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FULL PAPER

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Palladium(II)-*N*-Heterocyclic Carbene Complexes: Efficient Catalysts for the Direct C-H Bond Arylation of Furans with Aryl Halides

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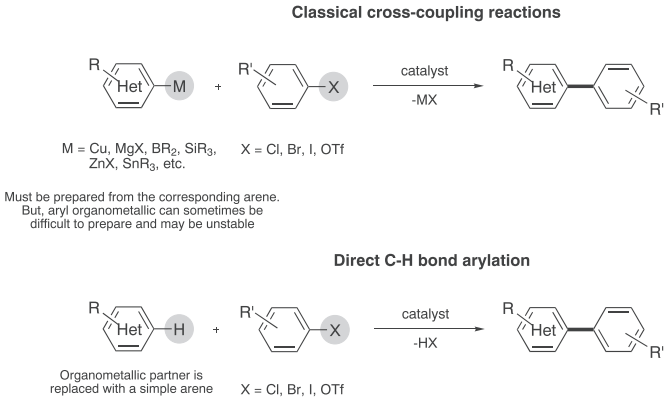
This paper contains the synthesis and characterization of the seven new benzimidazolium salts and their corresponding new palladium(II)-NHC complexes with the general formula $[PdX_2(NHC)_2]$, (NHC = *N*-heterocyclic carbene, X = Cl or Br), and also their catalytic activity in direct C-H bond arylation of 2-substituted furan derivatives with aryl bromides and aryl chlorides. Under the optimal conditions, these palladium(II)-NHC complexes showed the good catalytic performance for the direct C-H bond arylation of 2-substituted furans with (hetero)aryl bromides, and with readily available and inexpensive aryl chlorides. The C-H bond arylation regioselectively produced C5-arylated furans by using 1 mol% of the palladium(II)-NHC catalysts in moderate to high yields.

KEYWORDS
benzimidazolium salt, direct C-H bond arylation, furan, *N*-Heterocyclic carbene, palladium

1 | INTRODUCTION

Bi(hetero)aryl compounds are important structural moieties with an extensive history of diverse applications in a variety of fields, such as biology or material sciences, since, numerous economically important pharmaceuticals or agrochemicals have bi(hetero)aryl units as indispensable substructures.[1–3] The traditional method for the construction of bi(hetero)aryl moieties is transition metal-catalyzed cross-coupling between aryl(pseudo) halides and aryl organometallic reagents. However, the syntheses of aryl organometallic reagents require a number of steps from the arene and generate undesired byproducts. Therefore, the direct coupling between aryl(pseudo) halides and (hetero)arenes is advantageous with respect to a minimization of reaction steps and a reduction of byproduct formation. In the recent years, various methods have been developed for the direct C-H bond arylation of a variety of (hetero)arenes.[4,5] Compared to the classical cross-coupling reactions, direct C-H bond arylation not only initiate new stream for C-C bonds construction but also comply with the requirements of 'green' and 'sustainable' development in chemistry (Scheme 1). To date, palladium catalysis is the most widely developed method for the direct C-H bond arylation reactions,[6] but several contributions have been reported using ruthenium catalysis,[7] or other transitions metals.[8] Transition metal-free conditions for such cross-couplings have been also described.[9] Early examples of palladium-catalyzed direct arylation were reported by Ames *et al.*[10] Later development in this area focused on intermolecular direct arylation and expanded the substrate scope to include various (hetero)arenes containing directing groups and electron-deficient arenes. In recent



SCHEME 1 Comparison of classical cross-coupling reactions and direct C-H bond arylation

years, a wide variety of studies in this field focused on the developments of new C-H bond transformations. After this development, various methods for direct arylation of other valuable heteroarenes such as pyrroles, azoles, (benzo)thiophenes and (benzo)furans have been developed.[11–32]

The furans are very important backbones in organic chemistry, and many of their derivatives possess medicinal and biological activities. Consequently, to develop an efficient strategy for the synthesis of furan derivatives is of great importance.[33] As selected examples, Dantrolene is a muscle relaxant commonly used for the treatment of life-threatening complications during anesthesia,[34] Guanidine exhibits high Na^+/H^+ exchange isoform-1 inhibitory activity,[35] and Bioymifi is a compound that binds to the extracellular domain of the DR 5 receptors and induces their aggregation[36] (Figure 1).

The direct arylation of furans generally gives the C2- and C5-arylated products with high regioselectivity, since, the C2- and C5-positions of furan are the most electron-rich as a consequence of the resonance. The C3- and C4-positions of furan are neither electron-rich nor electron poor and as such will only react under forcing conditions when the C2- and C5-positions are blocked (Figure 2). Therefore, the formation of mixtures of C2-arylated furans and C2,C5-diarylated furans was generally observed with unsubstituted furan. The use of a blocking group at the C2-position allowed the selective production of C5-monoarylated furans.[37]

The palladium-catalyzed direct arylation of furans with aryl halides at low catalyst loadings would provide an economically and environmentally attractive procedure for the preparation of such compounds. The first example of palladium-catalyzed direct arylation of furans was reported in 1990 by Ohta *et al*. Using $Pd(PPh_3)_4$ as the catalyst and KOAc as the base, the reaction of 4-bromobenzaldehyde with furan gave the C2-arylated furan in a low yield of 40%.[38] To date, series of electron-rich furan derivatives have been activated successfully, often by using palladium species to catalyze the direct arylation. Especially, Doucet and co-workers conducted an intense and fruitful activity in the area of the palladium-catalyzed intermolecular arylations of furan derivatives with (hetero)aryl halides since 2009.[39] But, only a few examples of palladium(II)-NHC-catalyzed direct arylation of furans were found in the literature to date.[40] In this connection, recently we have also reported direct arylation of furans with aryl halides

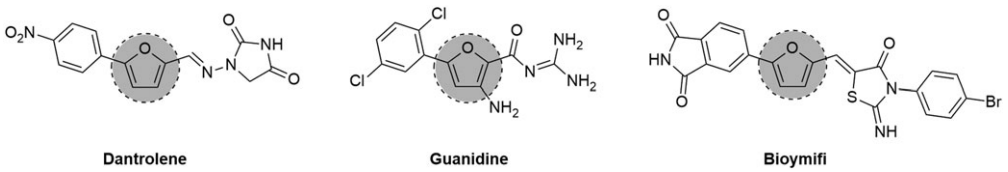


FIGURE 1 Examples of biologically active furan derivatives

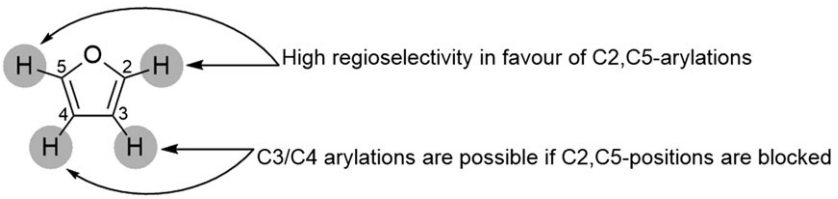


FIGURE 2 Most favourable positions of furans for direct C-H bond arylations

catalyzed by palladium(II)-NHC complexes.[41] In the present article, we now described the synthesis and characterization of seven new benzimidazolium salts (**2a-g**) and their corresponding seven new palladium(II)-NHC complexes (**3a-g**) of the general formula $[PdX_2(NHC)_2]$ (Figure 3). All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR spectroscopy and elemental analysis techniques. The palladium(II)-NHC complexes were tested in the direct C5-arylation of 2-substituted furans with aryl halides in moderate to high yields.

2 | EXPERIMENTAL

2.1 | Materials

All manipulations were carried out under argon using standard Schlenk line techniques. The solvents used were purified by distillation over the drying agents indicated and were transferred under argon. Elemental analyses were performed by İnönü University Scientific and Technological Research Center (Malatya, Turkey). Melting points were measures in open capillary tubes with an Electrothermal-9200 melting points apparatus. FT-IR spectra were recorded on ATR unit in the range of 400–4000 cm^{-1} with Perkin Elmer Spectrum 100 Spectrofotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker Avance AMX and Bruker Avance III spectrometer operating at 300, 400 and 500 MHz (^{1}H NMR) and at 75, 100 and 125 MHz (^{13}C NMR) in $CDCl_3$. The NMR studies were carried out in high-quality 5 mm NMR tubes. The chemical shifts (δ) are reported in ppm relative to $CDCl_3$. Coupling constants (J values) are given in hertz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, pent = pentet, m = multiplet. ^{1}H NMR spectra are referenced to residual protiated solvents (δ = 7.26 ppm for $CDCl_3$), ^{13}C chemical shifts are reported relative to deuteriated solvents (δ = 77.16 ppm for $CDCl_3$). All catalytic reactions were monitored on an Agilent 6890 N GC and Schimadzu 2010 Plus GC–MS system by GC-FID with an HP-5 column of 30 m length, 0.32 mm diameter, and 0.25 μm film thickness.

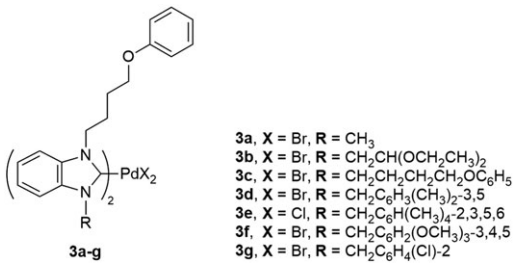


FIGURE 3 Palladium(II)-NHC complexes **3a-g** synthesised and assessed in the present study

2.2 | General procedure for the preparation of *N*-(4-phenoxybutyl) benzimidazole, (1)

For the preparation of *N*-(4-phenoxybutyl)benzimidazole (**1**), benzimidazole (5.90 g, 50.0 mmol) and potassium hydroxide (2.80 g, 50.0 mmol) were dissolved in ethyl alcohol (50 ml), the reaction mixture was stirred at room temperature for 1 h. Then, 4-phenoxybutyl bromide (11.45 g, 50.0 mmol) was slowly added, and the solution was heated to reflux for 5 h. The mixture cooled to room temperature, the precipitated potassium bromide was removed by filtration. The solvent was removed by distillation. The crude product was then distilled under vacuum.

2.2.1 | *N*-(4-Phenoxybutyl)benzimidazole, (1)

Yield: 9.72 g, 73%; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) = 1.84 (pent, J = 5.9 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 2.13 (pent, J = 7.4 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.00 (t, J = 6.0 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.30 (t, J = 7.1 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 6.90 (d, J = 7.1 Hz, 2H, arom C*H*s, $CH_2CH_2CH_2CH_2OC_6H_4$); 6.98 (t, J = 7.4 Hz, 1H, arom. CH, $CH_2CH_2CH_2CH_2OC_6H_4$); 7.29–7.36, 7.45–7.46 and 7.84–7.86 (m, 6H, arom. C*H*s, NC_6H_4N and $CH_2CH_2CH_2CH_2OC_6H_4$); 7.96 (s, 1H, NC*H*N). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) = 26.5 ($CH_2CH_2CH_2CH_2OC_6H_5$); 27.0 ($CH_2CH_2CH_2CH_2OC_6H_5$); 44.9 ($CH_2CH_2CH_2CH_2OC_6H_5$); 67.0 ($CH_2CH_2CH_2CH_2OC_6H_5$); 109.7, 114.4, 120.4, 120.9, 122.2, 123.0, 129.6, 133.8, 142.9, 158.7 (arom. *C*s, NC_6H_4N and $CH_2CH_2CH_2CH_2OC_6H_5$); 143.8 (N*C*HN). Elemental analysis calcd. (%) for $C_{17}H_{18}N_2O$ (Mr = 266.3): C 76.66, H 6.81, N 10.52; found (%): C 76.67, H 6.86, N 10.54.

2.3 | General procedure for the preparation of benzimidazolium salts, (2a-g)

For the preparation of benzimidazolium salts (**2a-g**), *N*-(4-phenoxybutyl)benzimidazole, **1**, (1.33 g, 5.0 mmol) was dissolved in degassed dimethylformamide, (DMF), (10 ml) and alkyl halide (5.0 mmol) was added at room temperature. The reaction mixture was stirred at 80 °C for 36 h. After completion of the reaction, the solvent was removed by vacuum and diethyl ether (15 ml) was added to obtain a white crystalline solid, which was

filtered off. The solid was washed with diethyl ether (3 × 10 ml) and dried under vacuum. The crude product was recrystallized from ethanol/diethyl ether mixture (1:2, *v/v*) and completely dried under vacuum.

2.3.1 | 1-(4-Phenoxybutyl)-3-(methyl) benzimidazolium Bromide, (2a)

Yield: 1.53 g, 85%; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) = 1.89 (pent, J = 5.8 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 2.24 (pent, J = 7.2 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 3.96 (t, J = 5.7 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.20 (s, 3H, CH_3); 4.67 (t, J = 7.4 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 6.73–7.70 (m, 9H, arom. C*H*s, NC_6H_4N and $CH_2CH_2CH_2CH_2OC_6H_5$); 11.21 (s, 1H, NC*H*N). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ (ppm) = 26.2 ($CH_2CH_2CH_2CH_2OC_6H_5$); 26.4 ($CH_2CH_2CH_2CH_2OC_6H_5$); 33.9 (CH_3); 47.4 ($CH_2CH_2CH_2CH_2OC_6H_5$); 66.7 ($CH_2CH_2CH_2CH_2OC_6H_5$); 113.0, 113.1, 114.4, 120.8, 127.3, 129.5, 131.1, 132.0, 158.5 (arom. *C*s, NC_6H_4N and $CH_2CH_2CH_2CH_2OC_6H_5$); 142.8 (NCHN). Elemental analysis calcd. (%) for $C_{18}H_{21}BrN_2O$ (Mr = 361.3): C 59.84, H 5.86, N 7.75; found (%): C 59.86, H 5.88, N 7.77.

2.3.2 | 1-(4-Phenoxybutyl)-3-(2,2-diethoxyethyl)benzimidazolium Bromide, (2b)

Yield: 2.08 g, 90%; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) = 1.07 (t, J = 7.2 Hz, 6H, $CH_2CH(OCH_2CH_3)_2$); 1.90 (pent, J = 5.7 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 2.26 (pent, J = 7.3 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 3.61 and 3.71 (qq, J = 7.2, 1.6 Hz, 4H, $CH_2CH(OCH_2CH_3)_2$); 3.98 (t, J = 5.6 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.63 (t, J = 7.4 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.72 (d, J = 4.2 Hz, 2H, $CH_2CH(OCH_2CH_3)_2$); 4.96 (t, J = 4.2 Hz, 1H, $CH_2CH(OCH_2CH_3)_2$); 6.76–7.79 (m, 9H, arom. C*H*s, NC_6H_4N and $CH_2CH_2CH_2CH_2OC_6H_5$); 11.24 (s, 1H, NC*H*N). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ (ppm) = 15.2 ($CH_2CH(OCH_2CH_3)_2$); 26.1 ($CH_2CH_2CH_2CH_2OC_6H_5$); 26.3 ($CH_2CH_2CH_2CH_2OC_6H_5$); 47.3 ($CH_2CH_2CH_2CH_2OC_6H_5$); 50.0 ($CH_2CH(OCH_2CH_3)_2$); 64.7 ($CH_2CH(OCH_2CH_3)_2$); 66.7 ($CH_2CH_2CH_2CH_2OC_6H_5$); 100.1 ($CH_2CH(OCH_2CH_3)_2$); 112.5, 114.4, 114.9, 120.9, 126.8, 126.9, 129.5, 130.9, 132.5, 158.5 (arom. *C*s, NC_6H_4N and $CH_2CH_2CH_2CH_2OC_6H_5$); 143.4 (NCHN). Elemental analysis calcd. (%) for $C_{23}H_{31}BrN_2O_3$ (Mr = 463.4): C 59.61, H 6.74, N 6.05; found (%): C 59.63, H 6.76, N 6.08.

2.3.3 | 1,3-Di(4-phenoxybutyl) benzimidazolium Bromide, (2c)

Yield: 2.30 g, 93%; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ (ppm) = 1.98 (pent, J = 5.8 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 2.31 (pent, J = 7.5 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.06 (t, J = 5.8 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.74 (t, J = 7.5 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 6.83–7.76 (m, 14H, arom. C*H*s, NC_6H_4N and $CH_2CH_2CH_2CH_2OC_6H_5$); 11.54 (s, 1H, NC*H*N). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ (ppm) = 26.1 ($CH_2CH_2CH_2CH_2OC_6H_5$); 26.4 ($CH_2CH_2CH_2CH_2OC_6H_5$); 47.3 ($CH_2CH_2CH_2CH_2OC_6H_5$); 66.7 ($CH_2CH_2CH_2CH_2OC_6H_5$); 113.2, 114.3, 120.8, 127.2, 129.5, 131.3, 158.5 (arom. *C*s, NC_6H_4N and $CH_2CH_2CH_2CH_2OC_6H_5$); 142.6 (NCHN). Elemental analysis calcd. (%) for $C_{27}H_{31}BrN_2O_2$ (Mr = 495.4): C 65.45, H 6.31, N 5.65; found (%): C 65.47, H 6.33, N 5.67.

2.3.4 | 1-(4-Phenoxybutyl)-3-(3,5-dimethylbenzyl)benzimidazolium Bromide, (2d)

Yield: 2.07 g, 89%; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ (ppm) = 1.99 (pent, J = 5.8 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 2.27 (s, 6H, $CH_2C_6H_3(CH_3)_2$–3,5); 2.35 (pent, J = 7.4 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.05 (t, J = 5.8 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.78 (t, J = 7.4 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 5.76 (s, 2H, $CH_2C_6H_3(CH_3)_2$–3,5); 6.82–7.76 (m, 12H, arom. C*H*s, NC_6H_4N, $CH_2CH_2CH_2CH_2OC_6H_5$ and $CH_2C_6H_3(CH_3)_2$–3,5); 11.61 (s, 1H, NC*H*N). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ (ppm) = 21.2 ($CH_2C_6H_3(CH_3)_2$–3,5); 26.2 ($CH_2CH_2CH_2CH_2OC_6H_5$); 26.4 ($CH_2CH_2CH_2CH_2OC_6H_5$); 47.5 ($CH_2CH_2CH_2CH_2OC_6H_5$); 51.5 ($CH_2C_6H_3(CH_3)_2$–3,5); 66.7 ($CH_2CH_2CH_2CH_2OC_6H_5$); 113.1, 113.9, 114.4, 125.9, 127.2, 129.5, 130.9, 131.2, 131.5, 132.4, 139.1, 158.5 (arom. *C*s, NC_6H_4N, $CH_2CH_2CH_2CH_2OC_6H_5$ and $CH_2C_6H_3(CH_3)_2$–3,5); 142.7 (NCHN). Elemental analysis calcd. (%) for $C_{26}H_{29}BrN_2O$ (Mr = 465.4): C 67.10, H 6.28, N 6.02; found (%): C 67.12, H 6.30, N 6.05.

2.3.5 | 1-(4-Phenoxybutyl)-3-(2,3,5,6-tetramethylbenzyl)benzimidazolium Chloride, (2e)

Yield: 1.77 g, 79%; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ (ppm) = 1.95 (pent, J = 5.8 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 2.22 (pent, J = 7.4 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 2.25 and 2.26 (s, 12H, $CH_2C_6H(CH_3)_4$–2,3,5,6); 4.04 (t, J = 5.8 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.84 (t, J = 7.4 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 5.88 (s, 2H, $CH_2C_6H(CH_3)_4$–

2,3,5,6); 6.82 and 7.74 (d, J = 7.9 Hz, 4H, arom. C*H*s, $CH_2CH_2CH_2CH_2OC_6H_4$); 7.25 (t, J = 7.9 Hz, 1H, arom. C*H*, $CH_2CH_2CH_2CH_2OC_6H_4$); 7.08 (s, 1H, arom. C*H*, $CH_2C_6H(CH_3)_4$–2,3,5,6); 6.94, 7.29, 7.48 and 7.59 (t, J = 7.8 Hz, 4H, arom. C*H*s, NC_6H_4N); 11.34 (s, 1H, NC*H*N). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ (ppm) = 16.2 and 20.6 ($CH_2C_6H(CH_3)_4$–2,3,5,6); 26.1 ($CH_2CH_2CH_2CH_2OC_6H_5$); 26.5 ($CH_2CH_2CH_2CH_2OC_6H_5$); 47.3 ($CH_2CH_2CH_2CH_2OC_6H_5$); 47.8 ($CH_2C_6H(CH_3)_4$–2,3,5,6); 66.7 ($CH_2CH_2CH_2CH_2OC_6H_5$); 113.0, 113.7, 114.3, 120.8, 127.1, 127.7, 129.5, 131.5, 131.6, 133.6, 134.1, 135.1, 158.5 (arom. *C*s, NC_6H_4N, $CH_2C_6H(CH_3)_4$–2,3,5,6 and $CH_2CH_2CH_2CH_2OC_6H_5$); 143.4 (N*C*HN). Elemental analysis calcd. (%) for $C_{28}H_{33}ClN_2O$ (Mr = 449.0): C 74.90, H 7.41, N 6.24; found (%): C 74.92, H 7.43, N 6.26.

2.3.6 | 1-(4-Phenoxybutyl)-3-(3,4,5-trimethoxybenzyl)benzimidazolium Bromide, (2f)

Yield: 2.11 g, 80%; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ (ppm) = 1.96 (pent, J = 5.8 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 2.31 (pent, J = 7.2 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 3.85 and 3.79 (s, 9H, $CH_2C_6H_2(OCH_3)_3$–3,4,5); 4.03 (t, J = 5.8 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.74 (t, J = 7.4 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 5.78 (s, 2H, $CH_2C_6H_2(OCH_3)_3$–3,4,5); 6.81–7.72 (m, 11H, arom. C*H*s, NC_6H_4N, $CH_2CH_2CH_2CH_2OC_6H_5$ and $CH_2C_6H_2(OCH_3)_3$–3,4,5); 11.76 (s, 1H, NC*H*N). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ (ppm) = 26.2 ($CH_2CH_2CH_2CH_2OC_6H_5$); 26.4 ($CH_2CH_2CH_2CH_2OC_6H_5$); 47.3 ($CH_2CH_2CH_2CH_2OC_6H_5$); 51.6 ($CH_2C_6H_3(CH_3)_2$–3,5); 56.7 and 60.8 ($CH_2C_6H_2(OCH_3)_3$–3,4,5); 66.7 ($CH_2CH_2CH_2CH_2OC_6H_5$); 106.1, 113.1, 113.7, 114.4, 120.9, 127.1, 128.4, 129.5, 131.3, 131.4, 138.5, 153.8, 158.5 (arom. *C*s, NC_6H_4N, $CH_2CH_2CH_2CH_2OC_6H_5$ and $CH_2C_6H_2(OCH_3)_3$–3,4,5); 143.5 (N*C*HN). Elemental analysis calcd. (%) for $C_{27}H_{31}BrN_2O_4$ (Mr = 527.4): C 61.48, H 5.92, N 5.31; found (%): C 61.49, H 5.93, N 5.33.

2.3.7 | 1-(4-Phenoxybutyl)-3-(2-chlorobenzyl)benzimidazolium Bromide, (2 g)

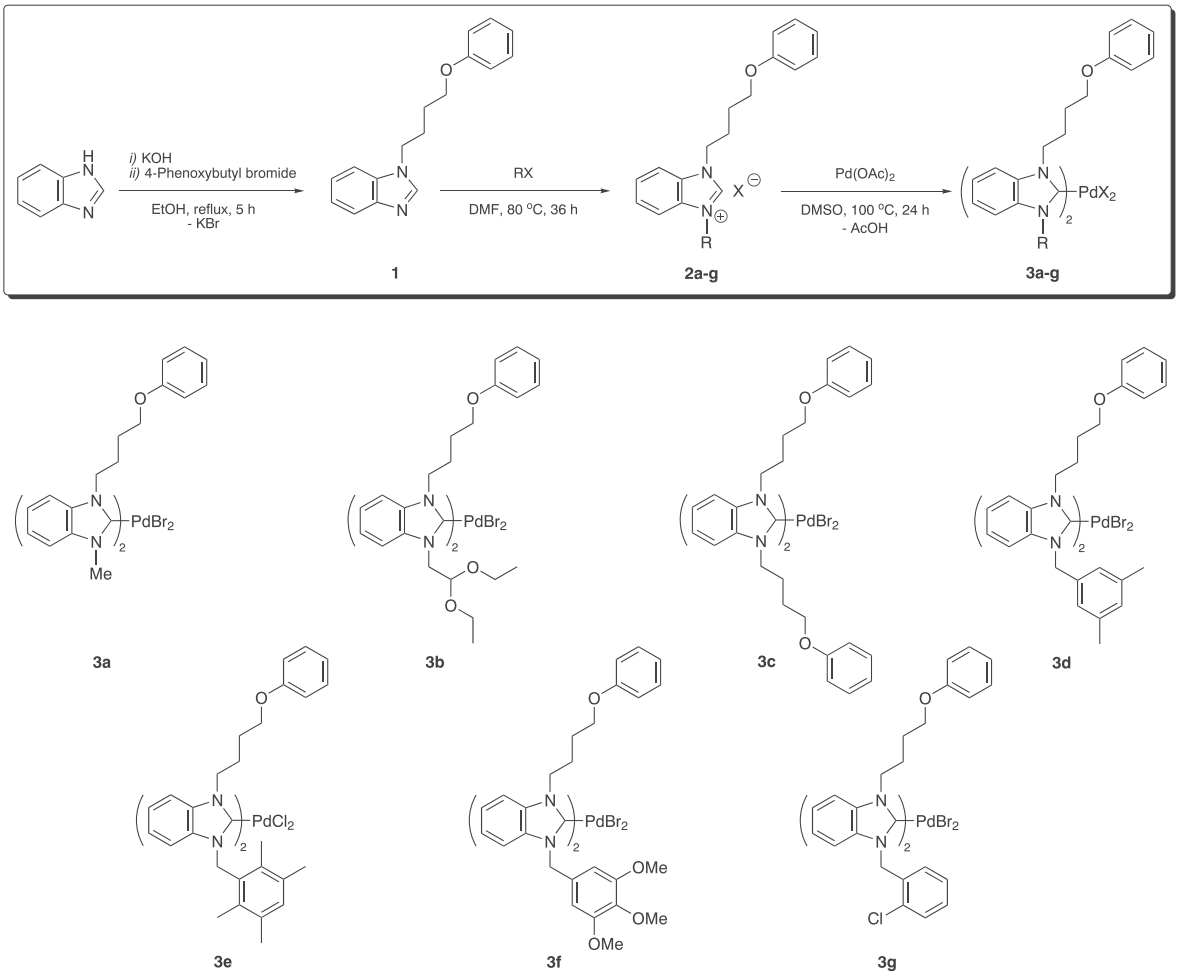
Yield: 1.95 g, 83%; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ (ppm) = 1.99 (pent, J = 5.8 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 2.34 (pent, J = 7.2 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.05 (t, J = 5.9 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.78 (t, J = 7.3 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 5.99 (s, 2H, $CH_2C_6H_4$(Cl)-2); 6.83–7.76 (m, 13H, arom. C*H*s, NC_6H_4N, $CH_2CH_2CH_2CH_2OC_6H_5$ and $CH_2C_6H_4$(Cl)-2); 11.53 (s, 1H, NC*H*N). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ (ppm) = 26.1 ($CH_2CH_2CH_2CH_2OC_6H_5$); 26.4 ($CH_2CH_2CH_2CH_2OC_6H_5$); 47.5 ($CH_2CH_2CH_2CH_2OC_6H_5$); 48.7 ($CH_2C_6H_4$(Cl)-2); 66.7 ($CH_2CH_2CH_2CH_2OC_6H_5$); 113.1, 113.8, 114.4, 120.8, 127.2, 127.3, 128.1, 129.5, 130.1, 130.2, 131.0, 131.2, 131.3, 131.4, 133.6, 158.5 (arom. *C*s, NC_6H_4N, $CH_2CH_2CH_2CH_2OC_6H_5$ and $CH_2C_6H_4$(Cl)-2); 143.3 (N*C*HN). Elemental analysis calcd. (%) for $C_{24}H_{24}ClBrN_2O$ (Mr = 471.8): C 61.10, H 5.13, N 5.94; found (%): C 61.13, H 5.14, N 5.95.

2.4 | General procedure for the preparation of palladium(II)-NHC complexes, (3a-g)

All benzimidazolium salts were converted, with moderated yields, into the palladium(II)-NHC complexes (**3a-g**). A suspension of the benzimidazolium salt (1.0 mmol) and $Pd(OAc)_2$ (0.50 mmol) in degassed DMSO (3 mL) was heated with vigorous stirring at 100 °C for 24 h. Volatiles were removed in vacuo, and the residue was washed with *n*-pentane (2 × 5 ml). The crude product was dissolved with CH_2Cl_2 then filtered through a pad of celite and silica gel to remove the unreacted $Pd(OAc)_2$ and benzimidazolium salt. Next, the crude complex was crystallized from dichloromethane/diethyl ether mixture (1:2, *v/v*) at room temperature and, completely dried under vacuum. All palladium complexes were isolated as air- and moisture-stable yellow solids and were isolated in 46–69% yields. All the new compounds were prepared according to general reaction pathway depicted in Scheme 2.

2.4.1 | *cis/trans*-Dibromo-bis[1-(4-phenoxybutyl)-3-(methyl)benzimidazol-2-ylidene]palladium(II), (3a)

Yield: 0.206 g, 50%; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) = 1.89 and 1.97 (pent, J = 5.9 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 2.42 and 2.44 (pent, J = 7.2 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 3.91 and 4.03 (t, J = 6.1 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.17 and 4.30 (s, 6H, CH_3); 4.79 and 4.85 (t, J = 7.5 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 6.78–6.80, 6.85–6.89, 7.15–7.23 and 7.29–7.35 (m, 18H, arom. C*H*s, NC_6H_4N and $CH_2CH_2CH_2CH_2OC_6H_5$). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) = 25.7 and 25.8 ($CH_2CH_2CH_2CH_2OC_6H_5$); 25.9 and 26.0 ($CH_2CH_2CH_2CH_2OC_6H_5$); 33.6 and 33.8 (CH_3); 47.0 and 47.1 ($CH_2CH_2CH_2CH_2OC_6H_5$); 66.2 and 66.3 ($CH_2CH_2CH_2CH_2OC_6H_5$); 113.4, 113.5, 113.6, 113.7, 119.6, 119.7, 121.9, 122.0, 128.4, 128.5, 133.5, 133.6,



SCHEME 2 Synthesis of palladium(II)-NHC complexes (**3a-g**)

134.1, 134.2, 157.8, 157.9 (arom. *C*s, NC_6H_4N and $CH_2CH_2CH_2CH_2OC_6H_5$); 180.2 and 180.3 (Pd-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{36}H_{40}Br_2N_4O_2Pd$ (Mr = 827.0): C 52.29, H 4.88, N 6.78; found (%): C 52.31, H 4.90, N 6.79.

2.4.2 | *cis/trans*-Dibromo-bis[1-(4-phenoxybutyl)-3-(2,2-diethoxyethyl) benzimidazol-2-ylidene] palladium(II), (3b)

Yield: 0.237 g, 46%; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) = 0.97 and 1.01 (t, J = 7.0 Hz, 12H, $CH_2CH(OCH_2CH_3)_2$); 1.92 and 1.97 (pent, J = 5.7 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 2.43 and 2.44 (pent, J = 7.3 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 3.36–3.49 and 3.65–3.75 (m, 8H, $CH_2CH(OCH_2CH_3)_2$); 3.92 and 3.99 (t, J = 6.1 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.84 and 4.85 (t, J = 7.3 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.86 and 4.87 (d, J = 5.7 Hz, 4H, $CH_2CH(OCH_2CH_3)_2$); 5.49 and 5.54 (t, J = 5.6 Hz, 2H, $CH_2CH(OCH_2CH_3)_2$); 6.78–6.88, 7.15–7.22, 7.30–7.35 and 7.56–7.62 (m, 18H, arom. C*H*s, NC_6H_4N and $CH_2CH_2CH_2CH_2OC_6H_5$). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) = 15.3 and 15.4 ($CH_2CH(OCH_2CH_3)_2$); 26.6 and 26.7 ($CH_2CH_2CH_2CH_2OC_6H_5$); 26.9 and 27.0 ($CH_2CH_2CH_2CH_2OC_6H_5$); 48.1 and 48.2 ($CH_2CH_2CH_2CH_2OC_6H_5$); 51.6 and 51.7 ($CH_2CH(OCH_2CH_3)_2$); 64.2 and 64.9 ($CH_2CH(OCH_2CH_3)_2$); 67.2 and 67.4 ($CH_2CH_2CH_2CH_2OC_6H_5$); 102.1 and 102.5 ($CH_2CH(OCH_2CH_3)_2$); 109.9, 110.0, 112.6, 113.0, 114.5, 114.6, 120.6, 120.7, 122.6, 122.8, 129.4, 129.5, 134.4, 135.6, 158.8, 158.9 (arom. *C*s, NC_6H_4N and $CH_2CH_2CH_2CH_2OC_6H_5$); 181.5 and 181.7 (Pd-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{46}H_{60}Br_2N_4O_6Pd$ (Mr = 1031.2): C 53.58, H 5.86, N 5.43; found (%): C 53.60, H 5.87, N 5.45.

2.4.3 | Dibromo-bis[1,3-di(4-phenoxybutyl) benzimidazol-2-ylidene]palladium(II), (3c)

Yield: 0.377 g, 69%; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ (ppm) = 1.90 (pent, J = 6.5 Hz, 8H, $CH_2CH_2CH_2CH_2OC_6H_5$); 2.43 (pent, J = 7.3 Hz, 8H, $CH_2CH_2CH_2CH_2OC_6H_5$); 3.91 (t, J = 6.0 Hz, 8H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.83 (t, J = 7.5 Hz, 8H,

$CH_2CH_2CH_2CH_2OC_6H_5$); 6.77–6.87, 7.14–7.21 and 7.33–7.36 (m, 28H, arom. C*H*s, NC_6H_4N and $CH_2CH_2CH_2CH_2OC_6H_5$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ (ppm) = 26.7 ($CH_2CH_2CH_2CH_2OC_6H_5$); 27.1 ($CH_2CH_2CH_2CH_2OC_6H_5$); 48.2 ($CH_2CH_2CH_2CH_2OC_6H_5$); 67.2 ($CH_2CH_2CH_2CH_2OC_6H_5$); 110.5, 114.5, 120.7, 122.9, 129.5, 134.7, 158.8 (arom. *C*s, NC_6H_4N and $CH_2CH_2CH_2CH_2OC_6H_5$); 181.2 (Pd-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{54}H_{60}Br_2N_4O_4Pd$ (Mr = 1095.3): C 59.21, H 5.52, N 5.12; found (%): C 59.23, H 5.55, N 5.14.

2.4.4 | *cis/trans*-Dibromo-bis[1-(4-phenoxybutyl)-3-(3,5-dimethylbenzyl) benzimidazol-2-ylidene] palladium(II), (3d)

Yield: 0.238 g, 46%; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) = 1.61 and 1.69 (pent, J = 6.0 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 2.11 and 2.18 (s, 12H, $CH_2C_6H_3(CH_3)_2$–3,5); 2.26 and 2.28 (pent, J = 7.3 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 3.66 and 3.94 (t, J = 6.0 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.76 and 4.88 (t, J = 7.2 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 5.79 and 6.00 (s, 4H, $CH_2C_6H_3(CH_3)_2$–3,5); 6.73–6.77, 6.85–6.88, 7.01–7.18 and 7.20–7.24 (m, 24H, arom. C*H*s, NC_6H_4N, $CH_2CH_2CH_2CH_2OC_6H_5$ and $CH_2C_6H_3(CH_3)_2$–3,5). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) = 20.1 and 20.2 ($CH_2C_6H_3(CH_3)_2$–3,5); 25.6 and 25.7 ($CH_2CH_2CH_2CH_2OC_6H_5$); 25.9 and 26.0 ($CH_2CH_2CH_2CH_2OC_6H_5$); 47.1 and 47.2 ($CH_2CH_2CH_2CH_2OC_6H_5$); 51.5 and 51.7 ($CH_2C_6H_3(CH_3)_2$–3,5); 66.1 and 66.3 ($CH_2CH_2CH_2CH_2OC_6H_5$); 109.2, 109.3, 113.4, 113.5, 121.7, 121.8, 124.3, 124.4, 124.5, 124.7, 124.8, 124.9, 128.3, 128.4, 128.5, 128.6, 133.4, 133.5, 133.8, 133.9, 134.2, 134.3, 137.0, 137.1, 137.2, 137.3, 138.2, 138.3, 157.9, 158.0 (arom. *C*s, NC_6H_4N, $CH_2CH_2CH_2CH_2OC_6H_5$ and $CH_2C_6H_3(CH_3)_2$–3,5); 180.7 and 180.8 (Pd-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{52}H_{56}Br_2N_4O_2Pd$ (Mr = 1035.3): C 60.33, H 5.45, N 5.41; found (%): C 60.35, H 5.47, N 5.43.

2.4.5 | Dichloro-bis[1-(4-phenoxybutyl)-3-(2,3,5,6-tetramethylbenzyl)benzimidazol-2-ylidene] palladium(II), (3e)

Yield: 0.275 g, 55%; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) = 1.93 (pent, J = 6.0 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 2.17 and 2.24 (s, 24H, $CH_2C_6H(CH_3)_4$–2,3,5,6); 2.47 (pent, J = 7.2 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 3.94 (t, J = 5.8 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.96 (t, J = 7.1 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 6.28 (s, 4H, $CH_2C_6H(CH_3)_4$–2,3,5,6); 6.31–6.35 and 6.70–7.29 (m, 20H, arom. C*H*s, NC_6H_4N, $CH_2CH_2CH_2CH_2OC_6H_4$ and $CH_2C_6H(CH_3)_4$–2,3,5,6). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) = 16.7 and 20.6 ($CH_2C_6H(CH_3)_4$–2,3,5,6); 27.1 ($CH_2CH_2CH_2CH_2OC_6H_5$); 29.7 ($CH_2CH_2CH_2CH_2OC_6H_5$); 47.9 ($CH_2CH_2CH_2CH_2OC_6H_5$); 50.9 ($CH_2C_6H(CH_3)_4$–2,3,5,6); 67.3 ($CH_2CH_2CH_2CH_2OC_6H_5$); 112.0, 114.4, 114.5, 120.6, 120.7, 122.9, 129.4, 129.5, 134.3, 134.8, 134.9, 135.0, 158.9 (arom. *C*s, NC_6H_4N, $CH_2C_6H(CH_3)_4$–2,3,5,6 and $CH_2CH_2CH_2CH_2OC_6H_5$); 181.9 (Pd-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{56}H_{64}Cl_2N_4O_2Pd$ (Mr = 1002.5): C 67.09, H 6.43, N 5.59; found (%): C 67.15, H 6.48, N 5.62.

2.4.6 | *cis/trans*-Dibromo-bis[1-(4-phenoxybutyl)-3-(3,4,5-trimethoxybenzyl) benzimidazol-2-ylidene] palladium(II), (3f)

Yield: 0.278 g, 48%; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ (ppm) = 1.68 and 1.95 (pent, J = 6.0 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 2.32 and 2.47 (pent, J = 7.2 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 3.68, 3.72, 3.73 and 3.74 (s, 18H, $CH_2C_6H_2(OCH_3)_3$–3,4,5); 3.84 and 3.95 (t, J = 6.0 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.82 and 4.91 (t, J = 7.4 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 5.89 and 6.04 (s, 4H, $CH_2C_6H_2(OCH_3)_3$–3,4,5); 6.75–6.88, 7.08–7.20 and 7.31–7.36 (m, 22H, arom. C*H*s, NC_6H_4N, $CH_2CH_2CH_2CH_2OC_6H_5$ and $CH_2C_6H_2(OCH_3)_3$–3,4,5). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ (ppm) = 25.7 and 25.9 ($CH_2CH_2CH_2CH_2OC_6H_5$); 26.0 and 26.2 ($CH_2CH_2CH_2CH_2OC_6H_5$); 46.8 and 46.9 ($CH_2CH_2CH_2CH_2OC_6H_5$); 51.7 and 51.8 ($CH_2C_6H_3(CH_3)_2$–3,5); 55.4, 55.6, 59.7 and 59.8 ($CH_2C_6H_2(OCH_3)_3$–3,4,5); 66.1 and 66.2 ($CH_2CH_2CH_2CH_2OC_6H_5$); 103.6, 103.7, 109.4, 110.3, 113.4, 113.5, 119.6, 119.7, 122.1, 122.2, 128.4, 128.5, 130.2, 130.4, 133.0, 133.2, 133.6, 133.7, 152.4,152.7, 157.8, 157.9 (arom. *C*s, NC_6H_4N, $CH_2CH_2CH_2CH_2OC_6H_5$ and $CH_2C_6H_2(OCH_3)_3$–3,4,5); 180.6 and 180.7 (Pd-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{54}H_{60}Br_2N_4O_8Pd$ (Mr = 1159.3): C 55.95, H 5.22, N 4.83; found (%): C 55.97, H 5.23, N 4.85.

2.4.7 | *cis/trans*-Dibromo-bis[1-(4-phenoxybutyl)-3-(2-chlorobenzyl) benzimidazol-2-ylidene] palladium(II), (3 g)

Yield: 0.241 g, 46%; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ (ppm) = 1.72 and 2.04 (pent, J = 5.9 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 2.35 and 2.57 (pent, J = 7.4 Hz, 2H, $CH_2CH_2CH_2CH_2OC_6H_5$); 3.78 and 4.05 (t, J = 6.0 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 4.84 and 4.97 (t, J = 7.5 Hz, 4H, $CH_2CH_2CH_2CH_2OC_6H_5$); 6.05 and 6.32 (s, 4H, $CH_2C_6H_4$(Cl)-2); 6.87 and 6.92 (d,

J = 7.8 Hz, 8H, arom. C*H*s, NC_6H_4N, $CH_2CH_2CH_2CH_2OC_6H_5$ and $CH_2C_6H_4$(Cl)-2); 6.97 (t, *J* = 7.3 Hz, 2H, arom. C*H*s, NC_6H_4N, $CH_2CH_2CH_2CH_2OC_6H_5$ and $CH_2C_6H_4$(Cl)-2); 7.14–7.47 (m, 16H, arom. C*H*s, NC_6H_4N, $CH_2CH_2CH_2CH_2OC_6H_5$ and $CH_2C_6H_4$(Cl)-2). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): *δ* (ppm) = 26.7 and 26.8 ($CH_2CH_2CH_2CH_2OC_6H_5$); 26.9 and 27.1 ($CH_2CH_2CH_2CH_2OC_6H_5$); 48.2 and 49.4 ($CH_2CH_2CH_2CH_2OC_6H_5$); 49.0 and 49.4 ($CH_2C_6H_4$(Cl)-2); 67.1 and 67.3 ($CH_2CH_2CH_2CH_2OC_6H_5$); 110.4, 110.5, 110.9, 111.0, 120.5, 120.7, 123.2, 123.3, 127.2, 127.4, 128.9, 129.0, 129.3, 129.4, 129.5, 129.6, 132.1, 132.2, 132.7, 132.8, 134.2, 134.4, 134.7, 134.9, 158.8, 158.9 (arom. *C*s, NC_6H_4N, $CH_2CH_2CH_2CH_2OC_6H_5$ and $CH_2C_6H_4$(Cl)-2); 182.2 and 182.5 (Pd-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{48}H_{46}Br_2Cl_2N_4O_2Pd$ (Mr = 1048.0): C 55.01, H 4.42, N 5.35; found (%): C 55.03, H 4.45, N 5.37.

2.5 | General procedure for the direct arylation of 2-substituted furan derivatives

An oven dried 10 ml Schlenk tube was charged with palladium(II)-NHC complex (0.01 mmol), 2-substituted furan derivative (2.0 mmol), aryl halide (1.0 mmol), KOAc (2.0 mmol), and DMAc (2 mL) under argon. The Schlenk tube was placed in a preheated oil bath at 120 °C, and the reaction mixture was stirred for different durations, as given in Table 3 and Table 4. Completion of the reaction, the solvent was removed under vacuum and the residue was charged directly onto a micro silica gel column. The products were eluted by using *n*-hexane/diethyl ether mixture (5:1, *v/v*). The chemical characterizations of the products were made by GC–MS spectrometry. The conversions were based on the aryl halide by GC and GC–MS.

3 | RESULTS AND DISCUSSION

3.1 | Synthesis of *N*-(4-phenoxybutyl) benzimidazole

The *N*-(4-phenoxybutyl)benzimidazole (**1**) were synthesized by the reaction of benzimidazole with 4-phenoxybutyl bromide in ethyl alcohol at 78 °C for 5 h. Compound **1** was isolated as a viscous liquid in moderate yield (73%). The compound **1** was fully characterised by elemental analysis, ^{1}H and ^{13}C NMR and FT-IR spectroscopies. In the ^{13}C NMR spectra of **1**, the characteristic peak of the imino carbon, (N*C*HN), resonance was detected as typical singlet at *δ* = 143.8 ppm. The signal of the NC*H*N proton was also detected as singlet at *δ* = 7.96 ppm for **1**. FT-IR spectra showed a broad band at 1493 cm^{-1} for the -C=N- bond vibration of **1**. (For the NMR and FT-IR spectrum of **1**, see SI, pp. S1–S2). Obtained spectroscopic values are consistent with those found in the literature for other *N*-(alkyl)benzimidazole compounds.[42]

3.2 | Synthesis of benzimidazolium salts

The benzimidazolium salts **2a-g** were synthesized by the reaction of *N*-(4-phenoxybutyl)benzimidazole (**1**) with different alkyl halides in anhydrous dimethylformamide (DMF) at 80 °C for 36 h. All compounds were isolated as air- and moisture-stable crystalline solids in high yields (79–93%). The structures of the **2a-g** were determined by their characteristic spectroscopic data and elemental analyses. In the ^{13}C NMR spectra of **2a-g**, the characteristic peak of the benzimidazolium C(2)-carbon, (N*C*HN), resonance were detected as typical singlets at between *δ* = 142.6–143.5 ppm. The ^{1}H NMR spectra of the **2a-g** further supported the assigned structures, the resonances for benzimidazolium C(2)H-proton (NC*H*N) were observed as sharp singlets at between *δ* = 11.21–11.76 ppm. The formation of the **2a-g** were also evident through their FT-IR spectra, which showed peaks $\nu_{(C=N)}$ at between 1556–1565 cm^{-1} for the -C=N- bond vibration of **2a-g**. (For the NMR and FT-IR spectrum of **2a-g**, see SI, pp. S3-S16). Obtained spectroscopic values are consistent with those found in the literature for other benzimidazolium salts.[30–32, 41a]

3.3 | Synthesis of palladium(II)-NHC complexes

The palladium(II)-NHC complexes **3a-g** were synthesized by the reaction of benzimidazolium salts, (**2a-g**), with $Pd(OAc)_2$ in degassed dimethyl sulfoxide (DMSO) at 100 °C for 24 h. The palladium(II)-NHC complexes were obtained as light yellow solids in 46–69% yields. The air- and moisture-stable palladium(II)-NHC complexes were soluble in organic solvents such as acetone, dichloromethane, chloroform, DMF, ethanol and acetonitrile. The structures of the **3a-g** complexes were also determined by their characteristic spectroscopic data and elemental analyses. In the ^{1}H NMR and ^{13}C NMR spectra of the all palladium(II)-NHC complexes, loss of the benzimidazolium C(2)H-proton (NC*H*N) and benzimidazolium C(2)-carbon (N*C*HN) signal suggests the formation of the palladium(II)-NHC complexes. The characteristic peak of the Pd-$C_{carbene}$ resonance for all palladium(II)-NHC complexes were detected at between *δ* = 180.2–182.5 ppm, however, NMR studies showed that all palladium(II)-NHC complexes except **3c** and **3e** were a mixture of *cis/trans* isomers in an approximate 40:60

ratio. The results of the elemental analysis were in good agreement with the theoretical values. Palladium(II)-NHC complexes exhibit a characteristic $\nu_{(NCN)}$ band typically at between 1395–1411 cm^{-1}. (For the NMR and FT-IR spectrum of **3a-g**, see SI, pp. S17–S30). The spectroscopic data are similar to those found for other palladium(II)-NHC complexes in the literature.[30, 41a] The analytical data are in good agreement with the compositions proposed for all the new compounds we prepared, and are summarized in the Table 1.

3.4 | Direct arylation of 2-substituted furan derivatives

Our first objective was to determine the most suitable reaction conditions using our palladium(II)-NHC complexes. For this purpose, we selected the complex **3c** as the model catalyst, and the 2-furaldehyde as the model heteroaromatic substrate with a blocked C2-position. We used the 4-bromoacetophenone or 4-chloroacetophenone as the model coupling partner. Also, we selected DMAc as the solvent, and KOAc as the base, because the DMAc/KOAc combination has been commonly used for the direct arylation of 5-membered heterocycles.[39] We focused on the direct arylation at the C5-position of 2-furaldehyde. The coupling reactions were regioselective, and in almost all cases, only the C5--arylated products were formed, namely, 5-(4-acetylphenyl)-2-furaldehyde. The results of varying the other reaction conditions including catalyst loading, reaction time and reaction temperature are given in Table 2. The chemical characterizations of the products were made by GC–MS spectrometry. The conversions were based on the aryl halide by GC and GC–MS.

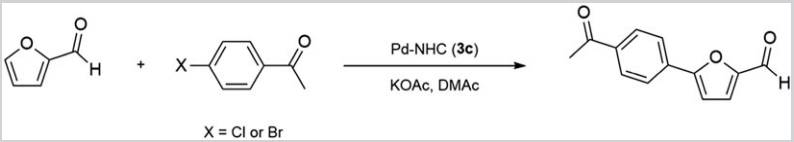
The arylation of 2-furaldehyde with 4-bromoacetophenone was first carried out at 150 °C for 2 h without the addition of **3c** complex in order to examine the effect of catalyst on the reaction. As attempt, no products were formed without the addition of **3c** complex (Table 2, entry 1). In the presence of 2 mol% of **3c** as the catalyst, KOAc as the base, DMAc as the solvent and 4-bromoacetophenone as the coupling partner at 150 °C for 2 h, the C5-arylated product was obtained full conversion with 91% isolated yield (Table 2, entry 2). When the amount of **3c** was decreased to 1 mol%, similar yield of product was observed (Table 2, entry 3). Decreasing the reaction temperature from 150 °C to 120 °C or 90 °C had a detrimental effect on the conversion (Table 2, entries 4 and 5). When the reaction time was reduced from 2 h to 1 h at 120 °C, no noticeable effect on the conversion with 83% isolated yield was observed (Table 2, entry 6), but when the reaction time was reduced to 0.5 h, the conversion dropped to 43% with 31% isolated yield (Table 2, entry 7). Finally, the best conditions leading to 94% conversion (with 83% isolated yield) of 4-bromoacetophenone with high selectivity in favor of the C5-arylated product were obtained, when the reaction was carried out in DMAc/KOAc combination in the presence of 1 mol% **3c** catalyst at 120 °C for 1 h (Table 2, entry 6).

TABLE 1 Physical and spectroscopic properties of the new compounds[a]

Compound	Molecular formula	Isolated yield [%]	M.p. [°C]	$\nu_{(CN)}$ [cm^{-1}]	H(2) ^{1}H NMR [ppm]	C(2) ^{13}C NMR [ppm]
1	$C_{17}H_{18}N_2O$	73	-	1493	7.96	143.8
2a	$C_{18}H_{21}BrN_2O$	85	108–109	1563	11.21	142.8
2b	$C_{23}H_{31}BrN_2O_3$	90	127–128	1565	11.24	143.4
2c	$C_{27}H_{31}BrN_2O_2$	93	82–83	1559	11.54	142.6
2d	$C_{26}H_{29}BrN_2O$	89	162–163	1560	11.61	142.7
2e	$C_{28}H_{33}ClN_2O$	79	176–177	1556	11.34	143.4
2f	$C_{27}H_{31}BrN_2O_4$	80	116–117	1558	11.76	143.5
2 g	$C_{24}H_{24}ClBrN_2O$	83	158–159	1557	11.53	143.3
3a	$C_{36}H_{40}Br_2N_4O_2Pd$	50	190–192	1404	-	180.2 and 180.3
3b	$C_{46}H_{60}Br_2N_4O_6Pd$	46	155–157	1407	-	181.5 and 181.7
3c	$C_{54}H_{60}Br_2N_4O_4Pd$	69	171–173	1407	-	181.2
3d	$C_{52}H_{56}Br_2N_4O_2Pd$	46	241–243	1404	-	180.7 and 180.8
3e	$C_{56}H_{64}Cl_2N_4O_2Pd$	55	128–130	1395	-	181.9
3f	$C_{54}H_{60}Br_2N_4O_8Pd$	48	214–216	1411	-	180.6 and 180.7
3 g	$C_{48}H_{46}Cl_2Br_2N_4O_2Pd$	46	138–140	1409	-	182.2 and 182.5

[a]As previously reported by several groups,[43] NMR data showed that all complexes except **3c** and **3e** were *cis*/*trans* mixtures.

TABLE 2 Influence of the reaction conditions for palladium(II)-NHC-catalyzed direct C5-arylation of 2-furaldehyde with 4-chloroacetophenone and 4-bromoacetophenone[a]



Entry	3c [mol-%]	X	Time [h]	Temperature [°C]	Conversion(Yield)[b,c] [%]
1	No	Br	2	150	-
2	2	Br	2	150	100(91)
3	1	Br	2	150	100(91)
4	1	Br	2	120	97(87)
5	1	Br	2	90	65(53)
6	**1**	**Br**	**1**	**120**	**94(83)**
7	1	Br	0.5	120	43(31)
8	1	Cl	1	120	-
9	1	Cl	2	120	7(—)
10	1	Cl	4	120	25(12)
11	1	Cl	8	120	50(36)
12	1	Cl	16	120	65(47)
13	**1**	**Cl**	**20**	**120**	**82(68)**
14	1	Cl	24	120	87(70)

[a]Conditions: 2-Furaldehyde (2.0 mmol), aryl halide (1.0 mmol), KOAc (2.0 mmol), DMAc (2 ml).

[b]Conversions were calculated with respect to aryl halide from the results of GC and GC–MS spectrometry.

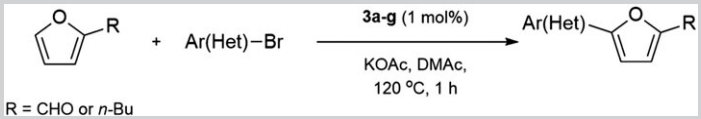
[c]Isolated yields were shown in parentheses.

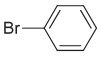
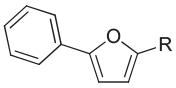
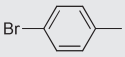
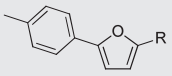
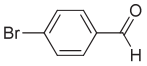
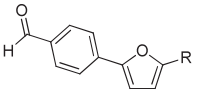
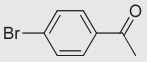
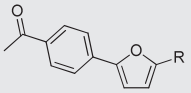
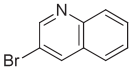
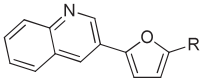
When the less reactive 4-chloroacetophenone was used as substrate in the presence of 1 mol% of **3c** catalyst and at 120 °C, the yields increased depending on the reaction time (Table 2, entries 9, 10, 11, 12), while no conversion was observed after lower reaction time such as 1 h (Table 2, entry 8). Interestingly, up to 68% yield were obtained, but for this, the reaction required a longer reaction time of 20 h (Table 2, entry 13). When the reaction time was increased from 20 h to 24 h at 120 °C, the very close yield of 4-chloroacetophenone was obtained (Table 2, entry 14). The conditions are commonly used for the direct arylation of 5-membered heterocycles. For this reason, the conditions are also consistent with the literature.[39]

Encouraged by the above successful results, we tried to evaluate the scope and limitations of the palladium(II)-NHC complexes **3a-g** for the direct arylation of 2-furaldehyde and 2-*n*-butylfuran with different aryl halides (Table 3 and Table 4). All reactions worked smoothly to give the desired C5-arylated products in moderate to high yields. A survey of coupling of (hetero)aryl bromides with 2-furaldehyde and 2-*n*-butylfuran, KOAc as the base in DMAc at 120 °C for 1 h is provided in Table 3. A variety of functional groups on (hetero)aryl bromide are tolerated. Quite similar yields were obtained (69–82% for 2-furaldehyde and 61–77% for 2-*n*-butylfuran) using the neutral aryl bromide such as bromobenzene (Table 3, entries 1–7). When the reaction of 2-furaldehyde and 2-*n*-butylfuran with electron-rich aryl bromide such as 4-bromotoluene was investigated, yields at between 69–82% and 58–78%, respectively (Table 3, entries 8–14). The coupling of 2-furaldehyde and 2-*n*-butylfuran with electron-poor aryl bromide such as 4-bromobenzaldehyde also proceeds nicely. 4-Bromobenzaldehyde gave the C5-arylated furan with 67–85% and 60–75% yields, respectively (Table 3, entries 15–21). The electron-poor 4-bromoacetophenone was also a good substrate to afford the corresponding products 5-(4-acetylphenyl)-2-furaldehyde and 5-(4-acetylphenyl)-2-*n*-butylfuran at between 63–83% and 71–83% yields, respectively (Table 3, entries 22–28). With 2-furaldehyde and 2-*n*-butylfuran, even the sterically hindered 3-bromoquinoline led to the expected coupling products with 58–79% and 68–78% yields, respectively (Table 1, entries 24–27).

Then, the scope and limitation of this reaction were examined by using a number of aryl chlorides (Table 4). A survey of coupling of aryl chlorides with 2-furaldehyde

TABLE 3 Palladium(II)-NHC-catalyzed direct C5-arylation of 2-substituted furan derivatives by using (hetero)aryl bromides[a]



Entry	(Hetero)aryl bromide	Catalyst	Product	Conversion(Yield)[b,c] [%] R = CHO	Conversion(Yield)[b,c] [%] R = *n*-Bu
1		**3a**		95(74)	81(68)
2		**3b**		90(71)	88(73)
3		**3c**		98(78)	90(77)
4		**3d**		97(75)	80(69)
5		**3e**		98(82)	75(62)
6		**3f**		90(77)	88(72)
7		**3 g**		88(69)	78(61)
8		**3a**		91(68)	89(74)
9		**3b**		92(77)	85(70)
10		**3c**		98(82)	90(78)
11		**3d**		97(70)	79(65)
12		**3e**		94(73)	89(72)
13		**3f**		90(74)	83(68)
14		**3 g**		85(69)	71(58)
15		**3a**		89(73)	86(74)
16		**3b**		95(82)	79(66)
17		**3c**		100(85)	87(75)
18		**3d**		91(73)	74(60)
19		**3e**		86(69)	80(65)
20		**3f**		95(70)	77(63)
21		**3 g**		90(67)	81(68)
22		**3a**		91(70)	90(79)
23		**3b**		84(77)	90(75)
24		**3c**		94(83)	97(83)
25		**3d**		78(63)	92(80)
26		**3e**		87(73)	84(71)
27		**3f**		88(72)	87(74)
28		**3 g**		74(67)	91(79)
29		**3a**		80(58)	90(77)
30		**3b**		84(68)	81(69)
31		**3c**		91(77)	95(78)
32		**3d**		85(71)	92(74)
33		**3e**		90(79)	90(72)
34		**3f**		88(72)	83(68)
35		**3 g**		80(65)	87(71)

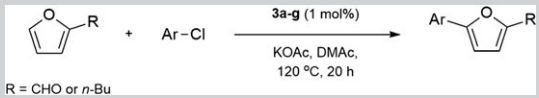
[a]Conditions: Pd-NHC, **3a-g** (0.01 mmol), furan derivative (2.0 mmol), (hetero)aryl bromide (1.0 mmol), KOAc (2.0 mmol), DMAc (2 ml), 120 °C, 1 h.

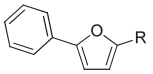
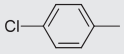
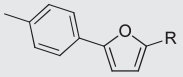
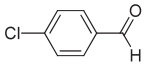
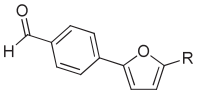
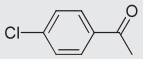
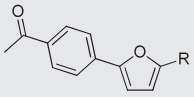
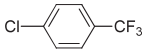
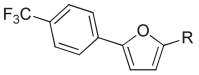
[b]Conversions were calculated with respect to (hetero)aryl bromide from the results of GC spectrometry.

[c]Isolated yields were shown in parentheses.

and 2-*n*-butylfuran, KOAc as the base in DMAc at 120 °C for 20 h is provided in Table 4. When the reaction of 2-furaldehyde with chlorobenzene, 4-chlorotoluene, 4-chlorobenzaldehyde, 4-chloroacetophenone and 4-chlorobenzotrifluoride was investigated, yields at between 51–72%, 52–69%, 50–76%, 53–69% and 60–76% were observed, respectively. When the reaction of 2-*n*-butylfuran with corresponding aryl chlorides was also investigated, yields at between 49–72%, 50–72%, 45–67%, 53–80% and 54–74% were observed, respectively. As can be seen from Table 4, substituents on the aryl chlorides had some effect on the reactions. For example, the electron-withdrawing groups such as -CHO, -$COCH_3$ and -CF_3 (Table 4, entries 15–35) were generally better

TABLE 4 Palladium(II)-NHC-catalyzed direct C5-arylation of 2-substituted furan derivatives by using aryl chlorides[a]



Entry	Aryl chloride	Catalyst	Product	Conversion(Yield)[b,c] [%] R = CHO	Conversion(Yield)[b,c] [%] R = *n*-Bu
1		**3a**		80(67)	69(54)
2		**3b**		75(63)	75(63)
3		**3c**		87(72)	85(72)
4		**3d**		69(53)	76(64)
5		**3e**		83(70)	82(68)
6		**3f**		84(70)	83(70)
7		**3 g**		65(51)	61(49)
8		**3a**		70(54)	60(50)
9		**3b**		73(58)	81(67)
10		**3c**		87(69)	86(72)
11		**3d**		70(52)	84(72)
12		**3e**		73(60)	81(69)
13		**3f**		75(62)	68(57)
14		**3 g**		71(58)	70(56)
15		**3a**		65(50)	68(55)
16		**3b**		68(53)	69(54)
17		**3c**		89(76)	81(67)
18		**3d**		80(68)	78(63)
19		**3e**		76(57)	73(60)
20		**3f**		84(72)	75(61)
21		**3 g**		80(65)	59(45)
22		**3a**		68(53)	82(67)
23		**3b**		73(61)	81(64)
24		**3c**		82(68)	95(80)
25		**3d**		72(60)	84(71)
26		**3e**		80(65)	75(62)
27		**3f**		82(69)	76(65)
28		**3 g**		75(63)	65(53)
29		**3a**		77(63)	78(64)
30		**3b**		79(68)	76(61)
31		**3c**		90(76)	88(74)
32		**3d**		82(69)	80(69)
33		**3e**		78(64)	74(61)
34		**3f**		88(75)	70(57)
35		**3 g**		74(60)	67(54)

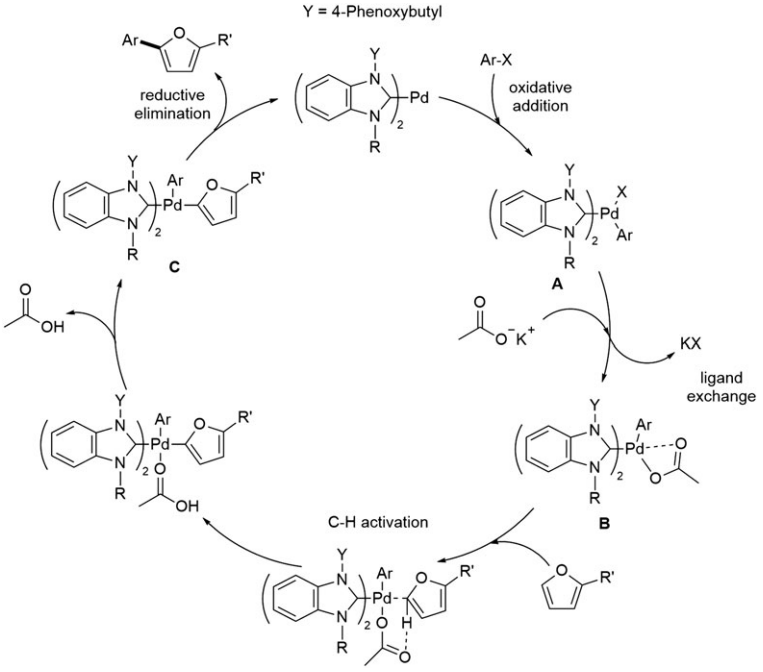
[a]Conditions: Pd-NHC, **3a-g** (0.01 mmol), furan derivative (2.0 mmol), aryl chloride (1.0 mmol), KOAc (2.0 mmol), DMAc (2 mL), 120 °C, 20 h.

[b]Conversions were calculated with respect to aryl chloride from the results of GC spectrometry.

[c]Isolated yields were shown in parentheses.

substrates, than those neutral aryl chloride such as chlorobenzene or 4-chlorotoluene having electron-donating substituent such as -CH_3 group (Table 4, entries 1–14).

Generally, the reactivity of 2-*n*-butylfuran was found to be less reactive than 2-furaldehyde. Also, when the performances of the complexes **3a-g** were compared in the direct C-H bond arylation of furans reaction, complex **3c** bearing NHC ligands with 1,3-di(4-phenoxybutyl) substituents exhibited better catalytic activity than the others. We attributed these performance differences to well-accordance electronic and steric properties of the NHC ligand. It is known that oxidative additions of electron-withdrawing substrates to electron rich palladium-complexes and reductive elimination of the product from large, sterically hindered palladium-complexes proceed more readily. Therefore, the presence of an NHC ligand



SCHEME 3 Proposed general catalytic pathway for the C-H bond arylation of 2-substituted furans

bearing a different second donating group such as ether side chains on the metal may radically increase the catalytic performance of the catalyst. The chelating nature of these ligands promotes production of highly stable complexes. The hemilabile part of such ligands is capable of reversible dissociation to produce vacant coordination sites, allowing complexation of substrates during the catalytic cycle. At the same time the strong-donor carbene moiety remains connected to the metal centre.[40b] In this direct C-H bond arylation, we believe that the bulky and electron-donor NHC ligands bearing 4-phenoxybutyl group in complexes **3a-g** provide the synergetic steric and electronic effects to confer the metal center the appropriate properties to make optimum for the key steps of the catalytic cycles. The proposed general catalytic pathway according to above explanations is shown in Scheme 3.

When the proposed catalytic pathway is examined, initially, oxidative addition of aryl halides to Pd(0) species affords a Pd(II)-aryl intermediate **A**. We believe that in the presence of electron-donor NHC ligands bearing 4-phenoxybutyl substituent, oxidative addition step more readily takes place and this is might be a key step. Then, followed by exchange of X ligand with KOAc to give **B**. The nature of the base used in this step is very important. Then, intermediate **B** reacts with 2-substituted furan to give **C** by C-H activation. In this step, the chelating nature of 4-phenoxybutyl substituent promotes production of highly stable complexes. Finally, the reductive elimination of intermediate **C** produces the desired C5-arylated furan products. It is clear that, reductive elimination of the product from large and sterically hindered NHC ligands bearing 4-phenoxybutyl substituent proceed more readily.

4 | CONCLUSIONS

In conclusion, seven new benzimidazolium salts and their corresponding new palladium(II)-NHC complexes were successfully synthesized and characterized by ^{1}H NMR, ^{13}C NMR and FT-IR spectroscopy, and microanalysis techniques. The catalytic activities of these new palladium(II)-NHC complexes were investigated as a broadly applicable catalysts in the direct C-H bond arylation of 2-substituted furan derivatives with different aryl halides. Under the optimal conditions, 2-substituted furans could be arylated solely in the C5-position with (hetero)aryl bromides. In addition, various substituents such as neutral, electron-donating and electron-withdrawing substrates could be tolerated, affording a efficient methodology for the direct C5-arylation of furans with economic and easily available aryl chlorides. Only a minor effect of the NHC ligand on the palladium complex was observed for the coupling of aryl halides with 2-substituted furan derivatives. Surprisingly, similar yields were obtained for the coupling of each aryl halides. We can say that there is no significant difference between these complexes on the catalytic activity of direct arylation of 2-substituted furan derivatives by aryl halides. The only significant difference between **3a-g** complexes indicates that electronic and steric properties are also playing some role in these processes. Finally, satisfactory results were obtained in presence of low catalyst

loading in this study. This low catalyst loading procedure is economically and environmentally attractive. Also, the only byproducts are AcOH/KX, (X = Cl or Br), instead of metallic salts with classical coupling procedures such as Suzuki, Stille, or Negishi reactions. Moreover, no preparation of an organometallic derivative is required, reducing the number of steps and consequently the amount of waste to prepare these compounds. It has to be emphasized that this procedure is environmentally more attractive than these classical coupling procedures.

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