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FULL PAPER

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Well-defined PEPPSI-themed palladium–NHC complexes: synthesis, and catalytic application in the direct arylation of heteroarenes

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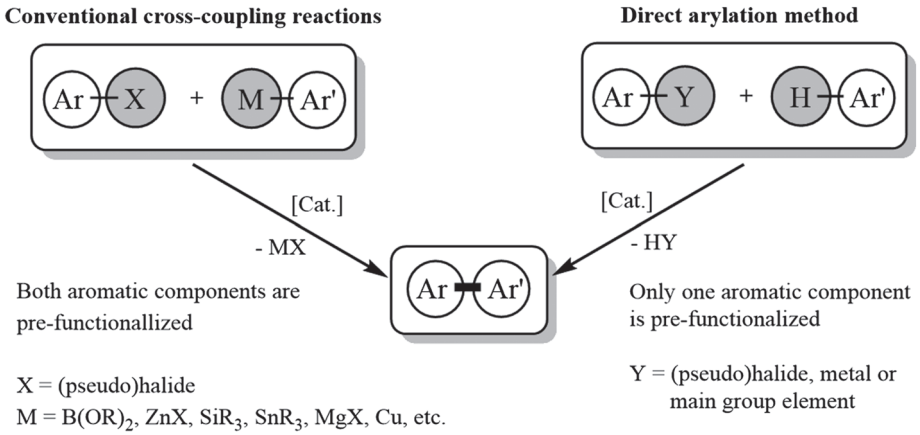
In this study, a series of benzimidazolium salts were synthesized as unsymmetrical *N*-heterocyclic carbene (NHC) precursors. Benzimidazolium salts were used for synthesis of the PEPPSI (pyridine enhanced precatalyst preparation stabilization and initiation)-themed, six new Pd-complexes with the general formula [PdX_2(NHC)(pyridine)]. The structures of all compounds were characterized by various spectroscopic techniques such as ^{1}H NMR, ^{13}C NMR and FT-IR. The more detailed structural characterization of four of the complexes was determined by single-crystal X-ray diffraction study. The catalytic activities of all Pd-complexes were evaluated in the direct arylation of the 2-acetylfuran and 2-acetylthiophene with aryl bromides in the presence of 1 mol% catalyst loading.

KEYWORDS
direct arylation, heteroarene, *N*-heterocyclic carbene, palladium, PEPPSI

1 | INTRODUCTION

Transition metal-catalyzed cross-coupling reactions have become one of the most important synthetic tools for synthesis of bi(hetero)aryl units in modern organic synthesis.[1–4] Suzuki,[5] Stille,[6] Negishi[7] or Kumada[8] type reactions are widely used in the metal-catalyzed synthesis of bi(hetero)aryls. Despite the large applicability of these reactions, in most of them, the starting coupling partners should bear either a metal-containing functionality or a halogen atom and related groups. In this case in fact the preliminary preparation of two independent, expensive, starting materials is required. These processes also have some disadvantages such as generating stoichiometric amounts of waste materials, the use of unstable and corrosive chemicals, etc.[9] Therefore, there is a need for more environmentally attractive and atom economical methods in which total synthesis steps and by-product formation are minimized. The direct arylation method represents an ideal alternative to conventional cross-coupling reactions in the synthesis of bi(hetero)aryls, because of its step-economic and eco-friendly advantages.[10] More importantly, this method not only minimizes by-product formation, but also has a great advantage as it makes organic synthesis easier (Scheme 1).

Over the last few decades, considerable advances have been achieved in direct arylation methods. Various transition metals such as Pd, Ru, Rh, etc., have been shown to be effective for the direct arylation reactions.[11] However, among them, the Pd-complexes are the most powerful



SCHEME 1 Comparison of conventional cross-coupling reactions and direct arylation method

and widely used catalysts in direct arylation. In recent years, Pd-catalyzed direct arylation of (hetero)arenes with (pseudo)halides have received significant attention as eco-friendly and economic alternatives to conventional methods. Here, aryl (pseudo)halides are the most commonly employed coupling partners for Pd-catalyzed direct arylation reactions.[12] Among these reactions, the direct arylation of heteroarenes is particularly attractive owing to the fact that these moieties are present in many biologically active compounds. One of the first examples of Pd-catalyzed direct arylation of heteroarenes was reported by Nakamura, Tajima and Sakai in 1982[13] and by Ohta in 1985.[14] Following these pioneering studies, Pd-catalyzed direct arylation of heteroarenes by aryl halides has been demonstrated to be a convenient and attractive methodology for the synthesis of bi(hetero)aryls. To date, Pd-catalyzed direct arylation of heteroarenes, especially five-membered heterocycles such as thiopene[15] and furan,[16] has been described by a large number of researchers.

N-Heterocyclic carbenes (NHCs) are neutral two-electron donors and they are known to be strong Lewis bases and excellent nucleophiles that bind metals better than phosphines.[17] One of the key features of NHCs compared with other classes of ligands is their stability. The strong σ-donating but poor π-accepting ability of NHC ligands leads to the formation of many stable metal–NHC complexes. Another features of NHCs is their tunability by the attachment of different substituents allowing the complexes to be obtained with desired electronic and steric properties.[17] In 1968, the first metal complexes containing NHC ligand were reported,[18] but these ligands received little attention in those years. However, after the first isolation and characterization of stable free NHC in 1991,[19] interest in these ligands increased exponentially. Next, the first use of the NHCs in Pd-catalyzed Heck reaction in 1995[20] presented a new class of ligands to the catalysis area. Nowadays, NHCs have become one of the most widely used ligand classes in organometallic chemistry and catalysis.

After the discovery of Organ's PEPPSI (pyridine enhanced precatalyst preparation stabilization and initiation)-themed Pd-complexes,[21] this type of complex has shown remarkable catalytic activities towards various carbon–carbon and carbon–heteroatom coupling reactions. PEPPSI-themed Pd–NHC complexes represent a new class of Pd-catalysts that are completely different from other Pd–NHC complexes and easier to synthesize and use.[22] In recent years, PEPPSI-themed Pd-complexes have been used as effective catalysts in direct arylation and successful results have been obtained.[23] In this context, recently we successfully reported the synthesis and structural characterization of PEPPSI-themed Pd-complexes with different NHC ligands, and we have investigated the atalytic activity of these complexes in direct arylation reactions.[12h, 15h] Herein, we now report the successful synthesis of six new PEPPSI-themed Pd–NHC complexes (**3a**–**3f**) of the general formula [PdX_2(NHC)(pyridine)], (X = Cl, Br; NHC = 1,3-disubstituted benzimidazole-2-ylidene), and their full characterization by various spectroscopic techniques. The solid-state structures of the four Pd-complexes (**3a**–**3c** and **3 f**) have been established by single-crystal X-ray diffraction study. In the present study, the catalytic application of all Pd-catalysts has been tested in the direct arylation of 2-acetylfuran and 2-acetylthiophene with aryl bromides in the presence of 1 mol% catalyst loading (Figure 1).

2 | EXPERIMENTAL SECTION

2.1 | Synthesis

The general procedures for the 1-(2,2-diethoxyethyl)benzimidazole (**1**), NHC ligand precursors (**2a**–**2f**) and their corresponding PEPPSI-themed Pd–carbene complexes (**3a**–**3f**) are shown in Scheme 2. Compounds **1**, **2b**, **2c**

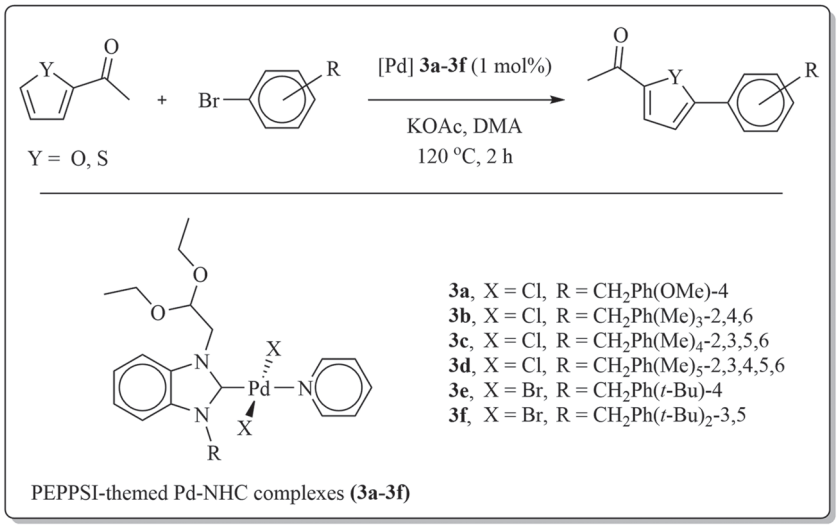


FIGURE 1 Pd-catalyzed direct arylation of C2-substituted furan and thiophene with aryl bromides

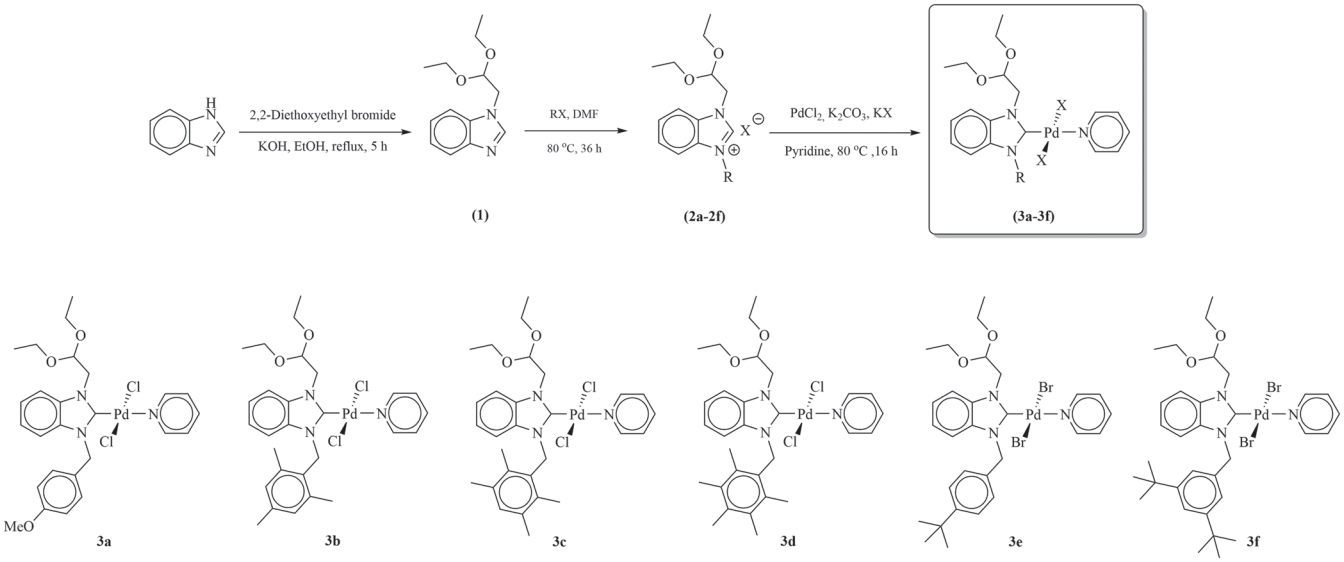
and **2d** were synthesized as previously described in the literature.[24]

2.2 | General procedure for the preparation of 1-(2,2-diethoxyethyl) benzimidazole (1)

For the preparation of 1-(2,2-diethoxyethyl)benzimidazole (**1**), benzimidazole (5.907 g, 50.0 mmol) and potassium hydroxide (2.805 g, 50.0 mmol) were dissolved in ethyl alcohol (50 ml), the reaction mixture was stirred at room temperature for 1 h. Then, 2,2-diethoxyethyl bromide (9.853 g, 50.0 mmol) was slowly added, and the solution was heated to reflux for 5 h. The mixture cooled to room temperature and the precipitated potassium bromide was removed by filtration. The solvent was removed by distillation. The crude product was then distilled under reduced vacuum. 1-(2,2-Diethoxyethyl)benzimidazole was isolated as a yellowish gel in 85% yields. For the ^{1}H NMR, ^{13}C NMR and FT-IR spectra of **1** see supporting information file, pages S1 and S2.

2.2.1 | 1-(2,2-Diethoxyethyl)benzimidazole, 1[24]

Yield 85%, 9.95 g (yellowish gel); b.p.: 140–150°C-(under ~50 Torr pressure); FT-IR ($\nu_{C(2)\text{-}N}$): 1494 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 1.14 [t, J = 7.0 Hz, 6H, $NCH_2CH(OCH_2CH_3)_2$]; 3.40 and 3.70 [dq, J = 9.2, 7.0 Hz, 4H, $NCH_2CH(OCH_2CH_3)_2$]; 4.25 [d, J = 5.3 Hz, 2H, $NCH_2CH(OCH_2CH_3)_2$]; 4.67 [t, J = 5.3 Hz, 1H, $NCH_2CH(OCH_2CH_3)_2$]; 7.25–7.32 (m, 2H, NC_6H_4N); 7.45 and 7.80 (dd, J = 6.8, 1.9 Hz, 2H, NC_6H_4N); 7.96 (s, 1H, NC*H*N). ^{13}C NMR



SCHEME 2 General pathway for the preparation of **1**, **2a–2f** and **3a–3f** compounds

(101 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 15.21 [$NCH_2CH(OCH_2CH_3)_2$]; 48.12 [$NCH_2CH(OCH_2CH_3)_2$]; 63.91 [$NCH_2CH(OCH_2CH_3)_2$]; 100.86 [$NCH_2CH(OCH_2CH_3)_2$]; 109.65, 120.31, 122.13, 122.92, 134.07 and 143.83 (NC_6H_4N); 143.55 (NCHN).

2.3 | General procedure for the preparation of NHC ligand precursors (2a–2f)

1-(2,2-Diethoxyethyl)benzimidazole (1.17 g, 5.0 mmol) was dissolved in degassed dimethylformamide (3 ml) and alkyl halide derivative (5.0 mmol) was added at room temperature. The reaction mixture was stirred at 80°C for 36 h under argon. After completion of the reaction, the solvent was removed by vacuum and Et_2O (15 ml) was added to obtain a white crystalline solid, which was filtered off. The solid was washed with Et_2O (3 × 10 ml) and dried under vacuum. The crude product was recrystallized from EtOH/Et_2O mixture (1:5, v/v) at room temperature, and completely dried under vacuum. All NHC ligand precursors (**2a–2f**) were isolated as air- and moisture-stable white solids in high yields. For the ^{1}H NMR, ^{13}C NMR and FT-IR spectrum of NHC ligand precursors (**2a–2f**) see supporting information file, pages S3–S14.

2.3.1 | 1-(2,2-Diethoxyethyl)-3-(4-methoxybenzyl)benzimidazolium chloride, 2a

Yield 87%, 1.70 g (white solid); m.p.: 130–131°C; FT-IR ($\nu_{C(2)\text{-}N}$): 1560 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 1.12 [t, J = 7.0 Hz, 6H, $NCH_2CH(OCH_2CH_3)_2$]; 3.67 and 3.77 [dq, J = 13.9, 7.0 Hz, 4H, $NCH_2CH(OCH_2CH_3)_2$]; 3.76 [s, 3H, $NCH_2C_6H_4(OCH_3)$-4); 4.79 (d, J = 4.2 Hz, 2H, $NCH_2CH(OCH_2CH_3)_2$]; 5.03 [t, J = 4.1 Hz, 1H, $NCH_2CH(OCH_2CH_3)_2$]; 5.77 [s, 2H, $NCH_2C_6H_4(OCH_3)$-4]; 6.88 [d, J = 8.3 Hz, 2H, $NCH_2C_6H_4(OCH_3)$-4]; 7.50 [d, J = 8.6 Hz, 2H, $NCH_2C_6H_4(OCH_3)$-4]; 7.52–7.64 (m, 3H, NC_6H_4N); 7.82 (d, J = 8.0 Hz, 1H, NC_6H_4N); 11.80 (s, 1H, NCHN). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 15.16 [$NCH_2CH(OCH_2CH_3)_2$]; 49.96 [$NCH_2CH(OCH_2CH_3)_2$]; 51.01 [$NCH_2C_6H_4(OCH_3)$-4]; 55.33 [$NCH_2C_6H_4(OCH_3)$-4]; 64.58 [$NCH_2CH(OCH_2CH_3)_2$]; 100.27 [$NCH_2CH(OCH_2CH_3)_2$]; 113.18, 114.67, 114.75, 124.77, 126.62, 126.80, 130.05, 130.76, 132.68 and 160.19 [NC_6H_4N and $NCH_2C_6H_4(OCH_3)$-4]; 144.12 (NCHN).

2.3.2 | 1-(2,2-Diethoxyethyl)-3-(2,4,6-trimethylbenzyl)benzimidazolium chloride, 2b[24]

Yield 76%, 1.53 g (white solid); m.p.: 172–173°C; FT-IR ($\nu_{C(2)\text{-}N}$): 1560 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 1.10 [t, J = 7.0 Hz, 6H, $NCH_2CH(OCH_2CH_3)_2$]; 2.30 and 2.33 [s, 9H, $NCH_2C_6H_2(CH_3)_3$-2,4,6]; 3.64 and 3.74 [dq, J = 14.1, 7.0 Hz, 4H, $NCH_2CH(OCH_2CH_3)_2$]; 4.84 [d, J = 3.9 Hz, 2H, $NCH_2CH(OCH_2CH_3)_2$]; 4.98 [t, J = 3.9 Hz, 1H, $NH_2CH(OCH_2CH_3)_2$]; 5.80 [s, 2H, $NCH_2C_6H_2(CH_3)_3$-2,4,6]; 6.95 [s, 2H, $NCH_2C_6H_2(CH_3)_3$-2,4,6]; 7.33 (d, J = 8.4 Hz, 1H, NC_6H_4N); 7.45–7.49 and 7.54–7.58 (m, 2H, NC_6H_4N); 7.84 (d, J = 8.4 Hz, 1H, NC_6H_4N); 10.78 (s, 1H, NCHN). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 15.10 [$NCH_2CH(OCH_2CH_3)_2$]; 20.18 and 21.07 [$NCH_2C_6H_2(CH_3)_3$-2,4,6]; 46.97 [$NCH_2CH(OCH_2CH_3)_2$]; 49.91 [$NCH_2C_6H_2(CH_3)_3$-2,4,6]; 64.41 [$NCH_2CH(OCH_2CH_3)_2$]; 99.87 [$NCH_2CH(OCH_2CH_3)_2$]; 113.09, 114.69, 125.07, 126.66, 126.88, 130.19, 130.97, 132.78, 137.99 and 139.77 [NC_6H_4N and $NCH_2C_6H_2(CH_3)_3$-2,4,6]; 143.92 (NCHN).

2.3.3 | 1-(2,2-Diethoxyethyl)-3-(2,3,5,6-tetramethylbenzyl)benzimidazolium chloride, 2c[24]

Yield 90%, 1.87 g (white solid); m.p.: 146–147°C; FT-IR ($\nu_{C(2)\text{-}N}$): 1563 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 1.08 [t, J = 7.0 Hz, 6H, $NCH_2CH(OCH_2CH_3)_2$]; 2.25 and 2.27 [s, 12H, $NCH_2C_6H(CH_3)_4$-2,3,5,6]; 3.63 and 3.72 [dq, J = 14.0, 7.0 Hz, 4H, $NCH_2CH(OCH_2CH_3)_2$]; 4.87 [d, J = 4.0 Hz, 2H, $NCH_2CH(OCH_2CH_3)_2$]; 4.96 [t, J = 4.0 Hz, 1H, $NCH_2CH(OCH_2CH_3)_2$]; 5.82 [s, 2H, $NCH_2C_6H(CH_3)_4$-2,3,5,6]; 7.09 [s, 1H, $NCH_2C_6H(CH_3)_4$-2,3,5,6]; 7.53–7.62 (m, 3H, NC_6H_4N); 7.89 (d, J = 7.8 Hz, 1H, NC_6H_4N); 10.06 (s, 1H, NCHN). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 15.05 [$NCH_2CH(OCH_2CH_3)_2$]; 15.99 and 20.55 [$NCH_2C_6H(CH_3)_4$-2,3,5,6]; 47.28 [$NCH_2CH(OCH_2CH_3)_2$]; 49.96 [$NCH_2C_6H(CH_3)_4$-2,3,5,6]; 64.29 [$NCH_2CH(OCH_2CH_3)_2$]; 99.99 [$NCH_2CH(OCH_2CH_3)_2$]; 113.12, 114.66, 126.87, 127.02, 127.63, 131.04, 132.79, 133.62, 134.12 and 135.08 [NC_6H_4N and $NCH_2C_6H(CH_3)_4$-2,3,5,6]; 142.96 (NCHN).

2.3.4 | 1-(2,2-Diethoxyethyl)-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazolium chloride, 2d[24]

Yield 95%, 2.04 g (white solid); m.p.: 120–121°C; FT-IR ($\nu_{C(2)\text{-}N}$): 1562 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ

(ppm) = 1.07 [t, J = 7.0 Hz, 6H, $NCH_2CH(OCH_2\ CH_3)_2$]; 2.25 and 2.29 [s, 15H, $NCH_2C_6(CH_3)_5$-2,3,4,5,6]; 3.64 and 3.74 [dq, J = 14.1, 7.0 Hz, 4H, $NCH_2CH(OCH_2\ CH_3)_2$]; 4.90 [d, J = 3.4 Hz, 2H, $NCH_2CH(OCH_2CH_3)_2$]; 4.97 [t, J = 3.3 Hz, 1H, $NCH_2CH(OCH_2CH_3)_2$]; 5.77 [s, 2H, $NCH_2C_6(CH_3)_5$-2,3,4,5,6]; 7.45 (d, J = 8.3 Hz, 1H, NC_6H_4N); 7.51 (t, J = 7.7 Hz, 1H, NC_6H_4N); 7.58 (t, J = 7.7 Hz, 1H, NC_6H_4N); 7.87 (d, J = 8.3 Hz, 1H, NC_6H_4N); 10.27 (s, 1H, NCHN). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 15.04 [$NCH_2CH(OCH_2CH_3)_2$]; 17.00, 17.05 and 17.34 [$NCH_2C_6(CH_3)_5$-2,3,4,5,6]; 47.77 [$NCH_2CH(OCH_2CH_3)_2$]; 50.03 [$NCH_2C_6(CH_3)_5$-2,3,4,5,6]; 64.37 [$NCH_2CH\ (OCH_2CH_3)_2$]; 99.80 [$NCH_2CH\ (OCH_2CH_3)_2$]; 112.86, 114.83, 124.83, 126.71, 126.83, 131.02, 132.93, 133.61, 133.98 and 137.42 [NC_6H_4N and $NCH_2C_6(CH_3)_5$-2,3,4,5,6]; 143.38 (NCHN).

2.3.5 | 1-(2,2-Diethoxyethyl)-3-(4-*tert*-butylbenzyl)benzimidazolium bromide, 2e

Yield 81%, 1.87 g (white solid); m.p.: 162–163°C; FT-IR ($\nu_{C(2)\text{-}N}$): 1557 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 1.05 [t, J = 7.0 Hz, 6H, $NCH_2CH\ (OCH_2CH_3)_2$]; 1.20 {s, 9H, $NCH_2C_6H_4\ [C(CH_3)_3]$-4}; 3.61 and 3.71 [dq, J = 13.9, 7.0 Hz, 4H, $NCH_2CH(OCH_2CH_3)_2$]; 4.73 [d, J = 4.1 Hz, 2H, $NCH_2CH\ (OCH_2CH_3)_2$]; 4.99 [t, J = 4.1 Hz, 1H, $NCH_2CH\ (OCH_2CH_3)_2$]; 5.69 {s, 2H, $NCH_2C_6H_4[C(CH_3)_3]$-4}; 7.32 {d, J = 8.3 Hz, 2H, $NCH_2C_6H_4[C(CH_3)_3]$-4}; 7.39 {d, J = 8.3 Hz, 2H, $NCH_2C_6H_4[C(CH_3)_3]$-4}; 7.45–7.58 (m, 3H, NC_6H_4N); 7.75 (d, J = 7.1 Hz, 1H, NC_6H_4N); 11.28 (s, 1H, NCHN). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 15.17 [$NCH_2CH(OCH_2CH_3)_2$]; 31.18 {$NCH_2C_6H_4[C(CH_3)_3]$-4}; 34.68 {$NCH_2C_6H_4[C(CH_3)_3]$-4}; 50.00 [$NCH_2CH\ (OCH_2CH_3)_2$]; 51.07 {$NCH_2C_6H_4\ [C(CH_3)_3]$-4}; 64.65 [$NCH_2CH(OCH_2CH_3)_2$]; 99.99 [$NCH_2CH(OCH_2CH_3)_2$]; 113.11, 114.71, 126.34, 126.73, 126.90, 128.20, 129.54, 130.82, 132.60 and 152.90 {NC_6H_4N and $NCH_2C_6H_4[C\ (CH_3)_3]$-4}; 143.58 (NCHN).

2.3.6 | 1-(2,2-Diethoxyethyl)-3-(3,5-di-*tert*-butylbenzyl)benzimidazolium bromide, 2f

Yield 73%, 1.89 g (white solid); m.p.: 166–167°C; FT-IR ($\nu_{C(2)\text{-}N}$): 1562 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 1.11 [t, J = 6.9 Hz, 6H, $NCH_2CH\ (OCH_2CH_3)_2$]; 1.28 {s, 18H, $NCH_2C_6H_3\ [C(CH_3)_3]_2$-3,5}; 3.68 and 3.77 [dq, J = 14.1, 7.0 Hz, 4H, $NCH_2CH\ (OCH_2CH_3)_2$]; 4.83 [d, J = 3.7 Hz, 2H, $NCH_2CH\ (OCH_2CH_3)_2$]; 5.07 [t, J = 3.7 Hz, 1H, $NCH_2CH\ (OCH_2CH_3)_2$]; 5.78 {s, 2H, $NCH_2C_6H_3\ [C(CH_3)_3]_2$-3,5}; 7.26 and 7.41 {s, 3H, $NCH_2C_6H_3\ [C(CH_3)_3]_2$-3,5}; 7.51–7.58 (m, 3H, NC_6H_4N); 7.84 (d, J = 8.5 Hz, 1H, NC_6H_4N); 11.30 (s, 1H, NCHN). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 15.18 [$NCH_2CH(OCH_2CH_3)_2$]; 31.36 {$NCH_2C_6H_3[C(CH_3)_3]_2$-3,5}; 34.94 {$NCH_2C_6H_3[C(CH_3)_3]_2$-3,5}; 49.97 [$NCH_2CH\ (OCH_2CH_3)_2$]; 52.09 {$NCH_2C_6H_3\ [C(CH_3)_3]_2$-3,5}; 64.65 [$NCH_2CH(OCH_2CH_3)_2$]; 100.08 [$NCH_2CH(OCH_2CH_3)_2$]; 113.12, 114.78, 122.42, 123.24, 126.68, 126.78, 130.88, 131.74, 132.74 and 152.18 {NC_6H_4N and $NCH_2C_6H_3\ [C(CH_3)_3]_2$-3,5}; 143.61 (NCHN).

2.4 | General procedure for the preparation of PEPPSI-themed palladium-carbene complexes (3a–3f)

NHC ligand precursors (**2a–2f**; 1.0 mmol) were converted with high yields into the PEPPSI-themed Pd–carbene complexes (**3a–3f**) by reaction with $PdCl_2$ (1.0 mmol) in refluxing pyridine in the presence of K_2CO_3 (5.0 mmol) as a base at 80°C for 16 h. Then, all volatiles were removed under vacuum, and the solid residue was washed with *n*-pentane (2 × 5 ml). The crude product was dissolved in CH_2Cl_2 (5 ml), then filtered through a pad of celite and silica gel (70–230 mesh) to remove the unreacted $PdCl_2$ and NHC ligand. The crude complex was crystallized from CH_2Cl_2–*n*-pentane mixture (1:5, v/v) at room temperature and completely dried under vacuum. All Pd-complexes were isolated as air- and moisture-stable bright yellow solids in moderate to high yields. For the ^{1}H NMR, ^{13}C NMR and FT-IR spectrum of **3a-3f** Pd-complexes see supporting information file, pages S15–S26.

2.4.1 | *Trans*-dichloro[1-(2,2-diethoxyethyl)-3-(4-methoxybenzyl)benzimidazole-2-ylidene]-(pyridine)-palladium (II), 3a

Yield 71%, 0.216 g (bright yellow solid); m.p.: 149–150°C; FT-IR ($\nu_{C(2)\text{-}N}$): 1405 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 1.04 [t, J = 7.0 Hz, 6H, $NCH_2CH(OCH_2CH_3)_2$]; 3.54 and 3.79 [dq, J = 9.4, 7.0 Hz, 4H, $NCH_2CH(OCH_2CH_3)_2$]; 3.70 [s, 3H, $NCH_2C_6H_4(OCH_3)$-4]; 4.94 [d, J = 5.5 Hz, 2H, $NCH_2CH\ (OCH_2CH_3)_2$]; 5.49 [t, J = 5.5 Hz, 1H, $NCH_2CH\ (OCH_2CH_3)_2$]; 6.09 [s, 2H, $NCH_2C_6H_4(OCH_3)$-4]; 6.79–6.83 [m, 2H, $NCH_2C_6H_4(OCH_3)$-4]; 7.03 (d, J = 3.9 Hz, 2H, NC_6H_4N); 7.12–7.15 (m, 1H, NC_6H_4N); 7.29–7.33 [m, 2H, $NCH_2C_6H_4(OCH_3)$-4]; 7.46 (d, J = 8.7 Hz, 2H, pyridine); 7.56 (d, J = 8.2 Hz, 1H, NC_6H_4N); 7.73 (tt, J = 7.7, 1.6 Hz, 1H, pyridine); 8.93 (dd, J = 6.5, 1.5 Hz, 2H, pyridine). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 15.35 [$NCH_2CH\ (OCH_2CH_3)_2$]; 51.52

[$NCH_2CH(OCH_2CH_3)_2$]; 52.80 [$NCH_2C_6H_4(OCH_3)$-4]; 55.26 [$NCH_2C_6H_4(OCH_3)$-4]; 64.65 [$NCH_2CH(OCH_2CH_3)_2$]; 102.66 [$NCH_2CH(OCH_2CH_3)_2$]; 111.10, 112.47, 114.25, 122.99, 123.08, 127.00, 129.41, 133.79, 135.92 and 159.90 [NC_6H_4N and $NCH_2C_6H_4(OCH_3)$-4]; 124.63, 138.25 and 151.20 (pyridine); 163.82 [Pd-*C*(2)].

2.4.2 | *Trans*-dichloro[1-(2,2-diethoxyethyl)-3-(2,4,6-trimethylbenzyl) benzimidazole-2-ylidene]-(pyridine)-palladium (II), 3b

Yield 64%, 0.199 g (bright yellow solid); m.p.: 192–193°C; FT-IR ($\nu_{C(2)\text{-}N}$): 1400 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 1.03 [t, J = 7.0 Hz, 6H, $NCH_2CH(OCH_2CH_3)_2$]; 2.25 and 2.26 [s, 9H, $NCH_2C_6H_2(CH_3)_3$-2,4,6]; 3.53 and 3.78 [dq, J = 9.4, 7.0 Hz, 4H, $NCH_2CH(OCH_2CH_3)_2$]; 4.93 [d, J = 5.5 Hz, 2H, $NCH_2CH(OCH_2CH_3)_2$]; 5.49 [t, J = 5.5 Hz, 1H, $NCH_2CH(OCH_2CH_3)_2$]; 6.11 [s, 2H, $NCH_2C_6H_2(CH_3)_3$-2,4,6]; 6.40 (d, J = 8.3 Hz, 1H, NC_6H_4N); 6.86 [s, 2H, $NCH_2C_6H_2(CH_3)_3$-2,4,6]; 6.90 (t, J = 7.4 Hz, 1H, NC_6H_4N); 7.08 (t, J = 7.4 Hz, 1H, NC_6H_4N); 7.31 (ddd, J = 7.6, 5.1, 1.3 Hz, 2H, pyridine); 7.54 (d, J = 8.2 Hz, 1H, NC_6H_4N); 7.73 (tt, J = 7.7, 1.6 Hz, 1H, pyridine); 8.89 (dd, J = 6.5, 1.5 Hz, 2H, pyridine). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 15.36 [$NCH_2CH(OCH_2CH_3)_2$]; 20.80 and 21.11 [$NCH_2C_6H_2(CH_3)_3$-2,4,6]; 49.96 [$NCH_2CH(OCH_2CH_3)_2$]; 51.53 [$NCH_2C_6H_2(CH_3)_3$-2,4,6]; 64.66 [$NCH_2CH(OCH_2CH_3)_2$]; 102.79 [$NCH_2CH(OCH_2CH_3)_2$]; 110.90, 112.36, 122.64, 123.06, 127.51, 129.66, 134.21, 135.70, 138.55 and 138.78 [NC_6H_4N and $NCH_2C_6H_2(CH_3)_3$-2,4,6]; 124.58, 138.15 and 151.18 (pyridine); 163.80 [Pd-*C*(2)].

2.4.3 | *Trans*-dichloro[1-(2,2-diethoxyethyl)-3-(2,3,5,6-tetramethylbenzyl)benzimidazole-2-ylidene]-(pyridine)-palladium (II), 3c

Yield 75%, 0.238 g (bright yellow solid); m.p.: 191–192°C; FT-IR ($\nu_{C(2)\text{-}N}$): 1403 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 1.03 [t, J = 7.0 Hz, 6H, $NCH_2CH(OCH_2CH_3)_2$]; 2.17 and 2.18 [s, 12H, $NCH_2C_6H(CH_3)_4$-2,3,5,6]; 3.53 and 3.77 [qq, J = 9.4, 7.0 Hz, 4H, $NCH_2CH(OCH_2CH_3)_2$]; 4.93 [d, J = 5.5 Hz, 2H, $NCH_2CH(OCH_2CH_3)_2$]; 5.49 [t, J = 5.5 Hz, 1H, $NCH_2CH(OCH_2CH_3)_2$]; 6.13 [s, 2H, $NCH_2C_6H(CH_3)_4$-2,3,5,6]; 6.37 (d, J = 8.3 Hz, 1H, NC_6H_4N); 6.88 (t, J = 7.4 Hz, 1H, NC_6H_4N); 7.01 [s, 1H, $NCH_2C_6H(CH_3)_4$-2,3,5,6]; 7.06 (t, J = 7.4 Hz, 1H, NC_6H_4N); 7.30 (ddd, J = 7.5, 5.1, 1.3 Hz, 2H, pyridine); 7.53 (d, J = 8.2 Hz, 1H, NC_6H_4N); 7.72 (tt, J = 7.7, 1.6 Hz, 1H, pyridine); 8.85 (dd, J = 6.4, 1.5 Hz, 2H, pyridine). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 15.36 [$NCH_2CH(OCH_2CH_3)_2$]; 16.48 and 20.63 [$NCH_2C_6H(CH_3)_4$-2,3,5,6]; 50.40 [$NCH_2CH(OCH_2CH_3)_2$]; 51.58 [$NCH_2C_6H(CH_3)_4$-2,3,5,6]; 64.64 [$NCH_2CH(OCH_2CH_3)_2$]; 102.78 [$NCH_2CH(OCH_2CH_3)_2$]; 110.86, 112.34, 122.57, 123.03, 130.50, 132.53, 134.34, 134.41, 135.05 and 136.62 [NC_6H_4N and $NCH_2C_6H(CH_3)_4$-2,3,5,6]; 124.56, 138.15 and 151.11 (pyridine); 163.77 [Pd-*C*(2)].

2.4.4 | *Trans*-dichloro[1-(2,2-diethoxyethyl)-3-(2,3,4,5,6-pentamethylbenzyl)benzimidazole-2-ylidene]-(pyridine)-palladium (II), 3d

Yield 77%, 0.250 g (bright yellow solid); m.p.: 215–216°C; FT-IR ($\nu_{C(2)\text{-}N}$): 1402 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 1.03 (t, J = 7.0 Hz, 6H, $NCH_2CH(OCH_2CH_3)_2$); 2.15, 2.22 and 2.24 [s, 15H, $NCH_2C_6(CH_3)_5$-2,3,4,5,6]; 3.53 and 3.78 [dq, J = 9.4, 7.0 Hz, 4H, $NCH_2CH(OCH_2CH_3)_2$]; 4.93 [d, J = 5.5 Hz, 2H, $NCH_2CH(OCH_2CH_3)_2$]; 5.49 [t, J = 5.5 Hz, 1H, $NCH_2CH(OCH_2CH_3)_2$]; 6.36 [s, 2H, $NCH_2C_6(CH_3)_5$-2,3,4,5,6]; 6.34 (d, J = 8.3 Hz, 1H, NC_6H_4N); 6.85 (t, J = 7.4 Hz, 1H, NC_6H_4N); 7.07 (t, J = 7.4 Hz, 1H, NC_6H_4N); 7.30 (ddd, J = 7.6, 5.2, 1.3 Hz, 2H, pyridine); 7.52 (d, J = 8.2 Hz, 1H, NC_6H_4N); 7.72 (tt, J = 7.7, 1.6 Hz, 1H, pyridine); 8.86 (dd, J = 6.4, 1.5 Hz, 2H, pyridine). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 15.36 [$NCH_2CH(OCH_2CH_3)_2$]; 16.95, 17.32 and 17.48 [$NCH_2C_6(CH_3)_5$-2,3,4,5,6]; 51.11 [$NCH_2CH(OCH_2CH_3)_2$]; 51.58 [$NCH_2C_6(CH_3)_5$-2,3,4,5,6]; 64.65 [$NCH_2CH(OCH_2CH_3)_2$]; 102.80 [$NCH_2CH(OCH_2CH_3)_2$]; 111.04, 112.25, 122.48, 122.98, 127.77, 133.36, 134.47, 134.63, 136.67 and 136.96 [NC_6H_4N and $NCH_2C_6(CH_3)_5$-2,3,4,5,6]; 124.54, 138.13 and 151.11 (pyridine); 163.57 [Pd-*C*(2)].

2.4.5 | *Trans*-dibromo[1-(2,2-diethoxyethyl)-3-(4-*tert*-butylbenzyl)benzimidazole-2-ylidene]-(pyridine)-palladium (II), 3e

Yield 61%, 0.221 g (bright yellow solid); m.p.: 91–92°C; FT-IR ($\nu_{C(2)\text{-}N}$): 1406 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 1.07 [t, J = 7.0 Hz, 6H, $NCH_2CH(OCH_2CH_3)_2$]; 1.22 {s, 9H, $NCH_2C_6H_4$ [$C(CH_3)_3$]-4}; 3.57 and 3.80 [dq, J = 9.4, 7.0 Hz, 4H, $NCH_2CH(OCH_2CH_3)_2$]; 4.91 [d, J = 5.5 Hz, 2H, $NCH_2CH(OCH_2CH_3)_2$]; 5.55 [t, J = 5.5 Hz, 1H, $NCH_2CH(OCH_2CH_3)_2$]; 6.07 {s, 2H, $NCH_2C_6H_4$ [$C(CH_3)_3$]-4}; 6.96–7.02 (m, 2H, NC_6H_4N); 7.13 (dd,

J = 8.2, 1.3 Hz, 1H, NC_6H_4N); 7.27–7.41 {m, 4H, NC_6H_4N and $NCH_2C_6H_4[C(CH_3)_3]$-4}; 7.45 (d, J = 8.2 Hz, 2H, pyridine); 7.57 (d, J = 8.2 Hz, 1H, NC_6H_4N); 7.75 (tt, J = 7.7, 1.6 Hz, 1H, pyridine); 8.95 (dd, J = 6.5, 1.5 Hz, 2H, pyridine). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 15.43 [$NCH_2CH(OCH_2CH_3)_2$]; 31.34 {$NCH_2C_6H_4[C(CH_3)_3]$-4}; 34.60 {$NCH_2C_6H_4[C(CH_3)_3]$-4}; 51.84 [$NCH_2CH(OCH_2CH_3)_2$]; 53.45 {$NCH_2C_6H_4$ $[C(CH_3)_3]$-4}; 64.63 [$NCH_2CH(OCH_2CH_3)_2$]; 102.10 [$NCH_2CH(OCH_2CH_3)_2$]; 111.20, 112.47, 122.83, 122.94, 125.77, 127.78, 131.77, 134.10, 136.12 and 151.12 [NC_6H_4N and $NCH_2C_6H_2(CH_3)_3$-2,4,6]; 124.67, 138.03 and 152.55 (pyridine); 163.43 [Pd-C(2)].

2.4.6 | *Trans*-dibromo[1-(2,2-diethoxyethyl)-3-(3,5-di-*tert*-butylbenzyl) benzimidazole-2-ylidene]-(pyridine)-palladium (II), 3f

Yield 69%, 0.269 g (bright yellow solid); m.p.: 151–152° C; FT-IR ($\nu_{C(2)\text{-}N}$): 1404 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 1.03 [t, J = 7.0 Hz, 6H, $NCH_2CH(OCH_2CH_3)_2$]; 1.20 {s, 18H, $NCH_2C_6H_3$ [C $(CH_3)_3]_2$-3,5}; 3.54 and 3.79 [dq, J = 9.4, 7.0 Hz, 4H, $NCH_2CH(OCH_2CH_3)_2$]; 4.91 [d, J = 5.6 Hz, 2H, $NCH_2CH(OCH_2CH_3)_2$]; 5.59 [t, J = 5.6 Hz, 1H, $NCH_2CH(OCH_2CH_3)_2$]; 6.11 {s, 2H, $NCH_2C_6H_3$ [C $(CH_3)_3]_2$-3,5}; 6.90 (d, J = 8.1 Hz, 1H, NC_6H_4N); 6.99 (t, J = 7.6 Hz, 1H, NC_6H_4N); 7.12 (t, J = 7.8 Hz, 1H, NC_6H_4N); 7.27 {s, 3H, $NCH_2C_6H_3[C(CH_3)_3]_2$-3,5); 7.28 (ddd, J = 7.6, 5.2, 1.3 Hz, 2H, pyridine); 7.57 (d, J = 8.2 Hz, 1H, NC_6H_4N); 7.69 (tt, J = 7.7, 1.6 Hz, 1H, pyridine); 8.97 (dd, J = 6.4, 1.4 Hz, 2H, pyridine). ^{13}C NMR (101 MHz, $CDCl_3$, 25°C, TMS): δ (ppm) = 15.40 [$NCH_2CH(OCH_2CH_3)_2$]; 31.47 {$NCH_2C_6H_3[C(CH_3)_3]_2$-3,5}; 34.97 {$NCH_2C_6H_3[C(CH_3)_3]_2$-3,5}; 51.71 [$NCH_2CH(OCH_2CH_3)_2$]; 54.34 {$NCH_2C_6H_3[C(CH_3)_3]_2$-3,5}; 64.74 [$NCH_2CH(OCH_2CH_3)_2$]; 102.03 [NCH_2CH $(OCH_2CH_3)_2$]; 111.28, 112.45, 121.78, 122.36, 122.70, 122.82, 133.86, 134.07, 136.11 and 151.32 [NC_6H_4N and $NCH_2C_6H_2(CH_3)_3$-2,4,6]; 124.64, 137.99 and 152.99 (pyridine); 163.38 [Pd-C(2)].

2.5 | X-Ray analysis of the palladium-carbene complexes

X-Ray diffraction data were recorded with a STOE IPDS II diffractometer at room temperature using graphite-monochromated Mo Kα radiation by applying the ω-scan method. Data collection and cell refinement were carried out using X-AREA[25] while data reduction was applied using X-RED32.[25] The structures were solved by direct methods with SIR2019[26] and refined by means of the full-matrix full-matrix least-squares calculations on F^2 using SHELXL-2018.[27] All carbon-bound H atoms were located in difference electron-density map and then treated as riding atoms in geometrically idealized positions, with C—H = 0.93 (aromatic CH), 0.97 (CH_2), 0.96 (CH_3) and 0.98 Å (methine CH), and with U_{iso} (H) = kU_{eq}(C), where k = 1.5 for the methyl groups and 1.2 for all other H atoms. In **3c**, there is a disordered solvent water molecule with very large displacement parameters which could not be modeled properly. The diffused electron densities resulting from this were removed by the SQUEEZE routine in PLATON.[28] There are two cavities of volume 105 Å^3 per unit cell centered at (0, 0.5, 0) and (0.5, 1, 0.5). Each cavity contains approximately 23 electrons which were assigned to two solvent water molecules. Since Z is equal to 4, each Pd complex has one solvent water equivalent. In the final refinement, these contributions were removed from the intensity data to produce better refinement results. The crystallographic data and refinement parameters are summarized in Table 1. Molecular graphic was created by using OLEX2.[29]

2.6 | General procedure for the direct arylation of C2-substituted heteroarenes

Typically, C2-substituted heteroarene (2.0 mmol), aryl bromide (1.0 mmol), KOAc (2.0 mmol), and DMA (2 ml) were added to an oven-dried Schlenk tube under argon atmosphere. Subsequently, the Pd–carbene catalyst (**3a–3f**) (0.01 mmol, 1 mol%) was added to stirred solution in a Schlenk tube, and the closed Schlenk tube was stirred at 120°C (oil bath temperature). At the end of the reaction, the solution was cooled to room temperature and dichloromethane (2 ml) was then added to the crude mixture. This solution was used for GC analysis and yields (%) were calculated according to aryl bromide.

3 | RESULTS AND DISCUSSION

3.1 | Synthesis of 1-(2,2-diethoxyethyl) benzimidazole

1-(2,2-Diethoxyethyl)benzimidazole (**1**) was synthesized as previously described in the literature.[24] Compound **1** was synthesized by the reaction of benzimidazole with 2,2-diethoxyethyl bromide in ethyl alcohol at 78°C for 5 h. Then it was isolated as a viscous liquid in moderate

TABLE 1 Crystal data and structure refinement parameters for **3a–3c** and **3f**

Parameters	3a	3b	3c	3f
CCDC depository	1944388	1944389	1944390	1944391
Color/shape	Yellow/prism	Yellow/prism	Yellow/prism	Yellow/prism
Chemical formula	$[PdCl_2(C_{21}H_{26}N_2O_3)(C_5H_5N)]$	$[PdCl_2(C_{23}H_{30}N_2O_2)(C_5H_5N)]$	$[PdCl_2(C_{24}H_{32}N_2O_2)(C_5H_5N)]\cdot H_2O$	$[PdBr_2(C_{28}H_{40}N_2O_2)(C_5H_5N)]$
Formula weight	610.84	622.89	654.93	781.94
Temperature (K)	296(2)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073 Mo Kα	0.71073 Mo Kα	0.71073 Mo Kα	0.71073 Mo Kα
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
Unit cell parameters				
a, b, c (Å)	16.6281(6), 19.8875(6), 8.2339(3)	8.6354(6), 10.7837(8), 16.0757(10)	8.7632(3), 21.2927(7), 16.9191(6)	12.8334(5), 14.2106(7), 22.7943(12)
α, β, γ (deg)	90, 92.511(3), 90	75.347(5), 82.221(5), 79.341(5)	90, 101.907(3), 90	79.628(4), 83.346(4), 63.310(3)
Volume (Å^3)	2720.26(16)	1417.13(17)	3089.05(19)	3650.5(3)
Z	4	2	4	4
$D_{calc.}$ (g/cm^3)	1.491	1.460	1.408	1.423
μ (mm^{-1})	0.910	0.873	0.807	2.727
Absorption correction	Integration	Integration	Integration	Integration
$T_{min.}$, $T_{max.}$	0.7306, 0.9406	0.8575, 0.9751	0.6126, 0.7988	0.2068, 0.8059
F_{000}	1248	640	1352	1584
Crystal size (mm^3)	0.69 × 0.20 × 0.07	0.32 × 0.11 × 0.03	0.79 × 0.36 × 0.34	0.70 × 0.40 × 0.09
Diffractometer	STOE IPDS II	STOE IPDS II	STOE IPDS II	STOE IPDS II
Measurement method	ω scan	ω scan	ω scan	ω scan
Index ranges	$-21 \le h \le 21$, $-25 \le k \le 25$, $-10 \le l \le 10$	$-11 \le h \le 11$, $-13 \le k \le 14$, $-20 \le l \le 20$	$-11 \le h \le 11$, $-27 \le k \le 27$, $-19 \le l \le 22$	$-16 \le h \le 16$, $-18 \le k \le 18$, $-29 \le l \le 29$
θ range for data collection (deg)	$2.048 \le \theta \le 27.754$	$2.410 \le \theta \le 27.705$	$1.913 \le \theta \le 27.721$	$1.740 \le \theta \le 27.727$
Reflections collected	32,424	14,709	21,431	47,604
Independent/observed reflections	6379/4510	6544/3566	7215/4603	17,087/6133
$R_{int.}$	0.0503	0.0839	0.0810	0.1383

(Continues)

TABLE 1 (Continued)

Parameters	3a	3b	3c	3f
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6379/0/319	6544/0/330	7215/0/340	17,087/0/755
Goodness-of-fit on F^2	0.978	0.911	0.930	0.867
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0407$, $wR_2 = 0.0733$	$R_1 = 0.0638$, $wR_2 = 0.0885$	$R_1 = 0.0494$, $wR_2 = 0.1104$	$R_1 = 0.0659$, $wR_2 = 0.1152$
R indices (all data)	$R_1 = 0.0718$, $wR_2 = 0.0807$	$R_1 = 0.1351$, $wR_2 = 0.1038$	$R_1 = 0.0840$, $wR_2 = 0.1227$	$R_1 = 0.2067$, $wR_2 = 0.1520$
$\Delta\rho_{max.}$, $\Delta\rho_{min.}$ (e/Å^3)	0.39, −0.42	0.79, −0.43	0.77, −0.75	1.19, −0.36

to high yield (85%). Compound **1** was characterized by ^{1}H NMR, ^{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 = 14,355 ppm. The signal of the NC*H*N proton was also detected as a singlet at δ = 7.96 ppm for **1**. FT-IR spectra showed a broad band at 1494 cm^{-1} for the -C=N- bond vibration of **1**.

3.2 | Synthesis of NHC ligand precursors

The NHC ligand precursors (**2a**–**2f**) were synthesized by the reaction of 1-(2,2-diethoxyethyl)-benzimidazole with substituted benzyl halides in dimethylformamide at 80° C for 36 h. The salts **2b**–**2d** were synthesized as previously described in the literature.[24] All NHC ligand precursors were characterized by various spectroscopic techniques such as ^{1}H NMR, ^{13}C NMR and FT-IR. The FT-IR data clearly indicated that the **2a–2f** ligand precursors exhibit a characteristic $\nu_{(CN)}$ band typically at 1560, 1560, 1563, 1562, 1557 and 1562 cm^{-1}, respectively. In the ^{1}H NMR spectra, the C(2)–*H* proton downfield resonances of **2a–2f** were observed as sharp singlets at δ = 11.80, 10.78, 10.06, 10.27, 11.28 and 11.30 ppm, respectively. In the ^{13}C NMR spectra, the *C*(2)-carbon resonance of **2a–2f** compounds appeared at δ = 144.12, 143.92, 142.96, 143.38, 143.58 and 143.61 ppm, respectively, as a single signal. These spectroscopic values are in line with those found for other benzimidazolium salts in the literature.[12e–h, 15f, 16h]

3.3 | Synthesis of PEPPSI-themed palladium–carbene complexes

The PEPPSI-themed Pd–carbene complexes (**3a–3f**) were synthesized according to procedures similar to those reported previously by Organ for other Pd–NHC–PEPPSI complexes.[21] The **3a–3f** complexes, which are highly moisture- and air-stable both in solution and in solid state against air, light and moisture, could be stored at room temperature for months without an obvious decline in catalytic efficiency. They are soluble in most organic solvents, such as dichloromethane, chloroform, ethanol and acetonitrile, with the exception of non-polar ones, such as pentane and hexane. Next, Pd-complexes were succesfully characterized by various spectroscopic techniques such as NMR, FT-IR and single-crystal X-ray analysis. In the ^{1}H NMR and ^{13}C NMR spectra of the Pd-complexes, the absence of the characteristic signals of the acidic C(2)-*H* proton and *C*(2)-carbon of the benzimidazolium salts suggests the formation of a Pd–carbene bond. Also, in the ^{13}C NMR spectra, the

characteristic *C*(2)-carbene signals of **3a–3f** complexes appear as singlets at δ = 163.82, 163.80, 163.77, 163.57, 163.43 and 163.38 ppm, respectively. The FT-IR data clearly indicate that the PEPPSI-themed Pd–carbene complexes exhibit a characteristic $\nu_{(CN)}$ band typically between 1400 and 1406 cm^{-1}. Owing to the flow of electrons from the NHC ligand to the Pd, the C–N bond is weakened, and as a result, a decrease in the $\nu_{(CN)}$ stretching frequency is expected. Also, for **3a–3c** and **3 f** complexes appropriate single crystals and structures of these complexes were elucidated by X-ray diffraction studies. These complexes show typical spectroscopic signatures, which are in line with those recently reported for other similar types of Pd–carbene complexes.[12h, 15h]

3.4 | Description of the crystal structures of the palladium–carbene complexes

The molecular diagrams of **3a–3c** and **3f** with the adopted atom-labeling scheme are shown in Figures 2–5, while important bond distances and angles are listed in Table 2. The asymmetric unit of **3f** contains the two independent molecules, labeled **A** and **B**. In the following discussion, parameters related to molecule **B** are given in square brackets.

The Pd–carbene complexes are structurally similar, in which Pd is surrounded by the carbon atom of NHC

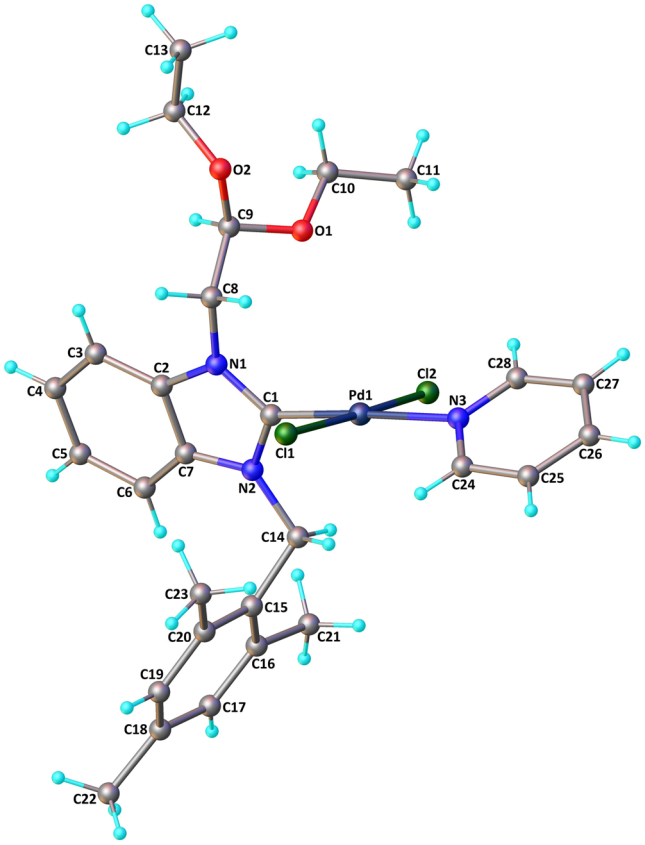


FIGURE 3 Molecular structure of **3b** showing the atom numbering scheme

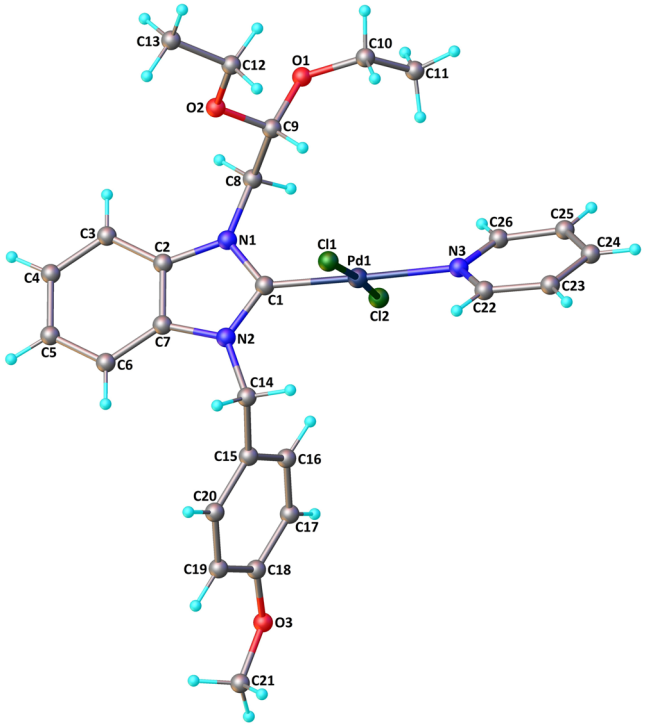


FIGURE 2 Molecular structure of **3a** showing the atom numbering scheme.

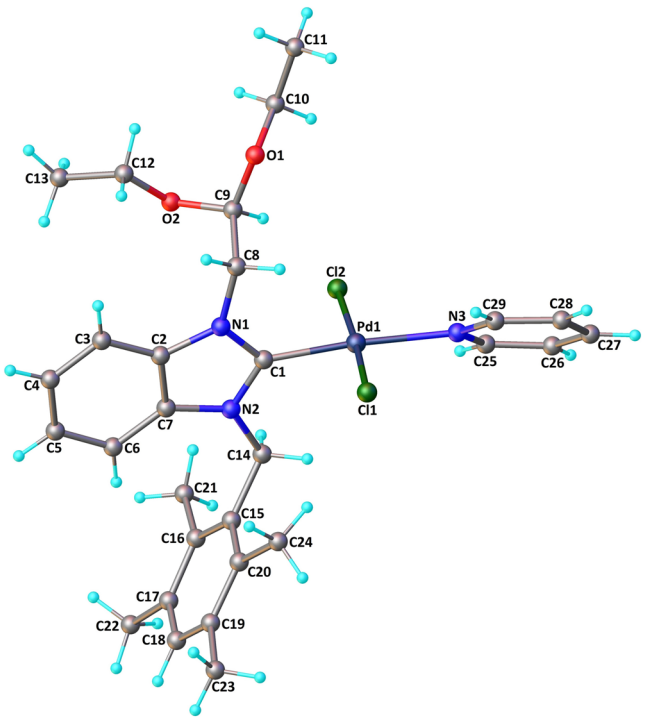


FIGURE 4 Molecular structure of **3c** showing the atom numbering scheme.

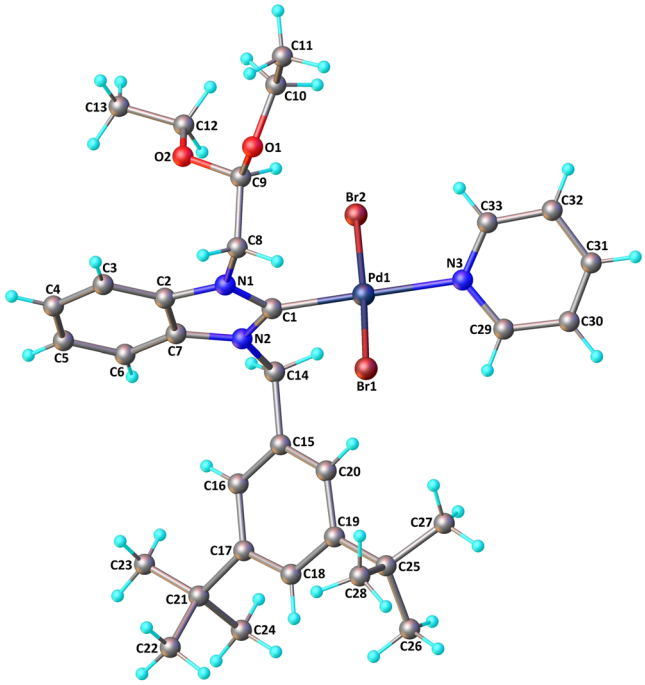


FIGURE 5 Molecular structure of **3f** showing the atom numbering scheme. For the sake of clarity, only molecule A is shown.

and the nitrogen atom of the pyridine ring. The remaining coordination sites are occupied by two chloride atoms in **3a–3c** and by two bromide atoms in **3f**. The metal coordination environments of the complexes feature a slightly distorted square-planar geometry, in which the NHC and pyridine ligands, and the anion atoms are *trans* to each other for all complexes. The *cis* angles varying from 86.0(2) to 92.6(2)° and the *trans* angles changing from 175.11(4) to 178.80(12)° are a little off from the ideal values of 90 and 180°. The two anion atoms are bent toward the NHC ligand rather than the non-bulky pyridine ligand, as evident from the X—Pd—C (X is the anion atom) angles smaller than those for X—Pd—$N_{pyridine}$. The four-coordinate geometry index, τ_4,[30] is 0.04 for **3a**, 0.05 for **3b**, 0.07 for **3c** and 0.05 for **3 f**, which has to be 0 for an ideal square-planar geometry and has to be 1 for a perfect tetrahedral geometry. The values of τ_4 indicate that the coordination polyhedron of the Pd atoms is a slightly distorted square-planar.

The average Pd—C_{NHC} bond distance [1.946 Å] is smaller than the sum of the individual covalent radii of the Pd and carbon atoms (2.12 Å), while the average Pd—$N_{pyridine}$ bond distance [2.109 Å] is nearly equal to the sum of the covalent individual radii of the Pd and nitrogen atoms (2.10 Å).[31] The Pd—Br and Pd—Cl bond lengths are in the typical range, and the internal N—C—N ring angle at the carbene centers varies from 105.9(7) to 107.6(2)° in the complexes. These values lie within the same range as those observed for analogous PEPPSI-themed Pd-complexes.[32] The carbene ring is nearly perpendicular to the $PdCNX_2$ coordination plane with a dihedral angle of 75.58(9)° in **3a**, 68.82(16)° in **3b**, 80.44(12)° in **3c** and 73.8(3)° [77.4(3)°] in **3 f**, which is typical for NHC complexes to reduce steric congestion.

TABLE 2 Selected geometric parameters for **3a–3c** and **3 f**

Parameters	3a	3b	3c	3f	
				Molecule A	Molecule B
Bond lengths (Å)					
Pd1—X1	2.3091(8)	2.305(2)	2.3008(11)	2.4273(12)	2.4286(12)
Pd1—X2	2.2993(9)	2.315(2)	2.3124(12)	2.4247(12)	2.4364(12)
Pd1—N3	2.114(2)	2.129(5)	2.113(3)	2.091(8)	2.096(8)
Pd1—C1	1.953(3)	1.944(5)	1.947(4)	1.946(8)	1.940(8)
N1—C1	1.351(4)	1.346(6)	1.351(5)	1.341(9)	1.357(10)
N2—C1	1.350(4)	1.365(6)	1.356(5)	1.362(8)	1.358(8)
Bond angles (deg)					
X1—Pd1—X2	175.23(3)	176.30(8)	175.11(4)	175.14(5)	175.91(5)
X1—Pd1—N3	92.16(8)	91.90(17)	91.33(10)	90.8(2)	92.6(2)
X2—Pd1—N3	92.40(8)	91.77(17)	92.43(10)	91.1(2)	91.4(2)
X1—Pd1—C1	88.10(8)	88.29(18)	86.33(12)	90.6(2)	89.9(2)
X2—Pd1—C1	87.38(8)	88.07(18)	90.12(12)	87.7(2)	86.0(2)
N3—Pd1—C1	178.80(12)	177.2(2)	175.62(13)	178.0(3)	177.4(3)
N1—C1—N2	107.6(2)	106.5(4)	107.1(3)	106.0(7)	105.9(7)

X1, Cl1 or Br1; X2, Cl2 or Br2.

On the other hand, the dihedral angle between the pyridine ring and the coordination plane is 37.68(14)° for **3a**, 35.8(3)° for **3b**, 41.35(17)° for **3c** and 56.1(6)° [48.7(5)°] for **3 f**.

3.5 | The direct arylation of 2-acetylfuran and 2-acetylthiophene with aryl bromides

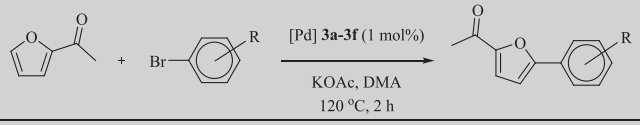
In 1990, the first examples of Pd-catalyzed direct arylation of furans and thiophenes were reported by Ohta.[14b] In this pioneering work, the direct C(2)-arylation of furan and thiophene was carried out in medium to good yields with electron-rich or electron-poor aryl bromides using [Pd $(PPh_3)_4$] as the catalyst, potassium acetate (KOAc) as the base and dimethylacetamide (DMA) as the solvent. In the last two decades, Pd-catalyzed direct arylation was successfully performed using DMA/KOAc combination.[15,16] Therefore, in this study, we selected DMA as the solvent, and KOAc as the base. The direct arylation of furan or thiophene itself to prepare C(2)-arylated products remains difficult as the formation of C(2)- and C(5)-diarylated products from C(2)-arylated products appears to be faster than the C(2)-arylation of furan or thiophene. Therefore, the use of a blocking group at the C(2)-position of furans and thiophenes in order to control the selectivity towards C(5)-arylation has also been described.[12d] Therefore, regioselective arylation on only the C(5)-position of C(2)-blocked furan or thiophene was observed. It is supposed that because the C(2)-position is blocked, the acidic C(5)-position is used for arylation and bonding of electron-deficient aryl groups is difficult compared with electron-rich aryl groups. For this reason, we selected C (2)-blocked 2-acetylfuran and 2-acetylthiophene as heteroaromatic subsrates, and we focused on the direct arylation at the C(5)-position of these heteroarenes.

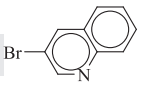
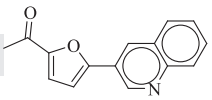
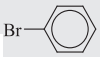
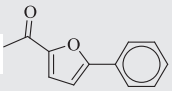
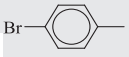
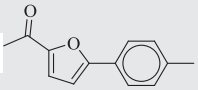
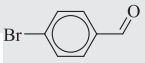
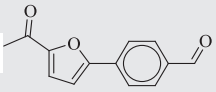
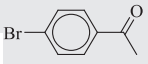
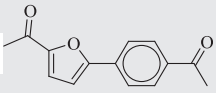
Initially, to optimize the reaction conditions, the arylation of 2-acetylfuran with 3-bromoquinoline was carried out at 120°C for 2 h without the addition of any Pd-catalyst in order to examine the effect of the catalyst on the reaction. No product was formed without the addition of Pd-catalyst (Table 3, entry 1). Then we examined the effect of the reaction time on the reaction. When the reaction time was reduced from 2 to 1 h in the presence of **3f** catalyst, 85% yield was observed (Table 3, entry 2). When the reaction time was reduced to 0.5 h in the presence of **3f** catalyst, the percentage conversion was significantly reduced to 60% with 81% yield (Table 3, entry 3). After these preliminary trials, it was concluded that the best conditions for the direct arlyation were achieved at 120° C, 2 h. Next, we evaluated the scope and limitations of the Pd-complexes **3a–3f** for the direct arylation of 2-acetylfuran and 2-acetylthiophene with different aryl bromides. The reaction worked well for a wide variety of aryl bromides such as 3-bromoquinoline, bromobenzene, 4-bromotoluene, 4-bromobenzaldehyde and 4-bromoacetophenone, affording 2-acetylfuran for 30 examples, and 2-acetylthiophene for another 30 examples, and the results are summarized in Tables 3 and 4, respectively.

Firstly, under the optimal conditions, direct arylation of 2-acetylfuran with aryl bromides was examined and the C (5)-arylated furan derivatives were obtained. Full conversion was obtained when 3-bromoquinoline was used with 2-acetylfuran with 71–85% GC yields (Table 3, entries 4–9). C(5)-arylated 2-acetylfuran was obtained with 85% GC yield in the presence of **3f** catalyst. Similar results were obtained when bromobenzene was used. In this case 2-acetyl-5-phenylfuran was obtained in 68–92% GC yield (Table 3, entries 10–15). 4-Bromotoluene, which contained an electron-rich aryl bromide, was also obtained at 69–87% GC yield with high conversion (Table 3, entries 16–21). 2-Acetyl-5-(4-methylphenyl)furan was obtained with 87% yield in the presence of **3d** catalyst (Table 3, entry 19). The coupling of 2-acetylfuran with electron-poor aryl bromide such as 4-bromobenzaldehyde proceeds nicely. 4-Bromobenzaldehyde gave the C(5)-arylated furan with 69–89% GC yields with full conversion (Table 3, entries 22–27). This product was obtained at 80% yield in the presence of **3f** catalyst (Table 3, entry 27). The electron-poor 4-bromoacetophenone was also a good substrate to afford the corresponding products 2-acetyl-5-(4-acetylphenyl) furan at between 76 and 80% CG yields (Table 3, entries 28–33).

Using the same reaction conditions, we investigated the reactivity of 2-acetylthiophene in Pd-catalyzed direct C(5)-arylation. As shown in Table 4, high-yield C(5)-arylated products were obtained. When 2-acetylthiophene was arylated with 3-bromoquinoline, bromobenzene, 4-bromotoluene, 4-bromobenzaldehyde and 4-bromoacetophenone, products were obtained using only 1 mol% Pd-complexes (**3a–3f**) as catalyst, and yields at 84–90, 67–88, 65–91, 69–85 and 81–92% were observed, respectively (Table 4, entries 1–30). When the reaction of 2-acetylthiophene with 3-bromoquinoline was investigated, C(5)-arylated product was obtained at 90% GC yield in the presence of **3d** catalyst (Table 4, entry 4). The reaction of 2-acetylthiophene with bromobenzene generated the 5-phenyl-2-acetylthiophene at 87 and 88% yield in the presence of **3b** and **3c** catalysts, respectively (Table 4, entries 8,9). The reaction of 2-acetylthiophene with 4-bromotoluene gave the expected product at 91 and 86% yield in the presence of **3b** and **3d** catalysts, respectively (Table 4, entries 14,16). The reaction of 2-acetylthiophene with 4-bromobenzaldehyde gave the expected product at 85% yield in the presence of **3e** catalyst (Table 4, entry 23).

TABLE 3 Pd-catalyzed direct C(5)-arylation of 2-acetylfuran with aryl bromides[a]



Entry	Aryl bromide	[Pd]	Product	Conversion (%)[b]	Yield (%)[c]
1[d]		None		—	—
2[e]		**3f**		85	85
3[f]		**3f**		60	81
4		**3a**		100	79
5		**3b**		100	71
6		**3c**		100	81
7		**3d**		100	74
8		**3e**		100	84
9		**3f**		100	85
10		**3a**		90	71
11		**3b**		96	68
12		**3c**		92	92
13		**3d**		100	90
14		**3e**		94	76
15		**3f**		100	90
16		**3a**		85	69
17		**3b**		100	86
18		**3c**		100	84
19		**3d**		100	87
20		**3e**		96	80
21		**3f**		100	85
22		**3a**		100	82
23		**3b**		100	69
24		**3c**		100	76
25		**3d**		100	75
36		**3e**		100	85
27		**3f**		100	89
28		**3a**		95	76
29		**3b**		95	78
30		**3c**		100	73
31		**3d**		100	71
32		**3e**		100	80
33		**3f**		100	80

[a]Conditions: [Pd] **3a–3f** (0.01 mmol, 1 mol%), 2-acetylfuran (2.0 mmol), aryl bromide (1.0 mmol), KOAc (2.0 mmol), DMA (2 ml), 120°C, 2 h.

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

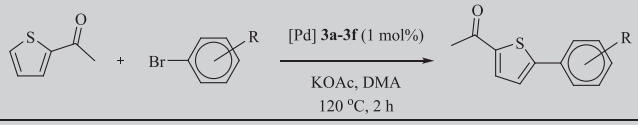
[c]GC yield.

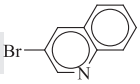
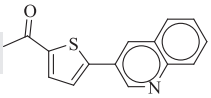
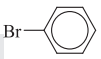
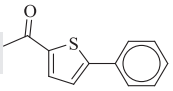
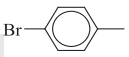
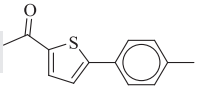
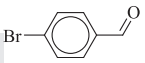
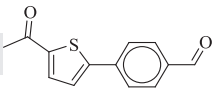
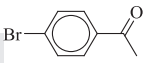
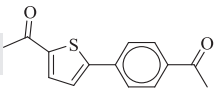
[d]Without any [Pd] catalyst.

[e]The reaction was carried out at 1 h.

[f]The reaction was carried out at 0.5 h.

TABLE 4 Pd-catalyzed direct C(5)-arylation of 2-acetylthiophene with aryl bromides[a]



Entry	Aryl bromide	[Pd]	Product	Conversion (%)[b]	Yield (%)[c]
1		**3a**		100	84
2		**3b**		97	89
3		**3c**		100	87
4		**3d**		100	90
5		**3e**		100	85
6		**3f**		100	88
7		**3a**		90	67
8		**3b**		95	87
9		**3c**		92	88
10		**3d**		95	85
11		**3e**		100	83
12		**3f**		94	83
13		**3a**		90	65
14		**3b**		100	91
15		**3c**		100	83
16		**3d**		100	86
17		**3e**		96	79
18		**3f**		100	84
19		**3a**		97	72
20		**3b**		100	69
21		**3c**		100	71
22		**3d**		100	74
23		**3e**		100	85
24		**3f**		100	74
25		**3a**		100	86
36		**3b**		95	81
27		**3c**		100	86
28		**3d**		100	89
29		**3e**		100	90
30		**3f**		100	92

[a]Conditions: [Pd] **3a–3f** (0.01 mmol, 1 mol%), 2-acetylthiophene (2.0 mmol), aryl bromide (1.0 mmol), KOAc (2.0 mmol), DMA (2 ml), 120°C, 2 h.

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

[c]GC yield.

Moderate to high yields of 5-(4-acetylphenyl)-2-acetylthiophene were obtained for the coupling with 4-bromoacetophenone (Table 4, entries 25–30).

The Pd-catalyzed direct arylation of furan and thiophene with a variety of electrophilic reagents has been previously described.[15,16] In previous studies, similar or close substrates have been employed with higher catalyst loading (1–20 mol%), and a higher reaction time (1–48 h) has been chosen for the direct arylation of furan and thiophene in the presence of Pd-catalysts. In the present work, 1 mol% catalyst loading was used, and the reaction time was shortened to 2 h. Moreover, thiophene and furan derivatives can be efficiently and selectively arylated at the C(5)-position. In this study, satisfactory

results were obtained as compared with previously reported similar studies.[15,16]

Finally, the catalytic activities of the PEPPSI-themed new Pd–carbene complexes were investigated in the direct C(5)-arylation of C(2)-blocked furan and thiophene. In most cases, high yields were observed with all complexes. Only a minor effect of the NHC ligand on the Pd-complex was observed for the coupling of aryl bromide with heteroaromatics. Surprisingly, similar conversions were obtained for the coupling of each aryl bromide. There is no significant difference between these complexes on the catalytic activity of direct arylation of heteroaromatics by aryl bromides. The only significant difference between **3a–3e** complexes indicates that electronic and steric effects also play some role in these processes.

4 | CONCLUSIONS

In summary, we have developed six new well-defined and air-stable PEPPSI-themed Pd–carbene complexes containing a benzimidazole-2-ylidene backbone. The catalytic activity of these Pd–carbene complexes was tested for the direct arylation of 2-acetylfuran and 2-acetylthiophene with aryl bromides using the C–H activation process. It was found that the new Pd-complexes were effective catalysts for this direct arylation. Overall, except in a few cases, satisfactory results were obtained. Since the NHC ligands were similar to each other, no significant difference was observed between the catalytic activities of the Pd-complexes. This study is of environmental and economic interest owing to the low catalyst loading and shorter reaction time. In this study, only AcOH and HBr were formed as a by-products by the use of direct arylation method and thus by-product formation was minimized compared with the multistep traditional transition metal-catalyzed reactions. Also, this study contributes to both organometallic synthesis and the literature in the preparation of bi(hetero)aryl derivatives. Further studies focused on its applicability to other reactions are currently underway in our laboratory.

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SUPPLEMENTARY DATA

CCDC 1944388–1944391 contain the supplementary crystallographic data for the compound reported in this article. These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk, https://www.ccdc.cam.ac.uk/structures/).

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