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The first use of [$PdBr_2$(imidazolidin-2-ylidene)(pyridine)] catalysts in the direct C-H bond arylation of C2-substituted furan and thiophene

Murat Kaloğlu[1,2] · Nazan Kaloğlu[1,2] · Namık Özdemir[3] · İsmail Özdemir[1,2]

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Abstract

N-Heterocyclic carbene (NHC)-linked PEPPSI-type palladium complexes have recently been used in the direct C-H bond arylation of heteroarenes. However, in most of the published works, NHC ligands containing benzimidazole and imidazole ring have been used, but using NHC ligands containing saturated imidazoline ring is quite rare. Therefore, in this study, four new 1,3-disubstituted imidazolinium salts as NHC ligand precursors, and their four new PEPPSI-type palladium complexes were synthesized. The structures of all new compounds were fully characterized by different spectroscopic and analytical techniques. The more detailed structural characterization of one of the palladium complexes was determined by single-crystal X-ray diffraction study. The catalytic activities of all palladium complexes were evaluated in the direct C-H bond arylation of the 2-acetylfuran and 2-acetylthiophene with (hetero) aryl bromides and readily available and inexpensive aryl chlorides in presence of 1 mol% catalyst loading at 120 °C. Under the given conditions, (hetero)aryl halides were successfully applied as the arylating reagents to achieve the C5-arylated furans and thiophenes in acceptable to high yields.

✉ İsmail Özdemir
ismail.ozdemir@inonu.edu.tr
https://www.inonu.edu.tr/

[1] Faculty of Science and Arts, Department of Chemistry, İnönü University, 44280 Malatya, Turkey

[2] Catalysis Research and Application Center, İnönü University, 44280 Malatya, Turkey

[3] Faculty of Education, Department of Mathematics and Science Education, Ondokuz Mayıs University, 55139 Samsun, Turkey

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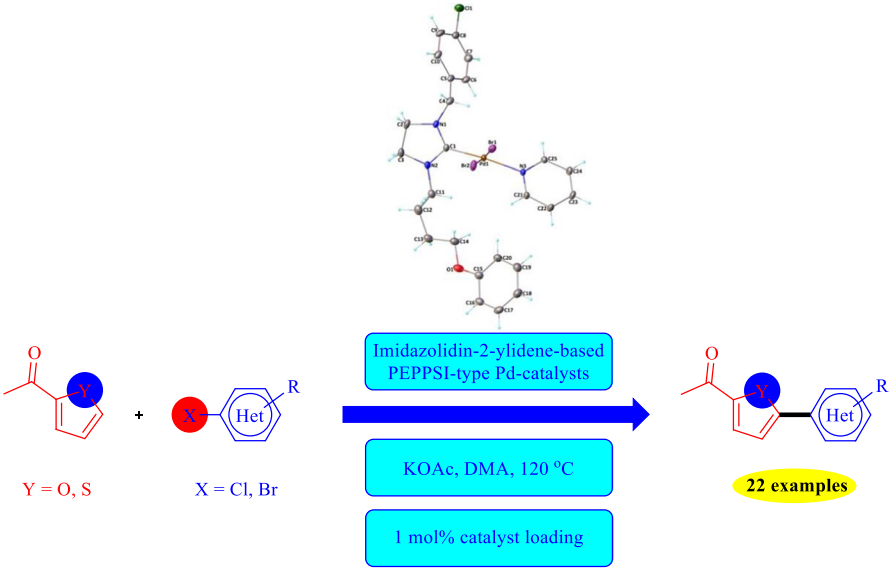
Graphic abstract



Keywords *N*-Heterocyclic carbene · Imidazolidin-2-ylidene · Palladium-PEPPSI complex · Direct C-H bond arylation · Furan · Thiophene

Introduction

Since the first isolation and characterization of stable free carbene by Arduengo in 1991, *N*-heterocyclic carbenes (NHCs) have played a central role as ligands in coordination chemistry [1–7]. In 1995, the first use of the NHCs in palladium-catalyzed Heck reaction by Herrmann revealed that NHCs are effective ligands, and they have emerged as a new ligand class in area of organometallic chemistry and catalysis [8]. The structural variability of NHCs makes them excellent scaffolds that allow to adapt the electronic and steric properties of a particular metal complex. Moreover, the strong σ-donating but poor π-accepting ability of NHCs leads to the formation of many stable metal complexes. Therefore, NHCs offer many advantages over phosphine ligands such as superior activity, stronger σ-donating properties, better stability and structural versatility [9, 10]. As a result of these, the importance of NHCs as ligands for metal complexes used in catalysis, material science and medical applications is unquestionable.

Bi(hetero)aryl substructures, which are important building units, are present in many natural products, biologically active molecules, functional materials and pharmaceuticals [11–13]. The robust synthetic routes for the synthesis of bi(hetero)aryls are still a challenging area of interest due to lower reactivity of heterocycles toward some of the recent booming arena of synthetic chemistry.

Today, developing efficient synthetic approaches to construct new $C(sp^2)$–$C(sp^2)$ bonds of bi(hetero)aryl units by transition-metal-catalyzed reactions is an important research area of modern organic synthesis [14]. Among these reactions, the Suzuki–Miyaura, Stille and Negishi couplings represent some of the important procedures [15–18]. However, they require the preliminary preparation of an organometallic derivative of an aryl derivative and provide an organometallic salt as the by-product. In this regard, the direct arylation of heteroarenes via C-H bond activation has emerged in recent years as an attractive alternative to traditional methods [19–25]. A chief advantage of this protocol is that the major by-products are HX along with a base instead of metallic salts obtained by traditional procedures. Moreover, no prior preparation of an organometallic derivative is required, reducing the number of steps to prepare these compounds [26]. Today, palladium-catalyzed direct arylation of heteroarenes with aryl (pseudo) halides offers a more economical and environmental-friendly approach for the construction of bi(hetero)aryl units because it obviates the use of organometallic reagents, which are generally difficult to synthesize and are, in some cases, unstable [27–32].

The palladium-catalyzed direct arylation of some five-membered heteroaromatics was firstly reported by Nakamura, Tajima and Sakai in 1982 [33]. In 1990, the first examples of palladium-catalyzed direct arylation of furans and thiophenes were reported by Ohta et al. [34]. Since then, the palladium-catalyzed direct arylation of five-membered heteroaromatics with aryl (pseudo)halides has emerged as one of the most powerful methods for the preparation of bi(hetero)aryls. To date, palladium-catalyzed direct arylation of a wide variety of heteroaromatics such as (benzo) furans, (benzo)thiophenes, pyrroles, indoles, thiazoles, oxazoles, imidazoles, pyrazoles or triazoles has been largely described by a large number of researchers [26, 35].

After the discovery of palladium-PEPPSI complexes by Organ et al. in 2006 [36], (PEPPSI = Pyridine Enhanced Precatalyst Preparation Stabilization and Initiation), PEPPSI complexes have shown remarkable catalytic activities toward many organic reactions. Pd-NHC-PEPPSI complexes represent a class of palladium catalysts completely different from other palladium-NHC complexes. Unlike other types of palladium complexes, Pd-NHC-PEPPSI complexes are easier to synthesize and use [37]. The high activity of Pd-NHC-PEPPSI complexes in catalysis has been based on to the presence of a loosely bound throw-away pyridine ligand that makes way for the incoming substrate [38]. Despite the fact that palladium-catalyzed direct arylation has become invaluable for catalysis chemistry, and significant advances have been reported, Pd-NHC-PEPPSI complexes have been weakly applied as catalysts in the direct arylation reactions to date [39]. However, in a limited number of studies, several examples about synthesis of Pd-NHC-PEPPSI complexes bearing (benz)imidazol-2-ylidene ligands and their catalytic application in the direct arylation reactions were reported to date by various research groups [40, 41]. In some cases, saturated ring imidazolidin-2-ylidene-based palladium complexes for the direct C-H bond arylation of heteroaromatic compounds are known to exhibit higher efficiency than their structurally analog unsaturated ring imidazol-2-ylidene-based palladium complexes [42,

43]. But, to the best of our knowledge, only very few reports are available on the direct arylation of heteroarenes with (hetero)aryl halides over Pd-NHC-PEPPSI complexes exploiting imidazolidin-2-ylidene ligand [44–46].

In the light of the information mentioned above, recently, we have reported the first examples of the direct C4-arylation of 3,5-dimethylisoxazole [47], and the direct C5-arylation of *N*-methylpyrrole-2-carboxaldehyde [48], with (hetero)aryl halides catalyzed by Pd-NHC-PEPPSI complexes bearing imidazolidin-2-ylidene ligand. These exciting results thus prompted us to further investigate its application on the direct arylation of other heteroarenes catalyzed by imidazolidin-2-ylidene-based palladium-PEPPSI catalysts. In this regard, herein, we have synthesized a series of new imidazolinium salts (**3a–3d**) as carbene precursors and their corresponding palladium-PEPPSI complexes (**4a–4d**) (Fig. 1). All new compounds were characterized by different techniques such as ^{1}H NMR, ^{13}C NMR, FT-IR and elemental analysis. Also, the solid-state structure of the palladium complex **4d** has been established by single-crystal X-ray diffraction study. Then, the catalytic properties of all palladium complexes were evaluated in the direct C5-arylation of the 2-acetylfuran and 2-acetylthiophene with (hetero)aryl halides in presence of 1 mol% palladium catalyst loading. The C5-arylated furans and thiophenes were selectively obtained in moderate to high yields. To the best of our knowledge, this work is the first report of the direct C5-arylation of 2-substituted furan and thiophene with (hetero)aryl halides in presence of imidazolidin-2-ylidene-based palladium-PEPPSI complexes.

Results and discussion

General procedure

The general synthesis pathway for the *N*-(4-phenoxybutyl)ethylenediamine (**1**), 1-(4-phenoxybutyl)imidazoline (**2**), 1,3-disubstituted imidazolinium salts (**3a**–**3d**), and their corresponding Pd-NHC-PEPPSI complexes (**4a–4d**) is shown in the Scheme 1. Some physical and spectroscopic data of the compounds **1–4** are summarized in Table 1.

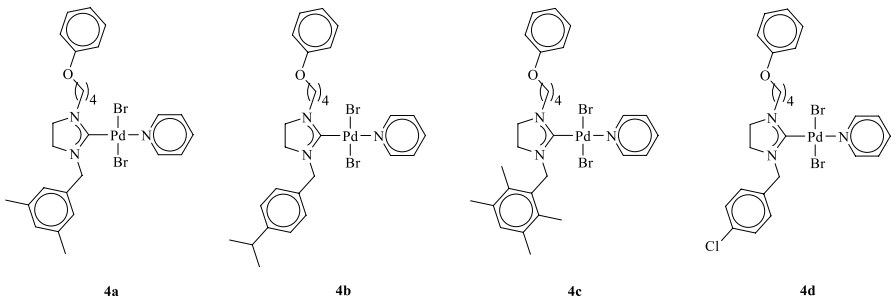
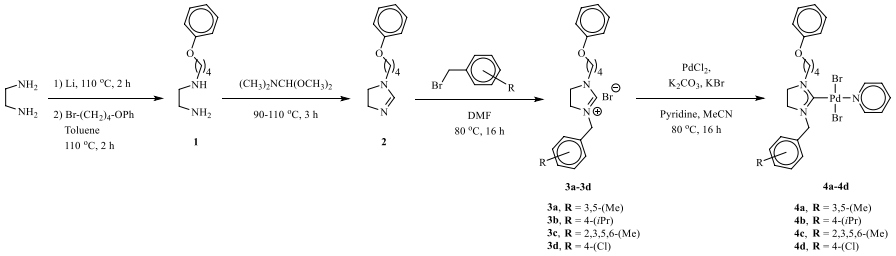


Fig. 1 Imidazolidin-2-ylidene based palladium-PEPPSI complexes used in this study



Scheme 1 The general synthesis pathway of compounds **1**–**4**

Table 1 Physical and spectroscopic properties of the compounds **1–4**

Compound	Formula	Isolated yield (%)	M.p. (°C)	IR ($\nu_{C(2)\text{-}N}$) (cm^{-1})	^{1}H NMR (C(2)-*H*) (ppm)	^{13}C NMR (*C*(2)) (ppm)
1	$C_{12}H_{20}N_2O$	75	110-115[a]	—	—	—
2	$C_{13}H_{18}N_2O$	91	125-130[a]	1598	6.87	158.86
3a	$C_{22}H_{29}BrN_2O$	80	79–80	1655	9.98	158.14
3b	$C_{23}H_{31}BrN_2O$	72	89–90	1661	10.00	158.13
3c	$C_{24}H_{33}BrN_2O$	69	134–135	1650	9.29	157.21
3d	$C_{20}H_{24}BrClN_2O$	78	79–80	1665	9.99	158.37
4a	$C_{27}H_{33}Br_2N_3OPd$	46	124–125	1602	—	180.70
4b	$C_{28}H_{35}Br_2N_3OPd$	42	69–70	1600	—	180.77
4c	$C_{29}H_{37}Br_2N_3OPd$	35	192–193	1600	—	181.40
4d	$C_{25}H_{28}Br_2ClN_3OPd$	50	120–121	1597	—	181.38

[a] Boiling point under ~ 50 Torr pressure

Preparation and characterization of *N*-(4-phenoxybutyl)ethylenediamine (1)

N-Alkylation of the ethylenediamine with 4-phenoxybutyl bromide gave the *N*-(4-phenoxybutyl)ethylenediamine (**1**) as colorless viscous liquid in 75% yield. This compound was characterized by ^{1}H NMR and ^{13}C NMR and IR spectroscopy, and elemental analysis studies. In the ^{1}H NMR spectra of the **1**, the signal of the N–H protons of ethylenediamine was detected as multiplet between $\delta = 1.54$–1.60 ppm, and aliphatic CH_2 protons of ethylenediamine were detected as multiplet between $\delta = 2.57$ and 2.61 ppm in accordance with the expected integrals. Aliphatic CH_2 protons of 4-phenoxybutyl substituent were detected as pentet at $\delta = 1.58$ and 1.74 ppm and were detected as triplet at $\delta = 2.71$ and 3.88 ppm. Aromatic ring protons of 4-phenoxybutyl substituent were detected as multiplet between $\delta = 6.79$ and 7.20 ppm with 5H intensity. In ^{13}C NMR spectra, aliphatic carbon resonances of ethylenediamine appeared at $\delta = 41.76$ and 49.52 ppm as single signal. Aliphatic carbon resonances of 4-phenoxybutyl substituent were detected at $\delta = 26.79$, 27.12, 52.47 and 67.60 ppm. Aromatic ring carbon resonances of

4-phenoxybutyl substituent appeared at $\delta = 114.48$, 120.53, 129.41 and 159.01 ppm. IR data clearly indicated that *N*-(4-phenoxybutyl)ethylenediamine exhibits a characteristic $\nu_{(C\text{-}N)}$ and $\nu_{(N\text{–}H)}$ band. In the IR spectra, C-N bond vibrations of the **1** were observed as sharp band at 1032 and 1241 cm^{-1}. N–H bond vibration also appeared as a broadband at 3290 cm^{-1}. Elemental analysis data of the **1** were also consistent with the expected structure.

Preparation and characterization of 1-(4-phenoxybutyl)imidazoline (2)

As can be seen in Scheme 1, the 1-(4-phenoxybutyl)imidazoline (**2**) was obtained by cyclization of the *N*-(4-phenoxybutyl)ethylenediamine (**1**) with *N*,*N*-dimethylformamide dimethyl acetal, as yellowish viscous liquid in 96% yield. The formation of the **2** was confirmed by the characteristic signals in ^{1}H NMR and ^{13}C NMR spectra, and elemental analysis data. In ^{1}H NMR spectra, characteristic C(2)-*H* proton down-field resonance of the **2** was observed as a sharp singlet at $\delta = 6.87$ ppm. Aliphatic C(4)-*H* and C(5)-*H* protons of imidazoline ring were detected as triplet at $\delta = 3.24$ and 3.84 ppm in accordance with the expected integrals, respectively. In ^{13}C NMR spectra, *C*(2) carbon resonance of imidazoline ring appeared at $\delta = 158.86$ ppm as a single signal, while *C*(4) and *C*(5) carbon resonances were observed at $\delta = 47.40$ and 48.39 ppm. The IR spectrum of the **2** displays the characteristic vibration band of C=N bond at 1598 cm^{-1}. Also, C-N bond vibrations of the **2** were observed as a sharp band at 1022 and 1240 cm^{-1}. These data suggest the formation of imidazoline ring. Elemental analysis data were also consistent with the expected structure.

Preparation and characterization of imidazolinium salts as carbene precursors (3a–3d)

The new imidazolinium salts **3a**-**3d** were synthesized as carbene precursors by interaction of the 1-(4-phenoxybutyl)imidazoline (**2**) with substituted benzyl bromides. The reactions were carried out in anhydrous dimethylformamide (DMF) at 80 °C for 16 h, and the target salts were obtained as white solids between 69 and 80% yields. The imidazolinium salts were fully characterized by the combination of ^{1}H NMR, ^{13}C NMR, and IR spectroscopic techniques and elemental analyses. In the ^{1}H NMR spectra, the signal of the acidic C(2)-*H* proton down-field resonance of imidazolinium ring for **3a–3d** salts was observed as sharp singlets at $\delta = 9.98$, 10.00, 9.29 and 9.99 ppm, respectively. Aliphatic CH_2 protons of benzyl substituents for imidazolinium salts **3a**–**3d** were detected as singlet at $\delta = 4.75$, 4.81, 4.87 and 4.88 ppm, respectively. In the ^{13}C NMR spectra, *C*(2)-carbon resonances of the **3a**–**3d** salts appeared at $\delta = 158.14$, 158.13, 157.21 and 158.37 ppm, respectively, as single signal. These downfield signals indicate the formation of imidazolinium salts. Also, aliphatic carbon resonances of benzyl substituents for the **3a**–**3d** salts were detected as single signal at $\delta = 52.25$, 51.94, 48.15 and 51.41 ppm, respectively. As shown in Table 1, the IR data clearly indicated that the imidazolinium salts **3a–3d** exhibit a characteristic $\nu_{C(2)\text{-}N}$ vibration band typically at 1655, 1661,

1650 and 1665 cm^{-1}, respectively. Elemental analysis data were also consistent with the expected structures.

Preparation and characterization of palladium-carbene complexes (4a–4d)

As can be seen in Scheme 1, the new palladium-carbene complexes **4a–4d** were prepared by metallation of the corresponding imidazolinium salts (**3a–3d**) with $PdCl_2$. The reactions were carried out in presence of pyridine as *N*-donor ligand in acetonitrile (MeCN) at 80 °C for 16 h, and the target complexes were obtained as yellow solids between 35 and 50% yields. These PEPPSI-type palladium-carbene complexes were very stable against air and moisture in the solid state. They are soluble in most organic solvents, such as CH_2Cl_2, $CHCl_3$, EtOAc and DMSO, with the exception of non-polar ones, such as pentane, hexane and Et_2O. Formation of palladium-carbene complexes is supported by NMR, IR spectroscopies and elemental analysis techniques. In the ^1H NMR spectra of complexes **4a–4d**, the characteristic down-field signals for the acidic C(2)–H protons of the imidazolinium salts **3a–3d** disappeared in the ^1H NMR spectra of the palladium-carbene complexes. In addition, the down-field signals of pyridine ligand between $\delta = 7.21$ and 8.97 ppm indicate the formation of PEPPSI-type palladium-carbene complexes. ^{13}C NMR chemical shifts provide a useful diagnostic tool for metal-carbene complexes. In the ^{13}C NMR spectra of complexes **4a–4d**, characteristic signal of *C*(2)-carbon of imidazolinium salts **3a–3d** between $\delta = 157.21$ and 158.37 ppm were completely disappeared, and the characteristic Pd–*C*(2) carbene bond signals of the complexes **4a–4d** were observed as singlet. In the ^{13}C NMR spectra, the carbene signals of the palladium-complexes **4a–4d** were observed at $\delta = 180.70$, 180.77, 181.40 and 181.38 ppm, respectively. Also, characteristic down-field signals of the aromatic carbons of the pyridine ligand support the formation of PEPPSI-type palladium-carbene complexes. The IR data clearly indicated that palladium-carbene complexes exhibit a characteristic $\nu_{(CN)}$ stretching frequency peaks typically between 1597 and 1602 cm^{-1}. Due to the flow of electrons from the imidazolidin-2-ylidene ligand to the palladium, the C-N bond is weakened, and as a result, a decreasing in the $\nu_{(CN)}$ stretching frequency is expected. Also, the microanalysis data of the palladium-carbene complexes agree closely with the theoretical requirements of their structures.

Description of the crystal structure of the palladium-carbene complex 4d

The molecular structure of complex **4d** with the adopted atom-labeling scheme is shown in Fig. 2, while important bond distances and angles are listed in Table 2. There are two crystallographically independent molecules in the asymmetric unit of the complex. In the following discussion, parameters related to the second molecule are given in square brackets.

The complex has a slightly distorted square-planar geometry, the metal center being coordinated to the carbenic carbon atom of NHC ligand, the nitrogen atom of the pyridine ring, and two bromo ligands in a *trans* configuration. In the square-planar coordination, atoms Pd1, Br1, Br2, N3 and C1 deviate by

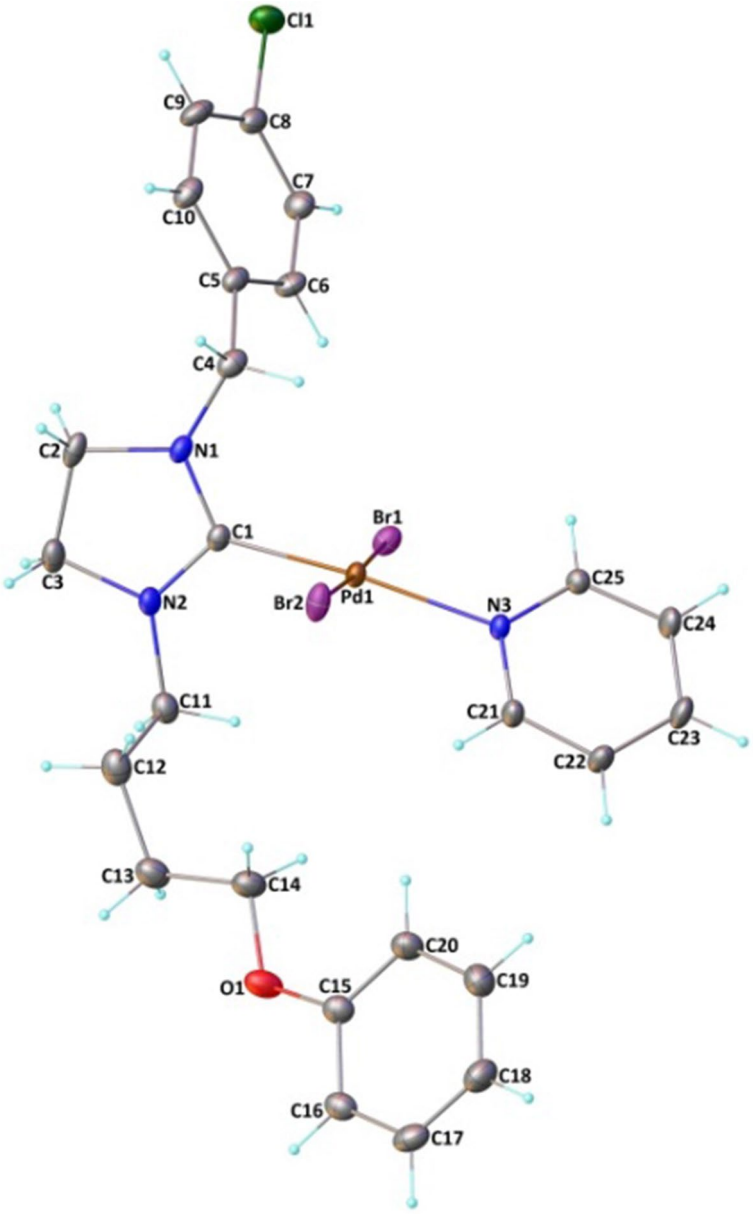


Fig. 2 Molecular structure of complex **4d**, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 10% probability level and H atoms are shown as small spheres of arbitrary radii. For the sake of clarity, only one of two molecules in the asymmetric unit is shown

0.0218(4) [0.0102(4)], 0.0529(6) [0.0957(6)], 0.0528(7) [0.0961(6)], − 0.060(4) [− 0.094(4)] and − 0.068(5) [− 0.108(4)] Å, respectively, from the mean plane through these five atoms. The *cis* angles varying from 88.08(13) to 92.03(10)°

Table 2 Selected geometric parameters for complex **4d**

Parameters	Molecule I	Molecule II
Bond lengths (Å)		
Pd1—Br1	2.4247(6)	2.4234(6)
Pd1—Br2	2.4263(7)	2.4262(6)
Pd1—N3	2.107(3)	2.110(4)
Pd1—C1	1.962(5)	1.959(5)
N1—C1	1.321(6)	1.322(6)
N1—C2	1.466(6)	1.462(6)
N2—C1	1.318(6)	1.319(6)
N2—C3	1.461(6)	1.459(7)
Bond angles (°)		
Br1—Pd1—Br2	176.96(3)	174.98(3)
Br1—Pd1—N3	90.69(10)	91.17(9)
Br2—Pd1—N3	92.03(10)	91.98(9)
Br1—Pd1—C1	89.32(13)	89.32(12)
Br2—Pd1—C1	88.08(13)	87.97(12)
N3—Pd1—C1	175.14(19)	173.72(19)
N1—C1—N2	110.3(4)	110.0(4)

[from 87.97(12) to 91.98(9)°] and the *trans* angles changing from 175.14(19) to 176.96(3)° [from 173.72(19) to 174.98(3)°] deviate from their expected values of 90 and 180°. For quantitative evaluation of the extent of distortion around the metal center, the structural indexes τ_4 [49] and $\tau_4^{'}$ [50] were employed; where α and β ($\beta > \alpha$) are the two greatest valence angles [$\beta = 176.96°$ and $\alpha = 175.14°$ for molecule **I** and $\beta = 174.98°$ and $\alpha = 173.72°$ for molecule **II**] and θ is the ideal tetrahedral angle ($\theta = 109.5°$).

$$\tau_4 = \frac{360° - (\alpha + \beta)}{360° - 2\theta} \quad \tau_4' = \frac{\beta - \alpha}{360° - \theta} + \frac{180° - \beta}{180° - \theta}$$

The calculated τ_4 and $\tau_4^{'}$ geometry indices are 0.06 [0.08] and 0.05 [0.08], respectively, pointing out a slightly distorted square-planar geometry.

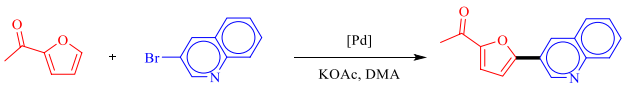
Although the Pd—C_{NHC} bond distance of 1.962(5) [1.959(5) Å] is smaller than the sum of the individual covalent radii of the palladium and carbon atoms (2.12 Å), the Pd—$N_{pyridine}$ bond distance of 2.107(3) [2.110(4) Å] is equal to the sum of the individual covalent radii of the palladium and nitrogen atoms (2.10 Å) [51]. The Pd—Br bond lengths are found in the typical range, and all the aforementioned values are comparable with those found in other Pd-NHC-Pyridine-Br_2 complexes [23, 52–57]. In the NHC ligands, the internal N—C—N ring angle at the carbene center is 110.3(4)° [110.0(4)]. The carbene ring is almost perpendicular to the $PdCNBr_2$ coordination plane with a dihedral angle of 88.4(2)° [83.9(2)°], which is typical for NHC complexes to reduce steric congestion. Furthermore, the dihedral angle between the pyridine ring and the coordination plane is found to be 49.8(2)° [48.1(2)°].

Influence of the reaction conditions for the palladium-carbene catalyzed direct arylation

In order to determine the most suitable conditions in the palladium-carbene catalyzed direct arylation of C2-substituted furan and thiophene, as can be seen in Eq. 1, the reaction of 2-acetylfuran with 3-bromoquinoline was examined as a model reaction. Last two decades, the palladium-catalyzed direct arylation of five-membered heterocycles was successfully performed using DMA/KOAc combination. Based on previously reported conditions for the direct arylation of furan and thiophene [58–71], we employed KOAc (2 equiv.) as the base and DMA as the solvent. The effect of the catalysts, temperature, reaction time and catalyst loading was examined on the reaction. Yields were calculated with respect to 3-bromoquinoline from the GC results. Selected results from our preliminary studies are summarized in Table 3.

The arylation of 2-acetylfuran with 3-bromoquinoline was carried out at 150 °C for 4 h without the addition of any palladium catalyst in order to examine the effect of the catalyst on the reaction. However, under these reaction conditions, no formation of the desired product was obtained (Table 3, entry 1). In order to identify the most active catalyst among complexes **4a–4d**, reactions were carried out at 150 °C in DMA with a palladium-loading of 1 mol% (Table 3, entries 2–5). In the presence of these catalysts, yields ranged from 90 to 97%. As a result of these preliminary studies, it was observed that the most active catalyst was complex **4c** with 97% yield

Table 3 The direct C5-arylation of 2-acetylfuran with 3-bromoquinoline[a]



Entry	[Pd] (mol-%)	Temperature (°C)	Time (h)	Yield (%)[b]
1	—	150	4	—
2	**4a** (1)	150	4	94
3	**4b** (1)	150	4	91
4	**4c** (1)	150	4	97
5	**4d** (1)	150	4	90
6	$PdCl_2$ (1)	150	4	78[c]
7	**4c** (1)	120	4	95
8	**4c** (1)	90	4	67
9	**4c** (1)	120	3	95
10	**4c** (1)	120	2	92
11	**4c** (1)	120	1	72
12	**4c** (0.5)	120	2	55

[a]Conditions: 2-acetylfuran (2 equiv.), 3-bromoquinoline (1 equiv.), KOAc (2 equiv.), DMA (2 mL)

[b]Yields were calculated with respect to 3-bromoquinoline from the results of GC spectrometry

[c]*In situ* generated catalytic system with **3c** salt as carbene precursor (2 equiv.) and $PdCl_2$ (1 equiv.) was used

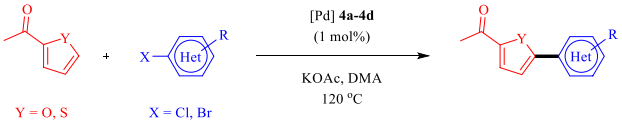
(Table 3, entry 4). It was observed that the catalytic activity of complexes **4a–4d** was enhanced by having sterically hindered and bulky groups on the NHC ligand.

When in situ generated palladium/ligand catalytic system with 2 mol% of **3c** NHC precursor and 1 mol% of $PdCl_2$ was used at 150 °C for 4 h, only 78% yield was observed (Table 3, entry 6). Thus, it was understood that isolated palladium complex **4c** was more active than in situ generated palladium/ligand system. Later, the effect of temperature on the yield was examined. When the temperature is reduced from 150 °C to 120 °C in presence of 1 mol% catalyst **4c**, the yield decreased to 95% (Table 3, entry 7). However, this decrease in the yield is within acceptable limits. When the reaction temperature was decreased from 120 °C to 90 °C in presence of 1 mol% catalyst **4c**, it was observed that the yield decreased up to 67% (Table 3, entry 8). At this temperature, the reaction did not take place in satisfactory yield. Therefore, it was decided that the optimum temperature for the model reaction was 120 °C. Next, the effect of the reaction time on the yield was examined. When the reaction time was regularly reduced from 4 to 2 h, no significant difference was observed on the yield (Table 3, entries 9,10). But, when the reaction time was reduced from 2 to 1 h, the yield dropped to 72% (Table 3, entry 11). Therefore, the optimum reaction time for the model reaction was decided to be 2 h. Finally, the effect of catalyst-loading on the yield was also investigated. When the catalyst-loading was decreased from 1 mol% to 0.5 mol% at 120 °C, only 55% yield was achieved after 2 h (Table 3, entry 12).

After these preliminary studies summarized in Table 3, we tried to evaluate the scope and limitations of the palladium-carbene catalysts **4a–4d** for the direct C5-arylation of 2-acetylfuran and 2-acetylthiophene with (hetero)aryl halides (Eq. 2). The reaction worked well for a wide variety of (hetero)aryl bromides, and even some aryl chlorides. The results of the direct C5-arylation of 2-acetylfuran and 2-acetylthiophene with (hetero)aryl halides are summarized in Table 4.

When the reaction of 2-acetylfuran with a neutral aryl bromide such as bromobenzene was investigated, yields at between 65 and 90%. When bromobenzene and 2-acetylthiophene were interacted, 71–88% yields were obtained (Table 4, entries 1–4). When chlorobenzene was used with both heterocycles in the presence of **4c** catalyst, which is the most active catalyst, high yields could not be obtained despite the 18 h reaction (Table 4, entry 3). When the reaction of both heterocycles with an electron-rich aryl bromide such as 4-bromotoluene was investigated, yields were obtained at between 60 and 88% for 2-acetylfuran and 71–91% for 2-acetylthiophene (Table 4, entries 5–8). When 4-chlorotoluene was used as aryl halide, after 18 h, moderate yields were obtained in presence of **4c** catalyst for both heterocycles (Table 4, entry 7). Similar yields were obtained for 2-acetylfuran (58–90%) and 2-acetylthiophene (55–87%) using 4-bromoanisole for 4 h by using only 1 mol% **4a**–**4d** complexes (Table 4, entries 9–12). But, when 4-chloroanisole was used in presence of **4c** catalyst, 55% and 61% yields were observed for the 2-acetylfuran and 2-acetylthiophene after 18 h, respectively (Table 4, entry 11). When the electron-withdrawing *para*-substituents such as aldehyde, acetyl, fluoro and trifluoromethyl on the aryl bromide were investigated with 2-acetylfuran, the target products were obtained in moderate to high yields in presence of 1 mol% **4a–4d** catalysts after 2 h. When electron-withdrawing *para*-substituents were used with 2-acetylthiophene,

Table 4 The Pd-carbene catalyzed direct C5-arylation of 2-acetylfuran and 2-acetylthiophene with (hetero)aryl halides[a]



(Eq. 2)

Entry	(Hetero)aryl halide	[Pd]	Product	Time (h)	Yield (%)[b,c]	
					Y = O	Y = S
1		**4a**		2	82	84
2		**4b**		2	71	79
3		**4c**		2	90 (66)	88 (57)
4		**4d**		2	65	71
5		**4a**		2	85	80
6		**4b**		2	76	71
7		**4c**		2	88 (70)	91 (73)
8		**4d**		2	60	75
9		**4a**		4	75	71
10		**4b**		4	58	55
11		**4c**		4	90 (55)	87 (61)
12		**4d**		4	74	60
13		**4a**		2	95 (82)	88
14		**4b**		2	81	75
15		**4c**		2	93	96 (87)
16		**4d**		2	76	79
17		**4a**		2	94	86
18		**4b**		2	88	80
19		**4c**		2	97 (84)	97 (83)
20		**4d**		2	78	79
21		**4a**		2	86	78
22		**4b**		2	81	69
23		**4c**		2	91	88
24		**4d**		2	73	76
25		**4a**		2	80	84
26		**4b**		2	62	80
27		**4c**		2	89 (75)	92 (81)
28		**4d**		2	70	67
29		**4a**		8	77	71
30		**4b**		8	58	52
31		**4c**		8	84	74
32		**4d**		8	45	39
33		**4a**		4	78	85
34		**4b**		4	64	62
35		**4c**		4	83	91
36		**4d**		4	55	67
37		**4a**		2	88	83
38		**4b**		2	81	70
39		**4c**		2	92	86
40		**4d**		2	83	67
41		**4a**		4	77	63
42		**4b**		4	61	60
43		**4c**		4	80	77
44		**4d**		4	48	49

[a] Conditions: [Pd] **4a–4d** (0.01 equiv., 1 mol%), 2-acetylfuran or 2-acetylthiophene (2 equiv.), (hetero) aryl halide (1 equiv.), KOAc (2 equiv.), DMA (2 mL), 120 °C

[b] Yields were calculated with respect to (hetero)aryl halide from the results of GC spectrometry

[c] Yields of the aryl chlorides obtained at 18 h were shown in parentheses

similar results were also obtained (Table 4, entries 13–28). However, the *para*-substituted 4-chlorobenzaldehyde, 4-chloroacetophenone and 4-chlorobenzotrifluoride led to the formation of the target products in moderate yields after 18 h. When

sterically hindered electron-donating 2-bromotoluene was used as aryl halide with 2-acetylfuran, 84% yield was obtained in the presence of **4c** catalyst after 8 h. When 2-acetylthiophene was used under the same conditions, the yield dropped to 74% (Table 4, entry 31). In the presence of 2-bromobenzonitrile, yields varying between 55 and 83% with 2-acetylfuran and 62–91% with 2-acetylthiophene were obtained after 4 h (Table 4, entries 33–36). Then, we examined the reactivities of electron-deficient heterocycles such as 3-bromoquinoline and 2-bromothiophene as heteroaryl bromides. When 3-bromoquinoline was used, high yields were obtained for both 2-acetylfuran and 2-acetylthiophene in the presence of **4e-4 h** catalysts after 2 h (Table 4, entries 37–40). When 2-bromothiophene was used as the coupling partner, a yield of 80% was obtained at the end of 4 h for 2-acetylfuran in the presence of **4c** of catalyst, while a yield of 77% was obtained for 2-acetylthiophene (Table 4, entry 43).

As a result, we investigated that the catalytic activities of imidazolidin-2-ylidene-linked palladium-PEPPSI complexes in the direct C5-arylation 2-acetylfuran were similar to 2-acetylthiophene with (hetero)aryl bromides and aryl chlorides by applying short time periods. The catalytic system was tolerable to a variety of functional groups such as aldehyde, acetyl, fluoro, trifluoromethyl and nitrile on the aryl halides, producing the corresponding products in moderate to high yields. Generally, the reactivity of 2-acetylfuran was similar to 2-acetylthiophene, and the yields for substrates containing electron-withdrawing groups were higher than those for substituents containing electron-donating group. Although small differences in reactivities were observed for **4a**-**4d** catalysts due to similar nature of the NHC moieties, it can be said that the most effective catalyst in the direct arylation of heteroaromatics is complex **4c** containing bulky 2,3,5,6-tetramethylbenzyl substituent.

Conclusion

In summary, we prepared a series of four new imidazolinium salts as imidazolidin-2-ylidene ligand precursors, and their four new PEPPSI-type palladium complexes. All new compounds were characterized using different spectroscopic and analitical techniques. The catalytic activities of the all palladium complexes were investigated in the direct C5-arylation of 2-acetylfuran and 2-acetylthiophene with (hetero)aryl halides. It was found that all the palladium complexes were effective catalysts for these reactions. Overall, except in a few cases, satisfactory results were obtained in all trials. This study was performed by using 1 mol% of palladium catalyst. Therefore, this low catalyst loading procedure was economically attractive. In this study, only AcOH and HBr were formed as a by-product by the use of direct arylation method and thus the by-product formation was minimized compared to the multi-step traditional transition metal-catalyzed reactions. To our knowledge, this study is the first report of the direct C5-arylation of 2-acetylfuran and 2-acetylthiophene with (hetero)aryl halides catalyzed by imidazolidin-2-ylidene-linked palladium-PEPPSI complexes. Moreover, further studies focused on the synthesis of new imidazolidin-2-ylidene-linked palladium-PEPPSI complexes and their catalytic application for the C-H bond arylation of heteroarenes are currently underway by our research group.

Experimental

General remarks

All manipulations were performed in Schlenk-type flasks under argon atmosphere. The melting point measurements were determined in open capillary tubes with an Electrothermal-9200 melting points apparatus. The C, H and N elemental analysis measurements were determined by LECO CHNS-932 elemental analyzer. The FT-IR spectra were recorded on GladiATR unit (Attenuated Total Reflection) in the range of 450–4000 cm^{-1} with a Perkin Elmer Spectrum 100 Fourier-transform infrared spectrometer. Routine ^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker Ascend™ 400 Avance III HD NMR spectrometer with sample solutions prepared in $CDCl_3$. The chemical shifts (δ) were reported in parts per million (ppm) relative to tetramethylsilane (TMS) as internal standard. Coupling constants (J values) were given in hertz. NMR multiplicities were abbreviated as follows: s = singlet, d = doublet, t = triplet, p = pentet, dd = doublet of doublets, tt = triplet of triplets, ddd = doublet of doublet of doublets, m = multiplet. ^{1}H NMR spectra were referenced to residual protiated solvents ($\delta = 7.28$ ppm for $CDCl_3$), ^{13}C NMR chemical shifts were reported relative to deuterated solvents ($\delta = 77.16$ ppm for $CDCl_3$). The catalytic solutions were analyzed with a Shimadzu GC 2025 equipped with GC-FID sensor and RX-5 ms column of 30 m length, 0.25 mm diameter and 0.25 μm film thickness.

Preparation of *N*-(4-phenoxybutyl)ethylenediamine (1)

The *N*-(4-phenoxybutyl)ethylenediamine (**1**) was prepared by the *N*-alkylation of the ethylenediamine with 4-phenoxybutyl bromide. Lithium (0.35 g; 50 mmol) was little by little added in freshly distilled and dried ethylenediamine (30 mL) under argon atmosphere at 110 °C. The solution, which was stirred for 1 h, was then cooled to room temperature, and 4-phenoxybutyl bromide (11.5 g; 50.2 mmol) was added to this solution. Then, anhydrous toluene (30 mL) was added to the solution. After 1 min, lithium bromide precipitate started to form. The mixture was stirred for a further 1 h at 110 °C, and it was then cooled to room temperature. The precipitated lithium bromide was removed by filtered off and was washed with 20 mL of toluene. Then, all volatiles were removed under vacuum. The crude product was distilled under reduced vacuum. The *N*-(4-phenoxybutyl)ethylenediamine was isolated as colorless gel in 75% yield.

Yield 75%, 7.880 g (colorless gel); bp: 110–115 °C (under ~ 50 Torr pressure); FT-IR ($\nu_{C\text{-}N}$): 1032 and 1241 cm^{-1}; ($\nu_{N\text{-}H}$): 3290 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 1.54–1.60 (m, 3H, N-*H*s of ethylenediamine); 1.58 (p, $J = 6.7$ Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 1.74 (p, $J = 6.7$ Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 2.57–2.61 (m, 4H, NCH_2CH_2N); 2.71 (t, $J = 5.9$ Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 3.88 (t, $J = 6.4$ Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 6.79–6.85 and 7.16–7.20 (m, 5H, arom. *H*s of $NCH_2CH_2CH_2CH_2OC_6H_5$). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 26.79 ($NCH_2CH_2CH_2CH_2OC_6H_5$);

27.12 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 41.76 and 49.52 (NCH_2CH_2N); 52.47 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 67.60 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 114.48, 120.53, 129.41 and 159.01 (arom. *C*s of $NCH_2CH_2CH_2CH_2OC_6H_5$). Elemental analysis calcd. (%) for $C_{12}H_{20}N_2O$: C 69.19, H 9.68, N 13.45; found (%): C 69.56, H 9.37, N 13.86. (For the ^{1}H NMR, ^{13}C NMR and IR spectrum of the **1**, see SI file, pages S1-S2).

Preparation of 1-(4-phenoxybutyl)imidazoline (2)

The 1-(4-phenoxybutyl)imidazoline (**2**) was prepared by the cyclization of the *N*-(4-phenoxybutyl)ethylenediamine (**1**) with *N*,*N*-dimethylformamide dimethyl acetal. For the preparation of the **2**, the *N*-(4-phenoxybutyl)ethylenediamine (**1**) (7,88 g; 37,8 mmol) was reacted with *N*,*N*-dimethylformamide dimethyl acetal (4,96 g; 41,6 mmol) at 90–110 °C for 3 h. End of the reaction, unreacted excess acetal were removed under vacuum. Then, the crude product was distilled under reduced vacuum. The 1-(4-phenoxybutyl)imidazoline was isolated as yellowish gel in 91% yield.

Yield 91%, 7.480 g (yellowish gel); bp: 125–130 °C (under ~ 50 Torr pressure); FT-IR ($\nu_{C\text{-}N}$): 1022 and 1240 cm^{-1}; ($\nu_{C=N}$): 1598 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 1.71–1.79 (m, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 1.81–1.87 (m, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 3.19 (t, J = 6.9 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 3.24 (t, J = 9.9 Hz, 2H, NCH_2CH_2N); 3.84 (td, J = 9.9, 1.6 Hz, 2H, NCH_2CH_2N); 4.01 (t, J = 6.0 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 6.87 (s, 1H, NC*H*N); 6.90–6.98 and 7.28–7.32 (m, 5H, arom. *H*s of $NCH_2CH_2CH_2CH_2OC_6H_5$). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 25.43 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 26.54 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 47.40 and 48.39 (NCH_2CH_2N); 54.74 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 67.22 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 114.45, 120.74, 129.49 and 157.78 (arom. *C*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 158.86 (NCHN). Elemental analysis calcd. (%) for $C_{13}H_{18}N_2O$: C 71.53, H 8.31, N 12.83; found (%): C 71.51, H 8.41, N 12.77. (For the ^{1}H NMR, ^{13}C NMR and IR spectrum of the **2**, see SI file, pages S3-S4).

General procedure for the preparation of imidazolinium salts as carbene precursors (3a–3d)

The new imidazolinium salts (**3a–3d**) were prepared by interaction of the 1-(4-phenoxybutyl)imidazoline (**2**) with substituted benzyl bromides. The 1-(4-phenoxybutyl)imidazoline (1,09 g; 5,0 mmol) and substituted benzyl bromide (5.0 mmol) were dissolved in degassed DMF (5 mL), and the solution was stirred at 80 °C for 16 h. After completion of the reaction, the mixture was allowed to cool to room temperature, and diethyl ether (15 mL) was added to solution. Then, obtained white solid was filtered off, was washed with diethyl ether (3 × 10 mL), and dried under vacuum. The crude product was recrystallized from EtOH/Et_2O solvent system (1:5, *v*/*v*) at room temperature and completely dried under vacuum. The new imidazolinium salts (**3a–3d**) were isolated as air- and moisture-stable white-brown crystalline solids.

1-(4-Phenoxybutyl)-3-(3,5-dimethylbenzyl)imidazolinium bromide (3a)

Yield 80%, 1.675 g (white solid); mp: 79–80 °C; FT-IR ($\nu_{C\text{-}N}$): 1038 and 1243 cm^{-1}; ($\nu_{C(2)\text{-}N}$): 1655 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 1.85–1.89 (m, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 1.91–1.95 (m, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 2.31 (s, 6H, $NCH_2C_6H_3(CH_3)_2$–3,5); 3.75 (t, J = 6.8 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 3.79–3.82 and 3.92–3.98 (m, 4H, NCH_2CH_2N); 4.00 (t, J = 5.6 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 4.75 (s, 2H, $NCH_2C_6H_3(CH_3)_2$–3,5); 6.87 (d, J = 7.8 Hz, 2H, arom. *H*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 6.94 (t, J = 7.4 Hz, 1H, arom. *H* of $NCH_2CH_2CH_2CH_2OC_6H_5$); 6.97 (m, 3H, arom. *H*s of $NCH_2C_6H_3(CH_3)_2$–3,5); 7.27 (dd, J = 8.7, 7.6 Hz, 2H, arom. *H*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 9.98 (s, 1H, NC*H*N). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 21.23 ($NCH_2C_6H_3(CH_3)_2$–3,5); 24.24 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 26.13 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 47.73 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 48.25 and 48.36 (NCH_2CH_2N); 52.25 ($NCH_2C_6H_3(CH_3)_2$–3,5); 66.80 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 114.43, 120.86, 129.55 and 158.61 (arom. *C*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 126.58, 130.73, 132.26 and 139.00 (arom. *C*s of $NCH_2C_6H_3(CH_3)_2$–3,5); 158.14 (N*C*HN). Elemental analysis calcd. (%) for $C_{22}H_{29}BrN_2O$: C 63.31, H 7.00, N 6.71; found (%): C 63.94, H 6.80, N 7.13. (For the ^1H NMR, ^{13}C NMR and IR spectrum of the **3a**, see SI file, pages S5-S6).

1-(4-Phenoxybutyl)-3-(4-isopropylbenzyl)imidazolinium bromide (3b)

Yield 72%, 1.561 g (white solid); mp: 89–90 °C; FT-IR ($\nu_{C\text{-}N}$): 1035 and 1237 cm^{-1}; ($\nu_{C(2)\text{-}N}$): 1661 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 1.22 (d, J = 6.9 Hz, 6H, $NCH_2C_6H_4(CH(CH_3)_2)$-4); 1.83–1.89 (m, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 1.90–1.94 (m, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 2.89 (hept, J = 6.9 Hz, 1H, $NCH_2C_6H_4(CH(CH_3)_2)$-4); 3.74 (t, J = 7.1 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 3.77–3.82 and 3.92–3.97 (m, 4H, NCH_2CH_2N); 4.00 (t, J = 5.7 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 4.81 (s, 2H, $NCH_2C_6H_4(CH(CH_3)_2)$-4); 6.87 (d, J = 7.9 Hz, 2H, arom. *H*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 6.93 (t, J = 7.3 Hz, 1H, arom. *H* of $NCH_2CH_2CH_2CH_2OC_6H_5$); 7.22 (d, J = 8.1 Hz, 2H, arom. *H*s of $NCH_2C_6H_4(CH(CH_3)_2)$-4); 7.26 (dd, J = 8.4, 7.5 Hz, 2H, arom. *H*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 7.32 (d, J = 8.1 Hz, 2H, arom. *H*s of $NCH_2C_6H_4(CH(CH_3)_2)$-4); 10.00 (s, 1H, NC*H*N). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 23.88 ($NCH_2C_6H_4(CH(CH_3)_2)$-4); 24.20 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 26.11 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 33.85 ($NCH_2C_6H_4(CH(CH_3)_2)$-4); 47.68 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 48.24 and 48.37 (NCH_2CH_2N); 51.94 ($NCH_2C_6H_4(CH(CH_3)_2)$-4); 66.77 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 114.42, 120.83, 129.53 and 158.59 (arom. *C*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 127.31, 128.95, 129.77 and 149.91 (arom. *C*s of $NCH_2C_6H_4(CH(CH_3)_2)$-4); 158.13 (N*C*HN). Elemental analysis calcd. (%) for $C_{23}H_{31}BrN_2O$: C 64.03, H 7.24, N 6.49; found (%): C 64.22, H 7.40, N 6.89. (For the ^1H NMR, ^{13}C NMR and IR spectrum of the **3b**, see SI file, pages S7-S8).

1-(4-Phenoxybutyl)-3-(2,3,5,6-tetramethylbenzyl)imidazolinium bromide (3c)

Yield 69%, 1.532 g (white solid); mp: 134–135 °C; FT-IR ($\nu_{C\text{-}N}$): 1037 and 1257 cm^{-1}; ($\nu_{C(2)\text{-}N}$): 1650 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 1.79–1.82 (m, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 1.84–1.89 (m, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 2.18 and 2.22 (s, 12H, $NCH_2C_6H(CH_3)_4$–2,3,5,6); 3.69 (t, J = 6.8 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 3.78–3.84 and 3.94–3.97 (m, 4H, NCH_2CH_2N); 4.01 (t, J = 6.7 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 4.87 (s, 2H, $NCH_2C_6H(CH_3)_4$–2,3,5,6); 6.79 (d, J = 7.9 Hz, 2H, arom. *H*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 6.89 (t, J = 7.3 Hz, 1H, arom. *H* of $NCH_2CH_2CH_2CH_2OC_6H_5$); 6.96 (s, 1H, arom. *H* of $NCH_2C_6H(CH_3)_4$–2,3,5,6); 7.21 (t, J = 8.0 Hz, 2H, arom. *H*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 9.29 (s, 1H, NC*H*N). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 16.11 and 20.51 ($NCH_2C_6H(CH_3)_4$–2,3,5,6); 24.24 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 25.97 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 46.85 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 48.15 ($NCH_2C_6H(CH_3)_4$–2,3,5,6); 48.18 and 48.48 (NCH_2CH_2N); 66.90 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 114.37, 120.82, 129.50 and 158.55 (arom. *C*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 128.09, 132.89, 133.82 and 134.76 (arom. *C*s of $NCH_2C_6H(CH_3)_4$–2,3,5,6); 157.21 (NCHN). Elemental analysis calcd. (%) for $C_{24}H_{33}BrN_2O$: C 64.71, H 7.47, N 6.29; found (%): C 64.89, H 7.53, N 6.70. (For the ^1H NMR, ^{13}C NMR and IR spectrum of the **3c**, see SI file, pages S9-S10).

1-(4-Phenoxybutyl)-3-(4-chlorobenzyl)imidazolinium bromide (3d)

Yield 78%, 1.642 g (white solid); mp: 79–80 °C; FT-IR ($\nu_{C\text{-}N}$): 1038 and 1241 cm^{-1}; ($\nu_{C(2)\text{-}N}$): 1665 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 1.83–1.86 (m, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 1.91–1.94 (m, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 3.71 (t, J = 6.9 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 3.77–3.82 and 3.92–3.97 (m, 4H, NCH_2CH_2N); 4.00 (t, J = 5.5 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 4.88 (s, 2H, $NCH_2C_6H_4$(Cl)-4); 6.87 (d, J = 8.0 Hz, 2H, arom. *H*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 6.94 (t, J = 7.3 Hz, 1H, arom. *H* of $NCH_2CH_2CH_2CH_2OC_6H_5$); 7.27 (t, J = 7.9 Hz, 2H, arom. *H*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 7.34 (d, J = 8.0 Hz, 2H, arom. *H*s of $NCH_2C_6H_4$(Cl)-4); 7.41 (d, J = 8.2 Hz, 2H, arom. *H*s of $NCH_2C_6H_4$(Cl)-4); 9.99 (s, 1H, NC*H*N). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 24.18 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 26.15 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 47.73 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 48.39 and 48.46 (NCH_2CH_2N); 51.41 ($NCH_2C_6H_4$(Cl)-4); 66.77 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 114.42, 120.89, 129.55 and 158.55 (arom. *C*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 129.43, 130.45, 131.15 and 136.06 (arom. *C*s of $NCH_2C_6H_4$(Cl)-4); 158.37 (NCHN). Elemental analysis calcd. (%) for $C_{20}H_{24}BrClN_2O$: C 56.69, H 5.71, N 6.61; found (%): C 56.84, H 5.68, N 6.93. (For the ^1H NMR, ^{13}C NMR and IR spectrum of the **3d**, see SI file, pages S11-S12).

General procedure for the preparation of palladium-carbene complexes (4a–4d)

An acetonitrile (10 mL) solution of imidazolinium salts **3a**-**3d** (1 mmol), $PdCl_2$ (0.177 g, 1 mmol), K_2CO_3 (0.691 g, 5 mmol), KBr (1.190 g, 10 mmol) and pyridine (0.119 g, 1.5 mmol) was stirred at 80 °C for 16 h. The reaction mixture was then filtered through Celite, the filtrate was evaporated under vacuum, and the solid residue was purified by column chromatography (CH_2Cl_2) to afford the corresponding palladium-carbene complex. Then, palladium-carbene complexes were recrystallized from CH_2Cl_2/*n*-pentane solvent system (1:5, *v/v*). The palladium-carbene complexes **4a–4d** were isolated as air- and moisture-stable yellow solids in 35–50% yields.

Dibromo-[1-(4-phenoxybutyl)-3-(3,5-dimethylbenzyl)imidazolidin-2-ylidene] (pyridine)palladium(II) (4a)

Yield 46%, 0.312 g (yellow solid); mp: 124–125 °C; FT-IR ($\nu_{C\text{-}N}$): 1071 and 1251 cm^{-1}; ($\nu_{C(2)\text{-}N}$): 1602 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 1.87–1.94 (m, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 1.96–2.02 (m, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 2.25 (s, 6H, $NCH_2C_6H_3(CH_3)_2$–3,5); 3.34–3.40 and 3.56–3.61 (m, 4H, NCH_2CH_2N); 4.03 (t, J = 5.9 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 4.14 (t, J = 7.3 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 5.17 (s, 2H, $NCH_2C_6H_3(CH_3)_2$–3,5); 6.84 (s, 1H, arom. *H* of $NCH_2C_6H_3(CH_3)_2$–3,5); 6.86 (d, J = 6.5 Hz, 2H, arom. *H*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 7.11 (s, 2H, arom. *H*s of $NCH_2C_6H_3(CH_3)_2$–3,5); 7.17–7.19 (m, 2H, arom. *H*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 7.21 (ddd, J = 7.9, 5.2, 1.4 Hz, 2H, arom. *H*s of pyridine); 7.64 (tt, J = 7.4, 1.5 Hz, 1H, arom. *H* of pyridine); 8.87 (dd, J = 6.3, 1.4 Hz, 2H, arom. *H*s of pyridine). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 21.30 ($NCH_2C_6H_3(CH_3)_2$–3,5); 24.32 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 26.51 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 47.72 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 48.41 and 50.34 (NCH_2CH_2N); 54.90 ($NCH_2C_6H_3(CH_3)_2$–3,5); 67.26 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 114.56, 120.60, 129.45 and 158.98 (arom. *C*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 126.67, 129.70, 135.10 and 137.79 (arom. *C*s of $NCH_2C_6H_3(CH_3)_2$–3,5); 124.49, 138.31 and 152.45 (arom. *C*s of pyridine); 180.70 (Pd-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{27}H_{33}Br_2N_3OPd$: C 47.56, H 4.88, N 6.16; found (%): C 47.59, H 4.81, N 6.13. (For the ^{1}H NMR, ^{13}C NMR and IR spectrum of the **4a**, see SI file, pages S13-S14).

Dibromo-[1-(4-phenoxybutyl)-3-(4-isopropylbenzyl)imidazolidin-2-ylidene] (pyridine)palladium(II) (4b)

Yield 42%, 0.289 g (yellow solid); mp: 69–70 °C; FT-IR ($\nu_{C\text{-}N}$): 1069 and 1238 cm^{-1}; ($\nu_{C(2)\text{-}N}$): 1600 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 1.27 (d, J = 6.8 Hz, 6H, $NCH_2C_6H_4(CH(CH_3)_2)$-4); 2.02–2.04 (m, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 2.05–2.08 (m, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 2.93 (hept, J = 6.8 Hz, 1H, $NCH_2C_6H_4(CH(CH_3)_2)$-4); 3.46 and 3.68 (t, J = 9.8 Hz, 4H, NCH_2CH_2N); 4.13 (t, J = 5.3 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 4.24 (t, J = 6.8 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 5.34 (s, 2H, $NCH_2C_6H_4(CH(CH_3)_2)$-4); 6.94–6.96

(m, 3H, arom. *H*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 7.25–7.30 (m, 6H, arom. *H*s of $NCH_2CH_2CH_2CH_2OC_6H_5$ and $NCH_2C_6H_4(CH(CH_3)_2)$-4); 7.51 (ddd, J=7.6, 5.0, 1.3 Hz, 2H, arom. *H*s of pyridine); 7.74 (tt, J=7.3, 1.4 Hz, 1H, arom. *H* of pyridine); 8.97 (dd, J=6.5, 1.5 Hz, 2H, arom. *H*s of pyridine). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)=24.03 ($NCH_2C_6H_4(CH(CH_3)_2)$-4); 24.30 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 26.51 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 33.88 ($NCH_2C_6H_4(CH(CH_3)_2)$-4); 47.65 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 48.43 and 50.34 (NCH_2CH_2N); 54.70 ($NCH_2C_6H_4(CH(CH_3)_2)$-4); 67.28 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 114.58, 120.60, 129.45 and 158.99 (arom. *C*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 126.80, 128.85, 132.56 and 148.76 (arom. *C*s of $NCH_2C_6H_4(CH(CH_3)_2)$-4); 124.49, 137.78 and 152.44 (arom. *C*s of pyridine); 180.77 (Pd-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{28}H_{35}Br_2N_3OPd$: C 48.33, H 5.07, N 6.04; found (%): C 48.00, H 5.01, N 6.06. (For the ^{1}H NMR, ^{13}C NMR and IR spectrum of the **4b**, see SI file, pages S15-S16).

Dibromo-[1-(4-phenoxybutyl)-3-(2,3,5,6-tetramethylbenzyl) imidazolidin-2-ylidene](pyridine)palladium(II) (4c)

Yield 35%, 0.247 g (yellow solid); mp: 192–193 °C; FT-IR ($\nu_{C\text{-}N}$): 1071 and 1250 cm^{-1}; ($\nu_{C(2)\text{-}N}$): 1600 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)=1.89–1.94 (m, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 1.96–1.99 (m, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 2.17 and 2.26 (s, 12H, $NCH_2C_6H(CH_3)_4$–2,3,5,6); 3.08 and 3.47 (t, J=9.2 Hz, 4H, NCH_2CH_2N); 4.03 (t, J=5.7 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 4.13 (t, J=7.1 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 5.30 (s, 2H, $NCH_2C_6H(CH_3)_4$–2,3,5,6); 6.83–6.87 (m, 3H, arom. *H*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 6.90 (s, 1H, arom. *H* of $NCH_2C_6H(CH_3)_4$–2,3,5,6); 7.16–7.19 (m, 2H, arom. *H*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 7.23 (ddd, J=7.5, 5.0, 1.3 Hz, 2H, arom. *H*s of pyridine); 7.66 (tt, J=7.8, 1.6 Hz, 1H, arom. *H* of pyridine); 8.91 (dd, J=6.6, 1.5 Hz, 2H, arom. *H*s of pyridine). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)=16.54 and 20.53 ($NCH_2C_6H(CH_3)_4$–2,3,5,6); 24.38 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 26.50 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 47.79 and 47.87 (NCH_2CH_2N); 49.30 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 50.59 ($NCH_2C_6H(CH_3)_4$–2,3,5,6); 67.28 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 114.56, 120.57, 129.43 and 158.98 (arom. *C*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 131.05, 131.84, 134.03 and 134.52 (arom. *C*s of $NCH_2C_6H(CH_3)_4$–2,3,5,6); 124.49, 137.76 and 152.44 (arom. *C*s of pyridine); 181.40 (Pd-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{29}H_{37}Br_2N_3OPd$: C 49.07, H 5.25, N 5.92; found (%): C 48.42, H 5.32, N 5.87. (For the ^{1}H NMR, ^{13}C NMR and IR spectrum of the **4c**, see SI file, pages S17-S18).

Dibromo-[1-(4-phenoxybutyl)-3-(4-chlorobenzyl)imidazolidin-2-ylidene] (pyridine)palladium(II) (4d)

Yield 50%, 0.345 g (yellow solid); mp: 120–121 °C; FT-IR ($\nu_{C\text{-}N}$): 1071 and 1235 cm^{-1}; ($\nu_{C(2)\text{-}N}$): 1597 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm)=1.89–1.95 (m, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 1.97–2.02 (m, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 3.35 and 3.61 (dd, J=11.5, 8.4 Hz, 4H, NCH_2CH_2N); 4.03 (t, J=5.8 Hz, 2H, $NCH_2CH_2CH_2CH_2OC_6H_5$); 4.14 (t, J=7.3 Hz, 2H,

$NCH_2CH_2CH_2CH_2OC_6H_5$); 5.24 (s, 2H, $NCH_2C_6H_4$(Cl)-4); 6.84–6.88 (m, 3H, arom. *H*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 7.20 (dd, $J = 15.9$, 8.2 Hz, 4H, arom. *H*s of $NCH_2C_6H_4$(Cl)-4); 7.27 (d, $J = 8.4$ Hz, 2H, arom. *H*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 7.45 (ddd, $J = 8.3$, 5.1, 1.4 Hz, 2H, arom. *H*s of pyridine); 7.66 (tt, $J = 7.6$, 1.5 Hz, 1H, arom. *H* of pyridine); 8.86 (dd, $J = 6.3$, 1.4 Hz, 2H, arom. *H*s of pyridine). ^{13}C NMR (101 MHz, $CDCl_3$, 25 °C, TMS): δ (ppm) = 24.28 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 26.49 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 47.61 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 48.52 and 50.37 (NCH_2CH_2N); 54.29 ($NCH_2C_6H_4$(Cl)-4); 67.22 ($NCH_2CH_2CH_2CH_2OC_6H_5$); 114.56, 120.63, 129.46 and 158.95 (arom. *C*s of $NCH_2CH_2CH_2CH_2OC_6H_5$); 128.96, 130.25, 133.80 and 133.98 (arom. *C*s of $NCH_2C_6H_4$(Cl)-4); 124.54, 137.86 and 152.43 (arom. *C*s of pyridine); 181.38 (Pd-$C_{carbene}$). Elemental analysis calcd. (%) for $C_{25}H_{28}Br_2ClN_3OPd$: C 43.63, H 4.10, N 6.11; found (%): C 43.27, H 4.16, N 6.12. (For the ^{1}H NMR, ^{13}C NMR and IR spectrum of the **4d**, see SI file, pages S19-S20).

X-Ray analysis of the complex 4d

X-ray data were collected 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 [72] while data reduction was applied using X-RED32 [72]. The structure was solved using the charge-flipping algorithm by SUPERFLIP [73] and refined by means of the full-matrix least-squares calculations on F^2 using SHELXL-2018 [74]. All H atoms were placed geometrically and treated using a riding model, fixing the bond lengths at 0.93 and 0.97 Å for CH and CH_2 atoms, respectively. The displacement parameters of the H atoms were fixed at U_{iso} (H) = $1.2U_{eq}$ of their parent atoms. The phenoxybutyl moiety in one of two molecules in the asymmetric unit of the compound was disordered over two positions with the occupancy factors of 0.520(5)/0.480(5)%. Crystal data, data collection and structure refinement details are collected in Table 5. Molecular diagram was drawn by using OLEX2 [75].

General procedure for the direct C5-arylation of furan and thiophene with (hetero)aryl halides

An oven dried Schlenk flask was charged with palladium catalyst (0.01 equiv., 1 mol%), 2-acetylfuran or 2-acetylthiophene (0.5 mmol, 2 equiv.), (hetero)aryl halide derivative (0.25 mmol, 1 equiv.), KOAc (0.5 mmol, 2 equiv.) and DMA (2 mL) under argon atmosphere. Then, the reaction mixture was stirred at 120 °C for different durations, as given in Table 4. Completion of the reaction, the solution cooled to room temperature, and CH_2Cl_2 (1 mL) was added to Schlenk tube to dilute the solution. The solution filtered through a pad of celite to remove the solid particles, then, was used for GC analysis. The yields (%) were calculated according to (hetero)aryl halide by GC analysis.

Table 5 Crystal data and structure refinement parameters for complex **4d**

CCDC depository	2,050,747
Color/shape	Dark yellow/block
Chemical formula	$[PdBr_2(C_{20}H_{23}ClN_2O)(C_5H_5N)]$
Formula weight	688.17
Temperature (K)	296(2)
Wavelength (Å)	0.71073 Mo Kα
Crystal system	Triclinic
Space group	$P\,\bar{1}$ (No. 2)
Unit cell parameters	
a, b, c (Å)	9.0803(4), 13.8072(6), 22.2565(10)
α, β, γ (°)	73.515(4), 88.742(4), 81.980(4)
Volume (Å^3)	2649.0(2)
Z	4
$D_{calc.}$ (g/cm^3)	1.726
μ (mm^{-1})	3.841
Absorption correction	Integration
$T_{min.}, T_{max}$	0.1897, 0.5027
F_{000}	1360
Crystal size (mm^3)	$0.75\times0.29\times0.20$
Diffractometer	STOE IPDS II
Measurement method	ω scan
Index ranges	$-11\le h\le 11, -18\le k\le 18, -28\le l\le 29$
θ range for data collection (°)	$1.909\le\theta\le 27.754$
Reflections collected	59,552
Independent/observed reflections	12,375/7782
R_{int}	0.0840
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	12,375/409/686
Goodness-of-fit on F^2	0.978
Final R indices [$I>2\sigma(I)$]	$R_1=0.0495$, $wR_2=0.0811$
R indices (all data)	$R_1=0.0962$, $wR_2=0.0923$
$\Delta\rho_{max.}, \Delta\rho_{min.}$ (e/Å^3)	$0.83, -0.58$

CRediT authorship contribution statement

Murat Kaloğlu contributed to conceptualization, methodology, investigation, writing-original draft, writing-review and editing, funding acquisition. Nazan Kaloğlu contributed to conceptualization, writing-original draft, methodology, investigation. Namık Özdemir contributed to software, writing-original draft, investigation. İsmail Özdemir contributed to conceptualization, resources, writing-original draft, supervision.

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