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Ruthenium *N*-heterocyclic–carbene catalyzed diarylation of arene C–H bond

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Novel ruthenium-1,3-dialkylimidazolin-2-ylidene complexes (2a–e) have been prepared and characterized by C, H, N analysis, ^{1}H-NMR and ^{13}C-NMR. The *ortho* position of the aromatic ring of pyridyl group substituted aromatic compound was directly arylated with aryl bromides and chlorides in the presence of a catalytic amount of [RuCl$_2$(1,3-dialkylimidazolin-2-ylidene)] complexes. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: imidazolin-2-ylidene; *N*-heterocyclic carbene; C–H activation; arylation

Introduction

Transition metal-based catalysis has gained much attention for diverse applications ranging from materials to pharmaceuticals.[1] The design of transition metal catalysts has to take into account several basic characteristics including high efficiencies and selectivities as well as economic and environmental considerations. The availability of catalysts to perform specific transformations is critical for both industry and academia. Over the years, the success of homogeneous catalysis can be attributed largely to the development of a diverse range of ligand frameworks that have been used to tune the behavior of a variety of metal-containing systems.

Advances in ligand design have allowed not only for improvements of known processes in terms of scope, mildness and catalyst loadings, but also for the discovery of new selective reactions. In the past few years, *N*-heterocyclic carbenes (NHCs) have emerged as versatile ligational building blocks for a large variety of coordination compounds in organometallic chemistry and homogeneous catalysis.[2–7] Several advantages have been gained in using NHCs rather than their phosphine analogs; these include tighter binding, greater thermal stability, and increased basicity. For these reasons, the metal–NHCs have been widely used as highly reactive and rather selective catalysts for numerous chemical transformations.

Owing to the usefulness of the metal–NHC complexes, many synthetic methods have been explored. According to the reports published on metal–NHCs, the most widely used preparation methods can be divided broadly into five types: (i) reaction of free NHCs with metal precursors;[8] (ii) reaction of electron-rich olefin dimers with organometallic fragments;[9] (iii) reaction of imidazolium salts with suitable basic transition metal salts;[10] (iv) reaction of azolium salts with metal precursors under basic phase transfer catalysis (PTC) conditions;[11] and (v) transmetallation with Ag(I)–NHCs.[12] Additionally, NHC–metal complexes can usually be made *in situ* with high yields.

We have previously reported the use of a *in situ* formed imidazolidin-2-ylidene, tetrahydropyrimidin-2-ylidene and tetrahydrodiazepin-2-ylidene/palladium(II) system, which exhibits high activity in various coupling reactions of aryl bromides and aryl chlorides. In order to obtain a more stable, efficient and active system, we have also investigated benzo-annelated derivatives.[13] Recently our group reported that novel complexes of rhodium(I) based on 1,3-dialkylimidazolidin-2-ylidenes give good yields for the addition of phenylboronic acid to aldehydes.[14]

Metal-mediated cross-coupling reactions of organometallic reagents and halides constitute an essential class of C–C bond forming reactions[15] and provide access to a wide array of natural products, pharmaceuticals, ligands and other materials. Not only are the organometallic starting materials frequently not commercially available or expensive, but they also give rise to undesired by-products. These problems can potentially be circumvented by developing protocols for the direct cross-coupling of organic compounds via C–H-bond functionalization. Comparably few examples of such intermolecular transformations have been described.[16] Methodologies for both the directed *ortho*-arylation of benzene derivatives[17,18] and the regioselective arylation of heterocyclic compounds[19] using aryl iodides and bromides have been developed. In particular, a general protocol for ruthenium-catalyzed arylations[18,20] employing inexpensive, but less reactive, aryl chlorides has proven elusive.[21]

Based on these findings and our continuing interest in developing more efficient and stable catalysts, we wished to examine whether we could influence the catalytic activity of ruthenium-1,3-dialkylimidazolin-2-ylidene complexes for the arylation of 2-phenylpyridine. (Scheme 1). We now report: (i) preparation of new RuCl$_2$(1,3-dialkylimidazolin-2-ylidene) complexes and (ii) their efficient catalysis of the arylation of 2-phenylpyridine.

Results and Discussion

Synthesis and characterization of RuCl$_2$NHC

The tetraaminoethene (**1a–e**) were synthesized using a method similar to that reported by Lappert *et al.*[22] The reaction of

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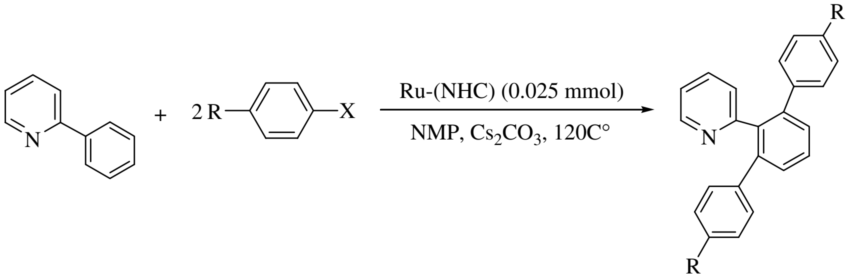
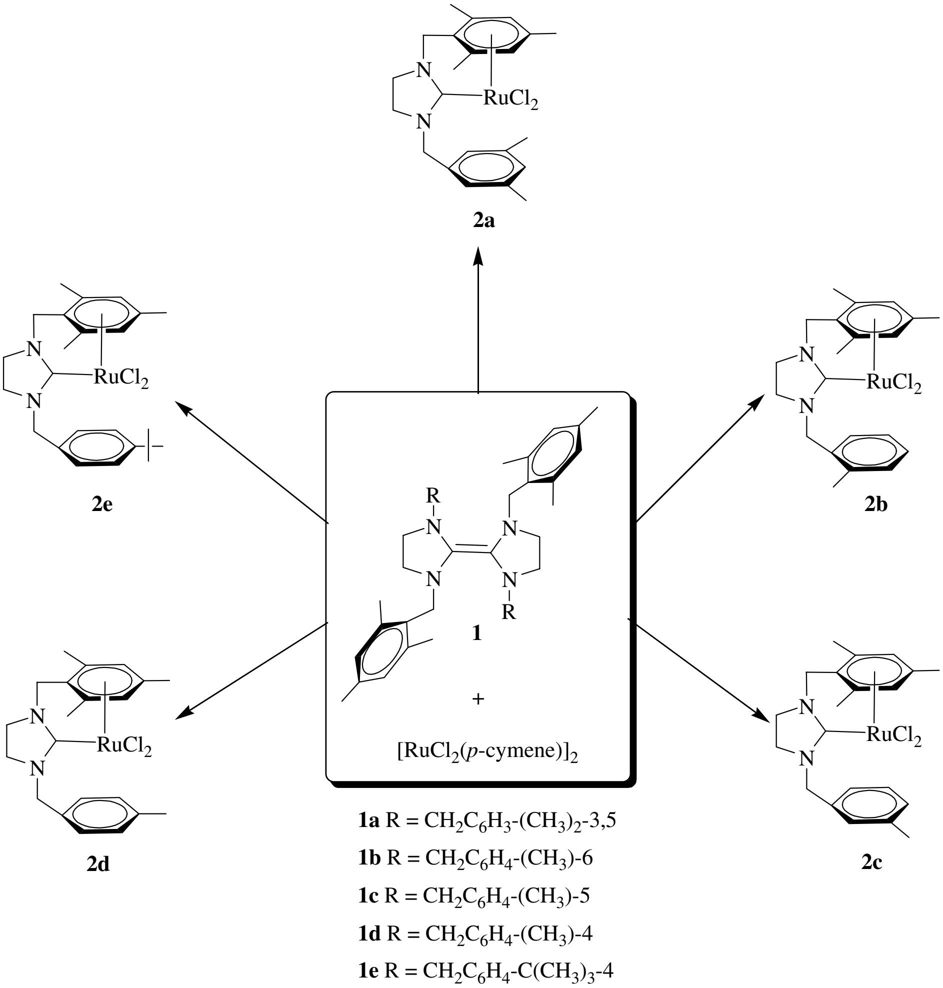


Scheme 1. Arylatin of 2-phenylpyridine by Ru–NHC complexes.



1a R = $CH_2C_6H_3$-$(CH_3)_2$-3,5
1b R = $CH_2C_6H_4$-(CH_3)-6
1c R = $CH_2C_6H_4$-(CH_3)-5
1d R = $CH_2C_6H_4$-(CH_3)-4
1e R = $CH_2C_6H_4$-$C(CH_3)_3$-4

Scheme 2. Synthesis of ruthenium-carbene complexes (**2a–2e**).

tetraaminoethene (**1a–e**) with the binuclear $[RuCl_2(arene)]_2$ complex proceeded smoothly in refluxing toluene to give the $[RuCl_2(NHC)]$ (**2a–e**) complexes as crystalline solids in 76–87% yields (Scheme 2).

Complexes (**2a–e**), which are very stable in the solid state, have been characterized by analytical and spectroscopic techniques. The molecular structures of complexes **2a** and **2b** have been confirmed by X-ray single-crystal analyses.[23] Ruthenium complexes exhibit a characteristic $\upsilon_{(NCN)}$ band typically at 1497–1508 cm^{-1}.[55–61] ^{13}C chemical shifts, which provide a useful diagnostic tool for metal carbene complexes, show that C_{carb} is substantially deshielded. Values of δ ($^{13}C_{carb}$) are in the 199.7–200.5 ppm range and are similar to those found for other carbene complexes. These new complexes show typical spectroscopic signatures which are in line with those recently reported for other $[RuCl_2(NHC)(arene)]$ complexes.[24]

Arylation of 2-phenylpyridine

The general application of C–H activation has been hampered by requirements of either highly specific or minimal functionality. The Sames group has made significant recent contributions towards addressing these limitations by developing a variety of direct arylations of functionalized and unprotected heterocycles, the products of which are analogous to those obtained from Pd-catalyzed cross coupling reactions, without the requirement for a metallated aryl species. Drawing on precedents for C–H activation of azines by $Ru_3(CO)_{12}$, as well as related catalytic C–H acylation reactions of nitrogen-containing heterocycles by Fukuyama[25] and Moore,[26] Ackermann has reported the site-specific arylation of 2-phenylpyridine by electron rich phosphine oxides and $[RuCl_2(p\text{-cymene})]_2$ catalyst system. This complex was discovered during mechanistic investigations into the catalytic role of $Ru_3(CO)_{12}$ in this reaction.[19e] This simple transformation serves as a model for C–H arylation of electron-deficient heteroaromatics, which are indispensable pharmaceutical motifs.

Here, various ruthenium–carbene complexes (**2a–e**) were compared as catalysts under the same reaction conditions. To survey the reaction parameters for the arylation of 2-phenylpyridine we chose to examine Cs_2CO_3, K_2CO_3 and $KOBu^t$ as base and NMP as solvent. We found that the reactions performed in NMP with Cs_2CO_3 or $KOBu^t$ as the base at 120 °C appeared to be best. We started our investigation with the arylation of 2-phenylpyridine with bromobenzene, in the presence of $[RuCl_2(NHC)]$ (**2**). Table 1 summarizes the results obtained in the presence of **2a–e** (Table 1, entries 1–5).

The control experiment indicated that the arylation of 2-phenylpyridine with bromobenzene reaction did not occur in the absence of **2a**. Under the determined reaction conditions, a wide range of aryl halides bearing electron-donating or electron-withdrawing groups can react with 2-phenylpyridine, affording the arylated products in excellent yields (Table 1 entries 4, 9, 14, 16, 19 and 24).

Table 1. Arylation of 2-phenylpyridine

Entry	Catalyst	R	X	Yield[a] (%)
1	2a	H	Br	73
2	2b	H	Br	68
3	2c	H	Br	82
4	2d	H	Br	95
5	2e	H	Br	83
6	2a	OCH_3	Br	74
7	2b	OCH_3	Br	81
8	2c	OCH_3	Br	95
9	2d	OCH_3	Br	98
10	2e	OCH_3	Br	79
11	2a	OCH_3	Cl	88
12	2b	OCH_3	Cl	96
13	2c	OCH_3	Cl	95
14	2d	OCH_3	Cl	98
15	2e	OCH_3	Cl	96
16	2a	CH_3	Cl	98
17	2b	CH_3	Cl	94
18	2c	CH_3	Cl	97
19	2d	CH_3	Cl	98
20	2e	CH_3	Cl	96
21	2a	$COCH_3$	Cl	76
22	2b	$COCH_3$	Cl	71
23	2c	$COCH_3$	Cl	73
24	2d	$COCH_3$	Cl	82
25	2e	$COCH_3$	Cl	77

[a] Yield determined by NMR and based on 2-phenylpyridine; 120 °C, 20 h.

Conclusion

In summary, from readily available starting materials, such as bis(1,3-dialkylimidazolin-2-ylidene), four novel ruthenium–carbenes (**2a–e**) have been prepared and characterized. Also, we have investigated the arylation of 2-phenylpyridine with aryl halides in the presence of the Ru–NHC complexes resulting in the formation of the corresponding arylated pyridine derivatives. Mechanistic studies as well as further applications of the present catalytic system are ongoing and will be reported in due course.

Experimental

Materials

All reactions for the preparation of **1** and **2** were carried out under Ar in flame-dried glass-ware using standard Schlenk-type flasks. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Na/K alloy), CH_2Cl_2 (P_4O_{10}), hexane and toluene (Na). Flash chromatography: Merck silica gel 60 (230–400 mesh). The complex $[RuCl_2(p\text{-cymene})]_2$ [27] and **1** and **2** were prepared according to known methods.[22] All reagents were purchased from Aldrich Chemical Co.

Melting point determination

Melting point were determined in glass capillaries under air with an Electrothermal-9200 melting point apparatus.

IR spectroscopy

FT-IR spectra were recorded as KBr pellets in the range 400–4000 cm^{-1} on a ATI Unicam 1000 spectrometer.

NMR spectroscopy

^1H NMR and ^{13}C NMR spectra were recorded using a Varian As 400 Merkur spectrometer operating at 400 MHz (^1H) and 100 MHz (^{13}C) in $CDCl_3$ with tetramethylsilane as an internal reference. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The NMR studies were carried out in high-quality 5 mm NMR tubes. Signals are quoted in parts per million as δ downfield from tetramethylsilane (δ 0.00) as an internal standard. Coupling constants (J values) are given in hertz. NMR multiplicities are abbreviated as fallows: s = singlet, d = doublet, t = triplet, m = multiplet signal.

Gas chromatography

All reactions were monitored on a Agilent 6890N GC system by GC-FID with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 µm film thickness.

Column chromatography

Column chromatography was performed using silica gel 60 (70–230 mesh). Solvent ratios are given as v/v.

Elemental analyses

Elemental analyses were performed by the Turkish Research Council (Ankara, Turkey), Microlab and Centre Régional de Mesures Physiques de l'Ouest, Université de Rennes.

General procedure for the preparation of the ruthenium-carbene complexes (2a–e)

A solution of bis(1,3-dialkylimidazolinylidene) (**1**) (0.5 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (0.5 mmol) in toluene (15 ml) was heated under reflux for 4 h. Upon cooling to room temperature, orange crystals of **2a–e** were obtained. The crystals were filtered, washed with diethyl ether (3 × 15 ml) and dried under vacuum. The crude product was recrystallized from CH_2Cl_2–Et_2O.

Dichloro-[1-(2,4,6-trimethylbenzyl)-3-(3,5-dimethylbenzyl-imidazolidin-2-iliden)]ruthenium (II) (2a)

Yield: 0.285 g (85%): m.p. 307–308 °C; $\nu_{(NCN)} = 1501\ cm^{-1}$. Anal. calcd for $RuC_{22}H_{28}N_2Cl_2$: C,53.66; H,5.73; N, 5.69. Found: C, 53.80; H, 5.86: N,5.82%. ^1H NMR (399.9 Hz, $CDCl_3$) δ = 2.19 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,6), 2.32 [s, 3H, $CH_2C_6H_2(CH_3)_3$-4], 2.27 [s, 6H, $CH_2C_6H_4(CH_3)_2$-3,5], 3.51(t, *J* 9.9) and 3.78 (t, *J* 10.2, 4H, NCH_2CH_2N), 4.13 [s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 4.77 [s, 2H, $CH_2C_6H_3(CH_3)_2$-3,5], 5.49 [s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 6.95 and 6.87 [s, 3H, $CH_2C_6H_3(CH_3)_2$-3,5]. $^{13}C\{H\}$NMR (100.5 Hz, $CDCl_3$) δ = 16.8 [$CH_2C_6H_2(CH_3)_3$-2,6], 17.5 [$CH_2C_6H_2(CH3)_3$-4], 21.3 [$CH_2C_6H_3(CH_3)_2$-3,5], 49.4 [$CH_2C_6H_2(CH_3)_3$-2,4,6], 47.5 and 49.5 (NCH_2CH_2N), 53.4 [$CH_2C_6H_4(CH_3)_2$-3,5], 89.0, 93.9, 98.7 and 101.2 [$CH_2C_6H_2(CH_3)_3$-2,4,6], 127.0, 129.1, 136.4 and 137.7 [$CH_2C_6H_4(CH_3)_2$-3,5], 199.7 (NCHN).

Dichloro-[1-(2,4,6-trimethylbenzyl)-3-(2-methylbenzyl)-imidazolidin-2-iliden]ruthenium (II) (2b)

Yield: 0.285 g (76%); m.p. 295–296 °C, $\nu_{(NCN)} = 1500\ cm^{-1}$. Anal. calcd for $RuC_{21}H_{26}N_2Cl_2$: C, 52.72; H, 5.48; N, 5.86. Found: C:52.83; H, 5.55; N, 5.96%. ^1H NMR (399.9 Hz, $CDCl_3$) δ = 2.67 (s, 3H, $CH_2C_6H_4(CH_3)$-4), 2.17 [s, 6H, $CH_2C_6H_2(CH_3)_3$-2,6], 3.72 (t, *J* 6.9) and 3.46(t, *J* 8.1) (4H, NCH_2CH_2N), 4.12 [s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 4.95 [s, 2H, $CH_2C_6H_4(CH_3)$-2], 2.28 ([, 3H, $CH_2C_6H_4(CH_3)$-2] 5.45 [s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 7.06–7.28 [m, 4H, $CH_2C_6H_4(CH_3)$-2].

$^{13}C\{H\}$NMR (100.5 Hz, $CDCl_3$) δ = 17.6 [$CH_2C_6H_4(CH_3)$-2], 17.1 [$CH_2C_6H_2(CH_3)_3$-2,6], 19.7 [$CH_2C_6H_2(CH_3)_3$-6], 49.6 [$CH_2C_6H_2(CH_3)_3$-2,4,6], 47.2 and 48.0 (NCH_2CH_2N), 50.9 [$CH_2C_6H_4(CH_3)$-4], 89.5, 93.4, 98.7 and 101.9 [$CH_2C_6H_2(CH_3)_3$-2,4,6], 126.3, 127.6, 129.7, 130.4, 134.9 and 137.1 [$CH_2C_6H_4(CH_3)$-2], 200.5 (NCHN).

Dichloro-[1-(2,4,6-trimethylbenzyl)-3-(3-methylbenzyl)-imidazolidin-2-iliden]ruthenium (II) (2c)

Yield: 0.293 g (78%); m.p. 305–306 °C; $\nu_{(NCN)} = 1505\ cm^{-1}$. Anal. calcd for $RuC_{21}H_{26}N_2Cl_2$: C,52.72; H, 5.48; N, 5.86. Found: C,52.60; H, 5.52; N, 5.94%.^1H NMR (399.9 Hz, $CDCl_3$) δ = 2.28 [s, 3H, $CH_2C_6H_4(CH_3)$-4], 2.15 [s, 6H, $CH_2C_6H_2(CH_3)_3$-2,6], 3.70 (t, *J* 6.9 Hz) and 3.48(t, *J* 5.7 Hz) (4H, NCH_2CH_2N), 4.78 [s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 4.1 [s, 2H, $CH_2C_6H_4(CH_3)$-2], 2.28 [s, 3H, $CH_2C_6H_4(CH_3)$-3] 5.45 [s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 7.36–7.28 [m, 4H, $CH_2C_6H_4(CH_3)$-3]. $^{13}C\{H\}$NMR (100.5 Hz, $CDCl_3$) δ = 17.7 [$CH_2C_6H_4(CH_3)$-3], 17.0 [$CH_2C_6H_2(CH_3)_3$-2,6], 21,6 [$CH_2C_6H_2(CH_3)_3$-4], 49.6 [$CH_2C_6H_2(CH_3)_3$-2,4,6], 47.2 and 48.0 (NCH_2CH_2N), 53.7 [$CH_2C_6H_4(CH_3)$-3], 101.24, 9.1, 93.7 and 89.1, [$CH_2C_6H_2(CH_3)_3$-2,4,6], 138.0, 136.7, 130.1, 128.5 and 126.5 [$CH_2C_6H_4(CH_3)$-3], 200.5 (NCHN).

Dichloro-[1-(2,4,6-trimethylbenzyl)-3-(4-methylbenzyl)-imidazolidin-2-iliden-ruthenium(II) (2d)

Yield: 0.308 g (82%); m.p. 334–335 °C; $\nu_{(NCN)} = 1508\ cm^{-1}$. Anal. calcd for $RuC_{21}H_{26}N_2Cl_2$: C,52.72; H,5.48; N, 5.86. Found: C,52.62; H, 5.55; N, 5.95%.^1H NMR (399.9 Hz, $CDCl_3$) δ = 2.15 (s, 6H, $CH_2C_6H_2(CH_3)_3$-2,6), 2.29 (s, 3H, $CH_2C_6H_2(CH_3)_3$-4), 2.28 (s, 3H, $CH_2C_6H_4(CH_3)$-4), 3.69(t, *J* 6,9 Hz) and 3.48 (t, *J* 5.7 Hz, 4H, NCH_2CH_2N), 4.77 [s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 4.1 [s, 2H, $CH_2C_6H_4(CH_3)$-4], 5.46 [s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 7.23, 7.20, 7.05 and 7.03 [m, 3H, $CH_2C_6H_4(CH_3)$-4]. $^{13}C\{H\}$NMR (100.5 Hz, $CDCl_3$): δ = 17.0 [$CH_2C_6H_2(CH_3)_3$-2,6], 21,3 [$CH_2C_6H_2(CH_3)_3$-4], 17.6 [$CH_2C_6H_4(CH_3)$-4], 53.4 [$CH_2C_6H_2(CH_3)_3$-2,4,6], 47.9 and 47.2 (NCH_2CH_2N), 49.5 [$CH_2C_6H_4(CH_3)$-4], 101.2, 99.13, 93.63 and 89.02 [$CH_2C_6H_2(CH_3)_3$-2,4,6], 137.24, 133.71, 129.34 and 129.2 [$CH_2C_6H_4(CH_3)$-4], 200.0 (NCHN).

Dichloro-1-(2,4,6-trimethylbenzyl)-3-(4-terbutyllbenzyl)-imidazolidin-2-iliden-ruthenium (II) (2e)

Yield: 0.326 g (87%); m.p. 305–306 °C; $\nu_{(NCN)} = 1497\ cm^{-1}$. Anal. calcd for $RuC_{24}H_{32}N_2Cl_2$: C, 55.38; H, 6.20; N, 5.38. Found: C, 55.28; H, 6.25; N, 5.41.^1H NMR (399.9 Hz, $CDCl_3$) δ = 2.17 [s, 6H, $CH_2C_6H_2(CH_3)_3$-2,6], 2.30 [s, 3H, $CH_2C_6H_2(CH_3)_3$-4], 1.27 [s, 9H, $CH_2C_6H_4(CH_3)_3$-4], 3.70 (t, *J* 5,7 Hz) and 3.53 (t, *J* 5.7 Hz, 4H, NCH_2CH_2N), 4.81 [s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 4.1 [s, 9H, $CH_2C_6H_4(CH_3)_3$-4], 5.48 [s, 2H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 7.26, 7.25 [s, 3H, $CH_2C_6H_4(CH_3)_3$-4]. $^{13}C\{H\}$NMR (100.5 Hz, $CDCl_3$) δ = 17.0 [$CH_2C_6H_2(CH_3)_3$-2,6], 34.6 [$CH_2C_6H_2(CH_3)_3$-4], 31.5 [$CH_2C_6H_4(CH_3)_3$-4], 53.3 [$CH_2C_6H_2(CH_3)_3$-2,4,6], 47.2 and 48.1 (NCH_2CH_2N), 49.6 [$CH_2C_6H_4(CH_3)_3$-4], 101.2, 98.9, 93.7 and 89.02 [$CH_2C_6H_2(CH_3)_3$-2,4,6], 150.4, 133.7, 129.1, 125.4 [$CH_2C_6H_4(CH_3)$-4], 200.1 (NCHN).

General procedure for ruthenium-carbene catalyzed arylation of 2-phenylpyridine

2-Phenylpyridine (1.0 mmol), arylhalide (2.2 mmol), ruthenium–carbene catalyst (0.025 mmol), Cs_2CO_3 (3 mmol) and NMP (2 ml) were introduced into a Schlenk tube. The resulting mixture was stirred at 120 °C for 20 h, cooled to ambient temperature after that H_2O (60 ml) and EtOAc (40 ml) were added to cold mixture. The contained aqueous layers were extracted with EtOAc. The organic phase was dried over $MgSO_4$ and concentrated in vacuum. The remain residue was purified by flash chromatography (hexane–ethyl acetate, 10 : 1). Analysis of the reaction product was carried out by NMR spectroscopy and GC.

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