

N-Heterocyclic carbene (NHC) palladium(II) complexes bearing chiral oxazoline ligands and their catalytic activities in allylic alkylation reactions

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Abstract: NHC–Pd(II) complexes bearing a chiral oxazoline ligand (**IIIa–f**) were synthesized by cleavage of dimeric palladium complexes with the oxazoline ligand. They were fully characterized by ^1H and ^{13}C NMR and elemental analyses. The catalytic activity of the complexes (**IIIa–f**) in allylic alkylation reactions was evaluated. The complex **IIIa** was found to be the most active catalyst. Very low *ee* values indicate that the oxazoline is dissociated from the active catalytic species.

Key words: N-heterocyclic carbene, oxazoline, palladium complexes, allylic alkylation

1. Introduction

N-Heterocyclic carbenes (NHCs) have emerged as important ligands for transition metals in organometallic catalysis. In contrast to phosphine complexes, their tight binding to the metal and high temperature, air, and moisture stability have led to the popularity of these compounds as ligands. The steric and electronic properties of these ligands can be modified by altering the substituents at the nitrogen atoms and heterocycle. Therefore, they can be used as ancillary ligands for the preparation of various complexes.^{1–6} Although palladium NHC complexes have been successfully developed as highly active precatalysts for C–C coupling reactions (e.g., Mizoroki-Heck and Suzuki-Miyaura couplings),^{7–13} the allylic alkylation reaction using a NHC–Pd has not been studied extensively. This reaction has proven to be a powerful method for C–C bond forming reactions, which are synthetically useful. Trost et al. have used the asymmetric allylic alkylation reaction for the total synthesis of galanthamine, which is utilized in the treatment of Alzheimer's disease.¹⁴ The first example of allylic alkylation using NHC–Pd complexes was published by Mori and Sato.^{15,16} In more recent years, enantioselective versions of allylic alkylation have been reported by several groups.^{17–26} However, to the best of our knowledge, allylic alkylation by chiral oxazoline bearing NHC–Pd complexes has not been investigated. To find a more active catalyst for this reaction and to throw light on the proposed mechanism, herein we report the preparation of benzimidazol-2-ylidene palladium(II) complexes containing a chiral oxazoline ligand.

2. Results and discussion

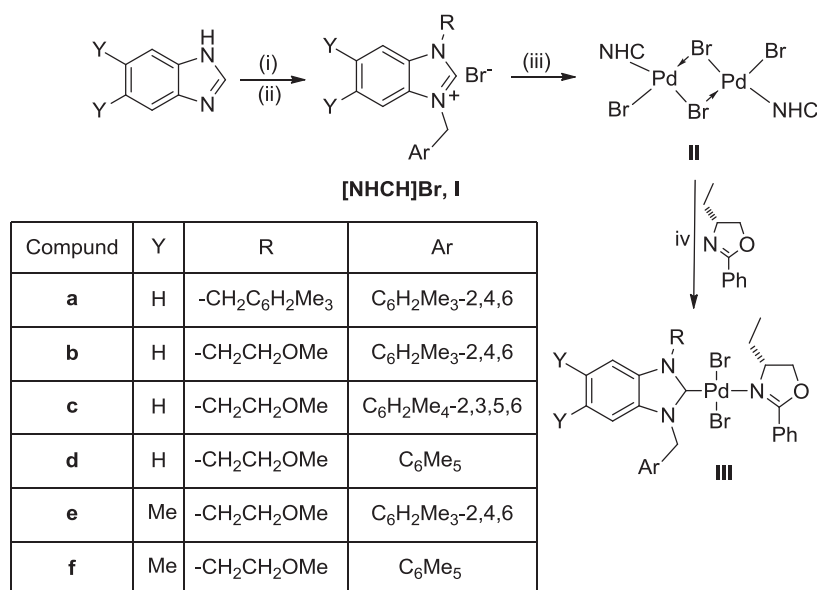
2.1. Synthesis and characterization of NHC precursors and NHC–Pd(II) complexes (I–III)

The (5,6-dimethyl)benzimidazolium salts synthesized (almost quantitative yield by quarternization of 1-substituted (5,6-dimethyl)benzimidazole²⁷ with benzyl bromides) were characterized by ^1H and ^{13}C NMR spectroscopy.

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^1H NMR chemical shifts were consistent with the proposed structures. The resonances for C_2 -hydrogens were observed as sharp singlets between 9.49 and 10.78 ppm. ^{13}C NMR of these salts showed the C-carbons at 140.4–143.2 ppm. These salts are air- and moisture-stable solids.

The synthesis of dinuclear and monomeric NHC–Pd complexes was carried out according to the literature.^{28,29} The dinuclear NHC–Pd(II) complexes (**IIa–f**) were air-stable orange solids slightly soluble in halogenated solvents (Scheme). Dinuclear palladium complexes (**IIa–f**) and chiral oxazoline were reacted in dichloromethane to give mixed-NHC–oxazoline complexes of Pd(II) (**IIIa–f**) as air-stable yellow solids soluble in halogenated solvents. NMR analyses of the complexes revealed that nitrogen atoms of the chiral oxazoline ligand are coordinated to the palladium center. ^{13}C NMR spectra of the complexes (**IIIa–f**) indicated a $\text{C}_{\text{carbene}}$ resonance between δ 167.1 and 167.3 ppm. The C=N signal in the oxazoline ring was observed between 163.6 and 165.6 ppm.



Scheme. (i) RX, KOH, toluene, EtOH or BuOH; (ii) ArCH_2Br , toluene, reflux; (iii) $\text{Pd}(\text{OAc})_2$, NaBr, DMSO, 90°C ; (iv) (4*S*)-4-ethyl-2-phenyl-4,5-dihydro-1,3-oxazole, CH_2Cl_2 , 25°C .

2.2. Allylic alkylation reactions with NHC–Pd(II) complexes (**IIIa–f**)

NHC–Pd(II) complexes **IIIa–f** were screened as catalysts for the allylic alkylation reaction of (*E*)-1,3-diphenyl-3-en-yl acetate using diethyl malonate as a nucleophile. The catalytic experiments were carried out using 2.5% mmol palladium complexes **IIIa–f** as catalysts in the presence of Cs_2CO_3 in THF at 50°C . The results are summarized in the Figure. The complex **IIIa** was found to be the most active catalyst (Figure). The activities of these complexes decreased in the order: **IIIa** > **IIIb** > **IIIc** > **IIIId** > **IIIe** > **IIIIf**. A comparison of **IIIb**, **IIIe** and **IIIId**, **IIIIf** showed that the methyl groups on the benzimidazole ring decrease the catalytic activity. The low reaction rate in the complexes with the methylated groups could be explained by the strong α -donating effect of the NHC ligand, which disfavors the nucleophilic addition step. These observations are consistent with previous work by Flahaut et al.²⁰ Although the complexes **IIIa–f** are chiral, very low enantioselectivity was observed (*ee*'s up to 3%). This result indicates that the chiral oxazoline ligand leaves the metal center early in

the catalytic cycle.^{35,36} Moreover, the development of chiral ligands disconnected to the NHC ligand does not appear to be promising for chiral induction in the allylic alkylation.

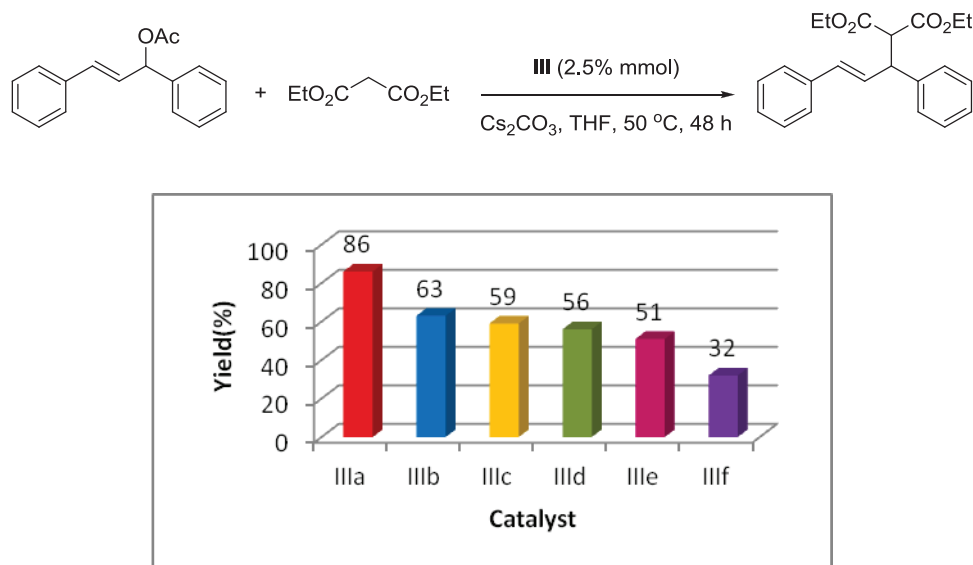


Figure. Allylic alkylation reaction of (*E*)-1,3-diphenyl-3-en-yl acetate catalyzed by NHC-Pd(II) complexes **IIIa-f**.

In conclusion, NHC-Pd(II) complexes bearing chiral oxazoline substituents (**IIIa-f**) were synthesized, characterized, and used for the allylic alkylation reaction of (*E*)-1,3-diphenyl-3-en-yl acetate. The complex **IIIa** is the most active catalyst. Catalytic activity decreased in the sequence: **IIIa** > **IIIb** > **IIIc** > **III d** > **III e** > **III f**. The results indicated that electron donating groups on the benzene ring of the NHC core or benzyl substituent decrease the catalytic activity. Unfortunately, no enantioselectivity could be observed. This behavior seems to be related to the departure of the oxazoline ligand from the metal center early in the catalytic cycle. Although we failed to achieve asymmetric induction, the yields of the alkylated reaction products are comparable or even higher than those reported for alternative procedures.^{19,20}

3. Experimental

All manipulations were performed in air unless stated otherwise. All solvents were used as received. 2,4,6-Trimethylbenzyl bromide, 2,3,5,6-tetramethylbenzyl bromide, and 2,3,4,5,6-pentamethylbenzyl bromide were synthesized according to methods previously described.³⁰ 1-Substituted-(5,6-dimethyl)benzimidazoles and benzimidazolium salts (**Ia-I d**) were prepared according to a slightly modified procedure from the literature.³¹⁻³⁴ All reagents were purchased from Merck, Fluka, Alfa Aesar, and Acros Organics. Melting points were recorded with a Gallenkamp electrothermal melting point apparatus. FTIR spectra were recorded on a PerkinElmer Spectrum 100 series spectrometer. ¹H NMR and ¹³C NMR spectra were recorded with a Varian AS 400 Mercury instrument. Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz. Optical rotations were taken on a Rudolph Research Analytical Autopol I automatic polarimeter with a wavelength of 589 nm. The concentration 'c' has units of g/100 mL. Elemental analyses were performed on a PerkinElmer PE 2400 elemental analyzer. Quantitative analyses were performed by gas chromatography (Thermo-Finnigan on an HP-5 capillary column and equipped with a FID detector) at Ege University Faculty of Science.

3.1. General procedure for the synthesis of 1,3-disubstituted (5,6-dimethyl)benzimidazolium salts (Ie, f)

1-Methoxyethyl-(5,6-dimethyl)benzimidazole or 1-(2,4,6-trimethyl)benzyl-benzimidazole (5.7 mmol) was dissolved in toluene and then 2,4,6-trimethylbenzyl bromide or 2,3,4,5,6-pentamethylbenzyl bromide (5.7 mmol) was added. The mixture was refluxed for 4 h. The solid that separated out after cooling was filtered off and washed with diethyl ether (5 mL). The product was recrystallized from CH₂Cl₂/Et₂O.

Ie: Yield 98%. Anal. Calc. C₂₂H₂₉BrN₂O: C, 63.25; H, 6.95; N, 6.71. Found: C, 62.98; H, 6.89; N, 6.67%. mp 210–214 °C. IR: $\tilde{\nu}$ = 1565 (ν CN) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 2.31 (s, 3 H, CH₂C₆H₂(CH₃)₃), 2.32 (s, 6 H, CH₂C₆H₂(CH₃)₃), 2.35 (s, 3 H, CH₃-Ar), 2.42 (s, 3 H, CH₃-Ar), 3.30 (s, 3 H, OCH₃), 3.87 (t, *J* = 4.4 Hz, 2 H, NCH₂CH₂O), 4.83 (t, *J* = 4.4 Hz, 2 H, NCH₂CH₂O), 5.70 (s, 2 H, CH₂C₆H₂(CH₃)₃), 6.95 (s, 2 H, CH₂C₆H₂(CH₃)₃), 7.15 (s, 1 H, Ar-*H*), 7.64 (s, 1 H, Ar-*H*), 10.24 (s, 1 H, NCHN). ¹³C NMR (100 MHz, CDCl₃) δ = 20.4 (CH₂C₆H₂(CH₃)₃-o), 20.8 (CH₂C₆H₂(CH₃)₃-p), 20.9 (CH₃-Ar), 21.3 (CH₃-Ar), 46.9 (CH₂C₆H₂(CH₃)₃), 47.8 (NCH₂CH₂O), 59.1 (NCH₂CH₂O), 70.1 (OCH₃), 113.2, 113.8 (Ar-*C*-o), 125.2, 129.9 (Ar-*C*), 130.3 (CH₂C₆H₂(CH₃)₃-o), 130.9 (CH₂C₆H₂(CH₃)₃-m), 137.4 (CH₂C₆H₂(CH₃)₃-p), 137.5, 138.2 (Ar-*C*-m), 140.0 (CH₂C₆H₂(CH₃)₃-o), 141.4 (NCHN).

If: Yield 80%. Anal. Calc. C₂₄H₃₃BrN₂O: C, 64.65; H, 7.41; N, 6.29. Found: C, 64.38; H, 7.32; N, 6.17%. mp 109–110 °C. IR: $\tilde{\nu}$ = 1566 (ν CN) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 2.26 (s, 6 H, CH₂C₆(CH₃)₅), 2.27 (s, 6 H, CH₂C₆(CH₃)₅), 2.29 (s, 3 H, CH₂C₆(CH₃)₅), 2.41 (s, 3 H, CH₃-Ar), 2.45 (s, 3 H, CH₃-Ar), 3.27 (s, 3 H, OCH₃), 3.83 (t, *J* = 4.8 Hz, 2 H, NCH₂CH₂O), 4.87 (t, *J* = 4.8 Hz, 2 H, NCH₂CH₂O), 5.30 (s, 2 H, CH₂C₆(CH₃)₅), 7.42 (s, 1 H, Ar-*H*), 7.72 (s, 1 H, Ar-*H*), 9.49 (s, 1 H, NCHN). ¹³C NMR (100 MHz, CDCl₃) δ = 17.1 (CH₂C₆(CH₃)₅-m), 17.2 (CH₂C₆(CH₃)₅-o), 17.5 (CH₂C₆(CH₃)₅-p), 20.8 (CH₃-Ar), 20.9 (CH₃-Ar), 47.5 (CH₂C₆(CH₃)₅-2,3,4,5,6), 48.0 (NCH₂CH₂O), 59.1 (NCH₂CH₂O), 70.3 (OCH₃), 112.9, 114.0 (Ar-*C*-o), 124.9 (Ar-*C*), 129.9 (CH₂C₆(CH₃)₅), 130.9 (Ar-*C*), 133.7 (CH₂C₆(CH₃)₅-m), 134.2 (CH₂C₆(CH₃)₅-p), 137.5 (CH₂C₆(CH₃)₅-o), 137.6, 137.7 (Ar-*C*-m), 140.4 (NCHN).

3.2. Synthesis of dimeric NHC-Pd(II) complexes (IIa–f)

A mixture of salt (Ia–f) (1.2 mmol), Pd(OAc)₂ (1.2 mmol), and NaBr (3.6 mmol) in DMSO was stirred at 90 °C for 24 h. The solvent was removed by vacuum distillation. The resulting residue was suspended in CH₂Cl₂ and then H₂O was added and the organic phase dried over Na₂SO₄. Concentration of the organic phase and the addition of Et₂O afforded complexes IIa–f as an orange solid.

3.3. Synthesis of mixed NHC-oxazoline Pd(II) complexes (IIIa–f)

A mixture of dinuclear complex (IIa–f) (0.17 mmol) and (4*R*)-4-ethyl-2-phenyl-4,5-dihydro-1,3-oxazole was suspended in CH₂Cl₂ (5 mL) and stirred at room temperature for 3 h. After removal of the solvent, complexes IIIa–f were obtained as yellow solids, which were washed with Et₂O and dried.

IIIa: Yield 45%. Anal. Calc. C₃₈H₄₃Br₂N₃OPd: C, 55.39; H, 5.26; N, 5.10. Found: C, 55.32; H, 5.23; N, 5.07%. mp 119–122 °C. IR: $\tilde{\nu}$ = 1643 (ν CN-ox) cm⁻¹. [α] = -37.50 (c. 0.16, 24.6 °C). ¹H NMR (400 MHz, CDCl₃) δ = 1.11 (t, *J* = 8.0 Hz, 3 H, Ox-CH₂CH₃), 2.05–2.12 (m, 1 H, Ox-CH₂CH₃), 2.33 (s, 12 H, CH₂C₆H₂(CH₃)₃), 2.35 (s, 6 H, CH₂C₆H₂(CH₃)₃), 2.66–2.72 (m, 1 H, Ox-CH₂CH₃), 4.27 (m, 1 H, Ox-

CH), 4.62–4.69 (m, 2 H, Ox-*CH*₂), 6.19 (s, 4 H, *CH*₂*C*₆*H*₂(*CH*₃)₃), 6.18–6.21 (m, 2 H, Ar-*H*), 6.70–6.73 (m, 2 H, Ar-*H*), 6.94 (s, 4 H, *CH*₂*C*₆*H*₂(*CH*₃)₃), 7.39–7.46 (m, 3 H, Ox-Ar-*H*), 8.82 (d, *J* = 8.0 Hz, 2 H, Ox-Ar-*H*). ¹³C NMR (100 MHz, CDCl₃) δ = 10.0 (Ox-*CH*₂*CH*₃), 21.2 (*CH*₂*C*₆*H*₂(*CH*₃)₃-o), 21.3 (*CH*₂*C*₆*H*₂(*CH*₃)₃-p), 28.5 (Ox-*CH*₂*CH*₃), 51.6 (*CH*₂*C*₆*H*₂(*CH*₃)₃), 68.2 (Ox-*CH*), 72.9 (Ox-*CH*₂), 111.3 (Ar-*C*-o), 122.7 (Ar-*C*-m), 126.9 (Ox-Ar-*C*-p), 127.8 (Ox-Ar-*C*-m), 128.2 (Ox-Ar-*C*-o), 129.8 (*CH*₂*C*₆*H*₂(*CH*₃)₃-m), 130.5 (Ar-*C*), 132.7 (*CH*₂*C*₆*H*₂(*CH*₃)₃-p), 135.2 (Ox-Ar-*C*), 138.9 (*CH*₂*C*₆*H*₂(*CH*₃)₃-o), 139.1 (*CH*₂*C*₆*H*₂(*CH*₃)₃), 166.1 (Ox-*CN*), 167.3 (*C*_{carbene}).

IIIb: Yield 40%. Anal. Calc. C₃₁H₃₇Br₂N₃O₂Pd: C, 49.65; H, 4.97; N, 5.60. Found: C, 49.59; H, 4.94; N, 5.59%. mp 173–177 °C. IR: $\tilde{\nu}$ = 1644 (ν CN-ox) cm⁻¹. [α] = -31.21 (c. 0.26, 26.6 °C). ¹H NMR (400 MHz, CDCl₃) δ = 1.10 (t, *J* = 7.6 Hz, 3 H, Ox-*CH*₂*CH*₃), 2.06–2.13 (m, 1 H, Ox-*CH*₂*CH*₃), 2.32 (s, 6 H, *CH*₂*C*₆*H*₂(*CH*₃)₃), 2.36 (s, 3 H, *CH*₂*C*₆*H*₂(*CH*₃)₃), 2.66–2.73 (m, 1 H, Ox-*CH*₂*CH*₃), 3.35 (s, 3 H, *OCH*₃), 4.15 (t, *J* = 6.0 Hz, 2 H, *NCH*₂*CH*₂*O*), 4.27 (t, *J* = 6.4 Hz, 1 H, Ox-*CH*), 4.62–4.68 (m, 2 H, Ox-*CH*₂), 5.02 (t, *J* = 6.0 Hz, 2 H, *NCH*₂*CH*₂*O*), 6.12 (s, 2 H, *CH*₂*C*₆*H*₂(*CH*₃)₃), 6.15 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 6.85 (t, *J* = 8.0 Hz, 1 H, Ar-*H*), 6.96 (s, 2 H, *CH*₂*C*₆*H*₂(*CH*₃)₃), 7.10 (t, *J* = 8.0 Hz, 1 H, Ar-*H*), 7.45–7.55 (m, 4 H, Ox-Ar-*H*, Ar-*H*), 8.76 (d, *J* = 7.6 Hz, 2 H, Ox-Ar-*H*). ¹³C NMR (100 MHz, CDCl₃) δ = 10.1 (Ox-*CH*₂*CH*₃), 21.1 (*CH*₂*C*₆*H*₂(*CH*₃)₃-o), 21.3 (*CH*₂*C*₆*H*₂(*CH*₃)₃-p), 28.5 (Ox-*CH*₂*CH*₃), 48.8 (*NCH*₂*CH*₂*O*), 51.4 (*CH*₂*C*₆*H*₂(*CH*₃)₃), 59.4 (*OCH*₃), 68.3 (Ox-*CH*), 71.5 (*NCH*₂*CH*₂*O*), 72.9 (Ox-*CH*₂), 111.2, 111.4 (Ar-*C*-o), 122.8, 123.2 (Ar-*C*-m), 126.8 (*CH*₂*C*₆*H*₂(*CH*₃)₃-m), 127.6 (Ox-Ar-*C*-o), 128.3 (Ox-Ar-*C*-m), 129.8 (Ox-Ar-*C*-p), 130.4, 132.7 (Ar-*C*), 134.7 (*CH*₂*C*₆*H*₂(*CH*₃)₃-p), 135.9 (Ox-Ar-*C*), 139.1 (*CH*₂*C*₆*H*₂(*CH*₃)₃-o), 139.3 (*CH*₂*C*₆*H*₂(*CH*₃)₃), 165.6 (Ox-*CN*), 167.3 (*C*_{carbene}).

IIIc: Yield 56%. Anal. Calc. C₃₂H₃₉Br₂N₃O₂Pd: C, 50.31; H, 5.15; N, 5.50. Found: C, 50.25; H, 5.11; N, 5.48%. mp 192–195 °C. IR: $\tilde{\nu}$ = 1642 (ν CN-ox) cm⁻¹. [α] = -35.81 (c. 0.25, 26.9 °C). ¹H NMR (400 MHz, CDCl₃) δ = 1.12 (t, *J* = 7.2 Hz, 3 H, Ox-*CH*₂*CH*₃), 2.07–2.14 (m, 1 H, Ox-*CH*₂*CH*₃), 2.26 (s, 3 H, *CH*₂*C*₆*H*(*CH*₃)₄), 2.29 (s, 3 H, *CH*₂*C*₆*H*(*CH*₃)₄), 2.69–2.74 (m, 1 H, Ox-*CH*₂*CH*₃), 3.35 (s, 3 H, *OCH*₃), 4.16 (t, *J* = 5.6 Hz, 2 H, *NCH*₂*CH*₂*O*), 4.27 (t, *J* = 6.4 Hz, 1 H, Ox-*CH*), 4.62–4.69 (m, 2 H, Ox-*CH*₂), 5.03 (t, *J* = 5.6 Hz, 2 H, *NCH*₂*CH*₂*O*), 6.01 (d, *J* = 8.0 Hz, 1 H, Ar-*H*), 6.22 (s, 2 H, *CH*₂*C*₆*H*(*CH*₃)₄), 6.81 (t, *J* = 8.0 Hz, 1 H, Ar-*H*), 7.09 (t, *J* = 8.0 Hz, 1 H, Ar-*H*), 7.12 (s, 1 H, *CH*₂*C*₆*H*(*CH*₃)₄), 7.44–7.56 (m, 4 H, Ox-Ar-*H*, Ar-*H*), 8.78 (d, *J* = 7.2 Hz, 2 H, Ox-Ar-*H*). ¹³C NMR (100 MHz, CDCl₃) δ = 10.1 (Ox-*CH*₂*CH*₃), 16.8 (*CH*₂*C*₆*H*(*CH*₃)₄-o), 20.7 (*CH*₂*C*₆*H*(*CH*₃)₄-m), 28.5 (Ox-*CH*₂*CH*₃), 48.8 (*NCH*₂*CH*₂*O*), 52.4 (*CH*₂*C*₆*H*(*CH*₃)₄), 59.4 (*OCH*₃), 68.3 (Ox-*CH*), 71.5 (*NCH*₂*CH*₂*O*), 72.9 (Ox-*CH*₂), 111.2, 111.6 (Ar-*C*-o), 122.6, 123.1 (Ar-*C*-m), 126.8 (*CH*₂*C*₆*H*(*CH*₃)₄-p), 128.3 (Ox-Ar-*C*-o), 130.4 (Ox-Ar-*C*-m), 130.5 (Ox-Ar-*C*-p), 132.7 (*CH*₂*C*₆*H*(*CH*₃)₄-o), 132.9 (*CH*₂*C*₆*H*(*CH*₃)₄-m), 134.6, 134.9 (Ar-*C*), 135.6 (Ox-Ar-*C*), 135.9 (*CH*₂*C*₆*H*(*CH*₃)₄), 165.6 (Ox-*CN*), 167.2 (*C*_{carbene}).

III d: Yield 78%. Anal. Calc. C₃₃H₄₁Br₂N₃O₂Pd: C, 50.95; H, 5.31; N, 5.40. Found: C, 50.86; H, 5.29; N, 5.36%. mp 199–201 °C. IR: $\tilde{\nu}$ = 1639 (ν CN-ox) cm⁻¹. [α] = -38.46 (c. 0.26, 26.8 °C). ¹H NMR (400 MHz, CDCl₃) δ = 1.11 (t, *J* = 7.2 Hz, 3 H, Ox-*CH*₂*CH*₃), 2.09–2.14 (m, 1 H, Ox-*CH*₂*CH*₃), 2.27 (s, 6 H, *CH*₂*C*₆(*CH*₃)₅), 2.31 (s, 6 H, *CH*₂*C*₆(*CH*₃)₅), 2.34 (s, 3 H, *CH*₂*C*₆(*CH*₃)₅), 2.68–2.73 (m, 1 H, Ox-*CH*₂*CH*₃), 3.36 (s, 3 H, *OCH*₃), 4.16 (t, *J* = 6.0 Hz, 2 H, *NCH*₂*CH*₂*O*), 4.29 (t, *J* = 6.8 Hz, 1 H, Ox-*CH*), 4.63–4.68 (m, 2 H, Ox-*CH*₂), 5.03 (t, *J* = 6.0 Hz, 2 H, *NCH*₂*CH*₂*O*), 6.06 (d, *J* = 7.2 Hz, 1 H, Ar-*H*), 6.23 (s, 2 H, *CH*₂*C*₆(*CH*₃)₅), 6.79 (t, *J* = 7.2 Hz, 1 H, Ar-*H*), 7.08 (t, *J* = 7.2 Hz, 1 H, Ar-*H*),

7.44–7.55 (m, 4 H, Ox-Ar-*H*, Ar-*H*), 8.79 (d, $J = 7.2$ Hz, 2 H, Ox-Ar-*H*). ^{13}C NMR (100 MHz, CDCl_3) $\delta =$ 10.1 (Ox- CH_2CH_3), 17.1 ($\text{CH}_2\text{C}_6(\text{CH}_3)_5\text{-o}$), 17.5 ($\text{CH}_2\text{C}_6(\text{CH}_3)_5\text{-p}$), 17.8 ($\text{CH}_2\text{C}_6(\text{CH}_3)_5\text{-m}$), 28.5 (Ox- CH_2CH_3), 48.7 ($\text{NCH}_2\text{CH}_2\text{O}$), 52.9 ($\text{CH}_2\text{C}_6(\text{CH}_3)_5$), 59.4 (OCH_3), 68.3 (Ox-*CH*), 71.4 ($\text{NCH}_2\text{CH}_2\text{O}$), 72.9 (Ox- CH_2), 111.1, 111.7 (Ar-*C-o*), 122.6, 123.1 (Ar-*C-m*), 126.8 (Ox-Ar-*C-o*), 127.9 (Ox-Ar-*C-m*), 128.3 (Ox-Ar-*C-p*), 130.4 ($\text{CH}_2\text{C}_6(\text{CH}_3)_5\text{-m}$), 132.7 ($\text{CH}_2\text{C}_6(\text{CH}_3)_5\text{-o}$), 133.4 ($\text{CH}_2\text{C}_6(\text{CH}_3)_5\text{-p}$), 134.9, 135.1 (Ar-*C*), 135.9 (Ox-Ar-*C*), 136.5 ($\text{CH}_2\text{C}_6(\text{CH}_3)_5$), 165.5 (Ox-*CN*), 167.2 (*C_{carbene}*).

IIIe: Yield 79%. Anal. Calc. $\text{C}_{33}\text{H}_{41}\text{Br}_2\text{N}_3\text{O}_2\text{Pd}$: C, 50.95; H, 5.31; N, 5.40. Found: C, 50.91; H, 5.28; N, 5.41%. mp 174–176 °C. IR: $\tilde{\nu} = 1639$ ($\nu\text{CN-ox}$) cm^{-1} . $[\alpha] = -9.17$ (c. 0.11, 28.2 °C). ^1H NMR (400 MHz, CDCl_3) $\delta =$ 1.14 (t, $J = 7.6$ Hz, 3 H, Ox- CH_2CH_3), 2.01 (s, 3 H, $\text{CH}_2\text{C}_6\text{H}_2(\text{CH}_3)_3$), 2.09–2.14 (m, 1 H, Ox- CH_2CH_3), 2.26 (s, 6 H, $\text{CH}_2\text{C}_6\text{H}_2(\text{CH}_3)_3$), 2.33 (s, 3 H, $\text{CH}_3\text{-Ar}$), 2.38 (s, 3 H, $\text{CH}_3\text{-Ar}$), 2.65–2.71 (m, 1 H, Ox- CH_2CH_3), 3.35 (s, 3 H, OCH_3), 4.13 (t, $J = 6.4$ Hz, 2 H, CH_2), 4.28 (t, $J = 6.8$ Hz, 1 H, Ox-*CH*), 4.62–4.70 (m, 2 H, Ox- CH_2), 4.94 (t, $J = 6.4$ Hz, 2 H, CH_2), 5.85 (s, 1 H, Ar-*H*), 6.04 (s, 2 H, $\text{CH}_2\text{C}_6\text{H}_2(\text{CH}_3)_3$), 6.95 (s, 2 H, $\text{CH}_2\text{C}_6\text{H}_2(\text{CH}_3)_3$), 7.19 (s, 1 H, Ar-*H*), 7.47–7.55 (m, 3 H, Ox-Ar-*H*), 8.77 (d, $J = 8.0$ Hz, 2 H, Ox-Ar-*H*). ^{13}C NMR (100 MHz, CDCl_3) $\delta =$ 10.1 (Ox- CH_2CH_3), 20.3, 20.6 (Ar- CH_3), 21.1 ($\text{CH}_2\text{C}_6\text{H}_2(\text{CH}_3)_3\text{-o}$), 21.3 ($\text{CH}_2\text{C}_6\text{H}_2(\text{CH}_3)_3\text{-p}$), 28.4 (Ox- CH_2CH_3), 48.5 ($\text{NCH}_2\text{CH}_2\text{O}$), 51.1 ($\text{CH}_2\text{C}_6\text{H}_2(\text{CH}_3)_3$), 59.4 (OCH_3), 68.2 (Ox-*CH*), 71.5 ($\text{NCH}_2\text{CH}_2\text{O}$), 72.7 (Ox- CH_2), 111.3, 111.9 (Ar-*C-o*), 126.9 ($\text{CH}_2\text{C}_6\text{H}_2(\text{CH}_3)_3\text{-m}$), 127.9 (Ox-Ar-*C-o*), 128.2 (Ox-Ar-*C-m*), 129.5 (Ox-Ar-*C-p*), 130.4 (Ar-*C*), 131.6, 132.5 (Ar-*C-m*), 133.3 ($\text{CH}_2\text{C}_6\text{H}_2(\text{CH}_3)_3\text{-p}$), 134.5 (Ox-Ar-*C*), 138.7 ($\text{CH}_2\text{C}_6\text{H}_2(\text{CH}_3)_3\text{-o}$), 139.4 ($\text{CH}_2\text{C}_6\text{H}_2(\text{CH}_3)_3$), 163.7 (Ox-*CN*), 167.1 (*C_{carbene}*).

IIIf: Yield 77%. Anal. Calc. $\text{C}_{35}\text{H}_{45}\text{Br}_2\text{N}_3\text{O}_2\text{Pd}$: C, 52.16; H, 5.63; N, 5.21. Found: C, 52.13; H, 5.61; N, 5.20%. mp 162–165 °C. IR: $\tilde{\nu} = 1640$ ($\nu\text{CN-ox}$) cm^{-1} . $[\alpha] = -8.77$ (c. 0.11, 26.8 °C). ^1H NMR (400 MHz, CDCl_3) $\delta =$ 1.14 (t, $J = 7.6$ Hz, 3 H, Ox- CH_2CH_3), 1.96 (s, 3 H, $\text{CH}_2\text{C}_6(\text{CH}_3)_5$), 2.08–2.16 (m, 1 H, Ox- CH_2CH_3), 2.21 (s, 3 H, $\text{CH}_3\text{-Ar}$), 2.29 (s, 6 H, $\text{CH}_2\text{C}_6(\text{CH}_3)_5$), 2.32 (s, 6 H, $\text{CH}_2\text{C}_6(\text{CH}_3)_5$), 2.38 (s, 3 H, $\text{CH}_3\text{-Ar}$), 2.68–2.74 (m, 1 H, Ox- CH_2CH_3), 3.37 (s, 3 H, OCH_3), 4.14 (t, $J = 5.6$ Hz, 2 H, CH_2), 4.28 (t, $J = 6.8$ Hz, 1 H, Ox-*CH*), 4.63–4.70 (m, 2 H, Ox- CH_2), 4.94 (t, $J = 5.6$ Hz, 2 H, CH_2), 5.76 (s, 1 H, Ar-*H*), 6.14 (s, 2 H, $\text{CH}_2\text{C}_6(\text{CH}_3)_5$), 7.18 (s, 1 H, Ar-*H*), 7.47–7.55 (m, 3 H, Ox-Ar-*H*), 8.79 (d, $J = 7.2$ Hz, 2 H, Ox-Ar-*H*). ^{13}C NMR (100 MHz, CDCl_3) $\delta =$ 10.1 (Ox- CH_2CH_3), 17.1 ($\text{CH}_2\text{C}_6(\text{CH}_3)_3\text{-o}$), 17.5 ($\text{CH}_2\text{C}_6(\text{CH}_3)_3\text{-p}$), 17.9 ($\text{CH}_2\text{C}_6(\text{CH}_3)_3\text{-m}$), 20.3 (Ar- CH_3), 20.6 (Ar- CH_3), 28.4 (Ox- CH_2CH_3), 48.5 ($\text{NCH}_2\text{CH}_2\text{O}$), 52.6 ($\text{CH}_2\text{C}_6(\text{CH}_3)_5$), 59.4 (OCH_3), 68.3 (Ox-*CH*), 71.4 ($\text{NCH}_2\text{CH}_2\text{O}$), 72.7 (Ox- CH_2), 111.2, 112.3 (Ar-*C-o*), 126.9 (Ox-Ar-*C-p*), 128.2 (Ox-Ar-*C-m*), 130.4 (Ox-Ar-*C-o*), 131.3, 131.4 (Ar-*C*), 132.6 ($\text{CH}_2\text{C}_6(\text{CH}_3)_5\text{-p}$), 133.0, 133.5 (Ar-*C-m*), 134.6 ($\text{CH}_2\text{C}_6(\text{CH}_3)_5\text{-o}$), 135.2 (Ox-Ar-*C*), 136.1 ($\text{CH}_2\text{C}_6(\text{CH}_3)_5$), 163.6 (Ox-*CN*), 167.1 (*C_{carbene}*).

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