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Synthesis, Characterization, and Catalytic Studies of Unsymmetrical Chiral NCC Pincer Pd(II) and Ni(II) Complexes Bearing (Imidazolinyl)aryl NHC Ligands

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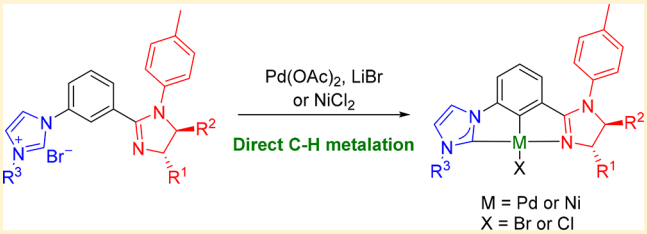
Supporting Information

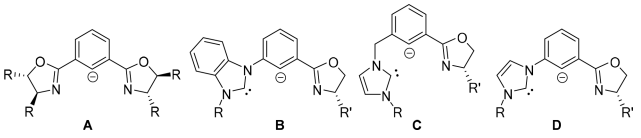
ABSTRACT: A series of palladium(II) and nickel(II) complexes based on unsymmetrical chiral (imidazolinyl)aryl NHC ligands are reported. The new ligand presursors **3a−g** were prepared from commercially available 3-bromobenzoic acid, in which the carboxyl and bromo functionalities were converted to chiral imidazoline and NHC moieties, respectively, in three steps. Treatment of **3a−g** with $Pd(OAc)_2$ in dimethylacetamide in the presence of NaOAc, followed by addition of LiCl, gave the seven palladium(II) pincer complexes **4a−g** via direct aryl C−H activation. Likewise, the six nickel(II) pincer complexes **5a−f** were obtained by reacting **3a−f** with anhydrous $NiCl_2$. All of the ligand precursors and pincer complexes are bench-stable and were fully characterized. The absolute configurations of palladium complexes **4a,c** and **5e** were further determined by X-ray diffraction. Finally, Pd pincer complex catalyzed asymmetric Friedel−Crafts alkylation and aza-Morita−Baylis−Hillman reactions were briefly assessed.



INTRODUCTION

Organometallic pincer complexes bearing tridentate ligands have been extensively investigated owing to their wide applications in organic catalysis, materials science, and chemical biology.[1,2] The incorporation of pincer ligands around the metal center enables the generation of efficient and stable catalysts with versatile reactivities via structural and electronic modifications of ligand frameworks.[3] Inspired by the pioneering work of Shaw, van Koten, and Noltes,[4] great progress has been achieved for symmetrical NCN,[5] NCN,[6] PCP,[7] and PNP[1i,8] type ligands in the past few decades. As another representative donor moiety, N-heterocyclic carbenes (NHCs) have gained tremendous attention due to their better σ-donating ability to form stable metal-NHC complexes.[9] A diversity of NHCs could be easily achieved by variation of substituents on the heterocycles. Consequently, NHC-based C donors have been commonly employed in symmetrical NCN,[10] CCC,[11] and CNC[12] type ligands.

Recently, NHC-containing unsymmetrical pincer-type ligands have also been reported by adding different donors to the pincer architectures.[13−17] This strategy allows fine modulation of stereoelectronic parameters and liabilities of ligands, which has a great influence on the reactivities of pincer complexes.[18] Several successful transformations have already been reported for ester hydrogenation,[13] Kumada cross-coupling,[14] Suzuki−Miyaura cross-coupling,[15] and reduction of ketones and aldehydes[16] catalyzed by unsymmetrical pincer Ru, Ir, and Ni complexes. However, the research on NHC pincer complexes with both unsymmetrical and chiral parameters has been less explored.[19] Anionic bis(oxazolinyl)-phenyl (Phebox, **A**) moieties have been widely utilized as chiral ligand precursors, which could coordinate with multiple metals to achieve ample asymmetrical transformations.[20] In 2015, the Shi group reported NHC-oxazoline CCN pincer complexes (**B**), which were utilized to support Au metal in cycloaddition/oxidation reactions of enyones with alkenes.[19a] In 2016, the Ito and Nishiyama groups developed a series of chiral CCN ligands (**C** and **D**) and their pincer Rh and Ru pincer complexes for asymmetrical hydrogenation, conjugate reduction,[19b] and alkynylation of ketones.[19c]



On the other hand, bis(imidazolinyl)phenyl[21,22] (Phebim, **E**) and bis(imidazolidine)phenyl[23] (**F**) frameworks have recently emerged as promising alternatives in asymmetrical catalyzations. In comparison with the corresponding oxazoline ligands, chirality in the imidazolines could be easily introduced through different chiral amino alcohols. Meanwhile, the NR group in imidazolines could provide higher tunability of conformational and electronic properties. We have studied imidazoline-based symmetrical[21] and unsymmetrical[24] chiral

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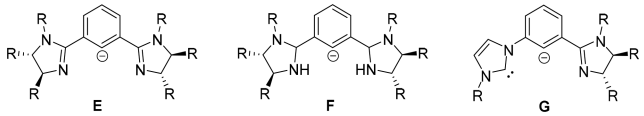
pincer Pt, Pd, Ni, and Rh complexes, which have been employed in asymmetric Friedel–Crafts alkylation,[21b,d] allylation,[21e,24a] alknylation,[21f] and diphenylphosphine[21g,24c,d] reactions.[1b] As a continuation of our previous work, we herein designed the new unsymmetrical chiral CCN pincer ligand **G** with both NHC and imidazole donor moieties. The corresponding CCN pincer Pd and Ni complexes have also been synthesized for the first time. Additionally, preliminary investigations on pincer Pd-catalyzed Friedel–Crafts alkylation and aza-Morita–Baylis–Hillman (aza-MBH) reactions are described.

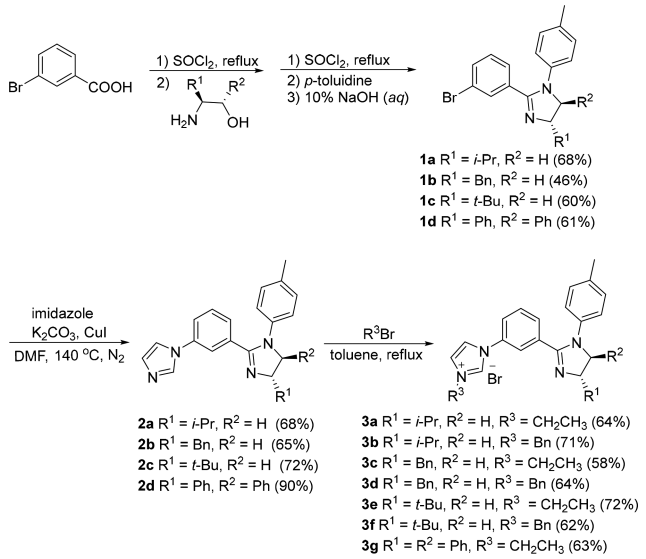


RESULTS AND DISCUSSION

The synthesis of unsymmetrical chiral ligand precursors **3a–i** is illustrated in Scheme 1. Initially, the carboxylic acid group of 3-bromobenzoic acid was converted to an imidazoline moiety in two steps according to a previous procedure.[21,25] 3-Bromobenzoic acid was refluxed in thionyl chloride to give 3-bromobenzoyl chloride, which reacted with chiral amino alcohols to afford the corresponding amido alcohols under basic conditions without further purification. The obtained amido alcohols were then treated with an excess of thionyl chloride, followed by arylamination and workup with 10% NaOH to provide **1a–d** in 46–68% yields. Next, compounds **1a–d** reacted with imidazole in the presence of CuI and K_2CO_3 to generate **2a–d** in 65–90% yields. Finally, treatment of **2a–d** with ethyl bromide or benzyl bromide in CH_3CN furnished the imidazoline-imidazolium ligands **3a–g** in 58–72% yields. The formation of the imidazolium salt was further confirmed by the characteristic signal at δ 10.86–11.20 ppm in the ^{1}H NMR spectra.

With the NHC-imidazoline ligands in hand, cyclometalation was carried out to form palladium(II) and nickel(II) pincer complexes via direct C–H activation, as shown in Scheme 2.

Scheme 1. Preparation of Unsymmetrical Chiral NHC-Imidazoline Ligand Precursors 3a–g

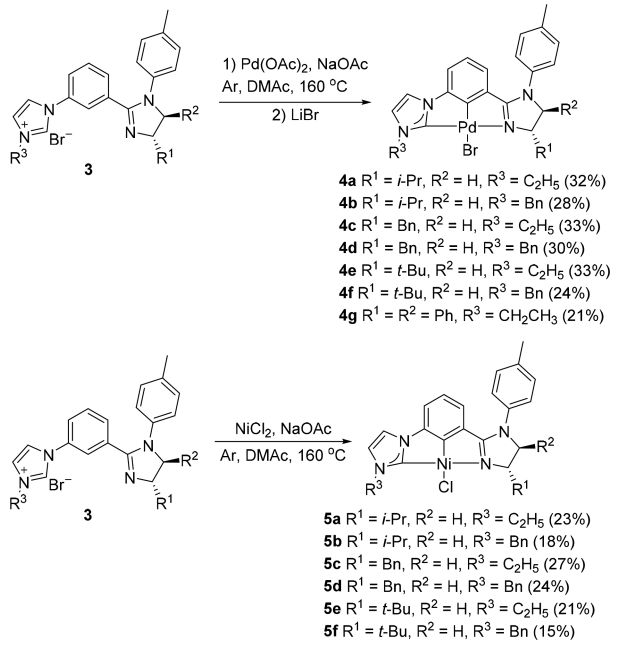


1a R^1 = *i*-Pr, R^2 = H (68%)
1b R^1 = Bn, R^2 = H (46%)
1c R^1 = *t*-Bu, R^2 = H (60%)
1d R^1 = Ph, R^2 = Ph (61%)

2a R^1 = *i*-Pr, R^2 = H (68%)
2b R^1 = Bn, R^2 = H (65%)
2c R^1 = *t*-Bu, R^2 = H (72%)
2d R^1 = Ph, R^2 = Ph (90%)

3a R^1 = *i*-Pr, R^2 = H, R^3 = CH_2CH_3 (64%)
3b R^1 = *i*-Pr, R^2 = H, R^3 = Bn (71%)
3c R^1 = Bn, R^2 = H, R^3 = CH_2CH_3 (58%)
3d R^1 = Bn, R^2 = H, R^3 = Bn (64%)
3e R^1 = *t*-Bu, R^2 = H, R^3 = CH_2CH_3 (72%)
3f R^1 = *t*-Bu, R^2 = H, R^3 = Bn (62%)
3g R^1 = R^2 = Ph, R^3 = CH_2CH_3 (63%)

Scheme 2. Preparation of Unsymmetrical Chiral CCN Pincer Pd and Ni Complexes 4a–g and 5a–f



4a R^1 = *i*-Pr, R^2 = H, R^3 = C_2H_5 (32%)
4b R^1 = *i*-Pr, R^2 = H, R^3 = Bn (28%)
4c R^1 = Bn, R^2 = H, R^3 = C_2H_5 (33%)
4d R^1 = Bn, R^2 = H, R^3 = Bn (30%)
4e R^1 = *t*-Bu, R^2 = H, R^3 = C_2H_5 (33%)
4f R^1 = *t*-Bu, R^2 = H, R^3 = Bn (24%)
4g R^1 = R^2 = Ph, R^3 = CH_2CH_3 (21%)

5a R^1 = *i*-Pr, R^2 = H, R^3 = C_2H_5 (23%)
5b R^1 = *i*-Pr, R^2 = H, R^3 = Bn (18%)
5c R^1 = Bn, R^2 = H, R^3 = C_2H_5 (27%)
5d R^1 = Bn, R^2 = H, R^3 = Bn (24%)
5e R^1 = *t*-Bu, R^2 = H, R^3 = C_2H_5 (21%)
5f R^1 = *t*-Bu, R^2 = H, R^3 = Bn (15%)

First, a mixture of ligands **3** and $Pd(OAc)_2$ was refluxed in dimethylacetamide in the presence of NaOAc for 48 h, followed by addition of LiCl, under a nitrogen atmosphere. After removal of solvent and purification by preparative TLC on silica gel plates, the cyclopalladated complexes **4a–g** were obtained in 21–33% yields. Encouraged by the above results, we also easily synthesized the unsymmetrical chiral CCN pincer Ni(II) complexes **5a–f** and isolated them in 15–27% yields using $NiCl_2$ as the nickel source.

All of the obtained neutral metal complexes **4a–g** and **5a–f** are air- and moisture-stable in both solution and the solid state and were fully characterized. When ligands **3a–g** were cyclometalated, the signals at δ 10.86–11.20 and 7.74–7.94 ppm both disappeared for the NHC and central Ar protons, indicating the formation of the corresponding Pd and Ni pincer complexes. Additionally, similarly to our previous reports, the chemical shifts of protons on the central Ar and NHC rings were shifted upfield, while proton signals on NAr and imidazoline ring were observed downfield due to C–M bonds formation and N–M bond coordination. In the $^{13}C\{^1H\}$ NMR spectra of the above Pd and Ni complexes, the appearance of signals at δ 168–171 ppm corresponded to the carbon atom of C=N, which shifted downfield in comparison to those of the ligand precursors (δ 160–161 ppm). Likewise, two new carbon signals observed in the range of δ 158–170 ppm due to C–M bond formations were assigned as the carbene carbon of NHC and the C-2 carbon of the central Ar.

The molecular structures of pincer Pd(II) complexes **4a,c** as well as Ni(II) complex **5e** were confirmed by X-ray analysis (Figures 1–3). In each pincer complex, the metal(II) atom displays a distorted-square-planar geometry coordinated by one imidazolinyl nitrogen atom, one central aryl carbon atom, one carbene carbon atom, and one halogen (Br or Cl) atom. Through the coordination of the metal center with tridentate ligands, a polycyclic system composed of four five-membered rings and one six-membered ring is formed, which are

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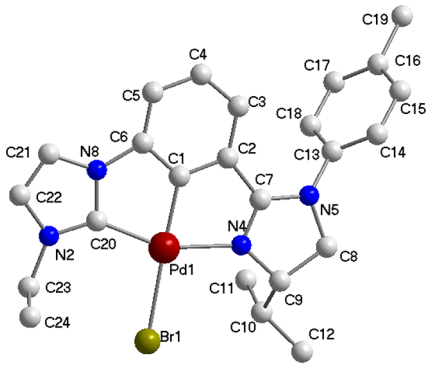

Figure 1. ORTEP diagram of the molecular structure of **4a** at the 30% probability level. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1), 1.931(6); Pd(1)−N(4), 2.109(5); Pd(1)−C(20), 2.005(6); Pd(1)−Br(1), 2.5132(9); N(4)−C(7), 1.297(8); N(5)−C(7), 1.357(8); N(8)−C(20), 1.366(8); N(2)−C(20), 1.341(8); C(20)−Pd(1)−N(4), 157.3(3); C(1)−Pd(1)−Br(1), 177.92(19); N(4)−C(7)−N(5), 116.3(6); N(2)−C(20)−N(8), 104.8(5).

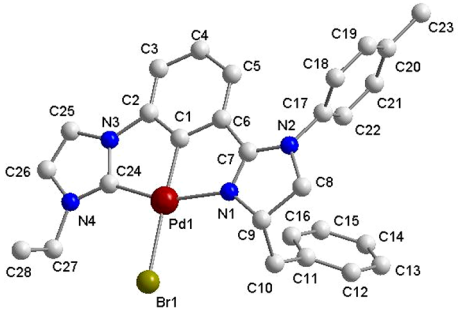

Figure 2. ORTEP diagram of the molecular structure of **4c** at the 30% probability level. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1), 1.938(6); Pd(1)−N(1), 2.112(5); Pd(1)−C(24), 2.010(7); Pd(1)−Br(1), 2.5224(9); N(1)−C(7), 1.307(8); N(2)−C(7), 1.345(8); N(3)−C(24), 1.37(1); N(4)−C(24), 1.340(9); C(24)−Pd(1)−N(1), 157.4(3); C(1)−Pd(1)−Br(1), 177.67(18); N(1)−C(7)−N(2), 114.8(5); N(3)−C(24)−N(4), 104.6(6).

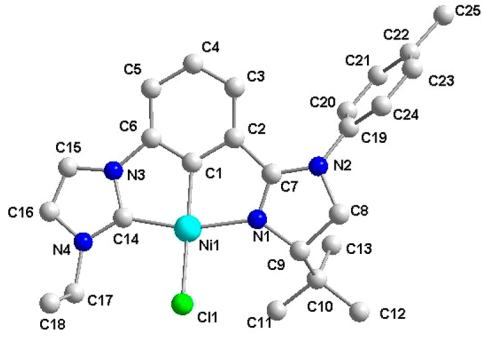

Figure 3. ORTEP diagram of the molecular structure of **5e** at the 30% probability level. Selected bond lengths (Å) and angles (deg): Ni(1)−C(1), 1.860(4); Ni(1)−N(1), 1.955(4); Ni(1)−C(14), 1.911(5); Ni(1)−Cl(1), 2.2146(15); N(1)−C(7), 1.308(6); N(2)−C(7), 1.336(6); N(3)−C(14), 1.378(6); N(4)−C(14), 1.331(7); C(14)−Ni(1)−N(1), 161.10(19); C(1)−Ni(1)−Cl(1), 168.79(16); N(1)−C(7)−N(2), 115.6(4); N(3)−C(14)−N(4), 104.9(5).

approximately coplanar. Select bond lengths and angles are reported in Table 1. Due to the ring strain within the system, the C_{Ar}−M−N (78−81°), C_{NHC}−M−C_{Ar} (79−82°), and C_{NHC}−M−N (157−162°) angles deviate from the perfect values (90 and 180°), in accordance with our previous reports.[21,24]

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes 4a,c and 5e

	4a	4c	5e
M−C_{Ar}	1.931(6)	1.938(6)	1.860(4)
M−C_{NHC}	2.005(6)	2.010(7)	1.911(5)
M−N	2.109(5)	2.112(5)	1.955(4)
M−X (X = Br, Cl)	2.5132(9)	2.5224(9)	2.2146(15)
C_{Ar}−M−N	78.2(2)	78.1(2)	80.70(19)
N−M−X (X = Br, Cl)	100.07(15)	99.65(14)	97.28(12)
X−M−C_{NHC} (X = Br, Cl)	102.7(2)	103.0(2)	101.53(16)
C_{NHC}−M−C_{Ar}	79.0(3)	79.3(3)	81.2(2)
C_{Ar}−M−X (X = Br, Cl)	177.92(19)	177.67(18)	168.79(16)
C_{NHC}−M−N	157.3(3)	157.4(3)	161.10(19)

Pd(II) complexes **4a,c** have similar bond lengths and angles. In comparison with the symmetrical NCN bis(imidazoline) pincer Pd−Br complex (Pd−N, 2.022 Å), the Pd−N distances (2.109 and 2.112 Å) are slightly longer.[21g] When Ni metal was incorporated, complex **5e** exhibited bond lengths shorter than those of Pd complexes **4a,c**, accompanied by increased angles of C_{Ar}−Ni−N, C_{NHC}−Ni−C_{Ar}, and C_{NHC}−M−N as well as decreased angles of N−Ni−Cl and Cl−Ni−C_{NHC}. In comparison to the related symmetrical carbene CCC pincer Ni−Cl complexes (Ni−C_{Ar}, 1.8503 Å; Ni−C_{NHC}, 1.9188 and 1.9202 Å; Ni−Cl, 2.1878 Å),[26] complex **5e** displays comparable Ni−C_{Ar} (1.860 Å) and Ni−C_{NHC} (1.911 Å) lengths and a slightly longer Ni−Cl (2.2146 Å) length. Meanwhile, Ni complex **5e** has slightly longer Ni−C_{Ar} and Ni−C_{NHC} bond lengths but a decreased Ni−Cl bond length in comparison to the corresponding bond lengths in the symmetrical NCN bis(imidazoline) pincer Ni−Cl complex (Ni−C_{Ar}, 1.836−1.848 Å; Ni−N,1.878−1.920 Å; Ni−Cl, 2.2249−2.2462 Å).[21c] Notably, while most of the bond angles around the Ni metal compare favorably with previous reports, the C_{Ar}−Ni−Cl bond angle of 168.79° deviates significantly from the normal angle range.

In complex **4a**, Pd atom forms a CH···Pd hydrogen bond with the adjacent C−H group of the imidazoline ring (Pd1···H8A = 2.9110(5) Å), which gives a one-dimensional chain structure (Figure 4). Likewise, in complex **4c**, a CH···Pd bond

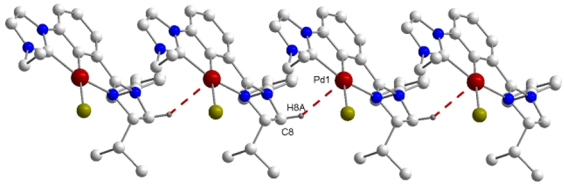

Figure 4. One-dimensional chain structure of complex **3a** formed by CH···Pd hydrogen bonds. Non-hydrogen-bonding H atoms are omitted for clarity.

between the Pd atom and the adjacent C−H group of the NAr ring (Pd1···H18 = 2.9007(1) Å) also results in a one-dimensional chain structure (Figure 5). In complex **5e**, two types of CH−Cl hydrogen bonds between the same Cl atom and adjacent C−H groups from the NHC ring (Cl1−H15 = 2.841(2) Å and Cl1−H17B = 2.6344(14) Å) contribute to the formation of a three-dimensional helix structure (Figure 6).

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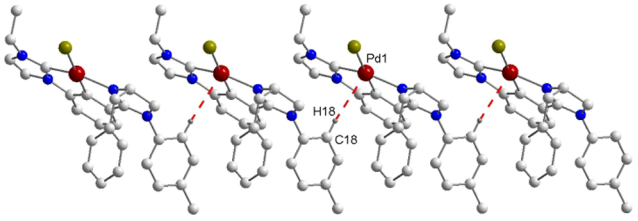


Figure 5. One-dimensional chain structure of complex **3c** formed by CH···Pd hydrogen bonds. Non-hydrogen-bonding H atoms are omitted for clarity.

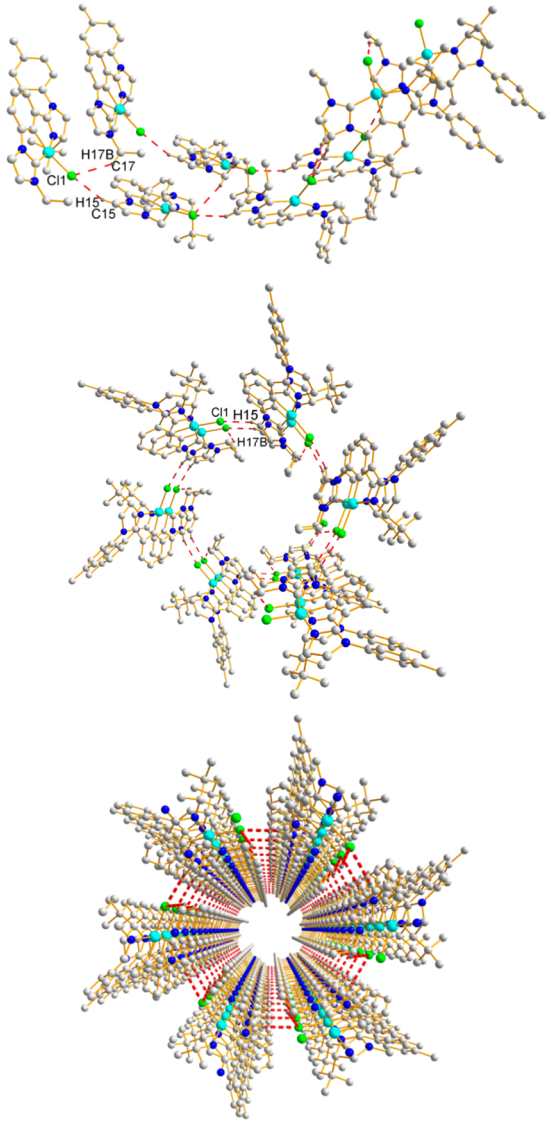
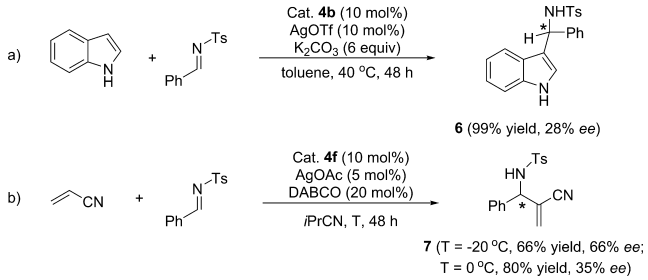


Figure 6. Two-dimensional helix structure of complex **5e** formed by CH···Cl hydrogen bonds: (top) side view; (middle and bottom) top view.

Asymmetric addition to C═N functionalities is an important strategy to construct chiral molecules with a carbon stereocenter bonded to nitrogen, which are important precursors for various biologically active compounds.[27] With Johannsen's pioneering work as inspiration,[28a] catalytic asymmetric aza-Friedel–Crafts reactions of aromatics with unsaturated imines have been realized by utilization of chiral transition-metal catalysts, chiral thiourea organocatalysts, and chiral phosphoric acids.[28] Recently, the Arai group reported nucleophilic addition of *N*-Boc imines under basic conditions in the presence of a chiral imidazolidine-based Pd-OTf catalyst, which gave the 3-indolyl methanamines in up to 99% yield and 98% ee.[23c] On the other hand, enantioselective aza-Morita–Baylis–Hillman (aza-MBH) reactions represent an effective strategy to prepare chiral α-methylene β-amino carbonyl compounds.[22b,29] Recently, the Nakamura and Shibata group developed aza-MBH reactions of acrylonitrile and imines (up to 98% yield and 98% ee) in the presence of a chiral Phebim-Pd pincer complex.[22b] On the basis of previous literature, we herein conducted a preliminary investigation on pincer Pd complex catalyzed asymmetric aza-Friedel–Crafts reactions of indole with N-Ts imine (Scheme 3a). The best result was

Scheme 3. (a) Asymmetric Aza-Friedel–Crafts Reactions and (b) Asymmetric Aza-MBH Reactions



achieved using Pd complex **4b** as the catalyst, which provided the desired product **6** in 99% yield and 28% ee. Subsequently, enantioselective aza-MBH reactions of acrylonitrile and N-Ts imine were also investigated (Scheme 3b). When Pd complex **4f** was employed at −20 °C, the corresponding product **7** was obtained in 66% yield and 66% ee. In addition, it was found that increased yield (80%) and decreased ee (35%) were observed when the temperature was elevated to 0 °C. Further reaction optimizations are currently in progress in our group.

CONCLUSION

In conclusion, we have synthesized a series of unsymmetrical chiral NHC-containing pincer Pd and Ni complexes via direct C–H activation from commercially available starting materials. All of the organometallic complexes are bench-stable and have been fully characterized. Preliminary evaluation reveals that Pd complexes showed moderate stereoselectivities in the asymmetric Friedel–Crafts alkylation and aza-MBH reactions. Further investigations are still in progress to optimize the conditions and expand the substrate scope for the above reactions.

EXPERIMENTAL SECTION

General Procedures. All air- and moisture-sensitive reactions were carried out in oven-dried Schlenk tubes under an Ar atmosphere. Solvents were dried by standard methods and freshly distilled prior to use if needed. Column chromatography was performed using 200–300 mesh silica gel. Analytical and preparative thin-layer chromatography (TLC) plates coated with commercial silica gel GF254 were used to monitor the reactions and purify products. Compounds **1a–e** were synthesized according to previous literature.[21,24] ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz using TMS as an internal standard. Data are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constants (J) in hertz (Hz). HRMS were determined on a Q-Tof Micro or AB SCIEX TripleTOF

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6600 MS/MS System ESI spectrometer. The structures of pincer complexes **4a** (CCDC file number 1839754), **4c** (CCDC 1841152), and **5e** (CCDC file number 1839755) were further confirmed by X-ray diffraction collected on a diffractometer with graphite-monochromated Cu Kα radiation.

1-((*S*)-4-Isopropyl-1-*p*-tolyl-4,5-dihydro-1*H*-imidazol-2-yl)-3-bromobenzene (1a). Yellow oil. Yield: 68%. $[\alpha]_D^{20}$ = +2.2 (*c* 0.52, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (t, *J* = 1.7 Hz, 1H), 7.45 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.32−7.27 (m, 1H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.70−6.64 (m, 2H), 4.09−4.01 (m, 2H), 3.67−3.55 (m, 1H), 2.25 (s, 3H), 1.90 (dt, *J* = 11.9, 6.7 Hz, 1H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.3, 140.5, 133.6, 133.4, 132.8, 131.7, 129.52, 129.46, 127.3, 122.9, 122.3, 70.3, 56.8, 33.1, 20.8, 18.9, 17.9. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{19}H_{22}BrN_2^+$ 357.0961, found 357.0957.

1-((*S*)-4-Benzyl-1-*p*-tolyl-4,5-dihydro-1*H*-imidazol-2-yl)-3-bromobenzene (1b). Yellow oil. Yield: 46%. $[\alpha]_D^{20}$ = +57.1 (*c* 1.18, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.76 (t, *J* = 1.7 Hz, 1H), 7.43 (ddd, *J* = 8.0, 1.9, 1.0 Hz, 1H), 7.30−7.15 (m, 6H), 7.05 (t, *J* = 7.9 Hz, 1H), 6.92−6.87 (m, 2H), 6.53−6.48 (m, 2H), 4.56−4.47 (m, 1H), 3.96 (t, *J* = 9.8 Hz, 1H), 3.64 (dd, *J* = 9.5, 7.2 Hz, 1H), 3.20 (dd, *J* = 13.6, 4.6 Hz, 1H), 2.82 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.21 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.8, 140.2, 138.2, 133.7, 133.3, 132.9, 131.8, 129.54, 129.45, 128.4, 127.4, 126.4, 123.1, 122.3, 65.4, 58.6, 42.3, 20.8. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{23}H_{22}BrN_2^+$ 405.0961, found 405.0957.

1-((*S*)-4-(*tert*-Butyl)-1-*p*-tolyl-4,5-dihydro-1*H*-imidazol-2-yl)-3-bromobenzene (1c). Yellow oil. Yield: 60%. $[\alpha]_D^{20}$ = +41.1 (*c* 0.90, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (t, *J* = 1.7 Hz, 1H), 7.42−7.38 (m, 1H), 7.32−7.28 (m, 1H), 7.03 (t, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 2H), 6.66 (d, *J* = 8.3 Hz, 2H), 4.07 (dd, *J* = 10.8 Hz, 9.4 Hz, 1H), 3.96 (dd, *J* = 10.9 Hz, 7.5 Hz, 1H), 3.60 (dd, *J* = 9.2 Hz, 7.6 Hz, 1H), 2.22 (s, 3H), 0.97 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 160.4, 140.6, 133.7, 133.4, 132.7, 131.7, 129.5, 127.4, 123.0, 122.3, 74.0, 55.7, 34.2, 26.0, 20.8. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{20}H_{24}BrN_2^+$ 371.1117, found 371.1113.

1-((4*S*,5*S*)-4,5-Diphenyl-1-*p*-tolyl-4,5-dihydro-1*H*-imidazol-2-yl)-3-bromobenzene (1d). Yellow oil. Yield: 61%. $[\alpha]_D^{20}$ = +217.5 (*c* 0.80, $CHCl_3$). ^1H NMR (400 Mhz, $CDCl_3$): δ 8.05−8.02 (m, 1H), 7.56−7.52 (m, 1H), 7.49 (ddd, *J* = 8.0, 1.9, 1.0 Hz, 1H) 7.44−7.24 (m, 10H), 7.13 (t, *J* = 7.9 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 2H), 6.64 (d, *J* = 8.3 Hz, 2H), 5.11 (d, *J* = 6.8 Hz, 1H), 4.70 (d, *J* = 6.8 Hz, 1H), 2.18 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.0, 143.4, 143.3, 140.6, 134.9, 133.3, 133.22, 132.16, 129.7, 129.1, 128.8, 127.9, 127.7, 127.5, 126.7, 126.6, 124.3, 122.4, 79.0, 78.7, 20.9. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{28}H_{24}BrN_2^+$ 467.1117, found 467.1117.

General Procedure for the Synthesis of Compounds 2a−d. In a 50 mL round-bottom flask were stirred complex **1** (2.80 mmol), imidazole (0.46 g, 6.72 mmol), K_2CO_3 (0.93 g, 6.72 mmol), and CuI (0.21 g, 1.09 mmol) in DMF (20 mL) at 140 °C for 21 h. The mixture was cooled to room temperature, diluted with ethyl acetate, and washed with water and brine. The organic layer was dried over Na_2SO_4 and then concentrated. The crude product was purified by column chromatography on silica gel with a mixture of ethyl acetate and CH_2Cl_2 (1/10 to 1/0) to give compounds **2**.

*(S)-3-(4-Isopropyl-1-p-tolyl-4,5-dihydro-1H-imidazol-2-yl)-1-(1H-imidazolyl)benzene (**2a**).* Yellow oil. Yield: 68%. $[\alpha]_D^{20}$ = −13.0 (*c* 0.60, $CHCl_3$). ^1H NMR (400 Mz, $CDCl_3$): δ 7.70 (s, 1H), 7.55 (t, *J* = 1.8 Hz, 1H), 7.50−7.47 (m, 1H), 7.40−7.33 (m, 2H), 7.19−7.15 (m, 2H), 7.03−6.97 (m, 2H), 6.74−6.69 (m, 2H), 4.13−4.04 (m, 2H), 3.69−3.61 (m, 1H), 2.27 (s, 3H), 2.00−1.87 (m, 1H), 1.06 (d, *J* = 6.8 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.5, 140.5, 137.1, 135.5, 133.8, 133.4, 130.5, 129.65, 129.55, 127.8, 123.2, 122.5, 121.8, 118.1, 70.5, 56.9, 33.2, 20.8, 18.9, 18.0. HRMS (positive ESI): $[M + H]^+$, calcd for $C_{22}H_{25}N_4^+$ 345.2074, found 345.2076.

*(S)-3-(4-Benzyl-1-p-tolyl-4,5-dihydro-1H-imidazol-2-yl)-1-(1H-imidazolyl)benzene (**2b**).* Yellow oil. Yield: 65%. $[\alpha]_D^{20}$ = +38.3 (*c* 0.63, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.69−7.67 (m, 1H), 7.52−7.49 (m, 1H), 7.47−7.43 (m, 1H), 7.37−7.32 (m, 2H), 7.28−7.24 (m, 4H), 7.23−7.17 (m, 1H), 7.16−7.13 (m, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.58−6.53 (m, 2H), 4.62−4.52 (m, 1H), 4.03 (t, *J* = 9.9 Hz, 1H), 3.69 (dd, *J* = 9.6, 7.2 Hz, 1H), 3.20 (dd, *J* = 13.6, 4.8 Hz, 1H), 2.88 (dd, *J* = 13.6, 8.2 Hz, 1H), 2.23 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.0, 140.1, 138.0, 137.0, 135.5, 135.1, 134.1, 133.0, 130.5, 129.7, 129.5, 128.4, 127.8, 126.4, 123.4, 122.6, 121.8, 118.1, 65.4, 58.6, 42.2, 20.8. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{26}H_{25}N_4^+$ 393.2074, found 393.2081.

*(S)-3-(4-(tert-Butyl)-1-p-tolyl-4,5-dihydro-1H-imidazol-2-yl)-1-(1H-imidazolyl)benzene (**2c**).* Yellow oil. Yield: 72%. $[\alpha]_D^{20}$ = +39.0 (*c* 0.41, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.57−7.53 (m, 1H), 7.52−7.47 (m, 1H), 7.40−7.32 (m, 2H), 7.19−7.14 (m, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.75−6.69 (m, 2H), 4.12 (dd, *J* = 10.9, 9.4 Hz, 1H), 4.00 (dd, *J* = 10.9, 7.7 Hz, 1H), 3.65 (dd, *J* = 9.3, 7.8 Hz, 1H), 2.27 (s, 3H), 0.99 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.6, 140.6, 137.1, 135.6, 133.9, 133.4, 130.5, 129.7, 129.6, 127.8, 123.4, 122.5, 121.8, 118.1, 74.1, 55.7, 34.3, 25.9, 20.8. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{23}H_{27}N_4^+$ 359.2230, found 359.2234.

*3-((4S,5S)-4,5-Diphenyl-1-p-tolyl-4,5-dihydro-1H-imidazol-2-yl)-1-(1H-imidazolyl)benzene (**2d**).* Yellow oil. Yield: 90%. $[\alpha]_D^{20}$ = +159.2 (*c* 1.77, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.77−7.75 (m, 1H), 7.75−7.71 (m, 1H), 7.70−7.68 (m, 1H), 7.61 (s, 1H), 7.46−7.35 (m, 9H), 7.34−7.30 (m, 2H), 7.18−7.15 (m, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.71−6.66 (m, 2H), 5.15 (d, *J* = 7.1 Hz, 1H), 4.75 (d, *J* = 7.1 Hz, 1H), 2.22 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 162.1, 143.1, 143.0, 140.5, 137.2, 135.6, 135.3, 132.9, 130.5, 129.8, 129.7, 129.1, 128.8, 128.2, 128.0, 127.6, 126.8, 126.6, 124.7, 122.9, 122.2, 118.1, 79.0, 78.6, 20.8. HRMS (positive ESI): $[M + H]^+$ calcd for $C_{31}H_{27}N_4^+$ 455.2230, found 455.2233.

General Procedure for the Synthesis of Compounds 3a−g. In a 100 mL round-bottom flask was stirred a mixture of **2** (2.91 mmol) and ethyl bromide or benzyl bromide (2.91 mmol) in toluene (50 mL). The solution was stirred at 110 °C for 48 h under an argon atmosphere. After removal of solvent under reduced pressure, the residue was purified by column chromatography on silica gel with $CHCl_3$/MeOH (50/1 to 20/1) to give ligands **3**.

*(S)-3-Ethyl-1-(3-(4-isopropyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)phenyl)-1H-imidazol-3-ium (**3a**).* Yellow oil. Yield: 64%. $[\alpha]_D^{20}$ = +132.0 (*c* 0.67, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 11.15 (s, 1H), 8.09−8.04 (m, 1H), 7.86−7.82 (m, 1H), 7.57 (t, *J* = 1.8 Hz, 1H), 7.52 (t, *J* = 1.7 Hz, 1H), 7.49−7.42 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 8.3 Hz, 2H), 4.69 (q, *J* = 7.3 Hz, 2H), 4.15−4.04 (m, 2H), 3.68−3.63 (m, 1H), 2.28 (s, 3H), 1.96−1.90 (m, 1H), 1.67 (t, *J* = 7.6 Hz, 3H), 1.06 (d, *J* = 6.7 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.0, 140.1, 135.9, 134.33, 134.31, 133.7, 130.7, 130.4, 129.8, 123.8, 123.4, 122.8, 121.5, 120.5, 70.4, 57.1, 45.9, 33.1, 20.8, 18.9, 18.0, 15.8. HRMS (positive ESI): $[M - Br^-]^+$ calcd for $C_{24}H_{29}N_4^+$ 373.2387, found 373.2387.

*(S)-3-Benzyl-1-(3-(4-isopropyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)phenyl)-1H-imidazol-3-ium (**3b**).* Yellow oil. Yield: 71%. $[\alpha]_D^{20}$ = +58.0 (*c* 0.27, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 11.20 (s, 1H), 8.04−7.97 (m, 1H), 7.80−7.77 (m, 1H), 7.60−7.56 (m, 2H), 7.46−7.38 (m, 7H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 8.3 Hz, 2H), 5.84 (d, *J* = 1.1 Hz, 2H), 4.10−4.02 (m, 2H), 3.65−3.60 (m, 1H), 2.26 (s, 3H), 1.94−1.86 (m, 1H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.94 (d, *J* = 6.7 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.1, 140.0, 135.7, 134.4, 134.3, 133.6, 132.8, 130.6, 130.5, 129.8, 129.5, 129.3, 129.0, 123.7, 123.5, 122.9, 121.7, 120.6, 70.3, 57.1, 53.5, 33.1, 20.8, 18.8, 18.0. HRMS (positive ESI): $[M - Br^-]^+$ calcd for $C_{29}H_{31}N_4^+$ 435.2543, found 435.2539.

*(S)-1-(3-(4-Benzyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)-phenyl)-3-ethyl-1H-imidazol-3-ium (**3c**).* Yellow oil. Yield: 58%. $[\alpha]_D^{20}$ = +79.0 (*c* 0.77, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 10.90 (s, 1H), 8.03−7.95 (m, 1H), 7.87 (s, 1H), 7.70 (s, 1H), 7.49 (s, 1H), 7.39 (d, *J* = 4.7 Hz, 2H), 7.25−7.14 (m, 5H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.51 (d, *J* = 8.2 Hz, 2H), 4.63 (q, *J* = 7.3 Hz, 2H), 4.57−4.47 (m, 1H), 3.99 (t, *J* = 9.9 Hz, 1H), 3.64 (dd, *J* = 9.3, 7.5 Hz, 1H), 3.14 (dd, *J* = 13.6, 4.7 Hz, 1H), 2.82 (dd, *J* = 13.6, 8.1 Hz, 1H), 2.20 (s,

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3H), 1.68−1.53 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.3, 139.8, 137.9, 135.7, 134.5, 134.3, 133.4, 130.6, 130.4, 129.7, 129.5, 128.4, 126.5, 123.9, 123.5, 123.2, 121.5, 120.4, 65.4, 58.8, 45.9, 42.1, 20.8, 15.9. HRMS (positive ESI): $[M - Br^-]^+$ calcd for $C_{28}H_{29}N_4^+$ 421.2387, found 421.2390.

(S)-3-Benzyl-1-(3-(4-benzyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)phenyl)-1H-imidazol-3-ium ***(3d)***. Yellow oil. Yield: 64%. $[\alpha]_D^{20}$ = +31.0 (*c* 0.28, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 11.18 (s, 1H), 8.03−7.99 (m, 1H), 7.74 (s, 1H), 7.63−7.58 (m, 2H), 7.55−7.49 (m, 1H), 7.47−7.36 (m, 6H), 7.29−7.19 (m, 5H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.55 (d, *J* = 8.2 Hz, 2H), 5.84 (s, 2H), 4.61−4.51 (m, 1H), 4.03 (t, *J* = 9.7 Hz, 1H), 3.74−3.65 (m, 1H), 3.18 (dd, *J* = 13.7, 4.7 Hz, 1H), 2.86 (dd, *J* = 13.8, 8.5 Hz, 1H), 2.24 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.3, 139.7, 137.8, 136.1, 134.6, 134.3, 133.3, 132.9, 130.7, 130.5, 129.8, 129.6, 129.49, 129.48, 129.4, 128.4, 126.5, 123.9, 123.6, 122.8, 121.5, 120.4, 65.3, 58.8, 53.7, 42.1, 20.8. HRMS (positive ESI): $[M - Br^-]^+$ calcd for $C_{33}H_{31}N_4^+$ 483.2543, found 483.2549

(S)-1-(3-(4-(tert-Butyl)-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)-phenyl)-3-ethyl-1H-imidazol-3-ium ***(3e)***. Yellow oil. Yield: 72%. $[\alpha]_D^{20}$ = +23° (*c* 0.409, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 10.86 (s, 1H), 8.05−7.99 (m, 1H), 7.94 (s, 1H), 7.79 (s, 1H), 7.60−7.55 (m, 1H), 7.50−7.40 (m, 2H), 7.05−6.97 (m, 2H), 6.76−6.68 (m, 2H), 4.73−4.62 (m, 2H), 4.16−4.06 (m, 1H), 4.03−3.94 (m, 1H), 3.71−3.61 (m, 1H), 2.27 (d, *J* = 2.0 Hz, 3H), 1.66 (td, *J* = 7.2, 2.3 Hz, 3H), 0.98 (d, *J* = 2.3 Hz, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 160.0, 140.2, 135.6, 134.3, 134.2, 133.7, 130.6, 130.3, 129.7, 123.7, 123.5, 123.2, 121.4, 120.4, 74.0, 55.8, 45.8, 34.2, 25.9, 20.8, 15.8. HRMS (positive ESI): $[M - Br^-]^+$ calcd for $C_{25}H_{31}N_4$ 387.2543, found 387.2543.

(S)-3-Benzyl-1-(3-(4-(tert-butyl)-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)phenyl)-1H-imidazol-3-ium ***(3f)***. Yellow oil. Yield: 62%. $[\alpha]_D^{20}$ = +83.0 (*c* 0.25, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 10.96 (s, 1H), 7.96 (s, 2H), 7.76 (s, 1H), 7.74−7.68 (m, 2H), 7.54 (s, 1H), 7.52−7.29 (m, 5H), 7.05−6.98 (m, 2H), 6.76−6.69 (m, 2H), 5.87 (s, 2H), 4.16−4.06 (m, 1H), 4.05−3.94 (m, 1H), 3.70−3.62 (m, 1H), 2.29−2.22 (m, 3H), 0.98 (s, 9H). $^{13}C\{^1H\}$ NMR(100 MHz, $CDCl_3$): δ 160.0, 140.1, 135.4, 134.29, 134.26, 133.5, 133.2, 130.5, 130.3, 129.8, 129.4, 129.3, 123.7, 123.5, 121.6, 120.5, 73.9, 55.9, 53.3, 34.2, 25.9, 20.8. HRMS (positive ESI): $[M - Br^-]^+$ calcd for $C_{30}H_{33}N_4$ 449.2700, found 449.2698.

1-(3-((4S,5S)-4,5-Diphenyl-1-(p-tolyl)-4,5-dihydro-1H-imidazol-2-yl)phenyl)-3-ethyl-1H-imidazol-3-ium ***(3g)***. Yellow oil. Yield: 63%. $[\alpha]_D^{20}$ = +59.0 (*c* 0.27, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 11.03 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.90 (s, 1H), 7.66 (s, 1H), 7.58−7.51 (m, 3H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.28−7.19 (m, 6H), 7.17−7.10 (m, 4H), 6.98 (d, *J* = 8.2 Hz, 2H), 5.05 (d, *J* = 7.3 Hz, 1H), 4.66 (d, *J* = 7.3 Hz, 1H), 4.68 (q, *J* = 7.3 Hz, 2H), 2.35 (s, 3H), 1.66 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 161.6, 142.8, 142.6, 140.0, 136.2, 135.7, 134.5, 133.3, 130.8, 130.7, 130.0, 129.1, 128.9, 128.1, 127.7, 126.8, 126.6, 124.8, 124.3, 122.4, 121.9, 120.5, 79.2, 78.6, 45.9, 20.8, 15.7. HRMS (positive ESI): $[M - Br^-]^+$ calcd for $C_{33}H_{31}N_4^+$ 483.2543, found 483.2544.

General Procedure for the Synthesis of Pd(II) Complexes 4a−g. In a 25 mL two-necked Schlenk tube were placed **3** (0.44 mmol), NaOAc (0.36 g, 4.40 mmol), and $Pd(OAc)_2$ (0.12 g, 0.53 mmol) in dry DMAc (10 mL). The mixture was refluxed under an Ar atmosphere for 48 h. After the mixture was cooled and concentrated in vacuo, the residue was purified by passing through a short column containing a layer of Celite and a layer of silica with dichloromethane as eluent. The solvent was removed under reduced pressure, and a solution of lithium bromide (467 mg, 5.38 mmol) in acetone/water (3/2, 50 mL) was added. The resulting solution was stirred at room temperature for 48 h and extracted with dichloromethane. The organic layer was washed with brine, dried over $MgSO_4$, and evaporated. The final products **4** were purified once again by preparative TLC on silica gel plates with CH_2Cl_2/EtOAc 10/1 as eluent.

Pd(II) Complex ***4a***. Yield: 32%. Mp = 258−259 °C. $[\alpha]_D^{20}$ = +123° (*c* 0.06, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, *J* = 2.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.95−6.91 (m, 2H), 6.81 (t, *J* = 7.8, 1H), 6.26 (d, *J* = 7. Two Hz, 1H), 4.81−4.64 (m, 2H), 4.41 (ddd, *J* = 11.2, 5.3, 3.4 Hz, 1H), 4.08 (dd, *J* = 11.1, 10.0 Hz, 1H), 3.82 (dd, *J* = 9.9, 5.4 Hz, 1H), 2.90−2.78 (m, 1H), 2.42 (s, 3H), 1.52 (t, *J* = 7.3 Hz, 3H), 0.92 (dd, *J* = 10.6, 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.7, 168.7, 160.2, 144.0, 137.58, 137.55, 134.9, 130.2, 126.2, 123.4, 122.0, 119.5, 114.2, 112.0, 66.1, 55.3, 46.1, 30.4, 29.7, 21.2, 18.7, 14.3. HRMS (positive ESI): $[M - Br^-]^+$ calcd for $C_{24}H_{27}N_4Pd^+$ 477.1265, found 477.1274. Anal. Calcd for $C_{24}H_{27}N_4PdBr$: C, 51.68; H, 4.88; N, 10.04. Found: C, 51.63; H, 5.00; N, 9.90.

Pd(II) Complex ***4b***. Yield: 28%. Mp > 300 °C. $[\alpha]_D^{20}$ = +187° (*c* 0.04, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 6.8 Hz, 2H), 7.37−7.29 (m, 3H), 7.26−7.22 (m, 3H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.85−6.77 (m, 2H), 6.28 (d, *J* = 7.5 Hz, 1H), 6.07 (d, *J* = 14.3 Hz, 1H), 5.80 (d, *J* = 14.3 Hz, 1H), 4.43 (ddd, *J* = 11.1, 5.3, 3.4 Hz, 1H), 4.10 (t, *J* = 10.6 Hz, 1H), 3.84 (dd, *J* = 9.9, 5.4 Hz, 1H), 2.93−2.81 (m, 1H), 2.42 (s, 3H), 0.94 (dd, *J* = 6.9, 3.9 Hz, 6H). $^{13}C\{^1H\}$ NMR(100 MHz, $CDCl_3$): 171.0, 168.6, 159.9, 144.2, 137.7, 137.6, 135.1, 130.2, 128.9, 128.8, 128.1, 126.3, 123.3, 122.1, 119.8, 114.6, 111.9, 66.2, 55.4, 53.6, 30.0, 21.2, 18.8, 14.5. HRMS (positive ESI): $[M - Br^-]^+$ calcd for $C_{29}H_{29}N_4Pd^+$ 539.1422, found 539.1429. Anal. Calcd for $C_{29}H_{29}N_4PdBr$: C, 56.19; H, 4.72; N, 9.04. Found: C, 56.41; H, 4.82; N, 8.74.

Pd(II) Complex ***4c***. Yield: 33%. Mp = 257−258 °C. $[\alpha]_D^{20}$ = +149° (*c* 0.11, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 6.3 Hz, 2H), 7.33 (d, *J* = 1.9 Hz, 1H), 7.24−7.17 (m, 4H), 7.14 (d, *J* = 8.2 Hz, 2H), 6.99−6.93 (m, 2H), 6.78 (t, *J* = 7.8 Hz, 2H), 6.12 (d, *J* = 7.7 Hz, 1H), 4.83−4.68 (m, 3H), 4.09 (t, *J* = 10.2 Hz, 1H), 3.80 (dd, *J* = 9.9, 4.0 Hz, 1H), 3.40 (dd, *J* = 13.4, 3.4 Hz, 1H), 3.17 (dd, *J* = 13.4, 7.6 Hz, 1H), 2.37 (s, 3H), 1.54 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.8, 168.9, 160.1, 144.2, 137.66, 137.61, 137.1, 135.0, 130.2, 130.0, 128.1, 126.3, 126.2, 123.2, 121.9, 119.4, 114.4, 111.9, 62.1, 59.0, 45.4, 40.1, 29.7, 21.1. HRMS (positive ESI): $[M - Br^-]^+$ calcd for $C_{28}H_{27}N_4Pd^+$ 525.1265, found 525.1281. Anal. Calcd for $C_{28}H_{27}N_4PdBr$: C, 55.51; H, 4.49; N, 9.25. Found: C, 55.89; H, 4.58; N, 9.09.

Pd(II) Complex ***4d***. Yield: 30%. Mp > 300 °C. $[\alpha]_D^{20}$ = +239° (*c* 0.04, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 6.8 Hz, 2H), 7.43 (d, *J* = 6.6 Hz, 2H), 7.39−7.29 (m, 3H), 7.28 (d, *J* = 1.9 Hz, 1H), 7.25−7.17 (m, 4H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.89−6.74 (m, 3H), 6.17−6.10 (m, 2H), 5.90 (d, *J* = 14.3 Hz, 1H), 4.82−4.69 (m, 1H), 4.12 (t, *J* = 10.1 Hz, 1H), 3.83 (dd, *J* = 9.9, 3.9 Hz, 1H), 3.43 (dd, *J* = 13.4, 3.5 Hz, 1H), 3.20 (dd, *J* = 13.3, 7.6 Hz, 1H), 2.38 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 171.2, 169.2, 160.5, 144.0, 137.7, 137.6, 137.0, 136.5, 135.0, 130.2, 130.1, 128.8, 128.2, 128.1, 126.3, 123.4, 123.3, 122.0, 119.8, 114.7, 112.1, 62.3, 58.9, 54.4, 41.1, 21.2. HR-MS (positive ESI): $[M - Br^-]^+$ calcd for $C_{33}H_{29}N_4Pd^+$ 587.1422, found 587.1430. Anal. Calcd for $C_{33}H_{29}N_4PdBr$: C, 59.34; H, 4.38; N, 8.39. Found: C, 59.72; H, 4.51; N, 8.17.

Pd(II) Complex ***4e***. Yield: 33%. Mp = 191−192 °C. $[\alpha]_D^{20}$ = +177° (*c* 0.10, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.33 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 6.99−6.90 (m, 2H), 6.84−6.77 (m, 1H), 6.29 (d, *J* = 7.8 Hz, 1H), 4.84−4.64 (m, 2H), 4.15−4.05 (m, 2H), 3.98−3.89 (m, 1H), 2.41 (s, 3H), 1.50 (t, *J* = 7.2 Hz, 3H), 1.10 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 169.5, 168.8, 158.9, 144.1, 137.6, 137.5, 134.8, 130.2, 126.2, 123.3, 122.0, 119.5, 114.4, 112.0, 68.6, 58.0, 45.3, 35.7, 26.4, 21.2, 16.9. HRMS (positive ESI): $[M - Br^-]^+$ calcd for $C_{25}H_{29}N_4Pd^+$ 491.1422, found 491.1430. Anal. Calcd for $C_{25}H_{29}N_4PdBr$: C, 52.51; H, 5.11; N, 9.80. Found: C, 52.75; H, 5.38; N, 9.62.

Pd(II) Complex ***4f***. Yield: 24%. Mp > 300 °C. $[\alpha]_D^{20}$ = +168° (*c* 0.10, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 6.8 Hz, 2H), 7.36−7.22 (m, 6H), 7.15 (d, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 7.7 Hz, 1H), 6.85−6.75 (m, 2H), 6.30 (d, *J* = 7.8 Hz, 1H), 6.09 (d, *J* = 14.4 Hz, 1H), 5.83 (d, *J* = 14.4 Hz, 1H), 4.18−4.07 (m, 2H), 3.95 (d, *J* = 7.7 Hz, 1H), 2.42 (s, 3H), 1.12 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.1, 168.9, 159.0, 144.1, 137.7, 137.5, 136.6, 134.9, 130.2, 128.8, 128.8, 128.1, 126.3, 123.4, 122.1, 119.9, 114.7,

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112.0, 68.6, 58.1, 53.7, 35.8, 26.5, 21.2. HRMS (positive ESI): $[M - Br^-]^+$ calcd for $C_{30}H_{31}N_4Pd^+$ 553.1578, found 553.1574. Anal. Calcd for $C_{30}H_{31}N_4PdBr$: C, 56.84; H, 4.93; N, 8.84. Found: C, 56.47; H, 5.15; N, 8.72.

Pd(II) Complex ***4g***. Yield: 21%. Mp = 134−135 °C. $[\alpha]_D^{20}$ = +239° (*c* 0.10, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.49−7.43 (m, 2H), 7.40−7.26 (m, 10H), 7.17−7.07 (m, 2H), 7.05−7.01 (m, 1H), 6.92−6.83 (m, 3H), 6.32 (d, *J* = 7.8 Hz, 1H), 5.49−5.36 (m, 1H), 4.83 (dd, *J* = 7.4, 5.1 Hz, 1H), 4.74−4.62 (m, 2H), 2.34 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 170.5, 169.9, 161.0, 144.3, 143.4, 140.9, 138.1, 136.4, 134.7, 130.0, 129.1, 128.8, 128.5, 127.5, 127.0, 126.6, 123.6, 122.2, 119.5, 114.4, 112.4, 79.9, 74.2, 46.1, 21.2, 16.8. HRMS (positive ESI): $[M - Br^-]^+$ calcd for $C_{33}H_{29}N_4Pd^+$ 587.1422, found 587.1432. Anal. Calcd for $C_{33}H_{29}N_4PdBr$: C, 59.34; H, 4.38; N, 8.39. Found: C, 59.20; H, 4.70; N, 8.04.

General Procedure for the Synthesis of Ni(II) Complexes 5a−f. In a 25 mL two-necked Schlenk tube were placed **3** (0.44 mmol), NaOAc (0.36 g, 4.40 mmol), and $NiCl_2$ (0.11 g, 0.88 mmol) in dry DMAc (10 mL). The mixture was refluxed under an Ar atmosphere for 48 h. After the mixture was cooled and concentrated in vacuo, the residue was purified by passing through a short column containing a layer of Celite and a layer of silica with dichloromethane as eluent. The desired products **5** were purified once again by preparative TLC on silica gel plates with CH_2Cl_2/EtOAc 1/1 as eluent.

Ni(II) Complex ***5a***. Yield: 23%. Mp = 246−247 °C. $[\alpha]_D^{20}$ = +160° (*c* 0.25, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.24−7.19 (m, 3H), 7.17−7.12 (m, 2H), 6.79 (d, *J* = 2.0 Hz, 1H), 6.78−6.73 (m, 2H), 6.25 (dd, *J* = 6.2, 2.3 Hz, 1H), 4.72−4.61 (m, 2H), 4.19 (dt, *J* = 10.9, 3.5 Hz, 1H), 4.13−4.15 (m, 1H), 3.81 (dd, *J* = 9.6, 3.8 Hz, 1H), 2.65 (dtd, *J* = 13.9, 6.9, 3.0 Hz, 1H), 2.41 (s, 3H), 1.49 (t, *J* = 7.2 Hz, 3H), 0.90 (dd, *J* = 11.3, 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 168.8, 167.2, 162.7, 144.4, 137.24, 137.15, 135.3, 130.0, 125.6, 123.0, 121.1, 120.2, 113.0, 110.2, 63.8, 55.7, 44.7, 30.5, 21.1, 18.7, 17.1, 14.4. HRMS (positive ESI): $[M - Cl]^+$ calcd for $C_{24}H_{27}N_4Ni^+$ 429.1584, found 429.1584. Anal. Calcd for $C_{24}H_{27}N_4NiCl$: C, 61.91; H, 5.84; N, 12.03. Found: C, 62.22; H, 5.97; N, 11.81.

Ni(II) Complex ***5b***. Yield: 18%. Mp = 278−279 °C. $[\alpha]_D^{20}$ = +179° (*c* 0.26, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 7.0 Hz, 2H), 7.38−7.28 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.19−7.13 (m, 2H), 6.78−6.74 (m, 2H), 6.67 (d, *J* = 2.0 Hz, 1H), 6.26 (p, *J* = 4.2 Hz, 1H), 6.10 (d, *J* = 14.5 Hz, 1H), 5.76 (d, *J* = 14.5 Hz, 1H), 4.20 (dt, *J* = 10.8, 3.4 Hz, 1H), 4.11 (t, *J* = 10.3 Hz, 1H), 3.83 (dd, *J* = 9.7, 3.8 Hz, 1H), 2.73−2.61 (m, 1H), 2.41 (s, 3H), 0.92 (dd, *J* = 18.3, 7.0 Hz, 7H). $^{13}C\{^1H\}$ NMR(100 MHz, $CDCl_3$): δ 169.3, 167.3, 162.7, 144.4, 137.23, 137.19, 137.1, 135.4, 130.1, 128.7, 128.6, 127.9, 125.7, 123.1, 121.5, 120.3, 113.5, 110.3, 63.8, 55.7, 52.8, 30.5, 21.2, 18.7, 14.4. HRMS (positive ESI): $[M - Cl]^+$ calcd for $C_{29}H_{29}N_4Ni^+$ 491.1740, found 491.1740. Anal. Calcd for $C_{29}H_{29}N_4NiCl$: C, 66.00; H, 5.54; N, 10.62. Found: C, 65.65; H, 5.92; N, 10.46.

Ni(II) Complex ***5c***. Yield: 27%. Mp = 208−209 °C. $[\alpha]_D^{20}$ = +165° (*c* 0.27, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, *J* = 6.8 Hz, 2H), 7.25−7.17 (m, 4H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 7.9 Hz, 2H), 6.82 (d, *J* = 1.9 Hz, 1H), 6.78 (d, *J* = 7.2 Hz, 1H), 6.73 (t, *J* = 7.6 Hz, 1H), 6.14 (d, *J* = 7.4 Hz, 1H), 4.81−4.61 (m, 2H), 4.52−4.42 (m, 1H), 4.10 (t, *J* = 10.0 Hz, 1H), 3.79 (dd, *J* = 9.8, 3.3 Hz, 1H), 3.37 (dd, *J* = 13.3, 3.2 Hz, 1H), 3.02−2.93 (m, 1H), 2.37 (s, 3H), 1.52 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 Mz, $CDCl_3$) δ 169.0, 167.7, 163.0, 144.5, 138.1, 137.3, 136.8, 135.3, 130.1, 129.9, 128.1, 126.2, 125.7, 123.1, 121.1, 120.2, 113.1, 110.3, 60.2, 59.4, 44.8, 41.2, 21.1, 17.1. HRMS (positive ESI): $[M - Cl]^+$ calcd for $C_{28}H_{27}N_4Ni^+$ 477.1584, found 477.1584. Anal. Calcd for $C_{28}H_{27}N_4NiCl$: C, 65.47; H, 5.30; N, 10.91. Found: C, 65.71; H, 5.63; N, 10.75.

Ni(II) Complex ***5d***. Yield: 24%. Mp = 275−276 °C. $[\alpha]_D^{20}$ = +182° (*c* 0.25, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.2 Hz, 2H), 7.45 (d, *J* = 6.9 Hz, 2H), 7.38−7.33 (m, 2H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.24−7.13 (m, 6H), 6.87 (d, *J* = 7.9 Hz, 2H), 6.79−6.69 (m, 3H), 6.20−6.12 (m, 2H), 5.77 (d, *J* = 14.5 Hz, 1H), 4.55−4.45 (m, 1H), 4.11 (t, *J* = 10.0 Hz, 1H), 3.80 (dd, *J* = 9.9, 3.3 Hz, 1H), 3.37 (dd, *J* = 13.3, 3.2 Hz, 1H), 3.01 (dd, *J* = 13.3, 8.1 Hz, 1H), 2.38 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 169.5, 167.8, 163.0, 144.4, 138.1, 137.4, 137.1, 136.8, 135.3, 130.1, 130.0, 128.8, 128.5, 128.2, 128.0, 126.2, 125.7, 123.2, 121.5, 120.3, 113.6, 110.4, 60.2, 59.4, 52.8, 41.3, 21.1. HRMS (positive ESI): $[M - Cl]^+$ calcd for $C_{33}H_{29}N_4Ni^+$ 539.1740, found 539.1740. Anal. Calcd for $C_{33}H_{29}N_4NiCl$: C, 68.84; H, 5.08; N, 9.73. Found: C, 69.05; H, 5.34; N, 9.39.

Ni(II) Complex ***5e***. Yield: 21%. Mp = 192−193 °C. $[\alpha]_D^{20}$ = +155° (*c* 0.25, $CHCl_3$). ^1H NMR (400Mz, $CDCl_3$) δ 7.22 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 2.0 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 6.79 (d, *J* = 2.0 Hz, 1H), 6.77−6.74 (m, 2H), 6.29 (dd, *J* = 5.5, 3.0 Hz, 1H), 4.77−4.55 (m, 2H), 4.18 (t, *J* = 10.0 Hz, 1H), 3.99 (dd, *J* = 9.9, 2.2 Hz, 1H), 3.89 (dd, *J* = 10.1, 2.3 Hz, 1H), 2.41 (s, 3H), 1.50 (t, *J* = 7.2 Hz, 3H), 1.10 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 168.4, 166.9, 161.7, 144.4, 137.2, 137.1, 135.2, 130.0, 125.6, 123.0, 121.0, 120.4, 113.0, 110.2, 65.6, 58.3, 44.9, 35.6, 26.5, 21.2, 17.1. HRMS (positive ESI): $[M - Cl]^+$ calcd for $C_{25}H_{29}N_4Ni^+$ 443.1740, found 443.1740. Anal. Calcd for $C_{25}H_{29}N_4NiCl$: C, 62.60; H, 6.09; N, 11.68. Found: C, 62.24; H, 6.23; N, 11.41.

Ni(II) Complex ***5f***. Yield: 15%. Mp = 248−249 °C. $[\alpha]_D^{20}$ = +211° (*c* 0.10, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.57−7.51 (m, 2H), 7.38−7.28 (m, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.17−7.13 (m, 3H), 6.75 (dd, *J* = 8.2, 4.3 Hz, 2H), 6.68 (d, *J* = 2.0 Hz, 1H), 6.30 (p, *J* = 4.1 Hz, 1H), 6.01 (d, *J* = 14.4 Hz, 1H), 5.78 (d, *J* = 14.4 Hz, 1H), 4.19 (t, *J* = 10.0 Hz, 1H), 4.01 (dd, *J* = 9.9, 2.1 Hz, 1H), 3.90 (dd, *J* = 10.1, 2.2 Hz, 1H), 2.41 (s, 3H), 1.09 (d, *J* = 21.3 Hz, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 169.0, 166.9, 161.8, 144.3, 137.3, 137.2, 137.1, 135.3 130.1, 128.68, 128.65, 127.9, 125.6, 123.1, 121.4, 120.5, 113.4, 110.4, 65.7, 58.3, 53.0, 35.7, 26.5, 21.2. HRMS (positive ESI): $[M - Cl]^+$ calcd for $C_{30}H_{31}N_4Ni^+$ 505.1897, found 505.1990. Anal. Calcd for $C_{30}H_{31}N_4NiCl$: C, 66.51; H, 5.77; N, 10.34. Found: C, 66.80; H, 6.03; N, 9.98.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00300.

Crystallographic data of **4a,c** and **5e** and NMR spectra of **1**−**5** (PDF)

Accession Codes

CCDC 1839754−1839755 and 1841152 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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