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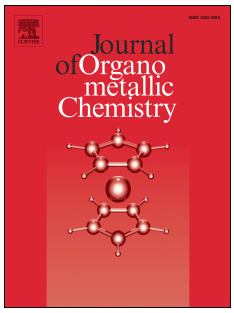

Large-scale synthesis of novel sterically hindered acenaphthene-based α-diimine ligands and their application in coordination chemistry

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Large-Scale Synthesis of Novel Sterically Hindered Acenaphthene-based α-Diimine Ligands and Their Application in Coordination Chemistry

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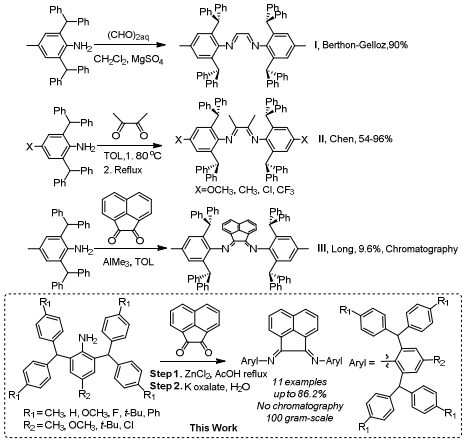
ABSTRACT: An efficient method to synthesize novel highly sterically hindered acenaphthene-based α-diimine ligands bearing bulky diarylmethyl moiety was achieved by two-step reactions. These reactions could be carried out on a scale of 100 grams with no chromatography involved. On the basis of this method, a series of novel highly sterically hindered acenaphthene-based α-diimine Pd(II) and Ni(II) complexes, imidazolium precursors and the corresponding NHCs-metal complexes were also successfully synthesized. These novel complexes can offer great potential for metal-catalyzed polymerizations and organic reactions.

Keywords: Diimine, Sterically hindered, α-diimine nickel complexes, α-diimine palladium complexes, N-heterocyclic carbene silver complexes, N-heterocyclic carbene palladium complexes

Introduction

The α-diimine ligands are well-known to stabilize organometallic complexes[1,2]. They are also the intermediate in the synthesis of N-heterocyclic carbenes (NHCs)[3,4]. The α-diimine ligands are usually derived from the condensation reaction of a diketone with two equivalents of an alkyl or arylamine, often catalyzed by a Lewis or Brönsted acid. The aryl substituent and the backbone of α-diimines can be easily tuned with appropriate substituents, thus enabling the preparation of arrays of ligands with independent control over the steric and electronic effects at the metal center. These ligands have been applied in metal-catalyzed polymerizations[5-10] and a significant number of useful organic reactions (supporting information, Scheme S1)[11-15]. It revealed that the increase of steric bulk at the *ortho* position of N-aryl moiety of the α-diimines can benefit these transformations. For example, Brookhart and coworkers[5-10] discovered that the incorporation of sterically bulky axial substituents (2,6-diisopropyl) in the Ni(II) and Pd(II) α-diimine catalysts is crucial in the generation of high molecular weight polymer because the bulky axial substituents dramatically retard the chain transfer rates. Using the more bulky dibenzhydryl instead of diisopropyl, the more thermally stable Ni(II) and Pd(II) α-diimine catalysts can be obtained[16-20]. These benzhydryl-derived Pd(II) α–diimine catalysts also generate polyolefins with high molecular weight and very low branching density[18]. The efficient and general synthetic methods for the glyoxal and 2,3-butadione derived ligands with bulky diarylmethyl moiety have been achieved in the recent work (Scheme 1, **I** and **II**)[18,21].



Scheme 1. Reported Procedure for the Synthesis of α-Diimines and Our Current Work.

α-Diimine of acenaphthenequinone, so-called BIAN ligands, are acknowledged as both oxdatively and thermally stable ligands for transition metal centers. The extensive π-system of the acenaphthene ring combined with the sterically modular aniline provide a broad range of π-acceptor frameworks, offer ing precise control over the steric, optical, and electronic properties.[22-28] These transition metal BIAN complexes are also used as popular olefin polymerization catalyst. Interestingly, polyolefin microstructure may be successfully tailored via in situ reduction of BIAN-ligated Ni(II)-based olefin polymerization catalysts[29,30]. Nevertheless, the synthesis of highly sterically hindered acenaphthene-based α-diimines bearing bulky diarylmethyl moiety is usually rather difficult since the reported strategies usually yield only monocondensed products[17,31,32]. Long recently reported a modified synthetic procedure using trimetylaluminum as catalysts for an acenaphthenequinone derived ligand bearing the bulky ben-

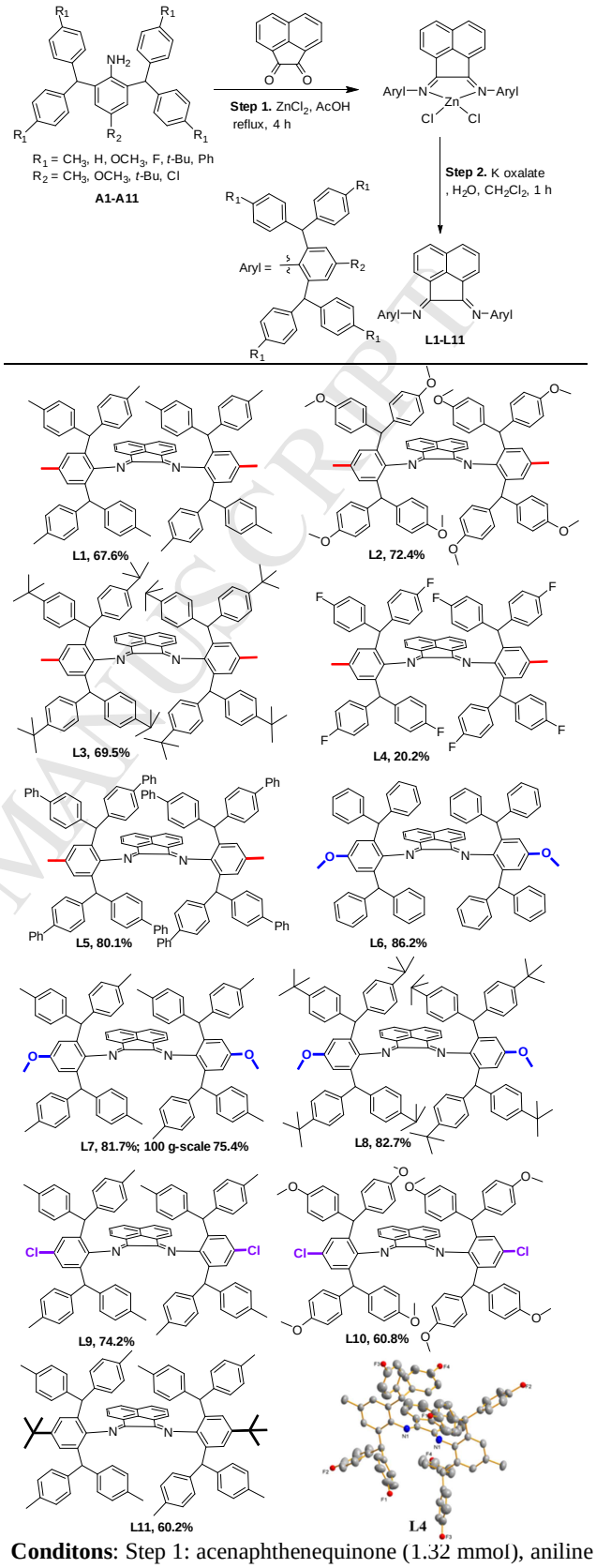
zhydryl moiety[17]. However, only ~10% yield is achieved and the column separation is also required, which is an obviously bottleneck for its wide applications (Scheme 1, **III**). In this work, an efficient and general method to synthesize highly sterically hindered acenaphthene-based α-diimine ligands bearing bulky diarylmethyl moiety was achieved by two-step reactions. On the basis of this method, a series of novel highly sterically hindered acenaphthene-based α-diimine Pd(II) and Ni(II) complexes, imidazolium precursors and the subsequent NHCs-metal complexes were also synthesized.

Results and discussion

Synthesis of sterically hindered acenaphthene-based α-diimine ligands.

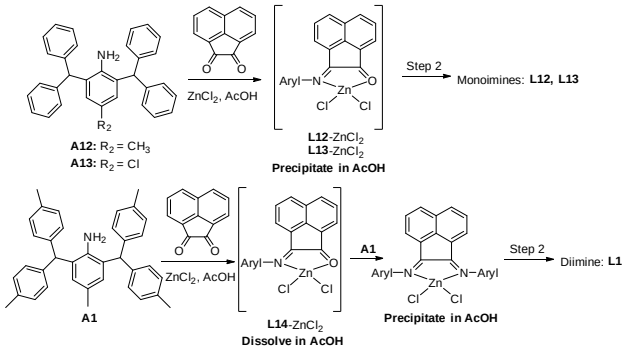
It was found that some sterically hindered diimines could be successfully prepared by the "template method" of Rosa[33]. Diimine-$ZnCl_2$ complex was synthesized by the reaction of aniline and acenaphthenequinone in the presence of $ZnCl_2$. Subsequent demetalation of the ligand was obtained by treating diimine-$ZnCl_2$ complex with an aqueous solution of potassium oxalate, leading to free ligand in high yield. Inspired by this work, this method is also applicable to the synthesis of sterically hindered acenaphthene-based α-diimines bearing bulky diarylmethyl moiety as indicated in Scheme 2. To test the limitations of this methodology, a number of hindered anilines with R_1 group in 4-position of diarylmethyl moiety and R_2 group in 4-position of N-aryl rings were investigated in the synthesis of acenaphthene-based dicondensed products. This method presented good compatibility and high isolated yields. Even the hindered group substituted anilines (R_1 = *tert*-butyl and phenyl) gave the products **L3** and **L5** in 69.5% and 80.1% yields respectively. Introducing the F group reduced the reaction efficiency (**L4**, 20.2%). Notably, 100 gram-scale preparation of **L7** was achieved in 75.4% yield, which makes it possible for large-scale synthesis of metal catalysts, especially robust α-diimine transition metal catalysts for olefin polymerization[16-18]. The solid structures of **L4** and **L5** were confirmed by single-crystal X-ray analysis (Scheme 2 and supporting information, Table S2). They exhibit *E*/*E* (C=N bond) isomeric preference in the crystalline state, like other α-diimine compounds[34]. The ^{1}H NMR spectrum, at room temperature, of a $CDCl_3$ solution of all diimines individually shows only one set of signals. **L7** was typically chosen to study time dependence by ^{1}H NMR analysis in $CDCl_3$ and no changes in the spectra can be observed within 36 h, indicating no isomerization occurs on the NMR time scale (supporting information, Figure S36). As a result, we predicted that the only isomer may be also *E*/*E* configuration in the solution.

An attempt to employ the anilines **A12** and **A13** as the substrates yielded the unexpected monoimine products (supporting information, Scheme S2), which was consistent with previous literature reports[17]. Our efforts to obtain the putative Zn(II) intermediate have been unsuccessful. MS analysis indicated the presence of the monoimine-Zn complex while the elemental analysis indicated the mixture of the monoimine and the monoimine-Zn complex. The monoimine-Zn complex may be unstable and free monoimine can be generated in the treatment process. We reasoned that one important factor was that the monoimine-Zn complexes exhibited poor solubility and precipitated in the acetic acid in the reaction of step 1,



Conditons: Step 1: acenaphthenequinone (1.32 mmol), aniline (3.0 mmol), $ZnCl_2$ (1.5 mmol), acetic acid (3 mL), refluxed for 4 h; Step 2: potassium oxalate (3.0 mmol), CH_2Cl_2 (20 mL), H_2O (3 mL), r. t. for 1 h. Isolated yields.

Scheme 2. Synthesis of α-Diimine Ligands.



Scheme 3. Plausible Explanation for the Production of Diimines and Monoimines.

preventing the formation of diimine- Zn complex (Scheme 3). In order to confirm this hypothesis, a monoimine **L14** (R_1 = CH_3, R_2 = CH_3) was purposefully synthesized using *p*-toluene sulfonic acid as conventional catalyst (see experimental section). **L12**, **L13**, **L14** and $ZnCl_2$ were in-situ added to the acetic acid respectively. The reaction mixture was refluxed under stirring for 4 hours. In monoimine **L14** system, solution was obtained, while insoluble substances were observed in monoimines **L12** and **L13** systems (supporting information, Figure S1). This experiment indicates that the modification of R_1 and R_2 can influence the solubility of monoimine-Zn complexes. As a result, the monocondensed products that are not precipitated in the solution can continue to react with anilines to form the dicondensed products (Scheme 3).

Synthesis of sterically hindered acenaphthene-based α-diimine palladium and nickel complexes.

A broad range of transition metal-BIAN complexes has now been described.[5-15] A focal point has been generation of robust, versatile α-diimine Pd(II) and Ni(II) catalysts for olefin polymerization and some important organic reactions. As a result, the coordination chemistry of these diimines with Pd(II) and Ni(II) was next evaluated (Figure 1). The palladium complex **1** was synthesized in 61.7% yield by the reaction of diimine **L7** with (COD)$PdCl_2$ (COD = 1,5-cyclooctadiene), while the nickel complex was generated in 83.9% yield by reaction of diimine **L7** with (DME)$NiBr_2$ (DME = 1,2-dimethoxyethane). The molecular structures of **1** and **2** were determined by X-ray diffraction analysis (Figure 1). Despite their large steric hindrance, the diimines leave sufficient room around the metal center. In the solid state, the Pd center adopts a square planar geometry while the Ni center adopts distorted tetrahedron geometry. The effective blockage of the axial positions of the Pd and Ni center can be observed from these structures. As mentioned in the introduction section, the presence of bulky ortho-aryl substituents in the ligand could retard the chain transfer process and generate high molecular weight polymer in olefin polymerization. Therefore, these Pd(II) and Ni(II) complexes may have the potential to produce some novel polyolefin materials.

Synthesis of the imidazolium chloride salts and corresponding NHCs-metal complexes.

The N-heterocyclic carbenes (NHCs) have emerged as the most powerful supporting ligands in metal-catalyzed organic transformations because of their strong σ-donation toward metal center. It has been reported the increase of steric bulk at the ortho position of N-aryl moiety of the NHCs could benefit the palladium-catalyzed organic reactions.[4] As a result, with an easy access to the highly steric diimine, the acenaphthene-based imidazolium precursors and the corresponding NHCs-metal complexes bearing bulky diarylmethyl moiety were also synthesized. Cyclocondensation with chloromethyl methyl ether provided the precipitate of the imidazolium chloride salts (Scheme 4a). These yellow solids were isolated by filtration and washed with Et_2O, giving in moderate to high yields of 74.1%, 89.5%, and 65.2% for **S1**, **S2**, and **S3**, respectively. All of the imidazolium slats were fully characterized by ^{1}H NMR, ^{13}C NMR and ESI-MS. The resonance of imidazolium C-H protons (NC*H*N) was observed downfield at δ =10.44, 10.47, and 13.17 ppm, respectively. Subsequently, the novel NHC-silver complex **3** which often acts as a NHC transfer agent in the presence of suitable metal precursors[35] and NHC-palladium complex **4** which can be generally used as catalyst in numerous cross-coupling reactions[36-42] were conveniently obtained in 70% and 81% yields, respectively (Scheme 4b). All of these prepared complexes are air and moisture stable and can be stored on a shelf for more than three months without noticeable decomposition. Complexes **3** and **4** were fully characterized by single crystal X-ray diffraction analysis (Figure 2). As expected, NHC-silver complex **3** is nearly linear (C_{NHC}-Ag-Cl 176.53(18)^o) and the Ag-C_{NHC} distance(2.101(6) Å) is close to that of other NHC-Ag complexes[21]. The solid structure of NHC-palladium complex **4** adopts slightly distorted square-planar coordination geometry with the NHC and pyridine *trans* to each other.

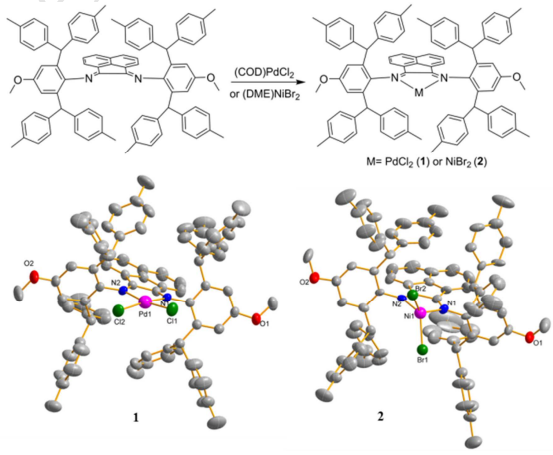
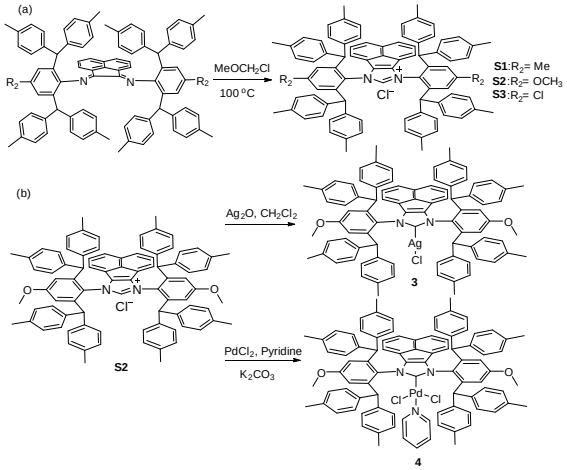


Figure 1. Synthesis and the ORTEP diagrams of complexes **1** and **2**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): complex **1**: Pd(1)-N(2) = 2.060(3), Pd(1)-N(1) = 2.071(3), Pd(1)-Cl(2) = 2 .2864(10), Pd(1)-Cl(1) = 2.2877(12), N(2)-Pd(1)-N(1) = 81.61(11), N(2)-Pd(1)-Cl(2) = 93.43(8), N(1)-Pd(1)-Cl(2) = 170.20(9), Cl(2)-Pd(1)-Cl(1) = 91.23(4); complex **2:** Ni(1)-N(2) = 2.037(7), Ni(1)-N(1) = 2.043(7), Ni(1)-Br(2) = 2.3005(18), Ni(1)-Br(1) = 2.3161(18), N(2)-Ni(1)-N(1) = 82.7(3), N(2)-Ni(1)-Br(2) = 102.7(2), N(1)-Ni(1)-Br(2) = 132.1(2), Br(2)-Ni(1)-Br(1) = 111.74(7).



Scheme 4. (a) Synthesis of the Imidazolium Chloride Salts; (b) Synthesis of Complexes **3** and **4**.

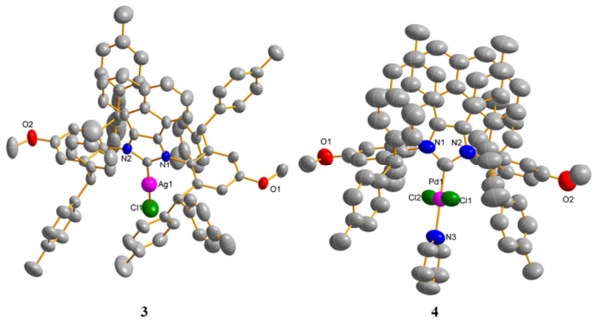


Figure 2. Synthesis and the ORTEP diagrams of complexes **3** and **4**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): complex **3**: Ag(1)-C(1) = 2.101(6), Ag(1)-Cl(1) = 2.350(2), C(1)-Ag(1)-Cl(1) = 176.53(18); complex **4**: Pd(1)-C(1) = 1.944(8), Pd(1)-N(3) = 2.117(7), Pd(1)-Cl(1) = 2.266(3), Pd(1)-Cl(2) = 2.287(3), C(1)-Pd(1)-N(3) = 179.1(4), C(1)-Pd(1)-Cl(1) = 87.2(3), N(3)-Pd(1)-Cl(1) = 91.9(2), C(1)-Pd(1)-Cl(2) = 90.3(3), N(3)-Pd(1)-Cl(2) = 90.6(2), Cl(1)-Pd(1)-Cl(2) = 177.48(8).

Conclusions

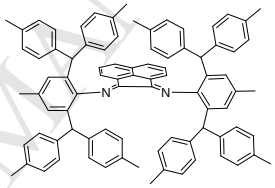
In summary, we have described an efficient method to synthesize acenaphthene-based α-diimine ligands bearing bulky diarylmethyl moiety. Most of products are accessible in moderate to high yields, with no tedious purification involved. These reactions also could be carried out on a scale of 100 grams. The coordination chemistry of these new bulky diimines was investigated through the synthesis of the corresponding Pd(II) and Ni(II) complexes. In addition, this methodology also enables us to synthesize the novel imidazolium precursors and the corresponding NHCs-metal complexes. These novel diimines should find application in the stabilization of reactive metallic species. Use of these diimines in olefin coordination polymerization catalysts is being actively pursued in our laboratory and we will continue to explore the use of these new diimines.

Experimental section

General Considerations.

All chemicals were commercially sourced, except those whose synthesis is described. Aniline compounds of 2,6-dibenzhydryl-4-methoxyaniline (**A6**), 2,6-dibenzhydryl-4-methylaniline (**A12**) and 2,6-dibenzhydryl-4-chloroaniline (**A13**), was synthesized according to previous methods[18]. The synthetic route for other anilines **A1-A5, A7-A11** was shown in supporting information. ^{1}H NMR spectra were acquired in 5 mm NMR tubes at 298 K on Bruker DPX 500 or Bruker Ascend Tm 400 spectrometers using TMS as an internal standard and $CDCl_3$ as solvent. ^{13}C NMR spectra were acquired in 5 mm NMR tubes at 298 K on Bruker DPX 500 or Bruker Ascend Tm 400 spectrometers. ^{13}C NMR chemical shifts were internally referenced to CH_3Cl (77.16 ppm) for chloroform-d_1. Coupling constants are in Hz. All data processing was carried out using XWIN-NMR version 3.6 (Bruker UK Ltd.). Elemental analysis was performed by the Analytical Center of the University of Science and Technology of China. Mass spectra of the anilines and some diimines were recorded on a Thermo LTQ Orbitrap XL (ESI+). Mass spectra of the complexes and some diimines were recorded on a Atouflex Speed MALDI-TOF MS. X-ray Diffraction data were collected at 298(2) K on a Bruker Smart CCD area detector with graphite-monochromated Mo K^{α} radiation (λ = 0.71073 Å).

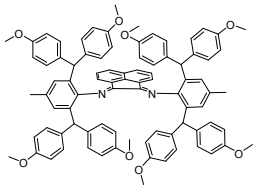
Procedure for the Synthesis of Acenaphthene-based α-Diimines.



Bis(2,6-bis(di-p-tolylmethyl)-4-methylphenyl)acenaphthylene-1,2-diimine (**L1**).

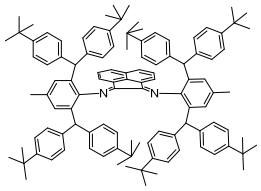
Step 1: $ZnCl_2$ (0.204 g, 1.5mmol) and acenaphthenequinone (0.241 g, 1.32mmol) were suspended in glacial acetic acid (3 mL). 2,6-Bis(di-p-tolylmethyl)-4-methylaniline (1.49 g, 3.0 mmol) was added, and the reaction mixture was refluxed under stirring for 4 h. The solution was allowed to cool to room temperature, and a bright orange-red solid precipitated. The solid was separated by filtration and washed with acetic acid (3 × 3 mL) and diethyl ether (5 ×6 mL), to remove remaining acetic acid. Drying under vacuum gave bright orange-red, poorly soluble solid (1.21 g, 72.2%). According to the reported literature[33,43,44], the solid is zinc diimine complex. Step 2: The zinc was removed from the zinc diimine complex. The product of the previous step was suspended in methylene chloride (20 mL), and a solution of potassium oxalate (0.553 g, 3 mmol) in water (3 mL) was added. The reaction mixture was stirred vigorously for 1 h. The two phases were separated, and the organic layer was washed with water (3×10 mL) and dried with $MgSO_4$. After filtration the solvent was removed under vacuum to afford the product as an orange powder (1.01 g, 93.6%), followed by recrystallization from dichloromethane and *n*-hexane. The total yield of two steps is 67.6%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.1 Hz, 2H, aryl-*H*), 6.99 – 6.83 (m, 22H, aryl-*H*), 6.72 (d, *J* = 5.6 Hz, 8H, aryl-*H*), 6.39 (d, *J* = 5.6 Hz, 8H, aryl-*H*), 6.12 (d, *J* = 5.1 Hz, 2H, aryl-*H*), 5.56 (s, 4H, C*H*(PhMe)$_2$), 2.27 (s, 6H, Ar-C*H*$_3$), 2.25 (s, 12H, CH(Ph*Me*)$_2$), 1.88 (s, 12H, CH(Ph*Me*)$_2$). ^{13}C NMR (126 MHz,

$CDCl_3$) δ 163.55 (*C*=N), 146.71, 141.19, 140.08, 139.84, 135.25, 134.81, 132.53, 131.87, 129.92, 129.51, 129.48, 129.23, 128.78, 128.60, 128.56, 127.10, 126.58, 124.52, 50.74 (*C*H(PhMe)$_2$), 21.64 (Ar-*C*H$_3$), 21.08(CH(Ph*Me*)$_2$), 20.68 (CH(Ph*Me*)$_2$). ESI-MS (m/z): calcd for $C_{86}H_{77}N_2$: $[M+H]^+$ 1137.6087, found: 1137.6063.



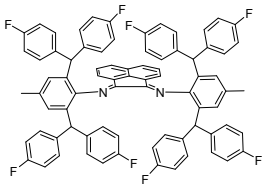
Bis(2,6-bis(bis(4-methoxyphenyl)methyl)-4-methylphenyl)acenaphthylene-1,2-diimine (**L2**).

Using the same procedure as for the synthesis of **L1**, **L2** was obtained as an orange powder. The yields of step 1 and step 2 are 75.1% (1.39 g) and 96.4% (1.21g), respectively. The total yield of two steps is 72.4%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.1 Hz, 2H, aryl-*H*), 7.00 (d, *J* = 8.4 Hz, 8H, aryl-*H*), 6.93 (t, *J* = 7.6 Hz, 2H, aryl-*H*), 6.86 (s, 4H, aryl-*H*), 6.76 (d, *J* = 8.3 Hz, 8H, aryl-*H*), 6.69 (d, *J* = 8.5 Hz, 8H, aryl-*H*), 6.11 (d, *J* = 8.3 Hz, 10H, aryl-*H*), 5.59 (s, 4H, C*H*Ar$_2$), 3.72 (s, 12H, OC*H*$_3$), 3.35 (s, 12H, OC*H*$_3$), 2.28 (s, 6H, aryl-C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.79 (*C*=N), 157.86 (*C*-O), 157.25 (*C*-O), 146.63, 139.75, 136.59, 135.17, 132.72, 132.19, 130.81, 130.51, 129.40, 129.16, 128.51, 127.58, 126.65, 124.48, 113.53, 113.25, 55.31 (O*C*H$_3$), 54.84 (O*C*H$_3$), 49.90 (*C*HAr$_2$), 21.65 (aryl-*C*H$_3$). ESI-MS (m/z): calcd for $C_{86}H_{77}N_2O_8$: 1265.5680, found: 1265.5701 $[M+H]^+$.



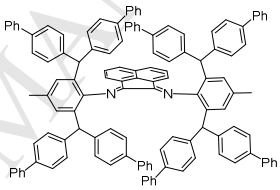
Bis(2,6-bis(bis(4-(tert-butyl)phenyl)methyl)-4-methylphenyl)acenaphthylene-1,2-diimine (**L3**).

Using the same procedure as for the synthesis of **L1**, **L3** was obtained as an orange powder. The yields of step 1 and step 2 are 78.1% (1.66 g) and 89.1% (1.36 g), respectively. The total yield of two steps is 69.5%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.0 Hz, 2H, aryl-*H*), 7.15 (d, *J* = 8.3 Hz, 8H, aryl-*H*), 7.04 (d, *J* = 8.2 Hz, 8H, aryl-*H*), 6.95 (s, 4H, aryl-*H*), 6.84 (dd, *J* = 16.8, 7.8 Hz, 10H, aryl-*H*), 6.70 (d, *J* = 8.1 Hz, 8H, aryl-*H*), 6.14 (d, *J* = 6.9 Hz, 2H, aryl-*H*), 5.66 (s, 4H, C*H*Ar$_2$), 2.32 (s, 6H, aryl-C*H*$_3$), 1.24 (s, 36H, (C(C*H*$_3$)$_3$), 0.98 (s, 36H, (C(C*H*$_3$)$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.64 (*C*=N), 148.40, 148.02, 146.68, 140.97, 140.03, 139.97, 132.45, 131.94, 129.58, 129.34, 129.26, 128.73, 128.01, 126.64, 124.95, 124.75, 124.65, 50.54 (*C*HAr$_2$), 34.40 (*C*(CH$_3$)$_3$), 34.08 (*C*(CH$_3$)$_3$), 31.52 (C(*C*H$_3$)$_3$), 31.26 (C(*C*H$_3$)$_3$), 21.71 (aryl-*C*H$_3$). ESI-MS (m/z): calcd for $C_{110}H_{125}N_2$: 1474.9876, found: 1474.9915 $[M+H]^+$.



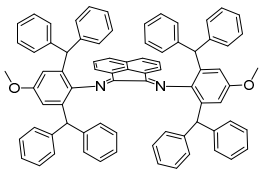
Bis(2,6-bis(bis(4-fluorophenyl)methyl)-4-methylphenyl)acenaphthylene-1,2-diimine (**L4**).

Using the same procedure as for the synthesis of **L1**, **L4** was obtained as an orange powder. The yields of step 1 and step 2 are 30.2% (0.52 g) and 67.0% (0.31 g), respectively. The total yield of two steps is 20.2%. A single crystal of **L4** was obtained by layering methanol onto the DCM solution at room temperature. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H, aryl-*H*), 6.95 (dt, *J* = 11.5, 5.9 Hz, 10H, aryl-*H*), 6.88 – 6.81 (m,12H, aryl-*H*), 6.75 (dd, *J* = 8.5, 5.4 Hz, 8H, aryl-*H*), 6.34 (t, *J* = 8.6 Hz, 8H, aryl-*H*), 6.08 (d, *J* = 7.1 Hz, 2H, aryl-*H*), 5.56 (s, 4H, C*H*Ar$_2$), 2.30 (s, 6H, Ar-C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.70 (*C*=N), 162.51 (*C*-F), 162.00 (*C*-F), 160.56 (*C*-F), 160.05 (*C*-F), 146.16, 139.85, 139.23, 139.21, 138.13, 138.10, 133.69, 131.61, 131.12, 131.06, 130.89, 130.82, 129.69, 129.62, 129.03, 128.01, 126.82, 124.33, 115.22, 115.05, 114.88, 50.04 (*C*HAr$_2$), 21.63 (Ar-*C*H$_3$). ^{19}F NMR (471 MHz, $CDCl_3$) δ -116.49 (s), -116.72 (s). MALDI-TOF-MS (m/z): 1169.06 $[M+H]^+$.



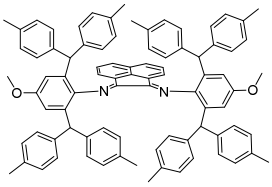
Bis(2,6-bis(di([1,1'-biphenyl]-4-yl)methyl)-4-methylphenyl)acenaphthylene-1,2-diimine (**L5**).

Using the same procedure as for the synthesis of **L1**, **L5** was obtained as a yellow powder. The yields of step 1 and step 2 are 96.5% (2.23 g) and 83.0% (1.71 g), respectively. The total yield of two steps is 80.1%. A single crystal of **L5** was obtained by layering methanol onto the DCM solution at room temperature. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.6 Hz, 8H, aryl-*H*), 7.36 (dd, *J* = 17.2, 8.0 Hz, 18H, aryl-*H*), 7.29 (s, 2H, aryl-*H*), 7.28 (s, 2H, aryl-*H*), 7.22 (d, *J* = 7.5 Hz, 20H, aryl-*H*), 7.07 – 7.00 (m, 20H, aryl-*H*), 6.86 (d, *J* = 8.0 Hz, 8H, aryl-*H*), 6.80 (t, *J* = 7.7 Hz, 2H, aryl-*H*), 6.23 (d, *J* = 7.1 Hz, 2H, aryl-*H*), 5.83 (s, 4H, C*H*Ar$_2$), 2.36 (s, 6H, Ar-C*H*$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.94 (*C*=N), 146.79, 142.93, 141.64, 140.99, 140.37, 139.69, 138.80, 138.48, 133.02, 131.46, 130.29, 129.91, 129.58, 129.28, 128.76, 128.62, 128.40, 128.22, 127.94, 127.01, 126.92, 126.83, 126.67, 126.60, 126.44, 124.51, 50.91 (*C*HAr$_2$), 21.58 (Ar-*C*H$_3$). MALDI-TOF-MS (m/z): 1634.18 $[M+H]^+$.



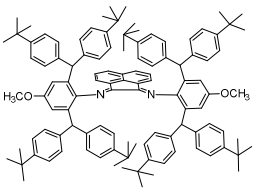
Bis(2,6-dibenzhydryl-4-methoxyphenyl)acenaphthylene-1,2-diimine (**L6**).

Using the same procedure as for the synthesis of **L1**, **L6** was obtained as a yellow powder. The yields of step 1 and step 2 are 98.7% (1.56 g) and 87.3% (1.20 g), respectively. The total yield of two steps is 86.2%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 2H, aryl-*H*), 7.10 (dd, *J* = 21.5, 6.6 Hz, 20H, aryl-*H*), 6.88 (d, *J* = 15.3 Hz, 10H, aryl-*H*), 6.66 (d, *J* = 15.1 Hz, 16H, aryl-*H*), 6.16 (d, *J* = 7.1 Hz, 2H, aryl-*H*), 5.68 (s, 4H, C*H*Ar_2), 3.66 (s, 6H, OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.24 (*C*=N), 155.69 (*C*-O), 143.51, 142.82, 142.33, 139.84, 133.02, 129.72, 129.47, 129.34, 128.51, 128.08, 128.00, 127.83, 126.64, 126.11, 125.81, 124.25, 114.51, 55.23 (OCH_3), 51.57 (*C*HAr_2). ESI-MS (m/z): calcd for $C_{78}H_{61}N_2O_2$: 1057.4733, found:1057.4777 $[M+H]^+$.



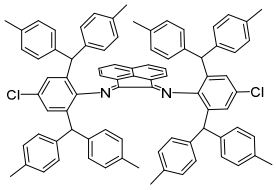
Bis(2,6-bis(di-p-tolylmethyl)-4-methoxyphenyl)acenaphthylene-1,2-diimine (**L7**).

Using the same procedure as for the synthesis of **L1**, **L7** was obtained as an orange powder. The yields of step 1 and step 2 are 93.0% (1.60 g) and 87.8% (1.26 g), respectively. The total yield of two steps is 81.7%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H, aryl-*H*), 6.96 (d, *J* = 8.1 Hz, 8H, aryl-*H*), 6.93 (d, *J* = 8.1 Hz, 8H, aryl-*H*), 6.90 – 6.86 (m, 2H, aryl-*H*), 6.70 (d, *J* = 8.0 Hz, 8H, aryl-*H*), 6.65 (s, 4H, aryl-*H*), 6.37 (d, *J* = 7.8 Hz, 8H, aryl-*H*), 6.15 (d, *J* = 7.1 Hz, 2H, aryl-*H*), 5.57 (s, 4H, C*H*Ar_2), 3.65 (s, 6H, Ar-OCH_3), 2.24 (s, 12H, Ar-CH_3), 1.86 (s, 12H, Ar-CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.31 (*C*=N), 155.67 (*C*-O), 142.98, 140.84, 139.81, 139.74, 135.39, 134.92, 133.38, 129.86, 129.51, 129.45, 128.84, 128.58, 128.54, 127.17, 126.61, 124.51, 114.26, 55.33 (Ar-OCH_3), 50.89 (*C*HAr_2), 21.07 (Ar-*C*H_3), 20.66 (Ar-*C*H_3). ESI-MS (m/z): calcd for $C_{86}H_{77}N_2O_2$: 1169.5985, found:1169.5999 $[M+H]^+$.



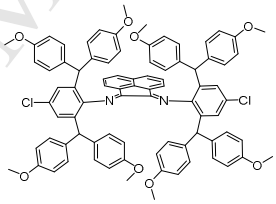
Bis(2,6-bis(bis(4-(tert-butyl)phenyl)methyl)-4-methoxyphenyl)acenaphthylene-1,2-diimine (**L8**).

Using the same procedure as for the synthesis of **L1**, **L8** was obtained as a yellow powder. The yields of step 1 and step 2 are 98.8% (2.11 g) and 83.7% (1.62 g), respectively. The total yield of two steps is 82.7%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.7 Hz, 2H, aryl-*H*), 7.17 (d, *J* = 7.2 Hz, 8H, aryl-*H*), 7.06 (d, *J* = 7.2 Hz, 8H, aryl-*H*), 6.86 (dd, *J* = 24.0, 7.4 Hz, 11H, aryl-*H*), 6.76 – 6.67 (m, 11H, aryl-*H*), 6.20 (d, *J* = 6.4 Hz, 2H, aryl-*H*), 5.67 (s, 4H, C*H*Ar_2), 3.69 (s, 6H, OCH_3), 1.24 (s, 36H, C(CH_3)$_3$), 0.97 (s, 36H, C(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.30 (*C*=N), 155.60 (*C*-O), 148.54, 148.17, 142.94, 140.53, 140.01, 139.75, 133.38, 129.54, 129.44, 129.21, 128.66, 128.14, 126.68, 125.01, 124.79, 124.66, 114.32, 55.35 (OCH_3), 50.70 (*C*HAr_2), 34.38 (*C*(CH_3)$_3$), 34.05 (*C*(CH_3)$_3$), 31.49 (C(*C*H_3)$_3$), 31.22 (C(*C*H_3)$_3$). ESI-MS (m/z): calcd for $C_{110}H_{125}N_2O_2$: 1505.9741, found: 1505.9735 $[M+H]^+$.



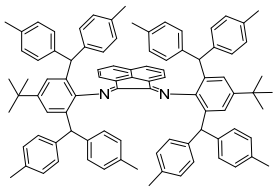
Bis(4-chloro-2,6-bis(di-p-tolylmethyl)phenyl)acenaphthylene-1,2-diimine (**L9**).

Using the same procedure as for the synthesis of **L1**, **L9** was obtained as a yellow powder. The yields of step 1 and step 2 are 75.1% (1.30 g) and 98.7% (1.15 g), respectively. The total yield of two steps is 74.2%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H, aryl-*H*), 7.05 (s, 4H, aryl-*H*), 6.92 (q, *J* = 8.2 Hz, 18H, aryl-*H*), 6.67 (d, *J* = 8.0 Hz, 8H, aryl-*H*), 6.40 (d, *J* = 7.9 Hz, 8H, aryl-*H*), 6.15 (d, *J* = 7.1 Hz, 2H, aryl-*H*), 5.52 (s, 4H, C*H*Ar_2), 2.25 (s, 12H, Ar-CH_3), 1.87 (s, 12H, Ar-CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.61 (*C*=N), 147.44, 140.09, 139.93, 139.10, 135.78, 135.32, 134.19, 129.75, 129.53, 129.33, 129.01, 128.98, 128.78, 128.60, 128.20, 127.62, 126.80, 124.51, 50.77 (*C*HAr_2), 21.07 (CH(Ph*Me*)$_2$), 20.67 (CH(Ph*Me*)$_2$). ESI-MS (m/z): calcd for $C_{84}H_{71}Cl_2N_2$: 1177.4994, found: 1177.4941 $[M+H]^+$.



Bis(2,6-bis(bis(4-methoxyphenyl)methyl)-4-chlorophenyl)acenaphthylene-1,2-diimine (**L10**).

Using the same procedure as for the synthesis of **L1**, **L10** was obtained as a yellow powder. The yields of step 1 and step 2 are 68.8% (1.37 g) and 88.4% (1.10 g), respectively. The total yield of two steps is 60.8%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H, aryl-*H*), 7.04 (s, 4H, aryl-*H*), 6.98 (dd, *J* = 16.5, 8.2 Hz, 10H, aryl-*H*), 6.72 (dd, *J* = 13.8, 8.6 Hz, 16H, aryl-*H*), 6.14 (dd, *J* = 10.6, 8.0 Hz, 10H, aryl-*H*), 5.56 (s, 4H, C*H*Ar_2), 3.73 (s, 12H, Ar-OCH_3), 3.36 (s, 12H, Ar-OCH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.93 (*C*=N), 158.15 (*C*-O), 157.53 (*C*-O), 147.36, 139.86, 135.48, 134.56, 134.16, 130.70, 130.40, 129.47, 129.16, 128.56, 128.13, 128.10, 126.86, 124.55, 113.77, 113.48, 55.34 (Ar-OCH_3), 54.87 (Ar-OCH_3), 49.95 (*C*HAr_2). ESI-MS (m/z): calcd for $C_{84}H_{71}Cl_2N_2O_8$: 1305.4587, found: 1305.4590 $[M+H]^+$.



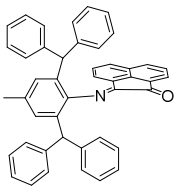
Bis(4-(tert-butyl)-2,6-bis(di-p-tolylmethyl)phenyl)acenaphthylene-1,2-diimine (**L11**).

Using the same procedure as for the synthesis of **L1**, **L11** was obtained as a yellow powder. The yields of step 1 and step 2 are 72.6% (1.29 g) and 82.9% (0.96 g), respectively. The total yield of two steps is 60.2%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H, aryl-*H*), 7.09 (s, 4H, aryl-*H*), 6.93 (q, *J* = 8.2 Hz, 16H, aryl-*H*), 6.87 – 6.83 (m, 2H, aryl-*H*), 6.69 (d, *J* = 7.9 Hz, 8H, aryl-*H*), 6.38 (d, *J* = 7.8 Hz, 8H, aryl-*H*), 6.01 (d, *J* = 7.1 Hz, 2H, aryl-*H*), 5.55 (s, 4H, C*H*Ar_2), 2.24 (s, 12H, Ar-CH_3), 1.86 (s, 12H, Ar-CH_3), 1.19 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.38 (*C*=N), 146.65, 145.70, 141.30, 140.31, 139.81, 135.08, 134.64, 131.10, 129.84, 129.61, 129.42, 128.67, 128.62, 128.46, 127.01, 126.56, 125.49, 124.31, 50.97 (*C*HAr_2), 34.52 (*C*(CH$_3$)$_3$), 31.58 (C(*C*H$_3$)$_3$), 21.05 (Ar-*C*H$_3$), 20.65 (Ar-*C*H$_3$). ESI-MS (m/z): calcd for $C_{92}H_{89}N_2$: 1221.7026, found: 1221.7052 $[M+H]^+$.

*Procedure for 100 gram-Scale Synthesis of **L7**.*

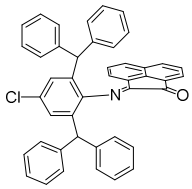
Step 1: $ZnCl_2$ (20.4 g, 150 mmol) and acenaphthenequinone (24.1 g, 132 mmol) were suspended in glacial acetic acid (300 mL). 2,6-Bis(di-p-tolylmethyl)-4-methylaniline (149 g, 300 mmol) was added, and the reaction mixture was refluxed under mechanical stirring for 4 h. The solution was allowed to cool to room temperature, and a bright orange-red solid precipitated. The solid was separated by filtration and washed with acetic acid (3 × 100 mL) and diethyl ether (5 ×150 mL), to remove remaining acetic acid. Drying under vacuum gave bright orange-red, poorly soluble solid (151 g, 87.8%). Step 2: The zinc was removed from the zinc diimine complex. The product of the previous step was suspended in methylene chloride (1000 mL), and a solution of potassium oxalate (55.3 g, 300 mmol) in water (500 mL) was added. The reaction mixture was stirred vigorously by mechanical agitator for 1 h. The two phases were separated, and the organic layer was washed with water (3×200 mL) and dried with $MgSO_4$. After filtration the solvent was removed under vacuum to afford the product as an orange powder (116 g, 85.9%). The total yield of two steps is 75.4%.

Procedure for the Synthesis of Acenaphthene-based Monoimines.



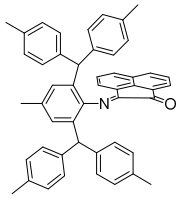
2-((2,6-Dibenzhydryl-4-methylphenyl)imino)acenaphthylen-1-one (**L12**).

Using the same procedure as for the synthesis of **L1**, **L12** was obtained as an orange powder. Our efforts to obtain the putative Zn(II) intermediate have been unsuccessful. MS analysis indicated the presence of the monoimine-Zn complex (MALDI-TOF-MS (m/z): 689.23 $[M-2Cl+Na]^+$, see supporting information, Figure S84) while the elemental analysis indicated the mixture of the monoimine ligands and the monoimine-Zn complexes (Anal. Calcd for $C_{45}H_{33}Cl_2NOZn$: C, 73.04; H, 4.49 N, 1.89; Found: C, 80.53; H, 5.10; N, 2.12). The total yield of two steps is 69.4% (0.55 g). This compound is previously known[36]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 – 7.99 (m, 2H, aryl-*H*), 7.70 (dt, *J* = 8.0, 3.4 Hz, 2H, aryl-*H*), 7.23 (t, *J* = 7.4 Hz, 4H, aryl-*H*), 7.17 (t, *J* = 7.3 Hz, 2H, aryl-*H*), 7.05 (dd, *J* = 7.4, 3.3 Hz, 5H, aryl-*H*), 6.85 (d, *J* = 7.2 Hz, 4H, aryl-*H*), 6.78 (s, 2H, aryl-*H*), 6.59 (t, *J* = 7.7 Hz, 4H, aryl-*H*), 6.42 (t, *J* = 7.4 Hz, 2H, aryl-*H*), 6.13 (d, *J* = 7.1 Hz, 1H, aryl-*H*), 5.42 (s, 2H, C*H*Ar_2), 2.26 (s, 3H, Aryl-CH_3). ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.82 (*C*=O), 162.41 (*C*=N), 145.96, 143.00, 142.49, 141.76, 133.26, 131.88, 131.79, 130.03, 129.90, 129.81, 129,71, 129.57, 129.56, 129.48, 128.72, 128.51, 128.47, 128.19, 127.84 , 127.57, 127.25, 126.97, 126.22, 125.55, 123.96, 121.54, 52.19 (*C*HAr_2), 21.58 (Aryl-*C*H$_3$). MALDI-TOF-MS (m/z): 604.07 $[M+H]^+$.



2-((2,6-Dibenzhydryl-4-chlorophenyl)imino)acenaphthylen-1-one (**L13**).

Using the same procedure as for the synthesis of **L1**, **L13** was obtained as an orange powder. Our efforts to obtain the putative Zn(II) intermediate have been unsuccessful. The total yield is 69.4% (0.57 g). This compound is previously known[45]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 6.1 Hz, 2H, aryl-*H*), 7.73 (t, *J* = 9.3 Hz, 2H, aryl-*H*), 7.32 – 7.19 (m, 5H, aryl-*H*), 7.05 (t, *J* = 11.1 Hz, 6H, aryl-*H*), 6.96 (s, 2H, aryl-*H*), 6.84 (d, *J* = 7.4 Hz, 5H, aryl-*H*), 6.60 (t, *J* = 7.4 Hz, 3H, aryl-*H*), 6.44 (t, *J* = 7.2 Hz, 2H, aryl-*H*), 6.16 (d, *J* = 7.0 Hz, 1H, aryl-*H*), 5.42 (s, 2H, C*H*Ar_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.45 (*C*=O), 162.62 (*C*=N), 146.87, 142.68, 142.01, 140.93, 134.16, 132.06, 129.97, 129.88, 129.67, 129.61, 129.48, 129.42, 128.95, 128.79, 128.47, 128.35, 128.16, 128.10, 127.80, 127.33, 126.69, 125.94, 123.92, 121.84, 52.21 (*C*HAr_2). ESI-MS (m/z): calcd for $C_{44}H_{31}ClNO$: 624.2094, found: 624.2007 $[M+H]^+$.



2-((2,6-Bis(di-p-tolylmethyl)-4-methylphenyl)imino)acenaphthylen-1-one **(L14).**

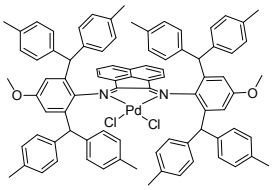
The monoimine ligand **L14** was purposefully synthesized to investigate the solubility of monoimine-Zn(II) intermediates in the acetic acid in the reaction of step 1. A mixture of 2,6-bis(di-p-tolylmethyl)-4-methylaniline (2.97 g, 6 mmol, 1.0 equiv.) and acenaphthenequinone (1.09 g, 6 mmol, 1.0 equiv.) were dissolved in 5 mL ethanol and 100 mL of CH_2Cl_2 containing a catalytic amount of *p*-toluenesulfonic acid and stirred for 48 h at room temperature. The solvent was evaporated at reduced pressure to give the crude product, which was chromatographed on silica gel with petroleum ether-ethyl acetate (v/v = 30:1). A 2.75 g amount of the product was obtained as red powder in 69.5% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 10.8, 7.6 Hz, 2H, aryl-*H*), 7.76 -7.66 (m, 2H,

aryl-*H*), 7.06-6.99 (m, 5H, aryl-*H*), 6.96 (t, *J* = 9.4 Hz, 4H, aryl-*H*), 6.77 (s, 2H, aryl-*H*), 6.71 (d, *J* = 7.9 Hz, 4H, aryl-*H*), 6.32 (d, *J* = 7.8 Hz, 4H, aryl-*H*), 6.03 (d, *J* = 7.1 Hz, 1H, aryl-*H*), 5.33 (s, 2H, C*H*(PhMe)$_2$), 2.29 (s, 6H, CH(Ph*Me*)$_2$), 2.25 (s, 3H, Ar-C*H*$_3$), 1.67 (s, 6H, *C*H(Ph*Me*)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.09 (*C*=O), 162.56 (*C*=N), 146.08, 142.38, 140.19, 139.12, 135.60, 134.86, 133.14, 132.77, 131.98, 131.67, 130.24, 129.97, 129.76, 129.47, 129.42, 129.31, 128.93, 128.64, 128.43, 127.58, 127.56, 127.33, 126.86, 124.29, 122.22, 121.50, 51.53(*C*HAr$_2$), 21.65 (Ar-*C*H$_3$), 21.14 (Ar-*C*H$_3$), 20.48 (Ar-*C*H$_3$). ESI-MS (m/z): calcd for $C_{49}H_{42}NO$: 660.3266, found: 660.3275 $[M+H]^+$.

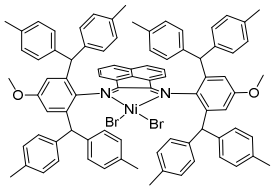
*In-situ Reaction of Monoimines **L12-L14** with $ZnCl_2$ in the Acetic Acid.*

Monoimine (0.2 mmol) and $ZnCl_2$ (0.2 mmol) were added in the glacial acetic acid (10 mL). The reaction mixture was refluxed under stirring for 4 h. In monoimine ligand **L14** system, solution is obtained, while insoluble substances are observed in monoimine ligand **L12** and **L13** systems (Figure S1).

Procedure for the Synthesis of α-Diimine Pd(II) and Ni(II) Complexes.

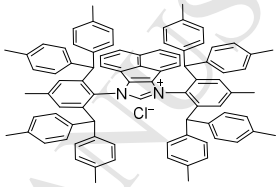


Complex 1: A mixture of **L7** (1.28 g, 1.1 mmol), (COD)$PdCl_2$ (0.286 g, 1 mmol) in CH_2Cl_2 (20 mL) was stirred for 3 days at room temperature. During stirring, the solid was completely dissolved and the color of the solution was changed from yellow to red. The desired compound can be isolated from repeated recrystallized from n-hexane and dichloromethane. Alternatively, the desired compound can be isolated at much higher yield using column chromatography. The mixture was eluted on silica gel with first 1:1 hexanes/CH_2Cl_2, then pure CH_2Cl_2 as the mobile phase. The pure compound was obtained as an orange solid (0.831 g, 61.7%). A single crystal of complex **1** was obtained by layering hexane onto the CH_2Cl_2 solution at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H, aryl-*H*), 7.27 (s, 3H, aryl-*H*), 7.26 – 7.24 (m, 5H, aryl-*H*), 6.97 (d, *J* = 7.8 Hz, 8H, aryl-*H*), 6.84 (t, *J* = 7.7 Hz, 2H, aryl-*H*), 6.73 (d, *J* = 7.7 Hz, 8H, aryl-*H*), 6.69 (s, 4H, aryl-*H*), 6.27 (d, *J* = 7.8 Hz, 8H, aryl-*H*), 6.12 (s, 4H, C*H*Ar$_2$), 6.04 (d, *J* = 6.9 Hz, 2H, aryl-*H*), 3.63 (s, 6H, Ar-OC*H*$_3$), 2.25 (s, 12H, Ar-C*H*$_3$), 1.82 (s, 12H, Ar-C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.00 (*C*=N), 158.69 (*C*-O), 145.61, 139.87, 138.86, 138.80, 136.24, 135.99, 135.41, 129.98, 129.90, 129.60, 128.99, 128.91, 127.39, 127.06, 123.52, 114.88, 55.31 (Ar-O*C*H$_3$), 51.67 (*C*HAr$_2$), 21.18 (Ar-*C*H$_3$), 20.70 (Ar-*C*H$_3$). MALDI-TOF-MS (m/z): 1309.36 $[M-Cl]^+$. Anal. Calcd for $C_{86}H_{76}Cl_2N_2O_2Pd$: C, 76.69; H, 5.69; N, 2.08; Found: C, 76.93; H, 5.57; N, 2.06.

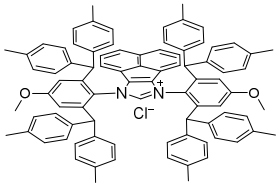


Complex 2: A mixture of **L7** (1.17 g, 1 mmol) and (DME)$NiBr_2$ (0.31 g, 1.0 mmol) (DME = 1,2-dimethoxyethane) were stirred in 10 mL of CH_2Cl_2 overnight at room temperature. The solvent was removed, and the resulting powder was washed with hexane (3×10 mL) and dried under vacuum to obtain a red solid (1.16 g, 83.9%). A single crystal of complex **2** was obtained by layering hexane onto the CH_2Cl_2 solution at room temperature. As a result of their paramagnetic nature, this complex could not be characterized by ^{1}H and ^{13}C NMR. MALDI-TOF-MS (m/z): 1307.33 $[M-Br]^+$. Anal. Calcd for $C_{86}H_{76}Br_2N_2O_2Ni$: C, 74.42; H, 5.52; N, 2.02; Found: C, 74.66; H, 5.47; N, 1.99.

Procedure for the Synthesis of the Imidazolium Chloride Salts.

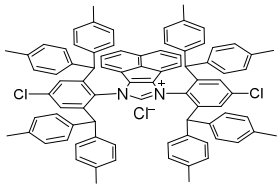


S1: L1 (1.32 mmol) and methoxy(methyl)chloride (65.9 mmol) were added to a nitrogen-flushed thick-walled reaction vessel. The vessel was sealed and the reaction mixture was stirred at 100℃ for 16h, during this time the mixture changed from a murky brown suspension to a clear red solution. Cooling of the reaction mixture to ambient temperature and the subsequent addition of 20 ml of diethyl ether resulted in the formation of a yellow precipitate. The resulting solid was filtered off and washed with 50 ml of diethyl ether and dried in vacuo to afford **S1**(1.16 g, 74.1%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.44 (s, 1H, N-C*H*), 7.79 (d, *J* = 8.2 Hz, 2H, aryl-*H*), 7.10 (t, *J* = 7.6 Hz, 2H, aryl-*H*), 7.00 (s, 4H, aryl-*H*), 6.90 (d, *J* = 6.5 Hz, 8H, aryl-*H*), 6.82 (d, *J* = 6.2 Hz, 8H, aryl-*H*), 6.52 (s, 16H, aryl-*H*), 6.28 (d, *J* = 6.9 Hz, 2H, aryl-*H*), 5.12 (s, 4H, C*H*Ar$_2$), 2.32 (s, 6H, Ar-C*H*$_3$), 2.22 (s, 12H, CH(Ph*Me*)$_2$), 1.96 (s, 12H, CH(Ph*Me*)$_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.09, 141.27, 139.31, 138.57, 138.19, 137.88, 136.60, 136.35, 130.69, 129.51, 129.33, 129.20, 129.06, 129.00, 128.55, 126.77, 123.68, 121.10, 51.00 (*C*HAr$_2$), 22.01 (Ar-*C*H$_3$), 21.03 (CH(Ph*Me*)$_2$), 20.73 (CH(Ph*Me*)$_2$). ESI-MS (m/z): calcd for $C_{87}H_{77}N_2$: 1149.6081, found: 1149.6082 $[M-Cl^-]^+$.



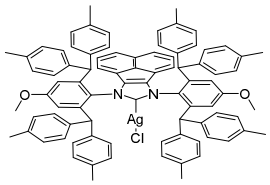
S2: Using the same procedure as for the synthesis of **S1**, **S2** was obtained as a yellow powder (1.44 g, 89.5%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.47 (s, 1H, N-C*H*), 7.79 (d, *J* = 8.1 Hz, 2H, aryl-*H*), 7.12 (t, *J* = 7.4 Hz, 2H, aryl-*H*), 6.89 (broad peak, 16H, aryl-*H*), 6.69 (s, 4H, aryl-*H*), 6.53 (s, 16H, aryl-*H*), 6.32

(d, J = 6.7 Hz, 2H, aryl-*H*), 5.12 (s, 4H, C*H*Ar$_2$), 3.66 (s, 6H, OC*H*$_3$), 2.22 (s, 12H, CH(Ph*M*e)$_2$), 1.96 (s, 12H, CH(Ph*M*e)$_2$). ^{13}C NMR (126 MHz, CDCl$_3$) δ 161.23 (*C*-O), 143.29, 138.36, 137.72, 136.70, 136.46, 129.52, 129.38, 129.19, 129.14, 129.09, 129.01, 128.56, 126.79, 124.16, 123.67, 121.15, 115.52, 55.57 (O*C*H$_3$), 51.22 (*C*HAr$_2$), 21.05 (CH(Ph*M*e)$_2$), 20.74 (CH(Ph*M*e)$_2$). ESI-MS (m/z): calcd for $C_{87}H_{77}N_2O_2$: 1181.5980, found: 1181.5978 [M-Cl$^-$]$^+$.

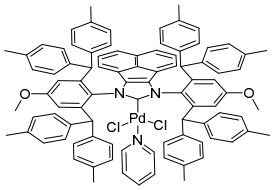


S3: Using the same procedure as for the synthesis of **S1**, **S3** was obtained as a yellow powder (1.03 g, 65.2%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 13.17 (s, 1H, N-C*H*), 7.68 (d, J = 8.2 Hz, 2H, aryl-*H*), 7.16 (s, 4H, aryl-*H*), 7.10 – 6.96 (m, 17H, aryl-*H*), 6.48 – 6.41 (m, 17H, aryl-*H*), 6.22 (d, J = 6.9 Hz, 2H, aryl-*H*), 5.25 (s, 4H, C*H*Ar$_2$), 2.18 (s, 12H, CH(Ph*M*e)$_2$), 1.93 (s, 12H, CH(Ph*M*e)$_2$). ^{13}C NMR (126 MHz, CDCl$_3$) δ 144.08, 138.18, 137.86, 137.75, 137.36, 136.55, 136.53, 130.36, 130.22, 129.57, 129.36, 129.21, 129.03, 128.65, 128.42, 126.58, 123.60, 121.58, 51.07 (*C*HAr$_2$), 21.11 (CH(Ph*M*e)$_2$), 20.79 (CH(Ph*M*e)$_2$). ESI-MS (m/z): calcd for $C_{85}H_{71}Cl_2N_2$: 1189.4989, found: 1189.4974 [M-Cl$^-$]$^+$.

Procedure for the Synthesis of N-heterocyclic Carbene (NHC) Complexes.



Complex 3: **S2** (254 mg, 0.21 mmol) was dissolved in CH_2Cl_2 (5 mL) and Ag_2O (23.2 mg, 0.1 mmol) was added. The mixture was sheltered from light and stirred at 25℃ for 16 h.The solution was filtered on a pad of celite and evaporated to give **3** as a yellow solid (70%, 189 mg). Single crystal of **3** was obtained by layering diethyl ether onto the CH_2Cl_2 solution at room temperature. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 (d, J = 7.8 Hz, 2H, aryl-*H*), 7.07 – 6.97 (m, 2H, aryl-*H*), 6.83 (d, J = 6.9 Hz, 7H, aryl-*H*), 6.76 (d, J = 7.2 Hz, 9H, aryl-*H*), 6.67 (s, 12H, aryl-*H*), 6.55 (d, J = 6.5 Hz, 8H, aryl-*H*), 6.19 (d, J = 6.4 Hz, 2H, aryl-*H*), 5.26 (s, 4H, C*H*Ar$_2$), 3.65 (s, 6H, OC*H*$_3$), 2.21 (s, 12H, CH(Ph*M*e)$_2$), 1.97 (s, 12H, CH(Ph*M*e)$_2$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 159.96 (*C*-O), 143.75, 139.56, 139.48, 139.20, 139.10, 139.09, 135.88, 135.73, 129.77, 129.55, 129.31, 129.16, 129.10, 129.00, 128.73, 128.53, 126.89, 126.18, 123.76, 121.77, 114.91, 55.28 (O*C*H$_3$), 50.86 (*C*HAr$_2$), 21.08 (CH(Ph*M*e)$_2$), 20.73 (CH(Ph*M*e)$_2$). MALDI-TOF-MS (m/z): 1287.27 [M-Cl]$^+$. Anal. Calcd for $C_{87}H_{76}AgClN_2O_2$: C, 78.87; H, 5.78; N, 2.11; Found: C, 78.99; H, 5.77; N, 2.16.



Complex 4: the mixture of $PdCl_2$ (44 mg, 0.25 mmol), **S2** (305 mg, 0.25 mmol), K_2CO_3 (344 mg, 2.5 mmol) and pyridine(1.4 mL) was stirred at 80 ^{o}C for 24 h under a nitrogen atmosphere. After cooling to room temperature,10 mL dichloromethane was added, and then the reaction mixture was diluted in CH_2Cl_2, pass through a pad of silica covered with celite, and eluted with CH_2Cl_2. The solvents were removed under reduced pressure to furnish the desired product, which was recrystallized in a CH_2Cl_2/hexane mixture to remove completely the pyridine. The pure palladium complex was finally obtained after filtration and drying under a high vacuum (Yellow solid，Yield: 288 mg, 81%). Single crystal of **4** was obtained by layering hexane onto the CH_2Cl_2 solution at room temperature. ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.25 (s, 2H, aryl-*H*), 7.76 (s, 1H, aryl-*H*), 7.35 (s, 2H, aryl-*H*), 7.14 (s, 10H, aryl-*H*), 6.89 (s, 12H, aryl-*H*), 6.51 (s, 2H, *C*HAr$_2$), 6.37 (d, J = 43.0 Hz, 12H, aryl-*H*), 6.10 (s, 8H, aryl-*H*), 5.64 (s, 2H, *C*HAr$_2$), 3.68 (s, 6H, OC*H*$_3$), 2.22 (s, 12H, CH(Ph*M*e)$_2$), 1.85 (s, 12H, CH(Ph*M*e)$_2$). ^{13}C NMR (101 MHz, CDCl$_3$) δ 158.81 (*C*-O), 157.72, 152.21, 144.39, 142.76, 140.95, 138.76, 138.00, 134.90, 131.25, 130.56, 129.59, 128.39, 127.89, 127.85, 127.37, 125.92, 125.18, 124.32, 124.28, 121.56, 116.41, 55.34 (O*C*H$_3$), 50.48 (*C*HAr$_2$), 21.04 (CH(Ph*M*e)$_2$), 20.81 (CH(Ph*M*e)$_2$). MALDI-TOF-MS (m/z): 1284.31 [M-C_5H_5N-2Cl]$^+$. Anal. Calcd for $C_{92}H_{81}Cl_2N_3O_2Pd$: C, 76.84; H, 5.68; N, 2.92; Found: C, 76.77; H, 5.80; N, 2.96.

Acknowledgment

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Appendix A

CCDC numbers of **L4**, **L5**, **1**, **2**, **3** and **4** are 1583392, 1583395, 1583396, 1583398, 1583400 and 1583401 respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/.

References

[1] G. Van Koten, K. Vrieze, Organomet. Chem. 21 (1982) 151.

[2] V. Rosa, S. A. Carabineiro, T. Aviles, P. T. Gomes, R. Welter, J. M. Campos, M. R. Ribeiro, J. Org. Chem. 693 (2008) 769.

[3] A. J. Arduengo, R. L. Harlow, M. A. Kline, J. Am. Chem. Soc. 113 (1991) 361.

[4] X. B. Lan, Y. W. Li, Y. F. Li, D. S. Shen, Z. F. Ke, F. S. Liu, J. Org. Chem. 82 (2017) 2914.
[5] L. K. Johnson, C. M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414.
[6] L. K. Johnson, S. Mecking, M. Brookhart J. Am. Chem. Soc. 118 (1996) 267.
[7] L. H. Guo, C. L. Chen, Sci. China Chem. 58 (2015) 1663.
[8] L. H. Guo, S. Y. Dai, X. L. Sui, C. L. Chen, ACS Catal. 6 (2016) 428.
[9] L. H. Guo, W. J. Liu, C. L. Chen, Mater. Chem. Front. 1 (2017), 2487.
[10] L. H. Guo, H. Y. Gao, Q. R. Guan, H. B. Hu, J. A. Deng, J. Liu, F. S. Liu, Wu, Q. Organometallics 31 (2012) 6054.
[11] A. M. Kluwer, T. S. Koblenz, T. Jonischkeit, K. Woelk, C. J. Elsevier, J. Am. Chem. Soc. 127 (2005) 15470.
[12] H. Guo, Z. Zheng, F. Yu, S. Ma, A. Holuigue, D. S. Tromp, C. J. Elsevier, Y. Yu, Angew. Chem., Int. Ed. 45 (2006) 4997.
[13] L. Li, P. S. Lopes, V. Rosa, C. A. Figueira, M. A. N. D. A. Lemos, M. T. Duarte, T. Aviles, P. T. Gomes, Dalton Trans. 41 (2012) 5144.
[14] L. Li, P. S. Lopes, C. A. Figueira, C. S. B. Gomes, M. T. Duarte, V. Rosa, C. Fliedel, T. Avilés, P. T. Gomes, Eur. J. Inorg. Chem. 2013 (2013) 1404.
[15] J. S. Ouyang, Y. F. Li, D. S. Shen, Z. F. Ke, F. S. Liu, Dalton Trans. 45 (2016) 14919.
[16] J. L. Rhinehart, L. A. Brown, B. K. Long, J. Am. Chem. Soc. 135 (2013) 16316.
[17] J. L. Rhinehart, N. E. Mitchell, B. K. Long, ACS Catal. 4 (2014) 2501.
[18] S. Y. Dai, X. L. Sui, C. L. Chen, Angew. Chem. Int. Ed. 54 (2015) 9948.
[19] L. H. Guo, C. Zou, S. Y. Dai, C. L. Chen, Polymers 9 (2017) 122.
[20] L. H. Guo, S. Y. Dai, C. L. Chen, Polymers 8 (2016) 37.
[21] B. G. Guillaume, A. S. Maxime, L. S. Anthony, T. Bernard, N. H. R. Joost, E. M. István, Dalton Trans. 39 (2010) 1444.
[22] K. Hasan, E. Zysman-Colman, J. Phys. Org. Chem. 26 (2013) 274.
[23] U. El-Ayaan, A. Paulovicova, S. Yamada, Y. J. Fukuda, Coord. Chem. 56 (2003) 373.
[24] J. Y. Wang, R. Ganguly, Y. X. Li, J. Diaz, H. S. Soo, F. Garcia, Inorg. Chem. 56 (2017) 7811.
[25] N. J. Hill, I. Vargas-Baca, A. H. Cowley, Dalton Trans. (2009) 240.
[26] I. L. Fedushkin, A. A. Skatova, V. A. Chudakova, G. K. Fukin, Angew. Chem. Int. Ed. 42 (2003) 3294.
[27] K. Vasudevan, A. H. Cowley, Chem. Commun. (2007) 3464.
[28] H. Schumann, M. Hummert, A. N. Lukoyanov, V. A. Chudakova, I. L. Fedushkin, Z. Naturforsch. B: Chem. Sci. 62 (2007) 1107.
[29] W. C. Anderson, J. L. Rhinehart, A. G. Tennyson, B. K. Long, J. Am. Chem. Soc. 138 (2016) 774.
[30] W. C. Anderson, B. K. Long, ACS Macro Lett. 5 (2016) 1029.
[31] Q. Ban, J. Zhang, T. L. Liang, C. Redshaw, W. H. J. Sun, Organomet. Chem. 713 (2012) 151.
[32] H. Liu, W. Z. Zhao, X. A. Hao, C. Redshaw, W. Huang, W. H. Sun, Organometallics 30 (2011) 2418.
[33] V. Lodeiro, T. Rosa, G. Avilés, B. Aullon, C. Covelo, Inorg. Chem. 47 (2008) 7734.
[34] J. A. Moore, K. Vasudevan, N. J. Hill, G. Reeske, A. H. Cowley, Chem. Commun. 27 (2006) 2913.
[35] J. A. Deng, H. Y. Gao, F. M. Zhu, Q. Wu, Organometallics 32 (2013) 4507.
[36] X. B. Lan, Y. W. Li, Y. F. Li, D. S. Shen, Z. F. Ke, F. S. Liu, J. Org. Chem. 82 (2017) 2914.
[37] X. B. Lan, F. M. Chen, B. B. Ma, D. S. Shen, F. S. Liu, Organometallics 35 (2016) 3852.
[38] C. J. O'Brien, E. A. B. Kantchev, C. Valente, N. Hadei, G. A. Chass, A. Lough, A. C. Hopkinson, M. G. Organ, Chem. Eur. J. 12 (2006) 4743.
[39] M. G. Organ, S. Calimsiz, M. Sayah, K. H. Hoi, A. J. Lough, Angew. Chem. Int. Ed. 48 (2009) 2383.
[40] A. Chartoire, X. Frogneux, A. Boreux, A. M. Z. Slawin, S. P. Nolan, Organometallics 31 (2012) 6947.
[41] T. Tu, W. W. Fang, J. Jiang, Chem. Commun. 47 (2011) 12358.
[42] T. Tu, Z. M. Sun, W. W. Fang, M. Z. Xu, Y. F. Zhou, Org. Lett. 14 (2012) 4250.
[43] D. Zhang, E. Nadres, M. Brookhart, O. Daugulis, Organometallics 32 (2013) 5136.
[44] K. V. Vasudevan, M. Findlater, A. H. Cowley, Chem. Commun. (2008) 1918.
[45] S. Kong, C. Y. Guo, W. Yang, L. Wang, W. H. Sun, R. Glaser, J. Org. Chem. 725 (2013) 37.

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Highlights

An efficient method to synthesize novel highly sterically hindered acenaphthene-based α-diimine ligands bearing bulky diarylmethyl moiety was achieved. On the basis of this method, novel highly sterically hindered acenaphthene-based α-diimine Pd(II) and Ni(II) complexes and N-heterocyclic carbenes-metal complexes were successfully synthesized.

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