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Novel chiral bisoxazoline ligands with a bipyridinyl backbone: preparation and interesting complexation behavior

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ABSTRACT

Novel C_2-symmetric chiral bisoxazoline ligands with a bipyridinyl backbone were prepared with ease from 3,3′-dicarbomethoxy-2,2′-bipyridine and enantiomerically pure 2-amino alcohols via a corresponding amide as intermediate. Interestingly, when these ligands were coordinated with Pd(II) and Cu(I), different complexation behaviors were found.

The design and development of effective chiral ligands have played a significant role in the advancement of asymmetric catalysis and have attracted a great deal of attention from both academics and industry. Thousands of ligands with various chiral elements have been developed and applied in many catalytic asymmetric reactions to produce enantiomerically pure compounds.[1] Among them, chiral pyridinyl-oxazoline compound is one type of important ligand, which was first prepared by Brunner and co-workers from readily available amino acids.[2] Afterward, these ligands have been found to have widespread use in metal-catalyzed asymmetric reactions, such as cyclopropanation,[3] Friedel–Crafts alkylation,[4] hydrosilylation,[5] aza-Wacker-type cyclization[6], and so on,[7] and extensive efforts have been devoted to the preparation of their efficient structural derivatives.

Most of the earlier pyridinyl-oxazoline ligands possess only the central chirality element in the oxazoline moiety. Within the coordination plane composed of two nitrogen atoms of the pyridine ring and the oxazoline ring and a metal ion, the planes of pyridine and oxazoline rings were involved, and the asymmetric induction is controlled only by the central chirality element in the oxazoline ring.[2–7] Axial chiral oxazoline ligands possess not only the central chirality element in the oxazoline moiety, but also an additional chirality element in the backbone.[8,9] Owing to the introduction of the chiral backbone, there is a possibility that the asymmetric induction by these ligands can be effectively controlled by a combination of the chirality elements in the oxazoline moiety and the backbone. Numbers of C_2-symmetric chiral oxazoline with an axially chiral biaryl backbone have been successfully employed as chiral ligands.[8] However, these axis-fixed ligands require inconvenient diastereomeric separation in their synthetic process, and generally, only one of the diastereomers works effectively in catalytic asymmetric reactions due to the configurational matching-mismatching effect. Our group has developed a series of axis-unfixed chiral oxazoline ligands based on our chelation-induced concept, which could afford only one of the two possible diastereomeric metal complexes during the coordinating process and showed excellent enantioselectivities in several asymmetric catalyses.[9] Herein we introduce a new type of chiral bisoxazoline ligand **1** bearing an axis-unfixed bipyridine backbone and report their preparation and interesting complexation behaviors (Fig. 1).

It was reported that chiral bisoxazoline ligands with a biphenyl backbone could be prepared with 2,2′-biphenyldicarboxylic acid dichloride.[9a–c] Therefore, we thought the chiral 2,2′-bis(oxazolinyl)pyridines ligands **1** could be prepared from 2,2′-bipyridinyl-3,3′-dicarboxylic acid with the same method. However, only a trace product was obtained. Fortunately, we obtained our ligands using 2,2′-bipyridinyl-3,3′-dicarboxylate as the starting material (Scheme 1). Thus, a mixture of 2,2′-bipyridinyl-3,3′-dicarboxylate **2** and aminoalcohol (3 equiv) was heated at 160 °C for 16 h to give the crude hydroxylethylamide **3**. The intermediate **3** was dissolved in dicholoromethane and to this solution $SOCl_2$ (5 equiv) was slowly added at 0 °C. After refluxing for 2 h, the reaction mixture was evaporated in vacuo to give crude chloroethylamide **4**. The crude **4** was dissolved in methanol and to this solution sodium hydroxide (3 equiv) was slowly added. After refluxing for 6 h, ligands **1a–d** were afforded in overall yields from 32% to 61%.[10]

It has been pointed out that enantiomerically stable biaryls require at least three *ortho*-substituents to avoid the racemization due to the rotation around the internal bond of the biaryls.[11] As

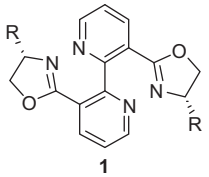

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Figure 1. The structure of the ligands **1**.

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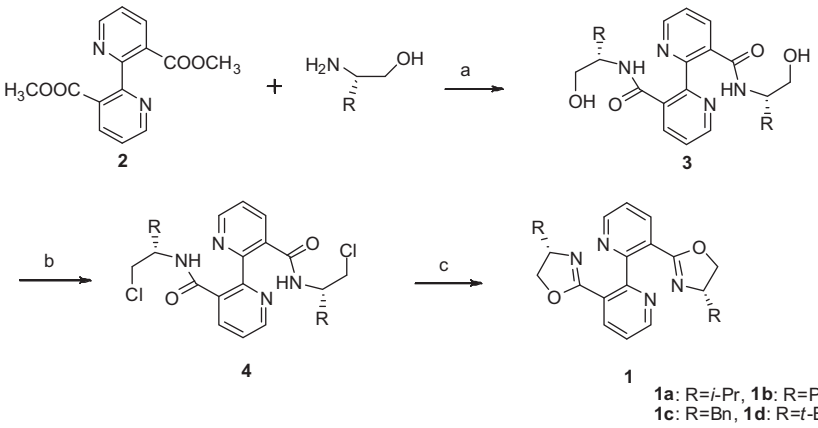
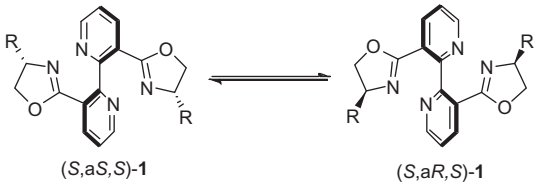


Scheme 1. Reagents and conditions: (a) 160 °C; (b) $SOCl_2$, CH_2Cl_2, reflux; (c) NaOH, MeOH, reflux (32–61%, overall yields).

same as the bisoxazoline ligands with biphenyl backbone,[9] the ligand **1** has only two *ortho*-substituents on the bipyridinyl backbone. So, two diastereomers, (*S, aS, S*)-**1** and (*S, aR, S*)-**1**, should be present in equilibrium in solution due to the rotation around the internal bond of the bipyridinyl backbone (Scheme 2). However, the two diastereomers of all the ligands were not observed by ^1H NMR determination in $CDCl_3$ and CD_3OD even at −60 °C. This result showed that for this type of ligand, the activation barrier to axial torsion is very small and the interconversion between the two diastereomers is very fast.

Different from the bisoxazoline ligands with biphenyl backbone, there may be two kinds of complexation behaviors when these ligands coordinate with different metal ions. The first one is that these ligands form pyridine-oxazoline-coordinated mono- or di-metal complexes **5** or **6** upon complexation with 1 or 2 equiv of metal ion (Fig. 2). The second one is that these ligands afford only one type of bisoxazoline-coordinated complex **7** upon complexation with 1 equiv of metal ion and the two pyridine rings do not coordinate to the metal ion (Fig. 2). The complexes **7** could produce a maximal or minimal dihedral angle because only lone pair electrons of the nitrogen atoms of the pyridine rings could affect the rotation around the internal bond of the bipyridine. So these ligands could match more reactions than that with a biphenyl backbone. However, as same as the oxazoline ligands with biphenyl backbone,[9] either of the two different complexation behaviors of these ligands may afford two diastereomer complexes, and one may form in greater preference to the other due to the difference in steric hindrance between them. If the ratio of the two diastereomer complexes is large enough, it may be possible to utilize the complex as a chiral catalyst in asymmetric reactions.

Then complexation behaviors of these ligands with different metal ions were investigated. At first, the complexation of ligand **1a** with Cu(I) in $CDCl_3$ was examined (Fig. 3, from top to bottom, the proportions of CuBr and **1a** are 0:1.0, 0.3:1.0, 0.5:1.0, 0.7:1.0, and 1.0:1.0). Upon treating **1a** with different portions of CuBr in $CDCl_3$, most of the proton signals of the ligand shifted gradually



Scheme 2. The equilibrium of the two diasteromers of the ligands.

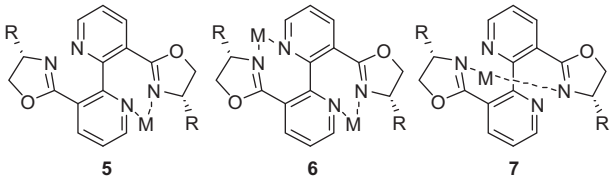


Figure 2. The possible complexes of ligands **1** with metal ions.

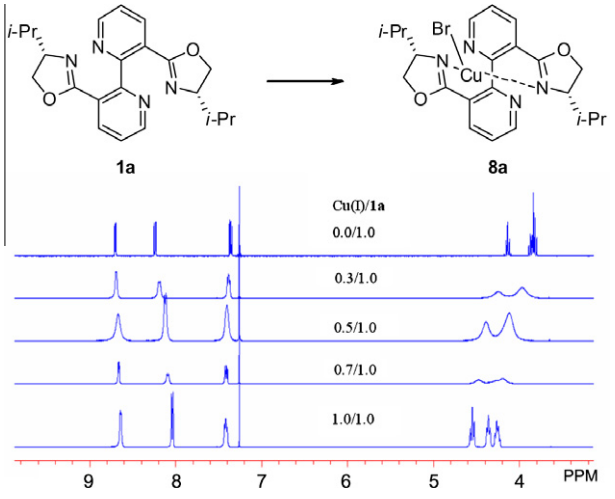


Figure 3. The complexation of ligands **1a** with CuBr.

to downfield in proportion to the amount of CuBr, indicating the rapid equilibrium between the free ligand and the ligand-CuBr complex on the NMR time-scale. However, when more than 1 equiv of CuBr was added, further downfield shift of the proton signals was not observed. This result showed the formation of a 1:1 *N,N*-chelating complex **8a** in solution, of which the coordination plane is composed of two nitrogen atoms of the two oxazoline rings and a Cu(I) ion. Ligands **1b**–**1d** showed a similar complexation behavior to that of **1a** toward CuBr to afford **8b–8d**, respectively.[12] When changing CuBr to CuOTf·0.5C_6H_6 and CuCl, similar complexation behaviors were observed.[13]

Since a metal ion has its own peculiar atomic radius and coordination structure, the complexation behavior of ligand **1a** with Pd(II) in CD_2Cl_2 was also examined. It was found that the complexation behavior of **1a** toward Pd(II) was quite different from that toward Cu(I) (Fig. 4, from top to bottom, the proportions of

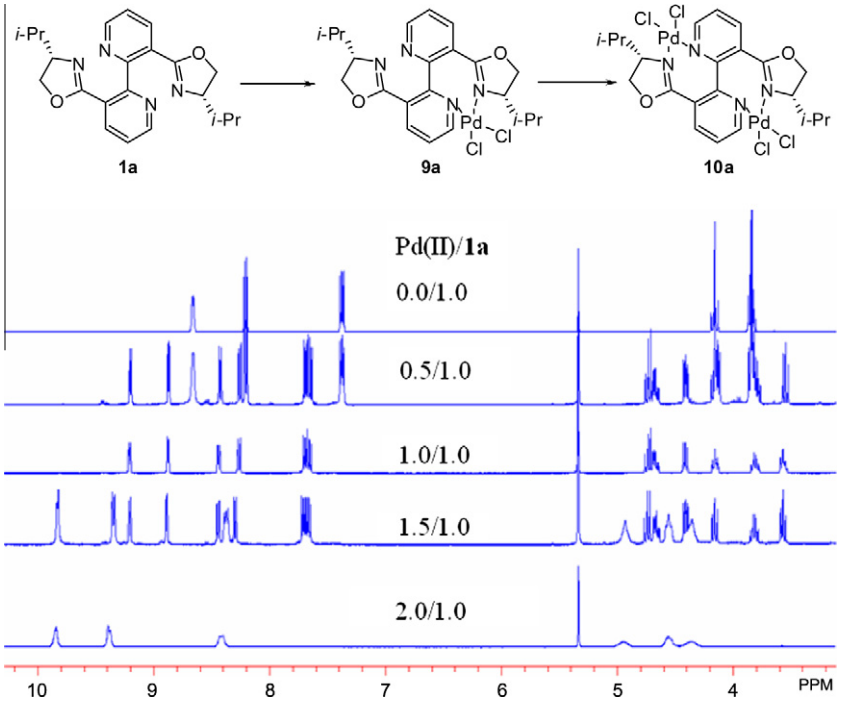


Figure 4. The complexation of ligands **1a** with $PdCl_2(CH_3CN)_2$.

$PdCl_2(MeCN)_2$ and the ligand are 0:1.0, 0.5:1.0, 1.0:1.0, 1.5:1.0, and 2.0:1.0). Upon the addition of 0.5 equiv of $PdCl_2(MeCN)_2$ to **1a** dissolved in CD_2Cl_2, the ^1H NMR spectrum showed complicated signals due to a mixture of resultant substance along with **1a**. When an additional 0.5 equiv of $PdCl_2(MeCN)_2$ was added, only one set of signals was observed in the ^1H NMR spectrum. This complex was assigned as **9a**, of which the coordination plane is composed of two nitrogen atoms of the pyridine ring and the oxazoline ring and a Pd(II) ion. When an additional 0.5 equiv of $PdCl_2(MeCN)_2$ was added, the ^1H NMR spectrum showed complicated signals due to another mixture of resultant substance along with **9a**. When 0.5 equiv of $PdCl_2(MeCN)_2$ was added again, only one set of signals was observed in the ^1H NMR spectrum, which was assigned as a C_2-symmertic dimetal complex **10a**. Further addition of $PdCl_2(MeCN)_2$ did not affect the ^1H NMR spectrum and the complex deposited quickly. Ligand **1d** bearing *t*-Bu on the oxazoline ring showed a similar complexation behavior to that of **1a** toward $PdCl_2(MeCN)_2$ to afford **9d** and **10d,** respectively. But ligand **1b** and **1c** only afforded **9b** and **9c**, respectively, and when additional 0.5 equiv of $PdCl_2(MeCN)_2$ was added, the ^1H NMR spectrum showed no change albeit with some deposition. When 0.5 equiv of $PdCl_2(MeCN)_2$ was added again, further deposition was found and the ^1H NMR spectrum of the solution showed that the proton signals of **9b** and **9c** disappeared, showing that all the ligands formed insoluble dimetal complexes **10b** and **10c**, respectively.[14] When changing the Cl anion to acetate, similar complexation behavior was observed.[15]

Then the circular dichroism (CD) spectra of the complexes **8a** and **9a** were measured in CH_3OH solution (Fig. 5). The cotton effects demonstrated that the induction of axial chirality occurred when the ligand was coordinated to the CuBr or $PdCl_2(MeCN)_2$.[16]

The absolute configuration of the complex **9d** was assigned to (*S*, a*R*, *S*)-**9d** by the NOESY experiment, because the NOE was observed between the methyl protons of oxazolinyl tertiary butyl and 6-proton of the pyridinyl group, and no obvious NOE was observed between the methyl protons of the oxazolinyl tertiary butyl and 4-proton of the pyridinyl group (Fig. 6). As for the absolute

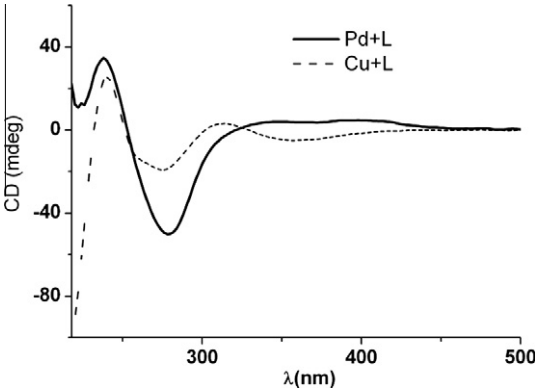


Figure 5. The CD spectra of the complexes **8a** and **9a**.

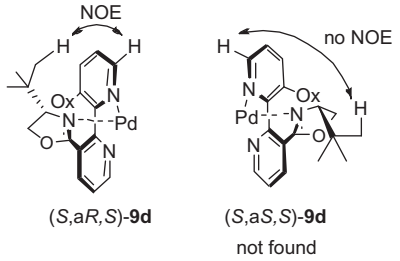


Figure 6. The two diasteromers of the complex **9d**.

configuration of the complex **10d**, we reasoned that it should be (*S*, a*R*, *S*)-**10d** because the torsion direction is the same as **9d**.

However, for the complex **8d**, no obvious NOEs were observed between the methyl protons of the oxazolinyl tertiary butyl and other protons, regardless of 6-proton of the pyridinyl group or 4-proton of the pyridinyl group. Because the complexation behavior of ligands **1** with Cu(I) is the same as that of bisoxazolines ligands with biphenyl backbone,[9a–c] we reasoned that the absolute config-

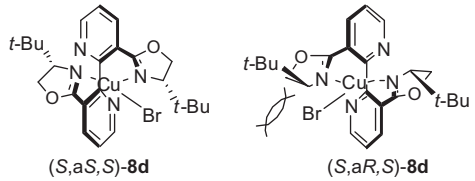


Figure 7. The two diasteromers of the complex **8d**.

uration of the complex **8d** should be (*S*, a*S*, *S*)-**8d** (Fig. 7). This complex has a trigonal planar coordination structure, in which the two planes of the oxazoline rings are inclined to the N-Cu(I)-N coordination plane by the introduction of the bipyridinyl backbone in the molecule. For (*S*, a*R*, *S*)-**8d**, the two substituents on the oxazoline rings are almost in the coordination plane, while for (*S*, a*S*, *S*)-**8d**, the two substituents are perpendicular to the plane in opposite directions and almost out of plane. Therefore, the steric repulsion between the substituents on the oxazoline rings and the Br coordinated to the Cu(I) in (*S*, a*S*, *S*)-**8d** is much smaller than that in (*S*, a*R*, *S*)-**8d**, resulting the formation of (*S*, a*S*, *S*)-**8d** other than (*S*, a*R*, *S*)-**8d**.

In summary, novel C_2-symmertic chiral bisoxazoline ligands with a bipyridinyl backbone were prepared with ease, and the complexation behaviors of these ligands toward Pd(II) and Cu(I) were studied. It was found that these ligands afforded pyridine-oxazoline-coordinated mono- or di-metal complexes upon complexation with $PdCl_2(MeCN)_2$. The axial chirality of these complexes was assigned as *aR*. However, upon complexation with CuBr, these ligands afforded only one type of bisoxazoline-coordinated complexes, the axial chirality of which was assigned as *aS*. Further study on the application of these ligands to asymmetric reactions is in progress in our laboratory.

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10. *Characterization data of the ligand* **1a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (dd, J = 2.0 Hz, 4.8 Hz, 2H), 8.24 (dd, J = 2.0 Hz, 8.0 Hz, 2H), 7.36 (dd, J = 4.8 Hz, 8.0 Hz, 2H), 4.15–4.11 (m, 2H), 3.87–3.79 (m, 4H), 1.64–1.59 (m, 2H), 0.78 (t, J = 6.0 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8, 158.4, 150.4, 137.4, 123.6, 122.6, 73.1, 70.6, 33.0, 18.9, 18.5; HR-MS calcd for $C_{22}H_{26}N_4O_2$, 378.2056, found 378.2059. *Characterization data of the ligand* **1b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 2H), 8.36–8.32 (m, 2H), 7.42–7.35 (m, 2H), 7.32–7.22 (m, 6H), 7.20–7.16 (m, 4H), 5.24 (dd, J = 8.4 Hz, 9.6 Hz, 2H), 4.54 (dd, J = 8.4 Hz, 9.6 Hz, 2H), 3.96 (t, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 150.7, 142.3, 138.0, 128.8, 127.7, 126.9, 122.9, 122.8, 75.3, 70.4; HR-MS calcd for $C_{28}H_{22}N_4O_2$, 446.1743, found 446.1735. *Characterization data of the ligand* **1c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (dd, J = 2.0 Hz, 5.0 Hz, 2H), 8.23 (dd, J = 2.0 Hz, 8.0 Hz, 2H), 7.37 (dd, J = 5.0 Hz, 8.0 Hz, 2H), 7.29–7.23 (m, 4H), 7.22–7.17 (m, 2H), 7.13–7.10 (m, 4H), 4.42–4.34 (m, 2H), 4.08 (t, J = 8.8 Hz, 2H), 3.87 (dd, J = 7.4 Hz, 8.0 Hz, 2H), 3.02–2.95 (m, 2H), 2.59–2.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 158.1, 150.7, 138.2, 137.6, 129.4, 128.7, 126.6, 123.8, 122.7, 72.3, 68.3, 41.6; HR-MS calcd for $C_{30}H_{26}N_4O_2$, 474.2056, found 474.2059. *Characterization data of the ligand* **1d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (dd, J = 2.0 Hz, 4.8 Hz, 2H), 8.25 (dd, J = 2.0 Hz, 8.0 Hz, 2H), 7.35 (dd, J = 4.8 Hz, 8.0 Hz, 2H), 4.11–4.05 (m, 2H), 3.92–3.78 (m, 4H), 0.72 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 158.7, 150.3, 137.3, 123.4, 122.5, 76.7, 68.7, 33.9, 26.0; HR-MS calcd for $C_{24}H_{30}N_4O_2$, 406.2369, found 406.2372.
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12. *Characterization data of the complex* **8a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68–8.61 (m, 2H), 8.04 (d, J = 8.0 Hz, 2H), 7.45–7.38 (m, 2H), 4.58–4.52 (m, 2H), 4.40–4.33 (m, 2H), 4.30–4.22 (m, 2H), 1.71–1.61 (m, 2H), 0.60 (d, J = 8.0 Hz, 6H), 0.51(d, J = 8.0 Hz, 6H); HR-MS calcd for $C_{22}H_{26}CuN_4O_2$ ([M−Br]$^+$), 441.1352, found 441.1351. *Characterization data of the complex* **8b**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (br s, 2H), 7.97 (d, J = 8.0 Hz, 2H), 7.34 (br s, 2H), 7.20–7.10 (m, 6H), 6.96–6.91 (m, 4H), 5.54–5.41 (m, 2H), 4.90–4.82 (m, 2H), 4.64–4.57 (m, 2H); HR-MS calcd for $C_{28}H_{22}CuN_4O_2$ ([M−Br]$^+$), 509.1039, found 509.1048. *Characterization data of the complex* **8c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (br s, 2H), 8.04 (d, J = 8.0 Hz, 2H), 7.45(br s, 2H), 7.26–7.15 (m, 6H), 7.09–7.05 (m, 4H), 4.62(br s, 2H), 4.52–4.36 (m, 4H), 2.86–2.75 (m, 2H), 2.06–1.92 (m, 2H); HR-MS calcd for $C_{30}H_{26}CuN_4O_2$ ([M−Br]$^+$), 537.1352, found 537.1364. *Characterization data of the complex* **8d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (br s, 2H), 8.11 (d, J = 8.0 Hz, 2H), 7.43(br s, 2H), 4.54–4.44 (m, 4H), 4.32–4.25 (m, 2H), 0.64 (s, 18H); HR-MS calcd for $C_{24}H_{30}CuN_4O_2$ ([M−Br]$^+$), 469.1665, found 469.1672.
13. *Characterization data of the complex of ligand* ***1c*** *with CuOTf·0.5C_6H_6*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (br s, 2H), 8.24 (br s, 2H), 7.42–7.00 (m, 12H), 4.40 (br s, 2H), 4.00 (br s, 2H), 3.81 (br s, 2H), 2.97 (br s, 2H), 2.52 (br s, 2H); HR-MS calcd for $C_{30}H_{26}CuN_4O_2$ ([M−OTf]$^+$), 537.1352, found, 537.1356. *Characterization data of the complex of ligand* ***1c*** *with CuCl*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (br s, 2H), 8.06 (br s, 2H), 7.48–7.00 (m, 12H), 4.70–4.30 (m, 6H), 2.79 (br s, 2H), 2.05 (br s, 2H); HR-MS calcd for $C_{30}H_{26}CuN_4O_2$ ([M−Cl]$^+$), 537.1352, found, 537.1351.
14. *Characterization data of the complex* **9a**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.19 (dd, J = 6.0 Hz, 4.0 Hz, 1H), 8.87 (dd, J = 6.0 Hz, 4.0 Hz, 1H), 8.43 (dd, J = 8.0 Hz, 6.0 Hz, 1H), 8.29 (dd, J = 8.0 Hz, 6.0 Hz, 1H), 7.63–7.71 (m, 2H), 4.66–4.76 (m, 2H), 4.38–4.43 (m, 1H), 4.12–4.18 (m, 1H), 3.79–3.82 (m, 1H), 3.54–3.59 (m, 1H), 2.39–2.44 (m, 1H), 1.65–1.73 (m, 1H), 0.87 (d, J = 7.2 Hz, 3H), 0.84 (d, J = 7.2 Hz, 6H), 0.58 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 164.8, 160.0, 156.8, 153.9, 153.3, 152.6, 141.3, 137.7, 129.4, 125.8, 124.7, 122.0, 73.3, 72.0, 71.6, 70.1, 32.6, 30.8, 18.7, 18.3, 17.8, 15.6; HR-MS calcd for $C_{24}H_{29}ClN_5O_2Pd$ ([M−Cl+CH_3CN]$^+$), 560.1045, found 560.1081. *Characterization data of the complex* **9b**: ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.91 (dd, J = 6.0 Hz, 4.0 Hz, 1H), 8.57 (dd, J = 6.0 Hz, 4.0 Hz, 1H), 8.47 (dd, J = 8.0 Hz, 6.0 Hz, 1H), 8.35 (dd, J = 8.0 Hz, 6.0 Hz, 1H), 7.70 (dd, J = 8.0 Hz, 4.0 Hz, 1H), 7.45–7.26 (m, 9H), 7.03–6.99 (m, 2H), 5.71–5.65 (m, 1H), 5.19–5.09 (m, 2H), 4.71–4.65 (m, 1H), 4.57–4.51 (m, 1H), 3.69–3.63 (m, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 164.5, 162.0, 155.9, 154.1, 153.3, 152.8, 141.7, 141.3, 138.7, 137.8,

129.6, 129.3, 129.1, 129.0, 128.7, 128.0, 127.1, 126.9, 126.8, 125.6, 124.9, 121.7, 77.3, 76.3, 70.6, 68.8; HR-MS calcd for $C_{30}H_{25}ClN_5O_2Pd$ ($[M-Cl+CH_3CN]^+$), 628.0732, found 628.0769. *Characterization data of the complex* **9c**: ^1H NMR (400 MHz, CD_2Cl_2): δ 9.02 (dd, J = 6.0 Hz, 4.0 Hz, 1H), 8.76 (dd, J = 6.0 Hz, 4.0 Hz, 1H), 8.40 (dd, J = 8.0 Hz, 6.0 Hz, 1H), 8.22 (dd, J = 8.0 Hz, 6.0 Hz, 1H), 7.64–7.58 (m, 2H), 7.32–7.26 (m, 6H), 7.17–7.13 (m, 2H), 7.12–7.08 (m, 2H), 5.08–5.04 (m, 1H), 4.75–4.69 (m, 1H), 4.45–4.40 (m, 1H), 4.32–4.25 (m, 1H), 4.20–4.14 (m, 1H), 3.61–3.54 (m, 2H), 2.95–2.88 (m, 1H), 2.79–2.65 (m, 2H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 165.2, 160.8, 156.6, 154.2, 153.1, 152.5, 141.1, 137.9, 137.8, 135.5, 129.6, 129.5, 129.3, 129.1, 128.6, 127.4, 126.7, 125.8, 124.5, 121.7, 74.7, 73.1, 68.5, 65.8, 41.1, 40.4; HR-MS calcd for $C_{32}H_{29}ClN_5O_2Pd$ ($[M-Cl+CH_3CN]^+$), 656.1045, found 656.1064. *Characterization data of the complex* **9d**: ^1H NMR (400 MHz, CD_2Cl_2): δ 9.17 (dd, J = 6.0 Hz, 4.0 Hz, 1H), 8.85 (dd, J = 6.0 Hz, 4.0 Hz, 1H), 8.45 (dd, J = 8.0 Hz, 6.0 Hz, 1H), 8.33 (dd, J = 8.0 Hz, 6.0 Hz, 1H), 7.73–7.66 (m, 2H), 4.75–4.69 (m, 1H), 4.55–4.45 (m, 2H), 4.10–4.05 (m, 1H), 3.78–3.72 (m, 1H), 3.70–3.64 (m, 1H), 0.95 (s, 9H), 0.79 (s, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 165.5, 159.8, 157.3, 153.8, 153.7, 152.7, 141.2, 137.9, 129.0, 125.8, 124.6, 122.1, 76.9, 73.9, 72.3, 69.9, 34.0, 33.7, 25.8, 25.7; HR-MS calcd for $C_{26}H_{33}ClN_5O_2Pd$ ($[M-Cl+CH_3CN]^+$), 588.1358, found 588.1382.

15. *Characterization data of the complex of ligand* ***1c*** *with Pd(OAc)$_2$*: ^1H NMR (400 MHz, CD_2Cl_2): δ 9.20 (dd, J = 6.0 Hz, 4.0 Hz, 1H), 8.81(dd, J = 6.0 Hz, 4.0 Hz, 1H), 8.35 (dd, J = 8.0 Hz, 6.0 Hz, 1H), 8.25 (dd, J = 8.0 Hz, 6.0 Hz, 1H), 7.68–7.64 (m, 1H), 7.60–7.55 (m, 1H), 7.32–7.24 (m, 6H), 7.19–7.15 (m, 2H), 7.10–7.07 (m, 2H), 4.63–4.58 (m, 1H), 4.45–4.25 (m, 2H), 4.18–4.13 (m, 1H), 3.80–3.75 (m, 1H), 3.60–3.54 (m, 1H), 2.98–2.92 (m, 1H), 2.78–2.72 (m, 1H), 2.64–2.55 (m, 2H), 1.88 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 177.5, 177.4, 165.9, 161.1, 157.2, 153.7, 153.0, 152.2, 140.9, 138.0, 137.9, 135.7, 129.6, 129.4, 129.3, 129.0, 128.6, 127.3, 126.7, 125.5, 124.4, 122.2, 74.1, 73.2, 68.5, 66.3, 41.3, 40.2, 22.8, 22.7; HR-MS calcd for $C_{32}H_{29}N_4O_4Pd$ ($[M-AcO]^+$), 639.1224, found 639.1326.
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