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Chiral Molecular Squares Based on Angular Bipyridines: Self-Assembly, Characterization, and Photophysical Properties

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Chiral molecular squares **1**–**12** based on $[M(dppe)]^{2+}$ metallocorners (M = Pd or Pt, and dppe = bis(diphenylphosphino)ethane) and new angular bipyridine bridging ligands derived from the 1,1′-binaphthyl framework were readily assembled and characterized by a variety of techniques including infrared, UV–vis, circular dichroism (CD), and NMR spectroscopy, and ESI mass spectrometry. All these chiral metallocycles are highly luminescent in solution at room temperature with quantum efficiency of 0.06–0.63. Interestingly, when equal molar enantiopure molecular squares of opposite handedness were mixed in solution, a new *meso* dimeric metallocycle with C_2 symmetry formed. This result indicates the lability of the M–pyridyl bonds in these metallocycles, which may hinder their applications in many enantioselective processes.

Introduction

Various biomolecules utilize a large number of sophisticated chemical interactions to direct the assembly of higher-ordered multicomponent systems that retain the structural and stereochemical nature of the subunits.[1] Interestingly, many biochemical functions that are critical to the biological systems can only be carried out by these self-assembled multicomponent systems, as exemplified by remarkable functions performed by processive multiprotein systems such as trimeric λ-exonuclease and much larger hexameric helicases.[1] Over the past decade, chemists have designed numerous artificial self-organized systems based on metal−ligand coordination.[2] Metallosupramolecular systems with interesting architectures such as triangles,[3] squares,[4] rectangles,[5] and higher polygons[6] can be readily obtained via such a metal coordination-directed self-assembly process. Our work focuses on the construction of chiral metallosupramolecular systems with the hope of utilizing the enzyme-like chiral cavities and functionalities for enantioselective processes.[3a,4a]

There are three general synthetic pathways to the construction of chiral metallocycles, namely (1) use of chiral auxiliary chelating ligands which will lead to chiral metal-containing building units (metallocorners);[7] (2) use of intrinsically chiral metallocorners owing to the specific arrangement of achiral components around the metal centers;[8] and (3) use of chiral bridging ligands.[3a,4a,9] We envisage that the third approach

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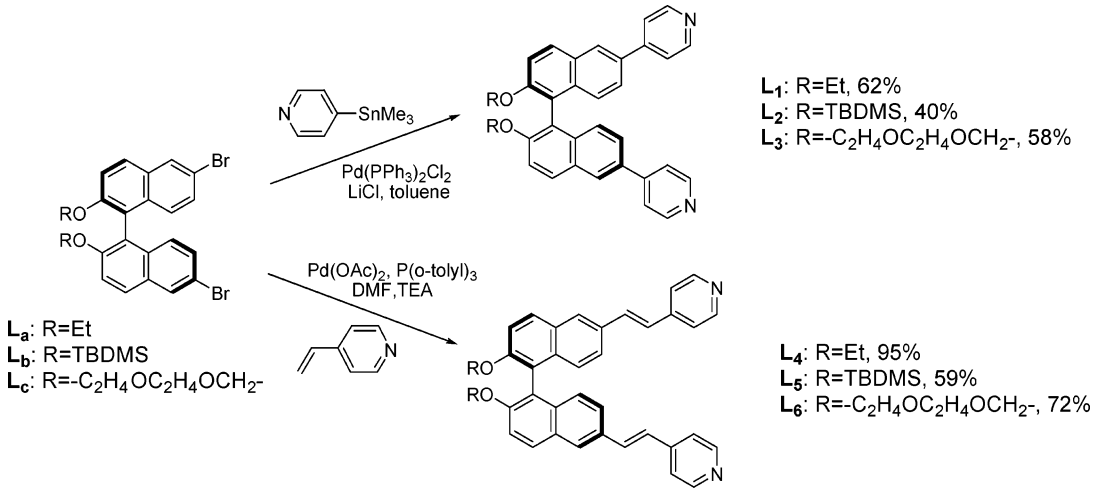
Scheme 1



is amenable to synthetic manipulations and thus the most versatile, and should allow the incorporation of novel functionalities into the final metallocyclic assemblies. In our previous papers, we have demonstrated the construction of chiral metallocycles based on atropisomeric linear bridging ligands and angular metallocorners and their utility in enantioselective sensing and asymmetric catalysis.[3a,4a] We wish to describe here the assembly of chiral molecular squares based on more flexible atropisomeric angular bridging ligands and angular metallocorners.[10] Specifically, a family of chiral angular bipyridines with various functionalities have been derived from readily available BINOL and combined with chelating phosphine-capped Pd(II) and Pt(II) centers to generate highly luminescent chiral molecular squares. We have also characterized these chiral molecular squares with a variety of techniques including NMR, IR, UV, mass spectrometry, and CD spectroscopy. The reassembly process of these chiral molecular squares (upon the mixing of molecular squares of opposite hands) has also been investigated by NMR spectroscopy.

Results and Discussion

1. Synthesis and Characterization. The chiral bridging ligands $\mathbf{L_{1-3}}$ were synthesized by Pd-catalyzed Stille coupling reactions between known enantiopure 6,6′-dibromo-1,1′-binaphthyl derivatives $\mathbf{L_{a-c}}$[11−13] and 4-trimethylstannylpyridine in 40−62% yields, while $\mathbf{L_{4-6}}$ were synthesized by Pd-catalyzed Heck coupling reactions between $\mathbf{L_{a-c}}$ and 4-vinylpyridine in 59−95% yields (Scheme 1). The bisphosphine-coordinated Pd(II) and Pt(II) triflates, M(dppe)$(OTf)_2$ (M = Pd, Pt; dppe = 1,2-bis(diphenylphosphino)ethane), were prepared by the modified published procedures.[14] Enantiopure metallocycles **1**−**12** were prepared in very high isolated yields by treating equal molar M(dppe)$(OTf)_2$ (M = Pd or Pt) and enantiopure bridging ligands $\mathbf{L_{1-6}}$ in CH_2Cl_2 (Scheme 2).

Enantiopure metallocycles **1**−**12** were characterized by a variety of analytical techniques including infrared, UV−vis, circular dichroism (CD), and NMR spectroscopy, and ESI mass spectrometry. Their respective ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra which show a single ligand environment are diagnostic for their highly symmetrical cyclic structure. For example, ^{1}H NMR spectroscopic data of **1**−**12** show a set of peaks assignable to the α and *β* protons in the pyridine rings, a set of peaks in aromatic region originating from a single binaphthyl moiety, a set of complicated aromatic resonances for the phenyl groups of the dppe ligands, and one set of peaks originating from the methylene protons of the dppe ligand (Figure 1). In the cases of crown-ether-containing metallocycles, the ^{1}H NMR spectra also exhibit a set of peaks originating from C_2 symmetric crown-ether moieties. Interestingly, the α protons of the pyridyl rings have significantly shifted downfield, consistent with the coordination of the pyridyl group to the metal centers. In contrast, all the other aromatic protons of the chiral bipyridyl ligands have shifted upfield, suggesting that they may have experienced ring currents from the adjacent ligands as a result of the formation of metallocycles. The H_7 and H_8 protons of the binaphthyl units have experienced the most upfield shifts, further indicating the reduction of dihedral angles between the naphthyl rings in order to accommodate the formation of metallocycles. Unfortunately, despite many

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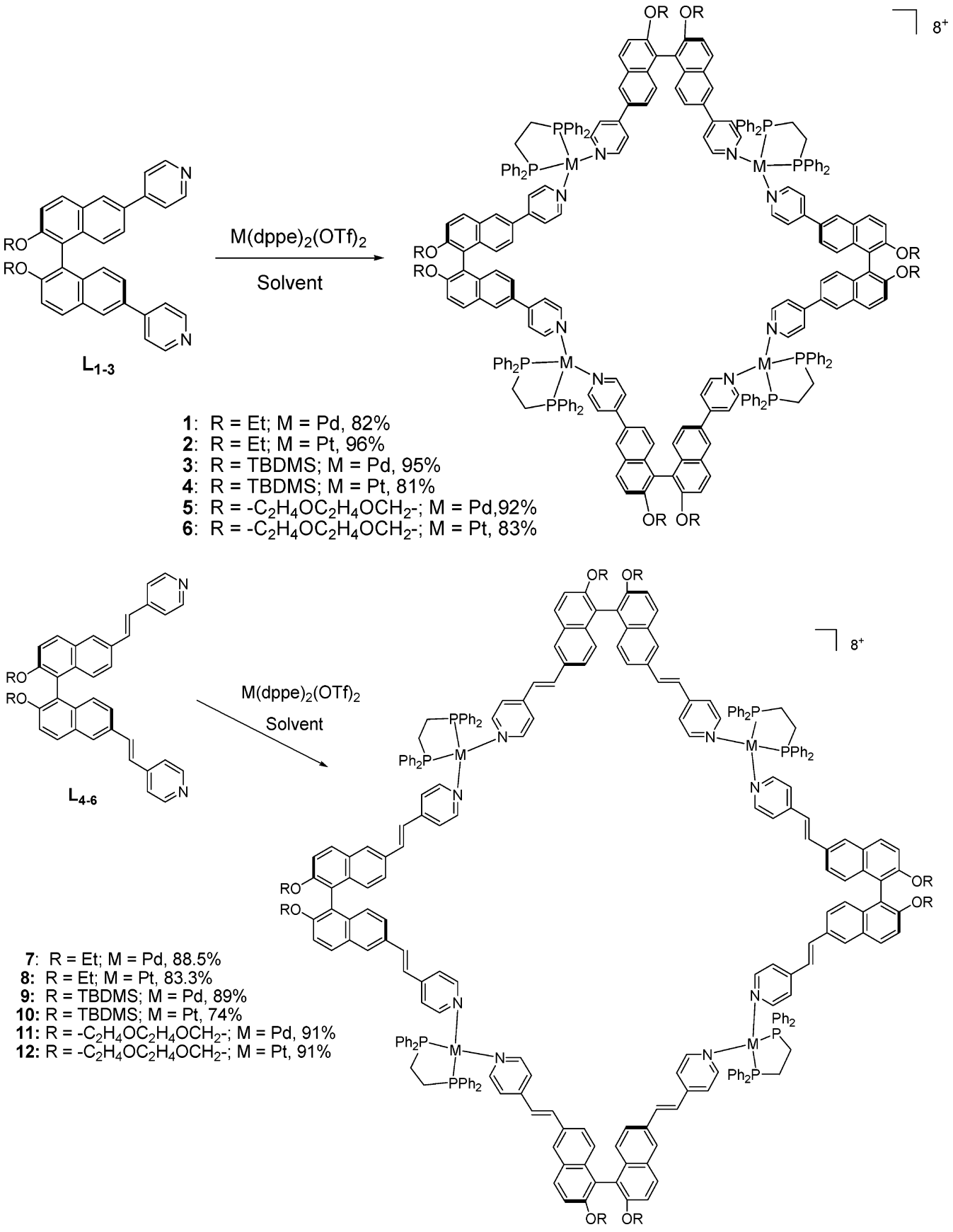
Scheme 2



attempts, we have failed to grow diffraction-quality single crystals of **1**−**12**.

Consistent with the ^{1}H NMR spectra, the ^{31}P{^{1}H} NMR spectra of Pd-containing metallocycles show a singlet around

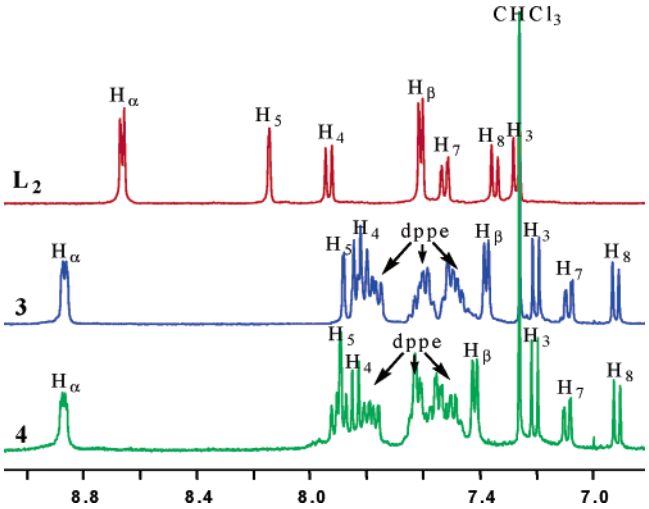


Figure 1. ^{1}H NMR spectra of $\mathbf{L}_2$, **3**, and **4**. Only the aromatic region is shown.

62 ppm while Pt-containing metallocycles show a sharp singlet around 34.5 ppm, with characteristic accompanying ^{195}Pt satellites (J_{Pt-P} = ~3210 Hz). ^{13}C{^{1}H} NMR spectra of **1**−**12** also exhibit a ligand environment consistent with the formation of highly symmetrical cyclic structures.

The electrospray mass spectra (ESI-MS)[15] showed the most compelling evidence for the formation of cyclic tetrameric structures of **1**−**12** (Table 1). For example, the ESI-MS spectrum of compound **1** showed the presence of multiply charged $[M - n\text{OTf}]^{n+}$ ion fragments at *m*/*z* ratios of 1149.2 for $[M - 4\text{OTf}]^{4+}$, 891.4 for $[M - 5\text{OTf}]^{5+}$, and 718.5 for $[M - 6\text{OTf}]^{6+}$. In the case of compound **3**, multiply charged $[M - n\text{OTf}]^{n+}$ ion fragments were found at *m*/*z* ratio of 1813.1 for $[M - 3\text{OTf}]^{3+}$, 1321.5 for $[M - 4\text{OTf}]^{4+}$, and 1028.5 for $[M - 5\text{OTf}]^{5+}$. For compound **5**, multiply charged $[M - n\text{OTf}]^{n+}$ ion fragments appeared at *m*/*z* ratio of 2743.1 for $[M - 2\text{OTf}]^{2+}$, 1176.8 for $[M - 3\text{OTf}]^{3+}$, 1295.5 for $[M - 4\text{OTf}]^{4+}$, and 814.1 for $[M - 6\text{OTf}]^{6+}$. The ESI-MS spectrum of compound **9** shows strong fragment peaks at *m*/*z* ratio of 2934.1 for $[M - 2\text{OTf}]^{2+}$, 1907.3 for $[M - 3\text{OTf}]^{3+}$, and 1083.3 for $[M - 5\text{OTf}]^{5+}$. Therefore, the ESI-MS data have unambiguously established the cyclic tetrameric structures for **1**−**12**.

2. Photophysical Properties. The electronic spectra of $\mathbf{L}_{1-3}$ are characterized by three major $\pi \rightarrow \pi^*$ transitions at ~229, ~270, and ~310 nm, while ligands $\mathbf{L}_{4-6}$ exhibit three major $\pi \rightarrow \pi^*$ transitions at ~236, ~292, and ~328 nm along with a shoulder peak at ~370 nm (Figure 2). The red-shift of $\pi \rightarrow \pi^*$ transitions for $\mathbf{L}_{4-6}$ in comparison to $\mathbf{L}_{1-3}$ is consistent with more conjugated nature of $\mathbf{L}_{4-6}$.

Upon the formation of metallocycles, the lower energy $\pi \rightarrow \pi^*$ transitions have red-shifted by 15−20 nm (Figure 2), while the highest energy peak remains relatively unchanged, presumably due to the mixing of phosphorus n → n* transitions of the dppe ligands. The small shoulder peaks at ~370 nm for $\mathbf{L}_{4-6}$ have experienced the largest red-shift (by ~23 nm) and have been significantly enhanced. Owing to the large intensity of the $\pi \rightarrow \pi^*$ transitions in these metallocycles, we have not been able to discern the MLCT transitions. All the UV−vis spectra are qualitatively the same between the Pd-based and Pt-based metallocycles.

Circular dichroism (CD) spectra of $\mathbf{L}_{1-3}$ are dominated by a major bisignate signal at ~260 nm that is due to the $\pi \rightarrow \pi^*$ transitions of chiral 1,1′-binaphthyl moieties (Figure 3). Upon the formation of metallocycles, three additional signals are evident in the CD spectra of **1**−**6**. The sharp, intense signal at ~220 nm is assigned to the phosphorus n → n* transitions of the dppe ligands. Although dppe is an achiral ligand, the phosphorus n → n* transitions become chiral upon forming metallocylces owing to their propeller arrangement relative to the chiral 1,1′-binaphthyl moieties. Such a chiral propeller arrangement of achiral phosphines has been previously observed in metallocycles built from atropisomeric linear bipyridines.[4a] Two new bisignate signals at ~290 and ~345 nm correspond to the $\pi \rightarrow \pi^*$ transitions of the $\mathbf{L}_{1-3}$ ligands. The significantly enhanced CD signals for two lower energy $\pi \rightarrow \pi^*$ transitions further suggest the formation of helical structures in these metallocycles.[16]

The CD spectra of $\mathbf{L}_{4-6}$ exhibit four signals corresponding to all the $\pi \rightarrow \pi^*$ transitions observed in their UV−vis

Table 1. Fragment Ions Observed in the ESI-MS Spectra of **1**−**12**

compd	obsd *m*/*z*	$(M - n\text{OTf})^{n+}$ fragment	calcd *m*/*z*
1	1149.2	$(M - 4\text{OTf})^{4+}$	1150.5
	891.4	$(M - 5\text{OTf})^{5+}$	890.6
	718.5	$(M - 6\text{OTf})^{6+}$	717.3
2	1238.3	$(M - 4\text{OTf})^{4+}$	1239.1
	962.1	$(M - 5\text{OTf})^{5+}$	961.5
3	1813.1	$(M - 3\text{OTf})^{3+}$	1813.7
	1321.5	$(M - 4\text{OTf})^{4+}$	1322.9
	1030.2	$(M - 5\text{OTf})^{5+}$	1028.5
4	1411.9	$(M - 4\text{OTf})^{4+}$	1411.6
	1098.3	$(M - 5\text{OTf})^{5+}$	1099.4
	893.2	$(M - 6\text{OTf})^{6+}$	891.3
5	2743.1	$(M - 2\text{OTf})^{2+}$	2742.4
	1176.8	$(M - 3\text{OTf})^{3+}$	1778.5
	1295.5	$(M - 4\text{OTf})^{4+}$	1296.7
	814.1	$(M - 6\text{OTf})^{6+}$	814.7
6	1895.6	$(M - 3\text{OTf})^{3+}$	1896.8
	1392.0	$(M - 4\text{OTf})^{4+}$	1395.3
	1074.1	$(M - 5\text{OTf})^{5+}$	1078.4
7	1653.4	$(M - 3\text{OTf})^{3+}$	1653.1
	1202.5	$(M - 4\text{OTf})^{4+}$	1202.6
	931.8	$(M - 5\text{OTf})^{5+}$	932.2
8	2731.4	$(M - 2\text{OTf})^{2+}$	2731.5
	1771.1	$(M - 3\text{OTf})^{3+}$	1771.3
	811.1	$(M - 6\text{OTf})^{6+}$	811.1
9	2934.1	$(M - 2\text{OTf})^{2+}$	2935.0
	1907.3	$(M - 3\text{OTf})^{3+}$	1907.0
	1083.3	$(M - 5\text{OTf})^{5+}$	1084.6
10	3076.6	$(M - 2\text{OTf})^{2+}$	3076.3
	2001.0	$(M - 3\text{OTf})^{3+}$	2001.2
	1463.5	$(M - 4\text{OTf})^{4+}$	1463.5
11	2845.2	$(M - 2\text{OTf})^{2+}$	2846.5
	1347.4	$(M - 4\text{OTf})^{4+}$	1348.7
12	3023.9	$(M - 2\text{OTf})^{2+}$	3023.8
	1964.2	$(M - 3\text{OTf})^{3+}$	1966.2
	1436.5	$(M - 4\text{OTf})^{4+}$	1437.4

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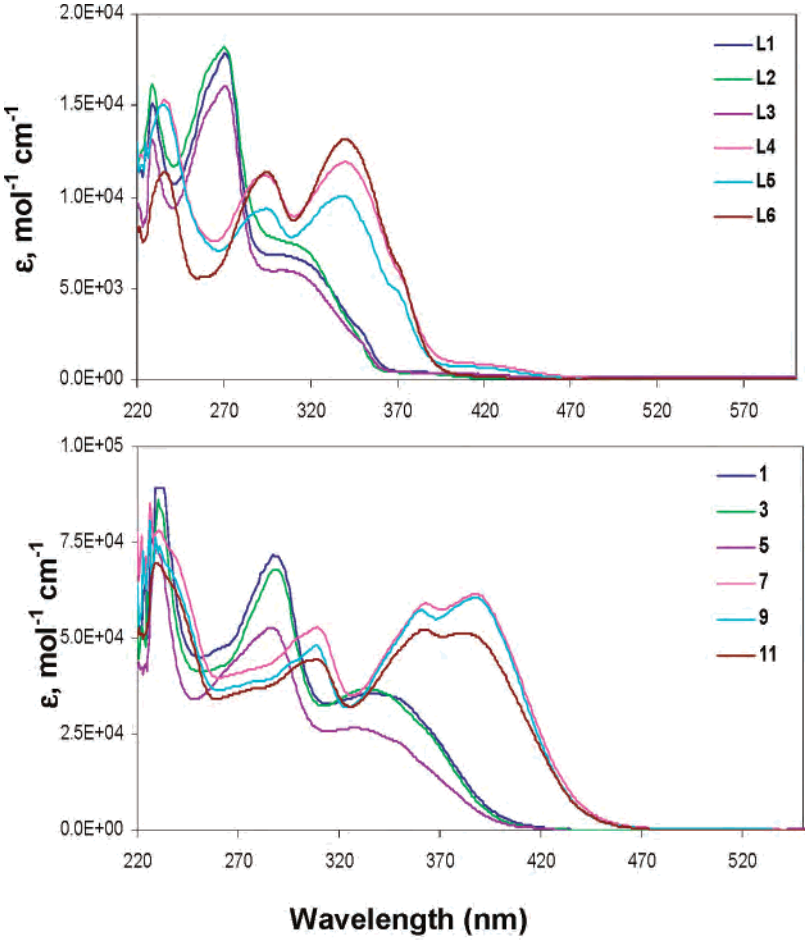


Figure 2. UV−vis spectra of $\mathbf{L_{1-6}}$ and Pd-based molecular squares.

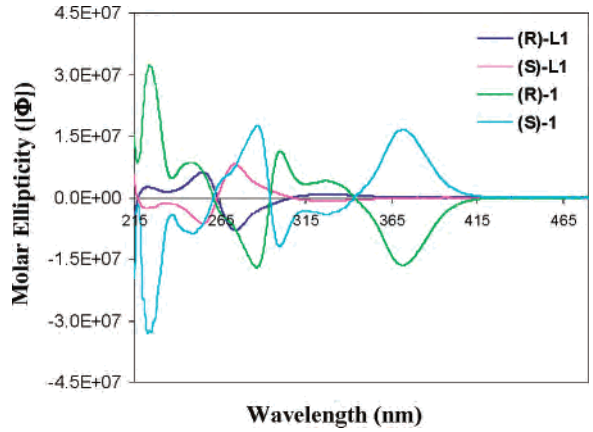


Figure 3. CD spectra of $\mathbf{L_1}$ and **1**.

spectra (Figure 4). The presence of CD signals corresponding to the lower energy $\pi \rightarrow \pi^*$ transitions in $\mathbf{L_{4-6}}$ is consistent with coplanar nature (hence reduced twisting motion) of the naphthyl and pyridyl rings linked by the olefinic moiety. Upon forming metallocycles, all these CD signals have been significantly enhanced. We believe that significant enhancement of CD signals in **7**−**12** is a result of both the presence of multiple ligands in each metallocycle and the formation of more rigid helical structures. We have prepared metallocycles **1**−**12** with both hands of ligands $\mathbf{L_{1-6}}$, and as expected, the CD spectra of all the enantiomeric pairs are mirror images of one another.

Ligands $\mathbf{L_{1-6}}$ are highly fluorescent in CH_2Cl_2 at room temperature. $\mathbf{L_{1-3}}$ emit at 385 nm with quantum efficiency of 0.36−0.90, while $\mathbf{L_{4-6}}$ emit less efficiently at ∼435 nm with quantum efficiency of 0.11−0.30 (Table 2). Metallocycles **1**−**12** are also highly luminescent in CH_2Cl_2 at room temperature (Figure 5). Compounds **1**−**6** each exhibit a fluorescence band at ∼435 nm, with a Stokes shift of ∼100 nm from the low energy absorption. Significant red-shifts

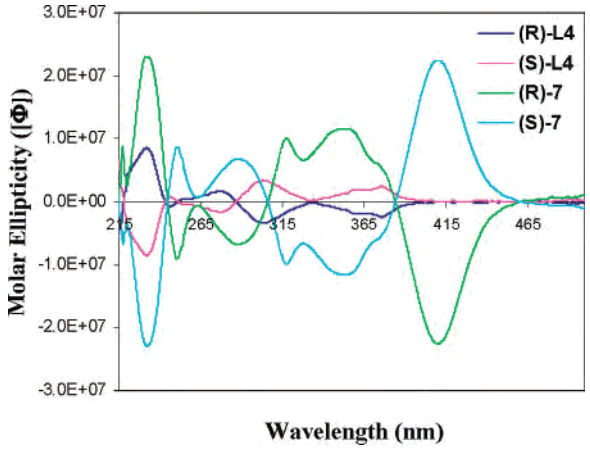


Figure 4. CD spectra of $\mathbf{L_4}$ and **7**.

Table 2. Luminescence Properties of $\mathbf{L_{1-6}}$ and **1**−**12** in CH_2Cl_2 at Room Temperature[a]

compd	excitation wavelength (nm)	emission wavelength (nm)	quantum yield
$\mathbf{L_1}$	340	386	0.43
$\mathbf{L_2}$	317	381	0.90
$\mathbf{L_3}$	340	387	0.36
$\mathbf{L_4}$	342	437	0.14
$\mathbf{L_5}$	342	432	0.11
$\mathbf{L_6}$	340	438	0.30
1	335	437	0.33
2	335	442	0.63
3	333	425	0.37
4	340	434	0.42
5	328	443	0.37
6	347.5	445	0.28
7	390	486	0.09
8	392	497	0.11
9	390	519	0.06
10	389	499	0.07
11	381.5	483	0.10
12	384.5	496	0.08

[a] Quantum yields were determined using anthracene (in cyclohexane) as the external standard. A solution of ~10^{-6} M of **1**−**12** was used to maintain the optical density under 0.1.

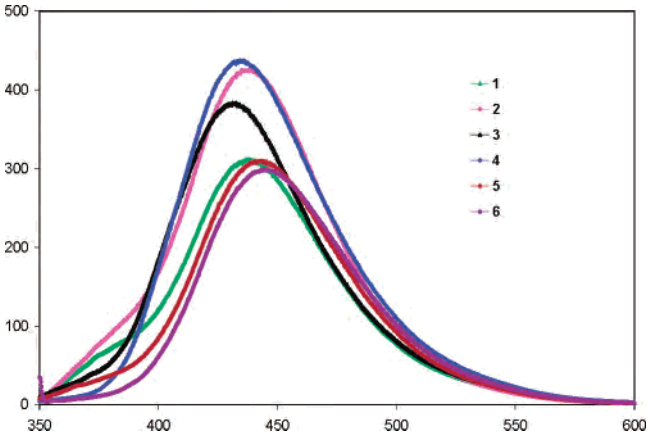


Figure 5. Luminescence spectra of **1**−**6** in CH_2Cl_2 at a concentration of ~10^{-6} M.

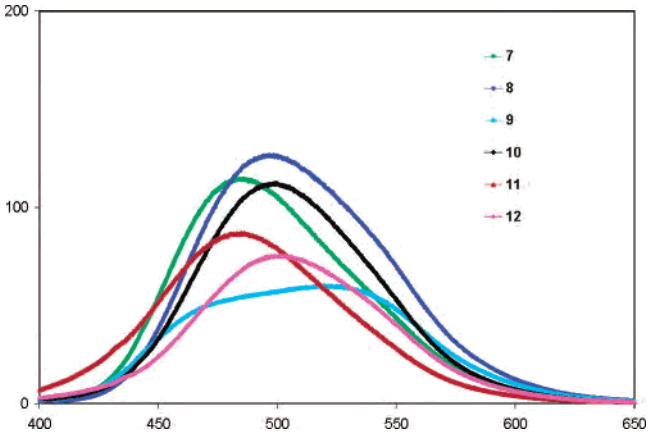
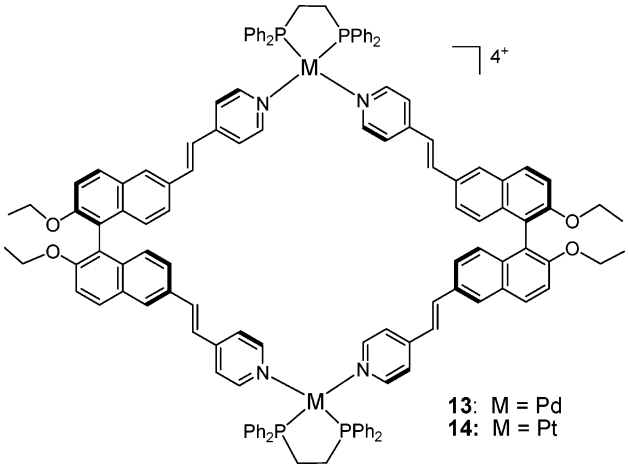


Figure 6. Luminescence spectra of **7**−**12** in CH_2Cl_2 at a concentration of ~10^{-6} M.

(~50 nm) of the luminescence of **1**−**6** compared to $\mathbf{L_{1-3}}$ are consistent with those observed in the UV−vis spectra. Luminescence quantum efficiency for **1**−**6** ranges from 0.28 to 0.63. Compounds **7**−**12** each exhibit a fluorescence band at ~495 nm, with a Stokes shift of ~110 nm from the low energy absorption. Consistent with their free ligands, compounds **7**−**12** are less fluorescent that **1**−**6**, with a quantum efficiency of 0.06−0.11. We tentatively assign the fluorescence bands for **1**−**12** as mostly intraligand (^{1}IL) in character. We have not observed any phosphorescence bands for fluid solutions of **1**−**12** at room temperature.

Scheme 3



3. Reassembly Process. When equal amounts of enantiomerically pure molecular squares were mixed in CH_2Cl_2, they rearranged to generate *meso* dimeric metallocycles (Scheme 3). For example, when (*R*)-**7** was combined with the same amount of (*S*)-**7** in CH_2Cl_2, the mixture (compound **13**) gave a more complicated set of peaks in the ^{1}H NMR spectrum, which as expected exactly matched the ^{1}H NMR spectrum of Pd-metallocycles made from Pd(dppe)$(OTf)_2$ and racemic $\mathbf{L_4}$. While we have shown that enantiopure **7** has a D_4 symmetry, compound **13** shows two sets of peaks due to the $\mathbf{L_4}$ ligand and thus exhibits a C_2 symmetry in solution. No mirror symmetry is present in **13** because of the relative orientation of the two coordinating pyridyl rings on the Pd center. The ESI-MS data of **13** indicated the presence of $[M - n\text{OTf}]^{n+}$ ion fragments at *m*/*z* ratios of 1201.0 and 751.1 that are assignable to $[M - 2\text{OTf}]^{2+}$ (expected 1202.6) and $[M - 3\text{OTf}]^{3+}$ (expected 752.2) of the dimeric metallocycle, respectively. An analogous metallocycle with Pt(dppe)$(OTf)_2$ metallocorner and racemic $\mathbf{L_4}$ bridging ligand, **14**, has been similarly prepared. The NMR and ESI-MS data of **14** are also consistent with the formulation of a *meso* dimeric metallocycle with C_2 symmetry. We have also followed the reassembly process by ^{1}H NMR spectroscopy. We have determined the half-life for the D_4 molecular squares of (*rac*)-**7** to be 2.57 h in CD_2Cl_2 at −20 °C. Similar experiments showed that the half-life for the D_4 molecular squares of (*rac*)- **8** is 3.15 h at 25 °C (Figure 7). This result is consistent with kinetic inertness of Pt(II) centers relative to Pd(II) centers.

4. Summary

The reaction of chelating phosphine-capped Pd(II) or Pt(II) triflates with properly designed chiral bridging ligands results in the formation of highly symmetrical chiral tetrameric cyclic complexes. All these chiral metallocycles are highly

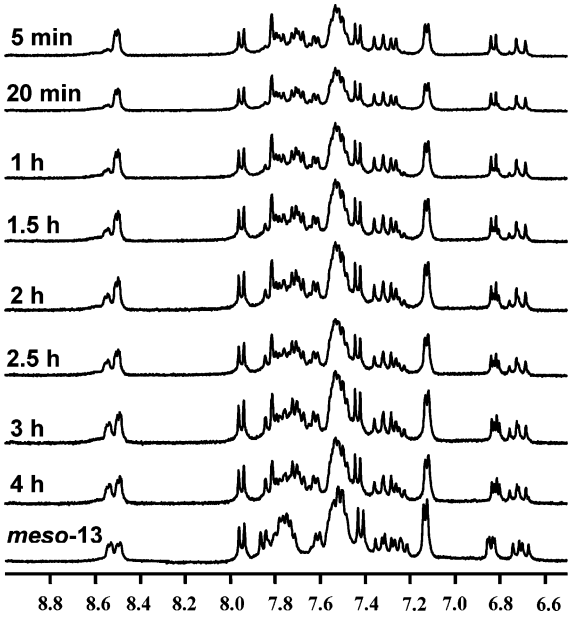


Figure 7. Reassembly process for (*rac*)-**7** followed by ^{1}H NMR spectroscopy in CD_2Cl_2 at −20 °C. (*rac*)-**7** slowly reassembles into *meso*-**13**.

luminescent in solution at room temperature with quantum efficiency of 0.06−0.63. Interestingly, mixing of equal molar enantiopure molecular squares of opposite handedness in solution led to a new *meso* dimeric metallocycle with C_2 symmetry. This result indicates the lability of the M−pyridyl bonds in these metallocycles, which may hinder their applications in many enantioselective processes.

5. Experimental Section

All of the chemicals were obtained from commercial sources and used without further purification. All of the reactions and manipulations were carried out under N_2 with the use of standard inert-atmosphere and Schlenk techniques. Solvents used in reactions were dried by standard procedures. 6,6′-Dibromo-2,2′-diethoxy-1,1′-binaphthalene, 6,6′-dibromo-2,2′-bis(*tert*-butyldimethylsiloxy)-1,1′-binaphthalene, and 6,6′-dibromo-2,2′-pentaethyleneglycol-1,1′-binaphthalene were prepared according to modified literature procedures.[11−13] Pd(dppe)(OTf)$_2$ and Pt(dppe)(OTf)$_2$ were also prepared by following literature procedures.[14]

UV−vis spectra were obtained using a Hewlett-Packard 8452A diode array spectrophotometer. Circular dichroism (CD) spectra were recorded on a Jasco J-710 spectropolarimeter. The IR spectra were recorded from KBr pellets on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. NMR spectra were recorded on Varian XL-400 and Bruker NMR 400 DRX spectrometer. ^{1}H NMR spectra were recorded at 400 MHz and referenced to the proton resonance resulting from incomplete deuteration of the dichloromethane (δ 5.32), or chloroform (δ 7.26). ^{13}C{^{1}H} NMR spectra were recorded at 100 MHz, and all of the chemical shifts are reported downfield in ppm relative to the carbon resonance of the methyl group of chloroform-d_1 (δ 77.0), or dichloromethane-d_2 (δ 53.8). Mass spectra were recorded on an Agilent 1100 series LC/MSD or an electrospray mass spectrometer at University of Illinois at Urbana−Champaign mass spectrometry laboratory.

Luminescence measurements were carried out on a Shimadzu RF-5301PC spectrafluorophotometer equipped with a xenon lamp. Quantum yield studies were performed using 1 cm closed-cap quartz spectrophotometer cells (Starna Cells, Inc.) on appropriate excitation wavelengths that were determined using a Shimadzu UV-2401PC UV−vis spectrophotometer. Anthracene in cyclohexane was used as the external standard.

6,6′-Bis(4″-pyridyl)-2,2′-diethoxy-1,1′-binaphthalene (L_1). To a 100 mL three-necked round-bottom flask equipped with a magnetic stirrer and a reflux condenser was added 6,6′-dibromo-2,2′-diethoxy-1,1′-binaphthalene (800 mg, 1.6 mmol), 4-trimethylstannylpyridine (1.0 g, 3.52 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (84.5 mg, 0.12 mmol), and LiCl (424 mg, 10 mmol) in toluene (25 mL). The mixture was degassed for 10 min and allowed to reflux for 72 h under N_2 atmosphere. The solvent was evaporated, and the residue was extracted with ethyl acetate followed by washing with water several times. The organic layer was dried over anhydrous $MgSO_4$ and evaporated to afford pure brown solid which was further purified by silica gel column chromatography [ethyl acetate/hexanes/triethylamine (6:3:1 v/v)] to afford pure 6,6′-bis(4″-pyridyl)-2,2′-diethoxy-1,1′-binaphthalene (493 mg, 62%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.67 (d, $^3J_{H-H}$ = 5.86 Hz, 4H), 8.65 (d, $^4J_{H-H}$ = 1.64 Hz, 2H), 8.05 (d, $^3J_{H-H}$ = 9.04, 2H), 7.59 (d, $^3J_{H-H}$ = 5.86 Hz, 4H), 7.50 (d, $^3J_{H-H}$ = 9.04 Hz, 4H), 7.26 (d, $^3J_{H-H}$ = 9.04 Hz, 2H), 4.10 (m, 4H), 1.11 (t, $^3J_{H-H}$ = 6.97 Hz, 6H). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 155.20, 150.24, 148.27, 134.28, 132.92, 129.97, 129.20, 126.49, 126.38, 124.78, 121.60, 120.09, 116.28, 65.10, 14.94. IR (cm^{-1}): 3456.7(br), 3062.8(br), 2975.9(br), 1622.5(m), 1590.0(s), 1545.6(m), 1490.9(m), 1465.6(m), 1412.5(m), 1368.3(m), 1200.1(w), 1236.9(s), 1110.4(m), 1091.9(m), 1053.1(s), 1032.6(s), 809.9(m). HR-MS (EI) *m*/*z* 496.2151 (calcd *m*/*z* 496.2151).

6,6′-Bis(4″-pyridyl)-2,2′-bis(*tert*-butyldimethylsiloxy)-1,1′-binaphthalene (L_2). To a 100 mL three-necked round-bottom flask equipped with a magnetic stirrer and a reflux condenser was added 6,6′-dibromo-2,2′-bis(*tert*-butyldimethylsiloxy)-1,1′-binaphthalene (673 mg, 1.0 mmol), 4-trimethylstannylpyridine (625 mg, 2.25 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (50 mg, 0.07 mmol), and LiCl (255 mg, 6 mmol) in toluene (15 mL). The mixture was degassed for 10 min and allowed to refulx for 72 h under N_2 atmosphere. The solvent was evaporated, and the residue was extracted with ethyl acetate followed by washing several times with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated to afford pure brown solid which was further purified by silica gel column chromatography [ethyl acetate/hexanes/triethylamine (5:4.75:0.25 v/v)] to afford pure 6,6′-bis(4″-pyridyl)-2,2′- bis(*tert*-butyldimethylsiloxy)-1,1′-binaphthalene (268 mg, 40%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.66 (d, $^3J_{H-H}$ = 5.69 Hz, 4H), 8.14 (d, $^4J_{H-H}$ = 1. 43 Hz, 2H), 7.93 (d, $^3J_{H-H}$ = 8.97, 2H), 7.61 (d, $^3J_{H-H}$ = 5.69 Hz, 4H), 7.52 (dd, $^3J_{H-H}$ = 8.90 Hz, $^4J_{H-H}$ = 1.43 Hz, 2H), 7.34 (d, $^3J_{H-H}$ = 8.97 Hz, 2H), 7.27 (d, $^3J_{H-H}$ = 8.90 Hz, 2H), 0.49 (s, 18H), 0.05 (s, 6H), −0.10 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.15, 150.13, 148.34, 134.69, 132.45, 129.58, 129.24, 126.82, 126.35, 124.52, 121.78, 121.52, 121.35, 24.98, 17.59, −4.24, −4.43. IR (cm^{-1}): 3419.9(br), 3028.7(br), 2926.8(m), 2855.4(m), 1718.8(w), 1623.9(m), 1590.3(s), 1547.7(m), 1487.7(s), 1471.1(s), 1413.9(m), 1356.4(s), 1284.5(s), 1250.1(s), 1186.7(m), 1137.3(s), 1087.5(m), 1044.6(m), 1000.9(s), 949.5(m), 870.9(s), 811.5(w), 779.0(s), 721.6(m), 680.6(w), 624.5(m). HR-MS (EI) *m*/*z* 668.3254 (calcd *m*/*z* 668.3254).

6,6′-Bis(4″-pyridyl)-2,2′-pentaethyleneglycol-1,1′-binaphthalene (L_3). To a 100 mL three-necked round-bottom flask equipped with a magnetic stirrer and a reflux condenser was added 6,6′-dibromo-2,2′-pentaethyleneglycol-1,1′-binaphthalene (517 mg, 0.8 mmol), 4-trimethystannylpyridine (500 g, 1.76 mmol), Pd(PPh$_3$)$_2$-Cl$_2$ (42.3 mg, 0.06 mmol), and LiCl (212 mg, 5 mmol) in toluene

(13 mL). The mixture was degassed for 10 min and allowed to stir for 72 h under N_2 atmosphere. The solvent was evaporated, and the residue was extracted with ethyl acetate followed by washing several times with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated to afford brown solid which was further purified by silica gel column chromatography [dichloromethane/methanol (10:0.5 v/v)] to afford pure 6,6′-bis(4″-pyridyl)-2,2′- pentaethyleneglycol-1,1′-binaphthalene (298 mg, 58%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.66 (d, $^3J_{H-H}$ = 6.25 Hz, 4H), 8.17 (d, $^4J_{H-H}$ = 1.78 Hz, 2H), 8.06 (d, $^3J_{H-H}$ = 9.55, 2H), 7.60 (d, $^3J_{H-H}$ = 6.25 Hz, 4H), 7.58 (d, $^3J_{H-H}$ = 9.55 Hz, 4H), 7.50 (dd, $^3J_{H-H}$ = 7.99 Hz, $^4J_{H-H}$ = 1.78 Hz, 2H), 7.25 (d, $^3J_{H-H}$ = 7.99 Hz, 2H), 4.26 (m, 2H), 4.11 (m, 2H), 3.64 (m, 4H), 3.54 (m, 8H), 3.42 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.39, 150.20, 148.25, 134.20, 133.11, 130.06, 129.38, 126.48, 126.38, 124.94, 121.55, 120.06, 116.70, 70.89, 70.68, 70.63, 69.78. IR (cm^{-1}): 3412.6(br), 3010.2(br), 2866.7(br), 1621.8(m), 1591.1(s), 1546.1(m), 1490.9(s), 1414.5(m), 1351.5(m), 1282.2(s), 1248.6(s), 1128.1(m), 1093.3(s), 1061.9(s), 992.1(m), 811.2(s). MS (LCMS) *m*/*z* 643 (calcd *m*/*z* 642.74).

6,6′-Bis(4″-vinylpyridyl)-2,2′-diethoxy-1,1′-binaphthalene (L_4). To a 100 mL three-necked round-bottom flask equipped with a magnetic stirrer and a reflux condenser were added 6,6′-dibromo-2,2′-diethoxy-1,1′-binaphthalene (2.0 g, 4.0 mmol), 4-vinylpyridine (1.07 mL, 10.0 mmol), palladium acetate (44.5 mg, 0.2 mmol), and tris(*o*-tolyl)phosphine (45 mg) in a mixture of DMF (50 mL) and triethylamine (50 mL). The mixture was degassed for 10 min and allowed to reflux for 24 h under N_2 atmosphere. The solvents were evaporated, and the residue was extracted with ethyl acetate followed by washing several times with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated to afford pure 6,6′-bis(4″-vinylpyridine)-2,2′-diethoxy-1,1′-binaphthalene (2.14 g, 95%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.57 (d, $^3J_{H-H}$ = 6.37 Hz, 4H), 7.97 (d, $^3J_{H-H}$ = 9.25 Hz, 2H), 7.94 (d, $^4J_{H-H}$ = 1.67 Hz, 2H), 7.47 (dd, $^3J_{H-H}$ = 9.02, $^4J_{H-H}$ = 1.67 Hz, 2H), 7.45 (d, $^3J_{H-H}$ = 9.02 Hz, 2H), 7.44 (d, $^3J_{H-H}$ = 16.66 Hz, 2H), 7.37 (d, $^3J_{H-H}$ = 6.37 Hz, 4H), 7.15 (d, $^3J_{H-H}$ = 9.25 Hz, 2H), 7.02 (d, $^3J_{H-H}$ = 16.66 Hz, 2H), 4.08 (m, 4H), 1.09 (t, $^3J_{H-H}$ = 7.40 Hz, 6H). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 155.09, 150.14, 144.87, 134.29, 133.31, 131.37, 129.66, 129.17, 128.01, 126.07, 123.69, 120.73, 120.42, 116.06, 65.07, 14.94. IR (cm^{-1}): 3468.9(br), 3033.7(br), 2979.1(br), 1629.0(m), 1591.8(s), 1560.3(m), 1546.8(m), 1465.5(s), 1439.8(m), 1411.7(s), 1350.9(m), 1332.7(m), 1275.7(s), 1244.8(s), 1264.7(s), 1170.7(m), 1109.5(w), 1087.4(m), 1047.8(s), 972.3(s), 859.3(m), 823.7(w), 800.0(s), 736.0(m), 668.7(w), 567.9(m). HR-MS (EI) *m*/*z* 548.2464 (calcd *m*/*z* 548.2464).

6,6′-Bis(4″-vinylpyridine)-2,2′-bis(*tert*-butyldimethylsiloxy)-1,1′-binaphthalene (L_5). To a 100 mL three-necked round-bottom flask equipped with a magnetic stirrer and a reflux condenser were added 6,6′-dibromo-2,2′-bis(*tert*-butyldimethylsiloxy)-1,1′-binaphthalene (1.35 g, 2.0 mmol), 4-vinylpyridine (0.8 mL, 7 mmol), palladium acetate (22.2 mg, 0.1 mmol), and tris(*o*-tolyl)-phosphine (22.2 mg) in a mixture of THF (7 mL) and TEA (7 mL). The mixture was degassed for 10 min and allowed to reflux for 72 h under N_2 atmosphere. The solvents were evaporated, and the residue was extracted with ethyl acetate followed by washing several times with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated to afford pure brown solid which was further purified by silica gel column chromatography [ethyl acetate/triethylamine (9.75:0.25 v/v)] to afford pure 6,6′-bis(4″-vinylpyridine)-2,2′-diethoxy-1,1′-binaphthalene (857 mg, 59%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.57 (d, $^3J_{H-H}$ = 5.63 Hz, 4H), 7.91 (d, $^4J_{H-H}$ = 1.50 Hz, 2H), 7.85 (d, $^3J_{H-H}$ = 8.81, 2H), 7.49 (dd, $^3J_{H-H}$ = 9.01 Hz, $^4J_{H-H}$ = 1.50 Hz, 2H), 7.43 (d, $^3J_{H-H}$ = 16.41 Hz, 4H), 7.38 (d, $^3J_{H-H}$ = 5.63 Hz, 4H), 7.23 (d, $^3J_{H-H}$ = 9.81 Hz, 2H), 7.21 (d, $^3J_{H-H}$ = 9.01 Hz, 2H), 7.03 (d, $^3J_{H-H}$ = 16.41 Hz, 4H), 0.49 (s, 18H), 0.05 (s, 6H), −0.14 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 152.02, 150.10, 144.91, 134.70, 133.46, 131.17, 129.26, 129.18, 127.93, 126.43, 124.96, 123.49, 122.10, 121.14, 120.72, 25.00, 17.59, −4.24, −4.49. IR (cm^{-1}): 3436.5(br), 3032.5(br), 2926.6(br), 2854.9(br), 1593.2(s), 1550.3(m), 1469.9(s), 1414.3(m), 1355.9(s), 1281.4(m), 1250.3(s), 1166.5(m), 1081.4(w), 1001.7(m), 990.2(m), 958.2(m), 901.9(w), 837.8(s), 821.6(s), 777.5(m). HR-MS (EI) *m*/*z* 720.3567 (calcd *m*/*z* 720.3567).

6,6′-Bis(4″-vinylpyridine)-2,2′-pentaethyleneglycol-1,1′-binaphthalene (L_6). To a 25 mL three-necked round-bottom flask equipped with a magnetic stirrer and a reflux condenser were added 6,6′-dibromo-2,2′-pentaethyleneglycol-1,1′-binaphthalene (300 mg, 0.47 mmol), 4-vinylpyridine (0.14 mL, 1.4 mmol), palladium acetate (10.4 mg, 0.048 mmol), and tris(*o*-tolyl)-phosphine (10.4 mg) in DMF (4 mL) and TEA (4 mL). The mixture was degassed for 10 min and allowed to reflux for 72 h under N_2 atmosphere. The solvents were evaporated, and the residue was extracted with ethyl acetate followed by washing several times with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated to afford pure brown solid which was further purified by silica gel column chromatography [CH_2Cl_2/ethyl acetate/MeOH (5:4:1 v/v)] to afford pure 6,6′-bis(4″-vinylpyridine)-2,2′-pentaethyleneglycol-1,1′-binaphthalene (230 mg, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.57 (d, $^3J_{H-H}$ = 6.4 Hz, 4H), 7.97 (d, $^3J_{H-H}$ = 9.0 Hz, 2H), 7.94 (d, $^4J_{H-H}$ = 1.8), 7.50 (d, $^3J_{H-H}$ = 9.0 Hz, 2H), 7.48 (dd, $^3J_{H-H}$ = 8.9 Hz and $^4J_{H-H}$ = 1.8, 2H), 7.44 (d, $^3J_{H-H}$ = 16.2 Hz, 2H), 7.37 (d, $^3J_{H-H}$ = 6.3, 4H), 7.15 (d, $^3J_{H-H}$ = 8.9, 2H), 7.02 (d, $^3J_{H-H}$ = 16.2 Hz, 2H), 4.24 (m, 2H), 4.08 (m, 2H), 3.63 (m, 4H), 3.53 (m, 8H), 3.41 (m, 4H). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.24, 150.15, 144.82, 134.20, 133.27, 131.56, 129.73, 129.35, 127.97, 126.05, 125.36, 123.84, 120.76, 120.35, 116.39, 70.89, 70.68, 70.62, 69.77. IR (cm^{-1}): 3476.8(br), 3033.7(br), 2873.3(br), 1631.3(m), 1617.0(m), 1593.2(s), 1548.7(m), 1473.5(m), 1414.7(m), 1351.7(m), 1329.9-(m), 1243.9(s), 1090.4(s), 989.6(m), 967.9(m), 821.1(m), 859.3(m), 798.8(m). MS (LCMS) *m*/*z* 694 (calcd *m*/*z* 694.81).

[Pd(dppe)(L_1)]$_4$[OTf]$_8$ (1). To a 25 mL two-necked round-bottom flask containing Pd(dppe)(OTf)$_2$ (80.3 mg, 0.1 mmol) and **L_1** (50 mg, 0.1 mmol) was added CH_2Cl_2 (14 mL), and the reaction mixture was allowed to stir at room temperature (rt) for 12 h. The resulting yellow clear solution was filtered to remove insoluble residue, and reduced to half of its volume. Diethyl ether was added to the CH_2Cl_2 solution to afford bright yellow precipitate, which was collected by filtration and dried in vacuo. Yield: 106.8 mg (82%). ^{1}H NMR ($CDCl_3$): δ 8.87 (d, $^3J_{H-H}$ = 6.10 Hz, 16H), 7.96 (d, $^3J_{H-H}$ = 9.10 Hz, 8H), 7.92 (s, 8H), 7.79 (m, 32H), 7.46 (m, 56H), 7.36 (d, $^3J_{H-H}$ = 6.10 Hz, 16H), 7.08 (d, $^3J_{H-H}$ = 8.99 Hz, 8H), 6.86 (d, $^3J_{H-H}$ = 8.99 Hz, 8H), 4.07 (m, 16H), 3.14 (m, 16H), 1.07 (t, $^3J_{H-H}$ = 7.23 Hz, 24H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 156.17, 151.41, 150.99, 135.04, 133.80, 133.73, 133.44, 130.29(m), 129.15, 127.58, 126.55, 126.34, 125.78, 124.59, 123.94, 121.56 (q, $^1J_{C-F}$ = 321.1 Hz, OTf), 119.76, 116.41, 65.27, 28.53 (dd, $^1J_{C-P}$ = 39.2 Hz, $^2J_{C-P}$ = 8.9 Hz), 15.05. ^{31}P{^{1}H} NMR (CD_2Cl_2): 62.01. IR (cm^{-1}): 3503.3(br), 3062.8(br), 2975.7(br), 1609.9(s), 1491.1(m), 1437.4(s), 1280.0(s), 1254.0(s), 1155.6(m), 1106.1(m), 1055.6(w), 1029.9(s), 997.6(m), 817.6(w), 748.5(w), 691.3(w), 637.7(s), 533.8(m).

[Pt(dppe)(L_1)]$_4$[OTf]$_8$ (2). To a 25 mL two-necked round-bottom flask containing Pt(dppe)(OTf)$_2$ (44.6 mg, 0.05 mmol) and **L_1** (25 mg, 0.05 mmol) was added CH_2Cl_2 (7 mL), and the reaction mixture was allowed to reflux for 12 h. The resulting yellow clear solution

was filtered to remove insoluble residue and reduced to half of its volume. Diethyl ether was added to the CH_2Cl_2 solution to afford a bright yellow precipitate, which was collected by filtration and dried in vacuo. Yield: 67 mg (96%). ^{1}H NMR ($CDCl_3$): δ 8.88 (d, $^3J_{H-H}$ = 5.48 Hz, 16H), 7.97 (d, $^3J_{H-H}$ = 9.26 Hz, 8H), 7.94 (s, 8H), 7.83 (m, 24H), 7.59 (m, 16H), 7.49 (m, 24H), 7.44 (d, $^3J_{H-H}$ = 9.26 Hz, 8H), 7.39 (d, $^3J_{H-H}$ = 5.48 Hz, 16H), 7.08 (d, $^3J_{H-H}$ = 9.21 Hz, 8H), 6.85 (d, $^3J_{H-H}$ = 9.21 Hz, 8H), 4.08 (m, 16H), 2.97 (m, 16H), 1.08 (t, $^3J_{H-H}$ = 7.03 Hz, 24H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 156.31, 152.03, 150.77, 135.15, 133.95, 133.81, 133.51, 130.84, 130.27(m), 129.12, 127.80, 126.61, 125.13, 124.50, 124.43, 121.64 (q, $^1J_{C-F}$ = 322.0 Hz, OTf), 119.72, 116.44, 65.28, 28.56 (dd, $^1J_{C-P}$ = 44.3 Hz, $^2J_{C-P}$ = 5.9 Hz), 15.05. ^{31}P{^{1}H} NMR (CD_2Cl_2): 34.90 (s, $^1J_{Pt-P}$ = 3218.0 Hz). IR (cm^{-1}): 3495.7(br), 3063.1(br), 2980.1(br), 1610.6(s), 1492.8(m), 1467.8(m), 1436.9(s), 1261.6(s), 1254.9(s), 1224.2(s), 1155.8(s), 1108.7(m), 1054.7(m), 1029.7(s), 997.9(w), 816.5(m), 709.8(m), 692.7(m), 637.5(s), 536.5(s), 516.8(m).

[Pd(dppe)(L$_2$)]$_4$[OTf]$_8$ (3). The preparation is similar to that of **1**. Yield: 95%. ^{1}H NMR ($CDCl_3$), δ 8.87 (d, $^3J_{H-H}$ = 5.75 Hz, 16H), 7.88 (d, $^4J_{H-H}$ = 1.72 Hz, 8H), 7.84 (d, $^3J_{H-H}$ = 9.40 Hz, 8H), 7.79 (m, 32H), 7.59 (m, 16H), 7.50 (m, 32H), 7.38 (d, $^3J_{H-H}$ = 5.75 Hz, 16H), 7.20 (d, $^3J_{H-H}$ = 9.40 Hz, 8H), 7.09 (dd, $^3J_{H-H}$ = 8.89 Hz, $^4J_{H-H}$ = 1.72 Hz, 8H), 6.92 (d, $^3J_{H-H}$ = 8.89 Hz, 8H), 3.08 (m, 16H), 0.49 (s, 72H), 0.08 (s, 24H), −0.24 (s, 24H). ^{13}C-{^{1}H} NMR (CD_2Cl_2): δ 153.40, 151.58, 151.00, 135.64, 133.74, 133.72, 133.47, 130.30(m), 129.37, 127.39, 126.97, 126.27, 125.72, 124.35, 123.97, 121.56 (q, $^1J_{C-F}$ = 322.1 Hz, OTf), 122.09, 122.00, 28.61 (dd, $^1J_{C-P}$ = 39.2 Hz, $^2J_{C-P}$ = 8.1 Hz), 25.20, 17.89, −3.99, −4.43. ^{31}P{^{1}H} NMR (CD_2Cl_2): 62.05. IR (cm^{-1}): 3503.3(br), 3059.1(br), 2929.0(m), 2856.3(br), 1610.3(s), 1490.5(m), 1472.5(s), 1437.2(s), 1361.3(m), 1284.2(s), 1252.7(s), 1223.9(m), 1159.8(m), 1105.1(w), 1030.3(s), 998.3(m), 948.9(w), 871.3(m), 840.9(m), 818.8(s), 779.9(m), 708.6(w), 690.9(w), 637.7(s), 533.1(m).

[Pt(dppe)(L$_2$)]$_4$[OTf]$_8$ (4). The preparation is similar to that of **2**. Yield: 81%. ^{1}H NMR ($CDCl_3$): δ 8.87 (d, $^3J_{H-H}$ = 6.65 Hz, 16H), 7.89 (d, $^4J_{H-H}$ = 1.63 Hz, 8H), 7.84 (d, $^3J_{H-H}$ = 9.12 Hz, 8H), 7.78 (m, 32H), 7.62 (m, 16H), 7.52 (m, 32H), 7.42 (d, $^3J_{H-H}$ = 6.65 Hz, 16H), 7.21 (d, $^3J_{H-H}$ = 9.12 Hz, 8H), 7.09 (dd, $^3J_{H-H}$ = 9.46 Hz, $^4J_{H-H}$ = 1.63 Hz, 8H), 6.92 (d, $^3J_{H-H}$ = 9.46 Hz, 8H), 2.91 (m, 16H), 0.48 (s, 72H), 0.08 (s, 24H), −0.24 (s, 24H). ^{13}C-{^{1}H} NMR (CD_2Cl_2): δ 153.56, 152.17, 150.80, 135.76, 133.79(m), 133.57, 130.40(m), 130.12, 129.34, 127.62, 127.02, 124.97, 124.42, 124.33, 124.25, 122.16, 121.97, 121.56 (q, $^1J_{C-F}$ = 321.1 Hz, OTf), 28.59 (dd, $^1J_{C-P}$ = 43.2 Hz, $^2J_{C-P}$ = 6.5 Hz), 25.19, 17.88, −3.99, −4.43. ^{31}P{^{1}H} NMR (CD_2Cl_2): 35.01 (s, $^1J_{Pt-P}$ = 3228.2 Hz). IR (cm^{-1}): 3490.3(br), 3061.1(br), 2961.6(m), 2927.9(w), 2856.9(w), 1611.3(s), 1480.2(m), 1472.5(m), 1437.4(m), 1360.3(m), 1265.1(m), 1256.8(s), 1224.2(m), 1157.6(s), 1106.1(m), 1034.3(s), 998.8(m), 841.9(w), 813.9(s), 721.1(m), 692.5(m), 637.7(s), 536.6(s), 536.5(m).

[Pd(dppe)(L$_3$)]$_4$[OTf]$_8$ (5). The preparation is similar to that of **1**. Yield: 92%. ^{1}H NMR ($CDCl_3$), δ 8.88 (d, $^3J_{H-H}$ = 5.27 Hz, 16H), 7.96 (d, $^3J_{H-H}$ = 9.12 Hz, 8H), 7.92 (s, 8H), 7.79 (m, 32H), 7.57 (m, 32H), 7.48 (m, 40H), 7.35 (d, $^3J_{H-H}$ = 5.27 Hz, 16H), 7.08 (d, $^3J_{H-H}$ = 8.88 Hz, 8H), 6.87 (d, $^3J_{H-H}$ = 8.88 Hz, 8H), 4.23 (m, 8H), 4.07 (m, 8H), 3.61 (m, 16H), 3.54 (m, 32H), 3.43 (m, 16H), 3.13 (m, 16H). δ 155.89, 151.73, 149.81, 135.91, 132.89, 132.76, 132.53, 131.02, 130.21(m), 128.98, 127.82, 126.83, 122.78, 124.96, 124.01, 119.73, 121.04 (q, $^1J_{C-F}$ = 321.9 Hz, OTf), 116.98, 71.15, 70.89, 70.67, 70.05, 28.29 (dd, $^1J_{C-P}$ = 41.3 Hz, $^2J_{C-P}$ = 6.04 Hz). ^{31}P{^{1}H} NMR ($CDCl_3$): 63.05. IR (cm^{-1}): 3482.8(br), 3058.4(br), 2869.3(br), 1609.4(s), 1491.2(m), 1436.8(m), 1280.9(s), 1254.6(s), 1223.6(s), 1153.8(m), 1100.6(m), 1065.1(m), 1029.4(s), 997.5(m), 818.7(w), 708.9(w), 691.3(m), 637.5(s), 532.4(w), 516.2(m).

[Pt(dppe)(L$_3$)]$_4$[OTf]$_8$ (6). The preparation is similar to that of **2**. Yield: 83%. ^{1}H NMR (CD_2Cl_2): δ 8.84 (d, $^3J_{H-H}$ = 5.60 Hz, 16H), 8.08 (d, $^3J_{H-H}$ = 1.83 Hz, 8H), 8.07 (d, $^3J_{H-H}$ = 9.40 Hz, 8H), 7.89 (m, 32H), 7.68 (m, 16H), 7.61 (d, $^3J_{H-H}$ = 9.40 Hz, 8H), 7.57 (m, 32H), 7.49 (d, $^3J_{H-H}$ = 5.60 Hz, 16H), 7.18 (dd, $^3J_{H-H}$ = 8.98 Hz, $^4J_{H-H}$ = 1.83 Hz, 8H), 6.94 (d, $^3J_{H-H}$ = 8.98 Hz, 8H), 4.30 (m, 4H), 4.15 (m, 4H), 3.59 (m, 28H), 3.48 (m, 16H), 3.02 (m, 16H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 156.61, 152.01, 150.79, 135.08, 133.88, 133.76, 133.53, 130.92, 130.33(m), 129.39, 127.81, 126.64, 124.59, 124.47, 124.39, 119.88, 121.38 (q, $^1J_{C-F}$ = 321.1 Hz, OTf), 117.26, 71.10, 70.99, 70.87, 70.06, 28.56 (dd, $^1J_{C-P}$ = 44.3 Hz, $^2J_{C-P}$ = 5.84 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): 34.92 (s, $^1J_{Pt-P}$ = 3227.9 Hz). IR (cm^{-1}): 3488.7(br), 3052.4(br), 2876.6(br), 1611.3(s), 1493.1(m), 1436.9(m), 1353.1(m), 1256.9(s), 1223.9(s), 1154.5(m), 1106.5(m), 1070.3(m), 1029.8(s), 997.8(m), 820.2(w), 709.7(w), 693.1(m), 637.7(s), 536.1(m).

[Pd(dppe)(L$_4$)]$_4$[OTf]$_8$ (7). The preparation is similar to that of **1**. Yield: 88.5%. ^{1}H NMR ($CDCl_3$): δ 8.69 (d, $^3J_{H-H}$ = 6.16 Hz, 16H), 7.92 (d, $^3J_{H-H}$ = 9.22 Hz, 8H), 7.82 (m, 40H), 7.55 (m, 48H), 7.40 (d, $^3J_{H-H}$ = 9.22 Hz, 8H), 7.31 (d, $^3J_{H-H}$ = 16.31 Hz, 8H), 7.24 (dd, $^3J_{H-H}$ = 9.43 Hz, $^4J_{H-H}$ = 1.37 Hz, 8H), 7.16 (d, $^3J_{H-H}$ = 6.14 Hz, 16H), 6.93 (d, $^3J_{H-H}$ = 9.43 Hz, 8H), 6.65 (d, $^3J_{H-H}$ = 16.31 Hz, 8H), 4.07 (m, 16H), 2.89 (m, 16H), 1.06 (t, $^3J_{H-H}$ = 7.07 Hz, 24H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 155.78, 150.78, 148.37, 137.13, 134.91, 133.79, 133.76, 133.49, 130.94, 130.35(m), 129.81, 129.30, 126.07, 123.58, 123.17, 123.11, 121.48 (q, $^1J_{C-F}$ = 326.5 Hz, OTf), 120.32, 116.10, 65.29, 28.64 (dd, $^1J_{C-P}$ = 39.1 Hz, $^2J_{C-P}$ = 8.8 Hz), 15.05. ^{31}P{^{1}H} NMR (CD_2Cl_2): 62.04. IR (cm^{-1}): 3479.1(br), 3059.8(br), 2984.7(br), 1603.8(s), 1534.5(m), 1507.2(m), 1469.2(m), 1437.2(s), 1383.6(m), 1333.8(m), 1262.6(s), 1258.1(s), 1159.2(m), 1105.7(m), 1029.2(s), 822.9(w), 747.6(w), 708.5(m), 691.5(w), 637.2(s), 537.1(m).

[Pt(dppe)(L$_4$)]$_4$[OTf]$_8$ (8). The preparation is similar to that of **2**. Yield: 83.3%. ^{1}H NMR ($CDCl_3$): δ 8.69 (d, $^3J_{H-H}$ = 6.10 Hz, 16H), 7.92 (d, $^3J_{H-H}$ = 9.61 Hz, 8H), 7.82 (m, 40H), 7.58 (m, 16H), 7.53 (m, 32H), 7.41 (d, $^3J_{H-H}$ = 9.61 Hz, 8H), 7.32 (d, $^3J_{H-H}$ = 16.56 Hz, 8H), 7.24 (d, $^3J_{H-H}$ = 9.18 Hz, 8H), 7.16 (d, $^3J_{H-H}$ = 6.10 Hz, 16H), 6.93 (d, $^3J_{H-H}$ = 9.18 Hz, 8H), 6.65 (d, $^3J_{H-H}$ = 16.56 Hz, 8H), 4.07 (m, 16H), 2.90 (m, 16H), 1.06 (t, $^3J_{H-H}$ = 7.13 Hz, 24H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 155.88, 150.54, 149.04, 137.86, 135.00, 133.83, 133.60, 130.82, 130.40(m), 130.08, 129.28, 126.03, 124.88, 124.23, 123.67, 123.57, 122.74, 121.62 (q, $^1J_{C-F}$ = 320.3 Hz, OTf), 120.31, 116.11, 65.29, 28.61 (dd, $^1J_{C-P}$ = 43.7 Hz, $^2J_{C-P}$ = 9.1 Hz), 15.05. ^{31}P{^{1}H} NMR (CD_2Cl_2): 35.10 (s, $^1J_{Pt-P}$ = 3214.1 Hz). IR (cm^{-1}): 3497.2(br), 3064.3(br), 2979.5(m), 1605.1(s), 1499.7(m), 1469.1(s), 1437.1(s), 1256.9(s), 1223.9(s), 1158.3(s), 1108.3(m), 1029.8(s), 997.9(m), 967.2(w), 826.3(m), 721.6(m), 709.7(w), 692.5(s), 637.4(s), 536.3(s), 516.1(m).

[Pd(dppe)(L$_5$)]$_4$[OTf]$_8$ (9). The preparation is similar to that of **1**. Yield: 89%. ^{1}H NMR (CD_2Cl_2), δ 8.69 (d, $^3J_{H-H}$ = 5.87 Hz, 16H), 7.78 (m, 56H), 7.53 (m, 40H), 7.29 (d, $^3J_{H-H}$ = 16.63 Hz, 8H), 7.25 (d, $^3J_{H-H}$ = 8.43 Hz, 8H), 7.17 (d, $^3J_{H-H}$ = 9.10 Hz, 8H), 7.13 (d, $^3J_{H-H}$ = 5.87 Hz, 16H), 7.01 (d, $^3J_{H-H}$ = 8.43 Hz, 8H), 6.67 (d, $^3J_{H-H}$ = 16.63 Hz, 8H), 3.09 (m, 16H), 0.45 (s, 72H), 0.04 (s, 24H), −0.15 (s, 24H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 152.87, 148.46, 137.31, 135.46, 133.84, 133.50, 133.48, 130.82, 130.33(m), 129.93, 129.73, 129.47, 126.55, 126.31, 125.76, 123.35, 123.18, 122.99, 121.09 (q, $^1J_{C-F}$ = 320.9 Hz, OTf), 121.57, 28.61 (dd, $^1J_{C-P}$ = 41.2 Hz, $^2J_{C-P}$ = 7.8 Hz), 25.18, 17.88, −4.07, −4.38. ^{31}P{^{1}H} NMR ($CDCl_3$): 62.01. IR (cm^{-1}): 3504.7(br), 3064.6(br), 2929.0(m), 2854.8(m), 1604.3(s), 1550.5(m), 1470.1(s), 1437.0(m), 1383.6(m),

1358.7(m), 1269.1(s), 1253.2(s), 1159.9(m), 1104.4(m), 1081.9(m), 1029.9(s), 998.2(m), 824.8(w), 779.8(w), 708.6(m), 690.3(w), 637.4(s), 533.0(m).

[Pt(dppe)(L$_5$)]$_4$[OTf]$_8$ (10). The preparation is similar to that of **2**. Yield: 74%. ^{1}H NMR ($CDCl_3$): δ 8.69 (d, $^3J_{H-H}$ = 6.45 Hz, 16H), 7.84 (m, 40H), 7.55 (m, 56H), 7.32 (d, $^3J_{H-H}$ = 16.63 Hz, 8H), 7.25 (dd, $^3J_{H-H}$ = 9.01 Hz, $^4J_{H-H}$ = 1.69 Hz, 8H), 7.18 (d, $^3J_{H-H}$ = 9.25 Hz, 8H), 7.16 (d, $^3J_{H-H}$ = 6.45 Hz, 16H), 7.01 (d, $^3J_{H-H}$ = 9.01 Hz, 8H), 6.67 (d, $^3J_{H-H}$ = 16.63 Hz, 8H), 2.92 (m, 16H), 0.45 (s, 72H), 0.04 (s, 24H), −0.14 (s, 24H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 152.96, 150.50, 149.09, 138.00, 135.54, 133.84, 133.56, 130.69, 130.35(m), 130.00, 129.45, 126.56, 124.86, 124.22, 123.64, 123.33, 122.62, 122.43, 121.60, 121.57 (q, $^1J_{C-F}$ = 320.7 Hz, OTf), 28.61 (dd, $^1J_{C-P}$ = 45.0 Hz, $^2J_{C-P}$ = 5.9 Hz), 25.12, 17.87, −4.07, −4.38. ^{31}P{^{1}H} NMR (CD_2Cl_2): 35.08 (s, $^1J_{Pt-P}$ = 3216.5 Hz). IR (cm^{-1}): 3487.1(br), 3054.2(br), 2982.5(w), 1601.8(s), 1482.1(m), 1471.1(s), 1452.6(s), 1321.8(w), 1251.8(s), 1235.1(s), 1192.2(w), 1163.3(s), 1112.3(m), 1020.9(s), 1000.3(m), 992.5(m), 982.6(w), 965.6(w), 856.3(m), 712.9(m), 711.7(w), 695.1(s), 641.1(s), 536.7(s), 515.3(m).

[Pd(dppe)(L$_6$)]$_4$[OTf]$_8$ (11). The preparation is similar to that of **1**. Yield: 91%. ^{1}H NMR ($CDCl_3$): δ 8.70 (d, $^3J_{H-H}$ = 5.74 Hz, 16H), 7.92 (d, $^3J_{H-H}$ = 9.51 Hz, 8H), 7.91 (m, 40H), 7.55 (m, 16H), 7.49 (m, 32H), 7.45 (d, $^3J_{H-H}$ = 9.51 Hz, 8H), 7.29 (d, $^3J_{H-H}$ = 17.11 Hz, 8H), 7.25 (d, $^3J_{H-H}$ = 8.56 Hz, 8H), 7.14 (d, $^3J_{H-H}$ = 5.74 Hz, 16H), 6.94 (d, $^3J_{H-H}$ = 8.56 Hz, 8H), 6.65 (d, $^3J_{H-H}$ = 17.11 Hz, 8H), 4.22 (m, 8H), 4.05 (m, 8H), 3.61 (m, 16H), 3.49 (m, 32H), 3.38 (m, 16H), 3.07 (m, 16H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 156.34, 150.42, 148.42, 137.15, 134.93, 133.85, 133.54, 131.21, 130.39(m), 129.77, 129.66, 126.14, 123.32, 123.25, 123.18, 122.13 (q, $^1J_{C-F}$ = 318.97 Hz, OTf), 119.98, 117.01, 71.17, 71.02, 70.93, 70.22, 70.12, 28.68 (dd, $^1J_{C-P}$ = 41.1 Hz, $^2J_{C-P}$ = 7.48 Hz). ^{31}P-{^{1}H} NMR ($CDCl_3$): 62.58. IR (cm^{-1}): 3476.2(br), 3051.8(br), 2918.5(br), 1684.6(m), 1654.1(m), 1604.1(s), 1476.3(m), 1437.4(m), 1258.3(s), 1223.4(s), 1152.5(m), 1098.6(m), 1029.5(s), 998.2(m), 877.9(w), 824.6(w), 749.3(w), 708.2(m), 690.9(m), 637.3(s), 571.3(m).

[Pt(dppe)(L$_6$)]$_4$[OTf]$_8$ (12). The preparation is similar to that of **2**. Yield: 91%. ^{1}H NMR ($CDCl_3$): δ 8.70 (d, $^3J_{H-H}$ = 6.48 Hz, 16H), 7.92 (d, $^3J_{H-H}$ = 9.36 Hz, 8H), 7.82 (m, 40H), 7.58 (m, 16H), 7.53 (m, 24H), 7.46 (d, $^3J_{H-H}$ = 9.36 Hz, 8H), 7.32 (d, $^3J_{H-H}$ = 16.45 Hz, 8H), 7.25 (dd, $^3J_{H-H}$ = 9.78 Hz, $^4J_{H-H}$ = 1.45 Hz, 8H), 7.17 (d, $^3J_{H-H}$ = 6.48 Hz, 16H), 6.93 (d, $^3J_{H-H}$ = 9.78 Hz, 8H), 6.65 (d, $^3J_{H-H}$ = 16.45 Hz, 8H), 4.22 (m, 4H), 4.05 (m, 4H), 3.61 (m, 16H), 3.50 (m, 24H), 3.38 (m, 16H), 2.89 (m, 16H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 156.31, 151.02, 149.01, 137.45, 134.98, 133.23, 132.78, 131.24, 130.09(m), 129.82, 129.54, 125.63, 123.32, 123.72, 122.80, 121.69 (q, $^1J_{C-F}$ = 320.56 Hz, OTf), 119.82, 117.21, 71.08, 70.92, 70.84, 70.15, 70.02, 28.54 (dd, $^1J_{C-P}$ = 45.3 Hz, $^2J_{C-P}$ = 5.73 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): 34.54 (s, $^1J_{Pt-P}$ = 3213.9 Hz). IR (cm^{-1}): 3471.1(br), 3051.2(br), 2975.5(br), 1654.5(m), 1605.7(s), 1540.1(m), 1473.6(m), 1437.2(s), 1258.1(s), 1223.4(s), 1162.6(m), 1106.9(m), 1030.0(m), 825.0(m), 754.8(w), 709.6(w), 692.6(m), 637.5(s), 535.6(w), 517.5(m).

[Pd(dppe)(L$_4$)]$_4$[OTf]$_8$ (13). The preparation is similar to that of **7** except racemic ligand was used. Yield: 95%. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.53 (d $^3J_{H-H}$ = 13.3 Hz, 4H), 8.51 (d $^3J_{H-H}$ = 15.3 Hz, 4H), 7.95 (d, $^3J_{H-H}$ = 8.0 Hz, 4H), 7.76 (m, 20H), 7.52 (m, 24H), 7.43 (d, $^3J_{H-H}$ = 7.3 Hz, 4H), 7.29 (dd, $^3J_{H-H}$ = 16.7 Hz, $^4J_{H-H}$ = 3.3 Hz, 4H), 7.22 (d, $^3J_{H-H}$ = 10.7 Hz, 4H), 7.14 (d, $^3J_{H-H}$ = 6.7 Hz, 8H), 6.85 (d, $^3J_{H-H}$ = 8.0 Hz, 2H), 6.84 (d, $^3J_{H-H}$ = 9.3 Hz, 2H), 6.73 (d, $^3J_{H-H}$ = 14.0 Hz, 2H), 6.68 (d, $^3J_{H-H}$ = 14.7 Hz, 2H), 4.05 (m, 8H), 3.05 (m, 8H), 1.10 (t, $^3J_{H-H}$ = 6.33 Hz, 12H). ^{31}P{^{1}H} NMR (CD_2Cl_2): 62.95. IR (cm^{-1}): 3490.79(br), 3058.29(br), 2979.84(br), 1604.07(s), 1469.96(w), 1437.22(m), 1277.67(s), 1258.61(s), 1159.40(m), 1106.62(m), 1029.77(s), 812.42(w), 691.78(w), 637.77(s), 533.40(m). MS (ES): *m*/*z* 1201.0 (M − 2OTf)$^{2+}$, calcd 1202.6; 751.1 (M − 3OTf)$^{3+}$, calcd 752.2.

[Pt(dppe)(L$_4$)]$_4$[OTf]$_8$ (14). The preparation is similar to that of **8** except racemic ligand was used. Yield: 93%. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.61 (d, $^3J_{H-H}$ = 6.10 Hz, 4H), 8.58 (d, $^3J_{H-H}$ = 6.10 Hz, 4H), 7.96 (d, $^3J_{H-H}$ = 9.61 Hz, 4H), 7.81 (m, 20H), 7.59 (m, 24H), 7.44 (d, $^3J_{H-H}$ = 9.61 Hz, 4H), 7.38 (d, $^3J_{H-H}$ = 16.56 Hz, 4H), 7.27 (d, $^3J_{H-H}$ = 9.18 Hz, 4H), 7.20 (d, $^3J_{H-H}$ = 6.10 Hz, 8H), 6.88 (d, $^3J_{H-H}$ = 9.18 Hz, 2H), 6.86 (d, $^3J_{H-H}$ = 9.18 Hz, 2H), 6.78 (d, $^3J_{H-H}$ = 9.18 Hz, 2H), 6.75 (d, $^3J_{H-H}$ = 9.18 Hz, 2H), 4.13 (q, $^3J_{H-H}$ = 5.20 Hz, 8H), 2.90 (m, 8H), 1.13 (t, $^3J_{H-H}$ = 6.40 Hz, 12H). ^{31}P{^{1}H} NMR (CD_2Cl_2): 37.40 (s, $^1J_{Pt-P}$ = 3880.0 Hz). IR (cm^{-1}): 3466.69(br), 3059.70(br), 2979.40(m), 1604.73(s), 1469.70(w), 1437.61(m), 1273.79(s), 1260.09(s), 1158.44((m), 1108.98(w), 1030.41(s), 823.30(w), 695.15(w), 637.84(m), 535.92(w). MS (ES): *m*/*z* 1290.0 (M − 2OTf)$^{2+}$, 1291.3; 810.2 (M − 3OTf)$^{3+}$, calcd 811.2.

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Supporting Information Available: Additional figures and experimental information. This material is available free of charge via the Internet at http://pubs.acs.org.

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