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Synthesis of Chiral Cleft *C,N*-Palladium and Iridium Complexes from 2,3:6,7-Dibenzobicyclo[3.3.1]nona-2,6-diene-4,8-dione and Their Synthetic Applications

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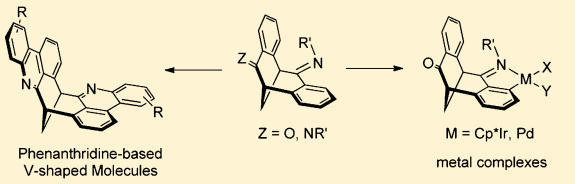
Supporting Information

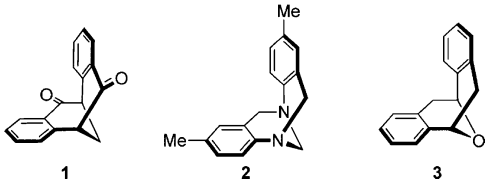
ABSTRACT: A transition-metal-mediated functionalization of 2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene-4,8-dione is reported. By the use of the corresponding imine, iridium or palladium complexes were prepared, and they were well characterized by NMR and single-crystal X-ray crystallographic analysis. The catalytic activity of these two metal complexes was briefly investigated in hydrogenation and 1,2-addition reactions. Finally, the catalytic bromination of 2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene-4,8-dione was realized in the presence of NBS and $Pd(OAc)_2$. Subsequently a new class of V-shaped molecules with biphenanthridine skeletons were synthesized.



INTRODUCTION

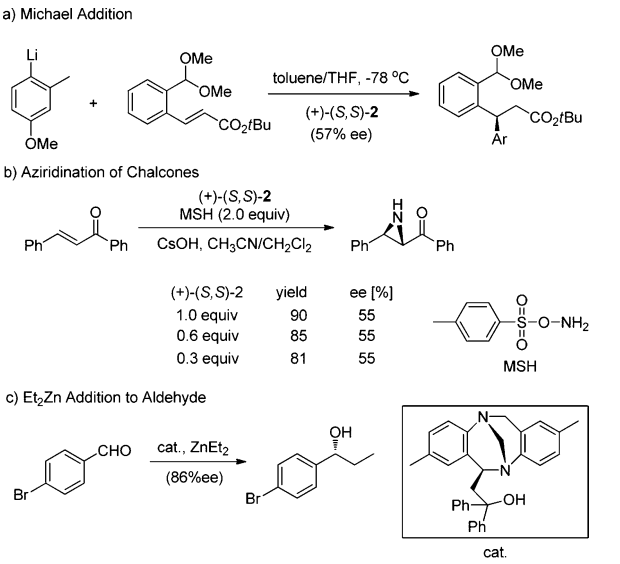
Cleftlike molecules, such as 2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene-4,8-dione **1**,[1] Tröger base **2**[2] and Kagan's ether **3**,[3] represent a class of unique chiral molecules (Chart 1). The

Chart 1. Cleftlike Molecules



bridged systems lead these molecules to be highly rigid, where two phenyl groups are almost perpendicular to each other. Tröger base **2** was an excellent module that could be used in host–guest[4] as well as "molecular torsion balance" studies.[5,6] Compound **2** was synthesized as early as 1887,[7] and it contains two nitrogen chiral centers stabilized by the rigid skeleton. Its enantiomers were easily obtained via dynamic kinetic resolution with (−)-1,1′-binaphthyl-2,2′-diyl hydrogen phosphate as the chiral reagent.[8] Recently, we reported a practical resolution of diketone **1** by the use of commercially available optically pure [1,1′-binaphthalene]-2,2′-diol (BINOL).[9] Multiple grams of optically pure **1** were obtained from 2-phenylacetonitrile without column chromatography, and BINOL was recovered over 95% yield. Despite these successes in the preparation of optically pure cleftlike molecules, there have only been a few studies on the catalytically asymmetric reactions by the use of these V-shaped chiral skeletons as ligands or catalysts.[10] As an example, optically active Tröger bases were used as ligands or catalysts in Michael addition and aziridination of unsaturated carbonyl compounds, and moderate asymmetric inductions were observed (Scheme 1a,b).[11] The amino alcohol derivative was also applied in the addition of Et_2Zn to aromatic aldehydes,

Scheme 1. Applications of Tröger Base Analogues in Asymmetric Catalysis



with up to 86% ee being achieved (Scheme 1c).[12] Herein we report our efforts on the synthesis and applications of *C,N*-palladium and iridium complexes based on chiral diketone **1**.

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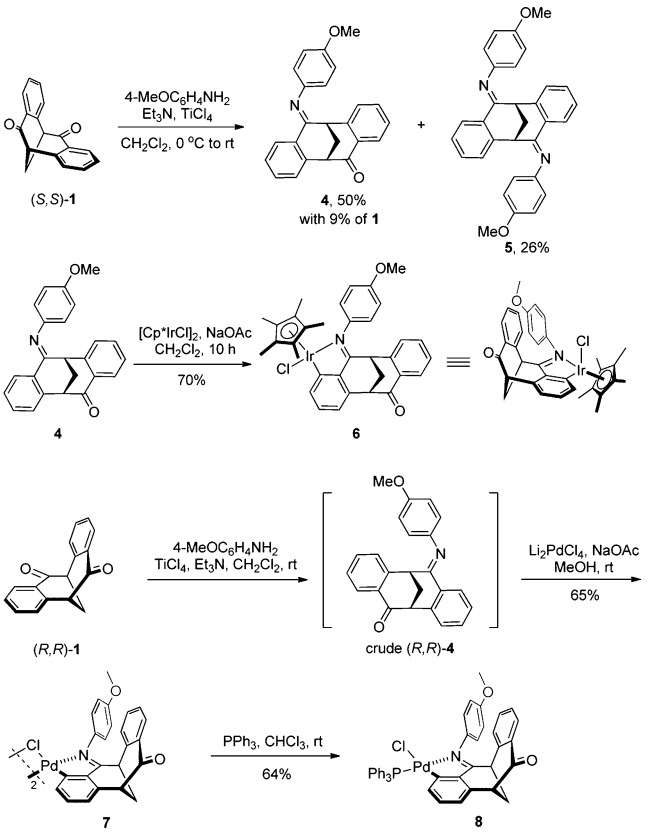
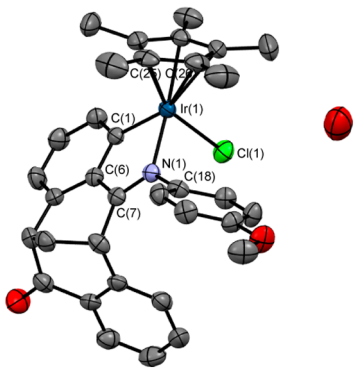
RESULTS AND DISCUSSION

Synthesis of Iridium and Palladium Complexes. The diketone compound has a rigid dihedral angle of around 100°. The chirality of **1** is more stable than that of Tröger base, which undergoes racemization via acid-mediated ring-opening and ring-closing processes.[13] As a synthetic organic research group, we have given our attention to the structures and catalytic activity of **1**-based metal complexes. It was anticipated that the highly rigid structure of these V-shaped molecules was beneficial for asymmetric induction. Furthermore, *C,N*-metallacycles, particularly for palladium complexes, have additional electronic advantages for minimizing transition states: neutral substrates bind trans to the N atom, and anionic ligands prefer the position trans to the C donor.[14] With this hypothesis in mind, the diketone (*S,S*)-**1** was converted to monoimine **4** along with 26% of diimine **5** under the catalysis of titanium tetrachloride. The monoimine **4** was usually contaminated with 9% of starting material (*S,S*)-**1** after purification, however, which did not affect the further synthesis of the metal complexes. The treatment of **4** and $[Cp^*IrCl_2]_2$ with NaOAc in CH_2Cl_2 successfully gave complex **6** in 70% yield (Scheme 2). Single crystals were obtained by slow volatilization of a solution of **6** in acetone (Figure 1).[15] It should be noted that the existence of diimine **5** and diketone **1** did not affect the reaction between imine **4** and $[Cp^*IrCl_2]_2$. The reaction uneventfully delivered the pure monometalated product **6** after column chromatographic purification on silica gel. The treatment of the crude imine **4** with Li_2PdCl_4 in the presence of NaOAc gave palladium dimer **7** in 58% overall yield. Pleasingly, single crystals that were suitable for X-ray analysis were obtained and the palladium dimer manifests a "Π-shaped" structure (Figure 2).[16] The dimer **7** was dissociated to monomer **8** by the treatment of 2.0 equiv of triphenylphosphine ligand.[17]

Scheme 2. Synthesis of Ir and Pd Complexes



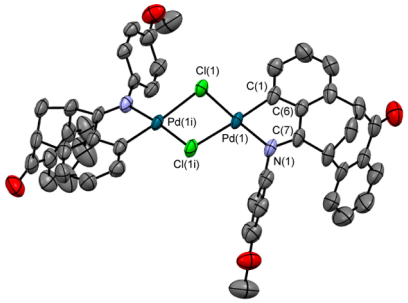


Selected bond distances (Å) and angles (°)

Ir(1)-Cl(1)	2.4058(17)
Ir(1)-N(1)	2.127(5)
Ir(1)-C(26)	2.273(8)
Ir(1)-C(25)	2.154(7)
Ir(1)-C(1)	2.029(6)
N(1)-Ir(1)-Cl(1)	88.22(15)
N(1)-Ir(1)-C(26)	104.3(3)
N(1)-Ir(1)-C(25)	101.6(3)
C(26)-Ir(1)-Cl(1)	116.1(2)
C(25)-Ir(1)-Cl(1)	153.8(2)
C(25)-Ir(1)-C(26)	38.0(3)
C(1)-Ir(1)-Cl(1)	89.12(19)
C(1)-Ir(1)-N(1)	77.9(2)
C(1)-Ir(1)-C(26)	154.6(3)
C(1)-Ir(1)-C(25)	116.6(3)

Figure 1. ORTEP drawing of iridium complex **6**.

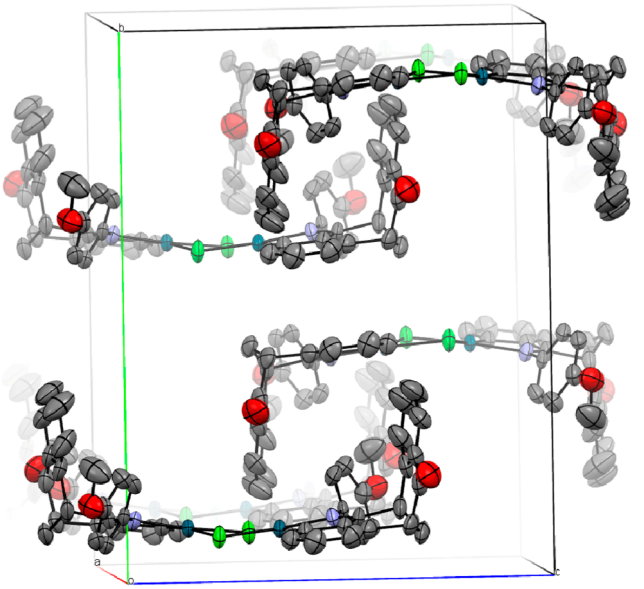
Synthetic Applications of Metal Complexes. Iridium and palladium complexes are widely used in reduction,[18] oxidation,[19] and C−C bond formation reactions.[20] With the



Selected bond distances (Å) and angles (°)

Pd(1)-C(1)	1.977(8)
Pd(1)-N(1)	2.039(6)
Pd(1)-Cl(1)	2.3375(16)
Pd(1)-Cl(1i)	2.4514(17)
Cl(1)-Pd(1i)	2.4513(17)
C(1)-Pd(1)-N(1)	80.9(3)
C(1)-Pd(1)-Cl(1)	95.0(2)
N(1)-Pd(1)-Cl(1)	174.31(17)
C(1)-Pd(1)-Cl(1i)	174.1(2)
N(1)-Pd(1)-Cl(1i)	98.90(18)
Cl(1)-Pd(1)-Cl(1i)	85.62(6)
Pd(1)-Cl(1)-Pd(1i)	93.38(6)

a) ORTEP drawing of **7**



b) packing of complex **7**

Figure 2. Structure of palladium dimer **7**.

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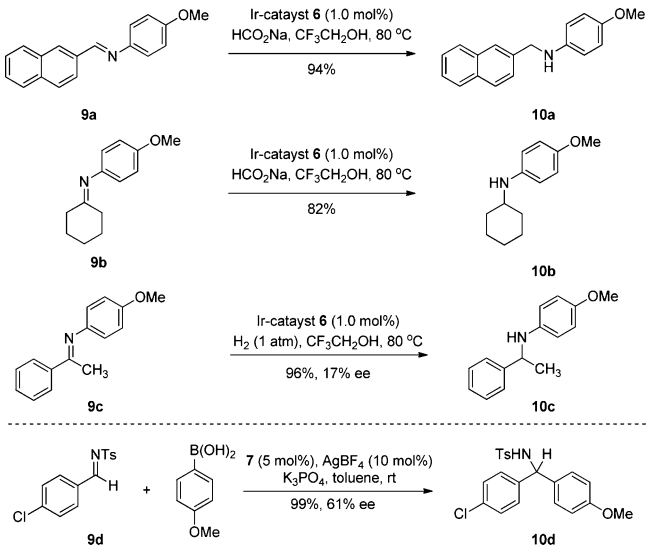
metal complexes **6** and **7** in hand, we briefly investigated their catalytic activity. In the presence of 1 mol % of iridium complex **6**, β-naphthaldehyde-derived imine **9a** was efficiently reduced to amine with HCO_2Na as the reagent (Scheme 3).[21] Under

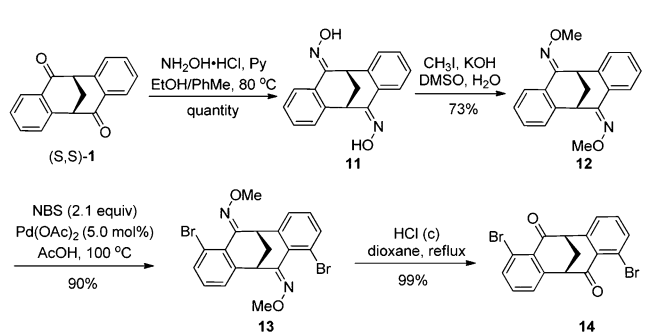
Scheme 3. Synthetic Applications of Metal Complexes



identical conditions, the cyclic ketone imine **9b** was reduced to the corresponding amine in 82% yield. Under 1 atm of hydrogen gas, acetophenone-derived imine **9c** was converted to **10c** in excellent yield, whereas only a low level of asymmetric induction was observed. A cationic palladium species from complex **7** was able to catalyze the 1,2-addition of aryl boronic acid to imines. For example, the reaction of **9d** with (4-methoxyphenyl)boronic acid in the presence of dimer **7** and $AgBF_4$ gave **10d** in quantitative yield with moderate enantioselectivity.[22]

Synthesis of Phenanthridine-Based V-Shaped Molecules. The synthesis of diketone **1** has poor functional group tolerance, since it requires a formidable amount of concentrated sulfuric acid in the acylation step. Thus, only extremely limited analogues of the diketone **1** have been synthesized until now. The synthesis of iridium and palladium complexes clearly indicated that the imines were promising directing groups for the C−H functionalization of the phenyl ring. Thus, the treatment of (*S*,*S*)-**1** with hydroxylamine hydrochloride in heated EtOH/PhMe afforded a quantitative yield of dioxime **11** with perfect *E* selectivity,[23] which was subsequently methylated to form **12** (Scheme 4). Bromination of *O*-methyl oxime was successfully realized with a catalytic amount of $Pd(OAc)_2$ in hot

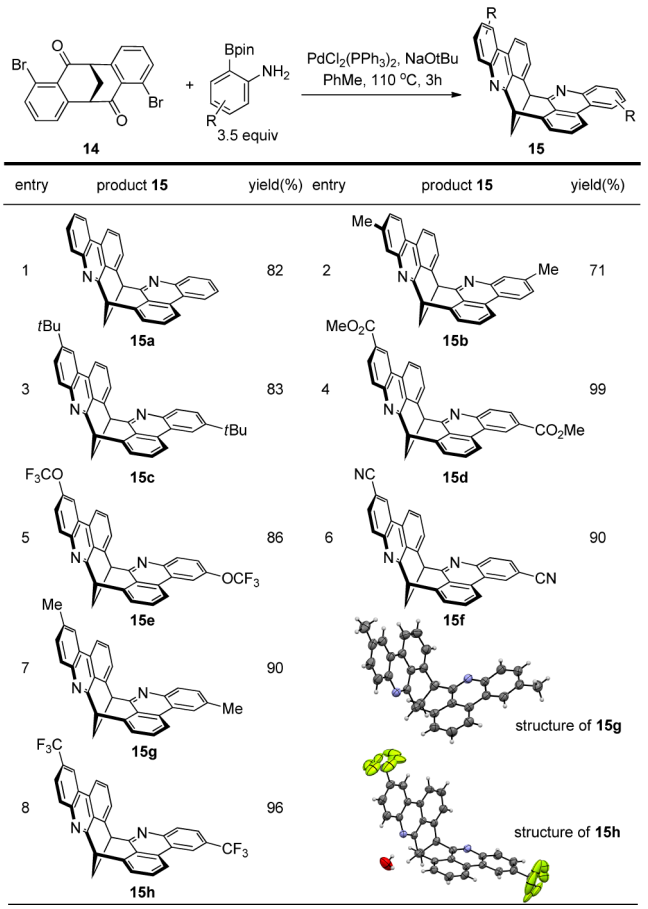
Scheme 4. Synthesis of Dibromo Ketone



acetic acid.[24] Finally, the exploration of **13** to HCl(c) delivered the dibrominated compound **14** in excellent yield.

Consequently, we proceeded to explore the feasibility of Suzuki cross-coupling with various substituted (2-aminophenyl)boronic esters (Scheme 5). The reactions

Scheme 5. Phenanthridine-Based V-Shaped Molecule Synthesis



proceeded uneventfully, and the products spontaneously aromatized to phenanthridine rings in good to excellent yields. Functional groups, such as methyl, *tert*-butyl, methyl ester, trifluoromethyl, trifluoromethoxyl, and nitrile, in (2-aminophenyl)boronic ester components were well tolerated. Single crystals for compounds **15g,h** were obtained, and an X-ray crystallographic analysis was performed. The structure clearly manifested that the dihedral angles of the two phenanthridine moieties were around 105−110°.[25,26]

CONCLUSION

In summary, we performed studies on the functionalization reactions of the optically active V-shaped molecule **1**. Metal complexes, such as iridium compound **6** and palladium complexes **7** and **8**, were prepared from the imine derivatives. The first two metal complexes were further characterized by X-ray crystallographic analysis and displayed moderate to excellent activity and selectivity in hydrogenations and 1,2-addition reactions. Finally, the direct bromination reaction of *O*-methyl oxime realized the functionalization of (*S*,*S*)-**1** to dibromo compound **14**, which provided an entry for the

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synthesis of phenanthridine-based V-shaped molecules **15** in good to excellent yields.

EXPERIMENTAL SECTION

General Information. All reactions were carried out under a nitrogen atmosphere in flame-dried glassware, unless the reaction procedure states otherwise. Anhydrous toluene was obtained by distillation from CaH_2, and anhydrous methanol was obtained by distillation from Mg powder. Other solvents were used without any further purification. Room-temperature reactions were carried out between 20 and 25 °C. Flash column chromatography was performed using 40−63 μm silica gel as the stationary phase. ^{1}H and ^{13}C NMR spectra were referenced by using the solvent residue as an internal reference (^{1}H NMR, 7.26 ppm for $CDCl_3$; ^{13}C NMR, 77.00 ppm for $CDCl_3$). Electron spray inization (ESI) mass spectrometry data were acquired by using an LTQ analyzer type instrument.

Synthesis of Ir Complex (*S,S*)-6. A solution of titanium(IV) chloride in dichloromethane (1.0 M, 4.0 mL) was added to a mixture of (*S,S*)-**1** (2.00 g, 8.06 mmol), 4-methoxyaniline (2.38 g, 19.3 mmol, 2.4 equiv), triethylamine (2.80 mL), and dichloromethane (40 mL) at 0 °C dropwise. After 10 h, the reaction mixture was quenched with water and extracted with dichloromethane. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on neutral alumina (hexane/ethyl acetate 5/1) to afford a yellow solid. Recrystallization of the above crude material was carried out in hot methanol, and the solid was collected by filtration to give pure bis-imine **5** (0.97 g, 15%). The filtrate was concentrated to afford the crude product imine (1.67 g, 50% of **4** and 9% of diketone **1**).

Analytical Data for Compound 4. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (dd, *J* = 7.6, 1.2 Hz, 1 H), 7.92 (dd, *J* = 8.0, 1.6 Hz, 1 H), 7.43−7.37 (m, 2 H), 7.35−7.30 (m, 2 H), 7.26 (td, *J* = 7.6, 1.2 Hz, 1 H), 7.03 (d, *J* = 8.8 Hz, 2 H), 6.85−6.80 (m, 3 H), 4.70 (t, *J* = 2.8 Hz, 1 H), 4.00 (t, *J* = 2.8 Hz, 1 H), 3.88 (s, 3 H), 2.81 (dt, *J* = 13.2, 3.2 Hz, 1 H), 2.75 (dt, *J* = 13.2, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.2, 163.4, 156.1, 144.0, 141.8, 136.2, 133.9, 131.5, 131.4, 129.4, 128.8, 128.6, 128.3, 128.04, 128.02, 127.1, 120.7, 114.6, 55.5, 48.6, 36.5, 31.9. HRMS (ESI): calcd for $C_{24}H_{20}NO_2$ $[M + H]^+$ 354.1494, found 354.1505.

Analytical Data for Compound 5. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16−8.12 (m, 2 H), 7.25−7.20 (m, 4 H), 7.03 (d, *J* = 8.8 Hz, 4 H), 6.87−6.82 (m, 6 H), 4.65 (t, *J* = 2.8 Hz, 2 H), 3.88 (s, 6 H), 2.60 (t, *J* = 2.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9, 156.0, 144.2, 138.5 131.9, 131.0, 128.5, 127.7, 127.0, 120.9, 114.6, 55.5, 36.4, 31.9. HRMS (ESI): calcd for $C_{31}H_{27}N_2O_2$ $[M + H]^+$ 459.2073, found 459.2084.

A mixture of the above crude **4** (70.7 mg, ∼ 0.178 mmol), $[Cp^*IrCl_2]_2$ (79.7 mg, 0.10 mmol), and NaOAc (82.0 mg, 1.0 mmol) in dichloromethane (4.0 mL) was stirred at room temperature for 10 h in air. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate 3/1) to afford (*S,S*)-**6** as a red solid (0.131 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (dd, *J* = 8.8, 2.4 Hz, 1 H), 7.86 (dd, *J* = 6.4, 2.8 Hz, 1 H), 7.66 (dd, *J* = 7.2, 0.4 Hz, 1 H), 7.22−7.19 (m, 2 H), 7.5 (t, *J* = 7.2 Hz, 1 H), 7.12 (dd, *J* = 8.8, 3.2 Hz, 1 H), 7.02 (d, *J* = 6.4 Hz, 2 H), 6.96 (dd, *J* = 8.4, 2.4 Hz, 1 H), 6.43−6.41 (m, 1 H), 4.61 (t, *J* = 2.8 Hz, 1 H), 3.93 (s, 3 H), 3.91 (t, *J* = 2.8 Hz, 1 H), 2.78 (dt, *J* = 13.6, 3.2 Hz, 1 H), 2.73 (dt, *J* = 13.2, 2.8 Hz, 1 H), 1.42 (s, 15 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.9, 180.8, 169.4, 158.1, 143.1, 142.2, 141.5, 137.4, 134.7, 133.8, 132.7, 129.1, 128.4, 128.3, 128.2, 126.2, 123.4, 121.1, 115.2, 112.6, 89.2, 55.6, 48.5, 37.4, 33.2, 8.6. HRMS (ESI): calcd for $C_{34}H_{33}IrNO_2$ $[M - Cl]^+$ 680.2141, found 680.2144.

Synthesis of Palladium Complex 7. A mixture of $PdCl_2$ (88.7 mg, 0.50 mmol) and LiCl (43.0 mg, 1.0 mmol) in methanol (5.0 mL) was stirred at room temperature for 24 h, and then a solution of crude (*R,R*)-**4** (0.177 g, ∼0.445 mmol) in methanol and NaOAc (45.1 mg, 0.55 mmol) was added to the mixture and stirred for another 12 h. The mixture was purified by column chromatography on silica gel (dichloromethane/methanol 50/1) to afford **7** as a yellow solid (143.5 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93−7.91 (m, 2 H), 7.32−7.26 (m, 4 H), 7.24−7.16 (m, 2 H), 7.12−6.89 (m, 12 H), 6.41−6.39 (m, 2 H), 4.41 (t, *J* = 2.8 Hz, 2 H), 3.91 (s, 6 H), 3.82 (t, *J* = 2.8 Hz, 2 H), 2.71 (dt, *J* = 13.2, 3.2 Hz, 2 H), 2.66 (dt, *J* = 13.6, 2.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.6, 181.4, 158.5, 141.4, 139.9, 138.6, 138.1, 134.0, 133.2, 132.0, 129.2, 128.9, 128.5, 127.2, 124.2, 123.9, 114.3, 113.8, 55.5, 47.9, 37.7, 33.3. HRMS (ESI): calcd for $C_{48}H_{36}ClN_2O_4Pd_2$ $[M - Cl]^+$ 951.0433, found 951.0513.

Synthesis of Monomer 8. A mixture of Pd complex **7** (24.7 mg, 0.025 mmol) and PPh_3 (13.1 mg, 0.050 mmol) in chloroform (1.25 mL) was stirred at room temperature for 10 h. The solvent was removed, and the residue was purified by flash chromatography on silica gel (dichloromethane/methanol 100/1) to afford **8** (24.3 mg, 64%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04−7.95 (m, 1 H), 7.70−7.66 (m, 6 H), 7.41−7.26 (m, 11 H), 7.18 (d, *J* = 8.4 Hz, 1 H), 7.08 (d, *J* = 8.4 Hz, 1 H), 7.01 (d, *J* = 8.8 Hz, 1 H), 6.99−6.91 (m, 2 H), 6.68−6.62 (m, 1 H), 6.54 (t, *J* = 7.6 Hz, 1 H), 6.37 (t, *J* = 6.8 Hz, 1 H), 4.66 (s, 1 H), 4.09−3.63 (m, 1 H), 3.84 (s, 3 H), 2.85−2.68 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.3, 181.4, 161.0, 157.8, 143.1, 140.7, 139.6, 138.5, 138.4, 137.9, 135.5, 135.4, 134.1, 131.52, 131.47, 131.2, 130.7, 130.60, 130.58, 129.4, 129.2, 128.6, 128.3, 128.0, 127.8, 124.0, 123.6, 113.5, 113.3, 55.4, 48.7, 38.2, 33.0. ^{31}P NMR (162 MHz, $CDCl_3$): δ 42.95. HRMS (ESI): calcd for $C_{42}H_{33}NO_2PPd$ $[M - Cl]^+$ 720.1284, found 720.1302.

4-Methoxy-*N*-(naphthalen-2-ylmethyl)aniline (10a). A mixture of **9a** (52.2 mg, 0.2 mmol), (*S,S*)-**6** (1.4 mg, 1 mol %), and sodium formate (68.0 mg, 1.0 mmol) in TFE (1.0 mL) was stirred at 80 °C for 90 min. The mixture was purified by column chromatography on silica gel (hexane/ethyl acetate 10/1) to afford **10a** as a solid (51.0 mg, 94%).

***N*-Cyclohexyl-4-methoxyaniline (10b).** A mixture of **9b** (34.7 mg, 0.2 mmol), (*S,S*)-**6** (1.4 mg, 1 mol %), and sodium formate (68.0 mg, 1.0 mmol) in TFE (1.0 mL) was stirred at 80 °C for 90 min. The mixture was purified by column chromatography on silica gel (hexane/ethyl acetate 10/1) to afford **10b** (28.6 mg, 82%).

4-Methoxy-*N*-(1-phenylethyl)aniline (10c). A mixture of **9c** (22.5 mg, 0.10 mmol) and (*S,S*)-**6** (0.70 mg, 1 mol %) was dissolved in trifluoroethanol, bubbled with hydrogen gas for 10 min, an then stirred at 85 °C under an H_2 atmosphere (1 atm) for 4 h. The mixture was purified by column chromatography on silica gel (hexane/ethyl acetate 10/1) to afford **10c** (22.0 mg, 96%, 17% ee) as a solid. HPLC (Daicel Chiracel OD-H column, column temperature 25 °C, *n*-hexane/2-propanol 95/5, flow rate 1.0 mL min^{-1}): 9.17 min (major enantiomer), 10.39 min (minor enantiomer).

***N*-((4-Chlorophenyl)(4-methoxyphenyl)methyl)-4-methylbenzenesulfonamide (10d).** A mixture of **9d** (29.3 mg, 0.1 mmol), (4-methoxyphenyl)boronic acid (30.4 mg, 0.2 mmol), (*R,R*)-**7** (4.9 mg, 5 mol %), $AgBF_4$ (2.0 mg, 10 mol %), and K_3PO_4 (64.0 mg, 0.3 mmol) in toluene (1.0 mL) was stirred at room temperature for 8 h. The mixture was purified by column chromatography on silica gel (hexane/ethyl acetate 5/1) to afford **10d** (40.0 mg, 99%, 61% ee) as a solid. HPLC (Daicel Chiracel OD column, column temperature 25 °C, *n*-hexane/2-propanol 80/20, flow rate 1.0 mL min^{-1}): 10.99 min (minor enantiomer), 14.21 min (major enantiomer).

Synthesis of Dibromo Ketone 14. A mixture of (*S,S*)-**1** (3.72 g, 15.0 mmol, 1.0 equiv), $NH_2OH{\cdot}HCl$ (3.13 g, 45.0 mmol, 3.0 equiv), and pyridine (7.5 mL) in ethanol and toluene (60 mL, 1/1 v/v) was stirred at 80 °C for 4 h. After it was cooled to room temperature, the mixture was added to ethyl acetate (200 mL) and extracted with HCl (1 N, 50 mL × 3). The organic layer was washed with brine and dried over Na_2SO_4. After filtration, the solvent was removed to obtain **11** (4.17 g, >99%) as a white solid. $[\alpha]_D^{23}$ = −496 (*c* 0.63, EtOAc). ^{1}H NMR (400 MHz, DMSO): δ 11.53 (s, 2 H), 7.82 (dd, *J* = 8.0, 0.8 Hz, 2 H), 7.59 (dd, *J* = 7.6, 0.8 Hz, 2 H), 7.28 (td, *J* = 7.2, 1.2 Hz, 2 H), 7.18 (td, *J* = 8.0, 1.2 Hz, 2 H), 4.91 (t, *J* = 2.8 Hz, 2 H), 2.17 (t, *J* = 2.8 Hz, 2 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 152.0, 137.5, 129.6, 129.1, 128.9, 127.0, 123.5, 31.2, 28.0.

Potassium hydroxide (8.0 g, 140 mmol, 14 equiv) was added to a solution of **11** (2.78 g, 10 mmol) in DMSO/H_2O (1/1 v/v, 100 mL). After the mixture was stirred for 15 min, CH_3I (4.4 mL, 70.0 mmol,

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7.0 equiv) was added and this mixture was stirred overnight. The reaction mixture was quenched by the addition of water and extracted with ethyl acetate (100 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate 50/1) to afford **12** (2.20 g, 73%) as a white solid. $[\alpha]_D^{23} = -571$ (*c* 0.87, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.94 (dd, *J* = 8.0, 1.2 Hz, 2 H), 7.55 (dd, *J* = 7.6, 1.2 Hz, 2 H), 7.26 (td, *J* = 7.2, 1.2 Hz, 2 H), 7.16 (td, *J* = 8.0, 1.2 Hz, 2 H), 4.91 (t, *J* = 2.8 Hz, 2 H), 4.08 (s, 6 H), 2.27 (t, *J* = 2.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 137.4, 129.6, 129.5, 128.4, 127.1, 124.4, 62.1, 32.1, 28.8. HRMS (ESI): calcd for $C_{19}H_{19}N_2O_2$ $[M + H]^+$ 307.1447, found 307.1443.

A mixture of **12** (1.0 g, 3.26 mmol, 1.0 equiv), *N*-bromosuccinimide (1.22 g, 6.85 mmol, 2.1 equiv), and $Pd(OAc)_2$ (36.6 mg, 5 mol %) in AcOH (20 mL) was heated to 100 °C and stirred for 90 min. After the mixture was cooled to room temperature, the solvent was removed and the residue was purified by chromatography on silica gel (hexane/ethyl acetate 40/1) to afford **13** (1.36 g, 90%). $[\alpha]_D^{23} = -507$ (*c* 0.87, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (dd, *J* = 8.0, 1.6 Hz, 2 H), 7.38 (dd, *J* = 8.0, 1.6 Hz, 2 H), 7.03 (t, *J* = 8.0 Hz, 2 H), 5.17 (t, *J* = 3.2 Hz, 2 H), 4.13 (s, 6 H), 2.28 (t, *J* = 3.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.4, 140.0, 135.0, 129.6, 129.0, 127.9, 120.6, 62.5, 33.0, 29.4. HRMS (ESI): calcd for $C_{19}H_{17}N_2O_2Br_2$ $[M + H]^+$ 462.9657, found 462.9655.

A mixture of **13** (1.00 g, 2.15 mmol, 1.0 equiv) and HCl (12 *N*, 10 mL, 60 equiv) in dioxane (6 mL) was stirred at reflux for 36 h. After the mixture was cooled to room temperature, water (50 mL) was added and the resulting mixture was extracted with dichloromethane (30 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel (hexane/ethyl acetate 10/1) to afford **14** as a white solid (0.86 g, 99%). $[\alpha]_D^{23} = -658$ (*c* 0.92, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (dd, *J* = 7.6, 0.8 Hz, 2 H), 7.46 (dd, *J* = 7.6, 1.2 Hz, 2 H), 7.30 (t, *J* = 7.6 Hz, 2 H), 4.10 (t, *J* = 2.8 Hz, 2 H), 2.95 (t, *J* = 3.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 142.5, 136.5, 134.2, 128.8, 126.4, 123.6, 51.0, 30.7. HRMS (ESI): calcd for $C_{17}H_{11}O_2Br_2$ $[M + H]^+$ 404.9126, found 404.9124.

General Procedure for Synthesis of Phenanthridine-Based V-Shaped Molecules. Preparation of 15a. A mixture of **14** (30.0 mg, 0.074 mmol, 1.0 equiv), 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (56.7 mg, 0.26 mmol, 3.5 equiv), $PdCl_2(PPh_3)_2$ (3.6 mg, 7 mol %), and NaO-*t*-Bu (35.6 mg, 0.37 mmol) in toluene (5.0 mL) was refluxed for 3 h. After it was cooled to room temperature, the mixture was directly submitted to column chromatography on silica gel (hexane/ethyl acetate/dichloromethane 5/1/1) to give **15a** (24.0 mg, 82%) as a white solid. $[\alpha]_D^{23} = -670$ (*c* 0.575, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.40 (d, *J* = 8.0 Hz, 2 H), 8.36 (d, *J* = 7.6 Hz, 2 H), 8.17 (dd, *J* = 8.4, 0.8 Hz, 2 H), 8.02 (d, *J* = 7.2 Hz, 2 H), 7.73 (d, *J* = 8.0 Hz, 2 H), 7.70 (td, *J* = 8.4, 1.6 Hz, 2 H), 7.56 (td, *J* = 7.2, 1.6 Hz, 2 H), 5.03 (t, *J* = 2.8 Hz, 2 H), 3.11 (t, *J* = 2.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 143.9, 139.4, 133.3, 131.0, 129.6, 128.7, 127.2, 126.5, 124.1, 122.2, 121.1, 120.3, 45.3, 31.1. HRMS (ESI): calcd for $C_{29}H_{19}N_2$ $[M + H]^+$ 395.1548, found 395.1551.

Characterization Data of Compound ***15b***. White solid (22.1 mg, 71%). $[\alpha]_D^{23} = -820$ (*c* 1.06, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, *J* = 8.0 Hz, 2 H), 8.30 (d, *J* = 8.4 Hz, 2 H), 7.98–7.96 (m, 4 H), 7.70 (t, *J* = 8.4 Hz, 2 H), 7.40 (dd, *J* = 8.4, 1.6 Hz, 2 H), 5.00 (t, *J* = 2.8 Hz, 2 H), 3.09 (t, *J* = 2.8 Hz, 2 H), 2.57 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 144.0, 139.5, 138.8, 133.3, 130.9, 129.2, 128.1, 126.6, 122.0, 121.8, 120.8, 120.0, 45.4, 31.2, 21.5. HRMS (ESI): calcd for $C_{31}H_{23}N_2$ $[M + H]^+$ 423.1861, found 423.1864.

Characterization Data of Compound ***15c***. White solid (31.0 mg, 83%). $[\alpha]_D^{23} = -458$ (*c* 0.95, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.43–8.41 (m, 4 H), 8.13 (d, *J* = 8.4 Hz, 2 H), 8.00 (d, *J* = 7.2 Hz, 2 H), 7.79 (dd, *J* = 8.4, 2.0 Hz, 2 H), 7.72 (t, *J* = 8.4 Hz, 2 H), 5.03 (t, *J* = 2.8 Hz, 2 H), 3.10 (t, *J* = 2.8 Hz, 2 H), 1.44 (s, 18 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 149.4, 142.0, 139.5, 133.4, 130.8, 129.1, 127.0, 123.5, 120.9, 120.4, 117.8, 45.3, 35.1, 31.4, 31.1. HRMS (ESI): calcd for $C_{37}H_{35}N_2$ $[M + H]^+$ 507.2800, found 507.2803.

Characterization Data of Compound ***15d***. White solid (41.1 mg, 99%). $[\alpha]_D^{23} = -386$ (*c* 1.15, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 9.18 (d, *J* = 1.6 Hz, 2 H), 8.52 (d, *J* = 8.0 Hz, 2 H), 8.31 (dd, *J* = 8.8, 2.0 Hz, 2 H), 8.20 (d, *J* = 8.4 Hz, 2 H), 8.07 (d, *J* = 7.6 Hz, 2 H), 7.82 (t, *J* = 8.0 Hz, 2 H), 5.06 (t, *J* = 2.8 Hz, 2 H), 3.99 (s, 6 H), 3.13 (t, *J* = 2.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 162.4, 146.4, 139.2, 133.4, 131.7, 129.7, 128.7, 127.8, 127.7, 124.9, 123.6, 121.5, 120.5, 52.3, 45.3, 31.0. HRMS (ESI): calcd for $C_{33}H_{23}N_2O_4$ $[M + H]^+$ 511.1658, found 511.1663.

Characterization Data of Compound ***15e***. White solid (35.8 mg, 86%). $[\alpha]_D^{23} = -371$ (*c* 0.635, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.4 Hz, 2 H), 8.22–8.19 (m, 4 H), 8.06 (d, *J* = 7.2 Hz, 2 H), 7.79 (t, *J* = 7.6 Hz, 2 H), 7.57 (dd, *J* = 8.8, 2.0 Hz, 2 H), 5.04 (t, *J* = 2.8 Hz, 2 H), 3.11 (t, *J* = 2.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 147.2, 142.2, 139.4, 132.7, 131.5, 131.4, 128.0, 124.9, 122.1, 121.3, 120.5 (q, J_{C-F} = 256 Hz), 120.3, 114.0, 45.1, 30.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.68. HRMS (ESI): calcd for $C_{31}H_{17}N_2O_2F_6$ $[M + H]^+$ 563.1194, found 563.1199.

Characterization Data of Compound ***15f***. White solid (29.4 mg, 90%). $[\alpha]_D^{23} = -327$ (*c* 0.28, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, *J* = 2.0 Hz, 2 H), 8.38 (d, *J* = 8.0 Hz, 2 H), 8.23 (d, *J* = 8.8 Hz, 2 H), 8.09 (d, *J* = 6.8 Hz, 2 H), 7.89 (dd, *J* = 8.4, 1.6 Hz, 2 H), 7.84 (t, *J* = 8.0 Hz, 2 H), 5.06 (t, *J* = 2.8 Hz, 2 H), 3.13 (t, *J* = 3.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1, 145.7, 139.2, 132.23, 132.15, 130.9, 130.4, 128.6, 127.9, 124.2, 121.3, 120.6, 119.0, 109.9, 45.2, 30.8. HRMS (ESI): calcd for $C_{31}H_{17}N_4$ $[M + H]^+$ 445.1453, found 445.1456.

Characterization Data of Compound ***15g***. White solid (28.1 mg, 90%). $[\alpha]_D^{23} = -398$ (*c* 0.583, CH_2Cl_2), ^1H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 8.0 Hz, 2 H), 8.20 (s, 2 H), 8.05 (d, *J* = 8.4 Hz, 2 H), 7.99 (d, *J* = 7.2 Hz, 2 H), 7.71 (t, *J* = 8.0 Hz, 2 H), 7.52 (dd, *J* = 8.4, 1.6 Hz, 2 H), 5.00 (t, *J* = 2.8 Hz, 2 H), 3.08 (t, *J* = 2.8 Hz, 2 H), 2.56 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 142.2, 139.5, 136.2, 133.0, 130.7, 130.3, 129.3, 127.0, 123.9, 121.8, 120.9, 120.4, 45.4, 31.2, 21.8. HRMS (ESI): calcd for $C_{31}H_{23}N_2$ $[M + H]^+$ 423.1861, found 423.1867.

Characterization Data of Compound ***15h***. White solid (37.7 mg, 96%). $[\alpha]_D^{23} = -428$ (*c* 0.925, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 2 H), 8.40 (d, *J* = 8.0 Hz, 2 H), 8.26 (d, *J* = 8.4 Hz, 2 H), 8.07 (d, *J* = 7.2 Hz, 2 H), 7.90 (dd, *J* = 8.8, 1.6 Hz, 2 H), 7.80 (t, *J* = 7.6 Hz, 2 H), 5.06 (t, *J* = 2.8 Hz, 2 H), 3.13 (t, *J* = 2.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.3, 145.5, 139.3, 133.0, 131.7, 130.6, 128.3 (q, J_{C-F} = 32.2 Hz), 128.1, 124.8 (q, J_{C-F} = 3.2 Hz), 124.3 (q, J_{C-F} = 270 Hz), 123.7, 121.3, 120.6, 120.0 (q, J_{C-F} = 4.0 Hz), 45.3, 30.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ −61.83. HRMS (ESI): calcd for $C_{31}H_{17}N_2F_6$ $[M + H]^+$ 531.1296, found 531.1293.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00024.

^1H and ^{13}C NMR spectra of new compounds and HPLC traces for **10c,d** (PDF)

Crystallographic data of **6**, **7**, and **15g,h** (CIF)

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(26) CCDC 1525817 contains supplementary crystallographic data for compound **15h**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

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