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C_2-Symmetric Hindered "Sandwich" Chiral *N*-Heterocyclic Carbene Precursors and Their Transition Metal Complexes: Expedient Syntheses, Structural Authentication, and Catalytic Properties

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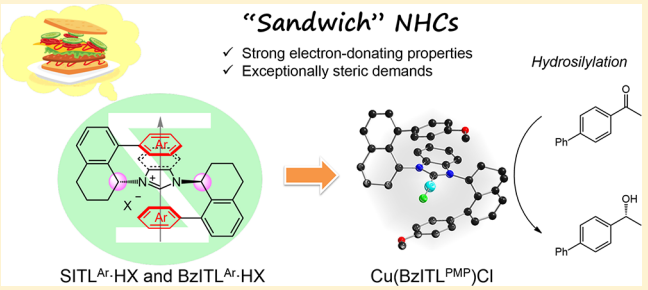
Supporting Information

ABSTRACT: We present here a new family of C_2-symmetric "sandwich" NHC ligands abbreviated as $SITL^{Ar}$ and $BzITL^{Ar}$ and their complexes. The chiral fragments incorporate bulky yet flexible cyclohexyl groups with α-stereocenters joined to nitrogens individually, which set up chiral pockets around pivotal carbene carbons (less than 2.5 Å). Full characterization revealed unique structures with roughly parallel aryl moieties above and below imidazoline and benzimidazole planes in the Z-shaped arrangement. Extra hydrogen bonding interactions and steric stress between the square-planar frameworks and aryl groups led to the exceptional confinement and reversed the configurations in the iridium complexes. In accordance with Tolman's electronic parameters and topographic steric maps of well-established metalated complexes, these new ligands possess strong electron-donating properties and exceptionally steric demands. Additionally, the preliminary results employing the $BzITL^{Ar}$ ligands allowed appropriate activities and provided potential applications for asymmetric induction in the enantioselective aryl transfer and hydrosilylation reactions with moderate enantioselectivity.



INTRODUCTION

N-Heterocyclic carbenes (NHCs) have emerged as a well-established and promising class of ligands in modern coordination chemistry since the auspicious start by Öfele and Wanzlick independently in 1968.[1] Benefiting from their impelling σ-donor, tunable π-acceptor, and steric properties, NHCs exhibit relevant high thermal and chemical stability to their complexes, and indeed, M−NHCs are more powerful tools in many catalytic transformations beyond simple phosphine surrogates.[2] Specifically, numerous metal−NHC complexes have displayed potentially antimicrobial and antitumor activities as metallopharmaceuticals, which are attributed to strong metal−carbon bonds coordinated to different metals.[3] In addition, the strategies of umpolung involving nucleophilic NHCs with both σ basicity and π acidity characteristics are recognized as "conventional weapons" to facilitate manifold organocatalytic reactions.[4]

The chemistry of NHCs has witnessed the leapfrog development since the X-ray structure of the stable 1,3-di-1-adamantylimidazol-2-ylidene was revealed by Arduengo's groundbreaking work in 1991.[5] With the development of fully fledged and versatile synthetic routes, an ever-growing variety of NHCs, encompassing their syntheses, structures, and applications, sprang up.[6] Structurally, (benz)imidazolium and imidazolinium salts still take up remarkable superiority as the core structures of NHC salts apart from the alternative families.[7] The backbone and both *N*-substituents adjacent to the core carbenic carbon are flexible and easily variable.

With the emergence of the chiral NHCs for asymmetric catalysis, saturated imidazoliniums based on chiral scaffolds (two stereocenters in the imidazoline ring) are of increasing interest especially for olefin metathesis, conjugated addition, allylic alkylation, and reductive coupling, which transfer the chirality remote from central metals to the active space effectively.[8] Alternatively, another possible manipulation to satisfy their sterically demanding structures is increasing access to introduce chiral *N*-substituents straightforward, since chiral elements surrounding the metal nuclei seem to be more targeted.[9] Usually, constructions of the scaffolds began from optically active amines, one of the most important chiral building blocks.[10] Among these, research in this field revealed the installations of bulky chiral fragments were roughly perpendicular to heterocyclic rings, which located separately on the left or right. Nitrogen-grafted substitutions with peculiar geometry that approximately coincide with the core framework of NHCs in the vertical view, by contrast, are still undeveloped (Scheme 1).[11] Encouraged by Brookhart's "sandwich" diimine ligands for olefin polymerizations,[12] we envision an appealing set of flexible NHC precursors abbreviated as $SITL^{Ar}$·HX and $BzITL^{Ar}$·HX.[13] Herein, two "pieces" of parallel aryl rings bound on opposite sides of the nucleus serve as the "sliced bread pocket", similar to the portable finger food. Starting from 1-aminotetralin, the synthetic challenges incorporate the

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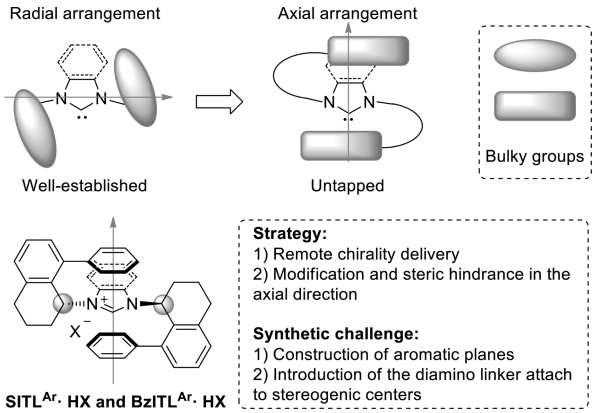
Scheme 1. Chiral "Sandwich" NHC Precursors

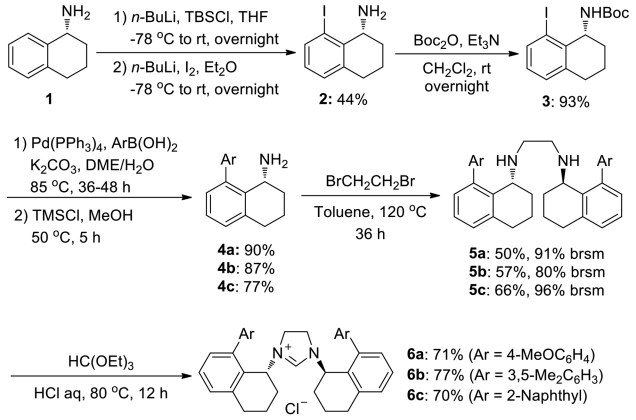


equipment of aromatic planes and diamino linkers without erosion of enantiopurity.[9f,14]

RESULTS AND DISCUSSION

Synthesis and Characterization of SITL^{Ar}·HCl. The synthetic approach in several straightforward steps was started from commercially available (*R*)-1-aminotetralin **1**. As illustrated in Scheme 2, a reliable regioselective iodation of

Scheme 2. Synthesis of SITL^{Ar}·HCl



The overall yields over 7 steps: **6a** (24%); **6b** (22%); **6c** (21%).

ortho C(sp^2)−H bond of chiral amine **1** was best performed under the neighboring group-directed lithiation condition on a multigram scale. Iodo compound **2** was directly converted to **3** using di-*tert*-butyl dicarbonate in excellent isolated yield. The palladium-catalyzed Suzuki−Miyaura couplings between Boc-protected amine **3** and arylboronic acids and the subsequent acid-promoted removal of Boc groups delivered corresponding amine intermediates **4** in 77−90% yields over 2 steps. Despite the failure of the diimine formation with glyoxal, the ethylene-diamine-based backbones were then installed with double alkylation reactions according to a modified procedure. Although this method has been diffusely utilized for the construction of saturated NHC linkers, it was disadvantageous and problematic to match easy-handling operation with reaction efficiency under neat conditions on a small scale, especially for multistep synthetic solids or viscous oils. Reactions of **4** with 1,2-dibromoethane serving as an alkylating agent in the presence of toluene led to diamines **5** in moderate yields with majority of remaining chiral amines recovered, which were then cyclized into the desired imidazolinium salts using HCl and triethyl orthoformate in fair yields.

A series of succinct ^{1}H NMR spectra confirmed the highly symmetrical geometry of **6a−c**. One distinctive character of these salts was the singlet peak corresponding to the imidazolinium protons at 7.76−8.27 ppm, which were shifted dramatically to higher fields compared to the analogue SICy·HCl (9.89 ppm, $CDCl_3$).[15] The proton resonances of iminium protons were plainly consistent with the high basicity of SITL^{Ar} salts. Besides, it is well-known that the NCN bond angles have a notable positive correlation with basicity of NHC precursors.[16] X-ray crystallographic analysis of SITL^{Xyl}·HCl **6b** revealed quite a large NCN bond angle (113.6(3) °) (Figure 1); thus, the pK_a values of these precursors could be comparable to the SIMes·HCl.[17]

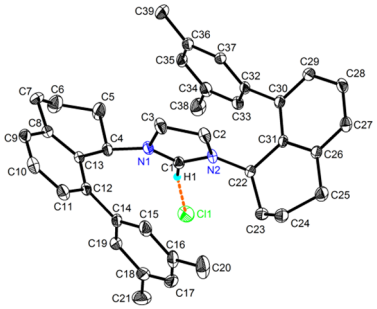
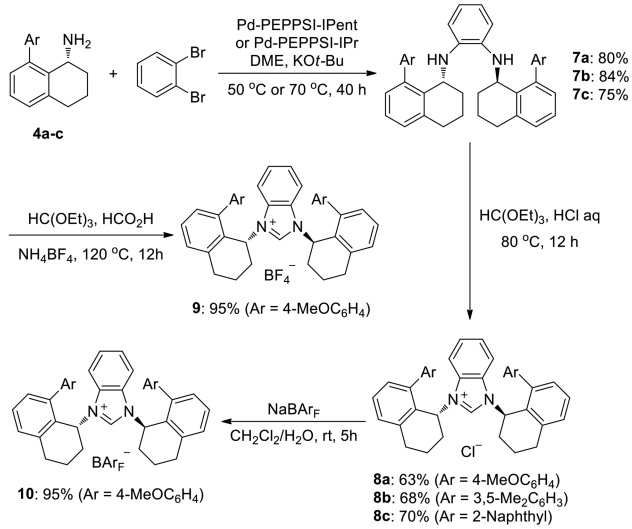


Figure 1. X-ray crystal structure of imidazolinium salt **6b** (ORTEP view with displacement ellipsoids drawn at 30% probably level. Hydrogen atoms and solvent molecules have been omitted for clarity. One of the conformations is listed herein. The same below). Selected bond lengths (Å): N(1)−C(1) 1.303(5), N(2)−C(1) 1.314(4), C(1)−H(1)···Cl(1) 2.31; selected bond angles (deg): N(1)−C(1)−N(2) 113.6(3), C(11)−C(12)−C(14)−C(15) −55.4(5), C(29)−C(30)−C(32)−C(33) 115.8(4).

Synthesis and Characterization of BzITL^{Ar}·HX. The synthetic route of NHCs **8a−c** was derived from the same key intermediates, **4a−c** (Scheme 3). Efficient synthesis posed by benzimidazole-based NHCs relies on the introduction of *N*,*N*′-dialkyl-*o*-phenylene-diamines, which is a long-standing chal-

Scheme 3. Synthesis of BzITL^{Ar}·HX



The overall yields from **1** over 7-8 steps: **8a** (19%); **8b** (20%); **8c** (17%); **9** (28%); **10** (18%).

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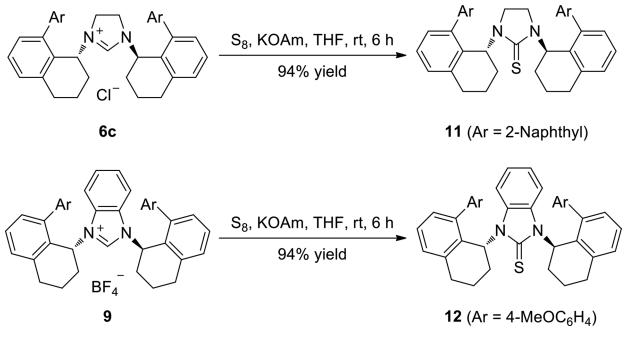
lenge and can often be accomplished based on aromatic C−N coupling reactions. Initial studies failed to furnish **7** under copper-catalyzed Ullmann coupling conditions. In implementing the synthetic strategy, we became intrigued by Buchwald−Hartwig catalytic systems in the sterically demanding environment. It is noteworthy that chiral amines equipped with stereogenic centers attached to nitrogens may undergo racemization in competition with palladium/triarylphosphine ligands-catalyzed cross-coupling reactions.[18] After exploring extensive approaches, Pd-PEPPSI precatalysts developed by Organ's group proved to be the most efficient to provide consecutively alkylated products with two secondary amine moieties in satisfactory yields.[19] Furthermore, attempts to optimize the reaction led to the observation that amounts of 5-substituted-1,2-dihydronaphthalenes as byproducts existed via *β*-H elimination to varying degrees. Unfortunately, increasing the steric hindrance of **4** by introducing bulky Ar groups such as 1,1′:3′,1″-terphenyl or 9-anthryl resulted in no formation of desired products with dominant side reactions. With **7** in hand, we proceeded to prepare benzimidazolium salts BzITL^{Ar}·HCl smoothly in the similar manner. Under analogous reaction conditions, new NHC salts with weakly coordinating anions[20] were synthesized. It was found to obtain higher yield of the NHC precursor for the synthesis of tetrafluoroborate salt **9** after purification by flash column chromatography. Instead, the late-stage anion exchange with the stoichiometric addition of sodium tetrakis[3,5-bis(trifluoro-methyl)phenyl]borate afforded BzITL^{PMP}·HBAr$_F$ in 95% yield.

The ^{1}H NMR spectra of BzITL^{Ar}·HCl displayed all the expected spectroscopic characteristics, similar to those of SITL^{Ar}·HCl. There are obvious distinctions in the proton resonances for the iminium protons (10.26−10.57 ppm), which are shifted to lower fields due to skeleton change. Notablely, BzITL^{Ar} salts with weakly coordinating anions led to higher basicity in accordance with more upfield benzimidazolium protons. The ^{11}B and ^{19}F NMR spectra of **9** and **10** exhibited characteristic singlets for the BF_4^- counterion at −0.7 and −151.1 ppm respectively, compared to −6.5 and −62.3 ppm for the BAr_F^- counterion.

Synthesis and Characterization of Thioureas. To further identify and compare structures of the aforementioned classes of BzITL^{Ar}, the selected NHC precursors were trapped as thioureas. In both case, the preparation of **11** and **12** involved deprotonation of model chloride salt **6c** and tetrafluoroborate salt **9** with KOAm, followed by trapping of the free carbenes *in situ* with sulfur in excellent yields (Scheme 4).

Scheme 4. Synthesis of Thioureas



Single crystals of thioureas **11** and **12** suitable for X-ray diffraction were subjected to crystal structure studies (Figure 2). There are no apparent structural differences despite

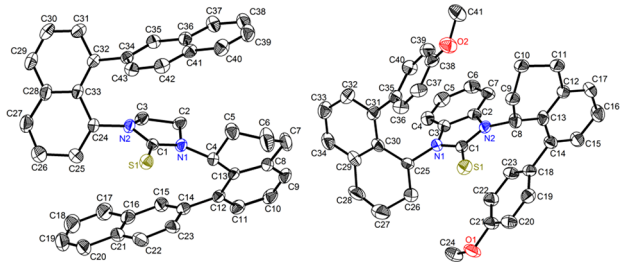
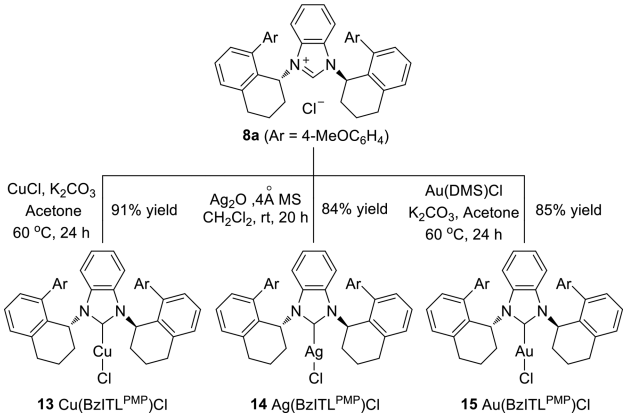


Figure 2. X-ray crystal structure of thiourea **11** (left) and **12** (right). For **11**: selected bond length (Å): C(1)−S(1) 1.684(3); selected bond angles (deg): N(1)−C(1)−N(2) 109.1(3), C(13)−C(14)−C(18)−C(19) −75.9(1), C(30)−C(31)−C(35)−C(36) −60.4(1). For **12**: selected bond length (Å): C(1)−S(1) 1.664(8); selected bond angles (deg): N(1)−C(1)−N(2) 107.2(6), C(11)−C(12)−C(14)−C(15) −53.8(4), C(31)−C(32)−C(34)−C(35) −56.7(4).

alterable Ar groups. Together with SITL^{Xyl}·HCl, the aryl rings, expecially for saturated imidazolinium derivatives, stand nearly parallel (dihedral angles of aromatic planes: 4.6° for **6b** and **11**; 11.2° for **12**) with similar distance (ca. 6.8 Å). In a word, the "sandwich" structures of aforementioned SITL^{Ar} and BzITL^{Ar} ligands are the Z-shaped distribution in accord with our original hypothesis elucidated by X-ray analysis.

Synthesis and Characterization of Corresponding Coinage Metal Complexes. Having successfully prepared BzITL^{PMP}·HCl **8a** on gram scale, we next focused on the coordination chemistry of complexes of group 11 elements with further applications (Scheme 5). The facile one-step

Scheme 5. Synthesis of Coinage Metal−NHC Complexes



synthetic route leading to CuCl-ligated benzimidazol-2-ylidene **13** was engaged in a protocol developed by Cazin and coworkers in the presence of 2 equiv of K_2CO_3.[21] Next, the reaction of Au(DMS)Cl and benzimidazolium salt **8a** was investigated in 85% yield, applying the similar condition for Au−NHC complex **15**.[22] Representative silver complex Ag(BzITL^{PMP})Cl **14**, which may serve as the vital carbene transfer agent, has been routinely carried out from benzimidazolium chloride **8a** using Ag_2O in CH_2Cl_2 in 84% yield on the basis of Lin's procedure.[23]

Next, all bench-stable solids **13**−**15** were fully characterized by NMR spectroscopy and electrospray mass spectrometry

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(ESI-MS). The disappearance of the iminium proton signals at ca. 10.5 ppm in the ^{1}H NMR spectra confirmed the formation of the resultant coinage metal complexes containing NHC ligands. The notable broadening of the signal may be correlated to the coordination of ligands with metal ions and fluxional behavior of the tetralin moiety on the NMR time scale. Furthermore, the individual signals of ^{13}C NMR spectra of **13** and **15** exhibited the metalated C_{NHC} resonances at 186.6 and 180.8 ppm in accordance with similar molecules, respectively.[24] Gratifyingly, carbene coupling to silver was displayed at 191.1 ppm in 175 MHz ^{13}C NMR spectrum of Ag(BzITL^{PMP})Cl **14**, although the majority showed no splitting pattern and even no observable carbene signals were recorded for a significant number of silver−NHC complexes.[24,25] It exhibited a complex splitting pattern (doublet of doublets) based upon the coupling constants J_{C-Ag} = 271 and 238 Hz for both ^{109}Ag and ^{107}Ag isotopes (48.162 and 51.840% natural abundance), respectively.

Single crystals of Cu(BzITL^{PMP})Cl suitable for X-ray diffraction study were obtained from acetone in the glovebox. As shown in Figure 3, Cu(BzITL^{PMP})Cl **13** deviates slightly

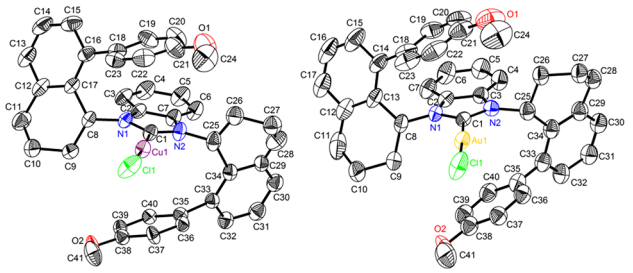


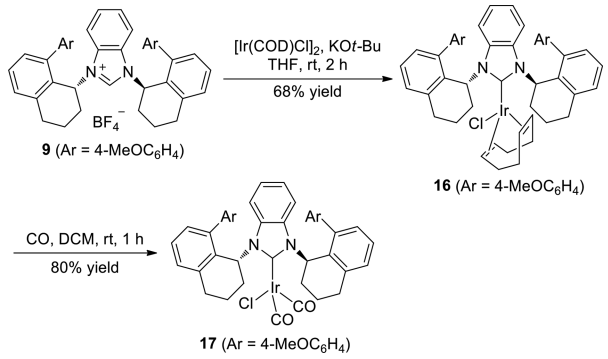
Figure 3. X-ray crystal structures of Cu(BzITL^{PMP})Cl **13** (left) and Au(BzITL^{PMP})Cl **15** (right). For **13**: selected bond lengths (Å): Cu(1)−C(1) 1.869(5), Cu(1)−Cl(1) 2.0880(15); selected bond angle (deg): C(1)−Cu(1)−Cl(1) 174.71(16). For **15**: selected bond lengths (Å): Au(1)−C(1) 1.976(10), Au(1)−Cl(1) 2.279(3); selected bond angle (deg): C(1)−Au(1)−Cl(1) 177.4(3).

from linearity (C(1)−Cu(1)−Cl(1) 174.71(16)°), and the Cu−C_{NHC} distance (1.869(5) Å) is at the short end of the normal range for similar molecules (1.87−1.96 Å).[26] The structure of gold(I) complex **15** has been established (Figure 3), which displays the same geometry, while being slightly more linear (C(1)−Au(1)−Cl(1) 177.4(3)°) and having a longer metal−NHC bond (1.976(10) Å) in good agreement with those in related complexes (1.94−2.02 Å).[27] As expected, the central metal atoms of complexes, bearing chloride atoms *trans* to the bulky BzITL^{PMP}, are both surrounded by the cavities of our well-defined NHC ligands.

Synthesis and Characterization of the Corresponding Iridium Complexes. To our delight, notwithstanding its rather enormous size, the BzITL^{Ar} ligands were also able to accommodate common ligands such as the η^4-1,5-cyclooctadiene moiety and CO (Scheme 6).[28] Deprotonation of BzITL^{PMP}·HBF$_4$ with KO*t*-Bu in the presence of the dimer [Ir(COD)Cl]$_2$ was converted smoothly to desired NHC complex **16** in 68% yield. The straightforward displacement of the COD ligand occurred by bubbling of CO through a solution of **16** in CH_2Cl_2, which was further converted into dicarbonyl analogue **17**.

The characteristic signals of NMR spectra relative to the symmetric positions in complex **16** were split in the

Scheme 6. Synthesis of NHC−Ir Complexes



nonequivalent pattern. Besides, the ^{13}C NMR data confirmed the formation of an iridium−carbene complex with a characteristic singlet at 195.1 ppm.[24,29] The ligating carbon atom of carbene ligand in the ^{13}C NMR spectrum was upfield at 179.3 ppm for **17**, indicating greater shielding of the carbene nucleus in Ir(BzITL^{PMP})(CO)$_2$Cl replaced with more electron-withdrawing π-acidic carbonyl ligands.

The air- and moisture-stable yellow crystals for X-ray quality were obtained from a saturated solution of complexes **16** in diethyl ether (Figure 4). The molecular structure features a pseudosquare-planar disposition of donors around the iridium center (Cl(1)−ct[C(46)−C(47)]−ct[C(42)−C(43)]−C(1) 0.94°). The Ir−$C_{carbene}$ distance measures 2.062(8) Å and falls into the reported range for analogous complexes (1.99−2.09 Å).[29] The cyclooctadiene fragment is close to a boat conformation and C_2 approximate symmetry, which elbows two "wings" of BzITL^{PMP} ligand aside from the metal. In general, the square-planar coordination mode is almost perpendicular to the carbene plane. As in other NHC-supported iridium complexes, the average distance of the iridium to the double bond of the COD-ring *trans* to the carbene ligand (ca. 2.078 Å) is slightly longer than that *trans* to the chloro ligand (ca. 2.019 Å) because of the stronger *trans* effect of the carbene.

The X-ray analysis permitted to unambiguously confirm the intimate structure of Ir(BzITL^{PMP})(CO)$_2$Cl (Figure 4), although NMR spectra of complex **17** revealed broad resonances, indicating the rapid dynamic exchange. Similarity, it shows the expected square-planar core geometry around the iridium center as expected for d^8 metals in strong ligand field environment. All bond lengths and angles are consistent with analogous compounds reported in the literature,[29] and suggest exclusive σ-bond characteristics.[30] The Ir−CO bond *trans* to the NHC (1.889(10) Å) is much longer than that in *cis* orientation (1.823(19) Å).

It is noteworthy that major differences are observed in the molecular structures, associated with the geometric arrangement of tetralin moieties compared to group 11 element complexes mentioned above. Both of the fragments are significantly twisted and keep apart from the iridium coordination plane, leading to the "sandwich" structure migrating toward the backbone of the ligand. After re-examination of crystal structures, the exceptional confinement could be attributed to intramolecular hydrogen bonding interactions between the chloro atoms and the hydrogens of cyclohexyl rings, except for the steric stress between the square-planar nuclei frameworks and side-chain Ar groups.

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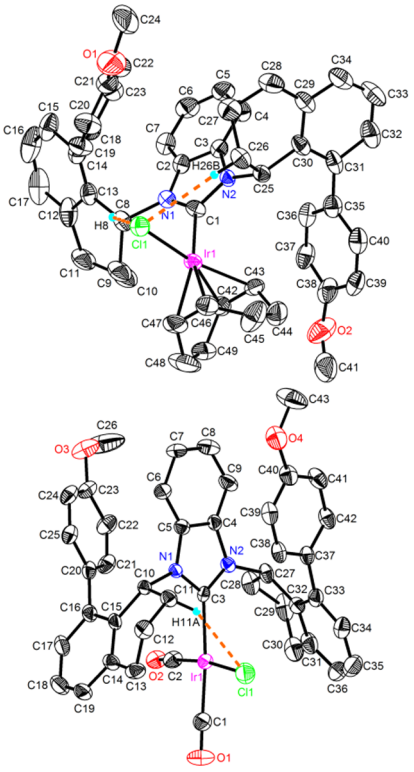
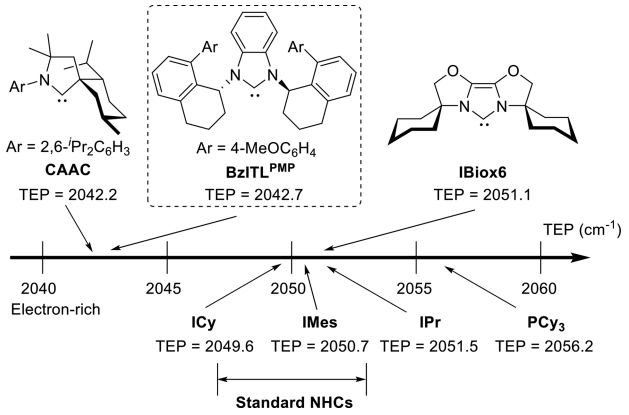


Figure 4. X-ray crystal structure of Ir(BzITL^{PMP})(COD)Cl **16** (up) and Ir(BzITL^{PMP})(CO)$_2$Cl **17** (down). For **16**: selected bond lengths (Å): Ir(1)−C(1) 2.062(8), Ir(1)−Cl(1) 2.364(2), Ir(1)−ct[C(42)−C(43)] 2.019, Ir(1)−ct[C(46)−C(47)] 2.078, C(8)−H(8)···Cl(1) 2.84, C(26)−H(26B)···Cl(1) 2.78; selected bond angles (deg): C(1)−Ir(1)−Cl(1) 90.8(3), ct[C(42)−C(43)−Ir(1)−ct[C(46)−C(47)] 85.9(2), Cl(1)−ct[C(46)−C(47)]−ct[C(42)−C(43)]−C(1) 0.94. ct[C(X)−C(Y)]: centroid of the C(X)−C(Y) bond. For **17**: selected bond lengths (Å): Ir(1)−C(3) 2.094(7), Ir(1)−Cl(1) 2.329(7), Ir(1)−C(1) 1.889(10), Ir(1)−C(2) 1.823(19), C(11)−H(11A)···Cl(1) 2.68; selected bond angles (deg): C(1)−Ir(1)−Cl(1) 88.4(4), C(2)−Ir(1)−C(3) 91.6(16), C(2)−C(1)−Cl(1)−C(3) 0.65.

Quantification of Electronic Properties of BzITL^{Ar} Ligands. The electronic impact of monodentate electron-rich NHC ligands on a metal center is typically measured by using Tolman's electronic parameter (TEP)[31] to evaluate their donor capabilities. Correlation studies developed by Crabtree[32] and Nolan[29] extended the methodology to *cis*-[M(NHC)(CO)$_2$X] (M = Ir or Rh, X = halide) and allowed the electronic properties of a wider range of organometallic ligands to be quantified via the empirical expression.[33] The infrared spectroscopic determination for a solution of Ir(BzITL^{PMP})(CO)$_2$Cl **17** in CH_2Cl_2 recorded an intense absorption band with the wavenumbers of 1969.24 and 2057.97 cm^{-1}, which can be ascribed to the stretching frequencies of a *cis*-M(CO)$_2$ unit, respectively. The TEP effect of BzITL^{PMP} was calculated into the value of 2042.7 cm^{-1}, indicating that the electron donor property was apparently enhanced compared to that of the other representative NHC ligands (Scheme 7).[29,34] On the basis of these data, it is remarkable that BzITL^{Ar} ligands behave with electron ability close to electron-rich CAACs (cyclic alkyl amino carbenes). Despite no exact TEP values of SITL^{Ar} with ethylene linkers for comparison, the saturated NHC complexes are predicted to exhibit marginally higher TEP values.[35]

Scheme 7. TEP Values for a Series of NHC Ligands



Evaluation of Steric Properties of BzITL^{Ar} Ligands. Having arrived at the crystal structures of complexes **13**, **15**, and **17**, we set out to estimate their steric properties introducing the terms of percent buried volumes and topographic steric maps.[36,37] The %V_{bur} values of linear complexes calculated via the application of Samb*V*ca software[36] are 53.6 and 51.0% among the most sterically demanding monodentate carbene ligands (Table 1), although

Table 1. Summary of %V_{bur} for a Series of NHC Ligands

		M(NHC)Cl		Ir(NHC)(CO)$_2$Cl
entry[a]	NHC	%V_{bur} (Cu)	%V_{bur} (Au)	%V_{bur} (Ir)
1	ICy	28.8[b]	27.4[b]	27.6[b]
2	BzICy		32.8[c]	
3	IAd	42.5[d]	39.8[e]	37.4[b]
4	IPr	47.6[b]	44.5[b]	34.5[b]
5	CAAC		51.2[b]	
6[f]	BzITL^{PMP}	53.5 (53.6)	51.0 (50.0)	47.4 (46.5)

[a]Parameters used for Samb*V*ca calculations: sphere radius, 3.50 Å; M−NHC length, 2.00 Å; Bondi radius, 1.17. H atoms are excluded. [b]Taken from ref 38. [c]Calcd based on ref 39. [d]Calcd based on ref 26d. [e]Taken from ref 37a. [f]Both of the conformations were considered.

it is generally acknowledged that NHCs bearing *N*-cyclohexyl substituents (ICy and BzICy) represent one of the less bulkier analogues.[38] Herein, we reaped another avenue to manipulate flexible cyclohexyl groups to design sterically hindered carbene ligands, different from IBOX and CAAC ligands.[9i,38] As expected, a very pronounced decrease on the buried volume of Ir(NHC)(CO)$_2$Cl emerged dependent on the nature of the metal complexes when switched to square-planar complex **17**. Indeed, the fact that repulsive interaction between aryl groups and highly coordinated plane and hydrogen bonding interaction have a clear impact on the steric influence of BzITL^{PMP} derivatives is in accordance with the aforementioned comparative analysis of X-ray structures. As shown in topographic steric maps (Figure 5), this same reason could explain why two distinctive subtypes polarize on the unique inverse arrangement of steric impact. Contrary to those for coinage metal complexes, the main steric hindrance for **17** is located in the low latitude regions near the equator.

Catalytic Studies. Since Fürstner reported a practical method for Rh/IPr-catalyzed aryl transfer reactions from arylboronic acids to aldehydes in 2001,[40] various sterically hindered and chiral NHC ligands were developed for the

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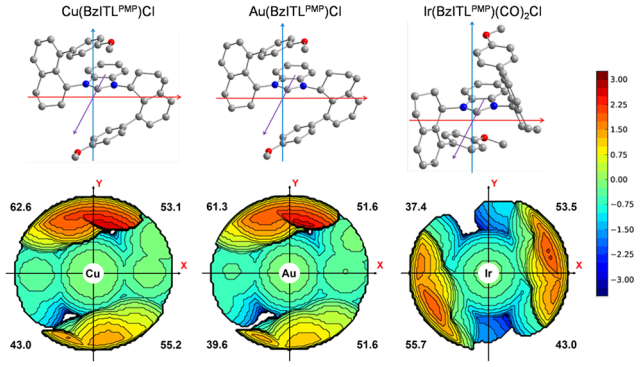
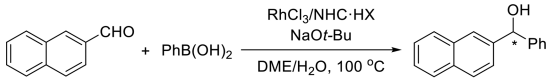


Figure 5. Steric maps for one of the conformations of BzITL^{PMP} ligand in complexes **13**, **15**, and **17**.

preparation of chiral benzylic alcohols in the rhodium-catalyzed 1,2-addition reactions.[41] Hitherto, it is regrettable that the stereodiscrimination process in these transformations is quite challenging, and only a few examples have been accomplished with unsatisfied enantioselectivities. Therefore, we focused on a series of SITL^{Ar} and BzITL^{Ar} ligands for the catalytic addition of phenylboronic acid to 2-naphthaldehyde according to Fürstner's procedure (Table S9).[40] The representative optimization results for the identification of the best NHC precursor are summarized in Table 2.

Table 2. Screening of Aryl Transfer Conditions



18 19 20

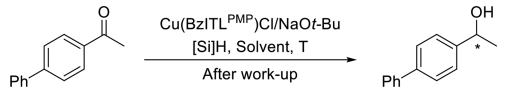
entry[a]	NHC·HX	yield (%)[b]	ee (%)[c]
1	**6a**	18	14
2	**6b**	20	0
3	**6c**	11	10
4	**8a**	78	25
5	**8b**	63	4
6	**8c**	67	27
7	**9**	84	1
8	**10**	96	0
9[d]	**8a**	84	25 (*R*)
10[e]	**8a**	25	32

[a]Reaction conditions: **18** (0.20 mmol), **19** (0.40 mmol), $RhCl_3$ (0.006 mmol, 3 mol %), NHC·HX (0.006 mmol, 3 mol %), NaO*t*-Bu (0.40 mmol), DME/H_2O (2.5 mL/0.5 mL), 24 h. [b]Isolated yields. [c]Determined by chiral HPLC. [d]At 36 h. [e]At 60 °C, 48 h.

Interestingly, low conversions were detected by using SITL^{Ar} ligand (entries 1−3), whereas a range of BzITL^{Ar} species efficiently catalyzed the formation of desired product **20** in good yields with the stereochemical control slightly improved (entries 4−6). These results of ligand screening indicated that the *o*-phenylene moiety on the ligand backbone played a subtle role in the catalytic process. The introduction of weakly coordinating counterions gave negative enantioselective results (entries 7−8). Without further optimization, BzITL^{PMP} exhibited the best result considering two aspects of reaction efficiency and enantioselectivity comprehensively so far. The prolonged time led to the corresponding alcohol in satisfied yield (entry 9). In addition, the reaction rate was significantly diminished when the temperature was decreased to 60 °C (entry 10).

Afterward, we turned our attention to their application in Cu-catalyzed asymmetric hydrosilylation of ketones. The catalytic activity of the copper−carbene complexes was realized in reduction of simple carbonyl compounds under mild condition.[26a,b,d,42] No more copper−carbene precatalysts parallel Cu(IPhEt)Cl developed by Gawley in the asymmetric induction so far, especially for reduction of dialkyl ketones.[9j,11,43] With the candidate ligand BzITL^{PMP} in mind, we examined reaction efficiency in asymmetric hydrosilylation of 4-acetylbiphenyl (Table S10). As outlined in Table 3,

Table 3. Screening of Hydrosilylation Conditions



21 22

entry[a]	[Si]H	solvent	*T* (°C)	yield (%)[b]	ee (%)[c]
1	PMHS	toluene	80	17	16
2	Et_3SiH	toluene	80	23	23
3	Ph_2SiH_2	toluene	80	45	23
4	$PhSiH_3$	toluene	80	79	26
5	$PhMeSiH_2$	toluene	80	>95	24
6	$PhMeSiH_2$	toluene	28	>95	35
7	$PhMeSiH_2$	THF	28	86	32
8	$PhMeSiH_2$	CH_2Cl_2	28	>95	31
9[d]	$PhMeSiH_2$	toluene	0	>95 (99)	43 (*R*)
10[e]	$PhMeSiH_2$	toluene	−40	52	57

[a]Reaction conditions: **21** (0.10 mmol), [Si]H (0.30 mmol), Cu(BzITL^{PMP})Cl (0.003 mmol, 3 mol %), NaO*t*-Bu (0.006 mmol, 12 mol %), toluene (1 mL), 1−18 h. Basic hydrolysis of the silyl ethers led to the desired alcohols. [b]Crude yields determined by ^{1}H NMR (isolated yield in the parentheses). [c]Determined by chiral HPLC. [d]At 0.20 mmol scale, 8 h. [e]At 72 h.

hydrosilanes had a pivotal influence on the conversion (entries 1−5).[44] Only reactions with methylphenylsilane proceeded smoothly with rising enantioselectives even at room temperature, albeit with various solvents (entries 6−8). The desired product was obtained in excellent yield and moderate 43% ee using toluene as the solvent when the temperature dropped to 0 °C (entry 9). Further optimization revealed that Cu(BzITL^{PMP})Cl precatalyst remained active at lower temperature with moderate yield (entry 10).

CONCLUSIONS

To summarize, we have developed a series of C_2-symmetric "sandwich" NHC ligands BzITL^{Ar} and BzITL^{Ar} bearing chiral *N*-substituents of hindered cyclohexyl derivatives in the expedient synthetic sequence. The well-defined and tunable structures of precursors and corresponding thioureas were unequivocally characterized, which coincided with our preceding hypothesis. It is worth noting that aryl moieties stretch closely parallel to each other in the axial direction. Connected by the (benz)imidazole and imidazoline nuclei, these NHCs spread in the Z-shaped arrangement. As indicated in the X-ray structures, the noncovalent hydrogen bonding interactions help to elucidate the differences in geometries, when switching from linear coinage metal complexes to square-planar iridium congeners. Subsequently, these new ligands

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have been evaluated and corroborated as one of the most σ-donating and sterically hindered yet flexible NHCs based upon the related metalated complexes. Finally, the preliminary study in asymmetric aryl transfer and hydrosilylation exhibited appropriate catalytic activities with potential chirality discrimination. Further applications of these unique NHCs are ongoing in our laboratory currently.

EXPERIMENTAL SECTION

General Considerations. All experimental procedures were carried out using the standard Schlenk techniques under an atmosphere of dry nitrogen or in a glovebox, unless otherwise stated. Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. ^{1}H, ^{11}B, ^{13}C, and ^{19}F NMR spectra were recorded at room temperature in $CDCl_3$ on a Bruker AVANCE III 400 MHz instrument at 400, 128, 100, and 376 MHz, respectively. The ^{13}C NMR spectrum for **14** was recorded at room temperature in $CDCl_3$ on a Bruker AVANCE III HD 700 MHz instrument at 175 MHz. ^{1}H and ^{13}C NMR chemical shifts (ppm) were referenced to solvent residues, while ^{11}B and ^{19}F NMR chemical shifts (ppm) were referenced to external $BF_3{\cdot}Et_2O$ and $CFCl_3$, respectively. Coupling constants (J) were reported in Hz. Melting points were measured on a Beijing Tech X-4 apparatus from and uncorrected. The enantiomeric excesses of the products were determined by HPLC analysis on an Agilent 1200 HPLC using chiral column described below in detail. Optical rotations were measured using an Anto Parr MCP 200 polarimeter at the sodium line (589 nm) in $CHCl_3$ solution (concentrations were given in the units of 10^{-2} g/mL). High-resolution mass spectra were obtained from Agilent 1290 Infinity/6540 UHD Q-TOF LC/MS System. The infrared spectra were obtained on a Nicolet iS50 FT-IR spectrometer equipped with a universal ATR sampling accessory and reported in wavenumbers (cm^{-1}). Flash column chromatography was carried out on silica gel (200−300 mesh) using the indicated solvent system. TLC was visualized with UV light (254 nm) or stained using phosphomolybdic acid solution followed by heating if necessary. X-ray crystal structures and data for compounds **6b**, **11**−**13**, and **15**−**17** were collected on a Bruker SMART APEX diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å).

Synthesis of (*R*)-8-Iodo-1,2,3,4-tetrahydronaphthalen-1-amine (2). Under nitrogen atmosphere, to a solution of (*R*)-1,2,3,4-tetrahydronaphthalen-1-amine **1** (7.36 g, 50 mmol) in 80 mL of THF at −78 °C was dropwise added 1.6 M *n*-BuLi solution in hexane (34.3 mL, 55 mmol, 1.1 equiv), and the resulting mixture was stirred at the same temperature for 30 min. Subsequently, a solution of TBSCl (8.29 g, 55 mmol, 1.1 equiv) in 40 mL of THF was slowly added at −78 °C. The reddish brown solution was warmed to room temperature naturally and stirred overnight. After removal of the THF solvent on the rotavapor, the yellow residue was redissolved in 150 mL of diethyl ether, which was used for the next reaction without further purification. This solution was recooled to −78 °C before 1.6 M *n*-BuLi solution in hexane (93.8 mL, 150 mmol, 3 equiv) was added dropwise. The reaction mixture was allowed to slowly warm to room temperature during 3 h carefully. After 1 h of stirring at room temperature followed by recooling to −78 °C, I_2 (25.4 g, 100 mmol, 2 equiv) was added in portions. The resulting solution was warmed to room temperature naturally and stirred overnight. Saturated $Na_2S_2O_3$ solution (80 mL) was added slowly under the ice bath. The resulting mixture was stirred vigorously for 15 min until a clear two-phase solution appeared. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (100 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was further purified by flash chromatography to give (*R*)-8-iodo-1,2,3,4-tetrahydronaphthalen-1-amine **2** (5.97 g, 44% yield). New compound, reddish brown solid, mp = 38−39 °C. $[\alpha]_D^{20}$ + 17.54 (*c* 1.63, $CHCl_3$). R_f = 0.36 (hexanes/ethyl acetate/triethylamine 20:2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.8 Hz, 1H), 7.06 (d, J = 7.6 Hz, 1H), 6.83 (t, J = 7.7 Hz, 1H), 4.04−4.03 (m, 1H), 2.82−2.66 (m, 2H), 2.02−1.98 (m, 1H), 1.95−1.87 (m, 1H), 1.85−1.74 (m, 2H), 1.65 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 138.9, 137.6, 130.0, 128.4, 102.7, 52.2, 31.5, 29.9, 17.5. HRMS Calcd for $C_{10}H_{13}IN$ $(M + H)^+$: 274.0087, found: 274.0091.

Synthesis of *tert*-Butyl (*R*)-(8-Iodo-1,2,3,4-tetrahydronaphthalen-1-yl)carbamate (3). To a solution of (*R*)-8-iodo-1,2,3,4-tetrahydronaphthalen-1-amine **2** (5.46 g, 20 mmol) and triethylamine (3.04 g, 30 mmol, 1.5 equiv) in 50 mL of CH_2Cl_2, $(Boc)_2O$ (5.24 g, 24 mmol, 1.2 equiv) dissolved in 50 mL of CH_2Cl_2 was added dropwise at 0 °C. The clear solution was then warmed to room temperature naturally and stirred overnight. After completion, the reaction was quenched with water (50 mL) and extracted with CH_2Cl_2 (100 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to furnish the crude product, which was further purified by flash chromatography to afford intermediate **3** (6.94 g, 93% yield). New compound, viscous yellow oil. $[\alpha]_D^{20}$ + 41.06 (*c* 0.85, $CHCl_3$). R_f = 0.45 (hexanes/ethyl acetate 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.7 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 6.87 (t, J = 7.7 Hz, 1H), 4.73−4.17 (m, 2H), 2.80−2.65 (m, 2H), 2.22 (d, J = 11.9 Hz, 1H), 1.78−1.62 (m, 3H), 1.46 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 140.5, 138.0, 129.6, 129.2, 103.2, 79.3, 52.4, 29.8, 29.7, 28.6, 17.8. HRMS Calcd for $C_{15}H_{20}INNaO_2$ $(M + Na)^+$: 396.0431, found: 396.0428.

Synthesis of (*R*)-8-(4-Methoxyphenyl)-1,2,3,4-tetrahydronaphtha-len-1-amine (4a). A flask was charged with *tert*-butyl (*R*)-(8-iodo-1,2,3,4-tetrahydronaphthalen-1-yl)carbamate **3** (6.72 g, 18 mmol) and 4-methoxyphenylboronic acid (4.10 g, 27 mmol, 1.5 equiv) in 180 mL of DME under nitrogen. When 2 mol/L K_2CO_3 (4.98 g, 36 mmol, 2 equiv) aqueous solution was added, the mixture was subsequently degassed for 20 min. After addition of $Pd(PPh_3)_4$ (1.04 g, 0.9 mmol, 5 mol %), the reaction flask was then fitted with a reflux condenser, and the brown suspension was stirred at 85 °C for 36 h until consumption of substrate **3** as monitored by TLC. After cooling to room temperature, the resulting mixture was poured into water (50 mL) and extracted with ethyl acetate (100 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the crude product containing a trace amount of substrate **3** and deiodination product. TMSCl (19.56 g, 180 mmol, 10 equiv) was added to methanol (100 mL) carefully, and the resulting solution was stirred for 30 min before being added to a solution of the crude intermediate above in methanol (50 mL) at 0 °C. The clear mixture was heated at 50 °C for 5 h and cooled to room temperature after completion. After removal of methanol and excess TMSCl, the residue was diluted with EtOAc (100 mL) and washed with 1:1 saturated aqueous $NaHCO_3$ solution/brine (50 mL × 2) and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by a silica gel column to give **4a** (4.09 g, 90% yield in 2 steps). New compound, brown oil. $[\alpha]_D^{20}$ + 65.55 (*c* 0.90, $CHCl_3$). R_f = 0.30 (dichloromethane/methanol 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.7 Hz, 2H), 7.18 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 7.4 Hz, 1H), 7.02 (d, J = 7.3 Hz, 1H), 6.97 (d, J = 8.7 Hz, 2H), 4.25 (t, J = 3.4 Hz, 1H), 3.86 (s, 3H), 2.94−2.78 (m, 2H), 1.96−1.76 (m, 4H), 1.43 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 142.1, 138.8, 136.8, 133.9, 130.2, 128.8, 128.5, 126.3, 113.9, 55.3, 45.2, 31.6, 30.1, 17.7. HRMS Calcd for $C_{17}H_{20}NO$ $(M + H)^+$: 254.1539, found: 254.1543.

Synthesis of (*R*)-8-(3,5-Dimethylphenyl)-1,2,3,4-tetrahydronaphthalen-1-amine (4b). The desired product was obtained in 87% overall yield (1.10 g) on 5 mmol scale according to the procedure described above. New compound, yellow oil. $[\alpha]_D^{20}$ + 36.25 (*c* 1.68, $CHCl_3$). R_f = 0.32 (dichloromethane/methanol 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, J = 7.5 Hz, 1H), 7.11 (d, J = 7.5 Hz, 1H), 7.03−6.99 (m, 4H), 4.28 (s, 1H), 2.95−2.80 (m, 2H), 2.38 (s, 6H), 2.04−1.78 (m, 4H), 1.18 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 141.7, 138.9, 137.9, 136.6, 128.8, 128.7, 128.2, 127.0,

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126.2, 45.2, 31.7, 30.2, 21.5, 17.8. HRMS Calcd for $C_{18}H_{22}N$ (M + H)$^+$: 252.1747, found: 252.1745.

Synthesis of (*R*)-5,6,7,8-Tetrahydro-[1,2′-binaphthalen]-8-amine (4c). The desired product was obtained in 77% overall yield (2.53 g) on 12 mmol scale according to the procedure described above. New compound, viscous yellow oil. $[\alpha]_D^{20}$ + 51.08 (*c* 1.11, $CHCl_3$). R_f = 0.30 (dichloromethane/methanol 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.81 (m, 4H), 7.52−7.48 (m, 3H), 7.22−7.19 (t, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.3 Hz, 1H), 4.30−4.29 (m, 1H), 2.95−2.79 (m, 2H), 2.02−1.76 (m, 4H), 1.13 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 139.4, 139.0, 136.9, 133.4, 132.5, 129.1, 128.5, 128.1, 128.0, 127.9, 127.8, 127.7, 126.4, 126.1, 45.2, 31.8, 30.1, 17.7. HRMS Calcd for $C_{20}H_{20}N$ (M + H)$^+$, 274.1590, found: 274.1589.

Synthesis of N^1,N^2-Bis((*R*)-8-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)ethane-1,2-diamine (5a). Amino intermediate **4a** (253 mg, 1.0 mmol, 2 equiv), dibromoethane (43 μL, 0.5 mmol) and toluene (5 mL) were placed in to a dried Young Teflon tube under nitrogen, which was flushed with nitrogen and sealed. The reaction mixture was heated at 120 °C for 36 h. The cooled brown mixture was poured into 2 mol/L NaOH aqueous solution (10 mL), and the aqueous phase was extracted with ethyl acetate (30 mL × 3). The combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. Purification by column chromatography afforded diamino product **5a** (134 mg, 50% yield, 91% brsm) with partial substrate **4a** recovered (114 mg, 45% recovery). New compound, waxy yellow solid, mp = 68−69 °C. $[\alpha]_D^{20}$ + 10.86 (*c* 0.58, $CHCl_3$). R_f = 0.50 (hexanes/ethyl acetate/triethylamine 20:2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−7.15 (m, 6H), 7.09 (d, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 7.2 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 4H), 3.86−3.76 (m, 8H), 2.93−2.74 (m, 4H), 2.20−2.11 (m, 2H), 1.99−1.85 (m, 4H), 1.76−1.65 (m, 4H), 1.56−1.49 (m, 2H), 1.07 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 142.3, 137.7, 137.3, 134.0, 130.3, 128.4, 128.3, 126.5, 113.3, 55.2, 51.7, 47.3, 29.9, 26.6, 17.4. HRMS Calcd for $C_{36}H_{41}N_2O_2$ (M + H)$^+$: 533.3163, found: 533.3165.

Synthesis of N^1,N^2-Bis((*R*)-8-(3,5-dimethylphenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)ethane-1,2-diamine (5b). The desired product was obtained in 57% yield (300 mg, 80% brsm) with the partial substrate **4b** recovered (148 mg, 29% recovery) on 1.0 mmol scale according to the procedure described above. New compound, yellow oil. $[\alpha]_D^{20}$ + 0.85 (*c* 1.30, $CHCl_3$). R_f = 0.38 (hexanes/ethyl acetate/triethylamine 20:2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.5 Hz, 2H), 7.08 (d, *J* = 7.3 Hz, 2H), 6.99 (d, *J* = 6.5 Hz, 2H), 6.95 (s, 6H), 3.77 (t, *J* = 3.4 Hz, 2H), 2.93−2.75 (m, 4H), 2.27 (s, 12H), 2.11−2.05 (m, 2H), 1.99−1.91 (m, 2H), 1.88−1.84 (m, 2H), 1.81−1.76 (m, 2H), 1.70−1.63 (m, 2H), 1.58−1.50 (m, 2H), 0.95 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 141.6, 137.8, 137.5, 137.0, 128.5, 127.9, 127.0, 126.4, 51.7, 47.2, 29.9, 26.7, 21.3, 17.6. HRMS Calcd for $C_{38}H_{45}N_2$ (M + H)$^+$: 529.3577, found: 529.3576.

Synthesis of N^1,N^2-Bis((*R*)-5,6,7,8-tetrahydro-[1,2′-binaphthalen]-8-yl)ethane-1,2-diamine (5c). The desired product was obtained in 66% yield (188 mg, 96% brsm) with the partial substrate **4c** recovered (84 mg, 31% recovery) on 0.5 mmol scale according to the procedure described above. New compound, foamy tan solid, mp = 81−82 °C. $[\alpha]_D^{20}$ − 29.78 (*c* 0.90, $CHCl_3$). R_f = 0.40 (hexanes/ethyl acetate/triethylamine 20:2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.73 (s, 2H), 7.56 (d, *J* = 8.3 Hz, 2H), 7.48−7.37 (m, 6H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 7.4 Hz, 2H), 7.07 (d, *J* = 7.3 Hz, 2H), 3.54 (s, 2H), 2.91−2.73 (m, 4H), 1.92 (d, *J* = 6.0 Hz, 2H), 1.74−1.53 (m, 6H), 1.37−1.30 (m, 4H), 0.67 (br, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 139.2, 137.9, 137.5, 133.1, 132.3, 128.7, 128.3, 128.1, 128.0, 127.8, 127.6, 127.3, 126.6, 126.1, 125.8, 51.6, 47.1, 30.0, 26.2, 17.1. HRMS Calcd for $C_{42}H_{41}N_2$ (M + H)$^+$: 573.3264, found: 573.3265.

Synthesis of 1,3-Bis((*R*)-8-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-4,5-dihydro-1*H*-imidazol-3-ium Chloride (6a). To a solution of diamine **5a** (266 mg, 0.5 mmol) in $HC(OEt)_3$ (8 mL) was added concentrated HCl (aqueous) (50 μL) at room temperature. The mixture was stirred for 30 min under nitrogen atmosphere and then heated to 80 °C until condensation was observed on the neck of the flask (approximately 0.5 h). At that moment, the mixture was allowed to stir open to the air for 12 h. After cooling to room temperature, diethyl ether (20 mL) was added to the suspension obtained. The precipitate was collected by filtration and washed with diethyl ether (5 mL × 3). The residual solvent was removed *in vacuo* to afford desired 4,5-dihydroimidazolinium salt **6a** (205 mg, 71% yield). New compound, off-white solid, mp = 242−243 °C. $[\alpha]_D^{20}$ − 122.52 (*c* 0.75, $CHCl_3$). R_f = 0.38 (dichloromethane/methanol 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 8.7 Hz, 6H), 6.97 (d, *J* = 8.2 Hz, 4H), 6.91 (d, *J* = 7.4 Hz, 2H), 5.46 (s, 2H), 3.84 (s, 6H), 3.15−3.00 (m, 4H), 2.78 (t, *J* = 5.4 Hz, 4H), 1.82−1.81 (m, 4H), 1.62−1.59 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 158.1, 142.1, 139.3, 132.4, 129.3, 129.2, 128.7, 127.6, 114.7, 55.5, 53.7, 45.4, 29.9, 29.0, 19.4. HRMS Calcd for $C_{37}H_{39}N_2O_2$ (M − Cl)$^+$: 543.3006, found: 543.3007.

Synthesis of 1,3-Bis((*R*)-8-(3,5-dimethylphenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-4,5-dihydro-1*H*-imidazol-3-ium Chloride (6b). The desired product was obtained in 77% yield (221 mg) on 0.5 mmol scale according to the procedure described above. New compound, white solid, mp = 155−156 °C. $[\alpha]_D^{20}$ − 173.97 (*c* 0.93, $CHCl_3$). R_f = 0.20 (dichloromethane/methanol 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 7.0 Hz, 2H), 6.99 (s, 2H), 6.96 (d, *J* = 7.4 Hz, 2H), 6.77 (s, 4H), 5.43 (t, *J* = 5.1 Hz, 2H), 3.39−3.30 (m, 2H), 3.12−3.06 (m, 2H), 2.82 (t, *J* = 6.1 Hz, 4H), 2.38 (s, 12H), 1.95−1.87 (m, 4H), 1.82−1.76 (m, 2H), 1.58−1.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 142.8, 140.1, 138.7, 138.6, 129.7, 129.1, 129.0, 128.8, 127.6, 125.9, 53.3, 46.9, 29.6, 28.3, 21.5, 18.8. HRMS Calcd for $C_{39}H_{43}N_2$ (M − Cl)$^+$: 539.3421, found: 539.3421.

Synthesis of 1,3-Bis((*R*)-5,6,7,8-tetrahydro-[1,2′-binaphthalen]-8-yl)-4,5-dihydro-1*H*-imidazol-3-ium Chloride (6c). The desired product was obtained in 70% yield (130 mg) on 0.3 mmol scale according to the procedure described above. New compound, off-white solid, mp = 178−179 °C. $[\alpha]_D^{20}$ − 208.83 (*c* 1.13, $CHCl_3$). R_f = 0.45 (dichloro-methane/methanol 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.00−7.87 (m, 6H), 7.60−7.41 (m, 8H), 7.18−7.17 (m, 2H), 7.03−6.98 (m, 4H), 5.39 (s, 2H), 2.85−2.44 (m, 8H), 1.41 (s, 2H), 1.17 (s, 2H), 0.80 (s, 2H), 0.30 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 141.9, 139.5, 138.6, 133.3, 132.6, 129.5, 129.2, 128.5, 128.1, 128.0, 127.4, 126.8, 126.5, 126.2, 53.9, 44.3, 29.9, 28.4, 19.9. HRMS Calcd for $C_{43}H_{39}N_2$ (M − Cl)$^+$: 583.3108, found: 583.3107.

Synthesis of N^1,N^2-Bis((*R*)-8-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)benzene-1,2-diamine (7a). To a Schlenk flask, equipped with a magnetic stir bar was added KO*t*-Bu (1.35 g, 12 mmol, 3 equiv) and Pd-PEPPSI-IPent (158 mg, 0.2 mmol, 5 mol %) (prepared by literature procedure)[19c], and the flask was evacuated and backfilled with argon (3 times), after which amine **4a** (2.44 g, 9.6 mmol, 2.4 equiv) and DME (25 mL) were added. After stirring for 2−3 min, 1,2-dibromobenzene (482 μL, 4 mmol) was added finally, and the sealed reaction vessel was placed into a preheated 50 °C oil bath with vigorous stirring for 40 h. Upon completion, the mixture was cooled to room temperature. The dark brown suspension was filtered through a bed of Celite and washed with ethyl acetate (25 mL). The filtrate was concentrated in vacuo and purified via silica gel flash chromatography to provide intermediate **7a** (1.85 g, 80% yield). New compound, foamy yellow solid, mp = 76−77 °C. $[\alpha]_D^{20}$ − 31.23 (*c* 1.14, $CHCl_3$). R_f = 0.50 (hexanes/ethyl acetate 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 4H), 7.10 (d, *J* = 7.5 Hz, 2H), 7.05 (d, *J* = 7.4 Hz, 2H), 6.68 (d, *J* = 8.5 Hz, 4H), 6.49 (dd, *J* = 5.7, 3.5 Hz, 2H), 6.20 (dd, *J* = 5.6, 3.6 Hz, 2H), 4.47 (s, 2H), 3.67 (s, 6H), 3.15 (s, 2H), 2.91−2.72 (m, 4H), 2.05 (d, *J* = 11.6 Hz, 2H), 1.95−1.83 (m, 2H), 1.67−1.63 (m, 2H), 1.56−1.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 143.1, 138.1, 136.2, 136.0, 133.3, 130.0, 128.6, 128.3, 127.1, 118.7, 113.5, 112.7, 55.4, 48.2, 29.7, 26.9, 17.7. HRMS Calcd for $C_{40}H_{41}N_2O_2$ (M + H)$^+$: 581.3163, found: 581.3165.

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Synthesis of N^1,N^2-Bis((*R*)-8-(3,5-dimethylphenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)benzene-1,2-diamine (7b). The desired product was obtained in 84% yield (482 mg) with Pd-PEPPSI-IPr[19a,b] at 70 °C instead on a 1.0 mmol scale according to the procedure described above. New compound, foamy yellow solid, mp = 59−60 °C. $[\alpha]_D^{20}$ − 68.85 (*c* 0.87, $CHCl_3$). R_f = 0.25 (hexanes/ethyl acetate 100:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 6.6 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 7.4 Hz, 2H), 6.80 (s, 4H), 6.74 (s, 2H), 6.50 (dd, *J* = 5.6, 3.2 Hz, 2H), 6.23 (dd, *J* = 5.7, 3.2 Hz, 2H), 4.39 (s, 2H), 3.22 (s, 2H), 2.93−2.72 (m, 4H), 2.05−1.98 (m, 16H), 1.67−1.64 (m, 2H), 1.55−1.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 140.6, 138.0, 137.4, 136.1, 135.5, 128.6, 128.3, 128.0, 127.1, 126.8, 118.4, 111.6, 48.0, 29.7, 27.1, 21.1, 17.7. HRMS Calcd for $C_{42}H_{45}N_2$ $(M + H)^+$: 577.3577, found: 577.3577.

Synthesis of N^1,N^2-Bis((*R*)-5,6,7,8-tetrahydro-[1,2′-binaphthalen]-8-yl)benzene-1,2-diamine (7c). The desired product was obtained in 75% yield (302 mg) with Pd-PEPPSI-IPr at 70 °C instead on a 0.65 mmol scale according to the procedure described above. New compound, foamy yellow solid, mp = 87−88 °C. $[\alpha]_D^{20}$ − 24.27 (*c* 0.82, $CHCl_3$). R_f = 0.30 (hexanes/ethyl acetate 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 4H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.44−7.37 (m, 6H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 4H), 6.24−6.22 (m, 2H), 6.04−6.02 (m, 2H), 4.57 (s, 2H), 3.37 (s, 2H), 3.00−2.94 (m, 2H), 2.86−2.78 (m, 2H), 2.09−1.95 (m, 4H), 1.70−1.66 (m, 2H), 1.57−1.50 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 138.4, 138.2, 136.2, 135.8, 133.2, 132.3, 128.9, 128.5, 128.0, 127.9, 127.6, 127.5, 127.2, 126.0, 125.8, 119.0, 113.3, 48.5, 29.7, 26.8, 17.6. HRMS Calcd for $C_{46}H_{41}N_2$ $(M + H)^+$: 621.3264, found: 621.3265.

Synthesis of 1,3-Bis((*R*)-8-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-1*H*-benzo[*d*]imidazol-3-ium Chloride (8a). The desired product was obtained in 63% yield (199 mg) on a 0.5 mmol scale according to the procedure described for **6a**. New compound, white solid, mp = 194−195 °C. $[\alpha]_D^{20}$ − 206.99 (*c* 1.20, $CHCl_3$). R_f = 0.30 (dichloromethane/methanol 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.57 (s, 1H), 7.31−6.60 (m, 18H), 6.25 (dd, *J* = 6.2, 3.1 Hz, 2H), 3.83 (s, 6H), 3.03 (s, 4H), 2.24−2.18 (m, 2H), 2.06−1.99 (m, 2H), 1.89−1.84 (m, 2H), 1.69−1.62 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 143.8, 142.7, 139.2, 132.0, 130.2, 129.5, 128.9, 128.8, 128.5, 128.1, 125.2, 114.1, 113.9, 57.0, 55.3, 32.5, 30.2, 20.3. HRMS Calcd for $C_{41}H_{39}N_2O_2$ $(M - Cl)^+$: 591.3006, found: 591.3010.

Synthesis of 1,3-Bis((*R*)-8-(3,5-dimethylphenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-1*H*-benzo[*d*]imidazol-3-ium Chloride (8b). The desired product was obtained in 68% yield (169 mg) on a 0.4 mmol scale according to the procedure described for **6a**. New compound, off-white solid, mp = 146−147 °C. $[\alpha]_D^{20}$ − 78.95 (*c* 1.24, $CHCl_3$). R_f = 0.50 (dichloromethane/methanol 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.26 (s, 1H), 7.31−7.23 (m, 6H), 7.07−7.06 (m, 2H), 6.81 (d, *J* = 7.1 Hz, 2H), 6.69 (s, 4H), 6.37 (s, 2H), 5.60 (br, 2H), 3.08−2.97 (m, 4H), 2.31−2.00 (m, 14H), 1.78−1.68 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 143.5, 139.8, 139.0, 138.0, 130.7, 129.5, 129.2, 129.1, 128.9, 128.0, 125.3, 113.8, 56.7, 32.2, 30.3, 21.4, 20.4. HRMS Calcd for $C_{43}H_{43}N_2$ $(M - Cl)^+$: 587.3421, found: 587.3422.

Synthesis of 1,3-Bis((*R*)-5,6,7,8-tetrahydro-[1,2′-binaphthalen]-8-yl)-1*H*-benzo[*d*]imidazol-3-ium Chloride (8c). The desired product was obtained in 70% yield (187 mg) on 0.4 mmol scale according to the procedure described for **6a**. New compound, off-white solid, mp = 151−152 °C. $[\alpha]_D^{20}$ − 203.71 (*c* 1.18, $CHCl_3$). R_f = 0.25 (dichloromethane/methanol 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 7.78 (s, 4H), 7.40−7.19 (m, 12H), 7.08−7.06 (m, 2H), 6.81 (d, *J* = 7.1 Hz, 2H), 6.15 (s, 4H), 2.81 (s, 4H), 1.55 (s, 2H), 1.31 (s, 2H), 0.95 (s, 2H), 0.32 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 142.4, 139.1, 137.5, 132.6, 132.2, 129.8, 129.7, 129.2, 128.7, 127.8, 126.1, 126.0, 125.6, 125.2, 113.6, 56.9, 30.6, 29.9, 20.2. HRMS Calcd for $C_{47}H_{39}N_2$ $(M - Cl)^+$: 631.3108, found: 631.3107.

Synthesis of 1,3-Bis((*R*)-8-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-1*H*-benzo[*d*]imidazol-3-ium Tetrafluoroborate (9). To a solution of diamine **7a** (581 mg, 1.0 mmol) and ammonium tetrafluoroborate (105 mg, 1.0 mmol) in $HC(OEt)_3$ (8 mL) was added a few drops of formic acid under nitrogen. The vessel was sealed and then heated to 120 °C for 12 h. After cooling to room temperature and evaporation to dryness, the residue was purified by flash chromatography to afford title compound **9** (644 mg, 95% yield). New compound, white solid, mp = 184−185 °C. $[\alpha]_D^{20}$ − 184.65 (*c* 1.33, $CHCl_3$). R_f = 0.40 (dichloromethane/methanol 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.32−7.25 (m, 4H), 7.04 (dd, *J* = 6.4, 3.1 Hz, 2H), 6.83−6.67 (m, 8H), 6.30−6.24 (m, 4H), 3.83 (s, 6H), 3.04 (t, *J* = 6.0 Hz, 4H), 2.21−2.15 (m, 2H), 2.04−1.96 (m, 2H), 1.89−1.85 (m, 2H), 1.70−1.62 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 143.0, 142.8, 139.4, 132.0, 130.4, 129.6, 129.2, 129.1, 128.4, 128.0, 125.6, 114.1, 57.5, 55.3, 32.4, 30.3, 20.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −151.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ −0.7. HRMS Calcd for $C_{41}H_{39}N_2O_2$ $(M - BF_4)^+$: 591.3006, found: 591.3005; calculated for $(^{11}BF_4)^-$ 87.0035, found: 87.0034.

Synthesis of 1,3-Bis((*R*)-8-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-1*H*-benzo[*d*]imidazol-3-ium Tetrakis-(3,5-bis(trifluoromethyl)phenyl)borate (10). Benzimidazolium chloride **8a** (67.8 mg, 0.10 mmol) was dissolved in dichloromethane (2 mL), and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (96.2 mg, 0.10 mmol) aqueous solution (2 mL) was added sequentially. The reaction mixture was then vigorously stirred for 5 h. The phases were separated, and aqueous phase was extracted with dichloromethane (15 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography to give benzimidazolium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate salt **10** (138.1 mg, 95% yield). New compound, foamy off-white solid, mp = 49−50 °C. $[\alpha]_D^{20}$ − 36.00 (*c* 0.80, $CHCl_3$). R_f = 0.63 (dichloromethane/methanol 20:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 8H), 7.58 (s, 4H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.30 (dd, *J* = 6.4, 3.1 Hz, 2H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 6.9 Hz, 2H), 6.99 (s, 1H), 6.91 (dd, *J* = 6.2, 3.0 Hz, 2H), 6.57−6.51 (m, 8H), 5.99 (t, *J* = 4.7 Hz, 2H), 3.57 (s, 6H), 2.95 (t, *J* = 5.6 Hz, 4H), 2.30−2.21 (m, 2H), 2.00−1.96 (m, 4H), 1.53−1.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9 (q, $^1J_{C-B}$ = 50 Hz), 159.1, 142.7, 138.9, 138.1, 135.0, 131.4, 130.3, 129.6 (d, $^3J_{C-F}$ = 4.7 Hz), 129.1 (qq, $^3J_{C-B}$ = 2.7 Hz, $^2J_{C-F}$ = 31 Hz), 128.7−128.6 (m), 128.5, 127.3, 126.9, 124.7 (q, $^1J_{C-F}$ = 271 Hz), 117.7−117.6 (m), 114.1, 113.1, 55.6, 55.1, 30.6, 29.1, 18.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.3. ^{11}B NMR (128 MHz, $CDCl_3$) δ −6.5. HRMS Calcd for $C_{41}H_{39}N_2O_2$ $(M - BAr_F)^+$: 591.3006, found: 591.3003; calcd for $C_{32}H_{12}{}^{11}BF_{24}$ $(BAr_F)^-$ 863.0654, found: 863.0650.

Synthesis of 1,3-Bis((*R*)-5,6,7,8-tetrahydro-[1,2′-binaphthalen]-8-yl)imidazolidine-2-thione (11). To a stirred solution of imidazolium salt **6c** (92.9 mg, 0.15 mmol) in THF (4 mL) were added S_8 (9.6 mg, 0.30 mmol, 2 equiv) and KOAm (37.9 mg, 0.30 mmol, 2 equiv) in turn at 0 °C under nitrogen. The suspension was warmed to room temperature and stirred for 6 h. After removing solvents under reduced pressure, the residue was separated by column chromatography to obtain desired thiourea **11** (86.8 mg, 94% yield). New compound, white solid, mp = 124−125 °C. $[\alpha]_D^{20}$ − 172.15 (*c* 0.97, $CHCl_3$). R_f = 0.63 (hexanes/ethyl acetate 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79−7.75 (m, 6H), 7.58 (s, 2H), 7.44−7.42 (m, 4H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 2H), 7.03 (t, *J* = 7.1 Hz, 4H), 5.51 (t, *J* = 7.3 Hz, 2H), 2.68−2.54 (m, 4H), 2.35−2.27 (m, 2H), 2.05−1.96 (m, 2H), 1.48−1.42 (m, 2H), 1.29−1.21 (m, 2H), 0.91−0.88 (m, 2H), 0.07−0.01 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 141.9, 139.5, 133.3, 132.5, 132.2, 129.3, 129.0, 128.2, 127.7, 127.5, 126.9, 126.5, 125.9, 125.5, 125.2, 52.2, 41.7, 30.8, 24.9, 20.9. HRMS Calcd for $C_{43}H_{39}N_2S$ $(M + H)^+$: 615.2828, found: 615.2829.

Synthesis of 1,3-Bis((*R*)-8-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-1,3-dihydro-2*H*-benzo[*d*]imidazole-2-thione (12). The desired product was obtained in 94% yield (58.4 mg) on 0.10 mmol scale according to the above procedure. New compound, white solid, mp = 208−209 °C. $[\alpha]_D^{20}$ − 9.83 (*c* 1.18, $CHCl_3$). R_f = 0.40 (hexanes/ethyl acetate 10:1). ^{1}H NMR (400 MHz,

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$CDCl_3$) δ 7.25−7.22 (m, 4H), 6.76 (t, J = 4.2 Hz, 2H), 6.61 (dd, J = 5.9, 3.1 Hz, 2H), 6.52−6.39 (m, 8H), 6.23 (t, J = 6.8 Hz, 2H), 5.81 (dd, J = 5.8, 3.2 Hz, 2H), 3.72 (s, 6H), 3.08−2.96 (m, 4H), 1.99−1.81 (m, 6H), 1.52−1.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.9, 157.9, 142.9, 139.0, 133.3, 131.3, 131.0, 129.5, 128.7, 128.0, 127.5, 120.7, 113.0, 110.0, 55.0, 53.9, 30.9, 29.4, 20.6. HRMS Calcd for $C_{41}H_{39}N_2O_2S$ $(M + H)^+$: 623.2727, found: 623.2724.

Synthesis of (1,3-Bis((*R*)-8-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-ylidene)-copper(I) Chloride (13). An oven-dried Young Teflon tube containing CuCl (24.8 mg, 0.25 mmol), benzimidazolium salt **8a** (156.8 mg, 0.25 mmol), and finely powdered K_2CO_3 (69.1 mg, 0.5 mmol, 2 equiv) was evacuated and refilled with nitrogen three times. After acetone (1.5 mL) was added to this tube under nitrogen, the resulting suspension was then heated at 60 °C for 24 h. The cooled mixture was filtered through a short silica column using CH_2Cl_2 as eluent and concentrated *in vacuo*. Pentane (5 mL) was added, thereby precipitating the desired product. Filtration and subsequent drying afforded title compound **13** (157.5 mg, 91% yield). New compound, off-white solid, mp = 240−241 °C. $[\alpha]_D^{20}$ − 112.57 (c 0.97, $CHCl_3$). R_f = 0.20 (hexanes/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.22 (m, 4H), 6.81−6.14 (m, 16H), 3.78 (s, 6H), 3.09−2.97 (m, 4H), 2.14−2.11 (m, 2H), 1.93 (s, 4H), 1.76 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.6, 158.1, 143.2, 139.2, 133.2, 132.3, 130.6, 129.1, 128.8, 128.5, 128.1, 122.3, 114.2, 112.2, 58.5, 55.3, 32.6, 30.5, 20.9. HRMS Calcd for $C_{41}H_{38}{}^{63}CuN_2O_2$ $(M - Cl)^+$: 653.2224, found: 653.2228.

Synthesis of (1,3-Bis((*R*)-8-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-ylidene)-silver(I) Chloride (14). Benzimidazolium salt **8a** (250.9 mg, 0.40 mmol), Ag_2O (46.3 mg, 0.20 mmol, 0.5 equiv), and 4 Å molecular sieves (100 mg) were placed in a dried Schlenk tube under nitrogen. After CH_2Cl_2 (10 mL) was added via syringe, the reaction mixture was stirred at room temperature for 20 h in the absence of light (aluminum foil). The brownish suspension was filtered through Celite and concentrated *in vacuo*. The residue was washed with Et_2O (10 mL) to obtain desired silver complex **14** (247.3 mg, 84% yield). New compound, white solid, mp = 229−230 °C. $[\alpha]_D^{20}$ − 77.45 (c 1.18, $CHCl_3$). R_f = 0.38 (hexanes/ethyl acetate 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20−7.17 (m, 4H), 6.72−5.92 (m, 16H), 3.74 (s, 6H), 2.96 (s, 4H), 2.02 (s, 2H), 1.85 (s, 4H), 1.67 (s, 2H). ^{13}C NMR (175 MHz, $CDCl_3$) δ 191.1 (dd, $^1J(^{109}Ag-^{13}C)$ = 271 Hz, $^1J(^{107}Ag-^{13}C)$ = 238 Hz), 158.3, 143.4, 139.3, 133.2, 132.3, 130.4, 129.2, 128.7, 128.3, 122.6, 114.2, 112.7, 59.3, 55.4, 32.6, 30.6, 21.0. HRMS Calcd for $C_{41}H_{38}{}^{107}AgN_2O_2$ $(M - Cl)^+$: 697.1979, found: 697.1979; $C_{41}H_{38}{}^{109}AgN_2O_2$ $(M - Cl)^+$ calcd: 699.1975, found: 699.1970.

Synthesis of (1,3-Bis((*R*)-8-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-ylidene)-gold(I) Chloride (15). The desired product was obtained in 85% yield (70.1 mg) on a 0.10 mmol scale according to the procedure described for complex **13**. New compound, white solid, mp >250 °C. $[\alpha]_D^{20}$ − 61.72 (c 0.93, $CHCl_3$). R_f = 0.40 (hexanes/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.23 (m, 6H), 6.81−6.60 (m, 10H), 6.38 (t, J = 7.4 Hz, 2H), 6.11−6.07 (m, 2H), 3.81 (s, 6H), 3.09−2.97 (m, 4H), 2.19−2.12 (m, 2H), 1.96−1.87 (m, 4H), 1.75−1.66 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.8, 158.3, 143.4, 139.3, 132.8, 132.0, 130.3, 129.2, 128.7, 128.2, 122.7, 114.3, 112.6, 58.8, 55.3, 32.3, 30.7, 20.9. HRMS Calcd for $C_{41}H_{38}AuN_2O_2$ $(M - Cl)^+$: 787.2593, found: 787.2598.

Synthesis of (1,3-Bis((*R*)-8-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-ylidene)-(1,5-cyclooctadiene)-iridium(I) Chloride (16). To an oven-dried Schlenk tube equipped with a magnetic stir bar was added KO*t*-Bu (22.4 mg, 0.20 mmol, 1.1 equiv), $[Ir(COD)Cl]_2$ (67.2 mg, 0.10 mmol, 0.56 equiv), and THF (5 mL) under nitrogen. The mixture was stirred at room temperature for 10 min, and then benzimidazolium salt **9** (122.1 mg, 0.18 mmol) was added. After stirring for 2 h at room temperature, the mixture was concentrated under reduced pressure. It was purified by column chromatography to get desired iridium complex **16** (114.3 mg, 68% yield). New compound, yellow solid, mp = 129−130 °C. $[\alpha]_D^{20}$ + 73.41 (c 0.85, $CHCl_3$). R_f = 0.50 (hexanes/diethyl ether 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.28 (m, 6H), 6.95−6.87 (m, 4H), 6.65−6.62 (m, 2H), 6.53 (d, J = 8.7 Hz, 2H), 6.47−6.41 (m, 4H), 6.13 (s, 1H), 5.97−5.95 (m, 1H), 5.90−5.88 (m, 1H), 4.58−4.53 (m, 1H), 4.43−4.38 (m, 1H), 4.02−3.95 (m, 1H), 3.70 (s, 3H), 3.68 (s, 3H), 3.23−3.14 (m, 2H), 3.04−3.00 (m, 2H), 2.36−2.34 (m, 1H), 2.24−1.97 (m, 6H), 1.86−1.72 (m, 3H), 1.64−1.51 (m, 2H), 1.44−1.19 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 159.2, 158.5, 144.6, 144.5, 140.0, 139.3, 137.1, 136.6, 134.2, 132.8, 132.6, 132.3, 130.1, 129.8, 129.7, 129.4, 128.6, 128.2, 128.1, 121.6, 121.1, 113.6, 112.7, 111.9, 84.6, 83.4, 58.2, 57.7, 55.3, 54.5, 52.6, 34.3, 33.2, 33.0, 30.7, 30.5, 30.3, 29.2, 28.6, 18.3, 18.1. HRMS Calcd for $C_{49}H_{50}{}^{193}IrN_2O_2$ $(M - Cl)^+$: 891.3496, found: 891.3495.

Synthesis of (1,3-Bis((*R*)-8-(4-methoxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)-1,3-dihydro-2*H*-benzo[*d*]imidazol-2-ylidene)-bis(carbon monoxide)-iridium(I) Chloride (17). Complex Ir(NHC)(COD)Cl **16** (55.6 mg, 0.06 mmol) was introduced into an oven-dried Schlenk tube under nitrogen. After CH_2Cl_2 (5 mL) was injected into the tube, CO gas was bubbled into the solution at room temperature for 1 h. Removal of the volatiles followed by washing with pentane afforded desired iridium complex **17** (41.8 mg, 80% yield). New compound, yellow solid, mp = 201−202 °C. $[\alpha]_D^{20}$ − 21.73 (c 0.98, $CHCl_3$). R_f = 0.25 (hexanes/ethyl acetate 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−5.58 (m, 20H), 3.67−3.46 (m, 6H), 3.02−1.68 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.8, 179.3, 168.2, 158.6, 144.0, 139.4, 135.0, 133.2, 130.9, 130.3, 129.0, 128.7, 128.1, 122.5, 113.7, 110.1, 59.1, 55.0, 32.8, 30.4, 28.1. IR (KBr, solution in CH_2Cl_2, cm^{-1}): 2934.25, 2865.60, 2836.18, 2057.97 (CO), 1969.24 (CO), 1610.02, 1514.15, 1462.87, 1425.75, 1397.47, 1343.25, 1284.81, 1245.00, 1195.55, 1177.11, 1034.44, 830.99, 791.90, 778.35, 736.45. HRMS Calcd for $C_{43}H_{38}{}^{193}IrN_2O_4$ $(M - Cl)^+$: 839.2455, found: 839.2453.

General Procedure for Rhodium-Catalyzed Enantioselective Addition of Phenylboronic Acid to 2-Naphthaldehyde. To an oven-dried Schlenk tube containing a magnetic stirring bar were added $RhCl_3$ (1.2 mg, 0.006 mmol, 3 mol %), $BzITL^{PMP}$ (3.8 mg, 0.006 mmol, 3 mol %), NaO*t*-Bu (38.4 mg, 0.40 mmol, 2 equiv), and DME (1 mL) under nitrogen. The mixture was stirred at room temperature for 30 min, and to this suspension were added 2-naphthaldehyde (31.2 mg, 0.20 mmol) and phenylboronic acid (48.8 mg, 0.40 mmol, 2 equiv) introduced in one portion. The resulting mixture was heated at 100 °C until full consumption of the starting aldehyde. Upon completion (36 h), the reaction was cooled to room temperature and diluted with ethyl acetate and water. The phases were separated, and the aqueous phase was extracted with ethyl acetate (10 mL × 3). After drying over Na_2SO_4, the organic phase was evaporated, and the residue was purified by flash chromatography (hexanes/ethyl acetate, 10/1), affording the title compound (39.1 mg, 84% yield, 25% ee) that slowly crystallized upon standing at room temperature. Known compound, white solid. $[\alpha]_D^{20}$ − 4.17 (c 1.20, $CHCl_3$) [lit.:[45] (−)-(*R*) $[\alpha]_D^{28}$ = −9.3 (c 0.43, $CHCl_3$) for 79% ee]. R_f = 0.40 (hexanes/ethyl acetate 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.87−7.80 (m, 3H), 7.53−7.48 (m, 2H), 7.45−7.43 (m, 3H), 7.36 (t, J = 7.4 Hz, 2H), 7.32−7.28 (m, 1H), 5.98 (s, 1H), 2.60 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 141.2, 133.4, 133.0, 128.7, 128.4, 128.2, 127.8, 126.8, 126.3, 126.1, 125.1, 124.9, 76.5. HPLC (OD-H column, *i*-PrOH/*n*-hexane 20/80, 0.8 mL/min, 254 nm): t_1 = 11.6 min (maj), t_2 = 13.3 min.

General Procedure for Cu-Catalyzed Enantioselective Hydrosilylation of 4-Acetylbiphenyl. To an oven-dried Schlenk tube containing a magnetic stirring bar were added $Cu(BzITL^{PMP})Cl$ **13** (4.1 mg, 0.006 mmol, 3 mol %), NaO*t*-Bu (2.3 mg, 0.024 mmol, 12 mol %), and dry toluene (2 mL) under nitrogen. The mixture was stirred at room temperature for 10 min, and to this solution was added $PhMeSiH_2$ (82 μL, 0.60 mmol, 3 equiv) with a micro syringe. After 20 min of stirring, the mixture was cooled to 0 °C, and 4-acetylbiphenyl (39.2 mg, 0.20 mmol) was then introduced in one portion. The resulting mixture was allowed to proceed at 0 °C until full consumption of the starting ketone. Upon completion (8 h), the

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reaction was quenched with 2 mol/L aqueous NaOH (2 mL), and MeOH (1 mL) was added with vigorous stirring for 12 h. The phases were separated, and the aqueous phase was extracted with ethyl acetate (10 mL × 3). After drying over Na_2SO_4 and evaporation of the solvent, purification by column chromatography with hexanes/ethyl acetate (30:1, v/v) afforded the desired product (39.5 mg, >99% yield, 43% ee). Known compound, white solid. $[\alpha]_D^{20}$ + 17.09 (*c* 0.79, $CHCl_3$) [lit.:[46] (+)-(*S*) $[\alpha]_D^{28}$ − 43.7 (c 0.75, $CHCl_3$) for 99% ee]. R_f = 0.25 (hexanes/ethyl acetate 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.62−7.59 (m, 4H), 7.47−7.44 (m, 4H), 7.36 (t, *J* = 7.3 Hz, 1H), 4.96 (q, *J* = 6.3 Hz, 1H), 2.01 (s, 1H), 1.55 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 141.0, 140.6, 128.9, 127.4, 127.2, 126.0, 70.3, 25.3. HPLC (AD-H column, *i*-PrOH/*n*-hexane 5/95, 0.7 mL/min, 254 nm): t_1 = 17.1 min, t_2 = 18.9 min (major).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00492.

X-ray crystal structures, topographic steric maps, NMR spectra (^1H, ^{13}C, ^{11}B, ^{19}F), IR spectra and HPLC spectra (PDF)

Accession Codes

CCDC 1815955, 1815957−1815960, 1818774, and 1822763 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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