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Chiral, Sterically Demanding N-Heterocyclic Carbenes Fused into a Heterobiaryl Skeleton: Design, Synthesis, and Structural Analysis

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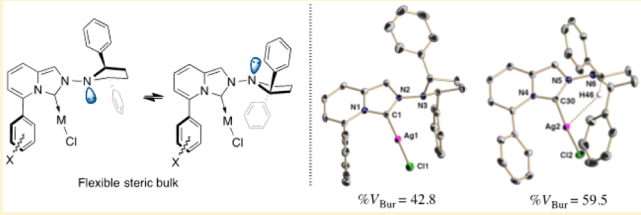
Supporting Information

ABSTRACT: A series of Cu(I), Ag(I), and Au(I) complexes incorporating a new family of imidazopyridin-3-ylidene ligands substituted by a diphenylpyrrolidino group at N(1) and aryl groups at C(5) has been synthesized and their structures determined by X-ray diffraction analysis. This structural study has revealed an extremely high steric protection of the metal center by the bulky heterobicyclic carbenes, while the inversion at the exocyclic N(sp^3) atom provides a remarkable flexibility.



INTRODUCTION

The design of new ligands with tailored steric and electronic properties is one of the essential tools for the development of new catalytic reactions and/or the resolution of activity or (stereo)selectivity issues. In particular, very strong ligand effects have been observed in Au(I)[1] and Ag(I)[2] catalyzed reactions, where electron-rich phosphorus-based ligands in a biaryl framework (Figure 1) constitute one of the most successful

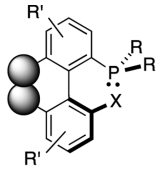
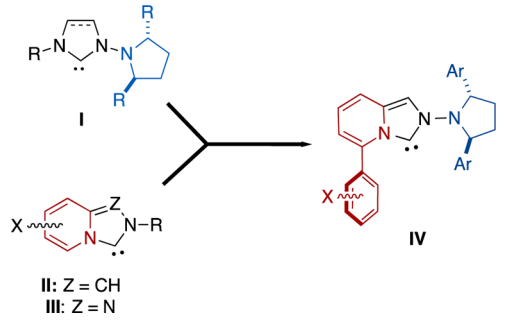


Figure 1. Biaryl phosphine ligands.

families of ligands. The dialkyl biphenylphosphine family (X-PHOS) developed by Buchwald and co-workers,[3] on one side, and the chiral C2-symmetric bidentate phosphines such as BINAP[3] and functionalized analogues (including BIPHEP, SEGPHOS, GARPHOS, DIFLUOROPHOS, etc.),[4] as well as heterobidentate X-MOP[5] ligands benefit from a biaryl framework that provides a considerable steric protection by the aromatic shield. We have been interested in the design and applications of new families of N-heterocyclic carbene (NHC) ligands, an area where we have initially reported on the introduction of *N*-dialkylamino groups as a strategy to incorporate chirality into NHCs of type **I**[6] (Scheme 1). Our work has also shown that the electronic properties of these ligands can be tuned by inclusion of the diamino carbene

Scheme 1. Heterobicyclic Carbenes in a Biaryl Skeleton



system in a heterobicyclic skeleton. In particular, NHCs derived from the imidazo[1,5-*a*]pyridin-3-ylidene **II**[7] and the 1,2,4-triazolo[4,3-*a*]- pyridin-3-ylidene **III**[8] moieties have been developed and their transition metal complexes have been applied in catalysis.[9] We have now focused on merging the successful design elements of Buchwald's biaryl phosphine X-PHOS ligands with the excellent catalytic properties of NHCs and, at the same time, incorporate a chiral element for potential applications in asymmetric catalysis. On this basis, we envisaged that the combination of the strategies leading to **I** and **II**/**III**, *i.e.*, the introduction of C2-symmetric cyclic *N*,*N*-dialkylamino groups into a heterobicyclic framework, would result in a system **IV**, which, incorporating aryl groups at position 5, should closely mimic the privileged X-PHOS architecture. It is worth highlighting that the inclusion of the diamino carbene in the heterobicyclic system avoids N−C(carbene) rotations,

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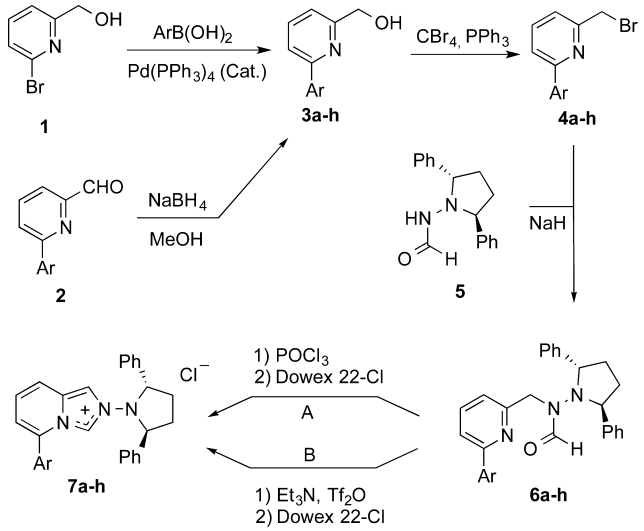
thereby fixing the direction of the σ-orbital parallel to the biaryl axis. In this contribution, we disclose the results collected on the basis of this rational design from which a series of coinage metal complexes have been prepared and characterized. The effect of the ligand onto the pocket around the metal center has been investigated providing general features about the steric protection that bulky heterobicyclic carbene ligands infer on those complexes.

RESULTS AND DISCUSSION

Synthesis of Ligand Precursors. The synthesis of ligands **IV** and their metal complexes is envisaged by deprotonation or direct metalation of the corresponding imidazo[1,5-*a*]-pyridinium salts **7**. The synthesis of the latter was planned through a two-step sequence route: (a) base-promoted alkylation of *N*-[(2*S*,5*S*)-2,5-diphenylpyrrolidin-1-yl]formamide **5**[10] with 6-aryl-2-bromomethylpyridines **4** and (b) cyclization of the resulting *N*-formylhydrazines **6** (Scheme 2). The

Scheme 2. Synthesis of the Ligand Precursors



required bromomethylpyridines **4** were readily prepared from the parent alcohols **3**, obtained by Suzuki−Miyaura coupling of 6-bromopyridine methanol **1** and aryl boronic acids (Ar = 4-*t*Bu-C_6H_4, 3,5-$(CF_3)_2$-C_6H_3, and Mes) or by reduction of aldehydes **2** [Ar = 4-F-C_6H_4, 4-OMe-C_6H_4, and 2,4,6-$(i\text{Pr})_3$-C_6H_2]. Following this simple sequence, a series of 5-aryl-*N*-[(2*S*,5*S*)-2,5-diphenylpyrrolidino]-imidazo[1,5-*a*]pyridinium chlorides **7a−h** were obtained via formylhydrazines **6a−h** in satisfactory yields (Table 1). The cyclization was performed by treatment with $POCl_3$ except for the most hindered substrate (Ar = 2,4,6-$(i\text{Pr})_3$-C_6H_2) **7h**, which was best obtained using Tf_2O/Et_3N as the condensation agent.[11] In both cases the azolium products were transformed into the chlorides **7a−h** after anion exchange (Dowex 22-Cl). The azolium **7b** was crystallized, and its structure was analyzed by X-ray diffraction studies (Figure 2).

Synthesis of Metal Complexes. With the ligand precursors in hand, we started the metalation studies using the method developed by Lin and co-workers[12] for the synthesis of silver carbenes. Thus, treatment of azolium salts **7a−h** with Ag_2O smoothly afforded the expected complexes **8a−h** in good to excellent yields (Scheme 3 and Table 2). These complexes were used as carbene transfer agents in

Table 1. Synthesis of Imidazopyridinium Salts 7a−h[a]

4	Ar	6 (%)[b]	method	7 (%)[b]
4a	Ph	**6a** (59)	A	**7a** (74)
4b	4-F-C_6H_4	**6b** (90)	A	**7b** (83)
4c	4-OMe-C_6H_4	**6c** (76)	A	**7c** (86)
4d	4-*t*Bu-C_6H_4	**6d** (78)	A	**7d** (80)
4e	3,5-$(CF_3)_2$-C_6H_3	**6e** (59)	A	**7e** (73)
4f	2,6-$(OMe)_2$-C_6H_3	**6f** (77)	A	**7f** (89)
4g	Mes	**6g** (64)	A	**7g** (80)
4h	2,4,6-$(i\text{Pr})_3$-C_6H_2	**6h** (84)	B	**7h** (86)

[a]Reactions performed at 1−6 mmol scale. [b]Isolated yields after column chromatography.

subsequent transmetalations to access the corresponding gold complexes **9a−h**. Finally, copper−NHC complexes **10a,b,f−h** were obtained after deprotonation of the azolium salts **7** with KO^{t}Bu and coordination of the resulting free carbenes to CuCl.

In order to have a reference compound to evaluate the steric and structural effects by the chiral diphenylpyrrolidino group compared with a very bulky group, we decided to synthesize also the *N*-adamantyl analogues, substituted at C5 by the bulky 2,4,6-triisopropylphenyl group (Scheme 4). A similar approach starting from **4h** and *N*-(1)-adamantyl formamide **11** provided intermediate **12** in 70% yield. As for **6h**, the cyclization of this bulky formamide worked best using Tf_2O/Et_3N as the condensation agent. The resulting azolium **13** was then transformed into the silver and gold complexes **14** and **15** using the same procedures as for the dialkylamino-substituted derivatives.

Structural Analysis. In addition to the azolium **7b**, silver and gold complexes **8a,b,e,h** and **6a,h** could be crystallized as single crystals and their structures were analyzed by X-ray diffraction. As it was previously observed in 1,3-Bis(*N*,*N*-dialkylamino)-imidazolin-2-ylidenes[5a] and *N*-dialkylamino-*N*′-alkylimidazol-2-ylidenes,[5b] the X-ray structures of compounds **8** and **9** revealed in general no conjugation between the dialkylamino group and the diaminocarbene electronic system, as deduced by the degree of pyramidalization observed at the exocyclic nitrogen and the low coplanarity between the pyrrolidine ring and the heterocycle (expressed by the C2(5)−N3−N2−C1 dihedral angles). The steric bulk of the NHC ligands in these structures were estimated using the percent buried volume (%V_{Bur}) descriptor introduced by Clavier and Nolan,[13] using the Samb*V*ca software developed by Cavallo and co-workers.[14,15] In all cases, the steric bulkiness proved to be exceptionally high, with %V_{Bur} values ranging from 41.5 to a record 59.9% (Figure 2). Not surprisingly, with the exception of **8e**, the high steric demand of the ligands favor a linear coordination mode.[16]

The structure of the azolium salt **7b** exhibits some interesting singularities. The %V_{Bur} values of 58.0 and 58.2 observed for the two independent molecules in the molecular cell of azolium **7b** are, in average, the highest within the series, as the smaller H atom at C(1) allows nonpermitted conformations in other cases. In particular, the heterobiaryl moiety can reach conformations closer to coplanarity [dihedral angles of ca. 44° for both **7b(1)** and **7b(2)** were observed], and one of the molecules [**7b(1)**] also showed a significant conjugation between the pyrrolidine ring and the heterocycle, as inferred from the coplanarity of both rings and the low pyramidalization of the exocyclic N(sp^3) atom. The structures of metal complexes **8** and **9** also showed a remarkable degree of

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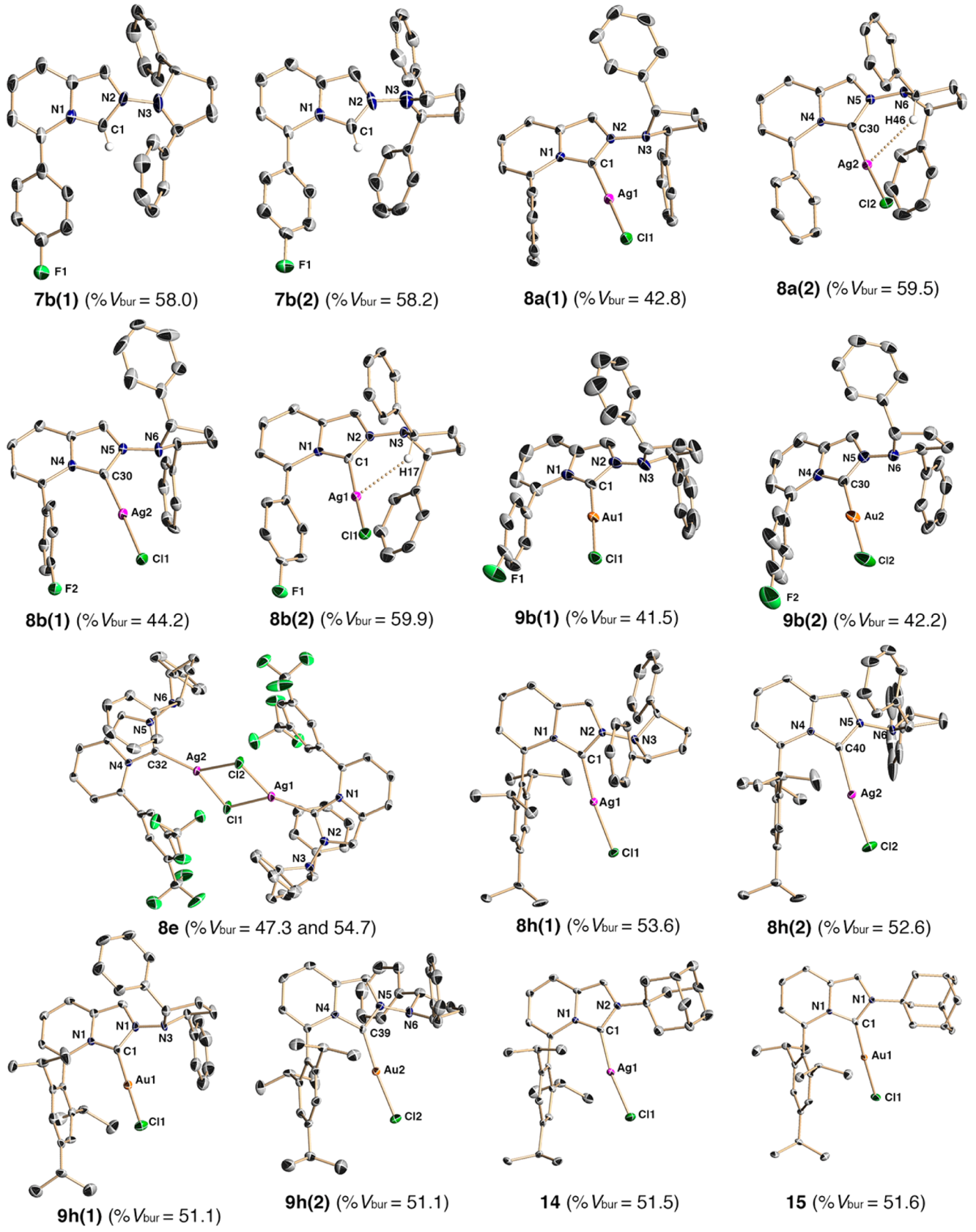

Figure 2. X-ray structures of **7b**, **8a**, **8b**, **9b**, **8e**, **8h**, **9h**, **14**, and **15**. Chloride counteranions (for **7b**) and H atoms (except those involved in CH–metal interactions) are omitted for clarity.

flexibility:[17] although the coplanarity of the heterobiaryl unit is obviously more hindered (dihedral angles >64° were observed in all cases), there is still some flexibility associated with N–N bond rotations [see, for instance, structures of **9h(1)** versus

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Scheme 3. Metalation Reactions

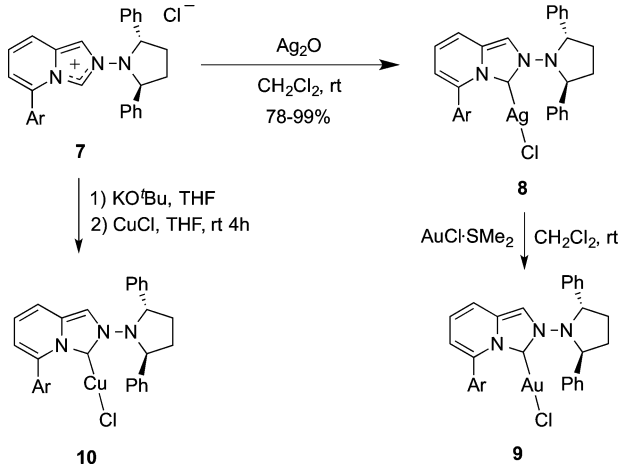
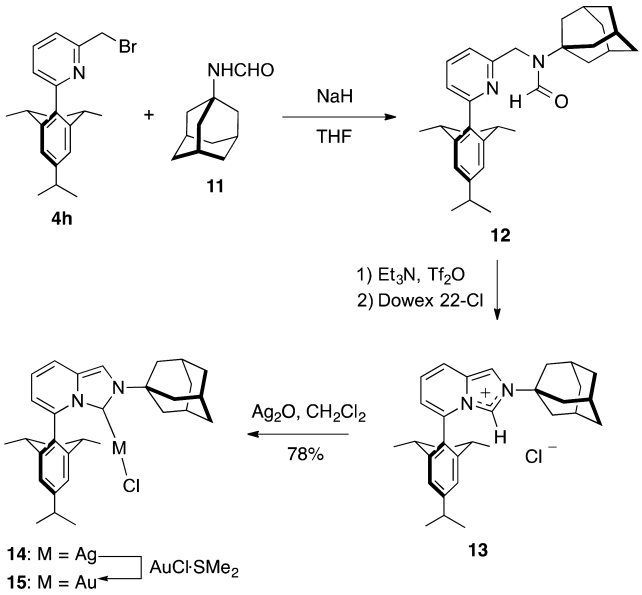


Table 2. Synthesis of Complexes 8, 9, and 10

Ar	8 (%)	9 (%)	10 (%)
Ph	**8a** (98)	**9a** (67)	**10a** (59)
4-F-C_6H_4	**8b** (97)	**9b** (97)	**10b** (55)
4-OMe-C_6H_4	**8c** (98)	**9c** (74)	
4-*t*Bu-C_6H_4	**8d** (99)	**9d** (74)	
3,5-$(CF_3)_2$-C_6H_3	**8e** (78)	**9e** (90)	
2,6-$(OMe)_2$-C_6H_3	**8f** (97)	**9f** (81)	**10f** (50)
Mes	**8g** (98)	**9g** (68)	**10g** (60)
2,3,6-$(i\mathrm{Pr})_3$-C_6H_2	**8h** (80)	**9h** (95)	**10h** (55)

Scheme 4. Synthesis of *N*-Adamantyl Derivatives



9h(2)] and/or Walden inversions at N(3) resulting in structures with the N lone pair oriented in *syn*- or *anti*-periplanar arrangements with respect to the C(carbene)−metal bond. Thus, in several cases the two independent molecules in the molecular cell [**8a(1)** vs **8a(2)** and **8b(1)** vs **8b(2)**] or the two ligands in the same molecule (**8e**) show a dramatic increase of the bulkiness as a consequence of that inversion, as represented in Figure 3. Thus, the $\%V_{Bur}$ steric descriptor rises from 42.8 to 59.5% in **5a**, from 44.2 to 59.9% in **8b**, and from 47.3 to 54.7% in **8e**. Remarkably, the values recorded for

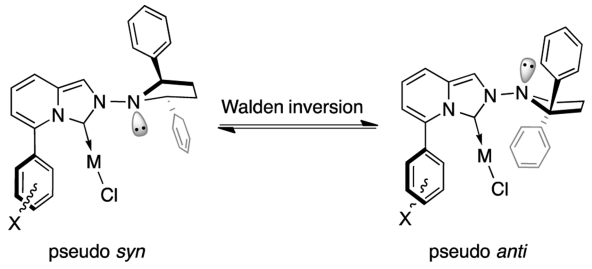


Figure 3. Conformational flexibility in the diphenylpyrrolidino group.

8a(2) and **8b(2)** are, to the best of our knowledge, the highest reported for any monodentate NHC ligand so far.[18] The folding in this conformation also results in a weak but significant C(2)H−Ag interaction (distances, Ag(2)−H(46) of 2.57 Å and Ag(1)−H(17) of 2.56 Å). Even the triisopropylphenyl derivatives **8h** and **9h**, with the pyrrolidine N-pyramidalized in the less hindered pseudo *syn*-conformation, present lower $\%V_{Bur}$ values (between 51.5 and 53.6%), demonstrating that the effect of the N(3) Walden inversion is more determining than the substitution pattern at the aryl group at C(5). Finally, the *N*-adamantyl silver and gold analogues **11** and **12** are also crystalline compounds, suitable for X-ray diffraction analysis. The comparison of these structures with the diphenylpyrrolidine analogues **5h** and **6h** revealed that the diphenylpyrrolidine is a very bulky group, providing quantifiable levels of steric bulk similar or higher than the adamantyl group, even in the less demanding conformation (these structures are in all cases characterized by the less hindered Walden conformation in the pyrrolidine ring).

CONCLUSIONS

In summary, the introduction of the (2*S*,5*S*)-2,5-diphenylpyrrolidino group into the N(2) position of 5-aryl substituted imidazo[1,5-*a*]pyridin-3-ylidenes provides an NHC ligand family that mimics the privileged architecture of Buchwald's biaryl phosphines. Moreover, the synthesis and structural analysis of several coinage metal complexes containing these ligands reveal exceptionally high levels of steric bulk, reaching record $\%V_{Bur}$ values within the NHC family of ligands. Moreover, this structural study reveals also a considerable level of flexibility associated with the conformational changes in the pyrrolidine ring.

EXPERIMENTAL SECTION

General Considerations. Air- and moisture-sensitive manipulations were carried out under an argon atmosphere using standard Schlenk techniques. All solvents were dried using a Solvent Purification System (Innovative Technologies). ^{1}H NMR spectra were recorded at 300, 400, or 500 MHz; ^{13}C NMR spectra were recorded at 75, 100, or 125 MHz with the solvent peak used as the internal reference. Column chromatography was performed on silica gel (Merck Kieselgel 60). Analytical TLC was performed on aluminum backed plates (1.5 × 5 cm) precoated (0.25 mm) with silica gel (Merck, Silica Gel 60 F_{254}). Compounds were visualized by exposure to UV light or by dipping the plates in a solution of 5% $(NH_4)_2Mo_7O_{24}\cdot 4H_2O$ in 95% EtOH (w/v) followed by heating. The following starting materials were purchased from commercial sources and used without further purification: 6-(bromopyridin-2-yl)methanol (**1**), phenylboronic acid, 4-(*tert*-butyl)phenyl)boronic acid, [3,5-bis(trifluoromethyl)phenyl]boronic acid, (2,6-dimethoxyphenyl)boronic acid, mesitylboronic acid, 6-(4-fluorophenyl)-2-pyridinecarboxaldehyde (**2b**), and 6-(4-methoxyphenyl)-2-pyridinecarboxaldehyde (**2c**). *N*-(Adamantyl)-formamide[19] and 1-amino-

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(2*S*,5*S*)-2,5-diphenylpyrrolidine[10] were prepared according to literature procedures.

Cross-Coupling of 6-(Bromopyridin-2-yl)methanol 1 with Aryl Boronic Acids. General Procedure for the Synthesis of 3a,d−g. Compound **1** (5−10 mmol) was added to a solution of $Pd(PPh_3)_4$ (3 mol %) in DME (20 mL), and the mixture was stirred for 30 min. The aryl boronic acid (1.4 equiv) and a solution of 2 M Na_2CO_3 (2 equiv) were added, and the mixture was stirred at 90 °C overnight. Upon cooling, the organic layer was collected and the water layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was dried over Na_2SO4, concentrated, and the residue was purified by flash chromatography on silica gel. Starting materials, yields, solvents used for chromatography, and characterization data for compounds **3a,d−g** are as follows.

*[(6-Phenyl)pyridin-2-yl]methanol (**3a**).*[20] From **1** (1.00 g, 5.10 mmol) and phenylboronic acid (0.87 g, 7.14 mmol), the general procedure was applied, and the product was purified by flash chromatography (1:3 AcOEt/cyclohexane) to yield 0.77 g (82%) of know **3a** as a white solid.

*[6-(4-tert-Butylphenyl)pyridin-2-yl]methanol (**3d**).*[21] From **1** (1.00 g, 5.10 mmol) and (4-(*tert*-butyl)phenyl)boronic acid (1.27 g, 7.14 mmol), the general procedure was applied, and the product was purified by flash chromatography (1:4 AcOEt/*n*-hexane) to yield 1.19 g (97%) of **3d** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.76 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.65 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.53 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 7.15 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 4.83 (s, 2H), 4.23 (s, 1H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 156.0, 152.3, 137.3, 135.9, 126.5, 125.6, 118.6, 118.3, 63.8, 34.6, 31.2. HRMS (CI) *m*/*z* calcd for $C_{16}H_{20}NO$ (M + H) 242.1545, found 242.1539. Mp: 54−56 °C.

*[6-(3,5-Bis(trifluoromethyl)phenyl)pyridin-2-yl]methanol (**3e**).* From **1** (0.90 g, 4.57 mmol) and [3,5-bis(trifluoromethyl)phenyl]-boronic acid (1.65 g, 6.4 mmol), the general procedure was applied, and the product was purified by flash chromatography (1:5 AcOEt/*n*-hexane) to yield 1.37 g (93%) of **3e** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 2H), 7.91 (s, 1H), 7.83 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.70 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.31 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 4.84 (s, 2H), 3.67 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 152.9, 140.7, 137.8, 132.0 (q, $^2J_{CF}$ = 33.1 Hz), 126.8, 123.2 (q, $^1J_{CF}$ = 271.0 Hz), 122.5, 120.3, 119.2, 64.1. HRMS (CI) *m*/*z* calcd for ($C_{14}H_{10}F_6NO$ (M + H) 322.0667, found 322.0675. Mp: 93−95 °C.

*[6-(2,6-Dimethoxyphenyl)pyridin-2-yl]methanol (**3f**).* From **1** (2.00 g, 10.64 mmol) and (2,6-dimethoxyphenyl)boronic acid (2.70 g, 14.89 mmol), the general procedure was applied, and the product was purified by flash chromatography (3:1 AcOEt/cyclohexane) to yield 2.30 g (88%) of **3f** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74−7.59 (m, 1H), 7.56−7.43 (m, 1H), 7.30 (t, $^3J_{HH}$ = 8.4 Hz, 1H), 7.18 (dd, $^3J_{HH}$ = 10.9, 7.7 Hz, 1H), 6.63 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 4.76 (s, 2H), 3.87 (s, 1H), 3.69 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 157.9, 153.2, 136.3, 131.9, 129.7, 128.5, 124.7, 118.7, 118.4, 104.2, 64.2, 55.9. HRMS (CI) *m*/*z* calcd for $C_{14}H_{16}NO_3$ (M + H) 246.1130, found 246.1122. Mp: 121−123 °C.

*(6-Mesitylpyridin-2-yl)methanol (**3g**).*[22] From **1** (1.00 g, 5.10 mmol) and mesitylboronic acid (1.17 g, 7.14 mmol), the general procedure was applied, and the product was purified by flash chromatography (1:3 AcOEt/cyclohexane) to yield 1.15 g (99%) of **3f** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 7.16 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 7.12 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 6.96 (s, 2H), 4.79 (s, 2H), 4.04 (s, 1H), 2.34 (s, 3H), 2.03 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 158.6, 137.6, 137.3, 136.8, 135.7, 128.3, 123.2, 118.1, 63.9, 20.9, 20.1. HRMS (CI) *m*/*z* calcd for $C_{15}H_{17}NO$ 227.1310, found 227.1302. Mp: 126−128 °C.

*6-(2,4,6-Triisopropylphenyl)picolinaldehyde **2h**.* This compound was prepared by a modification of the known procedure:[23] *t*BuLi (1.7 M in pentane, 1.5 mL, 2.5 mmol) was added to a cooled (−78 °C) solution of 2-bromo-6-(2,4,6-triisopropylphenyl)pyridine (533 mg, 1.48 mmol) in anhydrous THF (10 mL). The reaction mixture was allowed to warm to room temperature and stirred for 2 h. DMF (0.34 mL, 4.44 mmol) was added, and the mixture was stirred for 12 additional hours, then cooled to −40 °C, diluted with Et_2O (40 mL), and quenched by addition of saturated $NaHCO_3$ solution (40 mL). The aqueous layer was extracted with Et_2O (3 × 10 mL), and the combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (15:1 cyclohexane/Et_2O) to afford 350 mg (77%) of **2h** as a light yellow crystalline solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.95−7.88 (m, 2H), 7.50 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 7.09 (s, 2H), 2.93 (hept, $^3J_{HH}$ = 6.5 Hz, 1H), 2.42 (hept, $^3J_{HH}$ = 7.0 Hz, 2H), 1.27 (d, $^3J_{HH}$ = 7.0 Hz, 6H), 1.11 (d, $^3J_{HH}$ = 7.0 Hz, 6H), 1.08 (d, $^3J_{HH}$ = 6.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.0, 160.9, 152.4, 149.3, 146.1, 136.6, 129.3, 120.9, 119.3, 114.1, 34.4, 30.4, 24.1, 24.0, 23.9. HRMS (CI) *m*/*z* calcd for $C_{21}H_{27}NO$ 309.2093, found 309.2097. Mp: 210−211 °C.

General Procedure for the Aldehyde Reduction. Synthesis of Compounds 3b,c,h. $NaBH_4$ (2 equiv) was added to a cooled (0 °C) solution of **2b,c,h** (ca. 5 mmol) in MeOH (50 mL) and the mixture was stirred at room temperature for 10 h. Saturated NH_4Cl (30 mL) and K_2CO_3 (1 equiv) were added and the mixture was stirred for 15 min. The solids were removed by filtration and washed with CH_2Cl_2 (3 × 15 mL). The combined organic layer was washed with brine (15 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure and the resulting residue was purified by flash chromatography on silica gel. Starting materials, yields, solvents used for chromatography and characterization data for compounds **3b,c,h** are as follows:

*[6-(4-Fluorophenyl)pyridin-2-yl]methanol (**3b**).*[24] From **2b** (1.08 g, 5.37 mmol), the general procedure was applied, and the product was purified by flash chromatography (1:3 AcOEt/*n*-hexane) to yield 1.07 g (97%) of known **3b** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.92 (m, 2H), 7.71 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.56 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.16−7.08 (m, 3H), 4.78 (s, 2H), 4.18−3.85 (sa, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7 (d, $^1J_{CF}$ = 248.8 Hz), 158.8, 155.2, 137.7, 135.0 (d, $^4J_{CF}$ = 3.8 Hz), 128.8 (d, $^3J_{CF}$ = 8.5 Hz), 118.8, 115.7 (d, $^2J_{CF}$ = 21.7 Hz), 64.1.

*[6-(4-Methoxyphenyl)pyridin-2-yl]methanol (**3c**).*[25] From 6-(4-methoxyphenyl)picolinaldehyde (1.09 g, 5.12 mmol), the general procedure was applied, and the product was purified by flash chromatography (1:2 AcOEt/*n*-hexane) to yield 1.00 g (90%) of **3c** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 7.67 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 7.54 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.06 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 6.97 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 4.76 (s, 2H), 4.13 (sa, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 158.2, 155.6, 137.2, 131.3, 128.0, 118.1, 117.8, 114.0, 63.8, 55.2. HRMS (CI) *m*/*z* calcd for $C_{13}H_{13}NO_2$ 215.0946, found 215.0946.

*(6-(2,4,6-Triisopropylphenyl)pyridin-2-yl)methanol (**3h**).* From **2h** (1.70 g, 5.50 mmol), the general procedure was applied, and the product was purified by flash chromatography (1:9 AcOEt/toluene) to yield 1.15 g (67%) of **3h** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 7.20 (dd, $^3J_{HH}$ = 7.7, 3.0 Hz, 2H), 7.09 (s, 2H), 4.81 (s, 2H), 4.02 (s, 1H), 2.95 (hept, $^3J_{HH}$ = 6.9 Hz, 1H), 2.46 (hept, $^3J_{HH}$ = 6.9 Hz, 2H), 1.30 (d, $^3J_{HH}$ = 6.9 Hz, 6H), 1.11 (dd, $^3J_{HH}$ = 7.7, 6.9 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 158.5, 149.2, 146.6, 136.6, 136.1, 123.9, 121.1, 118.5, 64.2, 34.7, 30.7, 24.4, 24.4, 24.4. HRMS (CI) *m*/*z* calcd for $C_{21}H_{30}NO$ (M + H) 312.2327, found 312.2328. Mp: 164−166 °C.

Synthesis of 2-Bromomethylpyridines 4a−h. General Procedure. To a cooled (0 °C) solution of **3a−h** (typically 5 mmol) in dry CH_2Cl_2 (10 mL/mmol) were added CBr_4 (1.2 equiv) and PPh_3 (1.2 equiv), and the mixture was stirred for 3 h. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel. Starting materials, yields, solvents used for chromatography, and characterization data for compounds **4a−h** are as follows.

*2-(Bromomethyl)-6-phenylpyridine (**4a**).*[26] From **3a** (0.77 g, 4.17 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:4 AcOEt/cyclohexane) to yield 0.94 g (91%) of known **4a** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06−7.98 (m, 2H), 7.76 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.64 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.52−7.37 (m, 4H), 4.64 (s, 2H). ^{13}C NMR (100

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MHz, $CDCl_3$) δ 157.1, 156.6, 138.8, 137.6, 129.1, 128.7, 126.9, 121.6, 119.6.

*2-(Bromomethyl)-6-(4-fluorophenyl)pyridine (**4b**).* From **3b** (1.00 g, 4.92 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:3 AcOEt/cyclohexane) to yield 1.20 g (91%) of **4b** as a white solid. ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.15−7.90 (m, 2H), 7.74 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.59 (dd, $^3J_{HH}$ = 7.8, 0.6 Hz, 1H), 7.38 (dd, $^3J_{HH}$ = 7.7, 0.7 Hz, 1H), 7.22−7.07 (m, 2H), 4.61 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.72 (d, $^1J_{CF}$ = 248.9 Hz), 156.8, 156.2, 137.9, 135.1 (d, $^4J_{CF}$ = 3.3 Hz), 128.9 (d, $^3J_{CF}$ = 8.4 Hz), 121.8, 119.4, 115.7 (d, $^2J_{CF}$ = 21.5 Hz), 34.2.

*2-(Bromomethyl)-6-[(4-methoxy)phenyl]pyridine (**4c**).* From **3c** (1.15 g, 5.32 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:3 AcOEt/cyclohexane) to yield 1.28 g (87%) of **4c** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.95 (m, 2H), 7.71 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.57 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.33 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.03−6.95 (m, 2H), 4.62 (s, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 156.7, 156.4, 137.6, 131.4, 128.2, 120.9, 118.8, 114.0, 55.2, 34.2. HRMS (CI) *m*/*z* calcd for $C_{13}H_{13}NOBr$ (M + H) 279.0082, found 279.0074. Mp: 87−90 °C.

*2-(Bromomethyl)-6-[4-(tert-butyl)phenyl]pyridine (**4d**).* From **3d** (1.23 g, 5.10 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:10 AcOEt/cyclohexane) to yield 1.49 g (96%) of **4d** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.72 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.60 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.49 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.36 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 4.63 (s, 2H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 156.8, 152.7, 138.1, 136.3, 127.1, 126.1, 121.8, 119.9, 35.0, 34.5, 31.6. HRMS (CI) *m*/*z* calcd for $C_{16}H_{19}NBr$ (M + H) 304.0701, found 304.0687. Mp: 78−83 °C.

*2-(3,5-Bis-trifluoromethyl)phenyl-6-(bromomethyl)pyridine (**4e**).*[27] From **3e** (1.37 g, 4.27 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:5 AcOEt/*n*-hexane) to yield 1.55 g (95%) of **4e** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 2H), 7.93 (s, 1H), 7.86 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.73 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.53 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 4.65 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 153.6, 140.5, 138.3, 131.9 (q, $^2J_{CF}$ = 33.3 Hz), 126.9, 123.3, 123.1 (q, $^1J_{CF}$ = 270.7 Hz), 122.5, 119.6, 33.4. HRMS (CI) *m*/*z* calcd for $C_{14}H_8NBrF_6$ 382.9744, found 382.9737. Mp: 87−90 °C.

*2-(Bromomethyl)-6-[(2,6-dimethoxy)phenyl]pyridine (**4f**).* From **3f** (2.6 g, 10.64 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:3 AcOEt/cyclohexane) to yield 1.66 g (51%) of **4f** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 7.42 (dd, $^3J_{HH}$ = 7.7, 0.8 Hz, 1H), 7.31 (t, $^3J_{HH}$ = 8.4 Hz, 1H), 7.21 (dd, $^3J_{HH}$ = 7.7, 0.8 Hz, 1H), 6.64 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 4.64 (s, 2H), 3.73 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 156.2, 154.5, 136.7, 129.9, 125.5, 121.6, 118.8, 104.5, 56.1, 34.5. HRMS (CI) *m*/*z* calcd for ($C_{14}H_{15}NO_2Br$ (M + H) 308.0286, found 308.0276. Mp: 108−111 °C.

*2-(Bromomethyl)-6-mesitylpyridine (**4g**).* From **3g** (1.16 g, 5.10 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:4 AcOEt/*n*-hexane) to yield 1.20 g (81%) of **4g** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 7.41 (dd, $^3J_{HH}$ = 7.7, 0.8 Hz, 1H), 7.15 (dd, $^3J_{HH}$ = 7.7, 0.8 Hz, 1H), 6.94 (s, 2H), 4.61 (s, 2H), 2.32 (s, 3H), 2.04 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 157.1, 138.1, 137.8, 137.5, 136.1, 128.9, 124.4, 121.6, 34.5, 21.5, 20.6. HRMS (CI) *m*/*z* calcd for $C_{15}H_{17}NBr$ (M + H) 290.0544, found 290.0529. Mp: 56−59 °C.

*2-(Bromomethyl)-6-[(2,4,6-triisopropyl)phenyl]pyridine (**4h**).* From **3h** (1.15 g, 3.69 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:3 AcOEt/cyclohexane) to yield 1.06 g (77%) of **4h** as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 7.33 (dd, $^3J_{HH}$ = 7.8, 0.6 Hz, 1H), 7.15 (t, $^3J_{HH}$ = 9.0 Hz, 1H), 6.99 (s, 2H), 4.52 (s, 2H), 2.85 (hept, $^3J_{HH}$ = 6.9 Hz, 1H), 2.47−2.31 (m, 2H), 1.20 (d, $^3J_{HH}$ = 6.9 Hz, 6H), 1.12−0.94 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6, 156.8, 149.4, 146.6, 137.2, 124.7, 121.5, 121.3, 120.8, 34.9, 34.6, 30.8, 24.6, 24.5, 24.4. HRMS (CI) *m*/*z* calcd for $C_{21}H_{28}NBr$ (M + H) 374.1883, found 374.1458. Mp: 179−181 °C.

*Synthesis of N-[(2S,5S)-2,5-Diphenylpyrrolidin-1-yl]formamide (**5**).* Acetic formic anhydride (1.18 g, 13.36 mmol) was added dropwise over 10 min to a solution of 1-amino-(2*S*,5*S*)-2,5-diphenylpyrrolidine (2.12 g, 8.9 mmol) in THF (30 mL), and the mixture was stirred for 1 h at room temperature. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (1:2 EtOAc/*n*-hexane to afford 2.11 g (89%) of **5** as a crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, $^3J_{HH}$ = 10.8 Hz, 1H), 7.44−7.27 (m, 10H), 5.73 (d, $^3J_{HH}$ = 10.8 Hz, 1H), 4.32−4.19 (m, 2H), 2.64−2.48 (m, 2H), 2.21−2.07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 139.3, 128.7, 128.3, 128.0, 68.1, 30.1. HRMS (CI) *m*/*z* calcd for $C_{17}H_{19}N_2O$ (M + H) 267.1497, found 267.1499. $[\alpha]^{20}_D$ −242.3 (*c*, 0.8, $CHCl_3$). Mp: 126−129 °C. The enantiomeric excess (ee >99%) was determined by HPLC (Chiralpak AD, *n*-Hex-^{i}PrOH 95:5, 1 mL/min, 30 °C, $t_{r(minor)}$ = 12.5 min, $t_{r(major)}$ = 19.4 min, $t_{r(meso)}$ = 22.9 min).

General Procedure for the Synthesis of Formamides 6a−h. Formyl hydrazine **5** (1.78−5.86 mmol) was added portionwise to a suspension of NaH (2.2 equiv) in dry THF (10 mL/mmol), and the mixture was stirred for 5 min. Bromomethylpyridine **4a−h** (1 equiv) was then added in portions, and the mixture was stirred at room temperature overnight and quenched with water, and the insoluble materials were removed by filtration. The aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL), and the combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure furnished the crude product, typically as solid, which was purified by flash chromatography. Starting materials, yields, solvents used for chromatography, and characterization data for compounds **6a−h** are as follows.

*Data for **6a**.* From **4a** (0.94 g, 3.80 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:5 AcOEt/cyclohexane) to yield 967 mg (59%) of **6a** as a yellow foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.96 (d, $^3J_{HH}$ = 7.7 Hz, 2H), 7.52−7.36 (m, 5H), 7.31−7.08 (m, 10H), 6.55 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 4.63−4.50 (m, 3H), 3.68 (d, $^2J_{HH}$ = 15.8 Hz, 1H), 2.61−2.42 (m, 2H), 2.12−2.08 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 162.1, 156.3, 155.5, 140.5, 136.8, 128.7, 128.5, 128.4, 127.8, 127.6, 126.7, 121.0, 118.4, 66.3, 50.7, 30.9. HRMS (CI) *m*/*z* calcd for $C_{29}H_{28}N_3O$ (M + H) 434.2232, found 434.2243. $[\alpha]^{20}_D$ −102.2 (*c*, 0.5, $CHCl_3$).

*Data for **6b**.* From **4b** (1.10 g, 4.13 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:3 AcOEt/*n*-hexane) to yield 1.68 g (90%) of **6b** as a white foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.95−7.87 (m, 2H), 7.39 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.32−7.08 (m, 13H), 6.54 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 4.64−4.58 (m, 2H), 4.49 (d, $^2J_{HH}$ = 15.8 Hz, 1H), 3.63 (d, $^2J_{HH}$ = 15.8 Hz, 1H), 2.59−2.49 (m, 2H), 2.12−2.02 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 163.4 (d, $^1J_{CF}$ = 246.7 Hz), 162.2, 156.4, 154.5, 140.5, 136.8, 128.5, 128.4, 127.9, 127.7, 120.8, 118.1, 115.4 (d, $^2J_{CF}$ = 21.5 Hz), 65.8, 50.5, 30.7. HRMS (CI) *m*/*z* calcd for $C_{29}H_{27}N_3OF$ (M + H) 452.2138, found 452.2139. $[\alpha]^{20}_D$ −145.2 (*c* 0.5, $CHCl_3$).

*Data for **6c**.* From **4c** (1.00 g, 3.60 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:3 AcOEt/*n*-hexane) to yield 1.28 g (76%) of **6c** as a white foam. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.91 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 7.37 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.30−7.09 (m, 11H), 6.99 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 6.50 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 4.62−4.58 (m, 2H), 4.51 (d, $^2J_{HH}$ = 14.9 Hz, 1H), 3.86 (s, 3H), 3.62 (d, $^2J_{HH}$ = 14.9 Hz, 1H), 2.57−2.45 (m, 2H), 2.16−1.99 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 162.4, 160.4, 156.5, 155.5, 140.8, 136.8, 128.6, 128.1, 127.9, 125.1, 120.5, 117.7, 114.1, 65.6, 55.4, 51.1, 31.1. HRMS (CI) *m*/*z* calcd for $C_{30}H_{30}N_3O_2$ (M + H) 464.2338, found 464.2330. $[\alpha]^{20}_D$ −146.8° (*c* 1.0, $CHCl_3$).

*Data for **6d**.* From **4d** (0.76 g, 2.50 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:4 AcOEt/cyclohexane) to yield 957 mg (78%) of **6d** as a yellow foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H),

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7.92 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.52 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.43 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.32−7.12 (m, 11H), 6.55 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 4.64−4.58 (m, 2H), 4.55 (d, $^2J_{HH}$ = 15.0 Hz, 1H), 3.65 (d, $^2J_{HH}$ = 15.0 Hz, 1H), 2.64−2.44 (m, 2H), 2.23−2.01 (m, 2H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 156.3, 155.6, 140.5, 136.6, 128.4, 127.9, 127.7, 126.4, 125.5, 120.8, 120.1, 118.1, 66.1, 50.8, 34.5, 31.2, 30.9. HRMS (CI) m/z calcd for $C_{33}H_{36}N_3O$ (M + H) 490.2858, found 490.2852. $[\alpha]^{20}_D$ −126.7 (c 0.3, $CHCl_3$).

Data for ***6e***. From **4e** (0.89 g, 2.31 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:4 AcOEt/cyclohexane) to yield 775 mg (59%) of **6e** as a yellow foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 2H), 8.33 (s, 1H), 7.92 (s, 1H), 7.52 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.35−7.08 (m, 11H), 6.62 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 4.63−4.55 (m, 2H), 4.51 (d, $^2J_{HH}$ = 15.9 Hz, 1H), 3.62 (d, $^2J_{HH}$ = 15.9 Hz, 1H), 2.65−2.48 (m, 2H), 2.22−1.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 157.2, 151.9, 140.8, 140.5, 137.2, 131.9 (q, $^2J_{CF}$ = 33.2 Hz), 128.5, 127.8, 126.7, 123.3 (q, $^1J_{CF}$ = 271.1 Hz), 122.5, 122.2, 118.3, 66.1, 49.9, 30.8. HRMS (CI) m/z calcd for $C_{31}H_{26}N_3OF_6$ (M + H) 570.1980, found 570.1969. $[\alpha]^{20}_D$ −126.4 (c 1.0, $CHCl_3$).

Data for ***6f***. From **4f** (1.49 g, 4.83 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:2 AcOEt/cyclohexane) to yield 2.05 g (77%) of **6f** as a yellow foam. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.39−7.25 (m, 2H), 7.26−7.09 (m, 10H), 7.05 (dd, $^3J_{HH}$ = 9.3, 2.3 Hz, 1H), 6.73−6.59 (m, 3H), 4.68−4.60 (m, 3H), 3.89 (d, $^2J_{HH}$ = 15.3 Hz, 1H), 3.70 (s, 6H), 2.55−2.35 (m, 2H), 2.23−2.05 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.1, 158.1, 156.7, 153.1, 135.9, 129.6, 128.9, 128.5, 128.2, 127.8, 127.6, 124.4, 121.3, 119.3, 104.3, 68.2, 55.8, 52.3, 31.1. HRMS (CI) m/z calcd for $C_{31}H_{31}N_3O_3$ (M + H) 494.2444, found 494.2432. $[\alpha]^{20}_D$ −136.6 (c 0.5, $CHCl_3$).

Data for ***6g***. From **4g** (1.70 g, 5.86 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:4 AcOEt/cyclohexane) to yield 1.79 g (64%) of **6g** as a yellow foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.32−7.11 (m, 11H), 6.95−6.90 (m, 3H), 6.45 (d, $^3J_{HH}$ = 7.7 Hz, 1H), 4.62−4.55 (m, 2H), 4.44 (d, $^2J_{HH}$ = 16.3 Hz, 1H), 3.85 (d, $^2J_{HH}$ = 16.3 Hz, 1H), 2.55−2.48 (m, 2H), 2.31 (s, 3H), 2.16−2.05 (m, 2H), 2.01 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 158.3, 156.2, 137.5, 137.2, 136.0, 135.5, 128.5, 128.3, 128.0, 127.8, 122.4, 119.6, 65.4, 51.3, 30.9, 20.8, 20.1. HRMS (CI) m/z calcd for $C_{32}H_{34}N_3O$ (M + H) 476.2702, found 476.2709. $[\alpha]^{20}_D$ −103.3 (c 1.0, $CHCl_3$).

Data for ***6h***. From **4h** (655 mg, 1.75 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:10 AcOEt:cyclohexane) to yield 819 mg (84%) of **6h** as a yellow foam. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.28−7.18 (m, 11H), 7.12−7.06 (m, 2H), 6.98 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 6.45 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 4.64−4.56 (m, 2H), 4.47 (d, $^2J_{HH}$ = 16.5 Hz, 1H), 3.89 (d, $^2J_{HH}$ = 16.5 Hz, 1H), 2.98−2.92 (m, 1H), 2.62−2.56 (m, 1H), 2.47−2.41 (m, 3H), 2.21−2.13 (m, 2H), 1.29 (d, $^3J_{HH}$ = 6.9 Hz, 6H), 1.18 (d, $^3J_{HH}$ = 6.9 Hz, 3H), 1.12 (d, $^3J_{HH}$ = 6.9 Hz, 3H), 1.10 (d, $^3J_{HH}$ = 4.3 Hz, 3H), 1.07 (d, $^3J_{HH}$ = 4.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.3, 158.9, 156.5, 149.1, 146.6, 146.5, 136.7, 135.9, 129.2, 128.6, 128.3, 123.3, 121.3, 121.2, 120.1, 66.8, 51.7, 31.6, 34.9, 30.8, 30.5, 24.8, 24.7, 24.5, 24.4, 24.2. HRMS (CI) m/z calcd for $C_{38}H_{46}N_3O$ (M + H) 560.3641, found 560.3621. $[\alpha]^{20}_D$ −97.2 (c 0.9, $CHCl_3$).

Synthesis of *N*-(Adamantyl)-*N*-{[6-(2,4,6-triisopropyl)-phenyl]pyridin-2-methyl}formamide (12). Formamide **12** was prepared following the general procedure for the synthesis of compounds **6a−h**, but using *N*-(adamantyl)-formamide **11** (0.8 mmol) and **4h** (1 equiv) as starting materials and allowing the reaction to complete at 50 °C for 48 h. The crude mixture was purified by flash chromatography (1:4 AcOEt/*n*-hexane) to yield 0.27 g (70%) of **12** as a crystalline white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.68 (t, $^3J_{HH}$ = 8.0 Hz, 1H), 7.24 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.15 (d, $^3J_{HH}$ = 7.2 Hz, 1H), 7.08 (s, 2H), 4.85 (s, 2H), 2.94 (hept, $^3J_{HH}$ = 6.8 Hz, 1H), 2.49 (hept, $^3J_{HH}$ = 6.8 Hz, 2H), 2.13−2.09 (m, 3H), 1.94−1.90 (m, 6H), 1.72−1.58 (m, 6H), 1.28 (d, $^3J_{HH}$ = 7.2 Hz, 6H), 1.15−1.07 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 159.0, 159.0, 148.8, 146.1, 136.4, 136.2, 123.1, 120.8, 119.4, 57.1, 45.5, 42.4, 35.9, 34.5, 30.3, 29.5, 24.2, 24.1, 23.8. HRMS (CI) m/z calcd for $C_{32}H_{44}N_2O$ 472.3454, found 472.3446. Mp: 137−140 °C.

Synthesis of Azolium Chlorides 7a−g Using $POCl_3$: General Procedure. $POCl_3$ (1.1 equiv) was added to a solution of formamide **6a−h** (1.50−5.86 mmol) in toluene (10 mL/mmol), and the mixture was stirred at 80 °C overnight. The reaction mixture was quenched with a solution of satd. $NaHCO_3$, and the resulting suspension was filtered. The filtrate was extracted with CH_2Cl_2 (3 × 15 mL), and the combined organic layer was washed with brine and dried over anhydrous Na_2SO_4, and the solvent was removed in vacuo. The residue was dissolved in MeOH and treated with Dowex 22-Cl for 3 h. The solvent was removed in vacuo, and the residue was purified by flash chromatography. Starting materials, yields, solvents used for chromatography, and characterization data for compounds **7a−h** are as follows.

Data for ***7a***. From **6a** (0.94 g, 3.80 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (15:1 CH_2Cl_2:MeOH) to yield 1.92 g (74%) of **7a** as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 8.52 (s, 1H), 7.70 (d, $^3J_{HH}$ = 9.3 Hz, 1H), 7.60−7.50 (m, 3H), 7.46 (d, $^3J_{HH}$ = 7.6 Hz, 4H), 7.30−7.16 (m, 8H), 7.07 (dd, $^3J_{HH}$ = 9.3, 6.9 Hz, 1H), 6.75 (d, $^3J_{HH}$ = 6.9 Hz, 1H), 5.38−5.34 (m, 2H), 2.83−2.57 (m, 2H), 2.42−2.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 134.7, 131.2, 130.3, 129.9, 129.1, 128.8, 128.6, 128.1, 128.0, 124.7, 121.8, 117.9, 117.8, 115.5, 68.5, 31.4. HRMS (FAB) m/z calcd for $C_{29}H_{26}N_3$ (M − Cl) 416.2127, found 416.2112. $[\alpha]^{20}_D$ −130.0 (c 0.1, $CHCl_3$).

Data for ***7b***. From **6b** (1.68 g, 3.72 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (15:1 CH_2Cl_2:MeOH) to yield 1.45 g (83%) of **7b** as a brown foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.47 (s, 1H), 7.61 (d, $^3J_{HH}$ = 9.3 Hz, 1H), 7.49 (d, $^3J_{HH}$ = 7.6 Hz, 4H), 7.42−7.36 (m, 2H), 7.33−7.18 (m, 8H), 7.12−7.06 (m, 1H), 6.77 (d, $^3J_{HH}$ = 6.9 Hz, 1H), 5.44−5.38 (m, 2H), 2.79−2.65 (m, 2H), 2.45−2.38 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8 (d, $^1J_{CF}$ = 251.4 Hz), 137.7, 134.0, 130.6 (d, $^3J_{CF}$ = 8.5 Hz), 129.0, 128.8, 128.5, 128.1, 127.6, 126.3, 124.8, 122.9, 118.0, 117.6, 117.1 (d, $^2J_{CF}$ = 21.9 Hz), 114.5, 68.2, 31.2. HRMS (FAB) m/z calcd for $C_{29}H_{25}N_3F$ (M − Cl) 434.2033, found 434.2025. $[\alpha]^{20}_D$ −94.5 (c 0.1, $CHCl_3$).

Data for ***7c***. From **6c** (1.18 g, 2.54 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (15:1 CH_2Cl_2:MeOH) to yield 1.05 g (86%) of **7c** as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.55 (s, 1H), 7.60 (d, $^3J_{HH}$ = 9.3 Hz, 1H), 7.44 (d, $^3J_{HH}$ = 6.9 Hz, 4H), 7.29−7.15 (m, 8H), 7.07−6.98 (m, 3H), 6.70 (d, $^3J_{HH}$ = 6.9 Hz, 1H), 5.37−4.30 (m, 2H), 3.87 (s, 3H), 2.76−2.63 (m, 2H), 2.42−2.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5, 137.6, 134.7, 129.6, 129.2, 128.8, 128.6, 128.1, 124.8, 122.3, 122.0, 117.4, 117.2, 115.2, 114.9, 68.3, 55.5, 31.2. HRMS (FAB) m/z calcd for $C_{30}H_{28}N_3O$ (M − Cl) 446.2232, found 446.2239. $[\alpha]^{20}_D$ −61.4 (c 0.1, $CHCl_3$).

Data for ***7d***. From **6d** (0.96 g, 1.93 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (20:1 CH_2Cl_2:MeOH) to yield 0.80 g (81%) of **7d** as a brown foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.34 (s, 1H), 7.70 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 7.54 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.47 (d, $^3J_{HH}$ = 6.8 Hz, 4H), 7.33−7.15 (m, 8H), 7.07 (dd, $^3J_{HH}$ = 9.2, 6.8 Hz, 1H), 6.74 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 5.38−5.32 (m, 2H), 2.81−2.64 (m, 2H), 2.49−2.28 (m, 2H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 137.6, 134.6, 129.3, 128.8, 128.6, 128.1, 127.7, 127.4, 126.7, 124.7, 121.5, 117.8, 117.7, 115.6, 68.6, 35.0, 31.3, 31.0. HRMS (FAB) m/z calcd for $C_{33}H_{34}N_3$ (M − Cl) 472.2753, found 472.2774. $[\alpha]^{20}_D$ −63.7 (c 0.1, $CHCl_3$).

Data for ***7e***. From **6e** (0.78 mg, 1.37 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (20:1 CH_2Cl_2:MeOH) to yield 0.59 g (73%) of **7e** as a brown foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (s, 1H), 8.97 (s, 1H), 8.10 (s, 1H), 7.82−7.75 (m, 3H), 7.51 (d, $^3J_{HH}$ = 7.2 Hz, 4H), 7.32−7.18 (m, 6H), 7.14 (t, $^3J_{HH}$ = 6.9 Hz, 1H), 6.85 (d, $^3J_{HH}$ = 6.9 Hz, 1H), 5.46−5.42 (m, 2H), 2.79−2.64 (m, 2H), 2.51−2.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 133.2 (q, $^2J_{CF}$ = 34.2 Hz),

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132.5, 131.5, 128.9, 128.7, 128.7, 128.6, 128.1, 124.9, 124.5, 123.3, 122.5 (q, $^1J_{CF}$ = 271.5 Hz), 119.7, 119.2, 115.3, 68.5, 31.8. HRMS (FAB) m/z calcd for $C_{31}H_{24}N_3F_6$ (M − Cl) 552.1874, found 552.1887. $[\alpha]^{20}_D$ −57.1 (c 0.2, $CHCl_3$).

*Data for **7f**.* From **6f** (0.72 g, 1.50 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (15:1 CH_2Cl_2:MeOH) to yield 1.76 g (89%) of **7f** as a brown foam. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.34 (s, 1H), 7.61 (d, $^3J_{HH}$ = 9.3 Hz, 1H), 7.51 (t, $^3J_{HH}$ = 8.7 Hz, 1H), 7.42 (d, $^3J_{HH}$ = 7.2 Hz, 4H), 7.30−7.11 (m, 6H), 7.05 (dd, $^3J_{HH}$ = 9.3, 7.2 Hz, 1H), 6.78−6.63 (m, 3H), 5.34−5.27 (m, 2H), 3.64 (s, 3H), 3.60 (s, 3H), 2.82−2.60 (m, 2H), 2.46−2.25 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.8, 157.7, 137.4, 133.2, 128.7, 128.6, 128.4, 128.3, 127.8, 124.5, 122.5, 120.2, 117.3, 113.9, 106.8, 104.4, 104.2, 68.5, 56.3, 56.1, 31.3. HRMS (FAB) m/z calcd for $C_{31}H_{30}N_3O_2$ (M − Cl) 476.2338, found 476.2331. $[\alpha]^{20}_D$ −75.9 (c, 0.1, $CHCl_3$).

*Data for **7g**.* From **6g** (0.72 g, 1.50 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (9:1 CH_2Cl_2:MeOH) to yield 0.59 g (80%) of **7g** as a brown foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 7.93 (d, $^3J_{HH}$ = 9.4 Hz, 1H), 7.44 (s, 1H), 7.38 (d, $^3J_{HH}$ = 7.5 Hz, 4H), 7.23−7.13 (m, 6H), 7.10 (dd, $^3J_{HH}$ = 9.4, 6.8 Hz, 1H), 6.96 (s, 2H), 6.64 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 5.27−5.21 (m, 2H), 2.73−2.62 (m, 2H), 2.43−2.29 (m, 5H), 1.60 (s, 3H), 1.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 137.1, 136.72, 136.69, 132.8, 129.2, 129.1, 128.9, 128.7, 128.5, 127.9, 125.9, 124.8, 120.2, 118.7, 118.2, 116.5, 68.1, 31.1, 21.2, 18.9, 18.5. HRMS (FAB) m/z calcd for $C_{32}H_{32}N_3$ (M − Cl) 458.2596, found 458.2593. $[\alpha]^{20}_D$ −86.9 (c, 0.1, $CHCl_3$).

Synthesis of Azolium Chlorides 7h,13 Using Tf_2O: General Procedure. Dry Et_3N (1.1 equiv) was added dropwise to a cooled (−40 °C) solution of formamides **6h** or **12** (0.55−1.36 mmol) in dry CH_2Cl_2 (6 mL/mmol), and the mixture was stirred for 5 min. Tf_2O (1.1 equiv) was slowly added, and the mixture was allowed to warm to room temperature and stirred for 4 h. The residue was purified by flash chromatography (30:1 CH_2Cl_2/MeOH). The product was dissolved in MeOH and treated with Dowex 22-Cl for 3 h. Starting materials, yields, and characterization data for compounds **7h** and **13** are as follows.

*Data for **7h**.* From **6h** (0.76 g, 1.36 mmol), the general procedure was applied to yield 0.68 g (86%) of **7h** as a brown foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.87 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.63 (s, 1H), 7.47−7.40 (m, 3H), 7.24−7.09 (m, 9H), 6.69 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 5.36−5.30 (m, 2H), 3.02−2.94 (m, 1H), 2.68−2.63 (m, 2H), 2.41−2.36 (m, 2H), 1.99−1.93 (m, 1H), 1.76−1.70 (m, 1H), 1.31 (d, $^3J_{HH}$ = 6.8 Hz, 6H), 1.02 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 0.93 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 0.86 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 0.66 (d, $^3J_{HH}$ = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 147.9, 147.7, 137.3, 132.4, 129.4, 128.9, 128.7, 128.1, 124.4, 124.1, 122.4, 122.3, 120.6, 119.6, 118.7, 117.6, 69.1, 34.5, 32.1, 31.0, 30.9, 24.9, 24.8, 24.0, 23.9, 23.8, 23.8. HRMS (FAB) m/z calcd for $C_{38}H_{44}N_3$ (M − Cl) 542.3535, found 542.3541. $[\alpha]^{20}_D$ −106.0 (c 0.1, $CHCl_3$).

*Data for **13**.* From **12** (0.26 g, 0.55 mmol), the general procedure was applied to yield 0.24 g (90%) of **13** as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 8.37 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 7.81 (s, 1H), 7.28 (dd, $^3J_{HH}$ = 6.8, 4.8 Hz, 1H), 7.16 (s, 2H), 6.86 (d, $^3J_{HH}$ = 6.4 Hz, 1H), 2.96 (hept, $^3J_{HH}$ = 6.8 Hz, 1H), 2.28−2.18 (m, 3H), 2.17−2.10 (m, 8H), 1.75−1.72 (m, 6H), 1.28 (d, $^3J_{HH}$ = 6.8 Hz, 6H), 1.07 (d, $^3J_{HH}$ = 6.8 Hz, 6H), 0.98 (d, $^3J_{HH}$ = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 147.9, 133.0, 131.6, 124.5, 124.2, 122.6, 119.9, 119.9, 117.4, 116.0, 62.3, 43.1, 35.1, 34.4, 31.1, 29.4, 24.8, 24.3, 23.8. HRMS (FAB) m/z calcd for $C_{32}H_{43}N_2$ (M − Cl) 455.3426, found 455.3416. Mp: 148−150 °C. Crystallization was performed at room temperature by slow diffusion of n-hexane in a CH_2Cl_2 solution of the complex.

General Procedure for Synthesis of Silver Complexes 8a−h and 14. To a solution of **7a−h** or **13** (typically 0.1 mmol) in dry CH_2Cl_2 (20 mL/mmol) was added solid Ag_2O (1.2 equiv), and the mixture was stirred in the darkness at room temperature for 3 h. The solution was filtered through a Celite plug, and the filtrate was evaporated in vacuo. Starting materials, yields, and characterization data for compounds **8a−h** and **14** are as follows.[28]

*Data for **8a**.* From **7a** (45 mg, 0.1 mmol), the general procedure was applied to yield 55 mg (98%) of **8a** as a yellow solid. ^{1}H NMR (500 MHz, CDCl3) δ 7.63−7.40 (m, 3H), 7.33−7.13 (m, 12H), 6.96 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 6.79 (s, 1H), 6.73 (dd, $^3J_{HH}$ = 9.2, 6.8 Hz, 1H), 6.33 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 5.40−4.59 (m, 2H), 2.72−2.60 (m, 2H), 2.35−2.17 (m, 2H). ^{13}C NMR (125 MHz, CDCl3) δ 171.4 (d, $^1J_{CAg}$ = 275, 238 Hz), 171.4 (d, $^1J_{CAg}$ = 238 Hz), 139.4, 138.9, 133.2, 130.4, 129.6, 128.9, 128.8, 128.2, 128.1, 127.5, 122.5, 116.4, 114.9, 110.3, 110.3, 67.6, 30.7. $[\alpha]^{20}_D$ −130.9 (c, 0.1, $CHCl_3$). Crystallization was performed at −28 °C by slow diffusion of pentane in a CH_2Cl_2 solution of the complex.

*Data for **8b**.* From **7b** (47 mg, 0.1 mmol), the general procedure was applied to yield 56 mg (97%) of **8b** as a white solid. ^{1}H NMR (400 MHz, CDCl3) δ 7.35−7.14 (m, 14H), 7.01 (d, $^3J_{HH}$ = 9.3 Hz, 1H), 6.82 (s, 1H), 6.75 (dd, $^3J_{HH}$ = 9.3, 6.4 Hz, 1H), 6.34 (d, $^3J_{HH}$ = 6.4 Hz, 1H), 5.38−4.50 (m, 2H), 2.74−2.62 (m, 2H), 2.33−2.21 (m, 2H). ^{13}C NMR (100 MHz, CDCl3) δ 170.3 (d, $^1J_{CAg}$ = 275 Hz), 170.3 (d, $^1J_{CAg}$ = 237 Hz), 164.1 (d, $^1J_{CF}$ = 212.2 Hz), 138.8, 138.4, 131.0 (d, $^3J_{CF}$ = 6.7 Hz), 130.1, 128.9, 128.8, 128.2, 128.1, 127.6, 125.1, 122.4, 116.9 (d, $^2J_{CF}$ = 18.9 Hz), 115.3, 110.5, 110.6, 67.5, 30.7. $[\alpha]^{20}_D$ −115.2 (c, 0.2, $CHCl_3$). Crystallization was performed at −28 °C by slow diffusion of pentane in a CH_2Cl_2 solution of the complex.

*Data for **8c**.* From **7c** (48 mg, 0.1 mmol), the general procedure was applied to yield 58 mg (98%) of **8c** as a yellow solid. ^{1}H NMR (400 MHz, CDCl3) δ 7.29−7.19 (m, 10H), 7.18−7.12 (m, 2H), 7.05 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 6.95 (d, $^3J_{HH}$ = 9.3 Hz, 1H), 6.77 (d, $^3J_{HH}$ = 1.8 Hz, 1H), 6.73 (dd, $^3J_{HH}$ = 9.3, 6.6 Hz, 1H), 6.34 (dd, $^3J_{HH}$ = 6.6, 1.0 Hz, 1H), 5.61−4.61 (m, 2H), 3.95 (s, 3H), 2.83−2.53 (m, 2H), 2.33−2.17 (m, 2H). ^{13}C NMR (100 MHz, CDCl3) δ 171.4 (d, $^1J_{CAg}$ = 276 Hz), 171.4 (d, $^1J_{CAg}$ = 239 Hz), 161.4, 139.5, 138.9, 130.2, 128.8, 128.2, 128.1, 127.5, 125.3, 122.5, 116.2, 115.4, 114.7, 110.1, 110.0, 67.5, 56.0, 30.9. $[\alpha]^{20}_D$ −98.0 (c 0.1, $CHCl_3$).

*Data for **8d**.* From **7c** (51 mg, 0.1 mmol), the general procedure was applied to yield 61 mg (99%) of **8d** as a white solid. ^{1}H NMR (500 MHz, CDCl3) δ 7.56 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.37−7.18 (m, 12H), 6.92 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 6.76−6.69 (m, 2H), 6.37−6.32 (m, 1H), 5.72−4.18 (m, 2H), 2.74−2.61 (m, 2H), 2.32−2.20 (m, 2H), 1.45 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6 (d, $^1J_{CAg}$ = 275 Hz), 171.6 (d, $^1J_{CAg}$ = 238 Hz), 153.8, 139.7, 138.9, 130.2, 130.1, 130.1, 128.8, 128.5, 128.2, 127.5, 126.6, 122.5, 116.3, 114.6, 109.6, 109.6, 67.4, 35.0, 31.5, 31.2. $[\alpha]^{20}_D$ −156.3 (c 0.1, $CHCl_3$).

*Data for **8e**.* From **7e** (59 mg, 0.1 mmol), the general procedure was applied to yield 54 mg (78%) of **8e** as a yellow solid. ^{1}H NMR (500 MHz, CDCl3) δ 8.06 (s, 1H), 7.72 (sa, 1H), 7.56 (sa, 1H), 7.32−7.18 (m, 9H), 7.16−7.08 (m, 2H), 7.10 (d, $^3J_{HH}$ = 9.1 Hz, 1H), 6.93 (s, 1H), 6.80 (dd, $^3J_{HH}$ = 9.1, 6.8 Hz, 1H), 6.41 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 5.15−4.95 (m, 2H), 2.77−2.55 (m, 2H), 2.31−2.24 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5 (d, $^1J_{CAg}$ = 274 Hz), 170.5 (d, $^1J_{CAg}$ = 238 Hz), 138.6, 136.1, 135.1, 133.8 (q, $^2J_{CF}$ = 33.2 Hz), 129.5, 128.9, 128.4, 128.2, 124.5, 122.8 (q, $^1J_{CF}$ = 271.6 Hz), 122.2, 118.1, 116.5, 111.7, 111.6, 67.7, 30.9. $[\alpha]^{20}_D$ −130.1 (c 0.1, $CHCl_3$). Crystallization was performed at −28 °C by slow diffusion of pentane in a CH_2Cl_2 solution of the complex.

*Data for **8f**.* From **7f** (51 mg, 0.1 mmol), the general procedure was applied to yield 60 mg (97%) of **8f** as a yellow solid. ^{1}H NMR (500 MHz, CDCl3) δ 7.57 (t, $^3J_{HH}$ = 8.4 Hz, 1H), 7.37−7.12 (m, 10H), 6.93 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 6.79−6.66 (m, 3H), 6.63 (s, 1H), 6.37 (d, $^3J_{HH}$ = 6.6 Hz, 1H), 5.46−4.52 (m, 2H), 3.72 (s, 3H), 3.59 (s, 3H), 2.70−2.65 (m, 2H), 2.30−2.27 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8 (d, $^1J_{CAg}$ = 278 Hz), 170.8 (d, $^1J_{CAg}$ = 241 Hz), 158.0, 158.0, 138.9, 133.2, 132.5, 130.1, 130.1, 128.6, 128.5, 128.1, 127.5, 126.8, 126.4, 125.1, 122.5, 116.3, 116.2, 110.8, 108.9, 108.8, 105.1, 105.0, 68.5, 65.7, 56.1, 56.1, 31.9, 29.4. $[\alpha]^{20}_D$ −141.8 (c, 0.1, $CHCl_3$).

*Data for **8g**.* From **7g** (49 mg, 0.1 mmol), the general procedure was applied to yield 59 mg (98%) of **8g** as a yellow solid. ^{1}H NMR (500 MHz, CDCl3) δ 7.37−7.14 (m, 10H), 7.04 (d, $^3J_{HH}$ = 11.2 Hz, 2H), 6.99 (d, $^3J_{HH}$ = 9.3 Hz, 1H), 6.82 (s, 1H), 6.77 (dd, $^3J_{HH}$ = 9.3, 6.7 Hz, 1H), 6.30 (d, $^3J_{HH}$ = 6.7 Hz, 1H), 5.34−5.26 (m, 1H), 4.84−

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4.77 (m, 1H), 2.70−2.64 (m, 2H), 2.45 (s, 3H), 2.34−2.22 (m, 2H), 1.82 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5 (d, $^1J_{CAg}$ = 273 Hz), 170.5 (d, $^1J_{CAg}$ = 239 Hz), 141.2, 138.8, 138.1, 138.1, 136.2, 136.2, 129.6, 129.6, 129.4, 129.4, 129.3, 128.7, 128.7, 128.1, 127.6, 122.6, 116.2, 114.8, 110.2, 110.2, 67.9, 66.7, 31.4, 29.6, 21.6, 19.47, 19.20. $[\alpha]^{20}_D$ −150.3 (*c*, 0.1, $CHCl_3$).

Data for ***8h***. From **7g** (100 mg, 0.17 mmol) and Ag_2O (85.7 mg 0.37 mmol), the general procedure was applied to yield 95 mg (80%) of **8h** as a white solid. ^{1}H NMR (500 MHz, CDCl3) δ 7.38−7.31 (m, 2H), 7.21−7.15 (m, 10H), 6.93 (d, $^3J_{HH}$ = 9.3 Hz, 1H), 6.74 (dd, $^3J_{HH}$ = 9.3, 6.7 Hz, 1H), 6.69 (s, 1H), 6.34 (d, $^3J_{HH}$ = 6.7 Hz, 1H), 5.32−5.27 (m, 1H), 4.75−4.70 (m, 1H), 3.04−2.98 (m, 1H), 2.64−2.78 (m, 2H), 2.30−2.26 (m, 1H), 2.18−2.13 (m, 2H), 2.05−1.98 (m, 1H), 1.38 (d, $^3J_{HH}$ = 6.9 Hz, 6H), 1.19 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 1.05 (d, $^3J_{HH}$ = 6.5 Hz, 3H), 1.00 (d, $^3J_{HH}$ = 6.6 Hz, 3H), 0.98 (d, $^3J_{HH}$ = 6.7 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4 (d, $^1J_{CAg}$ = 273 Hz), 171.4 (d, $^1J_{CAg}$ = 236 Hz), 151.9, 146.5, 146.4, 138.7, 137.5, 129.58, 129.52, 128.4, 128.0, 127.4, 127.2, 126.6, 126.2, 122.2, 122.1, 122.0, 116.1, 115.5, 109.1, 109.0, 68.5, 65.8, 34.4, 32.7, 31.1, 30.9, 28.9, 24.9, 24.8, 24.2, 24.1, 24.0. Crystallization was performed at −28 °C by slow diffusion of pentane in a CH_2Cl_2 solution of the complex.

Data for ***14***. From **13** (152 mg, 0.31 mmol), the general procedure was applied to yield 167 mg (78%) of **14** as a white crystalline solid. ^{1}H NMR (400 MHz, CDCl3) δ 7.64 (s, 1H), 7.44 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 7.23 (s, 2H), 6.96 (dd, $^3J_{HH}$ = 9.1, 6.6 Hz, 1H), 6.53 (d, $^3J_{HH}$ = 6.0 Hz, 1H), 3.04 (hept, $^3J_{HH}$ = 7.2 Hz, 1H), 2.42−2.40 (m, 6H), 2.39−2.29 (m, 2H), 2.28−2.25 (m, 3H), 1.84−1.68 (m, 6H), 1.41 (d, $^3J_{HH}$ = 6.9 Hz, 6H), 1.23 (d, $^3J_{HH}$ = 6.9 Hz, 6H), 1.12 (d, $^3J_{HH}$ = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 146.7, 138.2, 130.2, 130.1, 127.7, 122.7, 122.0, 116.9, 116.0, 109.0, 108.9, 59.6, 44.7, 35.8, 34.6, 31.3, 29.9, 25.1, 24.4, 24.2. Crystallization was performed at room temperature by slow diffusion of *n*-hexane in a CH_2Cl_2 solution of the complex.

General Procedure for Synthesis of Gold Complexes 8a−h and 15. To a solution of silver(I) complex **8a−h** or **14** (0.05−0.24 mmol) in dry CH_2Cl_2 (20 mL/mmol) was added $AuCl(SMe_2)$ (1 equiv), and the mixture was stirred in the darkness, at room temperature for 3 h. The mixture was filtered through a Celite plug, the solvent was evaporated in vacuo, and the residue was purified by flash chromatography. Starting material, yields, solvents used for chromatography, and characterization data for compounds **9a−h** and **15** are as follows.

Data for ***9a***. From **8a** (138 mg, 0.24 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:3 AcOEt/*n*-hexane) to yield 104 mg (67%) of **9a** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.63 (m, 1H), 7.62−7.36 (m, 5H), 7.33−7.19 (m, 9H), 6.92 (d, $^3J_{HH}$ = 9.3 Hz, 1H), 6.74 (dd, $^3J_{HH}$ = 9.3, 6.6 Hz, 1H), 6.67 (s, 1H), 6.38 (d, $^3J_{HH}$ = 6.6 Hz, 1H), 5.59−5.52 (m, 1H), 4.78−4.73 (m, 1H), 2.87−2.73 (m, 1H), 2.65−2.59 (m, 1H), 2.38−2.32 (m, 1H), 2.24−2.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 139.0, 138.8, 134.0, 130.1, 129.7, 129.5, 129.0, 128.7, 128.5, 128.4, 128.0, 127.6, 122.4, 116.5, 115.8, 108.4, 68.8, 65.3, 33.2, 28.5. HRMS (FAB) *m*/*z* calcd for $C_{29}H_{25}N_3CAu$ (M − Cl) 612.1714, found 612.1715. $[\alpha]^{20}_D$ −135.8 (*c*, 0.05, CH_2Cl_2). Mp: 193−195 °C.

Data for ***9b***. From **8b** (34 mg, 0.06 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:3 AcOEt/*n*-hexane) to yield 38 mg (97%) of **9a** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52−7.41 (m, 2H), 7.39−7.29 (m, 2H), 7.25−7.11 (m, 10H), 6.89 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 6.70 (dd, $^3J_{HH}$ = 9.2, 6.7 Hz, 1H), 6.65 (s, 1H), 6.31 (d, $^3J_{HH}$ = 6.7 Hz, 1H), 5.50−5.46 (m, 1H), 4.76−4.72 (m, 1H), 2.75−2.70 (m, 1H), 2.62−2.55 (m, 1H), 2.32−2.27 (m, 1H), 2.23−2.17 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2 (d, $^1J_{CF}$ = 248.8 Hz), 163.9, 138.8, 138.0, 131.8, 130.0, 129.5, 128.7, 128.6, 128.5, 128.1, 127.9, 127.7, 127.4, 122.3, 116.8, 116.4, 116.2, 108.7, 68.9, 65.5, 32.2, 28.6. HRMS (FAB) *m*/*z* calcd for $C_{32}H_{32}FN_3O_2SAu$ [M − Cl + thioglycerol (matrix)] 738.1865, found 738.1860. $[\alpha]^{20}_D$ −171.8 (*c*, 0.1, $CHCl_3$). Mp: 121−123 °C. Crystallization was performed at −28 °C by slow diffusion of pentane in a CH_2Cl_2 solution of the complex.

Data for ***9c***. From **8c** (133 mg, 0.22 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:3 AcOEt/*n*-hexane) to yield 110 mg (74%) of **9c** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.46 (m, 2H), 7.36−7.29 (m, 1H), 7.27−7.21 (m, 9H), 7.17−7.08 (m, 2H), 6.89 (d, $^3J_{HH}$ = 9.3 Hz, 1H), 6.72 (dd, $^3J_{HH}$ = 9.3, 6.6 Hz, 1H), 6.64 (s, 1H), 6.37 (d, $^3J_{HH}$ = 6.6 Hz, 1H), 5.55−5.50 (m, 1H), 4.79−4.73 (m, 1H), 3.97 (s, 3H), 2.78−2.74 (m, 1H), 2.66−2.62 (m, 1H), 2.41−2.38 (m, 1H), 2.24−2.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 161.6, 139.0, 138.9, 131.1, 129.6, 128.7, 128.6, 128.4, 128.0, 127.6, 126.3, 122.5, 116.3, 115.8, 114.9, 108.3, 69.0, 65.3, 56.1, 33.4, 28.4. HRMS (FAB) *m*/*z* calcd for $C_{30}H_{27}N_3OAu$ (M − Cl) 642.1820, found 642.1833. $[\alpha]^{20}_D$ −73.4 (*c*, 0.1, CH_2Cl_2). Mp: 113−115 °C.

Data for ***9d***. From **8d** (126 mg, 0.20 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:2 AcOEt/*n*-hexane) to yield 103 mg (74%) of **9d** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65−7.56 (m, 2H), 7.55−7.49 (m, 2H), 7.42−7.33 (m, 1H), 7.28−7.16 (m, 9H), 6.88 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 6.73 (dd, $^3J_{HH}$ = 9.2, 6.6 Hz, 1H), 6.63 (s, 1H), 6.37 (d, $^3J_{HH}$ = 6.6 Hz, 1H), 5.55−5.49 (m, 1H), 4.78−4.73 (m, 1H), 2.84−2.71 (m, 1H), 2.66−2.56 (m, 1H), 2.43−2.30 (m, 1H), 2.25−2.14 (m, 1H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 153.7, 139.0, 138.7, 130.8, 129.4, 129.2, 128.5, 128.4, 128.2, 127.8, 127.4, 125.9, 122.3, 116.1, 115.5, 107.8, 68.8, 64.9, 34.9, 33.3, 31.4, 28.1. HRMS (FAB) *m*/*z* calcd for $C_{33}H_{33}N_3ClAu$ (M − Cl) 668.2340, found 668.2346. $[\alpha]^{20}_D$ −109.0 (*c*, 0.1, CH_2Cl_2). Mp: 108−110 °C.

Data for ***9e***. From **8e** (121 mg, 0.17 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:3 AcOEt/*n*-hexane) to yield 120 mg (90%) of **9e** as a light−yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.81 (s, 1H), 7.70 (s, 1H), 7.50−7.43 (m, 2H), 7.32−7.19 (m, 8H), 7.05 (d, $^3J_{HH}$ = 9.1 Hz, 1H), 6.83 (s, 1H), 6.81 (dd, $^3J_{HH}$ = 9.1, 6.4 Hz, 1H), 6.45 (d, $^3J_{HH}$ = 6.4 Hz, 1H), 5.62−5.57 (m, 1H), 4.82−4.77 (m, 1H), 2.74−2.62 (m, 2H), 2.35−2.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 138.9, 138.5, 135.8, 135.7, 132.2 (q, $^2J_{CF}$ = 34.2 Hz), 130.2, 130.2, 129.4, 128.7, 128.3, 127.9, 124.1, 123.2 (q, $^1J_{CF}$ = 273.1 Hz), 123.1 (q, $^1J_{CF}$ = 273.6 Hz), 122.2, 118.1, 117.1, 109.9, 68.9, 66.3, 33.0, 29.6. HRMS (FAB) *m*/*z* calcd for ($C_{31}H_{23}N_3F_6Au$−Cl) 748.1462, found 748.1486. $[\alpha]^{20}_D$ −106.9 (*c*, 0.1, CH_2Cl_2). Mp: 104−106 °C.

Data for ***9f***. From **8f** (133 mg, 0.21 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:3 AcOEt/*n*-hexane) to yield 177 mg (81%) of **9f** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (t, $^3J_{HH}$ = 8.4 Hz, 1H), 7.54−7.48 (m, 2H), 7.30−7.11 (m, 8H), 6.85 (d, $^3J_{HH}$ = 9.3 Hz, 1H), 6.75−6.67 (m, 3H), 6.51 (s, 1H), 6.38 (d, $^3J_{HH}$ = 6.6 Hz, 1H), 5.49−5.45 (m, 1H), 4.72−4.65 (m, 1H), 3.82 (s, 3H), 3.63 (s, 3H), 2.81−2.68 (m, 1H), 2.66−2.54 (m, 1H), 2.39−2.29 (m, 1H), 2.24−2.10 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 158.5, 158.4, 132.6, 132.0, 129.5, 128.6, 128.4, 128.3, 128.2, 127.6, 122.6, 117.0, 116.2, 112.0, 107.4, 105.0, 104.7, 68.8, 64.8, 56.1, 56.0, 33.4, 27.7. HRMS (FAB) *m*/*z* calcd for $C_{34}H_{37}N_3O_4SAu$ [M − Cl + thioglycerol (matrix)] 780.2170, found 780.2150. $[\alpha]^{20}_D$ −211.4 (*c*, 0.02, CH_2Cl_2). Mp: 130−132 °C.

Data for ***9g***. From **8g** (134 mg, 0.22 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:3 AcOEt/*n*-hexane) to yield 100 mg (68%) of **9g** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.46 (m, 2H), 7.29−7.13 (m, 8H), 7.10 (s, 1H), 7.07 (s, 1H), 6.92 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 6.76 (dd, $^3J_{HH}$ = 9.2, 6.6 Hz, 1H), 6.69 (s, 1H), 6.32 (d, $^3J_{HH}$ = 6.2 Hz, 1H), 5.58−5.50 (m, 1H), 4.82−4.76 (m, 1H), 2.81−2.68 (m, 1H), 2.65−2.54 (m, 1H), 2.49 (s, 3H), 2.43−2.33 (m, 1H), 2.28−2.15 (m, 1H), 1.98 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 140.7, 137.7, 137.0, 136.8, 130.3, 129.1, 128.9, 128.8, 128.6, 128.5, 128.4, 127.9, 127.5, 122.6, 116.2, 115.7, 108.4, 68.5, 65.5, 33.3, 28.7, 21.5, 19.7. HRMS (FAB) *m*/*z* calcd for $C_{32}H_{31}N_3Au$ (M − Cl) 654.2184, found 654.2216. $[\alpha]^{20}_D$ −211.4 (*c*, 0.02, CH_2Cl_2). Mp: 134−136 °C.

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Data for ***9h***. From **8g** (31 mg, 0.05 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:2 AcOEt/*n*-hexane) to yield 34 mg (95%) of **9h** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, $^3J_{HH}$ = 7.2 Hz, 2H), 7.20−7.10 (m, 10H), 6.87 (d, $^3J_{HH}$ = 9.2 Hz, 1H), 6.70 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 6.63 (s, 1H), 6.31 (d, $^3J_{HH}$ = 6.5 Hz, 1H), 5.52−5.47 (m, 1H), 4.78−4.73 (m, 1H), 3.02−2.99 (m, 1H), 2.71−2.65 (m, 1H), 2.56−2.50 (m, 1H), 2.38−2.34 (m, 1H), 2.25−2.20 (m, 1H), 2.15−2.06 (m, 1H), 2.02−1.99 (m, 1H), 1.41−1.33 (m, 9H), 1.14 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 1.08 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 0.96 (d, $^3J_{HH}$ = 6.7 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 152.0, 147.0, 146.9, 139.0, 138.9, 137.5, 129.1, 128.6, 128.5, 128.4, 128.3, 127.8, 127.4, 122.2, 122.0, 121.9, 116.4, 116.2, 108.1, 68.3, 65.4, 34.8, 33.6, 31.6, 31.4, 28.5, 25.3, 25.1, 24.5, 24.5, 23.9, 23.9. HRMS (FAB) *m*/*z* calcd for $C_{38}H_{43}N_3Au$ (M − Cl) 738.3123, found 738.3026. $[\alpha]^{20}_D$ −139.9 (*c*, 0.1, $CHCl_3$). Mp: 286−288 °C. Crystallization was performed at −28 °C by slow diffusion of pentane in a CH_2Cl_2 solution of the complex.

Data for ***15***. From **14** (167 mg, 0.24 mmol), the general procedure was applied, and the crude mixture was purified by flash chromatography (1:7 AcOEt/toluene) to yield 180 mg (97%) of **15** as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.42 (d, $^3J_{HH}$ = 9.1 Hz, 1H), 7.17 (s, 2H), 6.95 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 6.52 (d, $^3J_{HH}$ = 6.4 Hz, 1H), 3.02 (hept, $^3J_{HH}$ = 7.0 Hz, 1H), 2.69−2.65 (m, 6H), 2.36−2.29 (m, 2H), 2.28−2.23 (m, 3H), 1.84−1.71 (m, 6H), 1.40 (d, $^3J_{HH}$ = 6.9 Hz, 6H), 1.29 (d, $^3J_{HH}$ = 6.4 Hz, 6H), 1.10 (d, $^3J_{HH}$ = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 151.8, 146.8, 138.0, 129.7, 129.3, 122.1, 121.0, 117.0, 116.9, 108.6, 60.8, 43.9, 35.8, 34.7, 31.6, 30.0, 25.3, 24.4, 23.7. HRMS (FAB) *m*/*z* calcd for $C_{32}H_{42}N_2Au$ (M − Cl) 651.3014, found 651.2996. Mp: 228−231 °C. Crystallization was performed at room temperature by slow diffusion of *n*-hexane in a CH_2Cl_2 solution of the complex.

General Procedure for Synthesis of Copper Complexes 10a,b,f−h. To a solution of **7a,b,f−h** (typically 0.1 mmol) in dry THF (10 mL) was added KO^{t}Bu (1.2 equiv), and the mixture was stirred for 1 h at room temperature. The suspension was filtered through Celite, and the solvent was removed in vacuo. A solution of CuCl (1.2 equiv) in dry THF was added (10 mL), and the mixture was stirred for 4 h at room temperature, filtered, and concentrated in vacuo to afford the product **10**. Starting material, yields, and characterization data for compounds **10a,b,f−h** are as follows.

Data for ***10a***. From **7a** (100 mg, 0.22 mmol), the general procedure was applied to yield 67 mg (59%) of **10a** as a brown solid. ^{1}H NMR (500 MHz, CDCl3) δ 7.63−7.37 (m, 3H), 7.31−7.19 (m, 12H), 6.89 (d, $^3J_{HH}$ = 9.3 Hz, 1H), 6.72 (ddd, $^3J_{HH}$ = 9.3, 6.6, 1.0, Hz, 1H), 6.64 (s, 1H), 6.35 (dt, $^3J_{HH}$ = 6.8, 1.0 Hz, 1H), 5.50 (m, 1H), 4.73 (m, 1H), 2.34 (m, 2H), 2.20 (m, 2H). ^{13}C NMR (125 MHz, CDCl3) δ 164.69, 139.90, 139.67, 134.90, 131.95, 131.12, 130.99, 130.67, 130.37, 130.14, 130.05, 129.87, 129.61, 129.56, 129.45, 129.37, 128.88, 128.76, 128.53, 128.33, 123.33, 118.08, 117.42, 117.27, 116.73, 109.21, 71.58, 69.74, 66.19, 54.41, 34.16, 33.27, 30.65, 29.35. HRMS (FAB) *m*/*z* calcd for $C_{30}H_{29}N_3Cu$ (M − Cl) 529.1346, found 529.1340.

Data for ***10b***. From **7b** (50 mg, 0.10 mmol), the general procedure was applied to yield 33 mg (55%) of **10b** as a brown solid. ^{1}H NMR (500 MHz, CDCl3) δ 7.55−7.41 (m, 2H), 7.28−7.15 (m, 13H), 6.91 (dd, $^3J_{HH}$ = 9.3, 1.2 Hz, 1H), 6.72 (dd, $^3J_{HH}$ = 9.3, 6.6 Hz, 1H), 6.64 (s, 1H), 6.34 (dt, $^3J_{HH}$ = 6.6, 0.9 Hz, 1H), 5.48 (s, 1H), 4.75 (s, 1H), 2.67−2.55 (m, 2H), 2.32 (m, 2H), 2.19 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.7 (d, $^1J_{CF}$ = 251.3 Hz), 139.6, 139.0, 131.8 (d, $^3J_{CF}$ = 8.5 Hz), 130.8, 130.0 (d, $^3J_{CF}$ = 4.7 Hz), 129.6, 129.0, 128.9, 128.4, 123.2, 117.7 (d, $^2J_{CF}$ = 18.6 Hz), 117.7, 117.5, 116.1, 111.3, 72.7, 32.8, 30.6. HRMS (FAB) *m*/*z* calcd for $C_{30}H_{28}N_3FCu$ (M − Cl) 547.1252, found 547.1246.

Data for ***10f***. From **7f** (50 mg, 0.10 mmol), the general procedure was applied to yield 28 mg (50%) of **10f** as a brown solid. ^{1}H NMR (500 MHz, CDCl3) δ 7.57 (td, $^3J_{HH}$ = 8.5, 1.0 Hz, 1H), 7.23 (dd, $^3J_{HH}$ = 15.7, 8.7 Hz, 9H), 6.92 (dt, $^3J_{HH}$ = 9.3, 1.3 Hz, 1H), 6.80−6.67 (m, 3H), 6.63 (d, $^3J_{HH}$ = 1.9 Hz, 1H), 6.37 (dt, $^3J_{HH}$ = 6.6, 1.1 Hz, 1H), 3.72 (d, $^3J_{HH}$ = 1.1 Hz, 3H), 3.58 (d, $^3J_{HH}$ = 1.0 Hz, 3H), 2.66 (d, $^3J_{HH}$ = 11.3 Hz, 2H), 2.25 (s, 2H). δ ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 148.5, 148.3, 137.8, 132.8, 130.0, 129.5, 129.3, 129.2, 128.6, 125.0, 124.7, 122.9, 122.8, 121.1, 120.2, 119.4, 118.0, 69.6, 64.1, 35.1, 32.6, 31.4, 25.4, 24.6. HRMS (FAB) *m*/*z* calcd for $C_{32}H_{33}N_3O_2Cu$ (M − Cl) 589.1157, found 589.1139.

Data for ***10g***. From **7g** (50 mg, 0.10 mmol), the general procedure was applied to yield 36 mg (60%) of **10g** as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, $^3J_{HH}$ = 7.1 Hz, 3H), 7.26 (d, $^3J_{HH}$ = 1.1 Hz, 1H), 7.19 (s, 8H), 7.06 (d, $^3J_{HH}$ = 12.7 Hz, 2H), 6.95−6.87 (m, 1H), 6.66 (d, $^3J_{HH}$ = 1.2 Hz, 1H), 6.30 (dd, $^3J_{HH}$ = 6.6, 1.3 Hz, 1H), 5.52 (s, 1H), 4.76 (s, 1H), 2.46 (s, 4H), 1.95 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 140.9, 139.1, 138.9, 137.9, 137.2, 137.1, 130.5, 129.3, 129.1, 129.0, 128.8, 128.7, 128.6, 128.5, 128.1, 127.6, 122.8, 116.4, 115.9, 108.5, 108.4, 68.7, 65.6, 33.5, 28.8, 21.7, 20.0. HRMS (FAB) *m*/*z* calcd for $C_{33}H_{35}N_3Cu$ (M − Cl) 571.1816, found 571.1808.

Data for ***10h***. From **7h** (50 mg, 0.09 mmol), the general procedure was applied to yield 35 mg (55%) of **10h** as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.44 (m, 5H), 7.25−7.21 (m, 8H), 6.98 (d, $^3J_{HH}$ = 9.1, 3H), 6.77 (m, 2H), 6.34 (d, $^3J_{HH}$ = 6.0 Hz, 1H), 5.43 (bs, 1H), 4.84 (bs, 1H), 2.98 (m, 1H), 2.16 (m, 1H), 2.04 (m, 1H), 1.36 (d, $^3J_{HH}$ = 6.6 Hz, 6H), 1.20 (d, $^3J_{HH}$ = 6.4 Hz, 3H), 1.07 (d, $^3J_{HH}$ = 6.5 Hz, 6H), 1.00 (d, $^3J_{HH}$ = 6.5 Hz, 3H). ^{13}C NMR (80 MHz, $CDCl_3$) δ 152.1, 146.9, 146.9, 137.8, 129.4, 128.6, 128.2, 122.5, 122.4, 122.4, 116.1, 115.7, 115.5, 109.2, 94.5, 68.7, 53.1, 34.9, 33.1, 31.4, 31.4, 30.3, 29.7, 25.0, 24.2, 23.9. HRMS (FAB) *m*/*z* calcd for $C_{39}H_{47}N_3Cu$ (M − Cl) 655.2755, found 655.2746.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and characterization data for new compounds and crystallographic data for **5**, **7b**, **8a**, **8b**, **8e**, **8h**, **9b**, **9h**, **14**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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