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Modular Synthesis of Chiral NHC Precursors and Their Silver and Gold Complexes

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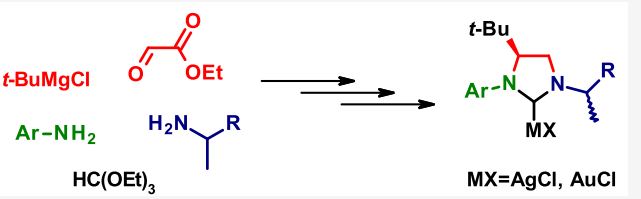
ABSTRACT: The stereoselective synthesis of chiral heterocyclic carbene precursors and the structural features of their silver and gold complexes were investigated. The prepared compounds are all based on the imidazolidine scaffold and bear the bulky *tert*-butyl substituent on the backbone in a stereocontrolled manner. The majority of the synthesized carbene precursors carry an additional element of central chirality in the side chain, and for some of them on formation of their silver or gold complexes a third element of asymmetry, axial chirality through hindered rotation of the aromatic substituent, is also present. The systematic study of the stereoselective formation of the NHC precursors led to scalable routes without the need for chiral chromatography. The NHC precursors were transformed efficiently into their silver and gold complexes, whose structural features were studied in detail both in solution and in the solid phase.



INTRODUCTION

The first isolation of a free N-heterocyclic carbene (NHC) by Arduengo[1] initiated a rapid development of this field.[2] This was fueled by the easily tunable electronic and steric properties of NHC ligands through structural modifications and the strength of the NHC−metal bond resulting in stable complexes. In addition to the utility of their metal complexes in catalysis, these carbenes have found widespread use in organocatalysis[3] and in materials science;[4] for some of their transition-metal complexes antibacterial and anticancer effects have also been reported.[5]

The increasing prominence of asymmetric transformations led to the development of chiral NHC precursors and their metal complexes. Several enantioselective transformations were reported employing C_2-symmetrical NHCs.[6] The research into C_1-symmetrical NHCs has also developed dynamically in recent years due to reports of an improved control of stereoselectivity over C_2-symmetrical analogues in several transformations.[7] The majority of the C_1-symmetrical NHC precursors reported to date possess a dihydroimidazole core with symmetrical C4 and C5 substituents and different substituents on the two nitrogen atoms of the carbene center (Figure 1). Alternatively, the symmetry of the central core can be broken through cyclization, resulting in a bi- or polycyclic carbene core. The number of examples with a nonsymmetrical monocyclic core (i.e., thiazole, triazole)[8] is more limited, and only a few examples of imidazolium[9] or dihydroimidazolium[10] salts, having different substituents at C4 and C5, have been reported.

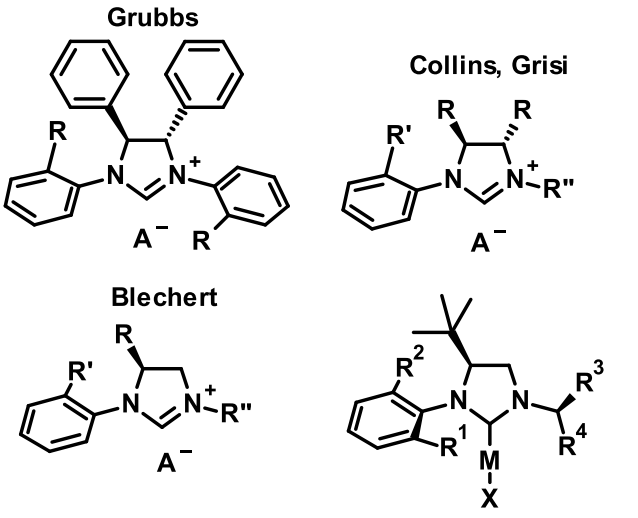


Figure 1. Representative examples of C_2- and C_1-symmetrical chiral NHC precursors and our target NHC carbene complex structures (bottom right).

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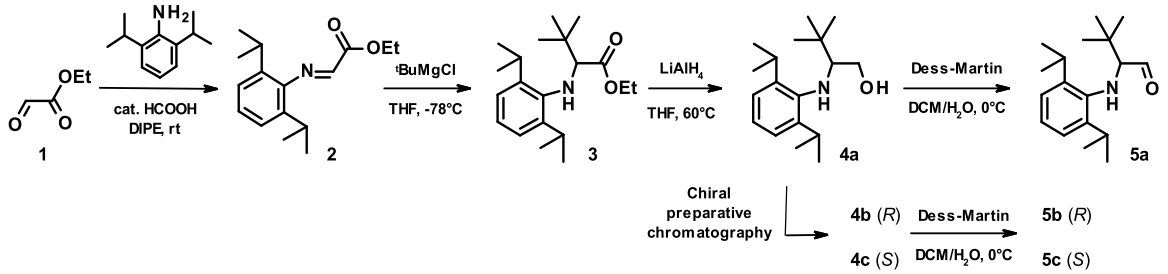
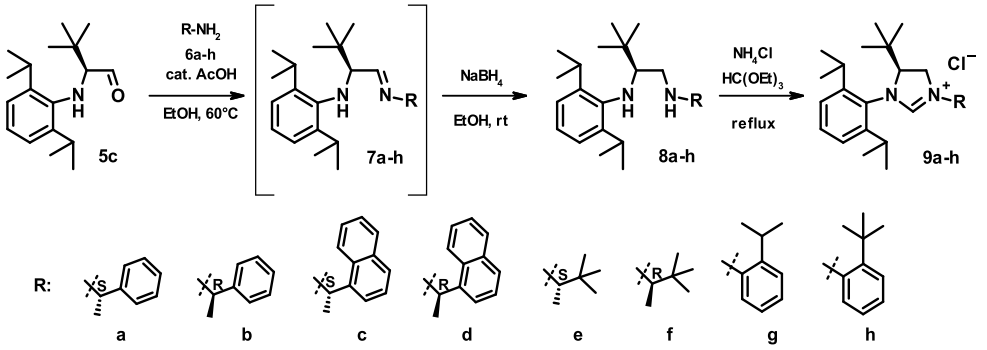
Scheme 1. Synthesis of the Key Intermediates 5a−c



Scheme 2. Synthesis of NHC Precursors 9a−h Using Amines as Diversity Sources



In NHCs bearing the stereodirecting group in the backbone, the chiral information is typically remote from the catalytically active metal center. The transfer of chirality can further be complicated by freely rotating N substituents, resulting in poor enantioselectivities. In the more successful examples this difficulty is countered by the fact that the generation of the NHC complex generates axial chirality at a hitherto freely rotating substituent, which is in the proximity of the catalytically active site, as first reported for C_2-symmetrical NHC complexes by Grubbs and co-workers (Figure 1).[11]

This concept was successfully extended to C_1-symmetrical NHCs having a symmetrical[12] or asymmetrical backbone substitution[13] (Figure 1). In a recent example achiral NHC precursors were transformed into chiral NHC-copper complexes, the asymmetry being generated on complex formation through hindered rotation, and the enantiomers could be separated by chiral chromatography.[14]

In asymmetric transformations optimization of the constitution of the NHC and, in case axial chirality is generated on complex formation, its conformational properties are equally important. This implies that the development of modular and scalable synthetic routes to chiral NHCs are a prerequisite of catalyst development.[15] Understanding the interplay of inherent backbone and side-chain chirality of NHCs and the way axial chirality emerges during complex formation is important to arrive at efficient enantioselective catalysts. With these principles in mind, we set out to develop a synthetic route that is applicable to a diverse set of NHC precursors starting from easily accessible reagents, is easy to execute, and is scalable. In addition to preparing chiral NHC precursors, we also wanted to synthesize the corresponding NHC-silver and NHC-gold complexes to study their structure and dynamic behavior.

The general structure of the targeted NHC complexes is shown in Figure 1. All target molecules are based on the imidazolidine framework, with backbone chirality being derived from a nonsymmetrical *tert*-butyl substitution. All NHCs carried a chiral side chain, and to ensure the stability of the NHC complexes, all molecules carried a bulky aromatic substituent. In certain cases, this aromatic substituent was such that it could be a source of axial chirality on complex formation.

RESULTS AND DISCUSSION

Our synthetic approach relied on the synthesis of the appropriately substituted ethylenediamine derivative followed by ring closure with a C1 synthon. The first key intermediate we wanted to prepare was the aminoaldehyde **5**, which already incorporated the *tert*-butyl group and the bulky aromatic substituent on the nitrogen atom (Scheme 1). We first synthesized the racemic aldehyde **5a** in four steps. The reaction of glyoxal acid ethyl ester (**1**) and diisopropylaniline in the presence of a catalytic amount of formic acid at ambient temperature showed complete conversion after 3 h. The resulting Schiff base **2** was purified by column chromatography to give a honey-like liquid, which was reacted with *t*BuMgCl in anhydrous THF at 0 °C. The formed racemic amino ester mixture **3** was converted to amino alcohol **4a** by reduction with $LiAlH_4$ in THF. The enantiomers **4b**,**c** could be separated at this stage by chiral chromatography. Both the racemic amino alcohol **4a** and also the pure compounds **4b**,**c** were oxidized to the desired aminoaldehyde at 0 °C with Dess−Martin periodinane. We noted that it was important to add 1.1 equiv of water for an improved reaction profile and higher yield. After complete conversion the products **5a−c** were isolated by a simple workup without chromatography.

The second stage of the process was the generation of the appropriate NHC precursors. With the homochiral aminoaldehyde **5b** or **5c** as the starting material, a set of diamines (**8a−l**) were prepared, the synthetic route depending on the nature of the substituent. The first approach relied on the introduction of diversity by the appropriate amine reagents

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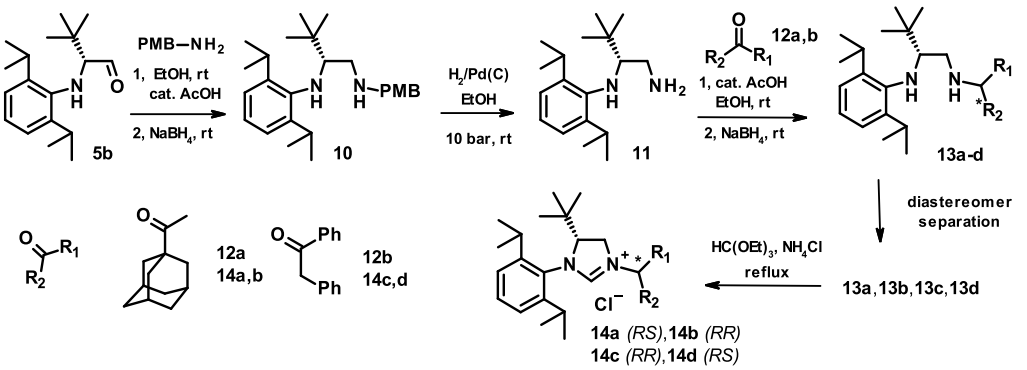
Scheme 3. Synthesis of NHC Precursors 14a−d through the Diversification of Diamine 11



using reductive amination (Scheme 2). **5c** was reacted with the corresponding amines **6a−h** followed by the in situ reduction of the formed Schiff bases using $NaBH_4$ or $LiAlH_4$. Although the imines **7a−h** could be isolated in the process, this did not lead to improved overall yields. Amines **6a,b**, **6c,d**, and **6e,f** resulted in the diastereoisomeric product pairs **8a,b**, **8c,d**, and **8e,f**, respectively. Their ^1H NMR spectra not only confirmed their structure but also provided evidence that the stereochemical integrity was not modified during the preparation. The concluding step of this sequence was the ring closure of the diamines to give carbene precursors **9a−h**. Using triethyl orthoformate as the solvent and ammonium chloride as the anion source we isolated the (4*S*)-4-*tert*-butyldihydroimidazolium salts in good yield.

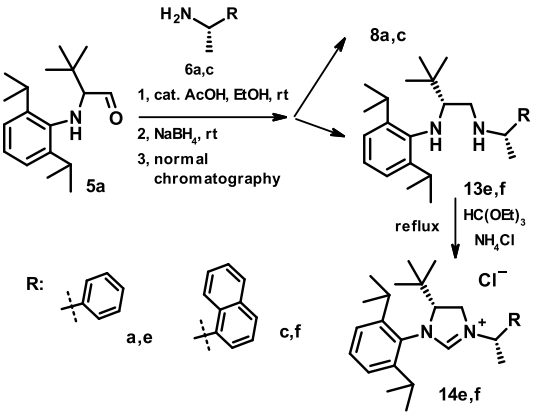
The next synthesis route was inspired by the fact that not all amines are commercially available in optically pure form (Scheme 3). We produced the enantiomerically pure diamine **11** in two steps from aldehyde **5b**. The condensation of **5b** with 4-methoxybenzylamine, followed by reduction with sodium borohydride, gave the PMB-protected diamine **10**. Removal of the PMB group by hydrogenolysis afforded the free diamine **11**, which was reacted with nonsymmetrical ketones **12a,b** following a reductive amination protocol. The diastereomeric pairs thus obtained could be separated by normal phase chromatography to give enantiopure diamines **13a−d**. The synthetic sequence was completed by the imidazolidine ring closure using the previous conditions, and we obtained the homochiral carbene precursors **14a−d**.

The ease of separation of the diastereoisomeric diamines **13a−d** prompted us to investigate briefly if the combination of racemic aldehyde **5a** with enantiomerically pure amines, followed by normal-phase chromatographic separation, would be an equally feasible approach to the homochiral diamines (Scheme 4). **5a** was reacted with commercially available enantiomerically pure phenethylamine (**6a**) and 1-naphthylamine (**6c**).

The obtained diastereomeric mixtures (**8a** and **13e**, **8c** and **13f**) were separated efficiently by normal-phase column chromatography to give the appropriate enantiopure compounds, with two of them, **8a,c**, showing the same NMR spectra and chromatographic properties as the previously prepared batches. The ring closure of the new diamines **13e,f**, under standard conditions, gave the new carbene precursors **14e,f**, respectively.

The weakness of the synthesis route described in Scheme 1 is the need for chiral chromatography. This could, in principle, be avoided if we used a chiral ester of glyoxalic acid as the

Scheme 4. Synthesis of Enantiopure Diamines and NHC Precursors Starting from Racemic Aminoaldehyde 5a



starting material. To test this hypothesis, we choose the L-menthyl ester **17a**, which was prepared from glyoxalic acid (**16**) and L-menthol (**15a**) in a biphasic reaction in the presence of a catalytic amount of H_2SO_4 (Scheme 5). After separation of the two phases the oxoacetate **17a** in diisopropyl ether was reacted with diisopropylaniline in the presence of a catalytic amount of formic acid at room temperature. The resulting Schiff base **18a** was purified by normal-phase column chromatography. Then *t*BuMgCl in anhydrous THF was added to the Schiff base at 0 °C. Under these reaction conditions the diastereomer ratio obtained for **19a** and **19c** was 3:7. The temperature dependence of the diastereomer ratio was also investigated. Unfortunately, running the reaction at −80 °C or at boiling temperature led to the same diastereoisomer ratio as that at 0 °C.

From the diastereomer mixture we were able to isolate the major component **19c** by stirring the mixture overnight in 1.25 M ethanolic hydrochloric acid. Sequential recrystallizations from hexane gave pure **19c** as a white crystalline hydrochloric acid salt. The NMR spectra of the obtained salt confirmed the presence of a single diastereoisomer.

Compound **19c** was converted to the desired amino alcohol by reduction with $LiAlH_4$. Since the crude product was contaminated by menthol, it was purified as an HBF_4 salt. After filtration and setting of the pH to 7 the amino alcohol **4c** was obtained as a colorless oil. Enantiomerically pure **4c** was oxidized to aldehyde **5c** at 0 °C with Dess−Martin periodinane under the aforementioned conditions and was isolated in high purity. An X-ray crystallography study of the gold complexes

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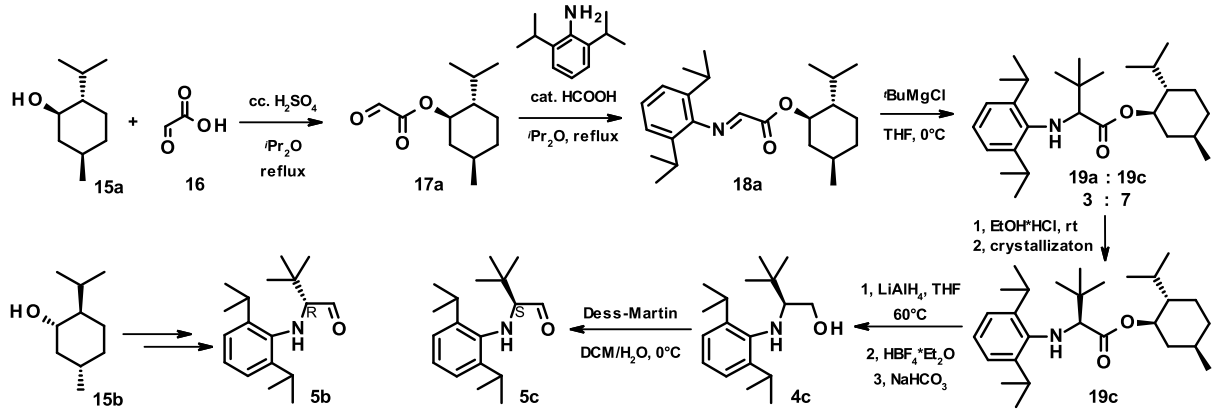
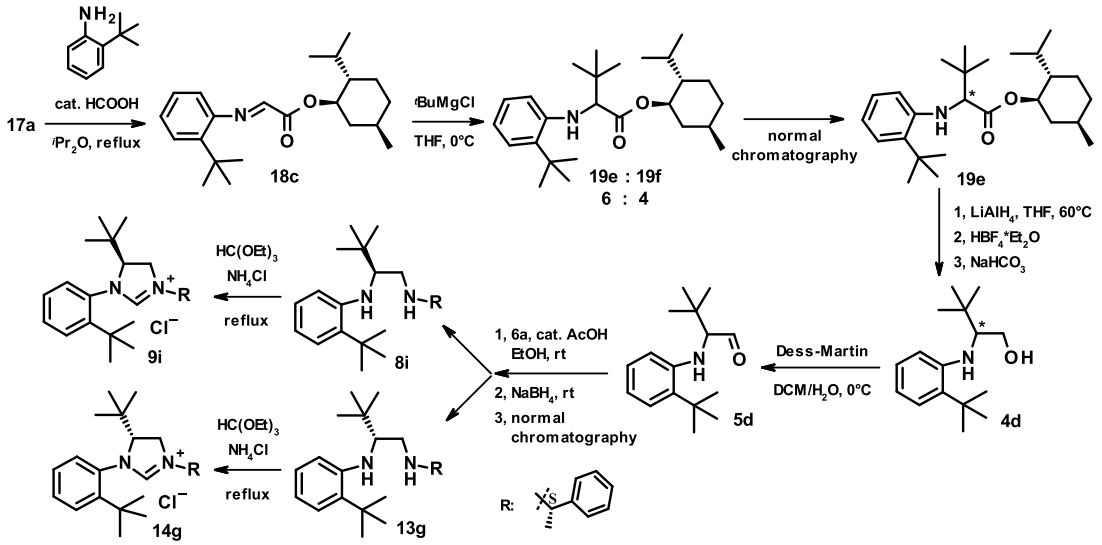
Scheme 5. Synthesis of the Enantiopure Aminoaldehydes 5b,c Using Menthol as Chiral Inducer



Scheme 6. Synthesis of NHC Precursors 9i and 14g



(see later) revealed that starting from L-menthol **4c** and **5c** (compounds with *S* configuration at C4) are formed, while when D-menthol was used, their enantiomers **4b** and **5b** (compounds with *R* configuration at C4) are formed. The mother liquor from the recrystallization of the different **19a−c** mixtures could also be reused by reduction of the ester and separation of the enantiomers **4b** and **4c** by chiral chromatography.

Although we were able to obtain **19c** in an enantiopure form, the observed asymmetric induction (7:3 ratio) during its formation was suboptimal. To better understand the addition step, we repeated it using the *o-tert*-butylaniline analogue **18c** (Scheme 6). The reaction of **18c** and *t*BuMgCl yielded a mixture of diastereomers (**19e,f**) in a 6:4 ratio that is inferior even to the previous case. In contrast to **19a,c**, diastereomers **19e,f** could only be separated by normal-phase chromatography. The pure diastereomers were converted to the amino alcohols **4d,e** in good yield by reduction with $LiAlH_4$. However, when the amino alcohol **4d** was oxidized using the standard conditions, we obtained a racemic aldehyde as the product, probably due to stability problems. **5d** was not sufficiently stable for purification; therefore, the crude product was carried on to the next reductive amination step. Chromatographic purification yielded the two compounds **8i** and **13g**, whose structure analysis confirmed that they were diastereoisomers. After the usual ring-closure procedure we obtained a pair of new, diastereomeric carbene precursors, **9i** and **14g**.

Having obtained a diverse set of heterocyclic carbene precursors, we converted them into their silver complexes. Fourteen dihydroimidazolium salts (**9a−i**, **14a-d,g**) were treated with silver oxide in DCM at ambient temperature, and the appropriate silver-NHC chloride complexes (**20a−i**, **21a−d,g**) were isolated (Scheme 7). These complexes not only are interesting in their own right but can also serve as the source of other metal-NHC complexes through transmetalation.

Exploiting this possibility, we treated the silver complexes with gold(I) chloride dimethyl sulfide reagent to yield the corresponding gold(I)-carbene chloride complexes **22a−i**, **23a−d,g**. The structures of the formed late-transition-metal-NHC complexes was characterized both by NMR spectroscopy and X-ray crystallography.

The NMR spectra of the silver complexes **20a−h** and **21a−e** agreed well with their structures. The complex formation led to a restricted conformational freedom of the benzene ring attached to N3, which was evident from the NMR spectra. Despite the presence of a symmetrically trisubstituted benzene

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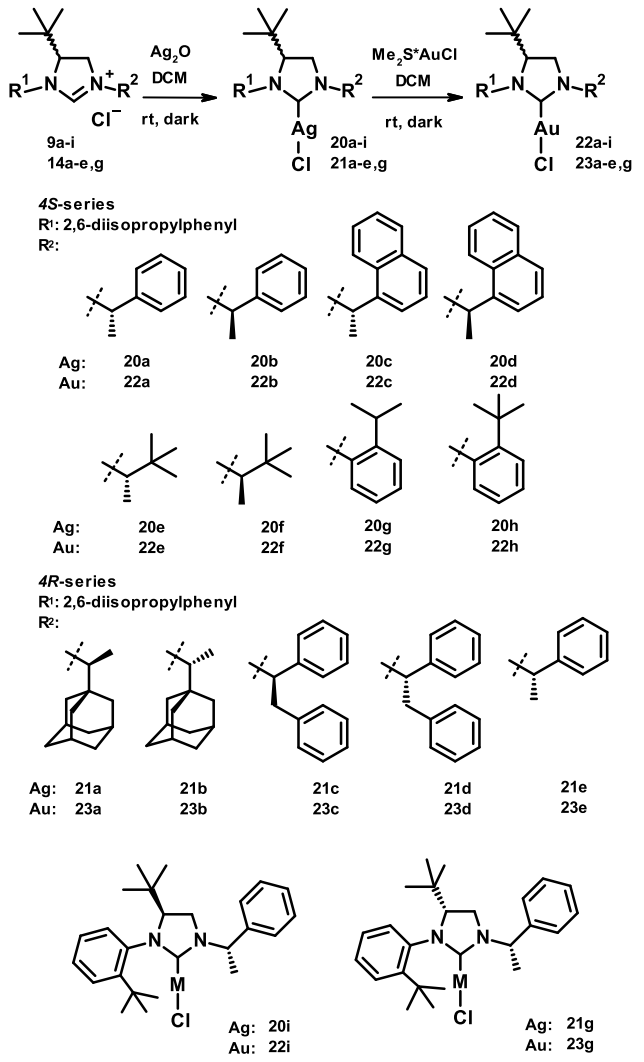
Scheme 7. Transformation of the N-Heterocyclic Carbene Precursors to NHC-Silver and NHC-Gold Complexes



ring, a spin system with three diastereotopic aromatic hydrogens was identified for the phenyl group. The different chemical environment supports that there is a hindered rotation around the bond connecting the benzene and imidazolidine rings. Consequently, the two isopropyl groups are also diasteretopic on the benzene ring: i.e., two CH and four CH_3 groups are visible in the ^{1}H NMR spectrum.

Another interesting phenomenon was observed in the DEPTQ NMR spectra of the NHC silver complexes. Silver has two NMR-active spin 1/2 isotopes, ^{107}Ag and ^{109}Ag (natural abundances 51.8% and 48.2%, respectively): i.e., in the vicinity of the silver atom a doublet is expected on the ^{13}C signals as the silver couples with carbons. Two doublet signals ($J_{C,Ag}$ = 240 Hz) were observed at 208.9 ppm corresponding to the carbene carbon atom in the imidazolidine ring. The large coupling constant is in line with the direct bonding between the Ag and carbene atoms in the NHC-silver complex. The two doublets can be explained by the isotope shift of the silver atom: i.e., there is a small chemical shift difference (δ(C−^{107}Ag) − δ(C−^{109}Ag) = 0.14 ppm) between the carbon atoms connecting to ^{107}Ag or ^{109}Ag. In addition four additional vicinal C−Ag couplings were detected in the DEPTQ spectrum: two for the imidazolidine ring ($^3J_{CH,Ag}$ = 8.2 Hz and $^3J_{CH_2,Ag}$ = 7.5 Hz) and two on the connecting carbon atoms ($^3J_{C,Ag}$ = 0.8 Hz and $^3J_{CH(CH_3),Ag}$ = 2.1 Hz). Unexpectedly, an additional $J_{C,Ag}$ = 1.4 Hz coupling was observed on one of the methyls of the isopropyl groups. This phenomenon cannot be explained by scalar coupling, since six chemical bonds separate these atoms, but rather by a through-space coupling, which suggests a very stable conformation of the benzene ring stabilized by the two ortho-positioned isopropyl groups.

In a study of the NMR spectra of the gold complex **22g** two sets of signals were observed in a 2:1 ratio, despite the fact that this molecule has only one chiral carbon atom. Analogously to the results of Dorta, who isolated and characterized chiral NHC-Pd complexes starting from symmetrical ligands,[16] this indicates the hindered rotation between the asymmetrically substituted benzene ring and the imidazolidine ring, generating axial chirality in the molecule and resulting in a diastereomeric mixture. In order to prove this, we registered a series of temperature-dependent ^{1}H NMR spectra in CD_3CN. By elevation of the temperature, the two signal sets collapsed into one and we were able to determine the coalescence temperature of this exchange process ($T_{coalescence}$ = 353 K, Figure 2). On consideration of the initial signal split of the CH

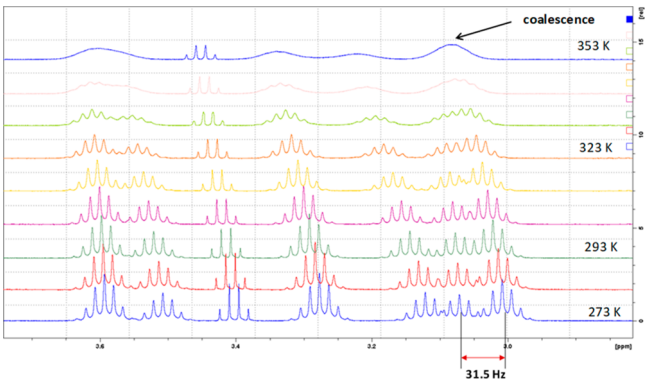


Figure 2. Temperature-dependent ^{1}H NMR spectra of **22g** (aliphatic section).

signals at T = 273 K (31.5 Hz), an approximate 17.8 kcal/mol free activation enthalpy can be calculated for the hindered rotation.[17]

We observed the same behavior in the case of **22h**, where the two sets of signals appeared in the NMR spectra in a 3:1 ratio. We failed to determine the coalescence temperature of this hindered rotation, since at the highest available temperature with our cryo NMR probehead (T = 353 K) the two signal sets still did not collapse into one, suggesting a much higher free activation enthalpy for the hindered rotation of this molecule. This observation is in line with the increased steric bulk of the *tert*-butyl substituent in comparison to isopropyl.

For the diastereomeric mixture of **22h** it was possible to determine the axial chirality of the two components. By selectively irradiating the two *tert*-butyl groups in a gradient-selective 1D ROESY NMR experiment, we could unequivocally prove that the major signal set belongs to the diasteroisomer where the two *tert*-butyl groups are on the opposite side of the plane of the imidazolidine ring, whereas in the minor diastereoisomer the two *tert*-butyl groups are on the same side of the plane. In both compounds the *tert*-butyl group on the imidazolidine ring shows steric proximity with the

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isopropyl moiety on the same side of the plane. In case of the minor signal set, the *tert*-butyl group on the benzene ring interacted with the same isopropyl group, whereas the major component showed correlation with the isopropyl which is on the opposite side of the plane (Figure 3).

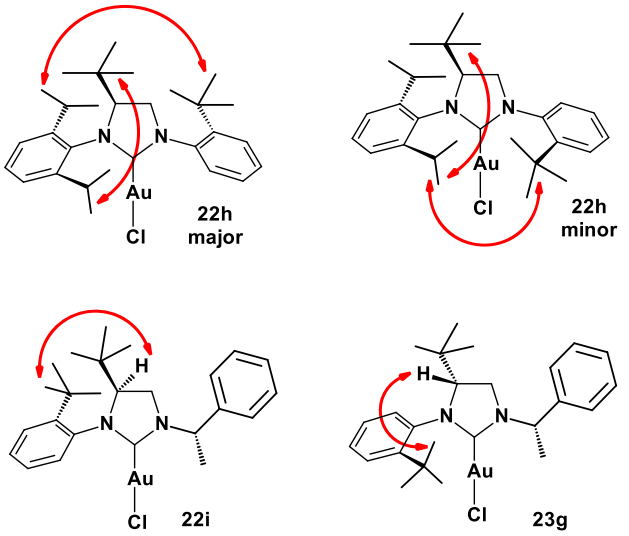

Figure 3. Relevant NOE interactions in the diastereomers of **22h**, **22i**, and **23g**.

By analogy we could anticipate the appearance of axial chirality through hindered rotation in case of the silver and gold complexes **20i**, **21g**, **22i**, and **23g**. Of these complexes **22i** and **23g** were investigated in detail. The NMR spectra suggested the presence of a single diastereoisomer in both cases. In the selective 1D ROE NMR experiment the *tert*-butyl moiety had strong interaction with the NCH in the ring, proving that in both molecules the two *tert*-butyl groups are located on the opposite side of the plane of the imidazolidine ring (Figure 3). To corroborate the axial chirality of these molecules determined by NMR spectroscopy, we also determined the X-ray structures of some complexes, including **22i**.

Crystals suitable for X-ray structure determination were grown of the NHC-gold complexes **22i** and **23a,c,d,e**. In case of **23a** there is also a solvent molecule (dichloromethane) in the lattice. The determination of the absolute configuration of the complexes was based on anomalous X-ray scattering and was unambiguous. The Flack parameters[18] in all cases are in the range of 0.003−0.07, and the refinement did not prove the presence of the other enantiomer.

The X-ray structure of **22i** is in complete agreement with the NMR measurements (Figure 4). The bulky *tert*-butyl substituents on the imidazolidine ring and on the benzene ring are on the opposite sides of the carbene ring's plane, and the chirality at the C4 position is also unambiguous. For the diastereomeric complexes **23c,d** the X-ray structures also define the chirality at the benzylic position. For complexes **22i** and **23a,e** the observed arrangement of substituents in the benzylic position is in line with the chirality of the used reagents.

The obtained X-ray structures resemble those of the known NHC-gold(I) complexes. The C4−C5 distances also support the C−C bond by lengths of 1.50−1.54 Å. The coordination around the Au(I) is highly planar with the C−Au−Cl angle being close to 180°. The Au−Cl distances are 2.27−2.28 Å, while the Au−C distances are 1.976−2.03 Å. Further details of the X-ray diffraction measurements can be found in the Tables S1 and S2 in the Supporting Information.

CONCLUSIONS

In summary, we developed a scalable synthetic route to a new class of C_1-symmetrical chiral NHC precursors. The common feature of these dihydroimidazolium salts is the presence of a bulky *tert*-butyl substituent in the C4 position in a homochiral form and a center of chirality in the substituent attached to the NHC core at N1. All NHC precursors bore an aromatic substituent on N3 and were prepared as a single enantiomer

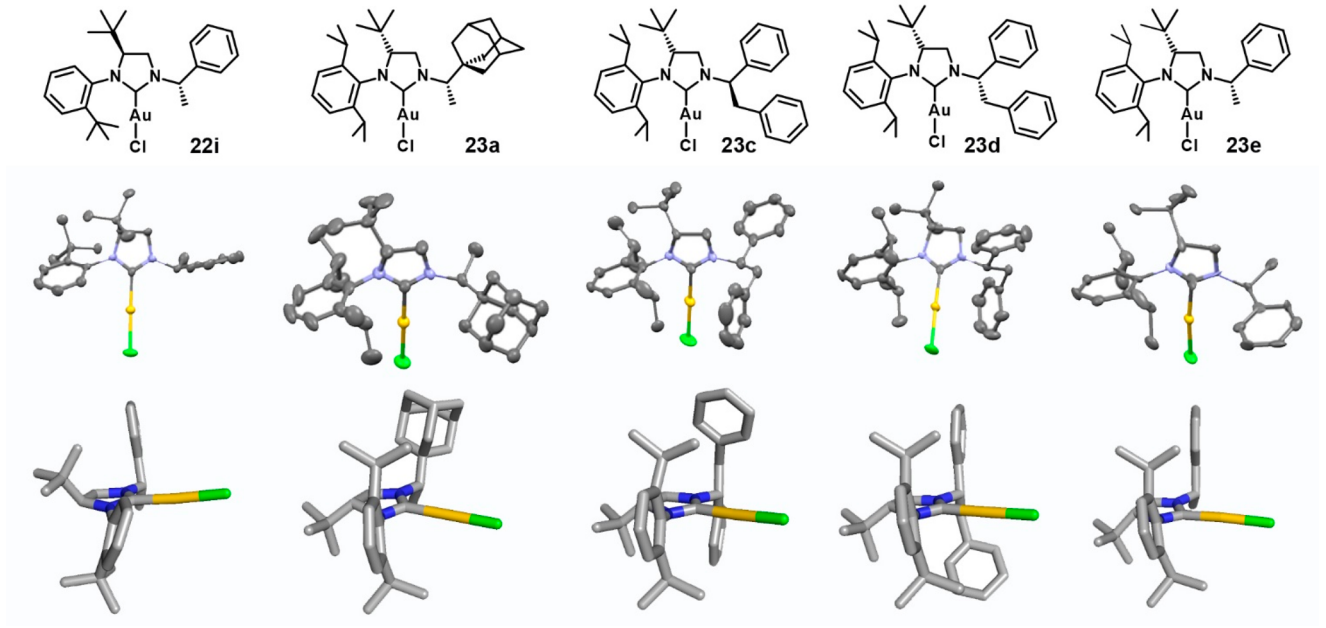

Figure 4. X-ray structures of complexes **22i** and **23a,c,d,e** in two different representations. The solvent molecule of **23a** is omitted for clarity.

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using stereoselective transformations. The prepared carbene precursors were converted to the corresponding NHC-silver and NHC-gold complexes. The structures of the complexes were characterized extensively in solution by NMR spectroscopy. Several complexes were also crystallized and their solid-state structures determined by X-ray crystallography. Both the solution and solid-state structures revealed that the complex formation resulted in the hindered rotation of the aromatic substituent. In certain complexes this also led to the emergence of axial chirality, with different degrees of stereoselectivity. Testing of the utility of the prepared chiral NHC-silver and NHC-gold complexes in asymmetric transformations is in progress in our laboratory.

EXPERIMENTAL SECTION

All reagents obtained from commercial sources were used without further purification. Anhydrous solvents were obtained from commercial sources and used without further drying. The reactions were monitored using LCMS and GCMS instruments. Analytical LC-MS: Agilent HP1200 LC with Agilent 6140 quadrupole MS, operating in positive or negative ion electrospray ionization mode. The molecular weight scan range was m/z 100−1350. Parallel UV detection was done at 210 and 254 nm. Samples were supplied as 1 mM solutions in MeCN or in THF/water (1/1) with 5 μL loop injection. LCMS analyses were performed on two instruments, one of which was operated with basic and the other with acidic eluents. Basic LCMS: Gemini-NX, 3 μm, C18, 50 mm × 3.00 mm i.d. column at 23 °C, flow rate of 1 mL min^{-1} using 5 mM aqueous NH_4HCO_3 solution and MeCN as eluents. Acidic LCMS: ZORBAX Eclipse XDB-C18, 1.8 μm, 50 mm × 4.6 mm i.d. column at 40 °C, flow rate of 1 mL min^{-1} using water and MeCN as eluents, both containing 0.02 v/v% formic acid. Combination gas chromatography and low-resolution mass spectrometry were performed on an Agilent 6850 gas chromatograph and Agilent 5975C mass spectrometer using a 15 m × 0.25 mm column with 0.25 μm HP-5MS coating and helium as the carrier gas. Ion source: EI$^+$, 70 eV, 230 °C, quadrupole 150 °C, interface 300 °C. Flash chromatography was performed on a ISCO CombiFlash Rf 200i instrument with prepacked silica gel cartridges (Redi*Sep*R_f Gold High Performance). Chiral separations were performed on a KNAUER Smartline Preparative HPLC system with a (R,R) WHELKO O-1 50 mm × 500 mm, 10 μm column running at a flow rate of 50 mL min^{-1} with UV diode array detection (210−285 nm). Chiral purity was determined on an Agilent 1100 HPLC system with a WHELKO O-1, 250 mm × 4.6 mm, 10 μm column running at a flow rate of 1 mL min^{-1} with UV diode array detection (210−285 nm).^{1}H NMR and proton-decoupled ^{13}C NMR measurements were performed on a Bruker Avance III 500 MHz spectrometer and a Bruker Avance III 400 MHz spectrometer, using DMSO-d_6 or $CDCl_3$ as solvent. ^{1}H and ^{13}C NMR data are in the form of δ values, given in parts per million (ppm), using the residual peak of the solvent as an internal standard (DMSO-d_6, 2.50 ppm (^{1}H)/39.5 ppm (^{13}C); $CDCl_3$, 7.26 ppm (^{1}H)/77.0 ppm (^{13}C)). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), sp (septet), m (multiplet), br s (broad singlet), dd (doublet of doublets), td (triplet of doublets), and qd (quartet of doublets). In some cases two sets of signals appear in the spectra due to hindered rotation. HRMS measurements were determined on a Shimadzu IT-TOF, ion source temperature 200 °C, ESI±, ionization voltage (+,−)4.5 kV. The mass resolution was a minimum of 10000. Melting points were determined by an OptiMelt melting view apparatus at ramp rates of 2 °C min^{-1} in sealed glass capillaries and are uncorrected. All products had an LC purity above 95% that was corroborated by their ^{1}H NMR spectra unless specifically mentioned otherwise.

Ethyl 2-(2,6-Diisopropylphenyl)iminoacetate (2). A 52 mL portion of 2,6-diisopropylaniline (250 mmol) was added to 51 mL of **1** (250 mmol) dissolved in 1000 mL DIPE, and 0.5 mL of formic acid was also added. The resulting mixture was stirred at room temperature for 6 h, at which point complete conversion was observed by GC-MS. The crude product was purified via column chromatography using heptane and EtOAc as eluents. **2** was collected as a yellow oil (58.5 g, 224 mmol, 89.5%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.76 (s, CH, 1 H), 7.21−7.07 (m, Ar-H, 3 H), 4.34 (q, J = 7.0 Hz, CH_2, 2 H), 2.73 (sp, J = 6.9 Hz, CH, 2 H), 1.32 (t, J = 7.0 Hz, CH_3, 3 H), 1.09 (d, J = 6.9 Hz, CH_3, 12 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 162.3, 155.8, 146.6, 135.9, 125.1, 123.0, 61.6, 27.3, 23.3, 14.0. HRMS: calcd for $C_{16}H_{23}NO_2$ [M]$^+$ 261.1729, found 261.1714.

2-(2,6-Diisopropylanilino)-3,3-dimethylbutanoic Acid (3). A solution of 40 g of **2** (153 mmol) in 765 mL of THF was cooled to −78 °C under an inert atmosphere, and then 140 mL of *t*BuMgCl (230 mmol) was added dropwise over 90 min. The resulting mixture was stirred at −78 °C for 60 min, at which point complete conversion was observed by GC-MS. The reaction mixture was quenched by the addition of saturated aqueous NH_4Cl solution, was warmed to room temperature, and then was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, and the volatiles were removed under reduced pressure. The crude product was purified via column chromatography using heptane and EtOAc as eluents. **3** was collected as a dark yellow oil (42.6 g, 133 mmol, 87.1%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.01 (d, J = 7.1 Hz, Ar-H, 2 H), 6.93 (dd, J = 8.1, 7.1 Hz, Ar-H, 1 H), 3.87 (m, NH, 1 H), 3.86 (m, CH, 1 H), 3.52 (d, J = 12.6 Hz, CH, 1 H), 3.32 (sp, J = 6.9 Hz, CH, 2 H), 1.15 (d, J = 6.8 Hz, CH_3, 12 H), 1.10 (s, CH_3, 9 H), 0.93 (t, J = 7.1 Hz, CH_3, 3 H), 1.09 (d, J = 6.9 Hz, CH_3, 12 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 172.9, 140.6, 140.4, 123.4, 123.0, 70.2, 59.6, 34.0, 26.7, 26.2, 24.2, 24.0, 13.9. HRMS: calcd for $C_{20}H_{34}NO_2$ [M + H]$^+$ 320.2584, found 320.2582.

2-(2,6-Diisopropylanilino)-3,3-dimethylbutanol (4a). A 10.8 g portion of $LiAlH_4$ (284 mmol) was suspended in 284 mL of THF at 0 °C, and 30.2 g of **3** (94.5 mmol) was added in small portions. Then the reaction mixture was warmed to 60 °C and stirred at that temperature for 45 min, at which point complete conversion was observed by LC-MS. The reaction mixture was cooled to 0 °C, and 10.8 mL of water, 21.6 mL of 2 N NaOH, and 21.6 mL of water were added slowly to the mixture. MTBE was added to the mixture at the previous temperature, and this mixture was stirred for 10 min. The mixture was filtered and washed with MTBE. The crude product was purified via column chromatography using heptane and EtOAc as eluents. **4a** was collected as a colorless oil (12.0 g, 43.3 mmol, 49.4%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.01 (d, J = 7.6 Hz, Ar-H, 2 H), 6.89 (t, J = 7.6 Hz, Ar-H, 1 H), 4.40 (t, J = 4.2 Hz, OH, 1 H), 3.40/3.28 (m, CH_2, 2 H), 3.39 (d, J = 12.7 Hz, NH, 1 H), 3.36 (sp, J = 6.7 Hz, CH, 2 H), 2.73 (dm, J = 11.9 Hz, CH, 1 H), 1.16 (d, J = 6.7 Hz, CH_3, 6 H), 1.12 (d, J = 6.7 Hz, CH_3, 6 H), 1.09 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 142.1, 140.9, 123.2, 122.0, 67.5, 59.5, 34.8, 27.7, 26.6, 24.1, 23.9. HRMS: calcd for $C_{18}H_{32}NO$ [M + H]$^+$ 278.2478, found 278.2323.

(2*R*)-2-(2,6-Diisopropylanilino)-3,3-dimethylbutanol (4b). By chiral HPLC analysis **4b** was a single enantiomer and was eluted first from the racemate **4a** on the (R,R) WHELK O-1 column using 2-PrOH and heptane (0.5/99.5) as eluents. **4b** was collected as a colorless oil (5.0 g, 18.0 mmol, 50.0%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.01 (d, J = 7.6 Hz, Ar-H, 2 H), 6.89 (t, J = 7.6 Hz, Ar-H, 1 H), 4.39 (t, J = 4.2 Hz, OH, 1 H), 3.40/3.28 (m, CH_2, 2 H), 3.39 (d, J = 12.7 Hz, NH, 1 H), 3.36 (sp, J = 6.7 Hz, CH, 2 H), 2.73 (dm, J = 11.9 Hz, CH, 1 H), 1.15 (d, J = 6.7 Hz, CH_3, 6 H), 1.13 (d, J = 6.7 Hz, CH_3, 6 H), 1.09 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 142.1, 140.9, 123.2, 122, 67.4, 59.5, 34.8, 27.6, 26.6, 24.1, 23.9. HRMS: calcd for $C_{18}H_{32}N$ [M + H]$^+$ 278.2478, found 278.2479.

(2*S*)-2-(2,6-Diisopropylanilino)-3,3-dimethylbutanol (4c). By chiral HPLC analysis **4c** was a single enantiomer and was eluted second from the racemate **4a** on the (R,R) WHELK O-1 column using 2-PrOH and heptane (0.5/99.5) as eluents. **4c** was collected as a colorless oil (5.0 g, 18.0 mmol, 50.0%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.01 (d, J = 7.6 Hz, Ar-H, 2 H), 6.89 (t, J = 7.6 Hz, Ar-H, 1 H), 4.39 (t, J = 4.2 Hz, OH, 1 H), 3.40/3.28 (m, CH_2, 2 H), 3.39 (d, J = 12.6 Hz, NH, 1 H), 3.36 (sp, J = 6.7 Hz, CH, 2 H), 2.73 (dm, J = 12.0 Hz, CH, 1 H), 1.15 (d, J = 6.7 Hz, CH_3, 6 H), 1.13 (d, J = 6.7

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Hz, CH_3, 6 H), 1.09 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 142.1, 140.9, 123.2, 122, 67.4, 59.5, 34.8, 27.6, 26.6, 24.1, 23.9. HRMS: calcd for $C_{18}H_{32}N$ $[M + H]^+$ 278.2478, found 278.2470.

2-(2-*tert*-Butylanilino)-3,3-dimethylbutanol (4d). This compound was prepared following the synthetic procedure described for **4a** starting from 15.7 g of **19e** (39.1 mmol). **4d** was collected as a colorless oil (8.09 g, 32.4 mmol, 83.0%). By chiral HPLC analysis **4d** was a single enantiomer and eluted second from the racemate on the (R,R) WHELK O-1 column using 2-PrOH and heptane (1/99) as eluents. ^1H NMR (500 MHz, DMSO-d_6): δ 7.10 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.98 (td, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.70 (dm, J = 7.7 Hz, Ar-H, 1 H), 6.49 (td, J = 7.7, 1.4 Hz, Ar-H, 1 H), 4.65 (t, J = 4.5 Hz, OH, 1 H), 4.27 (d, J = 9.3 Hz, NH, 1 H), 3.60/3.57 (m+m, CH_2, 2 H), 3.28 (m, CH, 1 H), 1.39 (s, CH_3, 9 H) 1.01 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 146.4, 132.0, 126.8, 125.9, 115.3, 111.0, 60.9, 59.9, 35.0, 33.7, 29.7, 27.5. HRMS: calcd for $C_{16}H_{28}NO$ $[M + H]^+$ 250.2165, found 250.2162.

2-(2-*tert*-Butylanilino)-3,3-dimethylbutanol (4e). This compound was prepared following the synthetic procedure described for **4a** starting from 6.22 g of **19f** (15.5 mmol). **4e** was collected as a colorless oil (3.43 g, 13.7 mmol, 88.7%). By chiral HPLC analysis **4e** was a single enantiomer and eluted first from the racemate on the (R,R) WHELK O-1 column using 2-PrOH and heptane (1/99) as eluents. ^1H NMR (500 MHz, DMSO-d_6): δ 7.10 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.98 (td, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.70 (dm, J = 7.7 Hz, Ar-H, 1 H), 6.49 (td, J = 7.7, 1.4 Hz, Ar-H, 1 H), 4.65 (t, J = 4.5 Hz, OH, 1 H), 4.26 (d, J = 9.3 Hz, NH, 1 H), 3.60/3.57 (m+m, CH_2, 2 H), 3.28 (m, CH, 1 H), 1.39 (s, CH_3, 9 H) 1.01 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 146.4, 132.0, 126.8, 125.9, 115.3, 111.0, 60.9, 59.9, 35.0, 33.7, 29.7, 27.5. HRMS: calcd for $C_{16}H_{28}NO$ $[M + H]^+$ 250.2165, found 250.2160.

2-(2,6-Diisopropylanilino)-3,3-dimethylbutanal (5a). A 6.34 g portion of **4a** (22.9 mmol) was dissolved in 549 mL of DCM and then cooled to 0 °C, and 10.7 g of Dess-Martin periodine (25.1 mmol) was added in small portions. Then 453 μL of water (25.1 mmol) was also added and this mixture was stirred for 1.5 h, at which point complete conversion was observed by LC-MS. The reaction mixture was quenched with pentane and then filtered through a pad of Celite. The solvent was removed under vacuum, and then more pentane was added and the mixture filtered again. This method was repeated twice, and **5a** was collected as a yellow solid (6.29 g, 22.8 mmol, 99.9%). Mp: 35−40 °C. ^1H NMR (500 MHz, DMSO-d_6): δ 9.64 (d, J = 5.1 Hz, CH, 1 H), 7.02 (m, Ar-H, 2 H), 6.97 (dd, J = 8.7, 6.3 Hz, Ar-H, 1 H), 4.02 (d, J = 10.9 Hz, NH, 1 H), 3.33 (sp, J = 6.8 Hz, CH, 2 H), 3.06 (dd, J = 10.9 Hz, J = 5.1 Hz, CH, 1 H), 1.17 (d, J = 6.8 Hz, CH_3, 6 H), 1.12 (d, J = 6.8 Hz, CH_3, 6 H), 1.12 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 203.9, 142.2, 139.9, 123.9, 123.6, 75.7, 33.9, 27.0, 26.5, 24.2, 24.1. HRMS: calcd for $C_{18}H_{30}NO$ $[M + H]^+$ 276.2322, found 276.2323.

(2*R*)-2-(2,6-Diisopropylanilino)-3,3-dimethylbutanal (5b). This compound was prepared following the synthetic procedure described for **5a** starting from 4.20 g of **4b** (15.1 mmol). **5b** was collected as a yellow solid (4.12 mg, 15.0 mmol, 98.8%). Mp: 65−75 °C. ^1H NMR (500 MHz, DMSO-d_6): δ 9.64 (d, J = 5.1 Hz, CH, 1 H), 7.02 (m, Ar-H, 2 H), 6.97 (dd, J = 8.7, 6.3 Hz, Ar-H, 1 H), 4.02 (d, J = 11.0 Hz, NH, 1 H), 3.33 (sp, J = 6.8 Hz, CH, 2 H), 3.07 (dd, J = 11.0 Hz, J = 5.1 Hz, CH, 1 H), 1.16 (d, J = 6.8 Hz, CH_3, 6 H), 1.12 (d, J = 6.8 Hz, CH_3, 6 H), 1.11 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 203.9, 142.2, 139.9, 123.9, 123.6, 75.7, 33.9, 27.0, 26.5, 24.2, 24.1. HRMS: calcd for $C_{18}H_{30}NO$ $[M + H]^+$ 276.2322, found 276.2325.

(2*S*)-2-(2,6-Diisopropylanilino)-3,3-dimethylbutanal (5c). This compound was prepared following the synthetic procedure described for **5a** starting from 3.40 g of **4c** (12.3 mmol). **5c** was collected as a yellow solid (3.36 g, 12.2 mmol, 99.5%). Mp: 70−80 °C. ^1H NMR (500 MHz, DMSO-d_6): δ 9.64 (d, J = 5.1 Hz, CH, 1 H), 7.02 (m, Ar-H, 2 H), 6.97 (dd, J = 8.7, 6.2 Hz, Ar-H, 1 H), 4.03 (d, J = 10.6 Hz, NH, 1 H), 3.33 (sp, J = 6.8 Hz, CH, 2 H), 3.07 (dd, J = 10.6 Hz, J = 5.1 Hz, CH, 1 H), 1.17 (d, J = 6.8 Hz, CH_3, 6 H), 1.12 (d, J = 6.8 Hz, CH_3, 6 H), 1.12 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 203.9, 142.2, 139.9, 123.9, 123.6, 75.7, 33.9, 27.0, 26.5, 24.2, 24.1. HRMS: calcd for $C_{18}H_{30}NO$ $[M + H]^+$ 276.2322, found 276.2320.

2-(2-*tert*-Butylanilino)-3,3-dimethylbutanal (5d). This compound was prepared following the synthetic procedure described for **5a** by starting from 2.97 g of **4e** (11.9 mmol). **5d** (racemic, 2.35 g) was collected as a yellow solid and used without further purification for the synthesis of **8i** and **13g**. ^1H NMR (500 MHz, DMSO-d_6): δ 9.83 (d, J = 1.8 Hz, CH, 1 H), 7.16 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.98 (td, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.60 (td, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.58 (d, J = 7.7 Hz, Ar-H, 1 H), 4.51 (d, J = 8.2 Hz, NH, 1 H), 4.17 (dd, J = 8.2, 1.8 Hz, CH, 1 H), 1.44 (s, CH_3, 9 H), 1.08 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 205.2, 145.1, 132.9, 126.8, 126.1, 117.1, 111.4, 68.5, 35.3, 33.8, 29.7, 26.8. HRMS: calcd for $C_{16}H_{26}NO$ $[M + H]^+$ 248.2009, found 248.2005.

(2*S*)-*N*-(2,6-Diisopropylphenyl)-3,3-dimethyl-*N*′-[(1*S*)-1-phenylethyl]butane-1,2-diamine (8a). A 1.3 mL portion of (1*S*)-1-phenylethanamine (10.5 mmol) was dissolved in 48 mL of EtOH under an inert atmosphere, and then 2.62 g of **5c** (9.51 mmol) was added in one portion and 55 μL of acetic acid (0.95 mmol) was also added. The mixture was stirred at 60 °C. The mixture in the first reaction step was stirred for 1 h, until all of the **5c** had reacted, ass observed by GC-MS. When the starting material was reacted, the mixture was cooled to room temperature and 1.44 g of $NaBH_4$ (38.1 mmol) was added carefully. The mixture in the second reaction step was stirred for 4 h at room temperature and observed by LC-MS. The reaction mixture was quenched with the addition of saturated aqueous NH_4Cl solution, and then it was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$. The volatiles were removed under reduced pressure, and the residue was purified via column chromatography using heptane and EtOAc as eluents. **8a** was collected as a yellow oil (3.08 mg, 8.09 mmol, 85.0%). ^1H NMR (500 MHz, DMSO-d_6): δ 7.26−7.04 (m, Ar-H, 5 H), 7.03 (d, J = 7.5 Hz, Ar-H, 2 H), 6.93 (t, J = 7.5 Hz, Ar-H, 1 H), 3.32 (sp, J = 6.7 Hz, CH, 2 H), 3.32 (q, J = 6.6 Hz, CH, 1 H), 3.25 (d, J = 11.4 Hz, NH, 1 H), 2.96 (m, CH, 1 H), 2.48/2.32 (m+m, CH_2, 2 H), 1.20 (br s, NH, 1 H), 1.17 (d, J = 6.7 Hz, CH_3, 6 H), 1.12 (d, J = 6.7 Hz, CH_3, 6 H), 0.96 (d, J = 6.6 Hz, CH_3, 3 H), 0.94 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 146.0, 142.3, 140.5, 128.0, 126.4, 126.2, 123.5, 122.1, 67.3, 57.6, 48.8, 35.1, 27.1, 27.0, 24.6, 24.1, 23.9. HRMS: calcd for $C_{26}H_{41}N_2$ $[M + H]^+$ 381.3264, found 381.3254.

(2*S*)-*N*-(2,6-Diisopropylphenyl)-3,3-dimethyl-*N*′-[(1*R*)-1-phenylethyl]butane-1,2-diamine (8b). This compound was prepared following the synthetic procedure described for **8a** starting from 1.33 mL of (1*R*)-1-phenylethanamine (10.5 mmol) and 2.62 g of **5c** (9.51 mmol). The reaction time for the first step was 2.5 h and for the second step was 4 h. **8b** was collected as a yellow oil (2.78 g, 7.30 mmol, 76.8%). ^1H NMR (500 MHz, DMSO-d_6): δ 7.23−7.04 (m, Ar-H, 5 H) 6.69 (d, J = 7.5 Hz, Ar-H, 2 H), 6.89 (t, J = 7.5 Hz, Ar-H, 1 H), 3.44 (q, J = 6.5 Hz, CH, 1 H), 3.35 (m, NH, 1 H), 3.35 (m, CH, 2 H), 3.01 (m, CH, 1 H), 2.37/2.34 (m+m, CH_2, 2 H), 1.32 (br s, NH, 1 H), 1.16 (d, J = 6.8 Hz, CH_3, 6 H), 1.12 (d, J = 6.8 Hz, CH_3, 6 H), 1.01 (d, J = 6.5 Hz, CH_3, 3 H), 0.94 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 145.9, 142.6, 139.9, 128.1, 126.4, 126.2, 123.4, 121.8, 66.0, 57.2, 48.4, 35.2, 27.2, 27.0, 24.4, 24.0, 23.9. HRMS: calcd for $C_{26}H_{41}N_2$ $[M + H]^+$ 381.3264, found 381.3250.

(2*S*)-*N*-(2,6-Diisopropylphenyl)-3,3-dimethyl-*N*′-[(1*S*)-1-(1-naphthyl)ethyl]butane-1,2-diamine (8c). This compound was prepared following the synthetic procedure described for **8a** starting from 1.38 mL of (1*S*)-1-(1-naphthyl)ethanamine (8.59 mmol) and 2.15 g of **5c** (7.81 mmol). The reaction time for the first step was 1.5 h and for the second step was 2 h. **8c** was collected as a yellow oil (2.83 g, 6.58 mmol, 84.3%). ^1H NMR (500 MHz, DMSO-d_6): δ 8.18−7.25 (m, Ar-H, 7 H), 7.00 (d, J = 7.6 Hz, Ar-H, 2 H), 6.89 (t, J = 7.6 Hz, Ar-H, 1 H), 4.32 (q, J = 6.8 Hz, CH, 1 H), 3.39 (br d, NH, 1 H), 3.37 (sp, J = 6.8 Hz, CH, 2 H), 3.07 (m, CH, 1 H), 2.53 (m, CH_2, 2 H), 1.56 (br s, NH, 1 H), 1.16 (d, J = 6.7 Hz, CH_3, 6 H), 1.16 (d, J = 6.4 Hz, CH_3, 3 H), 1.11 (d, J = 6.7 Hz, CH_3, 6 H), 0.93 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 142.6, 141.3, 139.9, 133.4, 130.7, 128.7, 126.6, 125.7, 125.6, 125.2, 123.4, 122.8, 122.4,

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121.8, 66.5, 52.9, 48.5, 27.2, 27.0, 24.0, 23.9, 23.6. HRMS: calcd for $C_{30}H_{42}N_2$ $[M + H]^+$ 431.3420, found 431.3418.

(2*S*)-*N*-(2,6-Diisopropylphenyl)-3,3-dimethyl-*N*′-[(1*R*)-1-(1-naphthyl)ethyl]butane-1,2-diamine (8d). This compound was prepared following the synthetic procedure described for **8a** starting from 1.28 mL of (1*R*)-1-(1-naphthyl)ethanamine (7.99 mmol) and 2.00 g of **5c** (7.26 mmol). The reaction time for the first step was 1 h and for the second step was 4 h. **8d** was collected as a yellow oil (2.25 g, 5.22 mmol, 71.9%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.18−7.37 (m, Ar-H, 7 H), 7.01 (d, J = 7.6 Hz, Ar-H, 2 H), 6.89 (t, J = 7.6 Hz, Ar-H, 1 H), 4.20 (q, J = 6.8 Hz, CH, 1 H), 3.39 (sp, J = 6.8 Hz, CH, 2 H), 3.34 (d, J = 11.7 Hz, NH, 1 H), 3.09 (m, CH, 1 H), 2.62/2.46 (m +dd, J = 11.7, 6.9 Hz, CH_2, 2 H), 1.17 (d, J = 6.8 Hz, CH_3, 6 H), 1.14 (d, J = 6.8 Hz, CH_3, 6 H), 1.10 (d, J = 6.8 Hz, CH_3, 3 H), 0.91 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 142.5, 141.2, 140.1, 133.5, 130.7, 128.6, 126.7, 125.6, 125.5, 125.2, 123.4, 123.0, 122.5, 121.9, 67.4, 54.0, 49.6, 27.1, 27.0, 24.1, 23.9, 23.8. HRMS: calcd for $C_{30}H_{42}N_2$ $[M + H]^+$ 431.3420, found 431.3427.

(2*S*)-*N*-(2,6-Diisopropylphenyl)-3,3-dimethyl-*N*′-[(1*S*)-1,2,2-trimethylpropyl]butane-1,2-diamine (8e). This compound was prepared following the synthetic procedure described for **8a** starting from 1.07 mL of (2*S*)-3,3-dimethylbutan-2-amine (7.99 mmol) and 2.00 g of **5c** (7.26 mmol). The reaction time for the first step was 2 h and for the second step was 4 h. **8e** was collected as a yellow oil (1.95 g, 5.41 mmol, 74.5%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.00 (d, J = 7.7 Hz, Ar-H, 2 H), 6.86 (t, J = 7.7 Hz, Ar-H, 1 H), 3.35 (sp, J = 6.7 Hz, CH, 2 H), 3.29 (d, J = 11.7 Hz, NH, 1 H), 3.06 (m, CH, 1 H), 2.74/2.51 (dd+m, J = 11.7, 7.5 Hz, CH_2, 2 H), 1.90 (br., CH, 1 H), 1.18 (d, J = 6.7 Hz, CH_3, 12 H), 1.00 (s, CH_3, 9 H), 0.67 (d, J = 6.5 Hz, CH_3, 3 H), 0.60 (s, CH_3, 9 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 142.7, 139.6, 123.4, 121.7, 67.3, 61.4, 51.1, 34.9, 34.2, 27.2, 27.1, 26.1, 24.0, 23.8, 14.2. HRMS: calcd for $C_{24}H_{44}N_2$ $[M + H]^+$ 361.3577, found 361.3583.

(2*S*)-*N*-(2,6-Diisopropylphenyl)-3,3-dimethyl-*N*′-[(1*R*)-1,2,2-trimethylpropyl]butane-1,2-diamine (8f). This compound was prepared following the synthetic procedure described for **8a** starting from 1.12 mL of (2*R*)-3,3-dimethylbutan-2-amine (8.39 mmol) and 2.10 g of **5c** (7.63 mmol). The reaction time for the first step was 2 h and for the second step was 4 h. **8f** was collected as a yellow oil (1.84 g, 5.09 mmol, 66.7%). A yellow oil was obtained. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.01 (d, J = 7.7 Hz, Ar-H, 2 H), 6.86 (t, J = 7.7 Hz, Ar-H, 1 H), 3.32 (sp, J = 6.8 Hz, CH, 2 H), 3.29 (d, J = 8.2 Hz, NH, 1 H), 3.01 (m, CH, 1 H), 2.84/2.28 (m+dd, J = 11.6, 6.2 Hz, CH_2, 2 H), 1.90 (q, J = 6.3 Hz, CH, 1 H), 1.18 (d, J = 6.8 Hz, CH_3, 6 H), 1.17 (d, J = 6.8 Hz, CH_3, 6 H), 1.01 (s, CH_3, 9 H), 0.79 (br s, NH, 1 H), 0.68 (d, J = 6.3 Hz, CH_3, 3 H), 0.58 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 142.2, 139.8, 123.5, 121.8, 67.2, 61.9, 49.6, 35.2, 33.8, 27.1, 26.1, 24.0, 14.2. HRMS: calcd for $C_{24}H_{44}N_2$ $[M + H]^+$ 361.3577, found 361.3588.

(2*S*)-*N*-(2,6-Diisopropylphenyl)-*N*′-(2-isopropylphenyl)-3,3-dimethylbutane-1,2-diamine (8g). This compound was prepared following the synthetic procedure described for **8a** starting from 1.13 mL of 2-isopropylaniline (7.99 mmol) and 2.10 g of **5c** (7.63 mmol). The reaction time for the first step was 7 h and for the second step was 30 min with 827 mg of $LiAlH_4$ (21.8 mmol) as the reductive agent. **8g** was collected as a yellow oil (2.26 g, 5.74 mmol, 79.0%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.02 (d, J = 7.6 Hz, Ar-H, 2 H), 6.93 (dm, J = 7.4 Hz, Ar-H, 1 H), 6.92 (t, J = 7.6 Hz, Ar-H, 1 H), 6.90 (td, J = 7.4, 1.1 Hz, Ar-H, 1 H), 6.52 (td, J = 7.4, 1.1 Hz, Ar-H, 1 H), 6.34 (dd, J = 7.4, 1.1 Hz, Ar-H, 1 H), 4.12 (d, J = 6.7 Hz, NH, 1 H), 3.50 (d, J = 11.1 Hz, NH, 1 H), 3.49/2.98 (m+m, CH_2, 2 H), 3.30 (sp, J = 6.8 Hz, CH, 2 H), 3.22 (m, CH, 1 H), 2.04 (m, J = 6.8 Hz, CH, 1 H), 1.10/1.06 (d+d, J = 6.8 Hz, J = 6.8 Hz, CH_3, 12 H), 1.06 (s, CH_3, 9 H), 0.95/0.94 (d+d, J = 6.8 Hz, J = 6.8 Hz, CH_3, 6 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 144.6, 142.5, 140.0, 131.6, 126.3, 124.3, 123.7, 122.0, 116.2, 109.3, 65.2, 45.6, 35.6, 27.1, 27.0, 25.7, 24.1, 24.0, 22.2, 22.1. HRMS: calcd for $C_{27}H_{43}N_2$ $[M + H]^+$ 395.3421, found 395.3436.

(2*S*)-*N*′-(2-*tert*-Butylphenyl)-*N*-(2,6-diisopropylphenyl)-3,3-dimethylbutane-1,2-diamine (8h). This compound was prepared following the synthetic procedure described for **8a** starting from 1.25 mL of 2-*tert*-butylaniline (7.99 mmol) and 2.00 g of **5c** (7.26 mmol). The reaction time for the first step was 16 h and for the second step was 3 h at 60 °C with 827 mg of $LiAlH_4$ (21.8 mmol) as the reductive agent. **8h** was collected as a yellow oil (2.15 g, 5.26 mmol, 72.4%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.08 (dd, J = 7.7, 1.2 Hz, Ar-H, 1 H), 6.98 (td, J = 7.7, 1.2 Hz, Ar-H, 1 H), 6.97 (d, J = 7.7 Hz, Ar-H, 2 H), 6.83 (t, J = 7.7 Hz, Ar-H, 1 H), 6.55 (td, J = 7.7, 1.2 Hz, Ar-H, 1 H), 6.51 (dd, J = 7.7, 1.2 Hz, Ar-H, 1 H), 4.60 (d, J = 6.2 Hz, NH, 1 H), 3.76 (d, J = 11.6 Hz, NH, 1 H), 3.46/3.04 (m+m, CH_2, 2 H), 3.38 (m, CH, 1 H), 3.30 (sp, J = 6.7 Hz, CH, 2 H), 1.25 (s, CH_3, 9 H), 1.11 (d, J = 6.7 Hz, CH_3, 12 H), 0.93 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 146.7, 143.0, 138.8, 132.9, 126.8, 125.6, 123.6, 121.3, 116.3, 111.5, 65.1, 44.9, 36.5, 33.8, 31.3, 29.4, 27.3, 27.1, 24.4. HRMS: calcd for $C_{27}H_{43}N_2$ $[M + H]^+$ 409.3577, found 409.3567.

(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*S*)-1-phenylethyl]-4,5-dihydroimidazolium Chloride (9a). A 2.50 g portion of **8a** (6.49 mmol) was dissolved in 33 mL of $HC(OEt)_3$ (194 mmol), and 382 mg of NH_4Cl (7.14 mmol) was added in one portion. The mixture was heated to reflux temperature and was stirred for 75 min, at which point complete conversion was observed by HPLC-MS. The volatiles were removed under reduced pressure, and the residue was purified via column chromatography using DCM and 1.2% methanolic ammonia as eluents. The crude product was recrystallized from DCM-Et_2O. **9a** was collected as a white solid (1.27 g, 2.97 mmol, 45.8%). Mp: 213-215 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.05 (s, CH, 1 H), 7.52−7.40 (m, Ar-H, 5 H), 7.49 (t, J = 7.7 Hz, Ar-H, 1 H), 7.39 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 7.38 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 5.05 (q, J = 7.0 Hz, CH, 1 H), 4.44 (dd, J = 12.3, 9.2 Hz, CH, 1 H), 4.13/3.94 (t+dd, J = 12.3 Hz, J = 12.3, 9.2 Hz, CH_2, 2 H), 3.20 (sp, J = 6.8 Hz, CH, 1 H), 2.90 (sp, J = 6.8 Hz, CH, 1 H), 1.72 (d, J = 7.0 Hz, CH_3, 3 H), 1.31 (d, J = 6.8 Hz, CH_3, 3 H), 1.29 (d, J = 6.8 Hz, CH_3, 3 H), 1.23 (d, J = 6.8 Hz, CH_3, 3 H), 1.18 (d, J = 6.8 Hz, CH_3, 3 H), 0.73 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 158.5, 145.5, 145.2, 138.5, 132.1, 130.4, 129.2, 128.8, 126.5, 125.5, 125.3, 73.8, 57.6, 49.4, 34.9, 28.3, 28, 25.8, 25.5, 25.2, 23.2, 22.6, 19.1. HRMS: calcd for $C_{27}H_{39}N_2$ $[M - Cl^-]^+$ 391.3108, found 391.3113.

(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*R*)-1-phenylethyl]-4,5-dihydroimidazolium Chloride (9b). This compound was prepared following the synthetic procedure described for **9a** starting from 2.78 g of **8b** (7.30 mmol). **9b** was collected as a white solid (1.12 g, 2.62 mmol, 35.9%). Mp: 164−166 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.12 (s, CH, 1 H), 7.55−7.41 (m, Ar-H, 5 H), 7.47 (t, J = 7.8 Hz, Ar-H, 1 H), 7.38 (dd, J = 7.8, 1.5 Hz, Ar-H, 1 H), 7.35 (dd, J = 7.8, 1.5 Hz, Ar-H, 1 H), 5.27 (q, J = 7.0 Hz, CH, 1 H), 4.37 (dd, J = 12.4, 8.8 Hz, CH, 1 H), 4.07/3.94 (t+dd, J = 12.4 Hz, J = 12.4, 8.8 Hz, CH_2, 2 H), 3.23 (sp, J = 6.7 Hz, CH, 1 H), 2.83 (sp, J = 6.7 Hz, CH, 1 H), 1.76 (d, J = 7.0 Hz, CH_3, 3 H), 1.30 (d, J = 6.7 Hz, CH_3, 3 H), 1.29 (d, J = 6.7 Hz, CH_3, 3 H), 1.23 (d, J = 6.7 Hz, CH_3, 3 H), 1.11 (d, J = 6.7 Hz, CH_3, 3 H), 0.76 (s, CH_3, 9 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.3, 145.5, 145.3, 137.7, 132.1, 130.3, 129.1, 128.8, 126.9, 125.4, 125.3, 74.1, 56.9, 47.8, 35.1, 28.3, 28.0, 26.0, 25.4, 25.2, 23.2, 22.6, 17.7. HRMS: calcd for $C_{27}H_{39}N_2$ $[M - Cl^-]^+$ 391.3108, found 391.2852.

(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*S*)-1-(1-naphthyl)ethyl]-4,5-dihydroimidazolium Chloride (9c). This compound was prepared following the synthetic procedure described for **9a** starting from 2.84 g of **8c** (6.580 mmol). **9c** was collected as a white solid (2.03 mg, 4.26 mmol, 64.7%). Mp: 272−274 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.87 (s, CH, 1 H), 8.21−7.58 (m, Ar-H, 6 H), 7.79 (d, J = 7.0 Hz, Ar-H, 1 H), 7.43 (t, J = 7.8 Hz, Ar-H, 1 H), 7.30 (d, J = 7.8 Hz, Ar-H, 2 H), 6.03 (q, J = 6.8 Hz, CH, 1 H), 4.37 (dd, J = 12.5, 8.5 Hz, CH, 1 H), 4.19/3.97 (dd+t, J = 12.5, 8.5 Hz, J = 12.5 Hz, CH_2, 2 H), 2.95 (sp, J = 6.8 Hz, CH, 1 H), 2.71 (sp, J = 6.8 Hz, CH, 1 H), 1.94 (d, J = 6.8 Hz, CH_3, 3 H), 1.21 (d, J = 6.8 Hz, CH_3, 3 H), 1.20 (d, J = 6.8 Hz, CH_3, 3 H), 1.02 (d, J = 6.8 Hz, CH_3, 3 H), 0.91 (d, J = 6.8 Hz, CH_3, 3 H), 0.77 (s, CH_3, 9 H), ^{13}C NMR (125 MHz, DMSO-d_6): δ 159.0, 145.3, 145.0, 133.7, 131.9, 131.6, 130.4, 130.2, 129.8, 129.2, 127.1, 126.3, 125.5, 125.4, 125.2, 122.6,

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73.8, 53.2, 48.0, 35.1, 28.1, 28.0, 25.5, 25.2, 23.2, 22.5, 17.9. HRMS: calcd for $C_{31}H_{41}N_2$ $[M - Cl^-]^+$ 441.3264, found 441.3253.

(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*R*)-1-(1-naphthyl)ethyl]-4,5-dihydroimidazolium Chloride (9d). This compound was prepared following the synthetic procedure described for **9a** starting from 2.25 g of **8d** (5.22 mmol). **9d** was collected as a white solid (1.90 g, 3.98 mmol, 76.1%). Mp: 261−263 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.40 (s, CH, 1 H), 8.72 (d, J = 8.5 Hz, Ar-H, 1 H), 8.00−7.32 (m, Ar-H, 6 H) 7.35 (t, J = 7.8 Hz, Ar-H, 1 H), 7.19/7.17 (dd+dd, J = 7.8, 1.5 Hz, J = 7.8, 1.5 Hz, Ar-H, 2 H), 4.21 (m, CH, 1 H), 4.20/3.25 (m+dd, J = 8.7, 4.0 Hz, CH_2, 2 H), 3.00 (sp, J = 6.8 Hz, CH, 1 H), 2.89 (sp, J = 6.8 Hz, CH, 1 H), 2.02 (d, J = 6.8 Hz, CH_3, 3 H), 1.45 (d, J = 6.8 Hz, CH_3, 3 H), 1.34 (d, J = 6.8 Hz, CH_3, 3 H), 1.27 (d, J = 6.8 Hz, CH_3, 3 H), 1.18 (d, J = 6.8 Hz, CH_3, 3 H), 0.36 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.3, 145.6, 145.3, 134.3, 132.3, 131.8, 131.3, 130.5, 130.3, 129.2, 127.7, 126.6, 125.7, 125.6, 124.9, 124.6, 124.0, 73.5, 53.4, 46.6, 35.5, 29.5, 28.6, 26.9, 25.8, 25.5, 23.8, 23.0, 17.1. HRMS: calcd for $C_{31}H_{41}N_2$ $[M - Cl^-]^+$ 441.3264, found 441.3265.

(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*S*)-1,2,2-trimethylpropyl]-4,5-dihydroimidazolium Chloride (9e). This compound was prepared following the synthetic procedure described for **9a** starting from 1.95 g of **8e** (5.41 mmol). **9e** was collected as a white solid (1.80 g, 4.42 mmol, 81.8% Yield). Mp: 130−148 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.00 (s, CH, 1 H), 7.49 (t, J = 7.7 Hz, Ar-H, 1 H), 7.38 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 7.37 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 4.55 (dd, J = 12.0, 10.2 Hz, CH, 1 H), 4.48/4.02 (t+dd, J = 12.0 Hz, J = 12.0, 10.2 Hz, CH_2, 2 H), 3.77 (q, J = 7.1 Hz, CH, 1 H), 3.18 (sp, J = 6.8 Hz, CH, 1 H), 2.98 (sp, J = 6.8 Hz, CH, 1 H), 1.37 (d, J = 7.1 Hz, CH_3, 3 H), 1.34 (d, J = 6.8 Hz, CH_3, 3 H), 1.30 (d, J = 6.8 Hz, CH_3, 3 H), 1.19 (d, J = 6.8 Hz, CH_3, 3 H), 1.13 (d, J = 6.8 Hz, CH_3, 3 H), 0.99 (s, CH_3, 9 H), 0.82 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 162.9, 160.5, 145.8, 145.5, 131.8, 130.5, 125.5, 125.2, 73.9, 62.9, 50.8, 35.0, 34.6, 28.2, 28.2, 26.4, 25.9, 25.5, 25.4, 23.0, 22.5, 13.3. HRMS: calcd for $C_{25}H_{43}N_2$ $[M - Cl^-]^+$ 371.3426, found 371.3423.

(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*R*)-1,2,2-trimethylpropyl]-4,5-dihydroimidazolium Chloride (9f). This compound was prepared following the synthetic procedure described for **9a** starting from 1.84 g of **8f** (5.09 mmol). **9f** was collected as a white solid (845 mg, 2.08 mmol, 40.8%). Mp: 259−261 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.95 (s, CH, 1 H), 7.47 (t, J = 7.7 Hz, Ar-H, 1 H), 7.37 (dm, J = 7.7 Hz, Ar-H, 2 H), 4.45/4.07 (m+m, CH_2, 2 H), 4.45 (m, CH, 1 H), 3.80 (q, J = 7.0 Hz, CH, 1 H), 3.26 (sp, J = 6.8 Hz, CH, 1 H), 2.97 (sp, J = 6.8 Hz, CH, 1 H), 1.37 (d, J = 7.0 Hz, CH_3, 3 H), 1.35 (d, J = 6.8 Hz, CH_3, 3 H), 1.29 (d, J = 6.8 Hz, CH_3, 3 H), 1.21 (d, J = 6.8 Hz, CH_3, 3 H), 1.10 (d, J = 6.8 Hz, CH_3, 3 H), 0.99 (s, CH_3, 9 H), 0.81 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 160.4, 145.8, 145.6, 131.9, 130.4, 125.4, 125.2, 74.1, 62.9, 49.5, 34.8, 34.6, 28.2, 27.9, 26.5, 26.0, 25.6, 25.3, 23.2, 22.5, 13.2. HRMS: calcd for $C_{25}H_{43}N_2$ $[M - Cl^-]^+$ 371.3426, found 371.3422.

(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-(2-isopropylphenyl)-4,5-dihydroimidazolium Chloride (9g). This compound was prepared following the synthetic procedure described for **9a** starting from 2.26 g of **8g** (5.73 mmol). **9g** was collected as a yellowish white solid (1.94 g, 4.39 mmol, 76.7%). Mp: 60−65 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.27 (s, CH, 1 H), 7.67 (dd, J = 7.9, 1.2 Hz, Ar-H, 1 H), 7.60 (dd, J = 7.9, 1.2 Hz, Ar-H, 1 H), 7.57 (td, J = 7.9, 1.2 Hz, Ar-H, 1 H), 7.51 (t, J = 7.7 Hz, Ar-H, 1 H), 7.46 (td, J = 7.9, 1.2 Hz, Ar-H, 1 H), 7.41 (dm, J = 7.7 Hz, Ar-H, 1 H), 7.41 (dm, J = 7.7 Hz, Ar-H, 1 H), 4.85/4.47 (t+dd, J = 11.8 Hz, J = 11.8, 10.2 Hz, CH_2, 2 H), 4.72 (dd, J = 11.8, 10.2 Hz, CH, 1 H), 3.33 (sp, J = 6.8 Hz, CH, 1 H), 3.15 (sp, J = 6.8 Hz, CH, 1 H), 3.06 (sp, J = 6.8 Hz, CH, 1 H), 1.42/1.16 (d+d, J = 6.8 Hz, J = 6.8 Hz, CH_3, 6 H), 1.36/1.19 (d+d, J = 6.8 Hz, J = 6.8 Hz, CH_3, 6 H), 1.30/1.26 (d+d, J = 6.8 Hz, J = 6.8 Hz, CH_3, 6 H), 0.88 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 160.8, 145.6, 145.3, 144.6, 133.0, 131.4, 130.7, 127.4, 127.3, 126.9, 125.6, 125.3, 75.0, 55.1, 34.9, 28.5, 28.2, 27.8, 25.8, 25.7, 25.4, 23.7, 23.6, 23.1, 22.5. HRMS: calcd for $C_{28}H_{41}N_2$ $[M - Cl^-]^+$ 405.3270, found 405.3255.

(4*S*)-4-*tert*-Butyl-1-(2-*tert*-butylphenyl)-3-(2,6-diisopropylphenyl)-4,5-dihydroimidazolium Chloride (9h). This compound was prepared following the synthetic procedure described for **9a** starting from 2.10 g of **8h** (5.14 mmol). **9h** was collected as a yellowish white solid (1.90 mg, 4.16 mmol, 81.0%). Mp: 230−245 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.26 (s, CH, 1 H), 7.75−7.45 (m, Ar-H, 4 H), 7.53 (t, J = 7.9 Hz, Ar-H, 1 H), 7.40 (d, J = 7.9 Hz, Ar-H, 2 H), 4.88 (t, J = 11.3 Hz, CH, 1 H), 4.82/4.42 (t+t, J = 11.3 Hz, J = 11.3 Hz, CH_2, 2 H), 3.33 (sp, J = 6.7 Hz, CH, 1 H), 3.16 (sp, J = 6.7 Hz, CH, 1 H), 1.48 (s, CH_3, 9 H), 1.43/1.16 (d+d, J = 6.7 Hz, J = 6.7 Hz, CH_3, 3 H), 1.38/1.19 (d+d, J = 6.7 Hz, J = 6.7 Hz, CH_3, 3 H), 0.87 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 145.4, 138.0, 133.8, 130.8, 130.7, 130.1, 129.4, 128.1, 125.6, 56.8, 34.6, 32.0, 28.2, 26.0, 25.7, 25.4, 23.0. HRMS: calcd for $C_{28}H_{41}N_2$ $[M - Cl^-]^+$ 419.3426, found 419.3404.

(4*S*)-4-*tert*-Butyl-3-(2-*tert*-butylphenyl)-1-[(1*S*)-1-phenylethyl]-4,5-dihydroimidazolium Chloride (9i). This compound was prepared following the synthetic procedure described for **9a** starting from 315 mg of **8i** (0.893 mmol). **9i** was collected as a light yellow solid (63 mg, 0.158 mmol, 17.7%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.13 (s, CH, 1 H), 7.71 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 7.62 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 7.48−7.40 (m, Ar-H, 5 H), 7.49 (td, J = 7.7, 1.4 Hz, Ar-H, 1 H), 7.39 (td, J = 7.7, 1.4 Hz, Ar-H, 1 H), 4.98 (q, J = 7.0 Hz, CH, 1 H), 4.51 (dd, J = 11.0, 8.1 Hz, CH, 1 H), 3.87 (m, CH_2, 2 H), 1.72 (d, J = 7.0 Hz, CH_3, 3 H), 1.40 (s, CH_3, 9 H), 0.71 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 157.6, 146.5, 138.4, 134.5, 131.6, 130.3, 130.1, 129.1, 128.7, 127.1, 126.8, 73.1, 57.5, 49.5, 35.4, 31.8, 25.2, 19.5. HRMS: calcd for $C_{25}H_{35}N_2$ $[M - Cl^-]^+$ 363.2800, found 363.2787.

(2*R*)-*N*-(2,6-Diisopropylphenyl)-*N*′-[(4-methoxyphenyl)methyl]-3,3-dimethylbutane-1,2-diamine (10). This compound was prepared following the synthetic procedure described for **8a** starting from 3.94 mL of 4-methoxyphenyl)methanamine (30.2 mmol) and 7.55 g of **5b** (27.4 mmol). The reaction time for the first step was 2 h and for the second step was 16 h. **10** was collected as a colorless oil (7.01 g, 17.7 mmol, 64.5%). A colorless oil was obtained. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.00 (d, J = 7.6 Hz, Ar-H, 2 H), 6.97 (m, Ar-H, 2 H), 6.89 (t, J = 7.6 Hz, Ar-H, 1 H), 6.76 (m, Ar-H, 2 H), 3.69 (s, CH_3, 3 H), 3.39 (s, CH_2, 2 H), 3.36 (sp, J = 6.8 Hz, CH, 2 H), 3.35 (m, NH, 1 H), 3.01 (m, CH, 1 H), 2.61/2.51 (dd+dm, J = 12.4, 4.2 Hz, J = 4.2 Hz, CH_2, 2 H), 1.33 (brs, NH, 1 H), 1.15 (d, J = 6.8 Hz, CH_3, 6 H), 1.13 (d, J = 6.8 Hz, CH_3, 6 H), 0.99 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 157.8, 142.5, 140.1, 132.6, 128.5, 123.4, 121.9, 113.4, 66.7, 54.9, 52.6, 50.2, 35.3, 27.3, 26.9, 24.1, 24.0. HRMS: calcd for $C_{26}H_{41}N_2O$ $[M + H]^+$ 397.3213, found 397.3217. The stereochemical integrity of the product was not investigated.

(2*R*)-*N*-(2,6-Diisopropylphenyl)-3,3-dimethylbutane-1,2-diamine (11). A 1.80 g portion of **10** (4.54 mmol) was dissolved in 23 mL of EtOH, and 483 mg of palladium (0.454 mmol) was added carefully. The reaction was carried out in an autoclave under 10 bar pressure at room temperature. After 24 h complete conversion was observed by HPLC-MS. The crude product was purified via column chromatography using DCM and 1.2% methanolic ammonia as eluents. **11** was collected as a colorless oil (1.19 g, 4.32 mmol, 95.2%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.00 (d, J = 7.6 Hz, Ar-H, 2 H), 6.87 (t, J = 7.6 Hz, Ar-H, 1 H), 3.38 (sp, J = 6.8 Hz, CH, 2 H), 3.38 (d, J = 5.0 Hz, NH, 1 H), 2.85 (m, CH, 1 H), 2.66/2.58 (dd+dd, J = 13.1, 5.0 Hz, J = 13.1 Hz, J = 5.0 Hz, CH_2, 2 H), 1.20 (br s, NH_2, 2 H), 1.16 (d, J = 6.8 Hz, CH_3, 6 H), 1.15 (d, J = 6.8 Hz, CH_3, 6 H), 0.99 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 142.7, 140.0, 123.4, 121.6, 69.3, 42.8, 35.3, 27.4, 26.9, 24.1, 24.0. HRMS: calcd for $C_{18}H_{30}N_2O$ $[M + H]^+$ 277.2638, found 277.2641. The stereochemical integrity of the product was not investigated.

(2*R*)-*N*′-[(1*S*)-1-(1-Adamantyl)ethyl]-*N*-(2,6-diisopropylphenyl)-3,3-dimethylbutane-1,2-diamine (13a) and (2*R*)-*N*′-[(1*R*)-1-(1-Adamantyl)ethyl]-*N*-(2,6-diisopropylphenyl)-3,3-dimethylbutane-1,2-diamine (13b). These compounds were prepared following the synthetic procedure described for **8a** starting from 1.03 g of 1-(1-adamantyl)ethanone (5.77 mmol) and 1.45 g of **11**

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(5.24 mmol). The reaction time for the first step was 3.5 h and for the second step was 2 h. **13a,b** were collected as a diastereomeric mixture (695 mg, 0.64 mmol, 30.2%). Diastereomers were separated via column chromatography using heptane and EtOAc as eluents. The earlier eluting diastereoisomer was collected as **13a** and the later eluting diastereoisomer as **13b**.

13a was collected as a colorless oil (483 mg, 1.10 mmol, 21.0%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.01 (d, J = 7.6 Hz, Ar-H, 2 H), 6.86 (t, J = 7.6 Hz, Ar-H, 1 H), 3.30 (sp, J = 6.8 Hz, CH, 2 H), 3.02 (m, CH, 1 H), 2.84/2.24 (m+m, CH_2, 2 H), 1.81−1.14 (m, CH/CH_2, 15 H), 1.70 (q, J = 6.4 Hz, 1 H), 1.19/1.18 (d+d, J = 6.8 Hz, J = 6.8 Hz, CH_3, 12 H), 1.01 (s, CH_3, 9 H), 0.66 (d, J = 6.4 Hz, CH_3, 3 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 142.3, 139.8, 123.5, 121.7, 67.3, 62.2, 50.1, 37.8, 37.6, 37.0, 36.8, 35.3, 35.2, 27.8, 27.8, 27.2, 27.1, 24.0, 12.9. HRMS: calcd for $C_{30}H_{51}N_2$ $[M + H]^+$ 439.4047, found 439.4037.

13b was collected as a yellowish oil (194 mg, 0.44 mmol, 8.4%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.00 (d, J = 7.7 Hz, Ar-H, 2 H), 6.85 (t, J = 7.7 Hz, Ar-H, 1 H), 3.36 (sp, J = 6.8 Hz, CH, 2 H), 3.07 (m, CH, 1 H), 2.75/2.48 (m+m, CH_2, 2 H), 1.84−1.10 (m, CH/CH_2, 15 H), 1.73 (q, J = 6.4 Hz, CH, 1 H), 1.19/1.18 (d+d, J = 6.8 Hz, J = 6.8 Hz, CH_3, 12 H), 0.99 (s, CH_3, 9 H), 0.66 (d, J = 6.4 Hz, CH_3, 3 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 143.0, 130.5, 129.1, 121.5, 67.4, 61.7, 51.0, 37.9, 36.9, 27.9, 27.2, 27.1, 24.1, 20.8, 12.9. HRMS: calcd for $C_{30}H_{51}N_2$ $[M + H]^+$ 439.4047, found 439.4047.

(2*R*)-*N*-(2,6-Diisopropylphenyl)-*N*′-[(1*R*)-1,2-diphenylethyl]-3,3-dimethylbutane-1,2-diamine (13c) and (2*R*)-*N*-(2,6-Diisopropylphenyl)-*N*′-[(1*S*)-1,2-diphenylethyl]-3,3-dimethylbutane-1,2-diamine (13d). These compounds were prepared following the synthetic procedure described for **8a** starting from 1.70 g of **11** (6.15 mmol) and 1.11 mL of 1,2-diphenylethanone (6.76 mmol). The reaction time for the first step was 5 h and for the second step was 2 h. **13c,d** were collected as a diastereomeric mixture (950 mg, 0.21 mmol, 33.8%). Diastereomers were separated via column chromatography using heptane and EtOAc as eluents. The earlier eluting diastereoisomer was collected as **13c** and the later eluting diastereoisomer as **13d**.

13c was collected as a yellow oil (507 mg, 1.11 mmol, 18.1%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.25−6.83 (m, Ar-H, 13 H), 3.43 (dd, J = 7.9, 6.0 Hz, CH, 1 H), 3.22 (sp, J = 6.7 Hz, CH, 2 H), 3.10 (d, J = 11.6 Hz, NH, 1 H), 2.81 (m, CH, 1 H), 2.62/2.56 (dd+dd, J = 13.4, 6.0 Hz, J = 13.4, 6.0 Hz, CH_2, 2 H), 2.45/2.17 (dm+dd, J = 12.6 Hz, J = 12.6, 5.0 Hz, CH_2, 2 H), 1.40 (br s, NH, 1 H), 1.14 (d, J = 6.7 Hz, CH_3, 6 H) 1.03 (d, J = 6.7 Hz, CH_3, 6 H), 0.82 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 144.0, 142.1, 140.4, 138.6, 129.0, 128.0, 127.9, 127.0, 126.5, 126.0, 123.4, 122.1, 67.1, 63.9, 47.7, 44.5, 27.0, 26.9, 24.0, 23.8. HRMS: calcd for $C_{32}H_{45}N_2$ $[M + H]^+$ 457.3577, found 457.3566.

13d was collected as a yellow oil (411 mg, 0.90 mmol, 14.6%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.20−6.85 (m, Ar-H, 13 H), 3.56 (t, J = 7.0 Hz, CH, 1 H), 3.25 (sp, J = 6.8 Hz, CH, 2 H), 3.21 (d, J = 11.7 Hz, NH, 1 H), 2.91 (m, CH, 1 H), 2.65/2.56 (dd+dd, J = 13.2, 7.0 Hz, J = 13.2, 7.0 Hz, CH_2, 2 H), 2.34 (d, J = 4.4 Hz, CH_2, 2 H), 1.35 (br s, NH, 1 H), 1.14 (d, J = 6.8 Hz, CH_3, 6 H) 1.07 (d, J = 6.8 Hz, CH_3, 6 H), 0.87 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 143.3, 142.4, 140.1, 138.7, 129.2, 127.9, 126.9, 126.5, 125.9, 123.4, 121.9, 66.4, 63.9, 48.3, 44.3, 27.0, 27.0, 24.0, 23.8. HRMS: calcd for $C_{32}H_{45}N_2$ $[M + H]^+$ 457.3577, found 457.3562.

(2*R*)-*N*-(2,6-Diisopropylphenyl)-3,3-dimethyl-*N*′-[(1*S*)-1-phenylethyl]butane-1,2-diamine (13e). This compound was prepared following the synthetic procedure described for **8a** starting from 0.77 mL of (1*S*)-1-phenylethanamine (6.00 mmol) and 1.50 g of **5a** (5.45 mmol). The reaction time for the first step was 2.5 h and for the second step was 4 h. **8a** and **13e** were collected as a diastereomeric mixture (1.75 g, 4.60 mmol, 84.4%). Diastereomers were separated via column chromatography using heptane and EtOAc as eluents. The later eluting diastereoisomer, **13e**, was collected as a yellow oil (832 mg, 2.19 mmol, 40.2%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.25−7.04 (m, Ar-H, 5 H) 7.00 (d, J = 7.6 Hz, Ar-H, 2 H), 6.89 (t, J = 7.6 Hz, Ar-H, 1 H), 3.44 (q, J = 6.5 Hz, CH, 1 H), 3.35 (d, J = 11.4 Hz, NH, 1 H), 3.35 (sp, J = 6.8 Hz, CH, 2 H), 3.01 (m, CH, 1 H), 2.39/2.35 (m+m, CH_2, 2 H), 1.32 (br s, NH, 1 H), 1.16 (d, J = 6.8 Hz, CH_3, 6 H), 1.12 (d, J = 6.8 Hz, CH_3, 6 H), 1.00 (d, J = 6.5 Hz, CH_3, 3 H), 0.94 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 145.9, 142.6, 139.9, 128.1, 126.4, 126.2, 123.4, 121.8, 66.0, 57.2, 48.4, 35.2, 27.2, 27.0, 24.4, 24.0, 23.9. HRMS: calcd for $C_{26}H_{41}N_2$ $[M + H]^+$ 381.3264, found 381.3257.

(2*R*)-*N*-(2,6-Diisopropylphenyl)-3,3-dimethyl-*N*′-[(1*S*)-1-(1-naphthyl)ethyl]butane-1,2-diamine (13f). This compound was prepared following the synthetic procedure described for **8a** starting from 0.55 mL of (1*S*)-1-(1-naphthyl)ethanamine (3.40 mmol) and 850 mg of **5a** (3.086 mmol). The reaction time for the first step was 1 h and for the second step was 4 h. **8c** and **13f** were collected as a diastereomeric mixture (620 mg, 1.44 mmol, 46.6%). Diastereomers were separated via column chromatography using heptane and EtOAc as eluents. The later eluting diastereoisomer, **13f**, was collected as a yellow oil (327 mg, 0.76 mmol, 24.6%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.10−7.27 (m, Ar-H, 7 H), 7.01 (d, J = 7.6 Hz, Ar-H, 2 H), 6.90 (t, J = 7.6 Hz, Ar-H, 1 H), 4.20 (q, J = 6.4 Hz, CH, 1 H), 3.39 (sp, J = 6.7 Hz, CH, 2 H), 3.34 (br d, NH, 1 H), 3.08 (m, CH, 1 H), 2.61/2.46 (m+m, CH_2, 2 H), 1.17 (d, J = 6.7 Hz, CH_3, 6 H), 1.14 (d, J = 6.4 Hz, CH_3, 3 H), 1.10 (d, J = 6.7 Hz, CH_3, 6 H), 0.92 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 142.5, 141.3, 140.1, 133.5, 130.7, 128.6, 126.7, 125.6, 125.6, 125.2, 123.5, 123.0, 122.5, 121.9, 67.4, 54.0, 49.5, 27.1, 27.0, 24.1, 24.0, 23.8. HRMS: calcd for $C_{30}H_{42}N_2$ $[M + H]^+$ 431.3420, found 431.3411.

(2*S*)-*N*-(2-*tert*-Butylphenyl)-3,3-dimethyl-*N*′-[(1*S*)-1-phenylethyl]butane-1,2-diamine (8i) and (2*R*)-*N*-(2-*tert*-Butylphenyl)-3,3-dimethyl-*N*′-[(1*S*)-1-phenylethyl]butane-1,2-diamine (13g). These compounds were prepared following the synthetic procedure described for **8a** starting from 2.35 g of crude **5d** (4.75 mmol) and 0.67 mL of (1*S*)-1-phenylethanamine (5.22 mmol). The reaction time for the first step was 20 h and for the second step was 2 h. **8i** and **13g** were collected as a diastereomeric mixture (605 mg, 1.72 mmol, 38.1%). Diastereomers were separated via column chromatography using heptane and EtOAc as eluents. The earlier eluting diastereoisomer was collected as **8i** and the later eluting diastereoisomer as **13g**.

8i was collected as a yellow oil (317 mg, 0.90 mmol, 18.9%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.33−7.14 (m, Ar-H, 5 H), 7.11 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.98 (td, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.77 (d, J = 7.7 Hz, Ar-H, 1 H), 6.50 (td, J = 7.7, 1.4 Hz, Ar-H, 1 H), 3.89 (d, J = 9.0 Hz, NH, 1 H), 3.63 (q, J = 6.6 Hz, CH, 1 H), 3.43 (td, J = 8.0, 3.8 Hz, CH, 1 H), 2.66/2.45 (dd+dd, J = 11.8, 3.8 Hz, J = 11.8, 8.0 Hz, CH_2, 2 H), 1.38 (s, CH_3, 9 H), 1.15 (d, J = 6.6 Hz, CH_3, 3 H), 0.90 (s, CH_3, 9 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 146.6, 146.0, 131.5, 128.1, 126.8, 126.5, 126.4, 126.0, 115.3, 111.1, 60.2, 58.0, 48.8, 35.3, 33.7, 29.8, 27.7, 27.1, 24.3. HRMS: calcd for $C_{24}H_{36}N_2$ $[M + H]^+$ 353.2951, found 353.2962.

13g was collected as a yellow oil (249 mg, 0.71 mmol, 14.9%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.30−7.15 (m, Ar-H, 5 H), 7.10 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.98 (td, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.77 (d, J = 7.7 Hz, Ar-H, 1 H), 6.48 (td, J = 7.7, 1.4 Hz, Ar-H, 1 H), 4.02 (d, J = 8.9 Hz, NH, 1 H), 3.58 (q, J = 6.7 Hz, CH, 1 H), 3.47 (m, CH, 1 H), 2.61/2.38 (dd+dd, J = 12.1, 2.5 Hz, J = 12.1, 7.1 Hz, CH_2, 2 H), 1.68 (br, NH, 1 H), 1.39 (s, CH_3, 9 H), 1.14 (d, J = 6. Hz, CH_3, 3 H), 0.90 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 146.6, 145.9, 131.5, 128.2, 126.8, 126.6, 126.4, 126.0, 115.3, 110.8, 59.1, 57.8, 48.2, 35.5, 33.8, 29.8, 27.1, 24.4. HRMS: calcd for $C_{24}H_{36}N_2$ $[M + H]^+$ 353.2951, found 353.2968.

(4*R*)-1-[(1*S*)-1-(1-Adamantyl)ethyl]-4-*tert*-butyl-3-(2,6-diisopropylphenyl)-4,5-dihydroimidazolium Chloride (14a). This compound was prepared following the synthetic procedure described for **9a** starting from 800 mg of **13a** (1.82 mmol). **14a** was collected as a yellowish white solid (216 mg, 0.445 mmol, 24.4%). Mp: 120−140 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.82 (s, CH, 1 H), 7.47 (t, J = 7.7 Hz, Ar-H, 1 H), 7.36 (dm, J = 7.7 Hz, Ar-H, 1 H), 7.36 (dm, J = 7.7 Hz, Ar-H, 1 H), 4.48 (dd, J = 12.0, 9.6 Hz, CH, 1 H), 4.42/4.04 (t +dd, J = 12.0 Hz, J = 12.0, 9.6 Hz, CH_2, 2 H), 3.57 (q, J = 7.1 Hz, CH, 1 H), 3.28 (sp, J = 6.9 Hz, CH, 1 H), 2.99 (sp, J = 6.9 Hz, CH, 1

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H), 2.00 (br s., CH, 3 H), 1.71/1.64 (m+m, CH_2, 6 H), 1.64/1.51 (m +m, CH_2, 6 H), 1.36 (d, J = 6.8 Hz, CH_3, 3 H), 1.33 (d, J = 7.1 Hz, CH_3, 3 H), 1.30 (d, J = 6.8 Hz, CH_3, 3 H), 1.20 (d, J = 6.7 Hz, CH_3, 3 H), 1.10 (d, J = 6.7 Hz, CH_3, 3 H), 0.81 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 162.9, 160.4, 145.8, 145.6, 132.0, 130.4, 125.5, 125.2, 74.1, 63.3, 50.1, 38.1, 36.1, 36.0, 34.7, 28.4, 27.9, 27.8, 25.9, 25.7, 25.2, 23.2, 22.5, 11.5. HRMS: calcd for $C_{31}H_{49}N_2$ [M − Cl^-]$^+$ 449.3896, found 449.3874.

(4*R*)-1-[(1*R*)-1-(1-Adamantyl)ethyl]-4-*tert*-butyl-3-(2,6-diisopropylphenyl)-4,5-dihydroimidazolium Chloride (14b). This compound was prepared following the synthetic procedure described for **9a** starting from 485 mg of **13b** (1.11 mmol). **14b** was collected as a yellowish white solid (114 mg, 0.235 mmol, 21.3%). Mp: 173-175 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.89 (s, 1 H), 7.49 (t, J = 7.8 Hz, Ar-H, 1 H), 7.38 (m, Ar-H, 1 H), 7.38 (m, Ar-H, 1 H), 4.56 (t, J = 11.6 Hz, CH, 1 H), 4.44/4.04 (t+t, J = 11.6 Hz, CH, J = 11.6 Hz, CH_2, 2 H), 3.51 (q, J = 7.2 Hz, CH, 1 H), 3.20 (sp, J = 6.8 Hz, CH, 1 H), 2.99 (sp, J = 6.7 Hz, CH, 1 H), 2.02 (br s, CH, 3 H), 1.72/1.61 (m+m, CH_2, 6 H), 1.56 (m, CH_2, 6 H), 1.35 (d, J = 6.8 Hz, CH_3, 3 H), 1.33 (d, J = 7.3 Hz, CH_3, 3 H), 1.31 (d, J = 6.8 Hz, CH_3, 3 H), 1.19 (d, J = 6.8 Hz, CH_3, 3 H), 1.14 (d, J = 6.8 Hz, CH_3, 3 H), 0.83 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 162.9, 160.2, 145.8, 145.5, 131.9, 130.5, 125.5, 125.2, 73.8, 63.3, 51.8, 38.2, 37.8, 36.4, 36.2, 36.1, 34.6, 29.2, 28.7, 28.2, 28.2, 27.7, 27.5, 25.9, 25.4, 25.3, 23.1, 22.6, 21, 12.0. HRMS: calcd for $C_{31}H_{49}N_2$ [M − Cl^-]$^+$ 449.3896, found 449.3880.

(4*R*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*R*)-1,2-diphenylethyl]-4,5-dihydroimidazolium Chloride (14c). This compound was prepared following the synthetic procedure described for **9a** starting from 507 mg of **13c** (1.11 mmol). **14c** was collected as a white solid (518 mg, 1.03 mmol, 92.7%). Mp: 268−270 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.31 (s, CH, 1 H), 7.60−7.28 (m, Ar-H, 10 H), 7.46 (t, J = 7.7 Hz, Ar-H, 1 H), 7.34 (dm, J = 7.7 Hz, Ar-H, 1 H), 7.34 (dm, J = 7.7 Hz, Ar-H, 1 H), 5.48 (dd, J = 11.7, 5.3 Hz, CH, 1 H), 4.21 (m, CH, 1 H), 4.21/3.86 (m+dd, J = 10.3, 5.4 Hz, CH_2, 2 H), 3.61/3.41 (dd+dd, J = 15.1, 11.7 Hz, J = 15.1, 5.3 Hz, CH_2, 2 H), 2.79 (sp, J = 6.7 Hz, CH, 1 H), 2.65 (sp, J = 6.7 Hz, CH, 1 H), 1.25 (d, J = 6.7 Hz, CH_3, 3 H), 1.20 (d, J = 6.7 Hz, CH_3, 3 H), 1.19 (d, J = 6.7 Hz, CH_3, 3 H) 1.06 (d, J = 6.7 Hz, CH_3, 3 H), 0.56 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 159.0, 145.3, 145.0, 137.3, 136.4, 131.9, 130.4, 129.1, 129.0, 128.8, 128.7, 127.0, 127.0, 125.4, 125.3, 73.7, 62.1, 50.5, 38.1, 28.3, 27.8, 26.0, 25.2, 25.0, 23.2, 22.5. HRMS: calcd for $C_{33}H_{43}N_2$ [M − Cl^-]$^+$ 467.3426, found 467.3424.

(4*R*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*S*)-1,2-diphenylethyl]-4,5-dihydroimidazolium Chloride (14d). This compound was prepared following the synthetic procedure described for **9a** starting from 411 mg of **13d** (0.900 mmol). **14d** was collected as a white solid (437 mg, 0.868 mmol, 96.5%). Mp: 277−279 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.03 (s, CH, 1 H), 7.64−7.32 (m, Ar-H, 10 H), 7.42 (t, J = 7.8 Hz, Ar-H, 1 H), 7.30 (dm, J = 7.8 Hz, Ar-H, 1 H), 7.30 (dm, J = 7.8 Hz, Ar-H, 1 H), 5.71 (dd, J = 12.0, 4.4 Hz, CH, 1 H), 4.42 (dd, J = 12.6, 10.3 Hz, CH, 1 H), 4.05/3.80 (dd+t, J = 12.6, 10.3 Hz, J = 12.6 Hz, CH_2, 2 H), 3.75/3.41 (dd+dd, J = 14.4, 12.0 Hz, J = 14.4, 4.4 Hz, CH_2, 2 H), 2.73 (sp, J = 6.8 Hz, CH, 1 H), 2.42 (sp, J = 6.8 Hz, CH, 1 H), 1.23 (d, J = 6.8 Hz, CH_3, 3 H) 1.14 (d, J = 6.8 Hz, CH_3, 3 H), 1.05 (d, J = 6.8 Hz, CH_3, 3 H) 0.96 (d, J = 6.8 Hz, CH_3, 3 H), 0.61 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 159.4, 145.4, 145.2, 136.7, 136.0, 131.3, 130.4, 129.2, 129.1, 128.7, 127.7, 127.0, 125.3, 125.2, 73.8, 61.8, 46.5, 34.8, 28.3, 27.6, 26.1, 25.6, 25.2, 22.7, 22.2. HRMS: calcd for $C_{33}H_{43}N_2$ [M − Cl^-]$^+$ 467.3426, found 467.3422.

(4*R*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*S*)-1-phenylethyl]-4,5-dihydroimidazolium Chloride (14e). This compound was prepared following the synthetic procedure described for **9a** starting from 832 mg of **13e** (2.19 mmol). **14e** was collected as a white solid (460 mg, 1.08 mmol, 49.2%). Mp: 170−172 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.05 (s, CH, 1 H), 7.52−7.40 (m, Ar-H, 5 H), 7.48 (t, J = 7.7 Hz, Ar-H, 1 H), 7.38 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 7.35 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 5.23 (q, J = 7.0 Hz, CH, 1 H), 4.37 (dd, J = 12.1, 8.8 Hz, CH, 1 H), 4.07/3.93 (t+dd, J = 12.1 Hz, J = 12.1, 8.8 Hz, CH_2, 2 H), 3.23 (sp, J = 6.8 Hz, CH, 1 H), 2.83 (sp, J = 6.8 Hz, CH, 1 H), 1.76 (d, J = 7.0 Hz, CH_3, 3 H), 1.30 (d, J = 6.8 Hz, CH_3, 3 H), 1.29 (d, J = 6.8 Hz, CH_3, 3 H), 1.23 (d, J = 6.8 Hz, CH_3, 3 H), 1.11 (d, J = 6.8 Hz, CH_3, 3 H), 0.76 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 159.2, 145.5, 145.3, 137.7, 132.1, 130.3, 129.1, 128.8, 126.9, 125.4, 125.3, 74.1, 57, 47.8, 35.1, 28.3, 28, 26, 25.4, 25.2, 23.2, 22.6, 17.7. HRMS: calcd for $C_{27}H_{39}N_2$ [M − Cl^-]$^+$ 391.3108, found 391.3113.

(4*R*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*S*)-1-(1-naphthyl)ethyl]-4,5-dihydroimidazolium Chloride (14f). This compound was prepared following the synthetic procedure described for **9a** starting from 327 mg of **13f** (0.759 mmol). **14f** was collected as a white solid (232 mg, 0.488 mmol, 64.3%). Mp: 270−272 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.21 (s, CH, 1 H), 8.21 (d, J = 8.2 Hz, Ar-H, 1 H), 8.14−7.55 (m, Ar-H, 6 H), 7.79 (d, J = 7.0 Hz, Ar-H, 1 H), 7.48 (t, J = 7.8 Hz, Ar-H, 1 H), 7.38 (m, Ar-H, 2 H), 6.01 (q, J = 7.0 Hz, CH, 1 H), 4.42 (dd, J = 12.4, 8.7 Hz, CH, 1 H), 4.25/3.75 (t+dd, J = 12.4 Hz, J = 12.4, 8.7 Hz, CH_2, 2 H), 3.14 (sp, J = 6.8 Hz, CH, 1 H), 2.96 (sp, J = 6.8 Hz, CH, 1 H), 1.88 (d, J = 7.0 Hz, CH_3, 3 H), 1.32 (d, J = 6.8 Hz, CH_3, 3 H), 1.26 (d, J = 6.8 Hz, CH_3, 3 H), 1.25 (d, J = 6.8 Hz, CH_3, 3 H), 1.17 (d, J = 6.8 Hz, CH_3, 3 H), 0.59 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 158.8, 145.5, 145.1, 133.8, 132.9, 132.0, 130.4, 130.2, 129.5, 129.3, 127.0, 126.3, 125.6, 125.5, 125.3, 124.4, 122.3, 73.6, 53.9, 48.9, 34.9, 28.3, 27.9, 25.8, 25.3, 23.2, 22.6, 18.6. HRMS: calcd for $C_{31}H_{41}N_2$ [M − Cl^-]$^+$ 441.3264, found 441.3253.

(4*R*)-4-*tert*-Butyl-3-(2-*tert*-butylphenyl)-1-[(1*S*)-1-phenylethyl]-4,5-dihydroimidazolium Chloride (14g). This compound was prepared following the synthetic procedure described for **9a** starting from 245 mg of **13g** (0.695 mmol). **14g** was collected as a light yellow solid (70 mg, 0.175 mmol, 25.3%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.14 (s, CH, 1 H), 7.71 (dd, J = 7.9, 1.5 Hz, Ar-H, 1 H), 7.60 (dd, J = 7.9, 1.5 Hz, Ar-H, 1 H), 7.54−7.39 (m, Ar-H, 5 H), 7.49 (t, J = 7.9 Hz, Ar-H, 1 H), 7.39 (td, J = 7.9, 1.5 Hz, Ar-H, 1 H), 5.14 (q, J = 7.0 Hz, CH, 1 H), 4.53 (dd, J = 12.4, 6.8 Hz, CH, 1 H), 3.88/3.75 (t+dd, J = 12.4 Hz, J = 12.4, 6.8 Hz, CH_2, 2 H), 1.74 (d, J = 7.0 Hz, CH_3, 3 H), 1.38 (s, CH_3, 9 H), 0.70 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 158.3, 146.5, 137.6, 134.4, 131.6, 130.3, 130.1, 128.9, 128.8, 127.2, 127.1, 73.1, 57.0, 47.6, 36.0, 35.5, 31.8, 25.2, 17.9. HRMS: calcd for $C_{25}H_{35}N_2$ [M − Cl^-]$^+$ 363.2800, found 363.2784.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 2-Oxoacetate (17a). A 78.1 g portion of **15a** (500 mmol) and 166 mL of oxaldehydic acid (1500 mmol) with 25 mL of sulfuric acid (500 mmol) were stirred in 1000 mL of diisopropyl ether (DIPE) at reflux temperature for 3 days, at which point the maximum conversion (50%) was observed by GC-MS. The reaction mixture was cooled to room temperature, and it was extracted with NaCl solution. The organic layers were dried over $MgSO_4$ and filtered. No further purification was done; **17a** was collected (53.1 g, 250 mmol, 50.0%) in diisopropyl ether solution. MS (EI, 70 eV) m/z (% relative intensity, [ion]): 55 (48), 71 (100), 81 (97), 95 (90), 109 (18), 123 (46), 138 (27), 155 (1).

(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl 2-Oxoacetate (17b). This compound was prepared following the synthetic procedure described for **17a** starting from 78.1 g of **15b** (500 mmol). **17b** was collected (53.1 g, 250 mmol, 50.0%) in diisopropyl ether solution. MS (EI, 70 eV) m/z (% relative intensity, [ion]): 55 (48), 71 (100), 81 (97), 95 (90), 109 (18), 123 (46), 138 (27), 155 (1).

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 2-(2,6-Diisopropylphenyl)iminoacetate (18a). A 52 mL portion of 2,6-diisopropylaniline (250 mmol) was added to 53.1 g of **17a** (250 mmol) in 1000 mL of DIPE, and 0.5 mL of formic acid was also added. The resulting mixture was stirred at room temperature for 3 h, at which point complete conversion was observed by GC-MS. The solvent was completely removed under vacuum. The residue was purified via column chromatography using heptane and EtOAc as eluents. **18a** was collected as a yellow oil (76.4 g, 206 mmol, 82.2%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.77 (s, CH, 1 H), 7.22−7.06 (m,

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Ar-H, 3 H), 4.82 (tm, J = 10.9 Hz, CH, 1 H), 2.72 (sp, J = 6.8 Hz, CH, 2 H), 2.03/1.14 (m+m, CH_2, 2 H), 1.87 (spd, J = 7.0, 2.6 Hz, CH, 1H), 1.67/1.12 (m+m, CH_2, 2 H), 1.67/0.92 (m+m, CH_2, 2 H), 1.54 (m, CH, 1 H), 1.51 (m, CH, 1 H), 1.10 (d, J = 6.8 Hz, CH_3, 6 H), 1.09 (d, J = 6.8 Hz, CH_3, 6 H), 0.92 (d, J = 6.6 Hz, CH_3, 3 H), 0.88 (d, J = 7.0 Hz, CH_3, 3 H), 0.79 (d, J = 7.0 Hz, CH_3, 3 H), ^{13}C NMR (125 MHz, DMSO-d_6): δ 162.1, 155.9, 146.7, 135.8, 125.1, 123.1, 75.4, 46.4, 40.3, 33.6, 30.9, 27.4, 26.5, 23.7, 23.2, 23.1, 21.9, 20.2, 16.9. HRMS: calcd for $C_{24}H_{38}NO_2$ $[M + H]^+$ 372.2897, found 372.2883.

(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl 2-(2,6-Diisopropylphenyl)iminoacetate (18b). This compound was prepared following the synthetic procedure described for **18a** starting from 53.1 g of **17b** (250 mmol). **18b** was collected as a yellow oil (60.3 g, 162 mmol, 64.9%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.77 (s, CH, 1 H), 7.19−7.08 (m, Ar-H, 3 H), 4.82 (td, J = 10.8, 4.3 Hz, CH, 1 H), 2.72 (sp, J = 6.9 Hz, CH, 2 H), 2.03/1.14 (dm+m, J = 10.8 Hz, CH_2, 2 H), 1.87 (dsp, J = 7.0, 2.7 Hz, CH, 1H), 1.67/1.12 (m, CH_2, 2 H), 1.67/0.92 (m, CH_2, 2 H), 1.54 (m, CH, 1 H), 1.51 (m, CH, 1 H), 1.10 (d, J = 6.9 Hz, CH_3, 6 H), 1.09 (d, J = 6.9 Hz, CH_3, 6 H), 0.92 (d, J = 6.6 Hz, CH_3, 3 H), 0.88 (d, J = 7.0 Hz, CH_3, 3 H), 0.79 (d, J = 7.0 Hz, CH_3, 3 H), ^{13}C NMR (125 MHz, DMSO-d_6): δ 162.1, 155.9, 146.7, 135.8, 125.1, 123.0, 75.4, 46.4, 40.3, 33.6, 30.9, 27.4, 26.5, 23.2, 23.1, 21.8, 20.2, 16.9. HRMS: calcd for $C_{24}H_{38}NO_2$ $[M + H]^+$ 372.2897, found 372.2901.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl (2*E*)-2-(2-*tert*-Butylphenyl)iminoacetate (18c). This compound was prepared following the synthetic procedure described for **18a** starting from 26.5 g of **17a** (125 mmol) and 16 mL of 2-*tert*-butylaniline (100 mmol). **18c** was collected as a yellow oil (26.8 g, 78.0 mmol, 62.0%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.83 (s, CH, 1 H), 7.38 (m, Ar-H, 1 H), 7.25 (m, Ar-H, 1 H), 7.25 (m, Ar-H, 1 H), 7.02 (m, Ar-H, 1 H), 4.77 (td, J = 11.0, 4.4 Hz, CH, 1 H), 2.03/1.08 (m+m, CH_2, 2 H), 2.00 (spd, J = 7.0, 2.6 Hz, 1 H), 1.67/0.91 (m+m, CH_2, 2 H), 1.67/1.1 (m+m, CH_2, 2 H), 1.52 (m, CH, 1 H), 1.48 (m, CH, 1 H), 1.35 (s, CH_3, 9 H), 0.91 (d, J = 6.5 Hz, CH_3, 3 H), 0.88 (d, J = 7.0 Hz, CH_3, 3 H), 0.75 (d, J = 7.0 Hz, CH_3, 3 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 162.6, 149.9, 147.9, 143.5, 127.9, 127.2, 126.1, 118.9, 74.8, 46.6, 40.3, 35.2, 33.6, 30.8, 30.2, 25.7, 23.0, 21.9, 20.5, 16.3. HRMS: calcd for $C_{22}H_{34}NO_2$ $[M + H]^+$ 344.2584, found 344.2589.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl (2*S*)-2-(2,6-Diisopropylanilino)-3,3-dimethylbutanoate (19c). A solution of 55.0 g of **18a** (148 mmol) in 740 mL anhydrous THF was cooled to 0 °C under an inert atmosphere, and then 111 mL of *t*BuMgCl (222 mmol) was added dropwise over 30 min. The resulting mixture was stirred for 30 min, at which point complete conversion was observed by GC-MS. The reaction mixture was quenched by the addition of saturated aqueous NH_4Cl solution and then was warmed to room temperature and extracted with EtOAc. The combined organic layers were dried over $MgSO_4$, and the volatiles were removed under reduced pressure. The crude product was purified via column chromatography using heptane and EtOAc as eluents. The product was collected as a diastereomeric mixture. This mixture was dissolved in EtOH·HCl and the solution stirred overnight at room temperature. The product (**19c**) was recrystallized from hexane and collected as a white solid (15.5 g, 36.1 mmol, 34.8%). Mp: 90−92 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.99 (m, Ar-H, 2 H), 6.92 (dd, J = 8.3, 6.8 Hz, Ar-H, 1 H), 4.34 (td, J = 10.5, 4.7 Hz, 1 H), 3.88 (d, J = 12.8 Hz, NH, 1 H), 3.55 (d, J = 12.8 Hz, CH, 1 H), 3.31 (sp, J = 6.8 Hz, CH, 2 H), 1.73/0.84 (m+m, CH_2, 2 H), 1.54/0.74 (m+m, CH_2, 2 H), 1.43/0.82 (m+m, CH_2, 2 H), 1.34 (m, CH, 1 H), 1.16 (d, J = 6.8 Hz, CH_3, 6 H), 1.15 (d, J = 6.8 Hz, CH_3, 6 H), 1.10 (s, CH_3,9 H), 0.98 (m, CH, 1 H), 0.81 (d, J = 6.7 Hz, CH_3, 3 H), 0.59 (m, CH, 1 H), 0.49 (d, J = 6.8 Hz, CH_3, 3 H), 0.13 (d, J = 6.8 Hz, CH_3, 3 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 162.1, 155.9, 146.7, 135.8, 125.1, 123.1, 75.4, 46.4, 40.3, 33.6, 30.9, 27.4, 26.5, 23.7, 23.2, 23.1, 21.8, 20.2, 16.9. HRMS: calcd for $C_{28}H_{48}NO_2$ $[M + H]^+$ 430.3680, found 430.3670.

(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl (2*R*)-2-(2,6-Diisopropylanilino)-3,3-dimethylbutanoate (19d). This compound was prepared following the synthetic procedure described for **19c** starting from 55.0 g of **18b** (148 mmol). **19d** was collected as a yellow oil (55.0 g, 116 mmol, 86.5%). Mp: 86−88 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ 6.98 (m, Ar-H, 2 H), 6.91 (dd, J = 8.5, 6.8 Hz, Ar-H, 1 H), 4.34 (td, J = 10.9, 4.6 Hz, 1 H), 3.87 (d, J = 12.7 Hz, NH, 1 H), 3.55 (d, J = 12.5 Hz, CH, 1 H), 3.31 (sp, J = 6.8 Hz, CH, 2 H), 1.73/0.84 (m+m, CH_2, 2 H), 1.53/0.74 (m+m, CH_2, 2 H), 1.42/0.82 (m+m, CH_2, 2 H), 1.33 (m, CH, 1 H), 1.18 (d, J = 6.8 Hz, CH_3, 6 H), 1.15 (d, J = 6.8 Hz, CH_3, 6 H), 1.09 (s, CH_3,9 H), 0.97 (m, CH, 1 H), 0.81 (d, J = 6.7 Hz, CH_3, 3 H), 0.60 (m, CH, 1 H), 0.48 (d, J = 6.8 Hz, CH_3, 3 H), 0.13 (d, J = 6.8 Hz, CH_3, 3 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 172.3, 153.5, 140.2, 123.4, 122.9, 72.7, 70.1, 46.1, 40.1, 34.0, 33.5, 30.7, 26.8, 26.1, 24.5, 24.1, 23.8, 22.4, 21.9, 20.8, 15.6. HRMS: calcd for $C_{28}H_{48}NO_2$ $[M + H]^+$ 430.3680, found 430.3675.

(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 2-(2-*tert*-Butylanilino)-3,3-dimethylbutanoate (19e) and (1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl 2-(2-*tert*-Butylanilino)-3,3-dimethylbutanoate (19f). These compounds were prepared following the synthetic procedure described for **19c** starting from 26.8 g of **18c** (78.0 mmol). **19e**,**f** were collected as a diastereomer mixture (23.1 g, 57.4 mmol, 73.6%). Diastereomers (ratio 6/4) were separated via column chromatography using heptane and EtOAc as eluents.

19e was collected as a light yellow oil (15.7 g, 38.4 mmol, 83.5%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.15 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.96 (td, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.63 (td, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.60 (dm, J = 7.7 Hz, Ar-H, 1 H), 4.52 (td, J = 10.8, 4.2 Hz, CH, 1 H), 4.37 (d, J = 10.7 Hz, NH, 1 H), 3.97 (d, J = 10.7 Hz, CH, 1 H), 1.91 (spd, J = 7.0, 2.7 Hz, CH, 1 H), 1.80/0.28 (m+m, CH_2, 2 H), 1.60/0.96 (m+m, CH_2, 2 H), 1.60/0.81 (m+m, CH_2, 2 H), 1.40 (s, CH_3, 9 H), 1.39 (m, CH, 1 H), 1.35 (m, CH, 1 H), 1.08 (s, CH_3, 9 H), 0.84 (d, J = 7.0 Hz, CH_3, 3 H), 0.82 (d, J = 6.6 Hz, CH_3, 3 H), 0.54 (d, J = 7.0 Hz, CH_3, 3 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 172.5, 145.1, 133.4, 126.7, 126.0, 117.6, 111.5, 74.3, 64.3, 46.2, 40.3, 34.0, 33.7, 33.6, 30.8, 29.7, 26.7, 25.5, 22.4, 21.9, 20.6, 15.6. HRMS: calcd for $C_{26}H_{44}NO_2$ $[M + H]^+$ 402.3367, found 402.3372.

19f was collected as a light yellow oil (6.90 g, 16.9 mmol, 55.1%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.17 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 7.00 (td, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.63 (td, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.53 (dm, J = 7.7 Hz, Ar-H, 1 H), 4.50 (td, J = 10.9, 4.4 Hz, CH, 1 H), 4.35 (d, J = 10.6 Hz, NH, 1 H), 3.91 (d, J = 10.6 Hz, CH, 1 H), 1.80/0.89 (m+m, CH_2, 2 H), 1.58/0.77 (m+m, CH_2, 2 H), 1.49/0.87 (m+m, CH_2, 2 H), 1.40 (s, CH_3, 9 H), 1.39 (m, CH, 1 H), 1.13 (m, CH, 1 H), 1.09 (s, CH_3, 9 H), 1.02 (spd, J = 6.9, 2.6 Hz, CH, 1 H), 0.83 (d, J = 6.6 Hz, CH_3, 3 H), 0.52 (d, J = 6.9 Hz, CH_3, 3 H), 0.32 (d, J = 6.9 Hz, CH_3, 3 H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 171.9, 145.2, 133.0, 126.9, 126.0, 117.6, 111.3, 73.8, 65.4, 46.1, 40.6, 33.7, 33.5, 33.5, 30.8, 29.6, 26.9, 24.1, 21.9, 21.8, 20.8, 15.0. HRMS: calcd for $C_{26}H_{44}NO_2$ $[M + H]^+$ 402.3367, found 402.3372.

[(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*S*)-1-phenylethyl]imidazolidin-2-ylidene]silver(I) Chloride (20a). A 500 mg portion of **9a** (1.17 mmol) was dissolved in 6 mL of DCM, and 149 mg of Ag_2O (0.644 mmol) was added in one portion. The reaction mixture was stirred at room temperature in the dark for 1 h, at which point complete conversion was observed by NMR. The reaction mixture was filtered through a pad of Celite. The volatiles were removed under reduced pressure and then recrystallized from DCM/Et_2O. **20a** was collected as a brownish white solid (364 mg, 0.682 mmol, 58.2%). Mp: 216−218 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49−7.37 (m, Ar-H, 5 H), 7.35 (t, J = 7.7 Hz, Ar-H, 1 H), 7.22 (dd, J = 7.7, 1.0 Hz, Ar-H, 1 H), 7.17 (dd, J = 7.7, 1.0 Hz, Ar-H, 1 H), 5.57 (q, J = 7.1 Hz, CH, 1 H), 4.03 (dd, J = 11.8 Hz, J = 10.3 Hz, CH, 1 H), 3.75/3.16 (t+t, J = 11.8 Hz, J = 10.3 Hz, CH_2, 2 H), 3.44 (sp, J = 6.9 Hz, CH, 1 H), 2.76 (sp, J = 6.9 Hz, CH, 1 H), 1.78 (d, J = 7.1 Hz, CH_3, 3 H), 1.53 (d, J = 6.9 Hz, CH_3, 3 H), 1.36 (d, J = 6.9 Hz, CH_3, 3 H), 1.32 (d, J = 6.9 Hz, CH_3, 3 H), 1.23 (d, J = 6.9 Hz, CH_3, 3 H), 0.66 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.1, 146.5, 146.1, 138.2, 137.1, 129.5, 129.1, 128.5, 126.9, 125.5, 125.3, 75.7, 59.3, 46.4, 29.1, 28.3, 27.7, 26.4, 26.2, 23.8, 23.6, 17.5. HRMS: calcd for $C_{27}H_{38}AgClN_2$ $[M]^+$ 532.1774, found 532.1769.

[(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*R*)-1-phenylethyl]imidazolidin-2-ylidene]silver(I) Chloride (20b).

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This complex was prepared following the synthetic procedure described for **20a** starting from 500 mg of **9b** (1.17 mmol). **20b** was collected as a brownish white solid (410 mg, 0.768 mmol, 65.6%). Mp: 200−225 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48−7.35 (m, Ar-H, 5 H), 7.34 (t, J = 7.7 Hz, Ar-H, 1 H), 7.21 (dd, J = 7.7, 1.2 Hz, Ar-H, 1 H), 7.14 (dd, J = 7.7, 1.2 Hz, Ar-H, 1 H), 5.60 (q, J = 7.1 Hz, CH, 1 H), 3.91 (dd, J = 11.8, 10.2 Hz, CH, 1 H), 3.50/3.34 (m+t, J = 11.8 Hz, CH_2, 2 H), 3.47 (sp, J = 6.8 Hz, CH, 1 H), 2.64 (sp, J = 6.9 Hz, CH, 1 H), 1.74 (d, J = 7.1 Hz, CH_3, 3 H), 1.50 (d, J = 6.8 Hz, CH_3, 3 H), 1.32 (d, J = 6.8 Hz, CH_3, 3 H), 1.26 (d, J = 6.9 Hz, CH_3, 3 H), 1.22 (d, J = 6.9 Hz, CH_3, 3 H), 0.77 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 208.1, 146.6, 146.0, 138.3, 137.2, 129.5, 129.1, 128.6, 127.0, 125.6, 125.2, 76.1, 59.3, 46.1, 29.1, 28.2, 27.8, 26.5, 26.2, 23.7, 23.5, 17.1. HRMS: calcd for $C_{27}H_{38}AgClN_2$ $[M]^+$ 532.1774, found 532.1769.

[(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*S*)-1-(1-naphthyl)ethyl]imidazolidin-2-ylidene]silver(I) Chloride (20c). This complex was prepared following the synthetic procedure described for **20a** starting from 1.50 g of **9c** (3.14 mmol). **20c** was collected as an off-white solid (1.37 g, 2.34 mmol, 74.5%). Mp: 199−201 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32−7.49 (m, Ar-H, 7 H), 7.35 (t, J = 6.8 Hz, Ar-H, 1 H), 7.21 (dd, J = 7.7, 1.0 Hz, Ar-H, 1 H), 7.15 (dd, J = 7.7, 1.0 Hz, Ar-H, 1 H), 6.16 (q, J = 6.8 Hz, CH, 1 H), 3.96 (dd, J = 11.9, 10.4 Hz, CH, 1 H), 3.66/2.71 (t+t, J = 11.9 Hz, J = 10.4 Hz, CH_2, 2 H), 3.46 (sp, J = 6.7 Hz, CH, 1 H), 2.75 (sp, J = 6.9 Hz, CH, 1 H), 1.96 (d, J = 6.9 Hz, CH_3, 3 H), 1.61 (d, J = 6.9 Hz, CH_3, 3 H), 1.34 (d, J = 7.0 Hz, CH_3, 3 H), 1.27 (d, J = 6.9 Hz, CH_3, 3 H), 1.20 (d, J = 6.7 Hz, CH_3, 3 H), 0.40 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 208.2, 146.5, 146.1, 137.0, 134.1, 133.2, 131.4, 129.9, 129.5, 129.3, 126.8, 126.4, 125.5, 125.2, 124.6, 123.6, 75.4, 56.0, 47.1, 29.1, 28.1, 27.7, 26.3, 26.2, 23.7, 23.6, 18.6. HRMS: calcd for $C_{31}H_{40}AgClN_2$ $[M]^+$ 582.1931, found 582.1925.

[(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*R*)-1-(1-naphthyl)ethyl]imidazolidin-2-ylidene]silver(I) Chloride (20d). This complex was prepared following the synthetic procedure described for **20a** starting from 1.00 g of **9d** (2.10 mmol). **20d** was collected as an off-white solid (1.01 mg, 1.73 mmol, 82.7%). Mp: 230−252 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29−7.50 (m, Ar-H, 7 H), 7.36 (t, J = 7.7 Hz, Ar-H, 1 H), 7.23 (dd, J = 7.7, 1.1 Hz, Ar-H, 1 H), 7.15 (dd, J = 7.7, 1.0 Hz, Ar-H, 1 H), 6.19 (q, J = 6.8 Hz, CH, 1 H), 3.78 (t, J = 11.2 Hz, CH, 1 H), 3.48 (sp, J = 6.8 Hz, CH, 1 H), 3.40/2.87 (t+t, J = 11.2 Hz, J = 11.2 Hz, CH_2, 2 H), 2.59 (sp, J = 6.8 Hz, CH, 1 H), 1.94 (d, J = 6.9 Hz, CH_3, 3 H), 1.55 (d, J = 6.8 Hz, CH_3, 3 H), 1.34 (d, J = 6.8 Hz, CH_3, 3 H), 1.27 (d, J = 6.7 Hz, CH_3, 3 H), 1.15 (d, J = 6.8 Hz, CH_3, 3 H), 0.72 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 210.2, 146.6, 146.1, 137.1, 134.1, 132.8, 131.8, 129.9, 129.5, 129.2, 127.3, 126.5, 125.5, 125.3, 125.2, 124.8, 123.4, 76.0, 56.0, 46.5, 28.8, 28.2, 27.8, 26.5, 26.4, 23.7, 23.6, 19.0. HRMS: calcd for $C_{31}H_{40}AgClN_2$ $[M]^+$ 582.1931 found 582.1925.

[(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*S*)-1,2,2-trimethylpropyl]imidazolidin-2-ylidene]silver(I) Chloride (20e). This complex was prepared following the synthetic procedure described for **20a** starting from 900 mg of **9e** (2.21 mmol). **20e** was collected as a brownish white solid (677 mg, 1.32 mmol, 59.6%). Mp: 198−216 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (t, J = 7.7 Hz, Ar-H, 1 H), 7.18 (dd, J = 7.7, 1.3 Hz, Ar-H, 1 H), 7.13 (dd, J = 7.7, 1.3 Hz, Ar-H, 1 H), 4.15 (q, J = 7.0 Hz, CH, 1 H), 4.07 (dd, J = 11.9, 10.7 Hz, CH, 1 H), 3.88/3.63 (t+t, J = 11.9 Hz, J = 10.7 Hz, CH_2, 2 H), 3.41 (sp, J = 6.7 Hz, CH, 1 H), 2.69 (sp, J = 6.8 Hz, CH, 1 H), 1.43 (d, J = 6.7 Hz, CH_3, 3 H), 1.34 (d, J = 7.0 Hz, CH_3, 3 H), 1.33 (d, J = 6.8 Hz, CH_3, 3 H), 1.30 (d, J = 6.7 Hz, CH_3, 3 H), 1.18 (d, J = 6.8 Hz, CH_3, 3 H), 1.06 (s, CH_3, 9 H), 0.81 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.5, 146.8, 146.0, 137.2, 129.4, 125.4, 125.3, 76.3, 66.2, 48.5, 35.5, 34.9, 29.1, 28.2, 28.0, 27.4, 26.8, 26.2, 23.8, 23.5, 14.0. HRMS: calcd for $C_{25}H_{42}AgClN_2$ $[M]^+$ 512.2087, found 512.2082.

[(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*R*)-1,2,2-trimethylpropyl]imidazolidin-2-ylidene]silver(I) Chloride (20f). This complex was prepared following the synthetic procedure described for **20a** starting from 800 mg of **9f** (1.97 mmol). **20f** was collected as a white solid (804 mg, 1.57 mmol, 79.6%). Mp: 185−187 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (t, J = 7.8 Hz, Ar-H, 1 H), 7.18 (dd, J = 7.8, 1.3 Hz, Ar-H, 1 H), 7.13 (dd, J = 7.8, 1.3 Hz, Ar-H, 1 H), 4.18 (q, J = 7.0 Hz, CH, 1 H), 4.02 (t, J = 11.3 Hz, CH, 1 H), 3.79/3.61 (t+t, J = 11.3 Hz, J = 11.3 Hz, CH_2, 2 H), 3.40 (sp, J = 6.9 Hz, CH, 1 H), 2.78 (sp, J = 6.8 Hz, CH, 1 H), 1.45 (d, J = 6.9 Hz, CH_3, 3 H), 1.34 (d, J = 7.0 Hz, CH_3, 3 H), 1.32 (d, J = 6.9 Hz, CH_3, 3 H), 1.29 (d, J = 6.8 Hz, CH_3, 3 H), 1.16 (d, J = 6.8 Hz, CH_3, 3 H), 1.07 (s, CH_3, 9 H), 0.79 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.5, 146.6, 146.4, 137.0, 129.4, 125.5, 125.2, 75.8, 66.0, 48.1, 35.2, 34.7, 29.0, 28.1, 28.0, 27.7, 26.7, 26.2, 23.7, 23.5, 13.7. HRMS: calcd for $C_{25}H_{42}AgClN_2$ $[M]^+$ 512.2087, found 512.2082.

[(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-(2-isopropylphenyl)imidazolidin-2-ylidene]silver(I) Chloride (20g). This complex was prepared following the synthetic procedure described for **20a** starting from 500 mg of **9g** (1.14 mmol). **20g** was collected as a white solid (374 mg, 0.683 mmol, 60.2%). Mp: 200−209 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46−7.20 (m, Ar-H, 4 H), 7.36 (t, J = 7.7 Hz, Ar-H, 1 H), 7.22 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 7.18 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 4.25 (br m, CH, 1 H), 4.13/3.92 (br m+t, J = 11.2 Hz, CH_2, 2 H), 3.51 (sp, J = 6.8 Hz, CH, 1 H), 3.18 (br m, CH, 1 H), 2.93 (sp, J = 6.8 Hz, CH, 1 H), 1.46 (d, J = 6.8 Hz, CH_3, 3 H), 1.42 (d, J = 6.8 Hz, CH_3, 3 H), 1.36 (d, J = 6.8 Hz, CH_3, 3 H), 1.33 (br d, J = 6.8 Hz, CH_3, 6 H), 1.24 (d, J = 6.8 Hz, CH_3, 3 H), 0.88 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 208.0, 146.5, 145.9, 138.0, 130.0, 129.6, 128.0, 127.6, 125.6, 125.3, 56.3, 29.4, 28.4, 26.7, 26.2, 23.8, 23.6. HRMS: calcd for $C_{28}H_{40}AgClN_2$ $[M]^+$ 546.1931, found 546.1955.

[(4*S*)-4-*tert*-Butyl-1-(2-*tert*-butylphenyl)-3-(2,6-diisopropylphenyl)imidazolidin-2-ylidene]silver(I) Chloride (20h). This complex was prepared following the synthetic procedure described for **20a** starting from 200 mg of **9h** (0.440 mmol). **20h** was collected as a yellow solid (215 mg, 0.383 mmol, 87.1%). Mp: 122−124 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60−7.01 (m, Ar-H, 4 H), 7.37/7.36 (t, J = 7.7 Hz, Ar-H, 1 H), 7.23/7.21 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 7.19/7.18 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 7.08/7.06 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 4.44−3.69 (m, CH, CH_2, 3 H), 3.51/3.49 (sp, J = 6.8 Hz, CH, 1 H), 2.98/2.94 (sp, J = 6.8 Hz, CH, 1 H), 1.53/1.53 (s, CH_3, 9 H), 1.46/1.43 (d, J = 6.8 Hz, CH_3, 3 H), 1.40/1.40 (d, J = 6.8 Hz, CH_3, 3 H), 1.36/1.34 (d, J = 6.8 Hz, CH_3, 3 H), 1.20/1.20 (d, J = 6.8 Hz, CH_3, 3 H), 0.87/0.85 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 214.6, 147.0, 146.6, 146.4, 145.9, 145.6, 140.0, 131.5, 131.2, 129.7, 129.6, 129.6, 129.5, 129.3, 128.3, 128.2, 125.6, 125.3, 125.4, 125.3, 76.4, 76.3, 58.1, 58.0, 34.4, 34.3, 32.9, 32.6, 29.8, 29.5, 29.3, 28.4, 27.6, 27.2, 27.0, 26.4, 26.3, 23.9, 23.7, 23.7, 23.3. HRMS: calcd for $C_{29}H_{42}AgClN_2$ $[M]^+$ 560.2087, found 560.2247.

[(4*S*)-4-*tert*-Butyl-3-(2-*tert*-butylphenyl)-1-[(1*S*)-1-phenylethyl]imidazolidin-2-ylidene]silver(I) Chloride (20i). This complex was prepared following the synthetic procedure described for **20a** starting from 60 mg of **9i** (0.150 mmol). **20i** was collected as a yellowish white solid (64 mg, 0.127 mmol, 84.1%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (dd, J = 7.9, 1.5 Hz, Ar-H, 1 H), 7.45−7.33 (m, Ar-H, 5 H), 7.37 (dd, J = 7.9, 1.5 Hz, Ar-H, 1 H), 7.30 (td, J = 7.9, 1.5 Hz, Ar-H, 1 H), 7.21 (td, J = 7.9, 1.5 Hz, Ar-H, 1 H), 5.51 (q, J = 7.1 Hz, CH, 1 H), 4.25 (dd, J = 11.9, 6.0 Hz, CH, 1 H), 3.75/3.15 (t+dd, J = 11.9 Hz, J = 11.9, 6.0 Hz, CH_2, 2 H), 1.70 (d, J = 7.1 Hz, CH_3, 3 H), 1.43 (s, CH_3, 9 H), 0.54 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 204.9, 146.1, 140.0, 138.2, 133.0, 130.2, 129.0, 128.9, 128.6, 127.3, 127.3, 74.3, 74.3, 59.3, 46.7, 46.6, 36.4, 35.6, 32.5, 26, 17.3. HRMS: calcd for $C_{25}H_{34}AgClN_2$ $[M]^+$ 504.1461 found 504.1472.

[(4*R*)-1-[(1*S*)-1-(1-Adamantyl)ethyl]-4-*tert*-butyl-3-(2,6-diisopropylphenyl)imidazolidin-2-ylidene]silver(I) Chloride (21a). This complex was prepared following the synthetic procedure described for **20a** starting from 216 mg of **14a** (0.445 mmol). **21a** was collected as a pinkish solid (99 mg, 0.167 mmol, 37.6%). Mp: 223−234 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (t, J = 7.8 Hz, Ar-H, 1 H), 7.18 (dd, J = 7.8, 1.6 Hz, Ar-H, 1 H), 7.12 (dd, J = 7.8, 1.6 Hz, Ar-H, 1 H), 4.02 (t, J = 11.4 Hz, CH, 1 H), 3.98 (br., CH, 1 H), 3.78/3.61 (t+t, J = 11.4 Hz, J = 11.4 Hz, CH_2, 2 H), 3.42 (sp, J = 6.8 Hz,

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CH, 1 H), 2.82 (sp, J = 6.8 Hz, CH, 1 H), 2.04 (br., CH, 3 H), 1.75/1.66 (brd+brd, CH_2, 6 H), 1.67 (br., CH_2, 6 H), 1.44 (d, J = 6.8 Hz, CH_3, 3 H), 1.35 (d, J = 6.8 Hz, CH_3, 3 H), 1.29 (d, J = 6.8 Hz, CH_3, 3 H), 1.29 (brd, CH_3, 3 H), 1.17 (d, J = 6.8 Hz, CH_3, 3 H), 0.79 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 210.9, 146.7, 146.5, 129.4, 125.5, 125.2, 75.8, 66.5, 40.1, 36.9, 34.6, 29.1, 28.5, 28.1, 27.7, 26.8, 26.2, 23.7, 23.5. HRMS: calcd for $C_{31}H_{48}AgClN_2$ $[M]^+$ 590.2557, found 509.2880.

[(4*R*)-1-[(1*R*)-1-(1-Adamantyl)ethyl]-4-*tert*-butyl-3-(2,6-diisopropylphenyl)imidazolidin-2-ylidene]silver(I) Chloride (21b). This complex was prepared following the synthetic procedure described for **20a** starting from 114 mg of **14b** (0.235 mmol). **21b** was collected as a brown solid (118 mg, 0.199 mmol, 84.8%). Mp: 110−120 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (t, J = 7.8 Hz, Ar-H, 1 H), 7.18 (dd, J = 7.8, 1.6 Hz, Ar-H, 1 H), 7.13 (dd, J = 7.8, 1.6 Hz, Ar-H, 1 H), 4.05 (dd, J = 11.9, 10.5 Hz, CH, 1 H), 3.95 (br., CH, 1 H), 3.89/3.66 (t+t, J = 11.9 Hz, J = 10.5 Hz, CH_2, 2 H), 3.43 (sp, J = 6.8 Hz, CH, 1 H), 2.68 (sp, J = 6.8 Hz, CH, 1 H), 2.06 (br., CH, 3 H), 1.75/1.66 (brd+brd., CH_2, 6 H), 1.69/1.62 (br d+br d., CH_2, 6 H), 1.44 (d, J = 6.8 Hz, CH_3, 3 H), 1.33 (d, J = 6.9 Hz, CH_3, 3 H), 1.31 (d, J = 6.8 Hz, CH_3, 3 H), 1.31 (d, J = 6.8 Hz, CH_3, 3 H), 1.18 (d, J = 6.8 Hz, CH_3, 3 H), 0.82 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 210.7, 146.8, 146.0, 137.4, 129.4, 125.4, 125.2, 76.3, 66.9, 49.2, 40.1, 36.9, 32.0, 29.1, 28.5, 28.4, 28.4, 28.2, 26.9, 26.2, 23.8, 23.5, 22.8, 14.3. HRMS: calcd for $C_{31}H_{48}AgClN_2$ $[M]^+$ 590.2557, found 509. 3245.

[(4*R*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*R*)-1,2-diphenylethyl]imidazolidin-2-ylidene]silver(I) Chloride (21c). This complex was prepared following the synthetic procedure described for **20a** starting from 200 mg of **14c** (0.440 mmol). **21c** was collected as a white solid (215 mg, 0.383 mmol, 87.1%). Mp: 200−218 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53−7.25 (m, Ar-H, 10 H), 7.26 (t, J = 7.7 Hz, Ar-H, 1 H), 7.12 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 7.03 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 5.75 (dd, J = 11.8, 4.6 Hz, CH, 1 H), 3.83 (dd, J = 11.7, 10.3 Hz, CH, 1 H), 3.72/3.17 (t+t, J = 11.7 Hz, J = 10.3 Hz, CH_2, 2 H), 3.52/3.40 (dd+dd, J = 14.3, 4.6 Hz, J = 14.3, 11.8 Hz, CH_2, 2 H), 3.30 (sp, J = 6.8 Hz, CH, 1 H), 2.15 (sp, J = 6.8 Hz, CH, 1 H), 1.44 (d, J = 6.9 Hz, CH_3, 3 H), 1.25 (d, J = 6.7 Hz, CH_3, 3 H), 1.18 (d, J = 6.9 Hz, CH_3, 3 H), 0.85 (d, J = 6.7 Hz, CH_3, 3 H), 0.56 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 209.9, 146.4, 146.1, 137.6, 136.7, 129.3, 129.2, 129.0, 128.8, 127.5, 127.1, 125.3, 125.2, 75.2, 64.8, 46.9, 36.6, 34.7, 28.7, 28.2, 26.6, 26.4, 23.8, 23.5. HRMS: calcd for $C_{33}H_{42}AgClN_2$ $[M]^+$ 608.2087, found 608.2330.

[(4*R*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*S*)-1,2-diphenylethyl]imidazolidin-2-ylidene]silver(I) Chloride (21d). This complex was prepared following the synthetic procedure described for **20a** starting from 143 mg of **14d** (0.284 mmol). **21d** was collected as an off-white solid (94 mg, 0.154 mmol, 54.2%). Mp: 220−231 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56−7.29 (m, Ar-H, 10 H), 7.26 (t, J = 7.7 Hz, Ar-H, 1 H), 7.09 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 7.06 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 5.78 (dd, J = 12.1, 4.1 Hz, CH, 1 H), 3.90 (t, J = 11.5 Hz, CH, 1 H), 3.51/3.34 (dd+dd, J = 14.3, 4.1 Hz, J = 14.3, 12.1 Hz, CH_2, 2 H), 3.45/3.30 (t+t, J = 11.5 Hz, J = 11.5 Hz, CH_2, 2 H), 2.73 (sp, J = 6.8 Hz, CH, 1 H), 2.59 (sp, J = 6.8 Hz, CH, 1 H), 1.23 (d, J = 6.8 Hz, CH_3, 3 H), 1.18 (d, J = 6.8 Hz, CH_3, 3 H), 1.17 (d, J = 6.8 Hz, CH_3, 3 H), 1.16 (d, J = 6.8 Hz, CH_3, 3 H), 0.65 (s, CH_3, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 209.4, 146.7, 145.9, 137.6, 136.5, 129.6, 129.4, 129.3, 129.2, 128.8, 127.4, 127.3, 125.4, 125.0, 76.0, 65.1, 46.2, 36.1, 29.0, 27.8, 27.6, 26.9, 26.2, 23.5, 23.5. HRMS: calcd for $C_{33}H_{42}AgClN_2$ $[M]^+$ 608.2087, found 608.2404.

[(4*R*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*S*)-1-phenylethyl]imidazolidin-2-ylidene]silver(I) Chloride (21e). This complex was prepared following the synthetic procedure described for **20a** starting from 300 mg **14e** (0.702 mmol). **21e** was collected as an off-white solid (250 mg, 0.468 mmol, 66.8%). Mp: 220−222 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49−7.37 (m, Ar-H, 5 H), 7.35 (t, J = 7.8 Hz, Ar-H, 1 H), 7.22 (dd, J = 7.8, 1.1 Hz, Ar-H, 1 H), 7.15 (dd, J = 7.8, 1.1 Hz, Ar-H, 1 H), 5.62 (q, J = 7.1 Hz, CH, 1 H), 3.92 (dd, J = 11.9 Hz, J = 9.9 Hz, CH, 1 H), 3.52/3.36 (m+t, J = 11.9 Hz, CH_2, 2 H), 3.48 (sp, J = 6.8 Hz, CH, 1 H), 2.66 (sp, J = 6.8 Hz, CH, 1 H), 1.76 (d, J = 7.1 Hz, CH_3, 3 H), 1.52 (d, J = 6.8 Hz, CH_3, 3 H), 1.33 (d, J = 6.8 Hz, CH_3, 3 H), 1.28 (d, J = 6.8 Hz, CH_3, 3 H), 1.23 (d, J = 6.8 Hz, CH_3, 3 H), 0.79 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 207.1, 146.6, 146.0, 138.3, 137.2, 129.5, 129.1, 128.6, 127.0, 125.6, 125.2, 76.2, 59.3, 46.1, 29.1, 28.2, 27.8, 26.5, 26.2, 23.7, 23.5, 17.1. HRMS: calcd for $C_{27}H_{38}AgClN_2$ $[M]^+$ 532.1774, found 532.1769.

[(4*R*)-4-*tert*-Butyl-3-(2-*tert*-butylphenyl)-1-[(1*S*)-1-phenylethyl]imidazolidin-2-ylidene]silver(I) Chloride (21g). This complex was prepared following the synthetic procedure described for **20a** starting from 70 mg of **14g** (0.175 mmol). **21g** was collected as a yellowish white solid (60 mg, 0.119 mmol, 67.6%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50 (dd, J = 7.9, 1.5 Hz, Ar-H, 1 H), 7.42−7.32 (m, Ar-H, 5 H), 7.39 (dd, J = 7.9, 1.5 Hz, Ar-H, 1 H), 7.30 (td, J = 7.9, 1.5 Hz, Ar-H, 1 H), 7.22 (td, J = 7.9, 1.5 Hz, Ar-H, 1 H), 5.55 (q, J = 7.1 Hz, CH, 1 H), 4.19 (dd, J = 11.9, 5.7 Hz, CH, 1 H), 3.47/3.31 (m+t, J = 11.9 Hz, CH_2, 2 H), 1.73 (d, J = 7.1 Hz, CH_3, 3 H), 1.37 (s, CH_3, 9 H), 0.73 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.7, 146.1, 140.0, 138.1, 132.9, 130.1, 129.0, 128.9, 128.5, 127.4, 127.1, 74.2, 74.1, 59.2, 46.6, 46.6, 36.4, 35.9, 32.5, 26.1, 17.2. HRMS: calcd for $C_{25}H_{34}AgClN_2$ $[M]^+$ 504.1461 found 504.1473.

[(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*S*)-1-phenylethyl]imidazolidin-2-ylidene]gold(I) Chloride (22a). A 260 mg portion of **20a** (0.487 mmol) was dissolved in 2.5 mL of DCM, and 143 mg of Me_2SAuCl (0.487 mmol) was added in one portion. The reaction mixture was stirred at room temperature in the dark for 30 min, at which point complete conversion was observed by NMR. The reaction mixture was filtered through a pad of Celite. The volatiles were removed under reduced pressure, and the residue was then recrystallized from DCM/Et_2O. **22a** was collected as a purplish solid (259 mg, 0.416 mmol, 85.4%). Mp: 262−264 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48−7.34 (m, Ar-H, 5 H), 7.34 (t, J = 7.7 Hz, Ar-H, 1 H), 7.19 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 7.14 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.10 (q, J = 7.0 Hz, CH, 1 H), 3.93 (dd, J = 11.7 Hz, J = 10.5 Hz, CH, 1 H), 3.71/3.08 (t+t, J = 11.7 Hz, J = 10.5 Hz, CH_2, 2 H), 3.40 (sp, J = 6.8 Hz, CH, 1 H), 2.71 (sp, J = 6.8 Hz, CH, 1 H), 1.75 (d, J = 7.0 Hz, CH_3, 3 H), 1.60 (d, J = 6.8 Hz, CH_3, 3 H), 1.34 (d, J = 6.8 Hz, CH_3, 3 H), 1.30 (d, J = 6.8 Hz, CH_3, 3 H), 1.29 (d, J = 6.8 Hz, CH_3, 3 H), 0.64 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.6, 147.0, 146.0, 137.9, 136.7, 129.5, 129.0, 128.5, 127.1, 125.4, 125.2, 75.3, 58.2, 45.5, 34.8, 29.2, 28.4, 27.3, 26.3, 26.1, 23.9, 23.7, 16.6. HRMS: calcd for $C_{27}H_{38}AuClN_2$ $[M]^+$ 622.2389, found 622.2393.

[(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*R*)-1-phenylethyl]imidazolidin-2-ylidene]gold(I) Chloride (22b). This complex was prepared following the synthetic procedure described for **22a** starting from 260 mg of **20b** (0.487 mmol). **22b** was collected as a brownish white solid (250 mg, 0.401 mmol, 82.4%). Mp: 238−240 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52−7.36 (m, Ar-H, 5 H), 7.34 (t, J = 7.7 Hz, Ar-H, 1 H), 7.20 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 7.13 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.15 (q, J = 7.1 Hz, CH, 1 H), 3.81 (dd, J = 11.8, 10.3 Hz, CH, 1 H), 3.48/3.30 (t+t, J = 10.3 Hz, J = 11.8 Hz, CH_2, 2 H), 3.46 (sp, J = 6.8 Hz, CH, 1 H), 2.60 (sp, J = 6.8 Hz, CH, 1 H), 1.73 (d, J = 7.1 Hz, CH_3, 3 H), 1.58 (d, J = 6.8 Hz, CH_3, 3 H), 1.32 (d, J = 6.8 Hz, CH_3, 3 H), 1.30 (d, J = 6.8 Hz, CH_3, 3 H), 1.25 (d, J = 6.8 Hz, CH_3, 3 H), 0.78 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.4, 147.0, 145.9, 138.2, 137.0, 129.5, 129.0, 128.5, 127.1, 125.5, 125.2, 75.7, 58.0, 45.4, 34.9, 29.2, 28.4, 27.3, 26.5, 26.0, 23.8, 23.6, 16.2. HRMS: calcd for $C_{27}H_{38}AuClN_2$ $[M]^+$ 622.2389, found 622.2399.

[(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*S*)-1-(1-naphthyl)ethyl]imidazolidin-2-ylidene]gold(I) Chloride (22c). This complex was prepared following the synthetic procedure described for **22a** starting from 260 mg of **20c** (0.445 mmol). **22c** was collected as an off-white solid solid (152 mg, 0.226 mmol, 50.7%). Mp: 246−250 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50−7.48 (m, Ar-H, 7 H), 7.35 (t, J = 7.8 Hz, Ar-H, 1 H), 7.20 (dd, J = 7.8,

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1.5 Hz, Ar-H, 1 H), 7.14 (dd, J = 7.8, 1.5 Hz, Ar-H, 1 H), 6.62 (q, J = 6.8 Hz, CH, 1 H), 3.85 (dd, J = 11.9, 10.2 Hz, CH, 1 H), 3.53/2.48 (t +dd, J = 11.9 Hz, J = 11.9, 10.2 Hz, CH_2, 2 H), 3.42 (sp, J = 6.8 Hz, CH, 1 H), 2.73 (sp, J = 6.8 Hz, CH, 1 H), 1.94 (d, J = 6.8 Hz, CH_3, 3 H), 1.71 (d, J = 6.8 Hz, CH_3, 3 H), 1.33 (d, J = 6.8 Hz, CH_3, 3 H), 1.32 (d, J = 6.8 Hz, CH_3, 3 H), 1.25 (d, J = 6.8 Hz, CH_3, 3 H), 0.35 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.3, 147.0, 146.0, 136.6, 134.0, 133.1, 131.7, 129.8, 129.5, 129.1, 126.9, 126.5, 125.4, 125.1, 125.0, 124.6, 124.0, 74.9, 55.3, 46.1, 29.3, 28.3, 27.3, 26.1, 26.1, 23.8, 23.7, 17.7. HRMS: calcd for $C_{31}H_{40}AuClN_2$ $[M]^+$ 672.2546, found 672.3098.

[(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*R*)-1-(1-naphthyl)ethyl]imidazolidin-2-ylidene]gold(I) Chloride (22d). This complex was prepared following the synthetic procedure described for **22a** starting from 50 mg of **20d** (0.942 mmol). **22d** was collected as an off-white solid (592 mg, 0.880 mmol, 93.4%). Mp: 296−298 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.47−7.49 (m, Ar-H, 7 H), 7.35 (t, J = 7.7 Hz, Ar-H, 1 H), 7.21 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 7.12 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 6.62 (q, J = 6.8 Hz, CH, 1 H), 3.67 (t, J = 11.3 Hz, CH, 1 H), 3.46 (sp, J = 6.7 Hz, CH, 1 H), 3.33/2.78 (t+t, J = 11.3 Hz, 11.3 Hz, CH_2, 2 H), 2.55 (sp, J = 6.8 Hz, CH, 1 H), 1.92 (d, J = 6.8 Hz, CH_3, 3 H), 1.61 (d, J = 6.7 Hz, CH_3, 3 H), 1.35 (d, J = 6.8 Hz, CH_3, 3 H), 1.32 (d, J = 6.8 Hz, CH_3, 3 H), 1.11 (d, J = 6.7 Hz, CH_3, 3 H), 0.70 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.4, 147.1, 146.0, 134.1, 132.9, 132.0, 127.3, 126.6, 125.4, 125.2, 125.1, 124.9, 123.8, 75.4, 55.2, 45.8, 28.8, 28.4, 27.3, 26.5, 26.3, 23.8, 23.7, 18.0. HRMS: calcd for $C_{31}H_{40}AuClN_2$ $[M]^+$ 672.2546, found 672.2554.

[(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*S*)-1,2,2-trimethylpropyl]imidazolidin-2-ylidene]gold(I) Chloride (22e). This complex was prepared following the synthetic procedure described for **22a** starting from 400 mg of **20e** (0.7784 mmol). **22e** was collected as a purplish white solid (427 mg, 0.708 mmol, 91.0%). Mp: 232−234 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (t, J = 7.7 Hz, Ar-H, 1 H), 7.17 (dd, J = 7.7 Hz, J = 1.5 Hz, Ar-H, 1 H), 7.12 (dd, J = 7.7 Hz, J = 1.5 Hz, Ar-H, 1 H), 4.73 (q, J = 7.1 Hz, CH, 1 H), 3.99 (dd, J = 11.9, 10.8 Hz, CH, 1 H), 3.86/3.61 (t+t, J = 11.9 Hz, J = 10.8 Hz, CH_2, 2 H), 3.38 (sp, J = 6.8 Hz, CH, 1 H), 2.65 (sp, J = 6.8 Hz, CH, 1 H), 1.53 (d, J = 6.8 Hz, CH_3, 3 H), 1.33 (d, J = 6.8 Hz, CH_3, 3 H), 1.33 (d, J = 7.1 Hz, CH_3, 3 H), 1.30 (d, J = 6.8 Hz, CH_3, 3 H), 1.26 (d, J = 6.8 Hz, CH_3, 3 H), 1.08 (s, CH_3, 9 H), 0.81 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.5, 147.2, 145.8, 136.9, 129.4, 125.3, 125.2, 75.9, 64.7, 47.8, 35.3, 29.2, 28.4, 28.0, 27.0, 26.7, 26.0, 23.9, 23.6, 13.5. HRMS: calcd for $C_{25}H_{42}AuClN_2$ $[M]^+$ 602.2702, found 602.2697.

[(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*R*)-1,2,2-trimethylpropyl]imidazolidin-2-ylidene]gold(I) Chloride (22f). This complex was prepared following the synthetic procedure described for **22a** starting from 430 mg of **20f** (0.837 mmol). **22f** was collected as an off-white white solid (395 mg, 0.655 mmol, 78.3%). Mp: 230−232 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (t, J = 7.7 Hz, Ar-H, 1 H), 7.18 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 7.12 (dd, J = 7.7 Hz, J = 1.5 Hz, Ar-H, 1 H), 4.75 (q, J = 7.0 Hz, CH, 1 H), 3.95 (t, J = 11.3 Hz, CH, 1 H), 3.78/3.59 (t+t, J = 11.3 Hz, J = 11.3 Hz, CH_2, 2 H), 3.40 (sp, J = 6.7 Hz, CH, 1 H), 2.75 (sp, J = 6.8 Hz, CH, 1 H), 1.53 (d, J = 6.8 Hz, CH_3, 3 H), 1.34 (d, J = 6.8 Hz, CH_3, 3 H), 1.31 (d, J = 7.0 Hz, CH_3, 3 H), 1.29 (d, J = 6.7 Hz, CH_3, 3 H), 1.23 (d, J = 6.7 Hz, CH_3, 3 H), 1.09 (s, CH_3, 9 H), 0.80 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.5, 147.1, 146.3, 136.7, 129.5, 125.4, 125.1, 75.3, 64.6, 47.6, 35.1, 29.1, 28.3, 28.0, 27.2, 26.6, 25.9, 23.8, 23.6, 13.2. HRMS: calcd for $C_{25}H_{42}AuClN_2$ $[M]^+$ 602.2702 found 602.2696.

[(4*S*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-(2-isopropylphenyl)imidazolidin-2-ylidene]gold(I) Chloride (22g). This complex was prepared following the synthetic procedure described for **22a** starting from 364 mg of **20g** (0.664 mmol). **22g** was collected as a white solid (250 mg, 0.393 mmol, 59.1%). Mp: 211−213 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46−7.14 (m, Ar-H, 7 H), 4.23/4.17 (m, CH, 1 H), 4.17/3.89 + 4.08/3.89 (m+m, CH_2, 2 H), 3.58−2.84 (sp, J = 6.8 Hz, CH, 3 H), 1.61−1.26 (d, J = 6.8 Hz, CH_3,18 H), 0.88/0.87 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.8, 147.0, 146.0, 145.8, 145.7, 137.5, 136.5, 130.0, 129.9, 129.7, 129.6, 128.2, 128.0, 127.5, 127.4, 127.4, 125.6, 125.4, 125.3, 125.2, 76.1, 75.8, 56.1, 56.0, 34.8, 29.6, 29.4, 28.6, 28.5, 28.5, 28.4, 27.2, 27.0, 26.6, 24.5, 24.4, 24.1, 23.9, 23.7, 23.6. HRMS: calcd for $C_{28}H_{40}AuClN_2$ $[M]^+$ 636.2546 found 636.2806.

[(4*S*)-4-*tert*-Butyl-1-(2-*tert*-butylphenyl)-3-(2,6-diisopropylphenyl)imidazolidin-2-ylidene]gold(I) Chloride (22h). This complex was prepared following the synthetic procedure described for **22a** starting from 215 mg of **20h** (0.383 mmol). **22h** was collected as a yellowish white solid (35 mg, 0.054 mmol, 14.1%). Mp: 104−125 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60−7.08 (m, Ar-H, 7 H), 4.20 (m, CH, 1 H), 4.20/3.73 (m+m, CH_2, 2 H), 3.48 (sp, J = 6.8 Hz, CH, 1 H), 2.96 (sp, J = 6.8 Hz, CH, 1 H), 1.55 (s, CH_3, 9 H), 1.55/1.36 (d+d, J = 6.8 Hz, J = 6.8 Hz, CH_3, 6 H), 1.39/1.27 (d +d, J = 6.8 Hz, J = 6.8 Hz, CH_3, 6 H), 0.87/0.85 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.0, 147.1, 146.9, 145.7, 139.4, 136.1, 131.3, 129.7, 129.5, 129.4, 128.1, 125.5, 125.2, 75.6, 57.9, 34.3, 32.9, 32.6, 29.7, 29.3, 28.5, 27.2, 26.9, 26.2, 23.8, 23.8. HRMS: calcd for $C_{29}H_{42}AuClN_2$ $[M]^+$ 650.2702 found 650.2679.

[(4*S*)-4-*tert*-Butyl-3-(2-*tert*-butylphenyl)-1-[(1*S*)-1-phenylethyl]imidazolidin-2-ylidene]gold(I) Chloride (22i). This complex was prepared following the synthetic procedure described for **22a** starting from 60 mg of **20i** (0.119 mmol). **22i** was collected as a yellowish white solid (28 mg, 0.047 mmol, 39.7%). Mp: 238−240 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51−7.32 (m, Ar- H, 5 H), 7.50 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 7.47 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 7.30 (td, J = 7.7, 1.5 Hz, Ar-H, 1 H), 7.20 (td, J = 7.7, 1.5 Hz, Ar-H, 1 H), 6.07 (q, J = 7.0 Hz, CH, 1 H), 4.25 (dd, J = 11.8, 6.1 Hz, CH, 1 H), 3.73/3.09 (t+dd, J = 11.8 Hz, J = 11.8, 6.1 Hz, CH_2, 2 H), 1.69 (d, J = 7.0 Hz, CH_3, 3 H), 1.45 (s, CH_3, 9 H), 0.53 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.8, 146.2, 139, 137.9, 133.9, 130.1, 128.9, 128.6, 127.4, 126.9, 73.7, 58.1, 45.7, 36.5, 35.5, 32.5, 25.9, 16.4. HRMS: calcd for $C_{25}H_{34}AuClN_2$ $[M]^+$ 594.2076 found 594.2113.

[(4*R*)-1-[(1*S*)-1-(1-Adamantyl)ethyl]-4-*tert*-butyl-3-(2,6-diisopropylphenyl)imidazolidin-2-ylidene]gold(I) Chloride (23a). This complex was prepared following the synthetic procedure described for **22a** starting from 90 mg of **21a** (0.152 mmol). **23a** was collected as an off-white solid (55 mg, 0.081 mmol, 53.1%). Mp: 260−262 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 (t, J = 7.7 Hz, Ar-H, 1 H), 7.18 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 7.12 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 4.55 (q, J = 7.1 Hz, CH, 1 H), 3.95 (t, J = 11.5 Hz, CH, 1 H), 3.77/3.58 (t+t, J = 11.5 Hz, J = 11.5 Hz, CH_2, 2 H), 3.42 (sp, J = 6.8 Hz, CH, 1 H), 2.80 (sp, J = 6.8 Hz, CH, 1 H), 2.05 (br t, CH, 3 H), 1.77/1.66 (br d+br d., CH_2, 6 H), 1.75/1.66 (br d+br d, CH_2, 6 H), 1.53 (d, J = 6.8 Hz, CH_3, 3 H), 1.34 (d, J = 6.8 Hz, CH_3, 3 H), 1.29 (d, J = 6.8 Hz, CH_3, 3 H), 1.27 (d, J = 7.1 Hz, CH_3, 3 H), 1.24 (d, J = 6.8 Hz, CH_3, 3 H), 0.80 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.5, 147.1, 146.3, 136.7, 129.5, 125.4, 125.1, 75.2, 65.1, 48.6, 40.1, 37.0, 34.4, 29.2, 28.6, 28.3, 27.1, 26.7, 26.0, 23.8, 23.6, 11.8. HRMS: calcd for $C_{31}H_{48}AuClN_2$ $[M]^+$ 680.3172, found 680.3844.

[(4*R*)-1-[(1*R*)-1-(1-Adamantyl)ethyl]-4-*tert*-butyl-3-(2,6-diisopropylphenyl)imidazolidin-2-ylidene]gold(I) Chloride (23b). This complex was prepared following the synthetic procedure described for **22a** starting from 110 mg of **21b** (0.186 mmol). **23b** was collected as a purple solid (84 mg, 0.123 mmol, 66.4%). Mp: 103−118 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (t, J = 7.7 Hz, Ar-H, 1 H), 7.17 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 7.12 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 4.56 (q, J = 6.9 Hz, CH, 1 H), 3.98 (dd, J = 11.8, 10.6 Hz, CH, 1 H), 3.87/3.36 (t+t, J = 11.8 Hz, J = 10.6 Hz, CH_2, 2 H), 3.42 (sp, J = 6.8 Hz, CH, 1 H), 2.67 (sp, J = 6.9 Hz, CH, 1 H), 2.12−1.98 (m, CH, 3 H), 1.85−1.21 (m, CH_2, 12 H), 1.53 (d, J = 6.8 Hz, CH_3, 3 H), 1.32 (d, J = 6.9 Hz, CH_3, 3 H), 1.31 (d, J = 6.9 Hz, CH_3, 3 H), 1.28 (br d, CH_3, 3 H), 1.25 (d, J = 6.8 Hz, CH_3, 3 H), 0.84 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.4, 147.2, 145.8, 137.1, 129.4, 125.3, 125.2, 76.0, 65.5, 48.6, 40.0, 36.9, 31.7, 30.7, 29.2, 28.6, 27.0, 26.8, 26.0, 23.9, 23.6, 22.8, 14.3, 12.1. HRMS: calcd for $C_{31}H_{48}AuClN_2$ $[M]^+$ 680.3172, found 680.3184.

[(4*R*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*R*)-1,2-diphenylethyl]imidazolidin-2-ylidene]gold(I) Chloride (23c).

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This complex was prepared following the synthetic procedure described for **22a** starting from 37 mg of **21c** (0.061 mmol). **23c** was collected as a purple solid (40 mg, 0.057 mmol, 94.3%). Mp: 239−241 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63−7.27 (m, Ar-H, 10 H), 7.27 (t, J = 7.7 Hz, Ar-H, 1 H), 7.12 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 7.02 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.34 (dd, J = 11.8, 4.9 Hz, CH, 1 H), 3.69/3.15 (m+m, CH_2, 2 H), 3.69 (m, CH, 1 H), 3.54/3.39 (dd+dd, J = 14.5, 4.9 Hz, J = 14.5, 11.8 Hz, CH_2, 2 H), 3.28 (sp, J = 6.8 Hz, CH, 1 H), 2.02 (sp, J = 6.8 Hz, CH, 1 H), 1.53 (d, J = 6.8 Hz, CH_3, 3 H), 1.24 (d, J = 6.8 Hz, CH_3, 3 H), 1.14 (d, J = 6.8 Hz, CH_3, 3 H), 0.90 (d, J = 6.8 Hz, CH_3, 3 H), 0.59 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.4, 146.9, 146.2, 137.3, 136.4, 136.2, 129.4, 129.2, 129.1, 129.1, 128.7, 127.3, 127.2, 125.2, 125.1, 75.0, 63.0, 45.9, 36.1, 34.4, 28.7, 28.3, 27.3, 26.4, 23.8, 23.6. HRMS: calcd for $C_{33}H_{42}AuClN_2$ $[M]^+$ 698.2702 found 698.3581.

[(4*R*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*S*)-1,2-diphenylethyl]imidazolidin-2-ylidene]gold(I) Chloride (23d). This complex was prepared following the synthetic procedure described for **22a** starting from 83 mg of **21d** (0.136 mmol). **23d** was collected as a purple solid (75 mg, 0.107 mmol, 78.8%). Mp: 230−232 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60−7.28 (m, Ar-H, 10 H), 7.28 (t, J = 7.7 Hz, Ar-H, 1 H), 7.09 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 7.06 (dd, J = 7.7, 1.5 Hz, Ar-H, 1 H), 6.40 (dd, J = 11.9, 4.7 Hz, CH, 1 H), 3.82 (t, J = 11.9 Hz, CH, 1 H), 3.56/3.34 (dd+dd, J = 14.4, 4.7 Hz, J = 14.4, 11.9 Hz, CH_2, 2 H), 3.41/3.33 (t+m, J = 11.9 Hz, CH_2, 2 H), 2.76 (sp, J = 6.8 Hz, CH, 1 H), 2.56 (sp, J = 6.8 Hz, CH, 1 H), 1.33 (d, J = 6.8 Hz, CH_3, 3 H), 1.26 (d, J = 6.8 Hz, CH_3, 3 H), 1.22 (d, J = 6.8 Hz, CH_3, 3 H), 1.16 (d, J = 6.8 Hz, CH_3, 3 H), 0.61 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.4, 147.1, 145.8, 137.6, 136.2, 136.0, 129.8, 129.5, 129.2, 128.9, 128.7, 127.3, 127.3, 125.2, 125.0, 75.4, 62.7, 45.6, 35.7, 34.3, 29.1, 27.8, 27.3, 26.7, 26.0, 23.7, 23.6. HRMS: calcd for $C_{33}H_{42}AuClN_2$ $[M]^+$ 698.2702 found 698.2736.

[(4*R*)-4-*tert*-Butyl-3-(2,6-diisopropylphenyl)-1-[(1*S*)-1-phenylethyl]imidazolidin-2-ylidene]gold(I) Chloride (23e). This complex was prepared following the synthetic procedure described for **22a** starting from 200 mg of **21e** (0.395 mmol). **23e** was collected as a yellowish white solid (210 mg, 0.337 mmol, 85.7%). Mp: 245−247 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52−7.36 (m, Ar-H, 5 H), 7.34 (t, J = 7.7 Hz, Ar-H, 1 H), 7.20 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 7.13 (dd, J = 7.7, 1.4 Hz, Ar-H, 1 H), 6.14 (q, J = 7.0 Hz, CH, 1 H), 3.81 (dd, J = 11.8, 10.3 Hz, CH, 1 H), 3.48/3.30 (t+t, J = 10.3 Hz, J = 11.8 Hz, CH_2, 2 H), 3.46 (sp, J = 6.8 Hz, CH, 1 H), 2.60 (sp, J = 6.8 Hz, CH, 1 H), 1.73 (d, J = 7.0 Hz, CH_3, 3 H), 1.58 (d, J = 6.8 Hz, CH_3, 3 H), 1.32 (d, J = 6.8 Hz, CH_3, 3 H), 1.30 (d, J = 6.8 Hz, CH_3, 3 H), 1.25 (d, J = 6.8 Hz, CH_3, 3 H), 0.78 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.4, 147.0, 145.9, 138.2, 137.0, 129.5, 129.0, 128.5, 127.1, 125.5, 125.2, 75.7, 58.0, 45.4, 34.9, 29.2, 28.4, 27.3, 26.5, 26.0, 23.8, 23.6, 16.2. HRMS: calcd for $C_{27}H_{38}AuClN_2$ $[M]^+$ 622.2389, found 622.2390.

[(4*R*)-4-*tert*-Butyl-3-(2-*tert*-butylphenyl)-1-[(1*S*)-1-phenylethyl]imidazolidin-2-ylidene]gold(I) Chloride (23g). This complex was prepared following the synthetic procedure described for **22a** starting from 60 mg of **21g** (0.119 mmol). **23g** was collected as a brownish white solid (62 mg, 0.104 mmol, 87.9%). Mp: 191−198 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46−7.31 (m, Ar-H, 5 H), 7.50 (dd, J = 7.8, 1.5 Hz, Ar-H, 1 H), 7.48 (dd, J = 7.8, 1.5 Hz, Ar-H, 1 H), 7.30 (td, J = 7.8, 1.5 Hz, Ar-H, 1 H), 7.21 (td, J = 7.8, 1.5 Hz, Ar-H, 1 H), 6.10 (q, J = 7.1 Hz, CH, 1 H), 4.10 (dd, J = 11.9, 6.0 Hz, CH, 1 H), 3.43/3.26 (dd+t, J = 11.9, 6.0 Hz, J = 11.9 Hz, CH_2, 2 H), 1.72 (d, J = 7.1 Hz, CH_3, 3 H), 1.38 (s, CH_3, 9 H), 0.74 (s, CH_3, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 193.8, 146.2, 139, 137.9, 133.9, 130.1, 128.9, 128.5, 127.3, 127, 73.5, 58, 45.7, 36.4, 35.8, 32.5, 26.1, 16.4. HRMS: calcd for $C_{25}H_{34}AuClN_2$ $[M]^+$ 594.2076 found 594.2081.

■ ASSOCIATED CONTENT

Supporting Information

(PDF) The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00530.

Additional experimental data and NMR spectra of all compounds (PDF)

Accession Codes

CCDC 2011206−2011210 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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