Coinage Metal Complexes bearing Fluorinated N-Heterocyclic Carbene Ligands

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To the memory of Professor Pascual Royo, pioneer of Organometallic Chemistry in Spain

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Abstract. The synthesis of novel fluorinated symmetrical and unsymmetrical imidazolium salts as well as their corresponding coinage metal complexes is described. The silver derivatives were prepared using Ag_2O as the metal source and the subsequent (NHC)AgX complexes were successfully employed in the preparation of the corresponding Cu(I) and Au(I) complexes through transmetallation reactions. Halide extrusion from (NHC)AuCl complexes in the presence of labile ligands also allowed the isolation of Au(I) cationic complexes [(NHC)Au(L)]X. The molecular structures of relevant examples of the neutral and ionic complexes have been unambiguously determined by X-ray studies.

Keywords: fluorinated N-heterocyclic carbenes, silver carbene, gold carbene, copper carbene, neutral and cationic complexes

1. Introduction

Since the seminal work by Arduengo on the isolation of an N-heterocyclic carbene ligand (NHC) [1], their use in coordination and organometallic chemistry has continuously increased along the years. Their strong σ-donor abilities along with the straightforward tunability of the N-substituents have provided them a high degree of popularity within those fields [2]. In this context, the presence of fluorinated groups as part of NHC ligands has been described to significantly affect the ligand properties and the catalytic activity of their metal derivatives [3]. Additionally, fluorinated ligands are required in fluorous biphase media and in supercritical carbon dioxide applications since they enhance the metal complex solubility in these reaction media [4]. In the last two decades, the synthesis of complexes of the group 8, 9 and 10 transition metals containing fluorinated NHC ligands have been extensively studied [2,5,6,7,8,9,10,11,]. Xiao and co-workers were pioneering in this field by preparing polyfluoroalkylated NHC carbene palladium complexes [5a]. Later, the synthesis of several polyfluoroalkylated and trifluoromethylated NHC palladium complexes and their use as catalysts in homogeneous Suzuki-Miyaura cross coupling reactions [3j] and in fluorous biphasic Mizoroki-Heck arylations were disclosed [5b]. Moreover, fluorinated (NHC)-Ru complexes have been described and employed as efficient catalysts in olefin metathesis [3b-f]. Other ruthenium [6], iridium [6,7], rhodium [7,8] and platinum [9] complexes with fluorinated NHC ligands have also been prepared. In contrast, very few reports of fluorinated NHC-coinage metal

complexes are known [10,11]. Main examples consist in a gold(I) complex with a triazolium ligand bearing a pendant (diphenylfluoro)methyl moiety [10a], silver and copper complexes with an unsymmetrical NHC ligand with a hexafluoroisopropylmethoxy group at the *N*-aryl moiety [10b,11d] and a series of silver complexes with NHC ligands having a pentafluorobenzyl [11a] or polyfluoroalkyl [11b,11c] groups.

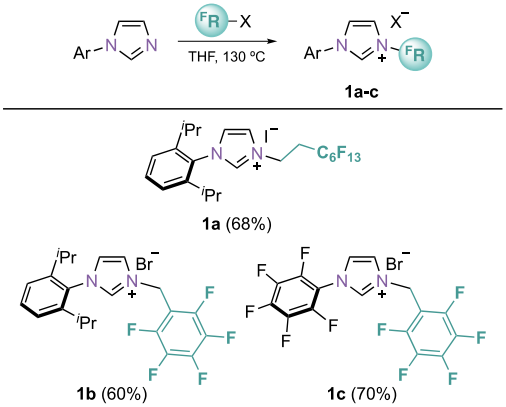
The growing interest in this area has encouraged us to focus on the preparation of fluorinated imidazolium salts as well as the corresponding group 11 metal complexes. Herein we describe the synthesis and characterization of four new fluorinated NHC ligands and the corresponding gold(I), silver(I) and copper(I) complexes, including structural characterization in solution and solid state. In all cases, bulky substituents are located at least in one of the two N-atoms of the NHC ligand, which is a non-common feature in the previous studies related to this chemistry.

2. Results and Discussion

*2.1. Synthesis of imidazolium salts **1a-d**.*

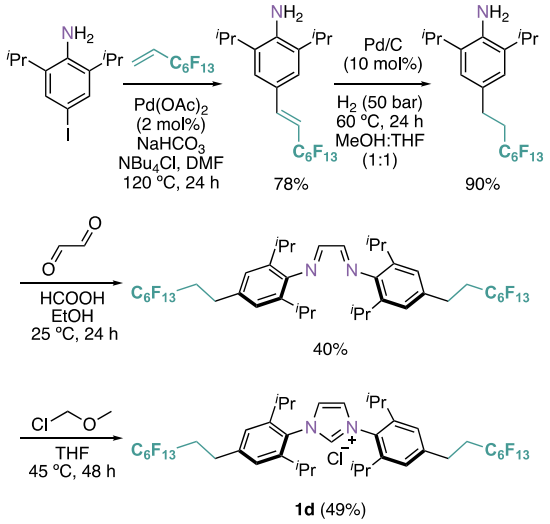
The fluorinated imidazolium salts **1a** and **1b** were prepared by direct alkylation of *N*-(2,6-diisopropylphenyl)imidazole [12] with the corresponding alkyl halide in 68% and 60% yields, respectively, after silica gel chromatography purification (Scheme 1). Similarly, the synthesis of the polyfluorinated imidazolium salt **1c** was carried out through direct alkylation of *N*-(perfluorophenyl)imidazole (the latter was obtained in 86% yield by slight modification of the procedure reported for the synthesis of the non-fluorinated aryl derivatives) [12] in 70% yield (Scheme 1).

Among the family of NHC ligands, the N-heterocyclic carbene IPr (1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]) is a well-known ancillary ligand for gold and copper catalysis. Thus, we next targeted the synthesis of the fluorinated and symmetrical imidazolium salt **1d** (Scheme 2), which resembles the IPr ligand and possesses two polyfluoroalkyl chains far away from the carbene center. For this purpose, 4-iodo-2,6-diisopropylaniline was prepared following a previously described procedure [13]. Then, a palladium-catalyzed Heck cross coupling of the aforementioned aniline with 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooct-1-ene allowed us to introduce the polyfluoroalkyl chain in an effective manner. Subsequent hydrogenation, condensation of the aniline with glyoxal to form the corresponding bisimine and reaction with chloromethyl methyl ether afforded the imidazolium salt **1d** as a yellow solid.



Scheme 1. Synthesis of imidazolium salts **1a-c**.

The hygroscopic imidazolium salts **1a-d** were characterized by spectroscopic and analytical methods. As representative data, the imidazolium N*C*(*H*)N resonances appeared in the 9.80-10.75 and 138.9-145.7 intervals in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra, respectively, within the range previously reported for other imidazolium salts (see Experimental Section for full characterization) [14].

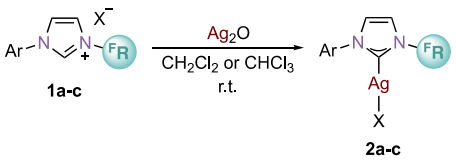


Scheme 2. Synthesis of imidazolium salts **1d**.

*2.2. Synthesis of group 11 neutral metal complexes (NHC)MX (M = Cu, Ag, Au, **2-4**).*

With the fluorinated imidazolium salts in hand, we targeted the preparation of the corresponding coinage metal complexes. We first focused on the preparation

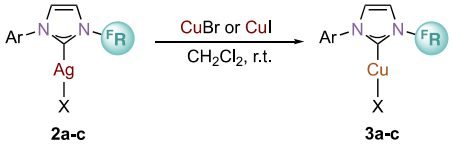
of the silver derivatives. The synthesis of **2a** and **2b** was carried out with 2 equiv of Ag_2O in CH_2Cl_2 at room temperature (Scheme 3). After stirring for 24 h, complexes **2a** and **2b** were obtained as brown solids in 56% and 67% yields, respectively. No reaction was observed with the imidazolium salt **1c** under the same conditions, albeit the use of $CHCl_3$ as solvent provided the complex **2c** in 49% yield.



2a (56%): Ar = 2,6-*i*PrC$_6$H$_3$, R = C$_2$H$_4$C$_6$F$_{13}$, X = I
2b (67%): Ar = 2,6-*i*PrC$_6$H$_3$, R = CH$_2$C$_6$F$_5$, X = Br
2c (49%): Ar = C$_6$F$_5$, R = CH$_2$C$_6$F$_5$, X = Br

Scheme 3. Synthesis of silver(I) complexes **2a-c**.

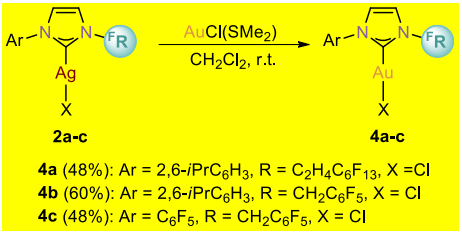
Attempts to prepare the corresponding copper complexes in a direct manner from the imidazolium salts **1a-c** were fruitless, even using potassium *tert*-butoxide or bis(trimethylsilyl)amide as bases to generate the corresponding free NHC ligand. Therefore, considering the well-known capabilities of (NHC)AgX as transmetallating agents [15], we explored the possibility of employing the previously prepared silver complexes **2a-c** to obtain the corresponding copper complexes. Thus, the synthesis of complex **3a** was obtained treating (NHC)AgX **2a** with CuI in CH_2Cl_2 at room temperature over 20 h under exclusion of light. Complexes **3b-c** were obtained using the same conditions but using CuBr. The transmetallation procedure proceeded satisfactorily in all the cases yielding copper complexes **3a-c** in 69-78% yields (Scheme 4).



3a (78%): Ar = 2,6-*i*PrC$_6$H$_3$, R = C$_2$H$_4$C$_6$F$_{13}$, X = I
3b (69%): Ar = 2,6-*i*PrC$_6$H$_3$, R = CH$_2$C$_6$F$_5$, X = Br
3c (44%): Ar = C$_6$F$_5$, R = CH$_2$C$_6$F$_5$, X = Br

Scheme 4. Synthesis of copper(I) complexes **3a-c**.

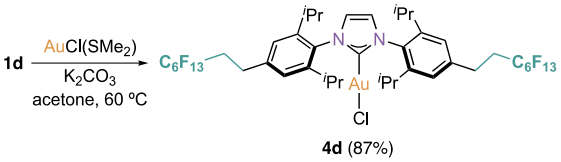
Likewise, the synthesis of the gold complexes **4a-c** was achieved from the previously prepared silver complexes **2a-c** using AuCl(SMe$_2$) as the gold source. The reactions were performed at room temperature using CH_2Cl_2 as solvent to afford complexes **4a-c** in good yields (Scheme 5).



4a (48%): Ar = 2,6-*i*PrC$_6$H$_3$, R = C$_2$H$_4$C$_6$F$_{13}$, X =Cl
4b (60%): Ar = 2,6-*i*PrC$_6$H$_3$, R = CH$_2$C$_6$F$_5$, X = Cl
4c (48%): Ar = C$_6$F$_5$, R = CH$_2$C$_6$F$_5$, X = Cl

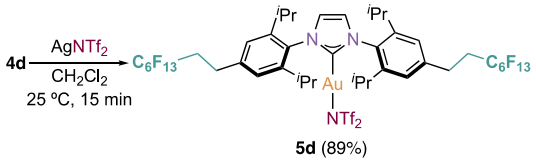
Scheme 5. Synthesis of gold complexes **4a-c**.

The transmetallation approach failed for the synthesis of gold complex **4d**. Instead, this complex could be prepared directly and in excellent yield from symmetrical imidazolium salt **1d** using K_2CO_3 as base and AuCl(SMe$_2$) in acetone at 60 ºC (Scheme 6).



Scheme 6. Synthesis of gold(I) complex **4d**.

Further treatment of complex **4d** with silver bis(trifluoromethanesulfonyl)imidate under exclusion of light led to the clean formation of a novel neutral complex **5d** in 89% yield (Scheme 7).



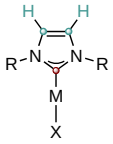
Scheme 7. Synthesis of gold(I) complex **5d**.

*2.3. Spectroscopic and structural characterization of complexes (NHC)MX (**2-4**).*

Relevant NMR data for complexes **2-4** are given in Table 1. As expected, the ^{1}H NMR spectra of these complexes show two different resonances at low field for the two backbone-ring protons (protons in green in the scheme of table 1) in the complexes with unsymmetrical ligands **2a-c**, **3a-c** and **4a-c**, and only one resonance in the complex **4d** bearing a symmetrical ligand. In comparison to the analogous nuclei of the imidazolium salts (8.26/7.22 ppm for **1a**, 8.01/7.36 ppm for **1b**, 8.14/8.09 for **1c**, 7.90 for **1d**), the resonances in the metal complexes appeared shifted upfield.

Data from $^{13}C\{^{1}H\}$ NMR spectra show that carbenic carbon (Table 1, C1 – circle red in the scheme of table 1) resonates at similar values to those reported for other group 11 metal NHC complexes [15c,16]. The signal related to the carbenic carbon (C1) for complexes **2c**, **3c** and **4c**, which bear two fluoroaromatic substituents, resonates slightly shifted downfield compared with the other members of the series. This could be related to the donor efficiency of these ligands to the metal center, having these the lowest donor ability among the family of ligands described herein. Considering this chemical shift as a qualitative measurement of the ligand-to-metal donation, the same trend is observed for copper, silver and gold complexes. It is also worth mentioning that Ag-carbene couplings were not observed in any of the members of the silver NHC-carbene complexes family described here [17].

Table 1. Selected measured NMR data for complexes **2a-c**, **3a-c** and **4a-d**.[a]



Complex	H_{imid} (ppm)	C_{imid} (ppm)	C1 (ppm)
2a	7.22/7.05	125.0/122.4	184.1
2b	7.30/7.08	125.2/121.4	183.2
2c	7.28/7.21	124.3/122.2	189.9
3a	7.17/6.95	124.1/121.2	182.7
3b	7.19/7.00	124.7/121.0	180.5
3c	7.23/7.15	123.8/121.9	183.2
4a	7.27/7.02	124.2/121.7	173.9
4b	7.21/7.02	124.7/120.9	174.9
4c	7.33/7.20	123.4/121.8	176.4
4d	7.16	124.3	175.6

[a]Data measured at 25 ºC in CD_2Cl_2.

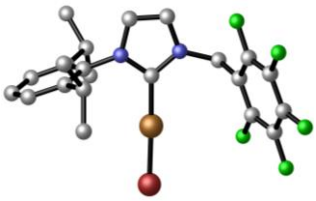


Figure 1. ORTEP plot of complex **3b**. Hydrogen atoms omitted for clarity.

Crystals of **3b** suitable for single-crystal X-ray diffraction studies were grown from a concentrated solution in CH_2Cl_2 and petroleum ether at -25 ºC. Figure 1 shows the molecular structure of this complex, which displays a two-coordinate metal atom in a linear environment with a C-Cu-Br bond angle of 177.88(12)º. The C-Cu bond length is similar to those found for other NHC-Cu complexes [14]. Additionally, as observed for other NHC complexes with aryl substituents, the aromatic ring plane is nearly orthogonal with respect to the imidazole plane [16,17].

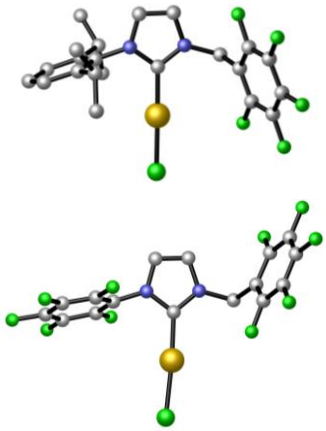


Figure 2. ORTEP plot of gold(I) complexes **4b** (up) and **4c** (bottom). Hydrogen atoms omitted for clarity.

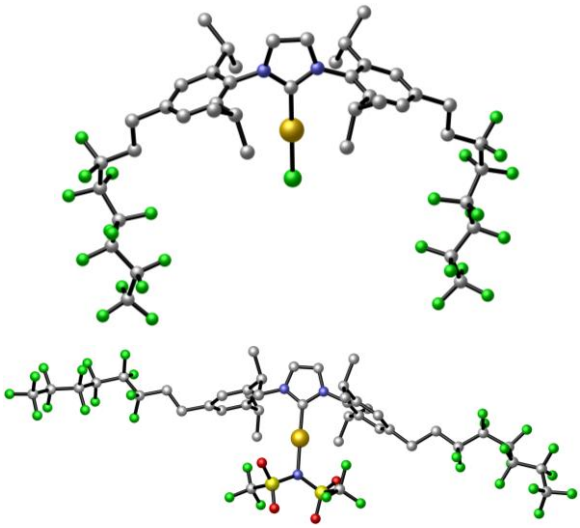
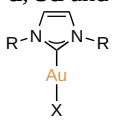


Figure 3. ORTEP plot of complexes **4d** (top) and **5d** (bottom). Hydrogen atoms omitted for clarity.

Single crystals suitable for X-ray diffraction were also obtained by diffusion of pentane or hexane into a concentrated solution of gold complexes **4b-d** and **5d** (see Experimental Section). Figure 2 and 3 contain the molecular structures for these complexes and selected bond distances and angles are being collected in Table 2. All of them display a two-coordinate metal atom in a linear environment with a C-Au-X angle within the range of 175.1(6) and 179.44(10)º. The C-Au bond distances are all close to 2.0 Å (Table 2, column 1). As for copper complex **3b**, the aromatic ring plane is nearly orthogonal to the imidazole plane. Interestingly, even if the fluorinated

NHC ligand is the same for complexes **4d** and **5d** (Figure 3), the polyfluoroalkyl chains display a different conformation in these two complexes. The two chains open up in complex **5d** (Figure 3) due to the increase of bulkinees introduced by ligand NTf_2^- compared to the less voluminous Cl^-.

Table 2. Selected bond distances and angles for gold(I) complexes **4b-d**, **5d** and **6c**.



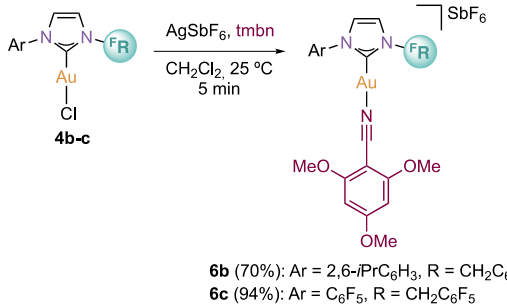
Complex	d (Au-C) (Å)	d (Au-X) (Å)	C-Au-X (º)
4b	1.979(3)	2.2951(7)	178.63(8)
4c	1.958(7)	2.3250(13)	175.3(2)
4d	1.987(3)	2.2773(9)	179.44(10)
5b	1.963(3)	2.086(3)	179.13(11)
6c	1.963(3)	2.001(10)	175.1(6)

X = Cl for **4b-d**, X = NTf_2 for **5d** and X = tmbn for **6c**. tmbn = trimethoxybenzonitrile.

*2.4. Synthesis and characterization of cationic gold complexes (**6b-d**).*

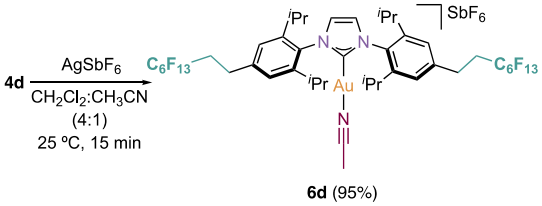
To be involved in catalysis, a coordination vacant must be generated from a linear dicoordinated gold(I) chloride complex. An effective procedure to avoid the *in situ* activation of gold(I) chloride complexes involves the use of cationic gold(I) complexes bearing weakly coordinating ligands. In this context, we next envisioned the preparation of cationic gold(I) complexes bearing fluorinated NHC ligands from the previously formed neutral gold(I) chloride complexes.[18] The initial attempts to obtain cationic complexes bearing acetonitrile as labile ligand from complexes **4b** and **4c** were unsuccessful. We could finally isolate cationic gold complexes **6b** and **6c** in good yield by treating the corresponding neutral gold complexes **4b** and **4c** with $AgSbF_6$ in the presence of trimethoxybenzonitrile in CH_2Cl_2 under the exclusion of light (Scheme 8). Furthermore, complex **6d** was prepared in a similar manner but using a 1:1 CH_2Cl_2:CH_3CN mixture as the reaction medium (Scheme 9). These results show that the electronic effect on the σ-donor abilities of NHC ligands induced by perfluoroalkyl chains located far away from the carbenic carbon is markedly lower than the effect produced by perfluorinatedaryl groups directly bound to the nitrogen atoms.

Complexes **6b** and **6c** exhibit NMR spectra in agreement with the presence of the coordinated NHC and nitrile ligands. Probably the most relevant feature is the upfield shift of the carbenic carbon nuclei when compared to the parent neutral complexes. Such resonance moves upfield from *ca.* 175 ppm in **4b-c** to *ca.* 167-169 ppm in **6b-c**.



6b (70%): Ar = 2,6-*i*PrC$_6$H$_3$, R = $CH_2C_6F_5$
6c (94%): Ar = C_6F_5, R = $CH_2C_6F_5$

Scheme 8. Synthesis of cationic gold(I) complexes **6b-c**.



6d (95%)

Scheme 9. Synthesis of cationic gold(I) complex **6d**.

Crystals of complex **6c** suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a solution of the complex in CH_2Cl_2 (Figure 4). The distance Au-C is 1.951(10) Å, nearly identical to that of the parent complex **4c** (Table 2). The distance Au(1)-N is 2.001(10) Å, and the angle C-Au-N is 175.1(6)°.

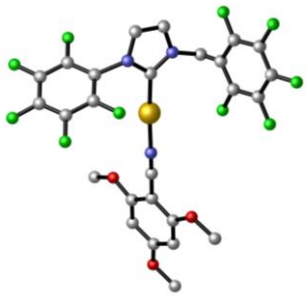


Figure 4. ORTEP plot of gold(I) complex **6c**. Hydrogen atoms omitted for clarity.

Stability of complexes 2-6.

We have checked the solubility of these complexes in supercritical carbon dioxide, since they could be potential catalysts for the functionalization of gaseous alkanes by carbene insertion from ethyl diazoacetate.[19] However, we have found that they decompose in such medium, leading to the appearance of colloidal metallic mixtures.

3. Conclusions

A series of copper(I), silver(I) and gold(I) complexes with highly fluorinated NHC ligands have been prepared and fully characterized, including structural X-ray studies in some cases. The stability in solution of neutral as well as some cationic derivatives could make them suitable for their use as catalyst precursors for reactions catalyzed by coinage metals.

4. Experimental

4.1. General procedures

All preparations and manipulations were carried out using Schlenk techniques or a glovebox. Solvents were dried using a Solvent Purification System (MBraun). All the reagents were purchased from commercial sources and used without further purification. Thin layer chromatography was carried out using TLC aluminium sheets coated with 0.2 mm of silica gel (Merck GF_{234}) using UV light as the visualizing agent and a solution of vanillin as stain. Chromatographic purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-60 µm) or automated flash chromatographer CombiFlash Companion. GC data were collected with a Varian 3900 instrument. NMR spectra were recorded on a Varian Mercury 400 MHz, Bruker Advance 400 Ultra Shield, Bruker 500 Ultrashield and Bruker 300 Ultrashield. Elemental analyses were carried out with a Perkin-Elmer EA 2400 analyzer and with LECO CHNS 932 micro-analyzer.

4.2. X-ray diffraction studies

Single crystals for the X-ray analyses were obtained from the preparations described below. The crystals were covered with perfluoropolyether oil (FOMBLIN®, Aldrich) and mounted in a fiber loop. X-ray data (T = 100(2) K) were obtained with a Bruker SMART APEX II CCD area detector on a D8 goniometer, using a graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), a Bruker Kappa APEX II DUO diffractometer equipped with an APPEX 2 4K CCD area detector, a Microsource with Mo_{ka} and Oxford Cryosystem Series 700 low-temperature device. Data were processed with the INTEGRATE program of the APEX2 software [20] for reduction and cell refinement. Multi-scan absorption corrections were applied by using the SCALE program for area detector. The structure was solved by direct methods and difference Fourier synthesis and refined by full-matrix least-squares procedures, with anisotropic thermal parameters in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms. Weighted R factors (*wR*) and all goodness-of-fit (S) are based on F^2, conventional *R* factors (*R*) are based on F. SHELXTL software package [21] (based on SHELXS and SHELXL) was used for structure solution and refinement. A summary of the fundamental crystal and refinement data are given in the Supporting Information. Atomic coordinates, anisotropic displacement parameters and bond lengths and angles can be found in the corresponding cif file.

4.3. Preparations

*4.3.1. 1-(2,6-diisopropylphenyl)-3-(1H,1H,2H,2H-perfluoro-octyl)-1H-imidazol-3-ium iodide (**1a**)*

1-(2,6-Diisopropylphenyl)imidazole (238 mg, 1.04 mmol), 1-iodo-1*H*,1*H*,2*H*,2*H*-perfluorooctane (0.30 mL, 1.15 mmol), and THF (1 mL) were placed in an ampoule. The reaction mixture was stirred for 24 h at 130 °C. Volatiles were removed under vacuum, and the residue was purified by silica gel chromatography (CH_2Cl_2/CH_3OH 10:1, R_f = 0.55) to give **1a** as a brown solid (500 mg, 68 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.94 (s, 1H, NC*H*N), 8.26 (br s, 1H, CH_{imid}), 7.55 (t, *J* = 7.8 Hz, 1H, CH_{arom}), 7.31 (d, *J* = 7.9 Hz, 2H, CH_{arom}), 7.22 (br s, 1H, CH_{imid}), 5.32 (t, *J* = 5.9 Hz, 2H, C$H_2CH_2(CF_2)_5CF_3$), 3.06 (tt, $^3J_{HH}$ = 5.9 Hz, $^3J_{HF}$ = 18.6 Hz, 2H, $CH_2CH_2(CF_2)_5CF_3$), 2.29 (hept, *J* = 6.8 Hz, 2H, C$H(CH_3)_2$), 1.21 (d, *J* = 6.8 Hz, 6H, CH(C$H_3)_2$), 1.14 (d, *J* = 6.8 Hz, 6H, CH(C$H_3)_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.4 (N*C*HN), 137.7 (*C*H_{arom}), 132.1 (*C*H_{arom}), 129.9 (*C*H_{arom}), 124.8 (*C*H_{arom}), 124.4 (*C*H_{imid}), 124.3 (*C*H_{imid}), 122-108 (m, 5C, *C*F_2, C*F*$_3$), 43.2 ($CH_2CH_2(CF_2)_5CF_3$), 32.0 (t, $^2J_{C-F}$ = 21 Hz, $CH_2CH_2(CF_2)_5CF_3$), 28.6 (*C*$H(CH_3)_2$), 24.3 (CH(*C*$H_3)_2$), 24.1 (CH(*C*$H_3)_2$). ^{19}F{^{1}H} NMR (376.6 MHz, $CDCl_3$): δ -80.8 (t, $^3J_{FF}$ = 10.0 Hz, 3F), -113.3 (t, $^3J_{FF}$ = 15.3 Hz, 2F), -121.9 (br s, 2F), -122.9 (br s, 2F), -123.3 (brs, 2F), -126.2 (m, 2F). HRMS calcd for $C_{23}H_{24}N_2IF_{13}$: 701.0698; Found: 701.0704.

*4.3.2. 1-(2,6-diisopropylphenyl)-3-[(perfluoro-phenyl)methyl]-1H-imidazol-3-ium bromide (**1b**).*

N-(2,6-Diisopropylphenyl)-imidazole (1000 mg, 4.39 mmol), 2,3,4,5,6-pentafluoro-benzyl bromide (0.74 mL, 4.83 mmol), and THF (5 mL) were placed in a ampoule. The reaction mixture was stirred for 24 h at

130 °C. Volatiles were removed under vacuum, and the residue was purified by silica gel chromatography (CH_2Cl_2/CH_3OH 10:1, R_f = 0.45) to give **1b** as a brown solid (1125 mg, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.56 (s, 1H, NC*H*N), 8.02 (br s, 1H, CH_{imid}), 7.47 (t, *J* = 7.8 Hz, 1H, CH_{arom}), 7.36 (br s, 1H, CH_{imid}), 7.23 (d, *J* = 7.8 Hz, 2H, CH_{arom}), 6.24 (s, 2H, C$H_2C_6F_5$), 2.21 (hept, *J* = 6.8 Hz, 2H, CH(CH_3)$_2$), 1.13 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.08 (d, *J* = 6.8 Hz, 6H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 147-136 (m, 5C, *C*F$_{arom}$), 145.3 (*C*H$_{arom}$), 138.9 (N*C*N), 132.0 (*C*H$_{arom}$), 129.9 (*C*H$_{arom}$), 125.5 (*C*H$_{imid}$), 124.6 (*C*H$_{arom}$), 123.3 (*C*H$_{imid}$), 107.3 (t, $^2J_{C\text{-}F}$ = 16 Hz, C_{ipso}), 41.8 (*C*H$_2C_6F_5$), 28.7 (*C*H(CH$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$). ^{19}F{^{1}H} NMR (376.6 MHz, $CDCl_3$): δ -141.6 (m, 2F, *o*-C*F*), -150.4 (t, $^3J_{F\text{-}F}$ = 21.0 Hz, 1F, *p*-C*F*), -159.7 (m, 2F, *m*-C*F*). Anal. Calcd. for $C_{22}H_{22}N_2BrF_5$ (%): C, 54.00; H, 4.53; N, 5.72; Found (%): C, 53.54; H, 4.81; N, 5.30.

*4.3.3. 1-(perfluorophenyl)-3-[(perfluorophenyl) methyl]-1H-imidazol-3-ium bromide (**1c**).*

2,3,4,5,6-Pentafluoroaniline (500 mg, 2.73 mmol), glyoxal (0.40 mL, 2.73 mmol, solution 40 % in water), and CH_3OH (6 mL) were placed in an ampoule. The reaction mixture was stirred for 16 h at 130 ºC. Then, NH_4Cl (292 mg, 5.46 mmol) was added followed by 37 % aq formaldehyde (0.41 mL, 5.46 mmol). The mixture was heated at 100 ºC for 1 h and H_3PO_4 (0.34 mL, 85 %) was added over a period of 10 min. The mixture was again stirred at 100 ºC during 6 h. Volatiles were removed under vacuum, and the residue was poured onto ice (40 mg) and neutralized with aq 40 % KOH solution until pH = 9. The resulting mixture was extracted with Et_2O (3 x 25 mL). The organic phases were combined and washed with H_2O, brine and dried with anhydrous Na_2SO_4. The solvent was removed affording the *N*-(perfluorophenyl)imidazole as a yellow oil (551 mg, 86 %)**.**

N-(perfluorophenyl)imidazole (551 mg, 2.35 mmol), 2,3,4,5,6-pentafluoro-benzyl bromide (0.40 mL, 2.59 mmol), and THF (1 mL) were placed in a ampoule. The reaction mixture was stirred for 24 h at 130 °C. Volatiles were removed under vacuum, and the residue was washed with ether to give **1c** as a brown solid (815 mg, 70 %). ^{1}H NMR (400 MHz, CD_3OD): δ 9.84 (s, 1H, NC*H*N), 8.14 (br s, 1H, CH_{imid}), 8.09 (br s, 1H, CH_{imid}), 5.89 (s, 2H, C$H_2C_6F_5$). ^{13}C{^{1}H} NMR (100 MHz, CD_3OD): δ 145-138 (m, 10C, *C*F$_{arom}$), 139.4 (N*C*N), 124.8 (*C*H$_{imid}$), 123.6 (*C*H$_{imid}$), 110.4 (t, $^2J_{C\text{-}F}$ = 17 Hz, C_{ipso}), 106.9 (t, $^2J_{C\text{-}F}$ = 17 Hz, C_{ipso}), 41.1 (*C*H$_2C_6F_5$). ^{19}F{^{1}H} NMR (376.6 MHz, CD_3OD): δ -146.7 (m, 2F, *o*-C*F*), -151.9 (m, 2F, *o*-C*F*), -155.4 (m, 1F, *p*-C*F*), -157.2 (m, 1F, *p*-C*F*), -165.9 (m, 2F, *m*-C*F*), -166.8 (m, 2F, *m*-C*F*). Anal. Calcd. for $C_{16}H_5N_2BrF_{10}$ (%): C, 38.81; H, 1.02; N, 5.66; Found (%): C, 38.70; H, 1.45; N, 5.84

4.3.4. (E)-2,6-Diisopropyl-4-(3,3,4,4,5,5,6,6,7,7, 8,8,8-tridecafluorooct-1-en-1-yl)aniline.

4-Iodo-2,6-diisopropylaniline (7.5 mmol, 2.27 g), $NaHCO_3$ (26.3 mmol, 2.20 g), Bu_4NCl (7.5 mmol, 2.08 g) and $Pd(OAc)_2$ (0.150 mmol, 34 mg) were dissolved in 10 mL of dry DMF under argon, followed by the addition of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooct-1-ene (9.75 mmol, 2.22 mL). The resulting mixture was stirred for 24 h at 120 ºC. It was treated with HCl 1M and extracted with ethyl acetate. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The resulting crude was purified using fluoroflash® cartridges. The sample was loaded in DMF:H_2O (8:2), fluorophobic elution was done with MeOH:H_2O (8:2) and fluorophilic elution with MeOH. The fluorophilic fraction was concentrated and the product was obtained as a dark red oil (3.05 g, 78% yield). ^{1}H NMR (400 MHz,$CDCl_3$): *δ* 7.17 (s, 2H), 7.10 (dt, $J_{H\text{-}H}$ = 16.0, $J_{H\text{-}F}$ = 2.3 Hz, 1H), 5.99 (dt, $J_{H\text{-}H}$ = 16.1, $J_{H\text{-}F}$ = 12.5 Hz, 1H), 4.01 (br s, 2H), 2.91 (hept, $J_{H\text{-}H}$ = 6.8 Hz, 2H), 1.31 (d, $J_{H\text{-}H}$ = 6.8 Hz, 24H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): *δ* 171.3, 142.9, 140.7 (t, $J_{C\text{-}F}$ = 9.6 Hz), 132.5, 126.9–125.5 (m), 123.7–123.4 (m), 123.0, 118.9 (t, $J_{C\text{-}F}$ = 34.5 Hz), 116.5–115.5 (m), 114.1–112.8 (m), 111.8–110.3 (m), 109.2 (t, $J_{C\text{-}F}$ = 23 Hz), 28.1, 22.3. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): *δ* -80.9 (t, $J_{F\text{-}F}$ = 9.8 Hz, 3F), -109.9 (t, $J_{F\text{-}F}$ = 13.1 Hz, 2F), -121.55, -121.80 (m, 2F), -122.83– -123.04 (m, 2F), -123.05 – -123.22 (m), -126.14 – -126.32 (m, 2F). HRMS (ESI) Calc. for $C_{20}H_{19}F_{13}N$ [M-H]$^-$: 520.1315. Found: 520.1330.

4.3.5. 2,6-diisopropyl-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctan-1-yl)aniline.

In a flask, (*E*)-2,6-diisopropyl-4-(3,3,4,4,5,5,6,6, 7,7,8,8,8-tridecafluorooct-1-en-1-yl)aniline (0.79 mmol, 413.5 mg) and 10% Pd/C (0.079 mmol, 84 mg) were suspended in 8 mL of MeOH:THF (1:1). It was stirred for 24 h at 60 ºC under 50 bar of H_2. After releasing the H_2 and cooling down to room temperature, the mixture was filtered through a pad of celite. The solvent was evaporated under reduced pressure and the crude was purified using fluoroflash® cartridges. The sample was loaded in DMF:H_2O (8:2), fluorophobic elution was done with MeOH:H_2O (8:2) and fluorophilic elution with

MeOH. The fluorophilic fraction was concentrated and the product was obtained as an orange oil (374 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.86 (s, 2H), 3.68 (br s, 2H), 2.93 (hept, J_{H-H} = 6.9 Hz, 2H), 2.87 – 2.78 (m, 2H), 2.43 – 2.25 (m, 2H), 1.28 (d, J_{H-H} = 6.8 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 139.1, 133.1, 129.0, 122.0, 121.9 – 120.3 (m), 119.4 – 117.8 (m), 116.6 – 115.3 (m), 114.6 – 112.9 (m), 112.1 – 110.0 (m), 109.5 – 107.6 (m), 33.8 (t, J_{C-F} = 22 Hz), 28.2 , 26.4 (t, J_{C-F} = 4.3 Hz), 22.5. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -81.00 (t, J_{F-F} = 10.3 Hz, 3F), -114.67 – -114.91 (m, 2F), -121.86 – -122.22 (m, 2F), -122.84 – -123.15 (m, 2F), -123.45 – -123.78 (m, 2F), -126.08 – -126.45 (m, 2F). HRMS (ESI-) Calc. for $C_{20}H_{21}F_{13}N$ $[M-H]^-$: 522.1472. Found: 522.1471.

4.3.6. Glyoxal-bis-(2,6-diisopropyl-4-(3,3,4,4,5,5,6,6, 7,7,8,8,8-tridecafluorooctyl)phenyl)imine.

In a flask, 2,6-diisopropyl-4-(3,3,4,4,5,5,6,6,7,7,8,8,8 -tridecafluorooctan-1-yl)aniline (3.04 g, 5.80 mmol) was dissolved in 30 mL of EtOH. 40% glyoxalaldehyde (0.333 mL, 2.90 mmol) and formic acid (11 μl, 0.29 mmol) were added to the solution. After 10 minutes, a yellow solid precipitated. The mixture was stirred at room temperature for 24 h. Afterwards, it was filtrated by gravity and the resulting solid was washed with cold EtOH (10 mL x 3), giving a bright yellow solid (2.45 g, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 2H), 7.00 (s, 4H), 3.04 – 2.78 (m, 8H), 2.49 – 2.29 (m, 4H), 1.21 (d, J_{H-H} = 6.9 Hz, 24H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 163.7, 147.1, 137.7, 136.1, 123.5, 121.3 – 120.2 (m), 119.2 – 117.9 (m), 116.5 (t, J_{C-F} = 33.0 Hz), 114.6 – 112.4 (m), 112.1 – 110.1 (m), 109.8 – 108.4 (m), 33.6 (t, J_{C-F} = 22.1 Hz), 28.4, 26.8 (t, J_{C-F} = 3.1 Hz), 23.6. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ -80.86 (t, J_{F-19F} = 10.0 Hz, 6F), -114.39 – -115.25 (m, 4F), -121.8 – -122.1 (m, 4F), -122.93 (br s, 4F) , -123.32 – -123.72 (m, 4F), -126.04 – -126.74 (m, 4F). HRMS (ESI+) Calc. for $C_{42}H_{43}F_{26}N_2$ $[M+H]^+$: 1069.3006. Found: 1069.2972.

*4.3.7. 1,3-bis-[2,6-diisopropyl-4-(3,3,4,4,5,5,6,6 ,7,7,8,8,8-tridecafluorooctyl)phenyl]1H-imidazol-3-ium chloride (**1d**).*

Glyoxal-bis-(2,6-diisopropyl-4-(3,3,4,4,5,5,6,6,7,7, 8,8,8-tridecafluorooctyl)phenyl)imine (571 mg, 0.534 mmol) was dissolved in 10 mL of dry THF under argon, followed by the addition of chloromethyl methyl ether in one pot (81 μL, 1.069 mmol). The resulting solution was stirred at 45 ºC for 48 h. The solvent was removed under reduced pressure and the resulting crude was dissolved in the minimum amount of CH_2Cl_2 and layered with pentane. After a while, a brown oil was separated by decantation and dried under vacuum to yield a brown solid. The resulting solid was dissolved in CH_2Cl_2 and filtered through a pad of silica first with CH_2Cl_2, then ethyl acetate (orange fraction) and finally MeOH (yellow fraction). The fraction obtained with methanol was evaporated to obtain the targeted compound as a yellow solid (264.3 mg, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.75 (t, J_{H-H} = 1.6 Hz, 1H), 7.90 (d, J_{H-H} = 1.6 Hz, 2H), 7.12 (s, 4H), 3.02 – 2.90 (m, 4H), 2.46 – 2.32 (m, 8H), 1.24 (d, J_{H-H} = 4.7 Hz, 12H), 1.22 (d, J_{H-H} = 4.9 Hz, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 145.7, 143.4, 140.2, 128.9, 126.3, 124.7, 121.1 – 120.0 (m), 119.2 – 118.3 (m), 118.4 – 117.6 (m), 116.3 – 115.3 (m), 111.7 – 110.6 (m), 109.3 – 108.3 (m), 32.7 (t, J_{C-F} = 22.2 Hz), 29.3, 26.8 (d, J_{C-F} = 3.9 Hz), 23.7. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -80.96 (t, J_{F-F} = 10.0 Hz, 6F), -114.57 – -114.70 (m, 4F), -121.66 – -122.21 (m, 4F), -122.98 (br s, 4F), -123.55 – -123.36 (m, 4F), -126.08 – -126.55 (m, 4F). HRMS (ESI+) Calc. for $C_{43}H_{43}F_{26}N_2$ $[M-Cl]^+$: 1081.3006. Found: 1081.3004.

*4.3.8. [1-(2,6-diisopropylphenyl)-3-(1H,1H,2H,2H -perfluorooctyl)-imidazolin-2-ylidene]silver iodide (**2a**).*

A Schlenk flask was charged with **1a** (384 mg, 0.55 mmol), silver oxide (127 mg, 0.55 mmol), and CH_2Cl_2 (40 mL). The reaction mixture was stirred at room temperature for 24 h in the dark and then filtered through Celite. The solvent was removed under vacuum and the residue was washed with petroleum ether to give **2a** as a brown solid (250 mg, 56%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.48 (br s, 1H, CH_{arom}), 7.22 (br s, 3H, CH_{imid}, CH_{arom}), 7.05 (br s, 1H, CH_{imid}), 4.56 (br s, 2H, CH_2CH$_2$(CF$_2$)$_5$CF$_3$), 2.69 (br s, 2H, CH$_2$CH_2(CF$_2$)$_5$CF$_3$), 2.31 (br s, 2H, CH(CH$_3$)$_2$), 1.07 (br s, 12H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 184.1 (N*C*N), 146.4 (*C*H$_{arom}$), 135.3 (*C*H$_{arom}$), 130.9 (*C*H$_{arom}$), 125.0 (*C*H$_{imid}$), 124.6 (*C*H$_{arom}$), 124-108 (m, 5C, *C*F$_2$, CF$_3$), 122.4 (*C*H$_{imid}$), 44.7 (*C*H$_2$CH$_2$(CF$_2$)$_5$CF$_3$), 32.7 (m, 1C, CH$_2$*C*H$_2$(CF$_2$)$_5$CF$_3$), 28.6 (*C*H(CH$_3$)$_2$), 24.8 (CH(*C*H$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$). ^{19}F{^{1}H} NMR (376.6 MHz, CD_2Cl_2): δ -81.5 (br s, 3F), -113.9 (br s, 2F), -122.2 (br s, 2F), -123.2 (br s, 2F), -123.5 (br s, 2F), -126.5 (br s, 2F).

*4.3.9. [1-(2,6-diisopropylphenyl)-3-((perfluoro-phenyl)methyl)-imidazolin-2-ylidene] silver bromide (**2b**)*

Following the above procedure, and using **1b** (244.7 mg, 0.5 mmol), silver oxide (139 mg, 0.6 mmol) and CH_2Cl_2 (30 mL), **2b** was isolated as a brown solid (200 mg, 67%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.50 (t, *J* = 7.8 Hz, 1H, C*H*$_{arom}$), 7.3-7.28 (m, 3H, C*H*$_{imid}$, C*H*$_{arom}$), 7.08 (br s, 1H, C*H*$_{imid}$), 5.56 (s, 2H, C*H*$_2$C$_6$F$_5$), 2.34 (hept, *J* = 6.7 Hz, 2H, C*H*(CH$_3$)$_2$), 1.20 (d, *J* = 6.6 Hz, 6H CH(C*H*$_3$)$_2$), 1.11 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 183.2 (N*C*N), 148-137 (m, 5C, *C*F$_{arom}$), 146.3 (*C*H$_{arom}$), 135.2 (*C*H$_{arom}$), 131.0 (*C*H$_{arom}$), 125.2 (*C*H$_{imid}$), 124.7 (*C*H$_{arom}$), 121.4 (*C*H$_{imid}$), 109.7 (t, $^2J_{C\text{-}F}$ = 16 Hz, *C*$_{ipso}$), 43.7 (*C*H$_2$C$_6$F$_5$), 28.8 (*C*H(CH$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$). ^{19}F{^{1}H} NMR (376.6 MHz, CD_2Cl_2): δ -141.5 (m, 2F, *o*-C*F*), -152.1 (t, $^3J_{F\text{-}F}$ = 21 Hz, 1F, *p*-C*F*), -160.8 (m, 2F, *m*-C*F*).

*4.3.10. 1-(perfluorophenyl)-3-(perfluorobenzyl) imidazolin-2-ylidene] silver bromide (**2c**)*

Following the procedure described for **2a**, and starting from **1c** (200 mg, 0.4 mmol), silver oxide (94 mg, 0.4 mmol), and CH_3CN (40 mL), **2c** was obtained as a brown solid (119 mg, 49 %). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.28 (br s, 1H, C*H*$_{imid}$), 7.22 (br s, 1H, C*H*$_{imid}$), 5.70 (s, 2H, C*H*$_2$C$_6$F$_5$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 189.9 (N*C*N), 148-137 (m, 10 C, *C*F$_{arom}$), 124.3 (*C*H$_{imid}$), 122.1 (*C*H$_{imid}$), 115.7 (t, $^2J_{C\text{-}F}$ = 14 Hz, *C*$_{ipso}$), 109.7 (t, $^2J_{C\text{-}F}$ = 18 Hz, *C*$_{ipso}$), 43.9 (*C*H$_2$C$_6$F$_5$). ^{19}F{^{1}H} NMR (376.6 MHz, CD_2Cl_2): δ -141.3 (m, 2F, *o*-C*F*), -146.0 (m, 2F, *o*-C*F*), -152.3 (m, 2F, *p*-C*F*), -161.2 (m, 4F, *m*-C*F*).

*4.3.11. [1-(2,6-diisopropylphenyl)-3-(1H,1H,2H, 2H-perfluorooctyl)-imidazolin-2-ylidene] copper iodide (**3a**)*

A mixture of the silver complex **2a** (118.1 mg, 0.15 mmol) and CuI (34.3 mg, 0.18 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 20 h in the dark. The mixture was filtered through Celite and the volatiles were then removed under reduced pressure. The residue was washed with petroleum ether to give **3a** as a brown solid (90 mg, 78%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.47 (t, *J* = 7.8 Hz, 1H, C*H*$_{arom}$), 7.27 (d, *J* = 7.8 Hz, 2H, C*H*$_{arom}$), 7.17 (br s, 1H, C*H*$_{imid}$), 6.95 (br s, 1H, C*H*$_{imid}$), 4.54 (br s, 2H, C*H*$_2$CH$_2$(CF$_2$)$_5$CF$_3$), 2.80 (m, 2H, CH$_2$C*H*$_2$(CF$_2$)$_5$CF$_3$), 2.40 (hept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 1.21 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.09 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 182.7 (N*C*N), 146.4 (*C*H$_{arom}$), 135.4 (*C*H$_{arom}$), 130.7 (*C*H$_{arom}$), 124.5 (*C*H$_{arom}$), 124.1 (*C*H$_{imid}$), 124-108 (m, 5C, *C*F$_2$, *C*F$_3$), 121.2 (*C*H$_{imid}$), 43.7 (*C*H$_2$CH$_2$(CF$_2$)$_5$CF$_3$), 33.3 (t, $^2J_{C\text{-}F}$ = 21 Hz, CH$_2$*C*H$_2$(CF$_2$)$_5$CF$_3$), 28.8 (*C*H(CH$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 24.6 (CH(*C*H$_3$)$_2$). ^{19}F{^{1}H} NMR (376.6 MHz, CD_2Cl_2): δ -81.2 (t, $^3J_{F\text{-}F}$ = 10.0 Hz, 3F), -113.8 (m, 2F), -122.1 (br s, 2F), -123.1 (br s, 2F), -123.6 (br s, 2F), -126.4 (m, 2F). Anal. Calcd. for $C_{23}H_{23}CuIF_{13}N_2$ (%): C, 40.18; H, 4.21; N, 3.35; Found (%): C, 40.43; H, 3.92; N, 3.81.

*4.3.12. [1-(2,6-diisopropylphenyl)-3-((perfluoro-phenyl)methyl)-imidazolin-2-ylidene] copper bromide (**3b**)*

A mixture of the silver complex **2b** (30 mg, 0.05 mmol) and CuBr (9 mg, 0.06 mmol) in CH_2Cl_2 (50 mL) was stirred at room temperature for 18 h in the dark. The mixture was filtered through Celite and the volatiles were then removed under reduced pressure to afford the copper complex **3b** as a white solid (19 mg, 69%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.50 (t, *J* = 7.8 Hz, 1H, C*H*$_{arom}$), 7.29 (d, *J* = 7.8 Hz, 2H, C*H*$_{arom}$), 7.19 (br s, 1H, C*H*$_{imid}$), 7.00 (br s, 1H, C*H*$_{imid}$), 5.53 (s, 2H, C*H*$_2$C$_6$F$_5$), 2.35 (hept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 1.21 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.12 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 180.5 (N*C*N), 148-137 (m, 5C, *C*F$_{arom}$), 146.3 (*C*H$_{arom}$), 134.9 (*C*H$_{arom}$), 130.9 (*C*H$_{arom}$), 124.7 (*C*H$_{imid}$), 124.6 (*C*H$_{arom}$), 121.0 (*C*H$_{imid}$), 109.8 (t, $^2J_{CF}$ = 15 Hz, *C*$_{ipso}$), 43.1 (*C*H$_2$C$_6$F$_5$), 28.8 (*C*H(CH$_3$)$_2$), 24.8 (CH(*C*H$_3$)$_2$), 24.3 (CH(*C*H$_3$)$_2$).^{19}F{^{1}H} NMR (376.6 MHz, CD_2Cl_2): δ -143.0 (m, 2F, *o*-C*F*), -152.5(m, 1F, *p*-C*F*), -161.5 (m, 2F, *m*-C*F*). Anal. Calcd. for $C_{22}H_{21}BrCuF_5N_2$ (%): C, 47.88; H, 3.84; N, 5.08; Found (%): C, 48.02: H, 4.39; N, 4.53.

4.3.13. [1-(perfluorophenyl)-3-((perfluorophenyl) methyl)-imidazolin-2-ylidene] copper bromide (**3c**).

Following the procedure described for **3b**, and using **2c** (50 mg, 0.08 mmol), CuBr (15 mg, 0.1 mmol) and CH_2Cl_2 (15 mL), **3c** was obtained as a brown tan solid (20.6 mg, 44%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.23 (br s, 1H, C*H*$_{imid}$), 7.15 (br s, 1H, C*H*$_{imid}$), 5.58 (s, 2H, C*H*$_2$C$_6$F$_5$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 183.2 (N*C*N), 148-137 (m, 10C, *C*F$_{arom}$), 123.8 (*C*H$_{imid}$), 121.9 (*C*H$_{imid}$), 115.3 (m, *C*$_{ipso}$), 109.2 (m, *C*$_{ipso}$), 43.3 (*C*H$_2$C$_6$F$_5$). ^{19}F{^{1}H} NMR (376.6 MHz, CD_2Cl_2): δ -140.8 (d, $^3J_{F\text{-}F}$ = 15.0 Hz, 2F, *o*-C*F*), -140.8 (d, $^3J_{F\text{-}F}$ = 15.0 Hz, 2F, *o*-C*F*), -151.4 (t, $^3J_{FF}$ = 21.6 Hz, 1F, *p*-C*F*), -151.9 (t, $^3J_{F\text{-}F}$ = 20.9 Hz, 1F, *p*-C*F*), -160.6 (m, 2F, *m*-C*F*), -160.7 (m, 2F, *m*-C*F*).

*4.3.14. [1-(2,6-diisopropylphenyl)-3-(1H,1H,2H, 2H-perfluorooctyl)-imidazolin-2-ylidene] gold chloride (**4a**).*

A mixture of the silver complex **2a** (101.1 mg, 0.125 mmol) and (SMe_2)AuCl (44.4 mg, 0.15 mmol) in CH_2Cl_2 (25 mL) was stirred at room temperature for 6 h in the dark. After filtration, activated carbon was added to the filtrate and the mixture was filtered through Celite. The volatiles were then removed under reduced pressure to afford complex **4a** as a brown solid (53 mg, 48%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.54 (t, *J* = 7.8 Hz, 1H, C*H*$_{arom}$), 7.31 (d, *J* = 7.9 Hz, 2H, C*H*$_{arom}$), 7.27 (br s, 1H, C*H*$_{imid}$), 7.02 (br s, 1H, C*H*$_{imid}$), 4.63 (t, *J* = 6.7 Hz, 2H, C*H*$_2$CH$_2$(CF$_2$)$_5$CF$_3$), 2.89 (m, 2H, CH$_2$C*H*$_2$(CF$_2$)$_5$CF$_3$), 2.37 (hept, *J* = 6.9 Hz, 2H, C*H*(CH$_3$)$_2$), 1.27 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.12 (d, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 173.9 (N*C*N), 146.3 (*C*H$_{arom}$), 134.7 (*C*H$_{arom}$), 131.2 (*C*H$_{arom}$), 125-108 (m, 5C, *C*F$_2$, *C*F$_3$),124.8 (*C*H$_{arom}$), 124.2 (*C*H$_{imid}$), 121.7 (*C*H$_{imid}$), 44.2 (*C*H$_2$CH$_2$(CF$_2$)$_5$CF$_3$), 32.8 (t, $^2J_{C\text{-}F}$ = 21 Hz, CH$_2$*C*H$_2$(CF$_2$)$_5$CF$_3$), 28.9 (*C*H(CH$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$).^{19}F{^{1}H} NMR (376.6 MHz, CD_2Cl_2): δ -81.2 (t, $^3J_{F\text{-}F}$ = 10.0 Hz, 3F), -113.8 (m, 2F), -122.1 (br s, 2F), -123.1 (br s, 2F), -123.6 (brs, 2F), -126.4 (m, 2F).

*4.3.15. [1-(2,6-diisopropylphenyl)-3-((perfluoro-phenyl)methyl)-imidazolin-2-ylidene] gold chloride (**4b**).*

A mixture of the silver complex **2b** (556.2 mg, 0.93 mmol) and (SMe_2)AuCl (329.7 mg, 1.12 mmol) in CH_2Cl_2 (70 mL) was stirred for 3 h at room temperature. Following the above work-up procedure, **4b** was obtained as a brown solid (323 mg, 60%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.53 (t, *J* = 7.5 Hz, 1H, C*H*$_{arom}$), 7.30 (d, *J* = 7.8 Hz, 2H, C*H*$_{arom}$), 7.21 (br s, 1H, C*H*$_{imid}$), 7.02 (brs, 1H, C*H*$_{imid}$), 5.62 (s, 2H, C*H*$_2$C$_6$F$_5$), 2.36 (hept, *J* = 6.8 Hz, 2H, C*H*(CH$_3$)$_2$), 1.26 (d, *J* = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 1.11 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 174.9 (N*C*N), 148-137 (m, 5C, *C*F$_{arom}$), 146.3 (*C*H$_{arom}$), 134.5 (*C*H$_{arom}$), 131.2 (*C*H$_{arom}$), 124.8 (*C*H$_{arom}$), 124.7 (*C*H$_{imid}$), 120.9 (*C*H$_{imid}$), 109.5 (t, $^2J_{C\text{-}F}$ = 17 Hz, *C*$_{ipso}$), 43.3 (*C*H$_2$C$_6$F$_5$), 28.9 (*C*H(CH$_3$)$_2$), 24.5 (CH(*C*H$_3$)$_2$), 24.4 (CH(*C*H$_3$)$_2$).^{19}F{^{1}H} NMR (376.6 MHz, CD_2Cl_2): δ -141.2 (m, 2F, *o*-C*F*), -152.1(t, $^3J_{F\text{-}F}$ = 21 Hz, 1F, *p*-C*F*), -161.0 (m, 2F, *m*-C*F*).

*4.3.16. [1-(perfluorophenyl)-3-((perfluorophenyl) methyl)-imidazolin-2-ylidene] gold chloride (**4c**).*

Following the procedure described for **4b**, and starting from **2c** (50 mg, 0.08 mmol) and (SMe_2)AuCl (29.5 mg, 0.1 mmol) in CH_2Cl_2 (15 mL), **4c** was isolated as a white solid (26 mg, 48%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.33 (br s, 1H, C*H*$_{imid}$), 7.20 (br s, 1H, C*H*$_{imid}$), 5.61 (s, 2H, C*H*$_2$C$_6$F$_5$). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 176.4 (N*C*N), 147-136 (m, 10 C, *C*F$_{arom}$), 123.4 (*C*H$_{imid}$), 121.8 (*C*H$_{imid}$), 114.0 (m, *C*$_{ipso}$), 108.1 (m, *C*$_{ipso}$), 42.9 (*C*H$_2$C$_6$F$_5$). ^{19}F{^{1}H} NMR (470.2 MHz, CD_2Cl_2): δ -140.2 (d, $^3J_{F\text{-}F}$ = 14.0 Hz, 2F, *o*-C*F*), -144.7 (d, $^3J_{F\text{-}F}$ = 18.6 Hz, 2F, *o*-C*F*), -149.7 (t, $^3J_{F\text{-}F}$ = 23.8 Hz, 1F, *p*-C*F*), -151.3 (t, $^3J_{F\text{-}F}$ = 20.8 Hz, 1F, *p*-C*F*), -159.8 (m, 2F, *m*-C*F*), -160.5 (m, 2F, *m*-C*F*).

*4.3.17. 1,3-bis-[2,6-diisopropyl-4-(3,3,4,4,5,5,6,6, 7,7,8,8,8-tridecafluorooctyl)phenyl]-imidazolin-2-ylidene] gold chloride (**4d**)*

In a Schlenk, ligand **1d** (600 mg, 0.537 mmol), (SMe_2)AuCl (158 mg, 0.537 mmol) and K_2CO_3 (1.611 mmol, 223 mg) were dissolved in dry acetone (10 mL) under argon atmosphere. The resulting violet suspension was stirred at 60 ºC. After 24 h, the solvent was evaporated and the crude was suspended in CH_2Cl_2 (10 mL). The violet suspension was filtered through a silica pad and washed with CH_2Cl_2 (10 mL). The colorless organic fraction was evaporated to yield a white solid which was next dissolved in CD_2Cl_2 (2 mL) and filtered again through a silica pad. The CD_2Cl_2 solution was layered with pentane (3 mL) and coled at -20 °C. After 1 h, a white crystalline solid precipitated which was separated by decantation and washed with pentane (3 x 1 mL) to yield the title complex as a white crystalline solid. The organic fraction was evaporated and the process was repeated to obtain more fractions of the pure complex. After repeating the process four times, the titled complex was obtained as a crystalline white solid (520.8 mg, 74%). Single crystals were obtained by diffusion of pentane to a CH_2Cl_2 solution of the complex. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.16 (s, 2H), 7.13 (s, 4H), 3.06 – 2.98 (m, 4H), 2.63 – 2.47 (m, 8H), 1.36 (d, *J* = 6.9 Hz, 12H), 1.24 (d, *J* = 6.9 Hz, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) *δ* 175.6, 146.1, 141.7, 132.7, 124.3, 123.2, 121.0 – 119.6 (m), 118.8 – 117.6 (m), 116.5 – 115.6 (m), 114.3 – 112.1 (m), 111.7 – 109.9 (m), 109.4 – 107.9 (m), 32.7 (t, $J_{C\text{-}F}$ = 22.2 Hz), 28.9, 26.7 (t, $J_{C\text{-}F}$ = 4.3 Hz), 24.4, 24.0. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$*) δ* -80.85 (t, $J_{F\text{-}F}$ = 10 Hz, 6F), -114.51 – -114.85 (m, 4F), -121.22 – -122.26 (m, 4F), -122.88 (br s, 4F), -123.08 – -124.00 (m, 4F), -125.70 – -126.79 (m, 4F). HRMS (ESI+) Calc. for $C_{43}H_{42}AuClF_{26}N_2Na$ $[M+Na]^+$: 1335.2179. Found:

1335.2161. Elemental Analysis calculated for $C_{43}H_{42}AuClF_{26}N_2$: C, 39.33; H, 3.22; N, 2.13. Found: C, 39.10; H, 3.08; N, 2.29.

*4.3.18. Synthesis of gold complex **5d.***

In a Schlenk flask, silver triflimide (26 mg, 0.067 mmol) was suspended in CH_2Cl_2 under exclusion of light and argon atmosphere. Then a solution of complex **4d** (80 mg, 0.061 mmol) in CH_2Cl_2 was added in one portion to the previous suspension. The resulting mixture was stirred for 15 min at room temperature and opened up to air. It was subsequently filtered through a pad of cotton/celite/cotton. The solvent was evaporated to obtain a pale yellow solid which was dissolved in the minimum amount of CH_2Cl_2, layered with hexane and kept at -20 ºC for 1 h. Complex **5d** precipitated as a white solid that was separated by decantation (84.6 mg, 89%). X-ray quality crystals were obtained by diffusion of hexane into a CH_2Cl_2 solution of the complex. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 2H), 7.16 (s, 4H), 3.07 – 2.95 (m, 4H), 2.49 (h, J_{H-H} = 6.8 Hz, 4H), 2.44 – 2.36 (m, 4H), 1.33 (d, J_{H-H} = 6.8 Hz, 12H), 1.25 (d, J_{H-H} = 6.8 Hz, 12H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 169.1, 146.8, 142.7, 132.8, 124.8, 124.4, 122.1 – 120.2 (m), 118.8 (q, J_{C-F} = 32.8 Hz), 116.6 (t, J_{C-F} = 32.7 Hz), 113.1 – 114.3 (m), 112.3 – 111.3 (m), 111.2 – 110.5 (m), 110.1 – 108.6 (m), 33.5 (t, J_{C-F} = 22.0 Hz), 29.5, 27.2 (t, J_{C-F} = 4.3 Hz), 24.6, 24.2.^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -76.22 (s, 6F), -80.72 – -81.00 (m, 6F), -114.67 (t, J_{F-F} = 13.8 Hz, 4F), -121.66 – -122.23 (m, 4F), -122.93 (br s, 4F), -123.36 – -123.98 (m, 4F), -125.98 – -126.49 (m, 4F). HRMS (ESI+) Calc. for $C_{43}H_{42}AuF_{26}N_2$ [M-$NS_2O_4C_2F_6$]$^+$: 1277.2593. Found: 1277.2580.

*4.3.19. Synthesis of gold complex **6b.***

Silver hexafluoroantimonate (68.7 mg, 0.2 mmol) was suspended in CH_2Cl_2 under exclusion of light and argon atmosphere. A solution of complex **4b** (128.4 mg, 0.2 mmol) and trimethoxybenzonitrile (38.7 mg, 0.2 mmol) in CH_2Cl_2 was added in one portion to the previous suspension. The resulting mixture was stirred for 5 minutes at room temperature and opened up to air. It was subsequently filtered through a pad of cotton/celite/cotton. The solvent was evaporated to yield the titled complex as an orange solid (145.5 mg, 70%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (br s, 1H), 7.54 (d, J_{H-H} = 7.8 Hz, 1H), 7.32 (d, J_{H-H} = 7.8 Hz, 2H), 7.10 (br s, 1H), 6.12 (br s, 2H), 5.70 (br s, 2H), 3.93 (br s, 9H), 2.36 (hept, J_{H-H} = 6.8 Hz, 2H), 1.27 (d, J_{H-H} = 6.8 Hz, 6H), 1.17 (d, J_{H-H} = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 166.5, 147.2 (ddt, J_{C-F} = 11.7, 8.0, 4.1 Hz), 146.4, 145.2 (ddt, J_{C-F} = 11.7, 8.0, 4.1 Hz), 144.1 – 143.6 (m), 141.8 (td, J_{C-F} = 13.3, 6.7 Hz), 139.6 (td, J_{C-F} = 14.3, 12.2, 5.0 Hz), 137.6 (td, J_{C-F} = 16.3, 15.5, 5.0 Hz), 134.1, 131.7, 131.2, 126.0, 125.8, 125.1, 124.7, 123.1, 121.6, 119.4, 91.6, 91.0, 43.6, 30.3, 29.0, 28.9, 24.6, 24.5. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -140.37 – -140.96 (m, 2F), -150.84 – -151.52 (m, 1F), -159.90 – -160.61 (m, 2F). HRMS (ESI+) Calc. for $C_{32}H_{32}AuF_5N_3O_3$ [M-SbF_6]$^+$: 798.2024. Found: 798.2025.

*4.3.20. Synthesis of gold complex **6c.***

Silver hexafluoroantimonate (17.2 mg, 0.05 mmol) was suspended in CH_2Cl_2 under exclusion of light and argon atmosphere. Afterwards, a solution of complex **4c** (32.4 mg, 0.05 mmol) and trimethoxybenzonitrile (10.63 mg, 0.05 mmol) in CH_2Cl_2 was added in one portion to the previous suspension. The resulting mixture was stirred for 5 minutes at room temperature and opened up to air. It was subsequently filtered through a pad of cotton/celite/cotton. The resulting mixture was concentrated and layered with diethyl ether. After cooling for 1h at -20 ºC, complex **6c** was separated by decantation as a white solid (49 mg, 94%).^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.57 (d, J_{H-H} = 2.1 Hz, 1H), 7.39 (d, J_{H-H} = 2.2 Hz, 1H), 6.15 (s, 2H), 5.63 – 5.60 (m, 2H), 3.93 (s, 6H), 3.92 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 169.8, 168.5, 166.6, 147.4 – 147.0 (m), 145.2 (d, J_{C-F} = 5.0 Hz), 144.9 – 144.5 (m), 144.4 – 143.8 (m), 143.3 – 142.9 (m), 142.9 – 142.5 (m), 142.3 – 141.8 (m), 140.1 – 139.3 (m), 138.1 – 137.1 (m), 125.4 (d, J_{C-F} = 5.0 Hz), 124.2, 119.6, 114.1, 109.1 – 108.2 (m), 91.7, 78.2 – 77.6 (m), 57.2, 56.9, 43.9.^{19}F{^{1}H} NMR (376 MHz, CD_2Cl_2) δ -139.99 – -140.63 (m, 2F), -144.51 – -145.01 (m, 2F), -149.22 – -149.45 (m, 1F), -150.80 – -1561.18 (m, 1F), -159.36 – -159.62 (m, 2F), -160.37 – -160.61 (m, 2F). HRMS (MALDI) Calc. for $C_{26}H_{15}AuF_{10}N_3O_3$ [M-SbF_6]$^+$: 804.0619. Found: 804.0486

*4.3.21. Synthesis of gold complex **6d.***

In a Schlenk, silver hexafluoroantimonate (39.2 mg, 0.114 mmol) was suspended in a mixture of CH_2Cl_2:CH_3CN (4:1) under exclusion of light and argon atmosphere. Afterwards, a solution of complex **4d** (150 mg, 0.114 mmol) in CH_2Cl_2:CH_3CN (4:1) was added in one pot to the previous suspension. The resulting mixture was stirred for 15 min at room temperature and opened up to air. It was subsequently filtered through a pad of cotton/celite/cotton. The

solvent was evaporated to obtain a yellow oil which was dried under high vacuum overnight to remove the excess of CH_3CN. The obtained yellow solid was dissolved in the minimum amount of CH_2Cl_2 and layered with pentane. The mixture was cooled at -20 ºC fridge until a yellow oil precipitated that was separated by decantation. Finally, the oil was dried under high vacuum overnight to yield the title complex as a white solid (169.1 mg, 95%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 2H), 7.19 (s, 4H), 3.12 – 3.01 (m, 4H), 2.57 – 2.40 (m, 8H), 2.35 (s, 3H), 1.34 (d, $J_{1H\text{-}1H}$ = 6.9 Hz, 12H), 1.27 (d, $J_{1H\text{-}1H}$ = 6.9 Hz, 12H.). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 166.8, 146.1, 142.7, 131.8, 124.9, 124.7, 120.5, 119.1 – 117.7 (m), 116.7 – 115.6 (m), 114.4 – 112.3 (m), 111.9 – 110.4 (m), 109.6 – 108.2 (m), 32.6 (t, $J_{C\text{-}F}$ = 22.1 Hz), 29.1, 26.9 (t, $J_{C\text{-}F}$ = 4.5 Hz), 24.1. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -80.85 (t, $J_{F\text{-}F}$ = 10.0 Hz, 6F), -114.19 – -114.64 (m, 2F), -121.53 – -122.23 (m, 2F), -122.89 (bs, 2F), -123.09 – -123.52 (m, 2F), -125.90 – -126.47 (m, 2F). HRMS (TOF-MS-ES+) Calc. for $C_{45}H_{45}AuF_{26}N_3$ $[M\text{-}SbF_6]^+$: 1318.2864. Found: 1318.2855.

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