Synthesis V. Dhayalan et al. Paper

Practical Synthesis of Chiral N-Heterocyclic Carbene Triazolium Salts Containing a Hydroxy Functional Handle

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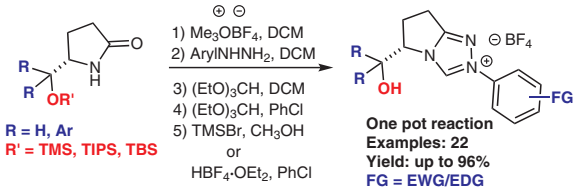

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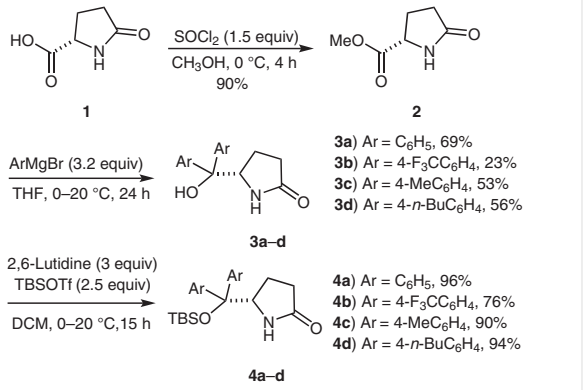
Abstract A library of functionalized chiral pyrrolidine-based N-heterocyclic carbene triazolium salts containing a hydroxy handle is prepared from readily accessible chiral (*S*)-pyroglutamic acid in eight steps. This improved synthetic protocol affords increased yields for known structures and 18 new NHCs are prepared by this method. The presence of a hydroxy handle offers potential for further functionalization and for non-covalent control over catalytic reactions in which the NHCs can serve as organocatalysts or ligands for organometallic catalysis.

Key words N-heterocyclic carbenes, triazolium salts, organocatalysis, organomagnesium reagents, arylhydrazines, benzyl alcohol, protecting groups, desilylation

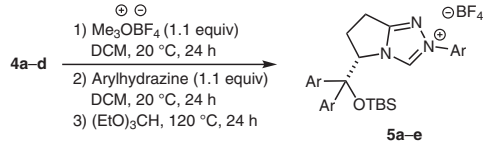
The introduction of functional groups capable of non-covalent interactions into the structure of organocatalysts is often beneficial for their selectivity.[1] For example, the highest enantioselectivity in the benzoin reaction afforded by an N-heterocyclic carbene (NHC) organocatalyst was the result of installing a hydroxy group in proximity to the catalytic center.[2] We have recently become interested in such motifs as secondary sphere non-covalent modifiers for organocatalysts; therefore, we sought to improve the synthetic protocol for the preparation of triazolium NHCs containing a hydroxy handle. In this article, we report a practical method for the preparation of functionalized chiral NHC triazolium salts in moderate to high yields. These chiral NHC salts are synthesized from readily accessible chiral (*S*)-pyroglutamic acid in eight steps. The described protocol enables the functionalization of pyrrolidine-based NHCs on either side of the carbene moiety using Grignard reagents and arylhydrazines. Synthetic protocols to modify the steric and electronic properties of NHC structures serve to tune selectivity, catalytic activity and basicity in organocatalytic reactions.[3] The presented synthetic protocol conserves this versatility, while introducing a hydroxy unit that adds a non-covalent component for controlling catalysis. The resulting NHCs can be further functionalized at the hydroxy handle to extend the library of catalysts by covalent and non-covalent modifiers.

Our synthetic protocol is based on previous literature reports with several modifications described below, which enabled the improvement of yields and the introduction of several new NHC scaffolds.[4] The protocol starts with commercially available (*S*)-pyroglutamic acid (**1**), which is converted into ester **2** in the presence of thionyl chloride ($SOCl_2$). By increasing the number of equivalents of $SOCl_2$, the time required for the reaction decreased to 4 hours compared to previous reports and the formation of by-products was mitigated.[5] In the subsequent Grignard reaction, the order of addition of phenylmagnesium bromide influenced the yield of the reaction and adding the ester to the Grignard reagent improved our yields by 10–15% for compound **3a**. The corresponding tertiary benzylic alcohol derivatives **3a–d** were obtained in up to 69% yield (Scheme



Scheme 1 Synthesis of functionalized pyrrolidinones **4a–d** via the addition of arylmagnesium reagents to pyroglutamic ester **2**

1). Selective silyl protection of the hydroxy functional group of **3a–d** with *tert*-butyldimethylsilyl triflate led to the corresponding silyl ethers **4a–d** in up to 96% yield. These silyl ethers were purified and subjected to a previously reported three-step, one-pot reaction affording chiral triazolium salts **5a–e** in up to 78% yield (Scheme 2).[5] It is noted that functionalized Grignard reagents were used, leading to three new chiral NHC triazolium salts.

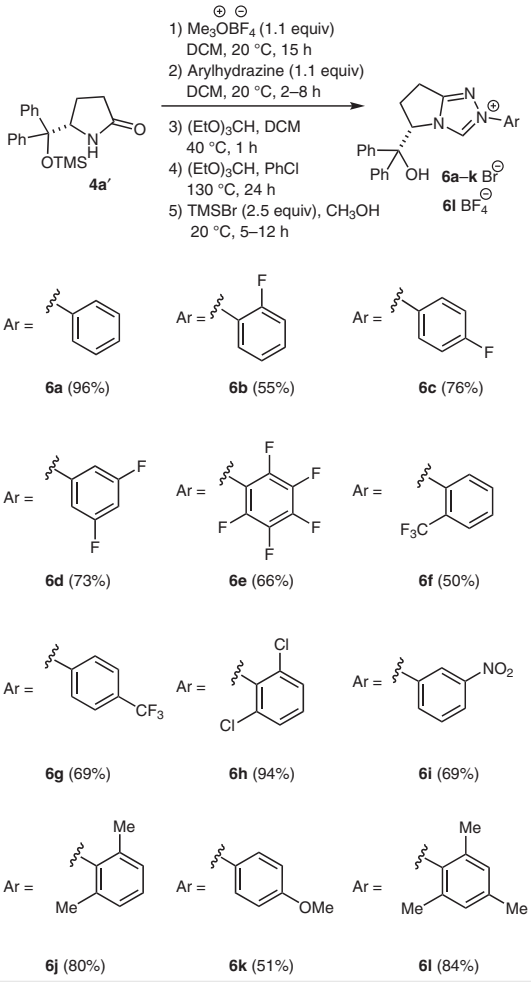


5a) Ar = C_6H_5; Ar = C_6H_5, 56%
5b) Ar = C_6H_5; Ar = C_6F_5, 44%
5c) Ar = 4-$F_3CC_6H_4$; Ar = C_6H_5, 78%
5d) Ar = 4-MeC_6H_4; Ar = C_6H_5, 59%
5e) Ar = 4-*n*-BuC_6H_4; Ar = C_6H_5, 70%

Scheme 2 Synthesis of chiral NHC triazolium salts **5a–e** by one-pot reactions of pyrrolidinones **4a–d** functionalized by Grignard reagents

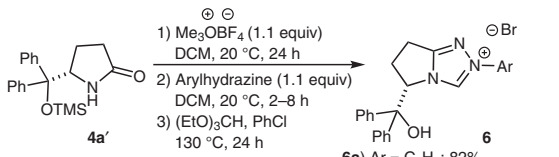
In order to obtain NHC salts with deprotected hydroxy groups, we opted for a more labile silyl protecting group following literature reports.[2b,4b] Trimethylsilyl (TMS)-protected pyrrolidinone **4a′** was prepared according the same procedure used for TBS protection (Scheme 1). Following the literature report, methylation of the TMS protected amide **4a′** was performed using Meerwein's reagent (trimethyloxonium tetrafluoroborate, $Me_3O^+BF_4^-$) to afford an imine intermediate (step 1), which was treated in situ with functionalized arylhydrazines to generate the corresponding coupled imine precursor (step 2). Serendipitously, we had started the next step by using DCM as the solvent instead of PhCl and obtained overall increased yields, therefore, we added one hour of reflux in DCM to the literature procedure. Following our modified protocol, triethyl orthoformate [$(EtO)_3CH$] was added in two batches, the first 8 equivalents were added in DCM (step 3), then DCM was removed by rotary evaporation, and the second batch was added in PhCl (step 4). Finally, deprotection of the TMS group (step 5) was performed according to the literature procedure using TMSBr (Scheme 3).

To ensure that the modified conditions (Scheme 3) using DCM in the third step of the reaction were improving the yields across the substrate scope, we selected several electron-donating and electron-withdrawing examples and performed the reaction in the absence of this step (Scheme 4). For all of these examples, the yields were improved by adding the DCM step (Scheme 3, step 3). The modified conditions afforded the chiral NHC salts in improved yields compared to previous reports and several new examples were prepared. We note that the improvement in yields was most remarkable for electron-withdrawing substituents on



Scheme 3 Synthesis of chiral NHC triazolium salts **6a–l** by a one-pot, five-step reaction sequence

the aryl ring compared to previous reports.[3a,4,5] Overall, fluorinated aryl substituents led to reduced yields compared to other substrates, even under our improved conditions.

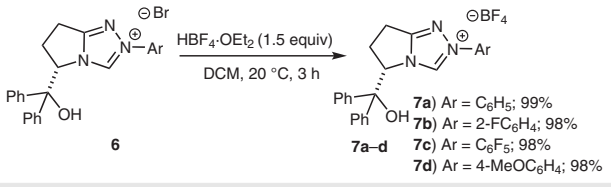


6a) Ar = C_6H_5; 82%
6e) Ar = C_6F_5; 30%
6h) Ar = 2,6-ClC_6H_3; 62%
6l) Ar = 2,4,6-$(Me)_3C_6H_2$; 71%

Scheme 4 Synthesis of chiral NHC triazolium salts **6** by a one-pot, four-step reaction sequence

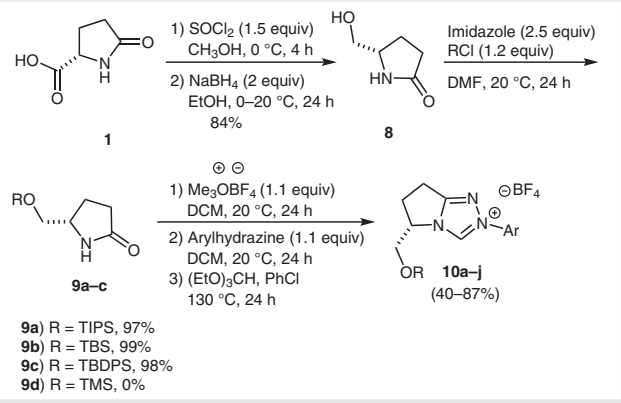
The silyl deprotection (step 5) was performed under similar conditions to previous literature reports, however, in these reports it was assumed that the counterion remained non-coordinating tetrafluoroborate (BF_4^-).[2b] By flu-

orine NMR analysis we noticed that in fact the characteristic BF_4^- peak does not appear; therefore, we assume that **6a–k** were obtained as bromine salts. As the counterion can influence catalytic properties, we tested whether it would be possible to exchange the counterion. The reaction of compounds **6a–b**, **e**, **k** with tetrafluoroboric acid diethyl ether complex (HBF_4·OEt_2) in DCM afforded the desired chiral NHC BF_4^- salts **7a–d** in excellent yields (Scheme 5).[4f]



Scheme 5 NHC triazolium counterion exchange

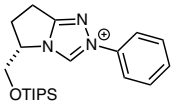
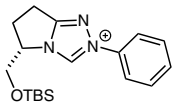
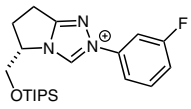
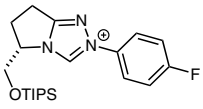
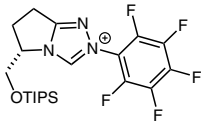
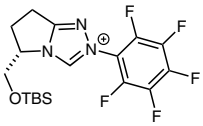
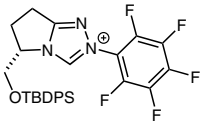
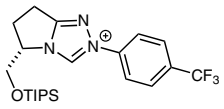
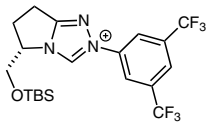
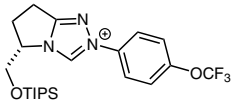
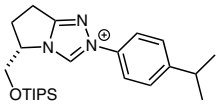
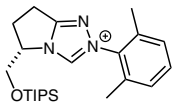
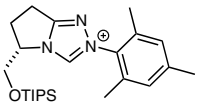
Hydroxy-functionalized pyrrolidinone **8** was prepared from commercially available (*S*)-pyroglutamic acid (**1**) in a one-pot reaction by esterification followed by reduction with $NaBH_4$ (Scheme 6). Following this reduction, a new family of chiral NHC triazolium salts with less steric hindrance near the hydroxy handle was prepared. Selective protection of the alcohol group was performed with different silylating reagents (RCl: TBSCl, TIPSCl, TBDPSCl, TMSCl) in excellent yields using a literature procedure.[6] The isolated silylated compounds **9a–c** were subjected to a three-step, one-pot procedure to afford the protected chiral NHC salts **10a–j** according to the literature (Scheme 6 and Table 1).[7]



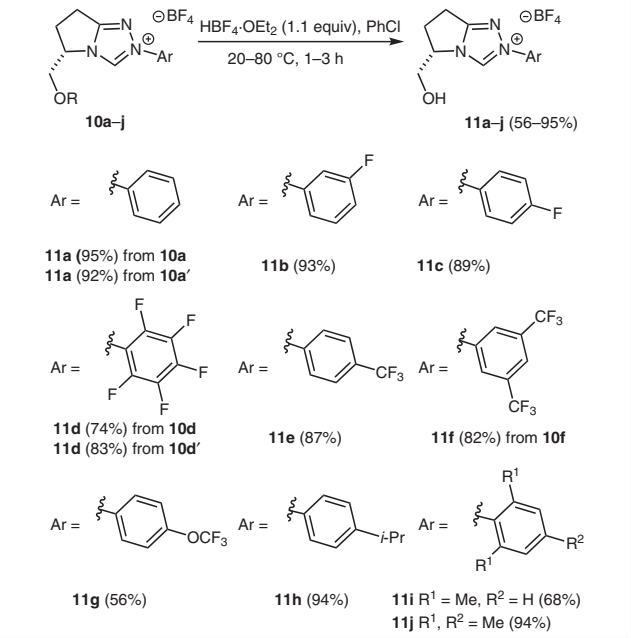
Scheme 6 Synthesis of NHC triazolium salts **10a–j** from (*S*)-pyroglutamic acid (**1**)

Because we had obtained improved yields for the previous set of substrates by adding a step, we tried our modified protocol for this new set. $(EtO)_3CH$ was added in two batches, the first 8 equivalents in DCM (according to Scheme 3, step 3) and the second batch was added in PhCl (according to Scheme 3, step 4). However, in this case, the yields were diminished using the modified protocol. Finally, the deprotection of the silyl groups on compounds **10a–j** (TIPS and TBS) efficiently proceeded with HBF_4·OEt_2 in dry PhCl, af-

Table 1 Substrate Scope of NHC Triazolium Salts **10a–j** Prepared from **9a–c**

Entry	R	$ArNHNH_2$	Product	10	Yield
1	**9a**	C_6H_5		**10a**	69%
2	**9b**	C_6H_5		**10a′**	70%
3	**9a**	3-FC_6H_4		**10b**	77%
4	**9a**	4-FC_6H_4		**10c**	84%
5	**9a**	C_6F_5		**10d**	56%
6	**9b**	C_6F_5		**10d′**	40%
7	**9c**	C_6F_5		**10d″**	48%
8	**9a**	4-$F_3CC_6H_4$		**10e**	67%
9	**9b**	3,5-$(F_3C)_2C_6H_3$		**10f**	66%
10	**9a**	4-$F_3COC_6H_4$		**10g**	61%
11	**9a**	4-*i*-PrC_6H_4		**10h**	73%
12	**9a**	2,6-$(Me)_2C_6H_3$		**10i**	73%
13	**9a**	2,4,6-$(Me)_3C_6H_2$		**10j**	87%

fording the desired chiral NHC triazolium salts **11a–j** in up to 95% yield (Scheme 7). By applying this protocol, nine new NHC scaffolds with hydroxy handles were prepared. We noticed that under the acidic conditions of the deprotection reaction and under column chromatography, NHC triazolium salts **11a–j** were prone to elimination; therefore, short reaction times and a purification process based on washing off impurities and recrystallization were opted for. This effect is most pronounced for electron-withdrawing substituents on the aryl ring.

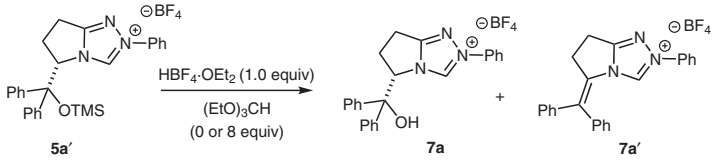


Scheme 7 Deprotection of NHC salts **10a–j** to afford **11a–j** with a free hydroxy group

To unravel the effect of DCM in our modified protocol for the synthesis of triazolium salts **6a–l**, we carried out several control experiments (Table 2). Based on plausible mechanisms for the one-pot NHC cyclization and previous literature reports, HBF_4 is a probable by-product of this reaction.[4f,p] Therefore, NHC catalyst **5a′** was subjected to this proposed by-product in the presence of different solvents to reveal potential side reactions. The labile TMS protecting group of **5a′** underwent smooth deprotection in the presence of $HBF_4{\cdot}OEt_2$ in DCM, affording **7a** (Table 2, entry 1). Under similar reaction conditions with PhCl as the solvent, **7a** underwent further elimination to afford a 41% yield of **7a′** (Table 2, entry 3), and over a longer reaction time **7a′** was isolated in 95% yield (Table 2, entry 5). In the presence of 8 equivalents of $(EtO)_3CH$ in DCM, **5a′** remained stable for 1 hour and could be recovered in quantitative yield. Under similar reaction conditions with PhCl as the solvent, a mixture of products was observed including a 1:3 ratio of **5a′** to **7a** along with additional unidentified by-products (Table 2, entry 4). From these control experiments, we conclude that using DCM as the solvent in the first hour of the reaction in the presence of $(EtO)_3CH$ can mitigate the cleavage of the TMS protecting group, the subsequent elimination process and additional side reactions. In contrast, due to the increased stability of the protecting groups used in the synthesis of **10a–j** (TIPS and TBS), DCM did not improve the observed yields for this new family of NHC triazolium salts.

In conclusion, a library of functionalized chiral pyrrolidine-based NHC triazolium salts containing a hydroxy handle has been prepared from readily accessible (*S*)-pyroglutamic acid in eight steps and with moderate to high reaction yields. These NHCs can serve as organocatalysts or ligands for organometallic catalysis, while the presence of a hydroxy handle could allow further functionalization and control of reactivity and selectivity through non-covalent interactions.

Table 2 Control Experiments[a]



Entry	$(EtO)_3CH$ (equiv)	Solvent	Temp (°C)	Time (h)	**5a′** (%)[b]	**7a** (%)[b]	**7a′** (%)[b]	Yield (%)[c]
1	–	DCM	40	1	0	100	0	92 (**7a**)
2	8	DCM	40	1	100	0	0	97 (**5a′**)
3	–	PhCl	110	1	0	59	41	–
4	8	PhCl	110	1	25	75	0	–
5	–	PhCl	110	15	0	0	100	95 (**7a′**)

[a] Unless otherwise stated, reactions were performed under a nitrogen atmosphere as follows: **5a′** (0.38 mmol, 1 equiv), $HBF_4{\cdot}OEt_2$ (0.38 mmol, 1 equiv), dry solvent (10 mL).
[b] The ratios of the three products were determined by ^1H NMR integration (see the Supporting Information).
[c] Yield of isolated product after recrystallization.

Reagents were purchased from commercial suppliers and used without further purification. $(EtO)_3CH$ was distilled before use. Anhydrous THF was prepared by adding molecular sieves (3 Å), that had been activated by microwave irradiation under vacuum (20% m/v), to commercial grade (AR) THF, which was used after 24–48 h. Similarly, activated molecular sieves (3 Å) were used for preparing the different anhydrous solvents used in this work: CH_3OH, DCM, Et_2O, DMF and PhCl. Unless otherwise stated, all operations were performed using high-vacuum standard Schlenk techniques under nitrogen/argon atmospheres. Thin-layer chromatography (TLC) analysis of reaction mixtures was performed using Merck silica gel 60 F254 TLC plates and samples were visualized under UV light or by staining with $KMnO_4$. Column chromatography was performed on Merck Silica Gel 60 Å (230–400 mesh). IR spectra were obtained using a Bruker Tensor II spectrophotometer equipped with a platinum attenuated total reflectance (ATR) accessory. Nuclear magnetic resonance (NMR) spectra were recorded using Bruker DPX400 or DMX500 instruments. The ^1H and ^{13}C chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to the residual solvent peaks ($CHCl_3$: δ_H = 7.26 ppm, δ_C = 77.0 ppm; DMSO: δ_H = 2.50 ppm, δ_C = 39.52 ppm; CH_3CN: δ_H = 1.94 ppm, δ_C = 1.32, 118.26 ppm). Multiplicities are reported using standard abbreviations. HRMS data were obtained using a Thermoscientific LTQU XL Orbitrap HRMS utilizing APCI (atmospheric-pressure chemical ionization).

(*S*)-Methyl 5-Oxopyrrolidine-2-carboxylate (2)

Precursor **2** was prepared according to a modified literature procedure.[5] A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with L-pyroglutamic acid (**1**) (10.00 g, 77 mmol, 1 equiv) in anhydrous CH_3OH (250 mL). $SOCl_2$ (8.30 mL, 116 mmol, 1.5 equiv) was added dropwise at 0 °C and the mixture then slowly warmed to 20 °C over 4 h. After full consumption of the starting material (TLC monitoring), CH_3OH was removed under reduced pressure and **2** was dried under high vacuum for 12 h. The crude product was used without further purification.

Phenylmagnesium Bromide

Phenylmagnesium bromide was prepared using a modified procedure based on a previous report.[8] A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with magnesium turnings (23.70 g, 975 mmol, 2.5 equiv) and heated with a heat gun under high vacuum for 5 min. After cooling to 0 °C, anhydrous THF (200 mL) was added and the magnesium turnings were activated using iodine (50 mg). The resulting suspension was cooled to 0 °C followed by the dropwise addition of bromobenzene (41.50 mL, 395 mmol, 1.0 equiv) in THF (50 mL). The reaction mixture was stirred at 0 °C for 30 min, warmed to 20 °C over 1 h and then heated at reflux for 2 h. The solids were allowed to settle and the yield of the insertion reaction was determined by iodometric titration of the supernatant solution (1.35 M in THF, 85%).[9]

(*S*)-5-(Hydroxydiphenylmethyl)pyrrolidin-2-one (3a)

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with phenylmagnesium bromide (183.00 mL, 248 mmol, 1.35 M in THF, 3.2 equiv). Methyl pyroglutamate **2** (11.10 g, 77.4 mmol, 1 equiv) in anhydrous THF (100 mL) was added dropwise at 0 °C and the mixture warmed to 20 °C and left to stir for 24 h (the duration of the reaction was initially determined by GC analysis until full consumption of the starting material was observed).[5] The reaction mixture was quenched with 3% aqueous HCl solution (600 mL). The organic layer was removed and the aqueous layer was washed with DCM (5 × 50 mL). The organic extracts were combined, dried over Na_2SO_4 and concentrated under reduced pressure. The product was purified by recrystallization with Et_2O (2 × 200 mL) to give pure **3a** (14.30 g, 69%).

4-(Trifluoromethyl)phenylmagnesium Bromide

4-(Trifluoromethyl)phenylmagnesium bromide was prepared using a modified procedure based on a previous report.[10] A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with magnesium turnings (11.70 g, 481 mmol, 2.5 equiv) and heated with a heat gun under high vacuum for 5 min. After cooling to 0 °C, anhydrous THF (100 mL) was added and the magnesium turnings were activated using iodine (50 mg). The suspension was cooled to 0 °C followed by the dropwise addition of 4-(trifluoromethyl)phenyl bromide (44 g, 195 mmol, 1.0 equiv) in THF (80 mL). The reaction mixture was stirred at 0 °C for 30 min, warmed to 20 °C over 1 h and then heated at reflux for 2 h. The solids were allowed to settle and the yield of the insertion reaction was determined by iodometric titration of the supernatant solution (0.6 M in THF, 56%).

(*S*)-5-{Hydroxy-bis[4-(trifluoromethyl)phenyl]methyl}pyrrolidin-2-one (3b)

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with methyl pyroglutamate **2** (5.5 g, 38.4 mmol, 1 equiv) in anhydrous THF (50 mL). 4-(trifluoromethyl)phenylmagnesium bromide (192.0 mL, 115 mmol, 0.6 M in THF, 3.0 equiv) was added dropwise at 0 °C and the mixture warmed to 20 °C and left to stir for 24 h. The reaction mixture was quenched with 3% aqueous HCl solution (300 mL). The organic layer was removed and the aqueous layer was washed with DCM (5 × 50 mL). The organic extracts were combined, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude residue was purified by flash column chromatography (silica gel pre-neutralized with triethylamine, *n*-hexane/EtOAc, 1:9) to furnish compound **3b**.

Yield: 3.50 g (23%); white solid.

^1H NMR (400 MHz, DMSO-d_6): δ = 1.73–1.82 (m, 1 H), 1.90–2.07 (m, 3 H), 4.88–4.90 (m, 1 H), 6.21 (s, 1 H), 7.40 (s, 1 H), 7.64–7.73 (m, 8 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.8, 29.9, 59.4, 78.8, 120.2 (q, *J* = 13.0 Hz), 124.3 (q, *J* = 270.0 Hz), 125.0 (q, *J* = 3.0 Hz), 127.0, 127.2, 127.3, 127.5 (q, *J* = 4.0 Hz), 128.1 (q, *J* = 40.0 Hz), 149.6, 177.7.

^{19}F NMR (376 MHz, DMSO-d_6): δ = –60.98 (s, 3 F), –60.91 (s, 3 F).

4-Methylphenylmagnesium Bromide

4-Methylphenylmagnesium bromide was prepared using a modified procedure based on a previous report.[11] A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with magnesium turnings (11.7 g, 481 mmol, 2.5 equiv) and heated with a heat gun under high vacuum for 5 min. After cooling to 0 °C, anhydrous THF (200 mL) was added and the magnesium turnings were activated using iodine (50 mg). The resulting suspension was cooled to 0 °C followed by the dropwise addition of *p*-tolyl bromide (33.4 g, 195 mmol, 1.0 equiv) in THF (30 mL). The reaction mixture was stirred at 0 °C for 30 min, warmed to 20 °C over 1 h and then heated at reflux for 2 h. The solids were allowed to settle and the yield of the insertion reaction was determined by iodometric titration of the supernatant solution (0.66 M in THF, 77%).

(*S*)-5-(Hydroxydi-*p*-tolylmethyl)pyrrolidin-2-one (3c)

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with methyl pyroglutamate **2** (5.5 g, 38.4 mmol, 1 equiv) in anhydrous THF (50 mL). 4-Methylmagnesium bromide (204.0 mL, 134 mmol, 0.66 M in THF, 3.5 equiv) was added dropwise at 0 °C and the mixture warmed to 20 °C and left to stir for 24 h. The reaction mixture was quenched with 3% aqueous HCl solution (300 mL). The organic layer was removed and the aqueous layer was washed with DCM (5 × 50 mL). The organic extracts were combined, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude residue was purified by flash column chromatography (silica gel was pre-neutralized with triethylamine, *n*-hexane/EtOAc, 1:9) to furnish compound **3c**.

Yield: 6.05 g (53%); white solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.76–1.93 (m, 4 H), 2.23 (s, 3 H), 2.25 (s, 3 H), 4.65–4.67 (m, 1 H), 5.58 (s, 1 H), 6.95 (s, 1 H), 7.07 (t, *J* = 8.0 Hz, 4 H), 7.31 (dd, *J* = 12.0, 8.0 Hz, 4 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.5, 20.6, 22.0, 29.9, 59.6, 78.4, 126.1, 126.4, 128.3, 128.4, 135.3, 142.8, 143.0, 177.4.

4-*n*-Butylphenylmagnesium Bromide

4-*n*-Butylphenylmagnesium bromide was prepared using a modified procedure based on a previous report.[12] A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with magnesium turnings (6.07 g, 250 mmol, 2.5 equiv) and heated with a heat gun under high vacuum for 5 min. After cooling to 0 °C, anhydrous THF (100 mL) was added and the magnesium turnings were activated using iodine (50 mg). The suspension was cooled to 0 °C followed by the dropwise addition of 4-(*n*-butyl)bromobenzene (21.3 g, 100 mmol, 1.0 equiv) in THF (20 mL). The reaction mixture was stirred at 0 °C for 30 min, warmed to 20 °C over 1 h and heated at reflux for 2 h. The solids were allowed to settle and the yield of the insertion reaction was determined by iodometric titration of the supernatant solution (0.67 M in THF, 80%).

(*S*)-5-[Bis(4-butylphenyl)(hydroxy)methyl]pyrrolidin-2-one (3d)

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with methyl pyroglutamate **2** (3.5 g, 24.5 mmol, 1 equiv) in anhydrous THF (50 mL). 4-*n*-Butylphenylmagnesium bromide (110.0 mL, 73 mmol, 0.67 M in THF, 3.0 equiv) was added dropwise at 0 °C and the mixture warmed to 20 °C and left to stir for 24 h. The reaction mixture was quenched with 3% aqueous HCl solution (300 mL). The organic layer was removed, and the aqueous layer was washed with DCM (5 × 50 mL). The organic extracts were combined, dried over Na_2SO_4 and concentrated under reduced pressure. The obtained crude residue was purified by flash column chromatography (silica gel was pre-neutralized with triethylamine, *n*-hexane/EtOAc, 1:9) to furnish compound **3d**.

Yield: 4.05 g (56%); white solid.

^{1}H NMR (400 MHz, CD_3OD): δ = 0.89–0.94 (m, 6 H), 1.28–1.39 (m, 4 H), 1.52–1.61 (m, 4 H), 1.96–2.12 (m, 4 H), 2.54–2.60 (m, 4 H), 4.76–4.79 (m, 1 H), 4.85 (s, 1 H), 7.09–7.16 (m, 4 H), 7.31–7.34 (m, 2 H), 7.38–7.41 (m, 2 H).

^{13}C NMR (100 MHz, CD_3OD): δ = 14.3, 23.2, 23.3, 31.1, 34.8, 36.1, 62.4, 80.1, 127.6, 129.0, 129.3, 142.7, 142.9, 143.1, 143.9, 181.9.

(*S*)-5-{[(*tert*-Butyldimethylsilyl)oxy]diphenylmethyl}pyrrolidin-2-one (4a)

Precursor **4a** was prepared using a previous literature report.[5] A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with alcohol **3a** (2.7 g, 10.2 mmol, 1 equiv) in anhydrous DCM (80 mL). 2,6-Lutidine (3.3 g, 31 mmol, 3 equiv) was slowly added at 0 °C and the mixture stirred for 5 min followed by the slow addition of *tert*-butyldimethylsilyl triflate (6.72 g, 26 mmol 2.5 equiv) at 0 °C. The reaction mixture was then stirred at 20 °C for 15 h, quenched with 0.5% aqueous HCl (100 mL) and extracted with DCM (5 × 30 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The obtained crude residue was purified by flash column chromatography (silica gel was pre-neutralized with triethylamine, *n*-hexane/EtOAc, 2:1) to furnish compound **4a** as a colorless solid (3.72 g, 96%).

(*S*)-5-[Diphenyl(trimethylsilyloxy)methyl]pyrrolidin-2-one (4a′)

Precursor **4a′** was prepared using a previous literature report.[5] A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with alcohol **3a** (14.00 g, 53 mmol, 1 equiv) in anhydrous DCM (400 mL). 2,6-Lutidine (18.40 mL, 159 mmol, 3 equiv) was slowly added at 0 °C and the mixture stirred for 5 min followed by the slow addition of trimethylsilyl triflate (24.00 mL, 133 mmol 2.5 equiv) at 0 °C. The reaction mixture was then stirred at 20 °C for 15 h, quenched with 0.5% aqueous HCl (200 mL) and extracted with DCM (5 × 60 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The obtained crude residue was purified by flash column chromatography (silica gel was pre-neutralized with triethylamine, *n*-hexane/EtOAc, 2:1) to furnish compound **4a′** as a colorless solid (16.50 g, 92%).

(*S*)-5-{[(*tert*-Butyldimethylsilyl)oxy]bis[4-(trifluoromethyl)phenyl]methyl}pyrrolidin-2-one (4b)

Precursor **4b** was prepared using a modified procedure based on previous reports. A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with alcohol **3b** (1.0 g, 2.5 mmol, 1 equiv) in anhydrous DCM (60 mL). 2,6-Lutidine (797 mg, 7.5 mmol, 3 equiv) was slowly added at 0 °C and the mixture stirred for 5 min followed by the slow addition of *tert*-butyldimethylsilyl triflate (1.63 g, 6.2 mmol, 2.5 equiv) at 0 °C. The reaction mixture was then stirred at 20 °C for 15 h, quenched with 0.5% aqueous HCl (60 mL) and extracted with DCM (5 × 20 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The obtained crude residue was purified by flash column chromatography (silica gel was pre-neutralized with triethylamine, *n*-hexane/EtOAc, 8:2) to furnish compound **4b**.

Yield: 970 mg (76%); white solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ = –0.46 (s, 3 H), –0.25 (s, 3 H), 0.76–0.89 (m, 1 H), 0.92 (s, 9 H), 1.75–1.92 (m, 2 H), 2.00–2.11 (m, 1 H), 4.75–4.78 (m, 1 H), 7.53 (t, *J* = 8.0 Hz, 4 H), 7.73 (t, *J* = 8.0 Hz, 4 H), 8.03 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = –3.6, –3.2, 18.5, 21.5, 25.9, 28.8, 58.2, 81.9, 120.0 (q, *J* = 13 Hz), 124.2, 124.2 (q, *J* = 270 Hz), 124.9 (q, *J* = 4 Hz), 128.3 (q, *J* = 32 Hz), 128.9, 129.6, 146.9, 147.5, 177.6.

^{19}F NMR (376 MHz, DMSO-d_6): δ = –61.03 (s, 3 F), –60.85 (s, 3 F).

(*S*)-5-{[(*tert*-Butyldimethylsilyl)oxy]di-*p*-tolylmethyl}pyrrolidin-2-one (4c)

Precursor **4c** was prepared using a modified procedure based on previous reports. A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with alcohol **3c** (2.4 g, 8.2 mmol, 1 equiv) in anhydrous DCM (80 mL). 2,6-Lutidine (2.6 g, 24.4 mmol, 3 equiv) was slowly added at 0 °C and the mixture stirred for 5 min followed by the slow addition of *tert*-butyldimethylsilyl triflate (5.3 g, 20 mmol, 2.5 equiv) at 0 °C. The reaction mixture was then stirred at 20 °C for 15 h, quenched with 0.5% aqueous HCl (60 mL) and extracted with DCM (5 × 30 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The obtained crude residue was purified by flash column chromatography (silica gel was pre-neutralized with triethylamine, *n*-hexane/EtOAc, 1:1) to furnish compound **4c**.

Yield: 3.01 g (90%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.40 (s, 3 H), –0.34 (s, 3 H), 0.93 (s, 9 H), 1.00–1.07 (m, 1 H), 1.82–1.88 (m, 1 H), 2.04–2.18 (m, 2 H), 2.34 (s, 3 H), 2.35 (s, 3 H), 4.58–4.60 (m, 1 H), 5.74 (s, 1 H), 7.12 (t, *J* = 8.0 Hz, 4 H), 7.17–7.18 (m, 2 H), 7.23 (d, *J* = 4.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –3.1, –3.0, 18.9, 21.2, 22.5, 26.2, 29.3, 60.2, 82.3, 128.5, 128.7, 128.8, 128.9, 137.6, 137.9, 139.5, 140.0, 178.8.

(*S*)-5-{[(*tert*-Butyldimethylsilyl)oxy]bis(4-butylphenyl)methyl}pyrrolidin-2-one (4d)

Precursor **4d** was prepared using a modified procedure based on previous reports. A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with alcohol **3d** (2.3 g, 6.1 mmol, 1 equiv) in anhydrous DCM (80 mL). 2,6-Lutidine (1.94 g, 18.2 mmol, 3 equiv) was slowly added at 0 °C and the mixture stirred for 5 min followed by the slow addition of *tert*-butyldimethylsilyl triflate (4.0 g, 15.1 mmol, 2.5 equiv) at 0 °C. The reaction mixture was then stirred at 20 °C for 15 h, quenched with 0.5% aqueous HCl (60 mL) and extracted with DCM (5 × 30 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The obtained crude residue was purified by flash column chromatography (silica gel was pre-neutralized with triethylamine, *n*-hexane/EtOAc, 2:1) to furnish compound **4d**.

Yield: 2.80 g (94%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.42 (s, 3 H), –0.36 (s, 3 H), 0.90–1.01 (m, 7 H), 0.92 (s, 9 H), 1.29–1.40 (m, 4 H), 1.55–1.64 (m, 4 H), 1.80–1.87 (m, 1 H), 2.03–2.21 (m, 2 H), 2.58–2.63 (m, 4 H), 4.58–4.61 (m, 1 H), 5.74 (s, 1 H), 7.10–7.13 (m, 4 H), 7.18–7.20 (m, 2 H), 7.24 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –3.2, –3.1, 14.1, 18.9, 22.4, 22.5, 26.2, 29.0, 33.6, 33.7, 35.3, 35.3, 60.2, 77.4, 82.2, 127.8, 128.2, 128.7, 128.9, 139.5, 140.1, 142.6, 143.0, 178.8.

Arylhydrazines from Arylhydrazine Salts (HCl); General Procedure

A 250 mL, single-neck, round-bottomed flask equipped with a magnetic stir bar and a septum was charged with the arylhydrazine salt (1.0 g) in Et_2O (50 mL) and 1 M aq NaOH (50 mL) was added at 0 °C. The reaction mixture was stirred at 0 °C for 1–2 h and then extracted with Et_2O (2 × 30 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The obtained residue was dried under high vacuum for 2–3 h to furnish the desired arylhydrazines.[4p]

TBS-Protected Pre-Catalysts 5 (Scheme 2); Typical Procedure 1 (TP1)

Catalysts **5a–e** were prepared based on previous reports.[3a,5]

(1) A dry, argon-flushed Schlenk flask equipped with a magnetic stir bar and a septum was charged with **4a–d** (10.0 mmol, 1 equiv) in anhydrous DCM (100 mL). $Me_3O^+BF_4^-$ (11.0 mmol, 1.1 equiv) was added and the reaction mixture was stirred at 20 °C for 24 h.

(2) The arylhydrazine (11.0 mmol, 1.1 equiv) was added to the solution and the mixture was stirred at 20 °C for 24 h. The solvent was removed in vacuo and the solid residue dried under high vacuum for 12 h. This product was then used in the next step without further purification.

(3) The solid from step 2 was dissolved in anhydrous $(EtO)_3CH$ (100 mL) and then stirred at 120 °C for 24 h under an argon atmosphere. The solvent was removed in vacuo and the residue dried under high vacuum for 3 h at 80 °C. The crude product was purified by flash column chromatography (silica gel, acetone/DCM) or by recrystallization from CH_3OH or Et_2O to give pure compounds **5a–e**.

(*S*)-5-{[(*tert*-Butyldimethylsilyl)oxy]diphenylmethyl}-2-phenyl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (5a)

NHC **5a**[5] was prepared according to TP1. (1) Compound **4a** (3.8 g, 10 mmol, 1 equiv), anhydrous DCM (100 mL) and $Me_3O^+BF_4^-$ (1.63 g, 11 mmol, 1.1 equiv). (2) Phenylhydrazine (1.3 g, 11 mmol, 1.1 equiv). (3) Anhydrous $(EtO)_3CH$ (100 mL). The crude product was recrystallized from CH_3OH to give the pure NHC compound **5a**.

Yield: 3.20 g (56%); white solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ = –0.37 (s, 3 H), –0.26 (s, 3 H), 0.91 (s, 9 H), 1.54–1.63 (m, 1 H), 2.77–2.94 (m, 2 H), 3.01–3.11 (m, 1 H), 6.00–6.02 (m, 1 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 7.38–7.47 (m, 8 H), 7.62–7.71 (m, 3 H), 7.81–7.86 (m, 2 H), 10.14 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = –3.6, –3.4, 18.5, 20.1, 26.0, 29.5, 65.6, 81.8, 121.9, 128.1, 128.3, 128.7, 128.7, 129.0, 129.1, 130.0, 130.8, 135.4, 138.5, 139.9, 140.0, 163.3.

(*S*)-5-{[(*tert*-Butyldimethylsilyl)oxy]diphenylmethyl}-2-(perfluorophenyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (5b)

NHC **5b**[4c] was prepared according to TP1. (1) Compound **4a** (3.8 g, 10 mmol, 1 equiv), anhydrous DCM (100 mL) and $Me_3O^+BF_4^-$ (1.63 g, 11 mmol, 1.1 equiv). (2) Pentafluorophenylhydrazine (2.18 g, 11 mmol, 1.1 equiv). (3) Anhydrous $(EtO)_3CH$ (100 mL). The crude product was recrystallized from EtOAc to give the pure NHC compound **5b**.

Yield: 2.90 g (44%); white solid.

^{1}H NMR (400 MHz, DMSO-d_6): δ = –0.41 (s, 3 H), –0.25 (s, 3 H), 0.90 (s, 9 H), 1.72–1.80 (m, 1 H), 2.81–2.87 (m, 1 H), 2.97–3.15 (m, 2 H), 6.11–6.13 (m, 1 H), 7.16–7.29 (m, 2 H), 7.40–7.52 (m, 8 H), 10.25 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = –3.6, –3.5, 18.4, 20.4, 25.9, 29.2, 66.5, 81.9, 110.0 (m), 128.0, 128.4, 128.6, 128.9, 129.2, 136.2 (m), 138.7 (m), 139.8, 139.8, 141.7 (m), 144.0 (m), 144.3, 164.4.

(*S*)-5-{[(*tert*-Butyldimethylsilyl)oxy]bis[4-(trifluoromethyl)phenyl]methyl}-2-phenyl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]-triazol-2-ium Tetrafluoroborate (5c)

NHC **5c** was prepared according to TP1. (1) Compound **4b** (518 mg, 1.0 mmol, 1 equiv), anhydrous DCM (10 mL) and $Me_3O^+BF_4^-$ (163 mg, 1.1 mmol, 1.1 equiv). (2) Phenylhydrazine (119 mg, 1.1 mmol, 1.1

equiv). (3) Anhydrous $(EtO)_3CH$ (10 mL). The crude product was purified by flash column chromatography (silica gel, acetone/DCM, 20:80) and washed with Et_2O to give the pure NHC compound **5c**.

Yield: 550 mg (78%); white solid.

IR (diamond-ATR, neat): 610, 717, 775, 837, 875, 1015, 1069, 1124, 1166, 1324, 2858, 2933 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = –0.40 (s, 3 H), –0.21 (s, 3 H), 0.92 (s, 9 H), 1.62–1.70 (m, 1 H), 2.80 (t, *J* = 12.0 Hz, 1 H), 2.92–3.11 (m, 2 H), 6.12 (dd, *J* = 8.0, 4.0 Hz, 1 H), 7.54–7.55 (m, 2 H), 7.65–7.73 (m, 5 H), 7.80 (d, *J* = 8.0 Hz, 2 H), 7.87 (t, *J* = 8.0 Hz, 4 H), 10.25 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = –3.7, –3.4, 18.5, 20.2, 25.9, 29.4, 64.9, 81.3, 121.3 (q, *J* = 270 Hz), 122.0, 125.4 (q, *J* = 3 Hz), 126.2 (q, *J* = 3 Hz), 128.0, 129.0, 129.4 (q, *J* = 32 Hz), 129.8, 129.9, 129.9, 130.9, 135.4, 138.8, 144.1, 144.3, 163.2.

^{19}F NMR (376 MHz, DMSO-d_6): δ = –148.33 (s, 4 F), –61.18 (s, 3 F), –61.05 (s, 3 F).

HRMS (ESI): *m*/*z* $[M - BF_4]^+$ calcd for $C_{32}H_{34}F_6N_3OSi$: 618.2370; found: 618.2331.

(*S*)-5-{[(*tert*-Butyldimethylsilyl)oxy]di-*p*-tolylmethyl}-2-phenyl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (5d)

NHC **5d** was prepared according to TP1. (1) Compound **4c** (1.23 g, 3.0 mmol, 1 equiv), anhydrous DCM (30 mL) and $Me_3O^+BF_4^-$ (488 mg, 3.3 mmol, 1.1 equiv). (2) Phenylhydrazine (357 mg, 3.3 mmol, 1.1 equiv). (3) Anhydrous $(EtO)_3CH$ (30 mL). The crude product was purified by flash column chromatography (silica gel, acetone/DCM, 20:80) and washed with Et_2O to give the pure NHC compound **5d**.

Yield: 1.05 g (59%); white solid.

IR (diamond-ATR, neat): 518, 584, 777, 834, 877, 1029, 1071, 1510, 1590, 2851, 2926 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = –0.37 (s, 3 H), –0.29 (s, 3 H), 0.90 (s, 9 H), 1.61–1.69 (m, 1 H), 2.33 (s, 3 H), 2.35 (s, 3 H), 2.77 (t, *J* = 12.0 Hz, 1 H), 2.86–2.92 (m, 1 H), 2.97–3.07 (m, 1 H), 5.94 (dd, *J* = 12.0, 4.0 Hz, 1 H), 7.14–7.21 (m, 4 H), 7.26–7.34 (m, 4 H), 7.64–7.70 (m, 3 H), 7.82 (d, *J* = 8.0 Hz, 2 H), 10.09 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = –3.5, –3.4, 18.4, 20.2, 20.6, 20.7, 25.9, 29.5, 65.7, 81.4, 121.9, 128.0, 128.7, 128.7, 129.4, 129.9, 130.8, 135.3, 136.9, 137.1, 138.0, 138.4, 163.3.

HRMS (ESI): *m*/*z* $[M - BF_4]^+$ calcd for $C_{32}H_{40}N_3OSi$: 510.2935; found: 510.2913.

(*S*)-5-{[(*tert*-Butyldimethylsilyl)oxy]bis(4-butylphenyl)methyl}-2-phenyl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (5e)

NHC **5e** was prepared according to TP1. (1) Compound **4d** (494 mg, 1.0 mmol, 1 equiv), anhydrous DCM (10 mL) and $Me_3O^+BF_4^-$ (163 mg, 1.1 mmol, 1.1 equiv). (2) Phenylhydrazine (119 mg, 1.1 mmol, 1.1 equiv). (3) Anhydrous $(EtO)_3CH$ (10 mL). The crude product was purified by flash column chromatography (silica gel, acetone/DCM, 10:90) to give the pure NHC compound **5e**.

Yield: 480 mg (70%); white solid.

IR (diamond-ATR, neat): 520, 687, 762, 777, 835, 881, 1018, 1055, 1253, 1465, 1511, 1592, 1698, 2857, 2928, 2955 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = –0.37 (s, 3 H), –0.28 (s, 3 H), 0.86–0.91 (m, 15 H), 1.25–1.35 (m, 4 H), 1.52–1.64 (m, 5 H), 2.25–2.57 (m, 4 H), 2.75 (t, *J* = 8.0 Hz, 1 H), 2.85–2.92 (m, 1 H), 2.99–3.09 (m, 1 H), 5.94 (dd, *J* = 8.0, 4.0 Hz, 1 H), 7.18–7.35 (m, 8 H), 7.65–7.71 (m, 3 H), 7.81 (d, *J* = 8.0 Hz, 2 H), 10.06 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = –3.6, –3.5, 13.7, 18.4, 20.1, 21.5, 21.6, 25.9, 29.5, 32.8, 32.9, 34.3, 66.0, 81.6, 121.9, 128.1, 128.6, 128.7, 130.0, 130.8, 135.3, 137.1, 138.3, 142.9, 143.2, 163.2.

HRMS (ESI): *m*/*z* $[M - BF_4]^+$ calcd for $C_{38}H_{52}N_3OSi$: 594.3874; found: 594.3857.

Deprotected Pre-Catalysts 6 (Scheme 3); Typical Procedure 2 (TP2)

NHCs **6a–l** were prepared using a modified procedure based on previous reports.[2b,4b]

(1) A dry, argon-flushed Schlenk flask equipped with a magnetic stir bar and a septum was charged with **4a′** (9.3 mmol, 1 equiv) in anhydrous DCM (60 mL). $Me_3O^+BF_4^-$ (10.2 mmol, 1.1 equiv) was added and the reaction mixture was stirred at 20 °C for 15 h.

(2) Arylhydrazine (10.2 mmol, 1.1 equiv) was added to the solution and the reaction mixture was stirred at 20 °C for 2–8 h. The solvent was removed in vacuo and the residue dried under high vacuum for 12 h. This product was used without further purification.

(3) The reaction mixture was dissolved in anhydrous DCM (80 mL) and $(EtO)_3CH$ (74 mmol, 8 equiv) was added. After refluxing this mixture for 1 h, the solvent was removed in vacuo and dried under high vacuum for 60 min.

(4) Anhydrous PhCl (80 mL) and $(EtO)_3CH$ (74 mmol, 8 equiv) were added and the reaction mixture was heated at reflux for 24 h under an argon atmosphere. The solvent was removed in vacuo and the residue dried under high vacuum for 12 h. The product was used without further purification.

(5) Anhydrous CH_3OH (300 mL) was added to the reaction flask followed by the addition of bromotrimethylsilane (TMSBr) (3.1 mL, 23 mmol, 2.5 equiv) dissolved in CH_3OH (30 mL). The reaction mixture was stirred at 20 °C for 5–12 h. The solvent was removed in vacuo and the residue dried under high vacuum for 3 h at 80 °C. The crude product was recrystallized from EtOAc/CH_3OH or was purified by column chromatography and washed with Et_2O to give the pure NHC compound **6a–l**. Care must be taken in running these columns as the products easily stick to the silica gel and decompose, thus they cannot be left on the column for prolonged periods of time and the chromatography should be performed expeditiously.

(*S*)-5-[Hydroxy(diphenyl)methyl]-2-phenyl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Bromide (6a)

NHC **6a**[2b] was prepared according to TP2. (1) Compound **4a′** (3.2 g, 9.3 mmol, 1 equiv), anhydrous DCM (60 mL) and $Me_3O^+BF_4^-$ (1.5 g, 10.2 mmol, 1.1 equiv). (2) Phenylhydrazine (1.1 g, 10.2 mmol, 1.1 equiv). (3) Anhydrous DCM (80 mL) and $(EtO)_3CH$ (12.3 mL, 74 mmol, 8 equiv). (4) Anhydrous PhCl (80 mL) and $(EtO)_3CH$ (12.3 mL, 74 mmol, 8 equiv). (5) Anhydrous CH_3OH (300 mL) and TMSBr (3.0 mL, 23 mmol, 2.5 equiv) dissolved in CH_3OH (30 mL). The crude product was recrystallized from CH_3OH/Et_2O (1:9) to give the pure NHC compound **6a**.

Yield: 4.0 g (96%); white solid.

IR (diamond-ATR, neat): 500, 617, 644, 685, 702, 755, 975, 1002, 1065, 1173, 1206, 1378, 1448, 1519, 1590, 2961, 3067, 3153 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.57–2.62 (m, 1 H), 2.90–3.02 (m, 2 H), 3.10–3.18 (m, 1 H), 6.18 (d, *J* = 8.0 Hz, 1 H), 6.55 (s, 1 H), 7.28 (t, *J* = 8.0 Hz, 1 H), 7.34–7.38 (m, 3 H), 7.44 (t, *J* = 8.0 Hz, 2 H), 7.53 (d, *J* = 8.0 Hz, 2 H), 7.59–7.68 (m, 5 H), 7.79 (d, *J* = 8.0 Hz, 2 H), 9.60 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.3, 29.9, 67.1, 79.0, 121.4, 126.0, 126.1, 127.5, 127.8, 128.4, 128.9, 130.1, 130.6, 135.3, 137.7, 143.3, 143.5, 163.6.

HRMS (ESI): *m*/*z* [M – Br]$^+$ calcd for $C_{24}H_{22}N_3O$: 368.1757; found: 368.1750.

(*S*)-5-[Hydroxy(diphenyl)methyl]-2-phenyl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Bromide(6a); Alternative Protocol without DCM Treatment

NHC **6a** was prepared according to TP2 but without treatment with DCM and $(EtO)_3CH$ (8 equiv) (see Scheme 4). (1) Compound **4a′** (3.2 g, 9.3 mmol, 1 equiv), anhydrous DCM (60 mL) and $Me_3O^+BF_4^-$ (1.5 g, 10.2 mmol, 1.1 equiv). (2) Phenylhydrazine (1.1 g, 10.2 mmol, 1.1 equiv). (3) Anhydrous PhCl (80 mL) and $(EtO)_3CH$ (12.3 mL, 74 mmol, 8 equiv). (4) Anhydrous CH_3OH (300 mL) and TMSBr (3.0 mL, 23 mmol, 2.5 equiv) dissolved in CH_3OH (30 mL). The crude product was recrystallized from CH_3OH/Et_2O (1:9) to give the pure NHC compound **6a**.

Yield: 3.53 g (82%); white solid.

(*S*)-2-(2-Fluorophenyl)-5-(hydroxydiphenylmethyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Bromide (6b)

NHC **6b** was prepared according to **TP2**. (1) Compound **4a′** (3.2 g, 9.3 mmol, 1 equiv), anhydrous DCM (60 mL) and $Me_3O^+BF_4^-$ (1.5 g, 10.2 mmol, 1.1 equiv). (2) 2-Fluorophenylhydrazine (1.28 g, 10.2 mmol, 1.1 equiv). (3) Anhydrous DCM (80 mL) and $(EtO)_3CH$ (12.3 mL, 74 mmol, 8 equiv). (4) Anhydrous PhCl (80 mL) and $(EtO)_3CH$ (12.3 mL, 74 mmol, 8 equiv). (5) Anhydrous CH_3OH (300 mL) and TMSBr (3.0 mL, 23 mmol, 2.5 equiv) dissolved in CH_3OH (30 mL). The crude product was recrystallized from CH_3OH/EtOAc (1:9) and washed with Et_2O to give the pure NHC compound **6b**.

Yield: 2.40 g (55%); white solid.

IR (diamond-ATR, neat): 621, 640, 660, 697, 751, 764, 779, 968, 1034, 1067, 1111, 1201, 1232, 1522, 1599, 3057, 3175, 3197, 3247 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.62–2.67 (m, 1 H), 2.93–3.04 (m, 2 H), 3.14–3.20 (m, 1 H), 6.23 (dd, *J* = 8.0, 4.0 Hz, 1 H), 6.64 (s, 1 H), 7.29 (t, *J* = 8.0 Hz, 1 H), 7.33–7.39 (m, 3 H), 7.43 (t, *J* = 8.0 Hz, 2 H), 7.48–7.54 (m, 3 H), 7.58–7.64 (m, 3 H), 7.69–7.73 (m, 1 H), 7.77 (td, *J* = 8.0, 2 Hz, 1 H), 9.34 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.3, 29.6, 67.5, 78.9, 117.2 (d, *J* = 14.0 Hz), 123.4 (d, *J* = 7.0 Hz), 125.7, 126.0, 126.5, 127.5, 127.8, 128.4, 128.8, 133.1 (d, *J* = 7.0 Hz), 140.7, 143.2, 143.4, 153.3, 155.3, 163.5.

^{19}F NMR (376 MHz, DMSO-d_6): δ = –123.19 (s, 1 F).

HRMS (ESI): *m*/*z* [M – Br]$^+$ calcd for $C_{24}H_{21}FN_3O$: 386.1663; found: 386.1649.

(*S*)-2-(4-Fluorophenyl)-5-(hydroxydiphenylmethyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Bromide (6c)

NHC **6c** was prepared according to TP2. (1) Compound **4a′** (1.05 g, 3.1 mmol, 1 equiv), anhydrous DCM (20 mL) and $Me_3O^+BF_4^-$ (503 mg, 3.4 mmol, 1.1 equiv). (2) 4-Fluorophenylhydrazine (428 mg, 3.4 mmol, 1.1 equiv). (3) Anhydrous DCM (30 mL) and $(EtO)_3CH$ (4.0 mL, 25 mmol, 8 equiv). (4) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (4.0 mL, 25 mmol, 8 equiv). (5) Anhydrous CH_3OH (100 mL) and TMSBr (1.0 mL, 8.0 mmol, 2.5 equiv) dissolved in CH_3OH (10 mL). The crude product was purified by flash column chromatography (silica gel, acetone/CH_3OH, 200:20), recrystallized from CH_3OH/EtOAc (1:9) and washed with Et_2O to give the pure NHC compound **6c**.

Yield: 1.12 g (76%); white solid

IR (diamond-ATR, neat): 521, 615, 640, 705, 734, 752, 839, 1151, 1204, 1238, 1382, 1449, 1501, 1522, 1583, 2964, 3060, 3175, 3272 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.54–2.61 (m, 1 H), 2.89–3.00 (m, 2 H), 3.09–3.17 (m, 1 H), 6.18 (d, *J* = 4.0 Hz), 6.54 (s, 1 H), 7.28 (t, *J* = 8.0 Hz, 1 H), 7.34–7.38 (m, 3 H), 7.44 (t, *J* = 8.0 Hz, 2 H), 7.51–7.60 (m, 6 H), 7.83–7.87 (m, 2 H), 9.34 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.2, 29.9, 67.1, 79.0, 117.1 (d, *J* = 24.0 Hz), 124.3 (d, *J* = 9.0 Hz), 126.1 (d, *J* = 15.0 Hz), 127.4, 127.8, 128.4, 128.9, 131.8 (d, *J* = 2.0 Hz), 138.0, 143.3, 143.5, 161.4, 163.6, 163.9.

^{19}F NMR (376 MHz, DMSO-d_6): δ = –109.92 (s, 1 F).

HRMS (ESI): *m*/*z* [M – Br]$^+$ calcd for $C_{24}H_{21}FN_3O$: 386.1663; found: 386.1644.

(*S*)-2-(3,5-Difluorophenyl)-5-(hydroxydiphenylmethyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Bromide (6d)

NHC **6d** was prepared according to TP2. (1) Compound **4a′** (1.05 g, 3.1 mmol, 1 equiv), anhydrous DCM (20 mL) and $Me_3O^+BF_4^-$ (503 mg, 3.4 mmol, 1.1 equiv). (2) 3,5-Difluorophenylhydrazine (490 mg, 3.4 mmol, 1.1 equiv). (3) Anhydrous DCM (30 mL) and $(EtO)_3CH$ (4.0 mL, 25 mmol, 8 equiv). (4) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (4.0 mL, 25 mmol, 8 equiv). (5) Anhydrous CH_3OH (100 mL) and TMSBr (1.0 mL, 8.0 mmol, 2.5 equiv) dissolved in CH_3OH (10 mL). The crude product was recrystallized from EtOAc and washed with Et_2O to give the pure NHC compound **6d**.

Yield: 1.10 g (73%); white solid.

IR (diamond-ATR, neat): 505, 615, 618, 625, 641, 655, 672, 694, 704, 732, 748, 849, 864, 882, 984, 1128, 1175, 1438, 1589, 1615, 2954, 3060, 3178, 3230, 3331 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.55–2.61 (m, 1 H), 2.80–2.88 (m, 1 H), 2.93–3.02 (m, 1 H), 3.09–3.15 (m, 1 H), 6.16 (d, *J* = 8.0 Hz, 1 H), 6.58 (s, 1 H), 7.28 (t, *J* = 8.0 Hz, 1 H), 7.33–7.38 (m, 3 H), 7.42–7.50 (m, 4 H), 7.57 (d, *J* = 8.0 Hz, 2 H), 7.63 (tt, *J* = 8.0, 4.0 Hz, 1 H), 7.79 (d, *J* = 4.0 Hz, 2 H), 9.89 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.2, 30.0, 67.4, 79.0, 105.6 (d, *J* = 11.0 Hz), 105.7 (d, *J* = 30.0 Hz), 106.2 (t, *J* = 25.0 Hz), 126.2 (d, *J* = 14.0 Hz), 127.5, 127.9, 128.4, 129.0, 137.0 (t, *J* = 14.0 Hz), 138.8, 143.3 (d, *J* = 14.0 Hz), 161.3, 163.7 (d, *J* = 14.0 Hz), 163.8.

^{19}F NMR (376 MHz, DMSO-d_6): δ = –106.25 (s, 2 F).

HRMS (ESI): *m*/*z* [M – Br]$^+$ calcd for $C_{24}H_{20}F_2N_3O$: 404.1569; found: 404.1551.

(*S*)-5-(Hydroxydiphenylmethyl)-2-pentafluorophenyl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Bromide (6e)

NHC **6e**[2b] was prepared according to TP2. (1) Compound **4a′** (3.2 g, 9.3 mmol, 1 equiv), anhydrous DCM (60 mL) and $Me_3O^+BF_4^-$ (1.5 g, 10.2 mmol, 1.1 equiv). (2) Pentafluorophenylhydrazine (2.00 g, 10.2 mmol, 1.1 equiv). (3) Anhydrous DCM (80 mL) and $(EtO)_3CH$ (12.3 mL, 74 mmol, 8 equiv). (4) Anhydrous PhCl (80 mL) and $(EtO)_3CH$ (12.3 mL, 74 mmol, 8 equiv). (5) Anhydrous CH_3OH (300 mL) and TMSBr (3.0 mL, 23 mmol, 2.5 equiv) dissolved in CH_3OH (30 mL). The crude product was recrystallized from EtOAc and washed with Et_2O. We noted that the catalyst contained EtOAc in most cases, which was removed

by dissolving the product in distilled THF and removing the solvent in vacuo. Finally, the product was washed with Et_2O to give the pure NHC compound **6e**.

Yield: 3.30 g (66%); white solid.

IR (diamond-ATR, neat): 610, 635, 678, 697, 739, 871, 972, 1002, 1069, 1375, 1448, 1510, 1522, 1542, 1595, 2954, 3142 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.64–2.70 (m, 1 H), 2.87–2.92 (m, 1 H), 2.99–3.09 (m, 1 H), 3.16–3.23 (m, 1 H), 6.19 (dd, *J* = 12.0, 4.0 Hz, 1 H), 6.80 (m, 1 H), 7.29–7.39 (m, 4 H), 7.42–7.48 (m, 4 H), 7.56 (d, *J* = 8.0 Hz, 2 H), 9.64 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.5, 29.7, 68.1, 78.8, 111.1 (m), 126.1, 127.7, 128.0, 128.5, 128.9, 136.2 (m), 138.7 (m), 141.2 (m), 142.9, 143.2, 143.5, 143.9 (m), 164.7.

HRMS (ESI): *m*/*z* [M – Br]$^+$ calcd for $C_{24}H_{17}F_5N_3O$: 458.1286; found: 458.1289.

(*S*)-5-(Hydroxydiphenylmethyl)-2-pentafluorophenyl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4] triazol-2-ium Bromide (6e); Alternative Protocol without DCM Treatment

NHC **6e** was prepared according to TP2 but without treatment with DCM and $(EtO)_3CH$ (8 equiv) (see Scheme 4). (1) Compound **4a′** (3.2 g, 9.3 mmol, 1 equiv), anhydrous DCM (60 mL) and $Me_3O^+BF_4^-$ (1.5 g, 10.2 mmol, 1.1 equiv). (2) Pentafluorophenylhydrazine (2.00 g, 10.2 mmol, 1.1 equiv). (3) Anhydrous PhCl (80 mL) and $(EtO)_3CH$ (12.3 mL, 74 mmol, 8 equiv). (4) Anhydrous CH_3OH (300 mL) and TMSBr (3.0 mL, 23 mmol, 2.5 equiv) dissolved in CH_3OH (30 mL). The crude product was recrystallized from EtOAc and washed with Et_2O. We noted that the catalyst contained EtOAc in most cases, which was removed by dissolving the product in distilled THF and removing the solvent in vacuo. Finally, the product was washed with Et_2O to give the pure NHC compound **6e**.

Yield: 1.51 g (30%); white solid.

(*S*)-5-(Hydroxydiphenylmethyl)-2-[2-(trifluoromethyl)phenyl]-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Bromide (6f)

NHC **6f** was prepared according to TP2. (1) Compound **4a′** (3.2 g, 9.3 mmol, 1 equiv), anhydrous DCM (60 mL) and $Me_3O^+BF_4^-$ (1.5 g, 10.2 mmol, 1.1 equiv). (2) 2-(Trifluoromethyl)phenylhydrazine (1.8 g, 10.2 mmol, 1.1 equiv). (3) Anhydrous DCM (80 mL) and $(EtO)_3CH$ (12.3 mL, 74 mmol, 8 equiv). (4) Anhydrous PhCl (80 mL) and $(EtO)_3CH$ (12.3 mL, 74 mmol, 8 equiv). (5) Anhydrous CH_3OH (300 mL) and TMSBr (3.0 mL, 23 mmol, 2.5 equiv) dissolved in CH_3OH (30 mL). The crude product was recrystallized from CH_3OH/acetone (1:9) and washed with Et_2O to give the pure NHC compound **6f**.

Yield: 2.40 g (50%); white solid.

IR (diamond-ATR, neat): 503, 627, 699, 758, 779, 1065, 1074, 1116, 1132, 1178, 1316, 1446, 1599, 2998, 3187 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.65–2.70 (m, 1 H), 2.79–2.85 (m, 1 H), 3.05–3.12 (m, 2 H), 6.16 (d, *J* = 8.0 Hz, 1 H), 6.72 (s, 1 H), 7.30–7.41 (m, 6 H), 7.47 (d, *J* = 4.0 Hz, 2 H), 7.53 (d, *J* = 8.0 Hz, 2 H), 7.77 (d, *J* = 8.0 Hz, 1 H), 7.93–8.01 (m, 2 H), 8.08 (d, *J* = 8.0 Hz, 1 H), 9.62 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.1, 29.9, 67.5, 78.7, 122.4 (q, *J* = 272.0 Hz), 125.0 (q, *J* = 31.0 Hz), 126.0, 126.3, 127.6 (q, *J* = 4.0 Hz), 127.8, 128.4, 128.7, 130.1, 132.4, 132.8, 134.3, 141.9, 143.1, 143.3, 163.2.

^{19}F NMR (376 MHz, DMSO-d_6): δ = –57.76 (s, 3 F).

HRMS (ESI): *m*/*z* [M – Br]$^+$ calcd for $C_{25}H_{21}F_3N_3O$: 436.1631; found: 436.1631.

(*S*)-5-(Hydroxydiphenylmethyl)-2-[4-(trifluoromethyl)phenyl]-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Bromide (6g)

NHC **6g** was prepared according to TP2. (1) Compound **4a′** (1.05 g, 3.1 mmol, 1 equiv), anhydrous DCM (20 mL) and $Me_3O^+BF_4^-$ (503 mg, 3.4 mmol, 1.1 equiv). (2) 4-(Trifluoromethyl)phenylhydrazine (598 mg, 3.4 mmol, 1.1 equiv). (3) Anhydrous DCM (30 mL) and $(EtO)_3CH$ (4.0 mL, 25 mmol, 8 equiv). (4) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (4.0 mL, 25 mmol, 8 equiv). (5) Anhydrous CH_3OH (100 mL) and TMSBr (1.0 mL, 8.0 mmol, 2.5 equiv) dissolved in CH_3OH (10 mL). The crude product was purified by flash column chromatography (silica gel, acetone/CH_3OH, 200:20), recrystallized from EtOAc and washed with Et_2O to give the pure NHC compound **6g**.

Yield: 1.10 g (69%); white solid.

IR (diamond-ATR, neat): 597, 640, 705, 845, 1068, 1111, 1131, 1169, 1321, 1589, 1615, 3068, 3170, 3190, 3411 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.57–2.62 (m, 1 H), 2.89–3.01 (m, 2 H), 3.11–3.19 (m, 1 H), 6.21 (d, *J* = 4.0 Hz, 1 H), 6.56 (s, 1 H), 7.28 (t, *J* = 8.0 Hz, 1 H), 7.36 (t, *J* = 8.0 Hz, 3 H), 7.44 (t, *J* = 8.0 Hz, 2 H), 7.52 (d, *J* = 8.0 Hz, 2 H), 7.60 (d, *J* = 8.0 Hz, 2 H), 8.04–8.07 (m, 4 H), 9.85 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.2, 29.9, 67.3, 79.0, 122.3, 123.5 (q, *J* = 271.0 Hz), 126.0, 126.2, 127.3 (q, *J* = 3.0 Hz), 127.5, 127.8, 128.4, 128.9, 130.4 (q, *J* = 32.0 Hz), 138.2, 138.7, 143.3, 143.4, 163.9.

^{19}F NMR (376 MHz, DMSO-d_6): δ = –61.25 (s, 3 F).

HRMS (ESI): *m*/*z* [M – Br]$^+$ calcd for $C_{25}H_{21}F_3N_3O$: 436.1631; found: 436.1611.

(*S*)-2-(2,6-Dichlorophenyl)-5-(hydroxydiphenylmethyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Bromide (6h)

NHC **6h** was prepared according to TP2. (1) Compound **4a′** (1.05 g, 3.1 mmol, 1 equiv), anhydrous DCM (20 mL) and $Me_3O^+BF_4^-$ (503 mg, 3.4 mmol, 1.1 equiv). (2) 2,6-Dichlorophenylhydrazine (602 mg, 3.4 mmol, 1.1 equiv). (3) Anhydrous DCM (30 mL) and $(EtO)_3CH$ (4.0 mL, 25 mmol, 8 equiv). (4) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (4.0 mL, 25 mmol, 8 equiv). (5) Anhydrous CH_3OH (100 mL) and TMSBr (1.0 mL, 8.0 mmol, 2.5 equiv) dissolved in CH_3OH (10 mL). The crude product was purified by flash column chromatography (silica gel, acetone/CH_3OH, 200:20), recrystallized from EtOAc and washed with Et_2O to give the pure NHC compound **6h**.

Yield: 1.50 g (94%); white solid.

IR (diamond-ATR, neat): 605, 629, 652, 699, 749, 755, 764, 795, 1066, 1194, 1411, 1443, 1572, 1593, 3055, 3138 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.67–2.76 (m, 1 H), 2.81–2.90 (m, 1 H), 3.12–3.24 (m, 2 H), 6.23 (d, *J* = 8.0 Hz, 1 H), 6.82 (s, 1 H), 7.32–7.49 (m, 10 H), 7.75–7.85 (m, 3 H), 9.59 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.4, 29.9, 68.0, 78.8, 126.1, 126.4, 127.8, 128.0, 128.5, 128.8, 129.4, 131.0, 132.6, 134.4, 142.8, 142.9, 143.0, 164.2.

HRMS (ESI): *m*/*z* [M – Br]$^+$ calcd for $C_{24}H_{20}Cl_2N_3O$: 436.0978; found: 436.0963.

(*S*)-2-(2,6-Dichlorophenyl)-5-(hydroxydiphenylmethyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Bromide (6h); Alternative Protocol without DCM Treatment

NHC **6h** was prepared according to TP2 but without treatment with DCM and $(EtO)_3CH$ (8 equiv) (see Scheme 4). (1) Compound **4a′** (1.05 g, 3.1 mmol, 1 equiv), anhydrous DCM (20 mL) and $Me_3O^+BF_4^-$ (503 mg, 3.4 mmol, 1.1 equiv). (2) 2,6-Dichlorophenylhydrazine (602 mg, 3.4 mmol, 1.1 equiv). (3) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (4.0

mL, 25 mmol, 8 equiv). (4) Anhydrous CH_3OH (100 mL) and TMSBr (1.0 mL, 8.0 mmol, 2.5 equiv) dissolved in CH_3OH (10 mL). The crude product was purified by flash column chromatography (silica gel, acetone/CH_3OH, 200:20), recrystallized from EtOAc and washed with Et_2O to give the pure NHC compound **6h**.

Yield: 1.0 g (62%); white solid.

(*S*)-5-(Hydroxydiphenylmethyl)-2-(3-nitrophenyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Bromide (6i)

NHC **6i** was prepared according to TP2. (1) Compound **4a′** (1.05 g, 3.1 mmol, 1 equiv), in anhydrous DCM (20 mL) and $Me_3O^+BF_4^-$ (503 mg, 3.4 mmol, 1.1 equiv). (2) 3-Nitrophenylhydrazine (524 mg, 3.4 mmol, 1.1 equiv). (3) anhydrous DCM (30 mL) and $(EtO)_3CH$ (4.0 mL, 25 mmol, 8 equiv). (4) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (4.0 mL, 25 mmol, 8 equiv). (5) Anhydrous CH_3OH (100 mL) and TMSBr (1.0 mL, 8.0 mmol, 2.5 equiv) dissolved in CH_3OH (10 mL). The crude product was purified by flash column chromatography (silica gel, acetone/CH_3OH, 200:20), recrystallized from EtOAc and washed with Et_2O to give the pure NHC compound **6i**.

Yield: 1.06 g (69%); yellow solid.

IR (diamond-ATR, neat): 501, 622, 635, 664, 702, 729, 752, 769, 1066, 1204, 1349, 1385, 1448, 1536, 1593, 3057, 3209, 3308 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.57–2.62 (m, 1 H), 2.86–2.99 (m, 2 H), 3.11–3.19 (m, 1 H), 6.20 (d, *J* = 8.0 Hz, 1 H), 6.57 (s, 1 H), 7.28–7.61 (m, 10 H), 7.95–7.99 (m, 1 H), 8.29 (d, *J* = 8.0 Hz, 1 H), 8.46 (d, *J* = 8.0 Hz, 1 H), 8.67 (s, 1 H), 9.97 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.2, 30.0, 67.3, 79.0, 117.0, 125.2, 126.0, 126.2, 127.5, 127.8, 128.1, 128.4, 128.9, 131.8, 135.9, 139.2, 143.4, 143.5, 148.2, 163.8.

HRMS (ESI): *m*/*z* [M – Br]$^+$ calcd for $C_{24}H_{21}N_4O_3$: 413.1608; found: 413.1590.

(*S*)-2-(2,6-Dimethylphenyl)-5-(hydroxydiphenylmethyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Bromide (6j)

NHC **6j** was prepared according to TP2. (1) Compound **4a′** (3.2 g, 9.3 mmol, 1 equiv), anhydrous DCM (60 mL) and $Me_3O^+BF_4^-$ (1.5 g, 10.2 mmol, 1.1 equiv). (2) 2,6-Dimethylphenylhydrazine (1.8 g, 10.2 mmol, 1.1 equiv). (3) Anhydrous DCM (80 mL) and $(EtO)_3CH$ (12.3 mL, 74 mmol, 8 equiv). (4) Anhydrous PhCl (80 mL) and $(EtO)_3CH$ (12.3 mL, 74 mmol, 8 equiv). (5) Anhydrous CH_3OH (300 mL) and TMSBr (3.0 mL, 23 mmol, 2.5 equiv) dissolved in CH_3OH (30 mL). The crude product was purified by flash column chromatography (silica gel, DCM/acetone, 2:1) and recrystallized from (hexane/Et_2O, 9:1) to give the pure NHC compound **6j**.

Yield: 3.55 g (80%); white solid.

IR (diamond-ATR, neat): 577, 614, 631, 658, 699, 754, 767, 968, 1181, 1385, 1448, 1585, 2961, 3057, 3153, 3223 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.00 (s, 6 H), 2.68–2.73 (m, 1 H), 2.91–3.01 (m, 1 H), 3.10–3.20 (m, 2 H), 6.18 (d, *J* = 4.0 Hz, 1 H), 6.76 (s, 1 H), 7.29–7.34 (m, 4 H), 7.38–7.41 (m, 4 H), 7.46 (t, *J* = 8.0 Hz, 1 H), 7.50 (d, *J* = 8.0 Hz, 4 H), 9.33 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 16.9, 21.5, 29.9, 67.5, 79.0, 125.9, 126.3, 127.7, 127.8, 128.5, 128.6, 128.8, 131.3, 134.3, 135.2, 141.0, 143.2, 143.4, 163.9.

HRMS (ESI): *m*/*z* [M – Br]$^+$ calcd for $C_{26}H_{26}N_3O$: 396.2070; found: 396.2061.

(*S*)-5-(Hydroxydiphenylmethyl)-2-(4-methoxyphenyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Bromide (6k)

NHC **6k**[4f] was prepared according to TP2. (1) Compound **4a′** (3.2 g, 9.3 mmol, 1 equiv), anhydrous DCM (60 mL) and $Me_3O^+BF_4^-$ (1.5 g, 10.2 mmol, 1.1 equiv). (2) 4-Methoxyphenylhydrazine (1.4 g, 10.2 mmol, 1.1 equiv). (3) Anhydrous DCM (80 mL) and $(EtO)_3CH$ (12.3 mL, 74 mmol, 8 equiv). (4) Anhydrous PhCl (80 mL) and $(EtO)_3CH$ (12.3 mL, 74 mmol, 8 equiv). (5) Anhydrous CH_3OH (300 mL) and TMSBr (3.0 mL, 23 mmol, 2.5 equiv) dissolved in CH_3OH (30 mL). The crude product was purified by flash column chromatography (silica gel, DCM/acetone, 80:20) and recrystallized from Et_2O to give the pure NHC compound **6k**.

Yield: 2.25 g (51%); white solid.

IR (diamond-ATR, neat): 500, 564, 609, 632, 649, 702, 744, 801, 834, 971, 1023, 1038, 1172, 1199, 1259, 1442, 1506, 1532, 1586, 2957, 3201 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.57–2.61 (m, 1 H), 2.90–3.00 (m, 2 H), 3.08–3.15 (m, 1 H), 3.84 (s, 3 H), 6.16 (d, *J* = 8.0 Hz, 1 H), 6.54 (s, 1 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 7.28 (t, *J* = 8.0 Hz, 1 H), 7.34–7.38 (m, 3 H), 7.44 (t, *J* = 8.0 Hz, 2 H), 7.53 (d, *J* = 8.0 Hz, 2 H), 7.59 (d, *J* = 8.0 Hz, 2 H), 7.70 (d, *J* = 8.0 Hz, 2 H), 9.48 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.3, 29.8, 55.8, 67.0, 79.0, 115.0, 123.2, 126.0, 126.1, 127.5, 127.8, 128.4, 128.5, 128.9, 137.1, 143.4, 143.6, 160.6, 163.4.

HRMS (ESI): *m*/*z* [M – Br]$^+$ calcd for $C_{25}H_{24}N_3O_2$: 398.1863; found: 398.1857.

(*S*)-5-(Hydroxydiphenylmethyl)-2-mesityl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (6l)

NHC **6l**[4b] was prepared according to TP2. (1) Compound **4a′**(3.2 g, 9.3 mmol, 1 equiv), anhydrous DCM (60 mL) and $Me_3O^+BF_4^-$ (1.5 g, 10.2 mmol, 1.1 equiv). (2) Mesitylhydrazine (1.53 g, 10.2 mmol, 1.1 equiv). (3) Anhydrous DCM (80 mL) and $(EtO)_3CH$ (12.3 mL, 74 mmol, 8 equiv). (4) Anhydrous PhCl (80 mL) and $(EtO)_3CH$ (12.3 mL, 74 mmol, 8 equiv). (5) Anhydrous CH_3OH (300 mL) and TMSBr (3.0 mL, 23 mmol, 2.5 equiv) dissolved in CH_3OH (30 mL). The obtained crude product was purified by flash column chromatography (silica gel, DCM/acetone, 2:1) and recrystallized from (benzene/Et_2O, 1:9) to give the pure NHC compound **6l**.

Yield: 3.90 g (84%); white solid.

IR (diamond-ATR, neat): 445, 507, 551, 587, 632, 658, 699, 764, 852, 971, 1015, 1189, 1385, 1448, 1493, 1585, 2955, 3057, 3229 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 1.96 (s, 6 H), 2.32 (s, 3 H), 2.67–2.73 (m, 1 H), 2.88–2.98 (m, 1 H), 3.09–3.19 (m, 2 H), 6.13–6.15 (m, 1 H), 6.75 (s, 1 H), 7.11 (s, 2 H), 7.29–7.34 (m, 2 H), 7.39 (t, *J* = 8.0 Hz, 4 H), 7.50 (d, *J* = 8.0 Hz, 4 H), 9.26 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 16.8, 20.6, 21.5, 29.9, 67.5, 79.0, 126.0, 126.4, 127.7, 127.9, 128.5, 128.8, 129.1, 131.9, 134.8, 141.1, 141.2, 143.2, 143.4, 163.8.

HRMS (ESI): *m*/*z* [M – BF_4]$^+$ calcd for $C_{27}H_{28}N_3O$: 410.2227; found: 410.2223.

(*S*)-5-(Hydroxydiphenylmethyl)-2-mesityl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (6l); Alternative Protocol without DCM Treatment

NHC **6l** was prepared according to TP2 but without treatment with DCM and $(EtO)_3CH$ (8 equiv) (see Scheme 4). (1) Compound **4a′** (3.2 g, 9.3 mmol, 1 equiv), anhydrous DCM (60 mL) and $Me_3O^+BF_4^-$ (1.5 g, 10.2 mmol, 1.1 equiv). (2) Mesitylhydrazine (1.53 g, 10.2 mmol, 1.1

equiv). (3) Anhydrous PhCl (80 mL) and $(EtO)_3CH$ (12.3 mL, 74 mmol, 8 equiv). (4) Anhydrous CH_3OH (300 mL) and TMSBr (3.0 mL, 23 mmol, 2.5 equiv) dissolved in CH_3OH (30 mL). The crude product was purified by flash column chromatography (silica gel, DCM/acetone, 2:1) and recrystallized from (benzene/Et_2O, 1:9) to give the pure NHC compound **6l**.

Yield: 3.30 g (71%); white solid.

(*S*)-5-[Hydroxy(diphenyl)methyl]-2-phenyl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (7a)

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with NHC **6a** (110 mg, 0.25 mmol, 1 equiv) in anhydrous DCM (4 mL). $HBF_4{\cdot}OEt_2$ (51 µL, 0.36 mmol, 1.5 equiv) was added and the reaction mixture was stirred at 20 °C for 3 h. The reaction mixture was diluted with CH_3OH (10 mL) and then transferred into a single-neck flask. The solvent was removed in vacuo (the water bath should not exceed 50 °C). The obtained crude product was dissolved in 5mL of CH_3OH and the solvent was removed in vacuo (the water bath should not exceed 50 °C) to remove residual acids, this process was repeated twice. The residue was dried under high vacuum for 12 h at 60 °C to give the pure NHC compound **7a**.[2b]

Yield: 113 mg (99%); white solid.

IR (diamond-ATR, neat): 521, 629, 699, 761, 828, 972, 1036, 1051, 1198, 1286, 1390, 1449, 1493, 1519, 1587, 3032, 3064, 3151 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.55–2.62 (m, 1 H), 2.88–3.09 (m, 2 H), 3.09–3.17 (m, 1 H), 6.13 (d, *J* = 8.0 Hz, 1 H), 6.56 (s, 1 H), 7.29 (t, *J* = 8.0 Hz, 1 H), 7.35–7.39 (m, 3 H), 7.45 (t, *J* = 8.0 Hz, 2 H), 7.52 (d, *J* = 8.0 Hz, 2 H), 7.58 (d, *J* = 4.0 Hz, 2 H), 7.62–7.68 (m, 3 H), 7.78 (d, *J* = 4.0 Hz, 2 H), 9.59 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.2, 29.9, 67.1, 79.0, 121.4, 126.0, 126.1, 127.5, 127.9, 128.4, 128.9, 130.1, 130.7, 135.3, 137.7, 143.3, 143.5, 163.7.

^{19}F NMR (376 MHz, DMSO-d_6): δ = –148.29 (s, 4 F).

HRMS (ESI): *m*/*z* $[M - BF_4]^+$ calcd for $C_{24}H_{22}N_3O$: 368.1757; found: 368.1752.

(*S*)-2-(2-Fluorophenyl)-5-(hydroxydiphenylmethyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (7b)

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with NHC **6b** (100 mg, 0.21 mmol, 1 equiv) in anhydrous DCM (4 mL). $HBF_4{\cdot}OEt_2$ (43 µL, 0.32 mmol, 1.5 equiv) was added and the reaction mixture was stirred at 20 °C for 3 h. The reaction mixture was diluted with CH_3OH (10 mL) and then transferred into a single-neck flask. The solvent was removed in vacuo (the water bath should not exceed 50 °C). The obtained crude product was dissolved in 5 mL of CH_3OH and the solvent was removed in vacuo (the water bath should not exceed 50 °C) to remove residual acids, this process was repeated twice. The residue was dried under high vacuum for 12 h at 60 °C to give the pure NHC compound **7b**.

Yield: 97 mg (98%); white solid.

IR (diamond-ATR, neat): 521, 629, 648, 696, 762, 825, 969, 1033, 1049, 1200, 1232, 1289, 1369, 1448, 1495, 1523, 1592, 3027, 3058, 3111, 3177 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.61–2.68 (m, 1 H), 2.91–3.05 (m, 2 H), 3.12–3.21 (m, 1 H), 6.16 (d, *J* = 8.0 Hz, 1 H), 6.65 (s, 1 H), 7.30 (t, *J* = 8.0 Hz, 1 H), 7.36–7.46 (m, 5 H), 7.51 (t, *J* = 8.0 Hz, 3 H), 7.57–7.64 (m, 3 H), 7.69–7.77 (m, 2 H), 9.33 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.3, 29.7, 67.5, 78.9, 117.2 (d, *J* = 18.0 Hz), 123.4 (d, *J* = 11.0 Hz), 125.8 (d, *J* = 4.0 Hz), 126.0, 126.5, 127.6, 127.9, 128.4, 128.9, 133.2 (d, *J* = 8.0 Hz), 140.7 (d, *J* = 5.0 Hz), 143.1, 143.4, 153.1, 155.6, 163.6.

^{19}F NMR (376 MHz, DMSO-d_6): δ = –148.30 (s, 4 F), –123.22 (s, 1 F).

HRMS (ESI): *m*/*z* $[M - BF_4]^+$ calcd for $C_{24}H_{21}FN_3O$: 386.1663; found: 386.1659.

(*S*)-5-(Hydroxydiphenylmethyl)-2-pentafluorophenyl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (7c)

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with NHC **6e** (150 mg, 0.28 mmol, 1 equiv) in anhydrous DCM (4 mL). $HBF_4{\cdot}OEt_2$ (57 µL, 0.42 mmol, 1.5 equiv) was added and the reaction mixture was stirred at 20 °C for 3 h. The reaction mixture was diluted with CH_3OH (10 mL) and then transferred into a single-neck flask. The solvent was removed in vacuo (the water bath should not exceed 50 °C) to remove residual acids, this process was repeated twice. The residue was dried under high vacuum for 12 h at 60 °C to give the pure NHC compound **7c**.[2b] To test whether the obtained compound required further purification it was recrystallized from ether. While the yield was decreased by only 10%, the proton and fluorine NMR remained identical, therefore, the compound is reported without the recrystallization step.

Yield: 150 mg (98%); white solid.

IR (diamond-ATR, neat): 520, 635, 699, 738, 762, 872, 972, 1001, 1032, 1068, 1169, 1376, 1449, 1510, 1526, 1596, 2964, 3031, 3061, 3153 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.65–2.71 (m, 1 H), 2.86–2.95 (m, 1 H), 2.99–3.09 (m, 1 H), 3.15–3.23 (m, 1 H), 6.16 (dd, *J* = 8.0, 4.0 Hz, 1 H), 6.79 (s, 1 H), 7.31 (t, *J* = 8.0 Hz, 1 H), 7.34–7.40 (m, 3 H), 7.42–7.48 (m, 4 H), 7.56 (d, *J* = 4.0 Hz, 2 H), 9.62 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.4, 29.7, 68.1, 78.8, 111.1 (m), 126.1, 127.7, 128.1, 128.5, 128.9, 136.2 (m), 138.7 (m), 141.5 (m), 142.9, 143.2, 143.5, 144.1 (m), 164.8.

^{19}F NMR (376 MHz, DMSO-d_6): δ = –160.08 (t, *J* = 22.6 Hz, 2 F), –148.32 (s, 4 F), –147.71 (t, *J* = 22.3 Hz, 1 F), –145.44 (d, *J* = 15.0 Hz, 2 F).

HRMS (ESI): *m*/*z* $[M - BF_4]^+$ calcd for $C_{24}H_{17}F_5N_3O$: 458.1286; found: 458.1281.

(*S*)-5-(Hydroxydiphenylmethyl)-2-(4-methoxyphenyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (7d)

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with NHC **6k** (110 mg, 0.22 mmol, 1 equiv) in anhydrous DCM (4 mL). $HBF_4{\cdot}OEt_2$ (47 µL, 0.34 mmol, 1.5 equiv) was added and the reaction mixture was stirred at 20 °C for 3 h. The reaction mixture was diluted in CH_3OH (10 mL) and then transferred into a single-neck flask. The solvent was removed in vacuo (the water bath should not exceed 50 °C). The obtained crude product was dissolved in 5 mL of CH_3OH and the solvent was removed in vacuo (the water bath should not exceed 50 °C) to remove residual acids, this process was repeated twice. The residue was dried under high vacuum for 12 h at 60 °C to give the pure NHC compound **7d**.[4f]

Yield: 105 mg (98%); white solid.

IR (diamond-ATR, neat): 518, 561, 634, 701, 762, 832, 972, 1016, 1041, 1175, 1256, 1306, 1393, 1449, 1523, 1585, 2841, 3065, 3143 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.56–2.62 (m, 1 H), 2.89–3.00 (m, 2 H), 3.07–3.14 (m, 1 H), 3.84 (s, 3 H), 6.11 (d, *J* = 8.0 Hz, 1 H), 6.55 (s, 1 H), 7.19 (d, *J* = 12.0 Hz, 2 H), 7.29 (t, *J* = 8.0 Hz, 1 H), 7.34–7.39 (m, 3 H), 7.44 (t, *J* = 8.0 Hz, 2 H), 7.53 (d, *J* = 8.0 Hz, 2 H), 7.58 (d, *J* = 4.0 Hz, 2 H), 7.69 (d, *J* = 8.0 Hz, 2 H), 9.46 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.3, 29.8, 55.8, 67.1, 79.0, 115.0, 123.2, 126.0, 126.1, 127.5, 127.8, 128.4, 128.5, 128.9, 137.1, 143.3, 143.6, 160.6, 163.4.

^{19}F NMR (376 MHz, DMSO-d_6): δ = –148.31 (s, 4 F).

HRMS (ESI): *m*/*z* [M – BF_4]$^+$ calcd for $C_{25}H_{24}N_3O_2$: 398.1863; found: 398.1853].

(*S*)-5-(Hydroxymethyl)pyrrolidin-2-one (8)

Precursor **8** was prepared according to a modified literature procedure.[6] A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with acid **1** (20.0 g, 155 mmol, 1 equiv) in anhydrous CH_3OH (400 mL). $SOCl_2$ (17.0 mL, 233 mmol, 1.5 equiv) was added dropwise at 0 °C and the mixture slowly warmed to 20 °C over 4 h. After full consumption of the starting material (TLC monitoring), the CH_3OH was removed under reduced pressure and the residue dried under high vacuum for 4 h. The product was used in the next step without further purification. EtOH (300 mL) was added to the reaction flask followed by the portionwise addition of $NaBH_4$ (11.8 g, 310 mmol, 2.0 equiv) at 0 °C, after which the mixture was slowly warmed to 20 °C over 24 h. The mixture was quenched with a 5% aqueous solution of citric acid (800 mL) until the solution became clear with a solid grey precipitate. The solution was then decanted from the precipitate and the precipitate was washed with EtOH and decanted once more. The solvent from the combined supernatant was removed under reduced pressure. A solution of 35% CH_3OH in EtOAc (500 mL) was added to the obtained crude oil and the resulting mixture stirred for 0.5 h and then filtered. The solvents were removed under reduced pressure and the obtained solid was dissolved in DCM (800 mL) and filtered. The DCM was removed under reduced pressure to furnish **8** as a pure, colorless solid (15 g, 84%).

(*S*)-5-{[(Triisopropylsilyl)oxy]methyl}pyrrolidin-2-one (9a)

Precursor **9a** was prepared according to a previous report.[7b] A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with alcohol **8** (2.0 g, 17.4 mmol, 1 equiv) in anhydrous DMF (120 mL), imidazole (3.0 g, 43.6 mmol, 2.5 equiv) was added at 20 °C and the resulting mixture stirred for 5 min followed by the addition of triisopropylsilyl chloride (TIPSCl) (4.0 g, 20.9 mmol, 1.2 equiv). The mixture was stirred at 20 °C for 24 h, then quenched with sat. aqueous NH_4Cl (60 mL) and extracted with Et_2O (5 × 30 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The crude residue was purified by flash column chromatography (silica gel was pre-neutralized with triethylamine, *n*-hexane/EtOAc, 1:1) to furnish compound **9a** as a colorless oil (4.6 g, 97%).

(*S*)-5-{[(*tert*-Butyldimethylsilyl)oxy]methyl}pyrrolidin-2-one (9b)

Precursor **9b** was prepared according to a previous report.[7b] A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with alcohol **8** (3.0 g, 26.06 mmol, 1 equiv) in anhydrous DMF (180 mL), imidazole (4.4 g, 65.2 mmol, 2.5 equiv) was added at 20 °C and the resulting mixture stirred for 5 min followed by the addition of *tert*-butyldimethylsilyl chloride (TBSCl) (4.71 g, 31.26 mmol, 1.2 equiv). The mixture was stirred at 20 °C for 24 h, then quenched with sat. aqueous NH_4Cl (60 mL) and extracted with Et_2O (5 × 30 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The crude residue was purified by flash column chromatography (silica gel was pre-neutralized with triethylamine, *n*-hexane/EtOAc, 1:1) to furnish compound **9b** as a colorless oil (6.016 g, 99%).

(*S*)-5-{[(*tert*-Butyldiphenylsilyl)oxy]methyl}pyrrolidin-2-one (9c)

Precursor **9c** was prepared according to a previous report.[7c] A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with alcohol **8** (2.0 g, 17.4 mmol, 1 equiv) in anhydrous DMF (120 mL), imidazole (3.0 g, 43.6 mmol, 2.5 equiv) was added at 20 °C and the resulting mixture stirred for 5 min followed by the addition of *tert*-butyldiphenylsilyl chloride (TBDPSCl) (5.73 g, 20.88 mmol, 1.2 equiv). The mixture was stirred at 20 °C for 24 h, then quenched with sat. aqueous NH_4Cl (60 mL) and extracted with Et_2O (5 × 30 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The crude residue was purified by flash column chromatography (silica gel was pre-neutralized with triethylamine, *n*-hexane/EtOAc, 1:1) to furnish compound **9c** as a colorless oil (6.0 g, 98%).

(*S*)-5-{[(Trimethylsilyl)oxy]methyl}pyrrolidin-2-one (9d)

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with alcohol **8** (1.0 g, 8.7 mmol, 1 equiv) in anhydrous DMF (60 mL), imidazole (1.5 g, 22 mmol, 2.5 equiv) was added at 20 °C and the resulting mixture stirred for 5 min followed by the addition of trimethylsilyl chloride (TMSCl) (1.13 g, 10.44 mmol, 1.2 equiv). The mixture was stirred at 20 °C for 24 h, then quenched with sat. aqueous NH_4Cl (60 mL) and extracted with Et_2O (5 × 30 mL). The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The crude residue was analyzed by TLC and NMR revealing the recovery of 95% of the starting material.

TIPS/TBS-Protected Reduced Pre-Catalysts 10 (Scheme 6); Typical Procedure 3 (TP3)

(1) A dry, argon-flushed Schlenk flask equipped with a magnetic stir bar and a septum was charged with **9a–c** (3.9 mmol, 1 equiv) in anhydrous DCM (20 mL). $Me_3O^+BF_4^-$ (4.3 mmol, 1.1 equiv) was added and the reaction mixture was stirred at 20 °C for 24 h.

(2) Arylhydrazine (4.3 mmol, 1.1 equiv) was added to the solution and the reaction mixture was stirred at 20 °C for 24 h. The solvent was removed in vacuo and the residue dried under high vacuum for 12 h. This product was used in the next step without further purification.

(3) The reaction mixture was dissolved in anhydrous PhCl (30 mL), $(EtO)_3CH$ (31.2 mmol, 8 equiv) was added and the reaction mixture was stirred at 130 °C for 24 h under an argon atmosphere. The solvent was removed in vacuo and the residue was dried under high vacuum for 12 h at 30–40 °C and then purified by flash column chromatography (silica gel, acetone/DCM) or recrystallized from Et_2O to give compounds **10a–j**.

(*S*)-2-Phenyl-5-{[(triisopropylsilyl)oxy]methyl}-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (10a)

NHC **10a** was prepared according to TP3. (1) Compound **9a** (3.0 g, 11 mmol, 1 equiv), anhydrous DCM (70 mL) and $Me_3O^+BF_4^-$ (1.79 g, 12.2 mmol, 1.1 equiv). (2) Phenylhydrazine (1.2 mL, 12.2 mmol, 1.1 equiv). (3) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (14.6 mL, 88 mmol, 8 equiv). The crude product was purified by flash column chromatography (silica gel, DCM/acetone, 200:40) and washed with Et_2O to give the pure NHC compound **10a**.[7b]

Yield: 3.50 g (69%); white solid.

IR (diamond-ATR, neat): 520, 640, 687, 767, 881, 974, 1034, 1045, 1115, 1382, 1463, 1589, 2867, 2943, 3137 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 0.96–0.99 (m, 18 H), 1.04–1.13 (m, 3 H), 2.58–2.66 (m, 1 H), 2.89–2.99 (m, 1 H), 3.25 (t, *J* = 8.0 Hz, 2 H), 4.04–4.15 (m, 2 H), 4.95–5.00 (m, 1 H), 7.65 (t, *J* = 8.0 Hz, 1 H), 7.72 (t, *J* = 8.0 Hz, 2 H), 7.86 (d, *J* = 8.0 Hz, 2 H), 10.78 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 11.2, 17.7, 21.4, 29.5, 61.5, 64.0, 120.8, 130.9, 130.7, 135.5, 137.9, 163.1.

HRMS (ESI): *m*/*z* [M – BF_4]$^+$ calcd for $C_{21}H_{34}N_3OSi$: 372.2466; found: 372.2460.

(*S*)-5-{[(*tert*-Butyldimethylsilyl)oxy]methyl}-2-phenyl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (10a′)

NHC **10a′** was prepared according to TP3. (1) Compound **9b** (1.0 g, 4.36 mmol, 1 equiv), anhydrous DCM (70 mL) and $Me_3O^+BF_4^-$ (709 mg, 4.8 mmol, 1.1 equiv). (2) Phenylhydrazine (518 mg, 4.8 mmol, 1.1 equiv). (3) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (5.8 mL, 34.87 mmol, 8 equiv). The crude product was purified by flash column chromatography (silica gel, DCM/acetone, 200:50) and washed with Et_2O to give the pure NHC compound **10a′**.[7b]

Yield: 1.278 g (70%); white solid.

IR (diamond-ATR, neat): 520, 684, 778, 837, 1035, 1054, 1112, 1136, 1278, 1381, 1472, 1526, 1599, 2858, 2874, 2931, 2954 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 0.08 (s, 3 H), 0.11 (s, 3 H), 0.88 (s, 9 H), 2.51–2.60 (m, 1 H), 2.88–2.98 (m, 1 H), 3.15–3.29 (m, 2 H), 3.86 (dd, *J* = 12.0, 4.0 Hz, 1 H), 4.08 (dd, *J* = 8.0, 4.0 Hz, 1 H), 4.86–4.92 (m, 1 H), 7.65–7.70 (m, 3 H), 7.76–7.78 (m, 2 H), 9.59 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = –5.4, –5.3, 18.8, 22.6, 26.1, 30.1, 63.6, 63.6, 64.9, 122.4, 131.3, 131.9, 136.7, 137.7, 164.3.

HRMS (ESI): *m*/*z* [M – BF_4]$^+$ calcd for $C_{18}H_{28}N_3OSi$: 330.1996; found: 330.1994.

(*S*)-2-(3-Fluorophenyl)-5-{[(triisopropylsilyl)oxy]methyl}-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (10b)

NHC **10b** was prepared according to TP3. (1) Compound **9a** (1.06 g, 3.9 mmol, 1 equiv), anhydrous DCM (20 mL) and $Me_3O^+BF_4^-$ (635 mg, 4.3 mmol, 1.1 equiv). (2) 3-Fluorophenylhydrazine (542 mg, 4.3 mmol, 1.1 equiv). (3) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (5.2 mL, 31.2 mmol, 8 equiv). The crude product was purified by flash column chromatography (silica gel, DCM/acetone, 9:1) and washed with Et_2O to give the pure NHC compound **10b**.

Yield: 1.43 g (77%); white solid.

IR (diamond-ATR, neat): 504, 645, 679, 691, 768, 881, 1038, 1062, 1112, 1205, 1378, 1462, 1593, 2840, 2867, 2927 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 1.03–1.06 (m, 18 H), 1.11–1.20 (m, 3 H), 2.56–2.65 (m, 1 H), 2.90–3.00 (m, 1 H), 3.17–3.31 (m, 2 H), 3.98 (dd, *J* = 12.0, 4.0 Hz, 1 H), 4.16 (dd, *J* = 12.0, 4.0 Hz, 1 H), 4.90–4.96 (m, 1 H), 7.41 (t, *J* = 8.0 Hz, 1 H), 7.57–7.63 (m, 2 H), 7.67–7.70 (m, 1 H), 9.64 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 12.6, 18.2, 22.6, 30.2, 63.8, 65.3, 110.2 (d, *J* = 27.0 Hz), 118.9 (d, *J* = 21.0 Hz), 133.3 (d, *J* = 9.0 Hz), 137.7 (d, *J* = 10.0 Hz), 138.1, 162.6, 164.6, 165.0.

^{19}F NMR (376 MHz, CD_3CN): δ = –151.74 (s, 4 F), –110.81 (s, 1 F).

HRMS (ESI): *m*/*z* [M – BF_4]$^+$ calcd for $C_{21}H_{33}FN_3OSi$: 390.2371; found: 390.2366.

(*S*)-2-(4-Fluorophenyl)-5-{[(triisopropylsilyl)oxy]methyl}-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (10c)

NHC **10c** was prepared according to TP3. (1) Compound **9a** (1.0 g, 3.68 mmol, 1 equiv), anhydrous DCM (20 mL) and $Me_3O^+BF_4^-$ (599 mg, 4.1 mmol, 1.1 equiv). (2) 4-Fluorophenylhydrazine (510 mg, 4.1 mmol, 1.1 equiv). (3) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (4.9 mL, 29.4 mmol, 8 equiv). The crude product was purified by flash column chromatography (silica gel, DCM/acetone, 200:40) and washed with Et_2O to give the pure NHC compound **10c**.

Yield: 1.48 g (84%); white solid.

IR (diamond-ATR, neat): 518, 640, 680, 691, 764, 844, 882, 1009, 1034, 1058, 1109, 1238, 1384, 1454, 1523, 1592, 2867, 2891, 2944, 2958 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 1.03–1.06 (m, 18 H), 1.11–1.20 (m, 3 H), 2.55–2.64 (m, 1 H), 2.90–2.99 (m, 1 H), 3.16–3.30 (m, 2 H), 3.97 (dd, *J* = 12.0, 4.0 Hz, 1 H), 4.16 (dd, *J* = 8.0, 4.0 Hz, 1 H), 4.88–4.95 (m, 1 H), 7.38–7.43 (m, 2 H), 7.78 (dd, *J* = 8.0, 4.0 Hz, 2 H), 9.56 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 12.6, 18.2, 22.6, 30.1, 63.8, 65.3, 118.2 (d, *J* = 23.0 Hz), 125.2 (d, *J* = 8.0 Hz), 133.0 (d, *J* = 3.0 Hz), 137.9, 164.4, 164.6 (d, *J* = 248.0 Hz).

^{19}F NMR (376 MHz, CD_3CN): δ = –151.78 (s, 4 F), –110.67 (s, 1 F).

HRMS (ESI): *m*/*z* [M – BF_4]$^+$ calcd for $C_{21}H_{33}FN_3OSi$: 390.2371; found: 390.2365.

(*S*)-2-(Perfluorophenyl)-5-{[(triisopropylsilyl)oxy]methyl}-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (10d)

NHC **10d** was prepared according to TP3. (1) Compound **9a** (1.06 g, 3.9 mmol, 1 equiv), anhydrous DCM (20 mL) and $Me_3O^+BF_4^-$ (635 mg, 4.13 mmol, 1.1 equiv). (2) Perfluorophenylhydrazine (849 mg, 4.3 mmol, 1.1 equiv). (3) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (5.2 mL, 31.2 mmol, 8 equiv). The crude product was purified by flash column chromatography (silica gel, DCM/acetone, 200:30) and washed with Et_2O to give the pure NHC compound **10d**.

Yield: 1.20 g (56%); white solid.

IR (diamond-ATR, neat): 520, 680, 788, 881, 979, 1004, 1038, 1051, 1111, 1264, 1356, 1463, 1531, 1598, 2866, 2888, 2943, 2953 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 1.04–1.06 (m, 18 H), 1.11–1.20 (m, 3 H), 2.54–2.62 (m, 1 H), 2.91–3.00 (m, 1 H), 3.19–3.33 (m, 2 H), 3.98 (dd, *J* = 12.0, 8.0 Hz, 1 H), 4.18 (dd, *J* = 12.0, 4.0 Hz, 1 H), 4.93–5.00 (m, 1 H), 9.58 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 12.5, 18.2, 22.9, 30.1, 64.8, 65.0, 112.4 (m), 13.80 (m), 140.5 (m), 142.3 (m), 145.4 (m), 146.2 (m), 143.2, 165.6.

^{19}F NMR (376 MHz, CD_3CN): δ = –161.15 (t, *J* = 18.8 Hz, 2 F), –151.89 (s, 4 F), –148.98 (t, *J* = 22.6 Hz, 1 F), –146.87 (d, *J* = 18.8 Hz, 2 F).

HRMS (ESI): *m*/*z* [M – BF_4]$^+$ calcd for $C_{21}H_{29}F_5N_3OSi$: 462.1995; found: 462.1992.

(*S*)-5-{[(*tert*-Butyldimethylsilyl)oxy]methyl}-2-(perfluorophenyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (10d′)

NHC **10d′** was prepared according to TP3. (1) Compound **9b** (1.0 g, 4.36 mmol, 1 equiv), anhydrous DCM (30 mL) and $Me_3O^+BF_4^-$ (709 mg, 4.8 mmol, 1.1 equiv). (2) Perfluorophenylhydrazine (949 mg, 4.8 mmol, 1.1 equiv). (3) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (5.8 mL,

34.87 mmol, 8 equiv). The crude product was purified by flash column chromatography (silica gel, DCM/acetone, 200:50) and washed with Et_2O to give the pure NHC compound **10d′**.

Yield: 900 mg (40%); white solid.

IR (diamond-ATR, neat): 520, 744, 781, 835, 864, 978, 1001, 1029, 1064, 1092, 1259, 1526, 1603, 2860, 2887, 2931, 2953 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 0.09 (s, 3 H), 0.11 (s, 3 H), 0.88 (s, 9 H), 2.51–2.60 (m, 1 H), 2.90–3.00 (m, 1 H), 3.18–3.32 (m, 2 H), 3.88 (dd, *J* = 12.0, 8.0 Hz, 1 H), 4.10 (dd, *J* = 12.0, 4.0 Hz, 1 H), 4.94–5.00 (m, 1 H), 9.62 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = –5.5, –5.4, 18.8, 22.9, 26.1, 30.0, 64.6, 112.4 (m), 137.9 (m), 140.6 (m), 143.2, 143.3 (m), 145.5, (m), 146.1 (m), 165.5.

^{19}F NMR (376 MHz, CD_3CN): δ = –161.37 (t, *J* = 22.6 Hz, 2 F), –152.04 (s, 4 F), –149.32 (t, *J* = 22.6 Hz, 1 F), –146.90 (d, *J* = 18.8 Hz, 2 F).

HRMS (ESI): *m*/*z* $[M - BF_4]^+$ calcd for $C_{18}H_{23}F_5N_3OSi$: 420.1525; found: 420.1520.

(*S*)-5-{[(*tert*-Butyldiphenylsilyl)oxy]methyl}-2-(perfluorophenyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (10d″)

NHC **10d″** was prepared according to TP3. (1) Compound **9c** (2.14 g, 6.0 mmol, 1 equiv), anhydrous DCM (40 mL) and $Me_3O^+BF_4^-$ (900 mg, 4.8 mmol, 1.0 equiv). (2) Perfluorophenylhydrazine (1.2 g, 6.0 mmol, 1.0 equiv). (3) Anhydrous PhCl (60 mL) and $(EtO)_3CH$ (8.0 mL, 48 mmol, 8 equiv). The crude product was recrystallized from *i*-PrOH to give the pure NHC compound **10d″**.[7c]

Yield: 1.80 g (48%); white solid.

IR (diamond-ATR, neat): 508, 612, 704, 741, 857, 1068, 1115, 1263, 1429, 1489, 1530, 1605, 2861, 2934, 2959, 3068 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 1.03 (s, 9 H), 2.54–2.62 (m, 1 H), 2.90–3.00 (m, 1 H), 3.20–3.35 (m, 2 H), 3.98 (dd, *J* = 12.0, 4.0 Hz, 1 H), 4.10 (dd, *J* = 12.0, 4.0 Hz, 1 H), 5.04–5.11 (m, 1 H), 7.43–7.53 (m, 6 H), 7.64 (t, *J* = 8.0 Hz, 4 H), 9.68 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 19.7, 22.8, 27.1, 30.2, 64.4, 65.3, 112.4 (m), 129.0, 129.1, 131.3, 131.3, 133.1, 133.3, 136.4, 136.4, 138.0 (m), 140.6 (m), 143.2, 143.4 (m), 145.5 (m), 146.1 (m), 165.6.

^{19}F NMR (376 MHz, CD_3CN): δ = –161.20 (t, *J* = 15.0 Hz, 2 F), –151.90 (s, 4 F), –149.10 (t, *J* = 26.0 Hz, 1 F), –146.84 (d, *J* = 22.6 Hz, 2 F).

HRMS (ESI): *m*/*z* $[M - BF_4]^+$ calcd for $C_{28}H_{27}F_5N_3OSi$: 544.1838; found: 544.1838.

(*S*)-2-(Perfluorophenyl)-5-{[(triisopropylsilyl)oxy]methyl}-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (10d); Alternative Protocol with DCM Treatment

NHC **10d** was prepared according to TP3 modified with an additional step involving treatment with DCM and $(EtO)_3CH$ (8 equiv).

(1) Compound **9a** (1.06 g, 3.9 mmol, 1 equiv), anhydrous DCM (20 mL) and $Me_3O^+BF_4^-$ (635 mg, 4.13 mmol, 1.1 equiv). (2) Perfluorophenylhydrazine (849 mg, 4.3 mmol, 1.1 equiv). (3) Anhydrous DCM (30 mL) and $(EtO)_3CH$ (5.2 mL, 31.2 mmol, 8 equiv), 40 °C, 1 h. (4) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (5.2 mL, 31.2 mmol, 8 equiv). The crude product was purified by flash column chromatography (silica gel, DCM/acetone, 200:30) and washed with Et_2O to give the pure NHC compound **10d**.

Yield: 1.08 g (50%); white solid.

(*S*)-2-[4-(Trifluoromethyl)phenyl]-5-{[(triisopropylsilyl)oxy]methyl}-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (10e)

NHC **10e** was prepared according to TP3. (1) Compound **9a** (1.0 g, 3.68 mmol, 1 equiv), anhydrous DCM (30 mL) and $Me_3O^+BF_4^-$ (599 mg, 4.1mmol, 1.1 equiv). (2) 4-(Trifluoromethyl)phenylhydrazine (713 mg, 4.1 mmol, 1.1 equiv). (3) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (4.9 mL, 29.44 mmol, 8 equiv). The crude product was purified by flash column chromatography (silica gel, DCM/acetone, 200:40) and washed with Et_2O to give the pure NHC compound **10e**.

Yield: 1.30 g (67%); white solid.

IR (diamond-ATR, neat): 521, 602, 660, 681, 767, 839, 851, 977, 1034, 1047, 1068, 1112, 1138, 1168, 1324, 1381, 1463, 1531, 1605, 2866, 2890, 2938 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 1.03–1.06 (m, 18 H), 1.11–1.20 (m, 3 H), 2.58–2.66 (m, 1 H), 2.92–3.02 (m, 1 H), 3.19–3.33 (m, 2 H), 4.00 (dd, *J* = 12.0, 4.0 Hz, 1 H), 4.18 (dd, *J* = 12.0, 4.0 Hz, 1 H), 4.92–4.98 (m, 1 H), 7.95–8.01 (m, 4 H), 9.73 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 12.6, 18.2, 22.6, 30.2, 64.0, 65.3, 123.1, 124.6 (q, *J* = 270.0 Hz), 128.6 (q, *J* = 4.0 Hz), 132.9 (q, *J* = 33.0 Hz), 138.4, 139.3, 164.8.

^{19}F NMR (376 MHz, CD_3CN): δ = –151.73 (s, 4 F), –63.39 (s, 3 F).

HRMS (ESI): *m*/*z* $[M - BF_4]^+$ calcd for $C_{22}H_{33}F_3N_3OSi$: 440.2340; found: 440.2322.

(*S*)-2-[3,5-Bis(trifluoromethyl)phenyl]-5-{[(*tert*-butyldimethylsilyl)oxy]methyl}-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (10f)

NHC **10f** was prepared according to TP3. (1) Compound **9b** (1.0 g, 4.36 mmol, 1 equiv), anhydrous DCM (30 mL) and $Me_3O^+BF_4^-$ (709 mg, 4.8 mmol, 1.1 equiv). (2) [3,5-Bis(trifluoromethyl)phenyl]hydrazine (1.17 g, 4.8 mmol, 1.1 equiv). (3) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (5.8 mL, 34.87 mmol, 8 equiv). The crude product was purified by flash column chromatography (silica gel, DCM/acetone, 200:50) and washed with Et_2O to give the pure NHC compound **10f**.

Yield: 1.60 g (66%); white solid.

IR (diamond-ATR, neat): 521, 682, 698, 779, 836, 1029, 1066, 1136, 1183, 1278, 1364, 1381, 1528, 1603, 2863, 2887, 2933, 2957 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 0.11 (s, 3 H), 0.13 (s, 3 H), 0.90 (s, 9 H), 2.52–2.60 (m, 1 H), 2.90–3.00 (m, 1 H), 3.19–3.32 (m, 2 H), 3.87 (dd, *J* = 12.0, 8.0 Hz, 1 H), 4.09 (dd, *J* = 8.0, 4.0 Hz, 1 H), 4.90–4.96 (m, 1 H), 8.28–8.29 (m, 1 H), 8.37 (s, 2 H), 9.76 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = –5.4, –5.3, 18.9, 22.6, 26.2, 30.1, 64.2, 64.9, 123.6 (q, *J* = 3.0 Hz), 123.7 (q, *J* = 271.0 Hz), 125.7 (q, *J* = 3.0 Hz), 134.0 (q, *J* = 34.0 Hz), 137.8, 139.2, 164.8.

^{19}F NMR (376 MHz, CD_3CN): δ = –151.83 (s, 4 F), –63.58 (s, 6 F).

HRMS (ESI): *m*/*z* $[M - BF_4]^+$ calcd for $C_{20}H_{26}F_6N_3OSi$: 466.1744; found: 466.1738.

(*S*)-2-[4-(Trifluoromethoxy)phenyl]-5-{[(triisopropylsilyl)oxy]methyl}-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (10g)

NHC **10g** was prepared according to TP3. (1) Compound **9a** (1.06 g, 3.9 mmol, 1 equiv), anhydrous DCM (30 mL) and $Me_3O^+BF_4^-$ (635 mg, 4.3 mmol, 1.1 equiv). (2) 4-(Trifluoromethoxy)phenylhydrazine (826 mg, 4.3 mmol, 1.1 equiv). (3) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (5.2

mL, 31.2 mmol, 8 equiv). The crude product was purified by flash column chromatography (silica gel, DCM/acetone, 9:1) and washed with Et_2O to give the pure NHC compound **10g**.

Yield: 1.29 g (61%); white solid.

IR (diamond-ATR, neat): 500, 633, 772, 859, 919, 1035, 1046, 1108, 1169, 1256, 1520, 1598, 3024, 3091, 3194 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 1.03–1.06 (m, 18 H), 1.11–1.20 (m, 3 H), 2.58–2.66 (m, 1 H), 2.91–3.01 (m, 1 H), 3.17–3.31 (m, 2 H), 4.00 (dd, *J* = 12.0, 4.0 Hz, 1 H), 4.18 (dd, *J* = 12.0, 4.0 Hz, 1 H), 4.93–4.97 (m, 1 H), 7.58 (d, *J* = 8.0 Hz, 2 H), 7.87 (d, *J* = 8.0 Hz, 2 H), 9.67 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 12.6, 18.2, 22.6, 30.2, 63.9, 65.3, 121.1 (q, *J* = 265.0 Hz), 123.7, 124.7, 135.2, 138.1, 151.2, 164.6.

^{19}F NMR (376 MHz, CD_3CN): δ = –151.65 (s, 4 F), –58.73 (s, 3 F).

HRMS (ESI): *m*/*z* [M – BF_4]$^+$ calcd for $C_{22}H_{33}F_3N_3O_2Si$: 456.2289; found: 456.2283.

(*S*)-2-[4-(Trifluoromethoxy)phenyl]-5-{[(triisopropylsilyl)oxy]methyl}-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (10g); Alternative Protocol with DCM Treatment

NHC **10g** was prepared according to TP3 modified with an additional step involving treatment with DCM and $(EtO)_3CH$ (8 equiv).

(1) Compound **9a** (1.06 g, 3.9 mmol, 1 equiv), anhydrous DCM (30 mL) and $Me_3O^+BF_4^-$ (635 mg, 4.3 mmol, 1.1 equiv). (2) 4-(Trifluoromethoxy)phenylhydrazine (826 mg, 4.3 mmol, 1.1 equiv). (3) Anhydrous DCM (30 mL) and $(EtO)_3CH$ (5.2 mL, 31.2 mmol, 8 equiv), 40 °C, 1 h. (4) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (5.2 mL, 31.2 mmol, 8 equiv). The crude product was purified by flash column chromatography (silica gel, DCM/acetone, 9:1) and washed with Et_2O to give the pure NHC compound **10g**.

Yield: 860 mg (40%); white solid.

(*S*)-2-(4-Isopropylphenyl)-5-{[(triisopropylsilyl)oxy]methyl}-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (10h)

NHC **10h** was prepared according to TP3. (1) Compound **9a** (1.06 g, 3.9 mmol, 1 equiv), anhydrous DCM (30 mL) and $Me_3O^+BF_4^-$ (635 mg, 4.3 mmol, 1.1 equiv). (2) 4-Isopropylphenylhydrazine (646 mg, 4.3 mmol, 1.1 equiv). (3) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (5.2 mL, 31.2 mmol, 8 equiv). The crude product was purified by flash column chromatography (silica gel, DCM/acetone, 9:1) and washed with Et_2O to give the pure NHC compound **10h**.

Yield: 1.43 g (73%); white solid.

IR (diamond-ATR, neat): 483, 521, 642, 691, 837, 851, 882, 977, 1012, 1028, 1046, 1068, 1091, 1115, 1216, 1394, 1461, 1525, 1586, 2866, 2943, 2951 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 1.03–1.06 (m, 18 H), 1.11–1.20 (m, 3 H), 1.28 (s, 3 H), 1.29 (s, 3 H), 2.56–2.64 (m, 1 H), 2.90–3.09 (m, 2 H), 3.15–3.30 (m, 2 H), 3.97 (dd, *J* = 12.0, 8.0 Hz, 1 H), 4.16 (dd, *J* = 8.0, 4.0 Hz, 1 H), 4.87–4.93 (m, 1 H), 7.52–7.55 (m, 2 H), 7.66 (d, *J* = 8.0 Hz, 2 H), 9.56 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 12.6, 18.2, 22.6, 24.0, 30.2, 34.6, 63.6, 65.3, 122.3, 129.2, 134.5, 137.4, 153.4, 164.3.

HRMS (ESI): *m*/*z* [M – BF_4]$^+$ calcd for $C_{24}H_{40}N_3OSi$: 414.2935; found: 414.2917.

(*S*)-2-(2,6-Dimethylphenyl)-5-{[(triisopropylsilyl)oxy]methyl}-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (10i)

NHC **10i** was prepared according to TP3. (1) Compound **9a** (1.06 g, 3.9 mmol, 1 equiv), anhydrous DCM (30 mL) and $Me_3O^+BF_4^-$ (635 mg, 4.3 mmol, 1.1 equiv). (2) 2,6-Dimethylphenylhydrazine (585 mg, 4.3 mmol, 1.1 equiv). (3) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (5.2 mL, 31.2 mmol, 8 equiv). The crude product was purified by flash column chromatography (silica gel, DCM/acetone, 85:15) and washed with Et_2O to give the pure NHC compound **10i**.

Yield: 1.39 g (73%); white solid.

IR (diamond-ATR, neat): 521, 662, 681, 781, 855, 882, 974, 1025, 1055, 1099, 1196, 1288, 1386, 1462, 1588, 1689, 2865, 2890, 2942 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 1.04–1.07 (m, 18 H), 1.11–1.20 (m, 3 H), 2.11 (s, 6 H), 2.58–2.66 (m, 1 H), 2.93–3.03 (m, 1 H), 3.17–3.32 (m, 2 H), 4.00 (dd, *J* = 12.0, 8.0 Hz, 1 H), 4.19 (dd, *J* = 12.0, 4.0 Hz, 1 H), 4.93–4.99 (m, 1 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.48 (t, *J* = 8.0 Hz, 1 H), 9.37 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 12.5, 17.5, 18.3, 22.8, 30.0, 63.9, 65.1, 129.9, 132.7, 135.4, 136.5, 140.9, 164.8.

HRMS (ESI): *m*/*z* [M – BF_4]$^+$ calcd for $C_{23}H_{38}N_3OSi$: 400.2779; found: 400.2766.

(*S*)-2-Mesityl-5-{[(triisopropylsilyl)oxy]methyl}-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (10j)

NHC **10j** was prepared according to TP3. (1) Compound **9a** (1.06 g, 3.9 mmol, 1 equiv), anhydrous DCM (30 mL) and $Me_3O^+BF_4^-$ (635 mg, 4.3 mmol, 1.1 equiv). (2) Mesitylhydrazine (646 mg, 4.3 mmol, 1.1 equiv). (3) Anhydrous PhCl (30 mL) and $(EtO)_3CH$ (5.2 mL, 31.2 mmol, 8 equiv). The crude product was purified by flash column chromatography (silica gel, DCM/acetone, 85:15) and washed with Et_2O to give the pure NHC compound **10j**.

Yield: 1.70 g (87%); white solid.

IR (diamond-ATR, neat): 521, 662, 681, 707, 765, 854, 882, 945, 975, 1025, 1055, 1201, 1289, 1386, 1461, 1588, 2866, 2943 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 1.04–1.06 (m, 18 H), 1.10–1.19 (m, 3 H), 2.06 (s, 6 H), 2.37 (s, 3 H), 2.56–2.65 (m, 1 H), 2.92–3.01 (m, 1 H), 3.15–3.30 (m, 2 H), 3.40 (dd, *J* = 12.0, 4.0 Hz, 1 H), 4.18 (dd, *J* = 12.0, 4.0 Hz, 1 H), 4.91–4.97 (m, 1 H), 7.13 (s, 2 H), 9.39 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 12.5, 17.4, 18.3, 21.2, 22.8, 29.9, 63.8, 65.1, 130.4, 133.0, 136.1, 140.9, 143.2, 164.7.

HRMS (ESI): *m*/*z* [M – BF_4]$^+$ calcd for $C_{24}H_{40}N_3OSi$: 414.2935; found: 414.2932.

(*S*)-5-(Hydroxymethyl)-2-phenyl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (11a)

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with NHC **10a** (300 mg, 0.66 mmol, 1 equiv) in anhydrous PhCl (30 mL). HBF_4·OEt_2 (100 µL, 0.726 mmol, 1.1 equiv) was added and the reaction mixture was stirred at 20 °C for 10 h. The reaction mixture was diluted with CH_3OH (10 mL) and then transferred into a single-neck flask. The solvent was removed in vacuo at less than 50 °C. The obtained crude product was dissolved in 10 mL of CH_3OH and the solvent was removed in vacuo (the water bath should not exceed 50 °C) to remove residual acids and solvents, this process was repeated three times. The residue was dried under high vacuum for 12 h at 40 °C. The crude product was washed with Et_2O to give the pure compound **11a**.

Yield: 190 mg (95%); white solid.

IR (diamond-ATR, neat): 465, 508, 521, 689, 774, 972, 1028, 1054, 1224, 1380, 1466, 1515, 1585, 2956, 3075, 3120, 3499 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 2.51–2.56 (m, 1 H), 2.80–2.89 (m, 1 H), 3.17–3.34 (m, 2 H), 3.65–3.71 (m, 1 H), 3.88–3.93 (m, 1 H), 4.81–4.87 (m, 1 H), 5.44 (t, *J* = 8.0 Hz, 1 H), 7.63 (t, *J* = 8.0 Hz, 1 H), 7.69 (t, *J* = 8.0 Hz, 2 H), 7.94 (d, *J* = 8.0 Hz, 2 H), 10.81 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.2, 28.9, 61.6, 62.3, 120.6, 130.2, 130.4, 135.6, 138.2, 162.6.

HRMS (ESI): *m*/*z* [M – BF_4]$^+$ calcd for $C_{12}H_{14}N_3O$: 216.1131; found: 216.1129.

(*S*)-5-(Hydroxymethyl)-2-phenyl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (11a); Prepared from 10a′

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with NHC **10a′** (300 mg, 0.72 mmol, 1 equiv) in anhydrous PhCl (30 mL). HBF_4·OEt_2 (110 μL, 0.79 mmol, 1.1 equiv) was added and the reaction mixture was stirred at 20 °C for 1 h. The reaction mixture was diluted with CH_3OH (10 mL) and then transferred into a single-neck flask. The solvent was removed in vacuo (the water bath should not exceed 50 °C). The obtained crude product was dissolved in 10 mL of CH_3OH and the solvent was removed in vacuo (the water bath should not exceed 50 °C) to remove residual acids and solvents, this process was repeated three times. The residue was dried under high vacuum for 12 h at 40 °C. The crude product was washed with Et_2O to give the pure compound **11a**.

Yield: 200 mg (92%); white solid.

(*S*)-2-(3-Fluorophenyl)-5-(hydroxymethyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (11b)

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with NHC **10b** (200 mg, 0.42 mmol, 1 equiv) in anhydrous PhCl (20 mL). HBF_4·OEt_2 (64 μL, 0.46 mmol, 1.1 equiv) was added and the reaction mixture was stirred at 50 °C for 0.5 h. The reaction mixture was diluted with CH_3OH (10 mL) and then transferred into a single-neck flask. The solvent was removed in vacuo (the water bath should not exceed 50 °C). The obtained crude product was dissolved in 10 mL of CH_3OH and the solvent was removed in vacuo (the water bath should not exceed 50 °C) to remove residual acids and solvents, this process was repeated three times. The residue was dried under high vacuum for 12 h at 40 °C. The crude product was washed with hexane (3 × 10 mL) and Et_2O (3 × 10 mL) to give the pure compound **11b**.

Yield: 125 mg (93%); white semi-solid.

IR (diamond-ATR, neat): 454, 518, 677, 787, 867, 881, 981, 1032, 1049, 1221, 1286, 1386, 1461, 1522, 1592, 1609, 2961, 3105, 3135, 3541 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 2.47–2.55 (m, 1 H), 2.86–2.94 (m, 1 H), 3.20–3.26 (m, 2 H), 3.58–3.71 (m, 2 H), 4.00 (dd, *J* = 8.0, 4.0 Hz, 1 H), 4.81–4.87 (m, 1 H), 7.39 (t, *J* = 8.0 Hz, 1 H), 7.63–7.71 (m, 3 H), 9.78 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 22.5, 29.8, 63.2, 63.9, 110.0 (d, *J* = 28.0 Hz), 118.1 (d, *J* = 3.0 Hz), 118.8, 133.1 (d, *J* = 10.0 Hz), 137.7 (d, *J* = 10.0 Hz), 138.6, 163.8 (d, *J* = 246.0 Hz), 164.1.

^{19}F NMR (376 MHz, CD_3CN): δ = –151.29 (s, 4 F), –110.96 (s, 1 F).

HRMS (ESI): *m*/*z* [M – BF_4]$^+$ calcd for $C_{12}H_{13}FN_3O$: 234.1037; found: 234.1033.

(*S*)-2-(4-Fluorophenyl)-5-(hydroxymethyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (11c)

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with NHC **10c** (200 mg, 0.42 mmol, 1 equiv) in anhydrous PhCl (20 mL). HBF_4·OEt_2 (64 μL, 0.46 mmol, 1.1 equiv) was added and the reaction mixture was stirred at 50 °C for 1 h. The reaction mixture was diluted with CH_3OH (10 mL) and then transferred into a single neck-flask. The solvent was removed in vacuo (the water bath should not exceed 50 °C). The obtained crude product was dissolved in 10 mL of CH_3OH and the solvent was removed in vacuo (the water bath should not exceed 50 °C) to remove residual acids and solvents, this process was repeated three times. The residue was dried under high vacuum for 12 h at 40 °C. The crude product was washed with hexane (3 × 10 mL) and Et_2O (3 × 10 mL) and then washed with Et_2O to give the pure compound **11c**.

Yield: 120 mg (89%); white solid.

IR (diamond-ATR, neat): 521, 697, 849, 972, 1004, 1028, 1059, 1165, 1231, 1376, 1449, 1521, 1585, 2947, 3074, 3107, 3515 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 2.46–2.55 (m, 1 H), 2.84–2.94 (m, 1 H), 3.14–3.29 (m, 2 H), 3.60 (dd, *J* = 8.0, 4.0 Hz, 1 H), 3.66–3.72 (m, 1 H), 3.97–4.02 (m, 1 H), 4.80–4.86 (m, 1 H), 7.37–7.41 (m, 2 H), 7.83 (dd, *J* = 8.0, 4.0 Hz, 2 H), 9.72 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 22.4, 29.7, 63.2, 63.8, 124.9 (d, *J* = 9.0 Hz), 129.3, 133.1 (d, *J* = 2.0 Hz), 138.3, 164. 4 (d, *J* = 247.0 Hz), 165.6.

^{19}F NMR (376 MHz, CD_3CN): δ = –152.83 (s, 4 F), –111.07 (s, 1 F).

HRMS (ESI): *m*/*z* [M – BF_4]$^+$ calcd for $C_{12}H_{13}FN_3O$: 234.1037; found: 234.1027.

(*S*)-5-(Hydroxymethyl)-2-(perfluorophenyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (11d)

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with NHC **10d** (300 mg, 0.55 mmol, 1 equiv) in anhydrous PhCl (20 mL). HBF_4·OEt_2 (98 μL, 0.72 mmol, 1.3 equiv) was added and the reaction mixture was stirred at 80 °C for 2 h. The reaction mixture was diluted with CH_3OH (10 mL) and then transferred into a single-neck flask. The solvent was removed in vacuo (the water bath should not exceed 50 °C). The obtained crude product was dissolved in 10 mL of CH_3OH and the solvent was removed in vacuo (the water bath should not exceed 50 °C) to remove residual acids and solvents, this process was repeated three times. The residue was dried under high vacuum for 12 h at 40 °C. The crude product was washed with hexane (3 × 10 mL) and Et_2O (3 × 10 mL) and then washed with Et_2O to give the pure compound **11d**.

Yield: 160 mg (74%); white solid.

IR (diamond-ATR, neat): 523, 630, 744, 862, 976, 995, 1022, 1058, 1379, 1495, 1510, 1525, 1600, 1659, 3077, 3123, 3391 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 2.47–2.56 (m, 1 H), 2.86–2.95 (m, 1 H), 3.18–3.32 (m, 2 H), 3.63–3.74 (m, 2 H), 3.98–4.03 (m, 1 H), 4.87–4.93 (m, 1 H), 9.73 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.5, 28.9, 61.4, 63.3, 111.3 (m), 136.4 (m), 138.9 (m), 141.2 (m), 141.7 (m), 143.8, 143.9 (m), 164.0.

^{19}F NMR (376 MHz, CD_3CN): δ = –161.37 (t, *J* = 19.0 Hz, 2 F), –152.47 (s, 4 F), –149.39 (t, *J* = 23.0 Hz, 1 F), –146.70 (d, *J* = 19.0 Hz, 2 F).

HRMS (ESI): *m*/*z* [M – BF_4]$^+$ calcd for $C_{12}H_9F_5N_3O$: 306.0660; found: 306.0657.

(*S*)-5-(Hydroxymethyl)-2-(perfluorophenyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (11d); Prepared from 10d′

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with NHC **10d′** (300 mg, 0.59 mmol, 1 equiv) in anhydrous PhCl (30 mL). $HBF_4{\cdot}OEt_2$ (89 μL, 0.65 mmol, 1.3 equiv) was added and the reaction mixture was stirred at 20 °C for 1 h. The reaction mixture was diluted with CH_3OH (10 mL) and then transferred into a single-neck flask. The solvent was removed in vacuo (the water bath should not exceed 50 °C). The obtained crude product was dissolved in 10 mL of CH_3OH and the solvent was removed in vacuo (the water bath should not exceed 50 °C) to remove residual acids and solvents, this process was repeated three times. The residue was dried under high vacuum for 12 h at 40 °C. The crude product was washed with hexane (3 × 10 mL) and Et_2O (3 × 10 mL) and then washed with Et_2O to give the pure compound **11d**.

Yield: 192 mg (83%); white solid.

(*S*)-5-(Hydroxymethyl)-2-[4-(trifluoromethyl)phenyl]-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (11e)

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with NHC **10e** (300 mg, 0.56 mmol, 1 equiv) in anhydrous PhCl (20 mL). $HBF_4{\cdot}OEt_2$ (86 μL, 0.62 mmol, 1.1 equiv) was added and the reaction mixture was stirred at 50 °C for 1 h. The reaction mixture was diluted with CH_3OH (10 mL) and then transferred into a single-neck flask. The solvent was removed in vacuo (the water bath should not exceed 50 °C). The obtained crude product was dissolved in 10 mL of CH_3OH and the solvent was removed in vacuo (the water bath should not exceed 50 °C) to remove residual acids and solvents, this process was repeated three times. The residue was dried under high vacuum for 12 h at 40 °C. The crude product was recrystallized from benzene to give the pure compound **11e**.

Yield: 180 mg (87%); white solid.

IR (diamond-ATR, neat): 428, 480, 504, 523, 601, 661, 697, 754, 848, 974, 1029, 1054, 1065, 1115, 1165, 1322, 1381, 1421, 1446, 1529, 1595, 1755, 2867, 2948, 3087, 3118, 3535 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 2.46–2.57 (m, 1 H), 2.82–2.96 (m, 1 H), 3.15–3.32 (m, 2 H), 3.56–3.73 (m, 2 H), 3.92–4.04 (m, 1 H), 4.83–4.89 (m, 1 H), 7.93–8.03 (m, 4 H), 9.87 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 22.5, 29.8, 63.2, 64.0, 122.9, 124.6 (q, *J* = 270.0 Hz), 128.5 (q, *J* = 4.0 Hz), 132.7 (q, *J* = 33.0 Hz), 138.9, 139.4, 164.3.

^{19}F NMR (376 MHz, CD_3CN): δ = –152.12 (s, 4 F), –63.37 (s, 3 F).

HRMS (ESI): *m*/*z* $[M - BF_4]^+$ calcd for $C_{13}H_{13}F_3N_3O$: 284.1005; found: 284.1005.

(*S*)-2-[3,5-Bis(trifluoromethyl)phenyl]-5-(hydroxymethyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (11f)

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with NHC **10f** (200 mg, 0.36 mmol, 1 equiv) in anhydrous PhCl (20 mL). $HBF_4{\cdot}OEt_2$ (50 μL, 0.40 mmol, 1.1 equiv) was added and the reaction mixture was stirred at 20 °C for 0.5 h. The reaction mixture was diluted with CH_3OH (10 mL) and then transferred into a single-neck flask. The solvent was removed in vacuo (the water bath should not exceed 50 °C). The obtained crude product was dissolved in 10 mL of CH_3OH and the solvent was removed in vacuo (the water bath should not exceed 50 °C) to remove residual acids and solvents, this process was repeated three times. The residue was dried under high vacuum for 12 h at 40 °C. The crude product was washed with hexane (3 × 10 mL) and Et_2O (3 × 10 mL) and then recrystallized from acetone/$CHCl_3$/hexane (1:3:7) to give the pure compound **11f**.

Yield: 130 mg (82%); white solid.

IR (diamond-ATR, neat): 415, 524, 682, 702, 717, 845, 899, 976, 1008, 1054, 1135, 1189, 1285, 1364, 1518, 1598, 3081, 3105, 3132, 3498 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 2.47–2.56 (m, 1 H), 2.87–2.97 (m, 1 H), 3.24–3.29 (m, 2 H), 3.63–3.73 (m, 2 H), 4.02 (dt, *J* = 12.0, 4.0 Hz, 1 H), 4.85–4.92 (m, 1 H), 8.27 (s, 1 H), 8.41 (s, 2 H), 9.96 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 22.5, 29.7, 63.1, 64.3, 123.2, 123.3, 123.7 (q, *J* = 271.0 Hz), 125.5 (m), 133.9 (q, *J* = 35.0 Hz), 137.9, 139.6, 164.5.

^{19}F NMR (376 MHz, CD_3CN): δ = –151.92 (s, 4 F), –63.55 (s, 6 F).

HRMS (ESI): *m*/*z* $[M - BF_4]^+$ calcd for $C_{14}H_{12}F_6N_3O$: 352.0879; found: 352.0864.

(*S*)-5-(Hydroxymethyl)-2-[4-(trifluoromethoxy)phenyl]-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (11g)

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with NHC **10g** (300 mg, 0.55 mmol, 1 equiv) in anhydrous PhCl (20 mL). $HBF_4{\cdot}OEt_2$ (83 μL, 0.61 mmol, 1.1 equiv) was added and the reaction mixture was stirred at 50 °C for 1 h. The reaction mixture was diluted with CH_3OH (10 mL) and then transferred into a single-neck flask. The solvent was removed in vacuo (the water bath should not exceed 50 °C). The obtained crude product was dissolved in 10 mL of CH_3OH and the solvent was removed in vacuo (the water bath should not exceed 50 °C) to remove residual acids and solvents, this process was repeated three times. The residue was dried under high vacuum for 12 h at 40 °C. The crude product was washed with hexane (3 × 10 mL) and Et_2O (3 × 10 mL) and then washed with Et_2O to give the pure compound **11g**.

Yield: 120 mg (56%); white solid.

IR (diamond-ATR, neat): 458, 520, 568, 794, 854, 1015, 1162, 1179, 1189, 1238, 1269, 1526, 1599, 3097, 3130, 3537 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 2.47–2.55 (m, 1 H), 2.85–2.92 (m, 1 H), 3.16–3.30 (m, 2 H), 3.58–3.72 (m, 2 H), 4.01 (dt, *J* = 12.0, 4.0 Hz, 1 H), 4.81–4.88 (m, 1 H), 7.57 (d, *J* = 8.0 Hz, 2 H), 7.91 (d, *J* = 8.0 Hz, 2 H), 9.77 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.2, 28.9, 61.7, 62.5, 119.9 (q, *J* = 257.0 Hz), 122.8, 123.0, 134.4, 138.8, 149.0, 162.7.

^{19}F NMR (376 MHz, CD_3CN): δ = –151.78 (s, 4 F), –58.74 (s, 3 F).

HRMS (ESI): *m*/*z* $[M - BF_4]^+$ calcd for $C_{13}H_{13}F_3N_3O_2$: 300.0954; found: 300.0950.

(*S*)-5-(Hydroxymethyl)-2-(4-isopropylphenyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (11h)

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with NHC **10h** (300 mg, 0.6 mmol, 1 equiv) in anhydrous PhCl (20 mL). $HBF_4{\cdot}OEt_2$ (90 μL, 0.66 mmol, 1.1 equiv) was added and the reaction mixture was stirred at 20 °C for 0.5 h. The reaction mixture was diluted with CH_3OH (10 mL) and then transferred into a single-neck flask. The solvent was removed in vacuo (the water bath should not exceed 50 °C). The obtained crude product was dissolved in 10 mL of CH_3OH and the solvent was removed in vacuo (the water bath should not exceed 50 °C) to remove residual acids and solvents, this process was repeated three

times. The residue was dried under high vacuum for 12 h at 40 °C. The crude product was washed with hexane (3 × 10 mL) and Et_2O (3 × 10 mL) to give the pure compound **11h**.

Yield: 194 mg (94%); white semi-solid.

IR (diamond-ATR, neat): 521, 550, 647, 838, 975, 1012, 1032, 1049, 1286, 1389, 1421, 1452, 1525, 1586, 2873, 2933, 2963, 3137, 3539 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 1.28 (d, *J* = 8.0 Hz, 6 H), 2.47–2.58 (m, 1 H), 2.85–2.94 (m, 1 H), 3.00–3.07 (m, 1 H), 3.14–3.28 (m, 2 H), 3.57–3.59 (m, 1 H), 3.67–3.73 (m, 1 H), 3.98–4.03 (m, 1 H), 4.80–4.86 (m, 1 H), 7.51 (dd, *J* = 8.0, 4.0 Hz, 2 H), 7.72 (d, *J* = 8.0 Hz, 2 H), 9.72 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 22.4, 24.0, 29.8, 34.6, 63.2, 63.7, 122.2, 129.1, 134.7, 137.8, 153.1, 163.8.

HRMS (ESI): *m*/*z* [M – BF_4]$^+$ calcd for $C_{15}H_{20}N_3O$: 258.1601; found: 258.1594.

(*S*)-2-(2,6-Dimethylphenyl)-5-(hydroxymethyl)-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (11i)

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with NHC **10i** (300 mg, 0.62 mmol, 1 equiv) in anhydrous PhCl (20 mL). HBF_4·OEt_2 (93 µL, 0.67 mmol, 1.1 equiv) was added and the reaction mixture was stirred at 20 °C for 1 h. The reaction mixture was diluted with CH_3OH (10 mL) and then transferred into a single-neck flask. The solvent was removed in vacuo (the water bath should not exceed 50 °C). The obtained crude product was dissolved in 10 mL of CH_3OH and the solvent was removed in vacuo (the water bath should not exceed 50 °C) to remove residual acids and solvents, this process was repeated three times. The residue was dried under high vacuum for 12 h at 40 °C. The crude product was washed with hexane (3 × 10 mL) and Et_2O (3 × 10 mL) to give the pure compound **11i**.

Yield: 140 mg (68%); white semi-solid.

IR (diamond-ATR, neat): 521, 664, 784, 972, 1028, 1195, 1228, 1385, 1452, 1515, 1589, 1742, 2930, 2967, 3088, 3128, 3552 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 2.06 (s, 3 H), 2.13 (s, 3 H), 2.19 (s, 1 H), 2.57–2.68 (m, 1 H), 2.96–3.06 (m, 1 H), 3.19–3.32 (m, 2 H), 4.20–4.25 (m, 1 H), 4.63 (dd, *J* = 12.0, 4.0 Hz, 1 H), 5.04–5.10 (m, 1 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.48 (t, *J* = 8.0 Hz, 1 H), 9.47 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 17.5, 20.8, 22.5, 30.0, 60.9, 64.5, 129.9, 132.7, 135.3, 136.6, 141.5, 164.5, 171.3.

HRMS (ESI): *m*/*z* [M – BF_4]$^+$ calcd for $C_{14}H_{18}N_3O$: 244.1444; found: 244.1441.

(*S*)-5-(Hydroxymethyl)-2-mesityl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium Tetrafluoroborate (11j)

A dry, argon-flushed, two-neck Schlenk flask equipped with a magnetic stir bar and a septum was charged with NHC **10j** (1.0 g, 2.0 mmol, 1 equiv) in anhydrous PhCl (80 mL). HBF_4·OEt_2 (301 µL, 2.2 mmol, 1.1 equiv) was added and the reaction mixture was stirred at 20 °C for 8 h. The reaction mixture was diluted with CH_3OH (10 mL) and then transferred into a single-neck flask. The solvent was removed in vacuo (the water bath should not exceed 50 °C). The obtained crude product was dissolved in 10 mL of CH_3OH and the solvent was removed in vacuo (the water bath should not exceed 50 °C) to remove residual acids and solvents, this process was repeated three times. The residue was dried under high vacuum for 12 h at 40 °C. The crude product was washed with hexane (3 × 10 mL) and Et_2O (3 × 10 mL) and then recrystallized from Et_2O to give the pure compound **11j**.[7a]

Yield: 650 mg (94%); white solid.

IR (diamond-ATR, neat): 521, 674, 842, 871, 974, 1002, 1018, 1032, 1068, 1203, 1288, 1380, 1449, 1515, 1590, 2965, 3030, 3141 cm^{-1}.

^1H NMR (400 MHz, CD_3CN): δ = 2.07 (s, 6 H), 2.36 (s, 3 H), 2.47–2.56 (m, 1 H), 2.86–2.95 (m, 1 H), 3.19–3.24 (m, 2 H), 3.60 (t, *J* = 8.0 Hz, 1 H), 3.68–3.74 (m, 1 H), 3.97–4.02 (m, 1 H), 4.84–4.90 (m, 1 H), 7.13 (s, 2 H), 9.43 (s, 1 H).

^{13}C NMR (100 MHz, CD_3CN): δ = 16.9, 20.7, 21.4, 28.8, 61.5, 62.4, 129.1, 132.0, 134.8, 141.2, 141.5, 162.9.

HRMS (ESI): *m*/*z* [M – BF_4]$^+$ calcd for $C_{15}H_{20}N_3O$: 258.1601; found: 258.1599.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611786.

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