Supporting Information

Synthesis of 4- and 4,5-Functionalized Imidazol-2-Ylidenes from a Single 4,5-Unsubstituted Imidazol-2-Ylidene

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Contents:

Synthesis, physical and spectroscopic data for all new compounds

General Considerations:

All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques. Solvents were dried by standard methods and distilled under argon. ^{1}H, ^{31}P, ^{19}F and ^{13}C NMR spectra were recorded on Varian Inova 400, 500 and Bruker 300 spectrometers at 25 °C. NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *sept* = septet, *m* = multiplet, *b* = broad signal. Mass spectra were performed at the UC Riverside Mass Spectrometry Laboratory. HRMS and elemental analyses for the new carbenes **4a-f** and **7** are not available due to the known instability of these products for such characterization methods. Melting points were measured with a Büchi melting point apparatus system. N,N'-1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, IDipp (**1**)[1] and N,N'-1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazol-5-ylidene, *a*NHC (**2'**)[2] were prepared following the literature procedures while all other starting materials were purchased from commercial sources.

Synthesis and characterization

N,N'-1,3-bis(2,6-diisopropylphenyl)-2-benzoylimidazolium chloride [IDipp(PhC=O)][Cl] (3a). A diethyl ether (Et_2O) solution (5 mL) of benzoyl chloride (0.147 g, 1.05 mmol) was added slowly to an Et_2O solution of NHC **1** (0.407 g, 1.05 mmol). The resulting suspension was stirred for 1 h at room temperature. The supernatant was removed with a syringe, and the solid residue was then washed four times with Et_2O (4 x 10 mL). After drying under vacuum, a low temperature crystallization (-20 °C) from an CH_3CN/Et_2O (1:2) solution afforded **3a** as colorless crystals. Yield 79% (0.439 g, 0.830 mmol). Mp: 197-199 °C. ^{1}H NMR (CD_3CN, 300 MHz): δ 1.22 (d, 6.8 Hz, 12 H, $CH(C\mathit{H}_3)_2$), 1.25 (d, 6.8 Hz, 12 H, $CH(C\mathit{H}_3)_2$), 2.65 (sept, 6.8 Hz, 4 H, $C\mathit{H}(CH_3)_2$), 7.37 (d, 7.8 Hz, 4 H, CH_{ar}), 7.49 (t, 7.8 Hz, 2 H, CH_{ar}), 7.55 (t, 7.2 Hz, 2 H, CH_{ar}), 7.65 (d, 7.2 Hz, 2 H, CH_{ar}), 7.72 (t, 7.2 Hz, 1 H, CH_{ar}), 8.29 (s, 2 H, CH_{imid}). ^{13}C NMR (CD_3CN, 100 MHz): δ 22.7, 26.1 (CH(CH$_3$)$_2$), 30.2 (CH(CH$_3$)$_2$), 126.1 (CH$_{ar}$), 128.7 (C$_{ar}$), 129.9 (CH$_{ar}$), 130.4 (CH$_{ar}$), 131.0 (CH$_{ar}$), 133.5 (CH$_{imid}$), 134.3 (C$_{imid}$), 138.1 (CH$_{ar}$), 142.7 (C$_{ar}$), 146.5 (C$_{ar}$), 181.0 (C=O). HRMS (ESI; CH$_3$CN): m/z calculated for $C_{34}H_{41}N_2O$ 493.3213, found 493.3220.

N,N'-1,3-bis(2,6-diisopropylphenyl)-2-chloroimidazolium chloride [IDippCl][Cl] (3b). NHC **1** (0.402 g, 1.03 mmol) and 1,1,1,2,2,2-hexachloroethane (0.259 g, 1.09 mmol) were combined in a Schlenk flask and dissolved in acetonitrile (30 mL). The resulting amber solution was sonicated for 24 h. Removal of volatiles under vacuum gave a light brown solid that was washed with toluene (15 mL) and extracted with acetonitrile (5 mL). This extract was concentrated in vacuum to half the volume and placed at -20 °C to yield 0.392 g of compound **3b** as colorless crystals (0.853 mmol, 83% yield). Mp: 283-285 °C. ^{1}H NMR (CD$_3$CN, 300 MHz): δ 1.25 (d, 6.8 Hz, 12 H, CH(C$H$$_3$)$_2$), 1.30 (d, 6.8 Hz, 12 H, CH(C$H$$_3$)$_2$), 2.37 (sept, 6.8 Hz, 4 H, CH(CH$_3$)$_2$), 7.56 (d, 7.8 Hz, 4 H, CH$_{ar}$), 7.75 (t, 7.8 Hz, 2 H, CH$_{ar}$), 8.40 (s, 2 H, CH$_{imid}$). ^{13}C NMR (CD$_3$CN, 75 MHz): δ 23.6, 24.3 (CH(CH$_3$)$_2$), 30.2 (CH(CH$_3$)$_2$), 118.4 (C$_{ar}$), 125.6 (CH$_{ar}$), 126.9 (CH$_{imid}$), 127.8 (C$_{imid}$), 133.9 (CH$_{ar}$), 146.4 (C$_{ar}$). HRMS (ESI; CH$_3$CN): m/z calculated for $C_{27}H_{36}ClN_2$ 423.2562, found 423.2564.

N,N'-1,3-bis(2,6-diisopropylphenyl)-2-bromoimidazolium bromide [IDippBr][Br] (3c). Dibromine (0.168 g, 1.05 mmol) was added dropwise to a solution of NHC **1** (0.402 g, 1.03 mmol) in THF (30 mL) at room temperature. The white suspension was stirred for 3 h. The solid was filtered and washed with toluene (10 mL) and extracted with acetonitrile (5 mL). Crystallization at -20°C affords 0.486 g of **3c** as colorless crystals (0.886 mmol, 86% yield). Mp: 268 °C (decomp). ^{1}H NMR (CD$_3$CN, 300 MHz): δ 1.27 (d, 6.8 Hz, 12 H, CH(C$H$$_3$)$_2$), 1.28 (d, 6.8 Hz, 12 H, CH(C$H$$_3$)$_2$), 2.34 (sept, 6.8 Hz, 4 H, CH(CH$_3$)$_2$), 7.55 (d, 7.8 Hz, 4 H, CH$_{ar}$), 7.74 (t, 7.8 Hz, 2 H, C$H$$_{ar}$), 8.12 (s, 2 H, CH$_{imid}$). ^{13}C NMR (CD$_3$CN, 75 MHz): δ 23.6, 24.4

(CH(*C*H$_3$)$_2$), 30.2 (*C*H(CH$_3$)$_2$), 117.3 (C$_{ar}$), 126.3 (CH$_{ar}$), 128.2 (CH$_{imid}$), 130.9 (C$_{imid}$), 133.7 (CH$_{ar}$), 146.4 (C$_{ar}$). HRMS (ESI; CH$_3$CN): m/z calculated for $C_{27}H_{36}BrN_2$ 467.2056, found 467.2071.

N,N'-1,3-bis(2,6-diisopropylphenyl)-2-trifluoromethanesulfonylimidazolium triflate [IDipp(SO$_2$CF$_3$)][OTf] (3d). The procedure described for the preparation of imidazolium **3a** was followed, using in this case triflic anhydride (0.296 g, 1.05 mmol). Imidazolium salt **3d** was isolated as colorless crystals. Yield 72% (0.507 g, 0.756 mmol). Mp: 213-215 °C. ^{1}H NMR (CD$_3$CN, 400 MHz): δ 1.23 (d, 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.35 (d, 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 2.30 (sept, 6.8 Hz, 4 H, C*H*(CH$_3$)$_2$), 7.55 (d, 7.8 Hz, 4 H, CH$_{ar}$), 7.75 (t, 7.8 Hz, 2 H, C*H*$_{ar}$), 8.56 (s, 2 H, CH$_{imid}$).^{13}C NMR (CD$_3$CN, 100 MHz): δ 22.4, 26.2, (CH(*C*H$_3$)$_2$), 30.7 (*C*H(CH$_3$)$_2$), 124.2 (q, *J*(C,F) = 318 Hz), 126.2 (CH$_{ar}$), 127.4 (C$_{ar}$), 130.5 (CH$_{imid}$), 134.3 (C$_{imid}$), 134.7 (CH$_{ar}$), 146.1 (C$_{ar}$). ^{19}F NMR (CD$_3$CN, 282 MHz): δ −78.4. HRMS (ESI; CH$_3$CN): m/z calculated for $C_{28}H_{36}F_3N_2O_2S$ 521.2444, found 521.2465.

N,N'-1,3-bis(2,6-diisopropylphenyl)-2-trimethylsilylimidazolium triflate [IDipp(SiMe$_3$)][OTf] (3e). The procedure described for the preparation of imidazolium **3a** was followed, using in this case trimethylsilyl triflate (0.233 g, 1.05 mmol). Imidazolium salt **3e** was isolated as colorless crystals. Yield 80% (0.513 g, 0.840 mmol). Mp: 226-228 °C. ^{1}H NMR (CD$_3$CN, 300 MHz): δ -0.18 (s, 9 H, Si(CH$_3$)$_3$), 1.18 (d, 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.36 (d, 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 2.37 (sept, 6.8 Hz, 4 H, C*H*(CH$_3$)$_2$), 7.50 (d, 7.8 Hz, 4 H, CH$_{ar}$), 7.66 (t, 7.8 Hz, 2 H, CH$_{ar}$), 7.91 (s, 2 H, C*H*$_{imid}$). ^{13}C NMR (CD$_3$CN, 75 MHz): δ -0.5 (Si(CH$_3$)$_3$), 23.0, 26.8 (CH(*C*H$_3$)$_2$), 30.7 (*C*H(CH$_3$)$_2$), 126.4 (CH$_{ar}$), 126.5 (q, *J*(C,F) = 318 Hz), 127.7 (C$_{ar}$), 130.3 (CH$_{imid}$), 133.7 (C$_{imid}$), 134.0 (CH$_{ar}$), 147.1 (C$_{ar}$). ^{19}F NMR (CD$_3$CN, 282 MHz): δ −78.4. HRMS (ESI; CH$_3$CN): m/z calculated for $C_{27}H_{37}N_2$ – SiMe$_3$ 389.2951, found 389.2960.

N,N'-1,3-bis(2,6-diisopropylphenyl)-2-diphenylphosphinoimidazolium chloride [IDipp(Ph$_2$P)][Cl] (3f). The procedure described for the preparation of imidazolium **3a** was followed, using in this case diphenylphosphine chloride (0.231 g , 1.05 mmol). Yield 77% (0.492 g, 0.808 mmol). Imidazolium salt **3f** was isolated as colorless crystals. Mp: 198-200 °C. ^{1}H NMR (CD$_3$CN, 300 MHz): δ 1.13 (d, 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.16 (d, 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 2.55 (sept, 6.8 Hz, 4 H, C*H*(CH$_3$)$_2$), 7.10-7.12 (m, 3 H, CH$_{ar}$), 7.17-7.21 (m, 5 H, CH$_{ar}$), 7.24 (d, 7.8 Hz, 4 H, CH$_{ar}$), 7.33 (t, 7.8 Hz, 2 H, CH$_{ar}$), 7.49 (t, 7.8 Hz, 2 H, CH$_{ar}$), 8.20 (s, 2 H, CH$_{imid}$). ^{13}C NMR (CD$_3$CN, 100 MHz): δ 22.7, 26.9 (CH(*C*H$_3$)$_2$), 30.9 (*C*H(CH$_3$)$_2$), 126.1 (CH$_{ar}$), 126.4 (CH$_{ar}$), 130.7 (d, J_{CP} = 9.5 Hz, C$_{ar}$), 130.9 (CH$_{ar}$), 131.0 (CH$_{imid}$), 132.7 (d, J_{CP} = 7.5 Hz, C$_{imid}$), 133.8 (CH$_{ar}$), 136.1 (CH$_{ar}$), 136.5 (C$_{ar}$), 146.6 (C$_{ar}$). ^{31}P NMR (CD$_3$CN, 121 MHz): δ -12.9. HRMS (ESI; CH$_3$CN): m/z calculated for $C_{39}H_{46}N_2P$ 573.3393, found 573.3399.

General Synthesis for 4-substituted NHCs 4a-4f.

Potassium hexamethyldisilazide (0.213 g, 1.07 mmol) and the appropriate imidazolium salt (1.05 mmol) were combined in a Schlenk flask and dissolved in THF (18 mL) at -78°C. The reaction mixture was stirred for 30 minutes. The cold bath was removed and the reaction mixture was stirred for another 30 minutes. The THF was removed under vacuum, and the residue was extracted with 40 mL of hexane. The extract was dried under vacuum yielding the crude products as white or yellowish solids.

N,N'-1,3-bis(2,6-diisopropylphenyl))-4-benzoylimidazol-2-ylidene, [IDipp(PhC=O)] (4a). The crude material was cooled down to 0°C and washed with 10 mL of hexane. After filtration, the remaining solid was dried under vacuum yielding 0.331 g of [IDipp(PhC=O)] (**4a**) as a white solid (0.672 mmol, 64% yield). Single crystals were obtained by recrystallization from a saturated toluene/hexane (1:2) solution at -20°C. Mp: 115-117 °C. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ

1.24 (d, 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.38 (d, 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.40 (d, 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.45 (d, 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 3.08 (d, 6.9Hz, 2 H, C*H*(CH$_3$)$_2$), 3.15 (d, 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$), 7.10 (t, 7.9 Hz, 2 H, CH$_{ar}$), 7.16 (s, 1 H, CH$_{imid}$), 7.17 (d, 7.1 Hz, 1 H, CH$_{ar}$), 7.25 (d, 7.9 Hz, 2 H, CH$_{ar}$), 7.34 (d, 7.9 Hz, 2 H, CH$_{ar}$), 7.38-7.43 (m, 2 H, CH$_{ar}$), 7.89 (d, 7.2 Hz, 2 H, CH$_{ar}$). ^{13}C NMR (CD$_3$CN, 75 MHz): δ 23.6, 23.8, 25.0, 25.1 (CH(*C*H$_3$)$_2$), 29.3, 29.8 (*C*H(CH$_3$)$_2$), 123.9 (CH$_{ar}$), 124.2 (CH$_{ar}$), 129.0 (CH$_{ar}$), 129.3 (CH$_{ar}$), 129.5 (CH$_{ar}$), 129.8 (CH$_{ar}$), 130.8 (CH$_{ar}$), 132.8 (CH$_{imid}$), 133.1 (C$_{ar}$), 138.0 (C$_{imid}$), 138.3 (C$_{ar}$), 139.8 (C$_{ar}$), 146.2 (C$_{ar}$), 146.3 (C$_{ar}$), 183.6 (C=O), 227.2 (C$_{carbene}$).

N,N'-1,3-bis(2,6-diisopropylphenyl))-4-chloroimidazol-2-ylidene, [IDipp(Cl)] (4b). The crude material was cooled down to -78 °C and extracted with 10 mL of hexane. After filtration, the hexane was removed under vacuum yielding 0.186 g of [IDipp(Cl)] (**4b**) as a white solid (0.441 mmol, 42% yield). Mp: 132-134 °C. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 1.27 (d, 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.32 (d, 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.36 (d, 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.40 (d, 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 2.98-3.08 (m, 4 H, C*H*(CH$_3$)$_2$), 6.67 (s, 1 H, CH$_{imid}$), 7.24-7.30 (m, 4 H, CH$_{ar}$), 7.34-7.38 (m, 2 H, CH$_{ar}$). ^{13}C NMR (C$_6$D$_6$, 75 MHz): δ 23.4, 23.8, 25.1, 25.3 (CH(*C*H$_3$)$_2$), 29.1, 29.5 (*C*H(CH$_3$)$_2$), 121.8 (CH$_{ar}$), 124.1 (CH$_{ar}$), 124.3 (C$_{ar}$), 124.6 (CH$_{ar}$), 127.6 (CH$_{ar}$), 129.6 (C$_{ar}$), 130.0 (CH$_{imid}$), 130.3 (C$_{imid}$), 146.4 (C$_{ar}$), 147.1 (C$_{ar}$), 222.5 (C$_{carbene}$).

N,N'-1,3-bis(2,6-diisopropylphenyl))-4-bromoimidazol-2-ylidene, [IDipp(Br)] (4c). The purification procedure was performed as described for **4b**, yielding 0.191 g of [IDipp(Br)] (**4c**) as a white solid (0.410 mmol, 39% yield). Mp: 146 °C (decomp). ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 1.26 (d, 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.30 (d, 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.34 (d, 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.38 (d, 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 2.95-3.07 (m, 4 H, C*H*(CH$_3$)$_2$), 6.73 (s, 1 H, CH$_{imid}$), 7.25-7.32 (m, 4 H, CH$_{ar}$), 7.36-7.39 (m, 2 H, CH$_{ar}$). ^{13}C NMR (C$_6$D$_6$, 75 MHz): δ 23.4, 23.8, 25.2, 25.3 (CH(*C*H$_3$)$_2$), 29.1, 29.5 (*C*H(CH$_3$)$_2$), 121.9 (CH$_{ar}$), 124.0 (CH$_{ar}$), 124.1 (C$_{ar}$), 124.4 (CH$_{ar}$), 127.6 (CH$_{ar}$), 129.3 (C$_{ar}$), 129.7 (CH$_{imid}$), 130.3 (C$_{imid}$), 146.6 (C$_{ar}$), 147.2 (C$_{ar}$), 223.3 (C$_{carbene}$).

N,N'-1,3-bis(2,6-diisopropylphenyl))-4-trifluoromethanesulfonylimidazol-2-ylidene, [IDipp(SO$_2$CF$_3$)] (4d). The crude material was cooled down to 0^{o}C and washed with 10 mL of hexane. After filtration, the remaining solid was dried under vacuum yielding 0.393 g of [IDipp(SO$_2$CF$_3$)] (**4d**) as a white solid (0.756 mmol, 72% yield). Mp: 124-126 ^{o}C. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 1.14 (d, 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.24 (d, 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.34 (d, 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.42 (d, 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 2.74-3.91 (m, 4 H, C*H*(CH$_3$)$_2$), 7.17 (d, 7.8 Hz, 2 H, CH$_{ar}$), 7.26 (d, 7.8 Hz, 2 H, CH$_{ar}$), 7.29-7.39 (m, 2 H, CH$_{ar}$), 7.51(s, 1 H, CH$_{imid}$). ^{13}C NMR (C$_6$D$_6$, 125 MHz): δ 22.2, 23.7, 24.5, 26.4 (CH(*C*H$_3$)$_2$), 29.2, 30.1 (*C*H(CH$_3$)$_2$), 120.5 (q, *J* (C,F) = 323 Hz), 124.1 (CH$_{ar}$), 124.4 (CH$_{ar}$), 124.9 (C$_{ar}$), 130.5 (CH$_{ar}$), 130.7 (CH$_{ar}$), 134.8 (C$_{ar}$), 136.7 (CH$_{imid}$), 137.0 (C$_{imid}$), 145.8 (C$_{ar}$), 146.9 (C$_{ar}$), 231.6 (C$_{carbene}$). ^{19}F NMR (C$_6$D$_6$, 282 MHz): δ -77.8.

N,N'-1,3-bis(2,6-diisopropylphenyl))-4-trimethylsilylimidazol-2-ylidene, [IDipp(SiMe$_3$)] (4e). The crude material was cooled down to -78 ^{o}C and extracted with 10 mL of hexane. After filtration, the solvent was removed under vacuum yielding 0.169 g of [IDipp(SiMe$_3$)] (**4e**) as a white solid (0.367 mmol, 35% yield). Mp: 110-112 ^{o}C. ^{1}H NMR (C$_6$D$_6$, 300 MHz): δ 0.05 (s, 9 H, Si(CH$_3$)$_3$), 1.29 (d, 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.39 (d, 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.40 (d, 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.51 (d, 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$), 2.96 (sept, 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$), 3.13 (sept, 6.8 Hz, 2 H, C*H*(CH$_3$)$_2$), 7.01 (s, 1 H, CH$_{imid}$), 7.29 (d, 7.8 Hz, 2 H, CH$_{ar}$), 7.31 (d, 7.8 Hz, 2 H, CH$_{ar}$), 7.37-7.44 (m, 2 H, CH$_{ar}$). ^{13}C NMR (C$_6$D$_6$, 75 MHz): δ 0.0 (Si(CH$_3$)$_3$), 22.3, 23.9, 24.3, 26.8 (CH(*C*H$_3$)$_2$), 29.0, 29.5 (*C*H(CH$_3$)$_2$), 123.6 (CH$_{ar}$), 124.1 (CH$_{ar}$), 127.3 (C$_{ar}$), 127.7

(C_{ar}), 129.2 (CH_{ar}), 129.4 (CH_{ar}), 131.0 (CH_{imid}), 132.1 (C_{imid}), 146.6 (C_{ar}), 147.0 (C_{ar}), 223.7 ($C_{carbene}$).

N,N'-1,3-bis(2,6-diisopropylphenyl))-4-diphenylphosphinoimidazol-2-ylidene, [IDipp(Ph_2P)] (4f). The crude material was cooled down to 0°C and washed with 10 mL of hexane. After filtration, the remaining solid is dried under vacuum yielding 0.343 g of [IDipp(Ph_2P)] (**4f**) as a light yellowish solid (0.599 mmol, 57% yield). Single crystals were obtained by recrystallization from a concentrated toluene/hexane solution at -20°C. Mp: 202-204 °C. ^{1}H NMR (C_6D_6, 300 MHz): δ 1.19 (d, 6.9 Hz, 6 H, $CH(CH_3)_2$), 1.26 (d, 6.9 Hz, 6 H, $CH(CH_3)_2$), 1.40 (d, 6.9 Hz, 6 H, $CH(CH_3)_2$), 1.47 (d, 6.9 Hz, 6 H, $CH(CH_3)_2$), 2.96 (d, 6.9 Hz, 2 H, $CH(CH_3)_2$), 3.20 (d, 6.9 Hz, 2 H, $CH(CH_3)_2$), 6.83 (s, 1 H, CH_{imid}), 7.05-7.14 (m, 6 H, CH_{ar}), 7.25-7.31 (m, 6 H, CH_{ar}), 7.39 (t, 7.4 Hz, 2 H, CH_{ar}), 7.41-7.50 (m, 2 H, CH_{ar}). ^{13}C NMR (CD_3CN, 100 MHz): δ 22.6, 24.3, 24.7, 26.0 ($CH(CH_3)_2$), 29.1, 29.8 ($CH(CH_3)_2$), 123.9 (CH_{ar}), 124.1 (CH_{ar}), 129.2 (CH_{ar}), 129.4 (d, J_{CP} = 7.2 Hz, CH_{ar}), 129.8 (CH_{ar}), 130.5 (CH_{ar}), 132.6 (d, J_{CP} = 10.7 Hz, C_{ar}), 133.7 (CH_{imid}), 133.9 (CH_{ar}), 137.0 (d, J_{CP} = 9.5 Hz, C_{imid}), 137.7 (C_{ar}), 139.0 (C_{ar}), 146.3 (C_{ar}), 147.1 (C_{ar}), 223.5 ($C_{carbene}$). ^{31}P NMR (C_6D_6, 121 MHz): δ -39.3.

N,N'-1,3-bis(2,6-diisopropylphenyl)-2,4-dibenzoylimidazolium chloride [IDipp(PhC=O)$_2$][Cl] (5a). A solution of NHC **4a** (0.202 g, 0.410 mmol) in 15 mL of Et_2O was added slowly to a solution benzoyl chloride (0.057 g, 0.408 mmol) in 5 mL of Et_2O, and the reaction mixture was stirred for 12 hrs at room temperature. The solvent was removed under vacuum and the residue was washed twice with hexane (2 x 5 mL) and vacuum dried to give **5a** as a yellow oil. Yield 73% (0.189 g, 0.298 mmol) ^{1}H NMR (CD_3CN, 400 MHz): δ 1.09 (d, 7.2 Hz, 6 H, $CH(CH_3)_2$), 1.13 (d, 7.2 Hz, 6 H, $CH(CH_3)_2$), 1.25 (two doublets overlapping, 12 H, $CH(CH_3)_2$), 2.69 (sept, 6.8 Hz, 2 H, $CH(CH_3)_2$), 2.81 (sept, 6.8 Hz, 2 H, $CH(CH_3)_2$), 7.31 (d, 7.8

Hz, 2 H, CH_{ar}), 7.35 (d, 7.8 Hz, 2 H, CH_{ar}), 7.52 (t, 7.8 Hz, 2 H, CH_{ar}), 7.56-7.67 (m, 3 H, CH_{ar}), 7.72-7.77 (m, 3 H, CH_{ar}), 8.03 (d, 7.6 Hz, 2 H, CH_{ar}), 8.18 (d, 7.6 Hz, 2 H, CH_{ar}), 8.70 (s, 1 H, CH_{imid}). ^{13}C NMR (CD_3CN, 100 MHz): δ 22.6, 23.7, 25.2, 26.3, ($CH(\mathit{C}H_3)_2$), 30.3, 30.4 ($\mathit{C}H(CH_3)_2$), 126.4 (CH_{ar}), 126.5 (CH_{ar}), 129.4 (C_{ar}), 130.2 (CH_{ar}), 130.3 (CH_{ar}), 130.5 (CH_{ar}), 130.9 (CH_{ar}), 131.3 (CH_{ar}), 131.5 (CH_{ar}), 132.4 (CH_{ar}), 132.8 (C_{ar}), 133.3 (CH_{ar}), 134.1 (CH_{imid}), 135.9 (C_{imid}), 136.3 (C_{imid}), 136.9 (C_{ar}), 138.7 (C_{ar}), 146.4 (C_{ar}), 146.5 (C_{ar}), 180.2 (C=O), 182.9 (C=O). HRMS (ESI; CH_3CN): m/z calculated for $C_{41}H_{45}N_2O_2$ 597.3476, found 597.3544.

N,N'-1,3-bis(2,6-diisopropylphenyl)-2-benzoyl,4-diphenylphosphino-imidazolium chloride [IDipp (Ph_2P)(PhC=O)][Cl] (6). A solution of NHC **4f** (0.201 g, 0.351 mmol) in 15 mL of Et_2O was added slowly to a solution benzoyl chloride (0.0492 g, 0.350 mmol) in 5 mL of Et_2O, and the reaction mixture was stirred for 12 hrs at room temperature. The solvent was removed under vacuum and the residue was washed twice with hexane (2 x 5 mL) and vacuum dried to yield 0.216 g of **6** as a white solid (0.303 mmol, 87% yield). Mp: 227-229 °C. ^1H NMR (C_6D_6, 400 MHz): δ 1.01 (d, 6.4 Hz, 6 H, $CH(C\mathit{H}_3)_2$), 1.03 (d, 6.4 Hz, 6 H, $CH(C\mathit{H}_3)_2$), 1.16 (d, 6.4 Hz, 6 H, $CH(C\mathit{H}_3)_2$), 1.27 (d, 6.4 Hz, 6 H, $CH(C\mathit{H}_3)_2$), 3.02 (sept, 6.4 Hz, 2 H, $C\mathit{H}(CH_3)_2$), 3.31 (sept, 6.4 Hz, 2 H, $C\mathit{H}(CH_3)_2$), 6.82 (d, 7.6 Hz, 2 H, CH_{ar}), 6.89 (d, 7.8 Hz, 2 H, CH_{ar}), 6.95-7.01 (m, 4 H, CH_{ar}), 7.07 (t, 7.6 Hz, 2 H, CH_{ar}), 7.29-7.32 (m, 4 H, CH_{ar}), 7.60 (s, 1 H, CH_{imid}), 7.67 (t, 7.6 Hz, 3 H, CH_{ar}), 7.74 (d, 7.6 Hz, 1 H, CH_{ar}), 7.88 (d, 7.6 Hz, 1 H, CH_{ar}), 8.28 (d, 7.2 Hz, 2 H, CH_{ar}). ^{13}C NMR (C_6D_6, 100 MHz): δ 23.2, 25.1, 25.5, 27.0, ($CH(\mathit{C}H_3)_2$), 29.8, 30.0 ($\mathit{C}H(\mathit{C}H_3)_2$), 125.8 ($CH_{ar}$), 129.5 (d, J(C,P) = 10.3 Hz, CH_{ar}), 130.0 (C_{ar}), 130.5 (d, J(C,P) = 8.9 Hz, C_{ar}), 130.8 (CH_{ar}), 131.0 (CH_{ar}), 131.8 (d, J(C,P) = 10.3 Hz, C_{imid}), 132.9 (CH_{ar}), 132.5 (CH_{ar}), 133.0 (CH_{imid}), 133.9 (C_{imid}), 134.8 (CH_{ar}), 135.0 (CH_{ar}), 135.9 (CH_{ar}), 136.9 (CH_{ar}), 141.4 (C_{ar}), 141.6

(C_{ar}), 146.3(C_{ar}), 147.8 (C_{ar}), 181.6 (C=O). ^{31}P NMR (C_6D_6, 121 MHz): δ –36.8. HRMS (ESI; CH_3CN): m/z calculated for $C_{46}H_{50}N_2OP$ 677.3655, found 677.3662.

N,N'-1,3-bis(2,6-diisopropylphenyl))-4-benzoyl-5-diphenylphosphinoimidazol-2-ylidene, [IDipp(Ph_2P)(PhCO)] (7). Potassium hexamethyldisilazide (0.112 g, 0.561 mmol) and the imidazolium salt **6** (0.200 g, 0.280 mmol) were combined in a Schlenk flask and dissolved in Et_2O (18 mL) at -78°C. The reaction mixture was stirred for 30 minutes. The cold bath was removed and the reaction mixture was stirred for another 60 minutes. The Et_2O was removed under vacuum, and the residue was extracted with 20 mL of benzene. The benzene extract was dried under vacuum and the resulting brownish residue was washed with 10 mL of hexane and dried once more to give 0.097 g (0.143 mmol, 51% yield) of **7** as a beige solid. Mp: 205°C (decomp). ^{1}H NMR (C_6D_6, 300 MHz): δ 1.02 (d, 6.4 Hz, 6 H, $CH(CH_3)_2$), 1.12 (d, 6.4 Hz, 6 H, $CH(CH_3)_2$), 1.22 (d, 6.4 Hz, 6 H, $CH(CH_3)_2$), 1.41 (d, 6.4 Hz, 6 H, $CH(CH_3)_2$), 2.66 (sept, 6.4 Hz, 2 H, $CH(CH_3)_2$), 3.04 (sept, 6.6 Hz, 2 H, $CH(CH_3)_2$), 6.79 (bs, 3 H, CH_{ar}), 6.91-6.97 (m, 4 H, CH_{ar}), 7.01-7.06 (m, 4 H, CH_{ar}), 7.07-7.15 (m, 4 H, CH_{ar}), 7.49 (d, 7.2 Hz, 2 H, CH_{ar}), 8.18 (d, 7.2 Hz, 2 H, CH_{ar}), 8.20 (d, 7.4 Hz, 2 H, CH_{ar}). ^{13}C NMR (C_6D_6, 75 MHz): δ 22.4, 24.7, 24.8, 26.4, ($CH(CH_3)_2$), 29.5, 30.1 ($CH(CH_3)_2$), 124.3 (CH_{ar}), 124.5 (CH_{ar}), 127.3 (CH_{ar}), 129.1 (CH_{ar}), 129.5 (CH_{ar}), 129.8 (CH_{ar}), 130.8 (CH_{ar}), 132.4 (C_{ar}), 133.7 (d, *J*(C,P) = 11.6 Hz, CH_{ar}), 134.7 (CH_{ar}), 135.0 (CH_{ar}), 137.3 (d, *J*(C,P) = 9.7 Hz, C_{ar}), 137.4 (C_{ar}), 138.5 (C_{imid}), 140.1 (C_{ar}), 141.4 (d, *J*(C,P) = 9.0 Hz, C_{imid}), 145.0 (C_{ar}), 146.4 (C_{ar}), 182.9 (C=O), 217.7 ($C_{carbene}$). ^{31}P NMR (C_6D_6, 121 MHz): δ –37.5.

Reaction of *a*NCH 2' with 2-benzoyl-imidazolium salt 3a. A solution of imidazolium salt **3a** (0.098 g, 0.185 mmol) in 5 mL of THF was added to a solution of *a*NHC **2'** (0.100 g, 0.185 mmol) in 5 mL of THF, and the reaction mixture was stirred for 1 h at room temperature. The

THF of the brown suspension was removed under vacuum yielding a brown residue. Et_2O (12 mL) was added to the residue, and after filtration a beige solid and a greenish solution were obtained. NMR data for the solution was identical to that of NHC **1**, while the NMR data for the solid was consistent with the preparation of the pentasubstitued imidazolium salt **5b.** 73% yield (0.092 g, 0.135 mmol); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.72 (d, 6.8 Hz, 12H, $CH(CH_3)_2$), 0.88 (d, 6.8 Hz, 6 H, $CH(CH_3)_2$), 1.22 (d, 6.8 Hz, 6 H, $CH(CH_3)_2$), 2.23 (sept, 6.8 Hz, 2 H, $CH(CH_3)_2$), 2.40 (sept, 6.8 Hz, 2 H, $CH(CH_3)_2$), 6.79 (d, 7.8 Hz, 4H, CH_{ar}), 7.10 (d, 7.8 Hz, 2H, CH_{ar}), 7.11 (d, 7.8 Hz, 2H, CH_{ar}), 7.18-7.22 (m, 4H, CH_{ar}), 7.23-7.25 (m, 3H, CH_{ar}), 7.32 (t, 7.2 Hz, 2H, CH_{ar}), 7.45 (t, 7.8 Hz, 2H, CH_{ar}), 7.53 (t, 7.8 Hz, 2H, CH_{ar}). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.4, 23.2, 23.6, 25.4, ($CH(CH_3)_2$), 29.0, 29.3 ($CH(CH_3)_2$), 120.3 (CH_{ar}), 122.9 (C_{ar}), 123.2 (C_{imid}), 124.2 (CH_{ar}), 125.2 (CH_{ar}), 126.0 (CH_{ar}), 127.3 (C_{ar}), 127.6 (C_{imid}), 127.8 (C_{imid}), 128.4 (CH_{ar}), 129.1 (CH_{ar}), 129.3 (CH_{ar}), 129.4 (CH_{ar}), 129.8 (CH_{ar}), 130.6 (CH_{ar}), 132.3 (CH_{ar}), 132.8 (CH_{ar}), 132.9 (CH_{ar}), 136.8 (C_{ar}), 144.3 (C_{ar}), 144.5 (C_{ar}), 145.1 (C_{ar}), 149.3 (C_{ar}), 180.8 (C=O).

Reaction of 2,4-benzoyl-imidazolium salt 5a with NHC 1: A solution of NHC **1** (0.031 g, 0.0789 mmol) in 5 mL of Et_2O was added dropwise to a solution of the imidazolium salt **5a** (0.050 g, 0.079 mmol) in 5 mL of Et_2O. The resulting white suspension was stirred for 1 h at room temperature and filtered to yield a white solid and a light-yellow solution .NMR data for the solid and the solution were identical to those for the 2-benzoyl imidazolium **3a** and 4-benzoylimidazol-2-ylidene **4a**, respectively.

Crystal Structure Determination of compounds 4a and 4f.

The Bruker X8-APEX[3] X-ray diffraction instrument with Mo-radiation was used for data collection**.** All data frames were collected at low temperatures (T = 100 K) using an ω, φ-scan mode (0.3° ω-scan width, hemisphere of reflections) and integrated using a Bruker SAINTPLUS software package[4]. The intensity data were corrected for Lorentzian polarization. Absorption corrections were performed using the SADABS program.[5] The SIR97[6] software was used for direct methods solution and phase determination, and Bruker SHELXTL[7] for structure refinement and difference Fourier maps. Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms of three compounds were refined by means of a full matrix least-squares procedure on F^2.

Table 6. Crystallographic Data and Summary of Data Collection and Structure Refinement

	4a	**4f**
Formula	$C_{34}H_{39}N_2O$	$C_{39}H_{45}N_2P$
Fw	491.67	572.74
cryst syst	Monoclinic	Monoclinic
space group	$P2_1/c$	$P2_1/c$
Size (mm^3)	0.98 x 0.13 x 0.10	0.97 x 0.30 x 0.24
T, K	100(2)	100(2)
a, Å	12.148(3)	16.5148(17)
b, Å	11.807(2)	10.5459(12)
c, Å	20.471(3)	20.489(2)
α, deg	90	90
β, deg	90.269(15)	107.355(3)
γ, deg	90	90
V, A^3	2936.3(10)	3405.9(6)
Z	4	4
d_{calcd} g·cm^{-3}	1.112	1.117
μ, mm^{-1}	0.066	0.109
Refl collected	10652	47581
T_{min}/T_{max}	0.944	0.926
N_{measd}	2860	10025
[R_{int}]	[0.0435]	[0.0382]
R [I>2sigma(I)]	0.0763	0.0437
R_w[I>2sigma(I)]	0.2190	0.0998
GOF	1.114	1.025
Largest diff peak/hole[e·Å^{-3}]	0.364/-0.375	0.363/-0.304

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