Supplementary material for:

Novel expanded ring N-heterocyclic carbenes: free carbenes, silver complexes and structures

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Experimental

General Remarks. All manipulations were performed in air, except where otherwise noted. The solvents thf and hexane (analytical grade) were freshly distilled from sodium/potassium alloy, dichloromethane was distilled from calcium hydride, the other solvents (acetonitrile, diethylether, acetone) were used as purchased. Deuterated solvents for NMR measurements were distilled from the appropriate drying agents under N₂ immediately prior to use following standard literature methods. Air-sensitive compounds were stored and weighed in a glovebox. The reagents 1,2-dibromoethane, 1,3-dibromopropane, 1,4-diiodobutane, 2,6-dimethylaniline, 2,4,6-trimethylaniline, 2,6-diisopropylaniline, triethylorthoformate, sodium tetrafluoroborate, and potassium bis(trimethylsilyl)amide were used as received. ¹H and ¹³C NMR spectra were obtained on Bruker Avance AMX 400, 500 or Jeol Eclipse 300 spectrometers. The chemical shifts are given as dimensionless δ values and are frequency referenced relative to TMS. Coupling constants J are given in hertz (Hz) as positive values regardless of their real individual signs. Abbreviations used: st = septet, br = broad. Mass spectra (MS) and high-resolution
mass spectra (HRMS) were obtained in positive electrospray (ES) mode unless otherwise reported, on a
Waters Q-TOF micromass spectrometer.

1,3-Bis-(2,4,6-trimethylphenyl)-4,5,6,7-tetrahydro-3H-[1,3]diazepin-1-ium iodide, 7-Mes·HI. The
reaction was performed on a 71.0 mmol scale of amidine (19.90 g), 5.00 g of K₂CO₃ (36.0 mmol) and
22.00 g of 1,4-diiodobutane (71.0 mmol) in 1 L of acetonitrile. The solution was heated under reflux
for 5 hours to yield 29.20 g (63.0 mmol, 89%) of white, crystalline material.

1,3-Bis-(2,6-dimethylphenyl)-4,5,6,7-tetrahydro-3H-[1,3]diazepin-1-ium iodide, 7-Xyl·HI. The
reaction was performed on a 43.3 mmol scale of amidine (10.93 g), 5.8 mL of 1,4-diiodobutane (13.63
g, 44 mmol), 3.01 g of K₂CO₃ (22.5 mmol) in 0.5 L of acetonitrile. The solution was heated under
reflux for 5 hours to yield 14.85 g (34.2 mmol, 79%) of white, crystalline material.

1,3-Bis-(2,6-diisopropylphenyl)-4,5,6,7-tetrahydro-3H-[1,3]diazepin-1-ium iodide, 7-Pr·HI. The
reaction was performed on a 11.0 mmol scale of amidine (4.00 g), 0.78 g of K₂CO₃ (5.6 mmol), 1.6 mL
of 1,4-diiodobutane (3.76 g, 12.1 mmol) in 400 mL of acetonitrile. The solution was heated under
reflux for 17 hours to yield 3.87 g (7.1 mmol, 64%) of white, crystalline material.

2,4-Bis-(2,4,6-trimethylphenyl)-4,5-dihydro-1H-benzo[e][1,3]diazepin-2-ium bromide, Xyl7-
Mes·HBr. The reaction was performed on a 35.8 mmol scale of amidine (10.03 g), 36.0 mmol of α,α’-
dibromo-o-xylene (9.49 g), 2.49 g of K₂CO₃ (18.0 mmol) in 0.5 L of acetonitrile. The solution was
heated under reflux for 5 hours to yield 12.42 g (26.2 mmol, 73%) of white, crystalline material. ¹H
NMR (CD₃CN, 400 MHz, 298 K) δ 7.57 (1H, s, NCHN), 7.53 (2H, dd, 3J_HH = 3.4, 3J_HH = 5.5, Xy-CH),
7.46 (2H, dd, 3J_HH = 3.4, 3J_HH = 5.5, Xy-CH), 7.03 (4H, s, Ar-m-CH), 5.37 (4H, br s, NCH₂), 2.28 (6H,
s, p-CH₃), 2.22 (12H, s, o-CH₃). ¹³C NMR (CD₃CN, 100 MHz, 298 K) δ: 158.3 (1C, s, NCHN), 141.0
(2C, s, Ar-C), 135.5 (4C, s, Ar-C), 135.2 (2C, s, Ar-C), 131.1 (4C, s, Ar-CH), 130.6 (2C, s, Ar-CH), 130.2 (2C, s, Ar-CH), 56.6 (2C, s, NCH2), 20.9 (2C, s, p-CH3), 18.4 (2C, s, o-CH3).

2,4-Bis-(2,6-dimethylphenyl)-4,5-dihydro-1H-benzo[e][1,3]diazepin-2-ium bromide, Xyl7-Xyl-HBr. The reaction was performed on a 7.9 mmol scale of amidine (2.00 g), 2.09 g of α,α’-dibromo-o-xylene (7.9 mmol), 0.56 g of K₂CO₃ (4.05 mmol) in 75.0 mL of acetonitrile. The solution was heated under reflux for 5 hours to yield 3.00 g (6.9 mmol, 87%) of white, crystalline material. ¹H NMR (CD₃CN, 400 MHz, 298 K): 7.65 (1H, s, NC-HN), 7.56 (2H, dd, 3J_HH = 3.4, 3J_HH = 5.5, Xy-CH), 7.50 (dd, 3J_HH = 3.4, 3J_HH = 5.5, 2H, Xy-CH), 7.32 (dd, 3J_HH = 6.7, 3J_HH = 8.4, 2H, Xy-p-CH), 7.25 (4H, br d, 3J_HH = 7.4, Xy-m-CH), 5.46 (4H, br s, NCH₂), 2.31 (12H, s, CH₃). ¹³C NMR (CD₃CN, 100 MHz, 298 K): 158.2 (1C, s, N-C-HN), 143.2 (2C, s, Ar-C), 135.6 (4C, s, Ar-C), 131.1 (4C, s, Ar-C), 130.9 (2C, s, Ar-CH), 130.2 (2C, s, Ar-CH), 130.0 (2C, s, Ar-CH), 56.4 (2C, s, NCH₂), 18.5 (4C, s, CH₃).

2,4-Bis-(2,6-diisopropylphenyl)-4,5-dihydro-1H-benzo[e][1,3]diazepin-2-ium bromide, Xyl7-Pr₄-HBr. The reaction was performed on a 11.0 mmol scale of amidine (4.00 g), 0.76 g K₂CO₃ (5.5 mmol) and 2.90 g α,α’-dibromo-o-xylene (11.0 mmol) in 0.4 L acetonitrile. The solution was heated under reflux for 48 hours to yield 2.67 g (4.9 mmol, 45%) of white, crystalline material. ¹H NMR (CD₃CN, 400 MHz, 298 K): 7.87 (s, 1H, NCHN), 7.55 (2H, dd, 3J_HH = 3.4, 3J_HH = 5.4, Xy-CH), 7.51-7.43 (4H, m, Xy-CH and DIPP-p-CH), 7.35 (4H, br d, 3J_HH = 7.7, DIPP-m-CH), 5.4 (4H, br s, CH₂), 3.00 (4H, br s, CH(CH₃)₂), 1.30 (12H, d, 3J_HH = 6.7, CH(CH₃)₂), 1.16 (12H, d, 3J_HH = 6.7, CH(CH₃)₂). ¹³C NMR (CD₃CN, 100 MHz, 298 K): 157.7 (1C, s, N-C-HN), 143.2 (2C, s, Ar-C), 139.9 (2C, s, Ar-C), 134.9 (4C, s, Ar-C), 131.7 (2C, s, Ar-CH), 131.1 (2C, s, Ar-CH), 130.2 (2C, s, Ar-CH), 126.1 (4C, s, Ar-CH), 57.9 (NCH₂), 29.6 (4C, s, CH(CH₃)₂), 24.9 (4C, s, CH(CH₃)₂), 24.6 (CH(CH₃)₂).
1,3-Bis-(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydro-pyrimidin-1-ium bromide, 6-Mes·HBr. The reaction was performed on a 20.0 mmol scale of amidine (5.60 g), 1.40 g of K₂CO₃ (10.0 mmol) and 4.24 g of 1,3-dibromopropane (20.0 mmol) in 0.25 L of acetonitrile. The solution was heated under reflux for 17 hours to yield 6.55 g (16.0 mmol, 82%) of white, crystalline material.

1,3-Bis-(2,6-dimethylphenyl)-3,4,5,6-tetrahydro-pyrimidin-1-ium bromide, 6-Xyl·HBr. The reaction was performed on a 4.7 mmol scale of amidine (1.13 g), 0.6 mL of 1,3-dibromopropane (1.19 g, 5.9 mmol) and 0.32 g of K₂CO₃ (2.3 mmol) in 50 mL of acetonitrile. The solution was heated under reflux for 17 hours to yield 1.17 g (3.2 mmol, 69%) of white, crystalline material.

1,3-Bis-(2,6-diisopropylphenyl)-3,4,5,6-tetrahydro-pyrimidin-1-ium bromide, 6-Pr·HBr. The reaction was performed on a 6.9 mmol scale of amidine (2.51 g), 0.52 g of K₂CO₃ (3.8 mmol) and 1.1 mL of 1,3-dibromopropane (2.19 g, 10.9 mmol) in 0.1 L of acetonitrile. The solution was heated under reflux for 4 days to yield 2.39 g (4.9 mmol, 71%) of white, crystalline material.

1,3-Bis-(2,4,6-trimethylphenyl)-4,5-dihydro-3H-imidazol-1-ium bromide, 5-Mes·HBr. The reaction was performed on a 35.7 mmol scale of amidine (10.00 g), 2.59 g of K₂CO₃ (17.8 mmol) and 5.4 mL of 1,2-dibromoethane (7.38 g, 39.3 mmol) in 0.5 L of acetonitrile. The solution was heated under reflux for 3 days to yield 10.45 g of white, crystalline material (27.1 mmol, 76%). Spectroscopic data for 5-Mes·HBr are in agreement with those reported in the literature.¹⁷¹H NMR (DMSO-d₆, 400 MHz, 298 K) δ: 8.99 (1H, s, NCH), 7.09 (4H, s, Ar-m-CH), 4.44 (4H, s, NCH₂), 2.34 (12H, s, o-CH₃), 2.29 (6H, s, p-CH₃).¹³C NMR (DMSO-d₆, 100 MHz, 298 K) δ: 160.2 (1C, s, NCHN), 139.6 (2C, s, Ar-C), 135.4 (4C, s, Ar-C), 130.8 (2C, s, Ar-C), 129.3 (4C, s, Ar-CH), 50.8 (NCH₂), 20.6 (p-CH₃), 17.2 (o-CH₃).

1,3-Bis-(2,6-dimethylphenyl)-4,5-dihydro-3H-imidazol-1-ium bromide, 5-Xyl·HBr. The reaction was performed on a 10.3 mmol scale of amidine (2.60 g), 0.72 g of K₂CO₃ (5.2 mmol) and 2.0 mL of
1,2-dibromoethane (4.40 g, 23.2 mmol) in 80.0 mL of acetonitrile. The solution was heated under reflux for 10 days. The product is less soluble in dichloromethane than the other halide salts. Yield 2.75 g (7.1 mmol, 69%) of light yellow, crystalline material. 

$^1$H NMR (DMSO-d$_6$, 400 MHz, 298 K) δ: 9.07 (1H, s, NCH$_N$), 7.36 (2H, dd, $^3$J$_{HH} = 6.5$, $^3$J$_{HH} = 8.5$, p-CH), 7.29 (4H, br d, $^3$J$_{HH} = 7.6$, m-CH), 4.51 (4H, s, NCH$_2$), 2.41 (12H, s, CH$_3$)$_3$. 

$^{13}$C NMR (DMSO-d$_6$, 100 MHz, 298 K) δ: 160.1 (1C, s, NCH$_N$), 135.8 (2C, s, Ar-C), 133.3 (4C, s, Ar-C), 130.0 (4C, s, Ar-CH), 128.9 (2C, s, Ar-CH), 50.8 (2C, s, NCH$_2$), 17.3 (4C, s, CH$_3$). HRMS (ES): m/z 279.1848 (M – Br$^+$; C$_{19}$H$_{23}$N$_2$ requires 279.1861).

1,3-Bis-(2,6-diisopropylphenyl)-4,5-dihydro-3H-imidazol-1-ium bromide, 5-Pr$^1$HBr. The reaction was performed on a 7.7 mmol scale of amidine (2.82 g), 0.56 g of K$_2$CO$_3$ (4.0 mmol) and 2.0 mL of 1,2-dibromoethane (4.40 g, 23.2 mmol) in 80.0 mL of acetonitrile. The solution was heated under reflux for 10 days. The product is less soluble in dichloromethane than the other halide salts. Crude yield 3.44 g (7.3 mmol, 94%) of white, microcrystalline material, which was converted to the BF$_4$-salt without further purification. $^1$H NMR (DMSO-d$_6$, 400 MHz, 298 K) δ: 9.49 (1H, s, NCH$_N$), 7.55 (2H, m, $^3$J$_{HH} = 7.7$, p-CH), 7.42 (4H, d, $^3$J$_{HH} = 7.7$, m-CH), 4.55 (4H, s, NCH$_2$), 3.08 (4H, s, NCH$_2$)$_2$, 1.35 (12H, s, CH(CH$_3$)$_2$), 1.19 (12H, s, CH(CH$_3$)$_2$). $^{13}$C NMR (DMSO-d$_6$, 100 MHz, 298 K) δ: 160.0 (1C, s, NCH$_N$), 146.1 (2C, s, Ar-C), 131.1 (4C, s, Ar-C), 129.8 (4C, s, Ar-CH), 124.8 (2C, s, Ar-C), 53.7 (2C, s, NCH$_2$), 28.3 (4C, s, CH(CH$_3$)$_2$), 25.0 (4C, s, CH(CH$_3$)$_2$).

7-Mes·HBF$_4$. A solution of 7-Mes·HBr (2.51 g, 5.4 mmol) in acetone (25 mL) was added to a solution of NaBF$_4$ (0.93 g, 8.5 mmol) in water (10 mL). Yield 2.05 g (4.9 mmol, 89%) of white, crystalline material. $^1$H NMR (CDCl$_3$, 400 MHz, 298 K) δ: 7.21 (1H, s, NCH$_N$), 6.95 (4H, s, Ar-CH), 4.32 (4H, m, $^3$J$_{HH} = 5.6$, NCH$_2$), 2.52 (4H, m, $^3$J$_{HH} = 5.6$, NCH$_2$CH$_2$), 2.37 (12H, s, o-CH$_3$), 2.27 (6H, s, p-CH$_3$). $^{13}$C NMR (CDCl$_3$, 100 MHz, 298 K) δ: 158.2 (s, NCH$_N$), 140.3 (s, Ar-C), 139.2 (s, Ar-C), 133.5 (s,
7-Xyl-HBF₄. The reaction was performed on a 11.6 mmol scale of 7-Xyl-HBr (5.02 g) in 25 mL of acetone and 1.73 g of NaBF₄ (15.8 mmol) in 25 mL of H₂O, to yield a white crystalline material. Yield 3.97 g (10.1 mmol, 87%). ¹H NMR (CDCl₃, 400 MHz, 298 K) δ: 7.28 (1H, s, NCH₃), 7.23 (2H, dd, ³J_HH = 6.8, ³J_HH = 8.3, -C), 7.14 (4H, d, ³J_HH = 7.6, -CH₂), 4.37 (4H, m, ³J_HH = 5.4, NCH₂), 2.54 (4H, m, ³J_HH = 5.4, NCH₂CH₂), 2.42 (12H, s, CH₃). ¹³C NMR (CDCl₃, 100 MHz, 298 K) δ: 158.0 (s, NCH₃), 141.4 (s, Ar-C), 133.9 (s, Ar-C), 130.1 (s, Ar-CH), 129.7 (s, Ar-CH), 54.6 (s, NCH₂), 25.1 (s, NCH₂CH₂), 24.5 (s, CH(CH₃)₂). HRMS (ES): m/z 307.2168 (M – BF₄⁺; C₂₁H₂₇N₂ requires 307.2174).

7-Prⁱ-HBF₄. The reaction was performed on a 4.6 mmol scale of 7-Prⁱ-HBr (2.51 g) in 25 mL of acetone and 0.89 g of NaBF₄ (8.1 mmol) in 25 mL of water, to yield a white crystalline material. Yield 2.22 g (4.4 mmol, 95%). ¹H NMR (CDCl₃, 400 MHz, 298 K) δ: 7.41 (2H, m, ³J_HH = 7.8, -CH), 7.24 (4H, d, ³J_HH = 7.8, -CH₂), 4.42 (4H, br s, NCH₂), 3.15 (4H, st, ³J_HH = 6.7, CH(CH₃)₂), 2.56 (4H, br s, NCH₂CH₂), 1.38 (12H, d, ³J_HH = 6.7, CH(CH₃)₂), 1.24 (12H, d, ³J_HH = 6.7, CH(CH₃)₂). ¹³C NMR (CDCl₃, 100 MHz, 298 K) δ: 157.3 (s, NCH₃), 144.7 (s, Ar-C), 138.7 (s, Ar-C), 131.0 (s, Ar-CH), 125.3 (s, Ar-CH), 55.9 (s, NCH₂), 28.9 (s, CH(CH₃)₂), 24.9 (s, CH(CH₃)₂), 24.7 (s, NCH₂CH₂), 24.5 (s, CH(CH₃)₂). HRMS (ES): m/z 419.3426 (M – BF₄⁺; C₂₉H₄₃N₂ requires 419.3445).

Xyl7-Mes-HBF₄. The reaction was performed on a 10.8 mmol scale of Xyl7-Mes-HBr (5.01 g) in 50 mL acetone and 1.33 g of NaBF₄ (12.1 mmol) in 25 mL water. Fractional crystallization by dissolving the crude material in dichloromethane, adding ether until saturation, and cooling to -30°C afforded 4.02 g (8.5 mmol, 79%) of a beige, crystalline material. ¹H NMR (CDCl₃, 400 MHz, 298 K) δ: 7.49-7.43 (2H, m, Xy-CH), 7.33-7.27 (2H, m, Xy-CH), 7.11 (1H, s, NCH₃N), 6.94 (4H, s, -CH₂), 5.38 (4H, br s; Δνₜ = ~ 150 Hz, NCH₂), 2.27 (18H, s, o-CH₃ and p-CH₃). ¹³C NMR (CDCl₃, 100 MHz, 298 K) δ: 156.1
Xyl7-Xyl-HBF₄. The reaction was performed on a 2.3 mmol scale of Xyl7-Xyl-HBr (1.00 g) in 30 mL acetonitrile and 0.34 g NaBF₄ (3.1 mmol) in 10 mL water, to yield a white crystalline material. Yield 0.81 g (1.8 mmol, 79%). ¹H NMR (CDCl₃, 400 MHz, 298 K) δ: 7.48 (2H, dd, ³J_HH = 3.3, ³J_HH = 5.5, Xy-CH), 7.33 (2H, dd, ³J_HH = 3.3, ³J_HH = 5.5, Xy-CH), 7.25 (2H, dd, ³J_HH = 7.2, ³J_HH = 7.9, p-Ar-CH), 7.17 (1H, s, NCHN), 7.15 (4H, d, ³J_HH = 7.5 Hz, m-Ar-CH), 5.38 (4H, br s, Δν₂/₃ ~ 400 Hz, NCH₂), 2.33 (12H, s, CH₃). ¹³C NMR (CDCl₃, 100 MHz, 298 K) δ: 156.0 (s, XCHN), 142.4 (s, Ar-C), 134.4 (s, Ar-C), 134.2 (s, Ar-C), 130.4 (s, Ar-CH), 130.3 (s, Ar-CH), 129.6 (s, Ar-CH), 129.3 (s, Ar-CH), 56.3 (s, N-CH₂), 18.3 (s, CH₃). HRMS (ES): m/z 355.2162 (M – BF₄⁺; C₂₅H₂₇N₂ requires 355.2174). ¹H NMR (CD₃CN, 400 MHz, 298 K) δ: 7.61 (1H, s, NCHN), 7.58-7.52 (2H, m, Xy-CH), 7.51-7.46 (2H, m, Xy-CH), 7.25 (2H, dd, ³J_HH = 6.7, ³J_HH = 8.3, p-Ar-CH), 7.23 (4H, d, ³J_HH = 7.5, m-Ar-CH), 5.32 (4H, br s, Δν₂/₃ ~ 30 Hz, NCH₂), 2.28 (12H, s, CH₃). ¹³C NMR (CD₃CN, 100 MHz, 298 K) δ: 158.3 (1C, s, NCHN), 143.2 (2C, s, Ar-C), 135.5 (4C, s, Ar-C), 135.3 (2C, s, Ar-C), 131.3 (4C, s, Ar-CH), 130.9 (2C, s, Ar-CH), 130.2 (2C, s, Ar-CH), 130.1 (2C, s, Ar-CH), 56.2 (2C, s, N-CH₂), 18.4 (2C, s, CH₃).

Xyl7-Pr⁺-HBF₄. The reaction was performed on a 3.7 mmol scale of Xyl7-Pr⁺-HBr (2.00 g) in 50 mL acetonitrile and 0.56 g NaBF₄ (5.1 mmol) in 10 mL water. Yield 1.66 g (3.0 mmol, 82%) of white, crystalline material. ¹H NMR (CDCl₃, 400 MHz, 298 K) δ: 7.51-7.46 (2H, m, Xy-CH), 7.42 (2H, t,
$^3J_{HH} = 7.8$, $p$-Ar-CH, 7.33-7.27 (2H, m, Xy-CH), 7.25 (4H, d, $^3J_{HH} = 7.8$, m-Ar-CH), 7.23 (1H, s, NCHN), 3.09 (4H, br s, $\Delta v_{\nu_2} = 120$ Hz, $CH(CH_3)_2$), 1.34 (12H, br d, $J \sim 4.5$ Hz, $CH(CH_3)_2$), 1.17 (12H, br d, $J \sim 4.5$ Hz, $CH(CH_3)_2$). NCH$_2$ not observed in CDCl$_3$ at 298 K. $^{13}$C NMR (CDCl$_3$, 100 MHz, 298 K) $\delta$: 155.2 (1C, s, NCHN), 139.3 (s, Ar-C), 133.9 (s, Ar-C), 131.0 (s, Ar-CH), 130.2 (s, Ar-CH), 129.2 (s, Ar-CH), 125.4 (s, Ar-CH), 57.7 (s, NCH$_2$), 28.7 (s, CH($CH_3)_2$), 25.1 (s, CH($CH_3)_2$), 24.6 (s, CH($CH_3)_2$). One Ar-C not observed in CDCl$_3$. HRMS (ES): $m/z$ 467.3414 (M – BF$_4^+$; C$_{33}$H$_{43}$N$_2$ requires 467.3426). 

$^1$H NMR (CD$_3$CN, 100 MHz, 298 K) $\delta$: 7.88 (1H, s, NCHN), 7.59-7.54 (2H, m, Ar), 7.52-7.44 (4H, m, $p$-Ar-CH and Xy-CH), 7.36 (4H, d, $^3J_{HH} = 7.7$, m-CH), 5.36 (4H, br s, $\Delta v_{\nu_2} = 70$ Hz, NCH$_2$), 2.98 (4H, br s, $\Delta v_{\nu_2} = 30$ Hz, $CH(CH_3)_2$), 1.31 (12H, d, $^3J_{HH} = 6.7$, CH($CH_3)_2$), 1.16 (12H, d, $^3J_{HH} = 6.7$, CH($CH_3)_2$). $^{13}$C NMR (CD$_3$CN, 100 MHz, 298 K) $\delta$: 157.7 (1C, s, NCHN), 145.8 (2C, s, Ar-C), 139.9 (2C, s, Ar-C), 134.8 (4C, s, Ar-C), 131.7 (2C, s, Ar-CH), 131.2 (2C, s, Ar-CH), 130.2 (4C, s, Ar-CH), 126.0 (2C, s, Ar-CH), 57.7 (2C, s, NCH$_2$), 29.6 (4C, s, CH($CH_3)_2$), 24.8 (4C, s, CH($CH_3)_2$), 24.6 (4C, s, CH($CH_3)_2$).

6-Mes-HBF$_4$. The reaction was performed on a 5.0 mmol scale (2.00 g) of 6-Mes-HBr in 30 mL of acetone and 0.59 g of NaBF$_4$ (5.4 mmol) in 10 mL of water, to yield a white crystalline material. Yield 1.75 g (4.3 mmol, 86%).

6-Xyl-HBF$_4$. The reaction was performed on a 2.9 mmol scale of 6-Xyl-HBr (1.07 g) in 20 mL of acetonitrile and 0.56 g of NaBF$_4$ (5.1 mmol) in 10 mL of water. Yield 0.86 g (2.3 mmol, 79%) of white, crystalline material. $^1$H NMR (CDCl$_3$, 400 MHz, 298 K) $\delta$: 7.83 (1H, s, NCHN), 7.18 (2H, dd, $^3J_{HH} = 7.0$, $^3J_{HH} = 8.2$, $p$-Ar-CH), 7.08 (4H, d, $^3J_{HH} = 7.08$, m-Ar-CH), 3.82 (4H, m, $^3J_{HH} = 5.7$, NCH$_2$), 2.49 (2H, m, $^3J_{HH} = 5.7$, NCH$_2$CH$_2$), 2.26 (12H, s, CH$_3$). $^{13}$C NMR (CDCl$_3$, 100 MHz, 298 K) $\delta$: 154.3 (s, NCHN), 138.4 (s, Ar-C), 134.4 (s, Ar-C), 130.1 (s, Ar-CH), 129.3 (s, Ar-CH), 45.9 (s, NCH$_2$), 19.0 (s, NCH$_2$CH$_2$), 17.3 (s, CH$_3$). HRMS (ES): $m/z$ 293.2014 (M – BF$_4^+$; C$_{20}$H$_{25}$N$_2$ requires 293.2018).
6-Pr\texttext{1}·HBF\text{4}. The reaction was performed on a 3.4 mmol scale of 6-Pr\texttext{1}·HBr (1.67 g) in 50 mL of acetonitrile and 0.74 g of NaBF\text{4} (2.67 mmol) in 40 mL of water. Yield 1.32 g (2.7 mmol, 78\%) of white, crystalline material. \texttext{1}H NMR (CDCl\texttext{3}, 400 MHz, 298 K) δ: 7.57 (1H, s, NCHN), 7.46 (2H, m, \texttext{3}J_{HH} = 7.6, p-Ar-CH), 7.27 (4H, d, \texttext{3}J_{HH} = 7.6, m-Ar-CH), 4.01 (4H, m, \texttext{3}J_{HH} = 5.6, NCH\texttext{2}), 2.99 (4H, st, \texttext{3}J_{HH} = 6.7, CH(CH\texttext{3})\texttext{2}), 2.67 (2H, m, \texttext{3}J_{HH} = 5.6, NCH\texttext{2}), 1.38 (12H, d, \texttext{3}J_{HH} = 6.7, CH(CH\texttext{3})\texttext{2}), 1.25 (12H, d, \texttext{3}J_{HH} = 6.7, CH(CH\texttext{3})\texttext{2}). \texttext{13}C NMR (CDCl\texttext{3}, 100 MHz, 298 K) δ: 153.1 (s, NCHN), 145.5 (s, Ar-C), 135.6 (s, Ar-C), 131.2 (s, m-Ar-CH), 125.1 (s, p-Ar-CH), 48.4 (s, NCH\texttext{2}), 30.8 (s, CH(CH\texttext{3})\texttext{2}), 28.8 (s, CH(CH\texttext{3})\texttext{2}), 24.6 (s, CH(CH\texttext{3})\texttext{2}), 19.0 (s, NCH\texttext{2}CH\texttext{2}). HRMS (ES): m/z 405.3257 (M – BF\texttext{4}\texttext{+}; C\texttext{28}H\texttext{41}N\texttext{2} requires 405.3270).

5-Mes·HBF\text{4}. The reaction was performed on a 10.8 mmol scale of 5-Mes·HBr (4.18 g) in 50 mL of acetone and 1.18 g of NaBF\text{4} (10.8 mmol) in 25 mL water. Yield 3.78 g (9.6 mmol, 89\%) of white, crystalline material.

5-Xyl·HBF\text{4}. The reaction was performed on a 6.3 mmol scale of 5-Xyl·HBr (2.280 g) in 100 mL of acetone and 1.01 g of NaBF\text{4} (9.2 mmol) in 50 mL of water. Yield 1.84 g (5.0 mmol, 79\%) of white, crystalline material.

5-Pr\texttext{1}·HBF\text{4}. The reaction was performed on a 5.2 mmol scale of 5-Pr\texttext{1}·HBr (2.47 g) in 100 mL of acetone and 0.99 g of NaBF\text{4} (9.0 mmol) in 50 mL of water. Yield 1.62 g (3.4 mmol, 65\%) of white, crystalline material.

**General protocol for the one-pot synthesis of tetrafluoroborate salts.** A suspension of 25 mmol amidine, 1-2 eq. of the dihalide, and 12.5 mmol K\texttext{2}CO\texttext{3} (0.5 eq.) in 150 mL of acetonitrile was refluxed until the ring closure was finished (monitored by \texttext{1}H NMR). At the end of the reaction the mixture was allowed to cool down to RT and a solution of 40 mmol of sodium tetrafluoroborate in 25 mL of water.
was added. The reaction mixture was stirred for 10 minutes, and the acetonitrile was subsequently evaporated on a rotary evaporator, resulting in the product to precipitate in the remaining water. The product was isolated by filtration, washed thoroughly with water, and dissolved in dichloromethane. The residual water was separated, and the dichloromethane solution dried over MgSO₄. The solution was filtered, concentrated, and ether was slowly added to the solution to crystallize the product. The product was isolated by filtration.

1,3-Bis-(2,6-dimethylphenyl)-4,5,6,7-tetrahydro-3\textit{H}-[1,3]diazepin-1-ium tetrafluoroborate, 7-Xyl·HBF₄. The reaction was performed on a 9.3 mmol scale of amidine (2.337 g), 625 mg of K₂CO₃ (4.5 mmol), 2.5 mL (5.87 g, 19.0 mmol) of 1,4-diiodobutane in 100 mL of acetonitrile. The reaction was refluxed for 17 hours. After cooling to RT, 2.437 g of NaBF₄ (22.2 mmol) in 100 mL of water was added. Yield 2.939 g (7.5 mmol, 79%) of white, microcrystalline material. Spectroscopically identical to the product obtained above.

1,3-Bis-(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydro-pyrimidin-1-ium tetrafluoroborate. The reaction was performed on a 35.7 mmol scale of amidine (10.012 g), 2.5 g of K₂CO₃, (18.1 mmol) 8.0 mL of 1,3-dibromobutane (39.6 mmol, 15.9 g) in 200 mL of acetonitrile. The reaction was refluxed for 48 hours. After cooling to RT, 7.2 g of NaBF₄ (65.6 mmol) in 25 mL of water was added. Yield 7.460 g (18.3 mmol, 51%) of white, crystalline material. Spectroscopically identical to the product obtained above.

1,3-Bis-(2,6-dimethylphenyl)-3,4,5,6-tetrahydro-pyrimidin-1-ium tetrafluoroborate. The reaction was performed on a 21.7 mmol scale of amidine (5.477 g), 1.527 g of K₂CO₃ (11.1 mmol), and 6.0 mL of 1,3-dibromobutane (11.9 g, 59.1 mmol) in 150 mL of acetonitrile. The reaction was refluxed for 18 hours. After cooling to RT, 4.938 g of NaBF₄ (45.0 mmol) in 100 mL of water was added. Yield 5.608 g (14.7 mmol, 68%) of white, crystalline material. Spectroscopically identical to the product obtained above.
1,3-Bis-(2,6-diisopropylphenyl)-3,4,5,6-tetrahydro-pyrimidin-1-ium tetrafluoroborate. The reaction was performed on a 24.7 mmol scale of amidine (9.012 g), 14.5 mmol (2.0 g) of K₂CO₃, and 8.0 mL (15.9 g, 78.8 mmol) of 1,3-dibromobutane in 150 mL of acetonitrile. The reaction was refluxed for 48 hours. After cooling to RT, 4.2 g of NaBF₄ (38.3 mmol) in 25 mL of water was added. Yield 6.290 g (12.8 mmol, 52%) of white, crystalline material. Spectroscopically identical to the product obtained above.

5-Mes. Reaction performed on a mmol scale (1.026 g) of the salt in 40 mL of diethylether and mmol of KN(SiMe₃)₂ (407 mg). Yield 377 mg (46%) of a colorless, crystalline solid. ¹H NMR (C₆D₆, 400 MHz, 298 K) δ: 7.22 (2H, m, ³J_HH = 7.6, p-Ar-CH), 7.12 (4H, d, ³J_HH = 7.6, m-Ar-CH), 3.37 (4H, st, ³J_HH = 6.8, CH(CH₃)₂), 2.82 (4H, m, ³J_HH = 5.9, NCH₂), 1.69 (2H, m, ³J_HH = 5.7, NCH₂CH₂), 1.28 & 1.27 (12H, d, ³J_HH = 6.8, CH(CH₃)₂). ¹³C NMR (C₆D₆, 100 MHz, 298 K) δ: 245.1 (1C, s, NCHN), 149.8 (2C, s, Ar-C), 146.1 (4C, s, Ar-C), 145.5 (4C, s, Ar-CH), 124.0 (2C, s, Ar-CH), 44.3 (2C, s, NCH₂), 28.6 (4C, s, CH(CH₃)₂), 25.1 (4C, s, CH(CH₃)₂), 24.5 (4C, s, CH(CH₃)₂), 22.0 (2C, s, NCH₂CH₂).
Fig. 1 ORTEP ellipsoid plots at 30% probability of the 7-Xyl·H₂O, solvent molecules have been omitted for clarity.

Fig. 2 ORTEP ellipsoid plots at 30% probability of the Xyl7-Ph cation, solvent molecules and the PF₆⁻ anion have been omitted for clarity.