Neutral and cationic cyclic (Alkyl)(Amino)Carbene mercury, [cAAC-Hg(II)] complexes: Scope of hydroamination of alkynes with organomercury compounds†

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Experimental section

General considerations

All manipulations were performed under nitrogen/argon atmosphere using Schlenk line or glove box techniques. All chemicals were purchased from Sigma-Aldrich and used without further purification. The starting materials cyclic alkyl amino carbene cAAC\textsuperscript{Me} and cAAC\textsuperscript{cy} were prepared by following the reported procedures.\textsuperscript{1} FT-IR spectra of the complexes were recorded in the range 4000–400 cm\textsuperscript{–1} with a Perkin–Elmer Lambda 35-spectrophotometer. The elemental analysis for the cAAC-Hg complexes did not give satisfactory results due to traces of THF trapped. The \textsuperscript{1}H and \textsuperscript{13}C spectra were recorded with a Bruker 400 MHz spectrometer with TMS as external reference; chemical shift values are reported in ppm. High-resolution mass spectrometry was performed with a Waters SYNAPT G2-S.

\textbf{Important caution note!} Organomercury compounds are highly toxic. All necessary care in handling mercury compounds must be exercised.

Syntheses of cAAC-Hg(II) complexes

\textbf{Synthesis of [cAAC\textsuperscript{Me}-HgBr(μ‒Br)]\textsubscript{2} (1a).} A mixture of [cAAC\textsuperscript{Me}H]+Cl\textsuperscript{–} (0.44 g, 1.38 mmol) and K[N(SiMe\textsubscript{3})\textsubscript{2}] (0.28 g, 1.40 mmol) was taken in THF (25 mL). The resulting suspension was stirred at room temperature for 2 h. The solution was filtered to remove KCl and subsequently added to a suspension of HgBr\textsubscript{2} (0.47 g, 1.38 mmol) in THF (5 mL). The resulting suspension was stirred at room temperature for 3 h. The solution was filtered off and the precipitate obtained was further washed with THF (10 mL) to give \textit{1a} as a white solid. The colorless crystals of \textit{1a} were grown from DMSO solution at room temperature. Yield: 0.70 g, 78.60 %. Mp: 256-258 °C. IR (KBr, cm\textsuperscript{–1}) ν : 2968, 2928, 2867, 1550, 1462, 1390, 1370, 1325, 1205, 1125, 1052, 1008, 807, 771, 566. \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6): δ = 7.51 (t, 2H, pAr‒H, \textit{J}_\text{H–H} = 8 Hz), 7.41 (d, 4H, mAr‒H, \textit{J}_\text{H–H} = 8 Hz), 2.69 (sept, 4H, C\textsubscript{H}(CH\textsubscript{3})\textsubscript{2}, \textit{J}_\text{H–H} = 8 Hz), 2.25 (s, 4H, CH\textsubscript{2}), 1.62 (s, 4H, CH\textsubscript{2}), 1.44 (s, 4H, CH\textsubscript{2}), 1.25 (t, 24H, CH(C\textsubscript{H}\textsubscript{3})\textsubscript{2}, \textit{J}_\text{H–H} = 8 Hz). \textsuperscript{13}C NMR (100 MHz, DMSO-\textit{d}_6): δ = 144.34 (C\textsubscript{ortho}), 132.84 (C\textsubscript{para}), 130.67 (C\textsubscript{meta}), 125.75 (C\textsubscript{meta}), 84.30 (NCH\textsubscript{3}), 55.00 (CH\textsubscript{3}), 48.81, 28.57, 27.41, 26.80, 23.75. HRMS (ES\textsuperscript{+}): m/z calcd for C\textsubscript{40}H\textsubscript{62}N\textsubscript{2}Hg\textsubscript{2}Br\textsubscript{4}Na: 1315.0906; found: 1315.0880.

\textbf{Synthesis of [cAAC\textsuperscript{cy}-HgBr(μ‒Br)]\textsubscript{2} (1b).} A mixture of [cAAC\textsuperscript{cy}H]+Cl\textsuperscript{–} (0.50 g, 1.38 mmol) and K[N(SiMe\textsubscript{3})\textsubscript{2}] (0.28 g, 1.40 mmol) was taken in THF (25 mL). The resulting suspension was stirred at room temperature for 2 h. The solution was filtered to remove KCl and subsequently added to suspension of HgBr\textsubscript{2} (0.47 g, 1.38 mmol) in THF (5 mL). The resulting suspension was stirred at room temperature for 3 h. The solution was filtered off and the precipitate obtained was further washed
with THF (10 mL) to give 1b as a white solid. The colorless crystals of 1b were grown from DMSO solution at room temperature. Yield: 0.77 g, 81 %. Mp: 283–285 °C. IR (KBr, cm⁻¹) ν : 2972, 2934, 2859, 1595, 1554, 1462, 1449, 1387, 1370, 1264, 1141, 1110, 1049, 929, 906, 776. ¹H NMR (400 MHz, DMSO-d₆): δ = 7.52 (t, 2H, pAr-H, Jₜₚₚₚ = 8 Hz), 7.41 (d, 4H, mAr-H, Jₜₚₚₚ = 8 Hz), 2.69 (sept, 4H, CH(CH₃)₂, ³Jₚₚₚ = 6.4 Hz), 2.34 (s, 4H, CH₂), 1.90–1.30 (m, 2OH, Hcy), 1.44 (s, 12H, CH₃), 1.25 (d, 12H, CH(CH₃)₂, ³Jₚₚₚ = 6.4). ¹³C NMR (100 MHz, DMSO-d₆): δ = 242.56 (C–Hg), 144.37 (Cortho), 132.89 (Cpara), 130.75 (Cipsa), 125.71 (Cmeta), 84.15 (CCH₂), 59.58 (CH₃), 33.24 (H₂CCH), 29.10, 28.35, 26.59, 23.57, 21.12. HRMS (ES⁺): m/z calcd for C₆H₇N₂Hg₂Br₃: 1291.2458 [M–HBr]⁺; found: 1291.2565; m/z calcd for C₂₃H₃₆NHgBr: 606.1644 [M–HBr]⁺; found: 606.1647.

**Synthesis of [cAAC⁹⁺H⁺][HgCl₃]⁻ (2a).** A mixture of [cAAC⁹⁺H⁺]Cl⁻ (0.64 g, 2.00 mmol) and Hg(OAc)₂ (0.32 g, 1.00 mmol) was taken in MeOH (50 mL). The resulting suspension was stirred at room temperature for overnight. The mixture was filtered and the filtrate was concentrated and kept at room temperature for crystallization that afforded colorless crystals of 2a. Yield: 0.35 g, 29.5 %. Mp: 228–230 °C. IR (Nujol, cm⁻¹) ν : 3060, 3012, 2971, 2808, 1441, 1460, 1392, 1371, 1347, 1207, 1128, 1056, 933, 807, 766, 653, 561, 485, 420. ¹H NMR (400 MHz, CD₃OD): δ = 9.40 (s, 1H, CH=N), 7.60 (t, 1H, pAr-H, ³Jₚₚₚ = 8 Hz), 7.54 (d, 2H, mAr-H, ³Jₚₚₚ = 8 Hz), 7.28 (sept, 2H, CH(CH₃)₂, ³Jₚₚₚ = 8 Hz), 2.50 (s, 2H, CH₂), 1.62 (s, 6H, CH₃), 1.57 (s, 6H, CH₃), 1.38 (d, 6H, CH(CH₃)₂, ³Jₚₚₚ = 8 Hz), 1.13 (d, 6H, CH(CH₃)₂, ³Jₚₚₚ = 8 Hz). ¹³C NMR (100 MHz, CD₃OD): δ = 193.67 (N=CH), 145.79 (Cortho), 133.30 (Cpara), 126.69, 85.95 (CCH₂), 30.82, 28.59 CH(CH₃)₂, 26.30 (CH₃), 26.22 (CH₃), 22.22. HRMS (ES⁺): m/z calcd for HgCl₃: 306.8745 [M–cAAC⁺]; found: 306.8733.

**Synthesis of [cAAC⁻][HgCl₃]⁻ (2b).** A mixture of [cAAC⁻]Cl⁻ salt (0.72 g, 2.00 mmol) and Hg(OAc)₂ (0.32 g, 1.00 mmol) was taken in MeOH (50 mL). The resulting suspension was stirred at room temperature for overnight. The mixture was filtered and the filtrate was concentrated and kept at room temperature for crystallization that afforded colorless crystals of 2b. Yield: 0.39 g, 30.8%. Mp: 237–245 °C (decomp). IR (Nujol, cm⁻¹) ν : 2967, 2927, 2861, 1715, 1671, 1640, 1579, 1443, 1364, 1272, 1191, 1050, 950, 928, 808, 766. ¹H NMR (400 MHz, CD₃OD): δ = 9.47 (s, 1H, CH=N), 7.61 (t, 1H, pAr-H, ³Jₚₚₚ = 8 Hz), 7.50 (d, 2H, mAr-H, ³Jₚₚₚ = 8 Hz), 2.79 (sept, 2H, CH(CH₃)₂, ³Jₚₚₚ = 7 Hz), 2.55 (s, 2H, CH₂), 2.11–1.60 (m, 1OH, Hcy), 1.59 (s, 6H, CH₃), 1.39 (d, 6H, CH(CH₃)₂, ³Jₚₚₚ = 7 Hz), 1.15 (d, 6H, CH(CH₃)₂, ³Jₚₚₚ = 7 Hz). ¹³C NMR (100 MHz, CD₃OD): δ = 192.94 (N=CH), 145.79 (Cortho), 133.22 (Cpara), 126.65, 85.12 (CCH₂), 54.01 (Ccy), 46.27 (CH₃), 35.14, 30.73 CH(CH₃)₂, 29.05 (CH₃), 26.36 (CH₃), 25.79 (H₂CCH), 22.55 (CH₃), 22.45 (H₂CCH). HRMS (ES⁻): m/z calcd for HgCl₃⁻: 306.8745 [M–cAAC⁻]; found: 306.8734; HRMS (ES⁺): m/z calcd for C₂₃H₃₆N⁻: 326.2848 [M–HgCl₃⁺]; found: 326.2860.
Synthesis of [(cAAC\textsuperscript{cy})\textsubscript{2}Hg(H\textsubscript{2}O)]\textsubscript{2}\textsuperscript{2+}\text{2}[NO\textsubscript{3}]\textsuperscript{2‒} (3). A mixture of [cAAC\textsuperscript{cy}·HgBr(μ-Br)]\textsubscript{2} (1b) (0.69 g, 1.00 mmol) and AgNO\textsubscript{3} (0.34 g, 2.00 mmol) was taken in THF (30 mL). The resulting suspension was stirred at room temperature for overnight. The mixture was filtered and the clear filtrate was concentrated and subsequently kept for crystallization that afforded colorless crystals of 3 at room temperature. Yield: 0.20 g, 40.9 %. Mp: 215–217 °C. IR (Nujol, cm\textsuperscript{−1}): 2973, 2935, 2859, 1590, 1469, 1446, 1382, 1318, 1143, 1052, 931, 779, 594. \textsuperscript{1}H NMR (400 MHz, DMSO–d\textsubscript{6}): δ = 7.69 (t, 2H, pAr–H, 3\textsubscript{J}H–H = 8 Hz), 7.62 (d, 4H, mAr–H, 3\textsubscript{J}H–H = 8 Hz), 2.73 (sept, 4H, CH(CH\textsubscript{3})\textsubscript{2}, 3\textsubscript{J}H–H = 8 Hz), 2.38 (s, 4H, CH\textsubscript{2}), 180-1.60 (m, 12H, H\textsubscript{Cy}), 1.47 (s, 12H, CH\textsubscript{3}), 1.25 (d, 12H, CH(CH\textsubscript{3})\textsubscript{2}, 3\textsubscript{J}H–H = 8 Hz), 1.11 (d, 12H, CH(CH\textsubscript{3})\textsubscript{2}, 3\textsubscript{J}H–H = 8 Hz), 0.95-0.75 (m, 8H, H\textsubscript{Cy}). \textsuperscript{13}C NMR (100 MHz, DMSO–d\textsubscript{6}): δ = 237 (C–Hg), 145.02 (C\textsubscript{ortho}), 132.41 (C\textsubscript{para}), 127.04 (C\textsubscript{meta}), 88.00 (CCH\textsubscript{3}), 58.52, 43.16, 34.70, 28.85, 28.46, 27.79, 24.00, 20.61. HRMS (AP\textsuperscript{+}): m/z calcd for C\textsubscript{46}H\textsubscript{70}HgN\textsubscript{3}O\textsubscript{3}: 914.5132 [M–H\textsubscript{2}O–NO\textsubscript{3}]; found: 914.5161.

Fig S1. \textsuperscript{1}H NMR spectrum (400 MHz, d\textsubscript{6}-DMSO) of [cAAC\textsuperscript{Me}·HgBr(μ-Br)]\textsubscript{2} (1a). Insets (I)‒(III) show the expansion of selected spectral region.
Fig S2. $^{13}$C NMR spectrum (100 MHz, d$_6$-DMSO) of [cAAC$^\text{Me}$-HgBr($\mu$-Br)]$_2$ (1a). Insets (I) & (II) show the expansion of selected spectral region.

Fig S3. HRMS spectrum of [cAAC$^\text{Me}$-HgBr($\mu$-Br)]$_2$ (1a).
Fig S4. $^1$H NMR spectrum (400 MHz, d$_6$-DMSO) of [cAAC$^{cy}$·HgBr(μ-Br)]$_2$ (1b). Insets (I)-(III) show expansion of the selected spectral region.

Fig S5. $^{13}$C NMR spectrum (100 MHz, d$_6$-DMSO) of [cAAC$^{cy}$·HgBr(μ-Br)]$_2$ (1b).
Fig S6. HRMS spectrum of \([\text{cAAC}^{\text{cy}}\cdot\text{HgBr(μ-Br)}]_2\) (1b).

Fig S7. $^1$H NMR spectrum (400 MHz, CD$_3$OD) of \([\text{cAAC}^{\text{MeH}}][\text{HgCl}_3]^-\) (2a). Insets (I)–(III) show the expansion of selected spectral region.
Fig S8. $^{13}$C NMR spectrum (100 MHz, CD$_3$OD) of [cAAC$^\text{Me}$H]$^+[$HgCl$_3$]$^-$ (2a).

Fig S9. HRMS spectrum of [cAAC$^\text{Me}$H]$^+[$HgCl$_3$]$^-$ (2a).
**Fig S10.** $^1$H NMR spectrum (400 MHz, CD$_3$OD) of [cAAC$^{59}$H][HgCl$_3$]$^-$ (2b). Insets (I)-(III) show expansion of the selected spectral region.

**Fig S11.** $^{13}$C NMR spectrum (100 MHz, CD$_3$OD) of [cAAC$^{59}$H][HgCl$_3$]$^-$ (2b).
Fig S12. HRMS spectrum of [cAAC\textsuperscript{9}H]\textsuperscript{+}[HgCl\textsubscript{3}]\textsuperscript{−} (2b).

Fig S13. \textsuperscript{1}H NMR spectrum (400 MHz, d\textsubscript{6}-DMSO) of [(cAAC\textsuperscript{9}H)_2Hg(H\textsubscript{2}O)]\textsuperscript{2+}2[NO\textsubscript{3}−] (3). Insets show expansion for the aliphatic and aromatic regions.
Fig S14. $^{13}$C NMR spectrum (100 MHz, d$_6$-DMSO) of [(cAAC$^{\gamma}$)$_2$Hg(H$_2$O)]$^{2+}$2[NO$_3$]$^-$ (3).

Fig S15. HRMS spectrum of [(cAAC$^{\gamma}$)$_2$Hg(H$_2$O)]$^{2+}$2[NO$_3$]$^-$ (3).
Single crystal X-ray characterization of compounds 1a, 1b, 2a, 2b and 3

Single crystal X-ray diffraction data of 1a was collected on a Bruker \textit{AXS KAPPA APEX-II} CCD diffractometer with MoKα radiation using omega scans. Unit cell determination and refinement and data collection were done using the Bruker APPEX-II suite,\textsuperscript{2} data reduction and integration were performed using SAINT v8.34A (Bruker, 2013)\textsuperscript{3} and absorption corrections and scaling were done using SADABS-2014/5 (Bruker, 2014/5)\textsuperscript{4}. Single crystal X-ray diffraction data of 1b, 2a, 2b and 3 were collected using a Rigaku XtaLAB mini diffractometer equipped with Mercury375M CCD detector. The data were collected with MoKα radiation (\(\lambda = 0.71073 \text{ Å}\)) using omega scans. During the data collection, the detector distance was 49.9 mm (constant) and the detector was placed at \(2\theta = 29.85^\circ\) (fixed) for all the data sets. The data collection and data reduction were done using Crystal Clear suite,\textsuperscript{5} and all the crystal structures were solved through OLEX2\textsuperscript{6} package using XT\textsuperscript{7} and the structures were refined using XL.\textsuperscript{7} All non hydrogen atoms were refined anisotropically. All the figures were generated using Mercury 3.2 and Diamond 2.1d. The geometric parameters reported here are taken from the CIF data. In compound 1b the five member ring carbon (C\textsubscript{8}) was disordered at two positions that were treated with equal occupancy.

In the crystal lattice, compound 1a forms 1D network due to the weak intermolecular C–H···Br interactions (2.979 Å) between a hydrogen atom on one of the methyl groups (of the C\textsubscript{4}N five membered carbene ring) of a molecule of 1a with a terminal bromine atom of another molecule of 1a (Fig S16).

![Fig S16. Formation of 1D network in the solid state of 1a due to weak intermolecular C–H···Br interactions.](image)

Similar to compound 1a, compound 1b also showed the existence of weak intermolecular C–H···Br interactions in the crystal lattice. These C–H···Br interactions measure 3.024 Å &
2.863 Å and lead to the formation of a 3D network. In the first C–H···Br interaction, terminal bromine atoms of each molecule of 1b interact with a hydrogen atom of one of the methyl groups (of C₆N five membered ring of second molecule of 1b) and the second pair of C–H···Br interactions involve the p-H atom of the 2,6-iPr₂C₆H₃ substituent from the third molecule of 1b (2.863 Å) (Fig S17).

Fig S17. Formation of 3D network of 2b in the crystal lattice due to weak intermolecular C–H···Br interactions.

Fig S18. Single crystal X-ray structure of [cAAC⁶⁺H][HgCl₃]⁻ (2a) (left) and [cAAC⁶⁻H][HgCl₃]⁻ (2b) (right). Thermal ellipsoids are shown at 50 % probability levels. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°] for 2a: Hg1-Cl1 2.6129(11), Hg1-Cl2 2.3717(15), Hg1-Cl3 2.3615(11); Cl1-Hg1-Cl2 107.32(4), Cl2-Hg1-Cl3 132.00(5), Cl1-Hg1-Cl3 106.57(4); for 2b: Hg(1)-Cl(1) 2.3873(15), Hg(1)-Cl(3) 2.6077(14), Hg(1)-Cl(2) 2.3978(14); Cl1-Hg1-Cl2 130.79(7), Cl2-Hg1-Cl3 102.42(6), Cl1-Hg1-Cl3 112.03(7).
Table S1. Crystallographic data for compounds 1a, 1b, 2a, 2b and 3.

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[a] R1 = Σ ||Fo| – |Fc||/Σ|Fo|, wR2 = [Σw( ||Fo|^2 – |Fc|^2 ||/Σw|Fo|^2 ||]^{1/2}
Intermolecular hydroamination reaction of phenylacetylenes and anilines bearing different functional groups:

**General procedure for hydroamination:** A Schlenk flask was charged with an aniline (4.5 mmol), an alkyne (4.5 mmol) and catalyst 1b (1.3 mol%) in 30 mL THF. The reaction progress was monitored by TLC and NMR and the products were isolated after the removal of volatiles under vacuum followed by extraction with hexane. Whenever necessary the products were purified by column chromatography. The spectroscopic data for the products were compared to the literature wherever available.

**Synthesis of N‒(1‒phenylethylidene)‒aniline (4a)**

Phenylacetylene (0.50 mL, 4.5 mmol) was added to a mixture of aniline (0.40 mL, 4.5 mmol) and [cAAC\textsuperscript{Cy}•HgBr(μ-Br)]\textsubscript{2}, (1b) (84 mg, 0.06 mmol, 1.3 mol%) taken in a Schlenk flask in 30 mL THF. The resulting solution was reflux for 8 h. The volatiles were then removed under reduced pressure and the resulting residue was extracted with hexane. The hexane extract was dried under vacuum and the oily material obtained was purified by column chromatography on silica gel (eluent petroleum ether/ethyl acetate 4:1+2% triethylamine) to afford 4a as a yellow oil.

**\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}):** \(\delta = 8.03\) (d, 2H, ArH, \(^3J_{H-H} = 8\) Hz), 7.50 (s, br, 3H, ArH), 7.40 (t, 2H, ArH, \(^3J_{H-H} = 8\) Hz), 7.14 (t, 1H, ArH, \(^3J_{H-H} = 8\) Hz), 6.85 (d, 2H, ArH, \(^3J = 8\) Hz), 2.28 (s, 3H, N=CC\textsubscript{H}\textsubscript{3}); **\(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}):** \(\delta = 165.55\) (NCC\textsubscript{H}\textsubscript{3}), 151.72, 139.48, 130.53, 129.30, 129.01, 128.42, 123.27, 119.43, 119.43, 17.44.

**HRMS (ES\(^+\)):** \(m/z\) calcd for C\textsubscript{14}H\textsubscript{14}N: 196.1126 \([\text{M+H}]^+\); found: 196.1120.

**Synthesis of N‒(1‒(p‒methoxyphenyl)ethylidene)aniline (4b)**

**\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}):** \(\delta = 8.00\) (d, 2H, ArH, \(^3J_{H-H} = 8\) Hz), 7.39 (t, 2H, ArH, \(^3J_{H-H} = 8\) Hz), 7.12 (t, 1H, ArH, \(^3J_{H-H} = 8\) Hz), 6.99 (d, 2H, ArH, \(^3J_{H-H} = 8\) Hz), 6.86 (d, 2H, ArH, \(^3J_{H-H} = 8\) Hz), 3.85 (s, 3H, OCH\textsubscript{3}), 2.22 (s, 3H, N=CC\textsubscript{H}\textsubscript{3}); **\(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}):** \(\delta = 164.40\) (NCC\textsubscript{H}\textsubscript{3}), 161.39, 151.79, 131.99, 128.83, 122.92, 119.53, 113.46, 55.16 (OCH\textsubscript{3}), 17.00 (CH\textsubscript{3}.

**HRMS (ES\(^+\)):** \(m/z\) calcd for C\textsubscript{15}H\textsubscript{16}NO: 226.1232 \([\text{M+H}]^+\); found: 226.1211.

**Synthesis of N‒(1‒(p‒fluorophenyl)ethylidene)aniline (4c)**

**\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}):** \(\delta = 8.00\) (m, 2H, ArH), 7.38 (t, 2H, ArH, \(^3J_{H-H} = 8\) Hz), 7.14 (m, 3H, ArH), 6.80 (m, 2H, ArH) 2.23 (s, 3H, N=CC\textsubscript{H}\textsubscript{3}), 2.03 (s, 6H, o-CH\textsubscript{3}); **\(^{19}\)F NMR (376.4 MHz, CDCl\textsubscript{3}):** \(\delta = -105.29\).

**HRMS (ES\(^+\)):** \(m/z\) calcd for C\textsubscript{14}H\textsubscript{13}NF: 214.1032 \([\text{M+H}]^+\); found: 214.1023.

**Synthesis of N‒(1‒phenylethylidene)‒2,4,6‒trimethylaniline (5a)**

**\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}):** \(\delta = 8.05\) (d, 2H, ArH, \(^3J_{H-H} = 8\) Hz), 7.50 (s, br, 3H, ArH), 6.90 (s, 2H, ArH), 2.32 (s, 3H, N=CC\textsubscript{H}\textsubscript{3}), 2.03 (s, 6H, o-CH\textsubscript{3}); **\(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}):** \(\delta = 165.54\) (NCC\textsubscript{H}\textsubscript{3}), 146.57, 139.38,
131.98, 130.47, 128.93, 128.47, 127.16, 125.66, 20.86 (CH₃), 18.02 (CH₃), 17.53 (CH₃). HRMS (ES⁺): m/z calcd for C₁₇H₂₀N: 238.1596 [M-H]⁺; found: 238.1584.

**Synthesis of N–(1–(p–methoxyphenyl)ethylidene)–2,4,6–trimethylaniline (5b)**

**¹H NMR** (400 MHz, CDCl₃): δ = 8.17 (d, 2H, ArH, 3J₁₋₋ = 8 Hz), 7.10 (d, 2H, ArH, 3J₁₋₋ = 8 Hz), 7.03 (s, 2H, ArH), 3.95 (s, 3H, OCH₃), 2.45 (s, 3H, p-CH₃), 2.17 (two overlapped singlets, 9H, o-CH₃ and N=CCH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 161.51, 146.88, 131.76, 128.74, 122.90, 113.90, 113.63, 55.18 (OCH₃): m/z calcd for C₁₇H₂₀O: 288.2055 [M+H]⁺; found: 288.2065.

**Synthesis of N–(1–(p–fluorophenyl)ethylidene)–2,6–disiopropylaniline (5c)**¹²

**¹H NMR** (400 MHz, CDCl₃): δ = 8.03 (m, 2H, ArH), 7.14 (t, 2H, ArH, 3J₁₋₋ = 8 Hz), 6.92 (s, 2H, ArH), 2.34 (s, 3H, N=CCH₃), 2.04 (s, 6H, o-CH₃): ¹³C NMR (100 MHz, CDCl₃): δ = 164.17 (NCCH₃), 146.11, 135.23, 131.79, 129.01, 125.36, 115.01, 20.53 (CH₃), 17.67 (CH₃), 17.07 (CH₃); ¹⁹F NMR (376.4 MHz, CDCl₃): δ = -110.66. HRMS (ES⁺): m/z calcd for C₂₂H₁₃FN: 256.1501 [M+H]⁺; found: 256.1489.

**Synthesis of N–(1–phenylethylidene)–2,6–diisopropylaniline (6a)**⁹

**¹H NMR** (400 MHz, CDCl₃): δ = 8.06 (d, 2H, ArH, 3J₁₋₋ = 8 Hz), 7.51 (br, 3H, ArH), 7.18 (d, 2H, ArH, 3J₁₋₋ = 8 Hz), 7.11 (d, 1H, ArH), 2.78 (sept, 2H, CH(CH₃)₂, 3J₁₋₋ = 8 Hz), 2.13 (s, 3H, N=CCH₃), 1.17 (t, 12H, CH(C₆H₃); 3J₁₋₋ = 8 Hz); ¹³C NMR (100 MHz, CDCl₃): δ = 164.94 (NCCH₃), 146.83, 140.26, 136.22, 132.6, 130.52, 128.55, 127.25, 123.42, 123.06, 28.32 (CH(CH₃)₂), 23.36 (CH(CH₃)₂), 23.11 (CH(CH₃)₂), 18.25 (CH₃). HRMS (ES⁺): m/z calcd for C₂₀H₂₀N: 288.2055 [M+H]⁺; found: 288.2065.

**Synthesis of N–(1–(p–methoxyphenyl)ethylidene)–2,6–disiopropylaniline (6b)**

**¹H NMR** (400 MHz, CDCl₃): δ = 8.18 (d, 2H, ArH, 3J₁₋₋ = 8 Hz), 7.20 (m, 2H, ArH), 7.12 (d, 2H, ArH, 3J₁₋₋ = 8 Hz), 6.97 (d, 1H, ArH, 3J₁₋₋ = 8 Hz), 3.96 (s, 3H, OCH₃), 3.95 (sept, 2H, CH(CH₃)₂, 3J₁₋₋ = 8 Hz), 2.23 (s, 3H, N=CCH₃): m/z calcd for C₂₁H₂₁O: 310.2171 [M+H]⁺; found: 310.2157.

**Synthesis of N–(1–(p–fluorophenyl)ethylidene)–2,6–disiopropylaniline (6c)**¹²

**¹H NMR** (400 MHz, CDCl₃): δ = 8.08 (m, 2H, ArH), 7.12 (m, 5H, ArH), 2.77 (sept, 2H, CH(CH₃)₂, 3J₁₋₋ = 6.8 Hz), 2.13 (s, 3H, N=CCH₃): m/z calcd for C₂₂H₂₂FNO: 328.1584 [M-H]⁻; found: 328.1577.
\[ {^1}H \text{ NMR} \ (400 \text{ MHz, CDCl}_3): \delta = 7.97 \ (d, 2H, ArH, ^3J_{H-H} = 8 \text{ Hz}), 7.46 \ (m, 3H, ArH), 6.92 \ (d, 2H, ArH, ^3J = 8 \text{ Hz}), 6.74 \ (d, 2H, ArH, ^3J = 8 \text{ Hz}), 3.82 \ (s, 3H, OCH}_3); \]

\[ {^{13}}C \text{ NMR} \ (100 \text{ MHz, CDCl}_3): \delta = 166.74 \ (NCCH}_3), 164.33, 155.80, 144.31, 136.20, 130.80, 130.70, 115.52, 114.44, 55.43 \ (s, 3H, OCH}_3), 16.96 \ (CH}_3); \]

\[ {^{19}}F \text{ NMR} \ (376.4 \text{ MHz, CDCl}_3): \delta = -121.57. \]

HRMS (ES^+): m/z calcd for C_{15}H_{15}FNO: 244.1127; found: 244.1127.
Synthesis of N-(1-(p-fluorophenyl)ethyldiene)--p-fluoroaniline (8c)\(^\text{11}\)

\[\begin{align*}
\text{F} & \quad \text{N} \\
\text{N} & \quad \text{F}
\end{align*}\]

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta = 7.97\) (m, 2H, ArH), 7.12 (t, 2H, ArH, \(\text{J}_{\text{H-H}} = 8\) Hz), 7.05 (t, 2H, ArH, \(\text{J}_{\text{H-H}} = 8\) Hz), 6.75 (m, 2H, ArH), 2.22 (s, 3H, CH\(_3\)); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta = 165.17\) (NCH\(_3\)), 160.46, 158.30, 147.51, 135.65, 129.38, 120.85, 115.51, 115.30, 17.53 (CH\(_3\)); \(^{19}\text{F NMR}\) (376.4 MHz, CDCl\(_3\)): \(\delta = -110.21\) and \(-121.06\). \(\text{HRMS (ES\textsuperscript{*})}: m/z\) calcd for \(\text{C}_{14}\text{H}_{12}\text{F}_2\text{N}\): 232.0938 [M+H]\(^+\); found: 232.0929.

Synthesis of N-(1-phenylethyldiene)--p-chloroaniline (9a)\(^\text{10}\)

\[\begin{align*}
\text{Cl} & \quad \text{N} \\
\text{N} & \quad \text{Cl}
\end{align*}\]

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta = 7.97\) (d, 2H, ArH, \(\text{J}_{\text{H-H}} = 8\) Hz), 7.47 (d, 3H, ArH, \(\text{J}_{\text{H-H}} = 8\) Hz), 7.31 (d, 2H, ArH, \(\text{J}_{\text{H-H}} = 8\) Hz), 6.75 (d, 2H, ArH, \(\text{J}_{\text{H-H}} = 8\) Hz), 2.24 (s, 3H, CH\(_3\)); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta = 166.38\) (NCC\(_3\)), 150.25, 139.26, 130.82, 129.14, 128.54, 127.29, 120.92, 17.56 (CH\(_3\)). \(\text{HRMS (ES\textsuperscript{*})}: m/z\) calcd for \(\text{C}_{14}\text{H}_{13}\text{ClN}\): 230.0737 [M+H]\(^+\); found: 230.0742.

Synthesis of N-(1-(p-methoxyphenyl)ethyldiene)--p-chloroaniline (9b)\(^\text{11}\)

\[\begin{align*}
\text{Cl} & \quad \text{N} \\
\text{N} & \quad \text{Cl}
\end{align*}\]

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta = 7.92\) (d, 2H, ArH, \(\text{J}_{\text{H-H}} = 8\) Hz), 7.06 (d, 2H, ArH, \(\text{J}_{\text{H-H}} = 8\) Hz), 6.92 (d, 2H, ArH, \(\text{J}_{\text{H-H}} = 8\) Hz), 6.58 (d, 2H, ArH, \(\text{J}_{\text{H-H}} = 8\) Hz), 3.84 (s, 3H, OCH\(_3\)), 2.54 (s, 3H, N=CH\(_3\)); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta = 165.34\) (NCC\(_3\)), 145.14 (d), 130.62, 129.08, 122.99, 121.09, 116.26, 113.73, 55.49 (OCH\(_3\)), 26.36 (CH\(_3\)). \(\text{HRMS (ES\textsuperscript{*})}: m/z\) calcd for \(\text{C}_{15}\text{H}_{12}\text{ClN}O\): 260.0842 [M+H]\(^+\); found: 260.0831.

Synthesis of N-(1-(p-fluorophenyl)ethyldiene)--p-chloroaniline (9c)\(^\text{11}\)

\[\begin{align*}
\text{Cl} & \quad \text{N} \\
\text{N} & \quad \text{Cl}
\end{align*}\]

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta = 7.97\) (m, 2H, ArH), 7.32 (d, 2H, ArH, \(\text{J}_{\text{H-H}} = 8\) Hz), 7.10 (m, 2H, ArH), 6.72 (d, 2H, ArH, \(\text{J}_{\text{H-H}} = 8\) Hz), 2.21 (s, 3H, CH\(_3\)); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta = 165.09\) (NCC\(_3\)), 163.23, 150.04, 135.4, 129.46, 129.38, 123.18, 120.93, 115.34, 17.48 (CH\(_3\)); \(^{19}\text{F NMR}\) (376.4 MHz, CDCl\(_3\)): \(\delta = -105.24\). \(\text{HRMS (ES\textsuperscript{*})}: m/z\) calcd for \(\text{C}_{15}\text{H}_{12}\text{ClFNO}\): 248.0632.

Synthesis of N-(1-phenylethyldiene)--p-bromoaniline (10a)\(^\text{10}\)

\[\begin{align*}
\text{Br} & \quad \text{N} \\
\text{N} & \quad \text{Br}
\end{align*}\]

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta = 8.00\) (d, 2H, ArH, \(\text{J}_{\text{H-H}} = 8\) Hz), 7.50 (m, 5H, ArH), 6.73 (d, 2H, ArH), 2.25 (s, 3H, N=CH\(_3\)); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta = 166.36\) (NCC\(_3\)), 150.44, 138.93, 130.65, 128.31, 127.07, 121.18, 120.92, 17.43 (CH\(_3\)). \(\text{HRMS (ES\textsuperscript{*})}: m/z\) calcd for \(\text{C}_{14}\text{H}_{12}\text{BrN}\): 274.0231 [M+H]\(^+\); found: 274.0243.

Synthesis of N-(1-(p-methoxyphenyl)ethyldiene)--p-bromoaniline (10b)

\[\begin{align*}
\text{Br} & \quad \text{N} \\
\text{N} & \quad \text{Br}
\end{align*}\]

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)): \(\delta = 7.91\) (d, 2H, ArH, \(\text{J}_{\text{H-H}} = 8\) Hz), 7.42 (d, 2H, ArH, \(\text{J}_{\text{H-H}} = 8\) Hz), 6.93 (d, 2H, ArH, \(\text{J}_{\text{H-H}} = 8\) Hz), 6.66 (d, 2H, ArH, \(\text{J}_{\text{H-H}} = 8\) Hz), 6.54 (d, 2H, ArH, \(\text{J}_{\text{H-H}} = 8\) Hz), 2.61 (s, 3H, CH\(_3\)); \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)): \(\delta = 165.59\) (NCC\(_3\)), 160.46, 158.30, 147.51, 135.65, 129.38, 120.85, 115.51, 115.30, 17.53 (CH\(_3\)); \(^{19}\text{F NMR}\) (376.4 MHz, CDCl\(_3\)): \(\delta = -110.21\) and \(-121.06\). \(\text{HRMS (ES\textsuperscript{*})}: m/z\) calcd for \(\text{C}_{14}\text{H}_{12}\text{BrFNO}\): 272.0238 [M+H]\(^+\); found: 272.0243.
1H NMR (400 MHz, CDCl₃): δ = 7.95 (m, 2H, ArH), 7.45 (d, 2H, ArH, J_H-H = 8 Hz), 7.12 (t, 2H, ArH, J_H-H = 8 Hz), 6.67 (d, 2H, ArH, J_H-H = 8 Hz), 2.20 (s, 3H, CH₃); 13C NMR (100 MHz, CDCl₃): δ = 165.10 (NCCH₃), 163.15, 150.38, 135.30, 129.42, 129.34, 121.33, 115.30, 17.43 (CH₃); 19F NMR (376.4 MHz, CDCl₃): δ = -105.16. HRMS (ES⁺): m/z calcd for C₁₄H₁₂BrFN: 292.0137 [M+Na]+; found: 292.0125.

Synthesis of N-(1-(p-fluorophenyl)ethylidene)-p-bromoaniline (10c)

References:

5) CrystalClear 2.0; Rigaku Corporation: Tokyo, Japan, 2013.