## Supporting Information

# Ligand-Free Iron-Catalyzed C-F Amination of Diarylamines: A one-pot regioselective synthesis of diaryl dihydrophenazines 

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## 1. General

All reactions using air- and moisture-sensitive compounds were performed in dry reaction vessels under a positive pressure of dry argon. Air- and moisture-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula. Air- and moisturesensitive solids are handled in an argon-filled glovebox. Organic solutions were concentrated by rotary evaporation at $c a .30 \mathrm{mmHg}$. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with $0.25 \mathrm{~mm} 230-400$ mesh silica gel containing a fluorescent indicator (Merck, Silica gel 60 F254). The TLC plates were visualized by exposure to ultraviolet light ( 254 nm ). Flash column chromatography was performed on Wakogel 60N (38-100 $\mu \mathrm{m}$ ). Preparative recycling gel permeation chromatography (GPC) was performed with a Japan Analytical Industry LC9204 instrument equipped with JAIGEL-1H-40/JAIGEL-2H-40 columns using toluene as an eluent.

Proton nuclear magnetic resonance ( ${ }^{1} \mathrm{H}$ NMR), carbon nuclear magnetic resonance ( ${ }^{13} \mathrm{C}$ NMR), and fluorine nuclear magnetic resonance ( ${ }^{19} \mathrm{~F} \mathrm{NMR}$ ) spectra were recorded on JEOL ECS-400NR ( 392 MHz for ${ }^{1} \mathrm{H}, 98.5 \mathrm{MHz}$ for ${ }^{13} \mathrm{C}$, and 368 MHz for ${ }^{19} \mathrm{~F}$ ) NMR spectrometer. ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ chemical shift values are reported in parts per million ( ppm , $\delta$ scale), which are referenced to the tetramethylsilane ( $\delta 0$ ) in $\mathrm{CDCl}_{3}$, the proton resonance of $\mathrm{C}_{6} \mathrm{D}_{6}(\delta 7.16)$, the carbon resonance of $\mathrm{CDCl}_{3}$ ( $\delta$ 77.16), the carbon resonance of $\mathrm{C}_{6} \mathrm{D}_{6}(\delta 128.06)$ or the external standard fluorine signal of $\mathrm{CFCl}_{3}(\delta 0)$, respectively. Data are presented as: chemical shift, multiplicity ( $\mathrm{s}=$ singlet, $\mathrm{d}=$ doublet, $\mathrm{t}=$ triplet, $\mathrm{q}=$ quartet, quint $=$ quintet, sext $=$ sextet, $\mathrm{m}=$ multiplet and/or multiplet resonances, $\mathrm{br}=$ broad $)$, coupling constant in Hertz $(\mathrm{Hz})$ and signal area integration in natural numbers. Purities of isolated compounds were determined by GC analysis on a Shimadzu GC-2010 instrument equipped with an FID detector and a capillary column, ZB-1MS (Phenomenex Inc., $10 \mathrm{~m} \times 0.10 \mathrm{~mm}$ i.d., $0.10 \mu \mathrm{~m}$ film thickness) capillary column. IR spectra were recorded on a PerkinElmer Spectrum One FT-IR Spectrometer and characteristic IR absorptions are reported in $\mathrm{cm}^{-1}$. High-resolution mass spectra (HRMS) were obtained using fast atom bombardment (FAB) ionization on a JEOL JMS700 mass spectrometer. Melting points were determined using Yanaco MP-500D melting point apparatus.

Cyclopentyl methyl ether (CPME) was obtained from ZEON Co. Ltd. Other reaction solvents were obtained purchased from Wako Pure Chemical Industries, Ltd., and they
were dried over molecular sieves (Wako Pure Chemical Industries, Ltd., 137-06085) and distilled from calcium hydride or benzophenone ketyl at ambient pressure, and degassed prior to use. Water content of the solvent was determined with a Karl Fischer Moisture Titrator (MKC-610, Kyoto Electronics Manufacturing Co. Ltd.) to be less than 20 ppm .

Other materials were purchased from Wako Pure Chemical Industries, Ltd., Tokyo Chemical Industry Co., Ltd., Aldrich Inc., and other commercial suppliers, and were used after appropriate purification, unless otherwise noted. Florisil (100-200 mesh) was purchased from Wako Pure Chemical Industries, Ltd.. Purities, commercial suppliers and production numbers of specific reagents are as follows: $\mathrm{FeCl}_{2}$ (99.998\%, Aldrich Inc., 429368); $\mathrm{FeCl}_{3}$ (99.99+\%, Aldrich Inc., 451649); $\mathrm{NiCl}_{2}$ (99.99\%, Aldrich Inc., 451193); $\mathrm{CoCl}_{2}$ (99.999\%, Aldrich Inc., 409322); Ethylmagnesium bromide in $\mathrm{Et}_{2} \mathrm{O}$ (Aldrich Inc., 189871).

## 2. Experimental Procedures

## Preparation of diarylamines

## Synthesis of 2-fluoro- $N$-phenylaniline (1a, X = F) (General procedure)



1-Bromo-2-fluorobenzene ( $797 \mathrm{mg}, 4.98 \mathrm{mmol}$ ) was added to a mixture of aniline ( $705 \mathrm{mg}, 7.57 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium(0) ( $44.6 \mathrm{mg}, 199 \mu \mathrm{~mol}$ ), (+/-)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl ( $186 \mathrm{mg}, 300 \mu \mathrm{~mol}$ ), and sodium tertbutoxide ( $674 \mathrm{mg}, 7.01 \mathrm{mmol}$ ) in toluene $(5.0 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $110^{\circ} \mathrm{C}$ for 5 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(10 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate $(4 \times 20 \mathrm{~mL})$ and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane/toluene $=9 / 1$ ) to afford the title compound as a yellow oil ( $731 \mathrm{mg}, 78 \%$ yield, $>99 \%$ purity on GC analysis). Anal. calcd for $\mathrm{C}_{12} \mathrm{H}_{10} \mathrm{FN}$ : C, 76.99; H, 5.38; N, 7.48. Found: C, 77.10 ; H, 5.62; N, 7.55. Spectroscopic data for the title compound has been previously reported. ${ }^{1}{ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR spectra have been attached as Figures S 1 , S2, and S3.

## Synthesis of 2-chloro- N -phenylaniline (1a, $\mathrm{X}=\mathbf{C l}$ )



Iodobenzene ( $820 \mathrm{mg}, 4.02 \mathrm{mmol}$ ) was added to a mixture of 2-chloroaniline ( 610 $\mathrm{mg}, 4.78 \mathrm{mmol})$, palladium(II) acetate ( $44.9 \mathrm{mg}, 200 \mu \mathrm{~mol}$ ), 1,1 'bis(diphenylphosphino)ferrocene ( $222 \mathrm{mg}, 400 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( 538 mg ,

[^1]$5.60 \mathrm{mmol})$ in toluene $(5.0 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $110^{\circ} \mathrm{C}$ for 5 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(10 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate ( $4 \times 20 \mathrm{~mL}$ ) and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford the title compound as a yellow oil ( $367 \mathrm{mg}, 45 \%$ yield, $>99 \%$ purity on GC analysis). Anal. calcd for $\mathrm{C}_{12} \mathrm{H}_{10} \mathrm{ClN}$ : C, 70.77; H, 4.95; N, 6.88. Found: C, 70.96; H, 5.04; N, 7.01. Spectroscopic data for the title compound has been previously reported. ${ }^{2}{ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra have been attached as Figures S4 and S5.

## Synthesis of 2-bromo- $N$-phenylaniline (1a, $\mathrm{X}=\mathrm{Br}$ )



1-Bromo-2-iodobenzene ( $1.12 \mathrm{~g}, 3.96 \mathrm{mmol}$ ) was added to a mixture of aniline ( 450 $\mathrm{mg}, 4.83 \mathrm{mmol})$, palladium(II) acetate $(44.9 \mathrm{mg}, \quad 200 \mu \mathrm{~mol}), \quad 1,1$ 'bis(diphenylphosphino)ferrocene ( $222 \mathrm{mg}, 400 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( 538 mg , $5.60 \mathrm{mmol})$ in toluene $(5.0 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $110^{\circ} \mathrm{C}$ for 5 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(10 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate ( $4 \times 20 \mathrm{~mL}$ ) and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford the title compound as a yellow oil ( $727 \mathrm{mg}, 80 \%$ yield, $>99 \%$ purity on GC analysis). Anal. calcd for $\mathrm{C}_{12} \mathrm{H}_{10} \mathrm{BrN}$ : C, 58.09; H, 4.06; N, 5.65. Found: C, 58.31; H, 4.23; N, 5.67. Spectroscopic data for the title compound has been previously reported. ${ }^{3}{ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra have been attached as Figures S6 and S7.

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## Synthesis of 2-fluoro- $N$-(p-tolyl)aniline (1b)



1-Iodo-4-methylbenzene ( $773 \mathrm{mg}, 4.01 \mathrm{mmol}$ ) was added to a mixture of 2 fluoroaniline ( $534 \mathrm{mg}, 4.80 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium(0) $(73.6 \mathrm{mg}$, $80.4 \mu \mathrm{~mol}$ ), 2-dicyclohexylphosphino-2', $6^{\prime}$ 'dimethoxybiphenyl ( $78.7 \mathrm{mg}, 192 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( $577 \mathrm{mg}, 6.00 \mathrm{mmol}$ ) in toluene $(5.0 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $60^{\circ} \mathrm{C}$ for 9 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(7.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate $(4 \times 10 \mathrm{~mL})$ and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford the title compound as a colorless oil ( $686 \mathrm{mg}, 85 \%$ yield, $>99 \%$ purity on GC analysis). Anal. calcd for $\mathrm{C}_{13} \mathrm{H}_{12} \mathrm{FN}$ : C, $77.59 ; \mathrm{H}, 6.01 ; \mathrm{N}, 6.96$. Found: C, 77.83; H, 6.28; N, 7.06. Spectroscopic data for the title compound has been previously reported. ${ }^{4} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR spectra have been attached as Figures S 8 , S9, and S10.

## Synthesis of 2-fluoro- $\boldsymbol{N}$-(m-tolyl)aniline (1c)


$1 c$
1-Iodo-3-methylbenzene ( $874 \mathrm{mg}, 4.01 \mathrm{mmol}$ ) was added to a mixture of 2fluoroaniline ( $535 \mathrm{mg}, 4.81 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium(0) $(72.9 \mathrm{mg}$, $79.6 \mu \mathrm{~mol}$ ), 2-dicyclohexylphosphino-2', $6^{\prime}$-dimethoxybiphenyl ( $79.1 \mathrm{mg}, 193 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( $575 \mathrm{mg}, 5.98 \mathrm{mmol}$ ) in toluene ( 5.0 mL ) at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $60^{\circ} \mathrm{C}$ for 3 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(7.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate $(4 \times 10 \mathrm{~mL})$ and the combined organic extracts

[^3]were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford the title compound as a colorless oil ( $695 \mathrm{mg}, 86 \%$ yield, $>99$ purity on GC analysis). IR (neat, $\mathrm{cm}^{-1}$ ) $3410(\mathrm{~N}-\mathrm{H}), 3047,2912,1604,1587$, $1515,1459,1415,1326,1293,1242,1186,1166,1098,1133,942,856,800,773,740$, 690, 585, 553, 519; ${ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{CDCl}_{3}, 392 \mathrm{MHz}\right) \delta 2.32$ (s, 3H), 5.75 (s, 1H), 6.79-6.85 (m, 2H), 6.92-6.93 (m, 2H), 7.01 (d, $J=7.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), 7.07 (ddd, $J=1.2,7.8 \mathrm{~Hz}, J_{\mathrm{H}-\mathrm{F}}=$ $11 \mathrm{~Hz}, 1 \mathrm{H}$ ), 7.16-7.20 (m, 1H), 7.30 (td, 1.2, $7.8 \mathrm{~Hz}, 1 \mathrm{H}$ ); ${ }^{13} \mathrm{C}$ NMR ( $\mathrm{CDCl}_{3}, 98.5 \mathrm{MHz}$ ) $\delta 21.64,115.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=20 \mathrm{~Hz}\right), 115.9,117.3\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=1.9 \mathrm{~Hz}\right), 119.6,120.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=\right.$ $6.6 \mathrm{~Hz}), 122.9,124.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=3.8 \mathrm{~Hz}\right), 129.4,132.0\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=15 \mathrm{~Hz}\right), 139.5,142.1,153.1$ $\left(\mathrm{d}, J_{\mathrm{C}-\mathrm{F}}=242 \mathrm{~Hz}\right) ;{ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{CDCl}_{3}, 368 \mathrm{MHz}\right) \delta-132.6$; Anal. calcd for $\mathrm{C}_{13} \mathrm{H}_{12} \mathrm{FN}$ : C, $77.59 ; \mathrm{H}, 6.01$; N, 6.96. Found: C, 77.75; H, 6.26; N, 7.03. ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR spectra have been attached as Figures S11, S12, and S13.

## Synthesis of 2-fluoro- $N$-(4-chlorophenyl)aniline (1d)



1-Chloro-4-iodobenzene ( $715 \mathrm{mg}, 3.00 \mathrm{mmol}$ ) was added to a mixture of 2fluoroaniline ( $504 \mathrm{mg}, 4.54 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium( 0 ) ( 43.6 mg , $47.6 \mu \mathrm{~mol}$ ), 2-dicyclohexylphosphino-2', $6^{\prime}$-dimethoxybiphenyl ( $59.1 \mathrm{mg}, 144 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( $720 \mathrm{mg}, 7.49 \mathrm{mmol}$ ) in toluene $(5.0 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $70^{\circ} \mathrm{C}$ for 2 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(8.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate ( $4 \times 16 \mathrm{~mL}$ ) and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane/ethyl acetate $=9 / 1$ ) to afford the title compound as a yellow oil ( $629 \mathrm{mg}, 95 \%$ yield, $>99 \%$ purity on GC analysis). IR (neat, $\mathrm{cm}^{-1}$ ) 3417 (N-H), 3047, 1617, 1597, 1510, 1450, 1456, 1395, 1326, 1294, 1244, 1230, 1185, 1091, 1033, 1008, 924, 886, 807, 742, 716, 676, 601, 526; ${ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{CDCl}_{3}, 392 \mathrm{MHz}\right) \delta 5.74(\mathrm{~s}, 1 \mathrm{H}), 6.87$ (tdd, $\left.J=2.0,8.2 \mathrm{~Hz}, J_{\mathrm{H}-\mathrm{F}}=5.5 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.01-7.05(\mathrm{~m}, 3 \mathrm{H}), 7.09(\mathrm{ddd}, J=1.1,8.2 \mathrm{~Hz}$, $\left.J_{\mathrm{H}-\mathrm{F}}=5.5 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.23-7.27(\mathrm{~m}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 98.5 \mathrm{MHz}\right) \delta 115.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=\right.$ $20 \mathrm{~Hz}), 117.6\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=2.0 \mathrm{~Hz}\right), 119.8,121.3\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=7.5 \mathrm{~Hz}\right), 124.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=3.7 \mathrm{~Hz}\right)$,
126.6, 129.5, $131.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=11 \mathrm{~Hz}\right), 140.9,153.3\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=241 \mathrm{~Hz}\right) ;{ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{CDCl}_{3}\right.$, $368 \mathrm{MHz}) \delta-131.9$; Anal. calcd for $\mathrm{C}_{12} \mathrm{H}_{9} \mathrm{ClFN}$ : C, 65.02 ; H, 4.09; N, 6.32. Found: C, 65.12; H, 4.20; N, 6.36. ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR spectra have been attached as Figures S 14 , S15, and S16.

## Synthesis of $N$-(3-chlorophenyl)-2-fluoroaniline (1e)



1-Chloro-3-iodobenzene ( $957 \mathrm{mg}, 4.01 \mathrm{mmol}$ ) was added to a mixture of 2 fluoroaniline ( $535 \mathrm{mg}, 4.81 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium( 0 ) ( 73.6 mg , $80.4 \mu \mathrm{~mol}$ ), 2-dicyclohexylphosphino-2', $6^{\prime}$ 'dimethoxybiphenyl ( $78.3 \mathrm{mg}, 191 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( $578 \mathrm{mg}, 6.01 \mathrm{mmol}$ ) in toluene $(5.0 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $60^{\circ} \mathrm{C}$ for 3 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(8.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate $(4 \times 16 \mathrm{~mL})$ and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford the title compound as a colorless oil ( $687 \mathrm{mg}, 77 \%$ yield, $>99 \%$ purity on GC analysis). IR (neat, $\mathrm{cm}^{-1}$ ) $3418(\mathrm{~N}-\mathrm{H}), 3065,1619,1596,1588$, $1513,1479,1458,1411,1325,1276,1244,1225,1185,1154,1094,1075,1033,993,920$, $850,799,768,742,717,677,638,582,555 ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 392 \mathrm{MHz}\right) \delta 5.79(\mathrm{~s}, 1 \mathrm{H})$, 6.89-6.94 (m, 3H), 7.04-7.12 (m, 3H), $7.19(\mathrm{t}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.31(\mathrm{t}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 98.5 \mathrm{MHz}\right) \delta 115.9\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=20 \mathrm{~Hz}\right), 116.0,117.6,118.7,121.5,122.0$ $\left(\mathrm{d}, J_{\mathrm{C}-\mathrm{F}}=6.6 \mathrm{~Hz}\right), 124.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=3.7 \mathrm{~Hz}\right), 130.5,130.6\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=11 \mathrm{~Hz}\right), 135.3,143.9$, 153.7 (d, $\left.J_{\mathrm{C}-\mathrm{F}}=242 \mathrm{~Hz}\right)$; ${ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{CDCl}_{3}, 368 \mathrm{MHz}\right) \delta-131.0$; Anal. calcd for $\mathrm{C}_{12} \mathrm{H}_{9} \mathrm{ClFN}: \mathrm{C}, 65.02$; H, 4.09; N, 6.32. Found: C, 65.16; H, 4.19; N, 6.42. ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR spectra have been attached as Figures S17, S18, and S19.

## Synthesis of 4-chloro-2-fluoro- N -phenylaniline (1f)



Iodobenzene ( $1.03 \mathrm{~g}, 5.05 \mathrm{mmol}$ ) was added to a mixture of 4-chloro- 2-fluoroaniline ( $882 \mathrm{mg}, 6.06 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium(0) ( $92.3 \mathrm{mg}, 101 \mu \mathrm{~mol}$ ), 2-dicyclohexylphosphino-2', $6^{\prime}$-dimethoxybiphenyl ( $99.4 \mathrm{mg}, 242 \mu \mathrm{~mol}$ ), and sodium tertbutoxide ( $721 \mathrm{mg}, 7.50 \mathrm{mmol}$ ) in toluene $(8.0 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $70^{\circ} \mathrm{C}$ for 15 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(8.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate $(4 \times 16 \mathrm{~mL})$ and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford the title compound as a white solid ( $801 \mathrm{mg}, 72 \%$ yield, $>99 \%$ purity on GC analysis). Mp: 66.7-67.7 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) 3417 (N-H), 3076, 1593, 1583, 1505, $1476,1410,1318,1269,1224,1189,1073,902,891,853,825,806,747,704,694,663$, 646, 577, 568, 496; ${ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{CDCl}_{3}, 392 \mathrm{MHz}\right) \delta 5.74(\mathrm{~s}, 1 \mathrm{H}), 6.98-7.03(\mathrm{~m}, 2 \mathrm{H}), 7.09$ (dd, $J=1.6,7.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.11(\mathrm{dd}, J=2.4,8.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.21(\mathrm{t}, J=9.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.30(\mathrm{~m}$, $2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 98.5 \mathrm{MHz}\right) \delta 116.3\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=23 \mathrm{~Hz}\right), 117.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=2,9 \mathrm{~Hz}\right)$, $119.2,122.5,124.4,124.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=2,9 \mathrm{~Hz}\right), 129.7,130.9\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=11 \mathrm{~Hz}\right), 141.6,152.6$ (d, $J_{\mathrm{C}-\mathrm{F}}=244 \mathrm{~Hz}$ ); ${ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{CDCl}_{3}, 368 \mathrm{MHz}\right) \delta-129.9$; Anal. calcd for $\mathrm{C}_{12} \mathrm{H} 9 \mathrm{ClFN}$ : C, 65.02; H, 4.09; N, 6.32. Found: C, 65.01; H, 4.18; N, $6.32 .{ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19}$ F NMR spectra have been attached as Figures S20, S21, and S22.

## Synthesis of 4-chloro-2-fluoro- N -(p-tolyl)aniline (1g)



1-Iodo-4-methylbenzene ( $1.01 \mathrm{~g}, 4.63 \mathrm{mmol}$ ) was added to a mixture of 4-chloro-2 fluoroaniline ( $872 \mathrm{mg}, 5.99 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium(0) ( 90.8 mg ,
$99.2 \mu \mathrm{~mol}$ ), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl ( $100 \mathrm{mg}, 244 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( $720 \mathrm{mg}, 7.49 \mathrm{mmol}$ ) in toluene $(8.0 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $60^{\circ} \mathrm{C}$ for 33 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous HCl $(8.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate ( $4 \times 16 \mathrm{~mL}$ ) and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford the title compound as a white solid ( $603 \mathrm{mg}, 55 \%$ yield, $>99$ purity on GC analysis). Mp: 57.0-57.5 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) $3426(\mathrm{~N}-\mathrm{H}), 3070$, 3033, 2920, 2852, 1607, 1588, 1509, 1475, 1419, 1399, 1332, 1311, 1266, 1224, 1189, $1115,1074,905,861,828,802,697,667,633,590,574,528,500 ;{ }^{1} \mathrm{H}$ NMR ( $\mathrm{CDCl}_{3}, 392$ $\mathrm{MHz}) \delta 2.32(\mathrm{~s}, 3 \mathrm{H}), 5.66(\mathrm{~s}, 1 \mathrm{H}), 6.95\left(\mathrm{ddd}, J=2.4,8.6 \mathrm{~Hz}, J_{\mathrm{H}-\mathrm{F}}=3.5 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.01(\mathrm{~m}$, $2 \mathrm{H}), 7.08\left(\mathrm{dd}, J=2.4, J_{\mathrm{H}-\mathrm{F}}=11 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.11-7.13(\mathrm{~m}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 98.5\right.$ $\mathrm{MHz}) \delta 20.89,116.1\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=23 \mathrm{~Hz}\right), 116.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=2.8 \mathrm{~Hz}\right), 120.3,123.6\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=\right.$ $9.5 \mathrm{~Hz}), 124.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=3.8 \mathrm{~Hz}\right), 130.2,131.8\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=11 \mathrm{~Hz}\right), 132.6,138.7,152.2(\mathrm{~d}$, $\left.J_{\text {C-F }}=243 \mathrm{~Hz}\right) ;{ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{CDCl}_{3}, 368 \mathrm{MHz}\right) \delta-131.0$; Anal. calcd for $\mathrm{C}_{13} \mathrm{H}_{11} \mathrm{ClFN}: \mathrm{C}$, $66.25 ; \mathrm{H}, 4.70 ; \mathrm{N}, 5.94$. Found: C, $66.43 ; \mathrm{H}, 4.81 ; \mathrm{N}, 5.96 .{ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR spectra have been attached as Figures S23, S24, and S25.

## Synthesis of 4-chloro- N -(4-chlorophenyl)-2-fluoroaniline (1h)


$1 h$
1-Chloro-4-iodobenzene ( $1.20 \mathrm{~g}, 5.03 \mathrm{mmol}$ ) was added to a mixture of 4-chloro-2 fluoroaniline ( $875 \mathrm{mg}, 6.01 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium(0) $(92.2 \mathrm{mg}$, $101 \mu \mathrm{~mol}$ ), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl ( $99.4 \mathrm{mg}, 242 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( $720 \mathrm{mg}, 7.49 \mathrm{mmol}$ ) in toluene $(5.0 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $60^{\circ} \mathrm{C}$ for 4 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous HCl $(8.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate $(4 \times 16 \mathrm{~mL})$ and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by recycling GPC to afford the title compound as a white solid ( $952 \mathrm{mg}, 74 \%$ yield, $>99 \%$ purity on GC
analysis). Mp: 51.5-52.3 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) $3426(\mathrm{~N}-\mathrm{H}), 3068,1594,1506,1491,1472$, $1419,1395,1330,1304,1268,1225,1190,1116,1092,1075,1006,904,859,844,825$, 802, 713, 697, 666, 576, 553, 525, 499; ${ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{CDCl}_{3}, 392 \mathrm{MHz}\right) \delta 5.69(\mathrm{~s}, 1 \mathrm{H}), 6.98-$ $7.02(\mathrm{~m}, 3 \mathrm{H}), 7.11\left(\mathrm{dd}, J=2.4 \mathrm{~Hz}, J_{\mathrm{H}-\mathrm{F}}=11 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.15(\mathrm{t}, J=9.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.23-7.27$ $(\mathrm{m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 98.5 \mathrm{MHz}\right) \delta 116.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=23 \mathrm{~Hz}\right), 117.9\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=2.9 \mathrm{~Hz}\right)$, $120.2,127.2,124.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=3.7 \mathrm{~Hz}\right), 125.2\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=9.4 \mathrm{~Hz}\right), 129.6,130.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=11\right.$ $\mathrm{Hz}), 140.3,152.8\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=244 \mathrm{~Hz}\right) ;{ }^{19} \mathrm{~F} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 368 \mathrm{MHz}\right) \delta-129.2$; Anal. calcd for $\mathrm{C}_{12} \mathrm{H}_{8} \mathrm{Cl}_{2} \mathrm{FN}$ : C, $56.28 ; \mathrm{H}, 3.15$; N, 5.47. Found: C, $56.47 ; \mathrm{H}, 3.24 ; \mathrm{N}, 5.48 .{ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19}$ F NMR spectra have been attached as Figures S26, S27, and S28.

## Synthesis of $\boldsymbol{N}$-(4-bromophenyl)-2-fluoroaniline (1i)


$1 i$
1-Bromo-4-iodobenzene $(1.13 \mathrm{~g}, 3.99 \mathrm{mmol})$ was added to a mixture of 2 fluoroaniline ( $534 \mathrm{mg}, 4.80 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium(0) (73.4 mg, $80.2 \mu \mathrm{~mol}$ ), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl ( $79.3 \mathrm{mg}, 193 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( $576 \mathrm{mg}, 5.99 \mathrm{mmol}$ ) in toluene $(5.0 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $50^{\circ} \mathrm{C}$ for 30 minutes before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(7.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate $(4 \times 14 \mathrm{~mL})$ and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford the title compound as a white solid ( 244 mg , $23 \%$ yield, $>99 \%$ purity on GC analysis). Mp: 47.5-48.7 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) $3423(\mathrm{~N}-\mathrm{H})$, $1617,1585,1507,1488,1473,1454,1328,1245,1225,1186,1177,1119,1096,1072$, 1029, 1003, 925, 887, 823, 803, 745, 713, 695, 556, 520, 493; ${ }^{1} \mathrm{H}$ NMR (CDCl3, 392 $\mathrm{MHz}) \delta 5.75(\mathrm{~s}, 1 \mathrm{H}), 6.87\left(\mathrm{tdd}, J=2.0,8.2 \mathrm{~Hz}, J_{\mathrm{H}-\mathrm{F}}=5.1 \mathrm{~Hz}, 1 \mathrm{H}\right), 6.95-6.99(\mathrm{~m}, 2 \mathrm{H})$, $7.03(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.09\left(\mathrm{ddd}, J=1.6,8.2 \mathrm{~Hz}, J_{\mathrm{H}-\mathrm{F}}=10 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.26(\mathrm{td}, 2.0,7.8$ $\mathrm{Hz}, 1 \mathrm{H}), 7.36-7.40(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 98.5 \mathrm{MHz}\right) \delta 113.8,115.8\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=20\right.$ $\mathrm{Hz}), 117.9\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=1.6 \mathrm{~Hz}\right), 120.0,121.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=6.6 \mathrm{~Hz}\right), 124.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=3.7 \mathrm{~Hz}\right)$, $131.2\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=15 \mathrm{~Hz}\right), 132.4,141.4,153.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=241 \mathrm{~Hz}\right) ;{ }^{19} \mathrm{~F} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 368\right.$ $\mathrm{MHz}) \delta-131.6$; Anal. calcd for $\mathrm{C}_{12} \mathrm{H}_{9} \mathrm{BrFN}$ : C, $54.16 ; \mathrm{H}, 3.41$; N, 5.26. Found: C, 54.40;
$\mathrm{H}, 3.44 ; \mathrm{N}, 5.30 .{ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR spectra have been attached as Figures S29, S30, and S31.

## Synthesis of $\boldsymbol{N}$-(4-bromophenyl)-4-chloro-2-fluoroaniline (1j)



1-Bromo-4-iodobenzene ( $1.41 \mathrm{~g}, 5.03 \mathrm{mmol}$ ) was added to a mixture of 4-chloro-2 fluoroaniline ( $871 \mathrm{mg}, 5.98 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium(0) ( 91.3 mg , $99.7 \mu \mathrm{~mol}$ ), 2-dicyclohexylphosphino-2', $6^{\prime}$ 'dimethoxybiphenyl ( $98.2 \mathrm{mg}, 239 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( $720 \mathrm{mg}, 7.49 \mathrm{mmol}$ ) in toluene $(5.0 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $50^{\circ} \mathrm{C}$ for 30 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(8.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate ( $4 \times 16 \mathrm{~mL}$ ) and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford the title compound as a white solid ( $468 \mathrm{mg}, 31 \%$ yield, $>99 \%$ purity on GC analysis). Mp: 66.9-67.4 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) 3426 (N-H), 3069, 1584, 1501, 1488, 1472, 1418, 1391, 1328, 1305, 1267, 1224, 1190, 1177, 1119, 1073, $1004,903,859,842,824,801,708,695,656,575,540,519,496 ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 392\right.$ MHz) $\delta 5.69(\mathrm{~s}, 1 \mathrm{H}), 6.93-6.97(\mathrm{~m}, 2 \mathrm{H}), 7.01\left(\mathrm{ddd}, J=2.4,9.0 \mathrm{~Hz}, J_{\mathrm{H}-\mathrm{F}}=2.0 \mathrm{~Hz}, 1 \mathrm{H}\right)$, $7.12\left(\mathrm{dd}, J=2.0 \mathrm{~Hz}, J_{\mathrm{H}-\mathrm{F}}=11 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.17(\mathrm{t}, J=9.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.37-7.41(\mathrm{~m}, 2 \mathrm{H}),{ }^{13} \mathrm{C}$ NMR ( $\left.\mathrm{CDCl}_{3}, 98.5 \mathrm{MHz}\right) \delta 114.4,116.6\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=23 \mathrm{~Hz}\right), 118.2\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=3.8 \mathrm{~Hz}\right), 120.3$, $124.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=2.8 \mathrm{~Hz}\right), 125.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=9.5 \mathrm{~Hz}\right), 130.2\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=11 \mathrm{~Hz}\right), 132.6,140.9$, 152.9 (d, $\left.J_{\mathrm{C}-\mathrm{F}}=245 \mathrm{~Hz}\right)$; ${ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{CDCl}_{3}, 368 \mathrm{MHz}\right) \delta-129.0$; Anal. calcd for $\mathrm{C}_{12} \mathrm{H}_{8} \mathrm{BrClFN}: \mathrm{C}, 47.96$; H, 2.68; N, 4.66. Found: C, 48.02; H, 2.76; N, 4.66. ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR spectra have been attached as Figures S32, S33, and S34.

## Synthesis of $\boldsymbol{N}$-(3-bromophenyl)-2-fluoroaniline (1k)



1-Bromo-3-iodobenzene ( $1.13 \mathrm{~g}, 3.99 \mathrm{mmol}$ ) was added to a mixture of 2 fluoroaniline ( $536 \mathrm{mg}, 4.82 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium(0) ( 73.2 mg , $80.0 \mu \mathrm{~mol}$ ), 2-dicyclohexylphosphino-2', $6^{\prime}$-dimethoxybiphenyl ( $78.5 \mathrm{mg}, 191 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( $576 \mathrm{mg}, 5.99 \mathrm{mmol}$ ) in toluene ( 5.0 mL ) at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $50^{\circ} \mathrm{C}$ for 3 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(7.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate $(4 \times 14 \mathrm{~mL})$ and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford the title compound as a colorless oil ( $500 \mathrm{mg}, 47 \%$ yield, $98 \%$ purity on GC analysis). IR (neat, $\mathrm{cm}^{-1}$ ) $3406(\mathrm{~N}-\mathrm{H}), 3063,1618,1586,1512$, 1504, 1477, 1468, 1408, 1325, 1244, 1276, 1244, 1225, 1185, 1155, 1099, 1068, 1032, $990,908,848,799,766,743,711,678,666,635,581,551,520 ;{ }^{1} \mathrm{H}$ NMR ( $\mathrm{CDCl}_{3}, 392$ $\mathrm{MHz}) \delta 5.78(\mathrm{~s}, 1 \mathrm{H}), 6.88-6.93(\mathrm{~m}, 1 \mathrm{H}), 6.97(\mathrm{t}, J=1.6,7.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.03-7.14(\mathrm{~m}, 4 \mathrm{H})$, $7.30(\mathrm{t}, J=1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.30(\mathrm{td}, J=1.6,7.8 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 98.5 \mathrm{MHz}\right) \delta$ $115.9\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=19 \mathrm{~Hz}\right), 116.5,118.7,120.5,122.0\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=7.5 \mathrm{~Hz}\right), 123.3,124.4,124.5$ $\left(\mathrm{d}, J_{\mathrm{C}-\mathrm{F}}=3.7 \mathrm{~Hz}\right), 130.6\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=11 \mathrm{~Hz}\right), 130.8,144.0,153.6\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=242 \mathrm{~Hz}\right) ;{ }^{19} \mathrm{~F}$ NMR ( $\mathrm{CDCl}_{3}, 368 \mathrm{MHz}$ ) $\delta-130.9$; Anal. calcd for $\mathrm{C}_{12} \mathrm{H} 9 \mathrm{BrFN}$ : C, $54.16 ; \mathrm{H}, 3.41$; N, 5.26. Found: C, $54.25 ; \mathrm{H}, 3.50 ; \mathrm{N}, 5.31 .{ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR spectra have been attached as Figures S35, S36, and S37.

## Synthesis of 4-bromo-2-fluoro- $N$-phenylaniline (11)



4-Bromo-2-fluoro-1-iodobenzene ( $1.20 \mathrm{~g}, 3.99 \mathrm{mmol}$ ) was added to a mixture of aniline ( $452 \mathrm{mg}, 4.85 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium(0) ( $75.0 \mathrm{mg}, 81.9$
$\mu \mathrm{mol}$ ), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl ( $78.0 \mathrm{mg}, 190 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( $569 \mathrm{mg}, 5.92 \mathrm{mmol}$ ) in toluene ( 5.0 mL ) at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $50^{\circ} \mathrm{C}$ for 23 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous HCl $(7.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate ( $4 \times 14 \mathrm{~mL}$ ) and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford the title as compound a white solid ( $321 \mathrm{mg}, 30 \%$ yield, $>99 \%$ purity on GC analysis). Mp: 68.0-68.5 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) 3418 (N-H), 3069, 1594, 1579, 1501, 1492, 1476, 1398, 1316, 1268, 1227, 1188, 1176, 1119, 1067, 1027, 889, 862, 846, 824, 806, 746, 703, 694, 611, 570, 530, 494; ${ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{CDCl}_{3}, 392 \mathrm{MHz}\right)$ $\delta 5.75(\mathrm{~s}, 1 \mathrm{H}), 7.00-7.04(\mathrm{~m}, 1 \mathrm{H}), 7.16(\mathrm{t}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.07-7.14(\mathrm{~m}, 3 \mathrm{H}), 7.23(\mathrm{dd}$, $\left.J=1.6 \mathrm{~Hz}, J_{\mathrm{H}-\mathrm{F}}=11 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.28-7.33(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 98.5 \mathrm{MHz}\right) \delta 110.9$ $\left(\mathrm{d}, J_{\mathrm{C}-\mathrm{F}}=8.5 \mathrm{~Hz}\right), 117.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=2.8 \mathrm{~Hz}\right), 119.0\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=22 \mathrm{~Hz}\right), 119.4,122.6,127.4(\mathrm{~d}$, $\left.J_{\mathrm{C}-\mathrm{F}}=3.8 \mathrm{~Hz}\right), 129.7,131.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=11 \mathrm{~Hz}\right), 141.4,152.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=245 \mathrm{~Hz}\right) ;{ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{CDCl}_{3}, 368 \mathrm{MHz}\right) \delta-130.0$; Anal. calcd for $\mathrm{C}_{12} \mathrm{H} 9 \mathrm{BrFN}$ : C, 54.16 ; H, 3.41; N, 5.26. Found: C, 54.32; H, 3.52; N, 5.20. ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR spectra have been attached as Figures S38, S39, and S40.

## Synthesis of 4-bromo-2-fluoro- N -(p-tolyl)aniline (1m)



1 m
4-Bromo-2-fluoro-1-iodobenzene ( $1.19 \mathrm{~g}, 3.95 \mathrm{mmol}$ ) was added to a mixture of $p$ toluidine ( $513 \mathrm{mg}, 4.79 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium(0) ( $73.1 \mathrm{mg}, 79.8$ $\mu \mathrm{mol}$ ), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl ( $78.9 \mathrm{mg}, 192 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( $572 \mathrm{mg}, 5.95 \mathrm{mmol}$ ) in toluene ( 5.0 mL ) at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $50^{\circ} \mathrm{C}$ for 3 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous HCl $(7.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate $(4 \times 14 \mathrm{~mL})$ and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford the title compound as a white solid ( $335 \mathrm{mg}, 30 \%$
yield, $>99 \%$ purity on GC analysis). Mp: 66.6-67.2 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) $3425(\mathrm{~N}-\mathrm{H}), 2917$, $1605,1514,1505,1416,1396,1331,1310,1271,1263,1223,1189,1114,1067,892,861$, $839,828,801,703,696,656,628,580,567,527,499 ;{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{CDCl}_{3}, 392 \mathrm{MHz}\right) \delta$ 2.32 (s, 3H), 5.67 (s, 1H), 6.99-7.04 (m, 2H), 7.06-7.13 (m, 4H), 7.19-7.22 (m, 1H); ${ }^{13} \mathrm{C}$ NMR ( $\left.\mathrm{CDCl}_{3}, 98.5 \mathrm{MHz}\right) \delta 20.90,110.0\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=8.5 \mathrm{~Hz}\right), 116.8\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=2.8 \mathrm{~Hz}\right), 118.8$ $\left(\mathrm{d}, J_{\mathrm{C}-\mathrm{F}}=22 \mathrm{~Hz}\right), 120.4,127.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=2.9 \mathrm{~Hz}\right), 130.2,132.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=11 \mathrm{~Hz}\right), 132.7$, 138.5, $152.3\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=245 \mathrm{~Hz}\right) ;{ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{CDCl}_{3}, 368 \mathrm{MHz}\right) \delta-131.0$; Anal. calcd for $\mathrm{C}_{13} \mathrm{H}_{11} \mathrm{BrFN}: \mathrm{C}, 55.74 ; \mathrm{H}, 3.96$; N, 5.00. Found: C, 55.82 ; H, 4.02; N, 5.06. ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19}$ F NMR spectra have been attached as Figures S41, S42, and S43.

## Synthesis of 4-bromo- N -(4-chlorophenyl)-2-fluoroaniline (1n)



4-Bromo-2-fluoro-1-iodobenzene ( $1.19 \mathrm{~g}, 3.95 \mathrm{mmol}$ ) was added to a mixture of 4chloroaniline ( $614 \mathrm{mg}, 4.81 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium(0) $(73.0 \mathrm{mg}$, $79.7 \mu \mathrm{~mol}$ ), 2-dicyclohexylphosphino-2', $6^{\prime}$ 'dimethoxybiphenyl ( $79.6 \mathrm{mg}, 194 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( $564 \mathrm{mg}, 5.87 \mathrm{mmol}$ ) in toluene $(5.0 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $50^{\circ} \mathrm{C}$ for 30 minutes before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(7.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate ( $4 \times 14 \mathrm{~mL}$ ) and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford the title compound as a white solid ( 392 mg , $33 \%$ yield, $>99 \%$ purity on GC analysis). Mp: 55.5-56.0 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) $3425(\mathrm{~N}-\mathrm{H})$, 3059, 1591, 1506, 1490, 1471, 1414, 1393, 1329, 1303, 1266, 1224, 1190, 1115, 1095, 892, 859, 842, 826, 802, 713, 696, 676, 650, 569, 544, 524, 498, 446; ${ }^{1} \mathrm{H}$ NMR ( $\mathrm{CDCl}_{3}$, $392 \mathrm{MHz}) \delta 5.71(\mathrm{~s}, 1 \mathrm{H}), 6.99-7.03(\mathrm{~m}, 2 \mathrm{H}), 7.08-7.16(\mathrm{~m}, 2 \mathrm{H}), 7.23-7.28(\mathrm{~m}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 98.5 \mathrm{MHz}\right) \delta 111.6\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=9.4 \mathrm{~Hz}\right), 118.1\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=1.9 \mathrm{~Hz}\right), 119.2(\mathrm{~d}$, $\left.J_{\mathrm{C}-\mathrm{F}}=23 \mathrm{~Hz}\right), 120.4,127.4,127.6\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=3.7 \mathrm{~Hz}\right), 129.6,131.0\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=11 \mathrm{~Hz}\right), 140.1$, $152.8\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=246 \mathrm{~Hz}\right) ;{ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{CDCl}_{3}, 368 \mathrm{MHz}\right) \delta-129.3$; Anal. calcd for
$\mathrm{C}_{12} \mathrm{H} 8 \mathrm{BrClFN}: \mathrm{C}, 47.96$; H, 2.68; N, 4.66. Found: C, 48.02; H, 2.75; N, 4.64. ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19}$ F NMR spectra have been attached as Figures S44, S45, and S46.

## Synthesis of 4-bromo- N -(4-bromophenyl)-2-fluoroaniline (10)



4-Bromo-2-fluoro-1-iodobenzene ( $899 \mathrm{~g}, 2.99 \mathrm{mmol}$ ) was added to a mixture of 4bromoaniline ( $622 \mathrm{mg}, 3.62 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium(0) $(55.8 \mathrm{mg}$, $60.9 \mu \mathrm{~mol}$ ), 2-dicyclohexylphosphino-2', $6^{\prime}$-dimethoxybiphenyl ( $59.3 \mathrm{mg}, 144 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( $436 \mathrm{mg}, 4.54 \mathrm{mmol}$ ) in toluene $(5.0 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $50^{\circ} \mathrm{C}$ for 30 minutes before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(5.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate $(4 \times 10 \mathrm{~mL})$ and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford the title compound as a white solid ( 209 mg , $20 \%$ yield, $>99 \%$ purity on GC analysis). Mp: 71.7-72.5 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) $3425(\mathrm{~N}-\mathrm{H})$, $3062,1613,1592,1582,1511,1488,1471,1413,1389,1325,1304,1268,1223,1189$, $1176,1118,1072,1004,891,859,840,825,801,707,694,644,621,568,533,514,496$; ${ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{CDCl}_{3}, 392 \mathrm{MHz}\right) \delta 5.71$ (s, 1H), 6.94-6.98 (m, 2H), 7.09-7.16 (m, 2H), 7.25 $\left(\mathrm{dd}, J=2.4 \mathrm{~Hz}, J_{\mathrm{H}-\mathrm{F}}=10 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.39-7.42(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 98.5 \mathrm{MHz}\right) \delta$ $111.8\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=9.4 \mathrm{~Hz}\right), 114.6,118.3\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=2.9 \mathrm{~Hz}\right), 119.3\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=22 \mathrm{~Hz}\right), 120.5$, $127.6\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=2.7 \mathrm{~Hz}\right), 130.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=11 \mathrm{~Hz}\right), 132.6,140.7,152.9\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=246 \mathrm{~Hz}\right)$; ${ }^{19}$ F NMR ( $\left.\mathrm{CDCl}_{3}, 368 \mathrm{MHz}\right) \delta-129.1$; Anal. calcd for $\mathrm{C}_{12} \mathrm{H}_{8} \mathrm{Br}_{2} \mathrm{FN}$ : C, 41.78; H, 2.34; N, 4.06. Found: C, 41.85; H, 2.41; N, 4.07. ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR spectra have been attached as Figures S47, S48, and S49.

## Synthesis of 2-fluoro- $N$-(4-fluorophenyl)aniline (1p)



1-Fluoro-4-iodobenzene ( $879 \mathrm{mg}, 3.96 \mathrm{mmol}$ ) was added to a mixture of 2fluoroaniline ( $532 \mathrm{mg}, 4.78 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium(0) ( 73.8 mg , $80.6 \mu \mathrm{~mol}$ ), 2-dicyclohexylphosphino-2', $6^{\prime}$-dimethoxybiphenyl ( $79.2 \mathrm{mg}, 193 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( $577 \mathrm{mg}, 6.00 \mathrm{mmol}$ ) in toluene ( 5.0 mL ) at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $60^{\circ} \mathrm{C}$ for 45 minutes before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(7.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate $(4 \times 14 \mathrm{~mL})$ and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford the title compound as a colorless oil ( 420 mg , $52 \%$ yield, $>99 \%$ purity on GC analysis). IR (neat, $\mathrm{cm}^{-1}$ ) $3431(\mathrm{~N}-\mathrm{H}), 3046,1618,1504$, 1457, 1399, 1327, 1296, 1245, 1229, 1210, 1184, 1154, 1096, 1034, 1011, 922, 880, 822, $777,741,709,699,642,609,548,527,497 ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 392 \mathrm{MHz}\right) \delta 5.69(\mathrm{~s}, 1 \mathrm{H})$, 6.81 (tdd, $\left.J=2.0,8.2 \mathrm{~Hz}, J_{\mathrm{H}-\mathrm{F}}=5.1 \mathrm{~Hz}, 1 \mathrm{H}\right), 6.97-7.04(\mathrm{~m}, 3 \mathrm{H}), 7.04-7.10(\mathrm{~m}, 3 \mathrm{H}), 7.13$ $(\mathrm{td}, J=1.6,8.2 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 98.5 \mathrm{MHz}\right) \delta 115.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=19 \mathrm{~Hz}\right), 116.2$ $\left(\mathrm{d}, J_{\mathrm{C}-\mathrm{F}}=23 \mathrm{~Hz}\right), 116.2\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=1.9 \mathrm{~Hz}\right), 120.2\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=7.6 \mathrm{~Hz}\right), 121.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=7.5\right.$ $\mathrm{Hz}), 124.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=3.7 \mathrm{~Hz}\right), 132.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=15 \mathrm{~Hz}\right), 137.9\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=2.9 \mathrm{~Hz}\right), 152.7(\mathrm{~d}$, $\left.J_{\text {C-F }}=240 \mathrm{~Hz}\right), 158.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=242 \mathrm{~Hz}\right) ;{ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{CDCl}_{3}, 368 \mathrm{MHz}\right) \delta-133.4,-120.8$; Anal. calcd for $\mathrm{C}_{12} \mathrm{H}_{9} \mathrm{~F}_{2} \mathrm{~N}$ : C, 70.24; H, 4.42; N, 6.83. Found: C, 70.39; H, 4.60; N, 6.98. ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR spectra have been attached as Figures S 50 , S51, and S52.

## Synthesis of 4-chloro-2-fluoro- N -(4-fluorophenyl)aniline (1q)



1-Fluoro-4-iodobenzene $(1.11 \mathrm{~g}, 5.00 \mathrm{mmol})$ was added to a mixture of 4-chloro -2fluoroaniline ( $878 \mathrm{mg}, 6.03 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium(0) $(91.8 \mathrm{mg}$,
$100 \mu \mathrm{~mol}$ ), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl ( $98.6 \mathrm{mg}, 240 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( $720 \mathrm{mg}, 7.49 \mathrm{mmol}$ ) in toluene $(5.0 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $60^{\circ} \mathrm{C}$ for 33 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous HCl $(8.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate ( $4 \times 16 \mathrm{~mL}$ ) and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford the title compound as a purple oil ( $894 \mathrm{mg}, 75 \%$ yield, $>99$ purity on GC analysis). IR (neat, $\left.\mathrm{cm}^{-1}\right) 3425(\mathrm{~N}-\mathrm{H}), 3075,1611,1587,1506,1422$, 1397, 1328, 1265, 1210, 1187, 1154, 1118, 1097, 1075, 1012, 904, 844, 803, 780, 700, $669,629,592,574,532,496 ;{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{CDCl}_{3}, 392 \mathrm{MHz}\right) \delta 5.63(\mathrm{~s}, 1 \mathrm{H}), 6.92-7.11(\mathrm{~m}$, $7 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 98.5 \mathrm{MHz}\right) \delta 116.2\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=23 \mathrm{~Hz}\right), 116.3\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=23 \mathrm{~Hz}\right)$, $116.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=5.9 \mathrm{~Hz}\right), 122.1\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=7.5 \mathrm{~Hz}\right), 124.1\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=9.4 \mathrm{~Hz}\right), 124.6\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}\right.$ $=3.7 \mathrm{~Hz}), 131.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=11 \mathrm{~Hz}\right), 137.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=1.9 \mathrm{~Hz}\right), 152.2\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=243 \mathrm{~Hz}\right), 158.9$ $\left(\mathrm{d}, J_{\mathrm{C}-\mathrm{F}}=242 \mathrm{~Hz}\right) ;{ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{CDCl}_{3}, 368 \mathrm{MHz}\right) \delta-130.8,-119.9$; Anal. calcd for $\mathrm{C}_{12} \mathrm{H}_{8} \mathrm{ClF}_{2} \mathrm{~N}: \mathrm{C}, 60.14 ; \mathrm{H}, 3.36$; N, 5.84. Found: C, 60.35 ; H, 3.50; N, 5.85. ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19}$ F NMR spectra have been attached as Figures S53, S54, and S55.

## Synthesis of 4-bromo-2-fluoro- N -(4-fluorophenyl)aniline (1r)



4-Bromo-2-fluoro-1-iodobenzene ( $1.19 \mathrm{~g}, 3.95 \mathrm{mmol}$ ) was added to a mixture of 4fluoroaniline ( $538 \mathrm{mg}, 4.84 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium(0) ( 73.4 mg , $80.2 \mu \mathrm{~mol}$ ), 2-dicyclohexylphosphino-2', $6^{\prime}$-dimethoxybiphenyl ( $77.4 \mathrm{mg}, 189 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( $566 \mathrm{mg}, 5.89 \mathrm{mmol}$ ) in toluene ( 5.0 mL ) at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $55^{\circ} \mathrm{C}$ for 30 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(7.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate ( $4 \times 12 \mathrm{~mL}$ ) and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford the title compound as a yellow oil ( $386 \mathrm{mg}, 34 \%$ yield, $>99 \%$ purity on GC analysis). IR (neat, $\mathrm{cm}^{-1}$ ) $3417(\mathrm{~N}-\mathrm{H}), 3077,1610,1583,1506,1418$,

1396, 1327, 1299, 1263, 1209, 1186, 1154, 1116, 1097, 1067, 1011, 892, 839, 800, 780, 700, 655, 624, 582, 568, 529; ${ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{CDCl}_{3}, 392 \mathrm{MHz}\right) \delta 5.65$ (s, 1H), 6.95-7.11(m, $6 \mathrm{H}), 7.22\left(\mathrm{dd}, J=2.0 \mathrm{~Hz}, J_{\mathrm{H}-\mathrm{F}}=11 \mathrm{~Hz}, 1 \mathrm{H}\right) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 98.5 \mathrm{MHz}\right) \delta 110.5(\mathrm{~d}$, $\left.J_{\mathrm{C}-\mathrm{F}}=9.4 \mathrm{~Hz}\right), 116.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=23 \mathrm{~Hz}\right), 116.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=2.8 \mathrm{~Hz}\right), 119.0\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=22 \mathrm{~Hz}\right)$, $122.3\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=8.4 \mathrm{~Hz}\right), 127.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=3.7 \mathrm{~Hz}\right), 132.3\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=11 \mathrm{~Hz}\right), 137.2\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=\right.$ $2.8 \mathrm{~Hz}), 152.2\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=245 \mathrm{~Hz}\right), 159.0\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=242 \mathrm{~Hz}\right) ;{ }^{19} \mathrm{~F} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 368 \mathrm{MHz}\right)$ $\delta-130.8,-119.7$; Anal. calcd for $\mathrm{C}_{12} \mathrm{H}_{8} \mathrm{BrF}_{2} \mathrm{~N}$ : C, $50.73 ; \mathrm{H}, 2.84 ; \mathrm{N}, 4.93$. Found: C, $50.73 ; \mathrm{H}, 2.91 ; \mathrm{N}, 4.91 .{ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR spectra have been attached as Figures S 56 , S57, and S58.

## Synthesis of 2-fluoro- $N$-(3-fluorophenyl)aniline (1s)


$1 s$
1-Bromo-3-fluorobenzene ( $702 \mathrm{mg}, 4.01 \mathrm{mmol}$ ) was added to a mixture of 2fluoroaniline ( $534 \mathrm{mg}, 4.80 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium(0) ( 72.6 mg , $79.3 \mu \mathrm{~mol}$ ), 2-dicyclohexylphosphino-2', $6^{\prime}$ 'dimethoxybiphenyl ( $77.4 \mathrm{mg}, 189 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( $578 \mathrm{mg}, 6.01 \mathrm{mmol}$ ) in toluene $(5.0 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $60^{\circ} \mathrm{C}$ for 9 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(7.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate $(4 \times 14 \mathrm{~mL})$ and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford the title compound as a colorless oil ( $709 \mathrm{mg}, 86 \%$ yield, $>99 \%$ purity on GC analysis). IR (neat, $\mathrm{cm}^{-1}$ ) $3429(\mathrm{~N}-\mathrm{H}), 3066,1609,1589,1518$, 1490, 1460, 1424, 1331, 1284, 1256, 1244, 1187, 1167, 1140, 1099, 1074, 1034, 1001, $965,929,840,798,768,742,709,742,709,680,643,582,566,519 ;{ }^{1} \mathrm{H}$ NMR ( $\mathrm{CDCl}_{3}$, $392 \mathrm{MHz}) \delta 5.82(\mathrm{~s}, 1 \mathrm{H}), 6.63\left(\mathrm{tdd}, J=1.2,8.2 \mathrm{~Hz}, J_{\mathrm{H}-\mathrm{F}}=2.4 \mathrm{~Hz}, 1 \mathrm{H}\right), 6.79(\mathrm{td}, J=2.4$ $\left.\mathrm{Hz}, J_{\mathrm{H}-\mathrm{F}}=11 \mathrm{~Hz}, 1 \mathrm{H}\right), 6.80\left(\mathrm{~d}, J_{\mathrm{H}-\mathrm{F}}=9.4 \mathrm{~Hz}, 1 \mathrm{H}\right), 6.87-6.92(\mathrm{~m}, 1 \mathrm{H}), 7.05(\mathrm{t}, J=8.2 \mathrm{~Hz}$, $1 \mathrm{H}), 7.09$ (ddd, $\left.J=1.6,7.8 \mathrm{~Hz}, J_{\mathrm{H}-\mathrm{F}}=11 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.17-7.23(\mathrm{~m}, 1 \mathrm{H}), 7.33(\mathrm{td}, J=1.2$, $8.2 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 98.5 \mathrm{MHz}\right) \delta 104.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=25 \mathrm{~Hz}\right), 108.1\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=21\right.$ $\mathrm{Hz}), 113.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=2.9 \mathrm{~Hz}\right), 115.8\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=19 \mathrm{~Hz}\right), 118.8\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=1.4 \mathrm{~Hz}\right), 122.0(\mathrm{~d}$, $\left.J_{\text {C-F }}=7.5 \mathrm{~Hz}\right), 124.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=3.7 \mathrm{~Hz}\right), 130.6\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=13 \mathrm{~Hz}\right), 130.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=15 \mathrm{~Hz}\right)$,
$144.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=10 \mathrm{~Hz}\right), 153.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=242 \mathrm{~Hz}\right), 163.9\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=244 \mathrm{~Hz}\right) ;{ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{CDCl}_{3}, 368 \mathrm{MHz}\right) \delta-130.9$, -111.9; Anal. calcd for $\mathrm{C}_{12} \mathrm{H}_{9} \mathrm{~F}_{2} \mathrm{~N}: \mathrm{C}, 70.24 ; \mathrm{H}, 4.42 ; \mathrm{N}$, 6.83. Found: C, $70.51 ; \mathrm{H}, 4.55 ; \mathrm{N}, 6.89 .{ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR spectra have been attached as Figures S59, S60, and S61.

## Synthesis of 2,4-difluoro- $N$-phenylaniline (1t)



1t
1-Bromo-2,4-difluorobenzene ( $973 \mathrm{mg}, 5.04 \mathrm{mmol}$ ) was added to a solution of aniline ( $543 \mathrm{mg}, 5.83 \mathrm{mmol}$ ), tris(dibenzylideneacetone)dipalladium(0) $(91.2 \mathrm{mg}, 100$ $\mu \mathrm{mol}$ ), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl ( $98.5 \mathrm{mg}, 240 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( $720 \mathrm{mg}, 7.49 \mathrm{mmol}$ ) in toluene $(5.0 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ under argon. The reaction was stirred at $70^{\circ} \mathrm{C}$ for 22 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous HCl $(8.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with ethyl acetate ( $4 \times 16 \mathrm{~mL}$ ) and the combined organic extracts were concentrated under reduced pressure. The crude product was purified by column chromatography (hexane) to afford the title compound as a white solid ( $306 \mathrm{mg}, 30 \%$ yield, $>99 \%$ purity on GC analysis). Anal. calcd for $\mathrm{C}_{12} \mathrm{H}_{9} \mathrm{~F}_{2} \mathrm{~N}$ : C, $70.24 ; \mathrm{H}, 4.42 ; \mathrm{N}, 6.83$. Found: C, 70.36 ; H, 4.58; N, 6.69. Spectroscopic data for the title compound has been previously reported. ${ }^{5}{ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR spectra have been attached as Figures S62, 63, and S64.

[^4]Preparation of $N^{1}$-(2-fluorophenyl)- $N^{1}, N^{2}$-diphenylbenzene-1,2-diamine (3a, $\mathbf{X}=\mathbf{F}$ ) by Pd-catalyzed Buchwald-Hartwig reaction

$3 \mathbf{a}(\mathrm{X}=\mathrm{F})$
1-Bromo-2-fluorobenzene ( $178 \mathrm{mg}, 1.02 \mathrm{mmol}$ ) was added to a solution of $N^{1}, N^{2}-$ diphenylbenzene-1,2-diamine ( $264 \mathrm{mg}, 1.01 \mathrm{mmol}$ ), palladium(II) acetate ( $5.06 \mathrm{mg}, 22.5$ $\mu \mathrm{mol}$ ), tri-tert-butylphosphine ( $20.8 \mathrm{mg}, 103 \mu \mathrm{~mol}$ ), and sodium tert-butoxide ( 155 mg , $1.61 \mathrm{mmol})$ in toluene $(5.0 \mathrm{~mL})$ at $25^{\circ} \mathrm{C}$ under argon. The coupling reaction was carried out at $110^{\circ} \mathrm{C}$ for 18 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(2.0 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The aqueous layer was extracted with ethyl acetate $(4.0 \mathrm{~mL})$ four times. The combined organic extracts were concentrated in vacuo. The crude product was purified by column chromatography (hexane) to afford the title compound as a white solid ( $83.5 \mathrm{mg}, 23 \%$ yield, $97 \%$ purity on GC analysis). Mp: 86.3$87.2^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) $3402(\mathrm{~N}-\mathrm{H}), 3039,1587,1508,1492,1457,1416,1305,1272$, $1258,1219,1171,1155,1101,1076,1029,806,740,703,691,614,562 ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}\right.$, $392 \mathrm{MHz}) \delta 6.09(\mathrm{~s}, 1 \mathrm{H}), 6.77(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H}), 6.88(\mathrm{td}, 1.6,7.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.89(\mathrm{td}$, $7.1,7.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.96(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.04-7.13(\mathrm{~m}, 3 \mathrm{H}), 7.13-7.27(\mathrm{~m}, 7 \mathrm{H}), 7.35$ (dd, $J=1.6,8.6 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 98.5 \mathrm{MHz}\right) \delta 116.5,117.0\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=20 \mathrm{~Hz}\right)$, $117.7,119.3,120.8,120.9,121.7,125.1\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=3.7 \mathrm{~Hz}\right), 126.3\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=8.5 \mathrm{~Hz}\right), 127.2$, 128.2, 129.2, 129.3, 129.8, 133.9 (d, $J_{\mathrm{C}-\mathrm{F}}=11 \mathrm{~Hz}$ ), 134.0, 140.9, 142.5, 147.2, 158.1 (d, $\left.J_{\mathrm{C}-\mathrm{F}}=249 \mathrm{~Hz}\right) ;{ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{CDCl}_{3}, 368 \mathrm{MHz}\right) \delta-119.6$; Anal. calcd for $\mathrm{C}_{24} \mathrm{H}_{19} \mathrm{FN}$ : C, 81.33; H, 5.40; N, 7.90. Found: C, 81.55; H, 5.49; N, 7.87. ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19}$ F NMR spectra have been attached as Figures S65, S66, and S67.

## Iron-Catalyzed C-F Amination of Diarylamines: A One-Pot Regioselective

## Synthesis of Diaryl Dihydrophenazines

## A representative procedure for the reactions in Table S1: procedure A

A solution of ethylmagnesium bromide in $\mathrm{Et}_{2} \mathrm{O}(100 \mu \mathrm{~L}, 2.97 \mathrm{M}, 0.297 \mathrm{mmol})$ was added to a mixture of 2-fluoro- N -phenylaniline ( $53.6 \mathrm{mg}, 0.286 \mathrm{mmol}$ ) in $\mathrm{Et} 2 \mathrm{O}(1.0 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$. After stirring the mixture at $25^{\circ} \mathrm{C}$ for 10 minutes, the solvent was removed in vacuo. $\mathrm{FeCl}_{2}(1.90 \mathrm{mg}, 15.0 \mu \mathrm{~mol}$ ), 1,2-dibromoethane ( $112 \mathrm{mg}, 0.598 \mathrm{mmol}$ ), and toluene $(1.5 \mathrm{~mL})$ were added to the residual magnesium amide. The reaction mixture was stirred at $100^{\circ} \mathrm{C}$ for 12 h before being cooled to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. After the organics were extracted from the aqueous layer with toluene $(4 \times 3.0 \mathrm{~mL})$, the combined layers filtered through a pad of Florisil and the solvent was removed under reduced pressure. The yield of 5,10 -diphenyl-5,10-dihydrophenazine 2a and $N^{1}, N^{1}, N^{2}$-triarylbenzene-1,2-diamine 3a and recovery of diarylamine $\mathbf{1 a}$ were determined by GC analysis using undecane as the internal standard.

Table S1. Optimization of Reaction Conditions

|  <br> 1a |  | $\text { 1) } \begin{aligned} & \mathrm{EtMgBr}(1 \text { equiv) } \\ & \mathrm{Et}_{2} \mathrm{O}, 25^{\circ} \mathrm{C}, 10 \min \\ & \text { then, removal of } \mathrm{Et}_{2} \mathrm{O} \\ & \hline \text { 2) metal salt }(5 \mathrm{~mol} \%) \\ & \mathrm{BrCH}_{2} \mathrm{CH}_{2} \mathrm{Br}(\mathrm{Y} \text { equiv) } \\ & \text { solvent, } 100^{\circ} \mathrm{C}, 12 \mathrm{~h} \end{aligned}$ |  |  |  | + |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | yield (\%) ${ }^{b}$ |  |  | recovery of |
| entry | X | metal salt | Y | solvent | 2a (\%) | 3a (\%) | $1 \mathbf{1 a}(\%)^{b}$ |
| 1 | F | $\mathrm{FeCl}_{2}$ | 0 | toluene | 11 | 7 | 76 |
| 2 | F | $\mathrm{FeCl}_{3}$ | 0 | toluene | 11 | 2 | 62 |
| 3 | F | $\mathrm{FeCl}_{2}$ | 2 | toluene | $78\left(76{ }^{c}\right)$ | 0 | 20 |
| 4 | F | $\mathrm{FeCl}_{2}$ | 2 | CPME | 27 | 0 | 28 |
| 5 | F | none | 0 | toluene | 0 | 0 | >99 |
| 6 | F | $\mathrm{NiCl}_{2}$ | 2 | toluene | 34 | 7 | 47 |
| 7 | F | $\mathrm{CoCl}_{2}$ | 2 | toluene | 15 | 12 | 64 |
| 8 | Cl | $\mathrm{FeCl}_{2}$ | 2 | toluene | 0 | 0 | >99 |
| 9 | Br | $\mathrm{FeCl}_{2}$ | 2 | toluene | <1 | 0 | 99 |

 undecane as an internal standard. ${ }^{c}$ Isolated yield.

## Synthesis of 5,10-diphenyl-5,10-dihydrophenazine (2a)



2a
The reaction was carried out according to the procedure A on a 0.29 mmol scale using 2-fluoro- $N$-phenylaniline ( $53.6 \mathrm{mg}, 0.286 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}$ ( $1.90 \mathrm{mg}, 15.0 \mu \mathrm{~mol}$ ), and 1,2dibromoethane ( $112 \mathrm{mg}, 0.598 \mathrm{mmol}$ ). The reaction was stirred at $100^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene $(4 \times 3.0 \mathrm{~mL})$ and the solvent was removed was under reduced pressure. The crude product was purified by washing with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}$ ( $3 \times 1.0 \mathrm{~mL}$ ) to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene) and combined to give the title compound as a yellow solid ( $36.2 \mathrm{mg}, 76 \%$ yield, $>99 \%$ purity on GC analysis). Spectroscopic data for the title compound has been previously reported. ${ }^{6}$ HRMS (FAB) $m / z[\mathrm{M}]^{+}$calcd for $\mathrm{C}_{24} \mathrm{H}_{18} \mathrm{~N}_{2} 334.1470$; found 334.1466. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra have been attached as Figures S68 and S69.

## Synthesis of 5,10-di-p-tolyl-5,10-dihydrophenazine (2b)



2b
The reaction was carried out according to the procedure A on a 0.30 mmol scale using 2-fluoro- $N$-(p-tolyl)aniline ( $61.1 \mathrm{mg}, 0.304 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}$ ( $1.90 \mathrm{mg}, 15.0 \mu \mathrm{~mol}$ ), and 1,2dibromoethane ( $112 \mathrm{mg}, 0.596 \mathrm{mmol}$ ). The reaction was stirred at $120^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$ ). The organics were extracted from the aqueous layer with toluene ( $4 \times 3.0 \mathrm{~mL}$ ) and the solvent was removed was under reduced pressure. The crude product was purified

[^5]by washing with $\mathrm{Et}_{2} \mathrm{O}$ ( $3 \times 1.0 \mathrm{~mL}$ ) to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}$ ( $3 \times 1.0 \mathrm{~mL}$ ) to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene) and combined to give the title compound as a yellow solid ( $38.8 \mathrm{mg}, 70 \%$ yield, $>99 \%$ purity on GC analysis). Mp: 273.5-275.0 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) 1480, 1456, 1341, 1285, 1265, 1208, 1104, 1059, 1019, 907, 808, 725, 616, 592, 529; ${ }^{1} \mathrm{H}$ NMR (C6D6, 392 MHz ) $\delta 2.07$ (s, 6H), $5.84-5.96$ (m, 4H), 6.27-6.37 (m, 4H), 6.98 (d, $J=8.2 \mathrm{~Hz}, 4 \mathrm{H}), 7.10$ (d, $J=7.8 \mathrm{~Hz}, 4 \mathrm{H}$ ); ${ }^{13} \mathrm{C}$ NMR (C6$\left.{ }_{6}, 98.5 \mathrm{MHz}\right) \delta 21.08$, 113.1, 121.3, 131.4, 132.2, 137.4, 137.8, 138.2. Anal. calcd for $\mathrm{C}_{26} \mathrm{H}_{22} \mathrm{~N}_{2}$ : C, 86.15; H, 6.12; N, 7.73. Found: C, 86.29; H, 6.16; N, 7.48. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra have been attached as Figures S70 and S71.

## Synthesis of 5,10-di-m-tolyl-5,10-dihydrophenazine (2c)



The reaction was carried out according to the procedure A on a 0.31 mmol scale using 2-fluoro- $N$-( $m$-tolyl)aniline ( $61.8 \mathrm{mg}, 0.307 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}$ ( $2.00 \mathrm{mg}, 15.8 \mu \mathrm{~mol}$ ), and $1,2-$ dibromoethane ( $111 \mathrm{mg}, 0.591 \mathrm{mmol}$ ). The reaction was stirred at $120^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene $(4 \times 3.0 \mathrm{~mL})$ and the solvent was removed was under reduced pressure. The crude product was purified by washing with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}$ ( $3 \times 1.0 \mathrm{~mL}$ ) to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene) and combined to give the title compound as a yellow solid ( $30.0 \mathrm{mg}, 54 \%$ yield, $>99 \%$ purity on GC analysis). Mp: 232.5-234.0 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) 1597, 1580, 1484, 1339, 1267, 1229, 1217, 1058, 1002, 783, 736, 718, 701, 620; ${ }^{1} \mathrm{H}$ NMR (C6D6, 392 MHz ) $\delta 2.01$ (s, 6H), 5.855.92 (m, 4H), 6.26-6.33 (m, 4H), 6.90-7.14 (m, 8H); ${ }^{13} \mathrm{C}$ NMR (C6D6, 98.5 MHz$) \delta 21.16$, 113.1, 121.4, 128.6, 128.9, 131.2, 132.0, 137.3, 140.9, 141.6. Anal. calcd for $\mathrm{C}_{26} \mathrm{H}_{22} \mathrm{~N}_{2}$ :

C, 86.15; H, 6.12; N, 7.73. Found: C, 85.99; H, 6.04; N, 7.68. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra have been attached as Figures S72 and S73.

## Synthesis of 5,10-bis(4-chlorophenyl)-5,10-dihydrophenazine (2d)



2d
The reaction was carried out according to the procedure A on a 0.30 mmol scale using $N$-(4-chlorophenyl)-2-fluoroaniline ( $67.0 \mathrm{mg}, 0.302 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}(1.90 \mathrm{mg}, 15.0 \mu \mathrm{~mol})$, and 1,2-dibromoethane ( $110 \mathrm{mg}, 0.586 \mathrm{mmol}$ ). The reaction was stirred at $120^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene $(4 \mathrm{x}$ 3.0 mL ) and the solvent was removed was under reduced pressure. The crude product was purified by washing with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene) and combined to give the title compound as a yellow solid ( $48.3 \mathrm{mg}, 79 \%$ yield, $>98 \%$ purity on GC analysis). Mp: 308.0-309.0 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) 1482, 1454, 1396, 1339, 1286, 1267, 1085, 1058, 1014, 915, 843, 815, 759, 736, 717, 616, 525, 517; ${ }^{1} \mathrm{H}$ NMR (C6D6, 392 MHz ) $\delta 5.65-5.72(\mathrm{~m}, 4 \mathrm{H}), 6.29-6.36(\mathrm{~m}, 4 \mathrm{H}), 6.79-6.86(\mathrm{~m}, 4 \mathrm{H}), 7.04-7.11$ (m, 4H); ${ }^{13} \mathrm{C}$ NMR (C6D6, 98.5 MHz ) $\delta 113.2,121.7,131.8,133.0,134.0,136.7,139.0$. Anal. calcd for $\mathrm{C}_{24} \mathrm{H}_{16} \mathrm{Cl}_{2} \mathrm{~N}_{2}$ : C, 71.48; H, 4.00; N, 6.95. Found: C, 71.50; H, 4.09; N, 6.94. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra have been attached as Figures S 74 and S 75 .

## Synthesis of 5,10-bis(3-chlorophenyl)-5,10-dihydrophenazine (2e)



The reaction was carried out according to the procedure A on a 0.32 mmol scale using $N$-(3-chlorophenyl)-2-fluoroaniline ( $70.7 \mathrm{mg}, 0.319 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}(1.90 \mathrm{mg}, 15.0 \mu \mathrm{~mol})$,
and 1,2 -dibromoethane ( $113 \mathrm{mg}, 0.602 \mathrm{mmol}$ ). The reaction was stirred at $120^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene ( 4 x 3.0 mL ) and the solvent was removed was under reduced pressure. The crude product was purified by washing with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene) and combined to give the title compound as a yellow solid ( $39.5 \mathrm{mg}, 61 \%$ yield, $>99 \%$ purity on GC analysis). Mp: 206.0-207.0 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) 1582 , 1483, 1343, 1283, 1270, 1217, 1159, 1126, 1064, 1000, 956, 785, 735, 690, 642, 618; ${ }^{1} \mathrm{H}$ NMR (C6 ${ }_{6}$, 392 $\mathrm{MHz}) \delta 5.68-5.74(\mathrm{~m}, 4 \mathrm{H}), 6.22-6.29(\mathrm{~m}, 4 \mathrm{H}), 6.81-6.91(\mathrm{~m}, 4 \mathrm{H}), 7.00-7.06(\mathrm{~m}, 2 \mathrm{H})$, $7.18(\mathrm{t}, J=2.0 \mathrm{~Hz}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 98.5 \mathrm{MHz}\right) \delta 113.4,121.8,128.6,129.8,131.9$, 132.4, 136.5, 136.7, 142.0. Anal. calcd for $\mathrm{C}_{24} \mathrm{H}_{16} \mathrm{Cl}_{2} \mathrm{~N}_{2}$ : C, 71.48; H, 4.00; $\mathrm{N}, 6.95$. Found: C, $71.60 ; \mathrm{H}, 4.15 ; \mathrm{N}, 6.81 .{ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra have been attached as Figures S76 and S77.

## Synthesis of 2,7-dichloro-5,10-diphenyl-5,10-dihydrophenazine (2f)



The reaction was carried out according to the procedure A on a 0.30 mmol scale using 4-chloro-2-fluoro- $N$-phenylaniline ( $66.1 \mathrm{mg}, 0.298 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}(1.80 \mathrm{mg}, 14.7 \mu \mathrm{~mol})$, and 1,2 -dibromoethane ( $113 \mathrm{mg}, 0.604 \mathrm{mmol}$ ). The reaction was stirred at $100^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene ( 4 x 3.0 mL ) and the solvent was removed was under reduced pressure. The crude product was purified by washing with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene)
and combined to give the title compound as a yellow solid ( $49.8 \mathrm{mg}, 83 \%$ yield, $>99 \%$ purity on GC analysis). Mp: 291.0-292.0 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) 1482, 1417, 1352, 1323, 1282, 1267, 1172, 960, 839, 751, 692, 568, 530; ${ }^{1} \mathrm{H}$ NMR (C6D6, 392 MHz ) $\delta 5.49$ (dd, J $=1.6,8.6 \mathrm{~Hz}, 2 \mathrm{H}), 5.86(\mathrm{dd}, J=1.6,2.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.22$ (ddd, $J=1.2,2.4,8.6 \mathrm{~Hz}, 2 \mathrm{H})$, 6.91-7.00 (m, 6H), 7.02-7.10 (m, 4H); ${ }^{13} \mathrm{C}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 98.5 \mathrm{MHz}\right) \delta 113.0,114.0,120.8$, 127.1, 128.7, 130.8, 131.7, 135.2, 138.0, 139.3. Anal. calcd for $\mathrm{C}_{24} \mathrm{H}_{16} \mathrm{Cl}_{2} \mathrm{~N} 2$ : C, $71.48 ; \mathrm{H}$, 4.00; N, 6.95. Found: C, $71.49 ; \mathrm{H}, 4.12 ; \mathrm{N}, 6.86 .{ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra have been attached as Figures S78 and S79.

## Synthesis of 2,7-dichloro-5,10-di-p-tolyl-5,10-dihydrophenazine (2g)



The reaction was carried out according to the procedure A on a 0.29 mmol scale using 4-chloro-2-fluoro- $N$-( $p$-tolyl)aniline ( $70.1 \mathrm{mg}, 0.294 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}(1.90 \mathrm{mg}, 15.0 \mu \mathrm{~mol}$ ), and 1,2 -dibromoethane ( $112 \mathrm{mg}, 0.598 \mathrm{mmol}$ ). The reaction was stirred at $100^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene ( 4 x 3.0 mL ) and the solvent was removed under reduced pressure. The crude product was purified by washing with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene) and combined to give the title compound as a yellow solid ( $56.0 \mathrm{mg}, 88 \%$ yield, $97 \%$ purity on GC analysis). Mp: 313.0-314.3 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) 1479, 1426, 1416, 1353, 1329, 1290, 1271, 1255, 1177, 1098, 1019, 966, 944, 851, 800, 772, 610, 574, 535; ${ }^{1} \mathrm{H}$ NMR (C6D6, 392 MHz$) \delta 2.01$ (s, 6H), 5.57 (d, $J=2.4 \mathrm{~Hz}, 2 \mathrm{H}), 5.94$ (d, $J=8.6 \mathrm{~Hz}, 2 \mathrm{H}$ ), $6.26(\mathrm{dd}, J=2.0,8.6 \mathrm{~Hz}, 2 \mathrm{H}), 6.89(\mathrm{~s}, 8 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 98.5 \mathrm{MHz}\right) \delta 21.06,113.0$, $113.9,120.7,127.0,130.5,132.4,135.5,136.7,138.3,138.6$. Anal. calcd for $\mathrm{C}_{24} \mathrm{H}_{20} \mathrm{Cl}_{2} \mathrm{~N}_{2}$ : C, $72.40 ; \mathrm{H}, 4.67 ; \mathrm{N}, 6.49$. Found: C, $72.45 ; \mathrm{H}, 4.80 ; \mathrm{N}, 6.33$. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra have been attached as Figures S80 and S81.

## Synthesis of 2,7-dichloro-5,10-bis(4-chlorophenyl)-5,10-dihydrophenazine (2h)



The reaction was carried out according to the procedure A on a 0.30 mmol scale using 4-chloro- $N$-(4-chlorophenyl)-2-fluoroaniline ( $77.4 \mathrm{mg}, 0.302 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}$ ( 1.80 mg , $14.7 \mu \mathrm{~mol}$ ), and 1,2 -dibromoethane ( $112 \mathrm{mg}, 0.598 \mathrm{mmol}$ ). The reaction was stirred at $100^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene ( $4 \times 3.0 \mathrm{~mL}$ ) and the solvent was removed was under reduced pressure. The crude product was purified by washing with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene) and combined to give the title compound as a yellow solid ( $63.4 \mathrm{mg}, 89 \%$ yield, $96 \%$ purity on GC analysis). Anal. calcd for $\mathrm{C}_{24} \mathrm{H}_{14} \mathrm{Cl}_{4} \mathrm{~N}_{2}$ : C, $61.05 ; \mathrm{H}, 2.99$; N, 5.93. Found: C, 61.20 ; H, 3.27; N, 5.75. Spectroscopic data for the title compound has been previously reported. ${ }^{6} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra have been attached as Figures S82 and S83.

## Synthesis of 5,10-bis(4-bromophenyl)-5,10-dihydrophenazine (2i)


$2 i$
The reaction was carried out according to the procedure A on a 0.30 mmol scale using $N$-(4-bromophenyl)-2-fluoroaniline ( $78.9 \mathrm{mg}, 0.296 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}(1.90 \mathrm{mg}, 15.0 \mu \mathrm{~mol}$ ), and 1,2 -dibromoethane ( $113 \mathrm{mg}, 0.602 \mathrm{mmol}$ ). The reaction was stirred at $120^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene ( 4 x
3.0 mL ) and the solvent was removed was under reduced pressure. The crude product was purified by washing with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene) and combined to give the title compound as a yellow solid ( $50.4 \mathrm{mg}, 69 \%$ yield, $>99 \%$ purity on GC analysis). Mp: 322.0-324.0 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) 1482, 1455, 1392, 1341, 1287, 1268, 1092, 1066, 1011, 913, 813, 735, 617, 522; ${ }^{1} \mathrm{H}$ NMR ( $\mathrm{C}_{6} \mathrm{D}_{6}, 392 \mathrm{MHz}$ ) $\delta$ 5.64-5.71 (m, 4H), 6.28-6.36 (m, 4H), 6.71-6.78 (m, 4H), 7.19-7.26 (m, 4H); ${ }^{13} \mathrm{C}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}, 98.5 \mathrm{MHz}\right) \delta 113.2,121.7,122.1,133.4,134.9,136.6,139.6$. HRMS (FAB) $\mathrm{m} / \mathrm{z}$ $[\mathrm{M}]^{+}$calcd for $\mathrm{C}_{24} \mathrm{H}_{16} \mathrm{Br}_{2} \mathrm{~N}_{2}$ 489.9680; found 489.9677 . ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra have been attached as Figures S84 and S85.

## Synthesis of 5,10-bis(4-bromophenyl)-2,7-dichloro-5,10-dihydrophenazine (2j)



The reaction was carried out according to the procedure A on a 0.30 mmol scale using $N$-(4-bromophenyl)-4-chloro-2-fluoroaniline ( $90.2 \mathrm{mg}, 0.300 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}$ ( 1.90 mg , $15.0 \mu \mathrm{~mol}$ ), and 1,2 -dibromoethane ( $113 \mathrm{mg}, 0.604 \mathrm{mmol}$ ). The reaction was stirred at $100^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene ( $4 \times 3.0 \mathrm{~mL}$ ) and the solvent was removed was under reduced pressure. The crude product was purified by washing with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene) and combined to give the title compound as a yellow solid ( $72.4 \mathrm{mg}, 86 \%$ yield, $97 \%$ purity on GC analysis). Mp: 329.0-331.0 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) $1475,1416,1354,1323$, $1270,1258,1175,1162,1094,1066,1012,965,940,839,822,793,785,715,568,531 ;$ ${ }^{1} \mathrm{H}$ NMR (C6D6, 392 MHz$) \delta 5.34(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H}), 5.78$ (d, $\left.J=2.0 \mathrm{~Hz}, 2 \mathrm{H}\right), 6.27$ (dd,
$J=2.0,8.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.51-6.58(\mathrm{~m}, 4 \mathrm{H}), 7.10-7.16(\mathrm{~m}, 4 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 98.5 \mathrm{MHz}\right)$ $\delta 113.0,114.0,121.1,122.9,127.4,132.5,134.7,135.1,137.4,138.0$. HRMS (FAB) $m / z$ $[\mathrm{M}]^{+}$calcd for $\mathrm{C}_{24} \mathrm{H}_{14} \mathrm{Br}_{2} \mathrm{Cl}_{2} \mathrm{~N}_{2} 557.8901$; found $557.8900 .{ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra have been attached as Figures S86 and S87.

## Synthesis of 5,10-bis(3-bromophenyl)-5,10-dihydrophenazine (2k)



The reaction was carried out according to the procedure A on a 0.28 mmol scale using $N$-(3-bromophenyl)-2-fluoroaniline ( $74.7 \mathrm{mg}, 0.281 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}(1.90 \mathrm{mg}, 15.0 \mu \mathrm{~mol})$, and 1,2-dibromoethane ( $112 \mathrm{mg}, 0.596 \mathrm{mmol}$ ). The reaction was stirred at $120^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene $(4 \mathrm{x}$ 3.0 mL ) and the solvent was removed was under reduced pressure. The crude product was purified by washing with $E t_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene) and combined to give the title compound as a yellow solid ( $46.3 \mathrm{mg}, 67 \%$ yield, $>99 \%$ purity on GC analysis). Mp: $234.2-235.2^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) $1580,1558,1485,1473$, 1456, 1347, 1287, 1271, 1153, 1062, 998, 946, 779, 773, 747, 734, 689, 678, 639, 621; ${ }^{1} \mathrm{H}$ NMR (C6D6, 392 MHz ) $\delta 5.66-5.73(\mathrm{~m}, 4 \mathrm{H}), 6.21-6.28(\mathrm{~m}, 4 \mathrm{H}), 6.77(\mathrm{t}, J=8.2 \mathrm{~Hz}$, 2H), 6.89-6.95 (m, 2H), 7.15-7.23 (m, 2H), 7.35 (t, $J=2.0 \mathrm{~Hz}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (C6D6, $98.5 \mathrm{MHz}) \delta 113.4,121.8,124.5,130.3,131.6,132.7,134.7,136.5,142.2$. Anal. calcd for $\mathrm{C}_{24} \mathrm{H}_{16} \mathrm{Br}_{2} \mathrm{~N}_{2}$ : C, 58.56; H, 3.28; N, 5.69. Found: C, 58.82; H, 3.43; N, 5.56. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra have been attached as Figures S88 and S89.

## Synthesis of 2,7-dibromo-5,10-diphenyl-5,10-dihydrophenazine (21)



The reaction was carried out according to the procedure A on a 0.30 mmol scale using 4-bromo-2-fluoro- $N$-phenylaniline ( $79.1 \mathrm{mg}, 0.297 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}(2.00 \mathrm{mg}, 15.8 \mu \mathrm{~mol}$ ), and 1,2 -dibromoethane ( $111 \mathrm{mg}, 0.593 \mathrm{mmol}$ ). The reaction was stirred at $100^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene ( 4 x 3.0 mL ) and the solvent was removed under reduced pressure. The crude product was purified by washing with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene) and combined to give the title compound as a yellow solid ( $66.4 \mathrm{mg}, 91 \%$ yield, $>98 \%$ purity on GC analysis). Mp: $275.6-276.6^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) $1477,1412,1351,1320$, 1279, 1266, 1171, 1025, 953, 935, 838, 788, 778, 750, 692, 559, 527; ${ }^{1} \mathrm{H}$ NMR ( ${ }_{6} \mathrm{D}_{6}$, $392 \mathrm{MHz}) \delta 5.42(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H}), 5.98(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.35(\mathrm{dd}, J=2.4,8.6 \mathrm{~Hz}$, 2H), 6.90-6.97 (m, 6H), 7.02-7.08 (m, 4H); ${ }^{13} \mathrm{C}$ NMR (C6 $\left.\mathrm{D}_{6}, 98.5 \mathrm{MHz}\right) \delta 114.4,115.7$, 124.0, 127.9 (overlap with the related signal of $\mathrm{C}_{6} \mathrm{D}_{6}$ ), 128.8, 130.8, 131.7, 135.8, 138.2, 139.2. Anal. calcd for $\mathrm{C}_{24} \mathrm{H}_{16} \mathrm{Br}_{2} \mathrm{~N}_{2}$ : C, $58.56 ; \mathrm{H}, 3.28$; $\mathrm{N}, 5.69$. Found: C, $58.61 ; \mathrm{H}, 3.44$; N, 5.59. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra have been attached as Figures S 90 and S 91.

## Synthesis of 2,7-dibromo-5,10-di-p-tolyl-5,10-dihydrophenazine (2m)



The reaction was carried out according to the procedure A on a 0.30 mmol scale using 4-bromo-2-fluoro- $N$-( $p$-tolyl)aniline ( $84.4 \mathrm{mg}, 0.301 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}(1.90 \mathrm{mg}, 15.0 \mu \mathrm{~mol}$ ),
and 1,2 -dibromoethane ( $113 \mathrm{mg}, 0.602 \mathrm{mmol}$ ). The reaction was stirred at $100^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene ( 4 x 3.0 mL ) and the solvent was removed was under reduced pressure. The crude product was purified by washing with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene) and combined to give the title compound as a yellow solid ( $71.3 \mathrm{mg}, 91 \%$ yield, $98 \%$ purity on GC analysis). Mp: $293.5^{\circ} \mathrm{C}$ (dec); IR (neat, $\mathrm{cm}^{-1}$ ) 2917, 1475, 1413, 1351, 1321, $1282,1267,1255,1177,1164,1103,1087,1019,958,938,836,816,805,787,756,716$, 606, 560, 533; ${ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 392 \mathrm{MHz}\right) \delta 1.99(\mathrm{~s}, 6 \mathrm{H}), 5.50(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H}), 6.06$ (d, $J=2.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.40(\mathrm{dd}, J=2.4,8.6 \mathrm{~Hz}, 2 \mathrm{H}), 6.89(\mathrm{~s}, 8 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\mathrm{C}_{6} \mathrm{D}_{6}, 98.5$ $\mathrm{MHz}) \delta 21.06,114.3,114.4,115.6,123.8,127.9,130.5,132.5,136.0,136.6$, 138.5. Anal. calcd for $\mathrm{C}_{26} \mathrm{H}_{20} \mathrm{Br}_{2} \mathrm{~N}_{2}$ : C, 60.02 ; H, 3.87; N, 5.38. Found: C, $60.01 ; \mathrm{H}, 4.08 ; \mathrm{N}, 5.19 .{ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra have been attached as Figures S92 and S93.

## Synthesis of 2,7-dibromo-5,10-bis(4-chlorophenyl)-5,10-dihydrophenazine (2n)



The reaction was carried out according to the procedure A on a 0.30 mmol scale using 4-bromo- $N$-(4-chlorophenyl)-2-fluoroaniline ( $91.0 \mathrm{mg}, 0.302 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}$ ( 2.00 mg , $15.8 \mu \mathrm{~mol}$ ), and 1,2 -dibromoethane ( $114 \mathrm{mg}, 0.609 \mathrm{mmol}$ ). The reaction was stirred at $100^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene ( $4 \times 3.0 \mathrm{~mL}$ ) and the solvent was removed was under reduced pressure. The crude product was purified by washing with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with
toluene) and combined to give the title compound as a yellow solid ( $75.8 \mathrm{mg}, 89 \%$ yield, $>98 \%$ purity on GC analysis). Mp: 332.4-334.4 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) $1481,1412,1352$, 1321, 1282, 1258, 1088, 1015, 959, 937, 842, 824, 786, 781, 719, 560, 534, 526; ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}, 392 \mathrm{MHz}\right) \delta 5.27(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 5.91(\mathrm{~d}, J=1.6 \mathrm{~Hz}, 2 \mathrm{H}), 6.42(\mathrm{dd}, J=2.0$, $8.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.56-6.63(\mathrm{~m}, 4 \mathrm{H}), 6.93-6.99(\mathrm{~m}, 4 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (C6 $\left.\mathrm{D}_{6}, 98.5 \mathrm{MHz}\right) \delta 114.5$, 114.7, 115.7, 124.3, 127.9 (overlap with the related signal of $\mathrm{C}_{6} \mathrm{D}_{6}$ ), 132.1, 134.7, 135.3, 137.4, 137.7. HRMS (FAB) $m / z[M]^{+}$calcd for $\mathrm{C}_{24} \mathrm{H}_{14} \mathrm{Br}_{2} \mathrm{Cl}_{2} \mathrm{~N}_{2} 557.8901$; found $557.8900 .{ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra have been attached as Figures S 94 and S 95 .

## Synthesis of 2,7-dibromo-5,10-bis(4-bromophenyl)-5,10-dihydrophenazine (20)



The reaction was carried out according to the procedure A on a 0.30 mmol scale using 4-bromo- $N$-(4-bromophenyl)-2-fluoroaniline ( $104 \mathrm{mg}, 0.301 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}$ ( 2.00 mg , $15.8 \mu \mathrm{~mol}$ ), and 1,2 -dibromoethane ( $113 \mathrm{mg}, 0.598 \mathrm{mmol}$ ). The reaction was stirred at $100{ }^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene $(4 \times 3.0 \mathrm{~mL})$ and the solvent was removed was under reduced pressure. The crude product was purified by washing with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene) and combined to give the title compound as a yellow solid ( $80.7 \mathrm{mg}, 82 \%$ yield, $>98 \%$ purity on GC analysis). HRMS (APCI) $m / z[\mathrm{M}]^{+}$calcd for $\mathrm{C}_{24} \mathrm{H}_{14} \mathrm{Br}_{4} \mathrm{~N}_{2} 645.7891$; found 645.7887. Spectroscopic data for the title compound have been reported. ${ }^{6}{ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra have been attached as Figures S96 and S97.

## Synthesis of 5,10-bis(4-fluorophenyl)-5,10-dihydrophenazine (2p)



The reaction was carried out according to the procedure A on a 0.30 mmol scale using 2-fluoro- $N$-(4-fluorophenyl)aniline ( $62.4 \mathrm{mg}, 0.304 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}(1.80 \mathrm{mg}, 14.2 \mu \mathrm{~mol}$ ), and 1,2 -dibromoethane ( $111 \mathrm{mg}, 0.593 \mathrm{mmol}$ ). The reaction was stirred at $100^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene $(4 \mathrm{x}$ 3.0 mL ) and the solvent was removed was under reduced pressure. The crude product was purified by washing with $E t_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene) and combined to give the title compound as a yellow solid ( $40.6 \mathrm{mg}, 72 \%$ yield, $>99 \%$ purity on GC analysis). Mp: 302.3-303.6 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) $1486,1458,1347,1289$, 1269, 1210, 1146, 1087, 1066, 1013, 907, 844, 826, 816, 731, 616, 593, 535; ${ }^{1} \mathrm{H}$ NMR (C6D6, 392 MHz ) $\delta 5.67-5.74(\mathrm{~m}, 4 \mathrm{H}), 6.29-6.37(\mathrm{~m}, 4 \mathrm{H}), 6.72-6.81(\mathrm{~m}, 4 \mathrm{H}), 6.85-6.93$ (m, 4H); ${ }^{13} \mathrm{C}$ NMR (C6D6, 98.5 MHz$) \delta 113.1,118.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=23 \mathrm{~Hz}\right), 121.6,133.4(\mathrm{~d}$, $\left.J_{\mathrm{C}-\mathrm{F}}=9.4 \mathrm{~Hz}\right), 136.5\left(\mathrm{ddd}, J_{\mathrm{C}-\mathrm{F}}=2.8 \mathrm{~Hz}\right), 137.0,162.3\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=247 \mathrm{~Hz}\right) ;{ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right.$, $368 \mathrm{MHz}) \delta-112.7$; Anal. calcd for $\mathrm{C}_{24} \mathrm{H}_{16} \mathrm{~F}_{2} \mathrm{~N}_{2}$ : C, 77.82 ; H, 4.35; N, 7.56. Found: C, $77.83 ; \mathrm{H}, 4.43$; $\mathrm{N}, 7.48 .{ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR spectra have been attached as Figures S 98 , S99, and S100.

## Synthesis of 2,7-dichloro-5,10-bis(4-fluorophenyl)-5,10-dihydrophenazine (2q)



The reaction was carried out according to the procedure A on a 0.31 mmol scale using 4-chloro-2-fluoro- $N$-(4-fluorophenyl)aniline ( $73.2 \mathrm{mg}, 0.305 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}$ ( 1.80 mg ,
$14.7 \mu \mathrm{~mol}$ ), and 1,2 -dibromoethane ( $112 \mathrm{mg}, 0.598 \mathrm{mmol}$ ). The reaction was stirred at $100^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene ( $4 \times 3.0 \mathrm{~mL}$ ) and the solvent was removed was under reduced pressure. The crude product was purified by washing with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene) and combined to give the title compound as a yellow solid ( $60.3 \mathrm{mg}, 90 \%$ yield, $98 \%$ purity on GC analysis). Mp: 309.5-310.5 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) $1483,1418,1353,1327$, $1282,1269,1235,1221,1169,1147,1089,1012,966,954,841,832,823,789,778,717$, $611,569,541 ;{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 392 \mathrm{MHz}\right) \delta 5.37(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 5.78(\mathrm{~d}, J=2.0 \mathrm{~Hz}$, $2 \mathrm{H}), 6.28(\mathrm{dd}, J=2.4,8.6 \mathrm{~Hz}, 2 \mathrm{H}), 6.66(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 4 \mathrm{H}), 6.67(\mathrm{~s}, 4 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\mathrm{C}_{6} \mathrm{D}_{6}$, $98.5 \mathrm{MHz}) \delta 113.0,113.9,118.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=23 \mathrm{~Hz}\right), 121.0,127.3,132.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=8.5 \mathrm{~Hz}\right)$, $134.8\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=2.9 \mathrm{~Hz}\right), 135.0,137.8,162.6\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=249 \mathrm{~Hz}\right) ;{ }^{19} \mathrm{~F}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}, 368\right.$ $\mathrm{MHz}) \delta-111.2$; Anal. calcd for $\mathrm{C}_{24} \mathrm{H}_{14} \mathrm{Cl}_{2} \mathrm{~F}_{2} \mathrm{~N}_{2}$ : C, $65.62 ; \mathrm{H}, 3.21 ; \mathrm{N}, 6.38$. Found: C, $65.91 ; \mathrm{H}, 3.37 ; \mathrm{N}, 6.22 .{ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR spectra have been attached as Figures S 101 , S102, and S103.

## Synthesis of 2,7-dibromo-5,10-bis(4-fluorophenyl)-5,10-dihydrophenazine (2r)



The reaction was carried out according to the procedure A on a 0.30 mmol scale using 4-bromo-2-fluoro- $N$-(4-fluorophenyl)aniline ( $85.3 \mathrm{mg}, 0.300 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}$ ( 1.90 mg , $15.0 \mu \mathrm{~mol}$ ), and 1,2 -dibromoethane ( $113 \mathrm{mg}, 0.604 \mathrm{mmol}$ ). The reaction was stirred at $100^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene ( $4 \times 3.0 \mathrm{~mL}$ ) and the solvent was removed was under reduced pressure. The crude product was purified by washing with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under
reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene) and combined to give the title compound as a yellow solid ( $45.0 \mathrm{mg}, 57 \%$ yield, $>99 \%$ purity on GC analysis). Mp: 318.0-320.0 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) 1483, 1413, 1389, 1327, 1282, 1269, 1260, 1240, 1225, 1170, 1148, 1087, 1017, 957, 936, 844, 829, 823, 791, 763, 607, 564, 537; ${ }^{1} \mathrm{H}$ NMR (C6D6, 392 MHz ) $\delta 5.30$ (d, $J=8.6 \mathrm{~Hz}, 2 \mathrm{H}$ ), 5.90 (d, $J=2.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.42(\mathrm{dd}, J=2.0,8.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.62-6.68(\mathrm{~m}, 8 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (C6 $\mathrm{D}_{6}, 98.5$ $\mathrm{MHz}) \delta 114.4,114.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=19 \mathrm{~Hz}\right), 115.7,118.8\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=26 \mathrm{~Hz}\right), 124.1,132.6\left(\mathrm{~d}, J_{\mathrm{C}}\right.$ $\mathrm{F}=8.4 \mathrm{~Hz}), 134.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=3.7 \mathrm{~Hz}\right), 135.6,138.0,162.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=249 \mathrm{~Hz}\right) ;{ }^{19} \mathrm{~F}$ NMR ( $\mathrm{C}_{6} \mathrm{D}_{6}, 368 \mathrm{MHz}$ ) $\delta-111.1$; HRMS (FAB) $m / z[\mathrm{M}]^{+}$calcd for $\mathrm{C}_{24} \mathrm{H}_{14} \mathrm{Br}_{2} \mathrm{~F}_{2} \mathrm{~N}_{2} 525.9492$; found $525.9490 .{ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR spectra have been attached as Figures $\mathrm{S} 104, \mathrm{~S} 105$, and S106.

## Synthesis of 5,10-bis(3-fluorophenyl)-5,10-dihydrophenazine (2s)



The reaction was carried out according to the procedure A on a 0.30 mmol scale using 2-fluoro- $N$-(3-fluorophenyl)aniline ( $60.9 \mathrm{mg}, 0.297 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}(2.00 \mathrm{mg}, 15.8 \mu \mathrm{~mol}$ ), and 1,2 -dibromoethane ( $112 \mathrm{mg}, 0.596 \mathrm{mmol}$ ). The reaction was stirred at $120^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene ( 4 x 3.0 mL ) and the solvent was removed was under reduced pressure. The crude product was purified by washing with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene) and combined to give the title compound as a yellow solid ( $34.9 \mathrm{mg}, 63 \%$ yield, $>99 \%$ purity on GC analysis). Mp: 238.4-239.4 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) 1483, 1458, 1443, 1431, 1343, 1284, 1273, 1263, 1216, 1157, 1146, 1132, 1107, 1075, 1060, 977, 886, 855, 779, 732, 720, 690, 644, 624, 620; ${ }^{1} \mathrm{H}$ NMR (C6D6, 392 MHz ) $\delta 5.73-5.79$ (m, 4H), 6.26-6.32 (m, 4H), $6.72\left(\mathrm{tdd}, J=0.8,8.2 \mathrm{~Hz}, J_{\mathrm{H}-\mathrm{F}}=2.7 \mathrm{~Hz}, 2 \mathrm{H}\right), 6.80-6.88(\mathrm{~m}, 4 \mathrm{H}), 6.88-6.93(\mathrm{~m}$.
$2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6} 98.5 \mathrm{MHz}\right) \delta 113.4,115.4\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=21 \mathrm{~Hz}\right), 118.6\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=21 \mathrm{~Hz}\right)$, $121.8,127.1\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=2.8 \mathrm{~Hz}\right), 132.6\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=9.5 \mathrm{~Hz}\right), 136.5,142.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=9.5 \mathrm{~Hz}\right)$, $164.9\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=249 \mathrm{~Hz}\right)$; ${ }^{19} \mathrm{~F}$ NMR ( $\mathrm{C}_{6} \mathrm{D}_{6}, 368 \mathrm{MHz}$ ) $\delta-108.8$; Anal. calcd for $\mathrm{C}_{24} \mathrm{H}_{16} \mathrm{~F}_{2} \mathrm{~N}_{2}$ : C, $77.82 ; \mathrm{H}, 4.35$; N, 7.56. Found: C, $77.84 ; \mathrm{H}, 4.49 ; \mathrm{N}, 7.42 .{ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19}$ F NMR spectra have been attached as Figures S 107, S108, and S109.

## Synthesis of 2,7-difluoro-5,10-diphenyl-5,10-dihydrophenazine (2t)



The reaction was carried out according to the procedure A on a 0.30 mmol scale using 2,4-difluoro- $N$-phenylaniline ( $62.4 \mathrm{mg}, 0.304 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}(1.80 \mathrm{mg}, 14.2 \mu \mathrm{~mol}$ ), and 1,2-dibromoethane ( $112 \mathrm{mg}, 0.596 \mathrm{mmol}$ ). The reaction was stirred at $100^{\circ} \mathrm{C}$ for 12 h before cooling to $25^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(0.60 \mathrm{~mL})$ was added to the reaction mixture at $25^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene ( 4 x 3.0 mL ) and the solvent was removed was under reduced pressure. The crude product was purified by washing with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}(3 \times 1.0 \mathrm{~mL})$ to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene) and combined to give the title compound as a yellow solid ( $50.2 \mathrm{mg}, 89 \%$ yield, $>99 \%$ purity on GC analysis). Mp: 275.5-276.5 ${ }^{\circ} \mathrm{C}$; IR (neat, $\mathrm{cm}^{-1}$ ) 1480, 1435, 1363, 1324, 1280, 1260, 1189, 1109, 1001, 829, 786, 754, 692, 661, 588, 552; ${ }^{1} \mathrm{H}$ NMR (C6D6, 392 $\mathrm{MHz}) \delta 5.53\left(\mathrm{dd}, J=9.0 \mathrm{~Hz}, J_{\mathrm{H}-\mathrm{F}}=5.1 \mathrm{~Hz}, 2 \mathrm{H}\right), 5.67\left(\mathrm{dd}, J=2.7 \mathrm{~Hz}, J_{\mathrm{H}-\mathrm{F}}=11 \mathrm{~Hz}, 2 \mathrm{H}\right)$, 5.87-5.97 (m, 2H), 6.95-7.03 (m, 6H), 7.05-7.12 (m, 4H); ${ }^{13} \mathrm{C}$ NMR (C6D6, 98.5 MHz$)$ $\delta 101.1\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=19 \mathrm{~Hz}\right), 105.7\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=22 \mathrm{~Hz}\right), 113.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=9.4 \mathrm{~Hz}\right), 128.6,131.0$, $131.6,132.3\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=1.9 \mathrm{~Hz}\right), 138.5\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=10 \mathrm{~Hz}\right), 139.9,159.3\left(\mathrm{~d}, J_{\mathrm{C}-\mathrm{F}}=238 \mathrm{~Hz}\right) ;$ ${ }^{19}$ F NMR (C6D6, 368 MHz ) $\delta-122.0$; HRMS (FAB) $m / z[\mathrm{M}]^{+}$calcd for $\mathrm{C}_{24} \mathrm{H}_{16} \mathrm{~F}_{2} \mathrm{~N}_{2}$ : 370.1282; Found: 370.1279. ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR spectra have been attached as Figures S110, S111, and S112.

## Synthesis of 2,7-difluoro-5,10-diphenyl-5,10-dihydrophenazine (2t) (12 mmol scale)



The reaction was carried out according to the procedure A on a 12 mmol scale using 2,4-difluoro- $N$-phenylaniline ( $2.46 \mathrm{~g}, 12.0 \mathrm{mmol}$ ), $\mathrm{FeCl}_{2}$ ( $76.2 \mathrm{mg}, 0.601 \mathrm{mmol}$ ), and 1,2dibromoethane ( $4.37 \mathrm{~g}, 23.3 \mathrm{mmol}$ ). The reaction was stirred at $100^{\circ} \mathrm{C}$ for 12 h before cooling to $0^{\circ} \mathrm{C}$, and 1 N aqueous $\mathrm{HCl}(30 \mathrm{~mL})$ was added to the reaction mixture at $0^{\circ} \mathrm{C}$. The organics were extracted from the aqueous layer with toluene $(4 \times 60 \mathrm{~mL})$ and the solvent was removed was under reduced pressure. The crude product was purified by washing with $\mathrm{Et}_{2} \mathrm{O}(3 \times 30 \mathrm{~mL})$ to afford a dark yellow solid (first solid). After the rest of $\mathrm{Et}_{2} \mathrm{O}$ layers was combined, the solvent was removed under reduced pressure and washed with $\mathrm{Et}_{2} \mathrm{O}$ ( $3 \times 30 \mathrm{~mL}$ ) to afford a dark yellow solid (second solid). The first and second solids were filtered through a pad of Florisil (eluting with toluene) and combined to give the title compound as a yellow solid ( $1.40 \mathrm{~g}, 63 \%$ yield, $97 \%$ purity on GC analysis).
3. ${ }^{1} \mathrm{H},{ }^{13} \mathrm{C}$, and ${ }^{19} \mathrm{~F}$ NMR Spectra


Figure S1. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 a}(\mathrm{X}=\mathrm{F})$ in $\mathrm{CDCl}_{3}$.


Figure S2. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 a}(\mathrm{X}=\mathrm{F})$ in $\mathrm{CDCl}_{3}$.


Figure S3. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{1 a}(\mathrm{X}=\mathrm{F})$ in $\mathrm{CDCl}_{3}$.


Figure $\mathbf{S 4} .{ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 a}(\mathrm{X}=\mathrm{Cl})$ in $\mathrm{CDCl}_{3}$.


Figure S5. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 a}(\mathrm{X}=\mathrm{Cl})$ in $\mathrm{CDCl}_{3}$.


Figure S6. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 a}(\mathrm{X}=\mathrm{Br})$ in $\mathrm{CDCl}_{3}$.


Figure $\mathbf{S 7}{ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 a}(\mathrm{X}=\mathrm{Br})$ in $\mathrm{CDCl}_{3}$.


Figure S8. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 b}$ in $\mathrm{CDCl}_{3}$.


Figure S9. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 b}$ in $\mathrm{CDCl}_{3}$.


Figure S10. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{1 b}$ in $\mathrm{CDCl}_{3}$.


Figure $\mathbf{S} 11 .{ }^{1} \mathrm{H}$ NMR spectrum of $1 \mathbf{c}$ in $\mathrm{CDCl}_{3}$.


Figure S12. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 c}$ in $\mathrm{CDCl}_{3}$.


Figure S13. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{1 c}$ in $\mathrm{CDCl}_{3}$.


Figure S14. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 d}$ in $\mathrm{CDCl}_{3}$.


Figure S15. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 d}$ in $\mathrm{CDCl}_{3}$.


Figure S16. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{1 d}$ in $\mathrm{CDCl}_{3}$.


Figure S17. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 e}$ in $\mathrm{CDCl}_{3}$.


Figure S18. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 e}$ in $\mathrm{CDCl}_{3}$.


Figure S19. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{1 e}$ in $\mathrm{CDCl}_{3}$.


Figure S20. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 f}$ in $\mathrm{CDCl}_{3}$.


Figure S21. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 f}$ in $\mathrm{CDCl}_{3}$.


Figure S22. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{1 f}$ in $\mathrm{CDCl}_{3}$.


Figure $\mathbf{S 2 3} .{ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 g}$ in $\mathrm{CDCl}_{3}$.


Figure $\mathbf{S 2 4}{ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 g}$ in $\mathrm{CDCl}_{3}$.


Figure S25. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{1 g}$ in $\mathrm{CDCl}_{3}$.


Figure S26. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 h}$ in $\mathrm{CDCl}_{3}$.


Figure S27. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 h}$ in $\mathrm{CDCl}_{3}$.


Figure S28. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{1 h}$ in $\mathrm{CDCl}_{3}$.


Figure S29. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 i}$ in $\mathrm{CDCl}_{3}$.


Figure S30. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 i}$ in $\mathrm{CDCl}_{3}$.


Figure S31. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{1 i}$ in $\mathrm{CDCl}_{3}$.


Figure S32. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 j}$ in $\mathrm{CDCl}_{3}$.


Figure S33. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1} \mathbf{j}$ in $\mathrm{CDCl}_{3}$.


Figure S34. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{1 j}$ in $\mathrm{CDCl}_{3}$.


Figure S35. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 k}$ in $\mathrm{CDCl}_{3}$.


Figure S36. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 k}$ in $\mathrm{CDCl}_{3}$.


Figure $\mathbf{S 3 7}{ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{1 k}$ in $\mathrm{CDCl}_{3}$.


Figure S38. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 1}$ in $\mathrm{CDCl}_{3}$.


Figure S39. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 1}$ in $\mathrm{CDCl}_{3}$.


Figure S40. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{1 1}$ in $\mathrm{CDCl}_{3}$.


Figure S41. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 m}$ in $\mathrm{CDCl}_{3}$.


Figure S42. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 m}$ in $\mathrm{CDCl}_{3}$.


Figure S43. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{1 m}$ in $\mathrm{CDCl}_{3}$.


Figure $\mathbf{S 4 4} .{ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 n}$ in $\mathrm{CDCl}_{3}$.


Figure $\mathbf{S 4 5 .}{ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 n}$ in $\mathrm{CDCl}_{3}$.


Figure S46. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{1 n}$ in $\mathrm{CDCl}_{3}$.


Figure S47. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 0}$ in $\mathrm{CDCl}_{3}$.


Figure S48. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 0}$ in $\mathrm{CDCl}_{3}$.


Figure S49. ${ }^{19} \mathrm{~F}$ NMR spectrum of 1 o in $\mathrm{CDCl}_{3}$.


Figure S50. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 p}$ in $\mathrm{CDCl}_{3}$.


Figure S51. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 p}$ in $\mathrm{CDCl}_{3}$.


Figure S52. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{1 p}$ in $\mathrm{CDCl}_{3}$.


Figure S53. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 q}$ in $\mathrm{CDCl}_{3}$.


Figure $\mathbf{S 5 4 .}{ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 q}$ in $\mathrm{CDCl}_{3}$.


Figure S55. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{1 q}$ in $\mathrm{CDCl}_{3}$.


Figure S56. ${ }^{1} \mathrm{H}$ NMR spectrum of $1 \mathbf{r}$ in $\mathrm{CDCl}_{3}$.


Figure S57. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 r}$ in $\mathrm{CDCl}_{3}$.


Figure S58. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{1 r}$ in $\mathrm{CDCl}_{3}$.


Figure S59. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 s}$ in $\mathrm{CDCl}_{3}$.


Figure S60. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{1 s}$ in $\mathrm{CDCl}_{3}$.


Figure S61. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{1 s}$ in $\mathrm{CDCl}_{3}$.


Figure S62. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{1 t}$ in $\mathrm{CDCl}_{3}$.


Figure S63. ${ }^{13} \mathrm{C}$ NMR spectrum of $1 \mathbf{t}$ in $\mathrm{CDCl}_{3}$.


Figure S64. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{1 t}$ in $\mathrm{CDCl}_{3}$.


Figure S65. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{3 a}(\mathrm{X}=\mathrm{F})$ in $\mathrm{CDCl}_{3}$.


Figure S66. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{3 a}(\mathrm{X}=\mathrm{F})$ in $\mathrm{CDCl}_{3}$.


Figure S67. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{3 a}(\mathrm{X}=\mathrm{F})$ in $\mathrm{CDCl}_{3}$.


Figure S68. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 a}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S69. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{2 a}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S70. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 b}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S71. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{2 b}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S72. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 c}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S73. ${ }^{13} \mathrm{C}$ NMR spectrum of $2 \mathbf{c}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S74. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 d}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S75. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{2 d}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S76. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 e}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S77. ${ }^{13} \mathrm{C}$ NMR spectrum of 2 e in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S78. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 f}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure $\mathbf{S 7 9 .}{ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{2 f}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S80. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 g}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S81. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{2 g}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S82. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 h}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S83. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{2 h}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S84. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 i}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S85. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{2 i}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S86. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 j}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S87. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{2 j}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S88. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 k}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S89. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{2 k}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S90. ${ }^{1} \mathrm{H}$ NMR spectrum of 21 in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure $\mathbf{S 9 1} .{ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{2 1}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S92. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 m}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S93. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{2 m}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S94. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 n}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S95. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{2 n}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S96. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 o}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S97. ${ }^{13} \mathrm{C}$ NMR spectrum of 2 o in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S98. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 p}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S99. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{2 p}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S100. ${ }^{19}$ F NMR spectrum of $\mathbf{2 p}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S101. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 q}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S102. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{2 q}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S103. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{2 q}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S104. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 r}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S105. ${ }^{13} \mathrm{C}$ NMR spectrum of 2 r in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S106. ${ }^{19} \mathrm{~F}$ NMR spectrum of 2 r in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S107. ${ }^{1} \mathrm{H}$ NMR spectrum of 2 s in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S108. ${ }^{13} \mathrm{C}$ NMR spectrum of 2 s in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S109. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{2 s}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S110. ${ }^{1} \mathrm{H}$ NMR spectrum of $\mathbf{2 t}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S111. ${ }^{13} \mathrm{C}$ NMR spectrum of $\mathbf{2 t}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.


Figure S112. ${ }^{19} \mathrm{~F}$ NMR spectrum of $\mathbf{2 t}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$.

## 4. Single-Crystal X-ray Structure Determination

Single crystal X-ray diffraction data of diaryl dihydrophenazines were obtained by using synchrotron radiation of BL40XU (= $0.83136 \AA$ ) and BL02B1 (= $0.69980 \AA$ ) beam lines in SPring-8 (Hyogo, Japan) with use of Rigaku Saturn 724 and Mercury II CCD detectors, respectively. The molecular structures of diaryl dihydrophenazines 2a-g, 2i-m, 20-t, and the crystallographic data were summarized as Figures S113-S130 with Cambridge Crystallographic Data Centre: Deposition number.


Figure S113. Crystal structure of 2a.


Figure S114. Crystal structure of 2b.

$$
\begin{aligned}
& R_{\mathrm{all}}=0.1060 \\
& \mathrm{w} R_{2}=0.3836 \\
& \mathrm{GOF}=1.267
\end{aligned}
$$



Figure S115. Crystal structure of 2c.


Figure S116. Crystal structure of 2d.


Figure S117. Crystal structure of $\mathbf{2 e}$.
monoclinic, P21/c (\#14)
$R_{a| |}=0.0574$
$\mathrm{w} R_{2}=0.1182$
GOF $=1.053$
CCDC registry number is 1878778 .
Figure S118. Crystal structure of $\mathbf{2 f}$.


Figure S119. Crystal structure of $\mathbf{2 g}$.
monoclinic, P21/n (\#14)
$R_{a / l}=0.0605$
$\mathrm{w} R_{2}=0.1503$
$G O F=1.034$
CCDC registry number is 1878779 .


Figure S120. Crystal structure of $\mathbf{2 i}$.


Figure S121. Crystal structure of $\mathbf{2 j}$.
monoclinic, P21/c (\#14)
$R_{a / l}=0.0371$
$w R_{2}=0.1264$
$G O F=1.010$
CCDC registry number is 1878781 .

Figure S122. Crystal structure of $\mathbf{2 k}$.


Figure S123. Crystal structure of $\mathbf{2 1}$.


Figure S124. Crystal structure of $\mathbf{2 m}$.


CCDC registry number is 1878784 .

Figure S125. Crystal structure of $\mathbf{2 0}$.


Figure S126. Crystal structure of 2p.


CCDC registry number is 1878785 .
Figure S127. Crystal structure of $\mathbf{2 q}$.


Figure S128. Crystal structure of 2r.


Figure S129. Crystal structure of 2s.


CCDC registry number is 1878787 .
Figure S130. Crystal structure of $\mathbf{2 t}$.


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