## Supporting Information

# Tailoring Sensors and Solvents for Optimal Analysis of Complex Mixtures Via Discriminative ${ }^{19}$ F NMR Chemosensing 

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## General Methods and Materials:

Materials: All reactions were carried out under nitrogen using standard Schlenk techniques unless otherwise noted. All solvents were of ACS reagent grade or better unless otherwise noted. Silica gel ( $60 \mu \mathrm{~m}$ ) was purchased from SiliCycle Inc. All reagent grade materials were purchased from commercial sources and used without further purification.

NMR Spectroscopy: ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra for some compounds were acquired in $\mathrm{CDCl}_{3}$ and others which are difficult to dissolve in $\mathrm{OS}\left(\mathrm{CD}_{3}\right)_{2}, \mathrm{CD}_{3} \mathrm{CN}$ on a Bruker Avance 400 MHz or 600 MHz Spectrometer. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) and referenced with Solvent Peak for ${ }^{1} \mathrm{H}$ NMR. $\mathrm{CDCl}_{3}$, or $\mathrm{SO}\left(\mathrm{CD}_{3}\right)_{2}$ for ${ }^{13} \mathrm{C}$ NMR and $\mathrm{CFCl}_{3}$ for ${ }^{19} \mathrm{~F}$ NMR.

## General procedure for NMR experiments:

For Figures 2, at ambient temperature, complex $\mathbf{3}(\mathbf{3 a}, \mathbf{3 b}, \mathbf{3 c}, \mathbf{3 d}, \mathbf{3 e}$, or $\mathbf{3 f}$ ) was added to a mixture of phenethylamine, tyramine, tryptamine, and serotonin in $\mathrm{CDCl}_{3}$, and ${ }^{19} \mathrm{~F}$ NMR spectra were taken using a 600 MHz NMR spectrometer (typically 64 scans).

For Figure 3, complex $\mathbf{3 b}, \mathbf{3 g}$, or $\mathbf{3 h}$ was added to a mixture of phenethylamine, tyramine, tryptamine, and serotonin in $\mathrm{CDCl}_{3}$, and ${ }^{19} \mathrm{~F}$ NMR spectra were taken using a 600 MHz NMR spectrometer ( 64 scans).

For Figure 4, complex 3c was added to a mixture of phenethylamine, tyramine, tryptamine, and serotonin in diverse solvents, and ${ }^{19} \mathrm{~F}$ NMR spectra were taken using a 600 MHz NMR spectrometer ( 64 scans).

For Figure 5, complex 3a or 3c was mixture with different analytes in chlorobenzene:methanol (2:1), and ${ }^{19} \mathrm{~F}$ NMR spectra were taken using a 600 MHz NMR spectrometer (256 scans).

Infrared Spectroscopy: Infrared spectra were recorded on a HP5973 Fourier Transform Infrared Spectrometer (FT-IR).

Mass Spectrometry: High-resolution mass spectra (HRMS) were obtained at the SIOC Instrumentation Facility employing ESI or EI as the ionization technique.

General procedure for the coupling between 3,4,5-trifluoro-nitrobenzene and various nucleophiles.


A mixture of phenol ( $500 \mathrm{mg}, 5.31 \mathrm{mmol}, 1.0$ equiv) and $\mathrm{NaH}(60 \mathrm{w} / \mathrm{w} \%)(425 \mathrm{mg}$, $6.38 \mathrm{mmol}, 1.2$ equiv) was stirred in DMF ( 10 mL ) under $\mathrm{N}_{2}$ for 30 min before the addition of $3,4,5$-trifluoro-nitrobenzene ( $1.13 \mathrm{~g}, 6.38 \mathrm{mmol}, 1.2$ equiv). The mixture was stirred at rt for 5 hours. Then water $(10 \mathrm{~mL})$ was added to quench the reaction. The mixture was then extracted with EtOAc $(3 \times 10 \mathrm{~mL})$. The combined organic phase was washed with brine, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, and concentrated in vacuo. The residue was purified by silica gel chromatography $\left(\mathrm{PE} / \mathrm{CH}_{2} \mathrm{Cl}_{2}, 9: 1\right)$ to afford $\mathbf{1 b}$ as yellow solid (1.2 g, yield: $89 \%$ ). M.P. $75-77^{\circ} \mathrm{C}$. IR (KBr): 3419, 3086, 3047, 1591, 1536, 1501, 1488, $1459,1350,1236,1194,1046,878,856,777,748,715,684 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR $(400 \mathrm{MHz}$, Chloroform- $d$ ) $\delta 7.94(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.33(\mathrm{dd}, J=8.7,7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.14(\mathrm{t}, J=7.4$ $\mathrm{Hz}, 1 \mathrm{H}), 6.96(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{19}$ F NMR ( 376 MHz , Chloroform- $d$ ) $\delta-120.56$ (d, $J$ $=7.0 \mathrm{~Hz}) .{ }^{13} \mathrm{C}$ NMR ( 101 MHz , Chloroform- $d$ ) $\delta 156.85,155.43(\mathrm{dd}, J=256.5,5.0 \mathrm{~Hz}$ ), $143.51(\mathrm{t}, \mathrm{J}=9.2 \mathrm{~Hz}), 137.86(\mathrm{t}, J=14.5 \mathrm{~Hz})$, 129.90, 124.11, 115.74, $109.09(\mathrm{~m})$. HRMS (DART): calc for $\mathrm{C}_{12} \mathrm{H}_{7} \mathrm{O}_{3} \mathrm{NF}_{2}[\mathrm{M}]^{+} 251.0389$, found 251.0390.


800 mg , yield: $84 \%$. Colorless oil. IR (film): 3097, 2989, 1532, 1504,1476, 1391, $1347,1245,1044,1018,881,744 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz , Chloroform-d) $\delta 7.87-$
$7.81(\mathrm{~m}, 2 \mathrm{H}), 4.39(\mathrm{q}, J=7.0 \mathrm{~Hz}, 2 \mathrm{H}), 1.43(\mathrm{t}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , Chloroform- $d$ ) $\delta-111.18\left(\mathrm{~d}, J=8.1 \mathrm{~Hz}\right.$ ). ${ }^{13} \mathrm{C}$ NMR ( 151 MHz , Chloroform- $d$ ) $\delta 154.47$ (dd, $J=252.3,6.5 \mathrm{~Hz}), 141.71(\mathrm{t}, J=13.4 \mathrm{~Hz}), 141.08(\mathrm{t}, J=10.4 \mathrm{~Hz}), 108.95(\mathrm{~m})$, $70.74(\mathrm{t}, J=4.0 \mathrm{~Hz})$, 15.51. $\mathrm{HRMS}:$ calc for $\mathrm{C}_{8} \mathrm{H}_{8} \mathrm{O}_{3} \mathrm{NF}_{2}[\mathrm{M}+\mathrm{H}]^{+}$204.0467, found 204.0467.

1.3 g , yield: $87 \%$. Orange solid. M.P.: $105-107^{\circ} \mathrm{C}$. IR (KBr): 2986, 2900, 1588,1520 , 1483, 1459, 1438, 1408, 1321, 1271, $1178 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 500 MHz , Chloroform- $d$ ) $\delta$ $7.86(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.30(\mathrm{dd}, J=8.4,7.5 \mathrm{~Hz}, 4 \mathrm{H}), 7.12(\mathrm{t}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.02$ $(\mathrm{d}, J=7.6 \mathrm{~Hz}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 126 MHz , Chloroform- $d$ ) $\delta 158.36$ (dd, $J=257.0,6.3$ $\mathrm{Hz})$, 145.67, $143.49(\mathrm{t}, J=10.5 \mathrm{~Hz}), 129.80(\mathrm{t}, J=13.3 \mathrm{~Hz}), 129.47,124.21,122.21$, 109.21 (m). HRMS (ESI): calc for $\mathrm{C}_{18} \mathrm{H}_{13} \mathrm{O}_{2} \mathrm{~N}_{2} \mathrm{~F}_{2}[\mathrm{M}+\mathrm{H}]^{+} 327.0940$, found 327.0937.


1 g
1.96 g, yield: $87 \%$. Red solid. M.P.: $86-88^{\circ} \mathrm{C}$. IR (KBr): 2985, 2917, 1605, 1506, 1446, 1364, 1337, 1227, 1170, 1069, 1020, 963, 883, $787 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 600 MHz , Chloroform- $d$ ) $\delta 7.74$ (d, $J=10.5 \mathrm{~Hz}, 2 \mathrm{H}$ ), 3.06 (s, 6H). ${ }^{19} \mathrm{~F}$ NMR ( 565 MHz , Chloroform- $d$ ) $\delta-118.58--118.69$ (m). ${ }^{13} \mathrm{C}$ NMR ( 151 MHz , Chloroform- $d$ ) $\delta 154.23$ (dd, $J=248.7,9.1 \mathrm{~Hz}), 138.28,135.94(\mathrm{t}, J=11.6 \mathrm{~Hz}), 109.86-108.11(\mathrm{~m}), 43.02(\mathrm{t}$, $J=5.2 \mathrm{~Hz}$ ). HRMS (ESI): calc for $\mathrm{C}_{8} \mathrm{H}_{9} \mathrm{O}_{2} \mathrm{~N}_{2} \mathrm{~F}_{2}[\mathrm{M}+\mathrm{H}]^{+}$203.0627, found 203.0628 .


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1.2 g, yield: $87 \%$. Light green solid. M.P.: $54-56^{\circ} \mathrm{C}$. IR ( KBr ): $3665,3444,3287,2980$, 2021, 1682, 1622, 1493, 1427, 1230, 1035, 853, 746, 625, $609 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR (400 MHz, Chloroform-d) $\delta 7.98-7.92(\mathrm{~m}, 2 \mathrm{H}), 7.33$ (dd, $J=7.2,2.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.13-7.03$ $(\mathrm{m}, 2 \mathrm{H}), 6.55(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.48(\mathrm{~h}, J=6.9 \mathrm{~Hz}, 1 \mathrm{H}), 1.30(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , Chloroform- $d$ ) $\delta-121.16\left(\mathrm{~d}, J=7.1 \mathrm{~Hz}\right.$ ). ${ }^{13} \mathrm{C}$ NMR ( 151 MHz , Chloroform- $d$ ) $\delta 155.30(\mathrm{dd}, J=256.1,5.2 \mathrm{~Hz}), 154.35,143.20(\mathrm{t}, J=9.5 \mathrm{~Hz}), 138.42$ ( $\mathrm{t}, J=14.2 \mathrm{~Hz}$ ), 137.49, 127.22, 126.73, 124.30, 113.67, 109.18 (m), 27.23, 22.65. HRMS (EI): calc for $\mathrm{C}_{15} \mathrm{H}_{13} \mathrm{O}_{3} \mathrm{NF}_{2}[\mathrm{M}]^{+} 293.0858$, found 293.0864.

1.5 g, yield: $85 \%$. Yellow solid. M.P.: $112-114^{\circ} \mathrm{C}$. IR (KBr): 2965, 2870, 1630, 1534, $1502,1488,1450,1350,1244,1175,1082,1050,886,778,747 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR (400 MHz, Chloroform- $d$ ) $\delta 7.73$ (d, $J=9.6 \mathrm{~Hz}, 2 \mathrm{H}$ ), 6.73 (t, $J=2.1 \mathrm{~Hz}, 2 \mathrm{H}$ ), 1.73 (t, $J=$ $2.6 \mathrm{~Hz}, 3 \mathrm{H}), 1.22(\mathrm{~s}, 18 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , Chloroform- $d$ ) $\delta-100.39(\mathrm{~d}, J=9.5$ Hz ). ${ }^{13} \mathrm{C}$ NMR ( 151 MHz , Chloroform- $d$ ) $\delta 185.54$, 161.12 (dd, $J=255.5,8.8 \mathrm{~Hz}$ ), $147.14(\mathrm{t}, J=12.4 \mathrm{~Hz}), 145.55,142.11(\mathrm{t}, J=2.5 \mathrm{~Hz}), 126.10,108.77(\mathrm{~d}, J=33.9 \mathrm{~Hz})$, $42.28(\mathrm{t}), 34.83,29.27,26.91(\mathrm{t}, J=5.2 \mathrm{~Hz})$. HRMS (EI): calc for $\mathrm{C}_{21} \mathrm{H}_{25} \mathrm{O}_{3} \mathrm{NF}_{2}[\mathrm{M}]^{+}$ 377.1797, found 377.1804.

## General procedure for the reduction of various nitrobenzenes.



To a solution of $\mathbf{1 b}(0.50 \mathrm{~g}, 1.99 \mathrm{mmol}, 1.0$ equiv) in EtOH ( 16 mL ) was added tin(II) chloride dihydrate ( $1.97 \mathrm{~g}, 8.87 \mathrm{mmol}, 4.0$ equiv) and concentrated hydrochloric acid $(1 \mathrm{~mL})$. After heated to reflux for 6 h , the mixture was cooled to room temperature, diluted with water $(10 \mathrm{~mL})$. The pH of the solution was adjusted pH with sodium hydroxide solution and the mixture was extracted with EtOAc $(3 \times 20 \mathrm{~mL})$. The combined organic layers were dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$, filtered and concentrated under reduced pressure to give $\mathbf{2 b}$ as a white solid ( $0.40 \mathrm{~g}, 1.81 \mathrm{mmol}$, yield: $90 \%$ ). M.P.: $73-75^{\circ} \mathrm{C}$. IR (KBr): $3419,1591,1536,1501,1488,1350,1236,1046,878,777$, $748,715 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta 7.30-7.23(\mathrm{~m}, 2 \mathrm{H}), 7.01(\mathrm{t}, J=$ $7.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.92(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 2 \mathrm{H}), 6.28(\mathrm{~d}, J=9.4 \mathrm{~Hz}, 2 \mathrm{H}), 3.74(\mathrm{~s}, 2 \mathrm{H}) .{ }^{19}$ F NMR ( 376 MHz , Chloroform- $d$ ) $\delta-126.80\left(\mathrm{~d}, J=9.0 \mathrm{~Hz}\right.$ ) ${ }^{13} \mathrm{C}$ NMR ( 151 MHz , Chloroformd) $\delta 158.39,156.82(\mathrm{dd}, J=247.6,7.0 \mathrm{~Hz}), 144.31(\mathrm{t}, J=12.3 \mathrm{~Hz}), 129.53$, $122.62(\mathrm{t}$, $J=15.7 \mathrm{~Hz}) .122 .45,114.94,98.81(\mathrm{~m})$. HRMS (ESI): calc for $\mathrm{C}_{12} \mathrm{H}_{10} \mathrm{ONF}_{2}[\mathrm{M}+\mathrm{H}]^{+}$ 222.0725 , found 222.0727 .


300 mg , yield: $87 \%$. Yellow solid. M.P.: $90-92{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta 6.22-6.15(\mathrm{~m}, 2 \mathrm{H}), 4.05(\mathrm{q}, J=7.0 \mathrm{~Hz}, 2 \mathrm{H}), 1.35(\mathrm{t}, J=7.0 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR (376 MHz, Chloroform- $d$ ) $\delta-128.23(\mathrm{~d}, J=9.4 \mathrm{~Hz}) .{ }^{13} \mathrm{C}$ NMR ( 151 MHz , Chloroform- $d$ ) $\delta$
154.47 (dd, $J=252.3,6.5 \mathrm{~Hz}), 141.71(\mathrm{t}, J=13.4 \mathrm{~Hz}), 141.08(\mathrm{t}, J=10.4 \mathrm{~Hz}), 108.95$ (m), $70.74\left(\mathrm{t}, J=4.0 \mathrm{~Hz}\right.$ ), 15.51. HRMS (ESI): calc for $\mathrm{C}_{8} \mathrm{H}_{10} \mathrm{ONF}_{2}[\mathrm{M}+\mathrm{H}]^{+}$174.0725, found 174.0726 .


2c
400 mg , yield: $88 \%$. Brown solid. M.P.: $110-112{ }^{\circ} \mathrm{C}$. IR ( KBr ): 3483, 2922, 1936, 1646, 1586, 1513, 1319, 1294, 1011, 831, 751, 729, 695, $563 \mathrm{~cm}^{-1},{ }^{1} \mathrm{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta 7.28-7.19(\mathrm{~m}, 4 \mathrm{H}), 7.04(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 4 \mathrm{H}), 6.96(\mathrm{t}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H})$, $6.26(\mathrm{~d}, J=9.6 \mathrm{~Hz}, 2 \mathrm{H}), 3.62(\mathrm{~s}, 2 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , Chloroform- -d ) $\delta-118.28$ $(\mathrm{d}, J=9.5 \mathrm{~Hz}) .{ }^{13} \mathrm{C}$ NMR ( 151 MHz , Chloroform- $d$ ) $\delta 161.50(\mathrm{dd}, J=249.3,7.9 \mathrm{~Hz}$ ), $146.79,146.60(\mathrm{t}), 129.08,121.90,120.60,112.84(\mathrm{t}, J=16.4 \mathrm{~Hz}), 98.87(\mathrm{~m})$. HRMS (ESI): calc for $\mathrm{C}_{18} \mathrm{H}_{15} \mathrm{~N}_{2} \mathrm{~F}_{2}[\mathrm{M}+\mathrm{H}]^{+}$297.1198, found 297.1197.

$2 g$
379 mg , yield: $86 \%$. Yellow solid. M.P.: $86-88^{\circ} \mathrm{C}$. IR (KBr): 3431, 3330, 3208, 2938, $2870,1651,1508,1457,1450,1172,1156,1043,1013,1002,941,829,638 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR (400 MHz, Chloroform-d) $\delta 6.20-6.09$ (m, 2H), 3.66 ( $\mathrm{s}, 2 \mathrm{H}$ ), 2.76 (t, $J=1.2 \mathrm{~Hz}$, $6 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , Chloroform- $d$ ) $\delta-119.63$ (d, $J=10.4 \mathrm{~Hz}$ ). ${ }^{13} \mathrm{C}$ NMR ( 151 MHz, Chloroform- $d$ ) $\delta 160.83(\mathrm{dd}, J=246.3,9.9 \mathrm{~Hz}), 144.14(\mathrm{~d}, J=13.6 \mathrm{~Hz}), 120.12$, $98.95-98.56(\mathrm{~m}), 44.63-44.40(\mathrm{~m})$. HRMS (ESI): calc for $\mathrm{C}_{8} \mathrm{H}_{11} \mathrm{~N}_{2} \mathrm{~F}_{2}[\mathrm{M}+\mathrm{H}]^{+}$ 173.0885, found173.0885.


2m
470 mg , yield: $89 \%$, colorless oil. IR (film): 3396, 2962, 2925, 2852, 1647, 1603, 1515, $1487,1468,1234,1182,1161,1083,1027,863,828,753 \mathrm{c} \mathrm{m}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta 7.32-7.22(\mathrm{~m}, 1 \mathrm{H}), 7.08-6.96(\mathrm{~m}, 2 \mathrm{H}), 6.57(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H})$, $6.33(\mathrm{~d}, J=9.4 \mathrm{~Hz}, 2 \mathrm{H}), 3.70(\mathrm{~s}, 2 \mathrm{H}) 3.57(\mathrm{p}, J=6.9 \mathrm{~Hz}, 1 \mathrm{H}), 1.31(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H})$. ${ }^{19}$ F NMR ( 376 MHz , Chloroform- $d$ ) $\delta-126.83$ (d, $J=9.2 \mathrm{~Hz}$ ). ${ }^{13} \mathrm{C}$ NMR ( 101 MHz , Chloroform- $d$ ) $\delta 158.11(\mathrm{~d}, J=7.1 \mathrm{~Hz}), 155.65(\mathrm{~d}, J=7.7 \mathrm{~Hz}), 144.10(\mathrm{t}, J=12.3 \mathrm{~Hz})$, 136.80, $126.54(\mathrm{~d}, J=5.0 \mathrm{~Hz}$ ), 122.50, 112.55, 98.92 (m), 27.11, 22.64. HRMS (EI): calc for $\mathrm{C}_{15} \mathrm{H}_{15} \mathrm{ONF}_{2}[\mathrm{M}]^{+}$263.1116, found 263.1120 .


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400 mg , yield: $86 \%$. M.P.: $149-151^{\circ} \mathrm{C}$. Yellow solid. IR (KBr): 2777, 1653, 1621, 1455, 1369, 1164, 1038, 992, 907, 825, $774 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz , Chloroform-d) $\delta 6.77$ $(\mathrm{t}, J=2.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.28(\mathrm{~d}, J=11.3 \mathrm{~Hz}, 2 \mathrm{H}), 1.64(\mathrm{t}, J=2.3 \mathrm{~Hz}, 3 \mathrm{H}), 1.23(\mathrm{~s}, 18 \mathrm{H})$. ${ }^{19}$ F NMR ( 376 MHz , Chloroform-d) $\delta-105.80 .{ }^{13} \mathrm{C}$ NMR ( 126 MHz , Chloroform- $d$ ) $\delta$ $186.32,162.18(\mathrm{dd}, J=247.2,11.6 \mathrm{~Hz}), 146.97(\mathrm{t}, J=14.9 \mathrm{~Hz}), 145.31(\mathrm{~d}, J=2.5 \mathrm{~Hz})$, 143.45, 107.03, 100.29 - 96.83 (m), 41.32, 34.54, 29.36. HRMS (EI): calc for $\mathrm{C}_{21} \mathrm{H}_{27} \mathrm{ONF}_{2}[\mathrm{M}]^{+} 347.2055$, found 347.2060.

## Procedure for the preparation of aniline $\mathbf{2 h}$.



Bromo-3,5-difluoroaniline ( $3.12 \mathrm{~g}, 15.0 \mathrm{mmol}, 1.0$ equiv) and Xphos Pd G3 ( 1.27 g , $1.5 \mathrm{mmol}, 10 \mathrm{~mol} \%$ ) was added to a Schlenk tube ( 100 mL ), which was degassed and refilled with nitrogen before the addition of anhydrous 1,4 -dioxane ( 50 mL ). Then the $\mathrm{ZnMe}_{2}$ ( 1.0 M in Hexane, $30 \mathrm{~mL}, 30 \mathrm{mmol}, 2.0$ equiv) was added to the solution. The reaction was heated at $100^{\circ} \mathrm{C}$ for 15 h . After the reaction cooled, MeOH was added to quench the excess $\mathrm{ZnMe}_{2}$. EtOAc was added to dilute the reaction and the organic phase was washed with water and brine successively. The organic layer was dried with $\mathrm{Na}_{2} \mathrm{SO}_{4}$ for 0.5 h and then concentrated under reduced pressure, the residue was subject to purification using column chromatography (silica gel, 20:1 PE:ethyl acetate) to yield the desired product $\mathbf{2 h}$ as a yellowish solid ( 1.14 g , yield: $53 \%$ ). M.P.: $39-41^{\circ} \mathrm{C}$. IR (KBr): 3850, 3409, 2932, 2830, 1569, 1588, 1511, 1450, 1365, 1324, 1142, 1105, 823, $625,513 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta 6.21-6.10(\mathrm{~m}, 2 \mathrm{H}), 3.68(\mathrm{~s}, 2 \mathrm{H})$, $2.03(\mathrm{t}, J=1.7 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , Chloroform- $d$ ) $\delta-115.46(\mathrm{~d}, J=7.8 \mathrm{~Hz}$ ). ${ }^{13} \mathrm{C}$ NMR ( 151 MHz , Chloroform- $d$ ) $\delta 162.27$ (dd, $J=242.9$, 12.3 Hz ), $145.72(\mathrm{t}, J=$ $13.6 \mathrm{~Hz}), 102.51(\mathrm{t}, J=21.9 \mathrm{~Hz}), 78.21-76.12(\mathrm{~m}), 6.33(\mathrm{t}, J=3.8 \mathrm{~Hz})$. HRMS (ESI): calc for $\mathrm{C}_{7} \mathrm{H}_{8} \mathrm{NF}_{2}[\mathrm{M}+\mathrm{H}]^{+}$144.0619, found 144.0619.

## Procedure for the preparation of aniline $\mathbf{2 j}$.



Schlenk tube ( 50 mL ), which was degassed and refilled with nitrogen before the addition of anhydrous 1,2-dimethoxyethane ( 20 mL ). Then Benzophenone imine ( 1.81 $\mathrm{g}, 10 \mathrm{mmol}, 1.25$ equiv) was added to the solution using a syringe and the reaction was
heated at $110^{\circ} \mathrm{C}$ for 8 h . After the reaction cooled, $\mathrm{H}_{2} \mathrm{O}$ was added, and washed with ethyl acetate for three times. The combined EtOAc phase was washed with brine, dried with $\mathrm{Na}_{2} \mathrm{SO}_{4}$ for 0.5 h and then concentrated under reduced pressure, the residue was subject to purification using column chromatography (silica gel, 1:1 DCM:PE) to yield the crude coupling product. Then the crude product was dissolved in $\mathrm{MeOH}(10 \mathrm{~mL})$ and water $(1.0 \mathrm{~mL})$, then trifluoromethanesulfonic acid $(0.5 \mathrm{~mL})$ was added and the reaction was heated at $60^{\circ} \mathrm{C}$ for 0.5 h . The solvent was evaporated and residue was dissolved using ethyl acetate and $\mathrm{NaHCO}_{3}$ solution. Then the organic phase was separated and washed with brine. The organic phase was then concentrated and the residue was subject to purification using column chromatography (silica gel, 1:1 PE:ethyl acetate) to yield the desired product $\mathbf{2 j}$ as a yellow solid ( 554 mg , yield: $40 \%$ ) M.P.: $185-187{ }^{\circ} \mathrm{C}$. IR (KBr): 3512, 3406, 3087, 1633, 1576, 1506, 1308, 1223, 1205, $1076,1001,853 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 600 MHz , Acetone- $d_{6}$ ) $\delta 6.43(\mathrm{~d}, J=12.3 \mathrm{~Hz}, 2 \mathrm{H}$ ), $6.40(\mathrm{~s}, 2 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , Acetone- $d_{6}$ ) $\delta-119.42\left(\mathrm{~d}, J=12.3 \mathrm{~Hz}\right.$ ). ${ }^{13} \mathrm{C}$ NMR ( 151 MHz , Acetone- $d_{6}$ ) $\delta 157.46$ (dd, $J=255.6,4.4 \mathrm{~Hz}$ ), 154.38 (t, $J=15.1 \mathrm{~Hz}$ ), 96.81 - $96.21(\mathrm{~m}) .{ }^{13} \mathrm{C}$ NMR ( 151 MHz , Acetone- $d_{6}$ ) $\delta 157.46(\mathrm{dd}, J=255.5,4.5 \mathrm{~Hz}$ ), 154.38 (t, $J=15.1 \mathrm{~Hz}$ ), 118.39, 96.49 (dd, $J=24.1,2.0 \mathrm{~Hz}$ ). HRMS (ESI): calc for $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{O}_{2} \mathrm{~N}_{2} \mathrm{~F}_{2}$ $[\mathrm{M}+\mathrm{H}]^{+}$175.0314, found 175.0313 .

## Typical procedure for the preparation of pincer ligands 4.



Under a $\mathrm{N}_{2}$ atmosphere, a solution of 2,6-pyridinedicarbonyl dichloride ( $93 \mathrm{mg}, 0.45$ mmol, 1.0 equiv) and 4-phenoxyphenylamine ( $200 \mathrm{mg}, 4.9 \mathrm{mmol}, 2.0$ equiv) in toluene $(10 \mathrm{~mL})$ was refluxed for 3 h before the reaction was cooled to room temperature. The white precipitate was filtered off and washed with toluene ( 20 mL ) and hexane ( 20 mL ),
and then dried under air to give the product $\mathbf{4 b}$ as a white solid ( $240 \mathrm{mg}, 0.42 \mathrm{mmol}$, yield: $93 \%$ ). M.P. $>250^{\circ} \mathrm{C} . \operatorname{IR}(\mathrm{KBr}): 3684,2973,2899,1681,1666,1531,1507,1487$, 1455, 1407, 1231, 1177, 1042, 891, 863, 846, 745, 685, 627, $610 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR (400 MHz, DMSO- $d_{6}$ ) $\delta 11.18(\mathrm{~s}, 2 \mathrm{H}), 8.41(\mathrm{~d}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H}), 8.33(\mathrm{dd}, J=8.6,6.8 \mathrm{~Hz}$, $1 \mathrm{H}), 7.90$ (d, $J=10.2 \mathrm{~Hz}, 4 \mathrm{H}), 7.41-7.30(\mathrm{~m}, 4 \mathrm{H}), 7.09(\mathrm{t}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.96(\mathrm{~d}, J$ $=8.1 \mathrm{~Hz}, 4 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , Chloroform- $d$ ) $\delta-124.18\left(\mathrm{~d}, J=8.9 \mathrm{~Hz}\right.$ ) ${ }^{13} \mathrm{C}$ NMR ( 101 MHz, DMSO- $d_{6}$ ) $\delta 162.41,157.83,155.64(\mathrm{dd}, J=245.9,6.6 \mathrm{~Hz}$ ), 148.60, 140.87, $136.44(\mathrm{t}, J=12.9 \mathrm{~Hz}), 130.51,126.71(\mathrm{t}, J=15.8 \mathrm{~Hz}), 126.36,123.58,115.17,105.55$ ( $\mathrm{m}, J=26.0 \mathrm{~Hz}$ ). HRMS (ESI): calc for $\mathrm{C}_{31} \mathrm{H}_{20} \mathrm{O}_{4} \mathrm{~N}_{3} \mathrm{~F}_{4}[\mathrm{M}+\mathrm{H}]^{+}$574.1384, found 574.1390.


240 mg , yield: $96 \%$. White solid. M.P. > $250{ }^{\circ} \mathrm{C}$. IR (KBr): 2830, 2014, 1897, 1685, $1513,1366,1223,1180,1035,899,847,774,615 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 600 MHz , DMSO$\left.d_{6}\right) \delta 11.05(\mathrm{~s}, 2 \mathrm{H}), 8.41(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 2 \mathrm{H}), 8.35-8.29(\mathrm{~m}, 1 \mathrm{H}), 7.76(\mathrm{~d}, J=10.2 \mathrm{~Hz}$, $4 \mathrm{H}), 4.16(\mathrm{q}, J=7.0 \mathrm{~Hz}, 4 \mathrm{H}), 1.32(\mathrm{t}, J=7.0 \mathrm{~Hz}, 6 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 565 MHz , DMSO- $d_{6}$ ) $\delta-127.51(\mathrm{~d}, J=10.4 \mathrm{~Hz}) .{ }^{13} \mathrm{C}$ NMR ( 126 MHz , Acetone- $d_{6}$ ) $\delta 161.50,155.95(\mathrm{dd}, J$ $=244.1,7.6 \mathrm{~Hz}), 148.74,140.01,133.87(\mathrm{t}, J=13.1 \mathrm{~Hz}), 131.39(\mathrm{t}, J=15.0 \mathrm{~Hz}), 125.59$, $104.37(\mathrm{~m}), 70.27(\mathrm{t}, J=2.6 \mathrm{~Hz}), 14.79$. HRMS (ESI): calc for $\mathrm{C}_{23} \mathrm{H}_{20} \mathrm{O}_{4} \mathrm{~N}_{3} \mathrm{~F}_{4}[\mathrm{M}+\mathrm{H}]^{+}$ 478.1384, found 478.1386 .


228 mg , yield: $95 \%$. Green solid. M.P. $>250^{\circ} \mathrm{C}$. IR ( KBr ): 3688, 3673, 3658, 3365, 2974, 2900, 1589, 1531,1499, 1487, 1449, 1379, 1347, 1233, 1194, 1182, 1043, 877, 854, 775, 738, 715, $683 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz, DMSO- $d_{6}$ ) $\delta 11.17(\mathrm{~s}, 2 \mathrm{H}), 8.44-$ 8.37 (m, 2H), 8.32 (dd, $J=8.6,6.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.83$ (d, $J=10.6 \mathrm{~Hz}, 4 \mathrm{H}), 7.32-7.19$ (m, 8 H ), 6.98 (td, $J=7.4,1.3 \mathrm{~Hz}, 4 \mathrm{H}$ ), $6.94(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 8 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , DMSO- $d_{6}$ ) $\delta-117.67(\mathrm{~d}, J=10.5 \mathrm{~Hz}) .{ }^{13} \mathrm{C}$ NMR ( 126 MHz , Acetone- $d_{6}$ ) $\delta 163.48$, 162.11 (dd, $J=248.1,7.4 \mathrm{~Hz}$ ), 150.45, 148.21, $142.01,139.85(\mathrm{t}, J=13.7 \mathrm{~Hz}), 131.07$, 127.63, 124.23, 122.42, $119.88(\mathrm{t}, J=15.8 \mathrm{~Hz}), 106.36(\mathrm{~m})$. HRMS (ESI): calc for $\mathrm{C}_{43} \mathrm{H}_{30} \mathrm{O}_{2} \mathrm{~N}_{5} \mathrm{~F}_{4}[\mathrm{M}+\mathrm{H}]^{+} 724.2330$, found 724.2337.


263 mg , yield: $93 \%$. White solid. M.P. > $250{ }^{\circ} \mathrm{C}$. IR (KBr): 3528, 2832, 1609, 1511, 1438, 1366, 1232, 1044, 868, 775, 748, $699 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 600 MHz , DMSO- $d_{6}$ ) $\delta$ $10.56(\mathrm{~s}, 2 \mathrm{H}), 7.69(\mathrm{~d}, J=52.4 \mathrm{~Hz}, 3 \mathrm{H}), 7.24(\mathrm{~s}, 4 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , Chloroformd) $\delta 111.45(\mathrm{~d}, J=8.2 \mathrm{~Hz}) .{ }^{13} \mathrm{C}$ NMR ( $\left.126 \mathrm{MHz}, \mathrm{DMSO}-d_{6}\right) \delta 162.57,158.43$ (dd, $J=$ $245.1,5.2 \mathrm{~Hz}), 148.46,140.88,138.99(\mathrm{t}, J=13.1 \mathrm{~Hz}), 126.50,105.01(\mathrm{dd}, J=26.6$, 2.6 Hz ), 103.33 (t, $J=21.5 \mathrm{~Hz}$ ). HRMS (ESI): calc for $\mathrm{C}_{19} \mathrm{H}_{10} \mathrm{O}_{2} \mathrm{~N}_{3} \mathrm{Cl}_{2} \mathrm{~F}_{4}[\mathrm{M}+\mathrm{H}]^{+}$ 458.0082, found 458.0081 .


227 mg , yield: $90 \%$. White solid. M.P. > $250{ }^{\circ} \mathrm{C}$. IR (KBr): 3686, 3673, 3660, 3361, 2972, 2900, 1698,1670, 1514, 1473, 1407, 1259, 1163, 1076, 1051, 1025, 888, 848, 834, 743, 645, 624, $560 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 600 MHz, DMSO-d6) $\delta 11.24(\mathrm{~s}, 2 \mathrm{H}), 8.42(\mathrm{~d}$, $J=7.7 \mathrm{~Hz}, 2 \mathrm{H}), 8.36-8.32(\mathrm{~m}, 1 \mathrm{H}), 7.82(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 4 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , DMSO- $d_{6}$ ) $\delta$-93.30 (d, $J=8.9 \mathrm{~Hz}$ ). ${ }^{13} \mathrm{C}$ NMR ( 101 MHz , DMSO- $d_{6}$ ) $\delta 162.54,162.52$ (dd, $J=240.1,9.1 \mathrm{~Hz}), 148.53,141.14(\mathrm{t}, J=14.1 \mathrm{~Hz}), 140.88,126.48,104.20(\mathrm{dd}, J=$ $30.6,2.1 \mathrm{~Hz}), 66.00(\mathrm{t}, J=31.3 \mathrm{~Hz})$. HRMS (ESI): calc for $\mathrm{C}_{19} \mathrm{H}_{9} \mathrm{O}_{2} \mathrm{~N}_{3} \mathrm{~F}_{4} \mathrm{I}_{2} \mathrm{Na}[\mathrm{M}+\mathrm{Na}]^{+}$ 663.8612, found 663.8618 .


265 mg , yield: $95 \%$, White solid. M.P. > $250{ }^{\circ} \mathrm{C}$. IR (KBr): $1685,1605,1585,1530$, 1472, 1453, 1364, 1169, 1026, 861, $853 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz , Pyridine- $d_{5}$ ) $\delta 12.51$ $(\mathrm{s}, 2 \mathrm{H}), 8.88-8.73(\mathrm{~m}, 4 \mathrm{H}), 8.69(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 8.20(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.05(\mathrm{~s}$, $11 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , Pyridine- $d_{5}$ ) $\delta-119.72\left(\mathrm{~d}, J=11.9 \mathrm{~Hz}\right.$ ). ${ }^{13} \mathrm{C}$ NMR ( 151 MHz , Pyridine- $d_{5}$ ) $\delta 162.79,158.68(\mathrm{dd}, J=243.7,9.5 \mathrm{~Hz}), 149.76,138.52,135.76$, 125.59, 124.89 (t, $J=14.0 \mathrm{~Hz}$ ), $106.04-105.30(\mathrm{~m}), 43.63(\mathrm{t}, J=2.9 \mathrm{~Hz})$. HRMS (ESI): calc for $\mathrm{C}_{23} \mathrm{H}_{22} \mathrm{O}_{2} \mathrm{~N}_{5} \mathrm{~F}_{4}[\mathrm{M}+\mathrm{H}]^{+} 476.1704$, found 476.1705.


283 mg , yield: $98 \%$. White solid. M.P. $>250^{\circ} \mathrm{C}$. IR (KBr): 1669, 1640, 1602, 1589, $1504,1451,1426,1237,1171,1088,847,624 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 600 MHz , Acetone- $d_{6}$ ) $\delta 8.48(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 2 \mathrm{H}), 8.36(\mathrm{dd}, J=8.2,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.74-7.67(\mathrm{~m}, 4 \mathrm{H}), 2.17(\mathrm{t}$, $J=1.7 \mathrm{~Hz}, 6 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR $\left(565 \mathrm{MHz}\right.$, Acetone- $\left.d_{6}\right) \delta-115.87(\mathrm{~d}, J=9.0 \mathrm{~Hz}) .{ }^{13} \mathrm{C}$ NMR $\left(126 \mathrm{MHz}\right.$, Acetone $\left.-d_{6}\right) \delta 161.55,161.23(\mathrm{dd}, J=241.9,11.5 \mathrm{~Hz}), 148.80,139.88$, $137.63(\mathrm{t}, J=14.2 \mathrm{~Hz}), 125.60,108.16(\mathrm{t}, J=21.9 \mathrm{~Hz}), 103.21-102.66(\mathrm{~m}), 5.86(\mathrm{~d}$, $J=3.8 \mathrm{~Hz}$ ). HRMS (ESI): calc for $\mathrm{C}_{21} \mathrm{H}_{16} \mathrm{O}_{2} \mathrm{~N}_{3} \mathrm{~F}_{4}[\mathrm{M}+\mathrm{H}]^{+} 418.1173$, found 418.1173.


310 mg , yield: $83 \%$. White solid. M.P. > $250{ }^{\circ} \mathrm{C}$. IR (KBr): 3352, 1703, 1628, 1605, $1544,1525,1514,1428,1375,1347,1176,1062,854,640 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 600 MHz , Acetone- $d_{6}$ ) $\delta 11.15(\mathrm{~s}, 2 \mathrm{H}), 8.56(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 8.45(\mathrm{t}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 8.05(\mathrm{~d}$, $J=11.8 \mathrm{~Hz}, 4 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 565 MHz , Acetone- $d_{6}$ ) $\delta-119.20(\mathrm{~d}, J=11.9 \mathrm{~Hz}) .{ }^{13} \mathrm{C}$ NMR (151 MHz, Acetone- $d_{6}$ ) $\delta 163.97,157.19(\mathrm{dd}, ~ J=255.9,3.6 \mathrm{~Hz}$ ), 149.85, 145.06 (t, $J=13.9 \mathrm{~Hz}$ ), 142.37, 128.32, 105.81 (dd, $J=25.4,3.3 \mathrm{~Hz}$ ). HRMS (ESI): calc for $\mathrm{C}_{19} \mathrm{H}_{8} \mathrm{O}_{6} \mathrm{~N}_{5} \mathrm{~F}_{4}[\mathrm{M}+\mathrm{H}]^{+} 478.0416$, found 478.0416.


275 mg , yield: $95 \%$. White solid. M.P. $>250^{\circ} \mathrm{C}$. IR (KBr): 1670, 1599, 1526, 1443, 1231, 1048, 998, 747, $624 \mathrm{~cm}^{-1},{ }^{1} \mathrm{H}$ NMR ( 400 MHz, DMSO-d6) $\delta 11.13$ ( $\mathrm{s}, 2 \mathrm{H}$ ), 8.42 $-8.37(\mathrm{~m}, 2 \mathrm{H}), 8.31(\mathrm{dd}, J=8.7,6.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.93-7.85(\mathrm{~m}, 4 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , DMSO- $d_{6}$ ) $\delta-134.64(\mathrm{dd}, J=22.6,10.4 \mathrm{~Hz}, 4 \mathrm{~F}),-166.68(\mathrm{tt}, J=22.5,6.7 \mathrm{~Hz}, 2 \mathrm{~F}) .{ }^{13} \mathrm{C}$ NMR ( 126 MHz , Pyridine- $d_{5}$ ) $\delta 162.44,151.72(\mathrm{dd}, J=10.1,5.2 \mathrm{~Hz}$ ), 149.19, 139.63, $137.19(\mathrm{t}, J=15.6 \mathrm{~Hz}), 134.56(\mathrm{td}, J=11.6,4.0 \mathrm{~Hz}), 126.11,105.86-105.09(\mathrm{~m})$. HRMS (ESI): calc for $\mathrm{C}_{19} \mathrm{H}_{9} \mathrm{O}_{2} \mathrm{~N}_{3} \mathrm{~F}_{6} \mathrm{Na}[\mathrm{M}+\mathrm{Na}]^{+} 448.0491$, found 448.0494 .


230 mg , yield: $93 \%$. White solid. M.P. > $250{ }^{\circ} \mathrm{C}$. IR (KBr): 2964, 1666, 1607, 1513, 1486, 1365, 1235, 1178, 1044, 866, 849, $749 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta 9.49(\mathrm{~s}, 2 \mathrm{H}), 8.53(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 8.20(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.53(\mathrm{~d}, J=9.0 \mathrm{~Hz}$, 4H), 7.30 (dd, $J=6.8,2.7 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.04 (ddd, $J=6.1,3.3,2.0 \mathrm{~Hz}, 4 \mathrm{H}), 6.57$ (d, $J=7.2$ $\mathrm{Hz}, 2 \mathrm{H}$ ), $3.61-3.46(\mathrm{~m}, 1 \mathrm{H}), 1.32(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 12 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , Chloroform- $d$ ) $\delta-124.54\left(\mathrm{~d}, J=9.0 \mathrm{~Hz}\right.$ ). ${ }^{13} \mathrm{C}$ NMR ( 126 MHz , Acetone- $d_{6}$ ) $\delta 163.50$, 157.68 (dd, $J=246.2,6.6 \mathrm{~Hz}$ ), 157.02, 150.47, 141.99, 138.22, 137.78 ( $\mathrm{t}, J=12.8 \mathrm{~Hz}$ ), $128.95(\mathrm{t}, J=15.7 \mathrm{~Hz}), 128.56(\mathrm{~m}), 127.61,124.86,106.46(\mathrm{~m}), 28.72,23.83$. HRMS (ESI): calc for $\mathrm{C}_{37} \mathrm{H}_{32} \mathrm{O}_{4} \mathrm{~N}_{3} \mathrm{~F}_{4}[\mathrm{M}+\mathrm{H}]^{+} 658.2323$, found 658.2326 .


220 mg , yield: $92 \%$. White solid. M.P. $>250^{\circ} \mathrm{C}$. IR ( KBr ): 2946, 2830, 1616, 1498, 1454, 1362, 1163, 1038, 992, 824, 630, $535 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta 9.41(\mathrm{~s}, 2 \mathrm{H}), 8.50(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 8.18(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.33(\mathrm{~d}, J=11.3 \mathrm{~Hz}$, $3 \mathrm{H}), 7.19-7.13(\mathrm{~m}, 1 \mathrm{H}), 6.80(\mathrm{~d}, J=2.0 \mathrm{~Hz}, 4 \mathrm{H}), 1.70(\mathrm{t}, J=2.2 \mathrm{~Hz}, 6 \mathrm{H}), 1.23(\mathrm{~s}$, $36 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , Chloroform- $d$ ) $\delta-104.08$ (d, $J=11.6 \mathrm{~Hz}$ ). ${ }^{13} \mathrm{C}$ NMR ( 126 MHz , Chloroform- $d$ ) $\delta 186.08$, $161.60(\mathrm{dd}, J=249.5,10.8 \mathrm{~Hz}), 161.17$, 148.47, 144.38, 143.96, 140.03, $137.14(\mathrm{t}), 126.36,114.84(\mathrm{t}, J=14.3 \mathrm{~Hz}), 104.58(\mathrm{~m}), 41.72,34.70$, 29.36. HRMS (ESI): calc for $\mathrm{C}_{49} \mathrm{H}_{55} \mathrm{~F}_{4} \mathrm{~N}_{3} \mathrm{O}_{4} \mathrm{Na}[\mathrm{M}+\mathrm{Na}]^{+} 848.4021$, found 848.4017 .

General procedure for the Preparation of Various Palladium Pincer Complexes 3


Ligand 3b ( $200 \mathrm{mg}, 0.42 \mathrm{mmol}, 1.0$ equiv) was suspended in a solution of $\mathrm{Pd}(\mathrm{OAc})_{2}$ ( $82 \mathrm{mg}, 0.36 \mathrm{mmol}, 1.05$ equiv) in acetonitrile ( 5 mL ). The resulting mixture was stirred at $35^{\circ} \mathrm{C}$ for overnight, and filtered through $0.02 \mu \mathrm{M}$ syringe filter $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right.$ was added before the filtration 9if product is not soluble in $\mathrm{CH}_{3} \mathrm{CN}$ ). The filtrate was concentrated to give the crude product which was transferred to a filter funnel and washed extensively with water and hexane. The yellow powder was then dried under air to give product 3 b as a yellow solid ( $223 \mathrm{mg}, 0.35 \mathrm{mmol}$, yield: $89 \%$ ). M.P. $>250^{\circ} \mathrm{C}$. IR ( KBr ): 3688, 3673, 3382, 2975, 2900, 1588, 1503, 1486, 1393, 1230, 1050, 882, 863, 747, 687 $\mathrm{cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz , Acetonitrile- $d_{3}$ ) $\delta 8.27(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.84(\mathrm{~d}, J=7.8$
$\mathrm{Hz}, 2 \mathrm{H}), 7.41-7.31(\mathrm{~m}, 4 \mathrm{H}), 7.18-7.08(\mathrm{~m}, 6 \mathrm{H}), 6.97(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 4 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , Acetonitrile- $d_{3}$ ) $\delta-130.32\left(\mathrm{~d}, J=9.9 \mathrm{~Hz}\right.$ ). ${ }^{13} \mathrm{C}$ NMR ( 126 MHz , Chloroformd) $\delta 167.40,156.44,154.06(\mathrm{dd}, J=248.9,6.4 \mathrm{~Hz}), 150.50,142.46(\mathrm{t}, J=11.2 \mathrm{~Hz})$, $140.56,128.35,126.47(\mathrm{t}, J=15.5 \mathrm{~Hz}), 125.22,121.62,113.74,109.58(\mathrm{~m})$. For the ${ }^{13} \mathrm{C}$ NMR, $\mathrm{CD}_{3} \mathrm{CN}$ was added to prevent the formation of oligomer. The signals of $\mathrm{CH}_{3} \mathrm{CN}$ for ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR were omitted because the bound $\mathrm{CH}_{3} \mathrm{CN}$ was replaced by $\mathrm{CD}_{3} \mathrm{CN}$. HRMS (ESI): calc for $\mathrm{C}_{33} \mathrm{H}_{21} \mathrm{~F}_{4} \mathrm{~N}_{4} \mathrm{O}_{4} \mathrm{Pd}[\mathrm{M}+\mathrm{H}]^{+} 719.0528$, found 719.0528.


226 mg , yield: $86 \%$. Yellow solid. M.P. > $250^{\circ} \mathrm{C}$. IR (KBr):1650, 1609, 1595, 1537, $1505,1434,1365,1234,1030,902,775,756 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz , Acetonitrile- $d_{3}$ ) $\delta 8.24(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.79(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 2 \mathrm{H}), 6.96(\mathrm{~d}, J=10.0 \mathrm{~Hz}, 4 \mathrm{H}), 4.15(\mathrm{~d}$, $J=7.3 \mathrm{~Hz}, 4 \mathrm{H}), 1.33(\mathrm{t}, J=7.1 \mathrm{~Hz}, 6 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , Acetonitrile $-d_{3}$ ) $\delta-131.17$ (d, $J=9.9 \mathrm{~Hz}$ ). ${ }^{13} \mathrm{C}$ NMR ( 101 MHz , Acetonitrile- $d_{3}$ ) $\delta 168.72$, 155.44 (dd, $J=245.0$, $7.7 \mathrm{~Hz}), 151.85,142.31,142.16(\mathrm{t}, J=11.7 \mathrm{~Hz}), 131.79(\mathrm{t}, J=15.2 \mathrm{~Hz}), 126.17,110.49$ (m), 70.38, 14.94. For the ${ }^{13} \mathrm{C}$ NMR, $\mathrm{CD}_{3} \mathrm{CN}$ was added to prevent the formation of oligomer. The signals of $\mathrm{CH}_{3} \mathrm{CN}$ for ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR were omitted because the bound $\mathrm{CH}_{3} \mathrm{CN}$ was replaced by $\mathrm{CD}_{3} \mathrm{CN}$. HRMS (ESI): calc for $\mathrm{C}_{25} \mathrm{H}_{21} \mathrm{~F}_{4} \mathrm{~N}_{4} \mathrm{O}_{4} \mathrm{Pd}$ $[\mathrm{M}+\mathrm{H}]^{+} 623.0528$, found 623.0534 .


218 mg , yield $91 \%$. Orange solid. M.P. $>250^{\circ} \mathrm{C}$. IR (KBr): 3474, 3449, 1632, 1588, 1494, 1338, 1274, 1035, 756, 693, 566, $508 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz , Acetonitrile- $d_{3}$ ) $\delta 8.28(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.84(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.28(\mathrm{t}, J=7.8 \mathrm{~Hz}, 8 \mathrm{H}), 7.09(\mathrm{~d}, J$ $=9.9 \mathrm{~Hz}, 4 \mathrm{H}), 7.05-6.99(\mathrm{~m}, 12 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , Acetonitrile- $d_{3}$ ) $\delta-121.41$ $(\mathrm{d}, J=9.9 \mathrm{~Hz}){ }^{13} \mathrm{C}$ NMR ( 126 MHz , Pyridine- $d_{5}$ ) $\delta 170.02,161.05(\mathrm{dd}, J=250.2,7.3$ $\mathrm{Hz})$, 153.00, $148.22(\mathrm{t}, J=11.8 \mathrm{~Hz})$, 147.67, 142.79, 130.64, 127.26, 123.71, 121.97, $119.40(\mathrm{t}, J=15.7 \mathrm{~Hz}), 112.50(\mathrm{~m})$. HRMS (ESI): calc for $\mathrm{C}_{45} \mathrm{H}_{31} \mathrm{~F}_{4} \mathrm{~N}_{6} \mathrm{O}_{2} \mathrm{Pd}[\mathrm{M}+\mathrm{H}]^{+}$ 869.1474, found 869.1478.


238 mg , yield: $91 \%$. Yellow solid. M.P. > $250{ }^{\circ} \mathrm{C}$. IR (KBr): 3483, 3438, 1634, 1599, $1473,1427,1372,1334,1206,1129,1031,849,833,757,674 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 600 MHz , Acetonitrile- $d_{3}$ ) $\delta 8.30(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.86(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.13(\mathrm{~d}, J=9.2 \mathrm{~Hz}$, 4H). ${ }^{19}$ F NMR ( 565 MHz , Acetonitrile- $d_{3}$ ) $\delta-117.22\left(\mathrm{~d}, J=9.9 \mathrm{~Hz}\right.$ ). ${ }^{13} \mathrm{C}$ NMR ( 151 MHz , Chloroform- $d$ ) $\delta 167.36,156.91(\mathrm{dd}, J=248.4,5.2 \mathrm{~Hz}), 150.38$, $145.02(\mathrm{t}, J=$ $12.5 \mathrm{~Hz}), 140.59,125.30,109.21(\mathrm{dd}, J=21.9,3.8 \mathrm{~Hz}), 103.91(\mathrm{t}, J=21.3 \mathrm{~Hz})$. For the ${ }^{13} \mathrm{C}$ NMR, $\mathrm{CD}_{3} \mathrm{CN}$ was added to prevent the formation of oligomer. The signals of $\mathrm{CH}_{3} \mathrm{CN}$ for ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR were omitted because the bound $\mathrm{CH}_{3} \mathrm{CN}$ was replaced by $\mathrm{CD}_{3} \mathrm{CN}$. HRMS (ESI): calc for $\mathrm{C}_{21} \mathrm{H}_{11} \mathrm{Cl}_{2} \mathrm{~F}_{4} \mathrm{~N}_{4} \mathrm{O}_{2} \mathrm{Pd}[\mathrm{M}+\mathrm{H}]^{+} 602.9225$, found 602.9230 .


212 mg , yield $87 \%$. Yellow solid. M.P. > $250{ }^{\circ} \mathrm{C}$. IR (KBr): 3463, 1589, 1467, 1424, 1384, 1276, 1206, 1121, 1029, 837, 758, $580 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta 8.16(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.88(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.92-6.85(\mathrm{~m}, 4 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR (376 MHz , Chloroform- $d$ ) $\delta-94.42(\mathrm{~d}, J=7.6 \mathrm{~Hz}) .{ }^{13} \mathrm{C}$ NMR ( 126 MHz , Chloroform- $d$ ) $\delta$ $167.29,160.63(\mathrm{dd}, J=244.7,8.0 \mathrm{~Hz}), 150.37,147.95(\mathrm{t}, J=11.7 \mathrm{~Hz}), 140.60,125.28$, $108.60(\mathrm{dd}, J=25.8,2.8 \mathrm{~Hz}), 63.65(\mathrm{t}, J=29.7 \mathrm{~Hz})$. For the ${ }^{13} \mathrm{C}$ NMR, $\mathrm{CD}_{3} \mathrm{CN}$ was added to prevent the formation of oligomer. The signals of $\mathrm{CH}_{3} \mathrm{CN}$ for ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR were omitted because the bound $\mathrm{CH}_{3} \mathrm{CN}$ was replaced by $\mathrm{CD}_{3} \mathrm{CN}$. HRMS (ESI): calc for $\mathrm{C}_{21} \mathrm{H}_{11} \mathrm{~F}_{4} \mathrm{I}_{2} \mathrm{~N}_{4} \mathrm{O}_{2} \mathrm{Pd}[\mathrm{M}+\mathrm{H}]^{+} 786.7937$, found 786.7944.


249 mg , yield: $95 \%$. Yellow solid. M.P. > $250^{\circ} \mathrm{C}$. IR (KBr): 2878, 2769, 2362, 1595, $1505,1430,1366,1268,1201,1162,1021 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 600 MHz , Pyridine- $d_{5}$ ) $\delta$ $8.15(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 8.07(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 2 \mathrm{H}), 6.92(\mathrm{~d}, J=10.4 \mathrm{~Hz}, 4 \mathrm{H}), 2.66(\mathrm{~s}$, 12H). ${ }^{19} \mathrm{~F}$ NMR ( 565 MHz , Pyridine- $d_{5}$ ) $\delta-121.57\left(\mathrm{~d}, J=11.0 \mathrm{~Hz}\right.$ ). ${ }^{13} \mathrm{C}$ NMR ( 101 MHz, Pyridine- $d_{5}$ ) $\delta 169.02,158.42(\mathrm{dd}, J=246.1,9.7 \mathrm{~Hz}), 152.09$, $142.91(\mathrm{t}, J=12.4$ $\mathrm{Hz}), 141.46,125.77,125.32(\mathrm{t}, J=13.9 \mathrm{~Hz}), 110.96$ - 110.53 (m), 43.46. HRMS (ESI): calc for $\mathrm{C}_{25} \mathrm{H}_{23} \mathrm{~F}_{4} \mathrm{~N}_{6} \mathrm{O}_{2} \mathrm{Pd}[\mathrm{M}+\mathrm{H}]^{+}$621.0848, found 621.0851.


255 mg , yield: $95 \%$. Yellow solid. M.P. > $250^{\circ} \mathrm{C}$. IR (KBr): 2597, 2335, 1633, 1601, 1496, 1422, 1320, 1267, 1077, 999, $833 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta$
8.09 (d, $J=7.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.82(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 2 \mathrm{H}), 6.77(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 4 \mathrm{H}), 2.06(\mathrm{t}, J=$ $1.7 \mathrm{~Hz}, 6 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , Acetonitrile- $d_{3}$ ) $\delta-118.25\left(\mathrm{~d}, J=8.5 \mathrm{~Hz}\right.$ ). ${ }^{13} \mathrm{C}$ NMR (101 MHz, Pyridine- $d_{5}$ ) $\delta 176.97,169.09,160.90(\mathrm{dd}, J=243.5,11.6 \mathrm{~Hz}), 152.03$, $146.30(\mathrm{~d}, J=12.2 \mathrm{~Hz}), 141.50,125.84,110.09-109.21(\mathrm{~m}), 108.22(\mathrm{t}, J=21.7 \mathrm{~Hz})$, 23.25, 6.41 ( $\mathrm{t}, J=3.9 \mathrm{~Hz}$ ). HRMS (ESI): calc for $\mathrm{C}_{23} \mathrm{H}_{17} \mathrm{~F}_{4} \mathrm{~N}_{4} \mathrm{O}_{2} \mathrm{Pd}[\mathrm{M}+\mathrm{H}]^{+}$ 563.0317.found 563.0318.


241 mg , yield: $92 \%$. Yellow solid. M.P. $>250^{\circ} \mathrm{C}$. IR ( KBr ): 3055, 2878, 2768, 2300, 1637, 1606, 1522, 1477, 1431, 1336, $1055 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz , Pyridine- $d_{5}$ ) $\delta$ $8.30(\mathrm{dd}, J=8.3,7.2 \mathrm{~Hz}, 1 \mathrm{H}), 8.17(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.11-7.02(\mathrm{~m}, 4 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , Pyridine- $d_{5}$ ) $\delta-120.46$ (d, $J=10.9 \mathrm{~Hz}$ ). ${ }^{19} \mathrm{~F}$ NMR ( 376 MHz , Acetone $-d_{6}$ ) $\delta-123.63--125.66(\mathrm{~m}) .{ }^{13} \mathrm{C}$ NMR ( 101 MHz , Pyridine- $\mathrm{d}_{5}$ ) $\delta 169.18$, 154.75 (dd, $J=$ $258.5,3.7 \mathrm{~Hz}), 152.55(\mathrm{t}, J=12.1 \mathrm{~Hz}), 150.92,142.23,126.98,124.93(\mathrm{t}, J=15.2 \mathrm{~Hz})$, 117.25, 113.35 - 110.73 (m), 0.79. HRMS (ESI): calc for $\mathrm{C}_{21} \mathrm{H}_{11} \mathrm{~F}_{4} \mathrm{~N}_{6} \mathrm{O}_{6} \mathrm{Pd}[\mathrm{M}+\mathrm{H}]^{+}$ 624.9706, found 624.9700.


259 mg , yield: $96 \%$. Yellow solid. M.P. > $250^{\circ} \mathrm{C}$. IR (KBr): 3055, 2910, 2337, 1635, $1618,1520,1435,1337,1045,997,764 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 600 MHz , Acetonitrile- $d_{3}$ ) $\delta$ $8.26(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.82(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.06(\mathrm{dd}, J=9.5,6.8 \mathrm{~Hz}, 4 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 565 MHz, Acetonitrile- $d_{3}$ ) $\delta-138.20(\mathrm{dd}, J=20.3,10.0 \mathrm{~Hz}, 4 \mathrm{~F}),-167.68(\mathrm{tt}, J$
$=20.6,6.7 \mathrm{~Hz}, 2 \mathrm{~F}) .{ }^{13} \mathrm{C}$ NMR ( 151 MHz , Pyridine- $d_{5}$ ) $\delta 169.29,151.80,151.25,143.06$, 141.85, 126.27, 117.35, 111.30 (d, $J=18.2 \mathrm{~Hz}$ ). HRMS (ESI): calc for $\mathrm{C}_{21} \mathrm{H}_{11} \mathrm{~F}_{6} \mathrm{~N}_{4} \mathrm{O}_{2} \mathrm{Pd}$ $[\mathrm{M}+\mathrm{H}]^{+} 570.9816$, found 570.9821 .


217 mg , yield: $87 \%$. Yellow solid. M.P. $>250^{\circ} \mathrm{C}$. IR (KBr): 3442, 2964, 1600, 1505 , 1486, 1449, 1434, 1335, 1237, 1177, 1083, 1037, 1001, 867, 756, $635 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{HNMR}$ ( 600 MHz , Acetonitrile- $d_{3}$ ) $\delta 8.27(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), $7.84(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.36$ (dd, $J=7.5,2.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.13(\mathrm{~d}, J=9.7 \mathrm{~Hz}, 3 \mathrm{H}), 7.11-7.04(\mathrm{~m}, 5 \mathrm{H}), 6.61(\mathrm{~d}, J=7.9 \mathrm{~Hz}$, $2 \mathrm{H}), 3.50(\mathrm{p}, J=6.9 \mathrm{~Hz}, 2 \mathrm{H}), 1.31(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 12 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR ( 565 MHz , Acetonitrile- $d_{3}$ ) $\delta-130.62(\mathrm{~d}, J=10.2 \mathrm{~Hz}) .{ }^{13} \mathrm{C}$ NMR ( 126 MHz , Acetone- $d_{6}$ ) $\delta 163.50$, $157.68(\mathrm{dd}, J=246.2,6.6 \mathrm{~Hz}), 157.02,150.47,141.99,138.22,137.78(\mathrm{t}, J=12.8 \mathrm{~Hz})$, $128.95(\mathrm{t}, J=15.7 \mathrm{~Hz}), 128.63,128.48,127.61,124.86,114.34$, 106.46 (m), 28.72, 23.83. For the ${ }^{13} \mathrm{C}$ NMR, $\mathrm{CD}_{3} \mathrm{CN}$ was added to prevent the formation of oligomer. The signals of $\mathrm{CH}_{3} \mathrm{CN}$ for ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR were omitted because the bound $\mathrm{CH}_{3} \mathrm{CN}$ was replaced by $\mathrm{CD}_{3} \mathrm{CN}$. HRMS (ESI): calc for $\mathrm{C}_{39} \mathrm{H}_{33} \mathrm{~F}_{4} \mathrm{~N}_{4} \mathrm{O}_{4} \mathrm{Pd}[\mathrm{M}+\mathrm{H}]^{+}$803.1467, found 803.1476.


239 mg , yield: $89 \%$. Yellow solid. M.P. > $250{ }^{\circ} \mathrm{C}$. IR (KBr): 2957, 2350, 1693, 1659, $1620,1556,1470,1421,1364,1268,1201,1119,1098,1023,903,880,845,758,679$, $631 \mathrm{~cm}^{-1} .{ }^{1} \mathrm{H}$ NMR ( 400 MHz , Acetonitrile- $d_{3}$ ) $\delta 8.26(\mathrm{t}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.81(\mathrm{~d}, J=$ $7.9 \mathrm{~Hz}, 2 \mathrm{H}), 7.07-6.78(\mathrm{~m}, 8 \mathrm{H}), 1.69(\mathrm{t}, J=2.6 \mathrm{~Hz}, 6 \mathrm{H}), 1.22(\mathrm{~s}, 36 \mathrm{H}) .{ }^{19} \mathrm{~F}$ NMR (376 MHz , Acetonitrile- $d_{3}$ ) $\delta-109.44\left(\mathrm{~d}, J=13.0 \mathrm{~Hz}\right.$ ). ${ }^{13} \mathrm{C}$ NMR ( 126 MHz , Benzene- $d_{6}$ ) $\delta$ 186.01, 168.81, 161.23 (dd, $J=247.0,11.1 \mathrm{~Hz}), 151.76,148.48(\mathrm{t}, J=13.7 \mathrm{~Hz}), 144.61$, $144.54,141.45,126.26,113.97(\mathrm{t}, J=14.5 \mathrm{~Hz})$, 111.64 (m), 42.15, 34.99, 29.58. HRMS(ESI): calc for $\mathrm{C}_{51} \mathrm{H}_{57} \mathrm{~F}_{4} \mathrm{~N}_{4} \mathrm{O}_{4} \mathrm{Pd}[\mathrm{M}+\mathrm{H}]^{+} 971.3345$, found 971.3358 .

The investigation of solvent effect on the resolving ability of ${ }^{19} \mathrm{~F}$-labeled Sensors


Figure S1. The resolution of biogenic amines using 3a in diverse solvents. ${ }^{19} \mathrm{~F}$ NMR spectra of solutions containing four biogenic amines ( 0.5 mM each) and complex $\mathbf{3 a}$ (ca. 2.0 mM ) in diverse
solvents. Note: the ${ }^{19} \mathrm{~F}$ chemical shifts of complexes $\mathbf{3 a}$ with a bound phenethylamine were all adjusted to -127.33 ppm for facile comparison between resolving abilities.

d


Figure S2. The resolution of biogenic amines using 3b in diverse solvents. ${ }^{19} \mathrm{~F}$ NMR spectra of solutions containing four biogenic amines ( 0.5 mM each) and complex $\mathbf{3 b}(\mathrm{ca} .2 .0 \mathrm{mM})$ in diverse solvents. Note: the ${ }^{19} \mathrm{~F}$ chemical shifts of complexes $\mathbf{3 b}$ with a bound phenethylamine were all adjusted to -125.47 ppm for facile comparison between resolving abilities.



$\begin{array}{llllllllll}4.65 & -114.75 & -114.85 & -114.95 & -115.05 & -115.15 & -115.25 & -115.35 & -115.45 & \text { PPM }\end{array}$

Figure S3. The resolution of biogenic amines using 3d in diverse solvents. ${ }^{19} \mathrm{~F}$ NMR spectra of solutions containing four biogenic amines ( 0.5 mM each) and complex $\mathbf{3 d}$ (ca. 2.0 mM ) in diverse solvents. Note: the ${ }^{19} \mathrm{~F}$ chemical shifts of complexes $\mathbf{3 d}$ with a bound phenethylamine were all adjusted to -114.77 ppm for facile comparison between resolving abilities.


Figure S4. The resolution of biogenic amines using 3e in diverse solvents. ${ }^{19} \mathrm{~F}$ NMR spectra of solutions containing four biogenic amines ( 0.5 mM each) and complex $\mathbf{3 e}(\mathrm{ca} .2 .0 \mathrm{mM})$ in diverse solvents. Note: the ${ }^{19} \mathrm{~F}$ chemical shifts of complexes $\mathbf{3 e}$ with a bound phenethylamine were all adjusted to -106.96 ppm for facile comparison between resolving abilities.



Figure S5. The resolution of biogenic amines using $\mathbf{3 f}$ in diverse solvents. ${ }^{19} \mathrm{~F}$ NMR spectra of solutions containing four biogenic amines ( 0.5 mM each) and complex $\mathbf{3 f}(\mathrm{ca} .2 .0 \mathrm{mM}$ ) in diverse solvents. Note: the ${ }^{19} \mathrm{~F}$ chemical shifts of complexes $\mathbf{3 f}$ with a bound phenethylamine were all adjusted to -92.53 ppm for facile comparison between resolving abilities.

## Sensing experiment using sensor 3 k



Figure S6. Detection and differentiation of phenethylamine, tyramine, tryptamine, and serotonin ( 0.5 mM each) with ${ }^{19} \mathrm{~F}$-labeled sensors $\mathbf{3 k}$ (ca. 2.0 mM ).

## Investigation of the impact of mixed solvents on the resolving ability of the sensor.



Figure S7. Investigation of the impact of mixed solvents on the resolving ability of sensor 3d. (a-f) ${ }^{19} \mathrm{~F}$ NMR spectra of solutions containing four biogenic amines ( 0.5 mM each) and complex $\mathbf{3 d}$ (ca. 2.0 mM ) in diverse solvents. Note: the ${ }^{19} \mathrm{~F}$ chemical shifts of complexes 3d with a bound phenethylamine were all adjusted to -114.7 ppm for facile comparison between resolving abilities.

Investigation of the impact of water on the resolving ability of ${ }^{19}$ F NMR chromatography.


Figure S8. Investigation of the impact of water on the resolving ability of ${ }^{19} \mathrm{~F}$ NMR chromatography. (a-e) ${ }^{19} \mathrm{~F}$ NMR spectra of solutions containing four biogenic amines ( 0.5 mM each) and complex $\mathbf{3 a}$ (ca. 2.0 mM ) in a mixture of THF and water. Note: the ${ }^{19} \mathrm{~F}$ chemical shifts of complexes $\mathbf{3 a}$ with a bound phenethylamine were all adjusted to -129.1 ppm for facile comparison between resolving abilities.

## Quantitative experiment using A3 as an internal standard.



Figure S9. A plot of $\mathrm{C}_{\mathrm{A} 7 / \mathrm{A} 3}$ (concentration ratio between $\mathbf{A 7}$ and $\mathbf{A 3}$ ) versus $\mathrm{S}_{\mathrm{A} 7 / \mathrm{S} 3}$ (the ratio between ${ }^{19}$ F NMR signal integrations correlated to A7 and A3). A3 was used as an internal standard with a known concentration (ca. 0.46 mM ). The concentration range for $\mathbf{A 7}$ is $0-0.87 \mathrm{mM} . \boldsymbol{c}$ : concentration. $\boldsymbol{S}$ : peak area.

Table S1 Concentration and integration ratios used for plotting Figure S9

| $\boldsymbol{c}_{\mathrm{A} 7} / \boldsymbol{c}_{\mathrm{A} 3}$ | $\boldsymbol{S}_{\mathrm{A} 7} / \boldsymbol{S}_{\mathrm{A} 3}$ |
| :---: | :---: |
| 0.00 | 0.00 |
| 0.48 | 0.31 |
| 0.97 | 0.72 |
| 1.45 | 1.00 |
| 1.93 | 1.37 |

## Examination of the correlation between ${ }^{19} \mathrm{~F}$ NMR signals and the identity of the analyte



A1 A3


Figure S10. ${ }^{19}$ F NMR spectra of (a-d) a mixture of sensor 3a (ca. 2 mM ) and different analyte (ca. 0.25 mM ). (e) a mixture of A1-A4 and sensor 3a. (f) superimposition of the sensor 3a with each of the 4 analytes collected independently.


Figure S11. (a) ${ }^{19} \mathrm{~F}$ NMR spectra of solutions (chlorobenzene:methanol $=2: 1$ ) containing 21 different analytes (ca. 0.23 mM each) and complexes $\mathbf{3 c}$ (ca. 6.3 mM ) (b) superimposition of the sensor $\mathbf{3 c}$ with each of the 21 analytes collected independently.


Figure S12. (a) ${ }^{19} \mathrm{~F}$ NMR spectra of solutions (chlorobenzene:methanol $=2: 1$ ) containing 21 diverse analytes (ca. 0.01 mM each) and complexes $\mathbf{3 c}$ (ca. 0.28 mM ). (b) superimposition of the sensor $\mathbf{3 c}$ with each of the 21 analytes collected independently.


Figure S13 ${ }^{1} \mathrm{H}$ and ${ }^{19} \mathrm{~F}$ NMR spectra for the mixture of sensor 3a (ca. 3.5 mM ) and analyte A1 (ca. 2.1 mM )


Figure S14. (a-d) ${ }^{19}$ F NMR spectra for the mixture of sensor 3a (ca. 2.0 mM ) and varying amounts of analyte A3.

## ${ }^{1} \mathrm{H},{ }^{19} \mathrm{~F}$, and ${ }^{13} \mathrm{C}$ NMR spectrum of all new products:


$\left\{\begin{array}{r}1.4435 \\ 1.4259 \\ 1.4083\end{array}\right.$


-111.1705
-111.1921




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$\stackrel{0}{0}$
$\stackrel{0}{6}$
$\stackrel{0}{6}$


$\left[\begin{array}{r}7.9481 \\ 7.9298 \\ 7.3491 \\ 7.3300 \\ 7.3088 \\ 7.2417 \\ 7.1502 \\ 7.1316 \\ 7.1132 \\ 6.9629 \\ 6.9424\end{array}\right.$


$\left.\begin{array}{l}\text { 6LSG'OZL- } \\ \text { L8EG'ozL- }\end{array}\right\}$





f1 (ppm)










NMR



${ }^{9}$ F NMR


1g


## 



${ }^{1} \mathrm{H} \mathrm{NMR}$





[^0]

N
N
Ni
N N


$\begin{array}{llllllllllllllllllllllll}210 & 200 & 190 & 180 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 & 90 & 80 & 70 & 60 & 50 & 40 & 30 & 20 & 10 & 0 & -10 \\ (\mathrm{ppm})\end{array}$


${ }^{19} \mathrm{~F}$ NMR


1m





${ }^{1} \mathrm{H}$ NMR $\mathrm{NH}_{2}$





[^1]$$
{ }^{13} \mathrm{C} \mathrm{NMR}
$$



(2)








$\qquad$



${ }^{1} \mathrm{H} \mathrm{NMR}$




$\left.\begin{array}{l}\text { عとเの"6LL- } \\ 09 \text { L9 } 6 \text { LL- }\end{array}\right\rangle$

## 

${ }^{13} \mathrm{C} \mathrm{NMR}$

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| :---: | :---: | :---: | :---: | :---: |
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| － | $\checkmark$ | F | $\xrightarrow{\text { ® }}$ | 析 |



## ${ }^{1} \mathrm{H}$ NMR <br>  <br> 2h





[^2]${ }^{13} \mathrm{C} \mathrm{NMR}$





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\({ }^{19} \mathrm{~F}\) NMR
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2j
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${ }^{13} \mathrm{C} \mathrm{NMR}$








G978•9ZL-
LZZ8•9Zレ-


${ }^{13} \mathrm{C}$ NMR $\mathrm{NH}_{2}$


21



 f1 (ppm)

${ }^{19}$ F NMR


2m








[^3]



[^4]













-121.3967
-121.4233






$\stackrel{\stackrel{\circ}{q} \stackrel{n}{N}}{\underset{\sim}{N}}$



[^5]





[^6]







## 

$\stackrel{\text { 号 }}{\substack{\text { Tj }}}$









[^7]



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$\chi_{-109.4249}^{-109.4593}$







Nion

## 



$\begin{array}{llllllllllllll}210 & 200 & 190 & 180 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 & 90 \\ & & & & & & (\mathrm{ppm})\end{array}$






|  | 1 |  |  |  | , |  |  |  |  |  | , |  |  |  | 1 |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 30 | 20 | 10 | 0 | -10 | -20 | -30 | -40 | -50 | -60 | -70 | $\begin{aligned} & -80 \\ & \text { f1 } \end{aligned}$ | $\begin{gathered} -90 \\ (\mathrm{ppm}) \end{gathered}$ | $-100$ | $-110$ | $-120$ | -130 | $-140$ | -150 | -160 | -170 | -180 | -190 | $-20 c$ |



$\begin{array}{lllllllllllllllllllllllllllllllllllll}240 & 230 & 220 & 210 & 200 & 190 & 180 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 & 90 & 80 & 70 & 60 & 50 & 40 & 30 & 20 & 10 & 0 & -10 & -20 & -30 & -40\end{array}$
f1 (ppm)





[^8]










$\left.\begin{array}{l}9 S 1 \varepsilon^{\prime} \varepsilon 6^{-} \\ 0 Z 6 z^{-} \varepsilon 6^{-}\end{array}\right\}$





$\begin{array}{lllllllllllllllllllllllllllllllllllllllllll}240 & 230 & 220 & 210 & 200 & 190 & 180 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 & 90 & 80 & 70 & 60 & 50 & 40 & 30 & 20 & 10 & 0 & -10 & -20 & -30 & -40\end{array}$ f1 (ppm)





点点㗊















| 20 | 210 | 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 | -10 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |







##  


 f1 (ppm)












$\chi_{-104.0962}^{-104.0654}$





[^0]:    

[^1]:    

[^2]:    

[^3]:    $\begin{array}{llllllllllllllllllllllllllll}210 & 200 & 190 & 180 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 & 90 & 80 & 70 & 60 & 50 & 40 & 30 & 20 & 10 & 0 & -10 \\ (\mathrm{fpm})\end{array}$

[^4]:    

[^5]:    O甘 オ
    

[^6]:    

[^7]:    $\begin{array}{llllllllllll}210 & 200 & 190 & 180 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 \\ \mathrm{f} 1(\mathrm{ppm})\end{array}$

[^8]:    $\begin{array}{llllllllllllll}30 & 20 & 10 & 0 & -10 & -20 & -30 & -40 & -50 & -60 & -70 & -80 & -90 \\ & & & & & & & & & & & & & \\ \mathrm{ppm})\end{array}$

