Supporting Information

Tailoring Sensors and Solvents for Optimal Analysis of Complex Mixtures Via Discriminative ¹⁹F NMR Chemosensing

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General Methods and MaterialsS	2
General procedure for the coupling between 3,4,5-trifluoro-nitrobenzene and variou	IS
nucleophilesS	3
General procedure for the reduction of various nitrobenzeneS	6
General procedure for the preparation of pincer ligands	0
General procedure for the preparation of various palladium pincer complexes	6
The investigation of solvent effect on the resolving ability of ¹⁹ F-labeled SensorsS2	2
Sensing experiment using sensor 3k	7
Investigation of the impact of mixed solvents on the resolving ability of the sensorS27	
Investigation of the impact of water on the resolving ability of ¹⁹ F NM	R
chromatography	8
Quantitative experiment using A3 as an internal standard	8
Examination of the correlation between ¹⁹ F NMR signals and the identity of th	e
analyte	9
¹ H, ¹⁹ F, and ¹³ C NMR spectrum of all new products	2

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 μ m) was purchased from SiliCycle Inc. All reagent grade materials were purchased from commercial sources and used without further purification.

NMR Spectroscopy: ¹H and ¹³C NMR spectra for some compounds were acquired in CDCl₃ and others which are difficult to dissolve in OS(CD₃)₂, CD₃CN on a Bruker Avance 400 MHz or 600 MHz Spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and referenced with Solvent Peak for ¹H NMR. CDCl₃, or SO(CD₃)₂ for ¹³C NMR and CFCl₃ for ¹⁹F NMR.

General procedure for NMR experiments:

For Figures 2, at ambient temperature, complex **3** (**3a**, **3b**, **3c**, **3d**, **3e**, or **3f**) was added to a mixture of phenethylamine, tyramine, tryptamine, and serotonin in CDCl₃, and ¹⁹F NMR spectra were taken using a 600 MHz NMR spectrometer (typically 64 scans).

For Figure 3, complex **3b**, **3g**, or **3h** was added to a mixture of phenethylamine, tyramine, tryptamine, and serotonin in CDCl₃, and ¹⁹F 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 ¹⁹F 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 ¹⁹F 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 mg, 5.31 mmol, 1.0 equiv) and NaH (60 w/w%) (425 mg, 6.38 mmol, 1.2 equiv) was stirred in DMF (10 mL) under N₂ for 30 min before the addition of 3,4,5-trifluoro-nitrobenzene (1.13 g, 6.38 mmol, 1.2 equiv). The mixture was stirred at rt for 5 hours. Then water (10 mL) was added to quench the reaction. The mixture was then extracted with EtOAc (3×10 mL). The combined organic phase was washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by silica gel chromatography (PE/CH₂Cl₂,9:1) to afford **1b** as yellow solid (1.2 g, yield: 89%). M.P. 75–77 °C. IR (KBr): 3419, 3086, 3047, 1591, 1536, 1501, 1488, 1459, 1350, 1236, 1194, 1046, 878, 856, 777, 748, 715, 684 cm⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.2 Hz, 2H), 7.33 (dd, *J* = 8.7, 7.3 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 2H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ –120.56 (d, *J* = 7.0 Hz). ¹³C NMR (101 MHz, Chloroform-*d*) δ 156.85, 155.43 (dd, *J* = 256.5, 5.0 Hz), 143.51 (t, J = 9.2 Hz), 137.86 (t, *J* = 14.5 Hz), 129.90, 124.11, 115.74, 109.09 (m). HRMS (DART): calc for C₁₂H₇O₃NF₂ [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 cm⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 –

7.81 (m, 2H), 4.39 (q, J = 7.0 Hz, 2H), 1.43 (t, J = 7.0 Hz, 3H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ –111.18 (d, J = 8.1 Hz). ¹³C NMR (151 MHz, Chloroform-*d*) δ 154.47 (dd, J = 252.3, 6.5 Hz), 141.71 (t, J = 13.4 Hz), 141.08 (t, J = 10.4 Hz), 108.95(m), 70.74 (t, J = 4.0 Hz), 15.51. HRMS: calc for C₈H₈O₃NF₂ [M+H]⁺ 204.0467, found 204.0467.



1.3 g, yield: 87%. Orange solid. M.P.: 105–107 °C. IR (KBr): 2986, 2900, 1588, 1520, 1483, 1459, 1438, 1408, 1321, 1271, 1178 cm⁻¹. ¹H NMR (500 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.30 (dd, *J* = 8.4, 7.5 Hz, 4H), 7.12 (t, *J* = 7.4 Hz, 2H), 7.02 (d, *J* = 7.6 Hz, 4H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 158.36 (dd, *J* = 257.0, 6.3 Hz), 145.67, 143.49 (t, *J* = 10.5 Hz), 129.80 (t, *J* = 13.3 Hz), 129.47, 124.21, 122.21, 109.21 (m). HRMS (ESI): calc for C₁₈H₁₃O₂N₂F₂ [M+H]⁺ 327.0940, found 327.0937.



1.96 g, yield: 87%. Red solid. M.P.: 86–88 °C. IR (KBr): 2985, 2917, 1605, 1506, 1446, 1364, 1337, 1227, 1170, 1069, 1020, 963, 883, 787 cm⁻¹. ¹H NMR (600 MHz, Chloroform-*d*) δ 7.74 (d, J = 10.5 Hz, 2H), 3.06 (s, 6H). ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -118.58 – -118.69 (m). ¹³C NMR (151 MHz, Chloroform-*d*) δ 154.23 (dd, J = 248.7, 9.1 Hz), 138.28, 135.94 (t, J = 11.6 Hz), 109.86 – 108.11 (m), 43.02 (t, J = 5.2 Hz). HRMS (ESI): calc for C₈H₉O₂N₂F₂ [M+H]⁺ 203.0627, found 203.0628.



1.2 g, yield: 87%. Light green solid. M.P.: 54–56 °C. IR (KBr): 3665, 3444, 3287, 2980, 2021, 1682, 1622, 1493, 1427, 1230, 1035, 853, 746, 625, 609 cm⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.92 (m, 2H), 7.33 (dd, *J* = 7.2, 2.2 Hz, 1H), 7.13 – 7.03 (m, 2H), 6.55 (d, *J* = 8.3 Hz, 1H), 3.48 (h, *J* = 6.9 Hz, 1H), 1.30 (d, *J* = 6.9 Hz, 6H).¹⁹F NMR (376 MHz, Chloroform-*d*) δ –121.16 (d, *J* = 7.1 Hz). ¹³C NMR (151 MHz, Chloroform-*d*) δ 155.30 (dd, *J* = 256.1, 5.2 Hz), 154.35, 143.20 (t, *J* = 9.5 Hz), 138.42 (t, *J* = 14.2 Hz), 137.49, 127.22, 126.73, 124.30, 113.67, 109.18 (m), 27.23, 22.65. HRMS (EI): calc for C₁₅H₁₃O₃NF₂ [M]⁺ 293.0858, found 293.0864.



1.5 g, yield: 85%. Yellow solid. M.P.: 112–114 °C. IR (KBr): 2965, 2870, 1630, 1534, 1502, 1488, 1450, 1350, 1244, 1175, 1082, 1050, 886, 778, 747 cm⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, J = 9.6 Hz, 2H), 6.73 (t, J = 2.1 Hz, 2H), 1.73 (t, J = 2.6 Hz, 3H), 1.22 (s, 18H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ –100.39 (d, J = 9.5 Hz). ¹³C NMR (151 MHz, Chloroform-*d*) δ 185.54, 161.12 (dd, J = 255.5, 8.8 Hz), 147.14 (t, J = 12.4 Hz), 145.55, 142.11 (t, J = 2.5 Hz), 126.10, 108.77 (d, J = 33.9 Hz), 42.28 (t), 34.83, 29.27, 26.91 (t, J = 5.2 Hz). HRMS (EI): calc for C₂₁H₂₅O₃NF₂ [M]⁺ 377.1797, found 377.1804.

General procedure for the reduction of various nitrobenzenes.



To a solution of **1b** (0.50 g, 1.99 mmol, 1.0 equiv) in EtOH (16 mL) was added tin(II) chloride dihydrate (1.97 g, 8.87 mmol, 4.0 equiv) and concentrated hydrochloric acid (1 mL). After heated to reflux for 6 h, the mixture was cooled to room temperature, diluted with water (10 mL). The pH of the solution was adjusted pH with sodium hydroxide solution and the mixture was extracted with EtOAc (3×20 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure to give **2b** as a white solid (0.40 g, 1.81 mmol, yield: 90%). M.P.: 73–75 °C. IR (KBr): 3419, 1591, 1536, 1501, 1488, 1350, 1236, 1046, 878, 777, 748, 715 cm⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.23 (m, 2H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.28 (d, *J* = 9.4 Hz, 2H), 3.74 (s, 2H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ –126.80 (d, *J* = 9.0 Hz). ¹³C NMR (151 MHz, Chloroform-*d*) δ 158.39, 156.82 (dd, *J* = 247.6, 7.0 Hz), 144.31 (t, *J* = 12.3 Hz), 129.53, 122.62 (t, *J* = 15.7 Hz).122.45, 114.94, 98.81 (m). HRMS (ESI): calc for C₁₂H₁₀ONF₂ [M+H]⁺ 222.0725, found 222.0727.



300 mg, yield: 87%. Yellow solid. M.P.: 90–92 °C. ¹H NMR (400 MHz, Chloroform-*d*) δ 6.22 – 6.15 (m, 2H), 4.05 (q, *J* = 7.0 Hz, 2H), 1.35 (t, *J* = 7.0 Hz, 3H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ –128.23 (d, *J* = 9.4 Hz). ¹³C NMR (151 MHz, Chloroform-*d*) δ

154.47 (dd, J = 252.3, 6.5 Hz), 141.71 (t, J = 13.4 Hz), 141.08 (t, J = 10.4 Hz), 108.95 (m), 70.74 (t, J = 4.0 Hz), 15.51. HRMS (ESI): calc for C₈H₁₀ONF₂ [M+H]⁺ 174.0725, found 174.0726.



400 mg, yield: 88%. Brown solid. M.P.: 110–112 °C. IR (KBr): 3483, 2922, 1936, 1646, 1586, 1513, 1319, 1294, 1011, 831, 751, 729, 695, 563 cm⁻¹, ¹H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.19 (m, 4H), 7.04 (d, *J* = 8.0 Hz, 4H), 6.96 (t, *J* = 7.3 Hz, 2H), 6.26 (d, *J* = 9.6 Hz, 2H), 3.62 (s, 2H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ –118.28 (d, *J* = 9.5 Hz). ¹³C NMR (151 MHz, Chloroform-*d*) δ 161.50 (dd, *J* = 249.3, 7.9 Hz), 146.79, 146.60 (t), 129.08, 121.90, 120.60, 112.84 (t, *J* = 16.4 Hz), 98.87 (m). HRMS (ESI): calc for C₁₈H₁₅N₂F₂ [M+H]⁺ 297.1198, found 297.1197.



379 mg, yield: 86%. Yellow solid. M.P.: 86–88 °C. IR (KBr): 3431, 3330, 3208, 2938, 2870, 1651, 1508, 1457, 1450, 1172, 1156, 1043, 1013, 1002, 941, 829, 638 cm⁻¹.¹H NMR (400 MHz, Chloroform-*d*) δ 6.20 – 6.09 (m, 2H), 3.66 (s, 2H), 2.76 (t, *J* = 1.2 Hz, 6H).¹⁹F NMR (376 MHz, Chloroform-*d*) δ –119.63 (d, *J* = 10.4 Hz). ¹³C NMR (151 MHz, Chloroform-*d*) δ 160.83 (dd, *J* = 246.3, 9.9 Hz), 144.14 (d, *J* = 13.6 Hz), 120.12, 98.95 – 98.56 (m), 44.63 – 44.40 (m). HRMS (ESI): calc for C₈H₁₁N₂F₂ [M+H]⁺ 173.0885, found173.0885.



470 mg, yield: 89%, colorless oil. IR (film): 3396, 2962, 2925, 2852, 1647, 1603, 1515, 1487, 1468, 1234, 1182, 1161, 1083, 1027, 863, 828, 753c m⁻¹.¹H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.22 (m, 1H), 7.08 – 6.96 (m, 2H), 6.57 (d, *J* = 7.9 Hz, 1H), 6.33 (d, *J* = 9.4 Hz, 2H), 3.70 (s, 2H) 3.57 (p, *J* = 6.9 Hz, 1H), 1.31 (d, *J* = 6.9 Hz, 6H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ –126.83 (d, *J* = 9.2 Hz). ¹³C NMR (101 MHz, Chloroform-*d*) δ 158.11 (d, *J* = 7.1 Hz), 155.65 (d, *J* = 7.7 Hz), 144.10 (t, *J* = 12.3 Hz), 136.80, 126.54 (d, *J* = 5.0 Hz), 122.50, 112.55, 98.92 (m), 27.11, 22.64. HRMS (EI): calc for C₁₅H₁₅ONF₂ [M]⁺ 263.1116, found 263.1120.



400 mg, yield: 86%. M.P.: 149–151 °C. Yellow solid. IR (KBr): 2777, 1653, 1621, 1455, 1369, 1164, 1038, 992, 907, 825, 774 cm⁻¹. ¹ H NMR (400 MHz, Chloroform-*d*) δ 6.77 (t, *J* = 2.0 Hz, 2H), 6.28 (d, *J* = 11.3 Hz, 2H), 1.64 (t, *J* = 2.3 Hz, 3H), 1.23 (s, 18H). ¹⁹F NMR (376 MHz, Chloroform-d) δ –105.80. ¹³C NMR (126 MHz, Chloroform-*d*) δ 186.32, 162.18 (dd, *J* = 247.2, 11.6 Hz), 146.97 (t, *J* = 14.9 Hz), 145.31 (d, *J* = 2.5 Hz), 143.45, 107.03, 100.29 – 96.83 (m), 41.32, 34.54, 29.36. HRMS (EI): calc for C₂₁H₂₇ONF₂ [M]⁺ 347.2055, found 347.2060.

Procedure for the preparation of aniline 2h.



Bromo-3,5-difluoroaniline (3.12 g, 15.0 mmol, 1.0 equiv) and Xphos Pd G3 (1.27 g, 1.5 mmol, 10 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 ZnMe₂ (1.0 M in Hexane, 30 mL, 30 mmol, 2.0 equiv) was added to the solution. The reaction was heated at 100 °C for 15 h. After the reaction cooled, MeOH was added to quench the excess ZnMe₂. EtOAc was added to dilute the reaction and the organic phase was washed with water and brine successively. The organic layer was dried with Na₂SO₄ 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 **2h** as a yellowish solid (1.14 g, yield: 53%). M.P.: 39–41°C. IR (KBr): 3850, 3409, 2932, 2830, 1569, 1588, 1511, 1450, 1365, 1324, 1142, 1105, 823, $625, 513 \text{ cm}^{-1}$. ¹H NMR (400 MHz, Chloroform-*d*) δ 6.21 – 6.10 (m, 2H), 3.68 (s, 2H), 2.03 (t, J = 1.7 Hz, 3H).¹⁹F NMR (376 MHz, Chloroform-*d*) δ –115.46 (d, J = 7.8 Hz). ¹³C NMR (151 MHz, Chloroform-*d*) δ 162.27 (dd, J = 242.9, 12.3 Hz), 145.72 (t, J =13.6 Hz), 102.51 (t, J = 21.9 Hz), 78.21 – 76.12 (m), 6.33 (t, J = 3.8 Hz). HRMS (ESI): calc for C₇H₈NF₂ [M+H]⁺ 144.0619, found 144.0619.

Procedure for the preparation of aniline 2j.



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 g, 10 mmol, 1.25 equiv) was added to the solution using a syringe and the reaction was

heated at 110 °C for 8 h. After the reaction cooled, H₂O was added, and washed with ethyl acetate for three times. The combined EtOAc phase was washed with brine, dried with Na₂SO₄ 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 MeOH (10 mL) and water (1.0 mL), then trifluoromethanesulfonic acid (0.5 mL) was added and the reaction was heated at 60 °C for 0.5 h. The solvent was evaporated and residue was dissolved using ethyl acetate and NaHCO3 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 **2j** as a yellow solid (554 mg, yield: 40%) M.P.: 185-187 °C. IR (KBr): 3512, 3406, 3087, 1633, 1576, 1506, 1308, 1223, 1205, 1076, 1001, 853 cm⁻¹. ¹H NMR (600 MHz, Acetone- d_6) δ 6.43 (d, J = 12.3 Hz, 2H), 6.40 (s, 2H). ¹⁹F NMR (376 MHz, Acetone- d_6) δ –119.42 (d, J = 12.3 Hz). ¹³C NMR (151 MHz, Acetone- d_6) δ 157.46 (dd, J = 255.6, 4.4 Hz), 154.38 (t, J = 15.1 Hz), 96.81 -96.21 (m). ¹³C NMR (151 MHz, Acetone- d_6) δ 157.46 (dd, J = 255.5, 4.5 Hz), 154.38 $(t, J = 15.1 \text{ Hz}), 118.39, 96.49 \text{ (dd}, J = 24.1, 2.0 \text{ Hz}). \text{ HRMS (ESI): calc for } C_6H_5O_2N_2F_2$ [M+H]⁺ 175.0314, found 175.0313.

Typical procedure for the preparation of pincer ligands 4.



Under a N_2 atmosphere, a solution of 2,6-pyridinedicarbonyl dichloride (93 mg, 0.45 mmol, 1.0 equiv) and 4-phenoxyphenylamine (200 mg, 4.9 mmol, 2.0 equiv) in toluene (10 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 **4b** as a white solid (240 mg, 0.42 mmol, yield: 93%). M.P. > 250 °C. IR (KBr): 3684, 2973, 2899, 1681, 1666, 1531, 1507, 1487, 1455, 1407, 1231, 1177, 1042, 891, 863, 846, 745, 685, 627, 610 cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.18 (s, 2H), 8.41 (d, *J* = 7.4 Hz, 2H), 8.33 (dd, *J* = 8.6, 6.8 Hz, 1H), 7.90 (d, *J* = 10.2 Hz, 4H), 7.41 – 7.30 (m, 4H), 7.09 (t, *J* = 7.4 Hz, 2H), 6.96 (d, *J* = 8.1 Hz, 4H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ –124.18 (d, *J* = 8.9 Hz). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 162.41, 157.83, 155.64 (dd, *J* = 245.9, 6.6 Hz), 148.60, 140.87, 136.44 (t, *J* = 12.9 Hz), 130.51, 126.71 (t, *J* = 15.8 Hz), 126.36, 123.58, 115.17, 105.55 (m, *J* = 26.0 Hz). HRMS (ESI): calc for C₃₁H₂₀O₄N₃F₄ [M+H]⁺ 574.1384, found 574.1390.



240 mg, yield: 96%. White solid. M.P. > 250 °C. IR (KBr): 2830, 2014, 1897, 1685, 1513, 1366, 1223, 1180, 1035, 899, 847, 774, 615 cm⁻¹. ¹H NMR (600 MHz, DMSOd₆) δ 11.05 (s, 2H), 8.41 (d, J = 7.7 Hz, 2H), 8.35 – 8.29 (m, 1H), 7.76 (d, J = 10.2 Hz, 4H), 4.16 (q, J = 7.0 Hz, 4H), 1.32 (t, J = 7.0 Hz, 6H). ¹⁹F NMR (565 MHz, DMSO-d₆) δ –127.51 (d, J = 10.4 Hz). ¹³C NMR (126 MHz, Acetone-d₆) δ 161.50, 155.95 (dd, J = 244.1, 7.6 Hz), 148.74, 140.01, 133.87 (t, J = 13.1 Hz), 131.39 (t, J = 15.0 Hz), 125.59, 104.37 (m), 70.27 (t, J = 2.6 Hz), 14.79. HRMS (ESI): calc for C₂₃H₂₀O₄N₃F₄ [M+H]⁺ 478.1384, found 478.1386.



228 mg, yield: 95%. Green solid. M.P. > 250 °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 cm⁻¹. ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.17 (s, 2H), 8.44 – 8.37 (m, 2H), 8.32 (dd, *J* = 8.6, 6.9 Hz, 1H), 7.83 (d, *J* = 10.6 Hz, 4H), 7.32 – 7.19 (m, 8H), 6.98 (td, *J* = 7.4, 1.3 Hz, 4H), 6.94 (d, *J* = 8.0 Hz, 8H). ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ –117.67 (d, *J* = 10.5 Hz). ¹³C NMR (126 MHz, Acetone-*d*₆) δ 163.48, 162.11 (dd, *J* = 248.1, 7.4 Hz), 150.45, 148.21, 142.01, 139.85 (t, *J* = 13.7 Hz), 131.07, 127.63, 124.23, 122.42, 119.88 (t, *J* = 15.8 Hz), 106.36 (m). HRMS (ESI): calc for C₄₃H₃₀O₂N₅F₄ [M+H]⁺ 724.2330, found 724.2337.



263 mg, yield: 93%. White solid. M.P. > 250 °C. IR (KBr): 3528, 2832, 1609, 1511, 1438, 1366, 1232, 1044, 868, 775, 748, 699 cm⁻¹. ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.56 (s, 2H), 7.69 (d, *J* = 52.4 Hz, 3H), 7.24 (s, 4H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ 111.45 (d, *J* = 8.2 Hz). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 162.57, 158.43 (dd, *J* = 245.1, 5.2 Hz), 148.46, 140.88, 138.99 (t, *J* = 13.1 Hz), 126.50, 105.01 (dd, *J* = 26.6, 2.6 Hz), 103.33 (t, *J* = 21.5 Hz). HRMS (ESI): calc for C₁₉H₁₀O₂N₃Cl₂F₄ [M+H]⁺ 458.0082, found 458.0081.



227 mg, yield: 90%. White solid. M.P. > 250 °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 cm⁻¹. ¹H NMR (600 MHz, DMSO-*d*6) δ 11.24 (s, 2H), 8.42 (d, J = 7.7 Hz, 2H), 8.36 – 8.32 (m, 1H), 7.82 (d, J = 8.5 Hz, 4H). ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ –93.30 (d, J = 8.9 Hz). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 162.54, 162.52 (dd, J = 240.1, 9.1 Hz), 148.53, 141.14 (t, J = 14.1 Hz), 140.88, 126.48, 104.20 (dd, J = 30.6, 2.1 Hz), 66.00 (t, J = 31.3 Hz). HRMS (ESI): calc for C₁₉H₉O₂N₃F₄I₂Na [M+Na]⁺ 663.8612, found 663.8618.



265 mg, yield: 95%, White solid. M.P. > 250 °C. IR (KBr): 1685, 1605, 1585, 1530, 1472, 1453, 1364, 1169, 1026, 861, 853 cm⁻¹. ¹H NMR (400 MHz, Pyridine- d_5) δ 12.51 (s, 2H), 8.88 – 8.73 (m, 4H), 8.69 (d, J = 7.8 Hz, 2H), 8.20 (t, J = 7.8 Hz, 1H), 3.05 (s, 11H). ¹⁹F NMR (376 MHz, Pyridine- d_5) δ –119.72 (d, J = 11.9 Hz). ¹³C NMR (151 MHz, Pyridine- d_5) δ 162.79, 158.68 (dd, J = 243.7, 9.5 Hz), 149.76, 138.52, 135.76, 125.59, 124.89 (t, J = 14.0 Hz), 106.04 – 105.30 (m), 43.63 (t, J = 2.9 Hz). HRMS (ESI): calc for C₂₃H₂₂O₂N₅F₄ [M+H]⁺ 476.1704, found 476.1705.



283 mg, yield: 98%. White solid. M.P. > 250 °C. IR (KBr): 1669, 1640, 1602, 1589, 1504, 1451, 1426, 1237, 1171, 1088, 847, 624 cm⁻¹. ¹H NMR (600 MHz, Acetone-*d*₆) δ 8.48 (d, *J* = 7.7 Hz, 2H), 8.36 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.74 – 7.67 (m, 4H), 2.17 (t, *J* = 1.7 Hz, 6H).¹⁹F NMR (565 MHz, Acetone-*d*₆) δ –115.87 (d, *J* = 9.0 Hz). ¹³C NMR (126 MHz, Acetone-*d*₆) δ 161.55, 161.23 (dd, *J* = 241.9, 11.5 Hz), 148.80, 139.88, 137.63 (t, *J* = 14.2 Hz), 125.60, 108.16 (t, *J* = 21.9 Hz), 103.21 – 102.66 (m), 5.86 (d, *J* = 3.8 Hz). HRMS (ESI): calc for C₂₁H₁₆O₂N₃F₄ [M+H]⁺ 418.1173, found 418.1173.



310 mg, yield: 83%. White solid. M.P. > 250 °C. IR (KBr): 3352, 1703, 1628, 1605, 1544, 1525, 1514, 1428, 1375, 1347, 1176, 1062, 854, 640 cm⁻¹. ¹H NMR (600 MHz, Acetone-*d*₆) δ 11.15 (s, 2H), 8.56 (d, *J* = 8.5 Hz, 2H), 8.45 (t, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 11.8 Hz, 4H). ¹⁹F NMR (565 MHz, Acetone-*d*₆) δ –119.20 (d, *J* = 11.9 Hz). ¹³C NMR (151 MHz, Acetone-*d*₆) δ 163.97, 157.19 (dd, *J* = 255.9, 3.6 Hz), 149.85, 145.06 (t, *J* = 13.9 Hz), 142.37, 128.32, 105.81 (dd, *J* = 25.4, 3.3 Hz). HRMS (ESI): calc for C₁₉H₈O₆N₅F₄ [M+H]⁺ 478.0416, found 478.0416.



275 mg, yield: 95%. White solid. M.P. > 250 °C. IR (KBr): 1670, 1599, 1526, 1443, 1231, 1048, 998, 747, 624 cm⁻¹, ¹H NMR (400 MHz, DMSO-*d*6) δ 11.13 (s, 2H), 8.42 – 8.37 (m, 2H), 8.31 (dd, J = 8.7, 6.7 Hz, 1H), 7.93 – 7.85 (m, 4H). ¹⁹F NMR (376 MHz, DMSO-*d*6) δ –134.64 (dd, J = 22.6, 10.4 Hz, 4F), –166.68 (tt, J = 22.5, 6.7 Hz, 2F). ¹³C NMR (126 MHz, Pyridine-*d*₅) δ 162.44, 151.72 (dd, J = 10.1, 5.2 Hz), 149.19, 139.63, 137.19 (t, J = 15.6 Hz), 134.56 (td, J = 11.6, 4.0 Hz), 126.11, 105.86 – 105.09 (m). HRMS (ESI): calc for C₁₉H₉O₂N₃F₆Na [M+Na]⁺ 448.0491, found 448.0494.



230 mg, yield: 93%. White solid. M.P. > 250 °C. IR (KBr): 2964, 1666, 1607, 1513, 1486, 1365, 1235, 1178, 1044, 866, 849, 749 cm⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 9.49 (s, 2H), 8.53 (d, *J* = 7.8 Hz, 2H), 8.20 (t, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 9.0 Hz, 4H), 7.30 (dd, *J* = 6.8, 2.7 Hz, 2H), 7.04 (ddd, *J* = 6.1, 3.3, 2.0 Hz, 4H), 6.57 (d, *J* = 7.2 Hz, 2H), 3.61 – 3.46 (m, 1H), 1.32 (d, *J* = 6.9 Hz, 12H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ –124.54 (d, *J* = 9.0 Hz). ¹³C NMR (126 MHz, Acetone-*d*₆) δ 163.50, 157.68 (dd, *J* = 246.2, 6.6 Hz), 157.02, 150.47, 141.99, 138.22, 137.78 (t, *J* = 12.8 Hz), 128.95 (t, *J* = 15.7 Hz), 128.56 (m), 127.61, 124.86, 106.46 (m), 28.72, 23.83. HRMS (ESI): calc for C₃₇H₃₂O₄N₃F₄ [M+H]⁺ 658.2323, found 658.2326.



220 mg, yield: 92%. White solid. M.P. > 250 °C. IR (KBr): 2946, 2830, 1616, 1498, 1454, 1362, 1163, 1038, 992, 824, 630, 535 cm⁻¹.¹H NMR (400 MHz, Chloroform-*d*) δ 9.41 (s, 2H), 8.50 (d, *J* = 7.8 Hz, 2H), 8.18 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 11.3 Hz, 3H), 7.19 – 7.13 (m, 1H), 6.80 (d, *J* = 2.0 Hz, 4H), 1.70 (t, *J* = 2.2 Hz, 6H), 1.23 (s, 36H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ –104.08 (d, *J* = 11.6 Hz). ¹³C NMR (126 MHz, Chloroform-*d*) δ 186.08, 161.60 (dd, *J* = 249.5, 10.8 Hz), 161.17, 148.47, 144.38, 143.96, 140.03, 137.14 (t), 126.36, 114.84 (t, *J* = 14.3 Hz), 104.58 (m), 41.72, 34.70, 29.36. HRMS (ESI): calc for C₄₉H₅₅F₄N₃O₄Na [M+Na]⁺ 848.4021, found 848.4017. **General procedure for the Preparation of Various Palladium Pincer Complexes 3**



Ligand **3b** (200 mg, 0.42 mmol, 1.0 equiv) was suspended in a solution of Pd(OAc)₂ (82 mg, 0.36 mmol, 1.05 equiv) in acetonitrile (5 mL). The resulting mixture was stirred at 35 °C for overnight, and filtered through 0.02 μ M syringe filter (CH₂Cl₂ was added before the filtration 9if product is not soluble in CH₃CN). 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 **3b** as a yellow solid (223 mg, 0.35 mmol, yield: 89%). M.P. > 250 °C. IR (KBr): 3688, 3673, 3382, 2975, 2900, 1588, 1503, 1486, 1393, 1230, 1050, 882, 863, 747, 687 cm⁻¹. ¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 8.27 (t, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.8

Hz, 2H), 7.41 – 7.31 (m, 4H), 7.18 – 7.08 (m, 6H), 6.97 (d, J = 8.2 Hz, 4H). ¹⁹F NMR (376 MHz, Acetonitrile- d_3) δ –130.32 (d, J = 9.9 Hz). ¹³C NMR (126 MHz, Chloroform-d) δ 167.40, 156.44, 154.06 (dd, J = 248.9, 6.4 Hz), 150.50, 142.46 (t, J = 11.2 Hz), 140.56, 128.35, 126.47 (t, J = 15.5 Hz), 125.22, 121.62, 113.74, 109.58 (m). For the ¹³C NMR, CD₃CN was added to prevent the formation of oligomer. The signals of CH₃CN for ¹H NMR and ¹³C NMR were omitted because the bound CH₃CN was replaced by CD₃CN. HRMS (ESI): calc for C₃₃H₂₁F₄N₄O₄Pd [M+H]⁺719.0528, found 719.0528.



226 mg, yield: 86%. Yellow solid. M.P. > 250 °C. IR (KBr):1650, 1609, 1595, 1537, 1505, 1434, 1365,1234, 1030, 902, 775, 756 cm⁻¹. ¹H NMR (400 MHz, Acetonitrile- d_3) δ 8.24 (t, J = 7.6 Hz, 1H), 7.79 (d, J = 7.9 Hz, 2H), 6.96 (d, J = 10.0 Hz, 4H), 4.15 (d, J = 7.3 Hz, 4H), 1.33 (t, J = 7.1 Hz, 6H). ¹⁹F NMR (376 MHz, Acetonitrile- d_3) δ –131.17 (d, J = 9.9 Hz). ¹³C NMR (101 MHz, Acetonitrile- d_3) δ 168.72, 155.44 (dd, J = 245.0, 7.7 Hz), 151.85, 142.31, 142.16 (t, J = 11.7 Hz), 131.79 (t, J = 15.2 Hz), 126.17, 110.49 (m), 70.38, 14.94. For the ¹³C NMR, CD₃CN was added to prevent the formation of oligomer. The signals of CH₃CN for ¹H NMR and ¹³C NMR were omitted because the bound CH₃CN was replaced by CD₃CN. HRMS (ESI): calc for C₂₅H₂₁F₄N₄O₄Pd [M+H]⁺ 623.0528, found 623.0534.



218 mg, yield 91%. Orange solid. M.P. > 250 °C. IR (KBr): 3474, 3449, 1632, 1588, 1494, 1338, 1274, 1035, 756, 693, 566, 508 cm⁻¹. ¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 8.28 (t, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.8 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 8H), 7.09 (d, *J* = 9.9 Hz, 4H), 7.05 – 6.99 (m, 12H). ¹⁹F NMR (376 MHz, Acetonitrile-*d*₃) δ –121.41 (d, *J* = 9.9 Hz) ¹³C NMR (126 MHz, Pyridine-*d*₅) δ 170.02, 161.05 (dd, *J* = 250.2, 7.3 Hz), 153.00, 148.22 (t, *J* = 11.8 Hz), 147.67, 142.79, 130.64, 127.26, 123.71, 121.97, 119.40 (t, *J* = 15.7 Hz), 112.50 (m). HRMS (ESI): calc for C₄₅H₃₁F₄N₆O₂Pd [M+H]⁺ 869.1474, found 869.1478.



238 mg, yield: 91%. Yellow solid. M.P. > 250 °C. IR (KBr): 3483, 3438, 1634, 1599, 1473, 1427, 1372, 1334, 1206, 1129, 1031, 849, 833, 757, 674 cm⁻¹. ¹H NMR (600 MHz, Acetonitrile- d_3) δ 8.30 (t, J = 7.8 Hz, 1H), 7.86 (d, J = 7.8 Hz, 2H), 7.13 (d, J = 9.2 Hz, 4H). ¹⁹F NMR (565 MHz, Acetonitrile- d_3) δ –117.22 (d, J = 9.9 Hz). ¹³C NMR (151 MHz, Chloroform-d) δ 167.36, 156.91 (dd, J = 248.4, 5.2 Hz), 150.38, 145.02 (t, J = 12.5 Hz), 140.59, 125.30, 109.21 (dd, J = 21.9, 3.8 Hz), 103.91 (t, J = 21.3 Hz). For the ¹³C NMR, CD₃CN was added to prevent the formation of oligomer. The signals of CH₃CN for ¹H NMR and ¹³C NMR were omitted because the bound CH₃CN was replaced by CD₃CN. HRMS (ESI): calc for C₂₁H₁₁Cl₂F₄N₄O₂Pd [M+H]⁺ 602.9225, found 602.9230.



212 mg, yield 87%. Yellow solid. M.P. > 250 °C. IR (KBr): 3463, 1589, 1467, 1424, 1384, 1276, 1206, 1121, 1029, 837, 758, 580 cm⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.16 (t, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 2H), 6.92 – 6.85 (m, 4H). ¹⁹F NMR (376 MHz, Chloroform-*d*) δ –94.42 (d, *J* = 7.6 Hz). ¹³C NMR (126 MHz, Chloroform-*d*) δ 167.29, 160.63 (dd, *J* = 244.7, 8.0 Hz), 150.37, 147.95 (t, *J* = 11.7 Hz), 140.60, 125.28, 108.60 (dd, *J* = 25.8, 2.8 Hz), 63.65 (t, *J* = 29.7 Hz). For the ¹³C NMR, CD₃CN was added to prevent the formation of oligomer. The signals of CH₃CN for ¹H NMR and ¹³C NMR were omitted because the bound CH₃CN was replaced by CD₃CN. HRMS (ESI): calc for C₂₁H₁₁F₄I₂N₄O₂Pd [M+H]⁺786.7937, found 786.7944.



249 mg, yield: 95%. Yellow solid. M.P. > 250 °C. IR (KBr): 2878, 2769, 2362, 1595, 1505, 1430, 1366, 1268, 1201, 1162, 1021 cm⁻¹. ¹H NMR (600 MHz, Pyridine- d_5) δ 8.15 (t, J = 7.8 Hz, 1H), 8.07 (d, J = 7.7 Hz, 2H), 6.92 (d, J = 10.4 Hz, 4H), 2.66 (s, 12H). ¹⁹F NMR (565 MHz, Pyridine- d_5) δ -121.57 (d, J = 11.0 Hz). ¹³C NMR (101 MHz, Pyridine- d_5) δ 169.02, 158.42 (dd, J = 246.1, 9.7 Hz), 152.09, 142.91 (t, J = 12.4 Hz), 141.46, 125.77, 125.32 (t, J = 13.9 Hz), 110.96 – 110.53 (m), 43.46. HRMS (ESI): calc for C₂₅H₂₃F₄N₆O₂Pd [M+H]⁺ 621.0848, found 621.0851.



255 mg, yield: 95%. Yellow solid. M.P. > 250 °C. IR (KBr): 2597, 2335, 1633, 1601, 1496, 1422, 1320, 1267, 1077, 999, 833 cm⁻¹. ¹H NMR (400 MHz, Chloroform-*d*) δ

8.09 (d, J = 7.4 Hz, 1H), 7.82 (d, J = 7.6 Hz, 2H), 6.77 (d, J = 8.1 Hz, 4H), 2.06 (t, J = 1.7 Hz, 6H). ¹⁹F NMR (376 MHz, Acetonitrile- d_3) δ –118.25 (d, J = 8.5 Hz). ¹³C NMR (101 MHz, Pyridine- d_5) δ 176.97, 169.09, 160.90 (dd, J = 243.5, 11.6 Hz), 152.03, 146.30 (d, J = 12.2 Hz), 141.50, 125.84, 110.09 – 109.21 (m), 108.22 (t, J = 21.7 Hz), 23.25, 6.41 (t, J = 3.9 Hz). HRMS (ESI): calc for C₂₃H₁₇F₄N₄O₂Pd [M+H]⁺ 563.0317.found 563.0318.



241 mg, yield: 92%. Yellow solid. M.P. > 250 °C. IR (KBr): 3055, 2878, 2768, 2300, 1637, 1606, 1522, 1477, 1431, 1336, 1055 cm⁻¹. ¹H NMR (400 MHz, Pyridine- d_5) δ 8.30 (dd, J = 8.3, 7.2 Hz, 1H), 8.17 (d, J = 7.7 Hz, 2H), 7.11 – 7.02 (m, 4H). ¹⁹F NMR (376 MHz, Pyridine- d_5) δ –120.46 (d, J = 10.9 Hz). ¹⁹F NMR (376 MHz, Acetone- d_6) δ -123.63 – -125.66 (m). ¹³C NMR (101 MHz, Pyridine- d_5) δ 169.18, 154.75 (dd, J = 258.5, 3.7 Hz), 152.55 (t, J = 12.1 Hz), 150.92, 142.23, 126.98, 124.93 (t, J = 15.2 Hz), 117.25, 113.35 – 110.73 (m), 0.79. HRMS (ESI): calc for C₂₁H₁₁F₄N₆O₆Pd [M+H]⁺ 624.9706, found 624.9700.



259 mg, yield: 96%. Yellow solid. M.P. > 250 °C. IR (KBr): 3055, 2910, 2337, 1635, 1618, 1520, 1435, 1337, 1045, 997, 764 cm⁻¹. ¹H NMR (600 MHz, Acetonitrile-*d*₃) δ 8.26 (t, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.06 (dd, *J* = 9.5, 6.8 Hz, 4H). ¹⁹F NMR (565 MHz, Acetonitrile-*d*₃) δ –138.20 (dd, *J* = 20.3, 10.0 Hz, 4F), –167.68 (tt, *J*

= 20.6, 6.7 Hz, 2F). ¹³C NMR (151 MHz, Pyridine- d_5) δ 169.29, 151.80, 151.25, 143.06, 141.85, 126.27, 117.35, 111.30 (d, J = 18.2 Hz). HRMS (ESI): calc for C₂₁H₁₁F₆N₄O₂Pd [M+H]⁺ 570.9816, found 570.9821.



217 mg, yield: 87%. Yellow solid. M.P. > 250 °C. IR (KBr): 3442, 2964, 1600, 1505, 1486, 1449, 1434, 1335, 1237, 1177, 1083, 1037, 1001, 867, 756, 635 cm⁻¹. ¹HNMR (600 MHz, Acetonitrile- d_3) δ 8.27 (t, J = 7.8 Hz, 1H), 7.84 (d, J = 7.8 Hz, 2H), 7.36 (dd, J = 7.5, 2.0 Hz, 2H), 7.13 (d, J = 9.7 Hz, 3H), 7.11 – 7.04 (m, 5H), 6.61 (d, J = 7.9 Hz, 2H), 3.50 (p, J = 6.9 Hz, 2H), 1.31 (d, J = 6.9 Hz, 12H). ¹⁹F NMR (565 MHz, Acetonitrile- d_3) δ –130.62 (d, J = 10.2 Hz). ¹³C NMR (126 MHz, Acetone- d_6) δ 163.50, 157.68 (dd, J = 246.2, 6.6 Hz), 157.02, 150.47, 141.99, 138.22, 137.78 (t, J = 12.8 Hz), 128.95 (t, J = 15.7 Hz), 128.63, 128.48, 127.61, 124.86, 114.34, 106.46 (m), 28.72, 23.83. For the ¹³C NMR, CD₃CN was added to prevent the formation of oligomer. The signals of CH₃CN for ¹H NMR and ¹³C NMR were omitted because the bound CH₃CN was replaced by CD₃CN. HRMS (ESI): calc for C₃₉H₃₃F₄N₄O₄Pd [M+H]⁺ 803.1467, found 803.1476.



239 mg, yield: 89%. Yellow solid. M.P. > 250 °C. IR (KBr): 2957, 2350, 1693, 1659, 1620, 1556, 1470, 1421, 1364, 1268, 1201, 1119, 1098, 1023, 903, 880, 845, 758, 679, 631 cm⁻¹. ¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 8.26 (t, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 2H), 7.07 – 6.78 (m, 8H), 1.69 (t, *J* = 2.6 Hz, 6H), 1.22 (s, 36H). ¹⁹F NMR (376 MHz, Acetonitrile-*d*₃) δ –109.44 (d, *J* = 13.0 Hz). ¹³C NMR (126 MHz, Benzene-*d*₆) δ 186.01, 168.81, 161.23 (dd, *J* = 247.0, 11.1 Hz), 151.76, 148.48 (t, *J* = 13.7 Hz), 144.61, 144.54, 141.45, 126.26, 113.97 (t, *J* = 14.5 Hz), 111.64 (m), 42.15, 34.99, 29.58. HRMS(ESI): calc for C₅₁H₅₇F₄N₄O₄Pd [M+H]⁺971.3345, found 971.3358.

The investigation of solvent effect on the resolving ability of ¹⁹F-labeled Sensors



Figure S1. The resolution of biogenic amines using **3a** in diverse solvents. ¹⁹F NMR spectra of solutions containing four biogenic amines (0.5 mM each) and complex **3a** (ca. 2.0 mM) in diverse

solvents. *Note:* the ¹⁹F chemical shifts of complexes **3a** with a bound phenethylamine were all adjusted to -127.33 ppm for facile comparison between resolving abilities.



Figure S2. The resolution of biogenic amines using **3b** in diverse solvents. ¹⁹F NMR spectra of solutions containing four biogenic amines (0.5 mM each) and complex **3b** (ca. 2.0 mM) in diverse solvents. *Note:* the ¹⁹F chemical shifts of complexes **3b** with a bound phenethylamine were all adjusted to -125.47 ppm for facile comparison between resolving abilities.



Figure S3. The resolution of biogenic amines using 3d in diverse solvents. ¹⁹F NMR spectra of solutions containing four biogenic amines (0.5 mM each) and complex 3d (ca. 2.0 mM) in diverse solvents. *Note:* the ¹⁹F chemical shifts of complexes 3d 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. ¹⁹F NMR spectra of solutions containing four biogenic amines (0.5 mM each) and complex **3e** (ca. 2.0 mM) in diverse solvents. *Note:* the ¹⁹F chemical shifts of complexes **3e** 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 **3f** in diverse solvents. ¹⁹F NMR spectra of solutions containing four biogenic amines (0.5 mM each) and complex **3f** (ca. 2.0 mM) in diverse solvents. *Note:* the ¹⁹F chemical shifts of complexes **3f** with a bound phenethylamine were all adjusted to -92.53 ppm for facile comparison between resolving abilities.

Sensing experiment using sensor 3k



Figure S6. Detection and differentiation of phenethylamine, tyramine, tryptamine, and serotonin (0.5 mM each) with ¹⁹F-labeled sensors **3k** (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) ¹⁹F NMR spectra of solutions containing four biogenic amines (0.5 mM each) and complex **3d** (ca. 2.0 mM) in diverse solvents. *Note:* the ¹⁹F 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 ¹⁹F NMR chromatography.



Figure S8. Investigation of the impact of water on the resolving ability of ¹⁹F NMR chromatography. (a-e) ¹⁹F NMR spectra of solutions containing four biogenic amines (0.5 mM each) and complex **3a** (ca. 2.0 mM) in a mixture of THF and water. *Note:* the ¹⁹F chemical shifts of complexes **3a** 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 $C_{A7/A3}$ (concentration ratio between A7 and A3) versus $S_{A7/S3}$ (the ratio between ¹⁹F 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 A7 is 0-0.87 mM. *c*: concentration. *S*: peak area.

$oldsymbol{c}_{\mathrm{A7}} / oldsymbol{c}_{\mathrm{A3}}$	$S_{\rm A7} / S_{\rm A3}$
0.00	0.00
0.48	0.31
0.97	0.72
1.45	1.00
1.93	1.37

Table S1 Concentration and integration ratios used for plotting Figure S9

Examination of the correlation between ¹⁹F NMR signals and the identity of the analyte



Figure S10. ¹⁹F 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) ¹⁹F NMR spectra of solutions (chlorobenzene:methanol = 2:1) containing 21 different analytes (ca. 0.23 mM each) and complexes 3c (ca. 6.3 mM) (b) superimposition of the sensor 3c with each of the 21 analytes collected independently.



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



Figure S13 ¹H and ¹⁹F NMR spectra for the mixture of sensor **3a** (ca. 3.5 mM) and analyte **A1** (ca. 2.1 mM)



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

¹H, ¹⁹F, and ¹³C NMR spectrum of all new products:







30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 f1 (ppm)



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)












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 f1 (ppm)









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)











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)

















-80 -f1 (ppm) -20 -40 -60 -100 -120 -140 -160 -180



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)















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)











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)



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)































¹³C NMR

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)







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 f1 (ppm)






















30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 f1 (ppm)



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 fl (ppm)









30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 f1 (ppm)







210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2 f1 (ppm)











30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 f1 (ppm)





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)

















-94.4121 -94.4323







210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2 f1 (ppm)





















30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 f1 (ppm)





^{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)











-116.4 -116.8 -117.2 -117.6 -118.0 -118.4 -118.8 -119.2 -119.6 -120.0 -120.4 -120.8 -121.2 -121.6 -122.0 -122.4 -122.8 -122 fl (ppm)























10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)















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)











10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 f1 (ppm)


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)









-124.1731
<-124.1968</pre>





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 f1 (ppm)













220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fl (ppm)



















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 f1 (ppm)













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)





< -115.8656 < -115.8815



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)







-119.1936
 -119.2147



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













151.7787 151.7787 151.6985 151.6985 151.6985 151.6985 151.6985 151.6985 133.6256 133.6256 137.1882 137.1882 137.1886 137.1440 134.4765 134.4765 135.581 136.55337 105.55337 105.5337 105.5337 105.5337

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 f1 (ppm)









--124.5062 --124.5255 --124.5496 --124.5659

















