Supplementary Information for

A Multicolor and Ratiometric Fluorescent Sensing Platform for Metal Ions Based on Arene–Metal-Ion Contact

Anna Kanegae, Yusuke Takata, Ippei Takashima, Shohei Uchinomiya, Ryosuke Kawagoe, Akira Yamashita, Kazuteru Usui, Jirarut Wongkongkattep, Manabu Sugimoto, Akio Ojida*
**Supplementary Table 1.** Summary of the fluorescence emission shifts (nm) of Type-II probes 2–4 upon addition of metal ions.$^{a,b}$

![Chemical Structures](image)

|       | Cr(III) | Mn(II) | Co(II) | Ni(II) | Cu(II) | Zn(II) | Ag(I) | Cd(II) | Pb(II) |
|-------|--------|--------|--------|--------|--------|--------|-------|--------|--------|
| 2     | 0 (0.73)| 0 (1.0)| 0 (1.0)| 0 (1.0)| 0 (0.73)| 0 (1.0)| 0 (0.96)| 0 (1.0)| 0 (0.90)$^d$ |
| 3     | 0 (0.86)| 0 (1.04)| 0 (1.0)| 0 (1.0)| 1 (0.01)$^c$| 0 (0.96)| 0 (1.06)| 0 (1.0)| 0 (0.89)  |
| 4     | 0 (0.73)| 0 (1.0)| 0 (1.0)| 0 (1.0)| 0 (0.25)| 0 (0.96)| 0 (0.72)| 0 (1.0)| 0 (0.93)$^d$ |

$^a$Value in the parenthesis indicates fluorescence intensity ratio ($F_{\text{max}} / F_o$), where $F_o$ and $F_{\text{max}}$ designate fluorescence intensity in the absence and presence the maximum concentration of metal ions, respectively. $^b$Measurement conditions: [probe] = 25 µM, 50 mM HEPES (pH 7.4) / MeOH = 1 : 1, Unless otherwise noted, maximum concentration of metal ion is 1 mM. $\lambda_{ex} = 365$ nm, 25 °C. $^c$The maximum concentration of metal ion is 100 µM. $^d$The maximum concentration of metal ion is 50 µM.
**Supplementary Table 2.** Summary of the binding constants \((K_a, \text{M}^{-1})\) of probes 5 and 8–11 toward Zn(II) and Cd(II) ion determined by the fluorescence titration (Figure 2, 4, and Supplementary Figure 3).

|       | 5      | 8      | 9      | 10     | 11     |
|-------|--------|--------|--------|--------|--------|
| Zn(II)| 2.70 x 10^6 | 5.21 x 10^6 | 6.49 x 10^6 | 4.96 x 10^4 | 1.30 x 10^6 |
| Cd(II)| 9.50 x 10^6 | 1.80 x 10^6 | 3.73 x 10^6 | 7.79 x 10^6 | 2.86 x 10^6 |

*Each value was the average of the two independent experiments. Measurement conditions: [probe] = 1 μM, 50 mM HEPES (pH 7.4) / MeOH = 1 : 1, 25 °C.*

**Supplementary Table 3.** Summary of absorption shifts of probes 5 and 8–11 upon addition of various metal ions.

| probe | Cr^{3+} | Mn^{2+} | Co^{2+} | Ni^{2+} | Cu^{2+} | Zn^{2+} | Ag^{+} | Cd^{2+} | Hg^{2+} | Pb^{2+} |
|-------|---------|---------|---------|---------|---------|---------|--------|---------|---------|---------|
| 5     | .a      | .a      | 15      | 6       | 6       | 6       | 6      | 5       | 8       | 11      |
| 8     | .a      | .a      | 5       | <3      | <3      | 6       | <3     | 4       | 5       | .a      |
| 9     | .a      | .a      | <3      | <3      | 17      | 10      | 7      | 16      | 16      | .a      |
| 10    | .a      | .a      | <3      | <3      | 24      | 8       | 8      | 20      | 22      | .a      |
| 11    | .a      | .a      | 11      | 10      | 12      | 9       | 5      | 14      | 15      | <3      |

*Spectral change was scarcely observed.*
### Supplementary Table 4. Crystal data of the solved structures of the metal complexes.

|                  | 5-Zn(II)          | 5-Cu(II)          | 5-Cd(II)          | 5-Ag(I)          |
|------------------|-------------------|-------------------|-------------------|------------------|
| experimental formula | C$_{32}$H$_{33}$N$_4$O$_8$Cl$_2$Zn | C$_{32}$H$_{33}$N$_4$O$_8$Cl$_2$Cu | C$_{32}$H$_{33}$N$_4$O$_8$Cl$_2$Cd | C$_{32}$H$_{33}$N$_4$O$_4$CAg |
| formula weight   | 750.91            | 750.09            | 798.96            | 693.95           |
| counter anion    | ClO$_4^-$         | ClO$_4^-$         | ClO$_4^-$         | ClO$_4^-$        |
| crystal system   | orthorhombic      | orthorhombic      | monoclinic        | monoclinic       |
| a / Å            | 11.704 (2)        | 11.651 (19)       | 41.410 (5)        | 12.144 (15)      |
| b / Å            | 16.022 (3)        | 16.126 (3)        | 10.669 (13)       | 8.964 (11)       |
| c / Å            | 33.430 (6)        | 33.091 (5)        | 15.028 (18)       | 26.531 (3)       |
| α / °            | 90                | 90                | 90                | 90               |
| β / °            | 90                | 90                | 107.128 (14)      | 95.491 (10)      |
| γ / °            | 90                | 90                | 90                | 90               |
| V / Å            | 6269 (2)          | 6217.3 (18)       | 6345.2 (13)       | 2874 (6)         |
| μ (cm$^{-1}$)    | 1.013             | 0.937             | 0.919             | 0.84             |
| Z                | 8                 | 8                 | 8                 | 4                |
| Crystal size / nm | 0.2×0.2×0.2       | 0.2×0.3×0.2       | 0.3×0.2×0.05      | 0.2×0.2×0.2      |
| D$_{calc}$ / gcm$^{-3}$ | 1.561             | 1.603             | 1.673             | 1.608            |
| F$_{000}$        | 3040              | 3096              | 3248              | 1428             |
| radiation        | MoKα              | MoKα              | MoKα              | MoKα             |
| T / K            | 90                | 90                | 90                | 90               |
| No. reflections measured | 33682             | 34255             | 18178             | 16444            |
| No. unique reflections | 6835              | 6849              | 6912              | 6560             |
| No. reflections observed | 7328              | 7567              | 7540              | 6855             |
| No. parameters   | 465               | 437               | 469               | 420              |
| R$_1$ (I>2σ(I))$^a$ | 0.0307            | 0.0455            | 0.0361            | 0.0258           |
| wR$_2$ (all data)$^b$ | 0.0357            | 0.1228            | 0.0633            | 0.0279           |
| GOF              | 1.162             | 1.032             | 0.989             | 1.087            |

$^a$ R$_1$ = Σ||F$_o$|−|F$_c$|| / Σ|F$_o$|, $^b$ wR$_2$ = (Σw(F$_o^2$−F$_c^2$)$^2$ / Σw(F$_o^2$)$^2$)$^{1/2}$
**Supplementary Table 5.** Summary of selected distances and bend angles of the metal ion complexes of 5.

|       | distance (Å)                      | bend angle |
|-------|-----------------------------------|------------|
|       | C9-metal ion⁺⁺⁺⁺                  |            |
| 5-Zn(II) | 2.96 (1.39 + 1.77)                | 4.28       |
| 5-Cd(II) | 3.01 (1.58 + 1.77)                | 4.24       |
| 5-Ag(I)  | 3.28 (1.72 + 1.77)                | 4.51       |
| 5-Cu(II) | 3.14 (1.40 + 1.77)                | 4.48       |

*The values in the parentheses are the van der Waals radii of each metal ion and aromatic carbon. (1.77 Å).*
**Supplementary Table 6.** Summary of HOMO-LUMO energy gap levels and shape of molecular orbitals of the probes and their Zn(II) complexes.

| Environment     | Species | $\Delta E$ (eV) | Wavelength (nm) | $f$ | Occupied MO | Unoccupied MO | Coefficient |
|-----------------|---------|-----------------|-----------------|-----|-------------|---------------|-------------|
| PCM (water)     | 9       | 2.978           | 416.3           | 0.8078 | 138          | 139           | 0.697       |
|                 | 9+Zn(II)| 2.733           | 453.6           | 0.6177 | 147          | 148           | 0.698       |
| PCM (water)     | 5       | 3.596           | 344.8           | 0.1630 | 130          | 131           | 0.698       |
|                 | 5+Zn(II)| 3.520           | 352.2           | 0.1523 | 139          | 140           | 0.699       |

**probe 9**

138th MO (HOMO) [-0.20892 hartree]

139th MO (LUMO) [-0.02169 hartree]

**zinc complex 9-Zn(II)**

147th MO (HOMO) [-0.22262 hartree]

148th MO (LUMO) [-0.04705 hartree]

**probe 5**

130th MO (HOMO) [-0.23893 hartree]

131th MO (LUMO) [-0.02111 hartree]

**zinc complex 5-Zn(II)**

139th MO (HOMO) [-0.25795 hartree]

140th MO (LUMO) [-0.04308 hartree]
Supplementary Table 7. Summary of $S_0$-$S_1$ excitation of the probes with or without coordinated metal ion.

| species    | optimized geometry $^a$ | environment | $S_0$-$S_1$ excitation |
|------------|-------------------------|-------------|------------------------|
|            |                         |             | $\Delta E$ (eV) | $I$ (nm) | $f$  |
| 9+PC(0.0) | 9-Zn(II)                | vacuum      | 3.003                 | 412.9   | 0.570 |
| 9+Na(I)   | 9-Zn(II)                | vacuum      | 2.812                 | 441.0   | 0.494 |
| 9+Ca(II)  | 9-Zn(II)                | vacuum      | 2.451                 | 505.8   | 0.139 |
| 5+PC(0.0) | 5-Zn(II)                | vacuum      | 3.549                 | 349.3   | 0.113 |
| 5+Na(I)   | 5-Zn(II)                | vacuum      | 3.576                 | 346.7   | 0.114 |
| 5+Ca(II)  | 5-Zn(II)                | vacuum      | 3.555                 | 348.8   | 0.112 |

$^a$ Optimized geometry was calculated under vacuum conditions.
**Supplementary Figure 1.** Selected results of the fluorescence titration of Type-II probes (see Figure 1, Supplementary Table 1) 2, 3, and 4 with metal ions. Measurement conditions: [probe] = 25 µM, 50 mM HEPES (pH 7.4) / MeOH = 1 : 1, λ_ex = 365 nm, 25 °C. Counter anion of metal ions is chloride in all the experiments.
Supplementary Figure 2. Plot of the fluorescence intensity ($\lambda_{em} = 414 \text{ nm}$) of 5 upon addition of ZnCl$_2$. Measurement conditions: [5] = 25 µM, 50 mM HEPES (pH 7.4) / MeOH = 1 : 1, $\lambda_{ex} = 365 \text{ nm}$, 25 °C.
Supplementary Figure 3. Summary of the fluorescence titration profile of the probes with Zn(II) and Cd(II). Measurement conditions: [probe] = 1 µM, 50 mM HEPES (pH 7.4) / MeOH = 1 : 1, 25 °C. The fluorescence spectrum change of the probes is shown in Figure 2 and Figure 4. The data represent mean ± s.e. of three independent experiments.
Supplementary Figure 4. Fluorescence spectral changes of probes 6 and 7 upon addition of ZnCl$_2$ or CdCl$_2$. Measurement conditions: [6 or 7] = 25 µM, 50 mM HEPES (pH 7.4) / MeOH = 1 : 1, $\lambda_{\text{ex}}$ = 365 nm, 25 °C.
Supplementary Figure 5. UV absorption changes of probes 8, 9, 10, and 11 upon addition of ZnCl₂ or CdCl₂. Measurement conditions: [probe] = 5 µM (9, 10, 11) or 10 µM (8), 50 mM HEPES (pH 7.4) / MeOH = 1 : 1, 25 °C.
Supplementary Figure 6. Summary of fluorescence spectral changes of probes 5 and 8–11 upon addition of various metal ions. Measurement conditions: [probe] = 25 µM (5), 10 µM (8), or 5 µM (9, 10, 11) or, 50 mM HEPES (pH 7.4) / MeOH = 1 : 1, 25 °C. Each spectrum was obtained at the saturation point of the metal ion titration.
Supplementary Figure 7. Fluorescence spectral change of probe 5 with metal ions. Measurement conditions: [probe] = 25 µM, 50 mM HEPES (pH 7.4) / MeOH = 1 : 1, 25 °C, λ ex = 365 nm.
Supplementary Figure 8. Fluorescence spectral change of probe 8 with metal ions. Measurement conditions: [probe] = 10 μM, 50 mM HEPES (pH 7.4) / MeOH = 1 : 1, 25 °C, λ<sub>ex</sub> = 410 nm.
Supplementary Figure 9. Fluorescence spectral change of probe 9 with metal ions. Measurement conditions: [probe] = 5 µM, 50 mM HEPES (pH 7.4) / MeOH = 1 : 1, 25 °C, λ_ε = 488 nm.
Supplementary Figure 10. Fluorescence spectral change of probe 10 with metal ions. Measurement conditions: [probe] = 5 µM, 50 mM HEPES (pH 7.4) / MeOH = 1 : 1, 25 °C, λ<sub>e</sub> = 578 nm.
Supplementary Figure 11: Fluorescence spectral change of probe II with metal ions. Measurement conditions: [probe] = 5 μM, 50 mM HEPES (pH 7.4) / MeOH = 1 : 1, 25 °C, λ<sub>e</sub> = 674 nm.
Supplementary Figure 12. ORTEP diagrams (50% probability ellipsoids) of (a) 5-Cd$^{2+}$ ($C_{32}H_{32}N_4O_8Cl_2Cd$), (b) 5-Ag$^+$ ($C_{32}H_{32}N_4O_8ClAg$), and 5-Cu$^{2+}$ ($C_{32}H_{32}N_4O_6Cl_2Cu$). The perchlorate anions are omitted for clarity.
Supplementary Figure 13. Evaluation of the binding constant of probe 12 with Zn(II) under the neutral aqueous conditions: \([12] = 1 \mu M,\) 50 mM HEPES 100 mM NaCl, pH 7.4, 25 °C, \(\lambda_{ex} = 488\) nm.

Supplementary Figure 14. Fluorescence change of HeLa cells upon addition of Zn(II) detected by spectral scan mode. The cells were incubated with probe 12 (5 µM) followed by the treatment with ZnCl₂ (5 µM) in the presence of pyrithione (100 µM). The fluorescence intensities were measured at the different wavelengths from 499 to 607 nm with 8.8-nm interval.
Supplementary Figure 15. Fluorescence spectral change of probe 12 upon addition of Cd(II), Hg(II), and Cu(II) under the neutral aqueous conditions: [12] = 1 µM, 50 mM HEPES 100 mM NaCl, pH 7.4, 25 °C, λ_ex = 488 nm.
Supplementary Methods

General materials and methods for organic synthesis

Unless otherwise noted, chemical reagents were purchased from commercial suppliers (FUJIFILM Wako Pure Chemical Corporation, Tokyo Chemical Industry, Sigma-Aldrich, Watanabe Chemical Industries) and used without further purification. Reactions were carried out under a positive atmosphere of nitrogen, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on Merck TLC Silica gel 60 F_{254}. \(^1\)H-NMR spectra were recorded using a Varian UNITY-400 (400 MHz) spectrometer or Bruker Avance III HD 500 MHz spectrometer and chemical shifts (\(\delta\), ppm) were referenced to residual solvent peak (CDCl\(_3\): 7.26 ppm; MeOH-d\(_4\): 3.31 ppm; DMSO-d\(_6\): 2.50 ppm). ESI mass spectrometry was recorded using a MicroTOF II (Bruker Daltonics) spectrometer. HPLC purification was conducted with a HITACHI L-7000 (Hitachi).

Synthesis of probe 2

![Chemical structure of probe 2](image)

A solution of 2-1 (25 mg, 68.0 \(\mu\)mol), 2-2 (12 mg, 69.0 \(\mu\)mol) and K\(_2\)CO\(_3\) (40 mg, 0.29 mmol) in dry CHCl\(_3\) (10 mL) was stirred for 4 h at rt. After dilution with CHCl\(_3\), the organic layer was washed with sat. NaHCO\(_3\) aq. and brine followed by drying over Na\(_2\)SO\(_4\). After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO\(_2\) (CHCl\(_3\) : MeOH : NH\(_3\) aq. = 20 : 1 : 0.1) to give 2 (10 mg, 20%) as a colorless solid. \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 2.67 (16H, brs), 4.26-4.41 (4H, brs), 7.36-7.42 (4H, m), 7.95-7.97 (2H, d, \(J\) = 8.5 Hz), 8.47 (1H, s), 9.50 (1H, s). ESI-TOF-MS \(m/z\) calcd for C\(_{24}\)H\(_{31}\)N\(_4\) [M+H]\(^+\) = 375.2549, observed 375.2560.

Synthesis of probe 3

![Chemical structure of probe 3](image)

A solution of 2-1 (30 mg, 80.0 \(\mu\)mol), 3-1 (31 mg, 0.12 mmol) and K\(_2\)CO\(_3\) (68 mg, 0.50 mmol) in dry CHCl\(_3\) (10 mL) was stirred for 7 h at rt. After dilution with CHCl\(_3\), the organic layer was...
washed with sat. NaHCO$_3$ aq. and brine followed by drying over Na$_2$SO$_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO$_2$ (CHCl$_3$ : MeOH : NH$_3$ aq. = 200 : 10 : 1) to give 3 (13 mg, 39%) as a colorless solid. $^1$H-NMR (500 MHz, CD$_2$OD): $\delta$ 1.76 (4H, br s), 2.43-2.46 (4H, m), 2.52 (4H, br s), 2.65 (8H, br s), 3.35 (4H, s), 7.42-7.47 (4H, m), 8.03-8.05 (2H, d, $J = 8.5$ Hz), 8.57 (1H, s), 9.29 (1H, s). ESI-TOF-MS m/z calcd for C$_{26}$H$_{35}$N$_4$ [M+H]$^+$ = 403.2862, observed 403.2862.

Synthesis of probe 4

A solution of 2-1 (12 mg, 30 µmol), 4-1$^{1S}$ (14 mg, 30 µmol) and K$_2$CO$_3$ (29 mg, 0.21 mmol) in dry CHCl$_3$ (15 mL) was stirred for 2 h at 0 °C. After removal of K$_2$CO$_3$ by filtration, the solvent was evaporated. The residue was purified by reverse-phase HPLC (YMC-Triart C18, 250×10 mm I.D., mobile phase gradient: CH$_3$CN (0.1% TFA) / H$_2$O (0.1% TFA) = 5/95 → 60/40, linear gradient over 30 min) to give 4 (1.6 mg, 12%) as a colorless solid. $^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ 2.15-2.28 (4H, m), 2.36 (2H, s), 2.57-2.58 (4H, d, $J = 7.5$ Hz), 2.66-2.71 (4H, m), 3.19-3.21 (2H, m), 3.34-3.36 (2H, d, $J = 12$ Hz), 3.42-3.45 (4H, m), 3.49 (4H, s), 4.86-4.89 (2H, d, $J = 12$ Hz), 7.38-7.39 (2H, d, $J = 6.5$ Hz), 7.45-7.48 (2H, m), 8.03-8.04 (2H, d, $J = 8.5$ Hz), 8.55 (1H, s), 8.99 (1H, s). ESI-TOF-MS m/z calcd for C$_{28}$H$_{39}$N$_4$ [M+H]$^+$ = 431.3175, observed 431.3199.

Synthetic procedure of probe 5
Synthesis of 5-3
A solution of 5-1⁵³ (2.20 g, 3.81 mmol) and K₂CO₃ (1.80 g, 13.0 mmol) in MeOH (140 mL)-H₂O (7 mL) was heated at 80 °C for 2.5 h with stirring. After removal of the solvent in vacuo, the residue was filtered and washed with EtOH. The filtrate was concentrated by evaporation to give crude 5-2, which was dissolved in EtOH and concentrated by evaporation twice to azeotropically remove H₂O. To a solution of crude 5-2 in dry MeOH (30 mL) added 2-formylpyridine (898 mg, 8.38 mmol) dissolved in dry MeOH (10 mL), and the mixture was stirred overnight at rt. Sodium borohydride (361 mg, 9.53 mmol) was added portionwise at 0 °C and the mixture was further stirred for 3 h at rt. After removal of the solvent by evaporation, the residue was diluted with sat. NaHCO₃ aq. and extracted with CHCl₃ (x2). The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography on SiO₂ (CHCl₃ : MeOH : NH₃ aq. = 10 : 1 : 0.1 → 8 : 1 : 0.1) to give 5-3 (1.15 g, 78%) as a pale yellow viscous oil.

¹H-NMR (500 MHz, CDCl₃): δ 1.42 (9H, s), 2.80-2.83 (4H, t, J = 6.3 Hz), 3.38 (4H, s), 3.90 (4H, s), 7.13-7.15 (2H, m), 7.28-7.30 (2H, d, J = 8.0 Hz), 7.60-7.64 (2H, m), 8.53 (2H, d, J = 4.5 Hz).

¹³C-NMR (125 MHz, CDCl₃): δ 159.3, 155.3, 148.8, 136.0, 121.7, 121.5, 79.1, 77.2, 54.5, 47.5, 28.0.

ESI-TOF-MS m/z calcd for C₂₁H₃₂N₅O₂ [M+H]⁺ = 386.2556, observed 386.2498.

Synthesis of 5-4
To a solution of 5-3 (40.4 mg, 0.10 mmol), 2-1 (38 mg, 0.10 mmol) and triethylamine (29 µL, 211 mmol) in dry CHCl₃ (15 mL) was stirred at 40 °C for 24 h. After dilution with CHCl₃, the organic layer was washed with sat. NaHCO₃ aq. and brine followed by drying over Na₂SO₄. After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO₂ (CHCl₃ : MeOH : NH₃ aq. = 40 : 1 : 0.1) to give 5-3 (28.3 mg, 49%) as a yellow solid. ¹H-NMR (500 MHz, CDCl₃): δ 1.27 (9H, s), 2.85 (4H, brs), 3.69 (4H, brs), 3.77 (4H, s), 4.23 (4H, brs), 7.02 (2H, t, J = 5.5 Hz), 7.14 (2H, d, J = 7.5 Hz), 7.37-7.43 (6H, m), 7.96 (2H, d, J = 8.5 Hz). 8.45 (s, 2H), 10.1 (s, 1H). ESI-TOF-MS m/z calcd for C₂₁H₃₂N₅O₂ [M+H]⁺ = 588.3339, observed 588.3501.

Synthesis of 5
To an ice-cooled solution of 5-4 (28.0 mg, 48 µmol) in dry CH₂Cl₂ (1 mL) was added dropwise TFA (1 mL), and the mixture was stirred for 30 min at rt. After removal of the solvent in vacuo, the residue was dissolved in CHCl₃ and washed with sat. NaHCO₃ aq. and brine followed by drying over Na₂SO₄. After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO₂ (CHCl₃ : MeOH : NH₃ aq. = 40 : 1 : 0.1) to give 5 (14.4 mg, 63%) as a pale yellow solid. ¹H-NMR (500 MHz, CDCl₃): δ 2.90 (4H, brs), 3.05 (4H, brs), 3.76 (4H, brs), 6.94 (2H, t, J = 6.3 Hz), 7.03 (2H, t, J = 7.0 Hz), 7.19 (2H, td, J = 1.7 Hz, ), 7.37 (1H, d, J = 8.4 Hz).
Hz), 7.38 (1H, d, J = 8.4 Hz), 7.47 (2H, d, J = 6.5 Hz), 7.93 (2H, d, J = 8.5 Hz), 8.37 (2H, d, J = 4.3 Hz), 8.43 (1H, s), 9.38 (1H, brs).

$^{13}$C-NMR (125 MHz, CDCl$_3$): δ 160.1, 148.5, 136.0, 134.2, 132.0, 131.0, 131.0, 128.9, 127.9, 124.6, 121.4, 120.3, 60.9, 58.2, 55.9, 46.7. ESI-TOF-MS m/z calcd for C$_{32}$H$_{34}$N$_5$ [M+H]$^+$ = 488.2814, observed 488.2763.

Synthetic procedure of probe 6

![Synthetic procedure of probe 6](image)

Synthesis of 6-2

To a solution of 6-1 (1.57 g, 12 mmol) in dry MeOH (35 mL) was added 2-formyl pyridine (2.57 g, 24 mmol) and the mixture was stirred overnight at room temperature. Sodium borohydride (1.30 g, 34.3 mmol) was added and the mixture was further stirred overnight at rt. After removal of the solvent by evaporation, the residue was diluted with water and extracted with CHCl$_3$ followed by drying over Na$_2$SO$_4$. The organic layer was concentrated in vacuo and the residue was purified by column chromatography on SiO$_2$ (CHCl$_3$: MeOH: NH$_3$aq. = 10 : 1 : 0.1) to give 6-2 (1.01 g, 27%) as a colorless oil. $^1$H NMR (500 MHz, CDCl$_3$): δ 1.69-1.75 (4H, m), 2.67-2.73 (8H, m), 3.89 (4H, s), 7.13-7.16 (2H, m), 7.29-7.30 (2H, d, J = 7.5 Hz), 7.61-7.65 (2H, m), 8.54-8.56 (2H, m). ESI-TOF-MS m/z calcd for C$_{18}$H$_{28}$N$_5$ [M+H]$^+$ = 314.2345, observed 314.2501.

Synthesis of 6

A solution of 6-2 (50.3 mg, 0.16 mmol), 2-1 (58.4 mg, 0.16 mmol) and K$_2$CO$_3$ (44 mg, 0.32 mmol) in dry CHCl$_3$ (15 mL) was stirred for 3 h at rt. After dilution with CHCl$_3$, the organic layer was washed with sat. NaHCO$_3$ aq. and brine followed by drying over Na$_2$SO$_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO$_2$ (CHCl$_3$: MeOH: NH$_3$aq. = 20 : 10 : 0.1) to give 6 (11.5 mg, 14%) as a pale yellow solid. $^1$H-NMR (500 MHz, CDCl$_3$): δ 2.08 (4H, brs), 2.64 (4H, brs), 2.68-2.71 (4H, t, J = 5.5 Hz), 4.33 (4H, s), 4.38 (4H, brs), 7.16-7.18 (2H, m), 7.34-7.39 (6H, m), 7.60-7.64 (2H, m), 7.92-7.93 (2H, d, J = 8.0 Hz), 8.41 (1H, s), 8.60-8.61 (2H, d, J = 4.5 Hz), 9.27 (1H, s). ESI-TOF-MS m/z calcd for C$_{34}$H$_{38}$N$_5$NaBH$_4$dry MeOH N OH H N 6-1 H 2N NH 2N H N 6-2 Br Br N N H N 6-2 K$_2$CO$_3$ CHCl$_3$ 6-1 H 2-1 6-2 K$_2$CO$_3$ CHCl$_3$ 6 2-1
\[{\text{M+H}}]^+ = 516.3127, \text{ observed} 516.3343.\]

**Synthesis of 7**

A solution of **7-1**\(^{1}\) (29 mg, 0.077 mmol), **2-1** (28 mg, 0.077 mmol) and \(\text{K}_2\text{CO}_3\) (25 mg, 0.18 mmol) in dry DMF (10 mL) was stirred for 3 h at rt. After dilution with AcOEt, the organic layer was washed with sat. NaHCO\(_3\) aq. and brine followed by drying over Na\(_2\)SO\(_4\). After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO\(_2\) (CHCl\(_3\) : MeOH : NH\(_3\) aq. = 20 : 1 : 0.1) to give 7 (14.1 mg, 32\%) as a pale yellow solid. \(^1\text{H}-\text{NMR} (500\ MHz, \text{CDCl}_3): \delta 2.82-2.89 (8\text{H}, \text{ brs}), 3.59-3.69 (6\text{H}, \text{ brs}), 4.34 (4\text{H}, \text{ brs}), 6.90-6.93 (2\text{H}, \text{ m}), 6.99-7.05 (4\text{H}, \text{ m}), 7.14-7.17 (3\text{H}, \text{ m}), 7.37-7.39 (5\text{H}, \text{ m}), 7.94-7.96 (2\text{H}, \text{ dd, } J = 2.5, 7.0 \text{ Hz}), 8.36-8.43 (4\text{H}, \text{ m}). \text{ESI-TOF-MS } m/z \text{ calcd for } C_{38}H_{39}N_6 [\text{M+H}]^+ = 579.3236, \text{ observed} 579.3266.

**Synthetic procedure of probe 8**

A solution of **8-1**\(^{1}\) (660 mg, 2.59 mmol), benzyl bromide (0.93 mL, 7.76 mmol) and triethyl amine (0.54 mL, 3.88 mmol) in dry DMF (20 mL) was stirred for 15 h at 110 °C. After dilution
with sat. NaHCO₃ aq., the mixture was extracted with ethyl acetate (x2). The combined organic layers were washed with sat. NaHCO₃ aq. and brine followed by drying over Na₂SO₄. After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO₂ (hexane : AcOEt = 1 : 1) to give 8-2 (773 mg, 86%) as a yellow powder. ¹H-NMR (400 MHz, CDCl₃) : δ 1.42 (6H, s), 2.08 (3H, s), 2.33 (3H, s), 4.56 (1H, s), 5.41 (1H, s), 5.90 (1H, s), 6.12 (1H, s), 7.14 (1H, s), 7.22-7.32 (5H, m). ESI-TOF-MS m/z calcd for C₂₃H₂₄NO₂ [M+H]⁺ = 346.1807, observed 346.1810.

Synthesis of 8-3
A solution of 8-2 (867.2 mg, 2.50 mmol) and SeO₂ (777 mg, 7.50 mmol) in dry dioxane (50 mL) was refluxed for 22 h with stirring. After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO₂ (hexane : AcOEt = 1 : 1) to give 8-3 (621 mg, 69%) as a red powder. ¹H-NMR (400 MHz, CDCl₃) : δ 1.55 (6H, s), 4.61 (2H, s), 6.28 (1H, s), 6.36 (1H, s), 6.48 (1H, s), 7.24 (1H, s), 7.24-7.35 (5H, m), 9.37 (1H, s), 9.72 (1H, s). ESI-TOF-MS m/z calcd for C₂₃H₂₀NO₄ [M+H]⁺ = 374.1392, observed 374.1401.

Synthesis of 8-4
To a solution of 8-3 (421 mg, 1.13 mmol) in dry MeOH (20 mL) was added portionwise NaBH₄ (102 mg, 2.70 mmol) and the mixture was stirred for 12 h at rt. After addition of water, MeOH was removed by evaporation. The aqueous solution was neutralized with 1N HCl and extracted with CH₂Cl₂ (x4). The combined organic layers were dried over MgSO₄ and concentrated by evaporation. The residue was purified by column chromatography on SiO₂ (CHCl₃ : MeOH = 20 : 1) to give 8-4 (279 mg, 66 %) as a yellow powder. ¹H-NMR (400 MHz, CDCl₃) : δ 1.45 (6H, s), 4.52 (2H, d, J = 5.6 Hz), 4.57 (2H, s), 4.79-4.81 (2H, d, J = 5.6 Hz), 5.66 (1H, s), 6.18 (1H, s), 6.20 (1H, s), 7.23-7.30 (6H, m). ¹³C-NMR (125 MHz, CDCl₃) : δ 162.4, 155.6, 154.7, 147.9, 137.2, 130.7, 129.7, 128.8, 127.1, 125.9, 117.8, 117.2, 106.9, 106.1, 99.3, 63.1, 60.8, 57.9, 48.3, 29.0. ESI-TOF-MS m/z calcd for C₂₃H₂₀NO₄ [M+H]⁺ = 378.1705, observed 378.1714.

Synthesis of 8-5
To a solution of 8-4 (80.5 mg, 0.21 mmol) in dry DMF (4 mL) was added dropwise thionyl chloride (80 µL, 1.10 mmol) at rt. The mixture was stirred for 15 min at rt. After dilution with AcOEt, the organic layer with sat. NaHCO₃ aq. and brine followed by drying over Na₂SO₄. After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO₂ (hexane : AcOEt = 2 : 1) to give 8-5 (69 mg, 69%) as a yellow powder. ¹H-NMR (400 MHz, CDCl₃) : δ 1.47 (6H, s), 4.43 (2H, s), 4.57 (4H, s), 5.75 (1H, s), 6.17 (1H, s), 6.19 (1H, s), 7.24-7.31 (5H, m), 7.42 (1H, s). ¹³C-NMR (125 MHz, CDCl₃) : δ 161.2, 156.0, 149.7, 148.0, 136.7,
133.3, 128.8, 127.5, 127.2, 125.7, 118.9, 116.2, 109.8, 106.8, 99.6, 58.1, 48.3, 44.2, 41.4, 28.8. ESI-TOF-MS m/z calcd for C_{23}H_{22}Cl_{2}NO_{2} [M+H]^+ = 414.1028, observed 414.1036.

Synthesis of 8-6
A solution of 8-5 (42.2 mg, 0.10 mmol), 5-3 (50 mg, 0.13 mmol), potassium iodide (20 mg, 0.12 mmol), and K_{2}CO_{3} (45 mg, 0.33 mmol) in dry DMF (10 mL) was stirred for 9 h at rt. After dilution with AcOEt, the organic layer was washed with sat. NaHCO_{3} aq. (x2) and brine followed by drying over Na_{2}SO_{4}. The solvent was removed in vacuo and the residue was purified by column chromatography on SiO_{2} (CHCl_{3} : MeOH : NH_{3} aq. = 30 : 10 : 0.3) to give 8-6 (40 mg, 55%) as an orange solid. \(^1\)H-NMR (400 MHz, CDCl_{3}) : \(\delta\) 1.28 (9H, s), 1.39 (6H, s), 2.75-2.77 (4H, t, \(J = 4.0\) Hz), 3.51-3.54 (6H, d, \(J = 0.75\) Hz), 5.74 (1H, s, \(J = 13.2\) Hz), 7.12-7.24 (3H, m), 7.24-7.31 (7H, m), 7.55 (3H, t, \(J = 8.8\) Hz), 8.50 (2H, t, \(J = 5.2\) Hz). ESI-TOF-MS m/z calcd for C_{35}H_{36}N_{6}O_{4} [M+H]^+ = 727.3972, observed 727.3981.

Synthesis of 8
To an ice-cooled solution of crude 8-6 (14.7 mg, 20 \(\mu\)mol) in dry CH_{2}Cl_{2} (2 mL) was added dropwise TFA (2 mL), and the mixture was stirred for 30 min at rt. After removal of the solvent in vacuo, the mixture was purified by reverse-phase HPLC (YMC-Triart C18, 250×10 mm I.D., mobile phase: CH_{3}CN (0.1% TFA) / H_{2}O (0.1% TFA) = 20/80 \(\rightarrow\) 60/40, linear gradient over 40 min) to give 8 (6.8 mg, 54%) as an orange solid. The purity of 9 was confirmed to be > 95% by HPLC analysis. \(^1\)H-NMR (500 MHz, DMSO-d_{6}) : \(\delta\) = 1.36 (6H, s), 2.60-2.82 (8H, m), 3.42-3.95 (8H, m), 4.64 (2H, s), 5.74 (1H, s), 6.02 (1H, s), 6.09 (1H, s), 7.10-7.15 (1H, m), 7.18-7.29 (5H, m), 7.29-7.39 (3H, m), 7.47 (1H, td, \(J = 7.7\) Hz, 1.7 Hz), 7.58 (1H, td, \(J = 7.7\) Hz, 1.7 Hz), 7.99 (1H, s), 8.35 (1H, s), 8.41 (1H, dd, \(J = 4.8\) Hz, 0.75 Hz), 8.48 (1H, dd, \(J = 4.8\) Hz, 0.75 Hz). \(^{13}\)C-NMR (125 MHz, DMSO-d_{6}) : \(\delta\) = 160.1, 160.0, 158.8, 155.2, 152.5, 148.5, 148.4, 147.3, 138.2, 136.1, 135.8, 135.2, 128.5, 126.9, 126.6, 125.9, 122.9, 122.5, 121.8, 121.7, 121.2, 117.8, 111.8, 108.0, 98.3, 79.2, 79.0, 78.7, 69.8, 59.7, 59.5, 57.6, 57.3, 55.5, 55.2, 47.5, 45.3, 45.2, 28.4. ESI-TOF-MS m/z calcd for C_{39}H_{42}N_{6}O_{2} [M+H]^+ = 627.3447, observed 627.3506.
Synthetic procedure of probe 9

Synthesis of 9-2

A solution of 9-1 (60 mg, 76 µmol), 5-3 (42 mg, 0.11 mmol), potassium iodide (13 mg, 78 µmol) and K₂CO₃ (32 mg, 0.23 mmol) in dry DMF (6 mL) was stirred for 5.5 h at rt. After dilution with sat. NaHCO₃ aq., the mixture was extracted with AcOEt (x2). The combined organic layers were washed with sat. NaHCO₃ aq. and brine followed by drying over Na₂SO₄. After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO₂ (CHCl₃ : MeOH : NH₃ aq. = 80 : 1 : 0.1) to give 9-2 (51 mg, 61%) as a pale yellow oil. ¹H-NMR (500 MHz, CDCl₃): δ 1.09 (18H, s), 1.22 (9H, s), 2.52-2.54 (4H, d, J = 5.8 Hz), 3.29 (4H, s), 3.39 (4H, s), 3.42 (4H, s), 4.26 (2H, s), 6.26-6.27 (2H, d, J = 2.5 Hz), 6.45 (2H, d, J = 2.5 Hz), 6.97-6.99 (2H, d, J = 7.5 Hz), 7.05-7.08 (2H, m), 7.29-7.34 (12H, m), 7.41 (2H, s), 7.68-7.70 (8H, m), 8.44-8.45 (2H, d, J = 4.6 Hz). ESI-TOF-MS m/z calcd for C₆₈H₇₈N₅O₅Si₂ [M+H]⁺ = 1100.5541, observed 1100.4864.

Synthesis of 9-3

To a solution of 9-2 (51 mg, 46 µmol) in dry THF (2 mL) was added tetrabutylammonium fluoride in THF (1 M; 200 µL, 200 µmol), and the mixture was stirred for 1 h at rt. After removal of the solvent in vacuo, the residue was dissolved in dry EtOH (3 mL). 2,3-Dichloro-5,6-dicyano-p-benzoquinone (11 mg, 48 µmol) was added and the mixture was stirred for 15 min at rt. After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO₂ (CHCl₃ : MeOH : NH₃ aq. = 10 : 1 : 0.1) to give crude 9-3 (35 mg) as an orange oil. ¹H-NMR (500 MHz, CDCl₃): δ 1.27 (9H, s), 2.72 (4H, s), 3.53 (4H, s), 3.70 (4H, s), 3.90 (4H, s), 6.52 (2H, s), 6.73-6.74 (2H, d, J = 1.5 Hz), 7.12-7.14 (2H, m), 7.19-7.20 (2H, d, J = 7.5 Hz), 7.55-7.59 (2H, m), 8.46 (2H, d, J = 4.0 Hz), 10.09 (1H, s). ESI-TOF-MS m/z calcd for C₆₈H₆₈N₅O₅ [M+H]⁺ = 622.3027, observed 622.3277.

Synthesis of 9

To an ice-cooled solution of crude 9-3 (35 mg) in dry CH₂Cl₂ (2 mL) was added dropwise TFA
(2 mL), and the mixture was stirred for 30 min at rt. After removal of the solvent in vacuo, the mixture was purified by reverse-phase HPLC (YMC-Triart C18, 250×10 mm I.D., mobile phase: CH₃CN (0.1% TFA) / H₂O (0.1% TFA) = 20/80 → 60/40, linear gradient over 40 min) to give 9 (12.3 mg, 51% from 9-2) as an orange solid. The purity of 9 was confirmed to be > 95% by HPLC analysis.

1H-NMR (500 MHz, CD₃CN): 3.19 (4H, t, J = 4.7 Hz), 3.46 (4H, s), 3.93 (4H, s), 4.26 (4H, br s), 6.79 (2H, d, J = 1.5 Hz), 7.10 (2H, t, J = 6.2 Hz), 7.14 (2H, d, J = 7.9 Hz) 7.20 (2H, d, J = 2.0 Hz), 7.66 (2H, t, J = 6.5 Hz), 8.13 (2H, d, J = 4.5 Hz), 9.26 (1H, s).

13C-NMR (125 MHz, CD₃CN): δ 173.6, 160.0, 157.4, 147.2, 145.8, 141.3, 125.9, 125.3, 124.3, 115.7, 103.1, 57.9, 57.5, 52.8, 45.2.

ESI-TOF-MS m/z calcd for C₃₁H₃₂N₅O₃ [M+H]⁺ = 522.2505, observed 522.2524.

Synthetic procedure of probe 10

10-1(700 mg, 1.65 mmol) was converted to 10-2 according to the reported method.56 The crude 10-2 (1.15 g), trimethyl orthoformate (4.40 mL, 0.365 mmol), and tetrabutylammonium bromide (206 mg, 0.64 mmol) was dissolved in dry MeOH (20 mL)-dry THF (10 mL). The mixture was stirred for 36 h at 45 °C. After removal of the solvent by evaporation, the residue was purified by column chromatography on SiO₂ (CHCl₃ : MeOH = 30 : 1) to give a solid. This material was
washed with i-Pr₂O by filtration to give 10-3 as a beige solid (795 mg, 60% yield from 10-1) ¹H-NMR (500 MHz, DMSO-d₆): δ 3.38 (12H, s), 6.52 (2H, s), 6.76-6.77 (2H, d, J = 2.5 Hz), 7.08 (2H, d, J = 2.5 Hz). ¹³C-NMR (125 MHz, DMSO-d₆): δ 176.7, 161.9, 157.6, 141.9, 112.5, 111.4, 102.0, 100.9, 55.0. ESI-TOF-MS m/z calcd for C₁₉H₃₀NaO₈ [M+Na]⁺ = 399.1056, observed 399.1033.

Synthesis of 10-4
To an ice-cooled solution of 10-3 (350 mg, 0.93 mmol) in dry CH₂Cl₂ (15 mL) was added dry pyridine (1.13 mL, 14.0 mmol). Trifluoromethansulfonic anhydride (782 µL, 4.65 mmol) was added dropwise and the mixture was stirred for 15 min at 0 °C. After dilution with AcOEt, the organic layer was washed with sat. NaHCO₃ aq. and brine followed by drying over Na₂SO₄. After concentration in vacuo, the residues was purified by column chromatography on SiO₂ (hexane : AcOEt = 6 : 1) to give 10-4 (565 mg, 95%) as a colorless solid. ¹H-NMR (500 MHz, CDCl₃): δ 3.50 (12H, s), 6.59 (2H, s), 7.43-7.44 (2H, d, J = 3 Hz), 7.71 (2H, d, J = 3 Hz). ¹³C-NMR (125 MHz, CDCl₃): δ 177.0, 156.7, 152.2, 144.4, 119.9, 118.7 (q, J_C-F = 319 Hz), 116.6, 111.2, 99.9, 55.2. ESI-TOF-MS m/z calcd for C₂₁H₁₈F₆NaO₁₂S₂ [M+Na]⁺ = 663.0042, observed 663.0126.

Synthesis of 10-5
In a sealed glass tube, a mixture of 10-4 (540 mg, 0.84 mmol) and pyrrolidine (690 µL, 8.40 mmol) in dry DMSO (3.5 mL) was stirred for 1 h at 85 °C. After dilution with AcOEt, the organic layer was washed with sat. NaHCO₃ aq. and brine followed by drying over Na₂SO₄. After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO₂ (hexane : AcOEt = 1 : 1) to give 10-5 as a yellow solid (165 mg, 41%). ¹H-NMR (500 MHz, CD₂OD): 2.07-2.10 (8H, m), 3.41-3.43 (8H, t, J = 6.5 Hz), 6.38-6.39 (2H, d, J = 2.5 Hz), 6.75 (2H, s), 6.95-6.96 (2H, d, J = 2.5 Hz). ¹³C-NMR (125 MHz, CDCl₃): δ 177.4, 158.3, 150.4, 141.0, 110.2, 107.1, 101.7, 96.9, 55.5, 47.6. ESI-TOF-MS m/z calcd for C₂₇H₂₄N₂NaO₆ [M+Na]⁺ = 505.2315, observed 505.1919.

Synthesis of 10-6
To an ice-cooled solution of 10-5 (156 mg, 0.32 mmol) in chloroform (4 mL) and water (1 mL) was added dropwise TFA (1 mL), and the mixture was stirred for 15 min at rt. After dilution with sat. NaHCO₃ aq., the mixture was extracted with chloroform (x2). The combined organic layers were washed with water and brine followed by drying over Na₂SO₄. The solvent was removed in vacuo to give 10-6 (135 mg) as a yellow solid. ¹H-NMR (500 MHz, CDCl₃): δ 2.08-2.10 (8H, m), 3.43-3.46 (8H, t, J = 6.5 Hz), 6.49 (2H, d, J = 2.5 Hz), 6.94 (2H, J = 2.5 Hz), 11.12 (2H, s). ¹³C-NMR (125 MHz, CDCl₃): δ 194.6, 176.5, 157.8, 150.6, 139.6, 110.5, 109.1, 99.9, 47.9, 25.4.
ESI-TOF-MS m/z calcd for C_{23}H_{22}N_{2}NaO_{4} [M+Na]^+ = 413.1477, observed 413.1191.

Synthesis of 10-7

To an ice-cooled solution of crude 10-6 (135 mg) in dry THF (12 mL) was added dropwise borane-THF complex (0.89 M in THF solution, 2.88 mL, 2.56 mmol), and the mixture was stirred for 30 min at 60°C. After quenching the reaction with H_2O at 0 °C, the resultant mixture was extracted with AcOEt (x2). The combined organic layers were washed with sat. NaHCO_3 aq. and brine followed by drying over Na_2SO_4. The solvent was removed in vacuo to give 10-7 (135 mg, quant.) as a light purple solid. ^1H-NMR (500 MHz, CDCl_3): δ 1.99-2.02 (8H, m), 3.28-3.31 (8H, t, J = 6.5 Hz), 3.88 (2H, s), 4.70 (4H, s), 6.19-6.20 (2H, d, J = 2 Hz), 6.38 (2H, d, J = 2 Hz). ESI-TOF-MS m/z calcd for C_{23}H_{22}N_{2}NaO_{3} [M+Na]^+ = 403.1998, observed 403.1749.

Synthesis of 10-8

To a solution of 10-7 (65 mg, 0.16 mmol) in dry DMF (2 mL) was added dropwise thionyl chloride (46.5 µL, 0.64 mmol) at rt. The mixture was stirred for 20 min at rt. After dilution with AcOEt, the organic layer with sat. NaHCO_3 aq. and brine followed by drying over Na_2SO_4. After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO_2 (hexane : AcOEt = 1 : 1) to give 10-8 (43 mg) as purple solid. This material was used for the next reaction without further purification. The pure sample of 10-8 was obtained by column chromatography on SiO_2 (hexane : CH_2Cl_2 =1 : 1) for structural analysis. ^1H-NMR (500 MHz, CDCl_3): δ 2.00-2.25 (8H, m), 3.28-3.30 (8H, t, J = 6.5 Hz), 4.03 (2H, s), 4.62 (4H, s), 6.23 (2H, brs), 6.34 (2H, brs). ^13C-NMR (125 MHz, CDCl_3): δ 152.5, 147.4, 136.2, 108.4, 105.9, 99.6, 47.7, 44.7, 25.4, 20.2. ESI-TOF-MS m/z calcd for C_{23}H_{22}Cl_2N_2O [M+H]^+ = 417.1500, observed = 417.1529.

Synthesis of 10-9

A solution of crude 10-8 (43 mg), 5-3 (50 mg, 0.13 mmol), potassium iodide (17 mg, 0.10 mmol), and K_2CO_3 (42 mg, 0.30 mmol) in dry DMF (6 mL) was stirred for 8 h at rt. After dilution with AcOEt, the organic layer was washed with sat. NaHCO_3 aq. (x2) and brine followed by drying over Na_2SO_4. The solvent was removed in vacuo and the residue was purified by column chromatography on SiO_2 (CHCl_3 : MeOH : NH_3 aq. = 80 : 10 : 0.3) to give 10-9 (24 mg, 21%) as a red viscous oil. ^1H-NMR (500 MHz, CD_2OD): 1.21 (9H, s), 2.00-2.05 (10H, m), 2.68-2.73 (4H, m), 3.21-3.24 (8H, m), 3.35-3.40 (4H, m), 3.63-3.73 (8H, m), 4.18-4.24 (2H, m), 6.144 (4H, d, J = 2.5 Hz), 7.20 (2H, t, J = 6.5 Hz), 7.24 (2H, d, J = 8.0 Hz), 7.58-7.62 (2H, m), 8.35 (2H, d, J = 5.0 Hz). ESI-TOF-MS m/z calcd for C_{44}H_{56}N_{2}O_{3} [M+H]^+ = 730.4439, observed 730.4406.

Synthesis of 10

S32
A solution of 10-2 (24.7 mg, 34 µmol) and 2,3-dichloro-5,6-dicyano-\(\nu\)-benzoquinone (15 mg, 66 µmol) in dry EtOH (2 mL) was stirred for 1 h at rt. After removal of the solvent in vacuo, the residue was dissolved in dry CH\(_2\)Cl\(_2\) (2 mL). TFA (2 mL) was added at 0 °C, and the mixture was stirred for 30 min at rt. After removal of the solvent in vacuo, the residue was purified by reverse-phase HPLC (YMC-Triart C18, 250×10 mm I.D., mobile phase: CH\(_3\)CN (0.1% TFA) / H\(_2\)O (0.1% TFA) = 20/80 → 60/40, linear gradient over 40 min) to give 10 (8.2 mg, 38%) as a red oil. The purity of 10 was confirmed to be > 95% by HPLC analysis. \(^1\)H-NMR (500 MHz, CD\(_3\)CN): 1.98-2.06 (8H, m), 3.05-3.70 (20H, m), 3.98 (4H, s), 6.39 (2H, d, \(J = 2.0 \text{ Hz}\)), 7.02 (4H, d, \(J = 2.0 \text{ Hz}\)), 7.10 (2H, d, \(J = 7.5 \text{ Hz}\)), 7.59 (2H, t, \(J = 7.5 \text{ Hz}\)), 8.33 (2H, d, \(J = 4.0 \text{ Hz}\)), 8.92 (1H, d, \(J = 8.5 \text{ Hz}\)). \(^{13}\)C-NMR (125 MHz, CD\(_3\)CN): \(\delta\) 158.9, 158.6, 155.1, 148.4, 142.1, 141.1, 139.3, 125.0, 123.5, 119.5, 113.6, 96.8, 58.1, 57.7, 52.8, 49.8, 45.2, 25.8. ESI-TOF-MS m/z calcd for C\(_{39}\)H\(_{46}\)N\(_7\)O \([\text{M}]^+\) = 628.3758, observed 628.3759.

**Synthetic procedure of probe 11**

![Synthetic procedure of probe 11](image)

**Synthesis 11-2**

A solution of 11-1\(^{57}\) (833 mg, 3.40 mmol), 1,4-dibromobutane (950 mg, 4.40 mmol), K\(_2\)CO\(_3\) (1.4 g, 10.2 mmol) and potassium iodide (1.5 g, 8.8 mmol) in dry CH\(_3\)CN (24 mL) was refluxed for 35 h with stirring. After removal of K\(_2\)CO\(_3\) by filtration, the solution was diluted with AcOEt. The
organic layer was washed with sat. NaHCO₃ aq. and brine followed by drying over Na₂SO₄. After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO₂ (hexane : AcOEt = 10 : 1) to give 11-2 (891 mg, 88%) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) : δ 1.98-2.01 (4H, m), 3.25-3.28 (4H, m), 3.41 (3H, s), 4.50 (2H, s), 4.69 (2H, s), 6.44 (1H, s), 6.60 (1H, s), 6.77 (1H, s). ¹³C-NMR (125 MHz, CDCl₃): δ 148.9, 140.4, 123.3, 117.3, 113.5, 109.5, 95.6, 124.6, 68.8, 55.4, 47.6, 25.4. ESI-TOF-MS m/z calcd for C₁₃H₁₀BrNO₂ [M+H]⁺ = 300.0599, observed 300.0611.

Synthesis of 11-3
To a cooled (−78 °C) solution of 11-2 (891 mg, 3.0 mmol) in dry THF (9 mL) was added 1.6 M n-butyllithium solution in hexane (2.2 ml, 3.4 mmol). After stirring for 20 min at -78°C, dichlorodimethylsilane (291 µL, 3.0 mmol) was added dropwise and the mixture was stirred for 10 min at -78°C. The mixture was slowly warmed to rt and further stirred for 5 min at rt. After quenching the reaction with H₂O, the resultant mixture was diluted with AcOEt. The organic layer was washed with sat. NaHCO₃ aq. and brine followed by drying over Na₂SO₄. After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO₂ (hexane : AcOEt = 6 : 1) to give 11-3 (543 mg, 73%) as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) : δ 0.51 (6H, s), 1.98 (8H, m), 3.27 (8H, m), 3.40 (6H, s), 4.55 (4H, s), 4.69 (4H, s), 6.58 (2H, s), 6.68 (2H, s), 6.82 (2H, s). ESI-TOF-MS m/z calcd for C₂₈H₄₃N₂O₄Si [M+H]⁺ = 499.2992, observed 499.3003.

Synthesis of 11-4
A solution of 11-3 (543 mg, 2.20 mmol) in MeOH (5 mL)-5 N HCl aq. (5 mL) was stirred for 1 h at 50°C. After dilution with sat. NaHCO₃ aq., the resultant mixture was extracted with AcOEt. The organic layer was washed with NaHCO₃ aq. and brine followed by drying over Na₂SO₄. The solvent was removed in vacuo to give 11-4 (345 mg, 77%) as a yellow solid. ¹H-NMR (400 MHz, CDCl₃) : δ 0.53 (6H, s), 1.97-2.00 (8H, m), 3.27-3.30 (8H, t, J = 6.6 Hz), 4.62 (4H, s), 6.60 (2H, s), 6.69 (2H, s), 6.81 (2H, s). ESI-TOF-MS m/z calcd for C₂₄H₃₅N₂O₂Si [M+H]⁺ = 411.2468, observed 411.2488.

Synthesis of 11-5
To a solution of 11-4 (345 mg, 0.84 mmol), triethylamine (468 µL, 3.4 mmol) and 4-dimethylamino pyridine (34 mg, 0.28 mmol) in dry CH₂Cl₂ (10 mL) was added acetic anhydride (238 µL, 2.5 mmol), and the mixture was stirred for 3h at rt. After dilution with dichloromethane, the organic layer was washed with sat. NaHCO₃ aq. and brine followed by drying over Na₂SO₄. The solvent was removed by evaporation, and the residue was purified by column
chromatography on SiO$_2$ (hexane : ethyl acetate = 4 : 1) to give 11-5 (415 mg, quant.) as a colorless oil. $^1$H-NMR (400 MHz, CDCl$_3$) : $\delta$ 0.52 (6H, s), 1.97-2.00 (8H, m), 2.01 (6H, s), 3.26-3.29 (8H, t, $J$ = 6.6 Hz), 5.05 (4H, s), 6.55 (2H, s), 6.71 (2H, s), 6.81 (2H, s). $^{13}$C-NMR (125 MHz, CDCl$_3$) : $\delta$ 170.5, 147.2, 139.0, 135.7, 120.9, 117.0, 112.1, 66.8, 47.3, 25.2, 20.7, -2.4. ESI-TOF-MS $m/z$ calcd for C$_{28}$H$_{39}$N$_2$O$_4$Si [M+H]$^+$ = 495.2679, observed 495.2695.

Synthesis of 11-6
To the solution of 11-5 (415 mg, 0.84 mmol) in AcOH (5 mL) was added paraformaldehyde (37% solution in H$_2$O, 366 µL, 4.50 mmol) and the mixture was stirred for 1 h at 70 °C. After dilution with sat. NaHCO$_3$ aq., the mixture was extracted with chloroform (x2). The combined organic layers were washed with sat. NaHCO$_3$ aq. and brine followed by drying over N$_2$SO$_4$. The solvent was removed in vacuo to give crude 11-6 (401 mg) as a blue solid. $^1$H-NMR (400 MHz, CDCl$_3$) : $\delta$ 0.52 (6H, s), 1.96-2.02 (6H, m), 2.19 (6H, s), 3.26 (8H, t, $J$ = 7.5 Hz), 5.03 (4H, s), 6.56 (2H, s), 6.61 (2H, s), 6.81 (2H, s). ESI-TOF-MS $m/z$ calcd for C$_{28}$H$_{39}$N$_2$O$_4$Si [M+H]$^+$ = 507.2679, observed 507.2691.

Synthesis of 11-7
To a n iced-cooled solution of lithium borohydride (33.9 mg, 1.60 mmol) in dry THF (6 mL) was slowly added the crude 11-6 (401 mg, 0.79 mmol) dissolved in dry THF (12 mL). The mixture was stirred for 30 min at rt. 1N NaOH aq. (4 mL) and MeOH (4 mL) was added at 0 °C, and the mixture was further stirred for 20 min at rt. After dilution with sat NaHCO$_3$ aq., the resultant mixture was extracted with ethyl acetate (x2). The combined organic layers were washed with sat. NaHCO$_3$ aq. and brine followed by drying over N$_2$SO$_4$. After removal of the solvent in vacuo, residue was purified by column chromatography on SiO$_2$ (hexane : AcOEt = 1 : 1) to give 11-7 (128 mg, 36% from 11-5) as a colorless solid. $^1$H-NMR (400 MHz, CDCl$_3$) : $\delta$ 0.47 (6H, s), 1.98-2.01 (8H, m), 3.28-3.32 (8H, t, $J$ = 6.8 Hz), 4.10 (2H, s), 4.81 (4H, s), 6.53-6.54 (2H, d, $J$ = 2.8 Hz), 6.76-6.77 (2H, d, $J$ = 2.8 Hz). $^{13}$C-NMR (125 MHz, CDCl$_3$) : $\delta$ 145.6, 137.8, 137.4, 132.2, 64.2, 47.6, 28.5, 25.1, -3.1. ESI-TOF-MS $m/z$ calcd for C$_{25}$H$_{35}$N$_2$O$_2$Si [M+H]$^+$ = 423.2468, observed 423.2472.

Synthesis of 11-8
To a solution of 11-7 (46 mg, 0.11 mmol) in dry DMF (2 mL) was added dropwise thionyl chloride (40 µL, 0.55 mmol) at rt. The mixture was stirred for 20 min at rt. After dilution with AcOEt, the organic layer with sat. NaHCO$_3$ aq. and brine followed by drying over Na$_2$SO$_4$. After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO$_2$ (hexane : AcOEt = 10 : 1) to give 11-8 (28 mg, 55%) as a purple solid. $^1$H-NMR (400 MHz, CDCl$_3$) :
δ0.45 (6H, s), 2.01 (8H, m), 3.31 (8H, m), 4.16 (2H, s), 4.82 (4H, s), 6.56 (2H, s), 6.77 (2H, s).

13C-NMR (125 MHz, CDCl3) : δ 145.8, 137.9, 134.6, 131.4, 116.7, 114.5, 47.7, 46.3, 28.9, 25.4, -2.8. ESI-TOF-MS m/z calcd for C25H33Cl2N2O2Si [M+H]+ = 459.1790, observed 459.1801.

Synthesis of 11-9
A solution of 11-8 (48.5 mg, 0.11 mmol), 5-3 (55 mg, 0.14 mmol), potassium iodide (23.5 mg, 0.14 mmol) and K2CO3 (50 mg, 0.36 mmol) in dry DMF (10 mL) was stirred for 8 h at rt. After dilution with sat. NaHCO3 aq., the mixture was extracted with AcOEt (x2). The combined organic layers were washed with sat. NaHCO3 aq. and brine followed by drying over Na2SO4. After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO2 (CHCl3 : MeOH : NH3 aq. = 80 : 1 : 0.1) to give 11-9 (67 mg, 79%) as a blue solid. 1H-NMR (500 MHz, CDCl3) : δ 0.44 (6H, s), 1.23 (9H, s), 1.98-2.01 (8H, m), 2.73 (4H, brs), 3.28-3.31 (8H, t, J = 6.3 Hz), 3.62 (4H, brs), 3.71 (4H, s), 3.85 (4H, s), 4.43 (2H, t, J = 2.5 Hz), 6.73-6.74 (2H, d, J = 2.5 Hz), 7.04-7.07 (2H, q, J = 3.0 Hz), 7.26 (2H, m), 7.50 (2H, brs), 8.43-8.44 (2H, d, J = 2.5 Hz).

13C-NMR (125 MHz, CDCl3) : δ 170.7, 1159.7, 155.2, 148.5, 145.3, 137.4, 136.0, 135.5, 133.1, 123.0, 121.6, 117.2, 115.3, 80.2, 77.9, 60.5, 53.4, 47.7, 29.6, 28.2, 28.0, 25.4, -2.6. ESI-TOF-MS m/z calcd for C46H62N7O2Si [M+H]+ = 772.4734, observed 772.4711.

Synthesis of 11
A solution of 11-9 (16.5 mg, 21 µmol) and 2,3-dichloro-5,6-dicyano-p-benzoquinone (11 mg, 48 µmol) in dry EtOH (3 mL) was stirred for 15 min at rt. After removal of the solvent in vacuo, the residue was dissolved in dry CH2Cl2 (2 mL). TFA (2 mL) was added at 0 °C, and the mixture was stirred for 30 min at rt. After removal of the solvent in vacuo, the residue was purified by reverse-phase HPLC (YMC-Triart C18, 250×10 mm I.D., mobile phase: CH3CN (0.1% TFA) / H2O (0.1% TFA) = 5/95 → 60/40, linear gradient over 40 min) to give 11 (7.5 mg, 53%) as a blue solid. The purity of 11 was confirmed to be > 95% by HPLC analysis. 1H-NMR (500 MHz, CD3CN) : δ 0.31 (6H, s), 3.19 (4H, s), 3.44 (4H, s), 3.62 (8H, s), 4.00 (4H, s), 4.16 (4H, s), 6.80 (2H, d, J = 2.5 Hz), 6.83 (2H, s), 7.22 (2H, d, J = 7.5 Hz), 7.29 (2H, t, J = 6.5 Hz), 7.74 (2H, t, J = 7.5 Hz), 8.38 (2H, d, J = 4.5 Hz), 8.49 (1H, s).

13C-NMR (125 MHz, CD3CN) : δ 158.9, 152.4, 151.6, 149.8, 149.1, 147.9, 140.0, 127.1, 124.9, 123.8, 122.4, 121.2, 121.0, 59.5, 57.7, 53.4, 49.9, 25.8, -0.8. ESI-TOF-MS m/z calcd for C41H53N4Si [M+H]2+ = 335.7061, observed 335.7052.
Synthetic procedure of probe 12

A solution of 12-1 (1.06 mL, 10.0 mmol) and 2-formyl pyridine (2.1 g, 20 mol) in dry ethanol (10 mL) was stirred for 30 min at rt. Sodium sulfate (180 mg) was added and the mixture was further stirred overnight at rt. The solvent was removed by evaporation to give crude 12-2 (2.60 g). This material was used for the next reaction without further purification. ESI-TOF-MS m/z calc'd for C_{16}H_{19}N_{5}Na [M+Na]^+ = 304.1538, observed 304.1499.

A solution of crude 12-2 (454 mg) 2-bromoethyl ethyl ether (544 µL, 4.82 mmol) and triethylamine (270 µL, 1.94 mmol) in dry toluene (6.0 mL) was stirred for 38 h at 70 °C. After removal of the solvent in vacuo, the residue was diluted with dry EtOH (6 mL). Sodium tetrahydroborate (200 mg, 5.28 mmol) was slowly added and the mixture was stirred for 20 h at 40 °C. After dilution water, the resultant mixture was extracted with chloroform (x2). The combined organic layers was dried over Na_{2}SO_{4}. After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO\(_2\) (CHCl\(_3\) : MeOH : NH\(_3\) aq. = 10 : 1 : 0.1 → 5 : 1 : 0.1) to give 12-3 (112 mg, 39% from 12-1) as a yellow liquid. \(^1\)H-NMR (500 MHz, CDCl\(_3\)): \(\delta\) 1.15-1.20 (3H, m), 2.60-2.79 (10H, m), 3.42-3.52 (4H, m), 3.76-3.91 (4H, m), 7.10-7.16 (2H, m), 7.26-7.32 (1H, m), 7.47-7.49 (1H, m), 7.57-7.65 (2H, m), 8.49-8.54 (2H, m). \(^{13}\)C-NMR (125 MHz, CDCl\(_3\)): \(\delta\) 159.5, 149.1, 136.3, 122.1, 121.8, 68.8, 66.3, 54.8, 54.3, 53.9, 47.1,
15.0. ESI-TOF-MS m/z calcd for C\textsubscript{20}H\textsubscript{32}N\textsubscript{5}O \ [M+H]\textsuperscript{+} = 358.2607, observed 358.2400.

Synthesis of 12-4
A solution of 9-1\textsuperscript{86} (60 mg, 76 \(\mu\)mol), 12-3 (36 mg, 0.10 mmol), potassium iodide (13 mg, 78 \(\mu\)mol) and K\textsubscript{2}CO\textsubscript{3} (32 mg, 0.23 mmol) in dry DMF (6 mL) was stirred for 7 h at rt. After dilution with sat. NaHCO\textsubscript{3} aq., the mixture was extracted with AcOEt (x2). The combined organic layers were washed with sat. NaHCO\textsubscript{3} aq. and brine followed by drying over Na\textsubscript{2}SO\textsubscript{4}. After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO\textsubscript{2} (CHCl\textsubscript{3} : MeOH : NH\textsubscript{3} aq. = 30 : 1 : 0.1 \(\rightarrow\) 20 : 1 : 0.1) to give 12-4 (71 mg, 87\%) as a colorless oil.

\textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 1.09 (18H, s), 2.21 (2H, t, \(J = 7.5\) Hz), 2.44 (4H, brs), 2.49 (4H, brs), 2.66-2.75 (3H, m), 3.16 (6H, brs), 3.18 (2H, q, \(J = 9.0\) Hz), 3.41-3.50 (4H, m), 3.92 (1H, S), 4.41 (2H, s), 6.23 (2H, s), 6.51 (2H, s), 6.90 (2H, d, \(J = 9.5\) Hz), 7.00 (2H, dt, \(J = 1.0\) Hz, 7.5 Hz), 7.23-7.25 (2H, m), 7.27-7.34 (18H, m), 7.69 (4H, d, \(J = 2.5\) Hz), 7.71 (4H, d, \(J = 2.5\) Hz), 8.39 (2H, d, \(J = 2.5\) Hz), ESI-TOF-MS m/z calcd for C\textsubscript{67}H\textsubscript{78}N\textsubscript{5}O\textsubscript{4}Si\textsubscript{2} \[M+H\] = 1072.5592, observed 1072.5635.

Synthesis of 12
To a solution of 12-4 (24.7 mg, 23 \(\mu\)mol) in dry THF (2 mL) was added tetrabutylammonium fluoride in THF (1 mol/L; 73.7 \(\mu\)L, 73.7 \(\mu\)mol), and the mixture was stirred for 1 h at rt. After removal of the solvent in vacuo, the residue was dissolved in dry EtOH (2 mL). 2,3-Dichloro-5,6-dicyano-p-benzoquinone (8.5 mg, 37 \(\mu\)mol) was added and the mixture was stirred for 10 min at rt. After removal of the solvent in vacuo, the residue was purified by column chromatography on SiO\textsubscript{2} (CHCl\textsubscript{3} : MeOH = 5 : 1 \(\rightarrow\) 7 : 1 \(\rightarrow\) CHCl\textsubscript{3} : MeOH : NH\textsubscript{3} aq. = 7 : 1 : 0.1) to give 13 (6.4 mg, 47\%) as an orange oil.

\textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{3}): \(\delta\) 0.99 (3H, t, \(J = 7.0\) Hz), 2.50 (2H, s), 2.69 (8H, br), 3.16 (3H, br), 3.26 (2H, q, \(J = 7.0\) Hz), 3.34 (2H, br), 3.60 (4H, brs), 3.64 (1H, s), 6.51 (2H, s), 6.73 (2H, s), 7.06 (2H, t, \(J = 5.8\) Hz), 7.13 (2H, t, \(J = 6.8\) Hz), 7.47 (2H, t, \(J = 8.1\) Hz), 8.38 (2H, d, \(J = 4.1\) Hz), 9.89 (1H, brs). \textsuperscript{13}C-NMR (125 MHz, CDCl\textsubscript{3}): \(\delta\) 159.6, 158.9, 148.5, 141.3, 140.9, 136.2, 128.5, 127.5, 123.5, 121.8, 113.4, 102.8, 67.7, 66.3, 60.0, 57.0, 52.9, 51.9, 51.0, 15.1. ESI-TOF-MS m/z calcd for C\textsubscript{35}H\textsubscript{40}N\textsubscript{5}O\textsubscript{4} \[M+H\] = 594.3080, observed 594.3087.

Synthesis of 13
To a solution of 12 (9.5 mg, 16.0 \(\mu\)mol) and DIPEA (16.8 \(\mu\)L, 96.0 \(\mu\)mol) in dry DMF (1.5 mL) was added (4-bromomethyl)phenylacetate (13.2 mg, 57.6 \(\mu\)mol) and the mixture was stirred for 17 h at rt. After dilution with AcOEt, the organic layer was washed with sat. NaHCO\textsubscript{3} aq. and brine followed by drying over Na\textsubscript{2}SO\textsubscript{4}. After removal of the solvent, the residue was purified by reverse-phase HPLC (YMC-Triart C18, 250×10 mm I.D., mobile phase: CH\textsubscript{3}CN (0.1% TFA) /
H$_2$O (0.1% TFA) = 5/95 → 60/40, linear gradient over 40 min) to give 12 (1.2 mg, 11%) as a yellow solid. The purity of 13 was confirmed to be > 95% by HPLC analysis. $^1$H-NMR (500 MHz, CD$_3$CN): δ = 7.70 (2H, dd, $J = 3.5$ Hz, 5.0 Hz), 7.60 (2H, dt, $J = 1.5$ Hz, 8.0 Hz), 7.46 (2H, d, $J = 8.5$ Hz), 7.36 (2H, d, $J = 8.5$ Hz), 7.16 (2H, d, $J = 8.5$ Hz), 7.04-7.09 (5H, m), 6.76 (2H, d, $J = 8.5$ Hz), 4.56 (2H, s), 4.22-4.26 (4H, m), 3.52-3.75 (4H, m), 3.07-3.12 (4H, m), 2.24 (s, 3H), 0.89 (3H, t, $J = 3.5$ Hz). ESI-TOF-MS $m/z$ calcd for C$_{22}$H$_{25}$N$_{5}$O$_{6}$ [M+H]$^+$ = 742.3605, observed 742.3564.

Supplementary References

S1. Ojida, A.; Mito-oka, Y.; Inoue, M.; Hamachi, I. J. Am. Chem. Soc. 2002, 124, 6256-6258.
S2. Grisenti, A. L.; Smith, M. B.; Fang, L.; Bishop, N.; Wagenknecht, P. S.; Inorg. Chim. Acta 2010, 363, 157-162.
S3. Zhang, Y.-M.; Chang, D.-C.; Zhang, J.; Liu, Y.-H.; Yu, X.-Q. Bioorg. Med. Chem. 2015, 23, 5756-5763.
S4. Matouzenko, G. S.; Borshch, S. A.; Jeanneau, E.; Bushuev, M. B.; Chem. Eur. J. 2009, 15, 1252-1260.
S5. Atkins, R. L.; Bliss, D. E.; J. Org. Chem., 1978, 43, 1975-1980.
S6. Takashima, I.; Kanegae, A.; Sugimoto, M.; Ojida, A.; Inorg. Chem. 2014, 53, 7080-7082.
S7. Reuter, R.; Wegner, H. A.; Chem. Eur. J. 2011, 17, 2987-2995.
H-NMR spectrum of probe 5

Current Data Parameters
NAME Dec25-2020-ynth
EXPMOD 10
PROCNR 1

F2 - Acquisition Parameters
Date_ 20201225
Time 11.55 h
INSTRUM spect
PROBHD 2130033_0007
PULPROG zg30
TD 65336
SOLVENT CDC13
NS 16
DS 2
DMH 10000.000 Hz
FIDRES 0.030176 Hz
AQ 3.2767999 sec
RG 31.29
DM 50.000 usec
DE 13.555 usec
TE 300.0 K
DI 1.0000000 usec
DD 1
SP01 500.1730885 MHz
NUCl 1h
FO 4.00 usec
FI 12.00 usec
PLNI 13.5000000 N

F2 - Processing parameters
SI 65336
SF 500.1700121 MHz
WON IM
SSB 0
LB 0.30 Hz
GN 0
FC 1.00
C-NMR spectrum of probe 5

Current Data Parameters
NAME Dec25-2020-anth13C-2
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20201225
Time 17:04 h
INSTRUM spect
PROCNO Z139033_0007 { }
PROGPROG zpg30
TD 65536
SOLVENT CCC13
NS 272
DS 4
SWH 29761.904 Hz
FIDRES 0.908261 Hz
AQ 1.1010048 sec
RG 189.66
DE 16.800 usec
TE 11.00 usec
DD 300.0 Hz
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SF01 125.7804233 MHz
WD01 13C
P0 3.33 usec
P1 10.60 usec
PLM1 650000000 W
SF02 500.172007 MHz
WD02 1H
CF0DG12 wait65
FC0DG2 80.00 usec
PLM2 135000000 W
PLM12 0.30375001 W
PLM13 0.15278000 W

F2 - Processing parameters
ST 32768
SF 125.7678491 MHz
MDM 3 EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
H-NMR spectrum of probe 8
C-NMR spectrum of probe 8
H-NMR spectrum of probe 9
$^{13}$C-NMR spectrum of probe 9.
H-NMR spectrum of probe 10

Current Data Parameters
NAME   AY32001
EXPNO  10
PROCNO 1

F2 - Acquisition Parameters
DATE_   20210418
TIME   18.45 h
INSTRM  spect
PROCBD  Z130033_0007 C
PULPROG zg30
TD     65536
SOLVENT CD3CN
NS    32
DS     2
SWH   10000.000 Hz
FIDRES  0.365176 Hz
AQ     3.2767999 sec
AG     31.29
DE     50.000 usec
TE     200.0 K
DI    1.000000000 sec
TD0    1
SF01   500.1730885 MHz
MDC1   18
PG     4.00 usec
FL1    12.00 usec
PLM1   13.50000000 W

F2 - Processing parameters
SI     65536
SF    500.1700545 MHz
NROM  32
SNR     0
LB     0.30 Hz
PB      0
PC     1.00
$^{13}$C-NMR spectrum of probe 10

Current Data Parameters
NAME: AR30001
EXPNO: 20
PROCNO: 1

F2 - Acquisition Parameters
Data_20210426
Time: 7.45 h
INSTTRUM: spect
PROBHD: Z130033_0007
PULPROG: zpg30
TD: 65.536
SOLVENT: CD3CN
NS: 9600
DS: 4
SNR: 2976.1, 903 Hz
T1MES: 0.988261 Hz
AQ: 1.101048 sec
AQ: 189.66
DW: 16.800 usec
DE: 11.00 usec
TD: 300.0 X
D1: 2.00000000 sec
D11: 0.03000000 sec
TD2: 1
SFO1: 125.7804233 MHz
NUC1: 13C
F0: 3.33 usec
F1: 10.00 usec
PLM1: 65.00000000 W
SFO2: 500.1720007 MHz
NUC2: 1H
CEPFD2: 80.00 usec
PLM2: 13.50000000 W
PLL2: 0.30375001 W
PLM13: 0.12578000 W

F2 - Processing parameters
SI: 32768
SF: 125.7677734 MHz
NOW: EM
SSB: 0
LB: 1.00 Hz
GR: 0
FC: 1.40
H-NMR spectrum of probe 11
C NMR spectrum of probe 11

**Current Data Parameters**

**NAME**
AY30402

**EXPN0**
10

**FROCN0**
1

**F2 - Acquisition Parameters**

- **Date:** 20210410
- **Time:** 8:53 h
- **INSTRUM:** spect
- **FROBNR:** E130033_0007
- **FOPFN:** apyg10
- **TD:** 65536
- **SOLVENT:** CD3CN
- **NS:** 10100
- **DS:** 4
- **Rd:** 29761.904 Hz
- **FDRES:** 0.908261 Hz
- **AQ:** 1.1010048 sec
- **RG:** 189.66
- **DM:** 16.600 usec
- **DE:** 11.00 usec
- **TF:** 300.0 K
- **DU:** 2.0000000 sec
- **DI1:** 0.0300000 sec
- **TD:** 1
- **SF01:** 125.7804233 MHz
- **NUC1:** 13C
- **P0:** 3.33 usec
- **P1:** 10.00 usec
- **PLM1:** 65.00000000 MHz
- **SF02:** 500.1720007 MHz
- **NUC2:** 1H
- **CPDPRG[2]:** wait465
- **PCPD2:** 80.0 usec
- **PLM2:** 13.50000000 MHz
- **PLM12:** 0.30375501 W
- **PLM13:** 0.15278000 W

**F2 - Processing parameters**

- **SI:** 32168
- **SF:** 125.7677732 MHz
- **IMW:** EM
- **ZEB:** 0
- **LB:** 1.00 Hz
- **CB:** 0
- **PC:** 1.40
H-NMR spectrum of probe 12

Current Data Parameters
NAME: AY28102
EXPNO: 10
PROCNO: 1

F2 - Acquisition Parameters
Date: 20210423
Time: 21.38 h
INSTRUM: spect
PROBED: E130033_0007 (-)
FCLASS: 1g30
TD: 6.55 MHz
SOLVENT: CDC13
NS: 16
DS: 2
SNR: 1000.000 Hz
PDUES: 0.3053 Hz
AQ: 3.276999 sec
RD: 31.29
DN: 50.000 usec
DE: 13.55 usec
TZ: 300.0 K
D1: 1.00000000 sec
TDD: 1
SP01: 500.1730885 MHz
NUC1: 1H
PO: 4.00 usec
P1: 12.00 usec
PLW1: 13.5000000 W

F2 - Processing parameters
SI: 65536
SF: 500.1700107 MHz
MDW: 0
SSB: 0
LB: 0.30 Hz
GB: 0
PC: 1.00
C-NMR spectrum of probe 12