

## Supplementary Information

### **Bent-to-planar Si-rhodamines: a distinct rehybridization lights up NIR-II fluorescence for tracking nitric oxide in the Alzheimer's disease brain**

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## 1. Experimental Section

### Materials and General Methods

Unless special stated, all solvents and chemicals were purchased from commercial suppliers in analytical grade and used without further purification. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AM 400 spectrometer, using TMS as an internal standard. High resolution mass spectrometry data were obtained with a Waters LCT Premier XE spectrometer. Absorption spectra were collected on a Varian Cary 500 spectrophotometer, and fluorescence spectra measurements were performed on a Varian Cary Eclipse fluorescence spectrophotometer and a PTI-QM4 steady-state fluorimeter with a 75 W Xenon arc-lamp and a R928 PMT and an InGaAs photodetector. The time-dependent fluorescence measurements were conducted upon continuous illumination (Hamamatsu, LC8 Lightningcure, 300 W). The measurement of pH values in the context of buffer adjustments was performed on a SevenCompact pH-meter (Mettler Toledo). Femtosecond transient absorption (TA) spectra were collected using commercial femtosecond transient absorption spectrometer (Helios fire, Ultrafast System). In vitro PA images were scanned with a PA equipment (VEVO LAZR-X, Fujifilm VisualSonics, USA). IR images were monitored by a compact thermal imaging camera (FOTRIC 286). Confocal fluorescence images were taken on confocal laser scanning microscope (CLSM, Leica confocal microscope TCS SPS CFSMP and a Leica DMI8 microscope). Fluorescence signals in 96-well plates were recorded using a Series III 900/1700 animal imaging system (NIROPTICS, China). In vivo fluorescence images were measured with MARS-FAST in vivo imaging system (Artemis Intelligent Imaging, Shanghai, China). DEA-NONOate (Enzo Biochem, Inc.) was used as the source of NO, which is commercially available.<sup>S1-S2</sup> DEA-NONOate Notes: Dissociates to the free amine and nitric oxide in a pH-dependent manner following first order kinetics. To initiate the release of nitric oxide, add stock alkaline solution of DEA NONOate to excess buffer of pH 7.0 - 7.4. The half life in 0.1 M phosphate buffer, pH 7.4, is  $t_{1/2} = 16$  min. at 22 -25 °C or  $t_{1/2} = 2$  min. at 37 °C. Liberates 1.5 mol of NO per mol of parent compound. Decomposition is nearly instantaneous at pH 5.0.

DCM = dichloromethane

DMSO = dimethylsulfoxide

EtOH = ethanol

MeCN = acetonitrile

MeOH = methanol

THF = tetrahydrofuran

### Spectral measurement details of SiRhd probes

*B*-SiRhd-3 ( $\lambda_{\text{ex}} = 550$  nm) solution (10  $\mu\text{M}$ , including  $\text{Hg}^{2+}$ ) in PBS (0.01 M, pH 7.4) was placed into the wells of a quartz cuvette. Absorbance/FL intensities were continuously acquired using Varian Cary 500 spectrophotometer and Varian Cary Eclipse fluorescence spectrophotometer. Absorbance and fluorescence emission spectra ( $\lambda_{\text{ex}} = 550$  nm) of *B*-SiRhd-4 (10  $\mu\text{M}$ ) in the presence of phosgene in ethonal; absorbance and fluorescence emission spectra ( $\lambda_{\text{ex}} = 550$  nm) of *P*-SiRhd-1 (10  $\mu\text{M}$ ) in the presence of palladium ( $\text{Pd}(\text{PPh}_3)_4$ ) in a mixed solution of  $\text{CH}_3\text{CN}/\text{PBS}$  ( $v/v = 1/3$ ). Absorbance

and fluorescence emission spectra ( $\lambda_{\text{ex}} = 420 \text{ nm}$ ,  $\lambda_{\text{em}} = 808 \text{ nm}$ ) of *B*-SiRhd-7 (10  $\mu\text{M}$ ) in the presence of NO in a mixed solution of  $\text{CH}_3\text{CN}/\text{HEPES}$  ( $v/v = 1/1$ , 0.02 M, pH 7.4).

### Photophysical data

The fluorescence quantum yield ( $\Phi$ ) was measured following the previous method.<sup>53</sup> Briefly,  $\Phi$  was calculated by using the following equation:

$$\Phi_s = \Phi_r (A_r F_s / A_s F_r) (n_s^2 / n_r^2)$$

Where, s and r denote sample and reference, respectively. *A* is the absorbance. *F* is the relative integrated fluorescence intensity and *n* is the refractive index of the solvent. *B*-SiRhd-1, *P*-SiRhd-1, *B*-SiRhd-4, *B*-SiRhd-3 and *P*-SiRhd-3 were measured by using rhodamine 6G ( $\Phi = 88\%$  in ethanol) as a standard.<sup>54</sup> *P*-SiRhd-7 were measured by using IR-26 ( $\Phi = 0.05\%$  in dichloroethane) as a standard.<sup>55</sup>

## Cell Experiment

### Cell Lines

The human epithelioid cervical carcinoma cell line HeLa and the mouse macrophage cell line RAW 264.7 were purchased from the Institute of Cell Biology (Shanghai, China). Cells were all propagated in T-75 flasks cultured at 37  $^{\circ}\text{C}$  under a humidified 5%  $\text{CO}_2$  atmosphere in DMEM medium (GIBCO/Invitrogen, Camarillo, CA, USA), which were supplemented with 10 % fetal bovine serum (FBS, Biological Industry, Kibbutz Beit Haemek, Israel) and 1 % penicillin-streptomycin (10,000 U  $\text{mL}^{-1}$  penicillin and 10 mg  $\text{mL}^{-1}$  streptomycin, Solarbio life science, Beijing, China).

### In vitro Cellular Imaging

The cells at  $1 \times 10^5$  cells/well were seeded onto glass-bottom petri dishes with complete medium (1.5 mL) for 12 h. The cells pro-incubated with 10  $\mu\text{M}$  *B*-SiRhd-3 or *B*-SiRhd-7 for 0.5 h. Then the cells incubated with and without inducer. PBS was used to wash cells for three times to clean the background. The images were then photographed by using a confocal laser scanning microscope Leica TCS SP8 (63  $\times$  oil lens).

### Animals

All animal studies were approved by the Animal Care and Use Committee of East China Normal University in accordance with the guidelines for the care and use of laboratory animals. The 6-week-old female BALB/cA nude mice were produced from Shanghai SLAC Laboratory Animal Co. Ltd., and maintained under standard conditions. The animals were housed in sterile cages within laminar airflow hoods in a specific pathogen-free room with a 12-h light/12-h dark schedule and fed autoclaved chow and water *ad libitum*. Number of qualitative qualification: No.20220004001694. Production Permit No.: SCXK (Shanghai) 2022-0004. The 12-month-old male APP/PS1 transgenic mice and wild-type mice were produced from Jiangsu Huachuang Sino Pharmatech Co., Ltd. (Jiangsu, China), and

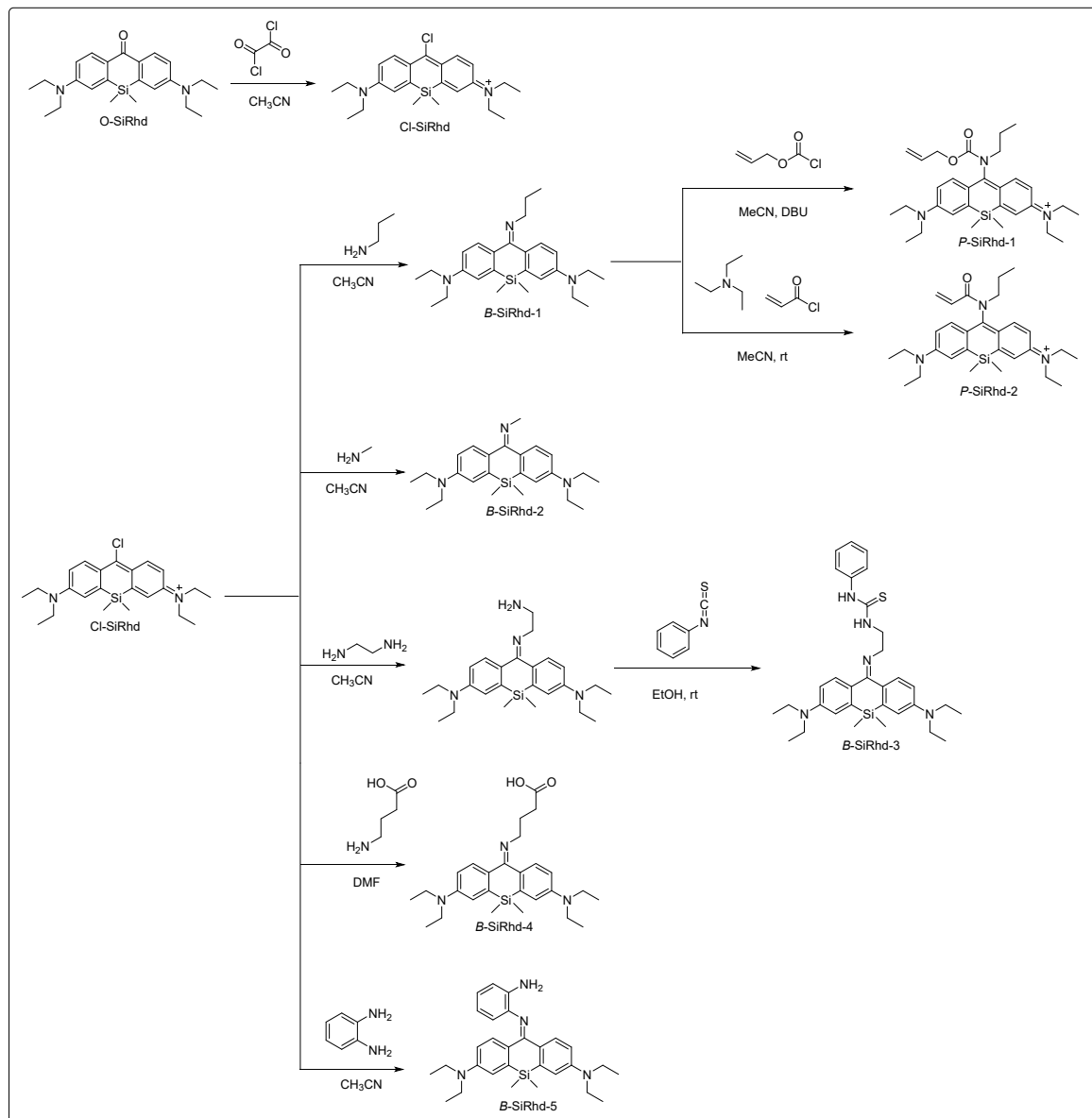
maintained under standard conditions. Number of qualitative qualification: No.20220168. Production Permit No.: SCXK (Jiangsu) 2020-0009.

### ***In vivo* NIR II fluorescence imaging**

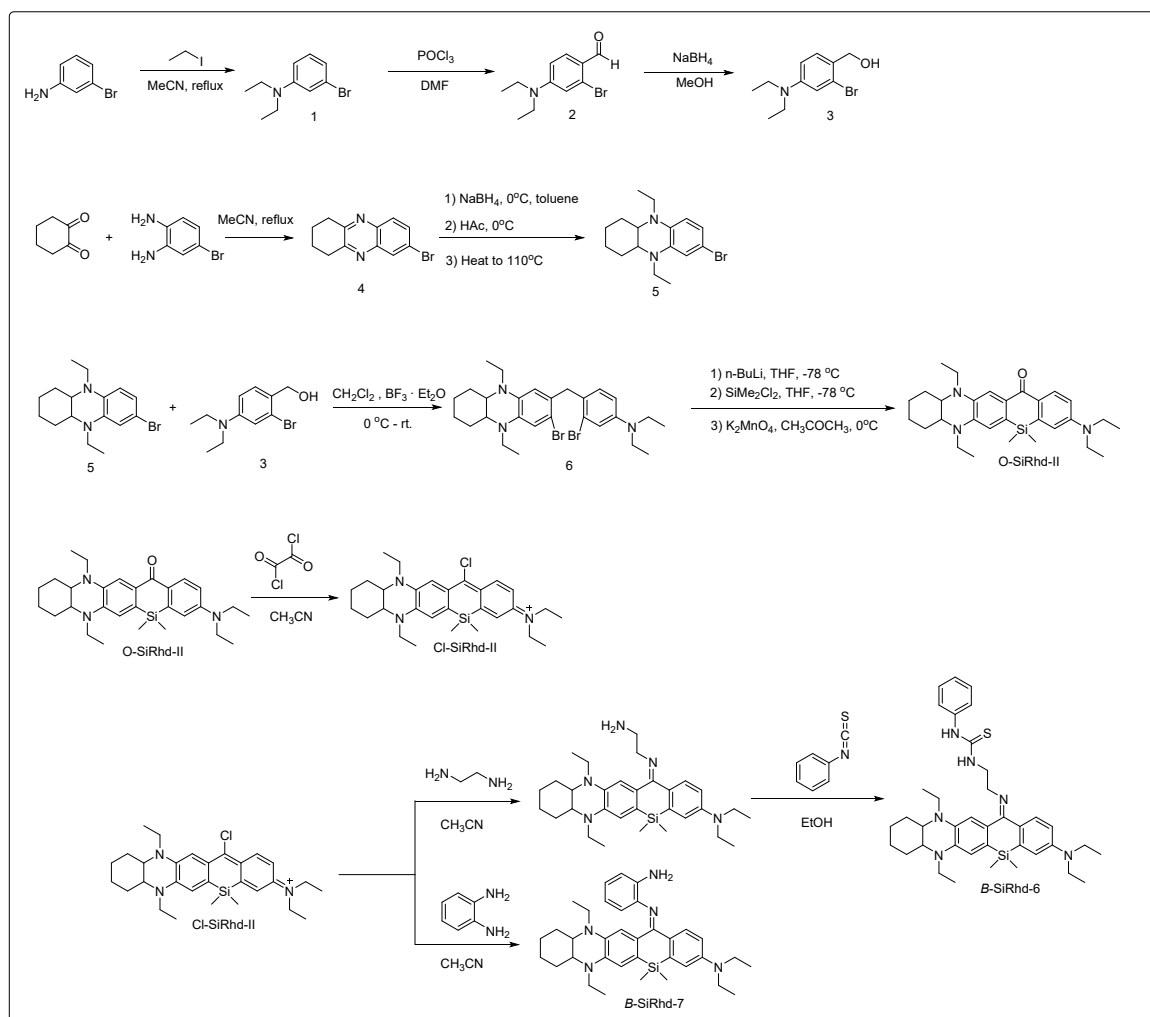
Mice were treated with either LPS (1 mg/mL, 4 mg/Kg) or a saline (as control group) intraperitoneally. After 6 h, the B-SiRhd-7@liposome (0.4 mM, 200  $\mu$ L) were tail intravenous injected into mice for in vivo imaging. NIR-II images of mice anesthetized with isoflurane were recorded at various time points post-injection through MARS-FAST in vivo imaging system (Artemis Intelligent Imaging, Shanghai, China). The excitation wavelength was 808 nm, and the NIR-II fluorescence signal was collected with 1100 nm LP filters (Thorlabs).

**Synthesis of Intermediate Compound 1-7 and *B*-SiRhd-1, *P*-SiRhd-1, *P*-SiRhd-2, *B*-SiRhd-3, *B*-SiRhd-4, *B*-SiRhd-5, *B*-SiRhd-6 and *B*-SiRhd-7**

The compound **O-SiRhd**<sup>56</sup> was synthesized by the established procedures from our group.



**Scheme S1.** Synthetic route of compound **Cl-SiRhd**, **B-SiRhd-1**, **P-SiRhd-1**, **P-SiRhd-2**, **B-SiRhd-3**, **B-SiRhd-4**, **B-SiRhd-5**.



**Scheme S2.** Synthetic route of compound **Cl-SiRhd-II**, **B-SiRhd-6** and **B-SiRhd-7**.

### Synthesis of compound **Cl-SiRhd**

A solution of compound **O-SiRhd** (100 mg, 0.26 mmol) in CH<sub>3</sub>CN (10 mL) was stirred at 0 °C under N<sub>2</sub> for 10 min, and then (COCl)<sub>2</sub> (0.10 mL) was added dropwise over 1 min. The reaction mixture was stirred for 10 min. The completion of reaction was monitored by TLC. After completion of the reaction, the solvents were removed under reduced pressure and the residue was purified by silica gel chromatography using dichloromethane/methanol (v/v, 20:1) as the eluent to afford **Cl-SiRhd** (30 mg): Yield 34%. <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>CN, ppm): δ 0.63 (s, 6H, -SiCH<sub>3</sub>), 1.2 (t, *J* = 7.2 Hz, 12H, -CH<sub>2</sub>CH<sub>3</sub>), 3.69 (q, *J* = 7.2 Hz, 8H, -CH<sub>2</sub>CH<sub>3</sub>), 7.87 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.4 Hz, 2H, Ph-H), 8.14 (d, *J* = 2.4 Hz, 2H, Ph-H), 8.54 (d, *J* = 8.4 Hz, 2H, Ph-H). High resolution mass spectrometry (ESI-MS, m/z): [M]<sup>+</sup> Calc for C<sub>23</sub>H<sub>32</sub>N<sub>2</sub>SiCl, 399.2023, Found, 399.2025.

### Synthesis of compound **B-SiRhd-1**

A solution of compound **O-SiRhd** (100 mg, 0.26 mmol) in CH<sub>3</sub>CN (10 mL) was stirred at 0 °C under N<sub>2</sub> for 10 min, and then (COCl)<sub>2</sub> (0.10 mL) was added dropwise over 1 min. The reaction mixture was stirred for 10 min. The solvents were removed under reduced pressure and the crude compound was used without further purification. To a solution crude compound in CH<sub>3</sub>CN (10 mL) at 0 °C was added phenyl n-propylamine (23.30 mg, 0.39 mmol). The mixture was stirred overnight at 25 °C. The completion of reaction was monitored by TLC. After completion of the reaction, the solvents were removed under reduced pressure and the residue was purified by silica gel chromatography using dichloromethane/methanol (v/v, 30:1) as the eluent to afford **B-SiRhd-1** as a red solid (30 mg): Yield 27%. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 0.49 (s, 6H, -SiCH<sub>3</sub>), 0.82 (t, *J* = 7.2 Hz, 3H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.14 (q, *J* = 6.4 Hz, 12H, -CH<sub>2</sub>CH<sub>3</sub>), 1.79 (q, *J* = 7.2 Hz, 2H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.50 (t, 8H, -CH<sub>2</sub>CH<sub>3</sub>), 3.85 (q, *J* = 6.4 Hz, 2H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 6.82-6.88 (m, 2H, Ph-H), 6.98 (d, *J* = 2.4 Hz, 1H, Ph-H), 7.06 (d, *J* = 2.4 Hz, 1H, Ph-H), 7.62 (d, *J* = 9.2 Hz, 1H, Ph-H), 7.79 (d, *J* = 9.2 Hz, 1H, Ph-H). High resolution mass spectrometry (ESI-MS, m/z): [M]<sup>+</sup> Calc for C<sub>26</sub>H<sub>40</sub>N<sub>3</sub>Si, 422.2992, Found, 422.2997.

### Synthesis of compound **B-SiRhd-2**

A solution of compound **O-SiRhd** (100 mg, 0.26 mmol) in CH<sub>3</sub>CN (10 mL) was stirred at 0 °C under N<sub>2</sub> for 10 min then (COCl)<sub>2</sub> (0.10 mL) was added dropwise over 1 min. After stirring 10 min of the reaction mixture, the solvents were removed under reduced pressure and the crude compound was used without further purification. To a solution crude compound in CH<sub>3</sub>CN (10 mL) at 0 °C was added phenyl methylamine (0.10 mL). The mixture was stirred overnight at 25 °C. The completion of reaction was monitored by TLC. After completion of the reaction, the solvents were removed under reduced pressure and the residue was purified by silica gel chromatography using dichloromethane/methanol (v/v, 30:1) as the eluent to afford **B-SiRhd-2** as an orange solid (30 mg): Yield 30%. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 0.46 (s, 6H, -SiCH<sub>3</sub>), 1.18-1.26 (m, 12H, -CH<sub>2</sub>CH<sub>3</sub>), 3.42-3.51 (m, 8H, -CH<sub>2</sub>CH<sub>3</sub>), 3.67 (s, 3H, -NCH<sub>3</sub>), 6.70-6.73 (m, 1H, Ph-H), 6.76 (d, *J* = 2.8 Hz, 1H, Ph-H), 6.88-6.91 (m, 2H, Ph-H), 7.57 (d, *J* = 8.8 Hz, 1H, Ph-H), 8.45 (d, *J* = 9.2 Hz, 1H, Ph-H). High resolution mass spectrometry (ESI-MS, m/z): [M+H]<sup>+</sup> Calc for C<sub>24</sub>H<sub>36</sub>N<sub>3</sub>Si, 394.2679, Found, 394.2679.

### Synthesis of compound **B-SiRhd-3**



A solution of compound **O-SiRh** (100 mg, 0.26 mmol) in CH<sub>3</sub>CN (10 mL) was stirred at 0 °C under N<sub>2</sub> for 10 min then (COCl)<sub>2</sub> (0.10 mL) was added dropwise over 1 min. The reaction mixture was stirred for 10 min then ethylenediamine (0.35 mL, 5.25 mmol) was added. The mixture was stirred 30 min at room temperature. The solvents were removed under reduced pressure and the crude compound was used without further purification. To a solution crude compound in ethanol (10 mL) at 0 °C was added phenyl isothiocyanate (0.10 mL). The mixture was stirred overnight at 25 °C. The completion of reaction was monitored by TLC. After completion of the reaction, the solvents were removed under reduced pressure and the residue was purified by silica gel chromatography using dichloromethane/methanol (v/v, 20:1) as the eluent to afford **B-SiRh-3** as a red solid (12 mg): Yield 8.2%. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 0.46 (s, 6H, -SiCH<sub>3</sub>), 1.14 (t, 12H, *J* = 6.8 Hz, -CH<sub>2</sub>CH<sub>3</sub>), 3.49 (d, 8H, *J* = 6.8 Hz, -CH<sub>2</sub>CH<sub>3</sub>), 4.05 (d, 4H, -CH<sub>2</sub>-), 6.79-6.88 (m, 2H, Ph-H), 6.97 (s, 1H, Ph-H), 7.04 (s, 1H, Ph-H), 7.10 (d, 1H, Ph-H), 7.24 (s, 4H, Ph-H), 7.66 (s, 1H, Ph-H), 7.83 (s, 1H, Ph-H), 8.03 (s, 1H, -NH-), 9.93 (s, 1H, -NH-). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, ppm): δ = -2.57, 12.32, 43.13, 43.86, 123.21, 124.27, 124.60, 128.63, 139.02, 180.57. Mass spectrometry (ESI-MS, *m/z*): [M+H]<sup>+</sup> Calc for C<sub>32</sub>H<sub>44</sub>N<sub>5</sub>SSi, 558.3087, Found, 558.3079.

#### Synthesis of compound **B-SiRh-4**

A solution of compound **O-SiRh** (100 mg, 0.26 mmol) in CH<sub>3</sub>CN (10 mL) was stirred at 0 °C under N<sub>2</sub> for 10 min then (COCl)<sub>2</sub> (0.10 mL) was added dropwise over 1 min. After stirring 10 min of the reaction mixture, the solvents were removed under reduced pressure and the crude compound was used without further purification. To a solution crude compound in DMF (30 mL) was added 4-aminobutyric acid (41 mg, 0.39 mmol). The mixture was heated to reflux in an argon atmosphere for 5 h. The completion of reaction was monitored by TLC. After completion of the reaction, the solvents were removed under reduced pressure and the residue was purified by silica gel chromatography using dichloromethane/methanol (v/v, 20:1) as the eluent to afford **B-SiRh-4** as a red solid (30 mg): Yield 27%. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 0.43 (s, 6H, -SiCH<sub>3</sub>), 1.12 (s, 12H, -CH<sub>2</sub>CH<sub>3</sub>), 1.85 (s, 2H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOH), 2.28 (s, 2H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOH), 3.41 (s, 8H, -CH<sub>2</sub>CH<sub>3</sub>), 3.77 (s, 2H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOH), 6.72 (s, 2H, Ph-H), 6.83 (s, 1H, Ph-H), 6.94 (s, 1H, Ph-H), 7.41 (d, *J* = 8.4 Hz, 1H, Ph-H), 7.66 (d, *J* = 8 Hz, 1H, Ph-H). Mass spectrometry (ESI-MS, *m/z*): [M+H]<sup>+</sup> Calc for C<sub>27</sub>H<sub>40</sub>N<sub>3</sub>O<sub>2</sub>Si, 466.2890, Found, 466.2885.

#### Synthesis of compound **B-SiRh-5**

A solution of compound **O-SiRh** (100 mg, 0.26 mmol) in CH<sub>3</sub>CN (10 mL) was stirred at 0 °C under N<sub>2</sub> for 10 min then (COCl)<sub>2</sub> (0.10 mL) was added dropwise over 1 min. After stirring 10 min of the reaction mixture, the solvents were removed under reduced pressure and the crude compound was used without further purification. To a solution crude compound in CH<sub>3</sub>CN (10 mL) at 0 °C was added *o*-phenylenediamine (0.32 g, 3 mmol). The mixture was stirred overnight at 25 °C. After completion of the reaction, the solvents were removed under reduced pressure and the residue was purified by silica gel chromatography using dichloromethane/methanol (v/v, 30:1) as the eluent to afford **B-SiRh-5** as a red solid (30 mg): Yield 30%. <sup>1</sup>H-NMR (400 Hz, CDCl<sub>3</sub>, ppm): δ 0.51 (s, 6H, -SiCH<sub>3</sub>), 1.18 (t, *J* = 7.2 Hz, 12H, -CH<sub>2</sub>CH<sub>3</sub>), 3.41 (q, *J* = 7.2 Hz, 8H, -CH<sub>2</sub>CH<sub>3</sub>), 6.56-6.58 (m, 2H, Ph-H), 6.81-6.82 (m, 3H, Ph-H), 7.02-7.12 (m, 3H, Ph-H),

7.73 (s, 2H, Ph-H). Mass spectrometry (ESI-MS, m/z): [M+H]<sup>+</sup> Calc for C<sub>29</sub>H<sub>39</sub>N<sub>4</sub>Si, 471.2944, Found, 471.2946.

### Synthesis of compound **P-SiRhd-1**

DBU (94 mg, 0.62 mmol) was added dropwise to the solution of compound **B-SiRhd-1** (130 mg, 0.31 mmol) in CH<sub>3</sub>CN (10 mL). Then allyl chloroformate (75 mg, 0.62 mmol) was added over 1 min at 0 °C. The reaction mixture was stirred for 2h at room temperature. The completion of reaction was monitored by TLC. After completion of the reaction, CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was added to the mixture, the combined organic layer was washed with brine. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The residue was purified by silica gel chromatography using dichloromethane/methanol (v/v, 30:1) as the eluent to afford **P-SiRhd-1** as a green solid (43 mg): Yield 35.9%. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 0.55 (d, *J* = 10.8 Hz, 6H, -SiCH<sub>3</sub>), 0.80-0.84 (m, 3H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.21-1.23 (t, 12H, *J* = 7.2 Hz, -CH<sub>2</sub>CH<sub>3</sub>), 1.54-1.60 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.52-3.56 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.72-3.74 (m, 8H, -CH<sub>2</sub>CH<sub>3</sub>), 4.49 (q, 2H, *J* = 1.6 Hz, -COOCH<sub>2</sub>-), 4.68 (d, 1H, *J* = 5.2 Hz, -OCH<sub>2</sub>CH=CH<sub>2</sub>), 4.90-5.02 (m, 2H, -OCH<sub>2</sub>CH=CH<sub>2</sub>), 7.06 (dd, *J*<sub>1</sub> = 9.6 Hz, *J*<sub>2</sub> = 2.8 Hz, 2H, Ph-H), 7.38 (d, *J* = 2.4 Hz, 2H, Ph-H), 7.59-7.62 (d, 2H, Ph-H). High resolution mass spectrometry (ESI-MS, m/z): [M]<sup>+</sup> Calc for C<sub>30</sub>H<sub>44</sub>N<sub>3</sub>O<sub>2</sub>Si, 506.3205, Found, 506.3205.

### Synthesis of compound **P-SiRhd-2**

Triethylamine (63 mg, 0.62 mmol) was added dropwise to the solution of compound **B-SiRhd-1** (130 mg, 0.31 mmol) in CH<sub>3</sub>CN (10 mL). Then acryloyl chloride (57 mg, 0.62 mmol) was added over 1 min at 0 °C. The reaction mixture was stirred for 2h at room temperature. The completion of reaction was monitored by TLC. After completion of the reaction, CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was added to the mixture, the combined organic layer was washed with brine. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The residue was purified by silica gel chromatography using dichloromethane/methanol (v/v, 20:1) as the eluent to afford **P-SiRhd-2** as a green solid (66 mg): Yield 58.5%. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 0.56 (s, 3H, -SiCH<sub>3</sub>), 0.62 (s, 3H, -SiCH<sub>3</sub>), 0.82 (t, *J* = 7.2 Hz, 3H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.22 (t, *J* = 7.2 Hz, 12H, -CH<sub>2</sub>CH<sub>3</sub>), 1.52-1.58 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.05-3.08 (m, 2H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.73 (s, 8H, -CH<sub>2</sub>CH<sub>3</sub>), 5.62-5.65 (m, 1H, -CH=CH<sub>2</sub>), 5.96-6.03 (m, 1H, -CH=CH<sub>2</sub>), 6.26-6.31 (m, 1H, -CH=CH<sub>2</sub>), 7.04-7.08 (m, 2H, Ph-H), 7.42 (d, *J* = 2.4 Hz, 2H, Ph-H), 7.49 (d, 2H, Ph-H). High resolution mass spectrometry (ESI-MS, m/z): [M]<sup>+</sup> Calc for C<sub>29</sub>H<sub>42</sub>N<sub>3</sub>O<sub>2</sub>Si, 476.3097, Found, 476.3092.

### Synthesis of compound **1**

3-bromoaniline (2.00 g, 11.70 mmol), EtI (7.30 g, 46.80 mmol), and K<sub>2</sub>CO<sub>3</sub> (1.60 g, 11.70 mmol) were dissolved in anhydrous CH<sub>3</sub>CN (50 mL). The mixture was heated to reflux in an argon atmosphere for 11 h. The completion of reaction was monitored by TLC. After completion, the reaction mixture was cooling to room temperature, the mixture was filtered. The organic layer was concentrated under vacuum, and then the crude product was purified by silica gel chromatography using dichloromethane/petroleum ether (v/v, 1:10) as the eluent to afford **compound 1** as a colorless liquid (1.6 g): Yield 60.3%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 1.15 (t, 6H, *J* = 7.2 Hz, -CH<sub>2</sub>CH<sub>3</sub>), 3.32 (q, 4H, *J* = 7.2 Hz, -CH<sub>2</sub>CH<sub>3</sub>), 6.57 (dd, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 2.4 Hz, 1H, Ph-H), 6.72-6.77 (m, 2H, Ph-H), 7.03 (t, *J* = 8 Hz, 1H, Ph-H). <sup>13</sup>C NMR (100

MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 12.57, 44.44, 110.26, 114.26, 117.95, 123.74, 130.56, 149.04. Mass spectrometry (ESI-MS, m/z): [M+H]<sup>+</sup> Calc for C<sub>10</sub>H<sub>15</sub>NBr, 228.0388, Found, 228.0380.

### Synthesis of compound 2

0.25 mL POCl<sub>3</sub> was added dropwise in anhydrous DMF (5 mL) in 0 °C and the reaction mixture was stirred at room temperature for 30 min. **Compound 1** (1.00 g, 4.40 mmol) was added in the reaction mixture. The mixture was stirred in an argon atmosphere at room temperature for 6 h. The reaction mixture was poured into 200 mL cool water. The mixture was filtered. The residue was washed by water for three times to afford **compound 2** as a white solid. Yield 41.24%. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  1.22 (t, *J* = 7.2 Hz, 6H, -CH<sub>2</sub>CH<sub>3</sub>), 3.42 (q, *J* = 7.2 Hz, 4H, -CH<sub>2</sub>CH<sub>3</sub>), 6.59-6.62 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.4 Hz, 1H, Ph-H), 6.76 (d, *J* = 2.4 Hz, 1H, Ph-H), 7.78 (d, *J* = 8.8 Hz, 1H, Ph-H), 10.05 (d, *J* = 0.4 Hz, 1H, -CHO). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 12.43, 44.81, 110.26, 114.32, 121.50, 131.32, 152.50, 190.03. Mass spectrometry (ESI-MS, m/z): [M+H]<sup>+</sup> Calc for C<sub>11</sub>H<sub>15</sub>NOBr, 256.0337, Found, 256.0334.

### Synthesis of compound 3

**Compound 2** (300 mg, 1.18 mmol) was dissolved in methanol (6.00 mL), and then sodium borohydride (67.11 mg, 1.76 mmol) was added into the solution. The reaction mixture was stirred for 2 h at room temperature. H<sub>2</sub>O was added to the residue, and the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The residue was purified by column chromatography using dichloromethane/petroleum ether (v/v, 1:2) as the eluent to afford **compound 3** as a colorless liquid (250 mg): Yield 83.36%. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  1.15 (t, *J* = 7.2 Hz, 6H, -CH<sub>2</sub>CH<sub>3</sub>), 1.81 (s, 1H, -CH<sub>2</sub>OH), 3.33 (q, *J* = 7.2 Hz, 4H, -CH<sub>2</sub>CH<sub>3</sub>), 4.62 (s, 2H, -CH<sub>2</sub>OH), 6.58 (dd, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 2.4 Hz, 1H, Ph-H), 6.83 (d, *J* = 2.8 Hz, 1H, Ph-H), 7.21 (d, *J* = 8.8 Hz, 1H, Ph-H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 12.46, 44.43, 64.98, 110.75, 115.17, 124.75, 125.97, 130.69, 148.48. Mass spectrometry (ESI-MS, m/z): [M+H]<sup>+</sup> Calc for C<sub>11</sub>H<sub>17</sub>NOBr, 258.0494, Found, 258.0494.

### Synthesis of compound 4

1,2-Cyclohexanedione (500 mg, 4.46 mmol) and 4-Bromobenzene-1,2-diamine (1.00 g, 5.53 mmol) was dissolved in acetonitrile. The reaction mixture was then stirred at 80 °C for 8 h. The completion of reaction was monitored by TLC. After completion, the reaction mixture was cooling to room temperature. The solvent was removed in a rotary evaporator and crude product was purified by column chromatography using ethanldan/petroleum ether (v/v, 1:4) as the eluent to afford **compound 4** as a pale yellow solid (890 mg): Yield 76.23%. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  2.03-2.06 (m, 4H, -CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>-), 3.15 (dd, *J*<sub>1</sub> = 4.8 Hz, *J*<sub>2</sub> = 2.4 Hz, 4H, -CH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>-), 7.73 (dd, *J*<sub>1</sub> = 8 Hz, *J*<sub>2</sub> = 2 Hz, 1H, Ph-H), 7.83 (d, *J* = 8 Hz, 1H, Ph-H), 8.15 (d, *J* = 2 Hz, 1H, Ph-H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  = 22.65, 33.19, 122.66, 129.68, 130.67, 132.47, 139.87, 141.74, 154.62, 155.21. Mass spectrometry (ESI-MS, m/z): [M+H]<sup>+</sup> Calc for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>Br, 263.0184, Found, 263.0181.

### Synthesis of compound 5

**Compound 4** (0.45 g, 1.70 mmol) was dissolved in dry toluene (80 mL) and cooled to 0 °C. To this cold solution was added sodium borohydride (0.65 g, 17.00 mmol) over a period of 15 min. The pale yellow slurry thus obtained was stirred for 10 min. Glacial acetic acid (3.40 mL, 0.60 mmol) was added to it drop wise over a period of 1 h maintaining the temperature 5-10 °C. The resulting brown slurry was stirred for another 1 h at 10 °C and allowed to attain room temperature. It was then heated to gentle reflux for 5 h. On cooling, a thick red resinous mass was obtained. To this red resinous mass water (250 mL) was added. The toluene layer formed was separated and aqueous layer was extracted with ethyl acetate (3 × 100 mL). Combined extracts and toluene layer were washed repeatedly with dilute sodium carbonate solution and then with water, dried over anhydrous sodium sulphate, filtered and vacuum evaporated. The dark brown oil obtained was purified by column chromatography using dichloromethane/petroleum ether (v/v, 1:10) as the eluent to afford **compound 5** as a pale yellow oil (0.17 g): Yield 31.05%. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 1.09-1.16 (m, 6H, -CH<sub>2</sub>CH<sub>3</sub>), 1.34-1.38 (m, 2H, -CH<sub>2</sub>-), 1.54-1.57 (m, 4H, -CH<sub>2</sub>-), 1.79-1.86 (m, 2H, -CH<sub>2</sub>-), 3.11-3.44 (m, 8H, -CH<sub>2</sub>CH<sub>3</sub>, -NCHCH<sub>2</sub>-), 6.39 (d, *J* = 8.8 Hz, 1H, Ph-H), 6.60 (d, *J* = 2 Hz, 1H, Ph-H), 6.67 (dd, *J*<sub>1</sub> = 8.4 Hz, *J*<sub>2</sub> = 2 Hz, 1H, Ph-H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 11.53, 22.39, 27.00, 27.63, 41.92, 54.65, 55.35, 109.54, 112.06, 113.16, 119.28, 133.99, 136.47. Mass spectrometry (ESI-MS, *m/z*): [M+H]<sup>+</sup> Calc for C<sub>16</sub>H<sub>24</sub>N<sub>2</sub>Br, 322.1123, Found, 322.1120.

### Synthesis of compound 6

**Compound 3** (1.95 g, 7.58 mmol) and **compound 5** (2.29 g, 7.11 mmol) were dissolved in methanol (6.00 mL), and then BF<sub>3</sub>·OEt<sub>2</sub> (1.92 mL, 15.16 mmol) was dripped into the solution. The reaction mixture was stirred for 24 h at room temperature, diluted with water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The residue was purified by column chromatography using dichloromethane/petroleum ether (v/v, 1:10) as the eluent to afford **compound 6** as a pale yellow oil (1.50 g): Yield 37.6%. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 0.99-1.03 (m, 3H, -CH<sub>2</sub>CH<sub>3</sub>), 1.11-1.16 (m, 9H, -CH<sub>2</sub>CH<sub>3</sub>), 1.32-1.37 (m, 2H, -CH<sub>2</sub>-), 1.50-1.57 (m, 4H, -CH<sub>2</sub>-), 1.79-1.84 (m, 2H, -CH<sub>2</sub>-), 3.01-3.42 (m, 10H, -NCH<sub>2</sub>CH<sub>3</sub>, -NCHCH<sub>2</sub>-), 3.94 (s, 2H, -PhCH<sub>2</sub>Ph-), 6.28 (s, 1H, Ph-H), 6.52 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.8 Hz, 1H, Ph-H), 6.67 (s, 1H, Ph-H), 6.86-6.88 (m, 2H, Ph-H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ = 11.42, 12.49, 22.26, 27.47, 40.16, 41.97, 44.42, 55.11, 111.40, 113.25, 113.98, 135.38, 125.66, 126.61, 127.26, 130.83, 134.45, 134.81, 147.16. Mass spectrometry (ESI-MS, *m/z*): [M+H]<sup>+</sup> Calc for C<sub>27</sub>H<sub>38</sub>N<sub>3</sub>Br<sub>2</sub>, 562.1432, Found, 562.1435.

### Synthesis of O-SiRhd-II

To a dried flask flushed with argon, **compound 6** (1.50 g, 2.67 mmol) and anhydrous THF (17 mL) were added. The solution was cooled to -78 °C, 2.4 M n-BuLi (3.20 mL, 8.01 mmol) was added, and the mixture was stirred for 0.5 h. At the same temperature, a solution of SiMe<sub>2</sub>Cl<sub>2</sub> (3.47 mmol) in anhydrous THF (10 mL) was slowly added, and the mixture was slowly warmed to room temperature, then stirred for 8 h. After completion, the reaction was quenched by addition of saturated NH<sub>4</sub>Cl aq and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with brine and dried over

Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the crude compound was used without further purification. To a solution crude compound in acetone (50 mL) at 0 °C was added KMnO<sub>4</sub> (1.26 g, 8.01 mmol) in small portions over a period of 1 h with stirring. The mixture was stirred for another 1 h at the same temperature, then diluted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL), filtered through paper filter and evaporated to dryness. The residue was purified by column chromatography using dichloromethane/petroleum ether (v/v, 2:1) as the eluent to afford **O-SiRhd-II** as a yellow solid (10 mg): Yield 1%. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 0.38 (d, *J* = 6 Hz, 6 H, -SiCH<sub>3</sub>), 1.08-1.16 (m, 12H, -CH<sub>2</sub>CH<sub>3</sub>), 1.34-1.38 (m, 2H, -CH<sub>2</sub>-), 1.47-1.48 (m, 2H, -CH<sub>2</sub>-), 1.56-1.61 (m, 2H, -CH<sub>2</sub>-), 1.72-1.82 (m, 2H, -CH<sub>2</sub>-), 3.20-3.64 (m, 10H, -NCH<sub>2</sub>CH<sub>3</sub>, -NCHCH<sub>2</sub>-), 6.68 (s, 1H, Ph-H), 6.80 (d, *J* = 9.2 Hz, 2H, Ph-H), 7.48 (s, 1H, Ph-H), 8.08 (d, *J* = 8.4 Hz, 1H, Ph-H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, ppm): δ = 0.00, 12.30, 13.52, 44.68, 111.43, 128.25, 129.03, 131.01, 136.22, 138.76, 141.60, 149.61, 184.54. Mass spectrometry (ESI-MS, *m/z*): [M+H]<sup>+</sup> Calc for C<sub>29</sub>H<sub>42</sub>N<sub>3</sub>OSi, 476.3097, Found, 476.3097.

### Synthesis of Cl-SiRhd-II

The mixture of **O-SiRhd-II** (100 mg, 0.21 mmol) in CH<sub>3</sub>CN (10 mL) was stirred at 0 °C under N<sub>2</sub> for 10 min then (COCl)<sub>2</sub> (0.1 mL) was added dropwise over 1 min. The mixture was stirred 30 min at room temperature. After completion, the solvents were removed under reduced pressure and the residue was purified by HPLC (eluent: CH<sub>3</sub>CN/H<sub>2</sub>O = 100/0, 14 min) to afford the pure product **Cl-SiRhd-II** (60 mg): Yield 58%. <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>CN, ppm): δ 0.55 (d, *J* = 4 Hz, 6 H, -SiCH<sub>3</sub>), 1.16 (t, *J* = 7.2 Hz, 6H, -CH<sub>2</sub>CH<sub>3</sub>), 1.24-1.26 (m, 3H, -CH<sub>2</sub>CH<sub>3</sub>), 1.32-1.39 (m, 2H, -CH<sub>2</sub>-), 1.44 (t, *J* = 8 Hz, 3H, -CH<sub>2</sub>CH<sub>3</sub>), 1.49-1.54 (m, 2H, -CH<sub>2</sub>-), 1.68-1.76 (m, 2H, -CH<sub>2</sub>-), 2.27-2.29 (m, 2H, -CH<sub>2</sub>-), 3.39-4.01 (m, 10H, -NCH<sub>2</sub>CH<sub>3</sub>, -NCHCH<sub>2</sub>-), 7.28 (s, 1H, Ph-H), 7.91 (dd, *J*<sub>1</sub> = 8.8 Hz, *J*<sub>2</sub> = 2.4 Hz, 2H, Ph-H), 8.08 (d, *J* = 2.4 Hz, 1H, Ph-H), 8.49 (d, *J* = 8.4 Hz, 1H, Ph-H). Mass spectrometry (ESI-MS, *m/z*): [M]<sup>+</sup> Calc for C<sub>29</sub>H<sub>41</sub>ClN<sub>3</sub>OSi, 494.2758, Found, 494.2754.

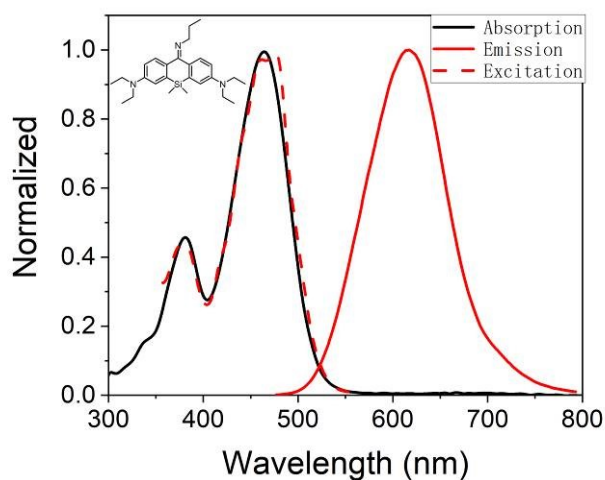
### Synthesis of B-SiRhd-6

The mixture of **O-SiRhd-II** (100 mg, 0.21 mmol) in CH<sub>3</sub>CN (10 mL) was stirred at 0 °C under N<sub>2</sub> for 10 min then (COCl)<sub>2</sub> (0.1 mL) was added dropwise over 1 min. The reaction mixture was stirred for 10 min then ethylenediamine (0.35 mL, 5.25 mmol) was added. The mixture was stirred 30 min at room temperature. The completion of reaction was monitored by TLC. After completion, solvents were removed under reduced pressure and the crude compound was used without further purification. To a solution crude compound in ethanol (10 mL) at 0 °C was added phenyl isothiocyanate (0.1 mL). The mixture was stirred overnight at 25 °C. The solvents were removed under reduced pressure and the residue was purified by HPLC (eluent: CH<sub>3</sub>CN/H<sub>2</sub>O = 90/10 to 80/20, 16 min) to afford the pure product **B-SiRhd-6** (12 mg): Yield 9%. <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 0.36-0.46 (m, 6H, -SiCH<sub>3</sub>), 1.04-1.14 (m, 12H, -CH<sub>2</sub>CH<sub>3</sub>), 1.41-1.86 (m, 8H, -CH<sub>2</sub>-), 3.17-3.63 (m, 10H, -NCH<sub>2</sub>CH<sub>3</sub>, -NCHCH<sub>2</sub>-), 3.97-4.11 (m, 4H, -NCH<sub>2</sub>CH<sub>2</sub>N-), 6.79 (s, 2H, Ph-H), 7.01-7.11 (m, 2H, Ph-H), 7.25 (s, 4H, Ph-H), 7.64-8.17 (m, 2H, Ph-H). Mass spectrometry (ESI-MS, *m/z*): [M+H]<sup>+</sup> Calc for C<sub>38</sub>H<sub>53</sub>N<sub>6</sub>SSi, 653.3822, Found, 653.3827.

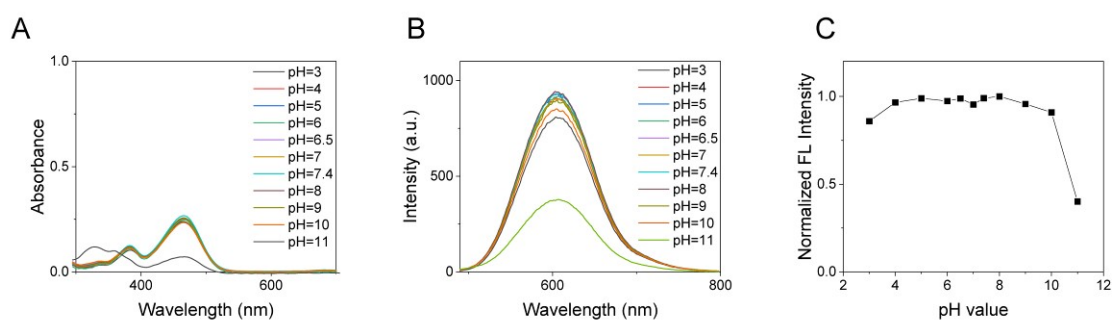
### Synthesis of **B-SiRhd-7**

The mixture of **O-SiRhd-II** (100 mg, 0.21 mmol) in CH<sub>3</sub>CN (10 mL) was stirred at 0 °C under N<sub>2</sub> for 10 min then (COCl)<sub>2</sub> (0.1 mL) was added dropwise over 1 min. The reaction mixture was stirred for 10 min then o-phenylenediamine (226 mg, 2 mmol) was added. The mixture was stirred overnight at 25 °C. The completion of reaction was monitored by TLC. After completion, the solvents were removed under reduced pressure and the residue was purified by flash chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 50/1) to afford the pure product **B-SiRhd-7** (10 mg). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 0.38-0.46 (m, 6 H, -SiCH<sub>3</sub>), 1.04-1.14 (m, 12H, -CH<sub>2</sub>CH<sub>3</sub>), 1.23-1.58 (m, 8H, -CH<sub>2</sub>CH<sub>2</sub>-), 3.13-3.43 (m, 10H, -NCH<sub>2</sub>CH<sub>3</sub>, -NCHCH<sub>2</sub>-), 4.66 (s, 2H, -NH<sub>2</sub>), 6.04 (s, 1H, Ph-H), 6.31-6.38 (m, 2H, Ph-H), 6.62-6.79 (m, 6H, Ph-H). <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>, ppm): δ -2.61, -0.99, 11.59, 12.32, 12.44, 21.97, 27.10, 41.04, 43.63, 54.10, 54.56, 54.89, 112.14, 113.40, 114.09, 116.68, 118.12, 122.38, 124.82, 128.46, 128.98, 133.67, 134.68, 135.10, 136.71, 139.25, 146.60, 164.01. Mass spectrometry (ESI-MS, m/z): [M+H]<sup>+</sup> Calc for C<sub>35</sub>H<sub>48</sub>N<sub>5</sub>Si, 566.3679, Found, 566.3678.

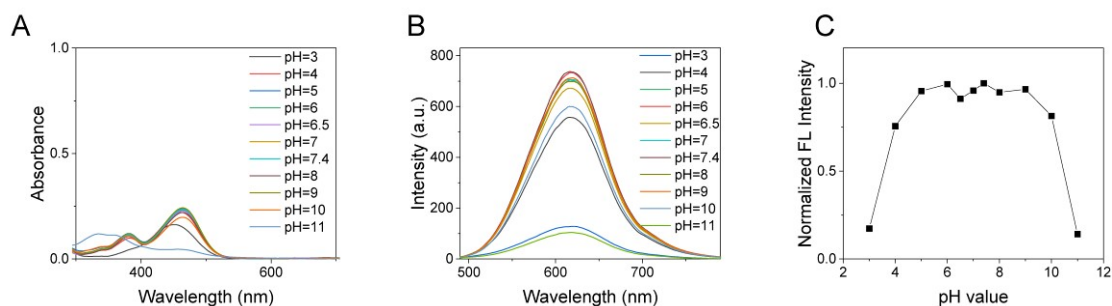
## 2. Figures of photophysical properties



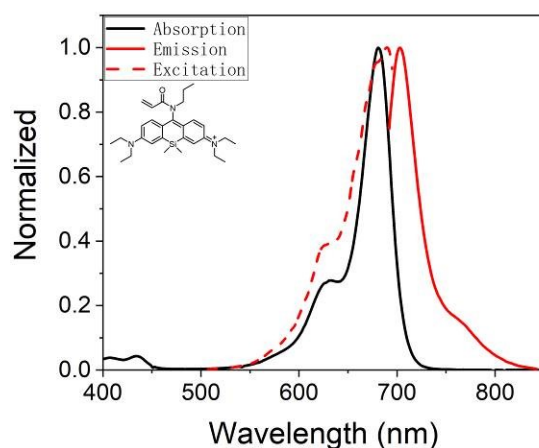
**Figure S1.** Absorption (black solid line), normalized emission (red solid lines;  $\lambda_{\text{ex}} = 460$  nm) and normalized excitation ( $\lambda_{\text{em}} = 615$  nm; red dotted line) spectra of *B*-SiRhd-1 in PBS solution (10  $\mu\text{M}$ , pH 7.4).



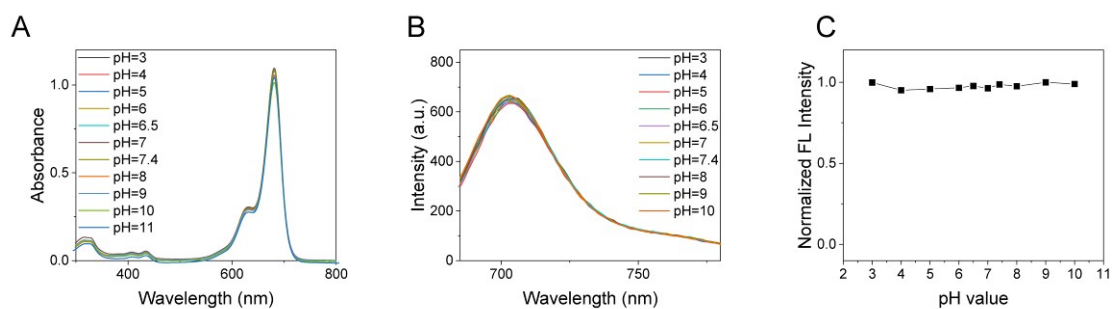
**Figure S2.** (A) Absorption of *B*-SiRhd-2 at various pH values in mixed solution of PBS/ $\text{CH}_3\text{CN}$  (10  $\mu\text{M}$ ,  $v/v = 3/1$ ). (B) Fluorescence intensities of *B*-SiRhd-2 at various pH values in mixed solution of PBS/ $\text{CH}_3\text{CN}$  (10  $\mu\text{M}$ ,  $v/v = 3/1$ ). (C) Normalized fluorescence intensities of *B*-SiRhd-2 at various pH values in mixed solution of PBS/ $\text{CH}_3\text{CN}$  (10  $\mu\text{M}$ ,  $v/v = 3/1$ ).



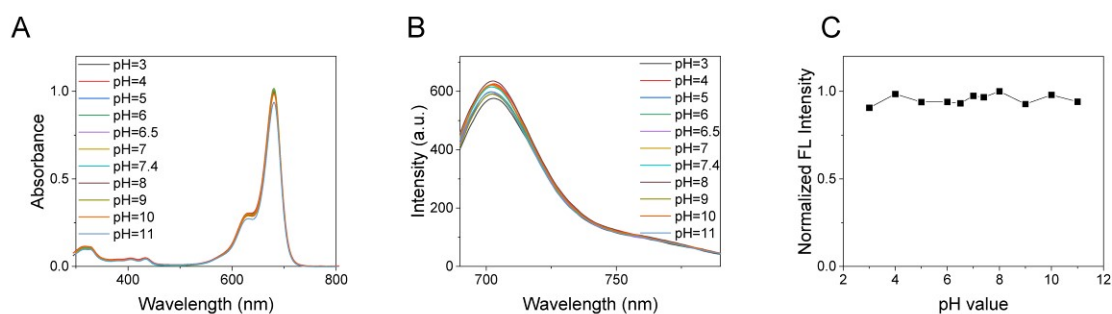
**Figure S3.** (A) Absorption of 10  $\mu\text{M}$  *B*-SiRhd-2 at various pH values in PBS. (B) Fluorescence intensities of 10  $\mu\text{M}$  *B*-SiRhd-2 at various pH values in PBS. (C) Normalized fluorescence intensities of 10  $\mu\text{M}$  *B*-SiRhd-2 at various pH values in PBS.



**Figure S4.** Absorption (black solid line), normalized emission (red solid lines;  $\lambda_{\text{ex}} = 680 \text{ nm}$ ) and normalized excitation ( $\lambda_{\text{em}} = 702 \text{ nm}$ ; red dotted line) spectra of *P*-SiRhd-2 in mixed solution of PBS/CH<sub>3</sub>CN (10  $\mu\text{M}$ ,  $v/v = 3/1$ , pH 7.4).

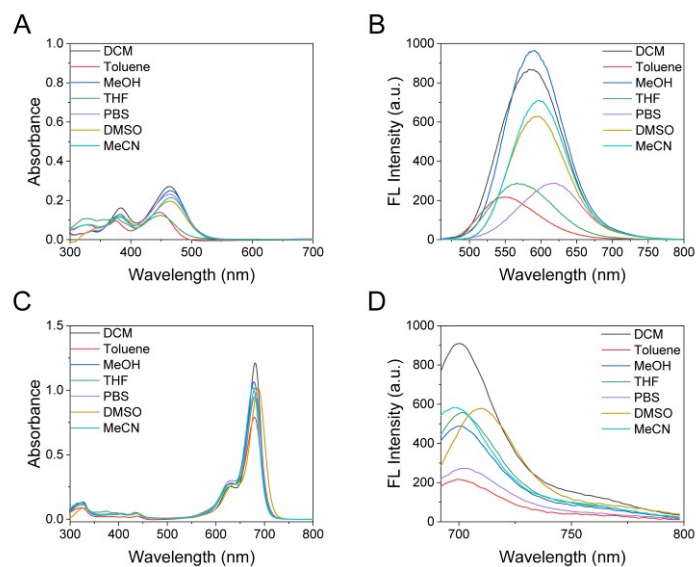


**Figure S5.** (A) Absorption of *P*-SiRhd-2 at various pH values in mixed solution of PBS/CH<sub>3</sub>CN (10  $\mu\text{M}$ ,  $v/v = 3/1$ ). (B) Fluorescence intensities of *P*-SiRhd-2 at various pH values in mixed solution of PBS/CH<sub>3</sub>CN (10  $\mu\text{M}$ ,  $v/v = 3/1$ ). (C) Normalized fluorescence intensities of *P*-SiRhd-2 at various pH values in mixed solution of PBS/CH<sub>3</sub>CN (10  $\mu\text{M}$ ,  $v/v = 3/1$ ).

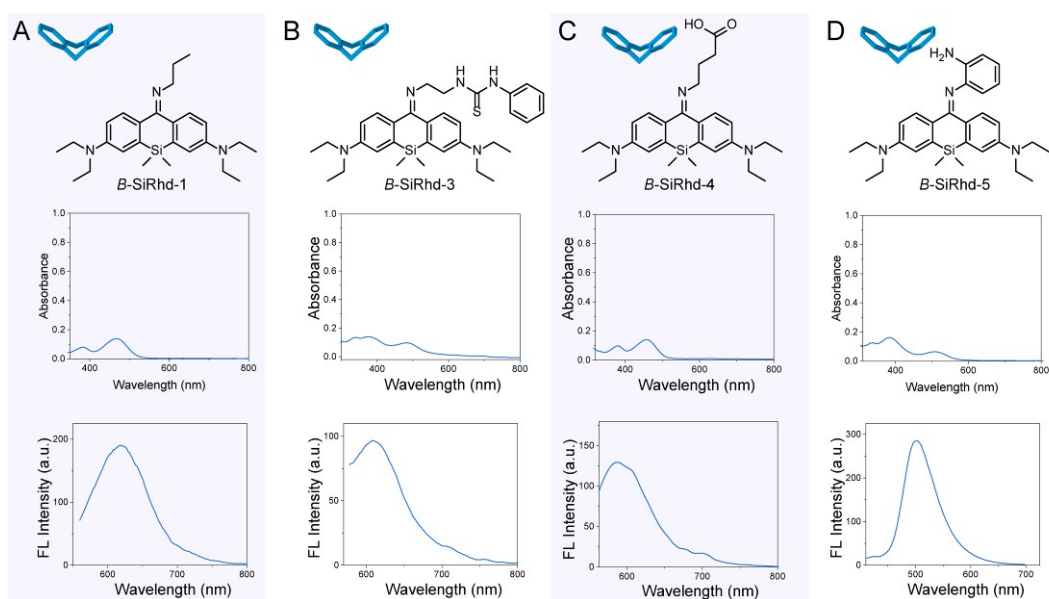


**Figure S6.** (A) Absorption of 10  $\mu\text{M}$  *P*-SiRhd-2 at various pH values in PBS. (B) Fluorescence intensities of 10  $\mu\text{M}$  *P*-SiRhd-2 at various pH values in PBS. (C) Normalized fluorescence intensities of 10  $\mu\text{M}$  *P*-SiRhd-2 at various pH values in PBS.

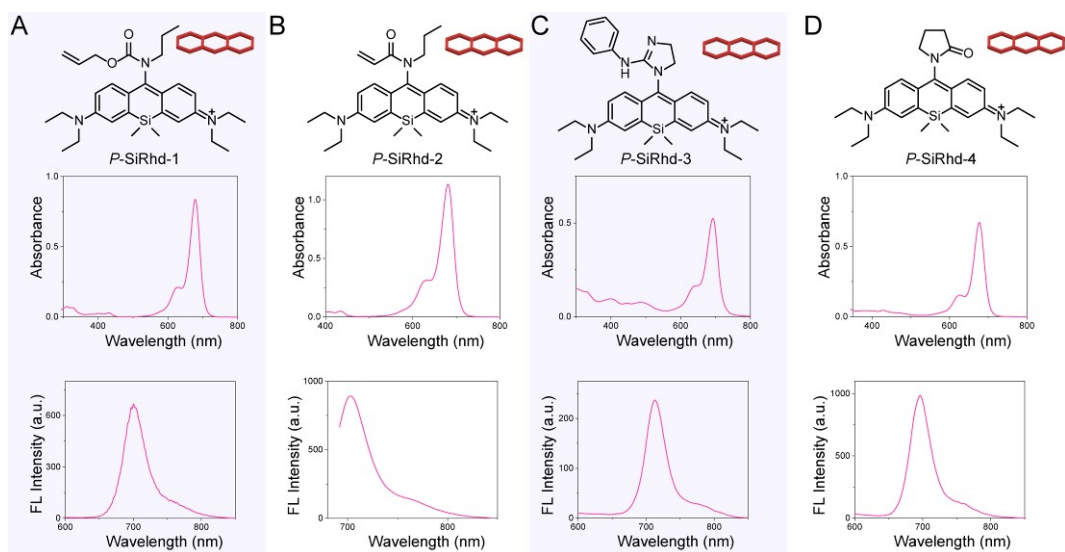




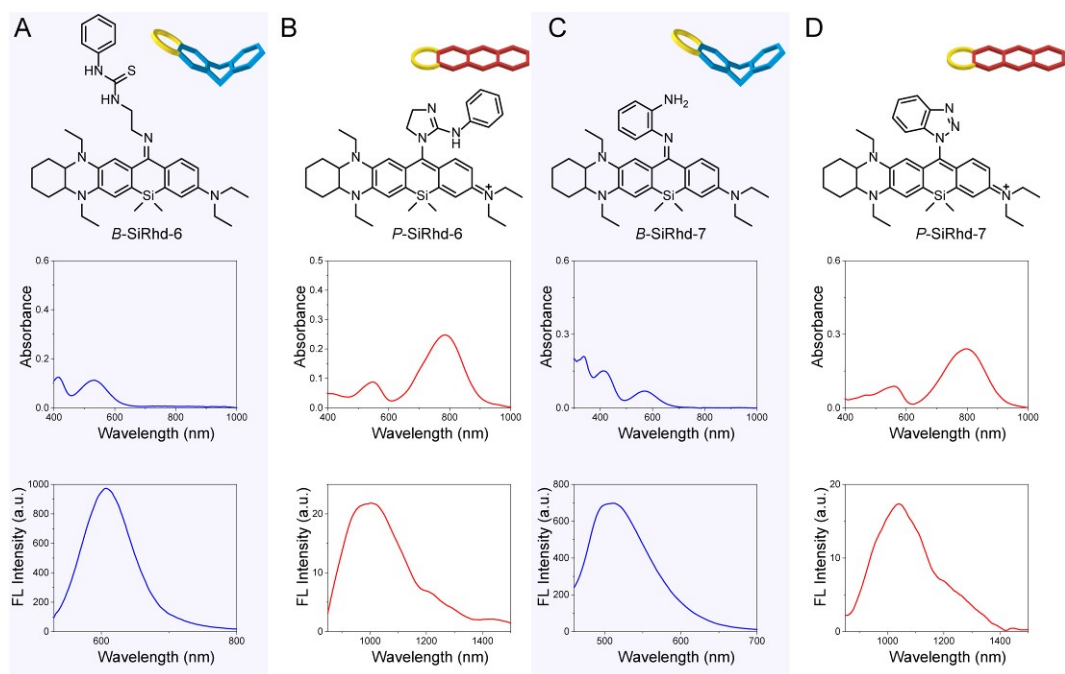
**Figure S7.** Absorption (A, C) and fluorescence (B, D) spectra of *B*-SiRhd-2 (A, B) and *P*-SiRhd-2 (C, D) in different solvents. For *P*-SiRhd-2, the solvent effect is negligible on the absorption and emission spectra.



**Figure S8.** Absorption and fluorescence emission spectra of *B*-SiRhd. (A) Absorption and fluorescence emission spectra ( $\lambda_{\text{ex}} = 550 \text{ nm}$ ) of *B*-SiRhd-1 (10  $\mu\text{M}$ ) in a mixed solution of  $\text{CH}_3\text{CN}/\text{PBS}$  ( $v/v = 1/3$ , pH 7.4, 0.01 M). (B) Absorbance and fluorescence emission spectra ( $\lambda_{\text{ex}} = 550 \text{ nm}$ ) of *B*-SiRhd-3 (10  $\mu\text{M}$ ) in PBS solution at pH 7.4. (C) Absorbance and fluorescence emission spectra ( $\lambda_{\text{ex}} = 550 \text{ nm}$ ) of *B*-SiRhd-4 (10  $\mu\text{M}$ ) in ethonal. (D) Absorbance and fluorescence emission spectra ( $\lambda_{\text{ex}} = 385 \text{ nm}$ ) of *B*-SiRhd-5 (10  $\mu\text{M}$ ) in a mixed solution of  $\text{CH}_3\text{CN}/\text{HEPES}$  ( $v/v = 3/7$ , pH 7.4, 0.02 M).

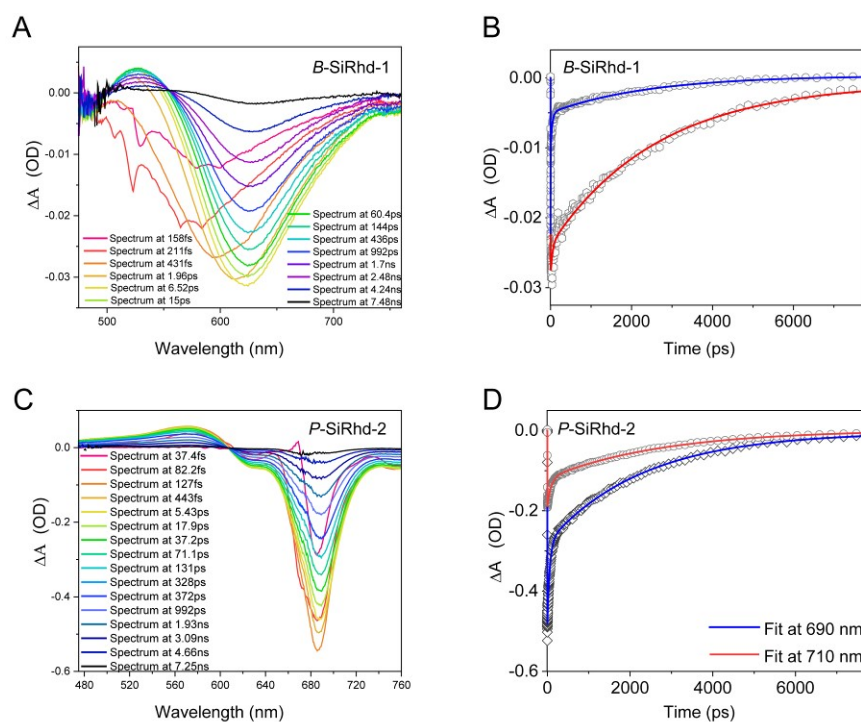


**Figure S9. Absorption and fluorescence emission spectra of P-SiRhd.** (a) Absorbance and fluorescence emission spectra ( $\lambda_{\text{ex}} = 550 \text{ nm}$ ) of P-SiRhd-1 (10  $\mu\text{M}$ ) in a mixed solution of  $\text{CH}_3\text{CN}/\text{PBS}$  ( $v/v = 1/3$ , pH 7.4, 0.01 M). (b) Absorbance and fluorescence emission spectra ( $\lambda_{\text{ex}} = 680 \text{ nm}$ ) of P-SiRhd-2 (10  $\mu\text{M}$ ) in a mixed solution of  $\text{CH}_3\text{CN}/\text{PBS}$  ( $v/v = 1/3$ , pH 7.4, 0.01 M). (c) Absorbance and fluorescence emission spectra ( $\lambda_{\text{ex}} = 550 \text{ nm}$ ) of P-SiRhd-3 (10  $\mu\text{M}$ ) in PBS solution at pH 7.4. (d) Absorbance and fluorescence emission spectra ( $\lambda_{\text{ex}} = 550 \text{ nm}$ ) of P-SiRhd-4 (10  $\mu\text{M}$ ) in ethonal.



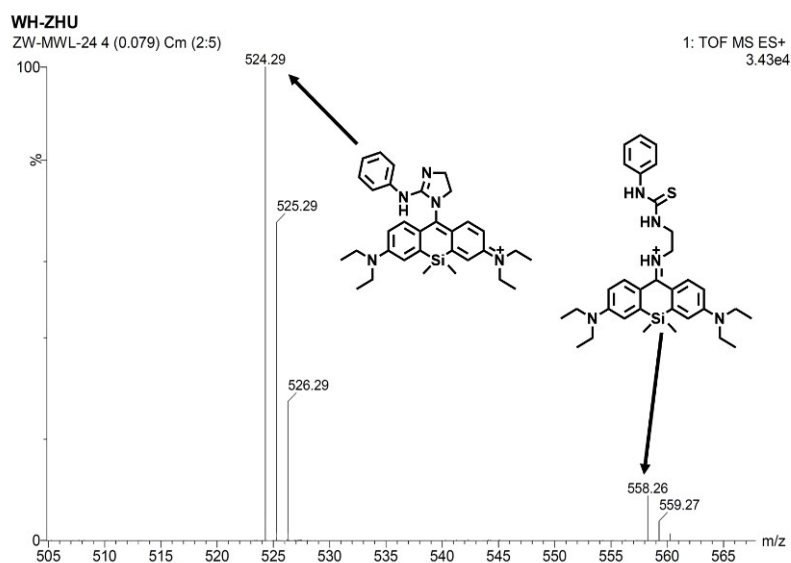
**Figure S10. Absorption and fluorescence emission spectra of SiRhd.** (A) Absorbance and fluorescence emission spectra ( $\lambda_{\text{ex}} = 510 \text{ nm}$ ) of B-SiRhd-6 (10  $\mu\text{M}$ ) in a mixed solution of DMSO/HEPES ( $v/v = 1/1$ , pH 7.4, 0.02 M). (B) Absorbance and fluorescence emission spectra ( $\lambda_{\text{ex}} = 800 \text{ nm}$ ) of P-SiRhd-6 (10  $\mu\text{M}$ ) in a mixed solution of DMSO/HEPES ( $v/v = 1/1$ , pH 7.4, 0.02 M). (C) Absorbance and fluorescence emission spectra ( $\lambda_{\text{ex}} = 420 \text{ nm}$ ) of B-SiRhd-7 (10  $\mu\text{M}$ ) in a mixed

solution of CH<sub>3</sub>CN/HEPES (v/v = 1/1, pH 7.4, 0.02 M). (D) Absorbance and fluorescence emission spectra ( $\lambda_{\text{ex}} = 800 \text{ nm}$ ) of *P*-SiRhd-7 (10  $\mu\text{M}$ ) in a mixed solution of CH<sub>3</sub>CN/HEPES (v/v = 1/1, pH 7.4, 0.02 M).

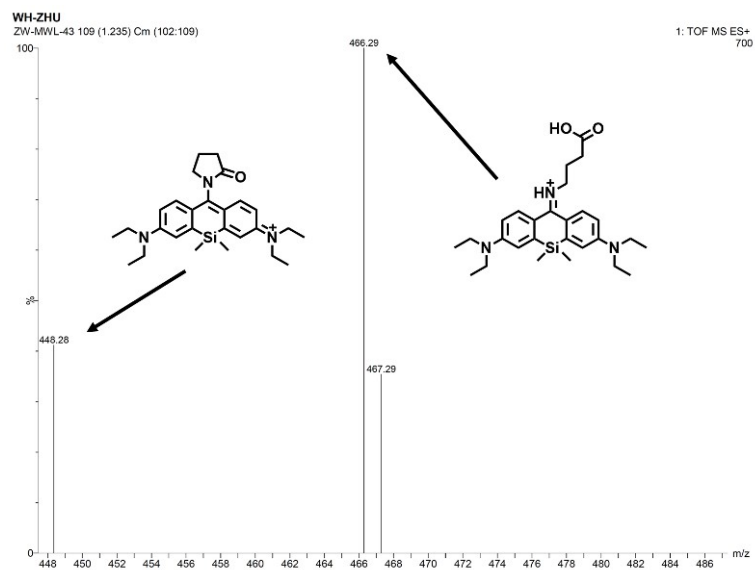


**Figure S11.** Femtosecond time-resolved transient absorption spectra and kinetics of SiRhd. Femtosecond time-resolved transient absorption spectra (A) and kinetics (B) of *B*-SiRhd-1 (excited at  $\lambda_{\text{ex}} = 460 \text{ nm}$ ). Femtosecond time-resolved transient absorption spectra (C) and kinetics (D) of *P*-SiRhd-2 (excited at  $\lambda_{\text{ex}} = 680 \text{ nm}$ ).

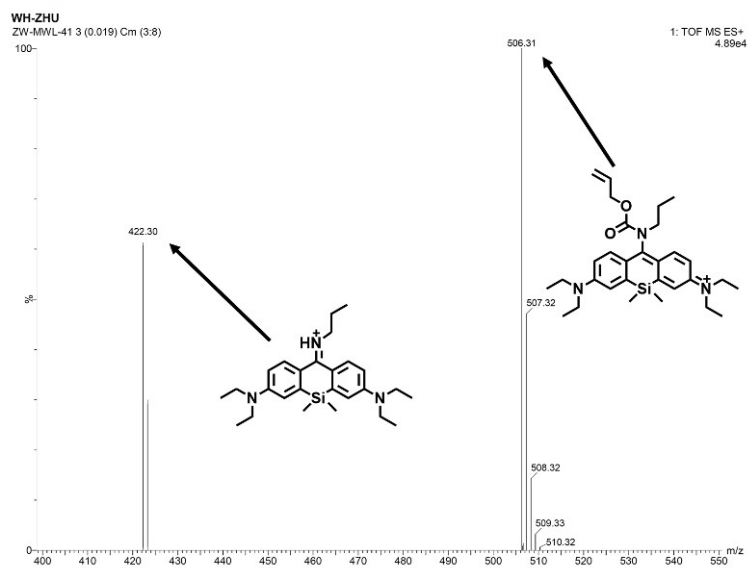
### 3. Responsive performance measurement of SiRhd probes



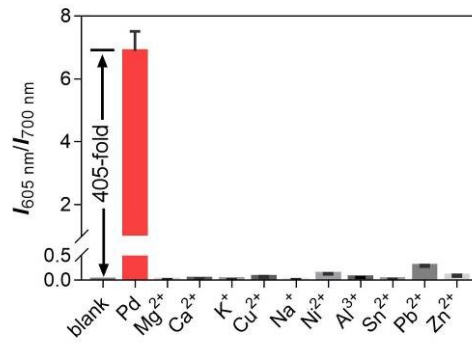
**Figure S12.** HRMS spectrum of the products from the reaction of *B*-SiRhd-3 with 1 equiv of Hg<sup>2+</sup>.



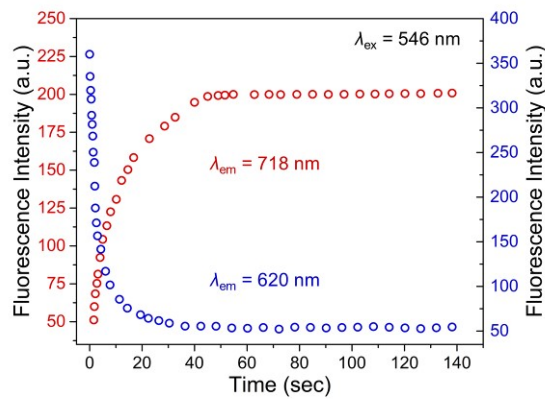
**Figure S13.** HRMS spectrum of the products from the reaction of *B*-SiRhd-4 with 1 equiv of phosgene.



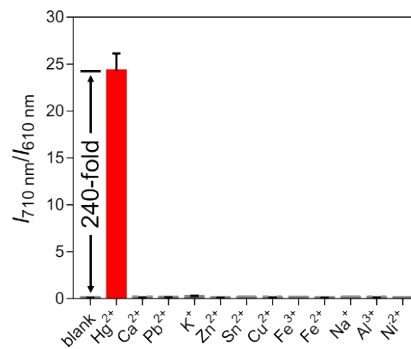
**Figure S14.** HRMS spectrum of the products from the reaction of *P*-SiRhd-1 with 1 equiv of Pd.



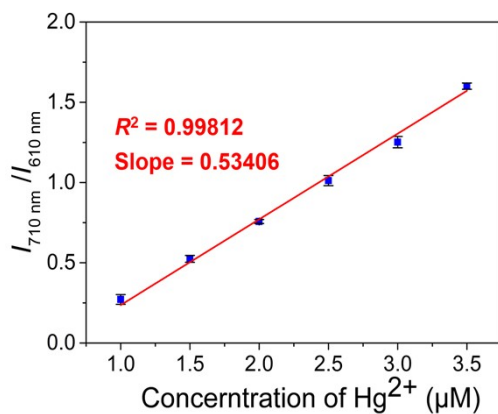
**Figure S15.** Fluorescence intensity ratio of 10  $\mu\text{M}$  *P*-SiRhd-1 ( $I_{605 \text{ nm}}/I_{700 \text{ nm}}$ ) in the present of different metal ions in a mixed solution of  $\text{CH}_3\text{CN}/\text{PBS}$  ( $v/v = 1/3$ ,  $\text{pH} = 7.4$ ,  $0.01 \text{ M}$ ).



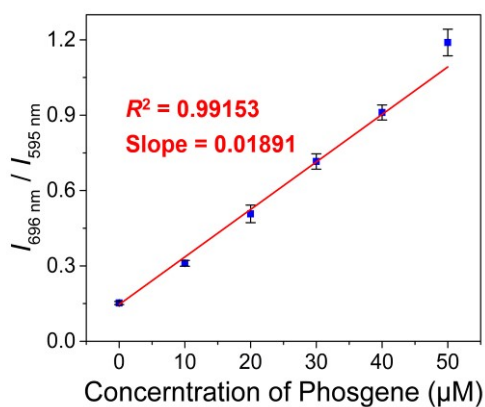
**Figure S16.** Time dependence of fluorescence intensity at 620 nm and 718 nm for *B*-SiRhd-3 (20  $\mu\text{M}$ ) in PBS solution ( $\text{pH} = 7.4$ ) in the presence of  $\text{Hg}^{2+}$  (20  $\mu\text{M}$ ).  $\lambda_{\text{ex}} = 546 \text{ nm}$ . Data was recorded every 0.5 s.



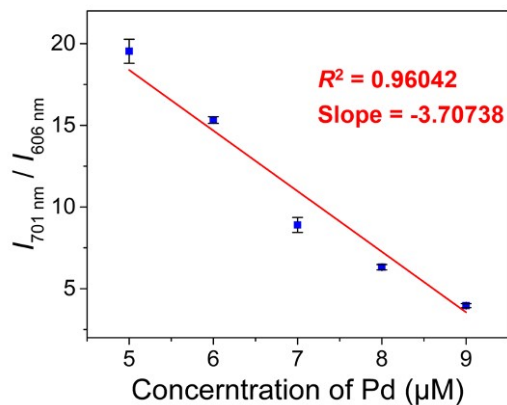
**Figure S17.** Fluorescence intensity ratio of 10  $\mu\text{M}$  *B*-SiRhd-3 ( $I_{710 \text{ nm}}/I_{610 \text{ nm}}$ ) in the present of different metal ions in PBS solution at  $\text{pH} 7.4$



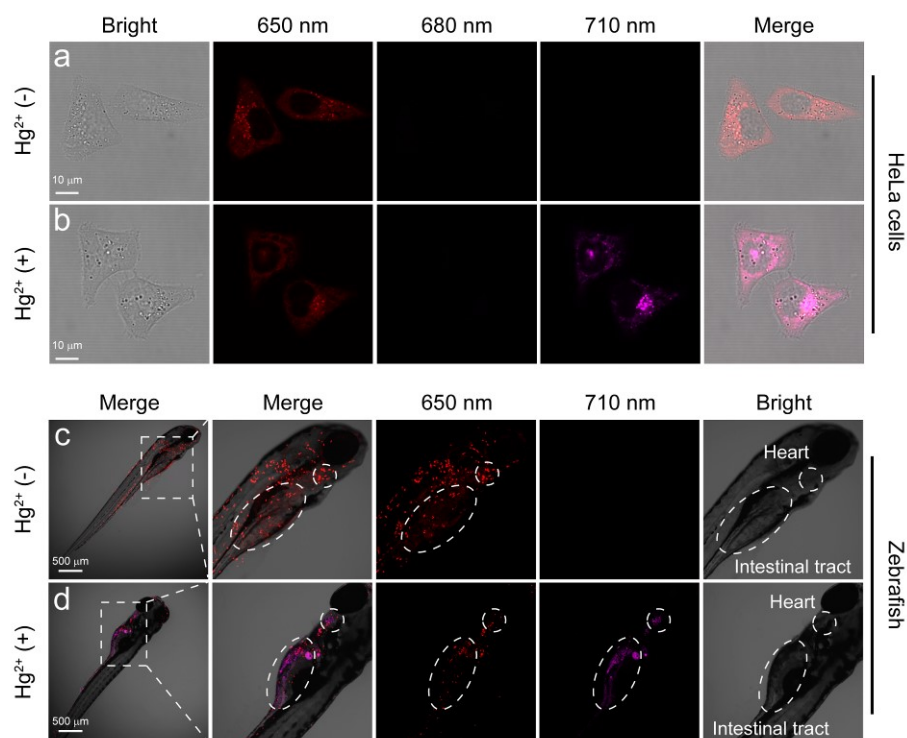
**Figure S18.** Dual-channel linear ratio analysis of *B*-SiRhd-3 for  $\text{Hg}^{2+}$ . A linear correlation between fluorescence ratio  $I_{710 \text{ nm}} / I_{610 \text{ nm}}$  and concentration of  $\text{Hg}^{2+}$ . Note: The detection limit was calculated to be  $0.062 \mu\text{M} \cdot \text{L}^{-1}$  ( $3\sigma/\text{slope}$ ).



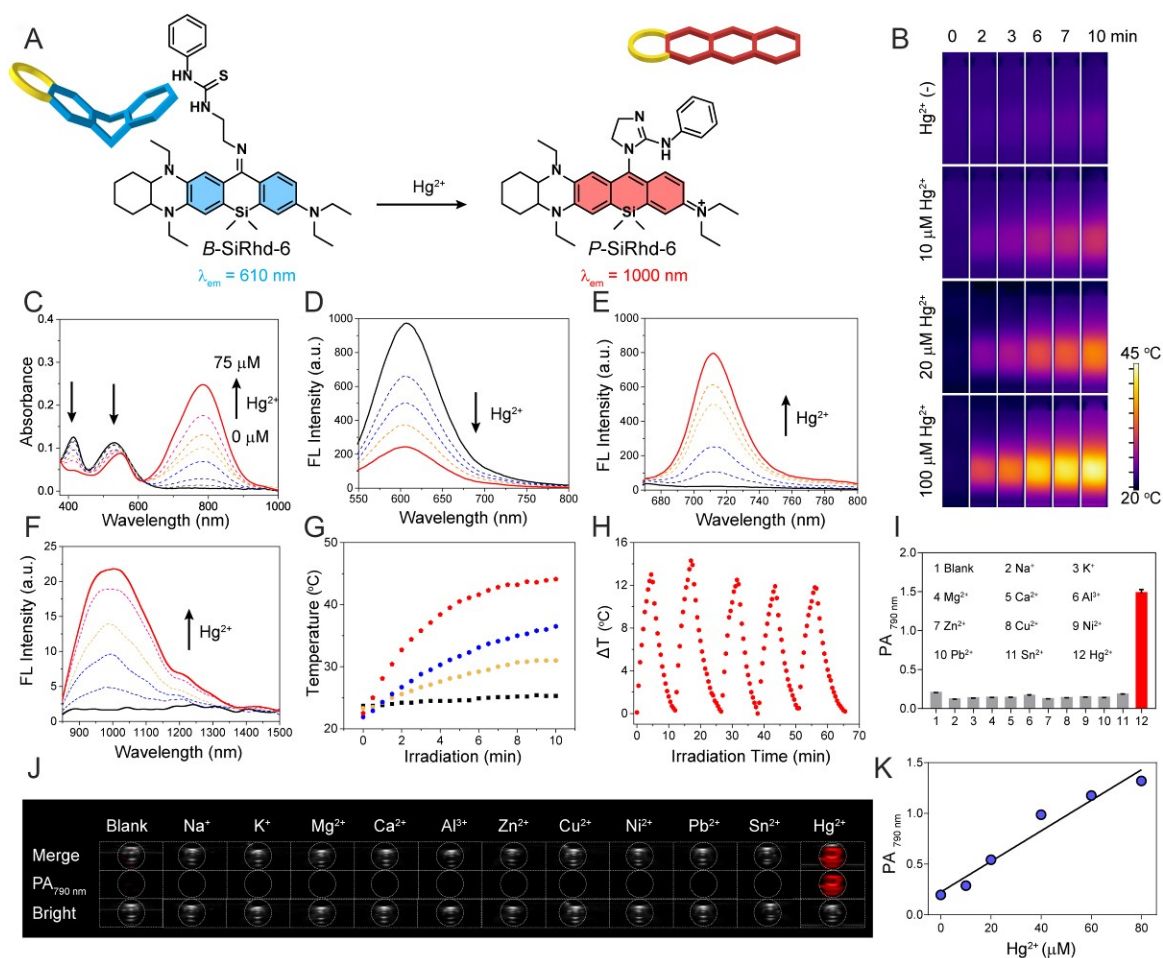
**Figure S19.** Dual-channel linear ratio analysis of *B*-SiRhd-4 for phosgene. A linear correlation between fluorescence ratio  $I_{696 \text{ nm}} / I_{595 \text{ nm}}$  and concentration of phosgene.



**Figure S20.** Dual-channel linear ratio analysis of *P*-SiRhd-1 for palladium. A linear correlation between fluorescence ratio  $I_{701 \text{ nm}} / I_{606 \text{ nm}}$  and concentration of palladium.

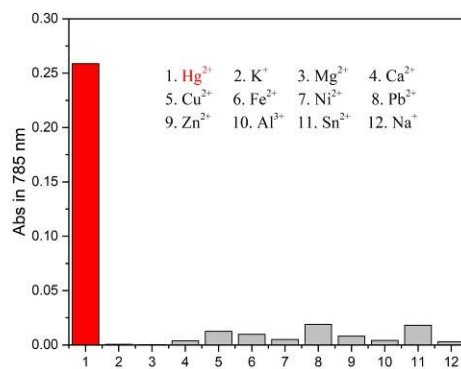


**Figure S21.** Initially, HeLa cells (incubated with *B*-SiRhd-3) exhibited bright fluorescence in the 650 nm channel and non-fluorescence in the 710 nm channel (Figure S21a). After incubation with  $\text{Hg}^{2+}$  (10  $\mu\text{M}$ ), the HeLa cells exhibited a sharply decreased fluorescence intensity in the 650 nm channel and a concomitant increase in the 710 nm channel (Figure S21b), which correspond to emission spectra of *B*-SiRhd-3 in the presence of  $\text{Hg}^{2+}$  (Figure 4D). Furthermore, similar emission profiles and ratiometric were observed in zebrafish. As shown in Figure S21c, the whole body of zebrafish larva was stained by *B*-SiRhd-3, and exhibited 650 nm fluorescence. Then, zebrafish (pre-stained by *B*-SiRhd-3) was incubated with 1  $\mu\text{M}$   $\text{Hg}^{2+}$  for 12 h, and emission at 710 nm was clearly observed mainly in the intestinal tract and heart (Figure S21d). This dual-channel imaging results suggested the activation of *B*-SiRhd-3 could real-time track the uptaken of  $\text{Hg}^{2+}$  in zebrafish. All these imaging experiments helped to establish how our bending/planar switchable Si-rhodamines enable cross-talk-free ratiometric analysis of biomolecules in living cells and zebrafish.

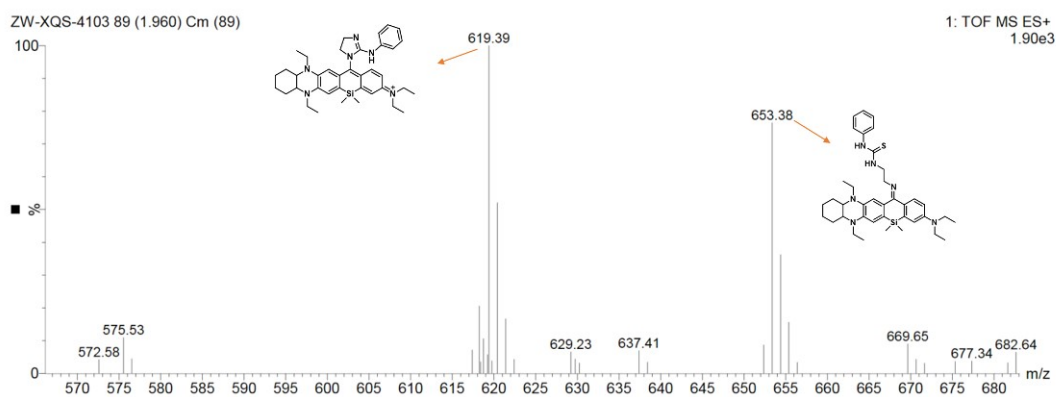


**Figure S22.** (A) Reaction of probe *B*-SiRhd-6 with  $\text{Hg}^{2+}$  and formation of *P*-SiRhd-6. Absorbance (C) and fluorescence emission (D, E, F) spectra of *B*-SiRhd-6 (10  $\mu\text{M}$ ) in the presence of  $\text{Hg}^{2+}$  in a mixed solution of DMSO/HEPES ( $v/v = 1/1$ ,  $\text{PH} = 7.4$ , 0.02 M). Temperature elevation curves (G) and infrared thermal (B) of *B*-SiRhd-6 (20  $\mu\text{M}$ ) with different concentrations of  $\text{Hg}^{2+}$  (0, 10, 20 and 100  $\mu\text{M}$ ) under 808 nm laser irradiation (2  $\text{W}/\text{cm}^2$ , 10 min). (H) The variation of temperatures during five cycles of heating-cooling processes under 808 nm laser irradiation of *B*-SiRhd-6 (20  $\mu\text{M}$ ) with 150  $\mu\text{M}$   $\text{Hg}^{2+}$ . (I) PA<sub>790 nm</sub> of the *B*-SiRhd-6 in the presence of various representative metal cations. (J) In vitro PA images of the solution of *B*-SiRhd-6 in the presence of various representative metal ions ( $\text{Na}^{2+}$ ,  $\text{K}^{+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sn}^{2+}$ , and  $\text{Hg}^{2+}$ ) at 790 nm. (K) Plot of PA<sub>790 nm</sub> of *B*-SiRhd-6 against the concentration of  $\text{Hg}^{2+}$ .

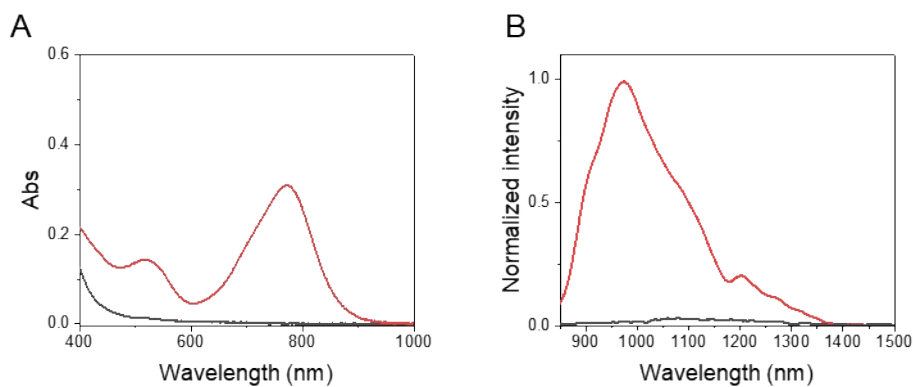




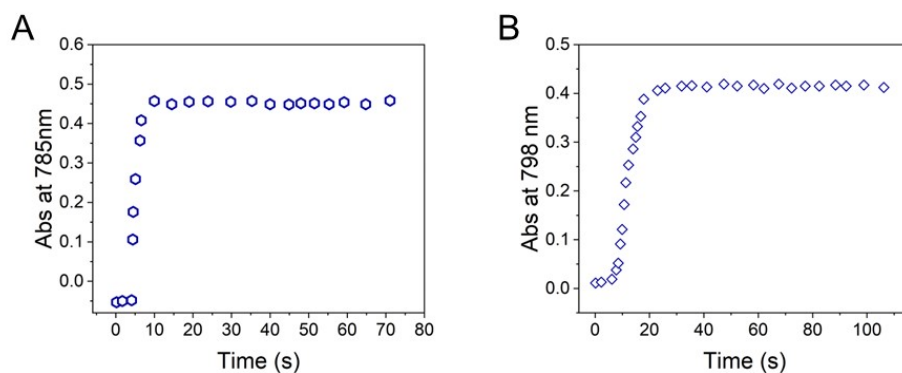
**Figure S23.** Absorbance intensity in 785 nm of 10  $\mu$ M *B*-SiRhd-6 in the present of different metal ions in a mixed solution of DMSO/HEPES (v/v =1/1 , PH = 7.4 , 0.02 M).



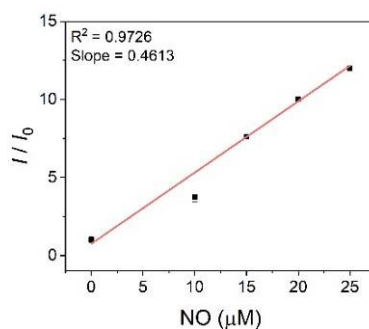
**Figure S24.** HRMS spectrum of the products from the reaction of *B*-SiRhd-6 with 1 equiv of Hg<sup>2+</sup>.



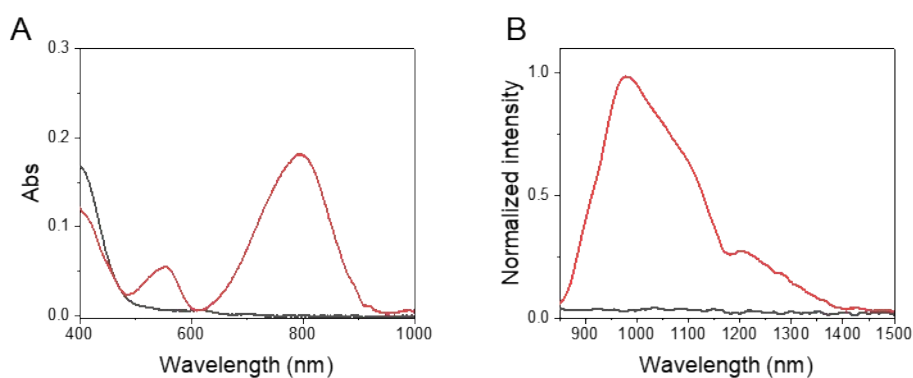
**Figure S25.** (A) Absorption spectra of *B*-SiRhd-6 (black) and *P*-SiRhd-6 (red) in DMSO. (B) Fluorescence spectra of *B*-SiRhd-6 (black) and *P*-SiRhd-6 (red) in DMSO.  $\lambda_{ex}$  = 800 nm.



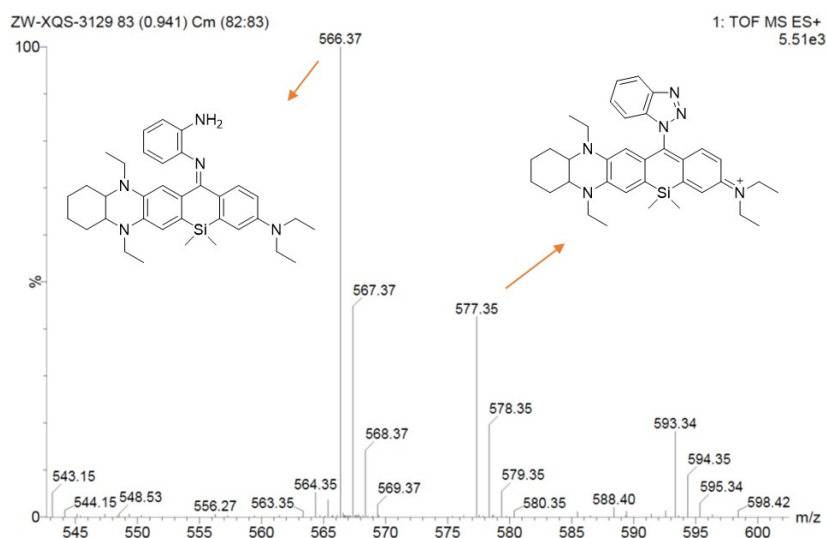
**Figure S26.** (A) Time dependence of absorption at 785 nm for B-SiRhd-6 (10 μM) in a mixed solution of DMSO/HEPES (v/v = 1/1, pH = 7.4, 0.02 M) in the presence of Hg<sup>2+</sup> (20 μM). (B) Time dependence of absorption at 798 nm for B-SiRhd-7 (10 μM) in a mixed solution of CH<sub>3</sub>CN/HEPES (v/v = 1/1, pH 7.4, 0.02 M) in the presence of NO (100 μM).



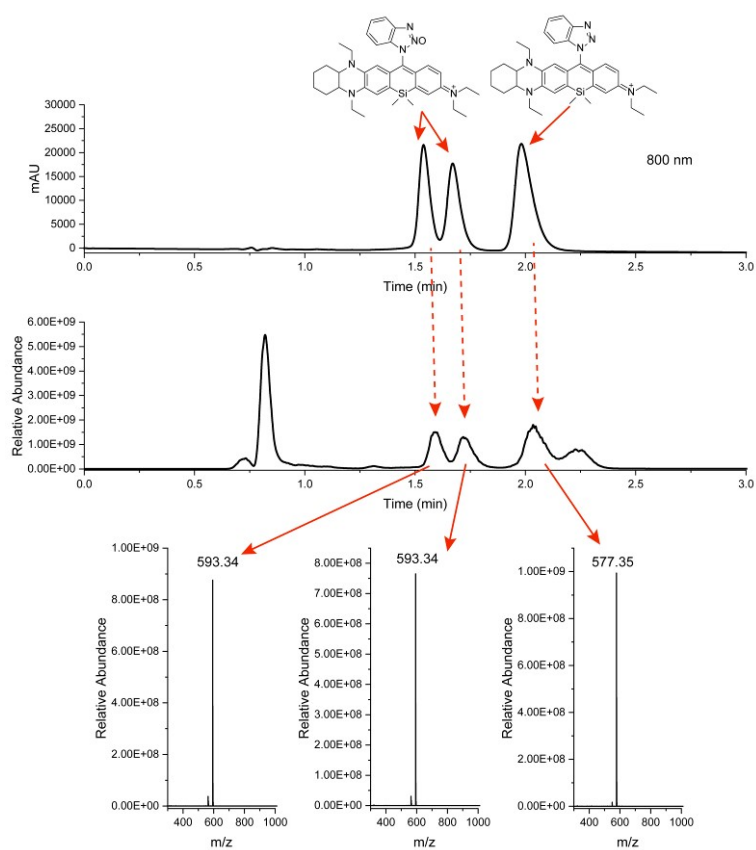
**Figure S27.** A linear correlation between fluorescence ratio  $I/I_0$  and concentration of NO. Note: The detection limit was calculated to be 0.3 μM ( $3\sigma/\text{slope}$ ).  $\lambda_{\text{ex}} = 808$  nm,  $\lambda_{\text{em}} = 1040$  nm.



**Figure S28.** (A) Absorption spectra of B-SiRhd-7 (black) and P-SiRhd-7 (red) in DMSO. (B) Fluorescence spectra of B-SiRhd-7 (black) and P-SiRhd-7 (red) in DMSO.  $\lambda_{\text{ex}} = 800$  nm.

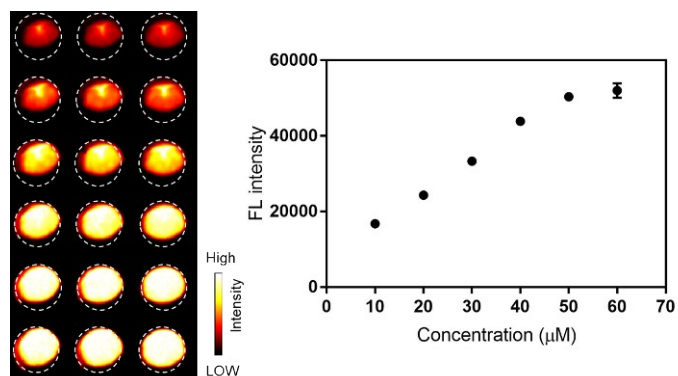


**Figure S29.** HRMS spectrum of the products from the reaction of *B*-SiRhd-7 with 1 equiv of DEA NONOate.

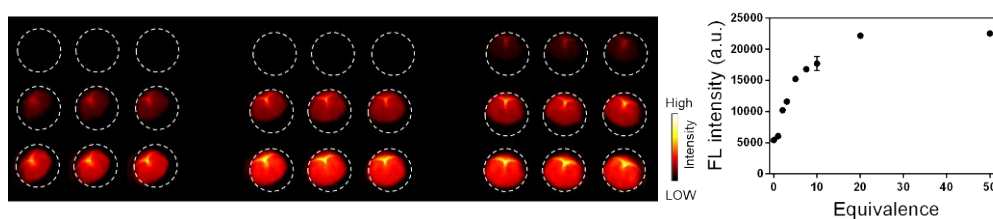


**Figure S30.** High resolution liquid chromatograph mass (LCMS) traces of probe *B*-SiRhd-7 with excess DEA NONOate.

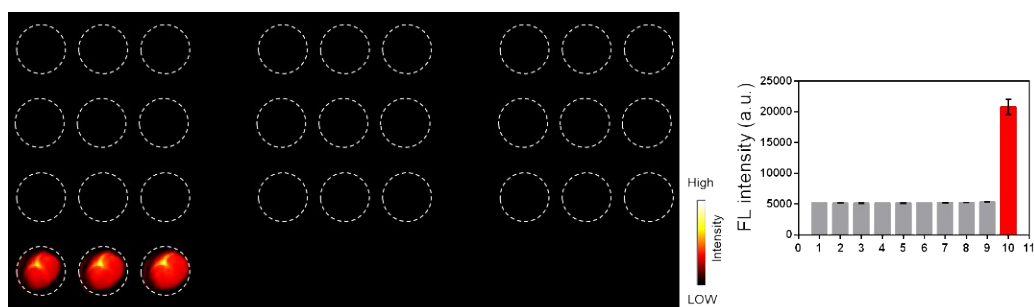
Absorption in 800 nm was verified belonging to *P*-SiRhd-7.



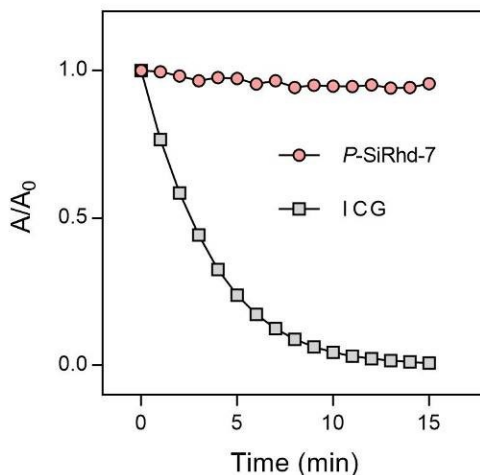
**Figure S31.** Fluorescence emission ( $\lambda_{\text{ex}} = 808 \text{ nm}$ , 880 nm long-pass filter) of *B*-SiRhd-7 with different concentrations (10, 20, 30, 40, 50, 60  $\mu\text{M}$ ) in the presence of DEA NONOate in a mixed solution of  $\text{CH}_3\text{CN}/\text{HEPES}$  ( $v/v = 1/1$ , PH = 7.4, 0.02 M).



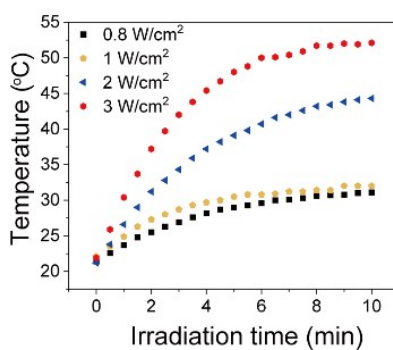
**Figure S32.** Fluorescence emission ( $\lambda_{\text{ex}} = 808 \text{ nm}$ , 880 nm long-pass filter) of *B*-SiRhd-7 (20  $\mu\text{M}$ ) in the presence of different equivalence of DEA NONOate in a mixed solution of  $\text{CH}_3\text{CN}/\text{HEPES}$  ( $v/v = 1/1$ , PH = 7.4, 0.02 M).



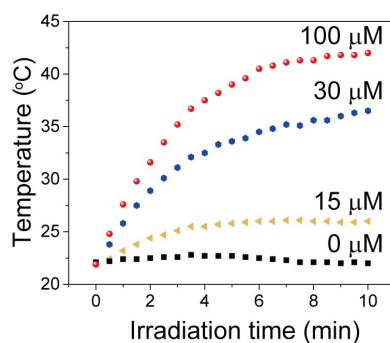
**Figure S33.** Fluorescence emission ( $\lambda_{\text{ex}} = 808 \text{ nm}$ , 880 nm long-pass filter) of *B*-SiRhd-7 (20  $\mu\text{M}$ ) over various species (1) Blank; (2) NaClO (0.1 mM); (3) H<sub>2</sub>O<sub>2</sub> (0.1 mM); (4) CaCl<sub>2</sub> (0.1 mM); (5) NaNO<sub>2</sub> (1 mM); (6) GSH (1 mM); (7) Glu (1 mM); (8) Cys (0.2 mM); (9) Na<sub>2</sub>SO<sub>3</sub> (1 mM), and (10) DEA NONOate in a mixed solution of DMSO/HEPES ( $v/v = 1/1$ , PH = 7.4, 0.02 M).



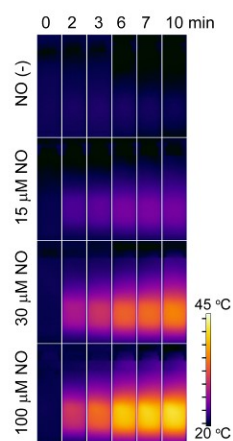
**Figure S34.** Photostability of ICG and *P*-SiRhd-7 under continuous-wave laser exposure with a power density of 1 W/cm<sup>2</sup> in HEPES/CH<sub>3</sub>CN solution (1:1, v/v, pH 7.4),  $\lambda_{ex}$ =808 nm. The photostability of NIR-II fluorophores is a key factor for practical application of in vivo bioimaging. These results demonstrated that *P*-SiRhd-7 possess better photostability than ICG.



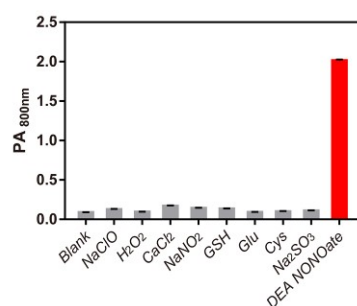
**Figure S35.** Photothermal conversion behavior of *B*-SiRhd-7 (20  $\mu$ M) with 500  $\mu$ M DEA NONOate after different irradiation at 808 nm laser irradiation (0.8–3 W/cm<sup>2</sup>). Note: Large excess nitric oxide is added here to only ensure as fast and complete response as possible from the probe, so as to choose the laser with optimal power density, while not priority for the sensitivity of NO with the probe.



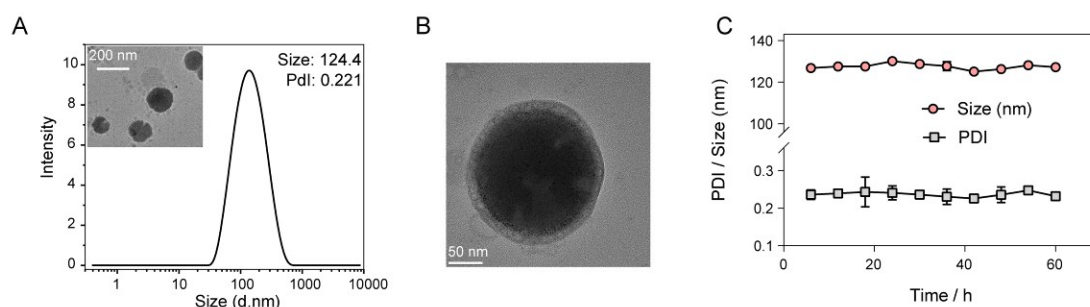
**Figure S36.** Temperature elevation curves of *B*-SiRhd-7 (20  $\mu$ M) with different concentrations of DEA NONOate (0, 15, 30 and 100  $\mu$ M) under 808 nm laser irradiation (2 W/cm<sup>2</sup>, 10 min).



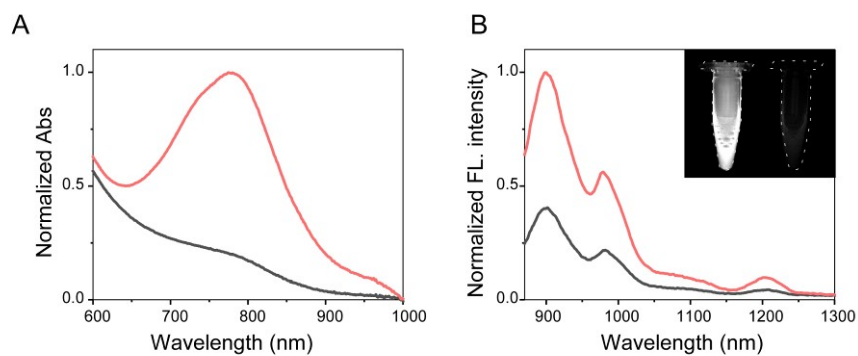
**Figure S37.** Infrared thermal of *B*-SiRhd-7 (20  $\mu\text{M}$ ) with different concentrations of DEA NONOate (0, 15, 30 and 100  $\mu\text{M}$ ) under 808 nm laser irradiation (2  $\text{W}/\text{cm}^2$ , 10 min).



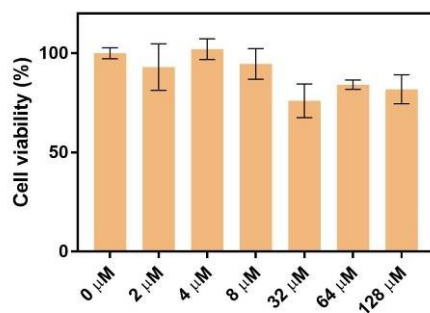
**Figure S38.**  $\text{PA}_{800\text{nm}}$  of the *B*-SiRhd-7 in the presence of various representative species (1) Blank; (2) NaClO (0.1 mM); (3)  $\text{H}_2\text{O}_2$  (0.1 mM); (4)  $\text{CaCl}_2$  (0.1 mM); (5)  $\text{NaNO}_2$  (1 mM); (6) GSH (1 mM); (7) Glu (1 mM); (8) Cys (0.2 mM); (9)  $\text{Na}_2\text{SO}_3$  (1 mM), and (10) DEA NONOate in a mixed solution of DMSO/HEPES (v/v = 1/1, PH = 7.4, 0.02 M).



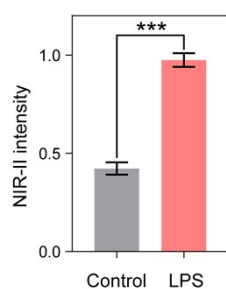
**Figure S39.** Representative size distribution graphs (A) and TEM images (B) of *B*-SiRhd-7@liposome depicting the hydrodynamic diameter after 48 h of synthesis. Insets show the TEM images of the liposomes. (A) Scale bar: 200 nm and (B) Scale bar: 50 nm. (C) Graph shows stability of *B*-SiRhd-7@liposome as a function of change in size distribution and PDI over time, measured by dynamic light scattering during storage condition at 4  $^{\circ}\text{C}$ . Sample size,  $n=3$ .



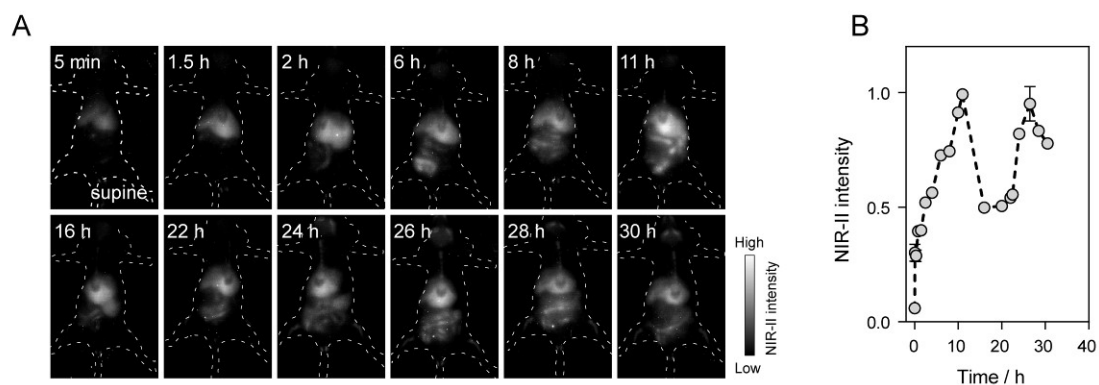
**Figure S40.** (A) Normalized absorption spectra of B-SiRhd-7@liposome (black) and B-SiRhd-7@liposome+NO (red) in PBS (pH=7.4). (B) Normalized fluorescence spectra of B-SiRhd-7@liposome (black) and B-SiRhd-7@liposome+NO (red) in PBS (pH=7.4).  $\lambda_{ex}$  = 808 nm.



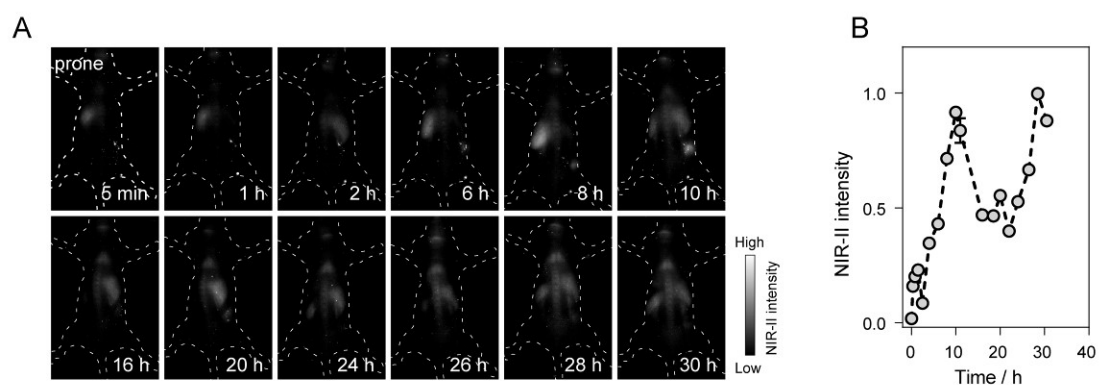
**Figure S41.** Viability of RAW264.7 cells incubated with B-SiRhd-7@liposome for 24 h.



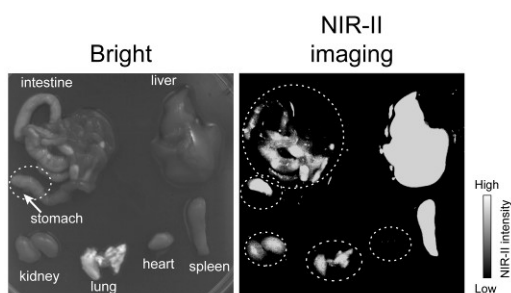
**Figure S42.** Comparison of fluorescence intensities at 11h in Figure 6D. Data are presented as the mean value, and the error bars represented the SD from the meanvalue (n = 3). \*\*\* P < 0.001.



**Figure S43.** In vivo circulation of *B*-SiRhd-7@liposome in LPS-pretreated mice in ventral view. (A) The representative time course images after administration of *B*-SiRhd-7@liposome (0.4 mM, 200  $\mu$ L) through tail vessel after LPS pretreated 6 h,  $\lambda_{ex}$  = 808 nm, 1100 nm long-pass filter. (B) The normalized fluorescence intensity of *B*-SiRhd-7@liposome in the mice versus time. The maximum fluorescence intensity (11 h in panel A) is defined as 1.0.

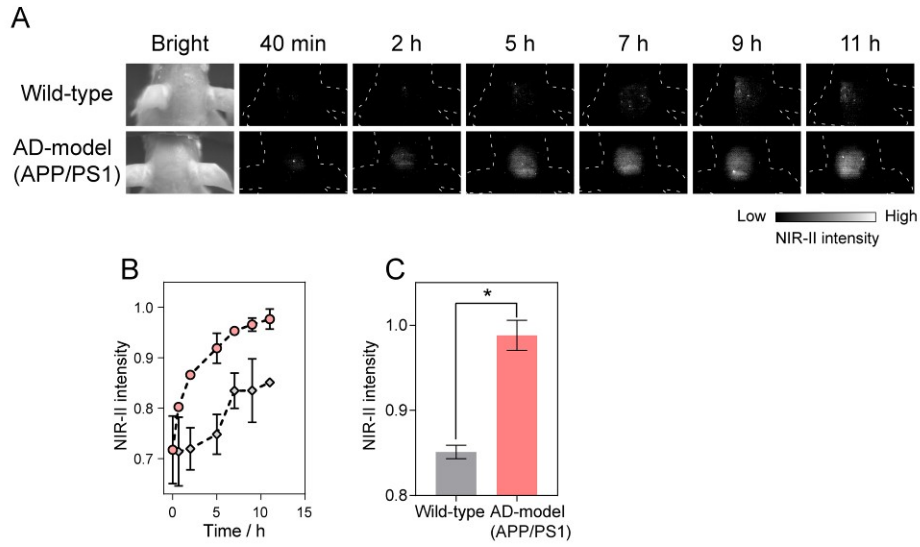


**Figure S44.** In vivo circulation of *B*-SiRhd-7@liposome in LPS-pretreated mice in dorsal view. (A) The representative time course images after administration of *B*-SiRhd-7@liposome (0.4 mM, 200  $\mu$ L) through tail vessel after LPS pretreated 6 h,  $\lambda_{ex}$  = 808 nm, 1100 nm long-pass filter. (B) The normalized fluorescence intensity of *B*-SiRhd-7@liposome in the mice versus time. The maximum fluorescence intensity (28 h in panel A) is defined as 1.0.



**Figure S45.** Bright-field image and NIR-II fluorescence imaging of different organs excised from the LPS-induced mouse at 9 h after tail-vein injection of *B*-SiRhd-7@liposome.





**Figure S46.** (A) In vivo fluorescence imaging of NO in wild-type and AD-model (APP/PS1) mice brains during 11 h via intravenous injection of 200  $\mu$ L 0.4 mM B-SiRhd-7@liposomes,  $\lambda_{ex}$  = 808 nm, 1100 nm long-pass filter. (B) Plots of in vivo fluorescence intensities versus time points for mice in image (A). The maximum fluorescence intensity (11 h) is defined as 1.0. (C) Comparison of fluorescence intensities at 11h for the two groups. Data are presented as the mean value, and the error bars represented the SD from the mean value (n = 3). \* P < 0.05.

#### 4. $^1\text{H}$ NMR, $^{13}\text{C}$ NMR, and HRMS spectra of the compounds

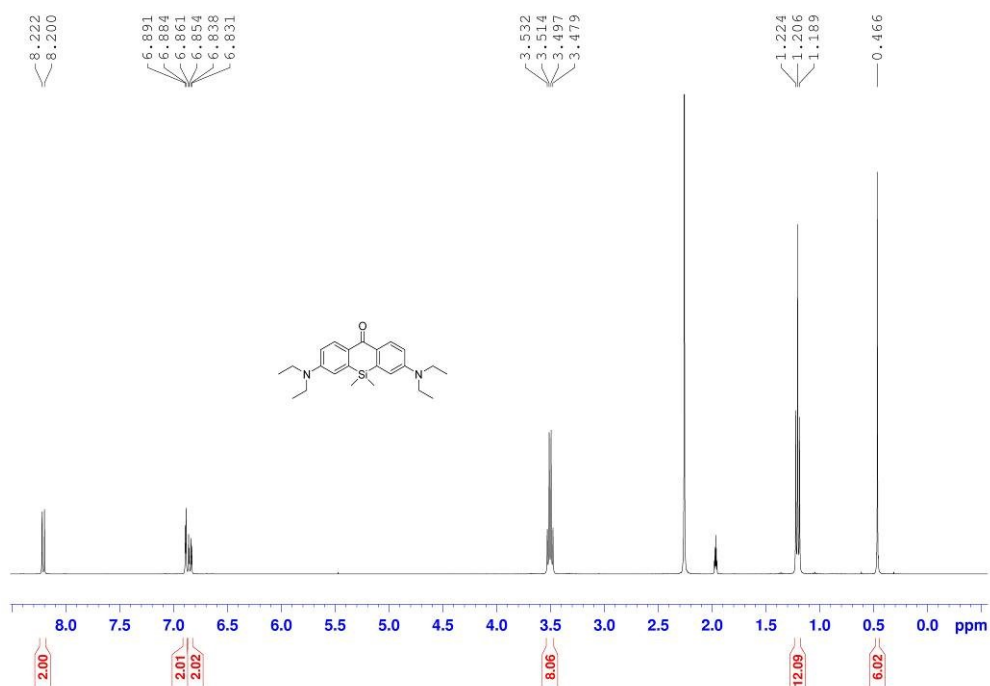


Figure S47.  $^1\text{H}$  NMR spectrum of **O-SiRhd** in  $\text{CD}_3\text{CN}$ .

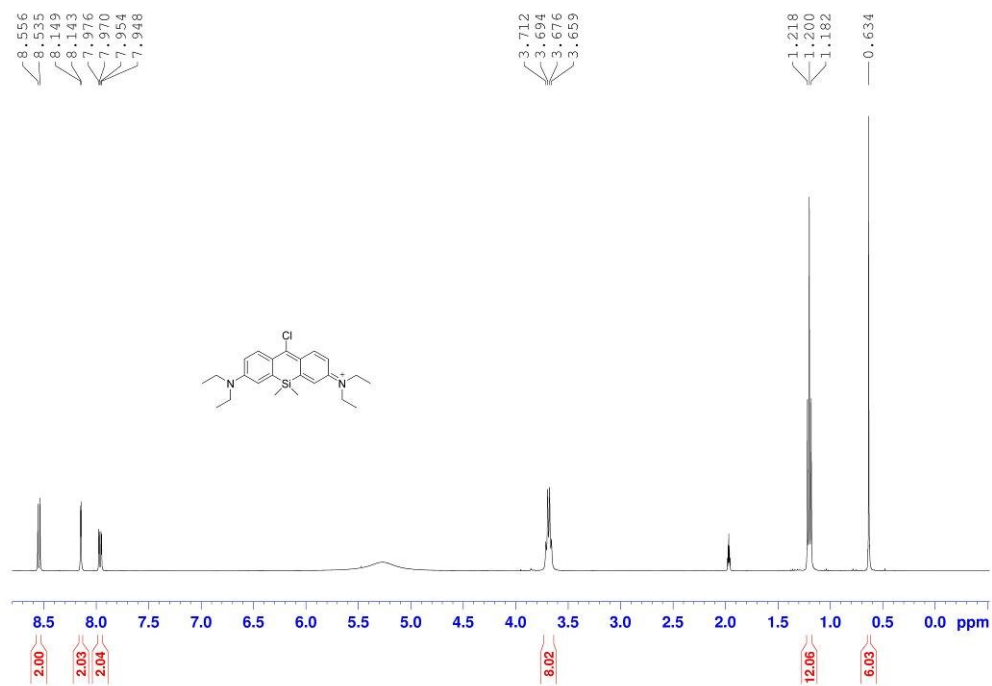


Figure S48.  $^1\text{H}$  NMR spectrum of **Cl-SiRhd** in  $\text{CD}_3\text{CN}$ .

Monoisotopic Mass, Even Electron Ions  
 25 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)  
 Elements Used:  
 C: 0-23 H: 0-36 N: 0-3 Si: 0-2 Cl: 0-1  
 WH-ZHU  
 ZW-XQS-4107 14 (0.300) Cm (14)

1: TOF MS ES+  
 7.45e+003

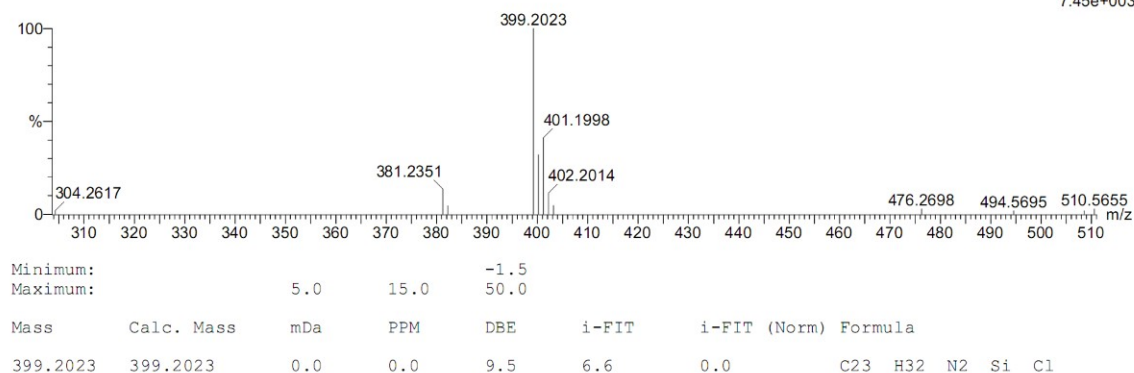


Figure S49. HRMS spectrum of Cl-SiRhd.

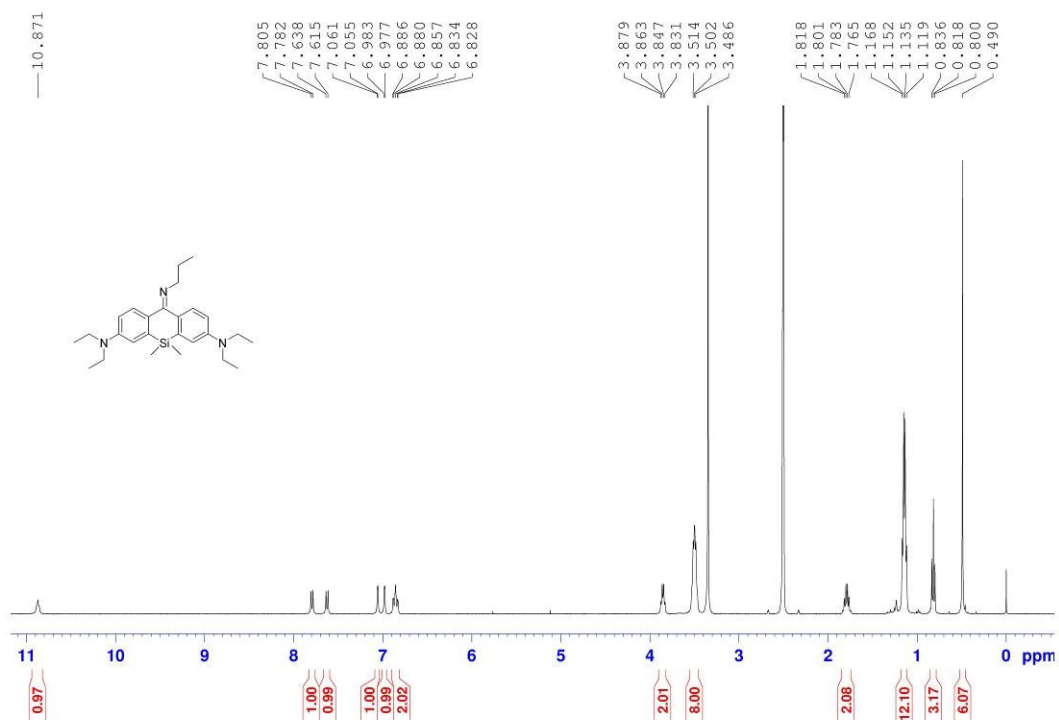


Figure S50. <sup>1</sup>H NMR spectrum of B-SiRhd-1 in DMSO-d<sub>6</sub>.

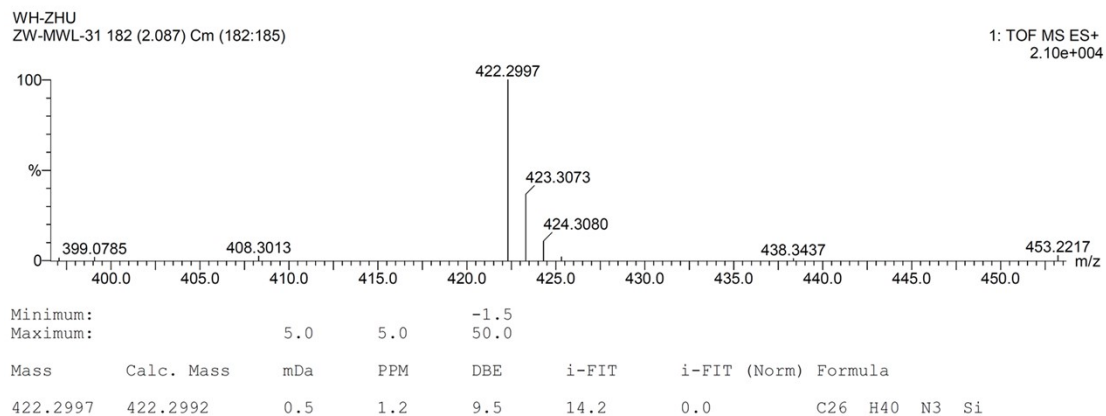


Figure S51. HRMS spectrum of *B*-SiRhd-1.

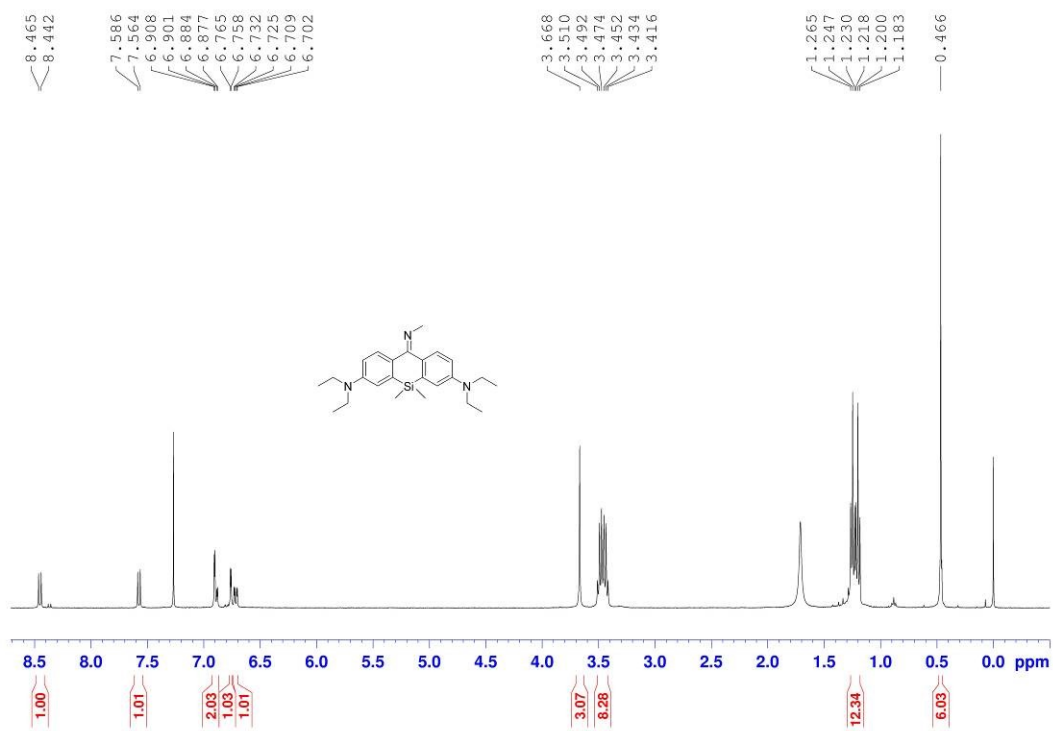


Figure S52.  $^1\text{H}$  NMR spectrum of *B*-SiRhd-2 in  $\text{CDCl}_3$ .



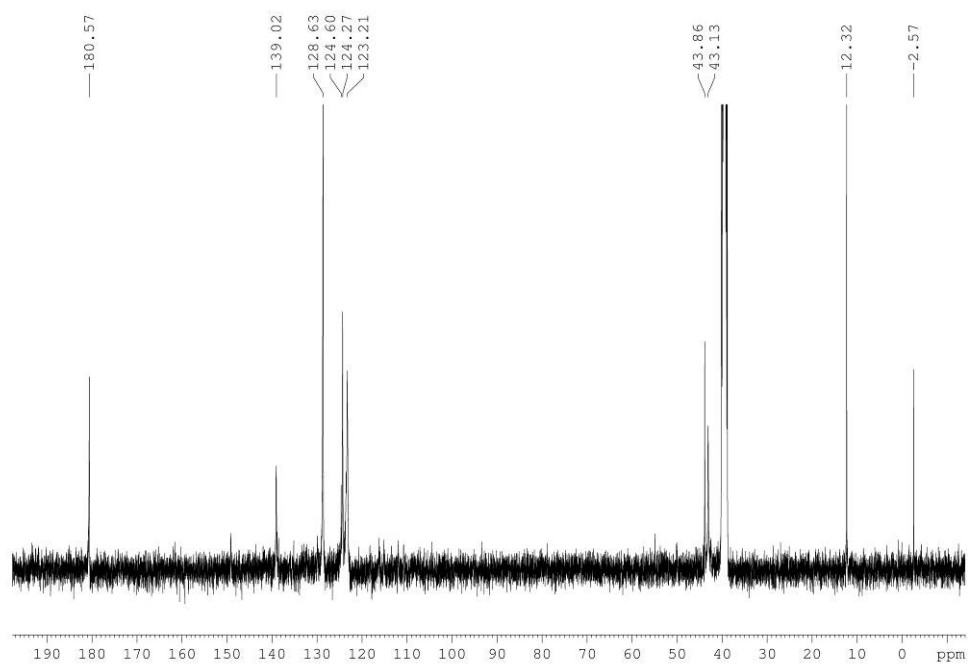


Figure S55.  $^{13}\text{C}$  NMR spectrum of *B-SiRhd-3* in  $\text{DMSO-}d_6$

### Elemental Composition Report

Page 1

#### Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

646 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

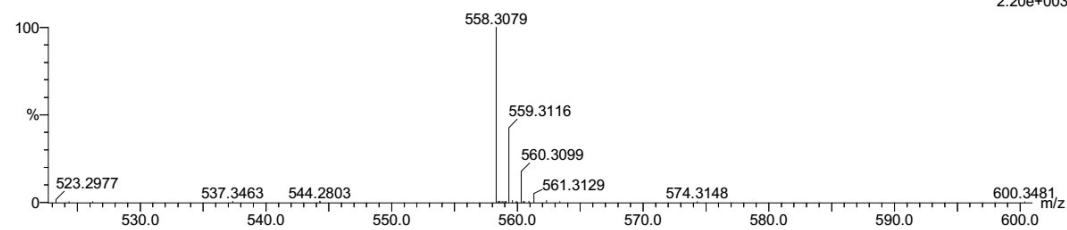
Elements Used:

C: 0-34 H: 0-50 N: 0-6 S: 0-2 Si: 0-8

WH-ZHU

ZW-MWL-25 153 (1.742) Cm (153:155)

1: TOF MS ES+  
2.20e+003



Minimum: -1.5  
Maximum: 5.0 5.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
558.3079	558.3087	-0.8	-1.4	14.5	48.3	0.0	C32 H44 N5 S Si

Figure S56. HRMS spectrum of *B-SiRhd-3*.

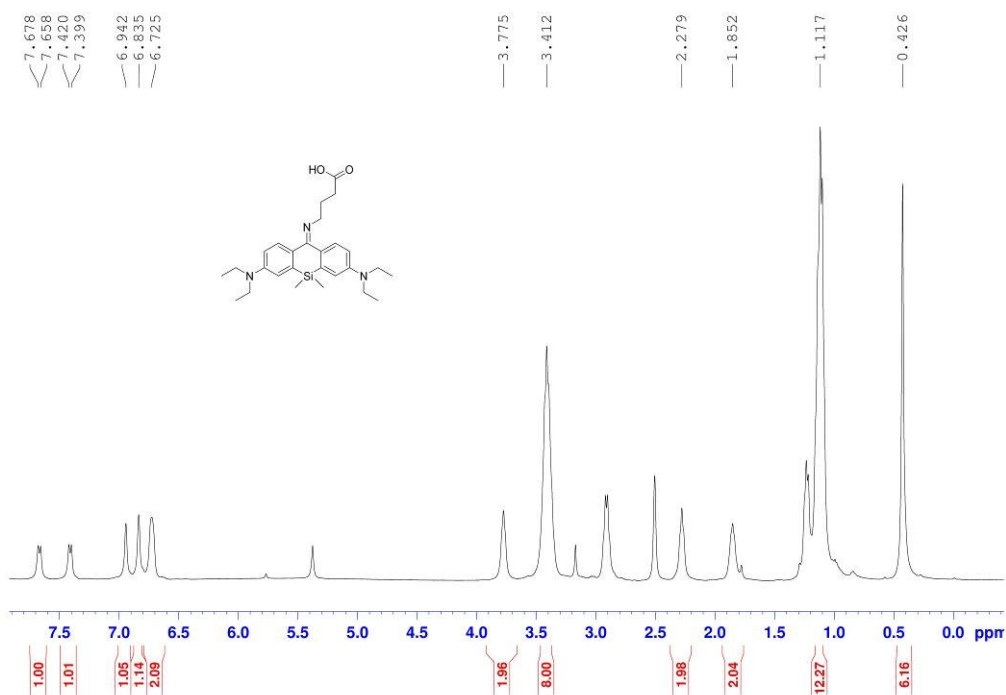


Figure S57.  $^1\text{H}$  NMR spectrum of **B-SiRhd-4** in  $\text{DMSO}-d_6$ .

### Elemental Composition Report

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#### Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

94 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

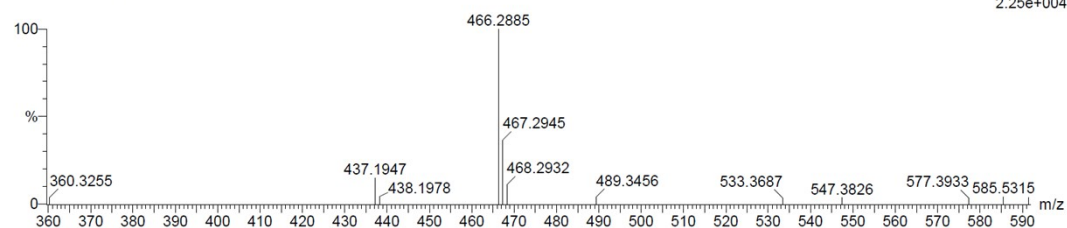
Elements Used:

C: 0-30 H: 0-45 N: 0-4 O: 0-4 Si: 0-1

WH-ZHU

ZW-MWL-31 86 (0.980) Cm (86:89)

1: TOF MS ES+  
2.25e+004



Minimum:  
Maximum:

5.0 10.0 50.0

Mass Calc. Mass mDa PPM DBE i-FIT i-FIT (Norm) Formula

466.2885 466.2890 -0.5 -1.1 10.5 12.2 0.0 C27 H40 N3 O2 Si

Figure S58. HRMS spectrum of **B-SiRhd-4**.

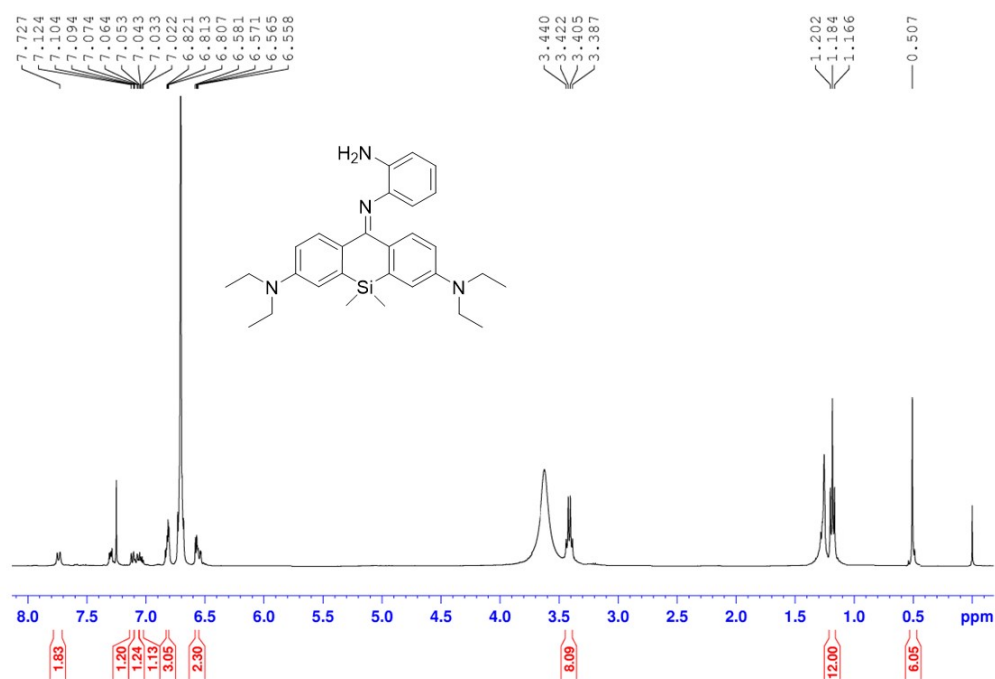


Figure S59. <sup>1</sup>H NMR spectrum of *B-SiRhd-5* in CDCl<sub>3</sub>.

Monoisotopic Mass, Even Electron Ions

15 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)

Elements Used:

C: 0-30 H: 0-40 N: 0-4 Si: 0-2

WH-ZHU

ECUST institute of Fine Chem

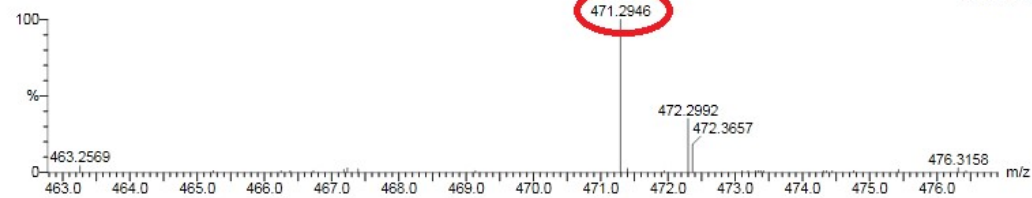
07-Sep-2016

ZW-TJM-0907 101 (0.715) Cm (95:103)

15:03:39

1: TOF MS ES+

2.09e+003



Minimum:

Maximum: 300.0 50.0 -1.5 100.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
471.2946	471.2944	0.2	0.4	13.5	75.6	0.0	C <sub>29</sub> H <sub>39</sub> N <sub>4</sub> Si

Figure S60. HRMS spectrum of *B-SiRhd-5*.





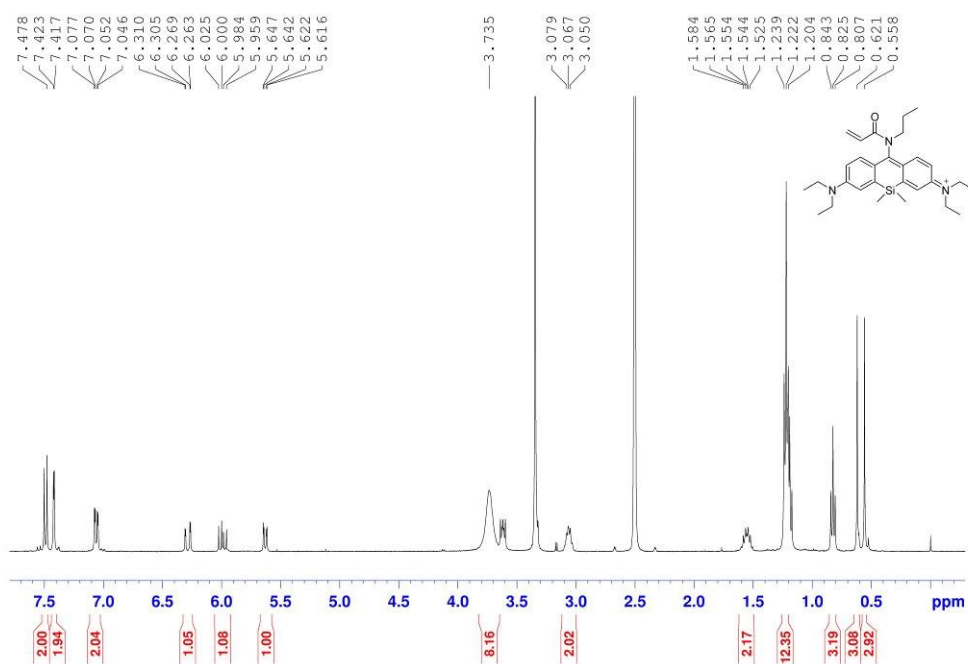


Figure S63.  $^1\text{H}$  NMR spectrum of *P*-SiRhd-2 in  $\text{DMSO-}d_6$ .

## Elemental Composition Report

Page 1

### Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions

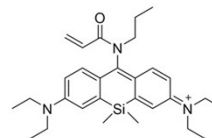
75 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

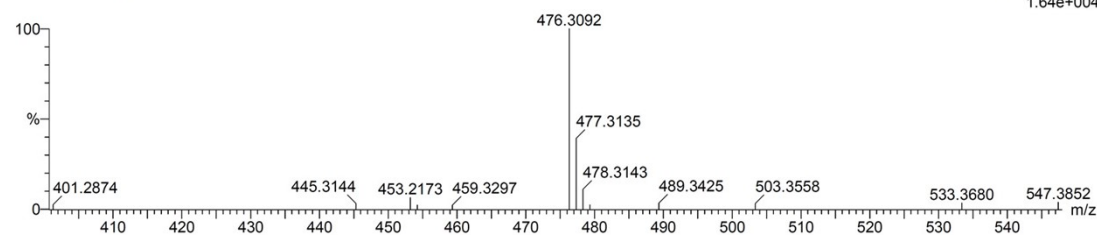
C: 0-30 H: 0-45 N: 0-3 O: 0-5 Si: 0-1

WH-ZHU

ZW-MWL-33 66 (0.749) Cm (60:66)



1: TOF MS ES+  
1.64e+004



Minimum:

Maximum: 5.0 5.0 -1.5

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
476.3092	476.3097	-0.5	-1.0	11.5	9.5	0.0	C <sub>29</sub> H <sub>42</sub> N <sub>3</sub> O Si

Figure S64. HRMS spectrum of *P*-SiRhd-2.

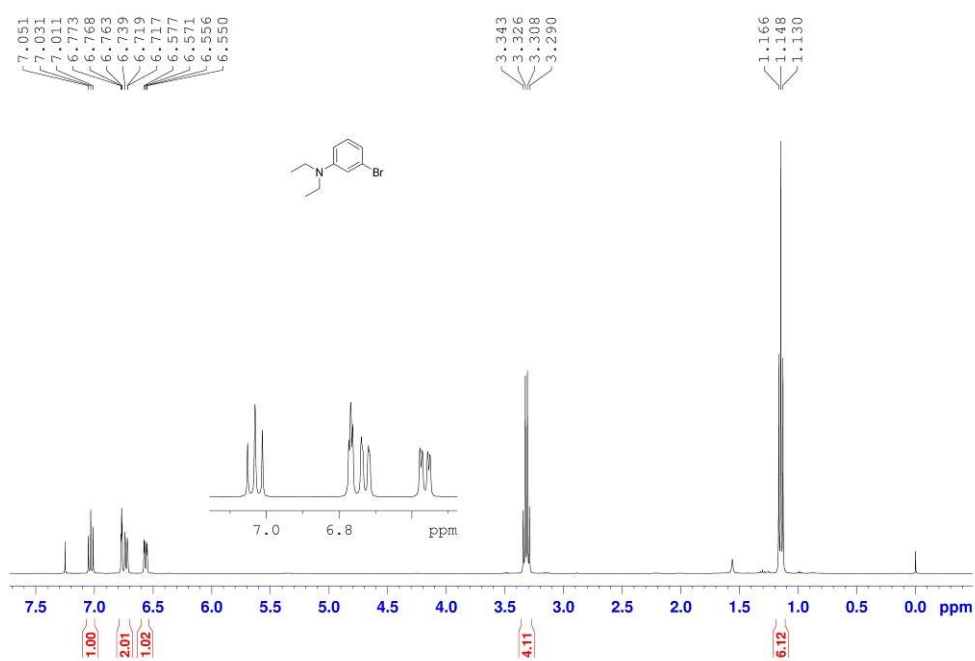


Figure S65. <sup>1</sup>H NMR spectrum of compound 1 in CDCl<sub>3</sub>

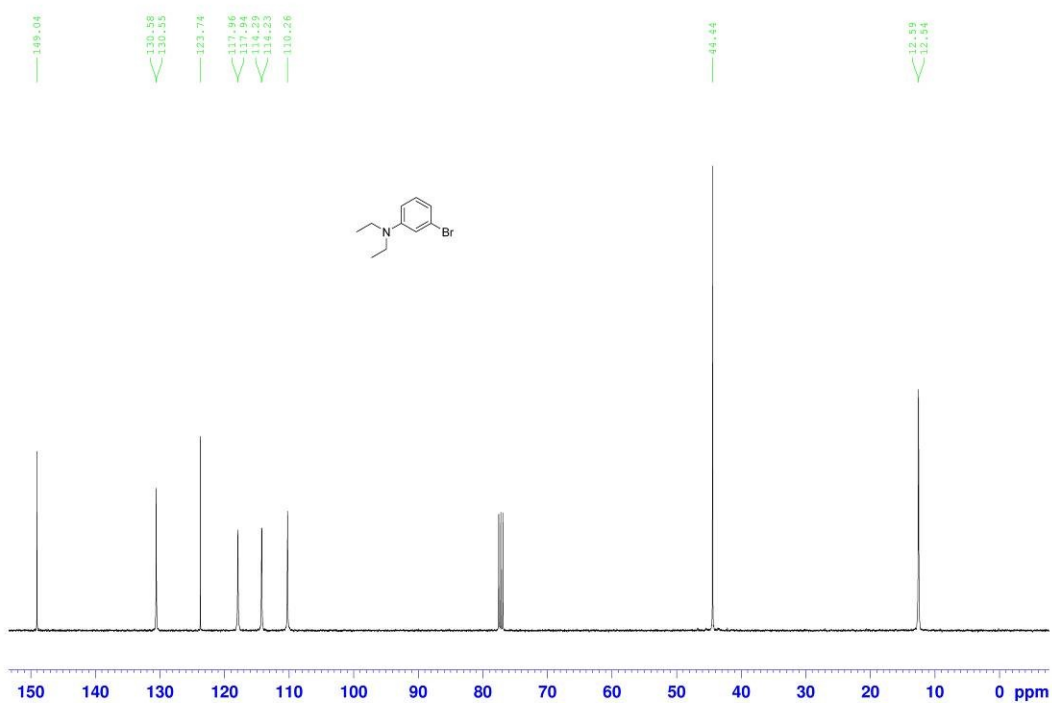
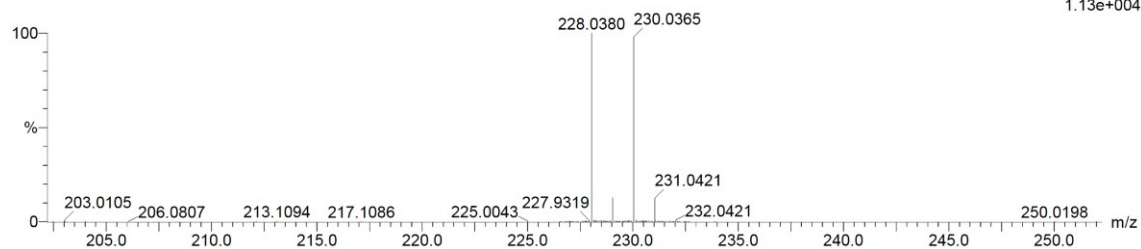


Figure S66. <sup>13</sup>C NMR spectrum of compound 1 in CDCl<sub>3</sub>

Monoisotopic Mass, Even Electron Ions  
 5 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)  
 Elements Used:  
 C: 0-12 H: 0-15 N: 0-1 Br: 0-1

WH-ZHU  
 ZW-XQS-3121 84 (0.950) Cm (84:86)

1: TOF MS ES+  
 1.13e+004



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
228.0380	228.0388	-0.8	-3.5	3.5	350.7	0.0	C10 H15 N Br

Figure S67. HRMS spectrum of compound 1.

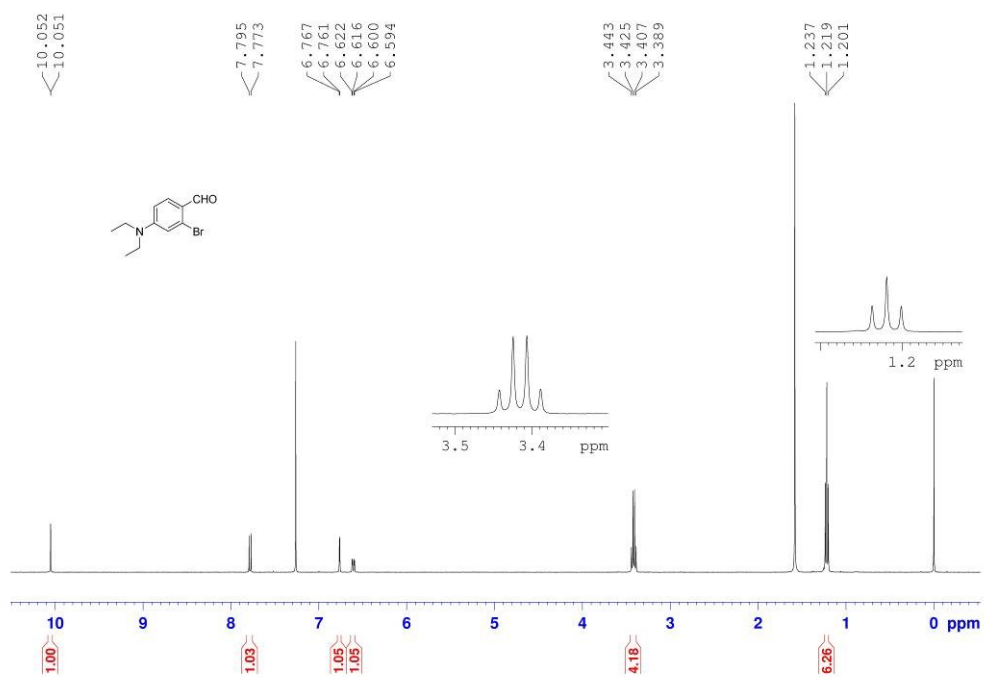


Figure S68. <sup>1</sup>H NMR spectrum of compound 2 in CDCl<sub>3</sub>

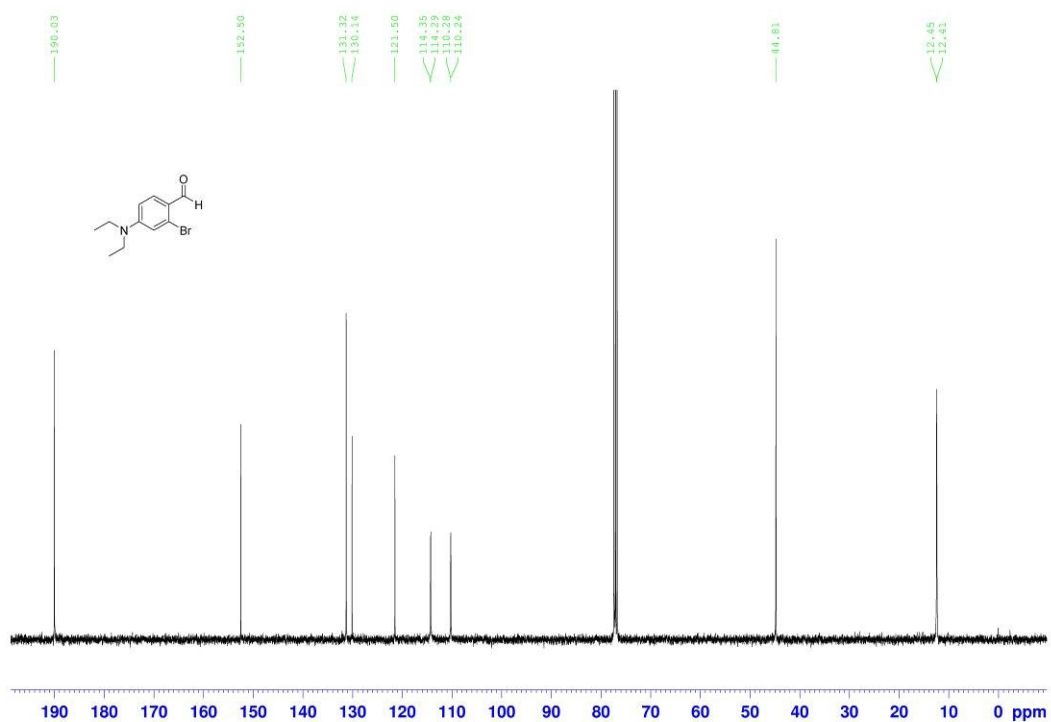


Figure S69. <sup>13</sup>C NMR spectrum of compound 2 in CDCl<sub>3</sub>

Monoisotopic Mass, Even Electron Ions

21 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

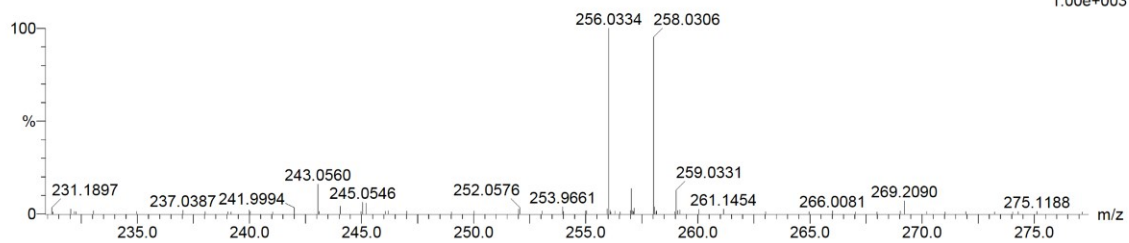
Elements Used:

C: 0-14 H: 0-15 N: 0-1 O: 0-4 Br: 0-1

WH-ZHU

ZW-XQS-3122 23 (0.250) Cm (23:26)

1: TOF MS ES+  
1.00e+003



Minimum:

Maximum: 5.0 10.0 -1.5

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
256.0334	256.0337	-0.3	-1.2	4.5	70.5	0.0	C11 H15 N O Br

Figure S70. HRMS spectrum of compound 2.

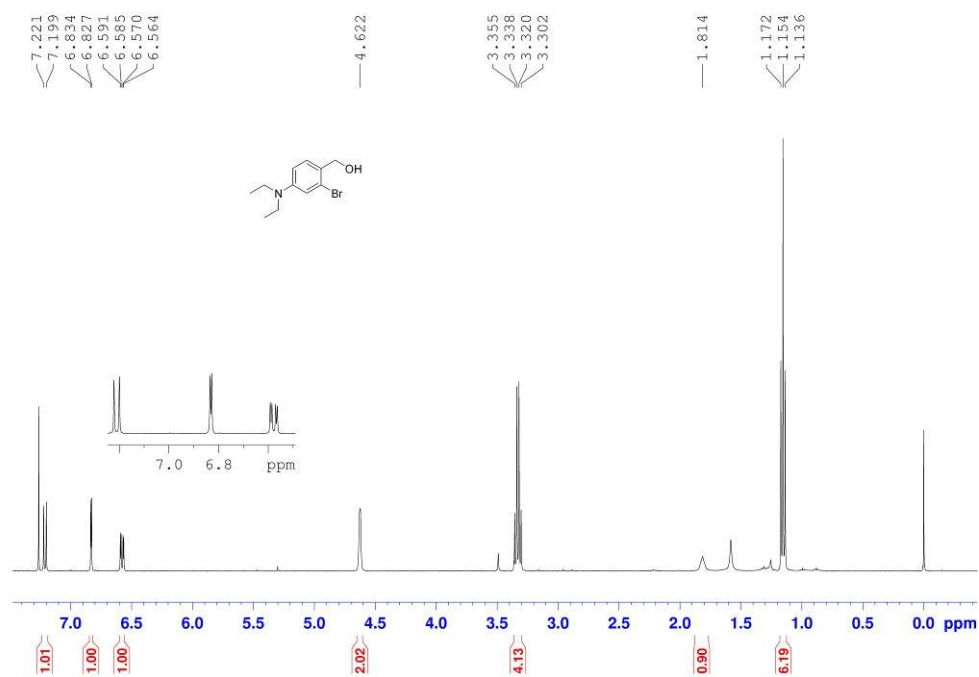


Figure S71. <sup>1</sup>H NMR spectrum of compound 3 in CDCl<sub>3</sub>

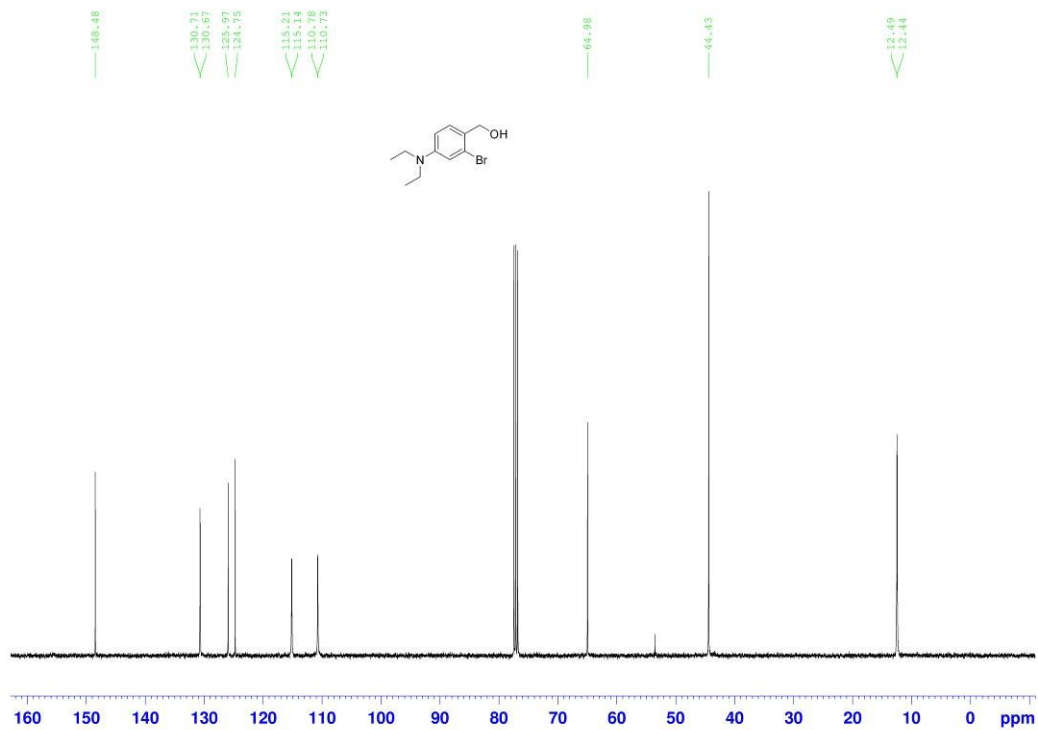
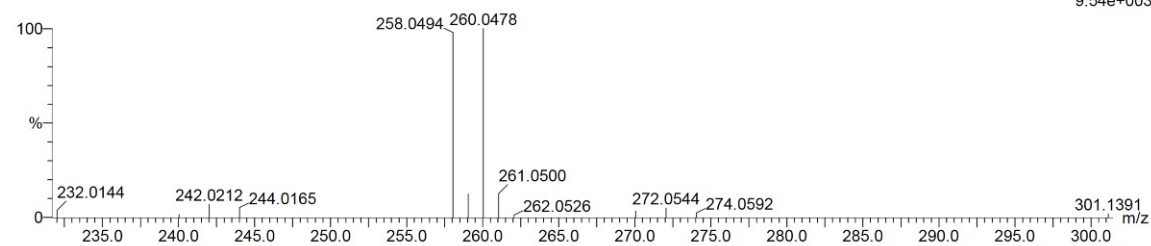


Figure S72. <sup>13</sup>C NMR spectrum of compound 3 in CDCl<sub>3</sub>

Monoisotopic Mass, Even Electron Ions  
 74 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)  
 Elements Used:  
 C: 0-25 H: 0-37 N: 0-3 O: 0-2 Br: 0-1

WH-ZHU  
 ZW-XQS-2123 103 (1.173) Cm (101:103)

1: TOF MS ES+  
 9.54e+003



Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
258.0494	258.0494	0.0	0.0	3.5	7.4	0.0	C11 H17 N O Br

Figure S73. HRMS spectrum of compound 3.

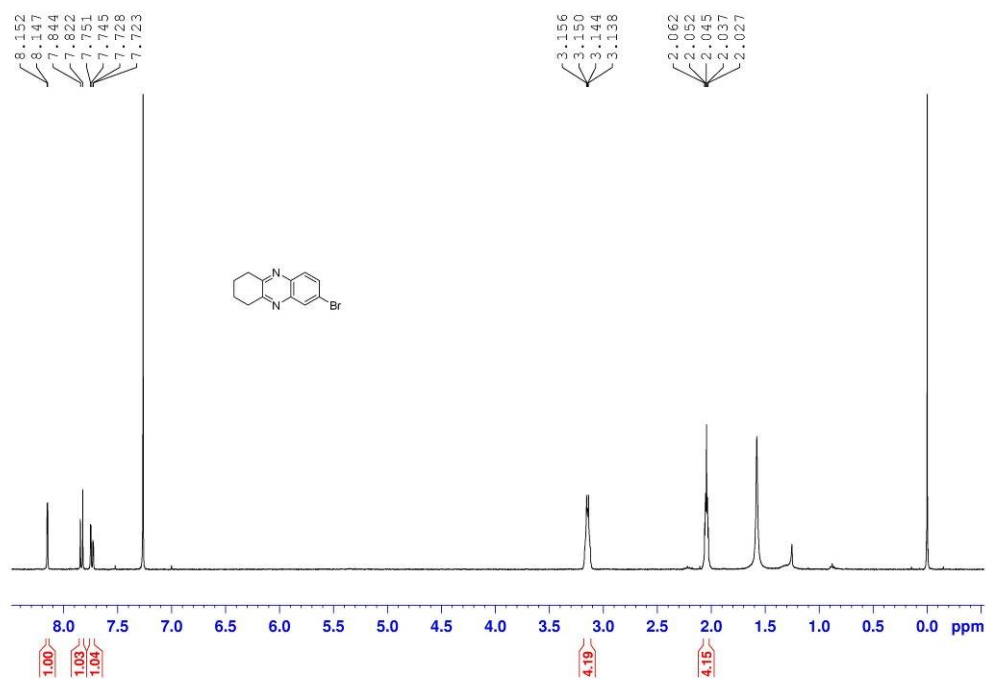


Figure S74. <sup>1</sup>H NMR spectrum of compound 4 in CDCl<sub>3</sub>

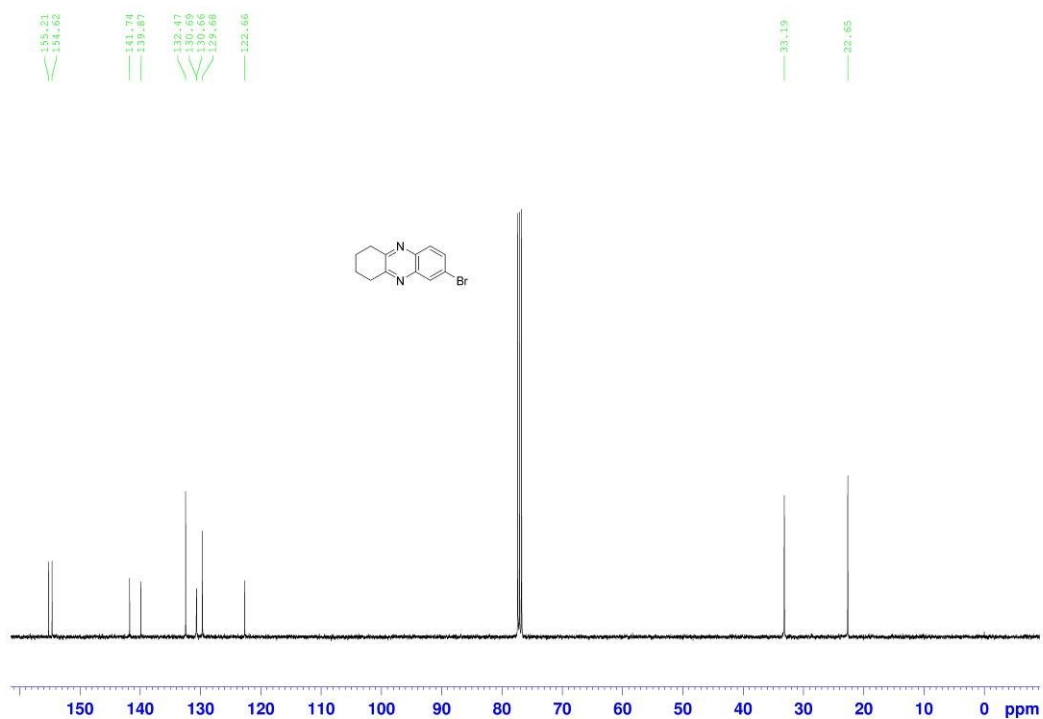


Figure S75.  $^{13}\text{C}$  NMR spectrum of compound 4 in  $\text{CDCl}_3$

Monoisotopic Mass, Even Electron Ions

7 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

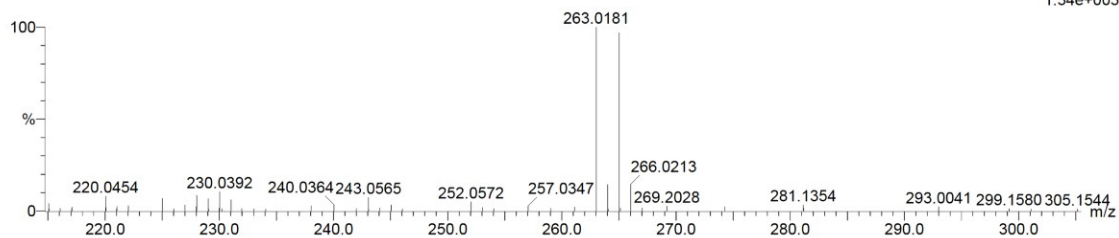
Elements Used:

C: 0-14 H: 0-15 N: 0-2 Br: 0-1

WH-ZHU

ZW-XQS-3124 163 (1.882) Cm (163:166)

1: TOF MS ES+  
1.34e+003



Minimum: -1.5  
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
263.0181	263.0184	-0.3	-1.1	7.5	15.1	0.0	C12 H12 N2 Br

Figure S76. HRMS spectrum of compound 4.



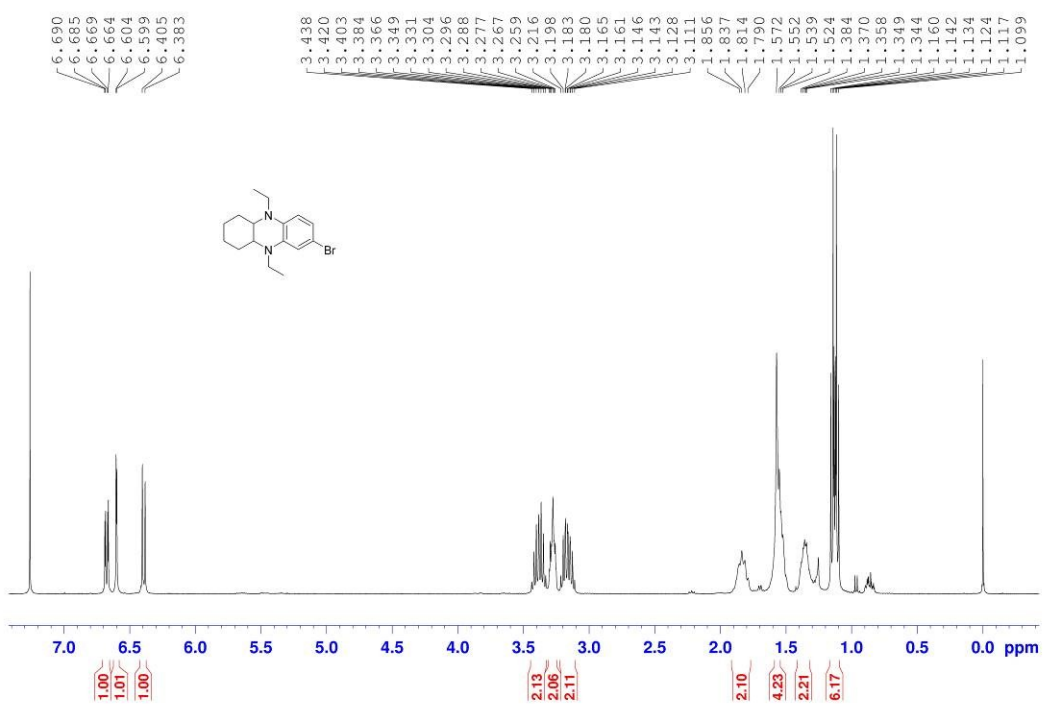


Figure S77. <sup>1</sup>H NMR spectrum of compound 5 in CDCl<sub>3</sub>

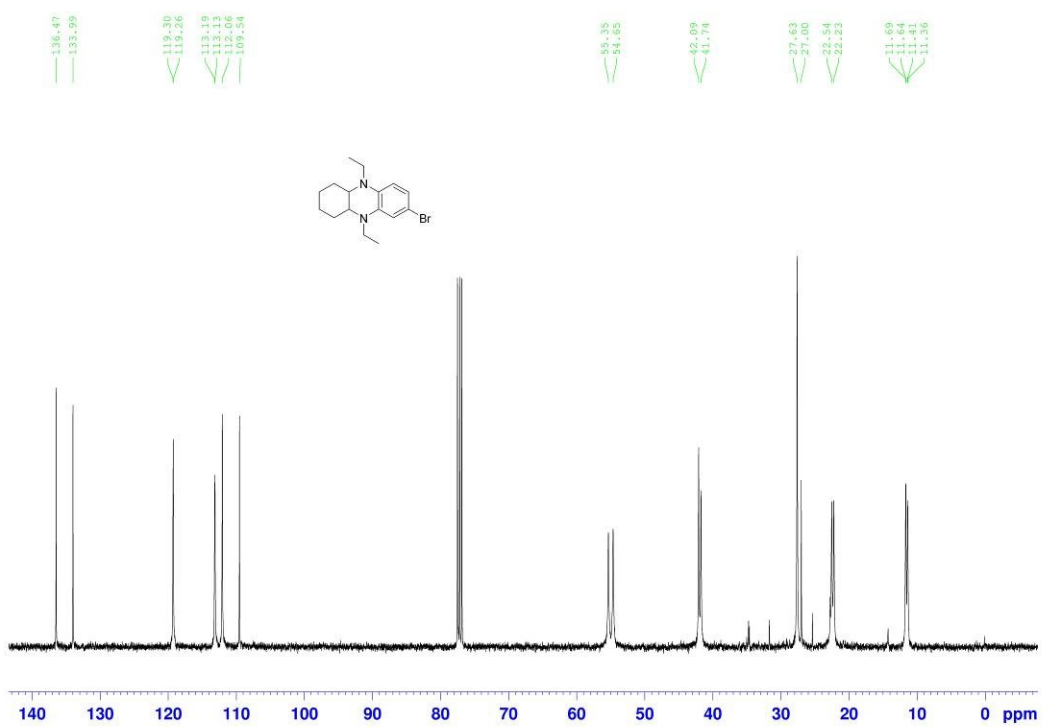


Figure S78. <sup>13</sup>C NMR spectrum of compound 5 in CDCl<sub>3</sub>

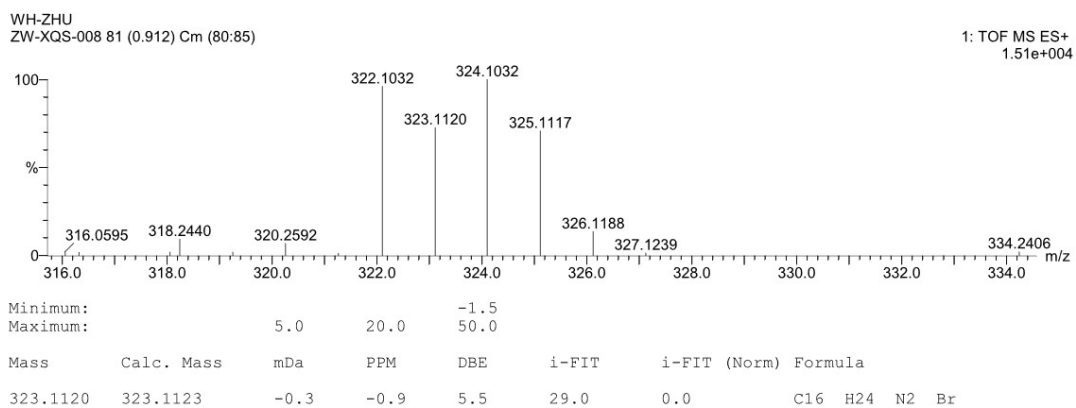


Figure S79. HRMS spectrum of compound 5.

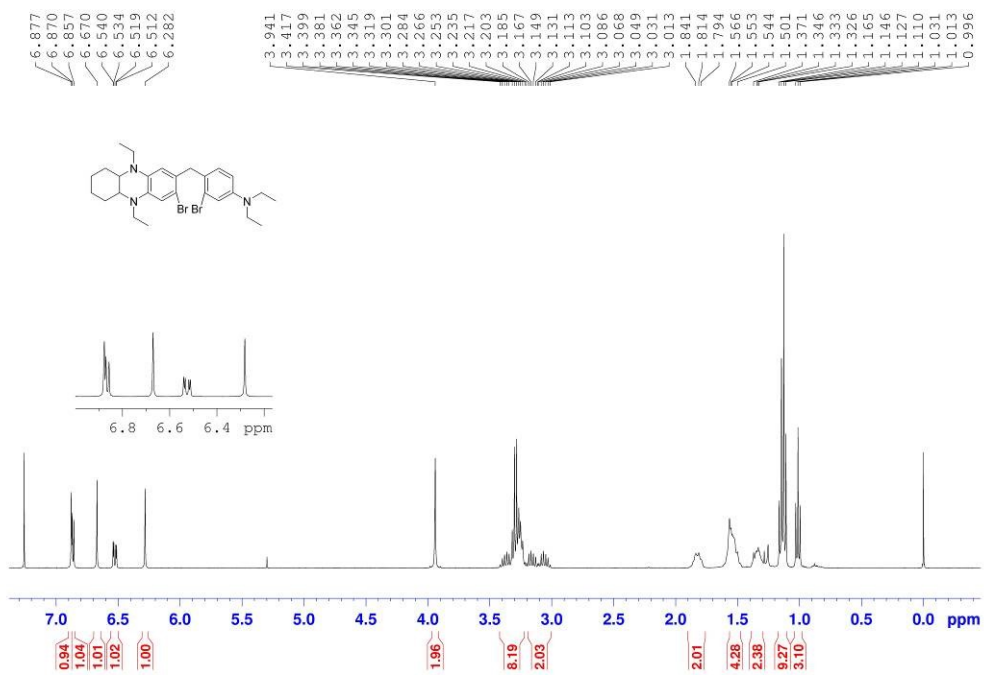


Figure S80.  $^1\text{H}$  NMR spectrum of compound 6 in  $\text{CDCl}_3$

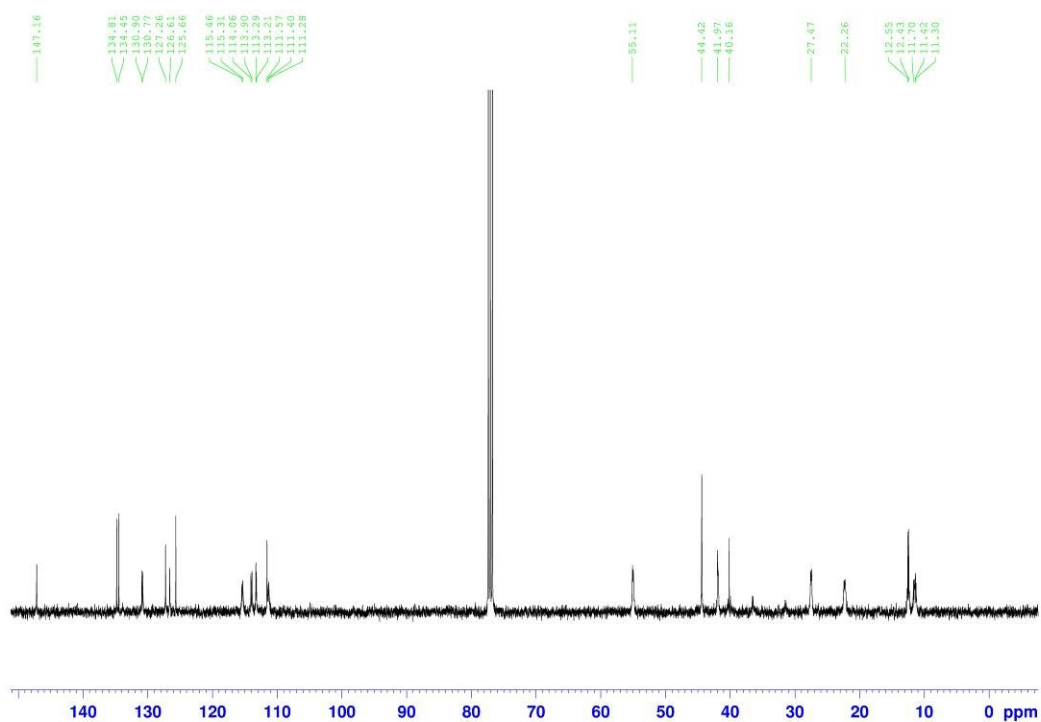


Figure S81.  $^{13}\text{C}$  NMR spectrum of compound 6 in  $\text{CDCl}_3$

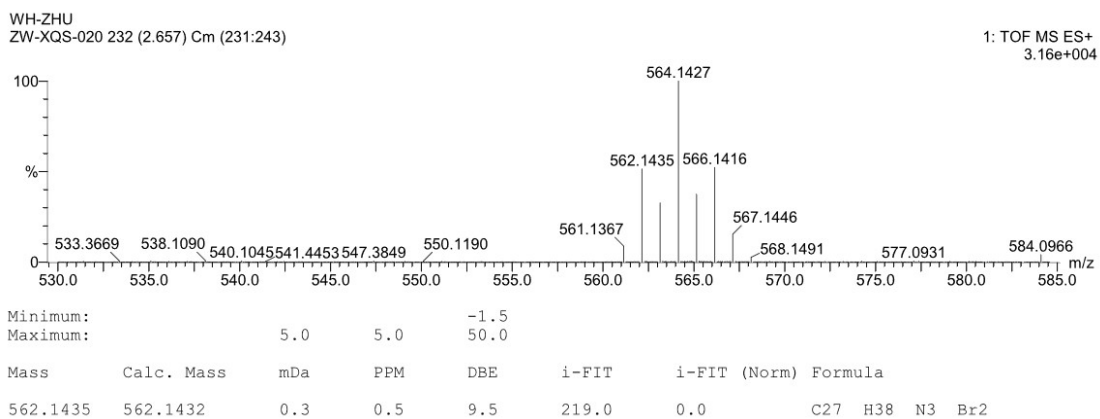


Figure S82. HRMS spectrum of compound 6.

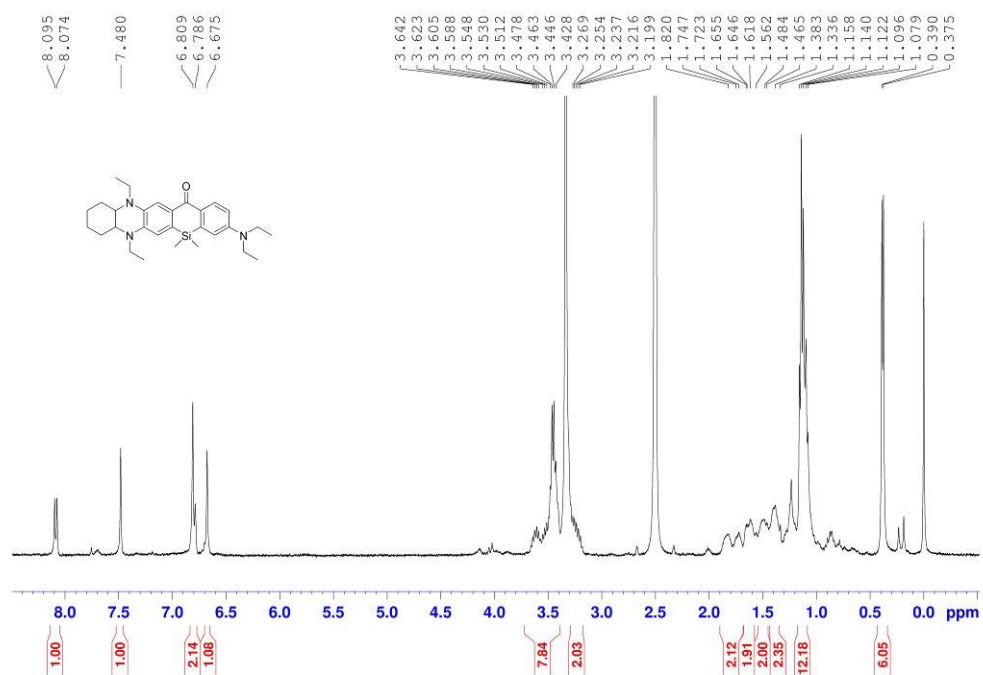


Figure S83. <sup>1</sup>H NMR spectrum of O-SiRhd-II in DMSO-*d*<sub>6</sub>.

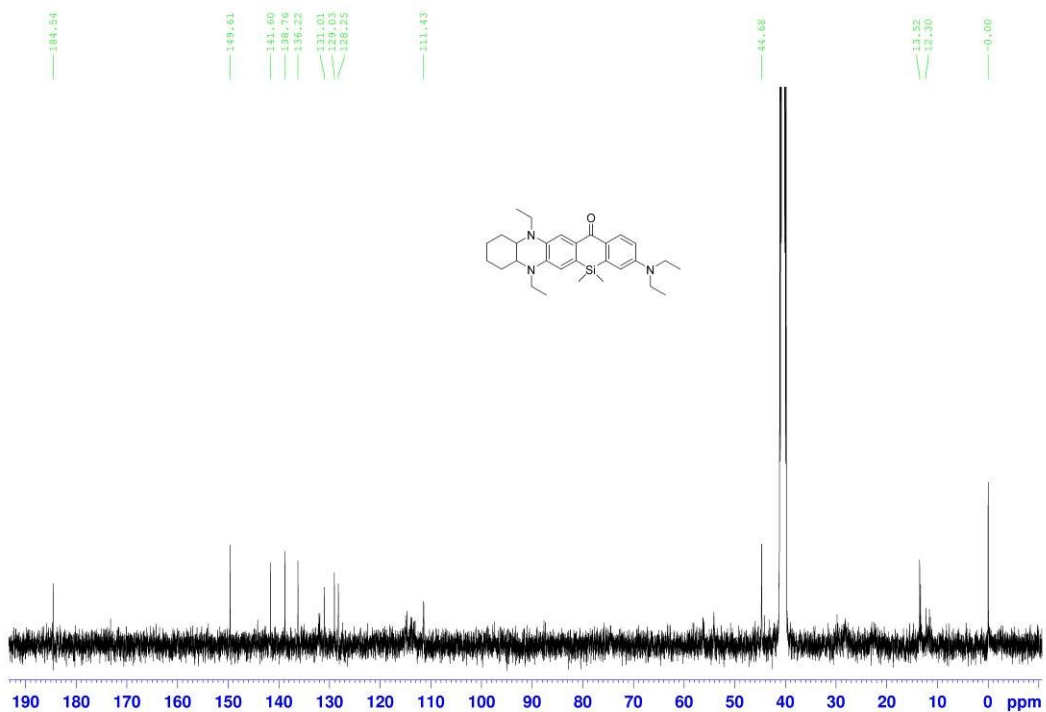


Figure S84. <sup>13</sup>C NMR spectrum of O-SiRhd-II in DMSO-*d*<sub>6</sub>.

WH-ZHU  
ZW-XQS-032 206 (2.364) Cm (206:210)

1: TOF MS ES+  
1.20e+004

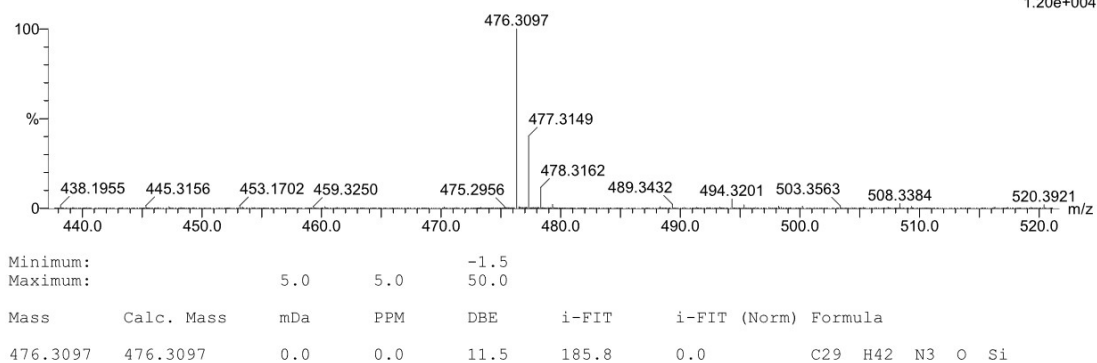


Figure S85. HRMS spectrum of O-SiRhod-III.

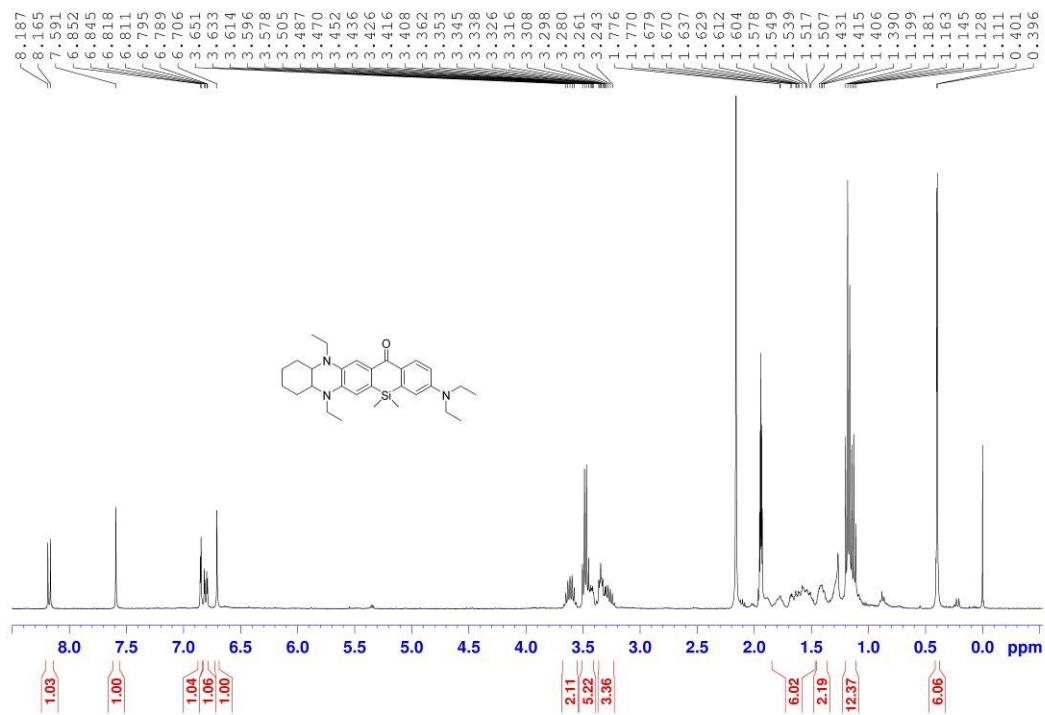


Figure S86. <sup>1</sup>H NMR spectrum of O-SiRhod-III in CD<sub>3</sub>CN.

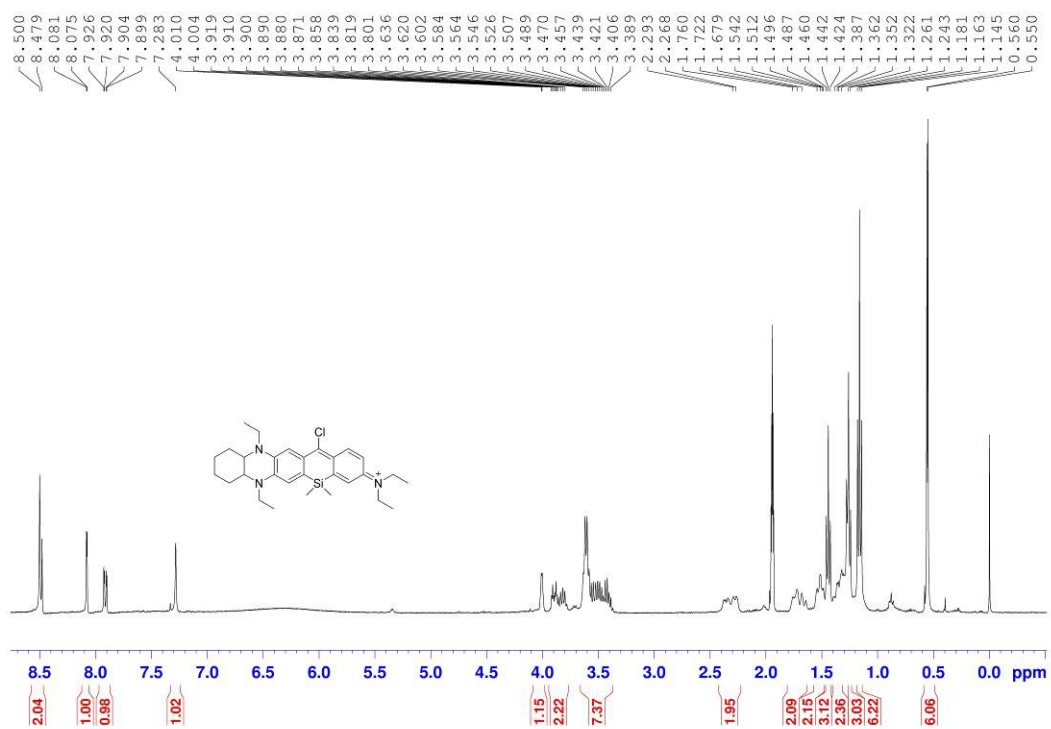


Figure S87. <sup>1</sup>H NMR spectrum of Cl-SiRhd-II in CD<sub>3</sub>CN.

Monoisotopic Mass, Even Electron Ions

35 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

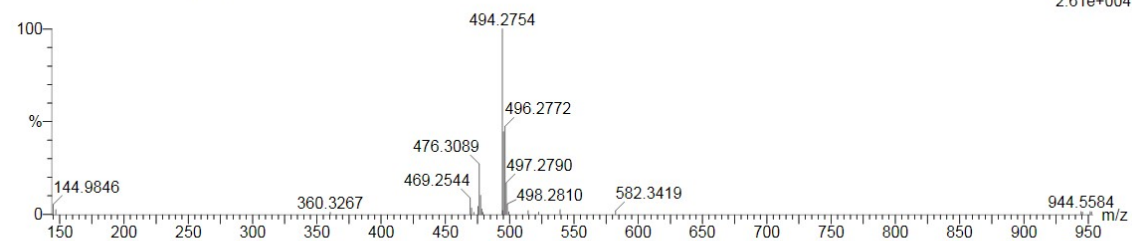
Elements Used:

C: 0-30 H: 0-43 N: 0-4 Cl: 0-1 Si: 0-2

WH-ZHU

ZW-XQS-4102 26 (0.548) Cm (25:26)

1: TOF MS ES+  
2.61e+004



Minimum:

Maximum: 5.0 15.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
494.2754	494.2758	-0.4	-0.8	11.5	33.1	0.0	C <sub>29</sub> H <sub>41</sub> N <sub>3</sub> Cl Si

Figure S88. HRMS spectrum of Cl-SiRhd-II.

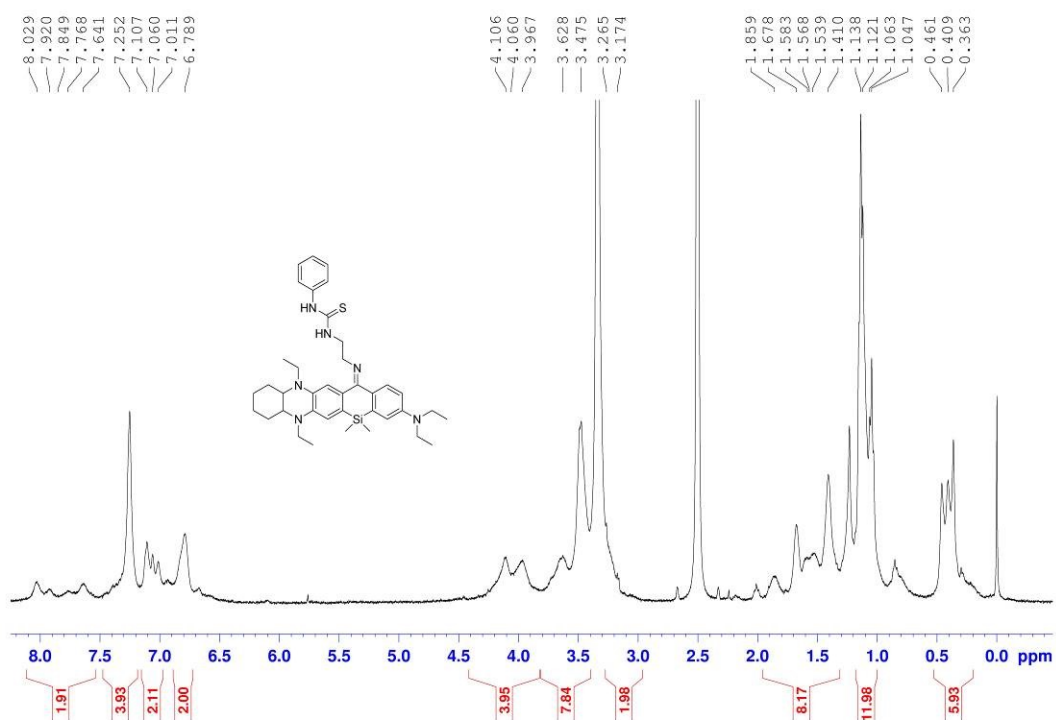


Figure S89. <sup>1</sup>H NMR spectrum of *B*-SiRhd-6 in DMSO-*d*<sub>6</sub>.

Monoisotopic Mass, Even Electron Ions

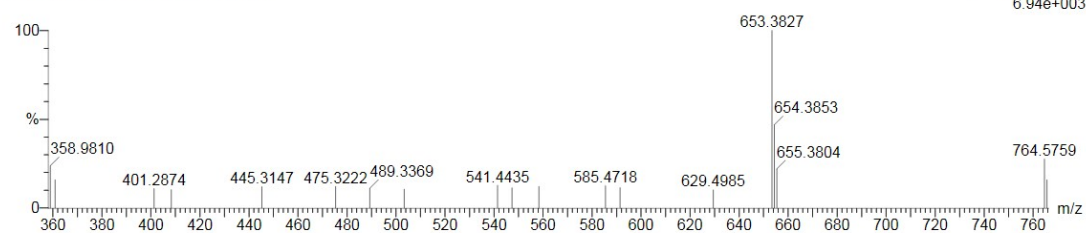
24 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)

Elements Used:

C: 0-38 H: 0-53 N: 0-6 Si: 0-1 S: 0-1

WH-ZHU

ZW-XQS-2101 16 (0.166) Cm (10:16)



Minimum:

Maximum:

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
653.3827	653.3822	0.5	0.8	16.5	15.6	0.0	C <sub>38</sub> H <sub>53</sub> N <sub>6</sub> Si S

Figure S90. HRMS spectrum of *B*-SiRhd-6.

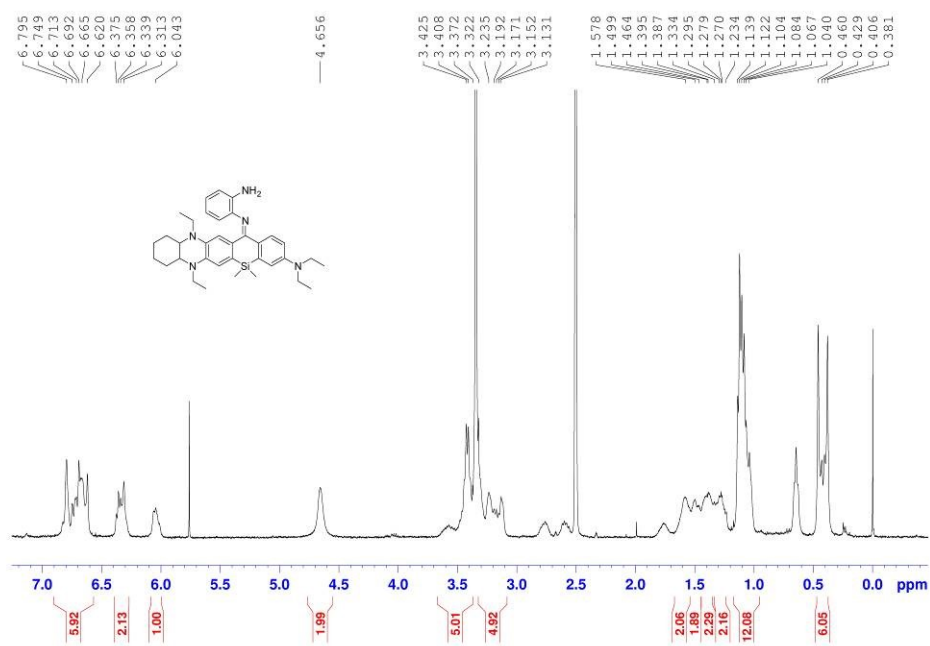


Figure S91. <sup>1</sup>H NMR spectrum of *B-SiRhd-7* in DMSO-*d*<sub>6</sub>.

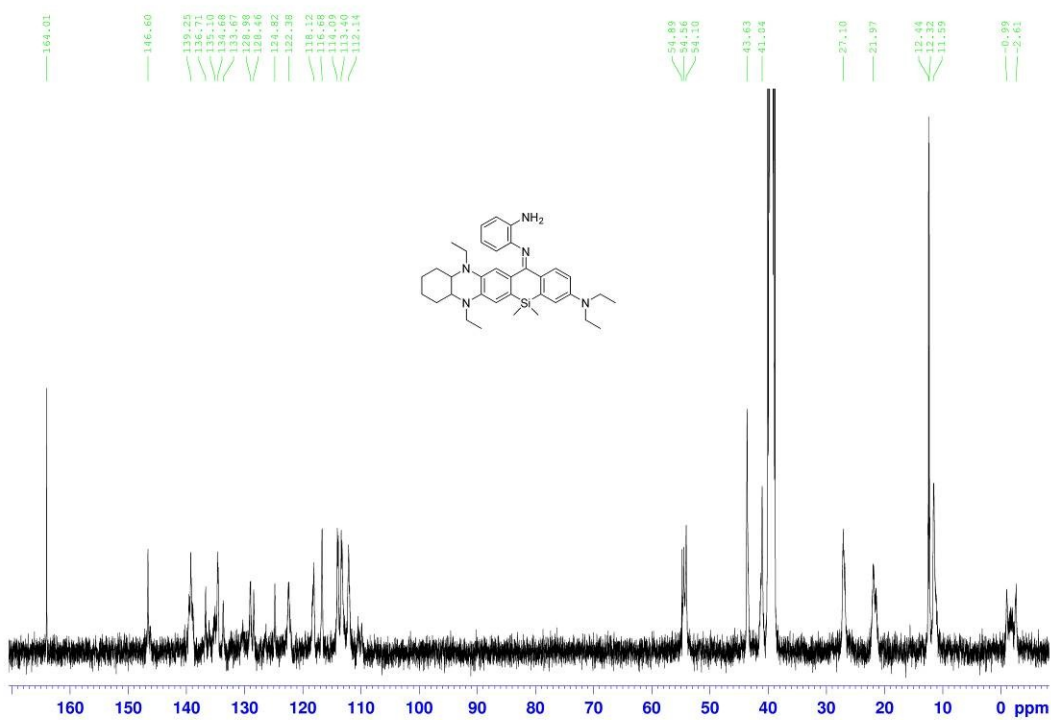
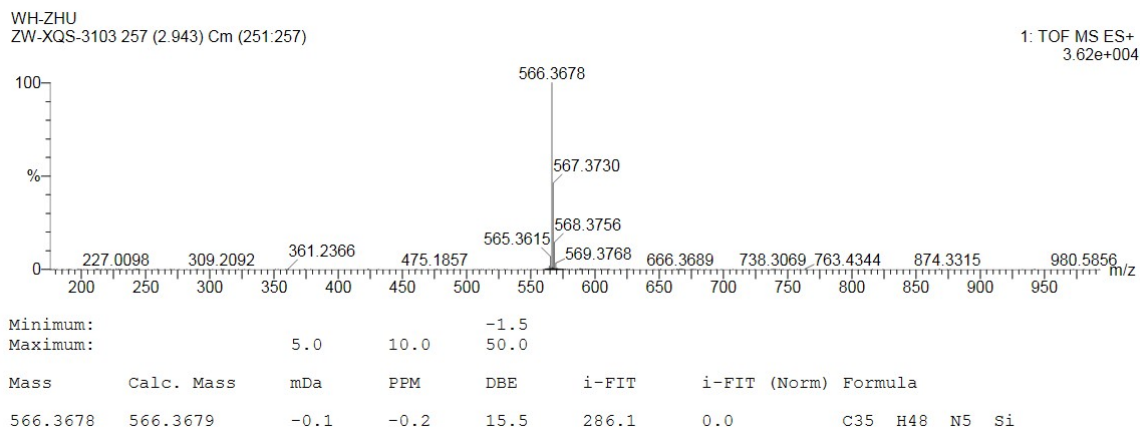


Figure S92. <sup>13</sup>C NMR spectrum of *B-SiRhd-7* in DMSO-*d*<sub>6</sub>.





**Figure S93.** HRMS spectrum of **B-SiRhd-7**.

## 5. Tables of photophysical data and crystal data

**Table S1.** Photophysical data of **B-SiRhds** and **P-SiRhds**.

Dye	$\lambda_{\text{abs}}$ (nm) <sup>[a]</sup>	$\epsilon_{\lambda_{\text{abs}}}$ ( $M^{-1}\cdot\text{cm}^{-1}$ ) <sup>[b]</sup>	$\lambda_{\text{em}}$ (nm) <sup>[c]</sup>	$\Phi_{\text{F}}$ (%)
<i>B</i> -SiRhd-1 <sup>[d]</sup>	460	17731	610	37 <sup>[g]</sup>
<i>P</i> -SiRhd-1 <sup>[d]</sup>	680	85276	701	31 <sup>[g]</sup>
<i>B</i> -SiRhd-4 <sup>[e]</sup>	460	14042	595	34 <sup>[g]</sup>
<i>B</i> -SiRhd-3 <sup>[d]</sup>	488	9677	610	51 <sup>[g]</sup>
<i>P</i> -SiRhd-3 <sup>[d]</sup>	690	52518	710	55 <sup>[g]</sup>
<i>P</i> -SiRhd-7 <sup>[f]</sup>	780	24035	1040	0.03 <sup>[f, h]</sup>

[a] Absorption peak.

[b] Molar absorptivity at the absorption peak.

[c] Fluorescence emission peak.

[d] Measured pH 7.4 PBS.

[e] Measured in methanol.

[f] Measured in a mixed solution of  $\text{CH}_3\text{CN}/\text{HEPES}$  ( $v/v = 1/1$ , pH 7.4).

[g] measured by using rhodamine 6G ( $\Phi = 88\%$  in ethanol) as a standard.

[h] measured by using IR-26 ( $\Phi = 0.05\%$  in dichloroethane) as a standard.

**Table S2.** Crystal data and structure refinement for *B*-SiRhd-5. The X-ray crystallographic coordinates for *B*-SiRhd-5 have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number: 2119838.

Identification code	<i>B</i> -SiRhd-5	
Empirical formula	C <sub>29</sub> H <sub>38</sub> N <sub>4</sub> Si	
Formula weight	470.72	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.4703(2) Å	α = 90°.
	b = 13.2994(3) Å	β = 90°.
	c = 24.4250(7) Å	γ = 90°.
Volume	2751.47(12) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.136 Mg/m <sup>3</sup>	
Absorption coefficient	0.108 mm <sup>-1</sup>	
F(000)	1016	
Crystal size	0.200 x 0.150 x 0.120 mm <sup>3</sup>	
Theta range for data collection	2.545 to 25.999°.	
Index ranges	-10<=h<=9, -16<=k<=16, -28<=l<=30	
Reflections collected	24545	
Independent reflections	5417 [R(int) = 0.0423]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6649	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	5417 / 2 / 321	
Goodness-of-fit on F <sup>2</sup>	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.1161	
R indices (all data)	R1 = 0.0566, wR2 = 0.1237	
Absolute structure parameter	0.05(5)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.737 and -0.326 e.Å <sup>-3</sup>	

**Table S3.** Crystal data and structure refinement for *P*-SiRhd-2. The X-ray crystallographic coordinates for *P*-SiRhd-2 have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number: 2119842.

Identification code	<i>P</i> -SiRhd-2	
Empirical formula	C30 H44 Cl3 N3 O Si	
Formula weight	597.12	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.8497(8) Å	$\alpha = 90^\circ$ .
	b = 15.4899(12) Å	$\beta = 97.135(2)^\circ$ .
	c = 20.3611(14) Å	$\gamma = 90^\circ$ .
Volume	3395.4(4) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.168 Mg/m <sup>3</sup>	
Absorption coefficient	0.331 mm <sup>-1</sup>	
F(000)	1272	
Crystal size	0.200 x 0.150 x 0.080 mm <sup>3</sup>	
Theta range for data collection	2.407 to 24.999°.	
Index ranges	-12 ≤ h ≤ 12, -16 ≤ k ≤ 18, -24 ≤ l ≤ 24	
Reflections collected	26357	
Independent reflections	5966 [R(int) = 0.0625]	
Completeness to theta = 25.242°	97.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6574	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	5966 / 12 / 369	
Goodness-of-fit on F <sup>2</sup>	1.034	
Final R indices [I > 2σ(I)]	R1 = 0.0718, wR2 = 0.1771	
R indices (all data)	R1 = 0.1143, wR2 = 0.2144	
Extinction coefficient	0.0048(13)	
Largest diff. peak and hole	0.739 and -0.462 e.Å <sup>-3</sup>	

**Table S4.** Crystal data and structure refinement for Cl-SiRhd. The X-ray crystallographic coordinates for Cl-SiRhd have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number: 2132279.

Identification code	Cl-SiRhd	
Empirical formula	C <sub>25</sub> H <sub>36</sub> Cl <sub>6</sub> N <sub>2</sub> Si	
Formula weight	605.35	
Temperature	272.0 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 22.2241(9) Å	α = 90°.
	b = 9.0072(3) Å	β = 90°.
	c = 30.4536(11) Å	γ = 90°.
Volume	6096.1(4) Å <sup>3</sup>	
Z	8	
Density (calculated)	1.319 Mg/m <sup>3</sup>	
Absorption coefficient	5.646 mm <sup>-1</sup>	
F(000)	2528	
Crystal size	0.1 x 0.05 x 0.02 mm <sup>3</sup>	
Theta range for data collection	2.902 to 68.298°.	
Index ranges	-26 ≤ h ≤ 26, -10 ≤ k ≤ 10, -34 ≤ l ≤ 36	
Reflections collected	54262	
Independent reflections	5562 [R(int) = 0.0784]	
Completeness to theta = 67.679°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.4474	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	5562 / 41 / 367	
Goodness-of-fit on F <sup>2</sup>	1.050	
Final R indices [I > 2σ(I)]	R1 = 0.0568, wR2 = 0.1454	
R indices (all data)	R1 = 0.0912, wR2 = 0.1648	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.340 and -0.453 e.Å <sup>-3</sup>	

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