Supporting Information

Synthesis of unsymmetrical Si-rhodamine fluorophores and application to a far-red to near-infrared fluorescence probe for hypoxia

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General Procedure and Materials

Reagents and solvents were of the best grade available, purchased from Tokyo Chemical Industries, Wako Pure Chemical, Aldrich Chemical Co., Dojindo, Watanabe Chemical Industries, Invitrogen and Biosearch Technologies, and were used without further purification. Mice (Jcl:ICR) were purchased from CLEA Japan. Somnopentyl® Injection was purchased from Kyoritsu Seiyaku Corporation. Special chemicals and DMSO (fluorometric grade) used for stock solutions were purchased from Dojindo. Saline was purchased from Otsuka Pharmaceutical Co. Ltd. Reactions were monitored by means of TLC and ESI mass spectrometry. All compounds were purified on a silica gel column and/or by preparative HPLC.

Instruments

NMR spectra were recorded on a JEOL JNM-LA300 instrument at 300 MHz for ^{1}H NMR and at 75 MHz for ^{13}C NMR, or a JEOL JNM-LA400 instrument at 400 MHz for ^{1}H NMR and at 100 MHz for ^{13}C NMR. Mass spectra (MS) were measured with a JEOL JMS-T100LC AccuToF (ESI). HPLC purifications were performed on an Inertsil ODS-3 (10.0 × 250 mm) column (GL Sciences Inc.) using an HPLC system composed of a pump (PU-2080, JASCO) and a detector (MD-2015 or FP-2025, JASCO) fitted with a reversed-phase column (GL Sciences (Tokyo, Japan), Inertsil ODS-3 10 mm × 250 mm, using eluent A (H_2O containing 0.1% TFA (v/v)) and eluent B (CH_3CN with 20% H_2O containing 0.1% TFA (v/v)), at the flow rate of 5 ml/min. HPLC analyses were performed on a system composed of a pump (PU-2080, JASCO) and a detector (MD-2015, JASCO), fitted with a reversed-phase column (Inertsil ODS-3 4.6 mm × 250 mm (GL Sciences, Tokyo, Japan)), using eluent A and eluent B at the flow rate of 1 mL/min. Absorption spectra were obtained with Shimadzu UV-1650 and UV-2550 instruments (Tokyo, Japan). Fluorescence spectroscopic studies were performed with a Hitachi F4500 or F-7000 spectrometer (Tokyo, Japan). The excitation and emission slit widths were 5 nm. UV-Visible spectra were obtained on a Shimadzu UV-1650. Fluorescence spectroscopic studies were performed on a Hitachi F4500. The slit width was 5 nm for both excitation and emission. The photomultiplier voltage was 700 V. Absolute quantum yields were determined with a Hamamatsu Photonics Quantaurus QY.

Optical Properties and Relative Fluorescence Quantum Efficiency

Optical properties of dyes except **azoSiR640** and **2,6-diMe SiR640** (**65**) were examined in 100 mM sodium phosphate buffer (pH 7.4) containing 1% (v/v) DMSO as a co-solvent. Those of

azoSiR640 and **2,6-diMe SiR640** (**65**) were measured in PBS (pH 7.4) containing 0.1% DMSO as a co-solvent. The absolute fluorescence quantum efficiencies (Φ_{fl}) of **28**, **29** and **30** were determined with a Hamamatsu Photonics Quantaurus QY. For determination of the fluorescence quantum efficiency (Φ_{fl}) of **25**, **azoSiR640** and **2,6-diMe SiR640** (**65**), Cresyl violet in MeOH (Φ_{fl} = 0.54) was used as a standard. For determination of the fluorescence quantum efficiencies (Φ_{fl}) of SiR640 (**26**), **27** and **31**, Cy5.5 in PBS (Φ_{fl} = 0.24) was used as a standard. Fluorescence quantum efficiencies were calculated according to the following equation.

$$\Phi_x/\Phi_{st} = [A_{st}/A_x][n_x^2/n_{st}^2][D_x/D_{st}]$$

where st: standard; x: sample; A: absorbance at the excitation wavelength; *n*: refractive index; D: area under the fluorescence spectra on an energy scale.

For determination of molar extinction coefficient (ε) of dyes, we firstly prepared the DMSO stock solution of each dye by dissolving several mg of dye in DMSO and then measured absorbance at the wavelength of absorbance maximum in 100 mM sodium phosphate buffer (pH 7.4) or PBS (pH 7.4) by using the DMSO stock solutions.

Preparation of Rat Liver Microsomes

All procedures were approved by the Animal Care and Use Committee of the University of Tokyo. Rats (Wistar, 6–7 weeks old) were purchased from CLEA Japan. Rats received intraperitoneal injection of 60 mg/kg sodium phenobarbital once daily for three days, then were fasted overnight and sacrificed by exsanguination from the abdominal aorta. The liver containing 0.15 M KCl (pH 7.4) was homogenized in 3 volumes of the same buffer. Microsomes were prepared according to the method of Omura and Sato.[S1] Microsomes contained 67.8 mg protein/mL and 1.82 nmol P450/mg protein. They were diluted with 0.1 M potassium phosphate buffer at pH 7.4 for assay and the final concentration was 226 μg/3 mL.

In vitro Assay with Rat Liver Microsomes

The hypoxic condition *in vitro* (enzyme assay in cuvette) was prepared by bubbling argon gas into the reaction solution (0.1 M potassium phosphate buffer (pH 7.4)) for 30 minutes. Rat liver microsomes (226 μg/3 mL) were preincubated at 37 °C for 5 min and then 1 μM probe containing 0.1% DMSO as a cosolvent was added. As a cofactor for reductases, 50 μM NADPH was added at 5 min.

Cell Lines and Culture Conditions

Human lung carcinoma cell line A549 were purchased from RIKEN Bioresource Center cell bank (Tsukuba, Japan). A549 cells were cultured in DMEM (Dulbecco's modified Eagle's medium) (Invitrogen) containing 10% fetal bovine serum (Invitrogen) and 1% penicillin streptomycin (Invitrogen). All cell lines were maintained at 37°C under 5% CO_2 in air (the standard conditions).

Hypoxic Conditions for Live Cell Fluorescence Imaging

An O_2 concentration of 0.1% was generated with an Anaero Pack® (Mitsubishi Gas Chemical Company, Inc.) and a 2.5 L rectangular jar (Mitsubishi Gas Chemical Company, Inc.). O_2 concentration in the range of 1–20% was controlled with a multi gas incubator (Sanyo) by means of N_2 substitution.

Fluorescence Confocal Microscopy

3 × 10^4 A549 cells were seeded on 8-chamber plates (NUNC™) and cultured for one day before assay. Cells were washed with PBS once, and then incubated in 200 μL DMEM containing 100 nM fluorescence probes and 0.1% DMSO as a cosolvent at various oxygen concentrations. Fluorescence confocal microscopic images were acquired by using a Leica Application Suite Advanced Fluorescence (LAS-AF) instrument with a TCS SP5 and a 63×, 40× or 10× objective lens. The light source was a white-light laser. The excitation and emission wavelengths were 640 and 660-750 nm for **2,6-diMe SiR640** and **azoSiR640**, respectively.

Inhibitor Assay with Diphenyliodonium Chloride

Diphenyliodonium chloride was purchased from Tokyo Chemical Industries and dissolved in MilliQ to make 20 mM stock solution. 3 × 10^4 A549 cells were seeded on 8-chamber plates and cultured for one day before assay. Cells in the presence or the absence of DPI (10 or 100 μM) were incubated under hypoxia (0.1% O_2 concentration) with 100 nM fluorescence probe for 6 hr. Cells were washed with PBS once, then taken up in 200 μL of PBS and images were obtained. An inverted microscope (IX 71, Olympus) equipped with a 20× objective lens (UPlan Apo 20×/0.70, Olympus) and an EM-CCD digital camera (C9000, Hamamatsu Photonics K.K.) was used to obtain fluorescence and DIC images. The fluorescence images were observed through a filter cube (Cy5 for azoSiR640, Olympus).

Fluorescence Confocal Microscopy of Cells under a Cover Glass

1.5 × 10^5 A549 cells were seeded on 35 mm poly-L-lysine-coated glass-bottomed dishes (Matsunami Glass Ind., Ltd.) and cultured for 2 days before assay. Cells were washed with PBS, then incubated in 1 mL DMEM containing 100 nM azoSiR640 containing 0.1% DMSO as a cosolvent. After incubation for 15 min, the cells were washed with PBS twice, and then a 13-mmdiameter cover glass (Matsunami Glass Ind., Ltd.) was gently placed on top of them. Fresh DMEM (2 mL) was then added and the culture was continued for 80 min under standard conditions. Fluorescence images were captured using a Leica Application Suita Advanced Fluorescence (LAS-AF) instrument with a Leica TCS SP5. The light source was a white-light laser. The excitation and emission wavelengths were 650 and 700-780 nm, respectively.

In vivo Imaging of Mice

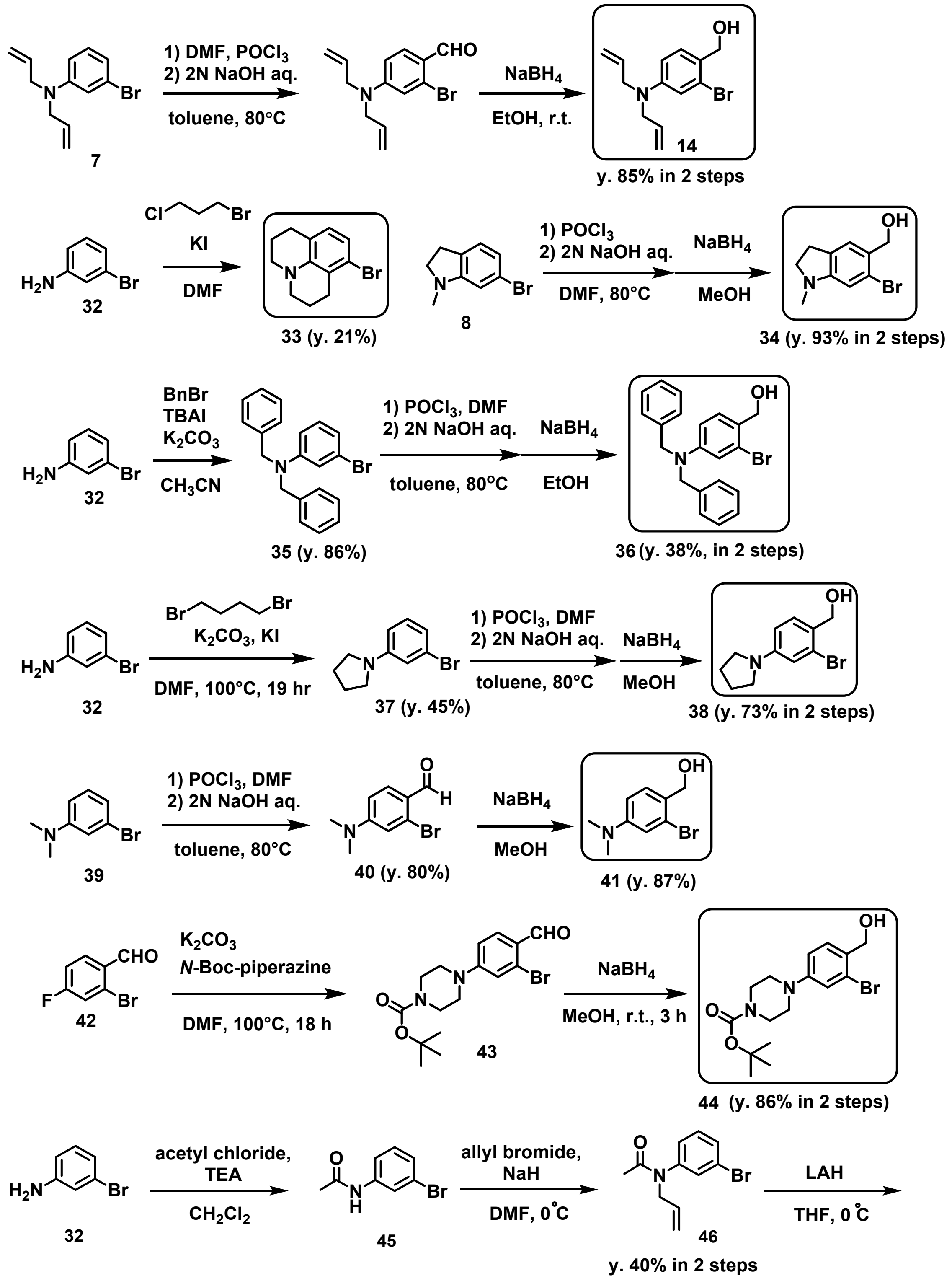
All procedures were approved by the Animal Care and Use Committee of the University of Tokyo. ICR mice (♂, 5 weeks) were anesthetized with Somnopentyl and azoSiR640 (100 μM in 100 μL saline solution) was administered through an orbital vein. Fluroescence images were taken for 32 min, then the portal vein and renal vein were ligated with clips at 36 min. Fluorescence images were taken for another 20 min. All animal experiments were conducted in accordance with institutional guidelines. Fluorescence images were captured with a Maestro In-vivo Imaging System (CRi Inc., Woburn, MA), with a red filter (Ex/Em = 616-661 nm / 675 nm L.P.).

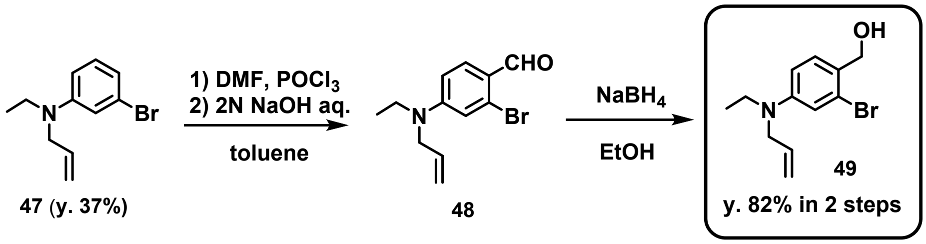
Computation Details

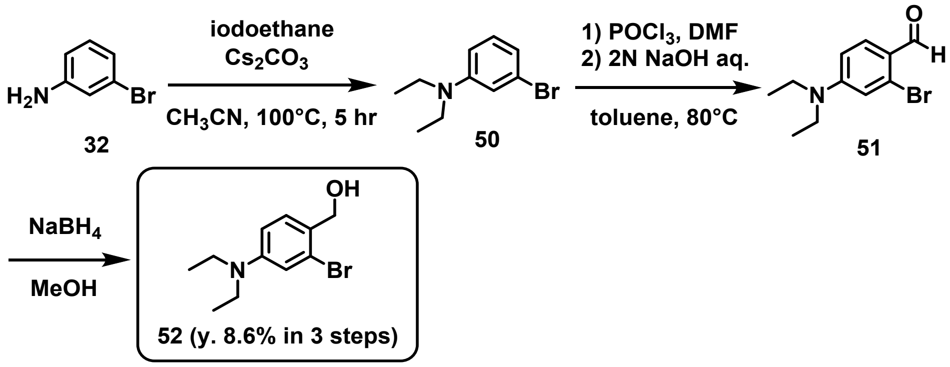
All density functional theory (DFT) calculations were performed at the B3LYP[S2-4] functional level as implemented in Gaussian 09[S5]. The 6-31+G(d) basis set was used for all atoms. The number of imaginary frequencies is 0 for all structures.

Synthesis and Characterization of Compounds

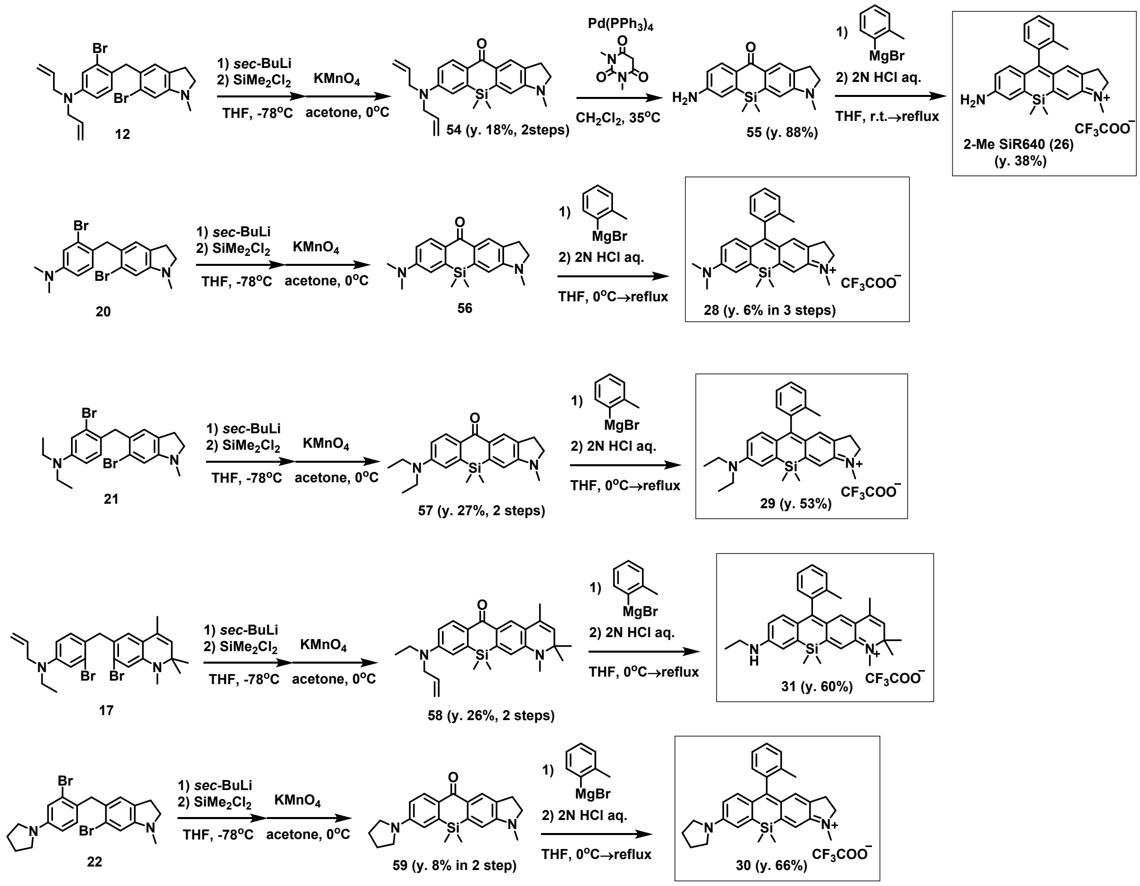
Scheme S1. Synthesis of anilines and hydroxymethylanilines.

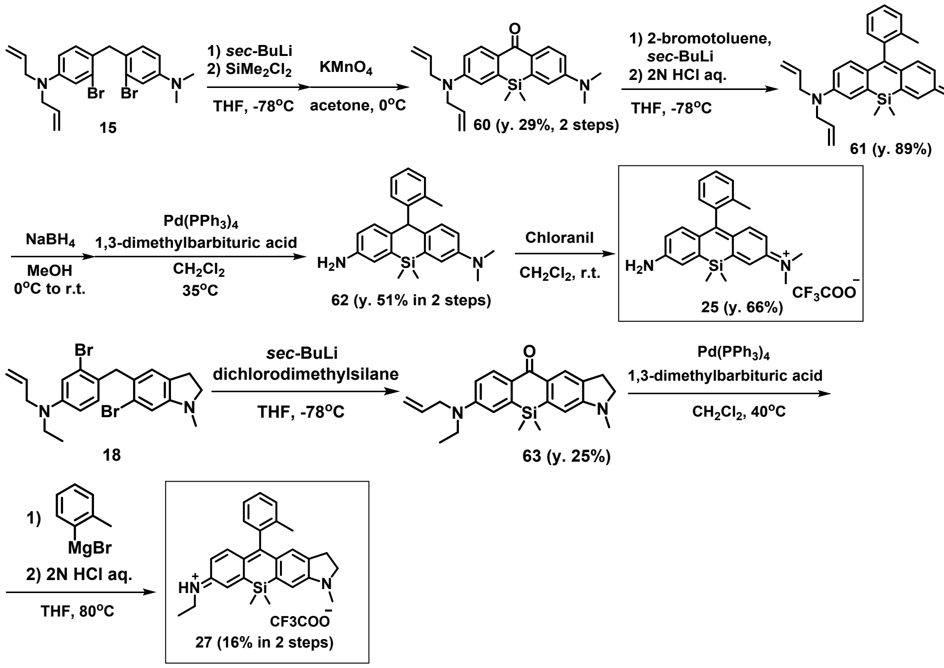




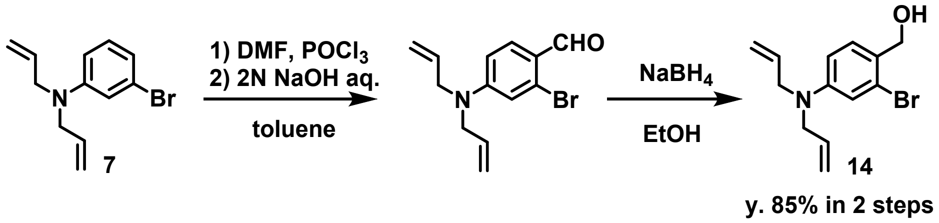


Scheme S2. Synthesis of unsymmetrical Si-rhodamines.

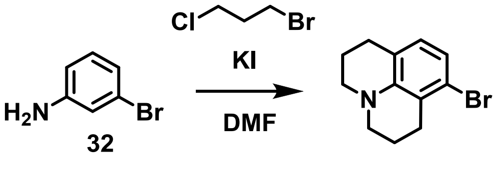




2-Me SiR600, 2-Me SiR650 and 2-Me SiR700 were prepared according to our previous reports.[S6,7]



To a solution of 3-bromo-*N*,*N*-diallylaniline[S6] (**7**) (1.21 g, 4.80 mmol) in toluene (20 mL) were added DMF (456 μL, 6.24 mmol) and phosphorus oxychloride (534 μL, 5.76 mmol) under an argon atmosphere. The reaction mixture was stirred for 21 hr at 80°C, then cooled in an ice bath, and an aqueous solution of 2 N NaOH was added. Stirring was continued for 5 minutes, and then the mixture was extracted with dichloromethane. The combined organic layer was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was taken up in ethanol (10 mL) and sodium borohydride (182 mg, 4.80 mmol), and the mixture was stirred for 1 hr at room temperature. The solvent was evaporated under reduced pressure, then water was added to the residue, and the mixture was extracted with dichloromethane. The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure to afford a residue, which was purified by column chromatography (silica gel, AcOEt/*n*-hexane) to afford **14** (1.15 g, 4.08 mmol, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.89-3.91 (m, 4H), 4.62 (d, *J* = 6.0 Hz, 2H), 5.12-5.19 (m, 4H), 5.76-5.88 (m, 2H), 6.60 (dd, *J* = 2.3, 8.6 Hz, 1H), 6.86 (d, *J* = 2.3 Hz, 1H), 7.20 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 52.7, 65.0, 111.3, 115.9, 116.3, 124.4, 127.0, 130.5, 133.0, 149.4; LRMS (ESI$^+$) 264 [M–OH]$^+$.

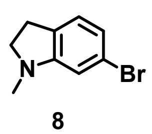


32

33 (y. 21%)

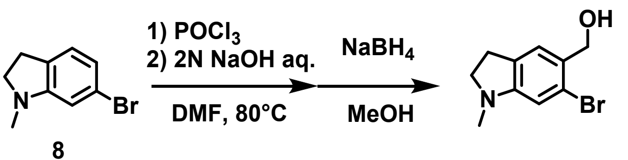
To a solution of 3-bromoaniline (**32**) (2 g, 11.6 mmol) in DMF (8 mL) was added KI (1.5 g, 9.3 mmol). The reaction mixture was stirred for 26 hr at 130°C. The mixture was concentrated *in vacuo* and H_2O was added to the residue. The aqueous layer was extracted with *n*-hexane. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, 10% AcOEt / *n*-hexane) and further purified by GPC to afford **33** (620 mg, 2.46 mmol, 21%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.90-2.01 (m, 4H), 2.69 (t, *J* = 6.6 Hz, 2H), 2.77 (t, *J* = 6.6 Hz, 2H), 3.08-3.15 (m, 4H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.8, 21.9, 27.6, 28.5, 49.7, 50.0, 119.4, 120.6, 120.7, 122.9, 127.7, 144.5; LRMS (ESI$^+$) 254 [M+H]$^+$.



8

Compound **8** was synthesized as reported previously.[S7]

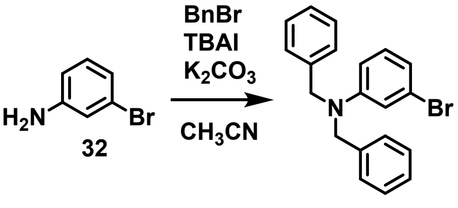


8

34 (y. 93% in 2 steps)

To a solution of 6-bromo-1-methylindoline (**8**) (212 mg, 1.00 mmol) in DMF (5 mL) was added phosphorus oxychloride (139 μL, 1.5 mmol) under an argon atmosphere. The reaction mixture was stirred for 14 hr at 80°C, then cooled in an ice bath, and an aqueous solution of 2 N NaOH was added. The mixture was stirred for 15 minutes, and then extracted with dichloromethane. The combined organic layer was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. Methanol (10 mL) and sodium borohydride (38 mg, 1.00 mmol) were added to the residue, and the mixture was stirred for 1 hr at room temperature, and then evaporated under reduced pressure. H_2O was added to the residue and the mixture was extracted with dichloromethane. The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, AcOEt/*n*-hexane) to afford **34** (224 mg, 0.926 mmol, 85%).

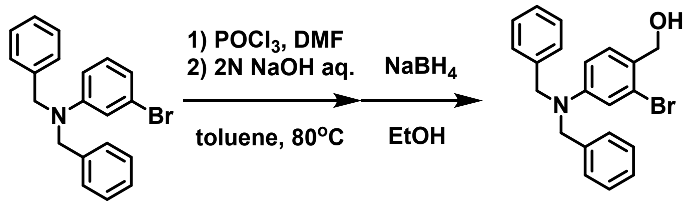
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.81 (t, *J* = 5.9 Hz, 1H), 2.74 (s, 3H), 2.90 (t, *J* = 8.0 Hz, 2H), 3.35 (t, *J* = 8.0 Hz, 2H),4.63 (d, *J* = 5.9 Hz, 2H), 6.60 (s, 1H), 7.10 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.1, 35.7, 56.1, 65.0, 110.6, 121.8, 125.3, 128.2, 130.0, 154.0; LRMS (ESI$^+$) 244 $[M+H]^+$.



35 (y. 86%)

To a solution of 3-bromoaniline (**32**) (2 g, 11.6 mmol) in CH_3CN (35 mL) were added K_2CO_3 (4 g, 29.0 mmol), benzyl bromide (3.45 mL, 29.1 mmol) and tetrabutylammonium iodide (429 mg, 1.16 mmol). The reaction mixture was stirred for 63 hr at 80°C. The mixture was concentrated *in vacuo* and H_2O was added to it. The aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, CH_2Cl_2/*n*-hexane) to afford **35** (3.54 g, 10.1 mmol, 21%).

^{1}H NMR (300 MHz, $CDCl_3$): 4.61 (s, 4H), 6.63 (dd, *J* = 8.3, 2.7 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.89 (s, 1H), 6.99 (t, *J* = 8.3 Hz, 1H), 7.20-7.36 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 54.0, 111.1, 115.1, 119.6, 123.5, 126.6, 127.1, 128.7, 130.4, 137.8, 150.5.

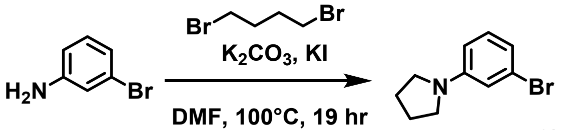


35

36 (y. 38%, in 2 steps)

To a solution of **35** (3.51 g, 9.97 mmol) in toluene (20 mL) were added DMF (946 μL, 13.0 mmol) and phosphorus oxychloride (1109 μL, 12.0 mmol) under an argon atmosphere. The reaction mixture was stirred for 15 hr at 80°C, then cooled in an ice bath, and an aqueous solution of 2 N NaOH was added. The mixture was stirred for 30 minutes, then extracted with dichloromethane. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated to dryness. Then, ethanol (20 mL) and sodium borohydride (379 mg, 9.97 mmol) were added to the residue. The mixture was stirred for 3 hr at room temperature and then evaporated to dryness under reduced pressure. H_2O was added to the residue and the mixture was extracted with dichloromethane. The organic layer was dried over Na_2SO_4, and evaporated to dryness under reduced pressure. The residue was purified by column chromatography (silica gel, AcOEt/*n*-hexane) to afford **36** (1.45 g, 3.79 mmol, 38%).

^{1}H NMR (300 MHz, $CDCl_3$): 4.58 (s, 2H), 4.60 (s, 4H), 6.63 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.94 (d, *J* = 2.5 Hz, 1H), 7.15 (d, *J* = 8.7 Hz, 1H), 7.18-7.34 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 54.0, 64.9, 111.5, 116.0, 124.5, 126.5, 127.0, 127.5, 128.7, 130.5, 137.6, 149.8; HRMS (ESI$^+$) Calcd for $[M+Na]^+$, 404.0626, Found, 404.0655 (+2.9 mmu).

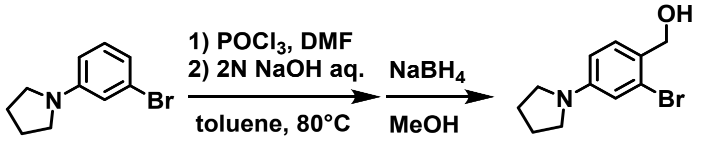


32

37 (y. 45%)

To a solution of 3-bromoaniline (**32**) (2.0 g, 11.6 mmol) in DMF (20 mL) were added K_2CO_3 (7.07 g, 51.2 mmol), 1,4-dibromobutane (2.76 g, 12.8 mmol) and KI (10 mg, 60.2 μmol). The reaction mixture was stirred for 19 hr at 100°C and then concentrated *in vacuo*. H_2O was added to the residue, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography (silica gel, CH_2Cl_2/*n*-hexane) to afford **37** (1.17 g, 5.18 mmol, 45%).

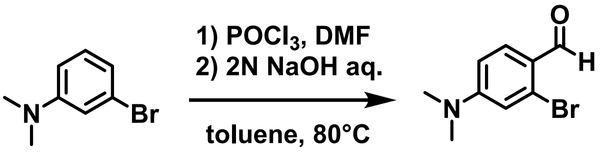
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.97-2.01 (m, 4H), 3.22-3.27 (m, 4H), 6.45 (dd, *J* = 8.0, 2.2 Hz, 1H), 6.67 (s, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 7.04 (t, *J* = 8.0 Hz, 1H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.4, 47.6, 110.2, 114.3, 118.0, 123.3, 130.3, 149.0; LRMS (ESI$^+$) 226 [M+H]$^+$.



37 **38 (y. 73% in 2 steps)**

To a solution of **37** (511 mg, 2.26 mmol) in toluene (6.0 mL) were added DMF (214 µL, 2.94 mmol) and phosphorus oxychloride (251 µL, 2.71 mmol) under an argon atmosphere. The reaction mixture was stirred for 14 hr at 80°C, then cooled in an ice bath, and an aqueous solution of 2 N NaOH was added. The mixture was stirred for 30 minutes, and then extracted with dichloromethane. The organic layer was washed with brine, dried over Na_2SO_4, and evaporated to dryness. Methanol (15 mL), CH_2Cl_2 (5 mL) and sodium borohydride (379 mg, 9.97 mmol) were added to the residue. The mixture was stirred for 6 hr at room temperature and then evaporated to dryness. H_2O was added to the residue and the mixture was extracted with dichloromethane. The organic layer was dried over Na_2SO_4, and evaporated to dryness. The residue was purified by column chromatography (silica gel, AcOEt/*n*-hexane) to afford **38** (421 mg, 1.64 mmol, 73%).

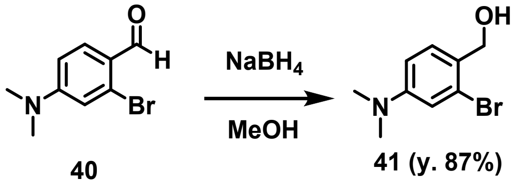
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.79 (t, *J* = 6.2 Hz, 1H), 1.98-2.03 (m, 4H), 3.24-3.28 (m, 4H), 4.64 (d, *J* = 6.2 Hz, 1H), 6.47 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.74 (d, *J* = 2.1 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 1H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.4, 47.6, 65.2, 110.8, 115.2, 124.5, 125.9, 130.6, 148.6; LRMS (ESI$^+$) 226 [M+H]$^+$.



39 **40 (y. 80%)**

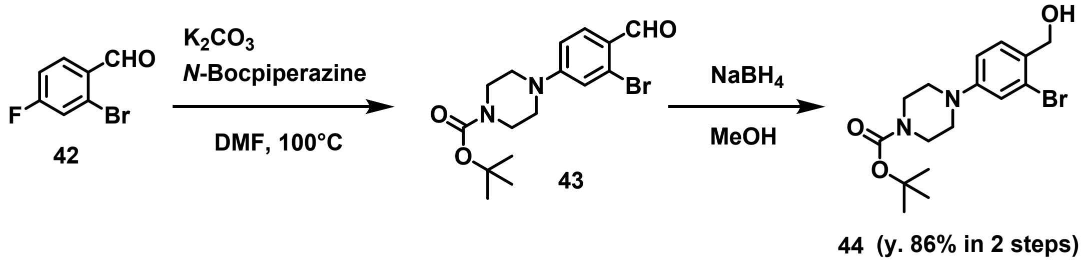
To a solution of 3-bromo-*N*,*N*-dimethylaniline (**39**) (516 mg, 2.58 mmol) in toluene (4 mL) were added DMF (245 µL, 3.35 mmol) and phosphorus oxychloride (287 µL, 3.10 mmol) under an argon atmosphere. The reaction mixture was stirred for 20 hr at 80°C, then 2 N NaOH aq. was added under cooling in a water bath. The mixture was stirred for 4 hr, and then extracted with dichloromethane. The organic solution was washed with brine, dried over Na_2SO_4, and evaporated, and the residue was purified by column chromatography (silica gel, AcOEt/*n*-hexane) to obtain **40** (470 mg, 2.06 mmol, 80%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 3.08 (s, 6H), 6.64 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.80 (d, *J* = 2.7 Hz, 1H), 7.80 (d, *J* = 9.0 Hz), 10.09 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.0, 110.5, 114.8, 122.0, 129.7, 131.0, 154.5, 190.1; HRMS (ESI$^+$) Calcd for $[M+H]^+$, 228.0024, Found, 228.0027 (+0.3 mmu).



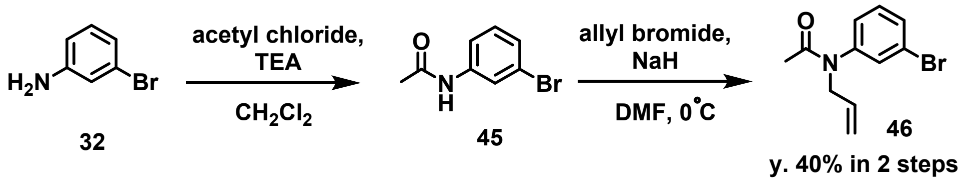
To a solution of **40** (433 mg, 1.90 mmol) in methanol (6.0 mL) was added sodium borohydride (74 mg, 1.90 mmol). The reaction mixture was stirred for 2 hr at room temperature and then concentrated *in vacuo*. H_2O was added to the residue, and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography (silica gel, AcOEt/*n*-hexane) to afford **41** (412 mg, 1.79 mmol, 87%).

^{1}H NMR (300 MHz, CD_2Cl_2): δ 2.93 (s, 6H), 4.60 (d, *J* = 6.6 Hz, 1H), 6.65 (dd, *J* = 8.1, 3.0 Hz, 1H), 6.89 (d, *J* = 3.0 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 1H) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.4, 65.0, 111.4, 116.0, 124.4, 127.0, 130.4, 151.1; HRMS (ESI$^+$) Calcd for $[M+H]^+$, 230.0181, Found, 230.0162 (–1.9 mmu).



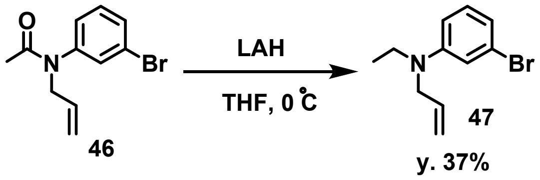
To a solution of 2-bromo-4-fluorobenzaldehyde (**42**) (2.41 g, 12.9 mmol) in DMF (30 mL) were added *N*-Boc-piperazine (2.19 g, 10.8 mmol) and K_2CO_3 (2.24 g, 16.2 mmol). The reaction mixture was stirred for 18 hr at 100°C, diluted with $NaHCO_3$ aq., and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4 and evaporated to dryness. The residue (crude **43**) was dissolved in methanol (30 mL) and sodium borohydride (494 mg, 13 mmol) was added to it. The reaction mixture was stirred for 3 hr at room temperature and then evaporated to dryness. H_2O was added to the residue and the mixture was extracted with dichloromethane. The organic layer was dried over Na_2SO_4, and evaporated to dryness. The residue was purified by column chromatography (NH silica gel, AcOEt / *n*-hexane) to afford **44** (3.46 g, 9.33 mmol, 86%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48 (s, 9H), 2.02 (t, *J* = 6.6 Hz, 1H), 3.13 (t, *J* = 5.1 Hz, 4H), 3.56 (t, *J* = 5.1 Hz, 4H), 4.66 (d, *J* = 6.6 Hz, 2H), 6.85 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.08 (d, *J* = 2.1 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.4, 48.9, 64.8, 80.1, 115.4, 120.1, 123.9, 130.0, 130.9, 151.8, 154.6; LRMS (ESI$^+$) 371 [M+H]$^+$.



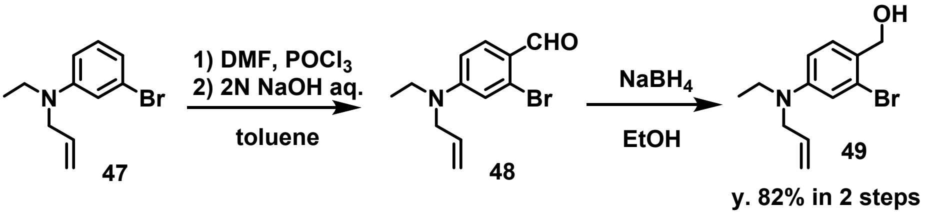
3-Bromoaniline (**32**) (4.3g, 25.0 mmol) was dissolved in CH_2Cl_2 (50 mL), and acetyl chloride (2.4 g, 30 mmol) was added to the solution. TEA (10 mL) was added dropwise, and the mixture was stirred for 3 hr. The reaction was quenched by adding H_2O, and the whole was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue (crude **45**) was dissolved in DMF (30 mL) and NaH (1.2 g, 50.0 mmol) was added to it. The mixture was stirred for 15 min at 0ºC. At the same temperature, allyl bromide (6.0g, 4.6 mL) was added, and stirring was continued for 2 hr. The reaction was quenched by adding H_2O, and the whole was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. Purification of the residue by column chromatography (silica, CH_2Cl_2/hexane = 1/1) provided *N*-allyl-3-bromoacetoanilide (**46**) (2.5 g, 9.84 mmol, 39%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.89 (s, 3H), 4.28 (d, *J* = 5.7 Hz, 2H), 5.10-1.15 (m, 2H), 5.80-5.89 (m, 1H), 7.15 (d, *J* = 7.2 HZ, 1H), 7.29 (t, *J* = 8.1 Hz, 1H), 7.36 (s, 1H), 7.48 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.6, 51.9, 118.1, 122.6, 126.6, 130.7, 131.0, 131.1, 132.7, 144.1, 169.6; LRMS (ESI$^+$) 254 [M+H]$^+$.



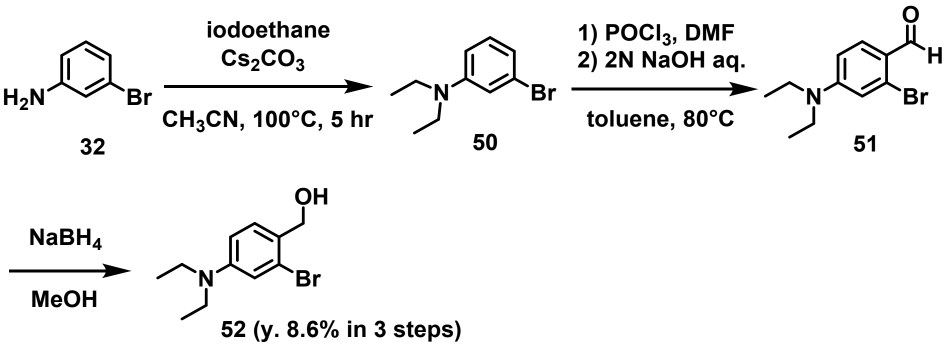
Compound **46** (2.5 g, 10 mmol) was dissolved in THF (30 mL) and lithium aluminium hydride (760 mg, 20 mmol) was added to the solution. The mixture was stirred for 4 hr, then the reaction was quenched by adding sat. potassium sodium tartrate aq. The whole was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. Purification of the residue by column chromatography (silica gel, CH_2Cl_2) provided **47** (880 mg, 3.66 mmol, 37 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.57 (t, *J* = 7.20 Hz, 3H), 3.35 (q, *J* = 7.2 Hz, 2H), 3.85-3.87 (m, 2H), 5.12-5.18 (m, 2H), 5.76-5.86 (m, 1H), 6.57 (dd, *J* = 2.1, 8.1 Hz 1H), 6.74-6.79 (m, 2H), 7.02 (d, *J* =7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.2, 44.8, 52.5, 110.5, 114.6, 116.0, 118.5, 123.4, 130.3, 133.6, 149.4; HRMS (ESI$^+$) Calcd for $[M+H]^+$, 240.0388, Found, 240.0387 (–0.1 mmu).



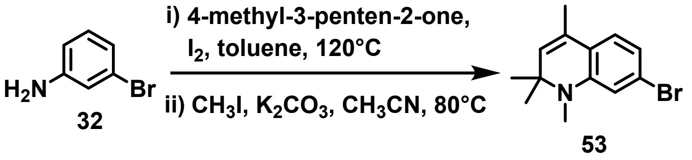
Compound **47** (750 mg, 2.95 mmol), DMF (297 mg, 4.1 mmol) and $POCl_3$ (576 mg, 3.8 mmol) were dissolved in toluene (20 mL), and the mixture was heated to 60°C and stirred for 2 hr. It was then cooled to r.t. and 2 N NaOH was added to it. Stirring was continued for 30 min, and then the mixture was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue (crude **48**) was dissolved in EtOH (20 mL) and cooled to 0°C. $NaBH_4$ (119 mg, 3.1 mmol) was added, and the mixture was stirred for 30 min. The reaction was quenched by adding H_2O, and the whole was extracted with CH_2Cl_2.The organic layer was dried over Na_2SO_4 and evaporated to dryness. Purification of the residue by column chromatography (silica gel, AcOEt/hexane = 3/7) provided **49** (693 mg, 2.44 mmol, 83%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.88 t, *J* = 7.5 Hz, 3H), 3.38 (q, *J* =7.5 Hz, 2H), 4.62 (d, *J* = 5.1 Hz, 2H), 5.12-5.18 (m, 2H), 5.77-5.86 (m, 2H), 6.60 (d, *J* = 8.1 Hz, 1H), 6.85 (d, *J* = 4.5 Hz, 1H), 7.20 (dd, *J* = 4.5, 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.2, 44.9, 52.5, 65.0, 111.1, 115.5, 116.1, 124.6, 126.4, 130.6, 133.4, 148.9; HRMS (ESI$^+$) Calcd for $[M+H]^+$, 270.0494, Found, 270.0510 (+1.6 mmu).

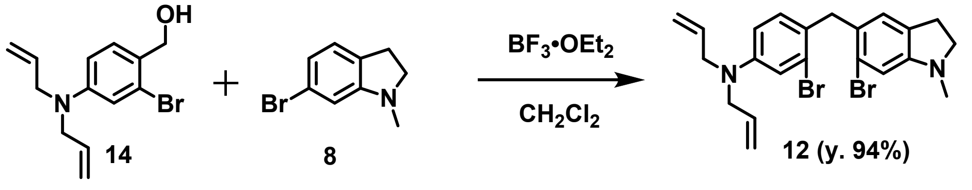


3-Bromoaniline (**32**) (1.70 g, 10.0 mmol), iodoethane (7.75 g, 50.0 mmol) and Cs_2CO_3 (16.3 g, 50.0 mol) were dissolved in CH_3CN (20 mL), and the mixture was refluxed at 100°C for 5 hr. H_2O was added to it, and the whole was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. Partial purification of the residue by column chromatography (silica gel, CH_2Cl_2/hexane = 2/8) provided crude **50**. Compound **50**, DMF (2.0 mL) and $POCl_3$ (2.0 mL) were dissolved in toluene (40 mL), and the mixture was heated to 60°C and stirred overnight. The mixture was cooled to r.t., 2 N NaOH was added to it, and stirring was continued for 30 min, followed by extraction with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue (crude **51**) was dissolved in MeOH (50 mL). The solution was cooled to 0°C, then $NaBH_4$ (227 mg, 5.97 mmol) was added to it, and the mixture was stirred for 30 min. The reaction was quenched by adding H_2O, and the whole was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. Purification of the residue by column chromatography (silica gel, AcOEt/hexane = 3/7) provided **52** (220 mg, 8.6%).

^1H NMR (300 MHz, $CDCl_3$): δ 1.14 (t, J = 7.2 Hz, 6H), 2.06 (t, J = 6.0 hz, 1H), 3.32 (q, J = 7.2 Hz, 4H), 4.50 (d, J = 6.0 Hz, 2H), 6.56 (dd, J = 2.1, 7.5 Hz, 1H), 6.82 (d, J = 2.1 Hz, 1H), 7.20 (d, J = 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.4, 44.3, 64.9, 110.7, 115.1, 124.7, 125.9, 130.6, 148.4; HRMS (ESI$^+$) Calcd for $[M+H]^+$, 258.0494, Found, 258.0497 (+0.3 mmu).

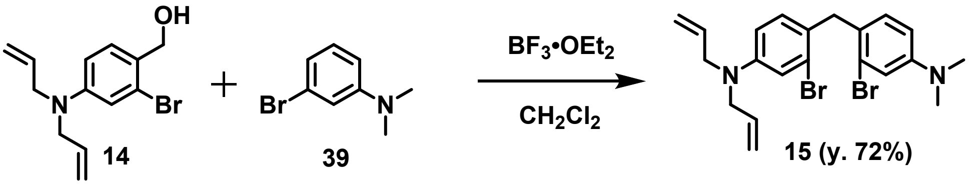


Compound **53** was synthesized as reported previously.[S7]



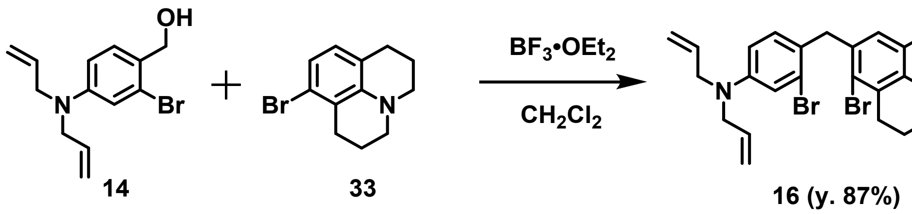
To a solution of **14** (73 mg, 0.260 mmol) and **8** (55 mg, 0.260 mmol) in CH_2Cl_2 (5 mL) was added $BF_3{\cdot}OEt_2$ (65 μL, 0.520 mmol). The reaction mixture was stirred for 24 hr at room temperature, diluted with water and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography (silica gel, CH_2Cl_2/*n*-hexane) to afford **12** (116 mg, 0.244 mmol, 94%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.73 (s, 3H), 2.83 (t, *J* = 8.1 Hz, 2H), 3.28 (t, *J* = 8.1 Hz, 2H), 3.87-3.88 (m, 4H), 3.97 (s, 2H), 5.14-5.20 (m, 4H), 5.76-5.89 (m, 2H), 6.64 (dd, *J* = 2.5, 8.2 Hz, 1H), 6.65 (s, 1H), 6.73 (s, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.90 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.4, 36.0, 40.1, 52.7, 56.3, 110.9, 111.6, 115.9, 116.3, 123.1, 125.5, 126.1, 127.1, 128.1, 130.2, 130.7, 133.5, 148.1, 153.0; LRMS (ESI$^+$) 477 $[M+H]^+$.



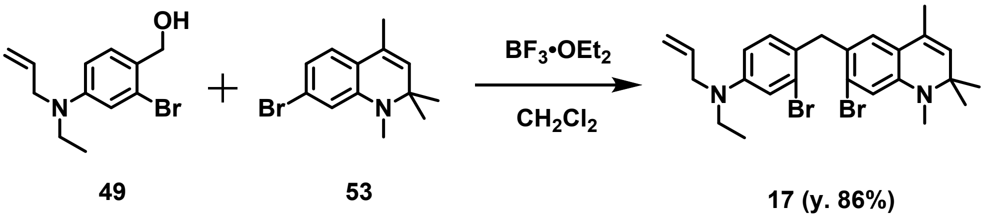
To a solution of **14** (18.1 mg, 64.4 μmol) and **39** (14.5 mg, 72.5 μmol) in CH_2Cl_2 (5 mL) was added $BF_3{\cdot}OEt_2$ (16 μL, 129 μmol). The reaction mixture was stirred for 8 hr at 37°C, diluted with water, and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography (silica gel, AcOEt/*n*-hexane) to afford **15** (21.5 mg, 46.3 μmol, 72%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.91 (s, 6H), 3.86-3.88 (m, 4H), 3.98 (s, 2H), 5.14-5.19 (m, 4H), 5.76-5.89 (m, 2H), 6.54 (dd, *J* = 2.5, 8.8 Hz, 1H), 6.59 (dd, *J* = 2.4, 8.5 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.90 (d, *J* = 2.5 Hz, 1H), 6.93 (d, *J* = 2.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 39.8, 40.5, 52.7, 111.7, 111.8, 116.0, 116.2, 125.5, 125.6, 126.9, 127.1, 130.7, 130.8, 133.5, 148.1, 150.0; LRMS (ESI$^+$) 465 $[M+H]^+$.



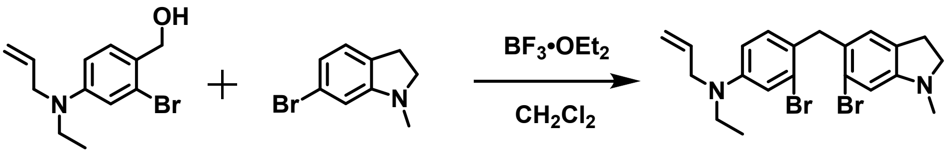
To a solution of **14** (25 mg, 89.0 μmol) and **33** (22 mg, 89.0 μmol) in CH_2Cl_2 (8 mL) was added $BF_3 \cdot OEt_2$ (22 μL, 178 μmol). The reaction mixture was stirred for 3 hr at room temperature, then diluted with water and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4. The solvent was evaporated to dryness, and the residue was purified by column chromatography (silica gel, CH_2Cl_2/*n*-hexane) to afford **16** (40 mg, 77.5 μmol, 87%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.89-2.03 (m, 4H), 2.64 (t, *J* = 6.6 Hz, 2H), 2.82 (t, *J* = 6.6 Hz, 2H), 3.05-3.12 (m, 4H), 3.86-3.88 (m, 4H), 3.95 (s, 2H), 5.14-5.19 (m, 4H), 5.76-5.89 (m, 2H), 6.49 (s, 1H), 6.54 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.79 (d, *J* = 9.0 Hz, 1H), 6.90 (d, *J* = 3.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.0, 22.3, 27.5, 29.4, 40.9, 49.6, 50.1, 52.8, 111.7, 116.0, 116.3, 120.8, 121.3, 125.6, 125.6, 127.0, 127.3, 128.6, 128.7, 130.7, 133.7, 143.0, 148.1; HRMS (ESI$^+$) Calcd for $[M+H]^+$, 515.0698 Found, 515.0712 (+1.5 mmu).



Compounds **49** (375 mg, 1.38 mmol) and **53** (795 mg, 3 mmol) were dissolved in CH_2Cl_2 (20 mL). $BF_3 \cdot OEt_2$ (391 mg, 346 μL, 2.76 mmol) was added, and the solution was stirred at r.t. for 23 hr. The reaction was quenched by adding H_2O, and the whole was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. Purification of the residue by column chromatography (silica gel, AcOEt/hexane = 1/9) provided **17** (614 mg, 86%).

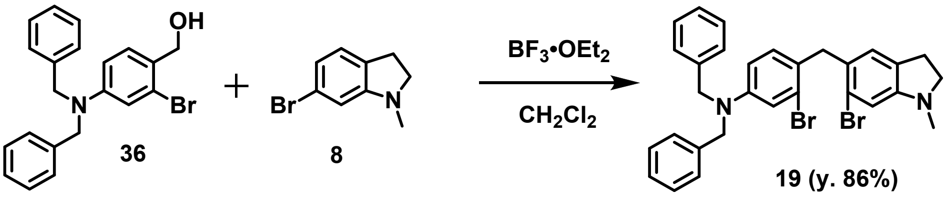
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.14 (t, *J* = 6.6 Hz, 3H), 1.29 (s, 6H), 1.86 (s, 3H), 2.77 (s, 3H), 3.32 (q, *J* = 6.6 Hz, 2H), 3.80-3.84 (m, 2H), 3.96 (s, 2H), 5.11-5.17 (m, 2H), 5.28 (s, 1H), 5.75-5.90 (m, 1H), 6.50 (dd, *J* = 2.1, 6.6 Hz, 1H), 6.69-6.89 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.2, 18.4, 27.2, 30.7, 39.9, 44.8, 52.6, 56.4, 113.4, 114.3, 115.7, 116.0, 122.8, 124.8, 125.5, 125.6, 126.4, 126.5, 127.6, 130.4, 130.5, 134.0, 144.7, 147.6; HRMS (ESI$^+$): Calcd for $[M+H]^+$, 519.0833; found, 519.0878 (+4.4 mmu).



49 8 18 (y. 70%)

Compounds **49** (693 mg, 2.6 mmol) and **8** (542 mg, 5.1 mmol) were dissolved in CH_2Cl_2 (20 mL). $BF_3\cdot OEt_2$ (623 μL, 5.0 mmol) was added, and the solution was stirred at r.t. for 23 hr. The reaction was quenched by adding H_2O, and the whole was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. Purification of the residue by column chromatography (silica gel, AcOEt/hexane = 1/9) provided **18** (825 mg, 1.78 mmol, 70 %).

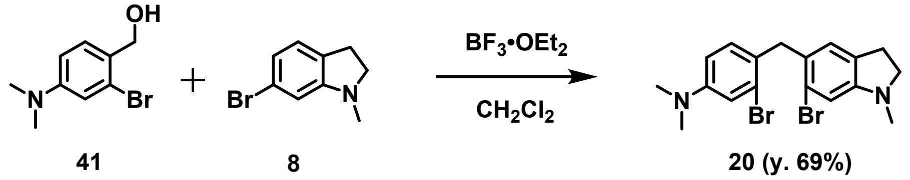
^{1}H NMR (300 MHz, $CDCl_3$): δ 1.15 (t, J = 6.6 Hz, 3H), 2.72 (s, 3H), 2.82 (t, J = 8.1 Hz, 2H), 3.28 (t, J = 8.1 Hz, 2H), 3.33 (q, J = 6.6 Hz, 2H), 3.84-3.85 (m, 2H), 3.97 (s, 2H), 5.13-5.19 (m, 2H), 5.78-5.88 (m, 1H), 6.53 (dd, J = 3.0, 8.1 Hz, 1H), 6.65 (s, 1H), 6.73 (s, 1H), 6.80 (d, J = 8.1 Hz, 1H), 6.88 (d, J = 3.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 12.2, 28.4, 36.0, 40.1, 44.8, 52.6, 56.3, 110.9, 111.4, 115.6, 116.0, 123.0, 125.7, 126.1, 126.5, 128.1, 130.2, 130.8, 134.0, 147.7, 153.0; HRMS (ESI$^+$): Calcd for $[M+H]^+$, 465.0364; found, 465.0380 (+1.6 mmu).



36 8 19 (y. 86%)

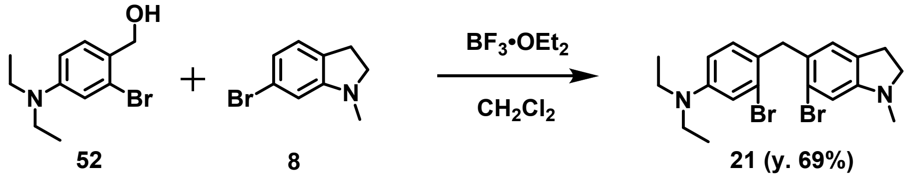
To a solution of **36** (40 mg, 105 μmol) and **8** (22 mg, 105 μmol) in CH_2Cl_2 (8 mL) was added $BF_3\cdot OEt_2$ (27 μL, 210 μmol). The reaction mixture was stirred for 17 hr at room temperature, diluted with water and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by GPC to afford **19** (52 mg, 90.2 μmol, 86%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.72 (s, 3H), 2.83 (t, J = 8.1 Hz, 2H), 3.28 (t, J = 8.1 Hz, 2H), 3.96 (s, 2H), 4.59 (s, 4H), 6.56 (dd, J = 8.7, 2.7 Hz, 1H), 6.63 (s, 1H), 6.74-6.77 (m, 2H), 6.98 (d, J = 2.7 Hz, 1H), 7.20-7.35 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.3, 36.0, 40.1, 54.1, 56.2, 110.8, 111.9, 116.0, 123.1, 125.6, 126.2, 126.7, 127.0, 127.7, 128.7, 130.2, 130.7, 138.1, 148.7, 153.1; HRMS (ESI$^+$) Calcd for $[M+H]^+$, 577.0677, Found, 577.0678 (+0.1 mmu).



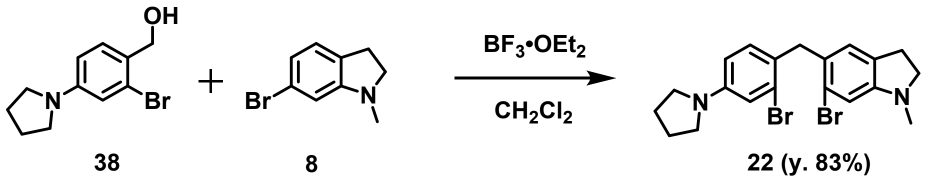
To a solution of **41** (25 mg, 109 μmol) and **8** (23 mg, 109 μmol) in CH_2Cl_2 (6 mL) was added $BF_3{\cdot}OEt_2$ (28 μL, 218 μmol). The reaction mixture was stirred for 17.5 hr at room temperature, diluted with water and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography (silica gel, AcOEt/*n*-hexane) to afford **20** (32 mg, 75.5 μmol, 69%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 2.73 (s, 3H), 2.81 (t, *J* = 8.1 Hz, 2H), 2.91 (s, 6H), 3.28 (t, *J* = 8.1 Hz, 2H), 3.98 (s, 2H), 6.59 (dd, *J* = 8.8, 2.2 Hz, 1H), 6.65 (s, 1H), 6.70 (s, 1H), 6.86 (d, *J* = 2.2 Hz, 1H), 6.93 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.3, 36.0, 40.2, 40.5, 56.3, 110.9, 111.8, 116.2, 123.0, 125.6, 126.0, 127.2, 128.1, 130.1, 130.7, 145.0, 153.0; HRMS (ESI$^+$) Calcd for $[M+H]^+$, 425.0051, Found, 425.0022 (–2.9 mmu).



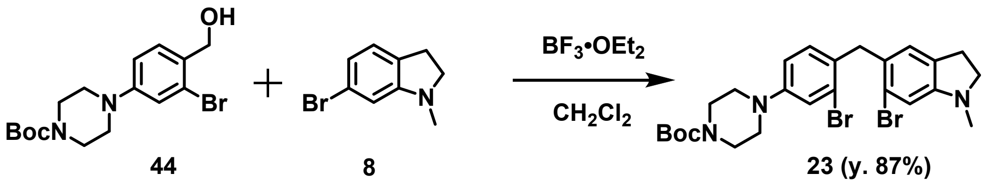
Compound **52** (220 mg, 0.86 mmol) and 6-bromo-1-methylindoline (**8**) (235 mg, 1.11 mmol) were dissolved in CH_2Cl_2 (20 mL). $BF_3{\cdot}OEt_2$ (130 μL, 1.1 mmol) was added, and the solution was stirred r.t. for 23 hr. The reaction was quenched by adding H_2O, and the whole was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. Purification of the residue by column chromatography (silica gel, AcOEt/hexane = 1/9) provided **21** (284 mg, 72%).

^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.05 (t, *J* = 8.4 Hz, 6H), 2.63 (s, 3H), 2.73 (t, *J* = 8.7 Hz, 2H), 3.17-3.26 (m, 5H), 3.85 (s, 2H), 6.44 (dd, *J* = 3.0, 8.1 Hz, 1H), 6.55 (s, 1H), 6.63 (s, 1H), 6.72 (d, *J* = 8.1 Hz, 1H), 6.78 (d, *J* = 3.0 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ 12.7, 28.7, 36.2, 40.5, 44.7, 56.6, 111.0, 111.5, 115.6, 123.2, 126.0, 126.2, 126.4, 128.4, 130.8, 131.3, 147.9, 153.7; HRMS (ESI$^+$) Calcd for [M+H]$^+$, 451.0385, Found, 451.0373 (–1.2 mmu).



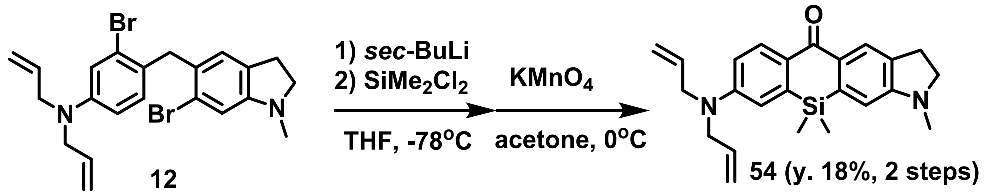
To a solution of **38** (39 mg, 152 µmol) and **8** (32 mg, 152 µmol) in CH_2Cl_2 (10 mL) was added BF_3· OEt_2 (38 µL, 304 µmol). The reaction mixture was stirred for 13 hr at room temperature, diluted with water, and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography (silica gel, CH_2Cl_2/*n*-hexane) to afford **22** (57.1 mg, 127 µmol, 83%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.96-2.01 (m, 4H), 2.72 (s, 3H), 2.81 (t, *J* = 8.0 Hz, 2H), 3.22-3.30 (m, 6H), 3.98 (s, 2H), 6.42 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.65 (s, 1H), 6.69 (s, 1H), 6.78 (d, *J* = 2.1 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.4, 28.3, 36.0, 40.2, 47.6, 56.3, 110.8, 111.0, 115.1, 123.0, 125.6, 125.9, 126.0, 128.3, 130.1, 130.9, 147.3, 152.9; HRMS (ESI$^+$) Calcd for [M+H]$^+$, 451.0208, Found, 451.0222 (+1.4 mmu).



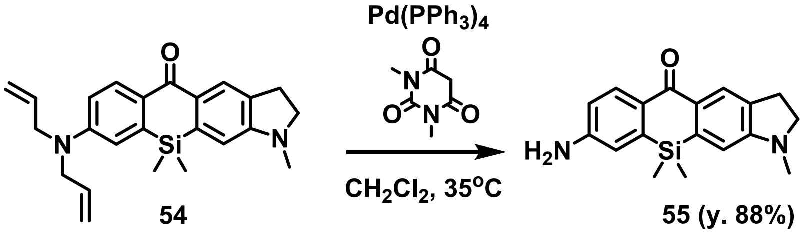
To a solution of **44** (41 mg, 110 µmol) and **8** (23 mg, 108 µmol) in CH_2Cl_2 (5 mL) was added BF_3· OEt_2 (28 µL, 220 µmol). The reaction mixture was stirred for 6 hr at room temperature, diluted with water and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography (silica gel, AcOEt/*n*-hexane) to afford **23** (53 mg, 93.7 µmol, 87%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48 (s, 9H), 2.73 (s, 3H), 2.82 (t, *J* = 8.1 Hz, 2H), 3.10 (t, *J* = 5.1 Hz, 4H), 3.30 (t, *J* = 8.1 Hz, 2H), 3.56 (t, *J* = 5.1 Hz, 4H), 4.00 (s, 2H), 6.65 (s, 1H), 6.70 (s, 1H), 6.77 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.88 (d, *J* = 8.7 Hz, 1H), 7.13 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.3, 28.4, 36.0, 40.4, 49.1, 56.2, 80.0, 110.8, 115.6, 120.3, 123.1, 125.4, 126.1, 127.5, 130.2, 130.8, 131.2, 150.5, 153.1, 154.7; HRMS (ESI$^+$) Calcd for $[M+H]^+$, 566.0841, Found, 566.0850 (+0.9 mmu).



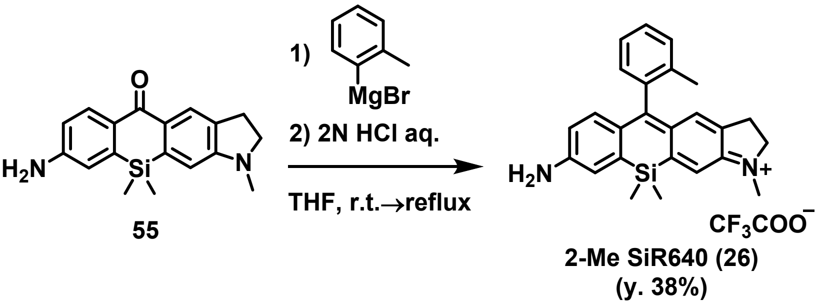
To a solution of **12** (207 mg, 0.434 mmol) in anhydrous THF (10 mL) was added 1 M THF solution of *sec*-BuLi (0.91 mL, 0.91 mmol) at –78 °C under an argon atmosphere. The reaction mixture was stirred for 20 min at the same temperature, and then dichlorodimethylsilane (112 mg, 0.868 mmol) in anhydrous THF (5 mL) was added. The mixture was warmed to room temperature and stirred for 1 hr, and 2 N HCl aq. was added to quench the reaction. The mixture was neutralized with $NaHCO_3$ aq. and extracted with CH_2Cl_2. The organic layer was collected, washed with brine, dried over Na_2SO_4 and evaporated to dryness. The residue was dissolved in acetone (30 mL) at 0°C and $KMnO_4$ (275 mg, 1.74 mmol) was added in small portions over 3 hr with stirring at the same temperature. Then the mixture was filtered through a Celite filter and the solution was evaporated to dryness. The residue was purified by column chromatography (silica gel, AcOEt/*n*-hexane) to afford **54** (30 mg, 77.3 μmol, 18%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.43 (s, 6H), 2.90 (s, 3H), 3.05 (t, J = 8.5 Hz, 2H), 3.47 (t, J = 8.5 Hz, 2H), 4.02-4.03 (m, 4H), 5.18-5.23 (m, 4H), 5.82-5.94 (m, 2H), 6.50 (s, 1H), 6.80-6.86 (m, 2H), 8.21 (s, 1H), 8.34 (d, J = 9.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –1.2, 28.0, 34.6, 52.7, 54.8, 107.9, 107.9, 113.4, 114.7, 116.5, 120.4, 126.0, 130.0, 131.5, 131.6, 132.1, 133.0, 140.1, 140.3, 150.0, 154.8, 185.1; HRMS (ESI$^+$) Calcd for $[M+H]^+$, 389.2049 Found, 389.2069 (+2.0 mmu).



To a solution of **54** (506 mg, 1.30 mmol) in CH_2Cl_2 (20 ml) were added 1,3-dimethylbarbituric acid (406 mg, 2.60 mmol) and $Pd(PPh_3)_4$ (225 mg, 0.145 mmol) under an argon atmosphere. The reaction mixture was stirred for 19 hr at 35°C. The reaction was quenched with sat. $NaHCO_3$ aq., and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with sat. $NaHCO_3$ aq. and brine, dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, AcOEt/CH_2Cl_2) to afford **55** (354 mg, 1.15 mmol, 88%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.43 (s, 6H), 2.90 (s, 3H), 3.04 (t, *J* = 8.2 Hz, 2H), 3.47 (t, *J* = 8.2 Hz, 2H), 6.49 (s, 1H), 6.76-6.82 (m, 2H), 8.20 (s, 1H), 8.31 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –1.3, 28.0, 34.4, 54.7, 107.8, 107.8, 116.1, 117.5, 126.1, 131.2, 131.8, 132.2, 140.1, 140.8, 148.8, 154.9, 185.1; HRMS (ESI$^+$) Calcd for $[M+H]^+$, 309.1423 Found, 389.1426 (+0.3 mmu).

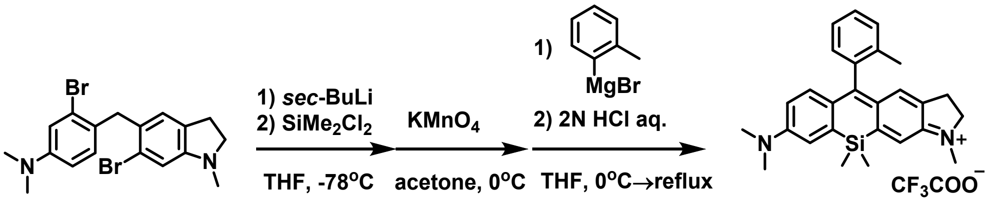


55

2-Me SiR640 (26)
(y. 38%)

To a solution of **55** (8.7 mg, 28.2 μmol) in anhydrous THF (5 mL) was added a 1 M THF solution of *o*-tolylmagnesium bromide (2.8 mL, 2.82 mmol), and the mixture was refluxed at 80°C for 2 hr under an argon atmosphere. It was cooled to room temperature, and 2 N HCl aq. was added to it. The mixture was diluted with sat. $NaHCO_3$ aq. and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by HPLC (eluent, 48% CH_3CN/0.1% TFA aq. (0 min) to 56% CH_3CN/0.1% TFA aq. (20 min); flow rate = 5.0 mL/min) to afford 2-Me SiR640 (**26**) (5.3 mg, 10.7 μmol, 38%).

^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.54 (s, 3H), 0.56 (s, 3H). 2.03 (s, 3H), 2.96 (t, *J* = 8.0 Hz, 2H), 3.21 (s, 3H), 3.83 (t, *J* = 8.0 Hz, 2H), 6.58 (d, *J* = 8.7 Hz, 1H), 6.79 (s, 1H), 6.91 (s, 1H), 6.95 (d, *J* = 8.7 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.29-7.43 (m, 4H)); ^{13}C NMR (100 MHz, CD_3OD) δ –1.6, -1.3, 19.4, 26.8, 33.9, 56.0, 116.3, 117.1, 123.4, 126.9, 128.6, 129.8, 129.9, 130.1, 131.3, 134.5, 135.4, 136.9, 140.7, 141.8, 147.8, 154.5, 156.6, 159.6, 168.6; HRMS (ESI$^+$) Calcd for [M+H]$^+$, 383.1944 Found, 383.1940 (–0.4 mmu).

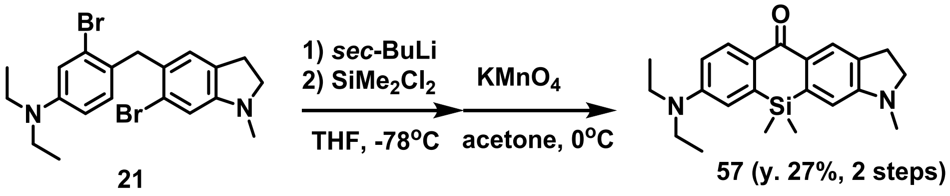


20

28 (y. 6% in 3 steps)

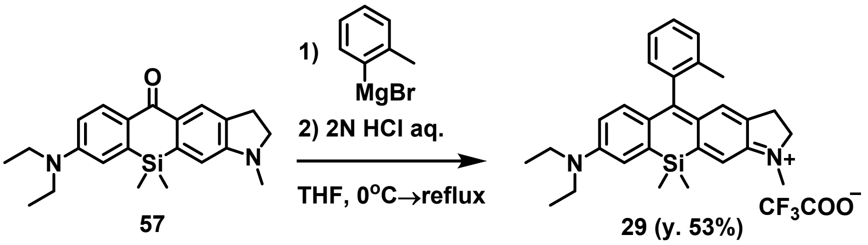
To a solution of **20** (354 mg, 0.835 mmol) in anhydrous THF (20 mL) was added a 1 M THF solution of *sec*-BuLi (1.7 mL, 1.7 mmol) at –78 °C under an argon atmosphere. The reaction mixture was stirred for 30 min at the same temperature, then dichlorodimethylsilane (118 µL, 1.02 mmol) in anhydrous THF (3 mL) was added to it. The mixture was warmed to room temperature and stirred for 5 hr. Then 2 N HCl aq. was added to quench the reaction, and the mixture was neutralized with NaHCO$_3$ aq. and extracted with CH$_2$Cl$_2$. The organic layer was collected, washed with brine, dried over Na$_2$SO$_4$ and evaporated to dryness. The residue was dissolved in acetone (30 mL) at 0°C and KMnO$_4$ (196 mg, 1.25 mmol) was added in small portions over 3 hr with stirring at the same temperature. Then the mixture was filtered through a Celite filter and the filtrate was evaporated to dryness. The residue was purified by column chromatography (silica gel, AcOEt/*n*-hexane) and GPC. The residue (crude **56**) was dissolved in anhydrous THF (10 mL), and a 1 M THF solution of *o*-tolylmagnesium bromide (10 mL, 10 mmol) was added to it. The mixture was refluxed at 80°C for 5 hr under an argon atmosphere, then cooled to room temperature, and 2 N HCl aq. was added to it. The mixture was diluted with sat. NaHCO$_3$ aq. and extracted with CH$_2$Cl$_2$. The combined organic layer was washed with brine, dried over Na$_2$SO$_4$ and concentrated *in vacuo*. The residue was purified by HPLC (eluent, 52% CH$_3$CN/0.1% TFA aq. (0 min) to 72% CH$_3$CN/0.1% TFA aq. (20 min); flow rate = 25.0 mL/min) to afford **28** (25 mg, 47.7 µmol, 6%).

^{1}H NMR (400 MHz, CD$_2$Cl$_2$): δ 0.47 (s, 3H), 0.50 (s, 3H), 1.95 (s, 3H), 2.88 (t, *J* = 7.2 Hz, 2H), 3.14 (s, 6H), 3.18 (s, 3H), 3.80 (t, *J* = 7.2 Hz, 2H), 6.46 (dd, *J* = 9.2, 2.0 Hz, 1H), 6.71 (s, 1H), 6.90-6.91 (m, 2H), 7.00-7.01 (m, 2H), 7.24-7.37 (m, 3H); ^{13}C NMR (100 MHz, CD$_2$Cl$_2$) δ –1.0, –0.7, 19.7, 26.8, 34.4, 40.9, 55.7, 113.9, 115.9, 120.3, 126.3, 128.1, 129.3, 129.5, 129.8, 130.9, 134.3, 134.5, 136.4, 140.8, 146.8, 153.8, 154.3, 158.7, 168.8; HRMS (ESI$^+$) Calcd for [M]$^+$, 411.2257, Found, 411.2219 (–3.8 mmu).



To a flame-dried flask flushed with argon were added **21** (280 mg, 0.62 mmol) and anhydrous THF (15 mL). The mixture was cooled to -78°C, and 1 M *sec*-BuLi (1.86 mL, 1.86 mmol) was added to it. The solution was stirred for 20 min at the same temperature, and then dichlorodimethylsilane (157 mg, 1.22 mmol) in anhydrous THF (3 mL) was added to it. The mixture was warmed to r.t. and stirred for 2 hr. The reaction was quenched by adding 2 N HCl, and the mixture was neutralized with sat $NaHCO_3$ aq.. The whole was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue was dissolved in acetone, and the solution was cooled to 0°C. To this solution, $KMnO_4$ (294 mg, 1.86 mmol) was added in small portions over a period of 2 hr with stirring. Stirring was continued for another 1 hr at the same temperature, then the mixture was diluted with CH_2Cl_2, filtered through a Celite filter and evaporated to dryness. The residue was purified by column chromatography (silica gel, AcOEt/hexane = 3/7) to give **57** (60 mg, 0.165 mmol, 27%).

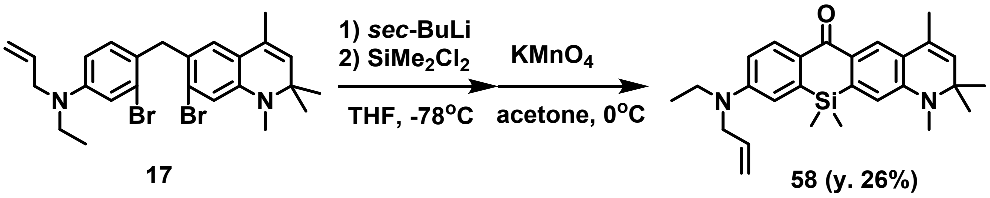
^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.46 (s, 6H), 1.24 (t, J = 6.6 Hz, 6H), 2.91 (s, 3H, 3.06 (t, J = 8.7 Hz, 2H), 3.44-3.50 (m, 6H), 6.61 (s, 1H), 6.76-6.82 (m, 2H), 8.23 (s, 3H), 8.37 (d, J = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, CD_2Cl_2): δ -0.55, 13.2, 28.9, 35.2, 45.3, 55.6, 108.9, 113.4, 114.6, 126.5, 129.5, 132.2, 132.4, 133.2, 140.8, 141.3, 150.0, 155.8, 185.3; LRMS (ESI$^+$) 365 [M+H]$^+$.



To a solution of **57** (10 mg, 27.4 μmol) in anhydrous THF (5 mL) was added a 1 M THF solution of *o*-tolylmagnesium bromide (10 mL, 10 mmol) and the mixture was refluxed for 5 hr under an argon atmosphere. It was cooled to room temperature, and 2 N HCl aq. was added to it.

The mixture was diluted with sat. $NaHCO_3$ aq., and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, MeOH/CH_2Cl_2) and HPLC (eluent, 56% CH_3CN/0.1% TFA aq. (0 min) to 72% CH_3CN/0.1% TFA aq. (20 min); flow rate = 5.0 mL/min) to afford **29** (8 mg, 14.5μmol, 53%).

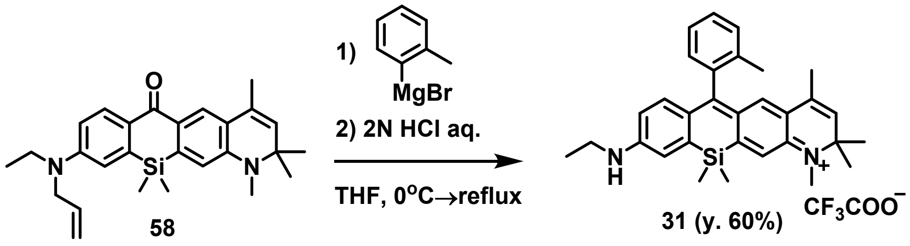
^{1}H NMR (300 MHz, CD_3CN): δ 0.55 (s, 3H), 0.56 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 6H), 2.02 (s, 3H), 2.90 (t, *J* = 8.1 Hz, 2H), 3.23 (s, 3H), 3.58 (q, *J* = 7.1 Hz, 4H), 3.85 (t, *J* = 8.1 Hz, 2H), 6.63 (dd, *J* = 9.9, 2.6 Hz, 1H), 6.72 (s, 1H), 6.88 (d, *J* = 9.9 Hz, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 7.15 (s, 1H), 7.20 (d, *J* = 2.6 Hz, 1H), 7.34-7.48 (m, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ –1.5, –1.2, 13.0, 19.4, 26.9, 33.9, 46.4, 56.0, 114.5, 116.8, 121.1, 126.9, 128.2, 129.9, 130.0, 130.1, 131.3, 134.3, 135.31, 137.0, 140.6, 141.3, 147.5, 152.9, 154.1, 159.4, 168.2; HRMS (ESI$^+$) Calcd for $[M]^+$, 439.2570, Found, 439.2566 (–0.4 mmu).



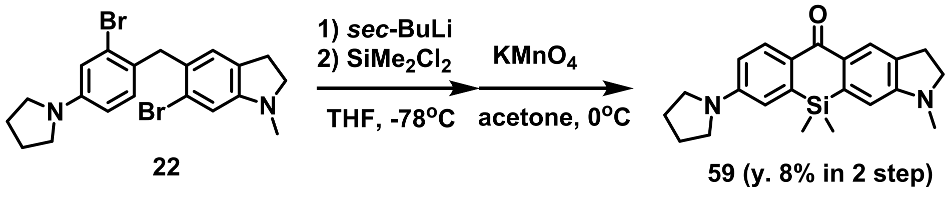
To a flame-dried flask flushed with argon were added **17** (614 mg, 1.19 mmol) and anhydrous THF (15 mL). The mixture was cooled to –78 °C, and 1 M *sec*-BuLi (3.6 mL, 3.6 mmol) was added. The solution was stirred for 20 min at the same temperature. Dichlorodimethylsilane (302 mg, 2.38 mmol) in anhydrous THF (3 mL) was added to it, then the mixture was warmed to r.t., and stirred for 2 hr. The reaction was quenched by adding 2 N HCl, and the mixture was neutralized with sat. $NaHCO_3$ aq. The whole was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue was dissolved in acetone, and the solution was cooled to 0°C. To this solution, $KMnO_4$ (940 mg, 5.95 mmol) was added in small portions over a period of 2 hr with stirring. Stirring was continued for another 1 hr at the same temperature, then the mixture was diluted with CH_2Cl_2, filtered through a Celite filter and evaporated to dryness. The residue was purified by column chromatography (silica gel, AcOEt/hexane = 3/7) to give **58** (134 mg, 0.311 mmol, 26 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.45 (s, 6H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.38 (s, 6H), 2.09 (s, 3H), 2.94 (s, 3H), 3.49 (q, *J* = 7.2 Hz, 2H), 4.00-4.02 (m, 2H), 5.18-5.23 (m, 2H), 5.33 (s, 1H), 5.82-

5.94 (m, 1H), 6.58 (s, 1H), 6.79 (d, *J* = 3.0 Hz, 1H), 6.82 (dd, *J* = 3.0, 8.7 Hz, 1H), 8.19 (s, 1H), 8.37 (d, *J* = 8. 7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ –1.1, 12.4, 18.7, 28.5, 30.9, 44.8, 52.4, 57.1, 112.4, 112.9, 114.2, 116.3, 123.3, 124.8, 128.0, 129.4, 129.6, 129.8, 131.6, 133.3, 140.4, 140.7, 146.8, 149.5, 185.0; HRMS (ESI$^+$): Calcd for $[M+H]^+$, 431.2529; found, 431.2503 (–1.5 mmu).

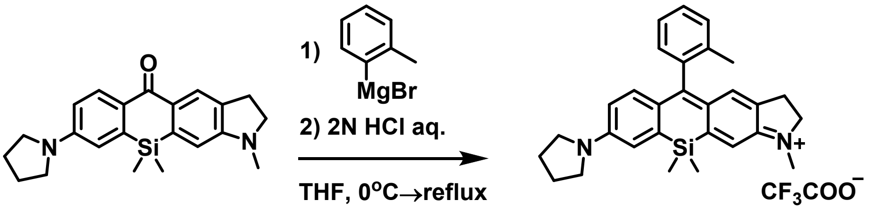


To a solution of **58** (20 mg, 46.4 µmol) in anhydrous THF (5 mL) was added a 1 M THF solution of *o*-tolylmagnesium bromide (10 mL, 10 mmol) and the mixture was refluxed at 65°C for 13 hr under an argon atmosphere. It was then cooled to room temperature, and 2 N HCl aq. was added to it. The mixture was diluted with sat. $NaHCO_3$ aq. and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by HPLC (eluent, 48% CH_3CN/0.1% TFA aq. (0 min) to 80% CH_3CN/0.1% TFA aq. (20 min); flow rate = 25.0 mL/min) to afford **31** (16 mg, 27.6 µmol, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.54 (s, 3H), 0.55 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.43 (s, 3H), 1.45 (s, 3H), 1.51 (s, 3H), 2.05 (s, 3H), 3.14 (s, 3H), 3.47 (q, *J* = 7.2 Hz, 2H), 5.29 (s, 1H), 6.63 (s, 1H), 6.85 (s, 1H), 7.06-7.08 (m, 2H), 7.27-7.42 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ –1.4, –1.1, 13.9 17.6, 19.4, 29.3, 32.1, 38.4, 59.4, 112.5, 115.5, 117.7, 118.4, 122.4, 125.6, 126.3, 127.5, 128.7, 128.9, 129.8, 130.1, 131.4, 135.7, 138.8, 148.2, 149.1, 156.0, 161.1, 161.4, 167.4; HRMS (ESI$^+$) Calcd for $[M]^+$, 465.2726, Found, 465.2676 (–4.1 mmu).



To a solution of **22** (336 mg, 0.747 mmol) in anhydrous THF (25 mL) was added a 1 M THF solution of *sec*-BuLi (1.64 mL, 1.64 mmol) at –78 °C under an argon atmosphere. The reaction mixture was stirred for 20 min at the same temperature, then dichlorodimethylsilane (134 μL, 1.12 mmol) in anhydrous THF (5 mL) was added to it. The mixture was warmed to room temperature and stirred for 2 hr, then 2 N HCl aq. was added to quench the reaction, and the mixture was neutralized with $NaHCO_3$ aq. The whole was extracted with CH_2Cl_2. The organic layer was collected, washed with brine, dried over Na_2SO_4 and evaporated to dryness. The residue was dissolved in acetone (30 mL) at 0°C, and $KMnO_4$ (472 mg, 2.99 mmol) was added in small portions over 2 hr with stirring at the same temperature. The mixture was filtered through Celite and the filtrate was evaporated to dryness. The residue was purified by column chromatography (silica gel, CH_2Cl_2/*n*-hexane) to afford **59** (21 mg, 58.0 μmol, 8%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.45 (s, 6H), 2.03-2.07 (m, 4H), 2.90 (s, 3H), 3.05 (t, *J* = 8.0 Hz, 2H), 3.39-3.50 (m, 6H), 6.51 (s, 1H), 6.64 (d, *J* = 2.1 Hz, 1H), 6.69 (dd, *J* = 8.1, 2.1 Hz, 1H), 8.22 (s, 1H), 8.39 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.5, 28.1, 34.6, 47.5, 54.8, 108.0, 113.1, 114.1, 126.0, 129.1, 131.6, 131.8, 132.1, 140.1, 140.5, 149.0, 154.8, 185.2; LRMS (ESI$^+$) 363 [M+H]$^+$.



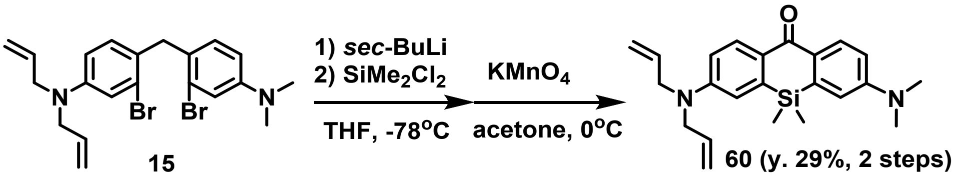
59

30 (y. 66%)

To a solution of **59** (15 mg, 41.4 μmol) in anhydrous THF (20 mL) was added a 1 M THF solution of *o*-tolylmagnesium bromide (1 mL, 1 mmol) and the mixture was refluxed for 4 hr under an argon atmosphere. It was cooled to room temperature, and 2 N HCl aq. was added to it. The mixture was diluted with sat. $NaHCO_3$ aq. and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by HPLC (eluent, 64% CH_3CN/0.1% TFA aq. (0 min) to 80% CH_3CN/0.1% TFA aq. (20 min); flow rate = 5.0 mL/min) to afford **30** (15 mg, 27.3 μmol, 66%).

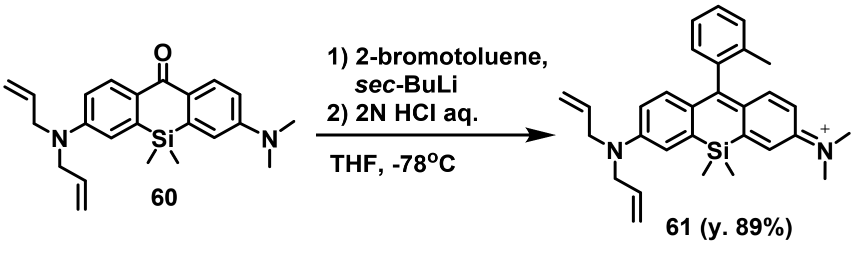
^{1}H NMR (400 MHz, CD_2Cl_2): δ 0.55 (s, 3H), 0.57 (s, 3H), 2.03 (s, 3H), 2.10 (t, *J* = 6.9 Hz, 4H), 2.96 (t, *J* = 7.2 Hz, 2H), 3.24 (s, 3H), 3.57 (t, *J* = 6.9 Hz, 4H), 3.86 (t, *J* = 7.2 Hz, 2H), 6.44 (dd, *J* = 9.2, 2.4 Hz, 1H), 6.78 (s, 1H), 6.93 (s, 1H), 6.98-7.00 (m, 2H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.33-

7.46 (m, 3H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ –1.0, –0.7, 19.7, 25.8, 26.8, 34.2, 49.3, 55.6, 114.8, 115.4, 121.4, 126.3, 128.1, 129.3, 129.5, 129.6, 130.9, 134.0, 136.4, 139.8, 141.2, 147.4, 151.6, 153.5, 158.4, 168.9; HRMS (ESI$^+$) Calcd for [M]$^+$, 437.2413, Found, 437.2387 (–2.6 mmu).



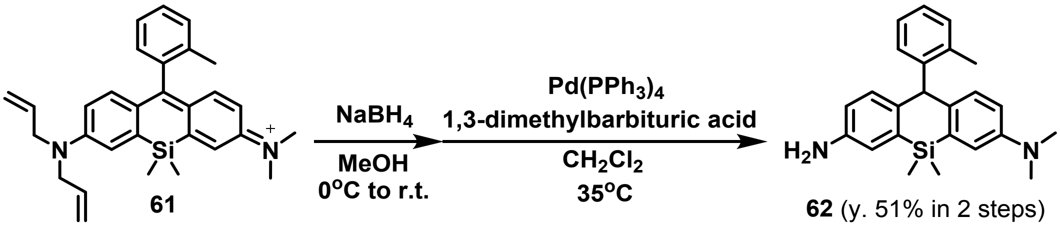
To a solution of **15** (19.9 g, 43.0 mmol) in anhydrous THF (120 mL) in a flame-dried flask was added a 1 M THF solution of *sec*-BuLi (120 mL, 120 mmol) at –78 °C under an argon atmosphere. The reaction mixture was stirred for 20 min at the same temperature, and then dichlorodimethylsilane (5.8 mL, 60 mmol) in anhydrous THF (40 mL) was slowly added to it. The mixture was warmed to room temperature and stirred for 1 hr, then 2 N HCl aq. was added to quench the reaction, and the mixture was neutralized with sat. $NaHCO_3$ aq. The whole was extracted with CH_2Cl_2. The organic layer was collected, washed with brine, dried over Na_2SO_4 and evaporated to dryness. The residue was dissolved in acetone (300 mL) at 0°C and $KMnO_4$ (19.4 g, 123 mmol) was added in small portions over 2 hr with stirring at the same temperature. The mixture was stirred for a further 1 hr at room temperature, filtered and evaporated to dryness. The residue was purified by column chromatography (silica gel, CH_2Cl_2) to afford **60** (4.68 g, 12.4 mmol, 29%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.44 (s, 6H), 3.09 (s, 6H), 4.03 (d, 4H, *J* = 4.4 Hz), 5.18-5.30 (m, 4H), 5.82-5.95 (m, 2H), 6.78-6.85 (m, 4H), 8.36 (d, 1H, *J* = 8.7 Hz), 8.39 (d, 1H, *J* = 9.0 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = −1.1, 40.0, 52.6, 113.1, 113.4, 114.2,114.7, 116.5, 129.6, 129.9, 131.6, 133.0, 140.4, 150.1, 151.4, 185.1; HRMS (ESI$^+$): Calcd for [M+H]$^+$, 377.2049, Found, 377.2019 (−3.0 mmu).



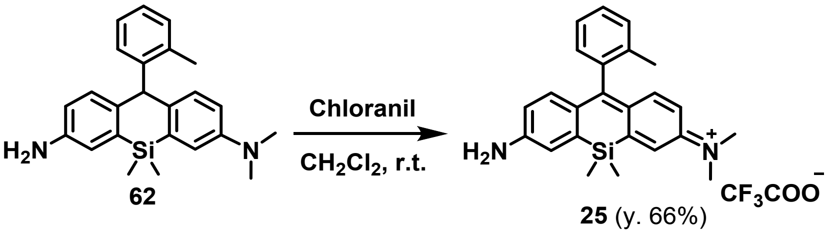
To a flame-dried flask flushed with argon was added a solution of 2-bromotoluene (14 mL, 110 mmol) in anhydrous THF (50 mL). The mixture was cooled to –78 °C, and then a 1 M THF solution of *sec*-BuLi (100 mL, 100 mmol) was added at –78 °C under an argon atmosphere. The reaction mixture was stirred for 20 min at the same temperature, and then a solution of **60** (930 mg, 2.47 mmol) in anhydrous THF (30 mL) was slowly added to it. The mixture was warmed to room temperature and stirred for 1 h, then 2 N HCl aq. (80 mL) was added, and the whole was extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography (silica gel, MeOH/CH_2Cl_2, 1/19 → 1/4) to afford **61** (1.07 g, 2.20 mmol, 89%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 0.61 (s, 3H), 0.63 (s, 3H), 2.04 (s, 3H), 3.49 (s, 6H), 4.21 (d, 4H, *J* = 5.1 Hz), 5.19–5.32 (m, 4H), 5.82-5.95 (m, 2H), 6.11 (dd, 1H, *J* = 1.5 Hz, 9.6 Hz), 6.69 (dd, 1H, *J* = 1.5 Hz, 10.2 Hz), 7.07 (d, 1H, *J* = 9.6Hz), 7.11-7.14 (m, 2H), 7.29 (d, 1H, *J* = 3.0 Hz), 7.35-7.49 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = −1.1, −0.8, 19.4, 41.6, 53.6, 114.0, 114.5, 118.1, 120.6, 121.7, 125.6, 127.6, 128.0, 128.8, 128.9, 130.2, 130.4, 130.8, 135.6, 138.3, 141.0, 142.2, 147.7, 153.2, 154.7, 170.0; HRMS (ESI$^+$): Calcd for $[M]^+$, 451.2569, Found, 451.2541 (−2.8 mmu).



Compound **61** (1.15 g, 2.36 mmol) was dissolved in MeOH (100 mL). The solution was cooled to 0°C, and $NaBH_4$ (367 mg, 9.72 mmol) was added to it. The reaction mixture was stirred for 30 min, washed with sat. $NaHCO_3$ aq. and brine, dried over Na_2SO_4 and evaporated to dryness. The residue was partially purified by column chromatography (silica gel, ethyl acetate/*n*-hexane 1/4) to provide crude reduced **61** (785 mg). To a flame-dried flask flushed with argon were added $Pd(PPh_3)_4$ (213 mg, 0.184 mmol) and 1,3-dimethylbarbituric acid (943 mg, 6.04 mmol). The crude reduced **61** in CH_2Cl_2 (50 mL) was then added to this flask, and the mixture was stirred at 35°C for 11 hr, and evaporated to dryness. The residue was suspended in sat. $NaHCO_3$ aq., and extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane 1/9 → 1/4) to obtain **62** (450 mg, 1.21 mmol, 51% in 2 steps).

^{1}H-NMR (300 MHz, CD_3OD): δ = 0.37 (s, 3H), 0.54 (s, 3H), 2.17 (s, 3H), 2.88 (s, 6H), 5.50 (s, 1H), 6.60 (dd, *J* = 8.4 Hz, 2.6 Hz, 1H), 6.69 (dd, *J* = 8.8 Hz, 2.9 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 1H), 6.97−7.09 (m, 6H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ = −1.0, −0.3, 20.5, 40.7, 49.9, 114.6, 116.3, 116.9, 119.0, 125.8, 126.1, 129.8, 130.1, 131.0, 131.1, 133.6, 134.4, 135.5, 137.2, 139.2, 143.3, 146.0, 147.9; HRMS (ESI+): Calcd for $[M+H]^+$, 373.2100, Found, 373.2071 (−2.9 mmu).

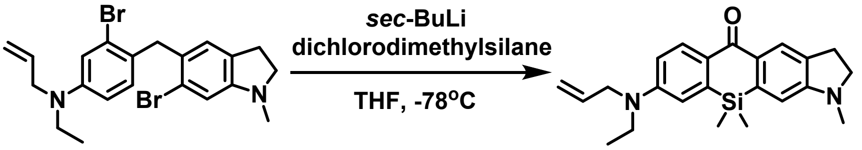


62

25 (y. 66%)

Compound **62** (121 mg, 0.324 mmol) and chloranil (159 mg, 0.647 mmol) were dissolved in CH_2Cl_2 (10 mL), and the mixture was stirred for 30 min. The solution was evaporated to dryness and the residue was purified by HPLC (eluent, 16% CH_3CN/0.1% TFA aq. (0 min) to 80% CH_3CN/0.1% TFA aq. (25 min); flow rate = 5.0 mL/min) to afford **25** (103 mg, 0.213 mmol, 66 %).

^{1}H NMR (300 MHz, CD_3OD): δ = 0.55 (s, 3H), 0.56 (s, 3H), 2.04 (s, 3H), 3.34 (s, 6H), 6.58 (dd, 1H, *J* = 2.1 Hz, 9.6 Hz), 6.76 (dd, 1H, *J* = 3.0 Hz, 9.6 Hz), 7.02 (d, 1H, 9.6 Hz), 7.07-7.13 (m, 2H), 7.20 (d, 1H, *J* = 2.1 Hz), 7.36-7.49 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −1.6, –1.3, 19.3, 40.4, 113.1, 117.5, 119.3, 125.5, 125.5, 127.4, 127.8, 128.7, 128.9, 130.1, 135.6, 138.6, 140.2, 143.5, 146.9, 150.1, 153.0, 158.1, 169.1; HRMS (ESI^+): Calcd for $[M]^+$, 371.1944, Found, 371.1974 (+3.1 mmu).

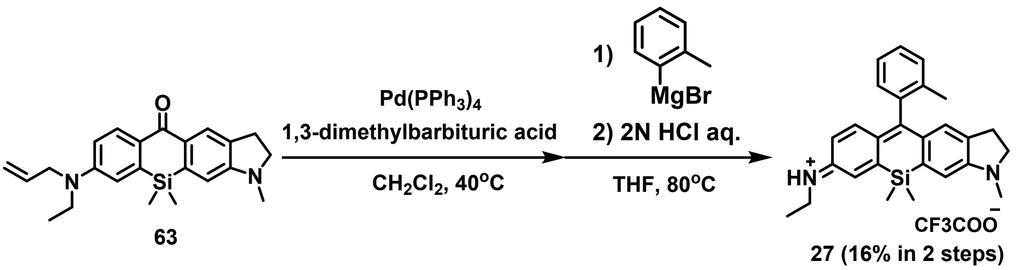


18

63 (y. 25%)

To a flame-dried flask flushed with argon were added **18** (825 mg, 1.79 mmol) and anhydrous THF (15 mL). The mixture was cooled to -78 °C, and 1 M *sec*-BuLI (4.3 mL, 4.3 mmol) was added to it. The solution was stirred for 20 min at the same temperature, and dichlorodimethylsilane (455 mg, 3.58 mmol) in anhydrous THF (3 mL) was added. The mixture was warmed to r.t. and stirred for 2 hr, then the reaction was quenched by adding 2 N HCl. The mixture was neutralized with sat. $NaHCO_3$ aq., and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. The residue was dissolved in acetone, and the solution was cooled to 0 ˚C. To this solution, $KMnO_4$ (1.414 g, 8.95 mmol) was added in small portions over a period of 2 hr with stirring. Stirring was continued for another 1 hr at the same temperature, then the mixture was diluted with CH_2Cl_2, filtered through a Celite filter, and evaporated to dryness. The residue was purified by column chromatography (silica gel, AcOEt/hexane = 3/7) to give **63** (170 mg, 0.451 mmol, 25%).

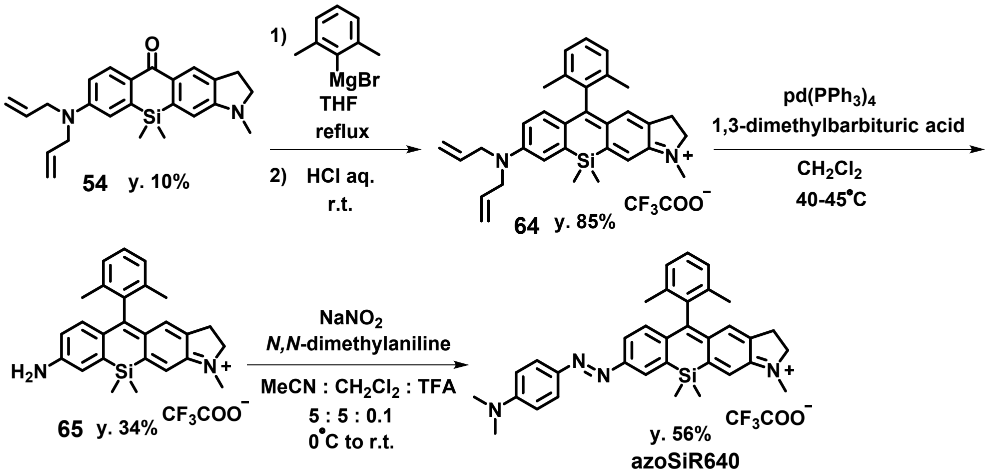
^{1}H NMR (300 MHz, CD_3CN): δ 0.29 (s, 6H), 0.97 (t, *J* = 6.6 Hz, 3H), 2.65 (s, 3H), 2.79 (t, *J* = 8.1 Hz, 2H), 3.22 (t, *J* = 8.1 Hz, 2H), 3.28 (q, *J* = 6.6 Hz, 2H), 3.81 (d, *J* = 5.4 Hz, 2H), 4.91-4.97 (m, 2H), 5.61-5.74 (m, 1H), 6.42 (s, 1H), 6.59 (dd, *J* = 3.0, 8.7 Hz, 1H), 6.65 (d, *J* = 3.0 Hz, 1H), 7.83 (s, 1H), 7.95 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (75 MHz, CD_3CN): δ –1.2, 12.6, 28.6, 34.7, 45.6, 52.9, 55.3, 109.3, 113.9, 115.4, 116.3, 126.2, 129.9, 131.9, 132.1, 133.4, 134.9, 141.0, 141,3, 150.5, 156.1, 185.0; HRMS (ESI$^+$): Calcd for [M+H]$^+$, 377.2049; found, 377.2051 (+0.2 mmu).

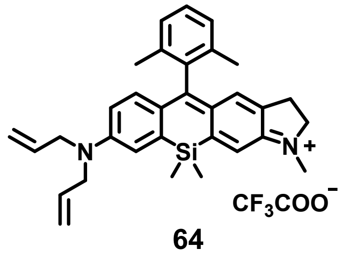


Compound **63** (183 mg, 0.5 mmol) and 1,3-dimethylbarbituric acid (312 mg, 2.0 mmol) were dissolved in CH_2Cl_2 under an Ar atmosphere. $Pd(PPh_3)_4$ (115 mg, 0.1 mmol) was added under Ar. The mixture was stirred for 18 hr at 40°C, and then evaporated to dryness. The residue was partially purified by column chromatography (silica gel, CH_2Cl_2) to give crude deprotected **63** (153 mg, 91%). HRMS (ESI$^+$): Calcd for [M+H]$^+$, 337.1736; found, 337.1738 (+0.2 mmu). To a flame-dried flask flushed with argon were added crude deprotected **63** (34 mg, 0.1 mmol) and anhydrous THF (5 mL). The solution was heated to 80°C, and 1 M *o*-tolylmagnesium bromide (3 mL) was added. The mixture was stirred for 2 hr, then cooled to r.t., and the reaction was quenched by addition of 2 N HCl. Stirring was continued at r.t. for 15 min, then the mixture was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated to dryness. Purification of the residue by HPLC (eluent, a 20-min linear gradient, from 20 % to 100 % solvent B; flow rate, 5.0 ml/min; detection wavelength, 680 nm) provided **27** (6.8 mg, 16% in 2 steps).

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.52 (s, 3H), 0.54 (s, 3H), 1.33 (t, J = 6.6 Hz, 3H), 2.04 (s, 3H), 2.94 (t, J = 8.1 Hz, 2H), 3.17 (s, 3H), 3.42 (q, J = 6.6 Hz, 2H), 3.78 (t, J = 8.1 Hz, 2H), 6.50 (d, J = 8.7 Hz, 1H), 6.70 (s, 1H), 6.80 (s, 1H), 6.97 (d, J = 9.0 HZ, 1H), 7.06 (d, J = 7.2 Hz, 1H), 7.30-7.35 (m, 3H), 7.45 (t, J = J = 8.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ -1.5, -1.2, 13.9, 19.5, 26.6, 33.7, 38.3, 54.6, 113.6, 125.7, 127.5, 128.7, 128.7, 129.0, 130.3, 132.5, 133.0, 135.8, 139.3, 142.5, 147.2, 150.9, 155.0, 156.9, 167.6; HRMS (ESI$^+$): Calcd for $[M]^+$, 411.2257; Found, 411.2228 (−2.8 mmu).

Scheme S3. Synthesis of azoSiR640.

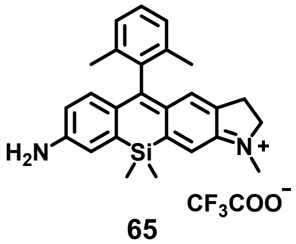




64

To a solution of **54** (160 mg, 412 μmol) in anhydrous THF (20 mL) was added a 1 M THF solution of 2,6-dimethylphenylmagnesium bromide (4.1 mL, 4.1 mmol) and the mixture was refluxed at 80°C for 2 hr under an argon atmosphere. Another portion of the Grignard reagent (1 M THF solution of 2,6-dimethylphenylmagnesium bromide; 2.0 mL, 2.0 mmol) was further added and the mixture was refluxed at 90°C for 5 hr. It was cooled to room temperature, and 2 N HCl was added to it. The resulting mixture was diluted with H_2O, and extracted with CH_2Cl_2. The organic layer was collected, washed with brine, dried over Na_2SO_4 and evaporated to dryness. The residue was purified by HPLC (gradient, A/B = 60/40 to 0/100, 15 min) to afford **64** as a blue solid (206 mg, 349 μmol, 85%).

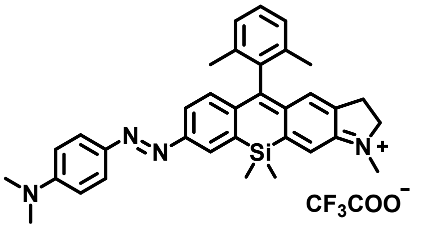
^{1}H NMR (400 MHz, CD_3OD): δ 0.55 (s, 6H), 1.99 (s, 6H), 2.99 (t, *J* = 7.2 Hz, 2H), 3.21 (s, 3H), 3.97 (t, *J* = 7.2 Hz, 2H), 4.10 (d, *J* = 4.8 Hz, 4H), 5.20 (d, *J* = 17.2 Hz, 2H), 5.29 (d, *J* = 10.4 Hz, 2H), 5.85 (m, 2H), 6.52 (dd, *J* = 9.6, 2.8 Hz, 1H), 6.75 (s, 1H), 6.93 (d, *J* = 9.6 Hz, 1H), 7.04 (d, *J* = 2.8 Hz, 1H), 7.14 (s, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OD): δ -1.5, 19.7, 25.9, 34.2, 53.2, 55.3, 113.8, 116.6, 117.8, 119.6, 127.4, 127.6, 128.5, 128.9, 131.1, 132.9, 134.5, 135.6, 138.3, 138.6, 145.3, 151.9, 154.4, 158.6, 167.2; LRMS (ESI$^+$): [M]$^+$, 477.



65

To a solution of **64** (83.6 mg, 142 μmol) in CH_2Cl_2 (20 mL) were added 1,3-dimethylbarbituric acid (81.9 mg, 525 μmol) and $Pd(PPh_3)_4$ (202 mg, 175 μmol), and the mixture was stirred for 17.5 hr at 40 °C under an argon atmosphere. It was cooled to room temperature, and H_2O was added to it. The aqueous layer was extracted with CH_2Cl_2. The organic layer was collected, dried over Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography (NH silica gel, CH_2Cl_2/MeOH = 98/2 to 94/6) and then HPLC (gradient, A/B = 70/30 to 0/100, 25 min) to afford **2,6-diMe SiR640** (**65**) as a blue solid (24.2 mg, 47.4 μmol, 34%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.53 (s, 6H), 1.98 (s, 6H), 2.97 (t, *J* = 8.1 Hz, 2H), 3.24 (s, 3H), 3.85 (t, *J* = 8.1 Hz, 2H), 6.53 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.75 (s, 1H), 6.89 (s, 1H), 6.92 (d, *J* = 9.0 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 2.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ -1.7, 19.6, 26.3, 33.7, 54.7, 114.3, 116.7, 123.8, 127.4, 127.6, 128.4, 128.5, 132.4, 133.2, 135.5, 138.7, 140.9, 147.7, 152.7, 155.6, 157.6, 168.8; HRMS (ESI$^+$): Calcd for $[M]^+$, 397.2100, Found, 397.2096 (–0.4 mmu).

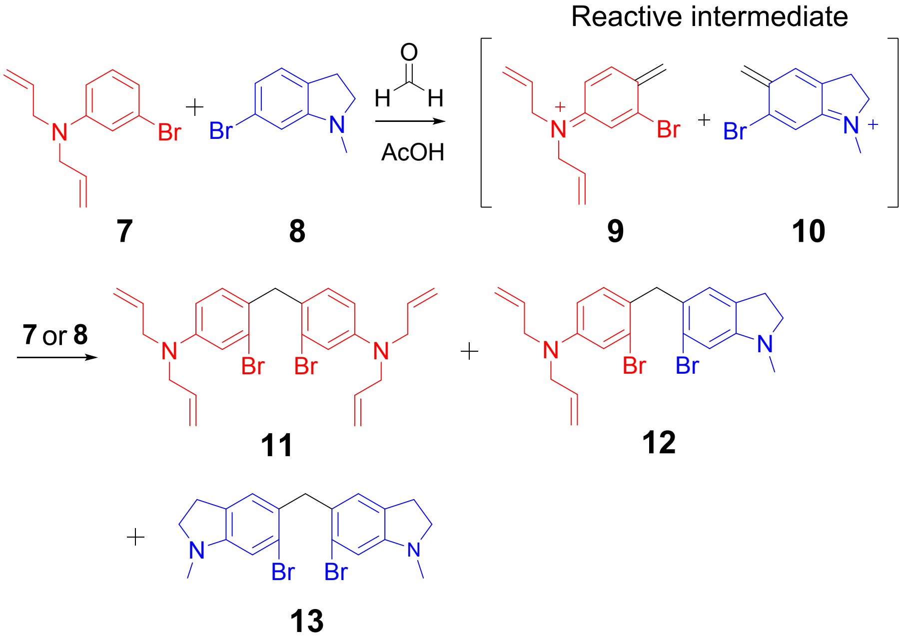


azoSiR640

2,6-diMe SiR640 (**65**) (13.0 mg, 25.4 μmol) was dissolved in MeCN/CH_2Cl_2 (1 : 1, 10 mL) containing 1% TFA and the mixture was stirred at 0 °C under an argon atmosphere. $NaNO_2$ (3.6 mg, 52.5 μmol) was added to it, and stirring was continued at 0°C for 2 min. *N,N*-Dimethylaniline (58.8 μL, 757 μmol) in MeCN (1 mL) was then added. After further stirring at room temperature for 1.5 hr, the mixture was diluted with H_2O and extracted with CH_2Cl_2. The organic layer was collected, washed with brine, dried over Na_2SO_4 and evaporated to dryness. The residue was purified by HPLC (gradient, A/B = 60/40 to 0/100, 20 min) to afford **azoSiR640** as a dark blue solid (8.9 mg, 14.2 μmol, 56%).

^{1}H NMR (300 MHz, CD_3OD): δ 0.67 (s, 6H), 2.02 (s, 6H), 3.06 (m, 2H), 3.15 (s, 6H), 3.58 (s, 3H), 4.15 (t, *J* = 6.6 Hz, 2H), 6.87 (d, *J* = 9.6 Hz, 2H), 6.91 (s, 1H), 7.15 (d, *J* = 8.7 Hz, 1H), 7.28 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.68–7.72 (m, 2H), 7.89 (d, *J* = 9.6 Hz, 2H), 8.25 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR (100 MHz, CD_3OD): δ –1.7, 19.9, 26.4, 35.5, 40.3, 58.1, 112.9, 122.0, 125.0, 127.2, 129.0, 129.7, 130.2, 133.8, 134.2, 135.7, 136.9, 139.6, 139.9, 140.7, 142.0, 145.4, 154.8, 155.3, 158.8, 161.4, 163.3; HRMS (ESI$^+$): Calcd for $[M]^+$, 529.2788, Found, 529.2743 (–4.5 mmu).

Table S1. Heterodimerization reaction of two anilines



Entry	Temp. (°C)	Time (min)	Recovery (%) **7**	Recovery (%) **8**	Conversion (%) **11**	Conversion (%) **12**	Conversion (%) **13**
1	60	15	86	9	0	2	16
2	80	90	11	0	13	0	0

Compounds **11** and **13** were identified based on the previous reports.[S6,7]

Initially, we tried to synthesize aniline heterodimers by exploring heterodimerization of allyl-protected aniline (**7**) and *N*-methylindoline (**8**) under the reaction conditions used for the synthesis of aniline homodimers.[S9] However, this reaction mainly afforded the homodimers **11** and **13** (Table S1). The use of formaldehyde (2.5 eq.) in acetic acid for 15 min at 60°C provided small amounts of homodimer **13** and heterodimer **12** (Table S1, entry 1). Under this condition, reactive **8** was thought to preferentially form the homodimer. Therefore, we performed the same reaction for 90 min at 80°C (Table S1, entry 2). However, we obtained only a small amount of homodimer **11**, probably because aniline **8** formed complex polymers consisting of **8** and **7**.

We anticipated that the reaction mechanism for aniline homodimers in Table S1 might be as follows. Formaldehyde forms *p*-hydroxymethyl aniline under the acidic condition, and then dehydration of *p*-hydroxymethyl aniline generates an electrophilic aza quinone methide (**9** or **10**), which is thought to be the reactive intermediate. Then, another aniline (**7** or **8**) reacts with **9** or **10**, generating aniline homodimer (**11** or **13**), which can be converted to symmetrical Si-rhodamine fluorophore. So, we expected that we would be able to obtain the aniline heterodimers by forming the reactive intermediate of one of the two anilines, followed by nucleophilic attack of another aniline (see Table 1 in the manuscript).

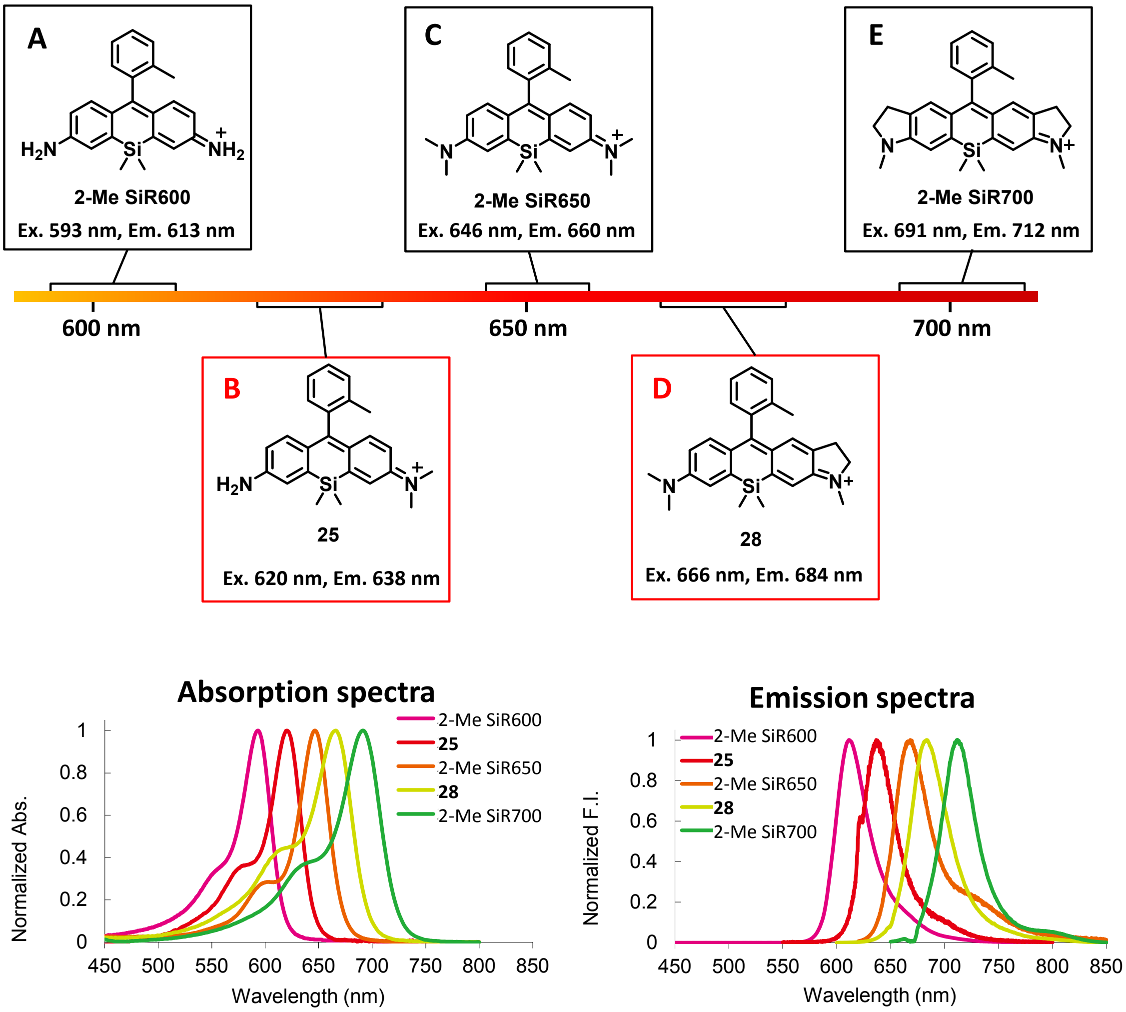


Fig. S1 Absorption and emission wavelengths of Si-rhodamines are fine-tunable by chemically introducing alkyl groups into the xanthene moieties. Photophysical properties and spectra were measured in 100 mM sodium phosphate buffer (pH 7.4) containing 1% DMSO as a co-solvent.

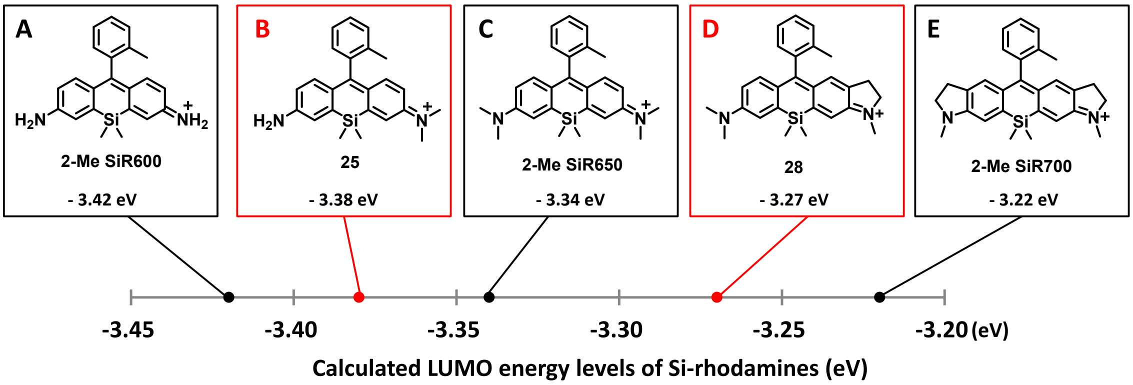


Fig. S2 Calculated LUMO energy levels of Si-rhodamines. Calculations were performed at the B3LYP/6-31+G(d) (gas phase) level.

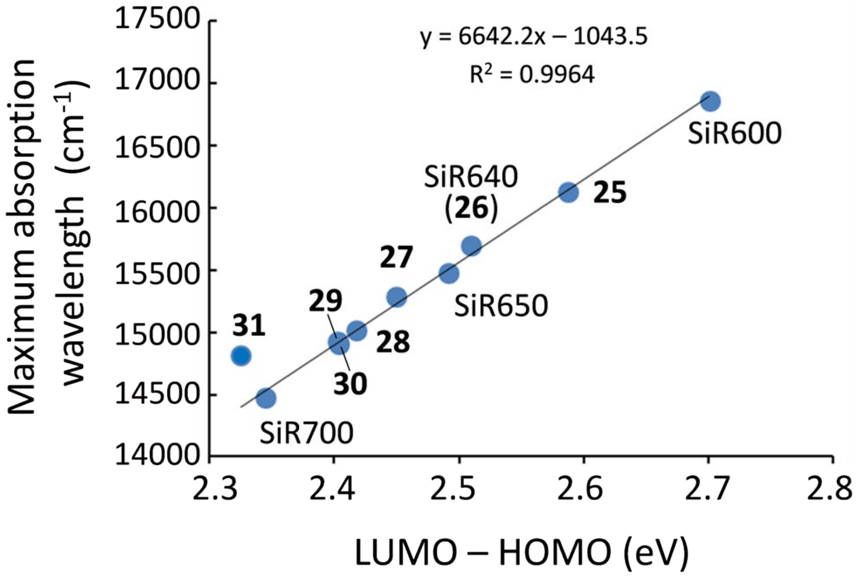


Fig. S3 Relationship between maximum absorption wavelength (cm^{-1}) and calculated LUMO energy level – HOMO energy difference (eV) of symmetrical and unsymmetrical Si-rhodamines. The HOMO and LUMO energies were calculated at the B3LYP/6-31+G(d) (gas phase) level. The solid line is the best linear fit to the points except for **31**.

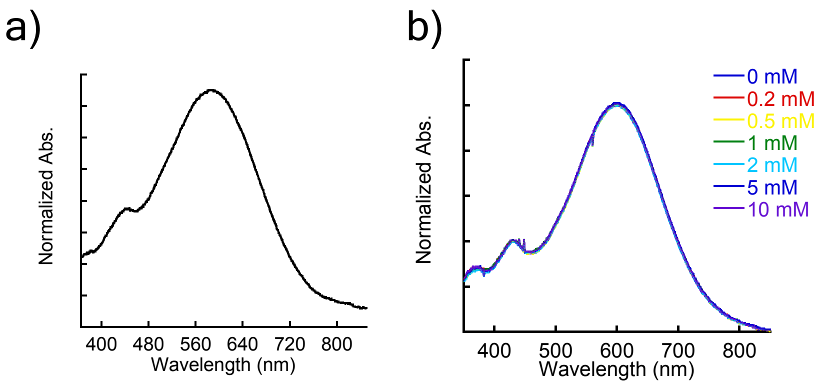


Fig. S4 (a) Normalized absorption of **azoSiR640** (1 μM) in PBS at pH 7.4, containing 0.1% DMSO as a cosolvent. (b) Normalized absorption spectra of **azoSiR640** (1 μM) in sodium phosphate buffer at pH 7.4 containing 1% DMSO and 0.03% Pluronic-F127 in the presence of various concentrations of GSH.

Table S2. Photophysical properties of **azoSiR640** and **2,6-diMe SiR640** in PBS (pH 7.4)

Dye	λ_{abs} (nm)	λ_{fl} (nm)	ε ($M^{-1}cm^{-1}$)	Φ_{fl}[a[
azoSiR640	590	N.D.	3.8×10^4	<0.001
2,6-diMe SiR640 (65)	637	670	5.4×10^4	0.15

[a] For the determination of the fluorescence quantum efficiency (Φ_{fl}), Cresyl violet in MeOH ($\Phi_{\mathrm{fl}} = 0.53$) was used. N.D. = not detectable.

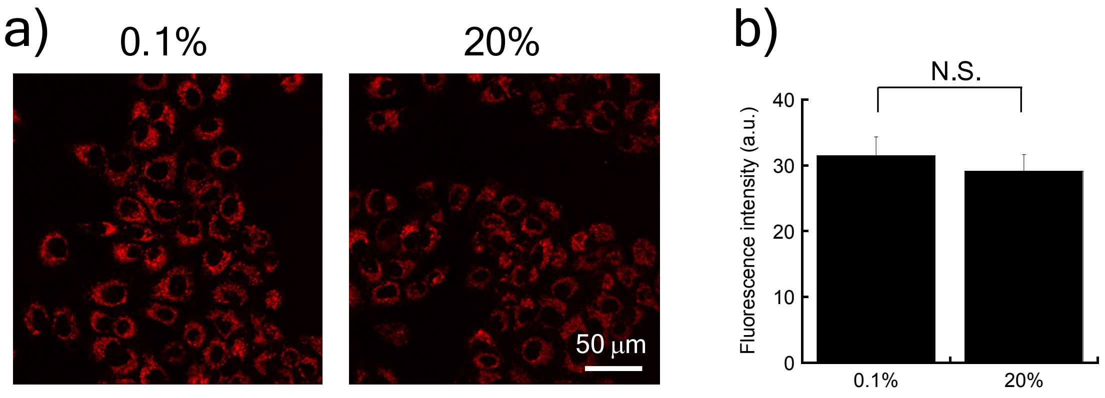


Fig. S5 Cellular assay with 100 nM **2,6-diMe SiR640** containing 0.1% DMSO as a co-solvent. **2,6-diMe SiR640** was loaded into A549 cells for 20 min, and then the cells were washed with

PBS twice. The medium was changed and the cells were incubated under normoxia or hypoxia (0.1% O_2) for 6 hrs. Then, fluorescence imaging was performed (a). Cellular fluorescence intensity was acquired at the fluorescent ROI in each cell. N.S. indicates not significant by Student's *t*-test (n = 4).

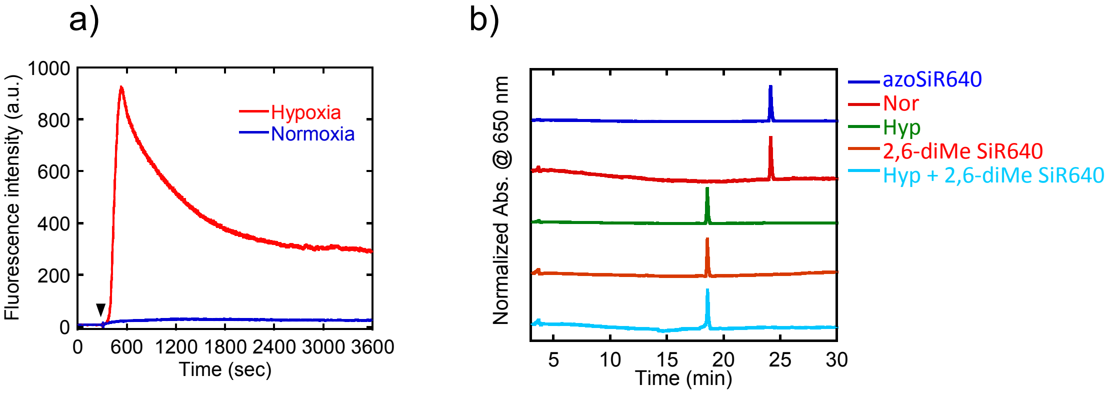


Fig. S6 (a) Time-dependent changes in the fluorescence intensity of **azoSiR640** (1 µM) in the presence of rat liver microsomes (226 µg/3 mL) under hypoxia or normoxia. Measurements were performed in potassium phosphate buffer (0.1 M; pH 7.4) containing DMSO (0.1%) as a cosolvent. As a cofactor for reductases, NADPH (50 µM) was added at 5 min (the black arrowhead indicates this time point). The excitation and emission wavelengths were 640 and 660 nm. (b) HPLC analyses of the reaction mixtures after *in vitro* assay. 5 µM **azoSiR640** was incubated with rat liver microsomes and 50 µM NADPH in 100 mM phosphate buffer (pH 7.4; 3 mL) at 37 °C for 10 min. Eluent A: H2O / 0.1% TFA, eluent B: 80% MeCN / 20% H2O / 0.1% TFA. A : B = 70 : 30 to 0 : 100 (20 min), linear gradient. **2,6-diMe SiR640** is the reaction product of **azoSiR640** after reduction under hypoxia.

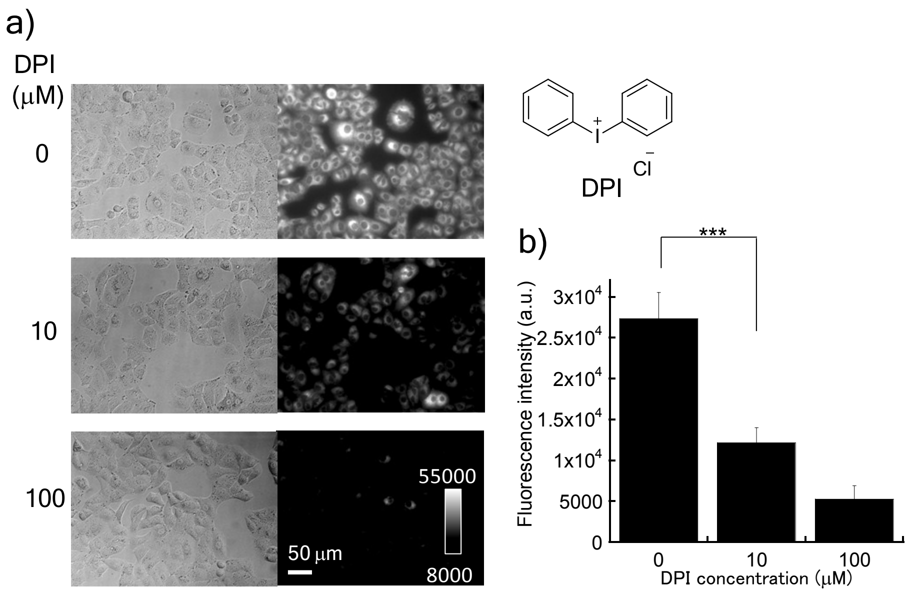


Fig. S7 (a) Fluorescence microscopy images of A549 cells under hypoxia (0.1% O_2) with or without DPI. A549 cells were incubated under hypoxia for 6 hr. (b) Fluorescence intensity of cells. Fluorescence intensity of each cell was determined at the fluorescent ROI of each cell. *** indicates $p<0.001$ by Student's t-test (n = 5).

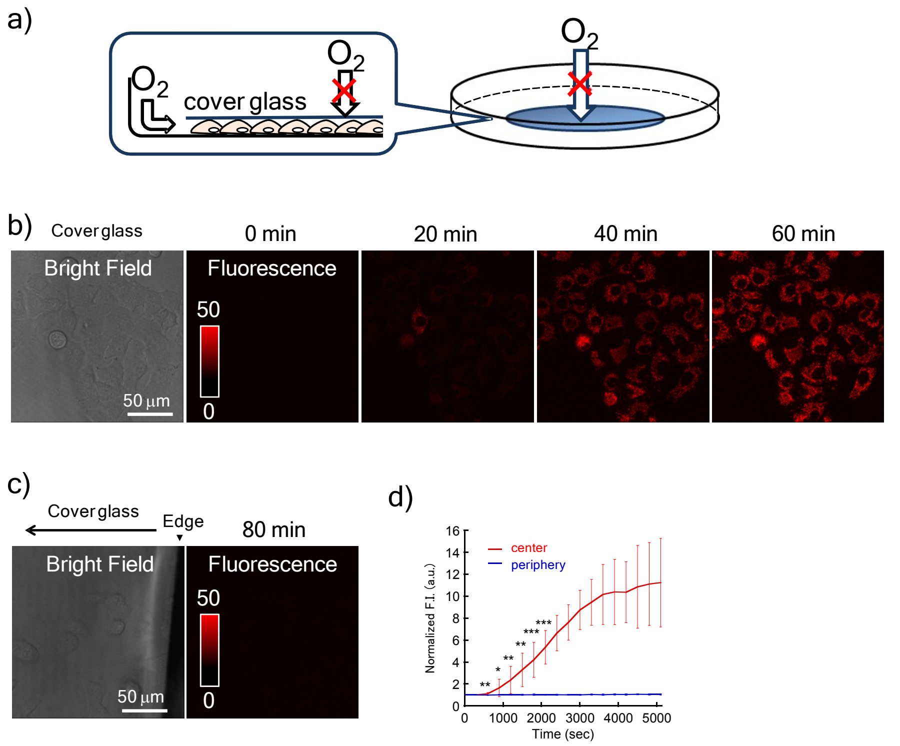


Fig. S8 (a) Schematic illustration of cellular hypoxia generated by a cover glass. (b) Confocal fluorescence microscopy images of A549 cell with 100 nM **azoSiR640** in the central part of the cover glass (center) at each time point. (c) Fluorescence image of A549 cells near the boundary of the cover glass (periphery) 80 min after mounting the cover glass. (d) Time-dependent change in fluorescence intensity at the center or periphery region of the cover glass. n=14, * indicates P<0.05, ** indicates P<0.01 and *** indicates P<0.001 by Student's *t*-test.

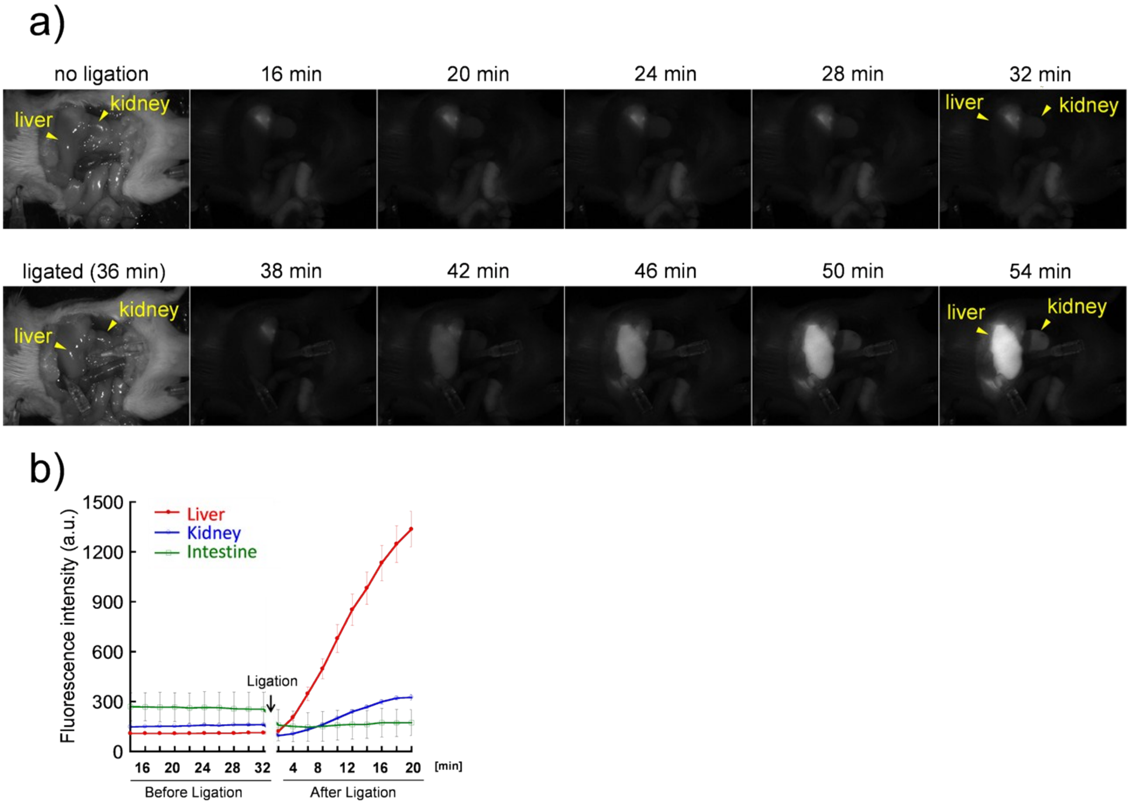


Fig. S9 Fluorescence images of mouse. ICR mouse was injected with 100 µM **azoSiR640** in 100 µL saline solution containing 1% DMSO as a co-solvent from an orbital vein. The portal vein and renal vein were ligated about 35 min after probe injection. Excitation and emission wavelengths were 635 nm and 700 nm, respectively. Exposure time: 300 ms.

Cartesian Coordinates and Total Electron Energies

2-Me SiR600

HOMO	-8.81 eV
LUMO	-6.11 eV

E(RB3LYP) = −1251.05125584 a.u.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	1.725592	2.870467	−0.046436
2	6	0	−1.010030	2.398801	−0.154223
3	6	0	0.826242	3.971549	−0.092622
4	6	0	−0.563618	3.698313	−0.145265
5	1	0	2.791193	3.091968	−0.004989
6	1	0	−2.078411	2.226371	−0.200088
7	6	0	1.290185	1.558369	−0.053524
8	6	0	−2.177893	−0.145721	−0.190250
9	6	0	0.048052	−1.284358	−0.108451
10	6	0	−0.121953	1.275460	−0.110296
11	6	0	1.485219	−1.376940	−0.053240
12	6	0	−0.677323	−0.046955	−0.126861
13	6	0	1.345392	−3.830443	−0.088172
14	6	0	−2.956614	−0.187877	0.987410
15	6	0	−2.795510	−0.193631	−1.449459
16	6	0	−0.068421	−3.744326	−0.137953
17	6	0	−0.683441	−2.515548	−0.148125
18	6	0	2.090938	−2.619717	−0.045547
19	6	0	−4.964584	−0.325483	−0.401929
20	6	0	−4.184632	−0.282815	−1.559398
21	6	0	−4.350149	−0.278805	0.851589
22	1	0	3.176702	−2.698436	−0.006255
23	1	0	−1.765437	−2.486670	−0.190976
24	1	0	−2.182305	−0.160363	−2.347035
25	1	0	−4.649163	−0.318487	−2.540729
26	1	0	−6.046536	−0.394585	−0.472204
27	1	0	−4.962184	−0.312687	1.749713
28	1	0	−0.663915	−4.652919	−0.170673
29	1	0	−1.274398	4.519736	−0.181391
30	6	0	−2.326323	−0.136766	2.361884

31	1	0	−3.091446	−0.184196	3.142135
32	1	0	−1.634207	−0.972515	2.524434
33	1	0	−1.754806	0.787556	2.513547
34	7	0	1.287807	5.243047	−0.086266
35	1	0	0.658321	6.032999	−0.122148
36	1	0	2.276991	5.446993	−0.052574
37	7	0	1.971381	−5.029617	−0.080845
38	1	0	2.978922	−5.100817	−0.049596
39	1	0	1.452031	−5.896077	−0.114510
40	14	0	2.561319	0.168609	0.019254
41	6	0	3.517747	0.232224	1.644923
42	1	0	4.220081	−0.606989	1.722326
43	1	0	4.103678	1.156597	1.721392
44	1	0	2.845493	0.188309	2.509305
45	6	0	3.720925	0.246136	−1.467125
46	1	0	4.316210	1.167603	−1.455781
47	1	0	4.424879	−0.595387	−1.463233
48	1	0	3.166715	0.215853	−2.412025

2-Me SiR650

HOMO -8.32 eV
LUMO -5.83 eV

E(RB3LYP) = −1408.28356535 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.750348	−1.617910	−0.036593
2	6	0	2.465052	1.138933	−0.151060
3	6	0	3.927046	−0.806217	−0.099092
4	6	0	3.731188	0.605071	−0.151514
5	1	0	2.869906	−2.695112	0.010235

6	1	0	2.370595	2.217277	−0.198402
7	6	0	1.472268	−1.089523	−0.032781
8	6	0	−0.000102	2.481993	−0.176400
9	6	0	−1.281509	0.336030	−0.097018
10	6	0	1.281587	0.336143	−0.096876
11	6	0	−1.472079	−1.089632	−0.032669
12	6	0	0.000007	0.978162	−0.113356
13	6	0	−3.926873	−0.806526	−0.099204
14	6	0	−0.000459	3.260146	1.002340
15	6	0	0.000111	3.105240	−1.433572
16	6	0	−3.731112	0.604760	−0.152099
17	6	0	−2.465016	1.138715	−0.151659
18	6	0	−2.750121	−1.618118	−0.036422
19	6	0	−0.000380	5.276243	−0.381694
20	6	0	−0.000048	4.497556	−1.540782
21	6	0	−0.000562	4.656946	0.870355
22	1	0	−2.869601	−2.695319	0.010630
23	1	0	−2.370620	2.217052	−0.199404
24	1	0	0.000383	2.492745	−2.332262
25	1	0	0.000110	4.965656	−2.521151
26	1	0	−0.000482	6.360633	−0.449437
27	1	0	−0.000780	5.267825	1.770021
28	1	0	−4.579296	1.276439	−0.197253
29	1	0	4.579329	1.276828	−0.196284
30	6	0	−0.000680	2.624489	2.375226
31	1	0	−0.000192	3.389005	3.157701
32	1	0	−0.883076	1.990932	2.529742
33	1	0	0.881020	1.989937	2.529590
34	7	0	5.168853	−1.352725	−0.107745
35	7	0	−5.168641	−1.353127	−0.107762
36	14	0	0.000139	−2.259089	0.082440
37	6	0	0.000303	−3.155047	1.745320
38	1	0	−0.883794	−3.796530	1.848488
39	1	0	0.884766	−3.796010	1.848588
40	1	0	0.000053	−2.446565	2.581589
41	6	0	0.000031	−3.488209	−1.351002

42	1	0	0.883490	−4.137876	−1.315779
43	1	0	−0.882417	−4.139177	−1.314465
44	1	0	−0.001057	−2.975132	−2.319415
45	6	0	−5.349472	−2.805486	−0.056505
46	1	0	−4.874737	−3.295578	−0.914970
47	1	0	−4.935139	−3.226364	0.867683
48	1	0	−6.414893	−3.031944	−0.084005
49	6	0	−6.356237	−0.496507	−0.167214
50	1	0	−6.406070	0.172326	0.700337
51	1	0	−6.363190	0.107825	−1.082148
52	1	0	−7.247385	−1.123352	−0.165978
53	6	0	5.349788	−2.805091	−0.057018
54	1	0	4.935400	−3.226344	0.866973
55	1	0	4.875172	−3.294899	−0.915712
56	1	0	6.415229	−3.031458	−0.084493
57	6	0	6.356388	−0.496002	−0.166930
58	1	0	6.363346	0.108551	−1.081720
59	1	0	6.406123	0.172627	0.700783
60	1	0	7.247583	−1.122780	−0.165783

2-Me SiR700

HOMO -8.02 eV

LUMO -5.68 eV

E(RB3LYP) = −1484.51498951 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.755047	−1.804307	0.011861
2	6	0	2.468668	0.996638	−0.100071
3	6	0	3.888978	−0.960193	−0.031953
4	6	0	3.721130	0.450853	−0.084373

5	1	0	2.889455	−2.882411	0.045080
6	1	0	2.360846	2.074130	−0.146495
7	6	0	1.477508	−1.258965	0.000043
8	6	0	0.000981	2.306335	−0.151528
9	6	0	−1.285666	0.166315	−0.103464
10	6	0	1.288966	0.168405	−0.063573
11	6	0	−1.473581	−1.261497	−0.048101
12	6	0	0.001333	0.801001	−0.096885
13	6	0	−3.883945	−0.966253	−0.138950
14	6	0	−0.015946	3.077364	1.031672
15	6	0	0.017824	2.938817	−1.403816
16	6	0	−3.716887	0.444975	−0.189396
17	6	0	−2.465250	0.992671	−0.172442
18	6	0	−2.750229	−1.808646	−0.065508
19	6	0	0.001521	5.103173	−0.337965
20	6	0	0.018226	4.331951	−1.502035
21	6	0	−0.015325	4.475176	0.909747
22	1	0	−2.884426	−2.886071	−0.014091
23	1	0	−2.357993	2.070331	−0.216318
24	1	0	0.030639	2.332088	−2.306372
25	1	0	0.031427	4.806736	−2.479190
26	1	0	0.001584	6.188047	−0.398463
27	1	0	−0.028275	5.079939	1.813546
28	6	0	−0.034586	2.431885	2.399764
29	1	0	−0.044961	3.190391	3.188134
30	1	0	−0.918524	1.796401	2.536688
31	1	0	0.844796	1.795738	2.560570
32	7	0	5.200355	−1.289996	−0.029472
33	7	0	−5.194081	−1.298343	−0.175614
34	14	0	0.001155	−2.423541	0.083302
35	6	0	−0.024275	−3.330008	1.740472
36	1	0	−0.910523	−3.971077	1.826085
37	1	0	0.858172	−3.972133	1.852885
38	1	0	−0.036490	−2.626366	2.580708
39	6	0	0.025230	−3.643056	−1.358333
40	1	0	0.907465	−4.293608	−1.311420

41	1	0	−0.858726	−4.292768	−1.342345
42	1	0	0.042204	−3.122971	−2.322842
43	6	0	−5.085561	1.087697	−0.300519
44	1	0	−5.233379	1.514939	−1.299988
45	1	0	−5.239885	1.893031	0.423805
46	6	0	−6.050998	−0.101099	−0.058585
47	1	0	−6.864400	−0.153320	−0.789088
48	1	0	−6.498314	−0.071111	0.945439
49	6	0	−5.747782	−2.626887	0.004507
50	1	0	−5.078379	−3.377718	−0.421854
51	1	0	−5.912052	−2.856226	1.067608
52	1	0	−6.707084	−2.690207	−0.517354
53	6	0	5.091940	1.098434	−0.083866
54	1	0	5.210833	1.847454	−0.872385
55	1	0	5.284796	1.598367	0.873377
56	6	0	6.047527	−0.106432	−0.280347
57	1	0	6.895971	−0.102703	0.411080
58	1	0	6.444939	−0.154795	−1.304488
59	6	0	5.747882	−2.629152	−0.134876
60	1	0	5.100503	−3.344821	0.377304
61	1	0	5.862822	−2.937909	−1.184280
62	1	0	6.730489	−2.654585	0.345160

Compound **25**

HOMO -8.55 eV

LUMO -5.96 eV

E(RB3LYP) = −1329.66757899 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.713242	−0.935327	−0.028700

2	6	0	1.560612	1.586810	−0.128820
3	6	0	3.567969	0.212842	−0.062682
4	6	0	2.929985	1.488065	−0.111322
5	1	0	3.172201	−1.917375	0.011020
6	1	0	1.125039	2.577936	−0.170729
7	6	0	1.334234	−0.845838	−0.043685
8	6	0	−1.201807	2.068130	−0.188013
9	6	0	−1.732935	−0.376860	−0.111220
10	6	0	0.696024	0.445154	−0.097945
11	6	0	−1.454034	−1.788658	−0.055152
12	6	0	−0.720726	0.643262	−0.122545
13	6	0	−3.860457	−2.285946	−0.102511
14	6	0	−1.466617	2.804096	0.987992
15	6	0	−1.384566	2.658686	−1.447703
16	6	0	−4.139305	−0.898086	−0.155243
17	6	0	−3.109292	0.012887	−0.160516
18	6	0	−2.499800	−2.694355	−0.052994
19	6	0	−2.092873	4.714920	−0.404245
20	6	0	−1.828827	3.977717	−1.560344
21	6	0	−1.911333	4.127728	0.850060
22	1	0	−2.295984	−3.763674	−0.012690
23	1	0	−3.360037	1.065674	−0.208409
24	1	0	−1.176519	2.079032	−2.344068
25	1	0	−1.965638	4.421435	−2.542458
26	1	0	−2.438696	5.742380	−0.475936
27	1	0	−2.118880	4.706361	1.747090
28	1	0	−5.170074	−0.555539	−0.194803
29	1	0	3.518417	2.396709	−0.137726
30	6	0	−1.283953	2.200375	2.363120
31	1	0	−1.524347	2.929208	3.142604
32	1	0	−1.932221	1.327870	2.513075
33	1	0	−0.252166	1.865358	2.527239
34	7	0	4.917974	0.094566	−0.048749
35	7	0	−4.859663	−3.200063	−0.099403
36	14	0	0.316044	−2.429889	0.020458
37	6	0	0.621620	−3.347853	1.641648

38	1	0	−0.002361	−4.247534	1.711962
39	1	0	1.667700	−3.669434	1.720430
40	1	0	0.398787	−2.716257	2.509133
41	6	0	0.690125	−3.528614	−1.468310
42	1	0	1.736100	−3.859851	−1.462230
43	1	0	0.063923	−4.429405	−1.462260
44	1	0	0.510400	−3.000885	−2.411849
45	6	0	5.556644	−1.223294	0.000023
46	1	0	5.274434	−1.768015	0.908836
47	1	0	5.289152	−1.827010	−0.875382
48	1	0	6.638326	−1.093563	0.004819
49	6	0	5.768434	1.288423	−0.084319
50	1	0	5.597133	1.868477	−0.998676
51	1	0	5.584225	1.930816	0.784714
52	1	0	6.813438	0.981294	−0.065948
53	1	0	−5.830052	−2.920860	−0.138763
54	1	0	−4.669282	−4.191809	−0.067787

Compound **26** (**2-Me SiR640**)
HOMO -8.37 eV
LUMO -5.87 eV

E(RB3LYP) = −1367.78379453 a.u.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	3.079817	−2.300720	−0.029719
2	6	0	3.176517	0.471590	−0.122407
3	6	0	4.341617	−1.648261	−0.052125
4	6	0	4.358057	−0.233578	−0.098867
5	1	0	3.075274	−3.389605	0.004479
6	1	0	3.230417	1.552732	−0.162012

7	6	0	1.884611	−1.602658	−0.051234
8	6	0	0.930762	2.141351	−0.187239
9	6	0	−0.646823	0.207611	−0.106372
10	6	0	1.896316	−0.165236	−0.098942
11	6	0	−1.032281	−1.183996	−0.060958
12	6	0	0.710198	0.652989	−0.121361
13	6	0	−3.377876	−0.546681	−0.069545
14	6	0	1.048624	2.917495	0.986837
15	6	0	1.019304	2.750900	−1.447977
16	6	0	−3.015988	0.829848	−0.116386
17	6	0	−1.701146	1.194155	−0.134873
18	6	0	−2.371563	−1.543109	−0.041996
19	6	0	1.342086	4.904056	−0.409062
20	6	0	1.224212	4.127312	−1.563547
21	6	0	1.254227	4.298450	0.846639
22	1	0	−2.657245	−2.590833	0.001863
23	1	0	−1.441630	2.245735	−0.174804
24	1	0	0.928423	2.139941	−2.343121
25	1	0	1.291857	4.584653	−2.546675
26	1	0	1.502605	5.976061	−0.483345
27	1	0	1.347632	4.907367	1.742744
28	1	0	5.307520	0.295242	−0.118590
29	6	0	0.959727	2.295757	2.363220
30	1	0	1.065420	3.057292	3.141440
31	1	0	−0.001422	1.790176	2.519903
32	1	0	1.745194	1.546316	2.522415
33	7	0	5.493929	−2.362223	−0.029806
34	1	0	6.395998	−1.907707	−0.050938
35	1	0	5.489881	−3.371994	−0.002829
36	7	0	−4.718200	−0.691867	−0.061654
37	14	0	0.262305	−2.554294	−0.026763
38	6	0	0.106021	−3.576501	1.552909
39	1	0	−0.862408	−4.090124	1.597943
40	1	0	0.885926	−4.346646	1.600715
41	1	0	0.197172	−2.951045	2.448170
42	6	0	0.103817	−3.643196	−1.560872

43	1	0	0.883909	−4.414420	−1.578030
44	1	0	−0.864965	−4.157628	−1.582335
45	1	0	0.192879	−3.055426	−2.481516
46	6	0	−4.283234	1.660020	−0.173479
47	1	0	−4.391614	2.139060	−1.153928
48	1	0	−4.305270	2.453017	0.579996
49	6	0	−5.402545	0.612093	0.059622
50	1	0	−6.211866	0.674025	−0.674897
51	1	0	−5.847386	0.694912	1.061003
52	6	0	−5.454417	−1.932495	0.096979
53	1	0	−4.885028	−2.767614	−0.316724
54	1	0	−5.672531	−2.136385	1.154909
55	1	0	−6.401360	−1.861522	−0.446416

Compound **27**

HOMO -8.21 eV

LUMO -5.76 eV

E(RB3LYP) = −1446.41115483 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−3.127430	−1.026159	−0.035986
2	6	0	−2.298886	1.626897	−0.138054
3	6	0	−4.105849	0.007700	−0.075131
4	6	0	−3.643153	1.350868	−0.126459
5	1	0	−3.469875	−2.056539	0.001148
6	1	0	−1.991806	2.664817	−0.181918
7	6	0	−1.767810	−0.757993	−0.045343
8	6	0	0.378110	2.451269	−0.189969
9	6	0	1.222343	0.103469	−0.067202
10	6	0	−1.299536	0.600292	−0.097269

11	6	0	1.123136	−1.335037	−0.009727
12	6	0	0.088220	0.975683	−0.108514
13	6	0	3.546646	−1.515412	0.010101
14	6	0	0.504584	3.040100	−1.457176
15	6	0	0.521949	3.236461	0.975153
16	6	0	3.662860	−0.098120	−0.042258
17	6	0	2.543811	0.683165	−0.081428
18	6	0	2.267063	−2.120127	0.025165
19	6	0	0.919277	5.189106	−0.442735
20	6	0	0.792650	4.604485	0.819593
21	6	0	0.774387	4.403908	−1.588367
22	1	0	2.186556	−3.203628	0.053417
23	1	0	2.650117	1.761004	−0.125540
24	1	0	0.905209	5.220302	1.708797
25	1	0	1.128957	6.251715	−0.528925
26	1	0	0.868842	4.845394	−2.576549
27	1	0	−4.364091	2.164429	−0.158882
28	7	0	−5.432846	−0.254219	−0.065490
29	1	0	−6.060756	0.539847	−0.097426
30	7	0	4.764182	−2.097889	0.040781
31	14	0	−0.553943	−2.194333	−0.002179
32	6	0	−0.745975	−3.276091	−1.538405
33	1	0	−0.005484	−4.085598	−1.545782
34	1	0	−1.739417	−3.740536	−1.570996
35	1	0	−0.617308	−2.694077	−2.458052
36	6	0	−0.769794	−3.212958	1.573374
37	1	0	−1.763594	−3.676411	1.609551
38	1	0	−0.030437	−4.021939	1.624453
39	1	0	−0.654609	−2.595259	2.471253
40	6	0	5.134297	0.265713	−0.012284
41	1	0	5.399931	0.734159	0.943168
42	1	0	5.416370	0.963286	−0.806502
43	6	0	5.838999	−1.106537	−0.170698
44	1	0	6.640165	−1.267410	0.557587
45	1	0	6.263063	−1.240563	−1.175899
46	6	0	5.040030	−3.520344	−0.035712

47	1	0	4.247525	−4.087300	0.458177
48	1	0	5.126655	−3.858907	−1.078283
49	1	0	5.982082	−3.731927	0.478445
50	1	0	0.389916	2.422843	−2.345229
51	6	0	0.391825	2.637316	2.358226
52	1	0	−0.594236	2.181765	2.512908
53	1	0	1.137898	1.851754	2.532445
54	1	0	0.528757	3.402504	3.127998
55	6	0	−6.052828	−1.579171	−0.015510
56	1	0	−5.722084	−2.167585	−0.881951
57	1	0	−5.716244	−2.102754	0.889331
58	6	0	−7.574686	−1.457925	−0.014986
59	1	0	−7.935113	−0.960860	−0.923275
60	1	0	−8.027158	−2.453472	0.021989
61	1	0	−7.929411	−0.896980	0.857625

Compound **28**

HOMO -8.16 eV

LUMO -5.74 eV

E(RB3LYP) = −1446.39942243 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	−3.020626	−1.471975	−0.035183
2	6	0	−2.510143	1.251141	−0.142309
3	6	0	−4.127129	−0.567714	−0.086399
4	6	0	−3.816553	0.822052	−0.137906
5	1	0	−3.226456	−2.536298	0.006215
6	1	0	−2.329617	2.318363	−0.188878
7	6	0	−1.703364	−1.048066	−0.035798
8	6	0	0.047832	2.393839	−0.177869

9	6	0	1.165134	0.161229	−0.067713
10	6	0	−1.396364	0.355877	−0.092518
11	6	0	1.236158	−1.278978	−0.005327
12	6	0	−0.063889	0.893766	−0.103137
13	6	0	3.664329	−1.171821	−0.011931
14	6	0	0.107993	3.002076	−1.440853
15	6	0	0.090180	3.183255	0.992507
16	6	0	3.612274	0.249141	−0.067225
17	6	0	2.408559	0.892844	−0.095493
18	6	0	2.465358	−1.923344	0.018392
19	6	0	0.254784	5.178871	−0.411421
20	6	0	0.195032	4.574837	0.846712
21	6	0	0.210856	4.389439	−1.562417
22	1	0	2.514390	−3.008748	0.050724
23	1	0	2.386042	1.975523	−0.142412
24	1	0	0.228583	5.193886	1.740180
25	1	0	0.333883	6.259656	−0.490170
26	1	0	0.255195	4.845604	−2.547454
27	1	0	−4.606954	1.561292	−0.178209
28	7	0	−5.410883	−1.011241	−0.086362
29	7	0	4.942525	−1.606569	0.006382
30	14	0	−0.328447	−2.329439	0.041531
31	6	0	−0.398191	−3.482094	−1.452736
32	1	0	0.437781	−4.192696	−1.445548
33	1	0	−1.324997	−4.069332	−1.454260
34	1	0	−0.354881	−2.921653	−2.393557
35	6	0	−0.414659	−3.305986	1.655874
36	1	0	−1.346507	−3.881877	1.717911
37	1	0	0.415893	−4.018648	1.733105
38	1	0	−0.371297	−2.643469	2.527865
39	6	0	5.030784	0.783907	−0.053796
40	1	0	5.249638	1.282584	0.898267
41	1	0	5.220160	1.508197	−0.851631
42	6	0	5.890458	−0.495973	−0.218911
43	1	0	6.713411	−0.559652	0.499977
44	1	0	6.315547	−0.581398	−1.229006

45	6	0	5.383326	−2.986709	−0.071790
46	1	0	4.672282	−3.641393	0.437532
47	1	0	5.491526	−3.317486	−1.114864
48	1	0	6.352453	−3.082798	0.426262
49	1	0	0.073012	2.381293	−2.333171
50	6	0	0.023430	2.564368	2.371387
51	1	0	−0.908842	2.005311	2.520493
52	1	0	0.848685	1.861847	2.542631
53	1	0	0.076138	3.334634	3.146479
54	6	0	−5.709478	−2.443629	−0.040308
55	1	0	−5.288850	−2.966127	−0.908106
56	1	0	−6.790239	−2.581616	−0.053345
57	6	0	−6.522802	−0.059004	−0.135536
58	1	0	−6.507340	0.613378	0.730610
59	1	0	−6.490078	0.542650	−1.051907
60	1	0	−7.463233	−0.609016	−0.122631
61	1	0	−5.318295	−2.903289	0.875541

Compound **29**

HOMO -8.08 eV

LUMO -5.68 eV

E(RB3LYP) = −1525.02742914 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	−2.658779	−1.115603	−0.142794
2	6	0	−1.910381	1.549515	−0.152762
3	6	0	−3.690178	−0.121484	−0.199094
4	6	0	−3.249056	1.236416	−0.182487
5	1	0	−2.947087	−2.160273	−0.119109
6	1	0	−1.640061	2.598765	−0.147787

7	6	0	−1.310707	−0.809906	−0.116287
8	6	0	0.741406	2.464651	−0.140480
9	6	0	1.654203	0.137835	−0.075767
10	6	0	−0.877923	0.562046	−0.127206
11	6	0	1.595529	−1.303295	−0.054993
12	6	0	0.494941	0.979172	−0.106352
13	6	0	4.023124	−1.415377	−0.022251
14	6	0	0.851124	3.098575	−1.387288
15	6	0	0.859344	3.215855	1.049702
16	6	0	4.098925	0.004958	−0.037704
17	6	0	2.957796	0.754963	−0.065415
18	6	0	2.761955	−2.056310	−0.031682
19	6	0	1.198691	5.225129	−0.302545
20	6	0	1.088159	4.595893	0.939702
21	6	0	1.079604	4.473496	−1.473398
22	1	0	2.712526	−3.142101	−0.030502
23	1	0	3.033032	1.836220	−0.082245
24	1	0	1.179694	5.185498	1.848892
25	1	0	1.375673	6.295946	−0.353562
26	1	0	1.161997	4.949617	−2.446492
27	1	0	−3.961744	2.050097	−0.190385
28	7	0	−5.011005	−0.444604	−0.268891
29	7	0	5.257799	−1.963852	0.002677
30	14	0	−0.056381	−2.210486	−0.073293
31	6	0	−0.201701	−3.287200	−1.618390
32	1	0	0.559335	−4.077442	−1.624386
33	1	0	−1.182233	−3.777371	−1.664973
34	1	0	−0.079370	−2.695355	−2.532657
35	6	0	−0.255593	−3.250548	1.491103
36	1	0	−1.233843	−3.746946	1.512404
37	1	0	0.509442	−4.035220	1.543391
38	1	0	−0.170342	−2.637440	2.395501
39	6	0	5.559171	0.409308	0.013293
40	1	0	5.805800	0.852237	0.985967
41	1	0	5.826383	1.140798	−0.755106
42	6	0	6.302767	−0.936795	−0.185440

43	1	0	7.111933	−1.093879	0.534712
44	1	0	6.725506	−1.029857	−1.196049
45	6	0	5.572195	−3.374881	−0.118899
46	1	0	4.801122	−3.977988	0.366325
47	1	0	5.656740	−3.681127	−1.171774
48	1	0	6.525130	−3.574955	0.379480
49	1	0	0.756166	2.507493	−2.295250
50	6	0	0.743174	2.568756	2.412257
51	1	0	−0.230218	2.081121	2.548488
52	1	0	1.510355	1.798965	2.563532
53	1	0	0.856676	3.312178	3.206813
54	6	0	−5.457867	−1.843613	−0.167621
55	1	0	−4.783866	−2.469315	−0.758500
56	1	0	−6.428143	−1.918831	−0.657297
57	6	0	−6.015431	0.647725	−0.265556
58	1	0	−5.951322	1.181421	0.693215
59	1	0	−5.732483	1.357934	−1.049765
60	6	0	−7.463464	0.228356	−0.509683
61	1	0	−8.076536	1.135963	−0.501999
62	1	0	−7.600358	−0.248938	−1.485732
63	1	0	−7.855034	−0.433838	0.268772
64	6	0	−5.558575	−2.355367	1.275314
65	1	0	−4.593661	−2.304100	1.791007
66	1	0	−6.280261	−1.767922	1.853396
67	1	0	−5.893885	−3.398976	1.277626

Compound **30**

HOMO -8.07 eV

LUMO -5.66 eV

E(RB3LYP) = −1523.82909578 a.u.

Center	Atomic	Atomic	Coordinates (Angstroms)		

Number	Number	Type	X	Y	Z
1	6	0	−2.676466	−1.110638	−0.018251
2	6	0	−1.910795	1.554607	−0.124928
3	6	0	−3.690613	−0.101973	−0.054670
4	6	0	−3.251224	1.253202	−0.106003
5	1	0	−2.990632	−2.148862	0.032782
6	1	0	−1.628179	2.599292	−0.176685
7	6	0	−1.326078	−0.815134	−0.030641
8	6	0	0.748413	2.441240	−0.197463
9	6	0	1.644009	0.111187	−0.067171
10	6	0	−0.886486	0.554884	−0.087742
11	6	0	1.576572	−1.327809	0.000916
12	6	0	0.489522	0.960191	−0.107454
13	6	0	4.003480	−1.456123	0.013445
14	6	0	0.852627	3.027290	−1.467981
15	6	0	0.886337	3.234589	0.962832
16	6	0	4.088199	−0.037925	−0.051650
17	6	0	2.951709	0.718860	−0.092163
18	6	0	2.738214	−2.087996	0.037700
19	6	0	1.233427	5.188537	−0.466347
20	6	0	1.128908	4.606955	0.799424
21	6	0	1.094374	4.395564	−1.607319
22	1	0	2.681333	−3.172816	0.074164
23	1	0	3.034646	1.798352	−0.145591
24	1	0	1.236760	5.228687	1.685117
25	1	0	1.421482	6.254683	−0.558822
26	1	0	1.171943	4.834451	−2.598160
27	1	0	−3.973859	2.059810	−0.147502
28	7	0	−5.002287	−0.419700	−0.041348
29	7	0	5.234985	−2.011926	0.045333
30	14	0	−0.080787	−2.223574	0.020303
31	6	0	−0.254547	−3.322160	−1.506455
32	1	0	0.503383	−4.115380	−1.511708
33	1	0	−1.237736	−3.808565	−1.530868
34	1	0	−0.143132	−2.744327	−2.431021

35	6	0	−0.269878	−3.236773	1.603191
36	1	0	−1.254067	−3.719888	1.646067
37	1	0	0.485867	−4.030279	1.657273
38	1	0	−0.164300	−2.610704	2.496486
39	6	0	5.551534	0.358032	−0.030202
40	1	0	5.811600	0.833075	0.923656
41	1	0	5.815041	1.060444	−0.826526
42	6	0	6.284285	−0.999239	−0.189868
43	1	0	7.100410	−1.136692	0.526448
44	1	0	6.695283	−1.130031	−1.201181
45	6	0	5.538628	−3.428431	−0.030480
46	1	0	4.769440	−4.008843	0.484578
47	1	0	5.608867	−3.772203	−1.072821
48	1	0	6.496022	−3.617639	0.463601
49	1	0	0.743235	2.403844	−2.352374
50	6	0	0.779203	2.639243	2.349500
51	1	0	−0.196108	2.164277	2.513515
52	1	0	1.542379	1.869736	2.521246
53	1	0	0.906425	3.410598	3.114841
54	6	0	−5.524479	−1.799282	−0.084426
55	1	0	−5.021877	−2.376219	−0.867659
56	6	0	−6.091591	0.576012	0.010577
57	1	0	−5.894365	1.319085	0.790125
58	1	0	−6.166430	1.100701	−0.952473
59	1	0	−5.347578	−2.299724	0.878456
60	6	0	−7.023699	−1.616195	−0.359435
61	1	0	−7.618375	−2.441480	0.041723
62	1	0	−7.202546	−1.566800	−1.440090
63	6	0	−7.343624	−0.264169	0.297809
64	1	0	−8.250258	0.202335	−0.097035
65	1	0	−7.472307	−0.386790	1.379822

Compound **31**

HOMO -8.02 eV

LUMO -5.69 eV

E(RB3LYP) = −1602.45157625 a.u.

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	1.696396	−1.837182	−0.002623
2	6	0	1.720685	0.926267	−0.090951
3	6	0	2.957128	−1.162027	−0.021627
4	6	0	2.936859	0.275977	−0.063673
5	1	0	1.693614	−2.920332	0.032853
6	1	0	1.727502	2.007250	−0.126596
7	6	0	0.481876	−1.176896	−0.028077
8	6	0	−0.580452	2.532262	−0.177373
9	6	0	−2.096173	0.543589	−0.099754
10	6	0	0.453867	0.259842	−0.077014
11	6	0	−2.444652	−0.850614	−0.048724
12	6	0	−0.746118	1.037158	−0.108937
13	6	0	−4.840344	−0.289175	−0.082562
14	6	0	−0.516869	3.316527	0.995550
15	6	0	−0.493821	3.141865	−1.438216
16	6	0	−4.495900	1.088879	−0.133420
17	6	0	−3.180135	1.479790	−0.142777
18	6	0	−3.776350	−1.234348	−0.041280
19	6	0	−0.280976	5.309807	−0.401527
20	6	0	−0.345308	4.525512	−1.555074
21	6	0	−0.365643	4.704380	0.854518
22	1	0	−4.029101	−2.290172	−0.004077
23	1	0	−2.962977	2.540199	−0.187694
24	1	0	−0.545023	2.525138	−2.332551
25	1	0	−0.281989	4.982888	−2.538539
26	1	0	−0.166900	6.387741	−0.476729
27	1	0	−0.315982	5.319339	1.750077
28	6	0	−0.611132	2.695711	2.371935

29	1	0	−0.525174	3.459883	3.150109
30	1	0	−1.567303	2.177749	2.518489
31	1	0	0.182171	1.956701	2.540119
32	7	0	4.120792	−1.852846	−0.000587
33	7	0	−6.139754	−0.666929	−0.075583
34	14	0	−1.111900	−2.179485	0.000043
35	6	0	−1.235167	−3.192716	1.589203
36	1	0	−2.188778	−3.732960	1.639222
37	1	0	−0.433374	−3.939607	1.644635
38	1	0	−1.163224	−2.555716	2.478104
39	6	0	−1.228187	−3.291492	−1.522000
40	1	0	−0.424674	−4.038596	−1.529131
41	1	0	−2.180654	−3.835729	−1.540288
42	1	0	−1.155712	−2.711008	−2.448756
43	6	0	−6.638774	−2.042008	−0.027394
44	1	0	−6.251018	−2.599323	−0.890815
45	1	0	−6.262159	−2.532805	0.880192
46	6	0	4.083324	−3.319220	0.040122
47	1	0	3.580681	−3.674149	0.946779
48	1	0	3.568189	−3.723625	−0.838233
49	1	0	5.096460	−3.712117	0.043401
50	6	0	5.354766	0.290878	−0.055107
51	1	0	6.310509	0.810379	−0.065105
52	6	0	5.474944	−1.210788	−0.019956
53	6	0	4.214771	0.998456	−0.077647
54	6	0	6.255172	−1.603199	1.259621
55	1	0	6.462031	−2.677015	1.310909
56	1	0	7.220297	−1.085766	1.269579
57	1	0	5.700959	−1.307513	2.156120
58	6	0	6.245692	−1.662692	−1.285686
59	1	0	7.211541	−1.148098	−1.326621
60	1	0	6.450124	−2.738240	−1.289042
61	1	0	5.684810	−1.407279	−2.190336
62	6	0	4.225867	2.506094	−0.117639
63	1	0	3.720769	2.889461	−1.013300
64	1	0	3.714910	2.937240	0.752689

65	1	0	5.252157	2.883686	−0.124271
66	1	0	−6.835686	0.068166	−0.108696
67	6	0	−8.165218	−2.058070	−0.036413
68	1	0	−8.563038	−1.597062	−0.948062
69	1	0	−8.526524	−3.090193	0.000441
70	1	0	−8.574298	−1.529578	0.832624
71	1	0	−5.284547	1.836875	−0.167873

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