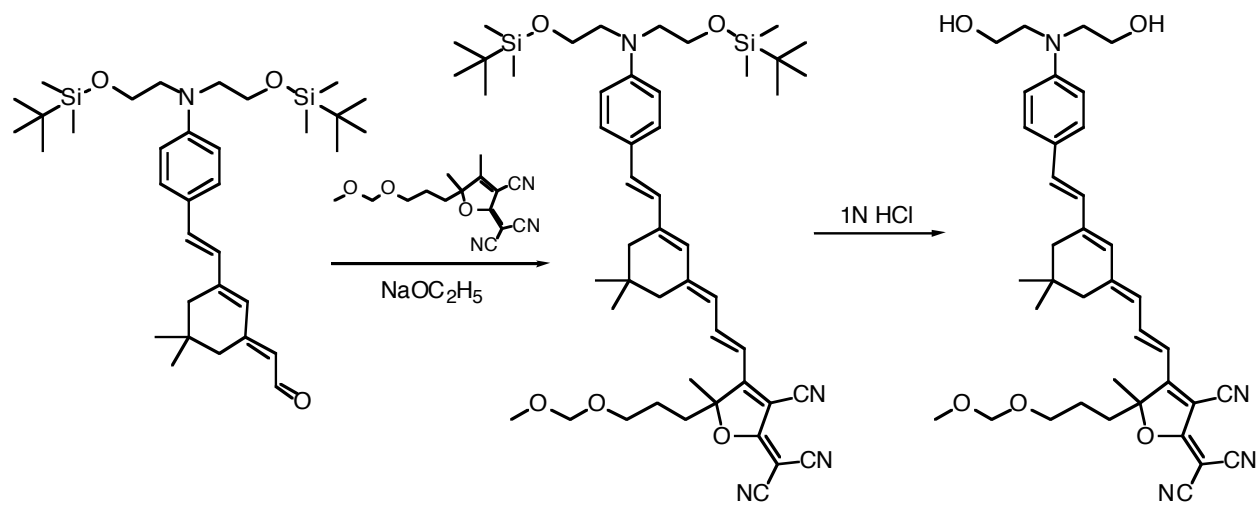


Supporting information

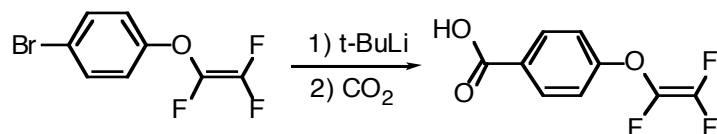


Preparation of 2-[4-(3-{3-[2-(4-{Bis-[2-(tert-butyl-dimethyl-silyloxy)-ethyl]-amino}-phenyl)-vinyl]-5,5-dimethyl-cyclohex-2-enylidene}-propenyl)-3-cyano-5-(3-methoxymethoxy-propyl)-5-methyl-5H-furan-2-ylidene]-malononitrile:

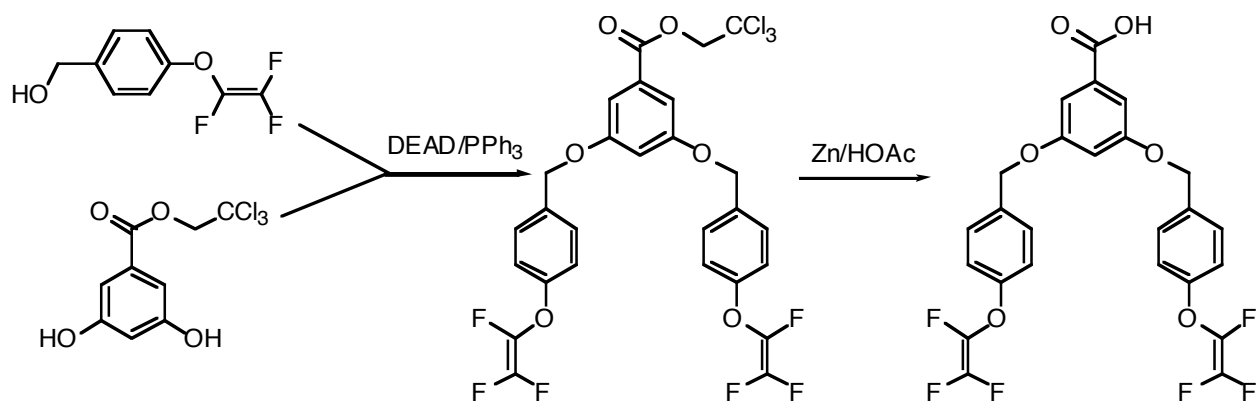
[3-(2-{4-[Bis-(2-trimethylsilyloxy-ethyl)-amino]-phenyl}-vinyl)-5,5-dimethyl-cyclohex-2-enylidene]-acetaldehyde, (1.0 g, 1.71 mmole) and 2-[3-Cyano-5-(3-methoxymethoxy-propyl)-4,5-dimethyl-5H-furan-2-ylidene]-malononitrile (0.59 g, 1.2 equivalent) and sodium ethoxide (0.036, 0.53 mmol) mixed in 3 mL ethanol. The mixture was heated by microwave oven for 16 mins and monitored by TLC. The crude mixture was directly loaded into a column of silica gel and eluted with ethylacetate/ hexane (2:3, v/v). The product was obtained as dark bluish solid in 0.36 g, yield 25%. ¹H NMR (CDCl₃, TMS), trans-form: δ 8.02 (q, 1H), 7.37 (d, 2H), 6.83 (m, 4H), 6.38 (s, 1H), 6.34 (d, 1H) 6.24 (d, 1H), 4.5 (s, 2H), 3.77 (t, 4H), 3.66 (t, 2H), 3.5 (t, 4H), 3.1 (s, 3H), 2.42 (s, 2H), 2.40 (s, 2H), 2.2 (m, 2H), 1.6 (s, 3H), 1.41 (m, 2H), 1.2 (s, 2H), 1.05 (s, 3H), 0.88 (s, 18H), 0.02 (s, 12 H). Anal. Calcd for C₄₉H₇₂N₄O₅Si₂: C, 68.97; H, 8.50; N, 6.57. Found: C, 68.91; H, 8.43; N, 6.73.

Preparation of 2-[4-{3-[3-(2-{4-[Bis-(2-hydroxy-ethyl)-amino]-phenyl}-vinyl)-5,5-dimethyl-cyclohex-2-enylidene]-propenyl}-3-cyano-5-(3-methoxymethoxy-propyl)-5-methyl-5H-furan-2-ylidene]-malononitrile (compound 8):

The above precursor was dissolved in 50 mL of acetone and then 11 mL of 1N HCl aqueous solution was added dropwise. The reaction mixture was allowed to stir at room temperature for 1 hour and monitored by TLC. After neutralized with dilute sodium bicarbonate solution, most of the solvent was removed by roto-evaporator. The resultant precipitation was collected by filtration, washed by methylene dichloride, dried in vacuum oven and used for next step without further purification.



Preparation of 4-Trifluorovinyl-oxy-benzoic acid (compound 9). To the solution of 1-Bromo-4-trifluorovinyl-oxy-benzene (2.53 g, 10 mmol) in 15 mL of dried diethyl ether at $-78\text{ }^{\circ}\text{C}$ was added dropwise 6 mL of tert-butyllithium (1.7 M in pentane, 10.2 mmol). The reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 hour. Then the stream of carbon dioxide was introduced to the reaction solution at the same temperature for 45 mins. After warmed up to room temperature, the reaction solution was neutralized by 55 mL of 1.2N HCl solution. Evaporation of the solvent afforded white precipitation, which was collected by filtration, washed by large amount of hexane, and dried in vacuum oven. Product: 1.21 g, and 55.5% yield. $^1\text{H NMR}$ (CDCl_3): δ 8.2 (d, $J = 8.8\text{ Hz}$, 2H), 7.18 (d, $J = 8.8\text{ Hz}$, 2H). Anal. Calcd for $\text{C}_9\text{H}_5\text{F}_3\text{O}_3$: C, 49.56; H, 2.31. Found: C, 49.62; H, 2.25.



Preparation of 3,5-Bis-(4-trifluorovinyloxy-benzyloxy)-benzoic acid 2,2,2-trichloro-ethyl ester.

To a solution of 3,5-Dihydroxy-benzoic acid 2,2,2-trichloro-ethyl ester (2.04 g, 7.14 mmol), 4-[(trifluoroethenyl)oxy]benzyl alcohol (3.2 g, 15.6 mmol), and triphenylphosphine (6.0 g, 22.9 mmol) in freshly distilled THF (40 mL) was added dropwise diethyl azocarboxylate (3.6 mL, 22.7 mmol). The reaction mixture was allowed to stir at room temperature overnight, and then all the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using CH₂Cl₂/hexane (1:3, v/v) as the eluent to afford 3,5-Bis-(4-trifluorovinyloxy-benzyloxy)-benzoic acid 2,2,2-trichloro-ethyl ester as colorless oil (3.39 g, yield 72 %).

Preparation of 3,5-Bis-(4-trifluorovinyloxy-benzyloxy)-benzoic acid (compound 14). To the solution of 3,5-Bis-(4-trifluorovinyloxy-benzyloxy)-benzoic acid 2,2,2-trichloro-ethyl ester (3.38 g, 5.14 mmol) in the mixture solvent of THF/acetic acid (10 mL/10 mL) was added 2.3 g of the zinc dust. The reaction mixture was allowed to stir vigorously under nitrogen for 3 h, and filtered. Most of the solvent was evaporated, and the residue of the filtration was redissolved in diethyl ether. The solution was washed by water (100 mL × 3), and dried over sodium sulfate. The crude product was purified by column chromatography using CH₂Cl₂/acetone (2:1, v/v) as the eluent to afford 3,5-Bis-(4-trifluorovinyloxy-benzyloxy)-benzoic acid as white solid (2.60 g, yield 96%). ¹H NMR (CDCl₃): δ 7.36 (d, J = 8.8 Hz, 4H), 7.26 (d, J = 2.6 Hz, 2H), 7.04 (d, J = 8.8 Hz, 4H), 6.72 (t, J = 2.6 Hz, 1H), 4.97 (s, 4H). Anal. Calcd for C₂₅H₁₆F₆O₆: C, 57.04; H, 3.06. Found: C, 57.15; H, 3.12.