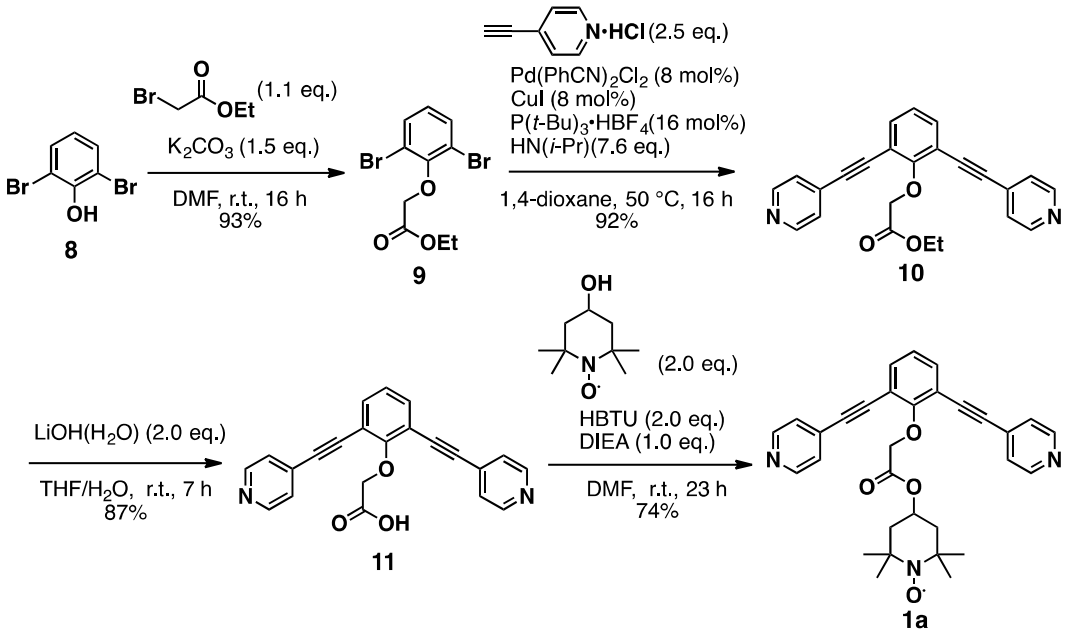
[Contents]

1. Genaral

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DRX-500 spectrometer equipped with a 5 mm BBO-Z-gradient probe, a Bruker AV-500 spectrometer equipped with a 5 mm TCI gradient cryo probe. All NMR spectral data were collected at 300 K and the chemical shift values reported here are with respect to an internal TMS standard for $CDCl_3$, and to a residual solvent signal for DMSO-d_6 and CD_3NO_2. Melting points were determined on a Yanaco MP-500V micro melting point apparatus. ESI-TOF-MS and CSI-TOF-MS spectra were measured on a Bruker maXis. The data analysis of mass spectra were processed on a Bruker Data Analysis (Version 4.0 SP 2) software and the simulations were performed on a Bruker IsotopePattern software. IR spectra for organic compounds were recorded with a JASCO FT/IR-6700 spectrometer. Optical rotation was measured with JASCO P-2200. Preparative size-exclusion chromatography (SEC) was carried out using a LC-908 (JAI) equipped with JAIGEL 1H and 2H columns (eluent: chloroform). Reagents and solvents were purchased from TCI, WAKO Pure Chemical Industries, Sigma-Aldrich or Kanto Chemical. $[Pd(CH_3CN)_4](BF_4)_2$ was purchased from Strem Chemicals. All the chemicals were of reagent grade and used without any further purification.

2. Synthetic Procedure and Physical Properties

• Synthesis and physical properties of ligand 1a



• Synthesis of Ethyl 2-(2,6-dibromophenoxy)acetate (9):

2,6-dibromophenol **8** (5.04 g, 20.0 mmol) and K_2CO_3 (4.15 g, 30.0 mmol) were dissolved in DMF (60 mL). Ethyl bromoacetate (2.44 mL, 22.0 mmol) was added, and the resulting mixture was stirred at room temperature for 16 h. The reaction mixture was diluted with H_2O (200 mL), and extracted with AcOEt (200 mL). The organic layer was washed with H_2O (3 x 25 mL), dried over anhydrous $MgSO_4$, filtrated and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (AcOEt/Hexane = 5:95) to give the title compound **9** (6.28 g, 18.6 mmol) as a colorless liquid in 93% yield.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 7.51 (d, J = 8.0 Hz, 2H), 6.91 (t, J = 8.0 Hz, 1H), 4.62 (s, 2H), 4.33 (q, J = 7.0 Hz, 2H), 1.35 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ 167.8 (C), 152.3 (C), 132.8 (CH), 127.0 (CH), 118.1 (C), 69.1 (CH_2), 61.4 (CH_2), 14.2 (CH_3); IR (ATR, cm^{-1}): 2936, 1762, 1734, 1448, 1431, 1296, 1199, 1076, 1051, 764, 719, 710, 499, 456, 429; HR-ESI-TOF-MS: *m/z* = 360.8876 (calculated for $C_{10}H_{10}Br_2O_3Na$: 360.8869 $[M+Na]^+$).

• Synthesis of Ethyl 2-(2,6-bis(pyridin-4-ylethynyl)phenoxy)acetate (10):

4-ethynyl pyridine hydrochloride (8.02 g, 57.5 mmol) was added to a mixture of compound **9** (7.77 g, 23.0 mmol), P(*t*-Bu)$_3$·HBF$_4$ (1.06 g, 3.68 mmol), CuI (350 mg, 1.84 mmol) and Pd(PhCN)$_2$Cl$_2$ (705 mg, 1.84 mmol), diisopropylamine (24.5 mL, 175 mmol) in degassed 1,4-dioxane (130 mL), and the resulting mixture was stirred at 50 °C for 16 h under Ar atmosphere. The reaction mixture was diluted with CHCl$_3$ (100 mL) and filtrated through celite pad. After washed with ethylenediamine aq., the water layer was extracted with CHCl$_3$ (2 x 100 mL). The combined organic layer was washed with brine and dried over anhydrous Na$_2$SO$_4$, then evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (MeOH/Et$_2$O = 0:10 → 1:9) to give the title compound **10** as a brown solid (8.13 g, 21.3 mmol) in 92% yield.

^{1}H NMR (500 MHz, CDCl$_3$, 300 K): δ 8.63 (d, *J* = 6.0 Hz, 4H), 7.55 (d, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 6.0 Hz, 4H), 7.16 (t, *J* = 7.5 Hz, 1H), 4.95 (s, 2H), 4.23 (q, *J* = 3.0 Hz, 2H), 1.23 (t, *J* = 3.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$, 300 K): δ 168.4 (C), 160.3 (C), 149.9 (CH), 134.7 (CH), 131.0 (C), 125.5 (CH), 124.2 (CH), 116.3 (C), 91.9 (C), 89.0 (C), 70.2 (CH$_2$), 61.4 (CH$_2$), 14.2 (CH$_3$); IR (ATR, cm^{-1}): 2925, 2210, 1765, 1592, 1444, 1376, 1187, 1084, 1057, 827, 791, 751, 545, 516; m.p.: 89.5–92.4 °C; HR-ESI-TOF-MS: *m/z* = 383.1399 (calculated for C$_{24}$H$_{19}$N$_2$O$_3$: 383.1390 [M+H]$^+$).

• Synthesis of 2-(2,6-bis(pyridin-4-ylethynyl)phenoxy)acetic acid (11):

To a solution of compound **10** (4.00 g, 10.5 mmol) in THF (10 mL) was added a solution of LiOH(H$_2$O) (878 mg, 21.0 mmol) in H$_2$O (21 mL) and the resulting mixture was stirred at room temperature for 7 h. After the removal of THF under reduced pressure, the solution was neutralized with 4N HCl aq. (5.25 mL). The resulting mixture was filtrated, and the residue was dried *in vacuo* to give a title compound **11** (3.25 g, 9.17 mmol) as a white solid in 87%.

^{1}H NMR (500 MHz, DMSO-d_6, 300 K): δ 8.62 (d, *J* = 7.2 Hz, 4H), 7.64 (d, *J* = 9.6 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 4H), 7.19 (t, *J* = 9.6 Hz, 1H), 4.84 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6, 300 K): δ 169.8 (C), 160.6 (C), 149.9 (CH), 135.0 (CH), 131.0 (C), 125.3 (CH), 123.6 (CH), 114.8 (C), 91.3 (C), 89.5 (C), 70.9 (CH$_2$); IR (ATR, cm^{-1}): 3364, 3055, 2215, 1603, 1500, 1449, 1410, 1016, 822, 538; m.p.: >255 °C (decomposed); HR-ESI-TOF-MS: *m/z* = 355.1074 (calculated for C$_{22}$H$_{15}$N$_2$O$_3$: 355.1077 [M+H]$^+$).

• Synthesis of 4-(2-(2,6-bis(pyridin-4-ylethynyl)phenoxy)acetoxy)-2,2,6,6-tetramethyl-piperidin-1-yloxyl (1a):

Compound **11** (1.00 g, 2.82 mmol) was dissolved in DMF (100 mL). *N*,*N*-diisopropyl-ethylamine (492 μL, 2.82 mmol), *O*-(Benzotriazol-1-yl)-*N,N,N',N'*-tetramethyluronium Hexafluorophosphate (2.14 g, 5.64 mmol) and 4-hydroxy-TEMPO (972 mg, 5.64 mmol) were added, and then the resulting mixture was stirred at room temperature for 23 h. The reaction mixture was diluted with H_2O (200 mL), and extracted with AcOEt (2 x 100 mL). The organic layer was washed with H_2O (100 mL) and brine (50 mL), dried over anhydrous $MgSO_4$, filtrated and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (MeOH/$CHCl_3$ =5:95) and GPC (Gel Permeation Chromatography) to give the title compound **1a** (1.07 g, 2.10 mmol) as a brown solid in 74% yield.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 8.64 (br, 4H), 7.57 (br, 2H), 7.43 (br, 4H), 7.25 (br, 1H), 4.97 (br, 2H); ^{1}H NMR (500 MHz, CD_3NO_2, 300 K): δ 8.63 (br, 4H), 7.68 (br, 2H), 7.51 (br, 4H), 7.28 (br, 1H), 5.10 (br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ 160.2 (C), 150.1 (CH), 134.9 (CH), 131.0 (C), 125.6 (CH), 124.3 (CH), 116.2 (C), 91.9 (C), 89.0 (C). (The signals of proton and carbon in the vicinity of nitroxyl radical were not detected by ^{1}H NMR and ^{13}C NMR.); IR (ATR, cm^{-1}): 2973, 1732, 1593, 1432, 1293, 1226, 1179, 1084, 1044, 992, 833, 820, 795, 752, 549, 536; m.p.: 129.5–132.0 °C; HR-ESI-TOF-MS: *m/z* = 509.2312 (calculated for $C_{31}H_{31}N_3O_4$: 509.2309 $[M+H]^+$).

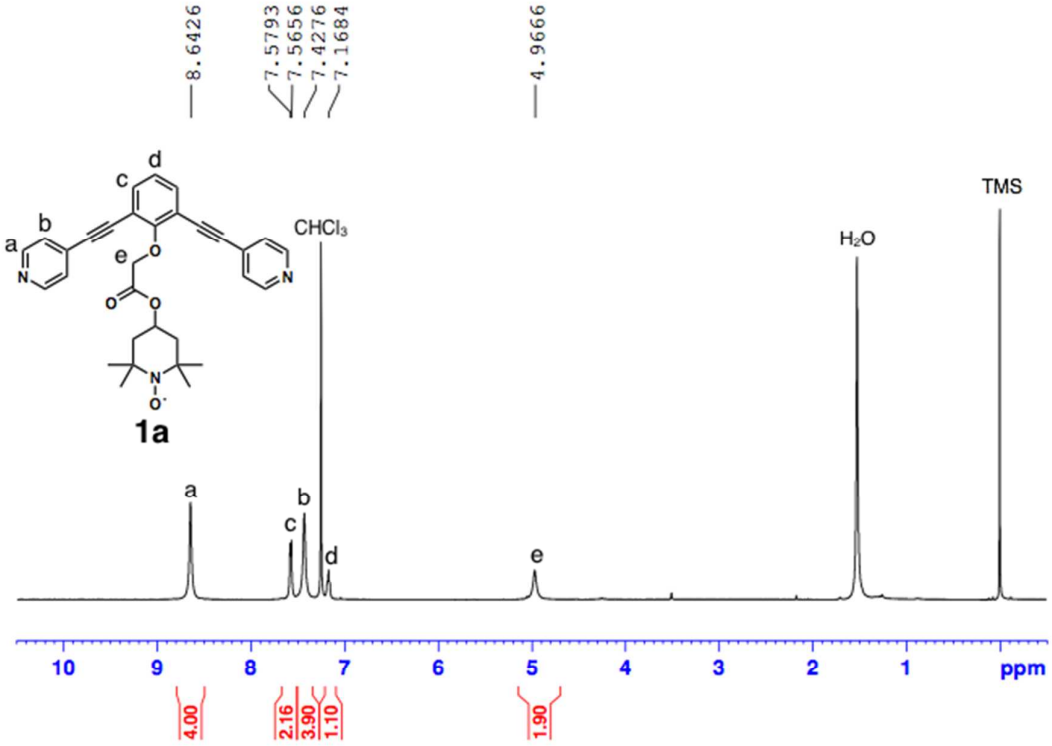


Figure S1. ^{1}H NMR spectrum of ligand **1a** (500 MHz, $CDCl_3$, 300 K).

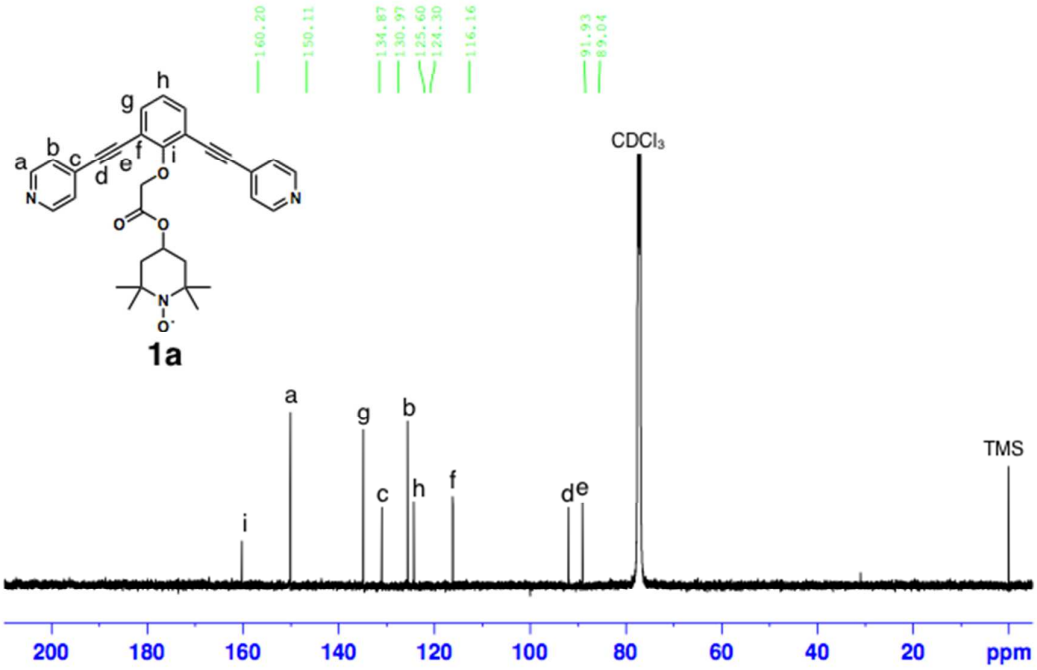
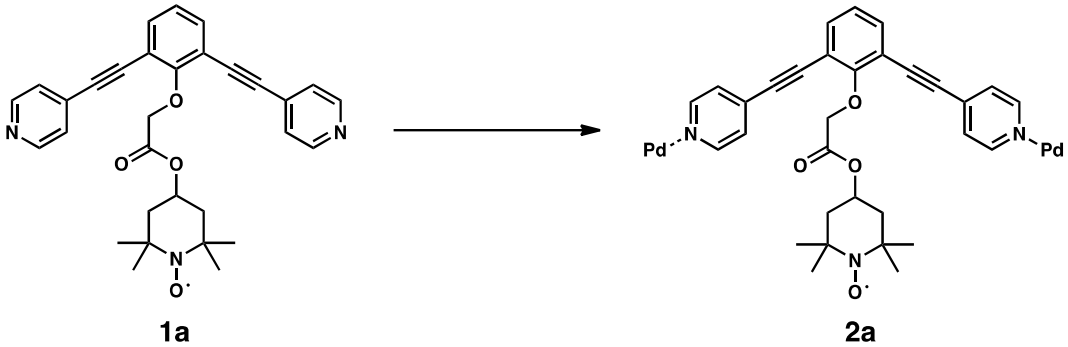


Figure S2. ^{13}C NMR spectrum of ligand **1a** (125 MHz, $CDCl_3$, 300 K).

• **Self-assembly of sphere 2a**



To a solution of compound **1a** (2.54 mg, 5.00 μmol) in CD_3NO_2 (250 μL) was added a solution of $[Pd(CH_3CN)_4](BF_4)_2$ (1.11 mg, 2.50 μmol) in CD_3NO_2 (250 μL) and the resulting mixture was stirred at room temperature for 30 min. The quantitative formation of sphere **2a** was confirmed by ^{1}H NMR and CSI-TOF-MS.

^{1}H NMR (500 MHz, CD_3NO_2, 300 K): no significant signal of **2a** was detected due to the paramagnetic shifts derived from the nitroxyl radical. CSI-TOF-MS (BF_4^- salt, CH_3CN): *m/z* = 1327.2044 (calculated for $[M - 11(BF_4^-)]^{11+}$ 1327.2037), *m/z* = 1209.3511 (calculated for $[M - 12(BF_4^-)]^{12+}$ 1209.3531), *m/z* = 1109.6377 (calculated for $[M - 13(BF_4^-)]^{13+}$ 1109.6334), *m/z* = 1024.1604 (calculated for $[M - 14(BF_4^-)]^{14+}$ 1024.1593), *m/z* = 950.0862 (calculated for $[M - 15(BF_4^-)]^{15+}$ 950.0818).

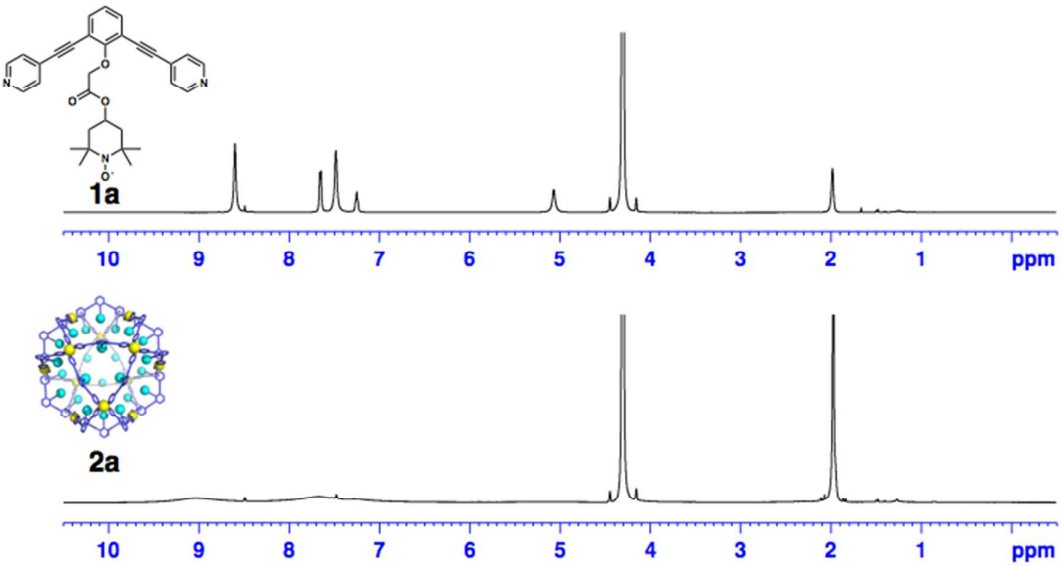


Figure S3. ^{1}H NMR spectra of ligand **1a** and sphere **1b** (500 MHz, CD_3NO_2, 300 K).

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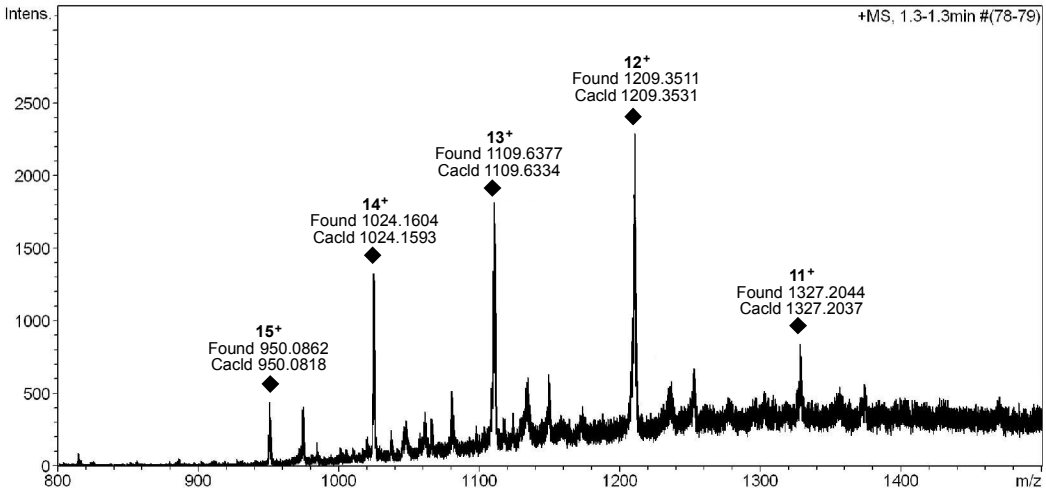


Figure S4. CSI-TOF-MS spectrum of sphere **2a** (BF_4^-salt, CH_3CN).

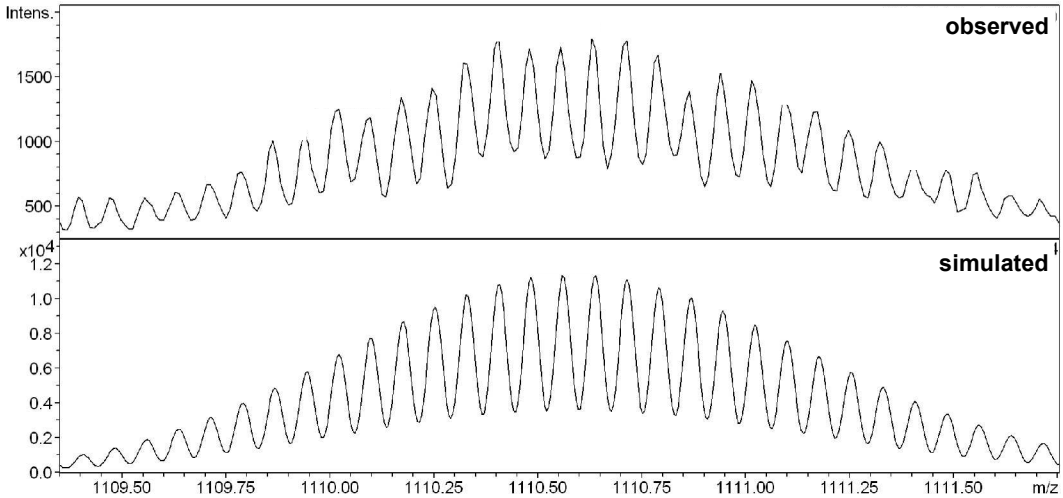
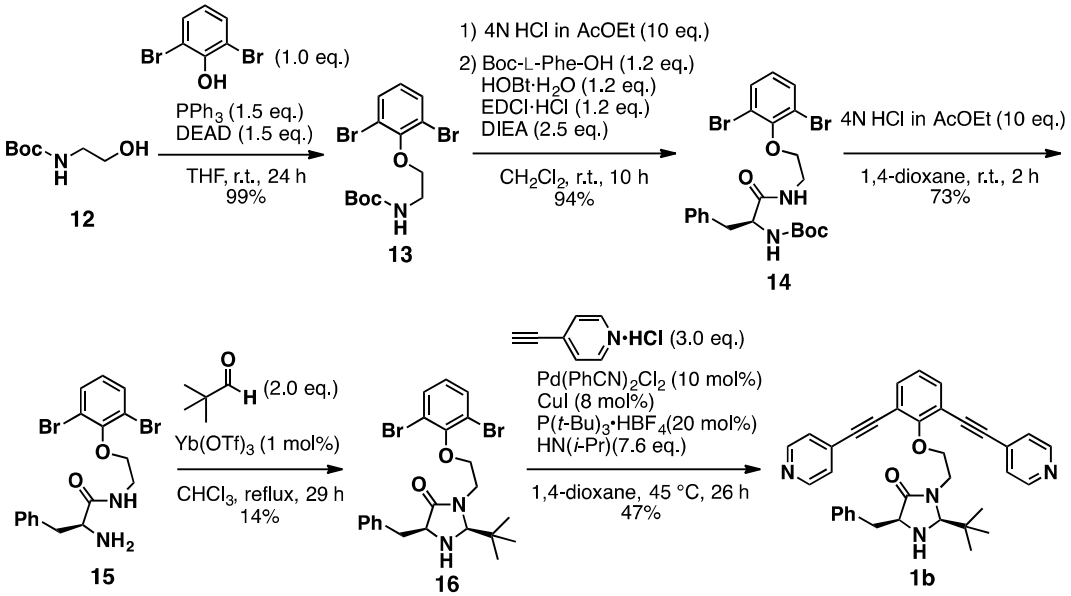


Figure S5. Isotopepattern of 13^+ ion peak (observed and simulated pattern) of CSI-TOF-MS spectrum of sphere **2a**.

• **Synthesis and physical properties of ligand 1b**



• **Synthesis of *tert*-butyl (2-(2,6-dibromophenoxy)ethyl)carbamate (13):**

Compound **12** (5.00 g, 31.0 mmol) and 2,6-dibromophenol (7.81 g, 31.0 mmol) were dissolved in THF (30 mL) and cooled to 0 °C. A solution of DEAD (40 wt% solution in toluene; 21.1 mL, 46.5 mmol) and triphenylphosphine (12.2 g, 46.5 mmol) in THF (50 mL), cooled to 0 °C, was added slowly. The resulting mixture was stirred at room temperature for 24 h, and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (AcOEt/Hexane = 1:9) to give the title compound **13** (12.1 g, 30.6 mmol) as a white solid in 99% yield.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 7.50 (d, J = 8.0 Hz, 2H), 6.87 (t, J = 8.0 Hz, 1H), 5.26 (br, 1H), 4.10 (br, 2H), 3.58 (br, 2H), 1.47 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ 156.0 (C), 152.8 (C), 132.8 (CH), 126.5 (CH), 118.3 (C), 79.4 (C), 72.3 (CH_2), 40.9 (CH_2), 28.5 (CH_3); IR (ATR, cm^{-1}): 3319, 2978, 2213, 1675, 1528, 1438, 1365, 1281, 1243, 1152, 1030, 998, 890, 722, 615; m.p.: 71.1–73.0 ºC; HR-ESI-TOF-MS: *m/z* = 417.9432 (calculated for $C_{13}H_{17}Br_2NO_3Na$: 417.9448 $[M+Na]^+$).

• **Synthesis of *tert*-butyl (S)-(1-((2-(2,6-dibromophenoxy)ethyl)amino)-1-oxo-3-phenylpropan-2-yl)carbamate (14):**

Compound **13** (17.1 g, 43.3 mmol) was dissolved in AcOEt (10 mL). To the solution, 4N HCl in AcOEt (108 mL, 433 mmol) was slowly added. After the mixture was stirred for 1 h at room temperature, the solvents were blown off under the stream of air and the resulting white solid was dried *in vacuo*. Quantitative removal of boc group was confirmed by ^{1}H NMR measurement. The obtained 2-(2,6-dibromophenoxy)ethan-1-amine hydrochloride (14.3 g, 43.3 mmol) and DIEA (18.8 mL, 108 mmol) were dissolved in CH_2Cl_2 (160 mL). To the solution, *N*-(*tert*-Butoxycarbonyl) -L-phenylalanine (13.7 g, 51.8 mmol), HOBt·H_2O (7.93 g, 51.8 mmol), EDCI·HCl (9.93 g, 51.8 mmol) were added. After the mixture was stirred for 10 h at room temperature, the solution was washed with sat. $NaHCO_3$ aq. (2 x 100 mL) and brine (50 mL), and then the organic layer was dried over anhydrous Na_2SO_4 and evaporated. The crude product was purified by column chromatography on silica gel (MeOH/$CHCl_3$ = 1:99) to give the title compound **14** (21.9 g, 40.5 mmol) as a white solid in 94% yield.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.29 (m, 3H), 6.88 (t, *J* = 8.0 Hz, 1H), 6.60 (br, 1H), 4.96 (br, 1H), 4.43 (br, 1H), 4.07 ~ 4.03 (m, 2H), 3.75–3.60 (m, 2H), 3.15–3.06 (m, 2H), 1.40 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ 171.3 (C), 155.3 (C), 152.4 (C), 136.7 (C), 132.8 (CH), 129.3 (CH), 128.7 (CH), 127.0 (CH), 126.7 (CH), 118.2 (C), 80.2 (C), 71.6 (CH_2), 55.9 (CH), 39.6 (CH_2), 38.8 (CH_2), 28.3 (CH_3); IR (ATR, cm^{-1}): 3311, 2920, 1690, 1650, 1550, 1525, 1434, 1232, 1166, 1022, 766, 711, 678, 514; m.p.: 123.0–124.1 ºC; HR-ESI-TOF-MS: *m/z* = 565.0121 (calculated for $C_{22}H_{26}Br_2N_2O_4Na$: 565.0133 $[M+Na]^+$).

• Synthesis of (*S*)-2-amino-*N*-(2-(2,6-dibromophenoxy)ethyl)-3-phenylpropanamide (15):

Compound **14** (25.9 g, 47.8 mmol) was dissolved in 1,4-dioxane (50 mL). To the solution, 4N HCl in 1,4-dioxane (120 mL, 478 mmol) was slowly added. After the mixture was stirred for 3 h at room temperature, the solvents were blown off under the stream of air and the resulting white solid was dried *in vacuo*. The resulting white solid was dissolved in sat. $NaHCO_3$ aq. (100 mL) and extracted with $CHCl_3$ (2 x 100 mL), and then the organic layer was dried over anhydrous Na_2SO_4 and evaporated. The crude product was purified by column chromatography on silica gel (AcOEt/Hexane = 8:2) to give the title compound **15** (15.5 g, 35.1 mmol) as a yellow oil in 73% yield.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 7.98 (br, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 (m, 3H), 6.88 (t, *J* = 8.0 Hz, 1H), 4.12 (m, 2H), 3.73 (m, 2H), 3.66 (dd, *J* = 4.0, 10.0 Hz, 1H), 3.32 (dd, *J* = 4.0, 14.0 Hz, 1H), 2.71 (dd, *J* = 10.0, 14.0 Hz, 1H); ^{13}C NMR (125

MHz, $CDCl_3$, 300 K): δ 174.4 (C), 152.6 (C), 138.0 (C), 132.8 (CH), 129.3 (CH), 128.7 (CH), 126.8 (CH), 126.6 (CH), 118.3 (C), 71.9 (CH_2), 56.7 (CH), 41.1 (CH_2), 39.3 (CH_2); IR (ATR, cm^{-1}): 3339, 2952, 1673, 1438, 1243, 1068, 1032, 754, 720, 701; HR-ESI-TOF-MS: *m/z* = 442.9787 (calculated for $C_{17}H_{19}Br_2N_2O_2$: 442.9788 $[M+H]^+$).

• **Synthesis of (2*S*,5*S*)-5-benzyl-2-(*tert*-butyl)-3-(2-(2,6-dibromophenoxy)ethyl)imidazo-ledin-4-one (16):**

$Yb(OTf)_3$ (48.7 mg, 78.5 μmol) was added to a mixture of compound **15** (3.47 g, 7.85 mmol) and pivalaldehyde (1.70 mL, 15.7 mmol) in $CHCl_3$ (80 mL), and then refluxed for 29 h. The resulting mixture was flitrated and evaporated under reduced pressure. The disasteroisomers were separated by column chromatography on silica gel (AcOEt/Hexane = 2:8) to give the title compound **16** (552 mg, 1.08 mmol) as a white solid in 14% yield.

^1H NMR (500 MHz, $CDCl_3$, 300 K) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.32–7.27 (m, 4H), 7.24–7.20 (m, 1H), 6.87 (t, *J* = 8.0 Hz, 1H), 4.67 (s, 1H), 4.25 (dt, *J* = 4.5, 9.0 Hz, 1H), 4.19 (dt, *J* = 4.5, 13.5 Hz, 1H), 4.09 (dt, *J* = 4.5, 9.0 Hz,1H), 3.78 (dd, *J* = 4.0, 8.0 Hz 1H), 3.69 (ddd, *J* = 4.5, 9.0, 13.5 Hz, 1H), 3.17 (dd, *J* = 4.0, 14.0 Hz 1H), 2.95 (dd, *J* = 4.5, 9.0 Hz, 1H), 1.78 (br, 1H), 0.92 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ 175.9 (C), 152.6 (C), 138.1 (C), 132.8 (CH), 129.7 (CH), 128.6 (CH), 126.6 (CH), 126.6 (CH), 118.4 (C), 80.1 (CH), 70.3 (CH_2), 59.4 (CH), 42.4 (CH_2), 38.2 (CH_2), 35.4 (C), 25.9 (CH_3); IR (ATR, cm^{-1}): 3339, 2952, 1673, 1438, 1243, 1068, 1032, 754, 720, 701; m.p.: 44.1–45.9 ºC; HR-ESI-TOF-MS: *m/z* = 511.0422 (calculated for $C_{22}H_{27}Br_2N_2O_2$: 511.0415 $[M+H]^+$).

• **Synthesis of (2*S*,5*S*)-5-benzyl-2-(*tert*-butyl)-3-(2-(2,6-bis(pyridin-4-ylethynyl)phenoxy) ethyl)imidazolidin-4-one (1b):**

4-ethynyl pyridine hydrochloride (410 mg, 2.94 mmol) was added to a mixture of compound **16** (500 mg, 0.980 mmol), $P(t\text{-}Bu)_3 \cdot HBF_4$ (56.9 mg, 0.196 mmol), CuI (14.9 mg, 78.4 μmol) $Pd(PhCN)_2Cl_2$ (37.6 mg, 98.0 μmol), and diisopropylamine (1.05 mL, 7.45 mmol) in degassed 1,4-dioxane (25 mL), and the resulting mixture was stirred at 45 °C for 26 h under Ar atmosphere. The reaction mixture was diluted with AcOEt (100 mL) and filtrated through celite pad. After washed with ethylenediamine aq., the water layer was extracted with AcOEt (2 x 50 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4, then evaporated under reduced pressure. The residue was purified by column chromatography

on silica gel (MeOH/AcOEt = 3:97) and GPC (Gel Permeation Chromatography) to give the title compound **1b** as a brown oil (253 mg, 0.456 mmol) in 47% yield.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 8.62 (d, *J* = 5.4 Hz, 4H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.43 (d, J = 5.4 Hz, 4H), 7.29–7.12 (m, 6H), 4.56 (m, 1H), 4.43 (s, 1H), 4.36 (m, 1H), 4.21 (dt, *J* = 6.2, 14.3 Hz, 1H), 3.68 (dt, *J* = 6.2, 14.3 Hz, 1H), 3.58 (br, 1H), 3.09 (dd, *J* = 3.7, 13.7 Hz, 1H), 2.82 (dd, *J* = 8.2, 13.7 Hz, 1H), 0.81 (s, 9H); ^{1}H NMR (500 MHz, CD_3NO_2, 300 K): δ 8.61 (d, *J* = 5.3 Hz, 4H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.55 (d, J = 5.3 Hz, 4H), 7.29–7.19 (m, 6H), 4.62–4.57 (m, 1H), 4.55–4.49 (m, 1H), 4.47 (s, 1H), 4.30–4.25 (m, 1H), 3.75–3.69 (m, 1H), 3.65 (br, 1H), 3.04 (dd, *J* = 3.3, 13.6 Hz, 1H), 2.72 (dd, *J* = 8.4, 13.6 Hz, 1H), 0.85 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ 175.9 (C), 160.5 (C), 149.9 (CH), 137.9 (C), 134.8 (CH), 131.0 (C), 129.4 (CH), 128.6 (CH), 126.6 (CH), 125.5 (CH), 124.2 (CH), 116.9 (C), 91.3 (C), 89.3 (C), 80.5 (CH), 70.6 (CH_2), 59.2 (CH), 42.7 (CH_2), 38.2 (CH_2), 35.4 (C), 25.6 (CH_3); IR (ATR, cm^{-1}): 2974, 2213, 1685, 1592, 1538, 1492, 1438, 1405, 1232, 1076, 989, 818, 747, 700, 612, 548, 428; HR-ESI-TOF-MS: *m/z* = 555.2763 (calculated for $C_{36}H_{35}N_4O_2$: 555.2755 $[M+H]^+$).

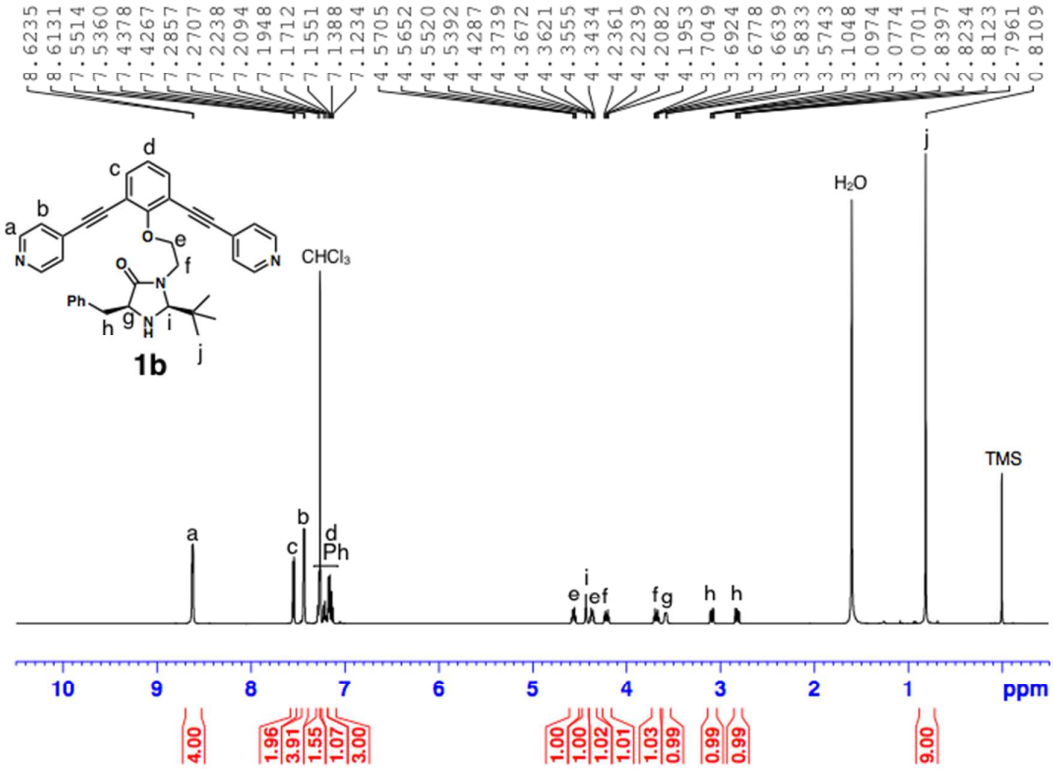


Figure S6. ^{1}H NMR spectrum of ligand **1b** (500 MHz, $CDCl_3$, 300 K).

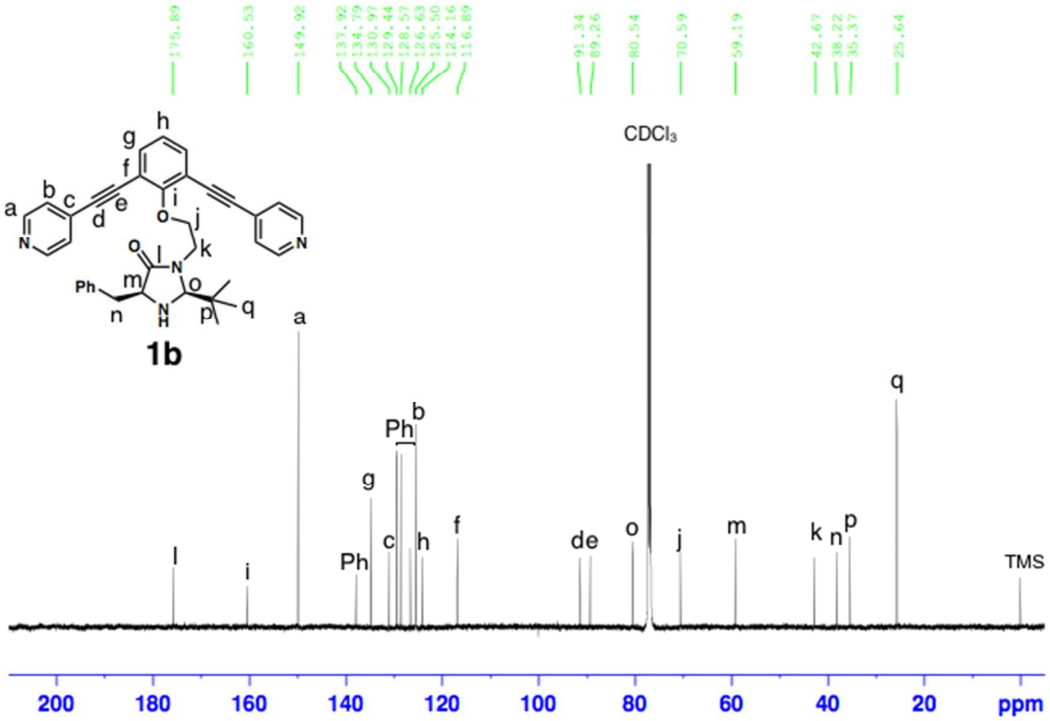
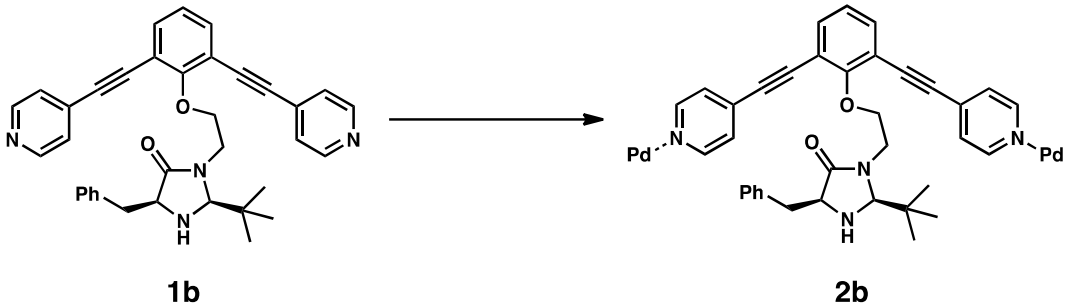


Figure S7. ^{13}C NMR spectrum of ligand **1b** (125 MHz, $CDCl_3$, 300 K).

• **Self-assembly of sphere 2b**



To a solution of compound **1b** (2.77 mg, 5.00 μmol) in CD_3NO_2 (250 μL) was added a solution of $[Pd(CH_3CN)_4](BF_4)_2$ (1.11mg, 2.50 μmol) in CD_3NO_2 (250 μL) and the resulting mixture was stirred at room temperature for 30 min. The quantitative formation of sphere **2b** was confirmed by ^{1}H NMR and CSI-TOF-MS.

^{1}H NMR (500 MHz, CD_3NO_2, 300 K): δ 9.10 (br, 96H), 7.82 (br, 144H), 7.24 (br, 144H), 4.32 (br, 96H), 3.68 (br, 48H), 2.88 (br, 48H), 0.76 (br, 216H); Diffusion coefficient (CD_3NO_2, 300 K, BF_4^-salt): $D = 6.3 \times 10^{-11}$ m^2 s^{-1}; CSI-TOF-MS (BF_4^- salt, CH_3CN): *m/z* = 1427.6672 (calculated for $[M - 11(BF_4^-)]^{11+}$ 1427.6645), *m/z* = 1301.4406 (calculated for $[M - 12(BF_4^-)]^{12+}$ 1301.4422), *m/z* = 1194.6378 (calculated for $[M - 13(BF_4^-)]^{13+}$ 1194.6387), *m/z* = 1103.0927 (calculated for $[M - 14(BF_4^-)]^{14+}$ 1103.0928), *m/z* = 1023.7463 (calculated for $[M - 15(BF_4^-)]^{15+}$ 1023.7531), *m/z* = 954.3288 (calculated for $[M - 16(BF_4^-)]^{16+}$ 954.3308).

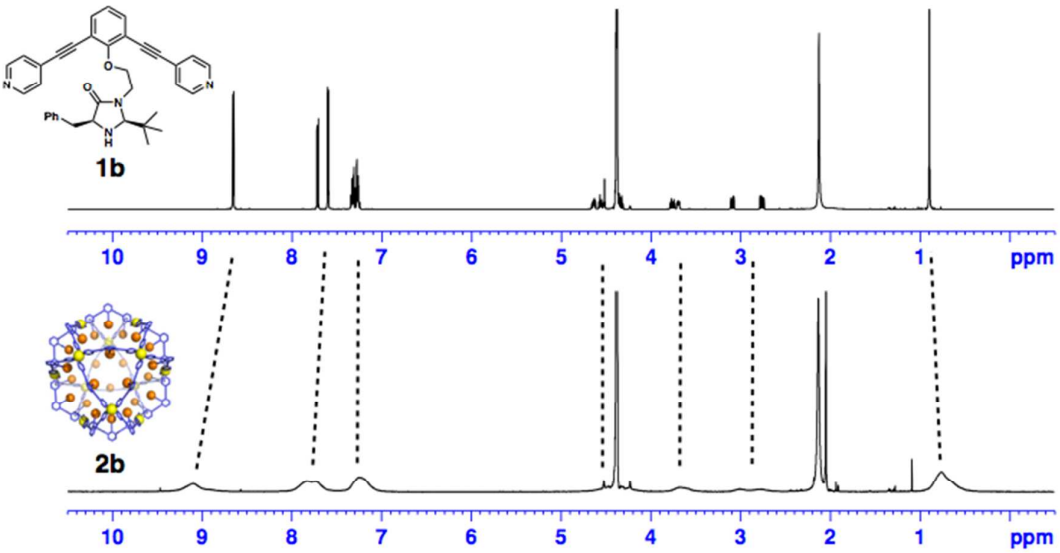


Figure S8. ^{1}H NMR spectra of ligand **2a** and sphere **2b** (500 MHz, CD_3NO_2, 300 K).

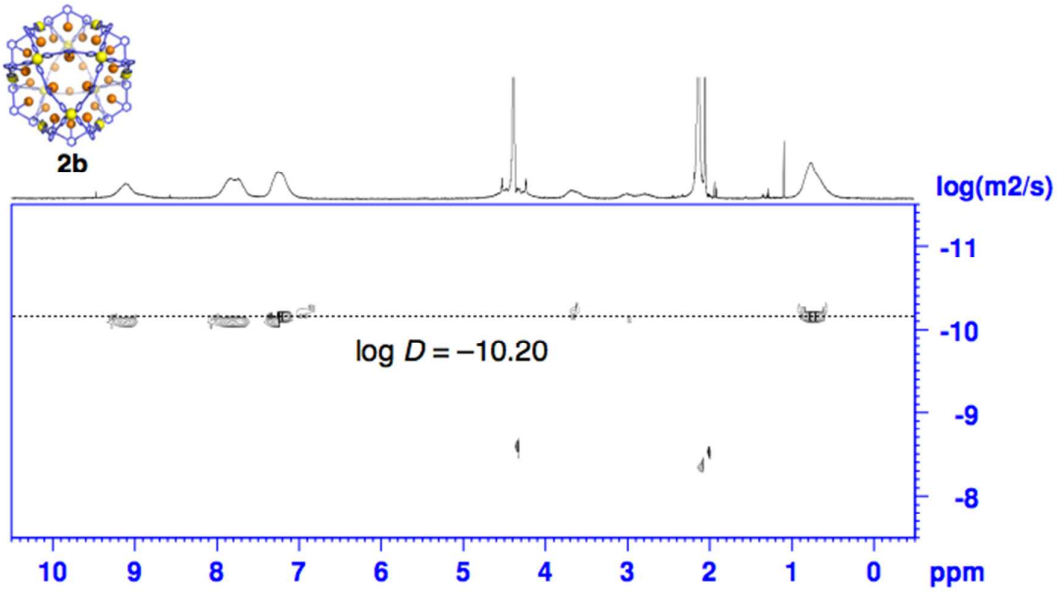


Figure S9. ^{1}H DOSY spectrum of sphere **2b** (BF_4^- salt, 500 MHz, CD_3NO_2, 300 K).

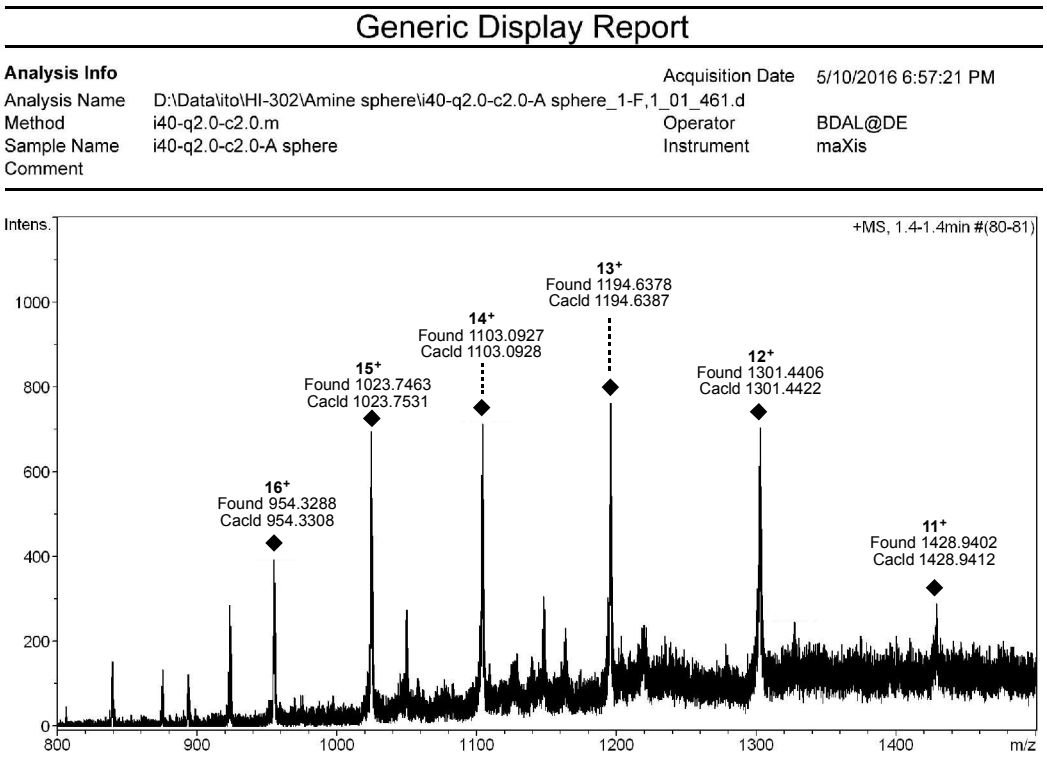


Figure S10. CSI-TOF-MS spectrum of sphere **2b** (BF_4^- salt, CH_3CN).

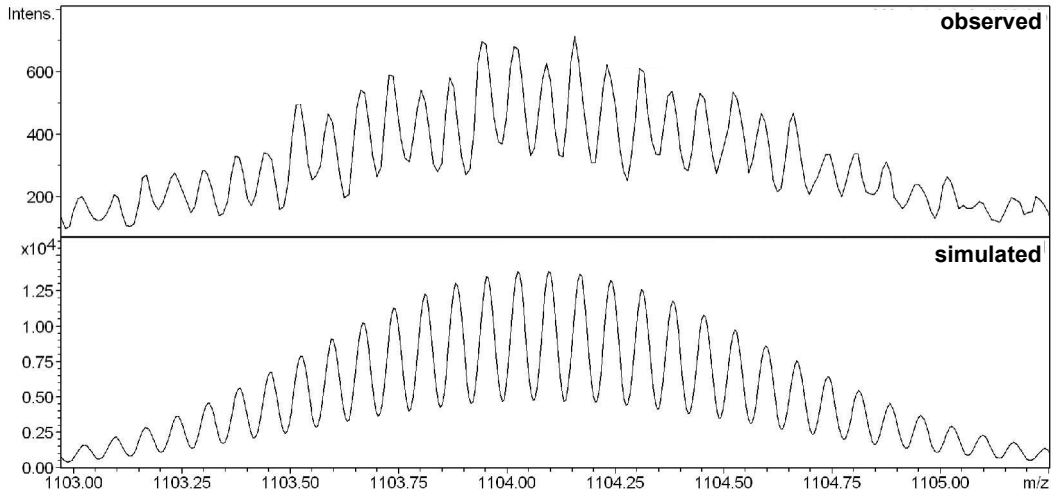
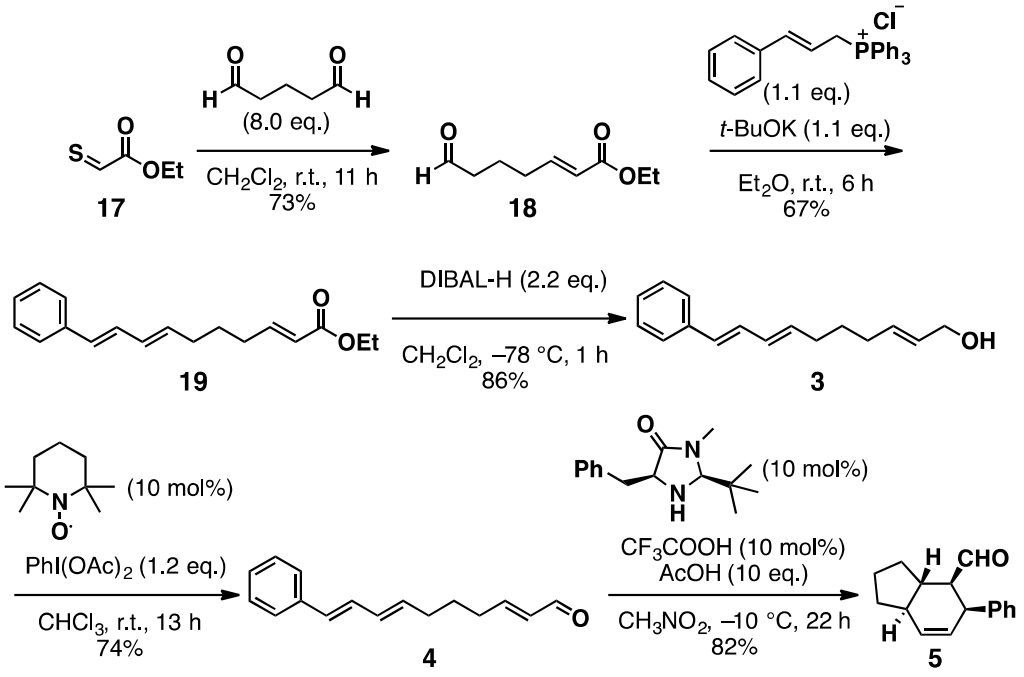


Figure S11. Isotopepattern of 14^+ ion peak (observed and simulated pattern) of CSI-TOF-MS spectrum of sphere **2b**.

• Synthesis and physical properties of compound 3–5



• Synthesis of ethyl (*E*)-7-oxohept-2-enoate (18):

To a solution of aqueous glutaraldehyde (25 w%, 11.5 g, 115 mmol) in CH_2Cl_2 (35 ml) was added a solution of (carbethoxymethylene)triphenylphosphorane (5.00 g, 14.4 mmol) in CH_2Cl_2

(35 mL) and the resulting mixture was stirred at room temperature for 11 h. The reaction mixture was diluted with AcOEt (400 mL), washed with water (2 x 100 mL) and brine (50 mL) and dried over anhydrous Na_2SO_4, then evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (AcOEt/Hexane = 1:9) to give the title compound **18** (1.80 g, 10.5 mmol) as a colorless oil in 73% yield.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 9.78 (s, 1H), 6.92 (dt, *J* = 7.0, 15.5 Hz, 1H), 5.84 (d, *J* = 15.5 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.49 (t, *J* = 7.2 Hz, 2H), 2.25 (dt, *J* = 7.0, 7.2 Hz, 2H), 1.81 (quint, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ 201.4 (CH), 166.5 (C), 147.5 (CH), 122.4 (CH), 60.2 (CH_2), 42.9 (CH_2), 31.2 (CH_2), 20.3 (CH_2), 14.2 (CH_3); IR (ATR, cm^{-1}): 2948, 2870, 2824, 2725, 1718, 1438, 1363, 1195, 1150, 1091, 1010, 882, 849, 761, 679; HR-ESI-TOF-MS: *m/z* = 193.0845 (calculated for $C_9H_{14}NaO_3$: 193.0841 $[M+Na]^+$).

• Synthesis of Ethyl-10-phenyldeca-2,7,9-trienoate (19):

Cinnamyltriphenylphosphonium chloride (3.22 g, 7.76 mmol) was added to *t*-BuOK (870 mg, 7.76 mmol) in Et_2O (25 mL), and the resulting mixture was stirred at room temperature for 30 min. The reaction mixture was cooled to 0 °C and a solution of compound **18** (1.20 g, 7.05 mmol) in Et_2O (2.5 mL) was added. The solution was warmed to room temperature and stirred for 6 h. The solution was poured into H_2O (150 mL) and extracted with Et_2O (3 x 70 mL). The combined organic layer was dried over anhydrous Na_2SO_4, then evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (AcOEt/Hexane = 8:92) to afford the trienyl ester as a 1:1 mixture of geometric isomers (2*E*,7*E*,9*E* and 2*E*,7*Z*,9*E*). The mixture was redissolved in CH_2Cl_2 (25 mL) and I_2 (125 mg, 0.98 mmol) was added. After the mixture was stirred for 30 min at room temperature, sat. Na_2SO_3 aq. (20 mL) were added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL) and the combined organic layer was dried over anhydrous Na_2SO_4, filtrated and evaporated under reduced pressure to give the title compound **19** (1.27 g, 4.70 mmol) as a colorless oil consisting of a 87:13 mixture of 2*E*,7*E*,9*E* and 2*E*,7*Z*,9*E* isomers in 67% yield.

Ethyl (2*E*,7*E*,9*E*)-10-phenyldeca-2,7,9-trienoate ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 7.37 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.4, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.96 (dt, *J* = 6.9, 15.9 Hz, 1H), 6.73 (dd, *J* = 10.4, 15.6 Hz, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 6.21 (dd, *J* = 10.4, 14.4 Hz, 1H), 5.83 (d, *J* = 15.9 Hz, 1H), 5.77 (dt, *J* = 7.0, 14.4 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.23 (dt, *J* = 6.9, 7.2 Hz, 2H), 2.18 (dt, *J* = 7.0, 7.4 Hz, 2H), 1.64–1.56 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C

NMR (125 MHz, $CDCl_3$, 300 K): δ 166.7 (C), 148.8 (CH), 137.6 (C), 134.5 (CH), 131.3 (CH), 130.5 (CH), 129.1 (CH), 128.6 (CH), 127.2 (CH), 126.2 (CH), 121.7 (CH), 60.2 (CH_2), 32.2 (CH_2), 31.6 (CH_2), 27.6 (CH_2), 14.3 (CH_3).

Ethyl (2*E*,7*Z*,9*E*)-10-phenyldeca-2,7,9-trienoate ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 7.40 (d, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.4, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.02 (dd, *J* = 10.4, 15.6 Hz, 1H), 6.96 (dt, *J* = 6.9, 15.9 Hz, 1H), 6.54 (d, *J* = 15.6 Hz, 1H), 6.21 (dd, *J* = 10.4, 14.4 Hz, 1H), 5.83 (d, *J* = 15.9 Hz, 1H), 5.48 (dt, *J* = 7.0, 14.4 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.32 (dt, *J* = 7.0, 7.4 Hz, 2H), 2.23 (dt, *J* = 6.9, 7.2 Hz, 2H), 1.64–1.56 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ 166.7 (C), 148.7 (CH), 137.5 (C), 132.6 (CH), 131.8 (CH), 129.5 (CH), 128.6 (CH), 127.5 (CH), 126.4 (CH), 124.2 (CH), 121.8 (CH), 60.2 (CH_2), 31.6 (CH_2), 27.9 (CH_2), 27.3 (CH_2), 14.3 (CH_3).

Analysis of mixture IR (ATR, cm^{-1}): 3341, 2930, 1714, 1653, 1441, 1265, 1183, 1040, 986, 756, 691, 508; HR-ESI-TOF-MS: *m/z* = 293.1512 (calculated for $C_{18}H_{22}NaO_2$: 293.1512 $[M+Na]^+$).

• Synthesis of 10-phenyldeca-2,7,9-trien-1-ol (3):

Compound **19** (1.20 g, 444 mmol) consisting of a 87:13 mixture of 2*E*,7*E*,9*E* and 2*E*,7*Z*,9*E* isomers was dissolved in CH_2Cl_2 (24 mL). The solution was cooled to –78 °C and a solution of DIBAL-H (1 M solution in hexane; 9.76 mL, 9.76 mmol) was added. After one hour, the reaction solution was warmed to 0 °C and MeOH (10 mL) was added to quench the remaining DIBAL-H. The slurry was then warmed to room temperature and treated with sat. Rochelle's salt aq. (30 mL). After stirring for 16 h, the layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine (40 mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (AcOEt/Hexane = 3:7) to give the title compound **3** (870 mg, 3.81 mmol) as a colorless oil consisting of a 87:13 mixture of 2*E*,7*E*,9*E* and 2*E*,7*Z*,9*E* isomers in 86% yield.

(2*E*,7*E*,9*E*)-10-phenyldeca-2,7,9-trien-1-ol ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 7.37 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.4, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.75 (dd, *J* = 10.4, 15.6 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 6.21 (dd, *J* = 10.4, 15.0 Hz, 1H), 5.81 (dt, *J* = 7.0, 15.0 Hz, 1H), 5.70–5.65 (m, 2H), 4.1–4.08 (m, 2H), 2.16 (dt, *J* = 7.0, 7.4 Hz, 2H), 2.09 (dt, *J* = 6.9, 7.4 Hz, 2H), 1.53 (quint, *J* = 7.4, 2H), 1.27 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ 137.6 (C), 135.2 (CH), 132.9 (CH), 130.9 (CH), 130.2 (CH), 129.3 (CH), 129.3 (CH), 128.6 (CH), 127.1 (CH),

126.1 (CH), 63.8 (CH_2), 32.3 (CH_2), 31.7 (CH_2), 28.7 (CH_2).

(2*E*,7*Z*,9*E*)-10-phenyldeca-2,7,9-trien-1-ol ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 7.40 (d, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.4, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.03 (dd, *J* = 10.4, 15.6 Hz, 1H), 6.53 (d, *J* = 15.6 Hz, 1H), 6.21 (dd, *J* = 10.4, 18.4 Hz, 1H), 5.74–5.71 (m, 1H5.61 (m, 1H), 5.50 (dt, *J* = 7.2, 18.4 Hz, 1H), 4.12–4.08 (m, 2H), 2.31 (dt, *J* = 7.0, 7.4 Hz, 2H), 2.09 (dt, *J* = 6.9, 7.4 Hz, 2H), 1.53 (quint, *J* = 7.4 Hz, 2H), 1.27 (br, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ 137.6 (C), 132.8 (CH), 132.6 (CH), 132.2 (CH), 129.5 (CH), 129.1 (CH), 128.6 (CH), 127.4 (CH), 126.3 (CH), 124.4 (CH), 63.8 (CH_2), 31.7 (CH_2), 29.0 (CH_2), 27.4 (CH_2).

Analysis of mixture IR (ATR, cm^{-1}): 3286, 2925, 2216, 1685, 1593, 1438, 1406, 1233, 990, 820, 747, 700, 546; HR-ESI-TOF-MS: *m/z* = 251.1411 (calculated for $C_{16}H_{20}NaO$: 251.1406 $[M+Na]^+$).

• Synthesis of 10-phenyldeca-2,7,9-trienal (4):

2,2,6,6-tetramethylpiperidine 1-oxyl (27.4 mg, 0.175 mmol) and $PhI(OAc)_2$ (677 mg, 2.10 mmol) were added to compound **3** (400 mg, 1.75 mmol) consisting of a 87:13 mixture of 2*E*,7*E*,9*E* and 2*E*,7*Z*,9*E* isomers in $CHCl_3$ (7 mL), and the resulting mixture was stirred at room temperature for 13 h. The solution was washed with sat. $Na_2S_2O_3$ aq. (2 x 50 mL), sat. $NaHCO_3$ aq. (50 mL) and brine (50 mL), and then the organic layer was dried over anhydrous Na_2SO_4 and evaporated. The crude product was purified by column chromatography on silica gel (AcOEt/Hexane = 1:9) to give the title compound **4** (295 mg, 1.30 mmol) as a colorless oil consisting of a 87:13 mixture of 2*E*,7*E*,9*E* and 2*E*,7*Z*,9*E* isomers in 74% yield.

(2*E*,7*E*,9*E*)-10-phenyldeca-2,7,9-trienal ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 9.52 (d, *J* = 7.9 Hz) 7.37 (d, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.85 (dt, *J* = 6.8, 15.6 Hz, 1H), 6.75 (dd, *J* = 10.4, 15.6 Hz, 1H), 6.46 (dd, *J* = 10.4, 15.6 Hz, 1H), 6.22 (dd, *J* = 10.4, 14.1 Hz, 1H), 6.14 (dd, *J* = 7.9, 15.6 Hz, 1H), 5.79 (dt, *J* = 7.1, 14.1 Hz, 1H), 2.42–2.33 (m, 2H), 2.21 (dt, *J* = 7.1, 7.4 Hz, 2H), 1.66 (quint, *J* = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ 194.0 (CH), 158.3 (CH), 137.5 (C), 134.0 (CH), 133.2 (CH), 131.6 (CH), 130.7 (CH), 129.0 (CH), 128.6 (CH), 127.3 (CH), 126.2 (CH), 32.2 (CH_2), 32.1 (CH_2), 27.4 (CH_2).

(2*E*,7*Z*,9*E*)-10-phenyldeca-2,7,9-trienal ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 9.52 (d, *J* = 7.9 Hz) 7.40 (d, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.4, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.01 (dd, *J* = 10.4, 15.6 Hz, 1H), 6.85 (dt, *J* = 6.8, 15.6 Hz, 1H), 6.54 (dd, *J* = 10.4, 15.6 Hz, 1H), 6.21 (dd, *J* = 10.4, 14.1 Hz, 1H), 6.14 (dd, *J* = 7.9, 15.6 Hz, 1H), 5.49 (dt, *J* = 7.1, 14.1 Hz, 1H), 2.42–2.33

(m, 4H), 1.67 (quint, J = 7.4, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ 194.0 (CH), 158.3 (CH), 137.4 (C), 133.2 (CH), 132.8 (CH), 131.4 (CH), 129.8 (CH), 128.6 (CH), 127.6 (CH), 126.4 (CH), 123.9 (CH), 32.1 (CH_2), 27.8 (CH_2), 27.3 (CH_2).

Analysis of mixture IR (ATR, cm^{-1}): 3352, 3021, 2928, 1638, 1447, 987, 746, 691, 507; HR-ESI-TOF-MS: *m/z* = 249.1248 (calculated for $C_{16}H_{18}NaO$: 249.1250 $[M+Na]^+$).

• Synthesis of (1*S*,2*R*,3*S*,6*R*)-3-phenylbicyclo[4.3.0]non-4-ene-2-carbaldehyde (5):

Compound **4** (mixture of *E*,*E*-diene geometry 90.5 mg, 400 μmol and *Z*,*E*-diene geometry 13.5 mg, 59.8 μmol)[1] was dissolved in CD_3NO_2/D_2O = 98:2 (2 mL). The solution was cooled to –10 °C, and a solution of (2*S*,5*S*)-5-benzyl-2-(*tert*-butyl)-3-methylimidazolidin-4-one (10.4 mg, 40.0 μmol), CF_3COOH (3.06 μL, 40.0 μmol) and AcOH (229 μL, 4.00 mmol) in CD_3NO_2/D_2O = 98:2 (2 mL) was added. After stirring for 22 h at –10 °C, the reaction mixture was warmed to room temperature. The crude reaction mixture was directly purified by column chromatography on silica gel (AcOEt/Hexane = 5:95) to give the title compound **5** (74.2 mg, 0.328 mmol) as a white solid as an >20:1 mixture of *endo*:*exo* product in 82% yield. HPLC analysis of **5** showed that it was formed in 93% ee (DAICEL CHIRALPAK IB column, IPA/Hexane = 1:99).

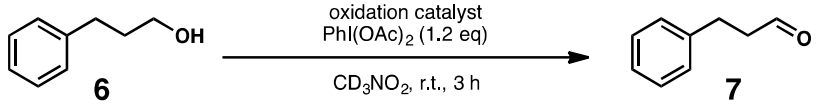
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 9.07 (d, J = 4.1 Hz, 1H) 7.30 (t, J = 7.5 Hz, 2H), 7.23 (d, J = 7.5, 1H), 7.19 (d, J = 7.5 Hz, 2H), 6.14 (d, J = 9.9 Hz, 1H), 5.63–5.57 (m, 1H), 4.01 (br, 1H), 2.73–2.64 (m, 1H), 2.01–1.74 (m, 6H), 1.39–1.23 (m, 1H), 1.15–1.04 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K): δ 204.9 (CH), 139.6 (C), 130.9 (CH), 129.7 (CH), 128.6 (CH), 128.5 (CH), 127.2 (CH), 56.8 (CH), 44.5 (CH), 43.9 (CH), 38.7 (CH), 28.6 (CH_2), 27.3 (CH_2), 22.4 (CH_2); IR (ATR, cm^{-1}): 3015, 2967, 2869, 2721, 1714, 1453, 1271, 807, 762, 701, 665, 626, 571; m.p.: 68.3–70.6 °C; HR-ESI-TOF-MS: *m/z* = 249.1240 (calculated for $C_{16}H_{18}NaO$: 249.1250 $[M+Na]^+$).

[1] *Z*,*E*-dienes of compound **4** were uniformly inert to this catalytic asymmetric Diels-Alder reaction.

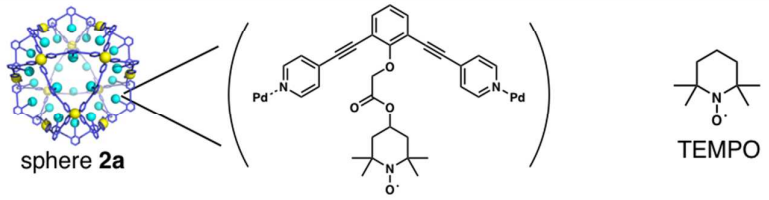
3. Catalysis

• Oxidation reaction catalyzed by sphere 2a

Table S1. Oxidation reaction profile catalyzed by sphere **2a** and TEMPO[a].



entry	oxidation catalyst	yield of **7**[b]	TOF_{ini}[c]
1	sphere **2a** (10/24 mol%)	96%	23.6
2	TEMPO (10 mol%)	91%	11.2



[a] Reaction conditions: each reagent and reactant was separately dissolved in CD_3NO_2 and certain volumes of each solution were taken and mixed into a test tube directly (with total volume = 500 uL), compound **6** (6.81 mg, 50.0 μmol) in CD_3NO_2 (133 μL), $PhI(OAc)_2$ (19.3 mg, 60.0 μmol) in CD_3NO_2 (250 μL), sphere **2a** was prepared in advance with ligand **1a** (2.54 mg, 5.00 μmol) and $[Pd(CH_3CN)_4](BF_4)_2$ (1.11 mg, 2.50 μmol) in CD_3NO_2 (167 μL), TEMPO (0.78 mg, 5.00 μmol) in CD_3NO_2 (167 μL). [b] The reactions were subsequently monitored by ^1H NMR and the yields of the product **7** were calculated based on the integration by using tetramethylsilane in $CDCl_3$ as an external standard. [c] The TOF_{ini} was calculated at conversion of 15 min reaction time.

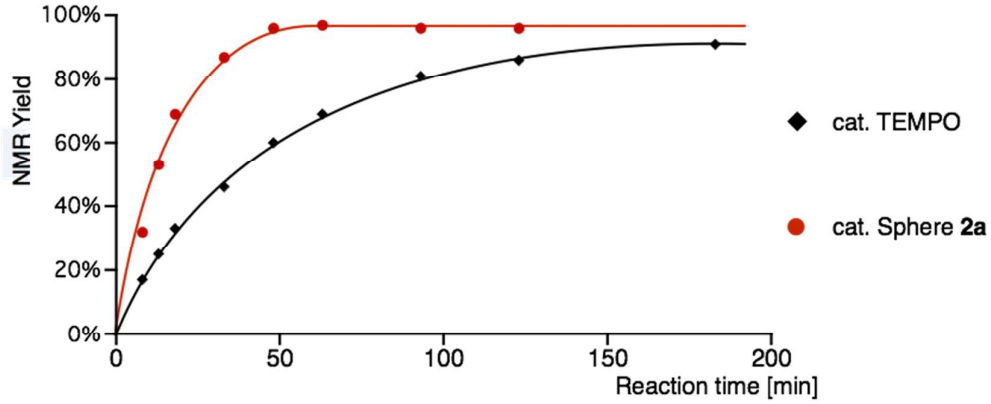
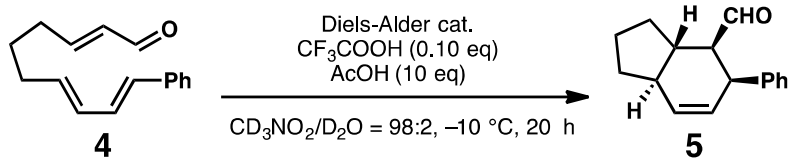


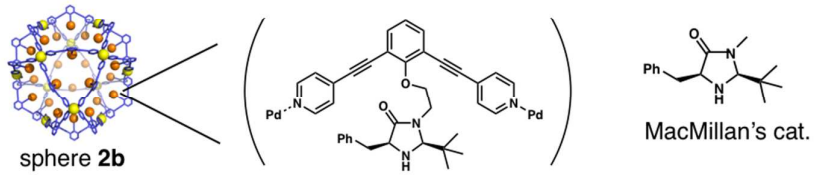
Figure S12. Oxidation reaction profile catalyzed by sphere **2a** and TEMPO.

• **Asymmetric Diels–Alder reaction catalyzed by sphere 2b**

Table S2. Asymmetric Diels-Alder reaction catalyzed by sphere **2b** and MacMillan's cat.[a].



entry	Diels-Alder catalyst	yield of **5**[b]	*endo*/*exo* of **5**	ee of **5**[c]
1	sphere **2b** (10/24 mol%)	86%	>20:1	93%
2	MacMillan's cat. (10 mol%)	88%	>20:1	96%

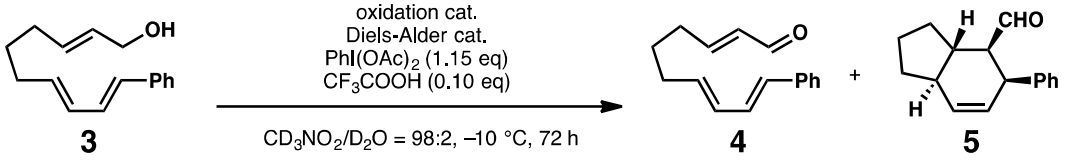


[a] Reaction conditions: each reagent and reactant was separately dissolved in CD_3NO_2/D_2O = 98:2 and certain volumes of each solution were taken and mixed into a test tube directly (with total volume = 800 μL), compound **4** (mixture of *E*,*E*-diene geometry 18.1 mg, 80.0 μmol and *Z*,*E*-diene geometry 2.7 mg, 12.0 μmol)[1] in CD_3NO_2/D_2O = 98:2 (400 μL), sphere **2b** was prepared in advance with ligand **1b** (4.44 mg, 8.00 μmol) and $[Pd(CH_3CN)_4](BF_4)_2$ (1.78 mg, 4.00 μmol) in CD_3NO_2/D_2O = 98:2 (400 μL), TFA (0.612 μL, 8.00 μmol) and AcOH (45.8 μL, 8.00 μmol) were added to sphere **2b** solution. [b] The reactions were subsequently monitored by ^{1}H NMR and the yields of the product **5** were calculated based on the integration by using tetramethylsilane in $CDCl_3$ as an external standard. Yield was based on the conversion of the *E*,*E*-diene substrate to product **5**. [c] The ee values were determined by HPLC with a DAICEL CHIRALPAK IB column (IPA/Hexane = 1:99). Absolute structure was determined by comparison of reported optical rotation[S1] and observed optical rotation value.

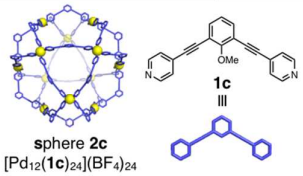
[1] *Z*,*E*-dienes of compound **4** were uniformly inert to this catalytic asymmetric Diels-Alder reaction, and equivalents of reagents were based on *E*,*E*-diene geometry of compound **4**.

• **Oxidation and asymmetric Diels-Alder cascade reaction catalyzed by sphere 2a and 2b**

Table S3. Effects of site-isolation of catalysts in $M_{12}L_{24}$ spherical complexes[a].



entry	oxidation cat. (mol%)	Diels-Alder cat. (mol%)	additive (mol%)	yield of **4**[b]	yield of **5**[b]
1	sphere **2a** (20/24)	sphere **2b** (10/24)	-	4%	56%[c]
2	TEMPO (20)	sphere **2b** (10/24)	-	79%	4%
3	sphere **2a** (20/24)	MacMillan's cat. (10)	-	76%	3%
4	TEMPO (20)	MacMillan's cat. (10)	-	90%	<1%
5	TEMPO (20)	MacMillan's cat. (10)	sphere **2c** (30/24)	64%	<1%
6	-	sphere **2b** (10/24)	-	<1%	<1%
7	sphere **2a** (20/24)	-	-	61%	<1%
8	-	sphere **2b** (10/24)	sphere **2c** (20/24)	69%	<1%
9	sphere **2a** (20/24)	-	sphere **2c** (10/24)	54%	4%
10	TEMPO (20)	sphere **2b** (10/24)	sphere **2c** (20/24)	58%	1%
11	sphere **2a** (20/24)	MacMillan's cat. (10)	sphere **2c** (10/24)	64%	<1%



[a] Compound **3**, CF_3COOH, MacMillan's cat., sphere **2b** and sphere **2c** were dissolved in CD_3NO_2/D_2O = 98:2 (267 μL) as 'solution A'. $PhI(OAc)_2$, TEMPO, sphere **2a** and sphere **2c** were dissolved in CD_3NO_2/D_2O = 98:2 (533 μL) as 'solution B'. Sphere **2a–c** were synthesized with 1.0 eq of ligand **1a–c** and 0.50 eq of $[Pd(CH_3CN)_4](BF_4)_2$ in CD_3NO_2/D_2O = 98:2. Ligand **1c** was synthesized according to the reported procedure.[S2] The equivalent of reactants/reagents is shown in Table S4. Certain volumes of each solution were taken and mixed into a test tube directly (with total volume = 800 μL). [b] The reactions were subsequently monitored by ^1H NMR and the yields of the products were calculated based on the integration by using tetramethylsilane in $CDCl_3$ as an external standard. [c] Product was formed in *endo*/*exo* = >20:1 and 93% ee. The ee values were determined by HPLC with a DAICEL CHIRALPAK IB column (IPA/Hexane = 1:99).

Table S4. Solution A and Solution B preparation for each entry in Table S3.

entry	solution A: CD_3NO_2/D_2O = 98:2 (267 μL)					solution B: CD_3NO_2/D_2O = 98:2 (533 μL)			
	substrate **3**[1] (μmol)	CH_3COOH (μmol)	MacMillan's cat. (μmol)	sphere **2b** (μmol)	Sphere **2c** (μmol)	$PhI(OAc)_2$ (μmol)	TEMPO (μmol)	sphere **2a** (μmol)	sphere **2c** (μmol)
1	80.0	8.00	-	8.00/24	-	92.0	-	16.0/24	-
2	80.0	8.00	-	8.00/24	-	92.0	16.0	-	-
3	80.0	8.00	8.00	-	-	92.0	-	16.0/24	-
4	80.0	8.00	8.00	-	-	92.0	16.0	-	-
5	80.0	8.00	8.00	-	8.0/24	92.0	16.0	-	16.0/24
6	80.0	8.00	-	8.00/24	-	92.0	-	-	-
7	80.0	8.00	-	-	-	92.0	-	16.0/24	-
8	80.0	8.00	-	8.00/24	-	92.0	-	-	16.0/24
9	80.0	8.00	-	-	8.0/24	92.0	-	16.0/24	-
10	80.0	8.00	-	8.00/24	-	92.0	16.0	-	16.0/24
11	80.0	8.00	8.00	-	8.0/24	92.0	-	16.0/24	-

[1]Amount of substance of *E*,*E*-diene of compound **3** (contaminated with *Z*,*E*-diene geometry 12.0 μmol). Equivalents of reagents were based on *E*,*E*-diene geometry of compound **3**.

4. References

(S1) Wilson, R. M.; Jen, W. S.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2005**, *127*, 11616.

(S2) Fujita, D.; Takahashi, A.; Sato, S.; Fujita, M. *J. Am. Chem. Soc*. **2011**, *133*, 13317.