Supporting Information

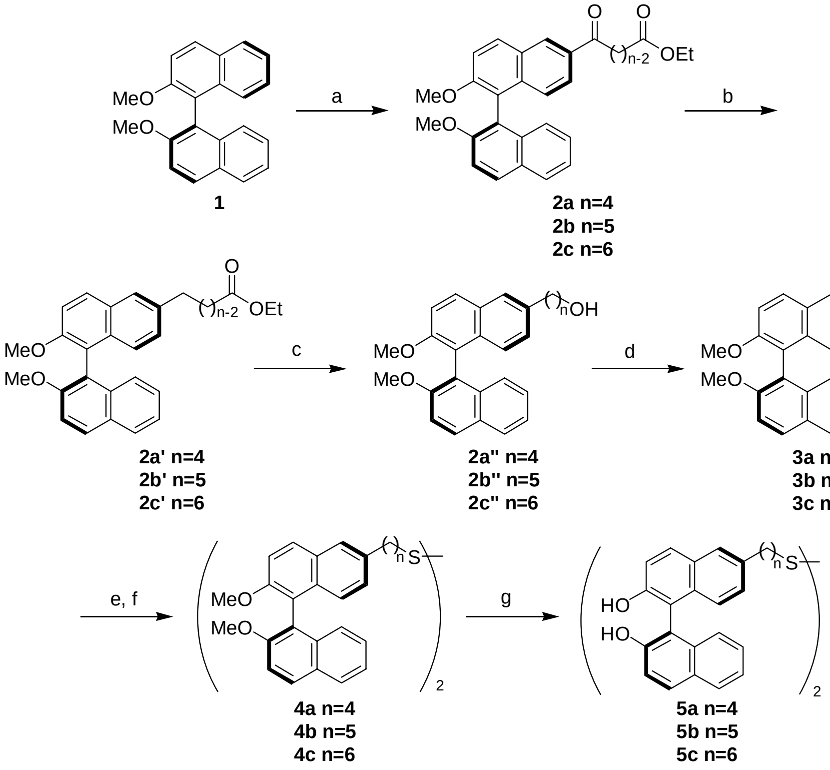
Monolayer-protected Au Cluster (MPC)-supported Ti-BINOLate Complex

Kazuyoshi Marubayashi, Shinobu Takizawa, Tetsuo Kawakusu, Takayoshi Arai, and Hiroaki Sasai*
The Institute of Scientific and Industrial Research (ISIR), Osaka University
Mihogaoka, Ibaraki, Osaka 567-0047, Japan
sasai@sanken.osaka-u.ac.jp

Experimental section

^{1}H and ^{13}C NMR spectra were recorded with JEOL JNM-EX270 FT NMR (^{1}H-NMR 270 MHz, ^{13}C-NMR 67.7 MHz). All signals are expressed as ppm down field from tetramethylsilane used as an internal standard. FT-IR spectra were recorded on a SHIMADZU FTIR-8300. Optical rotations were measured with JASCO P-1030 polarimeter. HPLC analyses were performed on a JASCO HPLC system (JASCO PU 980 pump and UV-975 UV/Vis detector) using a mixture of hexane and *i*-PrOH as the eluent. Mass spectra were obtained on JEOL JMS-700 (for FAB-MS). Elemental analysis was performed on PERKIN-ELMER 2400. Dynamic light scattering (DLS) was measured with Microtrac Version 10.0.4-J005 by NIKKISO Co. Ltd. Transmission electron microscope (TEM) was measured with JEM-3000F. Column chromatography on SiO_2 was performed with Kanto Silica Gel 60 (40-100 μm). Commercially available organic and inorganic compounds were used without further purification except for the solvent, which was distilled by the known method before use.

Synthesis of disulfides 5



Reagents and conditions: (a) $AlCl_3$, $EtO_2C(CH_2)_{n-2}COCl$, CH_2Cl_2; (b) TFA, Et_3SiH, CH_2Cl_2; (c) LAH, THF; (d) PPh_3, CBr_4, THF; (e) $(NH_2)_2C{=}S$, DMSO; (f) I_2, NaOH aq; (g) BBr_3, CH_2Cl_2

General procedure

Preparation of 2: To a solution of chiral 2,2'-dimethoxy-1,1'-binaphthyl (**1**) (29 mmol) in CH_2Cl_2 (250 mL) under argon atmosphere was added $AlCl_3$ (35 mmol) as a powder at 0 °C. After stirring for 10 minutes, corresponding acid chloride mono ethyl ester (32 mmol) was added dropwise to the above mixture. The reaction was quenched with water at 0 °C when the formation of small amount of diacylated compound at 6,6’ position of **1** was observed by TLC analysis. The mixture was extracted with EtOAc and then washed with 1N HCl, brine, dried over Na_2SO_4, filtered and concentrated. To the crude mixture was added a small amount of acetone. Compound **1**, which was unreacted, was precipitated and removed by Celite® filtration, and the filtrate was concentrated under vacuum to give an oil, which was subjected to column chromatography on SiO_2 with EtOAc-hexane (1/9) as the eluent. Compound **2** was obtained as a yellow oil.

2a (n=4) : 75 % yield. Known compound. Bayston, D. J.; Fraser, J. L.; Ashton, M. R.; Baxter, A. D.; Polywka, M. E. C.; Moses, E. *J. Org. Chem.* **1998**, *63*, 3137.

2b (n=5) : 62 % yield. IR(neat): ν_{max} 3059, 2978, 2941, 2905, 2837, 1728, 1676, 1616, 1593, 1508, 1479, 1466, 1443, 1375, 1246, 1173, 1148, 1094, 1065, 1045, 1020, 955, 907, 808, 750, 687, 596 cm^{-1}**.** $[\alpha]^{25}_{D}$ +4.5° (c 1.13, $CHCl_3$) (*R*)-isomer. ^{1}H-NMR ($CDCl_3$): δ 1.24 (t, *J*=7.0Hz, 3H), 1.97 (quin, *J*=7.3Hz, 2H), 2.09 (t, *J*=7.3Hz, 2H), 2.40 (t, *J*=7.3Hz, 2H), 3.74 (s, 3H), 3.77 (s, 3H), 4.12 (q, *J*=7.0Hz, 2H) 7.02-7.32 (m, 4H), 7.44 (d, *J*=9.0Hz, 1H), 7.49 (d, *J*=9.0Hz, 1H), 7.74 (dd, *J*=9.0, 1.8Hz, 1H), 7.85 (d, *J*=8.1Hz, 1H), 7.97 (d, *J*=9.0Hz, 1H), 8.08 (d, *J*=9.0Hz, 1H), 8.50 (d, *J*=1.8Hz, 1H)**.** ^{13}C-NMR ($CDCl_3$): δ 14.29, 19.71, 33.52, 37.39, 56.56, 56.78, 60.35, 113.91, 114.38, 118.55, 119.46, 123.46, 124.15, 124.74, 125.56, 126.33, 127.84, 127.90, 129.04, 129.58, 130.00, 131.20, 131.85, 133.63, 136.28, 154.72, 156.91, 173.17, 198.97**.** FAB-HRMS. Calcd for $C_{29}H_{28}O_5$ [M^+]: 456.1937, Found: 456.1934.

2c (n=6) : 69 % yield. IR(neat): ν_{max} 2978, 2941, 2866, 1730, 1707, 1622, 1456, 1373, 1267, 1248, 1178, 1148, 1096, 1067, 1030, 910, 808, 752 cm^{-1}. $[\alpha]^{25}_{D}$ –2.0° (c 1.94, $CHCl_3$) (*S*)-isomer. ^{1}H-NMR ($CDCl_3$): δ 1.23 (t, *J*=7.0Hz, 3H), 1.60-1.78 (m, 6H), 2.30 (t, *J*=7.6Hz, 2H), 3.06 (t, *J*=7.3Hz, 2H), 3.74 (s, 3H), 3.78 (s, 3H), 4.11 (q, *J*=7.0Hz, 2H), 7.00-7.31 (m, 4H), 7.43 (d, *J*=9.2Hz, 1H), 7.49 (d, *J*=9.2Hz, 1H), 7.72 (dd, *J*=9.2, 2.2Hz, 1H), 7.85 (d, *J*=9.2Hz, 1H), 7.97 (d, *J*=9.2Hz, 1H), 8.08 (d, *J*=9.2Hz, 1H), 8.48 (d, *J*=2.2Hz, 1H). ^{13}C-NMR ($CDCl_3$): δ 14.31, 24.14, 24.36, 33.64, 38.09, 56.62, 56.83, 60.34, 113.95, 114.41, 123.49, 124.24, 124.78, 125.57, 126.15, 126.36, 127.88, 127.92, 129.08, 129.61, 129.95, 131.22, 131.99, 156.91, 173.15, 173.39 , 198.90. FAB-MS m/z: 470 [M^+]. Anal. Calcd for $C_{30}H_{30}O_5 \bullet 19/3H_2O$: C, 61.63; H, 7.36. Found: C, 61.63; H, 7.45.

Preparation of 2': To a solution of compound **2** (18 mmol) in CH_2Cl_2 (10 mL) under argon atmosphere, trifluoroacetic acid (21 mL) and triethylsilane (7.2 mL) were added dropwise at 0 °C. The mixture was stirred at ambient temperature until the reaction had reached completion by monitoring with TLC analysis. The reaction was quenched with water in ice bath and then neutralized with saturated Na_2CO_3 aq, washed with brine, and dried over Na_2SO_4. The filtrate was concentrated under vacuum to give an oil, which was subjected to column chromatography on SiO_2 with EtOAc-hexane (1/9) as the eluent. Compound **2'** was obtained as a yellow oil.

2a' (n=4) : 89 % yield. Known compound. Bayston, D. J.; Fraser, J. L.; Ashton, M. R.; Baxter, A. D.; Polywka, M. E. C.; Moses, E. *J. Org. Chem.* **1998**, *63*, 3137.

2b' (n=5) : 72 % yield. IR(neat): ν_{max} 3059, 2934, 2837, 1730, 1620, 1593, 1505, 1481, 1462, 1433, 1371, 1352, 1331, 1246, 1177, 1148, 1134, 1094, 1067, 1047, 1020, 889, 806, 748, 689, 665, 592 cm^{-1}.

$[\alpha]^{25}_{D}$ +12.2° (c 1.94, $CHCl_3$) (*R*)-isomer. ^{1}H-NMR ($CDCl_3$): δ 1.24 (t, *J*=7.0Hz, 3H), 1.68-1.76 (m, 4H), 2.29-2.36 (m, 2H), 2.70-2.76 (m, 2H), 3.74 (s, 3H), 3.75 (s, 3H), 4.11 (q, *J*=7.0Hz, 2H) 7.00-7.33 (m, 5H), 7.41 (d, *J*=6.5Hz, 1H), 7.45 (d, *J*=6.5Hz, 1H), 7.63 (s, 1H), 7.86 (d, *J*=9.2Hz, 1H), 7.90 (d, *J*=9.2Hz, 1H), 7.96 (d, *J*=9.2Hz, 1H). ^{13}C-NMR ($CDCl_3$): δ 14.32, 24.74, 30.73, 34.28, 35.47, 56.90, 56.98, 60.20, 114.15, 114.31, 119.47, 119.64, 123.35, 125.17, 126.22, 127.67, 127.75, 128.69, 129.07, 129.18, 129.25, 132.37, 132.89, 137.00, 154.35, 154.77, 173.45. FAB-HRMS. Calcd for $C_{29}H_{30}O_4$ [M^+]: 442.2144, Found: 442.2143.

2c’ (n=6) : 80 % yield. IR(neat): ν_{max} 3059, 2934, 2853, 2837, 1732, 1622, 1593, 1558, 1541, 1508, 1464, 1373, 1352, 1333, 1265, 1178, 1148, 1134, 1096, 1067, 1018, 889, 808, 748, 590 cm^{-1}. $[\alpha]^{25}_{D}$ –13.7° (c 1.27, $CHCl_3$) (*S*)-isomer. ^{1}H-NMR ($CDCl_3$): δ 1.23 (t, *J*=7.0Hz, 3H), 1.36-1.44 (m, 2H), 1.68-1.76 (m, 4H), 2.29-2.36 (m, 2H), 2.70-2.76 (m, 2H), 3.74 (s, 3H), 3.75 (s, 3H), 4.11 (q, *J*=7.0Hz, 2H) 7.00-7.33 (m, 5H), 7.41 (d, *J*=6.5Hz, 1H), 7.44 (d, *J*=6.5Hz, 1H), 7.62 (s, 1H), 7.85 (d, *J*=9.2Hz, 1H), 7.89 (d, *J*=9.2Hz, 1H), 7.95 (d, *J*=9.2Hz, 1H). ^{13}C-NMR ($CDCl_3$): δ 14.30, 24.91, 28.85, 30.90, 30.95, 34.32, 35.60, 56.88, 56.98, 60.16, 114.13, 114.26, 119.43, 119.62, 123.33, 125.07, 125.16, 126.12, 126.16, 127.74, 128.66, 129.05, 129.17, 129.24, 132.31, 133.87, 137.34, 154.29, 154.76, 173.57. FAB-HRMS. Calcd for $C_{30}H_{32}O_4$ [M^+]: 456.2301, Found: 456.2292.

Preparation of 2”: To a solution of compound **2’** (20 mmol) in THF (150 mL) under argon atmosphere, $LiAlH_4$ (20 mmol) was added and stirred at 0 °C. The mixture was stirred until the reaction had reached completion by monitoring with TLC analysis. The reaction was quenched with water in ice bath and extracted with EtOAc. The organic layer was washed with 1N HCl and brine, dried over Na_2SO_4. The filtrate was concentrated under vacuum to give an oil, which was subjected to column chromatography on SiO_2 with EtOAc-hexane (1/4) as the eluent. Compound **2”** was obtained in quantitative yield as a colorless oil.

2a” (n=4) : IR(neat): ν_{max} 3393, 3059, 3007, 2934, 2837, 1620, 1594, 1505, 1480, 1460, 1351, 1330, 1263, 1178, 1148, 1092, 1067, 1047, 1018, 889, 808, 748, 689, 660 cm^{-1}. $[\alpha]^{25}_{D}$ +14.5° (c 1.19, $CHCl_3$) (*R*)-isomer. ^{1}H-NMR ($CDCl_3$): δ 1.37 (s, OH), 1.59-1.79 (m, 4H), 2.73 (t, *J*=7.6Hz, 2H), 3.64 (t, *J*=6.3Hz, 2H), 3.73 (s, 3H), 3.75 (s, 3H), 6.99-7.32 (m, 5H), 7.41 (d, *J*=7.0Hz, 1H), 7.44 (d, *J*=7.0Hz, 1H), 7.62 (s, 1H), 7.85 (d, *J*=9.2Hz, 1H), 7.88 (d, *J*=9.2Hz, 1H), 7.95 (d, *J*=9.2Hz, 1H). ^{13}C-NMR ($CDCl_3$): δ 27.37, 32.43, 35.52, 56.93, 57.00, 62.88, 114.13, 114.28, 119.42, 119.59, 123.37, 125.16, 126.16, 126.27, 127.73, 127.77, 128.70, 129.06, 129.22, 132.35, 133.87, 137.14, 154.33, 154.76. FAB-MS m/z 386 [M^+].

Anal. Calcd for $C_{26}H_{26}O_3 \cdot 2/3H_2O$: C,78.36; H, 6.91. Found: C, 78.18; H, 6.72.

2b'' (n=5) : IR(neat): ν_{max} 3377, 3058, 2999, 2932, 2837, 1622, 1593, 1506, 1481, 1460, 1352, 1331, 1256, 1178, 1148, 1134, 1094, 1065, 1047, 1018, 885, 806, 748, 689, 660 cm^{-1}. $[\alpha]^{25}_{D}$ –16.1° (c 1.19, $CHCl_3$) (*S*)-isomer. ^{1}H-NMR ($CDCl_3$): δ 1.36-1.47 (m, 2H), 1.54-1.75 (m, 4H), 2.71 (t, *J*=7.6Hz, 2H), 3.61 (t, *J*=6.5Hz, 2H) 3.73 (s, 3H), 3.75 (s, 3H), 7.00-7.33 (m, 5H), 7.41 (d, *J*=7.2Hz, 1H), 7.44 (d, *J*=7.2Hz, 1H), 7.62 (s, 1H), 7.85 (d, *J*=9.2Hz, 1H), 7.88 (d, *J*=9.2Hz, 1H), 7.95 (d, *J*=9.2Hz, 1H). ^{13}C-NMR ($CDCl_3$): δ 25.53, 31.10, 32.71, 35.80, 56.93, 57.01, 62.92, 114.17, 114.31, 119.47, 119.66, 123.37, 125.10, 125.19, 126.14, 126.20, 127.77, 128.69, 129.08, 129.20, 129.27, 132.33, 133.90, 137.41, 154.32, 154.78. FAB-MS m/z 400 [M$^+$]. Anal. Calcd for $C_{27}H_{28}O_3 \cdot 1/3H_2O$: C,79.77; H, 7.11. Found: C, 79.74; H, 7.11.

2c'' (n=6) : IR(neat): ν_{max} 3356, 3059, 2999, 2930, 2853, 1622, 1593, 1506, 1481, 1460, 1352, 1330, 1254, 1178, 1148, 1134, 1094, 1065, 1047, 1020, 889, 806, 748, 689, 664, 592 cm^{-1}. $[\alpha]^{25}_{D}$ –14.0° (c 0.56, $CHCl_3$) (*S*)-isomer. ^{1}H-NMR ($CDCl_3$): δ 1.36-1.41 (m, 4H), 1.55 (t, *J*=6.7Hz, 2H), 1.65-1.71 (m, 2H), 2.71 (t, *J*=7.8Hz, 2H), 3.60 (t, *J*=6.5Hz, 2H) 3.73 (s, 3H), 3.75 (s, 3H), 7.00-7.33 (m, 5H), 7.41 (d, *J*=7.2Hz, 1H), 7.44 (d, *J*=7.2Hz, 1H), 7.62 (s, 1H), 7.85 (d, *J*=9.2Hz, 1H), 7.88 (d, *J*=9.2Hz, 1H), 7.96 (d, *J*=9.2Hz, 1H). ^{13}C-NMR ($CDCl_3$): δ 25.67, 29.17, 31.25, 32.70, 35.76, 56.90, 56.99, 62.96, 114.15, 114.28, 119.44, 119.66, 123.35, 125.05, 125.18, 126.14, 127.76, 127.80, 128.67, 129.07, 129.18, 129.27, 132.30, 133.89, 137.57, 154.29, 154.76. FAB-HRMS. Calcd for $C_{28}H_{30}O_3$ [M$^+$]: 414.2195, Found: 414.2188.

Preparation of compound 3: To a mixture of compound **2''** (12 mmol), PPh_3 (24 mmol) in THF (150 mL) under argon atmosphere was added CBr_4 (24 mmol) at 0 °C. The mixture was stirred until the reaction had reached completion by monitoring with TLC analysis. The reaction mixture was diluted with hexane, PPh_3O was precipitated and filtered through Celite®. The filtrate was concentrated under vacuum to give an oil, which was subjected to column chromatography on SiO_2 with EtOAc-hexane (1/10) as the eluent. Compound **3** was obtained as a yellow oil.

3a (n=4) : 70 % yield. IR(neat): ν_{max} 3060, 2998, 2933, 2837, 1623, 1593, 1507, 1481, 1462, 1351, 1328, 1263, 1178, 1147, 1134, 1092, 1067, 1047, 1018, 889, 808, 748, 689 cm^{-1}. $[\alpha]^{25}_{D}$ –14.5° (c 1.12, $CHCl_3$) (*S*)-isomer. ^{1}H-NMR ($CDCl_3$): δ 1.76-1.97 (m, 4H), 2.74 (t, *J*=7.0Hz, 2H), 3.42 (t, *J*=6.5Hz, 2H) 3.75 (s, 3H), 3.76 (s, 3H), 7.00-7.34 (m, 5H), 7.42 (d, *J*=5.4Hz, 1H), 7.45 (d, *J*=5.4Hz, 1H), 7.63 (s, 1H), 7.86 (d, *J*=9.2Hz, 1H), 7.90 (d, *J*=9.2Hz, 1H), 7.97 (d, *J*=9.2Hz, 1H). ^{13}C-NMR ($CDCl_3$): δ 29.69, 32.32, 33.85, 34.86, 56.91, 56.97, 114.09, 114.30, 119.51, 123.37, 125.14, 125.24, 126.18, 126.31, 127.61, 127.79, 128.71, 129.04, 129.23, 132.40, 133.85, 136.60, 154.38, 154.75. FAB-MS m/z 448 [M^+]. Anal. Calcd for $C_{26}H_{25}BrO_2 \cdot 3/7H_2O$: C, 68.32; H, 5.70; Br, 17.48. Found: C, 68.05; H, 5.73; Br, 17.56.

3b (n=5) : quantitative yield. IR(neat): ν_{max} 3058, 2999, 2933, 2837, 1622, 1593, 1508, 1480, 1460, 1352, 1329, 1263, 1178, 1148, 1134, 1092, 1067, 1047, 1018, 889, 804, 748, 689 cm^{-1}. $[\alpha]^{25}_{D}$ –14.7^o (c 1.01, $CHCl_3$) (*S*)-isomer. ^{1}H-NMR ($CDCl_3$): δ 1.45-1.57 (m, 2H), 1.65-1.77 (m, 2H), 1.85-1.96 (m, 2H), 2.74 (t, *J*=7.3Hz, 2H), 3.40 (t, *J*=6.9Hz, 2H) 3.75 (s, 3H), 3.77 (s, 3H), 7.00-7.35 (m, 5H), 7.43 (d, *J*=5.9Hz, 1H), 7.46 (d, *J*=5.9Hz, 1H), 7.65 (s, 1H), 7.88 (d, *J*=9.2Hz, 1H), 7.92 (d, *J*=9.2Hz, 1H), 7.98 (d, *J*=9.2Hz, 1H). ^{13}C-NMR ($CDCl_3$): δ 27.92, 30.44, 32.75, 33.88, 35.61, 56.86, 56.95, 114.10, 114.27, 119.40, 119.56, 123.35, 125.14, 126.13, 126.20, 127.68, 127.77, 128.68, 129.04, 129.20, 132.33, 133.86, 137.10, 154.32, 154.75. FAB-HRMS. Calcd for $C_{27}H_{27}BrO_2$ [M^+]: 462.1194, Found: 462.1194.

3c (n=6) : 90 % yield. IR(neat): ν_{max} 3058, 2999, 2934, 2853, 1623, 1592, 1508, 1481, 1460, 1352, 1329, 1263, 1178, 1148, 1134, 1092, 1067, 1047, 1018, 889, 808, 748, 689 cm^{-1}. $[\alpha]^{25}_{D}$ –13.8^o (c 1.58, $CHCl_3$) (*S*)-isomer. ^{1}H-NMR ($CDCl_3$): δ 1.34-1.50 (m, 4H), 1.65-1.73 (m, 2H), 1.79-1.90 (m, 2H), 2.71 (t, *J*=7.5Hz, 2H), 3.36 (t, *J*=6.7Hz, 2H) 3.73 (s, 3H), 3.77 (s, 3H), 7.00-7.33 (m, 5H), 7.42 (d, *J*=5.9Hz, 1H), 7.45 (d, *J*=5.9Hz, 1H), 7.62 (s, 1H), 7.88 (d, *J*=9.2Hz, 1H), 7.90 (d, *J*=9.2Hz, 1H), 7.96 (d, *J*=9.2Hz, 1H). ^{13}C-NMR ($CDCl_3$): δ 28.06, 28.47, 31.04, 32.75, 33.98, 35.68, 56.88, 56.96, 114.16, 114.30, 119.48, 119.66, 123.35, 125.10, 125.17, 126.12, 126.17, 127.74, 128.66, 129.08, 129.17, 129.27, 132.33, 133.90, 137.37, 154.32, 154.77. FAB-MS m/z 477 [M^+]. Anal. Calcd for $C_{28}H_{29}BrO_2 \cdot 3/10H_2O$: C,69.65; H, 6.18; Br, 16.55. Found: C, 69.35; H, 6.23; Br, 16.84.

Preparation of compound 4: To a solution of compound **3** (12 mmol) in DMSO (100 mL) under argon atmosphere, thiourea (24 mmol) was added and stirred at 35 ^{o}C. The mixture was stirred until compound **3** was consumed completely by monitoring with TLC analysis. 20% NaOH aq was added to adjust the pH to 11. After 3h, the reaction mixture was acidified with 5N HCl to pH 3, and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4. The filtrate was concentrated under vacuum to give an oil, which was subjected to column chromatography on SiO_2 with EtOAc-hexane (1/4) as the eluent. A mixture of compound **4** and corresponding thiol was obtained as a colorless oil. The mixture was treated with iodine (6 mmol) in NaOH aq (12 mmol) to afford a red oil, which was purified through column chromatography on SiO_2 with EtOAc-hexane (1/4) as the eluent.

Compound **4** was obtained as a colorless oil.

4a (n=4) : 71 % yield. IR(neat): ν_{max} 3050, 3000, 2933, 2830, 1622, 1594, 1503, 1482, 1461, 1431, 1355, 1331, 1263, 1216, 1175, 1148, 1134, 1092, 1067, 1047, 1018, 889, 806, 748, 664, 592 cm^{-1}. $[\alpha]^{25}_{D}$ -15.5^{o} (c 1.13, $CHCl_3$) (*S*)-isomer. ^{1}H-NMR ($CDCl_3$): δ 1.59-1.82 (m, 8H), 2.61-2.74 (m, 8H), 3.74 (s, 6H), 3.76 (s, 6H), 7.00-7.33 (m, 10H), 7.38-7.45 (m, 4H), 7.62 (s, 2H), 7.83-7.90 (m, 4H), 7.95 (d, *J*=8.9Hz, 2H). ^{13}C-NMR ($CDCl_3$): δ 28.90, 30.03, 35.37, 39.07, 56.91, 56.99, 114.18, 114.35, 119.50, 119.66, 123.37, 125.18, 126.16, 126.27, 127.69, 127.77, 128.71, 129.09, 129.21, 129.27, 132.40, 133.91, 136.97, 154.38, 154.89. FAB-HRMS. Calcd for $C_{52}H_{50}O_4S_2$ [M^{+}]: 802.3150, Found: 802.3145.

4b (n=5) : 75 % yield. IR(neat): ν_{max} 3051, 3001, 2929, 2835, 1620, 1593, 1503, 1481, 1460, 1431, 1354, 1331, 1246, 1215, 1176, 1148, 1134, 1092, 1065, 1047, 1018, 889, 806, 748, 665, 592 cm^{-1}. $[\alpha]^{25}_{D}$ $+15.5^{o}$ (c 1.06, $CHCl_3$) (*R*)-isomer. ^{1}H-NMR ($CDCl_3$): δ 1.40-1.51 (m, 4H), 1.57-1.74 (m, 8H), 2.61 (t, *J*=7.3Hz, 4H), 2.70 (t, *J*=7.6Hz, 4H), 3.74 (s, 6H), 3.75 (s, 6H), 7.00-7.33 (m, 10H), 7.42 (d, *J*=8.6Hz, 2H), 7.44 (d, *J*=8.6Hz, 2H), 7.62 (s, 2H), 7.86 (d, *J*=8.9Hz, 2H), 7.88 (d, *J*=8.9Hz, 2H), 7.95 (d, *J*=8.9Hz, 2H). ^{13}C-NMR ($CDCl_3$): δ 28.64, 28.99, 30.71, 30.88, 30.98, 35.40, 35.69, 56.86, 56.95, 114.07, 114.21, 119.36, 119.55, 123.33, 125.05, 125.14, 126.13, 126.18, 127.75, 128.67, 129.02, 129.17, 129.20, 132.27, 133.84, 137.34, 154.26, 154.72. FAB-HRMS. Calcd for $C_{54}H_{54}O_4S_2$ [M^{+}]: 830.3463, Found: 830.3449.

4c (n=6) : 69 % yield. IR(neat): ν_{max} 3056, 3000, 2934, 2853, 1622, 1592, 1504, 1480, 1459, 1431, 1354, 1331, 1263, 1216, 1178, 1148, 1134, 1092, 1067, 1047, 1022, 889, 808, 748, 665, 592 cm^{-1}. $[\alpha]^{25}_{D}$ -14.2^{o} (c 1.14, $CHCl_3$) (*S*)-isomer. ^{1}H-NMR ($CDCl_3$): δ 1.36-1.41 (m, 4H), 1.64-1.69 (m, 4H), 2.62-2.71 (m, 4H), 3.74 (s, 6H), 3.75 (s, 6H), 7.02-7.32 (m, 10H), 7.42 (d, *J*=8.6Hz, 2H), 7.43 (d, *J*=8.6Hz, 2H), 7.61 (s, 2H), 7.84 (d, *J*=8.9Hz, 2H), 7.87 (d, *J*=8.9Hz, 2H), 7.95 (d, *J*=8.9Hz, 2H). ^{13}C-NMR ($CDCl_3$): δ 28.44, 29.00, 29.19, 31.15, 35.76, 39.15, 56.93, 57.02, 114.20, 114.32, 119.50, 119.71, 123.37, 125.09, 125.20, 126.15, 127.77, 128.70, 129.10, 129.20, 129.30, 132.33, 133.92, 137.54, 154.32, 154.80. FAB-HRMS. Calcd for $C_{56}H_{58}O_4S_2$ [M^{+}]: 858.3776, Found: 858.3751.

Preparation of compound 5: To a solution of compound **4** (8 mmol) in CH_2Cl_2 (80 mL) under argon atmosphere, 1M BBr_3 solution in CH_2Cl_2 (24mL, 24 mmol) was added at 0 ^{o}C. The mixture was stirred until the reaction had reached completion by monitoring with TLC analysis. The reaction was quenched with ice and extracted with EtOAc. The organic layer was washed with 1N HCl and brine, dried over Na_2SO_4. The filtrate was concentrated under vacuum to give an oil, which was subjected to column chromatography on SiO_2 with EtOAc-hexane (1/2) as the eluent. Compound **5** was obtained in quantitative yield as a yellow powder.

5a (n=4) : IR(neat): ν_{max} 3497, 3393, 3059, 3014, 2930, 2853, 1618, 1597, 1508, 1463, 1433, 1380, 1340, 1271, 1256, 1215, 1178, 1146, 1126, 1070, 1026, 982, 949, 818, 750, 667 cm^{-1}. $[\alpha]^{25}_{D}$ –44.8^o (c 1.00, $CHCl_3$) (*R*)-isomer. ^{1}H-NMR ($CDCl_3$): δ 1.57-1.79 (m, 8H), 2.59-2.74 (m, 8H), 5.04 (br, OH), 7.02-7.14 (m, 6H), 7.27-7.37 (m, 8H), 7.63 (s, 2H), 7.85-7.88 (m, 4H), 7.95 (d, *J*=8.9Hz, 2H). ^{13}C-NMR ($CDCl_3$): δ 28.53, 28.81, 29.94, 30.09, 30.81, 31.03, 35.28, 38.94, 110.60, 110.89, 11763, 123.88, 124.12, 126.84, 127.30, 128.25, 128.72, 129.27, 129.27, 129.43, 130.72, 131.19, 131.65, 133.25, 137.72, 151.96, 152.51. FAB-HRMS. Calcd for $C_{48}H_{42}O_4S_2$ [M^+]: 746.2524, Found: 746.2502. mp 103-105 ^{o}C (EtOAc-hexane).

5b (n=5) : IR(neat): ν_{max} 3504, 3422, 3059, 3014, 2926, 2853, 1618, 1597, 1508, 1463, 1433, 1381, 1340, 1315, 1271, 1256, 1215, 1178, 1146, 1126, 1070, 1026, 982, 949, 818, 750, 671 cm^{-1}. $[\alpha]^{25}_{D}$ –49.0^o (c 0.52, $CHCl_3$) (*R*)-isomer. ^{1}H-NMR ($CDCl_3$): δ 1.40-1.49 (m, 4H), 1.54-1.72 (m, 8H), 2.58 (t, *J*=7.3Hz, 4H), 2.70 (t, *J*=7.6Hz, 4H), 5.05 (br, OH), 7.03-7.15 (m, 6H), 7.24-7.38 (m, 8H), 7.63 (s, 2H), 7.85-7.88 (m, 4H), 7.94 (d, *J*=9.2Hz, 2H). ^{13}C-NMR ($CDCl_3$): δ 28.58, 28.98, 30.70, 30.96, 35.44, 35.64, 110.59, 110.90, 117.64, 123.88, 124.07, 124.13, 126.84, 127.33, 128.26, 128.80, 129.29, 129.47, 130.75, 131.21, 131.63, 133.26, 138.06, 151.98, 152.55. FAB-HRMS. Calcd for $C_{50}H_{46}O_4S_2$ [M^+]: 774.2837, Found: 774.2839. mp 74-75 ^{o}C (EtOAc-hexane).

5c (n=6) : IR(neat): ν_{max} 3489, 3420, 3059, 3007, 2926, 2853, 1618, 1597, 1506, 1464, 1437, 1379, 1344, 1313, 1271, 1256, 1213, 1178, 1144, 1124, 1070, 1026, 981, 947, 887, 862, 818, 748, 667 cm^{-1}. $[\alpha]^{25}_{D}$ –46.5^o (c 0.78, $CHCl_3$) (*R*)-isomer. ^{1}H-NMR ($CDCl_3$): δ 1.30-1.40 (m, 8H), 1.62-1.66 (m, 8H), 2.57-2.72 (m, 8H), 5.02 (br, OH), 7.00-7.15 (m, 6H), 7.24-7.38 (m, 8H), 7.63 (s, 2H), 7.82-7.88 (m, 4H), 7.94 (d, *J*=9.2Hz, 2H). ^{13}C-NMR ($CDCl_3$): δ 28.39, 28.77, 28.93, 29.02, 29.14, 30.85, 31.22, 35.69, 39.11, 110.67, 111.00, 117.60, 123.88, 124.05, 124.16, 127.31, 128.25, 128.82, 129.30, 129.50, 130.72, 131.17, 131.64, 133.30, 138.22, 151.97, 152.55. FAB-HRMS. Calcd for $C_{52}H_{50}O_4S_2$ [M^+]: 802.3150, Found: 802.3170. mp 77-78 ^{o}C (EtOAc-hexane).

General procedure for the synthesis of MPC 6

To a solution of tetraoctylammonium bromide (2.8 mmol) in toluene (120 mL) was added $HAuCl_4 \cdot 4H_2O$ (1.4 mml) in deionized water (50 mL). The yellow $HAuCl_4 \cdot 4H_2O$ aqueous solution quickly cleared and the toluene phase became orange-brown as the $AuCl_4^-$ was transferred into it. The organic layer was isolated, compound **5** (0.7 mmol) was added, and the resulting solution was stirred for 10 min at rt. The reaction solution was then vigorously stirred and $NaBH_4$ (14 mmol) in deionized water (50 mL) was added. The black organic phase was further stirred for another 12 h. The aqueous phase was removed, and the solvent was concentrated. The black residue was washed with EtOH, redissolved in toluene and precipitated from EtOH to afford the corresponding MPC **6** in quantitative yield.

Characterization of MPC 6a, 6b, and 6c

MPC **6a-c** were dried under reduced pressure at 50 ^{o}C for 1 d. MPC **6a-c** thus obtained were investigated by elemental analysis instrument. Furthermore, a suspension of MPC **6b** in THF was sonicated for 5 min. The resulting suspension of MPC **6b** was measured by DLS instrument and TEM instrument.