Transfer of Chiral Information via Achiral Ion Recognition by a Novel Pseudocrown Ether with a Binaphthyl Moiety

Tatsuya Nabeshima,* Akihiro Hashiguchi, Toshiyuki Saiki, and Shigehisa Akine

Synthesis and Physical Data of New Compounds

Scheme 1. Synthesis of Podands 1 and 2: a) 1) LDA, THF, r.t., 2) 1,2-bis(2-chloroethoxy)ethane, 29%; b) NBS, AIBN, benzene, reflux;[7b,c] c) NaH, p-xylene, reflux, 63%; d) NaH, THF, reflux, 73%.
4: To a solution of 3\textsuperscript{[7a]} (3.00 g, 7.57 mmol) in 1 L of dry THF was added 6.6 mL of 2.0 M LDA in heptane/THF/ethylbenzene solution at –35 °C to result in a dark blue solution. After the reaction mixture was stirred for 5 min at –35 °C, 9.44 mL of 1,2-bis(2-chloroethoxy)ethane (11.3 g, 60.4 mmol) was added, warmed to room temperature, and then stirred for 12 h. After evaporation of the solvent, the residue thus obtained was mixed with 500 mL of H\textsubscript{2}O, and extracted with CHCl\textsubscript{3} (500 mL x 3). The combined organic layers were dried over anhydrous MgSO\textsubscript{4} and concentrated in vacuo. The crude product was purified twice by alumina column chromatography (CH\textsubscript{2}Cl\textsubscript{2}, CHCl\textsubscript{3}, CH\textsubscript{2}Cl\textsubscript{2}:AcOEt = 10:1) and then silica gel column chromatography (CH\textsubscript{2}Cl\textsubscript{2}, CH\textsubscript{2}Cl\textsubscript{2}:AcOEt = 10:1, CH\textsubscript{2}Cl\textsubscript{2}:MeOH = 10:1) to give 4 (1.20 g, 2.19 mmol) as white powder in 29 % yield. m.p. 93.2-94.0 °C; \textsuperscript{1}H NMR (270 MHz, CDCl\textsubscript{3}, 25 °C, TMS): \(\delta = 8.47\) (s, 2H), 7.76-7.70 (m, 4H), 7.37 (s, 2H), 7.06-7.00 (m, 4H), 3.88 (s, 6H), 3.77-3.54 (m, 10H), 3.01 (t, \(J = 7.3\) Hz, 2H), 2.70 (s, 3H), 2.18 (quint, \(J = 7.0\) Hz, 2H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}, 25 °C, TMS): \(\delta = 131.01, 131.02, 128.30, 120.43, 120.03, 116.27, 116.09, 114.34, 114.31, 71.35, 70.84, 70.67, 70.15, 55.34, 42.69, 34.84, 29.52, 24.75; IR (KBr): \(v = 2958, 1609, 1594, 1548, 1514, 1439, 1291, 1251, 1177, 1112, 1074, 892, 830, 797, 509\) cm\textsuperscript{-1}; analysis calcd for C\textsubscript{32}H\textsubscript{35}ClN\textsubscript{2}O\textsubscript{4}: C 70.25, H 6.45, N 5.12; found: C 70.36, H 6.54, N 5.26.

1: A mixture of 4 (600 mg, 1.10 mmol), (\textit{R})-(\textit{+})-1,1’-binaphthol (130.9 mg, 0.457 mmol) and 60% NaH dispersion (40.2 mg, 1.01 mmol) in mineral oil in 10 ml of \(p\)-xylene was refluxed for 37 h. After evaporation of solvent, the residue thus obtained was mixed with 50 mL of H\textsubscript{2}O, and extracted with CHCl\textsubscript{3} (50 mL x 5). The combined organic layers were dried over anhydrous MgSO\textsubscript{4} and concentrated in vacuo. The crude product was purified by silica gel column chromatography (CHCl\textsubscript{3}, CH\textsubscript{2}Cl\textsubscript{2}:AcOEt = 20:1, CH\textsubscript{2}Cl\textsubscript{2}:MeOH = 20:1, and then 10:1) to give 1 (381 mg, 0.291 mmol) as pale yellow powder in 63 % yield. m.p. 91.4-92.0 °C; \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, 25 °C, TMS): \(\delta = 8.46\) (s, 4H), 7.86 (d, \(J = 9.3\) Hz, 2H), 7.77 (d, \(J = 8.1\) Hz, 2H), 7.75-7.65 (m, 8H), 7.39-7.30 (m, 6H), 7.27-7.22 (m, 2H), 7.18-7.07 (m, 4H), 7.00 (d, \(J = 9.0\) Hz, 8H), 4.05 (t, \(J = 5.7\) Hz, 4H), 3.85 (s, 6H), 3.84 (s, 6H), 3.48-3.36 (m, 8H), 3.18-3.05 (m, 8H), 2.92 (t, \(J = 7.8\) Hz, 4H), 2.69 (s, 6H), 2.08 (quint, \(J = 8.1\) Hz, 4H); \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}, 25 °C, TMS): \(\delta = 161.49, 160.24, 158.17, 156.59, 156.44, 154.24, 148.81, 134.01, 131.05, 131.03, 129.31, 129.20, 128.28, 127.76, 126.18, 125.41, 123.58, 120.42, 115.96, 116.22, 116.08, 115.57, 114.32,
Compound 5 [7b, c] (0.200 mg, 4.21 x 10^{-4} mol) was added to a mixture of 6 [7d] (77.8 mg, 1.68 x 10^{-4} mol) and 60% NaH dispersion (16.8 mg, 4.20 x 10^{-4} mol) in mineral oil in 5 mL of dry THF. The reaction mixture was refluxed for 24 h. After evaporation of the solvent, the residue was mixed with 50 mL of H₂O, and then extracted with CH₂Cl₂ (50 mL x 3). The organic layer was dried over anhydrous MgSO₄, and concentrated in vacuo. The crude product was purified by silica gel column chromatography (CHCl₃, CH₂Cl₂:AcOEt = 20:1, 10:1, CH₂Cl₂:MeOH = 20:1 and then 10:1) to give 2 (153 mg, 1.22 x 10^{-4} mol) as a white powder in 73 % yield. m.p. 104.7-105.8 °C; \(^1\)H NMR (300 MHz, CDCl₃, 25 °C, TMS): \(\delta = 8.54\) (d, \(J = 1.2\) Hz, 2H), \(8.43\) (d, \(J = 1.2\) Hz, 2H), \(7.80\) (d, \(J = 9.6\) Hz, 2H), \(7.76\)-7.66 (m, 10H), \(7.60\) (d, \(J = 2.1\) Hz, 2H), \(7.36\) (d, \(J = 1.8\) Hz, 2H), \(7.33\) (d, \(J = 8.7\) Hz, 2H), \(7.24\)-7.06 (m, 6H), \(7.04\)-6.92 (m, 8H), \(4.67\) (s, 4H), \(4.09\)-4.03 (m, 4H), \(3.85\) (s, 6H), \(3.83\) (s, 6H), \(3.47\) (t, \(J = 5.1\) Hz, 4H), \(3.31\) (t, \(J = 4.8\) Hz, 4H), \(3.17\)-3.12 (m, 4H), \(2.70\) (s, 6H); \(^{13}\)C NMR (75 MHz, CDCl₃, 25 °C, TMS): \(\delta = 160.37, 160.33, 158.66, 158.31, 156.33, 156.29, 154.21, 149.20, 148.94, 134.04, 131.03, 130.96, 129.32, 129.24, 128.42, 128.33, 127.78, 126.23, 125.42, 123.60, 120.59, 120.43, 118.28, 117.31, 116.11, 115.48, 114.36, 114.33, 74.09, 70.50, 69.99, 69.90, 69.58, 55.36, 24.79; ESIMS observed: \(m/z\) 1251.7 (\([M+H]^+\)), calcd for C₈₀H₇₅N₄O₁₀: \(m/z\) 1251.6; analysis calcd for C₈₀H₇₆N₄O₁₀•H₂O: C 75.69, H 6.03, N 4.41; found: C 75.61, H 6.13, N 4.47.
ESI-MS of $1\cdot\text{Cu}^\text{I}$ and $1\cdot\text{Cu}^\text{I}\cdot\text{Na}^+$

$1\cdot\text{Cu}^\text{I}$

$1\cdot\text{Cu}^\text{I}\cdot\text{Na}^+$ ($m/z = 2$)

Observed

Calculated
UV-Vis Spectral Changes of 1 by Addition of 1 equiv of CuCl.

Figure 4. UV-Vis spectral changes of 1 by addition of 1 equiv of CuCl in CH$_2$ClCH$_2$Cl. [1] = 6.00 x 10$^{-6}$ M. Insert shows the titration curve of 1 and CuCl at 480 nm in CH$_2$ClCH$_2$Cl:CH$_3$CN=50:1. [1] = 5.88 x 10$^{-5}$ M.