Supplementary Material (ESI) for Chemical Communications

Electronic Supplemental Information

Title A Novel Synthesis of Chiral Rotaxanes via Covalent Bond Formation

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Content

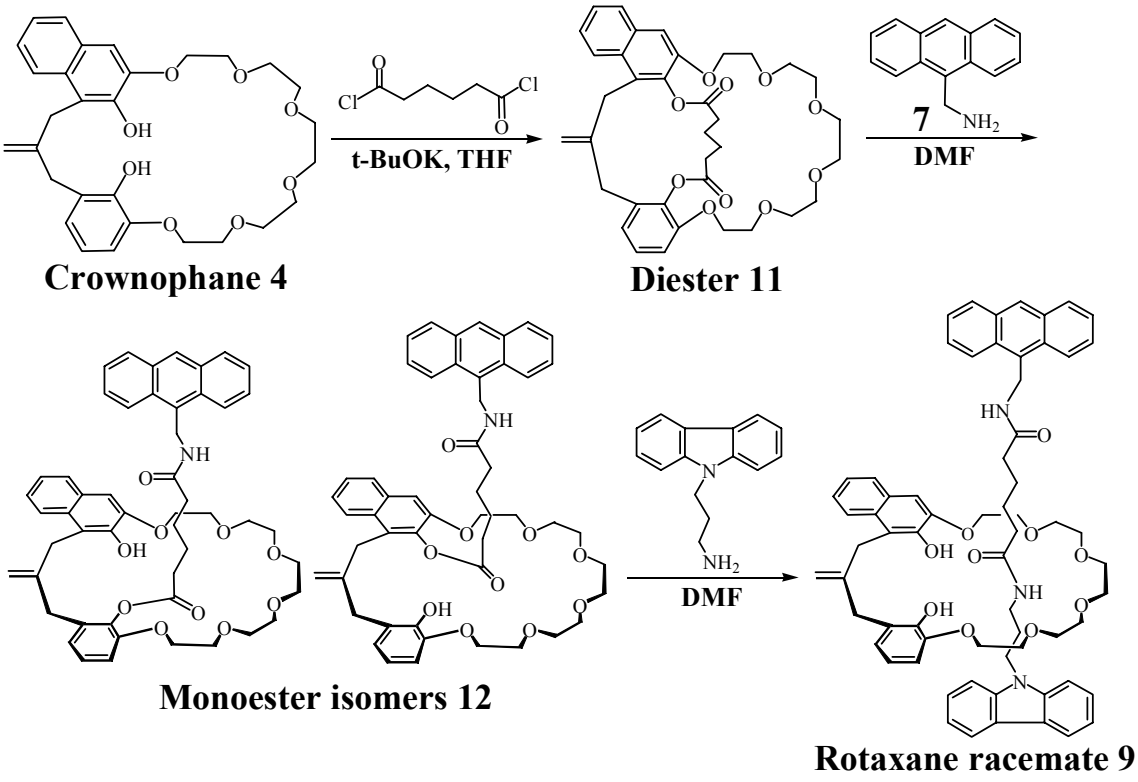
^{1}H NMR, IR, and ESI-MS data for crownophane **4**, monoesters **6**, **12**, diester **11**, and rotaxanes **8, 9, 10**.

Synthesis of rotaxane racemates **9**, **10** via diesterification and aminolysis (Scheme).

Crownophane **4**: ^{1}H NMR ($CDCL_3$) δ 3.51 (s, 2H, Ar-CH_2), 3.85 (s, 2H, Ar-CH_2), 3.69 (m, 14H, -O-CH_2CH_2-O-), 3.81, (m, 2H, -O-CH_2CH_2-O-), 4.13 (m, 2H, -O-CH_2CH_2-O-), 4.26 (m, 2H, -O-CH_2CH_2-O-), 4.48 (d, *J*=1.2, 1H, CH_2=C), 4.60 (d, *J*=1.2, 1H, CH_2=C), 6.72 (t, *J*=7.5, 1H, Ar), 6.84 (dd, *J*=7.5, *J*=1.8, 1H, Ar), 6.89 (dd, *J*=7.5, *J*=1.8, 1H, Ar), 7.13 (s, 1H, Ar), 7.27 (td, *J*=8.1, *J*=1.5, 1H, Ar), 7.34 (td, *J*=8.1, *J*=1.5, 1H, Ar), 7.63 (dd, *J*=8.1, *J*=1.5, 1H, Ar), 7.79 (d, *J*=8.1, 1H, Ar). ESI-MS (CH_3CN) m/z = 547 (Na^+).

Monoester isomers **6** : IR (KBr) 1755 cm^{-1} (ester, C=O), 1673 (amide, C=O). ESI-MS (CH_3CN) m/z = 657 (Na^+). ^{1}H-NMR spectrum of the monoester isomers **6** was complexities, therefore, the assignments for all peaks were not achieved. However, the number of protons corresponded to the monoester **6**.

Rotaxane **8**: ^{1}H NMR ($CDCL_3$) δ 1.30 (m, 2H, -CH_2-), 1.46 (m, 2H, -CH_2-), 1.72 (m, 4H, -$COCH_2$-), 2.64, 3.01, 3.13, 3.22, 3.36, 3.61, 3.68, 3.98, 4.12 (m, 20H, -O-CH_2CH_2-O-), 3.41 (s, 2H, Ar-CH_2), 3.55 (d, *J*=14, 1H, Ar-CH_2), 3.71 (d, *J*=14, 1H, Ar-CH_2), 4.32 (s, 1H, CH_2=C), 4.63 (s, 1H, CH_2=C), 5.14, 5.60 (m, 2H, Ar-CH_2), 5.95 (d, *J*=8.1, 1H, Ar), 6.54 (t, *J*=8.1, 1H, Ar), 6.83 (d, *J*=8.1, 1H, Ar), 6.86 (s, 1H, Ar), 7.26 (t, *J*=8.1, 1H, Ar), 7.28 (t, *J*=8.1, 1H, Ar), 7.52 (d, *J*=8.1, 1H, Ar), 7.88 (d, *J*=8.1, 1H, Ar), 7.04 (m, 6H, Ar), 7.19 (m, 9H, Ar), 7.51 (m, 4H, Ar), 8.00 (m, 2H, Ar), 8.50 (m, 2H, Ar), 8.42 (s, 1H, Ar), 6.27 (s, 1H, NH), 7.51 (br, 1H, NH), 6.98 (s, 1H, OH), 9.17 (s, 1H, OH). IR (KBr) 1677 cm^{-1} (br, amide, C=O). ESI-MS (CH_3CN) m/z = 1123 (Na^+).

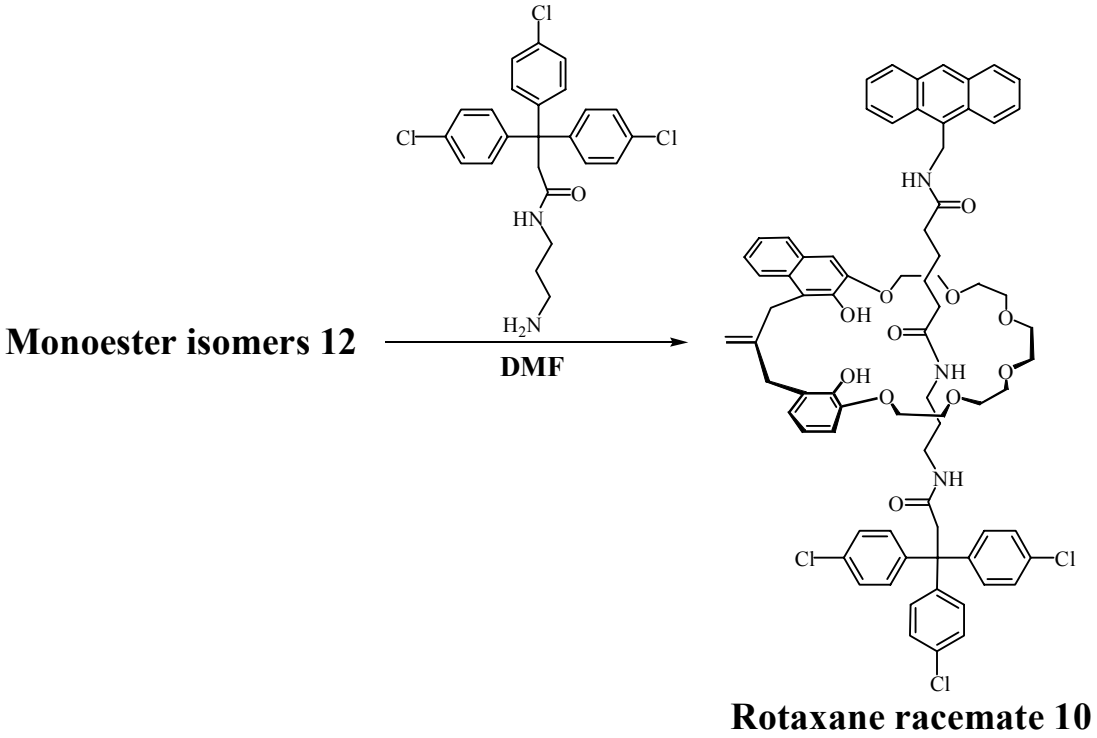


Scheme. Synthesis of rotaxane racemate **9** via diesterification and aminolysis.

Diester **11**: ^{1}H NMR ($CDCL_3$) δ 2.08 (br, 4H, -CH_2CH_2-), 2.75 (br, 4H, -COO-CH_2-), 3.41-4.29, (26H, -O-CH_2CH_2-O-, Ar-CH_2, CH_2=C), 6.87 (dd, *J*=7.8, *J*=1.5, 1H, Ar), 6.91 (dd, *J*=7.8, *J*=1.5, 1H, Ar), 7.14 (t, *J*=7.8, 1H, Ar), 7.13 (s, 1H, Ar), 7.38 (td, *J*=7.5, *J*=1.5, 1H, Ar), 7.43 (td, *J*=7.5, *J*=1.5, 1H, Ar), 7.73 (dd, *J*=7.5, *J*=1.5, 1H, Ar), 7.82 (d, *J*=7.5, 1H, Ar). IR (KBr) 1754 cm^{-1} (ester, C=O). ESI-MS (CH_3CN) m/z = 657 (Na^+).

Monoester isomers **12**: IR (KBr) 1754 cm^{-1} (ester, C=O), 1662 (amide, C=O). ESI-MS (CH_3CN) m/z = 864 (Na^+). ^{1}H-NMR spectrum of the monoester isomers **12** was complexities, therefore, the assignments for all peaks were not achieved. However, the number of protons corresponded to the monoester **12**.

Rotaxane **9**: ^{1}H NMR ($CDCL_3$) δ 1.42, 1.54, 1.82, 3.03, (m, 8H, -CH_2-), 4.02, (t, *J*=6.6, 2H, -N-CH_2-), 1.92, 2.05 (m, 4H, -$COCH_2$-), 3.18, 3.21, 3.41, 3.58, 3.61, 3.68, 3.95, 4.03 (m, 20H, -O-CH_2CH_2-O-), 3.38 (s, 2H, Ar-CH_2), 3.71 (s, 1H, Ar-CH_2), 3.88 (s, 1H, Ar-CH_2), 4.42 (s, 1H, CH_2=C), 4.68 (s, 1H, CH_2=C), 5.20, 5.47 (m, 2H, Ar-CH_2), 6.12 (d, *J*=7.8, 1H, Ar), 6.59 (t, *J*=7.8, 1H, Ar), 6.80 (d, *J*=7.8, 1H, Ar), 6.78 (s, 1H, Ar), 7.18 (t, *J*=8.1, 1H, Ar), 7.31 (t, *J*=8.1, 1H, Ar), 7.54 (d, *J*=8.1, 1H, Ar), 7.86 (d, *J*=8.1, 1H, Ar), 7.17-7.28 (6H, Ar), 8.03 (d, *J*=7.8, 2H, Ar), 7.48 (m, 4H, Ar), 7.98 (m, 2H, Ar), 8.35 (m, 2H, Ar), 8.36 (s, 1H, Ar), 6.11 (br, 1H, NH), 6.84 (br, 1H, NH), 7.14 (s, 1H, OH), 8.84 (s, 1H, OH). IR (KBr) 1647 cm^{-1} (br, amide, C=O). ESI-MS (CH_3CN) m/z = 1088 (Na^+).



Scheme. Synthesis of rotaxane racemate **10** via diesterification and aminolysis.

Rotaxane **10**: 1H NMR ($CDCL_3$) δ 1.36 (m, 2H, -CH_2-), 1.46 (m, 2H, -CH_2-), 1.88 (m, 2H, -$COCH_2$-), 2.06 (m, 2H, -CO-CH_2-), 2.96 (m, 2H, -CH_2-), 3.00 (m, 2H, -CH_2-), 3.17 (s, 2H, -CO-CH_2-C), 3.28, 3.35, 3.42, 3.51, 3.66, 3.92 (m, 4H, -O-CH_2CH_2-O-), 3.24 (s, 2H, Ar-CH_2), 3.49 (d, *J*=12, 1H, Ar-CH_2), 3.75 (d, *J*=12, 1H, Ar-CH_2), 4.41 (s, 1H, CH_2=C), 4.52 (s, 1H, CH_2=C), 5.31, 5.34 (m, 2H,

Ar-CH_2), 6.31 (d, *J*=7.8, 1H, Ar), 6.58 (t, *J*=7.8, 1H, Ar), 6.70 (d, *J*=7.8, 1H, Ar), 6.76 (s, 1H, Ar), 7.20 (t, *J*=7.8, 1H, Ar), 7.30 (t, *J*=7.8, 1H, Ar), 7.52 (d, *J*=7.8, 1H, Ar), 7.84 (d, *J*=7.8, 1H, Ar), 6.96 (d, *J*=8.4, 6H, Ar), 7.07 (d, *J*=8.4, 6H, Ar), 7.48 (t, *J*=7.8, 2H, Ar), 7.52 (t, *J*=7.8, 2H, Ar), 7.99 (d, *J*=7.8, 2H, Ar), 8.25 (d, *J*=7.8, 2H, Ar), 8.41 (s, 1H, Ar), 6.23 (br, 1H, NH), 6.47 (br, 1H, NH), 7.63 (s, 1H, OH), 8.38 (s, 1H, OH). IR (KBr) 1653 cm^{-1} (br, amide, C=O). ESI-MS (CH_3CN) m/z = 1311.5 (Na^+).