Synthesis of Cinchona Alkaloid Sulfonamidine Polymers as Sustainable Catalysts for the Enantioselective Desymmetrization of Cyclic Anhydrides

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Materials and general considerations. All solvents and reagents were purchased from Sigma-Aldrich, Wako Pure Chemical Industries, Ltd., or Tokyo Chemical Industry (TCI) Co., Ltd. at the highest available purity and were used as received, unless otherwise noted. Reactions were monitored by thin-layer chromatography using precoated silica gel plates (Merck 5554, 60F254). Column chromatography was performed using a silica gel column (Wakogel C-200, 100–200 mesh). Melting points were recorded using a Yanaco micro melting apparatus and were uncorrected. NMR spectra were recorded on JEOL JNM-ECS400 spectrometers in CDCl$_3$ or DMSO-$d_6$ at room temperature operating at 400 MHz ($^1$H) and 100 MHz ($^{13}$C{$^1$H}). TMS was used as an internal standard for $^1$H-NMR and CDCl$_3$ for $^{13}$C-NMR. Chemical shifts were reported in ppm using TMS as a reference, and the $J$ values were recorded in Hertz. IR spectra were recorded on a JEOL JIR-7000 FTIR spectrometer and are reported in cm$^{-1}$. Elemental analyses (carbon, hydrogen, nitrogen) were performed on a Yanaco-CHN coder MT-6 analyzer. HRMS (ESI) spectra
were recorded on a microTOF-Q II HRMS/MS instrument (BRUKER). HPLC analyses were performed with a JASCO HPLC system composed of a 3-line degasser DG-980, HPLC pump PV-980, column oven CO-965, equipped with a chiral column (CHIRALCEL AD-H, Daicel) using hexane/2-propanol as eluent. A UV detector (JASCO UV-975 for the JASCO HPLC system) was used for peak detection. Size exclusion chromatography (SEC) was performed using a Tosoh instrument with HLC 8020 UV (254 nm) or refractive index detection. DMF was used as the carrier solvent at a flow rate of 1.0 mL/min at 40 °C. Two polystyrene gel columns of bead size 10 μm were used. A calibration curve was made to determine the number-average molecular weight ($M_n$) and molecular weight distribution ($M_w/M_n$) values with polystyrene standards. Optical rotation was recorded using a JASCO DIP-149 digital polarimeter using a 10-cm thermostated microcell.
$^1$H NMR spectrum of 1C
$^1$H NMR spectrum of 1Q
$^1$H NMR spectrum of 3CI

3CI
$^1$H NMR spectrum of 3QI
$^1$H-NMR spectrum of 5Ca
$^1$H-NMR spectrum of $5C_b$
$^1$H-NMR spectrum of 5Cc
$^1$H-NMR spectrum of $5\text{Cd}$
$^1$H-NMR spectrum of P1C
$^1$H-NMR spectrum of P2Ca
$^1$H-NMR spectrum of P2Cba
$^1$H-NMR spectrum of P2Cca
$^1$H-NMR spectrum of P2Cda
$^1$H-NMR spectrum of P2Cbb
HPLC traces of the product obtained from asymmetric desymmetrization reaction

Table 2, entry 1
10% ee

Table 2, entry 2
49% ee
Table 2, entry 3
51% ee

Table 2, entry 4
37% ee
Table 2, entry 5
34% ee

Table 2, entry 6
20% ee
Table 2, entry 7
79% ee

Table 2, entry 8
94% ee
Table 2, entry 11
95% ee

Table 2, entry 12
93% ee
Table 3, entry 1
90% ee

Table 3, entry 2
91% ee
Table 3, entry 3
92% ee

Table 3, entry 4
93% ee
Table 3, entry 5
95% ee

Table 3, entry 6
93% ee
Table 3, entry 8
84% ee

Table 3, entry 9
65% ee
Table 3, entry 10
88% ee

Table 4, entry 1
95% ee
Table 4, entry 3
71% ee

Table 4, entry 4
95% ee