Supporting Information for:

Remarkable Enhancement of Enantioselectivity of Organocatalyzed Asymmetric Henry Reaction Assisted by Helical Poly(phenylacetylene)s Bearing Cinchona Alkaloid Pendants via an Amide Linkage

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Contents

1. Instruments

The melting points were measured on a Yanako melting point apparatus (Yanako, Kyoto, Japan) and were uncorrected. The NMR spectra were measured using a Varian VXR-500S spectrometer (Varian, Palo Alto, CA) operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C using tetramethylsilane (TMS) or a solvent residual peak as the internal standard. The IR spectra were recorded on a JASCO FT/IR-680 spectrophotometer (JASCO, Tokyo, Japan). The absorption and CD spectra were obtained in a 1.0 cm quartz cell using a JASCO V570 spectrophotometer and a JASCO J-820 spectropolarimeter, respectively. The temperature was controlled with a JASCO PTC-423L apparatus. The concentrations of the polymers were calculated based on the monomer units. The size exclusion chromatography (SEC) measurements were performed with a JASCO PU-980 liquid chromatograph equipped with a UV-visible detector (JASCO UV-1570, 280 nm) and a column oven (JASCO CO-1565). The number-average molecular weight (M_n) and its distribution (M_w/M_n) were determined at 40 °C using a Tosoh TSKgel MultiporeH_{XL}-M (30 cm) SEC column (Tosoh, Tokyo, Japan), and $CHCl_3/CF_3CH_2OH$ (9/1, v/v) containing 0.5 wt% tetrabutylammonium bromide (TBAB) was used as the eluent at a flow rate of 0.5 mL/min. The molecular weight calibration curve was obtained with polystyrene standards (Tosoh). The chiral HPLC analyses were performed on a JASCO PU-2080 Plus liquid chromatograph equipped with a Multi UV-visible detector (JASCO MD-2010 Plus) and an optical rotation detector (JASCO OR-2090 Plus, Hg–Xe without filter) using a Chiralcel OD or Chiralcel OJ-H column (0.46 (i.d.) x 25 cm, Daicel). A 2-propanol/*n*-hexane mixture was used as the eluent. The electron spray ionization mass spectra (ESI-MS) were recorded using a JEOL JMS-T100CS spectrometer (JEOL, Akishima, Japan). The laser Raman spectra were taken on a JASCO RMP-200 spectrophotometer.

2. Materials

All starting materials were purchased from Aldrich (Milwaukee, WI), Wako Pure Chemical Industries (Osaka, Japan), or Tokyo Kasei (TCI, Tokyo, Japan) and were used as received, except for triethylamine (NEt_3) and DMF. NEt_3 was dried over KOH pellets and distilled onto KOH under nitrogen. DMF was dried and deoxygenized by passing through purification columns (Glass Contour Solvent System, Nikko Hansen, Osaka, Japan) before use. Anhydrous THF (water content < 0.005%) was purchased from Wako (Osaka, Japan). (4-Carboxyphenyl)acetylene,[S1] 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methyl-morpholinium chloride (DMT-MM),[S2] **ACd**,[S3] **ACn**,[S3] **AQn**,[S3] and **AQd**[S3] were synthesized according to the previously reported methods.

3. Synthesis of Monomers and Polymers

Synthesis of Monomers (M-ACd, M-ACn, M-AQn, and M-AQd). A typical procedure for the synthesis of M-**ACd** is described below (Scheme 1). DMT-MM (3.39 g, 12.3 mmol) was added to a mixture of (4-carboxyphenyl)acetylene (896 mg, 6.13 mmol) and **ACd** (1.80 g, 6.13 mmol) in anhydrous THF (35 mL) and the mixture was stirred at room temperature overnight. Water (500 mL) was added to the reaction mixture and the mixture was extracted with EtOAc (250 mL x 5). The organic extracts were washed with brine (200 mL x 5) and dried over anhydrous Na_2SO_4. After filtration, the solvent was removed by evaporation, and the residue was then purified by column chromatographies ((SiO_2, $CHCl_3$/methanol = 1/0-20/3, v/v) and (NH-SiO_2, EtOAc/*n*-hexane = 2/1, v/v)) to afford M-**ACd** (1.61 g, 62%) as a white solid; mp 237-238 °C. IR (film, cm^{-1}): 3296 (ν_{N-H}), 2104 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=O}$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.89 (d, *J* = 4.6 Hz, 1H, Ar), 8.46 (d, *J* = 8.6 Hz, 1H, Ar), 8.14 (d, *J* = 7.5 Hz, 1H, Ar), 7.86 (bs, 1H, -N*H*CH-), 7.76-7.72 (m, 3H, Ar), 7.64 (t, *J* = 7.9 Hz, 1H, Ar), 7.54-7.52 (m, 2H, Ar), 7.50 (d, *J* = 4.5 Hz, 1H, Ar), 5.74-5.67 (m, 1H, -C*H*=CH_2), 5.41 (bs, 1H, -NHC*H*-), 5.00-4.94 (m, 2H, -CH=CH_2), 3.32-3.27 (m, 1H), 3.19 (s, 1H), 3.18-3.03 (m, 2H), 2.80-2.70 (m, 2H), 2.35-2.29 (m, 1H), 1.72-1.59 (m, 3H), 1.44-1.37 (m, 1H), 1.07-1.02 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.7, 150.2, 148.8, 141.33, 141.32, 134.0, 132.4, 130.7, 129.3, 127.3, 126.9, 125.7, 123.3, 119.5, 114.85, 114.81, 82.9, 79.7, 60.6, 56.2, 40.99, 40.97, 39.7, 28.0, 27.4, 26.1. HRMS (ESI+): *m/z* calcd for $C_{28}H_{27}N_3O$ ($M+H^+$), 422.2232; found, 422.2240. Anal. Calcd (%) for $C_{28}H_{27}N_3O$: C, 79.78; H, 6.46; N, 9.97. Found: C, 79.77; H, 6.39; N, 10.17.

The monomers (M-**ACn**, M-**AQn**, and M-**AQd**) were also prepared from **ACn**, **AQn**, and **AQd**, respectively, in the same way for the synthesis of M-**ACd** (Scheme 1).

Spectroscopic data of M-**ACn**. Yield: 31%. Mp 112-114 °C. IR (film, cm^{-1}): 3297 (ν_{N-H}), 2105 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=O}$). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.88 (d, *J* = 4.5 Hz, 1H, Ar), 8.42 (d, *J* = 8.4 Hz, 1H, Ar), 8.14 (dd, *J* = 8.5 Hz, 1H, Ar), 7.90 (bs, 1H, -N*H*CH-), 7.77-7.71 (m, 3H, Ar), 7.62 (t, *J* = 7.4 Hz, 1H, Ar), 7.54-7.53 (m, 2H, Ar), 7.49 (d, *J* = 4.6 Hz, 1H, Ar), 5.97-5.90 (m, 1H, -C*H*=CH_2), 5.39 (bs, 1H, -NHC*H*-), 5.20-5.10 (m, 2H, -CH=CH_2), 3.19 (s, 1H), 3.07-2.95 (m, 5H), 2.87-2.80 (m, 1H), 2.36-2.29 (m, 1H), 1.69 (bs, 1H), 1.55-1.48 (m, 1H), 1.45-1.38 (m, 1H), 1.05-0.97 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.7, 150.2, 148.8, 140.3, 140.2, 134.1, 132.4, 130.7, 129.3, 127.3, 126.8, 125.6, 123.3, 119.4, 115.23, 115.21, 82.9, 79.7, 60.6, 49.47, 49.45, 47.2, 39.3, 27.4, 26.8, 25.5. HRMS (ESI+): *m/z* calcd for $C_{28}H_{27}N_3O$ ($M+H^+$), 422.2232; found, 422.2252. Anal. Calcd (%) for $C_{28}H_{27}N_3O$: C, 79.78; H, 6.46; N, 9.97. Found: C, 79.80; H, 6.49; N, 9.97.

Spectroscopic data of M-**AQn**. Yield: 92%. Mp 231-233 °C. IR (film, cm^{-1}): 3295 (ν_{N-H}), 2105 ($\nu_{C\equiv C}$), 1637 ($\nu_{C=O}$). ^1H NMR (500 MHz, $CDCl_3$): δ 8.71 (d, J = 4.5 Hz, 1H, Ar), 8.03 (d, J = 9.2 Hz, 1H, Ar), 7.81 (bs, 1H, -N*H*CH-), 7.76-7.72 (m, 3H, Ar), 7.50 (d, J = 8.4 Hz, 2H, Ar), 7.40-7.37 (m, 2H, Ar), 5.76-5.69 (m, 1H, -C*H*=CH_2), 5.41 (bs, 1H, -NHC*H*-), 5.00-4.94 (m, 2H, -CH=CH_2), 3.98 (s, 3H, -OCH_3), 3.31-3.26 (m, 1H), 3.19 (s, 1H), 3.20-3.14 (m, 2H), 2.77-2.71 (m, 2H), 2.31 (bs, 1H), 1.70-1.61 (m, 3H), 1.48 (t, J = 11.6 Hz, 1H), 1.05-1.01 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.5, 157.9, 147.8, 145.0, 141.34, 141.31, 134.0, 132.4, 132.1, 128.4, 127.3, 125.7, 121.6, 114.9, 114.8, 102.0, 82.9, 79.7, 60.3, 56.2, 55.8, 41.1, 39.7, 31.7, 28.1, 27.5, 26.3. HRMS (ESI+): m/z calcd for $C_{29}H_{29}N_3O_2$ ($M+H^+$), 452.2338; found, 452.2356. Anal. Calcd (%) for $C_{29}H_{29}N_3O_2$: C, 77.13; H, 6.47; N, 9.31. Found: C, 76.99; H, 6.41; N, 9.29.

Spectroscopic data of M-**AQd**. Yield: 46%. Mp 114-116 °C. IR (film, cm^{-1}): 3295 (ν_{N-H}), 2103 ($\nu_{C\equiv C}$), 1638 ($\nu_{C=O}$). ^1H NMR (500 MHz, $CDCl_3$): δ 8.73 (d, J = 4.6 Hz, 1H, Ar), 8.02 (d, J = 9.2 Hz, 1H, Ar), 7.87 (bs, 1H, -N*H*CH-), 7.77 (d, J = 8.3 Hz, 2H, Ar), 7.64 (d, J = 2.7 Hz, 1H, Ar), 7.54 (d, J = 8.6 Hz, 2H, Ar), 7.43 (d, J = 4.6 Hz, 1H, Ar), 7.39-7.37 (m, 1H, Ar), 5.98-5.91 (m, 1H, -C*H*=CH_2), 5.37 (bs, 1H, -NHC*H*-), 5.16-5.13 (m, 2H, -CH=CH_2), 3.98 (s, 3H, -OCH_3), 3.19 (s, 1H), 3.11-2.91 (m, 5H), 2.36-2.34 (m, 1H), 1.73 (bs, 1H), 1.64-1.52 (m, 2H), 1.47-1.42 (m, 1H), 1.10-1.05 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.5, 157.9, 147.7, 145.0, 140.54, 140.52, 134.0, 132.4, 132.0, 128.3, 127.3, 125.6, 122.1, 115.01, 114.99, 101.3, 82.9, 79.7, 60.6, 55.64, 55.59, 49.5, 47.1, 39.1, 27.4, 26.9, 25.6. HRMS (ESI+): m/z calcd for $C_{29}H_{29}N_3O_2$ ($M+H^+$), 452.2338; found, 452.2320. Anal. Calcd (%) for $C_{29}H_{29}N_3O_2$: C, 77.13; H, 6.47; N, 9.31. Found: C, 76.97; H, 6.45; N, 9.28.

Polymerization. Polymerizations of M-**ACd**, M-**ACn**, M-**AQn**, and M-**AQd** were carried out according to Scheme 1 in a dry glass ampule under a dry nitrogen atmosphere using $[Rh(nbd)Cl]_2$ as a catalyst in a similar way as reported previously.[S4]

The monomer M-**ACd** (422 mg, 1.00 mmol) was placed in a dry ampule, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation-flush procedure was repeated for three times, a three-way stopcock was attached to the ampule, and anhydrous DMF (4.20 mL) and NEt_3 (140 μL, 1.00 mmol) were added with a syringe. To this was added a solution of $[Rh(nbd)Cl]_2$ (0.0125 M) in DMF (0.8 mL) at 30 °C. The concentrations of the monomer and the rhodium catalyst were 0.2 and 0.002 M, respectively. After 26 h, the resulting polymer (poly-**ACd**) was precipitated into a large amount of Et_2O, washed with Et_2O, and collected by centrifugation. The product was purified by reprecipitation from $CHCl_3$ to Et_2O, and the precipitated poly-**ACd** was washed with Et_2O and

dried *in vacuo* at room temperature overnight (312 mg, 74% yield). In the same way, poly-**ACn**, poly-**AQn**, and poly-**AQd** were prepared. The M_n and M_w/M_n of poly-**ACd**, poly-**ACn**, poly-**AQn**, and poly-**AQd** were determined by SEC using polystyrene standards in $CHCl_3/CF_3CH_2OH$ (9/1, v/v) containing 0.5 wt% TBAB as the eluent. The polymerization results are summarized in Table S1.

Table S1. Polymerization Results of M-ACd, M-ACn, M-AQn, and M-AQd with $[Rh(nbd)Cl]_2$[a]

		polymer				
entry	monomer	code	yield (%)	$M_n \times 10^{-4}$ [b]	M_w/M_n [b]	$\Delta\varepsilon_{1st}$ (λ)[c]
1	M-**ACd**	poly-**ACd**	74	21	1.7	-7.2 (454)
2	M-**ACn**	poly-**ACn**	83	16	1.3	5.6 (456)
3	M-**AQn**	poly-**AQn**	85	7.9	1.8	-7.6 (459)
4	M-**AQd**	poly-**AQd**	85	6.3	1.3	8.0 (468)

[a] Polymerized under nitrogen; [monomer] = 0.2 M, [monomer]/[Rh] = 100. [b] Determined by SEC (polystyrene standards) with $CHCl_3/CF_3CH_2OH$ (9/1, v/v) containing 0.5 wt% tetra-*n*-butylammonium bromide (TBAB) as the eluent. [c] Measured in $CHCl_3/CF_3CH_2OH$ (6/1, v/v, 0.02 mg/mL); $\Delta\varepsilon$ (M^{-1} cm^{-1}) and λ (nm).

Spectroscopic data of poly-**ACd**. IR (film, cm^{-1}): 3327 (ν_{N-H}), 1652 ($\nu_{C=O}$). ^{1}H NMR (500 MHz, $CDCl_3/CF_3CD_2OD$ (31/1, v/v), 55 °C): δ 8.60 (s, 2H, -N*H*CH-, Ar), 8.44 (s, 2H, Ar), 8.06 (s, 2H, Ar), 7.77-7.39 (m, 5H, Ar), 6.66 (s, 1H, -NHC*H*-), 5.80-5.38 (m, 2H, -C*H*=CH_2), 4.94 (s, 2H, -CH=CH_2), 3.34-2.64 (m, 3H), 2.59-1.80 (m, 3H), 1.66-0.84 (m, 5H). Anal. Calcd (%) for $(C_{28}H_{27}N_3O{\cdot}5/3H_2O)_n$: C, 74.48; H, 6.77; N, 9.31. Found: C, 74.63; H, 6.59; N, 9.09.

Spectroscopic data of poly-**ACn**. Yield: 83%. IR (film, cm^{-1}): 3309 (ν_{N-H}), 1647 ($\nu_{C=O}$). ^{1}H NMR (500 MHz, $CDCl_3/CF_3CD_2OD$ (31/1, v/v), 55 °C): δ 8.81 (s, 2H, -N*H*CH-, Ar), 8.42 (s, 2H, Ar), 8.12 (s, 2H, Ar), 7.80-7.35 (m, 5H, Ar), 6.24-5.38 (m, 3H, -NHC*H*-, -C*H*=CH_2), 5.15 (s, 2H, -CH=CH_2), 3.23-2.73 (m, 3H), 2.57-1.77 (m, 3H), 1.68-0.83 (m, 5H). Anal. Calcd (%) for $(C_{28}H_{27}N_3O)_n$: C, 79.78; H, 6.46; N, 9.97. Found: C, 79.98; H, 6.64; N, 9.98.

Spectroscopic data of poly-**AQn**. Yield: 85%. IR (film, cm^{-1}): 3326 (ν_{N-H}), 1652 ($\nu_{C=O}$). ^{1}H NMR (500 MHz, $CDCl_3/CF_3CD_2OD$ (31/1, v/v), 55 °C): δ 8.65 (s, 1H, -N*H*CH-), 8.50 (s, 2H, Ar), 7.96 (s, 2H, Ar), 7.69 (s, 1H, Ar), 7.46-7.04 (m, 4H, Ar), 6.69 (s, 1H, -NHC*H*-), 5.57

(s, 1H, -C*H*=CH_2), 5.37 (s, 1H), 4.94 (s, 2H, -CH=CH_2), 3.91 (s, 3H, -OCH_3), 3.07-2.79 (m, 3H), 2.48-1.94 (m, 3H), 1.63-0.86 (m, 5H). Anal. Calcd (%) for $(C_{29}H_{29}N_3O_2 \cdot H_2O)_n$: C, 74.18; H, 6.65; N, 8.95. Found: C, 74.36; H, 6.67; N, 8.88.

Spectroscopic data of poly-**AQd**. Yield: 85%. IR (film, cm^{-1}): 3310 (ν_{N-H}), 1646 ($\nu_{C=O}$). ^1H NMR (500 MHz, $CDCl_3/CF_3CD_2OD$ (31/1, v/v), 55 °C): δ 8.65 (s, 1H, -N*H*CH-), 8.34 (s, 2H, Ar), 7.92 (s, 2H, Ar), 7.59 (s, 1H, Ar), 7.46-7.04 (m, 4H, Ar), 6.64 (s, 1H, -NHC*H*-), 5.81 (s, 1H, -C*H*=CH_2), 5.55 (s, 1H), 5.02 (s, 2H, -CH=CH_2), 3.86 (s, 3H, -OCH_3), 3.10-2.52 (m, 3H), 2.33-1.97 (m, 3H), 1.63-0.88 (m, 5H). Anal. Calcd (%) for $(C_{29}H_{29}N_3O_2 \cdot 0.7H_2O)_n$: C, 75.04; H, 6.60; N, 9.05. Found: C, 75.01; H, 6.40; N, 8.92.

4. Characterization of Polymers

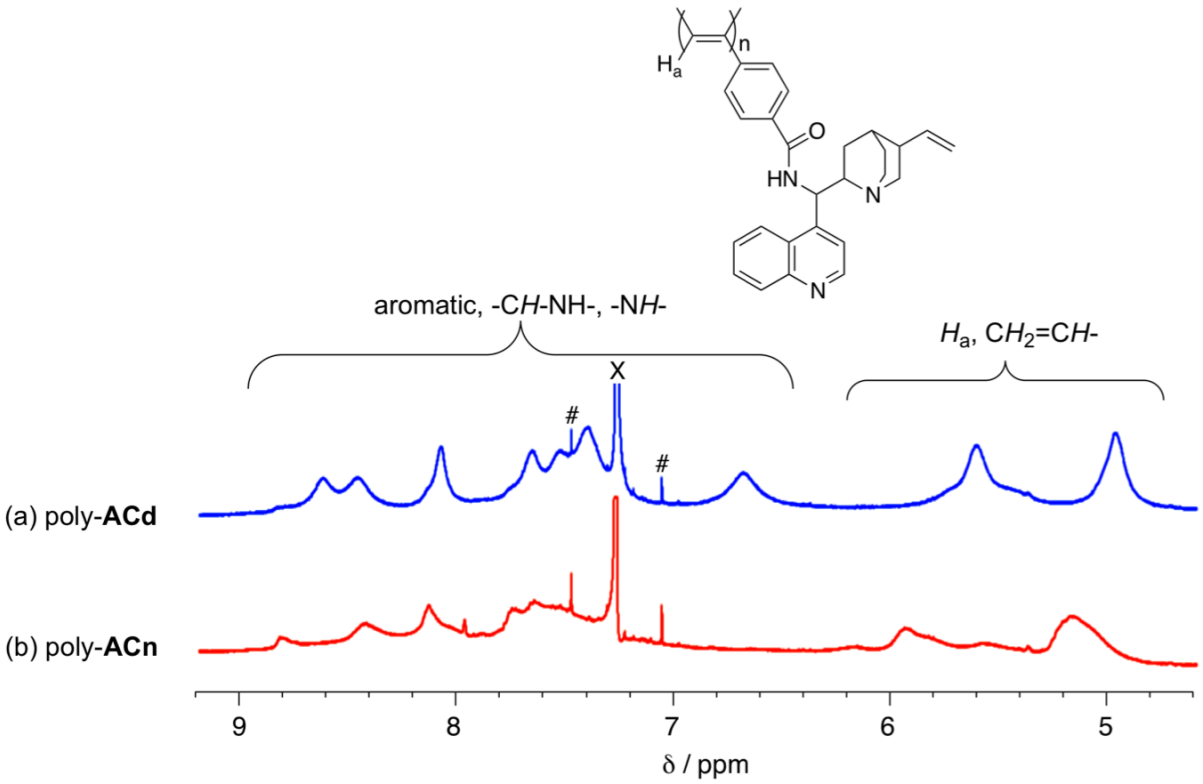


Figure S1. ^{1}H NMR spectra of poly-**ACd** (a) and poly-**ACn** (b) in $CDCl_3/CF_3CD_2OD$ (31/1, v/v) at 55 °C. X and # denote the proton from $CHCl_3$ and its ^{13}C satellite peaks, respectively.

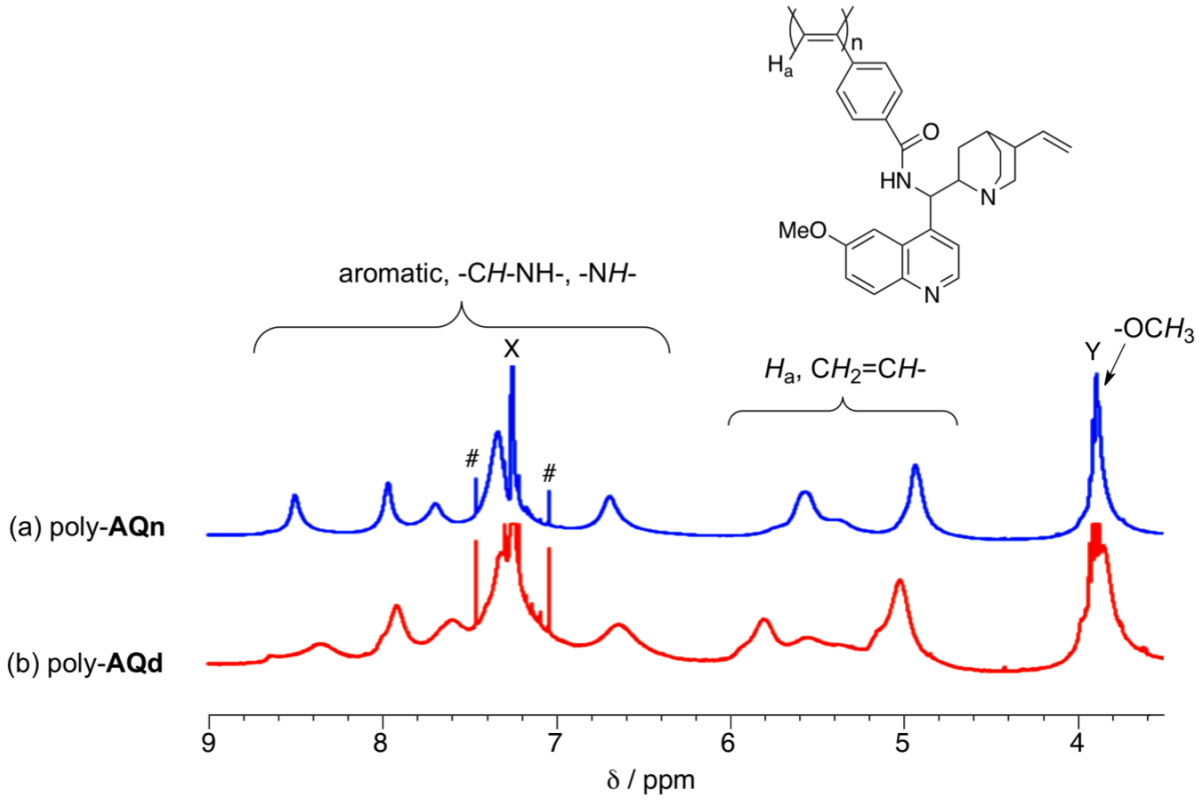


Figure S2. ^{1}H NMR spectra of poly-**AQn** (a) and poly-**AQd** (b) in $CDCl_3/CF_3CD_2OD$ (31/1, v/v) at 55 °C. X and Y denote the protons from $CHCl_3$ and CF_3CDHOD, and # denotes the ^{13}C satellite peaks of $CHCl_3$.

Figure S3 shows the Raman spectra of poly-**ACd**, poly-**ACn**, poly-**AQn**, and poly-**AQd** and poly-**AQn** and poly-**AQd** after grinding for 20 min. Before grinding, all the polymers showed intense peaks at 1551, 1348, 896 cm^{-1} (a), 1573, 1348, 903 cm^{-1} (b), 1570, 1345, 886 cm^{-1} (c), and 1567, 1348, 889 cm^{-1} (d), which can be assigned to the C=C, C-C, and C-H bond vibrations in the *cis* polyacetylenes, respectively.[S5] After grinding of poly-**AQn** and poly-**AQd**, new peaks appeared at 1500 and 1213 cm^{-1} (e) and 1497 and 1223 cm^{-1} (f), which can be assigned to the C=C and C-C bond vibrations in the *trans* acetylenes, respectively.

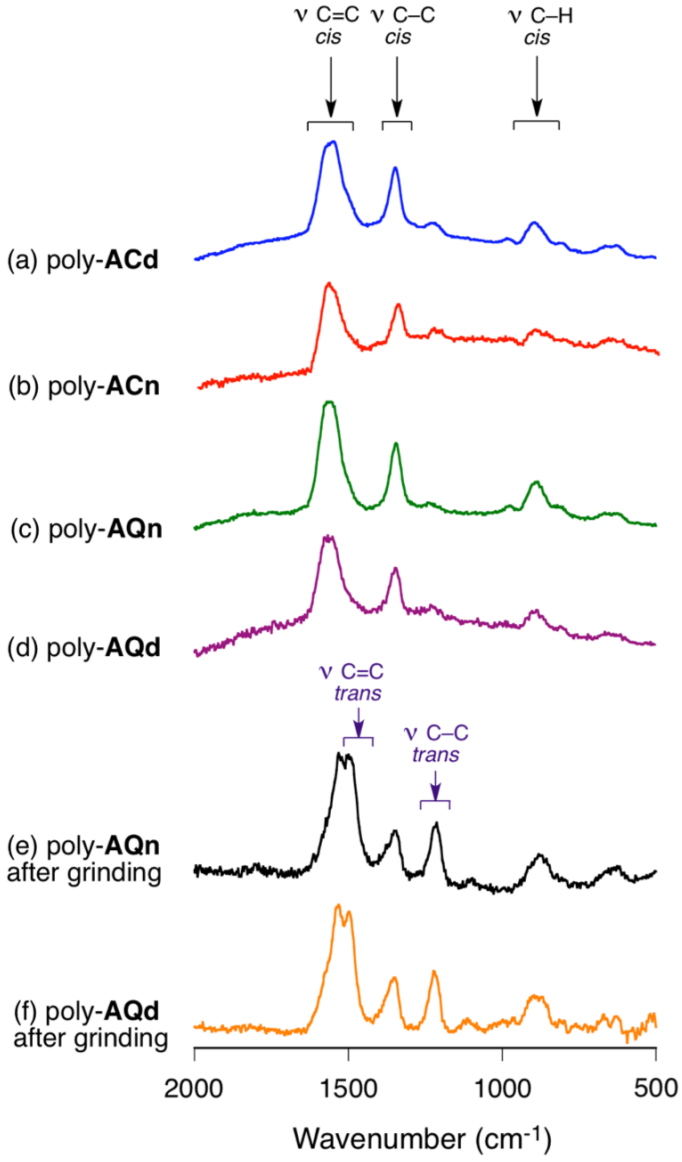


Figure S3. Raman spectra of poly-**ACd** (a), poly-**ACn** (b), poly-**AQn** (c), and poly-**AQd** (d) and poly-**AQn** (e) and poly-**AQd** (f) after grinding for 20 min.

The IR spectra of poly-**AQn**, poly-**ACd**, poly-**ACn**, poly-**AQd** as well as the monomer M-**AQn** showed the amide NH and carbonyl stretching (amide I) bands at approximately 3300–3330 and 1650-1660 cm^{-1}, respectively, in $CHCl_3$ or film state (Table S2). These wavenumbers are similar to those previously reported for the poly(phenylacetylene) bearing L- or D-alanine pendants linked via amide bonds in polar solvents such as THF where the pendant amide residues of the polymer hardly form intramolecular hydrogen-bonding networks.[S6] On the other hand, in a mixture of $CHCl_3$ and CF_3CH_2OH, the amide I bands of poly-**AQn** and M-**AQn** shifted to lower wavenumbers, whereas the NH bands showed almost no significant shift, resulting from intermolecular hydrogen-bonds between the amide carbonyl and the acidic hydrogen of CF_3CH_2OH. These results suggest that the present amide-linked poly(phenylacetylene)s may not form the intramolecular hydrogen-bonding networks through the neighboring amide groups because of the steric effect of the bulky pendant cinchona alkaloid residues (see also Figure S7).

Table S2. FT-IR Data of Polymers and Monomers[a]

		IR (cm^{-1})	
sample	condition	ν_{NH}	$\nu_{C=O}$ (amide I)
poly-**AQn**	$CHCl_3/CF_3CH_2OH$ (6/1, v/v)	nd[b]	1637
poly-**AQn**	$CHCl_3/CF_3CH_2OH$ (95/5, v/v)	nd[b]	1639
poly-**AQn**	$CHCl_3$[c]	3311	1650
poly-**AQn**	film	3326	1652
poly-**ACd**	film	3327	1652
poly-**ACn**	film	3309	1647
poly-**AQd**	film	3310	1646
M-**AQn**	$CHCl_3/CF_3CH_2OH$ (6/1, v/v)	3302	1644
M-**AQn**	$CHCl_3/CF_3CH_2OH$ (95/5, v/v)	3203	1651
M-**AQn**	$CHCl_3$	3301	1657

[a] FT-IR spectra were taken at ambient temperature in solution (2 mg/mL) in a 50-μm BaF_2 cell or in the film state. [b] Not detected due to overlapping with the OH vibration of CF_3CH_2OH. [c] The soluble part in $CHCl_3$ (ca. 1 mg/mL) was used.

5. CD Measurements of Monomers and Polymers

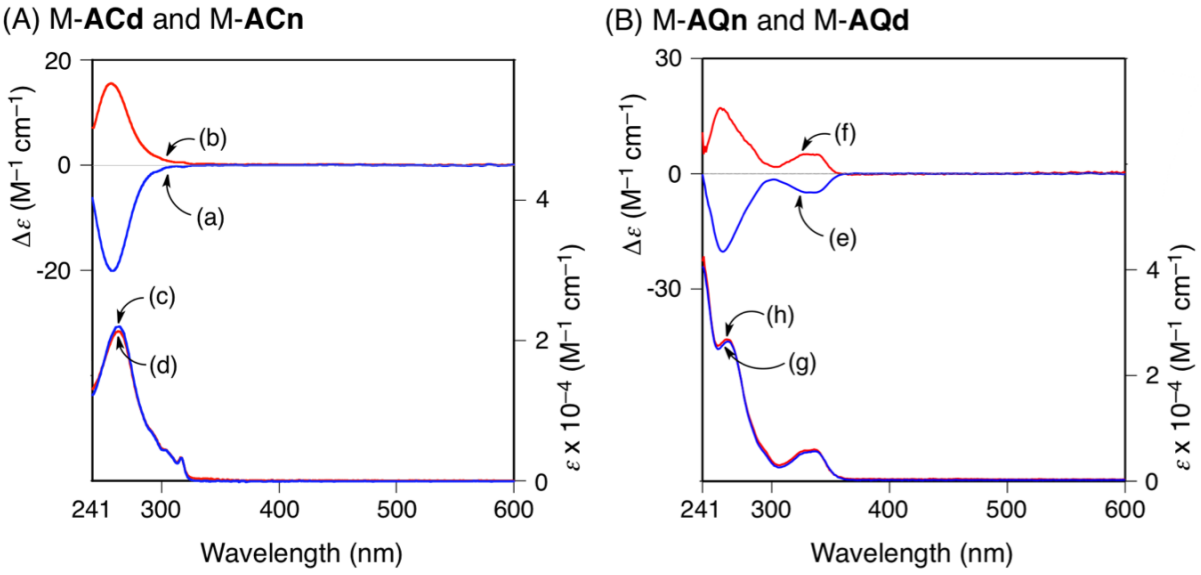


Figure S4. CD and absorption spectra of (A) M-**ACd** (a, c) and M-**ACn** (b, d), and (B) M-**AQn** (e, g) and M-**AQd** (f, h) in $CHCl_3$/CF_3CH_2OH (6/1, v/v, 0.02 mg/mL) at 25 ˚C.

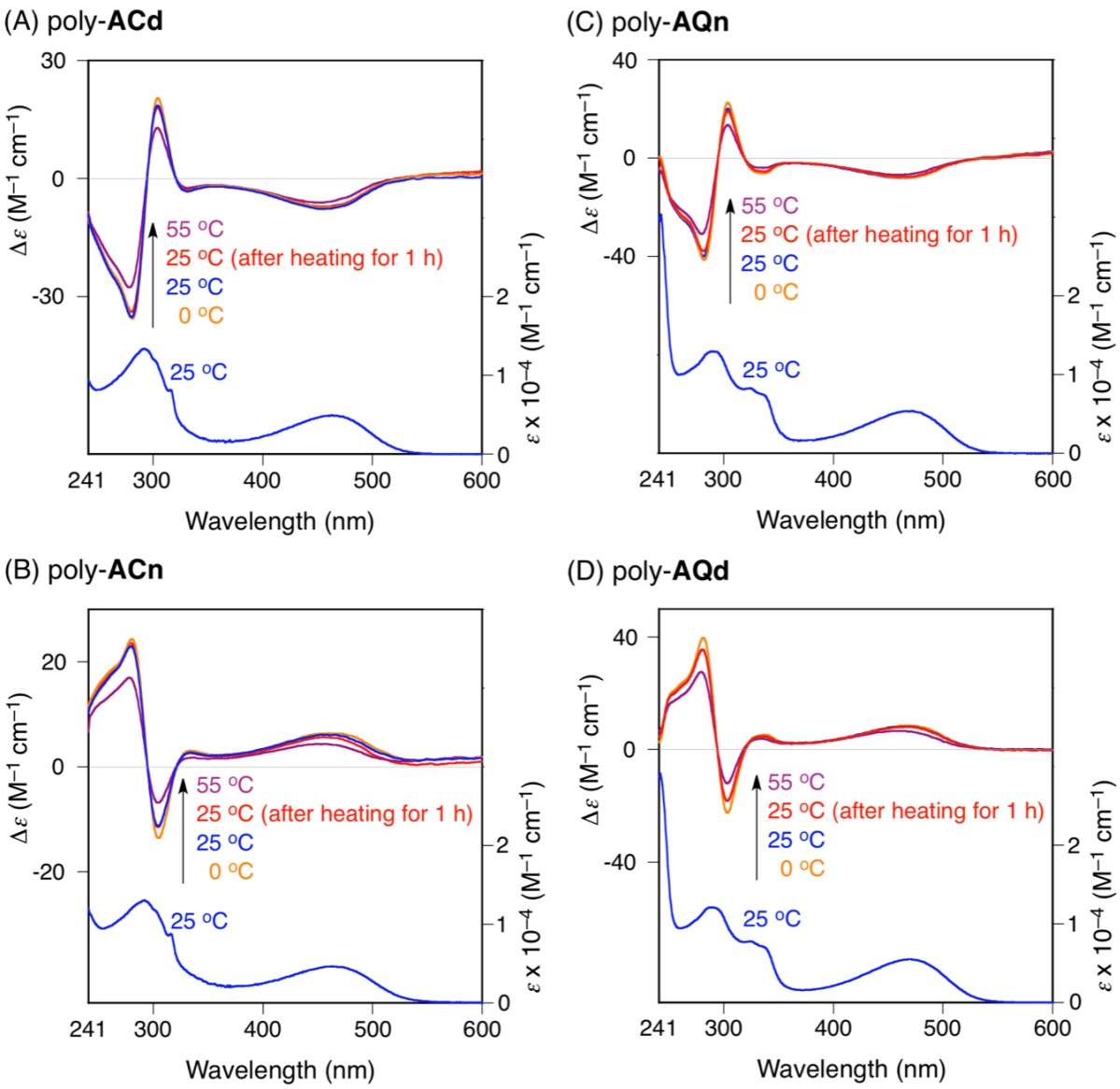
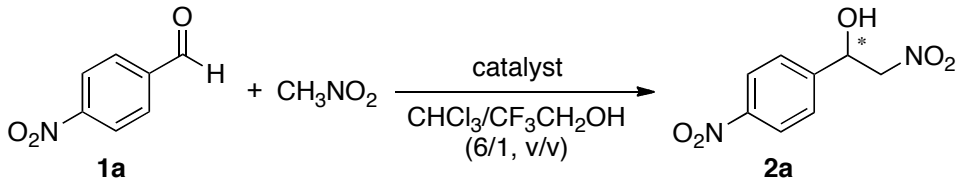


Figure S5. CD spectra of (A) poly-**ACd**, (B) poly-**ACn**, (C) poly-**AQn**, and (D) poly-**AQd** in $CHCl_3/CF_3CH_2OH$ (6/1, v/v, 0.02 mg/mL) at various temperatures and at 25 ˚C after heating at 55 ˚C for 1 h. Absorption spectra at 25 ˚C are also shown.

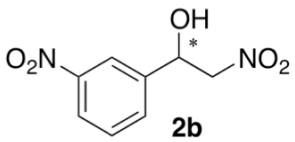
6. Enantioselective Henry Reaction Assisted by Helical Polymer Catalysts

Typical procedure for the enantioselective Henry reaction.

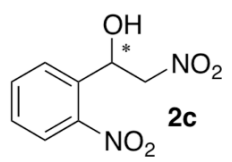


In a glass-reactor, a mixture of poly-**AQn** (9.0 mg, 0.02 mmol) and **1a** (15.1 mg, 0.1 mmol) in $CHCl_3$ (300 μL) and CF_3CH_2OH (50 μL) was stirred at -20 °C for 30 min. To this was added nitromethane (54.2 μL, 1.0 mmol), and the mixture was stirred at -20 °C for 7 days. The reaction mixture was directly subjected to flash column chromatography (SiO_2, EtOAc/*n*-hexane = 1/4, v/v) to give (*R*)-enriched 2-nitro-1-(4-nitrophenyl)ethanol (**2a**)[S7] (16.3 mg, 77%) as a white solid. The enantiomeric excess (ee) was determined to be 94% by HPLC analysis (Chiralcel OD column, 2-propanol/*n*-hexane = 1/9 (v/v), 1.0 mL/min, λ = 254 nm); $t_{(R)}$ = 32.7 min, $t_{(S)}$ = 42.0 min. IR (KBr, cm^{-1}): 3520 (ν_{O-H}), 1556 ($\nu_{N=O}$), 1520 ($\nu_{N=O}$), 1381 ($\nu_{N=O}$), 1348 ($\nu_{N=O}$), 1086 (ν_{C-O}). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28 (d, *J* = 9.1 Hz, 2H, Ar), 7.63 (d, *J* = 9.1 Hz, 2H, Ar), 5.63-5.60 (m, 1H, -C*H*OH), 4.63-4.55 (m, 2H, -CH_2NO$_2$), 3.12 (s, 1H, -CHO*H*). In same way, other polymers and monomers were also employed as a catalyst for the enantioselective Henry reaction of various aldehydes. These results are summarized in Tables 1, 2, S3, and S4.

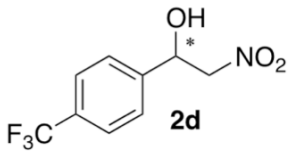
2-Nitro-1-(3-nitrophenyl)ethanol (2b):[S8] HPLC (Chiralcel OD column, 2-propanol/*n*-hexane = 1/9 (v/v), 0.7 mL/min, λ = 215 nm); $t_{(R)}$ = 45.0 min, $t_{(S)}$ = 52.1 min. IR (film, cm^{-1}): 3522 (ν_{O-H}), 1556 ($\nu_{N=O}$), 1530 ($\nu_{N=O}$), 1378 ($\nu_{N=O}$), 1352 ($\nu_{N=O}$), 1097 (ν_{C-O}). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.33 (s, 1H, Ar), 8.24 (d, *J* = 8.2 Hz, 1H, Ar), 7.77 (d, *J* = 7.8 Hz, 1H, Ar), 7.62 (t, *J* = 7.9 Hz, 1H, Ar), 5.63-5.60 (m, 1H, -C*H*OH), 4.66-4.57 (m, 2H, -CH_2NO$_2$), 3.13 (d, *J* = 4.2 Hz, 1H, -CHO*H*).



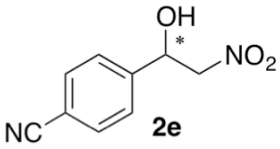
2-Nitro-1-(2-nitrophenyl)ethanol (2c):[S8] HPLC (Chiralcel OD column, 2-propanol/*n*-hexane = 1/9 (v/v), 0.3 mL/min, λ = 215 nm); $t_{(R)}$ = 58.1 min, $t_{(S)}$ = 64.0 min. IR (film, cm^{-1}): 3526 (ν_{O-H}), 1556 ($\nu_{N=O}$), 1523 ($\nu_{N=O}$), 1377 ($\nu_{N=O}$), 1345 ($\nu_{N=O}$), 1097 (ν_{C-O}). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.2 Hz, 1H, Ar), 7.96 (d, *J* = 7.9 Hz, 1H, Ar), 7.75 (t, *J* = 7.7 Hz, 1H, Ar), 7.56 (t, *J* = 7.8 Hz, 1H, Ar), 6.06 (d, *J* = 10.5 Hz, 1H, -C*H*OH), 4.89 (dd, *J* = 13.9, 2.4 Hz, 1H, -CH_2NO$_2$), 4.56 (dd, J_1 = 13.9, 9.1 Hz, 1H, -CH_2NO$_2$), 3.14 (d, *J* = 4.3 Hz, 1H, -CHO*H*).



2-Nitro-1-(4-trifluoromethylphenyl)ethanol (2d):[S9] HPLC (Chiralcel OD column, 2-propanol/*n*-hexane = 15/85 (v/v), 0.8 mL/min, λ = 230 nm); $t_{(R)}$ = 10.8 min, $t_{(S)}$ = 13.0 min. IR (film, cm^{-1}): 3524 (ν_{O-H}), 1556 ($\nu_{N=O}$), 1379 ($\nu_{N=O}$), 1165 (ν_{C-F}), 1067 (ν_{C-O}). ^1H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, J = 8.2 Hz, 2H, Ar), 7.56 (d, J = 8.7 Hz, 2H, Ar), 5.56 (d, J = 8.7 Hz, 1H, -C*H*OH), 4.63-4.53 (m, 2H, -C$H_2$$NO_2$), 2.96 (s, 1H, -CHO*H*).



2-Nitro-1-(4-cyanophenyl)ethanol (2e):[S10] HPLC (Chiralcel OD column, 2-propanol/*n*-hexane = 1/9 (v/v), 1.0 mL/min, λ = 230 nm); $t_{(R)}$ = 34.7 min, $t_{(S)}$ = 40.5 min. IR (KBr, cm^{-1}): 3429 (ν_{O-H}), 2239 ($\nu_{C\equiv N}$), 1557 ($\nu_{N=O}$), 1378 ($\nu_{N=O}$), 1084 (ν_{C-O}). ^1H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 8.4 Hz, 2H, Ar), 7.56 (d, J = 8.7 Hz, 2H, Ar), 5.57-5.54 (m, 1H, -C*H*OH), 4.61-4.55 (m, 2H, -C$H_2$$NO_2$), 3.08 (d, J = 4.1 Hz, 1H, -CHO*H*).



2-Nitro-1-(pyridin-3-yl)ethanol (2f):[S11] HPLC (Chiralcel OJ-H column, 2-propanol/*n*-hexane = 25/75 (v/v), 0.7 mL/min, λ = 214 nm); $t_{(R)}$ = 17.7 min, $t_{(S)}$ = 22.7 min. IR (film, cm^{-1}): 3058 (pyridine ring), 1591 (pyridine ring), 1552 ($\nu_{N=O}$), 1474 (pyridine ring), 1419 (pyridine ring), 1362 ($\nu_{N=O}$), 1095 (ν_{C-O}). ^1H NMR (500 MHz, $CDCl_3$): δ 8.65 (s, 1H, Ar), 8.61 (d, J = 4.8 Hz, 1H, Ar), 7.81-7.79 (m, 1H, Ar), 7.37 (dd, J = 7.9, 4.9 Hz, 1H, Ar), 5.55 (dd, J = 9.6, 3.0 Hz, 1H, -C*H*OH), 4.64 (dd, J = 13.6, 9.6 Hz, 1H, -C$H_2$$NO_2$), 4.55 (dd, J = 13.6, 3.1 Hz, 1H, -C$H_2$$NO_2$).

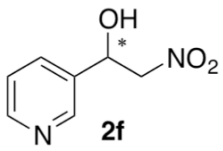
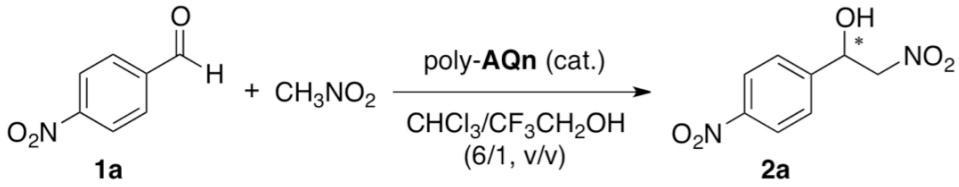


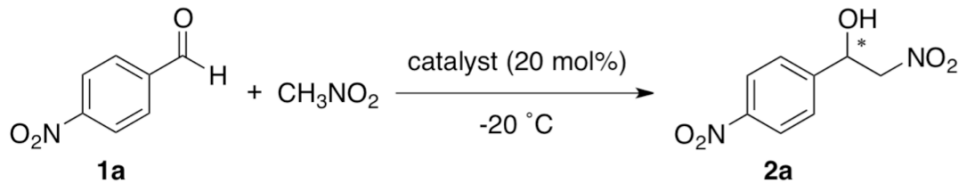
Table S3. Effect of Catalyst Loading and Temperature on Enantioselective Henry Reaction[a]



entry	poly-**AQn** (mol%)	*T* (°C)	time (d)	yield (%)[b]	*ee* (%)[c]
1	1	-20	7	23	66 (*R*)
2	5	-20	7	50	84 (*R*)
3	10	-20	7	82	86 (*R*)
4	20	-20	7	77	94 (*R*)
5	50	-20	3	53	77 (*R*)
5	20	25	4	84	7 (*R*)
6	20	-40	7	41	82 (*R*)

[a] The reactions of **1a** (0.3 M) with nitromethane (10 equiv) were carried out in the presence of poly-**AQn** in $CHCl_3/CF_3CH_2OH$ (6/1, v/v). [b] Isolated yield. [c] Determined by chiral HPLC analysis.

Table S4. Solvent Effect on Enantioselective Henry Reaction[a]



1a **2a**

entry	catalyst	solvent	yield (%)[b]	*ee* (%)[c]
1	poly-**AQn**	DMF[d]	52	28 (*R*)
2	poly-**AQn**	THF[d]	70	58 (*R*)
3	poly-**AQn**	$CHCl_3$[d]	87	35 (*R*)
4	poly-**AQn**	$CHCl_3/CF_3CH_2OH$ = (15/1, v/v)	68	73 (*R*)
5	poly-**AQn**	$CHCl_3/CF_3CH_2OH$ = (6/1, v/v)	77	94 (*R*)
6	poly-**AQn**	$CHCl_3/CF_3CH_2OH$ = (2/1, v/v)	93	79 (*R*)
7	poly-**AQn**	CF_3CH_2OH[d]	86	79 (*R*)
8	poly-**AQd**	DMF[d]	39	10 (*S*)
9	poly-**AQd**	$CHCl_3$[d]	46	46 (*S*)
10	poly-**AQd**	$CHCl_3/CF_3CH_2OH$ = (15/1, v/v)	87	66 (*S*)
11	poly-**AQd**	$CHCl_3/CF_3CH_2OH$ = (6/1, v/v)	68	64 (*S*)
12	poly-**AQd**	$CHCl_3/CF_3CH_2OH$ = (2/1, v/v)	66	46 (*S*)
13	poly-**AQd**	CF_3CH_2OH[d]	93	40 (*S*)

[a] The reactions of **1a** (0.3 M) with nitromethane (10 equiv) were carried out in the presence of poly-**ACd** or poly-**AQd** (20 mol%) in various solvents at -20 °C for 7 days. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] The polymer catalyst was almost insoluble in the solvent.

7. X-ray Crystallographic Data of M-AQn

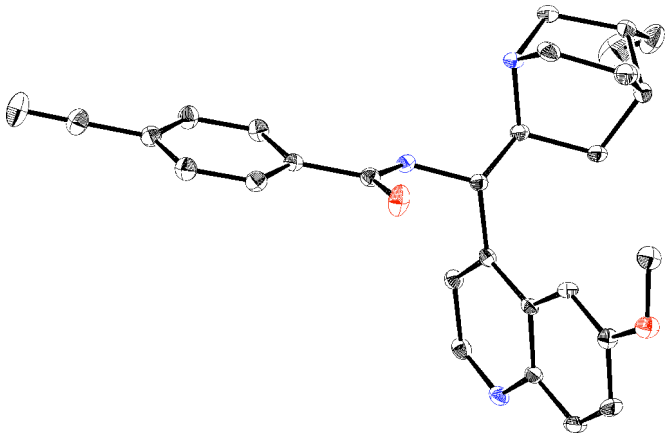


Figure S6. ORTEP drawing of the crystal structure of M-**AQn** with thermal ellipsoids at 30% probability.

Table S5. Crystal Data and Structure Refinement for M-AQn

Empirical formula	$C_{29}H_{29}N_3O_2$	
Formula weight	451.55	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 10.246(5) Å	α= 90°.
	b = 11.658(6) Å	β= 111.022(9)°.
	c = 10.679(5) Å	γ = 90°.
Volume	1190.8(10) Å^3	
Z	2	
Density (calculated)	1.259 Mg/m^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	480	
Crystal size	0.58 x 0.14 x 0.08 mm^3	
Theta range for data collection	2.04 to 25.00°.	
Index ranges	-12<=h<=9, -13<=k<=13, -12<=l<=12	
Reflections collected	6693	
Independent reflections	4044 [R(int) = 0.0398]	
Completeness to theta = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9936 and 0.9552	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	4044 / 1 / 320	
Goodness-of-fit on F2	1.087	
Final R indices [I>2sigma(I)]	R_1 = 0.0555, wR_2 = 0.1507	
R indices (all data)	R_1 = 0.0576, wR_2 = 0.1539	
Absolute structure parameter	1.7(17)	
Largest diff. peak and hole	0.219 and -0.334 e.Å^{-3}	
CCDC reference number	CCDC-852963	

8. Molecular Modeling and Calculations

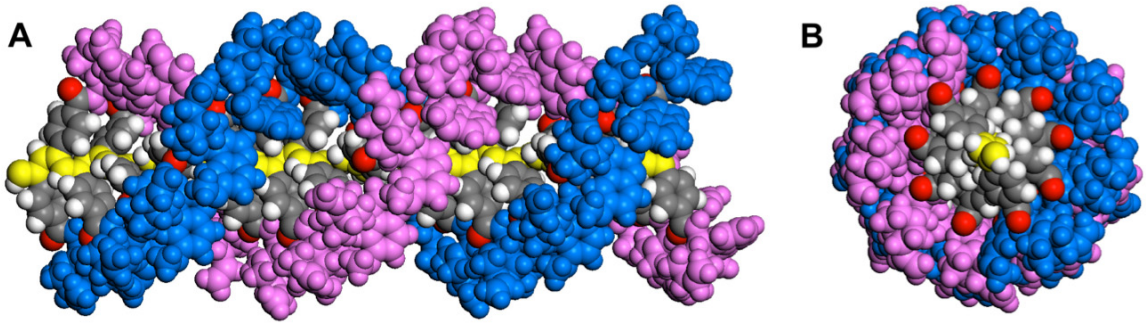


Figure S7. (A) Side view and (B) top view of a possible right-handed helical structure of poly-**AQn** (30-mer). The structure is shown using the space-filling model; two sets of helical arrays (n and n + 2) of the quinine pendants (blue and purple) and the main-chain atoms (yellow) are shown in different colors for clarity. The pendant quinine residues arrange in left-handed helical array along the right-handed helical poly-**AQn** backbone.

The molecular modeling and molecular mechanics (MM) calculations of poly-**AQn** were conducted with the Compass force field,[S12] as contained in the MS Modeling software (version 4.4, Accelrys, San Diego, CA) operated using a PC running under Windows XP. The initial monomer unit structure was constructed using the crystal structure of M-**AQn** (Figure S6). The main-chain helix sense of poly-**AQn** in $CHCl_3$/CF_3CH_2OH (6/1, v/v) where the negative first Cotton effect was observed at the main-chain region (350–550 nm) is assumed to be right-handed on the basis of the CD pattern of the analogous cyclodextrin-bound helical poly(phenylacetylene) whose main-chain helix sense was assigned by the calculations.[S13] When the main-chain of poly-**AQn** is right-handed, it possesses an opposite, left-handed helical array of the pendants. The polymer model (40 repeating monomer units) of poly-**AQn** was constructed using the Polymer Builder module in the MS Modeling software. The starting main-chain geometrical parameters, such as the bond lengths, the bond angles, and the internal rotation angles were defined as a 23 unit/10 turn (23/10) helix on the basis of the helical structure of a poly(phenylacetylene) bearing *N*,*N*-diisopropylaminomethyl pendants determined by X-ray analysis.[S14] The geometrical parameters for the helical poly-**AQn** backbone structure were fixed during the following force field optimization. The geometry optimizations were carried out without any cutoff by the smart algorithm in three steps. First, the starting conformations were subject to the steepest decent optimization to eliminate the worse steric conflicts. Second, subsequent optimization until the convergence using a conjugate gradient algorithm was performed. The fully optimized polymer models were

obtained by the further energy minimization using the Newton method with the 0.1 kcal mol^{-1} $Å^{-1}$ convergence criterion. The final right-handed helical poly-**AQn** model as shown in Figure S7 was reconstructed by adopting the geometry of the central monomer unit of the optimized poly-**AQn** structure to avoid the end-group effect. The poly-**AQn** model possesses no hydrogen bonding between the neighboring amide groups because of bulky pendant groups, which is consistent with the IR measurement results (Table S2).

9. Supporting References

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