Supplementary information

All the reactions were carried out under an atmosphere of dry nitrogen using flame-dried glassware and freshly distilled dry solvents. Routine monitoring of reactions was performed using Alugram SilG/UV_{254} (0.20 mm). All the chromatographic separations were performed using silica gel (Merck 60 230–400 mesh). ^{1}H NMR spectra were recorded on a Varian 200 MHz spectrometer with TMS as internal standard. Chemical shifts are reported in ppm and coupling constants in Hz. IR spectra of products **2**-**7** were recorded on an Avatar 360 FT-IR spectrophotometer. Self-supported wafers of the polymers were evacuated (< 10^{-4} Torr) at 50 °C and transmission FTIR spectra were taken with a Mattson Genesis Series FTIR. Ruthenium analyses were carried out by plasma emission spectroscopy on a Perkin-Elmer Plasma 40 emission spectrometer. Elemental analyses were carried out on a Perkin-Elmer 2400 elemental analyser. Results of the cyclopropanation reactions were determined by gas chromatography on a Hewlett-Packard 5890II with FID detector; helium as carrier gas, 20 p.s.i.; injector temperature: 230 °C; detector temperature: 250 °C.

4-Bromopyridine-2,6-dicarboxylic acid (2)

To a mixture of chelidamic acid monohydrate (**1**) (2.5 g, 12.43 mmol) in chlorobenzene (250 ml) was added dropwise a solution of phosphorus oxybromide (25.0 g, 87.1 mmol) in DMF (2.5 ml) with stirring at room temperature. The resulting orange solution was heated under reflux for 14 h and the solvent was removed under vacuum. Cold water (100 ml) was added to the black residue and the product was extracted with chlorobenzene/dichloromethane (1:1 v/v, 3 × 100 ml). The combined organic layers were evaporated and the solid residue was treated with 5 M NaOH (100 ml) and activated charcoal at room temperature. The solution was filtered and concentrated HCl was added to the filtrate to give a pH of 1. The white solid was filtered off and dried to give 1.68 g (55% yield) of 4-bromopyridine-2,6-dicarboxylic acid, which was used without further purification.

^{1}H NMR (dmso-d_6): 8.37 (2H, s)

IR(KBr, cm^{-1}): 3078, 1725.

4-Bromo-*N*,*N*′-bis[(*S*)-2-hydroxy-1-isopropylethyl]pyridine-2,6-dicarboxamide (3)

To a stirred mixture of 4-bromopyridine-2,6-dicarboxylic acid (**2**) (1.33 g, 5.74 mmol) in methylene chloride (130 ml) were added dropwise oxalyl chloride (1.95 ml, 21.9 mmol) and a catalytic amount DMF at room temperature. The reaction mixture was stirred at room temperature for 7 h. The solution was cooled and filtered through a pad of celite. The solvent and excess oxalyl chloride were removed under reduced pressure. 4-Bromopyridine-2,6-dicarbonyl chloride was obtained in 90% yield [IR (HATR, cm^{-1}): 3078, 1760]. The product was used without further purification.

To a stirred solution of (*S*)-(+)-valinol (837 mg, 8.13 mmol) in anhydrous methylene chloride (100 ml) at 0 ºC was added triethylamine (2.25 ml, 16.26 mmol). A solution of 4-bromopyridine-2,6-dicarbonylchloride (4.065 mmol) in methylene chloride (50 ml) was added dropwise to the above mixture over 30 min. After addition was complete, the mixture was stirred at room temperature for 24 h. The mixture was washed with 5% HCl (3 × 45 ml) and $NaHCO_3$ (3 × 45 ml). The organic layer was dried with $MgSO_4$ and the solvent was removed under reduced pressure to give 4-bromo-*N*,*N*′-bis[(*S*)-2-hydroxy-1-isopropylethyl]pyridine-2,6-dicarboxamide as a white solid (1.278 g, 75% yield) and this was used without further purification.

^{1}H NMR ($CDCl_3$): 8.45 (s, 2H), 7.95 (d, 2H, J = 8.4), 4.0–3.8 (m, 6H), 2.60 (s, 2H), 2.04 (m, 2H), 1.02 (d, 6H, J = 5.1), 0.99 (d, 6H, J = 5.4).

IR(cm^{-1}, KBr): 3310, 2961, 1657, 1533.

4-Bromo-*N*,*N*′-bis[(*S*)-2-chloro-1-isopropylethyl]pyridine-2,6-dicarboxamide (4)

To a stirred solution of 4-bromo-*N*,*N*′-bis[(*S*)-2-hydroxy-1-isopropylethyl]pyridine-2,6-dicarboxamide (**3**) (1.5 g, 3.54 mmol) in chloroform (100 ml) was added dropwise thionyl chloride (15 ml, 206.7 mmol) at room temperature. The resulting mixture was heated under reflux for 1.5 h until all the starting material had reacted (AcOEt, Rf = 0.9). The reaction mixture was allowed to cool and the solvent and excess thionyl chloride were removed under reduced pressure to give a solid, which was purified by column chromatography (hexanes/ethyl acetate = 7:3, Rf = 0.66). 4-Bromo-*N*,*N*′-bis[(*S*)-2-chloro-1-isopropylethyl]pyridine-2,6-dicarboxamide (1.144 g, 70% yield) was obtained as a white solid.

^{1}H NMR ($CDCl_3$): 8.49 (s, 2H), 7.89 (d, 2H, J = 10.2), 4.14 (m, 2H), 3.81 (dq, 4H, J = 3.6, J = 11.7), 2.04 (m, 2H), 1.03 (d, 6H, J = 7.0), 0.99 (d, 6H, J = 7.0).

IR (cm^{-1}, KBr): 3338, 1965, 1675, 1525.

Analysis: calc. for $C_{17}H_{24}BrCl_2N_3O_2$, C 45.05%, H 5.34%, N 9.27%; found C 45.27%, H 5.49%, N 8.99%.

4-Bromo-2,6-bis[(*S*)-4-isopropyloxazolin-2-yl]pyridine (5)

To a stirred suspension of NaH (120 mg, 3 mmol) in THF at 0 ºC was added 4-bromo-*N*,*N*′-bis[(*S*)-2-chloro-1-isopropylethyl]pyridine-2,6-dicarboxamide (**4**) (453 mg, 1 mmol). The solution was stirred at 0 ºC for 45 min. When all the starting material had reacted (hexanes/AcOEt) the mixture was filtered. The filtrate was concentrated under vacuum, redissolved in ethyl acetate (35 ml) and washed with brine (3 × 20ml). The organic layer was dried and the solvent was removed under reduced pressure to give an oil, which was purified by crystallization from hexanes. 4-Bromo-2,6-bis[(*S*)-4-isopropyloxazolin-2-yl]pyridine (270 mg, 70%) was obtained as white needles.

^{1}H NMR ($CDCl_3$): 8.37 (s, 2H), 4.56–4.48 (m, 2H), 4.25–4.10 (m, 4H), 1.85 (m, 2H), 1.03 (d, 6H, J = 6.6), 0.92 (d, 6H, J = 6.6).

IR (cm^{-1}, KBr): 2958, 1649, 1640, 1559.

Analysis: calc. for $C_{17}H_{22}BrN_3O_2$, C 53.70%, H 5.83%, N 11.05%; found C 53.48%, H 6.01%, N 11.22%.

***N*,*N*′-Bis[(*S*)-2-chloro-1-isopropylethyl]-4-vinylpyridine-2,6-dicarboxamide (6)**

To a solution of 4-bromo-*N*,*N*′-bis[(*S*)-2-chloro-1-isopropylethyl]pyridine-2,6-dicarboxamide (**4**) (747 mg, 1.65 mmol) in dry toluene (25 ml) was added a solution of tributylvinyltin (673 mg, 2.06 mmol) in toluene (5 ml) followed by $Pd(Ph_3P)_2Cl_2$ (59 mg 0.083 mmol) at room temperature. The resulting mixture was heated at 60 ºC for 6 h. When the starting material had completely reacted, the mixture was allowed to cool and was filtered through a pad of celite. The solvent was removed under reduced pressure. The crude solid was dissolved in acetonitrile (20 ml) and the solution was washed with hexanes (6 × 10 ml). The acetonitrile was evaporated under reduced pressure and the yellow solid was purified by column chromatography (hexanes/ethyl acetate = 7:3, Rf = 0.50) to give *N*,*N*′-bis[(*S*)-2-chloro-1-isopropylethyl]-4-vinylpyridine-2,6-dicarboxamide (363 mg, 55% yield) as a white solid.

^{1}H NMR ($CDCl_3$): 8.32 (s, 2H), 8.04 (s, 1H), 7.99 (s, 1H), 6.81 (dd, 1H, J = 11, J = 17), 6.20 (d, 1H, J = 17), 5.65 (d, 1H, J = 11), 4.14 (m, 2H), 3.81 (dq, 4H, J = 3.3, J = 11.4), 2.10 (m, 2H, J = 3.6), 1.00 (dd, 12H).
Analysis: calc. for $C_{19}H_{27}Cl_2N_3O_2$, C 57.00%, H 6.80%, N 10.50%; found C 56.81%, H 6.97%, N 10.43%.

2,6-Bis[(*S*)-4-isopropyloxazolin-2-yl]-4-vinylpyridine (7)

To a stirred suspension of NaH (120 mg, 3 mmol) in THF at 0 ºC was added *N*,*N*′-bis[(*S*)-2-chloro-1-isopropylethyl]-4-vinylpyridine-2,6-dicarboxamide (**6**) (300 mg, 0.75 mmol). The solution was heated at 45 ºC for 1.5 h. When all the starting material had reacted (AcOEt, Rf = 0.5) the mixture was allowed to cool. The mixture was filtered and the THF was removed under vacuum. The resulting yellow oil was dissolved in ethyl acetate (35 ml) and washed with brine (3 × 20 ml). The organic layer was dried and the solvent was removed under reduced pressure to give a yellow oil, which was dissolved in hot hexanes. 2,6-Bis[(*S*)-4-isopropyloxazolin-2-yl]-4-vinylpyridine (160 mg, 65% yield) was obtained as white crystals.
^{1}H NMR ($CDCl_3$): 8.17 (s, 2H), 6.72 (dd, 1H J = 11.0, J = 17.6), 6.13 (d, 1H, J = 17.6), 5.58 (d, 1H, J = 11.0), 4.56–4.48 (m, 2H), 4.25–4.10 (m, 4H), 1.85 (m, 2H), 1.04 (d, 6H, J = 6.6), 0.93 (d, 6H, J = 6.6).
Analysis: calc. for $C_{19}H_{25}N_3O_2$, C 69.70%, H 7.70%, N 12.83%; found C 69.67%, H 7.52%, N 12.96%.

Alternatively, 2,6-bis[(*S*)-4-isopropyloxazolin-2-yl]-4-vinylpyridine was prepared from 4-bromo-2,6-bis[(*S*)-4-isopropyloxazolin-2-yl]pyridine (**5**). To a solution of **5** (300 mg, 0.662 mmol) in dry toluene (20 ml) were added tributylvinyltin (649 mg, 1.99 mmol) and $Pd(Ph_3P)_2Cl_2$ (47 mg 0.066 mmol) at room temperature. The resulting mixture was heated at 75 ºC for 1 h. When the starting material had completely reacted, the mixture was allowed to cool, filtered through a pad of celite and the solvent removed under reduced pressure. The crude solid was dissolved in acetonitrile (20 ml) and washed with hexanes (4 × 15 ml). The acetonitrile was evaporated under reduced pressure and the residue was filtered through alumina (hexanes/ethyl acetate = 2:1). The yellow oil was purified by crystallization from hexanes to yield 2,6-bis[(*S*)-4-isopropyloxazolin-2-yl]-4-vinylpyridine (140 mg, 65% yield) as a white solid.

Polymerisation procedure (polymers P1, P2 and P3).

A solution of the monomers and AIBN in a mixture toluene/1-dodecanol (Table 1) was heated at 80±2ºC in a test tube for 24 h. The solid obtained was washed with THF, dried by suction and crushed in a mortar. The polymer was washed in a Soxhlet apparatus with THF for 24 h and dried under vacuum at 50ºC overnight. Typical yields were in the range 75-95%.

Table 1. Composition of the polymerisation mixtures.

	composition (mg)					
polymer	pybox (**7**)	styrene	DVB	toluene	1-dodecanol	AIBN
P1	50.0	91.4	142.6	436.0	0.0	2.9
P2	49.8	145.3	85.7	77.3	350.8	4.1
P3	50.0	101.8	151.3	77.6	361.0	3.0

Preparation of the catalysts.

The Ru complexes were prepared by adding the corresponding amount of polymer (**P1**-**P3**, 0.06 mmol of pybox) to a pre-filtered solution of $[Ru(p\text{-cymene})Cl_2]_2$ (18.7 mg, 0.03 mmol) in methylene chloride (5 ml). The suspension was stirred at room temperature for 24 h. The solid was filtered, thoroughly washed with methylene chloride and dried under vacuum at 50ºC overnight.

Preparation of polymer P4.

To a filtered solution of $[Ru(p\text{-cymene})Cl_2]_2$ (28 mg, 0.045 mmol) in methylene chloride (3 ml), 2,6-bis[(*S*)-4-isopropyloxazolin-2-yl]-4-vinylpyridine (**7**) (30 mg, 0.091 mmol) was added and the resulting solution was stirred at room temperature for 1 h. The solution was transferred to the polymerisation tube and the solvent was eliminated under reduced pressure. Styrene (57.5 mg), divinylbenzene (88.3 mg), toluene (271.3 mg) and AIBN (17 mg[*]) were added and the mixture was heated at 80±2ºC for 24 h. The resulting polymer was washed with THF, dried by suction, crushed in a mortar, Soxhlet extracted with CH_2Cl_2 for 3 days and dried at 50ºC under vacuum overnight.

[*] A larger excess of AIBN than in the case of polymers **P1**-**P3** was necessary in order to initiate the polymerisation. Complexation of AIBN with Ru may be the reason.

Cyclopropanation reactions.

To a suspension of the corresponding supported catalyst (0.02 mmol Ru) in a solution of styrene (278 mg, 2.67 mmol) and *n*-decane (25 mg) in methylene chloride (3 ml), was added ethyl diazoacetate (38 mg, 0.33 mmol) in methylene chloride (3 ml) during 6 h using a syringe pump. The reaction was monitored by gas chromatography, and after consumption of the diazoacetate, a second portion of this reagent was added in the same way. After the reaction the catalyst was filtered off, washed with methylene chloride and dried. The recovered catalysts were reused following the same method.

Yields and *trans*/*cis* selectivities were determined with a cross-linked methyl silicone column: 25 m x 0.2 mm x 0.33 μm. Oven temperature program: 70°C (3 min), 15°C/min to 200°C (5 min). Retention times: ethyl diazoacetate 4.28 min, styrene 5.03 min, *n*-decane 6.93 min, diethyl fumarate 8.73 min, diethyl maleate 9.04 min, *cis*-cyclopropanes (**9**) 11.84 min, *trans*-cyclopropanes (**8**) 12.35 min. The asymmetric induction (Figure 1) was determined with a Cyclodex-B column: 30 m x 0.25 mm x 0.25 μm. Oven temperature program: 125 °C isotherm. Retention times: (1*S*,2*R*)-cyclopropane (**9S**) 28.3 min, (1*R*,2*S*)-cyclopropane (**9R**) 29.1 min, (1*R*,2*R*)-cyclopropane (**8R**) 33.9 min, (1*S*,2*S*)-cyclopropane (**8S**) 34.3 min.

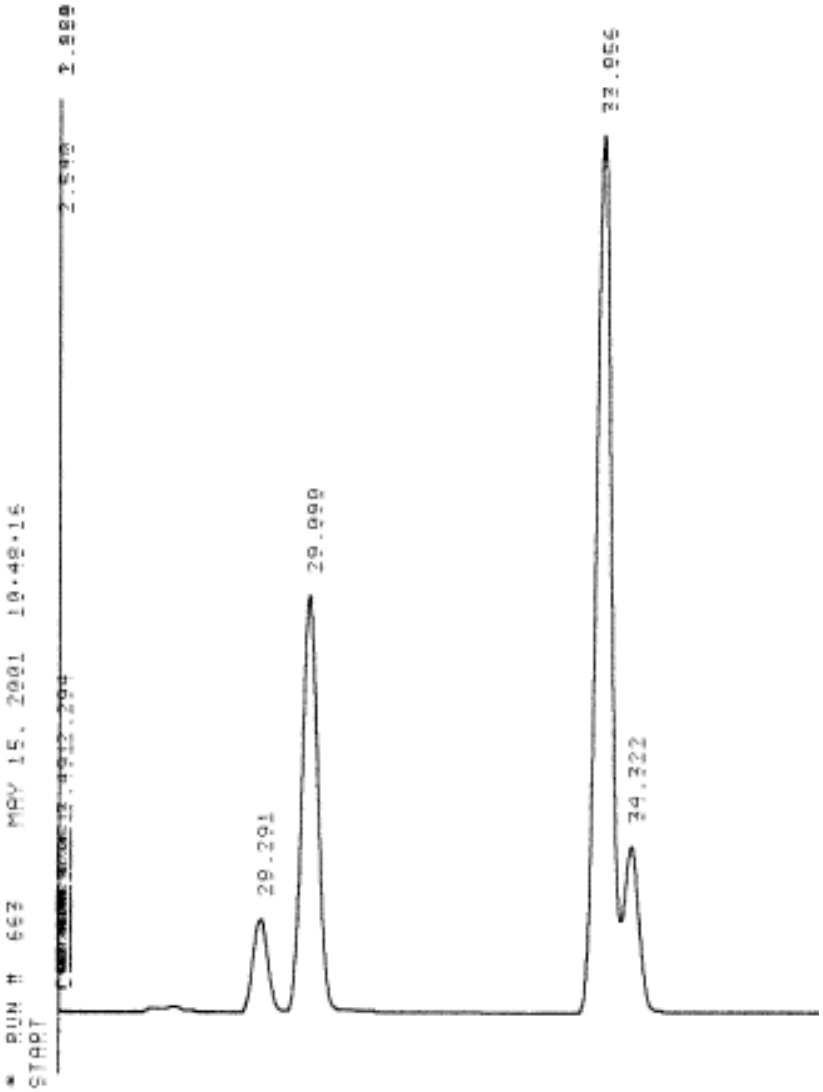

Figure 1