Supporting Information for:
Isospecific Polymerization of Epoxides: A Catalyst System for the Synthesis of Highly Isotactic Polyethers

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I. General Considerations

All air or water sensitive reactions were carried out under nitrogen in a Braun Labmaster drybox or using standard Schlenk techniques. NMR spectroscopy was performed using Varian Unity spectrometers INOVA 400 MHz, INOVA 500 MHz or INOVA 600 MHz. ^{1}H NMR spectra were referenced to residual non- or partially-deuterated solvent signals ($CHCl_3$ = 7.24 ppm, acetone-d_5 = 2.05 ppm, 1,1,2,2-tetrachloroethane-d_1 = 6.0 ppm, pyridine-d_4 = 8.74 ppm). ^{13}C NMR spectra were referenced to solvent signals ($CDCl_3$ = 77.23 ppm, acetone-d_6 = 29.92 ppm, 1,1,2,2-tetrachloroethane-d_2 = 73.78 ppm, pyridine-d_5 = 150.35 ppm). Mass spectrometry analyses were conducted at the School of Chemical Sciences Mass Spectrometry Laboratory at the University of Illinois at Urbana-Champaign or they were acquired using a JEOL GCMate II mass spectrometer operating at 3000 resolving power for high resolution measurements in positive ion mode and an electron ionization potential of 70 eV.

II. Determination of Epoxide Enantiomeric Excess

The enantiomeric excess (*ee*) of recovered propylene oxide was determined by chiral gas chromatography (GC). Gas chromatograms were obtained on a Hewlett-Packard 6890 series gas chromatograph using a flame ionization detector, He carrier gas, and an Alltech CHIRALDEX A-TA chiral capillary column (50 m x 0.25 mm). The absolute stereochemistry of the PO remaining after the polymerization was determined by comparison to a commercially available enantiopure sample.

III. Polymer Characterization

Number average molecular weights (M_n) and molecular weight distributions (M_w/M_n) were measured using high temperature gel-permeation chromatography (GPC) using a Waters Alliance GPCV 2000 size exclusion chromatograph equipped with a Waters differential refractometer detector and viscometer. The set of five sequential columns (four Waters HT 6E and one Waters HT 2) was eluted with 1,2,4-trichlorobenzene containing approximately 0.01 wt % 2,6-di-*tert*-butylhydroxytoluene at 1.0 mL/min at 140 ºC. The Waters refractometer processing method was used for data analysis. The chromatograms generated from the Waters refractometer were calibrated using polystyrene standards. Poly(1,1,1-trifluoro-2,3-epoxypropane) was examined using size-exclusion chromatography (SEC) at 35.0 °C in *N*,*N*-dimethylformamide containing 0.01 M lithium nitrate and 1% formic acid. The column set consisted of three 8 mm x 300 mm GRAM Linear M columns from Polymer Standards Services, calibrated with narrow-molecular-weight distribution poly(methyl methacrylate) standards. Polymer optical rotation was determined using a Perkin Elmer 241 Polarimeter. Polymer melting points were measured by differential scanning calorimetry (DSC) using a TA instruments Q1000 calorimeter equipped with an automated sampler. Analyses were performed in crimped aluminum pans under nitrogen and data were collected from the second heating run at a heating rate of 10 °C/min from -100 to 200 °C, and processed with the TA Q series software.

IV. NMR Quantification of Polymer Tacticity

The signals in the ^{13}C NMR spectra of the polyethers synthesized in this paper exhibit distinct resonances that result from stereochemical defects in the polymer chain. Many of the polyethers synthesized in this paper exhibit triad resolution of the methine carbon (previously assigned in literature);[1] however, poly(styrene oxide) and poly(3,3,3-trifluoromethyl oxirane) display significant overlap between the *mm*, *mr*, *rm*, and *rr* signals of the methine resonance. In these cases, the main-chain methylene resonances were used to quantify the triad integral values and calculate [*mm*]. Since the *mr* and *rm* triads are very small in comparison to the *mm*-triad, and occur in the same region as the ^{13}C-^{13}C satellite peaks of the *mm* triad, the distinct *rr* triad signal is instrumental in accurately calculating [*mm*] for highly isotactic samples, especially when the *mr* and *rm* triad peaks are smaller than the satellite signals. The integral value of the [*rr*] triad is multiplied by two (to equal the value of the *mr* and *rm* triads as a result of enantiomorphic site control statistics), and this value is subtracted from the integral value of the overlapping *mm*, *mr*, and *rm* triad region to give the value of the *mm* triad. For example, the [*mm*] of PPO can be calculated using the integral value of the [*rr*] triad, from which the value of [*mr*] and [*rm*] triads can be calculated and subtracted from the total integral value of [*mm*], [*mr*], and [*rm*]. This method is used due to the ^{13}C NMR baseline separation of the [*rr*] triad signal from the other triad signals and was used to calculate the [*mm*] for all polyethers in this paper. In some instances where the *rr* was not apparent, the tacticity was given as a lower limit ([*mm*] $\geq$ 0.97).

Calculation of polymer tacticity: (From ^{13}C NMR integrations of the methine resonances, Figure S1)

$[mm] + [mr] + [rm] + [rr] = 1$

$[rr] = 120/1120 = 0.11$

$[mr + rm] = 2[rr] = [2(120)]/1120 = 0.22$

$[mm] = [1000\text{-}2(120)]/1120 = 0.67$

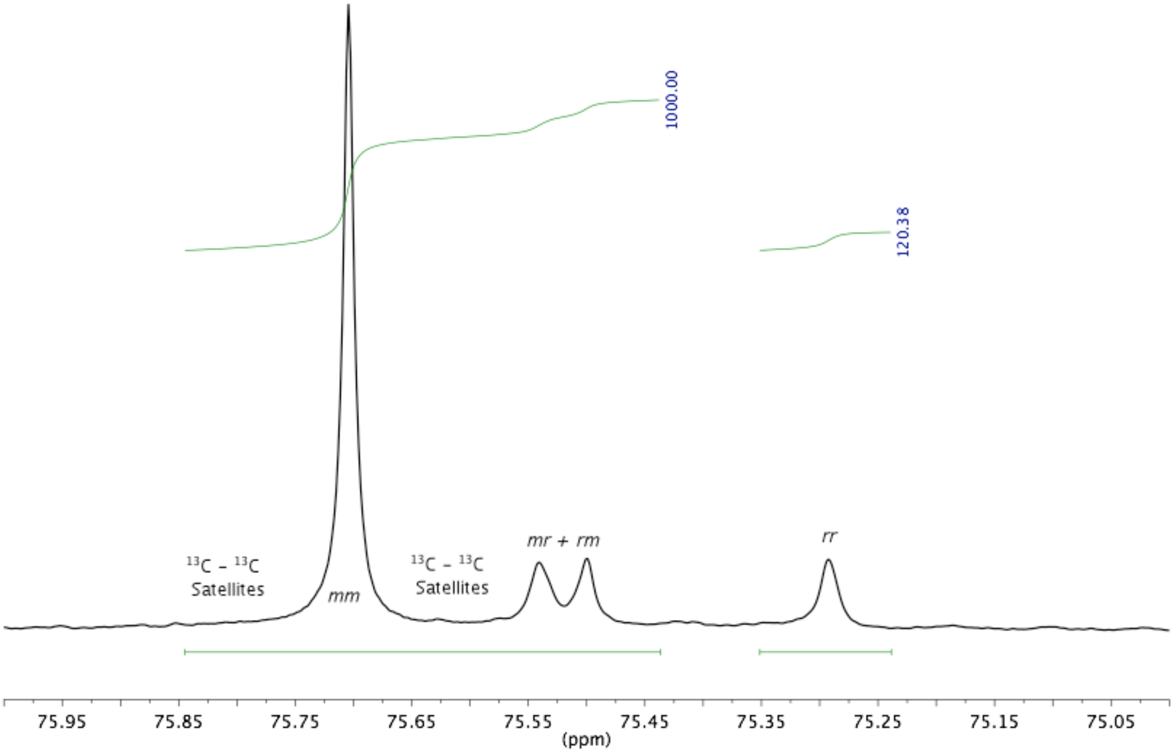


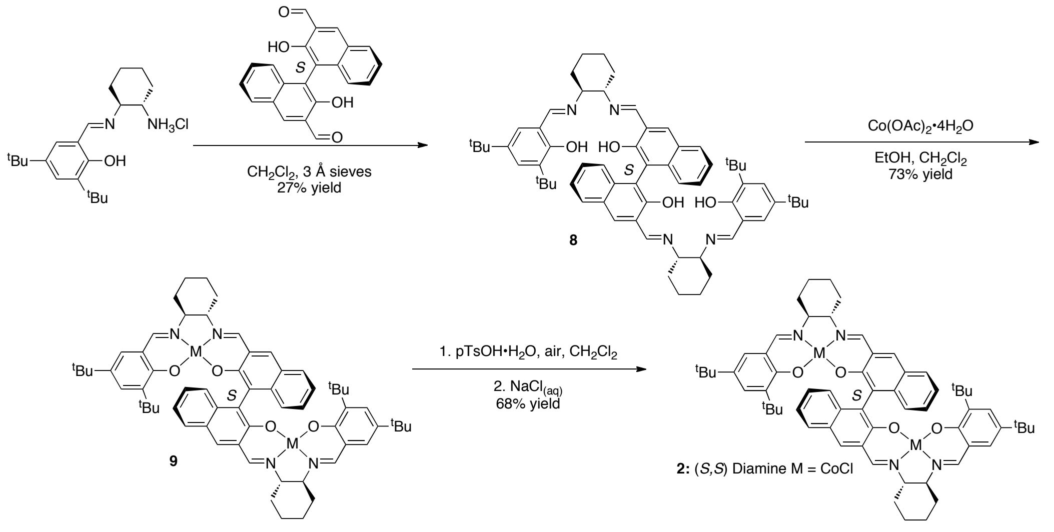
Figure S 1. Calculation of $ee_{(P)}$ for PPO by ^{13}C NMR spectroscopy using *rr* triad peak.

V. Materials

HPLC grade tetrahydrofuran, methylene chloride, and toluene were purchased from Fisher Scientific and purified over solvent columns. Reagent grade acetone, n-pentane, and chloroform, were purchased from Fisher Scientific and were used as received. Absolute ethanol and methanol were degassed by sparging with dry nitrogen, and stored over activated 3 Å molecular sieves. Styrene oxide was synthesized according to the procedure of Fringuelli and Pizzo,[2] dried over calcium hydride, degassed through several freeze-pump-thaw cycles, fractionally distilled under

N_2 and stored in the glovebox. All other epoxides were purchased from commercial sources and were dried over calcium hydride, degassed through several freeze-pump-thaw cycles, then vacuum transferred and stored under nitrogen in a glovebox. (1*S*,2*S*)-Diaminocyclohexane (99% *ee*) was purchased from Aldrich, 3,5-di-tert-butyl salicylaldehyde was purchased from Advanced Asymmetrics Inc. and (*S*)-1,1'-bi-2-naphthol was purchased from TCI. (1*S*,2*S*)- 2-(3,5-di-tert-butyl-2-hydroxybenzylideneamino)cyclohexanammonium chloride,[3] (*S*)-3,3'-diformyl-1,1'-bi-2-naphthol,[4] and bis(triphenylphosphine)iminium acetate ([PPN][OAc]), **4**[5] were prepared according to literature procedures. All other reagents were purchased from commercial sources and used as received.

VI. Synthetic Procedures



Scheme S 1. Synthesis of **2**.

Ligand 8.

A procedure analogous to the synthesis of the (*R₄S*) ligand was used for the synthesis of the (*S₅*) ligand **8**[6] Under nitrogen, molecular sieves (3 Å, 5.0 g), dichloromethane (50 ml), (*S*)-3,3'-diformyl-1,1'-bi-2-naphthol (1.11 g, 3.22 mmol), triethylamine (1.85 mL, 13.3 mmol) and (1*S*, 2*S*)- 2-(3,5-di-*tert*-butyl-2-hydroxybenzylideneamino)cyclohexanammonium chloride (2.43 g, 6.62 mmol) were added sequentially into a 200 mL Schlenk tube. After stirring for 24 hr, the reaction mixture was filtered through a pad of celite on a medium glass fritted funnel. The filtrate was washed with ammonium chloride aqueous solution, dried over $MgSO_4$, concentrated under reduced pressure and purified by chromatography on silica gel (12% EtOAc, 86% hexanes, 2%

Et_3N) to provide pure product as a yellow solid in 26.6% yield. ^1H NMR (600 MHz, $CDCl_3$) δ 13.79 (1H, s), 13.09 (1H, s), 8.54 (1H, s), 8.19 (1H, s), 7.80 (1H, s), 7.72 (1H, d, J = 8.8 Hz), 7.31 (1H, d, J = 2.5 Hz), 7.20 (1H, m), 7.15 (1H, m), 7.04 (1H, d, J = 8.8 Hz), 6.89 (1H, d, J = 2.5 Hz), 3.47 – 3.35 (1H, m), 3.21 (1H, m), 2.58 – 2.25 (1H, m), 2.16 (s, MeCN), 2.04 – 1.92 (1H, m), 1.92 – 1.82 (2H, m), 1.79 (1H, m), 1.76 – 1.52 (2H, m), 1.52 – 1.41 (1H, m), 1.45 (9H, s), 1.18 (9H, s). δ ^{13}C (151 MHz, $CDCl_3$) 166.09, 165.42, 158.18, 154.70, 140.14, 136.57, 135.29, 133.79, 128.95, 128.39, 127.70, 127.07, 126.05, 124.90, 123.34, 120.96, 117.94, 116.47, 73.48, 71.91, 35.21, 34.21, 33.48, 33.02, 31.59, 29.63, 24.48, 24.37. HRMS-EI (m/z): calcd for $C_{64}H_{78}N_4O_4$, 966.6023; found, 966.6055.

Complex 9.

Under nitrogen, $Co(OAc)_2$ (110 mg, 0.620 mmol) was added to a 50 mL Schlenk tube with a stir-bar. **8** (290 mg, 0.299 mmol) was dissolved in dichloromethane (3 mL) under nitrogen, and the ligand solution was cannulated into an anhydrous ethanol solution (8 mL) of $Co(OAc)_2$. The mixture was heated at 60 °C for 135 min, and then cooled slowly to room temperature. The solvent was removed in vacuo leaving a brick-red precipitate, which was collected by filtration using a fine glass-fritted funnel. The obtained solid was washed with pentane (20 mL) yielding a dark red powder, yield 262 mg, 73%. HRMS-EI (*m/z*): calcd for $C_{64}H_{74}Co_2N_4O_4$ 1080.4374; found, 1080.4392.

Complex 2.

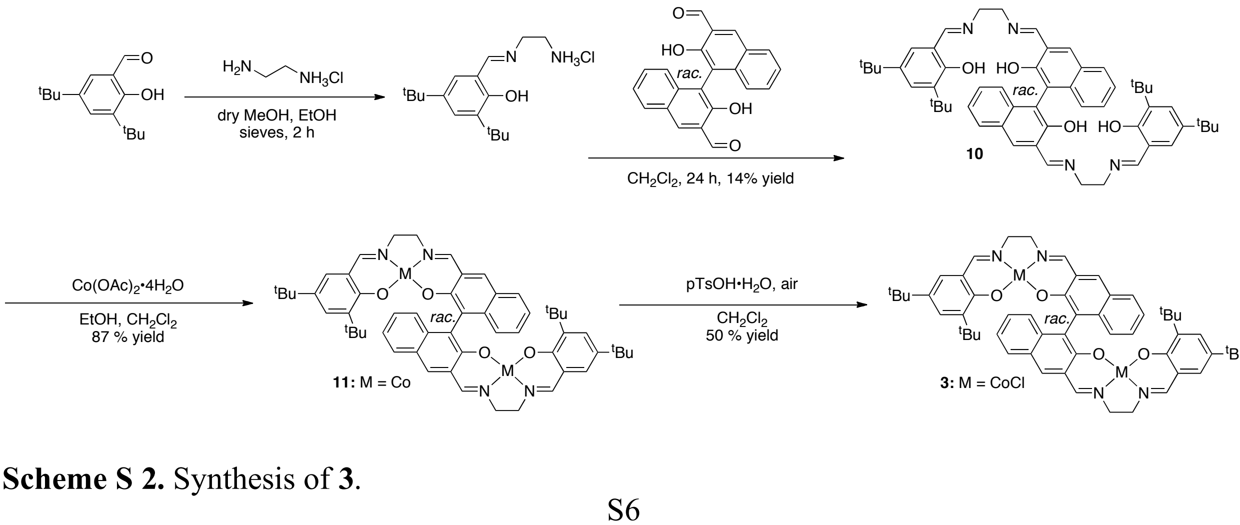
A procedure analogous to that reported by Jacobsen and co-workers for the synthesis of (*R*,*R*)-(salcy)CoCl[7] was applied for the synthesis of complex **2**. Complex **9** (262 mg, 0.242 mmol) was dissolved in 20 mL of methylene chloride in a beaker, and *para*-toluenesulfonic acid monohydrate (99 mg, 0.52 mmol) was added. The dark brown solution was stirred open to air for 24 h, during which all the methylene chloride evaporated. The dark shiny solids were redissolved in methylene chloride and washed three times with concentrated aqueous sodium chloride, then dried over $MgSO_4$ and filtered. Solvent was removed in vacuo, and the dark brown solids were washed with pentane to yield 189 mg of **2** as a dark brown powder (68% yield). ^1H NMR (600 MHz, pyridine-d_5) δ 9.21 (1H, s), 8.71 (s, d_4 pyridine), 8.59 (1H, s), 8.51 (1H, s), 7.99-1.97 (1H, m), 7.54 (s, d_4 pyridine), 7.49-7.48 (2H, m), 7.19-7.03 (2H, m), 7.18 (s, d_4 pyridine), 7.18 – 7.15 (2H, m), 7.03 – 7.01 (1H, m), 5.39-5.36 (1H, m), 3.27 (1H, m), 2.48 (1H, m), 2.13-2.07 (1H, m), 1.84-1.82 (2H, m), 1.70-1.67 (2H, m), 1.29 (9H, s), 1.19 (9H, s), 1.07-1.01 (2H, m). The complex was reduced to **9** during mass spectrometry analysis.

Ligand 10.

3,5-Di-tert-butyl salicylaldehyde (0.50 g, 2.2 mmol) was combined with ethylene diamine hydrochloride (0.21 g, 2.2 mmol) in a flask with activated 3Å molecular sieves (5.0 g). The flask was purged with N_2 and 25 mL of dry methanol and 25 mL of dry ethanol was added via cannula and stirred under N_2 at room temperature. The reaction was monitored by TLC until complete disappearance of salicylaldehyde was observed (2 h). At this point a solution of (*rac*)-3,3'-diformyl-1,1'-bi-2-naphthol 0.40 g (1.1 mmol) and triethylamine 0.25 mL were dissolved in 100 mL of anhydrous dichloromethane then cannulated into the reaction mixture and stirred overnight. The reaction was filtered through celite and rinsed with dichloromethane. The solution was concentrated, and purified by chromatography on silica gel (15%, EtOAc 84% hexanes, 1% Et_3N increased to 40%, EtOAc 59% hexanes, 1% Et_3N) The obtained yellow solid was rinsed with 4 x 5 mL of acetonitrile leaving pure ligand as a pale yellow solid. 0.1287 g 14% yield. Rf = 0.73 (40%, EtOAc / hexanes, 1% Et_3N). ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.59 (1H, s), 13.07 (1H, s), 8.62 (1H, s), 8.32 (1H, s), 7.92 (1H, s), 7.83-7.81 (2H, m), 7.33 (1H, s), 2.25 (1H, m) 7.24 (s, $CHCl_3$), 7.13 (1H, s), 6.99 (1H, s), 5.28 (s, CH_2Cl_2), 3.92-3.97 (4H, m), 3.86-3.88 (4H, m), 1.42 (9H, s), 1.23 (9H, s). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.92, 167.81, 167.75, 166.93, 158.14, 154.89, 154.77, 140.22, 136.74, 135.45, 134.18, 133.82, 130.07, 129.22, 129.08, 128.69, 128.54, 127.85, 127.71, 127.22, 126.25, 125.36, 124.92, 124.54, 124.47, 123.65, 123.49, 120.96, 117.89, 116.72, 77.48, 77.23, 76.98, 60.26, 59.44, 35.20, 35.05, 34.26, 31.65, 31.50, 29.63. HRMS-EI (m/z): calc for $C_{56}H_{66}N_4O_4$, 858.5084; found, 858.5084.

Complex 11.

Ligand **10** (227 mg, 0.264 mmol) was dissolved in 10 mL anhydrous degassed methylene chloride. In a separate flask $Co(OAc)_2{\cdot}4H_2O$ (145 mg, 0.581 mmol) was evacuated and dehydrated with a heat gun until solid changed color from pink to purple. The solid $Co(OAc)_2$ was then dissolved in 20 mL of anhydrous degassed EtOH via cannula. The ligand solution was transferred to the ethanol solution via cannula and a brown, red solid precipitate formed. The

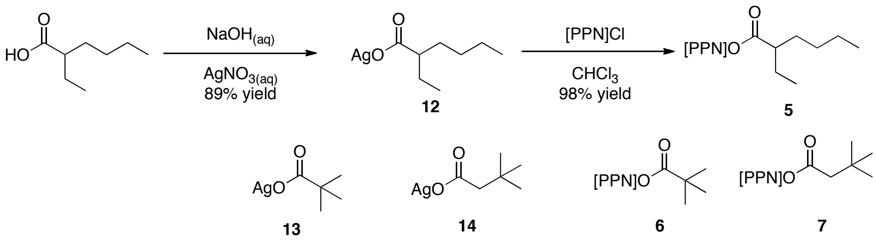


Scheme S 2. Synthesis of **3**.

suspension was heated to 60 °C for 2 h after which it was allowed to cool. The solvent was removed in vacuo to yield a brown precipitate. Product was collected by filtration using a fine frit, and rinsed with 3 x 100 mL pentanes yielding **11** as a brown powder. Yield: 225 mg (87 %). Compound is paramagnetic. HRMS-EI (m/z): calc for $C_{56}H_{62}N_4O_4,Co_2$ 972.3435; found, 972.3446.

Complex 3.

The cobalt complex **11** (142 mg, 0.146 mmol) was dissolved in 50 mL of methylene chloride. $TsOH{\cdot}H_2O$ (62 mg, 0.32 mmol) was added and the reaction mixture was stirred open to air in a beaker for 17 h over which time most of the solvent evaporated. Methylene chloride, 50 mL, was added and the solution was and rinsed with 3 x 50 mL brine, then dried over Na_2SO_4, filtered then solvent was removed in vacuo providing a shiny black solid which was rinsed with 4 x 100 mL pentanes. Yield: 76 mg 50%. ^1H NMR (300 MHz, pyridine-d_5) δ 9.42 (1H, s), 8.61 (s, d_4 pyridine), 8.40 (2H, m), 7.83 (1H, d, J = 8.3 Hz), 7.56 (s, d_4 pyridine) 7.55 (1H, m), 7.29 (s, d_4 pyridine), 7.26 – 7.04 (2H, m), 7.02 – 6.74 (1H, m), 6.65 (1H, d, J = 8.3 Hz), 4.97 (s, H_2O), 4.09-4.06 (2H, m), 3.57-3.50 (2H, m), 1.25 (9H, s), 1.18 (9H, s). The complex was reduced to **11** during mass spectroscopic analysis.



Scheme S 3. Synthesis of Silver Carboxylates: **12**, **13**, **14** and PPN Carboxylates: **5**, **6**, **7**.

Preparation of silver carboxylates

Representative synthesis of silver carboxylates 12, 13, 14.[8]

12. An aqueous solution of silver nitrate (50 mL, 1 M) was added to an aqueous sodium 2-ethylhexanoate solution (50 mL, 1.2 M). The resulting mixture was stirred in the absence of light for 15 min. The precipitate was filtered and rinsed with 50 mL water, 50 mL methanol, and 50 mL diethyl ether yielding a white solid which was dried in vacuo. Yield 1.31 g, 89% Elemental analysis; Found: C, 38.2; H, 5.9. Calc. for $C_8H_{15}AgO_2$: C, 38.3; H, 6.0%.

13. Yield 0.48 g, 39% Elemental analysis; Found: C, 29.0: H, 4.2. Calc. for $C_5H_9AgO_2$: C, 28.7; H, 4.3%.

14. Yield 1.09 g, 83% Elemental analysis; Found: C, 32.4; H, 4.8. Calc. for $C_6H_{11}AgO_2$: C, 32.3; H, 5.0%.

Representative synthesis of PPN carboxylates 5, 6, 7.[5]

Bis(triphenylphosphine)iminium chloride ([PPN]Cl) (561 mg, 0.976 mmol) and silver carboxylate **12** (250 mg, 0.996 mmol) were combined in 10 mL $CHCl_3$ and stirred at room temperature in the absence of light. After 3 days stirring was stopped and the gray solid was allowed to settle and the liquid was decanted. Any remaining solid was removed by centrifugation yielding a clear colorless liquid. Solvent was removed under vacuum yielding a clear viscous oil which solidified upon standing to give a white solid. Typical yields were 85-99%.

5. Isolated as a viscous clear oil in 98% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (6H, m), 7.52 – 7.36 (24H, m), 7.24 (s, $CHCl_3$), 2.31 – 2.21 (1H, m), 1.71 – 1.57 (2H, m), 1.46 – 1.17 (6H, m), 0.90 (3H, t, J = 7.4), 0.79 (3H, t, J = 7.2). ^{13}C NMR (151 MHz, $CDCl_3$) δ 134.05, 132.31 – 131.99 (m), 129.90 – 129.57 (m), 127.01 (dd, J = 1.9 Hz, J=110), 77.25 ($CDCl_3$), 49.25, 32.83, 30.17, 26.22, 23.24, 14.30, 12.48. Figure S 2.

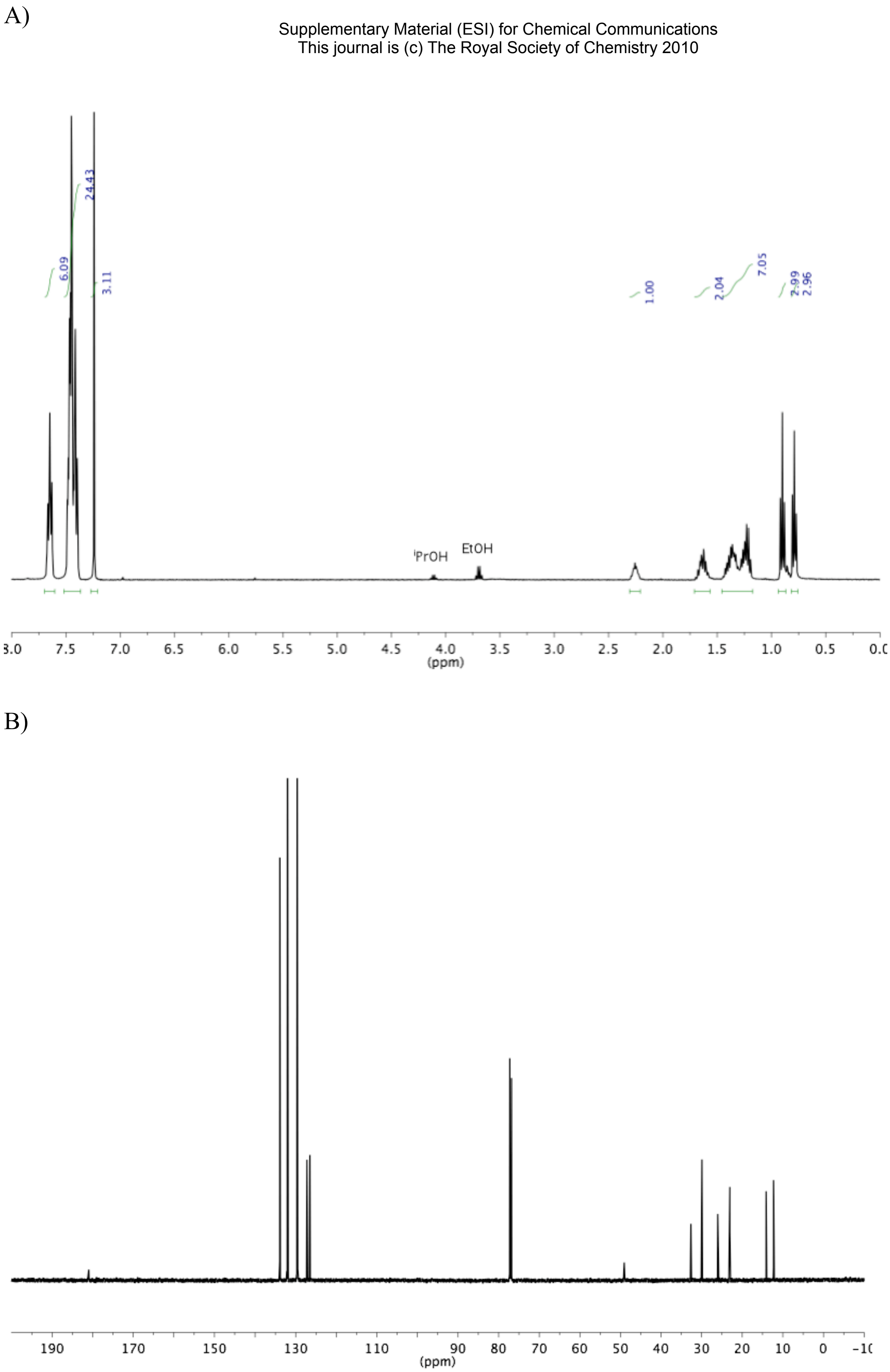
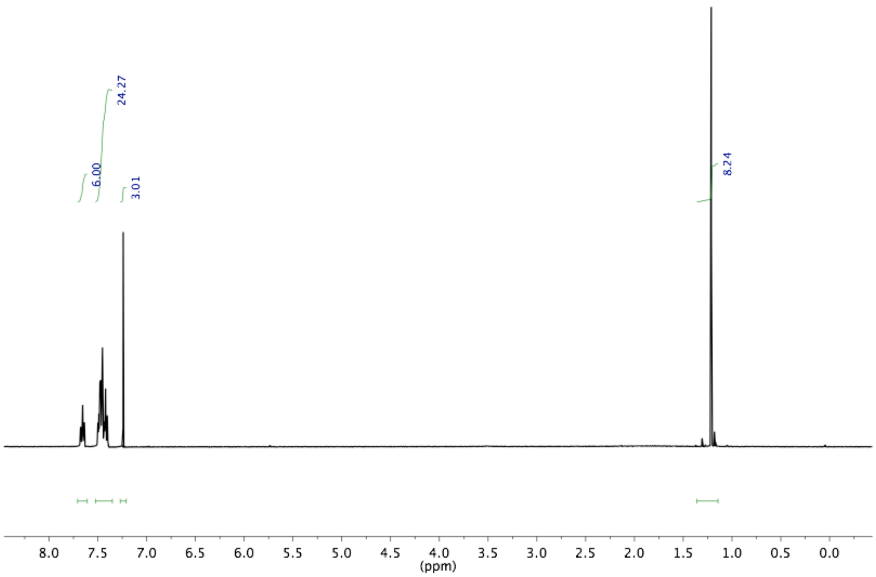


Figure S 2. NMR spectra of **5**. A) ^{1}H NMR. B) ^{13}C NMR.

6. Isolated as a white solid in 87% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.59 (6H, m), 7.53 – 7.35 (24H, m), 7.24 (s, $CHCl_3$), 1.19 (9H, s). ^{13}C NMR (151 MHz, $CDCl_3$) δ 181.13, 134.05, 132.31 – 131.99 (m), 129.90 – 129.57 (m), 127.01 (dd, J = 1.9 Hz, J=110), 77.25 ($CDCl_3$), 28.98. Figure S 3.

A)



B)

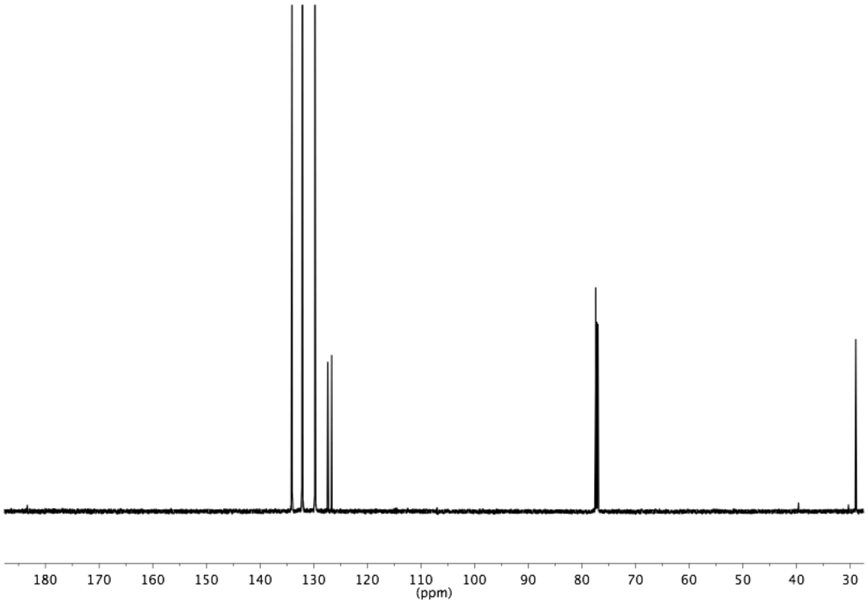
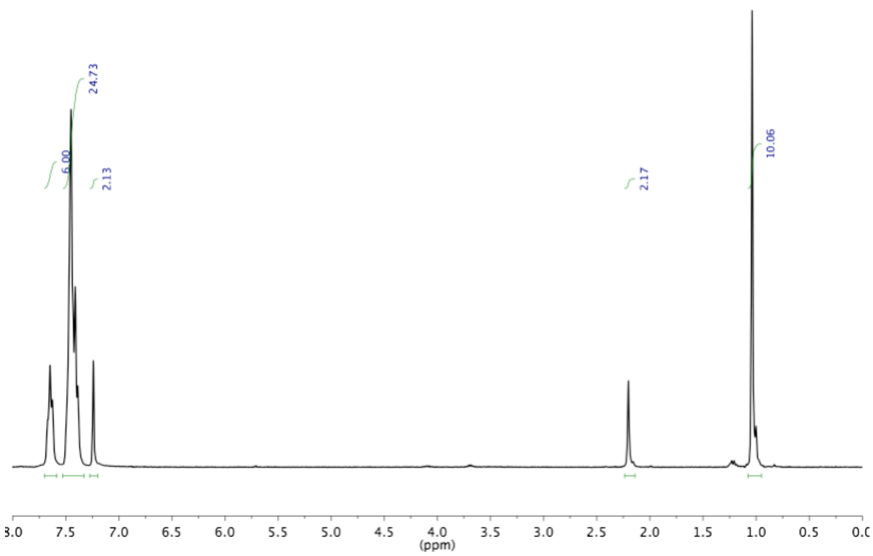


Figure S 3. NMR spectra of **6**. A) ^{1}H NMR. B) ^{13}C NMR.

7. Isolated as a white solid in 98% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.58 (6H, m), 7.53 – 7.33 (24H, m), 7.24 (s, $CHCl_3$), 2.20 (2H, s), 1.01 (9H, s). ^{13}C NMR (151 MHz, $CDCl_3$) δ 177.57, 134.05, 132.31 – 131.99 (m), 129.90 – 129.57 (m), 127.01 (dd, J = 1.9 Hz, J=110), 77.25 ($CDCl_3$), 51.79, 30.34. Figure S 4.

A)



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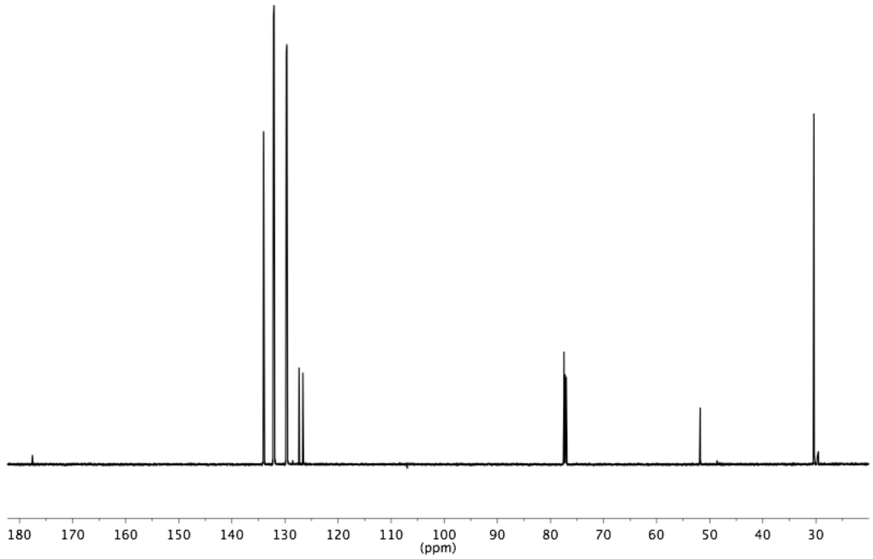

Figure S 4. NMR spectra of **7**. a) ^{1}H NMR. b) ^{13}C NMR.

VII. Polymerization of Epoxides

Determination of s-factor (k_s/k_r) of 2 for the enantiospecific polymerization of propylene oxide.

In a nitrogen drybox, **2** (4.2 mg, 0.0035 mmol) and **4** (4.4 mg, 0.0074 mmol) were added to a Schlenk tube containing a stir bar. A vacuum adapter was attached to the Schlenk tube, and was sealed under nitrogen before removing from the drybox. The Schlenk tube was placed under dry nitrogen on the Schlenk line, and subsequently cooled in an ice bath. Anhydrous toluene (6 mL) was added to the Schlenk tube via syringe, and the resulting solution was stirred for 15 min at 0 °C. Propylene oxide (0.831 g, 14.3 mmol) was added via syringe and the polymerization reaction was kept at 0 °C. After 90 min, the unreacted propylene oxide was vacuum transferred to another Schlenk tube cooled in liquid nitrogen. The remaining polymer solution was transferred to a pre-weighed round bottom flask and dried overnight under vacuum. Conversion was determined by polymer mass to be 22%. The *ee* of recovered propylene oxide was measured by chiral GC to be 23% (*R*)-propylene oxide, with t_R (major, *R*) = 14.2 min and t_R (minor, *S*) = 14.7 min. The absolute stereoconfiguration was confirmed by chiral GC using commercially available (*R*)-propylene oxide. The conditions for separation were: flow, 1.4 mL/min; velocity, 34 cm/sec; pressure, 7 psi; isothermal at 40 °C. The optical rotation of the polymer was measured ($[\alpha]_D^{23}$ = -24.7°, c = 1.5 g / 100 mL, $CHCl_3$) and matched closely that reported by Price et al.[9] The negative rotation shows that the polymer synthesized with **2** is (*S*)-poly(propylene oxide), giving evidence for epoxide ring-opening at the methylene carbon with retention of the configuration at the methine carbon. A concentrated sample of polymer in $CDCl_3$ was made for analysis by ^{13}C NMR spectroscopy to determine polymer tacticity. Polymer (50 mg) was dissolved in 0.5 mL of $CDCl_3$. An INOVA 500 Varian spectrometer was used to obtain the ^{13}C NMR spectrum (taken over 2 h, with more than 2000 scans), as well as a ^1H NMR spectrum of the dried polymer. Polymer tacticity (Figure S 5): [*mm*]:[*mr* + *rm*]:[*rr*] = [0.982]:[0.012]:[0.006], $ee_{(p)}$ = 0.988. The *s*-factor is calculated using equation:

$$s = k_s / k_r = \frac{\ln[1 - c(1 + ee_{(P)})]}{\ln[1 - c(1 - ee_{(P)})]}$$

where c is the conversion of epoxide, to give an estimated *s*-factor = 210. ^{13}C NMR ($CDCl_3$, 125 MHz): δ 75.70, 73.61, 17.64. ^1H NMR ($CDCl_3$, 500 MHz): δ 3.52 (2H, m), 3.39 (1H, m), 1.11 (3H, m). M_n = 36,800 g/mol, M_w/M_n = 7.8.

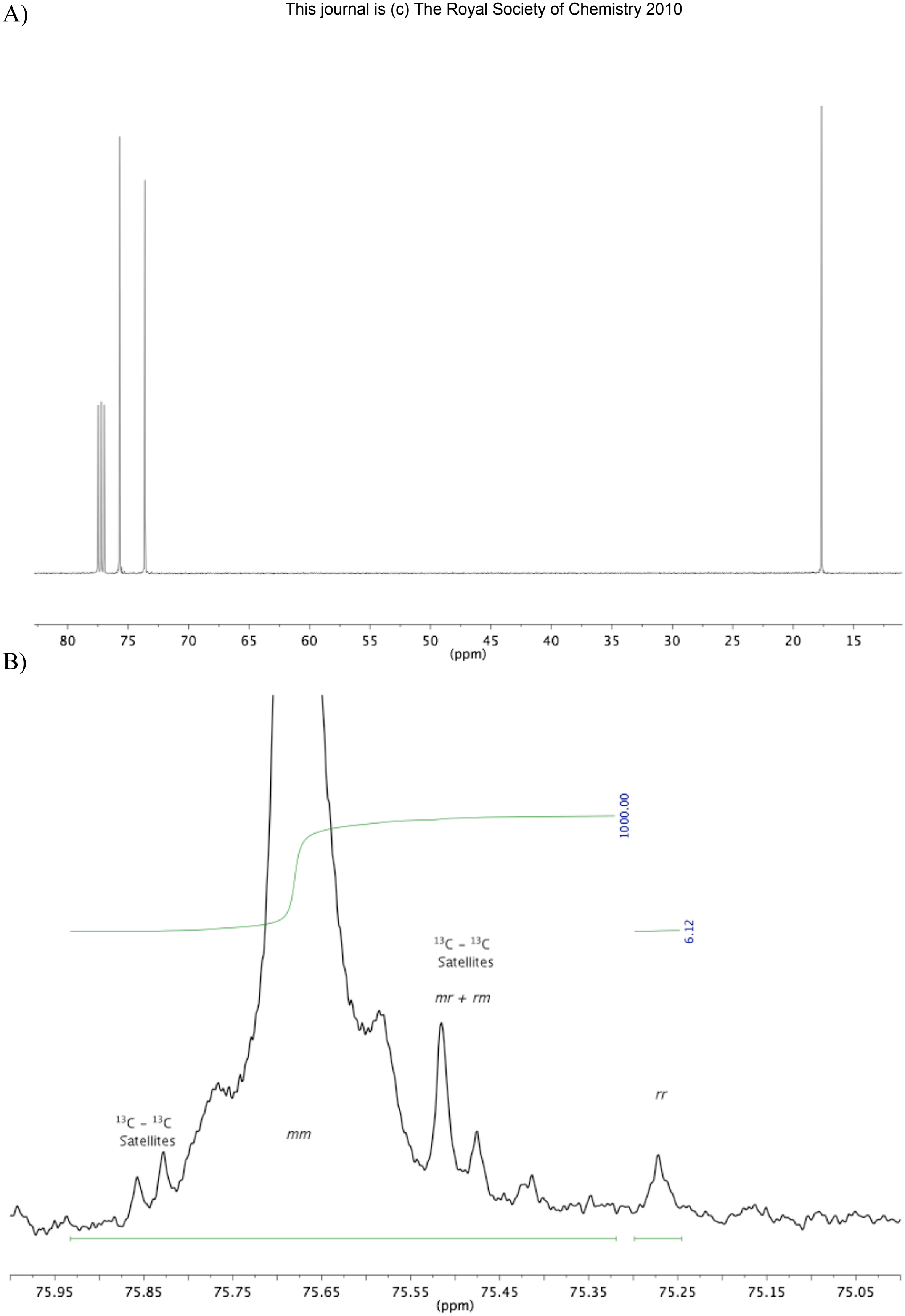

Figure S 5. ^{13}C NMR spectra of poly(propylene oxide). A) Full spectrum. B) Methine carbon.

Representative Isoselective Polymerization of Racemic Epoxides.

Polymerization of Racemic Propylene Oxide with (3/6) (table 2 entry 1).

In a drybox under nitrogen atmosphere, **3** (4.0 mg, 0.0038 mmol) and **6** (4.9 mg, 0.0076 mmol) were added to 6 mL of anhydrous toluene in a Schlenk tube containing a stir bar. The Schlenk tube was sealed under nitrogen and removed from the drybox. The Schlenk tube was placed under nitrogen on the Schlenk line, and subsequently cooled in an ice bath and stirred for 15 min at 0 °C. Propylene oxide (0.831 g, 14.3 mmol) was added via syringe. The polymerization was kept at in an ice bath during the course of the reaction. After 5 min an aliquot was taken for NMR analysis then 1 mL of methanol containing a trace amount of HCl was added to the mixture to quench the catalyst. Volatiles were then removed under vacuum. The remaining polymer solution was transferred to a pre-weighed round bottom flask and dried overnight under vacuum. Conversion was determined by ^{1}H NMR of the aliquot taken and determined to be 55%. An INOVA 500 Varian spectrometer was used to obtain the ^{13}C NMR spectrum (taken over 2 hrs, with more than 2000 scans), as well as a ^{1}H NMR spectrum of the dried polymer. Polymer tacticity[10] (Figure S 6) [*mm*] = 0.97. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.52 (2H, m), 3.39 (1H, m), 1.11 (3H, m). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 75.70, 73.61, 17.64. M_n = 134,000 g/mol, M_w/M_n = 1.8.

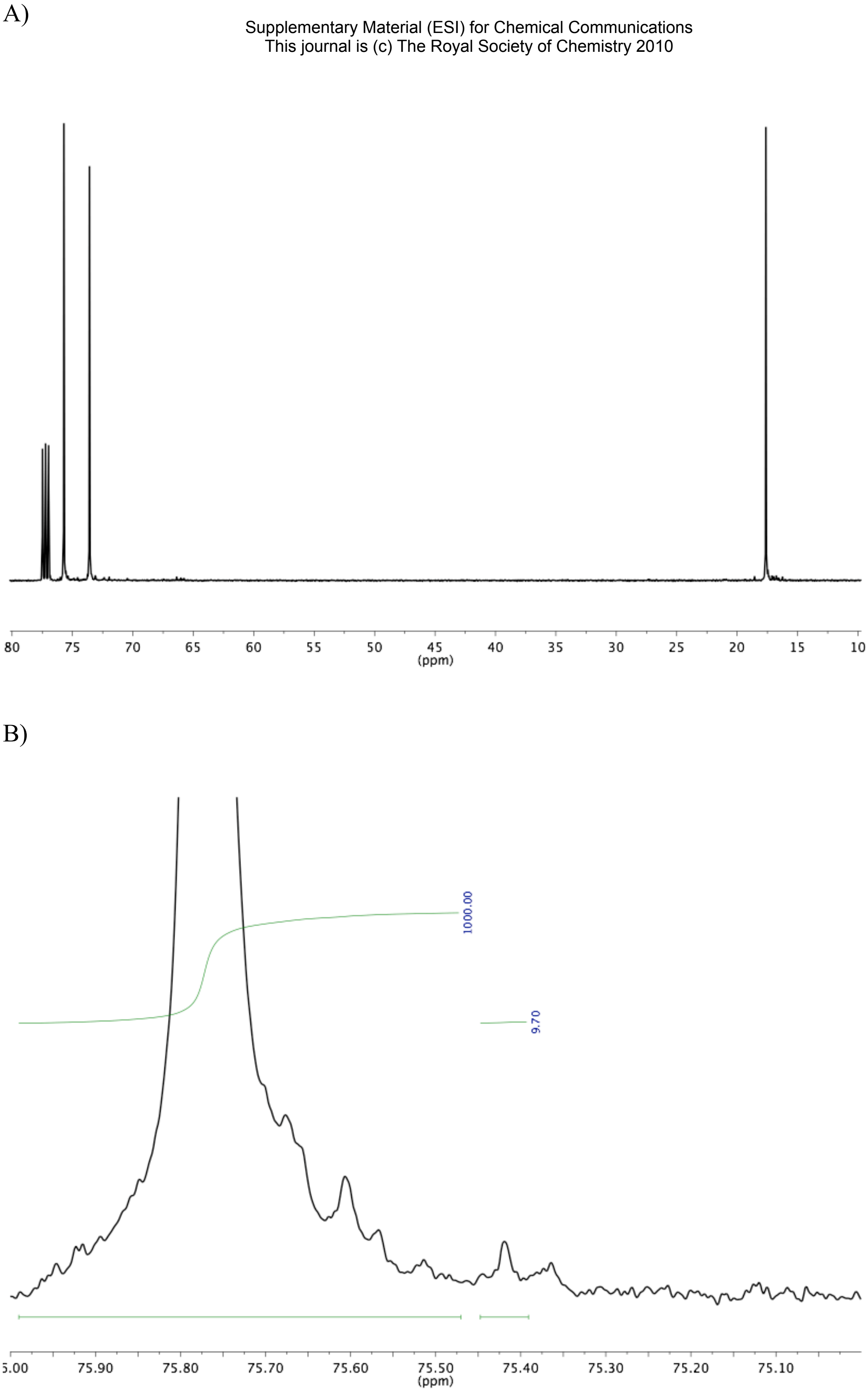

Figure S 6. ^{13}C NMR spectra of poly(propylene oxide). A) Full spectrum. B) Methine carbon.

Polymerization of Racemic 1-Butene Oxide (Table 2, entry 2).

The polymerization procedure was the same as that for propylene oxide except that 1.27 mL of butene oxide was used. Conversion was determined after 5 min by ^{1}H NMR to be 60%. Polymer tacticity[6] (Figure S 7) [*mm*] = 0.97. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.63 (1H, m), 3.56 – 3.49 (1H, m), 3.40 – 3.30 (1H, m), 1.62 – 1.48 (2H, m), 0.95 (3H, t, J = 7.4 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 81.07, 72.62, 25.04, 10.06. M_n = 239,000 g/mol, M_w/M_n = 1.5.

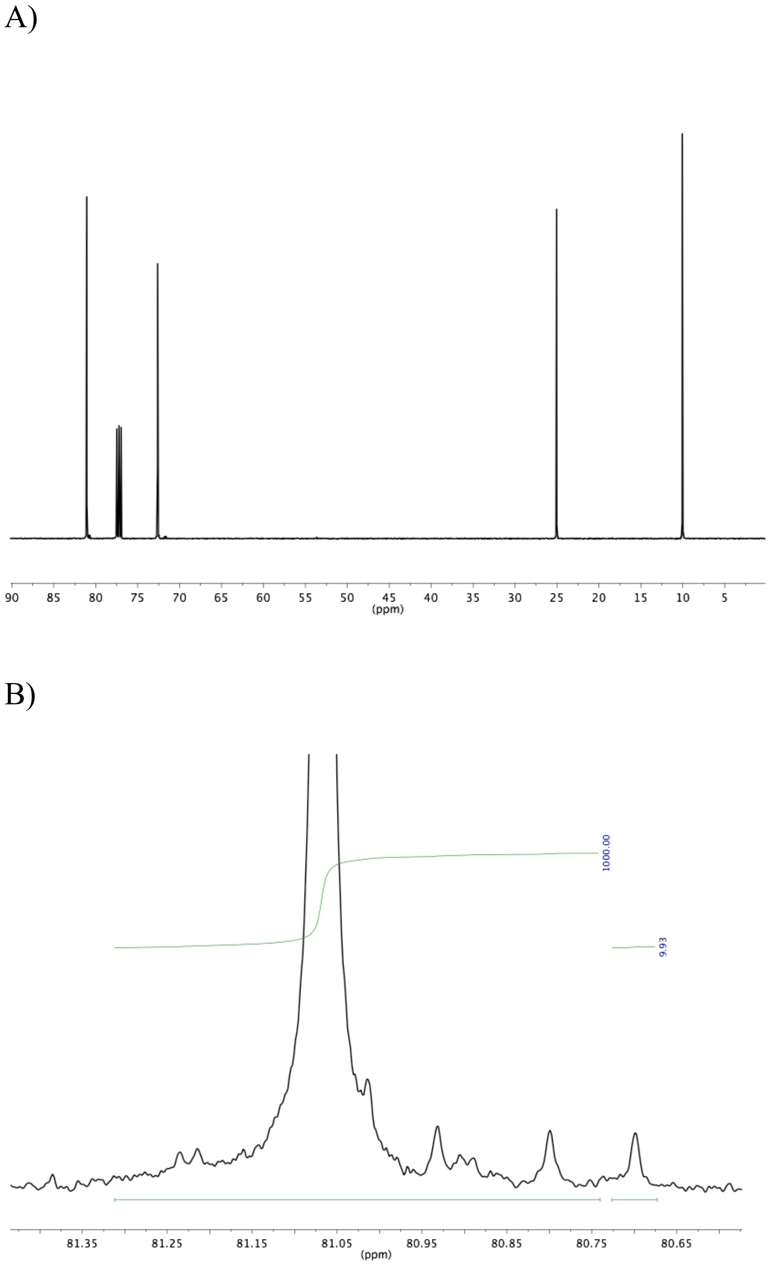

Figure S 7. ^{13}C NMR spectra of poly(butene oxide). a) Full spectrum. b) Methine carbon.

Polymerization of Racemic Phenyl Glycidyl Ether (Table 2, entry 3).

The polymerization procedure was the same as that for propylene oxide except that 1.98 mL of phenyl glycidyl ether was used. Conversion was determined after 1 min by ^{1}H NMR to be 89 %. Polymer tacticity[11] (Figure S 8) [*mm*] $\geq$ 0.97. ^{1}H NMR (500 MHz, 1,1,2,2,-tetrachloroethane-d_2 135 °C) δ 7.30 (2H, m), 6.94 (3H, m), 4.13 (1H, m), 4.08 (1H, m), 3.85 (3H, m). ^{13}C NMR (125 MHz, 1,1,2,2-tetrachloroethane-d_2 135°C) δ 158.91, 129.13, 120.76, 115.01, 78.47, 70.06, 68.64. M_n = 328,000 g/mol, M_w/M_n = 1.4.

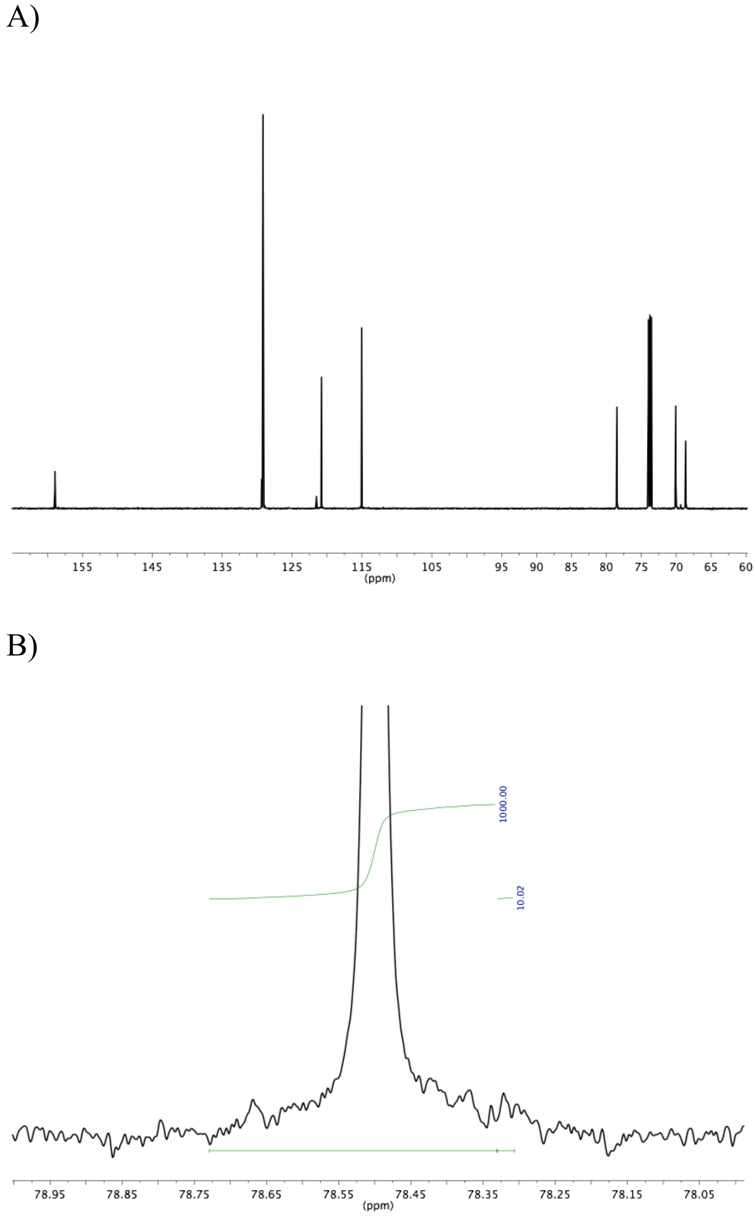

Figure S 8. ^{13}C NMR spectra of poly(phenyl glycidyl ether). A) Full spectrum. B) Methine carbon.

Polymerization of Racemic 3,4-Epoxy-1-Butene (Table 2, entry 4).

The polymerization procedure was the same as that for propylene oxide except that 1.18 mL of 3,4-epoxy-1-butene was used. Conversion was determined after 10 min by ^{1}H NMR to be 46%. Polymer tacticity (Figure S 9) [*mm*] = 0.92. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (1H, m), 5.32 (1H, m), 5.19 (1H, m), 4.08 – 3.80 (1H, m), 3.68 – 3.52 (1H, m), 3.45 (1H, m). ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.27, 117.64, 80.79, 72.31. M_n = 212,000 g/mol, M_w/M_n = 1.5.

(Note: The polymer appears to display tetrad resolution of the methylene carbon. The tacticity was confirmed by complete hydrogenation to poly(1-butene oxide), which had [*mm*] = 0.92)

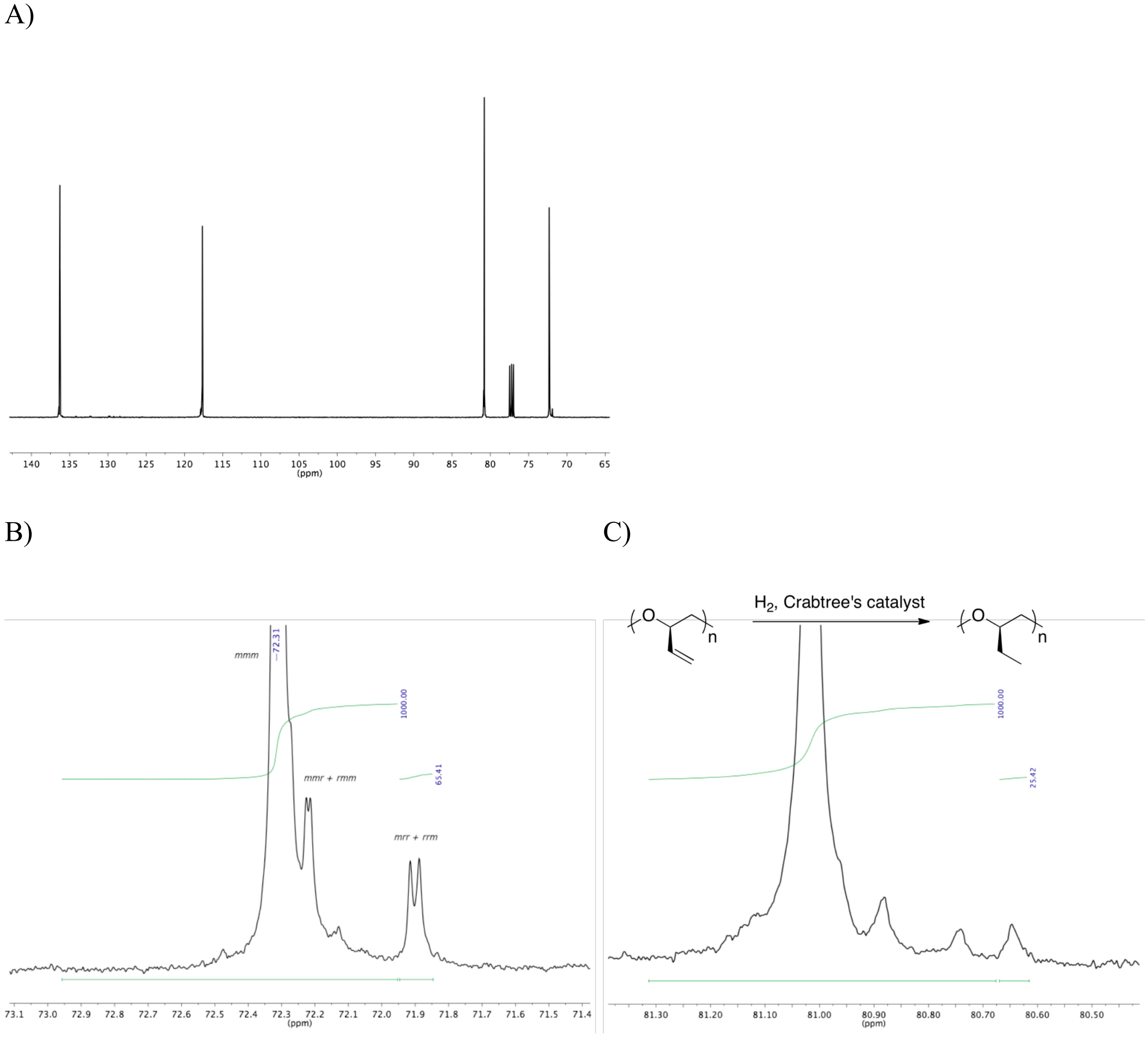

Figure S 9. ^{13}C NMR spectra of poly(3,4-epoxy-1-butene). A) Full spectrum. B) Methylene carbon. C) Hydrogenated polymer methine carbon.

Polymerization of Racemic Styrene Oxide (Table 2, entry 5).

The polymerization procedure was the same as that for propylene oxide except that 1.66 mL of styrene oxide was used. Conversion was determined after 45 min by ^{1}H NMR to be 23%. Polymer tacticity[12] (Figure S 10) [*mm*] ≥ 0.97. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (5H, s), 4.57 (1H, m), 3.69 (1H, m), 3.55 (1H, m). ^{13}C NMR (125 MHz, $CDCl_3$) δ 81.07, 72.62, 25.04, 10.06. $M_n = 77{,}000$ g/mol, $M_w/M_n = 1.9$.

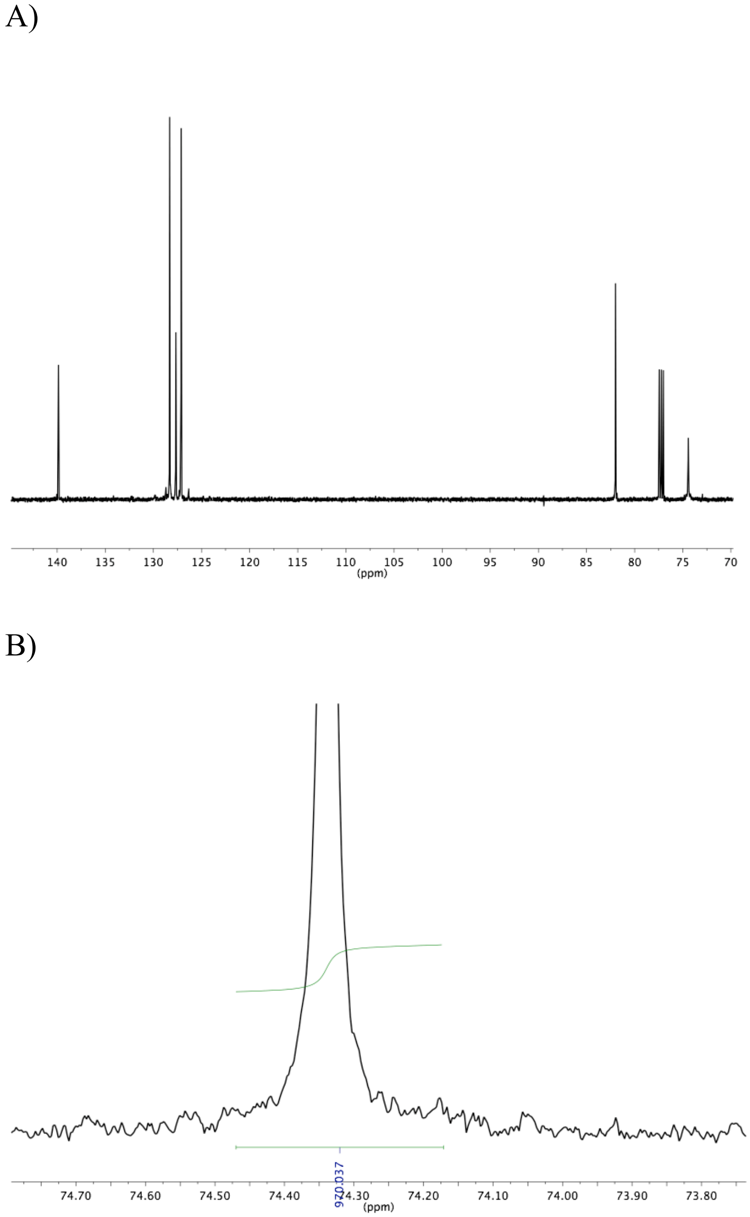

Figure S 10. ^{13}C NMR spectra of poly(styrene oxide). A) Full spectrum. B) Methylene carbon.

Polymerization of Racemic 1,1,1-trifluoro-2,3-epoxypropane (Table 2, entry 6).

The polymerization procedure was the same as that for propylene oxide except that 1.25 mL of 1,1,1-trifluoro-2,3-epoxypropane was used. Conversion was determined after 90 min by ^{1}H NMR to be 32%. Polymer tacticity[13] (Figure S 11) [*mm*] ≥ 0.97. ^{1}H NMR (500 MHz, Acetone-d_6) δ 4.35 (1H, m), 4.21 (1H, dd, J= 10.5, 3 Hz), 4.05 (1H, dd, J = 10.5, 7.5 Hz). ^{13}C NMR (125 MHz, Acetone-d_6) δ 125.00 (quartet, $^1J_{CF} = 282.2$ Hz), 78.84 (quartet, $^2J_{CF} = 29.8$ Hz), 71.45. $M_n = 20{,}000$ g/mol, $M_w/M_n = 13$.

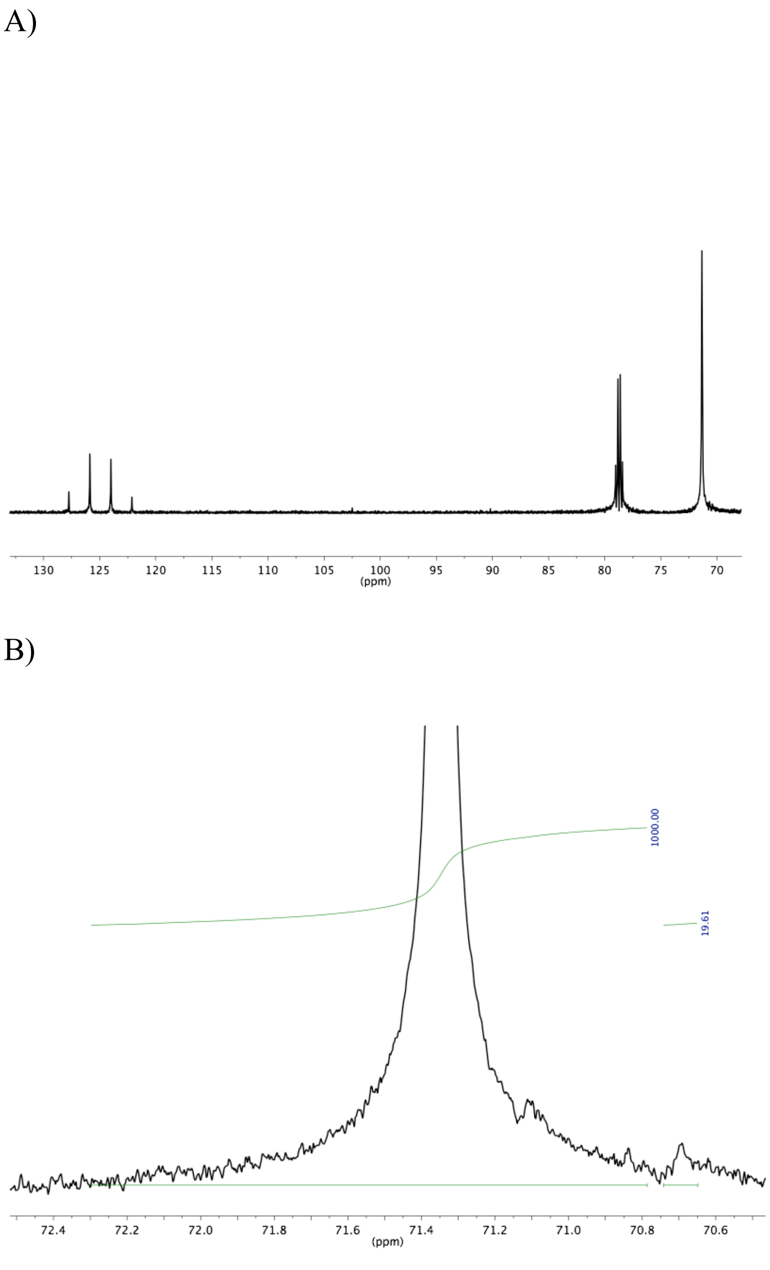

Figure S 11. ^{13}C NMR spectra of poly(1,1,1-trifluoro-2,3-epoxypropane). A) Full spectrum. B) Methylene carbon.

Representative Quantitative Isoselective Polymerization of Racemic Epoxides.

Polymerization of Racemic Propylene Oxide with (3/6) (table 3 entry 1).

In a drybox under nitrogen atmosphere, **3** (4.0 mg, 0.0038 mmol) and **6** (4.9 mg, 0.0076 mmol) were added to a Schlenk tube containing a stir bar. The Schlenk tube was sealed under nitrogen and removed from the drybox. The Schlenk tube was placed under dry nitrogen on the Schlenk line, and subsequently cooled in an ice bath. Anhydrous toluene (6 mL) was added to the Schlenk tube via syringe, and the resulting solution was stirred for 15 min at 0 °C. Propylene oxide (0.21 g, 3.7 mmol) was added via syringe. The polymerization was kept at 0 °C during the course of the reaction. After 60 min an aliquot was taken for NMR analysis, 1 mL of methanol containing a trace amount of HCl was added to the mixture to quench the catalyst, and volatiles were removed under vacuum. The remaining polymer solution was transferred to a pre-weighed round bottom flask and dried overnight under vacuum. Conversion was determined by ^{1}H NMR of the aliquot taken and determined to be over 99%. An INOVA 500 Varian spectrometer was used to obtain the ^{13}C NMR spectrum (taken over 2 h, with more than 2000 scans), as well as a ^{1}H NMR spectrum of the dried polymer. Polymer tacticity (Figure S 12) [*mm*] = 0.97. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.52 (2H, m), 3.39 (1H, m), 1.11 (3H, m). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 75.70, 73.61, 17.64. M_n = 107,000 g/mol, M_w/M_n = 1.8.

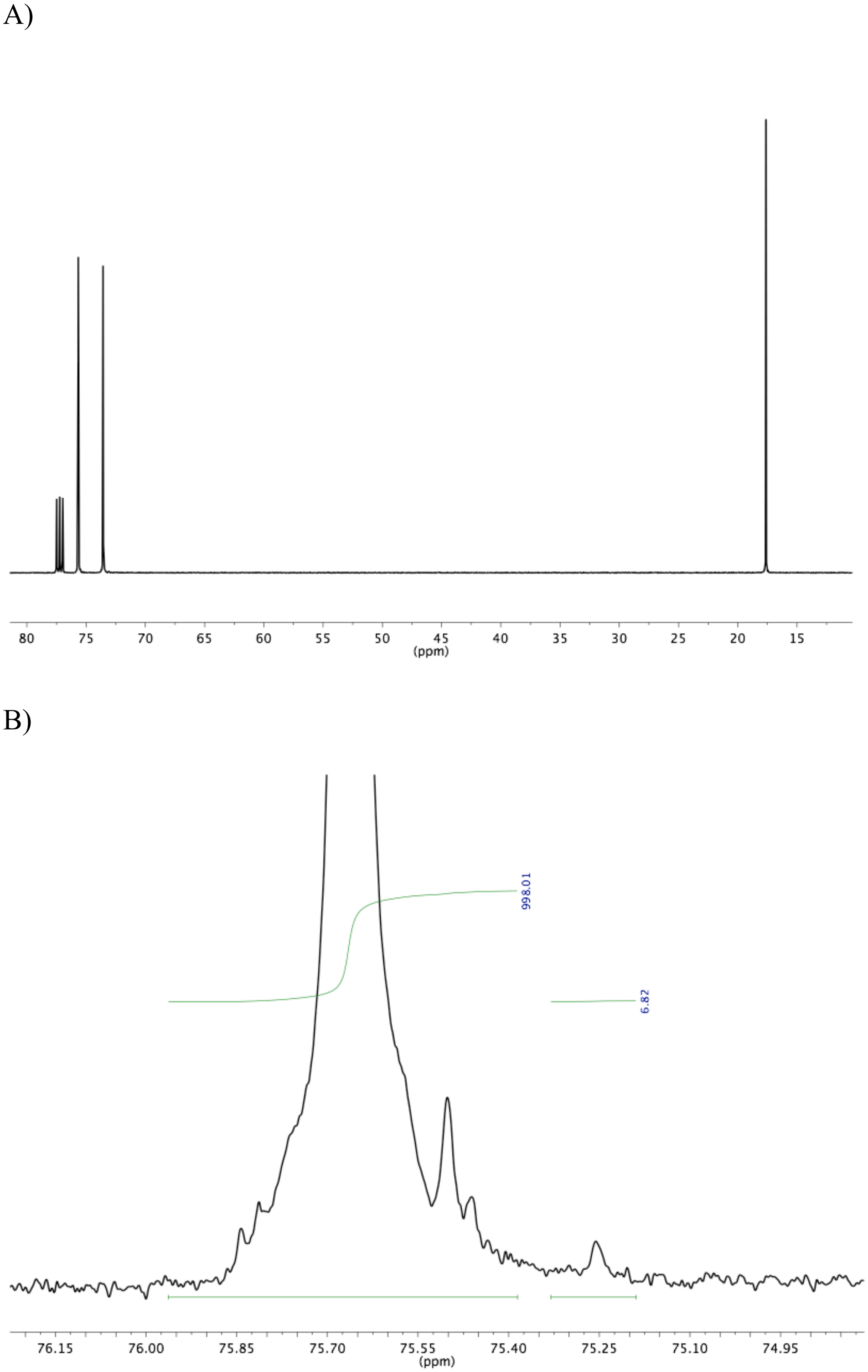

Figure S 12. ^{13}C NMR spectra of poly(propylene oxide). A) Full spectrum. b) Methine carbon.

VIII. Crystal Data and Refinement for **3**.

Table 1. Crystal data and structure refinement for **3**.

Identification code	pw2	
Empirical formula	$C_{86}H_{92}Cl_2Co_2N_{10}O_4$	
Formula weight	1518.46	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	Cc	
Unit cell dimensions	a = 23.7527(10) Å	a= 90°
	b = 37.5983(15) Å	b= 95.983(2)°
	c = 11.4249(4) Å	g = 90°
Volume	10147.6(7) Å^3	
Z	4	
Density (calculated)	0.994 Mg/m^3	
Absorption coefficient	0.424 mm^{-1}	
F(000)	3192	
Crystal size	0.50 x 0.30 x 0.15 mm^3	
Theta range for data collection	1.02 to 24.11°	
Index ranges	-27<=h<=27, -31<=k<=43, -13<=l<=13	
Reflections collected	31936	
Independent reflections	15586 [R(int) = 0.0368]	
Completeness to theta = 24.11°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9392 and 0.8161	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15586 / 41 / 937	
Goodness-of-fit on F^2	1.008	
Final R indices [I>2sigma(I)]	R1 = 0.0602, wR2 = 0.1522	
R indices (all data)	R1 = 0.0781, wR2 = 0.1625	
Absolute structure parameter	0.026(14)	
Largest diff. peak and hole	0.435 and -0.294 e·Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Co(1)	9539(1)	7104(1)	6205(1)	49(1)
Co(2)	8116(1)	8429(1)	8634(1)	46(1)
O(1)	8956(1)	6833(1)	6731(2)	48(1)
O(2)	9037(1)	7499(1)	6141(2)	47(1)
O(3)	8297(1)	8150(1)	7345(2)	44(1)
O(4)	8800(1)	8668(1)	8488(2)	43(1)
N(1)	10038(2)	6720(1)	6158(3)	57(1)
N(2)	10158(2)	7374(1)	5785(3)	52(1)
N(3)	7444(1)	8182(1)	8834(3)	50(1)
N(4)	7920(2)	8714(1)	9899(3)	53(1)
N(5)	9245(2)	6992(1)	4568(3)	50(1)
N(6)	9793(1)	7207(1)	7855(3)	53(1)
N(7)	7708(1)	8767(1)	7524(3)	47(1)
N(8)	8539(2)	8098(1)	9732(3)	54(1)
C(1)	8920(2)	6481(1)	6753(3)	53(1)
C(2)	8415(2)	6329(1)	7135(3)	50(1)
C(3)	8371(2)	5955(1)	7082(4)	72(1)
C(4)	8778(3)	5732(1)	6677(5)	81(2)
C(5)	9254(2)	5881(1)	6366(4)	76(1)
C(6)	9358(2)	6257(1)	6419(4)	61(1)
C(7)	9879(2)	6379(1)	6169(4)	61(1)
C(8)	10606(2)	6802(1)	5877(5)	82(2)
C(9)	10693(2)	7196(1)	6067(4)	63(1)
C(10)	10130(2)	7674(1)	5353(3)	57(1)
C(11)	9629(2)	7893(1)	5102(3)	55(1)
C(12)	9667(2)	8207(1)	4505(4)	61(1)
C(13)	9207(2)	8421(1)	4166(4)	65(1)
C(14)	9239(3)	8741(1)	3532(4)	70(1)
C(15)	8775(3)	8933(1)	3206(4)	81(2)
C(16)	8260(3)	8834(1)	3463(4)	76(2)
C(17)	8193(2)	8527(1)	4102(4)	65(1)
C(18)	8678(2)	8312(1)	4498(3)	55(1)
C(19)	8628(2)	7992(1)	5175(3)	47(1)
C(20)	9093(2)	7783(1)	5480(3)	45(1)
C(21)	8070(2)	7891(1)	5497(3)	48(1)
C(22)	7658(2)	7715(1)	4716(3)	52(1)
C(23)	7769(2)	7645(1)	3497(3)	59(1)
C(24)	7367(2)	7481(1)	2758(4)	74(1)
C(25)	6868(2)	7372(1)	3062(5)	83(2)
C(26)	6732(2)	7441(1)	4250(4)	71(1)
C(27)	7126(2)	7611(1)	5035(4)	57(1)
C(28)	6995(2)	7703(1)	6169(3)	55(1)
C(29)	7372(2)	7888(1)	6934(3)	47(1)
C(30)	7187(2)	7966(1)	8062(3)	56(1)
C(31)	7241(2)	8235(1)	10002(4)	67(1)
C(32)	7412(2)	8601(2)	10415(5)	90(2)
C(33)	8171(2)	9008(1)	10209(3)	50(1)

C(34)	8671(2)	9137(1)	9814(3)	38(1)
C(35)	8885(2)	9461(1)	10337(3)	46(1)
C(36)	9368(2)	9605(1)	10057(3)	51(1)
C(37)	9682(2)	9418(1)	9312(3)	46(1)
C(38)	9506(2)	9104(1)	8777(3)	44(1)
C(39)	8978(2)	8955(1)	9011(3)	43(1)
C(40)	7920(2)	7985(1)	6665(3)	45(1)
C(41)	8625(2)	5329(1)	6606(4)	117(2)
C(42)	8054(3)	5292(2)	5763(7)	172(4)
C(43)	8483(3)	5195(2)	7756(5)	135(3)
C(44)	9045(3)	5118(2)	5977(6)	138(3)
C(45)	7990(2)	6556(1)	7645(4)	59(1)
C(46)	8265(2)	6756(1)	8749(4)	77(2)
C(47)	7727(2)	6834(1)	6748(5)	85(2)
C(48)	7494(2)	6338(1)	8040(5)	78(2)
C(49)	9626(2)	9956(1)	10608(4)	64(1)
C(50)	10181(2)	9877(1)	11356(4)	79(2)
C(51)	9746(3)	10221(1)	9686(4)	85(2)
C(52)	9198(2)	10108(1)	11427(4)	77(2)
C(53)	9877(2)	8886(1)	7976(3)	53(1)
C(54)	10439(2)	9084(1)	7867(4)	64(1)
C(55)	9582(2)	8835(1)	6757(3)	55(1)
C(56)	10040(2)	8530(1)	8583(4)	68(1)
C(57)	8703(2)	6970(1)	4338(4)	57(1)
C(58)	8442(2)	6856(1)	3227(4)	56(1)
C(59)	8785(3)	6755(1)	2394(4)	77(2)
C(60)	9345(3)	6799(1)	2616(4)	74(2)
C(61)	9566(2)	6914(1)	3737(4)	63(1)
C(62)	9847(2)	7542(1)	8245(3)	61(1)
C(63)	10057(3)	7626(1)	9368(4)	81(2)
C(64)	10212(2)	7348(1)	10173(4)	79(2)
C(65)	10125(2)	7005(1)	9769(4)	73(1)
C(66)	9919(2)	6941(1)	8625(3)	55(1)
C(67)	7984(2)	8916(1)	6688(3)	52(1)
C(68)	7766(2)	9175(1)	5981(4)	59(1)
C(69)	7245(3)	9292(2)	6045(5)	90(2)
C(70)	6915(2)	9132(1)	6897(5)	76(2)
C(71)	7194(2)	8869(1)	7599(4)	62(1)
C(72)	8467(2)	7740(1)	9664(4)	66(1)
C(73)	8729(2)	7522(1)	10459(4)	75(2)
C(74)	9079(2)	7652(1)	11383(4)	70(1)
C(75)	9169(2)	8009(1)	11463(4)	65(1)
C(76)	8889(2)	8219(1)	10646(3)	57(1)
Cl(2)	5818(1)	7589(1)	8133(1)	90(1)
Cl(1)	5999(1)	8938(1)	9255(2)	132(1)
N(1P)	7769(2)	9698(2)	2253(5)	106(2)
C(1P)	7236(3)	9681(2)	1963(6)	113(2)
C(2P)	6853(4)	9831(2)	2659(7)	136(3)
C(3P)	7062(3)	10058(2)	3568(6)	112(2)
C(4P)	7629(3)	10065(2)	3841(7)	126(3)
C(5P)	7940(3)	9885(2)	3134(6)	117(2)
N(2P)	6373(3)	8881(2)	2629(5)	108(2)
C(6P)	6027(4)	9004(2)	3458(7)	124(3)
C(7P)	5988(4)	8819(2)	4476(7)	130(3)

C(8P)	6344(3)	8524(2)	4594(6)	122(3)
C(9P)	6682(3)	8460(2)	3748(8)	139(3)
C(10P)	6659(3)	8638(2)	2790(7)	110(2)

Table 3. Bond lengths [Å] and angles [°] for **3**.

Co(1)-O(1)	1.867(3)	C(17)-C(18)	1.443(6)
Co(1)-N(1)	1.872(3)	C(18)-C(19)	1.439(5)
Co(1)-N(2)	1.891(4)	C(19)-C(20)	1.371(6)
Co(1)-O(2)	1.902(3)	C(19)-C(21)	1.462(6)
Co(1)-N(6)	1.958(3)	C(21)-C(22)	1.417(6)
Co(1)-N(5)	1.972(3)	C(21)-C(40)	1.460(5)
Co(2)-N(3)	1.880(3)	C(22)-C(27)	1.409(6)
Co(2)-O(4)	1.879(3)	C(22)-C(23)	1.468(6)
Co(2)-O(3)	1.894(2)	C(23)-C(24)	1.355(6)
Co(2)-N(4)	1.897(3)	C(24)-C(25)	1.335(8)
Co(2)-N(8)	1.966(3)	C(25)-C(26)	1.452(7)
Co(2)-N(7)	1.978(3)	C(26)-C(27)	1.381(6)
O(1)-C(1)	1.329(5)	C(27)-C(28)	1.406(6)
O(2)-C(20)	1.322(4)	C(28)-C(29)	1.373(6)
O(3)-C(40)	1.282(5)	C(29)-C(40)	1.415(6)
O(4)-C(39)	1.284(4)	C(29)-C(30)	1.435(6)
N(1)-C(7)	1.336(6)	C(31)-C(32)	1.494(7)
N(1)-C(8)	1.453(6)	C(33)-C(34)	1.401(5)
N(2)-C(10)	1.230(5)	C(34)-C(39)	1.407(5)
N(2)-C(9)	1.442(6)	C(34)-C(35)	1.426(5)
N(3)-C(30)	1.304(5)	C(35)-C(36)	1.339(6)
N(3)-C(31)	1.479(5)	C(36)-C(37)	1.382(6)
N(4)-C(33)	1.287(5)	C(36)-C(49)	1.558(6)
N(4)-C(32)	1.461(6)	C(37)-C(38)	1.375(5)
N(5)-C(57)	1.291(6)	C(38)-C(39)	1.422(6)
N(5)-C(61)	1.311(5)	C(38)-C(53)	1.567(5)
N(6)-C(62)	1.337(6)	C(41)-C(43)	1.479(6)
N(6)-C(66)	1.346(5)	C(41)-C(44)	1.514(6)
N(7)-C(71)	1.292(6)	C(41)-C(42)	1.585(6)
N(7)-C(67)	1.336(5)	C(45)-C(47)	1.547(6)
N(8)-C(76)	1.345(5)	C(45)-C(48)	1.540(6)
N(8)-C(72)	1.356(6)	C(45)-C(46)	1.554(6)
C(1)-C(6)	1.422(6)	C(49)-C(51)	1.500(6)
C(1)-C(2)	1.435(6)	C(49)-C(50)	1.524(7)
C(2)-C(3)	1.410(6)	C(49)-C(52)	1.562(6)
C(2)-C(45)	1.487(6)	C(53)-C(55)	1.504(5)
C(3)-C(4)	1.396(7)	C(53)-C(56)	1.536(5)
C(4)-C(5)	1.344(8)	C(53)-C(54)	1.547(5)
C(4)-C(41)	1.557(7)	C(57)-C(58)	1.419(6)
C(5)-C(6)	1.432(7)	C(58)-C(59)	1.370(7)
C(6)-C(7)	1.378(6)	C(59)-C(60)	1.338(8)
C(8)-C(9)	1.511(7)	C(60)-C(61)	1.402(7)
C(10)-C(11)	1.453(6)	C(62)-C(63)	1.363(6)
C(11)-C(12)	1.369(6)	C(63)-C(64)	1.415(7)
C(11)-C(20)	1.446(6)	C(64)-C(65)	1.379(7)
C(12)-C(13)	1.381(7)	C(65)-C(66)	1.368(6)
C(13)-C(14)	1.409(6)	C(67)-C(68)	1.334(6)
C(13)-C(18)	1.410(7)	C(68)-C(69)	1.323(7)
C(14)-C(15)	1.339(8)	C(69)-C(70)	1.444(8)
C(15)-C(16)	1.339(8)	C(70)-C(71)	1.396(7)
C(16)-C(17)	1.383(7)	C(72)-C(73)	1.330(7)

C(73)-C(74)	1.363(7)
C(74)-C(75)	1.362(6)
C(75)-C(76)	1.344(6)
N(1P)-C(5P)	1.261(8)
N(1P)-C(1P)	1.276(8)
C(1P)-C(2P)	1.388(9)
C(2P)-C(3P)	1.396(9)
C(3P)-C(4P)	1.350(9)
C(4P)-C(5P)	1.332(9)
N(2P)-C(10P)	1.139(8)
N(2P)-C(6P)	1.397(9)
C(6P)-C(7P)	1.368(10)
C(7P)-C(8P)	1.391(10)
C(8P)-C(9P)	1.341(10)
C(9P)-C(10P)	1.280(10)

O(1)-Co(1)-N(1)	94.64(14)
O(1)-Co(1)-N(2)	175.70(13)
N(1)-Co(1)-N(2)	84.05(16)
O(1)-Co(1)-O(2)	87.48(11)
N(1)-Co(1)-O(2)	176.08(13)
N(2)-Co(1)-O(2)	94.07(13)
O(1)-Co(1)-N(6)	87.81(13)
N(1)-Co(1)-N(6)	92.77(14)
N(2)-Co(1)-N(6)	88.16(14)
O(2)-Co(1)-N(6)	90.61(12)
O(1)-Co(1)-N(5)	89.37(13)
N(1)-Co(1)-N(5)	88.36(14)
N(2)-Co(1)-N(5)	94.68(14)
O(2)-Co(1)-N(5)	88.36(12)
N(6)-Co(1)-N(5)	177.04(15)
N(3)-Co(2)-O(4)	177.87(13)
N(3)-Co(2)-O(3)	94.91(12)
O(4)-Co(2)-O(3)	85.88(10)
N(3)-Co(2)-N(4)	84.67(14)
O(4)-Co(2)-N(4)	94.60(13)
O(3)-Co(2)-N(4)	178.48(14)
N(3)-Co(2)-N(8)	89.70(14)
O(4)-Co(2)-N(8)	88.31(13)
O(3)-Co(2)-N(8)	90.20(12)
N(4)-Co(2)-N(8)	91.26(14)
N(3)-Co(2)-N(7)	91.69(14)
O(4)-Co(2)-N(7)	90.29(12)
O(3)-Co(2)-N(7)	89.61(12)
N(4)-Co(2)-N(7)	88.94(14)
N(8)-Co(2)-N(7)	178.61(15)
C(1)-O(1)-Co(1)	127.0(2)
C(20)-O(2)-Co(1)	123.6(2)
C(40)-O(3)-Co(2)	122.6(2)
C(39)-O(4)-Co(2)	127.4(2)
C(7)-N(1)-C(8)	118.3(4)
C(7)-N(1)-Co(1)	124.0(3)
C(8)-N(1)-Co(1)	116.6(3)
C(10)-N(2)-C(9)	121.6(4)
C(10)-N(2)-Co(1)	125.7(3)
C(9)-N(2)-Co(1)	112.6(3)
C(30)-N(3)-C(31)	121.4(4)
C(30)-N(3)-Co(2)	124.7(3)
C(31)-N(3)-Co(2)	113.8(3)
C(33)-N(4)-C(32)	121.3(4)
C(33)-N(4)-Co(2)	123.4(3)
C(32)-N(4)-Co(2)	114.9(3)
C(57)-N(5)-C(61)	118.8(4)
C(57)-N(5)-Co(1)	117.0(3)
C(61)-N(5)-Co(1)	124.0(3)
C(62)-N(6)-C(66)	118.4(3)
C(62)-N(6)-Co(1)	121.1(3)
C(66)-N(6)-Co(1)	120.5(3)
C(71)-N(7)-C(67)	117.5(4)
C(71)-N(7)-Co(2)	123.5(3)
C(67)-N(7)-Co(2)	118.9(3)
C(76)-N(8)-C(72)	116.3(4)
C(76)-N(8)-Co(2)	121.0(3)
C(72)-N(8)-Co(2)	122.5(3)
O(1)-C(1)-C(6)	122.3(4)
O(1)-C(1)-C(2)	117.4(4)
C(6)-C(1)-C(2)	120.3(4)
C(3)-C(2)-C(1)	116.3(4)
C(3)-C(2)-C(45)	122.5(4)
C(1)-C(2)-C(45)	121.0(4)
C(4)-C(3)-C(2)	124.3(5)
C(5)-C(4)-C(3)	117.8(5)
C(5)-C(4)-C(41)	126.3(5)
C(3)-C(4)-C(41)	115.9(5)
C(4)-C(5)-C(6)	123.2(5)
C(7)-C(6)-C(1)	123.8(4)
C(7)-C(6)-C(5)	118.3(4)
C(1)-C(6)-C(5)	117.8(4)
N(1)-C(7)-C(6)	125.6(4)
N(1)-C(8)-C(9)	107.1(4)
N(2)-C(9)-C(8)	108.6(4)
N(2)-C(10)-C(11)	127.5(4)
C(12)-C(11)-C(20)	120.1(4)
C(12)-C(11)-C(10)	119.4(4)
C(20)-C(11)-C(10)	120.6(4)
C(11)-C(12)-C(13)	123.4(5)
C(12)-C(13)-C(14)	123.9(5)
C(12)-C(13)-C(18)	117.0(4)
C(14)-C(13)-C(18)	119.0(5)
C(15)-C(14)-C(13)	121.1(5)
C(16)-C(15)-C(14)	122.1(5)
C(15)-C(16)-C(17)	120.5(5)
C(16)-C(17)-C(18)	120.0(5)
C(13)-C(18)-C(19)	121.0(4)
C(13)-C(18)-C(17)	117.1(4)
C(19)-C(18)-C(17)	121.9(4)
C(20)-C(19)-C(18)	120.3(4)
C(20)-C(19)-C(21)	120.9(3)

C(18)-C(19)-C(21)	118.8(4)
O(2)-C(20)-C(19)	118.9(4)
O(2)-C(20)-C(11)	123.0(3)
C(19)-C(20)-C(11)	118.1(3)
C(22)-C(21)-C(19)	123.2(3)
C(22)-C(21)-C(40)	118.0(4)
C(19)-C(21)-C(40)	118.8(3)
C(27)-C(22)-C(21)	123.2(4)
C(27)-C(22)-C(23)	116.7(4)
C(21)-C(22)-C(23)	120.0(4)
C(24)-C(23)-C(22)	119.3(5)
C(25)-C(24)-C(23)	124.4(5)
C(24)-C(25)-C(26)	118.6(5)
C(27)-C(26)-C(25)	119.3(5)
C(26)-C(27)-C(28)	120.8(5)
C(26)-C(27)-C(22)	121.7(4)
C(28)-C(27)-C(22)	117.3(4)
C(29)-C(28)-C(27)	121.3(4)
C(28)-C(29)-C(40)	123.0(4)
C(28)-C(29)-C(30)	115.8(4)
C(40)-C(29)-C(30)	121.1(3)
N(3)-C(30)-C(29)	124.8(4)
N(3)-C(31)-C(32)	107.8(4)
N(4)-C(32)-C(31)	110.5(4)
N(4)-C(33)-C(34)	126.5(4)
C(33)-C(34)-C(39)	123.7(3)
C(33)-C(34)-C(35)	116.0(3)
C(39)-C(34)-C(35)	120.2(3)
C(36)-C(35)-C(34)	121.4(4)
C(35)-C(36)-C(37)	118.2(4)
C(35)-C(36)-C(49)	123.8(4)
C(37)-C(36)-C(49)	117.7(4)
C(36)-C(37)-C(38)	123.5(4)
C(37)-C(38)-C(39)	119.2(3)
C(37)-C(38)-C(53)	123.0(4)
C(39)-C(38)-C(53)	117.6(3)
O(4)-C(39)-C(34)	122.9(4)
O(4)-C(39)-C(38)	119.8(3)
C(34)-C(39)-C(38)	117.2(3)
O(3)-C(40)-C(29)	126.4(3)
O(3)-C(40)-C(21)	116.6(4)
C(29)-C(40)-C(21)	117.0(3)
C(43)-C(41)-C(44)	117.8(5)
C(43)-C(41)-C(4)	111.0(5)
C(44)-C(41)-C(4)	111.8(5)
C(43)-C(41)-C(42)	104.5(5)
C(44)-C(41)-C(42)	103.3(5)
C(4)-C(41)-C(42)	107.4(5)
C(2)-C(45)-C(47)	111.8(4)
C(2)-C(45)-C(48)	112.4(4)
C(47)-C(45)-C(48)	106.6(4)
C(2)-C(45)-C(46)	110.5(4)
C(47)-C(45)-C(46)	108.4(4)
C(48)-C(45)-C(46)	106.8(4)
C(51)-C(49)-C(50)	107.9(4)
C(51)-C(49)-C(52)	111.1(4)
C(50)-C(49)-C(52)	108.3(4)
C(51)-C(49)-C(36)	112.0(3)
C(50)-C(49)-C(36)	110.1(4)
C(52)-C(49)-C(36)	107.4(4)
C(55)-C(53)-C(56)	112.3(3)
C(55)-C(53)-C(54)	108.0(3)
C(56)-C(53)-C(54)	106.0(3)
C(55)-C(53)-C(38)	111.7(3)
C(56)-C(53)-C(38)	108.8(3)
C(54)-C(53)-C(38)	109.7(3)
N(5)-C(57)-C(58)	122.3(4)
C(59)-C(58)-C(57)	118.0(5)
C(60)-C(59)-C(58)	119.1(5)
C(59)-C(60)-C(61)	118.8(5)
N(5)-C(61)-C(60)	122.7(5)
N(6)-C(62)-C(63)	122.9(4)
C(62)-C(63)-C(64)	119.1(5)
C(65)-C(64)-C(63)	117.0(5)
C(66)-C(65)-C(64)	120.6(4)
N(6)-C(66)-C(65)	121.9(4)
C(68)-C(67)-N(7)	123.3(4)
C(69)-C(68)-C(67)	121.2(5)
C(68)-C(69)-C(70)	118.3(5)
C(71)-C(70)-C(69)	115.1(5)
N(7)-C(71)-C(70)	124.6(4)
C(73)-C(72)-N(8)	121.7(4)
C(72)-C(73)-C(74)	120.8(4)
C(73)-C(74)-C(75)	118.9(4)
C(76)-C(75)-C(74)	118.0(4)
C(75)-C(76)-N(8)	124.1(4)
C(5P)-N(1P)-C(1P)	117.6(6)
N(1P)-C(1P)-C(2P)	121.5(7)
C(1P)-C(2P)-C(3P)	118.1(7)
C(4P)-C(3P)-C(2P)	116.9(7)
C(5P)-C(4P)-C(3P)	116.9(7)
N(1P)-C(5P)-C(4P)	127.9(7)
C(10P)-N(2P)-C(6P)	122.6(6)
C(7P)-C(6P)-N(2P)	120.3(6)
C(6P)-C(7P)-C(8P)	113.2(7)
C(9P)-C(8P)-C(7P)	118.5(7)
C(10P)-C(9P)-C(8P)	123.1(7)
N(2P)-C(10P)-C(9P)	122.0(8)

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2p^{2}[h^{2} a^{*2} U^{11} + ... + 2 h k a^{*} b^{*} U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Co(1)	66(1)	45(1)	36(1)	-1(1)	11(1)	11(1)
Co(2)	68(1)	40(1)	29(1)	-4(1)	7(1)	-2(1)
O(1)	67(2)	35(1)	45(1)	0(1)	12(1)	14(1)
O(2)	70(2)	43(1)	30(1)	2(1)	16(1)	7(1)
O(3)	66(2)	37(1)	30(1)	-9(1)	8(1)	-2(1)
O(4)	66(2)	36(1)	28(1)	-9(1)	6(1)	2(1)
N(1)	71(2)	54(2)	47(2)	-1(2)	9(2)	20(2)
N(2)	71(2)	57(2)	31(2)	-1(2)	10(2)	3(2)
N(3)	70(2)	51(2)	31(2)	-1(1)	14(2)	-3(2)
N(4)	70(2)	59(2)	31(2)	-7(2)	11(2)	-7(2)
N(5)	67(2)	48(2)	37(2)	2(1)	12(2)	12(2)
N(6)	69(2)	62(2)	31(2)	6(2)	13(2)	19(2)
N(7)	63(2)	41(2)	38(2)	-6(1)	6(2)	-3(2)
N(8)	80(2)	50(2)	33(2)	0(1)	10(2)	-3(2)
C(1)	75(3)	53(2)	33(2)	2(2)	7(2)	15(2)
C(2)	66(3)	45(2)	38(2)	1(2)	3(2)	6(2)
C(3)	98(3)	63(3)	56(3)	-2(2)	16(3)	-3(3)
C(4)	117(4)	56(3)	71(3)	-11(2)	14(3)	8(3)
C(5)	95(3)	69(3)	66(3)	0(2)	15(3)	23(3)
C(6)	83(3)	44(2)	56(3)	2(2)	10(2)	23(2)
C(7)	74(3)	56(3)	55(3)	-6(2)	18(2)	13(2)
C(8)	80(3)	81(3)	88(4)	1(3)	21(3)	13(3)
C(9)	62(3)	76(3)	49(2)	0(2)	4(2)	-2(2)
C(10)	81(3)	54(2)	38(2)	-5(2)	13(2)	3(2)
C(11)	86(3)	48(2)	33(2)	-4(2)	12(2)	0(2)
C(12)	85(3)	59(3)	39(2)	-4(2)	14(2)	-1(2)
C(13)	99(4)	61(3)	35(2)	-10(2)	4(2)	1(3)
C(14)	124(4)	52(3)	35(2)	1(2)	10(2)	-9(3)
C(15)	132(5)	58(3)	52(3)	6(2)	8(3)	-1(3)
C(16)	120(4)	59(3)	46(3)	6(2)	-10(3)	13(3)
C(17)	100(3)	55(3)	38(2)	-1(2)	2(2)	5(2)
C(18)	90(3)	42(2)	32(2)	-3(2)	3(2)	13(2)
C(19)	73(3)	46(2)	23(2)	-4(2)	6(2)	-1(2)
C(20)	70(3)	40(2)	27(2)	-2(2)	8(2)	9(2)
C(21)	72(3)	41(2)	29(2)	1(2)	-6(2)	14(2)
C(22)	78(3)	36(2)	40(2)	-2(2)	-7(2)	10(2)
C(23)	87(3)	52(2)	35(2)	0(2)	-3(2)	18(2)
C(24)	99(4)	65(3)	52(3)	-18(2)	-13(3)	18(3)
C(25)	89(4)	80(3)	75(3)	-22(3)	-21(3)	8(3)
C(26)	92(3)	65(3)	51(3)	-9(2)	-12(2)	10(3)
C(27)	80(3)	40(2)	46(2)	-5(2)	-11(2)	11(2)
C(28)	72(3)	52(2)	40(2)	-6(2)	-2(2)	12(2)
C(29)	75(3)	41(2)	26(2)	-7(2)	2(2)	-4(2)
C(30)	87(3)	44(2)	36(2)	2(2)	3(2)	-8(2)
C(31)	90(3)	80(3)	34(2)	-3(2)	19(2)	-16(3)
C(32)	95(4)	100(4)	78(3)	-38(3)	27(3)	-33(3)
C(33)	68(3)	52(2)	29(2)	-11(2)	1(2)	1(2)

C(34)	54(2)	34(2)	27(2)	3(1)	10(2)	4(2)
C(35)	68(3)	36(2)	33(2)	-2(2)	6(2)	7(2)
C(36)	73(3)	42(2)	37(2)	0(2)	7(2)	1(2)
C(37)	57(2)	42(2)	38(2)	-1(2)	-2(2)	-1(2)
C(38)	51(2)	47(2)	32(2)	-2(2)	1(2)	7(2)
C(39)	60(2)	45(2)	23(2)	-1(2)	1(2)	5(2)
C(40)	76(3)	37(2)	20(2)	-1(2)	2(2)	7(2)
C(41)	181(6)	59(3)	121(5)	8(3)	62(5)	15(4)
C(42)	186(9)	130(7)	189(9)	-1(7)	-32(7)	-20(6)
C(43)	170(7)	89(5)	149(7)	-6(5)	32(6)	-4(5)
C(44)	194(8)	81(4)	143(6)	-9(4)	36(6)	-10(5)
C(45)	69(3)	54(2)	54(2)	6(2)	6(2)	4(2)
C(46)	100(4)	67(3)	65(3)	-13(3)	16(3)	15(3)
C(47)	90(4)	71(3)	97(4)	9(3)	23(3)	12(3)
C(48)	92(4)	58(3)	86(4)	7(3)	15(3)	5(3)
C(49)	105(4)	42(2)	45(2)	-7(2)	5(2)	-8(2)
C(50)	96(4)	77(3)	63(3)	-8(3)	1(3)	-9(3)
C(51)	139(5)	53(3)	65(3)	-1(2)	17(3)	-16(3)
C(52)	116(4)	61(3)	55(3)	-14(2)	14(3)	-8(3)
C(53)	63(3)	51(2)	44(2)	-3(2)	12(2)	5(2)
C(54)	69(3)	65(3)	57(3)	-3(2)	6(2)	2(2)
C(55)	77(3)	47(2)	42(2)	-13(2)	11(2)	8(2)
C(56)	80(3)	56(3)	68(3)	-5(2)	11(2)	19(2)
C(57)	73(3)	54(2)	47(2)	3(2)	17(2)	18(2)
C(58)	78(3)	51(2)	39(2)	-2(2)	4(2)	8(2)
C(59)	130(4)	53(3)	49(3)	-1(2)	7(3)	-10(3)
C(60)	110(4)	64(3)	50(3)	-12(2)	17(3)	2(3)
C(61)	78(3)	59(3)	54(3)	-15(2)	18(2)	7(2)
C(62)	93(3)	58(3)	31(2)	1(2)	-1(2)	22(2)
C(63)	125(4)	68(3)	51(3)	-2(2)	7(3)	23(3)
C(64)	113(4)	79(3)	46(3)	3(2)	11(3)	27(3)
C(65)	104(4)	73(3)	45(2)	17(2)	21(2)	28(3)
C(66)	83(3)	44(2)	39(2)	6(2)	9(2)	16(2)
C(67)	69(3)	52(2)	39(2)	4(2)	22(2)	1(2)
C(68)	74(3)	63(3)	41(2)	2(2)	9(2)	3(2)
C(69)	114(4)	76(4)	81(4)	6(3)	13(3)	12(3)
C(70)	80(3)	69(3)	79(3)	11(3)	14(3)	12(3)
C(71)	71(3)	58(3)	58(3)	5(2)	10(2)	0(2)
C(72)	93(3)	48(2)	56(3)	-9(2)	4(2)	6(2)
C(73)	112(4)	52(3)	58(3)	-9(2)	2(3)	-2(3)
C(74)	112(4)	49(2)	45(3)	-1(2)	-9(3)	16(3)
C(75)	104(3)	60(3)	31(2)	-1(2)	8(2)	15(3)
C(76)	89(3)	50(2)	30(2)	-10(2)	5(2)	-1(2)
Cl(2)	115(1)	95(1)	61(1)	-2(1)	15(1)	-26(1)
Cl(1)	140(1)	161(2)	101(1)	-9(1)	35(1)	-8(1)
N(1P)	129(4)	111(4)	85(3)	-3(3)	39(3)	6(3)
C(1P)	166(7)	83(4)	92(4)	-6(3)	25(5)	-14(5)
C(2P)	148(6)	125(6)	142(7)	-5(5)	42(5)	-7(5)
C(3P)	127(5)	97(4)	116(5)	-19(4)	36(4)	2(4)
C(4P)	115(5)	136(6)	134(6)	-15(5)	41(5)	-15(5)
C(5P)	101(5)	157(7)	96(5)	-11(5)	22(4)	24(5)
N(2P)	137(4)	102(4)	86(3)	3(3)	18(3)	-1(3)
C(6P)	165(6)	73(4)	135(6)	-18(4)	28(5)	22(4)
C(7P)	159(7)	116(5)	121(6)	-23(5)	40(5)	-23(5)

C(8P)	161(7)	111(5)	91(5)	14(4)	-1(5)	-35(5)
C(9P)	115(6)	100(5)	197(9)	49(6)	-10(6)	13(4)
C(10P)	116(5)	98(5)	121(6)	10(4)	39(4)	23(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **3**.

	x	y	z	U(eq)
H(3A)	8043	5849	7339	86
H(5A)	9536	5731	6099	91
H(7A)	10149	6206	5989	73
H(8A)	10647	6739	5049	99
H(8B)	10889	6666	6395	99
H(9A)	10838	7243	6897	75
H(9B)	10974	7286	5557	75
H(10A)	10477	7774	5160	68
H(12A)	10029	8280	4314	73
H(14A)	9596	8821	3334	84
H(15A)	8811	9147	2779	97
H(16A)	7940	8975	3204	92
H(17A)	7826	8458	4279	78
H(23A)	8119	7713	3230	70
H(24A)	7446	7441	1971	88
H(25A)	6607	7252	2512	100
H(26A)	6377	7371	4486	85
H(28A)	6640	7636	6410	66
H(30A)	6854	7851	8261	67
H(31A)	7411	8055	10565	81
H(31B)	6824	8211	9944	81
H(32A)	7100	8769	10188	108
H(32B)	7486	8602	11284	108
H(33A)	8001	9151	10760	60
H(35A)	8679	9577	10897	55
H(37A)	10039	9511	9161	56
H(42A)	7938	5041	5724	258
H(42B)	8115	5375	4973	258
H(42C)	7758	5435	6070	258
H(43A)	8823	5199	8322	203
H(43B)	8341	4951	7666	203
H(43C)	8191	5347	8043	203
H(44A)	9410	5110	6465	207
H(44B)	9095	5232	5223	207
H(44C)	8904	4876	5837	207
H(46A)	8578	6904	8530	115
H(46B)	8410	6583	9348	115
H(46C)	7981	6908	9065	115
H(47A)	8028	6982	6482	128
H(47B)	7461	6984	7124	128
H(47C)	7527	6711	6072	128
H(48A)	7305	6209	7364	118
H(48B)	7223	6499	8358	118
H(48C)	7638	6168	8649	118
H(50A)	10340	10099	11700	119
H(50B)	10450	9770	10862	119

H(50C)	10111	9711	11987	119
H(51A)	9913	10436	10067	128
H(51B)	9392	10284	9211	128
H(51C)	10011	10118	9178	128
H(52A)	9352	10327	11800	115
H(52B)	9136	9933	12036	115
H(52C)	8838	10160	10960	115
H(54A)	10360	9314	7482	96
H(54B)	10678	8941	7397	96
H(54C)	10637	9122	8653	96
H(55A)	9487	9068	6404	82
H(55B)	9234	8698	6800	82
H(55C)	9832	8707	6273	82
H(56A)	10275	8393	8092	102
H(56B)	9696	8395	8693	102
H(56C)	10252	8576	9350	102
H(57A)	8470	7032	4933	69
H(58A)	8042	6850	3066	67
H(59A)	8628	6654	1670	93
H(60A)	9588	6753	2023	89
H(61A)	9965	6937	3902	76
H(62A)	9734	7730	7716	74
H(63A)	10098	7867	9606	98
H(64A)	10370	7396	10956	95
H(65A)	10209	6810	10290	88
H(66A)	9863	6702	8367	67
H(67A)	8355	8834	6593	63
H(68A)	7988	9276	5422	71
H(69A)	7092	9477	5542	108
H(70)	6535	9201	6974	91
H(71A)	6991	8758	8173	75
H(72A)	8223	7643	9033	79
H(73A)	8672	7273	10381	90
H(74A)	9257	7495	11960	84
H(75A)	9421	8107	12079	78
H(76A)	8942	8469	10719	68
H(1PA)	7098	9563	1254	136
H(2PA)	6460	9780	2520	163
H(3PA)	6817	10201	3977	134
H(4PA)	7799	10191	4506	152
H(5PA)	8338	9901	3316	141
H(6PA)	5819	9218	3314	148
H(7PA)	5743	8885	5046	156
H(8PA)	6347	8372	5258	146
H(9PA)	6951	8273	3865	167
H(10B)	6887	8567	2196	132

IX. References

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