Supporting Information

Copolymerization of CO_2 and *meso* Epoxides Using Enantioselective β–Diiminate Catalysts: A Route to Highly Isotactic Polycarbonates

W. Chadwick Ellis, Yukyung Jung, Michael Mulzer, Rocco Di Girolamo, Emil B. Lobkovsky, and Geoffrey W. Coates*

Department of Chemistry and Chemical Biology, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301

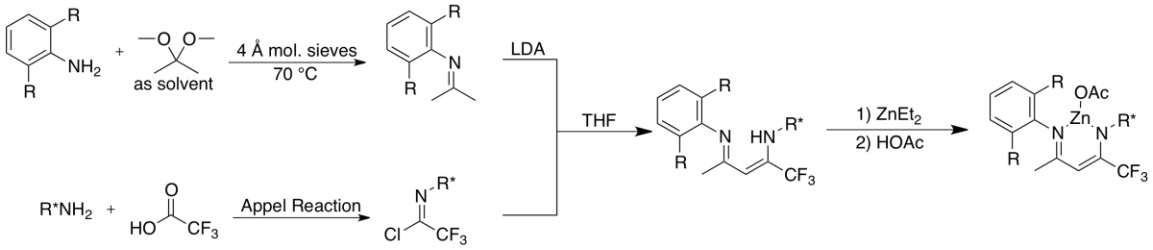
General considerations

Unless stated otherwise all synthetic manipulations were carried out using standard Schlenk techniques under a nitrogen atmosphere or in an MBraun Unilab glovebox under an atmosphere of purified nitrogen. Reactions were carried out in oven-dried glassware cooled under vacuum. Anhydrous toluene, hexanes and tetrahydrofuran were purchased from Fisher Scientific and sparged vigorously with nitrogen for 40 minutes prior to first use. The solvents were further purified by passing them under nitrogen pressure through two packed columns of neutral alumina (tetrahydrofuran was also passed through a third column packed with activated 4Å molecular sieves) or through neutral alumina and copper(II) oxide (for toluene and hexanes). All solvents used for recrystallization were purified to ensure that they were air and water free.[1] All non-dried solvents used were reagent grade or better and used as received.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian 400, 500 or 600 MHz instrument with shifts reported relative to the residual solvent peak. ^{19}F NMR spectra were recorded on a Varian 400 or 500 MHz instrument with shifts referenced to an external standard of neat $CFCl_3$ (0 ppm). NMR solvents were purchased from Cambridge Isotope Laboratories and used as received. Midwest Microlabs performed elemental analysis. High-resolution mass spectrometry (HRMS) analyses were performed by the Mass Spectrometry Lab at the University of Illinois at Urbana-Champaign. Analysis by gel permeation chromatography (GPC) was carried out using an Agilent PL-GPC 50 integrated system, (2 x PLgel Mini-MIX C columns, 5 micron, 4.6 mmID) equipped with UV and refractive index detectors. The GPC columns were eluted with tetrahydrofuran at 30 °C at 0.3 mL/min and were calibrated with monodisperse polystyrene standards. Gas-Liquid chromatography (GLC) analyses were performed on a Hewlett Packard 6890 gas chromatograph equipped with a Supelco β-Dex225 column and a flame ionization detector. Helium (Airgas, UHP grade) was used as carrier gas. Differential scanning calorimetry (DSC) of polymer samples was performed on a Mettler-Toledo Polymer DSC instrument equipped with a Julabo FT 100 chiller and autosampler. Typical DSC samples were prepared in aluminum pans and the experiments were performed under nitrogen with a heating rate of 10 °C/min from 25 °C to 260 °C. Data was processed using StarE software.

Carbon dioxide (Airgas, 99.999% purity) was dried over 3 Å molecular sieves overnight before use. Diethyl zinc (Aldrich) was stored in a glove box and used as received. Epoxides were dried under N_2 over freshly pulverized CaH_2 for several days, and then distilled and purified by 3 cycles of freeze-pump-thaw. Chiral primary amines were purchased from either Sigma-Aldrich or Alfa-Aesar and were ≥98% ee. If discolored, they were distilled prior to use. All other chemicals were purchased from Sigma-Aldrich, Acros, or Alfa-Aesar and used as received. Flash column chromatography was performed with silica gel (particle size 40-64 μm, 230-400 mesh) using mixtures of ethyl acetate and hexanes as eluent unless stated otherwise.

Synthetic procedures



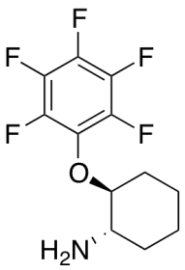
Scheme S1. Generalized synthetic steps to obtain BDI-Zn catalysts.

Preparation of amines

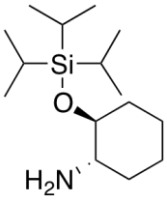
General procedure A: Synthesis of (1*S*,2*S*)-cyclohexanaminoethers.

(1*S*,2*S*)-Cyclohexanamino-2-ethers were synthesized from the corresponding (1*S*,2*S*)-2-cyclohexanolamine (*SS*-CHA) (>99% ee), which were prepared using the method of Jacobsen.[2] In a glove box, a Schlenk flask was charged with *SS*-CHA (8.68 mmol, 1.00 g) and sodium hexamethyldisilazide (8.68 mmol, 1.59 g). Under inert conditions on the bench, approximately 15 mL of THF was added to the Schlenk flask with stirring. After 1 h, the flask was cooled to 0 °C, and the neat electrophile (8.68 mmol) was added dropwise. The resulting mixture was stirred at 70 °C overnight. A precipitate formed. The resulting mixture was cooled to room temperature and extracted with 3 x 30 mL diethyl ether and washed with 50% saturated NaCl. The organic layers were combined, dried over $MgSO_4$, and filtered. The solvent was removed to yield crude product.

(1*S*,2*S*)-2-(Pentafluorophenoxy)cyclohexanamine. General Procedure A was performed at the 43.4 mmol (5.00 g *SS*-CHA) scale using hexafluorobenzene (8.07 g) as the electrophile. It yielded a cream solid which was recrystallized from 50 mL hexanes at −25 °C and filtered cold. The first crop of 7.38 g was obtained as tiny cream crystals in 60% yield. **^{1}H NMR** ($CDCl_3$): δ 3.84-3.86 (m, 1H), 3.02-2.91 (m, 1H), 2.1-2.1 (br s, 2H), 2.07-1.87 (m, 2H), 1.87-1.61 (m, 2H), 1.61-1.07 (m, 4H). **^{19}F NMR** ($CDCl_3$): δ −155.25 (d, J = 20.5 Hz, 2F), −163.08 (t, J = 21.8 Hz, 1F), −163.31-−163.61 (m, 2F).



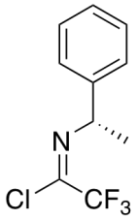
(1*S*,2*S*)-2-((Triisopropylsilyl)oxy)cyclohexanamine. Following general procedure A at the 12.5 mmol scale (1.44 g *SS*-CHA) using triisopropylsilylchloride (2.41 g) as the electrophile, 3.38 g of a crude yellow oil was obtained. This was distilled at < 400 mTorr. A small forerun (45-55 °C) was discarded, and the main fraction was retained as 2.49 g (73% yield) of colorless oil (75-85 °C). **^{1}H NMR** ($CDCl_3$): δ 3.41-3.31 (m, 1H), 2.67-2.46 (m, 1H), 2.0-1.75 (m overlapping br s, 4H), 1.76-1.57 (m, 2H), 1.46-0.82 (m with overlapping resonances, 25H).



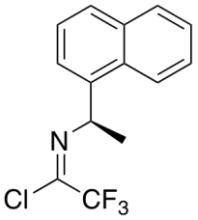
Preparation of imidoyl chlorides

General Procedure B: Imidoyl chlorides were prepared following the established literature procedure.[3] Carbon tetrachloride (approx. 4 mL, 4 mmol), triphenylphosphine (3.26 g, 12.4 mmol), and triethylamine (0.7 mL, 5 mmol) were combined in a round bottom flask of excess capacity. It was cooled to 0 °C under N_2. Trifluoroacetic acid (0.365 mL, 4.76 mmol) was added and stirred for 10 minutes. The amine of choice (4.97 mmol) was then added neat or dissolved in minimal CCl_4 or toluene, and the mixture was brought to room temperature with stirring. A reflux condenser was attached to the reaction vessel, and the mixture was brought to reflux slowly, using 10 °C increments. It was refluxed for 6h with a drying tube affixed to the top of the condenser. It was brought to room temperature after 6h, and the mixture was filtered through Celite and the pad was rinsed with copious hexanes. The liquor was combined and evaporated to leave the crude

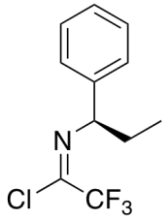
product. The crude product was purified by distillation, and the final product was stored in a desiccator. The authors noticed that an EXOTHERM occurs in this reaction near 70 °C on warming to reflux. Slow heating of the reaction mixture in glassware of excess capacity mitigated problems or runaway reactions. Take adequate precautions.



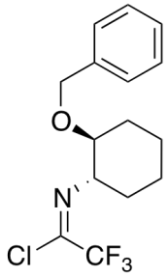
(*S*)-2,2,2-Trifluoro-N-(1-phenylethyl)acetimidoyl chloride. Following general procedure B using 5.00 g (41.3 mmol) (*S*)-1-phenylethanamine, the title compound was afforded as a tan oil with some residual solids. Filtering the crude oil through a plug of cotton and distilling the resulting oil (~200 mTorr, 30-40 °C) yields 5.26 g of a colorless oil in 54% yield, which was stored in a desiccator. **^{1}H NMR** ($CDCl_3$): δ 7.28-7.24 (m, 2H), 7.22-7.08 (m, 3H), 4.79 (q, J = 6.6 Hz, 1H), 1.25 (d, J = 6.6 Hz, 3H). **^{19}F NMR** ($CDCl_3$): δ −71.42 (s, 3F).

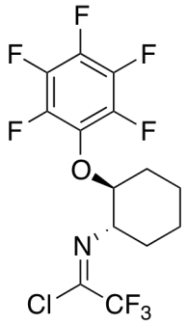


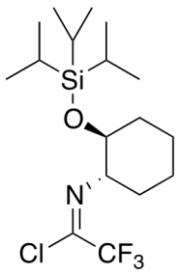
(*R*)-2,2,2-Trifluoro-N-(1-(naphthalen-1-yl)ethyl)acetimidoyl chloride. Following general procedure B using 2.49 g (14.5 mmol) (*R*)-1-(naphthalen-1-yl)ethanamine, the title compound was afforded as a light brown oil with some residual solids. Filtering the crude oil through a plug of cotton and distilling the resulting oil (~200 mTorr, 68-78 °C) yields 2.74 g of a colorless oil in 66% yield, which was stored in a desiccator. **^{1}H NMR** ($CDCl_3$): δ 8.16 (d, J = 8.3 Hz, 1H), 7.96-7.90 (m, 1H), 7.83 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 7.1 Hz, 1H), 7.65-7.45 (m, 3H), 1.72 (d, J = 6.7 Hz, 3H). **^{19}F NMR** ($CDCl_3$): δ −71.392 (s, 3F).



(*R*)-2,2,2-Trifluoro-N-(1-phenylpropyl)acetimidoyl chloride. Following general procedure B using 5.03 g (37.2 mmol) (*R*)-1-phenylpropan-1-amine, the title compound was afforded as a tan oil with some residual solids. Filtering the crude oil through a plug of cotton and distilling the resulting oil (20 Torr, 56-62 °C) yields 5.92 g of a colorless oil in 64% yield, which was stored in a desiccator. **^{1}H NMR** ($CDCl_3$): δ 7.47-7.27 (m, 5H), 4.77 (t, J = 6.8 Hz, 1H), 2.00-1.84 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H). **^{19}F NMR** ($CDCl_3$): δ −71.410 (s, 3F).

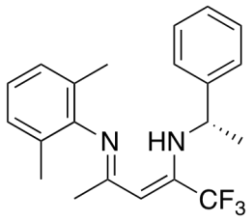
***N*-((1*S*,2*S*)-2-(Benzyloxy)cyclohexyl)-2,2,2-trifluoroacetimidoyl chloride.** 
Following general procedure B using 3.22 g (15.7 mmol) (1*S*,2*S*)-2-(benzyloxy)cyclohexanamine, the title compound was afforded as a tan oil with some residual solids. Filtering the crude oil through a plug of cotton and distilling the resulting oil (~200 mTorr, 85-94 °C) yields 3.46 g of a colorless oil in 69% yield, which was stored in a desiccator. **^{1}H NMR** ($CDCl_3$): δ 7.35-7.22 (m, 5H), 4.53 (dd, J = 42.6, 11.9 Hz, 2H), 3.79 (ddd, J = 11.5, 9.1, 4.2 Hz, 1H), 3.51 (ddd, J = 10.3, 8.9, 4.2 Hz, 1H), 2.21-2.11 (m, 1H), 1.85-1.68 (m, 3H), 1.59-1.43 (m, 1H), 1.43-1.23 (m, 3H). **^{19}F NMR** ($CDCl_3$): δ −71.608 (s, 3F).

2,2,2-Trifluoro-*N*-((1*S*,2*S*)-2-(pentafluorophenoxy)cyclohexyl)acetimidoyl chloride. 
Following general procedure B using 6.00 g (21.3 mmol) (1*S*, 2*S*)-2-(pentafluorophenoxy)cyclohexanamine, the crude title compound was afforded as a tan oil. Distillation of the oil (~200 mTorr, 2 inch Vigreux column, 60-70 °C) yields 4.25 g of a colorless oil in 50% yield, which was stored in a desiccator. **^{1}H NMR** ($CDCl_3$): δ 4.29-4.18 (m, 1H), 4.02-3.89 (m, 1H), 2.34-2.21 (m, 1H), 1.97-1.86 (m, 1H), 1.85-1.74 (m, 2H), 1.71-1.57 (m, 1H), 1.53-1.28 (m, 3H). **^{19}F NMR** ($CDCl_3$): δ −72.103 (s, 3F), −155.53 (d, J = 20.0, 2F), −163.2- −163.46, (m, 1F), −163.59- −163.80 (m, 2F).

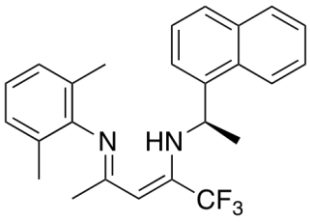
2,2,2-Trifluoro-*N*-((1*S*,2*S*)-2-((triisopropylsilyl)oxy)cyclohexyl)acetimidoyl chloride. 
Following general procedure B using 1.94 g (7.15 mmol) (1*S*,2*S*)-2-((triisopropylsilyl)oxy)cyclohexanamine, the title compound was afforded as a tan oil with some residual solids. Filtering out the solids with a plug of cotton and distilling the resulting oil (~200 mTorr, 78-86 °C) yields 1.31 g of a pale yellow oil in 47% yield, which was stored in a desiccator. **^{1}H NMR** ($CDCl_3$): δ 3.89 (ddd, J = 10.1, 8.2, 4.3 Hz, 1H), 3.70-3.62 (m, 1H), 2.07-1.94 (m, 1H), 1.87-1.63 (m, 3H), 1.51-1.26 (m, 4H), 1.15-0.89 (m, 21H). **^{19}F NMR** ($CDCl_3$): δ −71.737 (s, 3F).

Preparation of β–diiminate (BDI) ligands

General procedure C: Ligands were prepared by adding 2.41 mmol of the appropriate aryl imine (*N*-(2,6-diethyl)phenyl-acetimine or *N*-(2,6-dimethyl)phenyl-acetimine)[4] to a solution of 4.81 mmol lithium diisopropyl amide (LDA) at −78 °C in THF (~ 10 mL). The LDA was prepared *in situ* by combining *n*-butyl lithium (1.6 M in hexanes, 4.8 mmol) with diisopropyl amine (5.54 mmol) at 0 °C and stirring for 20m. The aryl imine solution was allowed to stir for 20m at −78 °C, at which time the corresponding imidoyl chloride (2.19 mmol) was added. This is similar to the literature procedure.[5] The reaction mixture was allowed to warm to room temperature over 30m, and quenched with aq. NH_4Cl. The mixture was extracted using diethyl ether. Organics were combined, dried, and the solvent removed to leave a crude oil. The crude ligand was purified by flash chromatography on silica gel.



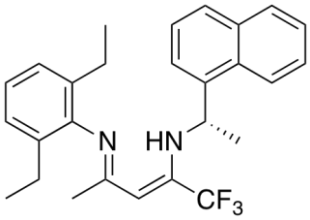
Ligand 1: 2,6-dimethyl-*N*-(5,5,5-trifluoro-4-(((*S*)-1-phenylethyl) amino) pent-3-en-2-ylidene)aniline. The crude product, a brown oil, was obtained using general procedure C. Imidoyl chloride was used at the 4.6 mmol scale, and all other reagents were scaled proportionately. The crude product was purified by flash chromatography on silica using 4:6 $CHCl_3$/hexanes. The title compound was obtained as a yellow oil in 58% yield (0.92 g). R_f = 0.83. **^{1}H NMR** ($CDCl_3$): δ 10.90 (d, J = 9.4 Hz, 1H), 7.34-7.13 (m, 5H), 7.05 (d, J = 7.5 Hz, 2H), 6.92 (t, J = 7.4 Hz, 1H), 5.31 (s, 1H), 4.86-4.68 (m, 1H), 2.06 (s, 3H), 2.01 (s, 3H), 1.72 (s, 3H), 1.48 (d, J = 6.7 Hz, 3H). **^{19}F NMR** ($CDCl_3$): δ −65.085 (s, 3F). **^{13}C NMR** ($CDCl_3$): δ 166.85, 148.21, 145.01, 142.19 (q, J = 30.6 Hz), 128.46, 127.91, 127.85, 127.45, 127.17, 126.90, 125.49, 123.04, 120.92 (q, J = 277.3 Hz), 93.89 (q, J = 6.0 Hz), 54.10, 25.28, 21.72, 18.34, 18.19. **HRMS** (ESI) *m/z* calculated for $C_{21}H_{24}F_3N_2^+$ ($M + H^+$) 361.1887, found 361.1897.



Ligand 2: 2,6-dimethyl-*N*-(5,5,5-trifluoro-4-(((*R*)-1-(naphthalen-1-yl)ethyl)amino)pent-3-en-2-ylidene)aniline. The crude product, a brown oil, was obtained using general procedure C. Imidoyl chloride was used at the 3.5 mmol scale,

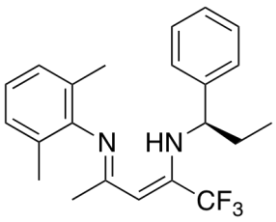
and all other reagents were scaled proportionately. The crude product was purified by flash chromatography on silica using 7.5% diethyl ether/pentane. The title compound was obtained as a yellow wax in 89% yield (1.28 g). R_f = 0.69. **^{1}H NMR** ($CDCl_3$): δ 11.11 (d, J = 9.2 Hz, 1H), 8.03 (d, J = 8.3 Hz, 1H), 7.86 (d, J = 7.4 Hz, 1H), 7.73 (d, J = 8.1 Hz, 1H), 7.56-7.44 (m, 3H), 7.39 (t, J = 7.6 Hz, 1H), 7.09 (d, J = 7.4 Hz, 2H), 6.95 (t, J = 7.5 Hz, 1H), 5.65-5.54 (m, 1H), 5.39 (s, 1H), 2.127 (s, 3H), 2.119 (s, 3H), 1.78 (s, 3H), 1.59 (d, J = 6.7 Hz, 3H). **^{19}F NMR** ($CDCl_3$): δ −65.482 (s, 3F). **^{13}C NMR** ($CDCl_3$): δ 167.26, 148.39, 142.24 (q, J = 29.9 Hz), 141.44, 133.96, 129.99, 129.08, 128.08, 128.03, 127.62, 127.55, 127.08, 126.27, 125.62, 125.59, 123.21, 122.69, 122.17, 120.98 (q, J = 277.4 Hz), 94.73 (q, J = 6.1 Hz), 50.76 (q, J = 2.1 Hz), 25.20, 21.95, 18.53, 18.40. **HRMS** (ESI) *m/z* calculated for $C_{25}H_{26}F_3N_2^+$ ($M + H^+$) 411.2043, found 411.2046.

Ligand 3: 2,6-diethyl-*N*-(5,5,5-trifluoro-4-(((*S*)-1-(naphthalen-1-yl)ethyl)amino)pent-3-en-2-ylidene)aniline.



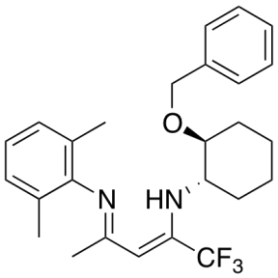
The crude product, a red/brown oil, was obtained using general procedure C. Imidoyl chloride was used at the 2.8 mmol scale, and all other reagents were scaled proportionately. The crude product was purified by flash chromatography on silica using 2:8 dichloromethane/hexanes. The title compound was obtained as a yellow oil in 36% yield (0.45 g). R_f = 0.62. **^{1}H NMR** ($CDCl_3$): δ 11.16 (d, J = 8.3 Hz, 1H), 8.03 (d, J = 7.9 Hz, 1H), 7.91-7.82 (m, 1H), 7.72 (d, J = 8.1 Hz, 1H), 7.56-7.44 (m, 3H), 7.43-7.35 (m, 1H), 7.12 (d, J = 8.2 Hz, 2H), 7.08-7.01 (m, 1H), 5.68-5.53 (m, 1H), 5.38 (s, 1H), 2.61-2.32 (m, 4H), 1.78 (s, 3H), 1.59 (d, J = 6.6 Hz, 3H), 1.18 (q, J = 7.6 Hz, 6H). **^{19}F NMR** ($CDCl_3$): δ −65.368 (s, 3F).

Ligand 4: 2,6-dimethyl-*N*-(5,5,5-trifluoro-4-(((*R*)-1-phenyl propyl)amino)pent-3-en-2-ylidene)aniline. The crude product, a gold oil, was obtained using general procedure C. Imidoyl chloride was used at the 4.3 mmol scale, and all other reagents were scaled proportionately. The crude product was purified by flash chromatography on silica using 1:19 ethyl acetate/hexanes. The title compound was obtained as a yellow oil in 80% yield (1.3 g). R_f = 0.65. **^{1}H NMR** ($CDCl_3$): δ 11.10 (d, J

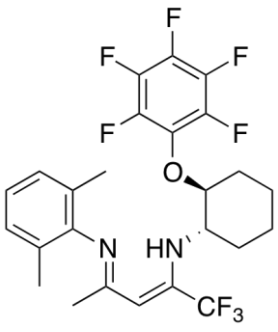


= 9.3 Hz, 1H), 7.38-7.22 (m, 5H), 7.16-7.10 (m, 2H), 7.03-6.96 (m, 1H), 5.38 (s, 1H), 4.66 (dd, *J* = 14.8, 8.2 Hz, 1H), 2.14 (d, *J* = 3.5 Hz, 6H), 1.92-1.70 (m, 5H), 0.98 (t, *J* = 7.4 Hz, 3H). **^{19}F NMR** ($CDCl_3$): δ −64.847 (s, 3F). **^{13}C NMR** ($CDCl_3$): δ 167.13, 148.35, 145.05, 142.96 (q, *J* = 29.9 Hz), 128.45, 128.03, 127.97, 127.62, 127.26, 126.96, 126.06, 123.15, 120.96 (q, *J* = 277.4 Hz), 93.60 (q, *J* = 6.0 Hz), 60.36 (q, *J* = 1.9 Hz), 32.49, 21.79, 18.41, 10.81. **HRMS** (ESI) *m/z* calculated for $C_{22}H_{26}F_3N_2^+$ ($M + H^+$) 375.2043, found 375.2045.

Ligand 5: *N*-(4-(((1*S*,2*S*)-2-(benzyloxy)cyclohexyl)amino)-5,5,5-trifluoropent-3-en-2-ylidene)-2,6-dimethylaniline. The crude product, a yellow oil, was obtained using general procedure C. Imidoyl chloride was used at the 4.5 mmol scale, and all other reagents were scaled proportionately. The crude product was purified by flash chromatography on silica using 3:20 diethyl ether/pentanes. The title compound was obtained as a yellow oil in 90% yield (1.8 g). R_f = 0.46 in 4% diethyl ether/pentane. **^{1}H NMR** ($CDCl_3$): δ 10.77 (d, *J* = 9.6 Hz, 1H), 7.34-7.20 (m, 5H), 7.10-7.01 (m, 2H), 6.92 (t, *J* = 7.5 Hz, 1H), 5.30 (s, 1H), 4.58 (dd, *J* = 11.7, 14.1 Hz, 2H), 3.62-3.51 (m, 1H), 3.27-3.18 (m, 1H), 2.08-1.99 (m, 4H), 1.99-1.91 (m, 4H), 1.74-1.63 (m, 4H), 1.63-1.55 (m, 1H), 1.49-1.14 (m, 4H). **^{19}F NMR** ($CDCl_3$): δ −64.761 (s, 3F). **^{13}C NMR** ($CDCl_3$): δ 166.90, 148.39, 143.24 (q, *J* = 29.7 Hz), 139.14, 128.33, 127.96, 127.91, 127.55, 127.41, 127.38, 123.03, 121.00 (q, *J* = 277.6 Hz), 92.71 (q, *J* = 6.0 Hz), 81.04, 71.95, 57.43, 32.78, 30.07, 23.62, 23.19, 21.75, 18.44, 18.29. **HRMS** (ESI) *m/z* calculated for $C_{26}H_{32}F_3N_2O^+$ ($M + H^+$) 445.2462, found 445.2460.



Ligand 6: 2,6-dimethyl-*N*-(5,5,5-trifluoro-4-(((1*S*,2*S*)-2-(pentafluorophenoxy)cyclohexyl)amino)pent-3-en-2-ylidene)aniline. The crude product, a red oil, was obtained using general procedure C. Imidoyl chloride was used at the 3.3 mmol scale, and all other reagents were scaled proportionately. The crude product was purified by flash chromatography on silica

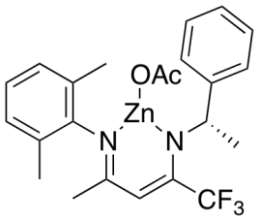


using 1:1 dichloromethane/hexanes. The title compound was obtained as a stiff yellow oil that solidified on standing in 77% yield (1.32 g). R_f = 0.88. **^{1}H NMR** ($CDCl_3$): δ 10.80 (d, J = 7.8 Hz, 1H), 7.05 (d, J = 7.6 Hz, 2H), 6.97-6.89 (m, 1H), 5.30 (s, 1H), 4.04-3.90 (m, 1H), 3.80-3.67 (m, 1H), 2.15-2.05 (m, 1H), 2.05-1.96 (m, 4H), 1.91 (s, 3H), 1.83-1.71 (m, 1H), 1.69 (s, 3H), 1.67-1.56 (m, 2H), 1.44-1.19 (m, 3H). **^{19}F NMR** ($CDCl_3$): δ −64.761 (s, 3F), −154.9- −155.4 (m, 2F), −163.6- −164.1 (m, 3F). **^{13}C NMR** ($CDCl_3$): δ 166.62, 147.63, 143.32 (q, J = 29.4 Hz), 143.15-143.03 (m), 141.28-140.86 (m), 139.25-138.82 (m), 138.64-138.05 (m), 137.38-136.68 (m), 136.68-136.09 (m), 133.37-132.68 (m), 128.03, 127.96, 127.90, 127.68, 123.37, 120.83 (q, J = 278.0 Hz), 93.58 (q, J = 5.8 Hz), 86.23, 57.21, 32.60, 29.92, 23.32, 22.86, 21.67, 18.38, 17.72. **HRMS** (ESI) *m/z* calculated for $C_{25}H_{25}F_8N_2O^+$ ($M + H^+$) 521.1834, found 521.1848.

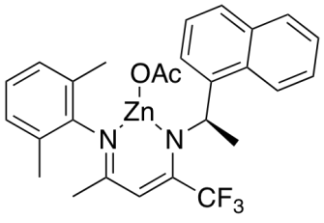
Ligand 7: 2,6-dimethyl-*N*-(5,5,5-trifluoro-4-(((1*S*,2*S*)-2-((triisopropylsilyl)oxy)cyclohexyl)amino)pent-3-en-2-ylidene)aniline. The crude product, a yellow oil, was obtained using general procedure C. Imidoyl chloride was used at the 3.1 mmol scale, and all other reagents were scaled proportionately. The crude product was purified by flash chromatography on silica using 1:1 dichloromethane/hexanes. The title compound was obtained as a stiff yellow oil that solidified on standing in 89% yield (1.43 g). R_f = 0.9. **^{1}H NMR** ($CDCl_3$): δ 10.72 (d, J = 10.5 Hz, 1H), 7.04 (d, J = 7.5 Hz, 2H), 6.90 (t, J = 7.5 Hz, 1H), 5.27 (s, 1H), 3.76-3.65 (m, 1H), 3.57-3.46 (m, 1H), 2.07-1.93 (m, 7H), 1.80-1.59 (m, 5H), 1.52-1.40 (m, 2H), 1.40-1.28 (m, 2H), 1.28-1.16 (m, 1H), 1.09-0.92 (m, 21H). **^{19}F NMR** ($CDCl_3$): δ −64.883 (s, 3F). **^{13}C NMR** ($CDCl_3$): δ 166.85, 150.60, 148.44, 143.42 (q, J = 29.8 Hz), 138.01, 127.97, 127.90, 127.59, 127.46, 123.00, 121.78, 121.43, 120.99 (q, J = 277.5 Hz), 92.40 (q, J = 6.0 Hz), 81.66, 72.88, 57.72, 34.92, 33.09, 31.60, 30.36, 23.88, 23.44, 21.74, 18.45, 18.36. **HRMS** (ESI) *m/z* calculated for $C_{28}H_{46}F_3N_2OSi^+$ ($M + H^+$) 511.3327, found 511.3328.

Preparation of complexes 1 - 7

General procedure D: The corresponding starting BDI ligand (2.5 mmol) was placed in an oven dried Schlenk flask under positive nitrogen flow, evacuated 3 times, and taken into the glove box. Dry toluene was added to dissolve the ligand, resulting in a 0.25 M solution. Neat diethyl zinc was added (8.75 mmol, 3.5 eq) with stirring. The flask was sealed and quickly placed on a Schlenk line under positive nitrogen pressure to avoid build-up of ethane gas. The mixture was warmed to 65 °C and stirred overnight, with noticeable evolution of bubbles occurring while warming to 65 °C. Volatiles were then removed from the mixture, leaving a yellow/brown oil or solid. Dry pentane was added to the mixture, resulting in a 0.25 M solution. If turbid, the solution was filtered under inert conditions. The solution was cooled to 0 °C, and then 2.38 mmol acetic acid (0.95 eq) was added *via* a 0.25 M stock solution in pentane. The solution was stirred at 0 °C for 10 m. The solution was allowed to come to room temperature and stirred overnight. In most cases, a dense white precipitate formed, which was typically isolated by cannula filtration.



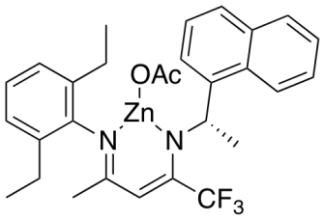
Complex 1: Following general procedure D, scaled to 2.55 mmol BDI ligand, a dense white precipitate formed in 10 minutes at room temperature, although stirring proceeded overnight. 50% of the solvent was removed in *vacuo* and the mixture was cooled to 0 °C. The liquor was cannula filtered, and the resulting solid washed 2 times with 1 mL pentane at 0 °C. The precipitate was recrystallized from approximately 20 mL cyclohexane to yield discrete white needles in 73% yield (0.90 g). **^{1}H NMR** of dimer (C_6D_6): δ 7.04-6.82 (m, 16H), 5.25 (s, 2H), 5.05 (q, J = 6 Hz, 2H), 2.11 (s, 6H), 2.02 (s, 6H), 1.90 (s, 3H), 1.39 (s, 6H), 1.15 (d, J = 6.5 Hz, 6H), 0.65 (s, 3H). **^{19}F NMR** ($CDCl_3$): δ −61.570 (s, 6F). Anal. Calcd for $C_{23}H_{25}F_3N_2O_2Zn$: C, 57.10; H, 5.21; N, 5.79. Found: C, 56.75; H, 5.04; N, 5.73.



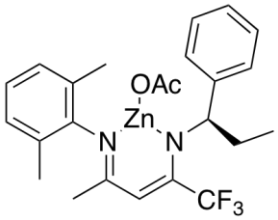
Complex 2: Following general procedure D, scaled to 1.58 mmol BDI ligand, a dense white precipitate formed in 10 minutes at room temperature, although stirring proceeded

overnight. 50% of the solvent was removed *in vacuo* and the mixture was cooled back to 0 °C. The liquor was cannula filtered, and the resulting solid washed with 1 mL hexanes at 0 °C. The precipitate was cannula filtered to isolate a white powder in 69% yield (0.58 g). **^{1}H NMR** of dimer (C_6D_6): 8.14 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 2H), 7.41-7.32 (m, 2H), 7.32-7.21 (m, 4H), 6.91-6.80 (m, 4H), 6.70-6.60 (m, 4H), 5.99-5.83 (m, 2H), 5.32 (s, 2H), 2.10 (s, 6H), 2.03 (s, 3H), 1.91 (s, 6H), 1.31 (m, 12H), 1.13 (s, 3H). **^{19}F NMR** ($CDCl_3$): δ −62.038 (s, 6F). Anal. Calcd for $C_{27}H_{27}F_3N_2O_2Zn$: C, 60.74; H, 5.10; N, 5.25. Found: C, 59.12; H, 5.21; N, 4.82.

Complex 3: Following general procedure D, scaled to 2.40 mmol BDI ligand, a dense white precipitate formed in 10 minutes at room temperature, although stirring proceeded overnight. 50% of the solvent was removed *in vacuo* and the mixture was cooled back to 0 °C. The liquor was cannula filtered leaving white microcrystals, and the resulting solid was recrystallized from approximately 1 mL toluene to yield small blocky crystals in 23% yield (0.31 g). **^{1}H NMR** of dimer (C_6D_6): *δ* 8.08 (d, *J* = 8.9 Hz, 2H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.41-7.28 (m, 4H), 7.28-7.17 (m, 2H), 6.98 (d, *J* = 7.4 Hz, 2H), 6.91-6.74 (m, 4H), 6.67 (d, *J* = 7.3 Hz, 2H), 5.95-5.77 (m, 2H), 5.28 (s, 2H), 2.73-2.55 (m, 2H), 2.54-2.35 (m, 4H), 2.35-2.15 (m, 2H), 1.99 (s, 3H), 1.31 (s, 6H), 1.25-1.08 (m, 15H), 0.91 (t, *J* = 7.6 Hz, 6H). **^{19}F NMR** ($CDCl_3$): *δ* −62.081 (s, 6F). Anal. Calcd for $C_{29}H_{31}F_3N_2O_2Zn$: C, 61.98; H, 5.56; N, 4.99. Found: C, 62.04; H, 5.47; N, 4.94.

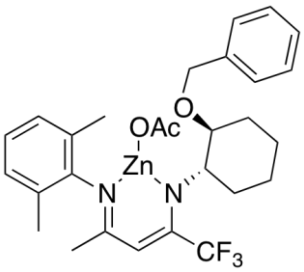


Complex 4: Following general procedure D scaled to 3.05 mmol BDI ligand, a dense white precipitate formed in 10 minutes at room temperature. The liquor was removed by cannula filtration. The resulting solid was dissolved in approximately 6 mL cyclohexane, and the mixture was filtered through Celite. The mixture was concentrated to a volume of about 2.5 mL and allowed to stand at 22 °C overnight. The crystalline product was isolated by cannula filtration in 60% yield (0.91 g). **^{1}H NMR** of mixture of dynamic species at −70 °C, integrated by

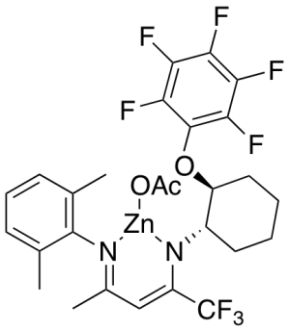


summing all methine proton resonances (near δ 5.25) to 1, (C_7D_8): δ 7.4-6.7 (m, 8H), 5.27-5.12 (m, 1H), 4.86-4.44 (m, 1H), 2.3-0.8 (m, 17H). **^{19}F NMR** (C_7D_8): δ −60.826, −61.129, −61.625, −64.526 (several singlets, 3F). Anal. Calcd for $C_{24}H_{27}F_3N_2O_2Zn$: C, 57.90; H, 5.47; N, 5.63. Found: C, 57.98; H, 5.66; N, 5.54.

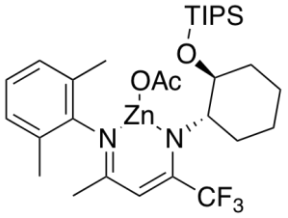
Complex 5: Following general procedure D scaled to 3.85 mmol BDI ligand, a dense white precipitate formed while stirring at room temperature overnight. The mixture was concentrated by 30%, and the remaining liquor was removed by cannula filtration at 0 °C. The resulting solid was dissolved in approximately 20 mL benzene, reduced in volume to approximately 7 mL, and the mixture was cooled to 22 °C. The crystalline product was isolated by cannula filtration in 48% yield (1.05 g). **^{1}H NMR** of mixture of dynamic species at −70 °C, integrated by summing all methine proton resonances (near δ 5.25) to 1, (C_7D_8): δ 7.35-6.75 (m, 8H), 5.28-5.16 (m, 1H), 4.6-2.9 (br m, 4H), 2.02-0.8 (br m, 20H). **^{19}F NMR** (C_7D_8): δ −72.569, −64.482, −61.397, −60.974 (br) (series of singlets, 3F). Anal. Calcd for $C_{28}H_{33}F_3N_2O_3Zn$: C, 59.21; H, 5.86; N, 4.93. Found: C, 58.90; H, 5.79; N, 4.70.



Complex 6: Following general procedure D scaled to 1.22 mmol BDI ligand, no precipitate formed overnight. The mixture was filtered through Celite and the volatiles removed to leave the product as a yellow crunchy foam in 51% yield (0.40 g). **^{1}H NMR** of mixture of dynamic species at −70 °C, integrated by summing all methine proton resonances (near δ 5.25) to 1, (C_7D_8): δ 7.01-6.54 (m, 3H), 5.53-5.07 (m, 1H), 4.66-3.795 (m, 2H), 2.25-0.25 (m, 20H). **^{19}F NMR** (C_7D_8): δ −60.328, −60.445, −60.785, −63.869 (several singlets, 3F), −155.4- −157.1 (m, 2F), −162.9- −166.3 (m, 3F). Anal. Calcd for $C_{27}H_{26}F_8N_2O_3Zn$: C, 50.37; H, 4.07; N, 4.35. Found: C, 50.53; H, 4.34; N, 4.36.

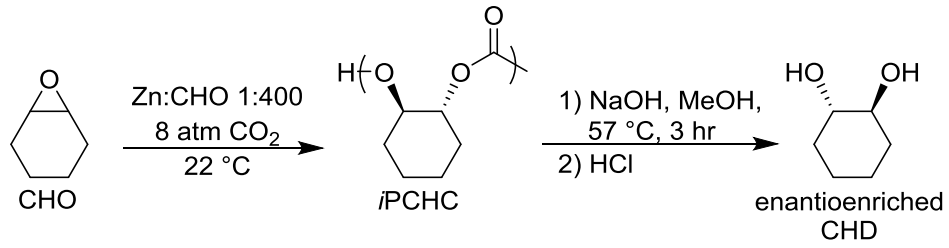


Complex 7: Following general procedure D scaled to 0.58 mmol BDI ligand and using hexanes as the solvent for acetic acid



metathesis, no precipitate formed after stirring for 2 h at 22 °C and at 55 °C for 3 h. The mixture was filtered through Celite and the volatiles removed to leave the product as a tan crunchy foam in 63% yield (0.23 g). **^{1}H NMR** of mixture of dynamic species at −70 °C, integrated relative to the sum of all methine proton resonances (near δ 5.25) to 1, (C_7D_8): δ 6.7-7.05 (m, 3H), 5.41-5.08 (m, 1H), 4.33-3.12 (br m, 2H), 2.6-0.46 (br m, 41H). **^{19}F NMR** (C_7D_8): δ −59.1- −61.02 (br), −63.937, −64.626, −72.879 (several singlets, 3F). Anal. Calcd for $C_{30}H_{47}F_3N_2O_3SiZn$: C, 56.82; H, 7.47; N, 4.42. Found: C, 56.81; H, 7.34; N, 4.39.

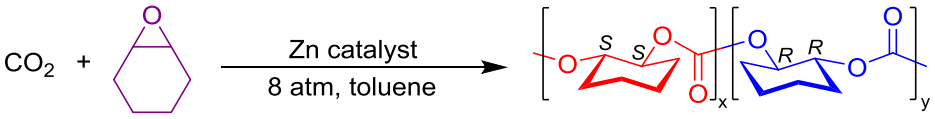
Polymerization, hydrolysis, and determination of catalyst enantioselectivity.



Scheme S2. Polymerization of CHO and CO_2, followed by hydrolysis of polymer to cyclohexane diol (CHD)

Polymerization of CO_2 and cyclohexene oxide. Screening reactions were performed as follows. An oven dried Fisher-Porter bottle was taken into the glove box. It was charged with a stir bar, 1.0 mL toluene, 1.0 mL cyclohexene oxide, and 0.25 mol % catalyst. The vessel was sealed with the reactor head and the apparatus was removed from the box. The vessel was placed in a 22 °C water bath and allowed to equilibrate for 10 minutes. The vessel was then charged to 8 atm CO_2, vented to ~2.4 atm, and recharged to 8 atm. The vessel was left open to 8 atm for 1 minute to allow saturation of the reaction mixture. The CO_2 pressure was then monitored as a gauge of conversion. The reaction was terminated when the mixture became too viscous for stirring, with a viscosity approaching that of honey. The vessel was vented to atmospheric pressure. The reaction mixture was diluted with ~2 mL $CDCl_3$ for a crude NMR, and then precipitated into 150 mL rapidly stirring methanol. The resulting white precipitate was isolated by vacuum filtration, dried on the filter pad for 15 minutes, and then dried *in vacuo* at 50 °C for several hours until the mass was constant.

Table S1. Polymerization conditions and polymer properties for figures 3 and 4.[a]



Entry	Figure	Catalyst	[CHO] (M)	[CHO]/[Zn]	t_{rxn} (h)	T_{rxn} (°C)	M_n[d] (kg/mol)	M_w/M_n[d]	% ee[e]
1	3	**5**	5	400	0.9	22	34	1.2	86
2	3	**6**	5	400	1.5	22	45	1.2	90
3	3	**6**	5	2000	28.0	0	34	1.3	92
4	3, 4a	*ent*-**5**	5	400	1.2	22	44	1.2	83
5[b]	3, 4c	**(EtZnO*i*Pr)$_4$**	3.2[c]	90	16	50	11	1.3	99
6	4b	**7**	9.9	2000	3.7	22	60	1.2	90

[a]Polymers were synthesized by copolymerization of CO_2 and CHO, with exception of entry 5. [b]Synthesized by ring-opening of optically pure cyclic *trans*-cyclohexene carbonate (see below for polymerization procedure). [c]Concentration of optically pure cyclic (*S*,*S*)-1,2-cyclohexene carbonate. [d]Determined by GPC in THF relative to polystyrene standards at 30 °C. [e]Enantiomeric excess of the trifluoroacetate-derivatized diol obtained upon hydrolysis of the polymer.

Polymerization of optically pure *trans*-cyclohexene carbonate. Optically pure cyclic (*S*,*S*)-1,2-cyclohexene carbonate[6] (0.50 g, 3.5 mmol), ethyl zinc isopropoxide (6 mg, 0.04 mmol), and toluene (1 mL) were mixed in a vial with a stirbar in the glovebox. On the bench, the vessel was heated to 50 °C and stirred for 16 h, at which time the reaction had solidified. The mixture was cooled to room temperature and then dissolved in dichloromethane (2 mL). This mixture was added to rapidly stirring methanol (40 mL), and the fine white powder was collected on glass filter paper. The polymer was isolated in 67% yield (0.335 g), and ^{1}H NMR analysis agreed with NMR spectra reported previously.[7,8]

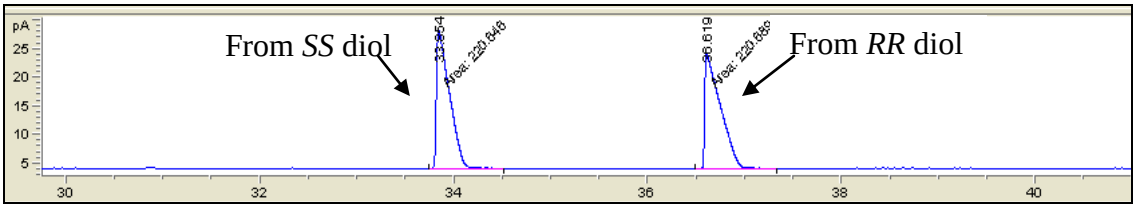
Thermolysis of poly(cyclohexene carbonate) to yield *trans*-cyclohexene carbonate. Isotactic poly(cyclohexene carbonate) (0.92 g) of 85% ee was placed into a 50 mL round bottom flask with a Schlenk side-arm and a stirbar. The vessel was sealed and vacuum was applied, pulling the vapors though a quick-trap cooled with liquid nitrogen. The vessel was heated to 250 °C in a sand bath, and a white crystalline material collected in the quick trap. After all polymer had disappeared, the apparatus was allowed to cool to room temperature, and the material in the quick trap was collected as a white, crystalline

solid (0.73 g, 79%). ^{1}H NMR analysis matched literature.[6] The material was recrystallized 4 times from 15% pentane/hexane to give 0.18 g material of 95% ee. At each recrystallization, approximately 100 mg of material was withdrawn for hydrolysis and analysis, which accounts for most of the loss in yield.

Hydrolysis of poly(cyclohexene carbonate) to yield *trans*-1,2-cyclohexanediol. Polycarbonate (approx. 100 mg polymer, 1 mmol of cyclohexene carbonate repeat units), sodium hydroxide (0.08 g, 2 mmol), and methanol (10 mL) were added to a scintillation vial and capped. The mixture was stirred at 57 °C for 3 h. The mixture was cooled to 22 °C, and then 3.1 mmol HCl was added via a 2.5 M aqueous stock solution with stirring. Volatiles were removed from the resulting mixture to leave a white solid. ^{1}H NMR analysis of the diol matched the literature.[9] If performed on the 10 mmol scale using *i*PCHC (86% ee), this procedure allowed for the isolation and enantioenrichment of the resulting cyclohexane diol. Recrystallization twice from hot acetone yielded cyclohexane diol in 59% yield (relative to the epoxide) and 99% ee.

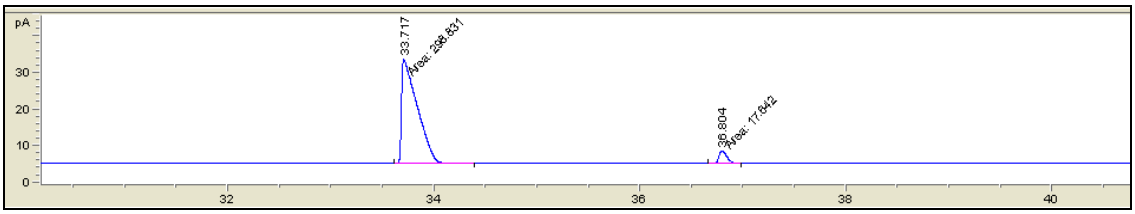
Bis(trifluoroacetyl) derivatization of the *trans*-1,2-diols.[10] Derivatization of the resulting diol could be achieved by modifying the hydrolysis procedure described in the previous paragraph. The white solid was extracted with 10 mL dichloromethane. A 2 mL aliquot of this solution was dried over $MgSO_4$ and placed in a 5 mL vial with a stir bar. 5 drops of pyridine were added with stirring. Then, 5 drops of trifluoroacetic anhydride were added. The mixture was allowed to stir for 3 minutes, and then quenched with 2 mL 2 M HCl. The organic phase was separated and dried through a 1.5" plug of silica gel in a glass Pasteur pipette (diameter ~0.24") to yield the sample for GLC analysis. ^{1}H and ^{19}F NMR analysis of the isolated colorless oil shows that the product is the bis(trifluoroacetyl)ester of the diol, *trans*-1,2-cyclohexadiyl bis(2,2,2-trifluoroacetate). **^{1}H NMR** ($CDCl_3$): δ 5.11-5.01 (m, 2H), 2.29-2.12 (m, 2H), 1.96-1.75 (m, 2H), 1.68-1.51 (m, 2H), 1.51-1.30 (m, 2H). **^{19}F NMR** ($CDCl_3$): δ −75.447 (s, 6F).

GLC of *trans*-1,2-cyclohexadiyl bis(2,2,2-trifluoroacetate). The sample in dichloromethane (~ 1mg/mL) was injected onto a Supelco *β*-Dex225 column and eluted using a temperature profile of: isotherm at 35 °C for 5 min, then 2 °C/min ramp up to 111 °C, then 111 °C isotherm for 1 min. Shown below is the chromatogram for a racemic sample, as well as a sample produced by *ent*-**5** (88.8% ee), and **5** (88.5% ee) at 0 °C (Table 1, Entry 7).



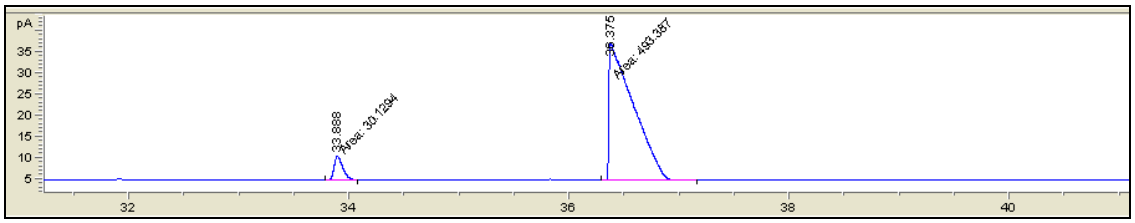
Peak #	Ret. Time [min]	Width [min]	Area [pA*s]	Area %
1	33.854	0.1533	220.6	49.995
2	36.619	0.1840	220.7	50.005

Figure S1. GLC trace of racemic *trans*-1,2-cyclohexadiyl bis(2,2,2-trifluoroacetate).



Peak #	Ret. Time [min]	Width [min]	Area [pA*s]	Area %
1	33.717	0.1758	298.8	94.425
2	36.804	0.0855	17.6	5.575

Figure S2. GLC trace of 1,2-cyclohexadiyl bis(2,2,2-trifluoroacetate) (88.8% ee, primarily derivatized *SS* diol) from hydrolysis of polymer produced by *ent*-**5** at 0 °C.



Peak #	Ret. Time [min]	Width [min]	Area [pA*s]	Area %
1	33.888	0.0908	30.1	5.755
2	36.375	0.2549	493.4	94.245

Figure S3. GLC trace of 1,2-cyclohexadiyl bis(2,2,2-trifluoroacetate) (88.5% ee, primarily derivatized *RR* diol) from hydrolysis of polymer produced by **5** at 0 °C.

Polymer characterization data

^{1}H NMR spectra

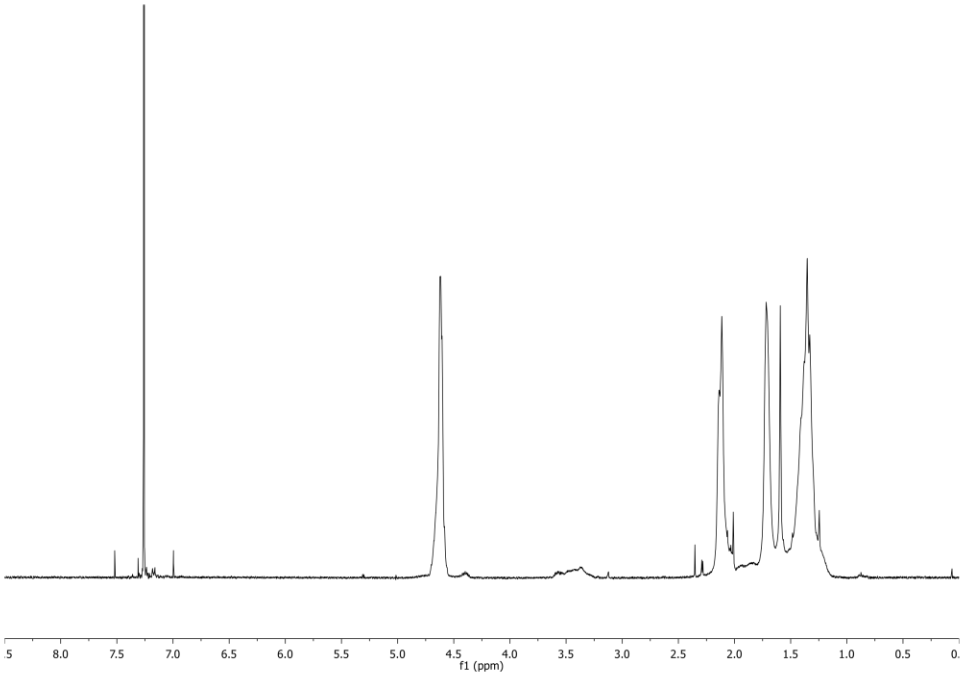


Figure S4. ^{1}H NMR spectrum for polymer reported in Table 1, entry 1.

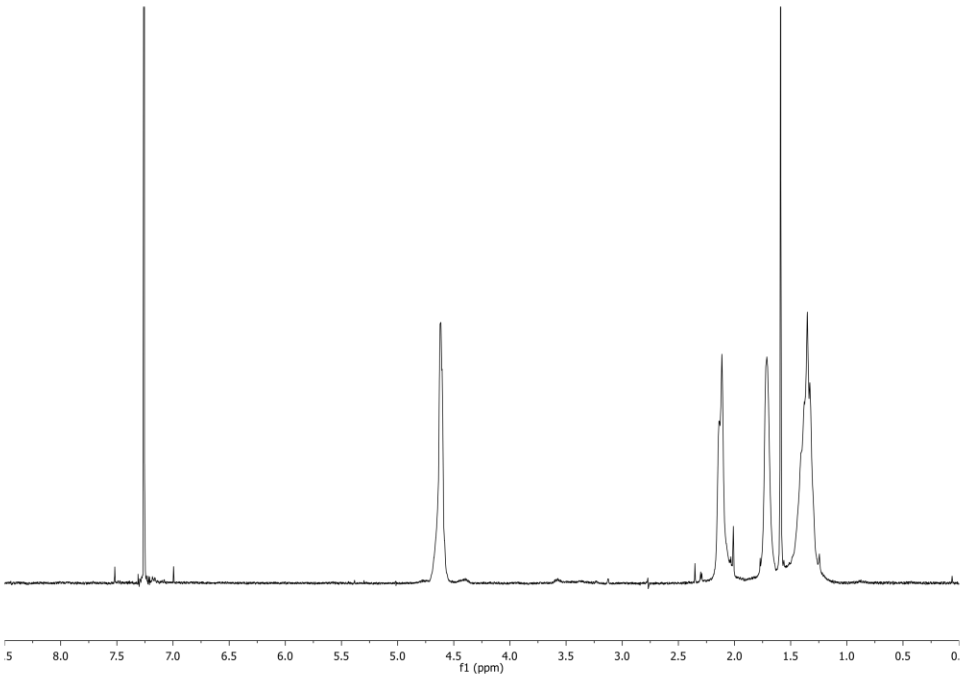


Figure S5. ^{1}H NMR spectrum for polymer reported in Table 1, entry 2.

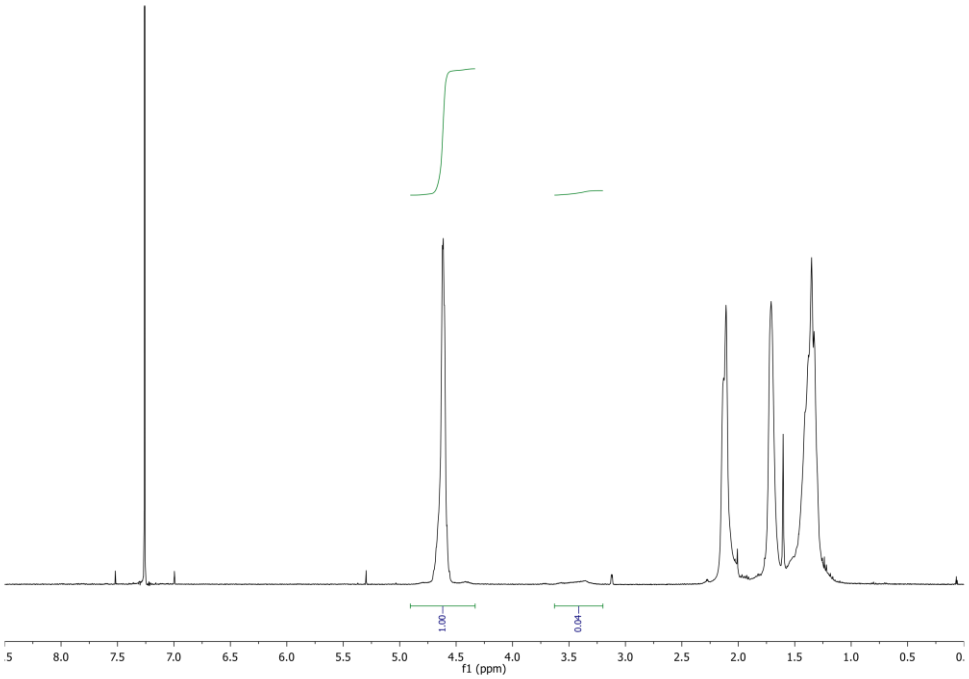


Figure S6. ^{1}H NMR spectrum for polymer reported in Table 1, entry 3.

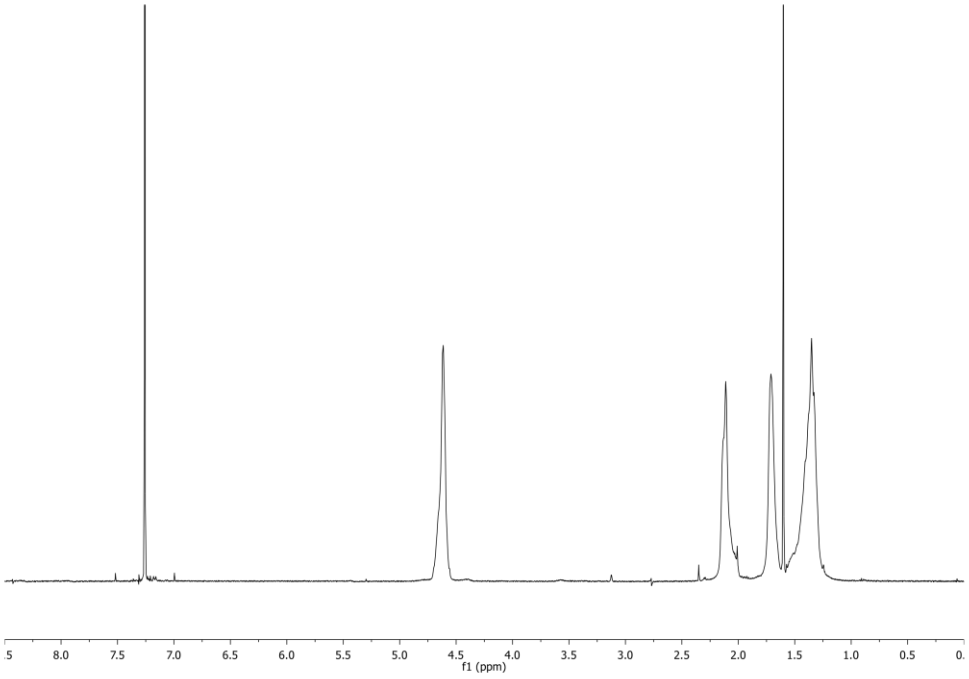


Figure S7. ^{1}H NMR spectrum for polymer reported in Table 1, entry 4.

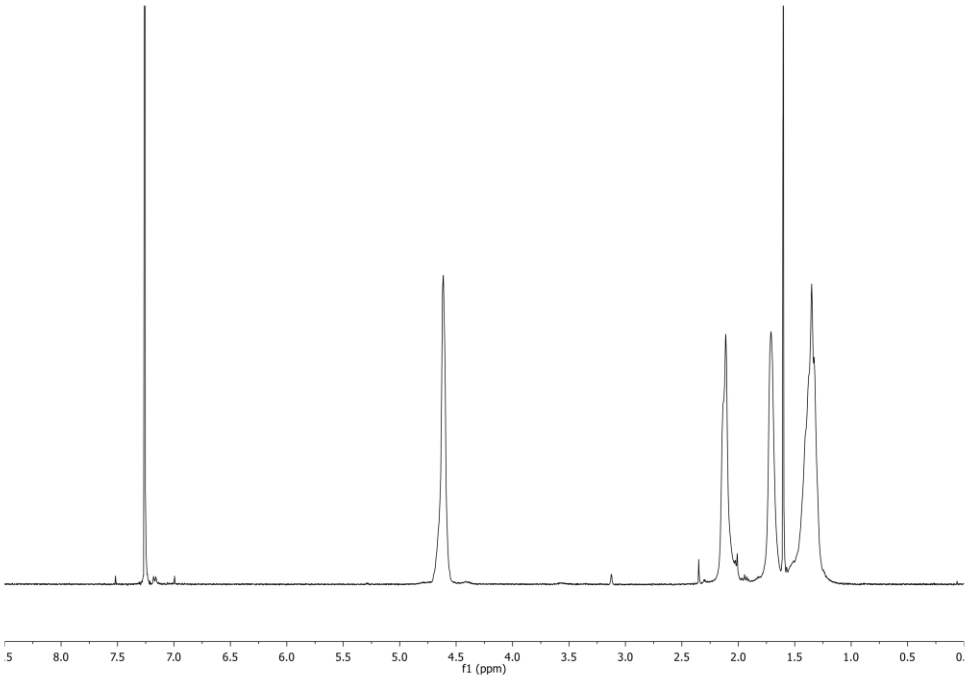


Figure S8. ^{1}H NMR spectrum for polymer reported in Table 1, entry 5.

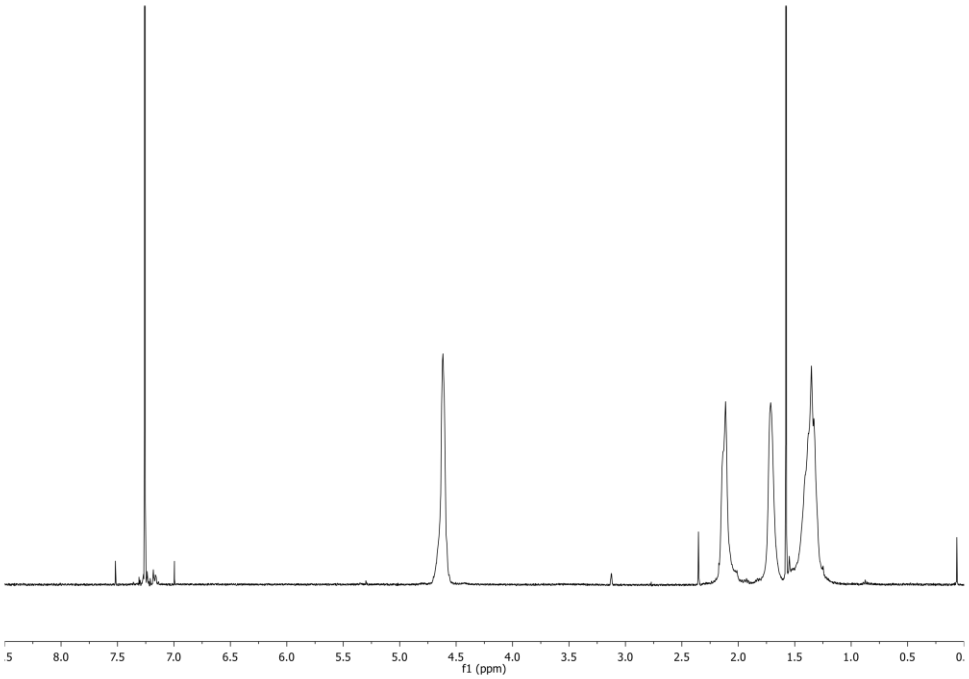


Figure S9. ^{1}H NMR spectrum for polymer reported in Table 1, entry 6.

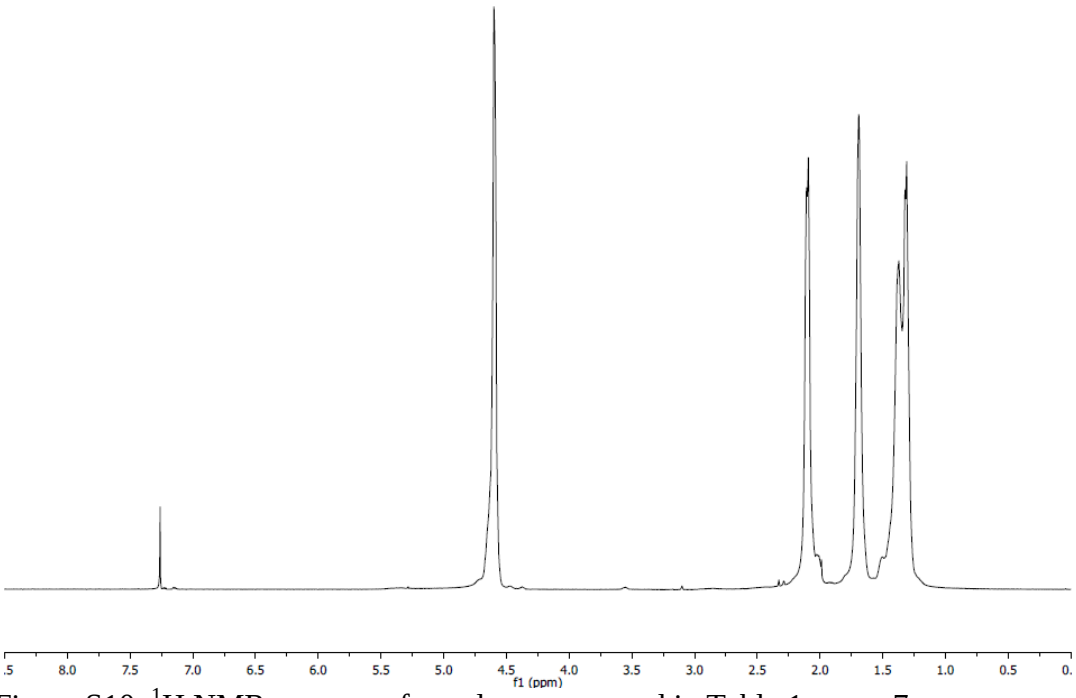


Figure S10. ^{1}H NMR spectrum for polymer reported in Table 1, entry 7.

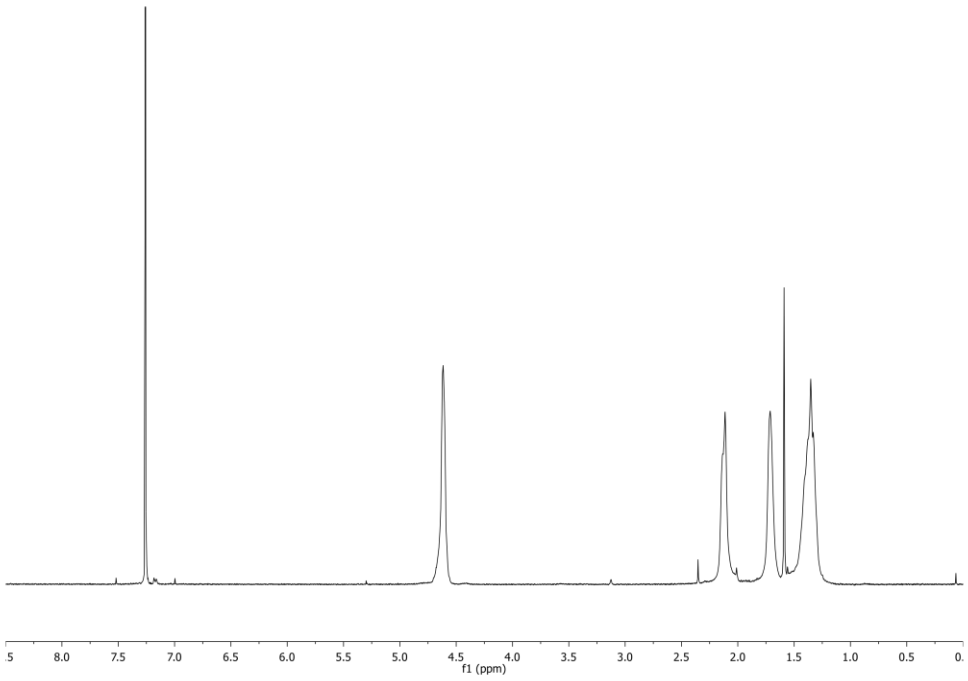


Figure S11. ^{1}H NMR spectrum for polymer reported in Table 1, entry 8.

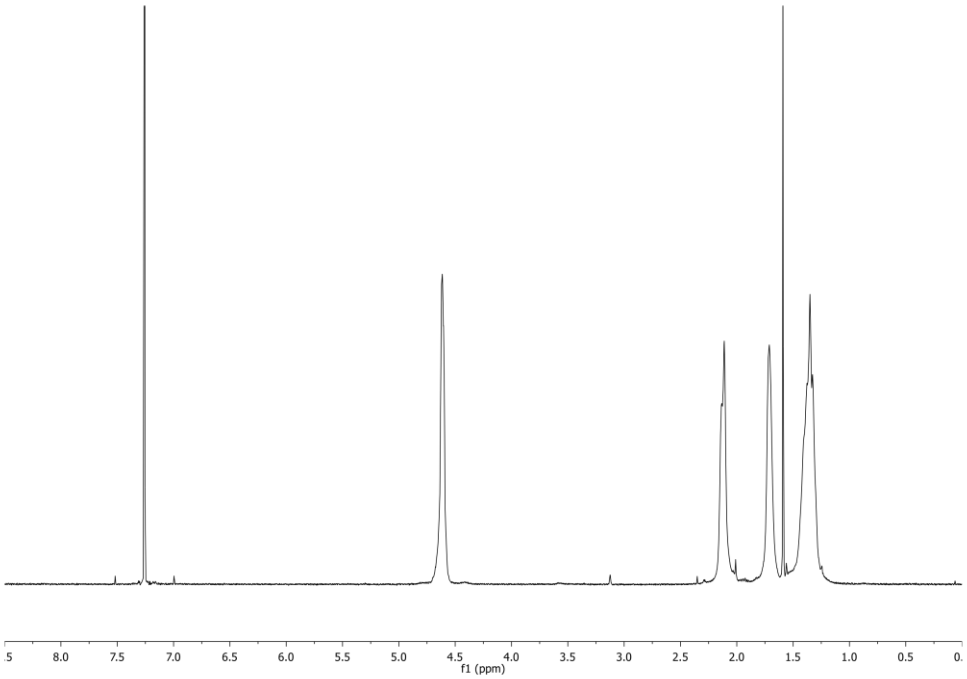


Figure S12. ^{1}H NMR spectrum for polymer reported in Table 1, entry 9.

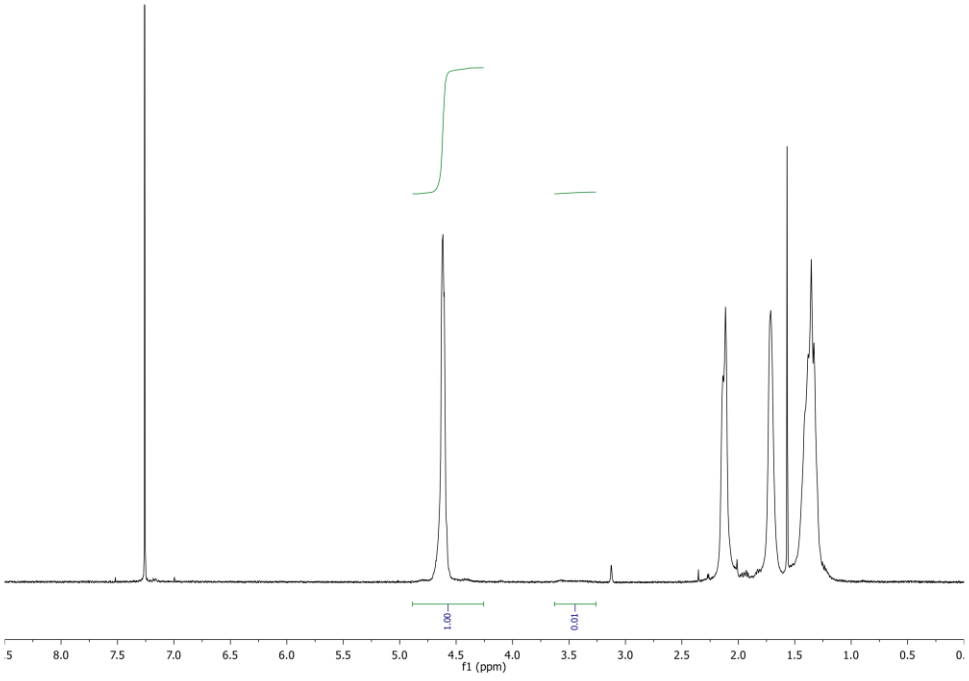


Figure S13. ^{1}H NMR spectrum for polymer reported in Table 1, entry 10.

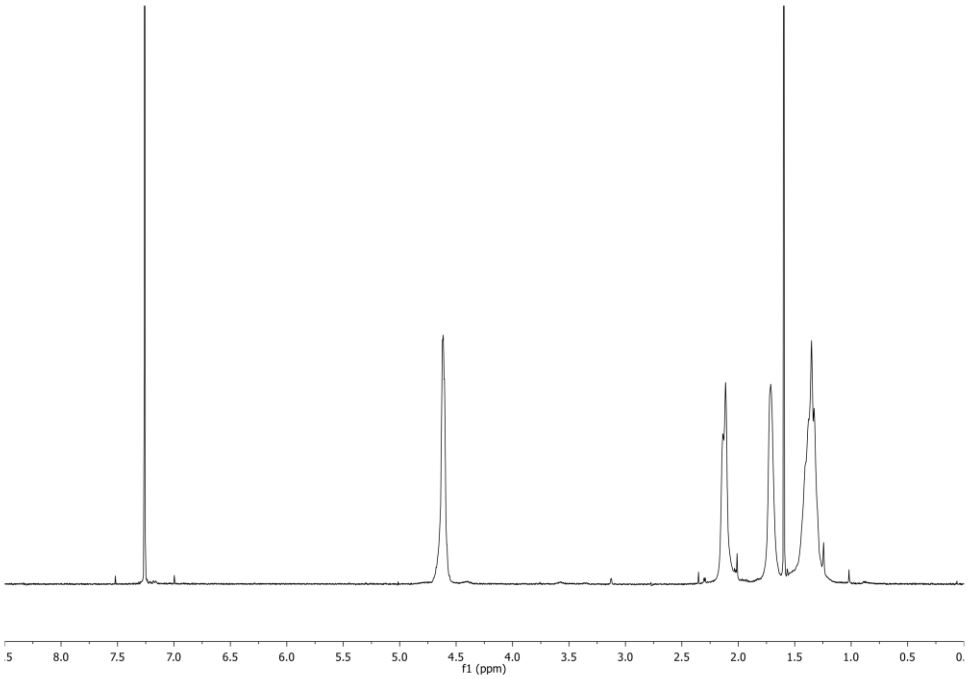


Figure S14. ^{1}H NMR spectrum for polymer reported in Table 1, entry 11.

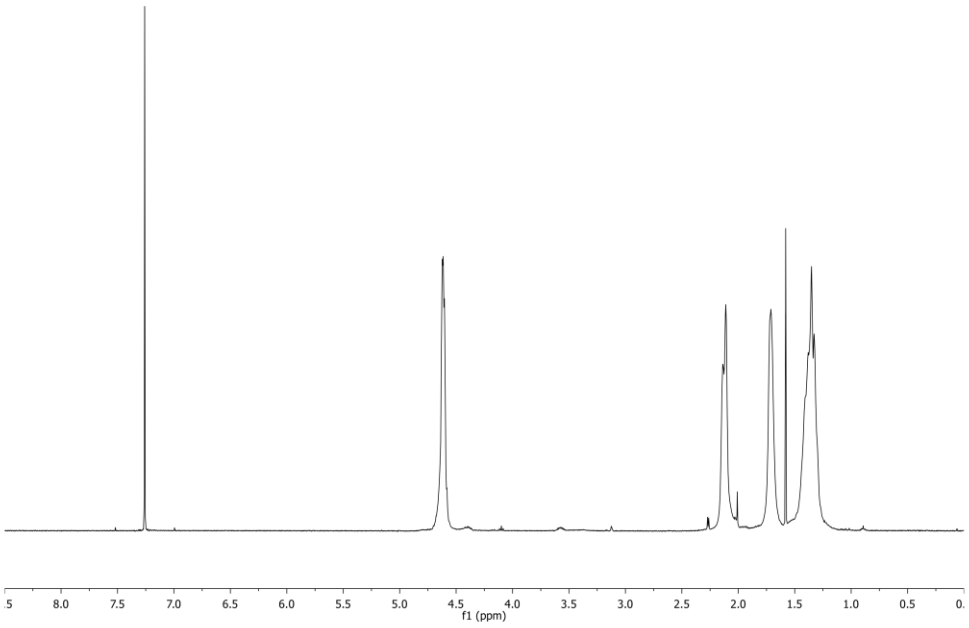


Figure S15. ^{1}H NMR spectrum for polymer reported in Table 1, entry 12.

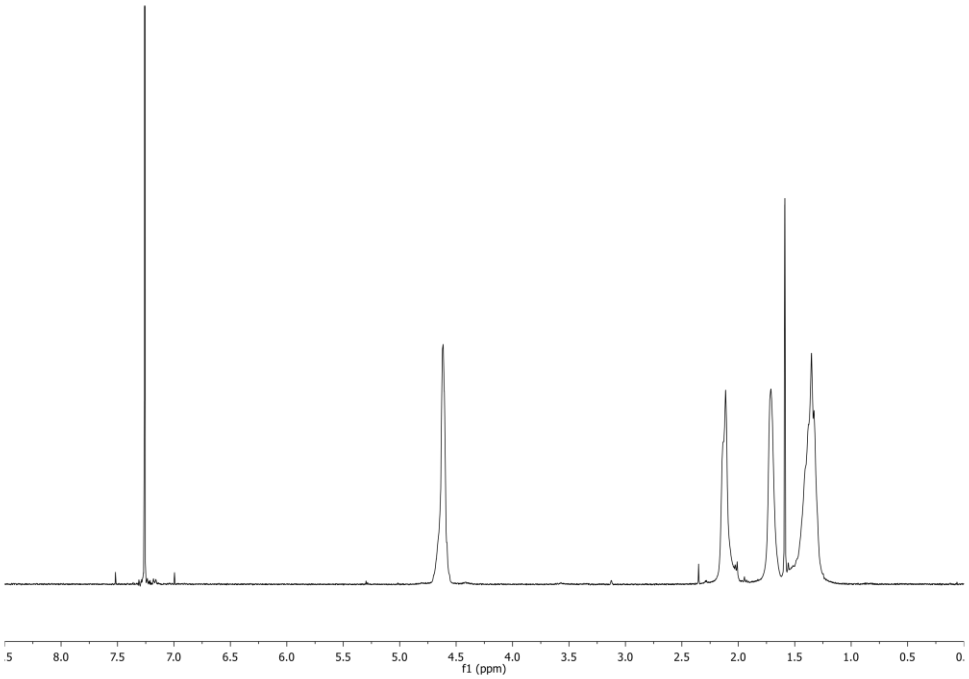


Figure S16. ^{1}H NMR spectrum for polymer reported in Figure 4a.

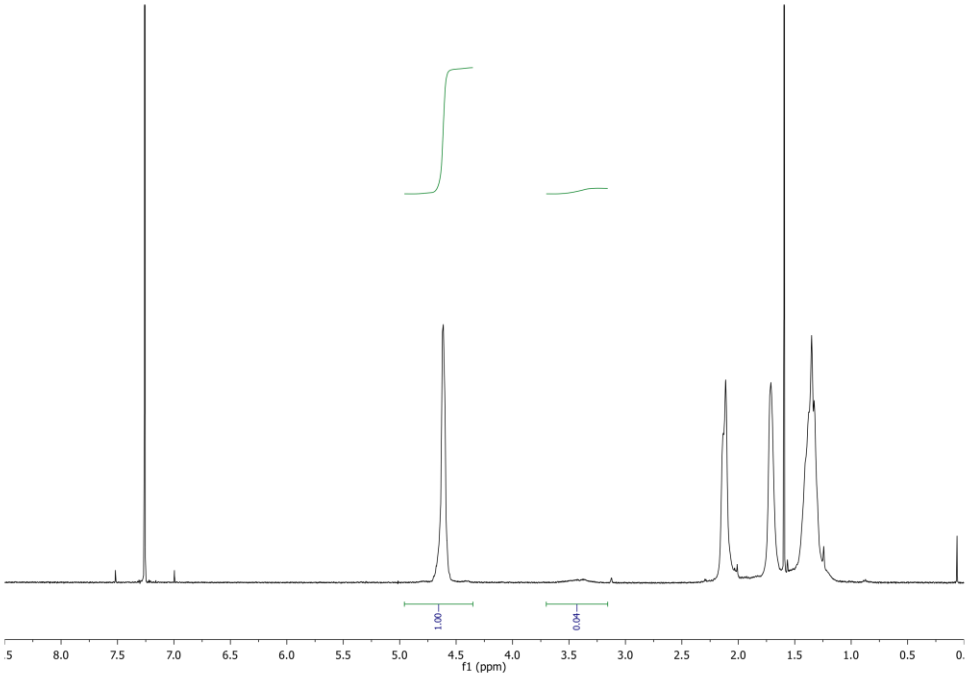


Figure S17. ^{1}H NMR spectrum for polymer reported in Figure 4b.

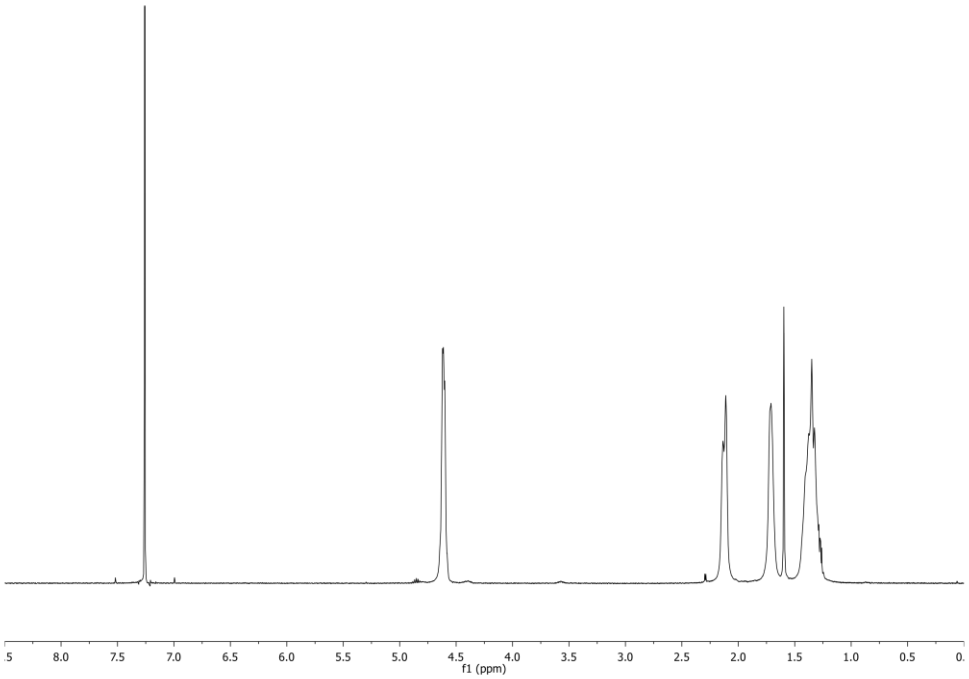


Figure S18. ^{1}H NMR spectrum for polymer reported in Figure 4c.

GPC traces

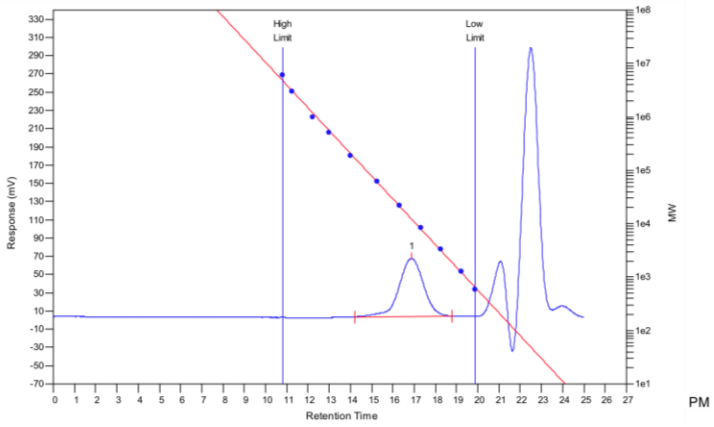


Figure S19. GPC trace for polymer reported in Table 1, entry 1.

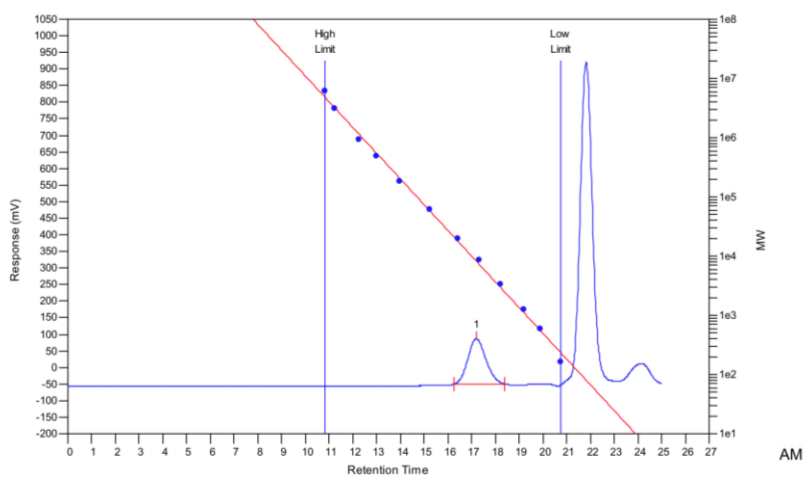


Figure S20. GPC trace for polymer reported in Table 1, entry 2.

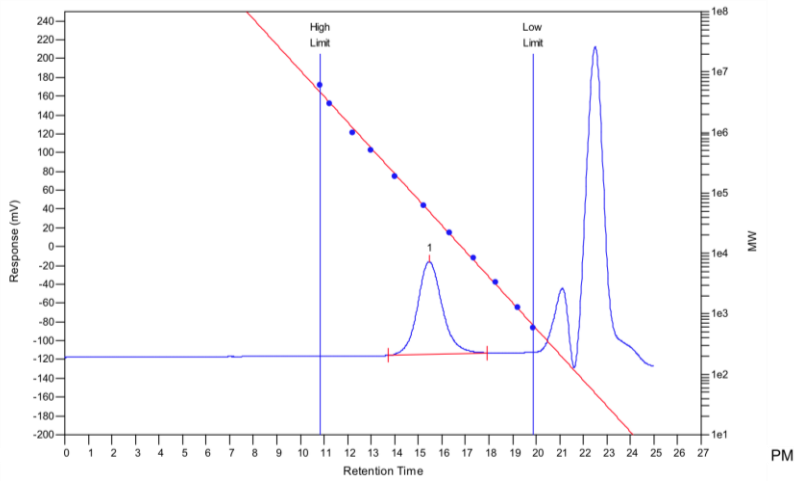


Figure S21. GPC trace for polymer reported in Table 1, entry 3.

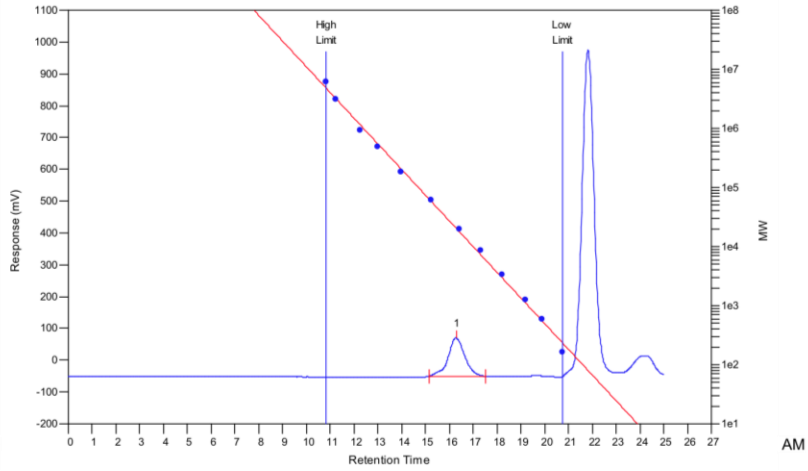


Figure S22. GPC trace for polymer reported in Table 1, entry 4.

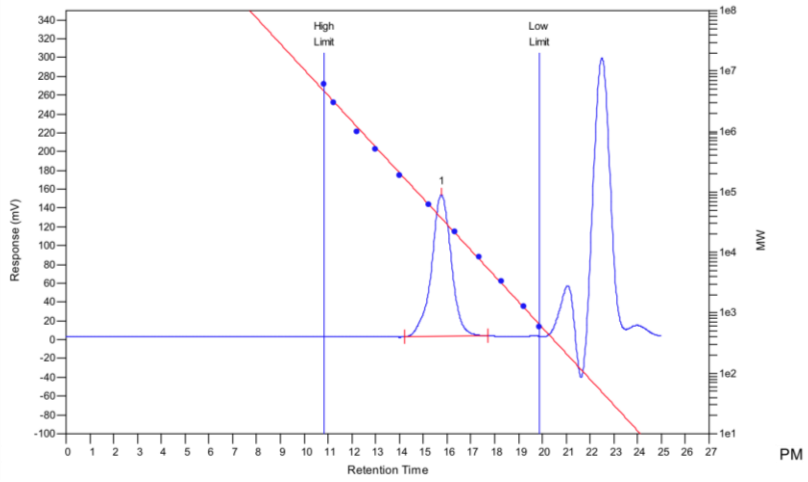


Figure S23. GPC trace for polymer reported in Table 1, entry 5.

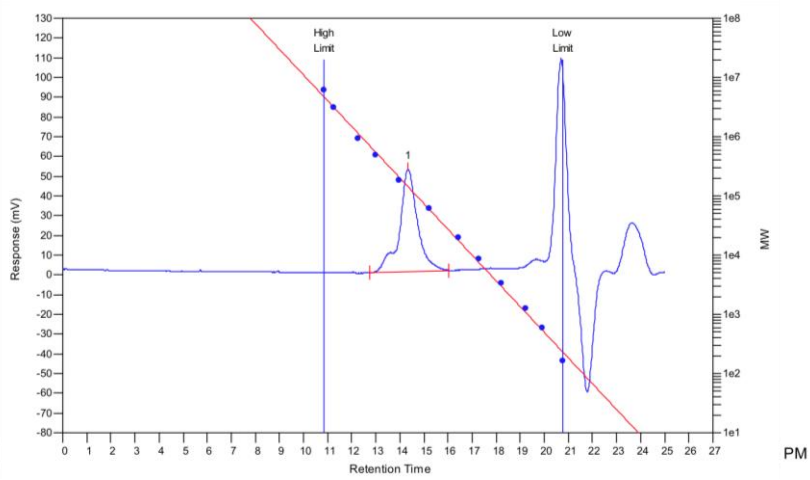


Figure S24. GPC trace for polymer reported in Table 1, entry 6.

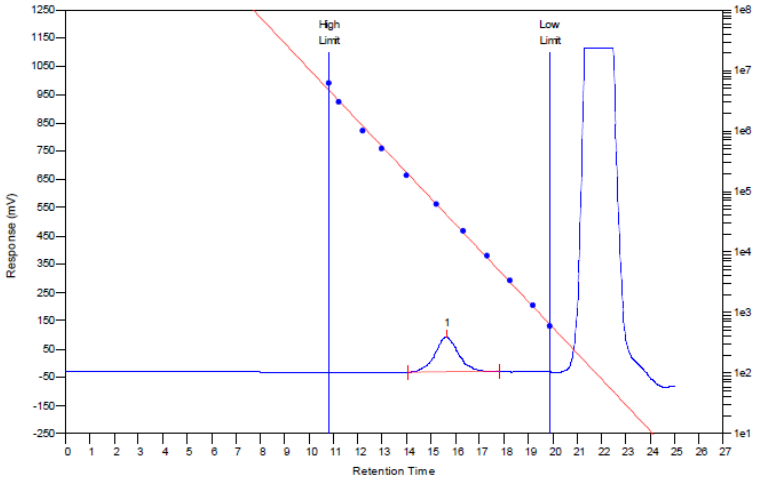


Figure S25. GPC trace for polymer reported in Table 1, entry 7.

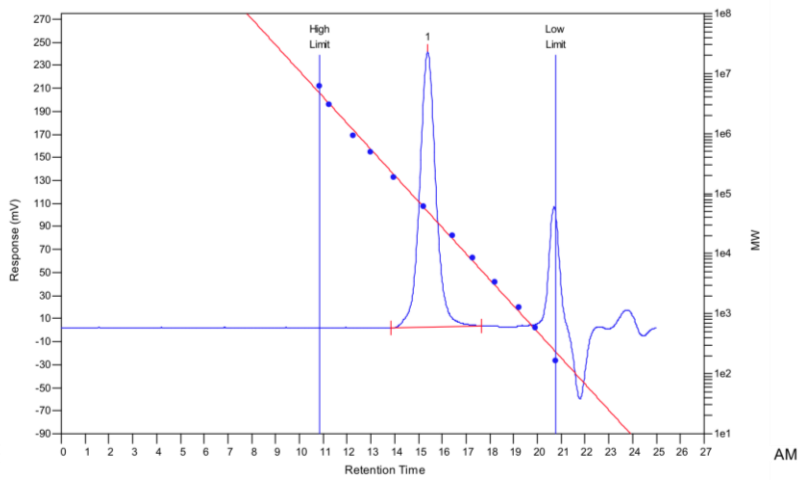


Figure S26. GPC trace for polymer reported in Table 1, entry 8.

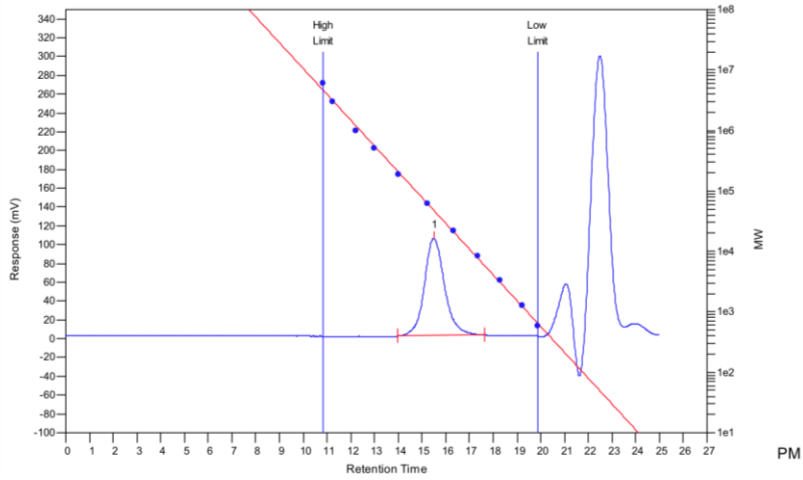


Figure S27. GPC trace for polymer reported in Table 1, entry 9.

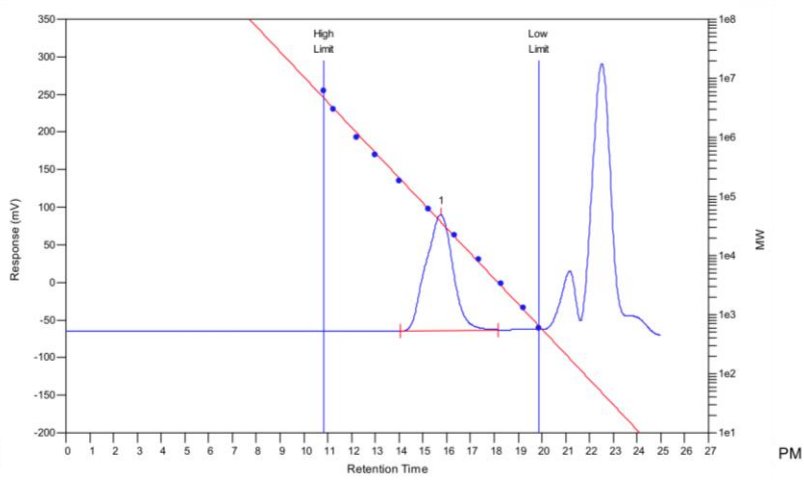


Figure S28. GPC thermogram for polymer reported in Table 1, entry 10.

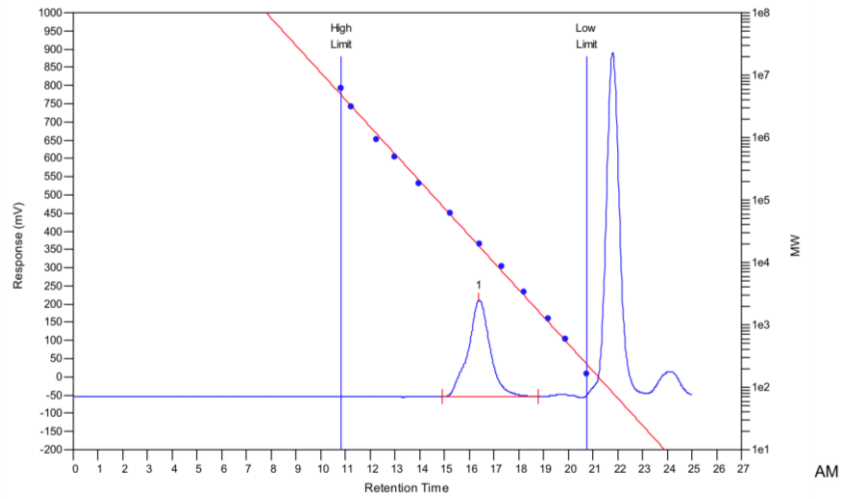


Figure S29. GPC trace for the polymer reported in Table 1, entry 11.

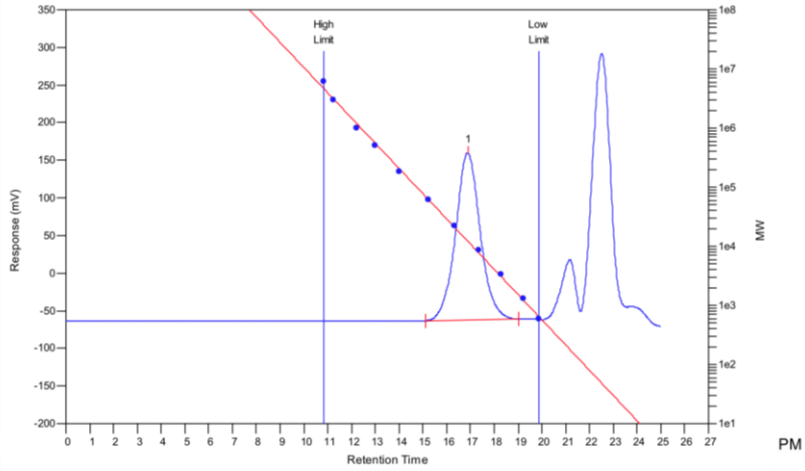


Figure S30. GPC trace for polymer reported in Table 1, entry 12.

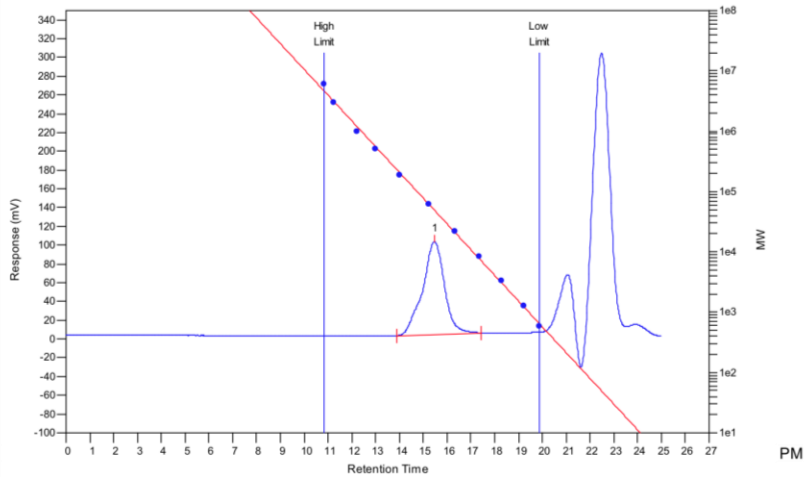


Figure S31. GPC trace for polymer reported in Figure 4a.

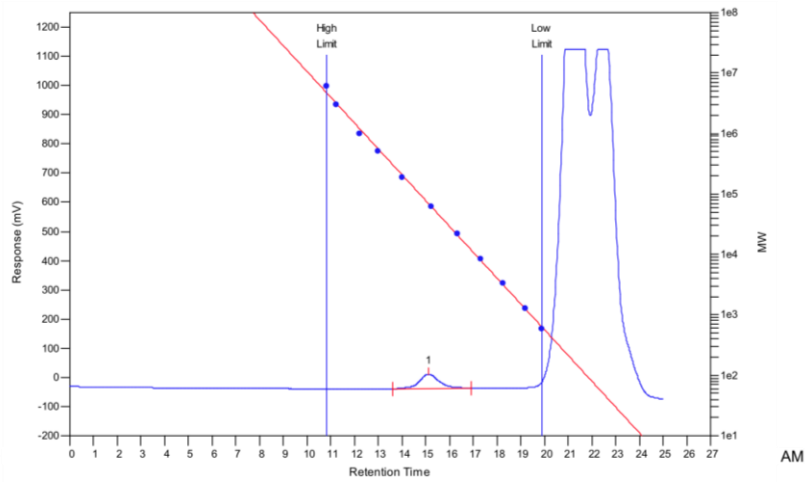


Figure S32. GPC trace for polymer reported in Figure 4b.

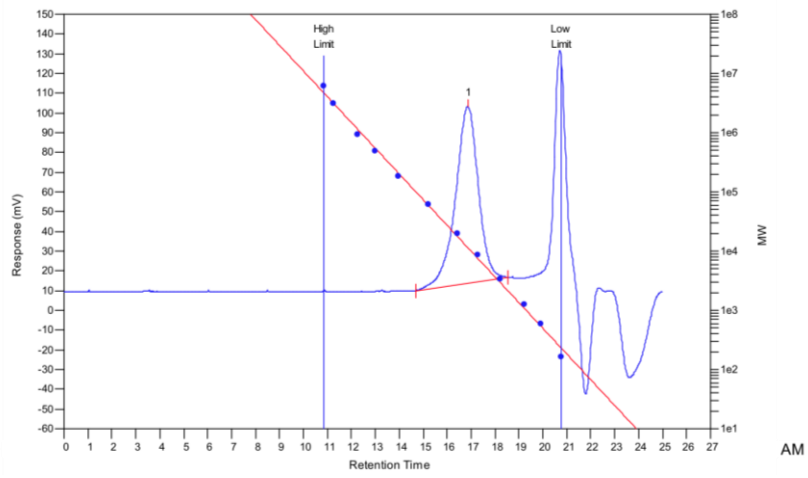


Figure S33. GPC trace for polymer reported in Figure 4c.

Representative DSC thermograms

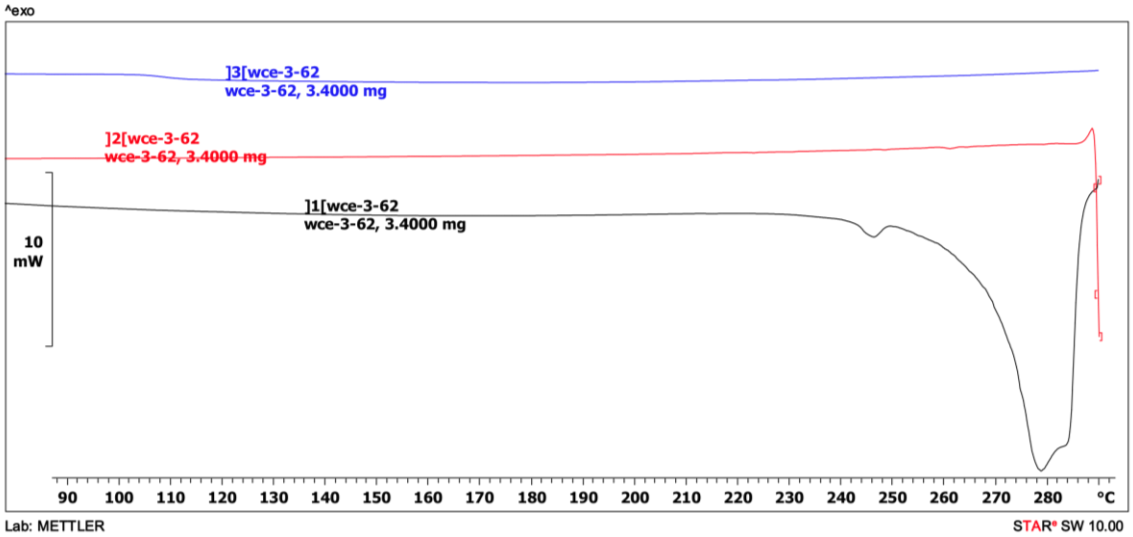


Figure S34. DSC thermogram for polymer reported in Table 1, entry 6. This sample was heated to 290 °C to examine total decomposition. The melting event occurs at approximately 248 °C. The second heating curve (blue line) shows no melting transition, demonstrating the complete decomposition of the polymer sample.

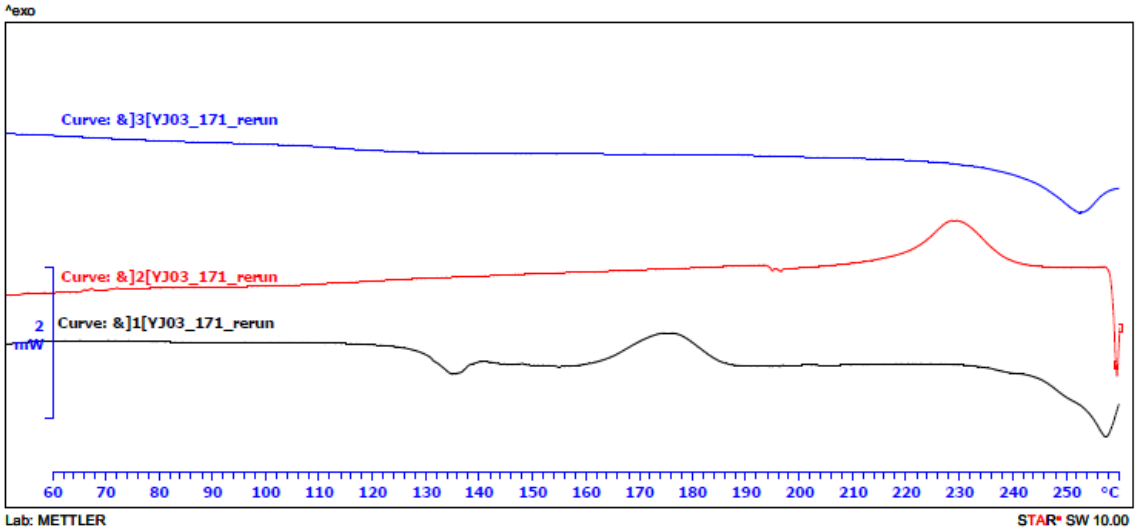


Figure S35. DSC thermogram for polymer reported in Table 1, entry 7. This sample shows a T_g at approx. 132 °C followed by a crystallization peak at approx. 175 °C, as well as a T_m at approx. 250 °C on the first heating cycle (black line). The T_m coincides with the onset of partial polymer decomposition. The second heating cycle (blue line) also shows a T_m at approx. 255 °C.

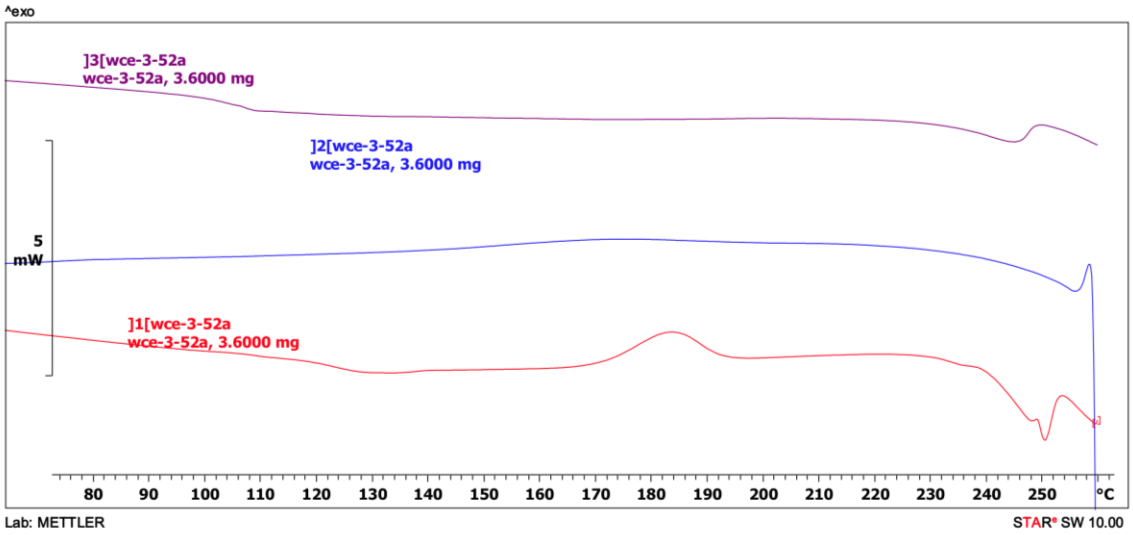


Figure S36. DSC thermogram for polymer reported in Table 1, entry 8. This sample shows a T_g at approx. 125 °C followed by a crystallization peak at approx. 185 °C during the first heating cycle (red line), as well as a T_m at approx. 250 °C. The second heating cycle (purple line) also shows a T_m at approx. 245 °C.

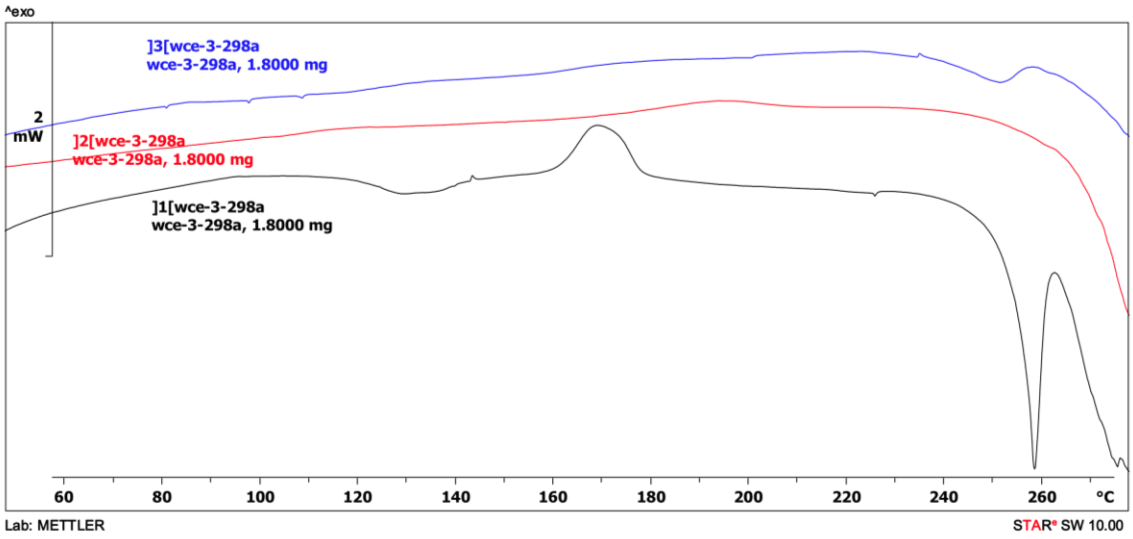


Figure S37. DSC thermogram for polymer reported in Table 1, entry 10. This sample was heated to 270 °C (compared to 260 °C), and it shows a T_g at approx. 125 °C followed by a crystallization peak at approx. 170 °C during the first heating cycle (black line), as well as a T_m at approx. 258 °C. The second heating cycle (blue line) also shows a T_m at approx. 250 °C.

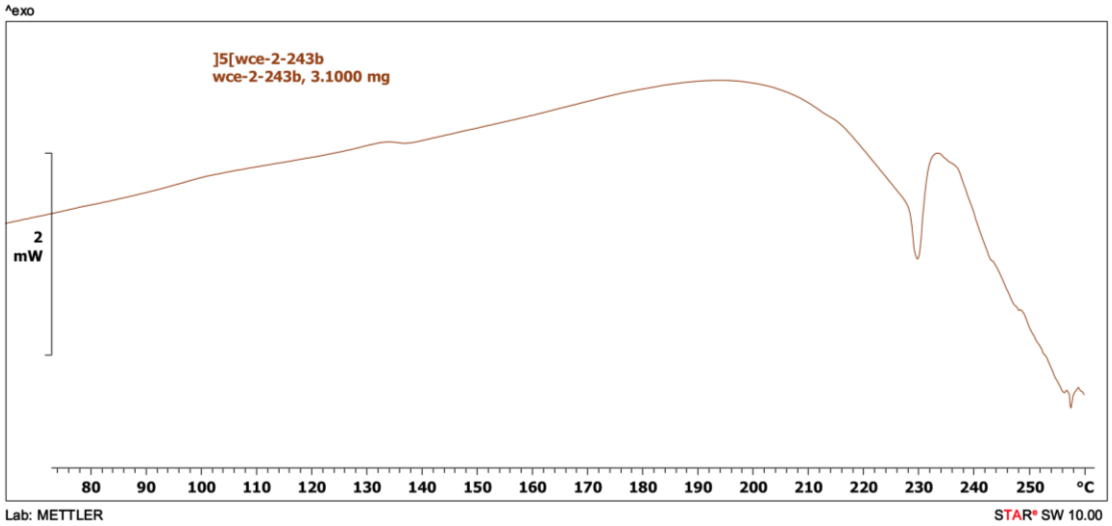


Figure S38. DSC thermogram for polymer reported in Figure 4a. This sample was annealed on the DSC by heating to 180 °C at a rate of 10 °C/min and cooling back to 40 °C before heating to 260 °C. The annealed sample shows a T_m at approx. 230 °C.

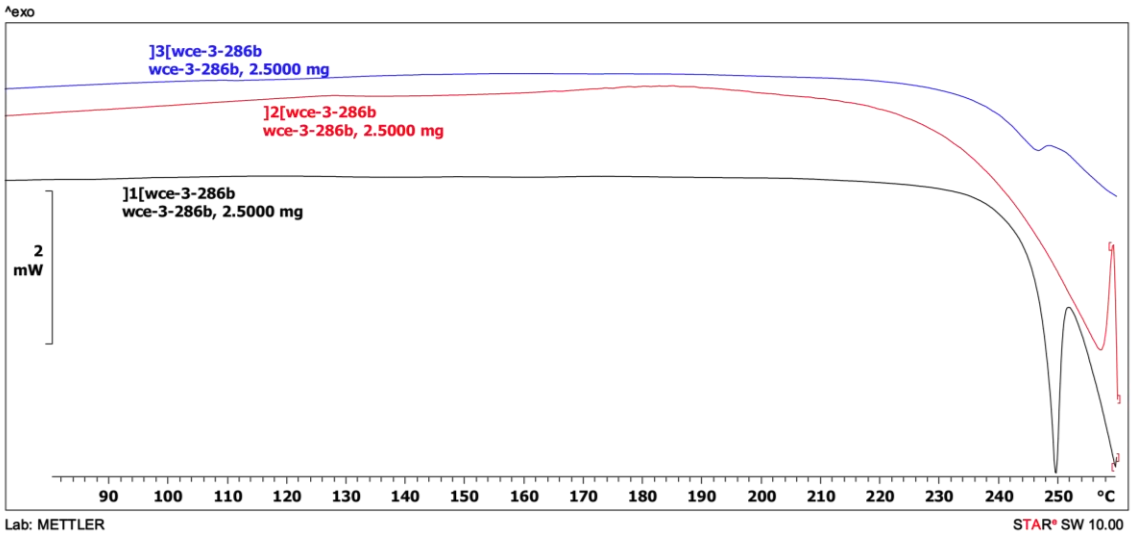


Figure S39. DSC thermogram for polymer reported in Figure 4b. This sample shows a T_m at approx. 250 °C that appears at approx. 245 °C in the second heating cycle (blue line).

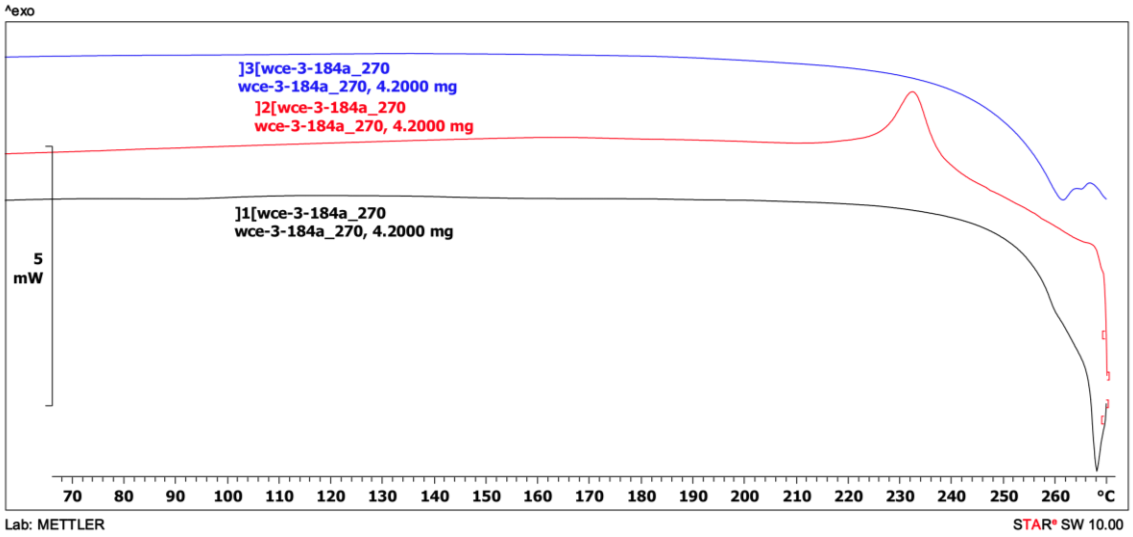


Figure S40. DSC thermogram for polymer reported in Figure 4c. This sample, which was heated to 270 °C to observe the T_m, shows a T_m at approx. 260 °C that is also visible in the second heating cycle (blue line).

Representative TGA thermograms

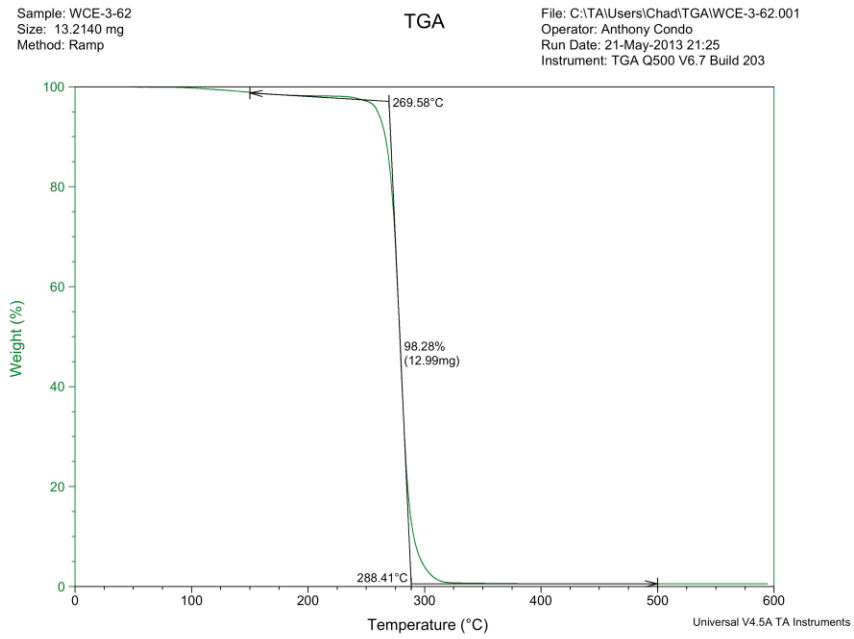


Figure S41. TGA thermogram for polymer reported in Table 1, entry 6.

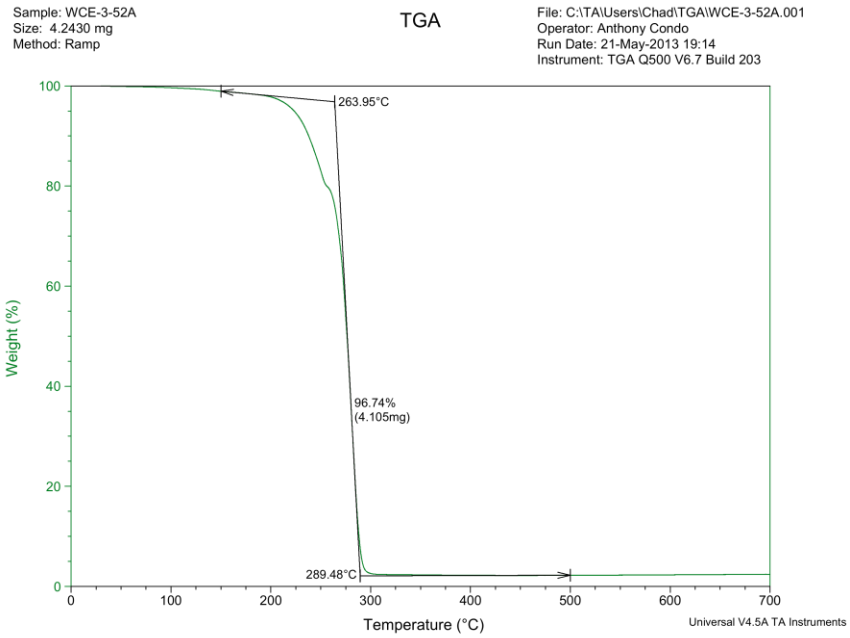


Figure S42. TGA thermogram for polymer reported in Table 1, entry 8.

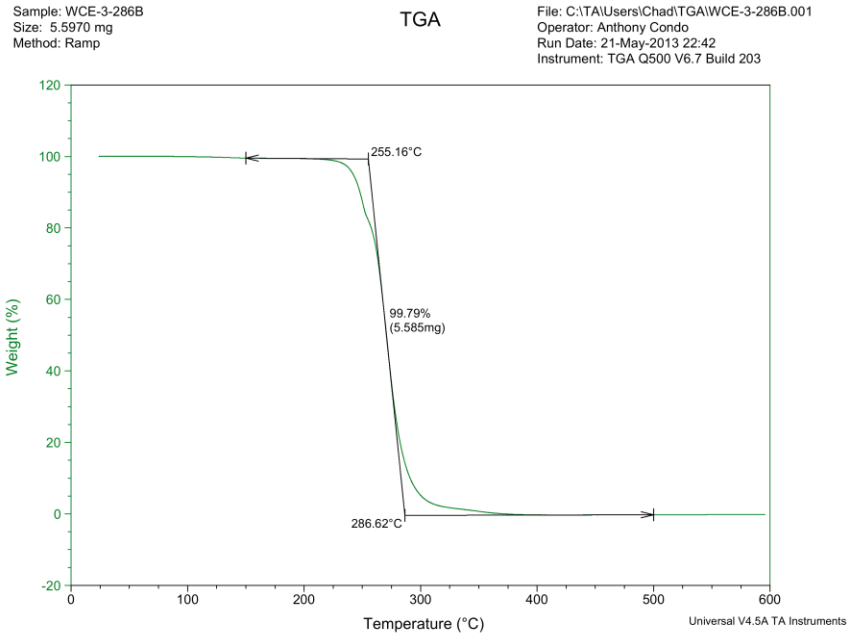


Figure S43. TGA thermogram for polymer reported in Figure 4b.

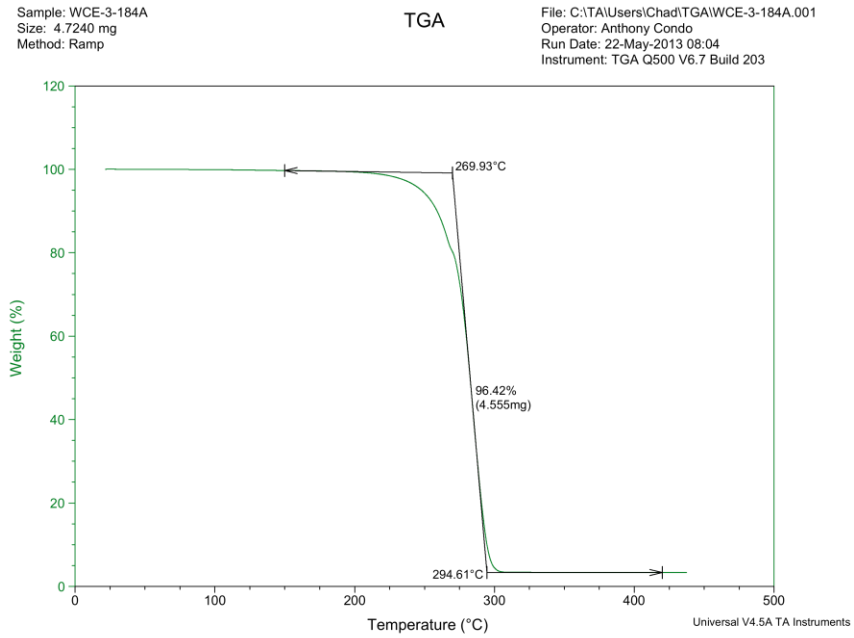


Figure S44. TGA thermogram for polymer reported in Figure 4c.

Representative ^{13}C NMR spectra

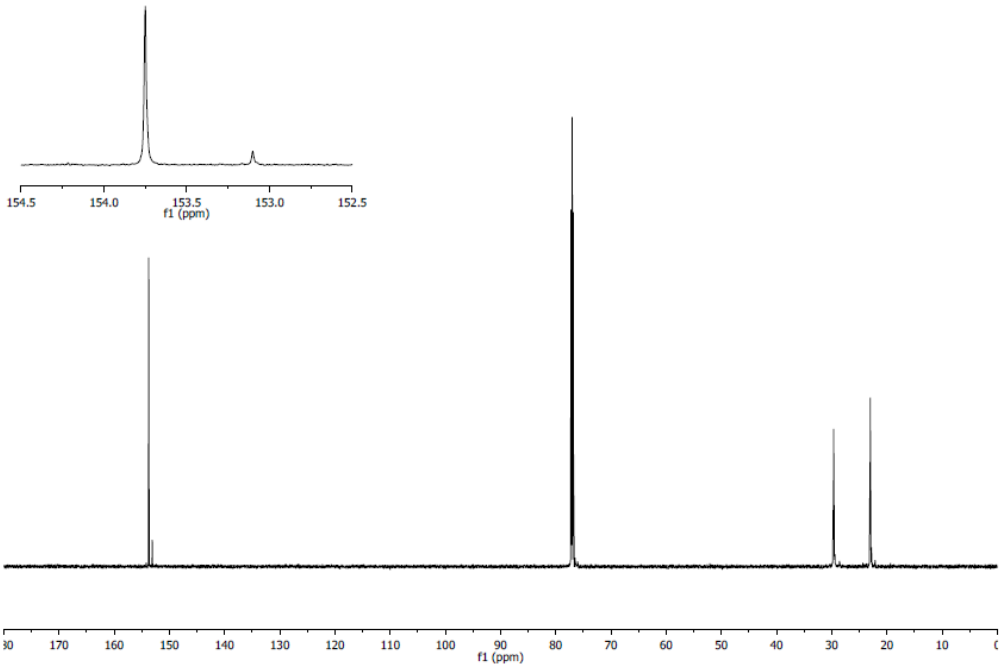


Figure S45. ^{13}C NMR spectrum for polymer reported in Table 1, entry 7.

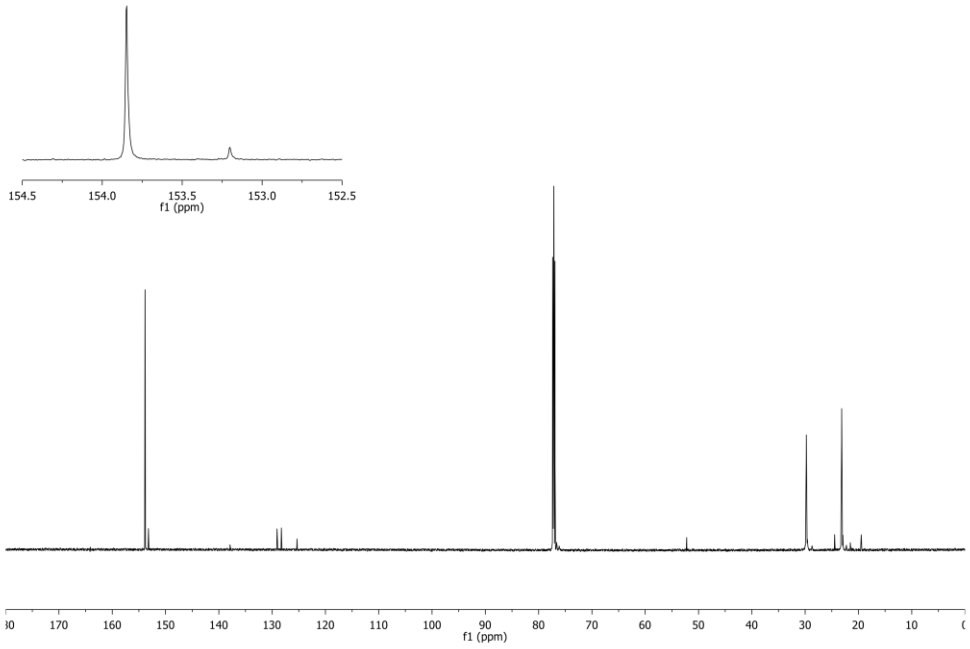


Figure S46. ^{13}C NMR spectrum for polymer reported in Table 1, entry 8. The peaks at δ19, 24, and 52, and those between δ125-140 are from residual CHO and toluene, respectively.

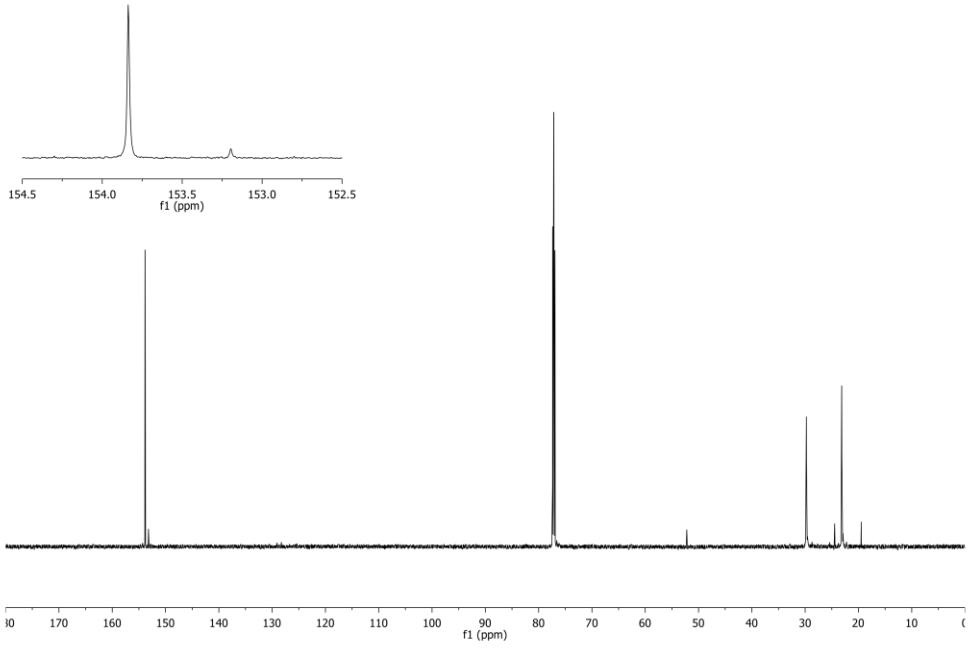


Figure S47. ^{13}C NMR spectrum for polymer reported in Table 1, entry 10.

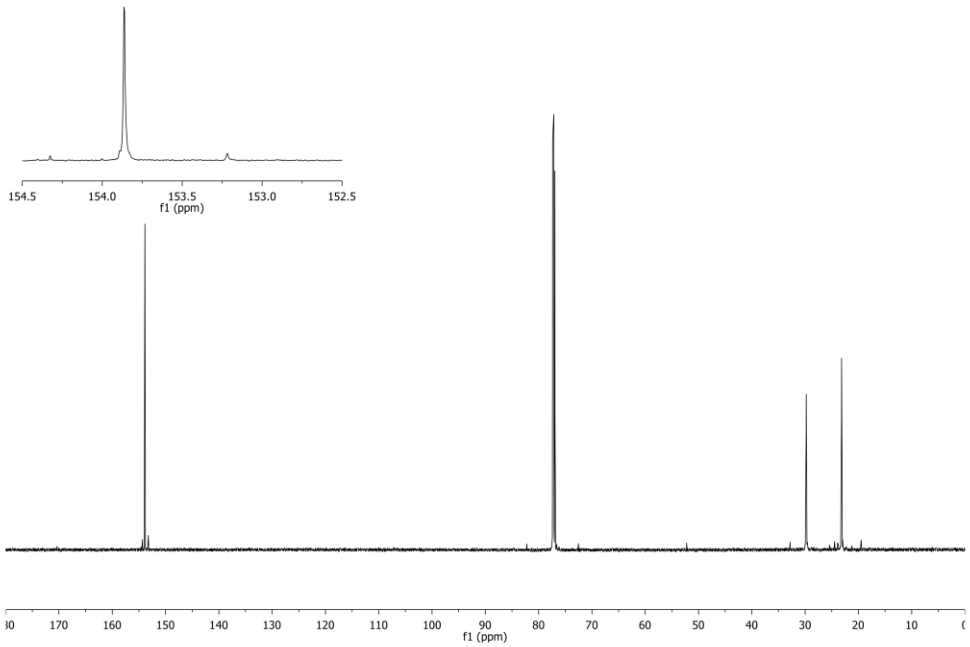


Figure S48. ^{13}C NMR spectrum for polymer reported in Table 1, entry 12.

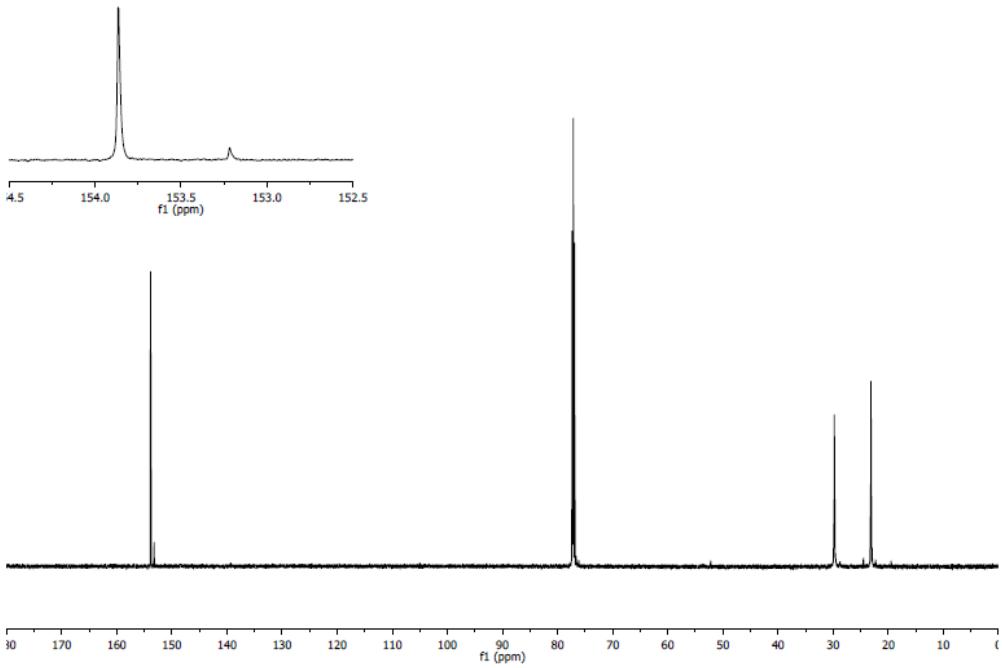


Figure S49. ^{13}C NMR spectrum for polymer reported in Figure 4b.

NMR analysis of catalyst 5

Various 1- and 2-D NMR spectroscopic techniques were used to study the solution state dynamics of catalyst **5**. At room temperature, ^{1}H and ^{19}F NMR spectra of catalyst **5** showed broad peaks suggestive of fluxional behavior. When cooled down to −70 °C, the peaks were able to be resolved such that two distinct species could be identified. The low temperature ^{1}H NMR spectrum also showed that the minor complex had a single methyl peak from the acetate (corresponding with carbon 26 in figure S18), while the major complex had two distinct methyl peaks for two different acetates (carbons 26 and 28). It seemed most likely that the species with two different acetates was the *anti*-dimer (**5-*anti***), but the other species could be either the monomer or the *syn*-dimer (**5-*syn***). DO-NMR spectroscopy at −80 °C was used to compare the translation diffusion coefficients of the two species, which appeared to be identical. We concluded from the VT ^{1}H NMR and DO-NMR spectra that the dimers **5-*syn*** and **5-*anti*** were in equilibrium, where they existed in a 1:1.8 ratio at −76 °C. Further characterization was done at −76 °C using COSY, HSQCAD, ROESY, and HMBC spectroscopy to confirm the structural assignments.

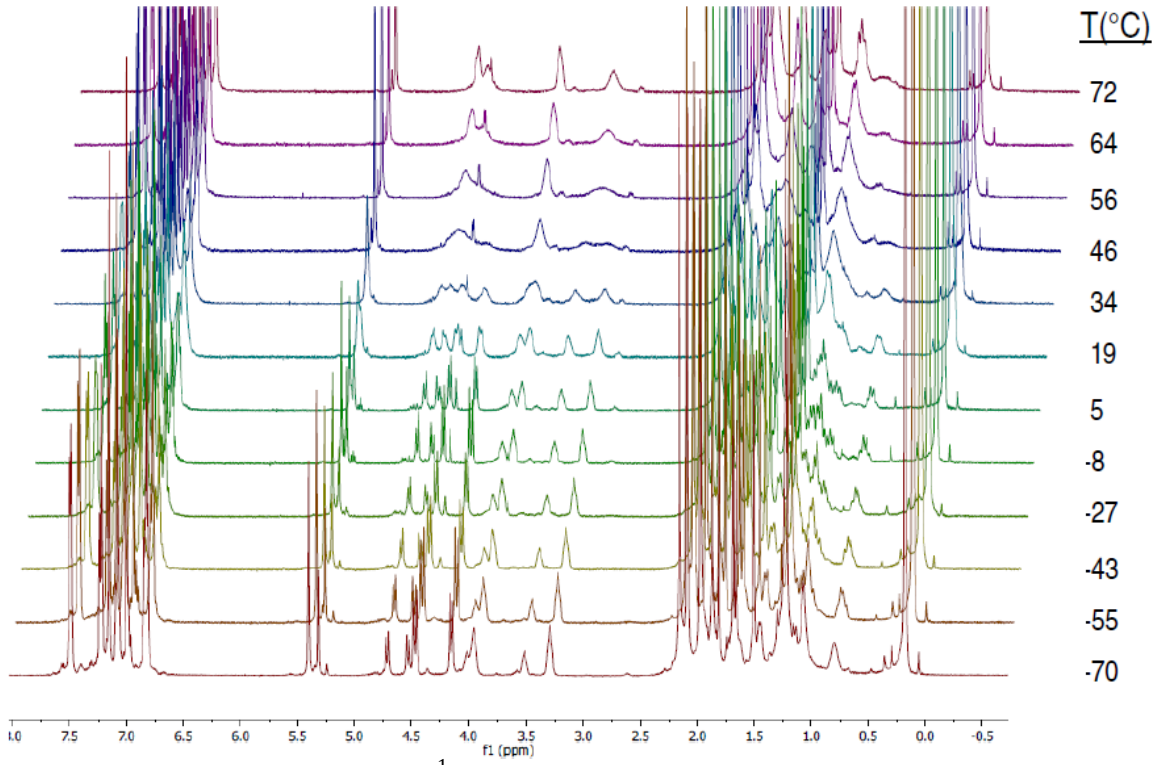


Figure S50. Variable temperature ^{1}H NMR spectra of catalyst **5** in toluene-d_8 with hexamethyldisiloxane (HMDS) as reference (full spectrum).

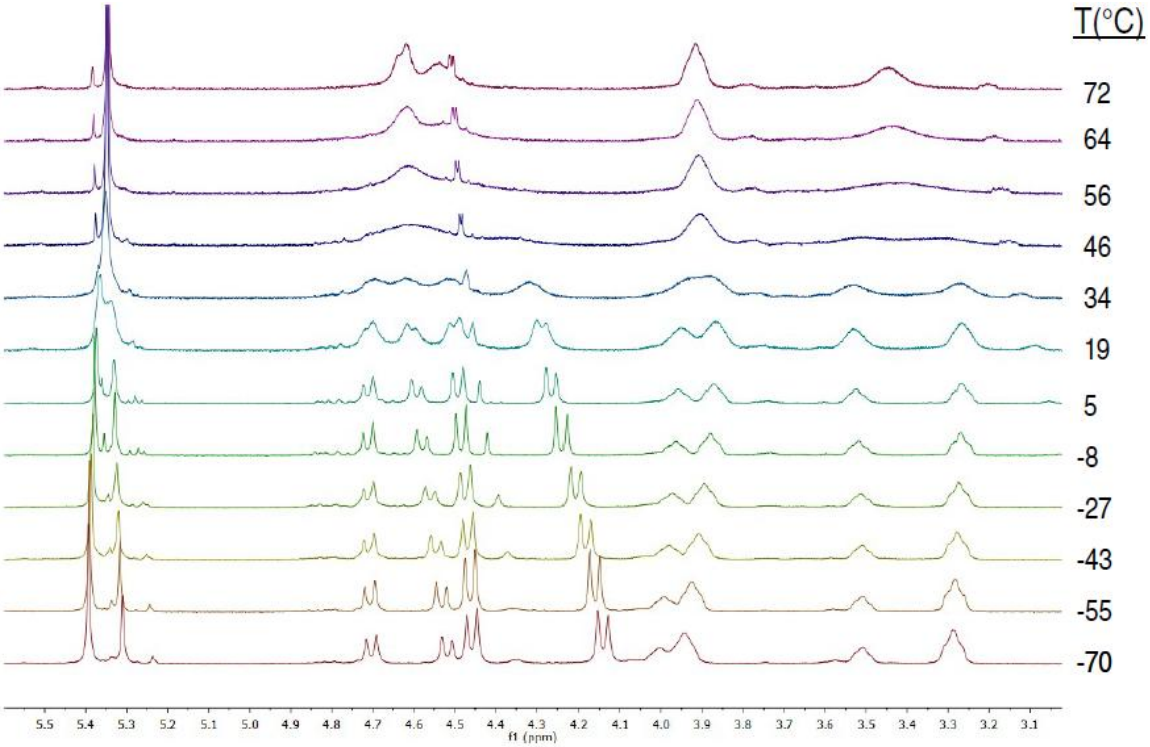


Figure S51. Variable temperature ^{1}H NMR spectra of catalyst **5** in toluene-d_8 with HMDS as reference. The region between 3.1 and 5.5 ppm was the best resolved and thus used to identify the two species in equilibrium.

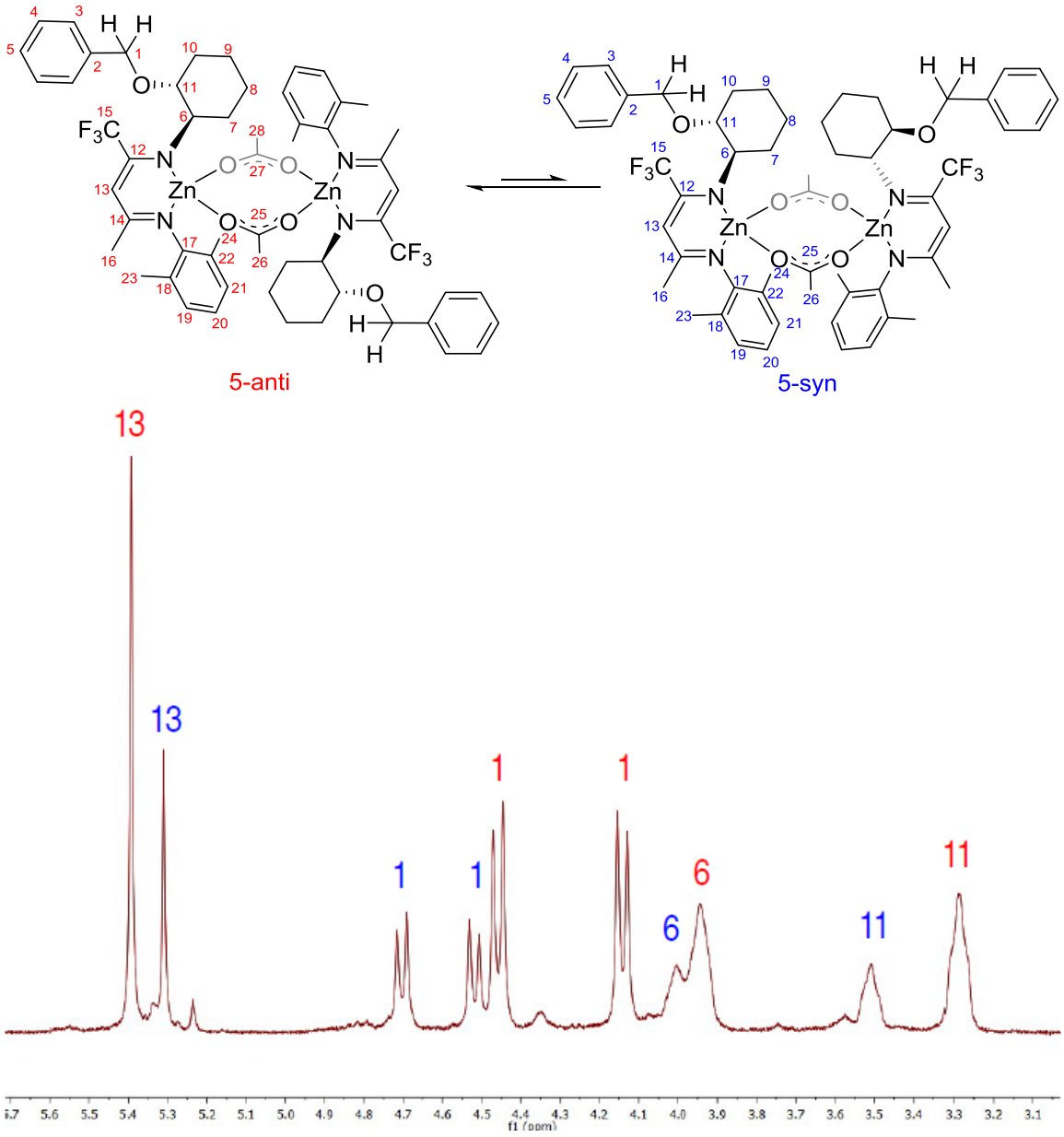


Figure S52. ^{1}H NMR spectrum of catalyst **5** at −70 °C in toluene-d_8 with assignments for the two dimers in equilibrium.

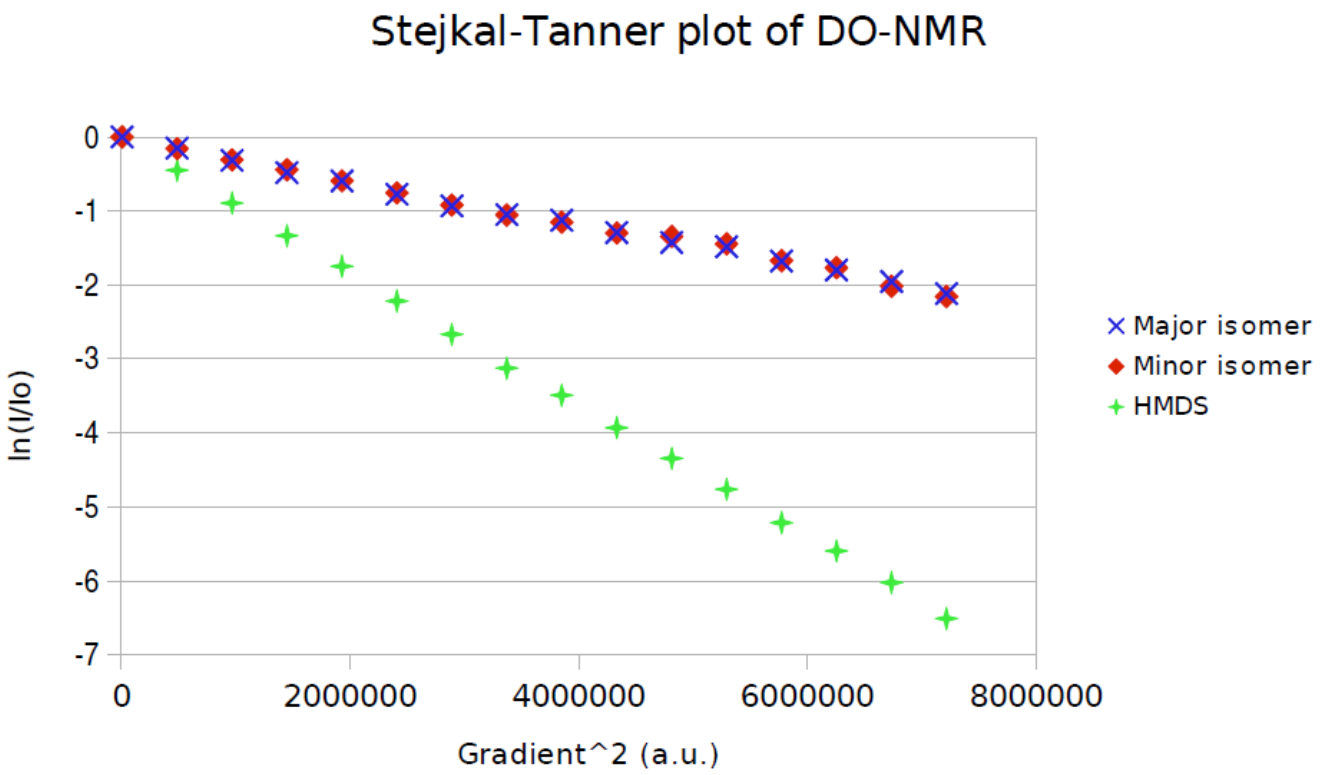


Figure S53. For the DO-NMR experiment, a double-stimulated-echo experiment with bipolar gradient pulses was performed on catalyst **5** in toluene-d_8 at −80 °C ([Zn]=28.2 M, HMDS as internal standard). A Stejkal-Tanner analysis was performed using the averaged integrations of peaks at 5.43 ppm, 4.49 ppm, 4.17 ppm, and 3.33 ppm for the major isomer, and the averaged integrations of peaks at 5.34 ppm, 4.74 ppm, 4.55 ppm, and 3.55 ppm for the minor isomer. For comparison, the integration of the HMDS peak at 0.2 ppm was also included. The Stejkal-Tanner plot shows that the major and minor isomer have essentially identical diffusion coefficients, where the diffusion coefficient D is equal to the absolute value of the slope. Thus, the DO-NMR results suggest that the equilibrium is between two dimers and not between monomer and dimer, since the monomer and dimer would have different diffusion coefficients (and different slopes) in the Stejkal-Tanner plot.

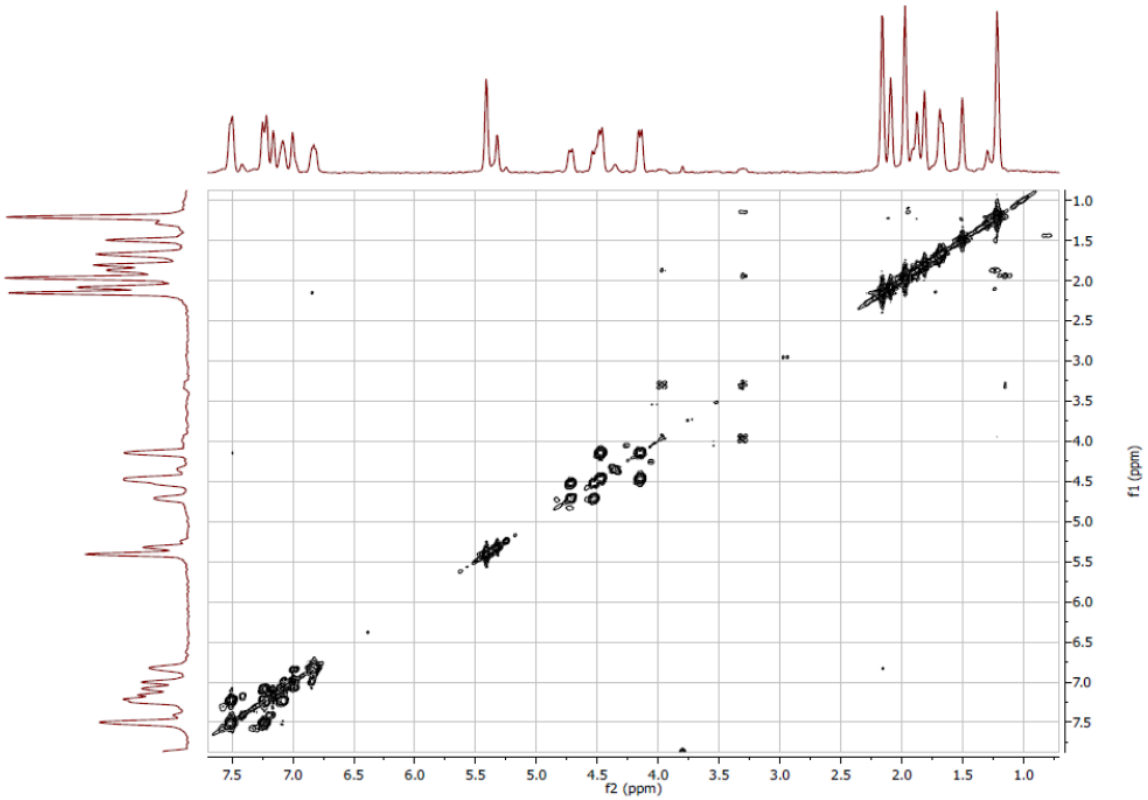


Figure S54. COSY spectrum of catalyst **5** at −76 °C in toluene-d_8.

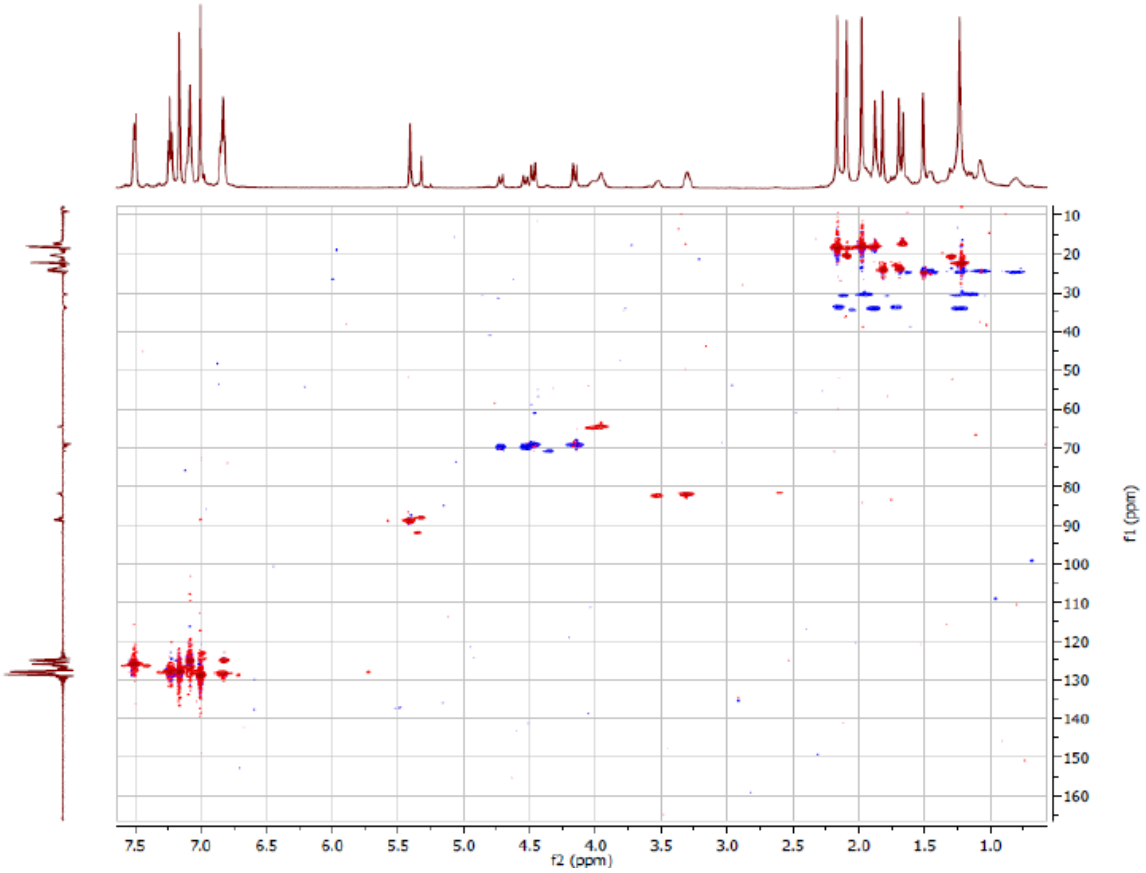


Figure S55. HSQC spectrum of catalyst **5** at −76 °C in toluene-d_8.

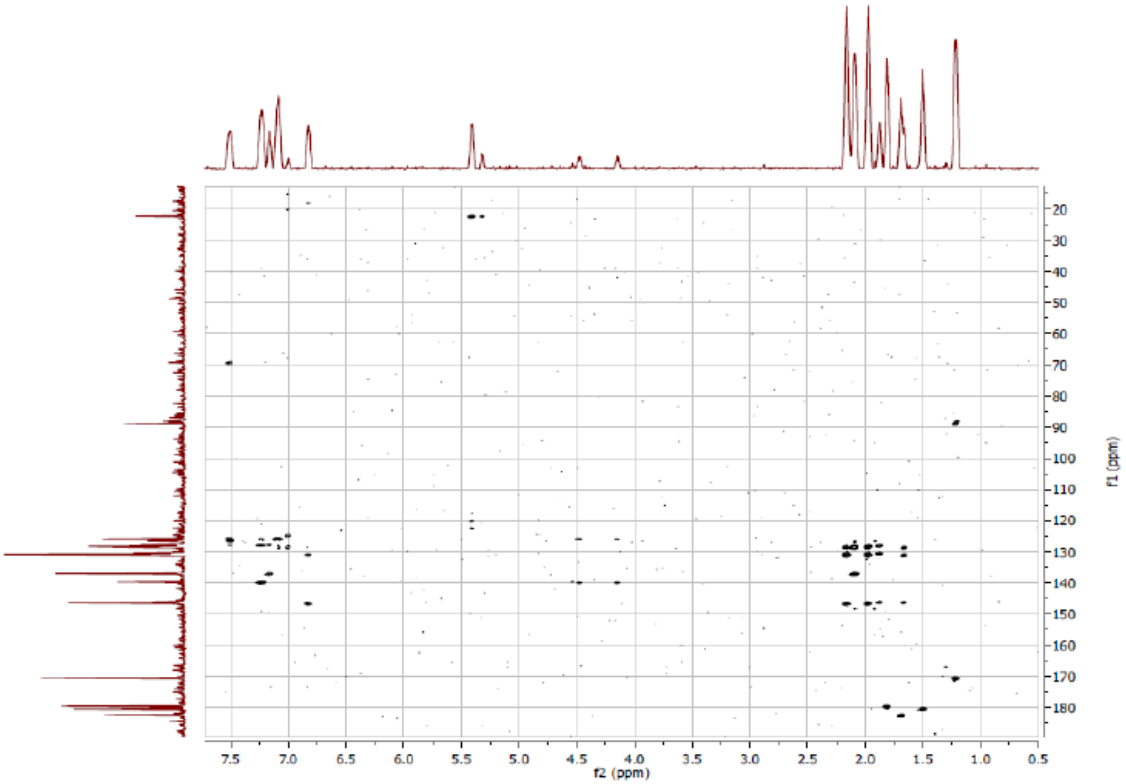


Figure S56. HMBC spectrum of catalyst **5** at −76 °C in toluene-d_8.

Table S2. ^{1}H and ^{13}C NMR spectral assignments for catalyst **5.**

Carbon atom # (figure S52)	5-anti		5-syn	
	^{1}H NMR δ	^{13}C {^{1}H} NMR δ	^{1}H NMR δ	^{13}C {^{1}H} NMR δ
1	4.47, 4.15	69.20	4.72, 4.52	69.81
2	-	139.92	-	139.74
3	7.50	125.87	7.50	125.93
4	7.23	127.90	7.23	127.90
5	7.08	126.65	7.08	125.12
6	3.96	64.55	4.03	64.80
7	nd	nd	nd	nd
8	nd	nd	nd	nd
9	nd	nd	nd	nd
10	1.95, 1.16	30.37	2.11, 1.24	30.67
11	3.30	82.01	3.53	82.44
12	-	nd	-	nd
13	5.41	88.77	5.32	88.08
14	-	170.69	-	170.57
15	-	121.28	-	nd
16	1.22	22.55	1.21	22.32
17	-	146.61	-	146.21
18	-	130.83	-	131.09
19	6.82	128.38	6.84	128.68
20	6.82	nd	6.82	nd
21	6.82	128.90	6.84	128.05
22	-	130.89	-	130.49
23	1.97	18.02	1.66	17.26
24	2.16	18.27	1.88	18.02
25	-	179.69	-	180.52
26	1.81	23.94	1.50	24.55
27	-	182.53	-	-
28	1.69	23.72	-	-

nd=could not be determined

Crystallographic data for complexes 1, 3, 4, and *ent*-5

Single-crystal X-ray crystallography:

Crystals were transferred from a crystallization vessel into a drop of viscous organic oil. Using a nylon loop, a suitable single crystal was chosen, mounted on a Bruker X8 APEX II diffractometer (MoK_α radiation) and cooled to −100 °C.

Data collection and reduction were done using Bruker APEX2[11] and SAINT+[12] software packages. An empirical absorption correction was applied with SADABS.[13] Structures were solved by direct methods and refined on F^2 by full matrix least-squares techniques using SHELXTL[14] software package. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were found in a difference Fourier map and refined isotropically.

For **1** 'ce4' the crystal size was 0.3 x 0.1x 0.025 mm^3. Overall 23467 reflections were collected, 9308 of which were symmetry independent (R_{int} = 0.0432); with 6898 'strong' reflections ($F_o > 4\sigma F_o$). Final R_1 = 4.38%

For **3**, 'ce1' the crystal size was 0.4 x 0.4 x 0.4 mm^3. Overall 25371 reflections were collected, 9628 of which were symmetry independent (R_{int} = 0.0203); with 8845 'strong' reflections ($F_o > 4\sigma F_o$). Final R_1 = 2.71%

For **4** 'ce10' the crystal size was 0.4 x 0.1x 0.1 mm^3. Overall 10724 reflections were collected, 8828 of which were symmetry independent (R_{int} = 0.0410); with 6611 'strong' reflections ($F_o > 4\sigma F_o$). Final R_1 = 4.34%

For *ent*-**5** 'ce5' the crystal size was 0.4 x 0.3x 0.2 mm^3. Overall 22854 reflections were collected, 12299 of which were symmetry independent (R_{int} = 0.0155); with 11150 'strong' reflections ($F_o > 4\sigma F_o$). Final R_1 = 2.54%

Table S3a. Crystal data and structure refinement for **1**.

Identification code	ce4	
Empirical formula	$C_{46}H_{50}F_6N_4O_4Zn_2$	
Formula weight	967.64	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 11.8212(9) Å	α= 90°
	b = 10.6057(8) Å	β= 97.779(4)°
	c = 18.6077(17) Å	γ = 90°
Volume	2311.4(3) $Å^3$	
Z	2	
Density (calculated)	1.390 Mg/m^3	
Absorption coefficient	1.107 mm^{-1}	
F(000)	1000	
Crystal size	0.30 x 0.10 x 0.03 mm^3	
Theta range for data collection	1.74 to 26.37°	
Index ranges	-14<=h<=14, -12<=k<=13, -23<=l<=23	
Reflections collected	19416	
Independent reflections	9308 [R(int) = 0.0432]	
Completeness to theta = 26.37°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9728 and 0.7323	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9308 / 1 / 592	
Goodness-of-fit on F^2	0.984	
Final R indices [I>2sigma(I)]	R1 = 0.0438, wR2 = 0.0738	
R indices (all data)	R1 = 0.0733, wR2 = 0.0841	
Absolute structure parameter	0.000(10)	
Largest diff. peak and hole	0.252 and -0.285 $e \cdot Å^{-3}$	

Table S3b. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zn(1)	8389(1)	3139(1)	7099(1)	39(1)
Zn(2)	7098(1)	1378(1)	8426(1)	37(1)
F(1)	11937(2)	4453(4)	6257(2)	110(1)
F(2)	12060(2)	4856(3)	7407(2)	95(1)
F(3)	11557(2)	6283(4)	6638(2)	130(2)
F(4)	4438(2)	3138(3)	9820(2)	95(1)
F(5)	5000(3)	1918(3)	10706(2)	104(1)
F(6)	3853(2)	1227(4)	9799(2)	98(1)
O(1)	7782(3)	1495(3)	6734(2)	69(1)
O(2)	6971(3)	421(3)	7542(2)	54(1)
O(3)	7886(2)	2926(2)	8099(1)	38(1)
O(4)	8626(3)	4809(3)	8165(2)	70(1)
N(1)	9991(3)	3501(3)	6970(2)	39(1)
N(2)	7648(3)	4380(3)	6388(2)	39(1)
N(3)	5719(3)	1712(3)	8881(2)	42(1)
N(4)	7994(3)	447(3)	9224(2)	38(1)
C(1)	7269(4)	587(4)	6932(3)	52(1)
C(2)	6989(7)	-465(6)	6387(3)	134(3)
C(3)	8139(3)	3992(4)	8454(2)	39(1)
C(4)	7804(4)	4115(4)	9191(2)	61(1)
C(5)	11422(4)	5077(5)	6773(4)	74(2)
C(6)	10204(3)	4646(4)	6746(2)	43(1)
C(7)	9400(3)	5516(4)	6426(2)	47(1)
C(8)	8234(3)	5349(4)	6192(2)	43(1)
C(9)	7680(3)	6307(5)	5649(3)	64(1)
C(10)	10874(4)	2520(4)	7128(3)	51(1)
C(11)	10599(9)	1394(13)	6701(6)	43(3)
C(12)	10389(10)	1430(13)	5958(6)	71(3)
C(13)	10098(12)	408(17)	5533(6)	95(5)
C(14)	10009(11)	-770(10)	5844(8)	84(3)
C(15)	10127(12)	-878(8)	6580(6)	106(5)

C(16)	10429(12)	160(8)	6990(6)	87(4)
C(11')	10440(20)	1440(30)	6487(15)	42(6)
C(12')	9927(18)	1760(20)	5818(13)	61(7)
C(13')	9610(20)	810(20)	5274(15)	88(9)
C(14')	10000(30)	-260(30)	5460(17)	92(11)
C(15')	10640(20)	-600(20)	6131(16)	88(8)
C(16')	10920(20)	330(30)	6692(17)	98(8)
C(17)	11011(5)	2224(5)	7935(3)	78(2)
C(18)	6473(3)	4236(4)	6077(3)	52(1)
C(19)	5625(4)	4879(5)	6400(3)	62(1)
C(20)	4502(4)	4662(7)	6109(4)	85(2)
C(21)	4223(5)	3856(8)	5548(4)	103(2)
C(22)	5062(5)	3255(7)	5229(3)	91(2)
C(23)	6207(4)	3411(5)	5489(3)	65(1)
C(24)	5919(4)	5767(5)	7027(3)	73(2)
C(25)	7122(4)	2789(5)	5134(3)	77(2)
C(26)	4784(5)	1972(5)	9986(3)	73(2)
C(27)	5783(3)	1564(4)	9590(2)	46(1)
C(28)	6699(3)	1061(4)	10054(2)	48(1)
C(29)	7685(3)	438(4)	9882(2)	42(1)
C(30)	8355(4)	-293(4)	10488(2)	61(1)
C(31)	4650(4)	2065(5)	8411(3)	59(1)
C(32)	4329(4)	996(5)	7872(3)	63(1)
C(33)	4130(6)	1170(8)	7130(4)	112(2)
C(34)	3823(9)	170(12)	6664(5)	158(4)
C(35)	3687(8)	-1007(11)	6946(6)	154(4)
C(36)	3884(6)	-1202(7)	7669(5)	120(3)
C(37)	4206(5)	-212(6)	8131(4)	84(2)
C(38)	4806(5)	3330(5)	8062(3)	95(2)
C(39)	8954(3)	-322(4)	9070(2)	36(1)
C(40)	8720(3)	-1499(3)	8741(2)	41(1)
C(41)	9641(4)	-2177(4)	8541(2)	49(1)
C(42)	10728(4)	-1714(4)	8666(2)	56(1)
C(43)	10944(4)	-562(4)	9009(2)	48(1)
C(44)	10064(4)	165(4)	9215(2)	42(1)
C(45)	7537(4)	-2041(4)	8631(3)	59(1)

C(46)	10309(3)	1411(5)	9585(2)	53(1)

Table S3c. Bond lengths [Å] and angles [°] for **1**.

Zn(1)-O(1)	1.972(3)	C(10)-C(11)	1.447(13)
Zn(1)-N(1)	1.979(3)	C(11)-C(16)	1.439(16)
Zn(1)-N(2)	1.984(3)	C(11)-C(12)	1.372(14)
Zn(1)-O(3)	2.041(2)	C(12)-C(13)	1.358(17)
Zn(2)-O(2)	1.920(3)	C(13)-C(14)	1.387(19)
Zn(2)-N(3)	1.968(3)	C(14)-C(15)	1.362(15)
Zn(2)-N(4)	1.968(3)	C(15)-C(16)	1.359(12)
Zn(2)-O(3)	2.021(2)	C(11')-C(12')	1.36(3)
F(1)-C(5)	1.373(6)	C(11')-C(16')	1.33(4)
F(2)-C(5)	1.332(6)	C(12')-C(13')	1.44(4)
F(3)-C(5)	1.317(6)	C(13')-C(14')	1.26(4)
F(4)-C(26)	1.326(6)	C(14')-C(15')	1.41(4)
F(5)-C(26)	1.331(6)	C(15')-C(16')	1.44(3)
F(6)-C(26)	1.362(6)	C(18)-C(19)	1.411(6)
O(1)-C(1)	1.221(5)	C(18)-C(23)	1.403(7)
O(2)-C(1)	1.247(5)	C(19)-C(20)	1.383(7)
O(3)-C(3)	1.323(5)	C(19)-C(24)	1.504(7)
O(4)-C(3)	1.206(5)	C(20)-C(21)	1.355(8)
N(1)-C(6)	1.319(5)	C(21)-C(22)	1.379(8)
N(1)-C(10)	1.475(5)	C(22)-C(23)	1.384(6)
N(2)-C(8)	1.318(5)	C(23)-C(25)	1.496(6)
N(2)-C(18)	1.439(5)	C(26)-C(27)	1.538(6)
N(3)-C(27)	1.319(5)	C(27)-C(28)	1.397(6)
N(3)-C(31)	1.485(6)	C(28)-C(29)	1.413(5)
N(4)-C(29)	1.325(5)	C(29)-C(30)	1.502(6)
N(4)-C(39)	1.457(5)	C(31)-C(32)	1.527(7)
C(1)-C(2)	1.514(7)	C(31)-C(38)	1.512(7)
C(3)-C(4)	1.483(6)	C(32)-C(37)	1.384(7)
C(5)-C(6)	1.506(6)	C(32)-C(33)	1.380(8)
C(6)-C(7)	1.397(6)	C(33)-C(34)	1.388(12)
C(7)-C(8)	1.400(6)	C(34)-C(35)	1.372(12)
C(8)-C(9)	1.518(6)	C(35)-C(36)	1.350(11)
C(10)-C(11')	1.69(3)	C(36)-C(37)	1.378(8)
C(10)-C(17)	1.520(6)	C(39)-C(40)	1.401(5)

C(39)-C(44)	1.401(5)	C(39)-N(4)-Zn(2)	119.1(2)
C(40)-C(41)	1.396(5)	O(1)-C(1)-O(2)	126.8(4)
C(40)-C(45)	1.501(5)	O(1)-C(1)-C(2)	116.8(4)
C(41)-C(42)	1.367(6)	O(2)-C(1)-C(2)	116.3(4)
C(42)-C(43)	1.386(6)	O(4)-C(3)-O(3)	118.7(4)
C(43)-C(44)	1.389(5)	O(4)-C(3)-C(4)	123.5(4)
C(44)-C(46)	1.501(6)	O(3)-C(3)-C(4)	117.7(4)
		F(3)-C(5)-F(2)	105.7(5)
O(1)-Zn(1)-N(1)	116.06(13)	F(3)-C(5)-F(1)	105.0(5)
O(1)-Zn(1)-N(2)	104.42(15)	F(2)-C(5)-F(1)	106.4(4)
N(1)-Zn(1)-N(2)	97.68(13)	F(3)-C(5)-C(6)	115.3(4)
O(1)-Zn(1)-O(3)	94.54(11)	F(2)-C(5)-C(6)	113.6(5)
N(1)-Zn(1)-O(3)	122.32(12)	F(1)-C(5)-C(6)	110.1(5)
N(2)-Zn(1)-O(3)	121.63(12)	N(1)-C(6)-C(7)	126.5(4)
O(2)-Zn(2)-N(3)	119.36(14)	N(1)-C(6)-C(5)	119.4(4)
O(2)-Zn(2)-N(4)	110.65(13)	C(7)-C(6)-C(5)	114.0(4)
N(3)-Zn(2)-N(4)	99.09(13)	C(6)-C(7)-C(8)	129.3(4)
O(2)-Zn(2)-O(3)	99.06(11)	N(2)-C(8)-C(7)	123.0(4)
N(3)-Zn(2)-O(3)	115.17(11)	N(2)-C(8)-C(9)	120.7(4)
N(4)-Zn(2)-O(3)	114.28(12)	C(7)-C(8)-C(9)	116.1(4)
C(1)-O(1)-Zn(1)	139.9(3)	N(1)-C(10)-C(11')	101.6(10)
C(1)-O(2)-Zn(2)	135.0(3)	N(1)-C(10)-C(17)	108.7(4)
C(3)-O(3)-Zn(2)	128.8(2)	C(11')-C(10)-C(17)	122.6(11)
C(3)-O(3)-Zn(1)	106.6(2)	N(1)-C(10)-C(11)	111.8(5)
Zn(2)-O(3)-Zn(1)	124.55(12)	C(11')-C(10)-C(11)	12.6(12)
C(6)-N(1)-C(10)	123.6(3)	C(17)-C(10)-C(11)	111.0(6)
C(6)-N(1)-Zn(1)	116.3(3)	C(16)-C(11)-C(12)	112.7(10)
C(10)-N(1)-Zn(1)	120.1(3)	C(16)-C(11)-C(10)	125.3(8)
C(8)-N(2)-C(18)	119.1(4)	C(12)-C(11)-C(10)	121.8(11)
C(8)-N(2)-Zn(1)	120.0(3)	C(13)-C(12)-C(11)	124.1(13)
C(18)-N(2)-Zn(1)	120.8(3)	C(12)-C(13)-C(14)	120.3(11)
C(27)-N(3)-C(31)	123.3(3)	C(15)-C(14)-C(13)	119.4(10)
C(27)-N(3)-Zn(2)	118.0(3)	C(16)-C(15)-C(14)	118.7(9)
C(31)-N(3)-Zn(2)	118.7(3)	C(11)-C(16)-C(15)	124.5(9)
C(29)-N(4)-C(39)	119.8(3)	C(12')-C(11')-C(16')	127(3)
C(29)-N(4)-Zn(2)	120.9(3)	C(12')-C(11')-C(10)	122(2)

C(16')-C(11')-C(10)	109(2)	C(27)-C(28)-C(29)	129.2(4)
C(13')-C(12')-C(11')	121(2)	N(4)-C(29)-C(28)	123.0(4)
C(14')-C(13')-C(12')	113(3)	N(4)-C(29)-C(30)	121.0(4)
C(13')-C(14')-C(15')	127(3)	C(28)-C(29)-C(30)	116.0(4)
C(14')-C(15')-C(16')	121(3)	N(3)-C(31)-C(32)	108.4(4)
C(11')-C(16')-C(15')	110(3)	N(3)-C(31)-C(38)	109.4(4)
C(19)-C(18)-C(23)	122.4(4)	C(32)-C(31)-C(38)	114.2(5)
C(19)-C(18)-N(2)	118.7(4)	C(37)-C(32)-C(33)	117.4(6)
C(23)-C(18)-N(2)	118.8(4)	C(37)-C(32)-C(31)	119.1(5)
C(20)-C(19)-C(18)	116.9(5)	C(33)-C(32)-C(31)	123.5(6)
C(20)-C(19)-C(24)	121.1(5)	C(32)-C(33)-C(34)	121.2(8)
C(18)-C(19)-C(24)	122.0(4)	C(35)-C(34)-C(33)	119.3(10)
C(21)-C(20)-C(19)	121.8(6)	C(36)-C(35)-C(34)	120.5(10)
C(20)-C(21)-C(22)	120.6(5)	C(35)-C(36)-C(37)	120.0(8)
C(23)-C(22)-C(21)	121.3(6)	C(36)-C(37)-C(32)	121.4(7)
C(22)-C(23)-C(18)	116.9(5)	C(40)-C(39)-C(44)	122.4(4)
C(22)-C(23)-C(25)	121.6(5)	C(40)-C(39)-N(4)	118.1(4)
C(18)-C(23)-C(25)	121.4(4)	C(44)-C(39)-N(4)	119.3(3)
F(5)-C(26)-F(4)	106.7(5)	C(39)-C(40)-C(41)	117.4(4)
F(5)-C(26)-F(6)	105.8(4)	C(39)-C(40)-C(45)	121.7(4)
F(4)-C(26)-F(6)	105.6(5)	C(41)-C(40)-C(45)	120.8(4)
F(5)-C(26)-C(27)	114.5(5)	C(42)-C(41)-C(40)	121.2(4)
F(4)-C(26)-C(27)	112.5(4)	C(41)-C(42)-C(43)	120.4(4)
F(6)-C(26)-C(27)	111.1(5)	C(44)-C(43)-C(42)	121.2(4)
N(3)-C(27)-C(28)	126.8(4)	C(43)-C(44)-C(39)	117.3(4)
N(3)-C(27)-C(26)	120.1(4)	C(43)-C(44)-C(46)	120.6(4)
C(28)-C(27)-C(26)	113.1(4)	C(39)-C(44)-C(46)	122.0(4)

Table S3d. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zn(1)	36(1)	39(1)	42(1)	3(1)	7(1)	-4(1)
Zn(2)	38(1)	34(1)	38(1)	3(1)	4(1)	-1(1)
F(1)	54(2)	137(3)	148(4)	26(3)	46(2)	-6(2)
F(2)	50(2)	80(2)	144(3)	9(2)	-27(2)	-13(2)
F(3)	53(2)	84(2)	246(5)	63(3)	-9(2)	-30(2)
F(4)	97(2)	76(2)	117(3)	-5(2)	39(2)	38(2)
F(5)	109(3)	139(3)	72(2)	-5(2)	43(2)	44(2)
F(6)	70(2)	112(3)	122(3)	0(3)	51(2)	-6(2)
O(1)	103(3)	53(2)	58(2)	-15(2)	35(2)	-34(2)
O(2)	77(2)	41(2)	47(2)	-6(1)	17(2)	-18(2)
O(3)	41(1)	32(2)	39(2)	-4(1)	3(1)	-4(1)
O(4)	97(3)	35(2)	85(3)	-12(2)	38(2)	-21(2)
N(1)	34(2)	43(2)	41(2)	1(2)	3(2)	2(2)
N(2)	28(2)	41(2)	49(2)	2(2)	5(2)	-4(2)
N(3)	38(2)	37(2)	51(2)	7(2)	7(2)	4(2)
N(4)	46(2)	31(2)	37(2)	0(2)	5(2)	0(2)
C(1)	59(3)	50(3)	48(3)	-13(2)	13(2)	-9(2)
C(2)	227(8)	96(5)	96(5)	-63(4)	82(6)	-97(6)
C(3)	41(3)	31(2)	43(3)	-4(2)	-1(2)	-1(2)
C(4)	80(3)	56(3)	45(3)	-17(2)	9(3)	-9(3)
C(5)	39(3)	69(4)	110(5)	22(3)	-3(3)	-6(3)
C(6)	30(2)	49(3)	51(3)	4(2)	6(2)	-7(2)
C(7)	40(2)	38(2)	63(3)	11(2)	9(2)	-6(2)
C(8)	39(2)	40(2)	50(3)	6(2)	7(2)	10(2)
C(9)	54(3)	57(3)	78(3)	26(3)	1(2)	7(3)
C(10)	42(3)	51(3)	57(3)	6(2)	1(2)	8(2)
C(11)	35(4)	58(6)	31(5)	-9(5)	-8(4)	21(4)
C(12)	78(7)	90(7)	46(6)	-3(6)	15(5)	-17(7)
C(13)	106(10)	145(14)	38(6)	-40(8)	22(7)	-40(11)
C(14)	107(9)	54(6)	89(10)	-28(6)	7(8)	-1(6)
C(15)	193(13)	45(5)	75(8)	-12(5)	-1(8)	-12(6)

C(16)	150(11)	40(5)	67(7)	0(4)	-3(7)	-4(6)
C(17)	88(4)	75(4)	64(4)	7(3)	-15(3)	26(3)
C(18)	30(2)	68(3)	54(3)	15(2)	-3(2)	-2(2)
C(19)	40(3)	77(4)	67(4)	18(3)	4(3)	5(3)
C(20)	33(3)	129(6)	92(5)	25(4)	6(3)	4(3)
C(21)	40(3)	178(8)	86(5)	16(5)	-15(3)	-20(4)
C(22)	66(3)	140(6)	60(4)	-4(4)	-13(3)	-19(4)
C(23)	50(3)	87(4)	54(3)	6(3)	-8(2)	-14(3)
C(24)	59(3)	75(4)	86(4)	5(3)	21(3)	14(3)
C(25)	79(4)	98(5)	47(3)	-13(3)	-7(3)	-4(3)
C(26)	69(4)	73(4)	80(4)	6(3)	28(3)	17(3)
C(27)	52(3)	38(3)	51(3)	2(2)	17(2)	7(2)
C(28)	59(3)	48(3)	39(3)	-3(2)	17(2)	2(2)
C(29)	55(3)	33(2)	38(3)	1(2)	6(2)	-3(2)
C(30)	85(4)	54(3)	43(3)	13(2)	13(3)	12(3)
C(31)	44(3)	65(3)	69(4)	10(3)	10(3)	10(3)
C(32)	40(3)	79(4)	69(4)	2(3)	0(3)	2(2)
C(33)	119(6)	133(7)	77(5)	5(5)	-12(4)	20(5)
C(34)	173(9)	197(12)	87(7)	-18(8)	-43(6)	43(9)
C(35)	128(7)	182(11)	135(10)	-59(8)	-43(7)	-21(7)
C(36)	121(6)	109(6)	124(7)	-25(5)	-2(6)	-26(5)
C(37)	78(4)	82(4)	91(5)	-3(4)	9(4)	-18(4)
C(38)	79(4)	78(5)	123(6)	42(4)	-9(4)	12(4)
C(39)	42(2)	34(2)	32(2)	6(2)	4(2)	4(2)
C(40)	51(3)	27(2)	43(2)	0(2)	5(2)	-2(2)
C(41)	63(3)	28(2)	57(3)	-1(2)	12(2)	7(2)
C(42)	63(3)	43(3)	65(3)	7(3)	18(2)	20(3)
C(43)	44(3)	51(3)	51(3)	5(2)	8(2)	5(2)
C(44)	45(3)	41(3)	36(3)	4(2)	-4(2)	4(2)
C(45)	63(3)	34(3)	77(3)	-5(2)	3(2)	-13(2)
C(46)	51(2)	54(3)	51(3)	-6(3)	-5(2)	-5(3)

Table S3e. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **1**.

	x	y	z	U(eq)
H(2A)	7113	-1273	6630	201
H(2B)	7478	-399	6010	201
H(2C)	6197	-398	6172	201
H(4A)	8041	4934	9390	91
H(4B)	8172	3457	9501	91
H(4C)	6982	4035	9163	91
H(7A)	9684	6329	6358	56
H(9A)	7528	5919	5174	95
H(9B)	8190	7019	5628	95
H(9C)	6968	6595	5798	95
H(10A)	11607	2859	7010	61
H(12A)	10449	2212	5728	85
H(13A)	9957	500	5026	114
H(14A)	9868	-1489	5549	101
H(15A)	10002	-1654	6800	127
H(16A)	10533	66	7497	105
H(12B)	9777	2615	5707	73
H(13B)	9153	978	4829	106
H(14B)	9857	-910	5115	110
H(15B)	10883	-1432	6212	105
H(16B)	11366	174	7140	118
H(17A)	11228	2984	8209	117
H(17B)	11598	1588	8047	117
H(17C)	10293	1911	8062	117
H(20A)	3917	5085	6307	102
H(21A)	3451	3706	5375	124
H(22A)	4852	2729	4827	109
H(24A)	6161	6570	6850	109
H(24B)	6534	5411	7365	109
H(24C)	5254	5893	7272	109

H(25A)	7532	3422	4895	115
H(25B)	6780	2184	4778	115
H(25C)	7649	2358	5498	115
H(28A)	6654	1149	10552	57
H(30A)	9010	-681	10315	91
H(30B)	7874	-942	10654	91
H(30C)	8614	273	10886	91
H(31A)	4036	2149	8720	71
H(33A)	4203	1981	6938	134
H(34A)	3710	297	6159	190
H(35A)	3454	-1682	6633	185
H(36A)	3801	-2014	7857	144
H(37A)	4346	-361	8633	101
H(38A)	5063	3944	8435	143
H(38B)	4086	3603	7796	143
H(38C)	5371	3255	7732	143
H(41A)	9510	-2967	8315	59
H(42A)	11334	-2179	8519	67
H(43A)	11699	-267	9105	58
H(45A)	7549	-2859	8399	88
H(45B)	7032	-1481	8325	88
H(45C)	7264	-2134	9096	88
H(46A)	11093	1652	9556	79
H(46B)	10194	1341	10090	79
H(46C)	9798	2046	9348	79

Table S4a. Crystal data and structure refinement for **3**.

Identification code	ce1	
Empirical formula	$C_{58}H_{60}F_6N_4O_4Zn_2$	
Formula weight	1121.84	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 13.5462(5) Å	α= 90°
	b = 19.2935(7) Å	β= 90°
	c = 20.7468(7) Å	γ = 90°
Volume	5422.3(3) $Å^3$	
Z	4	
Density (calculated)	1.374 Mg/m^3	
Absorption coefficient	0.955 mm^{-1}	
F(000)	2328	
Crystal size	0.40 x 0.40 x 0.40 mm^3	
Theta range for data collection	1.44 to 25.35°	
Index ranges	-8<=h<=16, -23<=k<=21, -20<=l<=24	
Reflections collected	18303	
Independent reflections	9628 [R(int) = 0.0203]	
Completeness to theta = 25.35°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7013 and 0.7013	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9628 / 0 / 677	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0271, wR2 = 0.0639	
R indices (all data)	R1 = 0.0319, wR2 = 0.0660	
Absolute structure parameter	0.005(7)	
Largest diff. peak and hole	0.296 and -0.201 $e \cdot Å^{-3}$	

Table S4b. 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)
Zn(1)	-6936(1)	4661(1)	1066(1)	23(1)
Zn(2)	-4415(1)	5133(1)	1160(1)	24(1)
F(1)	-9503(1)	6309(1)	845(1)	52(1)
F(2)	-10241(1)	5432(1)	437(1)	54(1)
F(3)	-10452(1)	5695(1)	1425(1)	56(1)
F(4)	-2796(1)	5202(1)	3088(1)	58(1)
F(5)	-1518(1)	4851(1)	2565(1)	48(1)
F(6)	-1724(1)	5930(1)	2760(1)	56(1)
O(1)	-6173(1)	4034(1)	532(1)	31(1)
O(2)	-4635(1)	4449(1)	466(1)	36(1)
O(3)	-5846(1)	5257(1)	1412(1)	26(1)
O(4)	-5127(1)	5936(1)	2120(1)	40(1)
N(1)	-7570(2)	4114(1)	1756(1)	27(1)
N(2)	-8093(1)	5180(1)	760(1)	25(1)
N(3)	-3811(1)	5969(1)	761(1)	24(1)
N(4)	-3354(1)	4891(1)	1768(1)	26(1)
C(1)	-5301(2)	4022(1)	329(1)	28(1)
C(2)	-5015(2)	3432(1)	-103(1)	44(1)
C(3)	-5880(2)	5719(1)	1886(1)	26(1)
C(4)	-6882(2)	5967(2)	2091(1)	41(1)
C(5)	-8940(2)	3846(2)	2497(1)	38(1)
C(6)	-8465(2)	4260(1)	1957(1)	27(1)
C(7)	-9048(2)	4802(1)	1690(1)	30(1)
C(8)	-8895(2)	5190(1)	1142(1)	28(1)
C(9)	-9770(2)	5655(1)	964(1)	37(1)
C(10)	-7520(2)	6243(1)	220(1)	40(1)
C(11)	-8032(2)	5546(1)	132(1)	29(1)
C(12)	-7498(2)	5079(1)	-352(1)	28(1)
C(13)	-6593(2)	5252(1)	-600(1)	36(1)
C(14)	-6101(2)	4842(1)	-1053(1)	41(1)
C(15)	-6520(2)	4245(2)	-1260(1)	40(1)

C(16)	-7444(2)	4024(1)	-1023(1)	34(1)
C(17)	-7881(2)	3402(1)	-1238(1)	42(1)
C(18)	-8778(2)	3197(2)	-1031(1)	48(1)
C(19)	-9287(2)	3606(2)	-579(1)	47(1)
C(20)	-8887(2)	4207(1)	-351(1)	34(1)
C(21)	-7951(2)	4440(1)	-563(1)	29(1)
C(22)	-7049(2)	3523(1)	2021(1)	32(1)
C(23)	-7074(2)	2906(1)	1671(2)	41(1)
C(24)	-6529(2)	2347(2)	1910(2)	59(1)
C(25)	-5991(2)	2411(2)	2473(2)	68(1)
C(26)	-5985(2)	3019(2)	2801(2)	59(1)
C(27)	-6509(2)	3599(2)	2591(1)	42(1)
C(28)	-7683(2)	2838(1)	1067(2)	47(1)
C(29)	-7422(3)	2264(2)	618(2)	95(2)
C(30)	-6476(3)	4275(2)	2953(2)	55(1)
C(31)	-5623(3)	4406(3)	3374(2)	134(2)
C(32)	-2637(2)	6946(1)	813(1)	39(1)
C(33)	-3112(2)	6295(1)	1076(1)	26(1)
C(34)	-2724(2)	6065(1)	1675(1)	28(1)
C(35)	-2808(2)	5424(1)	1963(1)	28(1)
C(36)	-2207(2)	5353(2)	2589(1)	41(1)
C(37)	-4086(2)	3734(2)	1875(2)	46(1)
C(38)	-3169(2)	4182(1)	1999(1)	31(1)
C(39)	-2278(2)	3854(1)	1665(1)	28(1)
C(40)	-1768(2)	3285(1)	1953(1)	30(1)
C(41)	-2014(2)	3008(1)	2565(1)	35(1)
C(42)	-1488(2)	2467(1)	2826(2)	45(1)
C(43)	-698(2)	2173(1)	2489(2)	48(1)
C(44)	-442(2)	2420(1)	1902(2)	45(1)
C(45)	-955(2)	2982(1)	1615(1)	35(1)
C(46)	-677(2)	3247(1)	1006(2)	41(1)
C(47)	-1178(2)	3786(2)	747(1)	40(1)
C(48)	-1982(2)	4089(1)	1073(1)	34(1)
C(49)	-4169(2)	6242(1)	160(1)	26(1)
C(50)	-3874(2)	5936(1)	-421(1)	34(1)
C(51)	-4252(2)	6210(2)	-996(1)	41(1)

C(52)	-4897(2)	6756(2)	-992(1)	43(1)
C(53)	-5193(2)	7045(1)	-416(1)	39(1)
C(54)	-4845(2)	6794(1)	171(1)	30(1)
C(55)	-3151(2)	5344(1)	-449(1)	41(1)
C(56)	-2092(2)	5583(2)	-536(2)	58(1)
C(57)	-5173(2)	7096(1)	805(1)	39(1)
C(58)	-5880(2)	7700(2)	776(2)	49(1)

Table S4c. Bond lengths [Å] and angles [°] for **3**.

Zn(1)-O(1)	1.9387(16)	C(12)-C(13)	1.371(3)
Zn(1)-N(2)	1.9657(19)	C(12)-C(21)	1.444(3)
Zn(1)-N(1)	1.977(2)	C(13)-C(14)	1.397(4)
Zn(1)-O(3)	2.0049(16)	C(14)-C(15)	1.354(4)
Zn(2)-N(4)	1.9682(19)	C(15)-C(16)	1.411(4)
Zn(2)-O(2)	1.9767(17)	C(16)-C(17)	1.411(4)
Zn(2)-N(3)	1.9880(19)	C(16)-C(21)	1.424(3)
Zn(2)-O(3)	2.0228(15)	C(17)-C(18)	1.349(4)
F(1)-C(9)	1.336(3)	C(18)-C(19)	1.406(4)
F(2)-C(9)	1.337(3)	C(19)-C(20)	1.365(4)
F(3)-C(9)	1.332(3)	C(20)-C(21)	1.415(3)
F(4)-C(36)	1.340(3)	C(22)-C(23)	1.395(4)
F(5)-C(36)	1.346(3)	C(22)-C(27)	1.398(4)
F(6)-C(36)	1.341(3)	C(23)-C(24)	1.398(4)
O(1)-C(1)	1.254(3)	C(23)-C(28)	1.505(4)
O(2)-C(1)	1.254(3)	C(24)-C(25)	1.380(5)
O(3)-C(3)	1.327(3)	C(25)-C(26)	1.357(5)
O(4)-C(3)	1.205(3)	C(26)-C(27)	1.396(4)
N(1)-C(6)	1.312(3)	C(27)-C(30)	1.505(4)
N(1)-C(22)	1.450(3)	C(28)-C(29)	1.490(4)
N(2)-C(8)	1.345(3)	C(30)-C(31)	1.472(5)
N(2)-C(11)	1.485(3)	C(32)-C(33)	1.512(3)
N(3)-C(33)	1.312(3)	C(33)-C(34)	1.421(3)
N(3)-C(49)	1.438(3)	C(34)-C(35)	1.377(4)
N(4)-C(35)	1.330(3)	C(35)-C(36)	1.539(4)
N(4)-C(38)	1.470(3)	C(37)-C(38)	1.536(4)
C(1)-C(2)	1.500(3)	C(38)-C(39)	1.528(3)
C(3)-C(4)	1.502(4)	C(39)-C(48)	1.369(4)
C(5)-C(6)	1.519(3)	C(39)-C(40)	1.428(3)
C(6)-C(7)	1.423(3)	C(40)-C(41)	1.417(4)
C(7)-C(8)	1.376(3)	C(40)-C(45)	1.430(4)
C(8)-C(9)	1.532(3)	C(41)-C(42)	1.374(4)
C(10)-C(11)	1.523(3)	C(42)-C(43)	1.400(4)
C(11)-C(12)	1.531(3)	C(43)-C(44)	1.351(4)

C(44)-C(45)	1.420(4)	C(8)-N(2)-Zn(1)	117.45(15)
C(45)-C(46)	1.415(4)	C(11)-N(2)-Zn(1)	118.74(15)
C(46)-C(47)	1.353(4)	C(33)-N(3)-C(49)	120.0(2)
C(47)-C(48)	1.410(4)	C(33)-N(3)-Zn(2)	118.62(16)
C(49)-C(50)	1.401(4)	C(49)-N(3)-Zn(2)	121.29(15)
C(49)-C(54)	1.406(4)	C(35)-N(4)-C(38)	121.7(2)
C(50)-C(51)	1.401(4)	C(35)-N(4)-Zn(2)	114.61(16)
C(50)-C(55)	1.506(4)	C(38)-N(4)-Zn(2)	123.66(16)
C(51)-C(52)	1.370(4)	O(1)-C(1)-O(2)	126.1(2)
C(52)-C(53)	1.380(4)	O(1)-C(1)-C(2)	117.2(2)
C(53)-C(54)	1.392(4)	O(2)-C(1)-C(2)	116.6(2)
C(54)-C(57)	1.506(4)	O(4)-C(3)-O(3)	120.3(2)
C(55)-C(56)	1.519(4)	O(4)-C(3)-C(4)	122.7(2)
C(57)-C(58)	1.511(4)	O(3)-C(3)-C(4)	117.0(2)
		N(1)-C(6)-C(7)	123.2(2)
O(1)-Zn(1)-N(2)	123.93(8)	N(1)-C(6)-C(5)	120.8(2)
O(1)-Zn(1)-N(1)	108.21(8)	C(7)-C(6)-C(5)	116.0(2)
N(2)-Zn(1)-N(1)	99.15(8)	C(8)-C(7)-C(6)	129.6(2)
O(1)-Zn(1)-O(3)	99.85(7)	N(2)-C(8)-C(7)	127.0(2)
N(2)-Zn(1)-O(3)	114.27(7)	N(2)-C(8)-C(9)	119.4(2)
N(1)-Zn(1)-O(3)	111.53(8)	C(7)-C(8)-C(9)	113.6(2)
N(4)-Zn(2)-O(2)	114.76(8)	F(3)-C(9)-F(1)	105.4(2)
N(4)-Zn(2)-N(3)	99.19(8)	F(3)-C(9)-F(2)	106.1(2)
O(2)-Zn(2)-N(3)	107.48(8)	F(1)-C(9)-F(2)	106.3(2)
N(4)-Zn(2)-O(3)	124.18(7)	F(3)-C(9)-C(8)	113.4(2)
O(2)-Zn(2)-O(3)	97.04(7)	F(1)-C(9)-C(8)	112.8(2)
N(3)-Zn(2)-O(3)	113.95(7)	F(2)-C(9)-C(8)	112.2(2)
C(1)-O(1)-Zn(1)	134.82(17)	N(2)-C(11)-C(10)	109.9(2)
C(1)-O(2)-Zn(2)	135.44(16)	N(2)-C(11)-C(12)	108.75(18)
C(3)-O(3)-Zn(1)	128.73(14)	C(10)-C(11)-C(12)	112.6(2)
C(3)-O(3)-Zn(2)	107.68(14)	C(13)-C(12)-C(21)	118.3(2)
Zn(1)-O(3)-Zn(2)	123.03(8)	C(13)-C(12)-C(11)	121.6(2)
C(6)-N(1)-C(22)	120.0(2)	C(21)-C(12)-C(11)	120.1(2)
C(6)-N(1)-Zn(1)	121.12(17)	C(12)-C(13)-C(14)	122.7(2)
C(22)-N(1)-Zn(1)	118.85(16)	C(15)-C(14)-C(13)	119.7(3)
C(8)-N(2)-C(11)	123.8(2)	C(14)-C(15)-C(16)	121.2(3)

C(15)-C(16)-C(17)	121.3(3)	F(6)-C(36)-C(35)	114.1(2)
C(15)-C(16)-C(21)	119.5(2)	F(5)-C(36)-C(35)	113.6(2)
C(17)-C(16)-C(21)	119.3(2)	N(4)-C(38)-C(39)	111.9(2)
C(18)-C(17)-C(16)	121.8(3)	N(4)-C(38)-C(37)	109.3(2)
C(17)-C(18)-C(19)	119.3(3)	C(39)-C(38)-C(37)	109.3(2)
C(20)-C(19)-C(18)	120.9(3)	C(48)-C(39)-C(40)	119.2(2)
C(19)-C(20)-C(21)	121.2(3)	C(48)-C(39)-C(38)	120.1(2)
C(20)-C(21)-C(16)	117.5(2)	C(40)-C(39)-C(38)	120.7(2)
C(20)-C(21)-C(12)	123.9(2)	C(41)-C(40)-C(39)	123.4(2)
C(16)-C(21)-C(12)	118.6(2)	C(41)-C(40)-C(45)	117.8(2)
C(23)-C(22)-C(27)	122.9(3)	C(39)-C(40)-C(45)	118.8(2)
C(23)-C(22)-N(1)	117.5(2)	C(42)-C(41)-C(40)	121.2(3)
C(27)-C(22)-N(1)	119.5(2)	C(41)-C(42)-C(43)	120.4(3)
C(22)-C(23)-C(24)	117.3(3)	C(44)-C(43)-C(42)	120.3(3)
C(22)-C(23)-C(28)	121.4(2)	C(43)-C(44)-C(45)	121.4(3)
C(24)-C(23)-C(28)	121.3(3)	C(46)-C(45)-C(44)	121.4(3)
C(25)-C(24)-C(23)	120.8(3)	C(46)-C(45)-C(40)	119.7(2)
C(26)-C(25)-C(24)	120.3(3)	C(44)-C(45)-C(40)	118.9(3)
C(25)-C(26)-C(27)	122.2(3)	C(47)-C(46)-C(45)	119.9(3)
C(26)-C(27)-C(22)	116.5(3)	C(46)-C(47)-C(48)	121.0(3)
C(26)-C(27)-C(30)	121.6(3)	C(39)-C(48)-C(47)	121.4(2)
C(22)-C(27)-C(30)	121.9(3)	C(50)-C(49)-C(54)	121.3(2)
C(29)-C(28)-C(23)	117.0(3)	C(50)-C(49)-N(3)	119.8(2)
C(31)-C(30)-C(27)	118.0(3)	C(54)-C(49)-N(3)	118.9(2)
N(3)-C(33)-C(34)	123.5(2)	C(49)-C(50)-C(51)	118.0(3)
N(3)-C(33)-C(32)	121.7(2)	C(49)-C(50)-C(55)	122.5(2)
C(34)-C(33)-C(32)	114.8(2)	C(51)-C(50)-C(55)	119.4(2)
C(35)-C(34)-C(33)	129.0(2)	C(52)-C(51)-C(50)	121.2(3)
N(4)-C(35)-C(34)	127.5(2)	C(51)-C(52)-C(53)	120.1(3)
N(4)-C(35)-C(36)	118.7(2)	C(52)-C(53)-C(54)	121.2(3)
C(34)-C(35)-C(36)	113.7(2)	C(53)-C(54)-C(49)	118.1(3)
F(4)-C(36)-F(6)	105.4(2)	C(53)-C(54)-C(57)	122.0(2)
F(4)-C(36)-F(5)	106.6(2)	C(49)-C(54)-C(57)	119.9(2)
F(6)-C(36)-F(5)	105.5(2)	C(50)-C(55)-C(56)	112.8(2)
F(4)-C(36)-C(35)	111.0(2)	C(54)-C(57)-C(58)	116.7(2)

Table S4d. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zn(1)	19(1)	25(1)	25(1)	2(1)	1(1)	1(1)
Zn(2)	20(1)	26(1)	28(1)	1(1)	2(1)	-1(1)
F(1)	45(1)	31(1)	80(1)	4(1)	3(1)	14(1)
F(2)	35(1)	63(1)	64(1)	-8(1)	-20(1)	14(1)
F(3)	31(1)	67(1)	69(1)	4(1)	13(1)	23(1)
F(4)	68(1)	83(1)	24(1)	5(1)	-2(1)	12(1)
F(5)	44(1)	51(1)	50(1)	3(1)	-18(1)	14(1)
F(6)	69(1)	50(1)	50(1)	-7(1)	-33(1)	5(1)
O(1)	26(1)	31(1)	36(1)	-6(1)	4(1)	0(1)
O(2)	33(1)	40(1)	34(1)	-10(1)	8(1)	-5(1)
O(3)	20(1)	29(1)	29(1)	-6(1)	1(1)	-1(1)
O(4)	34(1)	43(1)	45(1)	-15(1)	-2(1)	-4(1)
N(1)	24(1)	29(1)	28(1)	4(1)	2(1)	0(1)
N(2)	23(1)	26(1)	25(1)	0(1)	-3(1)	1(1)
N(3)	22(1)	27(1)	23(1)	2(1)	2(1)	-2(1)
N(4)	23(1)	30(1)	26(1)	2(1)	1(1)	6(1)
C(1)	31(2)	28(1)	26(2)	1(1)	0(1)	2(1)
C(2)	40(2)	41(2)	49(2)	-15(1)	2(1)	5(1)
C(3)	28(1)	25(1)	26(1)	-1(1)	3(1)	-3(1)
C(4)	36(2)	46(2)	42(2)	-16(1)	4(1)	6(1)
C(5)	28(2)	47(2)	40(2)	8(1)	8(1)	-5(1)
C(6)	22(1)	32(1)	27(1)	-1(1)	3(1)	-4(1)
C(7)	20(1)	36(1)	33(2)	-4(1)	5(1)	1(1)
C(8)	20(1)	28(1)	35(1)	-6(1)	-4(1)	2(1)
C(9)	28(1)	39(2)	44(2)	-1(1)	-2(1)	8(1)
C(10)	48(2)	30(1)	42(2)	2(1)	4(1)	-3(1)
C(11)	27(1)	28(1)	31(1)	2(1)	-5(1)	2(1)
C(12)	30(1)	29(1)	25(1)	3(1)	-6(1)	5(1)
C(13)	35(1)	37(2)	37(2)	2(1)	-1(1)	-6(1)
C(14)	33(1)	51(2)	41(2)	2(2)	9(1)	2(1)
C(15)	39(2)	45(2)	35(2)	-1(1)	7(1)	6(1)

C(16)	41(2)	34(1)	27(2)	4(1)	1(1)	6(1)
C(17)	56(2)	36(1)	33(2)	-6(1)	2(1)	5(1)
C(18)	66(2)	38(2)	40(2)	-11(1)	3(2)	-13(1)
C(19)	54(2)	44(2)	43(2)	-9(1)	7(2)	-17(2)
C(20)	35(2)	34(1)	32(2)	-4(1)	-1(1)	-5(1)
C(21)	31(1)	30(1)	25(1)	5(1)	-2(1)	1(1)
C(22)	21(1)	36(1)	39(2)	16(1)	8(1)	2(1)
C(23)	31(2)	33(1)	61(2)	15(1)	12(1)	-2(1)
C(24)	47(2)	34(2)	97(3)	22(2)	17(2)	4(1)
C(25)	42(2)	56(2)	107(3)	54(2)	7(2)	7(2)
C(26)	40(2)	70(2)	68(2)	50(2)	-1(2)	-1(2)
C(27)	27(2)	57(2)	41(2)	25(2)	4(1)	-2(1)
C(28)	41(2)	38(2)	64(2)	-7(2)	1(2)	0(1)
C(29)	91(3)	77(3)	116(4)	-47(3)	-15(3)	9(3)
C(30)	57(2)	59(2)	48(2)	7(2)	-19(2)	2(2)
C(31)	70(3)	218(6)	113(4)	-110(4)	-28(3)	48(4)
C(32)	40(2)	39(2)	38(2)	4(1)	-1(1)	-10(1)
C(33)	20(1)	28(1)	28(1)	-2(1)	3(1)	1(1)
C(34)	19(1)	36(1)	29(2)	-5(1)	-2(1)	2(1)
C(35)	22(1)	39(2)	25(1)	-3(1)	1(1)	7(1)
C(36)	47(2)	41(2)	36(2)	1(1)	-8(1)	9(1)
C(37)	33(2)	44(2)	61(2)	16(2)	11(2)	1(1)
C(38)	31(2)	34(1)	27(1)	6(1)	3(1)	4(1)
C(39)	26(1)	26(1)	32(2)	-1(1)	-2(1)	-2(1)
C(40)	28(1)	23(1)	38(2)	-1(1)	-8(1)	-3(1)
C(41)	38(2)	29(1)	39(2)	3(1)	-8(1)	-4(1)
C(42)	60(2)	30(1)	44(2)	5(1)	-21(2)	-8(1)
C(43)	50(2)	29(1)	66(2)	-1(2)	-27(2)	2(1)
C(44)	39(2)	28(1)	67(2)	-10(1)	-14(2)	5(1)
C(45)	31(1)	26(1)	48(2)	-7(1)	-10(1)	-2(1)
C(46)	33(2)	36(1)	53(2)	-13(1)	6(1)	3(1)
C(47)	39(2)	43(2)	38(2)	0(1)	10(1)	2(1)
C(48)	34(1)	35(1)	33(2)	6(1)	4(1)	5(1)
C(49)	29(1)	27(1)	23(1)	5(1)	-1(1)	-8(1)
C(50)	37(2)	37(1)	28(2)	2(1)	5(1)	-8(1)
C(51)	45(2)	53(2)	25(2)	3(1)	1(1)	-15(1)

C(52)	49(2)	50(2)	29(2)	12(1)	-11(1)	-13(1)
C(53)	39(2)	37(2)	39(2)	11(1)	-10(1)	-8(1)
C(54)	33(1)	29(1)	29(2)	4(1)	-5(1)	-7(1)
C(55)	49(2)	46(2)	28(2)	-5(1)	10(1)	-3(2)
C(56)	41(2)	67(2)	65(2)	-14(2)	-7(2)	2(2)
C(57)	44(2)	37(2)	36(2)	-3(1)	-8(1)	7(1)
C(58)	50(2)	43(2)	54(2)	-8(2)	-13(2)	13(1)

Table S4e. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **3**.

	x	y	z	U(eq)
H(2A)	-4670	3077	149	65
H(2B)	-4579	3602	-445	65
H(2C)	-5610	3230	-296	65
H(4A)	-6820	6247	2483	62
H(4B)	-7309	5567	2177	62
H(4C)	-7172	6249	1746	62
H(5A)	-8785	3353	2442	57
H(5B)	-9657	3911	2484	57
H(5C)	-8684	4006	2912	57
H(7A)	-9629	4913	1925	36
H(10A)	-7895	6526	526	60
H(10B)	-7486	6483	-196	60
H(10C)	-6851	6168	385	60
H(11A)	-8717	5631	-28	34
H(13A)	-6287	5668	-459	44
H(14A)	-5475	4981	-1214	50
H(15A)	-6185	3970	-1571	48
H(17A)	-7534	3120	-1538	50
H(18A)	-9063	2780	-1188	58
H(19A)	-9917	3461	-430	56
H(20A)	-9244	4474	-45	40
H(24A)	-6528	1920	1684	71
H(25A)	-5624	2027	2630	82
H(26A)	-5611	3051	3188	71
H(28A)	-8210	3148	976	57
H(29A)	-6718	2289	513	142
H(29B)	-7812	2307	222	142
H(29C)	-7565	1818	824	142
H(30A)	-6990	4606	2910	66
H(31A)	-5643	4088	3742	200

H(31B)	-5646	4885	3530	200
H(31C)	-5011	4332	3131	200
H(32A)	-3004	7104	433	59
H(32B)	-1952	6847	692	59
H(32C)	-2649	7309	1144	59
H(34A)	-2356	6399	1910	33
H(37A)	-4669	3963	2058	68
H(37B)	-3999	3280	2079	68
H(37C)	-4177	3672	1410	68
H(38A)	-3040	4198	2473	37
H(41A)	-2552	3199	2799	43
H(42A)	-1663	2292	3239	54
H(43A)	-340	1799	2672	58
H(44A)	93	2212	1677	54
H(46A)	-139	3047	778	49
H(47A)	-984	3963	338	48
H(48A)	-2324	4464	879	41
H(51A)	-4056	6013	-1396	50
H(52A)	-5141	6937	-1387	51
H(53A)	-5644	7423	-419	46
H(55A)	-3331	5034	-811	49
H(55B)	-3200	5072	-46	49
H(56A)	-2043	5871	-925	87
H(56B)	-1659	5179	-580	87
H(56C)	-1889	5855	-160	87
H(57A)	-4577	7246	1044	47
H(57B)	-5487	6722	1059	47
H(58A)	-5589	8073	517	73
H(58B)	-6009	7870	1213	73
H(58C)	-6501	7550	578	73

Table S5a. Crystal data and structure refinement for **4**.

Identification code	ce10	
Empirical formula	$C_{48}H_{54}F_6N_4O_4Zn_2$	
Formula weight	995.69	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 12.1107(3) Å	α= 90°
	b = 19.7360(8) Å	β= 90°
	c = 20.3350(8) Å	γ = 90°
Volume	4860.4(3) $Å^3$	
Z	4	
Density (calculated)	1.361 Mg/m^3	
Absorption coefficient	1.055 mm^{-1}	
F(000)	2064	
Crystal size	0.40 x 0.10 x 0.10 mm^3	
Theta range for data collection	1.96 to 25.35°	
Index ranges	-14<=h<=14, 0<=k<=23, 0<=l<=24	
Reflections collected	8828	
Independent reflections	8828 [R(int) = 0.0410]	
Completeness to theta = 25.35°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9018 and 0.6776	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8828 / 0 / 587	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	R1 = 0.0434, wR2 = 0.0788	
R indices (all data)	R1 = 0.0734, wR2 = 0.0909	
Absolute structure parameter	-0.004(10)	
Largest diff. peak and hole	0.347 and -0.367 $e \cdot Å^{-3}$	

Table S5b. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **4**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zn(1)	-725(1)	1102(1)	6022(1)	29(1)
Zn(2)	896(1)	1455(1)	7734(1)	30(1)
F(1)	-4523(2)	1224(1)	4836(1)	42(1)
F(2)	-4565(2)	1433(1)	5867(1)	41(1)
F(3)	-4497(2)	400(1)	5527(1)	41(1)
F(4)	4477(2)	2164(2)	8998(2)	78(1)
F(5)	4779(2)	1356(2)	8319(2)	67(1)
F(6)	4471(2)	2367(2)	7960(2)	70(1)
O(1)	221(2)	420(2)	6402(2)	42(1)
O(2)	377(2)	564(2)	7480(2)	42(1)
O(3)	-385(2)	2044(2)	6243(2)	45(1)
O(4)	209(2)	2208(2)	7265(2)	48(1)
N(1)	-416(2)	1003(2)	5076(2)	26(1)
N(2)	-2328(2)	964(2)	6006(2)	28(1)
N(3)	465(2)	1631(2)	8653(2)	32(1)
N(4)	2519(3)	1526(2)	7813(2)	34(1)
C(1)	429(3)	212(2)	6963(3)	33(1)
C(2)	775(5)	-513(2)	7028(3)	63(2)
C(3)	-156(3)	2406(2)	6727(3)	35(1)
C(4)	-367(5)	3148(2)	6651(3)	67(2)
C(5)	-964(3)	983(2)	3914(2)	42(1)
C(6)	-1214(3)	1041(2)	4641(2)	29(1)
C(7)	-2339(3)	1114(2)	4815(2)	30(1)
C(8)	-2836(3)	1041(2)	5430(2)	25(1)
C(9)	-4102(3)	1020(2)	5413(2)	33(1)
C(10)	712(3)	879(2)	4882(2)	28(1)
C(11)	1093(3)	209(2)	4852(2)	37(1)
C(12)	2212(4)	112(2)	4741(3)	50(1)
C(13)	2913(4)	652(3)	4656(3)	60(2)
C(14)	2516(4)	1301(3)	4680(3)	49(1)
C(15)	1414(3)	1428(2)	4789(2)	34(1)

C(16)	324(4)	-380(2)	4950(3)	49(1)
C(17)	991(4)	2143(2)	4793(2)	47(1)
C(18)	-2876(3)	725(2)	6612(2)	31(1)
C(19)	-2555(4)	-16(2)	6730(3)	40(1)
C(20)	-2356(4)	-269(3)	7347(3)	71(2)
C(21)	-2102(5)	-958(3)	7438(3)	89(2)
C(22)	-2044(5)	-1396(3)	6919(4)	78(2)
C(23)	-2213(4)	-1140(3)	6301(3)	68(2)
C(24)	-2454(4)	-461(2)	6206(3)	56(2)
C(25)	-2568(4)	1201(2)	7174(2)	43(1)
C(26)	-2956(4)	1930(2)	7065(3)	54(2)
C(27)	861(4)	1951(3)	9794(2)	64(2)
C(28)	1203(4)	1818(2)	9093(2)	40(1)
C(29)	2344(3)	1901(2)	8948(3)	41(1)
C(30)	2914(3)	1766(2)	8370(3)	39(1)
C(31)	4165(4)	1912(3)	8413(3)	54(1)
C(32)	-676(3)	1557(2)	8839(2)	30(1)
C(33)	-1380(3)	2120(2)	8818(2)	37(1)
C(34)	-2484(4)	2014(2)	8972(3)	49(1)
C(35)	-2877(4)	1394(3)	9150(2)	51(1)
C(36)	-2179(4)	847(2)	9169(2)	47(1)
C(37)	-1072(3)	915(2)	9011(2)	34(1)
C(38)	-969(4)	2812(2)	8638(3)	55(1)
C(39)	-303(4)	317(2)	9031(3)	57(2)
C(40)	3194(3)	1265(2)	7265(2)	40(1)
C(41)	3364(3)	498(2)	7335(3)	44(1)
C(42)	3126(4)	138(2)	7909(3)	47(1)
C(43)	3342(4)	-542(3)	7966(3)	62(2)
C(44)	3823(5)	-888(3)	7464(4)	79(2)
C(45)	4100(5)	-544(3)	6889(4)	98(2)
C(46)	3841(5)	139(3)	6829(3)	75(2)
C(47)	2696(4)	1483(2)	6615(2)	44(1)
C(48)	2791(4)	2239(3)	6501(3)	57(2)

Table S5c. Bond lengths [Å] and angles [°] for **4**.

Zn(1)-O(1)	1.928(3)	C(11)-C(12)	1.388(6)
Zn(1)-O(3)	1.955(3)	C(11)-C(16)	1.503(6)
Zn(1)-N(2)	1.960(3)	C(12)-C(13)	1.374(7)
Zn(1)-N(1)	1.970(3)	C(13)-C(14)	1.369(7)
Zn(2)-O(2)	1.937(3)	C(14)-C(15)	1.375(6)
Zn(2)-O(4)	1.952(3)	C(15)-C(17)	1.501(6)
Zn(2)-N(3)	1.972(4)	C(18)-C(25)	1.527(6)
Zn(2)-N(4)	1.977(3)	C(18)-C(19)	1.532(6)
F(1)-C(9)	1.343(5)	C(19)-C(20)	1.370(7)
F(2)-C(9)	1.352(4)	C(19)-C(24)	1.387(7)
F(3)-C(9)	1.333(4)	C(20)-C(21)	1.406(7)
F(4)-C(31)	1.344(6)	C(21)-C(22)	1.367(8)
F(5)-C(31)	1.339(5)	C(22)-C(23)	1.370(8)
F(6)-C(31)	1.338(6)	C(23)-C(24)	1.384(7)
O(1)-C(1)	1.238(5)	C(25)-C(26)	1.528(6)
O(2)-C(1)	1.262(5)	C(27)-C(28)	1.507(6)
O(3)-C(3)	1.250(5)	C(28)-C(29)	1.422(6)
O(4)-C(3)	1.242(5)	C(29)-C(30)	1.389(6)
N(1)-C(6)	1.312(5)	C(30)-C(31)	1.544(6)
N(1)-C(10)	1.442(5)	C(32)-C(37)	1.399(6)
N(2)-C(8)	1.330(5)	C(32)-C(33)	1.401(5)
N(2)-C(18)	1.478(5)	C(33)-C(34)	1.389(6)
N(3)-C(28)	1.317(5)	C(33)-C(38)	1.499(6)
N(3)-C(32)	1.440(5)	C(34)-C(35)	1.363(6)
N(4)-C(30)	1.317(5)	C(35)-C(36)	1.372(6)
N(4)-C(40)	1.474(5)	C(36)-C(37)	1.386(6)
C(1)-C(2)	1.496(6)	C(37)-C(39)	1.505(6)
C(3)-C(4)	1.494(6)	C(40)-C(47)	1.516(6)
C(5)-C(6)	1.513(6)	C(40)-C(41)	1.535(6)
C(6)-C(7)	1.415(5)	C(41)-C(46)	1.376(7)
C(7)-C(8)	1.396(5)	C(41)-C(42)	1.395(7)
C(8)-C(9)	1.535(5)	C(42)-C(43)	1.372(6)
C(10)-C(15)	1.392(5)	C(43)-C(44)	1.359(8)
C(10)-C(11)	1.401(5)	C(44)-C(45)	1.393(8)

C(45)-C(46)	1.390(7)	O(3)-C(3)-C(4)	116.2(5)
C(47)-C(48)	1.514(7)	N(1)-C(6)-C(7)	123.2(4)
		N(1)-C(6)-C(5)	120.4(3)
O(1)-Zn(1)-O(3)	116.49(14)	C(7)-C(6)-C(5)	116.4(4)
O(1)-Zn(1)-N(2)	119.87(13)	C(8)-C(7)-C(6)	128.9(4)
O(3)-Zn(1)-N(2)	110.13(13)	N(2)-C(8)-C(7)	126.9(3)
O(1)-Zn(1)-N(1)	102.09(13)	N(2)-C(8)-C(9)	118.6(4)
O(3)-Zn(1)-N(1)	106.18(13)	C(7)-C(8)-C(9)	114.4(4)
N(2)-Zn(1)-N(1)	99.07(14)	F(3)-C(9)-F(1)	106.9(3)
O(2)-Zn(2)-O(4)	114.97(14)	F(3)-C(9)-F(2)	106.6(3)
O(2)-Zn(2)-N(3)	109.08(13)	F(1)-C(9)-F(2)	105.0(3)
O(4)-Zn(2)-N(3)	102.46(14)	F(3)-C(9)-C(8)	112.3(3)
O(2)-Zn(2)-N(4)	114.12(14)	F(1)-C(9)-C(8)	113.0(4)
O(4)-Zn(2)-N(4)	114.20(14)	F(2)-C(9)-C(8)	112.4(3)
N(3)-Zn(2)-N(4)	100.01(14)	C(15)-C(10)-C(11)	121.8(4)
C(1)-O(1)-Zn(1)	136.2(3)	C(15)-C(10)-N(1)	119.0(3)
C(1)-O(2)-Zn(2)	134.9(3)	C(11)-C(10)-N(1)	118.9(3)
C(3)-O(3)-Zn(1)	140.5(3)	C(12)-C(11)-C(10)	117.4(4)
C(3)-O(4)-Zn(2)	145.2(3)	C(12)-C(11)-C(16)	121.3(4)
C(6)-N(1)-C(10)	121.6(3)	C(10)-C(11)-C(16)	121.3(4)
C(6)-N(1)-Zn(1)	120.8(3)	C(13)-C(12)-C(11)	121.1(4)
C(10)-N(1)-Zn(1)	117.6(3)	C(14)-C(13)-C(12)	120.3(4)
C(8)-N(2)-C(18)	124.2(3)	C(13)-C(14)-C(15)	121.2(4)
C(8)-N(2)-Zn(1)	117.2(3)	C(14)-C(15)-C(10)	118.2(4)
C(18)-N(2)-Zn(1)	118.3(3)	C(14)-C(15)-C(17)	120.3(4)
C(28)-N(3)-C(32)	120.1(4)	C(10)-C(15)-C(17)	121.5(4)
C(28)-N(3)-Zn(2)	120.9(3)	N(2)-C(18)-C(25)	108.6(3)
C(32)-N(3)-Zn(2)	119.0(3)	N(2)-C(18)-C(19)	108.8(3)
C(30)-N(4)-C(40)	125.0(3)	C(25)-C(18)-C(19)	114.1(4)
C(30)-N(4)-Zn(2)	117.1(3)	C(20)-C(19)-C(24)	117.2(5)
C(40)-N(4)-Zn(2)	117.7(3)	C(20)-C(19)-C(18)	122.4(5)
O(1)-C(1)-O(2)	125.0(4)	C(24)-C(19)-C(18)	120.4(4)
O(1)-C(1)-C(2)	117.1(4)	C(19)-C(20)-C(21)	120.7(6)
O(2)-C(1)-C(2)	117.9(5)	C(22)-C(21)-C(20)	121.5(6)
O(4)-C(3)-O(3)	126.4(4)	C(21)-C(22)-C(23)	117.7(6)
O(4)-C(3)-C(4)	117.4(4)	C(22)-C(23)-C(24)	121.2(6)

C(19)-C(24)-C(23)	121.6(5)	C(32)-C(33)-C(38)	121.9(4)
C(26)-C(25)-C(18)	113.3(4)	C(35)-C(34)-C(33)	122.1(4)
N(3)-C(28)-C(29)	123.4(4)	C(34)-C(35)-C(36)	120.0(4)
N(3)-C(28)-C(27)	120.3(4)	C(35)-C(36)-C(37)	120.8(4)
C(29)-C(28)-C(27)	116.3(4)	C(36)-C(37)-C(32)	118.6(4)
C(30)-C(29)-C(28)	129.5(4)	C(36)-C(37)-C(39)	121.0(4)
N(4)-C(30)-C(29)	128.1(4)	C(32)-C(37)-C(39)	120.4(4)
N(4)-C(30)-C(31)	118.2(4)	N(4)-C(40)-C(47)	109.8(3)
C(29)-C(30)-C(31)	113.8(4)	N(4)-C(40)-C(41)	110.5(4)
F(5)-C(31)-F(6)	107.3(4)	C(47)-C(40)-C(41)	114.4(4)
F(5)-C(31)-F(4)	105.8(4)	C(46)-C(41)-C(42)	116.8(5)
F(6)-C(31)-F(4)	106.5(4)	C(46)-C(41)-C(40)	119.6(5)
F(5)-C(31)-C(30)	112.5(4)	C(42)-C(41)-C(40)	123.4(5)
F(6)-C(31)-C(30)	111.0(4)	C(43)-C(42)-C(41)	121.9(5)
F(4)-C(31)-C(30)	113.3(4)	C(44)-C(43)-C(42)	120.6(6)
C(37)-C(32)-C(33)	121.1(4)	C(43)-C(44)-C(45)	119.3(6)
C(37)-C(32)-N(3)	119.1(3)	C(44)-C(45)-C(46)	119.5(6)
C(33)-C(32)-N(3)	119.7(4)	C(41)-C(46)-C(45)	121.8(6)
C(34)-C(33)-C(32)	117.4(4)	C(48)-C(47)-C(40)	112.5(4)
C(34)-C(33)-C(38)	120.7(4)		

Table S5d: Anisotropic displacement parameters ($Å^2 \times 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zn(1)	27(1)	35(1)	26(1)	-4(1)	-2(1)	0(1)
Zn(2)	26(1)	39(1)	25(1)	-3(1)	-2(1)	-2(1)
F(1)	26(1)	59(2)	40(2)	4(1)	-9(1)	3(1)
F(2)	28(1)	46(1)	49(2)	-8(1)	4(1)	6(1)
F(3)	33(1)	40(2)	51(2)	-2(1)	-1(1)	-11(1)
F(4)	42(2)	121(3)	70(2)	-36(2)	-16(2)	-17(2)
F(5)	33(1)	95(2)	74(3)	-14(2)	-13(2)	7(2)
F(6)	42(2)	87(2)	83(3)	-5(2)	5(2)	-29(2)
O(1)	46(2)	50(2)	30(2)	3(2)	-5(2)	15(2)
O(2)	50(2)	44(2)	33(2)	-5(2)	3(2)	-13(2)
O(3)	61(2)	39(2)	36(2)	-9(2)	1(2)	-13(2)
O(4)	65(2)	45(2)	33(2)	2(2)	-11(2)	18(2)
N(1)	22(2)	30(2)	27(2)	-5(2)	1(2)	3(1)
N(2)	29(2)	30(2)	25(2)	-2(2)	2(2)	2(1)
N(3)	29(2)	40(2)	27(2)	-1(2)	3(2)	-3(2)
N(4)	28(2)	48(2)	25(2)	-3(2)	-3(2)	-4(2)
C(1)	29(2)	29(2)	42(4)	0(2)	-1(2)	-3(2)
C(2)	77(3)	38(3)	74(4)	9(3)	-16(4)	7(3)
C(3)	37(3)	29(3)	38(3)	-1(2)	6(2)	-6(2)
C(4)	118(5)	33(3)	49(4)	1(2)	-20(4)	5(3)
C(5)	37(2)	64(3)	25(3)	-5(2)	-1(2)	6(2)
C(6)	32(2)	28(2)	27(3)	0(2)	2(2)	3(2)
C(7)	28(2)	33(2)	29(3)	-1(2)	-4(2)	3(2)
C(8)	19(2)	24(2)	32(3)	0(2)	-2(2)	3(2)
C(9)	28(2)	39(2)	33(3)	-4(2)	4(2)	1(2)
C(10)	26(2)	37(2)	19(3)	-7(2)	-1(2)	1(2)
C(11)	32(3)	39(3)	41(3)	-12(2)	-7(2)	5(2)
C(12)	36(3)	51(3)	62(4)	-20(3)	-4(3)	19(2)
C(13)	19(2)	79(4)	81(5)	-31(3)	2(3)	3(3)
C(14)	33(3)	58(4)	56(4)	-19(3)	1(2)	-12(2)
C(15)	30(2)	40(3)	33(3)	-8(2)	0(2)	-1(2)

C(16)	54(3)	34(3)	59(4)	-10(2)	-6(3)	5(2)
C(17)	49(3)	39(3)	53(4)	-1(2)	6(3)	-11(2)
C(18)	28(2)	41(3)	26(3)	6(2)	1(2)	1(2)
C(19)	33(2)	45(3)	41(4)	10(3)	10(2)	0(2)
C(20)	78(4)	77(4)	56(5)	23(3)	32(4)	31(3)
C(21)	106(5)	87(5)	75(6)	50(4)	43(4)	45(4)
C(22)	77(4)	53(4)	104(6)	31(4)	41(4)	16(3)
C(23)	79(4)	37(3)	88(5)	2(3)	-11(4)	-2(3)
C(24)	74(3)	43(3)	51(4)	3(3)	-7(3)	3(3)
C(25)	47(3)	55(3)	28(3)	-6(2)	10(2)	-5(2)
C(26)	64(3)	55(3)	43(4)	-21(3)	3(3)	4(3)
C(27)	55(3)	106(5)	31(3)	-18(3)	6(3)	-11(3)
C(28)	44(3)	49(3)	28(3)	-5(2)	-2(2)	-1(2)
C(29)	33(2)	60(3)	30(3)	-9(3)	-9(3)	-7(2)
C(30)	31(3)	49(3)	38(4)	-4(2)	-4(2)	-4(2)
C(31)	36(3)	69(4)	58(4)	-14(3)	-5(3)	-6(3)
C(32)	29(2)	42(2)	19(3)	-3(2)	3(2)	-1(2)
C(33)	39(3)	42(3)	30(3)	0(2)	7(2)	4(2)
C(34)	44(3)	57(3)	46(4)	0(3)	16(3)	16(2)
C(35)	34(2)	75(4)	43(4)	10(3)	10(2)	-3(3)
C(36)	45(3)	52(3)	44(4)	10(2)	6(3)	-9(2)
C(37)	35(2)	43(3)	23(3)	7(2)	0(2)	0(2)
C(38)	70(3)	36(3)	59(4)	-5(2)	20(3)	1(3)
C(39)	67(3)	43(3)	62(4)	23(3)	7(3)	6(2)
C(40)	24(2)	53(3)	43(3)	-5(2)	6(2)	-6(2)
C(41)	31(2)	51(3)	50(4)	3(3)	7(3)	2(2)
C(42)	42(3)	55(3)	45(4)	-1(3)	-7(3)	11(2)
C(43)	53(3)	62(4)	69(5)	14(3)	-13(3)	9(3)
C(44)	69(4)	59(4)	108(7)	2(4)	10(4)	22(3)
C(45)	95(5)	79(5)	120(7)	-15(4)	58(5)	24(4)
C(46)	85(4)	58(4)	80(5)	-4(3)	36(4)	10(3)
C(47)	38(2)	61(3)	32(3)	0(3)	7(2)	-6(2)
C(48)	64(3)	67(4)	39(4)	13(3)	3(3)	-14(3)

Table S5e. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **4**.

	x	y	z	U(eq)
H(2A)	194	-807	6853	95
H(2B)	901	-619	7492	95
H(2C)	1459	-586	6780	95
H(4A)	-53	3391	7027	100
H(4B)	-1164	3229	6631	100
H(4C)	-21	3309	6244	100
H(5A)	-479	1356	3781	63
H(5B)	-1655	1006	3664	63
H(5C)	-597	550	3827	63
H(7A)	-2823	1229	4465	36
H(12A)	2498	-336	4723	60
H(13A)	3677	575	4580	72
H(14A)	3010	1670	4622	58
H(16A)	710	-802	4842	73
H(16B)	-320	-329	4663	73
H(16C)	82	-394	5410	73
H(17A)	455	2203	4437	70
H(17B)	1609	2458	4730	70
H(17C)	634	2237	5216	70
H(18A)	-3693	748	6545	38
H(20A)	-2391	25	7717	85
H(21A)	-1968	-1122	7869	107
H(22A)	-1890	-1864	6984	94
H(23A)	-2164	-1432	5931	82
H(24A)	-2553	-297	5771	67
H(25A)	-2897	1028	7587	52
H(25B)	-1756	1200	7229	52
H(26A)	-2639	2104	6655	80
H(26B)	-2714	2213	7434	80
H(26C)	-3763	1939	7036	80

H(27A)	386	2353	9809	96
H(27B)	1519	2029	10064	96
H(27C)	456	1559	9963	96
H(29A)	2781	2073	9298	49
H(34A)	-2980	2386	8953	59
H(35A)	-3634	1340	9261	61
H(36A)	-2459	415	9291	56
H(38A)	-1594	3126	8613	82
H(38B)	-597	2793	8211	82
H(38C)	-448	2970	8974	82
H(39A)	273	396	9360	86
H(39B)	38	256	8598	86
H(39C)	-720	-92	9147	86
H(40A)	3938	1483	7300	48
H(42A)	2805	371	8270	57
H(43A)	3155	-773	8361	74
H(44A)	3968	-1359	7505	95
H(45A)	4464	-775	6541	117
H(46A)	3998	365	6427	89
H(47A)	3075	1241	6253	52
H(47B)	1908	1352	6605	52
H(48A)	2403	2481	6852	85
H(48B)	2459	2354	6076	85
H(48C)	3571	2370	6500	85

Table S6a. Crystal data and structure refinement for *ent*-**5**.

Identification code	ce5	
Empirical formula	$C_{56}H_{66}F_6N_4O_6Zn_2$	
Formula weight	1135.87	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 10.3348(8) Å	α= 113.176(3)°
	b = 10.8803(8) Å	β= 96.805(4)°
	c = 13.2532(11) Å	γ = 91.083(3)°
Volume	1356.84(18) $Å^3$	
Z	1	
Density (calculated)	1.390 Mg/m^3	
Absorption coefficient	0.957 mm^{-1}	
F(000)	592	
Crystal size	0.40 x 0.30 x 0.20 mm^3	
Theta range for data collection	1.69 to 28.28°	
Index ranges	-13<=h<=13, -14<=k<=14, -17<=l<=17	
Reflections collected	22196	
Independent reflections	12299 [R(int) = 0.0155]	
Completeness to theta = 28.28°	98.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8316 and 0.7007	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12299 / 3 / 776	
Goodness-of-fit on F^2	1.019	
Final R indices [I>2sigma(I)]	R1 = 0.0254, wR2 = 0.0562	
R indices (all data)	R1 = 0.0298, wR2 = 0.0573	
Absolute structure parameter	0.022(5)	
Largest diff. peak and hole	0.327 and -0.227 $e \cdot Å^{-3}$	

Table S6b. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for *ent*-**5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Zn(1)	4425(1)	-6190(1)	1462(1)	22(1)
Zn(2)	7206(1)	-2796(1)	2956(1)	24(1)
F(1)	1140(1)	-8048(2)	-2181(1)	44(1)
F(2)	2941(2)	-8987(2)	-2434(1)	42(1)
F(3)	2828(2)	-6945(2)	-2253(1)	43(1)
F(4)	10662(2)	-1240(2)	6432(1)	50(1)
F(5)	8939(2)	-273(2)	6931(1)	45(1)
F(6)	8983(2)	-2400(2)	6451(1)	52(1)
O(1)	6022(2)	-6483(2)	2273(1)	27(1)
O(2)	7258(2)	-4788(2)	2268(1)	28(1)
O(3)	5571(2)	-2435(2)	2226(2)	30(1)
O(4)	4488(2)	-4209(2)	2226(2)	30(1)
O(5)	5037(1)	-4995(1)	-880(1)	31(1)
O(6)	6482(2)	388(2)	5661(1)	46(1)
N(1)	2831(2)	-6896(2)	1820(2)	25(1)
N(2)	4059(2)	-6943(2)	-165(2)	22(1)
N(3)	8687(2)	-1908(2)	2611(2)	24(1)
N(4)	7652(2)	-2062(2)	4589(2)	28(1)
C(1)	7032(2)	-5687(2)	2614(2)	25(1)
C(2)	8051(2)	-5892(2)	3439(2)	35(1)
C(3)	4559(2)	-3236(2)	1954(2)	24(1)
C(4)	3408(3)	-2979(3)	1303(2)	44(1)
C(5)	602(3)	-8000(3)	1267(2)	41(1)
C(6)	1821(2)	-7429(2)	1029(2)	26(1)
C(7)	1801(2)	-7539(2)	-64(2)	27(1)
C(8)	2831(2)	-7377(2)	-610(2)	24(1)
C(9)	2433(3)	-7829(3)	-1861(2)	31(1)
C(10)	2719(2)	-6820(2)	2912(2)	31(1)
C(11)	2098(3)	-5754(3)	3619(2)	41(1)
C(12)	2000(3)	-5698(4)	4677(3)	65(1)
C(13)	2485(4)	-6657(4)	5007(3)	73(1)

C(14)	3099(3)	-7684(4)	4308(3)	63(1)
C(15)	3229(3)	-7799(3)	3235(2)	42(1)
C(16)	1545(3)	-4705(3)	3243(3)	53(1)
C(17)	3856(3)	-8963(3)	2445(3)	52(1)
C(18)	5146(2)	-7140(2)	-844(2)	23(1)
C(19)	6003(3)	-8178(3)	-650(2)	29(1)
C(20)	7167(3)	-8397(3)	-1287(2)	32(1)
C(21)	7964(3)	-7089(3)	-982(3)	38(1)
C(22)	7110(3)	-6071(3)	-1194(2)	31(1)
C(23)	5936(2)	-5820(2)	-569(2)	25(1)
C(24)	5579(2)	-3730(2)	-768(2)	34(1)
C(25)	4493(2)	-2957(2)	-1027(2)	32(1)
C(26)	4523(2)	-1580(2)	-470(2)	41(1)
C(27)	3502(2)	-857(2)	-687(2)	44(1)
C(28)	2466(3)	-1500(3)	-1455(3)	49(1)
C(29)	2419(3)	-2869(4)	-2036(3)	59(1)
C(30)	3438(3)	-3603(3)	-1819(2)	51(1)
C(31)	10846(3)	-683(3)	3111(2)	41(1)
C(32)	9713(2)	-1379(2)	3358(2)	28(1)
C(33)	9844(2)	-1364(2)	4439(2)	28(1)
C(34)	8886(2)	-1632(2)	4998(2)	26(1)
C(35)	9364(3)	-1368(3)	6210(2)	35(1)
C(36)	8670(2)	-1837(2)	1543(2)	30(1)
C(37)	9211(2)	-2856(3)	712(2)	38(1)
C(38)	9212(3)	-2744(4)	-300(3)	58(1)
C(39)	8669(4)	-1724(4)	-496(3)	70(1)
C(40)	8124(3)	-767(4)	300(3)	63(1)
C(41)	8102(3)	-779(3)	1364(2)	41(1)
C(42)	9796(2)	-3973(3)	934(2)	43(1)
C(43)	7484(3)	279(3)	2244(3)	61(1)
C(44)	6619(3)	-1938(3)	5284(2)	32(1)
C(45)	5846(3)	-3292(3)	4948(2)	39(1)
C(46)	4730(3)	-3137(4)	5637(3)	57(1)
C(47)	3835(3)	-2111(4)	5527(3)	61(1)
C(48)	4586(3)	-766(3)	5875(3)	52(1)
C(49)	5724(3)	-877(3)	5213(2)	40(1)

C(50)	6842(5)	959(4)	4900(4)	40(2)
C(50')	6066(5)	1274(5)	5343(5)	46(2)
C(51)	7287(4)	2392(3)	5627(2)	68(1)
C(52)	8611(5)	2411(4)	5871(3)	84(1)
C(53)	9339(5)	3603(6)	6379(5)	94(2)
C(54)	8778(4)	4756(4)	6647(3)	79(1)
C(55)	7482(4)	4768(3)	6415(2)	62(1)
C(56)	6727(3)	3580(3)	5903(2)	60(1)

Table S6c. Bond lengths [Å] and angles [°] for *ent*-**5**.

Zn(1)-O(1)	1.9622(16)	C(6)-C(7)	1.403(3)
Zn(1)-N(2)	1.967(2)	C(7)-C(8)	1.401(3)
Zn(1)-O(4)	1.9835(16)	C(8)-C(9)	1.533(3)
Zn(1)-N(1)	1.989(2)	C(10)-C(15)	1.387(4)
Zn(2)-O(3)	1.9703(17)	C(10)-C(11)	1.397(3)
Zn(2)-N(4)	1.981(2)	C(11)-C(12)	1.395(4)
Zn(2)-N(3)	1.985(2)	C(11)-C(16)	1.511(4)
Zn(2)-O(2)	1.9978(16)	C(12)-C(13)	1.363(5)
F(1)-C(9)	1.340(3)	C(13)-C(14)	1.365(5)
F(2)-C(9)	1.344(3)	C(14)-C(15)	1.401(4)
F(3)-C(9)	1.338(3)	C(15)-C(17)	1.506(4)
F(4)-C(35)	1.332(3)	C(18)-C(23)	1.528(4)
F(5)-C(35)	1.322(3)	C(18)-C(19)	1.529(3)
F(6)-C(35)	1.346(3)	C(19)-C(20)	1.521(3)
O(1)-C(1)	1.261(3)	C(20)-C(21)	1.513(4)
O(2)-C(1)	1.261(3)	C(21)-C(22)	1.519(4)
O(3)-C(3)	1.270(3)	C(22)-C(23)	1.518(3)
O(4)-C(3)	1.249(3)	C(24)-C(25)	1.502(3)
O(5)-C(24)	1.422(2)	C(25)-C(26)	1.384(3)
O(5)-C(23)	1.439(3)	C(25)-C(30)	1.380(3)
O(6)-C(50')	1.258(5)	C(26)-C(27)	1.397(3)
O(6)-C(49)	1.437(3)	C(27)-C(28)	1.351(4)
O(6)-C(50)	1.453(5)	C(28)-C(29)	1.378(5)
N(1)-C(6)	1.327(3)	C(29)-C(30)	1.403(4)
N(1)-C(10)	1.436(3)	C(31)-C(32)	1.519(4)
N(2)-C(8)	1.327(3)	C(32)-C(33)	1.416(4)
N(2)-C(18)	1.488(3)	C(33)-C(34)	1.395(4)
N(3)-C(32)	1.310(3)	C(34)-C(35)	1.534(3)
N(3)-C(36)	1.446(3)	C(36)-C(41)	1.391(3)
N(4)-C(34)	1.324(3)	C(36)-C(37)	1.400(3)
N(4)-C(44)	1.466(3)	C(37)-C(38)	1.394(4)
C(1)-C(2)	1.511(3)	C(37)-C(42)	1.482(4)
C(3)-C(4)	1.481(3)	C(38)-C(39)	1.352(5)
C(5)-C(6)	1.513(4)	C(39)-C(40)	1.346(6)

C(40)-C(41)	1.418(4)	C(49)-O(6)-C(50)	118.5(2)
C(41)-C(43)	1.497(4)	C(6)-N(1)-C(10)	118.7(2)
C(44)-C(49)	1.517(4)	C(6)-N(1)-Zn(1)	119.02(17)
C(44)-C(45)	1.537(4)	C(10)-N(1)-Zn(1)	122.28(16)
C(45)-C(46)	1.526(4)	C(8)-N(2)-C(18)	122.58(19)
C(46)-C(47)	1.503(5)	C(8)-N(2)-Zn(1)	116.71(16)
C(47)-C(48)	1.516(5)	C(18)-N(2)-Zn(1)	120.38(15)
C(48)-C(49)	1.529(4)	C(32)-N(3)-C(36)	118.6(2)
C(50)-C(51)	1.503(5)	C(32)-N(3)-Zn(2)	119.88(18)
C(50')-C(51)	1.638(6)	C(36)-N(3)-Zn(2)	121.50(15)
C(51)-C(52)	1.366(5)	C(34)-N(4)-C(44)	123.2(2)
C(51)-C(56)	1.358(4)	C(34)-N(4)-Zn(2)	116.88(17)
C(52)-C(53)	1.363(6)	C(44)-N(4)-Zn(2)	119.81(17)
C(53)-C(54)	1.327(6)	O(2)-C(1)-O(1)	123.9(2)
C(54)-C(55)	1.340(5)	O(2)-C(1)-C(2)	119.1(2)
C(55)-C(56)	1.374(4)	O(1)-C(1)-C(2)	116.9(2)
		O(4)-C(3)-O(3)	122.9(2)
O(1)-Zn(1)-N(2)	123.19(7)	O(4)-C(3)-C(4)	119.0(2)
O(1)-Zn(1)-O(4)	98.10(7)	O(3)-C(3)-C(4)	118.0(2)
N(2)-Zn(1)-O(4)	116.51(8)	N(1)-C(6)-C(7)	124.1(2)
O(1)-Zn(1)-N(1)	111.79(7)	N(1)-C(6)-C(5)	120.4(2)
N(2)-Zn(1)-N(1)	100.29(8)	C(7)-C(6)-C(5)	115.5(2)
O(4)-Zn(1)-N(1)	106.44(7)	C(6)-C(7)-C(8)	129.6(2)
O(3)-Zn(2)-N(4)	122.20(8)	N(2)-C(8)-C(7)	127.1(2)
O(3)-Zn(2)-N(3)	108.22(8)	N(2)-C(8)-C(9)	119.9(2)
N(4)-Zn(2)-N(3)	98.61(9)	C(7)-C(8)-C(9)	112.9(2)
O(3)-Zn(2)-O(2)	104.57(7)	F(3)-C(9)-F(2)	106.3(2)
N(4)-Zn(2)-O(2)	112.15(8)	F(3)-C(9)-F(1)	105.49(18)
N(3)-Zn(2)-O(2)	110.83(7)	F(2)-C(9)-F(1)	105.6(2)
C(1)-O(1)-Zn(1)	123.93(16)	F(3)-C(9)-C(8)	113.4(2)
C(1)-O(2)-Zn(2)	132.21(15)	F(2)-C(9)-C(8)	111.48(18)
C(3)-O(3)-Zn(2)	120.94(16)	F(1)-C(9)-C(8)	114.0(2)
C(3)-O(4)-Zn(1)	136.43(17)	C(15)-C(10)-C(11)	121.9(2)
C(24)-O(5)-C(23)	115.53(16)	C(15)-C(10)-N(1)	119.4(2)
C(50')-O(6)-C(49)	116.6(3)	C(11)-C(10)-N(1)	118.7(2)
C(50')-O(6)-C(50)	44.1(3)	C(12)-C(11)-C(10)	117.8(3)

C(12)-C(11)-C(16)	121.4(3)	F(4)-C(35)-F(6)	105.7(2)
C(10)-C(11)-C(16)	120.8(2)	F(5)-C(35)-C(34)	113.8(2)
C(13)-C(12)-C(11)	121.2(3)	F(4)-C(35)-C(34)	112.2(2)
C(12)-C(13)-C(14)	120.2(3)	F(6)-C(35)-C(34)	110.9(2)
C(13)-C(14)-C(15)	121.4(3)	C(41)-C(36)-C(37)	122.0(2)
C(14)-C(15)-C(10)	117.4(3)	C(41)-C(36)-N(3)	119.3(2)
C(14)-C(15)-C(17)	121.6(3)	C(37)-C(36)-N(3)	118.6(2)
C(10)-C(15)-C(17)	120.9(2)	C(36)-C(37)-C(38)	117.4(3)
N(2)-C(18)-C(23)	111.46(19)	C(36)-C(37)-C(42)	120.3(2)
N(2)-C(18)-C(19)	108.32(19)	C(38)-C(37)-C(42)	122.2(3)
C(23)-C(18)-C(19)	111.5(2)	C(39)-C(38)-C(37)	121.7(3)
C(20)-C(19)-C(18)	111.4(2)	C(38)-C(39)-C(40)	120.4(3)
C(21)-C(20)-C(19)	110.8(2)	C(39)-C(40)-C(41)	121.9(3)
C(20)-C(21)-C(22)	110.2(2)	C(36)-C(41)-C(40)	116.5(3)
C(23)-C(22)-C(21)	112.6(2)	C(36)-C(41)-C(43)	121.6(3)
O(5)-C(23)-C(22)	112.63(19)	C(40)-C(41)-C(43)	121.9(3)
O(5)-C(23)-C(18)	105.16(19)	N(4)-C(44)-C(49)	109.9(2)
C(22)-C(23)-C(18)	110.2(2)	N(4)-C(44)-C(45)	110.9(2)
O(5)-C(24)-C(25)	108.47(16)	C(49)-C(44)-C(45)	111.1(2)
C(26)-C(25)-C(30)	118.4(2)	C(46)-C(45)-C(44)	110.5(2)
C(26)-C(25)-C(24)	120.71(19)	C(47)-C(46)-C(45)	111.4(3)
C(30)-C(25)-C(24)	120.89(19)	C(46)-C(47)-C(48)	110.6(3)
C(25)-C(26)-C(27)	121.1(2)	C(47)-C(48)-C(49)	111.4(3)
C(28)-C(27)-C(26)	120.1(2)	O(6)-C(49)-C(44)	108.0(2)
C(27)-C(28)-C(29)	120.1(2)	O(6)-C(49)-C(48)	108.8(2)
C(28)-C(29)-C(30)	120.1(3)	C(44)-C(49)-C(48)	111.8(3)
C(25)-C(30)-C(29)	120.2(2)	O(6)-C(50)-C(51)	104.5(3)
N(3)-C(32)-C(33)	124.2(2)	O(6)-C(50')-C(51)	106.9(3)
N(3)-C(32)-C(31)	120.4(2)	C(52)-C(51)-C(56)	118.5(3)
C(33)-C(32)-C(31)	115.3(2)	C(52)-C(51)-C(50)	105.6(4)
C(34)-C(33)-C(32)	128.9(2)	C(56)-C(51)-C(50)	134.8(3)
N(4)-C(34)-C(33)	126.7(2)	C(52)-C(51)-C(50')	134.7(3)
N(4)-C(34)-C(35)	119.3(2)	C(56)-C(51)-C(50')	104.8(3)
C(33)-C(34)-C(35)	114.1(2)	C(50)-C(51)-C(50')	38.1(2)
F(5)-C(35)-F(4)	106.4(2)	C(53)-C(52)-C(51)	120.0(3)
F(5)-C(35)-F(6)	107.2(2)	C(54)-C(53)-C(52)	120.8(4)

C(53)-C(54)-C(55)	120.5(4)	C(51)-C(56)-C(55)	120.4(3)
C(54)-C(55)-C(56)	119.8(3)		

Table S6d. Anisotropic displacement parameters ($Å^2 \times 10^3$) for *ent*-**5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zn(1)	20(1)	23(1)	23(1)	9(1)	3(1)	-4(1)
Zn(2)	21(1)	25(1)	24(1)	7(1)	3(1)	-6(1)
F(1)	25(1)	68(1)	33(1)	16(1)	-7(1)	-6(1)
F(2)	44(1)	37(1)	32(1)	0(1)	6(1)	4(1)
F(3)	48(1)	51(1)	37(1)	29(1)	-6(1)	-7(1)
F(4)	32(1)	79(1)	38(1)	24(1)	-5(1)	4(1)
F(5)	41(1)	50(1)	27(1)	-4(1)	4(1)	-2(1)
F(6)	60(1)	56(1)	46(1)	30(1)	-3(1)	-9(1)
O(1)	22(1)	25(1)	35(1)	13(1)	-1(1)	-4(1)
O(2)	30(1)	26(1)	27(1)	10(1)	9(1)	1(1)
O(3)	22(1)	28(1)	39(1)	13(1)	2(1)	-3(1)
O(4)	32(1)	23(1)	35(1)	10(1)	7(1)	-4(1)
O(5)	25(1)	29(1)	43(1)	21(1)	2(1)	0(1)
O(6)	47(1)	47(1)	32(1)	5(1)	2(1)	-12(1)
N(1)	23(1)	27(1)	26(1)	11(1)	5(1)	-3(1)
N(2)	19(1)	22(1)	23(1)	9(1)	1(1)	-4(1)
N(3)	20(1)	22(1)	28(1)	9(1)	3(1)	-3(1)
N(4)	26(1)	32(1)	24(1)	6(1)	7(1)	-1(1)
C(1)	24(1)	25(1)	22(1)	5(1)	9(1)	3(1)
C(2)	29(1)	41(1)	34(1)	16(1)	-3(1)	-2(1)
C(3)	21(1)	24(1)	26(1)	6(1)	7(1)	-1(1)
C(4)	28(1)	57(2)	58(2)	38(1)	2(1)	0(1)
C(5)	31(1)	54(2)	35(1)	18(1)	2(1)	-16(1)
C(6)	18(1)	27(1)	31(1)	11(1)	4(1)	-3(1)
C(7)	21(1)	31(1)	25(1)	9(1)	-1(1)	-2(1)
C(8)	23(1)	22(1)	27(1)	10(1)	5(1)	3(1)
C(9)	24(1)	37(1)	31(1)	15(1)	-1(1)	-3(1)
C(10)	27(1)	38(1)	27(1)	13(1)	1(1)	-14(1)
C(11)	38(2)	47(2)	31(1)	5(1)	11(1)	-15(1)
C(12)	66(2)	76(2)	35(2)	2(2)	23(2)	-32(2)
C(13)	73(2)	109(3)	33(2)	29(2)	5(2)	-47(2)

C(14)	63(2)	91(3)	46(2)	48(2)	-15(2)	-38(2)
C(15)	36(1)	53(2)	39(1)	24(1)	-3(1)	-21(1)
C(16)	53(2)	35(1)	66(2)	7(1)	27(1)	2(1)
C(17)	44(2)	56(2)	72(2)	45(2)	-3(1)	-2(1)
C(18)	20(1)	28(1)	21(1)	9(1)	6(1)	0(1)
C(19)	28(1)	30(1)	37(2)	19(1)	13(1)	8(1)
C(20)	34(1)	34(1)	30(1)	15(1)	9(1)	10(1)
C(21)	28(1)	49(2)	44(2)	25(1)	10(1)	8(1)
C(22)	26(1)	39(1)	36(1)	21(1)	10(1)	0(1)
C(23)	24(1)	27(1)	27(1)	14(1)	3(1)	4(1)
C(24)	34(1)	30(1)	43(1)	19(1)	4(1)	-2(1)
C(25)	33(1)	31(1)	38(1)	20(1)	1(1)	-1(1)
C(26)	38(1)	31(1)	53(1)	21(1)	-2(1)	-5(1)
C(27)	48(2)	31(1)	58(2)	23(1)	6(1)	3(1)
C(28)	46(2)	50(2)	58(2)	32(1)	-4(1)	8(1)
C(29)	54(2)	48(2)	62(2)	21(1)	-30(2)	-9(1)
C(30)	63(2)	35(1)	49(2)	19(1)	-14(1)	-1(1)
C(31)	23(1)	52(2)	42(2)	15(1)	0(1)	-18(1)
C(32)	20(1)	25(1)	35(1)	9(1)	6(1)	0(1)
C(33)	17(1)	28(1)	36(2)	10(1)	2(1)	-1(1)
C(34)	25(1)	22(1)	24(1)	4(1)	0(1)	-1(1)
C(35)	30(1)	40(1)	33(2)	12(1)	1(1)	-2(1)
C(36)	22(1)	35(1)	35(1)	19(1)	1(1)	-11(1)
C(37)	24(1)	51(2)	34(1)	13(1)	3(1)	-16(1)
C(38)	56(2)	75(2)	37(2)	18(2)	10(1)	-30(2)
C(39)	72(2)	104(3)	44(2)	46(2)	-11(2)	-42(2)
C(40)	52(2)	75(2)	81(2)	63(2)	-27(2)	-35(2)
C(41)	33(1)	44(2)	53(2)	31(1)	-13(1)	-17(1)
C(42)	30(1)	45(2)	43(1)	3(1)	15(1)	-1(1)
C(43)	47(2)	37(2)	103(3)	33(2)	0(2)	4(1)
C(44)	27(1)	37(1)	22(1)	2(1)	3(1)	-6(1)
C(45)	32(1)	46(2)	31(2)	8(1)	8(1)	-16(1)
C(46)	48(2)	66(2)	49(2)	14(2)	13(2)	-23(2)
C(47)	28(2)	82(3)	53(2)	5(2)	18(2)	-17(2)
C(48)	32(2)	66(2)	44(2)	4(2)	17(1)	1(1)
C(49)	35(2)	44(2)	26(1)	-2(1)	5(1)	-5(1)

C(50)	48(3)	38(2)	33(2)	11(2)	7(2)	2(2)
C(50')	34(3)	50(3)	46(3)	13(2)	-7(2)	10(2)
C(51)	104(3)	43(2)	53(2)	26(1)	-33(2)	-10(2)
C(52)	125(4)	70(3)	68(2)	37(2)	16(2)	47(3)
C(53)	71(3)	137(5)	115(4)	91(4)	19(2)	14(3)
C(54)	101(3)	75(2)	77(2)	56(2)	-14(2)	-25(2)
C(55)	109(3)	45(2)	38(2)	24(1)	13(2)	14(2)
C(56)	60(2)	77(2)	63(2)	51(2)	0(1)	6(1)

Table S6e. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for *ent*-**5**.

	x	y	z	U(eq)
H(2A)	8633	-6562	3042	52
H(2B)	7619	-6206	3923	52
H(2C)	8561	-5043	3887	52
H(4A)	3280	-3681	551	65
H(4B)	3553	-2104	1270	65
H(4C)	2630	-2983	1659	65
H(5A)	708	-7876	2047	61
H(5B)	461	-8958	793	61
H(5C)	-151	-7535	1116	61
H(7)	987(18)	-7902(17)	-495(15)	19(5)
H(12)	1640(20)	-5060(20)	5130(20)	40(7)
H(13)	2420(30)	-6550(30)	5700(30)	70(9)
H(14A)	3446	-8336	4555	75
H(16A)	2215	-4358	2939	80
H(16B)	1270	-3969	3875	80
H(16C)	791	-5107	2670	80
H(17A)	3229	-9447	1780	78
H(17B)	4122	-9569	2804	78
H(17C)	4625	-8629	2236	78
H(18A)	4765	-7504	-1643	27
H(19A)	6350(20)	-7900(20)	159(18)	20(6)
H(19B)	5425(19)	-9010(20)	-880(15)	13(5)
H(20B)	7630(20)	-8980(20)	-1081(18)	28(6)
H(20A)	6950(30)	-8870(30)	-2040(30)	65(9)
H(21B)	8370(30)	-6700(30)	-180(30)	63(10)
H(21A)	8760(20)	-7230(20)	-1371(18)	37(6)
H(22B)	6860(20)	-6430(20)	-1970(20)	32(6)
H(22A)	7660(20)	-5300(20)	-1003(18)	33(6)
H(23A)	6238	-5388	246	30
H(24B)	6020(19)	-3170(20)	70(18)	35(6)

H(24A)	6218(19)	-3899(19)	-1328(16)	25(5)
H(26A)	5249	-1117	69	49
H(27A)	3536	88	-294	52
H(28A)	1769	-1008	-1596	59
H(29A)	1696	-3317	-2584	70
H(30A)	3401	-4547	-2218	61
H(31A)	11077	-1245	2381	62
H(31B)	11601	-535	3678	62
H(31C)	10592	182	3113	62
H(33A)	10701	-1142	4837	34
H(38A)	9605	-3402	-868	69
H(39)	8740(20)	-1760(30)	-1160(20)	54(7)
H(40)	7760(20)	-110(30)	200(20)	46(7)
H(42A)	10208	-4537	295	65
H(42B)	9111	-4513	1058	65
H(42C)	10454	-3610	1593	65
H(43A)	6801	-142	2481	92
H(43B)	7099	906	1949	92
H(43C)	8150	765	2880	92
H(44)	6987(19)	-1650(20)	6021(18)	28(5)
H(45A)	5489	-3640	4152	46
H(45B)	6437	-3946	5061	46
H(46B)	4340(30)	-4000(30)	5380(30)	67(9)
H(46A)	5150(20)	-2850(20)	6480(20)	40(7)
H(47B)	3380(20)	-2360(20)	4690(20)	34(7)
H(47A)	3210(30)	-2150(30)	5900(20)	56(8)
H(48B)	4920(20)	-440(20)	6630(20)	28(6)
H(48A)	4060(30)	-40(30)	5790(20)	64(10)
H(49)	5470(30)	-1130(30)	4470(20)	39(8)
H(50A)	6083	907	4350	48
H(50B)	7555	482	4503	48
H(50C)	5329	1694	5735	55
H(50D)	5760	874	4536	55
H(52A)	9025	1593	5686	101
H(53A)	10260	3609	6544	113
H(54A)	9299	5578	7005	94

H(55A)	7086	5597	6604	74
H(56A)	5808	3588	5741	72

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