



Supporting Information

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Supporting Information

Highly Active Polymer-Supported (salen)Al Catalysts for the Enantioselective Addition of Cyanide to α,β -Unsaturated Imides

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General methods and characterization data for compounds synthesized

Kinetics data provided for the studies with catalyst **1** and Jacobsen's catalyst.

¹H NMR Spectra provided for:

- 1) Salen Ligand **6**
- 2) Unmetallated monomer **7**
- 3) Metallated monomer **8**
- 4) Polymer **1**

General. All starting materials were obtained from commercial suppliers and were used without further purification unless otherwise stated. All air- or moisture-sensitive reactions were performed using oven-dried or flame-dried glassware under an inert atmosphere of dry argon or nitrogen. Air- or moisture-sensitive liquids and solutions were transferred via syringe or cannula. Dichloromethane was distilled from calcium hydride, benzene from sodium, and 2-propanol from calcium sulfate. CAUTION: Trimethylsilyl cyanide and hydrogen cyanide are highly toxic and should be handled extremely carefully in a fume hood as per the experimental protocol mentioned below.

Analytical thin layer chromatography (TLC) was performed using Silica XHL pre-coated (250 μm thickness) glass backed TLC plates from Sorbent Technologies. Eluting solvents are reported as volume ratios or volume percents. Compounds were visualized using UV light, potassium permanganate, *p*-anisaldehyde or iodine stains. Flash column chromatography was performed using silica gel 60 \AA (230 - 400 mesh). All ^1H and ^{13}C NMR spectra were recorded on Varian Mercury Vx 300 or Varian Mercury Vx 400 spectrometers using CDCl_3 as solvent. Chemical shifts are expressed in parts per million (δ), coupling constants (J) are reported in Hertz (Hz), and splitting patterns are reported as singlet (s), doublet (d), triplet (t), quartet (q), unresolved multiplet (m), and apparent (app). All NMR spectra are referenced using residual solvent peaks as the standard with δ values of 7.26 for CDCl_3 . High-resolution mass spectra were obtained from the Georgia Institute of Technology mass spectrometry lab. IR spectra were recorded using a Shimadzu FTIR-8400S instrument. Samples were prepared as thin

films on a KBr salt plate by evaporation of chloroform or dichloromethane solutions. Vibrational signals are reported in wavenumbers (cm^{-1}) as strong (s), medium (m), weak (w), or broad (br). Gel-permeation chromatography (GPC) analyses were performed on a Shimadzu-10A system referenced to poly(styrene) standards. THF was used as the mobile phase with a flow rate of 1.0 mL min^{-1} . Chiral HPLC analyses were performed on a Shimadzu-10A system, using a Pirkle-L-Leucine column from Regis Technologies, Inc.

Characterization of compounds.

Salen ligand 6: TLC $R_f = 0.14$ (5:1 Hexane/EtOAc); ^1H NMR (400 MHz, CDCl_3) $\delta =$ 13.72 (br s, 1H, OH); 13.67 (br s, 1H, OH); 8.33 (s, 1H, N=CH); 8.31 (s, 1H, N=CH); 7.31 (d, 1H, $J = 2.2 \text{ Hz}$, H_{Ar}), 7.23 (d, 1H, $J = 2.0 \text{ Hz}$, H_{Ar}), 6.99 (d, 1H, $J = 2.2 \text{ Hz}$, H_{Ar}), 6.91(d, 1H, $J = 2.2 \text{ Hz}$, H_{Ar}); 3.57 (t, 2H, $J = 6.5 \text{ Hz}$, CH_2OH); 3.33 (m, 2H, 2NCHCH₂); 1.86-1.97 (m, 4H, 2 CH_2); 1.73 (m, 2H, CH_2); 1.6 (m, 2H, CH_2); 1.43-1.53 (m, 6H, CH_2); 1.39-1.4 (s (overlapping), 18H, C(CH₃)₃); 1.24 (s, 9 H, C(CH₃)₃); 1.2 (s, 3H, CH_3), 1.19 (s, 3H, CH_3); 1.19-1.24 (m, 2H, CH_2); 1.01-1.1 (m, 2H, CH_2); ^{13}C NMR (75 MHz, CDCl_3) $\delta =$ 166.1, 166.0, 158.3, 158.2, 141.8, 140.2, 138.8, 136.5 (overlapping signals), 127.4, 127.0, 126.9, 126.3, 118.1, 72.6 (overlapping signals), 63.3, 44.5, 37.2, 35.18, 35.16, 34.3, 33.5, 33.0, 31.6, 30.2, 29.7, 29.6 (overlapping signals), 29.18, 29.15, 25.7, 24.8, 24.6; IR (thin film) ν 3452 (br), 3313 (br), 2932 (s), 2858(s), 1703(m), 1679 (s), 1634 (s), 1274 (m), 1174 (m), 734 (m), 717 (m) cm^{-1} ; MS (ESI $^+$) calcd for $\text{C}_{41}\text{H}_{65}\text{N}_2\text{O}_3$ (MH^+) 633.5, found 633.6. Anal. Calcd. for $\text{C}_{41}\text{H}_{64}\text{N}_2\text{O}_3$: C, 77.80; H, 10.19; N, 4.43; Found: C, 77.42, H, 10.18, N, 4.44.

Salen norbornene ester 7: TLC R_f = 0.63 (5:1 Hexane/EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 13.73 (br s, 1H, OH), 13.71 (br s, 1H, OH), 8.32 (s, 1H, $\text{N}=\text{CH}$), 8.3 (s, 1H, $\text{N}=\text{CH}$), 7.3 (d, 1H, J = 2.5 Hz, H_{Ar}), 7.21 (d, 1H, J = 2.4 Hz, H_{Ar}), 6.99 (d, 1H, J = 2.5 Hz, H_{Ar}), 6.91 (d, 1H, J = 2.3 Hz, H_{Ar}), 6.11 (m, 2H, $\text{CH}=\text{CH}$), 4.01 (t, 2H, J = 6.8 Hz, CH_2OH), 3.33 (m, 2H, 2NCHCH_2), 3.2 (m, 2H, CH_2), 3.0 (s, 1H, CH), 2.9 (s, 1H, CH), 2.2 (m, 1H, CH), 1.83-1.94 (m, 5H, 2 CH_2 , 1 CHH), 1.72 (m, 2H, CH_2), 1.4-1.6 (m, 6H, CH_2); 1.39-1.4 (s (overlapping), 18H, $\text{C}(\text{CH}_3)_3$), 1.25-1.4 (m, 3H, CHH), 1.24 (s, 9 H, $\text{C}(\text{CH}_3)_3$), 1.19-1.24 (m, 2H, CH_2), 1.19 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 1.01-1.1 (m, 2H, CH_2); ^{13}C NMR (75 MHz, CDCl_3) δ 176.6, 166.08, 166.01, 158.21, 158.16, 140.2, 138.7, 138.2, 136.6, 136.5, 127.4, 127.5, 127.4, 126.9, 126.3, 118.1, 118.07, 72.6 (overlapping signals), 64.8, 46.8, 46.5, 44.5, 43.4, 41.8, 37.2, 35.18, 35.16, 33.5, 33.4, 31.6, 30.5, 30.1, 29.7, 29.6 (overlapping signals), 29.22, 29.17, 28.9, 26.0, 24.7, 24.6; IR (thin film) ν 2950 (s), 2905 (s), 1728 (s), 1626 (s), 1469 (m), 1441 (m), 1273 (w), 1174 (m), 877 (w) cm^{-1} ; HRMS (ESI $^+$) calcd for $\text{C}_{49}\text{H}_{73}\text{N}_2\text{O}_4(\text{MH}^+)$ 753.5, found 753.5. Anal. Calcd. for $\text{C}_{49}\text{H}_{72}\text{N}_2\text{O}_4$: C, 78.15; H, 9.64; N, 3.72; Found: C, 77.82, H, 9.68, N, 3.94.

Al-Salen monomer 8: TLC R_f = 0.63 (5:1 Hexane/EtOAc); ^1H NMR (400 MHz, CDCl_3) δ 8.36 (s, 1H, $\text{N}=\text{CH}$), 8.18 (s, 1H, $\text{N}=\text{CH}$), 7.55 (d, 1H, J = 1.5 Hz, H_{Ar}), 7.47 (d, 1H, J = 1.2 Hz, H_{Ar}), 7.07 (br m, 1H, H_{Ar}), 7.0 (br m, 1H, H_{Ar}), 6.11 (m, 2H, $\text{CH}=\text{CH}$), 4.04 (t, 2H, J = 6.7 Hz, CH_2OH), 3.92 (m, 1H, NCHCH_2), 3.18 (m, 1H, NCHCH_2), 3.0 (br m, 1H, CH), 2.9 (br m, 1H, CH), 2.4-2.65 (m, 2H, CH_2), 2.2 (m, 1H, CH), 2-2.15 (m, 2H, CH_2), 1.7-1.94 (m, 5H, 2 CH_2 , 1 CHH), 1.4-1.6 (m, 6H, 3 CH_2), 1.53-1.54 (s (overlapping),

18H, C(CH₃)₃); 1.25-1.4 (m, 3H, CHH), 1.3 (s, 9 H, C(CH₃)₃), 1.27 (s, 6H C(CH₃)₃), 1.0-1.2 (m, 4H, CH₂); IR (thin film) ν 2950 (s), 2860 (m), 1715 (m), 1634 (s), 1539 (s), 1472 (m), 1390 (s), 1175 (m), 847 (m), 786 (m) cm⁻¹; HRMS (ESI⁺) calcd for C₄₉H₇₀N₂O₄Al (M-Cl⁺) 777.5151, found 777.5099. Anal. Calcd. for C₄₉H₇₀AlClN₂O₄: C, 72.34; H, 8.67; N, 3.44; Found: C, 71.99, H, 8.99, N, 3.44. ICP calcd: Al, 3.32. Found: Al, 3.5.

Al-salen 50mer 1: ¹H NMR (400 MHz, CDCl₃) δ 8.24 (br s, 1H, N=CH); 8.1 (brs, 1H, N=CH), 7.52 (br m, 1H, H_{Ar}), 7.44 (br m, 1H, H_{Ar}), 6.9 (br m, 1H, H_{Ar}), 6.86 (br m, 1H, H_{Ar}); 5.01-5.44 (br m, 2H, CH=CH), 3.97 (br m, 2H, CH₂OH), 3.61 (br m, 1H, NCHCH₂), 3.43 (br m, 1H, NCHCH₂), 2.86 - 3.1 (br m, 2H, CH), 2.28 - 2.86 (m, 2H, CH₂), 1.8-2.17 (br m, 3H, CH, CH₂), 1.38- 1.78 (br m, 11H, 5CH₂, 1CHH), 1.43-1.58 (br s (overlapping), 18H, C(CH₃)₃), 1.15-1.4 (br m, 3H, CHH), 1.29 (s, 9 H, C(CH₃)₃), 1.27 (s, 6H C(CH₃)₃), 1.0-1.2 (br m, 4H, CH₂); IR (thin film) ν 2950 (s), 2860 (s), 1732 (m), 1634 (s), 1558 (m), 1539 (m), 1472 (m), 1362 (m), 1176 (m), 846 (m), 786 (w) cm⁻¹; ICP calcd: Al, 3.32 . Found: Al, 4.1.

N-[3-(S)-Cyano-butryrl]-benzamide 9a: TLC R_f = 0.14 (3:1 hexane/EtOAc); ¹H NMR (300 MHz, CDCl₃) δ 8.88 (s, 1H, NH), 7.89 (dd, 2H, *J* = 8.0 Hz, *J* = 1.5 Hz, H_{Ar}), 7.64 (t, 1H, *J* = 7 Hz, H_{Ar}), 7.54 (t, 2H, *J* = 6.3 Hz, H_{Ar}), 3.47 (dd, 1H, *J* = 17.2 Hz, *J* = 7 Hz, CHCN), 3.31 (m, 1H CNCHCHH); 3.2 (m, 1H, NCCHCHH), 1.45 (d, 3H, *J* = 7.3 Hz, CH₃).

***N*-[3-(*S*)-Cyano-hexanoyl]-benzamide 9b:** TLC R_f = 0.2 (3:1 hexane/EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 9.38 (s, 1H, *NH*), 7.93 (dd, 2H, J = 8 Hz, J = 1.1 Hz, H_{Ar}), 7.6 (t, 1H, J = 6.2 Hz, H_{Ar}), 7.54 (t, 2H, J = 8.1 Hz, H_{Ar}), 3.45 (dd, 1H, J = 18.3 Hz, J = 8.8 Hz, *CHCN*), 3.3 (dd, 1H, J = 18.7 Hz, J = 5 Hz, *CNCHCHH*), 3.14 (m, 1H, *NCCHCHH*), 1.81 - 1.42 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 0.98 (t, 3H, J = 7.3 Hz, CH_3).

***N*-[3-(*S*)-Cyano-4-methyl-pentanoyl]-benzamide 9c:** TLC R_f = 0.2 (3:1 Hexane/EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 8.9 (s, 1H, *NH*), 7.87 (dd, 2H, J = 7.9 Hz, J = 1.5 Hz, H_{Ar}), 7.64 (t, 1H, J = 7.3 Hz, H_{Ar}), 7.54 (t, 2H, J = 7.3 Hz, H_{Ar}), 3.45 (dd, 1H, J = 18 Hz, J = 10 Hz, *CHCN*), 3.28 (dd, 1H, J = 18.6 Hz, J = 4.3 Hz, *CNCHCHH*); 3.12 (m, 1H, *NCCHCHH*), 2 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 1.14 (dd, 6H, J = 6.8 Hz, J = 3 Hz, $\text{CH}(\text{CH}_3)_2$).

***N*-[3-(*S*)-Cyano-5-phenyl-pentanoyl]-benzamide 9d:** TLC R_f = 0.2 (3:1 Hexane/EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 9.2 (s, 1H, *NH*), 7.89 (dd, 2H, J = 7.3 Hz, J = 1.5 Hz, H_{Ar}), 7.64 (t, 1H, J = 7.3 Hz, H_{Ar}), 7.53 (t, 2H, J = 6.9 Hz, H_{Ar}), 7.33 - 7.19 (m, 5H, H_{Ph}), 3.48 (dd, 1H, J = 18 Hz, J = 8.5 Hz, *CHCN*), 3.29 (dd, 1H, J = 18.7 Hz, J = 5.4 Hz, *CNCHCHH*), 3.11 (m, 1H, *NCCHCHH*), 2.96 (m, 1H, *NCCCHH*), 2.82 (m, 1H, *NCCCHH*), 21. - 1.96 (m, 2H, CH_2); ^{13}C NMR (75 MHz, CDCl_3) δ 172.8, 166.1, 139.98, 133.9, 132.2, 129.4, 128.9, 128.7, 128.1, 126.7, 121.4, 40.5, 33.7, 33.4, 26.4.

***N*-[3-(*S*)-Cyano-4,4-dimethyl-pentanoyl]-benzamide 9e:** TLC R_f = 0.26
(3:1 Hexane/EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 9.08 (s, 1H, *NH*), 7.9 (m, 2H, H_{Ar}),
7.6 (t, 1H, J = 6.5 Hz, H_{Ar}), 7.53 (t, 2H, J = 6.5 Hz, H_{Ar}), 3.4 - 3.3 (m, 2H, $CHCHHCH_3$),
3.01 (dd, 1H, J = 10.2 Hz, J = 4 Hz, $NCCHCHH$), 1.14 (s, 9H, $C(CH_3)_3$).

Kinetic graph for the catalysis:





