Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Exploring Ligand Substituent Effects in Stereoselective Polymerization of Racemic Lactide Using Aluminium Salen-Type Complexes

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Experimental Procedures

Materials

All the reagents were used as received without further purification unless mentioned otherwise. Racemic lactide (99%), L-lactide (99%), and D-lactide (99%) were purchased from Heowns and all of the lactides were recrystallized three times from anhydrous toluene under the stream of argon atmosphere to obtain white crystals. Aluminium isopropoxide (>98%) was purchased from TCI and used after activated. 2-Hydroxy-3-methylbenzaldehyde (>98%) was purchased from TCI. (*R,R*)-Cyclohexane-1,2-diamine (99%), (*S,S*)-Cyclohexane-1,2-diamine (99%), (*R,R*)-(-)-N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamine (99%), 2-Ethylphenol (98%), 2-Isopropylphenol (99%), 3-Bromo-2-hydroxybenzaldehyde (98%) and Paraformaldehyde (96%) were all purchased from Energy Chemical. Magnesium chloride (99%) was purchased from Macklin reagent. Salicylaldehyde (≥99%) was purchased from Aladdin. 3-Tert-butyl-2-hydroxybenzaldehyde (97%), 4-Tert-butyl-salicylaldehyde (95%), 5-Tert-butyl-2-hydroxy-benzaldehyde (98%) and 5-Bromo-3-tert-butyl-2-hydroxybenzaldehyde (95%) were purchased from Bidepharm. 3-Fluoro-2-hydroxybenzaldehyde (97%), 3-Chloro-2-hydroxy-benzaldehyde (97%) and 2-Iodophenol (98%) were purchased from Sigma Aldrich. Benzyl alcohol (BnOH, >99%) was purchased from Sigma Aldrich, distilled over calcium hydride (CaH_2), and then dissolved into anhydrous toluene to form a 1 M solution as the initiator. The anhydrous solvents, such as toluene and dichloromethane (DCM), were redistilled over CaH_2 and stored over molecular sieves (4 Å) in a glovebox for no more than 1 month. Chromatographic grade *n*-hexane, isopropanol and tetrahydrofuran were purchased from Honeywell LTD for the analysis of HPLC and GPC measurements. All other chemicals were commercially available and used appropriately according to practical use. The manipulations of air or moisture-sensitive compounds were operated by using Schlenk techniques or in an argon-filled glovebox.

Instrumentation

NMR: Nuclear magnetic resonance measurements were performed at room temperature on Bruker Advance instrument at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), $CDCl_3$ was used as an internal reference.

GPC: Molecular weights (M_n) and dispersities ($Đ$) of the polymers were determined by gel permeation chromatography (GPC, Agilent 1260 LC, USA) using THF as the eluent (flow rate: 1

mL/min, at 40 °C) and the sample concentration was 1 mg/mL.

MALDI-TOF: Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS) analyses were conducted on a Bruker Microflex LRF MS spectrometer equipped with a 337 nm nitrogen laser operating in a positive ion, linear mode. The sample solutions (10 mg/mL in THF), trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) solution (10 mg/mL in THF) and sodium trifluoroacetate aqueous solution (5 mg/mL) were mixed in a volume ratio of 5: 25: 1, 1 μL of which was then deposited on the target plate and dried before measurement.

HPLC: Shimadzu Prominence LC-20A Series High Performance Liquid Chromatography (HPLC) was applied to measure the enantiomeric excess (*ee*) of unreacted monomer using a UV (230 nm) detector (*n*-hexane: *i*-propanol = 9: 1, flow rate: 0.5 mL/min).

DSC: Differential scanning calorimetry (DSC) measurements were performed on DSC 3500 Sirius. The temperature was calibrated with $C_{10}H_{16}$, indium, tin, bismuth and zinc standard. Measurements were performed under N_2 atmosphere with a flow rate of 20 mL/min. Each sample with a mass of 10 mg was used for the measurement. The typical procedures for the measurements of samples were as follows: in the first heating scan, samples were heated from 20°C to 250°C at a heating rate of 10 K/min. In the second heating scan, samples were cooled to 0°C at 10 K/min and kept at 0°C for 20 min to eliminate any thermal history, and subsequently reheated to 250°C at 10 K/min.

General Procedure for the synthesis of Salcyc-(L1 - L15) ligands

Salcyc-L1 can be obtained commercially, whereas Salcyc-L2 - L15 were prepared according to typical procedures. Taking Salcyc-L2 as an example, a solution of (1*R*,2*R*)-Cyclohexane-1,2-diamine (4 g, 0.035 mol, 1 equiv.) and salicylaldehyde (8.5 g, 0.07 mol, 2 equiv.) in EtOH was stirred at 80℃ for 5 h under reflux. Once the reaction finished, the resulting mixture was cooled to room temperature, and the solvent was removed by a rotary evaporator. Next, the mixture was washed three times by 60 mL of hexane to give an analytically pure yellow powder.

Synthesis of Al(Salen) complexes

Complexes were prepared according to the literature reported before.[1] $Al(O^iPr)_3$ was activated by heating with a heat gun to a liquid state and maintained for 1 min, and then cooled to room temperature. This step was repeated four more times until there was no solid left.[2] The ligand was

dissolved in 2 mL toluene in a glovebox (1 mmol, 1 equiv.). The activated $Al(O^iPr)_3$ (1 mmol, 1 equiv.) was dissolved in 1 mL anhydrous toluene and added to the ligand solution. The solution was then stirred at 80°C for hours under the stream of argon atmosphere to afford a pale yellow powder. ^1H and ^{13}C NMR analysis for all the complexes were carried out to detect the structure of these complexes and crystal structures of complex (*R,R*)-Salen[6-Et] and (*R,R*)-Salen[6-^{i}Pr] were obtained.

However, the solubility of complexes with electron-withdrawing groups (F/Cl/Br/I) were not very well in $CDCl_3$ or many other deuterium reagents. In addition, carbon signals were fundamentally much weaker than proton signals. Thus, many efforts to obtain these complex's carbon spectra failed. But we acquired ^1H NMR spectra of these complexes (Salen[6-F/Cl/Br/I]) and crystal structure of the complex (*R,R*)-Salen[6-^{i}Pr].

Typical polymerization procedure

The standard protocol involved adding *rac*-LA (288 mg, 2 mmol) to a 10 mL glass Schlenk tube, along with 1.5 mL dry toluene and a metal initiator (0.02 mmol in 0.5 mL toluene). The resulting mixture was immediately stirred with a magnetic stir bar at 80°C for the expected time. An aliquot of the reaction mixture was taken after a designated time to determine the monomer conversion by ^1H NMR spectroscopy ($CDCl_3$, 400 MHz). The reaction was quenched, and the polymer was precipitated by adding excess methanol, then filtered and dried under vacuum. The probability of *rac* (P_r) or *meso* (P_m) enchainment was determined using homonuclear decoupled ^1H NMR spectroscopy.

Salcyc-L2: ^1H NMR (400 MHz, $CDCl_3$) δ 13.33 (s, 2H, OH), 8.26 (s, 2H, HC = N), 7.26 – 7.19 (m, 2H, ArH), 7.15 (d, *J* = 6.0 Hz, 1H, ArH), 7.15 (d, *J* = 9.4 Hz, 1H, ArH), 6.88 (d, *J* = 9.4 Hz, 1H, ArH), 6.88 (d, *J* = 7.2 Hz, 1H, ArH), 6.83 – 6.75 (m, 1H, ArH), 6.79 (t, *J* = 6.9 Hz, 1H, ArH), 3.40 – 3.26 (m, 2H, CH), 2.04 – 1.80 (m, 4H, CH), 1.80 – 1.65 (m, 2H, CH), 1.53 – 1.43 (m, 1H, CH), 1.48 (d, *J* = 19.0 Hz, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 161.1, 132.3, 131.6, 118.8, 118.7, 116.9, 72.8, 33.2, 24.3.

Salcyc-L3: ^1H NMR (400 MHz, $CDCl_3$) δ 13.63 (s, 2H, OH), 8.27 (s, 2H, HC = N), 7.18 – 7.09 (m, 2H, ArH), 7.01 (dd, *J* = 7.7, 1.7 Hz, 2H, ArH), 6.72 (t, *J* = 7.5 Hz, 2H, ArH), 3.45 – 3.16 (m, 2H), 2.24 (s, 6H, CH_3), 2.00 – 1.84 (m, 4H, CH), 1.81 – 1.64 (m, 2H, CH), 1.48 (td, *J* = 9.3, 4.4 Hz, 2H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 159.4, 133.3, 129.2, 125.8, 118.2, 118.0, 72.7,

33.3, 24.3, 15.6.

Salcyc-L4: ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.62 (s, 2H, OH), 8.28 (s, 2H, HC = N), 7.18 – 7.12 (m, 2H, ArH), 7.02 (d, *J* = 7.7 Hz, 1H, ArH), 7.02 (d, *J* = 7.7 Hz, 1H, ArH), 6.75 (t, *J* = 7.5 Hz, 2H, ArH), 3.39 – 3.27 (m, 2H, CH), 2.76 – 2.59 (m, 4H, CH_2), 1.98 – 1.82 (m, 4H, CH), 1.77 – 1.61 (m, 2H, CH), 1.56 – 1.41 (m, 2H, CH), 1.23 (s, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 159.1, 131.8, 131.6, 129.3, 118.3, 118.2, 72.7, 33.4, 24.4, 22.7, 13.9.

Salcyc-L5: ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.68 (s, 2H, OH), 8.28 (s, 2H, HC = N), 7.24 – 7.15 (m, 2H, ArH), 7.00 (dd, *J* = 7.7, 1.7 Hz, 2H, ArH), 6.77 (s, 2H, ArH), 3.34 (d, *J* = 6.8 Hz, 2H, ArCH, 2H, CH), 2.08 – 1.87 (m, 4H, CH), 1.71 (tt, *J* = 15.6, 12.6, 5.8 Hz, 2H, CH), 1.47 (tt, *J* = 9.3, 2.6 Hz, 2H, CH), 1.22 (d, *J* = 2.9 Hz, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 158.6, 136.2, 129.2, 128.9, 118.4, 118.2, 72.7, 33.4, 26.4, 24.4, 22.6, 22.5.

Salcyc-L6: ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.87 (s, 2H, OH), 8.29 (s, 2H, HC = N), 7.26 – 7.20 (m, 2H, ArH), 6.99 (d, *J* = 9.2 Hz, 1H, ArH), 6.99 (d, *J* = 6.0 Hz, 1H, ArH), 6.72 (t, *J* = 7.7 Hz, 2H, ArH), 3.48 – 3.13 (m, 2H, CH), 2.03 – 1.93 (m, 1H, CH), 2.06 – 1.94 (m, 1H, CH), 1.93 – 1.84 (m, 2H, CH), 1.82 – 1.69 (m, 2H, CH), 1.53 – 1.45 (m, 2H, CH), 1.41 (s, 18H, CCH3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 160.4, 137.2, 129.9, 129.4, 118.7, 117.8, 72.5, 34.9, 33.3, 29.5, 24.4.

Salcyc-L7: ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.25 (s, 2H, OH), 8.24 (s, 2H, HC = N), 7.09 (d, *J* = 8.1 Hz, 2H, ArCH), 6.91 (d, *J* = 1.9 Hz, 2H, ArCH), 6.84 (d, *J* = 8.1 Hz, 2H, ArCH), 3.35 – 3.24 (m, 2H, CH), 1.95 – 1.81 (m, 4H, CH), 1.70 (d, *J* = 11.2 Hz, 2H, CH), 1.46 (t, *J* = 10.0 Hz, 2H, CH), 1.27 (s, 18H, CCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 160.9, 156.3, 131.2, 116.5, 116.1, 113.9, 72.8, 35.1, 33.4, 31.2, 24.4.

Salcyc-L8: ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.14 (s, 2H, OH), 8.26 (s, 2H, HC = N), 7.33 – 7.23 (m, 2H, ArH), 7.12 (d, *J* = 2.5 Hz, 2H, ArH), 6.83 (d, *J* = 8.6 Hz, 2H, ArH), 3.40 – 3.23 (m, 2H, CH), 2.00 – 1.83 (m, 2H, CH), 1.94 – 1.78 (m, 2H, CH), 1.78 – 1.63 (m, 2H, CH),), 1.47 (d, *J* = 3.2 Hz, 1H, CH), 1.47 (d, *J* = 19.8 Hz, 1H, CH), 1.23 (s, 18H, CCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 158.7, 141.4, 129.6, 128.1, 118.1, 116.4, 72.9, 34.0, 33.4, 31.5, 24.4.

Salcyc-L9: ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.83 (s, 2H, OH), 8.17 (s, 2H, HC = N), 7.31 (d, *J* = 2.5 Hz, 2H, ArH), 7.08 (d, *J* = 2.4 Hz, 2H, ArH), 3.47 – 3.22 (m, 2H, CH), 2.06 – 1.97 (m, 2H,

CH), 1.94 – 1.86 (m, 2H, CH), 1.75 (d, J = 12.1 Hz, 2H, CH), 1.48 (td, J = 9.5, 4.5 Hz, 2H, CH), 1.39 (s, 18H, CCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 159.5, 140.0, 132.4, 131.7, 119.9, 109.9, 72.5, 35.2, 32.9, 29.2, 24.3.

(*S,S*)-Salcyc-L10: ^1H NMR (400 MHz, $CDCl_3$) δ 13.83 (s, 2H, OH), 8.17 (s, 2H, HC = N), 7.31 (d, J = 2.4 Hz, 2H, ArCH), 7.08 (d, J = 2.4 Hz, 2H, ArCH), 3.57 – 3.17 (m, 2H, CH), 2.07 – 1.96 (m, 2H, CH), 1.90 (dd, J = 7.3, 3.7 Hz, 2H, CH), 1.84 – 1.69 (m, 2H, CH), 1.48 (s, 2H), 1.39 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 159.5, 140.0, 132.5, 131.7, 119.9, 109.9, 72.5, 35.2, 32.9, 29.2, 24.3.

Salcyc-L11: ^1H NMR (400 MHz, $CDCl_3$) δ 13.66 (s, 2H, OH), 8.27 (d, J = 1.2 Hz, 2H, HC = N), 7.08 (d, J = 11.0 Hz, 1H, ArH), 7.11 – 7.04 (m, 1H, ArH), 7.05 (d, J = 1.5 Hz, 1H, ArH), 6.95 (dt, J = 7.7, 1.4 Hz, 2H, ArH), 6.77 – 6.66 (m, 1H, ArH), 6.75 – 6.64 (m, 1H, ArH), 3.35 (d, J = 9.8 Hz, 2H, CH), 2.09 – 1.84 (m, 4H, CH), 1.74 (d, J = 12.0 Hz, 2H, CH), 1.53 – 1.42 (m, 2H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 164.6, 152.6, 150.2, 150.0, 126.61, 126.57, 120.31, 120.26, 118.7, 118.6, 118.0, 117.9, 72.6, 33.1, 24.2.

Salcyc-L12: ^1H NMR (400 MHz, $CDCl_3$) δ 14.32 (s, 2H, OH), 8.24 (s, 2H, HC = N), 7.36 (dd, J = 7.9, 1.5 Hz, 2H, ArH), 7.08 (d, J = 7.7, 1.6 Hz, 2H, ArH), 6.74 (t, J = 7.8 Hz, 2H, ArH), 3.42 – 3.30 (m, 2H, CH), 2.04 – 1.84 (m, 4H, CH), 1.81 – 1.67 (m, 2H, CH), 1.48 (td, J = 9.5, 4.6 Hz, 2H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 157.7, 132.8, 130.2, 121.7, 119.2, 118.8, 72.3, 33.1, 24.2.

(*S,S*)-Salcyc-L13: ^1H NMR (400 MHz, $CDCl_3$) δ 14.31 (s, 2H, OH), 8.24 (s, 2H, HC = N), 7.34 (dd, J = 7.9, 1.5 Hz, 2H, ArH), 7.08 (dd, J = 7.7, 1.6 Hz, 2H, ArH), 6.73 (t, J = 7.8 Hz, 2H, ArH), 3.41 – 3.28 (m, 2H, CH), 2.02 – 1.83 (m, 4H, CH), 1.79 – 1.64 (m, 2H, CH), 1.47 (td, J = 9.5, 4.6 Hz, 2H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 157.7, 132.8, 130.1, 121.7, 119.2, 118.8, 72.2, 33.1, 24.1.

Salcyc-L14: ^1H NMR (400 MHz, $CDCl_3$) δ 14.45 (s, 2H, OH), 8.21 (s, 2H, HC = N), 7.52 (dd, J = 7.8, 1.5 Hz, 2H, ArH), 7.12 (d, J = 6.1 Hz, 1H, ArH), 7.12 (d, J = 9.2 Hz, 1H, ArH), 6.69 (t, J = 7.8 Hz, 2H, ArH), 3.43 – 3.30 (m, 2H, CH), 2.02 – 1.84 (m, 4H, CH), 1.73 (t, J = 11.6 Hz, 2H, CH), 1.48 (d, J = 10.7 Hz, 2H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 158.6, 135.8, 130.9, 119.4, 119.1, 111.2, 72.2, 33.1, 24.2.

Salcyc-L15: ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.60 (s, 2H, OH), 8.12 (s, 2H, HC = N), 7.73 (dd, *J* = 7.8, 1.6 Hz, 2H, ArH), 7.14 (d, *J* = 6.0 Hz, 1H, ArH), 7.14 (d, *J* = 9.2 Hz, 1H, ArH), 6.58 (t, *J* = 7.7 Hz, 2H, ArH), 3.41 – 3.29 (m, 2H, CH), 2.00 – 1.84 (m, 4H, CH), 1.70 (d, *J* = 9.8 Hz, 2H, CH), 1.46 (td, *J* = 9.4, 4.6 Hz, 2H, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 161.0, 141.9, 132.0, 120.2, 118.2, 86.2, 72.0, 33.1, 24.2.

NMR Spectroscopy

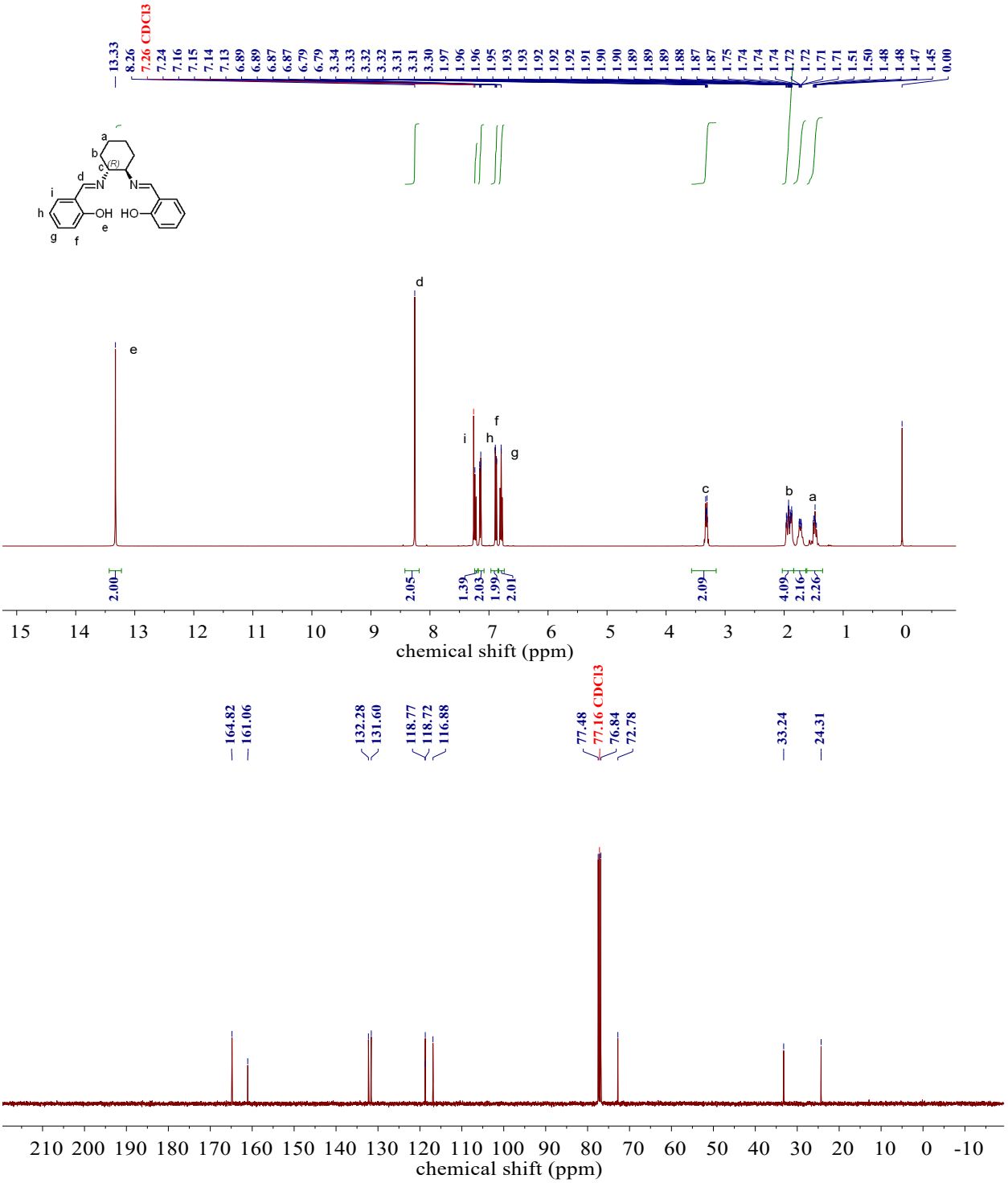


Figure S1. ^{1}H and ^{13}C NMR spectra for Salcyc-L2.

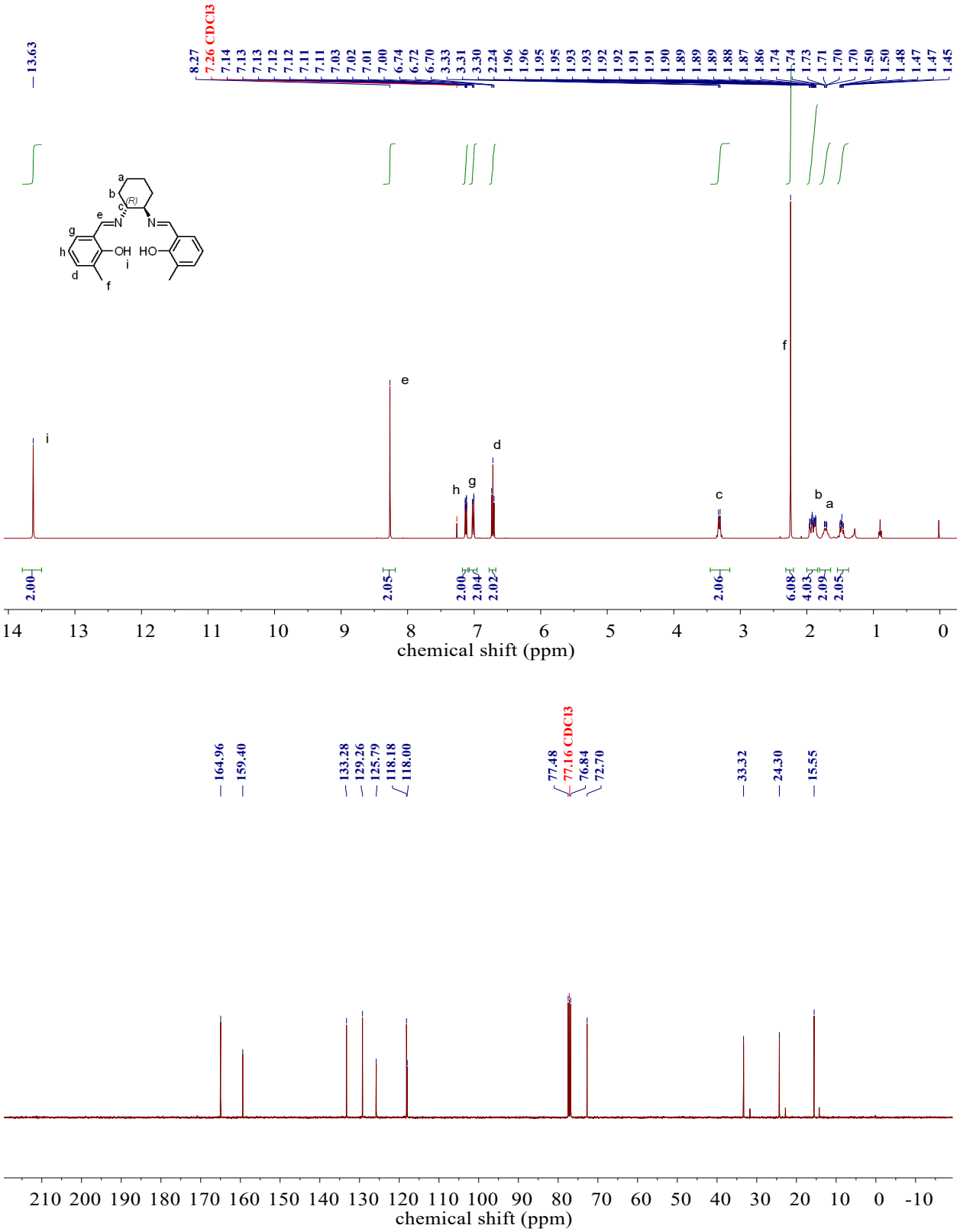


Figure S2. ^{1}H and ^{13}C NMR spectra for Salcyc-L3.

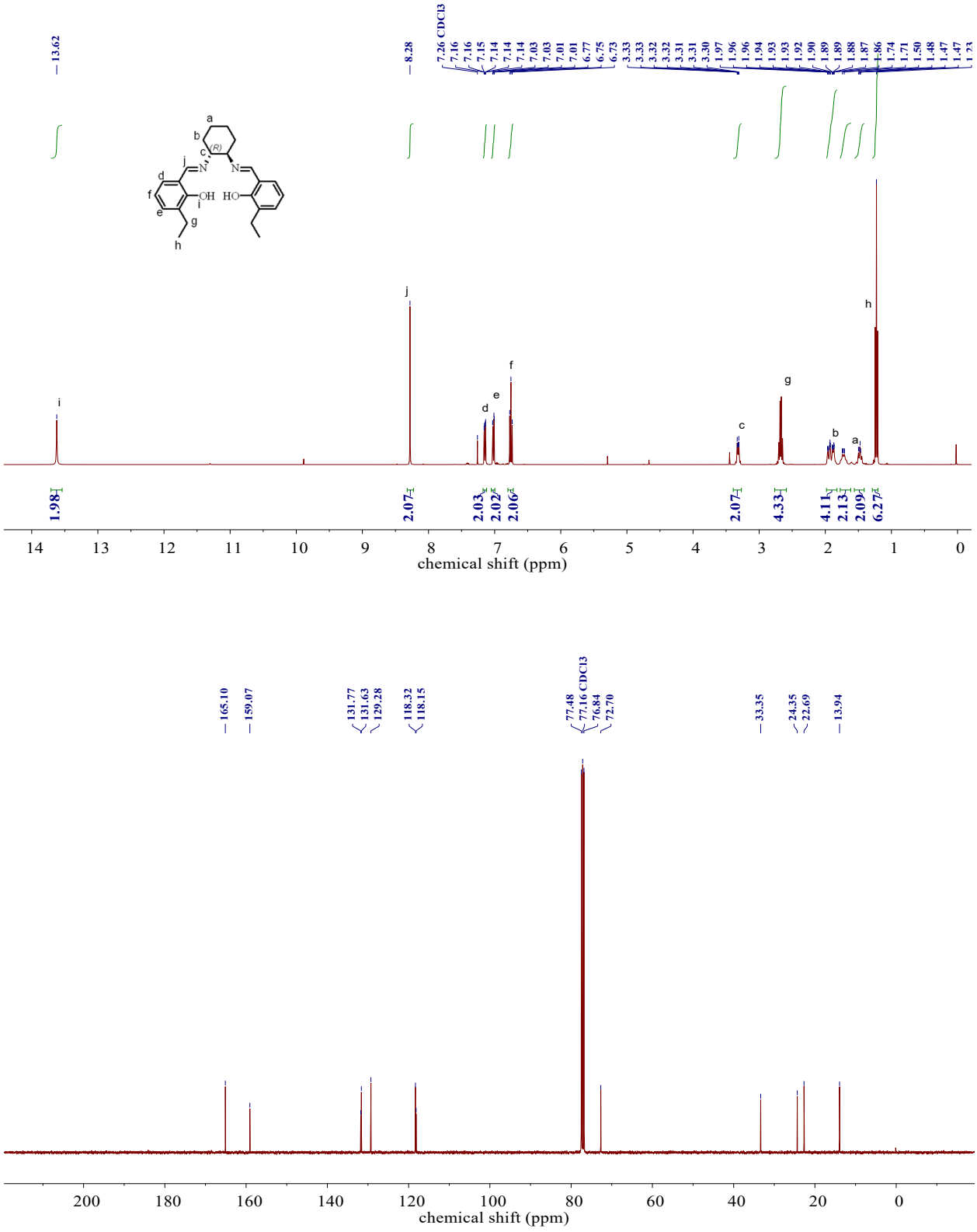


Figure S3. ^{1}H and ^{13}C NMR spectra for Salcyc-L4.

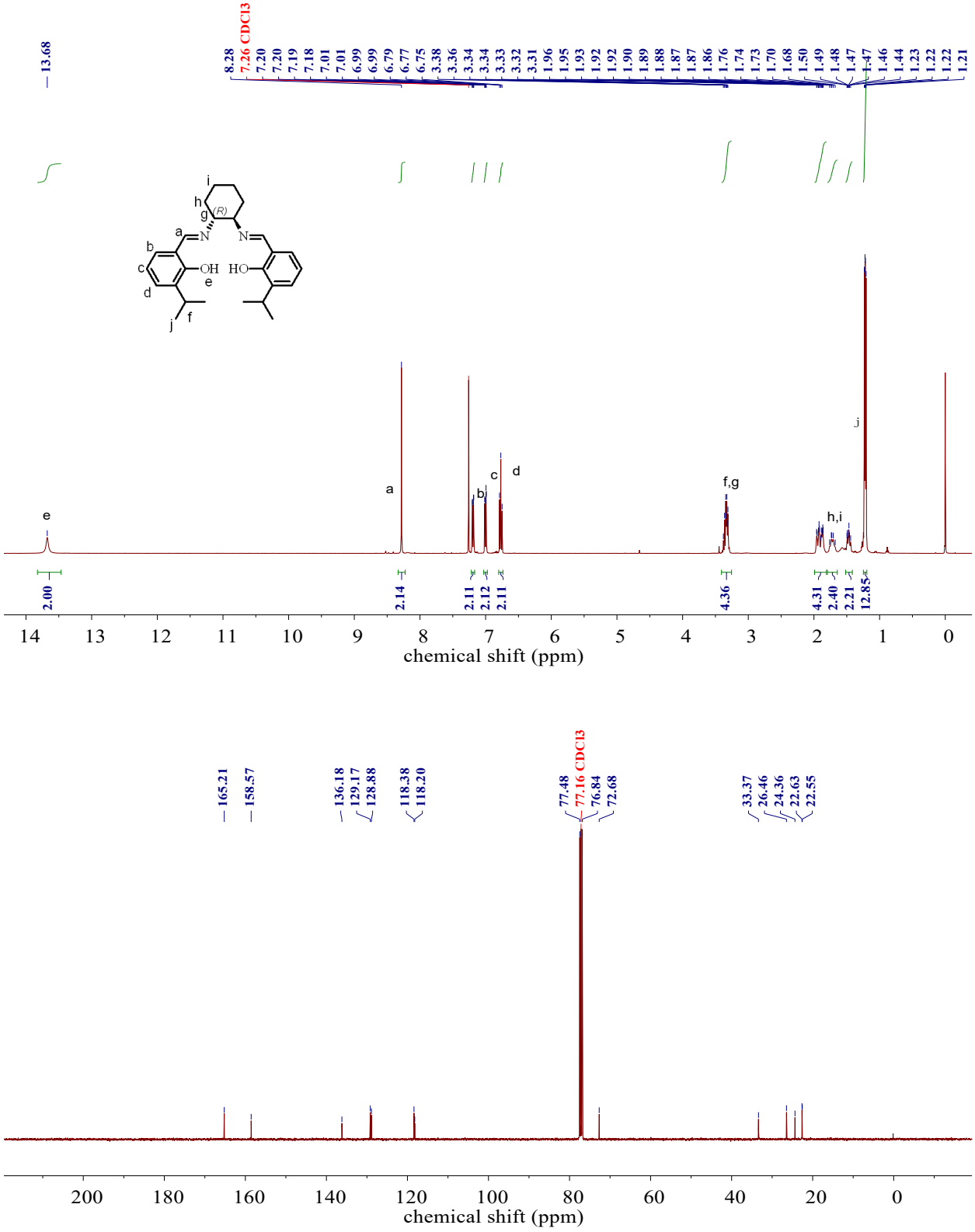


Figure S4. ^{1}H and ^{13}C NMR spectra for Salcyc-L5.

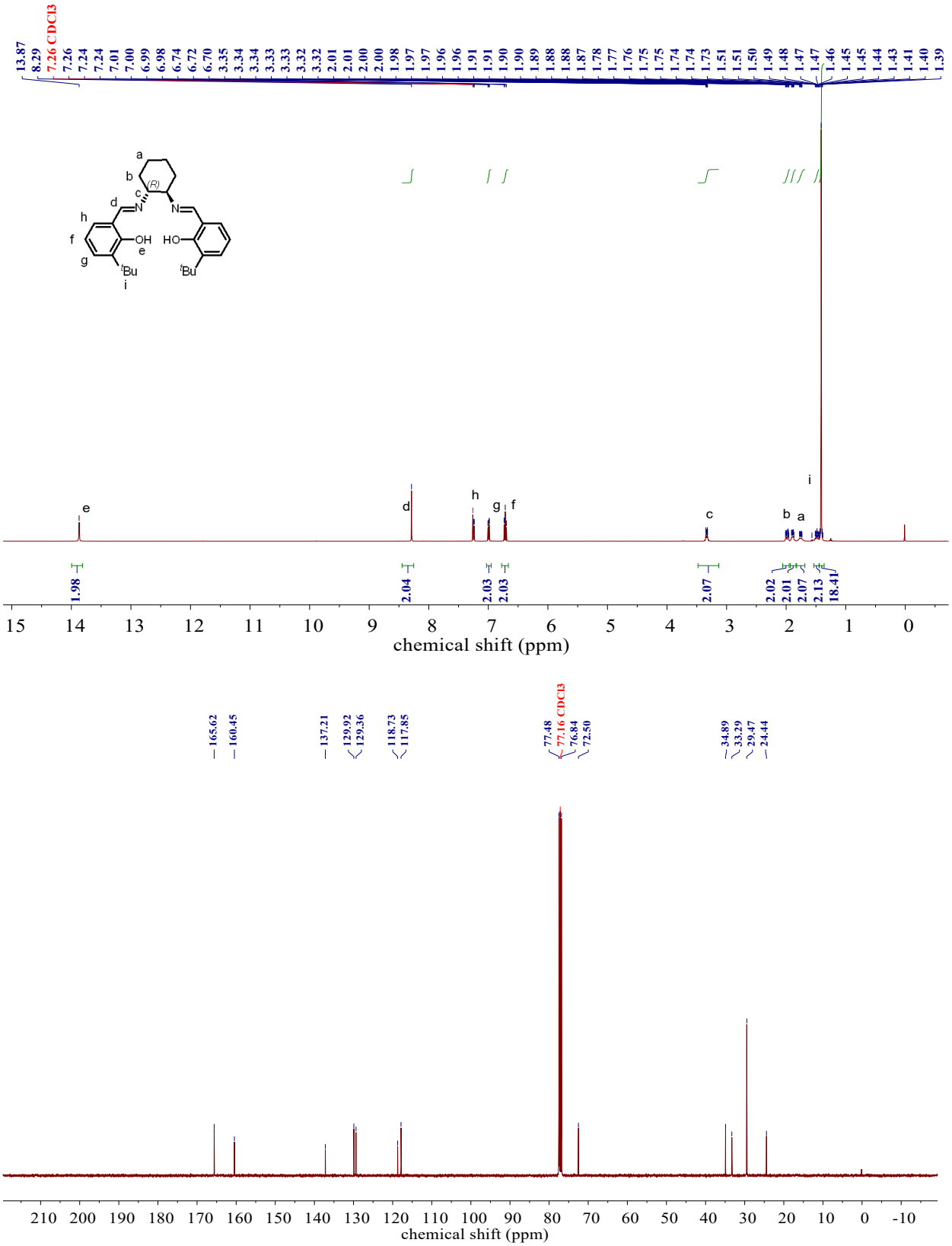


Figure S5. ^{1}H and ^{13}C NMR spectra for Salcyc-L6.

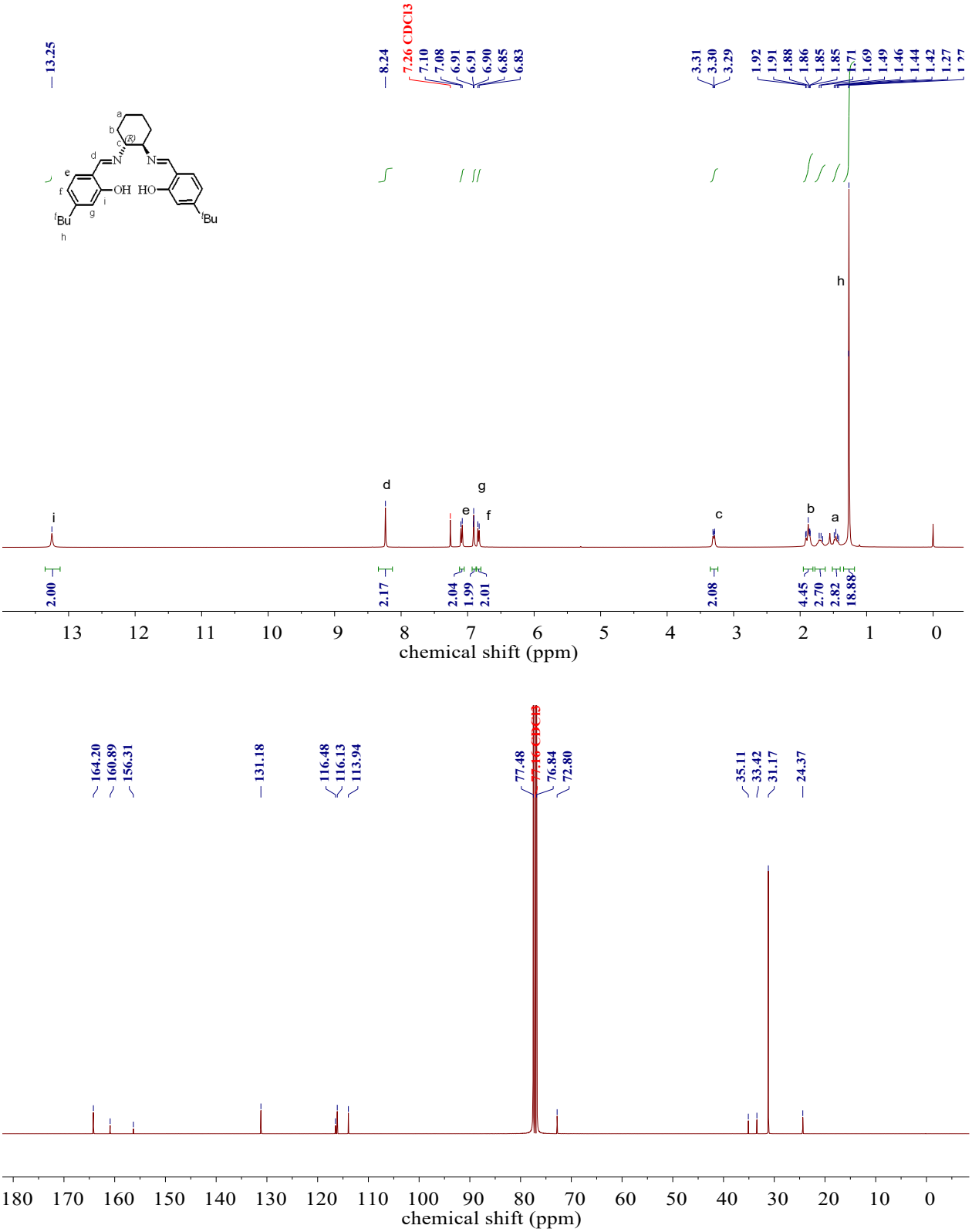


Figure S6. ^{1}H and ^{13}C NMR spectra for Salcyc-L7.

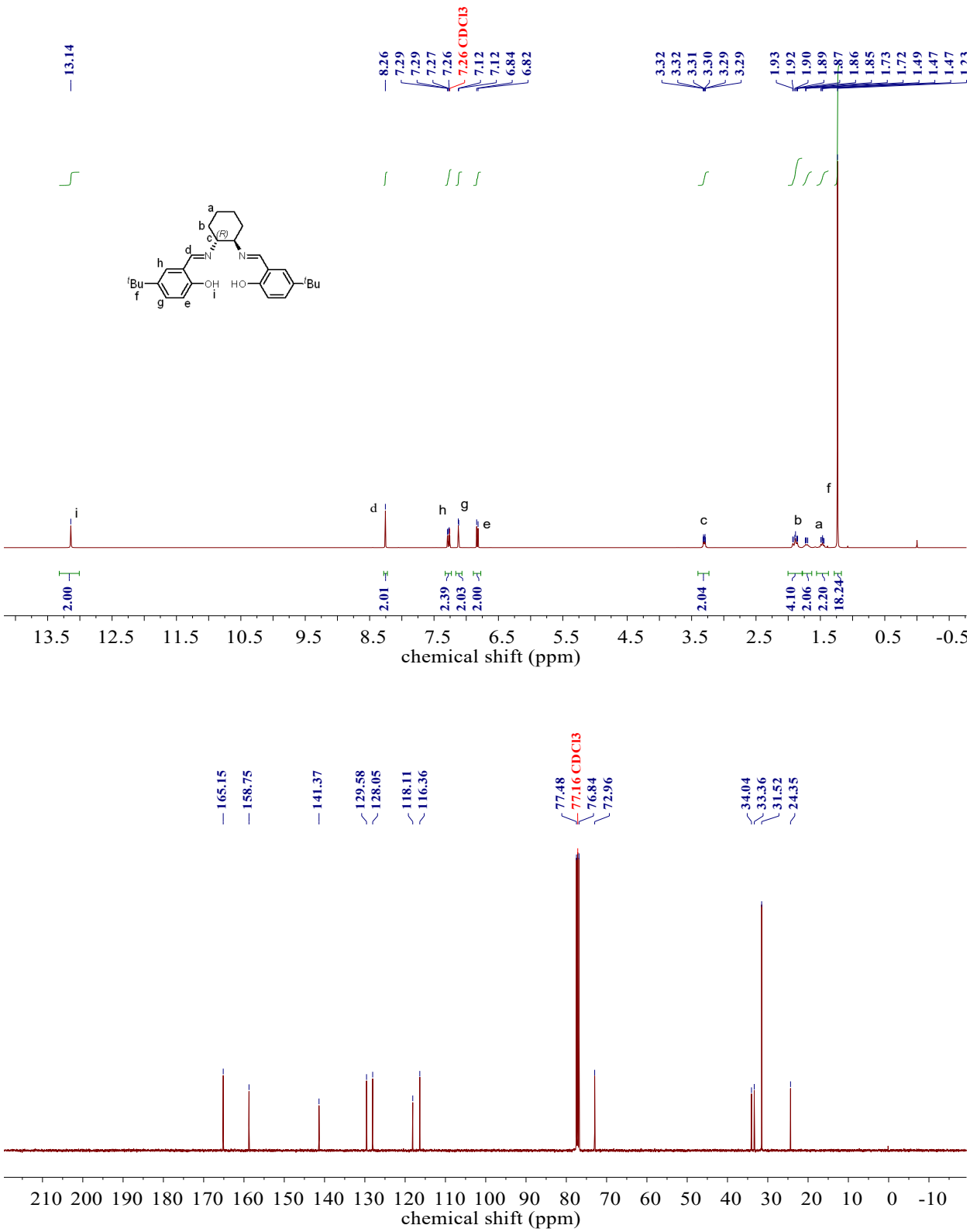


Figure S7. ^{1}H and ^{13}C NMR spectra for Salcyc-L8.

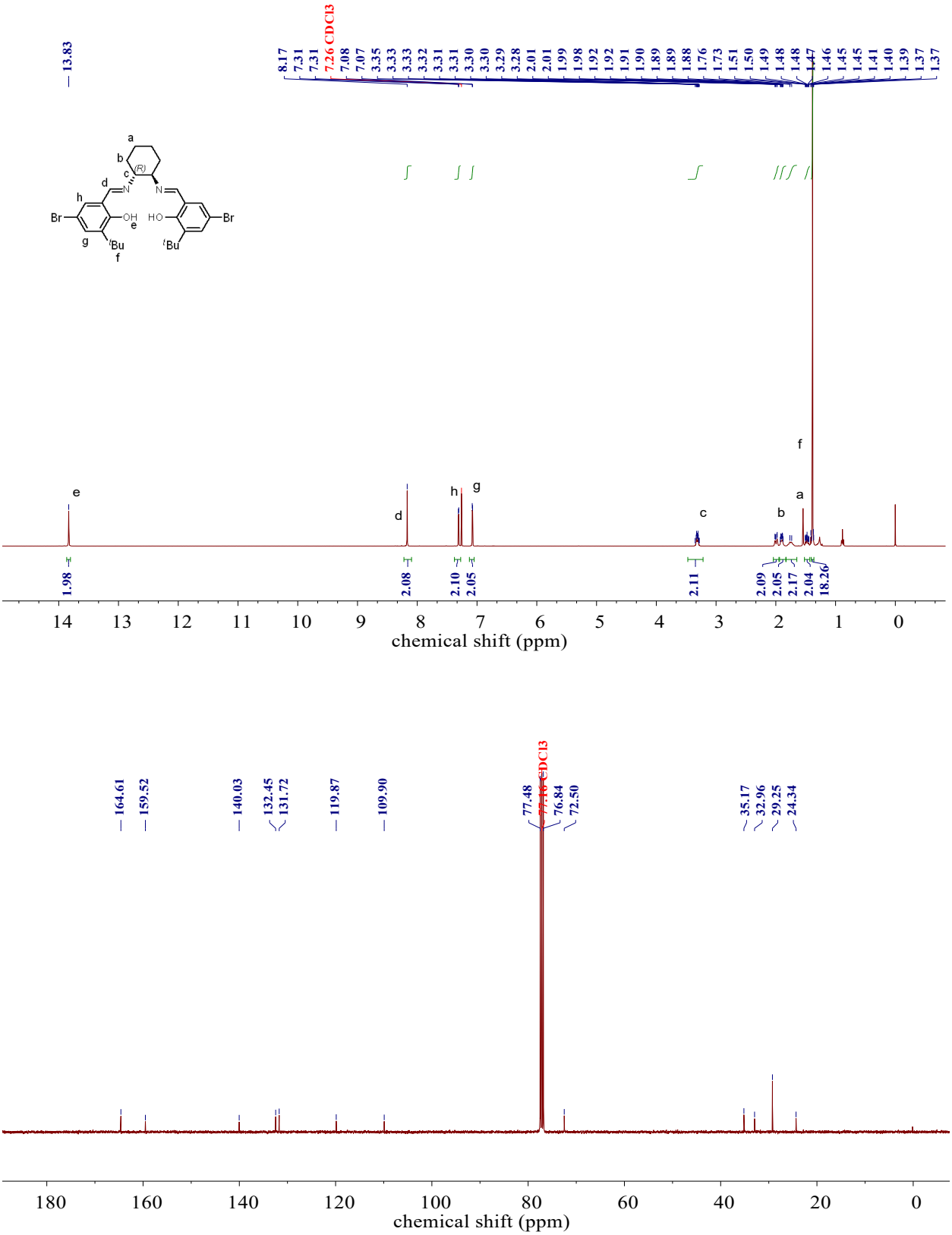


Figure S8. ^{1}H and ^{13}C NMR spectra for Salcyc-L9.

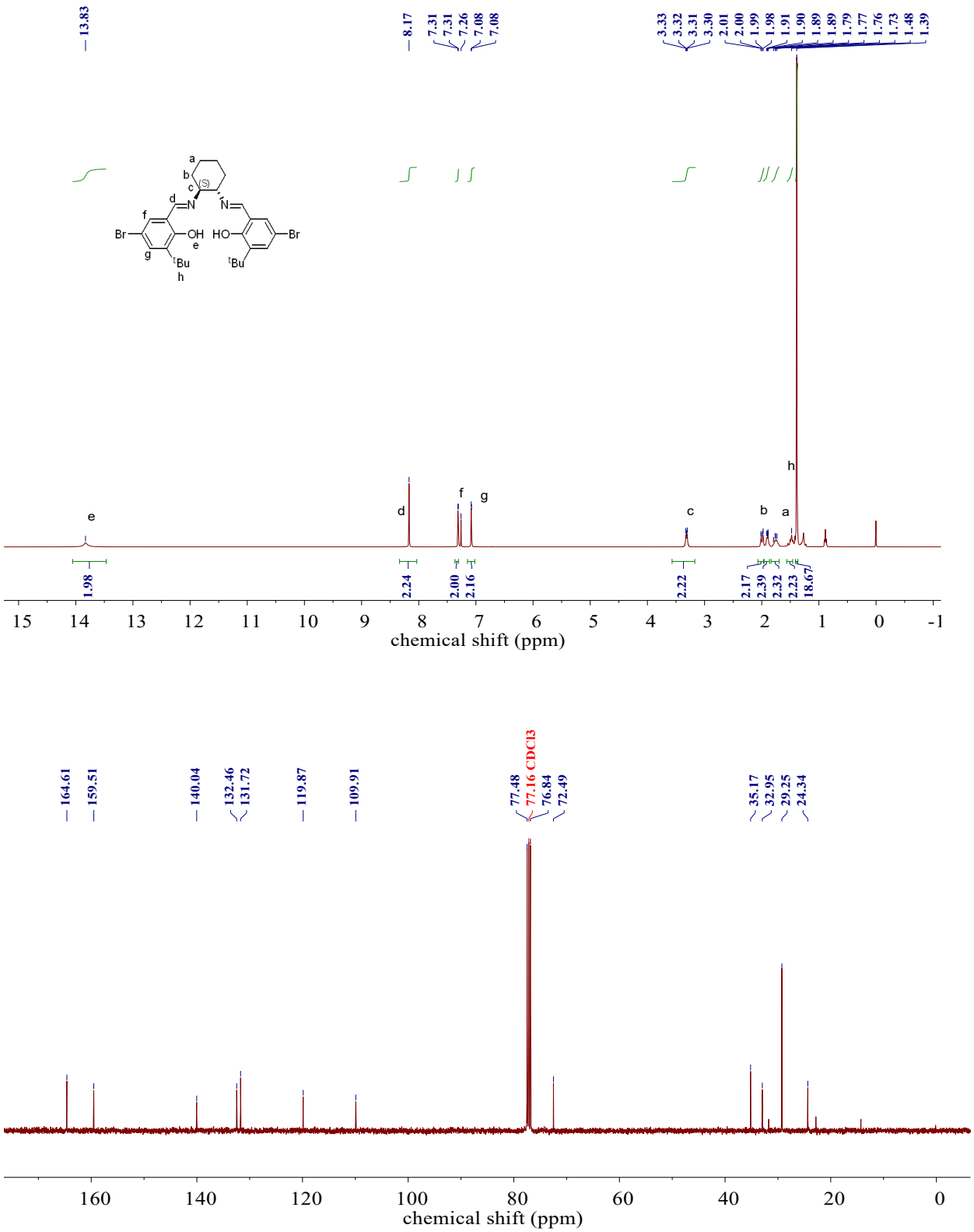


Figure S9. ^{1}H and ^{13}C NMR spectra for Salcyc-L10.

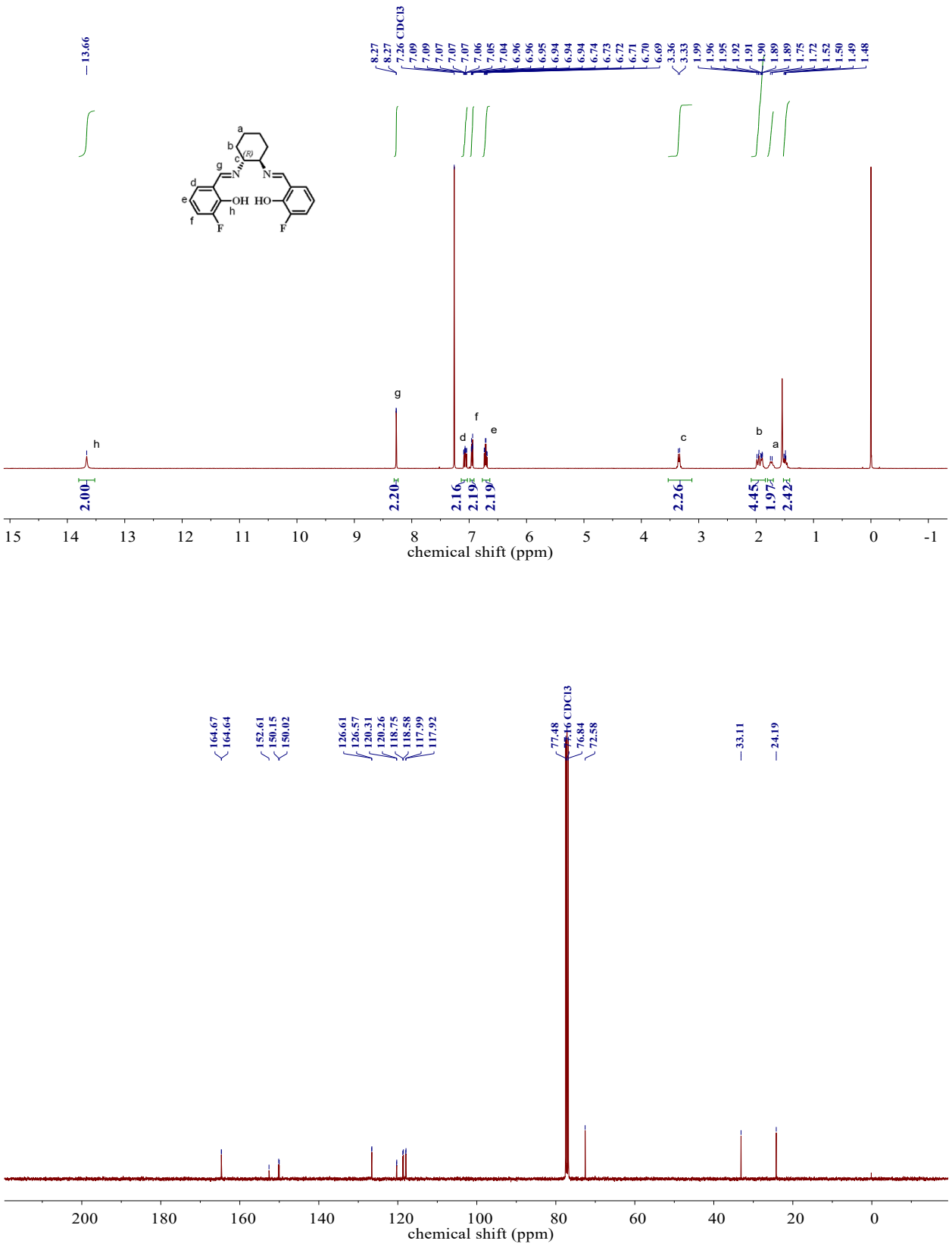


Figure S10. ^{1}H and ^{13}C NMR spectra for Salcyc-L11.

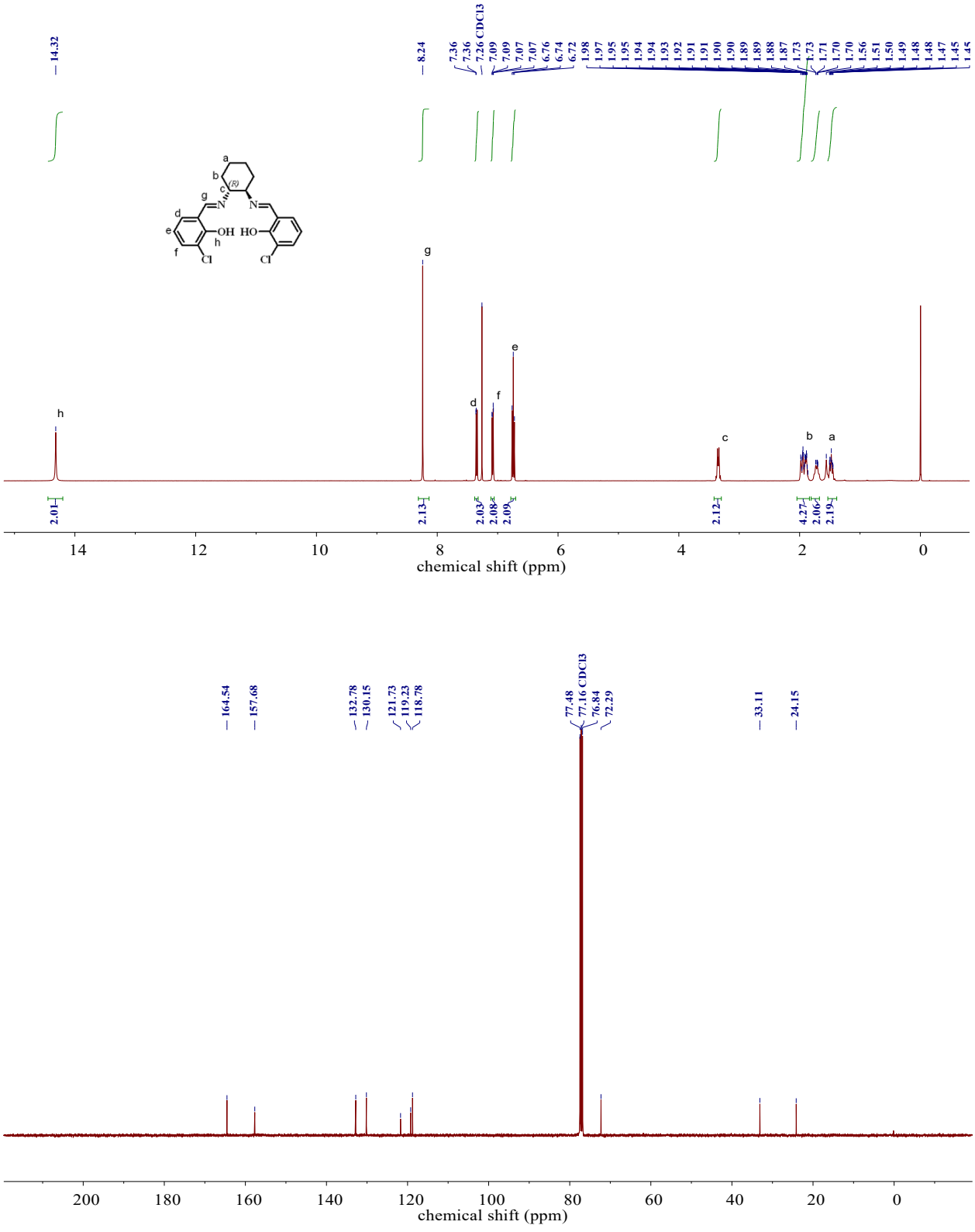


Figure S11. ^{1}H and ^{13}C NMR spectra for Salcyc-L12.

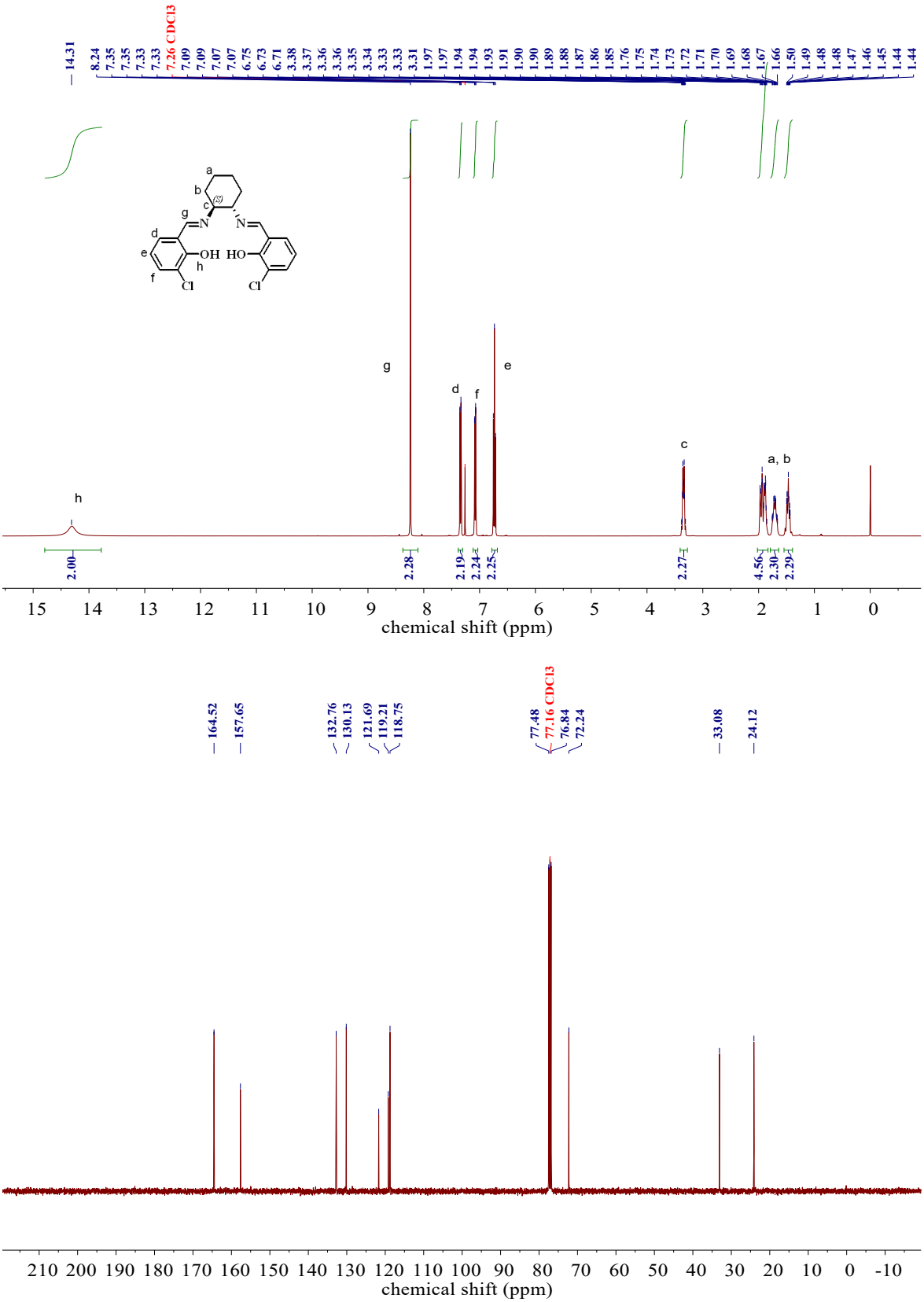
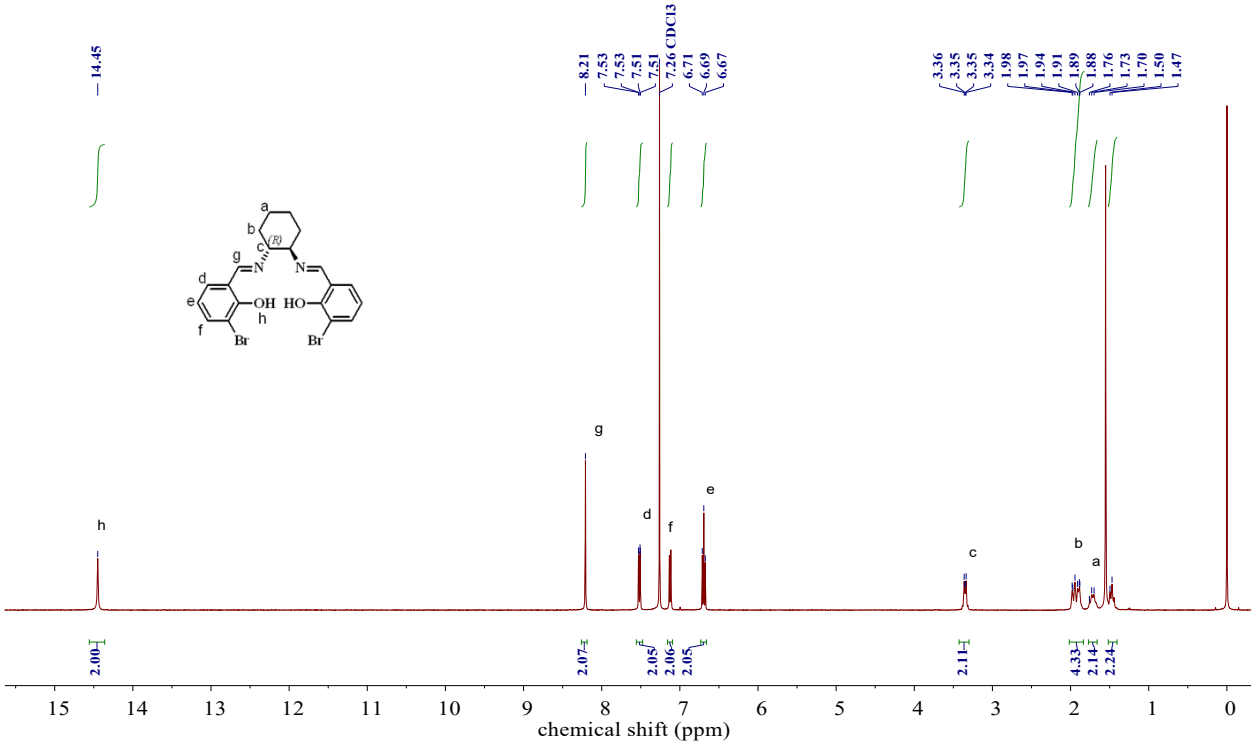


Figure S12. ^{1}H and ^{13}C NMR spectra for Salcyc-L13.



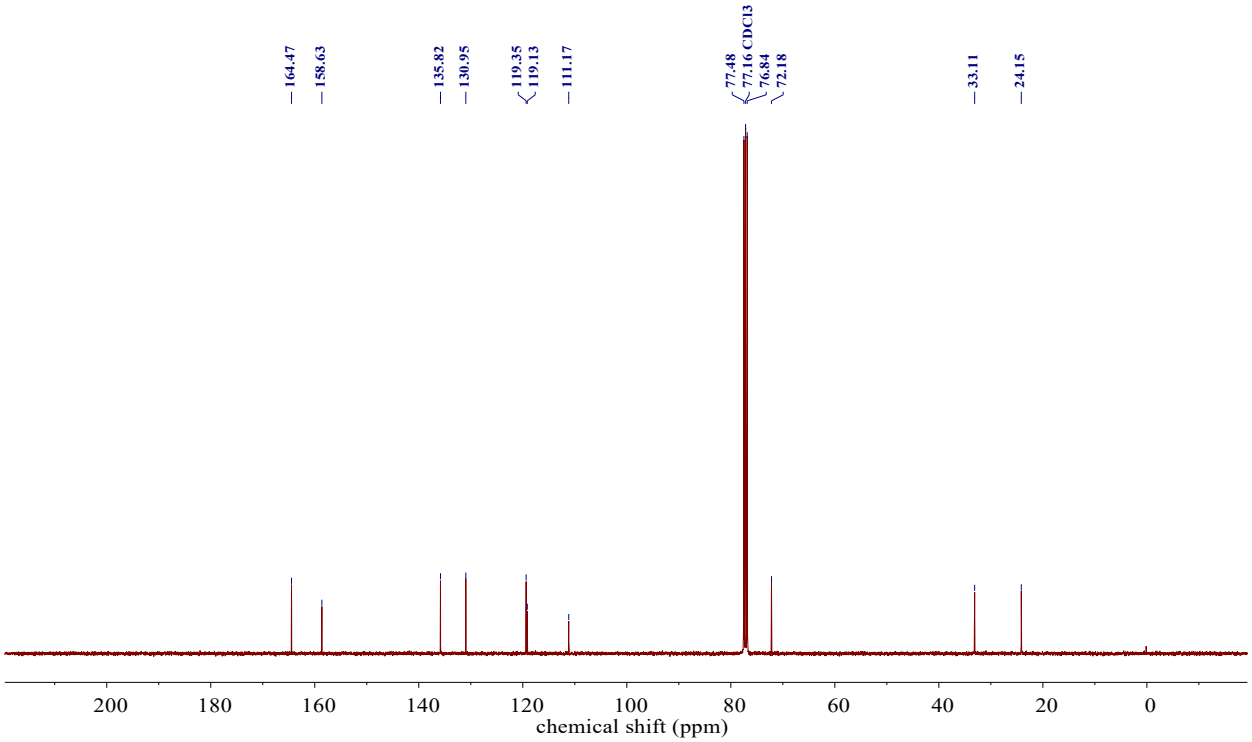


Figure S13. ^{1}H and ^{13}C NMR spectra for Salcyc-L14.

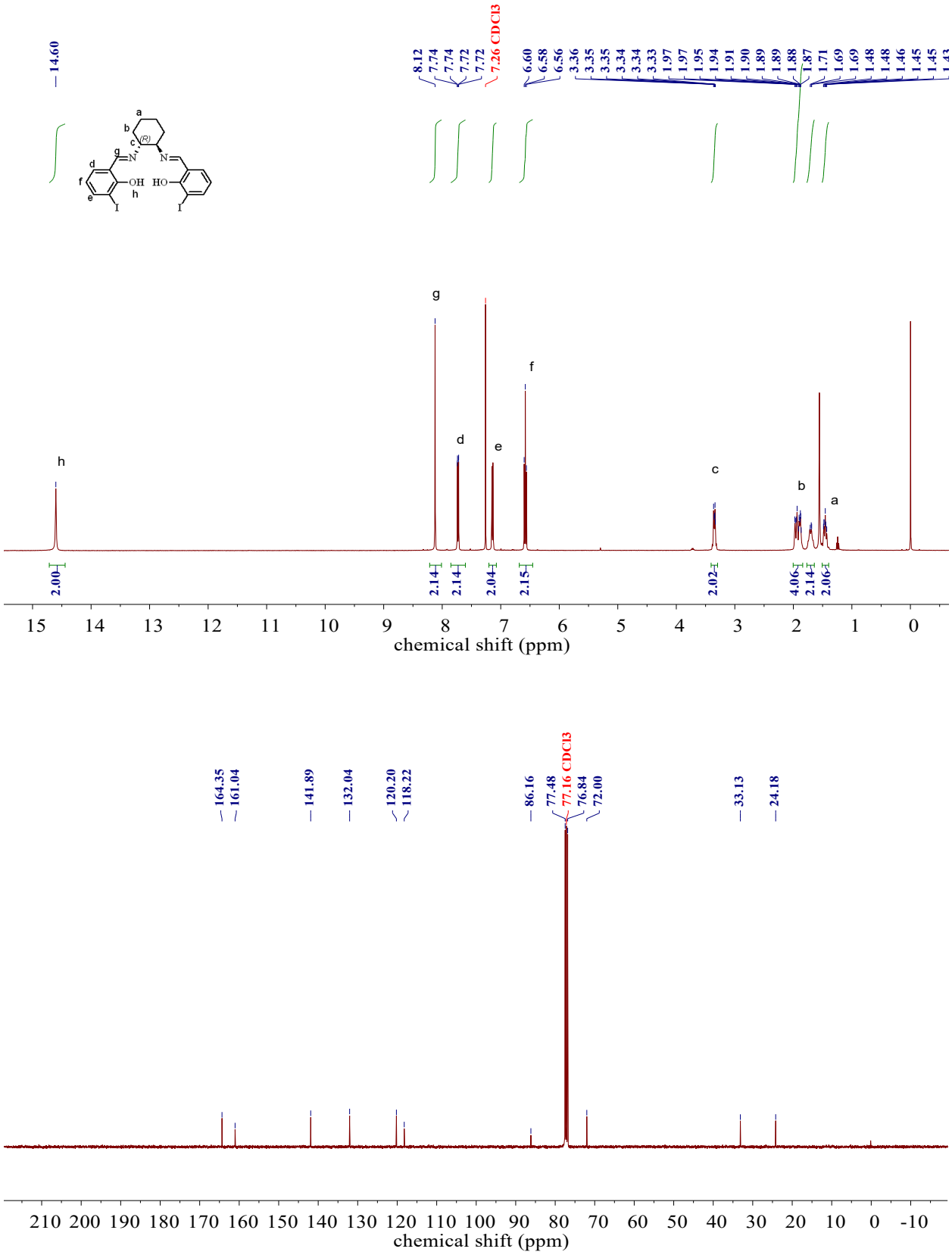


Figure S14. ^{1}H and ^{13}C NMR spectra for Salcyc-L15.

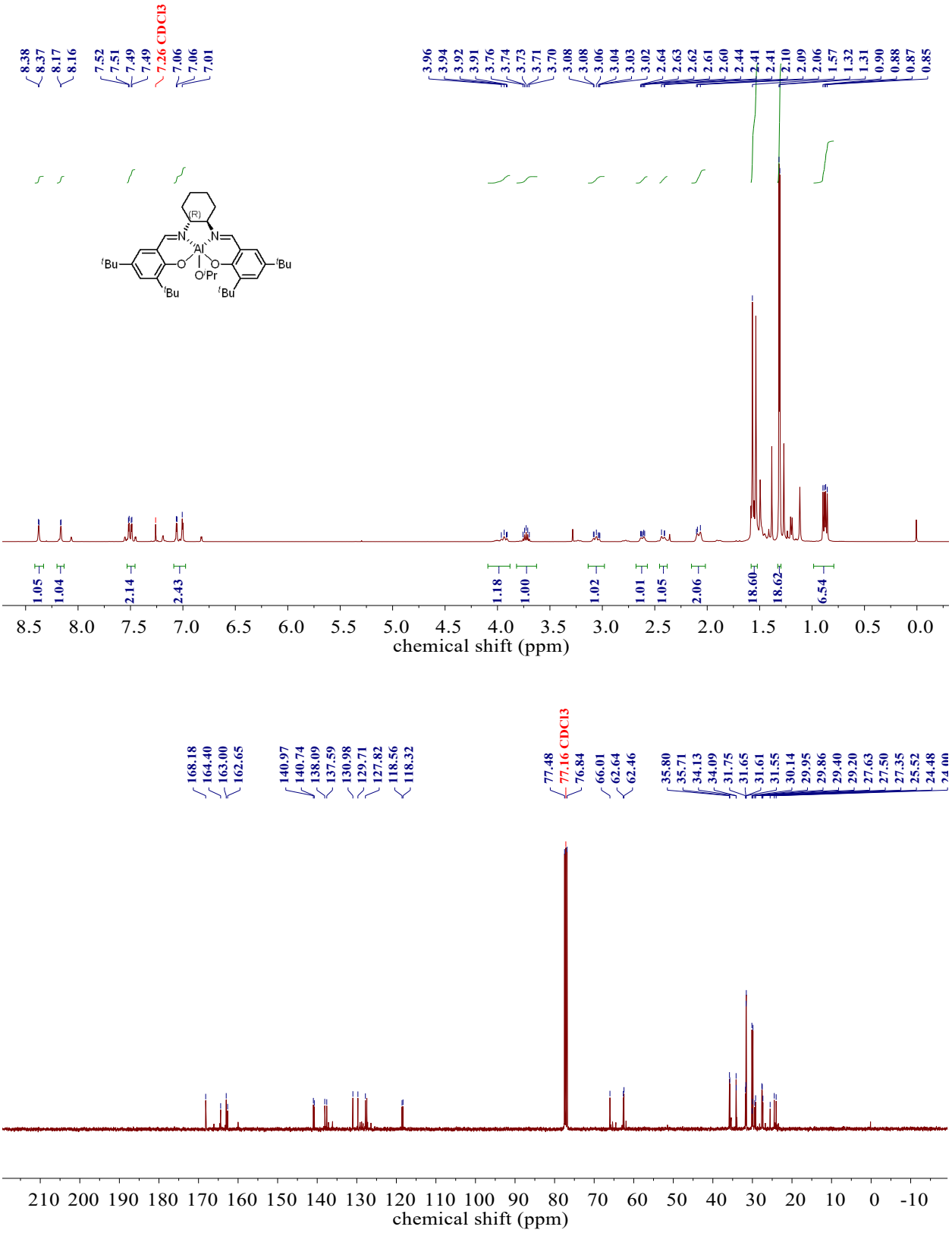


Figure S15. ^{1}H and ^{13}C NMR spectra for (*R,R*)-Salen[4,6-^{t}Bu].

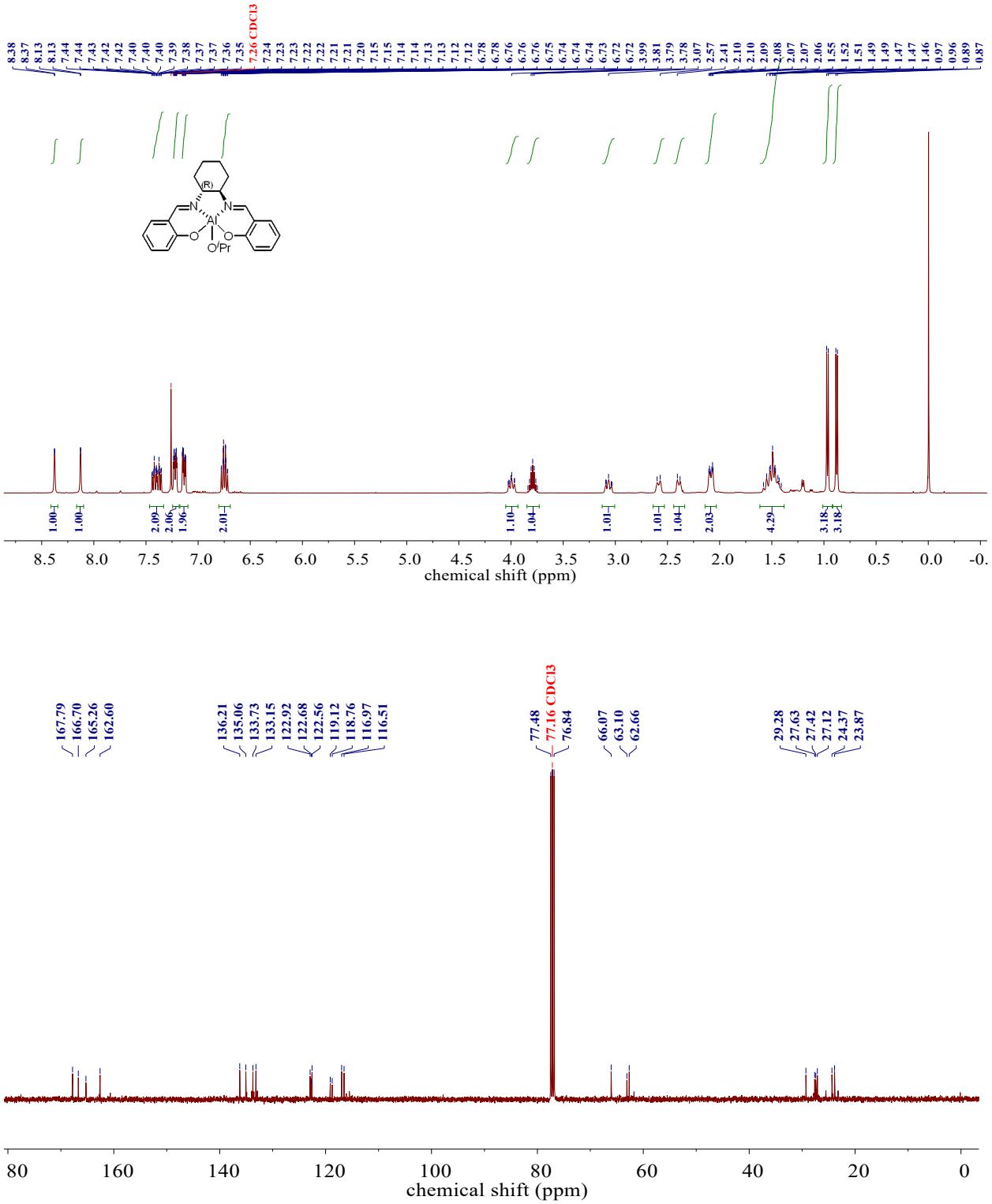


Figure S16. ^{1}H and ^{13}C NMR spectra for (*R,R*)-Salen[none].

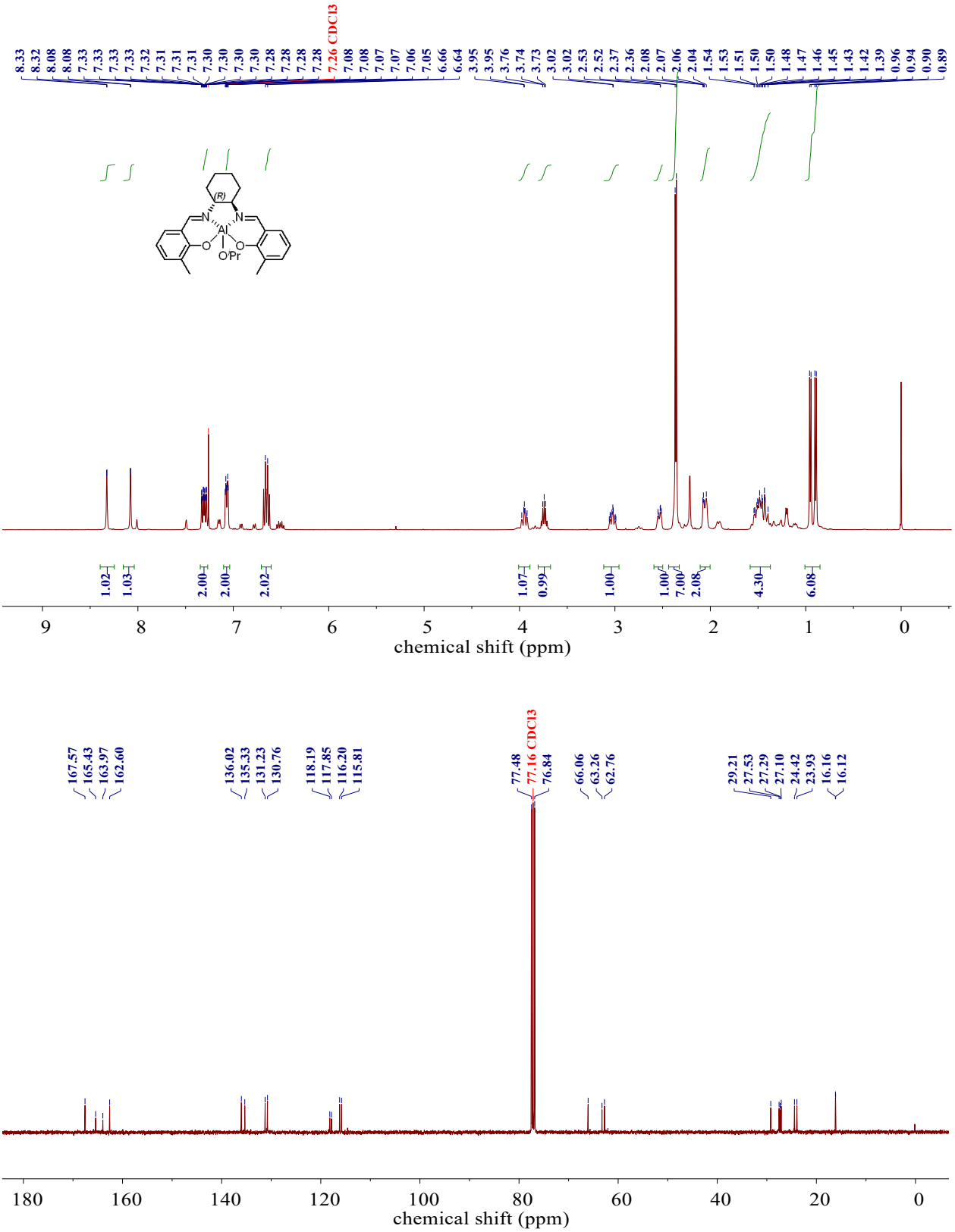


Figure S17. ^{1}H and ^{13}C NMR spectra for (*R,R*)-Salen[6-Me].

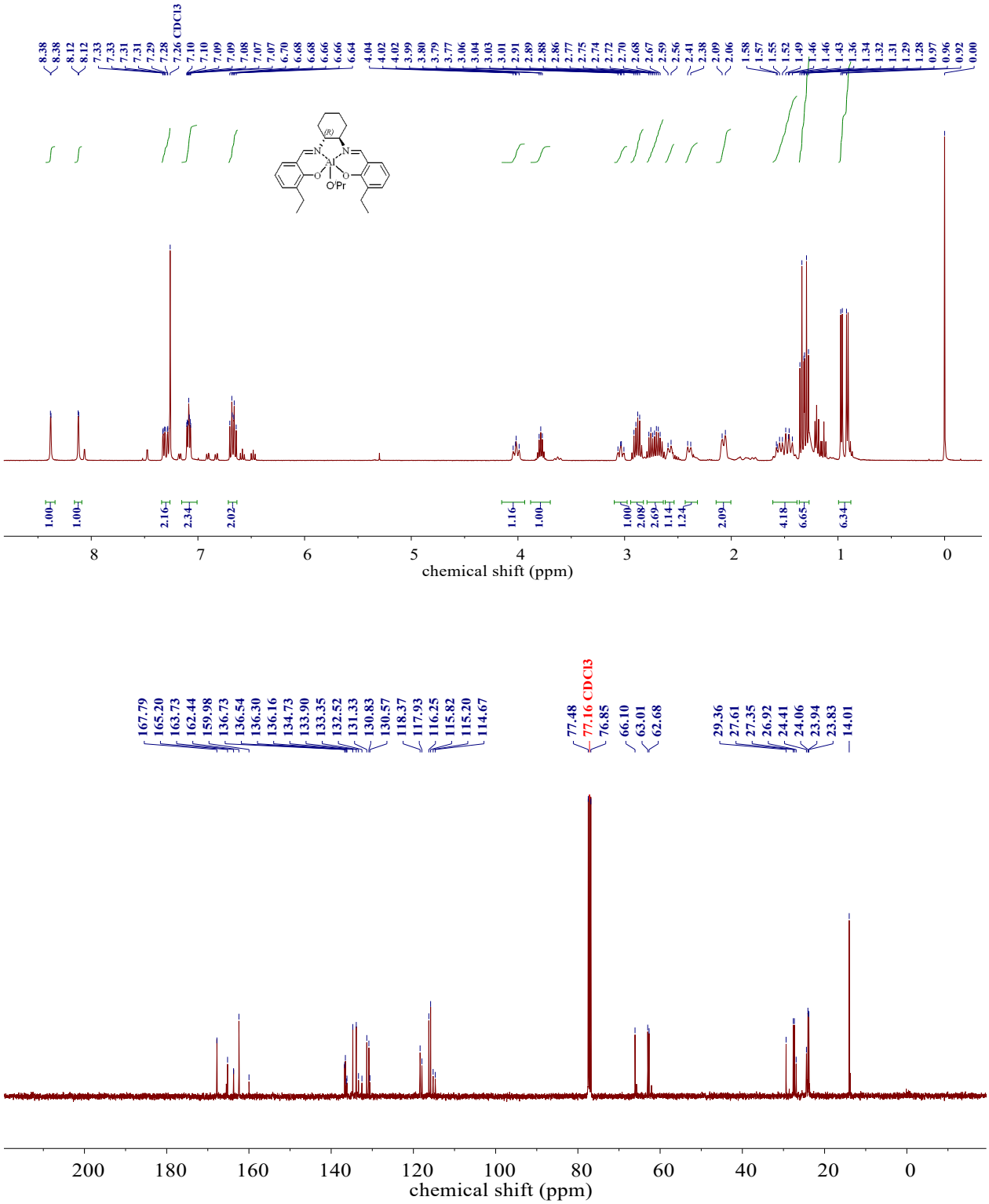


Figure S18. ^{1}H and ^{13}C NMR spectra for (*R,R*)-Salen[6-Et].

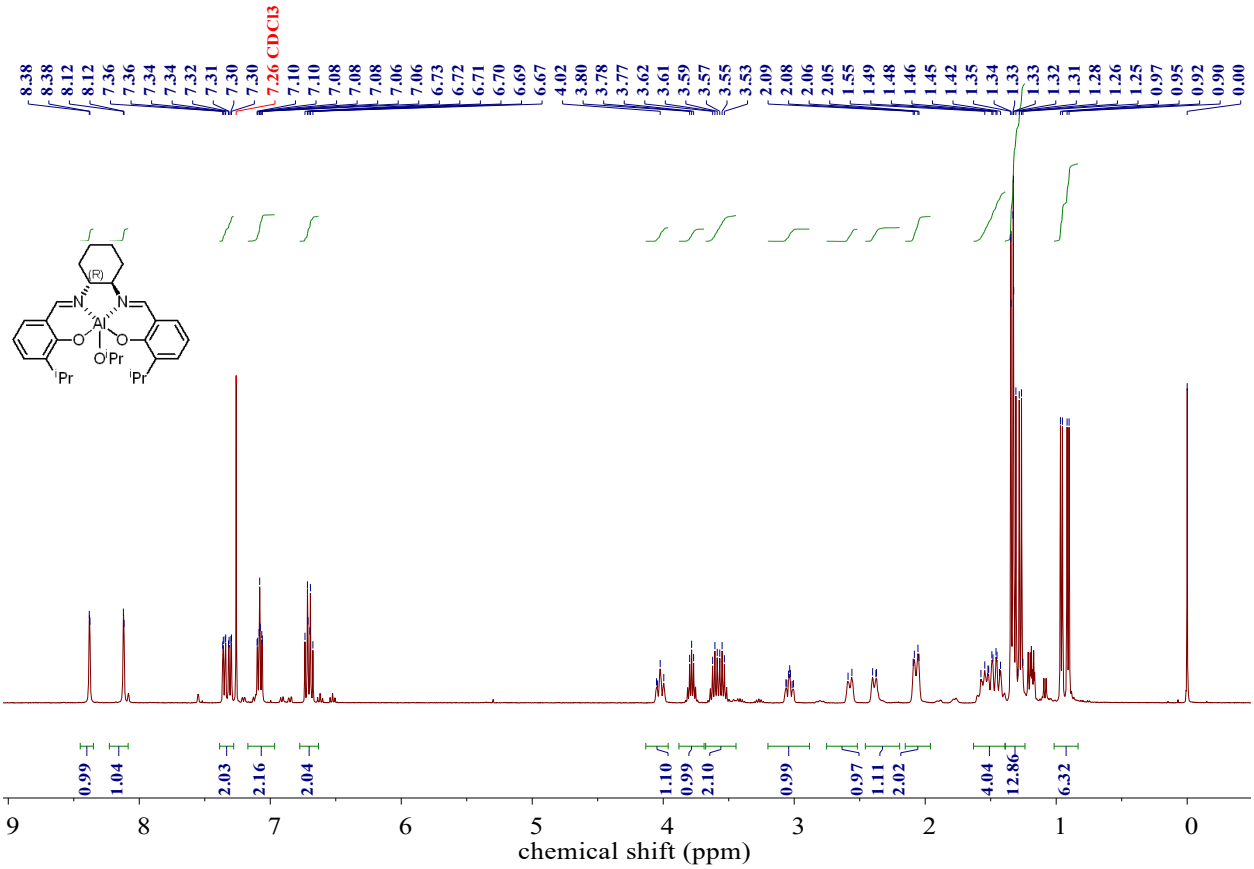


Figure S19. ^{1}H spectrum (*R,R*)-Salen[6-*i*Pr].

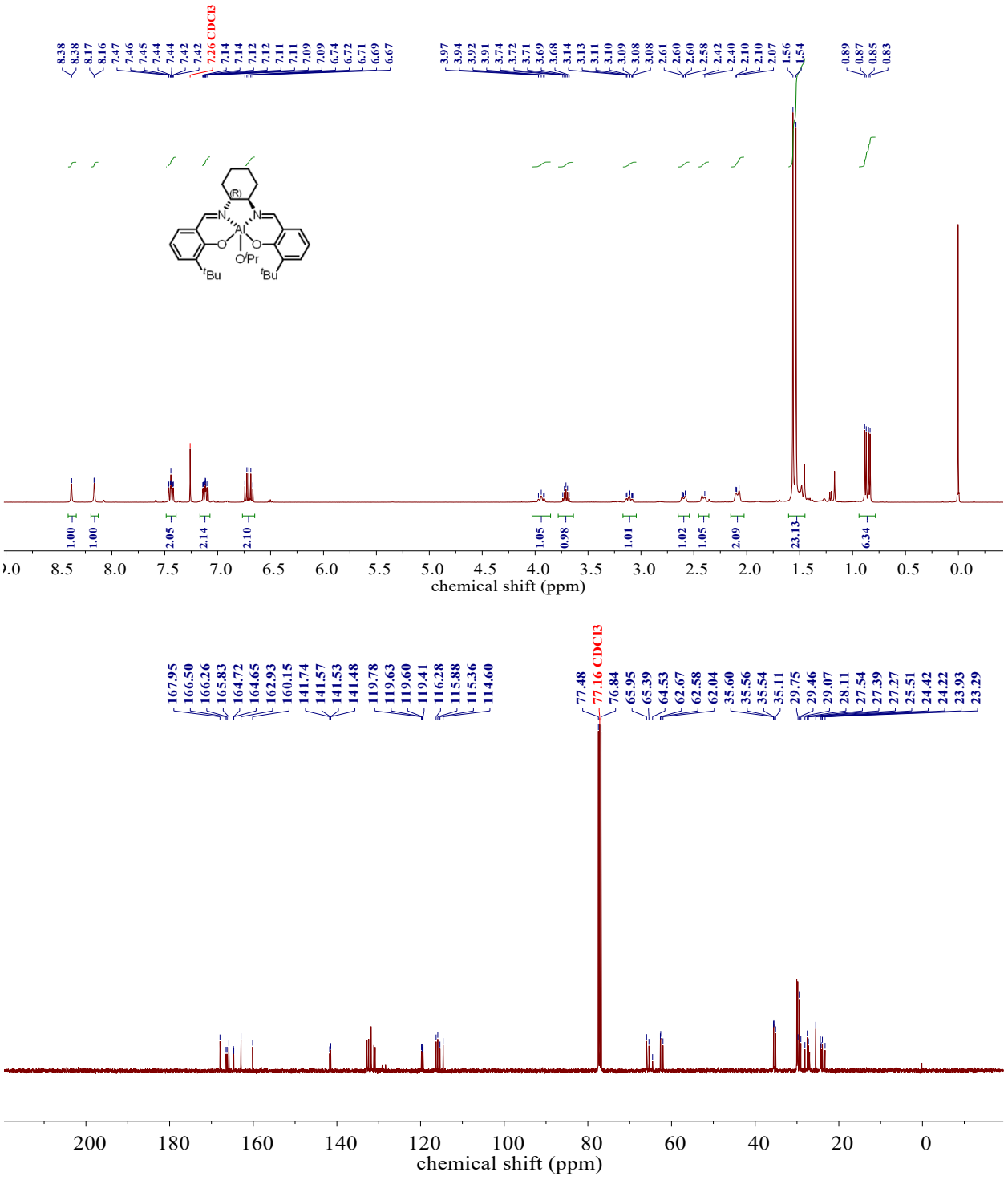


Figure S20. ^{1}H and ^{13}C NMR spectra for (*R,R*)-Salen[6-^{t}Bu].

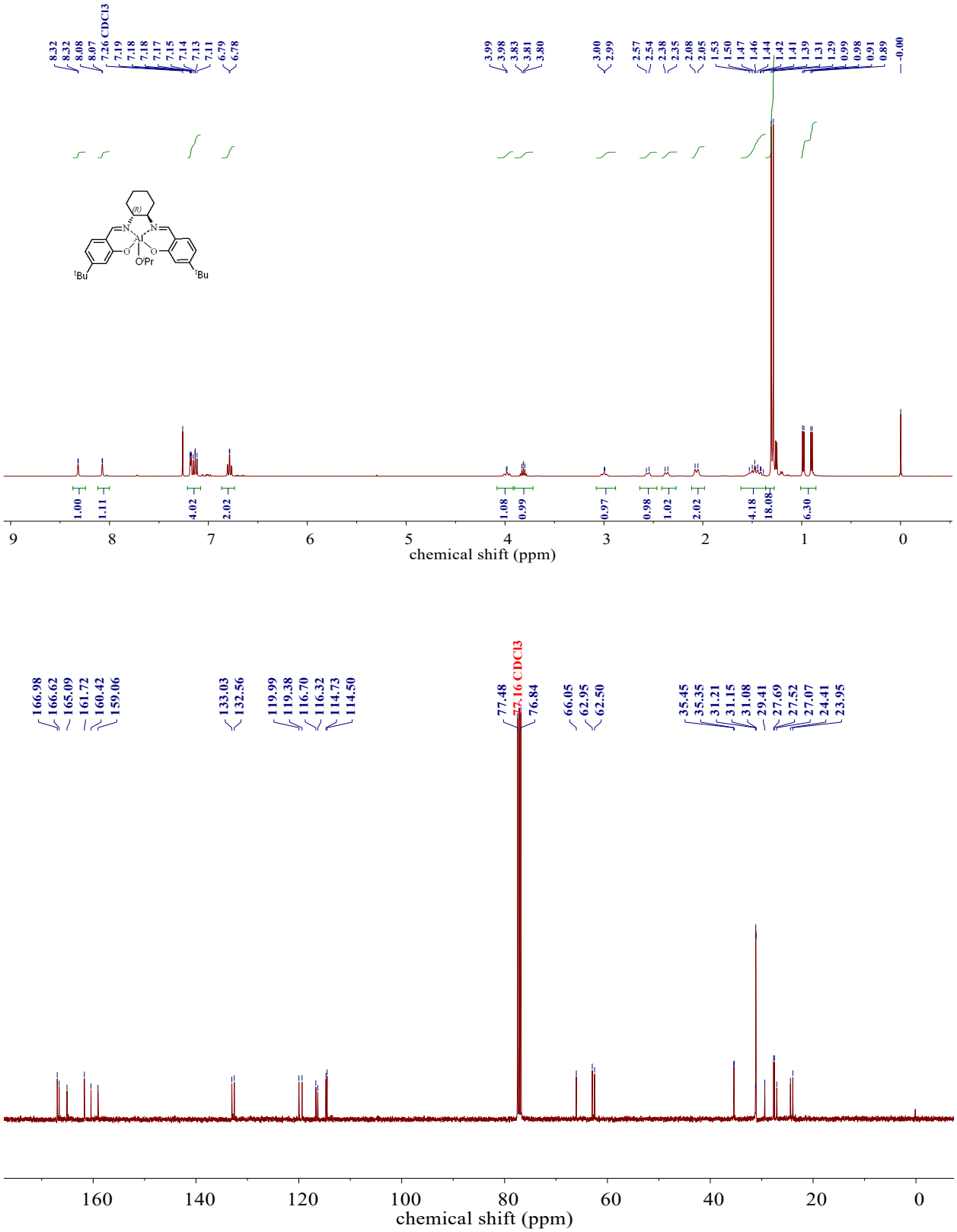


Figure S21. ^{1}H and ^{13}C NMR spectra for (*R,R*)-Salen[5-^{t}Bu].

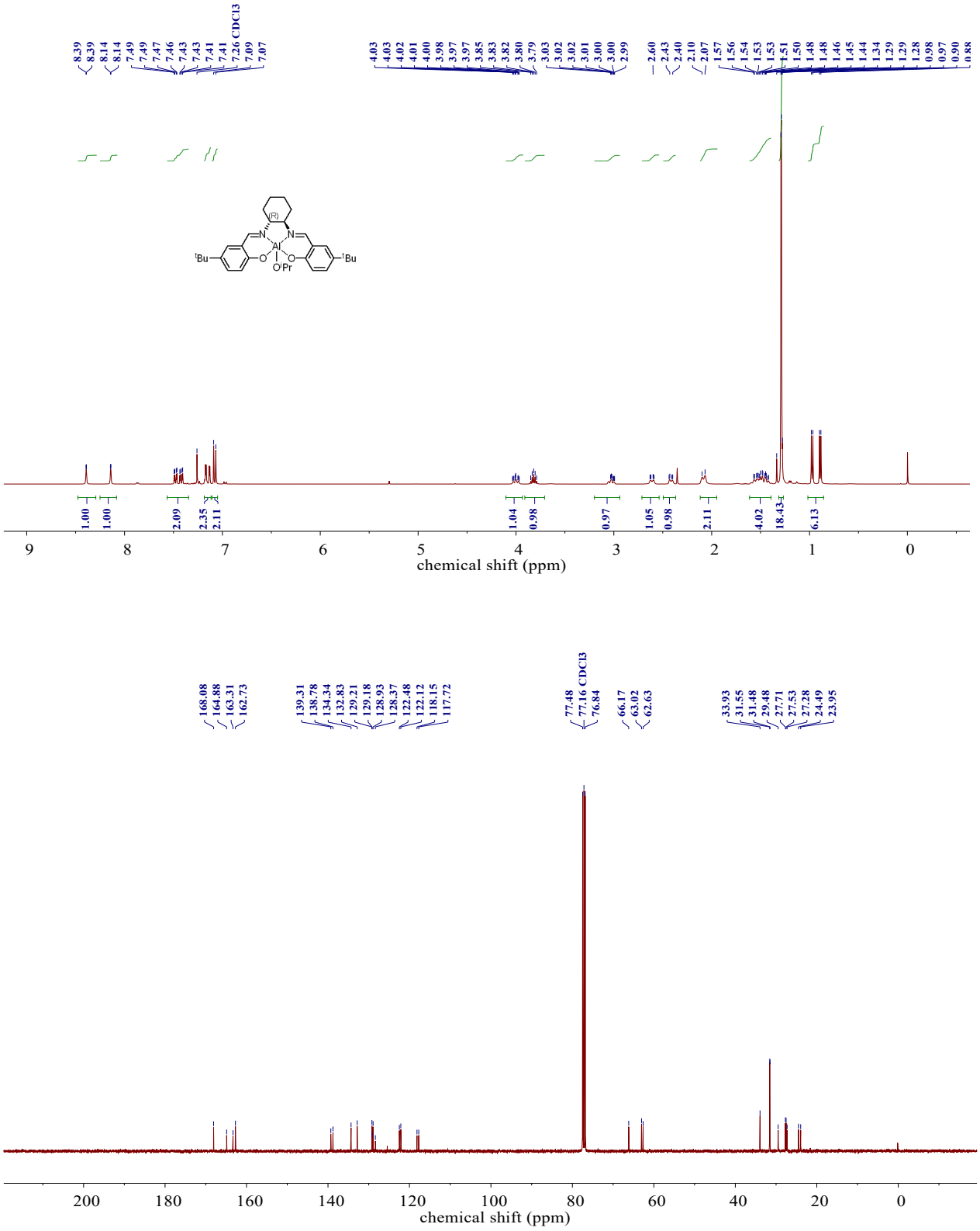


Figure S22. ^{1}H and ^{13}C NMR spectra for (*R,R*)-Salen[4-*t*Bu].

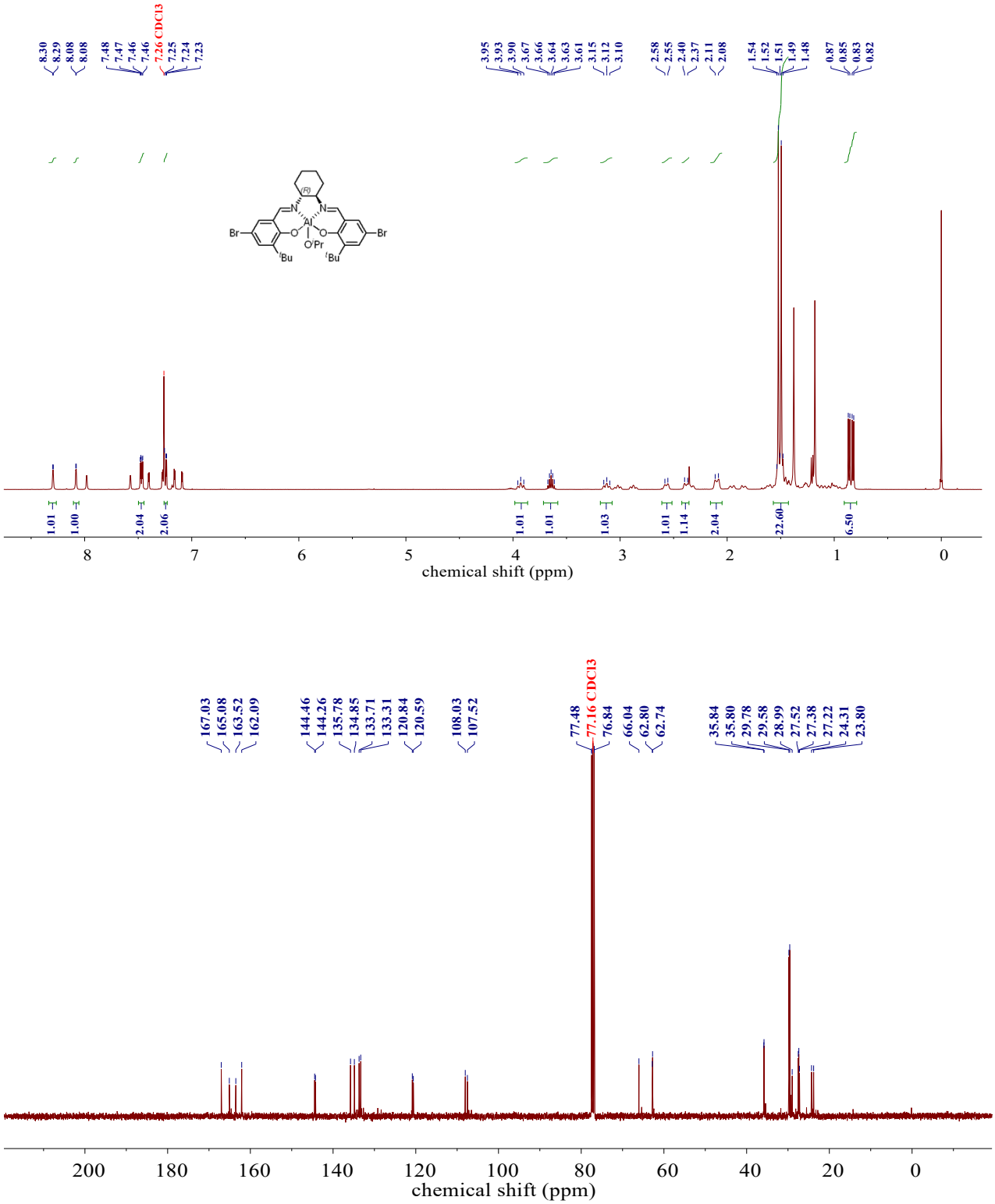


Figure S23. ^{1}H and ^{13}C NMR spectra for (*R,R*)-Salen[4,6-Br, ^{t}Bu].

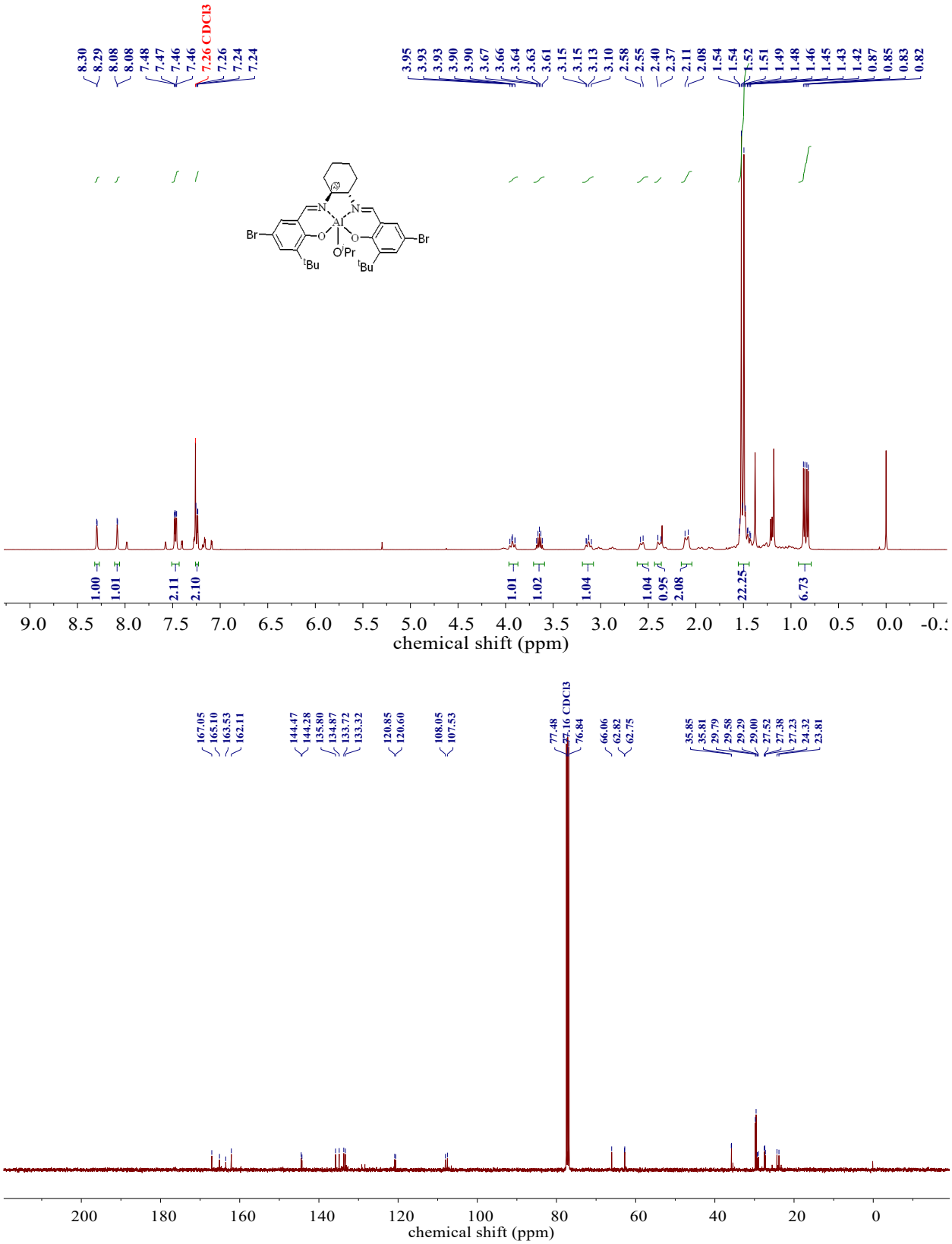


Figure S24. ^{1}H and ^{13}C NMR spectra for (*S,S*)-Salen[4,6-Br, ^{t}Bu].

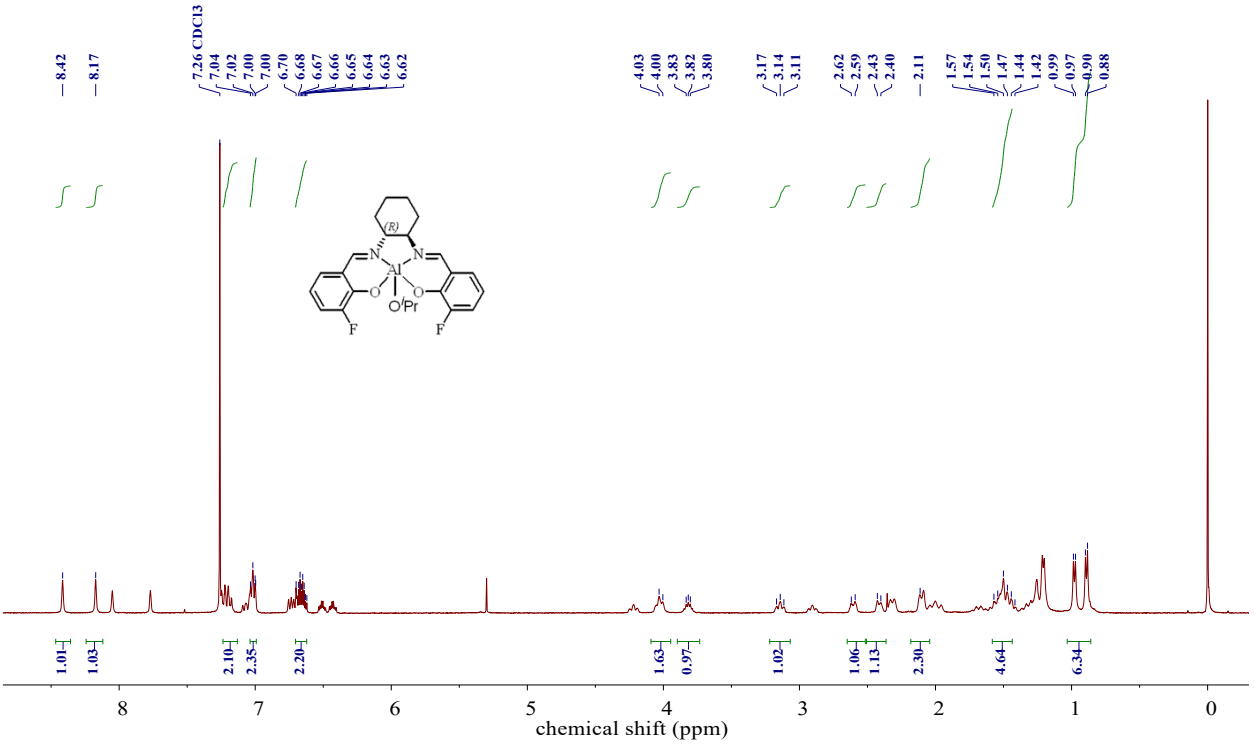


Figure S25. ^{1}H NMR spectra for (*R,R*)-Salen[6-F].

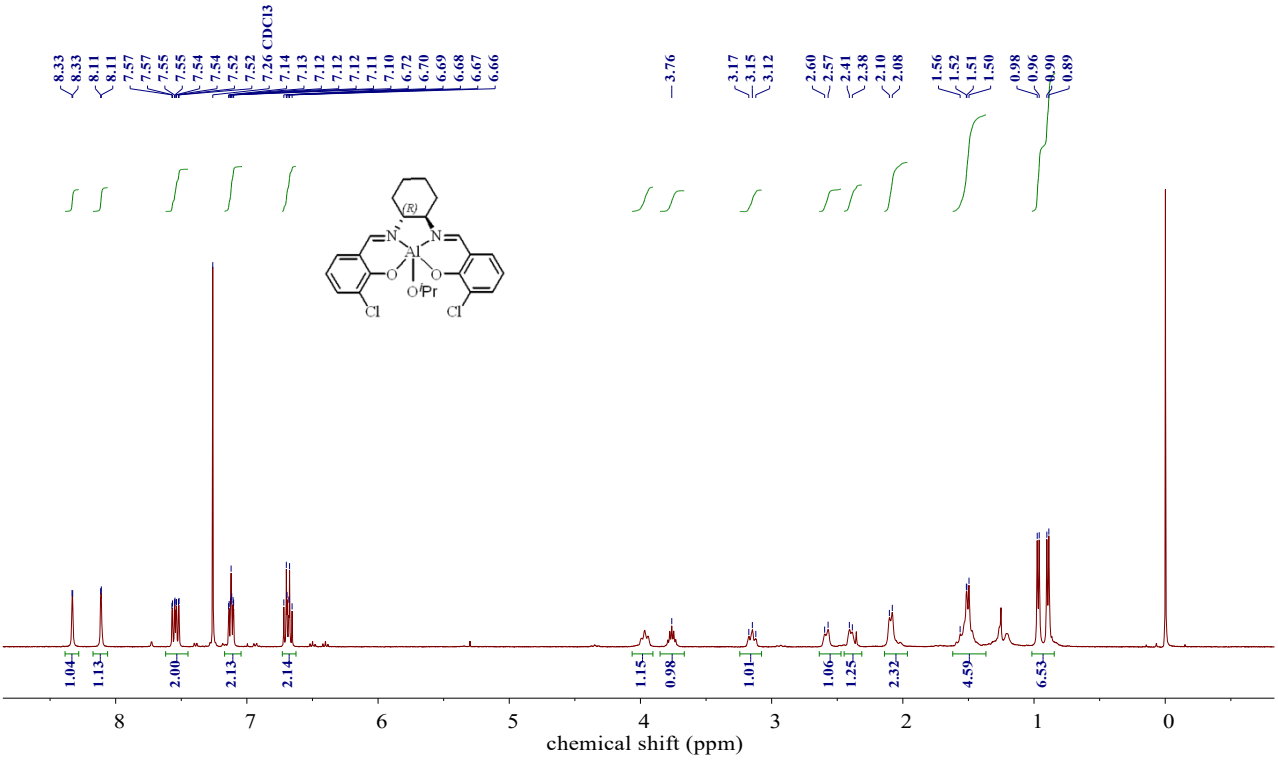


Figure S26. ^{1}H NMR spectra for (*R,R*)-Salen[6-Cl].

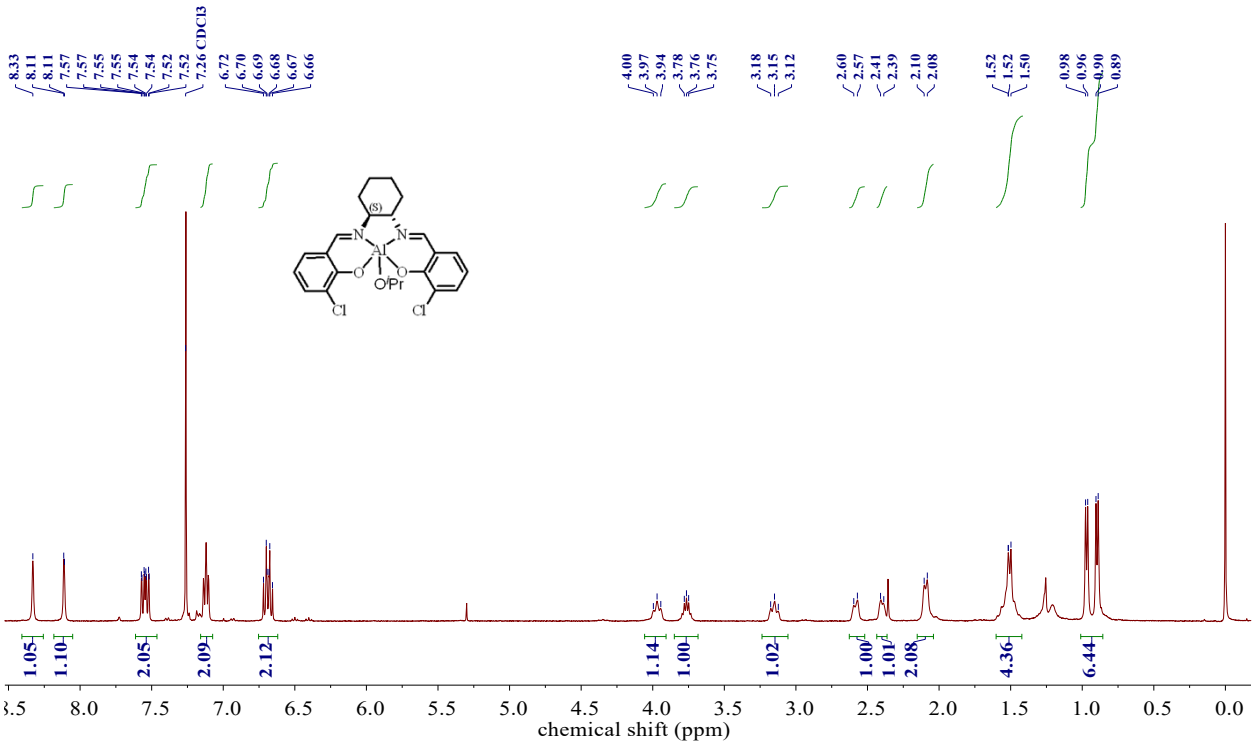


Figure S27. ^{1}H NMR spectra for (*S,S*)-Salen[6-Cl].

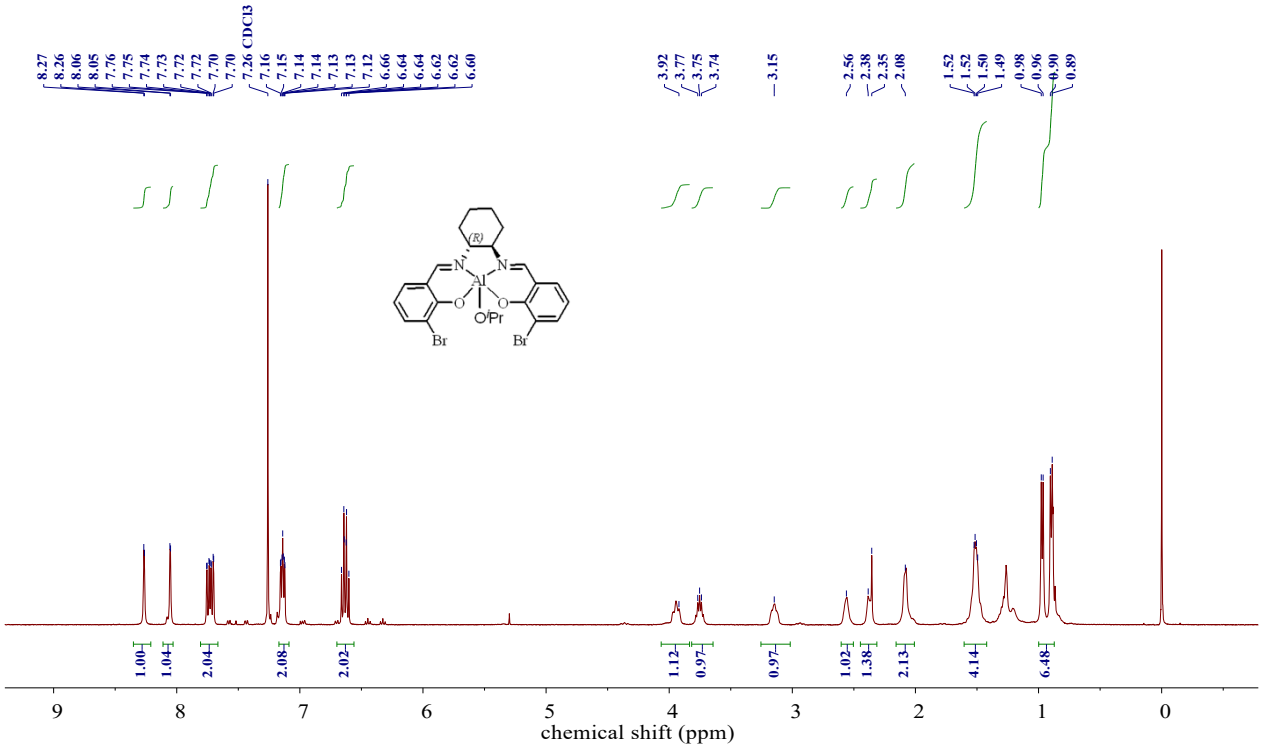


Figure S28. ^{1}H NMR spectra for (*R,R*)-Salen[6-Br].

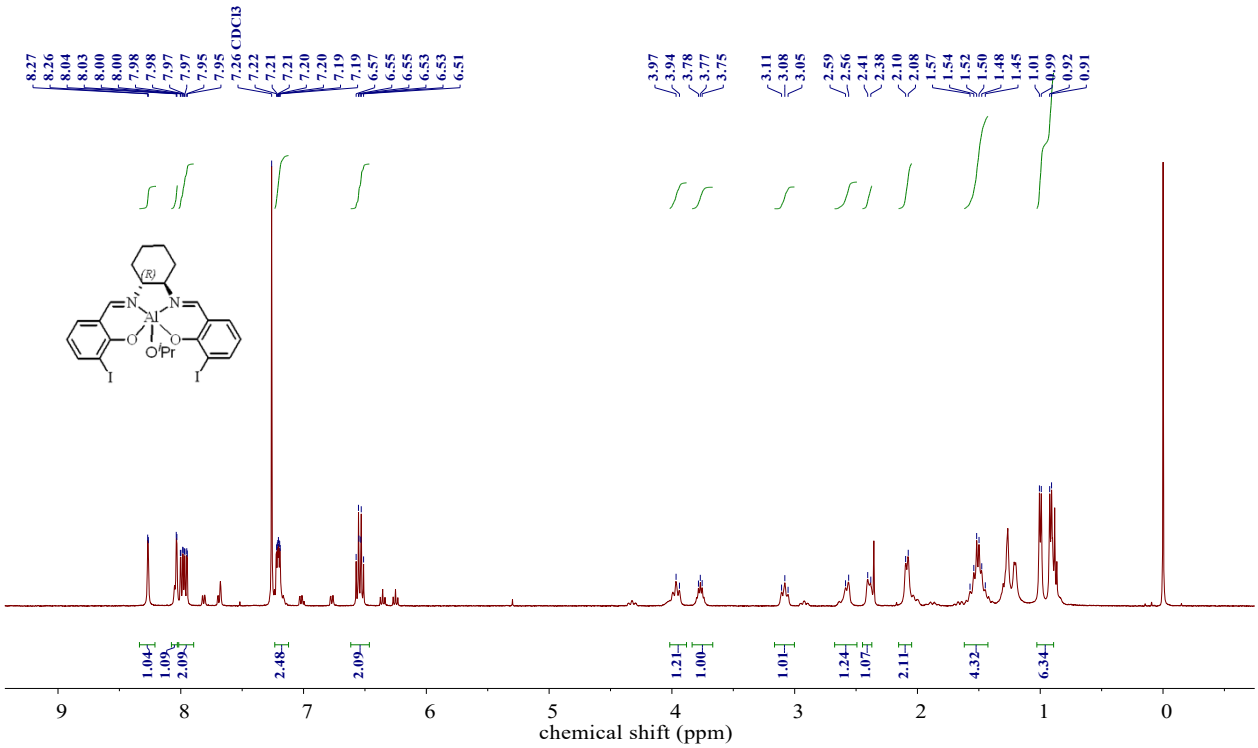
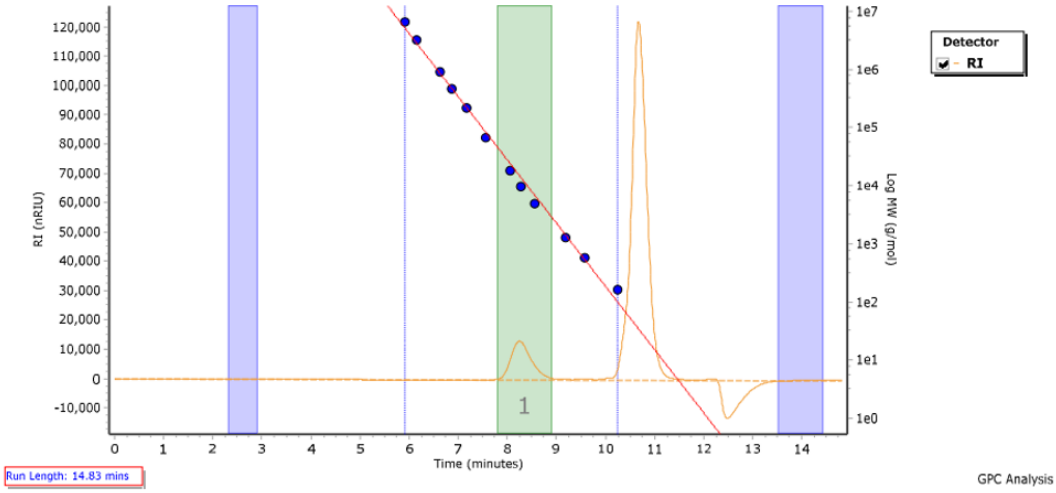


Figure S29. ^{1}H NMR spectra for (*R,R*)-Salen[6-I].



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	14708	11060	14239	17454	20586	16991	1.287

Figure S30. GPC trace of PLA (Table 1, entry 1).

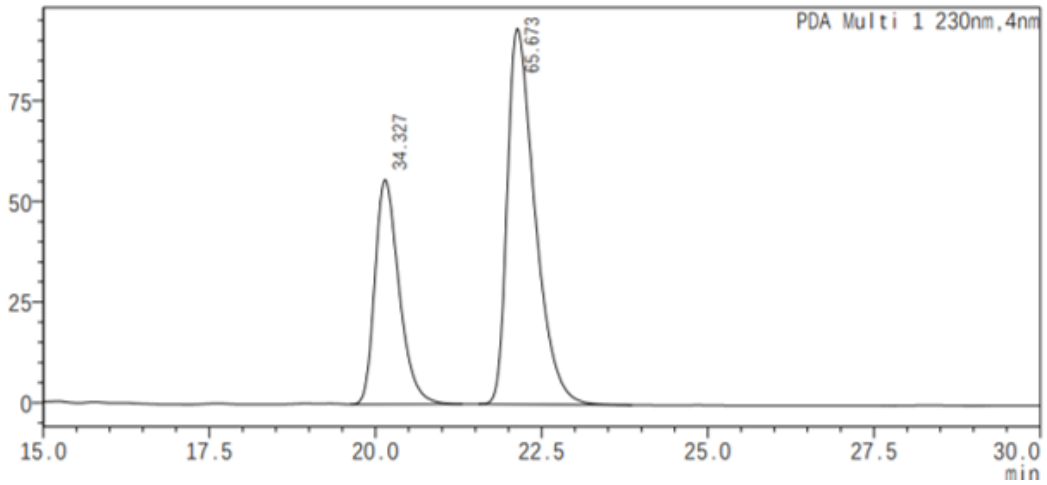
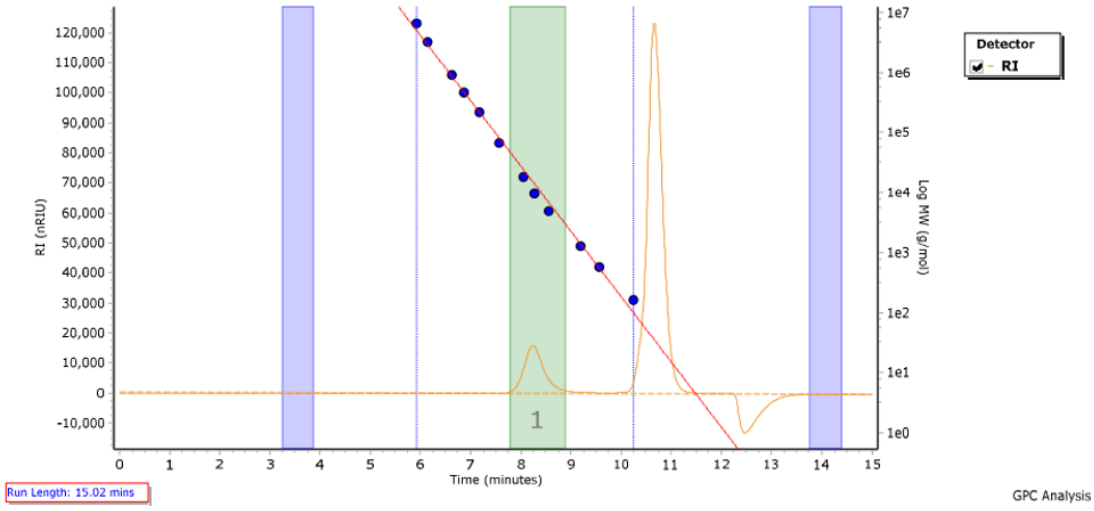


Figure S31. HPLC chromatogram of residual lactide monomer (Table 1, entry 1).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	15019	11482	14969	18544	22145	18019	1.304

Figure S32. GPC trace of PLA (Table 1, entry 2).

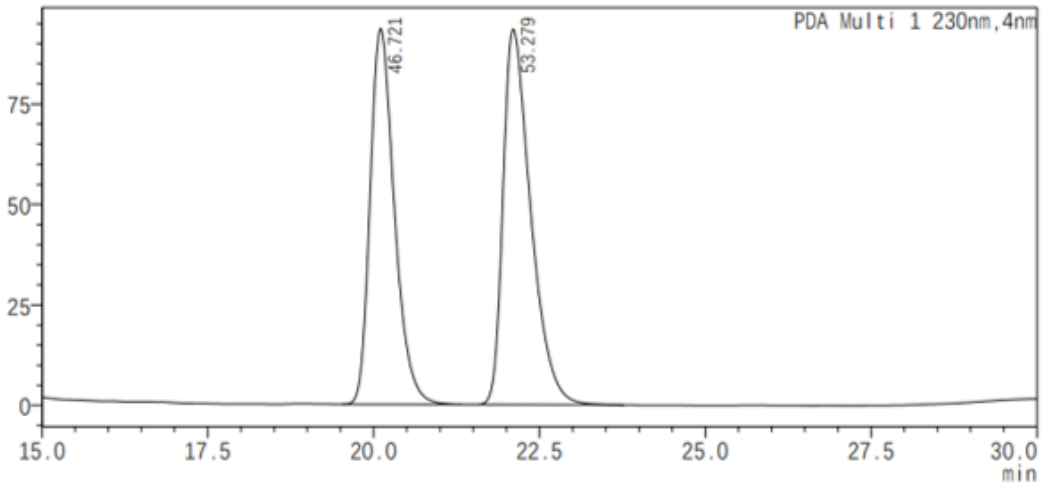
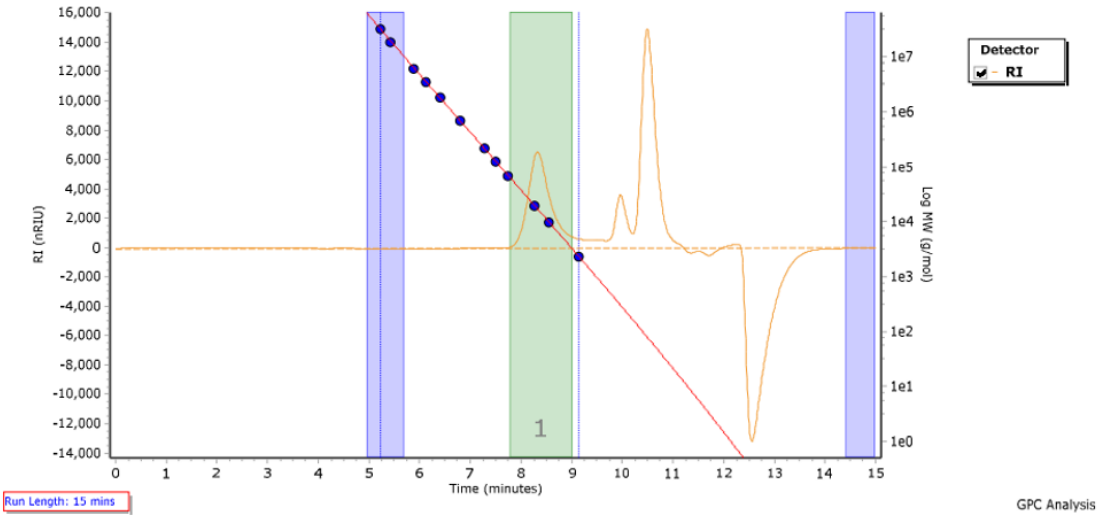


Figure S33. HPLC chromatogram of residual lactide monomer (Table 1, entry 2).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	16776	11937	16454	21222	26146	20519	1.378

Figure S34. GPC trace of PLA (Table 1, entry 3).

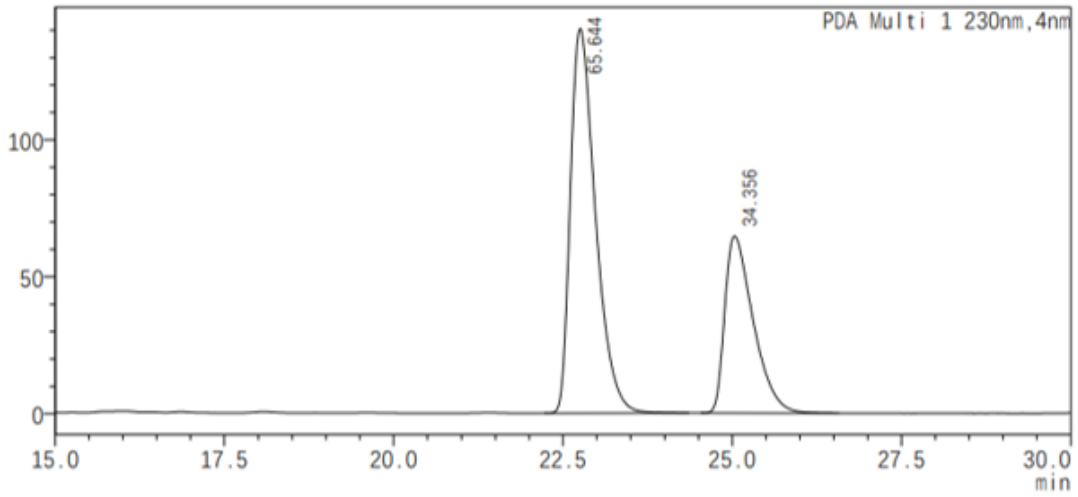
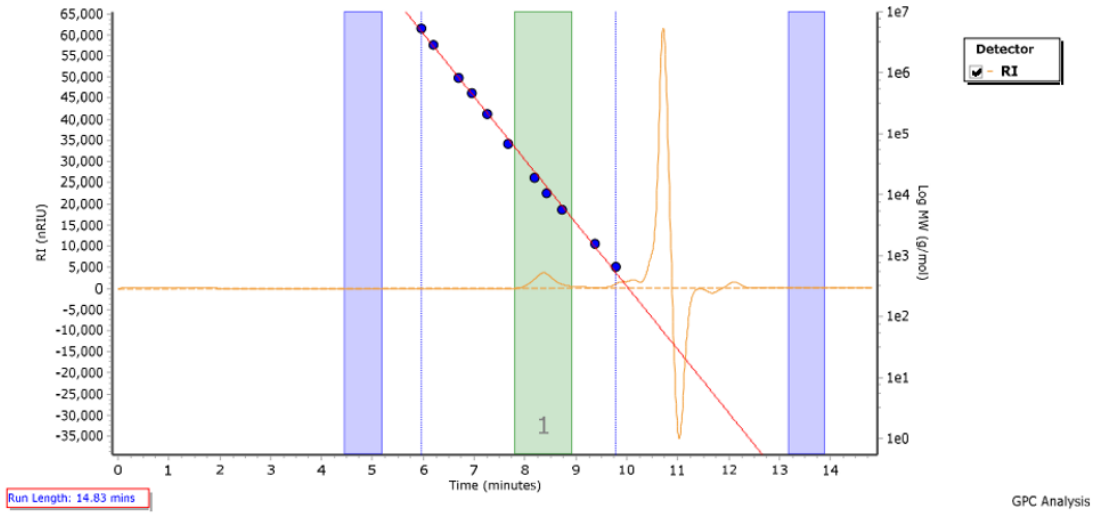


Figure S35. HPLC chromatogram of residual lactide monomer (Table 1, entry 3).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	15096	12455	15942	19773	23792	19195	1.28

Figure S36. GPC trace of PLA (Table 1, entry 4).

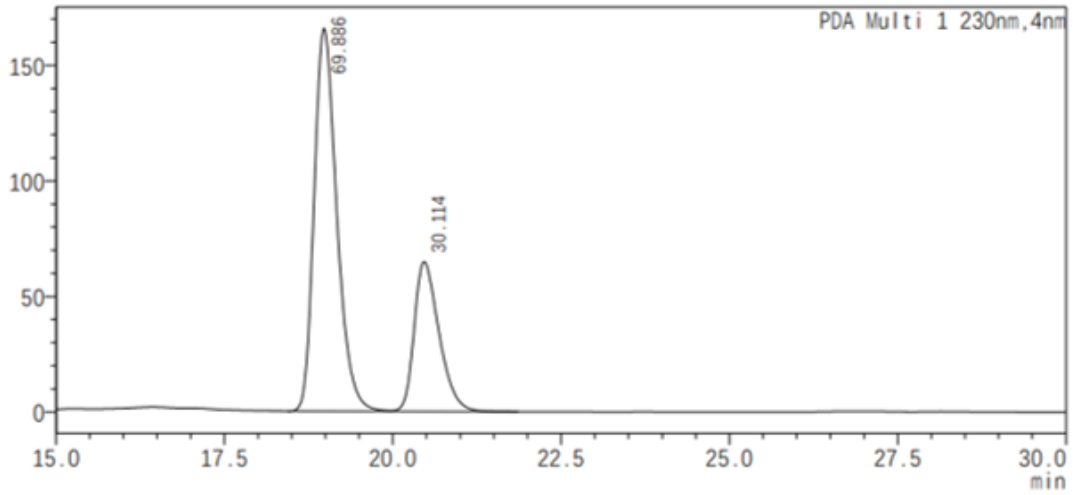
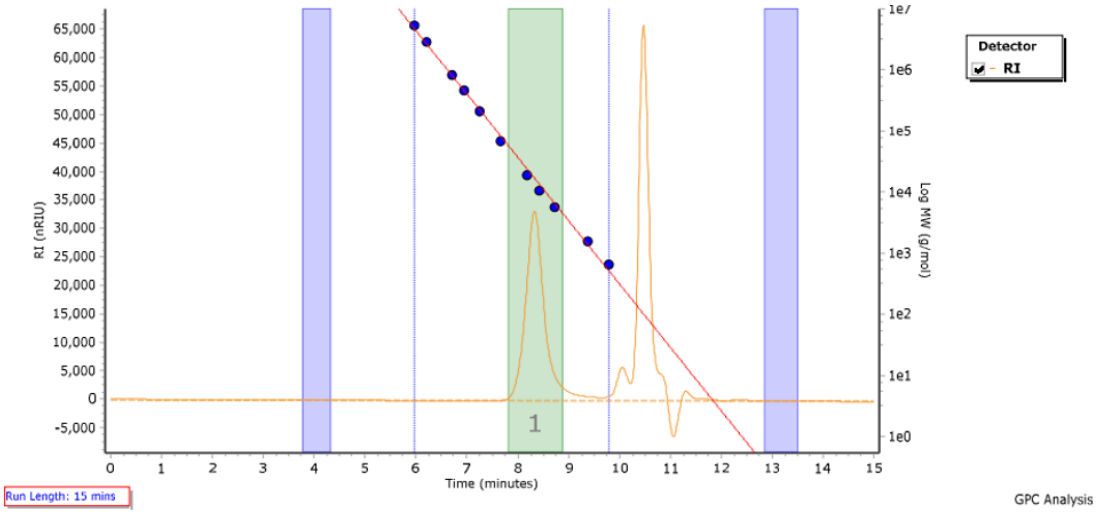


Figure S37. HPLC chromatogram of residual lactide monomer (Table 1, entry 4).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	16676	14219	17428	20887	24665	20356	1.226

Figure S38. GPC trace of PLA (Table 1, entry 5).

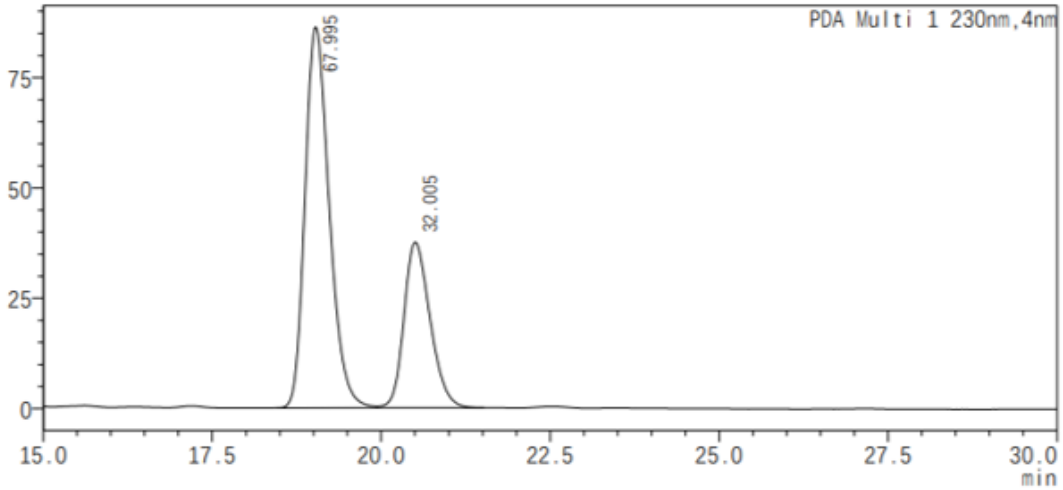
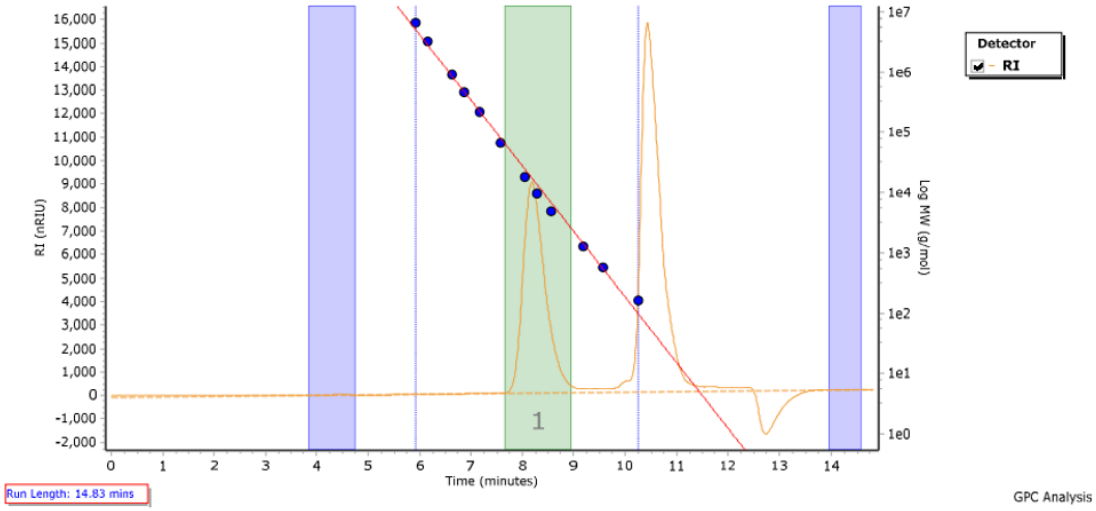


Figure S39. HPLC chromatogram of residual lactide monomer (Table 1, entry 5).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	17022	12094	16121	19978	23593	19437	1.333

Figure S40. GPC trace of PLA (Table 1, entry 6).

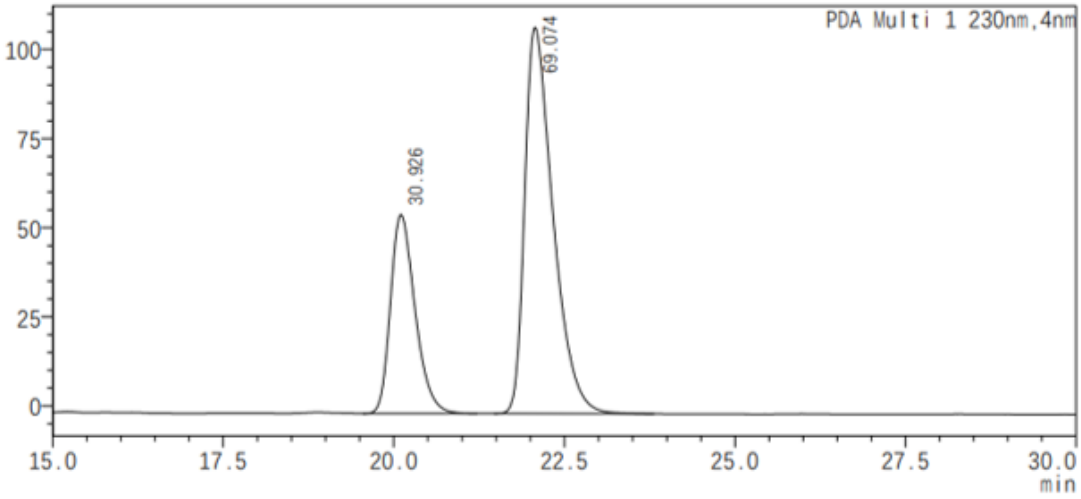
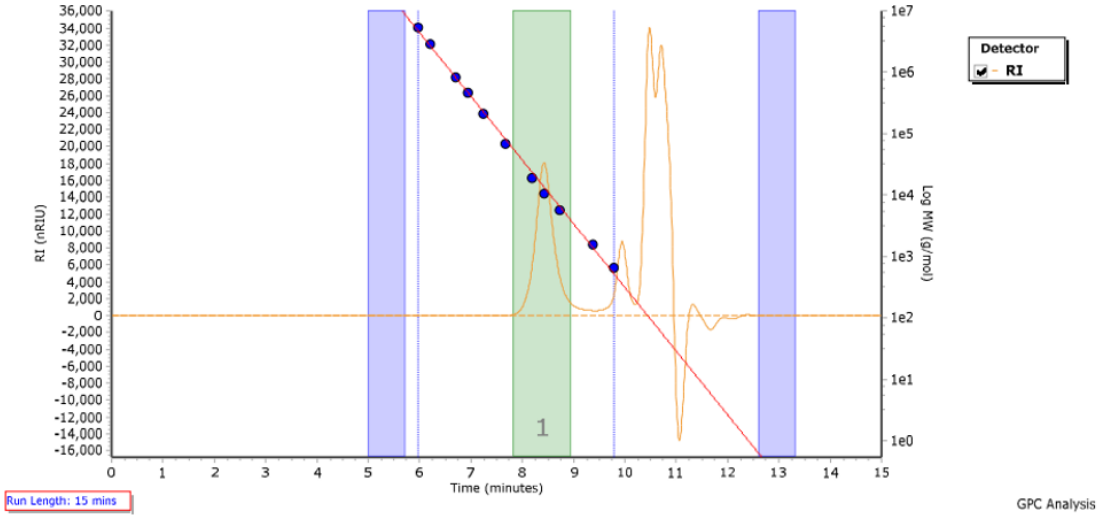


Figure S41. HPLC chromatogram of residual lactide monomer (Table 1, entry 6).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	13397	11356	13949	17011	20714	16515	1.228

Figure S42. GPC trace of PLA (Table 1, entry 7).

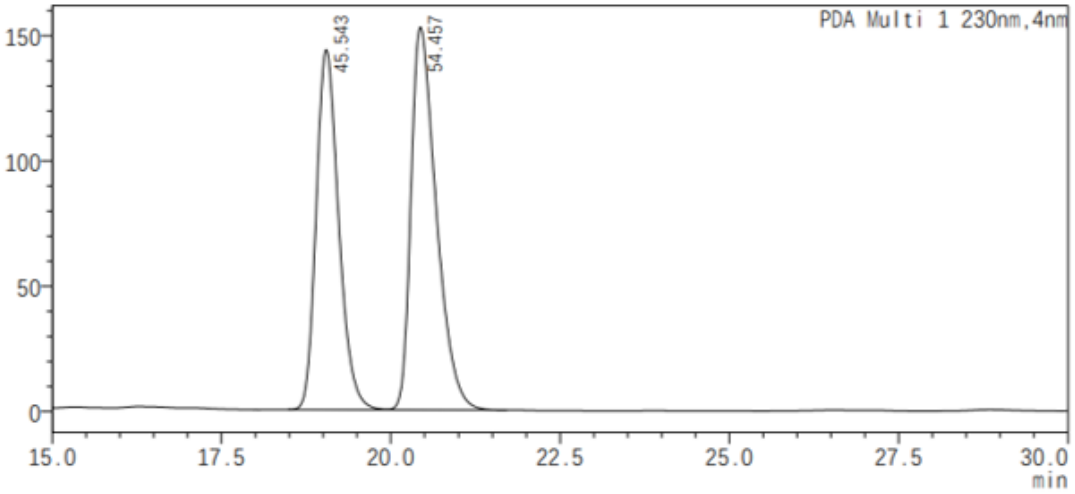
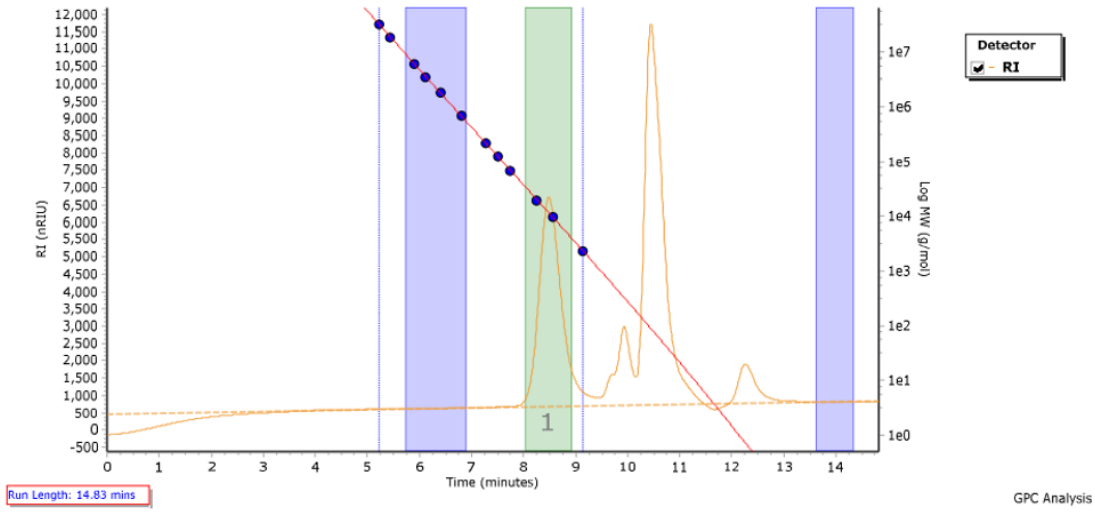


Figure S43. HPLC chromatogram of residual lactide monomer (Table 1, entry 7).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	11413	9691	11801	14176	16650	13816	1.218

Figure S44. GPC trace of PLA (Table 1, entry 8).

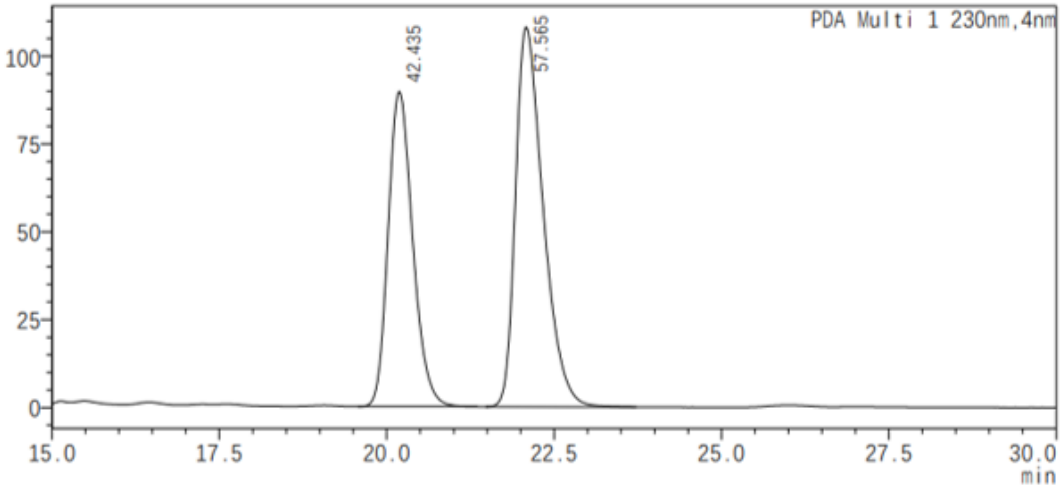
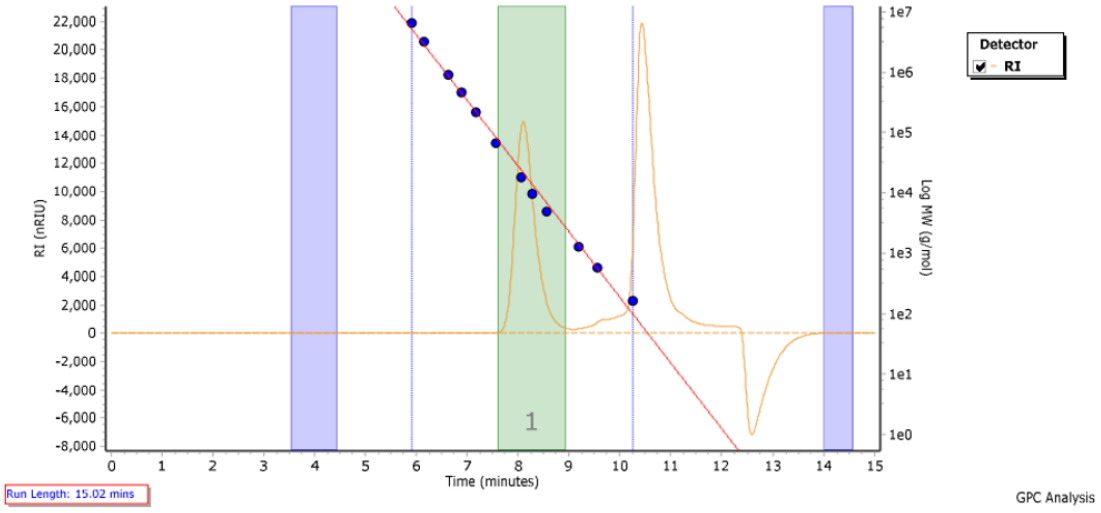


Figure S45. HPLC chromatogram of residual lactide monomer (Table 1, entry 8).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	21413	15299	20101	24470	28580	23859	1.314

Figure S46. GPC trace of PLA (Table 1, entry 9).

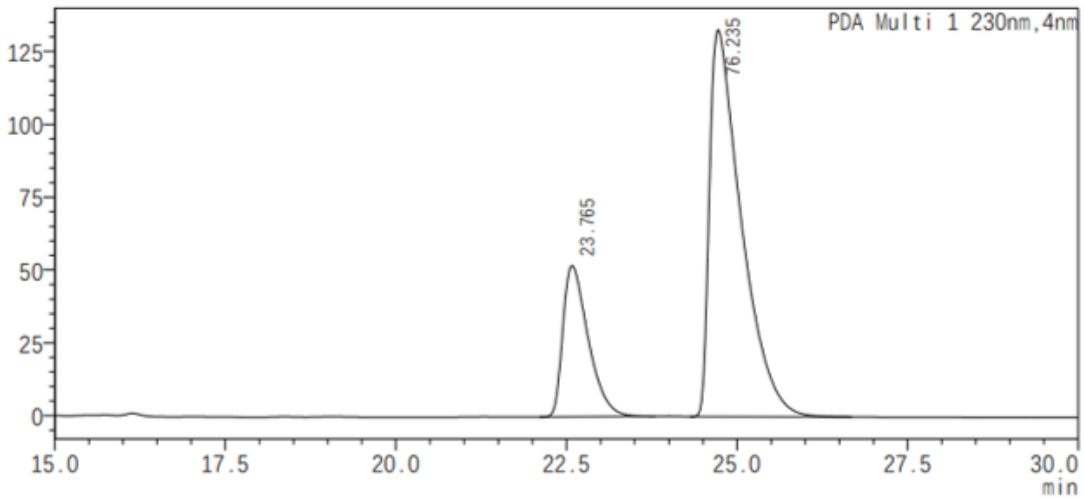
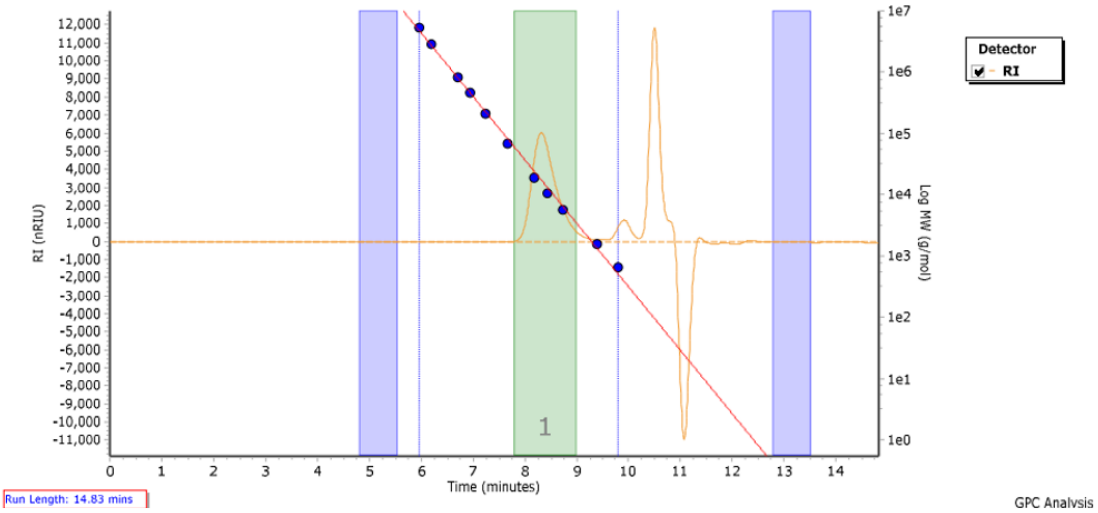


Figure S47. HPLC chromatogram of residual lactide monomer (Table 1, entry 9).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	17011	12002	16014	20071	23953	19495	1.334

Figure S48. GPC trace of PLA (Table 1, entry 10).

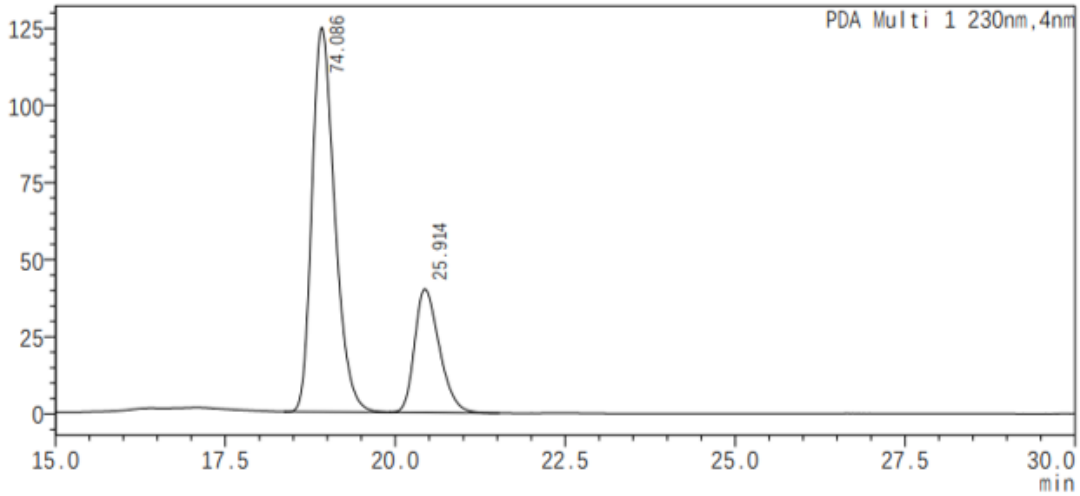
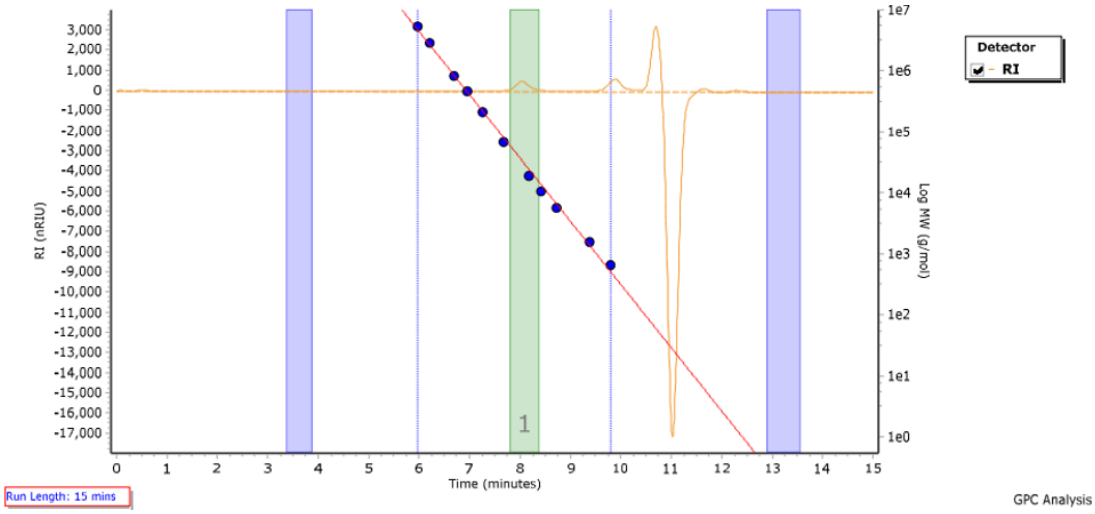


Figure S49. HPLC chromatogram of residual lactide monomer (Table 1, entry 10).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	33472	29457	32377	35189	37777	34789	1.099

Figure S50. GPC trace of PLA (Table 1, entry 11).

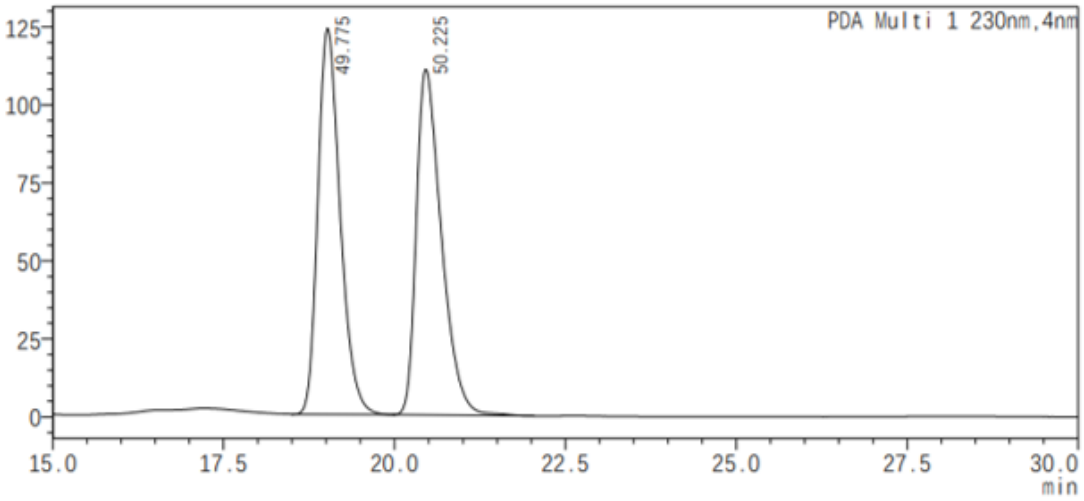
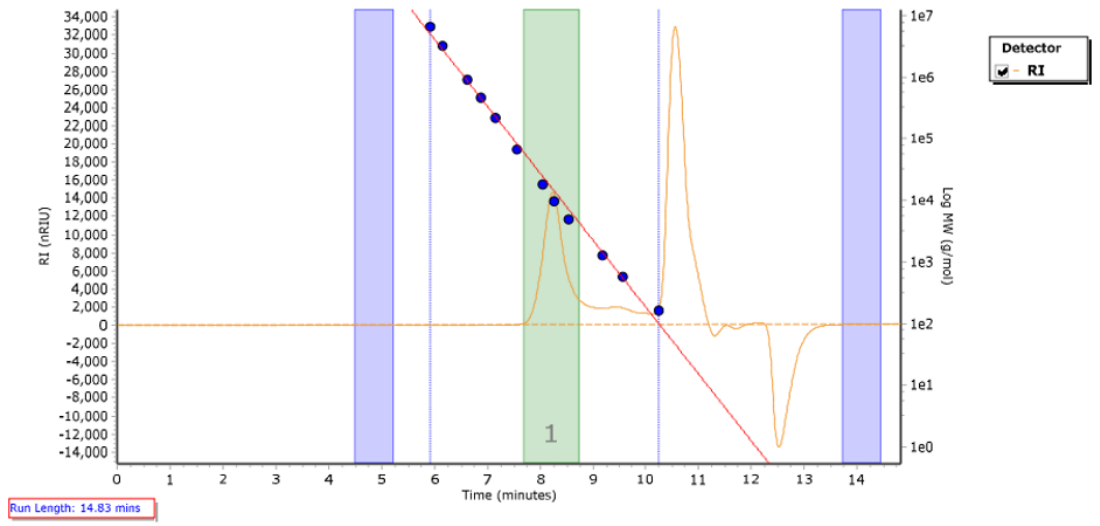


Figure S51. HPLC chromatogram of residual lactide monomer at 50.5% conversion (Table 1, entry 11).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	15019	12089	15567	19598	24016	18975	1.288

Figure S52. GPC trace of PLA (Table 2, entry 1).

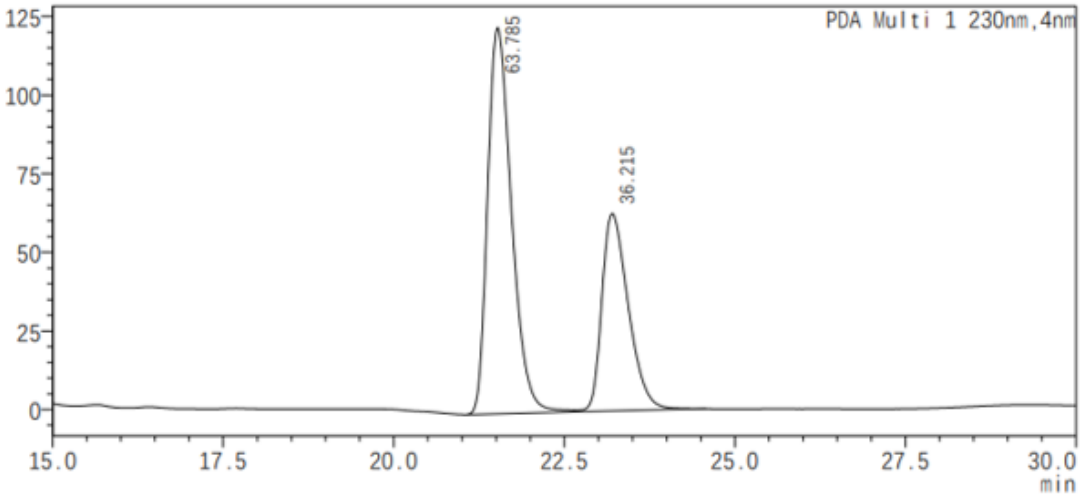
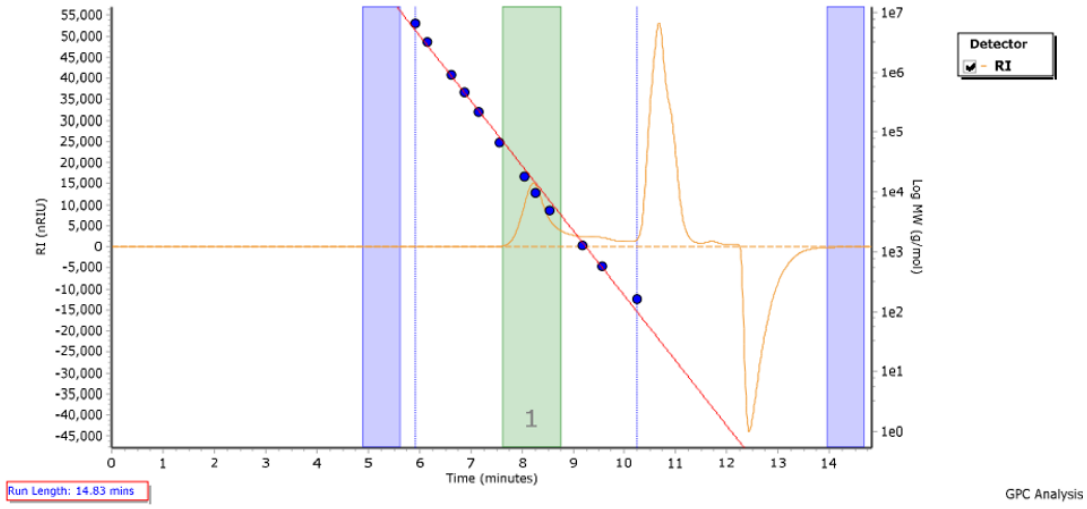


Figure S53. HPLC chromatogram of residual lactide monomer (Table 2, entry 1).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	15335	11818	16176	21463	27333	20644	1.369

Figure S54. GPC trace of PLA (Table 2, entry 2).

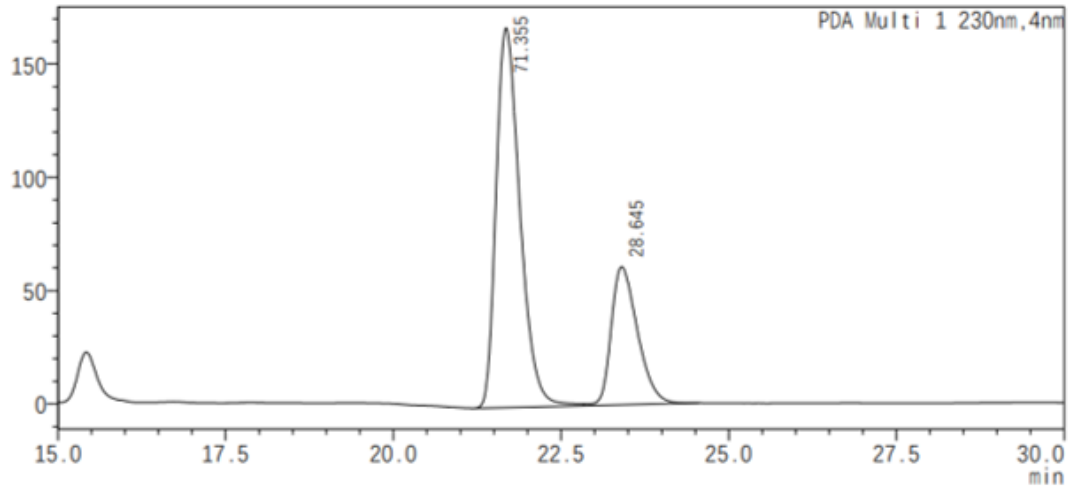
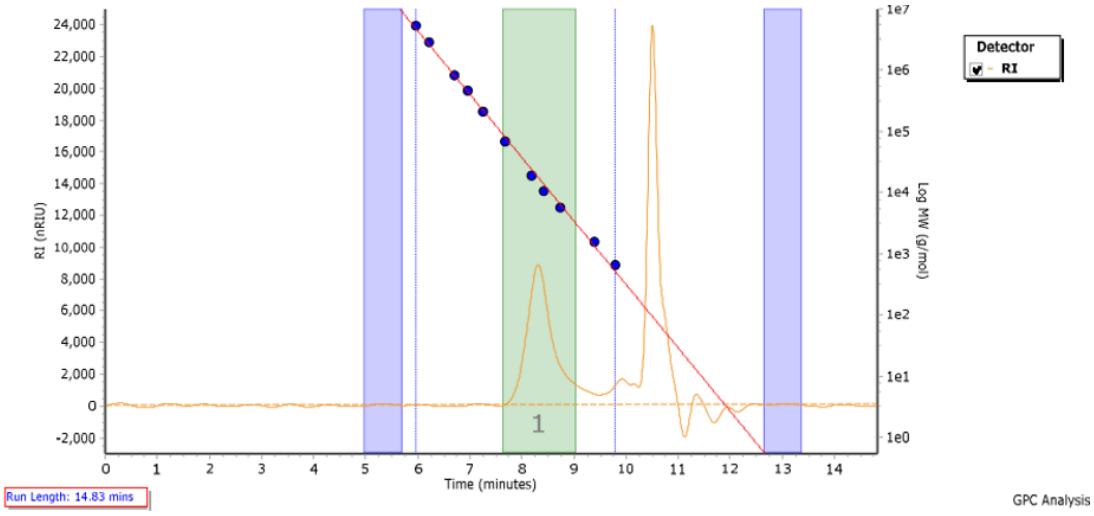


Figure S55. HPLC chromatogram of residual lactide monomer (Table 2, entry 2).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	17353	12142	17692	23682	29839	22801	1.457

Figure S56. GPC trace of PLA (Table 2, entry 3).

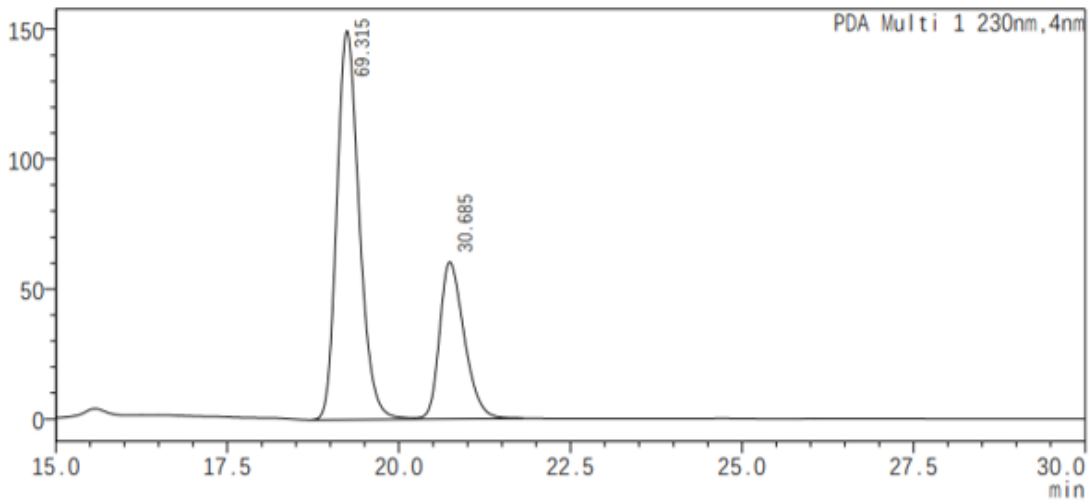
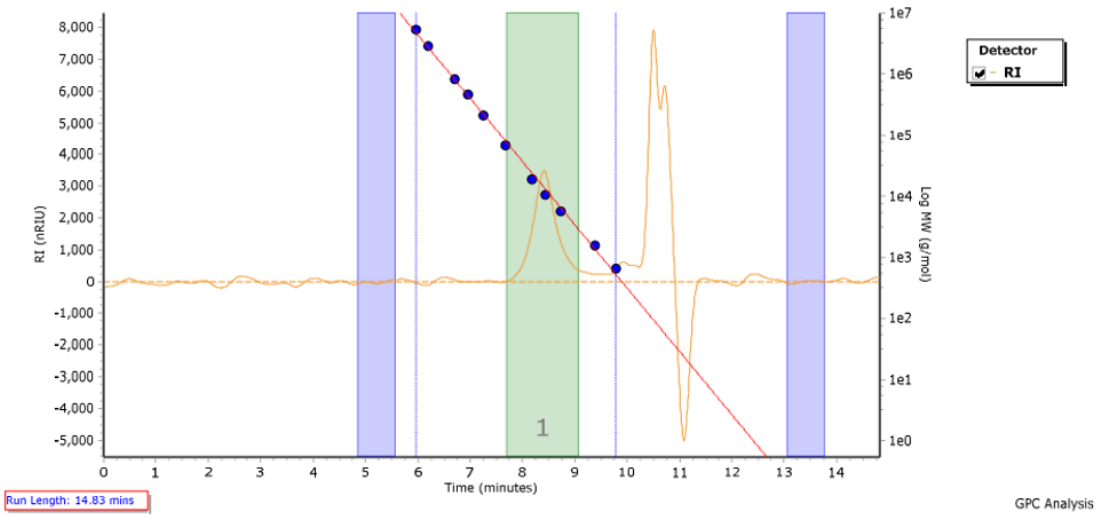


Figure S57. HPLC chromatogram of residual lactide monomer (Table 2, entry 3).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	13666	10558	14894	20418	27255	19514	1.411

Figure 58. GPC trace of PLA (Table 2, entry 4).

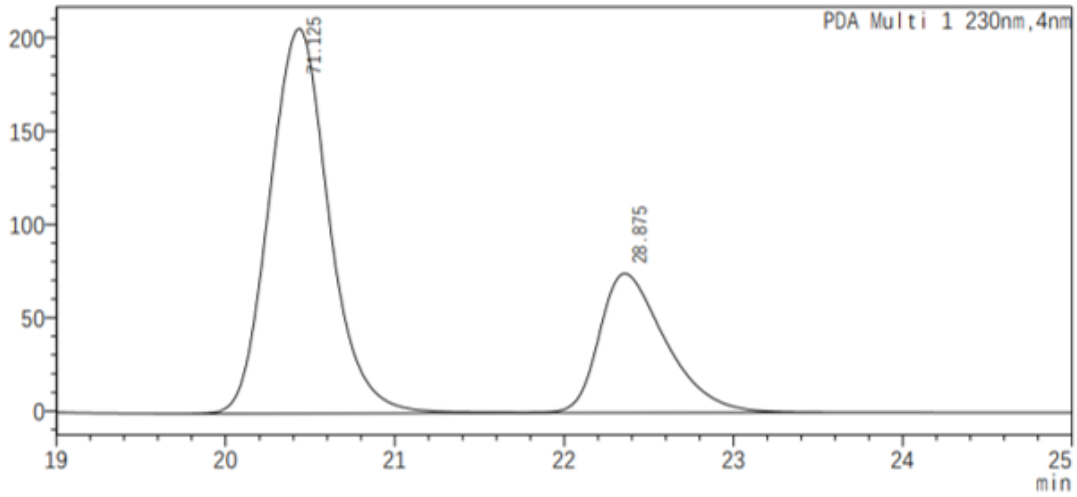
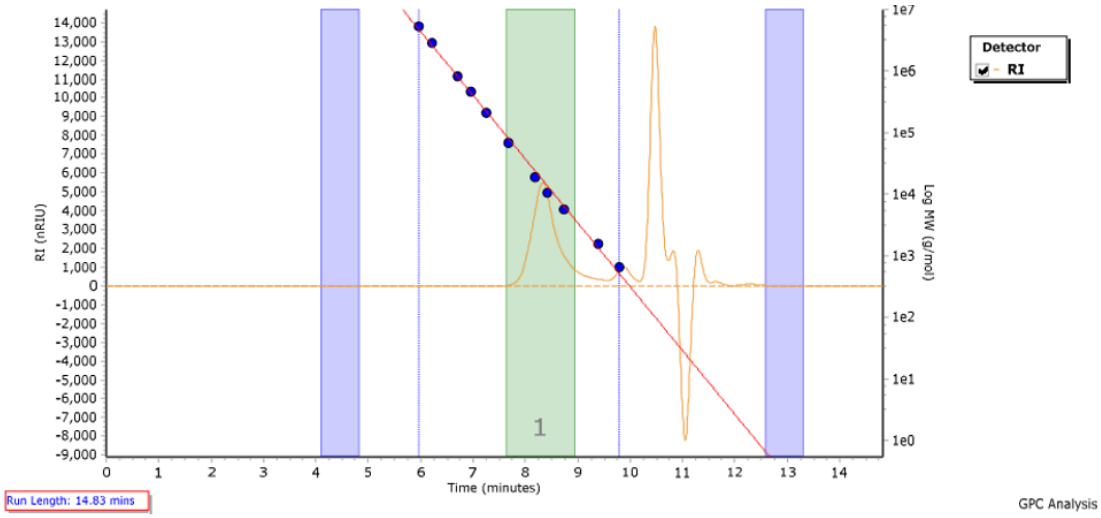


Figure S59. HPLC chromatogram of residual lactide monomer (Table 2, entry 4).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	16676	12573	17154	22512	28607	21679	1.364

Figure S60. GPC trace of PLA (Table 2, entry 5).

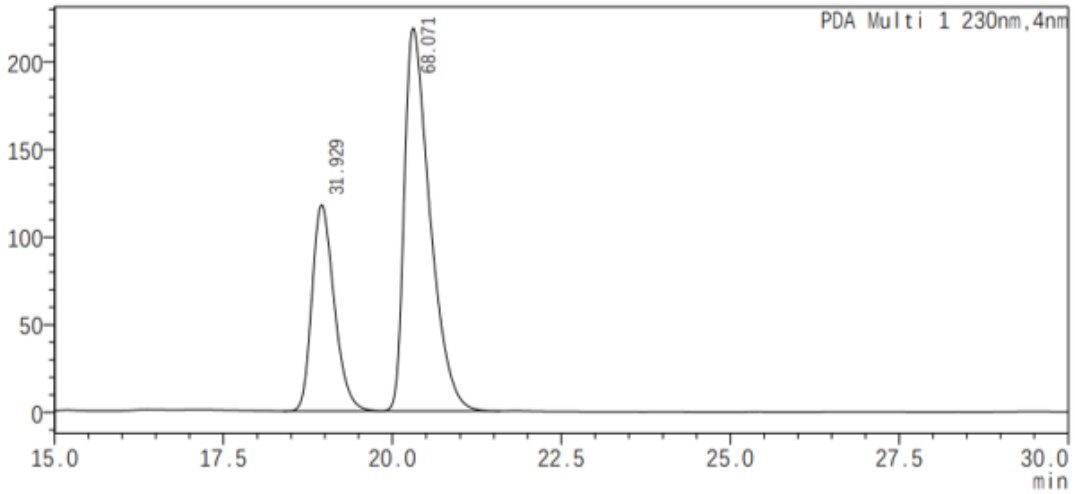
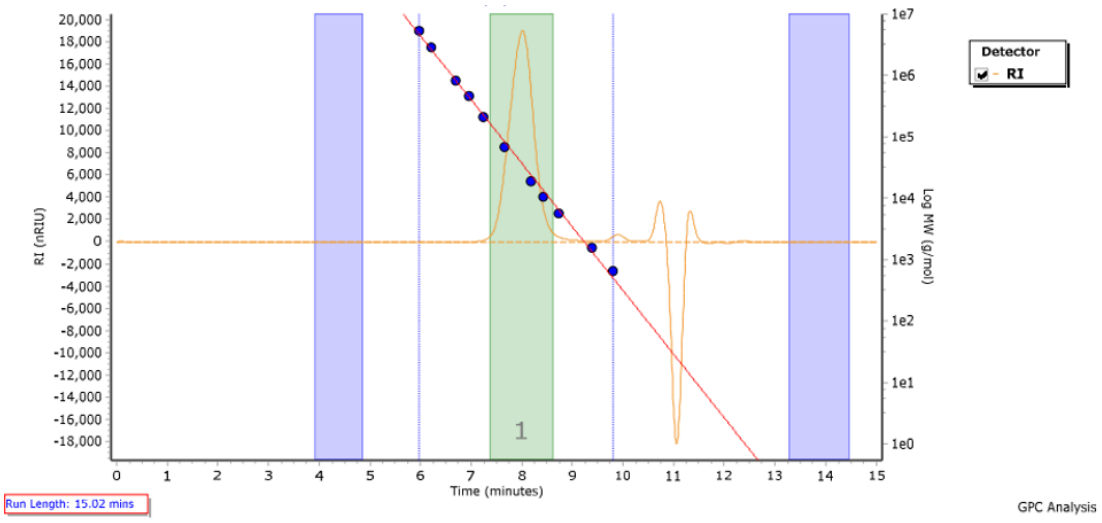


Figure S61. HPLC chromatogram of residual lactide monomer (Table 2, entry 5).



Molecular Weight Averages

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	35532	31932	42534	55744	70612	53658	1.332

Figure S62. GPC trace of PLA (Table 2, entry 6).

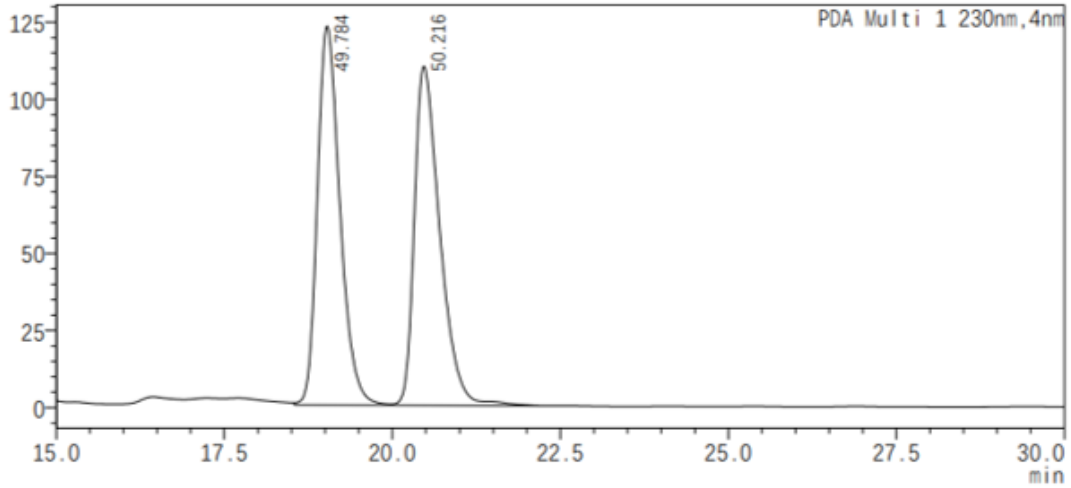


Figure S63. HPLC chromatogram of residual lactide monomer at 55.2% conversion (Table 2, entry 6).

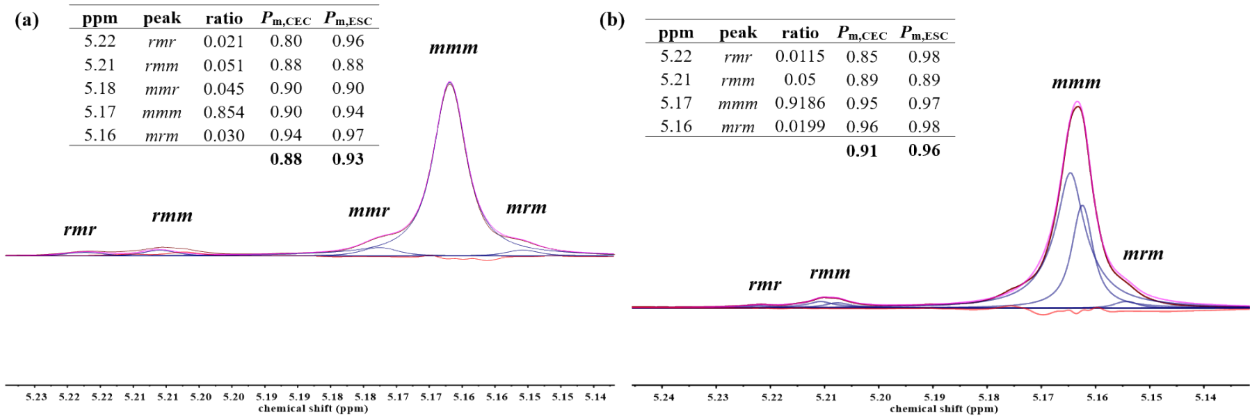


Figure S64. P_m value of PLA catalyzed by (a) (*R,R*)-Salen[4,6-Br, ^{t}Bu] and (b) *rac*-Salen[4,6-Br, ^{t}Bu].

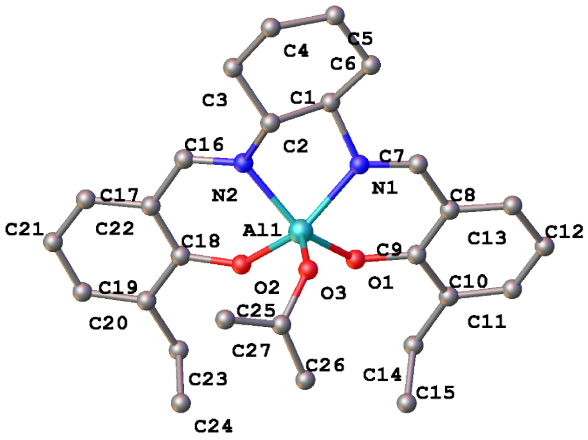


Figure S65. Crystal structure of (*R,R*)-Salen[6-Et] (H atoms were omitted for clarity). The CCDC number of (*R,R*)-Salen[6-Et] is 2244619.

Table S1. Crystal data and structure refinement for (*R,R*)-Salen[6-Et].

Identification code	221120f	
Empirical formula	C27 H35 Al N2 O3	
Formula weight	462.55	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.6431(11) Å	a= 102.572(3)°.
	b = 10.8092(15) Å	b= 96.872(2)°.
	c = 13.5182(16) Å	g = 102.262(3)°.
Volume	1323.4(3) $Å^3$	
Z	2	
Density (calculated)	1.161 Mg/m^3	
Absorption coefficient	0.105 mm^{-1}	
F(000)	496	
Crystal size	0.450 x 0.320 x 0.300 mm^3	
Theta range for data collection	1.992 to 25.018°.	
Index ranges	-11<=h<=11, -12<=k<=12, -14<=l<=16	
Reflections collected	6578	
Independent reflections	4520 [R(int) = 0.0338]	
Completeness to theta = 25.018°	96.6 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9753 and 0.9533
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4520 / 126 / 316
Goodness-of-fit on F^2	1.275
Final R indices [I>2sigma(I)]	R1 = 0.1210, wR2 = 0.3120
R indices (all data)	R1 = 0.1962, wR2 = 0.3414
Extinction coefficient	0.029(8)
Largest diff. peak and hole	0.295 and -0.255 e.Å^{-3}

Table S2. Selected bond lengths [Å] and angles [deg] for (*R,R*)-Salen[6-Et].

Al(1)-O(3)	1.745(5)
Al(1)-O(2)	1.795(5)
Al(1)-O(1)	1.811(4)
Al(1)-N(1)	1.996(5)
Al(1)-N(2)	1.997(6)
N(1)-C(7)	1.301(7)
N(1)-C(1)	1.563(18)
N(2)-C(16)	1.325(8)
N(2)-C(2)	1.546(15)
O(1)-C(9)	1.339(7)
O(2)-C(18)	1.343(8)
O(3)-C(25)	1.419(9)
C(1)-C(6)	1.516(9)
C(1)-C(2)	1.525(9)
C(2)-C(3)	1.538(9)
C(3)-C(4)	1.515(9)
C(4)-C(5)	1.487(9)
C(5)-C(6)	1.520(7)
C(7)-C(8)	1.456(8)
C(8)-C(13)	1.380(9)
C(8)-C(9)	1.399(8)
C(9)-C(10)	1.433(9)
C(10)-C(11)	1.396(10)
C(10)-C(14)	1.512(7)
C(11)-C(12)	1.353(10)
C(12)-C(13)	1.404(10)
C(14)-C(15)	1.515(8)
C(16)-C(17)	1.437(9)
C(17)-C(18)	1.387(9)
C(17)-C(22)	1.427(9)

C(18)-C(19)	1.426(11)
C(19)-C(20)	1.413(12)
C(19)-C(23)	1.532(8)
C(20)-C(21)	1.378(11)
C(21)-C(22)	1.356(10)
C(23)-C(24)	1.507(9)
C(25)-C(27)	1.384(11)
C(25)-C(26)	1.455(11)
O(3)-Al(1)-O(2)	111.5(2)
O(3)-Al(1)-O(1)	111.4(2)
O(2)-Al(1)-O(1)	87.9(2)
O(3)-Al(1)-N(1)	94.9(2)
O(2)-Al(1)-N(1)	152.7(2)
O(1)-Al(1)-N(1)	89.0(2)
O(3)-Al(1)-N(2)	103.5(2)
O(2)-Al(1)-N(2)	88.0(2)
O(1)-Al(1)-N(2)	143.8(2)
N(1)-Al(1)-N(2)	78.8(2)
C(7)-N(1)-C(1)	116.5(6)
C(7)-N(1)-Al(1)	126.1(4)
C(1)-N(1)-Al(1)	116.1(5)
C(16)-N(2)-C(2)	119.2(7)
C(16)-N(2)-Al(1)	128.1(5)
C(2)-N(2)-Al(1)	109.8(6)
C(9)-O(1)-Al(1)	131.2(4)
C(18)-O(2)-Al(1)	134.5(5)
C(25)-O(3)-Al(1)	131.4(6)
C(6)-C(1)-C(2)	113.8(11)
C(6)-C(1)-N(1)	113.5(11)
C(2)-C(1)-N(1)	102.3(10)
C(1)-C(2)-C(3)	111.3(14)
C(1)-C(2)-N(2)	100.6(9)
C(3)-C(2)-N(2)	118.8(11)
C(4)-C(3)-C(2)	111.4(12)
C(5)-C(4)-C(3)	116.0(12)
C(4)-C(5)-C(6)	119.9(8)
C(1)-C(6)-C(5)	111.5(8)
N(1)-C(7)-C(8)	124.5(6)
C(13)-C(8)-C(9)	120.9(6)
C(13)-C(8)-C(7)	118.5(7)
C(9)-C(8)-C(7)	120.5(6)
O(1)-C(9)-C(8)	123.1(6)
O(1)-C(9)-C(10)	117.6(7)
C(8)-C(9)-C(10)	119.2(6)
C(11)-C(10)-C(9)	116.8(7)
C(11)-C(10)-C(14)	123.6(7)

C(9)-C(10)-C(14)	119.6(7)
C(12)-C(11)-C(10)	124.4(8)
C(11)-C(12)-C(13)	118.2(8)
C(8)-C(13)-C(12)	120.5(8)
C(10)-C(14)-C(15)	111.7(7)
N(2)-C(16)-C(17)	123.5(7)
C(18)-C(17)-C(22)	120.6(7)
C(18)-C(17)-C(16)	121.0(7)
C(22)-C(17)-C(16)	118.4(7)
O(2)-C(18)-C(17)	123.0(7)
O(2)-C(18)-C(19)	117.3(8)
C(17)-C(18)-C(19)	119.7(7)
C(20)-C(19)-C(18)	116.9(9)
C(20)-C(19)-C(23)	121.4(9)
C(18)-C(19)-C(23)	121.1(8)
C(21)-C(20)-C(19)	123.1(9)
C(22)-C(21)-C(20)	119.6(9)
C(21)-C(22)-C(17)	120.1(8)
C(24)-C(23)-C(19)	102.1(10)
C(27)-C(25)-O(3)	116.6(7)
C(27)-C(25)-C(26)	125.8(9)
O(3)-C(25)-C(26)	114.0(8)

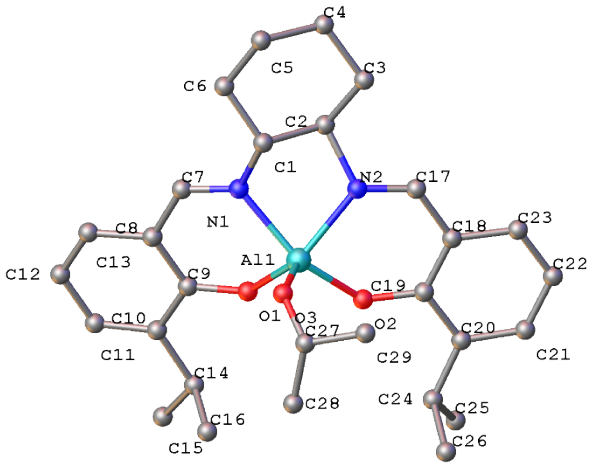


Figure S66. Crystal structure of (*R,R*)-Salen[6-^{i}Pr] (H atoms were omitted for clarity). The CCDC number of (*R,R*)-Salen[6-^{i}Pr] is 2244620.

Table S3. Crystal data and structure refinement for (*R,R*)-Salen[6-^{i}Pr].

Identification code	230210b	
Empirical formula	C29 H39 Al N2 O3	
Formula weight	490.60	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.6879(8) Å	a= 102.047(3)°.
	b = 11.1191(11) Å	b= 103.197(3)°.
	c = 14.2499(13) Å	g = 96.808(2)°.
Volume	1439.1(2) Å^3	
Z	2	
Density (calculated)	1.132 Mg/m^3	
Absorption coefficient	0.101 mm^{-1}	
F(000)	528	
Crystal size	0.480 x 0.280 x 0.250 mm^3	
Theta range for data collection	2.122 to 25.017°.	
Index ranges	-11<=h<=10, -13<=k<=13, -9<=l<=16	

Reflections collected	6822
Independent reflections	4943 [R(int) = 0.0397]
Completeness to theta = 25.017°	97.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9753 and 0.9533
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4943 / 102 / 336
Goodness-of-fit on F^2	1.080
Final R indices [I>2sigma(I)]	R1 = 0.1123, wR2 = 0.2835
R indices (all data)	R1 = 0.1655, wR2 = 0.3078
Extinction coefficient	0.013(3)
Largest diff. peak and hole	0.264 and -0.272 e.Å^{-3}

Table S4. Selected bond lengths [Å] and angles [deg] for (*R,R*)-Salen[6-^{i}Pr].

Al(1)-O(3)	1.734(5)
Al(1)-O(1)	1.823(4)
Al(1)-O(2)	1.823(4)
Al(1)-N(1)	2.029(5)
Al(1)-N(2)	2.042(5)
N(1)-C(7)	1.291(7)
N(1)-C(1)	1.508(16)
N(1)-C(1')	1.574(17)
N(2)-C(17)	1.292(8)
N(2)-C(2)	1.564(12)
N(2)-C(2')	1.575(14)
O(1)-C(9)	1.325(6)
O(2)-C(19)	1.334(7)
O(3)-C(27)	1.398(8)
C(1)-C(6)	1.530(9)
C(1)-C(2)	1.535(9)
C(2)-C(3)	1.532(9)
C(3)-C(4)	1.540(9)
C(4)-C(5)	1.537(9)
C(5)-C(6)	1.538(9)
C(7)-C(8)	1.439(8)
C(8)-C(13)	1.421(8)
C(8)-C(9)	1.440(7)
C(9)-C(10)	1.424(8)
C(10)-C(11)	1.375(9)
C(10)-C(14)	1.542(8)
C(11)-C(12)	1.420(10)

C(12)-C(13)	1.345(9)
C(14)-C(16)	1.482(11)
C(14)-C(15)	1.542(10)
C(17)-C(18)	1.440(9)
C(18)-C(19)	1.403(8)
C(18)-C(23)	1.441(9)
C(19)-C(20)	1.433(8)
C(20)-C(21)	1.406(10)
C(20)-C(24)	1.502(10)
C(21)-C(22)	1.388(11)
C(22)-C(23)	1.376(10)
C(24)-C(26)	1.524(16)
C(24)-C(25)	1.530(14)
C(27)-C(29)	1.430(10)
C(27)-C(28)	1.466(10)
O(3)-Al(1)-O(1)	110.3(2)
O(3)-Al(1)-O(2)	110.3(2)
O(1)-Al(1)-O(2)	88.76(19)
O(3)-Al(1)-N(1)	96.3(2)
O(1)-Al(1)-N(1)	87.93(19)
O(2)-Al(1)-N(1)	152.5(2)
O(3)-Al(1)-N(2)	105.5(3)
O(1)-Al(1)-N(2)	142.8(3)
O(2)-Al(1)-N(2)	88.0(2)
N(1)-Al(1)-N(2)	78.4(2)
C(7)-N(1)-C(1)	121.4(6)
C(7)-N(1)-Al(1)	125.7(4)
C(1)-N(1)-Al(1)	110.3(6)
C(17)-N(2)-C(2)	117.2(6)
C(17)-N(2)-Al(1)	126.0(5)
C(2)-N(2)-Al(1)	114.6(5)
C(9)-O(1)-Al(1)	133.3(4)
C(19)-O(2)-Al(1)	135.3(4)
C(27)-O(3)-Al(1)	137.0(6)
N(1)-C(1)-C(6)	119.5(12)
N(1)-C(1)-C(2)	101.4(10)
C(6)-C(1)-C(2)	112.0(14)
C(3)-C(2)-C(1)	114.9(11)
C(3)-C(2)-N(2)	111.8(9)
C(1)-C(2)-N(2)	101.8(9)
C(2)-C(3)-C(4)	109.0(11)
C(5)-C(4)-C(3)	116.0(13)
C(4)-C(5)-C(6)	112.1(16)
C(1)-C(6)-C(5)	111.3(16)
N(1)-C(7)-C(8)	125.1(5)
C(13)-C(8)-C(7)	118.9(5)

C(13)-C(8)-C(9)	119.9(5)
C(7)-C(8)-C(9)	121.1(5)
O(1)-C(9)-C(10)	120.2(5)
O(1)-C(9)-C(8)	121.0(5)
C(10)-C(9)-C(8)	118.8(5)
C(11)-C(10)-C(9)	118.5(6)
C(11)-C(10)-C(14)	122.6(6)
C(9)-C(10)-C(14)	118.8(5)
C(10)-C(11)-C(12)	122.5(7)
C(13)-C(12)-C(11)	120.1(7)
C(12)-C(13)-C(8)	120.3(6)
C(16)-C(14)-C(10)	111.8(6)
C(16)-C(14)-C(15)	109.2(7)
C(10)-C(14)-C(15)	113.4(6)
N(2)-C(17)-C(18)	126.3(6)
C(19)-C(18)-C(17)	121.3(6)
C(19)-C(18)-C(23)	120.4(6)
C(17)-C(18)-C(23)	118.3(6)
O(2)-C(19)-C(18)	121.7(5)
O(2)-C(19)-C(20)	118.6(6)
C(18)-C(19)-C(20)	119.8(6)
C(21)-C(20)-C(19)	117.5(7)
C(21)-C(20)-C(24)	121.5(6)
C(19)-C(20)-C(24)	121.0(6)
C(22)-C(21)-C(20)	122.8(7)
C(23)-C(22)-C(21)	120.4(7)
C(22)-C(23)-C(18)	119.1(7)
C(20)-C(24)-C(26)	111.4(9)
C(20)-C(24)-C(25)	113.8(9)
C(26)-C(24)-C(25)	107.1(9)
O(3)-C(27)-C(29)	113.5(7)
O(3)-C(27)-C(28)	114.1(7)
C(29)-C(27)-C(28)	116.9(8)

References

1. Z. Zhong, P. J. Dijkstra and J. Feijen, *J. Am. Chem. Soc.*, 2003, **125**, 11291–11298.

2. Y. Lu, J. H. Swisher, T. Y. Meyer, and G. W. Coates, *J. Am. Chem. Soc.* 2021, **143**, 4119–4124.