Supporting Information

For

Chirality-Driven Self-Assembly: Application Toward Renewable/Exchangeable Resin-Bound Catalysts

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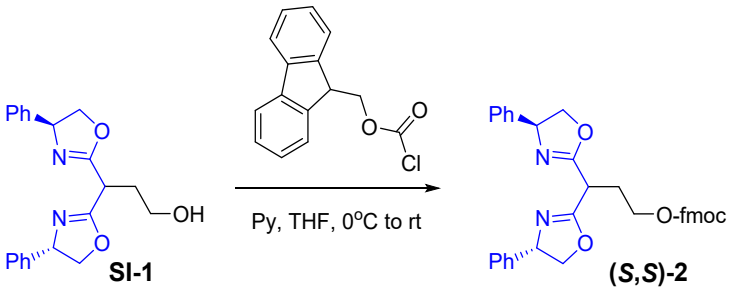
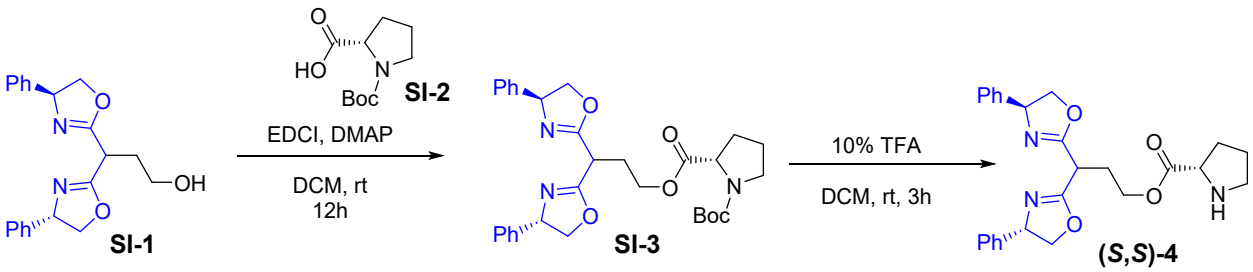
1. General Information

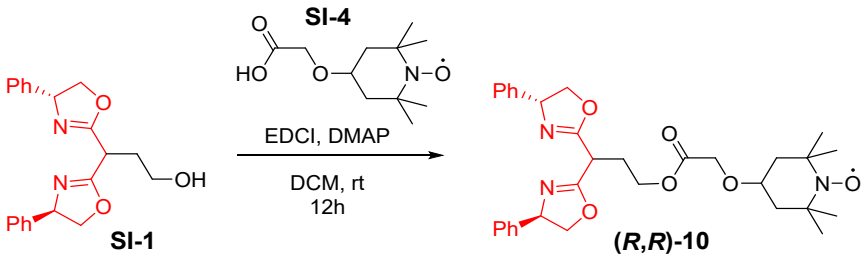
Solvents and materials were obtained from commercial suppliers (Fisher Scientific, Sigma-Aldrich, AA Block, Oakwood Chemicals, and Alfa Aesar) and used without further purification. Unless otherwise noted, all reactions were performed in standard dry glassware under an Argon atmosphere in dry solvents. Evaporation and concentration of solvents were carried out with Büchi Rotovapor R-200 attached to a Maximadry vacuum pump. Roto-evaporation for all zinc complexes were performed under rt, and the residue was further dried under high vacuum to obtain the complexed products. THF used for the synthesis of substituted box derivatives was dried using 4Å molecular sieves. Preparative separations were performed by silica gel gravity column chromatography using Silica Flash P60. TLC analyses were performed on Merck Kieselgel 60 F254 glass plates and were visualized with UV light or stains (iodine, vanillin, ninhydrin). ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 °C on Varian 400 MHz spectrometers using $CDCl_3$ and DMSO-d_6 as solvents purchased from Sigma Aldrich and Cambridge Isotope Laboratories, respectively. The solvent signals were used as internal standards for both ^{1}H NMR ($CDCl_3$ δ = 7.26 ppm) and ^{13}C NMR ($CDCl_3$ δ = 77.20 ppm) recordings. ^{1}H NMR data are reported as follows: chemical shift (reported in parts per million), multiplicity (s = singlet, d = doublet, t = triplet, quart = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, and m = multiplet), integration, and

coupling constants (reported in hertz). Mass spectra were measured with Thermo Fisher Scientific Q-Exactive Plus (ESI, APCI) spectrometer, ABI 4700 mass spectrometer. Infrared spectra were collected on a Nicolet iS10 FTIR spectrometer using a Smart iTR attenuated total reflectance sampling accessory with a single bounce ZnSe crystal plate. Polarimetry was measured in a Perkin Elmer Model 341 Polarimeter at 25 °C in a 100 mm cell at 589 nm using CH_2Cl_2 as the solvent.

2. Scheme for Chiral BOX Derived Functional Groups/Catalysts Preparations.

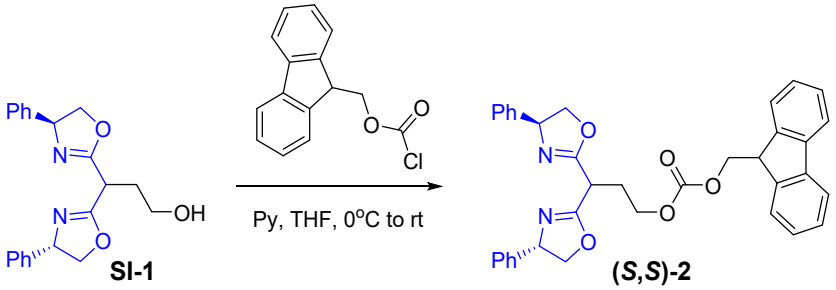






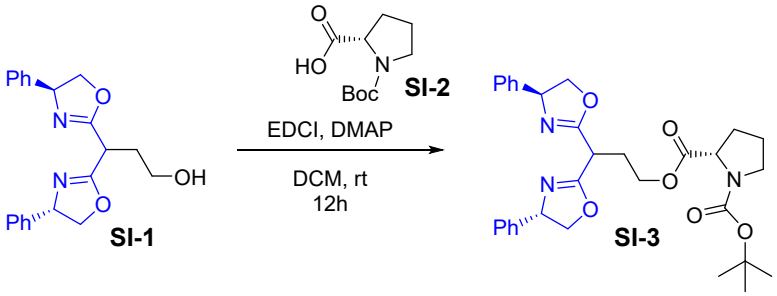
3. Procedure for Preparation of functionalized chiral BOX

i). Synthesis of **(*S*,*S*)-2**



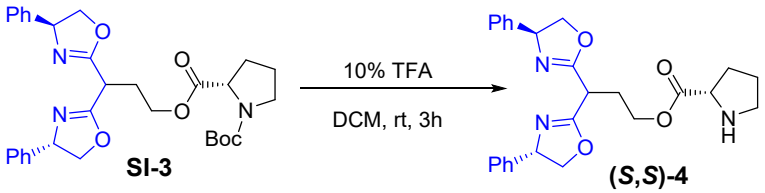
SI-**1** was prepared according to the published procedure.[1] To a solution of SI-**1** (3.0 g, 8.56 mmol) in pyridine (3 mL) was added 9-fluorenylmethoxycarbonyl chloride (2.65 g, 10.3 mmol, 1.2 equiv) in THF (15 ml) dropwise via cannula at room temperature. The reaction mixture was stirred overnight and quenched with water (5 ml). A crude product was washed with 2N HCl solution (3 X 10 ml) and extracted using ethyl acetate (3 X 20 ml), and combined organic layers were washed with brine (2X 20 ml). Solvents were evaporated under reduced pressure and the crude product was purified by column chromatography with DCM/MeOH (19:1) as eluent to give (*S*,*S*)-**2** (4.6 g, 93.8%) as off-white fluffy solid upon repeated drying under high vacuum: mp 113-115 °C; $[\alpha]_D^{25}$ = -11.5 (c = 0.8, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (dt, *J* = 6.1, 7.3 Hz, 2H), 3.79 (tt, *J* = 1.0, 7.4 Hz, 1H), 4.08 (td, *J* = 8.0, 8.6 Hz, 2H), 4.13 – 4.25 (m, 2H), 4.29 – 4.35 (m, 4H), 4.58 (ddd, *J* = 5.4, 8.4, 10.2 Hz, 2H), 5.12 – 5.19 (m, 2H), 7.14 – 7.27 (m, 14H), 7.50 – 7.56 (m, 2H), 7.64 – 7.70 (m, 2H). ^{13}C NMR (101 MHz,) δ 29.23, 36.43, 46.75, 46.85, 65.60, 69.58, 69.60, 69.65, 69.77, 75.28, 75.32, 76.84, 77.16, 77.48, 120.02, 120.06, 125.15, 125.23, 125.25, 126.66, 126.69, 126.80, 127.14, 127.20, 127.64, 127.77, 127.81, 127.88, 128.73, 128.75, 141.27, 141.29, 142.02, 142.03, 142.14, 143.38, 143.40, 143.56, 143.60, 155.07, 155.35, 165.34, 165.56. MS (ESI): *m/z* calculated for $C_{36}H_{33}N_2O_5$ $[M+H]^+$, 573.2384; found, 573.2648. FTIR: C=N 1655.41 cm^{-1}

ii). Synthesis of **SI-3**



At 0°C, EDCI (4.1 g, 21.4 mmol) was added to a stirring solution of *N*-(tert-Butoxycarbonyl)-*L*-proline (SI-**2**, Boc-Pro-OH, Sigma-Aldrich) (3.07 g, 14.3 mmol), **SI-1** (5.00 g, 14.27 mmol), and DMAP (0.70 g, 5.71 mmol) in DCM (10 mL) under argon. Reaction was warm to the room temperature and stirred overnight. The white solid was filtered off and washed with small amounts of ethyl acetate. The filtrate was concentrated under reduced pressure, and the crude product was purified by liquid chromatography on silica gel, eluting with methanol/DCM (3:97) to give **SI-3** (7.02 g, 89.8%) as a pale brown solid: mp 125-127 °C; $[\alpha]_D^{25}$ = -8.3 (c = 0.8, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (d, J = 8.0 Hz, 9H), 1.73 – 1.94 (m, 4H), 2.04 – 2.20 (m, 2H), 2.34 – 2.43 (m, 2H), 3.24 – 3.52 (m, 2H), 4.03 – 4.18 (m, 3H), 4.19 – 4.34 (m, 2H), 4.58 – 4.65 (m, 2H), 5.15 – 5.21 (m, 3H), 7.14 – 7.29 (m, 10H). ^{13}C NMR (101 MHz,) δ 23.71, 28.42, 28.53, 28.57, 29.18, 30.94, 31.00, 36.28, 36.31, 46.39, 46.43, 46.64, 58.91, 59.18, 59.42, 62.33, 62.36, 69.71, 69.75, 74.74, 75.35, 75.38, 75.42, 76.84, 77.16, 77.48, 79.83, 79.87, 79.97, 126.50, 126.52, 126.69, 126.74, 126.75, 127.68, 127.75, 127.86, 128.81, 128.84, 142.05, 142.15, 142.27, 153.88, 154.00, 165.31, 165.50, 165.71, 172.91, 173.16, 173.45. MS (ESI): *m/z* calculated for $C_{31}H_{38}N_3O_6$ $[M+H]^+$, 548.2755; found, 548.2832

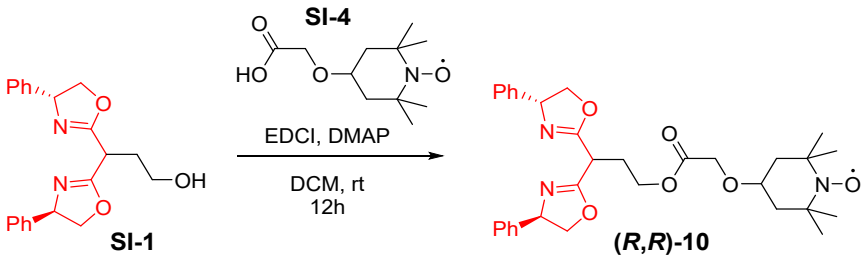
Synthesis of **(*S*,*S*)-4**



The 20% TFA solution in DCM (15 ml) was added to the solution of **SI-3** (6.5 g, 11.87 mmol) in DCM (100 mL), and the mixture was stirred 4 hours at room temperature. Upon completion of deprotection monitored by TLC, the mixture was basified through careful addition of saturated aqueous $NaHCO_3$. The crude product was extracted with DCM (3 x 30 ml), and the combined organic layer was washed with Brine (100 ml). The organic layer was dried over Na_2SO_4, and filtrate was concentrated to give **(*S*,*S*)-4** (5.20 g, 97.9%) as a pale brown oil which was used for next step without further purification. $[\alpha]_D^{25}$ = -7.5 (c = 0.8, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.56 – 1.68 (m, 3H), 1.73 – 1.84 (m, 1H), 1.96 – 2.09 (m, 1H), 2.35 (dd, *J* = 6.3, 7.5 Hz, 2H), 2.84 (dt, *J* = 6.8, 10.4 Hz, 1H), 2.97 (dt, *J* = 6.8, 10.4 Hz, 1H), 3.74 (ddd, *J* = 6.2, 8.1, 17.1 Hz, 2H), 4.05 (dt, *J* = 8.2, 9.6 Hz, 2H), 4.23 (td, *J* = 1.1, 6.3 Hz, 2H), 4.56 (ddd, *J* = 1.4, 8.4, 10.0 Hz, 2H), 5.03 – 5.21 (m, 2H), 7.14 – 7.21 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 24.91, 25.10, 28.95, 29.78, 29.95, 36.20, 46.49, 46.63, 59.46, 59.57, 62.46, 69.50, 69.56, 75.28, 77.05, 77.37, 77.68, 126.33, 126.59, 126.61,

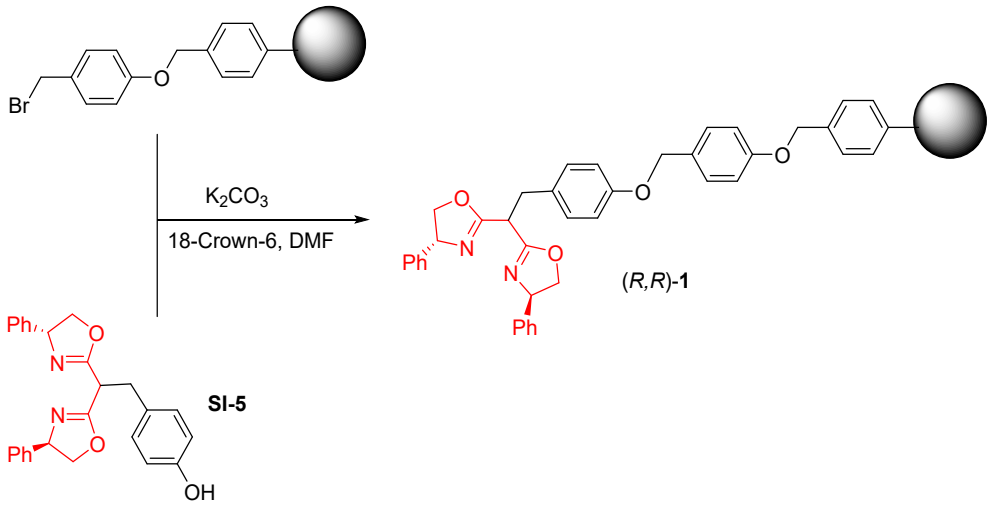
127.61, 127.76, 128.69, 128.71, 141.96, 141.98, 142.05, 142.08, 165.29, 165.41, 165.48, 174.20, 174.23. MS (ESI): *m/z* calculated for $C_{26}H_{30}N_3O_4$ $[M+H]^+$, 448.2231; found, 448.2287. FTIR: C=N 1657.41 cm^{-1}

iii). Synthesis of **(*R,R*)-10**



EDCI (4.10 g, 21.4 mmol) was added to a stirring solution of SI-**4**[2] (3.61 g, 0.485 mmol), SI-**1** ((*R,R*), 5.00 g, 14.27 mmol), and DMAP (0.7 g, 5.71 mmol) in DCM (30 mL) under argon. After stirring overnight at rt, the white solid was filtered off, and solids were washed three times with 20 mL of ethyl acetate. The filtrate was concentrated under reduced pressure, and the crude product was purified by liquid chromatography on silica gel, eluting with methanol/DCM (2:98) to give (*R,R*)-**10** (5.94 g, 74.0 %) as a red oil. $[\alpha]_D^{25}$ = +9.2 (c = 0.8, CH_2Cl_2); For the 1H NMR analysis, the (*R,R*)-**10** was reduced to TEMPO-H by the ascorbic acid using a standard procedure. ^{1}H NMR (400 MHz, DMSO-d_6) δ 0.96 – 1.14 (m, 12H), 1.27 (td, *J* = 4.4, 11.7 Hz, 2H), 1.85 (td, *J* = 3.9, 12.5 Hz, 2H), 2.29 (q, *J* = 6.6 Hz, 1H), 2.60 (t, *J* = 7.0 Hz, 1H), 3.40 – 3.49 (m, 3H), 3.62 (dddd, *J* = 2.9, 7.4, 11.0, 14.9 Hz, 1H), 3.76 (t, *J* = 7.8 Hz, 1H), 3.92 – 4.13 (m, 3H), 4.25 (t, *J* = 6.4 Hz, 2H), 4.67 (d, *J* = 1.7 Hz, 2H), 5.22 (dd, *J* = 7.8, 10.3 Hz, 2H), 7.22 – 7.40 (m, 9H), 8.25 (s, 1H). FTIR: C=N 1656.07 cm^{-1}

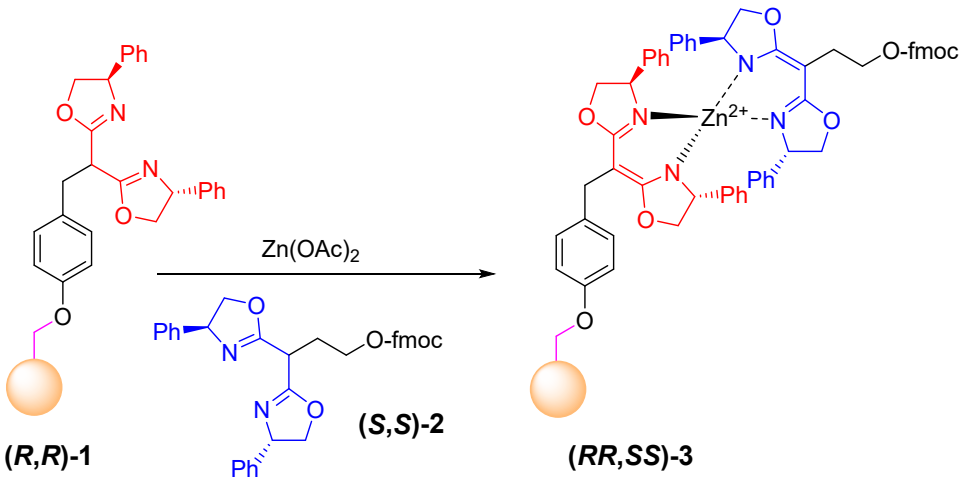
6. Procedure for Immobilization of SI-4 on Wang Resin.



The (*R*,*R*)-**1** was prepared according to the reported procedure.[3] Briefly, to the suspended solution of **SI-5**[1] (1.01 g, 2.45 mmol) in dry DMF (75ml) was added K_2CO_3 (450 mg, 3.26 mmol) and 18-crown-6 (90 mg, 0.326 mmol) at 0°C. The reaction mixture was warmed to room temperature and stirred for 2 hours. Reaction was cooled to 0°C and Wang-Br resin (0.5–1 mmol/g, 2.40 g) was added in one portion. The reaction mixture was gently stirred overnight under argon atmosphere at 50°C. The resin was filtered off and was washed successively with DMF (3x50mL), MeOH (2x50 mL), 50% MeOH in H_2O (2x50 mL), H_2O (4x50 mL), acetone (2x50 mL), and diethyl ether (3x50 mL). The resin was suspended on diethyl ether (75 ml) and left over night at ambient temperature. The resin was filtered off, and washed three times with diethyl ether (50 ml). The resin was dried at 40°C in vacuo for 72 hours to give (*R*,*R*)-**1** (2.60 g, 0.30mmol/g). FTIR: C=N 1655.1 cm^{-1}

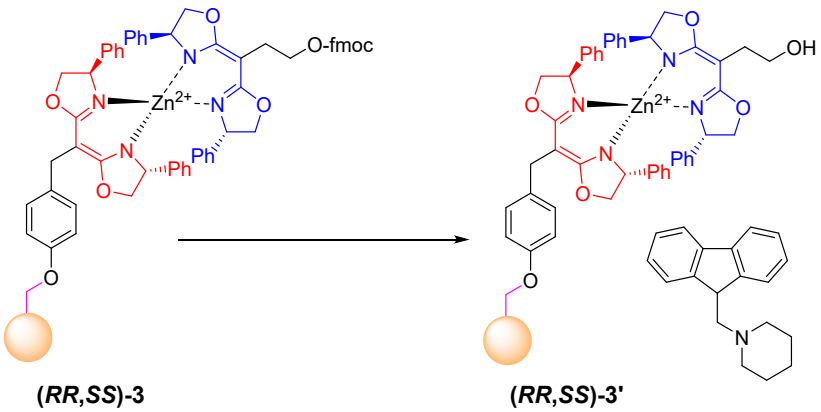
7. Spectroscopic quantification of functional (*R*,*R*)-BOX on the (*R*,*R*)-1.

a) Formation of Heterochiral (*RR*,*SS*)-**3**



The (*R*,*R*)-BOX functionalized resin (*R*,*R*)-**1** (1.00 g) was suspended in dry DCM and stirred at ambient temperature for 1 hour. To the solution was added fmoc-functionalized (*S*,*S*)-**2** (189 mg, 0.33 mmol) in 2 ml DCM, and mixture was stirred for 5 min. The solution of $Zn(OAc)_2$ (35 mg, 0.33 mmol) in MeOH (2.0 ml) was added to the mixture, and stirred for 30 min at room temperature. The resin was filtered off, and washed three times with DCM (10 ml), and three times with diethyl ether (10 ml). The resin was dried at 40°C in vacuo for 72 hours (until weight no longer changes) to give (*RR*,*SS*)-**3** (1.17 g), with a loading of 0.284 mmol of ligand per gram polymer (reported: 0.321 mmol/g). FTIR: C=N 1657.41 cm^{-1}

b) Quantification of functional BOX group on Wang resin using fmoc-derived (*RR*,*SS*)-**3**.

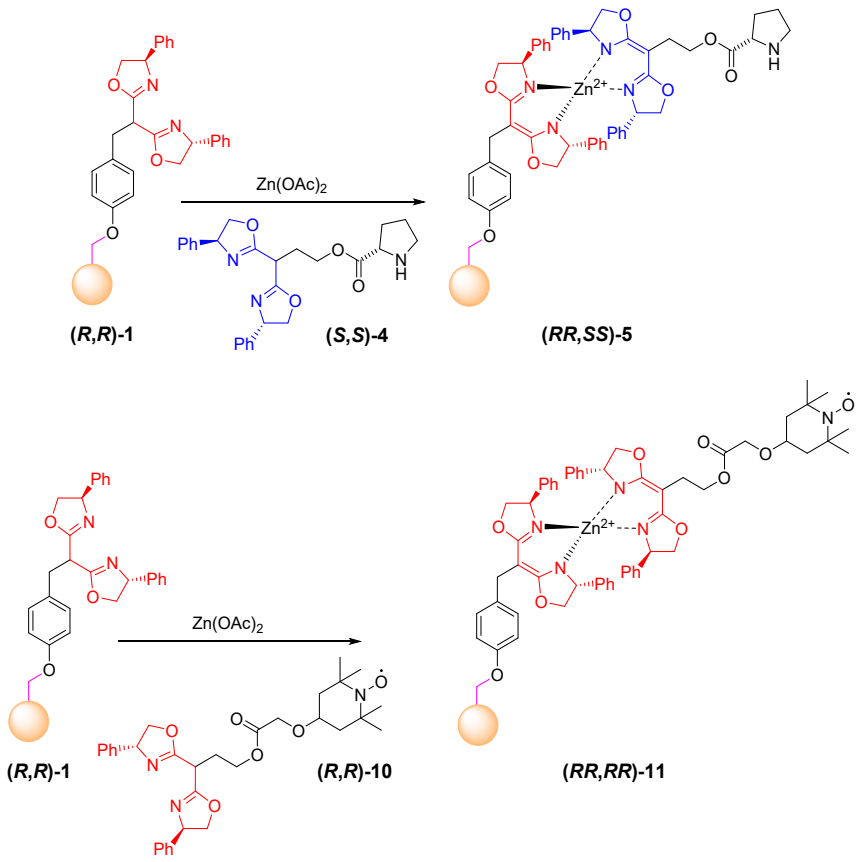


The measurement of loaded SI-**5** on Wang's resin (*RR*,*SS*)-**1** was conducted using standard fmoc quantification approach using (*RR*,*SS*)-**3**. The oven-dried (*RR*,*SS*)-**3** (0.03 g) was suspended in 0.8 ml of *N*,*N*-dimethylformamide (DMF) and allow the resin to swell for 15 minutes. Then 0.2 ml of piperidine was added to the mixture and stirred 30 h at room temperature. The 0.1ml of the supernatant solution was transferred to a 1cm quartz cuvette, and sample was diluted with 0.9ml DMF. UV absorbance measurement at 301 nm was recorded using standard protocol with 20% piperidine/DMF solution as blank. The mmol of Fmoc released during the deprotection reaction was calculated using L = (A x V x d)/(Ec x w x M) where L = Resin loading, A = Absorbance at 301 nm, V = Volume of the cleavage solution (= 1 mL), d = Dilution = 10, E = Extinction coefficient (= 7800 mL/mmol x cm), w = Width of the cuvette (= 1 cm), and M = Weight of the resin sample (=0.03g)

Measurement	A_{301}
1	0.683
2	0.629
3	0.644
4	0.672
Average	0.657

L = (10x0.657x10)/(7800x0.03) = 0.281 mmol/gram of Wang Resin

8. Catalyst immobilization onto the functionalized Wang resin (*R*,*R*)-1



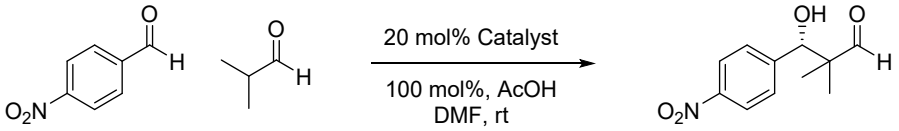
a) Preparation of (*RR*,*SS*)-**5**

The (*R*,*R*)-BOX functionalized resin (*R*,*R*)-**1** (1.00 g) was suspended in dry DCM (30 ml) and stirred at ambient temperature for 1 hour. To the solution was added (*S*,*S*)-**4** (134 mg, 0.30 mmol) in 2 ml DCM, and mixture was stirred for 5 min. The solution of $Zn(OAc)_2$ (55 mg, 0.30 mmol) in MeOH (2.0 ml) was added to the mixture, and stirred for 30 min at room temperature. The resin was filtered off, and washed three times with DCM (10 ml), and three times with diethyl ether (10 ml). The resin was dried at 40°C in vacuo for 72 hours (until weight no longer changes) to give (*RR*,*SS*)-**5** (1.145 g, 0.283 mmol/g). FTIR: C=N 1599.11 cm^{-1}

b) Preparation of (*RR*,*RR*)-**11**

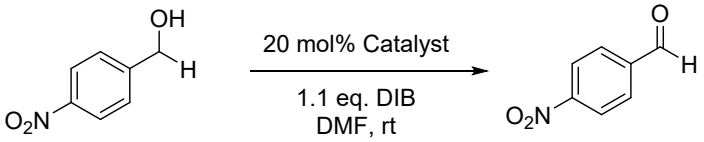
The (*R*,*R*)-BOX functionalized resin (*R*,*R*)-**1** (1.00 g) was suspended in dry DCM (30 ml) and stirred at ambient temperature for 1 hour. To the solution was added (*R*,*R*)-**10** (506 mg, 0.90 mmol) in 2 ml DCM, and mixture was stirred for 5 min. The solution of $Zn(OAc)_2$ (110 mg, 0.60 mmol) in MeOH (4.0 ml) was added to the mixture, and stirred for 30 min at room temperature. The resin was filtered off, and washed five times with DCM (10 ml), and three times with diethyl ether (10 ml). The resin was dried at 40°C in vacuo for 72 hours (until weight no longer changes) to give (*RR*,*RR*)-**11** (1.182 g, 0.289 mmol/g). FTIR: C=N 1601.36 cm^{-1}

9. Direct Aldol Reaction of Isobutyl aldehyde 6 and *p*-Nitrobenzaldehyde 7[4]



To the solution of isobutyraldehyde (91 μl, 1.0 mmol), *p*-Nitrobenzaldehyde (166 mg, 1.1 mmol), and acetic acid (57 μl, 1.0 mmol) was added catalyst (*RR*,*SS*)-**5** (712 mg, 0.2 mmol) in DMF (5 ml), and the mixture was gently stirred at room temperature for 5 h. The product was separated from catalytic resin through filtration, and the resin was washed four times with 10 ml of ethyl acetate. The filtrates were combined and washed three times with brine (10 ml), and concentrated under reduced pressure. The crude product was purified by liquid chromatography on silica gel, eluting with hexanes/ethyl acetate (Hexane/EtOAc = 60/40) afforded the 205 mg aldol product **8** ((*S*)-3-Hydroxy-2,2-dimethyl-3-(4-nitrophenyl)propanal, 91% yield) as clear crystal: mp 118-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (d, J = 1.0 Hz, 3H), 1.03 (d, J = 1.0 Hz, 3H), 2.94 (dd, J = 1.0, 3.4 Hz, 1H), 5.01 (d, J = 3.1 Hz, 1H), 7.48 (dtd, J = 0.9, 1.5, 8.1 Hz, 2H), 8.13 – 8.20 (m, 2H), 9.59 (d, J = 1.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 15.61, 19.84, 50.75, 76.17, 123.07, 128.39, 146.96, 147.56, 205.80. MS (ESI): *m/z* calculated for $C_{11}H_{13}NO_4$ $[M+H]^+$, 224.0917; found, 224.1005. HPLC (Chiralpak AD-H, i-PrOH/hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm): t_{major} =10.71 min, t_{minor} = 12.07 min, ee = 54%.

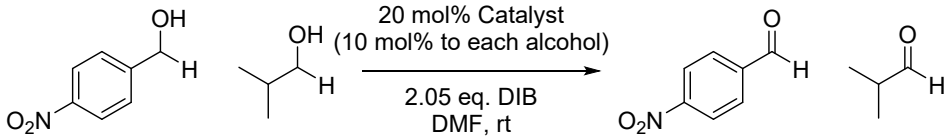
10. TEMPO Oxidation of *p*-Nitrobenzalcohol



The p-Nitrobenzyl alcohol **12** (153 mg, 1.0 mmol) was added TEMPO catalyst (*RR*,*RR*)-**11** (712 mg, 0.2 mmol) in DMF (5 ml) and stirred for 5 min at ambient temperature. The (diacetoxyiodo)benzene (328 mg, 1.02 mmol) was added to the mixture and reaction was gently stirred at room temperature for 5.5 hours. The product was separated from catalytic resin through filtration, and the resin was washed four times with 10 ml of ethyl acetate. The filtrates were combined and washed three times with brine (10 ml), and concentrated under reduced pressure. The crude product was purified by liquid chromatography on silica gel, eluting with hexanes/ethyl acetate (Hexane/EtOAc = 7/3 to 5/5) afforded the 220 mg p-Nitrobenzaldehyde **7** (98% yield) as pale yellow solid: mp 103-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, 2H), 8.38 (d, 2H), 10.15 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 76.73, 77.05, 77.37, 124.33, 130.50, 140.08, 151.16, 190.29.

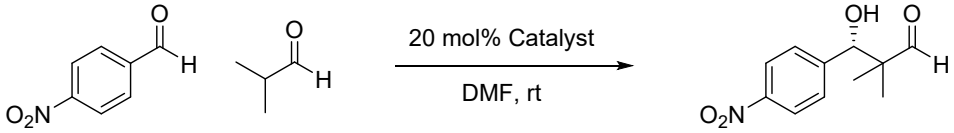
11. Sequential Oxidation/Aldol Reaction Using Catalyst Exchangeable Resin.

a) Oxidation Step



The *p*-Nitrobenzyl alcohol **12** (153 mg, 1.0 mmol) and isobutyl alcohol **13** (92 μl, 1.0 mmol) were added to the solution of TEMPO catalyst (*RR*,*RR*)-**12** (712 mg, 0.2 mmol) in DMF (5.0 ml). The oxidation reaction was initiated by adding (diacetoxyiodo)benzene (657 mg, 2.04 mmol) to the mixture and reaction was gently stirred at room temperature 7 hours. Upon completion of oxidation, monitored by GC, the product mixture was separated from catalytic resin through filtration, and the resin was washed three times with 3 ml of DMF. The organic layer was combined and saved for aldol step below.

b) Catalyst Exchange Step-aldol Step.



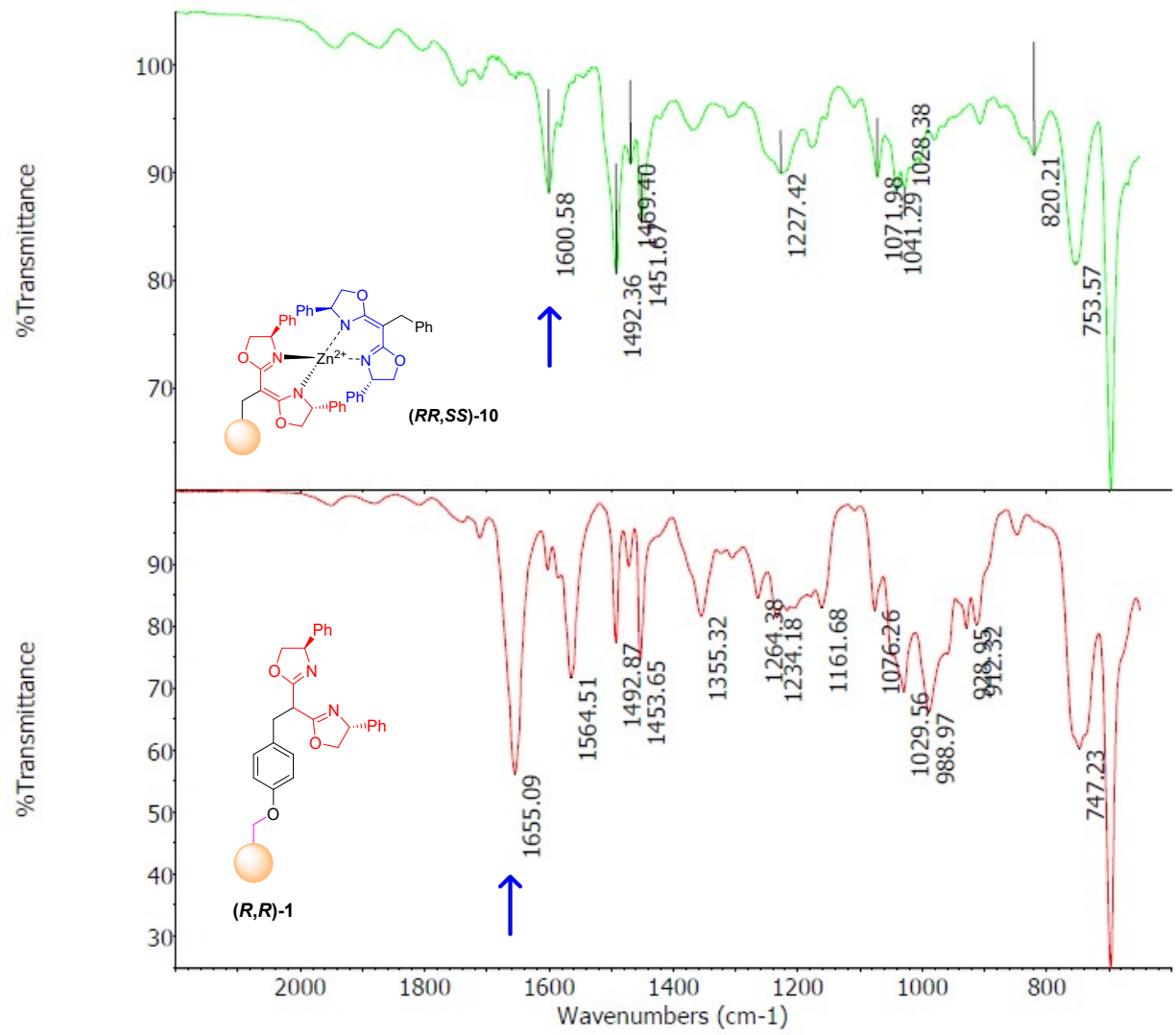
The washed resin (*RR*,*RR*)-**11** was resuspended in DMF (5 ml) and stirred for 15 min. To the mixture was added (*SS*,*SS*)-**4** (202 mg, 0.21 mmol), then the reaction was stirred for 15 min. The resulting pyrrolidine resin, (*RR*,*SS*)-**5**, was washed four times with 10 ml DMF. Washed resins were added to the solution of *p*-Nitrobenzaldehyde **7** and isobutyraldehyde **6** obtained from oxidation step above. Reaction was stirred gently at room temperature for 12 hours, and crude mixture containing aldol product was separated from resin through filtration. The product was separated from catalytic resin through filtration, and the resin was washed four times with 10 ml of ethyl acetate. The filtrates were combined and washed three times with brine (10 ml) and concentrated under reduced pressure. The crude product was purified by liquid chromatography on silica gel, eluting with hexanes/ethyl acetate (Hexane/EtOAc = 60/40) afforded the 182 mg aldol product **8** (((*S*)-3-Hydroxy-2,2-dimethyl-3-(4-nitrophenyl)propanal, 81% yield) as white solid: mp 118-120 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (d, *J* = 1.0 Hz, 3H), 1.03 (d, *J* = 1.0 Hz, 3H), 2.94 (dd, *J* = 1.0, 3.4 Hz, 1H), 5.01 (d, *J* = 3.1 Hz, 1H), 7.48 (dtd, *J* = 0.9, 1.5, 8.1 Hz, 2H), 8.13 – 8.20 (m, 2H), 9.59 (d, *J* = 1.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 15.61, 19.84, 50.75, 76.17, 123.07, 128.39, 146.96, 147.56, 205.80. MS (ESI): *m/z* calculated for $C_{11}H_{13}NO_4$ $[M+H]^+$, 224.0917; found, 224.1005. HPLC (Chiralpak AD-H, i-PrOH/hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm): t_{major} =10.72 min, t_{minor} = 12.08 min, ee = 54%.

Reference:

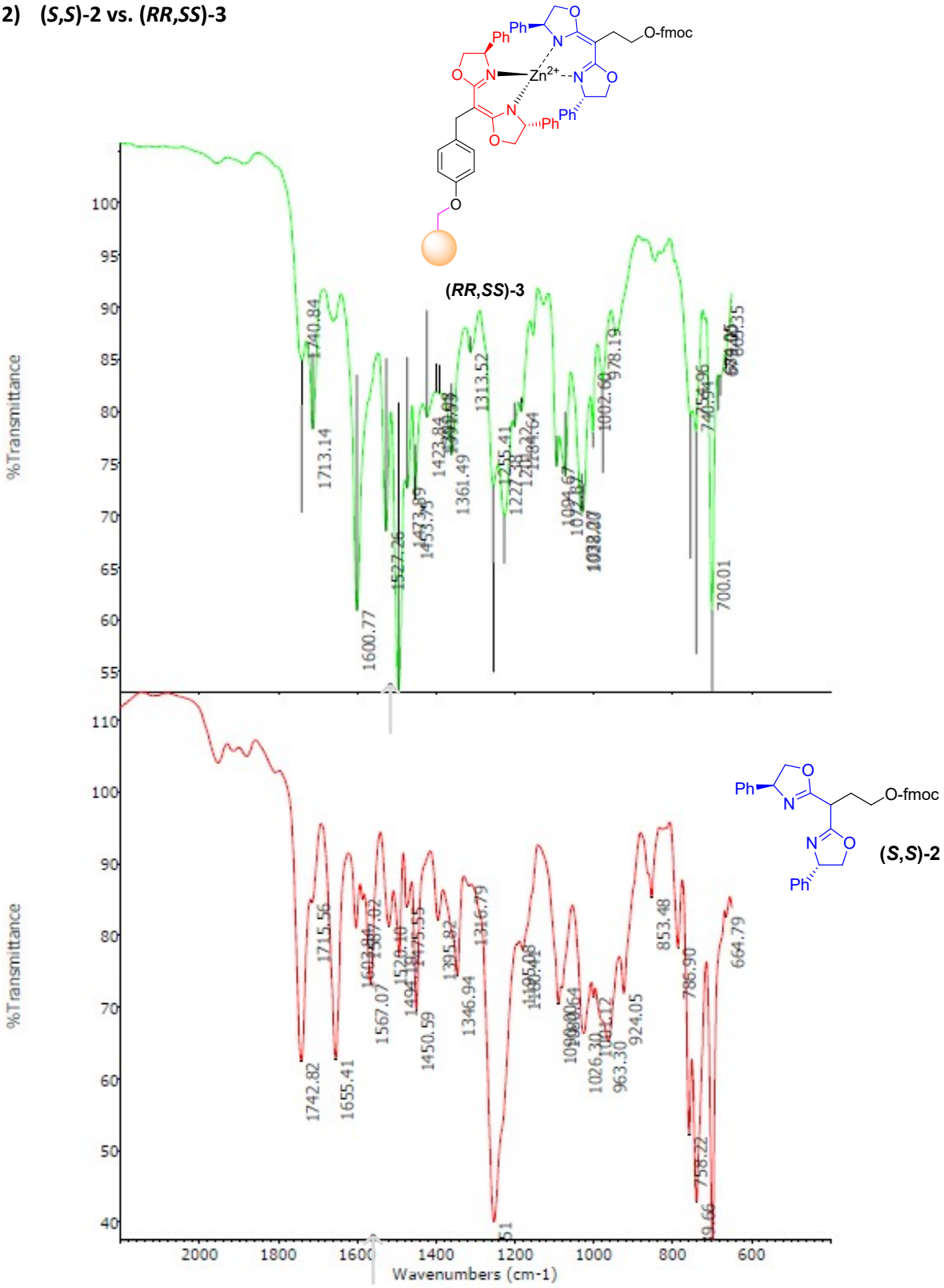
1. J. Zhou, A.M. Cole, E.M. Menuey, K.V. Kilway, S.A. Moteki, *Chem. Commun.* **2021**, *57*, 6404-6407.
2. J.-H. Guo, R.-W. Jiang, J.L. Andersen, M. Esmann, N.U. Fedosova, *FEBS Journal* **2018**, *285*, 2292-2305.
3. E.P. Carreiro, N.M.M. Moura, A.J. Burke, Anthony J. *Eur. J. Org. Chem*. **2012**, *3*, 518-528.
4. S. Luo, J. Li, H. Xu, L. Zhang, J-P.Cheng, Org. Lett. **2007**, *9*, 3675-3678.

Comparative FTIR Spectrum of Free vs. Zn(II) assembled functional Groups

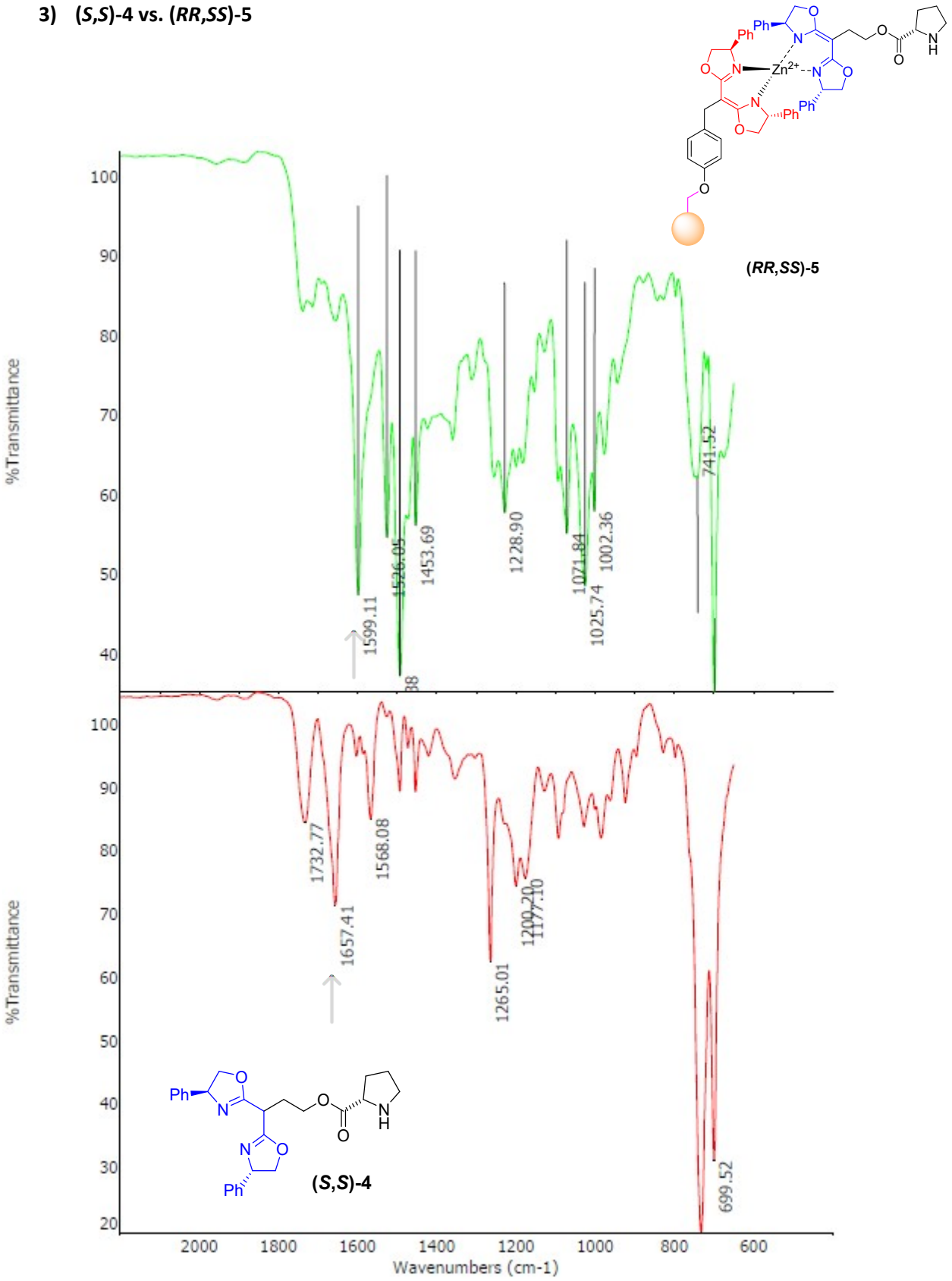
1) (*R*,*R*)-1 vs. (*RR*,*SS*)-10



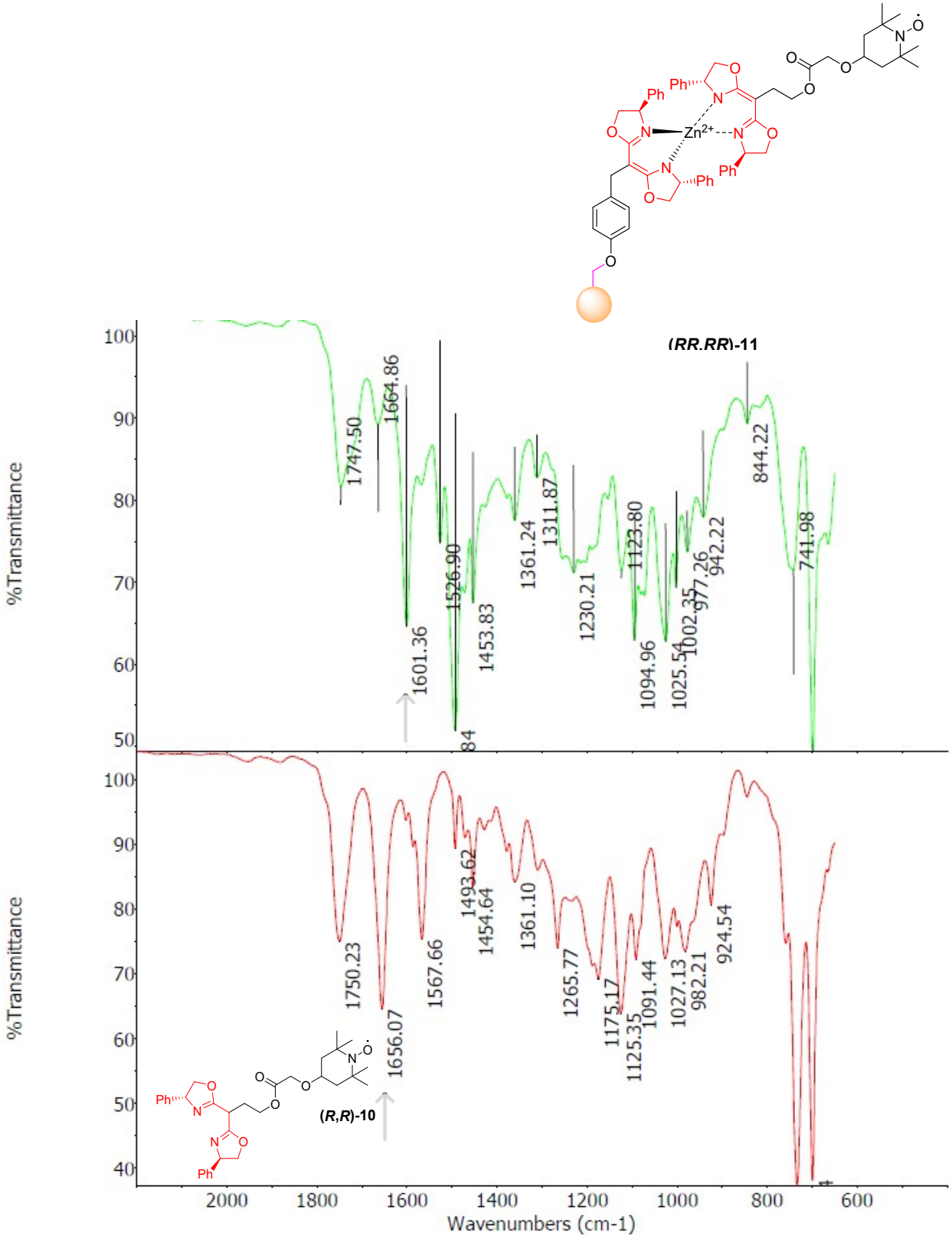
2) (*S,S*)-2 vs. (*RR,SS*)-3



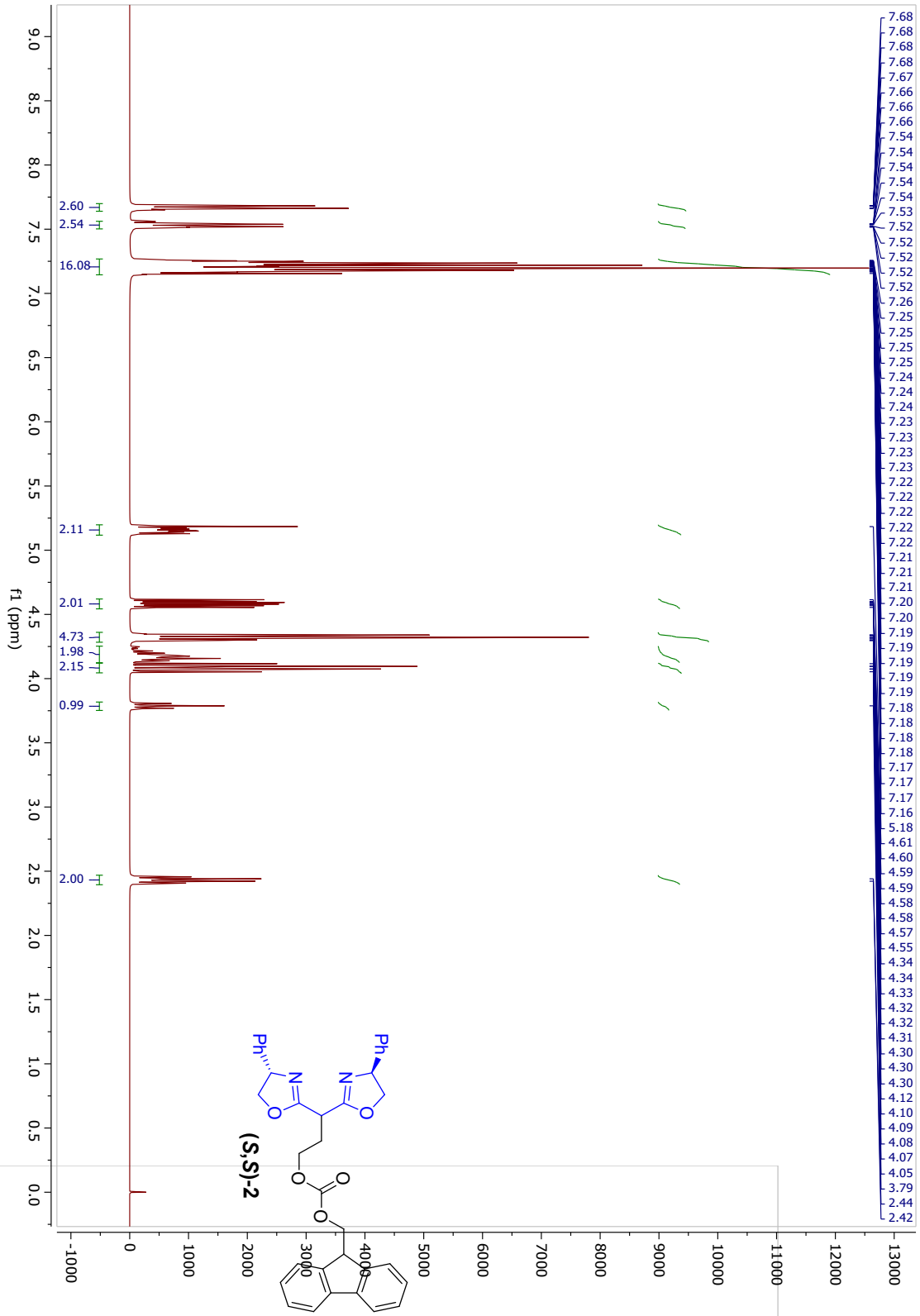
3) (*S,S*)-4 vs. (*RR,SS*)-5

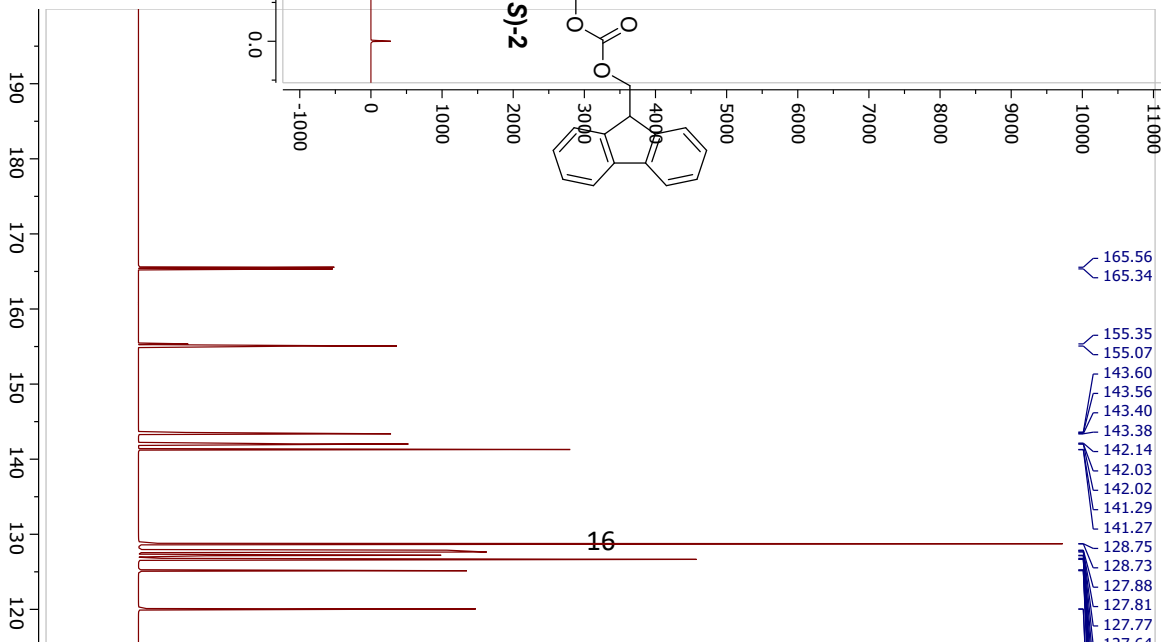


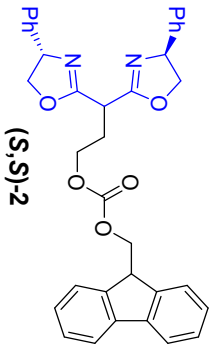
4) (*R*,*R*)-10 vs. (*RR*,*RR*)-11



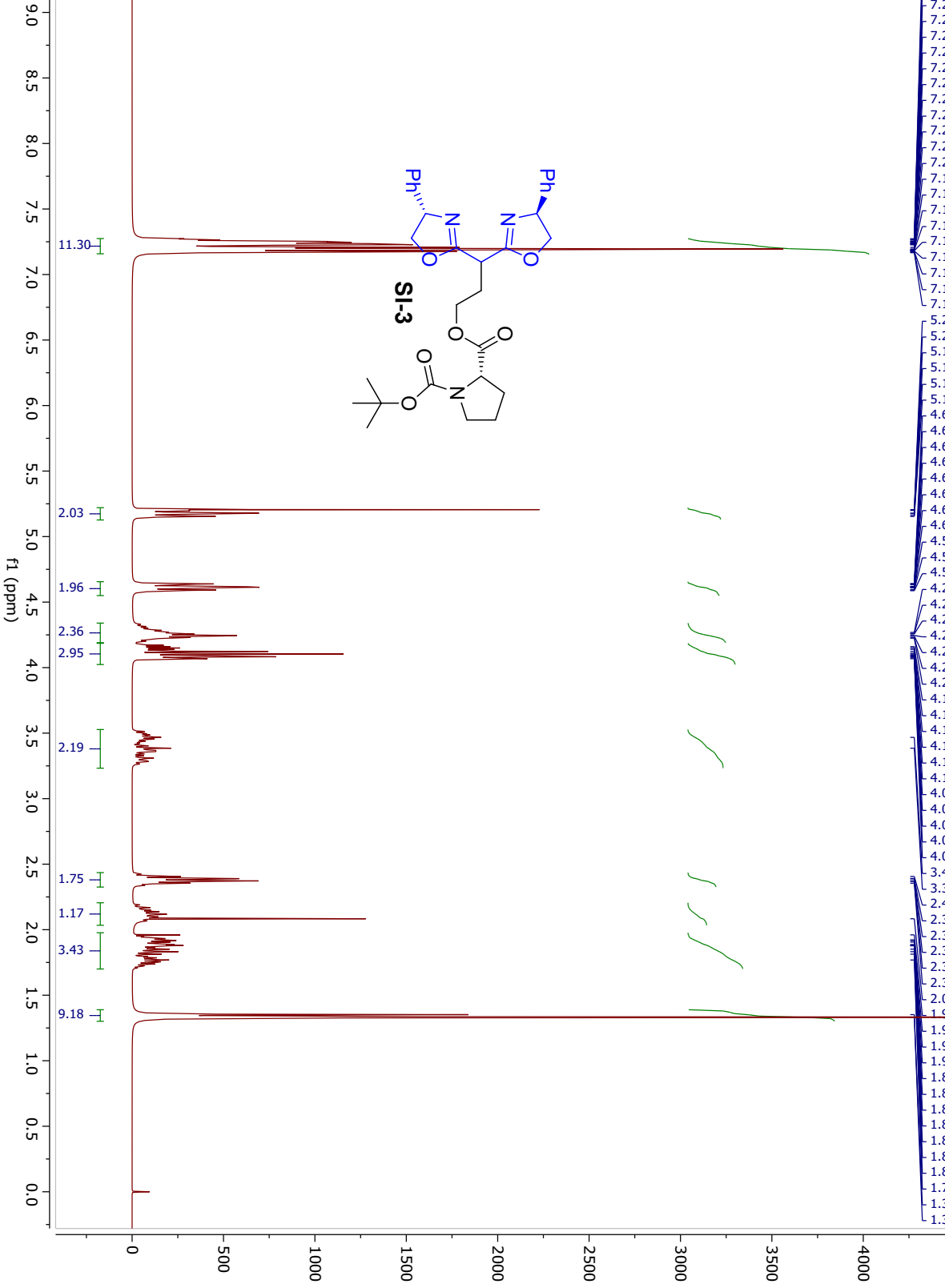
NMR Spectrum

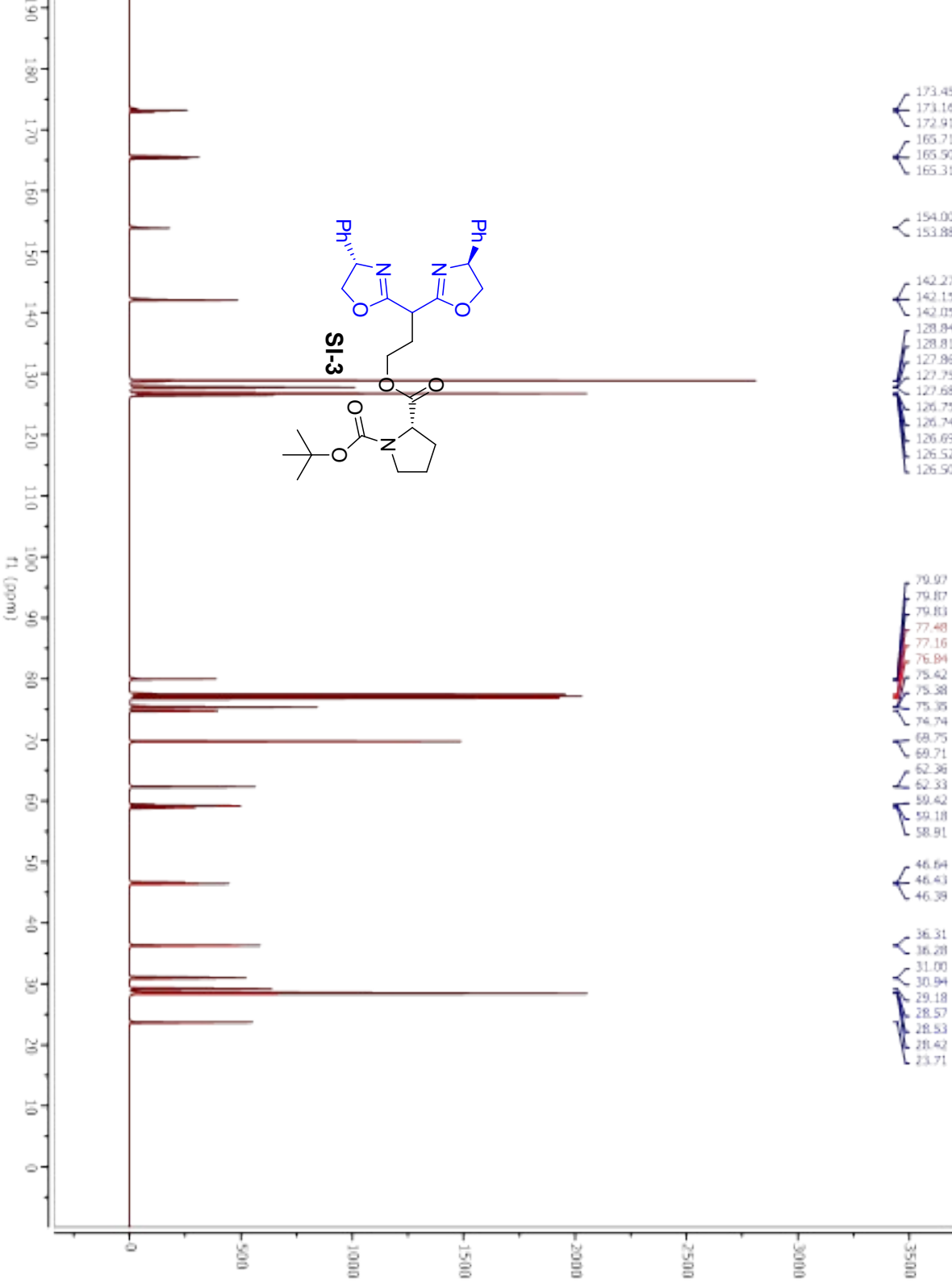


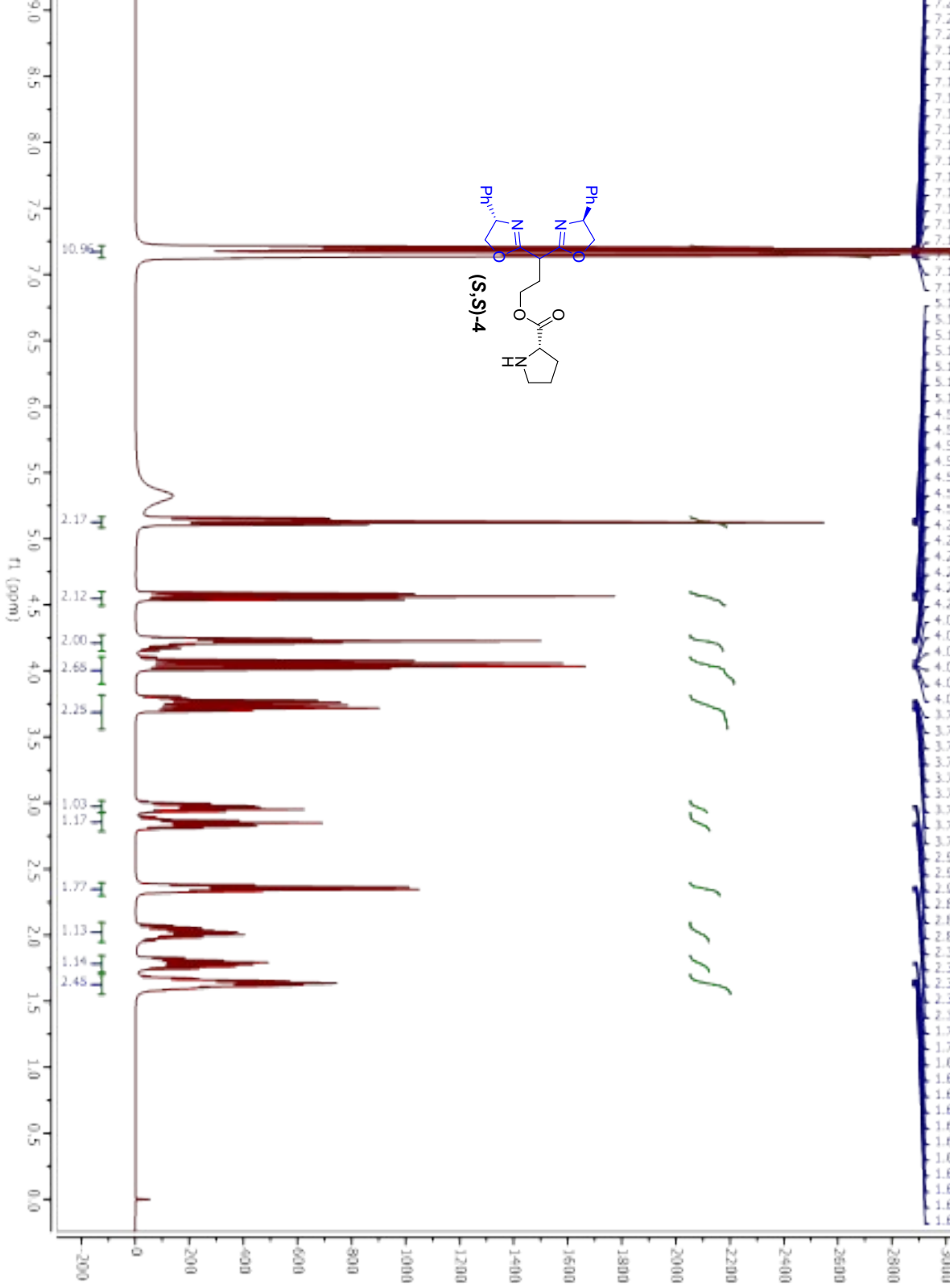


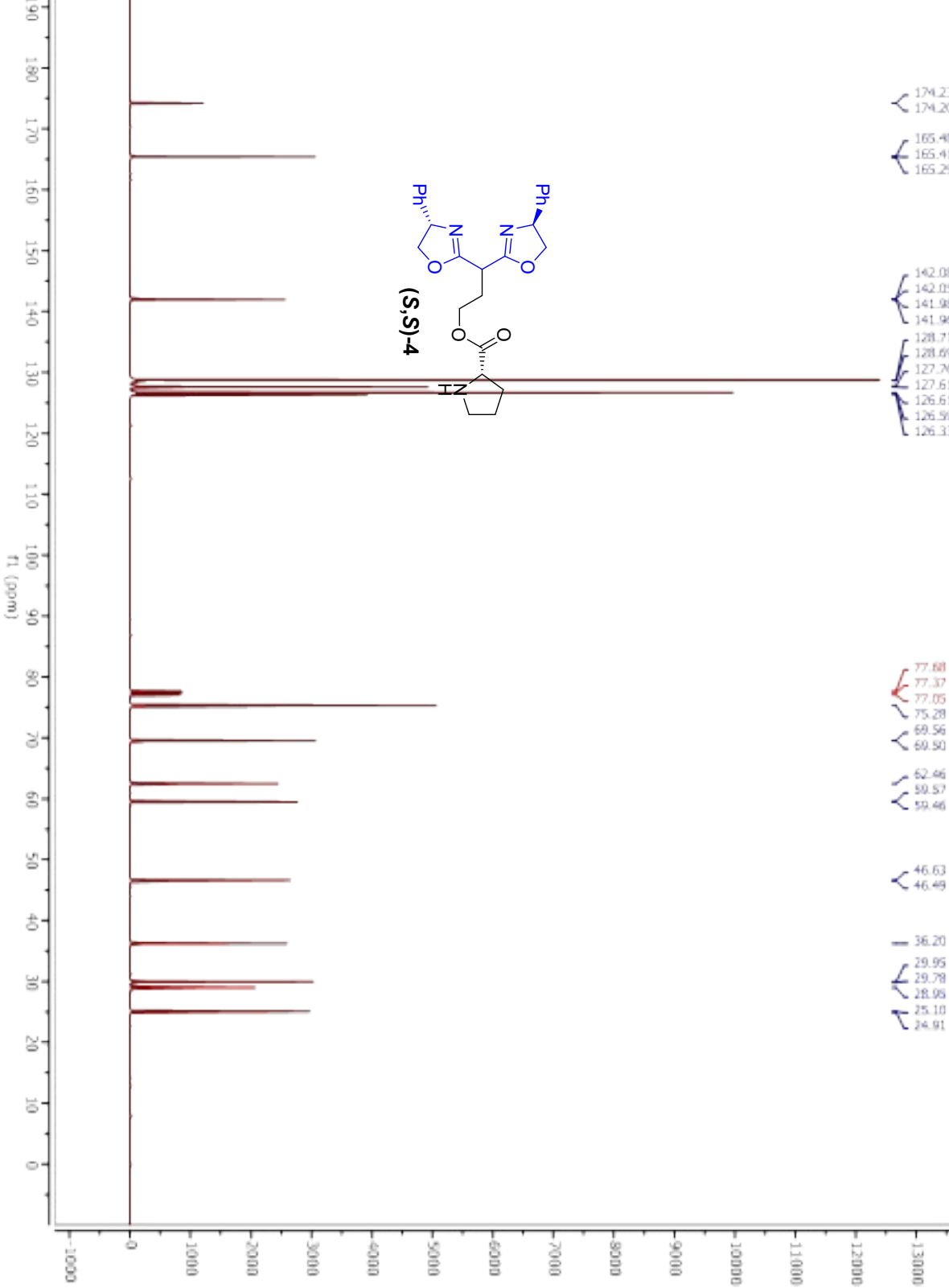


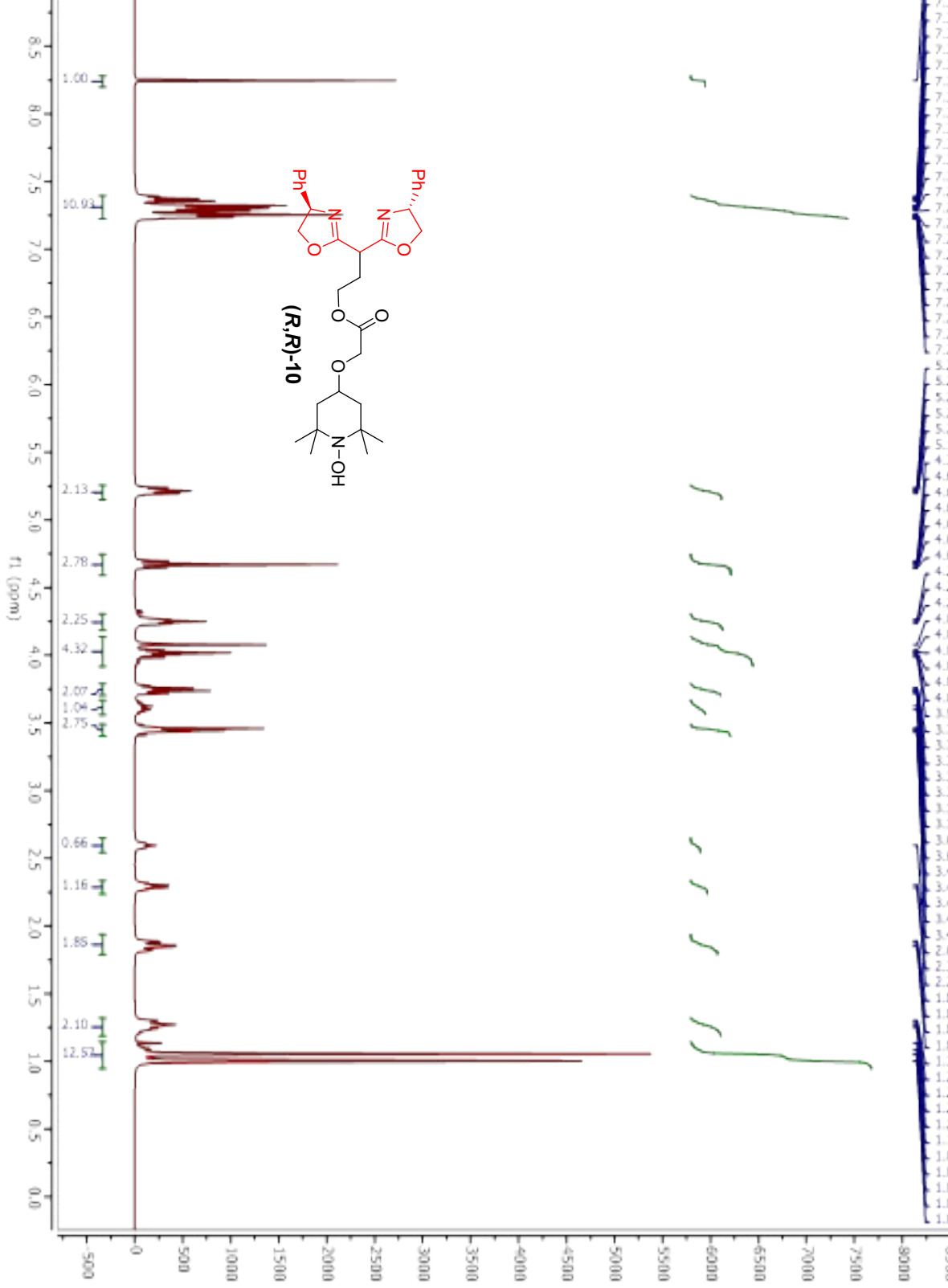
(S,S)-2

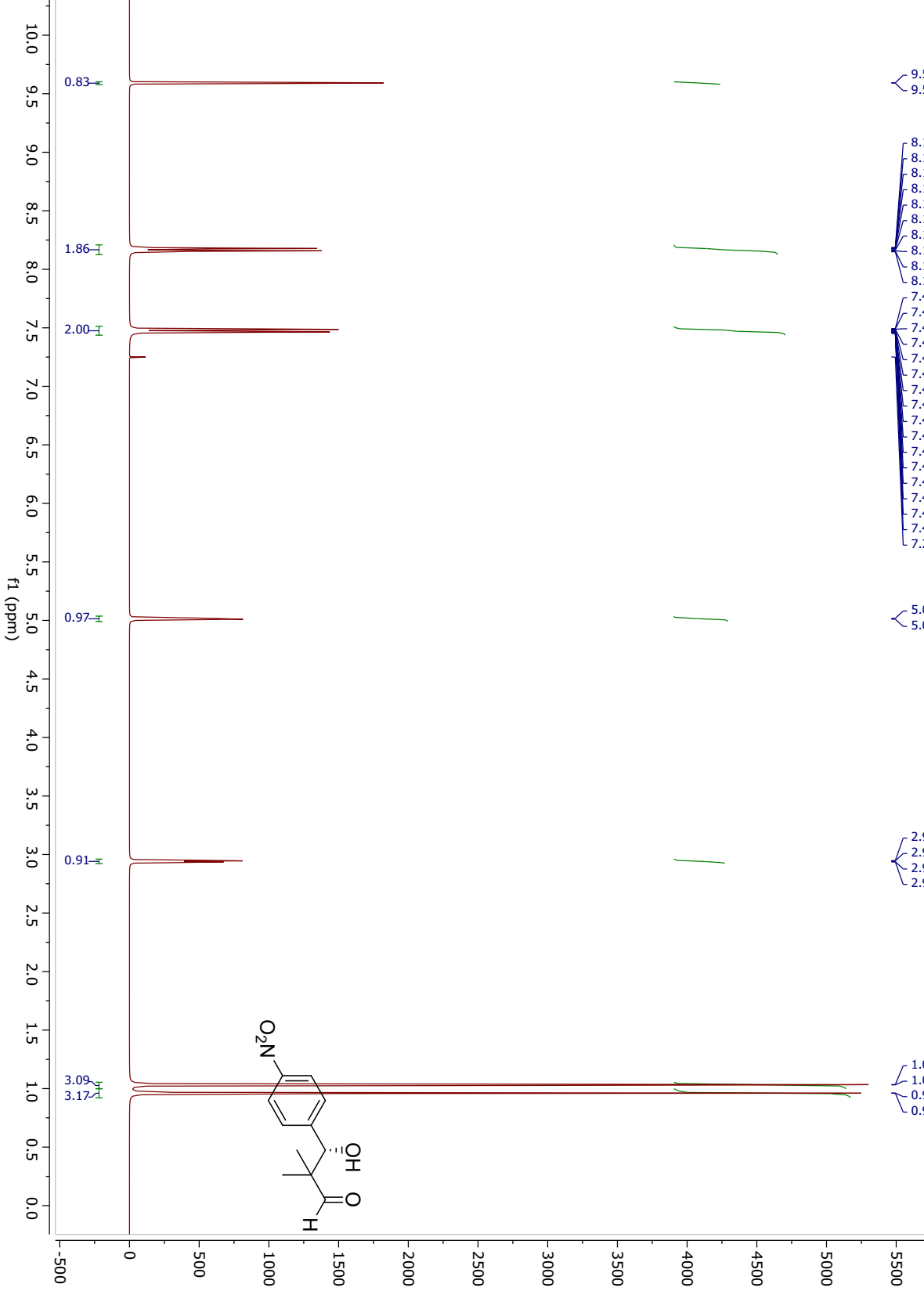

SI-3
11.30
2.03
1.96
2.36
2.95
2.19
1.75
1.17
3.43
9.18
f1 (ppm)


SI-3
Ph
Ph
N
N
O
O
O
O
O
O
N
f1 (ppm)


(S,S)-4
Ph
Ph
N
N
O
O
O
O
HN
10.96
2.17
2.12
2.00
2.68
2.25
1.03
1.17
1.77
1.13
1.14
2.45
f1 (ppm)


Ph
Ph
N
N
O
O
O
O
N
(S,S)-4
f1 (ppm)


(R,R)-10
Ph
Ph
N
O
O
N
O
O
O
N
OH
f1 (ppm)
1.00
10.93
2.13
2.78
2.25
4.32
2.07
1.04
2.75
0.66
1.16
1.85
2.10
12.57


f1 (ppm)
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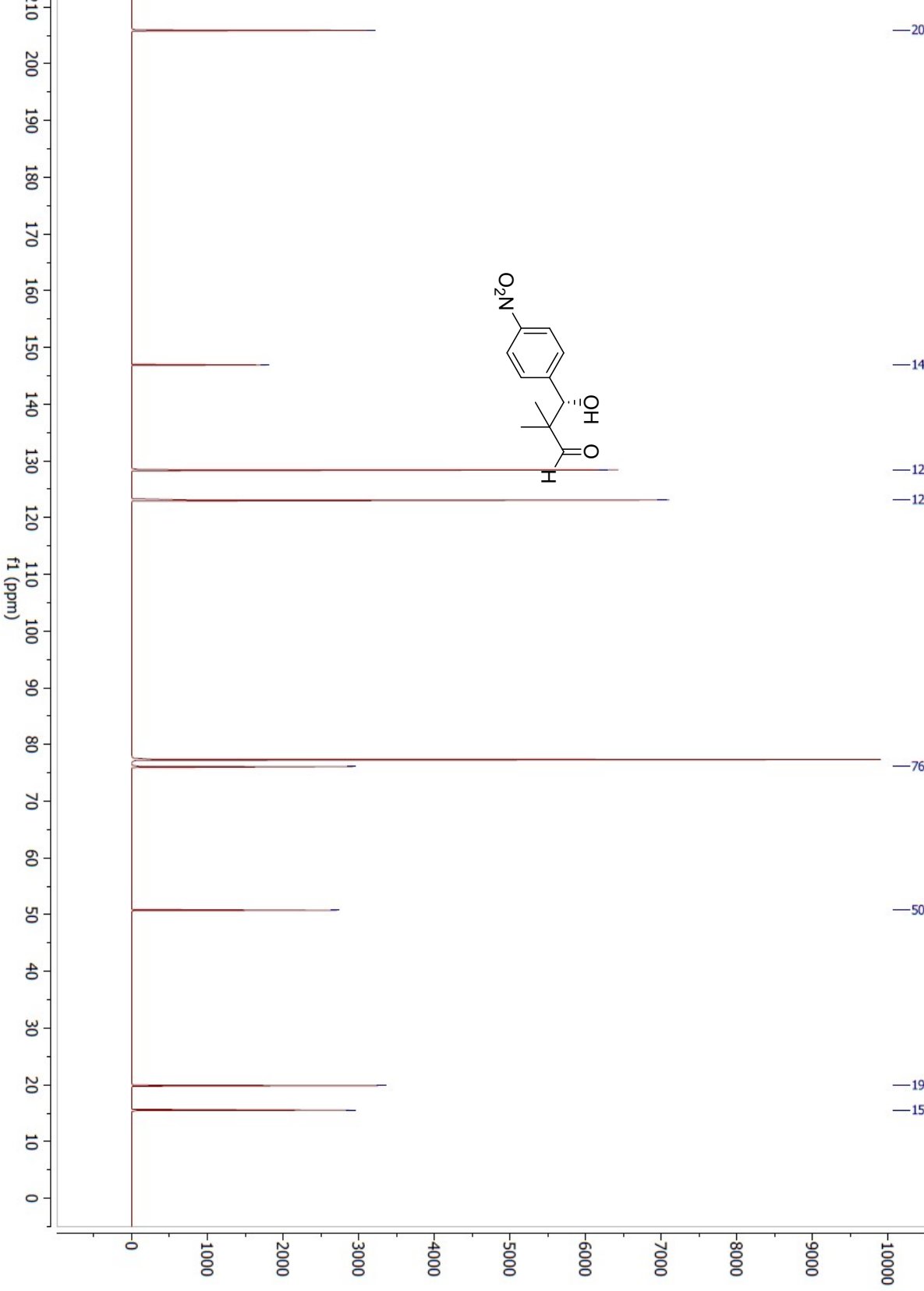
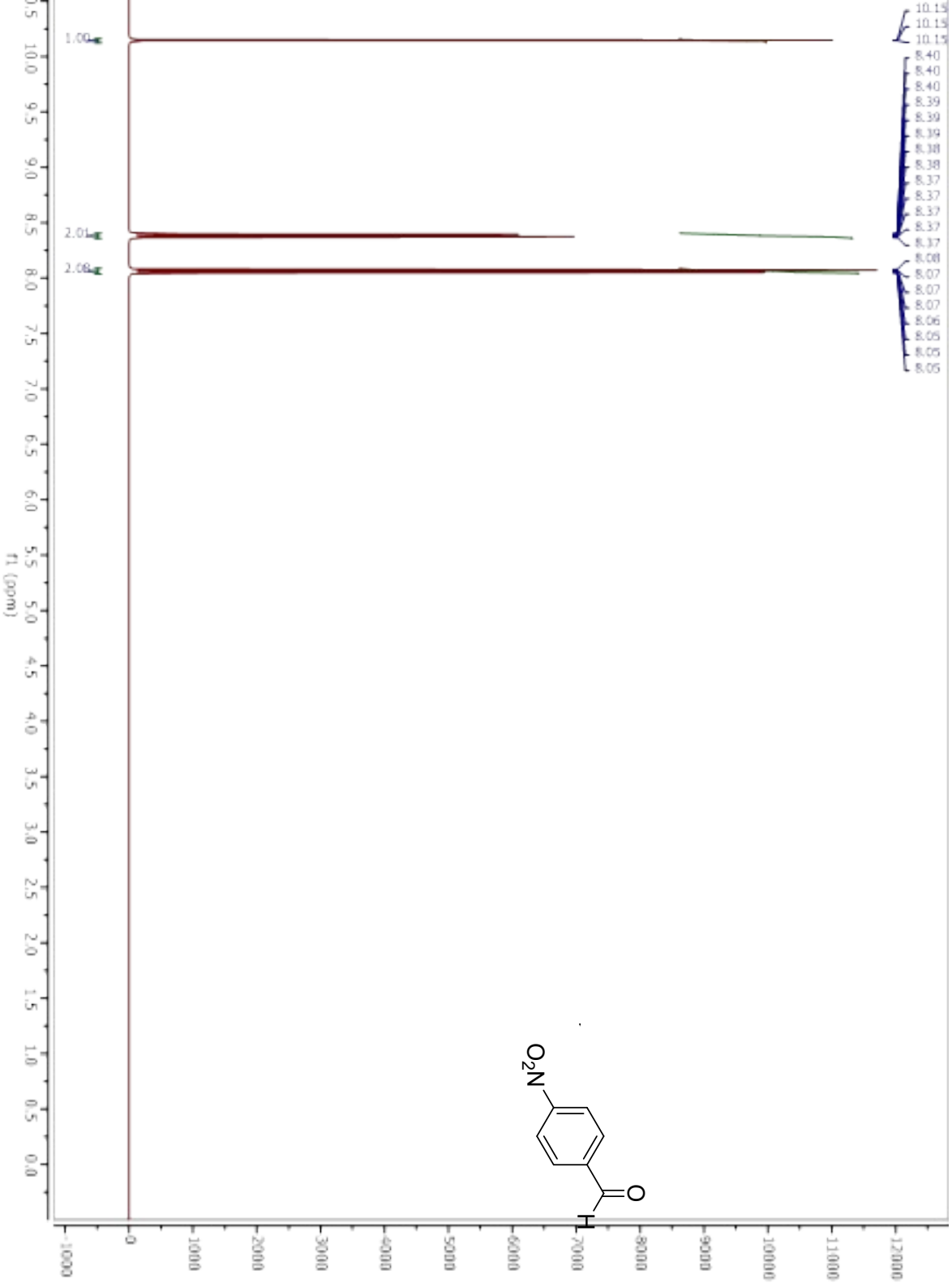
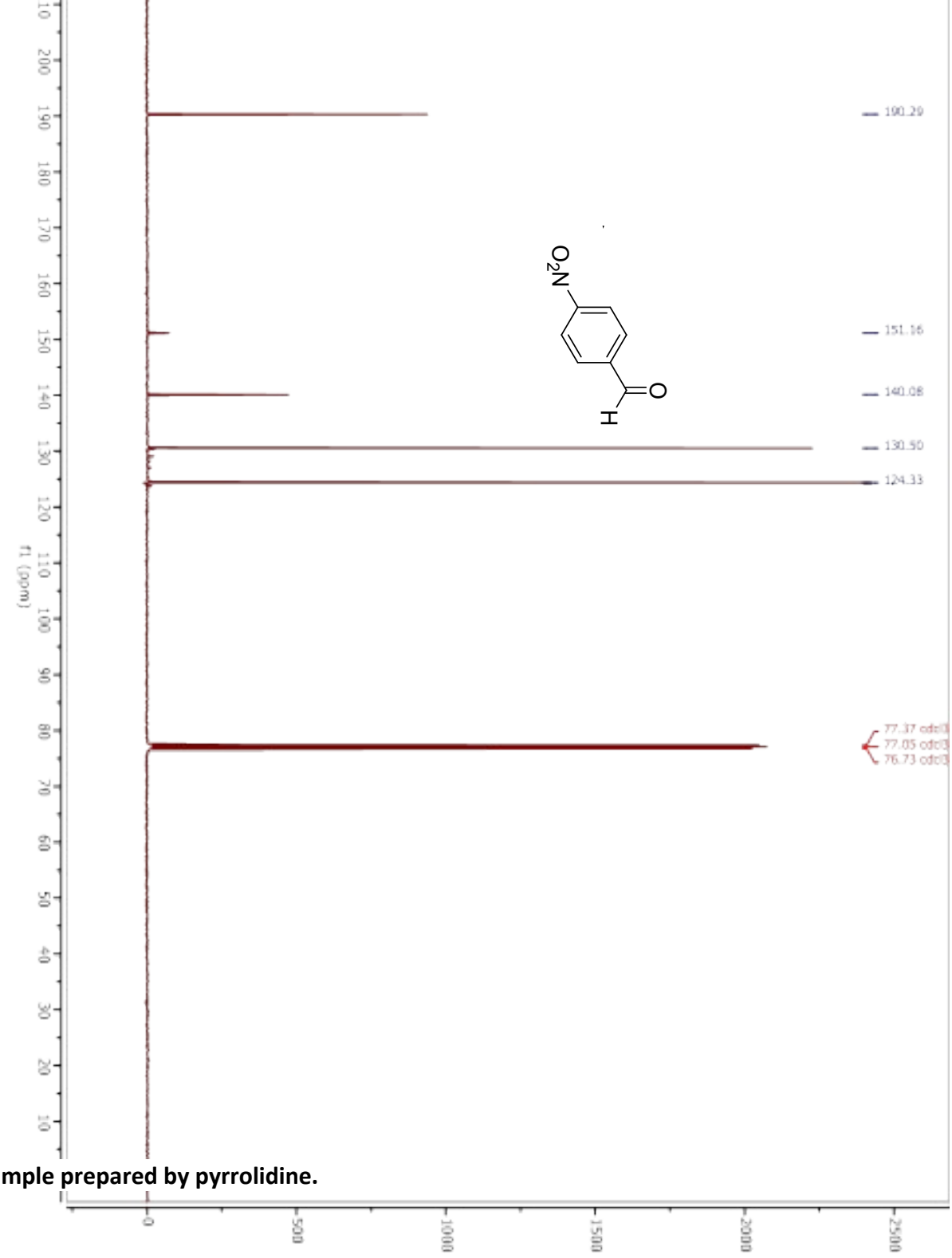
1.86
2.00
0.97
0.91
3.09
3.17
O2N
OH
O
H


f1 (ppm)
O2N
OH
O
H
20
14
12
12
76
50
19
15


10.15
10.15
10.15
8.40
8.40
8.40
8.39
8.39
8.39
8.38
8.38
8.37
8.37
8.37
8.37
8.37
8.08
8.07
8.07
8.07
8.06
8.05
8.05
8.05
1.00
2.01
2.08
f1 (ppm)
O2N
O
H



HPLC Spectrum

a) **Racemic sample prepared by pyrrolidine.**

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Area Percent Report

Signal 1: VWD1 A, Wavelength=210 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.726	MM	0.2206	5890.59961	445.11673	49.7040
2	12.081	MM	0.2536	5960.75049	391.73492	50.2960
Totals :				1.18514e4	836.85165	

b) Two-Step Oxidation/Aldol Reaction

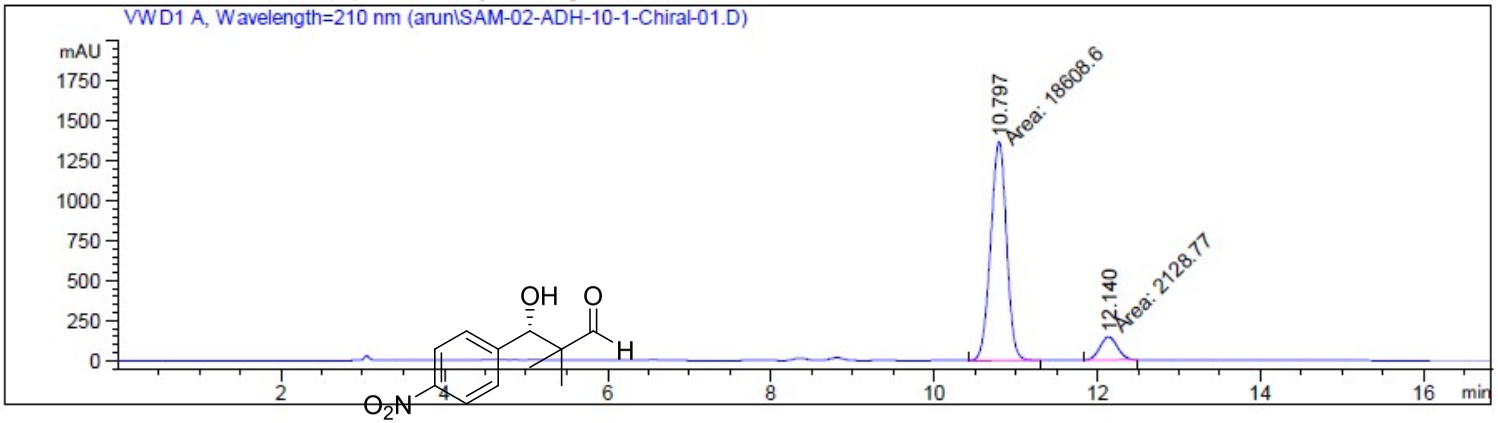
```
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=210 nm

Peak RetTime Type  Width     Area      Height    Area
  #  [min]       [min]  [mAU*s]      [mAU]      %
---|-------|----|-------|----------|----------|-------|
  1  10.724 BB   0.2080 9632.27246  720.49414  76.9174
  2  12.076 MM   0.2535 2890.60522  190.02315  23.0826

Totals :                1.25229e4   910.51729
```

c) Aldol product catalyzed by *L*-Proline



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Area Percent Report

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Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

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Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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2	12.140	MM	0.2464	2128.77417	143.98628	10.2654
Totals :				2.07374e4	1513.88057	