Supplementary Information for:

Efficient stereoselective synthesis of chiral 3,3′-dimethyl-(2,2′-bipyridine)-diol ligand and applications in Fe^{II}-catalysis

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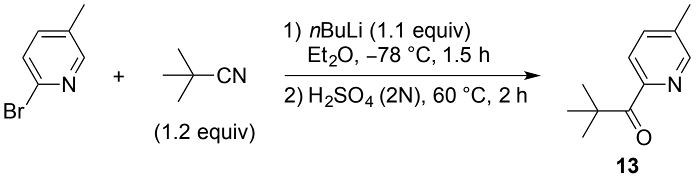
General Information

All reactions were performed in flame-dried glass and tubes under an atmosphere of argon. All solvents were commercially available, and they were distilled from CaH_2 (MeCN, CH_2Cl_2) or Na/benzophenone (THF, Et_2O, DME) prior to use. *N*,*N*-Dimethylformamide (DMF) was dried from P_2O_5 and distilled under reduced pressure (90 °C, 30 mmHg) prior to use. Triethylamine (Et_3N), 2,2,6,6-tetramethylpiperidine (TMPH), and diisopropylamine (DIPA) were distilled from CaH_2 prior to use. Powdered 4 Å MS was preactivated at 150 °C for 15 h under high vacuum prior to use. O_2 cylinder was purchased from Praxair Canada inc. and was passed through a plug of anhydrous Drierite™ prior to use. $Fe(ClO_4)_2{\cdot}6H_2O$ and $Fe(ClO_4)_3{\cdot}6H_2O$ were purchased from Alfa Aesar® (reagent grade purity). 2,2′-Bipyridinediol (*S*,*S*)-**1**,[1] Ru^{II} catalyst (*S*,*S*)-**14**,[2] (*Z*)-trimethyl((1-phenylprop-1-en-1-yl)oxy)silane **25** (*Z*/*E* = >99.5:0.5),[3] (*E*)-3-(but-2-enoyl)oxazolidin-2-one **28**,[4] and 3-acryloyloxazolidin-2-one **31**[5] were prepared from known procedures. Benzaldehyde **26** and cyclopentadiene **32**, which was obtained from dicyclopentadiene, were distilled prior to use. Distilled H_2O was degassed under argon atmosphere for 0.5 h prior to use. Other reagents were purchased directly from commercial suppliers (Alfa Aesar®, VWR® and Sigma-Aldrich®) and they were used without further purifications, unless otherwise noted. Thin-layer chromatography (TLC) was carried out on commercial silica gel plates (Silicycle F254, 250 mm) and compounds were visualized using UV light absorbance (254 nm) and/or aqueous $KMnO_4$. Flash column chromatography was performed on silica gel (Silicycle, 230–400 mesh) or Biotage® Isolera™ One automated chromatography system using a normal phase cartridge (Biotage®SNAP Ultra 25g packed with Biotage®HP-Sphere™ 25 µm). ^1H and $^{13}C\{H\}$ spectra were recorded on an Agilent Technologies DD2 500 MHz spectrometers in $CDCl_3$. For ^1H NMR, chemical shifts were reported in ppm downfield from tetramethylsilane (TMS) served as internal standard (δ = 0 ppm). Coupling constant are measured in hertz (Hz). For $^{13}C\{H\}$ NMR, $CDCl_3$ was used as internal standard (δ = 77.23 ppm) and spectra were obtained with complete proton decoupling. High-resolution mass spectra (HRMS) were recorded on an LC/MS-TOF (time of flight) Agilent 6210 mass spectrometer using electrospray ionization (ESI). IR spectra were recorded an ABB MB3000 FT-IR spectrometer with ABB MIRacle™ Diamond ATR accessory and they were reported in reciprocal centimeters (cm^{-1}). Melting points (mp) are uncorrected and they were recorded on a MEL-TEMP® capillary melting point apparatus. Enantiomeric ratios were determined on an Agilent 1100 Series HPLC system (hexane/*i*PrOH solvent mixture) using Daicel ChiralCel® OJ–H and OD–H and Daicel

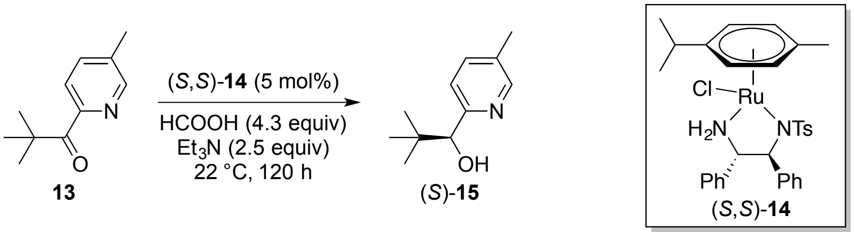
ChiralPak® AD–H columns. Optical rotations were measured on a Jasco DIP-360 digital polarimeter using a sodium lamp at ambient temperature.

Preparation of 2,2-dimethyl-1-(5-methylpyridin-2-yl)propan-1-one (13):[6]



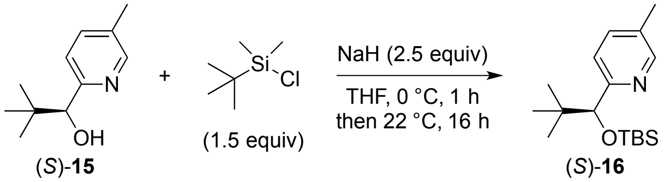
To a vacuum flame-dried 500 mL round bottom flask under argon atmosphere, 2-bromo-5-methylpyridine (6.88 g, 40.0 mmol, 1.0 equiv) was added to Et_2O (160 mL). The mixture was cooled to –78 °C before *n*-butyllithium (17.6 mL, 44.0 mmol, 1.1 equiv; 2.5 M in hexane) was added dropwise. The dark red solution was stirred at –78 °C for 0.5 h before pivalonitrile (5.3 ml, 48.0 mmol, 1.2 equiv) was added. The mixture was stirred at –78 °C for 1 h and was warmed up to 22 °C. An aqueous solution of H_2SO_4 (100 mL; 2 N) was added and the reaction was refluxed for 2 h at 60 °C. The mixture was cooled to 22 °C before the mixture was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with aqueous saturated $NaHCO_3$ (50 mL), brine (50 mL), and dried over $MgSO_4$. The drying agent was removed by filtration, and the filtrate was concentrated *in vacuo* (bath temperature 30 °C). The crude reaction product was purified by silica gel column chromatography using a gradient elution of hexane/EtOAc = 100:0–98:2 to give compound 13 as a yellowish oil (6.53 g, 36.8 mmol, 92% yield). R_f = 0.28 (hexane/EtOAc = 99:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.45 (m, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.58 (m, 1H), 2.39 (s, 3H), 1.46 (s, 9H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 206.5, 152.2, 148.1, 136.9, 136.0, 123.4, 44.1, 27.5, 18.6 ppm. IR (Diamond): 2955, 2928, 2868, 1684, 1481, 1296, 1198, 1028, 962, 849 cm^{-1}.

Preparation of (–)-(*S*)-2,2-dimethyl-1-(5-methylpyridin-2-yl)propan-1-ol (15):[6]



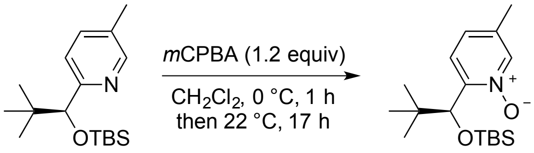
Ru^{II} catalyst (*S*,*S*)-14 (1.15 g, 1.80 mmol, 0.050 equiv) and 13 (6.38 g, 36.0 mmol, 1.0 equiv) were added to a vacuum flame-dried 100 mL flask under argon atmosphere. Freshly distilled Et_3N (12.6 mL, 90.0 mmol, 2.5 equiv) was added to the reaction, followed by a dropwise addition of formic acid (5.8 mL, 155 mmol, 4.3 equiv). The mixture was stirred at 22 °C for 120 h, and H_2O (50 mL) was added. The aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with aqueous saturated $NaHCO_3$ (50 mL), brine (50 mL), and dried over $MgSO_4$. The drying agent was removed by filtration, and the filtrate was concentrated *in vacuo* (bath temperature 40 °C). The crude reaction product was purified by silica gel column chromatography using a gradient elution of hexane/EtOAc = 95:5–80:20 to give compound (*S*)-15 as a colorless oil (5.29 g, 29.5 mmol, 82% yield, 86% *ee*). Recrystallization from hot hexane (16.0 mL, 70 °C) afforded the enantiomerically impoverished compound as white crystals (681 mg, 3.80 mmol, 11% yield, 38% *ee*). From the mother liquor, the enantiomerically enriched compound (*S*)-15 was obtained as a colorless oil (4.61 g, 25.7 mmol, 71% yield, 93% *ee*). R_f = 0.30 (hexane/EtOAc = 80:20). The *ee* was determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 95:5, flow rate = 0.5 mL/min, λ = 254 nm]: $t_R(S)$ = 19.3 min, $t_R(R)$ = 22.9 min; racemate: $t_R(S)$ = 18.4 min, $t_R(R)$ = 22.0 min. $[\alpha]_D^{22}$ = –16.6 (*c* = 1.00, CH_2Cl_2), $[\alpha]_D^{22}$ = –37.8 (*c* = 0.845, EtOH) (lit.[6] $[\alpha]_D^{24}$ = +32.4 (*c* = 1.03, EtOH), (*R*)-15). ^1H NMR (500 MHz, $CDCl_3$): δ_H 8.38 (m, 1H), 7.44 (m, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 4.33 (s, 1H), 4.26 (s, 1H), 2.34 (s, 3H), 0.91 (s, 9H) ppm. $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$): δ_C 157.1, 148.1, 136.1, 131.6, 122.2, 80.1, 36.2, 25.9, 18.1 ppm. IR (Diamond): 3402, 3209, 2953, 2868, 1605, 1485, 1364, 1238, 1016, 833 cm^{-1}. The absolute configuration of 15 was assigned as being *S*, by comparison of the optical rotation with a previous assignment.[7]

Preparation of (–)-(*S*)-2-(1-((*tert*-butyldimethylsilyl)oxy)-2,2-dimethylpropyl)-5-methylpyridine (16):[6]



Sodium hydride (2.57 g, 64.3 mmol, 2.5 equiv; 60% dispersion in mineral oil) was added to a vacuum flame-dried 250 mL round bottom flask under argon atmosphere. A solution of (*S*)-**15** (4.61 g, 25.7 mmol, 1.0 equiv, 93% *ee*) in THF (30 mL) was added dropwise to the flask at 0 °C. After the mixture had been stirred at 0 °C for 1 h, a solution of *tert*-butyldimethylsilyl chloride (5.81 g, 38.6 mmol, 1.5 equiv) in THF (20 mL) was added dropwise. The reaction was stirred at 0 °C for 5 min and brought up to 22 °C to stir an additional 16 h. An aqueous solution of saturated NH_4Cl (50 mL) was added to quench the reaction. The aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with brine (50 mL) and dried over $MgSO_4$. The drying agent was removed by filtration, and the filtrate was concentrated *in vacuo* (bath temperature 40 °C). The crude reaction product was purified by silica gel column chromatography using a gradient elution of hexane/EtOAc = 98:2–95:5 to give compound (*S*)-**16** as colorless oil (7.31 g, 24.9 mmol, 97% yield, 93% *ee*). R_f = 0.31 (hexane/EtOAc = 95:5). The *ee* was determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 99:1, flow rate = 0.5 mL/min, λ = 254 nm]: $t_R(R)$ = 8.7 min, $t_R(S)$ = 9.2 min; racemate: $t_R(R)$ = 8.6 min, $t_R(S)$ = 9.1 min. $[\alpha]_D^{22}$ = –66.1 (*c* = 1.07, CH_2Cl_2) (lit.[6] $[\alpha]_D^{27}$ = +67.2 (*c* = 1.07, CH_2Cl_2), (*R*)-**16**). ^1H NMR (500 MHz, $CDCl_3$): δ_H 8.30 (m, 1H), 7.45 (m, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 4.44 (s, 1H), 2.32 (s, 3H), 0.90 (s, 9H), 0.89 (s, 9H), 0.03 (s, 3H), –0.33 (s, 3H) ppm. $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$): δ_C 160.0, 147.7, 136.1, 131.0, 122.0, 83.4, 36.2, 26.0, 25.8, 18.1, 18.0 –4.8, –5.4 ppm. IR (Diamond): 2953, 2930, 2858, 1483, 1252, 1078, 1030, 872, 831, 773 cm^{-1}.

Preparation of (–)-(*S*)-2-(1-((*tert*-butyldimethylsilyl)oxy)-2,2-dimethylpropyl)-5-methylpyridine 1-oxide (17):[6]

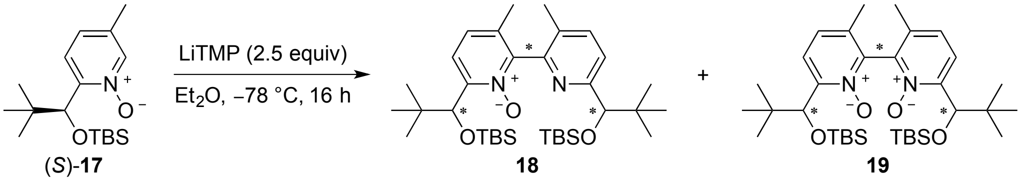


(*S*)-**16** (*S*)-**17**

To a 500 mL round bottom flask under argon atmosphere, *meta*-chloroperoxybenzoic acid (10.32 g, 29.9 mmol, 1.2 equiv; 50–55 wt%, cont. ca. 10% 3-chlorobenzoic acid, balance water) was added to CH_2Cl_2 (50 mL). A solution of (*S*)-**16** (7.31 g, 24.9 mmol, 1.0 equiv, 93% *ee*) in CH_2Cl_2 (40 mL) was added to the flask at 0 °C. The reaction was stirred at 0 °C for 1 h and brought up to 22 °C to stir for 17 h. An aqueous solution of KOH (100 mL; 40% m/v) was added, and the mixture was stirred at 22 °C for 1 h. The aqueous layer was extracted with CH_2Cl_2 (4 x 100 mL). The combined organic layers were washed with aqueous saturated $NaHCO_3$ (100 mL), brine (100 mL), and dried over $MgSO_4$. The drying agent was removed by filtration, and the filtrate was concentrated *in vacuo* (bath temperature 35 °C). The crude reaction product was purified by silica gel column chromatography using a gradient elution of CH_2Cl_2/MeOH = 100:0–95:5 to give compound (*S*)-**17** as a colorless oil (7.67 g, 24.8 mmol, 99% yield, 94% *ee*). R_f = 0.30 (CH_2Cl_2/MeOH = 98:2). The *ee* was determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 99:1, flow rate = 0.8 mL/min, λ = 254 nm]: $t_R(S)$ = 14.3 min, $t_R(R)$ = 16.1 min; racemate: $t_R(S)$ = 14.0 min, $t_R(R)$ =

15.6 min. $[\alpha]_D^{22}$ = –27.5 (c = 1.14, CH_2Cl_2) (lit.[6] $[\alpha]_D^{27}$ = +17.0 (c = 1.14, CH_2Cl_2), (*R*)-**17**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.05 (m, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.05 (m, 1H), 5.42 (s, 1H), 2.29 (s, 3H), 0.96 (s, 9H), 0.89 (s, 9H), 0.08 (s, 3H), –0.29 (s, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 150.9, 139.0, 134.2, 126.0, 125.6, 72.5, 37.7, 25.7, 25.4, 17.9, 17.8, –5.3, –5.4 ppm. IR (Diamond): 2953, 2930, 2858, 1472, 1383, 1252, 1070, 860, 839, 775 cm^{-1}.

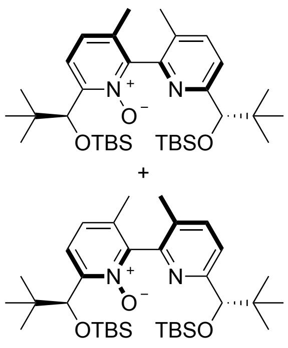
Preparation of the atropisomeric mixture of mono-*N*-oxides (18) and *N*,*N*′-dioxides (19):



LiTMP was prepared according to the following procedure: To a vacuum flame-dried 25 mL round bottom flask under argon atmosphere, freshly distilled TMPH (1.3 mL, 7.50 mmol, 2.5 equiv) was added to THF (7.5 mL). The mixture was cooled to 0 °C before *n*-butyllithium (3.0 mL, 7.50 mmol, 2.5 equiv; 2.5 M in hexane) was added dropwise. The reaction was stirred at 0 °C for 3 h.

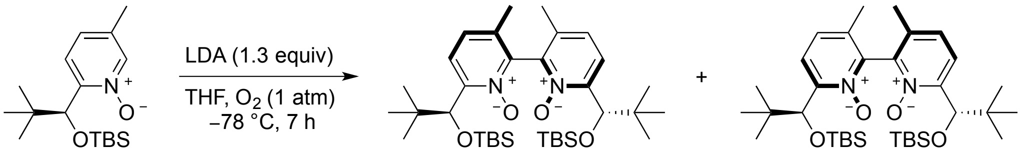
To the freshly prepared LiTMP mixture under argon atmosphere, a solution of (*S*)-**17** (928 mg, 3.0 mmol, 1.0 equiv, 90% *ee*) in Et_2O (6.0 mL) was added dropwise *via* cannula at –78 °C. The deep purple solution was stirred at –78 °C for 16 h, during which time the color of the reaction mixture gradually quenched to clear yellow. The reaction was then warmed up to 22 °C before H_2O (5 mL) was added. The reaction mixture was diluted with an aqueous ammonia solution (15 mL; 28–30 wt%) before the aqueous layer was extracted with CH_2Cl_2 (4 x 10 mL). The combined organic layers were washed with brine (20 mL) and dried over $MgSO_4$. The drying agent was removed by filtration, and the filtrate was concentrated *in vacuo* (bath temperature 35 °C). The crude reaction product was obtained as diastereoisomeric mixtures of mono-*N*-oxides **18** and *N*,*N'*-dioxides **19**. The crude product was purified by silica gel column chromatography to give compounds **18** as a white solid (487 mg, 0.810 mmol, 54% yield) and **19** as a yellowish solid (113 mg, 0.183 mmol, 12% yield). A fraction of (*RS**$_a$,*S*,*S*)-**18** was obtained pure and was characterized as a 71:29 atropisomeric mixture:

(*RS**$_a$)-(6,6'-bis((*S*)-1-((*tert*-butyldimethylsilyl)oxy)-2,2-dimethylpropyl)-3,3′-dimethyl-[2,2′-bipyridine] 1-oxide (18):



Product was obtained as a white solid (294 mg, 0.489 mmol, 33% yield). mp = 60–62 °C. R_f (major) = 0.52, R_f (minor) = 0.40 (hexane/EtOAc = 95:5). $[\alpha]_D^{22}$ = +79.8 (*c* = 1.00, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.58 (m, 0.29H, minor), 7.56 (m, 0.71H, major), 7.41 – 7.39 (m, 0.58H, minor), 7.39 – 7.37 (m, 1.42H, major), 7.11 (m, 0.29H, minor), 7.10 (m, 0.71H, major), 5.51 (s, 0.71H, major), 5.45 (s, 0.29H, minor), 4.50 (s, 0.71H, major), 4.48 (s, 0.29H, minor), 2.11 (s, 2.13H, major), 2.08 (s, 0.87H, minor), 2.04 (s, 2.13H, major), 2.02 (s, 0.87H, minor), 0.97 (s, 6.39H, major), 0.92 – 0.91 (m, 24.39H), 0.90 (s, 2.61H, minor), 0.86 (s, 2.61H, minor), 0.06 (s, 2.13H, major), 0.05 (s, 0.87H, minor), 0.04 (s, 0.87H, minor), 0.02 (s, 2.13H, major), –0.18 (s, 2.13H, major), –0.24 (s, 0.87H, minor), –0.27 (s, 0.87H, minor) –0.29 (s, 2.13H, major) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 160.8 (minor), 160.2 (major), 151.2 (minor), 151.0 (major), 149.7 (minor), 149.5 (major), 148.1 (major), 147.7 (minor), 137.2 (minor), 137.1 (major), 133.7 (major), 132.9 (minor), 132.2 (major), 131.0 (minor), 125.5 (major), 125.4 (minor), 124.7 (minor), 124.4 (major), 122.2 (major), 122.0 (minor), 83.2 (minor), 83.0 (major), 72.9 (minor), 72.7 (major), 37.7 (major), 37.6 (minor), 36.3, 26.2 (major), 25.89, 25.87 (minor), 25.83 (minor), 25.76 (minor), 25.6 (major), 25.4 (minor), 19.0 (major), 18.3 (minor), 18.1 (minor), 18.03 (major), 17.97 (major), 17.9 (minor), 17.5 (major), 17.1 (minor), –4.4 (major), –4.7 (minor), –4.9 (major), –5.18 (minor), –5.24, –5.3 (major), –5.4 (minor) ppm. IR (Diamond): 2953, 2930, 2856, 1462, 1360, 1250, 1074, 1030, 833, 775 cm^{-1}. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{34}H_{61}N_2O_3Si_2$ 601.4215; Found 601.4213.

Preparation of the atropisomeric mixture of *N*,*N*′-dioxides (19):



(*S*)-**17**

(*R*$_a$,*S*,*S*)-**19**

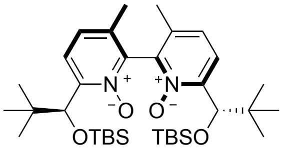
(*S*$_a$,*S*,*S*)-**19**

LDA was prepared according to the following procedure: To a vacuum flame-dried 250 mL round bottom flask under argon atmosphere, freshly distilled DIPA (3.7 mL, 26.0 mmol, 1.3 equiv) was added to THF (26 mL). The mixture was cooled to –78 °C before *n*-butyllithium (10.4 mL, 26.0

mmol, 1.3 equiv; 2.5 M in hexane) was added dropwise. The reaction was stirred at –78 °C for 20 min.

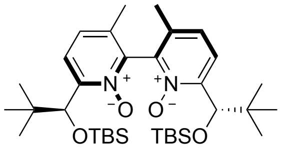
To the freshly prepared LDA mixture under argon atmosphere, a solution of (*S*)-**17** (6.19 g, 20.0 mmol, 1.0 equiv, 94% *ee*) in THF (30 mL) was added dropwise at –78 °C, whereas the color of the solution immediately turned to deep purple. Once the substrate was completely added, the inert atmosphere was quickly replaced by a positive flow of O_2 (balloon; 1 atm), and the mixture was stirred at –78 °C for 7 h, during which time the color of the reaction mixture gradually quenched to give a clear orange solution. Aqueous saturated $NaHCO_3$ (100 mL) was added to the reaction mixture at –78 °C before it was allowed to warm to 22 °C. The aqueous layer was extracted with Et_2O (3 x 100 mL). The combined organic layers were washed with aqueous saturated NH_4Cl (100 mL), brine (100 mL), and dried over $MgSO_4$. The drying agent was removed by filtration, and the filtrate was concentrated *in vacuo* (bath temperature 30 °C). The crude reaction product was obtained as a 75:19:3:3 diastereoisomeric mixture of (R_a,*S*,*S*)-**19**, (S_a,*S*,*S*)-**19**, (R_a,*S*,*R*)-**19**, and (S_a,*S*,*R*)-**19**, respectively, and was purified by silica gel column chromatography using a gradient elution of hexane/EtOAc = 98:2–95:5. In order of elution, compounds (R_a,*S*,*S*)-**19**, (RS^*_a,*S*,*R*)-**19**, and (S_a,*S*,*S*)-**19** were separated in fractions. Small amount of (R_a,*S*,*S*)-**19** and (S_a,*S*,*S*)-**19** were isolated within the fraction containing (RS^*_a,*S*,*R*)-**19** (638 mg, 1.03 mmol, 10% yield; (R_a,*S*,*S*)-**19**/(S_a,*S*,*S*)-**19**/(RS^*_a,*S*,*R*)-**19** = 47:18:34).

(+)-(R_a)-6,6'-bis((*S*)-1-((*tert*-butyldimethylsilyl)oxy)-2,2-dimethylpropyl)-3,3'-dimethyl-[2,2'-bipyridine] 1,1'-dioxide (19):[6]



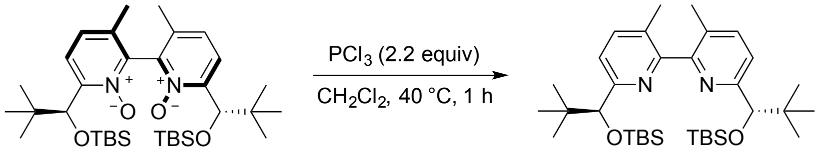
Product was obtained as a light yellow foam (2.75 g, 4.46 mmol, 45% yield). mp = 64–66 °C (lit.[6] mp = 67–69 °C). R_f = 0.63 (hexane/EtOAc = 95:5). $[\alpha]_D^{22}$ = +137.3 (*c* = 1.45, CH_2Cl_2) (lit.[6] $[\alpha]_D^{27}$ = –100.4 (*c* = 1.45, CH_2Cl_2), (*R*,*R*)-**19**). ^1H NMR (500 MHz, $CDCl_3$): δ_H 7.42 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 5.49 (s, 2H), 2.08 (s, 6H), 0.96 (s, 18H), 0.90 (s, 18H), 0.05 (s, 6H), –0.20 (s, 6H) ppm. $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$): δ_C 151.1, 142.2, 135.5, 125.2, 124.9, 72.3, 37.4, 25.8, 25.4, 17.9, 17.5, –5.2, –5.5 ppm. IR (Diamond): 2953, 2956, 1472, 1362, 1242, 1076, 1028, 891, 833, 775 cm^{-1}.

(–)-(S_a)-6,6'-bis((*S*)-1-((*tert*-butyldimethylsilyl)oxy)-2,2-dimethylpropyl)-3,3'-dimethyl-[2,2'-bipyridine] 1,1'-dioxide (19):



Product was obtained as a white solid (523 mg, 0.848 mmol, 8% yield). mp = 202–204 °C. R_f = 0.50 (hexane/EtOAc = 95:5). $[\alpha]_D^{22}$ = –12.5 (*c* = 1.45, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ_H 7.41 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 5.43 (s, 2H), 2.07 (s, 6H), 0.92 (s, 18H), 0.89 (s, 18H), 0.04 (s, 6H), –0.24 (s, 6H) ppm. $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$): δ_C 151.1, 142.2, 134.3, 125.1, 124.9, 72.9, 37.7, 25.8, 25.3, 17.9, 17.3, –5.3, –5.4 ppm. IR (Diamond): 2957, 2856, 1445, 1329, 1242, 1128, 1032, 866, 833, 775 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{34}H_{61}N_2O_4Si_2$ 617.4164; Found 617.4157.

Preparation of (–)-6,6'-bis((*S*)-1-((*tert*-butyldimethylsilyl)oxy)-2,2-dimethylpropyl)-3,3′-dimethyl-2,2′-bipyridine (24):

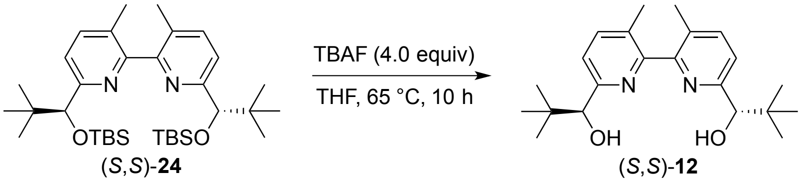


(R_a,*S*,*S*)-**19**

(*S*,*S*)-**24**

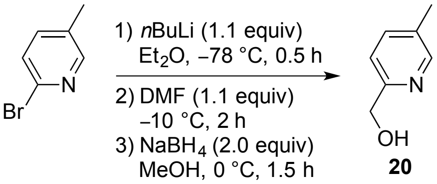
To a vacuum flame-dried 100 mL round bottom flask under argon atmosphere, (R_a,*S*,*S*)-**19** (3.09 g, 5.00 mmol, 1.0 equiv, 68% *de*$_a$) was added to CH_2Cl_2 (50 mL). Phosphorus trichloride (0.96 mL, 11.0 mmol, 2.2 equiv) was added dropwise at 0 °C, before the reaction was stirred at 40 °C for 1 h. The mixture was cooled to 22 °C and ice-cold H_2O (50 mL) and an aqueous solution of NaOH (50 mL; 10.0 M) were successively added. The aqueous layer was extracted with CH_2Cl_2 (3 x 60 mL). The combined organic layers were washed with brine (50 mL) and dried over $MgSO_4$. The drying agent was removed by filtration, and the filtrate was concentrated *in vacuo* (bath temperature 35 °C). The crude reaction product was purified by silica gel column chromatography using a gradient elution of hexane/EtOAc = 100:0–98:2 to give compound (*S*,*S*)-**24** as a colorless foam (2.89 g, 4.94 mmol, 99% yield). mp = 44–46 °C. R_f = 0.29 (hexane/EtOAc = 98:2). $[\alpha]_D^{22}$ = –23.5 (*c* = 1.00, CH_2Cl_2). ^1H NMR (500 MHz, $CDCl_3$): δ_H 7.56 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 4.50 (s, 2H), 2.07 (s, 6H), 0.92 (s, 18H), 0.89 (s, 18H), 0.04 (s, 6H), –0.28 (s, 6H) ppm. $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$): δ_C 160.0, 155.8, 137.8, 129.2, 121.6, 83.1, 36.3, 25.94, 25.90, 18.3, 18.1, –4.6, –5.2 ppm. IR (Diamond): 2955, 2930, 2858, 1585, 1472, 1360, 1252, 1078, 835, 773 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{34}H_{61}N_2O_2Si_2$ 585.4266; Found 585.4255.

Preparation of (–)-(1*S*,1'*S*)-1,1'-(3,3′-dimethyl-[2,2′-bipyridine]-6,6'-diyl)bis(2,2-dimethylpropan-1-ol) (12):[6]



To a vacuum flame-dried 50 mL round bottom flask under argon atmosphere, (*S*,*S*)-**24** (1.39 g, 2.38 mmol, 1.0 equiv) was added to THF (24 mL). Tetra-*n*-butylammonium fluoride (9.5 mL, 9.52 mmol, 4.0 equiv; 1.0 M in THF) was added dropwise at 22 °C, before the reaction was stirred at 65 °C for 10 h. The mixture was cooled to 22 °C and H_2O (20 mL) was added. The aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine (20 mL) and dried over $MgSO_4$. The drying agent was removed by filtration, and the filtrate was concentrated *in vacuo* (bath temperature 40 °C). The crude reaction product was purified by silica gel column chromatography using a gradient elution of hexane/EtOAc = 90:10–50:50 to give compound (*S*,*S*)-**12** as a white solid (824 mg, 2.31 mmol, 97% yield, 97% *de*, >99.5% *ee*). Recrystallization from hot hexane (17 mL, 70 °C) afforded the diastereo- and enantiomerically enriched compound as white crystals (648 mg, 1.82 mmol, 76% yield, 99% *de*, >99.5% *ee*). mp = 116–118 °C (lit.[6] mp = 107–110 °C). R_f = 0.27 (hexane/EtOAc = 70:30). *ee* and *de* were determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 95:5, flow rate = 0.8 mL/min, λ = 254 nm]: t_R(*S*,*S*) = 20.3 min, t_R(*R*,*R*) = 28.3 min, t_R(*meso*) = 30.0 min; racemate: t_R(*S*,*S*) = 20.7 min, t_R(*R*,*R*) = 28.7 min, t_R(*meso*) = 30.0 min. $[\alpha]_D^{22}$ = –13.9 (*c* = 1.86, EtOH) (lit.[6] $[\alpha]_D^{24}$ = +12.0 (*c* = 1.86, CH_2Cl_2), (*R*,*R*)-**12**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.60 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 4.42 – 4.36 (m, 4H), 2.18 (s, 6H), 0.94 (s, 18H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 156.4, 155.3, 138.2, 130.6, 122.0, 80.0, 36.3, 26.0, 18.6 ppm. IR (Diamond): 3454, 2962, 2864, 1583, 1452, 1394, 1364, 1068, 1014, 835 cm^{-1}.

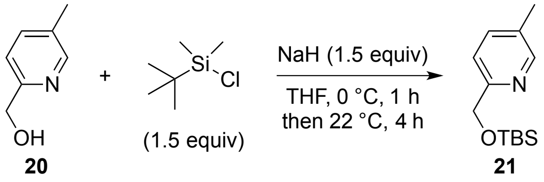
Preparation of (5-methylpyridin-2-yl)methanol (20):[8]



20

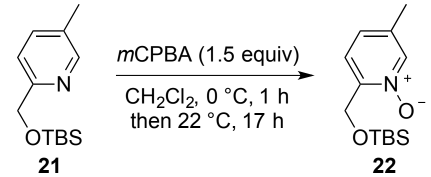
To a vacuum flame-dried 500 mL round bottom flask under argon atmosphere, 2-bromo-5-methylpyridine (5.16 g, 30.0 mmol, 1.0 equiv) was added to Et_2O (150 mL). The mixture was then cooled to –78 °C before *n*-butyllithium (13.2 mL, 33.0 mmol, 1.1 equiv; 2.5 M in hexane) was added dropwise and the reaction was stirred at –78 °C for 0.5 h. *N*,*N*-dimethylformamide (2.5 mL, 33.0 mmol, 1.1 equiv) was added dropwise to the dark red solution at –78 °C. The mixture was warmed up to –10 °C and stirred for 2 h. MeOH (75 mL) and sodium borohydride (2.27 g, 60.0 mmol, 2.0 equiv) were subsequently added and the resulting yellow solution was stirred for 1.5 h at 0 °C. An aqueous solution of saturated NH_4Cl (30 mL) was added dropwise at 0 °C to quench the reaction. The aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were washed with brine (50 mL) and dried over $MgSO_4$. The drying agent was removed by filtration, and the filtrate was concentrated *in vacuo* (bath temperature 35 °C). The crude product was purified by silica gel column chromatography using a gradient elution of hexane/EtOAc = 80:20–20:80 to give compound **20** as a yellow oil (2.77 g, 22.5 mmol, 75% yield). $R_f = 0.25$ (EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.38 (m, 1H), 7.49 (dd, *J* = 7.9, 2.2 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 4.73 (s, 2H), 3.93 (s, 1H) 2.34 (s, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 157.0, 148.7, 137.4, 131.7, 120.4, 64.2, 18.1 ppm. IR (Diamond): 3215, 2924, 2864, 1574, 1489, 1381, 1065, 1036, 824, 652 cm^{-1}.

Preparation of 2-(((*tert*-butyldimethylsilyl)oxy)methyl)-5-methylpyridine (21):



*Following the procedure described for the preparation of (S)-**16***: i) **20** (2.77 g, 22.5 mmol, 1.0 equiv), sodium hydride (1.35 g, 33.8 mmol, 1.5 equiv; 60% dispersion in mineral oil), THF (80 mL), 0 °C, 1 h; ii) *tert*-butyldimethylsilyl chloride (5.09 g, 33.8 mmol, 1.5 equiv) in THF (60 mL), 0 °C, 5 min; then 22 °C, 4 h. The crude product was purified by silica gel column chromatography using a gradient elution of hexane/EtOAc = 98:2–90:10 to give compound **21** as a colorless oil (5.12 g, 21.6 mmol, 96% yield). R_f = 0.27 (hexane/EtOAc = 90:10). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.34 (m, 1H), 7.51 (dd, J = 8.0, 2.2 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 4.81 (s, 2H), 2.33 (s, 3H), 0.96 (s, 9H), 0.12 (s, 6H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 158.3, 148.9, 137.1, 131.0, 119.6, 66.0, 25.9, 18.3, 18.1, –5.4 ppm. IR (Diamond): 2955, 2928, 2856, 1574, 1472, 1252, 1101, 835, 775, 667 cm^{-1}. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{13}H_{24}NOSi$ 238.1622; Found 238.1627.

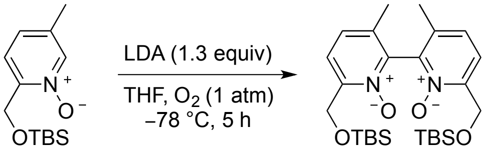
Preparation of 2-(((*tert*-butyldimethylsilyl)oxy)methyl)-5-methylpyridine 1-oxide (22):



21 **22**

*Following the procedure described for the preparation of (S)-**17***: **21** (5.12 g, 21.6 mmol, 1.0 equiv), *meta*-chloroperoxybenzoic acid (11.18 g, 32.4 mmol, 1.5 equiv; 50–55 wt%, cont. ca. 10% 3-chlorobenzoic acid, balance water), CH_2Cl_2 (86 mL), 0 °C, 1 h; then 22 °C, 17h. The crude product was purified by silica gel column chromatography using a gradient elution of CH_2Cl_2/MeOH = 100:0–98:2 to give compound **22** as a white solid (5.06 g, 20.0 mmol, 93% yield). mp = 42–44 °C. R_f = 0.27 (CH_2Cl_2/MeOH = 98:2). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.07 (m, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.15 (m, 1H), 4.91 (s, 2H), 2.31 (s, 3H), 0.97 (s, 9H), 0.15 (s, 6H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 148.9, 138.7, 133.9, 127.4, 122.2, 60.0, 25.9, 18.2, 17.9, –5.5 ppm. IR (Diamond): 2955, 2928, 2856, 1381, 1257, 1124, 1094, 835, 725, 669 cm^{-1}. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{13}H_{24}NO_2Si$ 254.1571; Found 254.1573.

Preparation of 6,6'-bis(((*tert*-butyldimethylsilyl)oxy)methyl)-3,3′-dimethyl-[2,2′-bipyridine] 1,1'-dioxide (23):

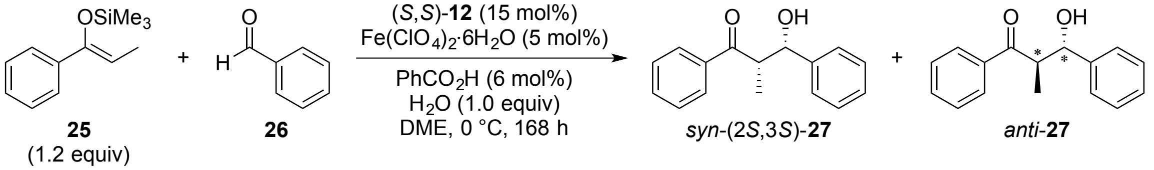


22 **23**

*Following the procedure described for the preparation of (S)-**19***: i) DIPA (2.2 mL, 15.6 mmol, 1.3 equiv), *n*-butyllithium (6.2 mL, 15.6 mmol, 1.3 equiv; 2.5 M in hexane), THF (16 mL), –78 °C, 20 min; ii) **22** (3.04 g, 12.0 mmol, 1.0 equiv) in THF (18 mL), O_2 (balloon; 1 atm.) –78 °C, 5 h. The crude product was purified by silica gel column chromatography using a gradient elution of

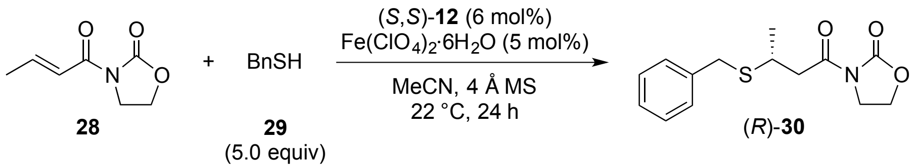
CH_2Cl_2/MeOH = 100:0–98:2 to give compounds **23** as a white crystals (1.61 g, 3.19 mmol, 53% yield), after recrystallisation from hot hexane/EtOAc 5:3 (75 mL, 70 °C), and **22** was recovered (1.01 g, 3.99 mmol, 33%). mp = 230–232 °C. R_f = 0.35 (CH_2Cl_2/MeOH = 98:2). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.56 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 4.97 (d, J = 17.3 Hz, 2H), 4.92 (d, J = 17.3 Hz, 2H), 2.10 (s, 6H), 0.98 (s, 18H), 0.15 (s, 12H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 149.3, 141.5, 134.1, 126.8, 122.2, 60.0, 25.9, 18.2, 17.4, –5.5 ppm. IR (Diamond): 2955, 2930, 2856, 1348, 1248, 1101, 835, 775, 725, 671 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{45}N_2O_4Si_2$ 505.2912; Found 505.2910.

Asymmetric Mukaiyama Aldol Reaction Catalyzed by Chiral Fe^{II} Complexes: Synthesis of Aldols (27):[9]



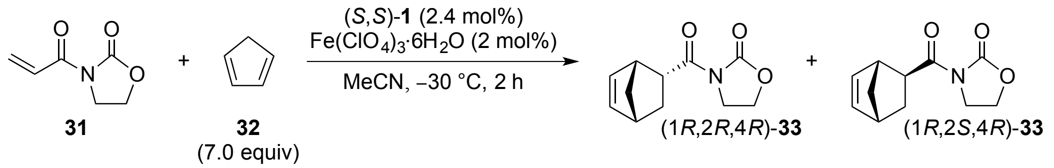
For the classical reaction procedure: see the supporting information of reference 9. *The modified reaction procedure:* To a vacuum flame-dried test tube under argon atmosphere, $Fe(ClO_4)_2·6H_2O$ (5.4 mg, 0.0150 mmol, 0.050 equiv) and (*S*,*S*)-**12** (16.0 mg, 0.0450 mmol, 0.15 equiv) was added to DME (0.3 mL) and the mixture was stirred at 22 °C for 1 h (pre-complexation). The resulting homogeneous yellow solution was cooled to 0 °C before benzoic acid (2.2 mg, 0.0180 mmol, 0.060 equiv), benzaldehyde **26** (30 μL, 0.300 mmol, 1.0 equiv), and degassed distilled H_2O (5.40 μL, 0.300 mmol, 1.0 equiv) were subsequently added. The mixture was stirred at 0 °C for 10 min. (*Z*)-Trimethyl((1-phenylprop-1-en-1-yl)oxy)silane **25** (74.3 mg, 0.360 mmol, 1.2 equiv) was added and the mixture was stirred at 0 °C for 168 h. Aqueous saturated $NaHCO_3$ (5 mL) was added to quench the reaction and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (10 mL) and dried over $MgSO_4$. The drying agent was removed by filtration, and the filtrate was concentrated *in vacuo* (bath temperature 30 °C). The crude reaction product was purified by a normal phase column chromatography (Biotage®SNAP Ultra 25g/Biotage®HP-Sphere™ 25 μm) using a gradient elution of hexane/EtOAc = 98:2–90:10 to give a diastereomeric mixture of aldols **27** as a white solid (68.9 mg, 0.287 mmol, 96% yield, 93% *de* (*syn*), 96% *ee* (*syn*, 2*S*,3*S*), 53% *ee* (*anti*)). mp = 44–46 °C (lit.[9] mp = 44–45 °C). R_f (*syn*) = 0.47, R_f (*anti*) = 0.43 (hexane/EtOAc = 80:20). The *de* was determined by ^{1}H NMR analysis of the crude reaction mixture and *ee*s were determined by HPLC [Daicel ChiralCel® OJ–H, hexane/*i*PrOH = 98:2, flow rate = 1.0 mL/min, λ = 220 nm]: t_R(*syn*, 2*R*,3*R*) = 35.3 min, t_R(*syn*, 2*S*,3*S*) = 49.1 min, t_R(*anti*, minor) = 62.1 min, t_R(*anti*, major) = 71.4 min; racemate (80% *de* (*syn*)): t_R(*syn*, 2*R*,3*R*) = 33.4 min, t_R(*syn*, 2*S*,3*S*) = 48.5 min, t_R(*anti*, 2*RS**,3*SR**) = 56.1 min, t_R(*anti*, 2*SR**,3*RS**) = 69.3 min. $[\alpha]_D^{22}$ = +10.7 (*c* = 1.00, $CHCl_3$) (lit.[9] $[\alpha]_D^{24}$ = +9.3 (*c* = 1.00, $CHCl_3$), 94% *de*, 97% *ee* of *syn*-(2*S*,3*S*)-**27**). ^1H NMR (500 MHz, $CDCl_3$): δ_H 8.00 – 7.98 (m, 0.07H, *anti*), 7.96 – 7.94 (m, 1.94H, *syn*), 7.62 – 7.59 (m, 1H), 7.51 – 7.47 (m, 2H), 7.43 – 7.41 (m, 2H), 7.38 – 7.35 (m, 2H), 7.29 – 7.26 (m, 1H), 5.26 (m, 0.97H, *syn*), 5.01 (dd, *J* = 7.9, 4.5, Hz, 0.03H, *anti*), 3.85 (m, 0.03H, *anti*), 3.72 (qd, *J* = 7.2, 3.0 Hz, 0.97H, *syn*), 3.66 (m, 0.97H, *syn*), 2.97 (d, *J* = 4.5 Hz, 0.03H, *anti*), 1.21 (d, *J* = 7.2 Hz, 2.91H, *syn*), 1.09 (d, *J* = 7.2 Hz, 0.10H, *anti*) ppm. $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$): δ_C 205.7 (*syn*), 205.0 (*anti*), 142.3 (*anti*), 141.9 (*syn*), 136.8 (*anti*), 135.7 (*syn*), 133.6 (*syn*), 133.3 (*anti*), 128.8 (*syn*), 128.7 (*anti*), 128.5, 128.3, 128.0 (*anti*), 127.4 (*syn*), 126.8 (*anti*), 126.1 (*syn*), 76.8 (*anti*), 73.2 (*syn*), 48.0 (*anti*), 47.2 (*syn*), 15.7 (*anti*), 11.3 (*syn*) ppm. IR (Diamond): 3520, 3059, 2988, 1670, 1597, 1448, 1325, 1219, 974, 696 cm^{-1}. The absolute configuration of *syn*-**27** was assigned as being 2*S*,3*S* by comparison of the optical rotation with a previous assignment.[10]

Asymmetric Thia-Michael Addition Reaction Catalyzed by Chiral Fe^{II} Complexes: Synthesis of β-Thioether (30):[4]



Accordingly to the published reaction procedure: To a vacuum flame-dried test tube under argon atmosphere, $Fe(ClO_4)_2{\cdot}6H_2O$ (9.1 mg, 0.0250 mmol, 0.050 equiv), (*S*,*S*)-**12** (10.7 mg, 0.0300 mmol, 0.060 equiv), and 4 Å molecular sieves (50.0 mg) were added to MeCN (0.5 mL) and the mixture was stirred at 22 °C for 2 h (pre-complexation). To the resulting homogeneous beige solution, (*E*)-3-crotonoyloxazolidin-2-one **28** (77.6 mg, 0.500 mmol, 1.0 equiv) and benzylthiol **29** (293 μL, 2.50 mmol, 5.0 equiv) were subsequently added and the mixture was stirred at 22 °C for 24 h. The reaction was filtered through a plug of Celite®, washed with three portions of Et_2O, and the filtrate was concentrated *in vacuo* (bath temperature 30 °C). The crude reaction product was purified by a normal phase column chromatography (Biotage®SNAP Ultra 25g/Biotage®HP-Sphere™ 25 μm) using a gradient elution of hexane/EtOAc = 80:20–50:50 to give compound (*R*)-**30** as a colorless oil (126.5 mg, 0.453 mmol, 91% yield, 90% *ee*). R_f = 0.39 (hexane/EtOAc = 70:30). The *ee* was determined by HPLC [Daicel ChiralCel® OJ–H, hexane/*i*PrOH = 70:30, flow rate = 1.0 mL/min, λ = 220 nm]: $t_R(R)$ = 48.6 min, $t_R(S)$ = 69.6 min; racemate: $t_R(R)$ = 50.0 min, $t_R(S)$ = 73.0 min. $[\alpha]_D^{22}$ = +13.5 (*c* = 1.00, $CHCl_3$) (lit.[4] $[\alpha]_D^{24}$ = +13.0 (*c* = 0.250, $CHCl_3$), 92% *ee* of (*R*)-**30**). ^1H NMR (500 MHz, $CDCl_3$): δ_H 7.36 – 7.30 (m, 4H), 7.24 (tt, *J* = 7.1, 1.5 Hz, 1H), 4.41 – 3.38 (m, 2H), 4.04 – 3.95 (m, 2H), 3.82 (d, *J* = 13.3 Hz, 1H), 3.79 (d, *J* = 13.3 Hz, 1H), 3.32 – 3.22 (m, 2H), 3.08 (m, 1H), 1.34 (d, *J* = 6.7 Hz, 3H) ppm. $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$): δ_C 170.9, 153.4, 138.4, 128.9, 128.5, 126.9, 62.1, 42.5, 42.4, 35.6, 35.3, 21.6 ppm. IR (Diamond): 2966, 2922, 1771, 1693, 1383, 1221, 1101, 1028, 758, 704 cm^{-1}. The absolute configuration of **30** was assigned as being *R* by comparison of the optical rotation with a previous assignment.[11]

Asymmetric Diels–Alder Addition Reaction Catalyzed by Chiral Fe^{III} Complexes: Synthesis of Cycloadducts (33):[5]



Accordingly to the published reaction procedure: To a vacuum flame-dried test tube under argon atmosphere, $Fe(ClO_4)_3{\cdot}6H_2O$ (4.6 mg, 0.0100 mmol, 0.020 equiv) and (*S*,*S*)-**1** (3.9 mg, 0.0120 mmol, 0.024 equiv) were added to MeCN (0.7 mL) and the mixture was stirred at 22 °C for 1.5 h (pre-complexation). 3- Acryloyloxazolidin-2-one **31** (70.6 mg, 0.500 mmol, 1.0 equiv) was added to the homogeneous dark red solution followed by the addition of MeCN (0.3 mL). The mixture was cooled to –30 °C and was stirred for 0.75 h. Freshly distilled cyclopentadiene **32** (294 μL, 3.50 mmol, 7.0 equiv) was introduced and the mixture was stirred at –30 °C for 2 h. Distilled H_2O (5 mL) was added to quench the reaction and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (10 mL) and dried over $MgSO_4$. The drying agent was removed by filtration, and the filtrate was concentrated *in vacuo* (bath temperature 30 °C). The crude reaction product was purified by a normal phase column chromatography (Biotage®SNAP Ultra 25g/Biotage®HP-Sphere™ 25 μm) using a gradient elution of hexane/EtOAc = 80:20–50:50 to give a diastereomeric mixture of cycloadducts **33** as a white solid (92.6 mg, 0.447 mmol, 89% yield, 89% *de* (*endo*), 98% *ee* (*endo*, 1*R*,2*R*,4*R*), 71% *ee* (*exo*, 1*R*,2*S*,4*R*)). mp = 56–58 °C (lit.[12] mp = 86–87 °C). R_f = 0.44 (hexane/EtOAc = 70:30). The *de* was determined by ^1H NMR analysis of the crude reaction mixture and *ee* values for *endo*- and *exo*-**33** were determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 95:5, flow rate = 1.0 mL/min, λ = 220 nm]: t_R(*exo*, 1*R*,2*S*,4*R*) = 20.1 min, t_R(*endo*, 1*R*,2*R*,4*R*) = 21.6 min, t_R(*exo*, 1*S*,2*R*,4*S*) = 26.6 min, t_R(*endo*, 1*S*,2*S*,4*S*) = 28.3 min; racemate (82% *de* (*endo*)): t_R(*exo*, 1*R*,2*S*,4*R*) = 20.1 min, t_R(*endo*, 1*R*,2*R*,4*R*) = 21.6 min, t_R(*exo*, 1*S*,2*R*,4*S*) = 26.6 min, t_R(*endo*, 1*S*,2*S*,4*S*) = 28.1 min. $[\alpha]_D^{22}$ = +148.7 (*c* = 1.00, $CHCl_3$) (lit.[12] $[\alpha]_D^{25}$ = –148.82 (*c* = 1.02, $CHCl_3$), 96% *de*, 98% *ee* of *endo*-(1*S*,2*S*,4*S*)-**33**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 6.26 (dd, *J* = 5.7, 3.1 Hz, 0.95H, *endo*), 6.20 – 6.17 (m, 0.10H, *exo*), 5.89 (dd, *J* = 5.7, 2.9 Hz, 0.95H, *endo*), 4.45 – 4.37 (m, 2H), 4.06 – 4.04 (m, 0.10H, *exo*), 4.03 – 3.93 (m, 2.85H, *endo*), 3.32 (m, 0.95H, *endo*), 3.29 (m, 0.05H, *exo*), 3.03 (m, 0.05H, *exo*), 2.97 – 2.94 (m, 1H), 1.99 – 1.94 (m, 1H), 1.54 (m, 0.05H, *exo*), 1.52 – 1.45 (m, 1.95H), 1.42 (m, 0.95H, *endo*), 1.39 (m, 0.05H, *exo*) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 176.1 (*exo*), 174.6 (*endo*), 153.42 (*endo*), 153.36 (*exo*), 138.2 (*exo*), 138.0 (*endo*), 135.9 (*exo*), 131.6 (*endo*), 62.0 (*endo*), 61.9 (*exo*), 50.1 (*endo*), 46.7 (*exo*), 46.3 (*endo*), 46.1 (*exo*), 43.1 (*endo*), 42.9, 42.8 (*endo*), 41.8 (*exo*), 30.3 (*exo*), 29.4 (*endo*) ppm. IR (Diamond): 2980, 2943, 1757, 1684, 1358, 1205, 1115, 1040, 860, 700 cm^{-1}. The absolute configuration of *endo*-**33** was assigned as being 1*R*,2*R*,4*R* by comparison of the optical rotation with a previous attribution.[13] The absolute configuration of *exo*-**33** was assigned as being 1*R*,2*S*,4*R* by comparison of the retention times observed on a Daicel ChiralCel® OD–H column with the chromatogram obtained from a ChiralCel® OD column of a previous assignment.[14]

Crystallization procedure for (S_a,*S*,*S*)-19:

(S_a,*S*,*S*)-**19** (30.0 mg, 48.6 µmol) was added to hexane (0.6 mL) and the mixture was heated to 70 °C to solubilize the solid. The solution was slowly cooled down to 22 °C and the crystals were gradually formed.

Crystallization procedure for [(*S*,*S*)-12·Fe·DME·H_2O]$^{2+}$·2ClO_4^-:

$Fe(ClO_4)_2\cdot 6H_2O$ (5.6 mg, 15.4 µmol, 1.0 equiv) and (*S*,*S*)-**12** (5.5 mg, 15.4 µmol, 1.0 equiv) were dissolved in DME (0.2 mL). The clear yellow homogeneous solution was stirred at 22 °C for 0.5 h. Vapor diffusion of diethyl ether (1.0 mL) into this solution afforded the crystals.

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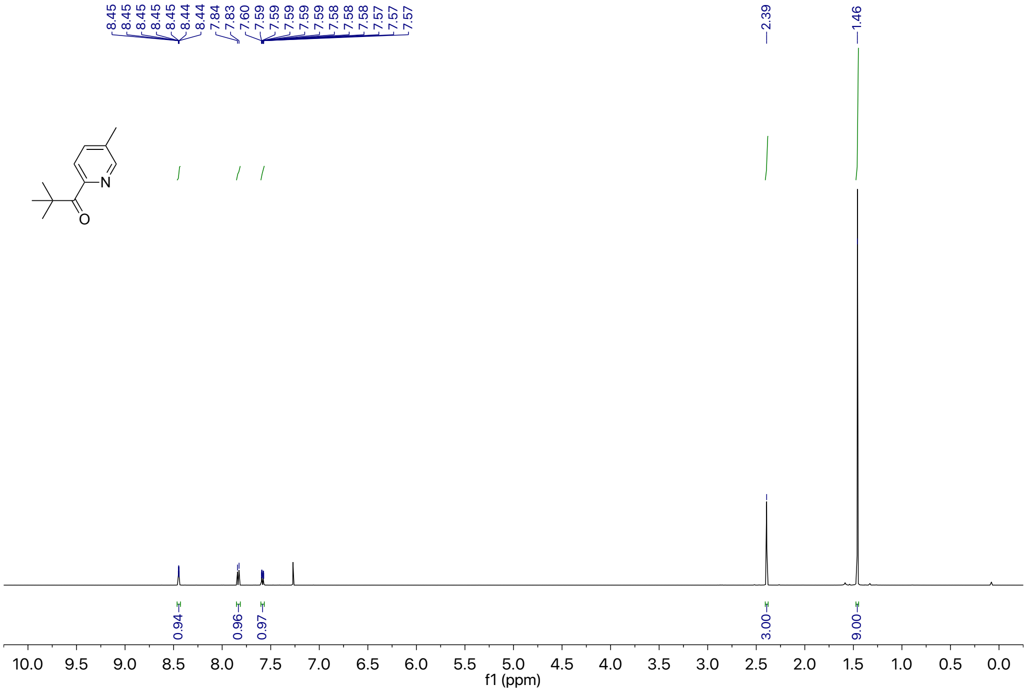
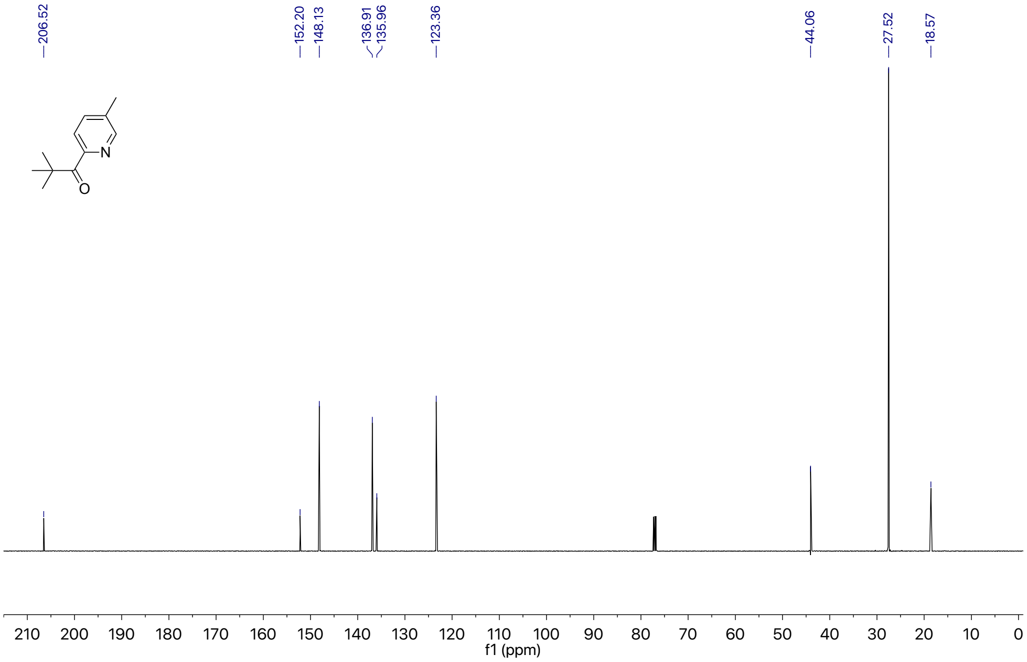
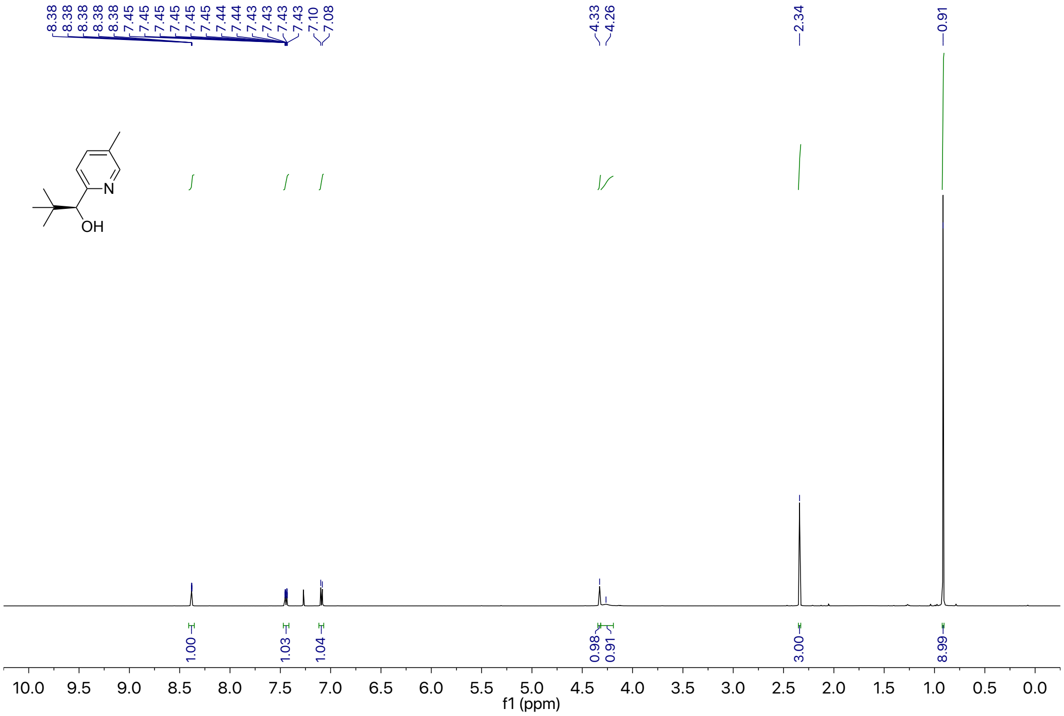
^{1}H and ^{13}C{H} NMR spectra



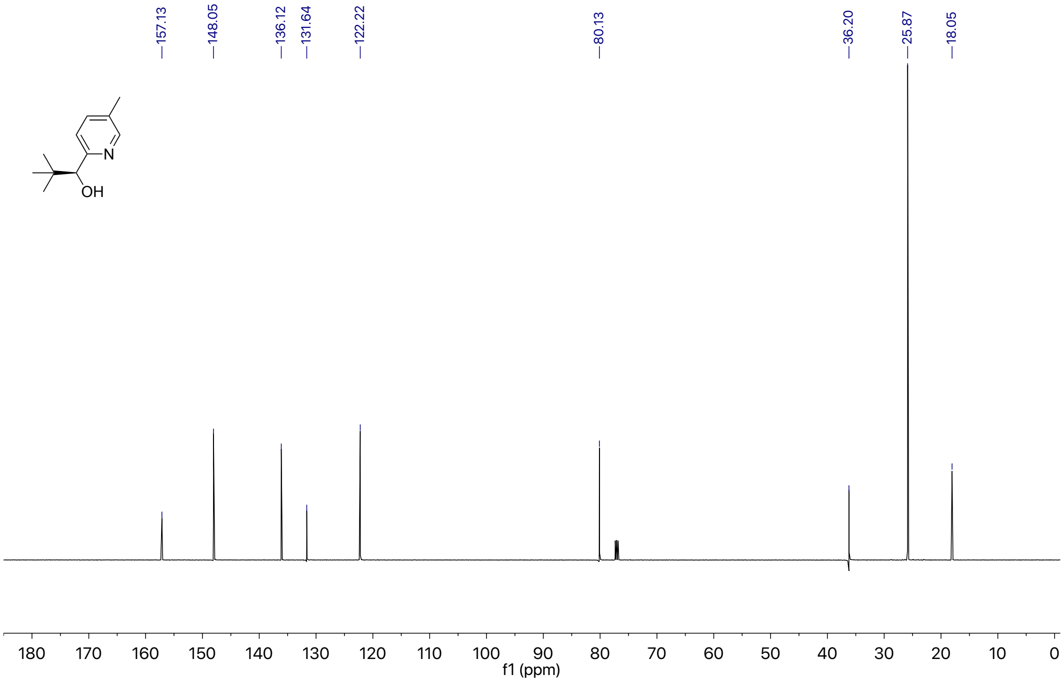
^{1}H NMR (500 MHz, CDCl$_3$) of **13**



^{13}C{H} NMR (126 MHz, CDCl$_3$) of **13**



^{1}H NMR (500 MHz, CDCl$_3$) of (*S*)-**15**



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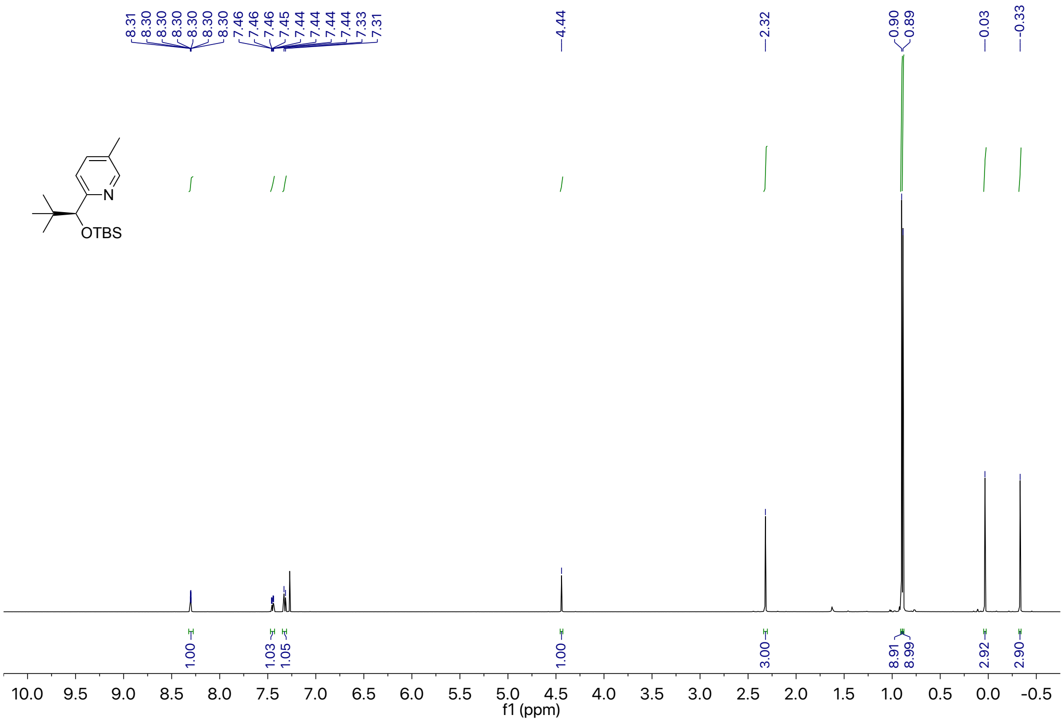
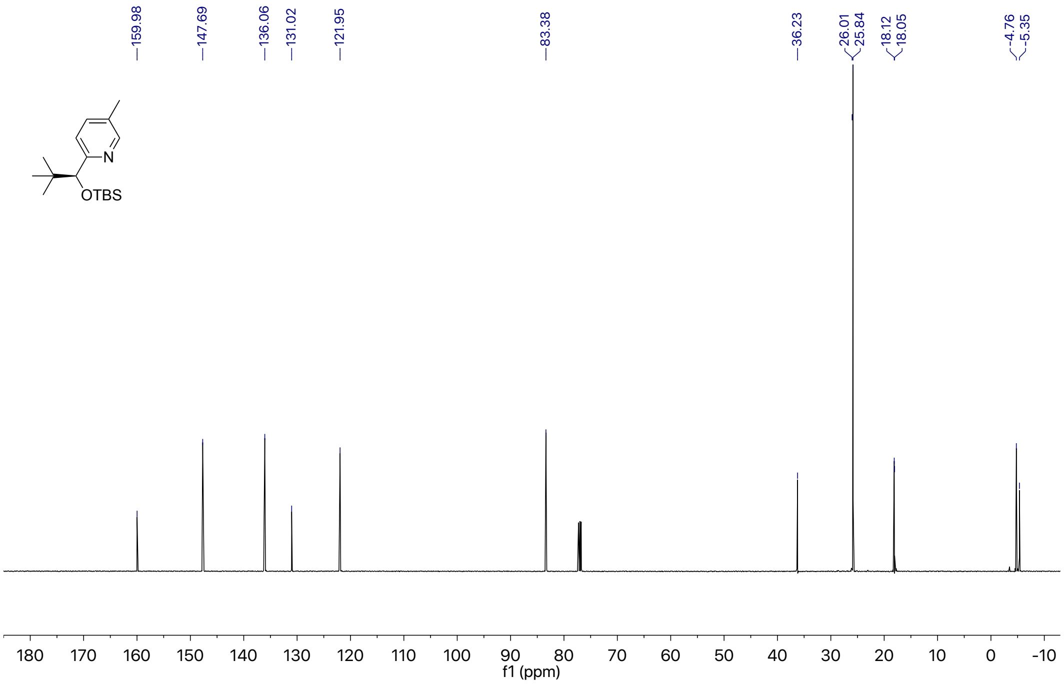


^{1}H NMR (500 MHz, CDCl$_3$) of (*S*)-**16**



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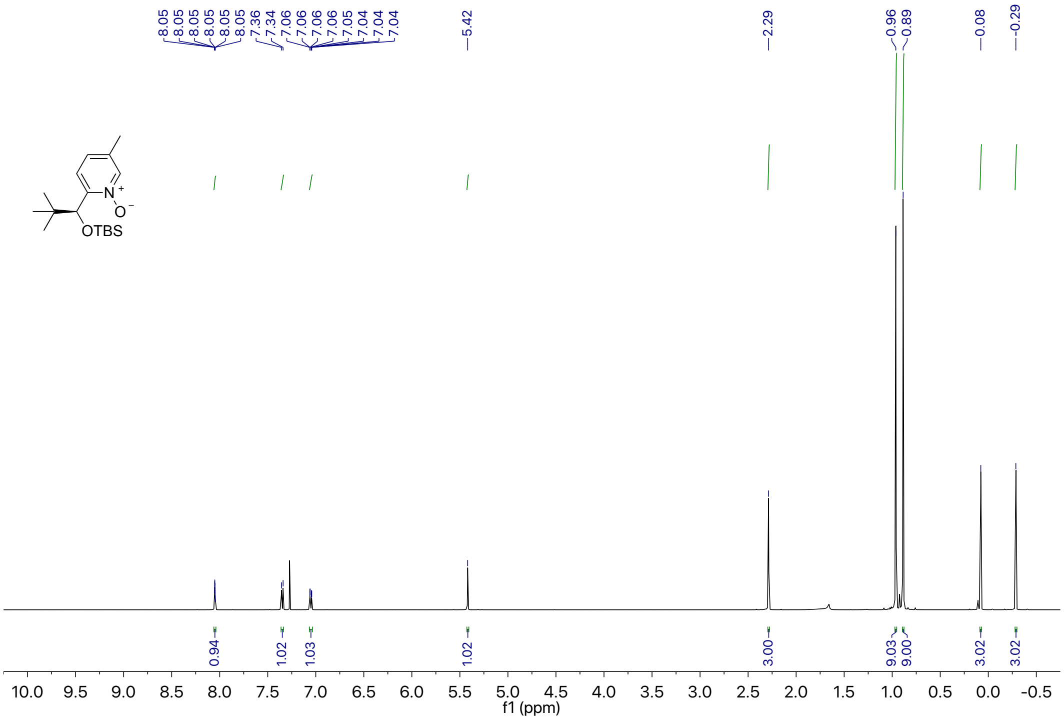

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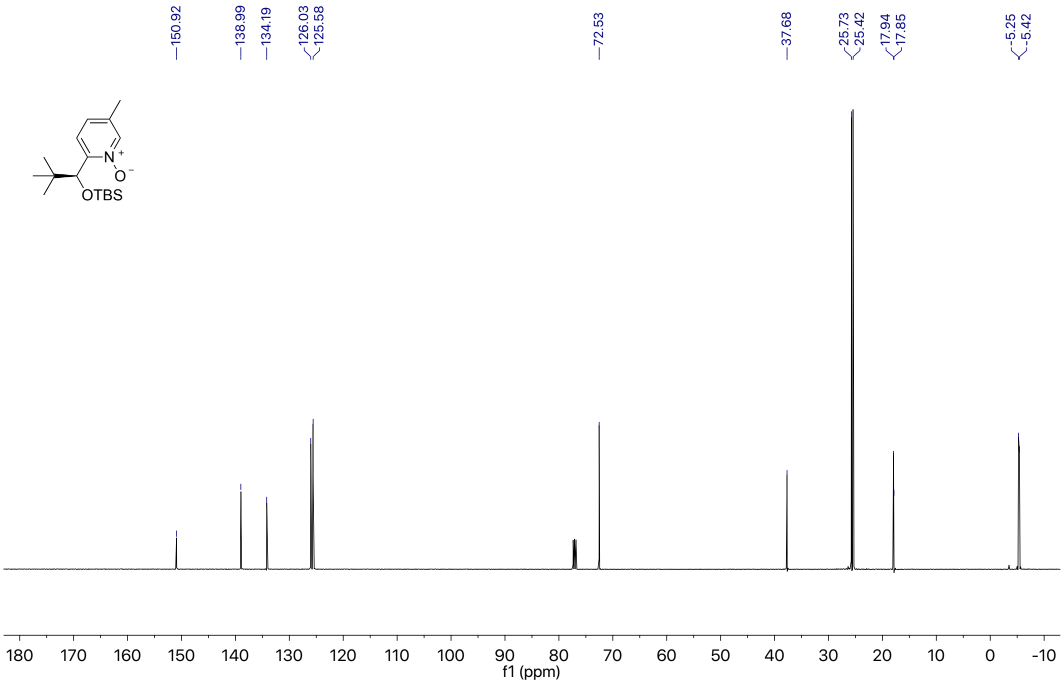

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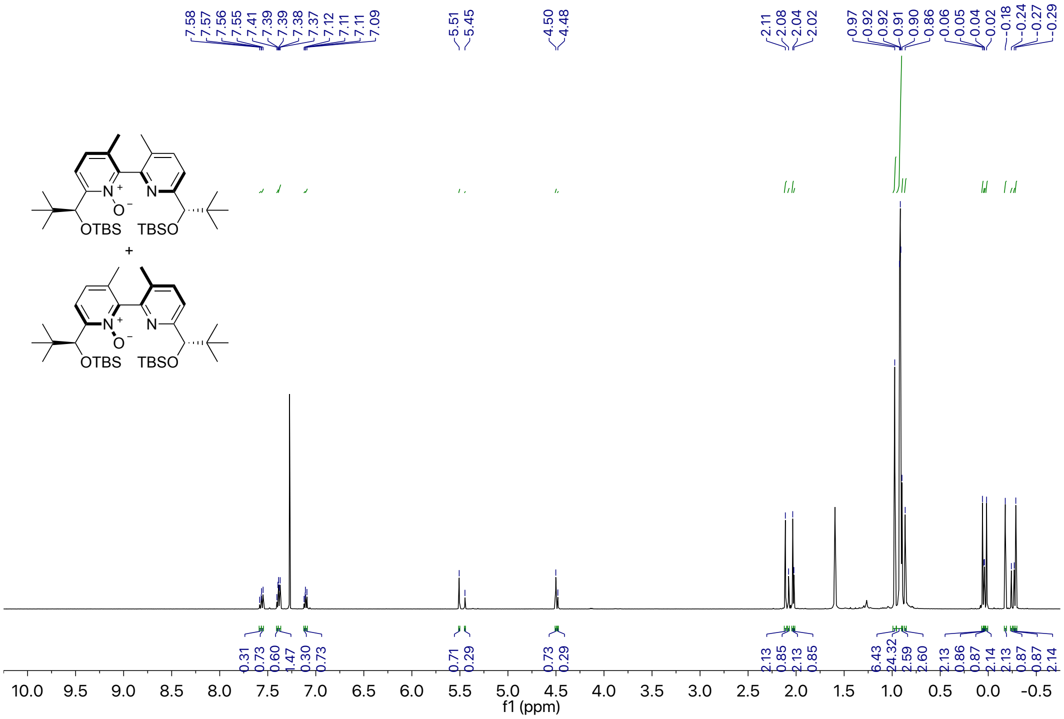
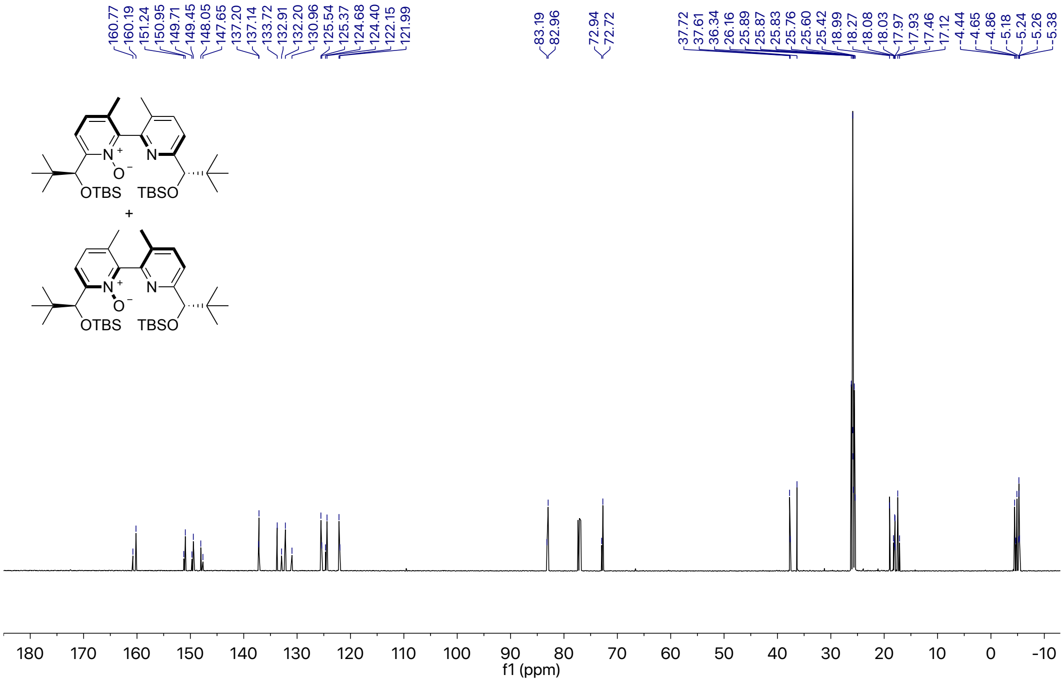


^{1}H NMR (500 MHz, CDCl$_3$) of (*R*$_a$,*S*,*S*)-**18** and (*S*$_a$,*S*,*S*)-**18**



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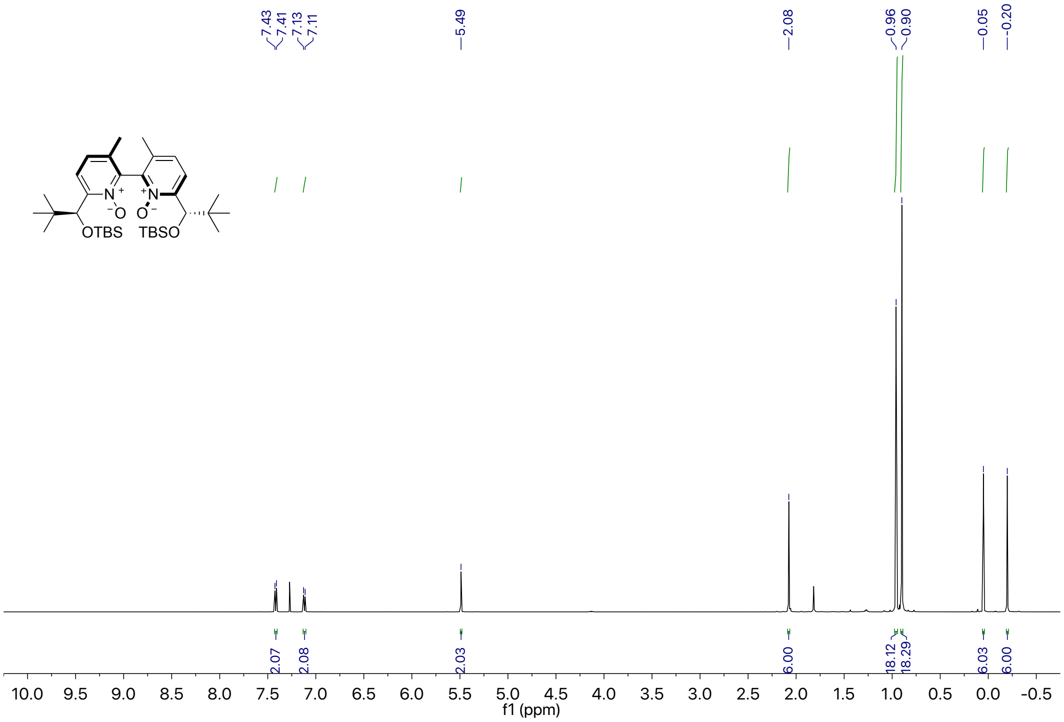

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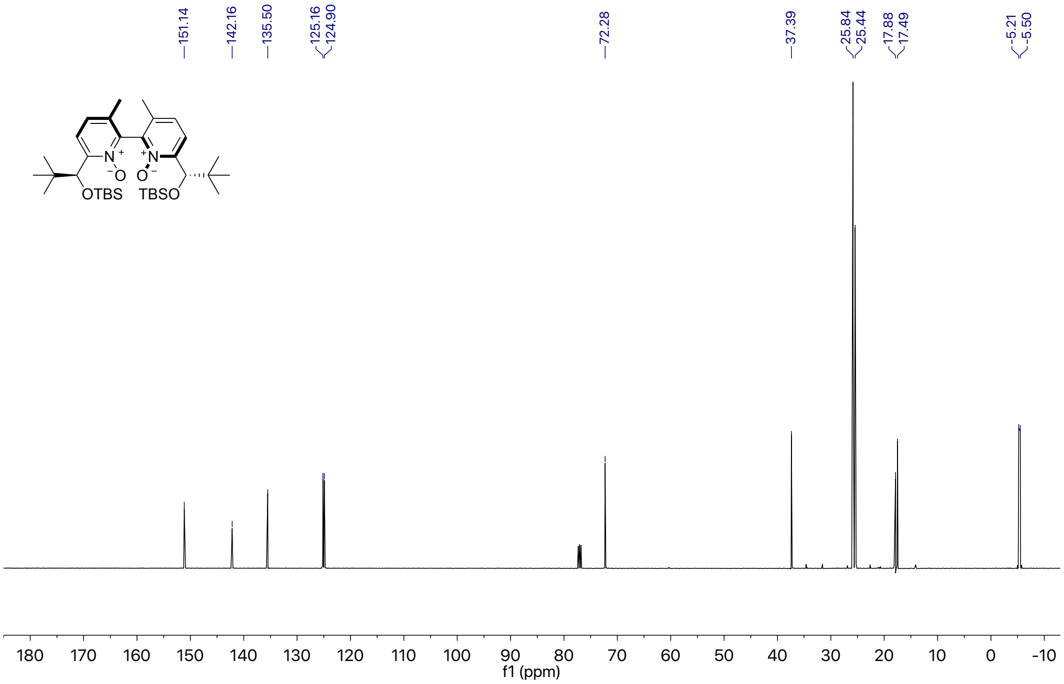

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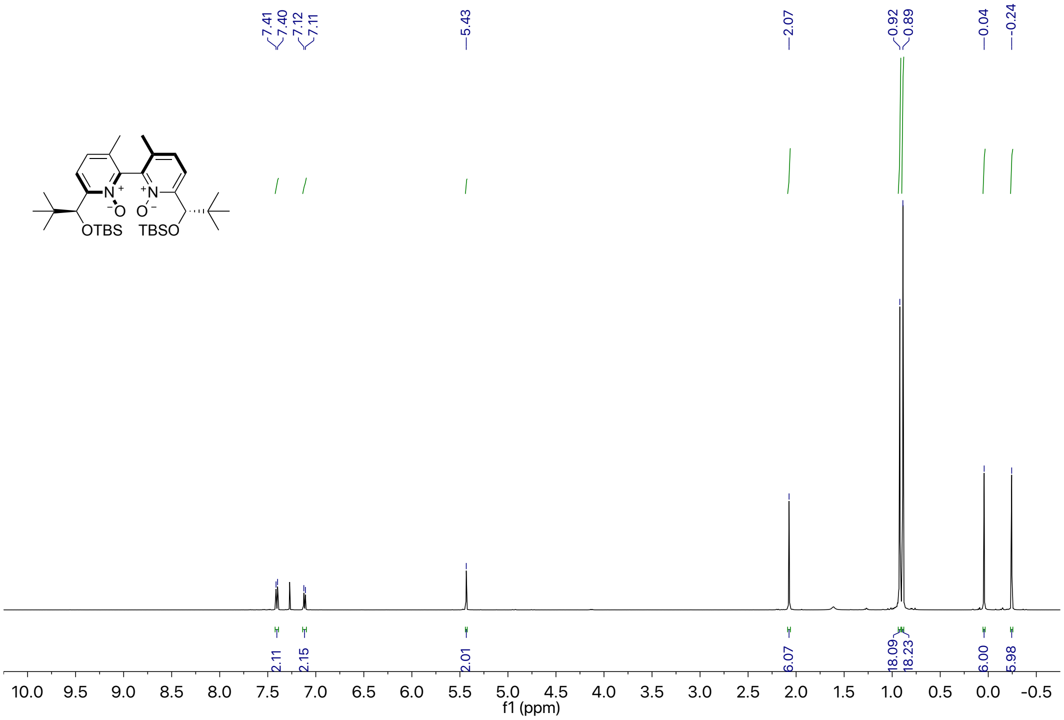

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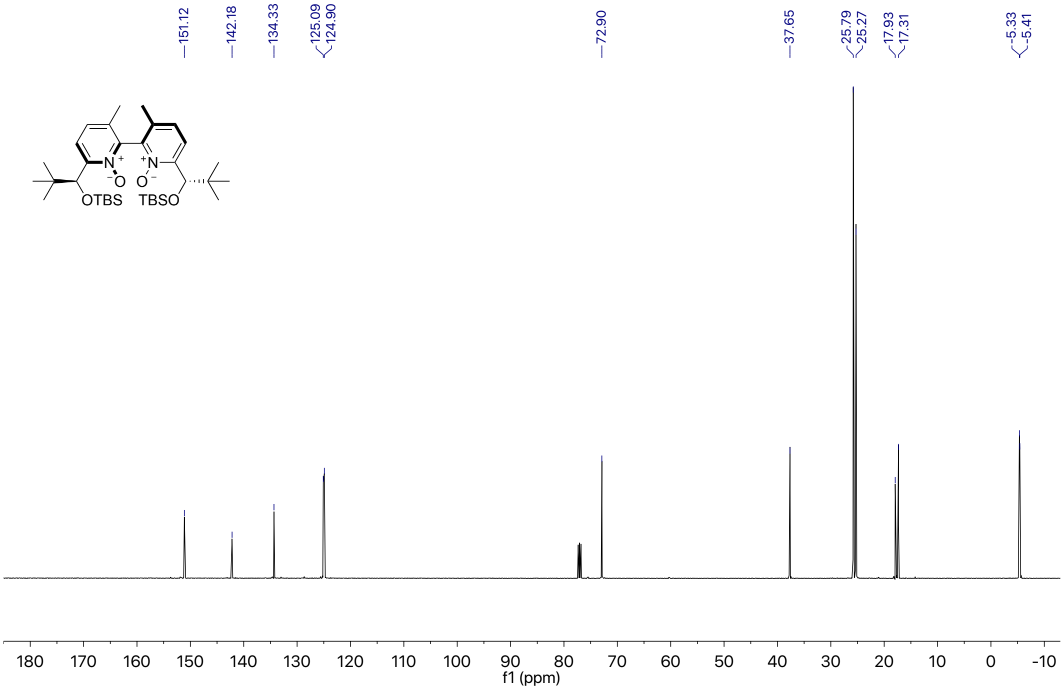

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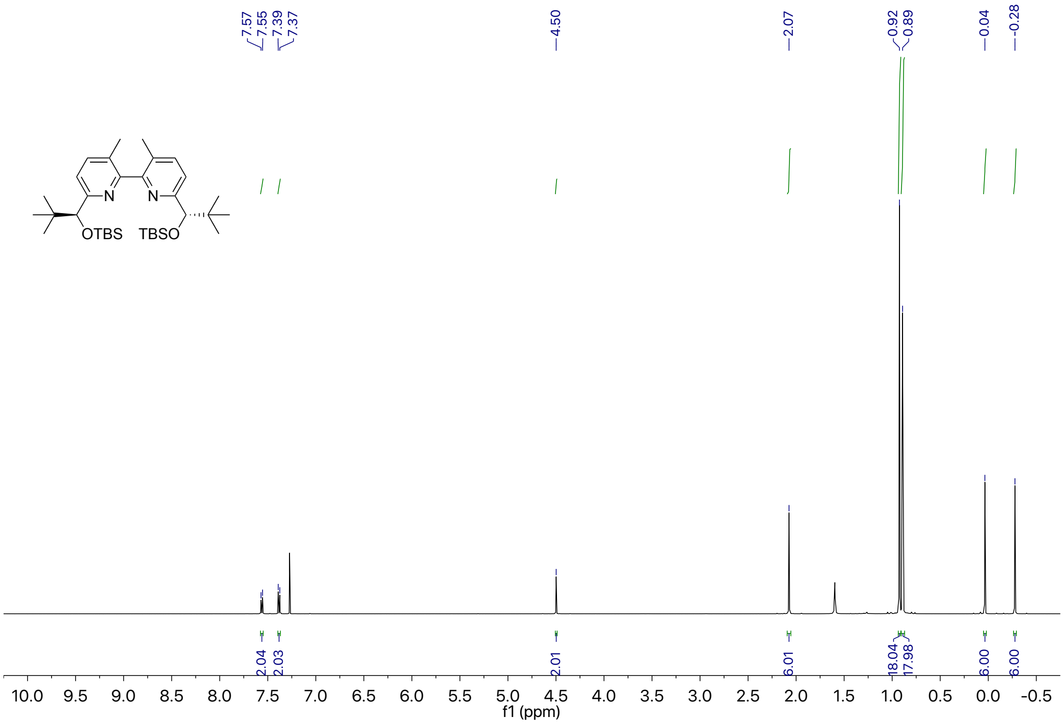
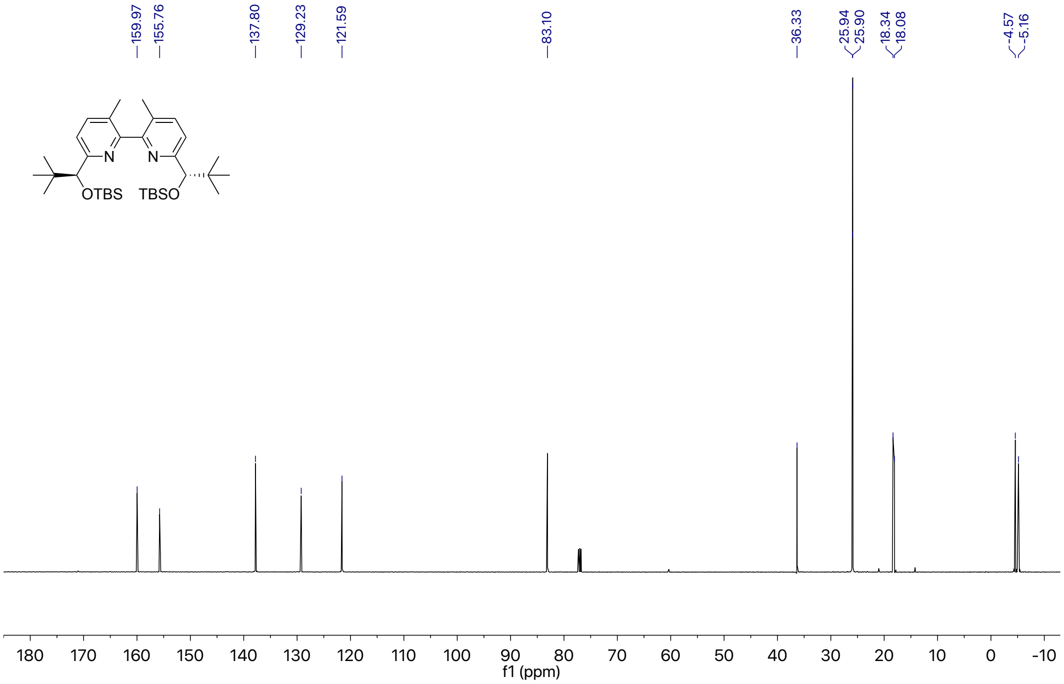


^{1}H NMR (500 MHz, CDCl$_3$) of (*S*,*S*)-**24**



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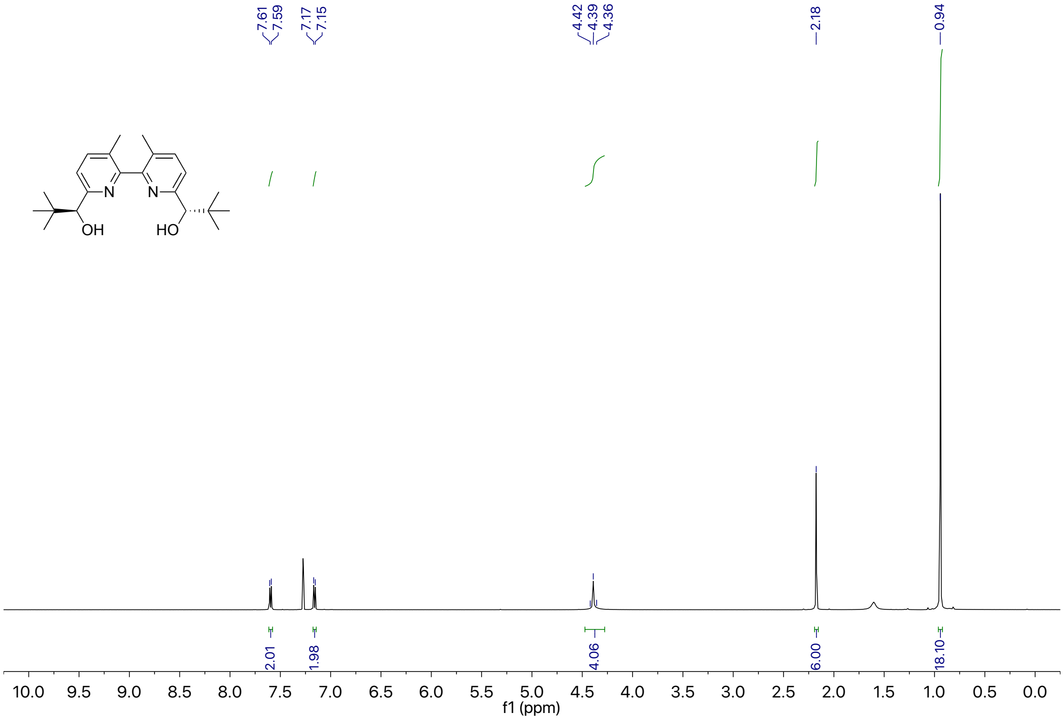

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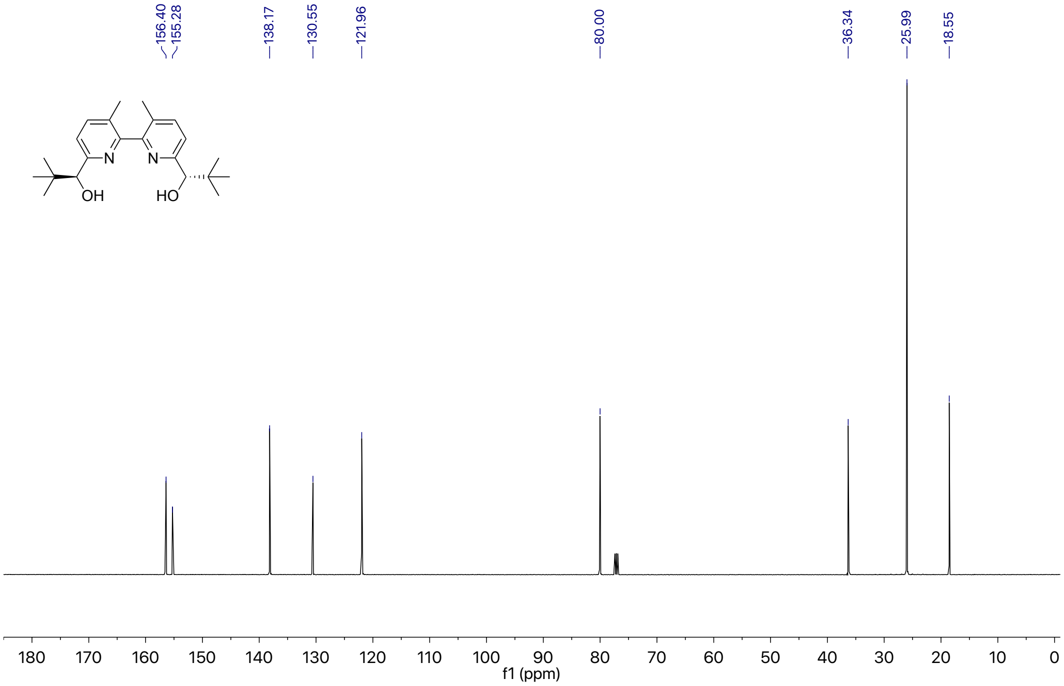

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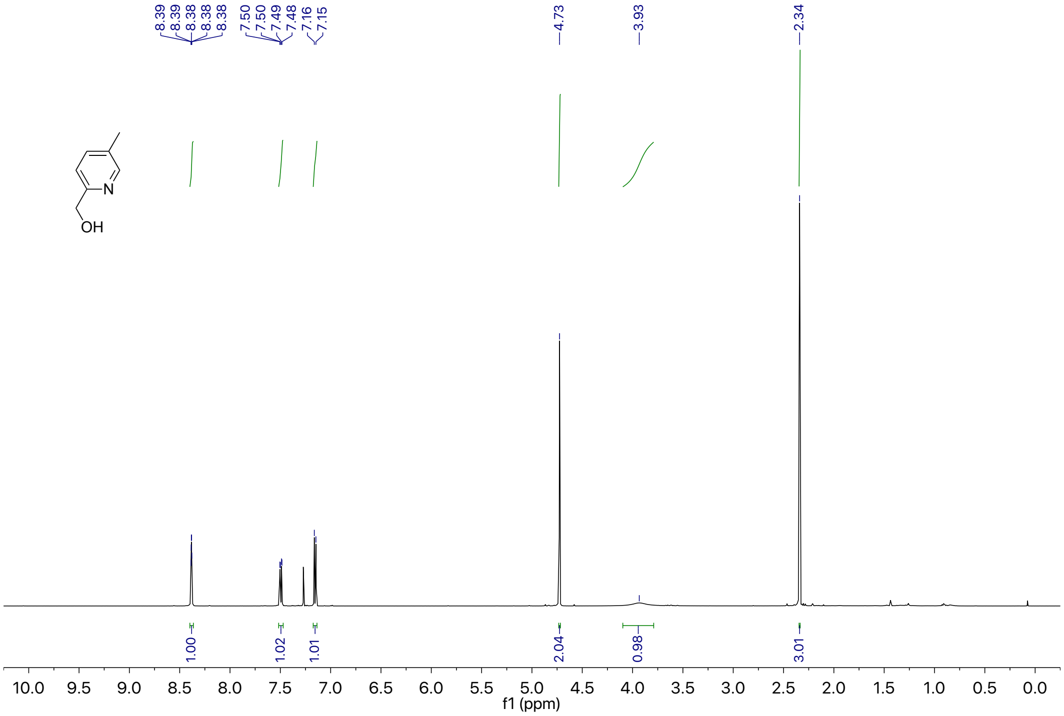
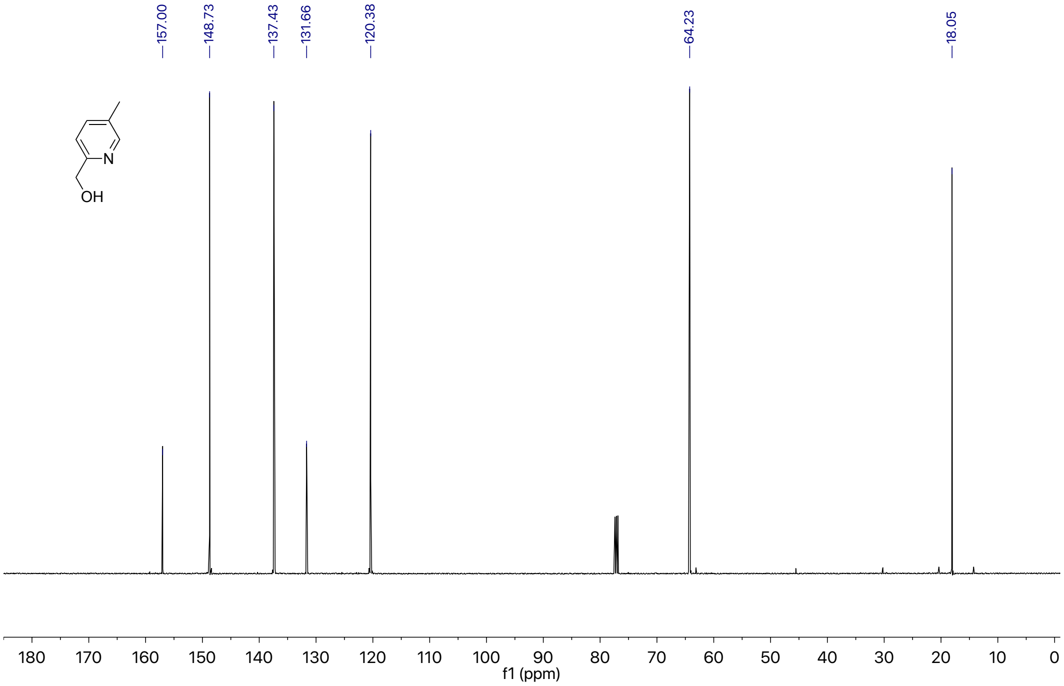
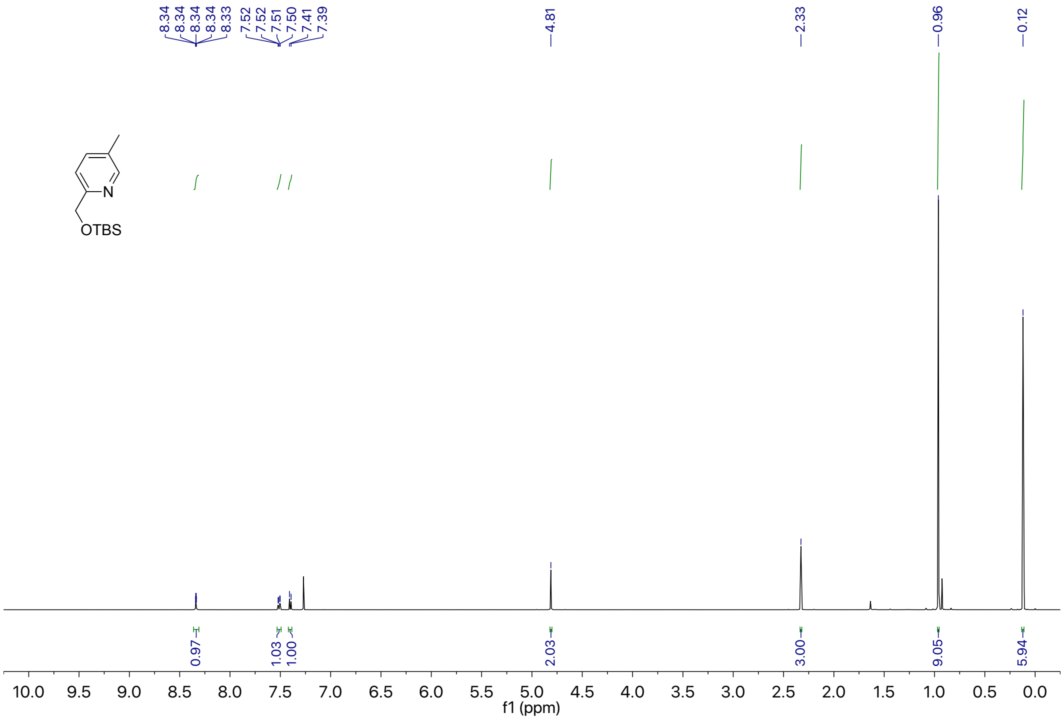


^{1}H NMR (500 MHz, CDCl$_3$) of **20**



^{13}C{H} NMR (126 MHz, CDCl$_3$) of **20**



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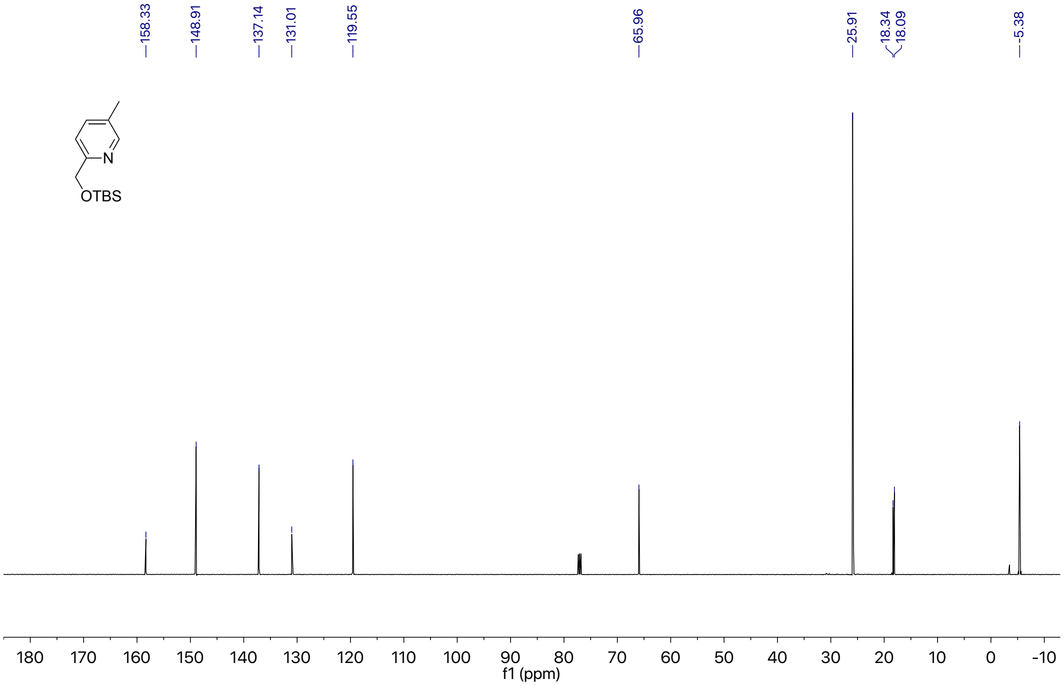

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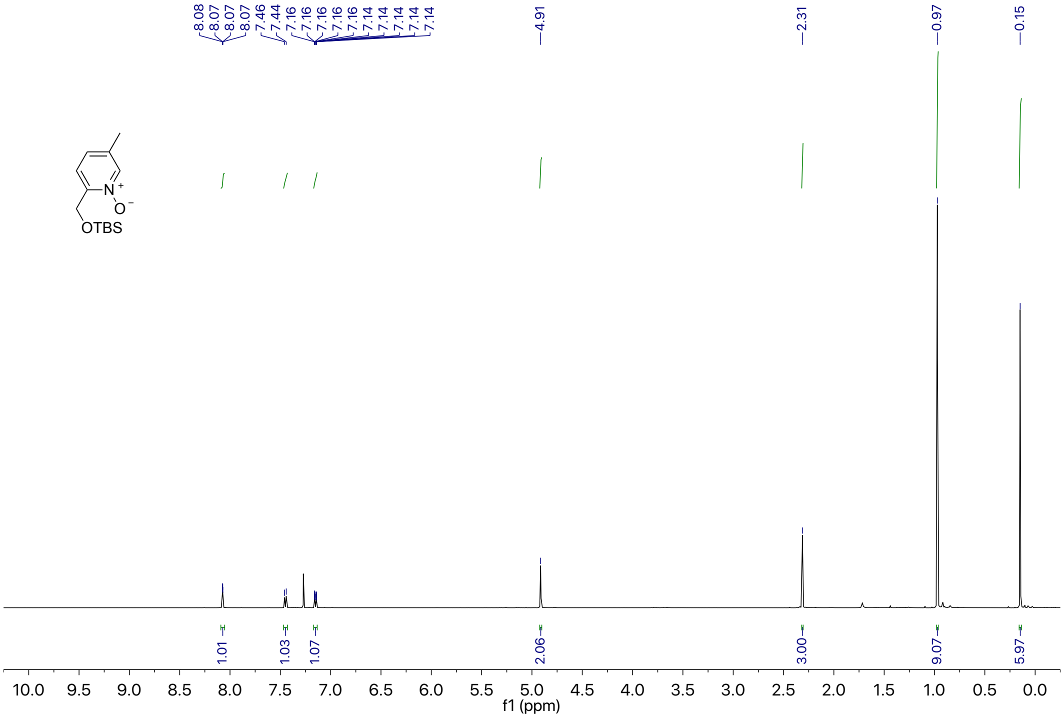

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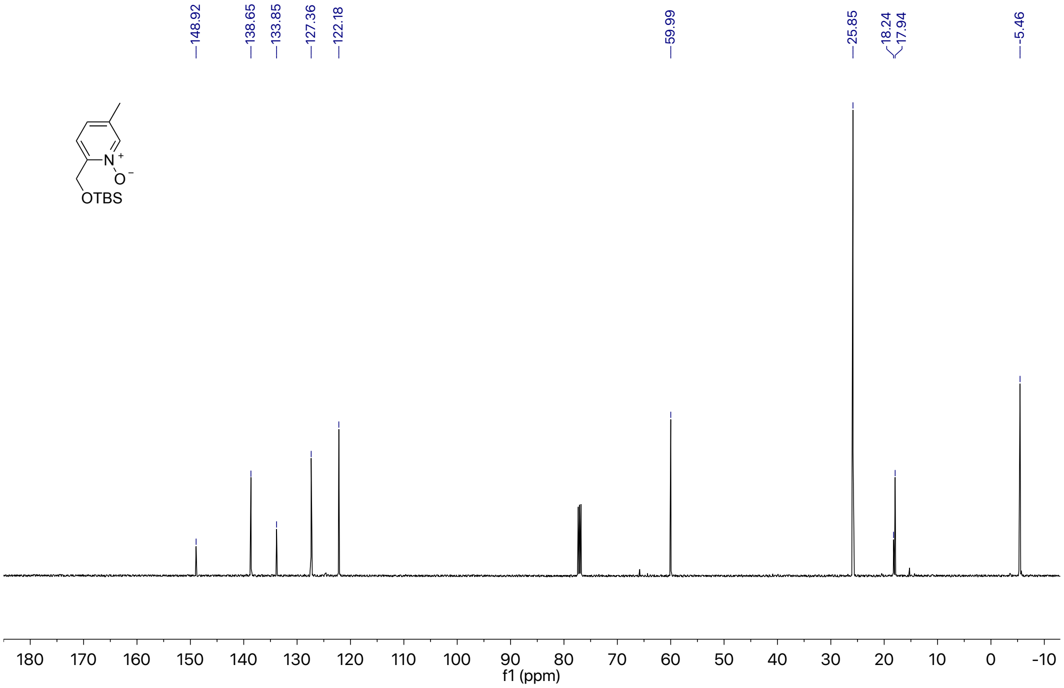

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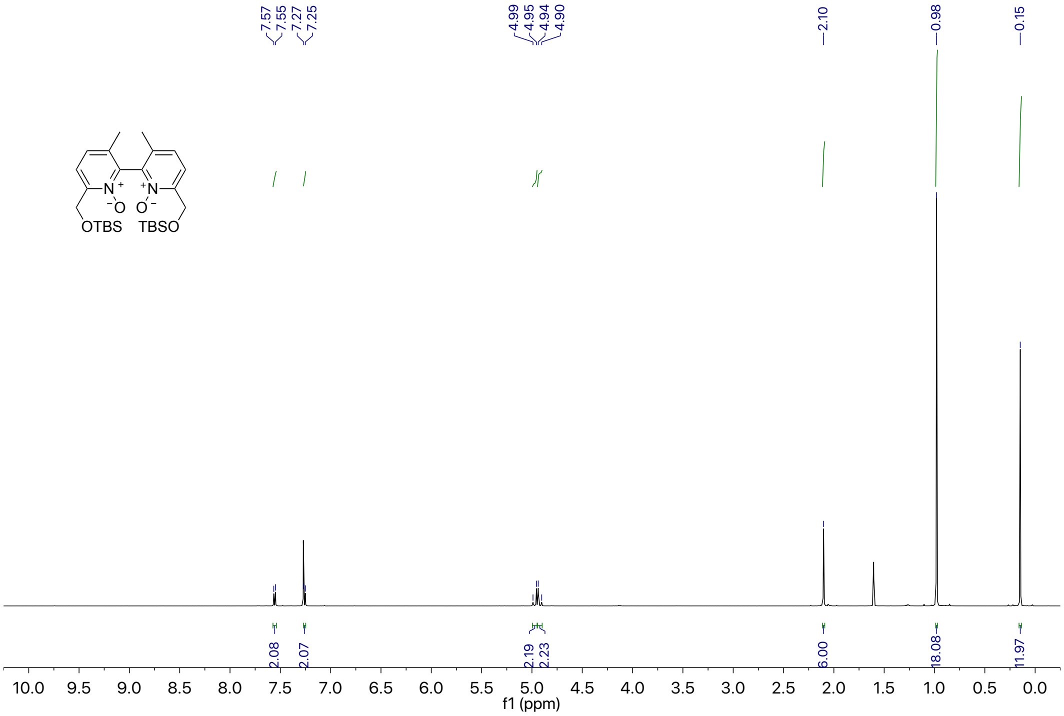

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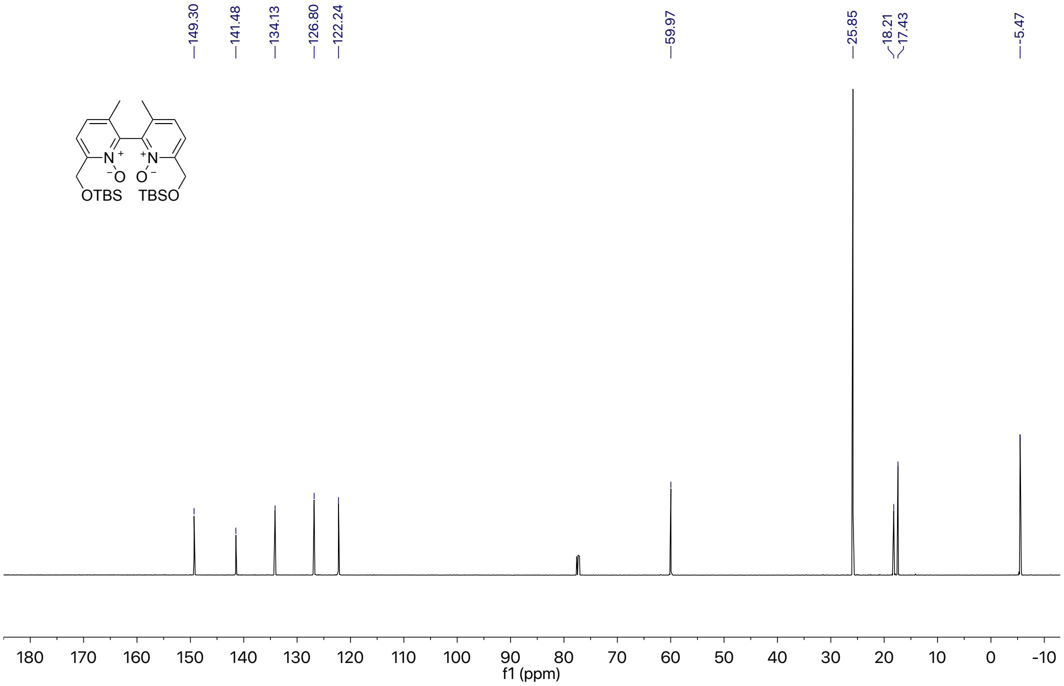

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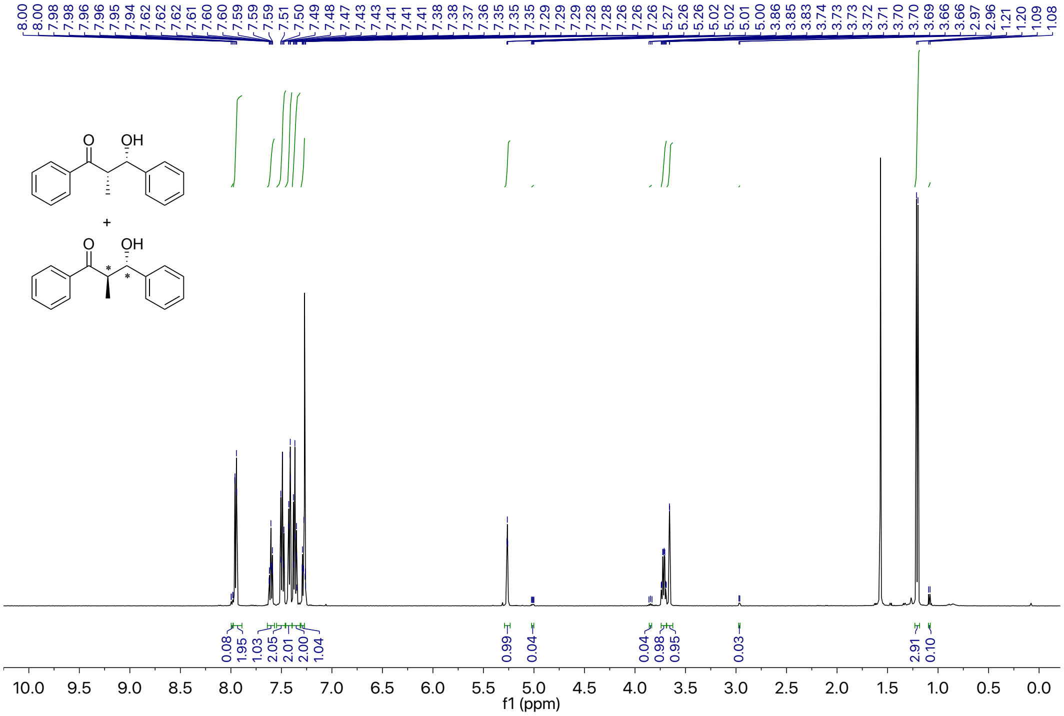
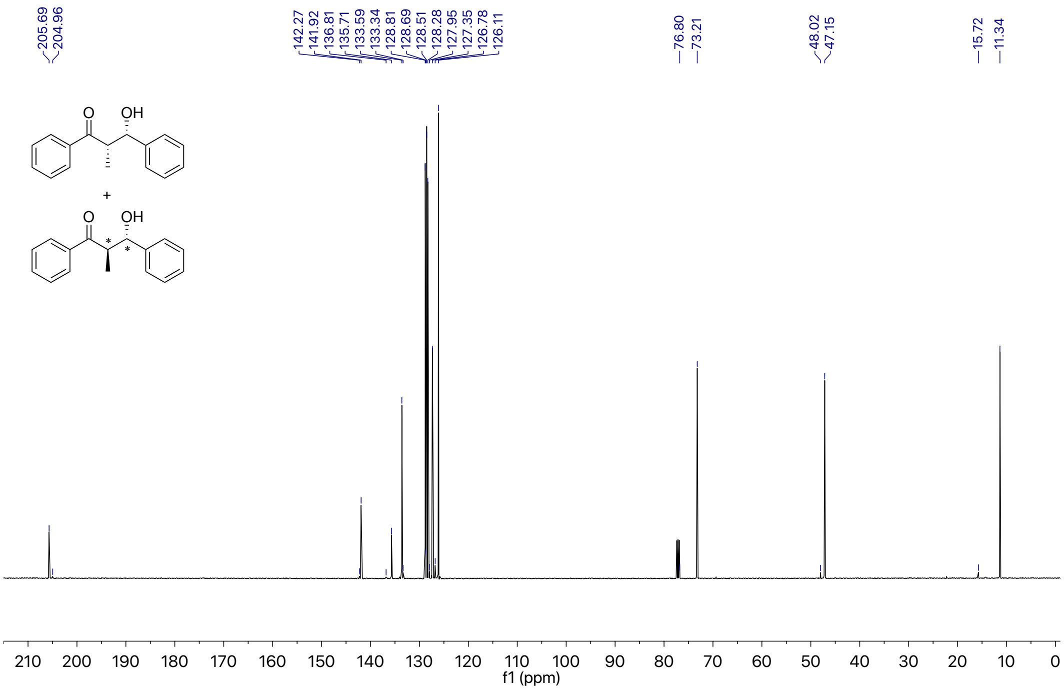
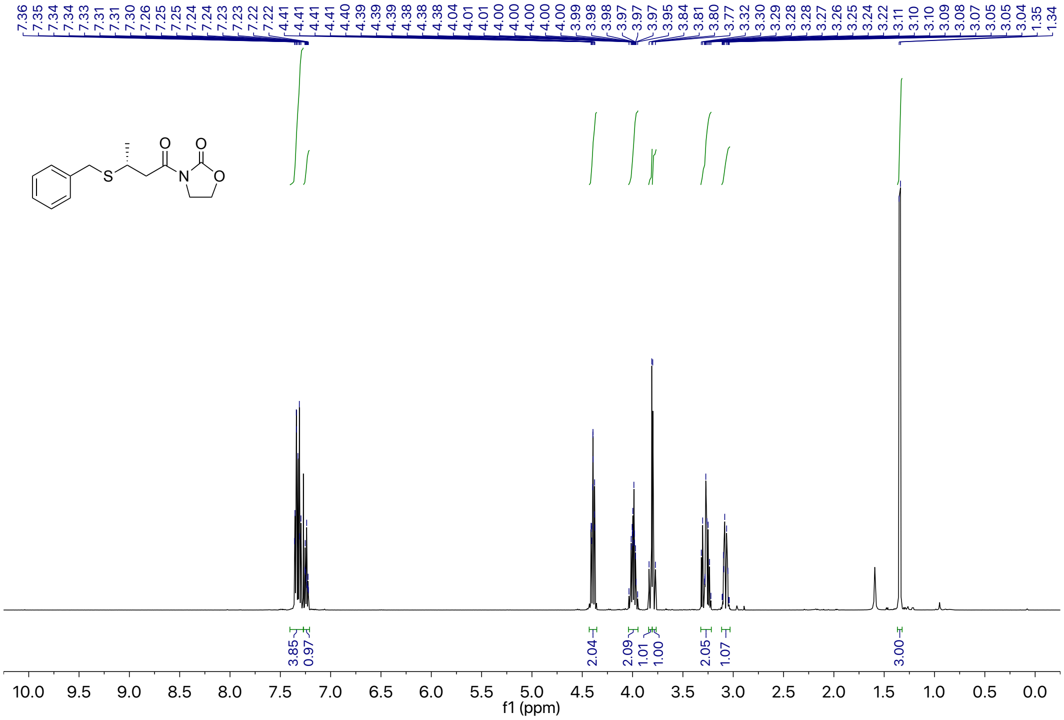


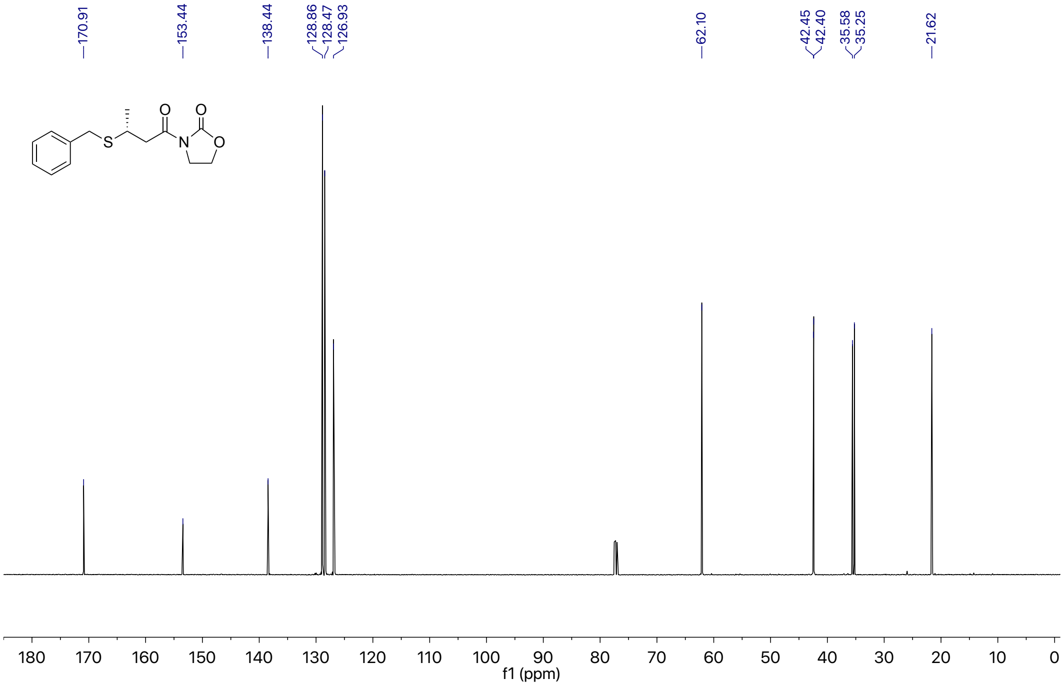
^{1}H NMR (500 MHz, CDCl$_3$) of *syn*-(2*S*,3*S*)-**27** and *anti*-**27**



^{13}C{H} NMR (126 MHz, CDCl$_3$) of *syn*-(2*S*,3*S*)-**27** and *anti*-**27**



^{1}H NMR (500 MHz, CDCl$_3$) of (*R*)-**30**



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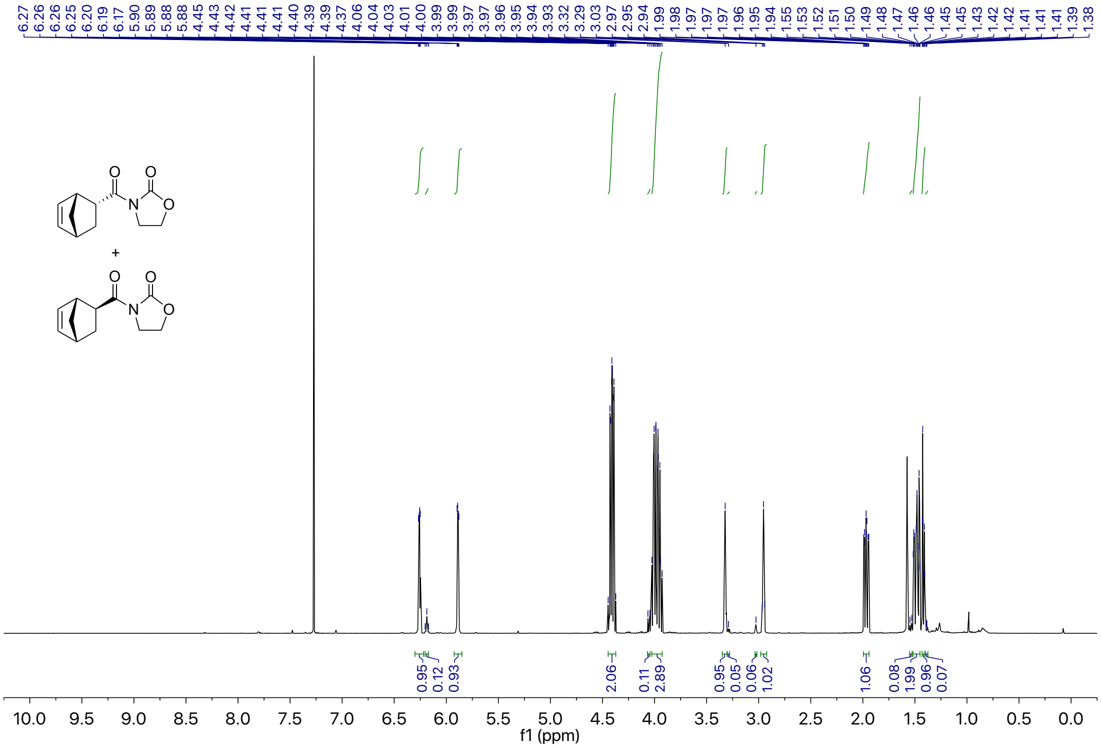

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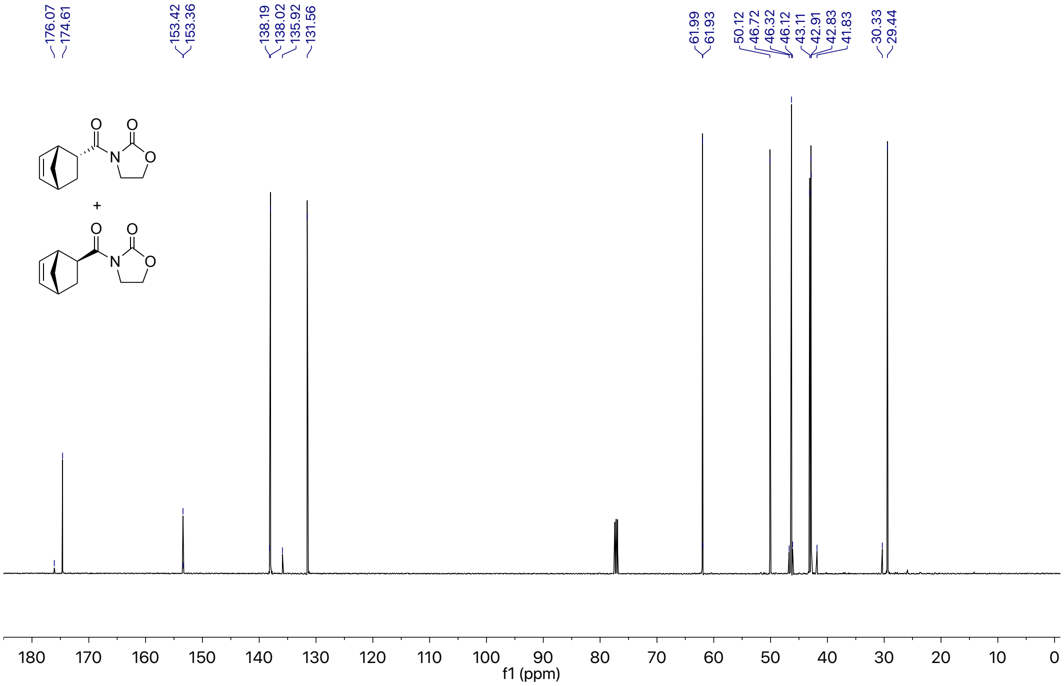
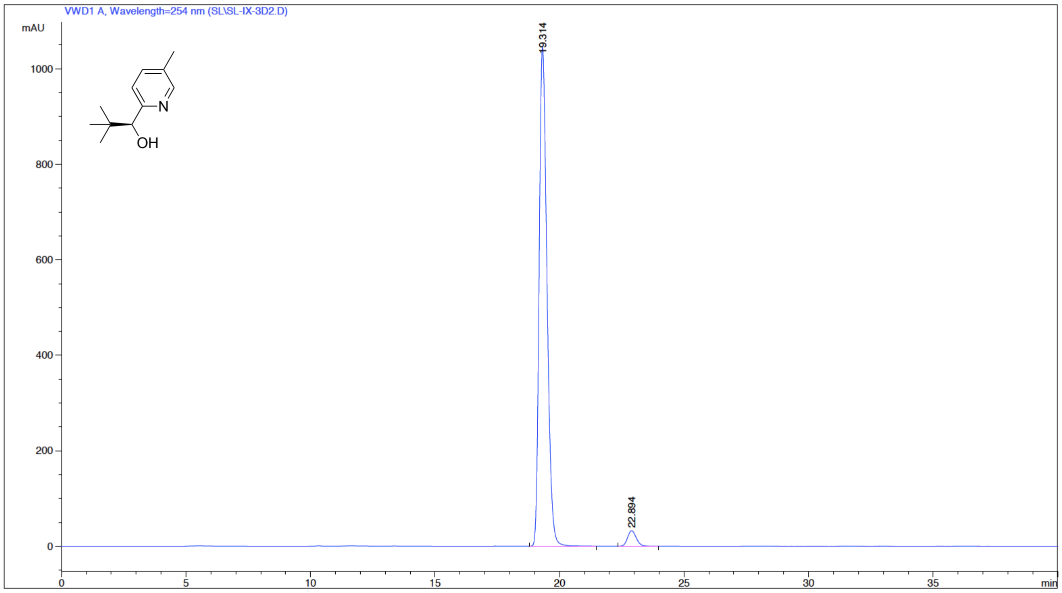


^{13}C{H} NMR (126 MHz, CDCl$_3$) of *endo*-(1*R*,2*R*,4*R*)-**33** and *exo*-(1*R*,2*S*,4*R*)-**33**

HPLC chromatograms



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   2  22.894 BB    0.3764  790.10681   32.54169  3.3505

Totals :                  2.35814e4 1077.92328
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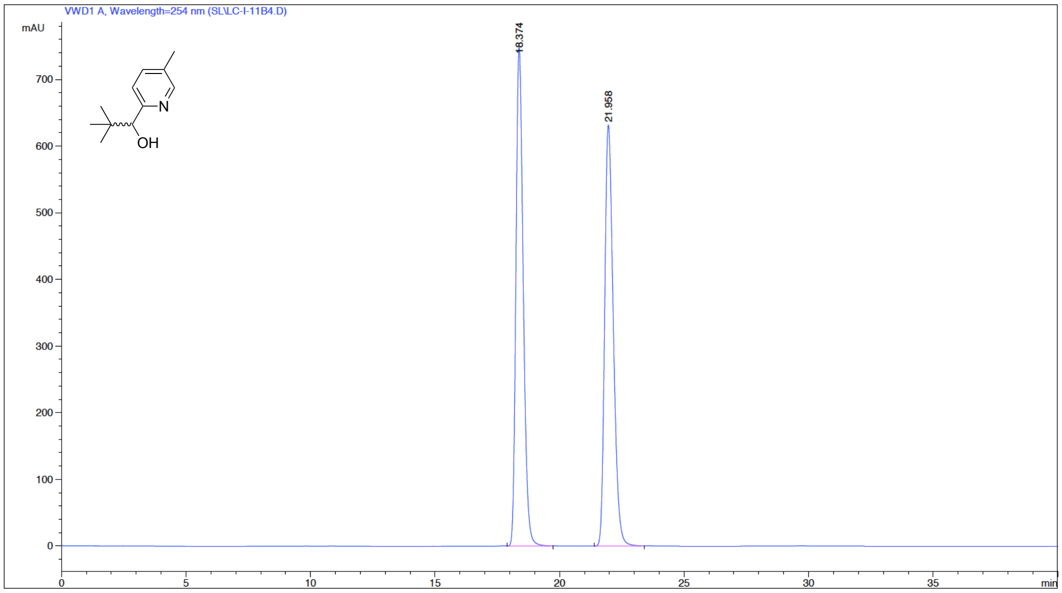
93% *ee* of (*S*)-**15**



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   2  21.958 BB    0.3621 1.51986e4  632.04688 49.8754

Totals :                  3.04732e4 1381.05890
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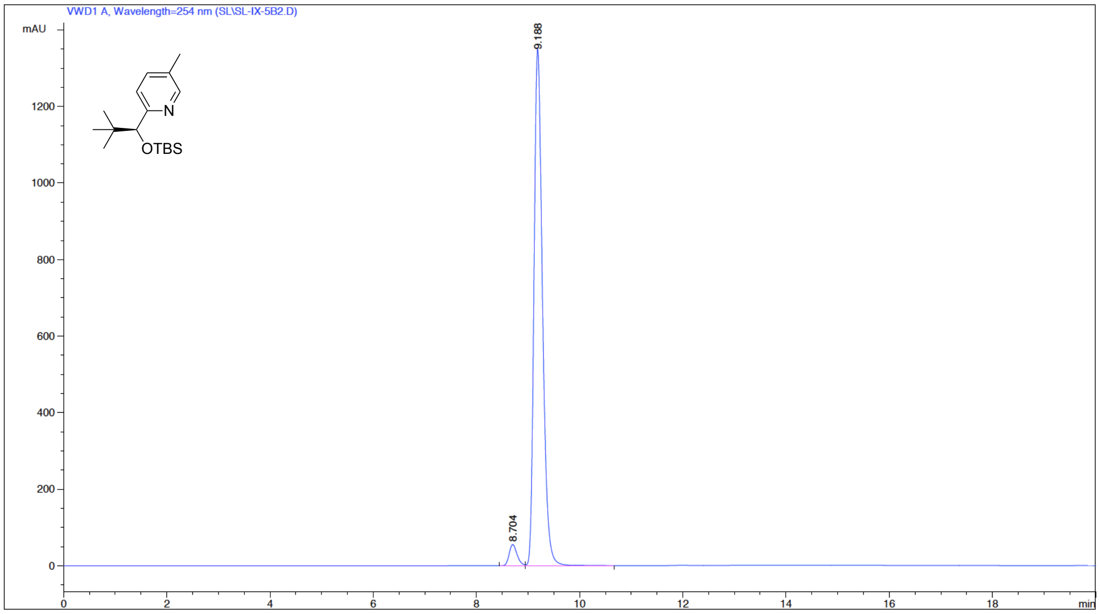
Racemate of **15**



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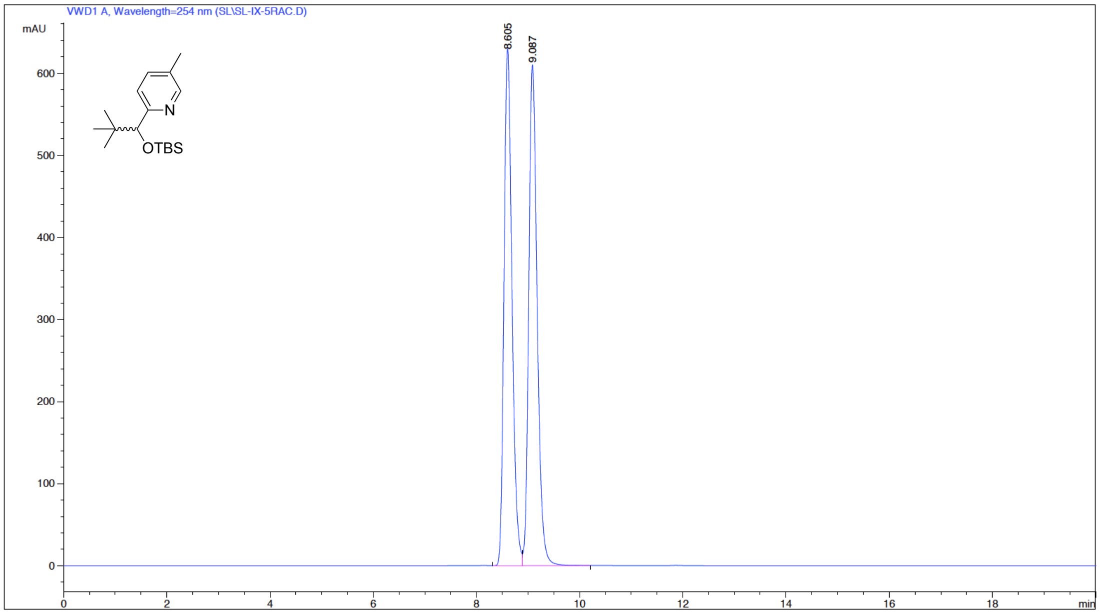
   2   9.188 VB     0.1796 1.54038e4  1351.11230  96.2882

Totals :                   1.59976e4  1406.49151
```

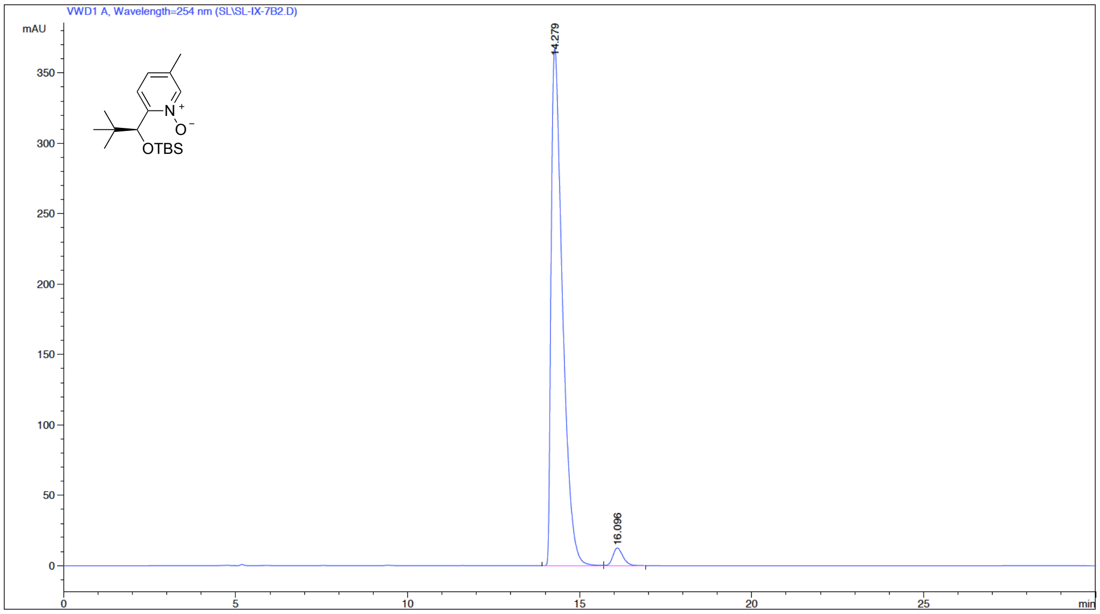
93% *ee* of (*S*)-**16**



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1   8.605 VV     0.1693 6780.62695  629.76501  49.4742
   2   9.087 VB     0.1762 6924.74316  609.69257  50.5258

Totals :                   1.37054e4  1239.45758
```

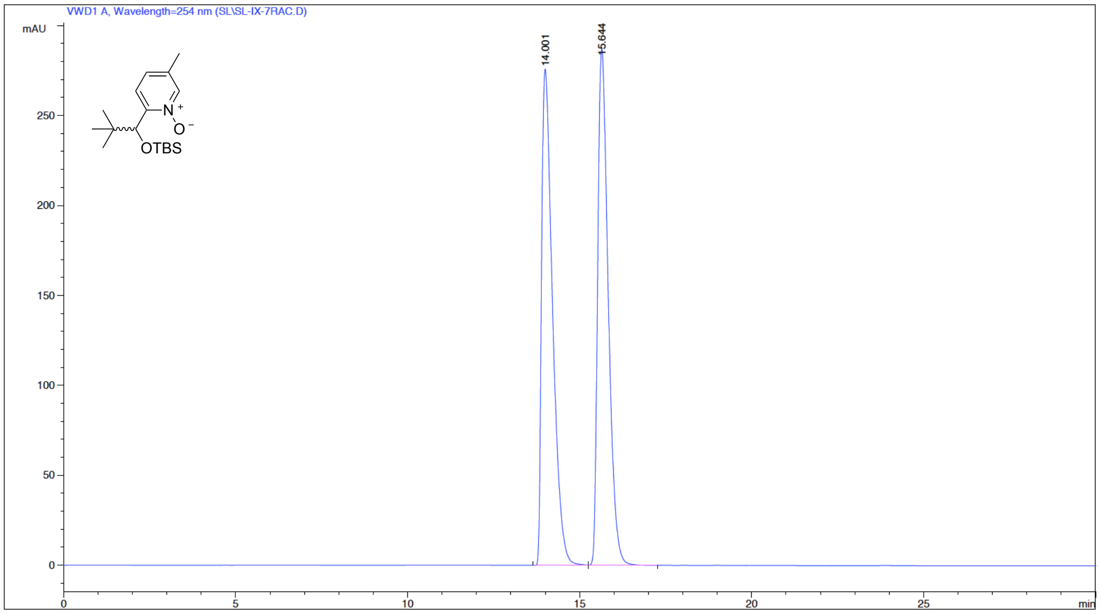
Racemate of **16**



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  14.279 BV     0.3486 8405.28418  367.18213 97.0274
   2  16.096 VB     0.3146  257.51065   12.57363  2.9726

Totals :                   8662.79483  379.75575
```

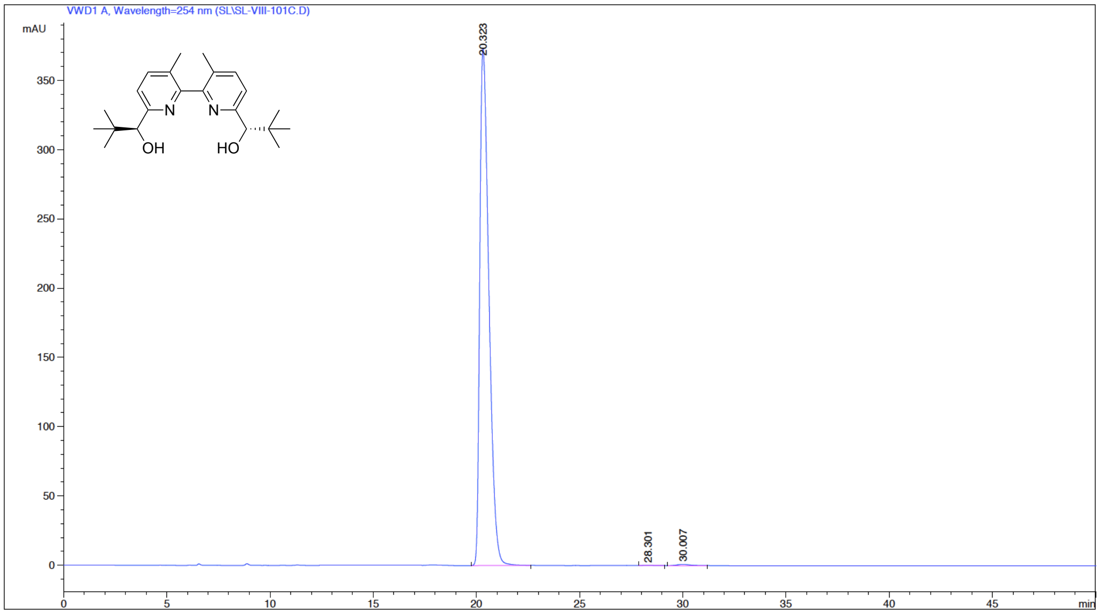
94% *ee* of (*S*)-**17**



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  14.001 BV     0.3370 6110.49414  275.93765 50.0057
   2  15.644 VB     0.3266 6109.11133  287.39175 49.9943

Totals :                   1.22196e4   563.32941
```

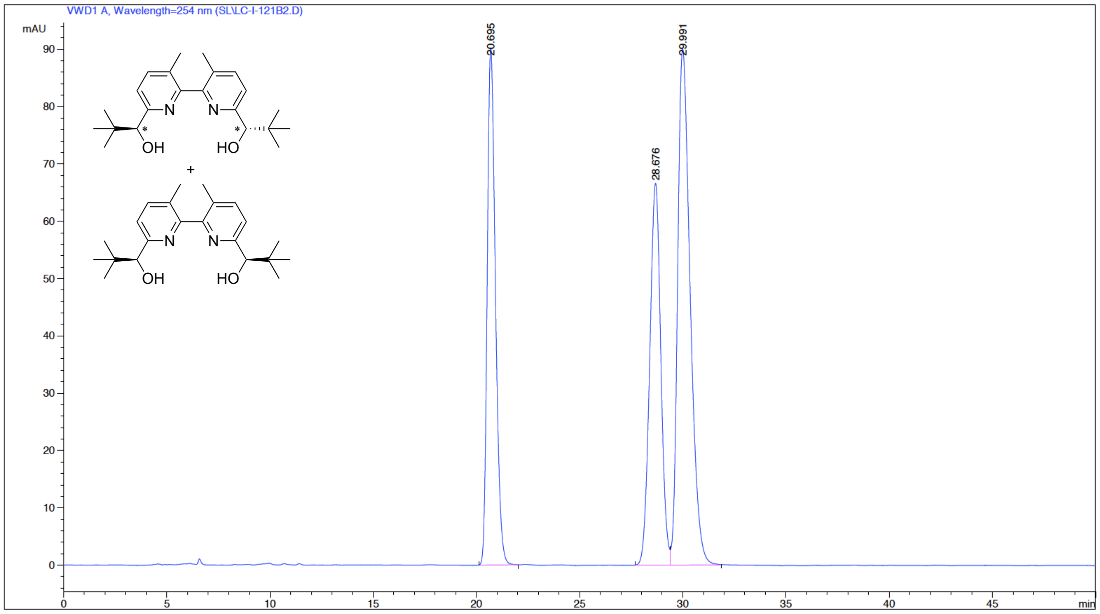
Racemate of **17**



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1  20.323 BB    0.4745 1.14535e4  373.20010 99.6148
   2  28.301 BB    0.5229    6.96210 1.75903e-1  0.0606
   3  30.007 BB    0.6732   37.32162 8.16338e-1  0.3246

Totals :                  1.14977e4  374.19234
```

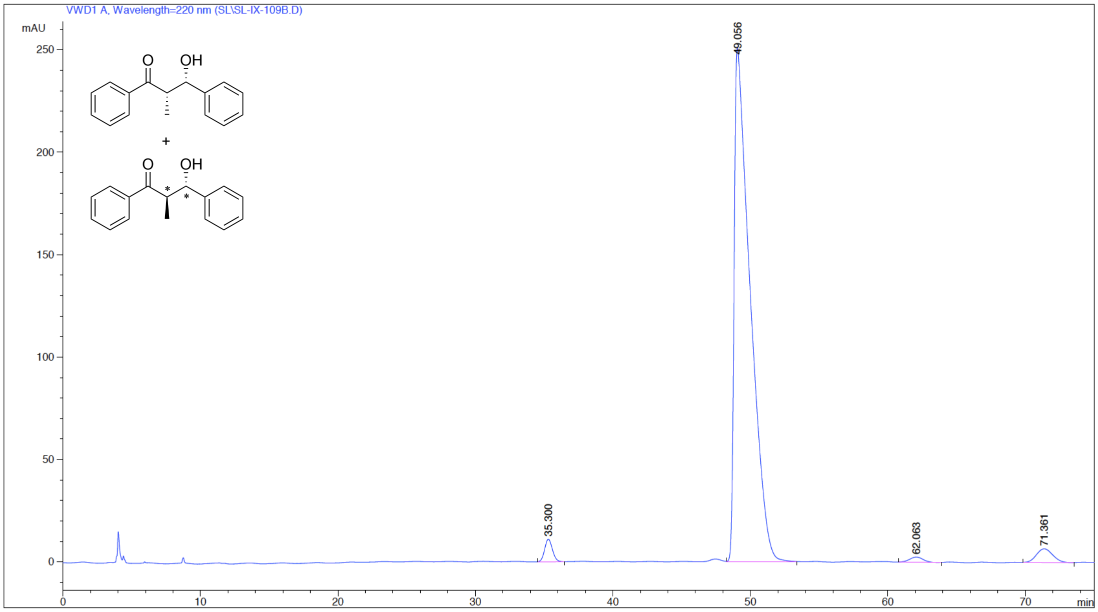
99% *de*, >99.5% *ee* of (*S*,*S*)-**12**



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1  20.695 BB    0.4274 2491.80518   90.12442 28.4234
   2  28.676 BV    0.5748 2485.19751   66.64484 28.3481
   3  29.991 VB    0.6511 3789.72876   90.05387 43.2285

Totals :                  8766.73145  246.82314
```

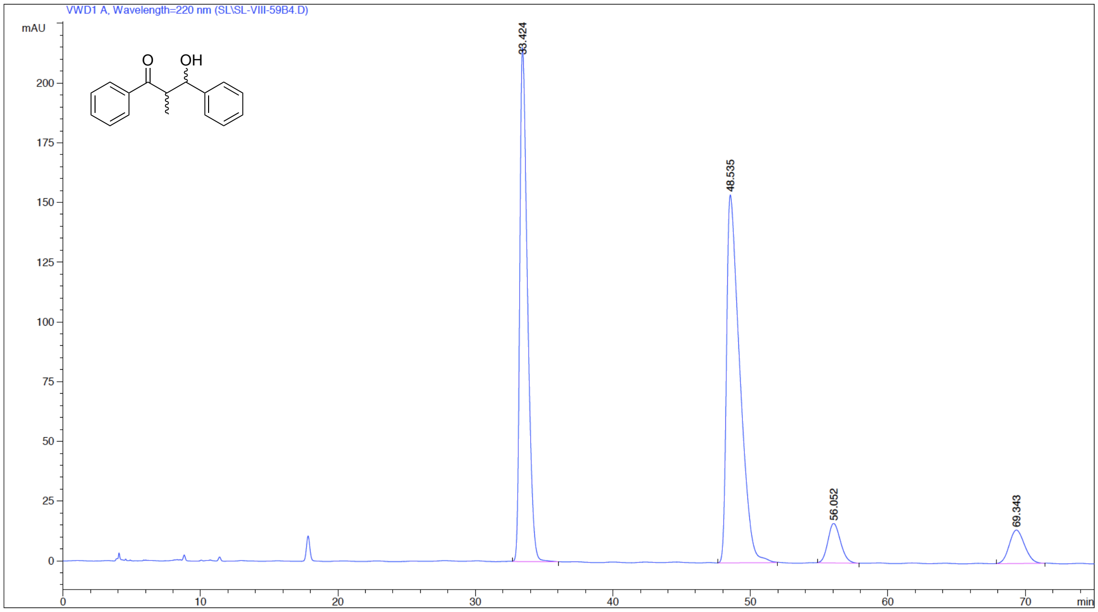
Racemate of **12**



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  35.300 BB     0.6120  435.46564   11.03047   2.0452
   2  49.056 VB     1.1347 2.01411e4  250.86353  94.5949
   3  62.063 BB     1.0172  169.34851    2.50986   0.7954
   4  71.361 BB     1.2568  546.03436    6.65765   2.5645

Totals :                  2.12919e4  271.06150
```

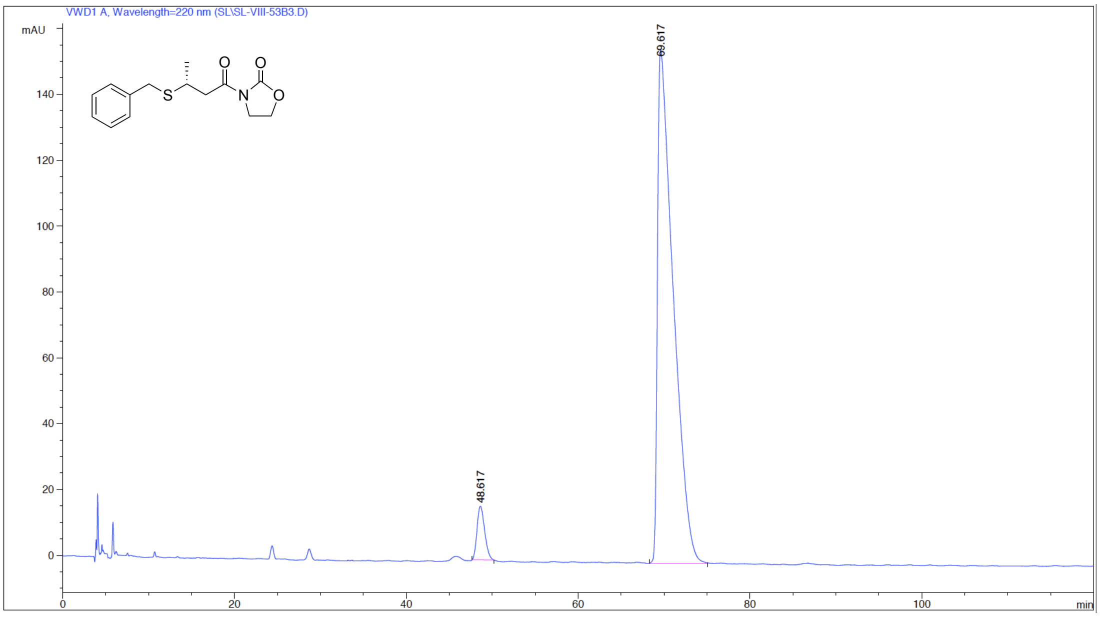
93% *de* (*syn*), 96% *ee* (*syn*, 2*S*,3*S*), 53% *ee* (*anti*) of **27**



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU    *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  33.424 BB     0.5962 8415.04883  215.10153  40.3453
   2  48.535 BB     1.0013 1.02963e4  154.00809  49.3650
   3  56.052 BB     0.9864 1056.31104   16.54786   5.0644
   4  69.343 BB     1.1995 1089.84875   14.04344   5.2252

Totals :                  2.08575e4  399.70092
```

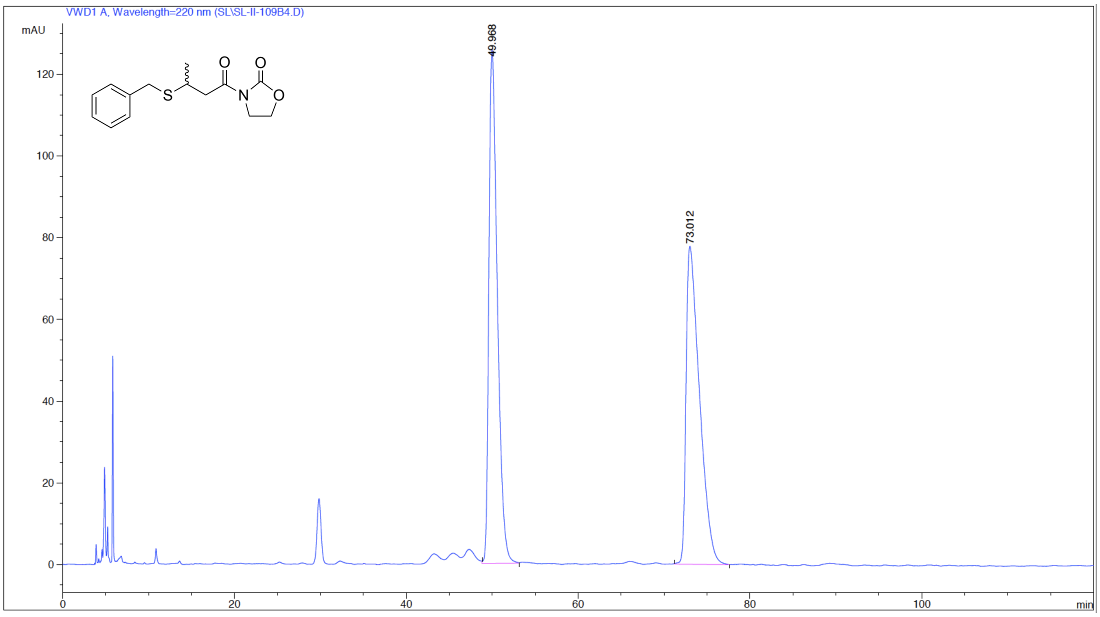
80% *de* (*syn*), racemate of **27**



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   mAU    *s  [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1  48.617 BBA    0.9686 1001.58405   16.26981   4.8342
   2  69.617 BB     1.7260 1.97173e4  155.89539  95.1658

Totals :                   2.07189e4  172.16519
```

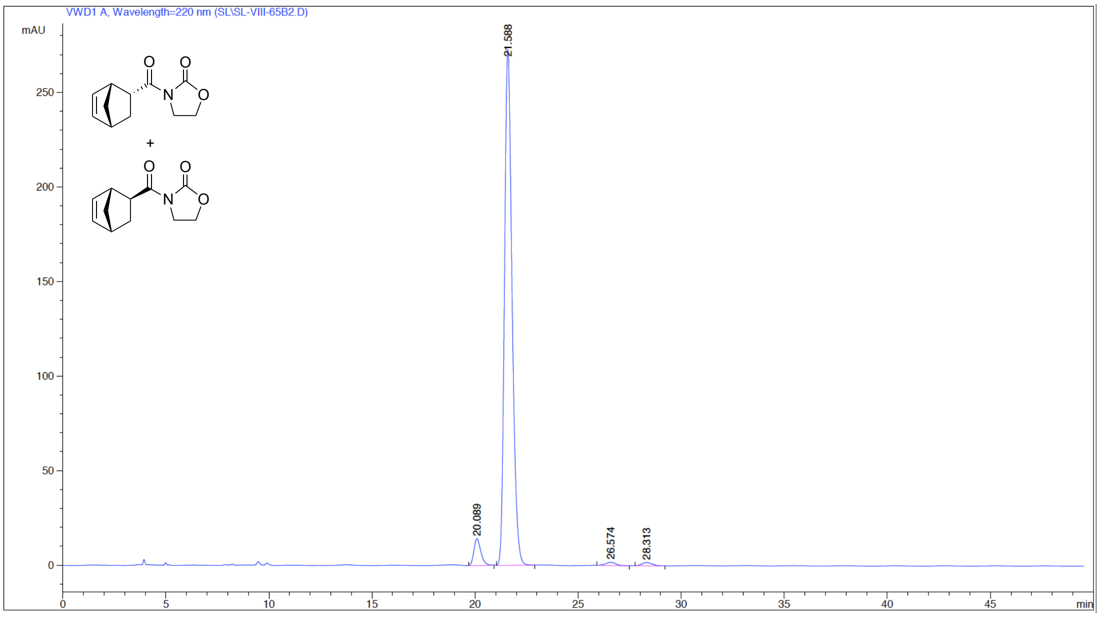
90% *ee* of (*R*)-**30**



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   mAU    *s  [mAU    ]     %
----|-------|----|-------|----------|----------|--------|
   1  49.968 VV     1.0539 8657.42969  125.70985  50.5610
   2  73.012 BB     1.5951 8465.32324   77.82642  49.4390

Totals :                   1.71228e4  203.53626
```

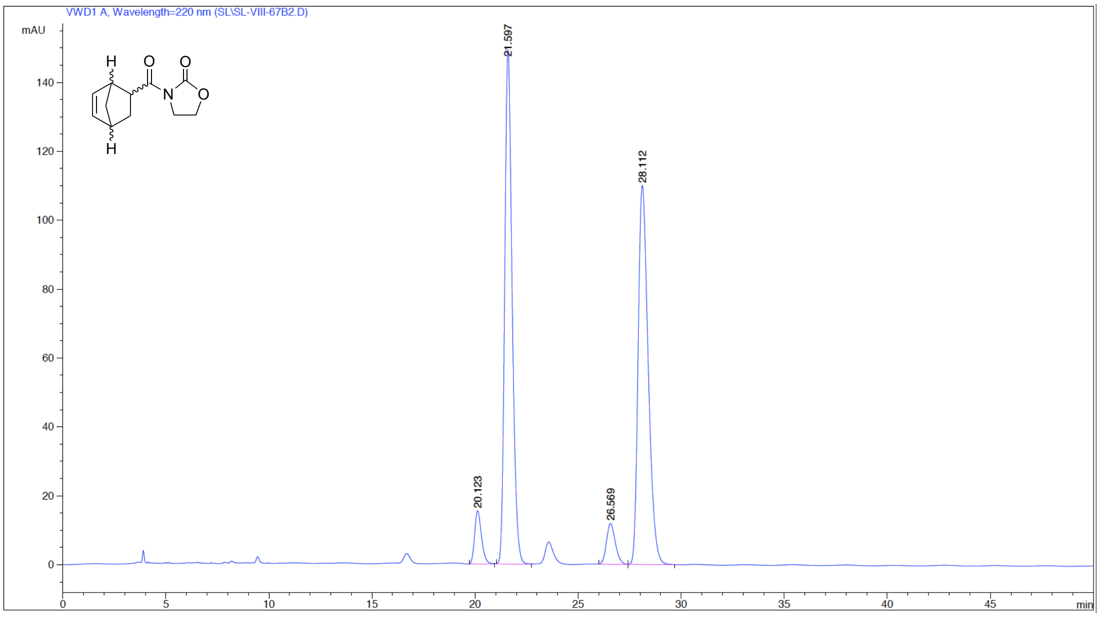
Racemate of **30**



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
  1  20.089 BB    0.3604  335.73639   14.19252   4.5183
  2  21.588 BB    0.3947 6979.44434  272.66684  93.9286
  3  26.574 BB    0.5340   57.20208    1.66827   0.7698
  4  28.313 BB    0.5154   58.20193    1.72733   0.7833

Totals :                 7430.58474  290.25495
```

89% *de* (*endo*), 98% *ee* (*endo*, 1*R*,2*R*,4*R*), 71% *ee* (*exo*, 1*R*,2*S*,4*R*) of **33**



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
  1  20.123 BB    0.3563  360.64661   15.47581   4.4076
  2  21.597 BB    0.3857 3743.47754  149.31416  45.7501
  3  26.569 BV    0.4594  354.53378   11.86197   4.3329
  4  28.112 VB    0.5230 3723.78809  110.02915  45.5095

Totals :                 8182.44601  286.68110
```

82% *de* (*endo*), racemate of **33**

Crystallographic data

X-ray structure and crystal data for (*S*$_a$,*S*,*S*)-19

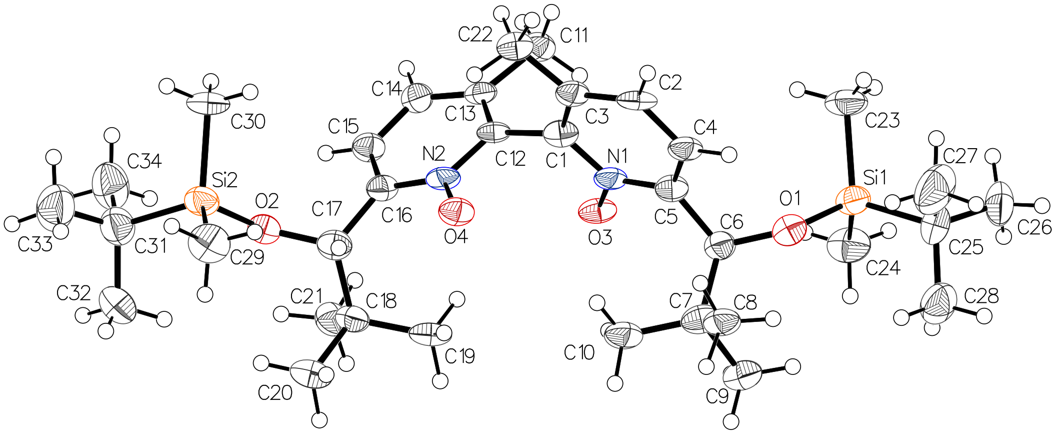


Table S1 Crystal data and structure refinement for (*S*$_a$,*S*,*S*)-19

Identification code	(*S*$_a$,*S*,*S*)-**19**
Empirical formula	$C_{17}H_{30}NO_2Si$
Formula weight	308.51
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.1449(4)
b/Å	39.232(2)
c/Å	7.1589(4)
α/°	90
β/°	109.605(3)
γ/°	90
Volume/Å^3	1890.37(19)
Z	4
ρ_{calc}g/cm^3	1.084
μ/mm^{-1}	1.121
F(000)	676.0
Crystal size/mm^3	0.17 × 0.09 × 0.01
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.504 to 140.218
Index ranges	$-8 \le h \le 8$, $-47 \le k \le 47$, $-7 \le l \le 8$
Reflections collected	7083
Independent reflections	7083 [R_{int} = ?, R_{sigma} = 0.0489]
Data/restraints/parameters	7083/7/399
Goodness-of-fit on F^2	1.067
Final R indexes [I>=2σ (I)]	R_1 = 0.0835, wR_2 = 0.2219
Final R indexes [all data]	R_1 = 0.0871, wR_2 = 0.2250
Largest diff. peak/hole / e Å^{-3}	0.85/-0.39
Flack parameter	0.04(4)

Table S2 Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2\times 10^3$) for (S_a,*S*,*S*)-19. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor

Atom	*x*	*y*	*z*	U(eq)
Si1	2966(4)	3415.9(7)	3014(4)	40.5(6)
Si2	2251(4)	6598.5(7)	3672(4)	39.9(6)
O1	1464(10)	3733.5(18)	3132(10)	40.4(15)
O2	2421(10)	6285.5(17)	2196(10)	36.8(14)
O3	3390(9)	4655.6(18)	2078(8)	35.3(14)
O4	1368(9)	5362.3(18)	4078(10)	37.8(14)
N1	3203(10)	4602(2)	3772(12)	34.9(16)
N2	3077(9)	5418(2)	3898(11)	32.4(16)
C1	3832(12)	4847(2)	5229(14)	32.5(19)
C2	3806(12)	4800(3)	7114(14)	34.3(19)
C3	3051(12)	4491(3)	7562(12)	35(2)
C4	2330(12)	4251(3)	6038(14)	36(2)
C5	2371(13)	4309(2)	4159(14)	33.4(18)
C6	1438(14)	4070(2)	2437(16)	38(2)
C7	-752(14)	4168(3)	1224(15)	41(2)
C8	-2093(13)	4075(3)	2440(16)	43(2)
C9	-1441(17)	3957(3)	-693(17)	49(3)
C10	-1000(14)	4542(3)	719(16)	44(2)
C11	4500(14)	5084(2)	8614(13)	35(2)
C12	4547(13)	5169(2)	4570(11)	29.3(17)
C13	6414(12)	5223(2)	4502(13)	31.6(18)
C14	6877(14)	5527(2)	3808(14)	37(2)
C15	5366(14)	5767(3)	3034(14)	35.7(19)
C16	3460(14)	5710(2)	3067(13)	33.6(18)
C17	1740(15)	5946(3)	2148(15)	38(2)
C18	528(14)	5854(3)	-64(15)	39(2)
C19	20(13)	5475(3)	-273(13)	40(2)
C20	-1382(16)	6061(3)	-709(17)	51(3)
C21	1791(17)	5942(3)	-1355(15)	43(2)
C22	7916(13)	4937(2)	5151(15)	37(2)
C23	5392(16)	3448(4)	5106(18)	55(3)
C24	3349(18)	3424(4)	534(16)	55(3)
C25	1540(20)	3023(3)	3310(20)	59(3)
C26	2740(30)	2704(3)	3080(30)	92(6)
C27	1210(30)	3036(5)	5290(30)	94(6)
C28	-480(18)	3009(3)	1690(20)	63(3)
C29	-172(15)	6576(3)	4150(20)	53(3)
C30	4347(15)	6569(4)	6097(16)	53(3)
C31	2461(18)	7002(3)	2290(20)	54(3)
C32	880(20)	6998(4)	210(20)	71(4)
C33	2160(30)	7312(4)	3440(30)	78(5)
C34	4540(20)	7025(4)	2070(30)	71(4)

Table S3 Anisotropic displacement parameters ($Å^2 \times 10^3$) for (S_a,S,S)-19. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	35.0(12)	46.2(14)	36.2(13)	-6.1(12)	6.5(10)	-0.8(11)
Si2	29.9(11)	45.8(15)	41.3(13)	-0.5(12)	8.6(10)	4.9(11)
O1	37(3)	44(4)	39(4)	-4(3)	12(3)	-4(3)
O2	35(3)	42(3)	33(3)	3(3)	10(3)	2(3)
O3	31(3)	55(4)	19(3)	0(3)	8(2)	-6(3)
O4	25(3)	50(4)	38(3)	4(3)	9(3)	-1(3)
N1	18(3)	44(4)	34(4)	-1(3)	-1(3)	1(3)
N2	14(3)	45(4)	36(4)	-4(3)	4(3)	1(3)
C1	16(3)	47(5)	37(5)	-2(4)	12(4)	1(3)
C2	18(4)	44(5)	38(5)	1(4)	7(4)	0(3)
C3	19(3)	64(6)	17(4)	6(4)	0(3)	-3(4)
C4	20(4)	48(5)	34(5)	4(4)	3(4)	-3(3)
C5	25(4)	42(5)	32(4)	-1(4)	8(3)	0(4)
C6	34(5)	38(5)	36(5)	2(4)	6(4)	-4(4)
C7	27(4)	58(6)	37(5)	-5(5)	11(4)	-6(4)
C8	24(4)	54(6)	44(5)	-3(4)	4(4)	0(4)
C9	43(5)	58(7)	40(6)	-8(5)	5(5)	-5(5)
C10	25(4)	58(6)	43(5)	3(5)	4(4)	-1(4)
C11	33(4)	52(6)	24(4)	-1(4)	13(3)	-3(4)
C12	29(4)	44(5)	12(3)	-2(3)	3(3)	-1(3)
C13	24(4)	40(5)	25(4)	-6(3)	0(3)	0(3)
C14	35(5)	39(5)	35(5)	-3(4)	10(4)	-1(4)
C15	30(4)	41(5)	36(5)	2(4)	10(4)	-1(4)
C16	32(4)	40(5)	26(4)	0(4)	5(3)	-2(4)
C17	36(5)	46(5)	33(5)	1(4)	11(4)	2(4)
C18	31(4)	45(6)	35(5)	3(4)	3(4)	5(4)
C19	24(4)	70(7)	23(4)	3(4)	3(3)	2(4)
C20	35(5)	68(7)	42(6)	7(5)	3(5)	10(5)
C21	50(6)	43(5)	36(5)	6(4)	16(5)	2(4)
C22	27(4)	43(6)	40(5)	6(4)	10(4)	0(4)
C23	32(5)	70(8)	48(6)	-2(6)	-5(4)	0(5)
C24	52(6)	75(8)	40(5)	-15(6)	17(5)	13(6)
C25	67(8)	33(6)	70(8)	-4(5)	13(7)	-11(5)
C26	78(10)	31(6)	137(17)	-5(8)	-4(10)	2(6)
C27	126(15)	73(10)	79(11)	3(9)	28(11)	-49(10)
C28	47(6)	52(7)	89(10)	-8(7)	21(7)	-10(5)
C29	30(4)	68(7)	72(7)	-4(6)	30(5)	7(5)
C30	32(5)	73(8)	37(5)	2(5)	-10(4)	2(5)
C31	50(6)	47(6)	63(7)	8(5)	17(6)	0(5)
C32	77(9)	55(8)	65(8)	19(6)	1(7)	6(6)

Table S4 Bond lengths for (S_a,S,S)-19

Atom	Atom	Length (Å)
Si1	O1	1.665(7)
Si1	C23	1.876(10)
C5	C6	1.514(13)
C6	C7	1.561(13)

Si1	C24	1.885(11)
Si1	C25	1.901(12)
Si2	O2	1.650(7)
Si2	C29	1.875(9)
Si2	C30	1.878(10)
Si2	C31	1.899(12)
O1	C6	1.407(12)
O2	C17	1.414(12)
O3	N1	1.281(10)
O4	N2	1.289(9)
N1	C1	1.380(12)
N1	C5	1.365(13)
N2	C12	1.398(12)
N2	C16	1.360(13)
C1	C2	1.369(14)
C1	C12	1.494(11)
C2	C3	1.407(13)
C2	C11	1.511(13)
C3	C4	1.402(13)
C4	C5	1.374(13)
C7	C8	1.539(14)
C7	C9	1.535(14)
C7	C10	1.510(16)
C12	C13	1.368(12)
C13	C14	1.375(13)
C13	C22	1.515(12)
C14	C15	1.400(13)
C15	C16	1.388(13)
C16	C17	1.503(13)
C17	C18	1.572(13)
C18	C19	1.524(16)
C18	C20	1.521(14)
C18	C21	1.533(14)
C25	C26	1.56(2)
C25	C27	1.51(2)
C25	C28	1.520(19)
C31	C32	1.537(19)
C31	C33	1.53(2)
C31	C34	1.548(19)

Table S5 Bond Angles for (*S*$_a$,*S*,*S*)-19

Atom	Atom	Atom	Angle (˚)
O1	Si1	C23	110.4(5)
O1	Si1	C24	109.6(5)
O1	Si1	C25	102.9(5)
C23	Si1	C24	111.3(6)
C23	Si1	C25	110.5(6)
C24	Si1	C25	111.9(6)
O2	Si2	C29	110.5(5)
O2	Si2	C30	109.8(5)
O2	Si2	C31	104.5(5)
C29	Si2	C30	109.1(6)
C29	Si2	C31	111.9(6)
C30	Si2	C31	110.8(6)
C6	O1	Si1	128.0(6)
C17	O2	Si2	128.1(6)
O3	N1	C1	119.2(8)
O3	N1	C5	121.5(8)
C5	N1	C1	119.3(8)
O4	N2	C12	118.3(8)
O4	N2	C16	121.6(8)
C16	N2	C12	120.1(7)
N1	C1	C12	114.2(8)
C2	C1	N1	122.7(9)
C2	C1	C12	123.0(9)
C1	C2	C3	118.4(9)
C1	C2	C11	119.4(9)
C9	C7	C8	107.7(9)
C10	C7	C6	112.9(8)
C10	C7	C8	108.6(9)
C10	C7	C9	109.5(9)
N2	C12	C1	113.7(8)
C13	C12	N2	120.6(8)
C13	C12	C1	125.7(8)
C12	C13	C14	120.2(8)
C12	C13	C22	118.2(8)
C14	C13	C22	121.5(8)
C13	C14	C15	118.7(9)
C16	C15	C14	121.0(9)
N2	C16	C15	119.1(8)
N2	C16	C17	117.1(8)
C15	C16	C17	123.7(9)
O2	C17	C16	110.2(8)
O2	C17	C18	108.1(8)
C16	C17	C18	113.1(8)
C19	C18	C17	110.9(8)
C19	C18	C21	109.3(8)
C20	C18	C17	108.5(9)
C20	C18	C19	109.3(9)
C20	C18	C21	110.2(9)
C21	C18	C17	108.6(8)
C26	C25	Si1	107.6(11)

C3	C2	C11	122.2(8)
C4	C3	C2	118.1(8)
C5	C4	C3	121.9(9)
N1	C5	C4	119.4(9)
N1	C5	C6	117.4(8)
C4	C5	C6	123.1(9)
O1	C6	C5	110.0(8)
O1	C6	C7	108.7(8)
C5	C6	C7	112.7(8)
C8	C7	C6	109.0(9)
C9	C7	C6	109.0(9)
C27	C25	Si1	109.6(9)
C27	C25	C26	113.2(15)
C27	C25	C28	108.2(14)
C28	C25	Si1	110.5(10)
C28	C25	C26	107.8(12)
C32	C31	Si2	109.7(9)
C32	C31	C34	108.6(13)
C33	C31	Si2	109.3(11)
C33	C31	C32	109.9(12)
C33	C31	C34	109.0(11)
C34	C31	Si2	110.3(9)

Table S6 Torsion angles for (S_a,*S*,*S*)-19

A	B	C	D	Angle (˚)
Si1	O1	C6	C5	-104.0(9)
Si1	O1	C6	C7	132.2(7)
Si2	O2	C17	C16	-104.9(8)
Si2	O2	C17	C18	131.1(7)
O1	C6	C7	C8	49.0(11)
O1	C6	C7	C9	-68.4(11)
O1	C6	C7	C10	169.7(8)
O2	Si2	C31	C32	54.9(10)
O2	Si2	C31	C33	175.5(9)
O2	Si2	C31	C34	-64.7(11)
O2	C17	C18	C19	171.3(7)
O2	C17	C18	C20	-68.7(10)
O2	C17	C18	C21	51.1(10)
O3	N1	C1	C2	-175.5(8)
O3	N1	C1	C12	4.4(11)
O3	N1	C5	C4	175.4(8)
O3	N1	C5	C6	-7.7(12)
O4	N2	C12	C1	6.2(11)
O4	N2	C12	C13	-176.7(8)
O4	N2	C16	C15	175.6(8)
O4	N2	C16	C17	-7.1(12)
N1	C1	C2	C3	-1.9(13)
N1	C1	C2	C11	-179.3(8)
N1	C1	C12	N2	93.3(8)
N1	C1	C12	C13	-83.6(12)
N1	C5	C6	O1	153.8(8)
N1	C5	C6	C7	-84.8(10)
N2	C12	C13	C14	1.3(12)
N2	C12	C13	C22	-176.9(8)
N2	C16	C17	O2	152.8(8)
N2	C16	C17	C18	-86.1(10)
C1	N1	C5	C4	-5.5(12)
C1	N1	C5	C6	171.5(8)
C1	C2	C3	C4	-1.2(12)
C3	C4	C5	N1	2.5(13)
C3	C4	C5	C6	-174.3(8)
C4	C5	C6	O1	-29.4(12)
C4	C5	C6	C7	92.0(11)
C5	N1	C1	C2	5.3(12)
C5	N1	C1	C12	-174.8(7)
C5	C6	C7	C8	-73.2(11)
C5	C6	C7	C9	169.5(9)
C5	C6	C7	C10	47.6(12)
C11	C2	C3	C4	176.1(8)
C12	N2	C16	C15	-4.8(13)
C12	N2	C16	C17	172.5(8)
C12	C1	C2	C3	178.3(8)
C12	C1	C2	C11	0.8(13)
C12	C13	C14	C15	-4.9(13)
C13	C14	C15	C16	3.7(14)
C14	C15	C16	N2	1.2(14)
C14	C15	C16	C17	-176.0(9)
C15	C16	C17	O2	-30.0(13)
C15	C16	C17	C18	91.1(11)
C16	N2	C12	C1	-173.4(8)
C16	N2	C12	C13	3.7(12)
C16	C17	C18	C19	49.0(11)
C16	C17	C18	C20	169.0(9)
C16	C17	C18	C21	-71.2(10)
C22	C13	C14	C15	173.3(9)
C23	Si1	O1	C6	82.6(9)
C24	Si1	O1	C6	-40.3(9)
C25	Si1	O1	C6	-159.5(9)
C29	Si2	O2	C17	-37.0(9)
C29	Si2	C31	C32	-64.7(11)
C29	Si2	C31	C33	55.8(11)
C29	Si2	C31	C34	175.7(10)
C30	Si2	O2	C17	83.5(9)

C1	C12	C13	C14	178.0(9)	C30	Si2	C31	C32	173.1(10)
C1	C12	C13	C22	-0.2(13)	C30	Si2	C31	C33	-66.3(11)
C2	C1	C12	N2	-86.9(11)	C30	Si2	C31	C34	53.6(12)
C2	C1	C12	C13	96.3(10)	C31	Si2	O2	C17	-157.6(8)
C2	C3	C4	C5	0.9(13)					

Table S7 Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for (*S*$_a$,*S*,*S*)-19

Atom	*x*	*y*	*z*	U(eq)
H3	3030.72	4446.4	8859.46	42
H4	1796.97	4042.34	6312.3	43
H6	2239.96	4077.64	1530.47	45
H8A	-1585.92	4184.93	3743.46	64
H8B	-2099.22	3827.38	2609.88	64
H8C	-3449.57	4154.41	1741.28	64
H9A	-582.62	4005.57	-1478.48	74
H9B	-2815.81	4016.79	-1461.42	74
H9C	-1364.14	3713.73	-361.97	74
H10A	-704.04	4675.77	1942.09	66
H10B	-2370.98	4586.44	-133.15	66
H10C	-87.03	4608.2	21.84	66
H11A	5870.2	5145.7	8755.44	53
H11B	4443.23	5007.49	9897.32	53
H11C	3637.56	5283.07	8163.73	53
H14	8196.13	5573.39	3851.78	44
H15	5648.52	5972.8	2478.66	43
H17	824.75	5933.83	2940.4	46
H19A	-758.3	5424.16	-1656.27	60
H19B	-756.21	5416.49	579.48	60
H19C	1249.45	5341.15	123.79	60
H20A	-1060.65	6303.96	-523.08	76
H20B	-2200.23	5995.54	91.49	76
H20C	-2116.96	6016.27	-2111.81	76
H21A	3075.54	5825.73	-839.25	64
H21B	2005.29	6189.18	-1329.91	64
H21C	1099.38	5868.57	-2721.71	64
H22A	8127.71	4879.3	6539.72	56
H22B	9176.68	5009.31	5015.63	56
H22C	7416.51	4735.77	4318.77	56
H23A	6383.74	3303.96	4818.4	82
H23B	5213.51	3370.99	6337.48	82
H23C	5846.28	3685.14	5253.44	82
H24A	4056.78	3632.38	421.19	83
H24B	2056.36	3417.85	-527.59	83
H24C	4133.32	3224.7	420.28	83
H26A	4146.36	2734.25	3876.25	138
H26B	2618.71	2676.61	1681.06	138
H26C	2224.1	2500.42	3530.66	138

H27A	2497.1	3027.9	6362.64	141
H27B	404.13	2840.03	5406.71	141
H27C	520.92	3247.31	5385.48	141
H28A	-1116.64	2789.61	1748.54	95
H28B	-309.23	3032.95	393.31	95
H28C	-1315.3	3194.52	1878.08	95
H29A	-1271.21	6594.84	2886.09	80
H29B	-247.36	6762.54	5025.05	80
H29C	-264.06	6357.11	4773.63	80
H30A	4366.94	6774.57	6882.34	79
H30B	5609.69	6549.15	5847.34	79
H30C	4158.34	6368.24	6828.41	79
H32A	802.17	6769.47	-363.3	107
H32B	1251.74	7162.28	-642.56	107
H32C	-410.25	7061.09	300.22	107
H33A	872.51	7292.88	3649.07	117
H33B	2175.66	7519.25	2686.47	117
H33C	3224	7321.75	4727.02	117
H34A	5562.98	7020.52	3383.34	106
H34B	4642.08	7237.35	1391.02	106
H34C	4728.35	6830.41	1288.35	106

X-ray structure and crystal data for $[(S,S)\text{-}12\cdot\text{Fe}\cdot\text{DME}\cdot\text{H}_2\text{O}]^{2+}\cdot 2\text{ClO}_4^{-}$

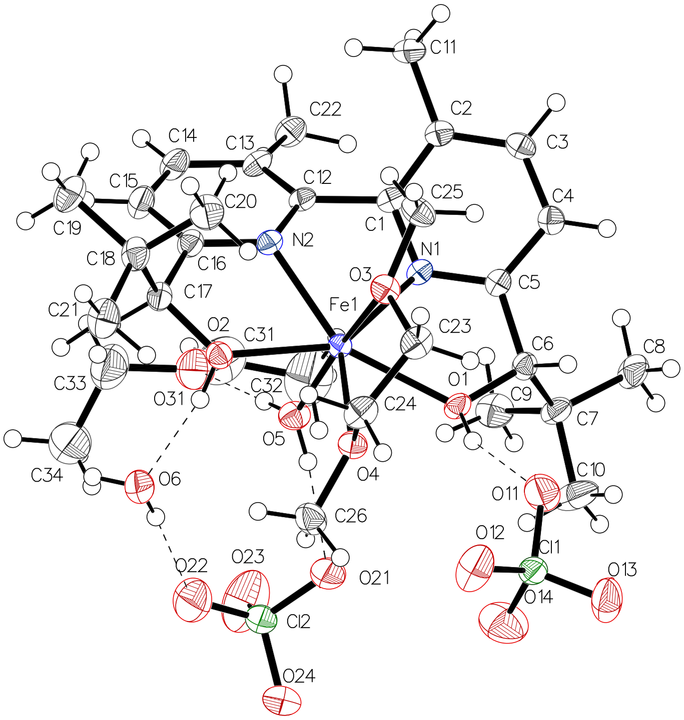


Table S8 Crystal data and structure refinement for $[(S,S)\text{-}12\cdot\text{Fe}\cdot\text{DME}\cdot\text{H}_2\text{O}]^{2+}\cdot 2\text{ClO}_4^{-}$

Identification code	$[(S,S)\text{-}\mathbf{12}\cdot\text{Fe}\cdot\text{DME}\cdot\text{H}_2\text{O}]^{2+}\cdot 2\text{ClO}_4^{-}$
Empirical formula	$C_{30}H_{55}Cl_2FeN_2O_{15}$
Formula weight	810.51
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.8528(6)
b/Å	11.1751(5)
c/Å	16.1835(8)
α/°	90
β/°	90.483(3)
γ/°	90
Volume/Å^3	1962.68(17)
Z	2
ρ_{calc}g/cm^3	1.371
μ/mm^{-1}	4.903
F(000)	858.0
Crystal size/mm^3	0.35 × 0.07 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.46 to 140.284
Index ranges	$-13 \leq h \leq 13$, $-13 \leq k \leq 13$, $-19 \leq l \leq 19$
Reflections collected	54206
Independent reflections	7289 [R_{int} = 0.0277, R_{sigma} = 0.0152]
Data/restraints/parameters	7289/9/482

Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	$R_1 = 0.0303$, $wR_2 = 0.0832$
Final R indexes [all data]	$R_1 = 0.0305$, $wR_2 = 0.0835$
Largest diff. peak/hole / e Å^{-3}	0.58/-0.22
Flack parameter	0.000(3)

Table S9 Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2\times 10^3$) for [(*S*,*S*)-12·Fe·DME·H_2O]$^{2+}$·2ClO_4^-. U_{eq} is defined as 1/3 of of the trace of the orthogonalized U_{IJ} tensor

Atom	*x*	*y*	*z*	U(eq)
Fe1	2892.2(4)	5848.4(4)	2172.0(2)	16.66(11)
O1	1685.6(18)	4303.3(17)	1787.6(13)	21.9(4)
O2	4708.6(18)	6412.6(19)	2652.4(12)	21.5(4)
O3	3445.8(19)	6092.9(19)	904.6(12)	23.3(4)
O4	4115.5(19)	4245.0(19)	1880.2(13)	23.6(4)
O5	2524(2)	5403(2)	3404.6(13)	26.2(4)
N1	995(2)	6469(2)	1853.3(15)	18.4(5)
N2	2812(2)	7784(2)	2467.3(15)	19.5(5)
C1	820(3)	7670(2)	1877.3(17)	18.6(5)
C2	20(3)	8260(3)	1333.2(18)	20.5(6)
C3	-659(3)	7538(3)	792.0(18)	22.3(6)
C4	-548(3)	6308(3)	800.2(18)	21.7(6)
C5	302(2)	5797(3)	1348.6(16)	18.8(5)
C6	499(3)	4467(3)	1410.5(18)	21.6(6)
C7	-525(3)	3815(3)	1911(2)	26.6(6)
C8	-1756(3)	3897(3)	1443(2)	34.9(8)
C9	-652(3)	4357(3)	2768(2)	35.7(8)
C10	-164(4)	2494(3)	1972(3)	46.9(10)
C11	-98(3)	9597(3)	1274(2)	26.0(6)
C12	1668(3)	8270(2)	2476.0(18)	20.0(5)
C13	1341(3)	9172(3)	3030.7(19)	23.5(6)
C14	2305(3)	9678(3)	3493(2)	29.2(7)
C15	3493(3)	9257(3)	3430(2)	29.2(7)
C16	3711(3)	8274(3)	2926.7(18)	22.5(6)
C17	4943(3)	7627(3)	2901.4(18)	22.0(6)
C18	5933(3)	8194(3)	2336(2)	28.6(7)
C19	6220(3)	9465(3)	2625(2)	37.3(8)
C20	5505(3)	8210(4)	1433(2)	36.1(8)
C21	7097(3)	7423(3)	2432(2)	34.9(7)
C22	36(3)	9535(3)	3201(2)	27.4(6)
C23	3963(3)	5046(3)	524.8(19)	28.0(6)
C24	4808(3)	4468(3)	1148(2)	28.4(6)
C25	2918(3)	6908(3)	321.1(19)	28.9(7)
C26	4785(3)	3523(3)	2464(2)	32.5(7)
Cl1	3181.3(6)	1279.3(6)	944.1(5)	25.34(16)
O11	2434(3)	2342(3)	797.2(18)	45.0(7)
O12	4455(3)	1569(3)	890(2)	49.7(7)
O13	2838(3)	341(3)	400(2)	59.3(9)

O14	2953(3)	901(4)	1782(2)	60.9(8)
Cl2	2930.6(8)	2991.6(7)	4848.2(5)	32.25(18)
O21	2398(4)	3114(3)	4040.1(18)	56.0(9)
O22	4077(3)	3610(3)	4903(2)	59.6(9)
O23	2124(4)	3501(4)	5427(3)	77.2(12)
O24	3081(3)	1744(3)	5002(2)	59.6(9)
O6	5562(3)	5239(2)	3962.9(17)	45.8(7)
O31	2046(3)	6919(3)	4667.5(17)	50.6(7)
C31	865(5)	7028(5)	5005(3)	63.2(13)
C32	12(5)	6231(6)	4516(4)	72.6(16)
C33	3028(6)	7495(5)	5139(3)	64.8(14)
C34	3430(6)	6775(5)	5873(3)	70.0(15)

Table S10 Anisotropic displacement parameters (Å^2×10^3) for [(*S*,*S*)-12·Fe·DME·H$_2$O]$^{2+}$·2ClO$_4^-$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe1	15.8(2)	16.44(19)	17.73(19)	-0.86(16)	0.86(14)	0.52(16)
O1	18.0(10)	15.2(9)	32.6(11)	-4.1(8)	-0.8(8)	2.3(7)
O2	19.6(9)	22.9(10)	22.1(9)	0.6(8)	-1.4(8)	0.3(8)
O3	24.7(10)	26.0(12)	19.2(9)	-1.4(8)	2.9(8)	3.0(8)
O4	20.1(10)	23.0(10)	27.6(10)	-1.7(8)	0.1(8)	5.1(8)
O5	32.4(11)	25.1(10)	21.4(10)	1.7(8)	4.4(9)	-0.3(9)
N1	17.1(11)	16.5(11)	21.6(11)	-1.3(9)	3.6(9)	-0.7(9)
N2	21.1(12)	17.3(11)	20.1(11)	0.7(9)	1.7(9)	-1.5(9)
C1	17.7(13)	17.2(13)	20.9(13)	-0.1(10)	4.8(11)	0.6(10)
C2	17.8(13)	19.6(13)	24.3(14)	2.0(11)	4.9(11)	-0.1(10)
C3	19.0(13)	26.1(14)	21.8(13)	3.2(11)	2.2(11)	3.8(11)
C4	17.9(13)	24.2(13)	23.0(13)	-1.8(11)	1.2(11)	1.2(11)
C5	16.5(12)	19.9(12)	20.1(12)	-2.1(11)	3.7(10)	-0.7(11)
C6	17.8(13)	20.5(14)	26.5(14)	-3.6(11)	-1.1(11)	0.4(11)
C7	20.4(14)	18.4(14)	40.9(17)	1.5(12)	1.5(13)	-1.6(11)
C8	21.4(15)	28.8(16)	55(2)	0.0(15)	-1.0(15)	-7.2(12)
C9	30.4(17)	39.2(19)	37.7(18)	8.0(15)	9.1(14)	-4.0(14)
C10	31.7(19)	23.4(17)	86(3)	11.6(19)	10(2)	-0.2(14)
C11	26.8(15)	19.4(14)	31.8(16)	5.4(11)	2.2(12)	2.9(12)
C12	21.2(13)	15.9(12)	23.1(13)	2.1(10)	1.8(11)	-1.9(10)
C13	27.6(15)	15.9(13)	27.2(14)	-2.5(11)	2.4(12)	-0.8(11)
C14	33.5(17)	21.2(14)	32.9(16)	-7.9(12)	0.5(13)	-1.2(12)
C15	28.7(16)	25.6(15)	33.2(16)	-7.1(13)	-2.2(13)	-4.0(12)
C16	23.1(14)	21.2(14)	23.2(14)	-0.2(11)	0.4(11)	-4.0(11)
C17	22.0(14)	23.1(14)	20.9(13)	-1.2(11)	-0.5(11)	-3.4(11)
C18	22.4(15)	33.6(17)	29.9(16)	0.4(13)	1.1(12)	-7.6(13)
C19	34.0(18)	31.9(18)	46(2)	0.2(15)	1.9(15)	-14.1(15)
C20	36.0(18)	43(2)	29.3(17)	8.3(15)	3.7(14)	-12.9(15)
C21	20.0(15)	43.0(19)	41.6(18)	-5.3(15)	5.8(13)	-4.1(14)
C22	28.9(16)	23.2(14)	30.1(15)	-4.7(12)	4.5(12)	1.1(12)
C23	32.7(16)	28.5(15)	22.9(14)	-4.5(12)	8.5(12)	-0.1(13)
C24	22.1(14)	26.1(15)	37.3(16)	-4.7(13)	8.5(12)	3.1(12)

C25	25.4(15)	38.6(18)	22.8(14)	8.4(13)	2.1(12)	3.5(13)
C26	32.5(17)	32.0(17)	32.8(16)	-4.9(13)	-6.5(14)	10.0(13)
Cl1	21.0(3)	22.3(3)	32.7(4)	0.1(3)	-1.3(3)	1.6(2)
O11	47.8(15)	40.7(14)	46.4(15)	-11.9(12)	-11.6(12)	15.5(12)
O12	30.8(13)	46.5(17)	72(2)	-21.6(14)	8.6(13)	-1.5(11)
O13	43.4(16)	46.5(17)	88(2)	-34.0(17)	-28.5(16)	15.4(14)
O14	64.1(19)	68(2)	50.2(16)	20.3(18)	5.5(14)	-2.2(18)
Cl2	40.4(4)	28.8(4)	27.5(4)	5.9(3)	-5.2(3)	-3.1(3)
O21	91(2)	36.5(14)	39.8(15)	12.1(12)	-26.3(15)	-13.3(15)
O22	47.6(17)	62(2)	69(2)	12.2(17)	-9.8(15)	-19.1(15)
O23	75(2)	84(3)	73(2)	-36(2)	25(2)	-11(2)
O24	72(2)	34.0(15)	72(2)	14.2(14)	-35.0(18)	0.0(14)
O6	63.0(18)	35.4(14)	38.5(14)	5.0(11)	-22.1(13)	-12.3(13)
O31	71(2)	44.8(16)	35.9(14)	-8.2(12)	-1.9(14)	4.0(15)
C31	81(4)	57(3)	51(3)	-15(2)	20(2)	4(3)
C32	48(3)	80(4)	90(4)	-32(3)	15(3)	11(3)
C33	93(4)	55(3)	46(2)	-1(2)	-12(2)	-23(3)
C34	100(4)	56(3)	54(3)	8(2)	-18(3)	-13(3)

Table S11 Bond lengths for [(*S*,*S*)-12·Fe·DME·H2O]$^{2+}$·2ClO$_4^-$

Atom	Atom	Length (Å)
Fe1	O1	2.252(2)
Fe1	O2	2.205(2)
Fe1	O3	2.160(2)
Fe1	O4	2.282(2)
Fe1	O5	2.098(2)
Fe1	N1	2.229(2)
Fe1	N2	2.218(2)
O1	C6	1.432(3)
O2	C17	1.438(4)
O3	C23	1.438(4)
O3	C25	1.428(4)
O4	C24	1.430(4)
O4	C26	1.435(4)
N1	C1	1.356(4)
N1	C5	1.337(4)
N2	C12	1.355(4)
N2	C16	1.339(4)
C1	C2	1.397(4)
C1	C12	1.490(4)
C2	C3	1.396(4)
C2	C11	1.502(4)
C3	C4	1.380(4)
C4	C5	1.397(4)
C5	C6	1.504(4)
C6	C7	1.562(4)
C7	C8	1.533(4)
C7	C9	1.521(5)
C7	C10	1.529(5)
C12	C13	1.398(4)
C13	C14	1.401(4)
C13	C22	1.501(4)
C14	C15	1.377(5)
C15	C16	1.390(4)
C16	C17	1.520(4)
C17	C18	1.553(4)
C18	C19	1.527(5)
C18	C20	1.530(5)
C18	C21	1.536(5)
C23	C24	1.504(5)
Cl1	O11	1.456(3)
Cl1	O12	1.423(3)
Cl1	O13	1.417(3)
Cl1	O14	1.444(3)
Cl2	O21	1.432(3)
Cl2	O22	1.425(3)
Cl2	O23	1.408(4)
Cl2	O24	1.425(3)
O31	C31	1.403(6)
O31	C33	1.455(6)
C31	C32	1.504(8)
C33	C34	1.496(7)

Table S12 Bond angles for [(*S*,*S*)-12·Fe·DME·H_2O]$^{2+}$·2ClO_4^-

Atom	Atom	Atom	Angle (˚)
O1	Fe1	O4	71.25(7)
O2	Fe1	O1	146.39(8)
O2	Fe1	O4	77.15(8)
O2	Fe1	N1	144.49(9)
O2	Fe1	N2	71.44(8)
O3	Fe1	O1	90.02(8)
O3	Fe1	O2	92.50(8)
O3	Fe1	O4	74.68(8)
O3	Fe1	N1	90.27(8)
O3	Fe1	N2	95.33(8)
O5	Fe1	O1	88.05(8)
O5	Fe1	O2	84.80(8)
O5	Fe1	O3	171.91(8)
O5	Fe1	O4	97.27(8)
O5	Fe1	N1	96.36(9)
O5	Fe1	N2	91.05(9)
N1	Fe1	O1	68.94(8)
N1	Fe1	O4	137.25(8)
N2	Fe1	O1	141.62(8)
N2	Fe1	O4	146.59(9)
N2	Fe1	N1	73.05(9)
C6	O1	Fe1	122.57(16)
C17	O2	Fe1	121.61(17)
C23	O3	Fe1	114.58(17)
C25	O3	Fe1	126.54(18)
C25	O3	C23	113.1(2)
C24	O4	Fe1	110.21(17)
C24	O4	C26	112.1(2)
C26	O4	Fe1	126.66(18)
C1	N1	Fe1	115.50(19)
C5	N1	Fe1	118.71(19)
C5	N1	C1	119.7(2)
C12	N2	Fe1	115.49(18)
C16	N2	Fe1	119.22(19)
C16	N2	C12	119.6(2)
N1	C1	C2	122.4(3)
N1	C1	C12	112.2(2)
C2	C1	C12	125.1(3)
C1	C2	C11	124.2(3)
C3	C2	C1	116.4(3)
C3	C2	C11	119.4(3)
C4	C3	C2	121.6(3)
C3	C4	C5	118.1(3)
N1	C5	C4	121.6(3)
N1	C5	C6	115.8(2)
C4	C5	C6	122.6(3)
O1	C6	C5	106.4(2)
O1	C6	C7	111.1(2)
C5	C6	C7	113.2(2)
C8	C7	C6	109.7(3)
C9	C7	C6	110.9(3)
C9	C7	C8	110.0(3)
C9	C7	C10	110.5(3)
C10	C7	C6	107.5(3)
C10	C7	C8	108.1(3)
N2	C12	C1	112.0(2)
N2	C12	C13	122.2(3)
C13	C12	C1	125.7(3)
C12	C13	C14	116.2(3)
C12	C13	C22	123.9(3)
C14	C13	C22	119.6(3)
C15	C14	C13	121.2(3)
C14	C15	C16	118.5(3)
N2	C16	C15	121.5(3)
N2	C16	C17	115.3(3)
C15	C16	C17	123.1(3)
O2	C17	C16	107.6(2)
O2	C17	C18	110.0(2)
C16	C17	C18	115.8(3)
C19	C18	C17	109.8(3)
C19	C18	C20	110.0(3)
C19	C18	C21	108.9(3)
C20	C18	C17	111.2(3)
C20	C18	C21	110.3(3)
C21	C18	C17	106.5(3)
O3	C23	C24	107.5(2)
O4	C24	C23	108.0(2)
O12	Cl1	O11	110.13(19)
O12	Cl1	O14	107.4(2)
O13	Cl1	O11	111.02(17)
O13	Cl1	O12	112.41(18)
O13	Cl1	O14	108.7(2)
O14	Cl1	O11	107.0(2)
O22	Cl2	O21	110.9(2)
O22	Cl2	O24	111.4(2)
O23	Cl2	O21	108.7(3)
O23	Cl2	O22	108.0(2)
O23	Cl2	O24	110.5(3)
O24	Cl2	O21	107.35(19)
C31	O31	C33	115.2(4)
O31	C31	C32	107.8(4)
O31	C33	C34	112.7(4)

Table S13 Hydrogen bonds for [(*S,S*)-12·Fe·DME·H_2O]$^{2+}$·2ClO_4^-

D	H	A	d(D-H) (Å)	d(H-A) (Å)	d(D-A) (Å)	D-H-A (°)
O1	H1	O11	0.8400(15)	2.042(15)	2.838(3)	158(4)
O2	H2	O6	0.8419(15)	1.825(9)	2.654(3)	168(4)
O5	H5A	O31	0.8398(15)	1.868(4)	2.708(4)	179(4)
O5	H5B	O21	0.8399(15)	1.931(9)	2.761(4)	169(4)
O6	H6A	O24[1]	0.8400(15)	1.965(12)	2.786(4)	166(4)
O6	H6B	O22	0.8400(15)	2.039(7)	2.876(4)	174(5)

[1] 1-X,1/2+Y,1-Z

Table S14 Torsion angles for [(*S,S*)-12·Fe·DME·H_2O]$^{2+}$·2ClO_4^-

A	B	C	D	Angle (˚)
Fe1	O1	C6	C5	0.0(3)
Fe1	O1	C6	C7	-123.7(2)
Fe1	O2	C17	C16	10.9(3)
Fe1	O2	C17	C18	-116.0(2)
Fe1	O3	C23	C24	-42.0(3)
Fe1	O4	C24	C23	-42.5(3)
Fe1	N1	C1	C2	145.8(2)
Fe1	N1	C1	C12	-28.0(3)
Fe1	N1	C5	C4	-147.0(2)
Fe1	N1	C5	C6	33.0(3)
Fe1	N2	C12	C1	-31.3(3)
Fe1	N2	C12	C13	144.7(2)
Fe1	N2	C16	C15	-150.9(3)
Fe1	N2	C16	C17	25.0(3)
O1	C6	C7	C8	-174.1(2)
O1	C6	C7	C9	64.3(3)
O1	C6	C7	C10	-56.7(4)
O2	C17	C18	C19	-177.5(3)
O2	C17	C18	C20	60.5(3)
O2	C17	C18	C21	-59.7(3)
O3	C23	C24	O4	55.4(3)
N1	C1	C2	C3	4.0(4)
N1	C1	C2	C11	-172.9(3)
N1	C1	C12	N2	39.1(3)
N1	C1	C12	C13	-136.8(3)
N1	C5	C6	O1	-20.3(3)
N1	C5	C6	C7	102.1(3)
N2	C12	C13	C14	9.4(4)
N2	C12	C13	C22	-165.2(3)
N2	C16	C17	O2	-22.3(3)
N2	C16	C17	C18	101.2(3)
C1	N1	C5	C4	4.4(4)
C1	N1	C5	C6	-175.7(2)
C1	C2	C3	C4	0.4(4)
C1	C12	C13	C14	-175.1(3)
C1	C12	C13	C22	10.4(5)
C2	C1	C12	N2	-134.5(3)
C2	C1	C12	C13	49.6(4)
C2	C3	C4	C5	-2.3(4)
C3	C4	C5	N1	-0.1(4)
C3	C4	C5	C6	180.0(3)
C4	C5	C6	O1	159.7(2)
C4	C5	C6	C7	-78.0(3)
C5	N1	C1	C2	-6.5(4)
C5	N1	C1	C12	179.7(2)
C5	C6	C7	C8	66.3(3)
C5	C6	C7	C9	-55.4(3)
C5	C6	C7	C10	-176.4(3)
C11	C2	C3	C4	177.5(3)
C12	N2	C16	C15	1.5(4)
C12	N2	C16	C17	177.4(2)
C12	C1	C2	C3	177.0(3)
C12	C1	C2	C11	0.0(5)
C12	C13	C14	C15	-3.3(5)
C13	C14	C15	C16	-3.2(5)
C14	C15	C16	N2	4.3(5)
C14	C15	C16	C17	-171.3(3)
C15	C16	C17	O2	153.6(3)
C15	C16	C17	C18	-83.0(4)
C16	N2	C12	C1	175.3(2)
C16	N2	C12	C13	-8.6(4)
C16	C17	C18	C19	60.2(3)
C16	C17	C18	C20	-61.8(4)
C16	C17	C18	C21	178.0(3)
C22	C13	C14	C15	171.5(3)
C25	O3	C23	C24	162.9(2)
C26	O4	C24	C23	170.7(3)
C31	O31	C33	C34	78.6(6)
C33	O31	C31	C32	-171.4(4)

Table S15 Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for [(*S*,*S*)-12·Fe·DME·H_2O]$^{2+}$·2ClO_4^-

Atom	*x*	*y*	*z*	U(eq)
H1	2010(30)	3670(19)	1610(20)	33
H2	4890(40)	5970(30)	3058(14)	32
H5A	2370(40)	5870(20)	3796(13)	39
H5B	2390(40)	4723(11)	3605(18)	39
H3	-1209.97	7903	408.74	27
H4	-1035.6	5823.14	443.11	26
H6	516.91	4125.24	839.81	26
H8A	-1652.02	3597.26	878.76	52
H8B	-2027.54	4732.77	1424.03	52
H8C	-2375.14	3413.02	1727.04	52
H9A	150.33	4344.49	3050.99	54
H9B	-1246.69	3890.47	3087.17	54
H9C	-940.41	5184.9	2719.13	54
H10A	602.84	2418.51	2291.29	70
H10B	-43.5	2170.7	1415.45	70
H10C	-820.62	2048.18	2247.2	70
H11A	-824.43	9858.24	1581.5	39
H11B	-187.7	9830.07	693.38	39
H11C	640.64	9973.25	1510.18	39
H14	2136.26	10323.51	3857.32	35
H15	4149.35	9630.7	3724.8	35
H17	5284.95	7608.12	3476.96	26
H19A	6449.47	9452.37	3212.14	56
H19B	5491.19	9970.73	2545.81	56
H19C	6905.26	9788.05	2303.28	56
H20A	5349.56	7388.84	1246.14	54
H20B	6146.42	8571.25	1090.44	54
H20C	4745.72	8679.54	1382.52	54
H21A	7325.05	7370.45	3018.42	52
H21B	7773.29	7789.05	2124.32	52
H21C	6935.4	6618.94	2216.04	52
H22A	-120.07	9477.56	3795.28	41
H22B	-529.92	9003.57	2901.22	41
H22C	-94.85	10361.86	3017.79	41
H23A	4429.05	5272.72	25.13	34
H23B	3300.25	4484.39	360.11	34
H24A	5134.59	3706.93	926.04	34
H24B	5511.47	5003.05	1274.8	34
H25A	2181.58	6548.11	70.1	43
H25B	3519.89	7084.37	-110.26	43
H25C	2691	7651	603.25	43
H26A	5554.66	3927.5	2617.66	49
H26B	4972.41	2745.5	2215.34	49
H26C	4284.25	3403.66	2958.68	49

H6A	5850(40)	5710(30)	4319(17)	69
H6B	5090(30)	4800(30)	4240(20)	69
H31	642.84	7517.3	5459.73	76
H32A	330.06	5410.71	4522.57	109
H32B	-41.46	6517.97	3944.97	109
H32C	-809.37	6246.08	4763.7	109
H33A	2740.18	8288.31	5328.64	78
H33B	3744.13	7623.34	4774.57	78
H34A	3715.14	5987.26	5689.61	105
H34B	2734.41	6675.77	6249.14	105
H34C	4102.93	7190.62	6160.58	105