Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary information for:

2,2′-Bipyridine-α,α′-trifluoromethyl-diol ligand: synthesis and application in the asymmetric Et_2Zn alkylation of aldehydes

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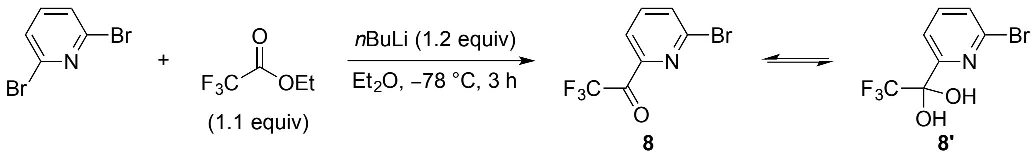
General information

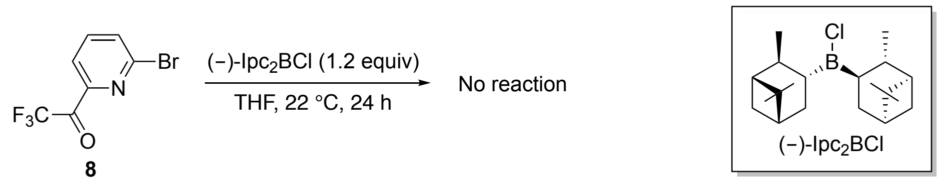
All solvents were commercially available and they were distilled from CaH_2 (CH_2Cl_2) or Na/benzophenone (Et_2O, PhMe) prior to use. *N*,*N*-Dimethylformamide (DMF) was dried from P_2O_5 and distilled under reduced pressure (90 °C, 30 mmHg) prior to use. Triethylamine (Et_3N) was distilled from CaH_2 prior to use. Ibuprofen *rac*-**10** was purchased from The Upjohn Company®. (–)-(*S*)-α-Methylbenzylamine **13** (98% *ee*) and diethylzinc solution (1.0 M in hexane) were purchased from Sigma-Aldrich®. Aldehydes **15a–v** were purchased from commercial suppliers (Sigma-Aldrich®, Alfa Aesar®, and TCI®) and they were distilled under reduced pressure prior to use. Other reagents were purchased directly from commercial suppliers (Sigma-Aldrich®, Alfa Aesar®, VWR®, TCI®, Strem®, and Acros®) 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 or 1000 μm) 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). ^{1}H, $^{13}C\{H\}$, and ^{19}F NMR spectra were recorded on an Agilent Technologies DD2 500 MHz spectrometers in $CDCl_3$. For ^{1}H 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. For ^{19}F NMR, no external standard was used. High-resolution mass spectra (HRMS) were recorded on an LC/MS-TOF (time of flight) Agilent 6210 mass spectrometer using electrospray ionization (ESI) or atmospheric pressure photoionization (APPI). IR spectra were recorded on an ABB MB3000 FT-IR spectrometer with ABB MIRacle™ Diamond ATR accessory and they were reported in reciprocal centimeters (cm^{-1}). Melting point (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 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 1-(6-bromopyridin-2-yl)-2,2,2-trifluoroethan-1-one (8) and 1-(6-bromopyridin-2-yl)-2,2,2-trifluoroethane-1,1-diol (8′):



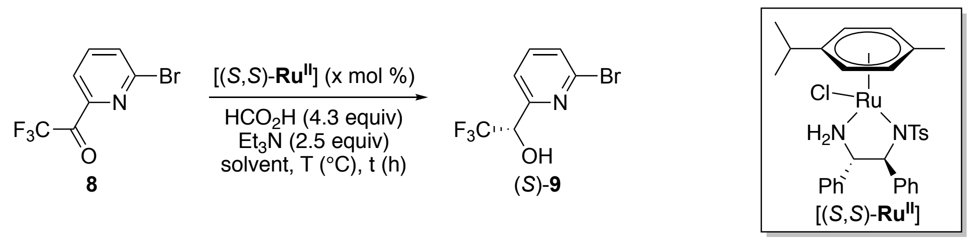
To a vacuum flame-dried 500 mL flask under argon, 2,6-dibromopyridine (7.11 g, 30.0 mmol, 1.0 equiv) was added to Et_2O (120 mL). The mixture was cooled to –78 °C before *n*-butyllithium (14.4 mL, 36.0 mmol, 1.2 equiv; 2.5 M in hexane) was added dropwise. The brown-yellow solution was stirred at –78 °C for 1 h. Ethyl 2,2,2-trifluoroacetate (3.9 mL, 33.0 mmol, 1.1 equiv) was added dropwise and the mixture was stirred at –78 °C for 2 h. The reaction was warmed to 22 °C and an aqueous solution of saturated NH_4Cl (15 mL) was added. The aqueous layer was extracted with Et_2O (3 x 75 mL) and dried over $MgSO_4$. The drying agent was removed by filtration and the filtrate was concentrated *in vacuo* (bath temperature 30 °C). Noteworthily, a minimal amount of aqueous solutions should be use during the workup to prevent the loss of **8′**. The crude product was purified by silica gel column chromatography using a gradient elution of hexane/EtOAc = 95:5–80:20 to give an 8:92 mixture of compounds **8** and **8′** as a light yellow solid (6.68 g, 24.7 mmol, 82% yield). mp = 68–70 °C. R_f = 0.32 (hexane/EtOAc = 80:20). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.13 (dd, *J* = 4.8, 3.7 Hz, 0.08H, **8**), 7.81 (m, 0.08H, **8**), 7.80 (m, 0.08H, **8**), 7.78 – 7.73 (m, 1.84H, **8′**), 7.64 (dd, *J* = 6.9, 1.9 Hz, 0.92H, **8′**), 4.95 (s, 1.84H, **8′**) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 179.5 (q, *J* = 35.3 Hz, **8**), 154.1, 148.8, 142.0, 140.3, 140.1, 139.3, 133.8, 129.8, 124.0 (m, **8**), 122.4 (q, *J* = 287.5 Hz, **8′**), 121.3 (q, *J* = 1.8 Hz, **8′**), 116.3 (q, *J* = 290.9 Hz, **8**), 91.8 (q, *J* = 33.5 Hz, **8′**) ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ_F –72.2 (s, 0.24F, **8**), –84.2 (s, 2.78F, **8′**) ppm. IR (Diamond): 3342, 1738, 1562, 1412, 1196, 1126, 1059, 953, 808, 716 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_7H_4BrF_3NO$ 253.9423; Found 253.9429. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_7H_6BrF_3NO_2$ 271.9529; Found 271.9534.

Asymmetric reduction of α-CF_3 ketone 8: Optimization studies



Scheme S1 Asymmetric hydroboration of **8** – (–)-Ipc$_2$BCl. Conditions: **8** (0.500 mmol), (–)-Ipc$_2$BCl (0.600 mmol), THF (0.5 mL), 22 °C, 24 h.

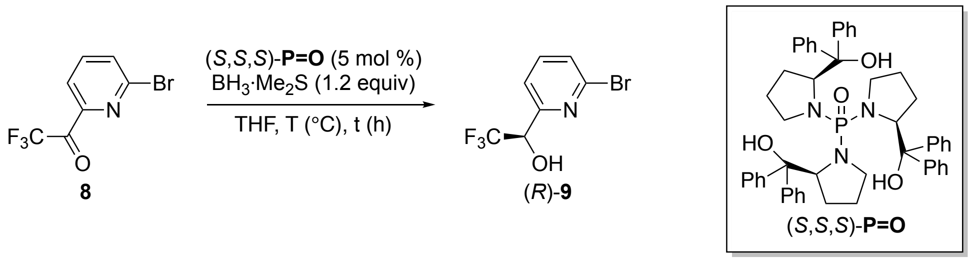
Table S1 Asymmetric transfer hydrogenation – RuCl(*p*-cymene)[(*S*,*S*)-TsDPEN][a]



Entry	solvent	x (mol %)	T (°C)	t (h)	Conv.[b] (%)	Yield (%)	*ee*[c] (%)
1	neat	1	22	1	78	68	34
2	neat	1	–20	48	NR	–	–
3	CH_2Cl_2	2	–20	24	20	14	44
4	PhMe	2	–20	68	32	27	46
5	Et_2O	2	–20	68	32	21	40
6	THF	2	–20	68	34	23	62
7	MeCN	2	–20	68	71	58	26
8	DMF	10	–20	48	100	91	42
9	THF	10	–20	21	89	74	64
10	THF	10	–78	94	5	4	92
11[d]	THF	15	–30	336	87	76	60

[a] Conditions: **8** (0.500 mmol), [Ru(*S*,*S*)-Ts-DPEN(*p*-cymene)]Cl (0.0500–0.750 mmol), HCO_2H (2.15 mmol), Et_3N (1.25 mmol), solvent (0.5 mL). [b] Conversion determined by ^{19}F NMR. [c] Determined by chiral HPLC (OJ–H column). [d] Using **8** (5.00 mmol), HCO_2H (43.0 mmol), and Et_3N (25.0 mmol).

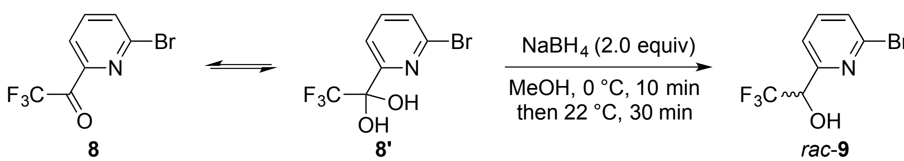
Table S2 Asymmetric transfer hydrogenation – tris((*S*)-prolinol)P=O/$BH_3{\cdot}Me_2S$[a]



Entry	T (°C)	t (h)	Conv.[b] (%)	Yield (%)	*ee*[c] (%)
1	70	1	53	44	10
2	22	3	43	33	14
3[d]	22	19	41	31	16

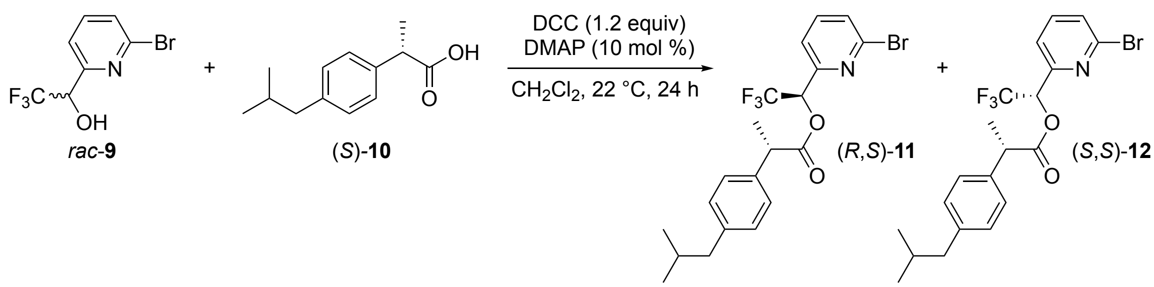
[a] Conditions: **8** (0.500 mmol), tris((*S*)-prolinol)phosphine oxide (0.0250 mmol), $BH_3{\cdot}Me_2S$ (0.600 mmol; 2.0 M in THF), THF (2.0 mL). [b] Conversion determined by ^{19}F NMR. [c] Determined by chiral HPLC (OJ–H column). [d] **8** was treated with $BF_3{\cdot}Et_2O$ (0.500 mmol) at 22 °C for 1 h (pre-complexation) and the corresponding adduct was used as the substrate.

Preparation of racemic 1-(6-bromopyridin-2-yl)-2,2,2-trifluoroethan-1-ol (9):



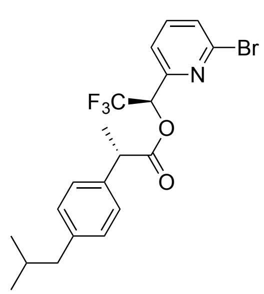
To a 500 mL flask, the mixture of compounds **8** and **8'** (6.63 g, 24.5 mmol, 1.0 equiv; **8**/**8'** = 8:92) was added to MeOH (250 mL). The mixture was cooled to 0 °C before sodium borohydride (1.85 g, 49.0 mmol, 2.0 equiv) was added in one portion. The reaction was stirred at 0 °C for 10 min, and it was further stirred at 22 °C for 30 min. Then, an aqueous solution of saturated NH_4Cl (35 mL) was slowly added to quench the reaction. The aqueous layer was extracted with Et_2O (3 x 75 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 30 °C). The crude product was purified by silica gel column chromatography using a gradient elution of hexane/EtOAc = 90:10–80:20 to give compound **9** as a white solid (6.17 g, 24.1 mmol, 98% yield). mp = 68–70 °C. R_f = 0.25 (hexane/EtOAc = 90:10). ^1H NMR (500 MHz, $CDCl_3$): δ_H 7.67 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.58 (m, 1H), 7.41 (m, 1H), 5.03 (p, *J* = 6.6 Hz, 1H), 4.77 (d, *J* = 7.6 Hz, 1H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 152.8 (q, *J* = 1.8 Hz), 141.2, 139.5, 129.1, 123.7 (q, *J* = 283.2 Hz), 121.5 (q, *J* = 1.8 Hz), 70.8 (q, *J* = 32.1 Hz) ppm. ^{19}F NMR (470 MHz, $CDCl_3$) δ_F –77.9 (d, *J* = 6.6 Hz, 3F) ppm. IR (Diamond): 3157, 2926, 2876, 1560, 1416, 1252, 1126, 997, 791, 681 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_7H_6BrF_3NO$ 255.9579; Found 255.9578.

Preparation of 1-(6-bromopyridin-2-yl)-2,2,2-trifluoroethyl (2*S*)-2-(4-isobutylphenyl)propanoate diastereoisomers (11 and 12):



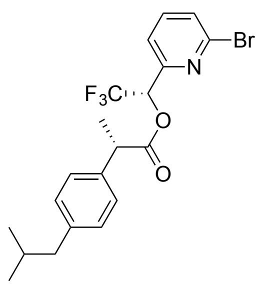
To a vacuum flame-dried 250 mL flask under argon, *rac*-**9** (6.14 g, 24.0 mmol, 1.0 equiv), (*S*)-**10** (4.95 g, 24.0 mmol, 1.0 equiv, 93% *ee*), 4-*N*,*N*-dimethylaminopyridine (293 mg, 2.40 mmol, 0.10 equiv), and *N*,*N'*-dicyclohexylcarbodiimide (5.94 g, 28.8 mmol, 1.2 equiv) were subsequently added to CH_2Cl_2 (120 mL) and the reaction was stirred at 22 °C for 24 h. The mixture was filtered through a plug of silica, washed with CH_2Cl_2 (3 x 50 mL), 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 = 100:0–95:5.

(+)-(*R*)-1-(6-Bromopyridin-2-yl)-2,2,2-trifluoroethyl (*S*)-2-(4-isobutylphenyl)propanoate (11):



Product was obtained as a light yellow oil (4.35 g, 9.79 mmol, 41% yield, 92% *ee*). The following characterization was performed using (*S*,*S*)-**11** in 98% *ee*: R_f = 0.70 (hexane/EtOAc = 90:10). The *ee* was determined by HPLC [Daicel ChiralCel® OJ–H, hexane/*i*PrOH = 98:2, flow rate = 0.5 mL/min, λ = 220 nm]: t_R(*S*,*R*) = 12.8 min, t_R(*R*,*S*) = 18.0 min; racemate: t_R(*S*,*R*) = 12.9 min, t_R(*R*,*S*) = 18.6 min. $[\alpha]_D^{22}$ = +105.1 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.43 (m, 1H), 7.31 (dd, *J* = 7.9, 7.9 Hz, 1H), 7.17 (dt, J = 8.1, 2.0 Hz, 2H), 7.10 (dt, J = 8.1, 2.0 Hz, 2H), 6.78 (m, 1H), 6.17 (q, J = 6.6 Hz, 1H), 3.90 (q, J = 7.2 Hz, 1H), 2.47 (d, J = 7.2 Hz, 2H), 1.86 (m, 1H), 1.55 (d, J = 7.2 Hz, 3H), 0.91 (d, J = 6.6 Hz, 6H) ppm. $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$): δ_C 171.9, 152.2 (m), 141.5, 141.1, 138.9, 136.5, 129.5, 128.9, 127.4, 122.6 (q, J = 281.3 Hz), 120.5, 72.4 (q, J = 32.7 Hz), 45.0, 44.7, 30.2, 22.3, 22.3, 17.8 ppm. ^{19}F NMR (470 MHz, $CDCl_3$) δ_F –74.98 (d, J = 6.6 Hz, 3F) ppm. IR (Diamond): 2955, 2935, 2870, 1755, 1437, 1186, 1138, 1072, 791, 685 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{22}BrF_3NO_2$ 444.0781; Found 444.0778.

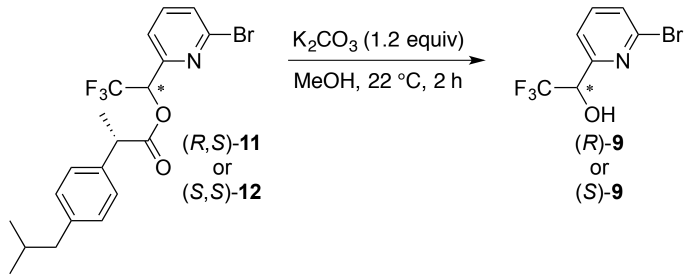
(+)-(*S*)-1-(6-Bromopyridin-2-yl)-2,2,2-trifluoroethyl (*S*)-2-(4-isobutylphenyl)propanoate (12):



Product was obtained as a light yellow oil (4.49 g, 10.1 mmol, 42% yield, 91% *ee*). The following characterization was performed using (*S*,*S*)-**12** in 98% *ee*: R_f = 0.57 (hexane/EtOAc = 90:10). The *ee* was determined by HPLC [Daicel ChiralCel® OJ–H, hexane/*i*PrOH = 98:2, flow rate = 0.5 mL/min, λ = 220 nm]: t_R(*S*,*S*) = 18.1 min, t_R(*R*,*R*) = 19.6 min; racemate: t_R(*S*,*S*) = 18.2 min, t_R(*R*,*R*) = 19.6 min. $[\alpha]_D^{22}$ = +9.6 (*c* = 1.0, $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$): δ_H 7.54 (dd, J = 7.9, 7.9 Hz, 1H), 7.51 (dd, J = 7.9, 1.3 Hz, 1H), 7.27 (m, 1H), 7.24 (dt, J = 8.1, 2.0 Hz, 2H), 7.13 (dt, J = 8.1, 2.0 Hz, 2H), 6.16 (q, J = 6.6 Hz, 1H), 3.89 (q, J = 7.2 Hz, 1H), 2.47 (d, J = 7.2 Hz, 2H), 1.86 (m, 1H), 1.58 (d, J = 7.2 Hz, 3H), 0.90 (d, J = 6.6 Hz, 6H) ppm. $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$): δ_C 172.2, 152.2 (m), 141.7, 141.1, 139.2, 136.2, 129.5, 129.1, 127.3, 122.6 (q, J = 281.5 Hz), 121.2, 72.4 (q, J = 32.8 Hz), 45.0, 44.9, 30.2, 22.3, 22.3, 17.9 ppm. ^{19}F NMR (470 MHz, $CDCl_3$) δ_F –75.04 (d, J = 6.6 Hz, 3F) ppm. IR (Diamond): 2955, 2934, 2870, 1755, 1437, 1186, 1138, 1072, 793, 685 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{22}BrF_3NO_2$ 444.0781; Found 444.0774.

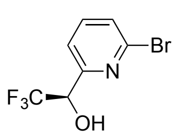
The resolution of *rac*-**9** was also investigated using enantiopure (*S*)-mandelic acid *O*-acetate[1] and (*S*)-mandelic acid *O*-*tert*-butyldimethylsilyl ether[2] but they both led to inseparable diastereoisomers by silica gel column chromatography.

Preparation of enantioenriched 1-(6-bromopyridin-2-yl)-2,2,2-trifluoroethan-1-ol (9):



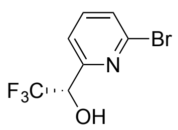
To a 250 mL flask, (*R*,*S*)-**11** (4.35 g, 9.79 mmol, 1.0 equiv, 92% *ee*) or (*S*,*S*)-**12** (4.49 g, 10.1 mmol, 1.0 equiv, 91% *ee*) was added to MeOH (100 mL). Anhydrous potassium carbonate (1.2 equiv) was added in one portion and the reaction was stirred at 22 °C for 2 h. Distilled water (40 mL) was added to quench the reaction, the mixture was concentrated *in vacuo* (bath temperature 45 °C), and the residue was extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with brine (1 x 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 product was purified by silica gel column chromatography using a gradient elution of hexane/EtOAc = 95:5–80:20. Characterization of (*R*)-**9** and (*S*)-**9**: *see the section for the preparation of rac-**9***.

(+)-(*R*)-1-(6-Bromopyridin-2-yl)-2,2,2-trifluoroethan-1-ol (9):



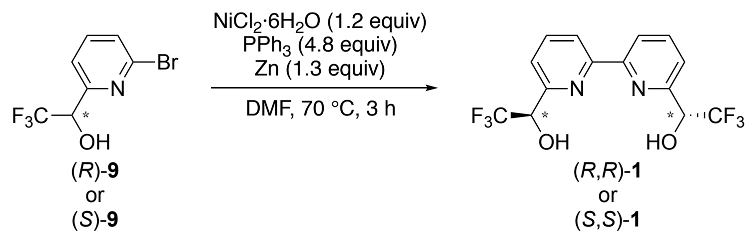
Product was obtained as a white solid (2.43 g, 9.49 mmol, 97% yield, 92% *ee*). Recrystallization from hot hexane (63.0 mL, 70 °C) afforded the enantiomerically enriched compound (*R*)-**9** as white crystals (1.81 g, 7.07 mmol, 72% yield, 96% *ee*). The following characterization was performed using (*R*)-**9** in >99.5% *ee*: The *ee* was determined by HPLC [Daicel ChiralCel® OJ–H, hexane/*i*PrOH = 95:5, flow rate = 0.5 mL/min, λ = 254 nm]: $t_R(R)$ = 38.8 min; racemate: $t_R(S)$ = 30.3 min, $t_R(R)$ = 38.8 min. $[\alpha]_D^{22}$ = +3.9 (*c* = 1.0, $CHCl_3$). The absolute configuration of **9** was determined as being *R* from single crystal X-ray analysis (CCDC 2098867).

(–)-(*S*)-1-(6-Bromopyridin-2-yl)-2,2,2-trifluoroethan-1-ol (9):



Product was obtained as a white solid (2.53 g, 9.88 mmol, 98% yield, 91% *ee*). Recrystallization from hot hexane (66.0 mL, 70 °C) afforded the enantiomerically enriched compound (*S*)-**9** as white crystals (1.98 g, 7.73 mmol, 77% yield, >99.5% *ee*). The *ee* was determined by HPLC [Daicel ChiralCel® OJ–H, hexane/*i*PrOH = 95:5, flow rate = 0.5 mL/min, λ = 254 nm]: t_R(*S*) = 30.4 min; racemate: t_R(*S*) = 30.3 min, t_R(*R*) = 38.8 min. $[\alpha]_D^{22}$ = –4.1 (*c* = 1.0, $CHCl_3$); $[\alpha]_D^{22}$ = +8.0 (*c* = 1.0, EtOH).

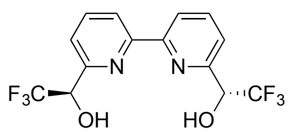
Preparation of 1,1'-([2,2'-bipyridine]-6,6'-diyl)bis(2,2,2-trifluoroethan-1-ol) (1):



To a vacuum flame-dried 250 mL flask under argon, freshly distilled DMF (8.0 mL per mmol of **9**) was added, and the solvent was degassed five times according to the *freeze-pump-thaw cycling* method. $NiCl_2{\cdot}6H_2O$ (1.2 equiv) was added and the mixture was stirred at 70 °C. Triphenylphosphine (4.8 equiv) and zinc powder (1.3 equiv) were subsequently added and the reaction was stirred at 70 °C for 1 h. (*R*)-**9** (1.79 g, 7.00 mmol, 1.0 equiv, 96% *ee*) or (*S*)-**9** (1.92 g, 7.50 mmol, 1.0 equiv, >99.5% *ee*) was added at 70 °C and the reaction was stirred for an additional 2 h. The mixture was cooled to 22 °C before an aqueous ammonia solution (13.5 mL per mmol of **9**; 5 wt%) was added to quench the reaction. The brown precipitate was extracted EtOAc (3 x 100 mL). The combined organic layers were washed with brine (1 x 100 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 product was purified by silica gel column chromatography using a gradient elution of hexane/EtOAc = 90:10–70:30. A non-negligible quantity of **1** was lost during the purification due to the presence of highly polarized CF_3 groups, which initiate aggregation and precipitation of the material on silica gel. Also, persistent organics contaminants, *i.e.* triphenylphosphine and DMF, were removed by recrystallization. Characterization of (*R*,*R*)-**1** or (*S*,*S*)-**1**: mp = 182–184 °C. R_f = 0.41 (hexane/EtOAc = 70:30). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.50 (m, 2H), 8.01

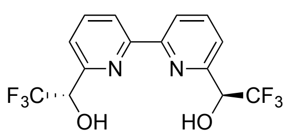
(dd, J = 7.8, 7.8 Hz, 2H), 7.53 (m, 2H), 5.36 (d, J = 7.2 Hz, 2H), 5.15 (p, J = 6.7 Hz, 2H) ppm. $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$): δ_C 153.7, 150.9 (m), 138.6, 124.0 (q, J = 283.2 Hz), 123.3 (m), 121.9, 70.8 (q, J = 31.8 Hz) ppm. ^{19}F NMR (470 MHz, $CDCl_3$) δ_F –77.9 (d, J = 6.6 Hz, 6F) ppm. IR (Diamond): 3373, 2934, 1574, 1448, 1356, 1261, 1124, 1078, 797, 694 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{11}F_6N_2O_2$ 353.0719; Found 353.0719. Stereoselectivities were determined based on the *ee* and *de* obtained on the corresponding dibenzoate **14** (*see the procedure described below*).

(–)-(1*R*,1′*R*)-1,1′-([2,2′-Bipyridine]-6,6′-diyl)bis(2,2,2-trifluoroethan-1-ol) (1):



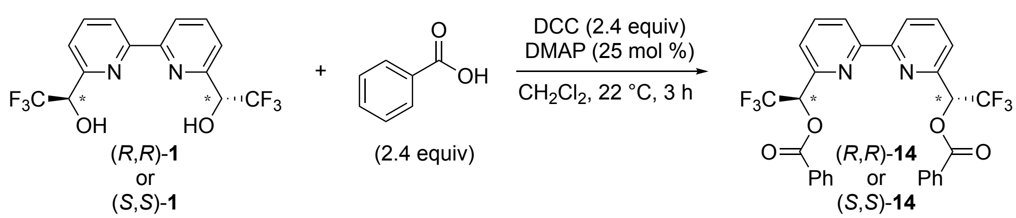
Product was obtained as a white solid (862 mg, 2.45 mmol, 70% yield). Recrystallization from hot hexane/EtOAc = 90:10 (85 mL, 77 °C) afforded the diastereo- and enantiomerically enriched compound (*R*,*R*)-**1** as white crystals (513 mg, 1.46 mmol, 42% yield, 97% *de*, >99.5% *ee*). $[\alpha]_D^{22}$ = –8.3 (c = 1.7, EtOH). (CCDC 2098890)

(+)-(1*S*,1′*S*)-1,1′-([2,2′-Bipyridine]-6,6′-diyl)bis(2,2,2-trifluoroethan-1-ol) (1):



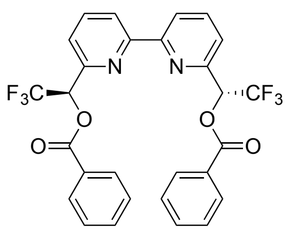
Product was obtained as a white solid (1.03 g, 2.92 mmol, 78% yield). Recrystallization from hot hexane/EtOAc = 90:10 (100 mL, 77 °C) afforded the diastereo- and enantiomerically enriched compound (*S*,*S*)-**1** as white crystals (680 mg, 1.93 mmol, 51% yield, >99.5% *de*, >99.5% *ee*). $[\alpha]_D^{22}$ = +8.8 (c = 1.7, EtOH).

Preparation of [2,2′-bipyridine]-6,6′-diylbis(2,2,2-trifluoroethane-1,1-diyl) dibenzoate (14):



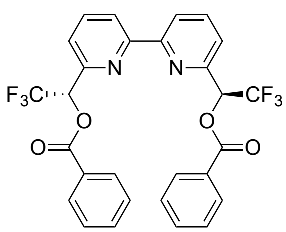
*Following the procedure described for the preparation of esters (R,S)-**11** and (S,S)-**12**:* (*R*,*R*)-**1** or (*S*,*S*)-**1** (35.2 mg, 0.100 mmol, 1.0 equiv), benzoic acid (29.3 mg, 0.240 mmol, 2.4 equiv), DCC (49.5 mg, 0.240 mmol, 2.4 equiv), DMAP (3.1 mg, 0.0250 mmol, 0.25 equiv), CH_2Cl_2 (1.0 mL), 22 °C, 3 h. After the filtration through a plug of silica, the crude product was sufficiently pure to be injected into the HPLC instrument without a prior purification. Characterization of (*R*,*R*)-**14** or (*S*,*S*)-**14**: R_f = 0.55 (hexane/EtOAc = 90:10). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.56 (m, 2H), 8.19 – 8.17 (m, 4H), 7.90 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.66 (m, 2H), 7.61 (m, 2H), 7.54 – 7.51 (m, 4H), 6.59 (q, *J* = 6.7 Hz, 2H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 164.4, 155.2, 150.7 (m), 138.0, 134.0, 130.1, 128.7, 128.6, 123.2 (q, *J* = 281.3 Hz), 122.4, 122.0, 73.5 (q, *J* = 32.4 Hz) ppm. ^{19}F NMR (470 MHz, $CDCl_3$) δ_F –74.7 (d, *J* = 6.8 Hz, 6F) ppm. IR (Diamond): 2978, 2934, 1736, 1441, 1244, 1178, 1134, 1090, 800, 706 cm^{-1}. HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{28}H_{19}F_6N_2O_4$ 561.1244; Found 561.1246.

(+)-(1*R*,1′*R*)-[2,2′-Bipyridine]-6,6′-diylbis(2,2,2-trifluoroethane-1,1-diyl) dibenzoate (14):



Product was obtained as a colorless sticky oil (53.1 mg, 0.0947 mmol, 95% yield, 97% *de*, >99.5% *ee*). *ee* and *de* were determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 80:20, flow rate = 1.0 mL/min, λ = 254 nm]: t_R(*R*,*R*) = 7.5 min, t_R(*meso*) = 16.7 min; racemate: t_R(*R*,*R*) = 7.5 min, t_R(*meso*) = 16.4 min, t_R(*S*,*S*) = 36.4 min. $[\alpha]_D^{22}$ = +201.7 (*c* = 1.0, $CHCl_3$).

(–)-(1*S*,1′*S*)-[2,2′-Bipyridine]-6,6′-diylbis(2,2,2-trifluoroethane-1,1-diyl) dibenzoate (14):

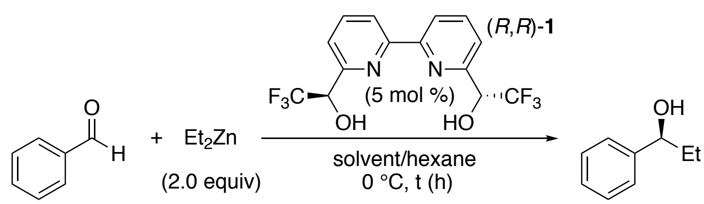


Product was obtained as a colorless sticky oil (51.5 mg, 0.0919 mmol, 92% yield, >99.5% *de*, >99.5% *ee*). *ee* and *de* were determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 80:20, flow rate = 1.0 mL/min, λ = 254 nm]: t_R(*meso*) = 16.5 min, t_R(*S*,*S*) = 35.8 min; racemate: t_R(*R*,*R*) = 7.5 min, t_R(*meso*) = 16.4 min, t_R(*S*,*S*) = 36.4 min. $[\alpha]_D^{22}$ = –202.6 (*c* = 1.0, $CHCl_3$).

General procedure for the asymmetric ethylation reaction of benzaldehyde catalyzed by Zn^{II} complexes: Optimization studies

To a vacuum flame-dried test tube under argon atmosphere, (*R*,*R*)-**1** (4.4 mg, 0.0125 mmol, 0.050 equiv) and benzaldehyde **15a** (25 μL, 0.250 mmol, 1.0 equiv) were added to the desired solvent and the mixture was stirred at the specified temperature for 10 min. A diethylzinc solution (0.5 mL, 0.500 mmol, 2.0 equiv; 1.0 M in hexane) was added dropwise and the reaction was stirred at –78–22 °C for 5–120 h. An aqueous solution of HCl (2 mL; 1.0 M) was added to quench the reaction and the aqueous layer was extracted with Et_2O (3 x 5 mL) The combined organic layers were washed with brine (2 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 alcohol (*S*)-**16a**.

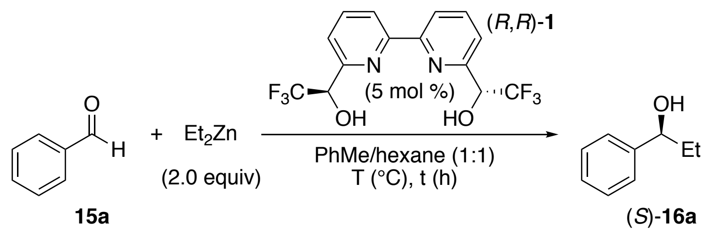
Table S3 Screening of solvents[a]



Entry	solvent/hexane	t (h)	Yield (%)	*ee*[b] (%)
1	MeCN (1:1)	72	16	67
2	THF (1:1)	72	10	17
3	CH_2Cl_2 (1:1)	48	59	85
4	Et_2O (1:1)	40	88	94
5	hexane	21	85	85
6	PhCl (1:1)	17	84	93
7	PhMe (1:1)	17	88	94

[a] Conditions: (*R*,*R*)-**1** (0.0125 mmol), **15a** (0.250 mmol), Et_2Zn (0.500 mmol), solvent (0.5 mL), 0 °C. [b] Determined by chiral HPLC (OJ–H column).

Table S4 Screening of temperatures[a]

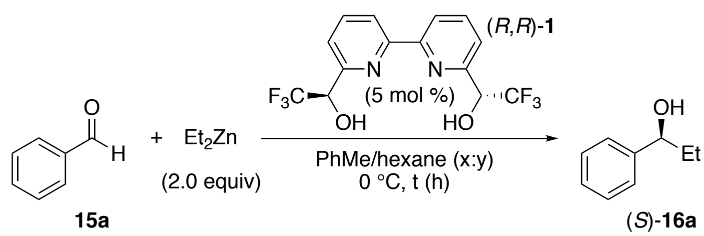


Entry	T (°C)	t (h)	Yield (%)	*ee*[b] (%)
1	22	5	89	89
2	0	17	88	94
3	–25	48	99	95
4	–78	96	<5	70

[a] Conditions: (*R*,*R*)-**1** (0.0125 mmol), **15a** (0.250 mmol), Et_2Zn (0.500 mmol), PhMe (0.5 mL).

[b] Determined by chiral HPLC (OJ–H column).

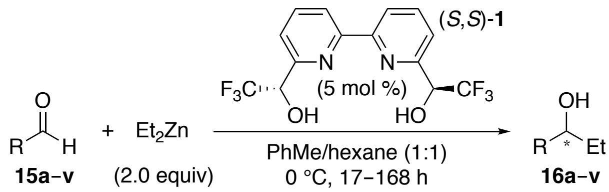
Table S5 Screening of concentrations and toluene proportions in hexane[a]



Entry	[**15a**] (M)	x	y	t (h)	Yield (%)	*ee*[b] (%)
1	0.250	1	1	17	88	94
2	0.250	1	3	21	90	92
3	0.375	1	3	17	83	92
4	0.050	1	1	120	69	93
5	0.050	2	1	120	55	92
6	0.050	4	1	120	38	90

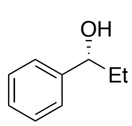
[a] Conditions: (*R*,*R*)-**1** (0.0125 mmol), **15a** (0.250 mmol), Et_2Zn (0.500 mmol), PhMe (0.17–4.0 mL) and hexane (0.00–2.0 mL), 0 °C. [b] Determined by chiral HPLC (OJ–H column).

General procedure for the asymmetric ethylation reaction of aldehydes catalyzed by Zn^{II} complexes: Synthesis of alcohols (16a–v)



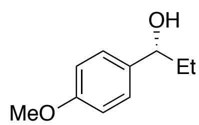
To a vacuum flame-dried test tube under argon atmosphere, (*S*,*S*)-**1** (8.8 mg, 0.0250 mmol, 0.050 equiv) and aldehyde **15a–v** (0.500 mmol, 1.0 equiv) were added to PhMe (1.0 mL) and the mixture was stirred at 0 °C for 10 min. To the resulting homogeneous solution, a diethylzinc solution (1.0 mL, 1.00 mmol, 2.0 equiv; 1.0 M in hexane) was added dropwise at 0 °C and the reaction was stirred at 0 °C for their respective reaction time. An aqueous solution of HCl (10 mL; 1.0 M) was added to quench the reaction and the aqueous layer was extracted with Et_2O (3 x 20 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 alcohols **16a–q**, **16t**, and **16u**. For alcohols **16r** and **16s**, the reaction was also quenched with HCl (5 mL; 1.0 M), but the aqueous layer was basified with aqueous saturated $NaHCO_3$ (10 mL) before it was extracted with EtOAc (3 x 20 mL). Also, the crude reaction product was purified using a gradient elution of hexane/EtOAc = 80:20–30:70. Absolute configurations were assigned by comparison of the optical rotation of a previous assignment, except for optically active **16c**, **16g**, and **16n** (unknown absolute configurations).

(+)-(*R*)-1-Phenylpropan-1-ol (16a):[3]



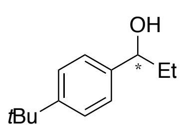
Product was obtained as a colorless oil (63.4 mg, 0.466 mmol, 93% yield, 95% *ee*). Reaction time = 17 h. R_f = 0.23 (hexane/EtOAc = 90:10). The *ee* was determined by HPLC [Daicel ChiralCel® OJ–H, hexane/*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 220 nm]: $t_R(S)$ = 22.6 min, $t_R(R)$ = 24.1 min; racemate: $t_R(S)$ = 22.4 min, $t_R(R)$ = 24.3 min. $[\alpha]_D^{22}$ = +48.0 (*c* = 0.90, $CHCl_3$) (lit.[4] $[\alpha]_D^{26}$ = +40.3 (*c* = 1.21, $CHCl_3$), 96% *ee* of (*R*)-**16a**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.38 – 7.35 (m, 4H), 7.29 (m, 1H), 4.62 (dd, J = 6.6, 6.6 Hz, 1H), 1.89 – 1.81 (m, 2H), 1.77 (m, 1H), 0.94 (dd, J = 7.4, 7.4 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 144.6, 128.4, 127.5, 126.0, 76.0, 31.9, 10.2 ppm. IR (Diamond): 3352, 2964, 2876, 1452, 1331, 1202, 1095, 1013, 972, 698 cm^{-1}.

(+)-(*R*)-1-(4-Methoxyphenyl)propan-1-ol (16b):[3]



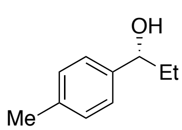
Product was obtained as a colorless oil (77.4 mg, 0.466 mmol, 93% yield, 93% *ee*). Reaction time = 24 h. R_f = 0.17 (hexane/EtOAc = 90:10). The *ee* was determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 220 nm]: t_R(*R*) = 28.0 min, t_R(*S*) = 31.5 min; racemate: t_R(*R*) = 28.3 min, t_R(*S*) = 31.8 min. $[\alpha]_D^{22}$ = +39.5 (c = 1.00, $CHCl_3$) (lit.[4] $[\alpha]_D^{26}$ = +38.9 (c = 1.23, $CHCl_3$), 96% *ee* of (*R*)-**16b**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.28 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 4.56 (ddd, J = 6.8, 6.8, 2.6 Hz, 1H), 3.82 (s, 3H), 1.83 (m, 1H), 1.79 – 1.69 (m, 2H), 0.91 (dd, J = 7.4, 7.4 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 158.9, 136.9, 127.2, 113.7, 75.6, 55.2, 31.8, 10.2 ppm. IR (Diamond): 3373, 2962, 2835, 1610, 1512, 1464, 1244, 1173, 1036, 827 cm^{-1}.

(+)-1-(4-(*tert*-Butyl)phenyl)propan-1-ol (16c):



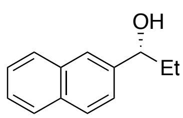
Product was obtained as a white solid (91.4 mg, 0.475 mmol, 95% yield, 92% *ee*). Reaction time = 48 h. R_f = 0.30 (hexane/EtOAc = 90:10). mp = 42–44 °C. The *ee* was determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 220 nm]: t_R(major) = 14.5 min, t_R(minor) = 16.1 min; racemate: t_R(*enant*-A) = 14.7 min, t_R(*enant*-B) = 16.3 min. $[\alpha]_D^{22}$ = +34.5 (c = 1.00, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.39 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 4.59 (ddd, J = 6.6, 6.6, 3.3 Hz, 1H), 1.84 (m, 1H), 1.81 – 1.72 (m, 2H), 1.33 (s, 9H), 0.94 (dd, J = 7.4, 7.4 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 150.4, 141.7, 125.8, 125.3, 75.8, 34.5, 31.7, 31.4, 10.3 ppm. IR (Diamond): 3265, 2962, 2878, 1512, 1462, 1333, 1269, 1111, 1009, 829 cm^{-1}. HRMS (APPI-TOF) m/z: $[M+H]^+[-H_2O]$ Calcd for $C_{13}H_{19}$ 175.1481; Found 175.1480.

(+)-(*R*)-1-(*p*-Tolyl)propan-1-ol (16d):[3]



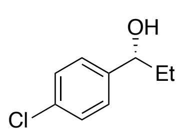
Product was obtained as a colorless oil (67.9 mg, 0.452 mmol, 90% yield, 95% *ee*). Reaction time = 17 h. R_f = 0.26 (hexane/EtOAc = 90:10). The *ee* was determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 220 nm]: $t_R(R)$ = 17.7 min, $t_R(S)$ = 20.3 min; racemate: $t_R(R)$ = 18.1 min, $t_R(S)$ = 20.8 min. $[\alpha]_D^{22}$ = +44.2 (*c* = 1.00, $CHCl_3$) (lit.[5] $[\alpha]_D^{20}$ = +26.3 (*c* = 1.00, $CHCl_3$), 94% *ee* of (*R*)-**16d**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.25 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 4.58 (ddd, *J* = 6.7, 6.7, 3.2 Hz, 1H), 2.36 (s, 3H), 1.83 (m, 1H), 1.79 – 1.71 (m, 2H), 0.92 (dd, *J* = 7.4, 7.4 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 141.7, 137.1, 129.1, 126.0, 75.8, 31.8, 21.1, 10.2 ppm. IR (Diamond): 3356, 2962, 2876, 1514, 1454, 1200, 1095, 1040, 972, 814 cm^{-1}.

(+)-(*R*)-1-(Naphthalen-2-yl)propan-1-ol (16e):[3]



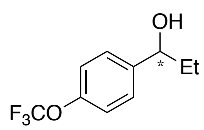
Product was obtained as a white solid (92.5 mg, 0.497 mmol, 99% yield, 86% *ee*). Reaction time = 41 h. R_f = 0.18 (hexane/EtOAc = 90:10). mp = 36–38 °C (lit.[6] mp = 37–38 °C). The *ee* was determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 220 nm]: $t_R(R)$ = 34.8 min, $t_R(S)$ = 37.0 min; racemate: $t_R(R)$ = 34.3 min, $t_R(S)$ = 36.2 min. $[\alpha]_D^{22}$ = +36.0 (*c* = 1.00, $CHCl_3$) (lit.[5] $[\alpha]_D^{20}$ = +32.8 (*c* = 1.00, $CHCl_3$), 95% *ee* of (*R*)-**16e**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.86 – 7.84 (m, 3H), 7.80 (m, 1H), 7.51 – 7.46 (m, 3H), 4.80 (ddd, *J* = 6.6, 6.6, 3.3 Hz, 1H), 1.97 – 1.90 (m, 2H), 1.86 (m, 1H), 0.96 (dd, *J* = 7.4, 7.4 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 142.0, 133.3, 133.01, 128.2, 128.0, 127.7, 126.1, 125.8, 124.8, 124.3, 76.1, 31.8, 10.2 ppm. IR (Diamond): 3254, 2928, 2864, 1454, 1331, 1128, 1018, 891, 825, 743 cm^{-1}.

(+)-(*R*)-1-(4-Chlorophenyl)propan-1-ol (16f):[3]



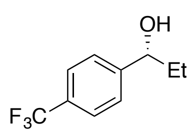
Product was obtained as a colorless oil (83.3 mg, 0.488 mmol, 98% yield, 93% *ee*). Reaction time = 17 h. R_f = 0.22 (hexane/EtOAc = 90:10). The *ee* was determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 220 nm]: $t_R(R)$ = 19.8 min, $t_R(S)$ = 20.8 min; racemate: $t_R(R)$ = 19.7 min, $t_R(S)$ = 20.7 min. $[\alpha]_D^{22}$ = +38.3 (*c* = 1.00, $CHCl_3$) (lit.[4] $[\alpha]_D^{26}$ = +30.6 (*c* = 2.08, $CHCl_3$), 96% *ee* of (*R*)-**16f**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.33 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 4.60 (ddd, *J* = 6.6, 6.6, 3.4 Hz, 1H), 1.84 (m, 1H), 1.82 – 1.69 (m, 2H), 0.92 (dd, *J* = 7.4, 7.4 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 143.0, 133.0, 128.5, 127.4, 75.2, 31.9, 10.0 ppm. IR (Diamond): 3354, 2966, 2878, 1597, 1491, 1410, 1323, 1090, 1013, 822 cm^{-1}.

(+)-1-(4-(Trifluoromethoxy)phenyl)propan-1-ol (16g):



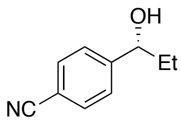
Product was obtained as a colorless oil (101.7 mg, 0.462 mmol, 92% yield, 95% *ee*). Reaction time = 17 h. R_f = 0.24 (hexane/EtOAc = 90:10). The *ee* was determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 99:1, flow rate = 0.5 mL/min, λ = 220 nm]: t_R(major) = 40.8 min, t_R(minor) = 42.0 min; racemate: t_R(*enant*-A) = 39.6 min, t_R(*enant*-B) = 40.8 min. $[\alpha]_D^{22}$ = +29.2 (*c* = 1.00, $CHCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.38 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 4.64 (ddd, *J* = 6.3, 6.3, 3.1 Hz, 1H), 1.88 – 1.79 (m, 2H), 1.75 (m, 1H), 0.93 (dd, *J* = 7.4, 7.4 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 148.4 (q, *J* = 1.8 Hz), 143.2, 127.32, 120.8, 120.5 (q, *J* = 256.8 Hz), 75.16, 31.94, 9.91 ppm. ^{19}F NMR (470 MHz, $CDCl_3$) δ_F –57.9 (s, 3F) ppm. IR (Diamond): 3340, 2970, 2881, 1510, 1254, 1211, 1155, 1018, 976, 851 cm^{-1}. HRMS (APPI-TOF) m/z: $[M+H]^+[-H_2O]$ Calcd for $C_{10}H_{10}F_3O$ 203.0678; Found 203.0686.

(+)-(*R*)-1-(4-(Trifluoromethyl)phenyl)propan-1-ol (16h):[3]



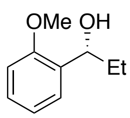
Product was obtained as a colorless oil (99.6 mg, 0.488 mmol, 98% yield, 90% *ee*). Reaction time = 17 h. R_f = 0.24 (hexane/EtOAc = 90:10). The *ee* was determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 220 nm]: t_R(*R*) = 15.7 min, t_R(*S*) = 16.5 min; racemate: t_R(*R*) = 15.7 min, t_R(*S*) = 16.5 min. $[\alpha]_D^{22}$ = +29.4 (*c* = 1.00, $CHCl_3$) (lit.[7] $[\alpha]_D^{25}$ = +15.8 (*c* = 1.30, $CHCl_3$), 72% *ee* of (*R*)-**16h**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.62 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 4.70 (ddd, *J* = 6.4, 6.4, 2.0 Hz, 1H), 1.92 (m, 1H), 1.87 – 1.73 (m, 2H), 0.94 (dd, *J* = 7.4, 7.4 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 148.5 (m), 129.6 (q, *J* = 32.3 Hz), 126.2, 125.3 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 271.6 Hz), 75.2, 31.9, 9.8 ppm. ^{19}F NMR (470 MHz, $CDCl_3$) δ_F –62.5 (s, 3F) ppm. IR (Diamond): 3352, 2972, 2881, 1418, 1323, 1163, 1117, 1067, 1016, 845 cm^{-1}.

(+)-(*R*)-4-(1-Hydroxypropyl)benzonitrile (16i):[8]



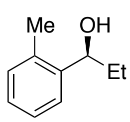
Product was obtained as a colorless oil (79.0 mg, 0.490 mmol, 98% yield, 91% *ee*). Reaction time = 17 h. R_f = 0.09 (hexane/EtOAc = 90:10). The *ee* was determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 220 nm]: $t_R(R)$ = 47.0 min, $t_R(S)$ = 50.8 min; racemate: $t_R(R)$ = 48.7 min, $t_R(S)$ = 52.1 min. $[\alpha]_D^{22}$ = +36.1 (*c* = 1.00, $CHCl_3$) (lit.[5] $[\alpha]_D^{20}$ = +28.8 (*c* = 1.00, $CHCl_3$), 94% *ee* of (*R*)-**16i**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.65 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 4.70 (ddd, *J* = 6.4, 6.4, 3.8 Hz, 1H), 1.95 (m, 1H), 1.83 – 1.73 (m, 2H), 0.94 (dd, *J* = 7.4, 7.4 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 150.3, 132.1, 126.7, 118.9, 110.7, 74.8, 32.0, 9.8 ppm. IR (Diamond): 3425, 2966, 2878, 2228, 1609, 1408, 1202, 1097, 978, 829 cm^{-1}.

(+)-(*R*)-1-(2-Methoxyphenyl)propan-1-ol (16j):[9]



Product was obtained as a colorless oil (78.0 mg, 0.469 mmol, 94% yield, 89% *ee*). Reaction time = 17 h. R_f = 0.27 (hexane/EtOAc = 90:10). The *ee* was determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 220 nm]: $t_R(S)$ = 25.1 min, $t_R(R)$ = 26.1 min; racemate: $t_R(S)$ = 25.4 min, $t_R(R)$ = 26.5 min. $[\alpha]_D^{22}$ = +18.7 (*c* = 1.00, $CHCl_3$) (lit.[4] $[\alpha]_D^{26}$ = +23.7 (*c* = 1.40, $CHCl_3$), 95% *ee* of (*R*)-**16j**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.31 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.25 (m, 1H), 6.97 (ddd, *J* = 7.5, 7.5, 1.1 Hz, 1H), 6.90 (dd, *J* = 8.2, 0.8 Hz, 1H), 4.79 (dd, *J* = 6.4, 6.4 Hz, 1H), 3.86 (s, 3H), 2.55 (m, 1H), 1.86 – 1.80 (m, 2H), 0.97 (dd, *J* = 7.4, 7.4 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 156.6, 132.5, 128.2, 127.1, 120.7, 110.5, 72.2, 55.2, 30.2, 10.5 ppm. IR (Diamond): 3391, 2964, 2837, 1601, 1489, 1464, 1234, 1028, 972, 750 cm^{-1}.

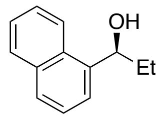
(–)-(*S*)-1-(*o*-Tolyl)propan-1-ol (16k):[3]



Product was obtained as a colorless oil (64.9 mg, 0.432 mmol, 86% yield, 86% *ee*). Reaction time = 168 h. R_f = 0.30 (hexane/EtOAc = 90:10). The *ee* was determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 220 nm]: $t_R(R)$ = 15.4 min, $t_R(S)$ = 17.6 min; racemate: $t_R(R)$ = 14.9 min, $t_R(S)$ = 17.0 min. $[\alpha]_D^{22}$ = –52.0 (*c* = 1.00, $CHCl_3$) (lit.[5] $[\alpha]_D^{20}$ =

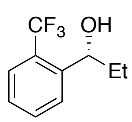
+36.3 (c = 28.6, $CHCl_3$), 96% *ee* of (*R*)-**16k**). ^{1}H NMR (500 MHz, $CDCl_3$): 7.48 (dd, J = 7.7, 1.2 Hz, 1H), 7.24 (m, 1H), 7.18 (ddd, J = 7.4, 7.4, 1.5 Hz, 2H), 7.15 (m, 1H), 4.89 (dd, J = 6.4, 6.4 Hz, 1H), 2.36 (s, 3H), 1.81 – 1.75 (m, 2H), 1.72 (m, 1H), 1.00 (dd, J = 7.4, 7.4 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 142.8, 134.6, 130.3, 127.1, 126.2, 125.3, 72.0, 30.9, 19.1, 10.4 ppm. IR (Diamond): 3342, 2962, 2876, 1460, 1379, 1265, 1090, 1053, 972, 748 cm^{-1}.

(–)-(*S*)-1-(Naphthalen-1-yl)propan-1-ol (16l):[3]



Product was obtained as a colorless oil (70.2 mg, 0.377 mmol, 75% yield, 77% *ee*). Reaction time = 48 h. R_f = 0.27 (hexane/EtOAc = 90:10). The *ee* was determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 220 nm]: t_R(*S*) = 27.8 min, t_R(*R*) = 30.9 min; racemate: t_R(*S*) = 28.3 min, t_R(*R*) = 31.5 min. $[\alpha]_D^{22}$ = –50.9 (c = 1.00, $CHCl_3$) (lit.[4] $[\alpha]_D^{26}$ = +60.3 (c = 1.11, $CHCl_3$), 97% *ee* of (*R*)-**16l**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.14 (m, 1H), 7.89 (m, 1H), 7.80 (m, 1H), 7.66 (m, 1H), 7.55 – 7.48 (m, 3H), 5.43 (m, 1H), 2.05 (m, 1H), 1.99 – 1.91 (m, 2H), 1.05 (dd, J = 7.4, 7.4 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 140.3, 133.9, 130.6, 128.9, 127.9, 125.9, 125.5, 125.5, 123.3, 123.0, 72.5, 31.1, 10.6 ppm. IR (Diamond): 3356, 2966, 2874, 1510, 1394, 1229, 1167, 1094, 966, 775 cm^{-1}.

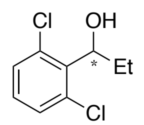
(+)-(*R*)-1-(2-(Trifluoromethyl)phenyl)propan-1-ol (16m):[10]



Product was obtained as a colorless oil (22.6 mg, 0.111 mmol, 22% yield, 24% *ee*). Reaction time = 72 h. R_f = 0.28 (hexane/EtOAc = 90:10). The *ee* was determined by HPLC [Daicel ChiralCel® OJ–H, hexane/*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 220 nm]: t_R(*S*) = 10.0 min, t_R(*R*) = 11.5 min; racemate: t_R(*S*) = 10.1 min, t_R(*R*) = 11.5 min. $[\alpha]_D^{22}$ = +9.5 (c = 0.27, $CHCl_3$) (lit.[11] $[\alpha]_D^{25}$ = –31.0 (c = 2.48, MeOH), 89% *ee* of **16m**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.77 (m, 1H), 7.63 (m 1H), 7.60 (m, 1H), 7.38 (m, 1H), 5.05 (dd, J = 6.3, 6.3 Hz, 1H), 1.93 (m, 1H), 1.81 – 1.76 (m, 2H), 1.01 (dd, J = 7.4, 7.4 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 143.9 (m), 132.2, 127.5, 127.4, 127.0 (q, J = 30.5 Hz), 125.4 (q, J = 5.8 Hz), 124.4 (q, J = 273.9 Hz), 70.9 (m), 32.1, 10.5 ppm. ^{19}F NMR (470 MHz, $CDCl_3$) δ_F –58.0 (s, 3F) ppm. IR (Diamond): 3387, 2970, 2880, 1454, 1310, 1159, 1115, 1034, 974, 768 cm^{-1}. The absolute configuration of **16m** was assigned as being

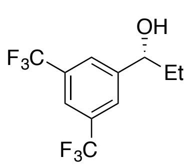
R by comparison of the retention times observed on a ChiralCel® OJ–H column with the chromatogram obtained from a ChiralPak® OJ–H column of a previous assignment.[10]

(–)-1-(2,6-Dichlorophenyl)propan-1-ol (16n):



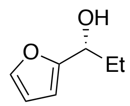
Product was obtained as a white solid (96.4 mg, 0.470 mmol, 94% yield, 74% *ee*). Reaction time = 72 h. R_f = 0.38 (hexane/EtOAc = 90:10). mp = 38–40 °C. The *ee* was determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 220 nm]: t_R(minor) = 13.9 min, t_R(major) = 15.3 min; racemate: t_R(*enant*-A) = 13.7 min, t_R(*enant*-B) = 15.1 min. $[\alpha]_D^{22}$ = –13.1 (*c* = 1.00, $CHCl_3$) (lit.[7] $[\alpha]_D^{25}$ = –16.4 (*c* = 1.82, $CHCl_3$), 87% *ee* of **16n**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.30 (d, *J* = 8.0 Hz, 2H), 7.14 (dd, *J* = 8.4, 8.4 Hz, 1H), 5.35 (ddd, *J* = 10.4, 8.3, 6.7 Hz, 1H), 2.83 (d, *J* = 10.4 Hz, 1H), 2.10 (ddq, *J* = 13.8, 8.4, 7.4 Hz, 1H), 1.98 (m, 1H), 1.01 (dd, *J* = 7.5, 7.5 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 137.9, 134.3, 129.3, 128.7, 73.5, 28.6, 10.5 ppm. IR (Diamond): 3254, 2986, 2881, 1560, 1435, 1340, 1200, 1084, 1022, 773 cm^{-1}. HRMS (APPI-TOF) m/z: $[M+H]^+[-H_2O]$ Calcd for $C_9H_9Cl_2$ 187.0076; Found 187.0072.

(+)-(*R*)-1-(3,5-Bis(trifluoromethyl)phenyl)propan-1-ol (16o):[12]



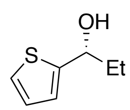
Product was obtained as a white solid (130.9 mg, 0.481 mmol, 96% yield, 76% *ee*). Reaction time = 17 h. R_f = 0.30 (hexane/EtOAc = 90:10). mp = 72–74 °C. The *ee* was determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 99:1, flow rate = 0.5 mL/min, λ = 220 nm]: t_R(*R*) = 19.3 min, t_R(*S*) = 20.3 min; racemate: t_R(*R*) = 18.9 min, t_R(*S*) = 20.1 min. $[\alpha]_D^{22}$ = +17.4 (*c* = 1.00, $CHCl_3$) (lit.[13] $[\alpha]_D^{25}$ = +21.02 (*c* = 1.0, $CHCl_3$), 80% *ee* of (*R*)-**16o**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.83 (m, 2H), 7.80 (m, 1H), 4.79 (ddd, *J* = 6.4, 6.4, 3.6 Hz, 1H), 2.02 (d, *J* = 3.6 Hz, 1H), 1.85 – 1.79 (m, 2H), 0.98 (dd, *J* = 7.4 Hz, 7.4 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 147.0, 131.6 (q, *J* = 33.3 Hz), 126.0 (m), 123.3 (q, *J* = 272.5 Hz), 121.3 (hept, *J* = 3.8 Hz), 74.6, 32.1, 9.6 ppm. ^{19}F NMR (470 MHz, $CDCl_3$) δ_F –62.8 (s, 6F) ppm. IR (Diamond): 3277, 2982, 2885, 1466, 1383, 1275, 1161, 1113, 899, 681 cm^{-1}.

(+)-(*R*)-1-(Furan-2-yl)propan-1-ol (16p):[3]



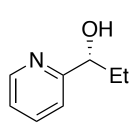
Product was obtained as a yellow oil (44.0 mg, 0.349 mmol, 70% yield, 78% *ee*). Reaction time = 17 h. R_f = 0.25 (hexane/EtOAc = 90:10). The *ee* was determined by HPLC [Daicel ChiralCel® OJ–H, hexane/*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 220 nm]: $t_R(S)$ = 19.3 min, $t_R(R)$ = 20.2 min; racemate: $t_R(S)$ = 20.3 min, $t_R(R)$ = 21.5 min. $[\alpha]_D^{22}$ = +14.7 (*c* = 1.00, $CHCl_3$) (lit.[14] $[\alpha]_D^{26}$ = +25.9 (*c* = 2.10, $CHCl_3$), 90% *ee* of (*R*)-**16p**). ^1H NMR (500 MHz, $CDCl_3$): δ_H 7.39 (m, 1H), 6.34 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.25 (dd, *J* = 3.2, 0.7 Hz, 1H), 4.62 (ddd, *J* = 6.6, 6.6, 6.6 Hz, 1H), 1.96 – 1.83 (m, 3H), 0.97 (dd, *J* = 7.4, 7.4 Hz, 3H) ppm. $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$): δ_C 156.7, 141.9, 110.1, 105.9, 69.2, 28.6, 9.9 ppm. IR (Diamond): 3360, 2966, 2878, 1504, 1464, 1149, 1007, 980, 879, 733 cm^{-1}.

(+)-(*R*)-1-(Thiophen-2-yl)propan-1-ol (16q):[15]



Product was obtained as a colorless oil (67.3 mg, 0.473 mmol, 95% yield, 92% *ee*). Reaction time = 41 h. R_f = 0.28 (Hexane/EtOAc = 90:10). The *ee* was determined by HPLC [Daicel ChiralCel® OJ–H, hexane/*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 220 nm]: $t_R(S)$ = 25.2 min, $t_R(R)$ = 29.2 min; racemate: $t_R(S)$ = 24.6 min, $t_R(R)$ = 29.0 min. $[\alpha]_D^{22}$ = +25.9 (*c* = 1.00, $CHCl_3$) (lit.[14] $[\alpha]_D^{28}$ = +26.4 (*c* = 2.20, $CHCl_3$), 95% *ee* of (*R*)-**16q**). ^1H NMR (500 MHz, $CDCl_3$): δ_H 7.26 (dd, *J* = 4.6, 1.7 Hz, 1H), 7.00 – 6.97 (m, 2H), 4.87 (ddd, *J* = 6.3, 6.3, 2.3 Hz, 1H), 1.97 – 1.90 (m, 2H), 1.86 (m, 1H), 0.98 (dd, *J* = 7.4, 7.4 Hz, 3H) ppm. $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$): δ_C 148.7, 126.6, 124.5, 123.8, 71.7, 32.2, 10.2 ppm. IR (Diamond): 3342, 2964, 2876, 1462, 1377, 1229, 1034, 968, 829, 692 cm^{-1}. HRMS (APPI-TOF) m/z: $[M+H]^+[-H_2O]$ Calcd for C_7H_9S 125.0419; Found 125.0420.

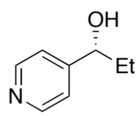
(+)-(*R*)-1-(Pyridin-2-yl)propan-1-ol (16r):[16]



Product was obtained as a colorless oil (34.5 mg, 0.251 mmol, 50% yield, 5% *ee*). Reaction time = 17 h. R_f = 0.32 (Hexane/EtOAc = 50:50). The *ee* was determined by HPLC [Daicel ChiralCel® OJ–H, hexane/*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 254 nm]: $t_R(R)$ = 14.5 min, $t_R(S)$ = 15.7 min; racemate: $t_R(R)$ = 14.5 min, $t_R(S)$ = 15.6 min. $[\alpha]_D^{22}$ = +1.8 (*c* = 0.72, $CHCl_3$) (lit.[17] $[\alpha]_D^{20}$ = +11.7 (*c* = 1.1,

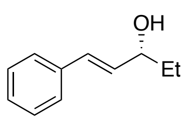
$CHCl_3$), >99% *ee* of (*R*)-**16r**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.56 (m, 1H), 7.69 (ddd, *J* = 7.7, 7.7, 1.7 Hz, 1H), 7.26 (m, 1H), 7.21 (m, 1H), 4.71 (dd, *J* = 7.2, 4.8 Hz, 1H), 4.19 (s, 1H), 1.90 (m, 1H), 1.73 (m, 1H), 0.96 (dd, *J* = 7.4, 7.4 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 162.1, 148.1, 136.6, 122.2, 120.4, 73.9, 31.3, 9.4 ppm. IR (Diamond): 3238, 2964, 2876, 1595, 1435, 1327, 1122, 1047, 982, 758 cm^{-1}.

(+)-(*R*)-1-(Pyridin-4-yl)propan-1-ol (16s):[3]



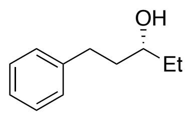
Product was obtained as a colorless oil (63.9 mg, 0.466 mmol, 93% yield, 3% *ee*). Reaction time = 17 h. R_f = 0.15 (Hexane/EtOAc = 50:50). The *ee* was determined by HPLC [Daicel ChiralCel® OJ–H, hexane/*i*PrOH = 95:5, flow rate = 0.8 mL/min, λ = 254 nm]: t_R(*R*) = 22.3 min, t_R(*S*) = 28.3 min; racemate: t_R(*R*) = 22.6 min, t_R(*S*) = 28.8 min. $[\alpha]_D^{22}$ = +1.8 (*c* = 1.00, $CHCl_3$) (lit.[18] $[\alpha]_D^{20}$ = +50.4 (*c* = 0.5, $CHCl_3$), 85% *ee* of (*R*)-**16s**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.57 (m, 2H), 7.28 (m, 2H), 4.66 (dd, *J* = 6.3, 6.3 Hz, 1H), 1.81 – 1.76 (m, 2H), 1.63 (m, 1H), 0.96 (dd, *J* = 7.4, 7.4 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 155.0, 148.8, 121.3, 73.7, 31.7, 9.8 ppm. IR (Diamond): 3194, 2966, 2876, 1605, 1414, 1219, 1065, 982, 816, 731 cm^{-1}.

(+)-(*R*,*E*)-1-Phenylpent-1-en-3-ol (16t):[3]



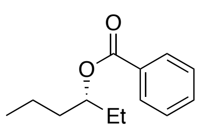
Product was obtained as a white semi-solid (69.1 mg, 0.426 mmol, 85% yield, 76% *ee*). Reaction time = 24 h. R_f = 0.17 (Hexane/EtOAc = 90:10). The *ee* was determined by HPLC [Daicel ChiralCel® OJ–H, hexane/*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 254 nm]: t_R(*S*,*E*) = 28.3 min, t_R(*R*,*E*) = 30.8 min; racemate: t_R(*S*,*E*) = 28.3 min, t_R(*R*,*E*) = 31.4 min. $[\alpha]_D^{22}$ = +5.4 (*c* = 1.00, $CHCl_3$) (lit.[4] $[\alpha]_D^{26}$ = +18.4 (*c* = 0.61, $CHCl_3$), 75% *ee* of (*R*,*E*)-**16t**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.41 – 7.39 (m, 2H), 7.35 – 7.32 (m, 2H), 7.25 (m, 1H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.23 (dd, *J* = 15.9, 6.8 Hz, 1H), 4.23 (ddd, *J* = 6.5, 6.5, 6.5 Hz, 1H), 1.74 – 1.64 (m, 2H), 1.60 (m, 1H), 0.99 (dd, *J* = 7.5, 7.5 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 136.8, 132.4, 130.4, 128.6, 127.6, 126.5, 74.4, 30.2, 9.8 ppm. IR (Diamond): 3431, 2970, 2876, 1450, 1338, 1126, 1072, 960, 752, 692 cm^{-1}.

(–)-(*R*)-1-Phenylpentan-3-ol (16u):[3]



Product was obtained as a colorless oil (42.4 mg, 0.258 mmol, 52% yield, 78% *ee*). Reaction time = 20 h. R_f = 0.22 (Hexane/EtOAc = 90:10). The *ee* was determined by HPLC [Daicel ChiralCel® OJ–H, hexane/*i*PrOH = 98:2, flow rate = 0.5 mL/min, λ = 220 nm]: $t_R(R)$ = 29.7 min, $t_R(S)$ = 30.9 min; racemate: $t_R(R)$ = 28.9 min, $t_R(S)$ = 30.0 min. $[\alpha]_D^{22}$ = –21.0 (*c* = 1.00, $CHCl_3$) (lit.[19] $[\alpha]_D^{20}$ = –12.2 (*c* = 2.45, $CHCl_3$), 55% *ee* of (*R*)-**16u**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.31 – 7.28 (m, 2H), 7.23 – 7.19 (m, 3H), 3.58 (m, 1H), 2.82 (m, 1H), 2.69 (m, 1H), 1.85 – 1.70 (m, 2H), 1.61 – 1.43 (m, 2H), 1.34 (d, *J* = 5.0 Hz, 1H), 0.96 (dd, *J* = 7.5, 7.5, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 142.3, 128.5, 128.4, 125.8, 72.7, 38.6, 32.1, 30.3, 9.9 ppm. IR (Diamond): 3346, 2928, 2876, 1603, 1454, 1119, 1030, 932, 743, 696 cm^{-1}.

(–)-(*R*)-Hexan-3-yl benzoate (16v):[20]

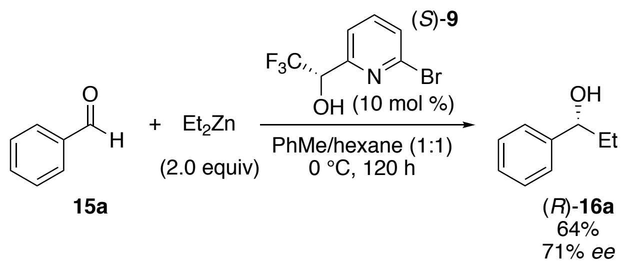


*In situ generated (R)-hexan-3-ol was transformed into benzoate **16v** according to the following procedure:* After the mixture was stirred at 0 °C for 24 h, CH_2Cl_2 (1.0 mL), Et_3N (139 μL, 1.00 mmol, 2.0 equiv), and benzoyl chloride (174 μL, 1.50 mmol, 3.0 equiv) were successively added into the test tube and the reaction was stirred at 22 °C for another 17 h. Product was obtained as a colorless oil (74.0 mg, 0.359 mmol, 72% yield, 73% *ee*). R_f = 0.30 (hexane/EtOAc = 98:2). The *ee* was determined by HPLC [Daicel ChiralPak® AD–H, hexane/*i*PrOH = 100:0, flow rate = 0.5 mL/min, λ = 220 nm]: $t_R(R)$ = 20.9 min, $t_R(S)$ = 22.9 min; racemate: $t_R(R)$ = 19.1 min, $t_R(S)$ = 20.4 min. $[\alpha]_D^{22}$ = –3.5 (*c* = 1.00, $CHCl_3$) (lit.[20] $[\alpha]_D^{23}$ = –4.8 (*c* = 1.0, $CHCl_3$), 89% *ee* of (*R*)-**16v**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.08 – 8.06 (m, 2H), 7.56 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.47 – 7.43 (m, 2H), 5.11 (m, 1H), 1.74 – 1.59 (m, 4H), 1.49 – 1.35 (m, 2H), 0.96 (dd, *J* = 7.4, 7.4 Hz, 3H), 0.94 (dd, *J* = 7.4, 7.4 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 166.4, 132.7, 130.9, 129.5, 128.3, 75.9, 35.9, 27.1, 18.7, 14.0, 9.7 ppm. IR (Diamond): 2962, 2876, 1715, 1450, 1269, 1105, 1070, 1026, 932, 708 cm^{-1}.

Asymmetric ethylation reaction of benzaldehyde catalyzed by Zn^{II} complexes:

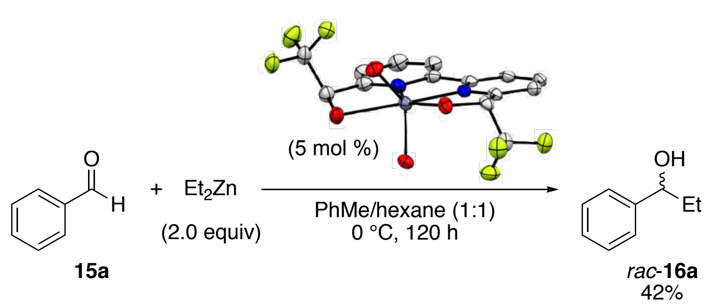
Control experiments

The use of 2,2′-bipyridine-α,α′-CF_3-diol **1** as ligand was necessary, as confirmed by the following experiment. When (*S*)-**9** was used as the chiral source under the optimized reaction conditions (Scheme S2), the ethylation reaction of **15a** occurred in a prolonged reaction time and both the yield and the enantiomeric excess of (*R*)-**16a** were diminished *vs.* (*S*,*S*)-**1** (93%, 95% *ee* of (*R*)-**16a**).



Scheme S2 Zn^{II}-catalyzed ethylation reaction of aldehyde **15a** using (*S*)-**9**. Conditions: (*S*)-**9** (0.0250 mmol), **15a** (0.250 mmol), Et_2Zn (0.500 mmol), PhMe (0.5 mL), 0 °C, 120 h.

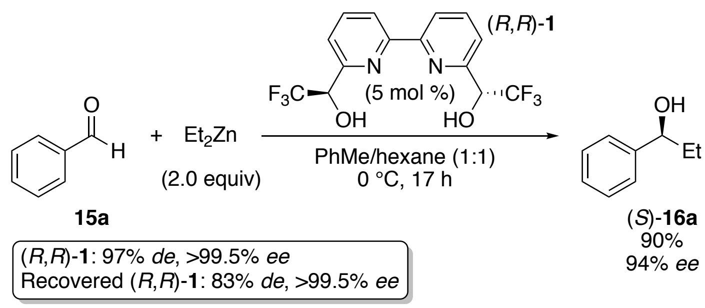
The preformed catalyst [(*R*,*R*)-**1**·Zn·$2H_2O$]$^{2+}$·2OTf$^{–}$ was employed in the ethylation reaction of **15a** (Scheme S3). The catalyst was obtained according to the crystallization procedure (described below) giving a homogeneous solution, which afforded the preformed catalyst as a white solid after evaporation of MeCN. Under the optimized reaction conditions, [(*R*,*R*)-**1**·Zn·$2H_2O$]$^{2+}$·2OTf$^{–}$ afforded **16a** in a moderate yield (42%) and no enantioselectivity *vs.* the *in situ* generated (*S*,*S*)-**1**/Zn^{II} catalyst. The low solubility of the preformed catalyst in PhMe suggests that *rac*-**16a** was obtained *via* an uncatalyzed pathway. This hypothesis was also supported by the incomplete conversion of **15a** even for a reaction time of 120 h.



Scheme S3 Zn^{II}-catalyzed ethylation reaction of aldehyde **15a** using preformed catalyst [(*R*,*R*)-**1**·Zn·$2H_2O$]$^{2+}$·2OTf$^{–}$ (CCDC 2099930). Conditions: (i) (*R*,*R*)-**1** (0.0250 mmol), $Zn(OTf)_2$

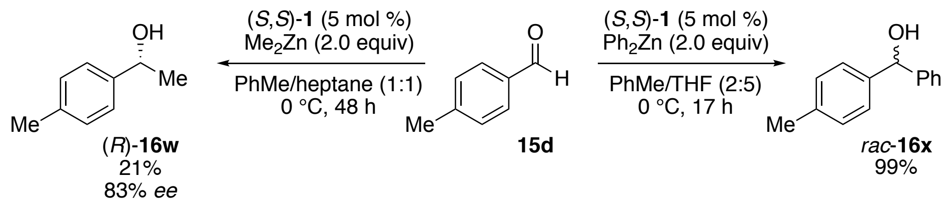
(0.0250 mmol), MeCN (0.3 mL), 22 °C, 0.5 h; then evaporated to dryness; (ii) **15a** (0.500 mmol), Et_2Zn (1.00 mmol), PhMe (1.0 mL), 0 °C, 120 h.

The feasibility of the general procedure was tested on a 2 mmol scale of benzaldehyde **15a** using the *R*,*R* enantiomer of 2,2′-bipyridine-α,α'-CF_3-diol **1** (Scheme S4). As expected, the reaction was completed in 17 h and (*S*)-**16a** was afforded with 90% yield and 94% *ee*. The recyclability of (*R*,*R*)-**1** was confirmed since the ligand was quantitatively recovered after the purification of (*S*)-**16a** using modified elution conditions (Biotage®SNAP Ultra 25g/Biotage®HP-Sphere™ 25 μm; gradient elution of hexane/EtOAc = 98:2–50:50). Importantly, epimerization of the 2,2′-bipyridine-α,α'-CF_3-diol ligand occurred to some extent during the reaction process based on the stereoselectivities obtained measured on recovered (*R*,*R*)-**1** (83% *de*, >99.5% *ee*). Interestingly, whereas the diastereoisomeric purity of the ligand was slightly decreased, its enantiomeric purity was also very slightly increased, as epimerization also occurred on the minor enantiomer.



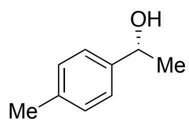
Scheme S4 Scale up of the Zn^{II}-catalyzed ethylation reaction of aldehyde **15a**. Conditions: (*R*,*R*)-**1** (0.100 mmol), **15a** (2.00 mmol), Et_2Zn (4.00 mmol), PhMe (4.0 mL), 0 °C, 17 h.

The protocol using (*S*,*S*)-**1**/Zn^{II} catalysis was further extended to the use of Me_2Zn (1.0 M in heptane; Sigma-Aldrich®) and Ph_2Zn (0.4 M in THF; prepared from PhMgBr and $ZnCl_2$ according to a known method)[22] for the alkylation of aldehyde **15d** (Scheme S5). Alcohol (*R*)-**16w** and *rac*-**16x** were afforded with respective yields of 21% and 99%, whereas a chiral induction was solely observed using Me_2Zn. Noteworthily, the reaction using Me_2Zn was stopped before complete conversion of **15d** (48 h).



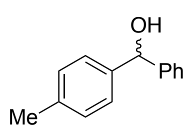
Scheme S5 Zn^{II}-catalyzed alkylation reaction of aldehyde **15d**. Conditions: (*S*,*S*)-**1** (0.0250 mmol), **15d** (0.500 mmol), Me_2Zn or Ph_2Zn (1.00 mmol), PhMe (1.0 mL), 0 °C, 17 h or 48 h.

(+)-(*R*)-1-(*p*-Tolyl)ethanol (16w):[3]



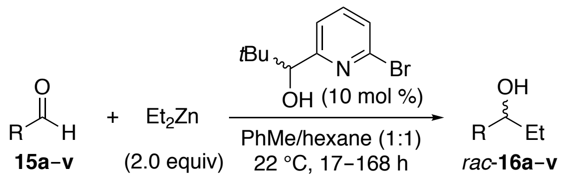
*Following the general procedure described for the synthesis of alcohols **16a–v**:* Product was obtained as a colorless oil (14.1 mg, 0.104 mmol, 21% yield, 83% *ee*). Reaction time = 48 h. R_f = 0.23 (Hexane/EtOAc = 90:10). The *ee* was determined by HPLC [Daicel ChiralCel® AD–H, hexane/*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 220 nm]: $t_R(R)$ = 19.3 min, $t_R(S)$ = 20.8 min; racemate: $t_R(R)$ = 19.1 min, $t_R(S)$ = 20.5 min. $[\alpha]_D^{22}$ = +38.9 (*c* = 0.67, $CHCl_3$) (lit.[21] $[\alpha]_D^{22}$ = +56.8 (*c* = 0.41, $CHCl_3$), 94% *ee* of (*R*)-**16w**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.28 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.89 (q, *J* = 6.4 Hz, 1H), 2.36 (s, 3H), 1.76 (m, 1H), 1.50 (d, *J* = 6.5 Hz, 3H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 143.0, 137.1, 129.2, 125.4, 70.2, 25.1, 21.1 ppm. IR (Diamond): 3348, 2972, 2924, 1514, 1450, 1070, 1009, 897, 816, 727 cm^{-1}.

***rac*-(*p*-Tolyl)phenylmethanol (16x):**[3]



Product was obtained in 99% yield (98.3 mg, 0.496 mmol). The ^{1}H NMR and ^{13}C NMR spectra of were in accordance with previously published data and the *ee* was determined by HPLC [Daicel ChiralCel® AD–H, hexane/*i*PrOH = 98:2, flow rate = 0.8 mL/min, λ = 220 nm]: t_R(*enant*-A) = 29.8 min, t_R(*enant*-B) = 32.6 min.

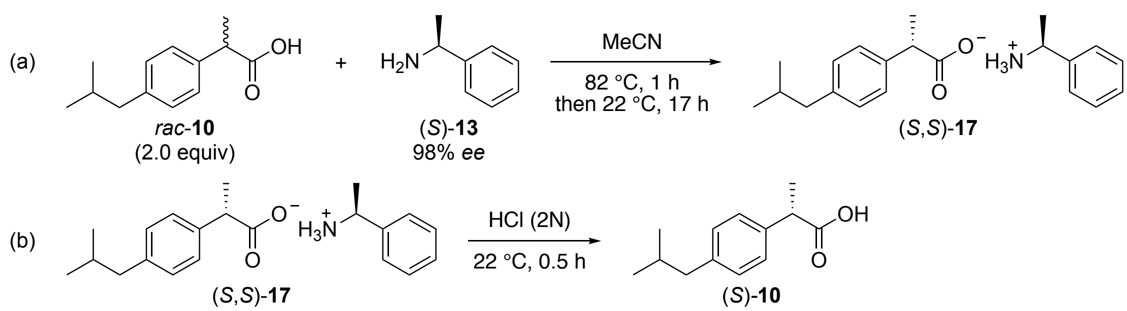
General procedure for the synthesis of racemates (16a–v)



*Following the procedure described for the preparation of enantioenriched alcohols **16a–v**:* *rac*-1-(6-bromopyridin-2-yl)-2,2-dimethylpropan-1-ol (*rac-t*Bu-alcohol; 12.2 mg, 0.0500 mmol, 0.010 equiv), **15a–v** (0.500 mmol, 1.0 equiv), Et_2Zn (1.0 mL, 1.00 mmol, 2.0 equiv; 1.0 M in hexane), PhMe (1.0 mL), 22 °C, 17–168 h.

Having similar polarities, *rac-t*Bu-alcohol was isolated within the fraction of *rac*-**16c**, *rac*-**16d**, *rac*-**16j–m**, and *rac*-**16q**. No interference of *rac-t*Bu-alcohol was noted for the HPLC chromatograms of the products.

Procedure for the resolution of 2-(4-isobutylphenyl)propanoic acid (10):[23]



(–)-(*S*)-α-Methylbenzylamine **13**, which is a relatively cheap enantiopure chiral precursor, was used as an efficient resolving agent of *rac*-**10** through the resolution of the diastereomeric salts (*S*,*S*)-**17** and (*R*,*S*)-**17**. The efficiency of the resolution relied mainly on the different solubility of (*S*,*S*)-**17** and (*R*,*S*)-**17**. Conceptually, all species are soluble at high temperature and a dynamic equilibrium, between (*S*)-**13** bonded with either the *S* or the *R* enantiomer of **10**, was established. By slowly lowering the temperature, the equilibrium was shifted in favor of (*S*,*S*)-**17**, which has a poor solubility in the chosen solvent. Thus, the unreacted (*R*)-**10** was then removed by filtration from the crystallized (*S*,*S*)-**17** salt. To reach higher diastereomeric enrichment of (*S*,*S*)-**17**, up to four recrystallization cycles were performed and, upon treatment with aqueous HCl, (*S*)-**10** was obtained with an excellent

93% *ee*. Since filtrates are generally enantiomerically impoverished in comparison with the crystals, the purity of the residual (*R*)-**10** was not verified and the filtrate was discarded.

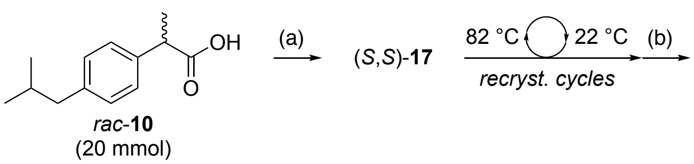
*Diastereomeric salt (S,S)-**17** was prepared according to the following procedure (eq. a):*
To a 1 L flask, *rac*-**10** (12.3 g, 60.0 mmol, 2.0 equiv) was added to MeCN (600 mL) followed by the addition of (–)-(*S*)-α-methylbenzylamine **13** (3.8 mL, 30.0 mmol, 1.0 equiv, 98% *ee*) at 22 °C. A white precipitate was formed instantly and the mixture was stirred at 82 °C for 1 h. Upon complete solubilization of the precipitate, the magnetic stir bar was removed before the mixture was allowed to cool down as slowly as possible to reach 22 °C. After standing at this temperature overnight, the white crystals were filtered, washed with portions of MeCN, and dried *in vacuo*. Three subsequent recrystallizations from hot MeCN (25 mL per mmol of (*S*,*S*)-**17**, 82°C) afforded the diastereomerically enriched compound as white crystals (7.20 g, 22.0 mmol, 73% yield).

*Ibuprofen (S)-**10** was prepared according to the following procedure (eq. b):*
To a 500 mL flask, (*S*,*S*)-**17** (9.82 g, 30 mmol) was added to EtOAc (200 mL) at 22 °C. An aqueous solution of HCl (100 mL; 2N) was slowly added and the reaction was stirred at 22 °C for 30 min. The aqueous layer was extracted with EtOAc (3 x 100 mL). The combined organic layers were washed with brine (100 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 product was purified by silica gel column chromatography using a gradient elution of hexane/EtOAc = 95:5–80:20 to give compound **10** as a white solid (6.11 g, 29.6 mmol, 99% yield, 93% *ee*). The following characterization was performed using (*S*)-**10** in 98% *ee*: mp = 42–44 °C (lit.[23] mp = 51–52 °C). R_f = 0.16 (Hexane/EtOAc = 90:10). $[\alpha]_D^{22}$ = +54.6 (*c* = 1.0, $CHCl_3$); (lit.[23] $[\alpha]_D^{20}$ = +52.3 (*c* = 1.0, $CHCl_3$), 98% *ee* of (*S*)-**10**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 10.72 (brs, 1H), 7.23 (dt, *J* = 8.1, 2.0 Hz, 2H), 7.11 (dt, *J* = 8.1, 2.0 Hz, 2H), 3.73 (q, *J* = 7.2 Hz, 1H), 2.46 (d, *J* = 7.2 Hz, 2H), 1.85 (m, 1H), 1.51 (d, *J* = 7.2 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 6H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 181.6, 140.9, 137.1, 129.5, 127.4, 45.2, 45.1, 30.3, 22.5, 18.2 ppm. IR (Diamond): 2953, 2870, 2633, 1701, 1418, 1281, 1230, 1184, 866,

779 cm^{-1}. The absolute configuration of **10** was assigned as being *S* by comparison of the optical rotation with a previous assignment. The enantioselectivity was determined based on the *ee* obtained on the corresponding propanoate **18** (*see the procedure described below*).

To illustrate the efficiency for the resolution of *rac*-**10** into (*S*)-**10**, the diastereoselective enrichment of (*S*,*S*)-**17** was determined after each recrystallization cycle (Table S6). On a 10 mmol reaction scale, the diastereomeric salt (*S*,*S*)-**17** was recrystallized according to the procedure of equation *a*. A small aliquot (32.7 mg, 0.100 mmol) was hydrolyzed into (*S*)-**10** in the reaction conditions of equation *b* and then, esterified into (*S*)-**18** to verify the *ee*. The recrystallization process was repeated up to 4 cycles with the remaining quantity of (*S*,*S*)-**17**.

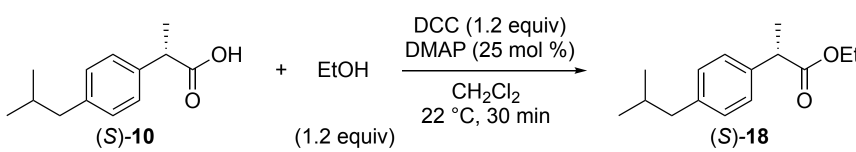
Table S6 Recrystallization cycles – yields of (*S*,*S*)-**17** and enantioselectivities of (*S*)-**10**



recryst. cycles	(*S*,*S*)-**17**			(*S*)-**10**
	m (g)	n (mmol)	Yield (%)	*ee*[a] (%)
1	2.82	8.61	86	68
2	2.68	8.18	82	84
3	2.32	7.08	71	94
4	2.07	6.32	63	98

[a] Determined by chiral HPLC (OJ–H column) from the corresponding (*S*)-**18**.

Preparation of (+)-(*S*)-ethyl 2-(4-isobutylphenyl)propanoate (18):[23]



*Following the procedure described for the preparation of esters (R,S)-**11** and (S,S)-**12**:*

(*S*)-**10** (20.6 mg, 0.100 mmol, 1.0 equiv), EtOH (7 μL, 0.120 mmol, 1.2 equiv), DCC (24.8 mg, 0.120 mmol, 1.2 equiv), DMAP (3.1 mg, 0.0250 mmol, 0.25 equiv), CH_2Cl_2 (0.5 mL), 22 °C, 30 min. After the filtration through a plug of silica, the crude product was sufficiently pure to be injected into the HPLC instrument without a prior purification. Product was obtained as a colorless oil (22.0 mg, 0.0939 mmol, 94% yield, 93% *ee*). The following characterization was performed using (*S*)-**18** in 98% *ee*: R_f = 0.42 (Hexane/EtOAc = 98:2). The *ee* was determined by HPLC [Daicel ChiralCel® OJ–H, hexane/*i*PrOH = 99.5:0.5, flow rate = 0.5 mL/min, λ = 220 nm]: $t_R(S)$ = 13.4 min, $t_R(R)$ = 14.6 min; racemate: $t_R(S)$ = 13.4 min, $t_R(R)$ = 14.5 min. $[\alpha]_D^{22}$ = +38.0 (*c* = 0.83, $CHCl_3$) (lit.[23] $[\alpha]_D^{20}$ = +33.9 (*c* = 1.1, $CHCl_3$), 76% *ee* of (*S*)-**18**). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.21 (dt, *J* = 8.1, 2.0 Hz, 2H), 7.10 (dt, *J* = 8.1, 2.0 Hz, 2H), 4.15 (m, 1H), 4.10 (m, 1H), 3.69 (q, *J* = 7.2 Hz, 1H), 2.45 (d, *J* = 7.2 Hz, 2H), 1.85 (m, 1H), 1.49 (d, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H) ppm. ^{13}C{H} NMR (126 MHz, $CDCl_3$): δ_C 174.8, 140.4, 137.9, 129.3, 127.1, 60.6, 45.2, 45.1, 30.2, 22.4, 18.6, 14.1 ppm. IR (Diamond): 2955, 2934, 2870, 2120, 1732, 1452, 1200, 1159, 1022, 847 cm^{-1}. The absolute configuration of **18** was assigned as being *S* by comparison of the optical rotation with a previous assignment

Crystallization procedure for (*R*)-9:

(*R*)-**9** (7.1 mg, 27.7 µmol) was added to hexane (1.0 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. (CCDC 2098867)

Crystallization procedure for (*R*,*R*)-1:

(*R*,*R*)-**1** (5.4 mg, 15.4 µmol) was added to hexane/EtOAc = 90:10 (0.53 mL) and the mixture was heated to 80 °C to solubilize the solid. The solution was slowly cooled down to 22 °C and the crystals were gradually formed. (CCDC 2098890)

Crystallization procedure for $[(R,R)\text{-}\mathbf{1}\cdot Zn\cdot 2H_2O]^{2+}\cdot 2OTf^-$:

$Zn(OTf)_2$ (5.6 mg, 15.4 µmol, 1.0 equiv) and (*R*,*R*)-**1** (5.4 mg, 15.4 µmol, 1.0 equiv) were dissolved in MeCN (0.2 mL). The colorless 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. (CCDC 2099930)

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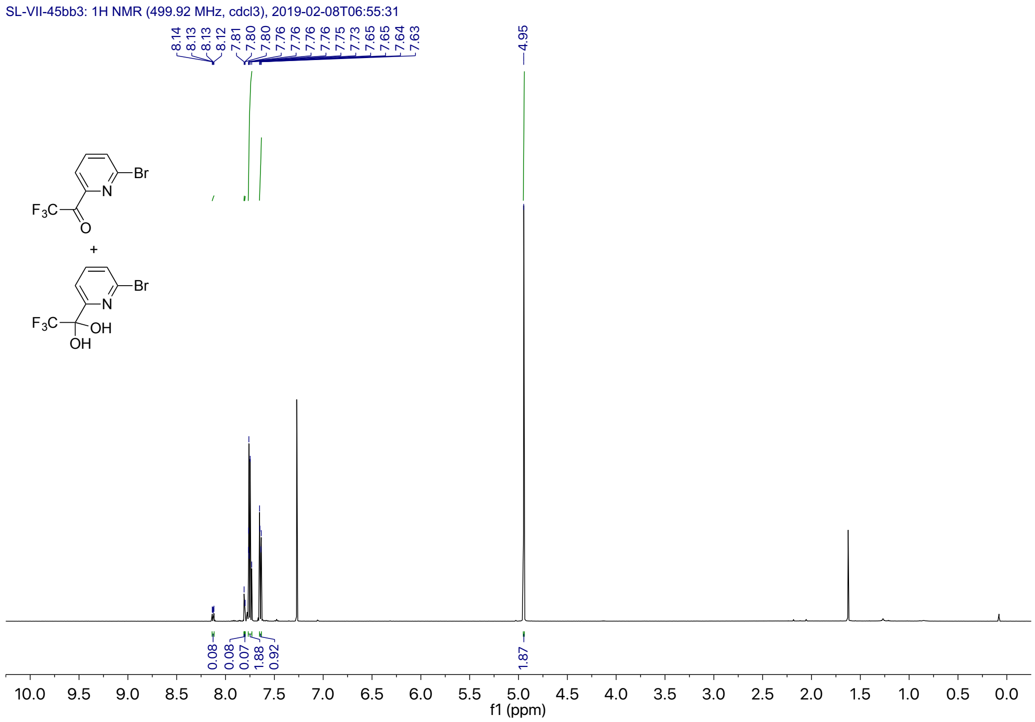
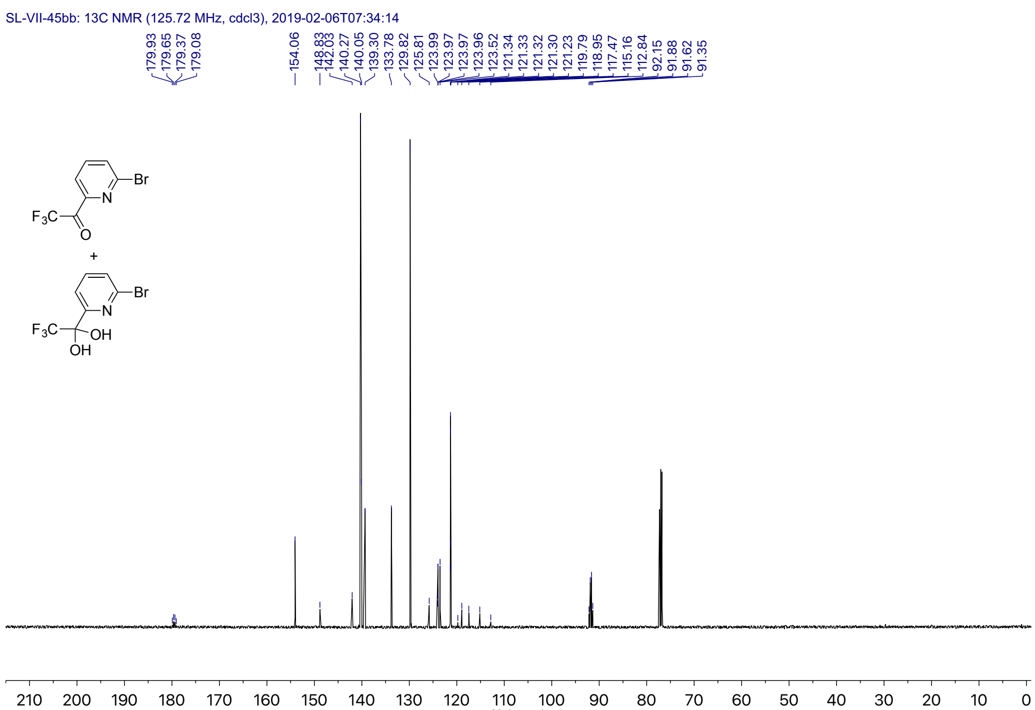
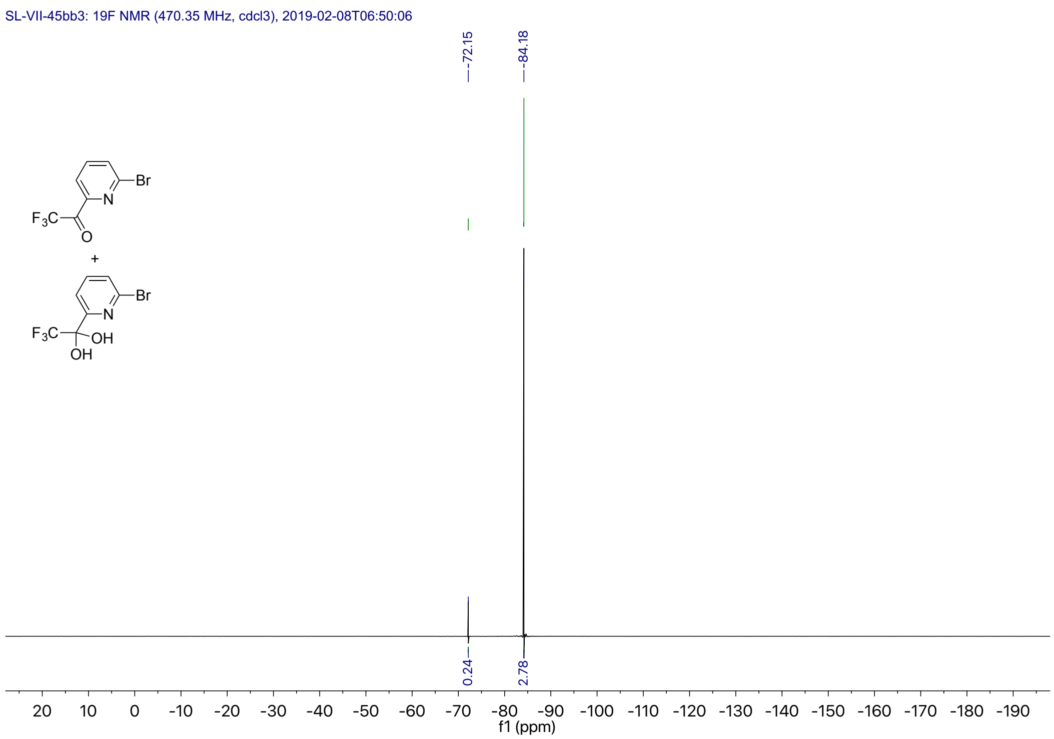
^{1}H, ^{13}C{H}, and ^{19}F NMR spectra



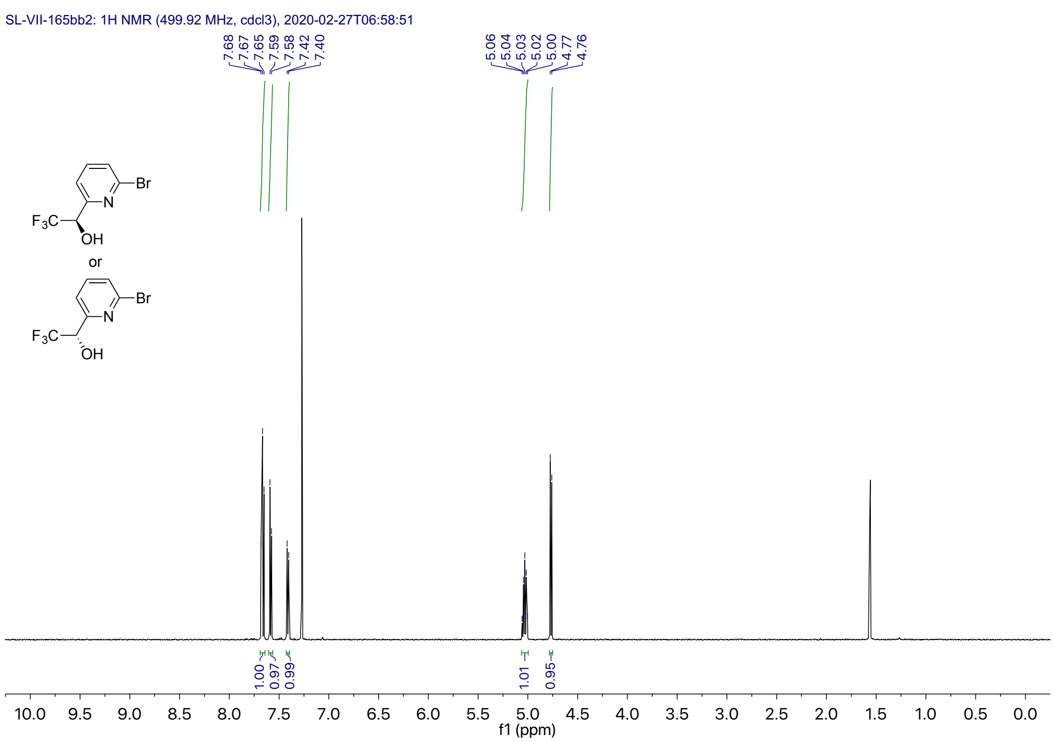
^{1}H NMR (500 MHz, $CDCl_3$) of **8** and **8'**



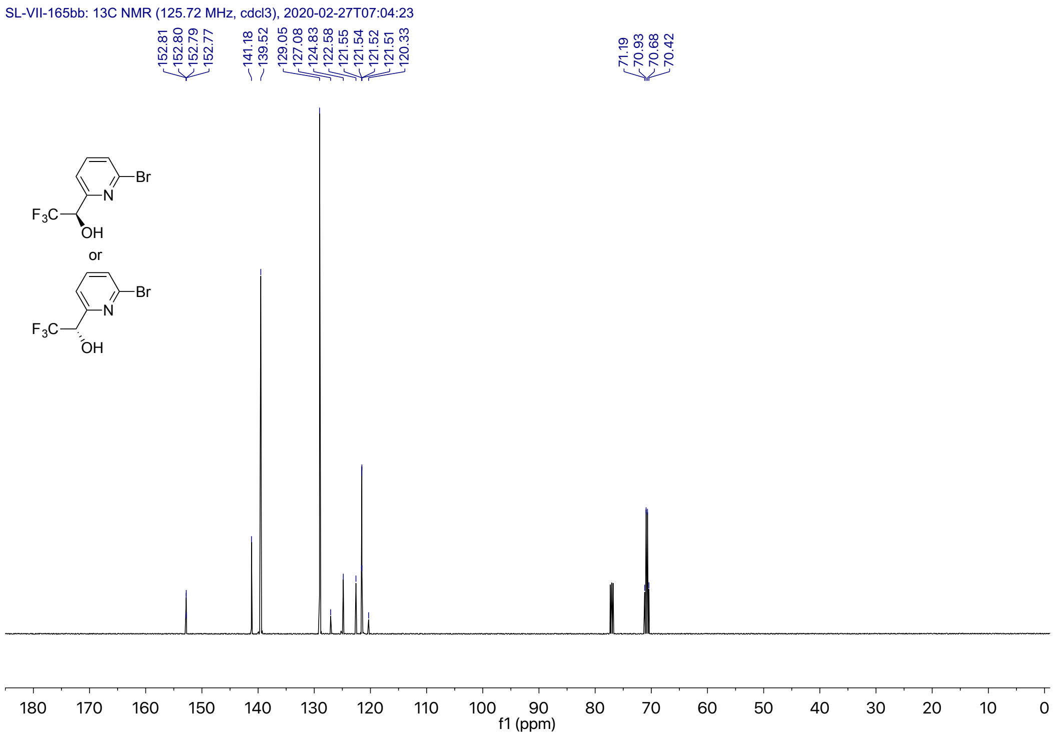
^{13}C{H} NMR (126 MHz, $CDCl_3$) of **8** and **8'**



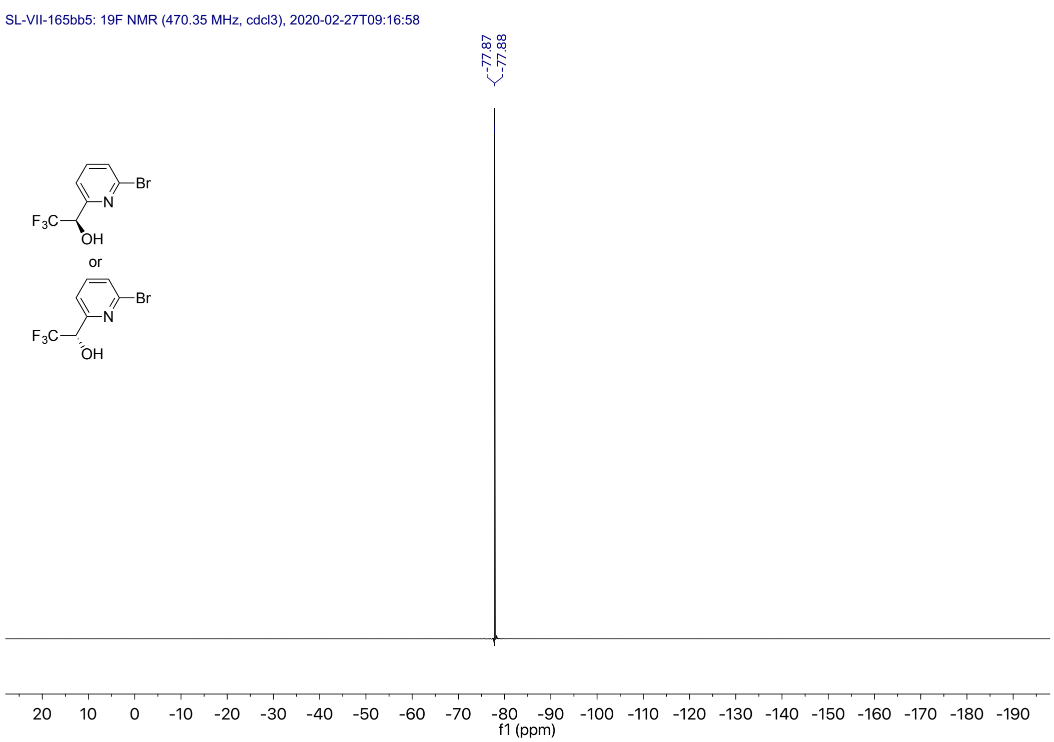
^{19}F NMR (470 MHz, $CDCl_3$) of **8** and **8'**



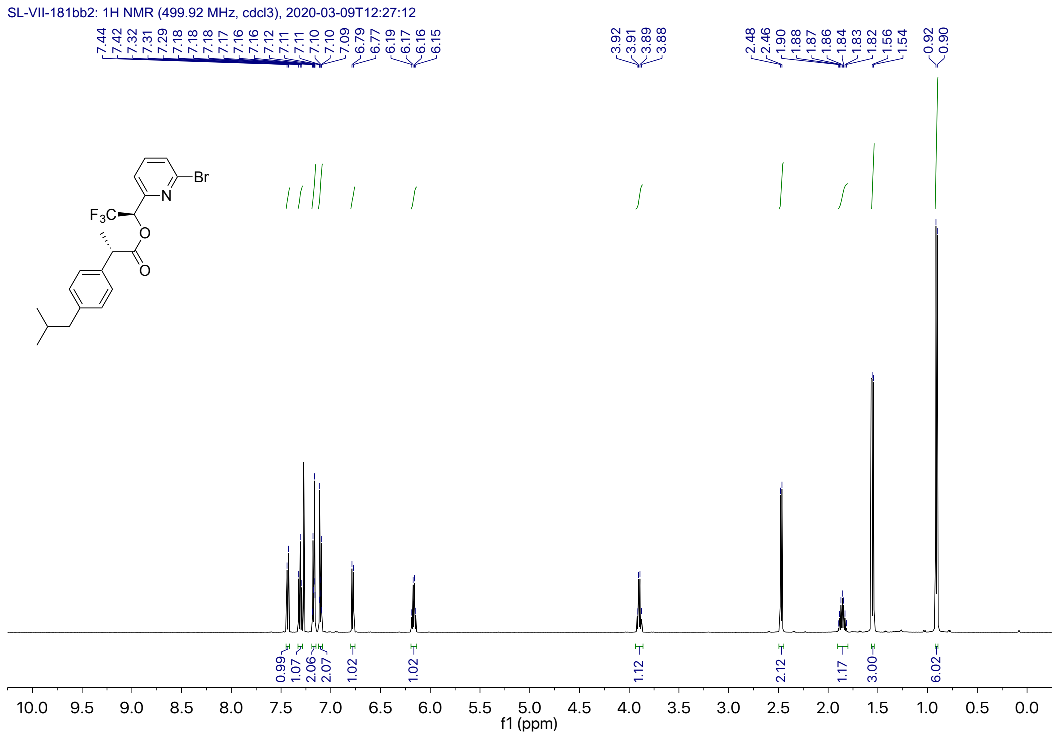
^{1}H NMR (500 MHz, $CDCl_3$) of (*R*)-**9** or (*S*)-**9**



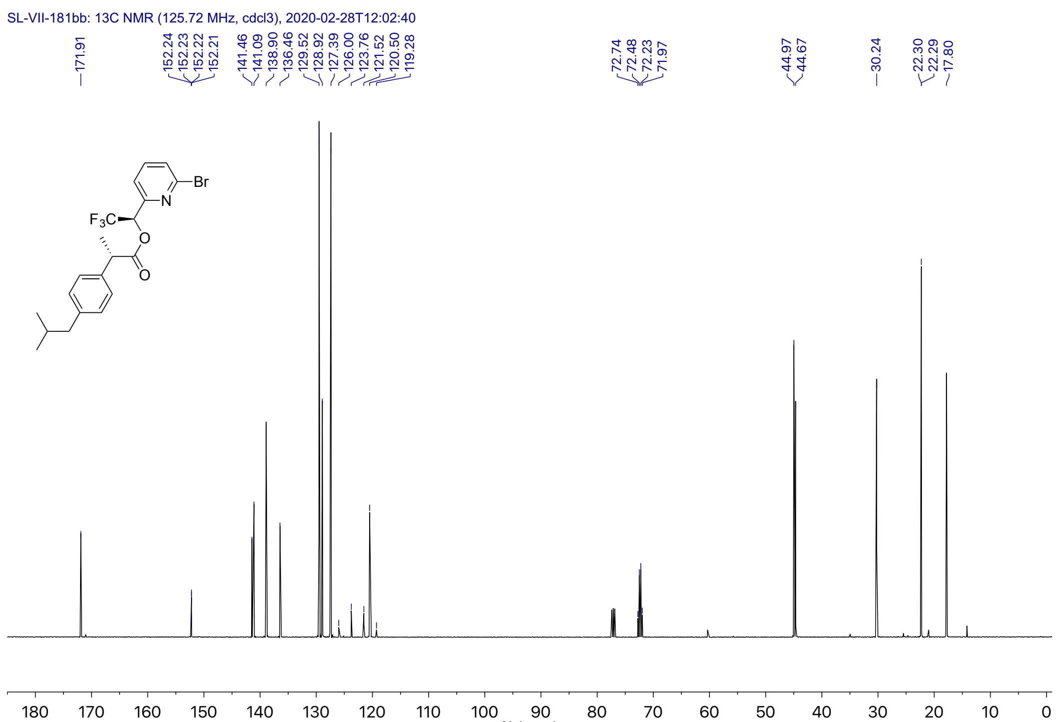
$^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) of (*R*)-**9** or (*S*)-**9**



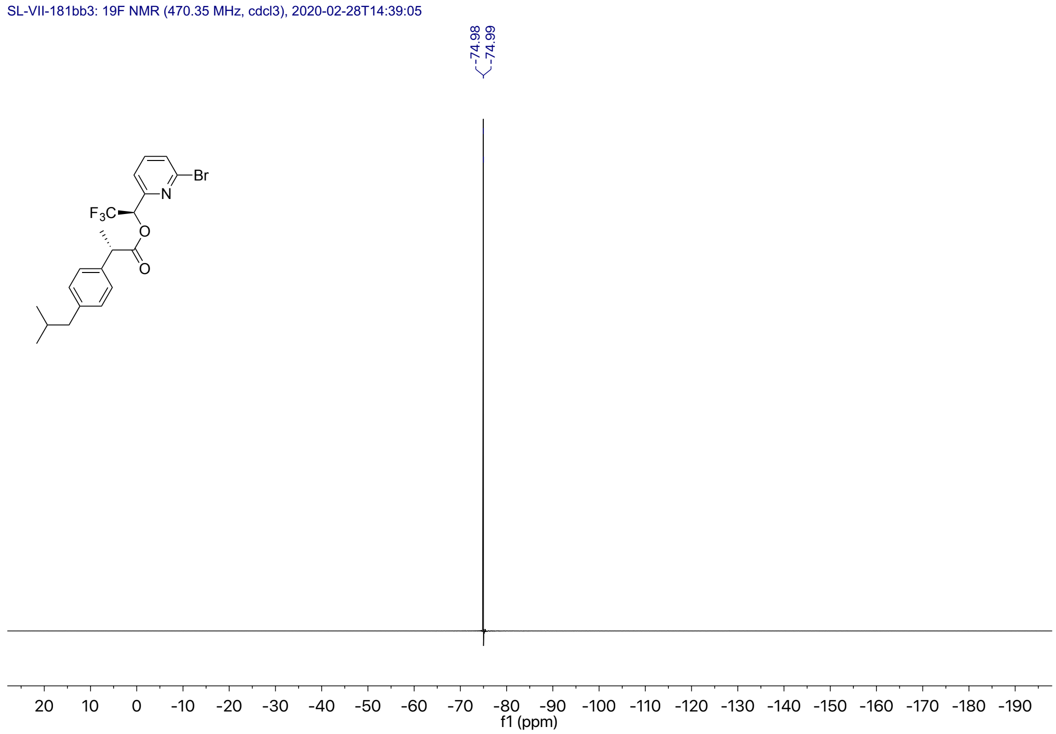
^{19}F NMR (470 MHz, $CDCl_3$) of (*R*)-**9** or (*S*)-**9**



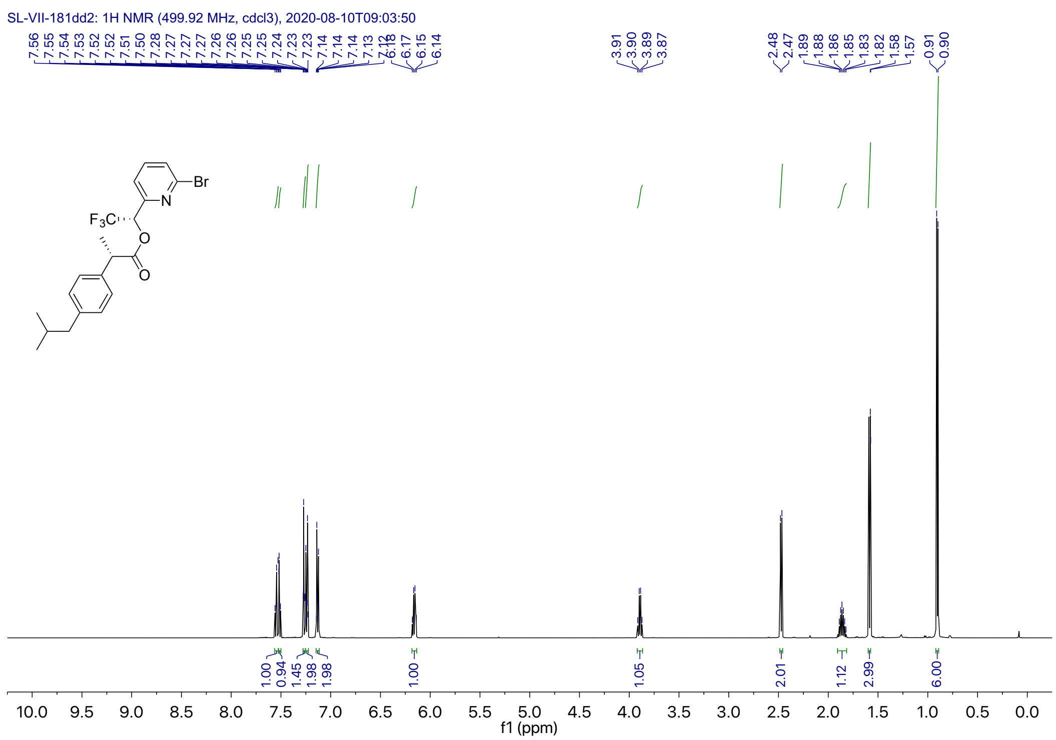
^{1}H NMR (500 MHz, CDCl$_3$) of (*R*,*S*)-**11**



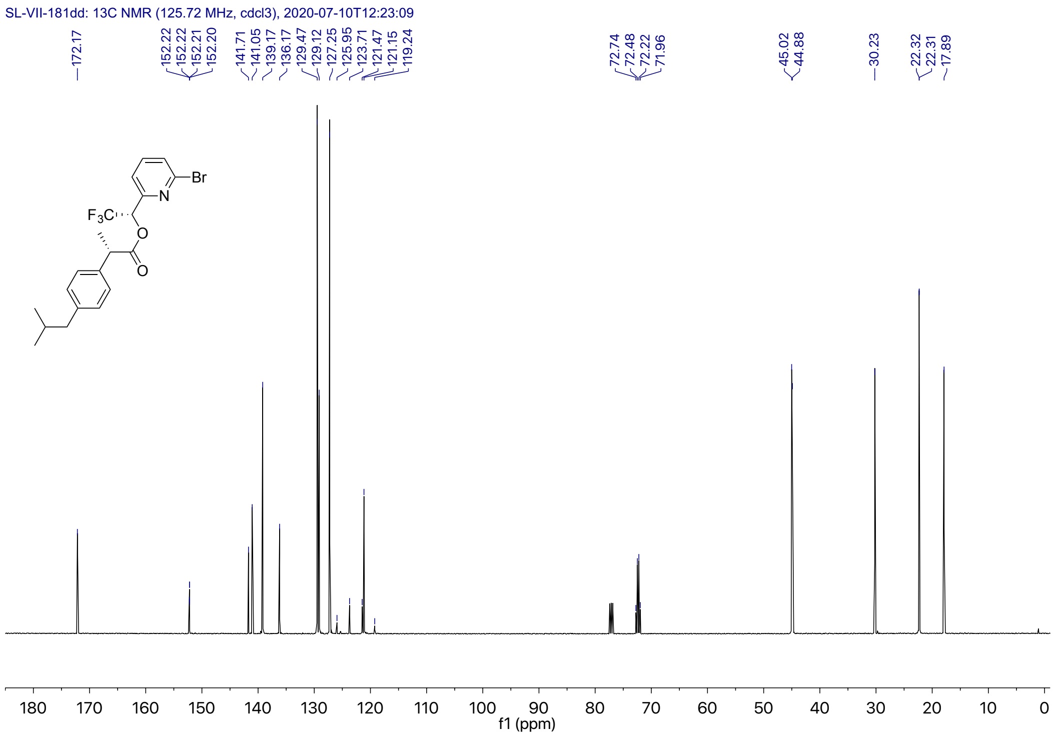
^{13}C{H} NMR (126 MHz, CDCl$_3$) of (*R*,*S*)-**11**



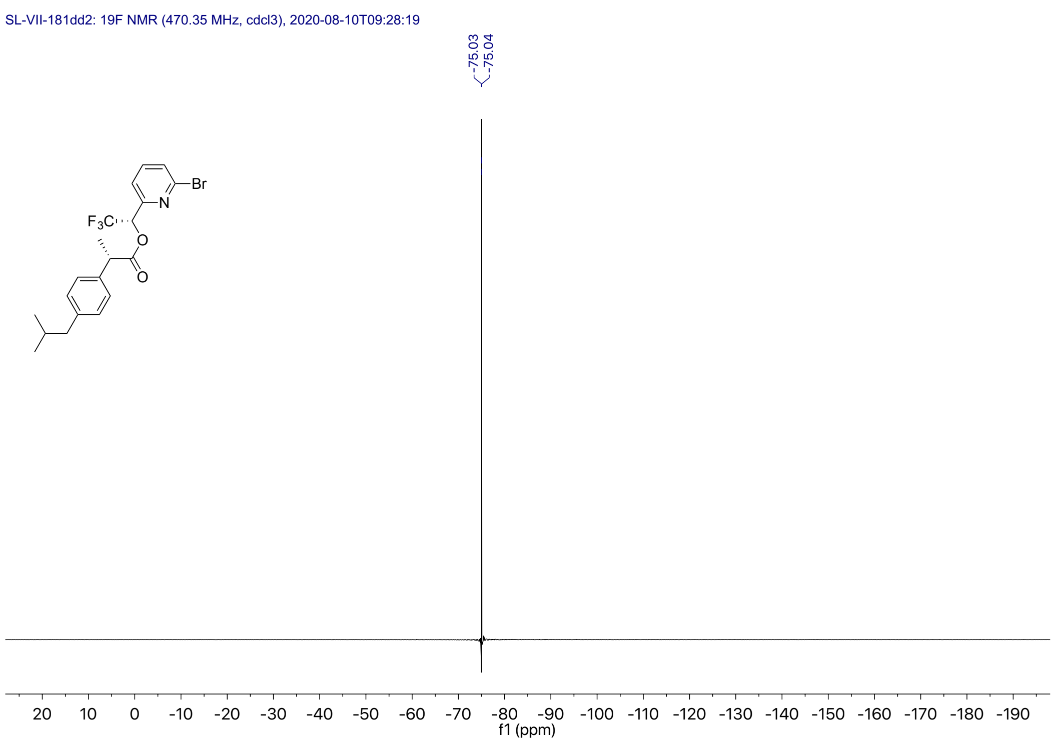
^{19}F NMR (470 MHz, $CDCl_3$) of (*R*,*S*)-**11**



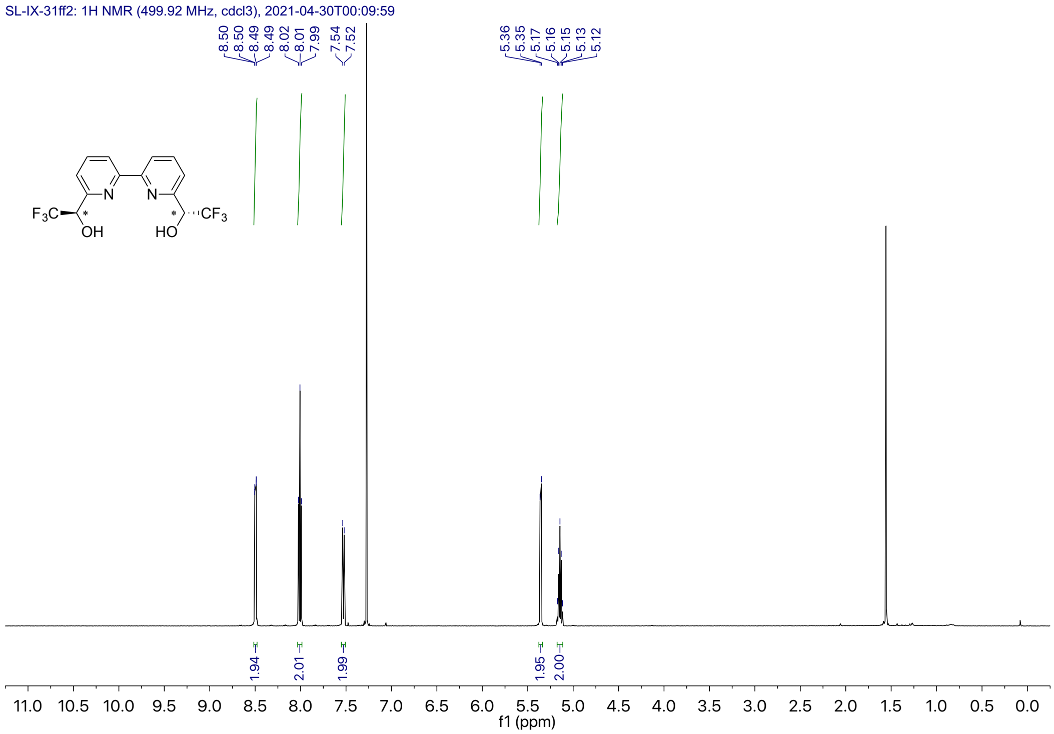
^1H NMR (500 MHz, $CDCl_3$) of (*S*,*S*)-**12**



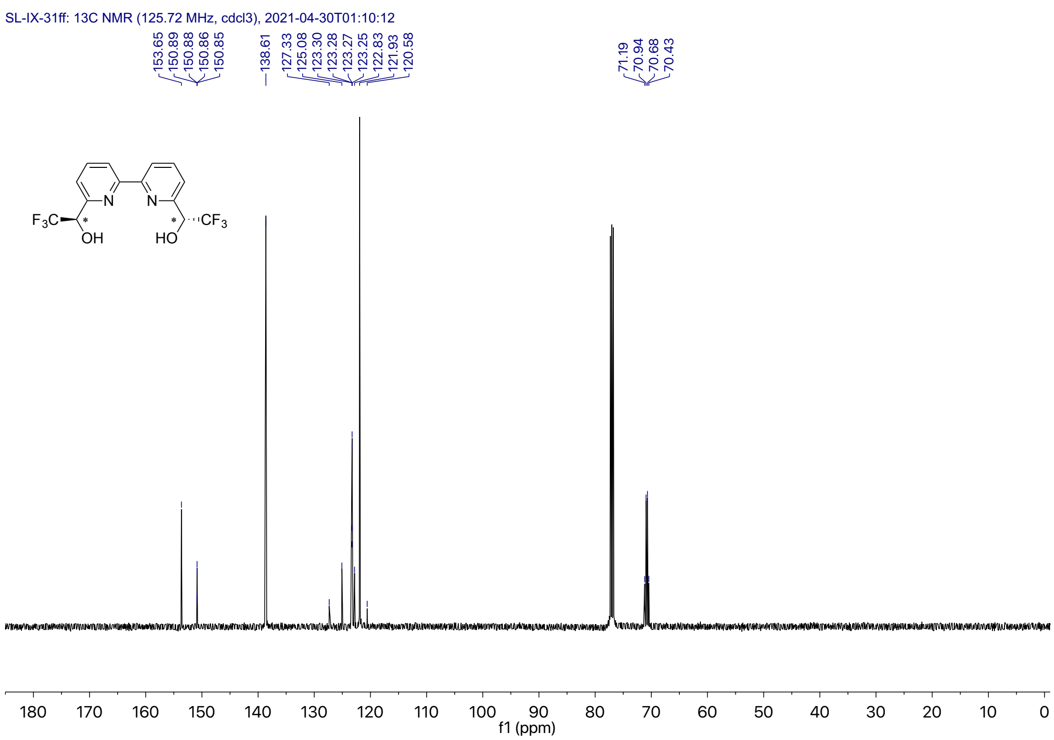
$^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) of (*S*,*S*)-**12**



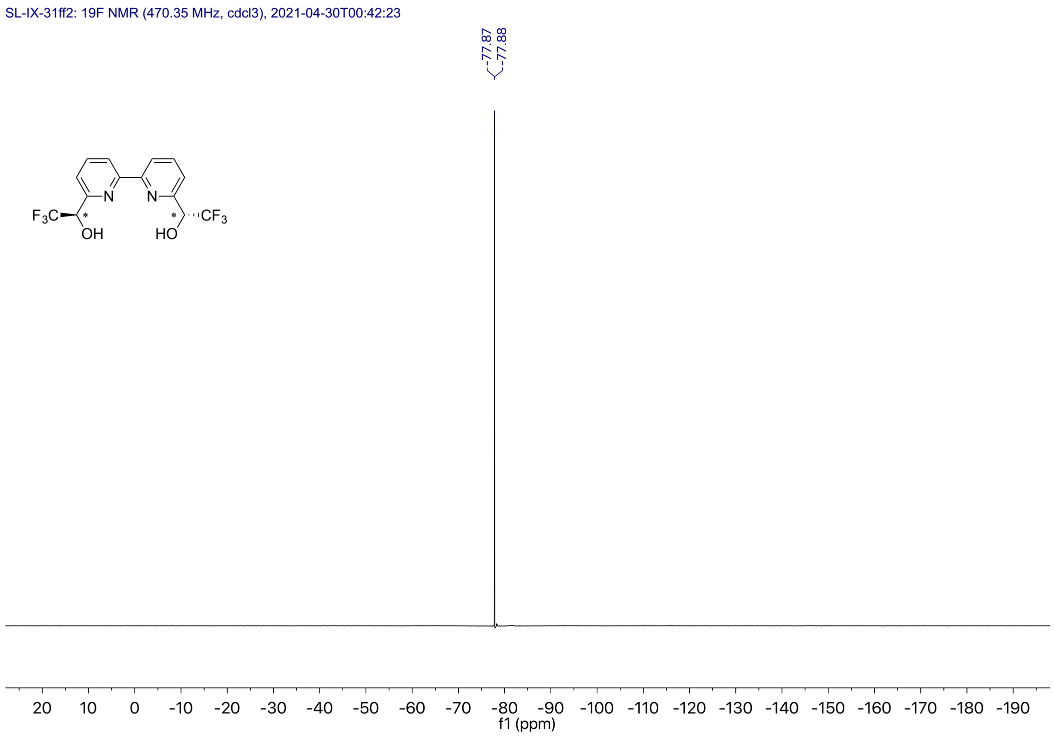
^{19}F NMR (470 MHz, $CDCl_3$) of (*S*,*S*)-**12**



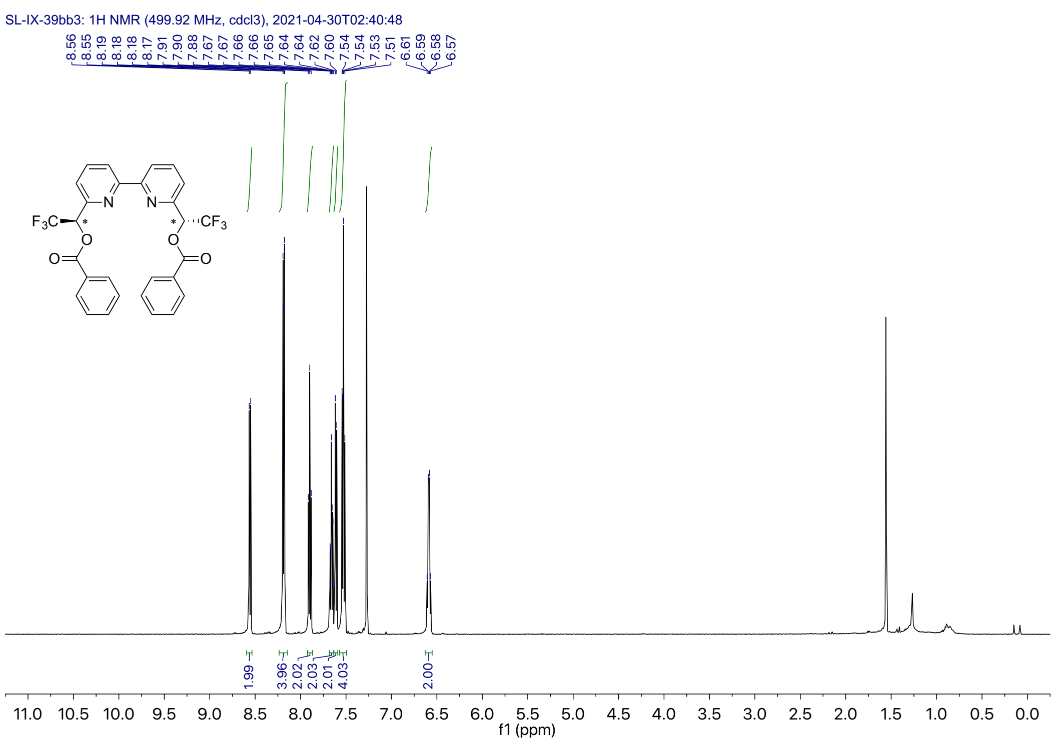
^{1}H NMR (500 MHz, CDCl$_3$) of (*R*,*R*)-**1** or (*S*,*S*)-**1**



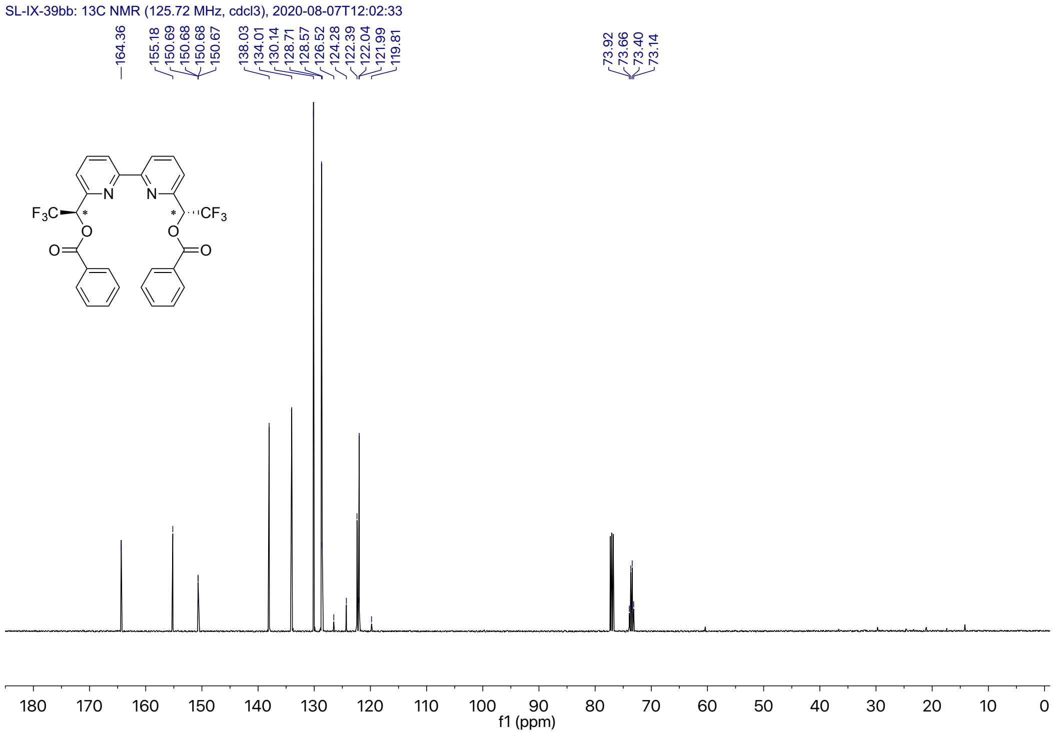
^{13}C{H} NMR (126 MHz, CDCl$_3$) of (*R*,*R*)-**1** or (*S*,*S*)-**1**



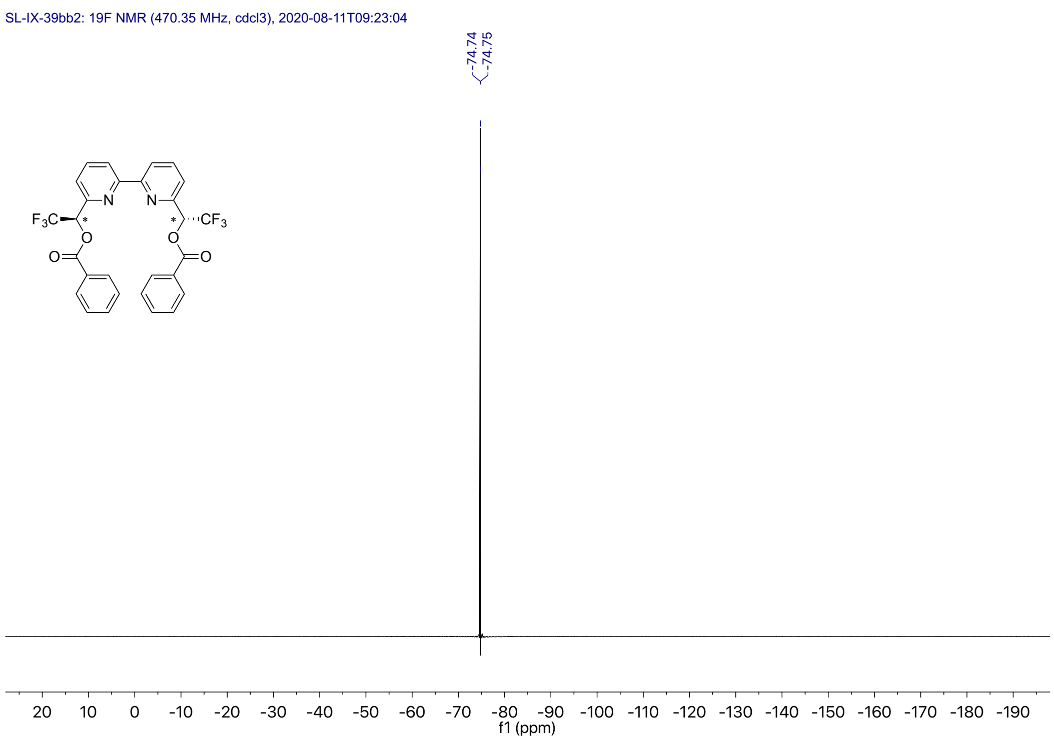
^{19}F NMR (470 MHz, $CDCl_3$) of (*R*,*R*)-**1** or (*S*,*S*)-**1**



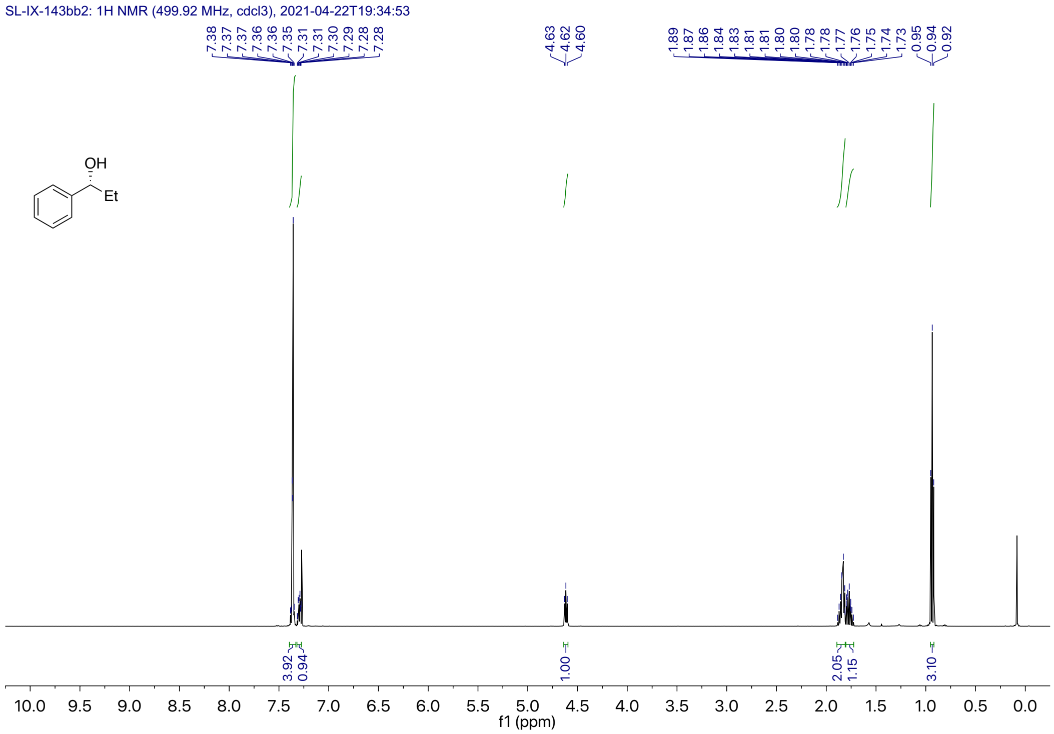
^{1}H NMR (500 MHz, $CDCl_3$) of (*R*,*R*)-**14** or (*S*,*S*)-**14**



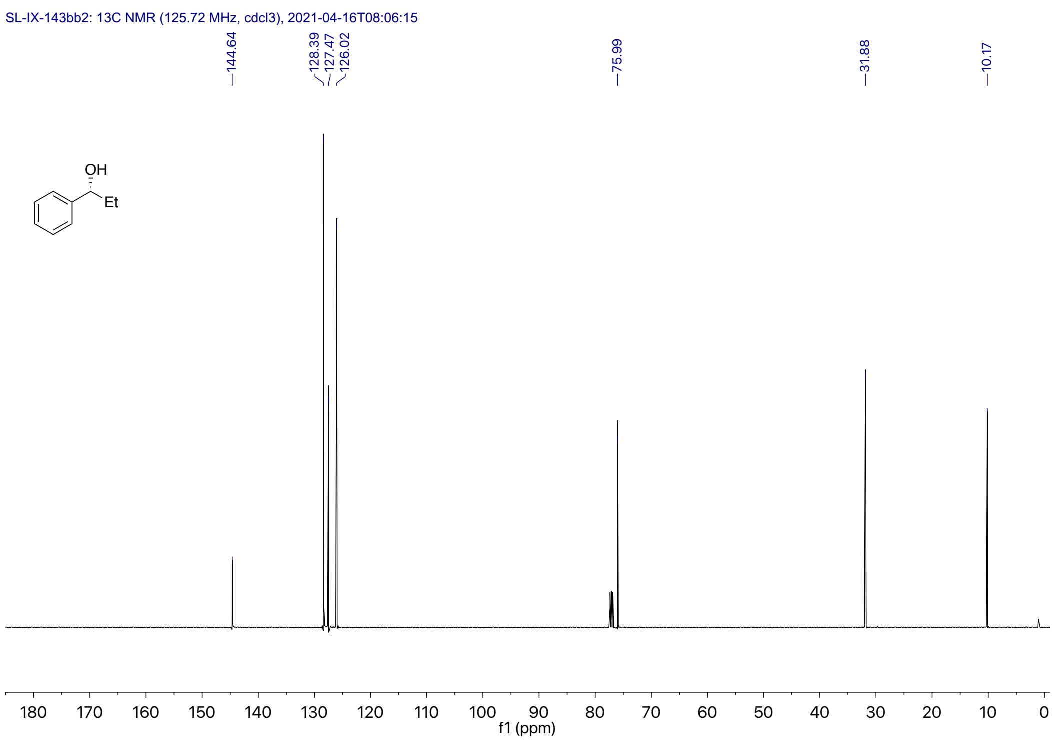
$^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) of (*R*,*R*)-**14** or (*S*,*S*)-**14**



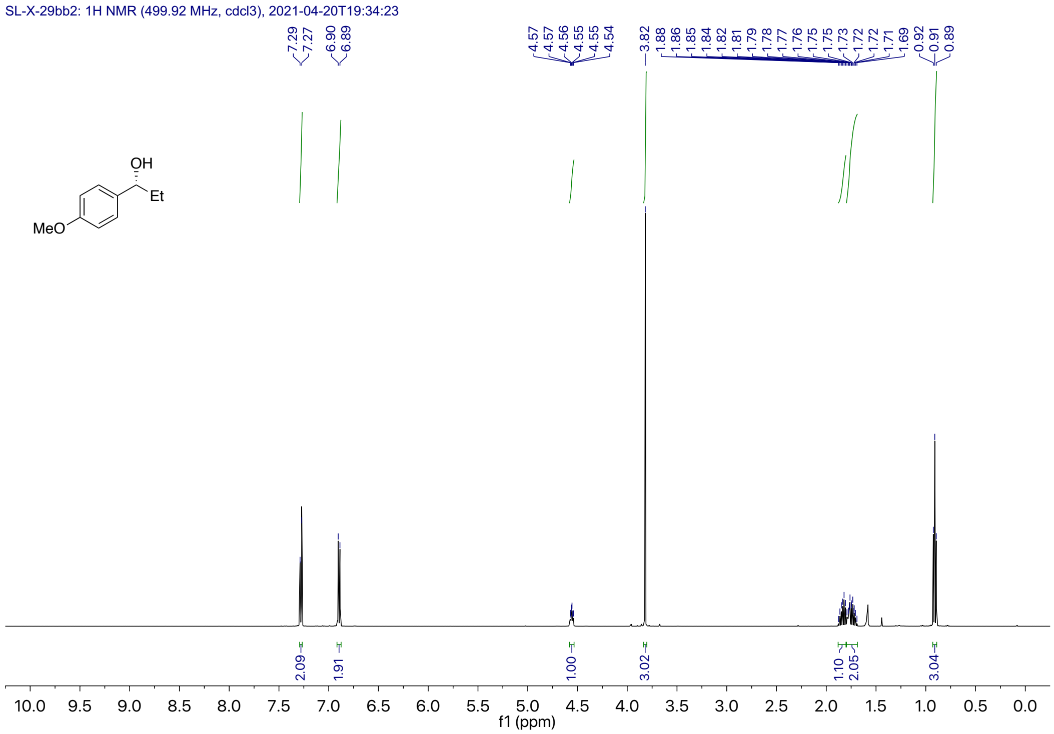
^{19}F NMR (470 MHz, $CDCl_3$) of (*R*,*R*)-**14** or (*S*,*S*)-**14**



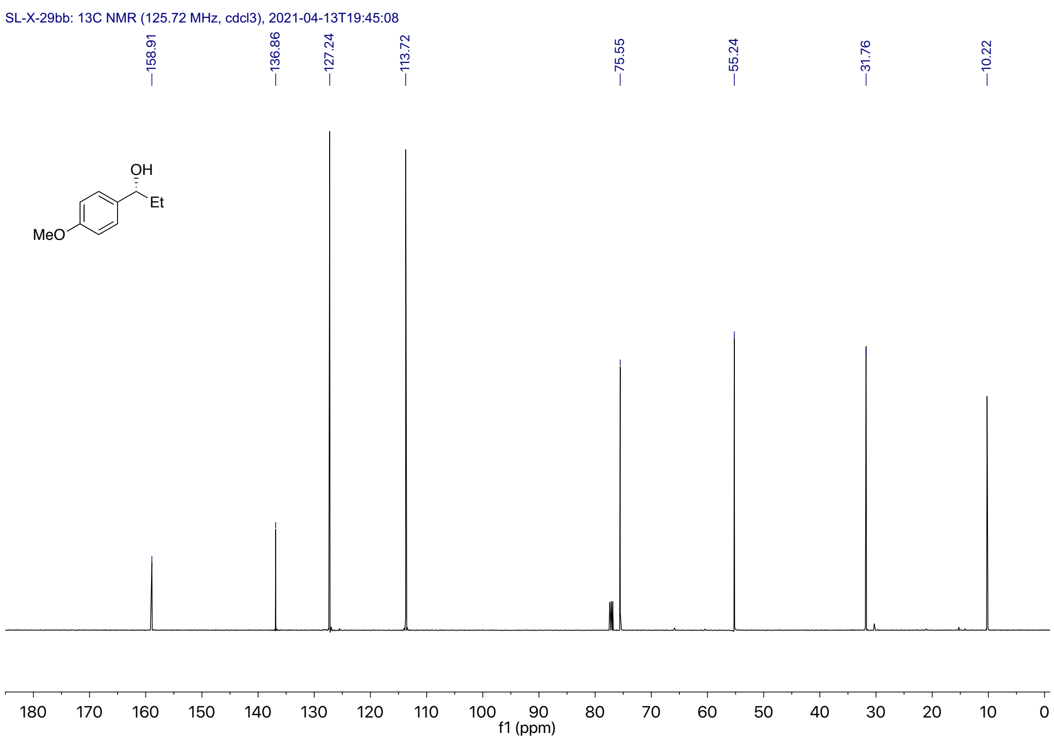
^1H NMR (500 MHz, $CDCl_3$) of (*R*)-**16a**



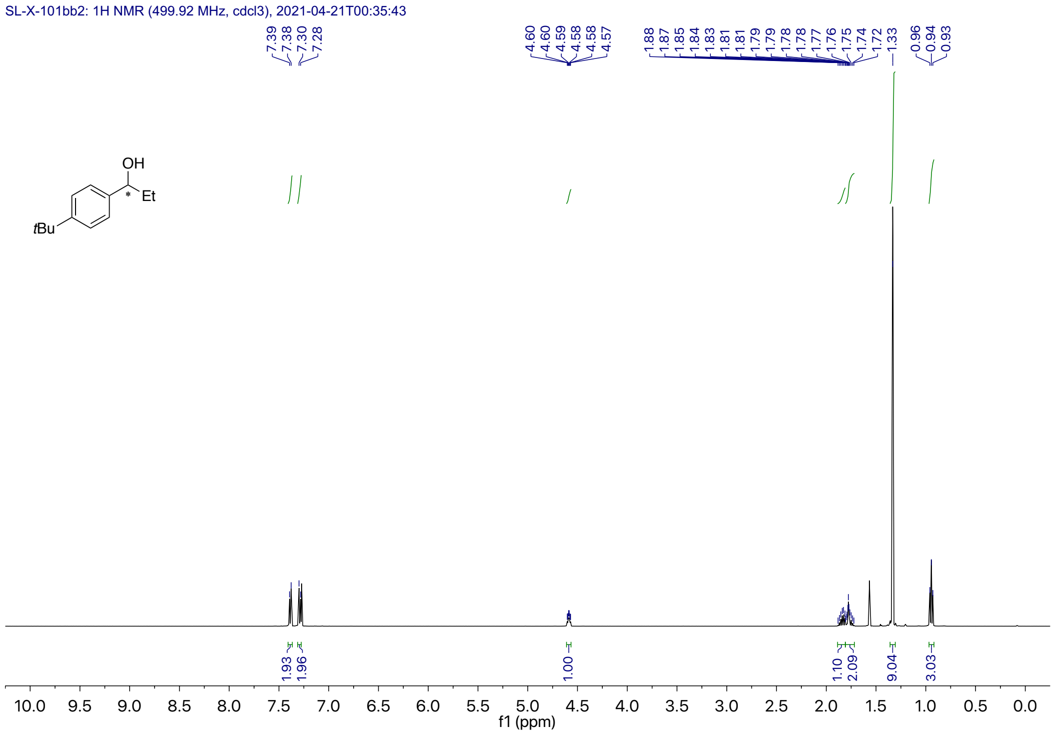
$^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) of (*R*)-**16a**



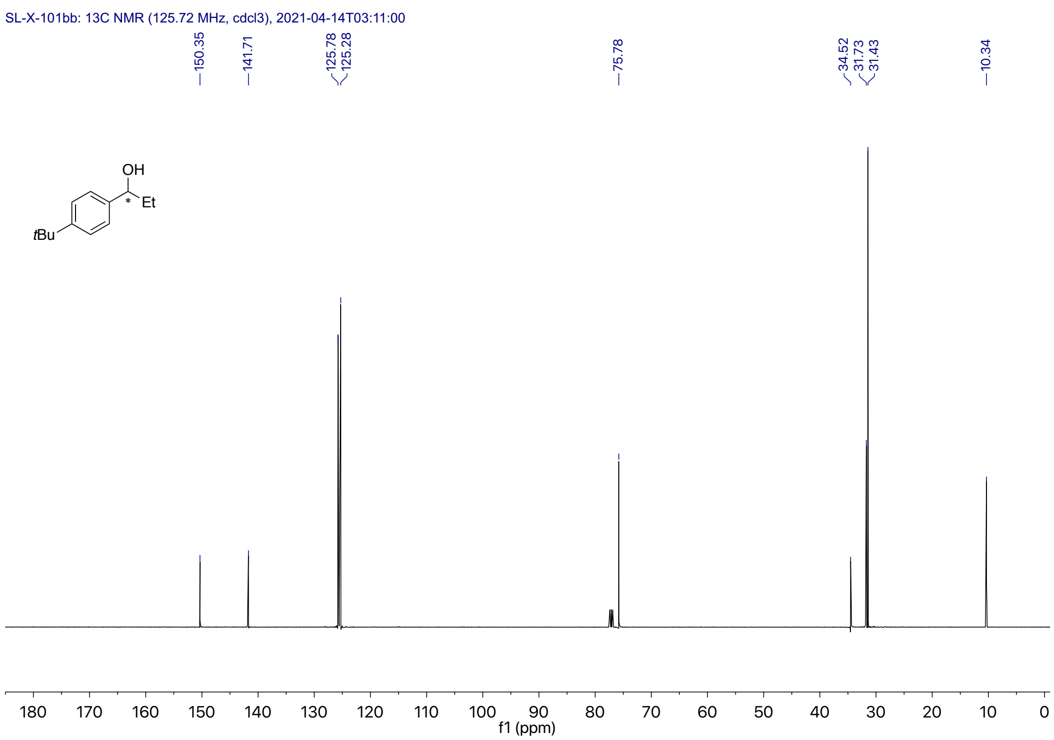
^{1}H NMR (500 MHz, $CDCl_3$) of (*R*)-**16b**



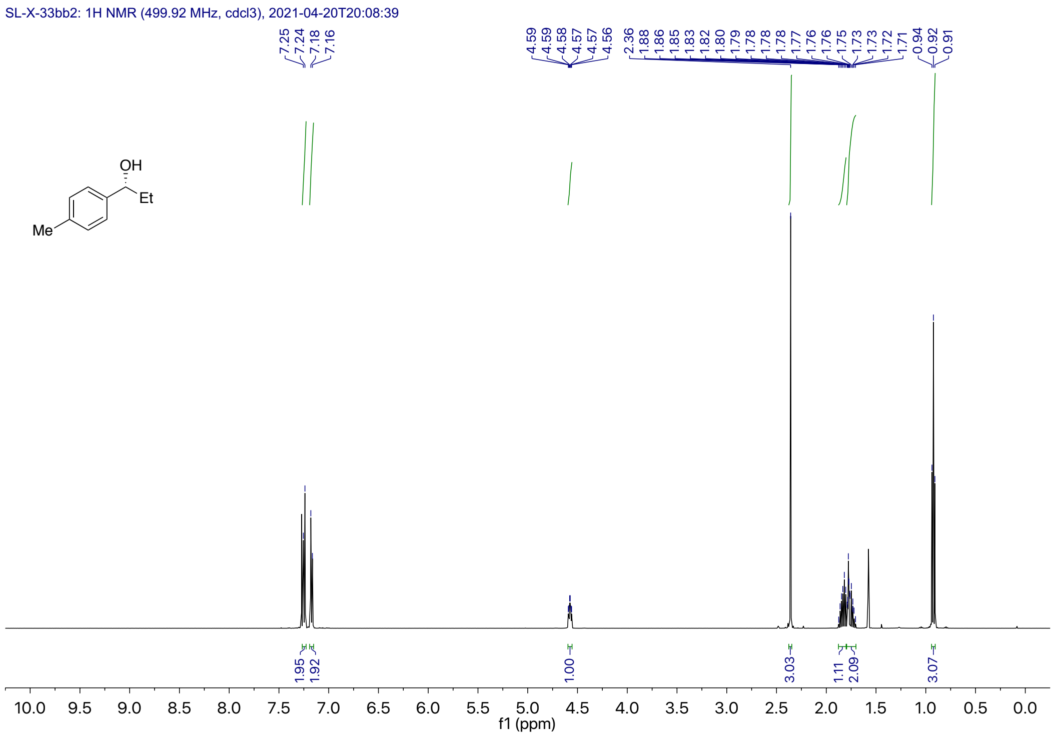
^{13}C{H} NMR (126 MHz, $CDCl_3$) of (*R*)-**16b**



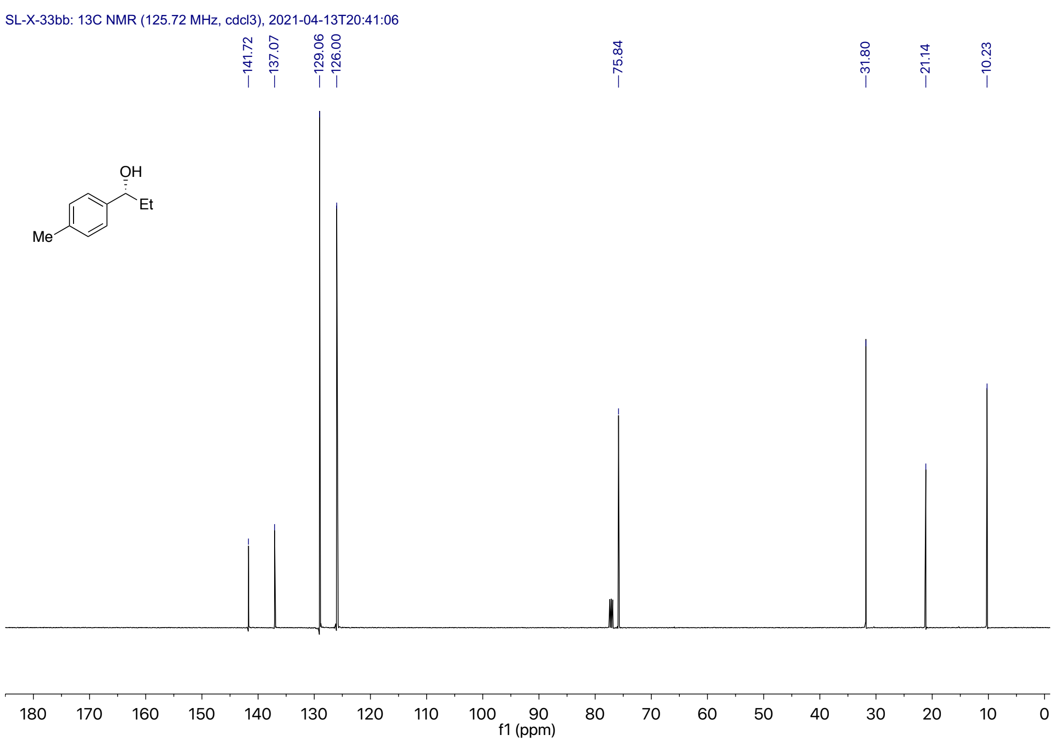
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**16c**



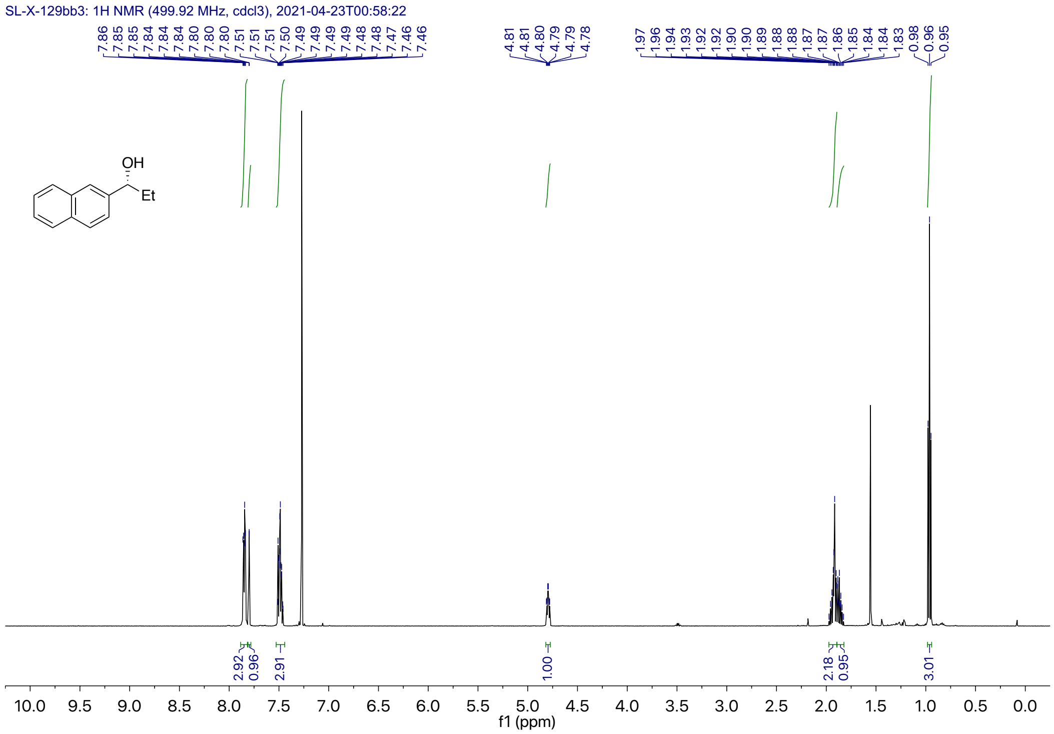
$^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) of (+)-**16c**



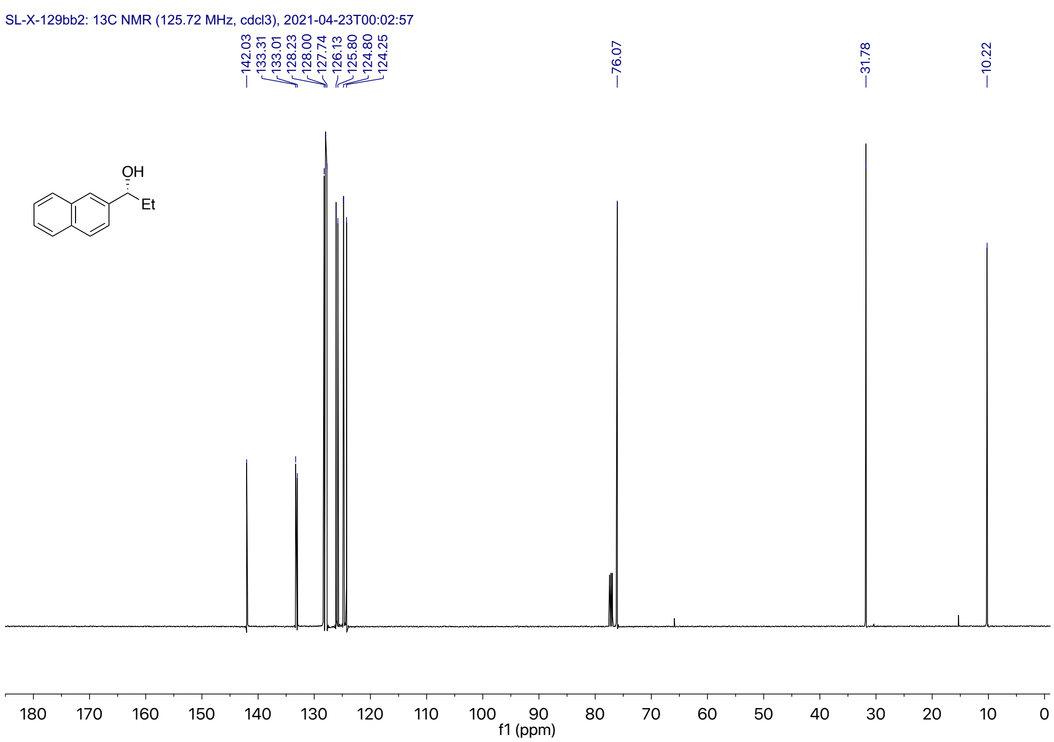
^{1}H NMR (500 MHz, $CDCl_3$) of (*R*)-**16d**



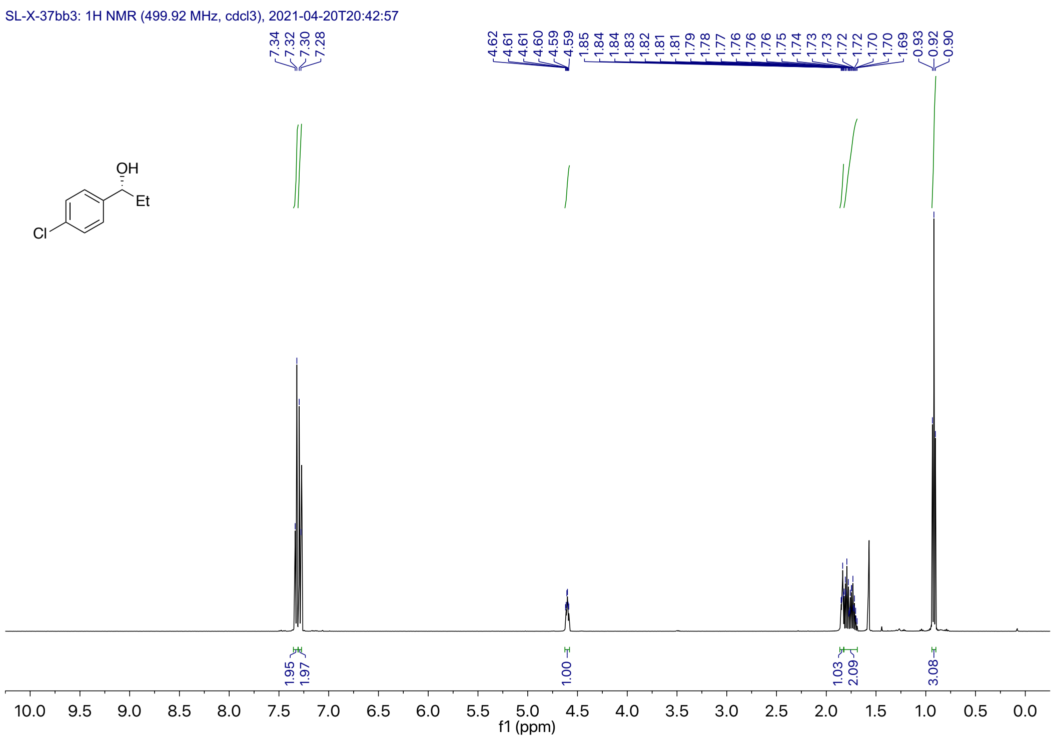
^{13}C{H} NMR (126 MHz, $CDCl_3$) of (*R*)-**16d**



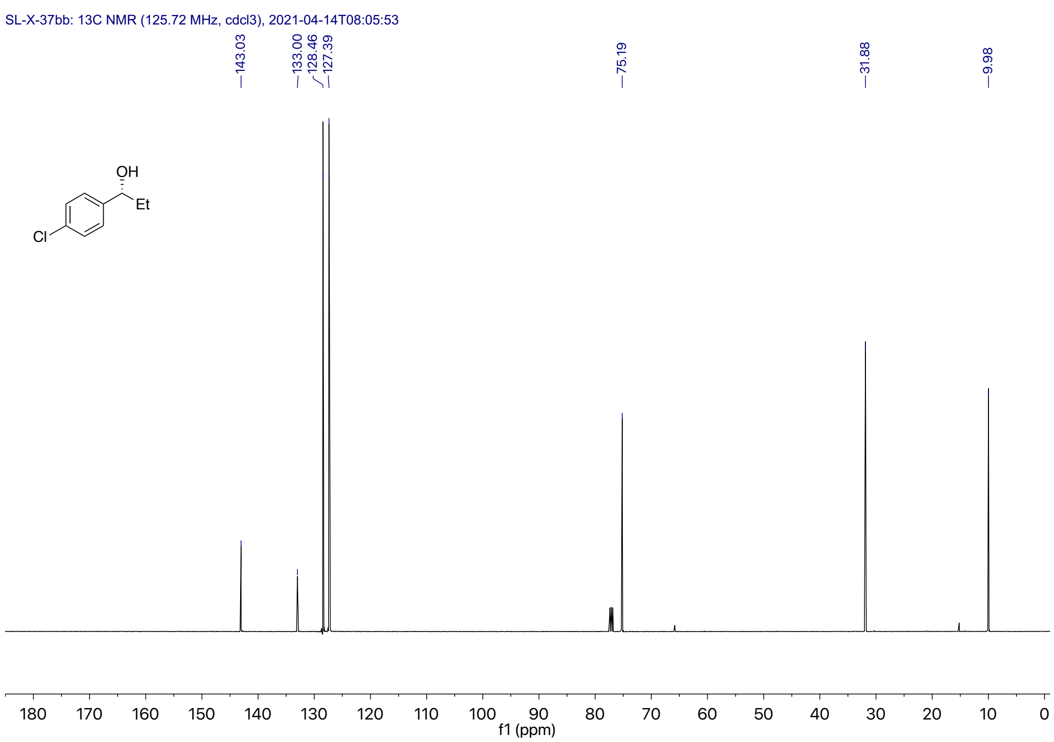
^{1}H NMR (500 MHz, $CDCl_3$) of (*R*)-**16e**



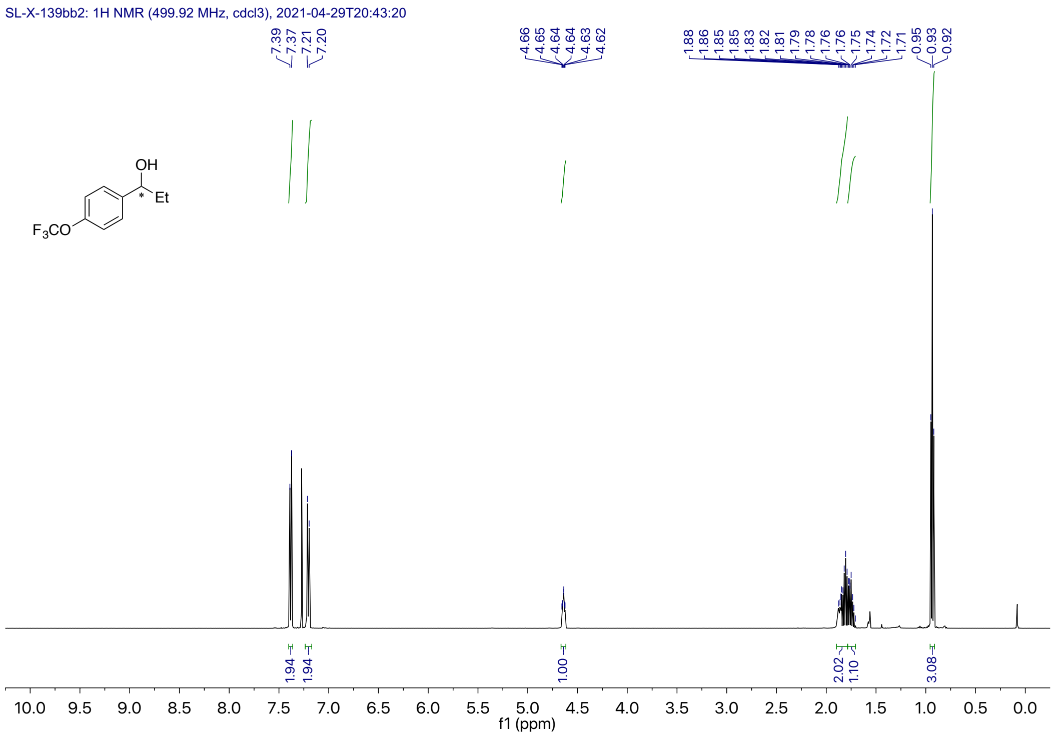
$^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) of (*R*)-**16e**



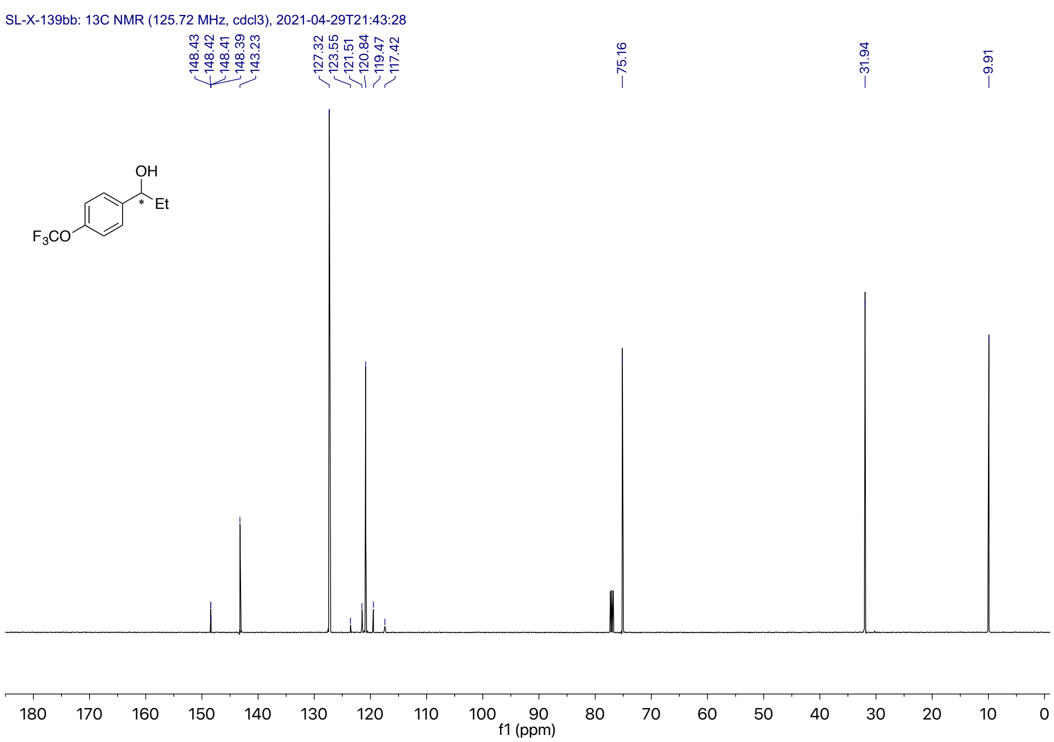
^{1}H NMR (500 MHz, $CDCl_3$) of (*R*)-**16f**



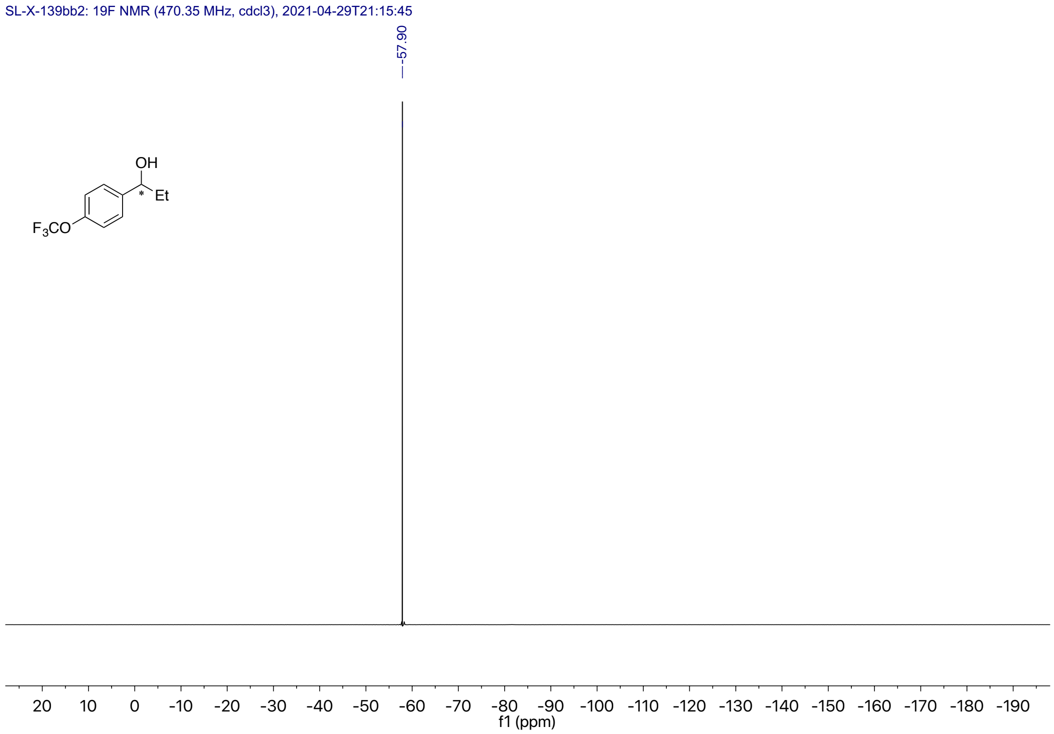
^{13}C{H} NMR (126 MHz, $CDCl_3$) of (*R*)-**16f**



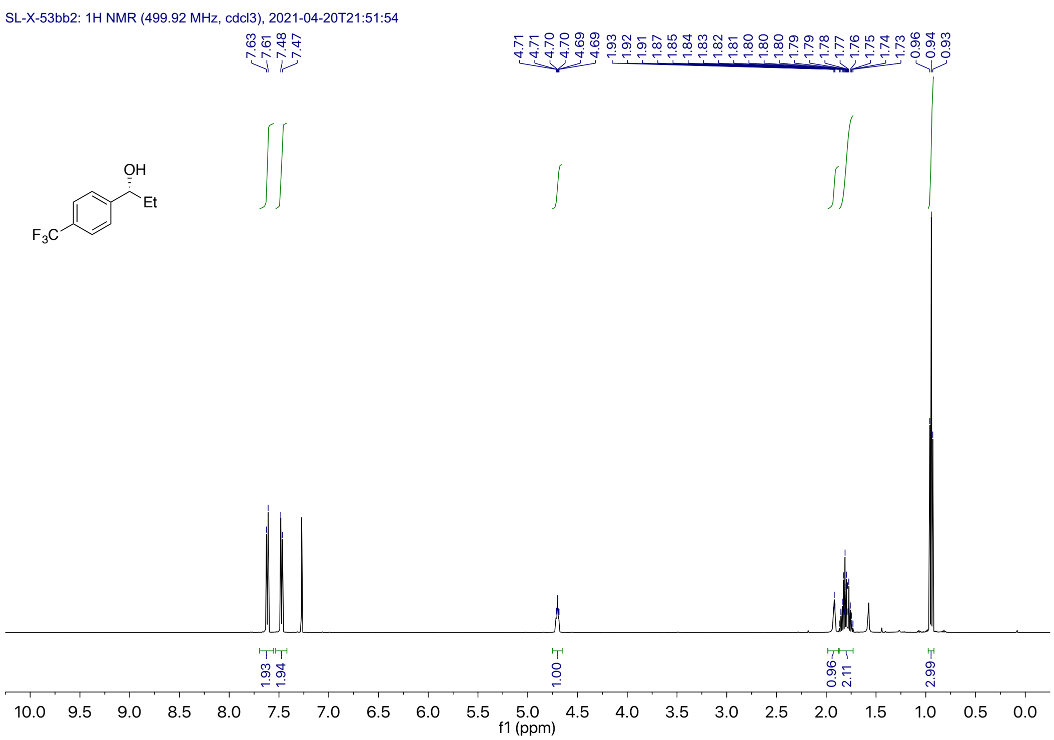
^{1}H NMR (500 MHz, $CDCl_3$) of (+)-**16g**



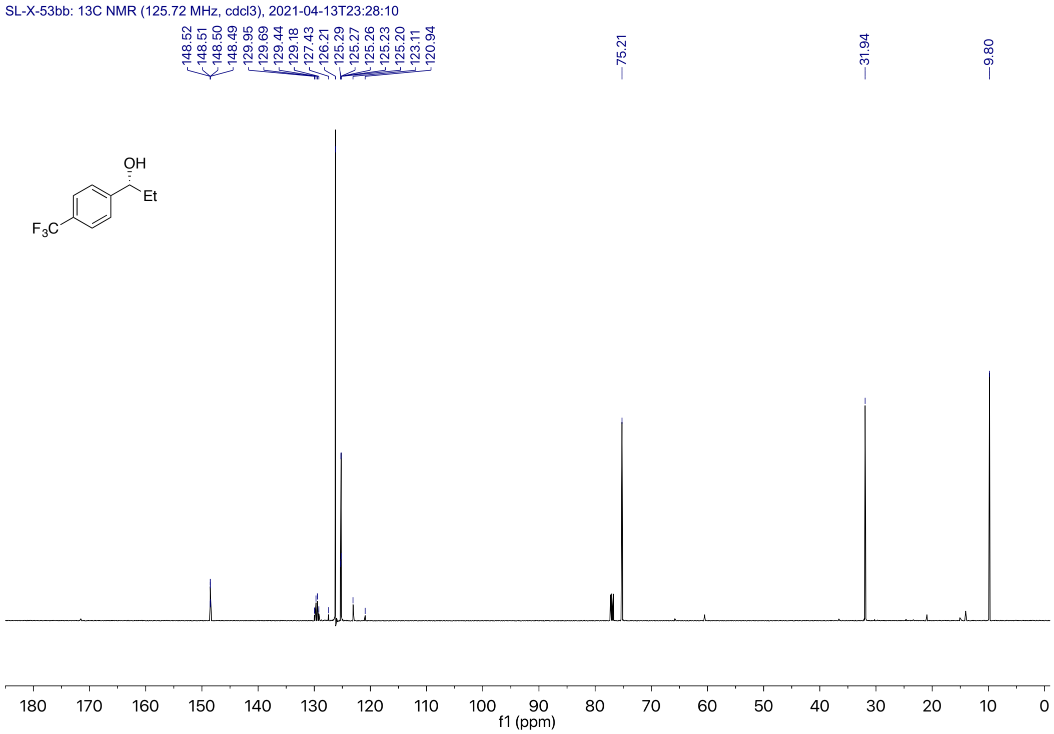
^{13}C{H} NMR (126 MHz, $CDCl_3$) of (+)-**16g**



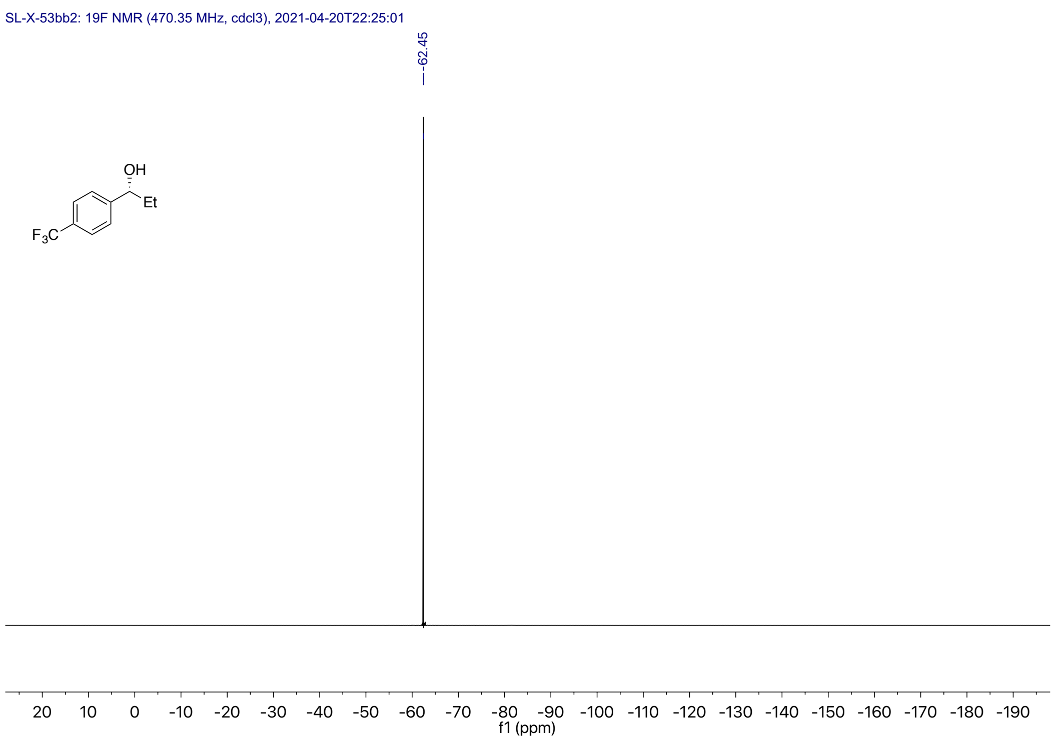
^{19}F NMR (470 MHz, $CDCl_3$) of (+)-**16g**



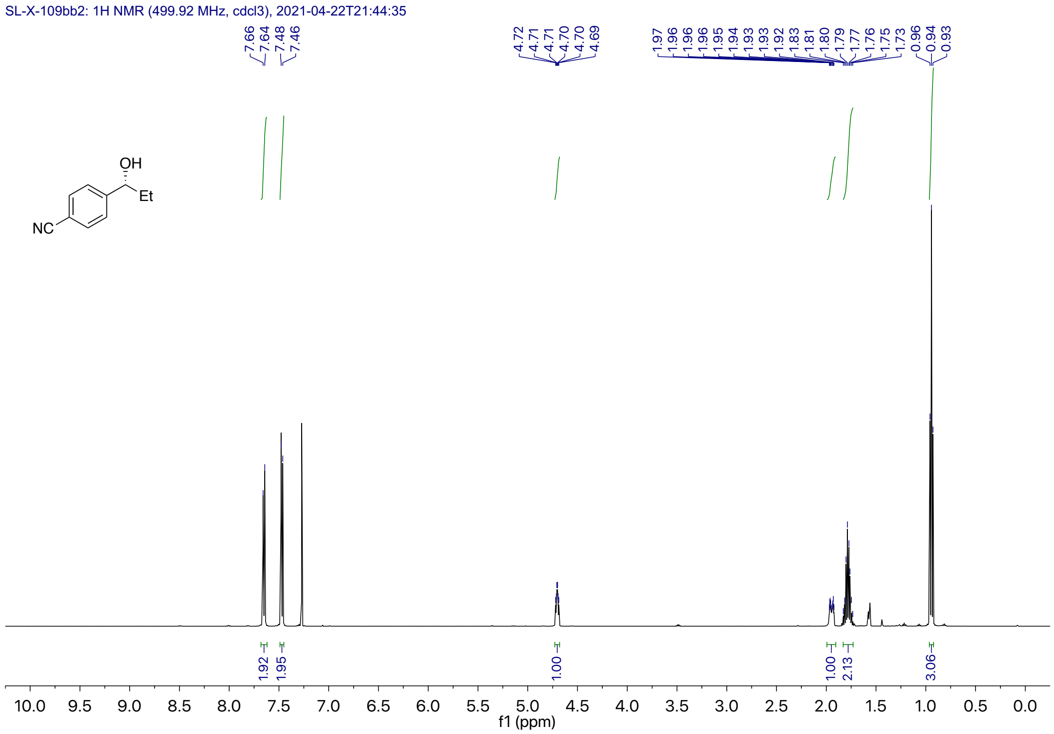
^{1}H NMR (500 MHz, $CDCl_3$) of (*R*)-**16h**



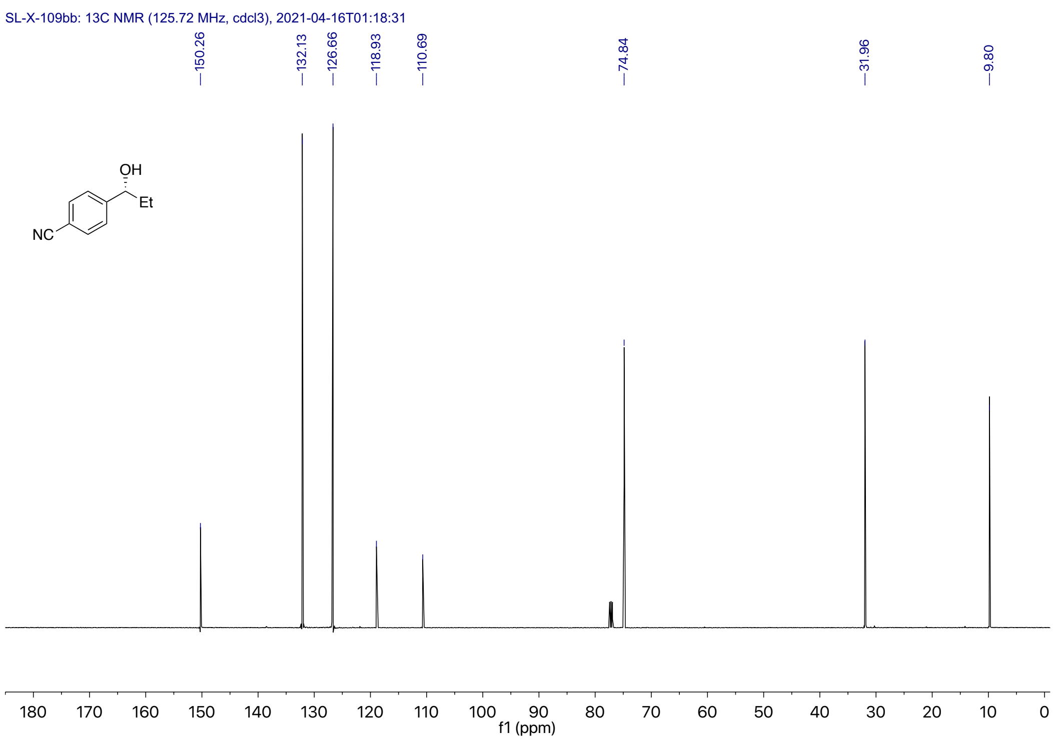
$^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) of (*R*)-**16h**



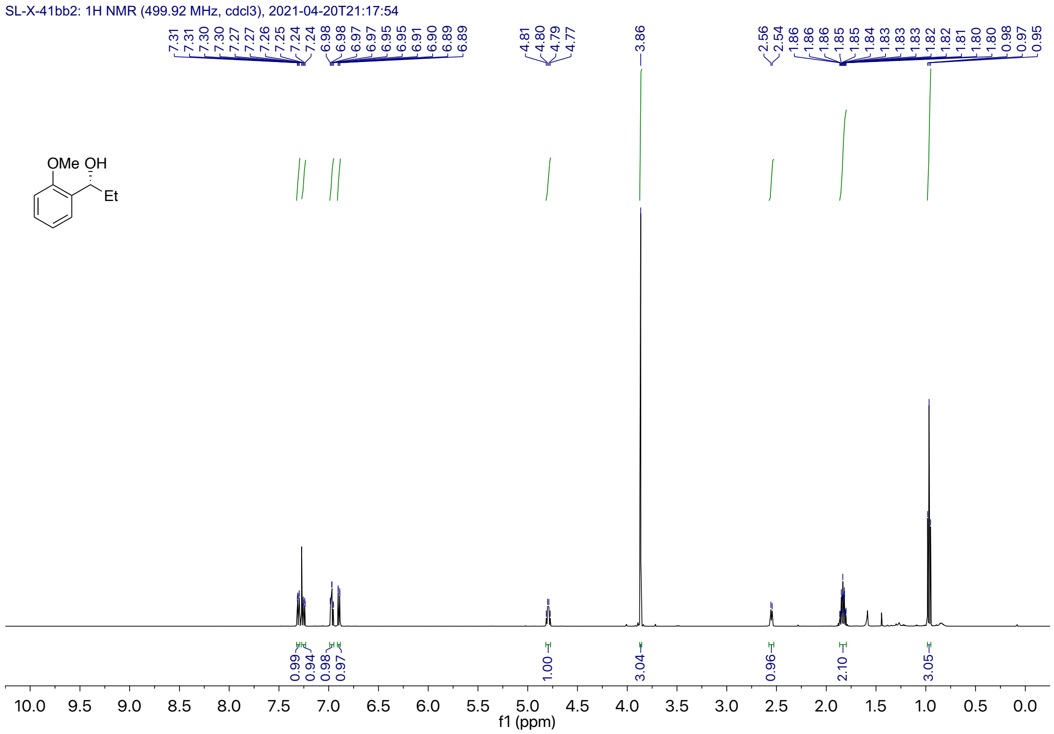
^{19}F NMR (470 MHz, $CDCl_3$) of (*R*)-**16h**



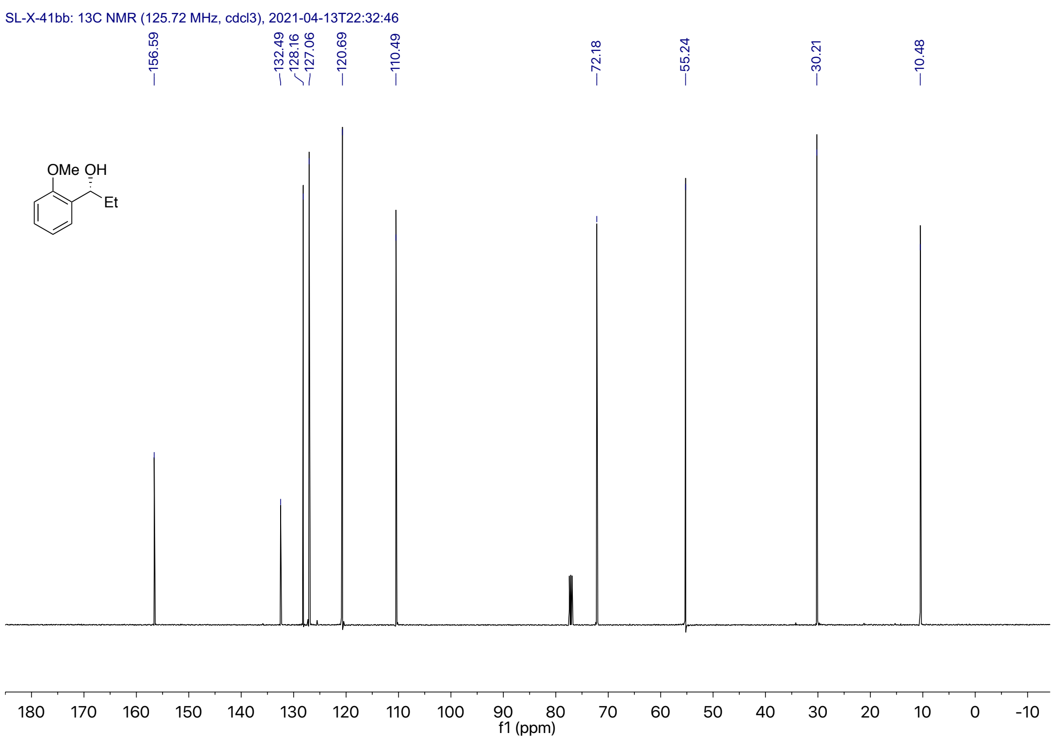
^{1}H NMR (500 MHz, $CDCl_3$) of (*R*)-**16i**



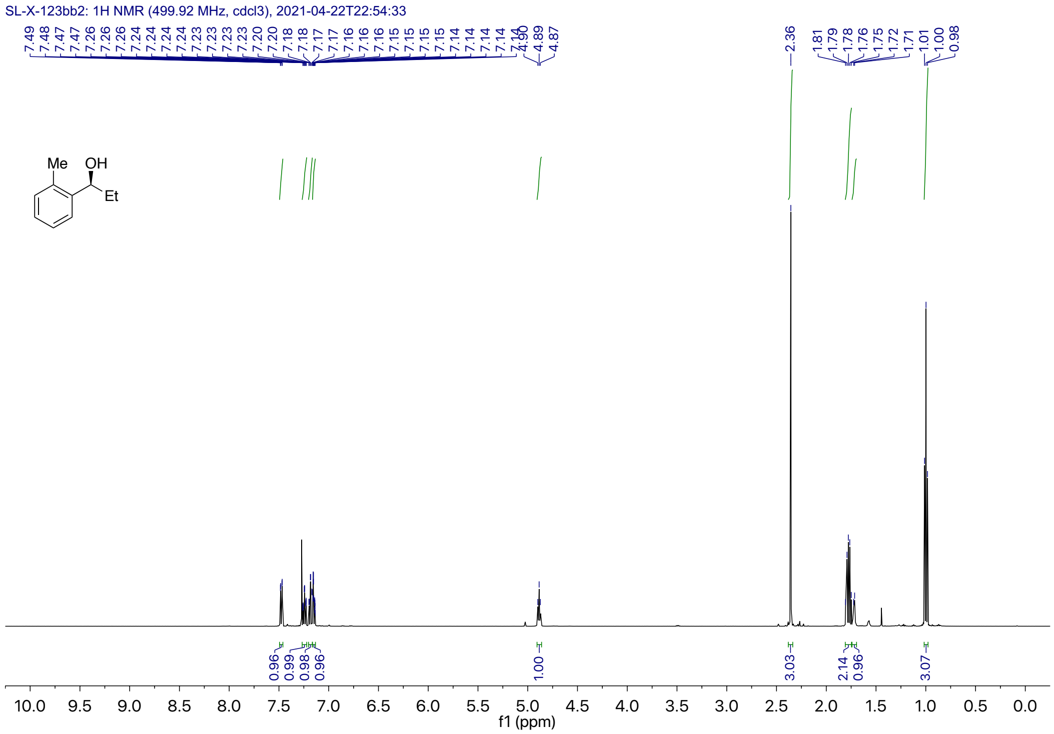
^{13}C{H} NMR (126 MHz, $CDCl_3$) of (*R*)-**16i**



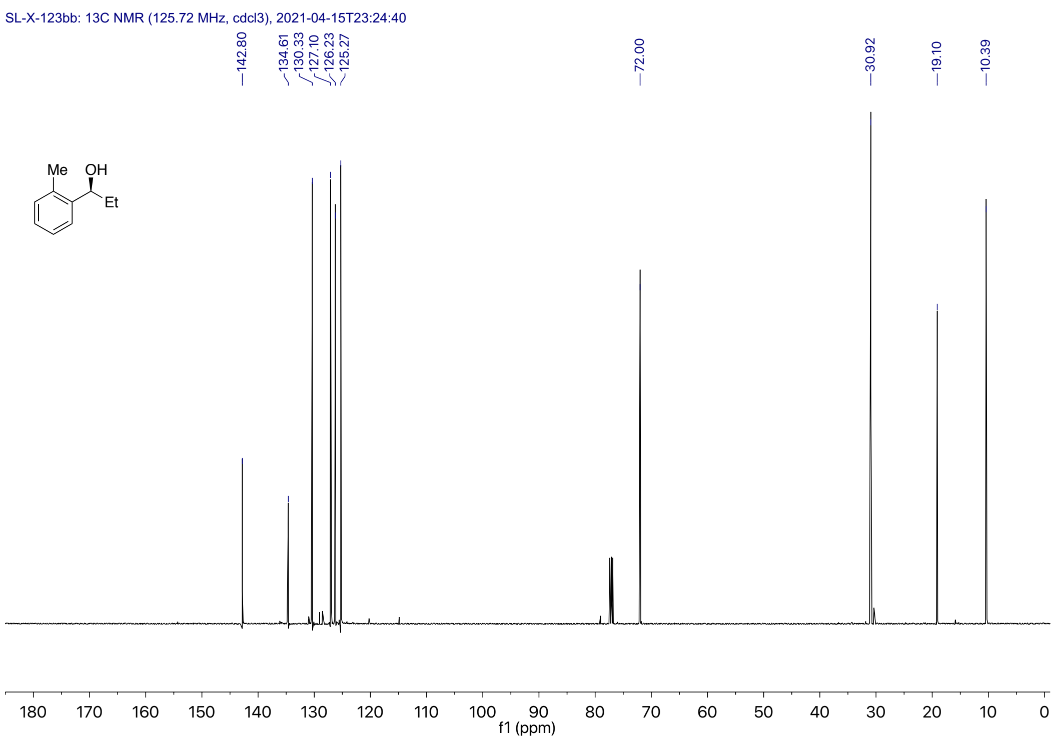
^{1}H NMR (500 MHz, CDCl$_3$) of (*R*)-**16j**



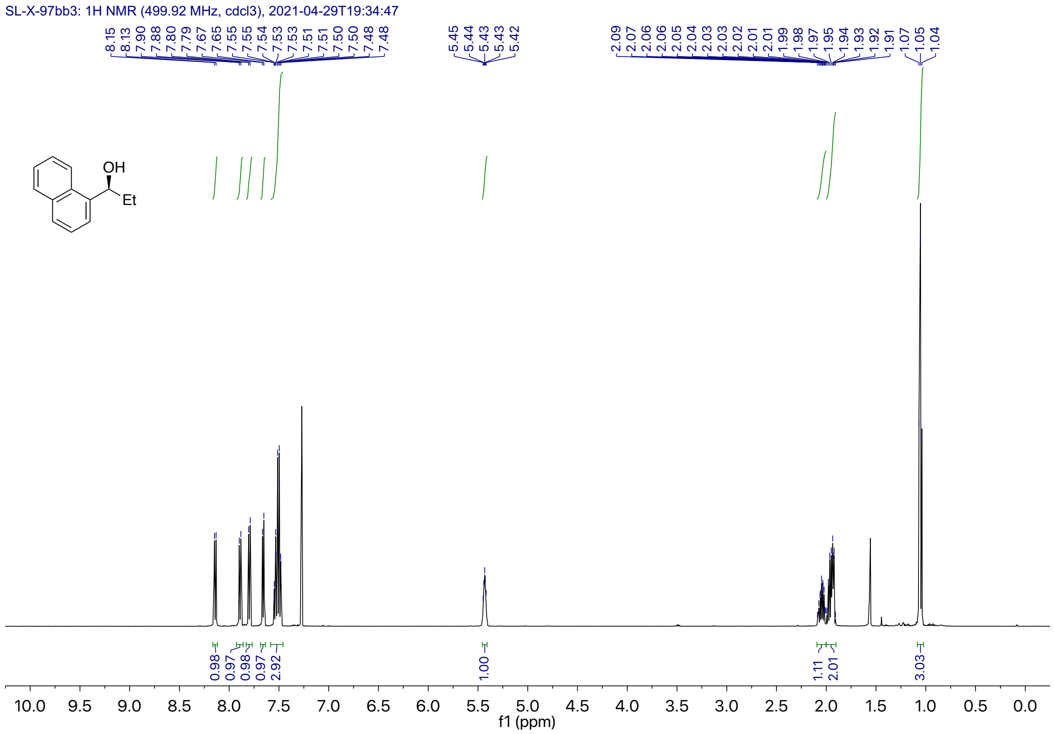
^{13}C{H} NMR (126 MHz, CDCl$_3$) of (*R*)-**16j**



^{1}H NMR (500 MHz, $CDCl_3$) of (*S*)-**16k**



$^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) of (*S*)-**16k**



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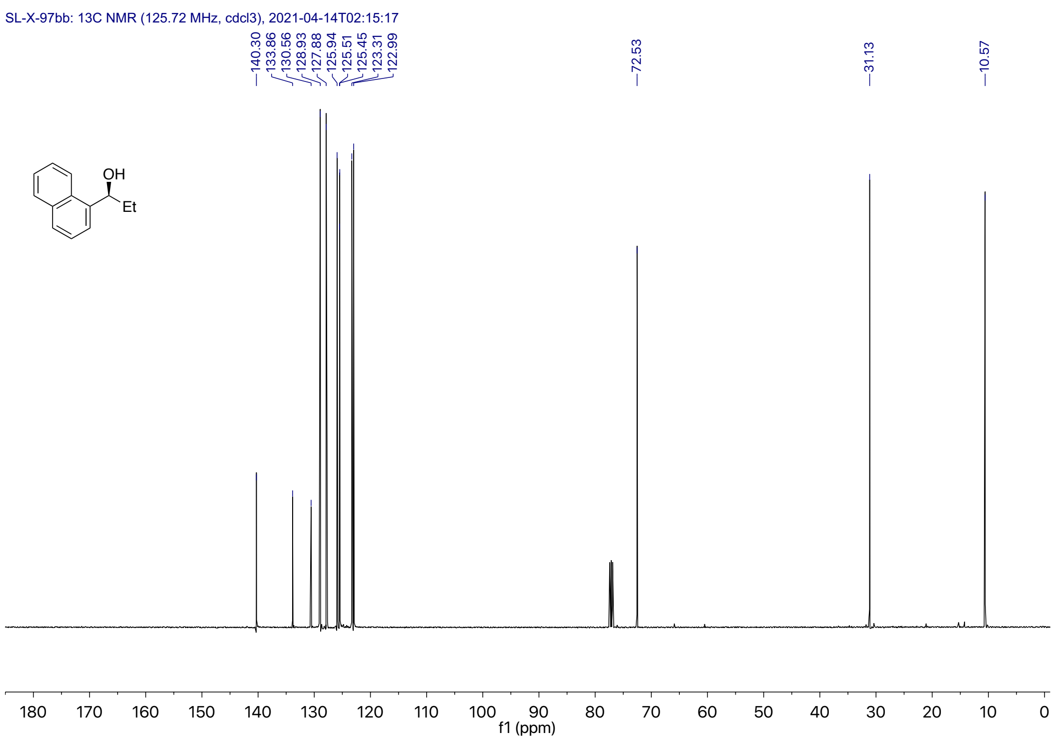
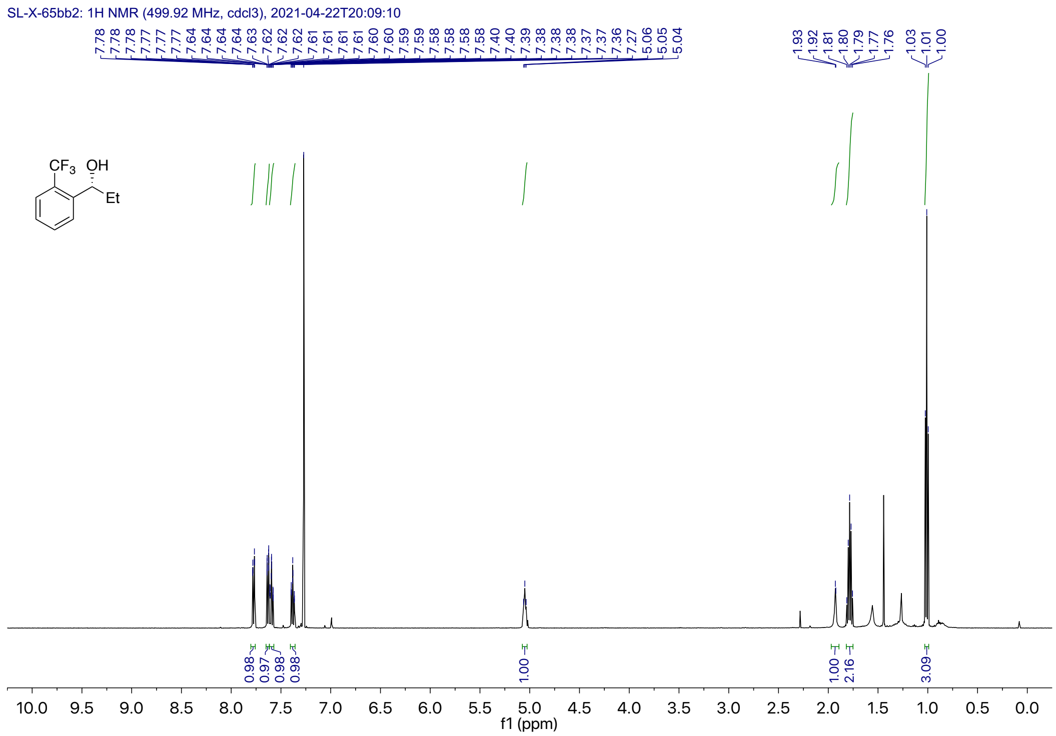


$^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) of (*S*)-**16l**



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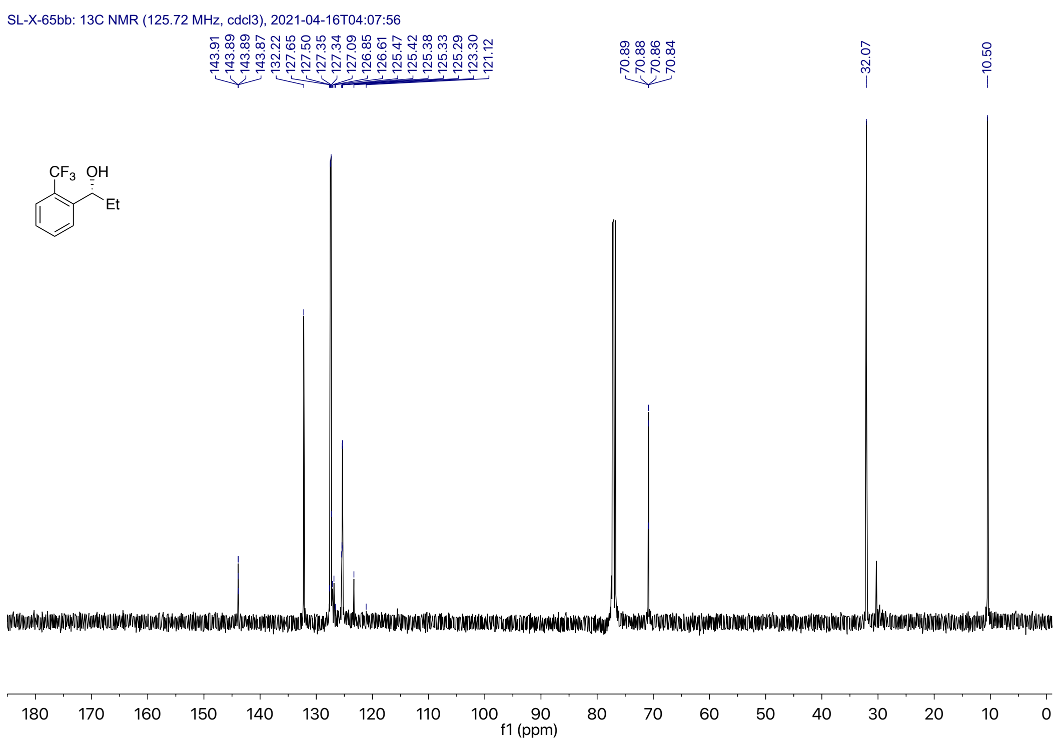
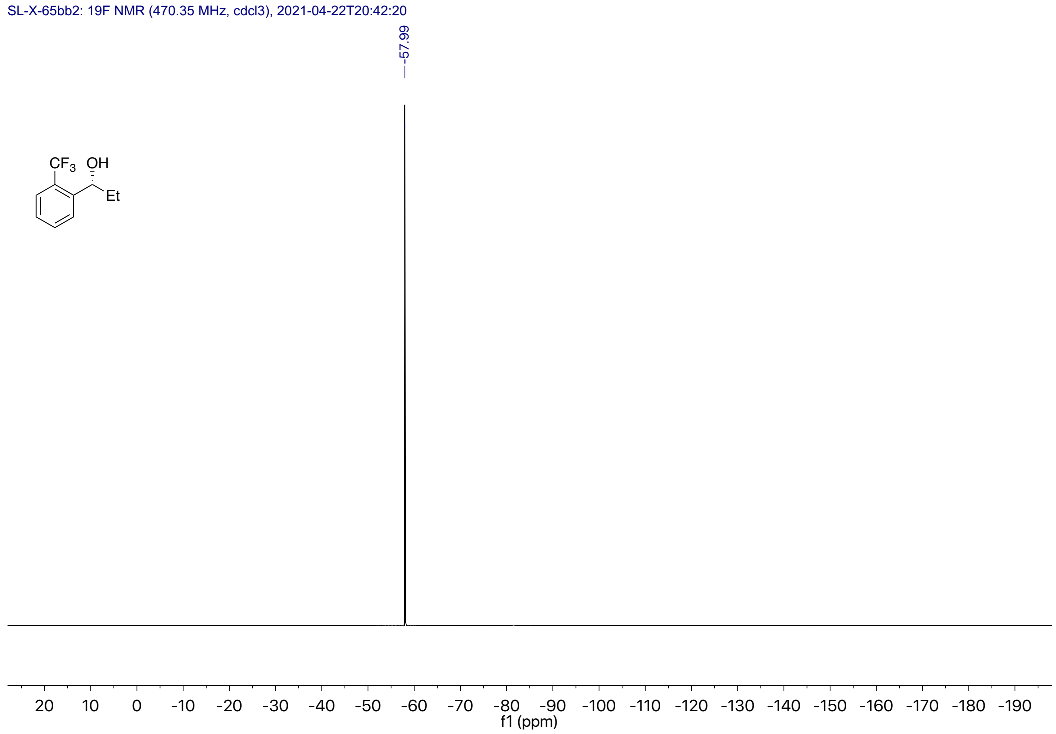
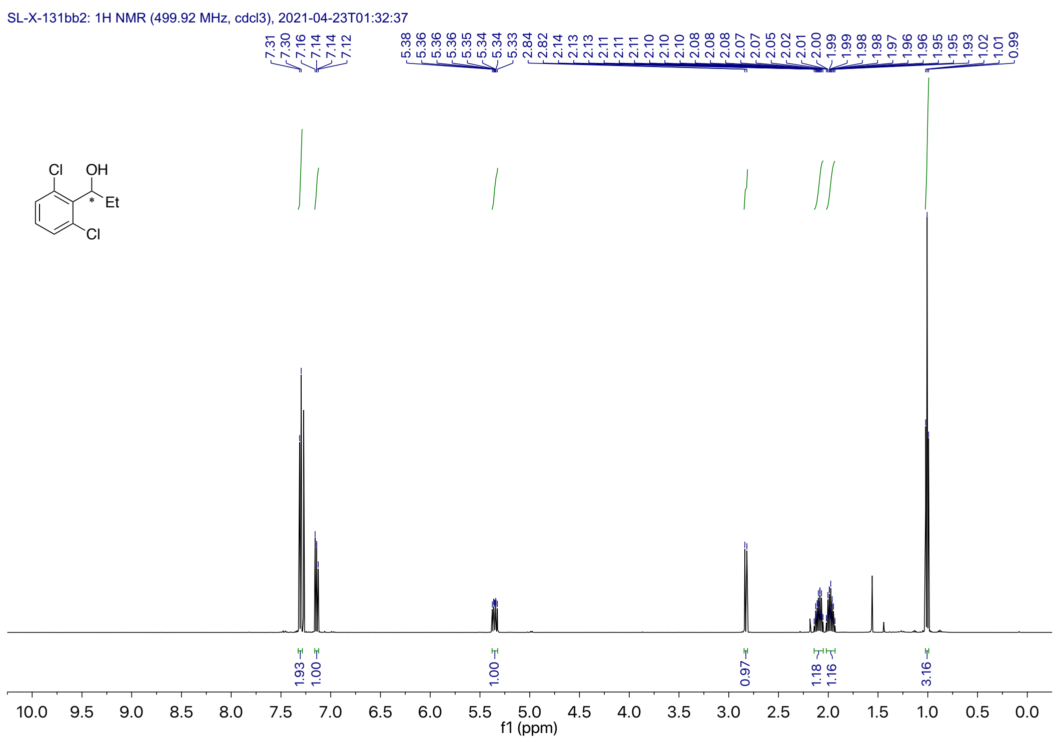


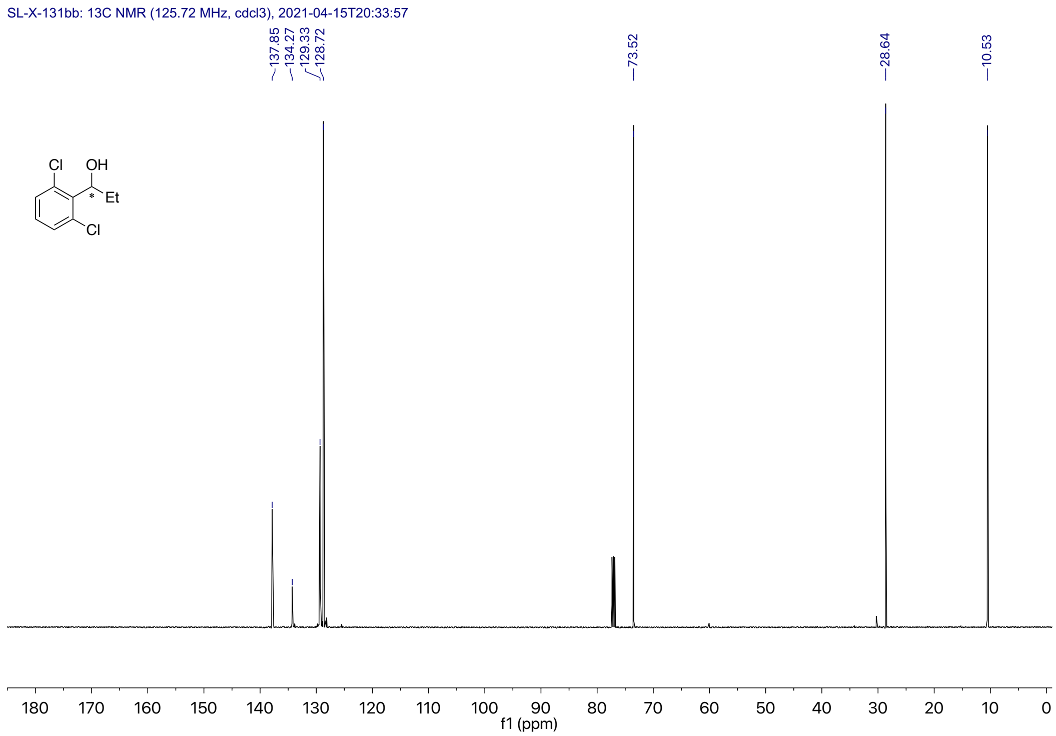
^{13}C{H} NMR (126 MHz, CDCl$_3$) of (*R*)-**16m**



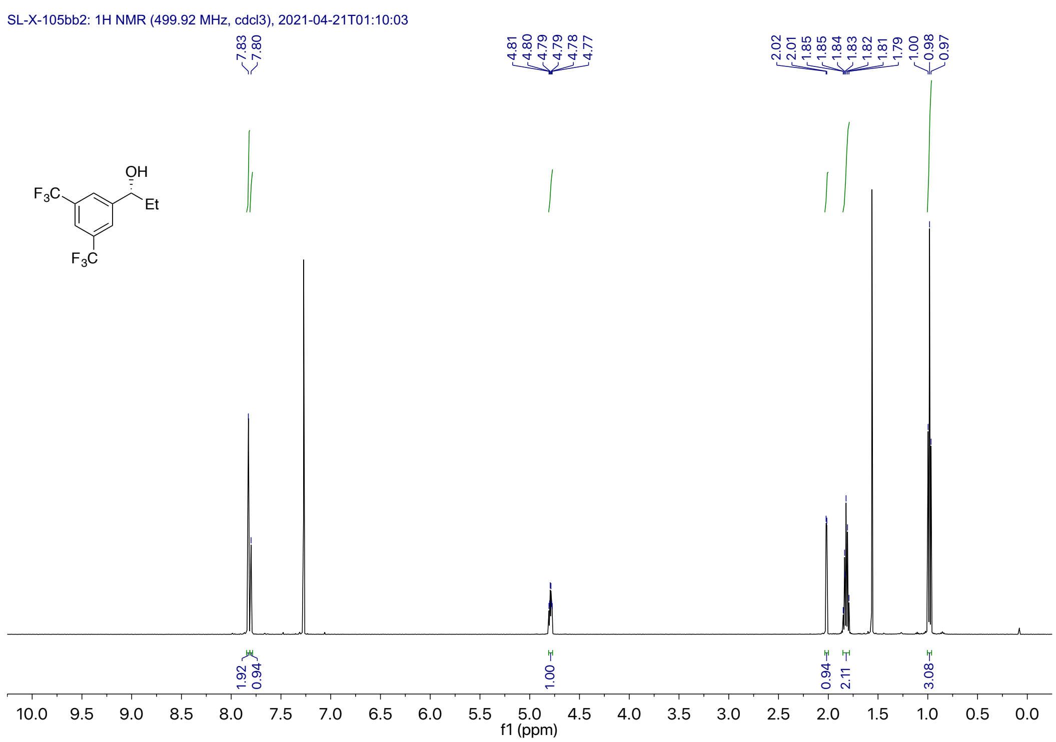
^{19}F NMR (470 MHz, $CDCl_3$) of (*R*)-**16m**



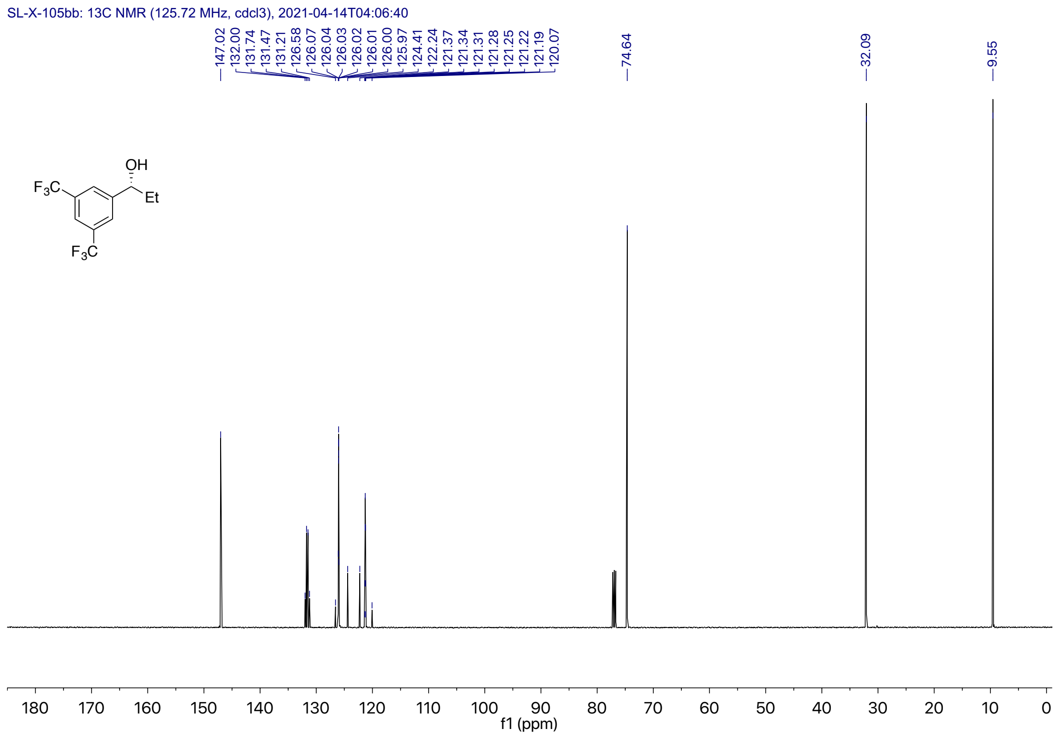
^{1}H NMR (500 MHz, $CDCl_3$) of (–)-**16n**



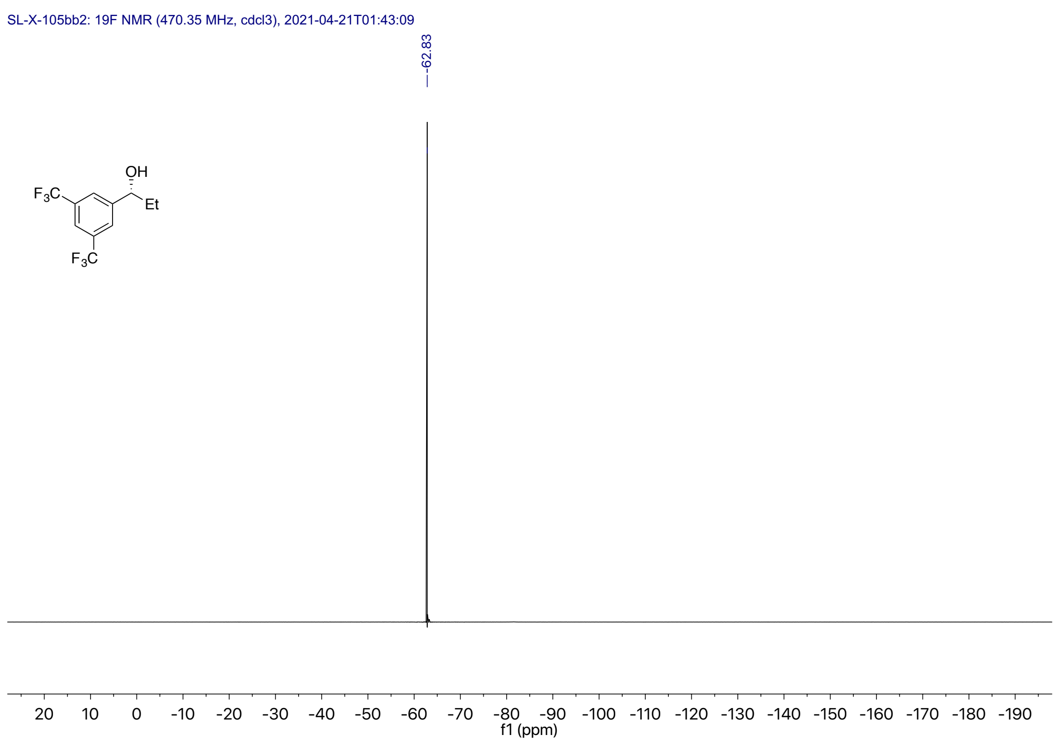
$^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) of (–)-**16n**



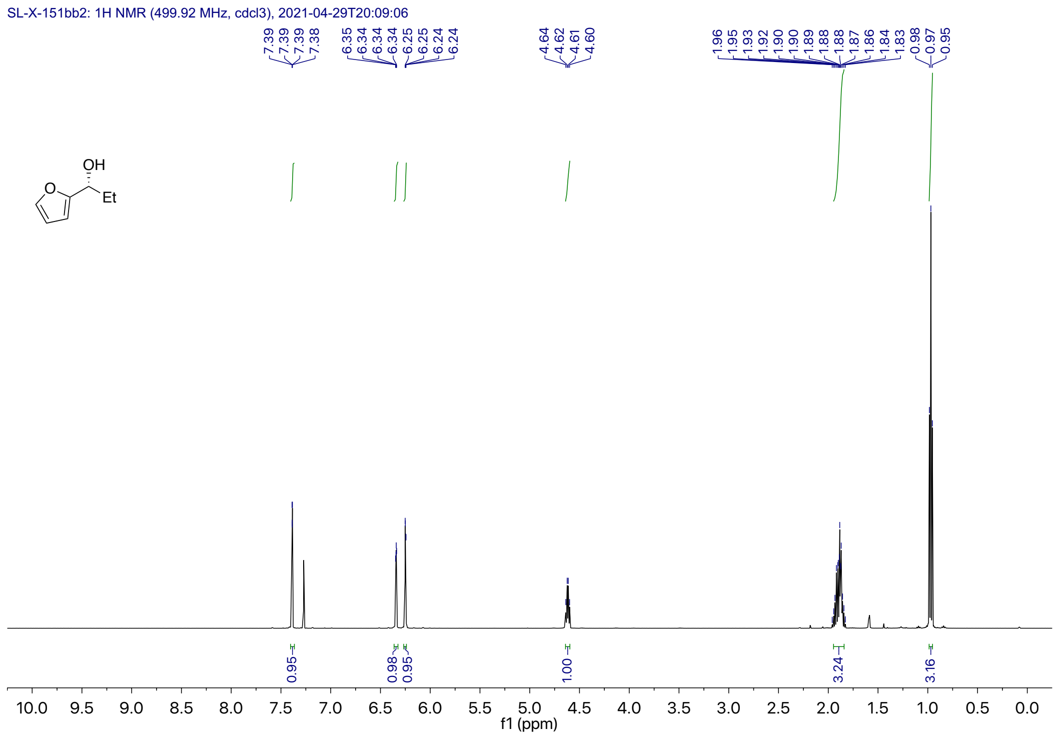
^{1}H NMR (500 MHz, $CDCl_3$) of (*R*)-**16o**



^{13}C{H} NMR (126 MHz, $CDCl_3$) of (*R*)-**16o**



^{19}F NMR (470 MHz, $CDCl_3$) of (*R*)-**16o**



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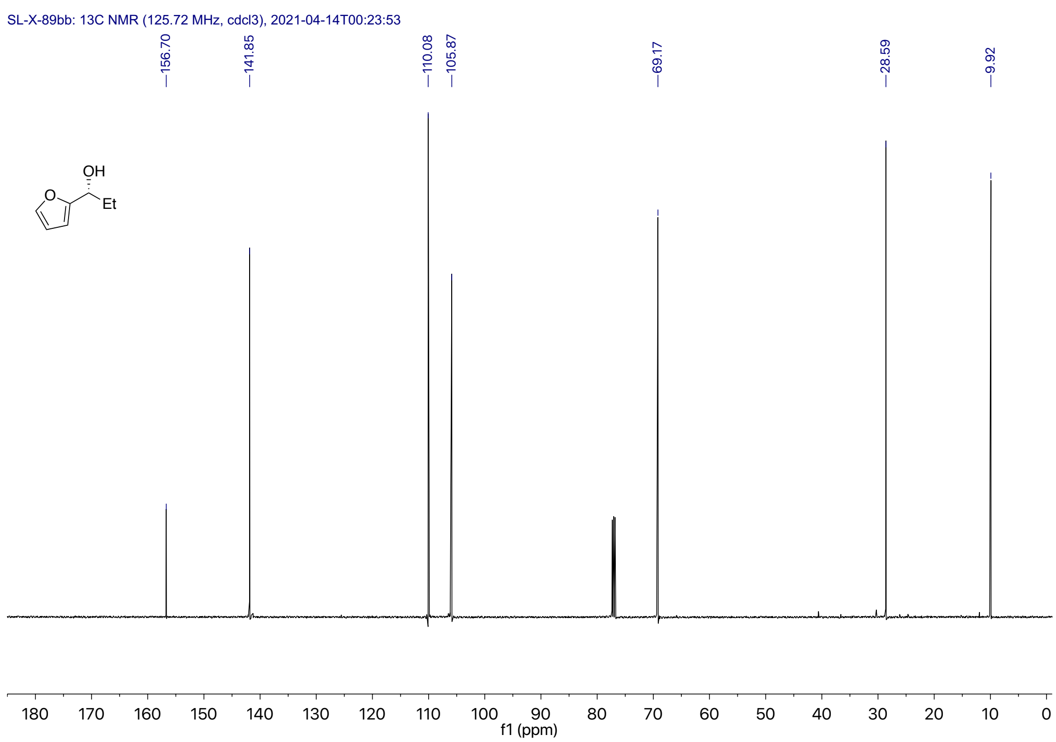
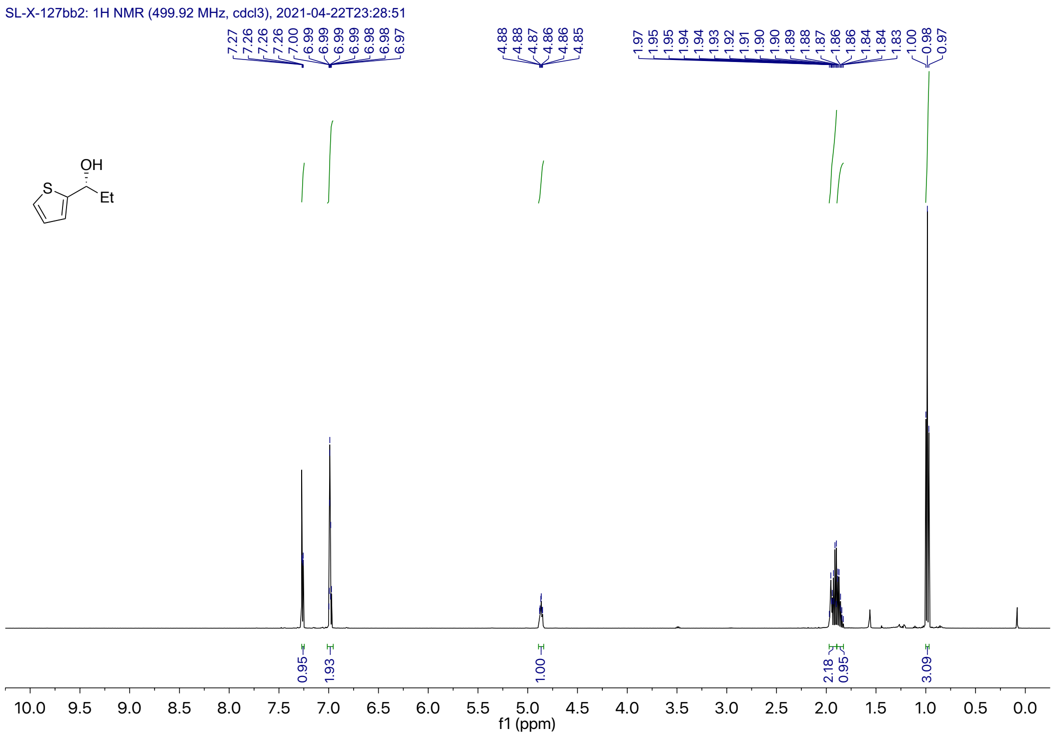
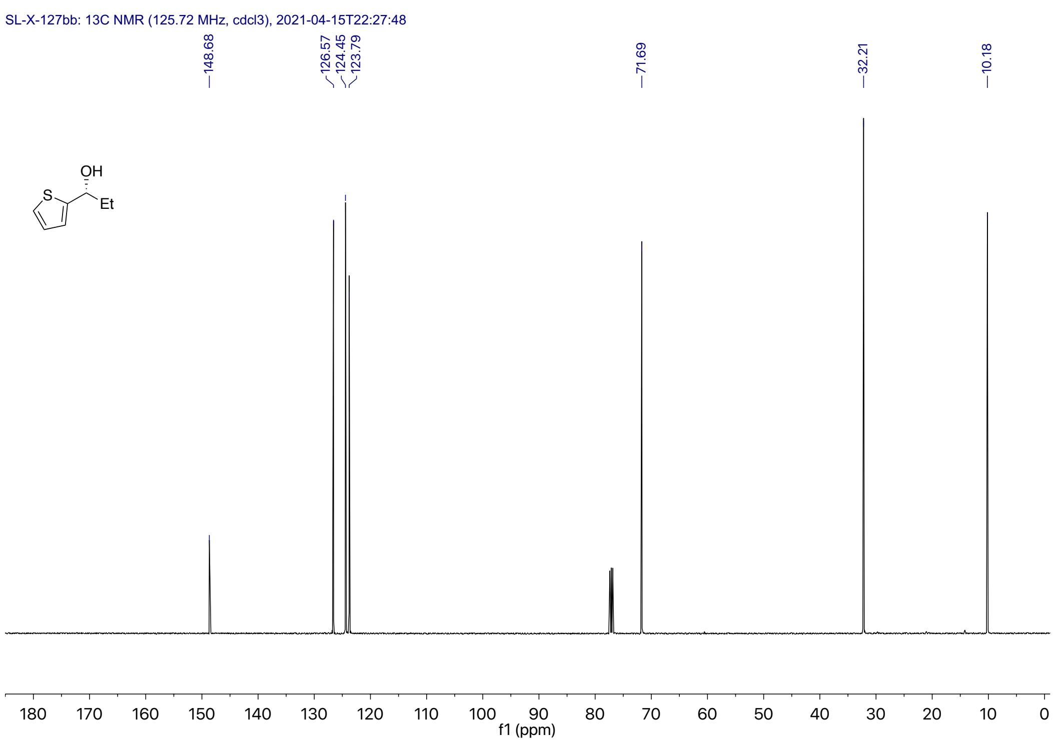


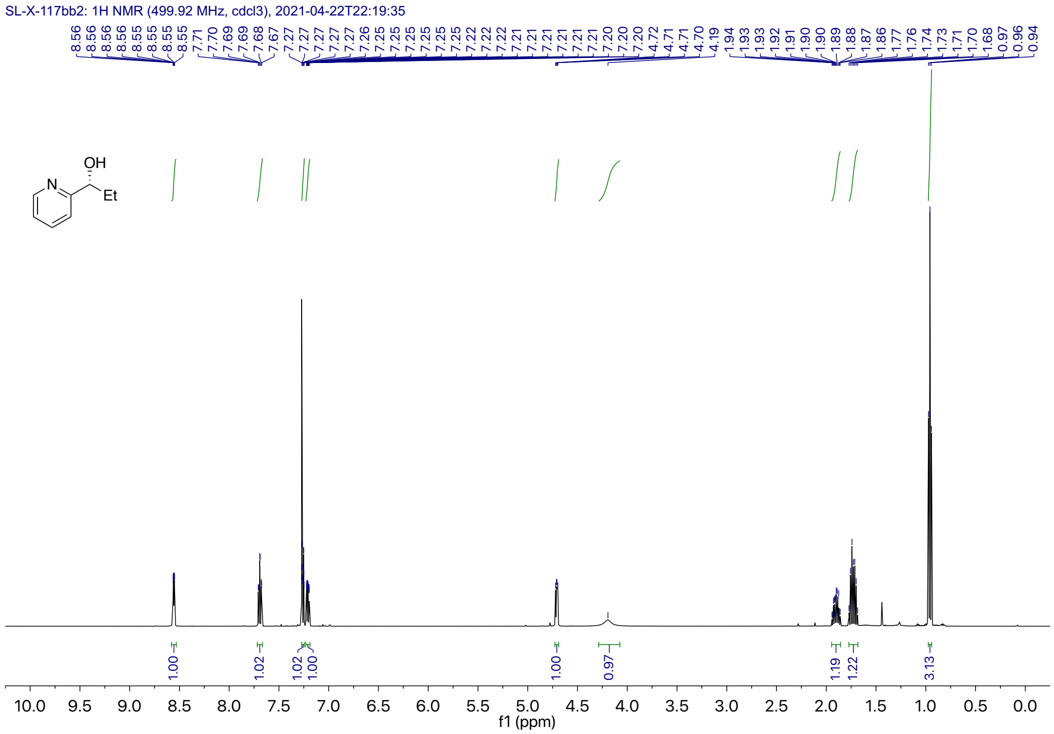
$^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) of (*R*)-**16p**



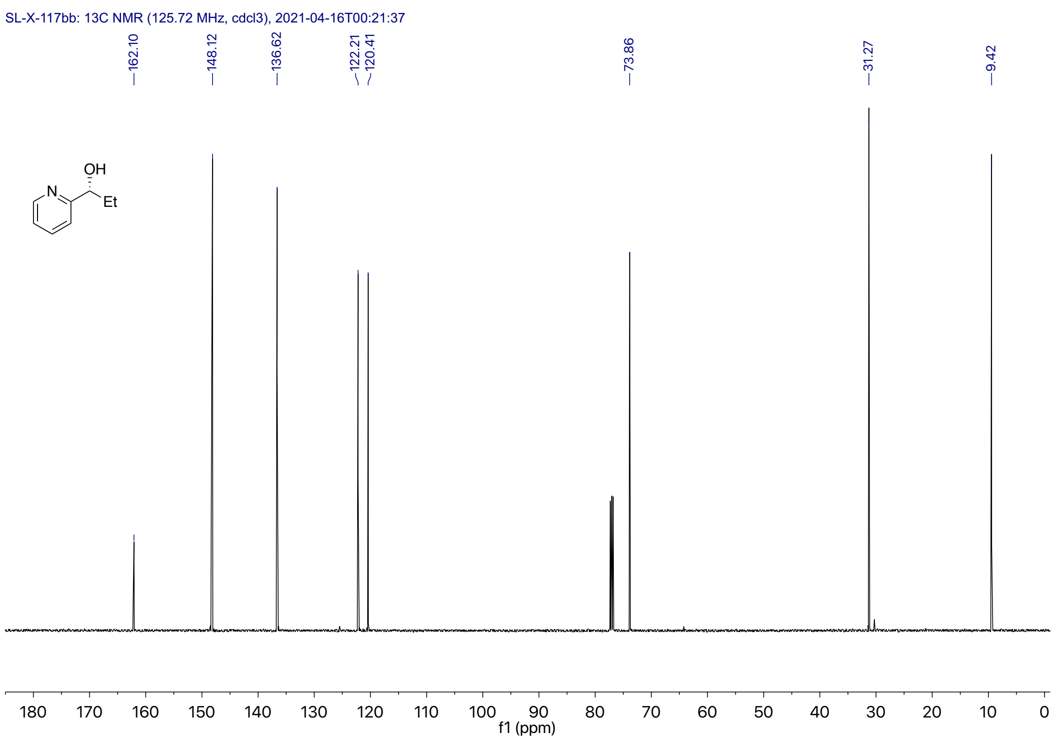
^{1}H NMR (500 MHz, $CDCl_3$) of (*R*)-**16q**



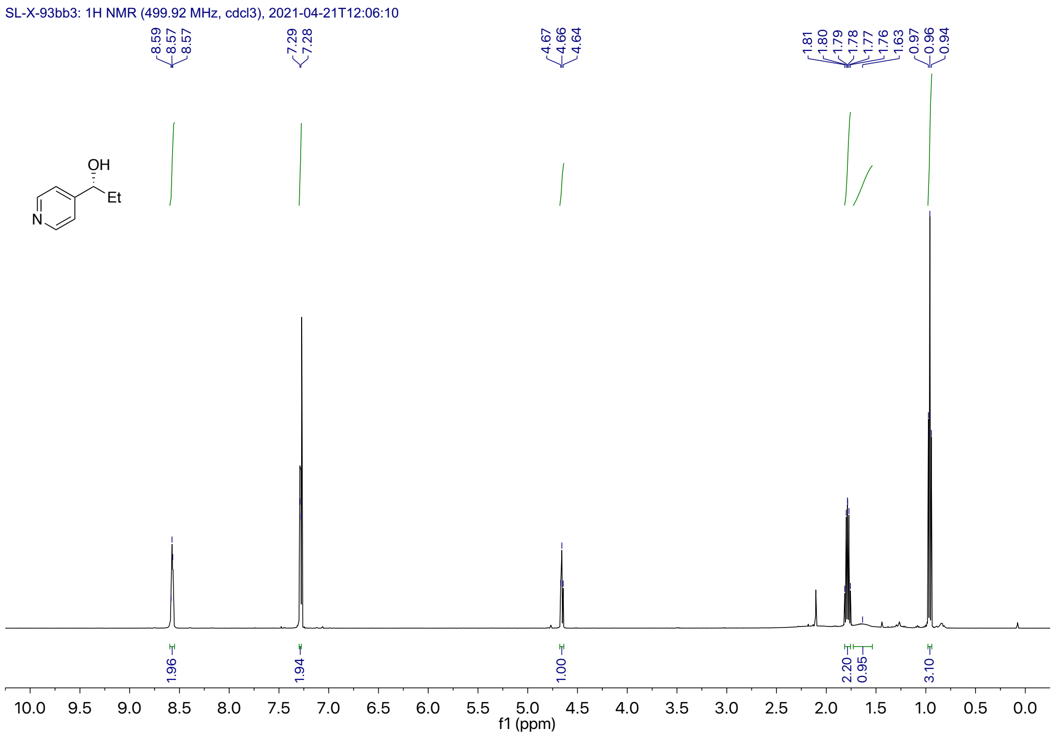
^{13}C{H} NMR (126 MHz, $CDCl_3$) of (*R*)-**16q**



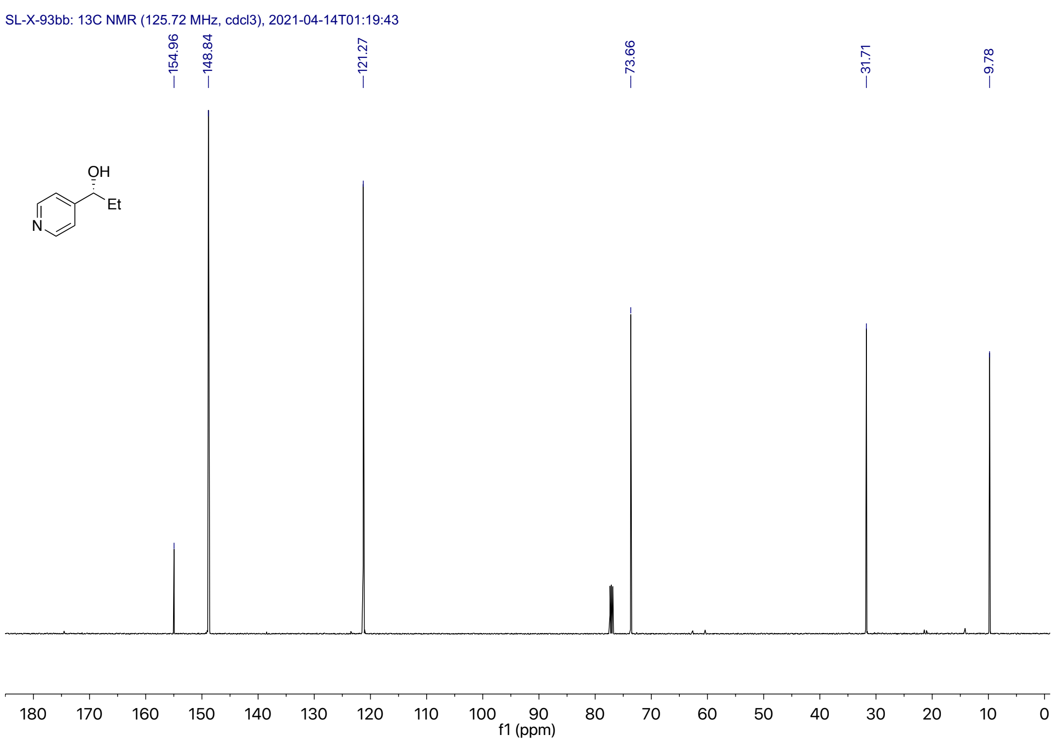
^{1}H NMR (500 MHz, $CDCl_3$) of (*R*)-**16r**



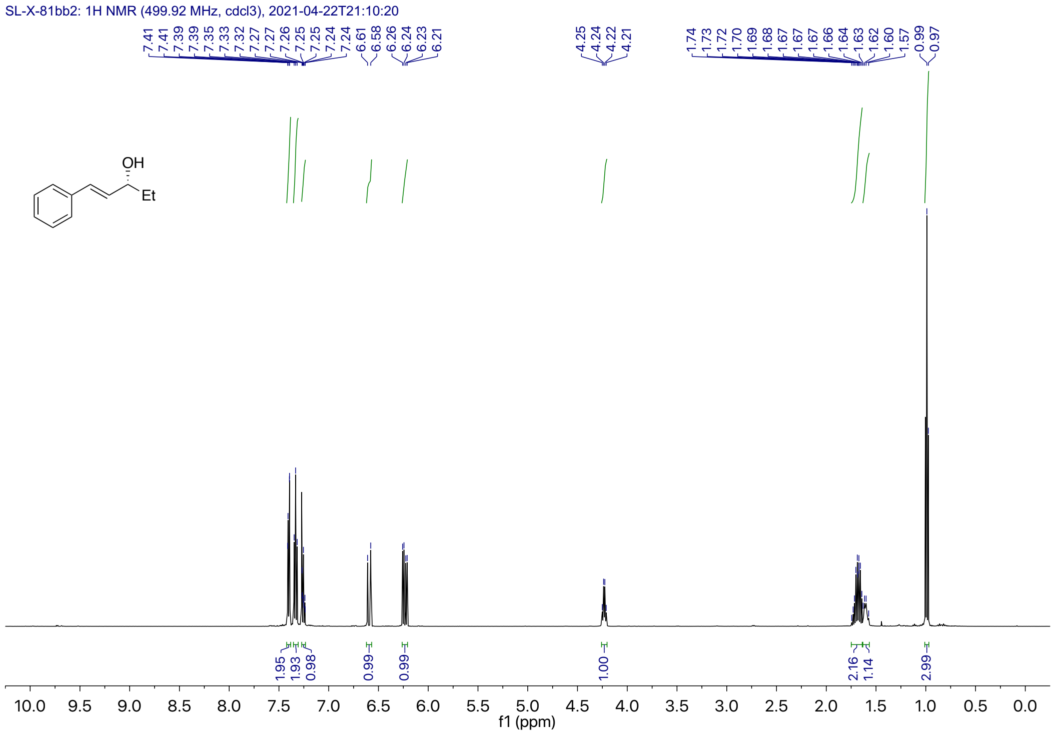
$^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) of (*R*)-**16r**



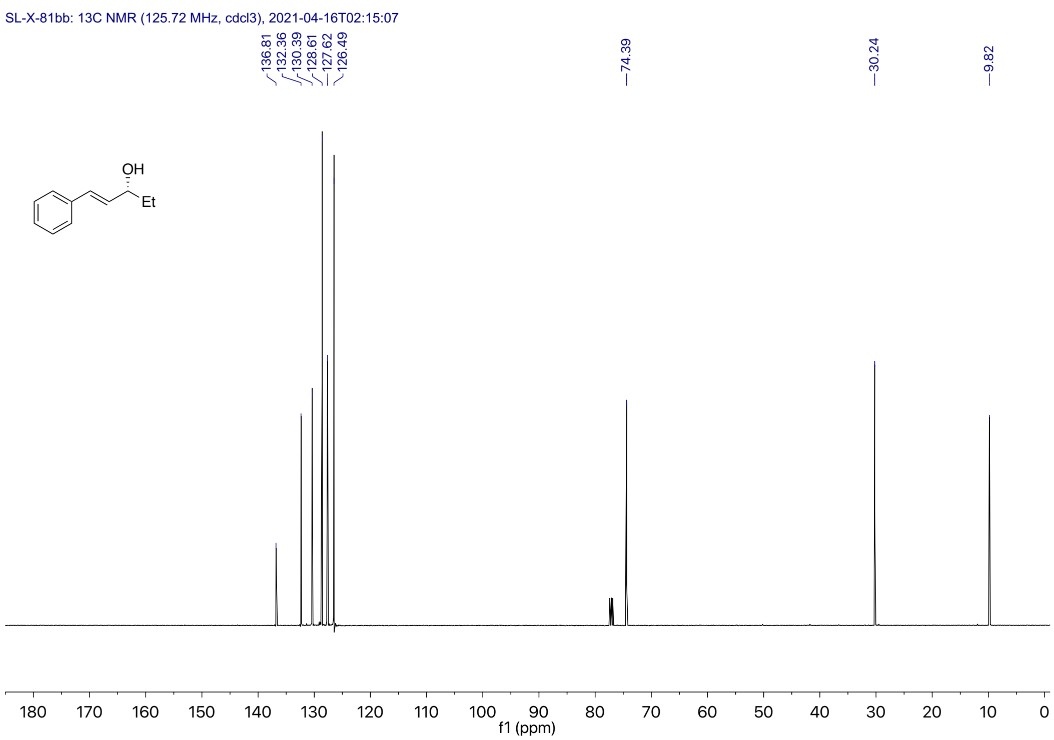
^{1}H NMR (500 MHz, $CDCl_3$) of (*R*)-**16s**



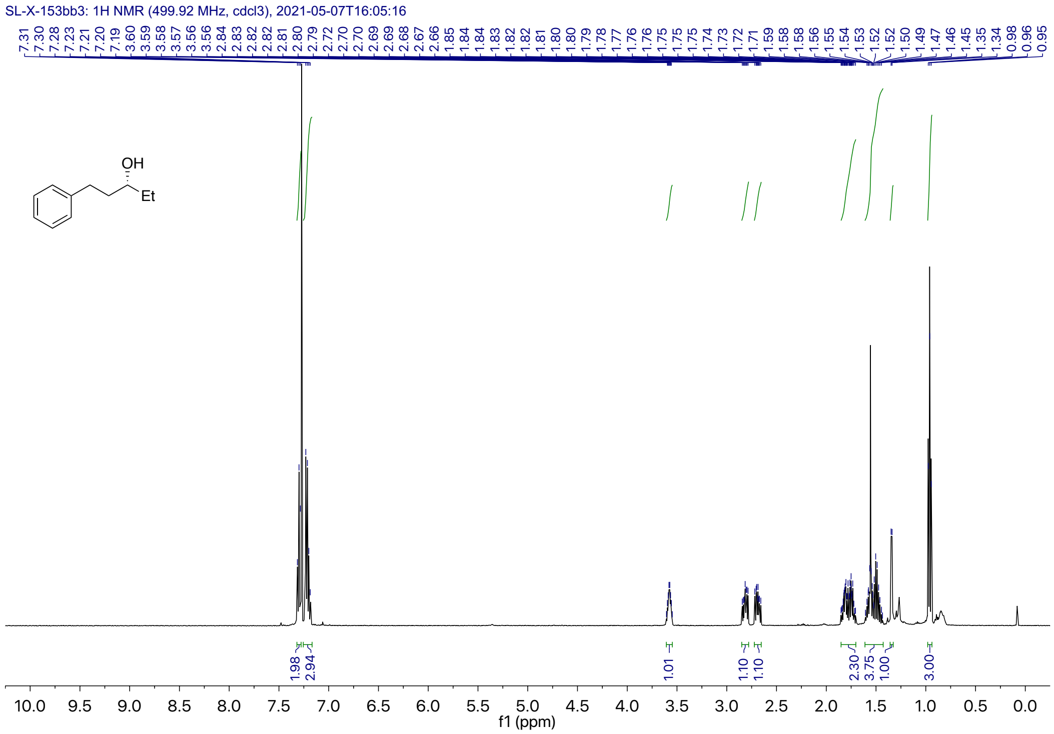
$^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) of (*R*)-**16s**



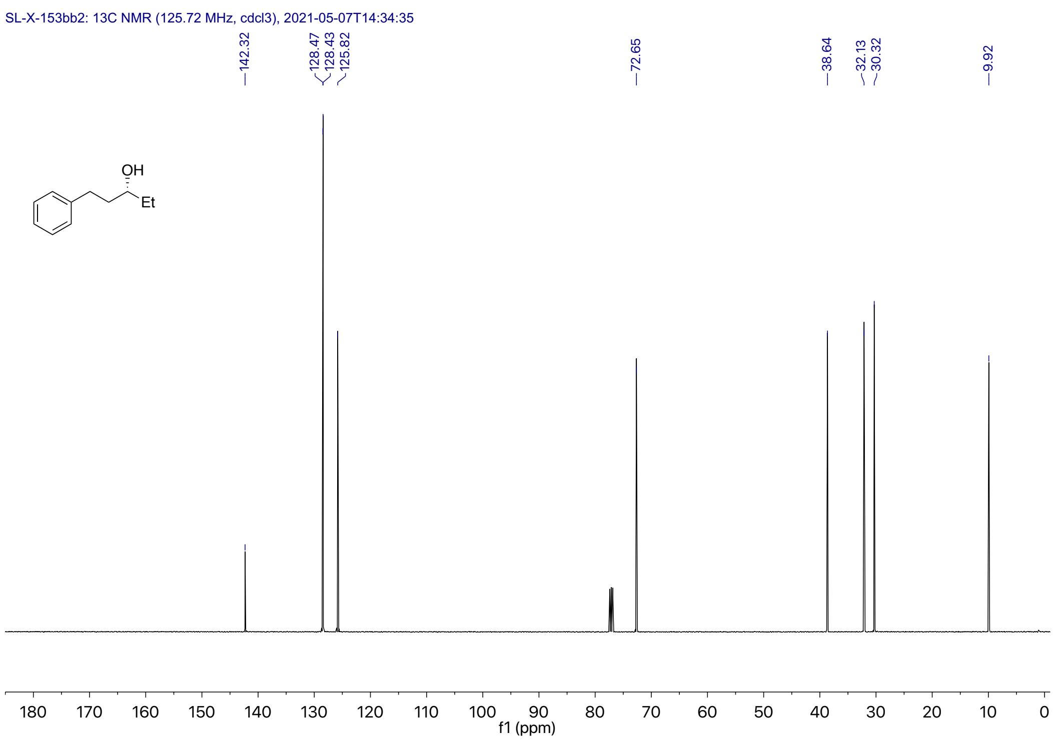
^{1}H NMR (500 MHz, CDCl$_3$) of (*R*)-**16t**



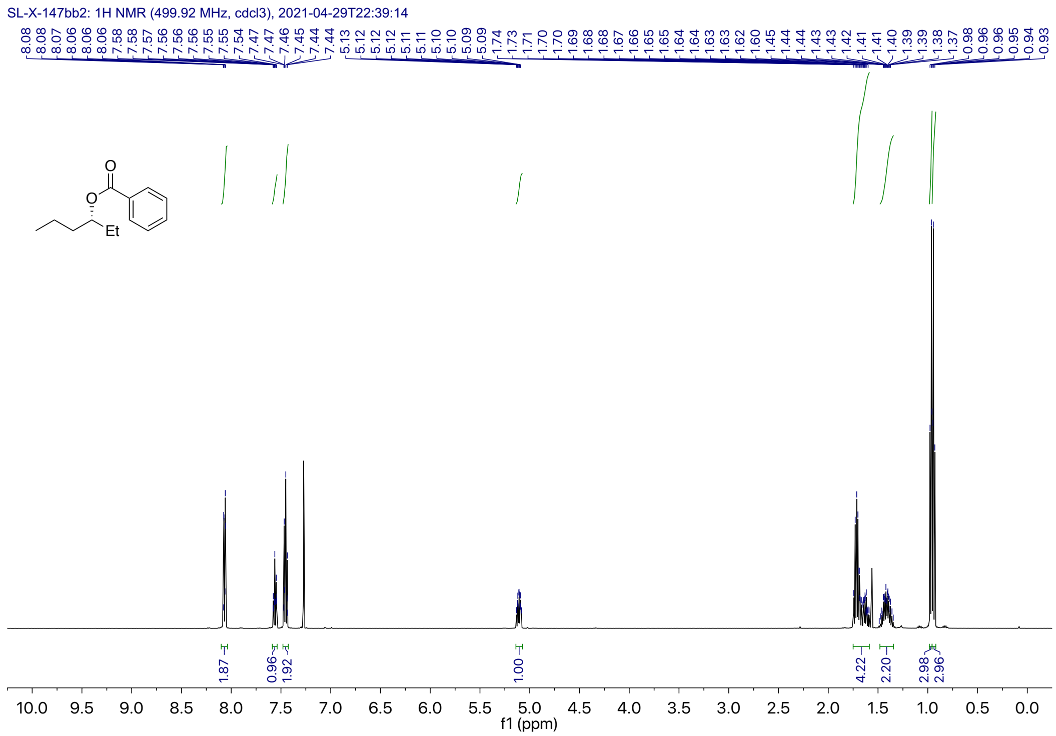
^{13}C{H} NMR (126 MHz, CDCl$_3$) of (*R*)-**16t**



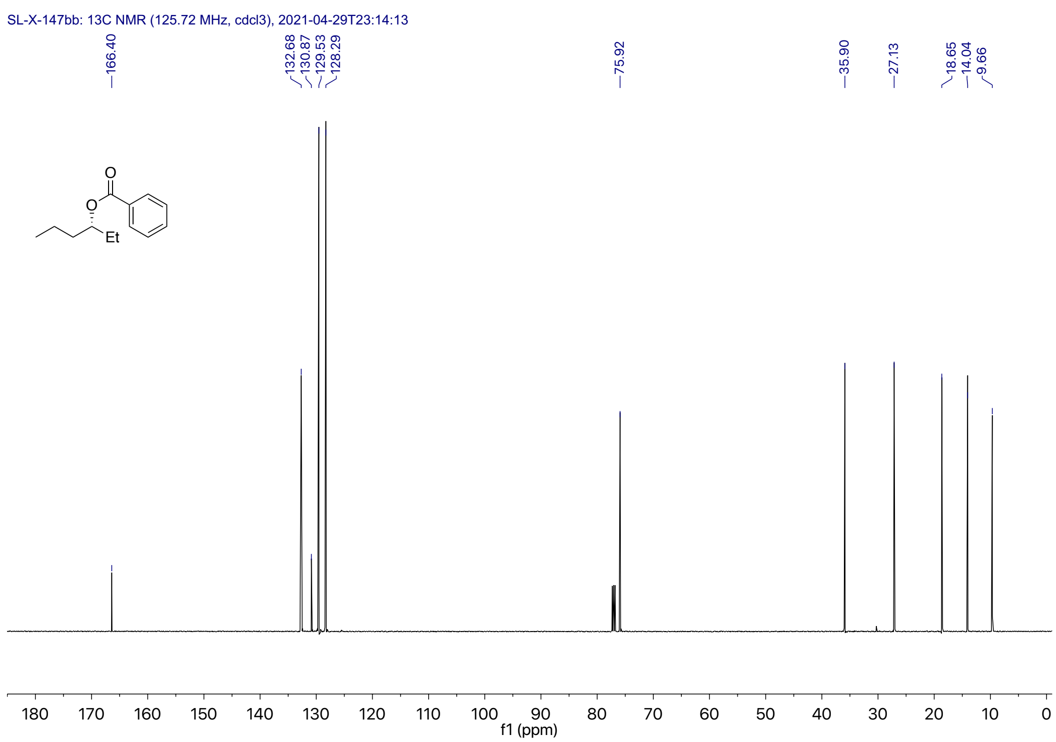
^{1}H NMR (500 MHz, $CDCl_3$) of (*R*)-**16u**



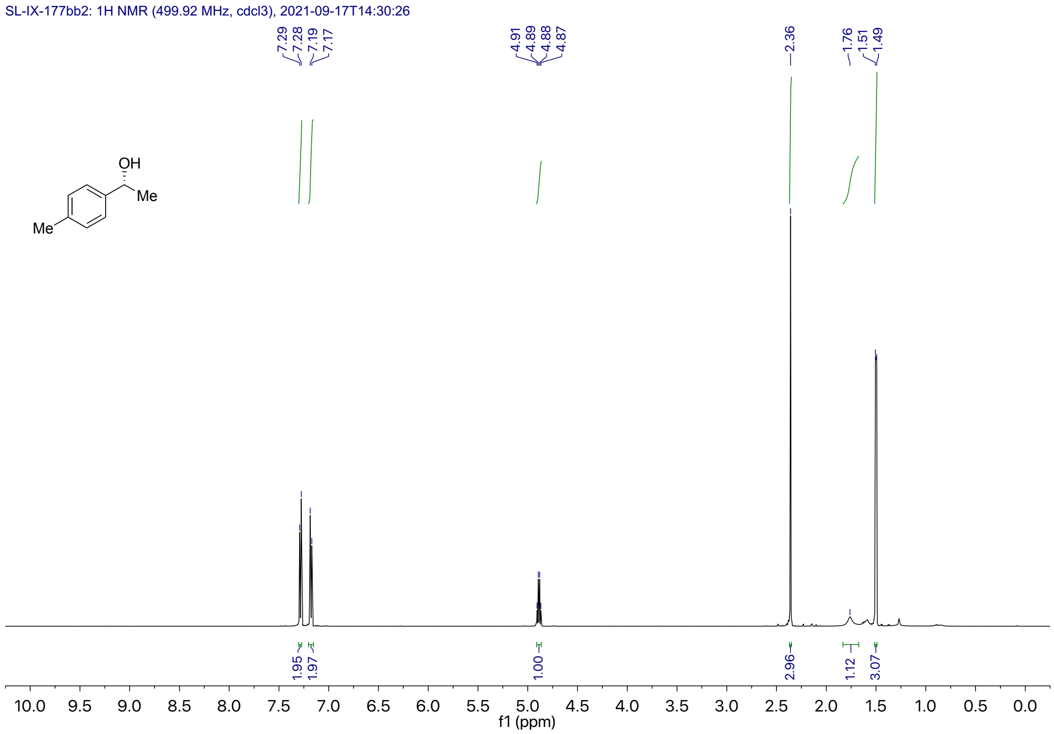
^{13}C{H} NMR (126 MHz, $CDCl_3$) of (*R*)-**16u**



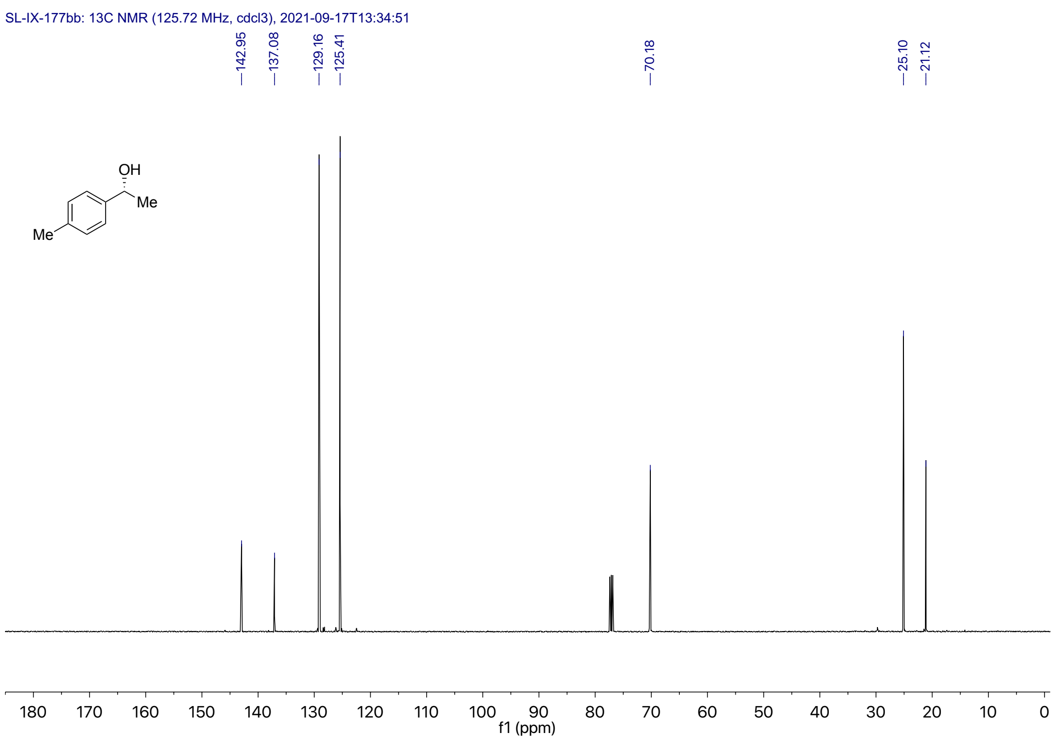
^{1}H NMR (500 MHz, $CDCl_3$) of (*R*)-**16v**



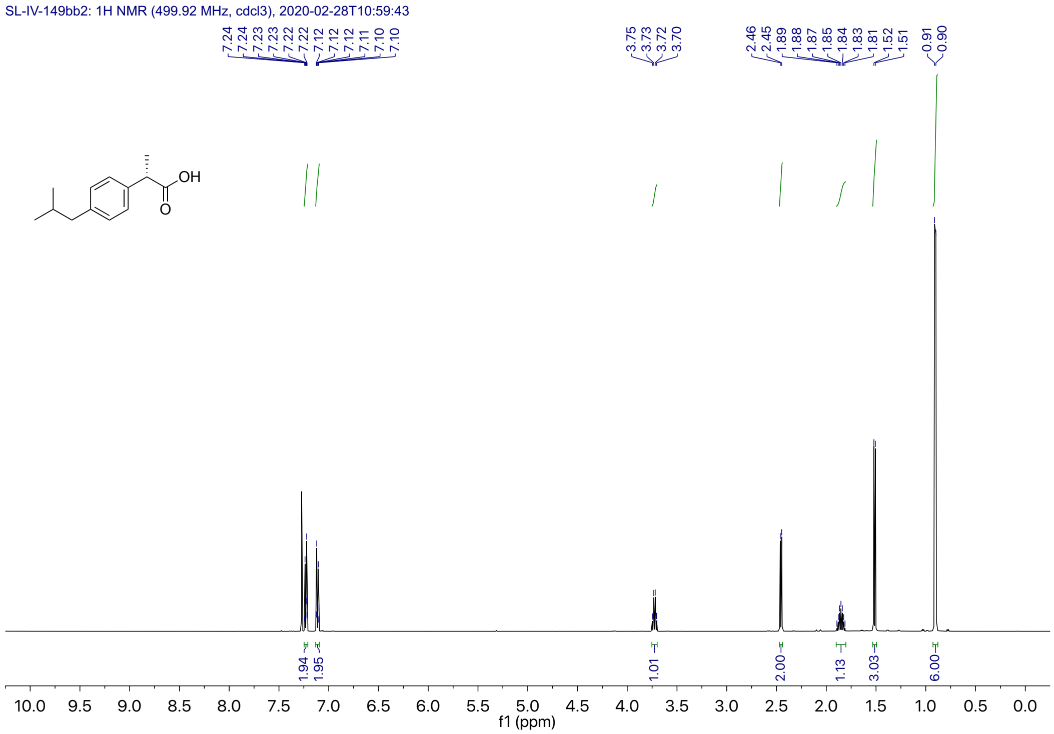
$^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) of (*R*)-**16v**



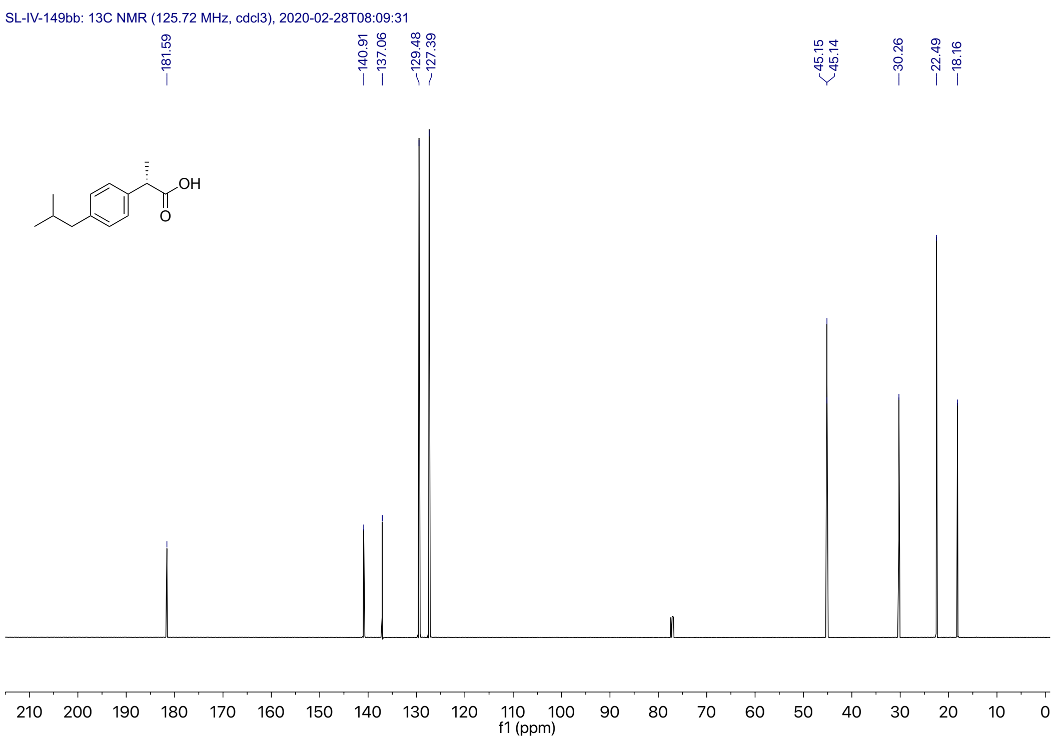
^{1}H NMR (500 MHz, $CDCl_3$) of (*R*)-**16w**



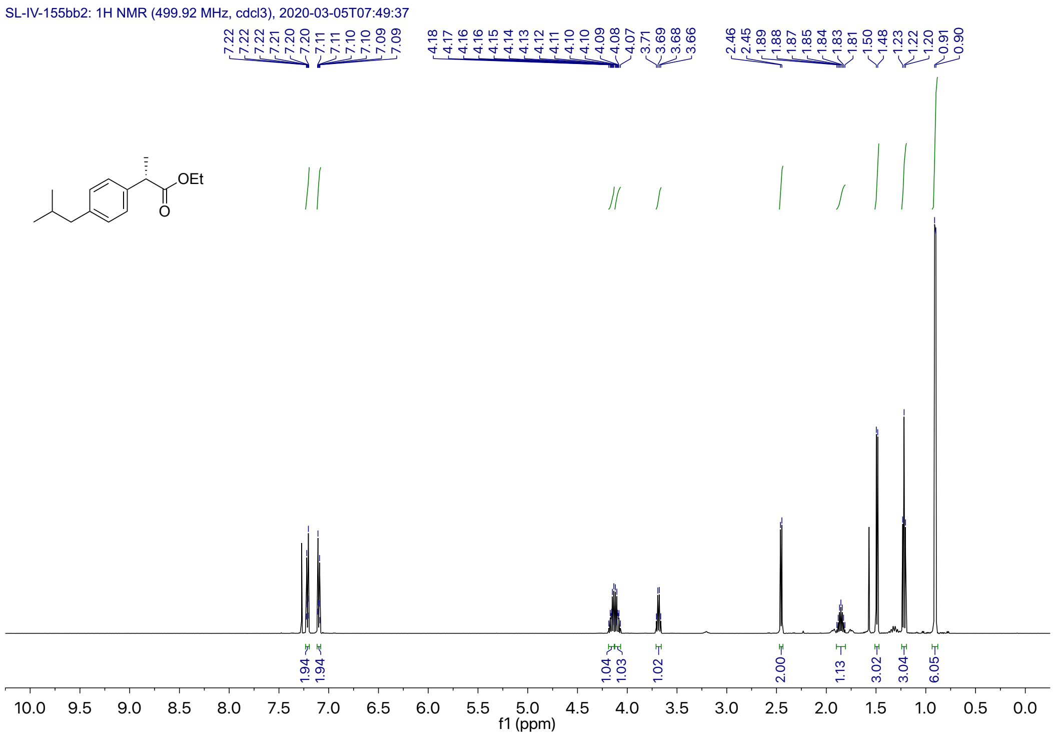
$^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) of (*R*)-**16w**



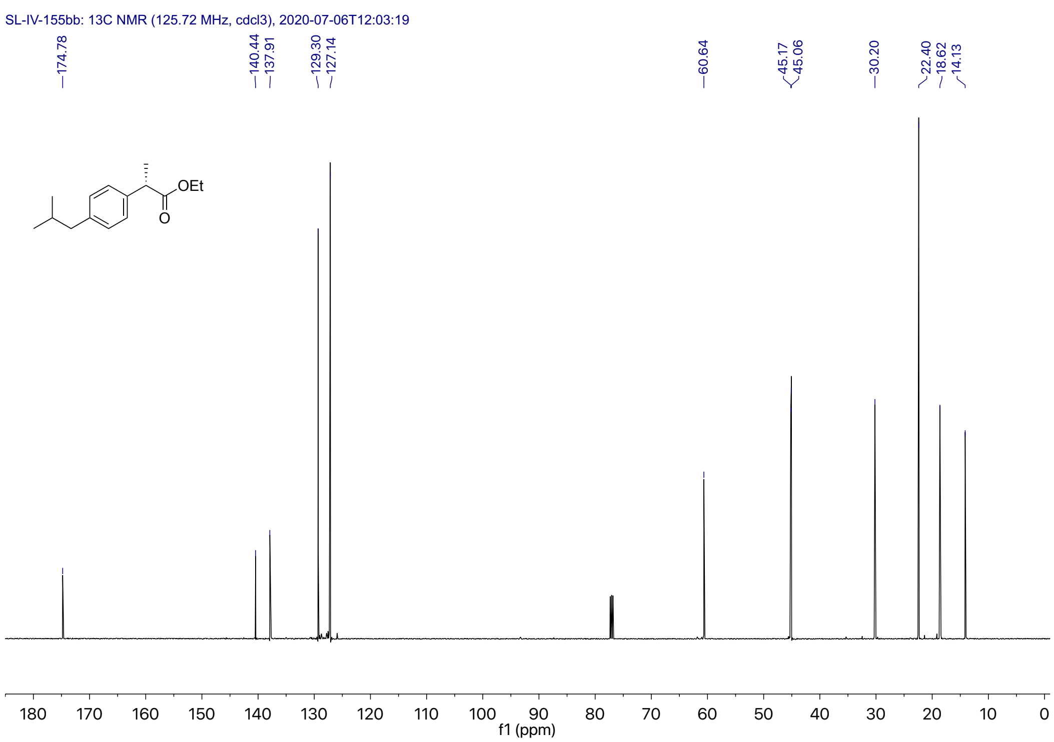
^{1}H NMR (500 MHz, $CDCl_3$) of (*S*)-**10**



^{13}C{H} NMR (126 MHz, $CDCl_3$) of (*S*)-**10**

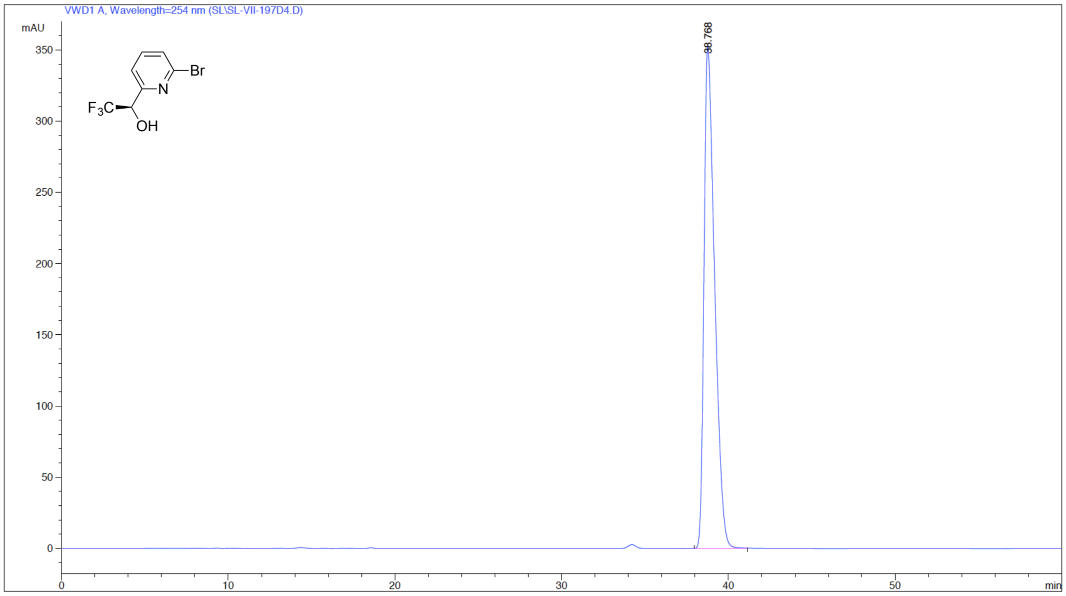


^{1}H NMR (500 MHz, $CDCl_3$) of (*S*)-**18**



$^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) of (*S*)-**18**

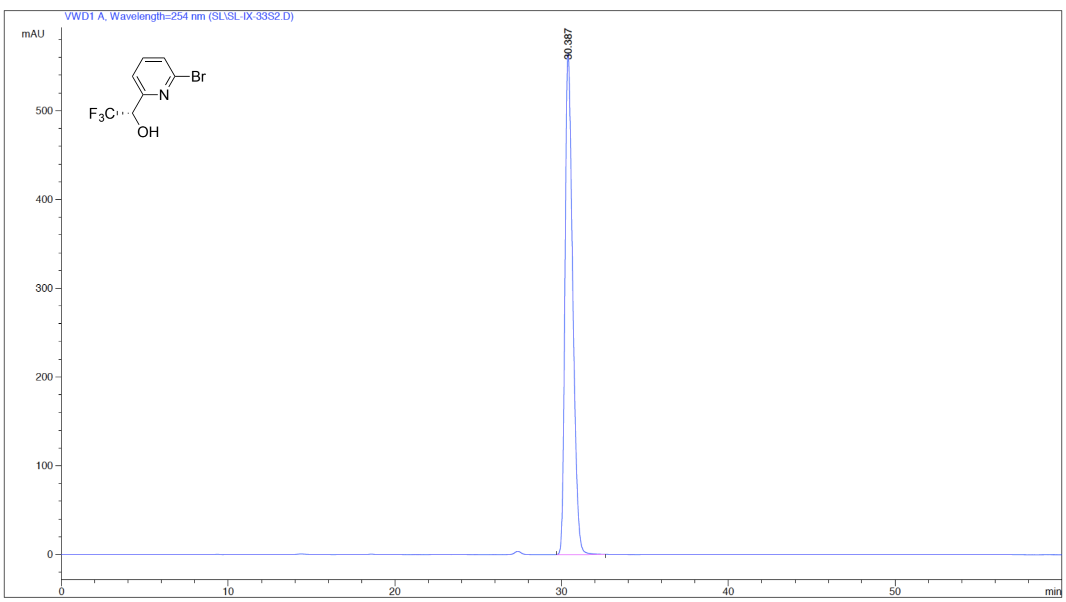
HPLC chromatograms



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	38.768	BB	0.6542	1.56241e4	352.31378	100.0000

Totals : 1.56241e4 352.31378

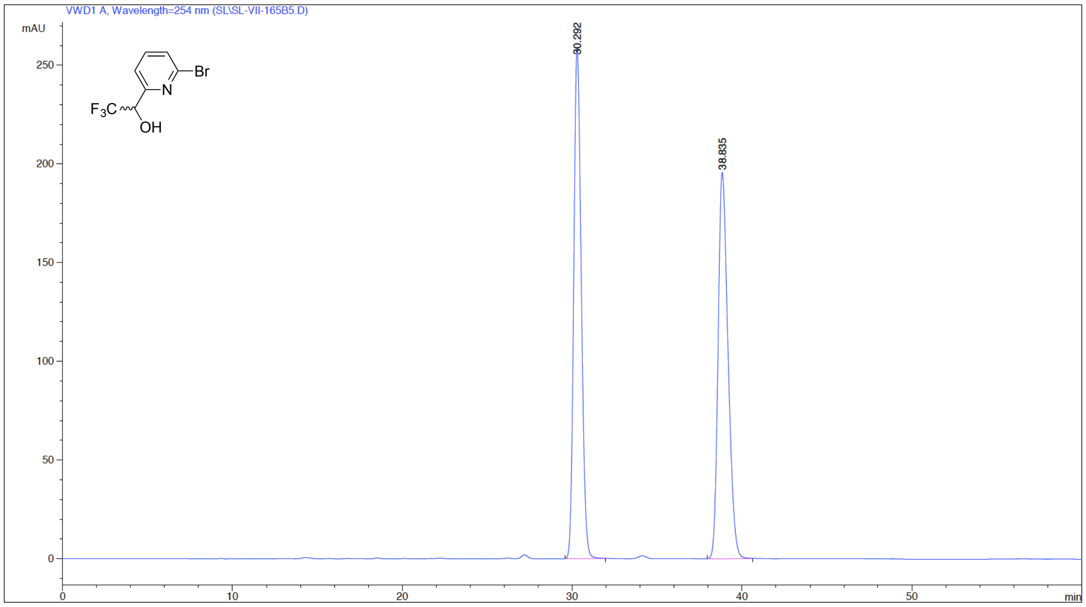
>99.5% *ee* of (*R*)-**9**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.387	BB	0.4788	1.82636e4	565.34698	100.0000

Totals : 1.82636e4 565.34698

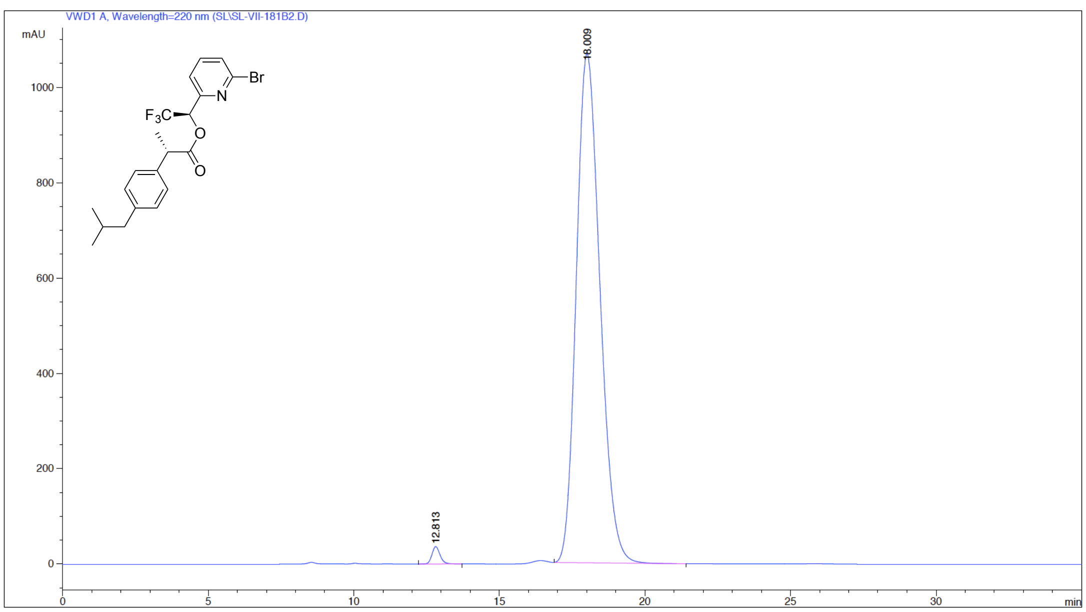
>99.5% *ee* of (*S*)-**9**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.292	BB	0.4623	7928.71826	258.74835	49.9432
2	38.835	BB	0.6077	7946.76270	195.68065	50.0568

Totals : 1.58755e4 454.42900

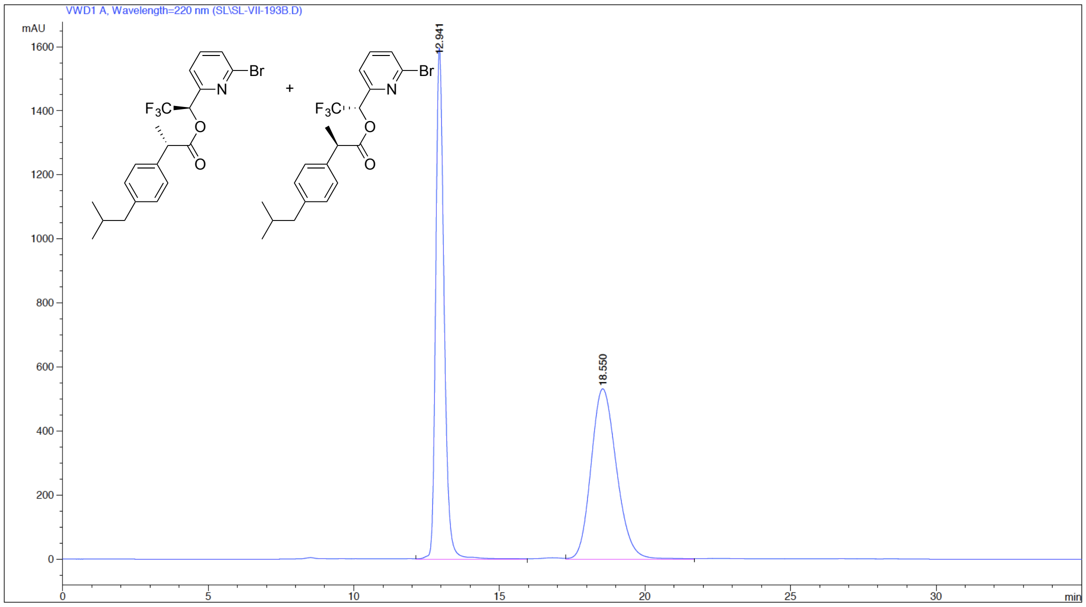
Racemate of **9**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.813	BBA	0.3021	705.85016	36.37053	1.1573
2	18.009	BB	0.8567	6.02876e4	1067.84644	98.8427

Totals : 6.09935e4 1104.21697

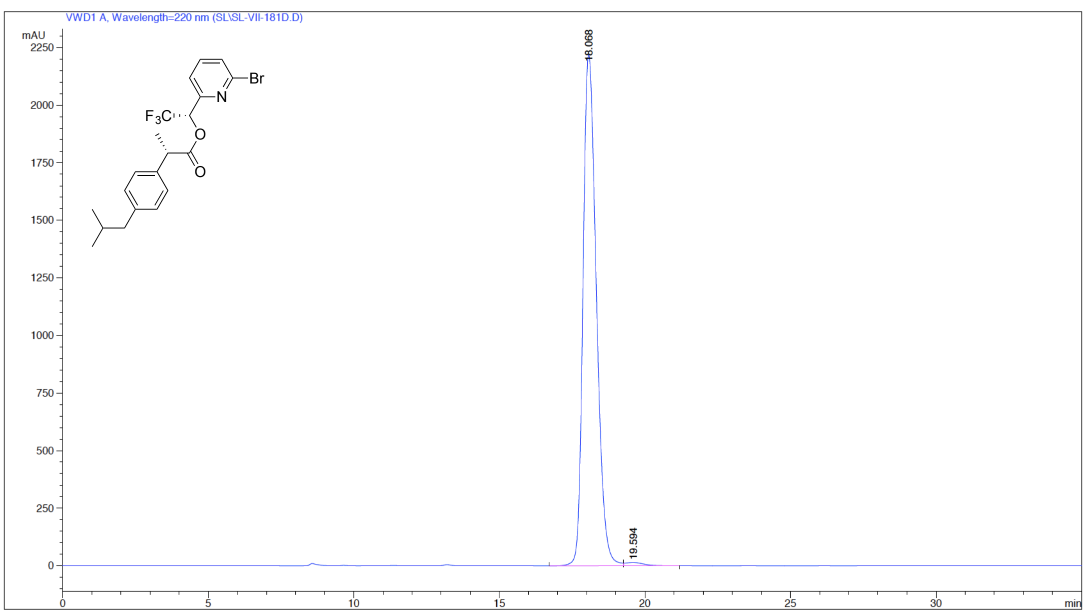
98% *ee* of (*R*,*S*)-**11**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.941	VV	0.3090	3.18945e4	1595.29480	49.7366
2	18.550	VV	0.9287	3.22323e4	531.60114	50.2634

Totals : 6.41268e4 2126.89594

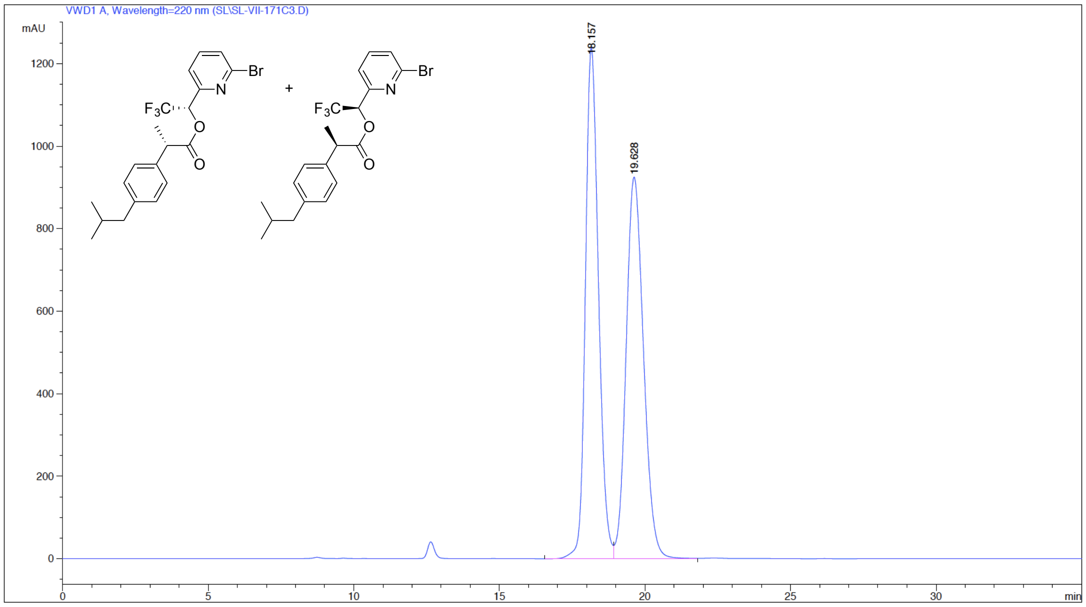
Racemate of **11**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.068	VV	0.4901	7.05066e4	2219.06616	99.1279
2	19.594	VB	0.6465	620.29785	14.11819	0.8721

Totals : 7.11269e4 2233.18435

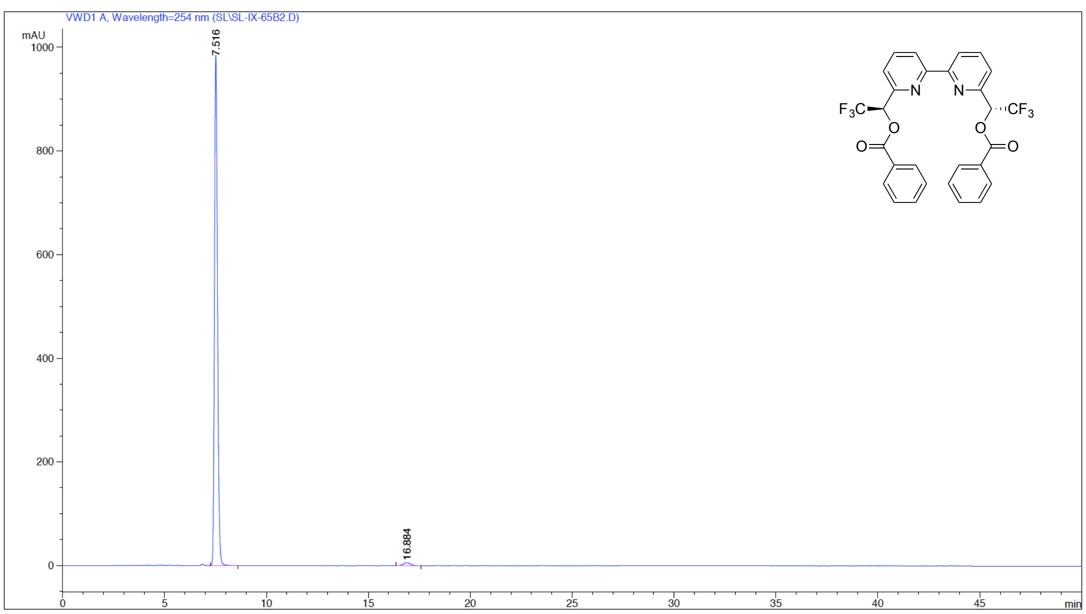
98% *ee* of (*S*,*S*)-**12**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.157	VV	0.4805	3.86549e4	1238.80432	50.1314
2	19.628	VV	0.6276	3.84523e4	925.21613	49.8686

Totals : 7.71072e4 2164.02045

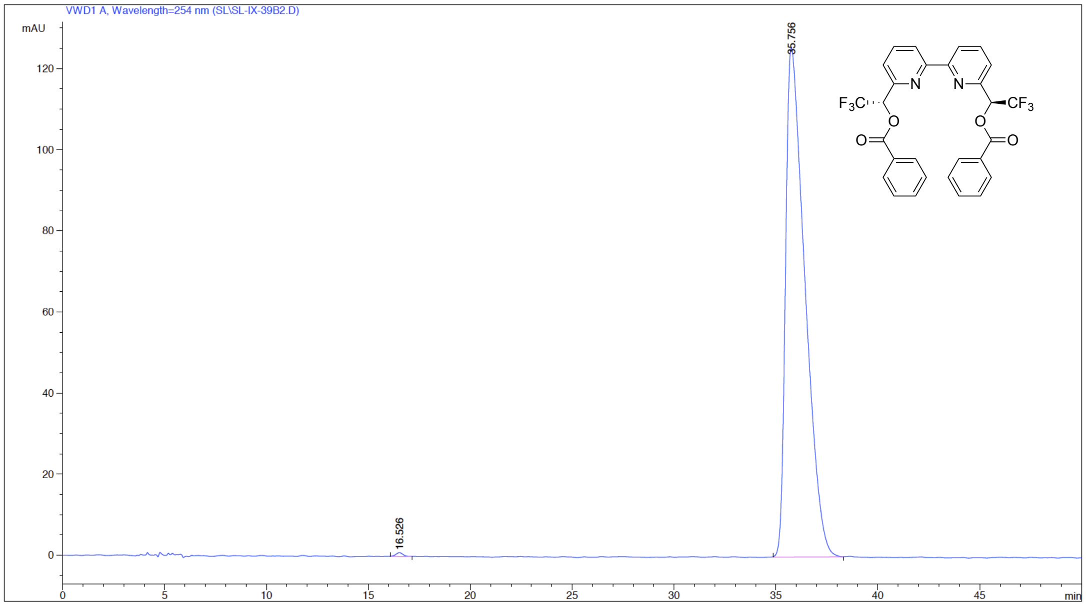
Racemate of **12**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.516	VB	0.1623	1.02636e4	985.65619	98.5978
2	16.884	BB	0.3992	145.95848	5.72842	1.4022

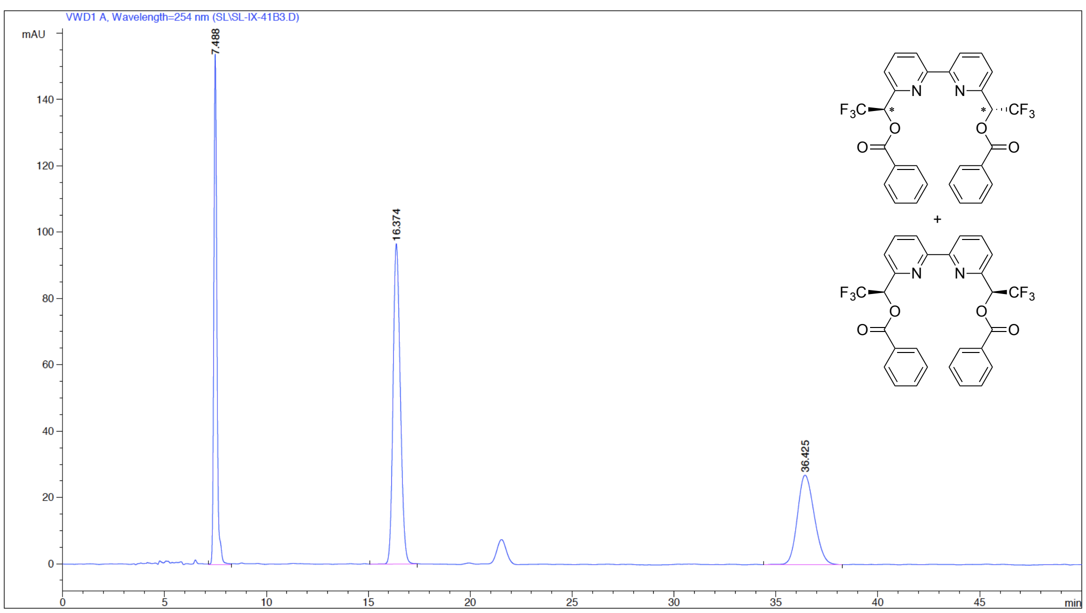
Totals : 1.04096e4 991.38460

97% *de*, >99.5% *ee* of (*R*,*R*)-**14**



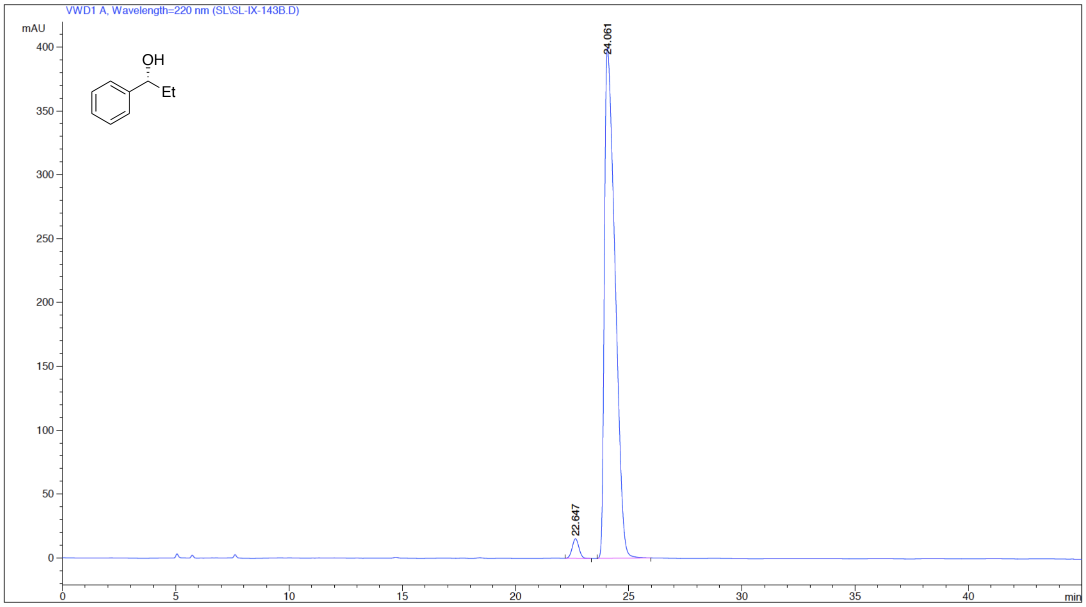
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.526	BB	0.3657	21.56781	9.13527e-1	0.2599
2	35.756	BB	0.9932	8277.66016	125.58489	99.7401
Totals :				8299.22796	126.49842	

>99.5% *de*, >99.5% *ee* of (*S*,*S*)-**14**



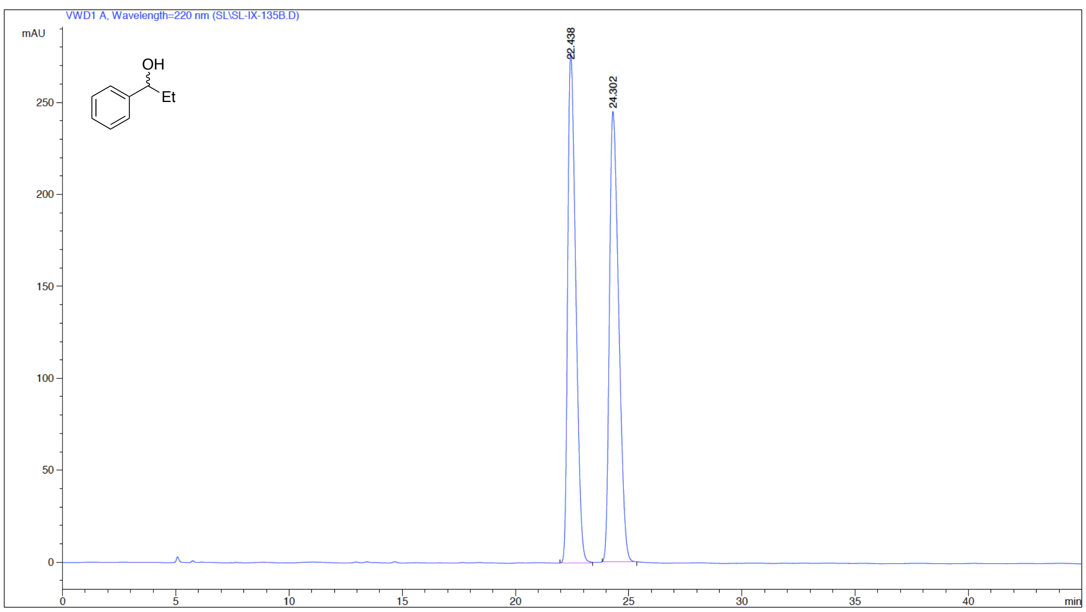
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.488	VB	0.1594	1602.65100	153.85120	28.8701
2	16.374	VB	0.3841	2383.29517	96.55835	42.9327
3	36.425	VB	0.8964	1565.29382	27.05115	28.1972
Totals :				5551.23999	277.46070	

Racemate of **14**



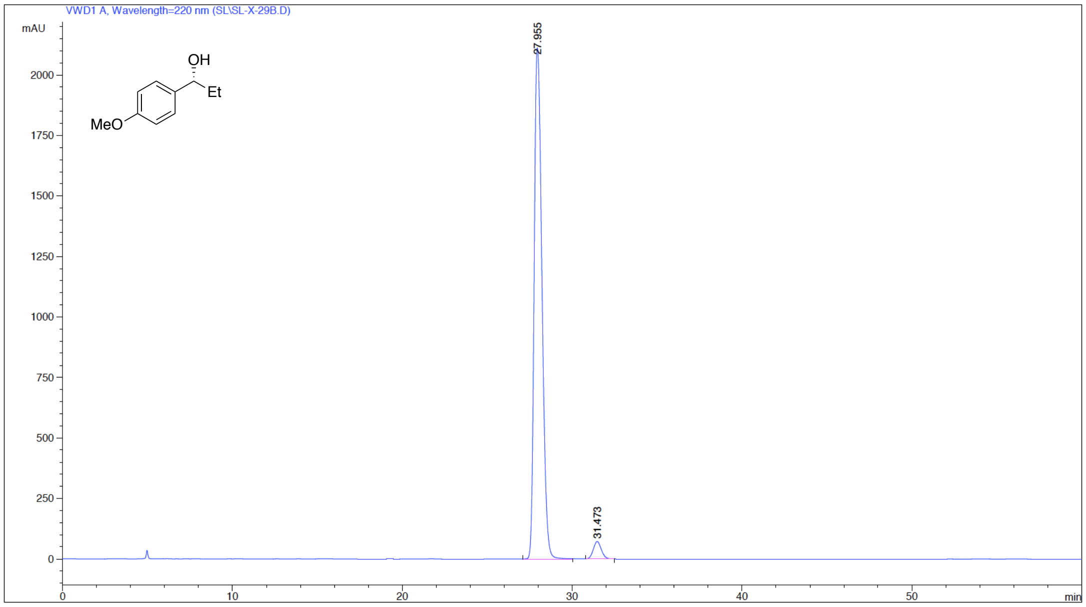

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  22.647 BB    0.3220  316.68661   15.36354   2.3745
   2  24.061 BB    0.5345 1.30204e4   399.57516  97.6255

Totals :                  1.33371e4   414.93871
```

95% *ee* of (*R*)-**16a**



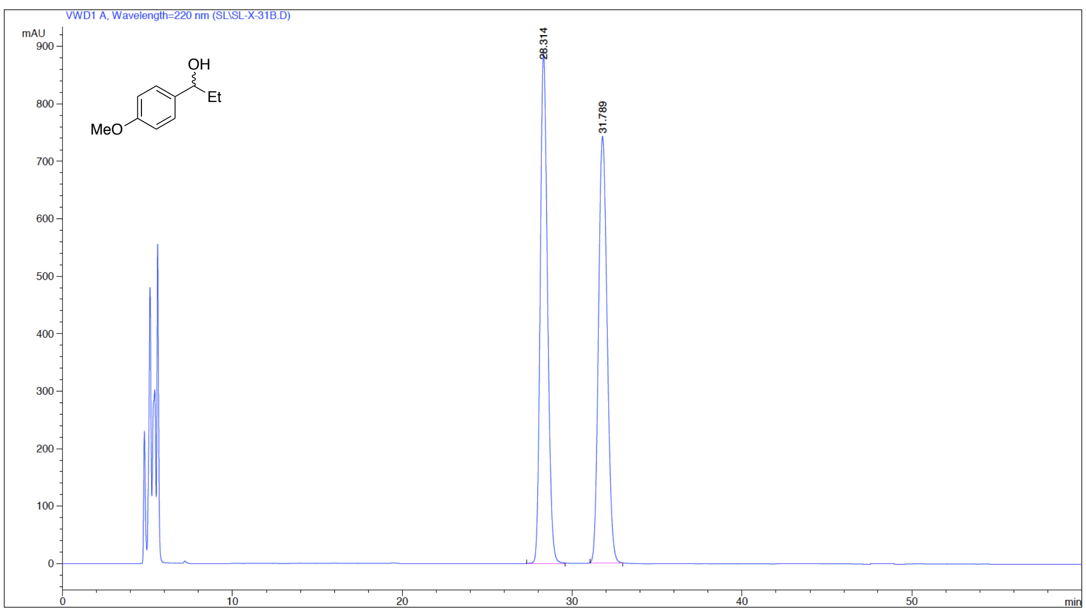

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   mAU   *s    [mAU   ]     %
----|-------|----|-------|----------|----------|--------|
   1  22.438 BBA   0.3899 6850.36963  277.50479  49.5029
   2  24.302 BBA   0.4522 6987.95996  244.97038  50.4971

Totals :                  1.38383e4   522.47517
```

Racemate of **16a**



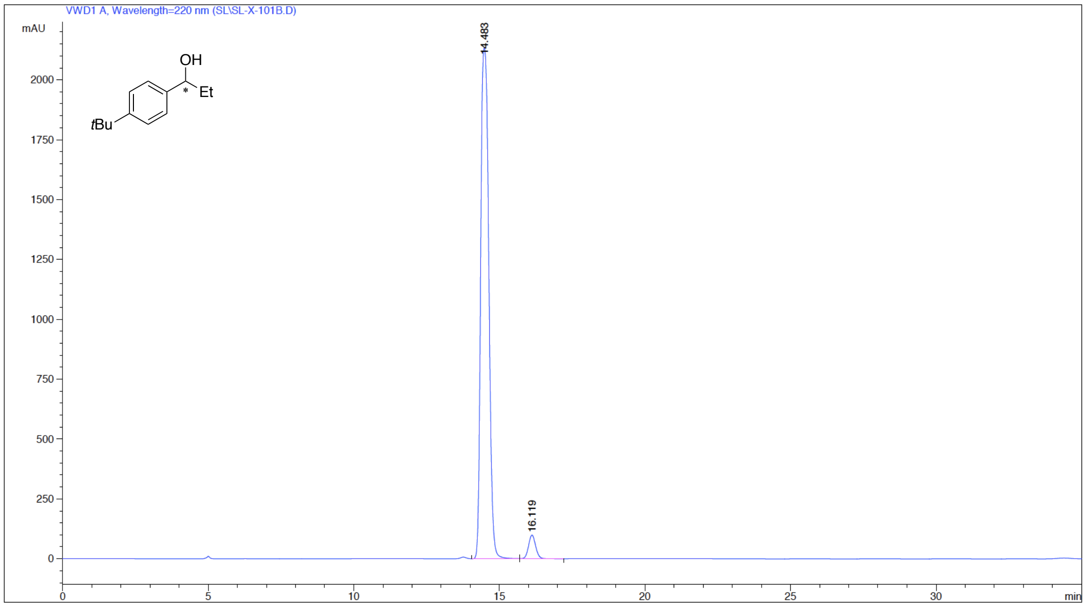
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.955	BBA	0.5011	6.70062e4	2112.19287	96.6131
2	31.473	BBA	0.5076	2349.00000	71.67091	3.3869
Totals :				6.93552e4	2183.86378	

93% *ee* of (*R*)-**16b**



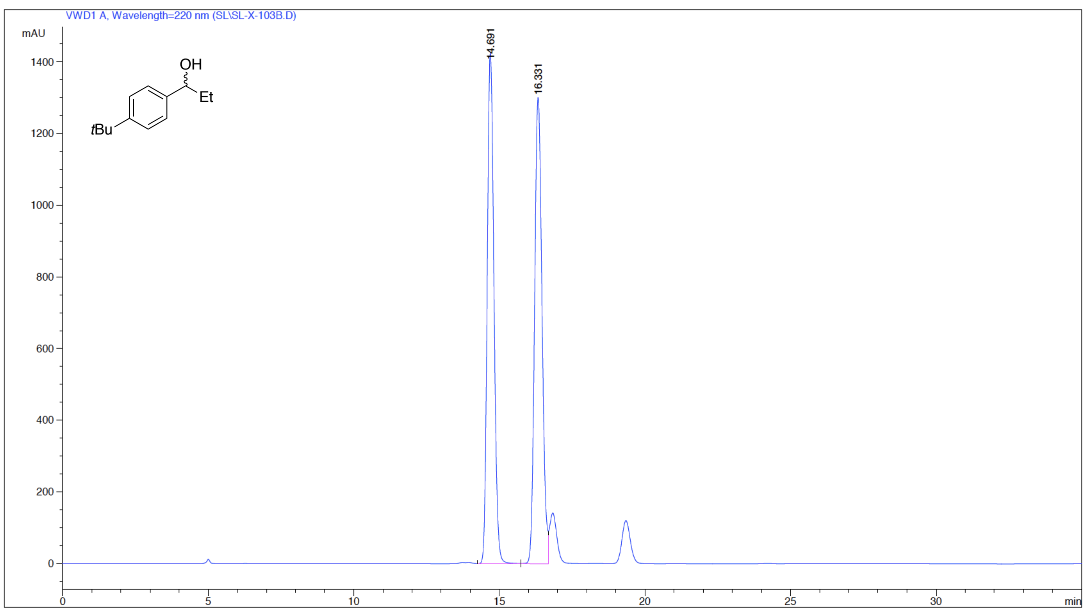
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.314	BBA	0.4597	2.63503e4	888.21442	49.9811
2	31.789	BBA	0.5599	2.63703e4	742.59167	50.0189
Totals :				5.27206e4	1630.80609	

Racemate of **16b**



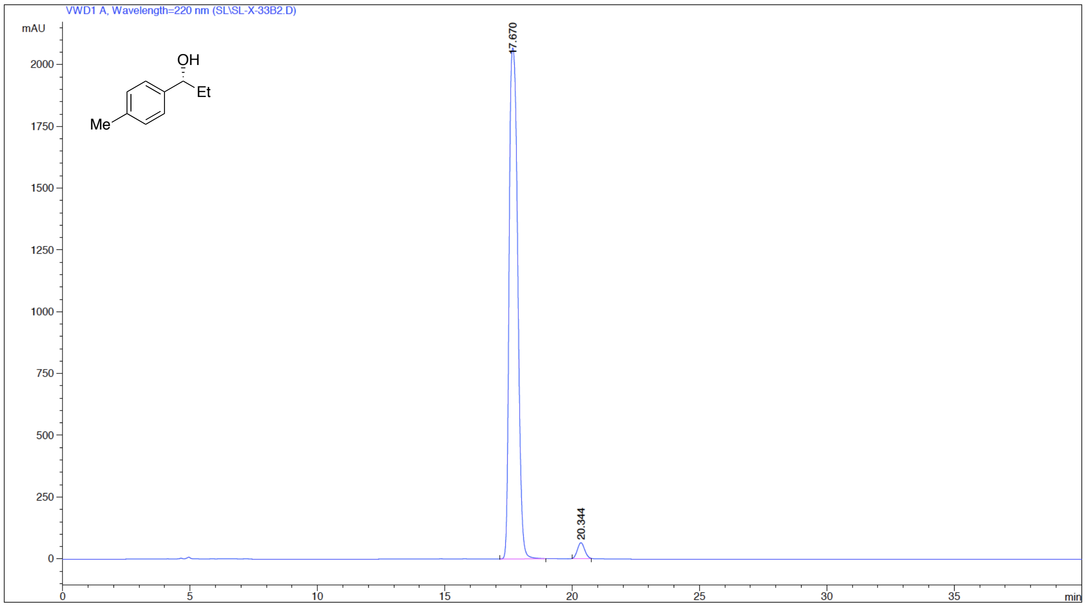
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.483	VV	0.3078	4.08665e4	2134.23486	95.9970
2	16.119	VB	0.2639	1704.11316	99.46891	4.0030
Totals :				4.25706e4	2233.70377	

92% *ee* of (+)-**16c**



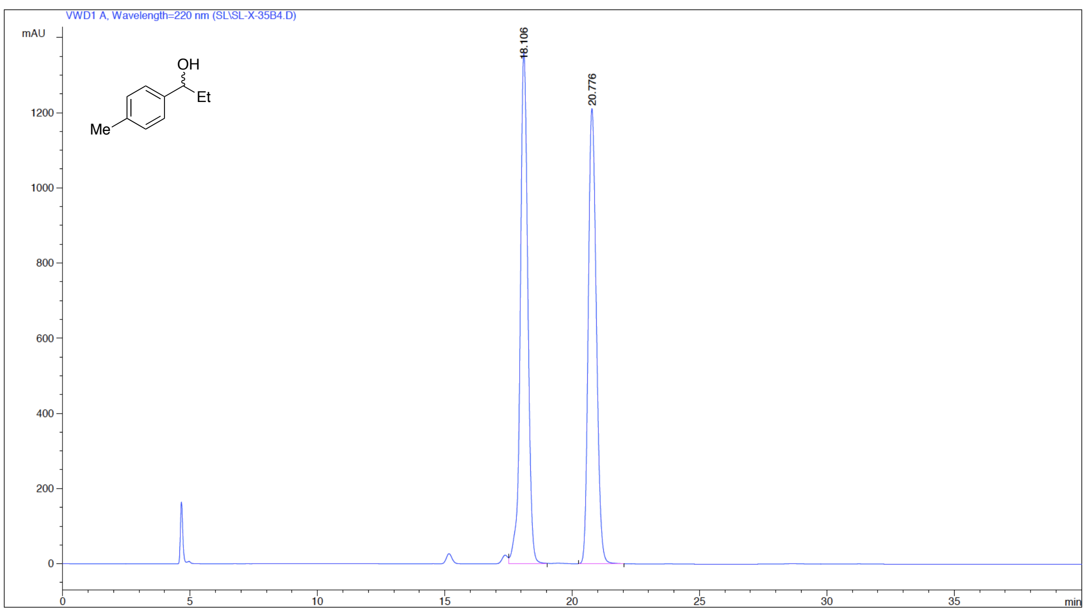
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.691	VV	0.2504	2.27803e4	1425.95032	49.7000
2	16.331	VV	0.2766	2.30553e4	1300.98596	50.3000
Totals :				4.58356e4	2726.93628	

Racemate of **16c**



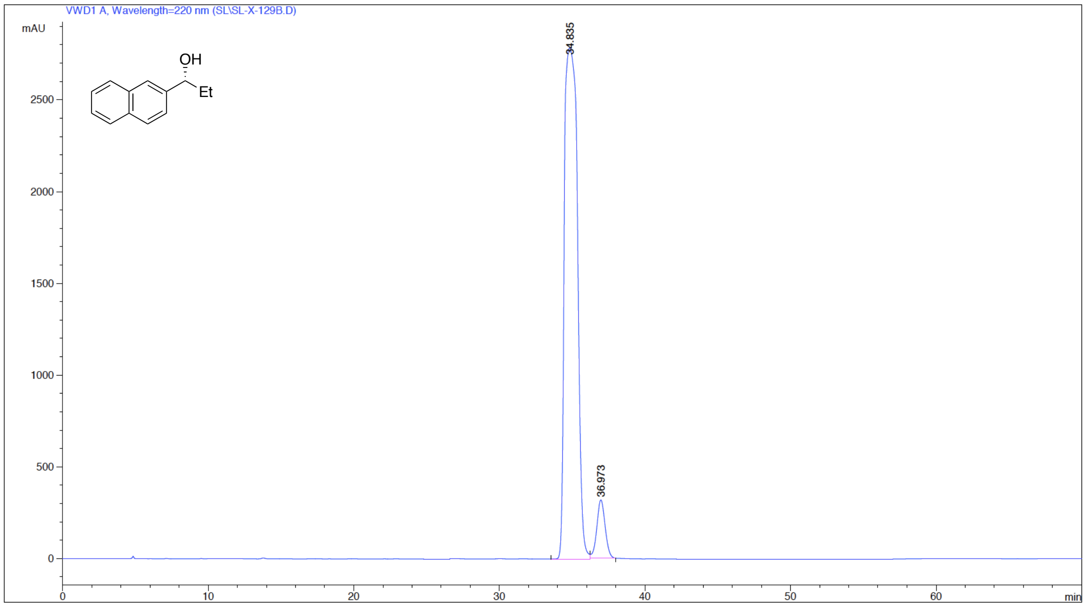
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.670	BBA	0.3744	4.77795e4	2068.07690	97.4471
2	20.344	BBA	0.3112	1251.71179	63.58452	2.5529
Totals :				4.90312e4	2131.66142	

95% *ee* of (*R*)-**16d**



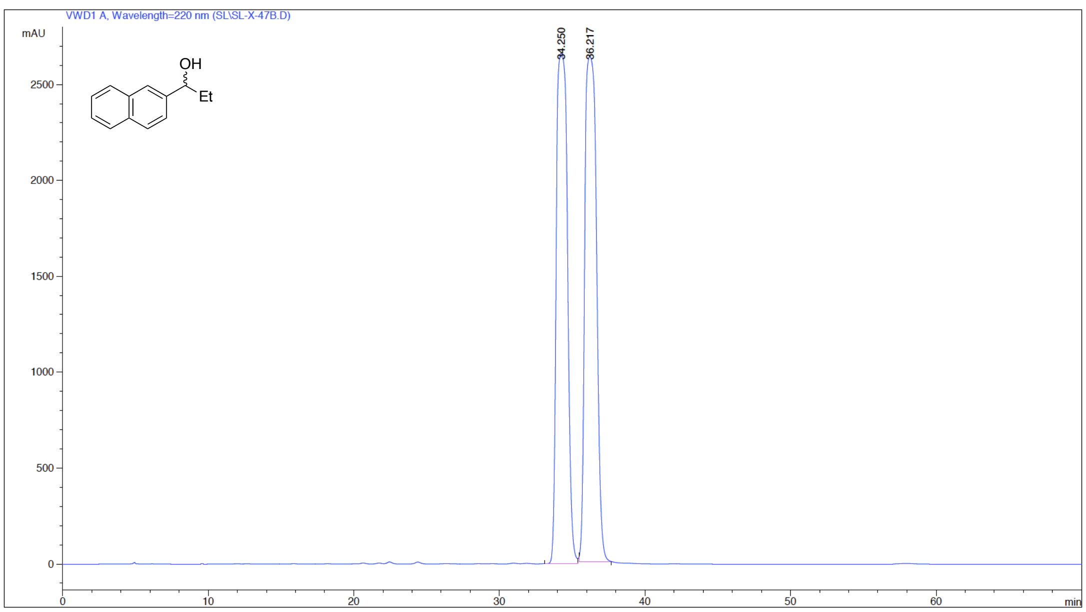
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.106	VBA	0.3187	2.79671e4	1359.36377	51.2968
2	20.776	BBA	0.3432	2.65531e4	1210.78772	48.7032
Totals :				5.45202e4	2570.15149	

Racemate of **16d**



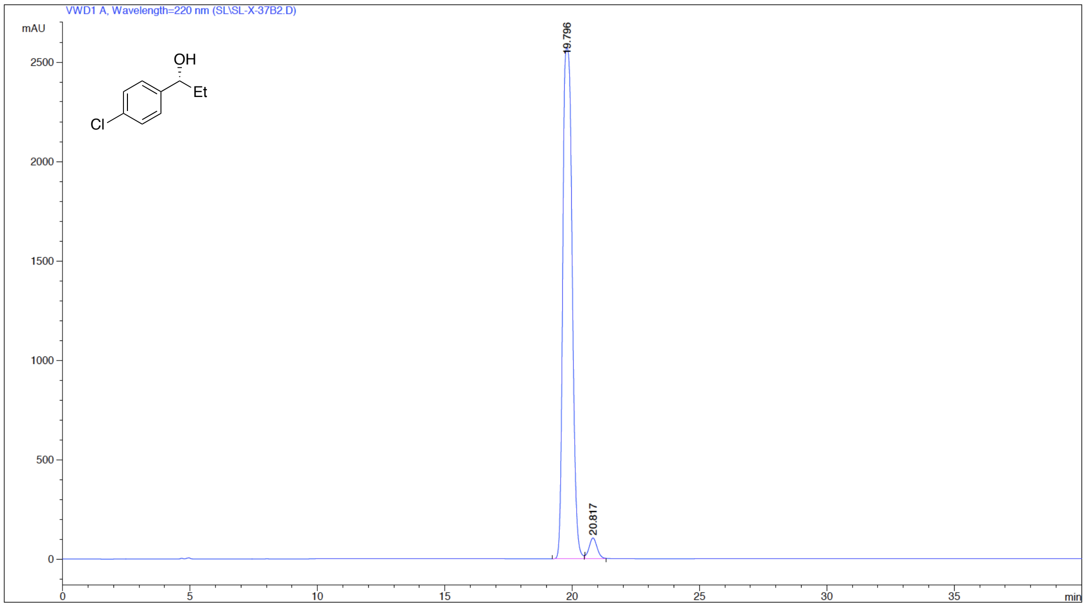
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.835	BBA	1.0011	1.72289e5	2785.79443	93.1588
2	36.973	BBA	0.6160	1.26522e4	317.72510	6.8412
Totals :				1.84941e5	3103.51953	

86% *ee* of (*R*)-**16e**



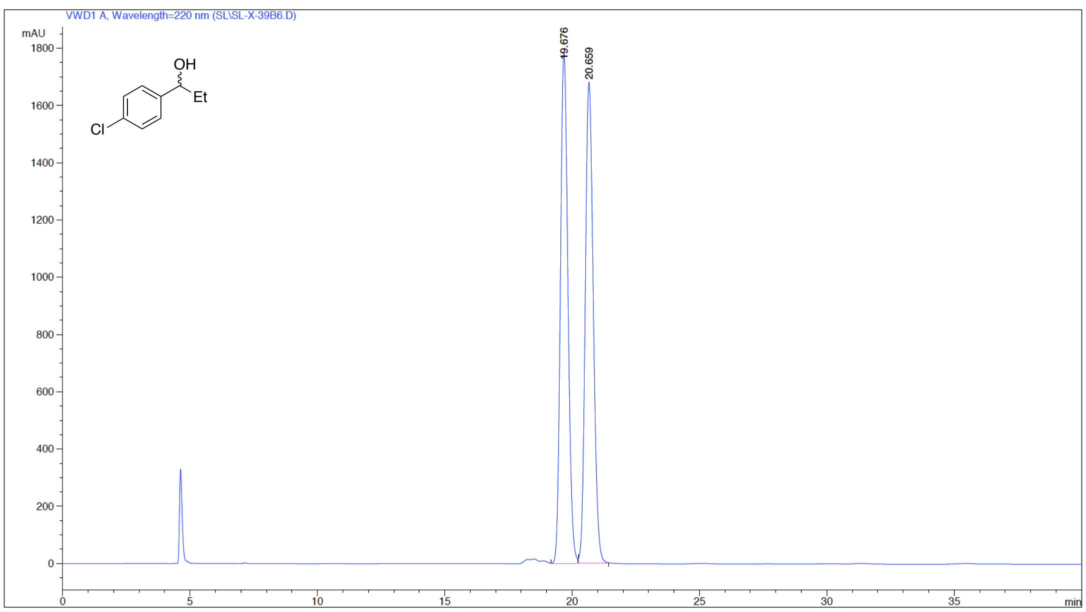
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.250	BV	0.8541	1.40473e5	2663.41309	48.9814
2	36.217	BBA	0.8927	1.46316e5	2633.77295	51.0186
Totals :				2.86789e5	5297.18604	

Racemate of **16e**



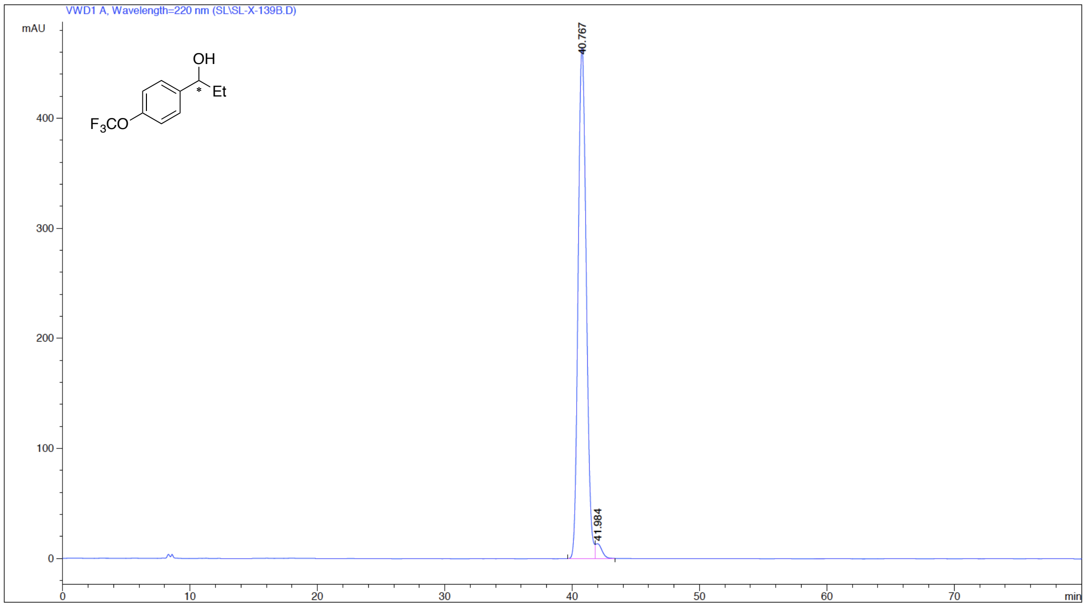
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.796	BBA	0.4038	6.52332e4	2570.90186	96.7260
2	20.817	BBA	0.3325	2208.04370	102.66486	3.2740
Totals :				6.74413e4	2673.56672	

93% *ee* of (*R*)-**16f**



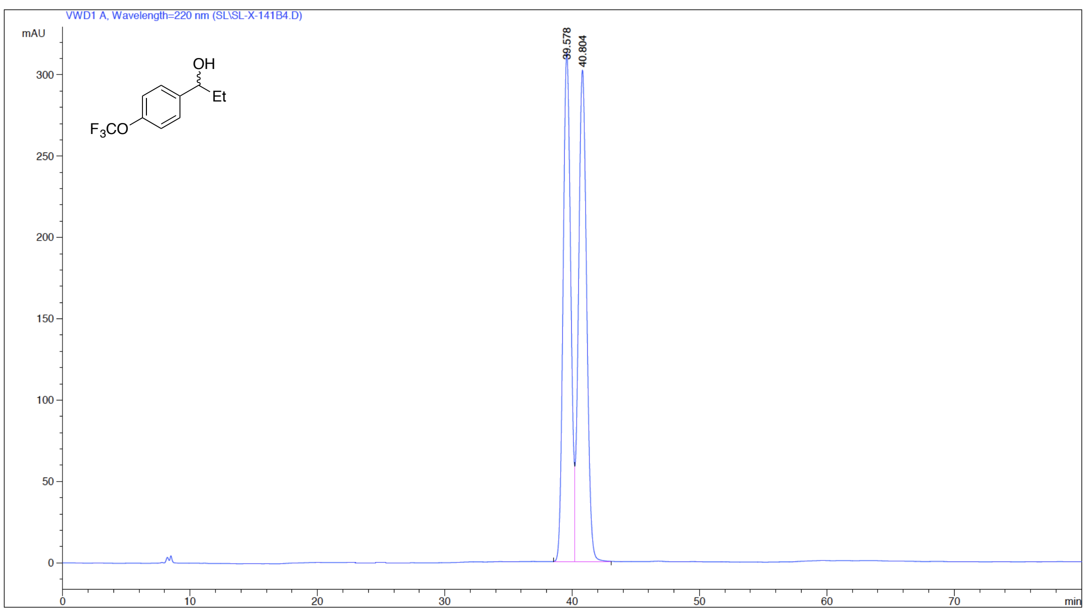
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.676	VBA	0.3248	3.67796e4	1785.06360	50.1113
2	20.659	BBA	0.3417	3.66162e4	1679.32312	49.8887
Totals :				7.33958e4	3464.38672	

Racemate of **16f**



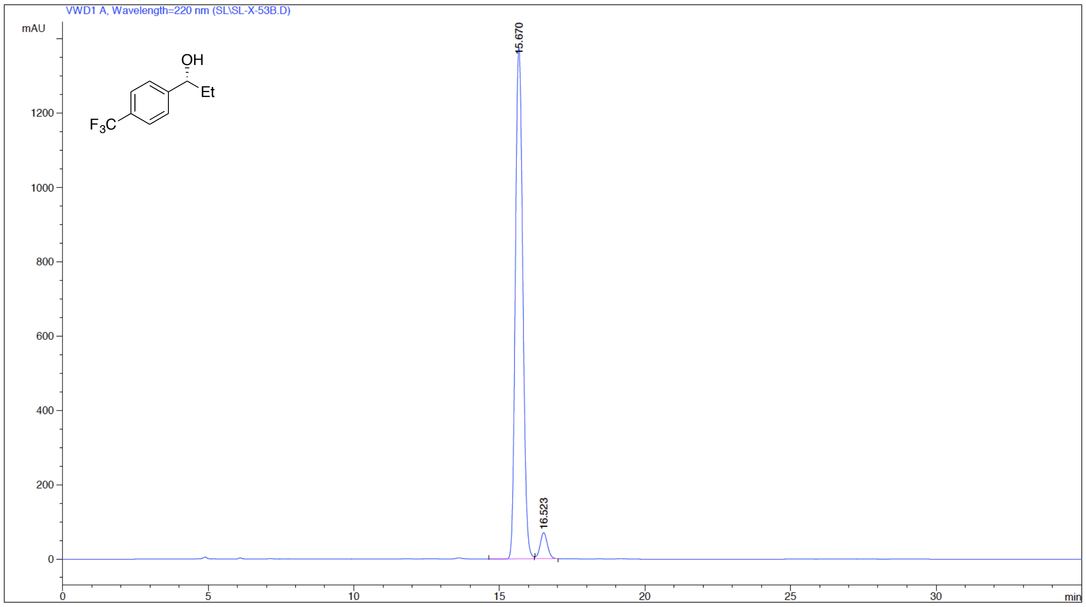
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	40.767	BBA	0.6964	2.06494e4	464.43008	97.7972
2	41.984	BBA	0.5182	465.10266	13.40983	2.2028
Totals :				2.11145e4	477.83992	

95% *ee* of (+)-**16g**



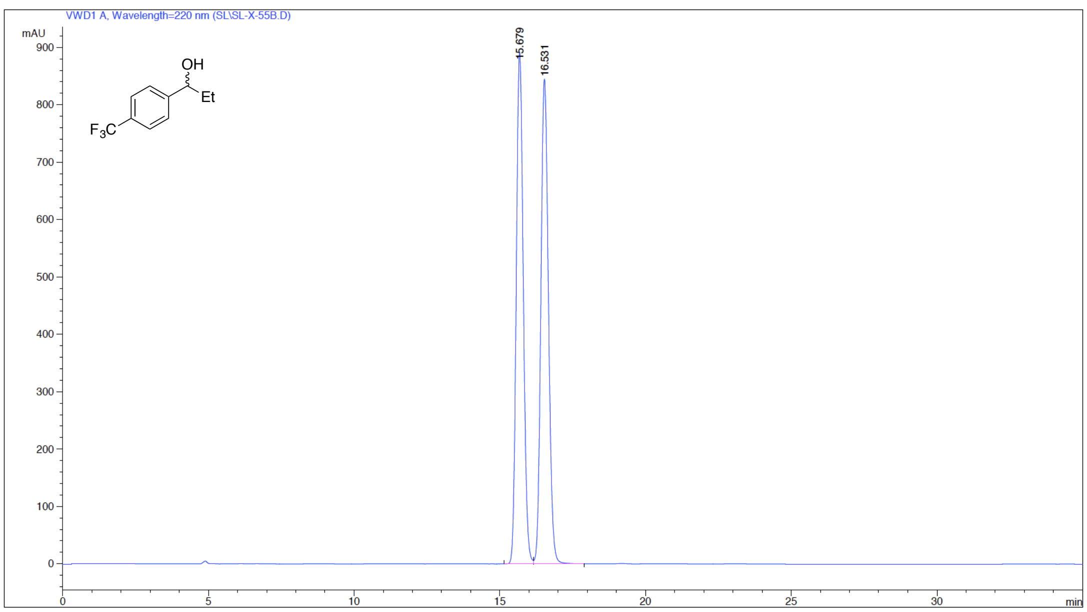
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	39.578	BV	0.6468	1.30508e4	312.90878	49.1930
2	40.804	VB	0.6805	1.34790e4	302.19992	50.8070
Totals :				2.65298e4	615.10870	

Racemate of **16g**



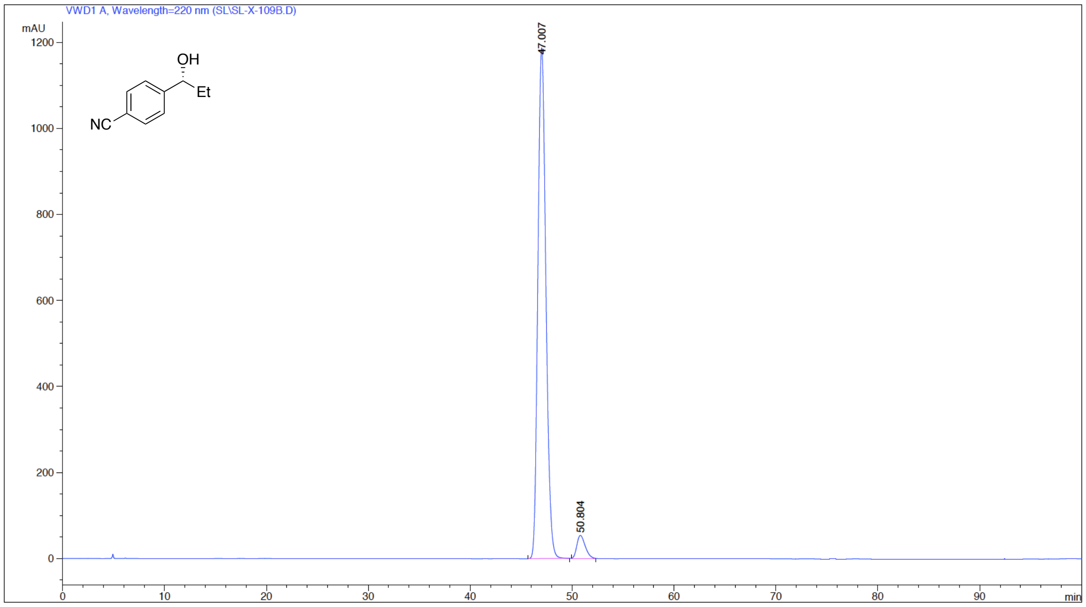
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.670	BBA	0.2825	2.43892e4	1376.07458	95.2488
2	16.523	BBA	0.2689	1216.58313	70.29205	4.7512
Totals :				2.56058e4	1446.36663	

90% *ee* of (*R*)-**16h**



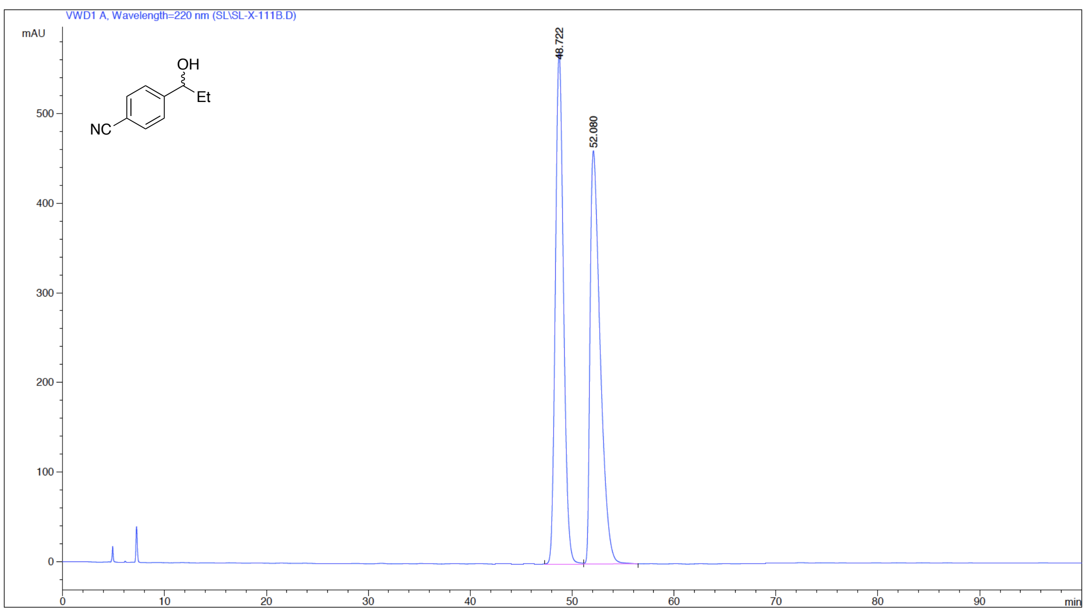
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.679	BV	0.2629	1.49572e4	890.62708	49.5915
2	16.531	VB	0.2828	1.52036e4	844.70703	50.4085
Totals :				3.01609e4	1735.33411	

Racemate of **16h**



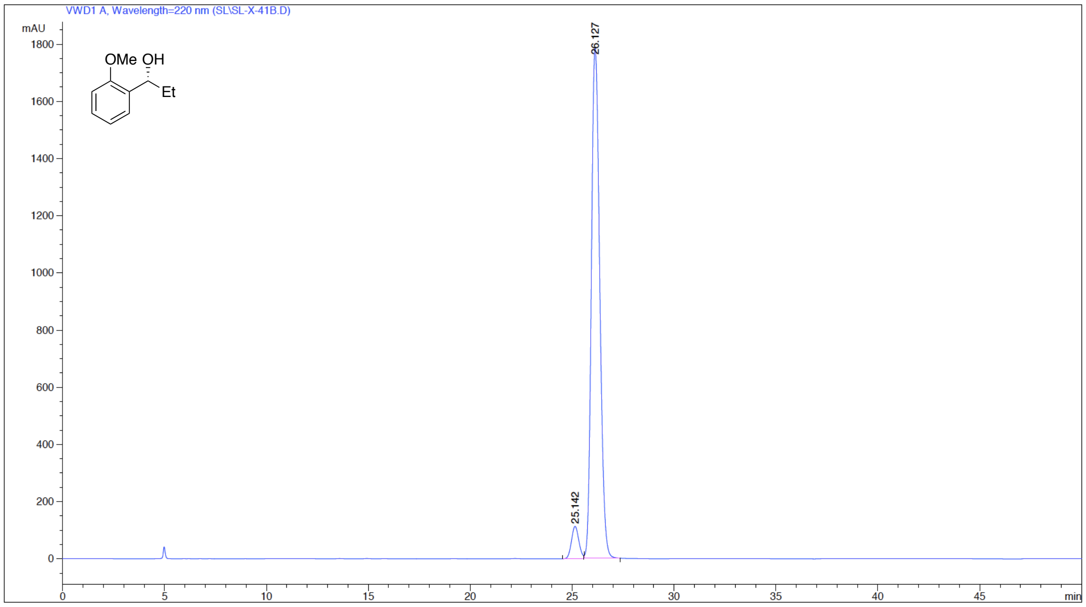
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	47.007	BBA	0.8466	6.45395e4	1187.61133	95.4910
2	50.804	BBA	0.8820	3047.47217	53.58073	4.5090
Totals :				6.75869e4	1241.19205	

91% *ee* of (*R*)-**16i**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	48.722	BV	0.8539	3.15226e4	570.85962	49.8190
2	52.080	VB	1.0531	3.17516e4	461.49625	50.1810
Totals :				6.32742e4	1032.35587	

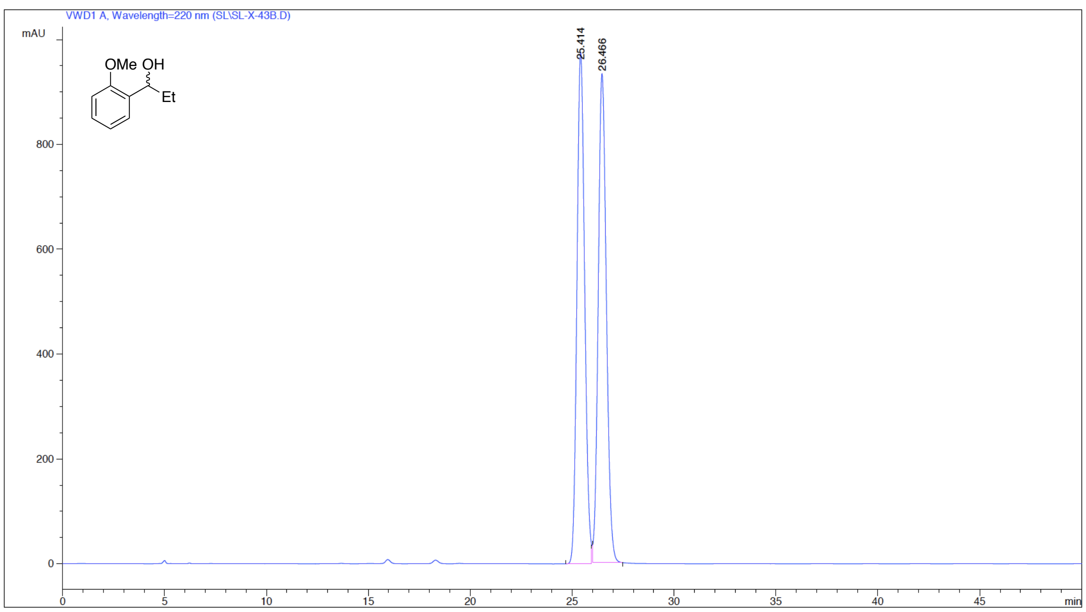
Racemate of **16i**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.142	BBA	0.3915	2854.02197	113.84367	5.3230
2	26.127	BBA	0.4481	5.07624e4	1785.73315	94.6770

Totals : 5.36164e4 1899.57683

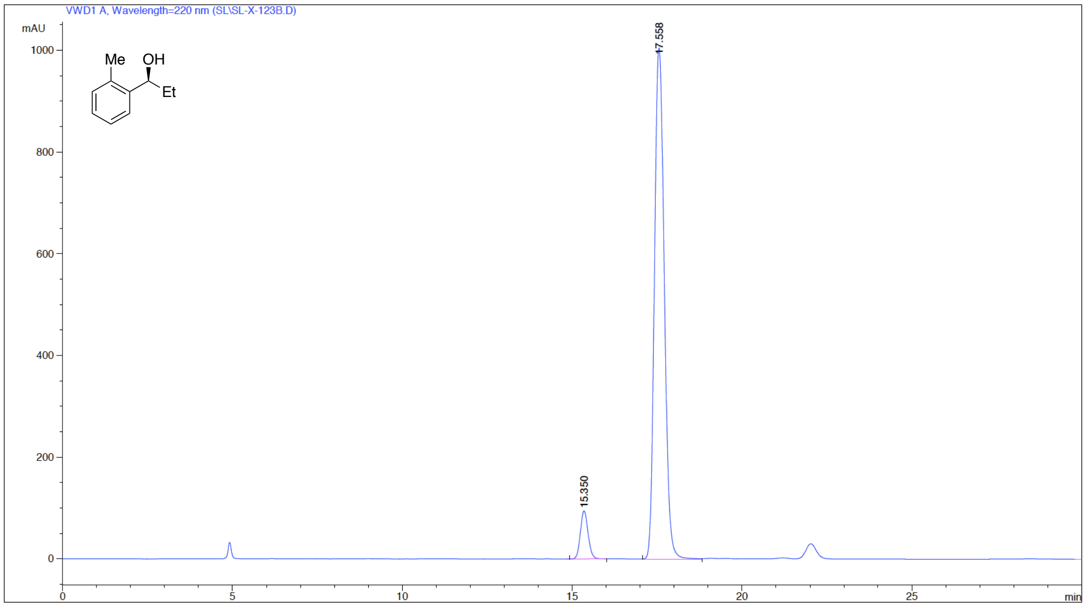
89% *ee* of (*R*)-**16j**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.414	BBA	0.4097	2.57277e4	975.16925	49.8675
2	26.466	BBA	0.4311	2.58645e4	933.07336	50.1325

Totals : 5.15922e4 1908.24261

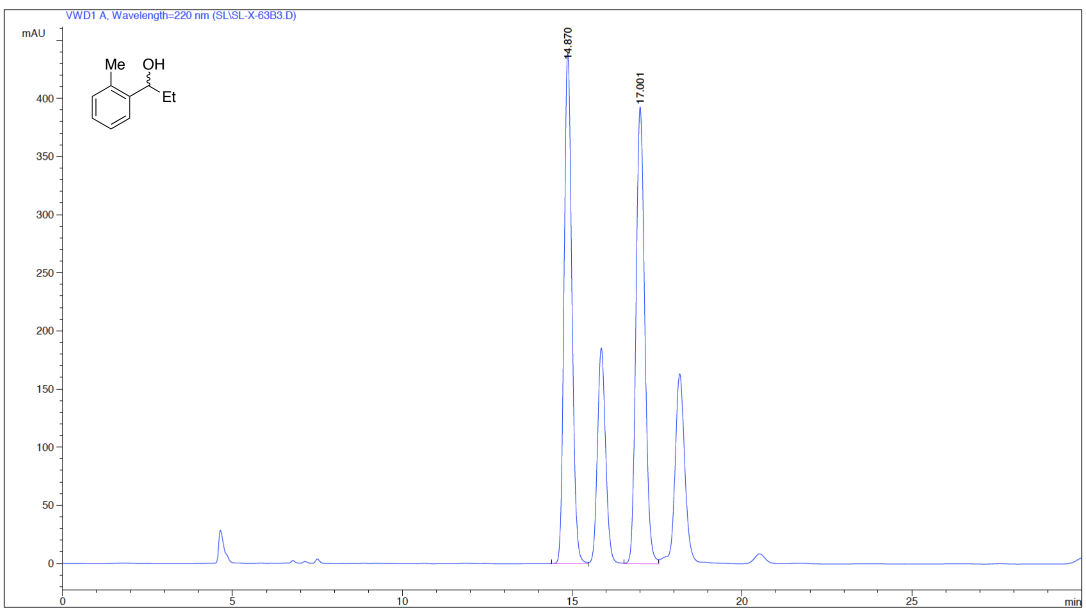
Racemate of **16j**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.350	BB	0.2445	1485.57239	94.51170	6.8691
2	17.558	BV	0.3183	2.01414e4	1005.02130	93.1309

Totals : 2.16269e4 1099.53300

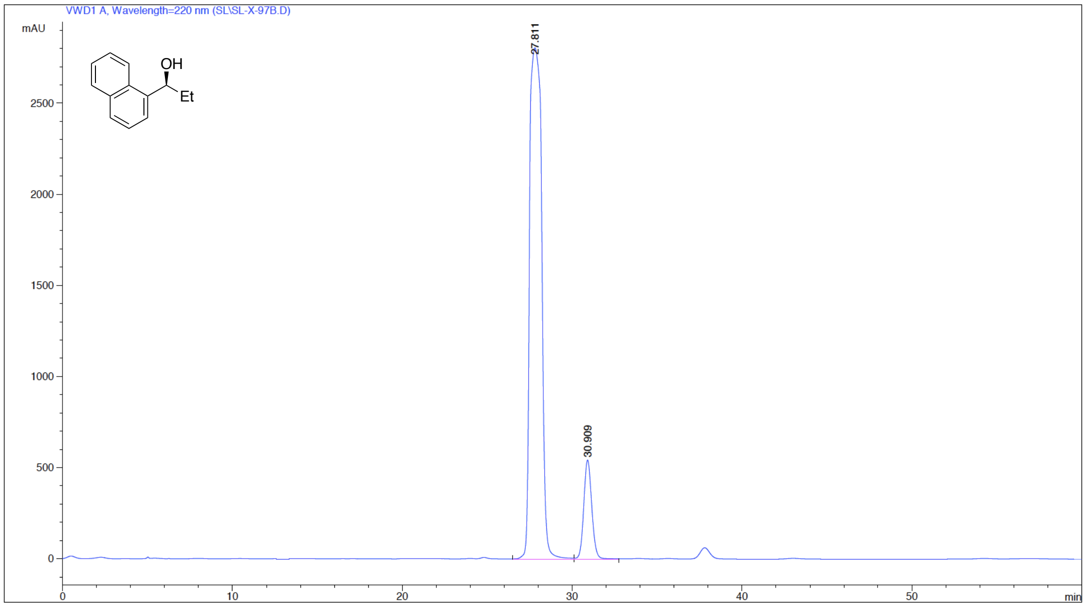
86% *ee* of (*S*)-**16k**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.870	BV	0.2503	7011.30518	439.20358	49.7790
2	17.001	VV	0.2799	7073.54688	392.90912	50.2210

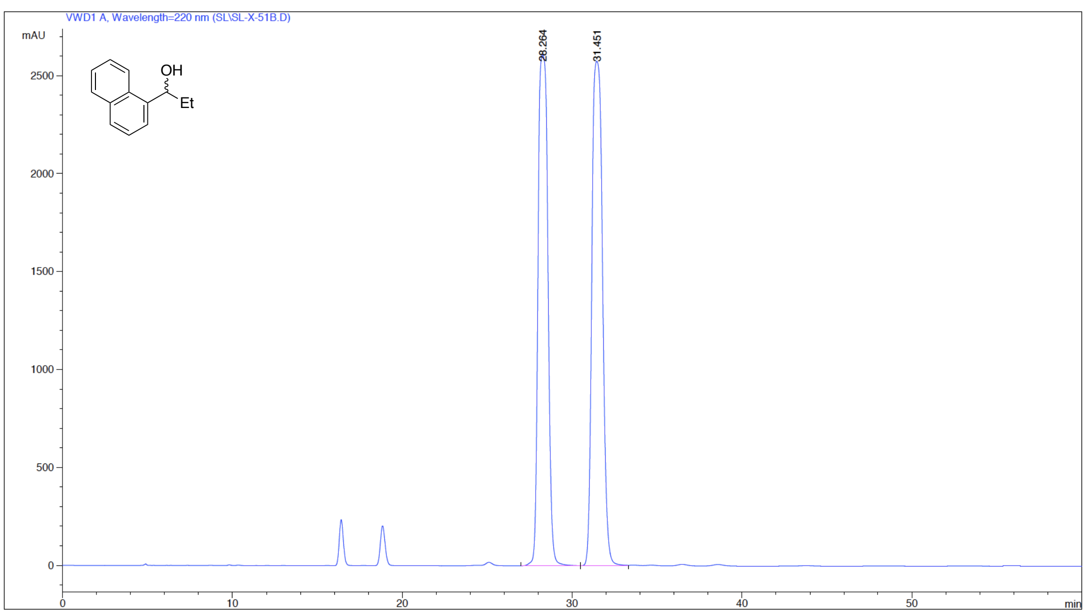
Totals : 1.40849e4 832.11270

Racemate of **16k**



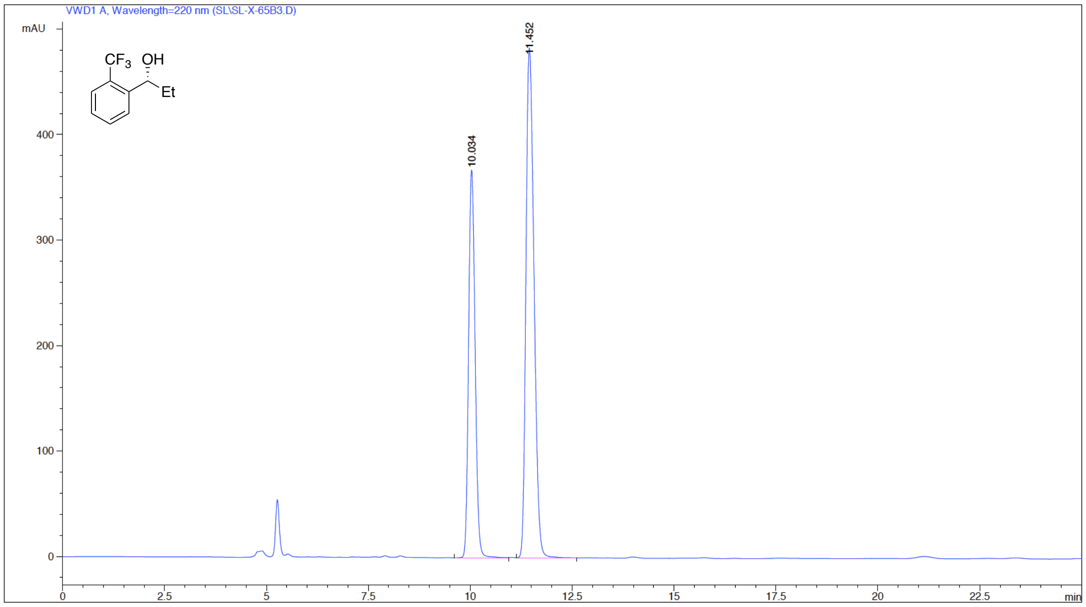
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.811	BV	0.7899	1.36671e5	2804.41968	88.5355
2	30.909	VB	0.5027	1.76976e4	542.83307	11.4645
Totals :				1.54369e5	3347.25275	

77% *ee* of (*S*)-**16l**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.264	BV	0.6386	1.04364e5	2608.40674	48.2717
2	31.451	VV	0.6930	1.11838e5	2575.46240	51.7283
Totals :				2.16202e5	5183.86914	

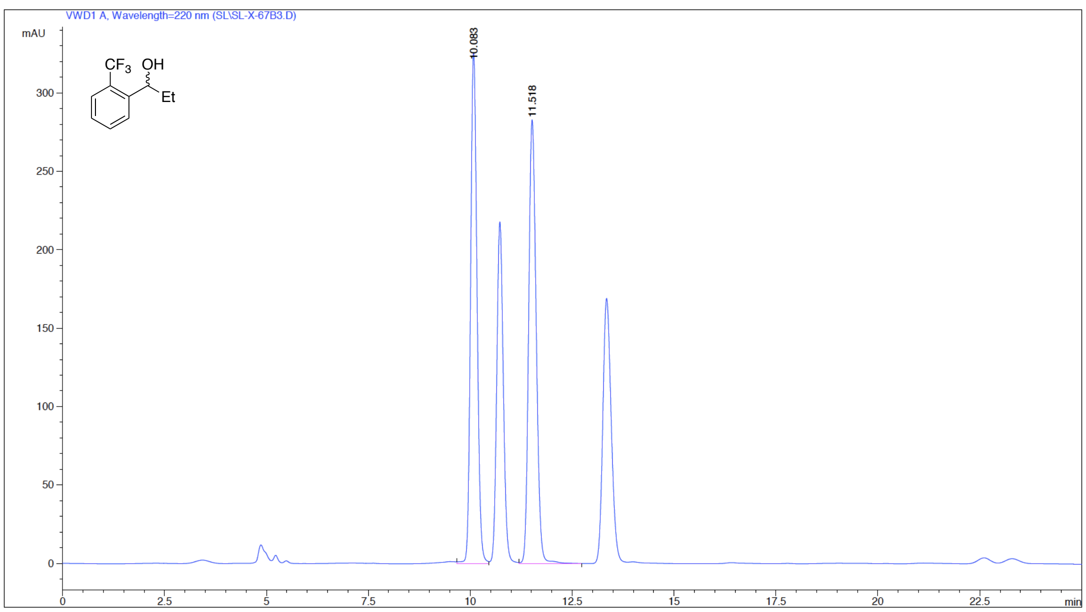
Racemate of **16l**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.034	VB	0.1760	4077.49658	367.72748	37.9964
2	11.452	VB	0.2190	6653.76660	482.85358	62.0036

Totals : 1.07313e4 850.58105

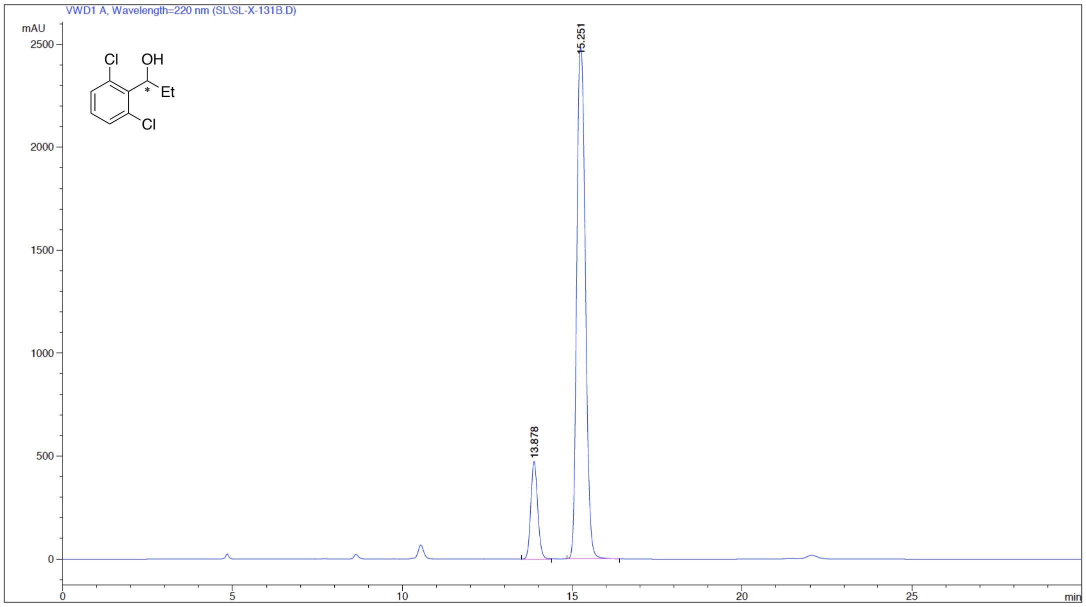
24% *ee* of (*R*)-**16m**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.083	VV	0.1746	3574.56836	325.81723	49.5142
2	11.518	VB	0.2026	3644.71411	283.06573	50.4858

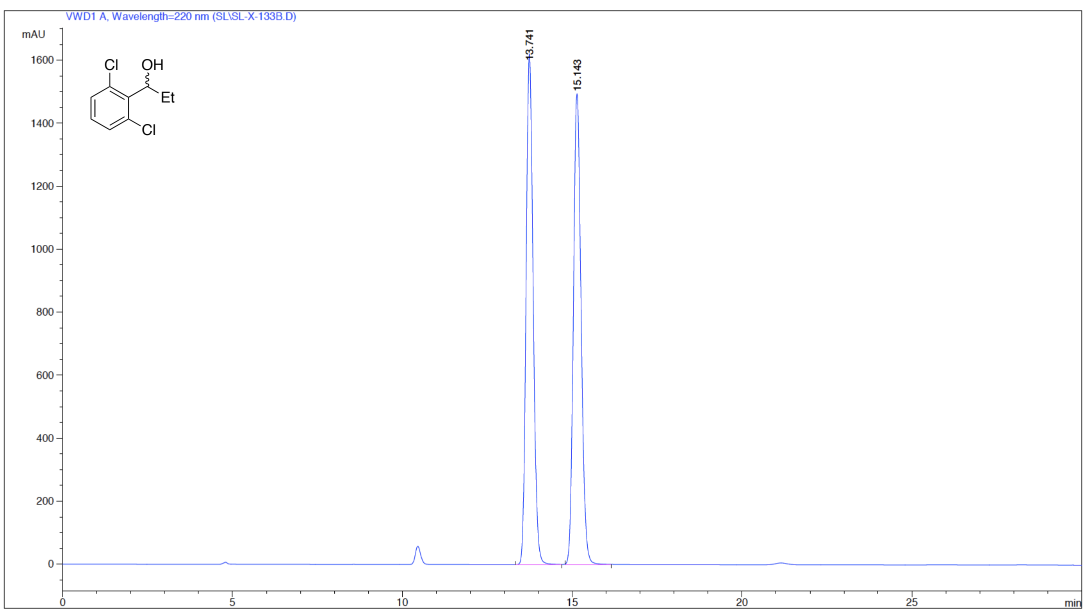
Totals : 7219.28247 608.88297

Racemate of **16m**



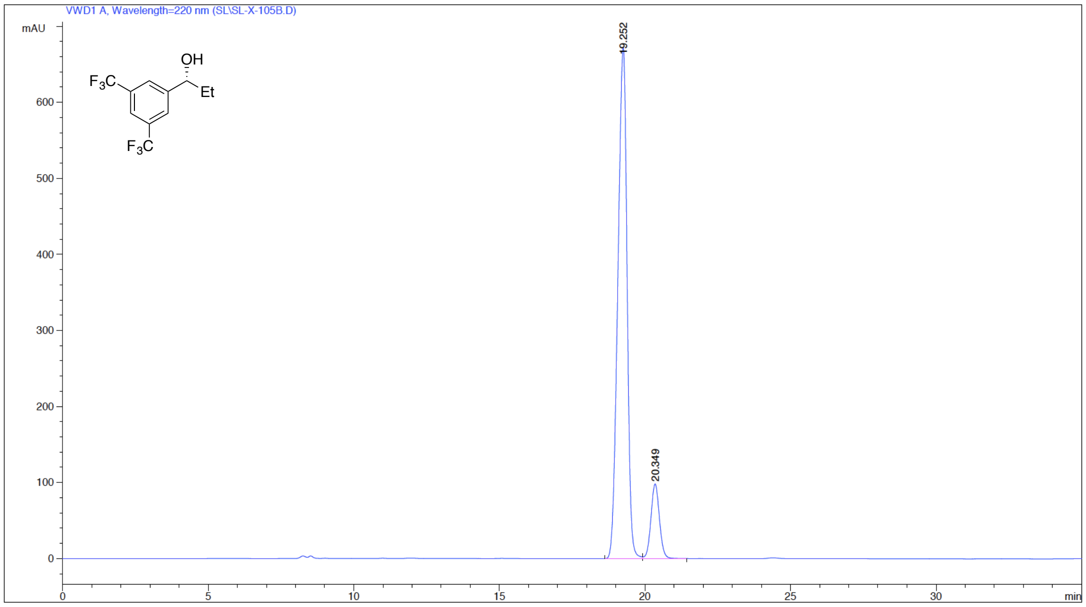
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.878	BBA	0.2164	6659.75049	473.86172	13.1805
2	15.251	BBA	0.2819	4.38674e4	2481.84131	86.8195
Totals :				5.05272e4	2955.70303	

74% *ee* of (–)-**16n**



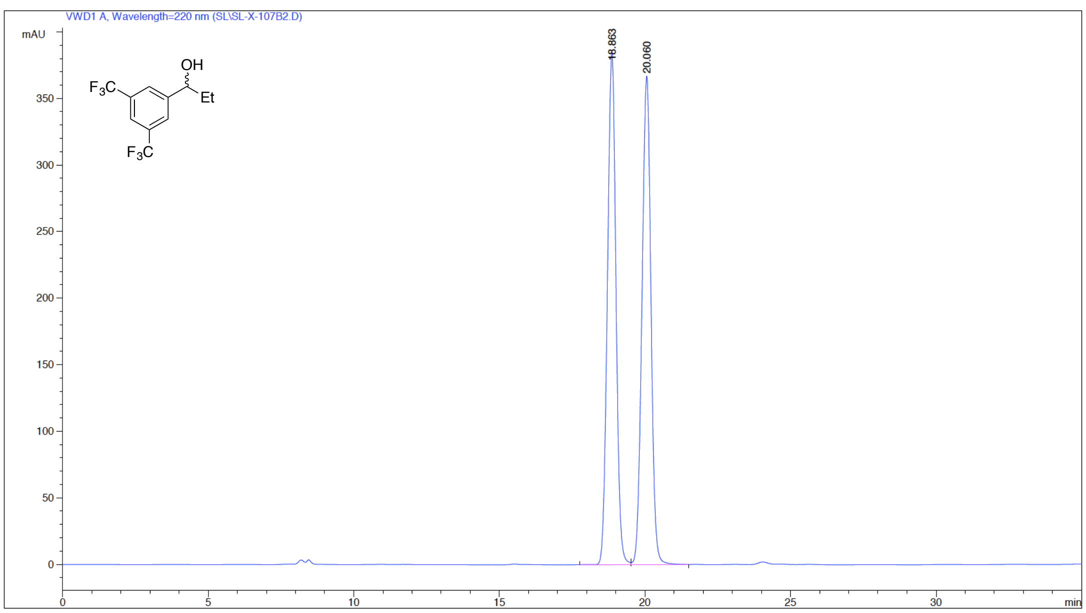
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.741	BV	0.2263	2.33626e4	1621.54492	49.8702
2	15.143	BBA	0.2445	2.34842e4	1494.04480	50.1298
Totals :				4.68468e4	3115.58972	

Racemate of **16n**



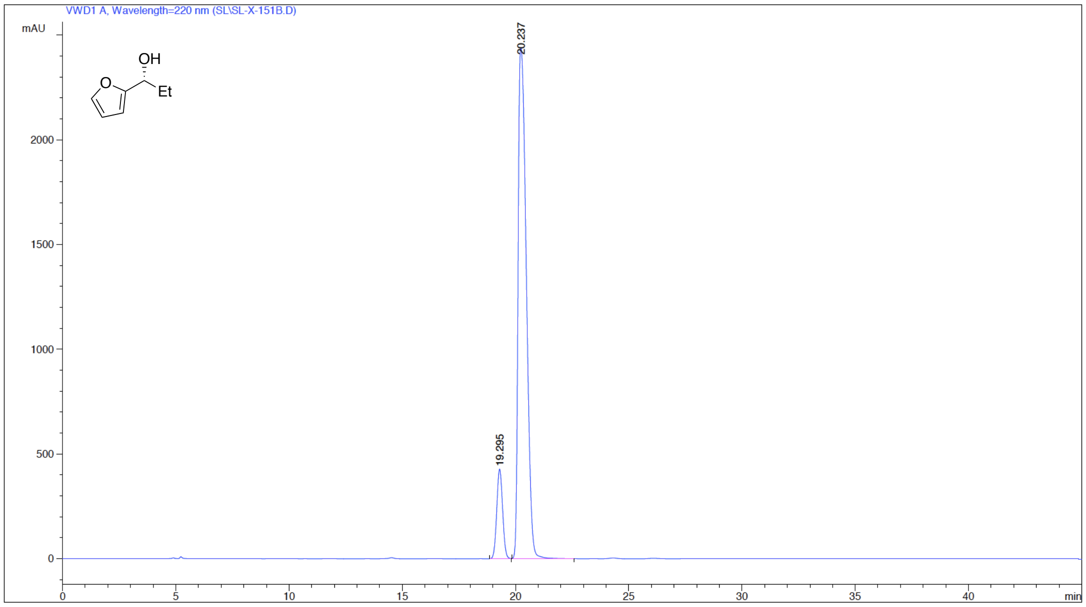
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.252	BV	0.3400	1.47146e4	671.80151	88.0290
2	20.349	VB	0.3163	2001.01392	98.23915	11.9710
Totals :				1.67156e4	770.04066	

76% *ee* of (*R*)-**16o**



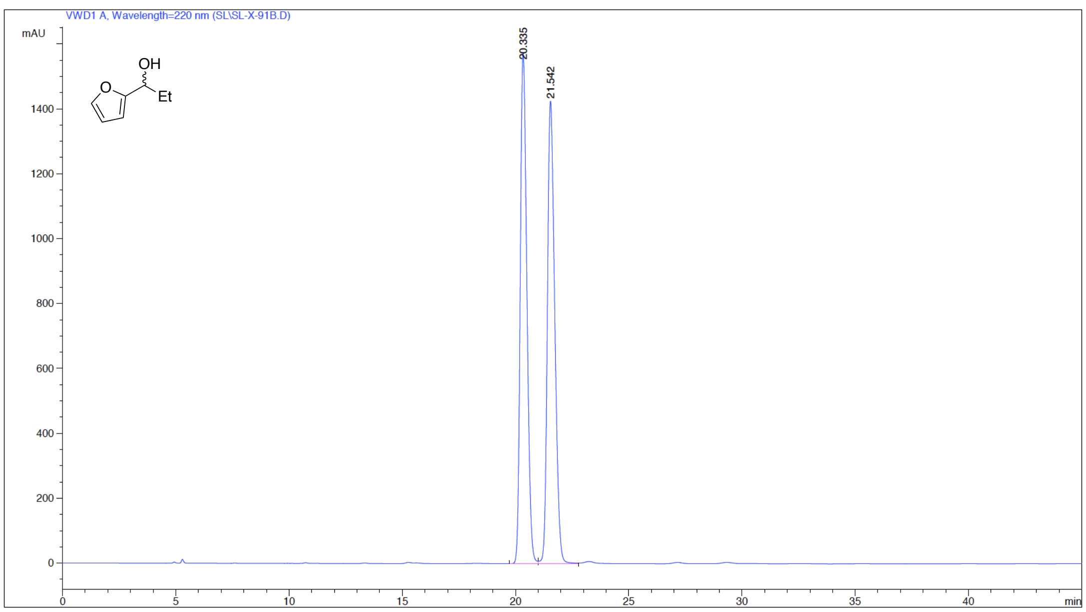
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.863	BV	0.3172	7849.87500	383.82141	49.9580
2	20.060	VB	0.3345	7863.06299	366.87363	50.0420
Totals :				1.57129e4	750.69504	

Racemate of **16o**



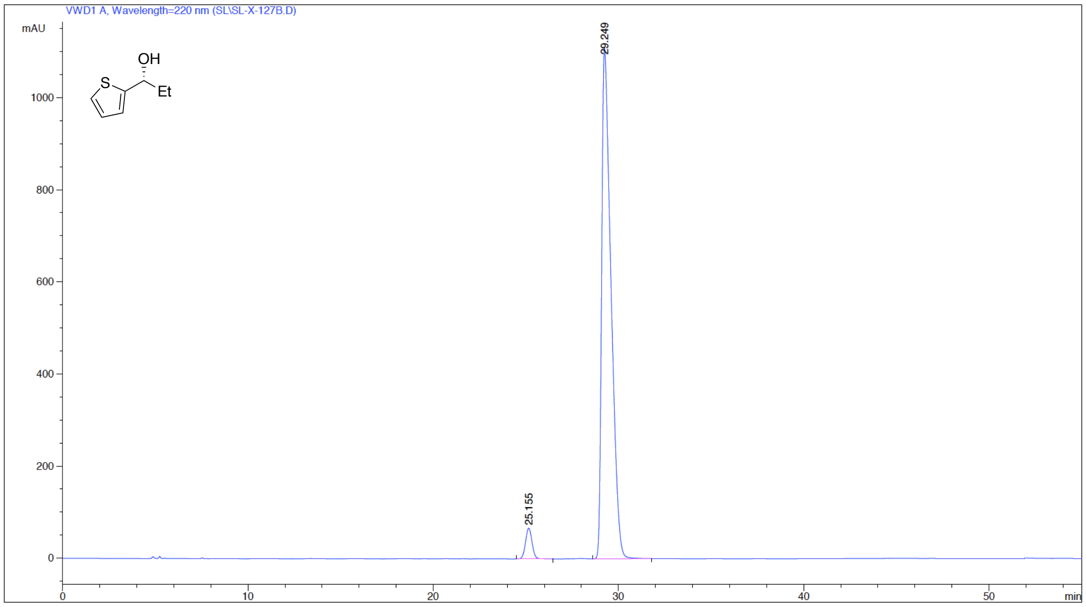
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.295	BBA	0.2796	7706.13525	428.68533	11.2086
2	20.237	BBA	0.3968	6.10460e4	2439.50171	88.7914
Totals :				6.87521e4	2868.18704	

78% *ee* of (*R*)-**16p**



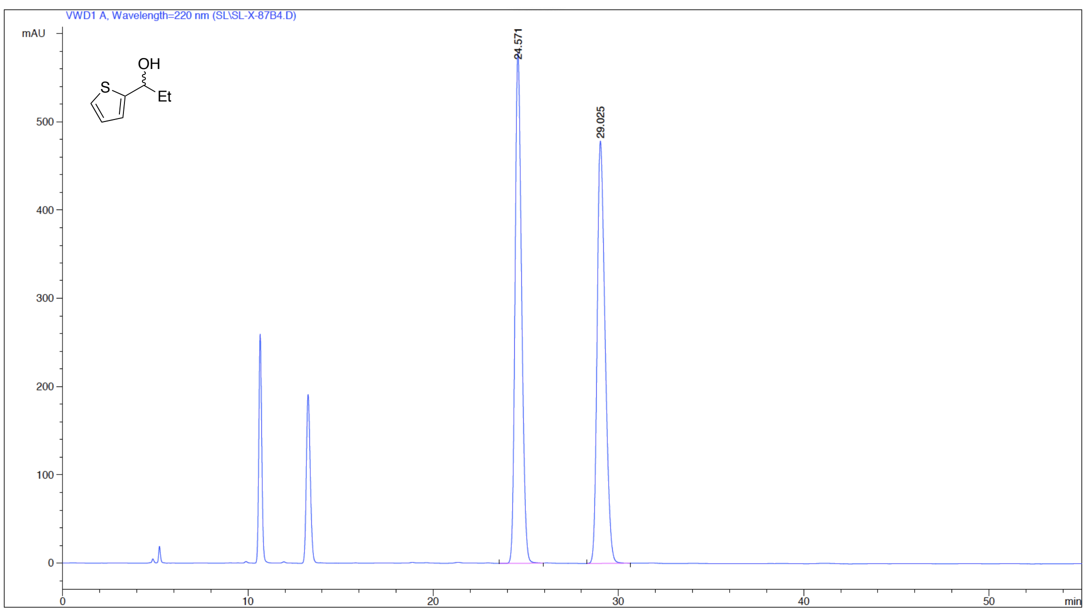
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.335	BV	0.3177	3.18766e4	1574.70471	49.7499
2	21.542	VV	0.3508	3.21971e4	1425.90894	50.2501
Totals :				6.40737e4	3000.61365	

Racemate of **16p**



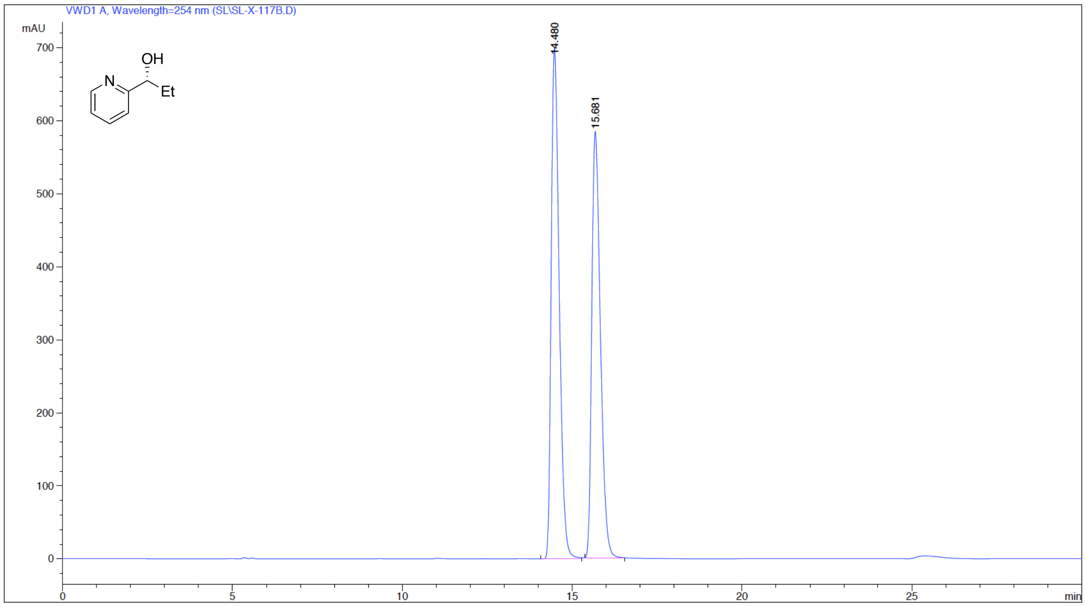
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	25.155	BB	0.3770	1624.93884	66.79941	4.0475
2	29.249	VB	0.5214	3.85215e4	1109.84888	95.9525
Totals :				4.01465e4	1176.64828	

92% *ee* of (*R*)-**16q**



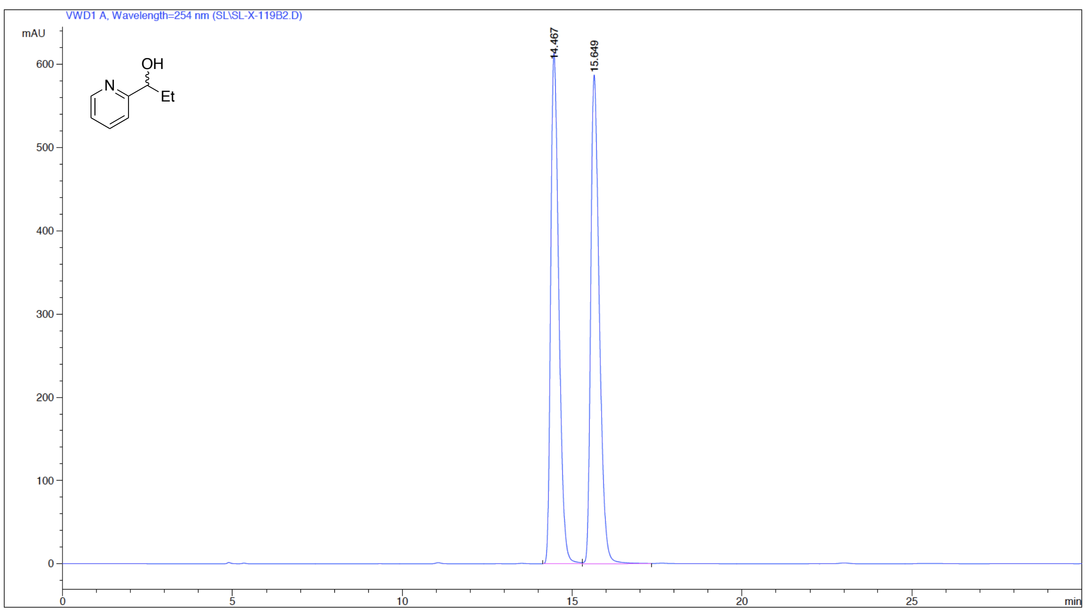
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.571	VB	0.3830	1.42220e4	578.30841	49.8977
2	29.025	BB	0.4590	1.42803e4	478.22913	50.1023
Totals :				2.85022e4	1056.53754	

Racemate of **16q**



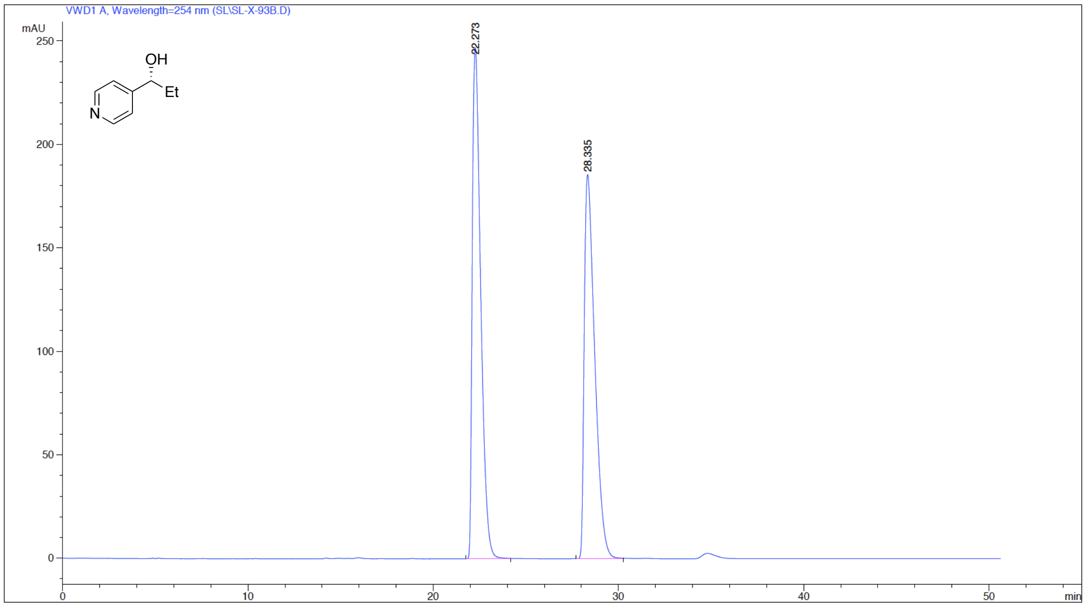
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.480	VBA	0.2520	1.14407e4	699.53473	52.6847
2	15.681	BBA	0.2722	1.02747e4	583.97156	47.3153
Totals :				2.17153e4	1283.50629	

5% *ee* of (*R*)-**16r**



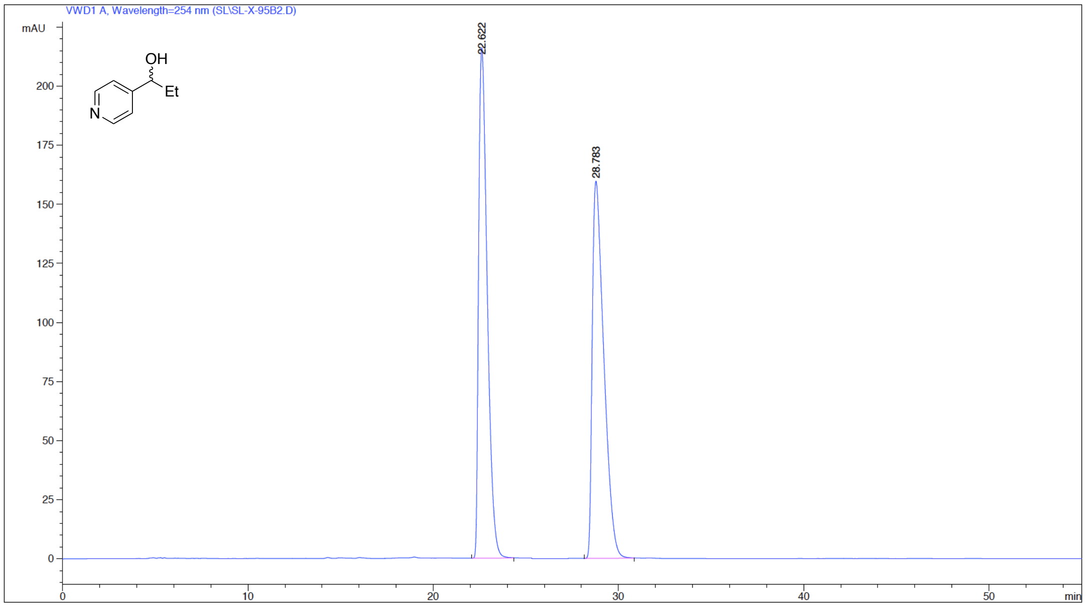
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.467	BV	0.2568	1.01447e4	613.94666	49.6283
2	15.649	VB	0.2687	1.02967e4	587.03424	50.3717
Totals :				2.04414e4	1200.98090	

Racemate of **16r**



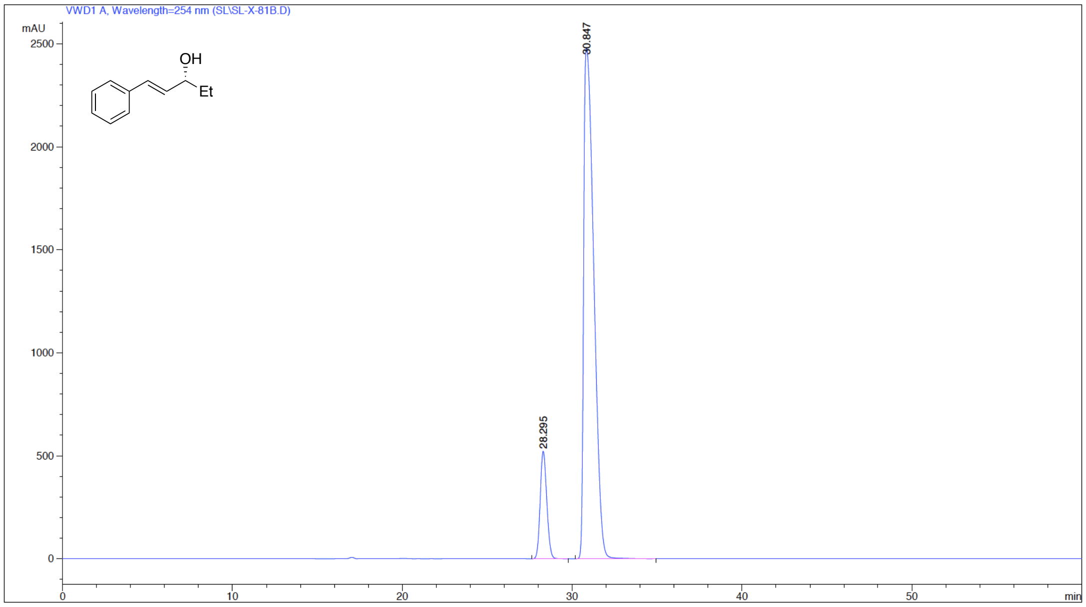
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.273	BB	0.4870	7782.95850	246.99620	51.6420
2	28.335	BB	0.5978	7288.01855	185.63200	48.3580
Totals :				1.50710e4	432.62820	

3% *ee* of (*R*)-**16s**



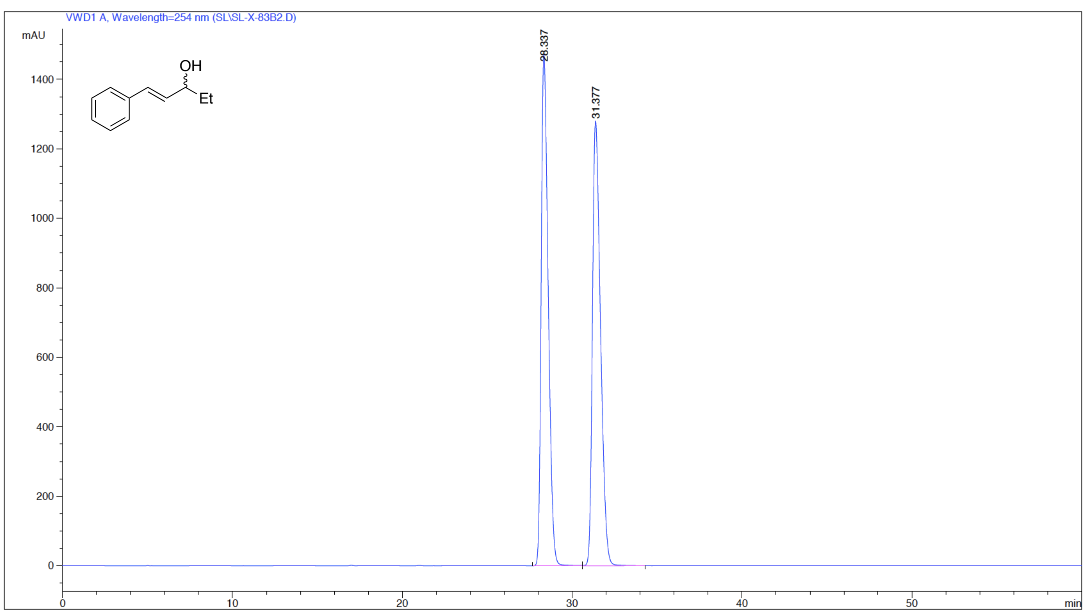
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.622	BB	0.5009	6953.20166	215.95317	50.1434
2	28.783	BB	0.6626	6913.43652	159.60739	49.8566
Totals :				1.38666e4	375.56056	

Racemate of **16s**



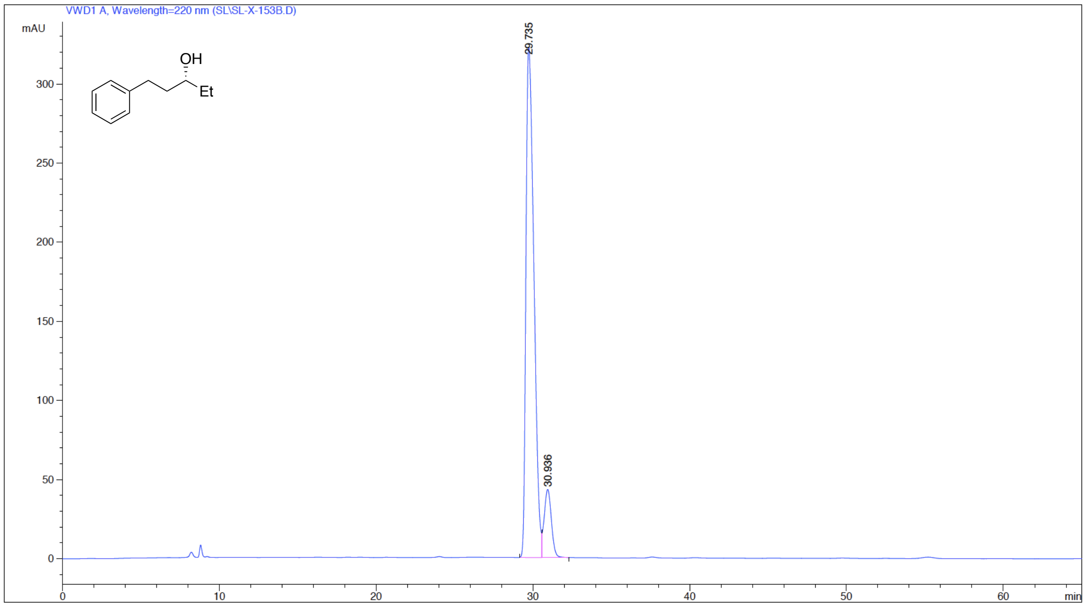
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.295	BB	0.4183	1.40412e4	522.51154	12.0901
2	30.847	BB	0.6491	1.02097e5	2480.24170	87.9099
Totals :				1.16138e5	3002.75323	

76% *ee* of (*R*)-**16t**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.337	BV	0.4417	4.21104e4	1471.16162	49.8520
2	31.377	VB	0.5055	4.23604e4	1280.08435	50.1480
Totals :				8.44708e4	2751.24597	

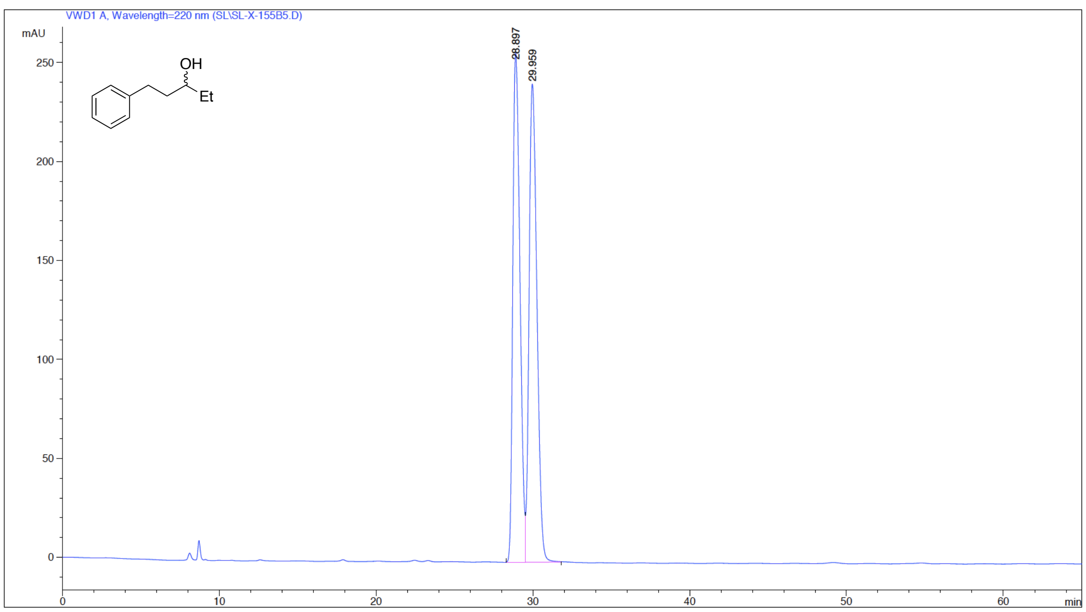
Racemate of **16t**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.735	BV	0.5491	1.12997e4	322.09839	89.0331
2	30.936	VB	0.4963	1391.87439	43.08772	10.9669

Totals : 1.26916e4 365.18610

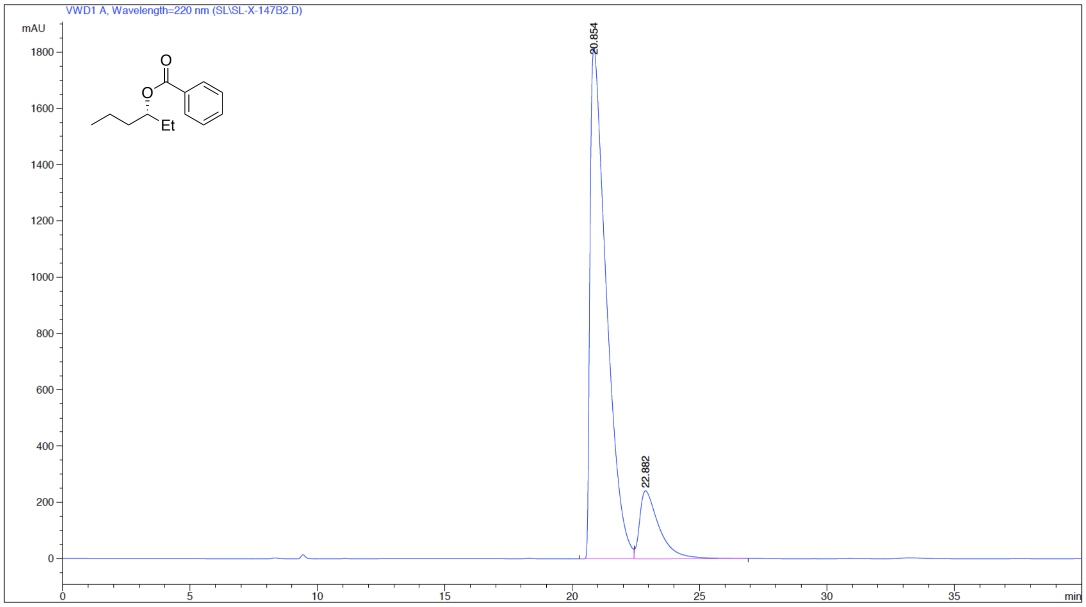
78% *ee* of (*R*)-**16u**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.897	BV	0.5021	8121.48730	257.34369	49.0856
2	29.959	VB	0.5553	8424.07617	241.58046	50.9144

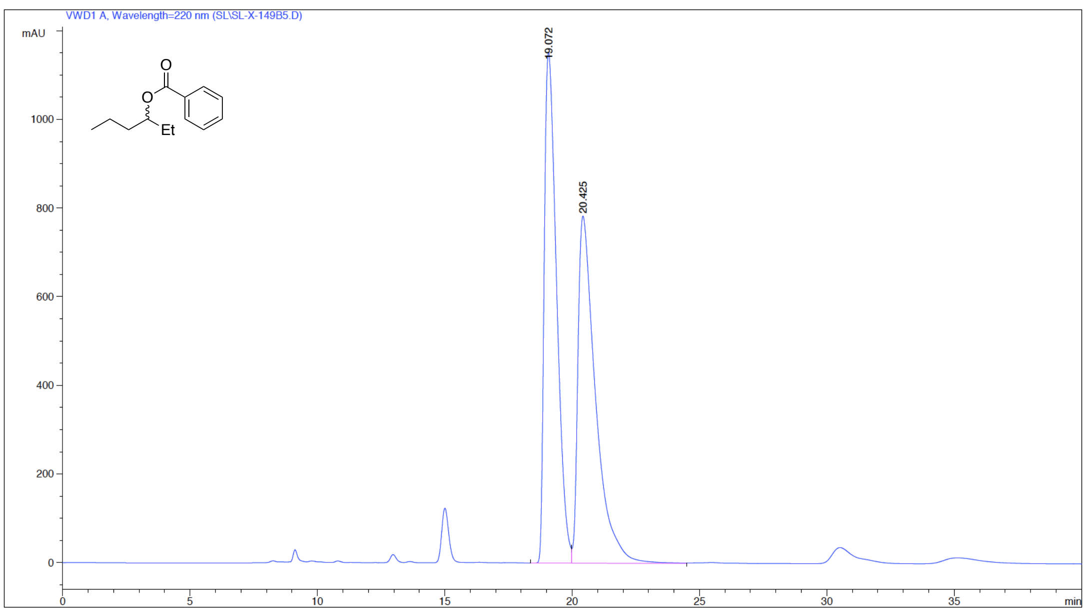
Totals : 1.65456e4 498.92415

Racemate of **16u**



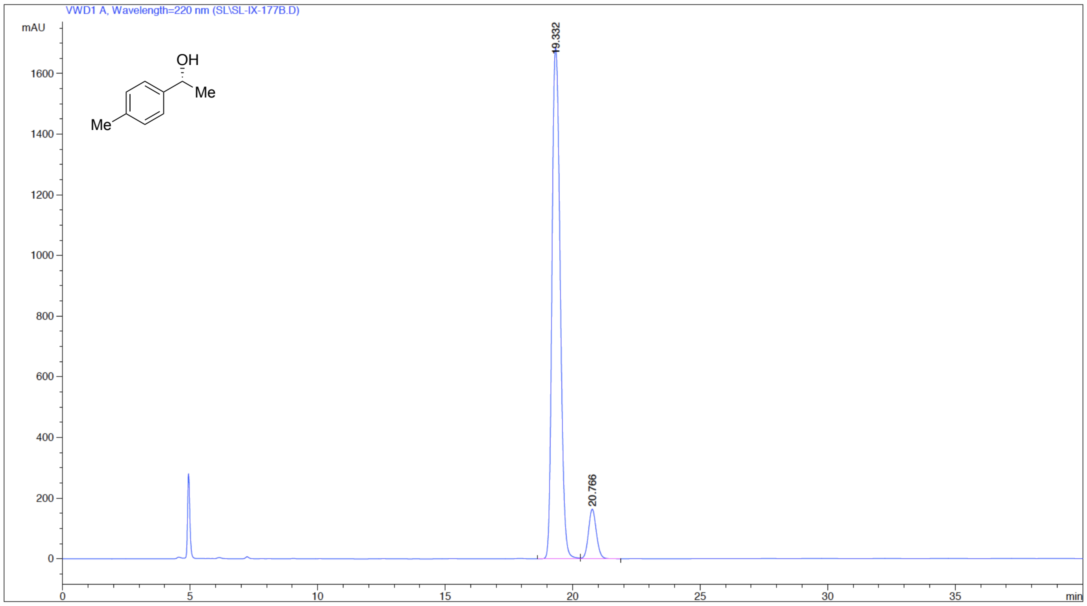
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.854	VV	0.6496	8.07439e4	1816.45264	86.3348
2	22.882	VB	0.7604	1.27802e4	241.38751	13.6652
Totals :				9.35241e4	2057.84015	

73% *ee* of (*R*)-**16v**



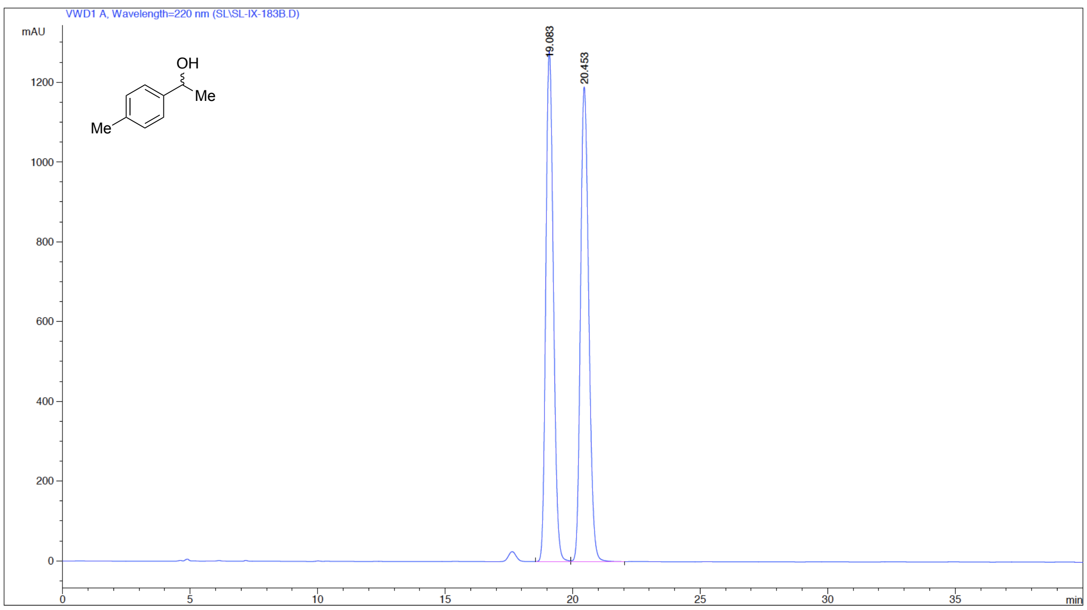
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.072	VV	0.5270	3.88016e4	1151.65271	50.7155
2	20.425	VV	0.7043	3.77068e4	783.30432	49.2845
Totals :				7.65084e4	1934.95703	

Racemate of **16v**



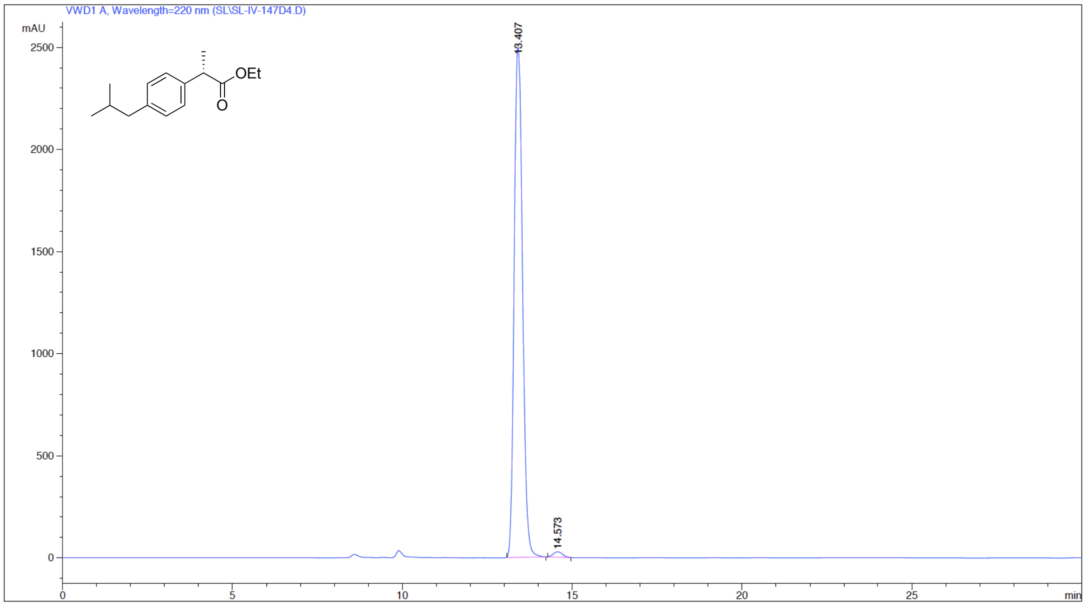
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.332	VV	0.3519	3.73826e4	1685.69824	91.4103
2	20.766	VB	0.3350	3512.78198	163.54077	8.5897
Totals :				4.08954e4	1849.23901	

83% *ee* of (*R*)-**16w**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.083	BV	0.3253	2.64211e4	1279.96167	49.6701
2	20.453	VB	0.3527	2.67721e4	1190.29553	50.3299
Totals :				5.31932e4	2470.25720	

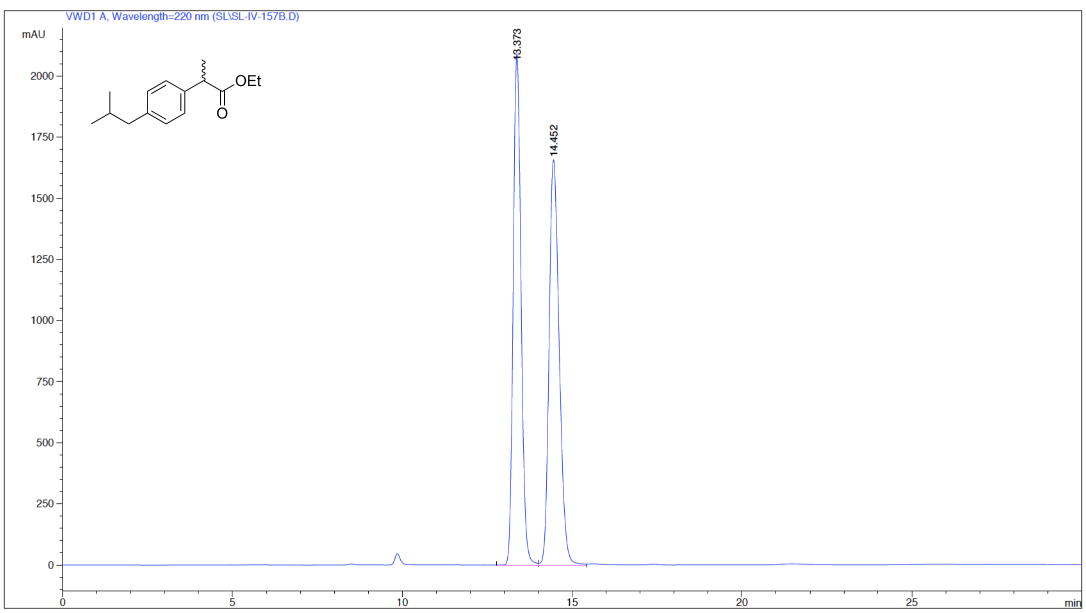
Racemate of **16w**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.407	BBA	0.2699	4.27737e4	2495.44043	98.8726
2	14.573	BBA	0.2893	487.71213	26.63586	1.1274

Totals : 4.32614e4 2522.07629

98% *ee* of (*S*)-**18**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.373	VV	0.2507	3.34521e4	2090.79541	49.3669
2	14.452	VV	0.3201	3.43101e4	1657.38879	50.6331

Totals : 6.77622e4 3748.18420

Racemate of **18**

Crystallographic data

X-ray structure and crystal data for (*R*)-9

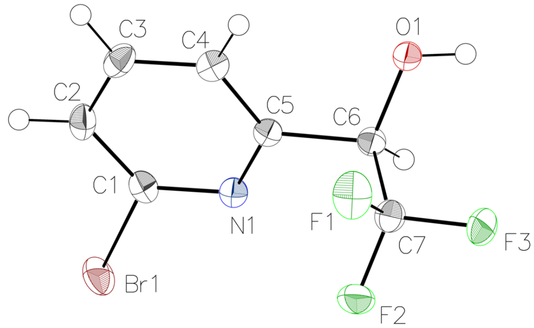


Table S7 Crystal data and structure refinement for (*R*)-**9**

Identification code	(*R*)-**9**
Empirical formula	$C_7H_5BrF_3NO$
Formula weight	256.03
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.2520(6)
b/Å	8.5655(8)
c/Å	13.9821(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	868.53(13)
Z	4
ρ_{calc}g/cm^3	1.958
μ/mm^{-1}	6.634
F(000)	496.0
Crystal size/mm^3	0.33 × 0.14 × 0.12
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	12.118 to 139.916
Index ranges	-8 ≤ h ≤ 8, -9 ≤ k ≤ 10, -17 ≤ l ≤ 17
Reflections collected	22485
Independent reflections	1620 [R_{int} = 0.0322, R_{sigma} = 0.0122]
Data/restraints/parameters	1620/0/122
Goodness-of-fit on F^2	1.173
Final R indexes [I>=2σ (I)]	R_1 = 0.0172, wR_2 = 0.0449
Final R indexes [all data]	R_1 = 0.0172, wR_2 = 0.0449
Largest diff. peak/hole / e Å^{-3}	0.43/-0.38
Flack parameter	-0.016(5)

Table S8 Fractional atomic coordinates (×10^{4}) and equivalent isotropic displacement parameters (Å^{2}×10^{3}) for (*R*)-**9**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor

Atom	*x*	*y*	*z*	U(eq)
Br1	2824.0(4)	2894.3(3)	5676.7(2)	28.16(11)
F3	2503(2)	9434(2)	8444.9(11)	30.3(4)
F2	1187(3)	7477(2)	7753.4(13)	34.2(4)
F1	1297(3)	9710(2)	7050.4(14)	35.0(4)
O1	5153(3)	9618(2)	6995.6(14)	22.6(4)
N1	3529(3)	5869(3)	6302.8(15)	17.4(4)
C1	3292(3)	5060(3)	5506.4(19)	18.9(5)
C2	3365(4)	5675(3)	4591.3(19)	22.0(6)
C5	3812(3)	7413(3)	6218.0(18)	15.9(5)
C6	4105(3)	8271(3)	7155.1(19)	17.3(5)
C7	2257(4)	8722(3)	7597.5(19)	22.9(5)
C3	3659(4)	7271(4)	4519.7(18)	23.6(6)
C4	3871(4)	8160(3)	5338.5(19)	20.3(5)

Table S9 Anisotropic displacement parameters (Å^{2}×10^{3}) for (*R*)-**9**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br1	33.93(17)	19.13(15)	31.43(16)	-6.66(11)	-2.78(12)	-4.31(12)
F3	31.3(9)	35.7(9)	24.0(8)	-12.8(7)	6.3(7)	-2.0(7)
F2	31.9(9)	35.8(11)	34.9(9)	-10.7(7)	14.2(8)	-13.5(8)
F1	30.9(8)	36.8(10)	37.3(10)	-6.1(8)	-5.2(8)	13.9(8)
O1	29.5(10)	21.1(9)	17.2(10)	-0.6(8)	1.5(8)	-7.5(8)
N1	16.2(10)	18.3(11)	17.8(10)	-0.8(8)	-0.8(9)	1.9(9)
C1	15.4(11)	17.7(12)	23.6(13)	-3.7(10)	-1.9(9)	2.3(9)
C2	18.3(13)	28.9(14)	18.7(12)	-6.4(11)	-3.2(9)	3.7(10)
C5	12.8(11)	17.2(12)	17.8(12)	-0.1(9)	0.1(9)	2.8(9)
C6	20.1(12)	14.5(12)	17.4(12)	0.6(10)	-0.3(10)	-0.2(9)
C7	24.8(13)	21.7(12)	22.3(12)	-4.7(10)	3.4(11)	-0.9(12)
C3	23.2(12)	31.3(14)	16.3(12)	3.6(11)	-0.7(10)	4.1(12)
C4	19.4(12)	20.3(14)	21.2(12)	1.7(10)	0.4(9)	2.9(10)

Table S10 Bond lengths for (*R*)-**9**

Atom	Atom	Length (Å)
Br1	C1	1.901(3)
F3	C7	1.345(3)
F2	C7	1.337(3)
F1	C7	1.337(4)
O1	C6	1.399(3)
N1	C1	1.323(3)
N1	C5	1.344(3)

Atom	Atom	Length(Å)
C1	C2	1.385(4)
C2	C3	1.387(4)
C5	C6	1.517(3)
C5	C4	1.387(4)
C6	C7	1.526(4)
C3	C4	1.384(4)

Table S11 Bond angles for (*R*)-**9**

Atom	Atom	Atom	Angle(˚)
C1	N1	C5	117.5(2)
N1	C1	Br1	115.43(19)
N1	C1	C2	125.0(2)
C2	C1	Br1	119.58(19)
C1	C2	C3	116.6(2)
N1	C5	C6	114.9(2)
N1	C5	C4	122.5(2)
C4	C5	C6	122.6(2)
O1	C6	C5	109.7(2)
O1	C6	C7	109.5(2)
C5	C6	C7	110.5(2)
F3	C7	C6	110.8(2)
F2	C7	F3	107.2(2)
F2	C7	C6	112.0(2)
F1	C7	F3	106.6(2)
F1	C7	F2	107.2(2)
F1	C7	C6	112.7(2)
C4	C3	C2	120.0(2)
C3	C4	C5	118.4(2)

Table S12 Hydrogen bonds for (*R*)-**9**

D	H	A	d(D-H) (Å)	d(H-A) (Å)	d(D-A) (Å)	D-H-A (°)
C6	H6	O1[1]	1.00	2.59	3.390(3)	136.7
O1	H1	N1[2]	0.84(5)	1.94(5)	2.779(3)	175(4)

[1]1-X,-1/2+Y,3/2-Z; [2]1-X,1/2+Y,3/2-Z

Table S13 Torsion angles for (*R*)-**9**

A	B	C	D	Angle (˚)
Br1	C1	C2	C3	178.2(2)
O1	C6	C7	F3	-61.2(3)
O1	C6	C7	F2	179.1(2)
O1	C6	C7	F1	58.2(3)
N1	C1	C2	C3	-1.9(4)
N1	C5	C6	O1	153.8(2)
N1	C5	C6	C7	-85.4(3)
N1	C5	C4	C3	-1.0(4)
C1	N1	C5	C6	-179.1(2)
C1	N1	C5	C4	-0.4(4)
C1	C2	C3	C4	0.3(4)
C2	C3	C4	C5	1.0(4)
C5	N1	C1	Br1	-178.17(18)
C5	N1	C1	C2	2.0(4)
C5	C6	C7	F3	177.8(2)
C5	C6	C7	F2	58.2(3)
C5	C6	C7	F1	-62.8(3)
C6	C5	C4	C3	177.5(2)
C4	C5	C6	O1	-24.8(3)
C4	C5	C6	C7	96.0(3)

Table S14 Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for (*R*)-**9**

Atom	*x*	*y*	*z*	U(eq)
H2	3221.12	5036.14	4040.69	26
H6	4782.83	7573.36	7608.02	21
H3	3715.04	7753	3908.6	28
H4	4053.49	9256.48	5298.99	24
H1	5610(60)	9970(60)	7510(40)	47(13)

X-ray structure and crystal data for (*R*,*R*)-1

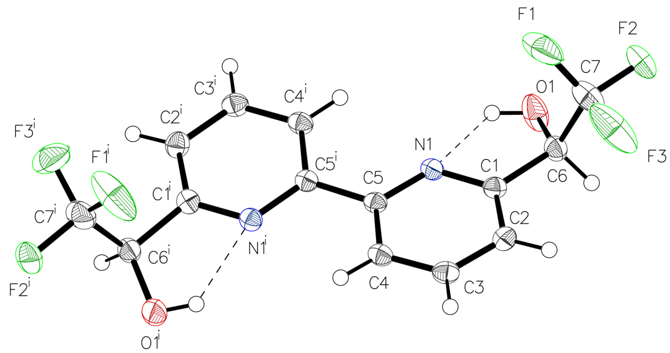


Table S15 Crystal data and structure refinement for (*R*,*R*)-**1**

Identification code	(*R*,*R*)-**1**
Empirical formula	$C_{14}H_{10}F_6N_2O_2$
Formula weight	352.24
Temperature/K	120
Crystal system	tetragonal
Space group	$P4_22_12$
a/Å	14.5873(2)
b/Å	14.5873(2)
c/Å	6.7844(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1443.65(6)
Z	4
ρ_{calc}g/cm^3	1.621
μ/mm^{-1}	0.919
F(000)	712.0
Crystal size/mm^3	0.201 × 0.109 × 0.085
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	7.456 to 121.076
Index ranges	-18 ≤ h ≤ 16, -17 ≤ k ≤ 18, -8 ≤ l ≤ 8
Reflections collected	21453
Independent reflections	1641 [R_{int} = 0.0331, R_{sigma} = 0.0150]
Data/restraints/parameters	1641/0/114
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0299, wR_2 = 0.0792
Final R indexes [all data]	R_1 = 0.0301, wR_2 = 0.0794
Largest diff. peak/hole / e Å^{-3}	0.22/-0.20
Flack parameter	0.02(3)

Table S16 Fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for (*R*,*R*)-**1**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor

Atom	*x*	*y*	*z*	U(eq)
F1	7867.0(12)	5865.7(15)	5506(2)	73.0(6)
F2	9088.7(8)	6111.3(9)	3853(2)	39.1(3)
F3	8700.7(12)	4732.5(11)	4574(3)	74.3(7)
O1	7571.3(10)	6358.8(10)	1542(3)	39.8(4)
N1	6208.5(9)	5261.9(9)	2337(2)	19.6(3)
C1	7016.0(11)	4833.8(11)	2327(2)	20.8(3)
C2	7113.0(11)	3886.7(11)	2454(3)	23.7(4)
C3	6321.5(11)	3363.1(11)	2587(3)	23.2(3)
C4	5476.5(11)	3793.7(11)	2572(2)	21.1(3)
C5	5443.4(10)	4748.8(10)	2458(2)	18.5(3)
C6	7835.4(11)	5476.4(12)	2117(3)	23.4(4)
C7	8371.0(15)	5543.0(15)	4025(3)	36.9(5)

Table S17 Anisotropic displacement parameters (Å^2×10^3) for (*R*,*R*)-**1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	71.7(11)	110.8(15)	36.4(7)	-29.8(9)	16.9(7)	-59.7(10)
F2	29.9(6)	41.8(7)	45.5(7)	2.6(5)	-8.5(5)	-15.9(5)
F3	74.7(11)	52.1(9)	96.1(14)	38.1(9)	-57.7(11)	-27.5(8)
O1	24.8(7)	25.4(7)	69.2(11)	14.0(7)	-5.6(7)	-4.7(5)
N1	20.2(6)	19.0(6)	19.8(6)	-1.2(5)	-0.7(5)	-1.9(5)
C1	21.4(7)	21.6(8)	19.3(7)	-2.5(6)	0.1(6)	-1.4(6)
C2	22.5(7)	22.6(8)	26.1(8)	-2.6(7)	0.1(7)	2.8(6)
C3	27.8(8)	17.0(7)	24.8(7)	-0.7(7)	-1.1(7)	-0.5(6)
C4	23.9(7)	19.1(7)	20.4(7)	-0.4(6)	-0.5(6)	-4.0(5)
C5	20.7(7)	18.9(7)	15.9(6)	-0.8(5)	-0.3(6)	-1.6(6)
C6	20.2(7)	22.3(8)	27.6(8)	0.4(6)	0.7(6)	-2.1(6)
C7	36.9(10)	38.5(11)	35.3(10)	5.0(8)	-7.3(8)	-16.6(8)

Table S18 Bond lengths for (*R*,*R*)-**1**

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
F1	C7	1.331(3)	C1	C6	1.526(2)
F2	C7	1.341(2)	C2	C3	1.387(2)
F3	C7	1.330(3)	C3	C4	1.384(2)
O1	C6	1.399(2)	C4	C5	1.396(2)
N1	C1	1.333(2)	C5	C5[1]	1.487(3)
N1	C5	1.3464(19)	C6	C7	1.515(3)
C1	C2	1.392(2)			

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

Table S19 Bond angles for (*R*,*R*)-**1**

Atom	Atom	Atom	Angle (˚)
C1	N1	C5	118.18(13)
N1	C1	C2	123.69(15)
N1	C1	C6	113.88(13)
C2	C1	C6	122.42(15)
C3	C2	C1	117.77(15)
C4	C3	C2	119.42(14)
C3	C4	C5	118.96(14)
N1	C5	C4	121.97(14)
N1	C5	C5[1]	116.56(16)
C4	C5	C5[1]	121.46(17)
O1	C6	C1	112.06(14)
O1	C6	C7	108.73(15)
C7	C6	C1	111.33(15)
F1	C7	F2	106.16(17)
F1	C7	C6	112.50(18)
F2	C7	C6	111.60(16)
F3	C7	F1	107.6(2)
F3	C7	F2	106.97(17)
F3	C7	C6	111.66(18)

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

Table S20 Hydrogen bonds for (*R*,*R*)-**1**

D	H	A	d(D-H) (Å)	d(H-A) (Å)	d(D-A) (Å)	D-H-A (°)
O1	H1	N1	0.83(3)	2.03(3)	2.6083(19)	126(3)

Table S21 Torsion angles for (*R*,*R*)-**1**

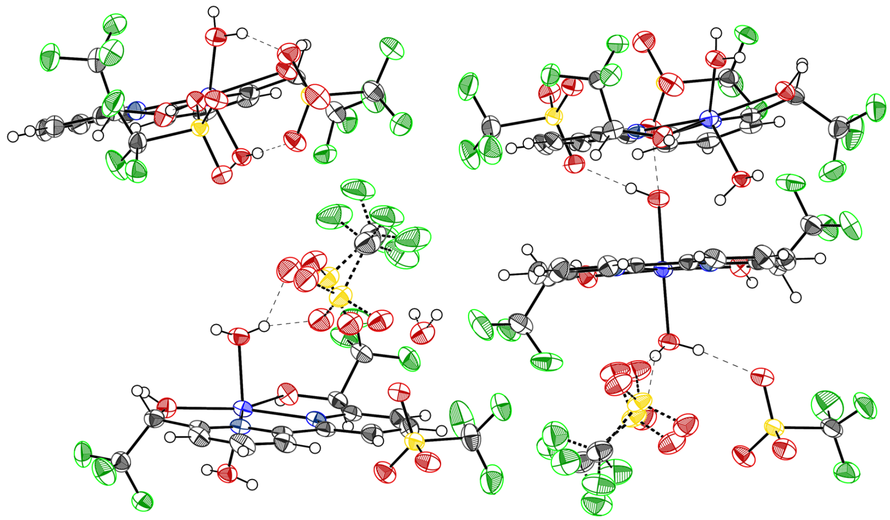
A	B	C	D	Angle (˚)
O1	C6	C7	F1	63.5(2)
O1	C6	C7	F2	-55.7(2)
O1	C6	C7	F3	-175.34(17)
N1	C1	C2	C3	0.4(3)
N1	C1	C6	O1	-13.3(2)
N1	C1	C6	C7	108.77(18)
C1	N1	C5	C4	0.1(2)
C1	N1	C5	C5[1]	-179.80(11)
C1	C2	C3	C4	0.5(2)
C1	C6	C7	F1	-60.4(2)
C1	C6	C7	F2	-179.61(16)
C1	C6	C7	F3	60.7(2)
C2	C1	C6	O1	165.49(16)
C2	C1	C6	C7	-72.5(2)
C2	C3	C4	C5	-1.1(2)
C3	C4	C5	N1	0.8(2)
C3	C4	C5	C5[1]	-179.35(11)
C5	N1	C1	C2	-0.7(3)
C5	N1	C1	C6	178.06(14)
C6	C1	C2	C3	-178.23(16)

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

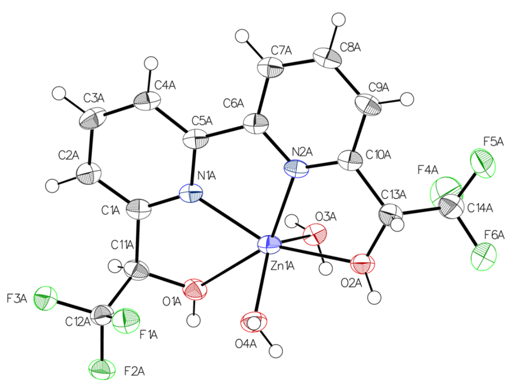
Table S22 Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for (*R*,*R*)-**1**

Atom	*x*	*y*	*z*	U(eq)
H2	7689.16	3613.78	2450.4	28
H3	6358.59	2728.3	2684.28	28
H4	4938.89	3452.35	2638.34	25
H6	8242.43	5226.88	1100.9	28
H1	7010(20)	6360(20)	1720(50)	54(9)

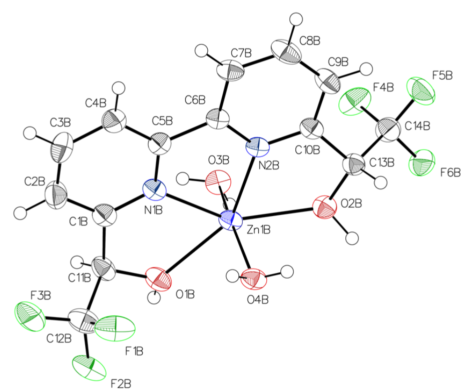
X-ray structure and crystal data for [(*R*,*R*)-1·Zn·2H$_2$O]$^{2+}$·2OTf^{-}



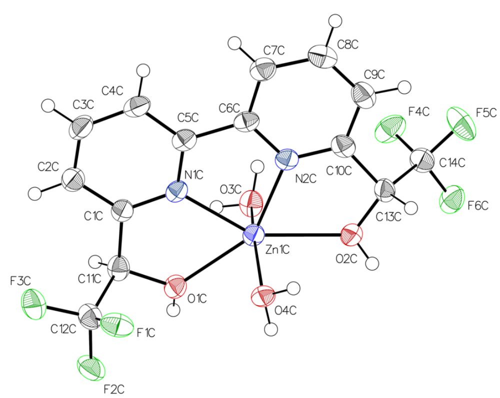
Complexes A–D



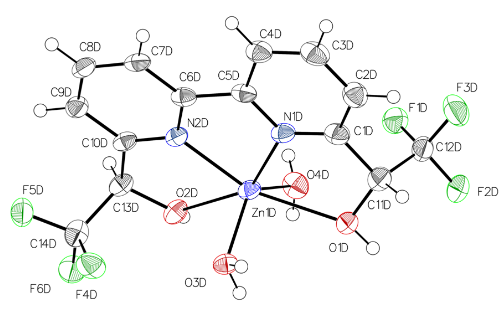
Complex A



Complex B



Complex C



Complex D

Table S23 Crystal data and structure refinement for $[(R,R)\text{-}\mathbf{1}\cdot Zn\cdot 2H_2O]^{2+}\cdot 2OTf^-$

Identification code	$[(R,R)\text{-}\mathbf{1}\cdot Zn\cdot 2H_2O]^{2+}\cdot 2OTf^-$
Empirical formula	$C_{16}H_{14.08}F_{12}N_2O_{10.04}S_2Zn$
Formula weight	752.50
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1$
a/Å	17.4342(4)
b/Å	12.8734(3)
c/Å	23.1114(6)
α/°	90
β/°	93.993(1)
γ/°	90
Volume/Å^3	5174.5(2)
Z	8
ρ_{calc}g/cm^3	1.932
μ/mm^{-1}	4.182
F(000)	2995.0
Crystal size/mm^3	0.09 × 0.07 × 0.02
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	3.832 to 144.45
Index ranges	-21 ≤ h ≤ 21, -15 ≤ k ≤ 15, -28 ≤ l ≤ 28
Reflections collected	88969
Independent reflections	20014 [R_{int} = 0.0646, R_{sigma} = 0.0500]
Data/restraints/parameters	20014/432/1666
Goodness-of-fit on F^2	0.992
Final R indexes [I>=2σ (I)]	R_1 = 0.0350, wR_2 = 0.0822
Final R indexes [all data]	R_1 = 0.0451, wR_2 = 0.0870
Largest diff. peak/hole / e Å^{-3}	0.36/-0.39
Flack parameter	0.010(7)

Table S24 Fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for $[(R,R)\text{-}\mathbf{1}\cdot Zn\cdot 2H_2O]^{2+}\cdot 2OTf^-$. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor

Atom	*x*	*y*	*z*	U(eq)
Zn1B	6149.1(3)	2401.8(5)	9990.8(3)	25.97(14)
F1B	4662.7(19)	2026(3)	8521.1(19)	53.2(10)
F2B	5079.0(19)	507(3)	8334.9(16)	48.3(8)
F3B	5258(3)	1784(4)	7756.1(16)	71.3(13)
F4B	7565.2(17)	3127(3)	11535.2(16)	47.2(8)
F5B	6924(2)	4070(3)	12096.3(14)	51.6(9)
F6B	6780(2)	2408(3)	12081.6(14)	46.7(8)
O1B	5978(2)	1345(3)	9213.7(17)	35.1(8)
O2B	6175(2)	2405(3)	10966.0(15)	31.3(7)
O3B	7251.2(19)	1902(3)	10068.2(15)	30.2(7)
O4B	4984.6(19)	2413(3)	10013.0(16)	31.8(7)
N1B	6241(2)	3312(3)	9220.9(17)	26.1(8)
N2B	6336(2)	3956(3)	10302.1(18)	24.5(8)

C1B	6162(3)	2924(4)	8690(2)	29.8(10)
C2B	6205(3)	3544(5)	8198(2)	40.7(13)
C3B	6318(4)	4599(5)	8278(2)	42.3(13)
C4B	6398(3)	5011(5)	8830(2)	35.3(11)
C5B	6355(3)	4333(4)	9294(2)	26.9(10)
C6B	6417(2)	4705(4)	9905(2)	25.3(10)
C7B	6548(3)	5736(4)	10059(2)	32.0(11)
C8B	6575(3)	6000(4)	10639(3)	40.0(13)
C9B	6482(3)	5237(4)	11050(2)	34.9(11)
C10B	6366(3)	4222(4)	10865(2)	26.7(10)
C11B	6007(3)	1756(5)	8654(2)	32.4(11)
C12B	5244(3)	1517(5)	8308(3)	42.4(13)
C13B	6233(3)	3339(4)	11277(2)	29.0(10)
C14B	6880(3)	3232(5)	11752(2)	37.2(12)
Zn1C	3833.9(3)	-125.5(5)	5026.6(3)	25.47(14)
F1C	2410.9(17)	500(3)	3580.3(14)	42.1(8)
F2C	3133(2)	-236(3)	2990.4(13)	43.1(8)
F3C	2963(2)	1421(3)	2950.8(15)	50.8(9)
F4C	5239.8(18)	-492(3)	6576.3(17)	45.1(8)
F5C	4545(2)	-820(4)	7289.8(14)	54.4(10)
F6C	4827.3(18)	-2035(3)	6697.4(15)	41.5(7)
O1C	3867(2)	-152(3)	4065.4(15)	29.2(7)
O2C	3985(2)	-1185(3)	5794.1(16)	32.2(8)
O3C	4996.6(19)	-136(3)	5024.3(16)	31.7(8)
O4C	2758.2(18)	-693(3)	4886.6(15)	29.3(7)
N1C	3656(2)	1419(3)	4706.2(18)	24.7(8)
N2C	3712(2)	772(3)	5786.4(17)	26.3(8)
C1C	3658(3)	1670(4)	4147(2)	26.8(10)
C2C	3592(3)	2686(4)	3954(2)	33.5(11)
C3C	3508(3)	3457(4)	4358(3)	38.1(12)
C4C	3509(3)	3214(4)	4940(2)	33.3(11)
C5C	3591(2)	2172(4)	5099(2)	26.7(10)
C6C	3622(2)	1814(4)	5713(2)	26.9(10)
C7C	3580(3)	2484(5)	6179(2)	34.0(11)
C8C	3633(3)	2053(5)	6731(2)	37.6(12)
C9C	3717(3)	995(5)	6807(2)	35.7(12)
C10C	3771(3)	381(4)	6317(2)	28.5(10)
C11C	3759(3)	765(4)	3740(2)	30.1(10)
C12C	3062(3)	610(5)	3314(2)	34.0(11)
C13C	3902(3)	-791(4)	6355(2)	28.5(10)
C14C	4639(3)	-1034(5)	6731(2)	35.2(11)
Zn1A	8928.0(3)	7475.5(5)	9767.9(3)	23.42(13)
F1A	10186.8(16)	8008(2)	8565.9(13)	33.6(6)
F2A	9791.0(17)	9468(2)	8198.9(13)	33.8(6)
F3A	9707.3(17)	8073(3)	7682.5(13)	36.5(7)
F4A	8021(2)	7117(3)	11359.4(18)	58.1(10)
F5A	8554(3)	5890(3)	11861.7(16)	62.3(12)
F6A	9051(2)	7410(3)	11900.6(14)	48.5(8)

O1A	8726(2)	8711(3)	8946.6(15)	28.7(7)
O2A	9344.8(18)	7390(3)	10764.2(14)	27.4(7)
O3A	7985.3(17)	8146(3)	10014.1(14)	24.4(6)
O4A	9923.8(19)	8171(3)	9768.8(15)	31.6(7)
N1A	8677(2)	6690(3)	8980.5(17)	21.5(7)
N2A	8777(2)	5963(3)	10064.7(17)	22.1(8)
C1A	8669(2)	7090(4)	8449(2)	24.7(9)
C2A	8531(3)	6507(4)	7955(2)	27.6(10)
C3A	8404(3)	5444(4)	8016(2)	32.6(11)
C4A	8399(3)	5019(4)	8565(2)	28.4(10)
C5A	8532(2)	5662(4)	9041(2)	23.6(9)
C6A	8527(2)	5278(4)	9649(2)	24.9(9)
C7A	8292(2)	4288(4)	9789(2)	25.9(9)
C8A	8324(3)	4000(4)	10365(2)	28.9(10)
C9A	8607(3)	4686(4)	10791(2)	27.3(10)
C10A	8834(2)	5677(4)	10617(2)	24.0(9)
C11A	8825(3)	8253(4)	8409(2)	26.5(10)
C12A	9641(3)	8446(4)	8213(2)	26.6(9)
C13A	9195(3)	6457(4)	11049(2)	27.6(10)
C14A	8692(3)	6713(5)	11543(3)	40.5(13)
Zn1D	8878.2(3)	-43.6(5)	4797.0(3)	24.73(14)
F1D	10094.8(18)	434(3)	3564.0(14)	38.5(7)
F2D	9747(2)	1933(3)	3233.5(15)	43.3(8)
F3D	9593(2)	569(3)	2695.6(14)	49.2(9)
F4D	7890.7(17)	-434(3)	6293.4(14)	41.5(7)
F5D	8339.6(19)	-1703(3)	6820.7(13)	39.7(7)
F6D	8831(2)	-176(3)	6927.7(13)	41.5(7)
O1D	8683(2)	1215(3)	3990.3(16)	33.9(8)
O2D	9271.4(18)	-129(3)	5809.0(15)	28.2(7)
O3D	7941.7(18)	639(3)	5043.6(14)	26.9(7)
O4D	9881.0(19)	625(3)	4801.9(16)	34.2(8)
N1D	8614(2)	-810(3)	4003.7(18)	26.7(8)
N2D	8736(2)	-1560(3)	5084.4(17)	23.3(8)
C1D	8570(3)	-376(4)	3481(2)	30.2(10)
C2D	8370(3)	-950(5)	2979(2)	35.3(11)
C3D	8241(3)	-2003(5)	3040(2)	37.5(12)
C4D	8296(3)	-2461(4)	3578(2)	32.6(11)
C5D	8475(3)	-1833(4)	4060(2)	27.1(10)
C6D	8505(2)	-2244(4)	4664(2)	26.2(10)
C7D	8309(3)	-3257(4)	4795(2)	29.1(10)
C8D	8381(3)	-3576(4)	5364(2)	31.2(11)
C9D	8640(3)	-2887(4)	5793(2)	30.2(10)
C10D	8808(2)	-1870(4)	5634(2)	24.8(9)
C11D	8742(3)	770(4)	3442(2)	33.2(11)
C12D	9557(3)	922(4)	3232(2)	34.5(11)
C13D	9109(3)	-1073(4)	6078(2)	26.9(10)
C14D	8538(3)	-842(5)	6530(2)	33.5(11)
S1J	5794.1(10)	2391.1(16)	5890.8(8)	40.0(4)

F1J	6999(3)	1232(5)	6071(3)	80.7(18)
F2J	6407(4)	1586(6)	6838(3)	79.3(17)
F3J	7101(3)	2732(5)	6468(3)	73.4(16)
O1J	5357(3)	1452(4)	5794(3)	49.3(13)
O2J	6111(4)	2819(6)	5389(3)	55.0(16)
O3J	5447(3)	3154(4)	6240(2)	41.0(11)
C1J	6616(5)	1959(7)	6343(4)	49.0(10)
S1L	6061(4)	1816(6)	5841(3)	40.0(4)
F1L	6700(11)	2478(15)	6827(11)	80.7(18)
F2L	6610(12)	824(16)	6761(10)	79.3(17)
F3L	7458(9)	1624(16)	6318(10)	73.4(16)
O1L	5321(10)	1924(17)	6074(10)	49.3(13)
O2L	6126(12)	833(15)	5533(9)	55.0(16)
O3L	6380(12)	2629(16)	5533(10)	41.0(11)
C1L	6737(11)	1675(16)	6471(9)	49.0(10)
S1G	4190.2(8)	4965.8(14)	9145.9(7)	38.3(4)
F1G	2897(2)	5211(4)	8527(2)	61.3(12)
F2G	2994(3)	3774(4)	8998(2)	65.8(13)
F3G	3605(3)	3990(4)	8233(2)	65.1(13)
O1G	3847(3)	5457(5)	9627(2)	48.3(12)
O2G	4540(3)	5681(4)	8762(2)	46.1(11)
O3G	4638(3)	4048(4)	9282(2)	49.1(12)
C1G	3375(4)	4455(6)	8699(3)	43.6(9)
S1M	3910(8)	4359(13)	9174(6)	38.3(4)
F1M	3250(20)	4920(30)	8180(17)	59(6)
F2M	3370(20)	3300(30)	8284(18)	62(8)
F3M	2520(20)	4090(30)	8690(19)	65(7)
O1M	3830(20)	3400(40)	9469(19)	48.3(12)
O2M	3540(30)	5040(40)	9510(20)	46.1(11)
O3M	4640(30)	4360(40)	8970(20)	49.1(12)
C1M	3190(30)	4150(30)	8510(30)	43.6(9)
S1I	9011.0(7)	564.4(10)	10490.0(5)	28.4(2)
F1I	8936(2)	-419(3)	11473.0(15)	48.6(9)
F2I	8601.4(19)	1188(3)	11497.9(16)	48.7(9)
F3I	9793.4(17)	789(3)	11489.0(14)	40.3(7)
O1I	8255(2)	139(3)	10339.8(17)	34.4(8)
O2I	9646(2)	-68(3)	10340.9(17)	41.0(9)
O3I	9071(2)	1651(3)	10353.2(18)	40.6(9)
C1I	9084(3)	525(4)	11283(2)	30.9(10)
S1K	8599.6(6)	1822.4(9)	8812.4(5)	24.6(2)
F1K	7951(3)	1045(4)	7859.0(17)	65.9(12)
F2K	9090(2)	1632(3)	7783.2(14)	52.6(9)
F3K	8138(3)	2695(4)	7829.8(16)	60.2(11)
O1K	8912(2)	812(3)	8955.7(16)	32.8(8)
O2K	7844(2)	2036(3)	9005.3(16)	35.3(8)
O3K	9138.2(19)	2665(3)	8915.9(15)	29.9(7)
C1K	8434(4)	1795(5)	8016(2)	41.9(13)
S1F	8675.7(6)	4266.5(9)	3886.9(5)	23.8(2)

F1F	8033(2)	3334(3)	2981.5(16)	54.7(10)
F2F	9086(2)	4136(4)	2827.7(15)	56.5(11)
F3F	8046.8(19)	5008(3)	2917.8(13)	41.7(7)
O1F	9036.9(19)	3282(3)	4037.5(15)	29.4(7)
O2F	7926(2)	4439(3)	4104.1(15)	34.1(8)
O3F	9188(2)	5152(3)	3954.8(16)	33.0(8)
C1F	8449(3)	4182(5)	3104(2)	34.1(11)
S1H	3686.4(7)	5885.6(11)	6104.7(5)	31.6(3)
F1H	3904(3)	4571(3)	6958.5(18)	76.3(15)
F2H	3043(2)	5728(4)	7085.2(17)	67.0(13)
F3H	4236(2)	6129(3)	7179.3(15)	48.3(8)
O1H	3144(2)	5142(3)	5842.1(17)	38.3(8)
O2H	4474(2)	5737(5)	5968.3(18)	54.4(13)
O3H	3426(2)	6947(3)	6070.3(18)	39.9(9)
C1H	3715(4)	5570(5)	6878(2)	42.4(13)
S1E	9073.7(7)	3015.9(9)	5546.0(5)	29.1(2)
F1E	8978(3)	1993(3)	6511.0(16)	55.9(10)
F2E	8639(2)	3601(3)	6556.2(16)	50.5(9)
F3E	9831.3(19)	3207(3)	6560.2(15)	45.8(8)
O1E	8322(2)	2598(3)	5378.6(16)	35.9(8)
O2E	9717(2)	2391(3)	5397.0(17)	41.2(9)
O3E	9138(2)	4109(3)	5426.6(18)	41.7(9)
C1E	9130(3)	2949(4)	6343(2)	34.6(11)
S1FL	3650.4(7)	3460.6(10)	11101.0(5)	28.8(2)
F1FL	2894(2)	3225(4)	12031.0(16)	57.5(10)
F2FL	4006(2)	3878(4)	12191.9(16)	68.3(14)
F3FL	3893(3)	2258(4)	12003(2)	77.0(14)
O1FL	3371(2)	4508(3)	11028.2(17)	38.7(9)
O2FL	3139(2)	2676(3)	10836.0(17)	38.1(9)
O3FL	4454(2)	3309(4)	11011.5(17)	46.7(10)
C1FL	3607(3)	3196(5)	11876(2)	39.6(13)
O1N	5282(14)	3810(20)	6649(12)	38(7)

Table S25 Anisotropic displacement parameters ($Å^2×10^3$) for $[(R,R)$-**1**$·Zn·2H_2O]^{2+}·2OTf^-$. 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}
Zn1B	20.8(3)	24.7(3)	31.9(3)	-3.7(3)	-1.5(2)	2.1(2)
F1B	28.7(16)	36.5(19)	93(3)	-4.4(19)	-6.9(17)	6.6(14)
F2B	40.8(17)	42(2)	59(2)	-19.6(17)	-12.4(15)	1.1(15)
F3B	74(3)	93(4)	42.2(19)	1(2)	-22.6(19)	-28(3)
F4B	24.0(14)	58(2)	59(2)	21.2(18)	-3.4(13)	2.6(14)
F5B	65(2)	50(2)	36.1(17)	-0.6(16)	-18.7(16)	-8.7(18)
F6B	53.3(19)	49(2)	36.9(16)	16.8(16)	-5.5(14)	-12.4(17)
O1B	40(2)	27.4(19)	37.0(19)	-6.0(16)	-4.2(16)	1.9(16)
O2B	34.1(17)	26.1(18)	33.3(17)	2.0(16)	0.2(14)	0.8(15)
O3B	26.6(16)	27.0(18)	36.9(17)	2.4(15)	0.7(13)	7.2(14)
O4B	21.5(14)	35(2)	39.0(18)	-5.0(16)	-1.0(13)	-0.9(13)
N1B	18.9(17)	28(2)	30.9(19)	-2.8(17)	-1.9(14)	4.9(15)

N2B	18.8(17)	22(2)	32(2)	-1.3(17)	-0.9(14)	2.5(15)
C1B	19(2)	35(3)	35(2)	-3(2)	-0.2(18)	3.8(19)
C2B	42(3)	50(4)	31(3)	-4(3)	7(2)	1(3)
C3B	50(3)	45(3)	33(3)	10(2)	10(2)	4(3)
C4B	37(3)	35(3)	34(3)	1(2)	2(2)	-3(2)
C5B	20(2)	29(3)	31(2)	1(2)	1.2(17)	4.2(18)
C6B	21(2)	24(2)	31(2)	-0.6(19)	-0.4(17)	2.5(17)
C7B	30(2)	23(2)	41(3)	1(2)	-5(2)	0(2)
C8B	49(3)	23(3)	46(3)	-7(2)	-12(2)	4(2)
C9B	41(3)	29(3)	33(2)	-6(2)	-7(2)	5(2)
C10B	19(2)	30(3)	31(2)	-3(2)	-2.6(17)	3.5(18)
C11B	27(2)	37(3)	33(2)	-12(2)	-0.3(19)	5(2)
C12B	36(3)	37(3)	51(3)	-5(3)	-12(2)	2(2)
C13B	26(2)	32(3)	29(2)	-1(2)	0.2(18)	-1(2)
C14B	32(3)	43(3)	35(3)	6(3)	-3(2)	-3(2)
Zn1C	21.1(3)	25.8(3)	29.1(3)	2.8(3)	-1.5(2)	-1.8(2)
F1C	30.3(15)	51(2)	44.0(17)	-13.8(16)	-0.6(13)	-4.6(14)
F2C	56.6(19)	44(2)	28.6(15)	-9.0(14)	-1.0(13)	5.9(16)
F3C	62(2)	48(2)	39.7(18)	9.1(16)	-14.8(16)	5.4(18)
F4C	28.5(15)	35.5(18)	70(2)	6.7(17)	-6.1(14)	-5.2(13)
F5C	54(2)	75(3)	32.7(16)	1.7(18)	-13.7(14)	14(2)
F6C	34.5(15)	35.3(18)	52.7(18)	12.5(15)	-11.0(13)	-2.3(13)
O1C	33.1(17)	24.1(17)	30.3(17)	1.3(15)	1.9(13)	4.4(15)
O2C	39(2)	24.6(19)	31.9(18)	2.7(15)	-4.7(15)	-2.4(16)
O3C	24.2(15)	36(2)	34.4(17)	5.7(15)	0.2(13)	2.1(14)
O4C	26.9(16)	29.2(18)	31.5(16)	-1.1(15)	0.6(13)	-7.0(14)
N1C	18.3(17)	23(2)	32(2)	3.6(17)	-1.3(15)	-1.5(15)
N2C	18.7(17)	29(2)	31(2)	0.5(18)	-1.5(15)	-4.4(16)
C1C	19(2)	29(3)	32(2)	4(2)	-4.5(17)	-2.6(18)
C2C	32(3)	32(3)	35(2)	5(2)	-5(2)	-4(2)
C3C	38(3)	25(3)	49(3)	9(2)	-11(2)	-5(2)
C4C	32(2)	23(2)	45(3)	-2(2)	-5(2)	-2(2)
C5C	16.1(19)	28(3)	36(2)	0(2)	-1.5(17)	-1.4(17)
C6C	18(2)	26(3)	36(2)	-3(2)	-1.0(17)	-1.6(18)
C7C	31(2)	32(3)	39(3)	-1(2)	0(2)	-4(2)
C8C	34(3)	43(3)	36(3)	-9(2)	0(2)	-4(2)
C9C	31(3)	45(3)	30(2)	2(2)	-1.2(19)	0(2)
C10C	19(2)	35(3)	30(2)	0(2)	-3.0(17)	-1.4(19)
C11C	26(2)	33(3)	31(2)	5(2)	1.8(18)	1(2)
C12C	35(3)	37(3)	30(2)	0(2)	-0.9(19)	5(2)
C13C	23(2)	35(3)	26(2)	6(2)	-3.6(17)	-5(2)
C14C	30(3)	39(3)	36(3)	4(2)	-8(2)	-4(2)
Zn1A	21.0(3)	18.4(3)	30.9(3)	-1.0(3)	2.5(2)	-1.0(2)
F1A	25.3(13)	35.5(17)	39.9(15)	-0.6(13)	0.9(11)	0.8(12)
F2A	38.6(15)	23.1(14)	40.8(15)	-1.7(13)	9.6(12)	-6.5(12)
F3A	39.5(16)	38.0(17)	32.9(14)	-7.7(14)	9.1(12)	-7.9(13)
F4A	37.6(18)	69(3)	70(2)	-14(2)	16.9(17)	6.4(17)
F5A	101(3)	47(2)	42.3(19)	-0.7(18)	31(2)	-21(2)

F6A	62(2)	49(2)	35.4(16)	-8.8(16)	7.5(15)	-13.0(18)
O1A	35.4(18)	17.4(16)	34.1(18)	0.2(14)	8.9(14)	0.3(14)
O2A	27.6(15)	25.7(17)	28.3(15)	2.5(15)	-2.3(12)	-5.6(14)
O3A	20.9(14)	23.0(16)	29.0(15)	-2.6(14)	-0.8(12)	3.0(12)
O4A	24.2(16)	33.6(19)	36.7(18)	-5.1(16)	0.9(13)	-8.2(14)
N1A	17.2(16)	17.3(18)	29.8(18)	-1.4(16)	0.8(14)	1.4(14)
N2A	17.7(16)	16.9(18)	31.6(19)	3.1(16)	0.1(14)	-0.6(14)
C1A	20(2)	22(2)	32(2)	1.6(19)	-1.4(17)	0.8(17)
C2A	29(2)	24(2)	30(2)	4(2)	-5.4(18)	0.7(19)
C3A	34(3)	27(3)	35(2)	-4(2)	-10(2)	-3(2)
C4A	28(2)	20(2)	36(2)	-1(2)	-3.3(18)	-3.5(19)
C5A	18.9(19)	18(2)	34(2)	0.1(19)	-1.4(16)	2.8(16)
C6A	17.2(19)	22(2)	35(2)	0(2)	2.3(17)	2.0(16)
C7A	20(2)	18(2)	40(2)	-2(2)	4.5(18)	3.4(17)
C8A	21(2)	21(2)	45(3)	7(2)	6.3(19)	0.5(17)
C9A	22(2)	23(2)	37(2)	8(2)	4.4(18)	2.1(17)
C10A	17.5(19)	21(2)	33(2)	1(2)	2.1(16)	2.1(17)
C11A	28(2)	18(2)	34(2)	3.9(19)	3.9(18)	0.4(18)
C12A	28(2)	23(2)	30(2)	-2.8(19)	2.2(18)	-2.8(18)
C13A	26(2)	28(2)	29(2)	3(2)	-0.2(18)	-0.7(19)
C14A	40(3)	42(3)	41(3)	-7(3)	11(2)	-10(3)
Zn1D	24.2(3)	18.6(3)	31.3(3)	-2.4(3)	1.9(2)	-1.3(2)
F1D	36.8(16)	35.0(17)	44.5(17)	2.8(14)	7.8(13)	-0.7(13)
F2D	55(2)	29.3(17)	46.9(17)	7.2(15)	15.6(15)	-6.4(15)
F3D	61(2)	55(2)	33.1(16)	-5.3(16)	13.8(15)	-11.5(18)
F4D	31.5(15)	50(2)	42.7(16)	0.3(15)	3.2(12)	11.0(14)
F5D	50.8(18)	36.4(18)	32.4(15)	3.4(14)	7.5(13)	-8.4(15)
F6D	53.9(19)	36.0(18)	34.1(15)	-6.3(14)	-1.4(13)	-7.3(15)
O1D	46(2)	23.1(18)	33.3(18)	0.9(15)	11.2(16)	-0.8(16)
O2D	26.3(15)	22.3(16)	35.0(17)	0.8(15)	-4.6(13)	-6.7(14)
O3D	24.8(15)	25.4(17)	29.9(16)	-1.5(14)	-2.0(12)	4.5(13)
O4D	26.1(16)	39(2)	37.8(18)	-3.1(17)	2.4(14)	-5.4(15)
N1D	26.6(19)	21(2)	33(2)	-5.1(17)	2.7(15)	-0.9(16)
N2D	17.8(16)	18.8(19)	33(2)	0.1(16)	2.3(14)	-0.3(14)
C1D	30(2)	29(3)	32(2)	-7(2)	3.4(19)	-0.7(19)
C2D	38(3)	37(3)	32(2)	-3(2)	4(2)	-2(2)
C3D	39(3)	38(3)	36(3)	-15(2)	4(2)	-6(2)
C4D	32(2)	27(3)	39(3)	-9(2)	5(2)	-5(2)
C5D	22(2)	25(2)	34(2)	-8(2)	5.3(17)	1.3(18)
C6D	17(2)	24(2)	38(2)	-6(2)	3.2(17)	0.5(17)
C7D	22(2)	20(2)	45(3)	-5(2)	6.4(19)	2.4(18)
C8D	26(2)	19(2)	50(3)	4(2)	9(2)	2.3(18)
C9D	28(2)	25(3)	39(3)	3(2)	8.3(19)	0.9(19)
C10D	20(2)	20(2)	34(2)	-1(2)	-0.9(17)	2.0(17)
C11D	38(3)	29(3)	33(2)	1(2)	3(2)	-1(2)
C12D	48(3)	27(3)	29(2)	2(2)	6(2)	-5(2)
C13D	22(2)	23(2)	34(2)	3(2)	-5.4(18)	0.7(18)
C14D	37(3)	33(3)	30(2)	2(2)	-4(2)	-5(2)

S1J	34.0(8)	34.9(9)	52.3(8)	-11.5(8)	12.2(7)	-11.7(7)
F1J	54(3)	55(3)	134(5)	-22(3)	9(3)	18(3)
F2J	75(4)	72(4)	88(4)	15(4)	-18(3)	6(3)
F3J	35(2)	66(3)	117(4)	-24(3)	-9(3)	-8(2)
O1J	40(3)	41(3)	67(4)	-17(3)	9(3)	-15(2)
O2J	51(3)	54(4)	61(4)	-17(3)	13(3)	-13(3)
O3J	36(2)	31(2)	57(3)	-1(2)	11(2)	-6(2)
C1J	41.3(18)	41.8(19)	64.6(19)	-9.6(18)	8.3(17)	-7.1(18)
S1L	34.0(8)	34.9(9)	52.3(8)	-11.5(8)	12.2(7)	-11.7(7)
F1L	54(3)	55(3)	134(5)	-22(3)	9(3)	18(3)
F2L	75(4)	72(4)	88(4)	15(4)	-18(3)	6(3)
F3L	35(2)	66(3)	117(4)	-24(3)	-9(3)	-8(2)
O1L	40(3)	41(3)	67(4)	-17(3)	9(3)	-15(2)
O2L	51(3)	54(4)	61(4)	-17(3)	13(3)	-13(3)
O3L	36(2)	31(2)	57(3)	-1(2)	11(2)	-6(2)
C1L	41.3(18)	41.8(19)	64.6(19)	-9.6(18)	8.3(17)	-7.1(18)
S1G	33.0(7)	36.8(8)	45.9(7)	9.5(7)	9.4(6)	13.7(6)
F1G	42(2)	58(3)	82(3)	16(2)	-10(2)	12(2)
F2G	53(3)	56(3)	90(3)	17(3)	11(2)	-9(2)
F3G	70(3)	64(3)	60(3)	-7(3)	-2(2)	6(3)
O1G	47(3)	53(3)	46(3)	9(2)	10(2)	15(2)
O2G	43(2)	34(2)	63(3)	4(2)	15(2)	10.0(19)
O3G	39(2)	41(3)	68(3)	16(2)	9(2)	17(2)
C1G	38.0(17)	40.3(18)	52.9(18)	6.7(17)	6.2(16)	9.2(17)
S1M	33.0(7)	36.8(8)	45.9(7)	9.5(7)	9.4(6)	13.7(6)
F1M	58(12)	62(13)	59(12)	23(12)	6(11)	8(12)
F2M	58(16)	63(17)	64(16)	-6(16)	-13(14)	29(15)
F3M	51(12)	64(13)	79(13)	0(13)	-8(12)	9(12)
O1M	47(3)	53(3)	46(3)	9(2)	10(2)	15(2)
O2M	43(2)	34(2)	63(3)	4(2)	15(2)	10.0(19)
O3M	39(2)	41(3)	68(3)	16(2)	9(2)	17(2)
C1M	38.0(17)	40.3(18)	52.9(18)	6.7(17)	6.2(16)	9.2(17)
S1I	25.2(5)	22.5(6)	36.9(6)	-0.2(5)	-2.3(4)	0.1(4)
F1I	62(2)	40(2)	43.9(18)	10.0(16)	-0.1(16)	-15.3(17)
F2I	36.8(17)	60(2)	49.4(19)	-19.1(18)	5.0(14)	5.1(16)
F3I	28.0(14)	49(2)	42.1(16)	0.9(15)	-7.9(12)	-6.9(14)
O1I	31.6(17)	22.8(18)	48(2)	-3.6(16)	-5.8(15)	-2.0(14)
O2I	38.5(19)	40(2)	44(2)	-5.1(19)	3.3(16)	7.9(18)
O3I	43(2)	25.9(19)	51(2)	1.1(18)	-7.3(17)	-4.7(16)
C1I	27(2)	30(3)	36(2)	-2(2)	1.5(19)	-2(2)
S1K	24.4(5)	22.3(6)	27.1(5)	-3.2(5)	1.3(4)	1.3(4)
F1K	68(3)	79(3)	49(2)	-30(2)	-12.0(18)	-15(2)
F2K	64(2)	63(2)	32.7(16)	-3.9(17)	14.0(15)	7(2)
F3K	75(3)	64(3)	38.9(18)	4.6(18)	-11.3(17)	23(2)
O1K	37.3(19)	19.2(17)	42.4(19)	-1.3(15)	5.3(15)	0.0(14)
O2K	26.7(17)	39(2)	40.1(18)	-10.6(17)	2.0(14)	0.4(15)
O3K	28.4(16)	23.0(17)	38.1(18)	1.2(15)	0.1(13)	2.6(13)
C1K	48(3)	47(4)	30(2)	-6(3)	-2(2)	3(3)

S1F	22.6(5)	22.7(6)	25.9(5)	-1.3(4)	-0.6(4)	1.8(4)
F1F	74(3)	39(2)	46.0(19)	-10.7(16)	-28.0(18)	2.4(18)
F2F	65(2)	73(3)	33.7(16)	10.7(18)	17.9(16)	30(2)
F3F	47.1(17)	42.7(19)	34.0(15)	3.6(15)	-7.0(13)	13.7(16)
O1F	32.4(17)	23.3(17)	31.7(16)	0.5(14)	-2.5(13)	1.0(14)
O2F	27.5(17)	40(2)	35.3(18)	-2.8(16)	4.0(14)	4.3(15)
O3F	28.2(16)	24.5(18)	45(2)	0.2(16)	-3.6(14)	0.3(14)
C1F	41(3)	35(3)	26(2)	-1(2)	-1(2)	11(2)
S1H	26.4(6)	33.8(7)	33.9(6)	-4.2(5)	-2.6(4)	3.5(5)
F1H	142(5)	33(2)	49(2)	1.8(18)	-23(3)	0(2)
F2H	69(3)	85(3)	48(2)	-15(2)	18.9(19)	-36(2)
F3H	60(2)	47(2)	36.5(17)	-7.2(16)	-5.7(15)	-10.1(17)
O1H	39.4(19)	31(2)	43(2)	-5.9(17)	-9.7(16)	4.2(16)
O2H	30(2)	90(4)	43(2)	-15(2)	-3.8(16)	12(2)
O3H	33.0(19)	34(2)	52(2)	3.0(19)	-3.3(16)	-5.3(16)
C1H	59(4)	34(3)	33(3)	-5(2)	1(2)	-10(3)
S1E	29.5(6)	21.4(6)	36.0(6)	0.8(5)	-1.9(5)	0.0(5)
F1E	83(3)	40(2)	43.1(18)	8.0(17)	-1.9(18)	-17(2)
F2E	44.2(19)	58(2)	49.4(19)	-16.4(18)	4.6(15)	6.5(17)
F3E	39.5(17)	50(2)	46.3(18)	-1.6(17)	-11.4(14)	-3.9(16)
O1E	35.5(19)	28(2)	42.3(19)	-2.6(16)	-9.5(15)	-0.8(15)
O2E	37.1(19)	41(2)	46(2)	-3.9(19)	2.9(16)	5.4(18)
O3E	50(2)	24.2(19)	50(2)	3.2(18)	-6.9(18)	-6.3(17)
C1E	35(3)	30(3)	37(3)	0(2)	-3(2)	-5(2)
S1FL	23.7(5)	30.7(6)	31.3(6)	-1.3(5)	-3.7(4)	0.7(5)
F1FL	35.2(17)	90(3)	47.5(19)	8(2)	1.3(14)	-13.2(19)
F2FL	55(2)	108(4)	40.1(19)	-8(2)	-7.2(17)	-40(2)
F3FL	87(3)	76(3)	67(3)	33(3)	-6(2)	23(3)
O1FL	36.0(19)	33(2)	46(2)	0.8(18)	-0.8(16)	-7.0(16)
O2FL	39(2)	27.2(19)	46(2)	-4.5(17)	-14.0(16)	3.0(15)
O3FL	27.9(19)	69(3)	42(2)	-4(2)	-4.5(15)	8.1(19)
C1FL	28(2)	56(4)	34(3)	4(3)	-6(2)	-7(2)
O1N	39(13)	31(13)	46(14)	6(11)	10(10)	-4(10)

Table S26 Bond lengths for [(*R*,*R*)-**1**·Zn·2H_2O]$^{2+}$·2OTf$^{–}$

Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Zn1B	O1B	2.257(4)	Zn1D	N1D	2.105(4)
Zn1B	O2B	2.251(3)	Zn1D	N2D	2.082(4)
Zn1B	O3B	2.022(3)	F1D	C12D	1.327(7)
Zn1B	O4B	2.034(3)	F2D	C12D	1.343(6)
Zn1B	N1B	2.146(4)	F3D	C12D	1.326(6)
Zn1B	N2B	2.144(4)	F4D	C14D	1.327(6)
F1B	C12B	1.331(7)	F5D	C14D	1.353(6)
F2B	C12B	1.334(7)	F6D	C14D	1.333(6)
F3B	C12B	1.322(8)	O1D	C11D	1.402(6)
F4B	C14B	1.333(6)	O2D	C13D	1.403(6)
F5B	C14B	1.339(7)	N1D	C1D	1.327(7)
F6B	C14B	1.325(7)	N1D	C5D	1.347(7)

O1B	C11B	1.401(7)	N2D	C6D	1.352(6)
O2B	C13B	1.401(6)	N2D	C10D	1.328(6)
N1B	C1B	1.322(7)	C1D	C2D	1.400(7)
N1B	C5B	1.338(7)	C1D	C11D	1.509(8)
N2B	C6B	1.345(6)	C2D	C3D	1.382(8)
N2B	C10B	1.343(6)	C3D	C4D	1.372(8)
C1B	C2B	1.398(8)	C4D	C5D	1.396(7)
C1B	C11B	1.528(8)	C5D	C6D	1.490(7)
C2B	C3B	1.383(9)	C6D	C7D	1.387(7)
C3B	C4B	1.381(8)	C7D	C8D	1.377(8)
C4B	C5B	1.388(8)	C8D	C9D	1.382(8)
C5B	C6B	1.488(6)	C9D	C10D	1.397(7)
C6B	C7B	1.389(7)	C10D	C13D	1.519(7)
C7B	C8B	1.382(8)	C11D	C12D	1.546(7)
C8B	C9B	1.384(8)	C13D	C14D	1.522(7)
C9B	C10B	1.385(8)	S1J	O1J	1.438(5)
C10B	C13B	1.510(7)	S1J	O2J	1.429(7)
C11B	C12B	1.535(7)	S1J	O3J	1.432(6)
C13B	C14B	1.525(7)	S1J	C1J	1.802(9)
Zn1C	O1C	2.226(3)	F1J	C1J	1.332(9)
Zn1C	O2C	2.239(4)	F2J	C1J	1.316(10)
Zn1C	O3C	2.028(3)	F3J	C1J	1.325(9)
Zn1C	O4C	2.018(3)	S1L	O1L	1.438(16)
Zn1C	N1C	2.137(4)	S1L	O2L	1.460(18)
Zn1C	N2C	2.125(4)	S1L	O3L	1.403(18)
F1C	C12C	1.335(6)	S1L	C1L	1.82(2)
F2C	C12C	1.332(7)	F1L	C1L	1.326(19)
F3C	C12C	1.343(7)	F2L	C1L	1.311(19)
F4C	C14C	1.328(6)	F3L	C1L	1.331(19)
F5C	C14C	1.342(7)	S1G	O1G	1.445(5)
F6C	C14C	1.333(7)	S1G	O2G	1.442(5)
O1C	C11C	1.404(6)	S1G	O3G	1.439(5)
O2C	C13C	1.409(6)	S1G	C1G	1.821(8)
N1C	C1C	1.334(6)	F1G	C1G	1.324(8)
N1C	C5C	1.339(7)	F2G	C1G	1.323(9)
N2C	C6C	1.360(7)	F3G	C1G	1.319(9)
N2C	C10C	1.323(7)	S1M	O1M	1.42(5)
C1C	C2C	1.383(7)	S1M	O2M	1.37(5)
C1C	C11C	1.515(7)	S1M	O3M	1.39(5)
C2C	C3C	1.379(8)	S1M	C1M	1.93(8)
C3C	C4C	1.381(8)	F1M	C1M	1.26(4)
C4C	C5C	1.395(7)	F2M	C1M	1.26(4)
C5C	C6C	1.488(7)	F3M	C1M	1.27(4)
C6C	C7C	1.386(7)	S1I	O1I	1.447(4)
C7C	C8C	1.389(8)	S1I	O2I	1.436(4)
C8C	C9C	1.380(9)	S1I	O3I	1.440(4)
C9C	C10C	1.391(8)	S1I	C1I	1.828(5)
C10C	C13C	1.527(7)	F1I	C1I	1.324(6)

C11C	C12C	1.523(7)	F2I	C1I	1.320(6)
C13C	C14C	1.532(7)	F3I	C1I	1.338(6)
Zn1A	O1A	2.483(4)	S1K	O1K	1.440(4)
Zn1A	O2A	2.368(3)	S1K	O2K	1.446(4)
Zn1A	O3A	1.975(3)	S1K	O3K	1.444(4)
Zn1A	O4A	1.953(3)	S1K	C1K	1.843(6)
Zn1A	N1A	2.101(4)	F1K	C1K	1.316(8)
Zn1A	N2A	2.087(4)	F2K	C1K	1.314(7)
F1A	C12A	1.334(6)	F3K	C1K	1.328(8)
F2A	C12A	1.342(6)	S1F	O1F	1.447(4)
F3A	C12A	1.329(6)	S1F	O2F	1.449(3)
F4A	C14A	1.323(7)	S1F	O3F	1.449(4)
F5A	C14A	1.323(7)	S1F	C1F	1.829(5)
F6A	C14A	1.344(7)	F1F	C1F	1.330(7)
O1A	C11A	1.397(6)	F2F	C1F	1.320(6)
O2A	C13A	1.403(6)	F3F	C1F	1.329(6)
N1A	C1A	1.331(6)	S1H	O1H	1.449(4)
N1A	C5A	1.357(6)	S1H	O2H	1.442(4)
N2A	C6A	1.354(6)	S1H	O3H	1.440(4)
N2A	C10A	1.325(6)	S1H	C1H	1.831(6)
C1A	C2A	1.375(7)	F1H	C1H	1.336(8)
C1A	C11A	1.525(6)	F2H	C1H	1.312(8)
C2A	C3A	1.395(7)	F3H	C1H	1.319(7)
C3A	C4A	1.383(7)	S1E	O1E	1.444(4)
C4A	C5A	1.383(7)	S1E	O2E	1.442(4)
C5A	C6A	1.488(7)	S1E	O3E	1.440(4)
C6A	C7A	1.384(7)	S1E	C1E	1.840(6)
C7A	C8A	1.380(7)	F1E	C1E	1.323(7)
C8A	C9A	1.387(8)	F2E	C1E	1.319(7)
C9A	C10A	1.403(7)	F3E	C1E	1.330(6)
C10A	C13A	1.521(7)	S1FL	O1FL	1.440(4)
C11A	C12A	1.544(6)	S1FL	O2FL	1.454(4)
C13A	C14A	1.524(7)	S1FL	O3FL	1.443(4)
Zn1D	O1D	2.475(4)	S1FL	C1FL	1.830(6)
Zn1D	O2D	2.393(3)	F1FL	C1FL	1.319(7)
Zn1D	O3D	1.973(3)	F2FL	C1FL	1.310(7)
Zn1D	O4D	1.948(4)	F3FL	C1FL	1.331(8)

Table S27 Bond angles for $[(R,R)\text{-}\mathbf{1}\cdot Zn\cdot 2H_2O]^{2+}\cdot 2OTf^{-}$

Atom	Atom	Atom	Angle (˚)	Atom	Atom	Atom	Angle (˚)
O2B	Zn1B	O1B	142.21(15)	O3D	Zn1D	O1D	81.55(13)
O3B	Zn1B	O1B	87.18(14)	O3D	Zn1D	O2D	85.68(13)
O3B	Zn1B	O2B	87.66(14)	O3D	Zn1D	N1D	108.96(15)
O3B	Zn1B	O4B	160.65(16)	O3D	Zn1D	N2D	101.90(14)
O3B	Zn1B	N1B	97.00(14)	O4D	Zn1D	O1D	77.96(15)
O3B	Zn1B	N2B	98.42(15)	O4D	Zn1D	O2D	79.55(13)
O4B	Zn1B	O1B	86.96(15)	O4D	Zn1D	O3D	124.19(16)
O4B	Zn1B	O2B	85.72(14)	O4D	Zn1D	N1D	110.74(15)

O4B	Zn1B	N1B	98.59(15)	O4D	Zn1D	N2D	122.62(16)
O4B	Zn1B	N2B	96.51(15)	N1D	Zn1D	O1D	68.92(15)
N1B	Zn1B	O1B	71.49(15)	N1D	Zn1D	O2D	149.35(15)
N1B	Zn1B	O2B	146.29(16)	N2D	Zn1D	O1D	147.20(15)
N2B	Zn1B	O1B	147.00(15)	N2D	Zn1D	O2D	71.20(14)
N2B	Zn1B	O2B	70.75(15)	N2D	Zn1D	N1D	79.33(16)
N2B	Zn1B	N1B	75.54(16)	C11D	O1D	Zn1D	113.5(3)
C11B	O1B	Zn1B	119.7(3)	C13D	O2D	Zn1D	114.9(3)
C13B	O2B	Zn1B	120.7(3)	C1D	N1D	Zn1D	126.2(4)
C1B	N1B	Zn1B	123.6(4)	C1D	N1D	C5D	120.0(4)
C1B	N1B	C5B	119.5(5)	C5D	N1D	Zn1D	113.8(3)
C5B	N1B	Zn1B	116.8(3)	C6D	N2D	Zn1D	114.7(3)
C6B	N2B	Zn1B	117.4(3)	C10D	N2D	Zn1D	125.5(3)
C10B	N2B	Zn1B	123.9(3)	C10D	N2D	C6D	119.7(4)
C10B	N2B	C6B	118.7(4)	N1D	C1D	C2D	121.8(5)
N1B	C1B	C2B	122.1(5)	N1D	C1D	C11D	117.9(5)
N1B	C1B	C11B	115.4(5)	C2D	C1D	C11D	120.3(5)
C2B	C1B	C11B	122.5(5)	C3D	C2D	C1D	117.7(5)
C3B	C2B	C1B	117.8(5)	C4D	C3D	C2D	120.9(5)
C4B	C3B	C2B	120.4(5)	C3D	C4D	C5D	118.1(5)
C3B	C4B	C5B	117.6(6)	N1D	C5D	C4D	121.4(5)
N1B	C5B	C4B	122.4(5)	N1D	C5D	C6D	116.3(4)
N1B	C5B	C6B	115.8(4)	C4D	C5D	C6D	122.2(5)
C4B	C5B	C6B	121.7(5)	N2D	C6D	C5D	115.5(4)
N2B	C6B	C5B	114.4(4)	N2D	C6D	C7D	121.5(5)
N2B	C6B	C7B	122.2(5)	C7D	C6D	C5D	123.0(5)
C7B	C6B	C5B	123.4(5)	C8D	C7D	C6D	118.8(5)
C8B	C7B	C6B	118.5(5)	C7D	C8D	C9D	119.9(5)
C7B	C8B	C9B	119.6(5)	C8D	C9D	C10D	118.5(5)
C8B	C9B	C10B	118.7(5)	N2D	C10D	C9D	121.7(5)
N2B	C10B	C9B	122.3(5)	N2D	C10D	C13D	116.7(4)
N2B	C10B	C13B	114.9(4)	C9D	C10D	C13D	121.6(4)
C9B	C10B	C13B	122.8(5)	O1D	C11D	C1D	108.5(4)
O1B	C11B	C1B	109.8(4)	O1D	C11D	C12D	111.0(4)
O1B	C11B	C12B	108.6(5)	C1D	C11D	C12D	109.5(4)
C1B	C11B	C12B	111.7(5)	F1D	C12D	F2D	107.0(4)
F1B	C12B	F2B	106.8(5)	F1D	C12D	C11D	112.7(4)
F1B	C12B	C11B	111.2(5)	F2D	C12D	C11D	110.7(5)
F2B	C12B	C11B	110.7(5)	F3D	C12D	F1D	107.5(5)
F3B	C12B	F1B	107.1(5)	F3D	C12D	F2D	107.9(4)
F3B	C12B	F2B	108.5(5)	F3D	C12D	C11D	110.7(5)
F3B	C12B	C11B	112.2(5)	O2D	C13D	C10D	110.8(4)
O2B	C13B	C10B	109.3(4)	O2D	C13D	C14D	107.3(4)
O2B	C13B	C14B	108.3(4)	C10D	C13D	C14D	112.6(4)
C10B	C13B	C14B	112.5(4)	F4D	C14D	F5D	106.8(4)
F4B	C14B	F5B	106.8(5)	F4D	C14D	F6D	107.7(5)
F4B	C14B	C13B	112.1(4)	F4D	C14D	C13D	111.9(4)
F5B	C14B	C13B	111.4(5)	F5D	C14D	C13D	112.5(5)

F6B	C14B	F4B	107.0(5)	F6D	C14D	F5D	106.5(4)
F6B	C14B	F5B	107.9(4)	F6D	C14D	C13D	111.1(4)
F6B	C14B	C13B	111.4(5)	O1J	S1J	C1J	102.8(4)
O1C	Zn1C	O2C	140.48(14)	O2J	S1J	O1J	115.3(4)
O3C	Zn1C	O1C	84.38(14)	O2J	S1J	O3J	113.3(4)
O3C	Zn1C	O2C	86.30(15)	O2J	S1J	C1J	104.7(4)
O3C	Zn1C	N1C	97.27(15)	O3J	S1J	O1J	115.1(3)
O3C	Zn1C	N2C	99.43(15)	O3J	S1J	C1J	103.6(4)
O4C	Zn1C	O1C	85.56(14)	F1J	C1J	S1J	110.3(6)
O4C	Zn1C	O2C	87.88(14)	F2J	C1J	S1J	111.1(6)
O4C	Zn1C	O3C	156.25(16)	F2J	C1J	F1J	109.5(8)
O4C	Zn1C	N1C	99.83(14)	F2J	C1J	F3J	107.2(8)
O4C	Zn1C	N2C	100.60(14)	F3J	C1J	S1J	111.3(6)
N1C	Zn1C	O1C	71.44(15)	F3J	C1J	F1J	107.3(7)
N1C	Zn1C	O2C	147.98(15)	O1L	S1L	O2L	111.6(12)
N2C	Zn1C	O1C	147.55(15)	O1L	S1L	C1L	105.0(12)
N2C	Zn1C	O2C	71.92(15)	O2L	S1L	C1L	103.7(12)
N2C	Zn1C	N1C	76.11(16)	O3L	S1L	O1L	121.0(14)
C11C	O1C	Zn1C	120.6(3)	O3L	S1L	O2L	110.7(14)
C13C	O2C	Zn1C	119.7(3)	O3L	S1L	C1L	102.8(12)
C1C	N1C	Zn1C	123.5(4)	F1L	C1L	S1L	111.3(17)
C1C	N1C	C5C	119.2(4)	F1L	C1L	F3L	106.9(16)
C5C	N1C	Zn1C	117.1(3)	F2L	C1L	S1L	111.7(16)
C6C	N2C	Zn1C	116.7(3)	F2L	C1L	F1L	108.5(18)
C10C	N2C	Zn1C	123.6(4)	F2L	C1L	F3L	106.8(17)
C10C	N2C	C6C	119.6(4)	F3L	C1L	S1L	111.4(16)
N1C	C1C	C2C	122.4(5)	O1G	S1G	C1G	104.3(3)
N1C	C1C	C11C	115.0(4)	O2G	S1G	O1G	114.1(3)
C2C	C1C	C11C	122.6(4)	O2G	S1G	C1G	103.2(3)
C3C	C2C	C1C	118.2(5)	O3G	S1G	O1G	116.0(3)
C2C	C3C	C4C	120.3(5)	O3G	S1G	O2G	114.4(3)
C3C	C4C	C5C	117.8(5)	O3G	S1G	C1G	102.5(3)
N1C	C5C	C4C	122.0(5)	F1G	C1G	S1G	110.7(6)
N1C	C5C	C6C	115.0(4)	F2G	C1G	S1G	110.1(5)
C4C	C5C	C6C	123.0(5)	F2G	C1G	F1G	108.4(6)
N2C	C6C	C5C	114.9(4)	F3G	C1G	S1G	110.9(5)
N2C	C6C	C7C	121.8(5)	F3G	C1G	F1G	108.1(6)
C7C	C6C	C5C	123.2(5)	F3G	C1G	F2G	108.6(7)
C6C	C7C	C8C	117.6(5)	O1M	S1M	C1M	100(2)
C9C	C8C	C7C	120.7(5)	O2M	S1M	O1M	102(3)
C8C	C9C	C10C	118.0(5)	O2M	S1M	O3M	133(3)
N2C	C10C	C9C	122.2(5)	O2M	S1M	C1M	104(3)
N2C	C10C	C13C	115.6(5)	O3M	S1M	O1M	107(3)
C9C	C10C	C13C	122.2(5)	O3M	S1M	C1M	107(3)
O1C	C11C	C1C	109.4(4)	F1M	C1M	S1M	107(4)
O1C	C11C	C12C	107.9(4)	F1M	C1M	F2M	113(4)
C1C	C11C	C12C	112.2(4)	F1M	C1M	F3M	111(4)
F1C	C12C	F3C	107.2(4)	F2M	C1M	S1M	106(4)

F1C	C12C	C11C	112.5(4)
F2C	C12C	F1C	106.7(5)
F2C	C12C	F3C	107.2(4)
F2C	C12C	C11C	111.6(4)
F3C	C12C	C11C	111.4(5)
O2C	C13C	C10C	109.1(4)
O2C	C13C	C14C	108.2(4)
C10C	C13C	C14C	110.6(4)
F4C	C14C	F5C	107.6(5)
F4C	C14C	F6C	106.8(4)
F4C	C14C	C13C	112.7(4)
F5C	C14C	C13C	110.5(4)
F6C	C14C	F5C	107.5(5)
F6C	C14C	C13C	111.4(4)
O2A	Zn1A	O1A	142.24(12)
O3A	Zn1A	O1A	82.15(12)
O3A	Zn1A	O2A	86.87(12)
O3A	Zn1A	N1A	109.40(14)
O3A	Zn1A	N2A	100.76(14)
O4A	Zn1A	O1A	77.64(14)
O4A	Zn1A	O2A	78.92(13)
O4A	Zn1A	O3A	123.83(15)
O4A	Zn1A	N1A	110.69(14)
O4A	Zn1A	N2A	124.03(16)
N1A	Zn1A	O1A	68.67(14)
N1A	Zn1A	O2A	148.33(14)
N2A	Zn1A	O1A	146.57(14)
N2A	Zn1A	O2A	70.99(14)
N2A	Zn1A	N1A	79.18(16)
C11A	O1A	Zn1A	112.9(3)
C13A	O2A	Zn1A	116.2(3)
C1A	N1A	Zn1A	126.9(3)
C1A	N1A	C5A	118.9(4)
C5A	N1A	Zn1A	114.1(3)
C6A	N2A	Zn1A	114.6(3)
C10A	N2A	Zn1A	125.0(3)
C10A	N2A	C6A	120.1(4)
N1A	C1A	C2A	123.0(5)
N1A	C1A	C11A	116.5(4)
C2A	C1A	C11A	120.5(4)
C1A	C2A	C3A	118.1(5)
C4A	C3A	C2A	119.5(5)
C5A	C4A	C3A	118.9(5)
N1A	C5A	C4A	121.5(4)
N1A	C5A	C6A	115.8(4)
C4A	C5A	C6A	122.7(4)
N2A	C6A	C5A	115.5(4)
N2A	C6A	C7A	121.3(4)
F2M	C1M	F3M	111(4)
F3M	C1M	S1M	109(4)
O1I	S1I	C1I	103.2(2)
O2I	S1I	O1I	115.6(2)
O2I	S1I	O3I	115.4(3)
O2I	S1I	C1I	102.9(2)
O3I	S1I	O1I	113.2(2)
O3I	S1I	C1I	104.2(3)
F1I	C1I	S1I	110.9(4)
F1I	C1I	F3I	108.1(4)
F2I	C1I	S1I	111.0(4)
F2I	C1I	F1I	108.9(4)
F2I	C1I	F3I	107.4(4)
F3I	C1I	S1I	110.4(3)
O1K	S1K	O2K	116.0(2)
O1K	S1K	O3K	114.1(2)
O1K	S1K	C1K	104.1(3)
O2K	S1K	C1K	103.2(3)
O3K	S1K	O2K	113.7(2)
O3K	S1K	C1K	103.6(3)
F1K	C1K	S1K	110.0(4)
F1K	C1K	F3K	108.9(5)
F2K	C1K	S1K	109.4(4)
F2K	C1K	F1K	109.1(5)
F2K	C1K	F3K	109.6(5)
F3K	C1K	S1K	109.8(4)
O1F	S1F	O2F	116.0(2)
O1F	S1F	O3F	114.1(2)
O1F	S1F	C1F	104.2(2)
O2F	S1F	O3F	113.9(2)
O2F	S1F	C1F	102.4(2)
O3F	S1F	C1F	104.1(3)
F1F	C1F	S1F	109.6(4)
F2F	C1F	S1F	110.5(4)
F2F	C1F	F1F	109.0(5)
F2F	C1F	F3F	108.8(5)
F3F	C1F	S1F	110.2(4)
F3F	C1F	F1F	108.7(4)
O1H	S1H	C1H	103.6(3)
O2H	S1H	O1H	115.1(3)
O2H	S1H	C1H	102.8(3)
O3H	S1H	O1H	114.2(2)
O3H	S1H	O2H	114.6(3)
O3H	S1H	C1H	104.6(3)
F1H	C1H	S1H	109.8(4)
F2H	C1H	S1H	110.9(5)
F2H	C1H	F1H	108.5(6)
F2H	C1H	F3H	108.8(5)

C7A	C6A	C5A	123.2(4)	F3H	C1H	S1H	111.4(4)
C8A	C7A	C6A	118.7(5)	F3H	C1H	F1H	107.3(5)
C7A	C8A	C9A	120.2(5)	O1E	S1E	C1E	103.6(2)
C8A	C9A	C10A	117.9(5)	O2E	S1E	O1E	115.8(2)
N2A	C10A	C9A	121.7(5)	O2E	S1E	C1E	103.0(2)
N2A	C10A	C13A	116.6(4)	O3E	S1E	O1E	113.2(2)
C9A	C10A	C13A	121.6(4)	O3E	S1E	O2E	115.3(3)
O1A	C11A	C1A	109.1(4)	O3E	S1E	C1E	103.8(3)
O1A	C11A	C12A	111.5(4)	F1E	C1E	S1E	109.9(4)
C1A	C11A	C12A	110.3(4)	F1E	C1E	F3E	108.6(5)
F1A	C12A	F2A	107.3(4)	F2E	C1E	S1E	110.7(4)
F1A	C12A	C11A	112.7(4)	F2E	C1E	F1E	109.5(5)
F2A	C12A	C11A	110.5(4)	F2E	C1E	F3E	107.7(5)
F3A	C12A	F1A	107.9(4)	F3E	C1E	S1E	110.5(4)
F3A	C12A	F2A	107.6(4)	O1FL	S1FL	O2FL	114.1(2)
F3A	C12A	C11A	110.7(4)	O1FL	S1FL	O3FL	115.7(3)
O2A	C13A	C10A	109.9(4)	O1FL	S1FL	C1FL	104.6(3)
O2A	C13A	C14A	107.5(4)	O2FL	S1FL	C1FL	102.5(3)
C10A	C13A	C14A	113.7(4)	O3FL	S1FL	O2FL	114.8(3)
F4A	C14A	F6A	107.4(5)	O3FL	S1FL	C1FL	102.8(2)
F4A	C14A	C13A	112.8(5)	F1FL	C1FL	S1FL	111.4(4)
F5A	C14A	F4A	107.6(5)	F1FL	C1FL	F3FL	108.1(5)
F5A	C14A	F6A	106.7(5)	F2FL	C1FL	S1FL	111.4(4)
F5A	C14A	C13A	112.3(5)	F2FL	C1FL	F1FL	107.7(5)
F6A	C14A	C13A	109.8(4)	F2FL	C1FL	F3FL	108.0(5)
O2D	Zn1D	O1D	141.35(13)	F3FL	C1FL	S1FL	110.2(5)

Table S28 Hydrogen bonds for $[(R,R)\text{-}\mathbf{1}\cdot Zn\cdot 2H_2O]^{2+}\cdot 2OTf^{-}$

D	H	A	d(D-H) (Å)	d(H-A) (Å)	d(D-A) (Å)	D-H-A (°)
O1B	H1B	O1FL[1]	0.879(13)	1.86(2)	2.699(5)	160(5)
O3B	H3BA	O2K	0.85	1.89	2.736(5)	170.7
O3B	H3BB	O1G[1]	0.85	2.27	2.794(6)	119.8
O3B	H3BB	O2M[1]	0.85	2.26	2.96(5)	139.8
O3B	H3BB	O1I	0.85	2.27	2.907(5)	131.4
O4B	H4BA	O3G	0.85	1.92	2.740(7)	161.0
O4B	H4BA	O1M	0.85	1.91	2.63(4)	141.4
O4B	H4BB	O3FL	0.85	1.95	2.795(6)	172.3
O1C	H1C	O3J[2]	0.84	1.83	2.608(6)	154.1
O1C	H1C	O1N[2]	0.84	1.85	2.66(2)	161.4
O2C	H2C	O3H[3]	0.81(7)	1.91(6)	2.688(6)	161(6)
O3C	H3CA	O1J	0.85	1.92	2.754(7)	164.4
O3C	H3CA	O2L	0.85	1.84	2.55(2)	139.6
O3C	H3CB	O2H[2]	0.85	1.92	2.770(6)	172.9
O4C	H4CA	O2F[2]	0.85	1.87	2.699(5)	162.4
O4C	H4CB	O2J[2]	0.85	2.28	2.853(7)	124.4
O4C	H4CB	O3L[2]	0.85	2.14	2.840(18)	138.9
O4C	H4CB	O1E[2]	0.85	2.39	2.933(5)	122.4
O1A	H1A	O1K[4]	0.872(13)	1.87(2)	2.724(5)	166(5)

O2A	H2A	O3K[5]	0.877(13)	1.96(3)	2.719(5)	143(3)
O3A	H3AA	O1I[4]	0.85	1.86	2.706(5)	177.3
O3A	H3AB	O2FL[6]	0.85	1.95	2.744(5)	153.9
O1D	H1D	O1F	0.881(13)	1.862(15)	2.732(5)	169(3)
O2D	H2D	O3F[7]	0.881(13)	1.95(3)	2.728(5)	147(4)
O3D	H3DA	O1E	0.85	1.86	2.707(5)	175.9
O3D	H3DB	O1H[2]	0.85	1.97	2.764(5)	155.0
C7D	H7D	O2F[3]	0.95	2.55	3.412(6)	150.9
O2B	H2B	O2G[1]	0.99(8)	1.76(8)	2.642(6)	147(7)

[1]1-X,-1/2+Y,2-Z; [2]1-X,-1/2+Y,1-Z; [3]+X,-1+Y,+Z; [4]+X,1+Y,+Z; [5]2-X,1/2+Y,2-Z; [6]1-X,1/2+Y,2-Z; [7]2-X,-1/2+Y,1-Z

Table S29 Torsion angles for [(*R*,*R*)-**1**·Zn·$2H_2O]^{2+}\cdot 2OTf^{-}$

A	B	C	D	Angle (˚)	A	B	C	D	Angle (˚)
Zn1B	O1B	C11B	C1B	0.1(5)	C5A	C6A	C7A	C8A	178.7(4)
Zn1B	O1B	C11B	C12B	-122.3(4)	C6A	N2A	C10A	C9A	-3.0(6)
Zn1B	O2B	C13B	C10B	-6.9(5)	C6A	N2A	C10A	C13A	174.0(4)
Zn1B	O2B	C13B	C14B	-129.7(3)	C6A	C7A	C8A	C9A	-1.8(7)
Zn1B	N1B	C1B	C2B	178.2(4)	C7A	C8A	C9A	C10A	1.8(7)
Zn1B	N1B	C1B	C11B	-0.7(6)	C8A	C9A	C10A	N2A	0.6(7)
Zn1B	N1B	C5B	C4B	-177.7(4)	C8A	C9A	C10A	C13A	-176.3(4)
Zn1B	N1B	C5B	C6B	1.0(5)	C9A	C10A	C13A	O2A	-178.2(4)
Zn1B	N2B	C6B	C5B	0.7(5)	C9A	C10A	C13A	C14A	-57.7(6)
Zn1B	N2B	C6B	C7B	-179.4(4)	C10A	N2A	C6A	C5A	-176.4(4)
Zn1B	N2B	C10B	C9B	-179.5(4)	C10A	N2A	C6A	C7A	3.1(6)
Zn1B	N2B	C10B	C13B	-1.8(5)	C10A	C13A	C14A	F4A	-59.9(6)
O1B	C11B	C12B	F1B	66.7(6)	C10A	C13A	C14A	F5A	61.9(6)
O1B	C11B	C12B	F2B	-51.9(6)	C10A	C13A	C14A	F6A	-179.6(5)
O1B	C11B	C12B	F3B	-173.3(5)	C11A	C1A	C2A	C3A	179.0(4)
O2B	C13B	C14B	F4B	65.5(6)	Zn1D	O1D	C11D	C1D	24.0(5)
O2B	C13B	C14B	F5B	-174.9(4)	Zn1D	O1D	C11D	C12D	-96.4(4)
O2B	C13B	C14B	F6B	-54.4(6)	Zn1D	O2D	C13D	C10D	7.3(4)
N1B	C1B	C2B	C3B	-1.3(8)	Zn1D	O2D	C13D	C14D	-116.0(3)
N1B	C1B	C11B	O1B	0.4(6)	Zn1D	N1D	C1D	C2D	-178.4(4)
N1B	C1B	C11B	C12B	121.0(5)	Zn1D	N1D	C1D	C11D	1.6(6)
N1B	C5B	C6B	N2B	-1.2(6)	Zn1D	N1D	C5D	C4D	-179.6(4)
N1B	C5B	C6B	C7B	178.9(4)	Zn1D	N1D	C5D	C6D	1.9(5)
N2B	C6B	C7B	C8B	-1.6(7)	Zn1D	N2D	C6D	C5D	6.6(5)
N2B	C10B	C13B	O2B	5.4(6)	Zn1D	N2D	C6D	C7D	-173.3(3)
N2B	C10B	C13B	C14B	125.8(5)	Zn1D	N2D	C10D	C9D	174.5(3)
C1B	N1B	C5B	C4B	-0.3(7)	Zn1D	N2D	C10D	C13D	-7.5(6)
C1B	N1B	C5B	C6B	178.5(4)	O1D	C11D	C12D	F1D	64.2(6)
C1B	C2B	C3B	C4B	1.0(9)	O1D	C11D	C12D	F2D	-55.7(6)
C1B	C11B	C12B	F1B	-54.6(7)	O1D	C11D	C12D	F3D	-175.3(4)
C1B	C11B	C12B	F2B	-173.2(5)	O2D	C13D	C14D	F4D	59.9(5)
C1B	C11B	C12B	F3B	65.4(6)	O2D	C13D	C14D	F5D	-179.8(4)
C2B	C1B	C11B	O1B	-178.6(5)	O2D	C13D	C14D	F6D	-60.6(5)
C2B	C1B	C11B	C12B	-58.0(7)	N1D	C1D	C2D	C3D	-1.9(8)
C2B	C3B	C4B	C5B	-0.4(8)	N1D	C1D	C11D	O1D	-18.4(6)

C3B	C4B	C5B	N1B	0.0(8)
C3B	C4B	C5B	C6B	-178.7(5)
C4B	C5B	C6B	N2B	177.6(4)
C4B	C5B	C6B	C7B	-2.3(7)
C5B	N1B	C1B	C2B	1.0(7)
C5B	N1B	C1B	C11B	-178.0(4)
C5B	C6B	C7B	C8B	178.3(5)
C6B	N2B	C10B	C9B	-0.3(7)
C6B	N2B	C10B	C13B	177.3(4)
C6B	C7B	C8B	C9B	0.8(8)
C7B	C8B	C9B	C10B	0.2(8)
C8B	C9B	C10B	N2B	-0.4(8)
C8B	C9B	C10B	C13B	-177.9(5)
C9B	C10B	C13B	O2B	-176.9(4)
C9B	C10B	C13B	C14B	-56.5(6)
C10B	N2B	C6B	C5B	-178.5(4)
C10B	N2B	C6B	C7B	1.4(7)
C10B	C13B	C14B	F4B	-55.5(6)
C10B	C13B	C14B	F5B	64.2(6)
C10B	C13B	C14B	F6B	-175.4(4)
C11B	C1B	C2B	C3B	177.6(5)
Zn1C	O1C	C11C	C1C	1.9(5)
Zn1C	O1C	C11C	C12C	-120.5(4)
Zn1C	O2C	C13C	C10C	-4.1(5)
Zn1C	O2C	C13C	C14C	-124.4(4)
Zn1C	N1C	C1C	C2C	-175.6(4)
Zn1C	N1C	C1C	C11C	2.8(5)
Zn1C	N1C	C5C	C4C	177.1(4)
Zn1C	N1C	C5C	C6C	-2.4(5)
Zn1C	N2C	C6C	C5C	2.4(5)
Zn1C	N2C	C6C	C7C	-176.4(3)
Zn1C	N2C	C10C	C9C	177.5(4)
Zn1C	N2C	C10C	C13C	-2.5(6)
O1C	C11C	C12C	F1C	65.3(6)
O1C	C11C	C12C	F2C	-54.5(5)
O1C	C11C	C12C	F3C	-174.4(4)
O2C	C13C	C14C	F4C	69.1(6)
O2C	C13C	C14C	F5C	-170.4(4)
O2C	C13C	C14C	F6C	-50.9(6)
N1C	C1C	C2C	C3C	-1.1(7)
N1C	C1C	C11C	O1C	-2.8(6)
N1C	C1C	C11C	C12C	116.9(5)
N1C	C5C	C6C	N2C	0.0(6)
N1C	C5C	C6C	C7C	178.7(4)
N2C	C6C	C7C	C8C	0.1(7)
N2C	C10C	C13C	O2C	4.1(6)
N2C	C10C	C13C	C14C	123.0(5)
C1C	N1C	C5C	C4C	1.5(7)
C1C	N1C	C5C	C6C	-178.0(4)
N1D	C1D	C11D	C12D	102.9(5)
N1D	C5D	C6D	N2D	-5.8(6)
N1D	C5D	C6D	C7D	174.2(4)
N2D	C6D	C7D	C8D	-2.3(7)
N2D	C10D	C13D	O2D	-1.0(6)
N2D	C10D	C13D	C14D	119.1(5)
C1D	N1D	C5D	C4D	1.0(7)
C1D	N1D	C5D	C6D	-177.5(4)
C1D	C2D	C3D	C4D	1.0(8)
C1D	C11D	C12D	F1D	-55.6(6)
C1D	C11D	C12D	F2D	-175.5(4)
C1D	C11D	C12D	F3D	64.9(6)
C2D	C1D	C11D	O1D	161.6(5)
C2D	C1D	C11D	C12D	-77.2(6)
C2D	C3D	C4D	C5D	0.8(8)
C3D	C4D	C5D	N1D	-1.9(7)
C3D	C4D	C5D	C6D	176.5(4)
C4D	C5D	C6D	N2D	175.8(4)
C4D	C5D	C6D	C7D	-4.3(7)
C5D	N1D	C1D	C2D	0.9(7)
C5D	N1D	C1D	C11D	-179.1(4)
C5D	C6D	C7D	C8D	177.7(4)
C6D	N2D	C10D	C9D	-0.9(6)
C6D	N2D	C10D	C13D	177.0(4)
C6D	C7D	C8D	C9D	0.3(7)
C7D	C8D	C9D	C10D	1.3(7)
C8D	C9D	C10D	N2D	-1.0(7)
C8D	C9D	C10D	C13D	-178.9(4)
C9D	C10D	C13D	O2D	177.0(4)
C9D	C10D	C13D	C14D	-62.9(6)
C10D	N2D	C6D	C5D	-177.4(4)
C10D	N2D	C6D	C7D	2.6(6)
C10D	C13D	C14D	F4D	-62.3(6)
C10D	C13D	C14D	F5D	58.0(6)
C10D	C13D	C14D	F6D	177.3(4)
C11D	C1D	C2D	C3D	178.1(5)
O1J	S1J	C1J	F1J	59.5(7)
O1J	S1J	C1J	F2J	-62.0(7)
O1J	S1J	C1J	F3J	178.6(6)
O2J	S1J	C1J	F1J	-61.3(7)
O2J	S1J	C1J	F2J	177.1(6)
O2J	S1J	C1J	F3J	57.7(7)
O3J	S1J	C1J	F1J	179.7(6)
O3J	S1J	C1J	F2J	58.1(7)
O3J	S1J	C1J	F3J	-61.2(7)
O1L	S1L	C1L	F1L	-57.4(18)
O1L	S1L	C1L	F2L	64.0(18)
O1L	S1L	C1L	F3L	-176.6(16)
O2L	S1L	C1L	F1L	-174.7(16)

C1C	C2C	C3C	C4C	1.5(8)	O2L	S1L	C1L	F2L	-53.2(18)
C1C	C11C	C12C	F1C	-55.3(6)	O2L	S1L	C1L	F3L	66.2(17)
C1C	C11C	C12C	F2C	-175.1(4)	O3L	S1L	C1L	F1L	70.0(18)
C1C	C11C	C12C	F3C	65.0(5)	O3L	S1L	C1L	F2L	-168.5(17)
C2C	C1C	C11C	O1C	175.6(4)	O3L	S1L	C1L	F3L	-49.1(18)
C2C	C1C	C11C	C12C	-64.7(6)	O1G	S1G	C1G	F1G	59.2(6)
C2C	C3C	C4C	C5C	-0.4(8)	O1G	S1G	C1G	F2G	-60.6(6)
C3C	C4C	C5C	N1C	-1.1(7)	O1G	S1G	C1G	F3G	179.2(5)
C3C	C4C	C5C	C6C	178.3(4)	O2G	S1G	C1G	F1G	-60.3(5)
C4C	C5C	C6C	N2C	-179.4(4)	O2G	S1G	C1G	F2G	179.9(5)
C4C	C5C	C6C	C7C	-0.7(7)	O2G	S1G	C1G	F3G	59.6(6)
C5C	N1C	C1C	C2C	-0.3(7)	O3G	S1G	C1G	F1G	-179.4(5)
C5C	N1C	C1C	C11C	178.1(4)	O3G	S1G	C1G	F2G	60.8(5)
C5C	C6C	C7C	C8C	-178.6(4)	O3G	S1G	C1G	F3G	-59.5(6)
C6C	N2C	C10C	C9C	2.4(7)	O1I	S1I	C1I	F1I	53.2(4)
C6C	N2C	C10C	C13C	-177.6(4)	O1I	S1I	C1I	F2I	-68.0(4)
C6C	C7C	C8C	C9C	-0.6(8)	O1I	S1I	C1I	F3I	173.1(4)
C7C	C8C	C9C	C10C	1.9(8)	O2I	S1I	C1I	F1I	-67.4(4)
C8C	C9C	C10C	N2C	-2.9(8)	O2I	S1I	C1I	F2I	171.4(4)
C8C	C9C	C10C	C13C	177.1(5)	O2I	S1I	C1I	F3I	52.4(4)
C9C	C10C	C13C	O2C	-175.9(4)	O3I	S1I	C1I	F1I	171.7(4)
C9C	C10C	C13C	C14C	-57.0(6)	O3I	S1I	C1I	F2I	50.5(4)
C10C	N2C	C6C	C5C	177.8(4)	O3I	S1I	C1I	F3I	-68.5(4)
C10C	N2C	C6C	C7C	-0.9(7)	O1K	S1K	C1K	F1K	59.8(5)
C10C	C13C	C14C	F4C	-50.3(6)	O1K	S1K	C1K	F2K	-60.0(5)
C10C	C13C	C14C	F5C	70.1(6)	O1K	S1K	C1K	F3K	179.6(4)
C10C	C13C	C14C	F6C	-170.4(4)	O2K	S1K	C1K	F1K	-61.8(5)
C11C	C1C	C2C	C3C	-179.5(5)	O2K	S1K	C1K	F2K	178.4(4)
Zn1A	O1A	C11A	C1A	25.4(4)	O2K	S1K	C1K	F3K	58.1(5)
Zn1A	O1A	C11A	C12A	-96.7(4)	O3K	S1K	C1K	F1K	179.4(4)
Zn1A	O2A	C13A	C10A	3.9(5)	O3K	S1K	C1K	F2K	59.6(5)
Zn1A	O2A	C13A	C14A	-120.3(4)	O3K	S1K	C1K	F3K	-60.7(5)
Zn1A	N1A	C1A	C2A	177.1(3)	O1F	S1F	C1F	F1F	54.6(4)
Zn1A	N1A	C1A	C11A	-3.0(6)	O1F	S1F	C1F	F2F	-65.5(5)
Zn1A	N1A	C5A	C4A	-176.3(3)	O1F	S1F	C1F	F3F	174.2(4)
Zn1A	N1A	C5A	C6A	3.6(5)	O2F	S1F	C1F	F1F	-66.6(4)
Zn1A	N2A	C6A	C5A	10.2(5)	O2F	S1F	C1F	F2F	173.2(4)
Zn1A	N2A	C6A	C7A	-170.3(3)	O2F	S1F	C1F	F3F	52.9(4)
Zn1A	N2A	C10A	C9A	169.7(3)	O3F	S1F	C1F	F1F	174.5(4)
Zn1A	N2A	C10A	C13A	-13.3(5)	O3F	S1F	C1F	F2F	54.3(5)
O1A	C11A	C12A	F1A	63.7(5)	O3F	S1F	C1F	F3F	-66.0(4)
O1A	C11A	C12A	F2A	-56.3(5)	O1H	S1H	C1H	F1H	56.1(5)
O1A	C11A	C12A	F3A	-175.3(4)	O1H	S1H	C1H	F2H	-63.7(5)
O2A	C13A	C14A	F4A	61.9(6)	O1H	S1H	C1H	F3H	174.9(4)
O2A	C13A	C14A	F5A	-176.3(5)	O2H	S1H	C1H	F1H	-64.0(5)
O2A	C13A	C14A	F6A	-57.8(6)	O2H	S1H	C1H	F2H	176.1(5)
N1A	C1A	C2A	C3A	-1.0(7)	O2H	S1H	C1H	F3H	54.7(5)
N1A	C1A	C11A	O1A	-17.0(6)	O3H	S1H	C1H	F1H	176.0(5)
N1A	C1A	C11A	C12A	105.8(5)	O3H	S1H	C1H	F2H	56.1(5)

N1A	C5A	C6A	N2A	-9.3(6)	O3H	S1H	C1H	F3H	-65.3(5)
N1A	C5A	C6A	C7A	171.3(4)	O1E	S1E	C1E	F1E	53.4(4)
N2A	C6A	C7A	C8A	-0.7(6)	O1E	S1E	C1E	F2E	-67.6(4)
N2A	C10A	C13A	O2A	4.7(6)	O1E	S1E	C1E	F3E	173.2(4)
N2A	C10A	C13A	C14A	125.3(5)	O2E	S1E	C1E	F1E	-67.6(4)
C1A	N1A	C5A	C4A	1.8(6)	O2E	S1E	C1E	F2E	171.4(4)
C1A	N1A	C5A	C6A	-178.3(4)	O2E	S1E	C1E	F3E	52.2(4)
C1A	C2A	C3A	C4A	1.9(7)	O3E	S1E	C1E	F1E	171.9(4)
C1A	C11A	C12A	F1A	-57.6(5)	O3E	S1E	C1E	F2E	50.8(4)
C1A	C11A	C12A	F2A	-177.6(4)	O3E	S1E	C1E	F3E	-68.3(4)
C1A	C11A	C12A	F3A	63.4(5)	O1FL	S1FL	C1FL	F1FL	63.3(5)
C2A	C1A	C11A	O1A	163.0(4)	O1FL	S1FL	C1FL	F2FL	-56.9(5)
C2A	C1A	C11A	C12A	-74.3(6)	O1FL	S1FL	C1FL	F3FL	-176.7(4)
C2A	C3A	C4A	C5A	-1.0(7)	O2FL	S1FL	C1FL	F1FL	-56.1(5)
C3A	C4A	C5A	N1A	-0.9(7)	O2FL	S1FL	C1FL	F2FL	-176.3(4)
C3A	C4A	C5A	C6A	179.2(4)	O2FL	S1FL	C1FL	F3FL	64.0(4)
C4A	C5A	C6A	N2A	170.7(4)	O3FL	S1FL	C1FL	F1FL	-175.5(5)
C4A	C5A	C6A	C7A	-8.8(7)	O3FL	S1FL	C1FL	F2FL	64.3(5)
C5A	N1A	C1A	C2A	-0.8(7)	O3FL	S1FL	C1FL	F3FL	-55.4(5)
C5A	N1A	C1A	C11A	179.2(4)					

Table S30 Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for [(*R*,*R*)-**1**·Zn·$2H_2O$]$^{2+}$·2OTf$^-$

Atom	*x*	*y*	*z*	U(eq)
H1B	6120(40)	690(15)	9196(13)	53
H3BA	7425.48	1870.64	9733.51	45
H3BB	7264.09	1277.07	10188.73	45
H4BA	4791.04	2831.87	9757.31	48
H4BB	4862.24	2668.62	10334.21	48
H2BA	6157.35	3251.25	7819.51	49
H3B	6341.8	5042.38	7951.2	51
H4B	6479.16	5734.11	8891.13	42
H7B	6616.98	6248.01	9770.91	38
H8B	6656.9	6701.36	10755.5	48
H9B	6497.72	5405.53	11450.96	42
H11B	6435.02	1413.6	8460.16	39
H13B	5738.8	3463.2	11461.83	35
H1C	4088.54	-596.36	3869.72	44
H2C	3840(30)	-1780(50)	5800(20)	24(15)
H3CA	5187.22	292.8	5275.97	48
H3CB	5131.02	100.58	4701.76	48
H4CA	2563.08	-788.33	5210.66	44
H4CB	2777.66	-1299.14	4739.32	44
H2CA	3604.46	2847.28	3553.39	40
H3C	3449.7	4159.35	4236.19	46
H4C	3454.57	3739.19	5223.57	40
H7C	3516.67	3210.61	6122.71	41
H8C	3611.36	2491.83	7060.23	45
H9C	3738.04	695	7183.63	43

H11C	4223.12	889.51	3518.57	36
H13C	3453.35	-1130.22	6524.64	34
H1A	8720(40)	9385(11)	8906(13)	43
H2A	9739(18)	7713(12)	10939(14)	41
H3AA	8085.66	8769.44	10115.69	37
H3AB	7659.37	8202.28	9724.27	37
H4AA	10320.31	7804.93	9856.92	47
H4AB	9986.9	8714.33	9975.38	47
H2AA	8521.1	6818.85	7581.66	33
H3A	8321.92	5014.97	7682.9	39
H4A	8305.7	4298.94	8615	34
H7A	8112.39	3815.59	9493.65	31
H8A	8151.52	3330.57	10470.28	35
H9A	8646.11	4490.26	11188.16	33
H11A	8443.24	8562.47	8114.59	32
H13A	9693.37	6166.27	11217.76	33
H1D	8800(40)	1878(14)	3957(13)	51
H2D	9693(17)	169(14)	5962(14)	42
H3DA	8044	1265.55	5136.9	40
H3DB	7612.69	684.96	4755.75	40
H4DA	10259.68	213.26	4861.6	51
H4DB	9967.15	1109.31	5048.14	51
H2DA	8325.02	-627.98	2608.11	42
H3D	8113.67	-2414.18	2706.21	45
H4D	8213.19	-3186.08	3619.83	39
H7D	8128.93	-3722.77	4496.31	35
H8D	8252.07	-4268.15	5462.66	37
H9D	8701.94	-3100.26	6187.13	36
H11D	8356.98	1101.34	3158.22	40
H13D	9593.97	-1344.73	6280.45	32
H2B	5880(40)	1920(60)	11200(30)	60(20)
H1NA	5554.13	3244.64	6661.87	58
H1NB	5608.84	4298.59	6754.3	58

Table S31 Atomic occupancy for [(*R*,*R*)-**1**·Zn·2H_2O]$^{2+}$·2OTf^{-}

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
S1J	0.785(2)	F1J	0.785(2)	F2J	0.785(2)
F3J	0.785(2)	O1J	0.785(2)	O2J	0.785(2)
O3J	0.785(2)	C1J	0.785(2)	S1L	0.215(2)
F1L	0.215(2)	F2L	0.215(2)	F3L	0.215(2)
O1L	0.215(2)	O2L	0.215(2)	O3L	0.215(2)
C1L	0.215(2)	S1G	0.900(3)	F1G	0.900(3)
F2G	0.900(3)	F3G	0.900(3)	O1G	0.900(3)
O2G	0.900(3)	O3G	0.900(3)	C1G	0.900(3)
S1M	0.100(3)	F1M	0.100(3)	F2M	0.100(3)
F3M	0.100(3)	O1M	0.100(3)	O2M	0.100(3)
O3M	0.100(3)	C1M	0.100(3)	O1N	0.160(11)
H1NA	0.160(11)	H1NB	0.160(11)		