Asymmetric Cooperative Catalysis of Strong Brønsted Acid-Promoted Reactions by Chiral Ureas

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Supporting Information

A. General Information

General Procedures. All reactions were performed in oven-dried or flame-dried round- bottom flasks and vials. Stainless steel syringes or cannulae were used to transfer air- and moisture-sensitive liquids. Flash chromatography was performed using silica gel 60 (230-400 mesh) from EM Science.

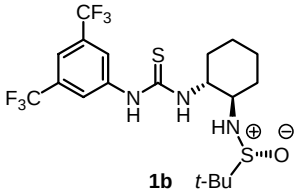
Materials. Commercial reagents were purchased from Sigma Aldrich, Fluka, EM Science, and Lancaster and used as received. All solvents were used after being freshly distilled unless otherwise noted.

Instrumentation. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Varian Mercury-400 (400 MHz), Inova-600 (600 MHz) and Inova-500 (500 MHz) NMR spectrometers. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to the NMR solvent residual peak ($CHCl_3$: δ 7.26). Chemical shifts for carbons are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the NMR solvent ($CDCl_3$: δ 77.0). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet), coupling constants in Hertz (Hz), and integration.
The mass spectroscopic data were obtained at the Harvard University mass spectrometry facility using a Micromass Platform II single quadrupole instrument. Infrared (IR) spectra were obtained using a Mattson Galaxy Series FTIR 3000 spectrophotometer referenced to a polystyrene standard. Data are represented as follows: frequency of absorption (cm^{-1}). Optical rotations were measured using a 2 mL cell with a 1 dm path length on a Jasco DIP 370 polarimeter at 589 nm, and are reported as $[\alpha]_D$ (concentration in grams/100 mL solvent). Chiral SFC analysis was performed on a Berger instrument. Chiral HPLC analysis was performed using a Shimadzu VP-series instrument.

Abbreviations used: EtOH – ethanol, EtOAc – ethyl acetate, THF – tetrahydrofuran, MeOH – methanol, Et_2O – diethyl ether, TEA – triethylamine, MS – molecular sieves, TLC – thin layer chromatography, *dr* – diastereomeric ratio, *ee* – enantiomeric excess, SFC – supercritical fluid chromatography.

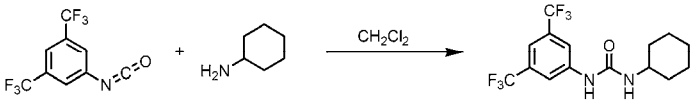
B. Synthesis of Catalysts:

Catalysts were prepared following a published procedure. (*1*)



Catalyst **1b**. ^{1}H NMR (500 MHz, $CDCl_3$): δ ppm 9.61 (s, 1 H) 8.32 (d, *J* = 7.78 Hz, 1 H) 7.98 (s, 2 H) 7.28 (s, 1 H) 6.29 (d, *J* = 2.75 Hz, 1 H) 4.45 (dd, *J* = 7.44, 3.32 Hz, 1 H) 2.96 - 3.04 (m, 1 H) 2.13 - 2.21 (m, 1 H) 2.01 - 2.09 (m, 1 H) 1.78 - 1.90 (m, 2 H) 1.27 - 1.57 (m, 4 H) 1.25 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$): δ ppm 182.2, 140.4, 131.1, 130.9, 122.0, 116.9, 63.9, 56.0, 55.8, 35.7, 32.9, 24.7, 24.5, 23.1. HRMS (ESI) calculated for $C_{19}H_{25}F_6N_3OS_2$ $[M+Na]^+$: 512.1241. Found 512.1247.

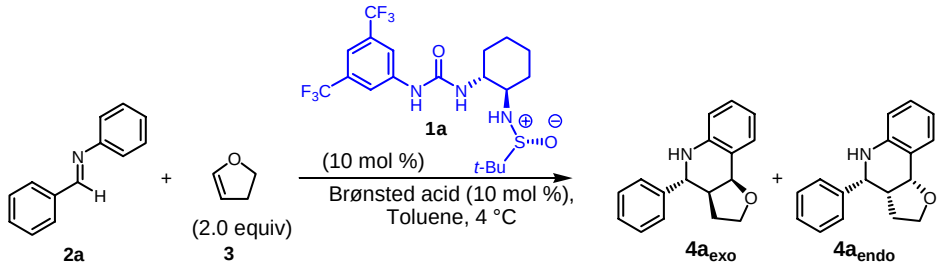
1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylurea (15).



A 10-ml round-bottomed flask equipped with a stir bar was charged with 3,5-bis(trifluoromethyl)phenyl isocyanate (0.61 mL, 3.5 mmol, 1.0 equiv) and CH_2Cl_2 (4.0 mL). Cyclohexylamine (0.59 ml, 5.2 mmol, 1.5 equiv) was added dropwise over 10 min with stirring. A white precipitate forms during addition of the amine. The reaction mixture was stirred for 30 min, concentrated under reduced pressure, and subjected to purification by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 12:1 to 8:1) to afford the product as a white powder (1.3 g, 3.6 mmol, quantitative yield). The product was further purified by recrystallization from 10:1 toluene/ethyl acetate (98% recovery). IR (film) ν_{max}, 3350 (br m), 2490 (m), 1658 (s), 1573 (s), 1545 (s), 1389 (s), 1272 (s), 1228 (m), 1176 (m), 1127 (s), 1047 (m) cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): δ 8.39 (1H, s) 8.13 (2H, s) 7.50 (1H, d, *J* = 0.8 Hz) 5.94 (1H, d, 1.6 Hz) 3.50–3.70 (1H, m), 1.86 - 1.96 (2H, m) 1.65 - 1.75 (2H, m) 1.54 - 1.63 (1H, m), 1.28 - 1.42 (2H, m) 1.14 - 1.29 (3H, m); ^{13}C NMR (100 MHz, acetone- d_6): δ ppm 154.8, 143.7, 132.3, 124.5, 118.3, 114.6, 49.5, 33.9, 26.3, 5.6. IR (thin film, cm^{-1}): 3350 (br m), 2490 (m), 2856 (w), 1658 (s), 1626 (w), 1573 (s), 1545 (s), 1477 (m), 1440 (w), 1389 (s), 1307 (w), 1272 (s), 1228 (m), 1176 (m), 1127 (s), 1047 (m), 1000

(w), 939 (m), 912 (w), 874 (s), 848 (w), 762 (w), 700 (s), 679 (s). LRMS (ESI) calculated for $C_{15}H_{17}F_6N_2O_2$ $[M+H]^+$: 355.1. Found 355.2.

C. Brønsted Acid Co-catalyst Structure-Reactivity/Enantioselectivity Studies of the Model Povarov Reaction



entry	Brønsted acid	reaction time (h)	dr (**exo**/**endo**)	**exo** ee (%)	**endo** ee (%)
a	HCl	26	0.5	56	29
b	HBr	20	1.0	61	31
c	HI	20	2.0	52	27
d	(+)CSA	16	2.0	79	44
e	(-)CSA	16	2.2	77	46
f	MsOH	16	1.3	66	13
g	TsOH	48	1.6	80	46
h	TfOH	3	2.0	81	24
i	NBSA	48	4.0	91	46
j	AcOH	48	NA	NA	NA
k	BzOH	48	NA	NA	NA
l	H_3PO_4	48	NA	NA	NA

Table S1. Brønsted acid co-catalyst structure-reactivity/enantioselectivity studies of the model Povarov reaction. NBSA =2-nitrobenzenesulfonic acid.

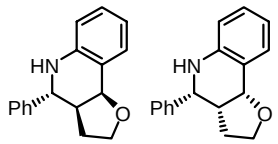
D. General Procedure for the Preparation of Racemic 4-Phenyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinolines

An 8 mL oven-dried vial was charged with *N*-benzylideneaniline **2a** (18 mg, 0.1 mmol) and toluene (1 mL) under a nitrogen atmosphere at room temperature. The mixture was cooled to –30 °C. Trifluoromethanesulfonic acid (TfOH) (0.15 mL of a 0.1 M diethyl ether stock solution) and 2,3-dihydrofuran **3** (15 μL, 0.2 mmol) were added dropwise carefully and the resulting solution was stirred

vigorously and gradually warmed up to 0 °C within 3 h. The reaction was quenched with pre-cooled TEA (0 °C, 140 μL, 1.0 mmol). The mixture was purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give **4a$_{exo}$/4a$_{endo}$** = (ca. 1 : 2) (21 mg, 86%) as a white foam.

E. General Procedure for the Preparation of Enantioenriched 4-Phenyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinolines

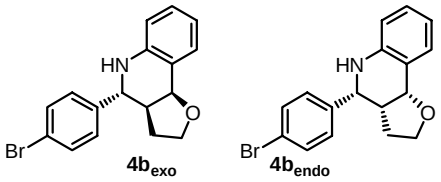
An 8 mL oven-dried vial was charged with *N*-benzylideneaniline **2a** (18 mg, 0.1 mmol), catalyst **1a** (4.7 mg, 0.01 mmol) and toluene (1 mL) under a nitrogen atmosphere at room temperature. The mixture was cooled to –55 °C. TfOH (0.15 mL of a 0.1 M diethyl ether stock solution) and dihydrofuran **3** (15 μL, 0.2 mmol) were added dropwise sequentially and the resulting solution was stirred vigorously for 48 h. The reaction was quenched with pre-cooled TEA (–30 °C, 140 μL, 1.0 mmol). The mixture was purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give **4a$_{exo}$/4a$_{endo}$** = (ca. 4 : 1) (21 mg, 86%) as a white foam.



4a$_{exo}$ **4a$_{endo}$**

4-phenyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinolines (**4a$_{exo}$/4a$_{endo}$**). The products were prepared by the general procedure. The reaction was run on 0.5 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give the title compounds **4a$_{exo}$/4a$_{endo}$** (4:1 *exo*/*endo*) as a foamy white solid (107 mg, 86%). The enantiomeric excesses of the *exo* and *endo* diastereomers were determined to be 96% and 34%, respectively, by chiral SFC (Daicel Chiralcel OD-H, 10% MeOH/CO_2, 4 ml/min, 240 nm, t_r(*exo* major): 4.1 min, t_r(*endo* major): 5.7 min, t_r(*endo* minor): 6.5 min, t_r(*exo* minor): 7.2 min). ^{1}H NMR (600 MHz, $CDCl_3$): *exo diastereomer* δ ppm 7.39-7.51 (m, 6 H) 7.17 (t, *J* = 7.8 Hz, 1 H) 6.84 (t, *J* = 7.2 Hz, 1 H) 6.67 (d, *J* = 7.8 Hz, 1 H) 4.65 (d, *J* = 4.8 Hz, 1 H) 4.18 (br. s., 1 H) 4.07 (td, *J* = 8.4, 6.6 Hz, 1 H) 3.89 (td, *J* = 9.0, 6.0 Hz, 1 H) 3.84 (d, *J* = 10.8 Hz, 1 H) 2.51 (m, 1 H) 2.06 (m, 1 H) 1.76 (m, 1 H); *endo diastereomer* δ ppm 7.39-7.51(m, 6 H) 7.13 (t, *J* = 7.8 Hz, 1 H) 6.85 (t, *J* = 7.2 Hz, 1 H) 6.64 (d, *J* = 7.8 Hz, 1 H) 5.32 (d, *J* = 7.8 Hz, 1 H) 4.74 (d, *J* = 3 Hz, 1 H) 3.87 (m, 1 H) 3.83 (s, 1 H) 3.76 (m, 1 H) 2.83 (m, 1 H) 2.25 (m, 1 H) 1.56 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): *exo diastereomer* δ ppm 145.3, 141.6, 131.1, 128.8, 128.5, 128.2, 128.0, 119.9, 118.2, 114.6, 76.1, 65.0, 57.6, 43.2, 28.7; *endo diastereomer* δ ppm 144.8, 142.1, 129.9, 128.5, 128.2,

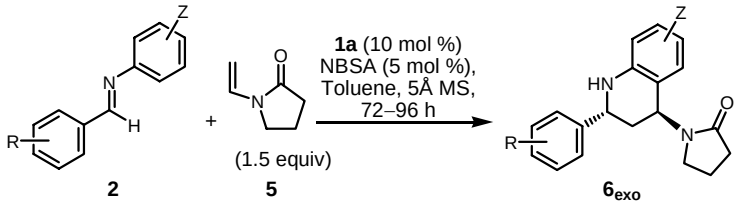
127.5, 126.4, 122.5, 119.0, 114.8, 75.8, 66.6, 57.3, 45.6, 24.5. HRMS (ESI) calculated for $C_{17}H_{18}NO$ $[M+H]^+$: 252.1388. Found 252.1386.



$\mathbf{4b_{exo}}$ $\mathbf{4b_{endo}}$

4-(4-bromophenyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinolines (**$\mathbf{4b_{exo}}$/$\mathbf{4b_{endo}}$**). The general procedure described above was performed on 1.0 mmol scale. The reaction was run at –30 ºC for 24 h. Chromatography on silica gel (hexanes:EtOAc, gradient from 20:1 to 4:1) yielded the title compounds (**$\mathbf{4b_{exo}}$/$\mathbf{4b_{endo}}$**) (4:1 *exo/endo*) as a white solid (309 mg, 94%). The enantiomeric excesses of the *exo* and *endo* diastereomers were determined to be 94% and 43%, respectively, by chiral SFC (Daicel Chiralcel OD-H, 20% MeOH/CO_2, 4 ml/min, 240 nm, t_r(*exo* major): 4.2 min, t_r(*endo* major): 5.0 min, t_r(*endo* minor): 6.2 min, t_r(*exo* minor): 8.9 min). ^{1}H NMR (600 MHz, $CDCl_3$): *exo diastereomer* δ ppm 7.56 (d, *J* = 7.2 Hz, 2 H) 7.44 (d, *J* = 7.8 Hz, 1 H) 7.36 (d, *J* = 7.2 Hz, 2 H) 7.17 (t, *J* = 7.8 Hz, 1 H) 6.85 (t, *J* = 8.4 Hz, 1 H) 6.67 (d, *J* = 8.4 Hz, 1 H) 4.63 (d, *J* = 5.4 Hz, 1 H) 4.13 (br. s., 1 H) 4.06 (td, *J* = 8.4, 6.0 Hz, 1 H) 3.88 (td, *J* = 9.0, 6.0 Hz, 1 H) 3.81 (d, *J* = 11.4 Hz, 1 H) 2.45 (m, 1 H) 2.06 (m, 1 H) 1.71 (m, 1 H); *endo diastereomer* δ ppm 7.56 (m, 2 H) 7.39 (d, *J* = 7.2 Hz, 2 H) 7.37 (m, 1 H) 7.14 (t, *J* = 7.8 Hz, 1 H) 6.87 (t, *J* = 8.4 Hz, 1 H) 6.65 (d, *J* = 8.4 Hz, 1 H) 5.31 (d, *J* = 7.8 Hz, 1 H) 4.71 (d, *J* = 2.4 Hz, 1 H) 3.88 (br. s., 1 H) 3.86 (m, 1 H) 2.78 (m, 1 H) 2.19 (m, 1 H) 1.54 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 145.4, 141.1, 132.0, 131.5, 130.2, 129.3, 122.2, 120.2, 118.8, 115.0, 76.3, 65.4, 57.4, 43.6, 29.0. HRMS (ESI) calculated for $C_{17}H_{17}BrNO$ $[M+H]^+$: 330.0493. Found 330.0483.

F. General Procedure for the Preparation of Enantioenriched and Racemic 1-(2-Phenyl-1,2,3,4-tetrahydroquinolin-4-yl)pyrrolidin-2-ones



entry	R	Z	yield (%)	ee (%)
a	3-Cl	H	90	98
b	3-Br	H	92	95
c	3,5-$(OMe)_2$	H	78	98
d	H	4-CO_2Me	75	96
e	H	H	92	97
f	4-F	H	72	95
g	4-Cl	H	87	97
h	4-Br	H	87	96
i	H	4-Cl	85	98
j	H	4-Br	87	98
k	H	3,5-$(Me)_2$	81	98
l	4-Me	H	84	97
m	3-Me	H	88	98
n	3,5-$(Me)_2$	H	86	99
o	H	4-Me	83	96

Table S2. Substrate scope of the asymmetric Povarov reaction between **2** and **5**. Reactions were carried out in toluene (0.1 M) at -60 °C for entries a–d; at -40 °C for entries e–k; at -30 °C for entries l–o. Isolated yields were obtained after purification using silica gel chromatography. Ee values were measured by chiral SFC analysis on commercial columns. NBSA =2-nitrobenzenesulfonic acid.

Method A:

An 8 mL oven-dried vial was charged with *N*-(3-chlorobenzylidene)benzenamine (43 mg, 0.2 mmol), 2-nitro-benzenesulfonic acid (2.0 mg, 0.01 mmol), catalyst **1a** (9.4 mg, 0.02 mmol), activated 5Å molecular sieves (40 mg) and toluene (2 mL) under a nitrogen atmosphere at room temperature. The mixture was cooled to –60 °C and stirred for 10 min. 1-vinylpyrrolidin-2-one **5** (0.30 mL of a 1.0 M toluene stock solution, 0.30 mmol) was added dropwise carefully and the resulting solution was stirred vigorously for 60 h. The reaction was quenched with pre-cooled TEA (–60 °C, 280 μL, 2.0 mmol). The mixture was purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to give **$6a_{exo}$** (59 mg, 90%) as a white foam.

Equal amounts of catalyst **1a** and its enantiomer were used to prepare the racemic sample of **6a$_{exo}$**.

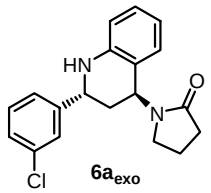
Method B:

An 8 mL oven-dried vial was charged with *N*-benzylidenebenzenamine (36 mg, 0.2 mmol), 2-nitro-benzenesulfonic acid (2.0 mg, 0.01 mmol), catalyst **1a** (9.4 mg, 0.02 mmol), activated 5Å molecular sieves (40 mg) and toluene (2 mL) under a nitrogen atmosphere at room temperature. The mixture was cooled to –40 °C and stirred for 10 min. 1-vinylpyrrolidin-2-one **5** (0.30 mL of a 1.0 M toluene stock solution, 0.30 mmol) was added dropwise carefully and the resulting solution was stirred vigorously for 72 h. The reaction was quenched with pre-cooled TEA (–40 °C, 280 μL, 2.0 mmol). The mixture was purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 1:1) to give **6e$_{exo}$** (53 mg, 92%) as a colorless oil.
Equal amounts of catalyst **1a** and its enantiomer were used to prepare the racemic sample of **6e$_{exo}$**.

Method C:

An 8 mL oven-dried vial was charged with *N*-(4-methylbenzylidene)benzenamine (39 mg, 0.2 mmol), 2-nitro-benzenesulfonic acid (2.0 mg, 0.01 mmol), catalyst **1a** (9.4 mg, 0.02 mmol), activated 5Å molecular sieves (40 mg) and toluene (2 mL) under a nitrogen atmosphere at room temperature. The mixture was cooled to –30 °C and stirred for 10 min. 1-vinylpyrrolidin-2-one **5** (0.30 mL of a 1.0 M toluene stock solution, 0.30 mmol) was added dropwise carefully and the resulting solution was stirred vigorously for 96 h. The reaction was quenched with pre-cooled TEA (–30 °C, 280 μL, 2.0 mmol). The mixture was purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to give **6l$_{exo}$** (51 mg, 84%) as a white foam.

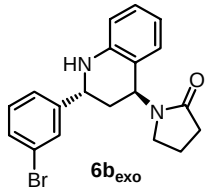
Equal amounts of catalyst **1a** and its enantiomer were used to prepare the racemic sample of **6l$_{exo}$**.



6a$_{exo}$

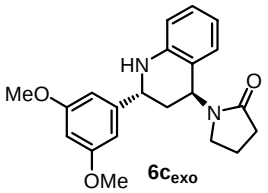
1-((2*R*,4*S*)-2-(3-chlorophenyl)-1,2,3,4-tetrahydroquinolin-4-yl)pyrrolidin-2-one (6a$_{exo}$). The product

was prepared by Method A. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to afford **6a$_{exo}$** (59 mg, 90%) as a colorless oil. **6a$_{exo}$** was determined to be 98% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 22% MeOH, t_r(minor) = 6.29 min, t_r(major) = 5.46 min). $[\alpha]^{25}_D$ = –72.2° (c = 2.5, CH_2Cl_2); IR (film) ν_{max}, 3358 (m), 3306 (m), 1667 (s), 1608 (s), 1494 (s), 1422 (m), 1316 (s), 1285 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.35 (s, 1 H) 7.21 - 7.29 (m, 3 H) 7.10 (t, *J* = 7.55 Hz, 1 H) 6.98 (d, *J* = 7.55 Hz, 1 H) 6.70 (t, *J* = 7.44 Hz, 1 H) 6.62 (d, *J* = 8.01 Hz, 1 H) 5.21 (t, *J* = 4.92 Hz, 1 H) 4.42 (dd, *J* = 9.96, 3.32 Hz, 1 H) 4.27 (br. s., 1 H) 3.32 - 3.39 (m, 1 H) 3.12 - 3.20 (m, 1 H) 2.45 (t, *J* = 8.13 Hz, 2 H) 2.23 - 2.31 (m, 1 H) 1.90 - 2.13 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 174.8, 145.6, 144.7, 134.4, 129.9, 129.2, 128.8, 127.8, 126.6, 124.5, 117.8, 114.5, 52.9, 46.1, 45.5, 36.1, 31.4, 18.3; HRMS (ESI-TOF) for $C_{19}H_{19}ClN_2O$ [M + Na^+] calcd 349.1078, found 349.1079.



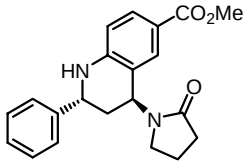
6b$_{exo}$

1-((2*R*,4*S*)-2-(3-bromophenyl)-1,2,3,4-tetrahydroquinolin-4-yl)pyrrolidin-2-one (6b$_{exo}$). The product was prepared by Method A. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to afford **6b$_{exo}$** (68 mg, 92%) as a colorless oil. **6b$_{exo}$** was determined to be 95% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 22% MeOH, t_r(minor) = 7.25 min, t_r(major) = 6.21 min). $[\alpha]^{25}_D$ = –61.3° (c = 2.4, CH_2Cl_2); IR (film) ν_{max}, 3315 (m), 2950 (m), 2928 (m), 1672 (s), 1608 (s), 1493 (s), 1421 (m), 1316 (m), 1285 (s), 1271 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.50 (s, 1 H) 7.40 (dd, *J* = 7.78, 0.92 Hz, 1 H) 7.28 (d, *J* = 7.78 Hz, 1 H) 7.20 (t, *J* = 7.78 Hz, 1 H) 7.09 (t, *J* = 7.67 Hz, 1 H) 6.98 (d, *J* = 7.55 Hz, 1 H) 6.70 (t, *J* = 7.44 Hz, 1 H) 6.61 (d, *J* = 8.01 Hz, 1 H) 5.21 (t, *J* = 4.92 Hz, 1 H) 4.40 (dd, *J* = 10.07, 3.43 Hz, 1 H) 4.27 (br. s., 1 H) 3.31 - 3.40 (m, 1 H) 3.12 - 3.20 (m, 1 H) 2.45 (t, *J* = 8.01 Hz, 2 H) 2.23 - 2.30 (m, 1 H) 1.90 - 2.12 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 174.8, 145.8, 144.7, 130.7, 130.3, 129.5, 129.3, 128.8, 125.0, 122.7, 117.8, 117.5, 114.5, 52.9, 46.0, 45.5, 36.2, 31.4, 18.3; HRMS (ESI-TOF) for $C_{19}H_{19}BrN_2O$ [M + Na^+] calcd 393.0573, found 393.0575.



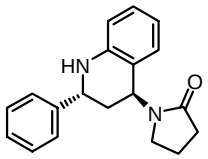
6c$_{exo}$

1-((2*R*,4*S*)-2-(3,5-dimethoxyphenyl)-1,2,3,4-tetrahydroquinolin-4-yl)pyrrolidin-2-one (6c$_{exo}$). The product was prepared by Method A. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to afford **6c$_{exo}$** (54 mg, 78%) as a colorless oil. **6c$_{exo}$** was determined to be 98% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 22% MeOH, t_r(minor) = 7.94 min, t_r(major) = 7.05 min). $[\alpha]^{25}_D$ = –68.1° (c = 1.5, CH_2Cl_2); IR (film) ν_{max}, 3336 (m), 2935 (m), 1672 (s), 1607 (s), 1597 (m), 1461 (s), 1428 (m), 1204 (m), 1155 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.06 - 7.16 (m, 1 H) 7.00 (d, *J* = 7.55 Hz, 1 H) 6.69 (t, *J* = 7.33 Hz, 1 H) 6.60 (d, *J* = 8.01 Hz, 1 H) 6.51 (d, *J* = 2.29 Hz, 2 H) 6.38 (t, *J* = 2.17 Hz, 1 H) 5.26 (t, *J* = 4.81 Hz, 1 H) 4.36 (dd, *J* = 10.19, 3.55 Hz, 1 H) 4.20 (br. s., 1 H) 3.77 (s, 6 H) 3.35 - 3.41 (m, 1 H) 3.14 - 3.20 (m, 1 H) 2.44 - 2.49 (m, 2 H) 2.25 - 2.31 (m, 1 H) 2.09 - 2.16 (m, 1 H) 1.91 - 2.03 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 174.7, 161.0, 145.9, 145.0, 129.5, 128.8, 117.7, 114.6, 110.7, 104.4, 99.4, 55.3, 53.6, 46.3, 36.3, 31.5, 18.4; HRMS (ESI-TOF) for $C_{21}H_{24}N_2O_3$ [M + Na^+] calcd 375.1679, found 375.1685.



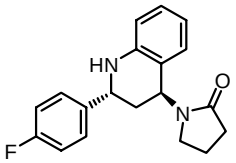
6d$_{exo}$

(2*R*,4*S*)-methyl-4-(2-oxopyrrolidin-1-yl)-2-phenyl-1,2,3,4-tetrahydroquinoline-6-carboxylate (6d$_{exo}$). The product was prepared by Method A. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to afford **6d$_{exo}$** (52 mg, 75%) as a colorless oil. **6d$_{exo}$** was determined to be 96% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 20% MeOH, t_r(minor) = 12.71 min, t_r(major) = 11.04 min). $[\alpha]^{25}_D$ = –105.8° (c = 0.9, CH_2Cl_2); IR (film) ν_{max}, 3350 (m), 2949 (m), 1704 (s), 1610 (s), 1519 (s), 1435 (m), 1286 (s), 1258 (m), 1194 (m), 1102 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.79 (dd, *J* = 8.47, 2.06 Hz, 1 H) 7.70 (d, *J* = 1.83 Hz, 1 H) 7.27 - 7.46 (m, 5 H) 6.58 (d, *J* = 8.47 Hz, 1 H) 5.22 (t, *J* = 5.04 Hz, 1 H) 4.71 (br. s., 1 H) 4.52 (dd, *J* = 9.39, 3.89 Hz, 1 H) 3.84 (s, 3 H) 3.30 - 3.38 (m, 1 H) 3.11 - 3.19 (m, 1 H) 2.44 - 2.52 (m, 2 H) 2.32 - 2.39 (m, 1 H) 1.96 - 2.13 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 177.0, 167.0, 142.3, 131.4, 130.8, 128.8, 128.0, 126.3, 122.2, 118.7, 116.5, 113.5, 53.3, 51.6, 46.2, 45.6, 35.3, 31.4, 18.4; HRMS (ESI-TOF) for $C_{21}H_{22}FN_2O_3$ [M + K^+] calcd 389.1262, found 389.1272.



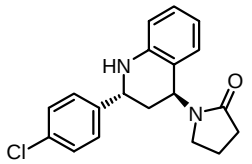
6e$_{exo}$

1-((2*R*,4*S*)-2-phenyl-1,2,3,4-tetrahydroquinolin-4-yl)pyrrolidin-2-one (6e$_{exo}$). The product was prepared by Method B. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to afford **6e$_{exo}$** (53 mg, 92%) as a colorless oil. **6e$_{exo}$** was determined to be 97% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 22% MeOH, t_r(minor) = 6.27 min, t_r(major) = 5.48 min). $[\alpha]^{25}_D$ = –79.7° (c = 1.2, CH_2Cl_2); IR (film) ν_{max}, 3346 (m), 3025 (m), 2972 (m), 1667 (s), 1608 (s), 1492 (m), 1420 (m), 1316 (m), 1279 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ ppm 7.27 - 7.39 (m, 5 H) 7.10 (t, *J* = 7.67 Hz, 1 H) 7.01 (d, *J* = 7.33 Hz, 1 H) 6.70 (t, *J* = 7.44 Hz, 1 H) 6.61 (d, *J* = 8.01 Hz, 1 H) 5.26 (t, *J* = 4.81 Hz, 1 H) 4.44 (dd, *J* = 10.07, 3.43 Hz, 1 H) 4.21 (br. s., 1 H) 3.33 - 3.48 (m, 1 H) 3.12 - 3.26 (m, 1 H) 2.47 (t, *J* = 8.01 Hz, 2 H) 2.24 - 2.35 (m, 1 H) 2.09 - 2.20 (m, 1 H) 1.90 - 2.08 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 174.7, 145.2, 143.4, 129.5, 128.7, 127.7, 126.4, 117.6, 114.4, 53.4, 46.2, 45.6, 36.3, 31.5, 18.4; HRMS (ESI-TOF) for $C_{19}H_{20}N_2O$ [M + H^+] calcd 293.1648, found 293.1648.



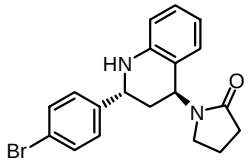
6f$_{exo}$

1-((2*R*,4*S*)-2-(4-fluorophenyl)-1,2,3,4-tetrahydroquinolin-4-yl)pyrrolidin-2-one (6f$_{exo}$). The product was prepared by Method B. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to afford **6f$_{exo}$** (45 mg, 72%) as a colorless oil. **6f$_{exo}$** was determined to be 95% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 22% MeOH, t_r(minor) = 5.37 min, t_r(major) = 4.89 min). $[\alpha]^{25}_D$ = –80.8° (c = 0.6, CH_2Cl_2); IR (film) ν_{max}, 3334 (m), 2930 (m), 1667 (s), 1607 (s), 1508 (m), 1280 (m), 1222 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ ppm 7.29 - 7.36 (m, 2 H) 7.10 (t, *J* = 7.67 Hz, 1 H) 6.97 - 7.07 (m, 3 H) 6.71 (t, *J* = 7.33 Hz, 1 H) 6.61 (d, *J* = 8.01 Hz, 1 H) 5.24 (t, *J* = 4.92 Hz, 1 H) 4.44 (dd, *J* = 9.96, 3.55 Hz, 1 H) 4.18 (br. s., 1 H) 3.32 - 3.42 (m, 1 H) 3.12 - 3.24 (m, 1 H) 2.46 (t, *J* = 8.01 Hz, 2 H) 2.23 - 2.31 (m, 1 H) 1.91 - 2.14 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 174.8, 161.2, 144.9, 139.2, 129.4, 128.8, 128.0, 127.9, 117.8, 115.4, 114.5, 52.8, 46.2, 45.6, 35.4, 31.5, 18.4; HRMS (ESI-TOF) for $C_{19}H_{19}FN_2O$ [M + Na^+] calcd 333.1373, found 333.1371.



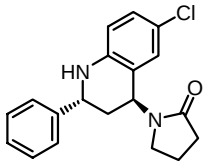
6g$_{exo}$

1-((2*R*,4*S*)-2-(4-chlorophenyl)-1,2,3,4-tetrahydroquinolin-4-yl)pyrrolidin-2-one (6g$_{exo}$). The product was prepared by Method B. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to afford **6g$_{exo}$** (56 mg, 87%) as a colorless oil. **6g$_{exo}$** was determined to be 97% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 22% MeOH, t_r(minor) = 7.75 min, t_r(major) = 6.90 min). $[\alpha]^{25}_D$ = -88.2° (c = 2.5, CH_2Cl_2); IR (film) ν_{max}, 3326 (m), 2990 (m), 2887 (m), 1663 (s), 1608 (m), 1485(s), 1320 (m), 1288 (s), 1268 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.27 - 7.32 (m, 4 H) 7.08 - 7.13 (m, 1 H) 6.98 (d, *J* = 7.33 Hz, 1 H) 6.68 - 6.73 (m, 1 H) 6.61 (d, *J* = 8.24 Hz, 1 H) 5.21 (t, *J* = 5.15 Hz, 1 H) 4.43 (dd, *J* = 9.73, 3.55 Hz, 1 H) 4.24 (br. s., 1 H) 3.26 - 3.53 (m, 1 H) 3.10 - 3.22 (m, 1 H) 2.45 (t, *J* = 8.13 Hz, 2 H) 2.23 - 2.30 (m, 1 H) 1.89 - 2.12 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 174.7, 144.8, 141.9, 33.2, 129.2, 128.7, 127.7, 117.8, 114.5, 52.8, 46.0, 45.5, 36.0, 31.4, 18.4; HRMS (ESI-TOF) for $C_{19}H_{19}ClN_2O$ [M + Na^+] calcd 349.1078, found 349.1083.



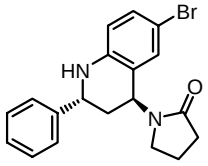
6h$_{exo}$

1-((2*R*,4*S*)-2-(4-bromophenyl)-1,2,3,4-tetrahydroquinolin-4-yl)pyrrolidin-2-one (6h$_{exo}$). The product was prepared by Method B. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to afford **6h$_{exo}$** (64 mg, 87%) as a colorless oil. **6h$_{exo}$** was determined to be 96% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 22% MeOH, t_r(minor) = 8.50 min, t_r(major) = 7.53 min). $[\alpha]^{25}_D$ = –78.5° (c = 1.9, CH_2Cl_2); IR (film) ν_{max}, 3324 (m), 2911 (m), 1664 (s), 1608 (s), 1591 (s), 1487 (s), 1421 (m), 1318 (m), 1286 (s), 1266 (m), 1009 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.45 (d, *J* = 8.47 Hz, 2 H) 7.23 (d, *J* = 8.47 Hz, 2 H) 7.10 (t, *J* = 7.55 Hz, 1 H) 6.98 (d, *J* = 7.55 Hz, 1 H) 6.70 (t, *J* = 7.44 Hz, 1 H) 6.61 (d, *J* = 8.24 Hz, 1 H) 5.21 (t, *J* = 5.15 Hz, 1 H) 4.42 (dd, *J* = 9.73, 3.55 Hz, 1 H) 4.25 (br. s., 1 H) 3.32 - 3.38 (m, 1 H) 3.12 - 3.20 (m, 1 H) 2.45 (t, *J* = 8.01 Hz, 2 H) 2.22 - 2.32 (m, 1 H) 1.90 - 2.13 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 174.7, 144.8, 142.5, 131.7, 129.2, 128.8, 128.0, 121.4, 117.8, 117.5, 114.5, 52.9, 46.1, 45.5, 35.9, 31.4, 18.4; HRMS (ESI-TOF) for $C_{19}H_{19}BrN_2O$ [M + Na^+] calcd 393.0573, found 393.0576.



6i$_{exo}$

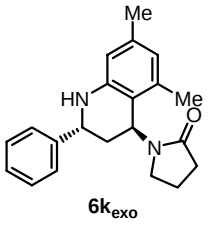
1-((2*R*,4*S*)-6-chloro-2-phenyl-1,2,3,4-tetrahydroquinolin-4-yl)pyrrolidin-2-one (6i$_{exo}$). The product was prepared by Method B. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to afford **6i$_{exo}$** (55 mg, 85%) as a colorless oil. **6i$_{exo}$** was determined to be 98% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 22% MeOH, t_r(minor) = 7.63 min, t_r(major) = 6.59 min). $[\alpha]^{25}_D$ = –83.1° (c = 3.1, CH_2Cl_2); IR (film) ν_{max}, 3336 (m), 1667 (s), 1605 (m), 1490 (m), 1420 (s), 1285 (m), 1269 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ ppm 7.25 - 7.37 (m, 5 H) 7.03 (dd, *J* = 8.58, 2.40 Hz, 1 H) 6.95 (d, *J* = 2.29 Hz, 1 H) 6.54 (d, *J* = 8.70 Hz, 1 H) 5.19 (t, *J* = 5.27 Hz, 1 H) 4.43 (dd, *J* = 9.61, 3.66 Hz, 1 H) 4.34 (br. s., 1 H) 3.35 - 3.42 (m, 1 H) 3.16 - 3.23 (m, 1 H) 2.44 (t, *J* = 8.13 Hz, 2 H) 2.23 - 2.30 (m, 1 H) 1.96 - 2.14 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 174.8, 143.7, 142.9, 128.7, 128.5, 127.8, 126.2, 126.2, 122.0, 119.1, 115.6, 53.4, 45.7, 45.2, 35.6, 31.2, 18.3; HRMS (ESI-TOF) for $C_{19}H_{19}ClN_2O$ [M + Na^+] calcd 349.1078, found 349.1078.



6j$_{exo}$

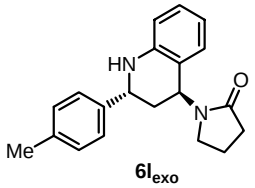
1-((2*R*,4*S*)-6-bromo-2-phenyl-1,2,3,4-tetrahydroquinolin-4-yl)pyrrolidin-2-one (6j$_{exo}$). The product was prepared by Method B. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to afford **6j$_{exo}$** (64 mg, 87%) as a colorless oil. **6j$_{exo}$** was determined to be 98% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 22% MeOH, t_r(minor) = 8.80 min, t_r(major) = 7.53 min). $[\alpha]^{25}_D$ = –75.1° (c = 2.5, CH_2Cl_2); IR (film) ν_{max}, 3326 (m), 2920 (m), 1667 (s), 1600 (s), 1487 (m), 1420 (s), 1311 (m), 1280 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ ppm 7.27 - 7.39 (m, 5 H) 7.17 (dd, *J* = 8.47, 2.29 Hz, 1 H) 7.09 (d, *J* = 2.29 Hz, 1 H) 6.50 (d, *J* = 8.47 Hz, 1 H) 5.20 (t, *J* = 5.15 Hz, 1 H) 4.43 (dd, *J* = 9.39, 3.66 Hz, 1 H) 4.32 (br. s., 1 H) 3.35 - 3.42 (m, 1 H) 3.16 - 3.24 (m, 1 H) 2.43 - 2.48 (m, 2 H) 2.22 - 2.31 (m, 1 H) 1.94 - 2.14 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 174.8, 144.2, 142.9, 131.5, 131.4, 128.7, 127.8, 126.3, 119.7, 116.0, 109.0, 53.5, 45.7, 45.3, 35.6, 31.2, 18.4; HRMS (ESI-TOF) for $C_{19}H_{19}BrN_2O$ [M + Na^+]

calcd 393.05733, found 393.0570.



6k$_{exo}$

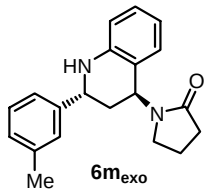
1-((2*R*,4*S*)-5,7-dimethyl-2-phenyl-1,2,3,4-tetrahydroquinolin-4-yl)pyrrolidin-2-one (6k$_{exo}$). The product was prepared by Method B. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to afford **6k$_{exo}$** (51 mg, 81%) as a colorless oil. **6k$_{exo}$** was determined to be 98% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 20% MeOH, t_r(minor) = 5.51 min, t_r(major) = 5.19 min). $[\alpha]^{25}_D$ = –89.3° (c = 4.1, CH_2Cl_2); IR (film) ν_{max}, 3325 (m), 2948 (m), 1671 (s), 1614 (m), 1584 (m), 1474 (s), 1416 (m), 1282 (s) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.23 - 7.48 (m, 5 H) 6.40 (s, 1 H) 6.28 (s, 1 H) 5.21 (dd, *J* = 4.24, 1.95 Hz, 1 H) 4.34 (dd, *J* = 12.48, 2.86 Hz, 1 H) 4.16 (br. s., 1 H) 3.34 - 3.45 (m, 1 H) 2.92 - 3.02 (m, 1 H) 2.42 - 2.50 (m, 2 H) 2.27 - 2.35 (m, 1 H) 2.22 (s, 3 H) 2.10 (s, 3 H) 1.85 - 2.07 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 174.1, 145.1, 143.4, 138.5, 138.0, 128.6, 127.7, 126.5, 120.3, 112.8, 112.0, 52.8, 47.4, 45.4, 38.3, 31.4, 21.0, 18.6; HRMS (ESI-TOF) for $C_{21}H_{24}N_2O$ [M + Na^+] calcd 343.1781, found 343.1785.



6l$_{exo}$

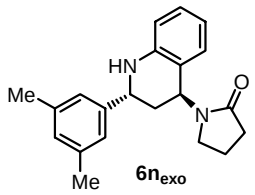
1-((2*R*,4*S*)-2-*p*-tolyl-1,2,3,4-tetrahydroquinolin-4-yl)pyrrolidin-2-one (6l$_{exo}$). The product was prepared by Method C. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to afford **6l$_{exo}$** (51 mg, 84%) as a colorless oil. **6l$_{exo}$** was determined to be 97% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 22% MeOH, t_r(minor) = 6.84 min, t_r(major) = 5.83 min). $[\alpha]^{25}_D$ = –84.4° (c = 0.6, CH_2Cl_2); IR (film) ν_{max}, 3325 (m), 2926 (m), 1668 (s), 1608 (m), 1494 (m), 1421 (s), 1317 (m), 1279 (s), 1129 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 6.86 - 6.94 (m, 2 H) 6.77 - 6.83 (m, 2 H) 6.71 - 6.76 (m, 1 H) 6.65 (d, *J* = 7.55 Hz, 1 H) 6.31 - 6.37 (m, 1 H) 6.24 (d, *J* = 8.01 Hz, 1 H) 4.90 (t, *J* = 4.81 Hz, 1 H) 4.05 (dd, *J* = 10.19, 3.32 Hz, 1 H) 3.77 - 3.89 (m, 1 H) 3.00 - 3.09 (m, 1 H) 2.78 - 2.88 (m, 1 H) 2.11 (t, *J* = 8.24 Hz, 2 H) 1.99 (s, 3 H) 1.88 - 1.93 (m, 1 H) 1.56 - 1.82 (m, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 174.7, 145.3, 137.4, 129.5, 128.7, 126.3, 117.6, 114.4, 110.7, 53.2, 46.4, 45.7, 36.4, 31.5, 21.1, 18.4;

HRMS (ESI-TOF) for $C_{20}H_{22}N_2O$ [M + Na^+] calcd 329.1624, found 329.1629.



6m$_{exo}$

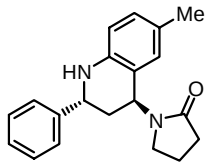
1-((2*R*,4*S*)-2-*m*-tolyl-1,2,3,4-tetrahydroquinolin-4-yl)pyrrolidin-2-one (6m$_{exo}$). The product was prepared by Method C. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to afford **6m$_{exo}$** (54 mg, 88%) as a colorless oil. **6m$_{exo}$** was determined to be 97% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 22% MeOH, t_r(minor) = 5.95 min, t_r(major) = 5.10 min). $[\alpha]^{25}_D$ = –108.0° (c = 3.0, $CHCl_3$); IR (film) ν_{max}, 3325 (m), 2953 (m), 2927 (m), 1673 (s), 1608 (s), 1493 (m), 1421 (s), 1317 (m), 1286 (s), 1270 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.23 (t, *J* = 7.44 Hz, 1 H) 7.13 - 7.19 (m, 2 H) 7.07 - 7.12 (m, 2 H) 7.01 (d, *J* = 7.55 Hz, 1 H) 6.69 (t, *J* = 7.44 Hz, 1 H) 6.60 (d, *J* = 8.01 Hz, 1 H) 5.25 (t, *J* = 4.69 Hz, 1 H) 4.39 (dd, *J* = 10.30, 3.43 Hz, 1 H) 4.24 (br. s., 1 H) 3.37 - 3.44 (m, 1 H) 3.15 - 3.22 (m, 1 H) 2.46 (t, *J* = 8.24 Hz, 2 H) 2.35 (s, 3 H) 2.24 - 2.30 (m, 1 H) 2.09 - 2.16 (m, 1 H) 1.89 - 2.07 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 174.7, 145.2, 143.3, 138.3, 129.4, 128.7, 128.5, 128.4, 127.0, 123.4, 117.5, 114.4, 53.3, 46.3, 45.7, 36.4, 31.4, 21.4; HRMS (ESI-TOF) for $C_{20}H_{22}N_2O$ [M + Na^+] calcd 329.1624, found 329.1631.



6n$_{exo}$

1-((2*R*,4*S*)-2-(3,5-dimethylphenyl)-1,2,3,4-tetrahydroquinolin-4-yl)pyrrolidin-2-one (6n$_{exo}$). The product was prepared by Method C. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to afford **6n$_{exo}$** (55 mg, 86%) as a colorless oil. **6n$_{exo}$** was determined to be 99% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 22% MeOH, t_r(minor) = 6.41 min, t_r(major) = 5.31 min). $[\alpha]^{25}_D$ = –86.9° (c = 3.3, CH_2Cl_2); IR (film) ν_{max}, 3325 (m), 2950 (m), 2920 (m), 1668 (s), 1609 (s), 1493 (m), 1421 (m), 1270 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.08-7.11 (m, 1 H) 7.02 (d, *J* = 7.10 Hz, 1 H) 6.98 (s,

2 H) 6.93 (s, 1 H) 6.66 - 6.72 (m, 1 H) 6.59 - 6.62 (m, 1 H) 5.26 (t, *J* = 4.58 Hz, 1 H) 4.35 (dd, *J* = 10.53, 3.43 Hz, 1 H) 4.21 (br. s., 1 H) 3.38 - 3.44 (m, 1 H) 3.15 - 3.21 (m, 1 H) 2.44 - 2.49 (m, 2 H) 2.31 (s, 6 H) 2.23 - 2.28 (m, 1 H) 2.08 - 2.15 (m, 1 H) 1.90 - 2.03 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 174.6, 145.3, 143.3, 138.2, 129.3, 128.7, 124.1, 117.5, 114.3, 53.3, 46.4, 45.8, 36.6, 31.4, 21.2, 18.3; HRMS (ESI-TOF) for $C_{21}H_{24}N_2O$ [M + Na^+] calcd 343.1780, found 343.1785.



6o$_{exo}$

1-((2*R*,4*S*)-6-methyl-2-phenyl-1,2,3,4-tetrahydroquinolin-4-yl)pyrrolidin-2-one (6o$_{exo}$). The product was prepared by Method C. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to afford **6o$_{exo}$** (50 mg, 83%) as a colorless oil. **6o$_{exo}$** was determined to be 96% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 22% MeOH, t_r(minor) = 5.59 min, t_r(major) = 5.05 min). $[\alpha]^{25}_D$ = –84.1° (c = 2.2, CH_2Cl_2); IR (film) ν_{max}, 3336 (m), 2952 (m), 1670 (s), 1508 (m), 1284 (s), 1269 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.23 - 7.42 (m, 5 H) 6.92 (dd, *J* = 8.13, 1.95 Hz, 1 H) 6.83 (s, 1 H) 6.53 (d, *J* = 8.01 Hz, 1 H) 5.24 (t, *J* = 4.81 Hz, 1 H) 4.41 (dd, *J* = 10.30, 3.43 Hz, 1 H) 4.10 (br. s., 1 H) 3.37 - 3.46 (m, 1 H) 3.14 - 3.26 (m, 1 H) 2.43 - 2.53 (m, 2 H) 2.22 - 2.25 (m, 2 H) 2.22 (s, 3 H) 2.08 - 2.18 (m, 1 H) 1.91 - 2.07 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ppm 174.7, 143.5, 142.9, 129.6, 129.5, 128.6, 127.6, 126.9, 126.4, 117.6, 114.5, 53.6, 46.2, 45.6, 36.6, 31.5, 20.4, 18.3; HRMS (ESI-TOF) for $C_{20}H_{22}N_2O$ [M + Na^+] calcd 329.1624, found 329.1630.

G. General Procedure for the Preparation of Racemic Benzyl 4-Phenyl-3,3a,4,5-tetrahydro-2*H*-pyrrolo[3,2-*c*]quinoline-1(9b*H*)-carboxylates

An 8 mL oven-dried vial was charged with *N*-benzylidenebenzenamine (18 mg, 0.1 mmol), benzyl 2,3-dihydropyrrole-1-carboxylate **7** (0.15 mL of a 1.0 M toluene stock solution, 0.15 mmol), activated 5Å molecular sieves (20 mg) and toluene (1 mL) under a nitrogen atmosphere at room temperature. The mixture was cooled to –30 °C. TfOH (0.05 mL of a 0.1 M ethyl ether stock solution) was added dropwise carefully and the resulting solution was stirred vigorously and gradually warmed up to 0 °C within 3 h. The reaction was quenched with pre-cooled TEA (0 °C, 140 μL, 1.0 mmol). The mixture was purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give **8e$_{exo}$** (21 mg, 57%) as a colorless oil and **8e$_{endo}$** (10 mg, 28%) as a white foam.

H. General Procedure for the Preparation of Enantioenriched Benzyl 4-Phenyl-3,3a,4,5-tetrahydro-2*H*-pyrrolo[3,2-*c*]quinoline-1(9b*H*)-carboxylates

Method D:

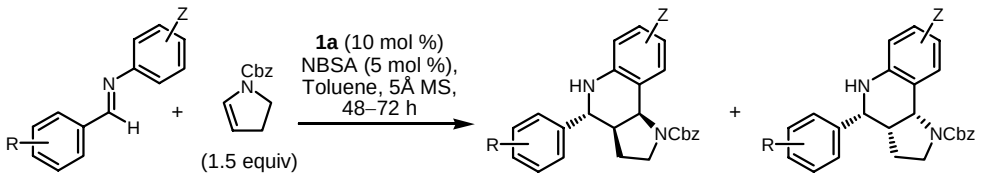
An 8 mL oven-dried vial was charged with *N*-(3-chlorobenzylidene)benzenamine (43 mg, 0.2 mmol), 2-nitro-benzenesulfonic acid (2.0 mg, 0.01 mmol), catalyst **1a** (9.4 mg, 0.02 mmol), activated 5Å molecular sieves (40 mg) and toluene (2 mL) under a nitrogen atmosphere at room temperature. The mixture was cooled to –60 °C and stirred for 10 min. Benzyl 2,3-dihydropyrrole-1-carboxylate **8** (0.30 mL of a 1.0 M toluene stock solution, 0.30 mmol) was added dropwise carefully and the resulting solution was stirred vigorously for 48 h. The reaction was quenched with pre-cooled TEA (–60 °C, 280 μL, 2.0 mmol). The mixture was purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give **8a**$_{\mathbf{exo}}$ (59 mg, 71%) as a white foam and **8a**$_{\mathbf{endo}}$ (16 mg, 19%) as a white foam.

Method E:

An 8 mL oven-dried vial was charged with *N*-benzylidenebenzenamine (36 mg, 0.2 mmol), 2-nitro-benzenesulfonic acid (2.0 mg, 0.01 mmol), catalyst **1a** (9.4 mg, 0.02 mmol), activated 5Å molecular sieves (40 mg) and toluene (2 mL) under a nitrogen atmosphere at room temperature. The mixture was cooled to –40 °C and stirred for 10 min. Benzyl 2,3-dihydropyrrole-1-carboxylate **7** (0.30 mL of a 1.0 M toluene stock solution, 0.30 mmol) was added dropwise carefully and the resulting solution was stirred vigorously for 60 h. The reaction was quenched with pre-cooled TEA (–40 °C, 280 μL, 2.0 mmol). The mixture was purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give **8e**$_{\mathbf{exo}}$ (42 mg, 57%) as a colorless oil and **8e**$_{\mathbf{endo}}$ (20 mg, 28%) as a white foam.

Method F:

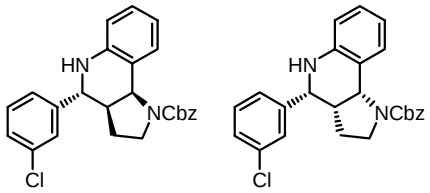
An 8 mL oven-dried vial was charged with *N*-(4-methylbenzylidene)benzenamine (39 mg, 0.2 mmol), 2-nitro-benzenesulfonic acid (2.0 mg, 0.01 mmol), catalyst **1a** (9.4 mg, 0.02 mmol), activated 5Å molecular sieves (40 mg) and toluene (2 mL) under a nitrogen atmosphere at room temperature. The mixture was cooled to –30 °C and stirred for 10 min. Benzyl 2,3-dihydropyrrole-1-carboxylate **7** (0.30 mL of a 1 M toluene stock solution, 0.30 mmol) was added dropwise carefully and the resulting solution was stirred vigorously for 72 h. The reaction was quenched with pre-cooled TEA (–30 °C, 280 μL, 2.0 mmol). The mixture was purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give **8l**$_{\mathbf{exo}}$ (42 mg, 54%) as a colorless oil and **8l**$_{\mathbf{endo}}$ (27 mg, 33%) as a white foam.



2 **7** **8_{exo}** **8_{endo}**

entry	R	Z	8_{exo} isolated yield (%)	dr (8_{exo}/8_{endo})	8_{exo} ee (%)
a	3-Cl	H	71	3.8	96
b	3-Br	H	73	4.2	96
c	3,5-$(OMe)_2$	H	53	2.1	98
d	H	4-CO_2Me	47	1.5	90
e	H	H	57	2.0	94
f	4-F	H	53	2.5	95
g	4-Cl	H	60	2.3	95
h	4-Br	H	60	2.5	97
i	H	4-Cl	62	3.6	93
j	H	4-Br	64	3.8	91
k	H	3,5-$(Me)_2$	45	1.4	96
l	4-Me	H	54	1.6	96
m	3-Me	H	55	1.6	95
n	3,5-$(Me)_2$	H	50	1.4	97

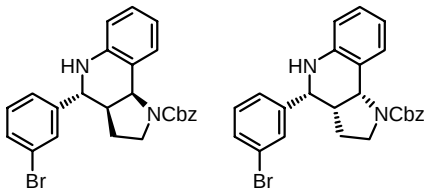
Table S3. Substrate scope of the asymmetric Povarov reaction between **2** and **7**. Reactions were carried out in toluene (0.1 M) at -60 °C for entries a–d; at -40 °C for entries e–k; at -30 °C for entries l–n. Isolated yields were obtained after purification using silica gel chromatography. ee values were measured by chiral SFC analysis on commercial columns. NBSA =2-nitrobenzenesulfonic acid. Cbz = carbobenzyloxy.



$8a_{exo}$ **$8a_{endo}$**

Benzyl-4-(3-chlorophenyl)-3,3a,4,5-tetrahydro-2*H*-pyrrolo[3,2-*c*]quinoline-1(9b*H*)-carboxylates ($8a_{exo}$/$8a_{endo}$). The products were prepared by Method D. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give **$8a_{exo}$** (59 mg, 71%) as a white foam and **$8a_{endo}$** (16 mg, 19%) as a white foam. **$8a_{exo}$** was determined to be 96% ee by Chiral HPLC analysis (Pirkle Covalent (*S*, *S*) Whelk, 1.0 mL/min, 230 nm, 20% EtOH/Hexanes, t_r(minor) = 12.00 min, t_r(major) = 10.29 min). $[\alpha]^{25}_D$ = –173.6° (c = 2.8, CH_2Cl_2); IR

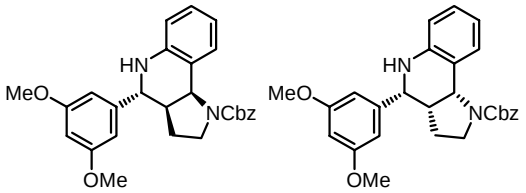
(film) ν_{max}, 3369 (m), 3058 (m), 2955 (m), 2892 (m), 1680 (s), 1607 (m), 1495 (s), 1359 (s), 1110 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.28 - 7.55 (m, 6 H) 7.18 - 7.25 (m, 3 H) 7.15 (dd, *J* = 6.07, 2.17 Hz, 1 H) 7.08 (t, *J* = 7.55 Hz, 1 H) 6.70 (br. s., 1 H) 6.58 (d, *J* = 8.01 Hz, 1 H) 5.23 (br. s., 1 H) 5.11 - 5.20 (m, 1 H) 4.89 (br. s., 1 H) 4.37 (br. s., 1 H) 4.26 (br. s., 1 H) 3.60 (q, *J* = 9.00 Hz, 1 H) 3.44 (br. s., 1 H) 2.56 - 2.65 (m, 1 H) 2.03 - 2.16 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 154.9, 146.9, 142.0, 134.5, 130.0, 128.4, 127.9, 127.5, 126.1, 123.9, 118.2, 113.5, 66.9, 55.3, 52.9, 44.8, 23.3; HRMS (ESI-TOF) for $C_{25}H_{23}ClN_2O_2$ [M + H^+] calcd 419.1520, found 419.1513. **8a$_{endo}$**: IR (film) ν_{max}, 3367 (m), 3032 (m), 2937 (m), 2892 (m), 1668 (s), 1607 (s), 1475 (s), 1319 (s), 1111 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.71 (d, *J* = 7.78 Hz, 0.6 H) 7.28 - 7.57 (m, 9.4 H) 7.08 (q, *J* = 7.86 Hz, 1 H) 6.79 (t, *J* = 7.44 Hz, 0.6 H) 6.70 (t, *J* = 7.33 Hz, 0.4 H) 6.56 - 6.65 (m, 1 H) 5.47 (d, *J* = 7.33 Hz, 0.6 H) 5.39 (d, *J* = 7.10 Hz, 0.4 H) 5.24 - 5.35 (m, 1 H) 5.15 - 5.25 (m, 1 H) 4.70 (d, *J* = 2.52 Hz, 1 H) 3.86 - 3.96 (m, 1 H) 3.32 - 3.56 (m, 2 H) 2.50 - 2.62 (m, 1 H) 2.07 - 2.27 (m, 1 H) 1.48 - 1.64 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 156.5, 143.9, 143.8, 143.3, 143.2, 139.1, 136.9, 134.6, 130.5, 129.9, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7, 126.6, 124.7, 124.6, 122.3, 121.1, 119.4, 119.0, 114.9, 114.8, 67.2, 66.9, 56.8, 56.5, 56.1, 55.8, 44.9, 44.8, 44.6, 44.1, 22.7, 21.7; HRMS (ESI-TOF) for $C_{25}H_{23}ClN_2O_2$ [M + H^+] calcd 419.1520, found 419.1518.



8b$_{exo}$ **8b$_{endo}$**

Benzyl-4-(3-bromophenyl)-3,3a,4,5-tetrahydro-2*H*-pyrrolo[3,2-*c*]quinoline-1(9b*H*)-carboxylates (8b$_{exo}$/8b$_{endo}$). The products were prepared by Method D. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give **8b$_{exo}$** (68 mg, 73%) as a white foam and **8b$_{endo}$** (16 mg, 18%) as a white foam. **8b$_{exo}$** was determined to be 96% ee by Chiral HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 230 nm, 20% EtOH/Hexanes, t_r(minor) = 16.30 min, t_r(major) = 18.20 min). $[\alpha]^{25}_D$ = –175.8° (c = 1.6, CH_2Cl_2); IR (film) ν_{max}, 3341 (m), 2973 (m), 1689 (s), 1475 (s), 1358 (m), 1300 (s), 1107 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.28 - 7.60 (m, 8 H) 7.18 - 7.25 (m, 1 H) 7.14 (t, *J* = 7.78 Hz, 1 H) 7.05 - 7.11 (m, 1 H) 6.70 (br. s., 1 H) 6.58 (dd, *J* = 8.01, 0.92 Hz, 1 H) 5.08 - 5.43 (m, 2 H) 4.89 (br. s., 1 H) 4.36 (br. s., 1 H) 4.27 (br. s., 1 H) 3.54 - 3.68 (m, 1 H) 3.44 (d, *J* = 6.18 Hz, 1 H) 2.55 - 2.66 (m, 1 H) 2.06 - 2.17 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 155.4, 147.2, 144.8, 141.9, 130.4, 129.1, 128.4, 128.3, 127.9, 124.3, 122.7,

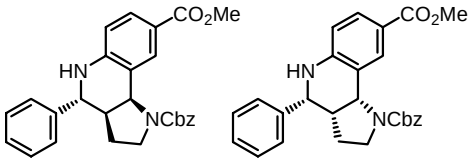
118.1, 113.5, 66.9, 55.3, 52.9, 44.8, 23.3; HRMS (ESI-TOF) for $C_{25}H_{23}BrN_2O_2$ [M + Na^+] calcd 485.0835, found 485.0830. **8b$_{endo}$**: IR (film) ν_{max}, 3366 (m), 2935 (m), 1693 (s), 1475 (s), 1414 (m), 1352 (s), 1263 (s), 1107 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.71 (d, *J* = 7.78 Hz, 0.6 H) 7.59 - 7.65 (m, 1 H) 7.43 - 7.49 (m, 2 H) 7.29 - 7.43 (m, 5 H) 7.23 - 7.28 (m, 1.4 H) 7.04 - 7.11 (m, 1 H) 6.79 (t, *J* = 7.44 Hz, 0.6 H) 6.69 (t, *J* = 7.44 Hz, 0.4 H) 6.56 - 6.62 (m, 1 H) 5.46 (d, *J* = 7.33 Hz, 0.6 H) 5.39 (d, *J* = 6.87 Hz, 0.4 H) 5.24 - 5.34 (m, 1 H) 5.17 - 5.24 (m, 2 H) 4.69 (d, *J* = 2.29 Hz, 1 H) 3.83 - 3.93 (m, 1 H) 3.34 - 3.52 (m, 2 H) 2.51 - 2.60 (m, 1 H) 2.07 - 2.25 (m, 1 H) 1.50 - 1.60 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 156.5, 155.3, 144.1, 144.0, 143.2, 142.6, 136.9, 136.6, 130.9, 130.8, 130.6, 130.2, 129.8, 129.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 127.7, 122.8, 122.4, 119.4, 119.0, 114.9, 114.8, 67.2, 66.9, 56.8, 56.6, 56.0, 55.8, 44.9, 44.8, 44.6, 44.2, 22.7, 21.7; HRMS (ESI-TOF) for $C_{25}H_{23}BrN_2O_2$ [M + K^+] calcd 501.0574, found 501.0576.



8c$_{exo}$ **8c$_{endo}$**

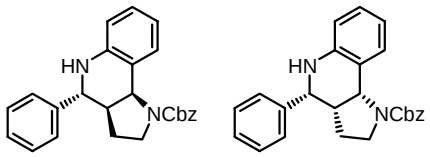
Benzyl-4-(3,5-dimethoxyphenyl)-3,3a,4,5-tetrahydro-2*H*-pyrrolo[3,2-*c*]quinoline-1(9b*H*)-carboxylates (8c$_{exo}$/8c$_{endo}$). The products were prepared by Method D. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give **8c$_{exo}$** (48 mg, 53%) as a colorless oil and **8c$_{endo}$** (21 mg, 26%) as a white foam. **8c$_{exo}$** was determined to be 98% ee by Chiral HPLC analysis (ChiralCel OD-H, 1.0 mL/min, 230 nm, 20% EtOH/Hexanes, t_r(minor) = 23.96 min, t_r(major) = 28.30 min). $[\alpha]^{25}_D$ = –170.9° (c = 2.3, CH_2Cl_2); IR (film) ν_{max}, 3360 (m), 2952 (m), 1607 (s), 1596 (s), 1457 (s), 1414 (m), 1204 (s), 1156 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.28 - 7.68 (m, 6 H) 7.06 (t, *J* = 7.44 Hz, 1 H) 6.60 - 6.87 (m, 1 H) 6.51 - 6.61 (m, 1 H) 6.42 (d, *J* = 2.29 Hz, 2 H) 6.33 (t, *J* = 2.17 Hz, 1 H) 5.21-5.29 (m, 1 H) 5.11 - 5.20 (m, 1 H) 4.92 (br. s., 1 H) 4.30 (d, *J* = 2.98 Hz, 1 H) 4.23 (br. s., 1 H) 3.72 (s, 6 H) 3.54 - 3.64 (m, 1 H) 3.38 - 3.48 (m, 1 H) 2.58 - 2.68 (m, 1 H) 2.06 - 2.17 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 161.0, 158.8, 147.4, 142.6, 142.5, 130.6, 128.4, 128.3, 127.8, 117.9, 113.5, 104.0, 98.7, 66.9, 56.0, 55.2, 53.3, 44.8, 28.1; HRMS (ESI-TOF) for $C_{27}H_{28}N_2O_4$ [M + Na^+] calcd 467.1941, found 467.1942. **8c$_{endo}$**: IR (film) ν_{max}, 3366 (m), 2997 (m), 1693 (s), 1607 (s), 1412 (s), 1337 (m), 1204 (s), 1175 (m), 1155 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.72 (d, *J* = 7.78 Hz, 0.6 H) 7.28 - 7.57 (m, 5.4 H) 7.07 (q, *J* = 7.71 Hz, 1 H) 6.77 (t, *J* = 7.44 Hz, 0.6 H) 6.65 - 6.73 (m, 0.4 H) 6.50 - 6.65 (m, 3 H) 6.42 (br. s., 1 H) 5.46 (d, *J* = 7.33 Hz, 0.6 H) 5.39 (d, *J* = 6.87 Hz, 0.4 H) 5.25 - 5.35 (m, 1 H) 5.16 - 5.24

(m, 1 H) 4.65 (br. s., 1 H) 3.94 (d, *J* = 14.42 Hz, 1 H) 3.81 (s, 6 H) 3.33 - 3.53 (m, 2 H) 2.51 - 2.63 (m, 1 H) 2.08 - 2.26 (m, 1 H) 1.54 - 1.68 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 160.9, 156.5, 144.2, 144.1, 143.5, 136.9, 136.6, 130.5, 129.8, 128.4, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 122.3, 121.1, 119.0, 118.7, 114.8, 114.7, 99.3, 99.2, 67.0, 66.8, 56.6, 56.4, 56.2, 55.3, 45.0, 44.9, 44.6, 44.2, 22.9, 21.9; HRMS (ESI-TOF) for $C_{27}H_{28}N_2O_4$ [M + K^+] calcd 467.1680, found 467.1680.



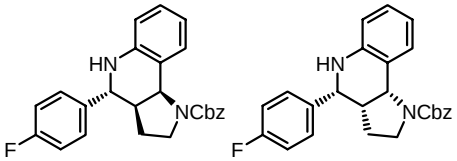
8d$_{exo}$ **8d$_{endo}$**

1-Benzyl-8-methyl-4-phenyl-3,3a,4,5-tetrahydro-2*H*-pyrrolo[3,2-*c*]quinoline-1,8(9b*H*)-dicarboxylate (8d$_{exo}$/8d$_{endo}$). The products were prepared by Method D. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to give **8d$_{exo}$** (42 mg, 47%) as a colorless oil and **8d$_{endo}$** (28 mg, 32%) as a white foam. **8d$_{exo}$** was determined to be 90% ee by Chiral HPLC analysis (ChiralPak AS-H, 1.0 mL/min, 230 nm, 10% EtOH/Hexanes, t_r(minor) = 17.91 min, t_r(major) = 19.63 min). $[\alpha]^{25}_D$ = –227.1° (c = 2.75, CH_2Cl_2); IR (film) ν_{max}, 3343 (m), 2950 (m), 1682 (s), 1610 (s), 1435 (s), 1328 (s), 1301 (m), 1281 (s), 1249 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 8.39 (br. s., 0.4 H) 8.17 (br. s., 0.6 H) 7.78 (dd, *J* = 8.47, 2.06 Hz, 1 H) 7.09 - 7.53 (m, 10 H) 6.57 (d, *J* = 8.47 Hz, 1 H) 5.11 - 5.35 (m, 2 H) 4.84 - 4.98 (m, 1 H) 4.80 (br. s., 1 H) 4.47 (br. s., 1 H) 3.80 (s, 3 H) 3.53 - 3.65 (m, 1 H) 3.43 (t, *J* = 9.39 Hz, 1 H) 2.54 - 2.65 (m, 1 H) 2.10 - 2.19 (m, 1 H) 1.97 - 2.09 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 167.2, 156.5, 146.4, 144.0, 132.3, 130.0, 128.8, 128.4, 127.8, 127.5, 125.5, 119.1, 112.9, 67.1, 55.4, 52.7, 51.5, 44.8, 28.0; HRMS (ESI-TOF) for $C_{27}H_{26}N_2O_4$ [M + Na^+] calcd 465.1785, found 465.1781. **8d$_{endo}$**: IR (film) ν_{max}, 3343 (m), 2975 (m), 1592 (s), 1514 (s), 1453 (s), 1359 (s), 1328 (s), 1242 (m), 1176 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 8.32 (s, 0.5 H) 8.23 (s, 0.5 H) 7.75 (d, *J* = 8.47 Hz, 1 H) 7.48 - 7.57 (m, 1 H) 7.29 - 7.45 (m, 9 H) 6.56 (dd, *J* = 8.47, 1.83 Hz, 1 H) 5.43 (d, *J* = 7.10 Hz, 0.5 H) 5.18 - 5.36 (m, 2.5 H) 4.77 (dd, *J* = 10.19, 2.63 Hz, 1 H) 4.42 (d, *J* = 15.80 Hz, 1 H) 3.83 (s, 1.5 H) 3.82 (br. s., 1.5 H) 3.33 - 3.50 (m, 2 H) 2.54 (br. s., 1 H) 1.99 - 2.15 (m, 1 H) 1.51 - 1.63 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 167.1, 166.9, 156.6, 155.5, 147.4, 147.3, 140.9, 140.8, 136.9, 132.5, 132.3, 130.0, 128.8, 128.6, 128.5, 128.4, 128.1, 127.8, 126.4, 121.2, 120.5, 120.2, 114.1, 67.6, 67.0, 56.5, 56.3, 56.1, 56.0, 51.6, 45.1, 44.9, 44.4, 43.9, 23.1, 22.2; HRMS (ESI-TOF) for $C_{27}H_{26}N_2O_4$ [M + Na^+] calcd 465.1785, found 465.1780.



8e$_{exo}$ **8e$_{endo}$**

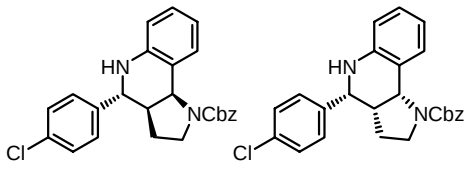
Benzyl-4-phenyl-3,3a,4,5-tetrahydro-2*H*-pyrrolo[3,2-*c*]quinoline-1(9b*H*)-carboxylates (8e$_{exo}$/8e$_{endo}$). The products were prepared by Method E. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give **8e$_{exo}$** (42 mg, 57%) as a colorless oil and **8e$_{endo}$** (20 mg, 28%) as a white foam. **8e$_{exo}$** was determined to be 94% ee by Chiral SFC analysis (ChiralPak AS-H, 3.0 mL/min, 230 nm, 12% MeOH, t_r(minor) = 8.95 min, t_r(major) = 7.66 min). $[\alpha]^{25}_D = -196.8°$ (c = 2.8, CH_2Cl_2); IR (film) ν_{max}, 3362 (m), 2951 (m), 2890 (m), 1695 (s), 1607 (s), 1497 (m), 1359 (s), 1299 (s), 1157 (m), 1029 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.44 - 7.64 (m, 0.4 H) 7.15 - 7.43 (m, 10.6 H) 7.09 (t, *J* = 7.55 Hz, 1 H) 6.70 (br. s., 1 H) 6.59 (dd, *J* = 8.01, 0.92 Hz, 1 H) 5.08 - 5.33 (m, 2 H) 4.92 (br. s., 1 H) 4.39 (d, *J* = 3.20 Hz, 1 H) 4.28 (br. s., 1 H) 3.60 (t, *J* = 8.81 Hz, 1 H) 3.46 (d, *J* = 6.41 Hz, 1 H) 2.59 - 2.67 (m, 1 H) 2.08 - 2.18 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 151.1, 149.6, 144.7, 142.6, 136.9, 130.1, 128.7, 128.4, 128.2, 127.8, 125.8, 117.8, 113.5, 66.9, 55.8, 53.10, 44.8, 28.2; HRMS (ESI-TOF) for $C_{25}H_{24}N_2O_2$ [M + Na^+] calcd 407.1735, found 407.1739. **8e$_{endo}$**: IR (film) ν_{max}, 3340 (m), 2953 (m), 1693 (s), 1483 (s), 1410 (s), 1329 (m), 1210 (s), 1175 (m), 1105 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.74 (d, *J* = 10.0 Hz, 0.6 H) 7.29 - 7.52 (m, 10.4 H) 7.08 (q, *J* = 8.09 Hz, 1 H) 6.79 (t, *J* = 7.44 Hz, 0.6 H) 6.69 (t, *J* = 7.33 Hz, 0.4 H) 6.59 (t, *J* = 6.87 Hz, 1 H) 5.49 (d, *J* = 7.33 Hz, 0.6 H) 5.41 (d, *J* = 6.87 Hz, 0.4 H) 5.24 - 5.37 (m, 1 H) 5.19-5.26 (m, 1 H) 4.73 (s, 1 H) 3.90 - 4.00 (m, 1 H) 3.31 - 3.54 (m, 2 H) 2.51 - 2.62 (m, 1 H) 2.12 - 2.33 (m, 1 H) 1.57 (dd, *J* = 12.71, 6.75 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 156.6, 155.4, 143.7, 141.7, 136.9, 136.6, 130.5, 129.8, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 127.7, 127.2, 127.6, 126.5, 126.4, 122.4, 121.1, 119.0, 118.7, 114.8, 114.7, 67.1, 66.8, 56.9, 56.6, 56.4, 56.2, 45.1, 45.0, 44.8, 44.3, 22.7, 21.8; HRMS (ESI-TOF) for $C_{25}H_{24}N_2O_2$ [M + Na^+] calcd 407.1735, found 407.1732.



8f$_{exo}$ **8f$_{endo}$**

Benzyl-4-(4-fluorophenyl)-3,3a,4,5-tetrahydro-2*H*-pyrrolo[3,2-*c*]quinoline-1(9b*H*)-carboxylates

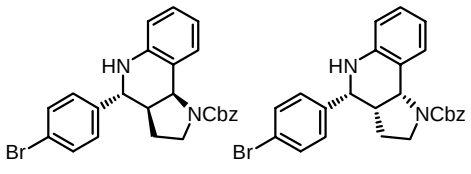
(8f$_{exo}$/8f$_{endo}$). The products were prepared by Method E. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give **8f$_{exo}$** (43 mg, 53%) as a colorless oil and **8f$_{endo}$** (17 mg, 22%) as a colorless oil. **8f$_{exo}$** was determined to be 95% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 20% MeOH, t_r(minor) = 8.70 min, t_r(major) = 7.53 min). $[\alpha]^{25}_D$ = –188.7° (c = 2.5, CH_2Cl_2); IR (film) ν_{max}, 3327 (m), 3055 (m), 2973 (m), 2890 (m), 1622 (s), 1508 (s), 1413 (m), 1357 (s), 1301 (m), 1106 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.29 - 7.61 (m, 6 H) 7.19 - 7.26 (m, 2 H) 7.08 (t, *J* = 7.67 Hz, 1 H) 6.97 (t, *J* = 8.58 Hz, 2 H) 6.69 (br. s., 1 H) 6.58 (d, *J* = 8.01 Hz, 1 H) 5.19 - 5.32 (m, 1 H) 5.11 - 5.18 (m, 1 H) 4.89 (br. s., 1 H) 4.37 (d, *J* = 3.20 Hz, 1 H) 4.25 (br. s., 1 H) 3.60 (q, *J* = 9.08 Hz, 1 H) 3.44 (d, *J* = 6.41 Hz, 1 H) 2.51 - 2.62 (m, 1 H) 2.06 - 2.17 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 162.9, 160.9, 142.3, 140.5, 128.4, 127.9, 127.5, 127.4, 118.0, 115.6, 115.5, 113.6, 110.7, 66.9, 55.2, 53.1, 44.9, 28.2; HRMS (ESI-TOF) for $C_{25}H_{23}FN_2O_2$ [M + H^+] calcd 403.1816, found 403.1813. **8f$_{endo}$**: IR (film) ν_{max}, 3327 (m), 3033 (m), 2951 (m), 1621 (s), 1485 (s), 1413 (m), 1358 (s), 1107 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.72 (d, *J* = 7.55 Hz, 0.6 H) 7.34 - 7.52 (m, 7 H) 7.32 (d, *J* = 6.64 Hz, 0.4 H) 7.04 - 7.12 (m, 3 H) 6.79 (t, *J* = 7.44 Hz, 0.6 H) 6.69 (t, *J* = 7.44 Hz, 0.4 H) 6.56 - 6.62 (m, 1 H) 5.47 (d, *J* = 7.10 Hz, 0.6 H) 5.39 (d, *J* = 6.87 Hz, 0.4 H) 5.25 - 5.35 (m, 1 H) 5.18 - 5.25 (m, 1 H) 4.71 (s, 1 H) 3.90 (d, *J* = 13.05 Hz, 1 H) 3.33 - 3.53 (m, 2 H) 2.48 - 2.57 (m, 1 H) 2.08 - 2.27 (m, 1 H) 1.50 - 1.61 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 163.2, 161.2, 156.5, 155.4, 143.5, 143.4, 137.4, 137.3, 136.9, 130.6, 129.8, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 127.6, 122.3, 121.1, 119.2, 119.1, 118.9, 115.6, 115.3, 114.8, 67.2, 66.8, 56.9, 56.6, 55.8, 55.6, 45.0, 44.9, 44.8, 44.4, 22.7, 21.7; HRMS (ESI-TOF) for $C_{25}H_{23}FN_2O_2$ [M + Na^+] calcd 441.1635, found 441.1630.



8g$_{exo}$ **8g$_{endo}$**

Benzyl-4-(4-chlorophenyl)-3,3a,4,5-tetrahydro-2*H*-pyrrolo[3,2-*c*]quinoline-1(9b*H*)-carboxylates (8g$_{exo}$/8g$_{endo}$). The products were prepared by Method E. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give **8g$_{exo}$** (51 mg, 60%) as a colorless oil and **8g$_{endo}$** (22 mg, 26%) as a colorless oil. **8g$_{exo}$** was determined to be 95% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 22% MeOH, t_r(minor) = 10.29 min, t_r(major) = 8.81 min). $[\alpha]^{25}_D$ = –204.9° (c = 3.3, CH_2Cl_2); IR (film) ν_{max}, 3368 (m), 2953 (m), 2891 (m), 1682 (s), 1607 (s), 1489 (m), 1412 (s), 1298 (m), 1098 (m) cm^{-1}; ^{1}H NMR (500

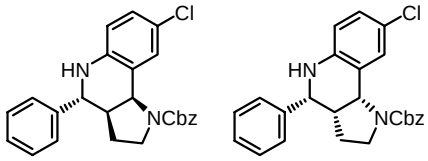
MHz, $CDCl_3$) rotamers, δ ppm 7.14 - 7.65 (m, 10 H) 7.08 (t, *J* = 7.55 Hz, 1 H) 6.69 (br. s., 1 H) 6.51 - 6.62 (m, 1 H) 5.20 - 5.33 (m, 1 H) 5.15 (d, *J* = 12.13 Hz, 1 H) 4.87 (d, *J* = 1.37 Hz, 1 H) 4.37 (d, *J* = 2.98 Hz, 1 H) 4.26 (br. s., 1 H) 3.54 - 3.67 (m, 1 H) 3.43 (br. s., 1 H) 2.50 - 2.61 (m, 1 H) 2.07 - 2.17 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 155.4, 143.3, 142.0, 137.3, 132.9, 128.8, 128.4, 127.9, 127.2, 117.9, 113.5, 66.9, 55.2, 53.2, 44.8, 28.2; HRMS (ESI-TOF) for $C_{25}H_{23}ClN_2O_2$ [M + Na^+] calcd 441.1340, found 441.1343. **8g$_{endo}$**: IR (film) ν_{max}, 3349 (m), 2974 (m), 2892 (m), 1693 (s), 1488 (m), 1411 (s), 1357 (m), 1109 (m), 1078 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.72 (d, *J* = 7.78 Hz, 0.6 H) 7.27 - 7.59 (m, 9.4 H) 7.08 (q, *J* = 7.78 Hz, 1 H) 6.76 - 6.84 (m, 0.6 H) 6.70 (t, *J* = 7.44 Hz, 0.4 H) 6.54 - 6.64 (m, 1 H) 5.46 (d, *J* = 7.10 Hz, 0.6 H) 5.39 (d, *J* = 6.64 Hz, 0.4 H) 5.24 - 5.35 (m, 1 H) 5.17 - 5.24 (m, 1 H) 4.70 (br. s., 1 H) 3.85 - 3.96 (m, 1 H) 3.29 - 3.53 (m, 2 H) 2.47 - 2.57 (m, 1 H) 2.07 - 2.26 (m, 1 H) 1.48 - 1.59 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 156.5, 143.4, 140.2, 140.1, 136.9, 133.4, 130.5, 129.8, 129.2, 128.5, 128.2, 128.0, 127.8, 127.6, 122.3, 119.3, 118.9, 115.0, 114.9, 114.8, 67.2, 66.8, 56.8, 56.5, 55.9, 55.7, 44.9, 44.6, 22.6, 21.7; HRMS (ESI-TOF) for $C_{25}H_{23}ClN_2O_2$ [M + Na^+] calcd 441.1340, found 441.1329.



8h$_{exo}$ **8h$_{endo}$**

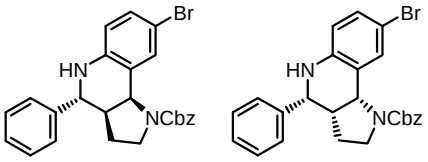
Benzyl-4-(4-bromophenyl)-3,3a,4,5-tetrahydro-2*H*-pyrrolo[3,2-*c*]quinoline-1(9b*H*)-carboxylates (8h$_{exo}$/8h$_{endo}$). The products were prepared by Method E. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give **8h$_{exo}$** (56 mg, 60%) as a colorless oil and **8h$_{endo}$** (22 mg, 24%) as a colorless oil. **8h$_{exo}$** was determined to be 97% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 22% MeOH, t_r(minor) = 12.07 min, t_r(major) = 10.27 min). $[\alpha]^{25}_D$ = –192.1° (c = 3.4, CH_2Cl_2); IR (film) ν_{max}, 3360 (m), 3031 (m), 2954 (m), 1689 (s), 1486 (s), 1413 (s), 1358 (m), 1267 (s), 1110 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.28 - 7.65 (m, 7 H) 6.91 - 7.20 (m, 4 H) 6.69 (br. s., 1 H) 6.45 - 6.62 (m, 1 H) 5.06 - 5.33 (m, 2 H) 4.87 (br. s., 1 H) 4.35 (d, *J* = 2.98 Hz, 1 H) 4.21 (br. s., 1 H) 3.53 - 3.67 (m, 1 H) 3.43 (br. s., 1 H) 2.48 - 2.62 (m, 1 H) 2.04 - 2.21 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 155.1, 144.9, 143.8, 131.8, 129.7, 1228.4, 128.3, 127.9, 127.6, 121.0, 118.1, 113.5, 66.9, 55.2, 52.9, 44.8, 28.1; HRMS (ESI-TOF) for $C_{25}H_{23}BrN_2O_2$ [M + Na^+] calcd 485.0835, found 485.0841. **8h$_{endo}$**: IR (film) ν_{max}, 3348 (m), 3032 (m), 2970 (m), 2891 (m), 1691 (s), 1458 (s), 1411 (m), 1357 (s), 1109 (m) cm^{-1}; ^1H

NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.71 (d, *J* = 7.78 Hz, 0.6 H) 7.28 - 7.62 (m, 9.4 H) 7.07 (q, *J* = 7.86 Hz, 1 H) 6.79 (t, *J* = 7.44 Hz, 0.6 H) 6.70 (t, *J* = 7.21 Hz, 0.4 H) 6.56 - 6.63 (m, 1 H) 5.46 (d, *J* = 7.33 Hz, 0.6 H) 5.39 (d, *J* = 6.87 Hz, 0.4 H) 5.24 - 5.35 (m, 1 H) 5.16 - 5.24 (m, 1 H) 4.68 (br. s., 1 H) 3.90 (d, *J* = 13.28 Hz, 1 H) 3.31 - 3.53 (m, 2 H) 2.48 - 2.58 (m, 1 H) 2.06 - 2.25 (m, 1 H) 1.48 - 1.59 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 156.5, 145.9, 143.5, 140.7, 139.4, 136.9, 131.7, 130.5, 129.8, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 127.7, 122.4, 121.4, 121.1, 119.3, 118.9, 114.9, 114.8, 67.2, 66.8, 56.8, 56.5, 55.9, 55.8, 44.9, 44.8, 44.6, 44.2, 22.6, 21.7; HRMS (ESI-TOF) for $C_{25}H_{23}BrN_2O_2$ [M + Na^+] calcd 485.0835, found 485.0821.



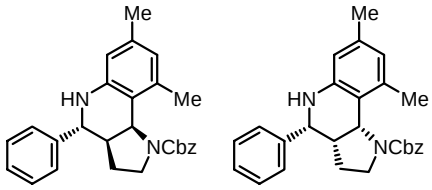
8i$_{exo}$ **8i$_{endo}$**

Benzyl-8-chloro-4-phenyl-3,3a,4,5-tetrahydro-2*H*-pyrrolo[3,2-*c*]quinoline-1(9b*H*)-carboxylates (8i$_{exo}$/8i$_{endo}$). The products were prepared by Method E. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give **8i$_{exo}$** (52 mg, 62%) as a colorless oil and **8i$_{endo}$** (14 mg, 17%) as a colorless oil. **8i$_{exo}$** was determined to be 93% ee by Chiral HPLC analysis (ChiralPak AS-H, 1.0 mL/min, 230 nm, 10% EtOH/Hexanes, t_r(minor) = 13.30 min, t_r(major) = 14.08 min). $[\alpha]^{25}_D$ = –179.1° (c = 2.5, CH_2Cl_2); IR (film) ν_{max}, 2926 (m), 2867 (m), 1720 (s), 1696 (s), 1490 (m), 1466 (s), 1453 (s), 1358 (m), 1289 (s), 1271 (m), 1119 (m), 1091 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.12 - 7.44 (m, 11 H) 7.02 (dd, *J* = 8.58, 2.40 Hz, 1 H) 6.51 (d, *J* = 8.47 Hz, 1 H) 5.20 (m, 2 H) 4.70 - 4.94 (m, 1 H) 4.38 (d, *J* = 2.98 Hz, 1 H) 4.29 (br. s., 1 H) 3.50 - 3.65 (m, 1 H) 3.44 (t, *J* = 8.93 Hz, 1 H) 2.50 - 2.67 (m, 1 H) 2.07 - 2.18 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 155.9, 144.3, 141.0, 130.7, 128.8, 128.5, 128.3, 128.0, 127.4, 125.6, 122.4, 114.7, 67.1, 55.7, 52.9, 44.9, 28.2; HRMS (ESI-TOF) for $C_{25}H_{23}ClN_2O_2$ [M + H^+] calcd 419.1520, found 419.1523. **8i$_{endo}$**: IR (film) ν_{max}, 2953 (m), 2866 (m), 1698 (s), 1490 (m), 1413 (s), 1359 (m), 1265 (s), 1119 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.28 - 7.82 (m, 11 H) 6.93 - 7.09 (m, 1 H) 6.42 - 6.61 (m, 1 H) 5.28 - 5.50 (m, 2 H) 5.21 (s, 1 H) 4.68 (d, *J* = 3.89 Hz, 1 H) 3.96 (d, *J* = 7.78 Hz, 1 H) 3.30 - 3.54 (m, 2 H) 2.48 - 2.63 (m, 1 H) 2.06 - 2.23 (m, 1 H) 1.50 - 1.63 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 156.6, 155.3, 142.3, 142.2, 141.3, 141.2, 136.8, 136.4, 130.0, 129.6, 128.7, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7, 126.5, 123.8, 123.5, 123.2, 116.0, 115.9, 67.4, 67.0, 56.7, 56.5, 56.4, 56.3, 45.1, 45.0, 44.6, 44.0, 22.7, 21.8; HRMS (ESI-TOF) for $C_{25}H_{23}ClN_2O_2$ [M + H^+] calcd 4519.1520, found 419.1523.



8j$_{exo}$ **8j$_{endo}$**

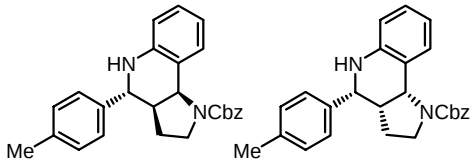
Benzyl-8-bromo-4-phenyl-3,3a,4,5-tetrahydro-2*H*-pyrrolo[3,2-*c*]quinoline-1(9b*H*)-carboxylates (8j$_{exo}$/8j$_{endo}$). The products were prepared by Method E. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give **8j$_{exo}$** (59 mg, 64%) as a colorless oil and **8j$_{endo}$** (15 mg, 17%) as white foam. **8j$_{exo}$** was determined to be 91% ee by Chiral HPLC analysis (ChiralPak AS-H, 1.0 mL/min, 230 nm, 10% EtOH/Hexanes, t_r(minor) = 13.81 min, t_r(major) = 15.16 min). $[\alpha]^{25}_D = -196.8°$ (c = 1.8, CH_2Cl_2); IR (film) ν_{max}, 3376 (m), 2953 (m), 1688 (s), 1598 (s), 1492 (m), 1415 (s), 1358 (m), 1307 (m), 1111 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.05 - 7.93 (m, 12.4 H) 6.29 - 6.63 (m, 0.6 H) 5.00 - 5.52 (m, 2 H) 4.65 - 4.99 (m, 1 H) 4.39 (d, *J* = 2.75 Hz, 1 H) 4.32 (br. s., 1 H) 3.54 - 3.65 (m, 1 H) 3.41 - 3.50 (m, 1 H) 2.54 - 2.66 (m, 1 H) 2.07 - 2.18 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 149.9, 149.7, 143.9, 141.5, 131.2, 128.8, 128.5, 128.0, 127.4, 125.6, 115.1, 109.4, 67.2, 67.1, 55.6, 52.8, 44.9, 28.3; HRMS (ESI-TOF) for $C_{25}H_{23}BrN_2O_2$ [M + Na^+] calcd 485.0835, found 485.0830. **8j$_{endo}$**: IR (film) ν_{max}, 3338 (m), 3062 (m), 2891 (m), 1693 (s), 1487 (m), 1413 (m), 1110 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.83 (s, 0.5 H) 7.60 (br. s., 0.5 H) 7.28 - 7.54 (m, 10 H) 7.09 - 7.19 (m, 1 H) 6.46 (dd, *J* = 8.36, 5.61 Hz, 1 H) 5.42 (d, *J* = 7.33 Hz, 0.5 H) 5.36 (d, *J* = 11.90 Hz, 0.5 H) 5.31 (d, *J* = 7.10 Hz, 0.5 H) 5.16 - 5.26 (m, 1.5 H) 4.68 (d, *J* = 4.81 Hz, 1 H) 3.95 (d, *J* = 7.10 Hz, 1 H) 3.30 - 3.51 (m, 2 H) 2.49 - 2.59 (m, 1 H) 2.02 - 2.24 (m, 1 H) 1.49 - 1.65 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 157.1, 155.3, 142.7, 141.3, 132.9, 132.5, 130.9, 128.7, 128.5, 128.4, 128.2, 127.9, 127.7, 126.5, 126.4, 116.4, 110.6, 110.3, 67.5, 67.0, 56.7, 56.4, 56.3, 56.2, 45.0, 44.5, 44.0, 22.8, 21.8; HRMS (ESI-TOF) for HRMS (ESI-TOF) for $C_{25}H_{23}BrN_2O_2$ [M + Na^+] calcd 485.0835, found 485.0825.



8k$_{exo}$ **8k$_{endo}$**

Benzyl-7,9-dimethyl-4-phenyl-3,3a,4,5-tetrahydro-2*H*-pyrrolo[3,2-*c*]quinoline-1(9b*H*)-carboxylates (8k$_{exo}$/8k$_{endo}$). The products were prepared by Method E. The reaction was run on 0.2 mmol scale, and

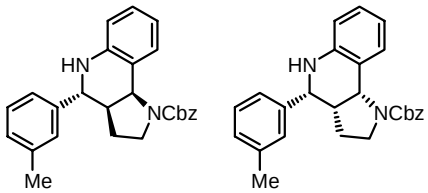
purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give **8k$_{exo}$** (37 mg, 45%) as a colorless oil and **8k$_{endo}$** (26 mg, 32%) as a white foam. **8k$_{exo}$** was determined to be 89% ee by Chiral HPLC analysis (ChiralCel OD-H, 1.0 mL/min, 230 nm, 30% EtOH/Hexanes, t_r(minor) = 8.08 min, t_r(major) = 18.93 min). $[\alpha]^{25}_D = -70.5°$ (c = 1.7, CH_2Cl_2); IR (film) ν_{max}, 3350 (m), 2957 (m), 2930 (m), 1703 (s), 1470 (m), 1410 (s), 1099 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.11 - 7.57 (m, 10 H) 6.31 - 6.47 (m, 1 H) 6.26 (s, 1 H) 5.07 - 5.17 (m, 1 H) 5.01 (d, *J* = 11.90 Hz, 1 H) 4.83 (br. s., 1 H) 4.20 (d, *J* = 6.41 Hz, 1 H) 4.14 (br. s., 1 H) 3.62 - 3.75 (m, 1 H) 3.46 - 3.59 (m, 1 H) 2.34 - 2.44 (m, 1 H) 2.25 (s, 3 H) 2.22 (s, 3 H), 1.85 - 2.09 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 152.9, 143.9, 143.6, 138.1, 128.7, 128.3, 127.9, 127.7, 127.6, 126.9, 121.1, 112.2, 66.6, 55.2, 43.9, 43.3, 21.0, 20.2; HRMS (ESI-TOF) for $C_{27}H_{28}N_2O_2$ [M + Na^+] calcd 435.2043, found 435.2040. **8k$_{endo}$**: IR (film) ν_{max}, 3350 (m), 2958 (m), 2930 (m), 1651 (s), 1614 (s), 1470 (m), 1337 (m), 1267 (s), 1092 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.29 - 7.71 (m, 10 H) 6.46 (br. s., 1 H) 6.32 (s, 1 H) 5.66 (br. s., 1 H) 5.13 - 5.32 (m, 2 H) 4.68 (br. s., 1 H) 3.68 - 3.92 (m, 2 H) 3.17 (br. s., 1 H) 2.54 - 2.77 (m, 1 H) 2.34 (s, 3 H) 2.24 (s, 3 H) 2.18 - 2.28 (m, 1 H) 1.49 - 1.68 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 156.0, 146.0, 141.9, 140.1, 137.6, 128.5, 128.4, 128.0, 127.8, 127.5, 126.3, 122.8, 113.7, 66.9, 66.8, 57.2, 56.5, 45.2, 44.9, 43.9, 20.8, 20.3; HRMS (ESI-TOF) for $C_{27}H_{28}N_2O_2$ [M + Na^+] calcd 435.2043, found 435.2039.



8l$_{exo}$ **8l$_{endo}$**

Benzyl-4-*p*-tolyl-3,3a,4,5-tetrahydro-2*H*-pyrrolo[3,2-*c*]quinoline-1(9b*H*)-carboxylates (8l$_{exo}$/8l$_{endo}$). The products were prepared by Method F. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give **8l$_{exo}$** (42 mg, 54%) as white foam and **8l$_{endo}$** (27 mg, 33%) as a white foam. **8l$_{exo}$** was determined to be 96% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 22% MeOH, t_r(minor) = 9.94 min, t_r(major) = 8.37 min). $[\alpha]^{25}_D = -198.6°$ (c = 2.5, CH_2Cl_2); IR (film) ν_{max}, 3343 (m), 2953 (m), 1698 (s), 1608 (m), 1512 (s), 1412 (s), 1302 (m), 1246 (s), 1175 (m), 1110 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.28 - 7.65 (m, 6 H) 7.03 - 7.23 (m, 5 H) 6.68 (br. s., 1 H) 6.53 - 6.62 (m, 1 H) 5.24 (br. s., 1 H) 5.08 - 5.19 (m, 1 H) 4.92 (br. s., 1 H) 4.33 (d, *J* = 3.20 Hz, 1 H) 4.23 (d, *J* = 14.19 Hz, 1 H) 3.54 - 3.69 (m, 1 H) 3.37 - 3.52 (m, 1 H) 2.55 - 2.68 (m, 1 H) 2.31 (s, 3 H) 1.98 - 2.16 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 152.8, 146.7, 141.0, 136.9, 129.4, 128.4, 128.3, 127.9, 125.8, 117.8, 113.6, 112.9, 66.9, 55.7, 53.2, 44.9, 27.9, 24.7; HRMS (ESI-TOF) for $C_{26}H_{26}N_2O_2$ [M + K^+] calcd 437.1625, found 437.1625.

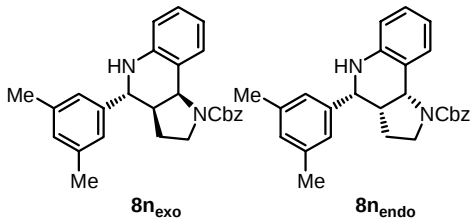
8l$_{endo}$: IR (film) ν_{max}, 3342 (m), 2935 (m), 1690 (s), 1486 (s), 1357 (m), 1327 (s), 1177 (m), 1103 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.72 (d, *J* = 7.78 Hz, 0.6 H) 7.28 - 7.51 (m, 7.4 H) 7.20 (d, *J* = 7.78 Hz, 2 H) 7.07 (q, *J* = 8.24 Hz, 1 H) 6.77 (t, *J* = 7.44 Hz, 0.6 H) 6.67 (t, *J* = 7.44 Hz, 0.4 H) 6.57 (t, *J* = 7.21 Hz, 1 H) 5.47 (d, *J* = 7.33 Hz, 0.6 H) 5.39 (d, *J* = 6.87 Hz, 0.4 H) 5.24 - 5.35 (m, 1 H) 5.21 (s, 1 H) 4.69 (d, *J* = 2.06 Hz, 1 H) 3.86 - 3.94 (m, 1 H) 3.32 - 3.52 (m, 2 H) 2.49 - 2.59 (m, 1 H) 2.38 (s, 3 H) 2.10 - 2.29 (m, 1 H) 1.53 - 1.66 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 156.6, 155.7, 143.7, 138.7, 138.6, 137.4, 130.6, 129.9, 129.3, 128.5, 128.4, 128.2, 128.0, 127.8, 127.7, 126.4, 122.4, 118.9, 114.7, 67.1, 66.8, 57.0, 56.7, 56.2, 56.0, 45.1, 45.0, 44.9, 44.5, 22.7, 21.8, 21.1; HRMS (ESI-TOF) for $C_{26}H_{26}N_2O_2$ [M + K^+] calcd 437.1625, found 437.1627.



8m$_{exo}$ **8m$_{endo}$**

Benzyl-4-*m*-tolyl-3,3a,4,5-tetrahydro-2*H*-pyrrolo[3,2-*c*]quinoline-1(9b*H*)-carboxylates (8m$_{exo}$/8m$_{endo}$). The products were prepared by Method F. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give **8m$_{exo}$** (44 mg, 55%) as white foam and **8m$_{endo}$** (27 mg, 34%) as white foam. **8m$_{exo}$** was determined to be 95% ee by Chiral HPLC analysis (Pirkle Covalent (*S*, *S*) Whelk, 1.0 mL/min, 230 nm, 20% EtOH/Hexanes, t_r(minor) = 11.23 min, t_r(major) = 9.43 min). $[\alpha]^{25}_D$ = –179.0° (c = 3.5, CH_2Cl_2); IR (film) ν_{max}, 3360 (m), 3030 (m), 2934 (m), 2890 (m), 1692 (s), 1607 (s), 1497 (m), 1414 (s), 1358 (m), 1107 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.28 - 7.70 (m, 6 H) 7.13 - 7.22 (m, 1 H) 7.00 - 7.12 (m, 4 H) 6.63 - 6.76 (m, 1 H) 6.58 (dd, *J* = 8.01, 1.14 Hz, 1 H) 5.27 (dd, 1 H) 5.16 (d, *J* = 12.36 Hz, 1 H) 4.93 (br. s., 1 H) 4.33 (d, *J* = 3.43 Hz, 1 H) 4.24 (br. s., 1 H) 3.61 (d, *J* = 9.39 Hz, 1 H) 3.40 - 3.52 (m, 1 H) 2.55 - 2.70 (m, 1 H) 2.32 (s, 3 H) 2.03 - 2.14 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 151.8, 144.7, 142.6, 138.4, 128.6, 128.4, 128.2, 128.0, 127.8, 126.6, 122.8, 117.8, 113.5, 66.9, 55.9, 53.2, 44.8, 28.2, 21.4; HRMS (ESI-TOF) for $C_{26}H_{26}N_2O_2$ [M + Na^+] calcd 421.1886, found 421.1886. **8m$_{endo}$**: IR (film) ν_{max}, 3341 (m), 2974 (m), 2952 (m), 2893 (m), 1693 (s), 1607 (s), 1412 (m), 1300 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.74 (d, *J* = 7.78 Hz, 0.6 H) 7.20 - 7.54 (m, 8.4 H) 7.15 (d, *J* = 7.10 Hz, 1 H) 7.08 (q, *J* = 8.09 Hz, 1 H) 6.79 (t, *J* = 7.44 Hz, 0.6 H) 6.69 (t, *J* = 7.55 Hz, 0.4 H) 6.59 (t, *J* = 6.87 Hz, 1 H) 5.48 (d, *J* = 7.33 Hz, 0.6 H) 5.41 (d, *J* = 7.10 Hz, 0.4 H) 5.26 - 5.37 (m, 1 H) 5.18 - 5.25 (m, 1 H) 4.70 (br. s., 1 H) 3.89 - 3.96 (m, 1 H) 3.34 - 3.54 (m, 2 H) 2.52 - 2.62 (m, 1 H) 2.40 (s, 3 H) 2.11 - 2.30 (m, 1 H) 1.54 - 1.66 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 156.6, 155.4, 143.7,

141.7, 138.3, 136.9, 130.8, 130.6, 129.9, 128.5, 128.4, 128.1, 128.0, 127.8, 127.7, 127.2, 127.1, 123.5, 123.4, 122.4, 118.9, 118.6, 114.7, 114.6, 67.1, 66.8, 57.1, 56.7, 56.4, 56.2, 45.1, 45.0, 44.8, 22.7, 21.8; HRMS (ESI-TOF) for $C_{26}H_{26}N_2O_2$ [M + Na^+] calcd 421.1886, found 421.1885.



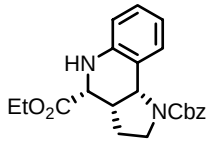
8n$_{exo}$ **8n$_{endo}$**

Benzyl-4-(3,5-dimethylphenyl)-3,3a,4,5-tetrahydro-2*H*-pyrrolo[3,2-*c*]quinoline-1(9b*H*)-carboxylates (8n$_{exo}$/8n$_{endo}$). The products were prepared by Method F. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 20:1 to 4:1) to give **8n$_{exo}$** (41 mg, 50%) as a colorless oil and **8n$_{endo}$** (29 mg, 35%) as white foam. **8n$_{exo}$** was determined to be 97% ee by Chiral HPLC analysis (Pirkle Covalent (*S*, *S*) Whelk, 1.0 mL/min, 230 nm, 20% EtOH/Hexanes, t_r(minor) = 10.91 min, t_r(major) = 9.00 min). $[\alpha]^{25}_D$ = –198.4° (c = 5.0, CH_2Cl_2); IR (film) ν_{max}, 3351 (m), 3030 (m), 2893 (m), 1691 (s), 1497 (s), 1413 (s), 1358 (s), 1319 (m), 1106 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.16 - 7.63 (m, 6 H) 7.08 (t, *J* = 7.55 Hz, 1 H) 6.87 (br. s., 3 H) 6.68 (br. s., 1 H) 6.57 (d, *J* = 8.01 Hz, 1 H) 5.23 (br. s., 1 H) 5.09 - 5.19 (m, 1 H) 4.93 (br. s., 1 H) 4.28 (d, *J* = 3.66 Hz, 1 H) 4.10 - 4.23 (m, 1 H) 3.54 - 3.66 (m, 1 H) 3.44 (d, *J* = 6.87 Hz, 1 H) 2.56 - 2.69 (m, 1 H) 2.27 (s, 6 H) 1.98 - 2.13 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 150.9, 142.7, 141.0, 138.3, 128.9, 128.4, 128.2, 127.9, 123.7, 117.8, 115.0, 113.6, 66.9, 55.9, 53.4, 44.8, 28.1, 21.4; HRMS (ESI-TOF) for $C_{27}H_{28}N_2O_2$ [M + H^+] calcd 413.2223, found 413.2221. **8n$_{endo}$**: IR (film) ν_{max}, 3342 (m), 2953 (m), 2894 (m), 1698 (s), 1480 (m), 1413 (s), 1357 (m), 1262 (s), 1104 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.74 (d, *J* = 7.55 Hz, 0.6 H) 7.29 - 7.53 (m, 5.4 H) 7.03 - 7.13 (m, 3 H) 6.97 (s, 1 H) 6.78 (t, *J* = 7.10 Hz, 0.6 H) 6.68 (t, *J* = 7.44 Hz, 0.4 H) 6.59 (t, *J* = 6.98 Hz, 1 H) 5.47 (d, *J* = 7.10 Hz, 0.6 H) 5.40 (d, *J* = 6.87 Hz, 0.4 H) 5.26 - 5.36 (m, 1 H) 5.22 (d, *J* = 1.37 Hz, 1 H) 4.66 (br. s., 1 H) 3.91 (d, *J* = 11.68 Hz, 1 H) 3.34 - 3.52 (m, 2 H) 2.54 - 2.60 (m, 1 H) 2.36 (s, 6 H) 2.12 - 2.28 (m, 1 H) 1.56 - 1.66 (m, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 156.6, 155.4, 143.7, 141.7, 141.6, 138.2, 136.9, 130.6, 129.8, 129.3, 129.2, 128.5, 128.4, 128.2, 128.0, 127.9, 127.8, 127.6, 124.2, 122.4, 121.1, 118.9, 118.5, 114.7, 114.6, 67.1, 66.8, 57.0, 56.7, 56.4, 56.2, 45.1, 45.0, 44.8, 44.3, 22.7, 21.8; HRMS (ESI-TOF) for $C_{27}H_{28}N_2O_2$ [M + Na^+] calcd 435.2043, found 413.2047.

I. General Procedure for the Preparation of Enantioenriched and Racemic Benzyl 4-ethyl 3,3a,4,5-tetrahydro-2*H*-pyrrolo[3,2-*c*]quinoline-1,4(9b*H*)-dicarboxylates

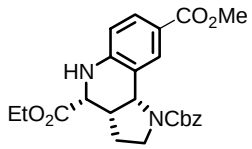
An 8 mL oven-dried vial was charged with (*E*)-ethyl 2-(phenylimino)acetate **9a** (35 mg, 0.2 mmol) (freshly made), catalyst **1a** (3.8 mg, 0.008 mmol), benzyl 2,3-dihydropyrrole-1-carboxylate **8** (0.22 mL of a 1.0 M toluene stock solution, 0.22 mmol), activated 5Å molecular sieves (40 mg) and toluene (2 mL) under a nitrogen atmosphere at room temperature. The mixture was cooled to –60 °C and stirred for 10 min. 2-Nitro-benzenesulfonic acid (0.8 mg, 0.004 mmol, as 0.1M stock solution in Et_2O), was added dropwise carefully and the resulting solution was stirred vigorously for 1.5 h. The mixture was purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to give **10a$_{endo}$** (59 mg, 78%) as a white foam.

Equal amounts of catalyst **1a** and its enantiomer were used to prepare the racemic sample of **10a$_{endo}$**.



10a$_{endo}$

(3a*R*,4*R*,9b*R*)-1-benzyl 4-ethyl 3,3a,4,5-tetrahydro-2*H*-pyrrolo[3,2-*c*]quinoline-1,4(9b*H*)-dicarboxylate (10a$_{endo}$). The product was prepared by the general procedure. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:1) to afford **10a$_{endo}$** (59 mg, 78%) as a white foam. **10a$_{endo}$** was determined to be 97% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 20% MeOH, t_r(minor) = 7.18 min, t_r(major) = 6.51 min). $[\alpha]^{25}_D$ =267.7° (c = 5.6, CH_2Cl_2); IR (film) ν_{max}, 3391 (m), 2980 (m), 1694 (s), 1491 (s), 1409 (s), 1268 (s), 1210 (m), 1106 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 7.66 (d, *J*=7.55 Hz, 0.4 H) 7.46 (d, *J*=7.10 Hz, 0.6 H) 7.29 - 7.43 (m, 5 H) 7.05 (d, *J*=8.01 Hz, 1 H) 6.74 (t, *J*=7.44 Hz, 0.6 H) 6.64 (t, *J*=7.44 Hz, 0.4 H) 6.53 - 6.61 (m, 1 H) 5.43 (d, *J*=7.55 Hz, 0.6 H) 5.15 - 5.37 (m, 2.4 H) 4.34 - 4.42 (m, 1 H) 4.21 - 4.36 (m, 3 H) 3.51 - 3.71 (m, 1 H) 3.31 - 3.47 (m, 1 H) 2.93 (d, *J*=4.35 Hz, 1 H) 1.94 - 2.14 (m, 1 H) 1.79 - 1.90 (m, 1 H) 1.34 (t, *J*=7.10 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 170.9, 156.3, 155.2, 141.7, 136.8, 136.5, 141.7, 136.8, 136.5, 130.2, 129.5, 128.5, 128.4, 128.2, 128.1, 128.0, 127.8, 127.6, 121.7, 118.9, 118.5, 114.5, 67.1, 66.8, 61.5, 56.2, 55.9, 53.9, 53.6, 44.7, 39.2, 38.8, 30.8, 23.0, 22.0, 14.2; HRMS (ESI-TOF) for $C_{22}H_{24}N_2O_4$ [M + Na^+] calcd 403.1634, found 403.1630.



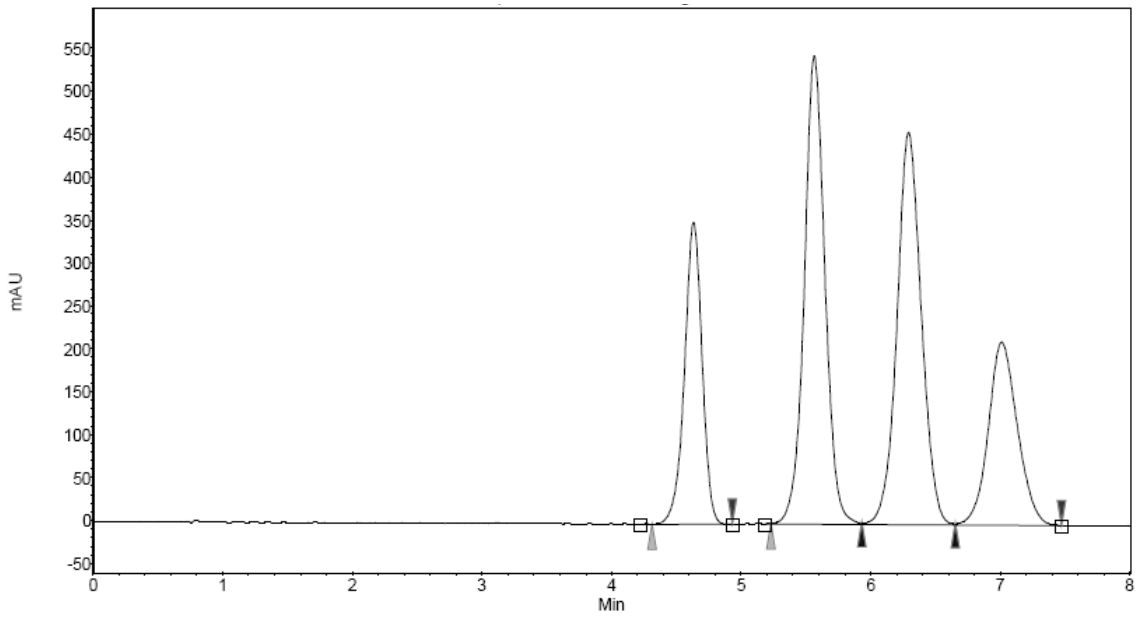
10b$_{endo}$

(3a*R*,4*R*,9b*R*)-1-benzyl 4-ethyl 8-methyl 3,3a,4,5-tetrahydro-2*H*-pyrrolo[3,2-*c*]quinoline-1,4,8(9b*H*)-

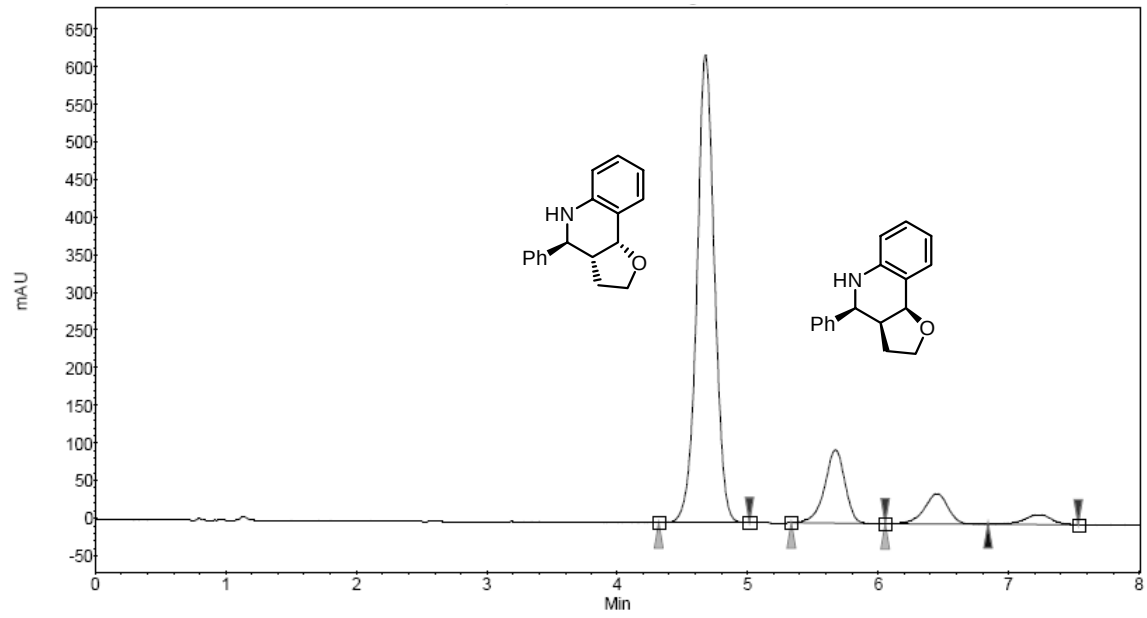
tricarboxylates (10b$_{endo}$). The product was prepared by the general procedure. The reaction was run on 0.2 mmol scale, and purified by flash column chromatography (silica gel, hexanes:EtOAc, gradient from 10:1 to 1:2) to afford **10b$_{endo}$** (66 mg, 76%) as a white foam. **10b$_{endo}$** was determined to be 95% ee by Chiral SFC analysis (Pirkle Covalent (*S*, *S*) Whelk, 3.0 mL/min, 230 nm, 20% MeOH, t_r(minor) = 14.31 min, t_r(major) = 13.31 min). $[\alpha]^{25}_D$ = 125.3° (c = 4.1, CH_2Cl_2); IR (film) ν_{max}, 3366 (m), 2951 (m), 1737 (s), 1698 (s), 1415 (s), 1281 (s), 1209 (m), 1131 (m), 1102 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) rotamers, δ ppm 8.26 (s, 0.5 H) 8.15 (s, 0.5 H) 7.74 (d, *J*=7.33 Hz, 0.5 H) 7.50 (d, *J*=7.33 Hz, 0.5 H) 7.28 - 7.45 (m, 5 H) 6.55 (d, *J*=8.70 Hz, 1 H) 5.18 - 5.48 (m, 2.5 H) 4.78 (d, *J*=12.13 Hz, 0.5 H) 4.21 - 4.41 (m, 4 H) 3.82 (d, *J*=8.70 Hz, 3 H) 3.50 - 3.72 (m, 1 H) 3.32 - 3.46 (m, 1 H) 2.92 (d, *J*=7.10 Hz, 1 H) 1.79 - 2.00 (m, 2 H) 1.33 (t, *J*=7.21 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) rotamers, δ ppm 170.4, 166.8, 156.3, 155.3, 145.4, 132.3, 131.9, 130.2, 128.5, 128.4, 127.8, 120.3, 113.8, 67.6, 67.0, 61.9, 55.8, 53.3, 53.2, 51.6, 44.7, 38.8, 38.3, 25.4, 23.3, 22.3, 14.2; HRMS (ESI-TOF) for $C_{24}H_{26}N_2O_6$ [M + Na^+] calcd 438.1791, found 438.1796.

J. Chiral SFC and HPLC Data

Racemic sample: ($4a_{exo}$/$4a_{endo}$)

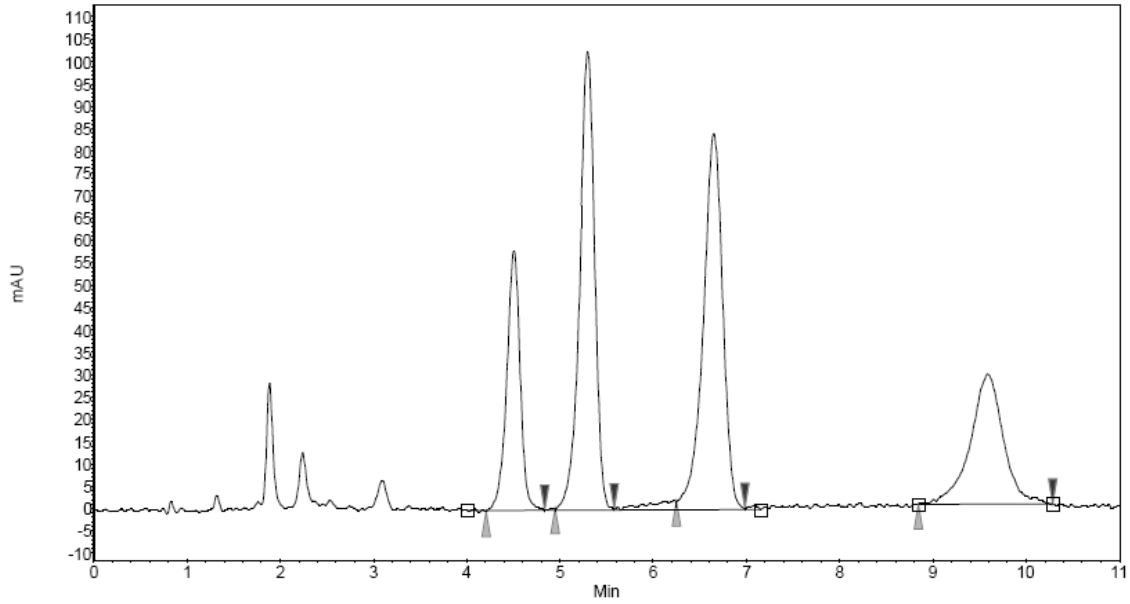


96% ee: The reaction was carried out with ***ent*-1a**.

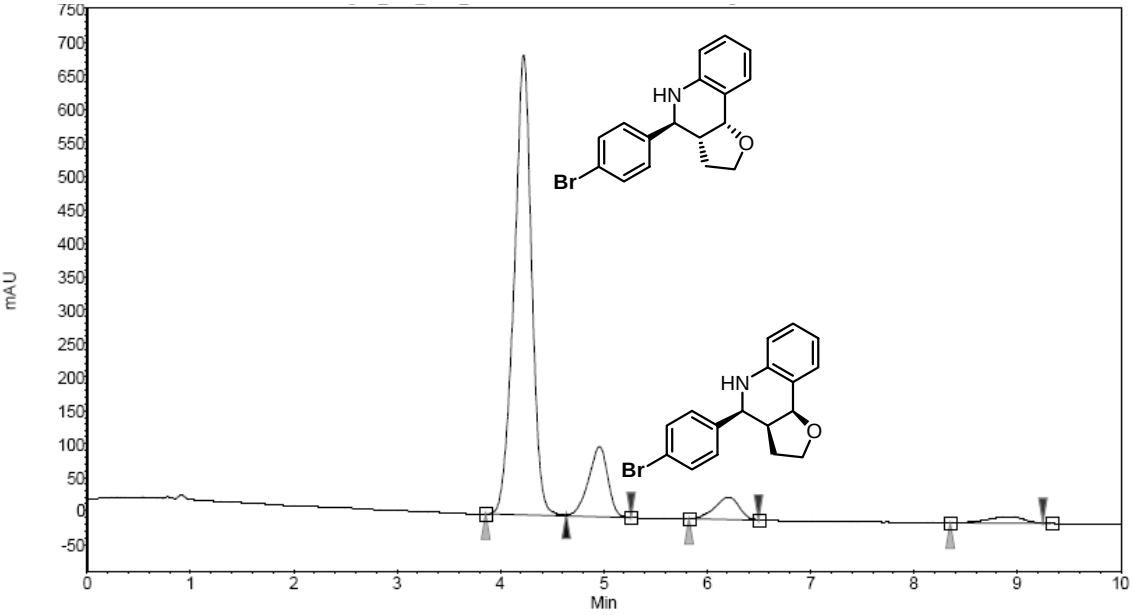


Index	Time	Height	Area	Area
	[Min]	[mAU]	[mAU*min]	[%]
1	4.68	621.62	97.13	76.709
2	5.67	97.65	17.61	13.911
3	6.45	40.72	8.62	6.807
4	7.23	13.36	3.26	2.574
Total			126.62	100.000

Racemic sample: (4b$_{exo}$/4b$_{endo}$)

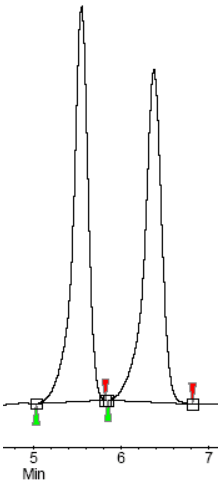


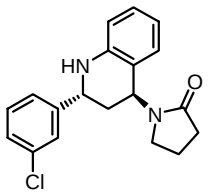
94% ee: The reaction was carried out with carried out with ***ent*-1a**.



Index	Time	Height	Area	Area
	[Min]	[mAU]	[mAU*min]	[%]
1	4.22	686.40	134.58	78.961
2	4.96	104.52	22.71	13.327
3	6.21	33.89	9.15	5.370
4	8.94	9.96	3.99	2.342
Total			170.43	100.000

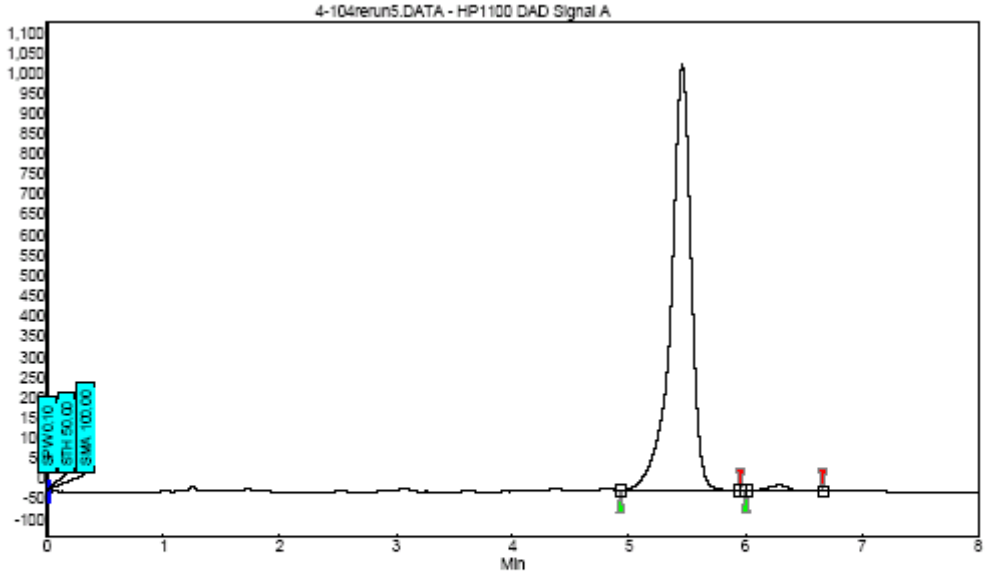
Racemic sample: ($6a_{exo}$)





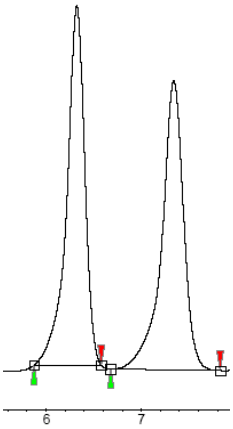
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.03	5.55	5.83	0.00	50.75	1015.1	202.7	50.751
2	UNKNOWN	5.86	6.38	6.82	0.00	49.25	855.5	196.7	49.249
Total						100.00	1870.6	399.5	100.000

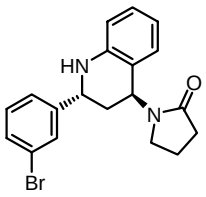
98% ee:



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.93	5.46	5.96	0.00	98.75	1047.7	210.1	98.753
2	UNKNOWN	6.00	6.29	6.66	0.00	1.25	13.2	2.7	1.247
Total						100.00	1060.8	212.7	100.000

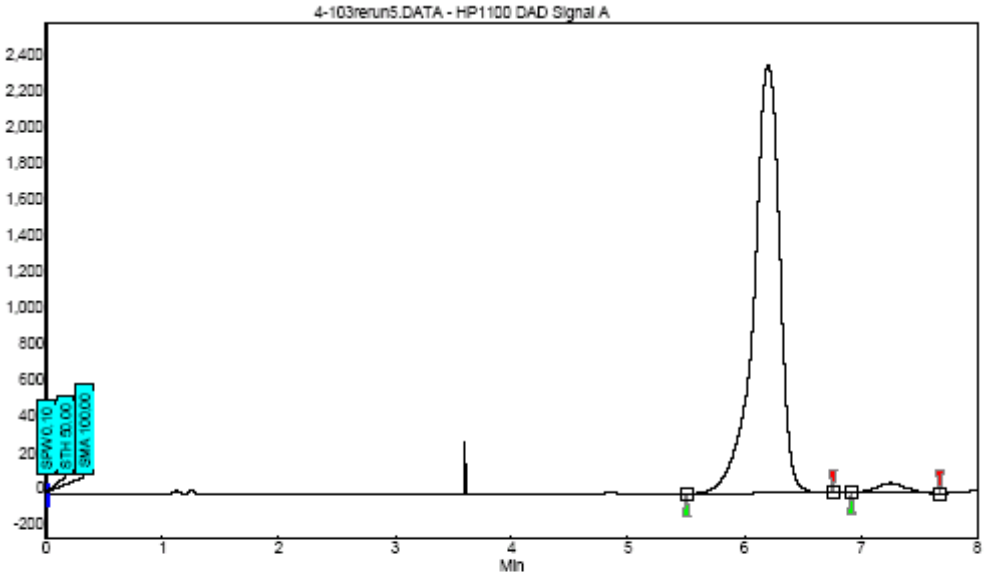
Racemic sample: ($6b_{exo}$)





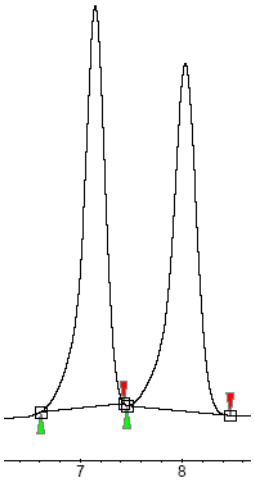
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	5.87	6.32	6.58	0.00	50.85	772.8	170.4	50.849
1	UNKNOWN	6.68	7.34	7.83	0.00	49.15	621.9	164.7	49.151
Total						100.00	1394.7	335.1	100.000

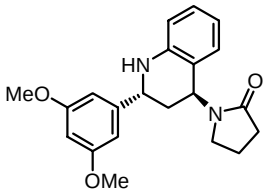
95% ee:



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.50	6.21	6.76	0.00	97.61	2361.4	610.7	97.609
2	UNKNOWN	6.92	7.25	7.68	0.00	2.39	53.1	15.0	2.391
Total						100.00	2414.5	625.6	100.000

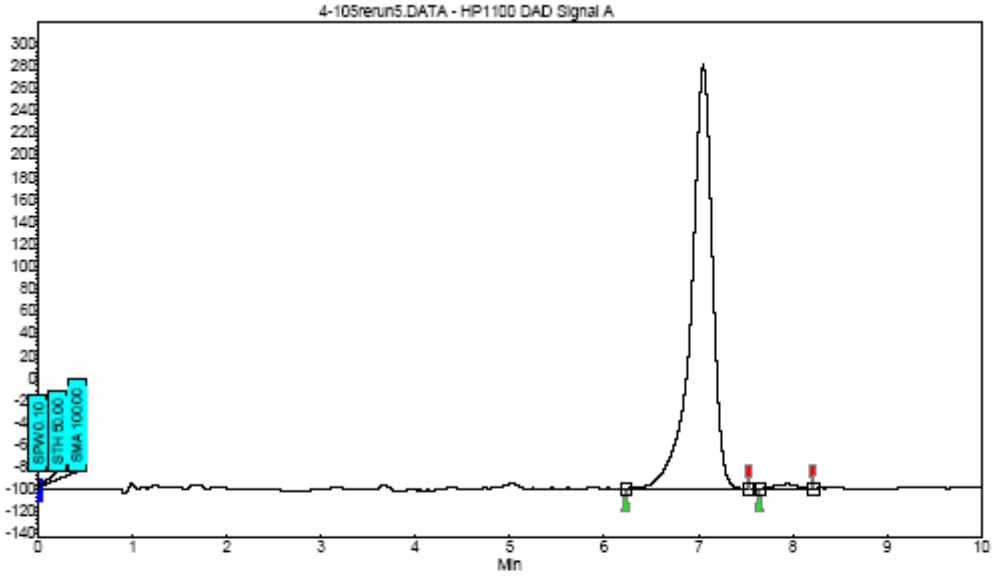
Racemic sample: ($6c_{exo}$)





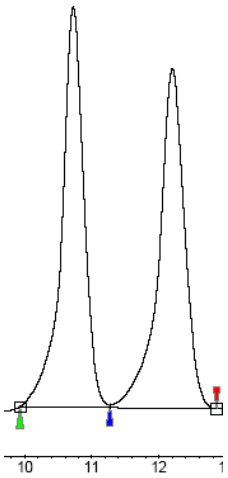
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.61	7.15	7.43	0.00	50.50	513.6	130.6	50.498
2	UNKNOWN	7.46	8.03	8.48	0.00	49.50	447.4	128.0	49.502
Total						100.00	961.0	258.5	100.000

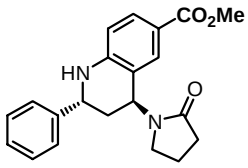
98% ee:



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.23	7.05	7.53	0.00	98.99	380.0	99.4	98.985
2	UNKNOWN	7.64	7.94	8.21	0.00	1.01	4.4	1.0	1.015
Total						100.00	384.3	100.4	100.000

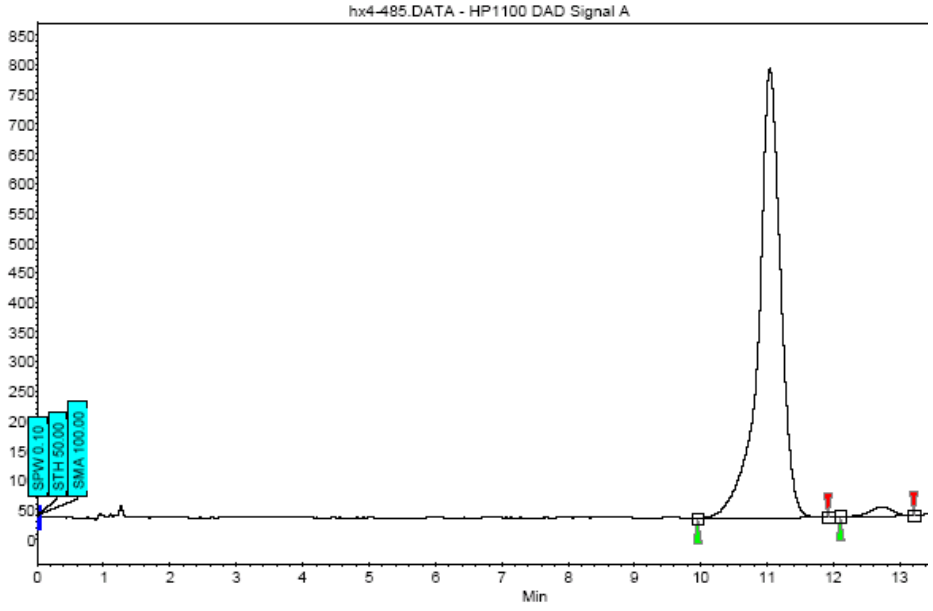
Racemic sample: ($6d_{exo}$)





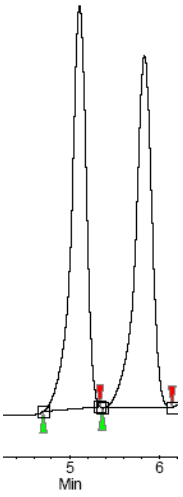
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	9.93	10.73	11.27	0.00	50.39	589.7	225.9	50.391
2	UNKNOWN	11.27	12.20	12.86	0.00	49.61	500.6	222.4	49.609
Total						100.00	1090.3	448.3	100.000

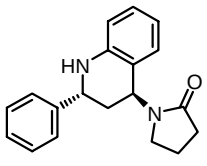
96% ee:



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	9.95	11.04	11.92	0.00	97.93	757.7	294.0	97.928
2	UNKNOWN	12.10	12.71	13.21	0.00	2.07	16.0	6.2	2.072
Total						100.00	773.7	300.2	100.000

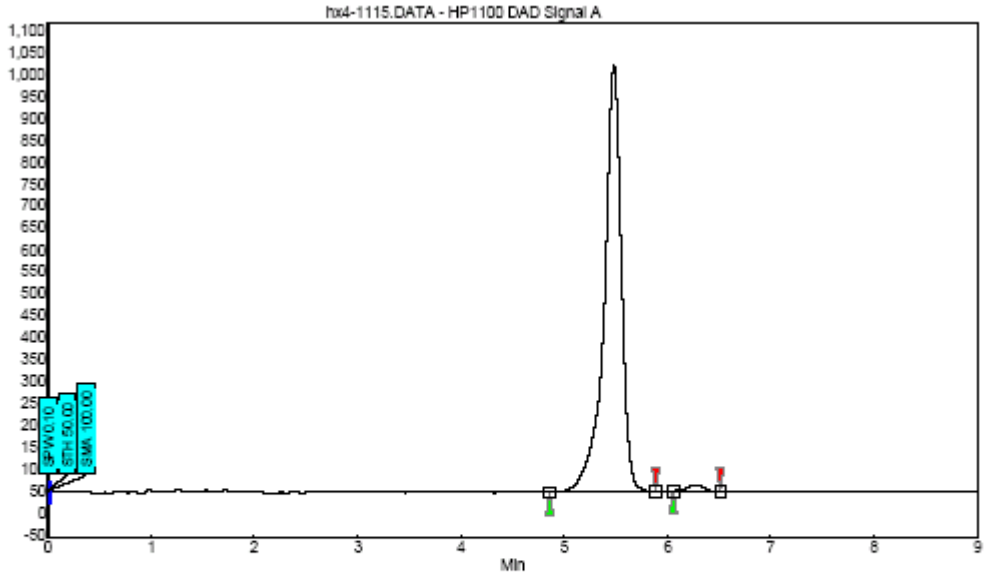
Racemic sample: (6e$_{exo}$)





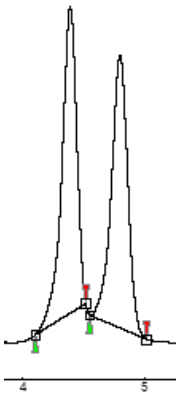
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	4.70	5.11	5.34	0.00	50.93	2157.3	420.5	50.930
1	UNKNOWN	5.37	5.83	6.15	0.00	49.07	1889.6	405.2	49.070
Total						100.00	4047.0	825.7	100.000

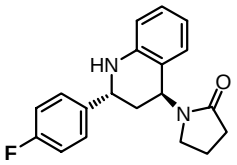
97% ee:



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.86	5.48	5.89	0.00	98.73	971.1	188.5	98.726
2	UNKNOWN	6.06	6.27	6.51	0.00	1.27	13.8	2.4	1.274
Total						100.00	984.9	190.9	100.000

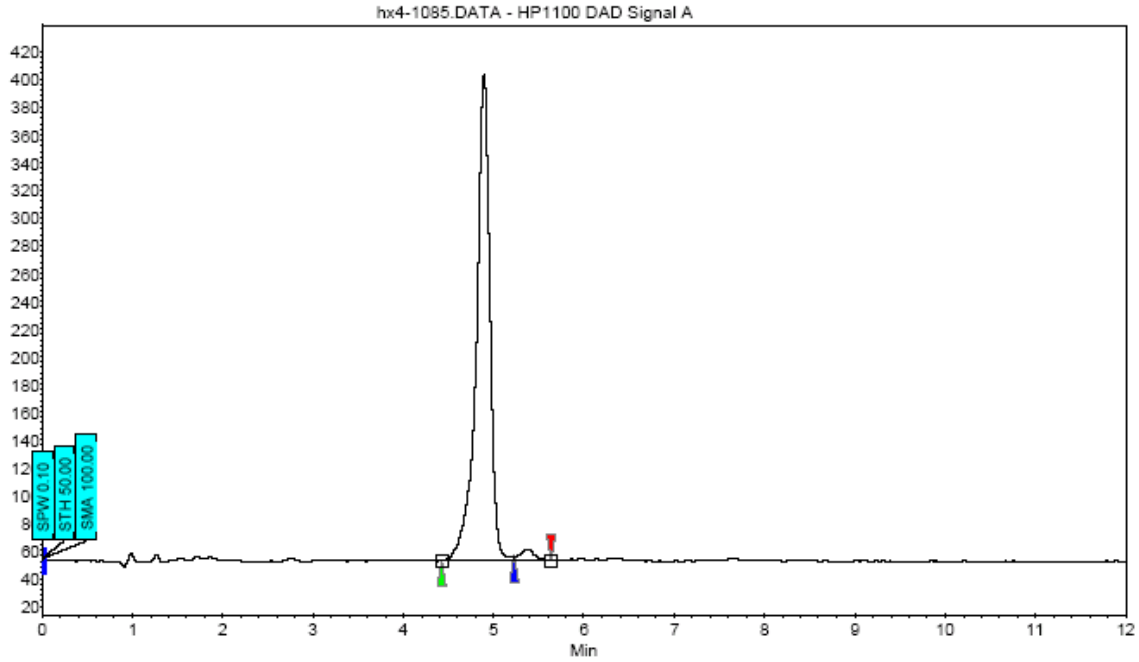
Racemic sample: (**6f$_{exo}$**)





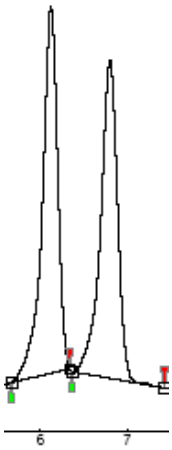
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	4.10	4.39	4.52	0.00	50.47	425.7	60.2	50.465
1	UNKNOWN	4.55	4.80	5.02	0.00	49.53	379.3	59.1	49.535
Total						100.00	805.0	119.3	100.000

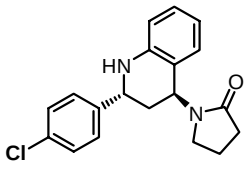
95% ee:



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.42	4.89	5.22	0.00	97.71	350.8	61.4	97.711
2	UNKNOWN	5.22	5.37	5.63	0.00	2.29	8.1	1.4	2.289
Total						100.00	358.9	62.9	100.000

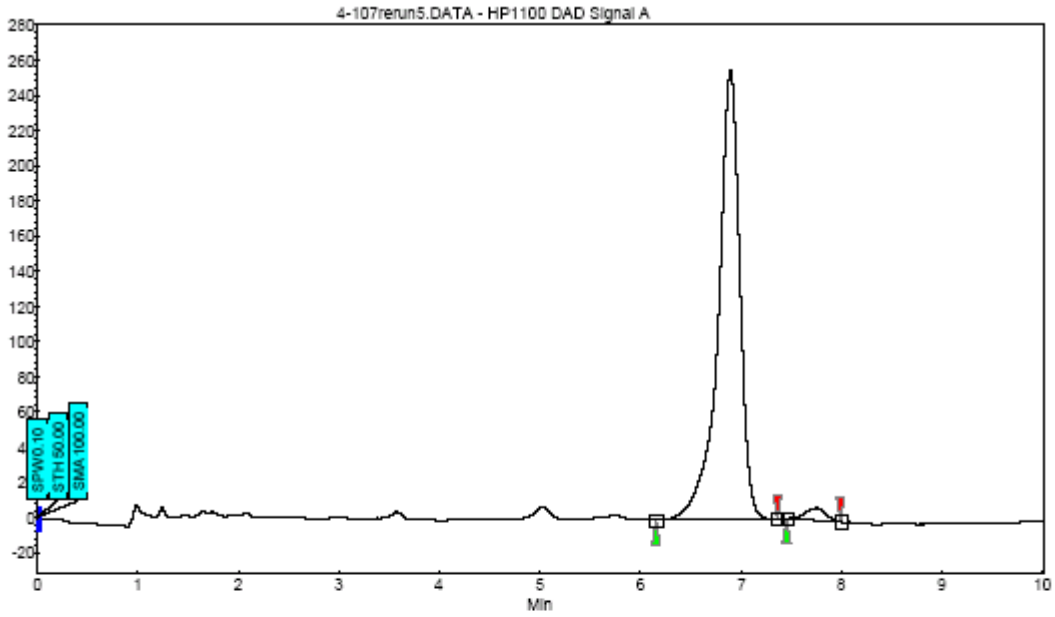
Racemic sample: ($6g_{exo}$)





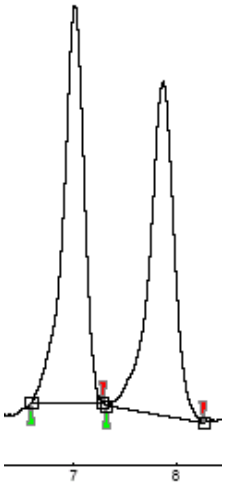
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	5.66	6.13	6.34	0.00	51.00	277.2	57.2	50.996
1	UNKNOWN	6.36	6.81	7.44	0.00	49.00	241.2	55.0	49.004
Total						100.00	518.4	112.2	100.000

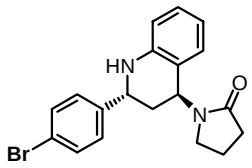
97% ee:



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.15	6.90	7.36	0.00	97.49	255.7	63.5	97.485
2	UNKNOWN	7.45	7.75	7.99	0.00	2.51	7.0	1.6	2.515
Total						100.00	262.7	65.1	100.000

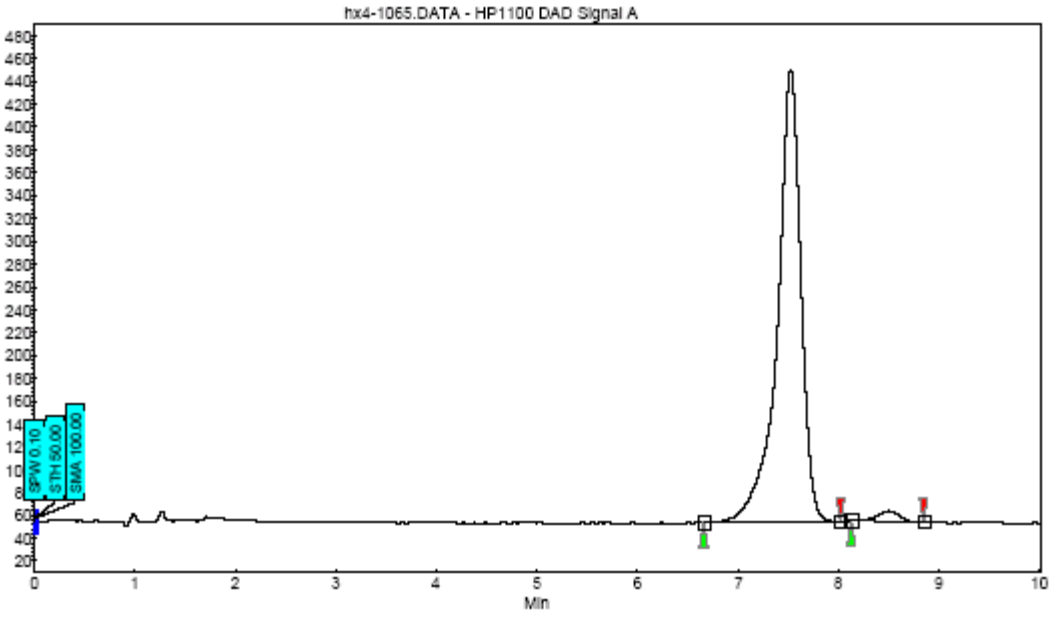
Racemic sample: ($6h_{exo}$)





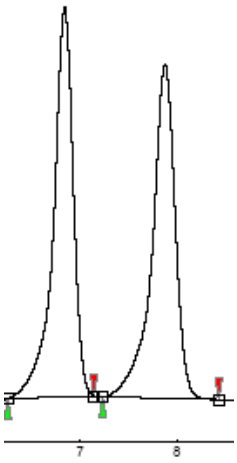
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	6.58	7.01	7.29	0.00	50.46	58.7	14.1	50.465
1	UNKNOWN	7.32	7.87	8.27	0.00	49.54	49.3	13.8	49.535
Total						100.00	107.9	27.9	100.000

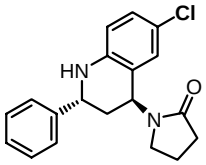
96% ee:



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.66	7.53	8.02	0.00	97.94	396.3	107.7	97.941
2	UNKNOWN	8.13	8.50	8.85	0.00	2.06	9.0	2.3	2.059
Total						100.00	405.3	110.0	100.000

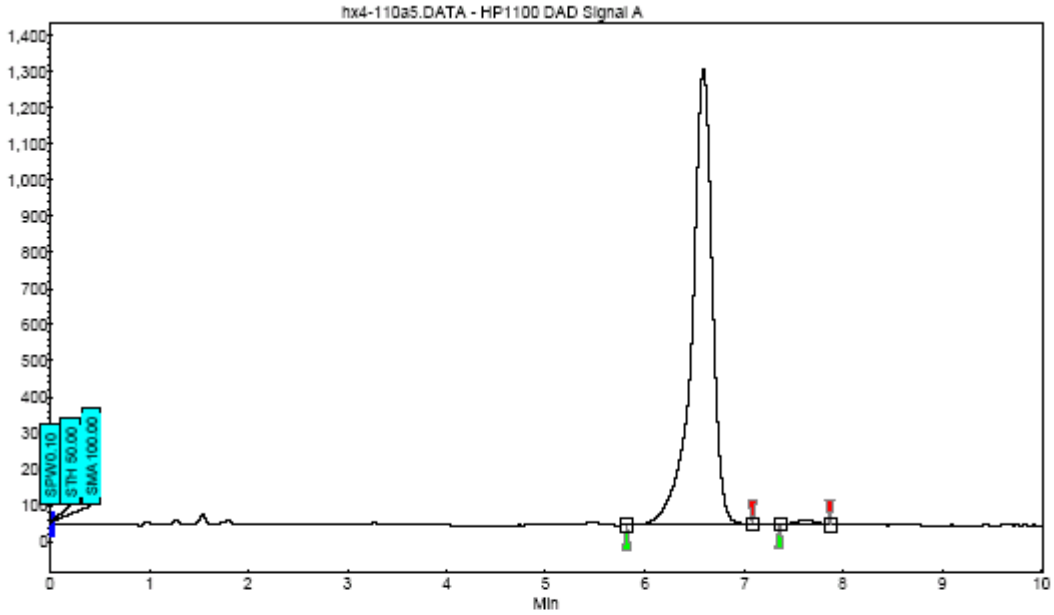
Racemic sample: (6i$_{exo}$)





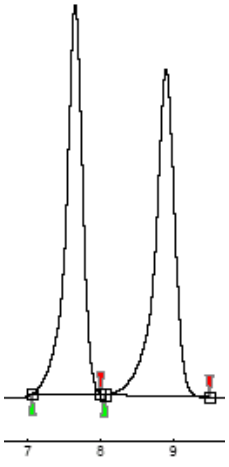
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	6.25	6.84	7.14	0.00	50.13	611.0	145.2	50.134
1	UNKNOWN	7.23	7.87	8.43	0.00	49.87	523.7	144.4	49.866
Total						100.00	1134.7	289.7	100.000

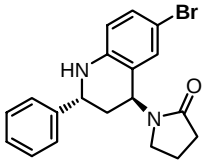
98% ee:



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.82	6.59	7.08	0.00	99.13	1259.3	299.0	99.131
2	UNKNOWN	7.36	7.63	7.87	0.00	0.87	12.0	2.6	0.869
Total						100.00	1271.3	301.6	100.000

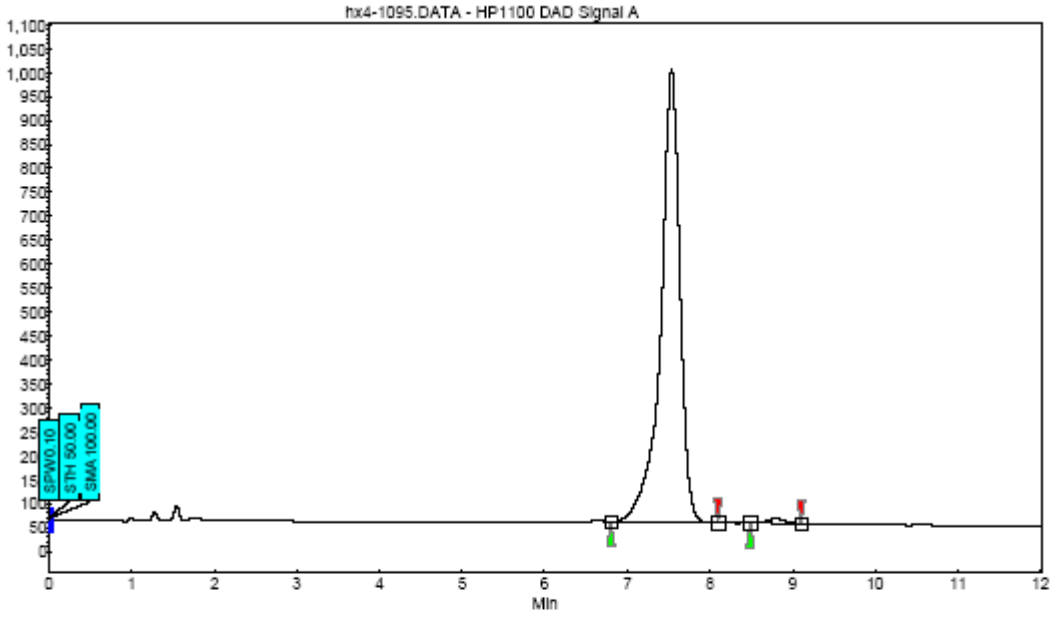
Racemic sample: (6j$_{exo}$)





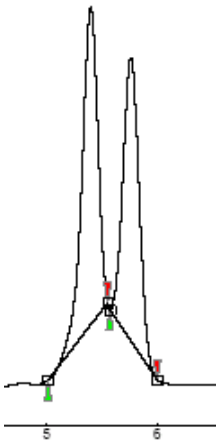
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	7.06	7.65	8.00	0.00	50.25	556.9	149.2	50.251
1	UNKNOWN	8.06	8.91	9.50	0.00	49.75	468.2	147.7	49.749
Total						100.00	1025.0	296.9	100.000

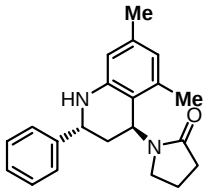
98% ee:



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.80	7.53	8.10	0.00	99.00	947.4	255.4	99.004
2	UNKNOWN	8.49	8.80	9.10	0.00	1.00	10.3	2.6	0.996
Total						100.00	957.7	257.9	100.000

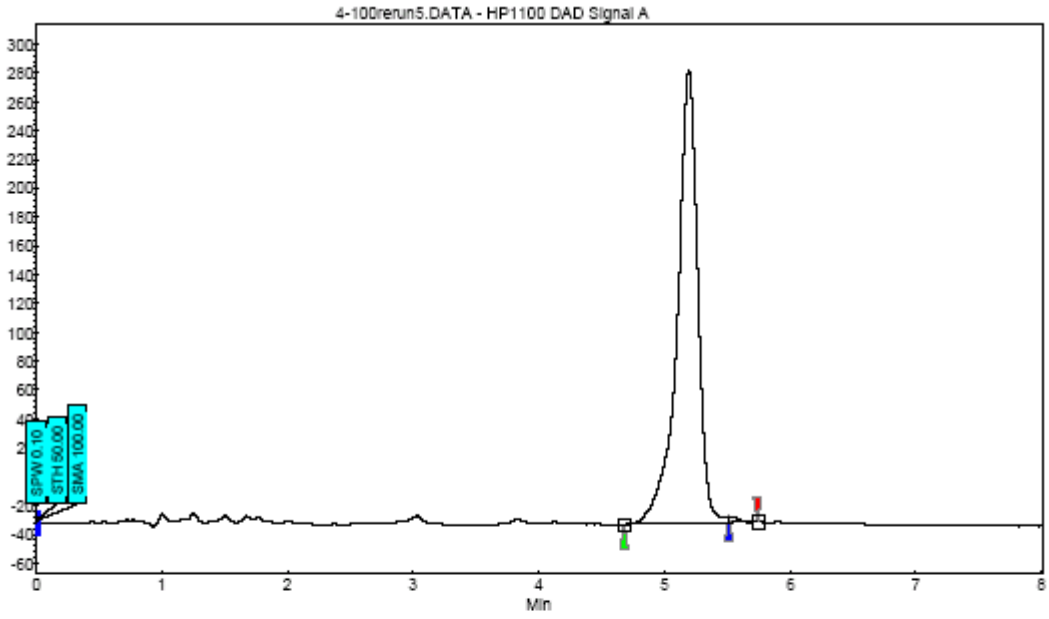
Racemic sample: (6k$_{exo}$)





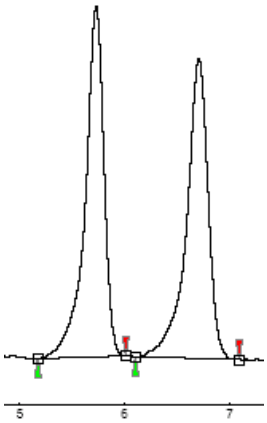
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.02	5.40	5.55	0.00	52.46	1365.5	223.4	52.456
2	UNKNOWN	5.57	5.77	6.00	0.00	47.54	1219.0	202.5	47.544
Total						100.00	2584.6	426.0	100.000

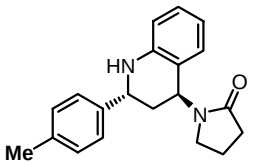
98% ee:



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.68	5.19	5.51	0.00	99.55	314.3	59.3	99.553
2	UNKNOWN	5.51	5.51	5.74	0.00	0.45	3.0	0.3	0.447
Total						100.00	317.4	59.6	100.000

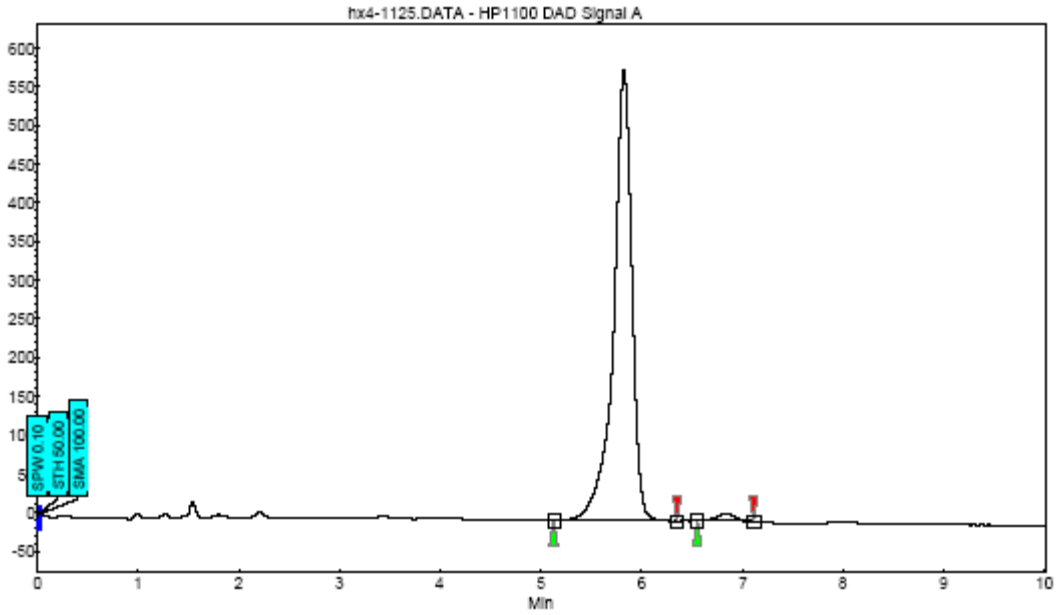
Racemic sample: (6l$_{exo}$)





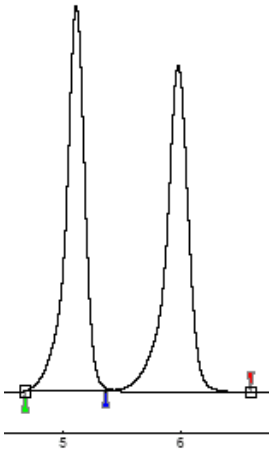
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.17	5.73	6.01	0.00	50.41	158.0	32.6	50.407
2	UNKNOWN	6.11	6.71	7.09	0.00	49.59	135.0	32.0	49.593
Total						100.00	293.0	64.6	100.000

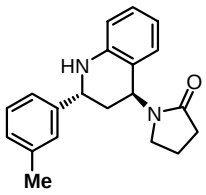
97% ee:



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	5.13	5.83	6.35	0.00	98.51	582.5	121.4	98.508
2	UNKNOWN	6.55	6.84	7.11	0.00	1.49	9.9	1.8	1.492
Total						100.00	592.4	123.2	100.000

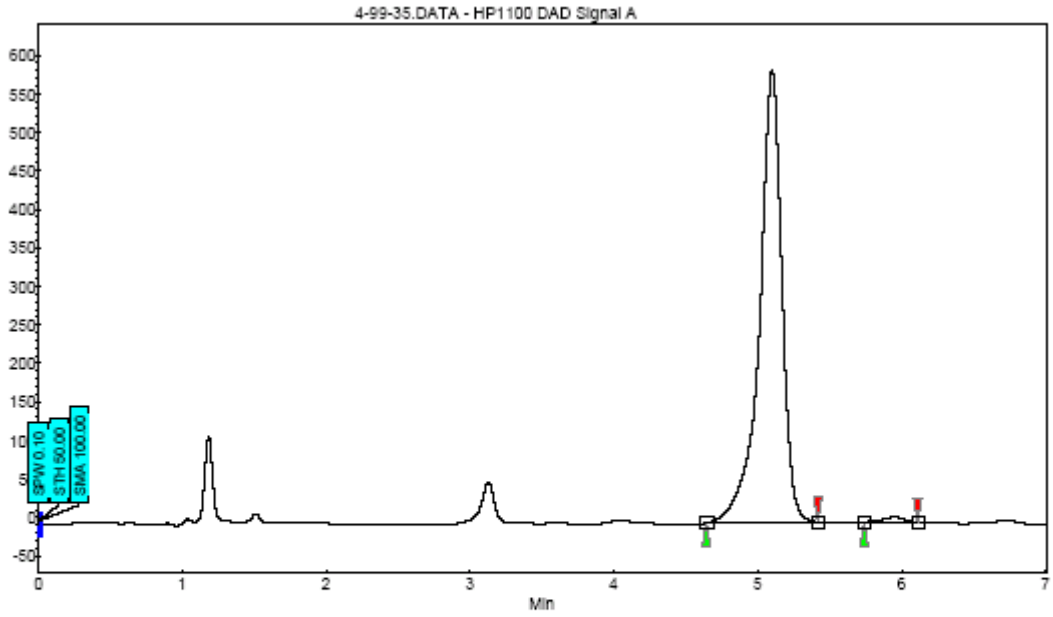
Racemic sample: (6m$_{exo}$)





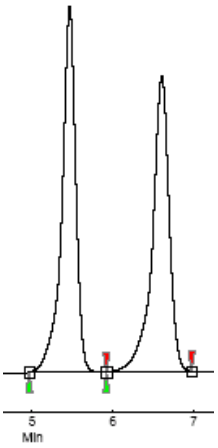
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.68	5.11	5.37	0.00	50.09	1389.6	260.4	50.091
2	UNKNOWN	5.37	5.98	6.59	0.00	49.91	1177.2	259.5	49.909
Total						100.00	2566.8	520.0	100.000

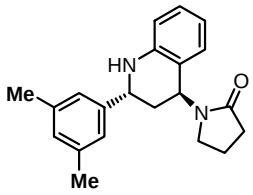
98% ee:



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.65	5.10	5.42	0.00	99.05	587.1	105.2	99.054
2	UNKNOWN	5.74	5.95	6.11	0.00	0.95	6.3	1.0	0.946
Total						100.00	593.4	106.2	100.000

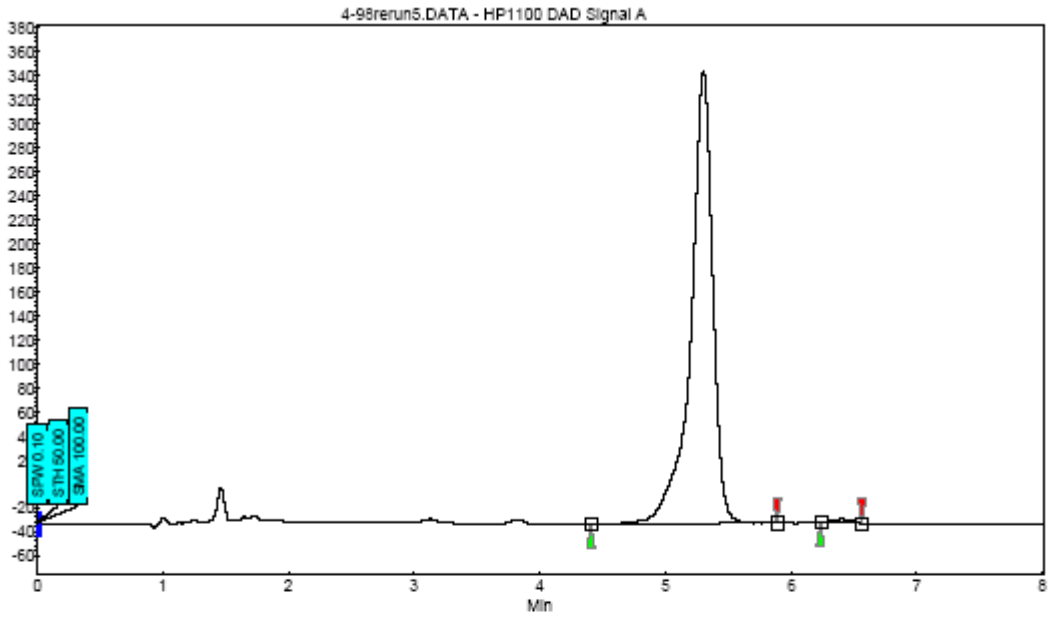
Racemic sample: ($6n_{exo}$)





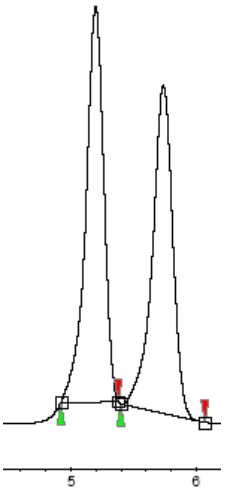
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.96	5.47	5.92	0.00	50.75	932.9	187.4	50.748
2	UNKNOWN	5.92	6.61	6.98	0.00	49.25	752.2	181.9	49.252
Total						100.00	1685.1	369.4	100.000

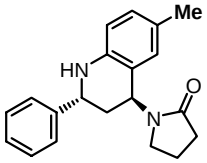
99% ee:



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.41	5.31	5.89	0.00	99.33	377.2	76.0	99.327
2	UNKNOWN	6.24	6.41	6.56	0.00	0.67	3.0	0.5	0.673
Total						100.00	380.2	76.5	100.000

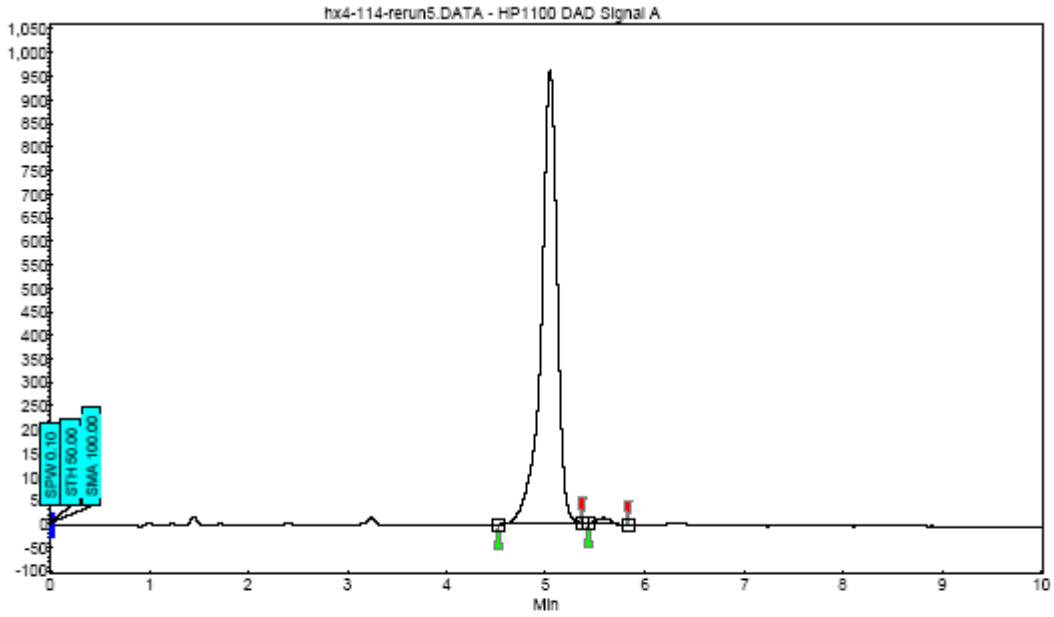
Racemic sample: (6o$_{exo}$)





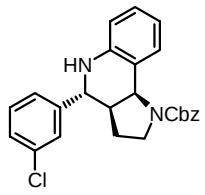
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.92	5.20	5.38	0.00	51.64	800.6	133.5	51.640
2	UNKNOWN	5.40	5.74	6.07	0.00	48.36	664.7	125.0	48.360
Total						100.00	1465.3	258.5	100.000

98% ee:

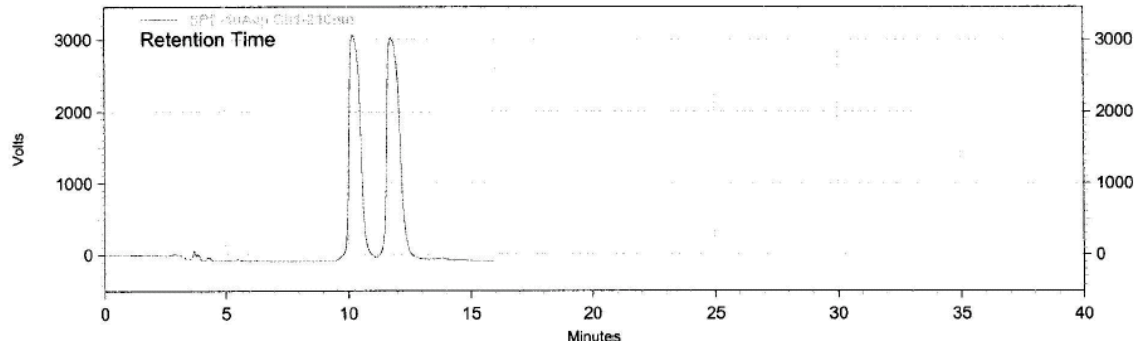


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	4.52	5.05	5.37	0.00	99.02	962.3	176.8	99.024
2	UNKNOWN	5.43	5.59	5.83	0.00	0.98	11.1	1.7	0.976
Total						100.00	973.4	178.5	100.000

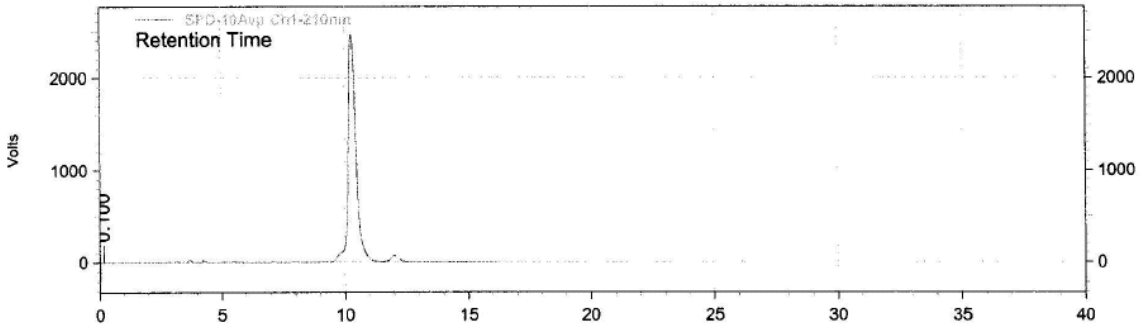
Racemic sample: ($8a_{exo}$)



14a



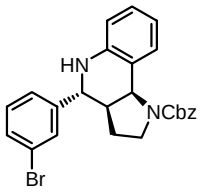
96% ee:

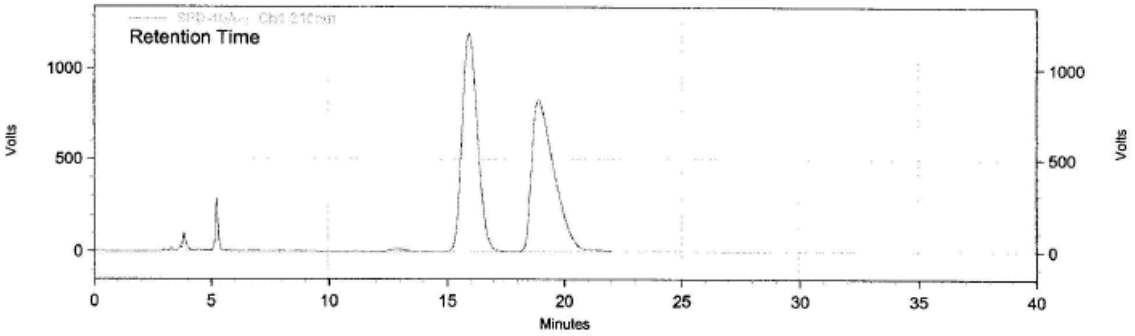


SPD-10Avp
Ch2-230nm
Results

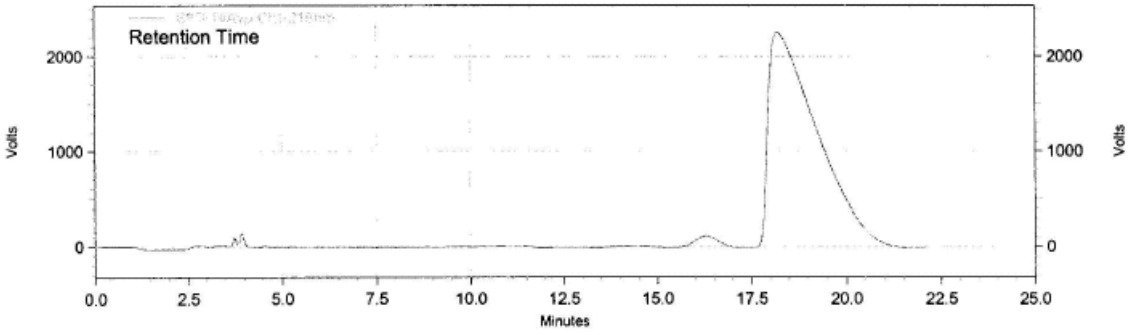
Retention Time	Area	Area %	Height	Height %
0.100	311	0.00	109	0.02
0.333	94	0.00	13	0.00
10.292	9418577	98.02	488242	98.03
12.008	189805	1.98	9702	1.95
Totals	9608787	100.00	498066	100.00

Racemic sample: ($8b_{exo}$)





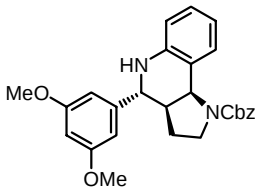
96% ee:

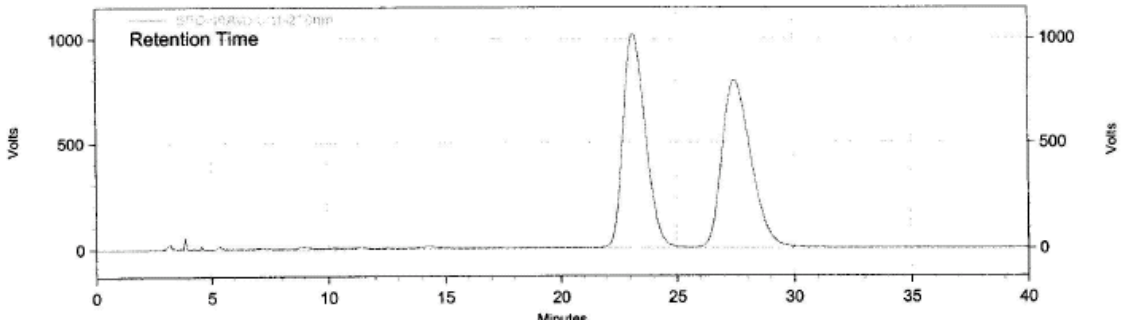


SPD-10Avp
Ch2-230nm
Results

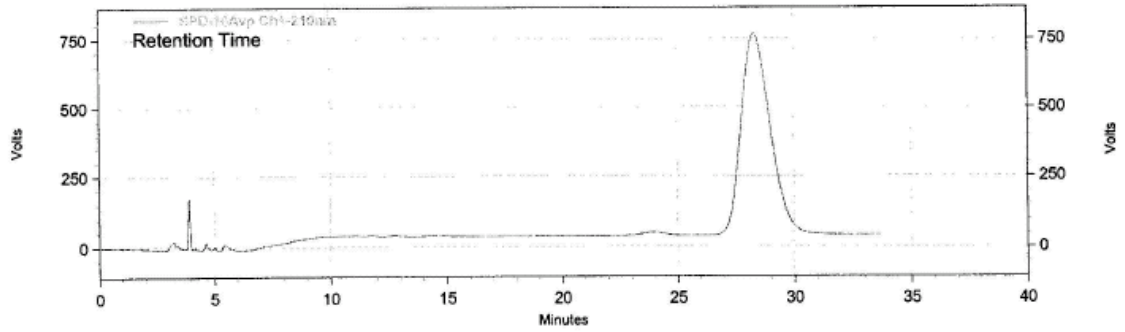
Retention Time	Area	Area %	Height	Height %
16.300	981653	2.19	23778	4.32
18.208	43840079	97.81	526840	95.68
Totals	44821732	100.00	550618	100.00

Racemic sample: ($8c_{exo}$)





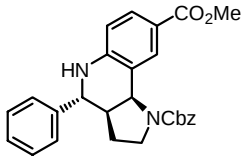
98% ee:



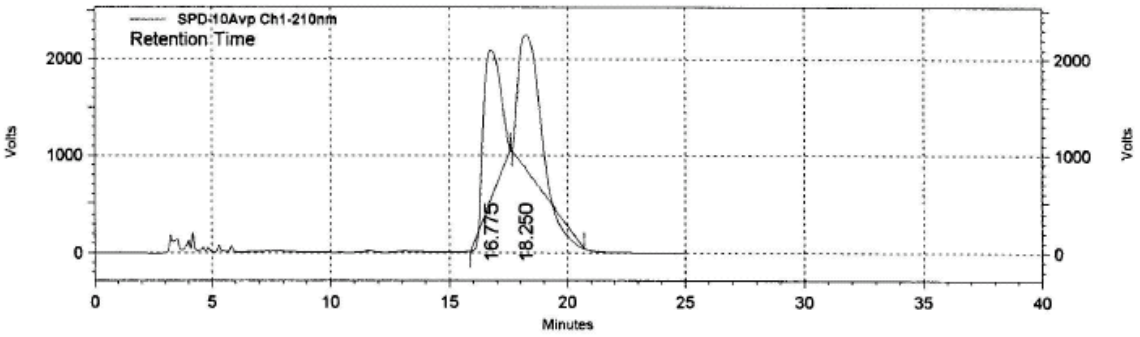
SPD-10Avp
Ch2-230nm
Results

Retention Time	Area	Area %	Height	Height %
23.967	173188	1.13	2607	1.43
28.308	15142553	98.87	179234	98.57
Totals	15315741	100.00	181841	100.00

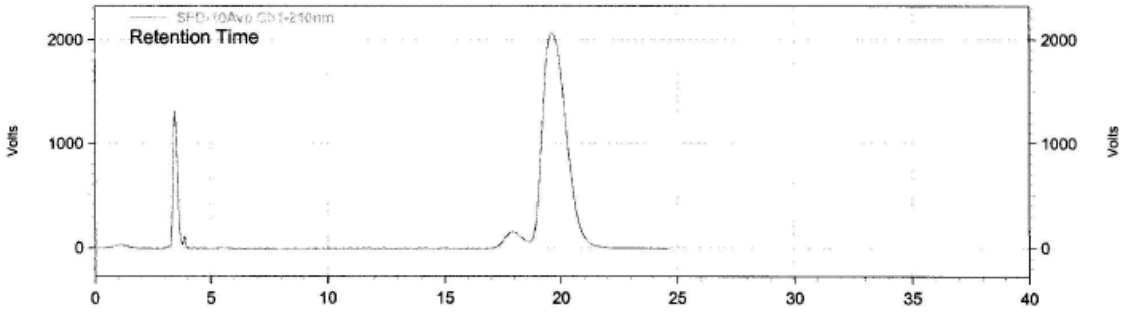
Racemic sample: ($8d_{exo}$)



14d



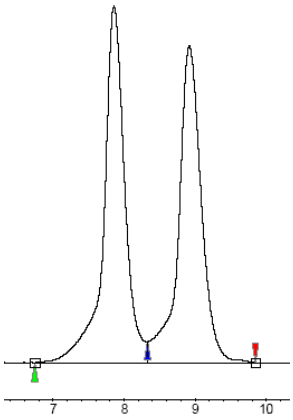
90% ee:

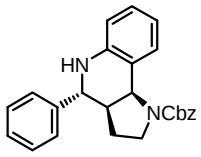


SPD-10Avp
Ch2-230nm
Results

Retention Time	Area	Area %	Height	Height %
17.917	3112827	5.00	55709	5.67
19.633	59099842	95.00	927438	94.33
Totals	62212669	100.00	983147	100.00

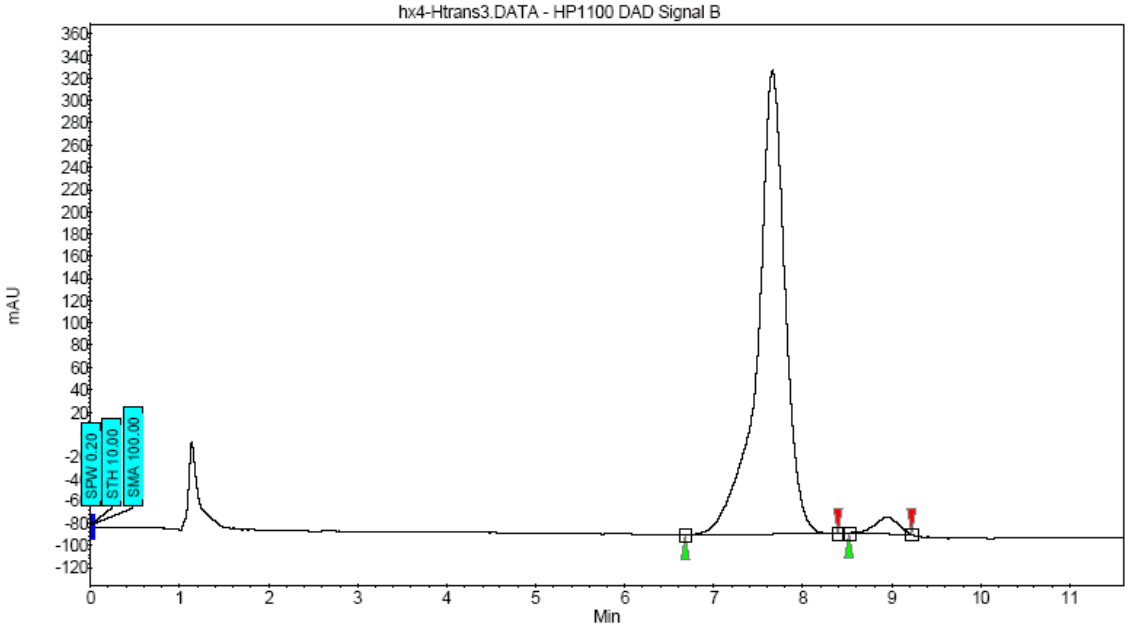
Racemic sample: ($8e_{exo}$)





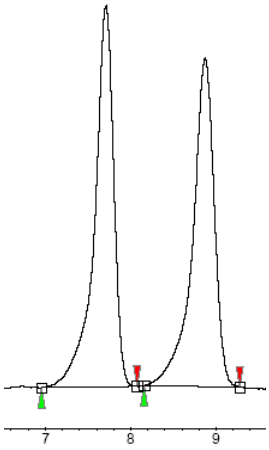
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.75	7.86	8.33	0.00	50.82	1170.2	401.0	50.824
2	UNKNOWN	8.33	8.92	9.85	0.00	49.18	1039.7	388.0	49.176
Total						100.00	2209.9	789.0	100.000

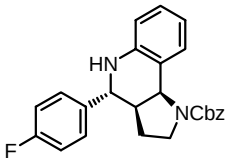
94% ee:



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.68	7.66	8.40	0.00	96.97	416.8	149.5	96.969
2	UNKNOWN	8.52	8.95	9.22	0.00	3.03	15.2	4.7	3.031
Total						100.00	432.0	154.1	100.000

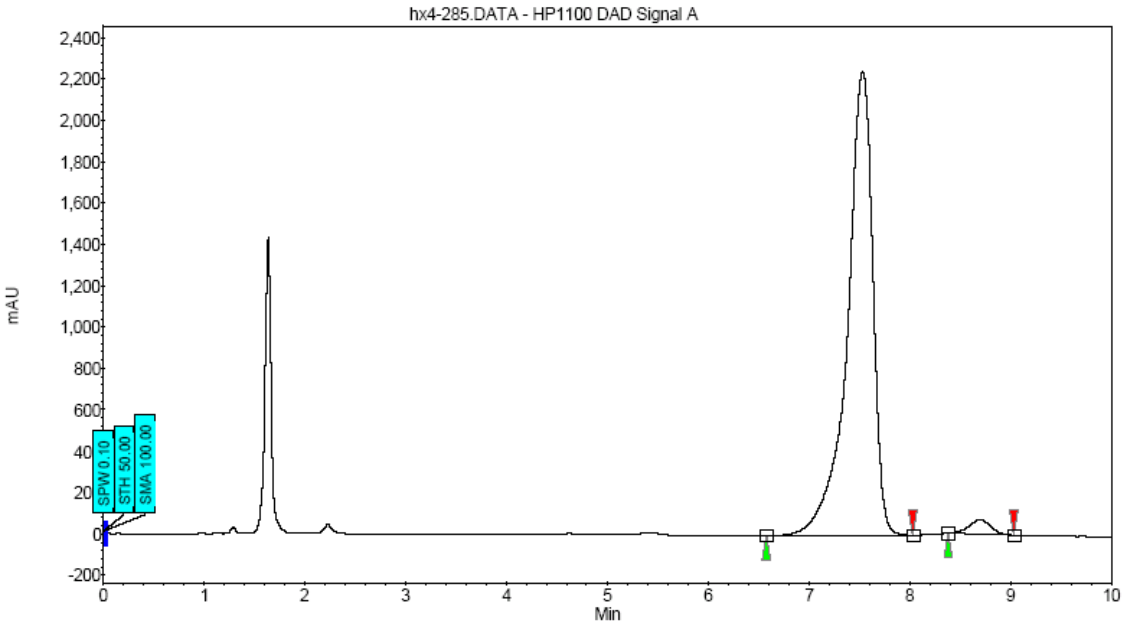
Racemic sample: (8f$_{exo}$)





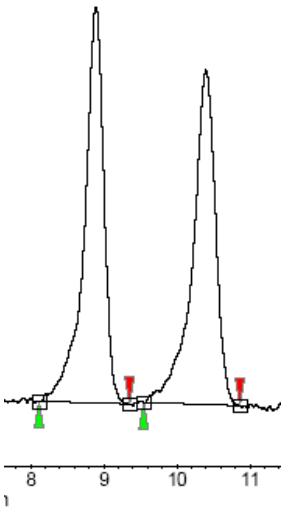
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.96	7.71	8.08	0.00	50.70	351.8	91.9	50.704
2	UNKNOWN	8.16	8.87	9.28	0.00	49.30	303.4	89.4	49.296
Total						100.00	655.2	181.3	100.000

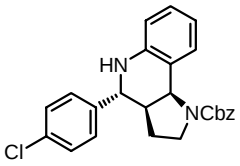
95% ee:



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.58	7.53	8.03	0.00	97.40	2238.4	653.4	97.400
2	UNKNOWN	8.38	8.70	9.03	0.00	2.60	69.1	17.4	2.600
Total						100.00	2307.5	670.9	100.000

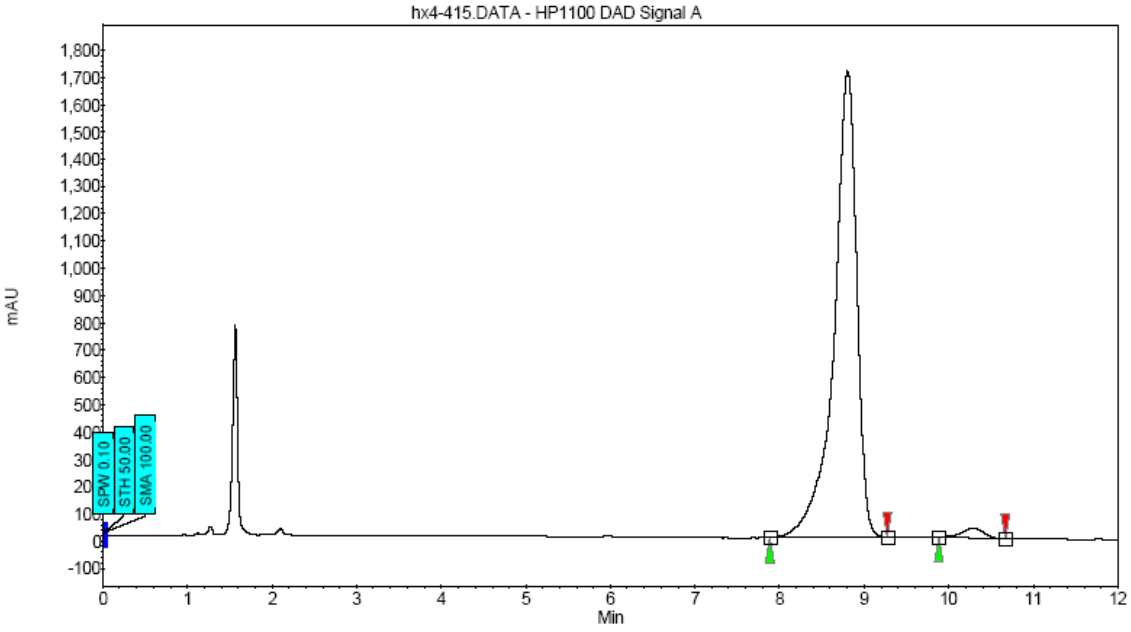
Racemic sample: ($8g_{exo}$)





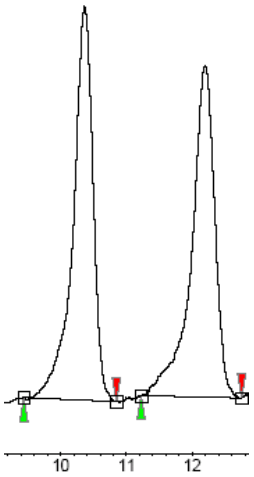
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	8.12	8.89	9.36	0.00	50.22	79.7	24.8	50.219
2	UNKNOWN	9.54	10.39	10.86	0.00	49.78	67.7	24.6	49.781
Total						100.00	147.4	49.4	100.000

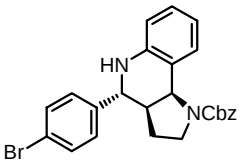
95% ee:



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	7.89	8.81	9.27	0.00	97.97	1707.5	529.3	97.966
2	UNKNOWN	9.88	10.29	10.67	0.00	2.03	36.2	11.0	2.034
Total						100.00	1743.8	540.2	100.000

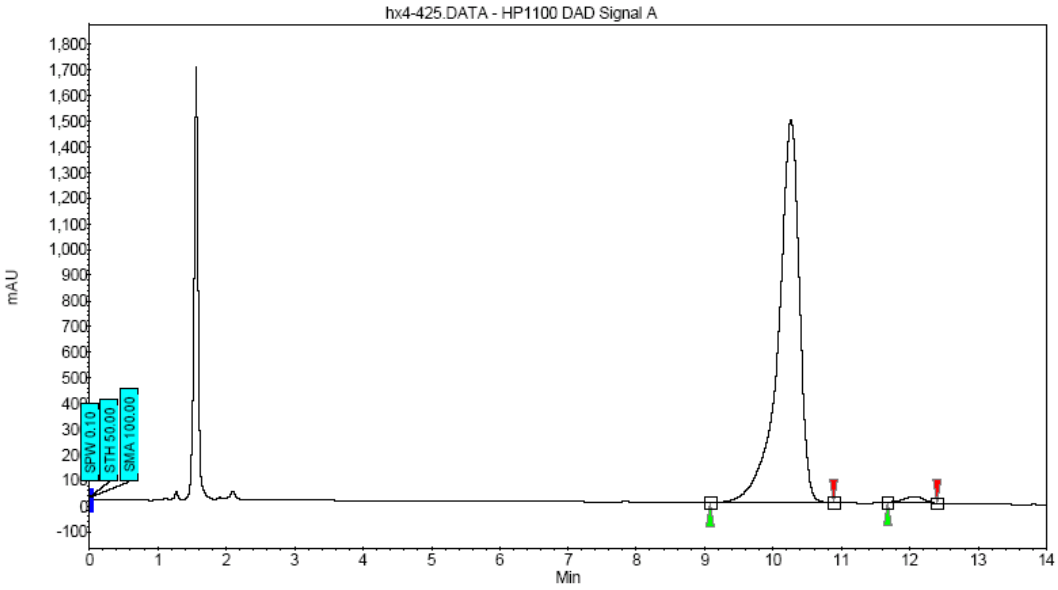
Racemic sample: (8h$_{exo}$)





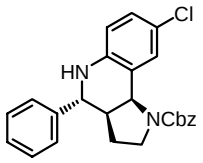
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	9.44	10.36	10.84	0.00	50.26	119.3	41.7	50.260
2	UNKNOWN	11.22	12.19	12.75	0.00	49.74	100.5	41.3	49.740
Total						100.00	219.8	83.0	100.000

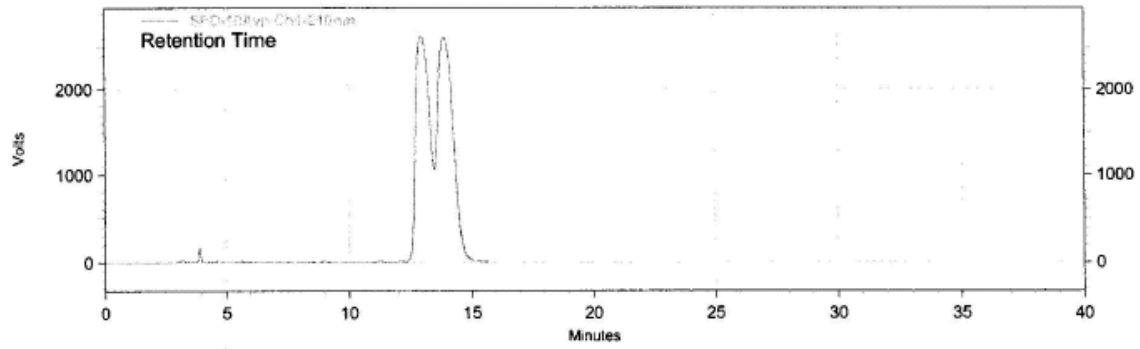
97% ee:



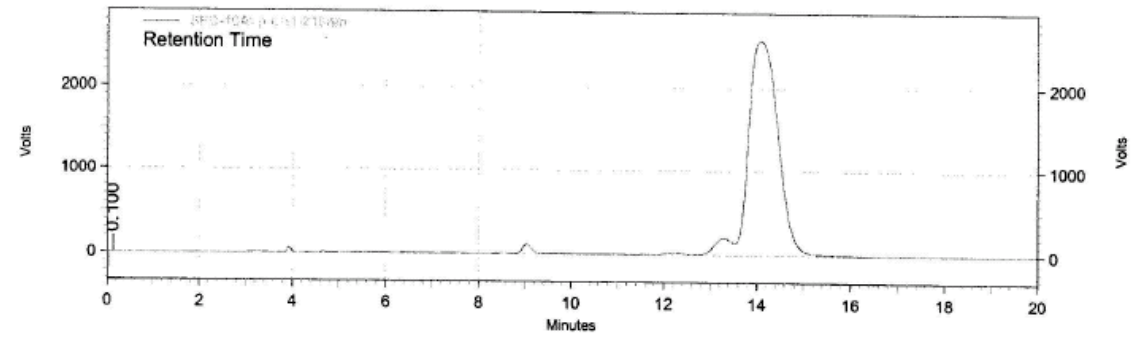
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	9.08	10.27	10.89	0.00	98.42	1489.8	532.0	98.425
2	UNKNOWN	11.68	12.07	12.40	0.00	1.58	25.5	8.5	1.575
Total						100.00	1515.3	540.5	100.000

Racemic sample: ($8i_{exo}$)





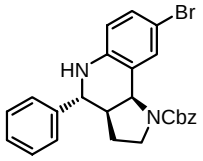
93% ee

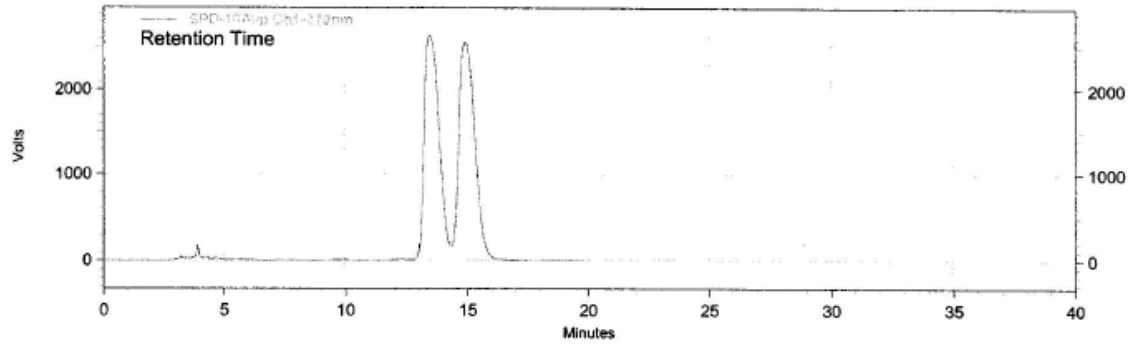


SPD-10Avp
Ch2-230nm
Results

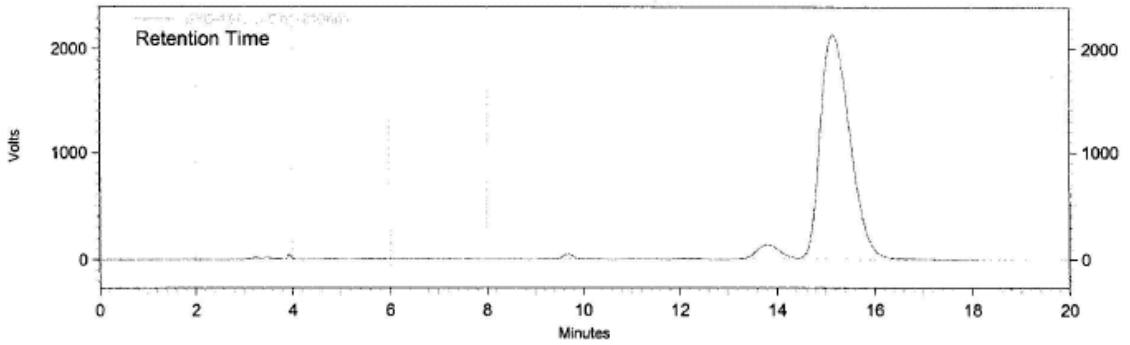
Retention Time	Area	Area %	Height	Height %
13.300	673905	3.65	26305	4.99
14.083	17794281	96.35	500790	95.01
Totals	18468186	100.00	527095	100.00

Racemic sample: ($8j_{exo}$)





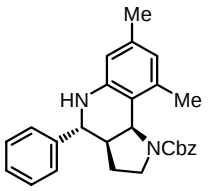
91% ee

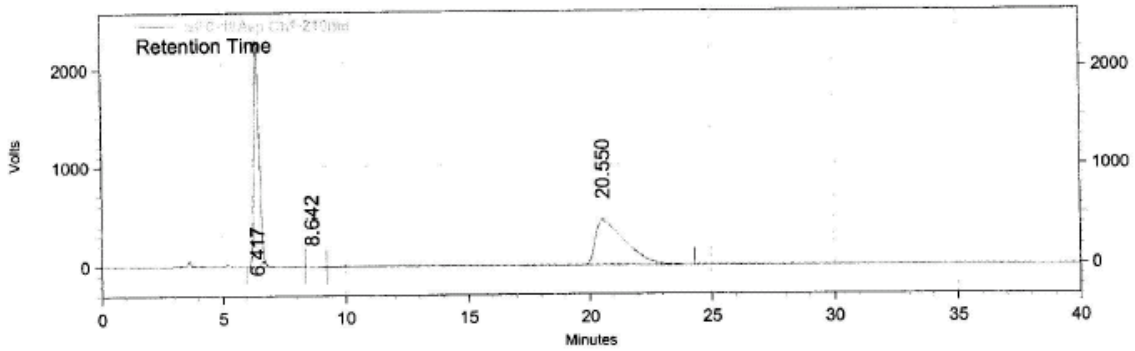


SPD-10Avp
Ch2-230nm
Results

Retention Time	Area	Area %	Height	Height %
0.367	150	0.00	6	0.00
13.808	706757	4.75	20993	5.51
15.158	14157974	95.24	360131	94.49
Totals	14864881	100.00	381130	100.00

Racemic sample: ($8k_{exo}$)

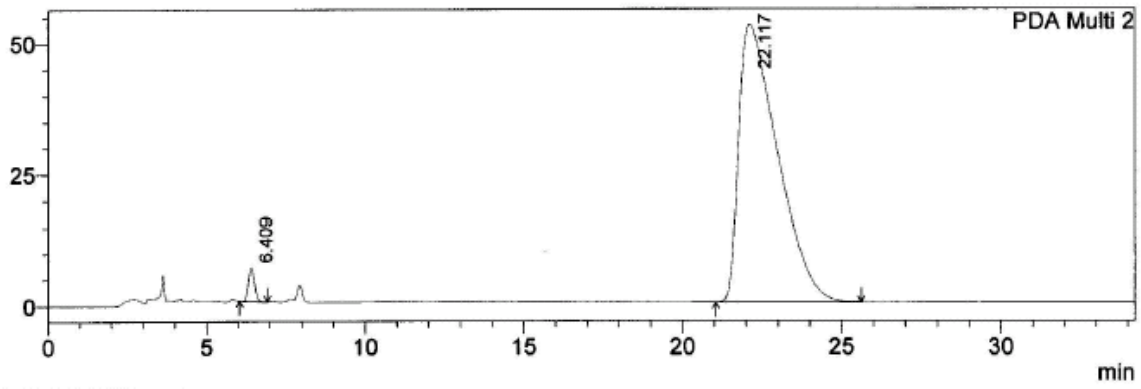




SPD-10Avp
Ch1-210nm
Results

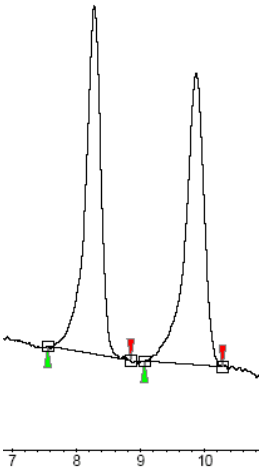
Retention Time	Area	Area %	Height	Height %
6.417	35276182	49.38	2285170	83.63
8.642	50664	0.07	92	0.00
20.550	36109789	50.55	447136	16.36
Totals	71436635	100.00	2732398	100.00

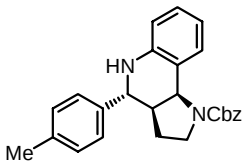
96% ee:



Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.409	86071	6493	1.888	10.938
2	22.117	4471974	52867	98.112	89.062
Total		4558045	59360	100.000	100.000

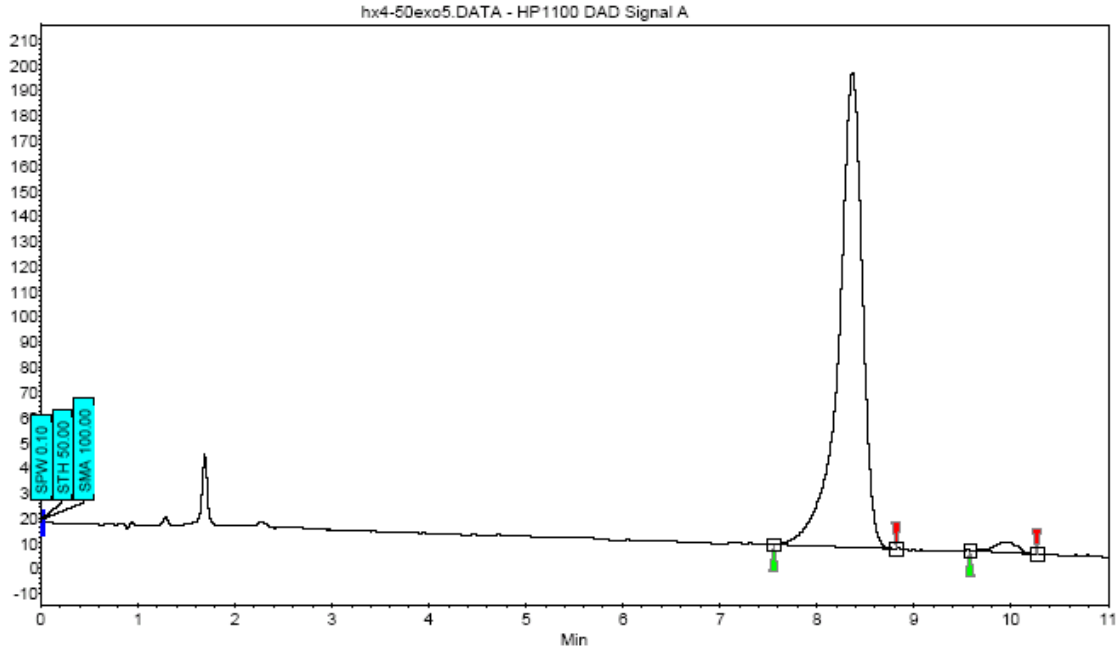
Racemic sample: (8l$_{exo}$)





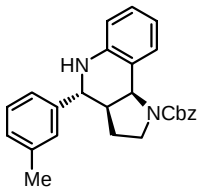
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	7.56	8.28	8.85	0.00	49.84	46.5	13.1	49.840
2	UNKNOWN	9.06	9.87	10.28	0.00	50.16	38.9	13.2	50.160
Total						100.00	85.5	26.3	100.000

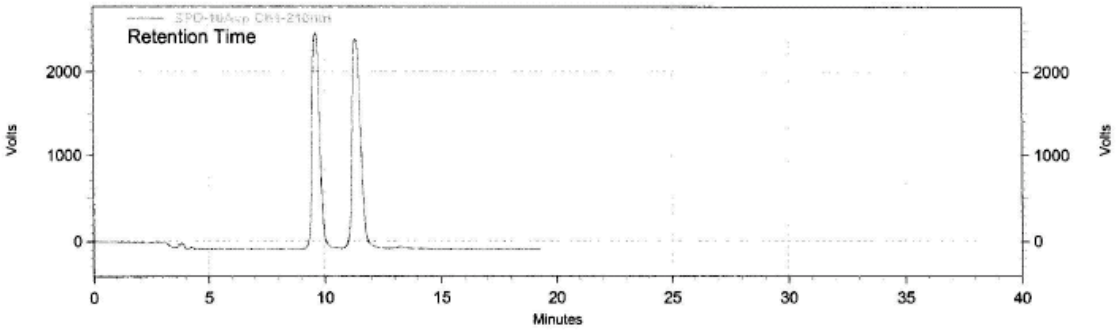
96% ee:



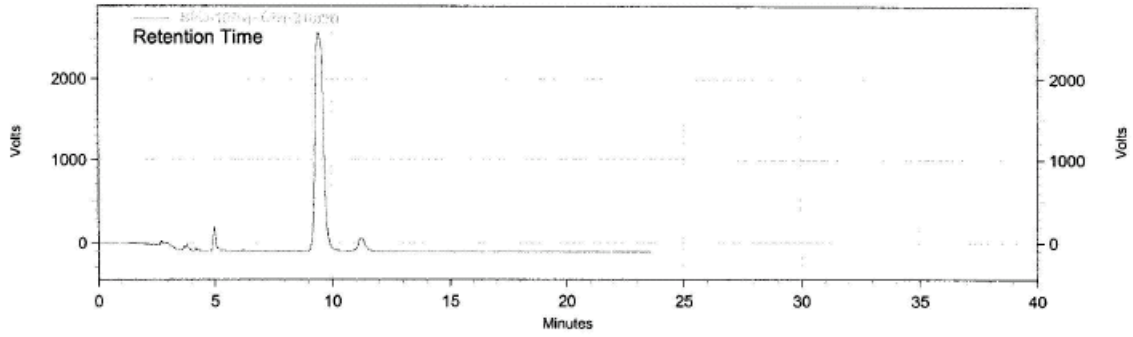
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	7.56	8.37	8.82	0.00	97.74	188.5	53.1	97.742
2	UNKNOWN	9.57	9.94	10.26	0.00	2.26	4.2	1.2	2.258
Total						100.00	192.7	54.4	100.000

Racemic sample: (8m$_{exo}$)





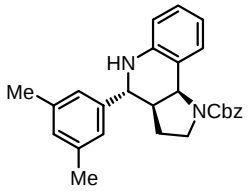
95% ee:

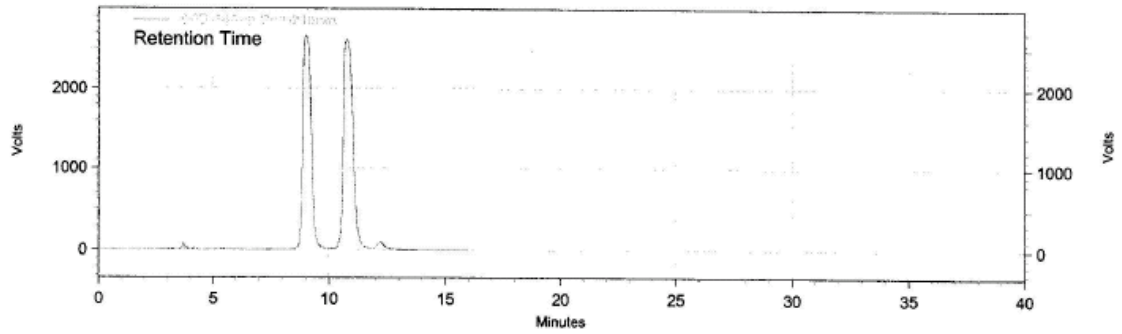


SPD-10Avp
Ch2-230nm
Results

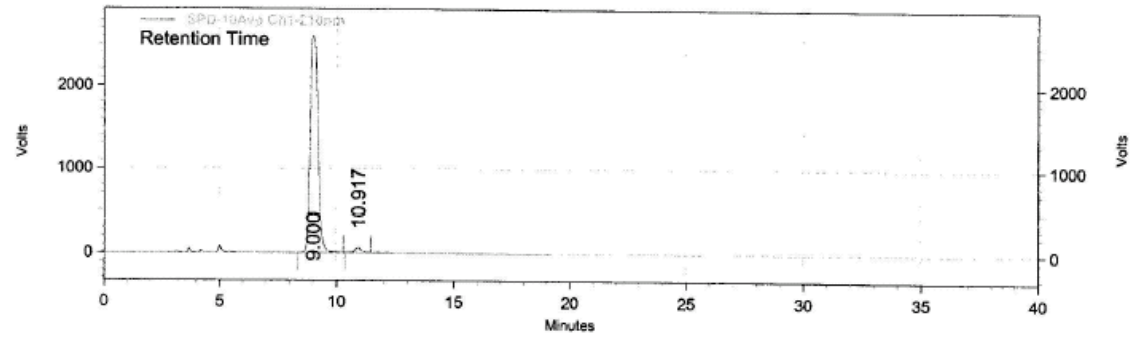
Retention Time	Area	Area %	Height	Height %
9.425	16612504	97.36	1038523	97.73
11.233	450665	2.64	24145	2.27
Totals	17063169	100.00	1062668	100.00

Racemic sample: ($8n_{exo}$)





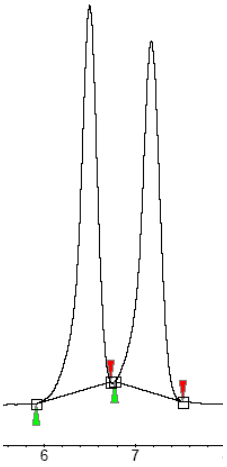
97% ee:

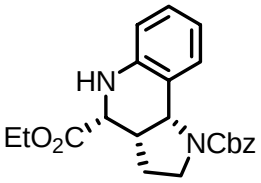


SPD-10Avp
Ch2-230nm
Results

Retention Time	Area	Area %	Height	Height %
9.000	15502077	98.57	980149	99.00
10.917	224673	1.43	9870	1.00
Totals	15726750	100.00	990019	100.00

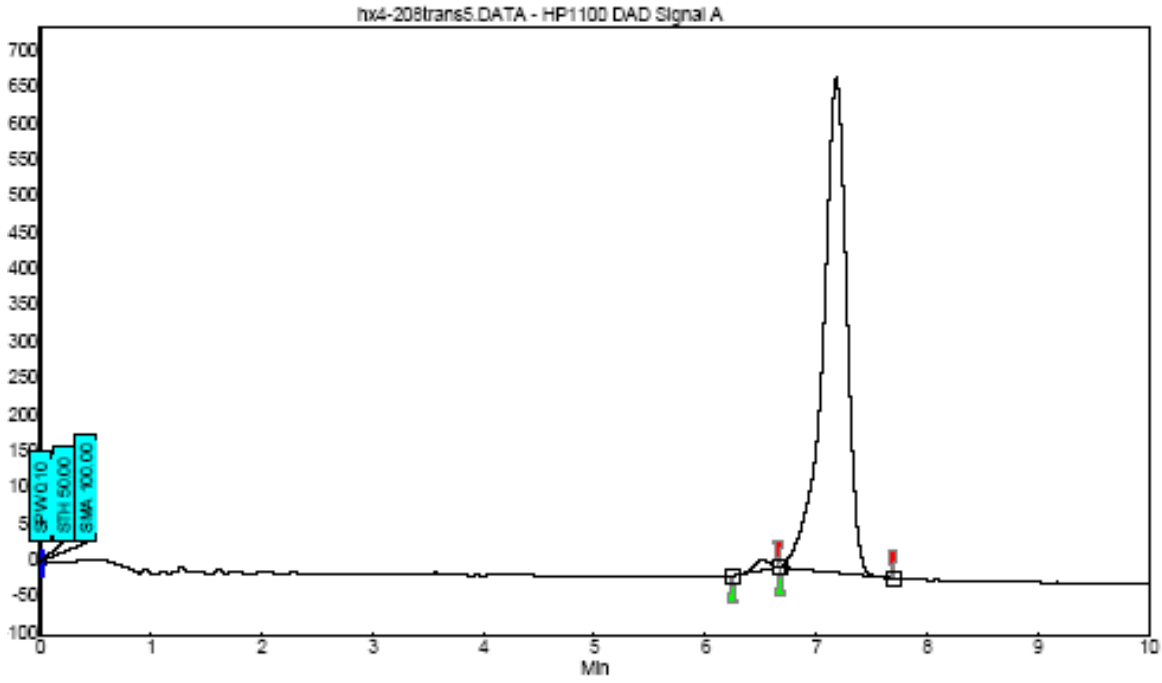
Racemic sample: (10a$_{endo}$)





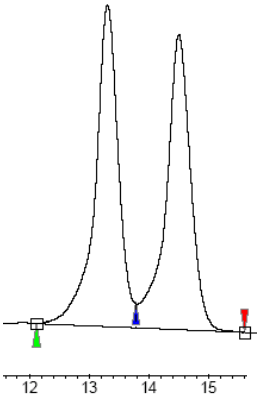
Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
2	UNKNOWN	5.91	6.50	6.73	0.00	50.43	988.2	219.4	50.428
1	UNKNOWN	6.78	7.18	7.53	0.00	49.57	907.5	215.7	49.572
Total						100.00	1895.7	435.1	100.000

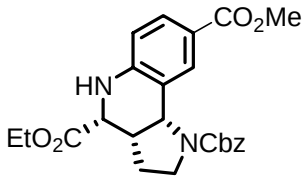
97% ee: The reaction was carried out with ***ent*-1a**.



Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	6.24	6.51	6.66	0.00	1.41	15.5	2.4	1.409
2	UNKNOWN	6.67	7.18	7.69	0.00	98.59	679.2	168.9	98.591
Total						100.00	694.7	171.3	100.000

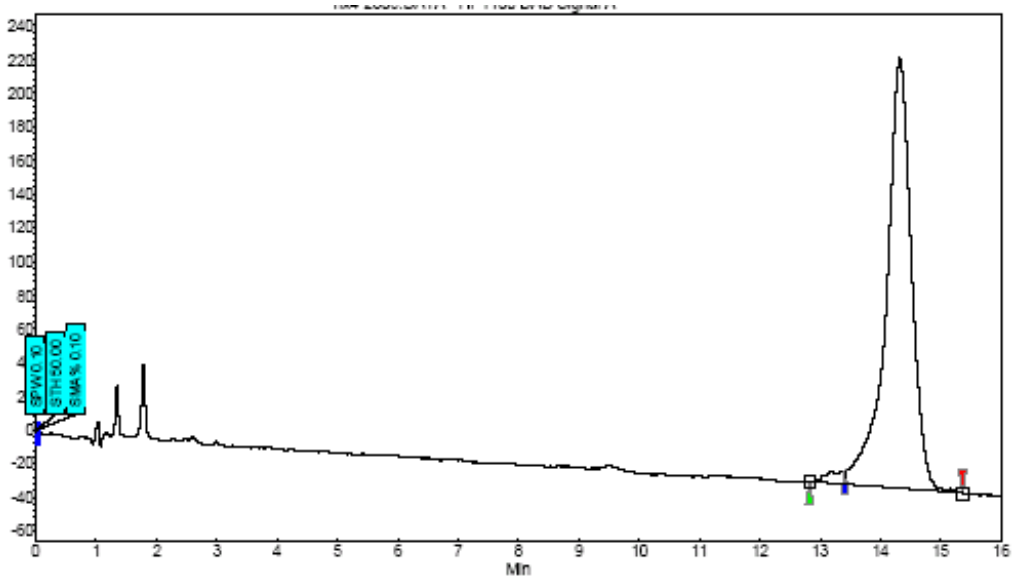
Racemic sample: (10b$_{endo}$)





Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	12.12	13.31	13.78	0.00	50.72	358.2	161.5	50.717
2	UNKNOWN	13.78	14.50	15.60	0.00	49.28	328.6	156.9	49.283
Total						100.00	686.8	318.4	100.000

95% ee: The reaction was carried out with ***ent*-1a**.

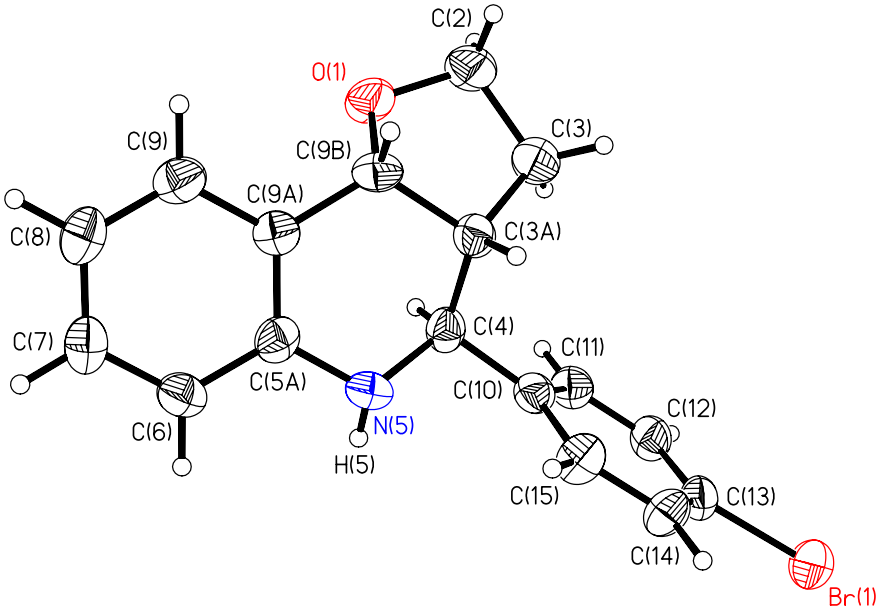


Index	Name	Start	Time	End	RT Offset	Quantity	Height	Area	Area
		[Min]	[Min]	[Min]	[Min]	[% Area]	[µV]	[µV.Min]	[%]
1	UNKNOWN	12.82	13.41	13.41	0.00	2.04	7.6	2.6	2.042
2	UNKNOWN	13.41	14.31	15.35	0.00	97.96	255.2	123.9	97.958
Total						100.00	262.8	126.5	100.000

K. X-ray Crystallographic Data

The enantiopure (3a*R*,4*S*,9b*R*)-4-(4-Bromophenyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinoline **4b$_{exo}$** was obtained after recrystallization from an ethyl acetate/hexane solvent mixture as the product of enantioselective reaction between *N*-(4-bromobenzylidene)benzenamine and 2,3−dihydrofuran **3** catalyzed by ***ent*-1a**.

A colorless chunk of the compound roughly 0.08 mm x 0.08 mm x 0.08 mm in size was transferred to a Bruker SMART CCD diffractometer equipped with an Oxford Cryosystems Cryostream Cooler and Mo Kα radiation (λ = 0.71073 Å). A total of 1305 frames were collected at 193 (2) K to θ_{max} = 25.00° with an oscillation range of 0.3°/frame, and an exposure time of 30 s/frame using SMART software. (Bruker AXS, 2001a) Unit cell refinement on all observed reflections, and data reduction with corrections for Lp and decay were performed using SAINT. (Bruker AXS, 2006) Scaling and a multi-scan absorption correction were done using SADABS. (Bruker AXS, 2004) The data was processed to θ_{max} = 25.00° rather than the routine value of θ_{max} = 27.50° because the quality and the completeness of the data at higher angles did not justify their inclusion. A total of 8182 reflections were collected, 6300 were unique (R_{int} = 0.0207), and 5665 had $I > 2\sigma(I)$. A lack of systematic absences was consistent with the compound having crystallized in the triclinic space group P1 or P-1. The chiral space group P1 (No. 1) was selected based on an observed mean $|E^2-1|$ value of 0.725 (versus the expectation values of 0.968 and 0.736 for centric and noncentric data, respectively).



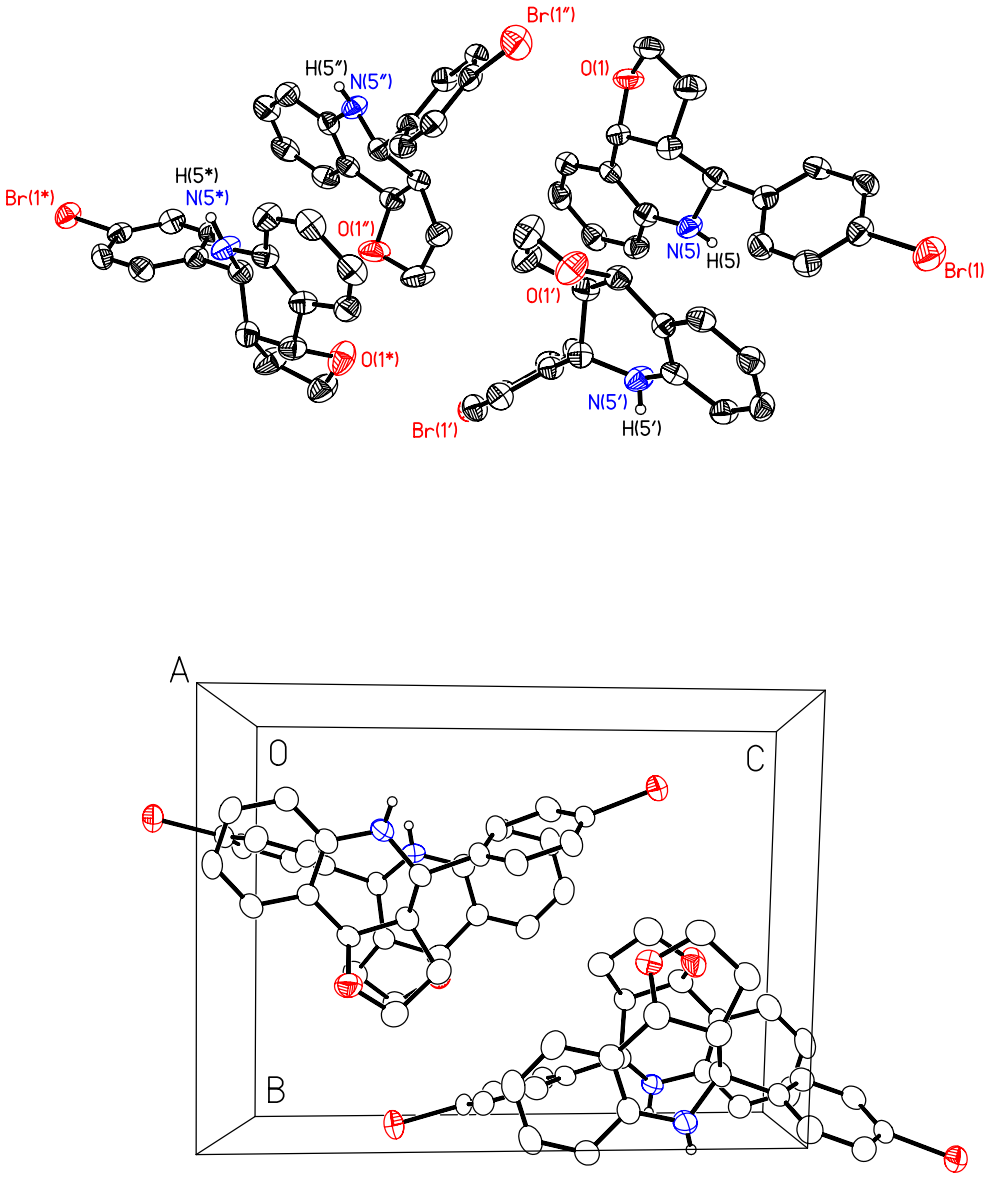


Figure S1. Perspective views showing 50% probability displacement ellipsoids.

Bruker AXS (2001a). *SMART V5.625(NT)*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.

Bruker AXS (2004). *SADABS*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA.

Bruker AXS (2006). *SAINT V7.34A*. Bruker Analytical X-ray Systems Inc., Madison, Wisconsin,USA.

Crystal data

$C_{17}H_{16}BrNO$	F_{000} = 672
M_r = 330.22	D_x = 1.526 Mg m^{-3}
Triclinic, *P*1	Melting point: ? K
Hall symbol: P 1	Mo *K*α radiation λ = 0.71073 Å
a = 9.685 (2) Å	Cell parameters from 3748 reflections
b = 10.643 (3) Å	θ = 2.4–25.0°
c = 14.121 (3) Å	μ = 2.86 mm^{-1}
α = 90.540 (4)°	*T* = 193 (2) K
β = 95.648 (4)°	Cell measurement pressure: ? kPa
γ = 97.136 (4)°	Chunk, colorless
V = 1437.0 (6) Å^3	0.08 × 0.08 × 0.08 mm
Z = 4	

Data collection

Bruker CCD diffractometer	8182 measured reflections
Radiation source: normal-focus sealed tube	6300 independent reflections
Monochromator: graphite	5665 reflections with $I > 2\sigma(I)$
Detector resolution: 836.6 pixels mm^{-1}	R_{int} = 0.021
T = 193(2) K	θ_{max} = 25.0°

P = ? kPa	θ_{min} = 1.5°
ω scans, 1305 0.3° rotations	h = −11 11
Absorption correction: multi-scan SADABS (Bruker AXS, 2004)	k = −12 12
T_{min} = 0.804, T_{max} = 0.804	l = −10 16

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.029	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.068	$w = 1/[\sigma^2(F_o^2) + (0.0221P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 0.98	$(\Delta/\sigma)_{max} < 0.001$
6300 reflections	$\Delta\rho_{max}$ = 0.56 e Å^{-3}
733 parameters	$\Delta\rho_{min}$ = −0.28 e Å^{-3}
3 restraints	Extinction correction: none
? constraints	Absolute structure: Flack H D (1983), Acta Cryst. A39, 876-881
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.001 (5)

Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) etc. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*-factors based on ALL data will be even larger.

The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL. (Bruker AXS, 2001b) The asymmetric unit was found to contain four molecules of (3a*R*,4*S*,9b*R*)-4- (4-Bromophenyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-*c*]quinoline. All of the nonhydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms were assigned isotropic displacement coefficients $U(H) = 1.2U(C)$ or $1.5U(N)$. The coordinates for the N-bound hydrogens were free to vary. The coordinates for the remaining hydrogens were allowed to ride on their respective carbons. The refinement converged to $R(F) = 0.0294$, $wR(F^2) = 0.0661$, and $S = 0.983$ for 5665 reflections with $I > 2\sigma(I)$, and $R(F) = 0.0337$, $wR(F^2) = 0.0676$, and $S = 0.983$ for 6300 unique reflections, 733 parameters, and 3 origin-defining restraints. The maximum $|\Delta/\sigma|$ in the final cycle of least-squares was less than 0.001, and the residual peaks on the final difference-Fourier map ranged from -0.280 to 0.561 eÅ^{-3}. Scattering factors were taken from the International Tables for Crystallography, Volume C. (Maslen *et al.*, 1992, and Creagh & McAuley, 1992)

The Flack absolute structure parameter refined to x = 0.001 (5) [versus the expectation values of 0 (within 3 esd's) for the correct and +1 for the inverted absolute structure] indicating that the coordinates provided below are for the correct hand [i.e., (3aR,4S,9bR)]. (Flack, 1983)

$R(F) = R1 = \Sigma ||F_o|-|F_c|| / \Sigma|F_o|$, $wR(F^2) = wR2 = [\ \Sigma\ w\ (F_o^2-F_c^2)^2 / \Sigma\ w\ (F_o^2)^2\ ]^{1/2}$, and *S* = Goodness-of-fit on $F^2 = [\ \Sigma\ w\ (F_o^2-F_c^2)^2\ /\ (n-p)\ ]^{1/2}$, where *n* is the number of reflections and *p* is the number of parameters refined.

L. Formyl ^{1}H NMR Chemical Shift Experiments to Probe Catalysts/Iminium Triflates Interaction

Iminium triflate **2a•HOTf** is a moisture-sensitive salt, obtained via the quantitative protonation of benzylidene aniline **2a** by HOTf. **2a•HOTf exists** as a tight ion pair and has a very limited solubility in non-poloar organic solvent, such as C_6D_6 (2 mM, determined by the internal standard 1,3,5-trimethoxybenzene). It is known that the ^{1}H NMR chemical shift of an iminium formyl H is a sensitive probe for the degree of ion pair (iminium cation and its counter ion) separation: A more magnetically shielded formyl H is correlated to a more separated ion pair, while a less magnetically shielded formyl H suggests the formation of a tighter ion pair. Mono-functional urea **15** and **1a** can both co-solubilize **2a•HOTf** in non-polar solvent (C_6D_6) through the formation of 1 : 1 dynamic complexes (8 mM and 35 mM, respectively). ^{1}H NMR experiments indicate that **15** binds triflate and induces a slightly more separated ion pair (the formyl H of **2a•HOTf** shifts ca. 0.1 ppm upfield), which is consistent with the anion-binding properties of **15**. On the other hand, **1a** induced a large (ca. 1 ppm) downfield shift of the formyl H on **2a•HOTf** in ^{1}H NMR. This unique phenomenon suggests the formation of a tighter ion pair and the existence of secondary interaction between the sulfinamide and **2a•HOTf**.

General Procedure for Complex Formation between 2a•HOTf and 15/1a under Solubility-Saturated Conditions

To an 8 mL oven-dried vial, was added **2a•HOTf** (16.6 mg, 0.05 mmol), catalyst **15**/**1a** (0.1 mmol), 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol), activated 5Å molecular sieves (10 mg) and C_6D_6 (1 mL) under a nitrogen atmosphere at room temperature. After stirring vigorously for 15 min, the vial was left unstirred for another 15 min, allowing for adequate precipitation. The clear sample was subsequently subjected for ^{1}H NMR analysis.

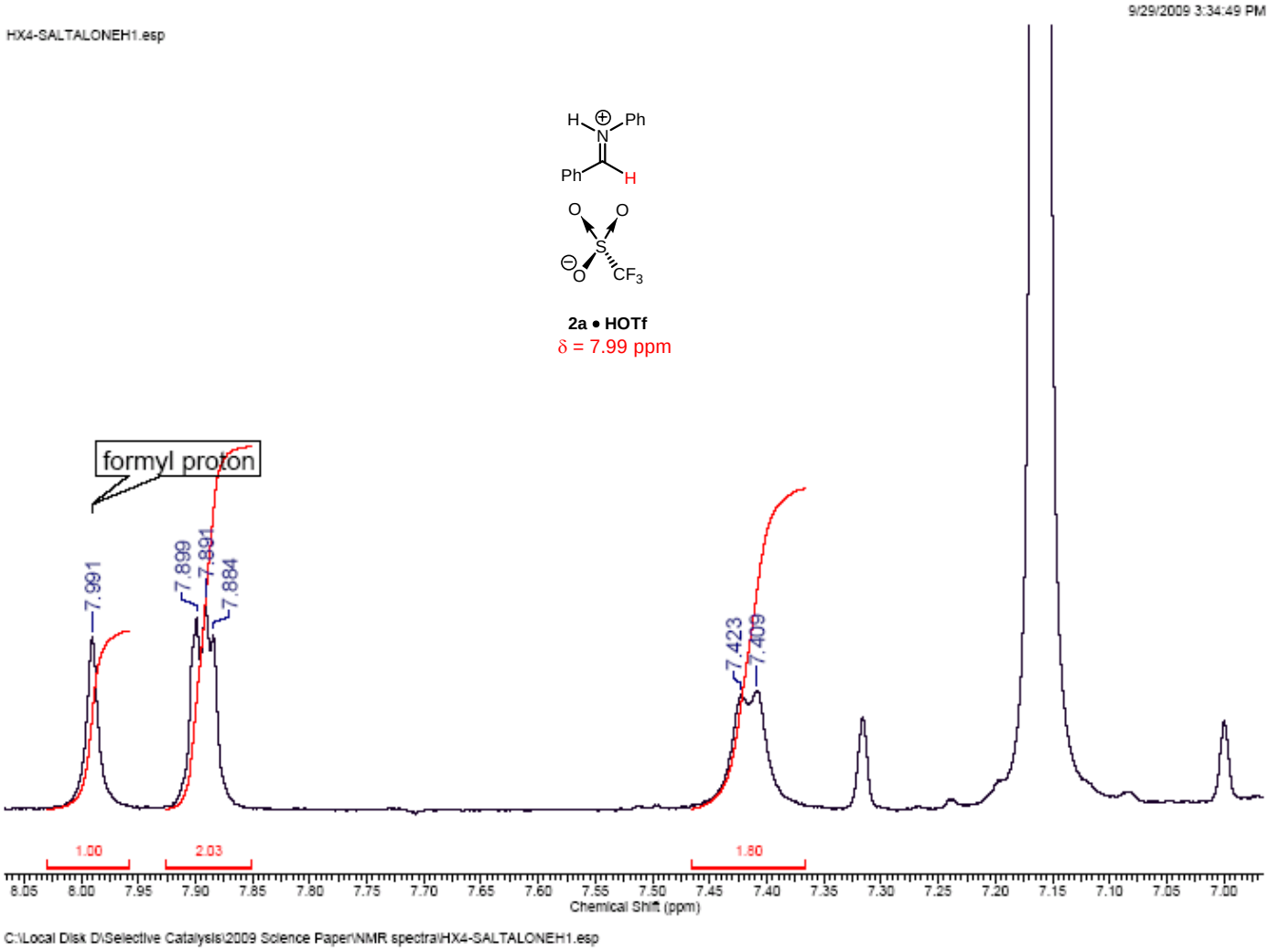


Figure S2. ^{1}H NMR Spectrum of **2a•HOTf** in C_6D_6

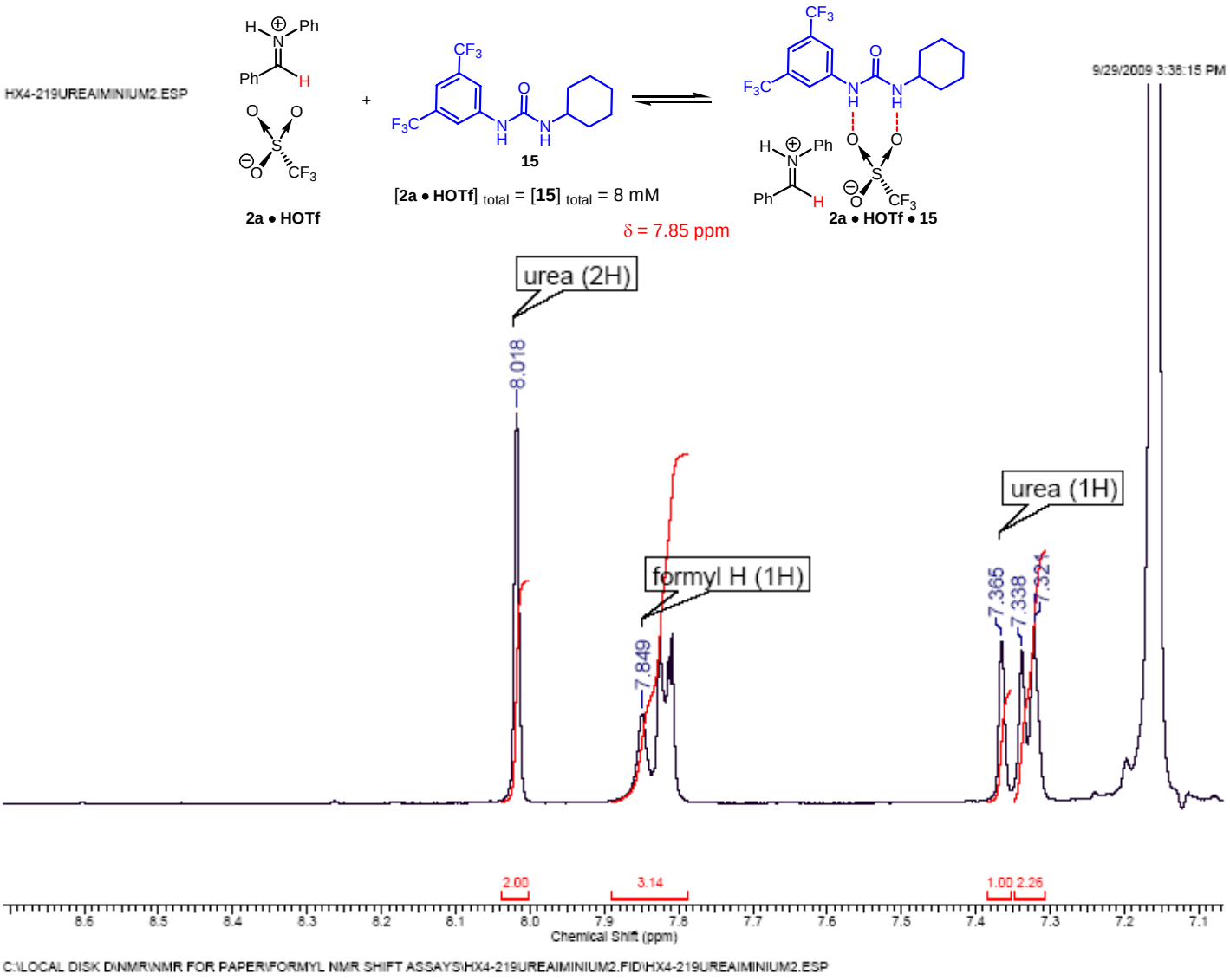


Figure S3. ^{1}H NMR Spectrum of **2a•HOTf/15** (1:1) in C_6D_6

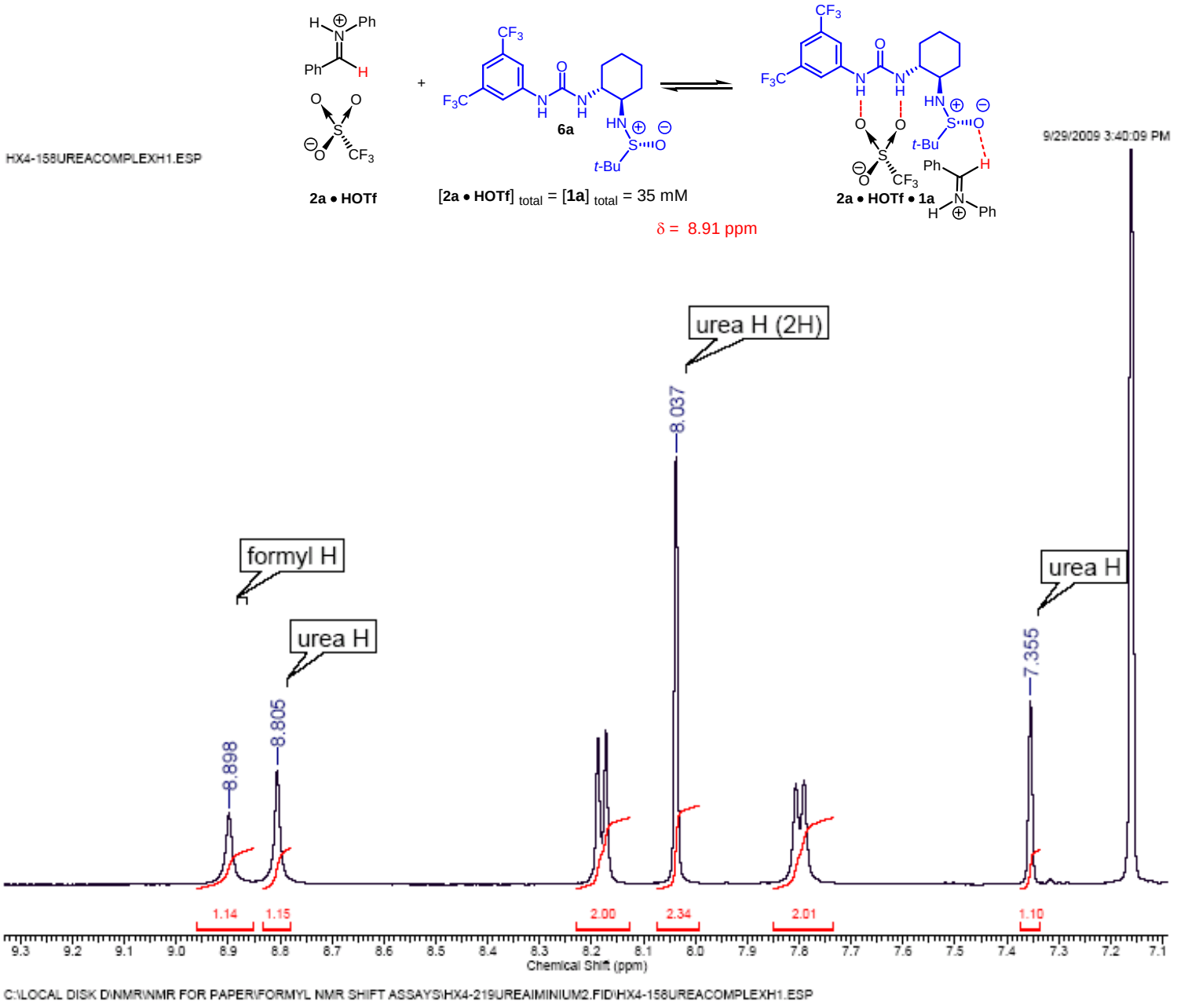


Figure S4. ^{1}H NMR Spectrum of **2a•HOTf/1a** (1:1) in C_6D_6

M. Kinetic Studies of Racemic and Enantioselective Povarov Reactions

General Information: Reactions were carried out in an Omnical reaction calorimeter. The instrument contains an internal magnetic stirrer and a differential scanning calorimeter (DSC), which compares the heat released or consumed in a sample vessel to an empty reference vessel. The vessels were 16 mL 21 mm x 70 mm borosilicate screw-thread vials fit with opentop black phenolic screw caps and white PTFE septa (KimbleBrand) charged with Teflon stir bars. Sample volumes did not exceed 3.5 mL. The temperature of the DSC was maintained constant at room temperature using a Neslab RTE-111 water circulator, ensuring that the reaction would proceed under isothermal conditions.

Representative calorimetry experiment: An oven-dried 16-mL glass vial equipped with a 3 mm x 12 mm stir bar was capped with a black phenolic cap fitted with a PTFE septum and was allowed to cool to room temperature. Imine **2a** (0.109 g, 0.600 mmol, 1 equiv) was added transferred to the vial, and the vial was immediately recapped. Anhydrous toluene (1.39 mL), a stock solution of urea catalyst **1a** in toluene (0.100 M, 1.50 mL), and 2,3-dihydrofuran (91. μL, 1.2 mmol. 2.0 equiv) were added sequentially via syringe. The vial was loaded into the calorimeter and the system was allowed to reach thermal equilibrium over 30 min. A freshly prepared stock solution of 0.30 M CF_3SO_3H in 10:1 of CH_2Cl_2/Et_2O (20.0 μL) was added via syringe. Heat release was monitored by the calorimeter and data were collected every 6 seconds until heat flow (mW) had decreased to background level.

Determination of diastereomeric ratio and enantiomeric excess of $\mathbf{4a_{exo}}$ and $\mathbf{4a_{endo}}$: The reaction mixture was quenched by addition of 200 μL of Et_3N. The solution was concentrated under reduced pressure, and the crude residue was dissolve in $CDCl_3$. The diastereomeric ratio was determined by ^{1}H NMR spectroscopic analysis of this sample by integration of the resonance of $\mathbf{4a_{endo}}$ at 5.4 ppm compared with the resonance of $\mathbf{4a_{exo}}$ at 4.6 ppm. The crude material was then subjection to purification by flash column chromatography (10:1 hexanes/Et_2O), the enantiomeric excess of a purified mixture of $\mathbf{4a_{exo}}$ and $\mathbf{4a_{endo}}$ was established by chiral SFC analysis (OD-H, 3 mL/min, 10% MeOH in CO_2, 30 °C, 210 nm, $\mathbf{4a_{exo}}$: t_R(major)= 11.4 min, t_R(minor) = 7.1 min; $\mathbf{4a_{endo}}$, t_R(major)= 9.7 min, t_R(minor) = 8.5 min).

Tau correction (Figure S5): Because heat transfer from the reactor vessel to sensors in the isothermal block of the calorimeter is not instantaneous, the raw data curve must be corrected to account for this heat response. In this procedure (termed τ-correction), a constant power was added to the sample via resistors built into the calorimeter. Using the WinCRC software, the resulting response curve was transformed into a square wave by manually adjusting two variables, τ_1 and τ_2. The square wave is the true power-vs-time

function of the resistor-generated power (A). The same τ_1 and τ_2 values obtained by this calibration were used to transform the raw data to generate the τ-corrected data curves (B).

A **B**

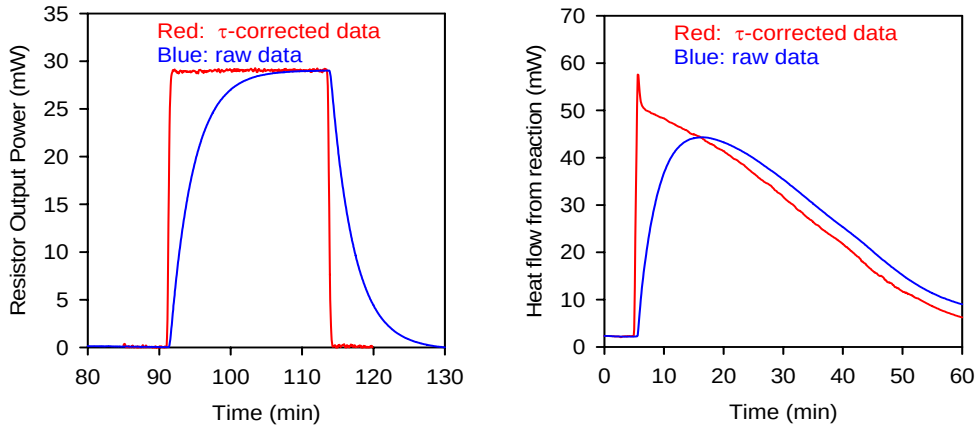


Figure S5. Calorimetry data after τ-correction

Conversion of calorimetry data (power versus time) to kinetic data (rate versus concentration): The procedure described below was executed in Microsoft Excel, using a spreadsheet analogous to the sample spreadsheet depicted below. The term "Letter(*n*)" represents the numerical value in column "Letter" and row '*n*' on the spread sheet. For example, D(2) = 27.6.

	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Conversion of limiting reagent	1.00	(fraction)	Raw TIME(min)	Raw POWER (mW)	Corr Time (min)	Corr Power (mW)	Δheat,(mW*min)	Σ Δheat,	conv lim rgt	mmol imine	[imine] (M)	RATE (M/s)
2	Maximum Power	70.75	mW	27.6	-1.03	0.00	0.00	0.00	0.00	0.000	0.400	0.0500	0.0000000
3	Maximum rate: - D[N]/Dt	0.00007	M s^{-1}	27.7	-1.09	0.10	1.62	0.16	0.16	0.000	0.400	0.0500	0.0000016
4	Total area under curve	865.14	mw*min	27.8	-1.12	0.20	5.68	0.57	0.73	0.001	0.400	0.0500	0.0000055
5	ΔH_{rxn}	31.02	kcal/mol	27.9	-1.17	0.30	11.15	1.12	1.85	0.002	0.399	0.0499	0.0000107
6	Reagent	mmol		28.0	-1.17	0.40	17.67	1.77	3.61	0.004	0.398	0.0498	0.0000170
7	imine	0.400		28.1	-1.13	0.50	25.01	2.50	6.11	0.007	0.397	0.0496	0.0000241
8	dihydrofuran	1.60		28.2	-1.10	0.60	32.97	3.30	9.41	0.011	0.396	0.0495	0.0000318
9	CF3SO3H	0.004		28.3	-1.01	0.70	40.01	4.00	13.41	0.016	0.394	0.0492	0.0000385
10	cat	0		28.4	-0.91	0.80	45.39	4.54	17.95	0.021	0.392	0.0490	0.0000437
11	Total volume (mL)	8.0		28.5	-0.85	0.90	49.79	4.98	22.93	0.027	0.389	0.0487	0.0000480
12				28.6	0.77	1.00	53.40	5.34	28.27	0.033	0.387	0.0484	0.0000514
13				28.7	4.84	1.10	56.39	5.64	33.91	0.039	0.384	0.0480	0.0000543
14				28.8	10.31	1.20	58.93	5.89	39.80	0.046	0.382	0.0477	0.0000568
15				28.9	16.82	1.30	61.13	6.11	45.92	0.053	0.379	0.0473	0.0000589
16				29.0	24.16	1.40	62.80	6.28	52.20	0.060	0.376	0.0470	0.0000605
17				29.1	32.13	1.50	64.28	6.43	58.62	0.068	0.373	0.0466	0.0000619
18				29.2	39.16	1.60	65.61	6.56	65.18	0.075	0.370	0.0462	0.0000632
19				29.3	44.54	1.70	66.76	6.68	71.86	0.083	0.367	0.0458	0.0000643
20				29.4	48.94	1.80	67.62	6.76	78.62	0.091	0.364	0.0455	0.0000651
21				29.5	52.56	1.90	68.35	6.83	85.46	0.099	0.360	0.0451	0.0000658
22				29.6	55.55	2.00	68.99	6.90	92.36	0.107	0.357	0.0447	0.0000665
23				29.7	58.09	2.10	69.46	6.95	99.30	0.115	0.354	0.0443	0.0000669
24				29.8	60.29	2.20	69.82	6.98	106.28	0.123	0.351	0.0439	0.0000673
25				29.9	61.95	2.30	70.17	7.02	113.30	0.131	0.348	0.0435	0.0000676
26				30.0	63.44	2.40	70.45	7.04	120.35	0.139	0.344	0.0430	0.0000679
27				30.1	64.77	2.50	70.57	7.06	127.40	0.147	0.341	0.0426	0.0000680
28				30.2	65.91	2.60	70.70	7.07	134.47	0.155	0.338	0.0422	0.0000681
29				30.3	66.78	2.70	70.75	7.08	141.55	0.164	0.335	0.0418	0.0000681
30				30.4	67.50	2.80	70.72	7.07	148.62	0.172	0.331	0.0414	0.0000681
31				30.5	68.15	2.90	70.62	7.06	155.68	0.180	0.328	0.0410	0.0000680
32				30.6	68.61	3.00	70.45	7.05	162.73	0.188	0.325	0.0406	0.0000679
33				30.7	68.98	3.10	70.29	7.03	169.76	0.196	0.322	0.0402	0.0000677
34				30.8	69.32	3.20	70.14	7.01	176.77	0.204	0.318	0.0398	0.0000676
35				30.9	69.60	3.30	69.92	6.99	183.76	0.212	0.315	0.0394	0.0000673
36				31.0	69.72	3.40	69.74	6.97	190.73	0.220	0.312	0.0390	0.0000672
37				31.1	69.85	3.50	69.53	6.95	197.69	0.229	0.309	0.0386	0.0000670
38				31.2	69.91	3.60	69.24	6.92	204.61	0.237	0.305	0.0382	0.0000667
39				31.3	69.87	3.70	69.10	6.91	211.52	0.244	0.302	0.0378	0.0000666
40				31.4	69.77	3.80	68.90	6.89	218.41	0.252	0.299	0.0374	0.0000664
41				31.5	69.61	3.90	68.58	6.86	225.27	0.260	0.296	0.0370	0.0000661
42				31.6	69.44	4.00	68.23	6.82	232.09	0.268	0.293	0.0366	0.0000657
43				31.7	69.29	4.10	67.92	6.79	238.89	0.276	0.290	0.0362	0.0000654
44				31.8	69.07	4.20	67.67	6.77	245.65	0.284	0.286	0.0358	0.0000652
45				31.9	68.89	4.30	67.28	6.73	252.38	0.292	0.283	0.0354	0.0000648
46				32.0	68.68	4.40	66.93	6.69	259.07	0.299	0.280	0.0350	0.0000645
47				32.1	68.39	4.50	66.72	6.67	265.75	0.307	0.277	0.0346	0.0000643
48				32.2	68.26	4.60	66.57	6.66	272.40	0.315	0.274	0.0343	0.0000641

Figure S6. A representative spreadsheet to calorimetry data to kinetic data

Columns D and E contain the τ-corrected raw data. The moment of addition of the last reagent is defined $t = 0$ (column F).

Thus, in this example,

$$F(n) = D(9 + n) - D(11) \quad (1)$$

The net power produced by the chemical reaction (heat flow) is obtained by subtracting from the power level recorded (column E) by the background power reached during the thermal equilibration, prior to the injection of the last reagent.

$$G(n) = E(9 + n) - E(11) \quad (2)$$

The power levels in column G are average values for the 6-second intervals. To obtain the heat released during each 6-second interval (column H), we multiply the power (mW) by time interval length (0.1 min).

$$H(n) = 0.1 \cdot G(n) \quad (3)$$

The total heat produced up to a certain time (column I) is found by summing all the intervals of heats produced up to that time point.

$$I(n) = \sum_{i=2}^{n} H(i) \quad (4)$$

The total heat produced by the reaction before it was either quenched or had reached completion is the largest value in column I. This value is recorded in cell B(4) using the Excel function MAX.

$$B(4) = MAX(I : I) \quad (5)$$

Conversion of the limiting reagent, imine **2a** (column J), is found by

$$J(n) = B(1) \cdot I(n) / B(4) \quad (6)$$

where B(1) is the conversion of the reaction when it was either quenched or reached completion. In the example given, the reaction had reached completion. Therefore, B(1) = 1. The use of eq 6 requires the explicit assumption that heat and reaction rate are proportional; this assumption is verified below.

The amount (mmol, column K) and concentration (mol/L, column L) of remaining imine, at any given time point is

$$K(n) = B(7) \cdot (1 - J(n)) \quad (7)$$

$$L(n) = K(n) / B(11) \quad (8)$$

where B(7) is the initial amount of substrate in mmol and B(11) is the total volume of the reaction in mL.

The rate of the reaction at any point (column M) is calculated by

$$M(n) = \frac{G(n)}{\frac{(60\ s/min)\cdot B(4)}{B(1)\cdot B(7)} B(11)} \quad (9)$$

By carrying out the corresponding dimensional analysis, it is readily appreciated that M(n) represents rate:

$$M(n) = \frac{[G(n)]}{\frac{[(60\ s/min)]\cdot[B(4)]}{[B(1)\cdot B(7)]}[B(11)]} = \frac{[mW]}{\frac{[(s/min)]\cdot[mw\ min]}{[1]\cdot[mmol]}[mL]} = \frac{M}{s} \quad (10)$$

Correlation of heat release with ^{1}H NMR conversion: Representative Povarov reaction experiments were set up in a reaction calorimeter under standard conditions (see above), with the exception that the reaction mixture contained 1,3,5-trimethoxybenzene as internal standard. Reactions set up with imine **2a** were allowed to proceed to partial %-conversion (10–90%), and then quenched by addition of Et_3N (200 μL). The cumulative heat release up to the point the reaction was quenched was determined using the spreadsheet described above (column I). The reaction mixtures were concentrated under reduced pressure, and %-conversion was determined by ^{1}H NMR spectroscopy by integration of recovered starting material relative to internal standard. With all three substrates, plots of cumulative heat versus imine consumption are linear, indicating that heat is proportional to conversion (Figure S7). The enthalpy of reaction can be calculated from the slope of the linear best-fit line, and is similar for the three substrates (31 ± 2 kcal/mol). This value was used for data processing all subsequent experiments in one of two ways, depending upon whether a particular reaction had reached completion. In cases in which the reaction was quenched before it had reached full conversion, the value in cell B(1) in the Excel worksheet was adjusted until the value in cell B(5) was in the range 31.0-31.1 kcal/mol. As described below, low levels of background nucleophile polymerization produces residual heat even after the Povarov reaction had reached full conversion, and including more data points in the heat summation artificially increases the value of B(5). Thus, in cases in which the reaction had been allowed to reach full conversion, the value in cell B(1) was set to '1', and the number of data points included in the summation (eq 4 above) was adjusted until the value in cell B(5) was in the range 31.0-31.1 kcal/mol.

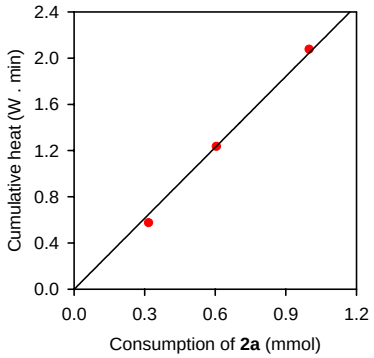
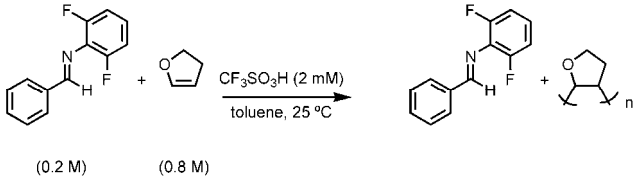


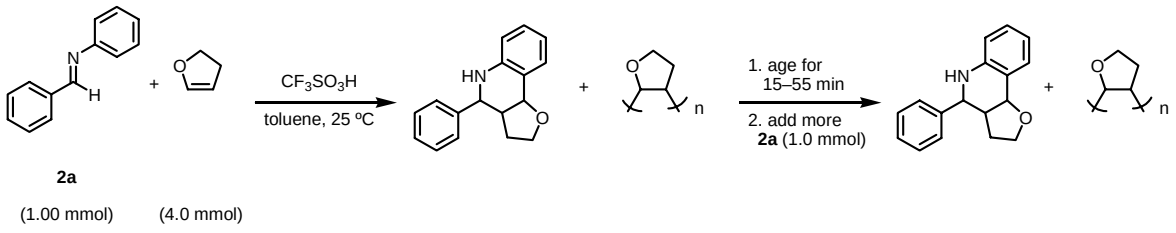
Figure S7. The demonstration of the generated heat is proportional to conversion

Extent of nucleophile polymerization: In the absence of an imine, CF_3SO_3H promotes rapid polymerization of DHF. This reaction is comparably slow when an imine such as **2c** is present in the reaction mixture, but it is not negligible. There are two possible errors that can result from DHF polymerization: (1) polymerization produces heat, and thus affects the observed enthalpy; (2) polymerization artificially lowers the concentration of DHF, and thus introduces error into the kinetic analysis.

Two different protocols were used to estimate the enthalpy of polymerization. (a) The enthalpy of polymerization of DHF was determined directly by allowing DHF to polymerize in the presence of an imine that does not react with DHF (*N*-benzylidene-2,6-difluorobenzenamine). The enthalpy of polymerization of DHF as determined by reaction calorimetry using this protocol is 8.3 kcal/mol.



(b) The enthalpy of polymerization was estimated under the actual reaction conditions using the following procedure: A standard Povarov experiment using 1.0 equiv of **2a** and 4 equiv of DHF was set up in the calorimeter ($[CF_3SO_3H]$ = 2.0 mM). This reaction was allowed to proceed to full conversion, and then aged for a specified time (15–55 min from the start of the first experiment). At this point, an additional 1.0 equiv of **2a** was added as a concentrated stock solution, and this second reaction was allowed to



proceed to full conversion.

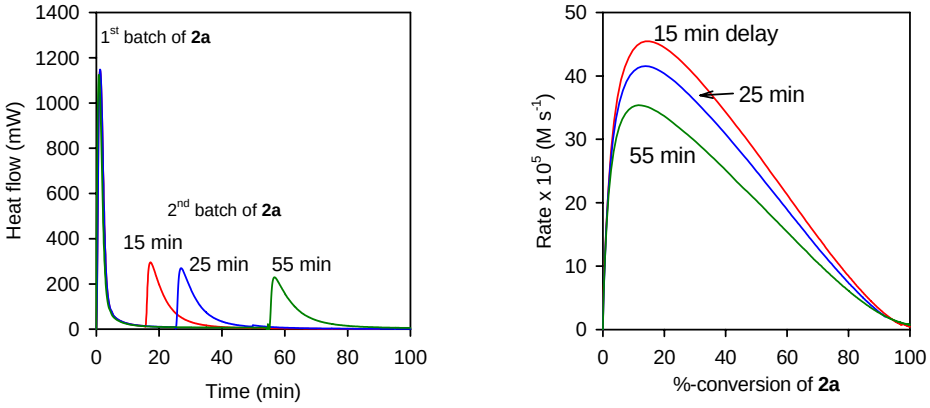


Figure S8. Detection of nucleophile polymerization by reaction calorimetry studies.

The raw heat flow versus time data for the reaction with the second batch of imine were converted to rate versus %-conversion data using the standard protocol. Analysis of these data demonstrates that as the delay time between the first and second reaction is increased, the rate of the second reaction decreases. This decrease in rate over time may be attributed to DHF polymerization, which decreases the amount of DHF available for reaction with **2a**. Using these data we can estimate the heat of nucleophile polymerization by making the following assumptions: (i) $H_{Povarov}$ = 31 kcal/mol, (ii) the decrease in initial rate of the second reaction can be ascribed to nucleophile depletion through polymerization, and (iii) the rate of the Povarov reaction has a first-order dependence on [DHF].

The total heat released in the first phase of the experiment (H_1)—between addition of the first batch of imine and addition of the second batch of imine—can be ascribed to two sources: (i) Povarov reaction and (ii) nucleophile polymerization.

$$H_{polymerization} = H_1 - H_{Povarov} \quad (11)$$

We wish to correlate the rate of the second reaction with the amount of DHF consumed during the first phase of the experiment. The concentration of DHF at 15 % conversion of the second batch of imine is given by:

$$[DHF] = (4 - 1 - 0.15 - (H_{polymerization} / x)) \text{ mmol} / 5 \text{ mL} \quad (12)$$

where $H_{polymerization}$ / x is the amount of nucleophile consumed by DHF polymerization during the first phase of the experiment, and x is the millimolar $H_{polymerization}$.

The rate of the Povarov reaction has a first-order dependence on [DHF]:

$$rate = k_{obsd}[DHF] \quad (13)$$

$$rate = k_{obsd}\,(2.85 - (H_{polymerization} / x))\ \text{mmol} / 5\ \text{mL} \quad (14)$$

$$(rate)\ (5\ \text{mL} / 2.85\ \text{mmol}) = -(k_{obsd} / x)\ (H_{polymerization} / 2.85\ \text{mmol}) + k_{obsd} \quad (16)$$

Expt	Length of phase 1 (min)	Heat release during phase 1 (mw · min)	$H_{polymerization}$ during phase 1[a] (mw · min)	Rate at 15 % conversion of phase 2 (M s^{-1})	*rate* · 1.7544 (s^{-1})	$H_{polymerization}$ / 2.85 (mw · min / mmol)
1	15	2730	571	0.000455	0.000797	200
2	25	2815	656	0.000415	0.000728	230
3	55	2953	794	0.000351	0.000615	278

a. Assuming $H_{Povarov}$ 2160 mw · min (i.e., 31.0 kcal/mol).

A least-squares fit to a plot of {$H_{polymerization}$ / 2.85} versus {*rate* · 1.7544} affords a straight line with y-intercept = k_{obsd} = 1.263 ± 0.007 x 10^{-3} s^{-1} and slope = – (k_{obsd} / x) = –2.33 ± 0.02 x 10^{-6} mmol mw^{-1} min^{-1} s^{-1}. The enthalpy of polymerization of DHF as determined by reaction calorimetry using this protocol is x = 542 mw · min $mmol^{-1}$ = 7.8 kcal/mol. This value is indistinguishable from the value determined using method (a) described above.

Two independent experiments have established that the enthalpy of polymerization of DHF is approximately 8 kcal/mol under conditions approximating the reaction conditions. Asymmetric Povarov reactions of **2a** run with 1.0 equiv DHF proceed to 60–85% conversion of imine. On the basis of these results, we estimate that approximately 5–15% of the total heat released during a Povarov reaction calorimetry experiment can be attributed to nucleophile polymerization. An error of this magnitude is unlikely to affect conclusions drawn from the experimental data.

(2) Polymerization of DHF lowers the actual concentration of DHF available for reaction, and thus introduces an error in the kinetic analysis. We address this issue by using a large excess of DHF in calorimetry experiments (typically 4.0 equiv), and by using data at low conversion in our kinetic analyses. Deviations from a strict first-order rate dependence on [DHF] are observed at low [DHF] in the asymmetric Povarov reaction, and this deviation can be ascribed at least in part to competitive DHF polymerization.

Inhibition by basic impurities: To test whether basic impurities that might be present in imines—Et_3N, aniline—inhibit the Povarov reaction, we added sub-stoichiometric amounts of these reagents to Povarov reactions. Experiments in which these reagents were added to a typical non-asymmetric Povarov reaction ([**2a**] = 0.10 M, [DHF] = 1.0 M, [CF_3SO_3H] = 1.0 mM, [additive] = 0.010 M) that had proceeded to approximately 30% conversion in a reaction calorimeter indicate that these reagents strongly inhibit the reaction (compare the red, blue, and green curves in the figure below).

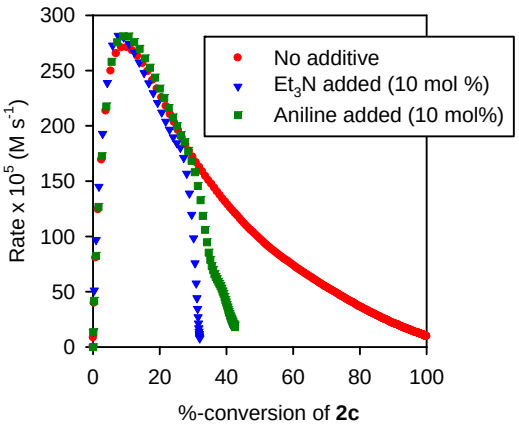


Figure S9. Rate inhibitory effect of basic impurities detected by reaction calorimetry studies.

Experimental rate data:

Table S4. Rates of Povarov reaction of imine **2c** with DHF catalyzed by CF_3SO_3H. Rates at 20 % conversion are provided in M s^{-1} (x 10^5).

[imine] (M)	[DHF] (M)	[CF_3SO_3H] (mM)	Rate
0.40	0.40	2.00	43
0.40	0.60	2.00	54
0.40	0.80	2.00	73
0.40	1.60	2.00	140
0.40	1.60	0.20	7
0.40	1.60	0.60	31
0.40	1.60	1.00	68
0.20	0.80	2.00	77

0.80	0.80	2.00	74

Table S5. Rates of Povarov reaction of imine **2a** ($[\mathbf{2a}]_i$ = 0.20 M) with DHF ($[DHF]_i$ = 1.6 M) co-catalyzed by CF_3SO_3H ($[CF_3SO_3H]_{tot}$ = 0.80 mM) and catalyst **15** in toluene at 25.0 °C. Rates are provided in M s^{-1} (x 10^5).

%-conversion	[cat] = 0 mM	[cat] = 0.10 mM	[cat] = 0.60 mM	[cat] = 1.6 mM
10	48.6	47.9	50.7	51.5
20	50.2	50.0	52.5	54.7
30	46.3	46.6	48.7	51.5
40	41.5	42.0	43.8	45.9
50	35.7	37.0	38.4	39.8
60	29.7	31.0	31.8	33.0
70	22.7	24.1	24.7	25.5
80	15.1	16.4	17.0	17.2

Table S6. Rates of Povarov reaction of imine **2a** ($[\mathbf{2a}]_i$ = 0.20 M) with DHF ($[DHF]_i$ = 1.6 M) co-catalyzed by CF_3SO_3H ($[CF_3SO_3H]_{tot}$ = 0.80 mM) and catalyst **1a** in toluene at 25.0 °C. Rates are provided in M s^{-1} (x 10^5).

%-conversion	[cat] = 0 mM	[cat] = 0.40 mM	[cat] = 0.60 mM	[cat] = 0.80 mM	[cat] = 1.4 mM
10	45.2	29.7	22.4	18.9	14.8
20	47.4	28.3	21.9	18.7	14.6
30	45.2	25.5	20.2	17.7	14.1
40	40.5	22.8	18.5	16.4	13.4
50	35.0	20.3	16.8	15.2	12.7
60	28.8	17.6	14.9	13.7	11.8
70	22.4	14.7	12.6	11.9	10.6
80	15.5	11.2	9.8	9.5	8.9
ee[a] (%)	0	28.9	42.5	51.3	63.5
dr[b]	0.37	0.5	0.59	0.71	0.88

%-con-version	[cat] = 2.4 mM	[cat] = 3.2 mM	[cat] = 8.0 mM	[cat] = 80 mM	[cat] = 150 mM
10	11.5	11.5	10.5	10.2	8.96
20	11.9	11.7	10.4	10.2	8.76
30	11.8	11.7	10.2	10.1	8.7
40	11.5	11.4	9.79	9.86	8.63
50	10.9	11.9	9.26	9.55	8.55
60	10.1	10.2	9.24	9.14	8.35
70	9.00	9.33	8.53	8.66	7.85
80	7.52	8.22	7.61	8.02	7.11
ee[a] (%)	72	nd	78.6	78.7	78.8
dr[b]	1.18	nd	1.35	1.35	1.35

a. enantiomeric excess of $\mathbf{4a_{exo}}$. b. diastereomeric ratio ($\mathbf{4a_{exo}}$/$\mathbf{4a_{endo}}$)

Table S7. Rates of Povarov reaction of imine **2a** ($[\mathbf{2a}]_i$ = 0.40 M) with DHF ($[DHF]_i$ = 1.6 M) co-catalyzed by CF_3SO_3H ($[CF_3SO_3H]_{tot}$ = 2.0 mM) and catalyst **1a** in toluene at 25.0 °C. Rates are provided in M s^{-1} (x 10^5).

%-con-version	[cat] = 0 mM	[cat] = 0.50 mM	[cat] = 1.0 mM	[cat] = 1.5 mM	[cat] = 2 mM
10	119	97	80	67	47
20	130	102	78	66	47
30	128	95	72	63	45
40	118	86	64	58	42
50	105	76	59	52	39
60	90	64	50	46	35
70	70	50	40	38	29
80	48	34	28	28	22
ee[a] (%)	0	11.9	25.5	41.2	52.3
dr[b]	0.36	0.41	0.5	0.66	0.8

%-con-version	[cat] = 4 mM	[cat] = 4 mM	[cat] = 8.0 mM	[cat] = 16 mM	[cat] = 30 mM
10	37	34	29	27	27
20	37	34	29	27	27
30	35	33	28	27	26
40	34	32	27	26	25
50	31	39	26	25	24
60	28	27	24	23	22
70	24	24	21	21	21
80	19	19	18	18	18
ee[a] (%)	62.1	70.3	73.6	77.8	78.9
dr[b]	1	1.4	1.46	1.4	1.63

a. enantiomeric excess of $\mathbf{4a_{exo}}$. b. diastereomeric ratio ($\mathbf{4a_{exo}}$/$\mathbf{4a_{endo}}$)

Table S8. Rates of Povarov reaction of imine **2a** ($[\mathbf{2a}]_i$ = 0.40 M) with DHF ($[DHF]_i$ = 1.6 M) co-catalyzed by CF_3SO_3H ($[CF_3SO_3H]_{tot}$ = 4.0 mM) and catalyst **1a** in toluene at 25.0 °C. Rates are provided in M s^{-1} (x 10^5).

%-con-version	[cat] = 0 mM	[cat] = 1.0 mM	[cat] = 2.0 mM	[cat] = 3.0 mM	[cat] = 4.0 mM
10	204	173	147	103	86
20	267	207	166	116	91
30	286	220	166	118	89
40	290	218	160	115	85
50	280	208	151	109	81
60	258	187	135	99	75
70	218	157	116	86	66
80	160	117	89	70	55
ee[a] (%)	0	12.7	29.1	42.5	53.9
dr[b]	0.32	0.36	0.44	0.55	0.74

%-con-version	[cat] = 6.0	[cat] = 8.0 mM	[cat] = 16 mM	[cat] = 32 mM	[cat] = 60 mM

	mM				
10	68	61	55	53	51
20	71	64	55	54	52
30	70	64	54	53	51
40	68	62	53	52	50
50	65	59	51	50	48
60	61	55	48	47	46
70	55	50	44	44	43
80	47	43	39	40	39
ee[a] (%)	64.6	69.1	76.8	78.1	82
dr[b]	0.98	1.14	1.43	1.48	1.54

a. enantiomeric excess of $\mathbf{4a_{exo}}$. b. diastereomeric ratio ($\mathbf{4a_{exo}}$/$\mathbf{4a_{endo}}$)

Table S9. Rates of Povarov reaction of imine **2c** ($[\mathbf{2c}]_i$ = 0.40 M) with DHF ($[DHF]_i$ = 1.6 M) co-catalyzed by CF_3SO_3H ($[CF_3SO_3H]_{tot}$ = 2.0 mM) and catalyst **1a** ($[\mathbf{1a}]_{tot}$ = 19 mM) in toluene at 25.0 °C. Rates are provided in M s^{-1} (x 10^5).

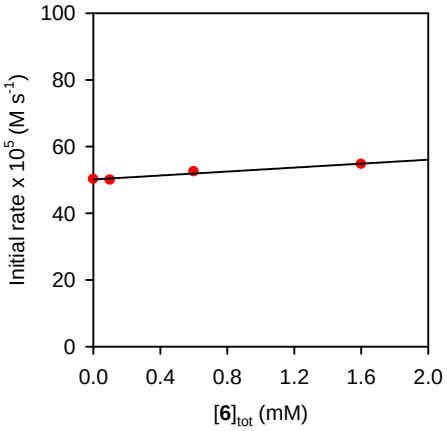
%-con-version	[DHF] = 0.4 M	[DHF] = 0.8 M	[DHF] = 1.2 M	[DHF] = 1.6 M
10	26.0	19.0	12.0	4.1
20	26.0	18.9	11.7	3.1
30	26.0	18.0	11.0	2.1
40	25.0	17.0	10.0	1.2
50	23.0	16.0	8.9	0.6
60	22.0	14.0	7.7	
70	20.0	13.0	6.3	
80	17.0	11.0	4.8	
ee[a] (%)	74.9	77	76.7	82.4
dr[b]	1.69	1.35	1.67	1.67

a. enantiomeric excess of $\mathbf{4a_{exo}}$. b. diastereomeric ratio ($\mathbf{4a_{exo}}$/$\mathbf{4a_{endo}}$)

Table S10. Rates of Povarov reaction of imine **2a** with DHF co-catalyzed by CF_3SO_3H ($[CF_3SO_3H]_{tot}$ = 2.0 mM) and catalyst **1a** ($[\mathbf{1a}]_{tot}$ = 50 mM) in toluene at 25.0 °C. Rates are provided in M s^{-1} (x 10^5).

%-con-version[a]	[**2a**] = 0.2 M	[**2a**] = 0.4 M	[**2a**] = 0.6 M
10	17.1	18.1	19.3
20	15.9	17.0	19.0
30	15.4	16.8	19.2
40	15.0	16.5	19.1
50	14.4	16.3	19.0
60	13.9	16.0	18.8
70	13.0	15.8	18.5
80	11.5	15.5	18.3
ee[b] (%)	77	85	87
dr[c]	1.5	1.9	1.8

a. enantiomeric excess of $\mathbf{4a_{exo}}$. b. diastereomeric ratio ($\mathbf{4a_{exo}}$/$\mathbf{4a_{endo}}$)



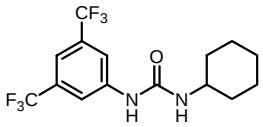


Figure S10. Rate dependence on $[\mathbf{15}]_{tot}$. Plot of instantaneous rate at 20% conversion (initial rate) of racemic Povarov reaction $[DHF]_i$ = 1.6 M, $[imine]_i$ = 0.20 M, $[CF_3SO_3H]_{tot}$ = 0.8 mM) co-catalyzed by CF_3SO_3H and **15** versus $[\mathbf{15}]_{tot}$. The black curve represents a least-squares fits to $f(x) = a + b\ x$, $a = 50.2 \pm 0.4 \times 10^{-5}$, $b = 3.0 \pm 0.4 \times 10^{-5}$.

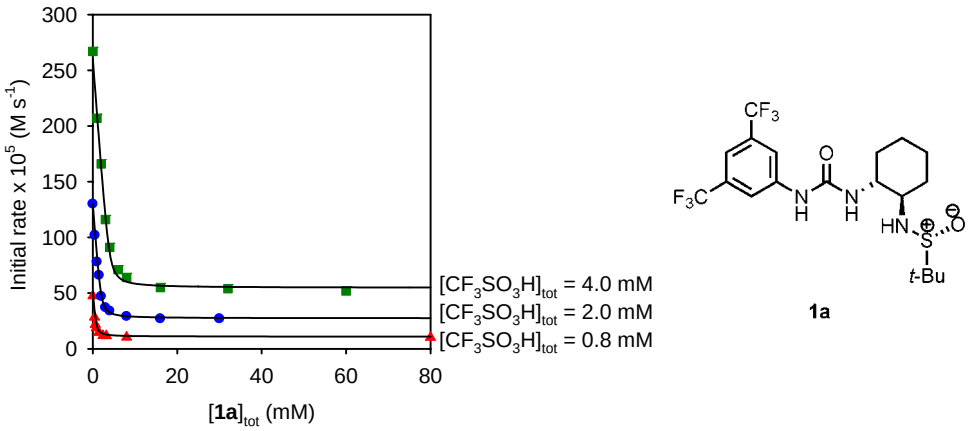
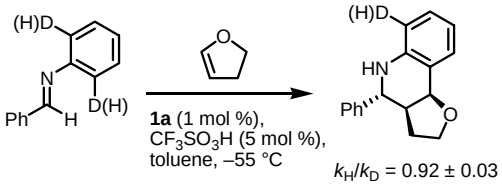


Figure S11. Rate dependence on $[\mathbf{1a}]_{tot}$. Plot of instantaneous rate at 20% conversion (initial rate) of asymmetric Povarov reaction $[DHF]_i$ = 1.6 M, $[imine]_i$ = 0.20 or 0.40 M) co-catalyzed by CF_3SO_3H and **1a** versus $[\mathbf{1a}]_{tot}$. The black curve represents a least-squares fits to eqs (1) and (2) , k_{rac} = 0.407 ± 0.004 x 10^{-5} M^{-1} s^{-1}, k_{asym} = 0.086 ± 0.03 M^{-1} s^{-1}, K = 9000 ± 2000 M^{-1}, R^2 = 0.9965.

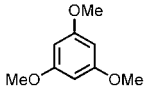
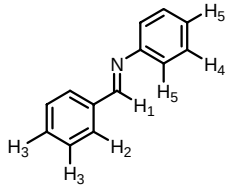
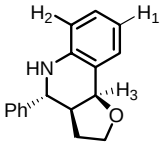
N. Kinetic Isotopic Effect Studies of Enantioselective Povarov Reactions

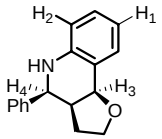


General: The kinetic isotope effect at the aniline *ortho* position in the Povarov reaction was measured through an intermolecular competition experiment between imine **2a** and **2a**-d_2. The synthesis and purification of **2c**-d_2 was described in Section 3.12.2. Isotope effects were determined by ^{1}H NMR spectroscopy. In general, the ^{1}H NMR spectrum of imines **2a** and **2a**-d_2 is poorly resolved, and most ^{1}H NMR spectroscopic analysis necessary for determination of isotope effects was carried out on the purified cycloadducts (**4a$_{exo}$** or **4a$_{endo}$**).

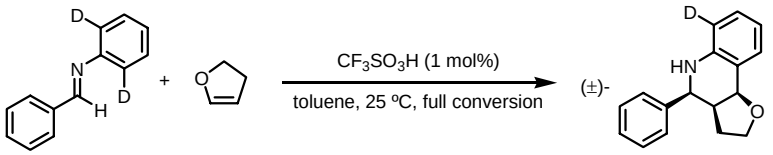
^{1}H NMR spectroscopic analysis were performed on 500 MHz and 600 MHz spectrometers at the Harvard University NMR facility. Unless otherwise specified, $CDCl_3$, relaxation delay time (d1) of 50 seconds, and 90^o pulses were used in the data collection. The NMR spectra were processed using the ACDLABS 9.0 software. The width of each interval of integration for a specific peak was constant across all spectra. Each peak was visually centered inside its interval of integration.

Table S11. Integration intervals used in kinetic isotope effect analysis:

Compound	Peak code	Integration interval (ppm)
		6.07–6.11
 **2a**	H 1	8.43–8.50
	H 2	7.87–7.94
	H 3	7.436–7.52
	H 4	7.37–7.43
	H 5	7.195–7.265
 **4a$_{exo}$**	H 1	6.79–6.85
	H 2	6.61–6.67
	H 3	4.59–4.64

 **4a$_{endo}$**	H 1	6.80–6.86
	H 2	6.59–6.64
	H 3	5.26–5.32
	H 4	4.68–4.74

Determination of the isotopic purity of **2a**-d_2: **2a**-d_2 was prepared via an iterative ortholithiation/CD_3OD quench route, as described in Section 3.12.2. The following protocol was used to determine isotopic purity of the deuterium-labeled starting material.

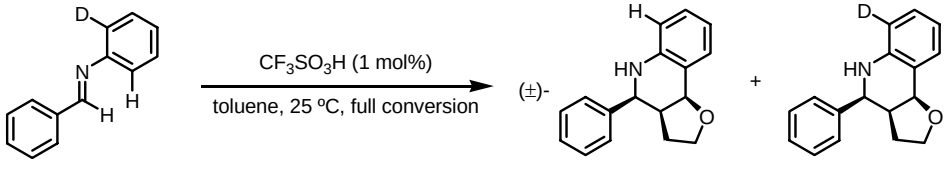


2a-d_2 **3** **4a$_{endo}$**-d

0.2 M 0.8 M

An oven-dried 16-mL glass reaction vessel was charged with **2a**-d_2 (73 mg, 0.4 mmol, 1.0 equiv), toluene (1.84 mL), and 2,3-dihydrofuran (121 μL, 1.6 mmol, 4.0 equiv). The reaction vessel was transferred into the calorimeter and allowed to equilibrate for 30 min. A 0.1 M solution of CF_3SO_3H in 10:1 of CH_2Cl_2/Et_2O (40 μL, 0.0040 mmol, 0.010 equiv) was added through the injection port. The reaction was monitored by calorimetry until its completion (20 minutes). The reaction mixture was concentrated under reduced pressure, and the crude material was then subjected to purification by flash column chromatography (25:1 hexanes/ethyl acetate). The diastereomeric mixture was further purified by preparatory thin-layer chromatography (20:1 hexanes/Et_2O). The diastereomers were separated completely, and each was dissolved in chloroform, filtered through a cotton plug, and concentrated under reduced pressure to yield **4a$_{exo}$** and **4a$_{endo}$**.

The primary isotopomeric impurity in **2a**-d_2 is presumably **2a**-d_1. In independent experiments of the type described below, it was established that **2a**-d_1 shows essentially no intramolecular kinetic isotope effect. On the basis of this observation, we assume that the isotopic purity of the product is proportional to the isotopic purity of the starting material.



2a-d_1 **4a$_{endo}$** **4a$_{endo}$**-d

4a$_{endo}$/4a$_{endo}$-d >>1

^{1}H NMR analysis of purified samples of **4a**$_{\mathbf{endo}}$-d_1 reveals approximately 1 % residual proton. This value indicates that **2a**-d_1 is approximately a 2 % impurity in **2a**-d_2, or that 99 % of all *ortho* positions are deuterium labeled in **2a**-d_2. By running this experiment in triplicate, we estimate 99.1 ± 0.2 % *ortho*-deuterium incorporation in **2a**-d_2.

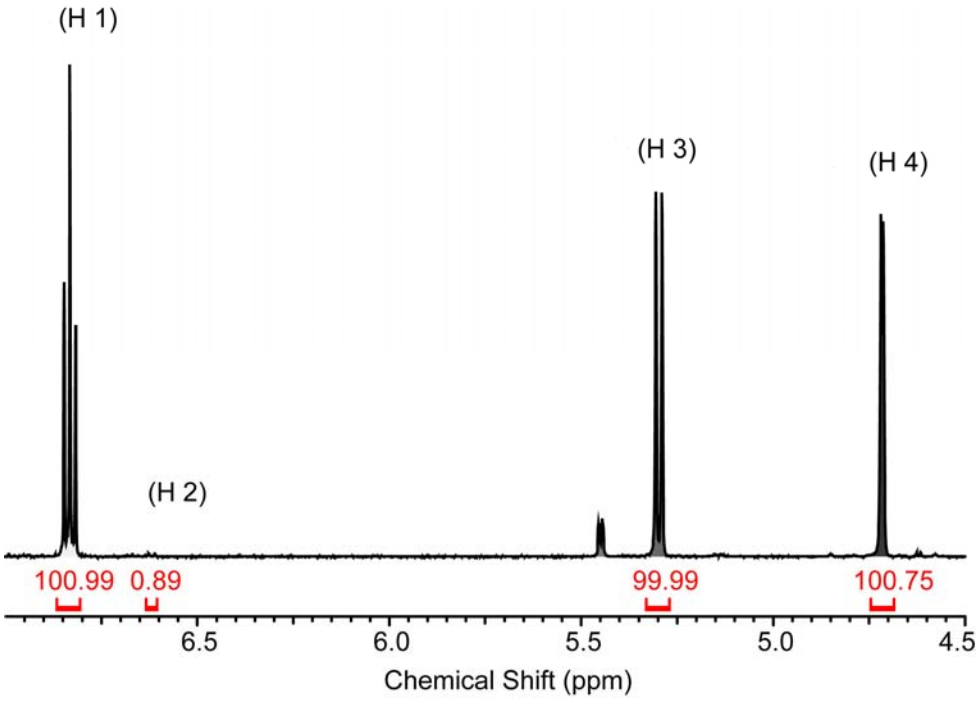


Figure S12. Partial ^{1}H NMR spectrum of **4a**$_{\mathbf{endo}}$ in C_6D_6 showing 99.1 % deuterium incorporation.

Isotopic competition experiments: A 25-mL oven-dried round-bottomed flask contained a stir bar was charged with imine **2a** (163 mg, 0.900 mmol, 0.500 equiv) and imine **2a**-d_2 (165 mg, 0.900 mmol, 0.500 equiv), catalyst **1a** (85 mg, 0.18 mmol, 0.10 equiv), and 1,3,5-trimethoxybenzene (101 mg, 0.600 mmol, 0.333 equiv). The flask was sealed with a rubber septum, and anhydrous toluene (8.58 mL) and 2,3-dihydrofuran (122 μL, 1.62 mmol, 0.900 equiv) were added via syringes. The stock solution was stirred at room temperature until all solids had dissolved. A separate oven-dried 6 mL glass vial was charged with CF_3SO_3H (102 mg, 0.68 mmol) and a solution of 10:1 anhydrous Et_2O/CH_2Cl_2 (2.27 ml).

Three oven-dried 6-mL glass vials equipped with stir bars were sealed with a rubber septum and charged with imine stock solution (1.93 mL) via syringe. The vials were cooled in a –55 °C bath for 30 min, and charged with CF_3SO_3H solution (67 μL, 0.020 mmol, 0.050 equiv). The reaction mixtures were stirred at –55 °C for 72, 90, and 96 h, and then quenched with Et_3N (200 μL) via syringe. Each reaction mixture

was concentrated under reduced pressure, and the %-conversion was determined by ^{1}H-NMR spectroscopy relative to internal standard. The residue was purified by flash column chromatography on silica gel (100:1 Hexanes/Et_3N). All fractions containing trace product were combined and concentrated under reduced pressure to yield **4a$_{exo}$** and **4a$_{endo}$** as a mixture of diastereomers. This mixture was further purified by prep-TLC (20:1 hexanes/Et_2O) to separate the diastereomeric products.

Determination of initial isotopic ratio in starting material stock solution: The initial isotopic ratio of the stock solution was determined to be $R_0 = [H]_0/[D]_0 = 1.042 \pm 0.013$ using the following protocols.

(a) An aliquot of the imine stock solution prepared above (1.0 mL) was concentrated under reduced pressure, dissolved in $CDCl_3$ (600 µL), and analyzed by ^{1}H-NMR spectroscopy (d1 = 80 s). Because the *ortho*- and *para*-protons overlap in the ^{1}H NMR spectrum, and because the *para*-proton is not deuterium-substituted, it is necessary to correct for this integral. The integral of a fully protonated position is:

$H_{average} = (H\ 1 + H\ 2 + H\ 3 + H\ 4) / 8 = 798.69 / 8 = 99.836$

The portion of the integral S_5 that can be attributed to each *ortho*-proton is:

$½\ (H\ 5 - H_{average}) = ½\ (201.71 - 99.836) = ½\ (101.874) = 50.937$

The initial proton/deuterium ratio at each *ortho*-position is:

$R_0 = 50.937 / (99.836 - 50.937) = 1.042$

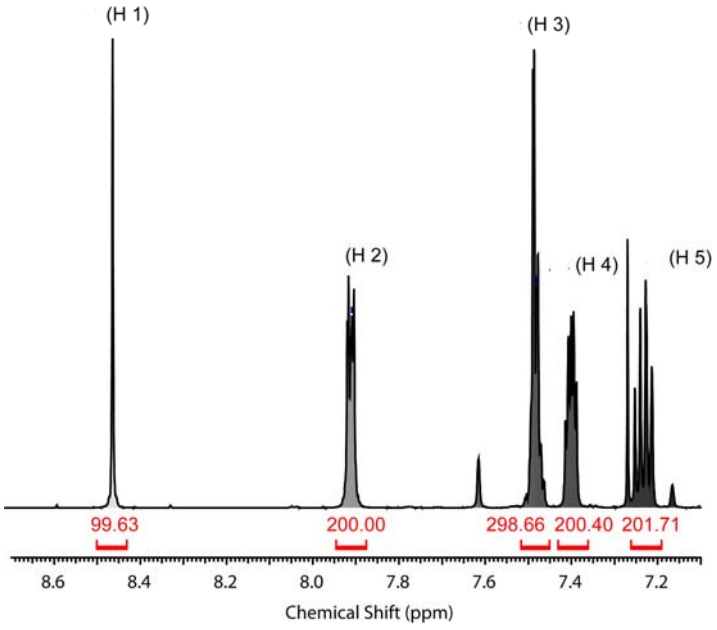


Figure S13. Partial ^{1}H NMR spectrum of the stock solution containing a mixture of **2a** and **2a**-d_2 in C_6D_6. The unlabeled resonances correspond to solvent or catalyst **1a**.

(b) An aliquot of the imine stock solution prepared above (1.0 mL) was concentrated under reduced pressure and the residue was subjected to purification by flash column chromatography (25:1 hexanes/Et_3N). The purified imine was dissolved in CD_3Cl and analyzed as described in (a).

$H_{average}$ = (H 1 + H 2 + H 3 + H 4) / 8 = 100.295

½ (H 5 – $H_{average}$) = ½ (202.27 – 100.295) = ½ (101.975) = 50.988

R_0 = 50.988 / (100.295 – 50.988) = 1.034

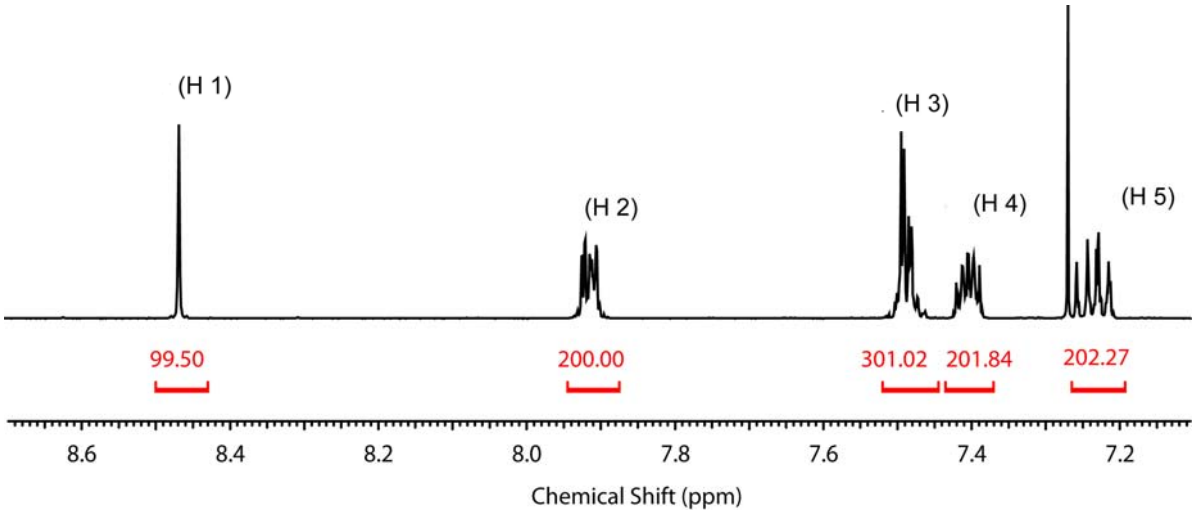


Figure S14. Partial ^{1}H NMR spectrum of the re-isolated and purified stock solution containing a mixture of **2a** and **2a**-d_2 in C_6D_6. The unlabeled resonance corresponds to solvent.

(c) A 6-mL oven-dried glass vial was charged with a mixture of imine isotopomers isolated from the stock solution as described in (b) (41 mg, 0.23 mmol, 1.0 equiv), catalyst **1b** (10 mg, 0.020 mmol, 0.10 equiv), 2,3-dihydrofuran (100 µL, 1.0 mmol, 4.6 equiv), and toluene (1.0 mL). The vial was sealed with a rubber septum and cooled in a –55 °C bath for 30 min. CF_3SO_3H (40 µL of a 0.30 M stock solution, 0.012 mmol, 0.050 equiv) was added via syringe, and the reaction mixture was stirred at –55 °C for 24 h. The reaction mixture was allowed to warm to room temperature, and another 1.0 mL of 2,3-dihydrofuran was added. The reaction mixture was aged for another 1 h at room temperature. The reaction mixture was concentrated under reduced pressure, and ^{1}H NMR analysis of the crude residue revealed no remaining starting material. The diastereomers were separated by prep-TLC, and each was analyzed by ^{1}H-NMR spectroscopy.

(i) Analysis of **4a$_{exo}$:**

$H_{average}$ = (H 1 + H 3) / 2 = 199.92 / 2 = 99.965

R_0 = 51.47 / (99.965 – 51.47) = 1.061

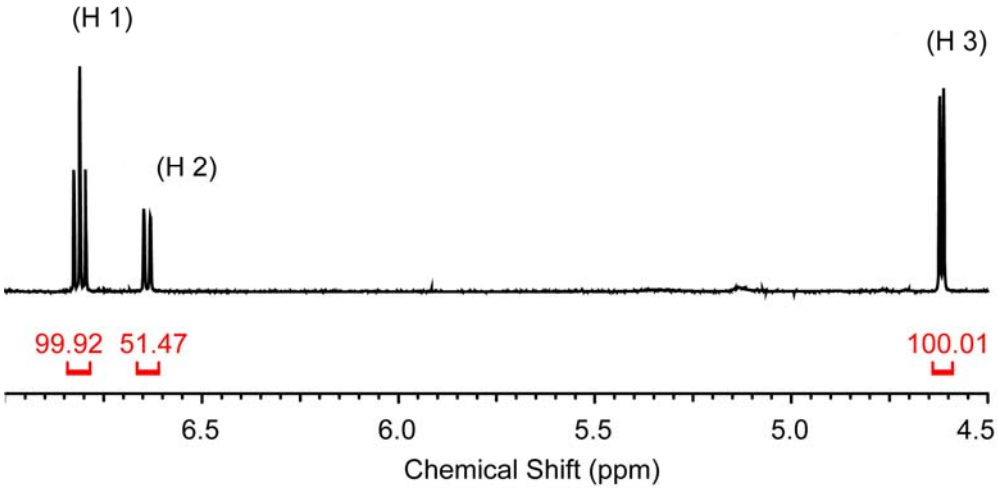


Figure S15. Partial ^{1}H NMR spectrum of **4a$_{exo}$** prepared from mixture of **2a** and **2a**-d_2 in C_6D_6.

(ii) Analysis of **4a$_{endo}$:**

$H_{average}$ = (H 1 + H 3 + H 4) / 3 = 298.25 / 3 = 99.417

R_0 = 50.50 / (99.417 – 50.50) = 1.032

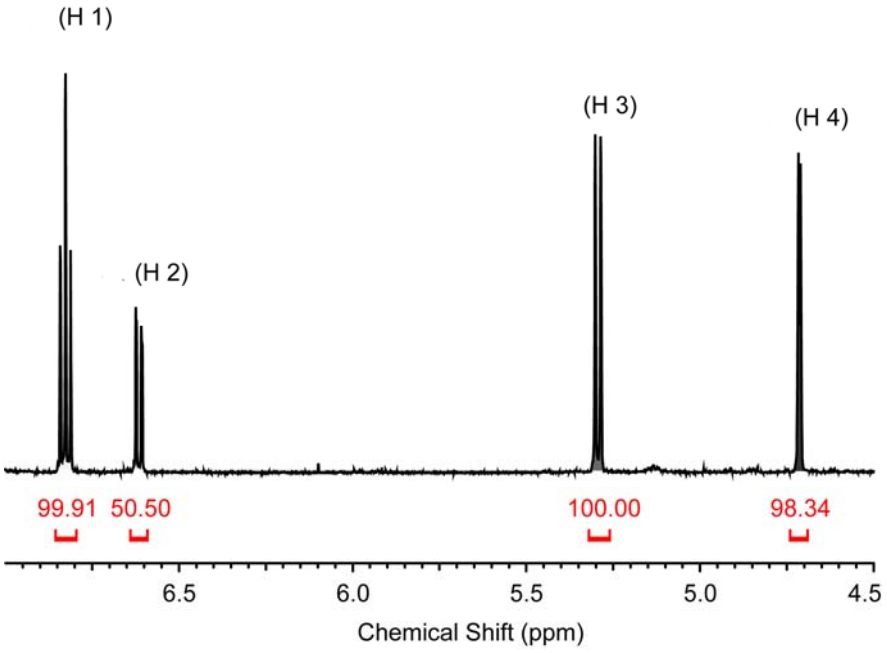


Figure S16. Partial ^{1}H NMR spectrum of **4a$_{endo}$** prepared from mixture of **2a** and **2a**-d_2 in C_6D_6.

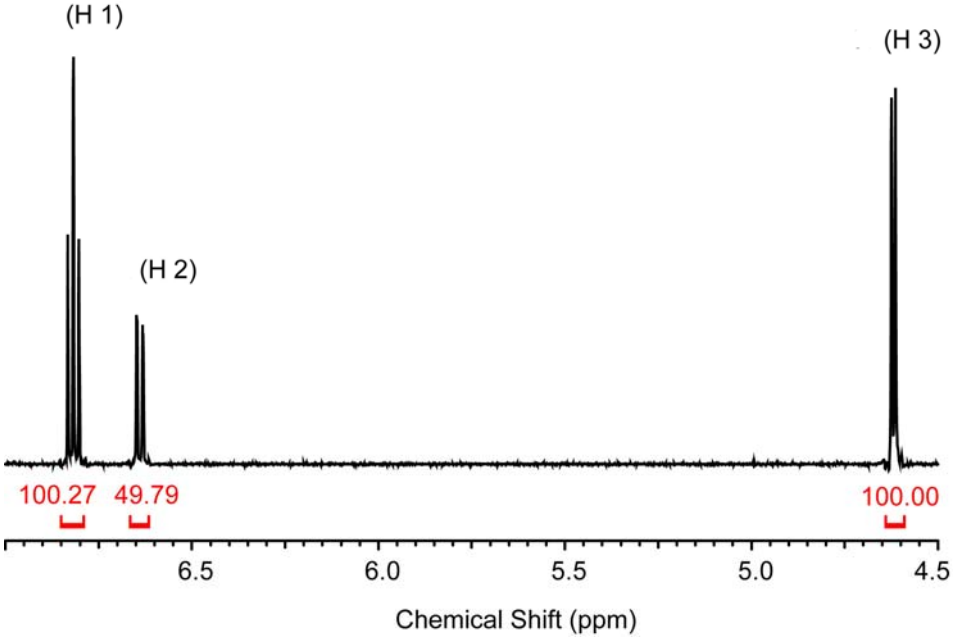
Determination of final isotopic ratio in Povarov addition products:

(a) Experiment 1: 64.1% conversion.

(i) Analysis of **4a$_{exo}$**

$H_{average}$ = (H 1 + H 3) / 2 = 200.27/ 2 = 100.135

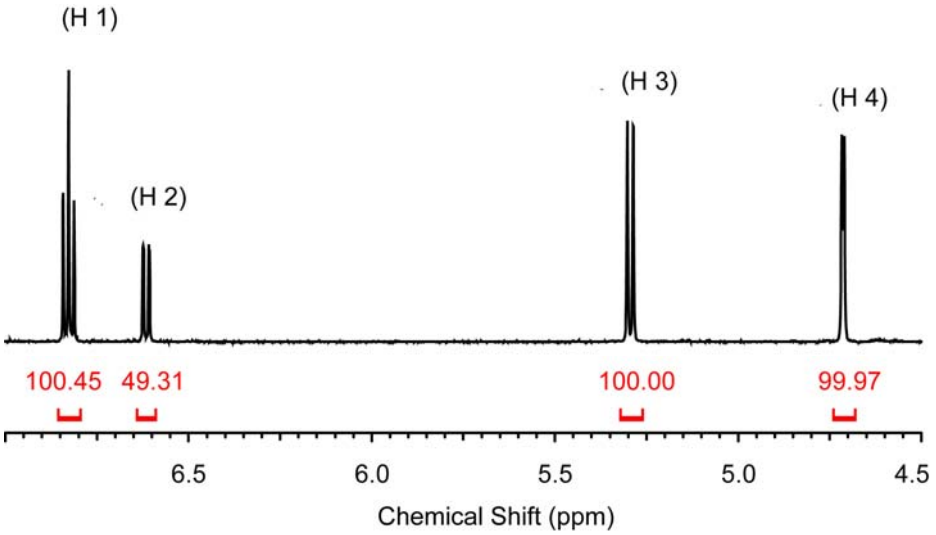
R_{prod} = 49.79 / (100.135 – 49.79) = 0.989



(ii) Analysis of **4a$_{endo}$**

$H_{average}$ = (H 1 + H 3 + H 4) / 3 = 300.42 / 3 = 100.140

R_{prod} = 49.31 / (100.140 – 49.31) = 0.970

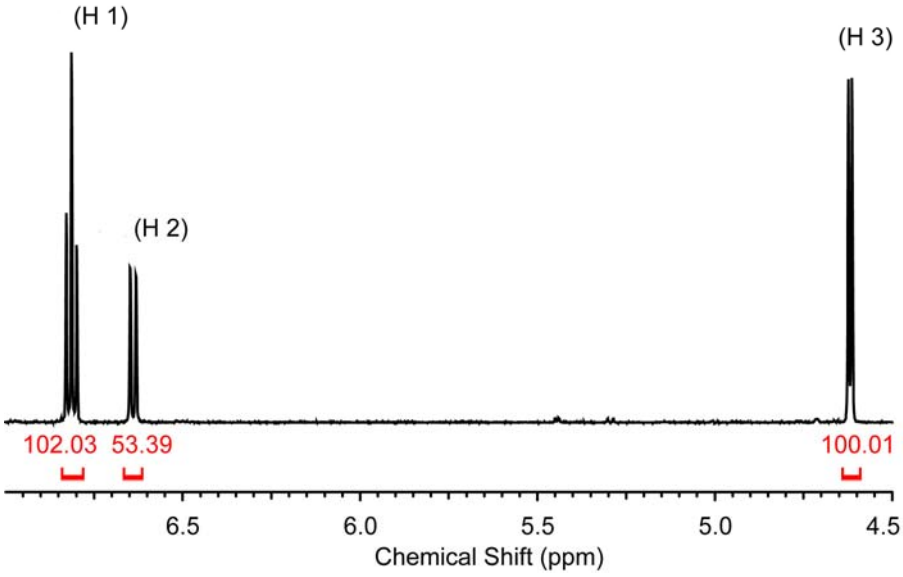


The recovered starting material from this experiment was re-subjected to the asymmetric Povarov reaction conditions. The reaction was allowed to proceed to full conversion, and the products were isolated and separated using the protocol described above.

(iii) Analysis of **4a$_{exo}$** derived from recovered starting material

$H_{average}$ = (H 1 + H 3) / 2 = 202.04/ 2 = 101.02

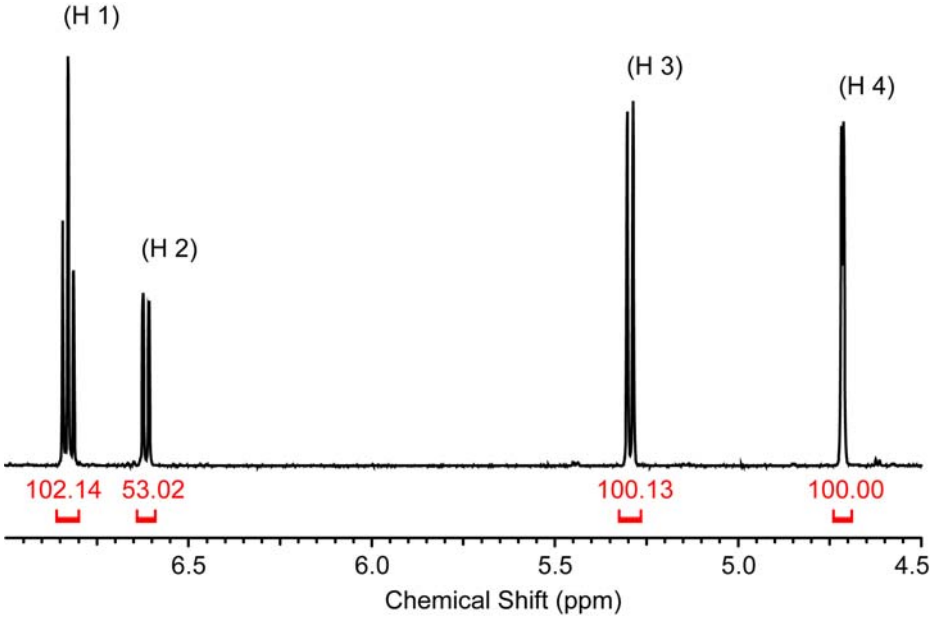
R_{recov} = 53.39 / (101.02 – 53.39) = 1.120



(iv) Analysis of **4a$_{endo}$** derived from recovered starting material

$H_{average}$ = (H 1 + H 3 + H 4) / 3 = 302.27 / 3 = 100.757

R_{recov} = 53.02 / (100.757 – 53.02) = 1.111



A qualitative analysis of these results demonstrate that $R_{recovered} > R_0 > R_{prod}$. Thus, in a Povarov reaction competion experiment, the starting material is preferentially enriched in *ortho*-hydrogen, whereas the product is preferentially enriched in *ortho*-deuterium. Stated differently, imine **2a**-d_2 is more reactive towards 2,3-dihydrofuran than **2a**, and the Povarov reaction displays an inverse secondary deuterium kinetic isotope effect ($k_H/k_D < 1$) at the *ortho*-anilino position.

The kinetic isotope effect experiment was run in triplicate, and yielded the following results:

(b) Experiment 2: 78.1% conversion.

	H 1	H 2	H 3	H 4	$H_{average}$	R_{prod}
4a$_{exo}$	100.64	50.33	100.00		100.320	1.007
4a$_{endo}$	100.85	50.57	100.00	99.80	100.217	1.019

(c) Experiment 3: 72.7% conversion.

	H 1	H 2	H 3	H 4	$H_{average}$	R_{prod}
4a$_{exo}$	100.99	50.48	100.00		100.495	1.009
4a$_{endo}$	101.37	50.87	100.77	100.00	100.713	1.021

Using $k_H/k_D = \ln (1 - F) / \ln (1 - F (R_0/R_{prod}))$, the following kinetic isotope effects can be calculated.

Expt	R_0	R_{4a}	R_{4b}	k_H/k_D for **4a$_{exo}$**	k_H/k_D for **4a$_{endo}$**
1	1.042 ± 0.013	0.989	0.970	0.911 ± 0.021	0.878 ± 0.021
2		1.007	1.019	0.920 ± 0.029	0.948 ± 0.029
3		1.009	1.021	0.934 ± 0.026	0.958 ± 0.026
Average				0.92 ± 0.03	0.93 ± 0.04

O. Hammett Study of Enantioselective Povarov Reactions

We measured the Povarov reaction rate of *para*-anilino substituted imines **2a** and its analogs by reaction calorimetry. A plot of $\log(k_{asym})$ versus σ_p provides an excellent linear fit with a large positive Hammett slope ($\rho = +1.96 \pm 0.06$). When taken together with the kinetic isotope effect data, the experimental and computational Hammett analysis is consistent with the hypothesis that the rate-limiting step is a highly asynchronous but formally concerted cycloaddition with all substrates examined.

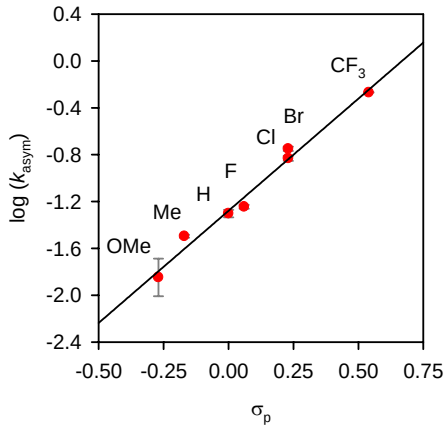


Figure S17. Rate dependence of the asymmetric Povarov reaction on substrate electronic properties. Logarithm of rate constant ($\log(k_{asym})$) versus σ_p for the Povarov reaction of *p*-substituted imines ($[imine]_i = 0.20$) with DHF ($[DHF]_i = 0.4 – 1.6$ M), co-catalyzed by CF_3SO_3H (2 – 4 mM)and urea catalyst **1a** (50 mM). The rate constants were derived from instantaneous rates at 20% conversion as described in the experimental section. The black curve represents a least-squares fit to $f(x) = a + \rho\, x$, $a = -1.28 \pm 0.02$, $\rho = +1.96 \pm 0.06$.

P. Computational Analysis of Catalytic Asymmetric Povarov Reactions

Calculations were executed at Harvard University using the Gaussian 03 program (*2*) with the B3LYP, (*3*) M05-2X, (*4*) or MP2 (*5*) methods, as specified. Unless otherwise noted, default convergence and integration grid settings were used. MP2 calculations employed the frozen core approximation. The 6-31G(d) and 6-31+G(d,p) basis sets of Pople and coworkers were used, as specified. (*6*) Stationary points were characterized by harmonic frequency calculations, and were shown to be first-order saddle points by the existence of a single imaginary frequency or local minima by the existence of no imaginary frequencies. Energies are uncorrected electronic energies at the B3LYP/6-31G(d) level, unless otherwise noted. Single-point energy calculations were performed at the M05-2X/6-31+G(d,p) or MP2/6-31G(d) levels of theory and employed fully optimized B3LYP/6-31G(d) geometries. Single-point energy calculations using the 6-31+G(d,p) basis set employed the keyword SCF=Tight. Relative energies reported in the main text of the paper do not include zero-point vibrational energy corrections or corrections for basis set superposition error. Unscaled zero-point vibrational energy (ZPVE) corrections or free energies at 298.15 K (G_{298}) derived from harmonic frequency calculations at the B3LYP/6-31G(d) level are included below. The following units are used: relative energy, kcal/mol; absolute energy, Hartree; distance, Å.

The four minima depicted in Fig. 4B were identified as follows. An initial study of the preferred catalyst conformation was carried out by subjecting a set of different starting catalyst rotamers to energy and geometry optimization. It was established that the minimum energy structure of the free catalyst displays an internal H-bond between the sulfinamide oxygen atom and the urea protons (shown below). Other rotamers—e.g. ones having the cyclohexyl ring rotated 180°—had substantially higher energies. For the optimal catalyst structure bears a close resemblance to the computed structures of related catalysts. (*7*) The computed structure differs from the crystal structure of **1a** in that the crystal structure displays an internal H-bond between the urea oxygen and the sulfinamide proton. (*1*)

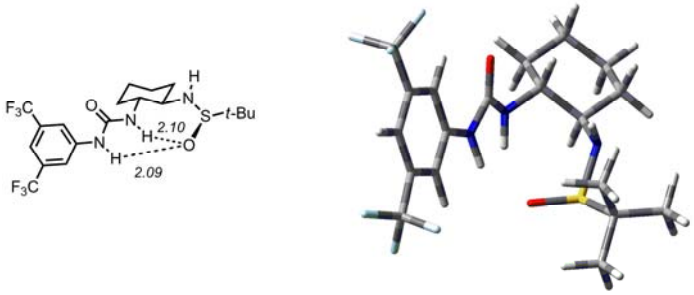


Figure S18. Computed structure of **1a**.

Table S12. Coordinate of computed structure of **1a**.

N	0.00000000	0.00000000	0.00000000
S	1.71138904	0.00000000	0.00000000
O	2.29988055	1.41033599	0.00000000
H	-0.38780058	0.54033420	-0.77376859
C	-1.18419587	1.78659360	1.33326573
C	-1.82691012	2.08243119	2.69972702
C	-2.95816217	1.09072554	3.00989495
C	-2.47081969	-0.36343980	2.92757941
C	-1.80152615	-0.66085319	1.57610648
H	-1.40147582	-1.68085744	1.55199846
H	-2.54340282	-0.59248721	0.76745470
H	-3.30425597	-1.05761903	3.08913789
H	-1.74835657	-0.55100713	3.73554338
H	-3.37621437	1.29609352	4.00264618
H	-3.77610613	1.24072004	2.29052559
H	-1.05284766	2.03023092	3.47921271
H	-2.19884841	3.11246434	2.69046521
H	-1.96150179	1.90311062	0.56660519
N	-0.11959018	2.72271579	0.98916100
C	-0.28948900	3.61300926	-0.05150774
N	0.92628664	3.99609790	-0.61735697
H	1.70049219	3.35779843	-0.44707257
O	-1.38876194	4.01274315	-0.42141151
H	0.83011526	2.39588195	1.13755973
C	-0.66154706	0.32888451	1.28667870
C	1.97095405	-0.65343378	-1.75641790
C	1.13928398	4.97512111	-1.59079611
C	2.43511190	5.08885828	-2.12052643
C	0.13917644	5.85169598	-2.04519605
C	2.72392010	6.05281150	-3.08312553
H	3.22076689	4.42567784	-1.77027830
C	0.45277246	6.81244925	-3.00556429
H	-0.86555755	5.75885335	-1.65850099
C	1.73746426	6.92740844	-3.53724536
H	1.96426959	7.67674013	-4.28536650
C	3.49787613	-0.64380890	-1.92803436
H	3.99132619	-1.27951756	-1.18355820
H	3.75081116	-1.03206263	-2.92117065
H	3.89997755	0.36895914	-1.83863064
C	1.41248563	-2.07841714	-1.81438256
H	1.62685265	-2.50813825	-2.80034564
H	1.88069948	-2.72379041	-1.06220896
H	0.33142968	-2.09552988	-1.65607268
C	1.31005685	0.28463789	-2.77048252
H	0.21884229	0.18766310	-2.78012372
H	1.57599308	1.32786217	-2.57285022
H	1.66140435	0.03442101	-3.77821575
H	0.09619678	0.21008444	2.07558889
C	-0.61054732	7.79099392	-3.43462841

C	4.10410292	6.10174657	-3.68249415
F	-1.84953129	7.26213874	-3.35635476
F	-0.42526941	8.20436748	-4.70924052
F	-0.60472628	8.90052890	-2.65918778
F	4.22564044	5.24437178	-4.72454177
F	4.40986548	7.33131515	-4.14829242
F	5.05567750	5.75825098	-2.78486692

Separately, the structure of the iminium triflate was studied by placing the triflate anion at different locations relative to the iminium cation, and subjecting the arrangements to energy and geometry optimization. This analysis revealed that the anion preferentially associated with the N-H or C-H protons. Initial structures having the catalyst, acid, and iminium at different locations relative to each other were subjected to energy and geometry minimization at the B3LYP/6-31G(d) level. These calculations each converged to one of the four complexes depicted in Fig. 3B. Other possible relative arrangements did not converge and displayed relative energies > 10 kcal/mol higher than the ones depicted in Fig. 4B.

These structures were in turn used as the basis for transition structure calculations. In transition structure calculations, the forming C–C bonds between iminium ion and 2,3-dihydrofuran were fixed at approximately 1.9 and 2.9 Å (estimated from the transition structure in the absence of catalyst and counteranion) and the rest of the molecule was relaxed. The resulting structure was analyzed by frequency calculation and subjected to transition structure search using the Gaussian keyword opt=ts.

Computational analysis of Aza-Diels–Alder reaction catalyzed by H^+

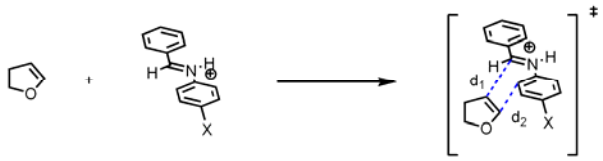


Table S13. Energies and free energies of cationic iminium ions and aza-Diels–Alder transition structures

X	$E_{imininum\ ion}$ (Hartree) [a]	$G_{298,imininum\ ion}$ (Hartree)	$E_{transition\ structure}$ (Hartree)	$G_{298,\ transition\ structure}$ (Hartree)
OMe-trans[b]	–671.6652565	–671.45756	–902.8792505	–902.581754
OMe-cis[b]	–671.6648817	–671.457069	–902.8793911	–902.582022
Me	–596.4577527	–596.254956	–827.6738596	–827.380857
H	–557.1367449	–556.957955	–788.3538914	–788.085817
F	–656.3661597	–656.196942	–887.583151	–887.324511

Cl	–1016.727241	–1016.560428	–1247.944974	–1247.68861
Br	–3128.236535	–3128.071217	–3359.454163	–3359.199264
CF_3	–894.1657169	–893.988709	–1125.384899	–1125.118449
CN	–649.3669573	–649.192621	–880.587095	–880.323317
NO_2	–761.6231318	–761.446303	–992.8441558	–992.57795

a. $E_{dihydrofuran}$ = –231.2217842; $G_{298,\ dihydrofuran}$ = –231.15621. b. OMe–*trans*: the methyl group of the methoxy substituent is *trans* relative to the formyl carbon of the iminium ion. OMe–*cis*: the methyl group of the methoxy substituent is *cis* relative to the formyl carbon of the iminium ion

2. Activation energies and free energies of cationic iminium ions and aza-Diels–Alder transition structures

X	σ_p [a]	Activation energy (ΔE_{act}, kcal/mol)	Activation free energy ($\Delta G_{298,act}$, kcal/mol)	d_1 (Å)	d_2 (Å)
OMe-trans[b]	–0.27	4.89	20.09	1.975	3.05
OMe-cis[b]	–0.27	4.56	19.61	1.993	3.026
Me	–0.17	3.56	19.02	1.998	3.045
H	0	2.91	17.79	2.004	3.059
F	0.06	3.01	17.97	1.997	3.071
Cl	0.23	2.54	17.59	2.008	3.079
Br	0.23	2.61	17.67	2.010	3.076
CF_3	0.54	1.63	16.61	2.026	3.098
CN	0.66	1.03	16.01	2.037	3.119
NO_2	0.78	0.48	15.41	2.047	3.136

Table S14. Activation energies and free energies of cationic iminium ions and aza-Diels–Alder transition structures. a. Extracted from: Hansch, C.; Leo, A.; Taft, R.W. *Chem. Rev.* **1991***, 91*, 165–195. b. OMe–trans: the methyl group of the methoxy substituent is *trans* relative to the formyl carbon of the iminium ion. OMe–cis: the methyl group of the methoxy substituent is *cis* relative to the formyl carbon of the iminium ion

Structures of iminium/sulfonate ion pair–catalyst complexes

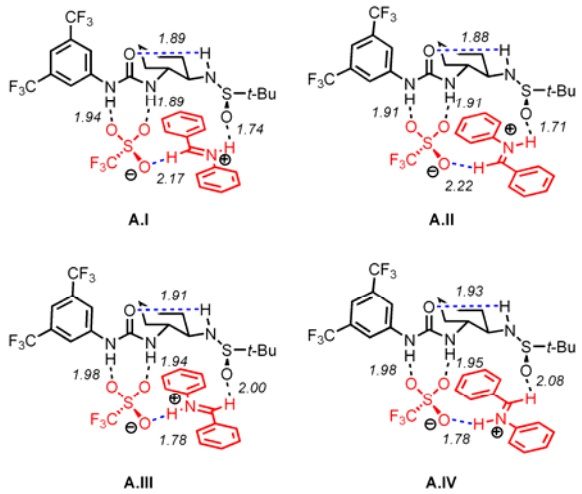
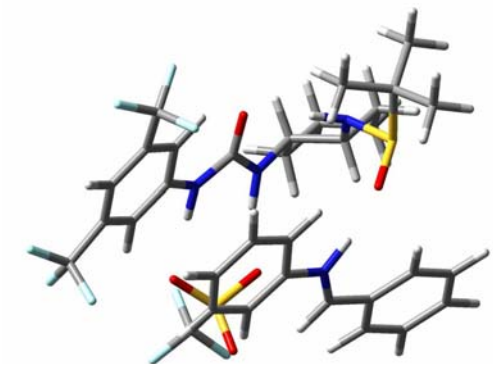


Table S15. The geometric and energetic parameters for iminium/sulfonate ion pair–catalyst **1a** complexes

	A.I	**A.II**	**A.III**	**A.IV**
E_{B3LYP}	-3569.870863	-3569.871504	-3569.870813	-3569.869314
$ZPVE_{B3LYP}$	0.689921	0.68972	0.690055	0.689846
$G_{298,\ B3LYP}$	-3569.274965	-3569.275546	-3569.274202	-3569.273241

A.I



N	-2.21499900	-2.65425900	-0.95573500
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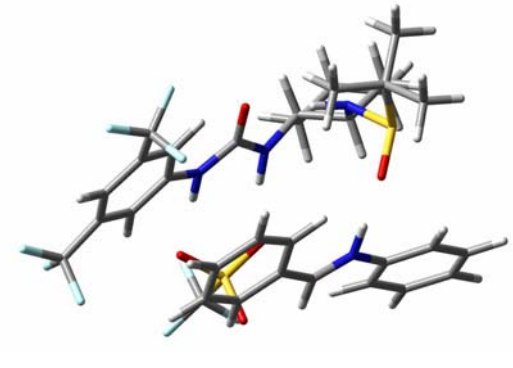
H	-1.22094100	-2.52530200	-1.19665600
C	-2.26904800	-0.65877300	-2.40766000
C	-3.16736400	0.42097900	-3.04234500
C	-4.42916500	-0.16148100	-3.69118300

A.II



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O	-2.23506900	-2.53724400	1.61465100
C	-2.21277900	-4.80302600	0.13107900
H	-1.48301600	-2.33039200	-1.23319800
C	-2.30418500	-0.33417700	-2.42855200
C	-3.06782500	0.85779700	-3.03833800

C	-5.22691800	-1.00644900	-2.69031000	C	-4.37492700	0.44367900	-3.72527400
C	-4.34267700	-2.10906600	-2.09515600	C	-5.27717300	-0.34220700	-2.76618500
H	-4.89990200	-2.70437000	-1.36081100	C	-4.52951900	-1.55641500	-2.20303300
H	-4.02820700	-2.80421700	-2.88588700	H	-5.16276600	-2.11440400	-1.50217500
H	-6.10488000	-1.45156000	-3.17421600	H	-4.27654700	-2.25013100	-3.01680600
H	-5.60569300	-0.36043200	-1.88481400	H	-6.19063300	-0.67018300	-3.27702300
H	-5.04716900	0.65284900	-4.08823400	H	-5.59577200	0.31212500	-1.94162000
H	-4.14639800	-0.78766300	-4.54963100	H	-4.89121400	1.33649300	-4.09798100
H	-3.45098100	1.14435500	-2.26559500	H	-4.15085800	-0.17853300	-4.60391400
H	-2.57356800	0.97481600	-3.77855200	H	-3.28459800	1.58104700	-2.24039700
H	-1.87412500	-1.31507900	-3.19369000	H	-2.40256500	1.36768300	-3.74448800
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C	0.11502100	-0.55681400	-1.74327500	N	-1.11483200	0.18423600	-1.75166300
N	1.12115200	0.33164500	-1.41566100	C	0.06854300	-0.49560400	-1.72605100
H	0.86442500	1.31690000	-1.30973100	N	1.16242100	0.28630800	-1.40765300
O	0.31108400	-1.76077300	-1.98774700	H	1.01362200	1.29428400	-1.30398900
H	-1.28187300	0.94386000	-1.41123900	O	0.14073900	-1.71442100	-1.96418100
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O	-0.63490900	3.80407500	1.31494700	O	1.00965500	3.10853900	-0.71055700
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C	1.15997500	1.24921300	2.55394100	C	-0.47859700	5.29974500	-0.65783200
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C	3.20715200	-0.04269300	2.71408200	C	-3.22412700	-1.15813400	-1.49383500
C	2.48258800	-1.22687300	2.57805000	N	-2.02614900	0.13407700	2.23556800
C	1.09681900	-1.18583200	2.43585300	C	-0.88707900	0.75513900	2.38532100
H	0.51618700	-2.09560200	2.32111600	C	-3.31743300	0.74104400	2.20583900
H	2.99765500	-2.18209800	2.55047100	C	-3.50228600	2.09034900	1.88260600
H	4.28834000	-0.06816000	2.80338400	C	-4.40750300	-0.08559300	2.50951400
H	3.11115700	2.10878700	2.76584800	C	-4.79528100	2.60962000	1.89139900
H	0.67432400	2.21732100	2.49992900	H	-2.66736200	2.71406700	1.58560600
N	-0.97928600	0.01794800	2.28756200	C	-5.69295000	0.45177300	2.51140600
C	-1.79164500	1.03824200	2.29315100	H	-4.23668700	-1.13104500	2.74722800

H	-1.35217000	2.03118400	2.33468300	C	-5.88967200	1.80029700	2.20738100
H	-1.36430100	-0.93590900	2.11269500	H	-4.94470800	3.65361100	1.63303500
C	-3.07865500	-1.54270200	-1.42689300	H	-6.53880700	-0.18515000	2.75302000
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C	-1.66761500	-4.95291800	0.38206200	H	-2.04776100	-0.89954700	2.07457800
C	-3.23472400	0.96281200	2.24438900	C	0.41205900	0.13527700	2.45650000
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C	-3.96585100	-0.23157400	2.42352500	C	0.62179400	-1.26400200	2.44758100
C	-5.31238200	2.19594200	2.00765500	C	2.80663200	0.49398300	2.66399800
H	-3.35252800	3.08980800	1.89497700	H	1.35055400	2.08112200	2.52847300
C	-5.35481000	-0.19970500	2.39040600	C	1.91241200	-1.76221100	2.54900800
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C	-6.02907300	1.00948300	2.18061900	C	3.00265700	-0.88854300	2.66005400
H	-5.83621200	3.13276900	1.84431200	H	3.65763400	1.16514500	2.70709500
H	-5.91699400	-1.11741200	2.53602000	H	2.08469200	-2.83366500	2.52115200
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C	2.45879700	0.03819300	-1.12986100	H	-0.91898900	1.83946000	2.46246700
C	3.29276500	1.12194900	-0.79936600	C	-0.69786600	-4.67888800	-0.05224800
C	2.99716700	-1.25851100	-1.13643900	H	-0.42770900	-4.18552500	-0.99005700
C	4.62742900	0.90424300	-0.47210200	H	-0.24821700	-4.12519200	0.77725100
H	2.88252600	2.12662600	-0.78384400	H	-0.25736000	-5.68310200	-0.06632300
C	4.33600100	-1.45033600	-0.79449000	C	-2.54887000	-5.56495800	1.42191400
H	2.36884500	-2.09372800	-1.40805200	H	-3.63185600	-5.64065600	1.57587300
C	5.16806200	-0.38281000	-0.46388200	H	-2.14869300	-6.58286000	1.35251000
H	6.20888600	-0.54599000	-0.21254600	H	-2.10730600	-5.07797900	2.29536700
C	-1.82591200	-5.62251700	1.75529100	C	-2.89637500	-5.43966700	-1.08312100
H	-2.88139600	-5.75680300	2.02037700	H	-2.53759900	-6.46991600	-1.19388400
H	-1.35909500	-6.61368500	1.72683500	H	-3.98508400	-5.47806700	-0.95949400
H	-1.34315600	-5.03472200	2.54043700	H	-2.67105700	-4.89322200	-2.00170100
C	-2.41012200	-5.73648700	-0.70546200	C	2.46162300	-0.14131200	-1.11554700
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H	-2.31000300	-5.25860700	-1.68269700	C	4.71997100	0.50710500	-0.50727400
C	-0.18913100	-4.74851400	0.04042900	H	3.12128000	1.90066200	-0.87788500

H	-0.04464300	-4.32475000	-0.95718000
H	0.29836900	-4.09632100	0.77094100
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H	-3.37323200	-0.89846600	-0.58441200
C	4.85823500	-2.85702300	-0.68656400
C	5.47325000	2.05997900	-0.01232200
F	4.60519300	-3.38080300	0.54473300
F	6.19529000	-2.92181500	-0.86468300
F	4.28704400	-3.68944000	-1.58208500
F	5.39161900	2.21989700	1.33906300
F	6.78111500	1.87582300	-0.29550200
F	5.09444300	3.22894300	-0.56387400
F	-1.43339600	4.86445300	-2.24902200
F	-0.37365800	6.01666100	-0.73745700
F	-2.44527800	5.43346500	-0.40808800

C	4.15856800	-1.81292800	-0.69565600
H	2.12979800	-2.26117600	-1.27995700
C	5.10987500	-0.83070600	-0.42518500
H	6.12689900	-1.09730700	-0.16472100
C	4.51370700	-3.25905600	-0.48599500
C	5.69980900	1.58527900	-0.13017000
F	3.81265300	-4.08688000	-1.28728000
F	5.82537200	-3.50154300	-0.69375700
F	4.24821000	-3.64287900	0.79572600
F	6.97395600	1.22776000	-0.40144900
F	5.65073500	1.84989600	1.20512500
F	5.45548500	2.74764200	-0.76480700
F	0.54827500	6.05855000	-0.26180300
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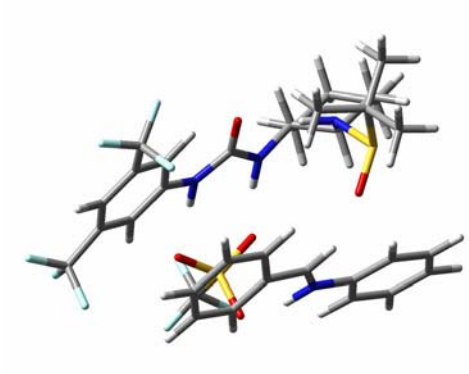
F	-1.61181700	5.81139600	-0.15617600

A.III



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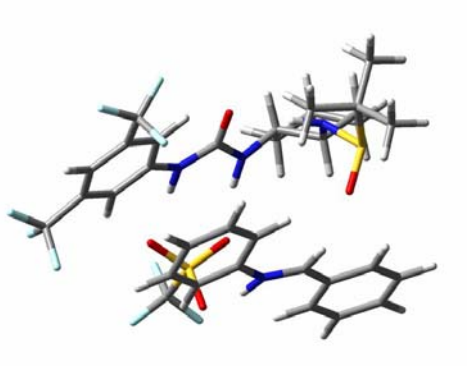
A.IV



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C	2.30398700	-0.65570000	2.39568400
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C	4.43126000	-0.04201000	3.69496300
C	5.27720700	-0.84312000	2.69851100

C	-4.45120000	-2.09702400	-2.00215200	C	4.45543300	-1.99481600	2.10983300
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H	-4.16545900	-2.81087400	-2.78706300	H	4.17291200	-2.69779000	2.90548500
H	-6.20226700	-1.39811100	-3.07273500	H	6.17847400	-1.23601500	3.18476600
H	-5.65439300	-0.30497200	-1.80457400	H	5.61937500	-0.18003300	1.89027600
H	-5.08179600	0.65403300	-4.03144000	H	4.99989100	0.80763600	4.09200500
H	-4.23212900	-0.82345800	-4.47374600	H	4.18101100	-0.68124300	4.55383600
H	-3.46719800	1.11964400	-2.22371900	H	3.39635100	1.20288800	2.26124800
H	-2.60166100	0.90599600	-3.73743900	H	2.51679700	0.99319700	3.76735500
H	-1.95791400	-1.39335000	-3.12271700	H	1.92531800	-1.32712300	3.17697500
N	-1.17691300	-0.06934600	-1.72228100	N	1.14702900	-0.03397300	1.74473800
C	0.05785800	-0.65105200	-1.70111800	C	-0.08403400	-0.62603200	1.70954300
N	1.09598600	0.22164800	-1.42125300	N	-1.12540400	0.24592400	1.44249600
H	0.87596200	1.21578300	-1.33727900	H	-0.91378200	1.24413300	1.40345400
O	0.22311700	-1.86455100	-1.90543700	O	-0.24045100	-1.84339000	1.89453100
H	-1.27940300	0.91989800	-1.49087800	H	3.42860900	-0.85034800	0.58290000
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O	0.75817700	3.10880300	-0.77649300	S	0.47831400	3.46531300	0.22873900
S	-0.58385000	3.48826200	-0.27601300	O	0.42622900	3.47856500	-1.26956600
O	-0.68102500	3.62259300	1.21304200	C	0.81723200	5.24354500	0.65385800
O	-1.69999600	2.70799900	-0.86742400	O	1.64236300	2.71642300	0.76602200
C	-3.19782500	1.25415800	2.12539800	C	3.16508300	-1.50579600	1.42821400
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C	-3.79930400	2.49248900	1.86816300	H	-1.41566000	2.17574500	-2.44217900
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H	-3.52016700	-0.85834400	2.53029800	H	-1.97834400	-2.75310300	-2.57234800
N	-1.77419000	1.23300100	2.17735300	H	-3.95892000	-1.28310000	-2.77234100
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H	-1.50105900	-0.79165400	2.36127700	C	2.00714400	0.31548200	-2.32793700
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C	-3.16152300	-1.56943200	-1.34885600	H	0.77728000	1.89761000	-2.00092900
C	-0.84911400	5.22844600	-0.87416800	C	3.28791300	0.96827000	-2.18971100
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H	0.75168300	2.34167300	2.55006900	H	4.26856200	-0.94407500	-2.39075900
C	2.43083700	-1.17559700	2.56923700	C	5.86283500	2.03142300	-1.95954600
H	0.42963700	-1.96609700	2.35219700	H	4.88174000	3.94307100	-1.74677200
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H	-1.59760300	-6.70315800	1.78373200	C	-3.33264200	0.99423000	0.89593400
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H	-2.17909500	-6.80376400	-0.72806500	C	-4.26820100	-1.60874600	0.68122800
H	-3.65972600	-5.87195600	-0.45818500	H	-2.27714500	-2.21934400	1.24719300
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C	-0.36905800	-4.83742700	0.14312600	H	-6.17860300	-0.73884200	0.17243000
H	-0.19548700	-4.40937700	-0.84817900	C	2.21276500	-5.75725500	-1.62919200
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C	2.42667700	-0.10627700	-1.13725500	H	3.28614400	-5.96654400	-1.70900800
C	3.29820100	0.95790200	-0.84039400	C	2.39404000	-5.74247500	0.89540900
C	2.92274200	-1.41999700	-1.10909500	H	1.91937300	-6.73047200	0.93798200
C	4.62609200	0.70499600	-0.51052000	H	3.47860700	-5.89695300	0.84968500
H	2.92232600	1.97566100	-0.84932200	H	2.16104800	-5.20484700	1.81727300
C	4.25577300	-1.64628900	-0.76556900	C	0.38012300	-4.69894600	-0.25662700

H	2.26623800	-2.24172700	-1.35343100	H	0.09850300	-4.19904700	0.67443400
C	5.12424600	-0.59848300	-0.46737400	H	0.05928100	-4.07879700	-1.09915200
H	6.16000700	-0.78907500	-0.21415500	H	-0.17242300	-5.64524100	-0.30527800
C	4.73113600	-3.06586900	-0.61459100	C	-4.73116800	-3.02048500	0.44654500
C	5.51271000	1.84218000	-0.08260800	C	-5.55730700	1.90562400	0.20486200
F	4.47290700	-3.53602400	0.63755800	F	-4.48130500	-3.40843400	-0.83525300
F	6.06340600	-3.18143400	-0.80150600	F	-4.10624600	-3.90926400	1.24613000
F	4.12316100	-3.90809900	-1.47460100	F	-6.06040300	-3.16180700	0.63869700
F	6.80932300	1.61569100	-0.38370400	F	-6.85527600	1.63187000	0.45984700
F	5.45857900	2.02196600	1.26896900	F	-5.23526900	3.02841100	0.87677800
F	5.15888300	3.01438800	-0.64271400	F	-5.48084500	2.20819000	-1.12064600
F	-0.81304400	5.26105000	-2.20981600	F	0.92271000	5.38356200	1.97857000
F	0.10095400	6.03432000	-0.39273900	F	-0.17094300	6.02385100	0.20986300
F	-2.04476000	5.67115900	-0.46236500	F	1.96720200	5.63257400	0.08524700

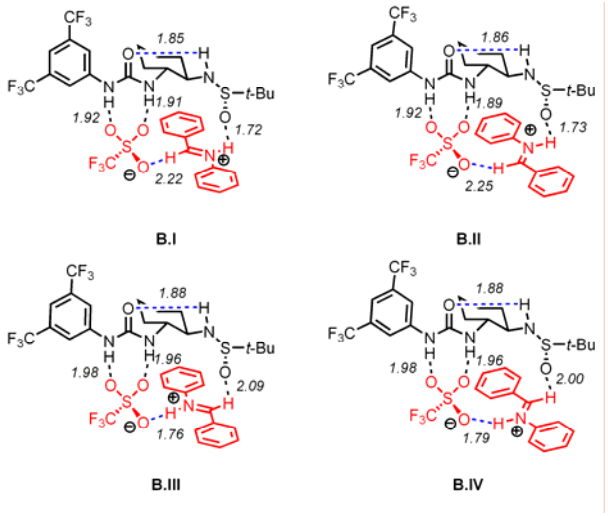
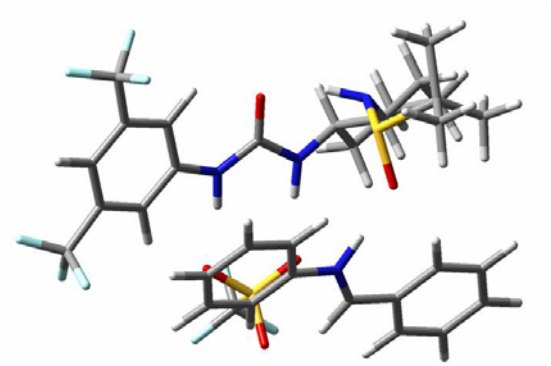


Table S16. The geometric and energetic parameters for iminium/sulfonate ion pair–catalyst **1c** complexes

	B.I	**B.II**	**B.III**	**B.IV**
E_{B3LYP}	-3569.864577	-3569.864519	-3569.863487	-3569.862508

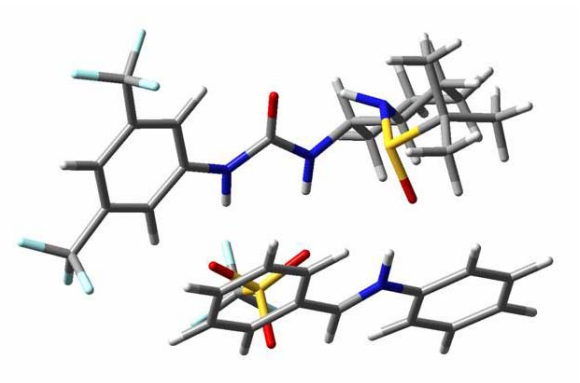
$ZPVE_{B3LYP}$	0.68998	0.69004	0.689522	0.690106
$G_{298,\ B3LYP}$	-3569.268772	-3569.26894	-3569.267583	-3569.268323

B.I



N -2.03451100 -2.85997200 -1.02006300
S -1.82207400 -3.22209400 0.62121600
O -2.36197800 -2.09268400 1.52607700
H -1.08735700 -2.75538100 -1.41588700
C -2.08892100 -0.73562400 -2.30657400
C -2.99211400 0.39612400 -2.82977400
C -4.16011000 -0.13948300 -3.66820000
C -4.96658700 -1.18937400 -2.89410900
C -4.05541500 -2.31336500 -2.38072200
H -4.63936500 -3.05470800 -1.82614900
H -3.60687700 -2.84758200 -3.23025000
H -5.75785600 -1.60906500 -3.52752900
H -5.46920000 -0.70906900 -2.04152700
H -4.80547900 0.69194500 -3.97655200
H -3.76974800 -0.59145000 -4.59130300
H -3.37647800 0.97048900 -1.97602100
H -2.38098400 1.09062600 -3.41726300
H -1.66183700 -1.27510600 -3.16289300
N -0.97266500 -0.15825700 -1.55660100
C 0.27599800 -0.71699300 -1.62251400

B.II



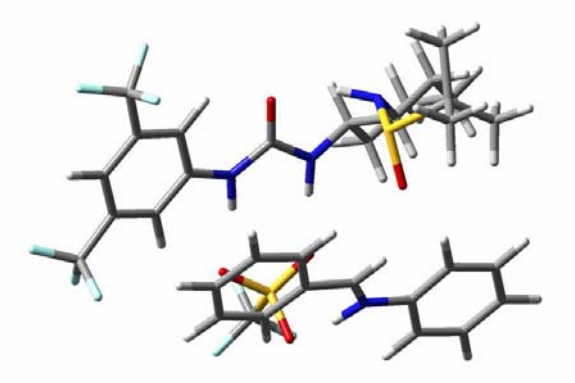
N 1.91219600 2.92273700 -0.98013200
S 1.62115200 3.15220800 0.68791500
O 2.41177900 2.12279500 1.52068400
H 0.98159500 2.79096800 -1.40474100
C 2.05706000 0.83117800 -2.31444400
C 3.00375300 -0.25639600 -2.85369100
C 4.17082700 0.34195700 -3.65000000
C 4.93588900 1.37973600 -2.81973900
C 3.98983100 2.46524000 -2.28649700
H 4.54505500 3.18408500 -1.67598100
H 3.55982300 3.03178600 -3.12443500
H 5.73168700 1.83965600 -3.41867200
H 5.42941200 0.87851800 -1.97411500
H 4.84279100 -0.46003300 -3.97877400
H 3.78413500 0.82005100 -4.56154000
H 3.39035300 -0.84509600 -2.01085200
H 2.42605200 -0.94997300 -3.47526800
H 1.62322600 1.37821700 -3.16232000
N 0.95014900 0.20072200 -1.59307800
C -0.31377600 0.72058300 -1.65116600
N -1.31314500 -0.14658400 -1.25506600

N	1.30279400	0.11900900	-1.23579100
H	1.07831500	1.09995400	-1.04623700
O	0.45078800	-1.89387700	-1.98545000
H	-1.07411100	0.81710100	-1.26562300
O	0.98879000	2.95586400	-0.57619700
S	-0.35887000	3.48867600	-0.24646200
O	-0.50569100	4.02851700	1.12734300
O	-1.46840700	2.58011800	-0.65781400
C	0.12690500	0.21689000	2.57275100
C	0.99973500	1.31258900	2.59382500
C	2.33546500	1.09879700	2.92436200
C	2.80149700	-0.18195800	3.23418200
C	1.92122200	-1.26420100	3.21582000
C	0.58219000	-1.07085800	2.88317200
H	-0.11334200	-1.90345900	2.86304600
H	2.27500000	-2.26377200	3.44990900
H	3.85184300	-0.33079500	3.46350600
H	3.02605100	1.93524300	2.91144000
H	0.67195200	2.30781500	2.31318700
N	-1.25556800	0.33730700	2.23558200
C	-1.93904600	1.44463900	2.15281700
H	-1.39907300	2.37314200	2.31305200
H	-1.70332400	-0.57408300	1.98513700
C	-2.92025000	-1.76894200	-1.49439800
C	-0.55366900	4.97308900	-1.34986500
C	-3.03117600	-4.63402000	0.96817700
C	-3.35172900	1.56179800	1.87143400
C	-3.83987500	2.87186700	1.68051400
C	-4.24325100	0.46920400	1.81440300
C	-5.19145600	3.08553200	1.43364200
H	-3.14168200	3.70319000	1.70019600
C	-5.59259200	0.69673300	1.57151200
H	-3.88354200	-0.54503700	1.95474200
C	-6.06859800	1.99980200	1.38148300
H	-1.05466700	-1.11448900	-1.04303200
O	-0.52940400	1.89074600	-2.01365200
H	1.08637300	-0.76962300	-1.29872700
H	3.25501600	1.34621000	-0.58598200
O	-0.90966500	-2.95746600	-0.50746300
S	0.46737400	-3.47048500	-0.28182300
O	0.70826000	-4.07040000	1.05299900
C	0.62847600	-4.89511200	-1.46680600
O	1.52839200	-2.51392200	-0.70909100
C	2.83960600	1.86591900	-1.45805800
N	2.35901800	-0.58992700	2.02515100
C	1.31251300	-1.30363900	2.33720300
C	3.66600700	-1.08872300	1.74580300
C	3.91259200	-2.44220500	1.48213800
C	4.70998100	-0.15441700	1.75159200
C	5.22262500	-2.85147500	1.24620900
H	3.10323300	-3.16003700	1.41579000
C	6.01412400	-0.58326700	1.51151700
H	4.48927600	0.89189000	1.93795900
C	6.27494900	-1.93183600	1.26394500
H	5.41704700	-3.89809400	1.03225700
H	6.82483000	0.13941700	1.52071000
H	7.29136500	-2.26516300	1.07555300
H	2.25974700	0.44152400	1.90444700
C	0.00277800	-0.79001700	2.65322600
C	-1.03730300	-1.73978300	2.76156600
C	-0.27515100	0.57931700	2.86472700
C	-2.33276100	-1.32423200	3.04848400
H	-0.82085200	-2.78648300	2.57129600
C	-1.57037300	0.97867500	3.16312000
H	0.51973900	1.31576900	2.80333300
C	-2.60040500	0.03201400	3.24539300
H	-3.13938400	-2.04735200	3.09466900
H	-1.78614700	2.03035300	3.32557200

H -5.55974300 4.09497100 1.27854600
H -6.28055000 -0.14297800 1.53441100
H -7.12580400 2.16628400 1.19341200
C 2.63565500 -0.23604300 -0.98568300
C 3.46693800 0.75742800 -0.43783400
C 3.17338700 -1.50700000 -1.24429900
C 4.79267100 0.46903700 -0.12754300
H 3.06443200 1.74789300 -0.25271700
C 4.50862300 -1.76785600 -0.93238800
H 2.54934500 -2.26805600 -1.68906800
C 5.33185800 -0.79569000 -0.36826900
H 6.36743200 -1.01007600 -0.13634800
C -2.61764700 -5.11536300 2.36975000
H -2.75628300 -4.32774000 3.11670100
H -3.23855000 -5.97187200 2.65669800
H -1.57078400 -5.43930700 2.39356600
C -4.47667200 -4.14048800 0.97786600
H -5.13015700 -4.94133200 1.34491400
H -4.58814700 -3.27775900 1.64053700
H -4.82005100 -3.86437500 -0.02186300
C -2.78044500 -5.71632200 -0.08439700
H -3.03719000 -5.36626200 -1.08712000
H -1.73159000 -6.03573900 -0.09310500
H -3.39363100 -6.59506600 0.14904100
H -3.34384300 -1.25803800 -0.62020600
C 5.04199000 -3.15740800 -1.16156600
C 5.62669600 1.51446500 0.56073100
F 4.71696700 -3.98914200 -0.14062900
F 6.38980400 -3.17414700 -1.26413300
F 4.54292500 -3.71302200 -2.28664700
F 5.43762000 1.48584000 1.91226800
F 6.94818700 1.32898900 0.35767200
F 5.32064800 2.76374200 0.15863700
F -0.44947200 4.60841800 -2.63394700
H -3.61738700 0.35246500 3.45093100
H 1.43142100 -2.38248100 2.34732300
C -2.65038300 0.17498600 -0.98734700
C -3.43738000 -0.82098800 -0.38052700
C -3.23561900 1.41631900 -1.28571100
C -4.76558300 -0.56275600 -0.05451700
H -2.99926800 -1.78962000 -0.16449700
C -4.57188400 1.64717600 -0.95511400
H -2.64570900 2.17807100 -1.77361900
C -5.35138100 0.67306700 -0.33526900
H -6.38898200 0.86389700 -0.09091200
C -5.15654500 3.00928600 -1.22204700
C -5.55492000 -1.59876600 0.69728300
F -4.66897900 3.55928400 -2.35426100
F -6.50297400 2.96992000 -1.33649000
F -4.87510500 3.87474400 -0.21607700
F -6.87755800 -1.51762100 0.44251700
F -5.41513100 -1.43945900 2.04732900
F -5.15782800 -2.85571600 0.41909400
F -0.28614400 -5.83102500 -1.19458200
F 0.45111600 -4.46916800 -2.72405500
F 1.84815100 -5.44107000 -1.36749000
C 2.50448800 4.77470600 1.07118900
C 4.01239300 4.64053000 0.87675900
H 4.26840200 4.53176900 -0.17978900
H 4.50976700 5.54384400 1.25081300
H 4.40456900 3.78201000 1.43014800
C 2.16035700 5.04346200 2.54493600
H 2.58486400 6.00815000 2.84588100
H 1.07671200 5.09299000 2.70545900
H 2.57445000 4.26842500 3.19664800
C 1.89051700 5.83398200 0.15124200
H 2.09544400 5.61158700 -0.89943000
H 0.80445100 5.90665700 0.28404800

F 0.38902500 5.88081300 -1.08006400
F -1.75777900 5.53095300 -1.15913700
H 2.32096600 6.81375400 0.39019600

B.III



N -2.14071900 -2.89802600 -1.01140300
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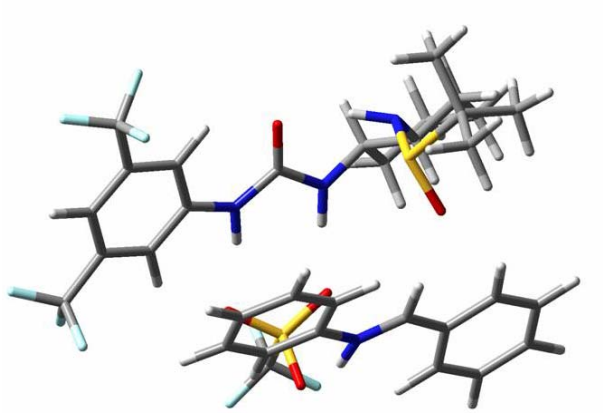
H -1.19101100 -2.83872500 -1.40276200
C -2.11830300 -0.79977000 -2.34939200
C -2.98202400 0.34660200 -2.90824300
C -4.18435400 -0.16576000 -3.71074200
C -5.02336100 -1.14722100 -2.88424000
C -4.15144400 -2.29047900 -2.34805900
H -4.75541900 -2.99147300 -1.76351500
H -3.73837000 -2.86792400 -3.18744000
H -5.84499200 -1.55305100 -3.48744100
H -5.48647900 -0.61321500 -2.04138800
H -4.79540800 0.68284400 -4.04157900
H -3.82948900 -0.66997000 -4.62105400
H -3.33103100 0.96837200 -2.07258600
H -2.34984700 0.99219800 -3.52852400
H -1.71365000 -1.38387500 -3.18728400
N -0.97912200 -0.22304800 -1.63106400

B.IV



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H -1.13383300 -2.77683100 -1.40076300
C -2.07606500 -0.77470700 -2.35682000
C -2.93173600 0.36847000 -2.93374400
C -4.13271300 -0.14771800 -3.73468300
C -4.98523300 -1.09994700 -2.88918000
C -4.13562400 -2.25313200 -2.33773000
H -4.75195600 -2.91227600 -1.71942700
H -3.75471100 -2.86592800 -3.16676600
H -5.81863300 -1.49944000 -3.48038400
H -5.43271500 -0.54206700 -2.05320200
H -4.73256200 0.69993200 -4.08797300
H -3.77767600 -0.67594600 -4.63120600
H -3.28306600 1.00210600 -2.10794000
H -2.29209200 1.00295800 -3.55814100
H -1.65015900 -1.35476900 -3.18658000
N -0.95543900 -0.19011900 -1.61276600

C	0.25033400	-0.82144900	-1.66018700
N	1.29994800	0.00053800	-1.28899100
H	1.10503700	0.99231900	-1.14201000
O	0.39958300	-2.01212300	-1.97920200
H	-1.04972100	0.76765200	-1.39574900
O	1.09979000	2.91257100	-0.65238100
S	-0.25598300	3.45245700	-0.39432500
O	-0.51150200	3.82009100	1.03652700
O	-1.35526300	2.65965500	-0.99818200
C	0.15518400	0.40675100	2.68038100
C	1.07696900	1.47794300	2.63898100
C	2.42521600	1.22991000	2.85526500
C	2.87412900	-0.07058300	3.11796000
C	1.96948600	-1.13366500	3.17489500
C	0.61668900	-0.89970500	2.95796300
H	-0.09809900	-1.71710500	2.96931100
H	2.32125800	-2.14159200	3.37238400
H	3.93578200	-0.24845500	3.25896400
H	3.14045000	2.04322800	2.79820100
H	0.74849400	2.48799100	2.41895900
C	-2.97688600	-1.77454100	-1.49388800
C	-0.30171500	5.09139000	-1.27176300
C	-3.27276100	-4.57026400	0.99024800
C	-3.28388600	1.76627900	1.84127500
C	-3.75809600	3.07367100	1.67867400
C	-4.15449800	0.67046900	1.78084200
C	-5.11990500	3.28762700	1.47935200
H	-3.06027800	3.90487600	1.69426500
C	-5.51345700	0.90562900	1.58159300
H	-3.78352900	-0.34816000	1.84414000
C	-6.00209800	2.20712200	1.43682400
H	-5.48755500	4.30144200	1.35278200
H	-6.19399300	0.06047600	1.53051500
H	-7.06364300	2.37557800	1.28043700

C	0.28876100	-0.76075800	-1.64078900
N	1.31710500	0.08496800	-1.26687500
H	1.10165400	1.07494100	-1.13881500
O	0.46315100	-1.94727900	-1.96086900
H	-1.05008400	0.79264600	-1.35381100
H	-3.30758200	-1.21013600	-0.63072100
O	1.04927000	2.99757600	-0.66989200
S	-0.29977300	3.44989400	-0.25660600
O	-0.44111000	3.70969300	1.21272200
C	-0.49967000	5.13783300	-1.01137600
O	-1.41309100	2.64312900	-0.81738600
C	-2.93679300	-1.75297200	-1.50966200
C	-3.48788700	1.38656300	1.79505700
C	-3.58952900	2.79081600	1.68200600
C	-4.63887700	0.58633000	1.61625300
C	-4.82019200	3.36842100	1.40061900
H	-2.71420400	3.42128100	1.79590200
C	-5.86508800	1.17783900	1.33281900
H	-4.54420900	-0.49374100	1.68907900
C	-5.95624200	2.56805100	1.22730000
H	-4.89698800	4.44755200	1.30987200
H	-6.74712000	0.55952800	1.19548100
H	-6.91381500	3.03233800	1.00776000
C	0.10367700	0.51058800	2.63724200
C	1.29921000	1.23876100	2.58293900
C	0.09738500	-0.83260800	3.03791900
C	2.49893100	0.61178500	2.91547600
H	1.28576300	2.27468300	2.25984700
C	1.30443000	-1.44042800	3.37091100
H	-0.82213200	-1.40592800	3.07790600
C	2.50483700	-0.72637600	3.30971900
H	3.42910500	1.16468800	2.83859900
H	1.30603400	-2.48222100	3.67736100
H	3.44070200	-1.21523400	3.56311600

C 2.61845900 -0.38219800 -1.01111400
C 3.48904600 0.61883500 -0.54382300
C 3.10624400 -1.69105700 -1.16147900
C 4.80376100 0.30568200 -0.20997900
H 3.12644200 1.63589600 -0.43745100
C 4.43020000 -1.97706000 -0.82608000
H 2.45276800 -2.46092500 -1.54451700
C 5.29295500 -0.99439400 -0.34423000
H 6.32031800 -1.22874500 -0.09560600
C -2.84968900 -5.13180700 2.35936400
H -2.85838600 -4.35104600 3.12675500
H -3.55032300 -5.91776200 2.66480400
H -1.84676000 -5.57248700 2.32288500
C -4.65840700 -3.93442800 1.08844000
H -5.37576800 -4.67671100 1.45997600
H -4.64536600 -3.09090900 1.78458000
H -5.01781600 -3.58222200 0.11842400
C -3.18101600 -5.64413600 -0.09479100
H -3.46493900 -5.25216900 -1.07408800
H -2.16500200 -6.04883100 -0.17475400
H -3.85063900 -6.47531600 0.15903100
H -3.35933300 -1.22174300 -0.62589600
C 4.90958500 -3.40114500 -0.93110600
C 5.67970400 1.37301800 0.38616900
F 4.58766000 -4.11496900 0.17677000
F 6.25271800 -3.47522800 -1.06475400
F 4.36100500 -4.04623800 -1.98201800
F 5.48705300 1.47511800 1.73513200
F 6.99223700 1.11571800 0.20924300
F 5.42636100 2.59262400 -0.12738300
F -0.09960100 4.91054500 -2.58051500
F 0.64751000 5.89913800 -0.79121100
F -1.49611500 5.66913600 -1.09364800
C -1.26256200 0.53975000 2.45410700
C 2.64962200 -0.26006700 -1.00428200
C 3.50681300 0.77534400 -0.59101400
C 3.16195000 -1.56274500 -1.11974600
C 4.83758300 0.50452000 -0.28445400
H 3.12395300 1.78758900 -0.51142600
C 4.49966200 -1.80725100 -0.80784300
H 2.51752500 -2.35939200 -1.46097000
C 5.35221700 -0.78825400 -0.38622000
H 6.39129100 -0.99061100 -0.15900400
C 5.01115300 -3.22261500 -0.86807600
C 5.70797800 1.61638800 0.23471800
F 4.42129800 -3.93747700 -1.84940200
F 6.34594200 -3.26992600 -1.07732700
F 4.77531300 -3.88364400 0.29288000
F 7.02015300 1.37370600 0.03143300
F 5.55110600 1.78382900 1.57849500
F 5.41697600 2.80278000 -0.33526100
F 0.44432800 5.96393500 -0.55406100
F -0.40101300 5.05483000 -2.34141700
F -1.70322300 5.63543300 -0.69655300
C -2.88976100 -4.84989800 0.82828200
C -4.37943200 -4.64657800 0.56548100
H -4.58017200 -4.51743700 -0.50067700
H -4.93848200 -5.52607200 0.90805000
H -4.75112700 -3.77174600 1.10873100
C -2.63966100 -5.23173000 2.29633500
H -3.10445600 -6.20233800 2.50524800
H -1.56852300 -5.32218400 2.51356100
H -3.07067900 -4.49064700 2.97635100
C -2.25649300 -5.86356000 -0.12773800
H -2.38418400 -5.55603300 -1.16917200
H -1.18435400 -5.98870100 0.06650400
H -2.73485200 -6.84117200 0.00831900
C -2.27284200 0.67547400 2.10978700

H	-1.86141900	-0.35398100	2.59203400	N	-1.09036600	1.20314500	2.27572200
N	-1.88375400	1.62057800	2.06657300	H	-0.94302500	2.20436100	2.03549900
H	-1.33136800	2.46696100	1.81446300	H	-2.34996600	-0.40748400	2.19110100

Cycloaddition transition structures mediated by chiral catalysts

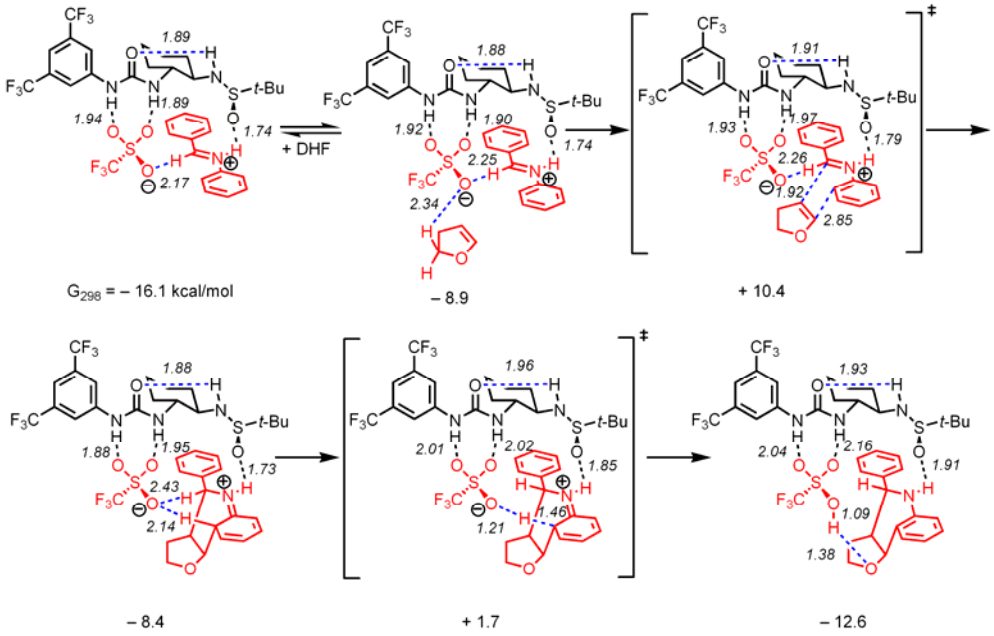
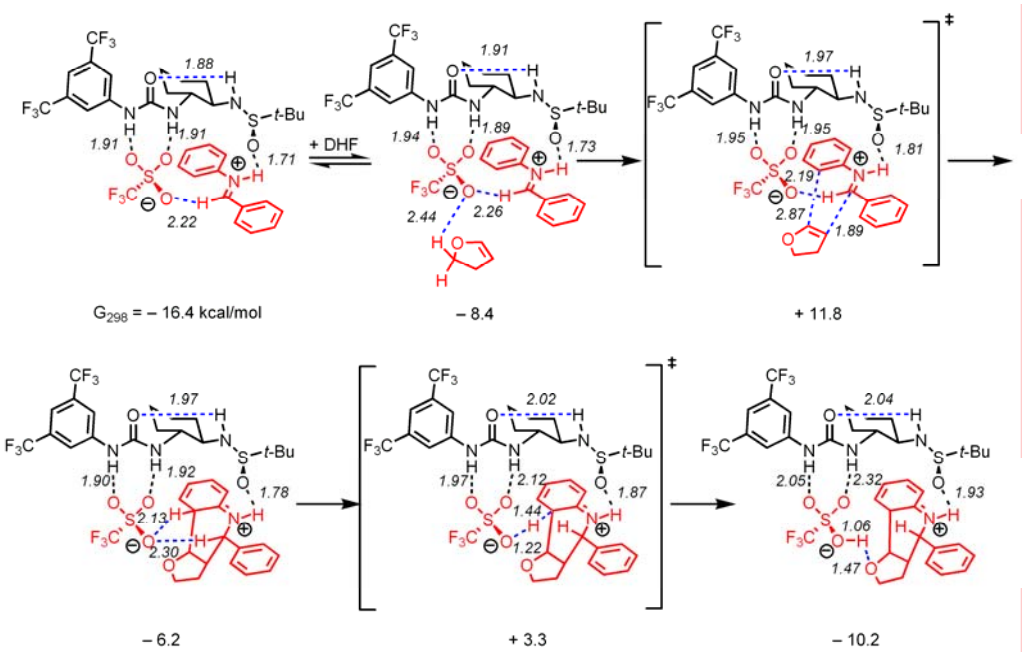
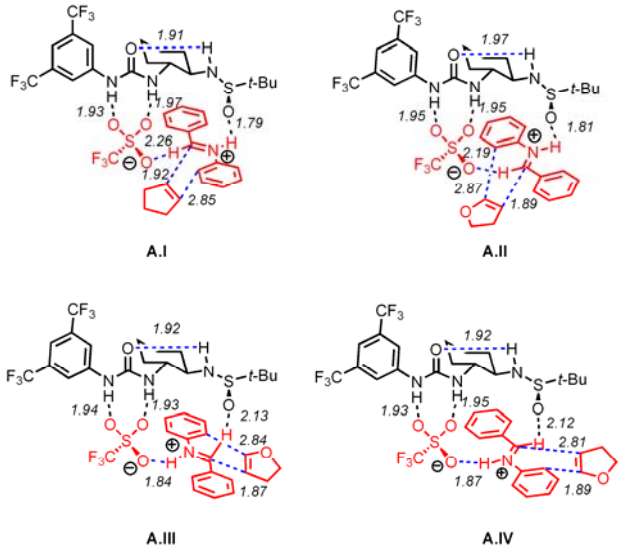


Figure S19:
Povarov reaction coordinate leading to (*R*)-**4a**$_{exo}$ catalyzed by CF_3SO_3H and **1a**.



Povarov reaction coordinate leading to (*S*)-**4a**$_{exo}$ catalyzed by CF_3SO_3H and **1a**.

Table S17. Transition state structures with catalyst **1a**



Absolute energies (Hartrees) of cycloaddition transition structures.

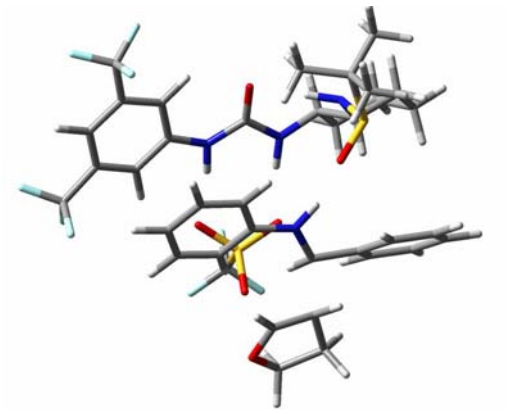
	A.I	A.II	A.III	A.IV
E_{B3LYP}	-3801.077165	-3801.07507	-3801.073169	-3801.071647
E_{MP2}	-3791.359193	-3791.35303	-3791.352477	-3791.353612

E_{M052x}	-3800.947411	-3800.941718	-3800.941344	-3800.940768
$ZPVE_{B3LYP}$	0.785296	0.785761	0.785875	0.786029
$G_{298,\ B3LYP}$	-3800.391411	-3800.389094	-3800.386934	-3800.384121

Relative energies (kcal/mol) of cycloaddition transition structures.

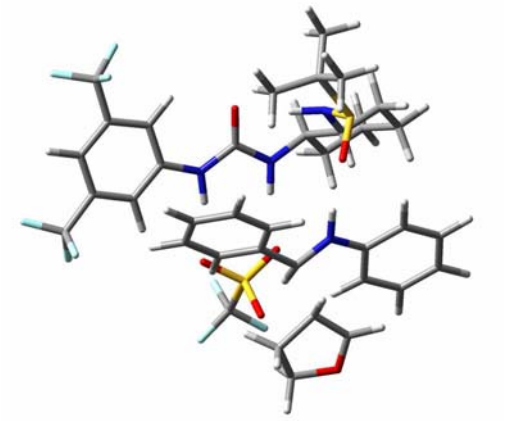
Transition structure	B3LYP/ 6-31G(d) E	B3LYP/ 6-31G(d) E + ZPVE	B3LYP/ 6-31G(d) G_{298}	MP2/ 6-31G(d) E	M05-2X/ 6-31+G(d,p) E
A.I	0.0	0.0	0.0	0.0	0.0
A.II	+ 1.3	1.6	1.5	3.9	3.6
A.III	2.5	2.9	2.8	4.2	3.8
A.IV	3.5	3.9	4.6	3.5	4.2

A.I



N 1.93328900 3.13057800 -0.78701200
S 2.41806000 3.55721300 0.76422000
O 1.81138800 2.66451200 1.86120800
H 0.92424700 2.98433500 -0.92552200
C 1.89955100 1.42856000 -2.57833500
C 2.76275200 0.52048800 -3.47543800
C 3.94631600 1.25957400 -4.11131300
C 4.81059700 1.93826800 -3.04134000

A.II



N -1.83330800 -2.65590500 -1.47805000
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O -2.31304300 -2.65160700 1.16821900
H -0.81449900 -2.53430700 -1.41528500
C -1.46570600 -0.67565500 -2.90105400
C -2.14856800 0.43603400 -3.72096900
C -3.25772100 -0.09417800 -4.63691200
C -4.29963500 -0.88639900 -3.83770700

C	3.95649100	2.87721000	-2.18164200	C	-3.62336500	-2.02197600	-3.06041600
H	4.56372100	3.35165700	-1.40090000	H	-4.35889700	-2.58429600	-2.47179200
H	3.55365400	3.68925000	-2.80286100	H	-3.17207600	-2.73730800	-3.76177600
H	5.63112400	2.49874900	-3.50623300	H	-5.06846800	-1.29625600	-4.50440600
H	5.27297700	1.17244500	-2.40193200	H	-4.81499000	-0.21260500	-3.13800300
H	4.54355100	0.55472800	-4.70274700	H	-3.72946500	0.74446400	-5.16332500
H	3.57405200	2.02002100	-4.81300800	H	-2.82198200	-0.74432000	-5.40946400
H	3.13571200	-0.31789800	-2.87213100	H	-2.56742100	1.17849600	-3.02898300
H	2.11818800	0.08328100	-4.24668300	H	-1.38120900	0.95849300	-4.30352300
H	1.42004700	2.20168800	-3.19239000	H	-0.93761400	-1.36144000	-3.57632500
N	0.83589200	0.61354500	-1.98880300	N	-0.46469000	-0.05218100	-2.02814800
C	-0.41970400	1.10680900	-1.77384900	C	0.73263300	-0.65714400	-1.76793000
N	-1.38298500	0.13938400	-1.56085100	N	1.71391100	0.18968500	-1.28924200
H	-1.09318400	-0.84004000	-1.61206800	H	1.46665000	1.16974700	-1.12892800
O	-0.65744200	2.32666900	-1.76676300	O	0.90533700	-1.87657900	-1.94214200
H	1.01086600	-0.39003000	-1.92138400	H	-0.56161700	0.95530500	-1.88490800
O	-0.81639400	-2.74716300	-1.44016100	H	-2.95618800	-0.84223200	-1.36980800
S	0.57313400	-3.22154800	-1.22178000	O	1.25955800	3.00214600	-0.51830300
O	0.83442100	-3.80156500	0.12077600	S	-0.11888100	3.53920900	-0.62841800
O	1.61211800	-2.25403600	-1.67089400	O	-0.79986500	3.79446600	0.67473100
C	-0.18875000	-0.20212500	2.14376700	O	-0.96702200	2.82679900	-1.61827200
C	-0.86621800	-1.43090800	2.01469000	C	-3.55182600	1.48446600	0.75132000
C	-2.21841500	-1.51339700	2.36890400	C	-4.40603500	0.36164300	0.73365500
C	-2.89834200	-0.39850100	2.84674200	C	-5.70473600	0.48498100	0.22077700
C	-2.22290900	0.82623000	2.96354900	C	-6.15785800	1.70012500	-0.27968100
C	-0.88400800	0.93207400	2.61931600	C	-5.29701900	2.81077100	-0.28035100
H	-0.35050900	1.87397000	2.70177500	C	-4.01245400	2.71507100	0.22826900
H	-2.75261900	1.70526800	3.32017500	H	-3.34178800	3.56814500	0.22586700
H	-3.95309400	-0.47020800	3.09176200	H	-5.63895300	3.76055400	-0.68201000
H	-2.74420900	-2.45349700	2.23523200	H	-7.16399200	1.78906700	-0.67870300
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N	1.16612200	-0.06930200	1.85626400	H	-4.04251300	-0.61524900	1.03382900
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H 1.53871900 0.89223900 1.89018000
C 2.77178900 2.15088700 -1.52079600
C 0.75637600 -4.66672600 -2.37863400
C 1.46982800 5.18366400 0.92229400
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C 2.95625700 -3.36754400 3.16029300
C 0.97677200 -2.43748600 3.93587500
H 2.73483300 -1.24030800 3.92736500
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H 3.64884800 -3.57634800 3.98356200
H 0.24757700 -1.84418800 4.47243100
H 1.43777700 -4.56693700 2.10434300
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C -1.70847800 -5.68860700 -1.42202100
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H -2.76332500 -5.86167500 -1.66628600

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C 1.77866000 5.67064000 2.34590700
H 2.85437500 5.82267000 2.49586200
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F -6.85712200 -1.82158900 -0.18216000
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A.III

H -1.25342300 -5.12929800 -2.24208700
C -0.09494700 -4.61746800 0.23202900
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C 3.59327300 -1.41183800 -1.11944400
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C 4.89640000 -1.65945100 -0.68328800
H 3.03272400 -2.16991900 -1.64603200
C 5.64001300 -0.69034700 -0.01463400
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C 5.47837700 -3.03127900 -0.89858000
C 5.80421000 1.58670400 1.00841800
F 5.08738400 -3.89472900 0.07207700
F 6.83006400 -3.01844300 -0.88684800
F 5.08848000 -3.56995700 -2.07434000
F 7.13508200 1.52646000 0.78290600
F 5.63569800 1.39809300 2.34800800
F 5.40007200 2.84374700 0.74144600
F 0.69998700 5.17128400 -2.53196200
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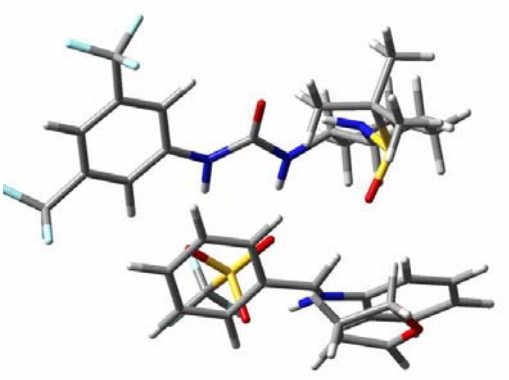
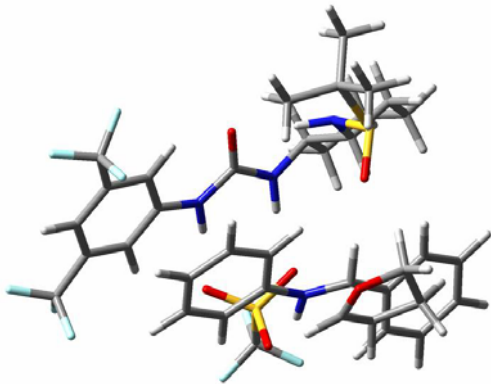
A.IV





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O	1.89145700	2.95552700	1.76946200
C	0.33873600	5.09253300	1.12766600
H	0.26811300	3.04847600	-0.79279600
C	1.31343900	1.81876100	-2.67625400
C	2.23491800	1.10115900	-3.68184300
C	3.22273300	2.05144400	-4.37015500
C	4.04963800	2.82786900	-3.33860600
C	3.12769200	3.58213600	-2.37385200
H	3.71344700	4.12937700	-1.62512600
H	2.54313300	4.33303400	-2.92310900
H	4.72571300	3.53277100	-3.83814000
H	4.68332300	2.12850500	-2.77420500
H	3.87669200	1.47838500	-5.03883000
H	2.67253700	2.76250800	-5.00345300
H	2.79066200	0.31550600	-3.15207900
H	1.60795700	0.59064900	-4.42208800
H	0.65762300	2.51908500	-3.20819400
N	0.45749200	0.81286300	-2.04048400
C	-0.84580400	1.07200900	-1.72599900
N	-1.60882600	-0.05325100	-1.47013200
H	-1.14059700	-0.96203800	-1.48615800
O	-1.29233000	2.22984200	-1.66837000
H	0.80067600	-0.14909600	-2.04333300

N	-2.20752300	-2.23834100	-1.81832500
S	-2.92351200	-3.12743700	-0.58470400
O	-2.50204800	-2.66837900	0.82224900
H	-1.18142600	-2.17222600	-1.80432300
C	-1.84980400	-0.12560600	-3.03813700
C	-2.53308800	1.10759600	-3.66325400
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References:

S1. K. L. Tan, E. N. Jacobsen, *Angew. Chem. Int. Ed.* **46**, 1315 (2007).

S2. Gaussian 03, Revision E.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

S3. B3LYP = Becke-3-Lee-Yang-Parr density functional theory. (a) Becke, A. D. *J. Chem. Phys.* **98**, 1372 (1993). (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **37**,785 (1988).

S4. Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2**, 364 (2006).

S5. Møller, C.; Plesset, M. S. *Phys. Rev.* **46**, 618 (1934).

S6. (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **54**,724 (1971). (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys*. **56,** 2257 (1972). (c) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta.* **28**,213 (1973).

S7. Zuend, S. J.; Jacobsen E. N. *J. Am. Chem. Soc.* **129**,15872 (2007).