Supplementary Methods

General Information:

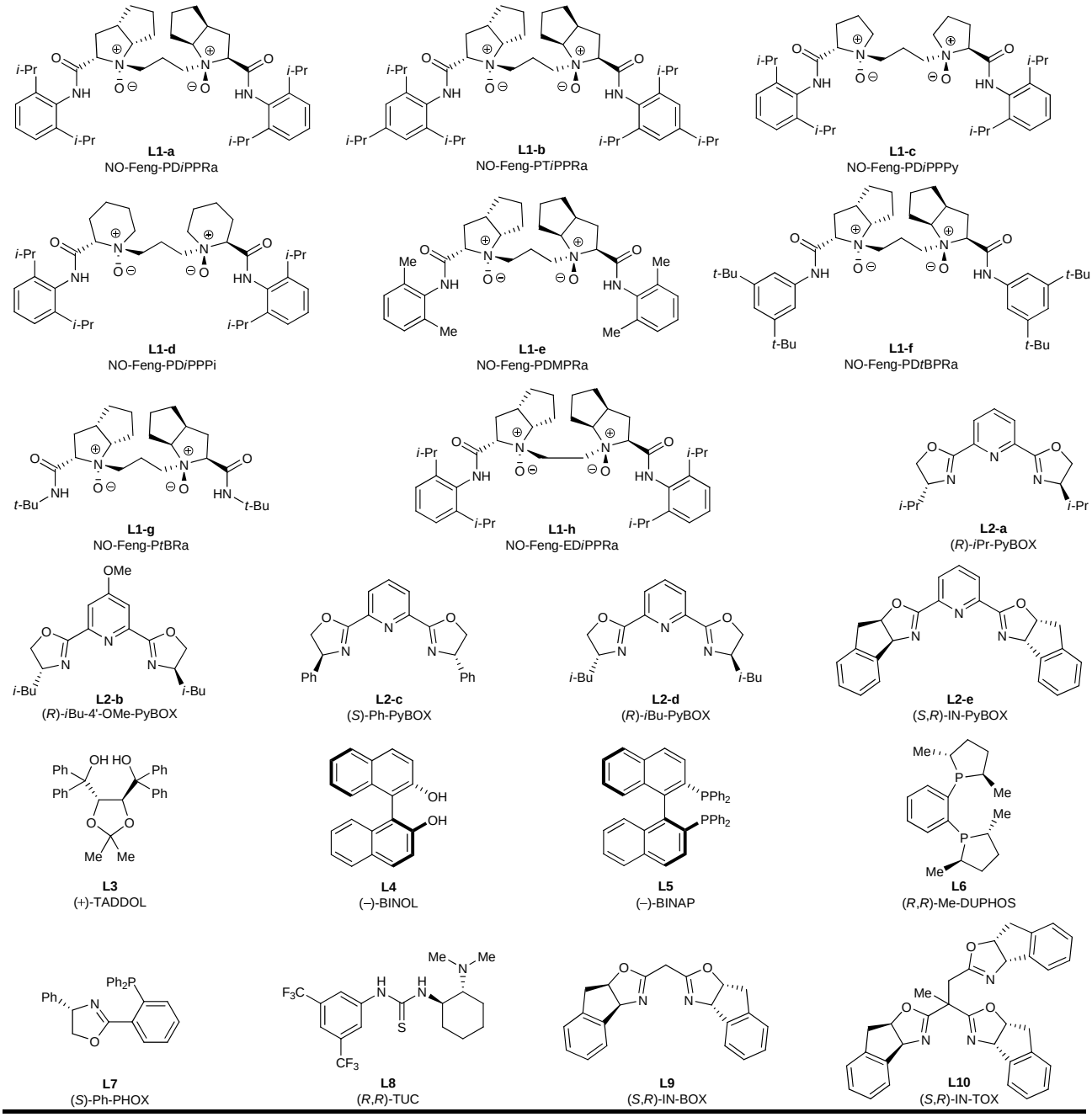
Melting points (mp) were determined on Buchi M-560 melting point apparatus and were uncorrected. Infrared (IR) spectra were measured with Nicolet FT-380 spectrometer using film KBr pellet techniques. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Advance III 400 MHz or Bruker Advance III 500 MHz spectrometer. Chemical shifts are expressed in parts per million (δ) referenced to tetramethyl silane (0.0 ppm), chloroform (7.26 ppm or 77.0 ppm), methanol (3.31 ppm or 49.0 ppm) and dimethyl sulfoxide (2.50 ppm or 39.5 ppm), respectively. The NMR data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt = doublet of triplet, dq = doublet of quartet, td = triplet of doublet, qd = quartet of doublet, ddd = doublet of doublet of doublet, m = multiplet, br = broad), coupling constant (Hz) and integration. High resolution mass spectra (HRMS) were recorded on Bruker 7.0 T FT-MS mass spectrometer. Mass spectra (MS) were measured with Bruker amaZon SL mass spectrometer. Optical rotations were measured using Anton Paar MCP-500 polarimeter. Diastereomeric ratios (dr) were determined by ^{1}H NMR analysis or HPLC analysis of the crude reaction mixtures. Enantiomeric excesses (ee) were determined by chiral HPLC analysis using Shimadzu LC-10ATVP (or Agilent HPLC 1260) with Lux (5 μm, 250×10 mm) Amylose-1 chiral column and ethanol (or isopropyl alcohol) in hexane.

Chemicals were used as received from commercial suppliers unless otherwise stated. The aromatic aldehydes used in the photo reactions were purified by passing through neutral alumina columns. 1,2-Dichloroethane (DCE), dichloromethane (DCM) and MeCN were both distilled over CaH_2 and bubbled with argon for one hour to remove dissolved oxygen. $Ru(bpy)_3(PF_6)_2$ was purchased from Sigma Aldrich. A PHILIPS 65 W (or 45 W) compact fluorescent lamp (CFL) was used as the light source. Flash chromatography was carried out using SiliCycle Silia*Flash* P60 (40−63 μm) silica gel.

Aldonitrones **1a**[1], **1e**[2], **1f**[1], **1g**[1], **1h**[1], **1i**[3], **1j**[3], **1n**[4] and **1o**[1] were prepared by condensation of commercially available *N*-alkyl hydroxylamine hydrochlorides with the corresponding aldehydes according to reported procedure[1]; ketonitrones **1b**[5], **1c**[6] and **1d**[7] were prepared by $Sc(OTf)_3$-promoted condensation of *N*-benzyl hydroxylamine with the corresponding ketones; cyclic nitrone **1k** was purchased from Matrix Scientific, **1l** and **1m** were prepared by MnO_2-oxidation of the corresponding cyclic hydroxylamines[8]. The spectroscopic characterization of above-mentioned nitrones matched those reported in the literatures.

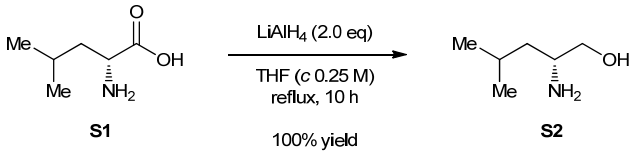
NO-Feng-PD*i*PPRa (**L1-a**), NO-Feng-PD*i*PPPy (**L1-c**), NO-Feng-PD*i*PPPi (**L1-d**), NO-Feng-PDMPRa (**L1-e**), (*R*)-*i*Pr-PyBOX (**L2-a**), (*S*)-Ph-PyBOX (**L2-c**), (*S*,*R*)-IN-PyBOX (**L2-e**) and **L3** to **L10** were commercially available chiral ligands. NO-Feng-PT*i*PPRa (**L1-b**) and other Feng's chiral *N*,*N*′-dioxide ligands **L1-f** to **L1-h** were prepared according to the reported procedure[9] (Supplementary Table 1).

Supplementary Table 1. Chiral ligands for optimization

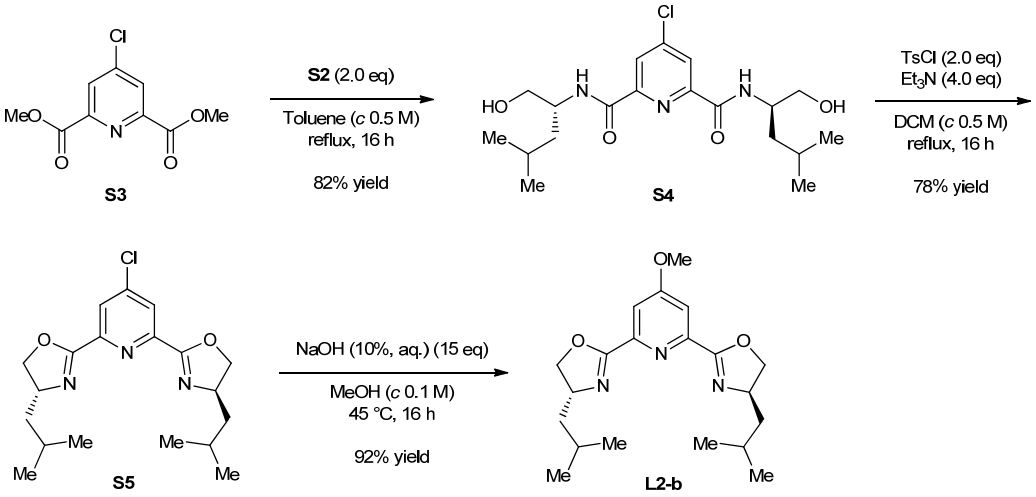


L1-b as a white solid: mp 128.5−129.2 ºC; $[\alpha]_D^{20}$ = −54.5 (*c* 1.0, $CHCl_3$); IR (film) ν_{max}: 3459, 2956, 2876, 1672, 1521 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.13−1.31 (m, 36H), 1.56−1.69 (m, 4H), 1.69−1.84 (m, 4H), 1.95−2.10 (m, 2H), 2.32−2.43 (m, 2H), 2.57−2.76 (m, 6H), 2.76−2.93 (m, 4H), 3.02 (heptet, *J* = 6.9 Hz, 4H), 3.28−3.41 (m, 2H), 3.43−3.56 (m, 2H), 3.90 (dd, *J* = 13.0, 5.2 Hz, 2H), 3.97−4.10 (m, 2H), 7.00 (s, 4H), 12.38−12.49 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.8, 23.2, 23.9, 27.0, 27.6, 28.9, 32.0, 34.1, 34.5, 42.4, 65.8, 80.8, 83.8, 121.1, 128.7, 144.3, 147.7, 166.1; HRMS calcd for $[C_{49}H_{77}N_4O_4]^+$ $(M + H)^+$: 785.5939; found: 785.5947.

(*R*)-*i*Bu-4′-OMe-PyBOX (**L2-b**) was prepared according to following procedures:



To a stirred 0 ºC suspension of $LiAlH_4$ (5.70 g, 150 mmol, 2.0 equiv.) and THF (300 mL) in a 500 mL two-necked round bottom flask was added **S1** (9.84 g, 75.0 mmol, 1.0 equiv.) portion wise under an argon atmosphere. The mixture was stirred at 0 ºC for 0.5 hour, and then was heated to reflux for 10 hours. To quench the reaction, the mixture was cooled to 0 ºC, slowly added water (16 mL) and stirred for 0.5 hour at 0 ºC. Anhydrous Na_2SO_4 was added to absorb the excess water. After filtration, the solvent was evaporated under reduced pressure to afford the desired product **S2** as a colorless oil (8.79 g, 75.0 mmol, quant. yield). The crude product was used for next step without further purification.



A mixture of **S3** (8.92 g, 38.8 mmol, 1.0 equiv.) and **S2** (9.11 g, 77.7 mmol, 2.0 equiv.) in toluene (78 mL) was heated to reflux for 16 hours. After cooling to room temperature, the solvent was evaporated under reduced pressure, and the residue was purified by flash chromatography on silica gel to afford **S4** as a yellow oil (eluent: EtOAc/PE = 3/1; 12.8 g, 32.0 mmol, 82% yield).

To a stirred solution of **S4** (12.8 g, 32.0 mmol, 1.0 equiv.) in CH_2Cl_2 (64 mL) was added Et_3N (17.8 mL, 128 mmol, 4.0 equiv.) and *p*-toluenesulfonyl chloride (12.2 g, 64.0 mmol, 2.0 equiv.). The mixture was heated to reflux for 16 hours. After cooling to room temperature, the mixture was washed with water (50 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford **S5** as a yellow oil (eluent: EtOAc/PE = 1/3 with 1% Et_3N; 9.03 g, 24.8 mmol, 78% yield).

To a stirred solution of **S5** (9.03 g, 24.8 mmol, 1.0 equiv.) in methanol (250 mL) was added aqueous NaOH solution (10% wt, 14.9 g NaOH in 134 mL water; 372 mmol, 15 equiv.). After being stirred at 45 ºC for 16 hours, the mixture was cooled and extracted with CH_2Cl_2 (3×150 mL). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford **L2-b** as a white solid (eluent: EtOAc/PE = 1/1 with 1% Et_3N; 8.23 g, 22.9 mmol, 92% yield). After being recrystallized in EtOAc, the ligand was stored at 4 ºC under an argon atmosphere: mp 108.6−109.2 ºC; $[\alpha]_D^{20}$ = +102.0 (*c* 1.0, $CHCl_3$); IR (film) ν_{max}: 3446, 2959, 2927, 2869, 1643, 1588, 1467, 1399, 1217, 1085, 1047 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.92−1.03 (m, 12H), 1.33−1.44 (m, 2H),

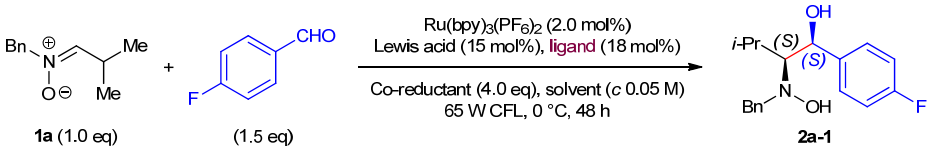
1.67−1.77 (m, 2H), 1.77−1.91 (m, 2H), 3.94 (s, 3H), 4.08 (dd, J = 8.5, 8.2 Hz, 2H), 4.31−4.43 (m, 2H), 4.59 (dd, J = 9.2, 8.5 Hz, 2H), 7.68 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6, 22.8, 25.4, 45.4, 55.8, 65.3, 73.8, 111.6, 148.4, 162.2, 166.6; HRMS calcd for $[C_{20}H_{30}N_3O_3]^+$ $(M + H)^+$: 360.2282; found: 360.2280.

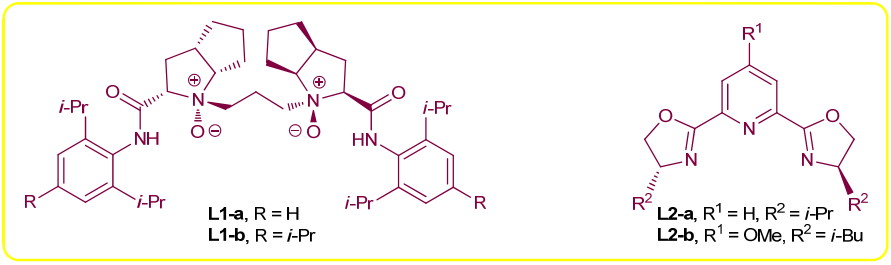
Optimization of the Reaction Conditions:

The optimization of the reaction conditions was conducted with the following procedure using nitrone **1a** and 4-fluorobenzaldehyde as the model reaction: an oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was added nitrone **1a** (53.2 mg, 0.30 mmol, 1.0 equiv.), chiral ligand (18 mol% for *N*,*N*′-dioxides, or 30 mol% for other ligands), $Ru(bpy)_3(PF_6)_2$ (5.2 mg, 0.006 mmol, 2.0 mol%) and Lewis acid (0.045 mmol, 15 mol%) in the glove box. When the tube was sealed and removed from the glove box, solvent (6.0 mL) was added, followed by 4-fluorobenzaldehyde (48 μL, 0.45 mmol, 1.5 equiv.) and the co-reductant (1.2 mmol, 4.0 equiv.). The tube was placed approximately 10 cm away from a 65 W CFL. After being stirred at 0 ºC under an argon atmosphere for 48 to 72 hours, the reaction mixture was filtered through a thin pad of silica gel (100 to 200 mesh), washed with EtOAc and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford **2a-1**. The yields were the combined yields for two diastereo isomers. The dr values were determined by ^{1}H NMR integral area of the crude products [δ_H 5.53 (*anti*), 4.87 (*syn*) in $CDCl_3$], and the ee values were determined by chiral HPLC analysis of the major diastereo isomers [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 85/15 (v/v), 1.0 mL/min, 220 nm; t_1 = 7.9 min, t_2 = 16.7 min].

Our investigation commenced with the general photocatalytic reductive condition (Supplementary Table 2 and Supplementary Table 3), and the desired diastereomeric mixture of vicinal hydroxyamino alcohols was obtained while a catalytic amount of Lewis acid was added (Supplementary Table 2, entries 1 and 2). By using a 45 W CFL in the presence of $La(OTf)_3$ (15 mol%) and *N*,*N*-diisopropylethylamine (DIPEA) (4.0 equiv.), the coupling of nitrone **1a** with 4-fluorobenzaldehyde in CH_3CN at 30 ºC for 48 hours offered (±)-**2a-1** in 92% combined yield (Supplementary Table 2, entry 1). Other photocatalysts, such as $Ir(ppy)_3$ and $Ir(ppy)_2(dtbbpy)(PF_6)$ also were used under this condition, but just the latter can give desired product in moderate yield (56%) (Supplementary Table 2, entries 3 and 4). To get enantioselective results, a series of factors such as chiral ligands, Lewis acids, co-reductants, temperature and solvents were studied. Fortunately, by using a 65 W CFL at 0 ºC with Feng's chiral *N*,*N*′-dioxides (**L1-a** to **L1-h**) and PyBOX ligands (**L2-a** and **L2-b**), mild to good ee were obtained (Supplementary Table 2, entries 5 to 8, and Supplementary Table 3). Noteworthily, complexes of $Sc(OTf)_3$ with Feng's chiral *N*,*N*′-dioxides should be used in CH_2Cl_2 (Supplementary Table 2, entries 5 and 6, and Supplementary Table 3), while complexes of $La(OTf)_3$ with PyBOX ligands should be used in CH_3CN (Supplementary Table 2, entries 7 and 8). When *N*,*N*,*N*′,*N*′-tetraethylethylenediamine (TEEDA) was used as co-reductant instead of DIPEA, a higher stereoselectivity was obtained in a slightly lower yield (Supplementary Table 2, entry 9 *vs.* entry 5, and entry 10 *vs.* entry 6). The complex of $Sc(OTf)_3$ with Feng's chiral *N*,*N*′-dioxide **L1-b** was the best chiral catalyst (Supplementary Table 2, entries 10 to 13). The best enantioselectivity was obtained at 0 ºC (Supplementary Table 2, entries 10, and 14 to 16). Finally, when DCE was used as solvent, the yield of desired product **2a-1** was increased to 93% without loss of ee (Supplementary Table 2, entries 17 and 18).

Supplementary Table 2. Optimization of Lewis acids, ligands, co-reductants, temperature and solvents

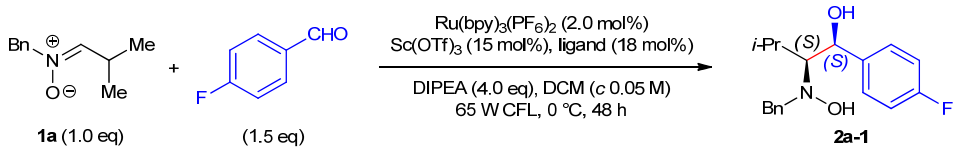


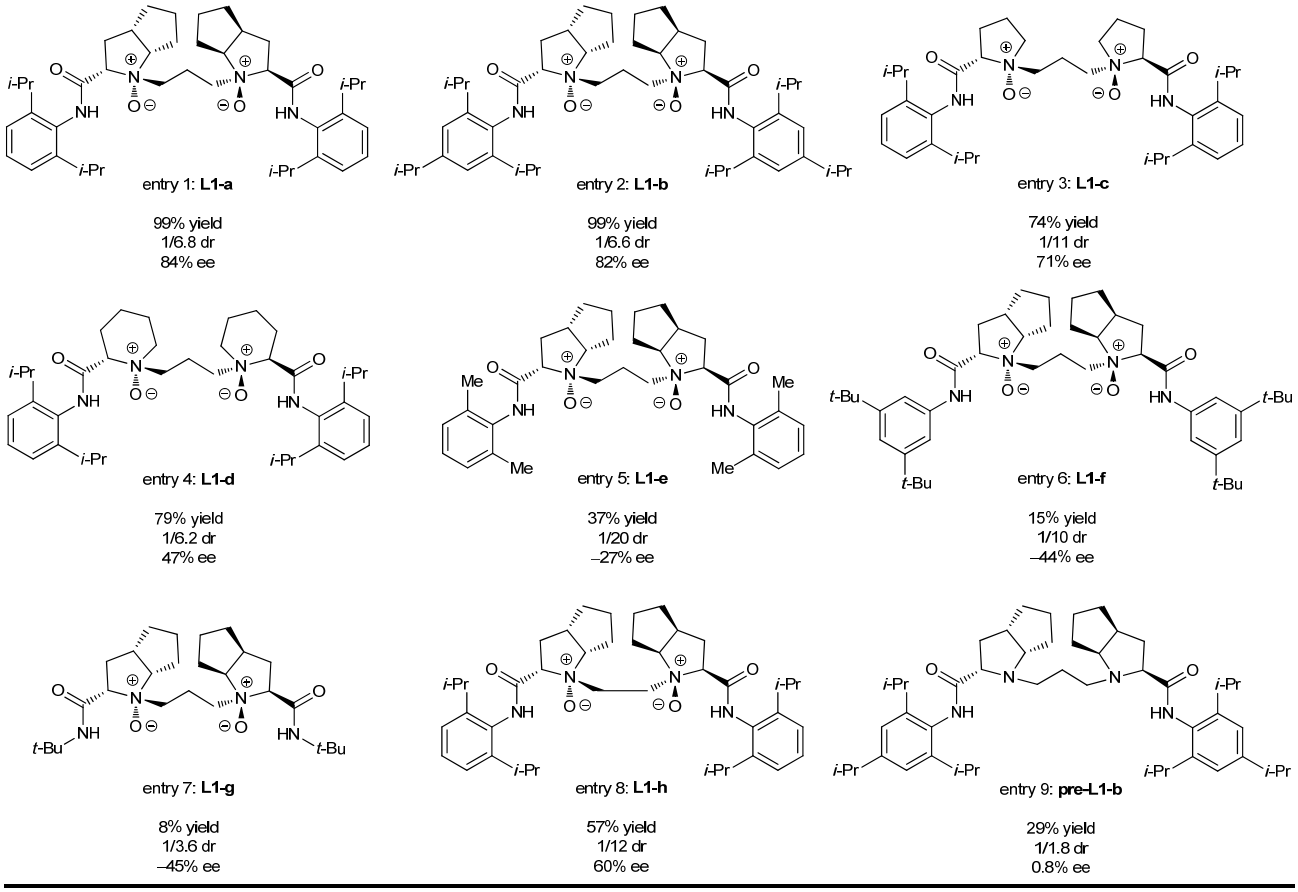


Entry	Lewis acid	Ligand	Co-reductant	Solvent	Yield (%)[h]	dr	ee (%)
1[a]	$La(OTf)_3$	_	iPr_2NEt	CH_3CN	92	1/3.4	_
2[a]	$Sc(OTf)_3$	_	iPr_2NEt	CH_3CN	39	1/2.0	_
3[b]	$La(OTf)_3$	_	iPr_2NEt	CH_3CN	trace (<5%)	_	_
4[c]	$La(OTf)_3$	_	iPr_2NEt	CH_3CN	56	1/3.4	_
5	$Sc(OTf)_3$	**L1-a**	iPr_2NEt	DCM	99	1/6.8	84
6	$Sc(OTf)_3$	**L1-b**	iPr_2NEt	DCM	99	1/6.6	82
7	$La(OTf)_3$	**L2-a**[g]	iPr_2NEt	CH_3CN	73	1/5.7	–16
8	$La(OTf)_3$	**L2-b**[g]	iPr_2NEt	CH_3CN	83	1/6.9	–24
9	$Sc(OTf)_3$	**L1-a**	TEEDA	DCM	81	1/10	89
10	$Sc(OTf)_3$	**L1-b**	TEEDA	DCM	73	1/11	92
11	$La(OTf)_3$	**L1-b**	TEEDA	DCM	57	1/20	12
12	$Eu(OTf)_3$	**L1-b**	TEEDA	DCM	30	1/10	11
13	$Y(OTf)_3$	**L1-b**	TEEDA	DCM	31	1/12	–0.6
14[d]	$Sc(OTf)_3$	**L1-b**	TEEDA	DCM	73	1/11	91
15[e]	$Sc(OTf)_3$	**L1-b**	TEEDA	DCM	71	1/11	91
16[f]	$Sc(OTf)_3$	**L1-b**	TEEDA	DCM	68	1/9.5	88
17	$Sc(OTf)_3$	**L1-b**	TEEDA	CH_3CN	46	1/3.7	92
18	$Sc(OTf)_3$	**L1-b**	TEEDA	DCE	93	1/12	92

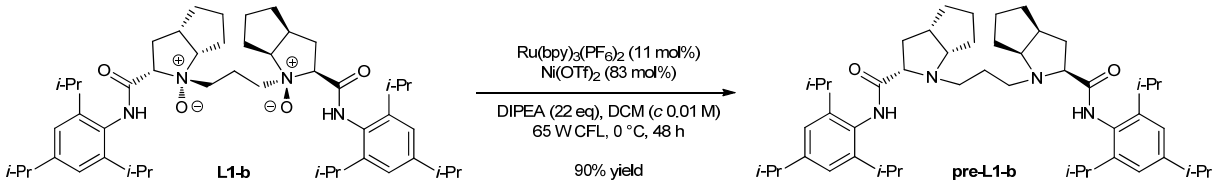
[a] T = 30 ºC, c = 0.1 M, 45 W CFL. [b] $Ir(ppy)_3$ instead of $Ru(bpy)_3(PF_6)_2$. [c] $Ir(ppy)_2(dtbbpy)(PF_6)$ instead of $Ru(bpy)_3(PF_6)_2$. [d] T = 20 ºC. [e] T = –10 ºC. [f] T = –20 ºC. [g] **L2** (30 mol%). [h] Yields were determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

Supplementary Table 3. Optimization of Feng's chiral *N*,*N*′-dioxide ligands





Supplementary Note 1. Photocatalytic reduction of Feng's ligands promoted by Lewis acid



Some Lewis acids can promote the reduction of Feng's ligands under reductive radical conditions. For example, **L1-b** can be reduced to its tertiary diamine precursor under a general photocatalytic reductive condition using $Ni(OTf)_2$ as the Lewis acid. Note that tertiary diamine precursors of Feng's ligands (such as **pre-L1-b**) showed poor catalytic activity in reductive coupling reaction of nitrones with aldehydes (see Supplementary Table 3, entry 9).

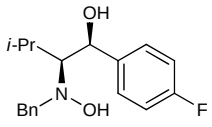
Photocatalytic Enantioselective Reductive Cross-Coupling of Nitrones with Aldehydes:

General procedure: An oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was added nitrone (0.30 mmol, 1.0 equiv.), **L1-b** (42.4 mg, 0.054 mmol, 18 mol%), $Ru(bpy)_3(PF_6)_2$ (5.2 mg, 0.006 mmol, 2.0 mol%) and $Sc(OTf)_3$ (22.1 mg, 0.045 mmol, 15 mol%) in the glove box. When the tube was sealed and removed from the glove box, DCE (or DCM) (6.0 mL) was added, followed by the aldehyde (0.45 mmol, 1.5 equiv.) and TEEDA (0.26 mL, 1.2 mmol, 4.0 equiv.). The tube was placed approximately 10 cm away from a 65 W CFL. After being stirred at 0 ºC under an argon atmosphere for 48 hours, the reaction mixture was filtered through a thin pad of silica gel (100 to 200 mesh), washed with EtOAc and concentrated under reduced pressure. The residue was purified by flash chromatography to afford desired vicinal hydroxyamino alcohols **2a** to **2j**. The yields were the combined yields of two diastereo isomers. The dr values were determined by ^{1}H NMR integral area or chiral HPLC analysis of the crude products, and the ee values were determined by chiral HPLC analysis. Unless otherwise noted, the characterization data and ee values are reported for the major diastereomer.

Modified method 1: An oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was added nitrone (0.30 mmol, 1.0 equiv.), **L1-a** (37.9 mg, 0.054 mmol, 18 mol%), $Ru(bpy)_3(PF_6)_2$ (5.2 mg, 0.006 mmol, 2.0 mol%) and $Sc(OTf)_3$ (22.1 mg, 0.045 mmol, 15 mol%) in the glove box. When the tube was sealed and removed from the glove box, DCM (6.0 mL) was added, followed by the aldehyde (0.45 mmol, 1.5 equiv.) and DIPEA (0.21 mL, 1.2 mmol, 4.0 equiv.). The tube was placed approximately 10 cm away from a 65 W CFL, and the reaction mixture was stirred at –5 ºC under an argon atmosphere for 48 hours to afford desired products **2k** to **2m**.

Modified method 2: An oven-dried 25 mL Schlenk tube equipped with a magnetic stir bar was added nitrone (0.30 mmol, 1.0 equiv.), **L2-b** (32.4 mg, 0.09 mmol, 30 mol%), $Ru(bpy)_3(PF_6)_2$ (5.2 mg, 0.006 mmol, 2.0 mol%) and $La(OTf)_3$ (26.4 mg, 0.045 mmol, 15 mol%) in the glove box. When the tube was sealed and removed from the glove box, CH_3CN (6.0 mL) was added, followed by the aldehyde (0.45 mmol, 1.5 equiv.) and TEEDA (0.26 mL, 1.2 mmol, 4.0 equiv.). The tube was placed approximately 10 cm away from a 65 W CFL, and the reaction mixture was stirred at –10 ºC under an argon atmosphere for 72 hours to afford desired products **2k** to **2m**.

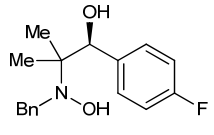
(1*S*,2*S*)-2-(Benzyl(hydroxy)amino)-1-(4-fluorophenyl)-3-methylbutan-1-ol (**2a-1**)



Following the **general procedure**, the asymmetric reductive coupling of nitrone **1a** (53.2 mg, 0.30 mmol, 1.0 equiv.) with 4-fluorobenzaldehyde (48 µL, 0.45 mmol, 1.5 equiv.) gave the desired product **2a-1** as the major diastereomer [dr = 1/12 (*anti*/*syn*), determined by ^{1}H NMR integral area of the crude product, δ_H 5.53 (*anti*), 4.87 (*syn*)] with 92% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 85/15 (v/v), 1.0 mL/min, 220 nm; t_1 = 7.9 min, t_2 = 16.7 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 1/5; 84.8 mg, 93% combined yield).

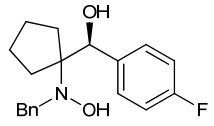
Major diastereomer (*syn*, more polar) as a white solid: mp 113.5−114.1 ºC; $[\alpha]_D^{20}$ = +64.5 (*c* 1.0, $CHCl_3$, 92% ee); IR (film) ν_{max}: 3366, 2949, 1505, 1217 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79 (d, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 7.0 Hz, 3H), 1.98−2.08 (m, 1H), 2.75 (dd, *J* = 8.2, 2.9 Hz, 1H), 3.98 (d, *J* = 13.3 Hz, 1H), 4.03−4.48 (br, 1H), 4.07 (d, *J* = 13.3 Hz, 1H), 4.87 (d, *J* = 8.2 Hz, 1H), 5.01−5.35 (br, 1H), 6.97−7.07 (m, 2H), 7.22−7.39 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 20.8, 27.0, 63.2, 72.3, 74.9, 115.1 (d, *J* = 21.3 Hz), 127.4, 128.4, 129.1 (d, *J* = 8.1 Hz), 129.2, 138.1, 138.3 (d, *J* = 3.0 Hz), 162.3 (d, *J* = 245.8 Hz); HRMS calcd for $[C_{18}H_{22}FNNaO_2]^+$ $(M + Na)^+$: 326.1527; found: 326.1528.

(*S*)-2-(Benzyl(hydroxy)amino)-1-(4-fluorophenyl)-2-methylpropan-1-ol (2b-1)



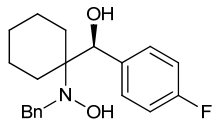
Following the **general procedure**, the asymmetric reductive coupling of nitrone **1b** (49.0 mg, 0.30 mmol, 1.0 equiv.) with 4-fluorobenzaldehyde (48 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2b-1** as a white solid (chromatography on silica gel, eluent: EtOAc/PE = 1/6; 62.4 mg, 72% yield) with 97% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 60/40 (v/v), 1.0 mL/min, 220 nm; t_1 = 17.4 min, t_2 = 26.9 min]: mp 148.5−149.2 ºC; $[\alpha]_D^{20}$ = –22.3 (*c* 1.0, $CHCl_3$, 97% ee); IR (film) ν_{max}: 3356, 1505, 1361, 1223, 1041 cm^{-1}; ^1H NMR (500 MHz, MeOD) δ 1.01 (s, 3H), 1.08 (s, 3H), 3.85 (d, *J* = 13.5 Hz, 1H), 3.99 (d, *J* = 13.5 Hz, 1H), 4.99 (s, 1H), 7.01−7.08 (m, 2H), 7.20−7.25 (m, 1H), 7.27−7.33 (m, 2H), 7.34−7.40 (m, 2H), 7.40−7.47 (m, 2H); ^{13}C NMR (125 MHz, MeOD) δ 18.4, 19.0, 57.4, 65.8, 77.8, 115.1 (d, *J* = 21.2 Hz), 127.8, 129.1, 130.3, 131.0 (d, *J* = 8.0 Hz), 138.3 (d, *J* = 2.6 Hz), 140.9, 163.6 (d, *J* = 243.7 Hz); HRMS calcd for $[C_{17}H_{20}FNNaO_2]^+$ $(M + Na)^+$: 312.1370; found: 312.1370.

(*S*)-(1-(Benzyl(hydroxy)amino)cyclopentyl)(4-fluorophenyl)methanol (2c)



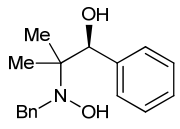
Following the **general procedure**, the asymmetric reductive coupling of nitrone **1c** (56.8 mg, 0.30 mmol, 1.0 equiv.) with 4-fluorobenzaldehyde (48 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2c** as a white solid (chromatography on silica gel, eluent: EtOAc/PE = 1/6; 47.4 mg, 50% yield) with 94% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 60/40 (v/v), 1.0 mL/min, 220 nm; t_1 = 14.8 min, t_2 = 18.4 min]: mp 136.9−137.4 ºC; $[\alpha]_D^{20}$ = –21.5 (*c* 1.0, $CHCl_3$, 94% ee); IR (film) ν_{max}: 3388, 2943, 1601, 1511, 1226 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.61−0.79 (m, 1H), 1.16−1.27 (m, 1H), 1.37−1.56 (m, 2H), 1.56−1.76 (m, 2H), 1.76−1.98 (m, 2H), 3.85 (d, *J* = 13.4 Hz, 1H), 3.95 (d, *J* = 13.4 Hz, 1H), 4.10−4.66 (br, 1H), 5.10 (s, 1H), 5.19−5.66 (br, 1H), 6.94−7.05 (m, 2H), 7.21−7.43 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.2, 25.6, 29.4, 30.0, 57.0, 75.8, 77.1, 114.5 (d, *J* = 21.2 Hz), 127.2, 128.3, 129.2, 129.6 (d, *J* = 7.9 Hz), 136.1 (d, *J* = 2.8 Hz), 138.6, 162.1 (d, *J* = 245.5 Hz); HRMS calcd for $[C_{19}H_{22}FNNaO_2]^+$ $(M + Na)^+$: 338.1527; found: 338.1529.

(*S*)-(1-(Benzyl(hydroxy)amino)cyclohexyl)(4-fluorophenyl)methanol (2d)



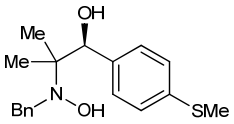
Following the **general procedure**, the asymmetric reductive coupling of nitrone **1d** (61.0 mg, 0.30 mmol, 1.0 equiv.) with 4-fluorobenzaldehyde (48 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2d** as a white solid (chromatography on silica gel, eluent: EtOAc/PE = 1/6; 64.0 mg, 65% yield) with 92% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 60/40 (v/v), 1.0 mL/min, 225 nm; t_1 = 4.4 min, t_2 = 5.5 min]: mp 147.4−148.2 ºC; $[\alpha]_D^{20}$ = –37.9 (*c* 1.0, $CHCl_3$, 92% ee); IR (film) ν_{max}: 3356, 2844, 1604, 1450, 1223, 1037 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.83−1.08 (m, 2H), 1.08−1.21 (m, 1H), 1.29−1.39 (m, 1H), 1.42−1.51 (m, 1H), 1.56−1.78 (m, 4H), 2.27−2.37 (m, 1H), 4.05 (d, *J* = 13.7 Hz, 1H), 4.20 (d, *J* = 13.7 Hz, 1H), 4.36−4.58 (br, 1H), 5.13 (s, 1H), 5.18−5.28 (br, 1H), 6.95−7.05 (m, 2H), 7.25−7.39 (m, 5H), 7.39−7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8 (2C), 26.1, 26.3, 32.6, 54.9, 64.6, 78.2, 114.4 (d, *J* = 21.2 Hz), 127.0, 128.4, 128.8, 129.6 (d, *J* = 8.0 Hz), 137.0 (d, *J* = 2.9 Hz), 139.3, 162.1 (d, *J* = 245.4 Hz); HRMS calcd for $[C_{20}H_{24}FNNaO_2]^+$ $(M + Na)^+$: 352.1683; found: 352.1684.

(*S*)-2-(Benzyl(hydroxy)amino)-2-methyl-1-phenylpropan-1-ol (2b-2)



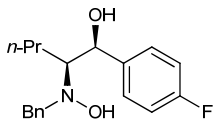
Following the **general procedure**, the asymmetric reductive coupling of nitrone **1b** (49.0 mg, 0.30 mmol, 1.0 equiv.) with benzaldehyde (46 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2b-2** as a white solid (chromatography on silica gel, eluent: EtOAc/PE = 1/6; 66.7 mg, 82% yield) with 99% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 60/40 (v/v), 1.0 mL/min, 220 nm; t_1 = 11.6 min, t_2 = 15.3 min]: mp 147.4−148.0 ºC; $[\alpha]_D^{20}$ = –24.1 (*c* 1.0, $CHCl_3$, 99% ee); IR (film) ν_{max}: 3359, 1457, 1358, 1037 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.96 (s, 3H), 1.01 (s, 3H), 3.76 (d, *J* = 13.1 Hz, 1H), 3.93 (d, *J* = 13.1 Hz, 1H), 4.03−4.42 (br, 1H), 4.83 (s, 1H), 5.30−5.49 (br, 1H), 7.20−7.38 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.3, 18.5, 56.1, 65.2, 76.8, 127.2, 127.3, 127.5, 128.1, 128.3, 129.4, 138.5, 140.0; HRMS calcd for $[C_{17}H_{21}NNaO_2]^+$ $(M + Na)^+$: 294.1465; found: 294.1466.

(*S*)-2-(Benzyl(hydroxy)amino)-2-methyl-1-(4-(methylthio)phenyl)propan-1-ol (2b-3)



Following the **general procedure**, the asymmetric reductive coupling of nitrone **1b** (49.0 mg, 0.30 mmol, 1.0 equiv.) with 4-(methylthio)benzaldehyde (60 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2b-3** as a white solid (chromatography on silica gel, eluent: EtOAc/PE = 1/5; 65.0 mg, 68% yield) with 94% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/*i*-PrOH = 85/15 (v/v), 1.0 mL/min, 259 nm; t_1 = 9.9 min, t_2 = 13.0 min]: mp 160.2−160.8 ºC; $[\alpha]_D^{20}$ = –25.4 (*c* 0.5, $CHCl_3$, 94% ee); IR (film) ν_{max}: 3347, 2917, 1434, 1370, 1041 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.00 (s, 3H), 1.05 (s, 3H), 2.49 (s, 3H), 3.80 (d, *J* = 13.1 Hz, 1H), 3.97 (d, *J* = 13.1 Hz, 1H), 4.06−4.21 (br, 1H), 4.78−4.86 (br, 1H), 4.87 (s, 1H), 7.19−7.25 (m, 2H), 7.26−7.41 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9, 16.3, 18.6, 56.2, 65.3, 76.6, 125.9, 127.4, 128.4, 128.6, 129.4, 137.1, 137.3, 138.4; HRMS calcd for $[C_{18}H_{23}NNaO_2S]^+$ $(M + Na)^+$: 340.1342; found: 340.1343.

(1*S*,2*S*)-2-(Benzyl(hydroxy)amino)-1-(4-fluorophenyl)pentan-1-ol (2e)



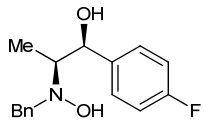
Following the **general procedure**, the asymmetric reductive coupling of nitrone **1e** (53.2 mg, 0.30 mmol, 1.0 equiv.) with 4-fluorobenzaldehyde (48 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2e** as the minor diastereomer [dr = 1.1/1 (*anti*/*syn*), determined by ^1H NMR integral area of crude product, δ_H 5.44 (*anti*), 4.43 (*syn*)]; major diastereomer (*anti*): 82% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 265 nm; t_1 = 5.7 min, t_2 = 6.0 min]; minor diastereomer (*syn*): 83% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 60/40 (v/v), 1.0 mL/min, 265 nm; t_1 = 5.1 min, t_2 = 12.7 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 1/5; 62.8 mg, 69% combined yield).

Major diastereomer (*anti*, less polar) as a white solid: mp 117.4−118.2 ºC; $[\alpha]_D^{20}$ = +3.5 (*c* 1.0, $CHCl_3$, 82% ee); IR (film) ν_{max}: 3366, 2956, 1508, 1220 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.69 (t, *J* = 7.0 Hz, 3H), 0.95−1.08 (m, 1H), 1.28−1.45 (m, 2H), 1.57−1.70 (m, 1H), 2.65−2.76 (m, 1H), 3.54−3.95 (br, 1H), 4.00 (d, *J* = 13.0 Hz, 1H), 4.07 (d, *J* = 13.0 Hz, 1H), 5.44 (s, 1H), 5.64−6.24 (br, 1H), 6.94−7.05 (m, 2H), 7.20−7.40 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 20.4, 26.0, 61.6, 70.2, 71.3, 114.9 (d, *J* = 21.3 Hz), 127.2 (d, *J* = 7.9 Hz), 127.6, 128.5, 129.4, 137.4, 137.8 (d, *J* = 3.0 Hz), 161.7 (d, *J* = 244.6 Hz); HRMS calcd for $[C_{18}H_{22}FNNaO_2]^+$ $(M + Na)^+$: 326.1527; found: 326.1525.

Minor diastereomer (**2e**, *syn*, more polar) as a white solid: mp 113.5−114.1 ºC; $[\alpha]_D^{20}$ = +23.0 (*c* 1.0, $CHCl_3$, 83% ee); IR (film) ν_{max}: 3366, 2950, 1505, 1217 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.68 (t, *J* = 7.0 Hz, 3H), 0.72−0.85

(m, 1H), 0.95−1.19 (m, 2H), 1.68−1.81 (m, 1H), 2.57−2.69 (m, 1H), 3.81 (d, J = 13.2 Hz, 1H), 4.05 (d, J = 13.2 Hz, 1H), 4.43 (d, J = 9.1 Hz, 1H), 5.03−6.09 (br, 1H), 6.93−7.06 (m, 2H), 7.21−7.40 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 21.4, 26.6, 61.0, 71.5, 74.6, 115.1 (d, J = 21.4 Hz), 127.4, 128.4, 129.1 (d, J = 8.1 Hz), 129.2, 136.9 (d, J = 2.8 Hz), 137.6, 162.4 (d, J = 245.9 Hz); HRMS calcd for $[C_{18}H_{22}FNNaO_2]^+$ $(M + Na)^+$: 326.1527; found: 326.1527.

(1*S*,2*S*)-2-(Benzyl(hydroxy)amino)-1-(4-fluorophenyl)propan-1-ol (2f-1)

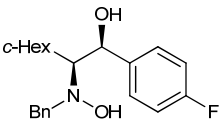


Following the **general procedure**, the asymmetric reductive coupling of nitrone **1f** (44.8 mg, 0.30 mmol, 1.0 equiv.) with 4-fluorobenzaldehyde (48 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2f-1** as the minor diastereomer [dr = 4.1/1 (*anti*/*syn*), determined by chiral HPLC analysis] of an inseparable diastereomeric mixture; major diastereomer (*anti*): 92% ee; minor diastereomer (*syn*): 42% ee [Lux® Amylose-1 column, Agilent HPLC, 30 ºC, hexane/EtOH = 90/10 (v/v), 1.0 mL/min, 220 nm; *anti*: t_1 = 13.9 min, t_2 = 17.8 min; *syn*: t_1 = 14.5 min, t_2 = 26.1 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 1/6; 59.7 mg, 72 % combined yield): IR (film) ν_{max}: 3426, 2913, 1604, 1510, 1222 cm^{-1}; HRMS calcd for $[C_{16}H_{18}FNNaO_2]^+$ $(M + Na)^+$: 298.1214; found: 298.1218.

Major diastereomer (*anti*, data read from spectrum of the diastereomeric mixture): ^{1}H NMR (500 MHz, MeOD) δ 1.12 (d, J = 6.6 Hz, 3H), 2.95 (qd, J = 6.6, 4.7 Hz, 1H), 3.81 (d, J = 13.4 Hz, 1H), 4.01 (d, J = 13.4 Hz, 1H), 5.09 (d, J = 4.7 Hz, 1H), 6.99−7.08 (m, 2H), 7.17−7.44 (m, 7H); ^{13}C NMR (125 MHz, MeOD) δ 8.8, 62.0, 67.6, 74.8, 115.4 (d, J = 21.5 Hz), 127.9, 129.0, 129.1 (d, J = 8.1 Hz), 130.2, 139.7, 140.5 (d, J = 3.0 Hz), 163.1 (d, J = 243.1 Hz).

Minor diastereomer (**2f-1**, *syn*, data read from spectrum of the diastereomeric mixture): ^{1}H NMR (500 MHz, MeOD) δ 0.88 (d, J = 6.5 Hz, 3H), 2.88 (dq, J = 9.0, 6.5 Hz, 1H), 3.82 (d, J = 13.3 Hz, 1H), 4.04 (d, J = 13.3 Hz, 1H), 4.52 (d, J = 9.0 Hz, 1H), 6.99−7.08 (m, 2H), 7.17−7.44 (m, 7H); ^{13}C NMR (125 MHz, MeOD) δ 7.9, 61.9, 67.8, 76.0, 115.9 (d, J = 21.3 Hz), 128.2, 129.2, 130.30, 130.32 (d, J = 8.1 Hz), 138.7 (d, J = 3.3 Hz), 139.5, 163.7 (d, J = 244.6 Hz).

(1*S*,2*S*)-2-(Benzyl(hydroxy)amino)-2-cyclohexyl-1-(4-fluorophenyl)ethanol (2g)



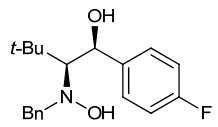
Following the **general procedure**, the asymmetric reductive coupling of nitrone **1g** (65.2 mg, 0.30 mmol, 1.0 equiv.) with 4-fluorobenzaldehyde (48 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2g** as the major diastereomer [dr = 1/3.0 (*anti*/*syn*), determined by ^{1}H NMR integral area of crude product, δ_H 5.53 (*anti*), 4.88 (*syn*)]; major diastereomer (*syn*): 74% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 225 nm; t_1 = 6.7 min, t_2 = 13.3 min]; minor diastereomer (*anti*): 89% ee [Lux® Amylose-1 column, Agilent HPLC, 30 ºC, hexane/EtOH = 85/15 (v/v), 1.0 mL/min, 225 nm; t_1 = 6.7 min, t_2 = 7.6 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 1/5; 89.6 mg, 87% combined yield).

Major diastereomer (**2g**, *syn*, more polar) as a white solid: mp 136.6−137.2 ºC; $[\alpha]_D^{20}$ = +42.7 (*c* 1.0, $CHCl_3$, 74% ee); IR (film) ν_{max}: 3379, 2927, 2853, 1515, 1441, 1220 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76−0.89 (m, 1H), 0.92−1.05 (m, 1H), 1.07−1.21 (m, 2H), 1.25−1.35 (m, 1H), 1.53−1.81 (m, 6H), 2.71 (dd, J = 8.2, 2.6 Hz, 1H), 3.95 (d, J = 13.3 Hz, 1H), 4.07 (d, J = 13.3 Hz, 1H), 4.13−4.71 (br, 1H), 4.88 (d, J = 8.2 Hz, 1H), 4.95−5.32 (br, 1H), 6.95−7.12 (m, 2H), 7.21−7.41 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.4, 26.8, 27.0, 31.1, 31.6, 37.5, 62.9, 71.9, 75.1, 115.1 (d, J = 21.4 Hz), 127.4, 128.4, 129.1 (d, J = 8.2 Hz), 129.2, 138.1, 138.4 (d, J = 3.0 Hz), 162.3 (d, J =

245.9 Hz); HRMS calcd for $[C_{21}H_{26}FNNaO_2]^+$ $(M + Na)^+$: 366.1840; found: 366.1839.

Minor diastereomer (*anti*, less polar) as a white solid: mp 140.1−140.6 ºC; $[\alpha]_D^{25}$ = +5.0 (*c* 1.0, $CHCl_3$, 89% ee); IR (film) ν_{max}: 3379, 2930, 2853, 1604, 1508, 1457, 1217 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.75−0.91 (m, 1H), 1.00−1.24 (m, 4H), 1.34−1.44 (m, 1H), 1.49−1.62 (m, 2H), 1.66−1.77 (m, 1H), 1.77−1.90 (m, 1H), 2.10−2.23 (m, 1H), 2.66 (dd, *J* = 6.4, 1.7 Hz, 1H), 3.36−3.56 (br, 1H), 3.93 (d, *J* = 13.1 Hz, 1H), 4.18 (d, *J* = 13.1 Hz, 1H), 4.90−5.09 (br, 1H), 5.48−5.58 (m, 1H), 6.96−7.06 (m, 2H), 7.25−7.40 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.40, 26.43, 26.6, 31.2, 31.9, 36.9, 62.6, 70.5, 74.6, 114.8 (d, *J* = 21.3 Hz), 127.0 (d, *J* = 7.9 Hz), 127.5, 128.4, 129.2, 137.9, 139.1 (d, *J* = 3.0 Hz), 161.5 (d, *J* = 244.5 Hz); HRMS calcd for $[C_{21}H_{26}FNNaO_2]^+$ $(M + Na)^+$: 366.1840; found: 366.1840.

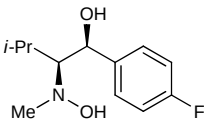
(1*S*,2*S*)-2-(Benzyl(hydroxy)amino)-1-(4-fluorophenyl)-3,3-dimethylbutan-1-ol (2h)



Following the **general procedure**, the asymmetric reductive coupling of nitrone **1h** (57.4 mg, 0.30 mmol, 1.0 equiv.) with 4-fluorobenzaldehyde (48 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2h** as the major diastereomer [dr = 1/5.0 (*anti*/*syn*), determined by ^1H NMR integral area of crude product, δ_H 5.57 (*anti*), 5.19 (*syn*)] with 38% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 230 nm; t_1 = 4.2 min, t_2 = 4.9 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 1/6; 24.9 mg, 26% combined yield).

Major diastereomer (*syn*, more polar) as a white solid: mp 126.1−127.0 ºC; $[\alpha]_D^{20}$ = +93.8 (*c* 0.5, $CHCl_3$, 38% ee); IR (film) ν_{max}: 3369, 2953, 1518, 1226 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.09 (s, 9H), 2.73 (d, *J* = 4.0 Hz, 1H), 3.61 (d, *J* = 13.5 Hz, 1H), 3.74 (d, *J* = 13.5 Hz, 1H), 4.45−4.76 (br, 1H), 5.03−5.29 (br, 1H), 5.19 (d, *J* = 4.0 Hz, 1H), 7.00−7.09 (m, 2H), 7.10−7.17 (m, 2H), 7.17−7.30 (m, 3H), 7.33−7.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.9, 36.5, 65.2, 74.6, 76.8, 114.9 (d, *J* = 21.3 Hz), 127.2, 128.18 (d, *J* = 7.8 Hz), 128.19, 128.9, 138.7, 140.6 (d, *J* = 3.0 Hz), 161.9 (d, *J* = 245.0 Hz); HRMS calcd for $[C_{19}H_{24}FNNaO_2]^+$ $(M + Na)^+$: 340.1683; found: 340.1683.

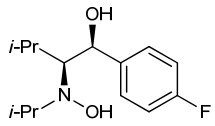
(1*S*,2*S*)-1-(4-Fluorophenyl)-2-(hydroxy(methyl)amino)-3-methylbutan-1-ol (**2i**)



Following the **general procedure**, the asymmetric reductive coupling of nitrone **1i** (30.3 mg, 0.30 mmol, 1.0 equiv.) with 4-fluorobenzaldehyde (48 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2i** as the major diastereomer [dr = 1/5.5 (*anti*/*syn*), determined by ^1H NMR integral area of crude product, δ_H 5.48 (*anti*), 4.79 (*syn*)] with 81% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 90/10 (v/v), 1.0 mL/min, 220 nm; t_1 = 6.7 min, t_2 = 8.2 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 1/2; 28.0 mg, 41% combined yield).

Major diastereomer (*syn*, more polar) as a colorless oil: $[\alpha]_D^{20}$ = +56.8 (*c* 0.5, $CHCl_3$, 81% ee); IR (film) ν_{max}: 3375, 2966, 2917, 1611, 1505, 1217 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.72 (d, *J* = 7.2 Hz, 3H), 0.96 (d, *J* = 7.0 Hz, 3H), 1.90−2.03 (m, 1H), 2.61 (dd, *J* = 8.4, 2.5 Hz, 1H), 2.78 (s, 3H), 4.79 (d, *J* = 8.4 Hz, 1H), 4.93−5.78 (br, 2H), 6.98−7.09 (m, 2H), 7.29−7.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.0, 21.1, 26.1, 46.3, 71.8, 76.2, 115.1 (d, *J* = 21.4 Hz), 129.1 (d, *J* = 8.1 Hz), 138.2 (d, *J* = 2.8 Hz), 162.3 (d, *J* = 245.7 Hz); HRMS calcd for $[C_{12}H_{18}FNNaO_2]^+$ $(M + Na)^+$: 250.1214; found: 250.1214.

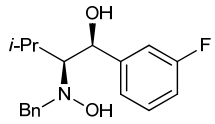
(1*S*,2*S*)-1-(4-Fluorophenyl)-2-(hydroxy(isopropyl)amino)-3-methylbutan-1-ol (2j)



Following the **general procedure**, the asymmetric reductive coupling of nitrone **1j** (38.8 mg, 0.30 mmol, 1.0 equiv.) with 4-fluorobenzaldehyde (48 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2j** as the major diastereomer [dr = 1/8.0 (*anti*/*syn*), determined by ^{1}H NMR integral area of crude product, δ_H 5.40 (*anti*), 4.75 (*syn*)] with 79% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 265 nm; t_1 = 4.4 min, t_2 = 5.2 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 1/3; 64.6 mg, 84% combined yield).

Major diastereomer (*syn*, more polar) as a white solid: mp 70.5−71.3 ºC; $[\alpha]_D^{20}$ = +39.4 (*c* 1.0, $CHCl_3$, 79% ee); IR (film) ν_{max}: 3372, 2962, 1614, 1505, 1210 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.62 (d, *J* = 7.2 Hz, 3H), 0.99 (d, *J* = 7.0 Hz, 3H), 1.05 (d, *J* = 6.2 Hz, 3H), 1.11 (d, *J* = 6.0 Hz, 3H), 1.99−2.13 (m, 1H), 2.78−2.92 (m, 1H), 3.12−3.27 (m, 1H), 4.75 (d, *J* = 8.2 Hz, 1H), 4.85−5.57 (br, 1H), 5.57−6.37 (br, 1H), 6.95−7.10 (m, 2H), 7.29−7.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 19.9, 21.2, 22.0, 25.7, 54.2, 70.1, 70.6, 114.9 (d, *J* = 21.4 Hz), 129.3 (d, *J* = 8.1 Hz), 138.3 (d, *J* = 2.6 Hz), 162.2 (d, *J* = 245.4 Hz); HRMS calcd for $[C_{14}H_{22}FNNaO_2]^+$ $(M + Na)^+$: 278.1527; found: 278.1527.

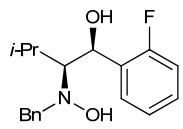
(1*S*,2*S*)-2-(Benzyl(hydroxy)amino)-1-(3-fluorophenyl)-3-methylbutan-1-ol (**2a-2**)



Following the **general procedure**, the asymmetric reductive coupling of nitrone **1a** (53.2 mg, 0.30 mmol, 1.0 equiv.) with 3-fluorobenzaldehyde (48 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2a-2** as the major diastereomer [dr = 1/7.2 (*anti*/*syn*), determined by ^{1}H NMR integral area of crude product, δ_H 5.56 (*anti*), 4.84 (*syn*)] with 79% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 220 nm; t_1 = 10.4 min, t_2 = 13.5 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 1/6; 83.5 mg, 92% combined yield).

Major diastereomer (*syn*, more polar) as a white solid: mp 84.4−85.0 ºC; $[\alpha]_D^{20}$ = +56.9 (*c* 1.0, $CHCl_3$, 79% ee); IR (film) ν_{max}: 3369, 2962, 2911, 1617, 1595, 1457, 1249 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (d, *J* = 7.0 Hz, 3H), 0.99 (d, *J* = 6.9 Hz, 3H), 1.95−2.08 (m, 1H), 2.72 (dd, *J* = 7.6, 3.3 Hz, 1H), 3.91 (d, *J* = 13.3 Hz, 1H), 4.00 (d, *J* = 13.3 Hz, 1H), 4.08−4.68 (br, 1H), 4.84 (d, *J* = 7.6 Hz, 1H), 5.15−5.65 (br, 1H), 6.90−7.00 (m, 1H), 7.02−7.13 (m, 2H), 7.20−7.37 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 20.7, 27.1, 63.1, 72.4, 74.7, 114.2 (d, *J* = 21.3 Hz), 114.4 (d, *J* = 20.9 Hz), 122.9 (d, *J* = 2.4 Hz), 127.4, 128.3, 129.2, 129.6 (d, *J* = 8.1 Hz), 138.1, 145.6 (d, *J* = 6.6 Hz), 162.8 (d, *J* = 245.7 Hz); HRMS calcd for $[C_{18}H_{22}FNNaO_2]^+$ $(M + Na)^+$: 326.1527; found: 326.1527.

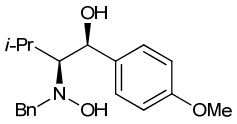
(1*S*,2*S*)-2-(Benzyl(hydroxy)amino)-1-(2-fluorophenyl)-3-methylbutan-1-ol (**2a-3**)



Following the **general procedure**, the asymmetric reductive coupling of nitrone **1a** (53.2 mg, 0.30 mmol, 1.0 equiv.) with 2-fluorobenzaldehyde (47 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2a-3** as the major diastereomer [dr = 1/12 (*anti*/*syn*), determined by ^{1}H NMR integral area of crude product, δ_H 5.83 (*anti*), 5.24 (*syn*)] with 66% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/*i*-PrOH = 85/15 (v/v), 1.0 mL/min, 225 nm; t_1 = 5.5 min, t_2 = 6.8 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 1/6; 39.2 mg, 43% combined yield).

Major diastereomer (*syn*, more polar) as a colorless oil: $[\alpha]_D^{20}$ = +59.8 (*c* 1.0, $CHCl_3$, 66% ee); IR (film) ν_{max}: 3366, 2956, 1492, 1454 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (d, *J* = 7.0 Hz, 3H), 1.00 (d, *J* = 6.9 Hz, 3H), 1.97−2.10 (m, 1H), 2.88 (dd, *J* = 7.0, 4.2 Hz, 1H), 3.87 (d, *J* = 13.4 Hz, 1H), 3.95 (d, *J* = 13.4 Hz, 1H), 4.09−4.54 (br, 1H), 5.24 (d, *J* = 7.0 Hz, 1H), 5.27−5.54 (br, 1H), 6.94−7.03 (m, 1H), 7.09−7.17 (m, 1H), 7.17−7.34 (m, 6H), 7.42−7.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 20.7, 27.5, 63.1, 67.5, 73.4, 115.2 (d, *J* = 22.2 Hz), 124.0 (d, *J* = 3.2 Hz), 127.2, 128.2, 128.9 (d, *J* = 8.3 Hz), 129.0, 129.1 (d, *J* = 4.4 Hz), 130.0 (d, *J* = 12.6 Hz), 138.3, 160.1 (d, *J* = 245.7 Hz); HRMS calcd for $[C_{18}H_{22}FNNaO_2]^+$ $(M + Na)^+$: 326.1527; found: 326.1528.

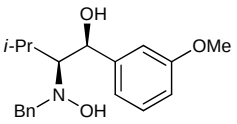
(1*S*,2*S*)-2-(Benzyl(hydroxy)amino)-1-(4-methoxyphenyl)-3-methylbutan-1-ol (2a-4)



Following the **general procedure**, the asymmetric reductive coupling of nitrone **1a** (53.2 mg, 0.30 mmol, 1.0 equiv.) with 4-methoxybenzaldehyde (55 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2a-4** as the major diastereomer [dr = 1/6.5 (*anti*/*syn*), determined by ^1H NMR integral area of crude product, δ_H 5.49 (*anti*), 4.87 (*syn*)] with 76% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 225 nm; t_1 = 9.0 min, t_2 = 12.9 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 1/4; 82.0 mg, 87% combined yield).

Major diastereomer (*syn*, more polar) as a white solid: mp 101.6−102.3 ºC; $[\alpha]_D^{20}$ = +53.9 (*c* 1.0, $CHCl_3$, 76% ee); IR (film) ν_{max}: 3379, 2956, 2921, 1614, 1515, 1246 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.78 (d, *J* = 7.1 Hz, 3H), 0.98 (d, *J* = 6.9 Hz, 3H), 1.89−2.06 (m, 1H), 2.80 (dd, *J* = 8.6, 2.6 Hz, 1H), 3.79 (s, 3H), 4.03 (d, *J* = 13.4 Hz, 1H), 4.10 (d, *J* = 13.4 Hz, 1H), 4.87 (d, *J* = 8.6 Hz, 1H), 4.99−5.27 (br, 1H), 6.81−6.95 (m, 2H), 7.21−7.43 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.59, 20.65, 27.0, 55.2, 63.2, 72.6, 74.9, 113.7, 127.3, 128.4, 128.7, 129.2, 134.5, 138.4, 159.2; HRMS calcd for $[C_{19}H_{25}NNaO_3]^+$ $(M + Na)^+$: 338.1727; found: 338.1725.

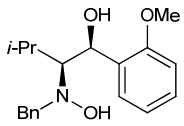
(1*S*,2*S*)-2-(Benzyl(hydroxy)amino)-1-(3-methoxyphenyl)-3-methylbutan-1-ol (**2a-5**)



Following the **general procedure**, the asymmetric reductive coupling of nitrone **1a** (53.2 mg, 0.30 mmol, 1.0 equiv.) with 3-methoxybenzaldehyde (55 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2a-5** as the major diastereomer [dr = 1/5.7 (*anti*/*syn*), determined by ^1H NMR integral area of crude product, δ_H 5.54 (*anti*), 4.84 (*syn*)] with 82% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 220 nm; t_1 = 11.4 min, t_2 = 18.2 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 1/4; 93.8 mg, 99% combined yield).

Major diastereomer (*syn*, more polar) as a colorless oil: $[\alpha]_D^{20}$ = +42.6 (*c* 1.0, $CHCl_3$, 82% ee); IR (film) ν_{max}: 3366, 2959, 1604, 1454, 1258 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.81 (d, *J* = 7.0 Hz, 3H), 0.98 (d, *J* = 6.9 Hz, 3H), 1.90−2.06 (m, 1H), 2.77 (dd, *J* = 8.0, 3.0 Hz, 1H), 3.75 (s, 3H), 3.97 (d, *J* = 13.4 Hz, 1H), 4.03 (d, *J* = 13.4 Hz, 1H), 4.11−4.62 (br, 1H), 4.84 (d, *J* = 8.0 Hz, 1H), 5.27−5.71 (br, 1H), 6.76−6.85 (m, 1H), 6.87−6.98 (m, 2H), 7.17−7.38 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 20.6, 27.1, 55.1, 63.1, 72.9, 74.5, 112.99, 113.00, 119.8, 127.2, 128.2, 129.1 (2C), 138.3, 144.3, 159.5; HRMS calcd for $[C_{19}H_{25}NNaO_3]^+$ $(M + Na)^+$: 338.1727; found: 338.1725.

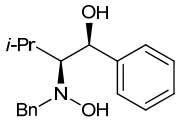
(1*S*,2*S*)-2-(Benzyl(hydroxy)amino)-1-(2-methoxyphenyl)-3-methylbutan-1-ol (2a-6)



Following the **general procedure**, the asymmetric reductive coupling of nitrone **1a** (53.2 mg, 0.30 mmol, 1.0 equiv.) with 2-methoxybenzaldehyde (54 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2a-6** as the major diastereomer [dr = 1/15 (*anti*/*syn*), determined by ^{1}H NMR integral area of crude product, δ_H 5.80 (*anti*), 5.34 (*syn*)] with 97% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 85/15 (v/v), 1.0 mL/min, 230 nm; t_1 = 6.4 min, t_2 = 9.0 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 1/4; 58.7 mg, 62% combined yield).

Major diastereomer (*syn*, more polar) as a colorless oil: $[\alpha]_D^{20}$ = +105.5 (*c* 1.0, $CHCl_3$, 97% ee); IR (film) ν_{max}: 3395, 2966, 1601, 1489, 1460, 1236, 1047 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (d, *J* = 6.9 Hz, 3H), 1.00 (d, *J* = 6.8 Hz, 3H), 1.92−2.06 (m, 1H), 2.96 (dd, *J* = 6.6, 4.6 Hz, 1H), 3.74 (s, 3H), 3.91 (s, 2H), 3.97−4.34 (br, 1H), 5.34 (d, *J* = 6.6 Hz, 1H), 5.36−5.57 (br, 1H), 6.78−6.85 (m, 1H), 6.93−7.00 (m, 1H), 7.16−7.29 (m, 6H), 7.41−7.49 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 20.7, 27.8, 55.0, 63.2, 69.0, 72.4, 110.3, 120.5, 126.9, 128.1, 128.2, 128.4, 129.0, 131.2, 138.7, 156.4; HRMS calcd for $[C_{19}H_{25}NNaO_3]^+$ $(M + Na)^+$: 338.1727; found: 338.1725.

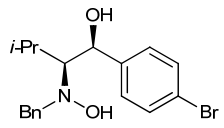
(1*S*,2*S*)-2-(Benzyl(hydroxy)amino)-3-methyl-1-phenylbutan-1-ol (**2a-7**)



Following the **general procedure**, the asymmetric reductive coupling of nitrone **1a** (53.2 mg, 0.30 mmol, 1.0 equiv.) with benzaldehyde (46 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2a-7** as the major diastereomer [dr = 1/9.8 (*anti*/*syn*), determined by ^{1}H NMR integral area of crude product, δ_H 5.56 (*anti*), 4.80 (*syn*)] with 92% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 220 nm; t_1 = 8.0 min, t_2 = 15.5 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 1/5; 73.4 mg, 86% combined yield).

Major diastereomer (*syn*, more polar) as a white solid: mp 88.0−88.6 ºC; $[\alpha]_D^{20}$ = +83.5 (*c* 1.0, $CHCl_3$, 92% ee); IR (film) ν_{max}: 3369, 2969, 2917, 1450, 1031 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 (d, *J* = 7.1 Hz, 3H), 0.95 (d, *J* = 7.0 Hz, 3H), 1.88−2.04 (m, 1H), 2.74 (dd, *J* = 8.2, 2.9 Hz, 1H), 3.91 (d, *J* = 13.3 Hz, 1H), 4.00 (d, *J* = 13.3 Hz, 1H), 4.14−4.72 (br, 1H), 4.80 (d, *J* = 8.2 Hz, 1H), 5.46−6.02 (br, 1H), 7.16−7.41 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 20.7, 26.8, 62.8, 72.8, 74.4, 127.1, 127.4, 127.5, 128.1, 128.2, 129.1, 138.2, 142.4; HRMS calcd for $[C_{18}H_{23}NNaO_2]^+$ $(M + Na)^+$: 308.1621; found: 308.1618.

(1*S*,2*S*)-2-(Benzyl(hydroxy)amino)-1-(4-bromophenyl)-3-methylbutan-1-ol (2a-8)

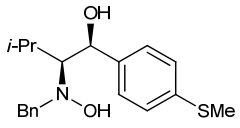


Following the **general procedure**, the asymmetric reductive coupling of nitrone **1a** (53.2 mg, 0.30 mmol, 1.0 equiv.) with 4-bromobenzaldehyde (83.2 mg, 0.45 mmol, 1.5 equiv.) gave the desired product **2a-8** as the major diastereomer [dr = 1/7.7 (*anti*/*syn*), determined by ^{1}H NMR integral area of crude product, δ_H 5.42 (*anti*), 4.83 (*syn*)] with 91% ee [Lux® Amylose-1 column, Agilent HPLC, 30 ºC, hexane/EtOH = 85/15 (v/v), 1.0 mL/min, 220 nm; t_1 = 9.5 min, t_2 = 19.6 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 1/6; 85.7 mg, 78% combined yield).

Major diastereomer (*syn*, more polar) as a white solid: mp 104.4−105.1 ºC; $[\alpha]_D^{25}$ = +78.5 (*c* 2.0, $CHCl_3$, 91% ee); IR (film) ν_{max}: 3341, 2960, 2917, 1488, 1385, 1071, 1010 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.81 (d, *J* = 7.1 Hz, 3H), 0.99 (d, *J* = 6.9 Hz, 3H), 1.96−2.06 (m, 1H), 2.73 (dd, *J* = 8.0, 3.2 Hz, 1H), 3.84−4.62 (br, 1H), 3.95 (d, *J* =

13.3 Hz, 1H), 4.04 (d, *J* = 13.3 Hz, 1H), 4.83 (d, *J* = 8.0 Hz, 1H), 5.04−5.39 (br, 1H), 7.19−7.23 (m, 2H), 7.24−7.35 (m, 5H), 7.42−7.47 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.6, 20.8, 27.0, 63.1, 72.3, 74.8, 121.4, 127.4, 128.4, 129.1, 129.2, 131.4, 138.1, 141.8; HRMS calcd for $[C_{18}H_{22}BrNNaO_2]^+$ $(M + Na)^+$: 386.0726; found: 386.0728.

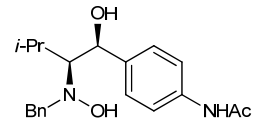
(1*S*,2*S*)-2-(Benzyl(hydroxy)amino)-3-methyl-1-(4-(methylthio)phenyl)butan-1-ol (**2a-9**)



Following the **general procedure**, the asymmetric reductive coupling of nitrone **1a** (53.2 mg, 0.30 mmol, 1.0 equiv.) with 4-(methylthio)benzaldehyde (60 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2a-9** as the major diastereomer [dr = 1/8.5 (*anti*/*syn*), determined by ^{1}H NMR integral area of crude product, δ_H 5.51 (*anti*), 4.79 (*syn*)] with 90% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 268 nm; t_1 = 10.1 min, t_2 = 15.8 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 1/5; 79.7 mg, 80% combined yield).

Major diastereomer (*syn*, more polar) as a white solid: mp 105.7−106.2 ºC; $[\alpha]_D^{20}$ = +85.2 (*c* 1.0, $CHCl_3$, 90% ee); IR (film) ν_{max}: 3369, 2962, 2917, 1499, 1085 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76 (d, *J* = 7.1 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H), 1.91−2.03 (m, 1H), 2.44 (s, 3H), 2.73 (dd, *J* = 8.4, 2.8 Hz, 1H), 3.96 (d, *J* = 13.3 Hz, 1H), 4.04 (d, *J* = 13.3 Hz, 1H), 4.14−4.63 (br, 1H), 4.79 (d, *J* = 8.4 Hz, 1H), 5.32−5.72 (br, 1H), 7.16−7.36 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.8, 20.5, 20.7, 26.8, 63.0, 72.4, 74.5, 126.4, 127.2, 128.0, 128.3, 129.1, 137.6, 138.2, 139.3; HRMS calcd for $[C_{19}H_{25}NNaO_2S]^+$ $(M + Na)^+$: 354.1498; found: 354.1497.

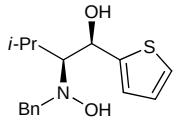
***N*-(4-((1*S*,2*S*)-2-(Benzyl(hydroxy)amino)-1-hydroxy-3-methylbutyl)phenyl)acetamide** (**2a-10**)



Following the **general procedure**, the asymmetric reductive coupling of nitrone **1a** (53.2 mg, 0.30 mmol, 1.0 equiv.) with *N*-(4-formylphenyl)acetamide (73.4 mg, 0.45 mmol, 1.5 equiv.) gave the desired product **2a-10** as the major diastereomer [dr = 1/5.3 (*anti*/*syn*), determined by ^{1}H NMR integral area of crude product, δ_H 5.53 (*anti*), 4.97 (*syn*)] with 82% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 240 nm; t_1 = 7.8 min, t_2 = 10.9 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 2/1; 102.1 mg, 99% combined yield).

Major diastereomer (*syn*, more polar) as a white solid: mp 89.9−90.6 ºC; $[\alpha]_D^{20}$ = +72.8 (*c* 1.0, $CHCl_3$, 82% ee); IR (film) ν_{max}: 3321, 2953, 2924, 1665, 1515, 1402 cm^{-1}; ^{1}H NMR (400 MHz, MeOD) δ 0.82 (d, *J* = 7.0 Hz, 3H), 0.98 (d, *J* = 6.9 Hz, 3H), 1.86−1.98 (m, 1H), 2.10 (s, 3H), 2.82 (dd, *J* = 8.2, 3.2 Hz, 1H), 4.08 (s, 2H), 4.97 (d, *J* = 8.2 Hz, 1H), 7.19−7.26 (m, 1H), 7.26−7.41 (m, 6H), 7.51−7.59 (m, 2H); ^{13}C NMR (100 MHz, MeOD) δ 20.8, 21.3, 23.8, 28.4, 64.4, 74.1, 75.2, 120.8, 128.0, 129.1 (2C), 130.3, 139.3, 139.9, 140.4, 171.5; HRMS calcd for $[C_{20}H_{26}N_2NaO_3]^+$ $(M + Na)^+$: 365.1836; found: 365.1834.

(1*S*,2*S*)-2-(Benzyl(hydroxy)amino)-3-methyl-1-(thiophen-3-yl)butan-1-ol (**2a-11**)

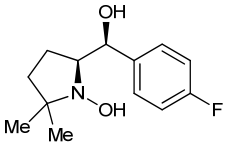


Following the **general procedure**, the asymmetric reductive coupling of nitrone **1a** (53.2 mg, 0.30 mmol, 1.0 equiv.) with thiophene-2-carbaldehyde (41 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2a-11** as the major diastereomer [dr = 1/6.2 (*anti*/*syn*), determined by ^{1}H NMR integral area of crude product, δ_H 5.63 (*anti*), 5.13 (*syn*)] with 73% ee [Lux® Amylose-1 column,

Shimadzu HPLC, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 235 nm; t_1 = 11.3 min, t_2 = 17.1 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 1/6; 63.8 mg, 73% combined yield).

Major diastereomer (*syn*, more polar) as a white solid: mp 85.9−86.5 ºC; $[\alpha]_D^{20}$ = +35.1 (*c* 1.0, $CHCl_3$, 73% ee); IR (film) ν_{max}: 3369, 2965, 2917, 1460, 1364 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.82 (d, *J* = 7.1 Hz, 3H), 1.01 (d, *J* = 6.9 Hz, 3H), 1.98−2.12 (m, 1H), 2.79 (dd, *J* = 8.2, 2.8 Hz, 1H), 3.98 (d, *J* = 13.3 Hz, 1H), 4.07 (d, *J* = 13.3 Hz, 1H), 4.21−4.79 (br, 1H), 5.13 (d, *J* = 8.2 Hz, 1H), 5.19−5.56 (br, 1H), 6.89−6.95 (m, 1H), 6.95−7.01 (m, 1H), 7.17−7.40 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 20.6, 27.0, 63.0, 68.7, 75.3, 125.0, 125.2, 126.2, 127.3, 128.3, 129.2, 138.1, 146.6; HRMS calcd for $[C_{16}H_{21}NNaO_2S]^+$ $(M + Na)^+$: 314.1185; found: 314.1184.

(*S*)-5-((*S*)-(4-Fluorophenyl)(hydroxy)methyl)-2,2-dimethylpyrrolidin-1-ol (**2k-1**)



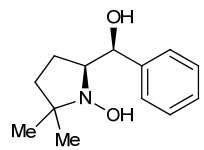
Following the **modified method 1**, the asymmetric reductive coupling of nitrone **1k** (33 μL, 0.30 mmol, 1.0 equiv.) with 4-fluorobenzaldehyde (48 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2k-1** as the major diastereomer [dr = 1/1.9 (*anti*/*syn*), determined by ^1H NMR integral area of crude product, δ_H 5.02 (*anti*), 4.70 (*syn*)]; major diastereomer (*syn*): 94% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 270 nm; t_1 = 7.7 min, t_2 = 8.5 min]; minor diastereomer (*anti*): 41% ee [Lux® Amylose-1 column, Agilent HPLC, 30 ºC, hexane/EtOH = 85/15 (v/v), 1.0 mL/min, 270 nm; t_1 = 7.7 min, t_2 = 9.5 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 1/2; 51.6 mg, 72% combined yield).

Following the **modified method 2**, the desired product **2k-1** was obtained as the major diastereomer [dr < 1/20 (*anti*/*syn*)] in 84% combined yield (60.3 mg) with 92% ee.

Major diastereomer (**2k-1**, *syn*, more polar) as a colorless oil: $[\alpha]_D^{20}$ = +27.1 (*c* 1.0, $CHCl_3$, 94% ee); IR (film) ν_{max}: 3324, 2972, 2933, 2873, 1604, 1511, 1220, 1153, 1149 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.09 (s, 3H), 1.24 (s, 3H), 1.28−1.37 (m, 1H), 1.47−1.64 (m, 3H), 3.26−3.36 (m, 1H), 4.70 (d, *J* = 8.2 Hz, 1H), 4.79−6.48 (br, 2H), 6.98−7.06 (m, 2H), 7.31−7.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 23.0, 26.4, 34.2, 65.4, 69.5, 77.5, 115.2 (d, *J* = 21.3 Hz), 128.5 (d, *J* = 8.0 Hz), 138.1 (d, *J* = 3.0 Hz), 162.3 (d, *J* = 245.5 Hz); HRMS calcd for $[C_{13}H_{19}FNO_2]^+$ $(M + H)^+$: 240.1394; found: 240.1396.

Minor diastereomer (*anti*, less polar) as a white solid: mp 87.2−87.5 ºC; $[\alpha]_D^{25}$ = +16.5 (*c* 1.0, $CHCl_3$, 41% ee); IR (film) ν_{max}: 3369, 2930, 2869, 2873, 1604, 1220, 1149 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.06 (s, 3H), 1.22 (s, 3H), 1.30−1.39 (m, 1H), 1.44−1.70 (m, 3H), 3.22 (ddd, *J* = 9.7, 7.0, 2.5 Hz, 1H), 3.48−4.60 (br, 2H), 5.02 (d, *J* = 1.6 Hz, 1H), 6.98−7.08 (m, 2H), 7.31−7.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.6, 18.0, 26.7, 34.3, 63.9, 69.5, 70.1, 115.0 (d, *J* = 21.2 Hz), 127.2 (d, *J* = 7.8 Hz), 136.8 (d, *J* = 2.9 Hz), 161.9 (d, *J* = 245.0 Hz); HRMS calcd for $[C_{13}H_{19}FNO_2]^+$ $(M + H)^+$: 240.1394; found: 240.1397.

(*S*)-5-((*S*)-Hydroxy(phenyl)methyl)-2,2-dimethylpyrrolidin-1-ol (**2k-2**)



Following the **modified method 1**, the asymmetric reductive coupling of nitrone **1k** (33 μL, 0.30 mmol, 1.0 equiv.) with benzaldehyde (46 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2k-2** as the major diastereomer [dr = 1/1.9 (*anti*/*syn*), determined by ^1H NMR integral area of crude product, δ_H 5.05 (*anti*), 4.70 (*syn*)]; major diastereomer (*syn*): 92% ee [Lux®

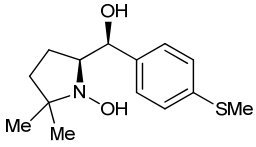
Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 220 nm; t_1 = 8.1 min, t_2 = 8.8 min]; minor diastereomer (*anti*): 36% ee [Lux® Amylose-1 column, Agilent HPLC, 30 ºC, hexane/EtOH = 95/5 (v/v), 1.0 mL/min, 220 nm; t_1 = 17.8 min, t_2 = 19.2 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 1/2; 48.5 mg, 73% combined yield).

Following the **modified method 2**, the desired product **2k-2** was obtained as the major diastereomer [dr < 1/20 (*anti*/*syn*)] in 76% combined yield (50.3 mg) with 87% ee.

Major diastereomer (**2k-2**, *syn*, more polar) as a colorless oil: $[\alpha]_D^{20}$ = +32.8 (*c* 1.0, $CHCl_3$, 92% ee); IR (film) ν_{max}: 3334, 2972, 2927, 2869, 1454, 1079 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.08 (s, 3H), 1.24 (s, 3H), 1.38−1.48 (m, 1H), 1.48−1.68 (m, 3H), 3.29−3.39 (m, 1H), 4.70 (d, *J* = 7.2 Hz, 1H), 7.24−7.42 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 23.0, 26.4, 34.3, 65.3, 69.6, 78.1, 126.9, 127.7, 128.4, 142.3; HRMS calcd for $[C_{13}H_{20}NO_2]^+$ $(M + H)^+$: 222.1489; found: 222.1488.

Minor diastereomer (*anti*, less polar) as a white solid: mp 65.6−66.6 ºC; $[\alpha]_D^{25}$ = +17.7 (*c* 1.0, $CHCl_3$, 36% ee); IR (film) ν_{max}: 3401, 2965, 2869, 1450, 1361, 1194 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.06 (s, 3H), 1.23 (s, 3H), 1.32−1.60 (m, 3H), 1.64−1.76 (m, 1H), 3.26 (ddd, *J* = 9.8, 7.1, 2.5 Hz, 1H), 3.37−4.74 (br, 2H), 5.05 (d, *J* = 1.8 Hz, 1H), 7.20−7.28 (m, 1H), 7.28−7.36 (m, 2H), 7.36−7.44 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.7, 18.0, 26.8, 34.4, 63.8, 69.5, 70.6, 125.6, 126.9, 128.1, 141.2; HRMS calcd for $[C_{13}H_{20}NO_2]^+$ $(M + H)^+$: 222.1489; found: 222.1488.

(*S*)-5-((*S*)-Hydroxy(4-(methylthio)phenyl)methyl)-2,2-dimethylpyrrolidin-1-ol (**2k-3**)



Following the **modified method 1**, the asymmetric reductive coupling of nitrone **1k** (33 μL, 0.30 mmol, 1.0 equiv.) with 4-(methylthio)benzaldehyde (60 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2k-3** as the major diastereomer [dr = 1/2.0 (*anti*/*syn*), determined by ^1H NMR integral area of crude product, δ_H 5.01 (*anti*), 4.67 (*syn*)]; major diastereomer (*syn*): 95% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 270 nm; t_1 = 12.0 min, t_2 = 16.3 min]; minor diastereomer (*anti*): 49% ee [Lux® Amylose-1 column, Agilent HPLC, 30 ºC, hexane/EtOH = 85/15 (v/v), 1.0 mL/min, 270 nm; t_1 = 13.5 min, t_2 = 21.3 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc/PE = 1/2; 75.6 mg, 94% combined yield).

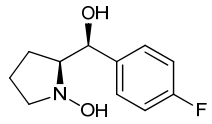
Following the **modified method 2**, the desired product **2k-3** was obtained as the major diastereomer [dr < 1/20 (*anti*/*syn*)] in 94% combined yield (75.2 mg) with 89% ee.

Major diastereomer (**2k-3**, *syn*, more polar) as a colorless oil: $[\alpha]_D^{20}$ = +33.6 (*c* 1.0, $CHCl_3$, 95% ee); IR (film) ν_{max}: 3403, 2965, 2834, 1514, 1248, 1035, 1001 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.08 (s, 3H), 1.24 (s, 3H), 1.28−1.37 (m, 1H), 1.45−1.63 (m, 3H), 2.46 (s, 3H), 3.25−3.41 (m, 1H), 4.67 (d, *J* = 8.5 Hz, 1H), 5.01−7.01 (br, 2H), 7.16−7.25 (m, 2H), 7.25−7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.8, 20.0, 23.1, 26.2, 34.2, 65.5, 69.5, 77.6, 126.5, 127.4, 137.6, 139.2; HRMS calcd for $[C_{14}H_{22}NO_2S]^+$ $(M + H)^+$: 268.1366; found: 268.1366.

Minor diastereomer (*anti*, less polar) as a white solid: mp 110.5−111.1 ºC; $[\alpha]_D^{25}$ = +21.5 (*c* 1.0, $CHCl_3$, 49% ee); IR (film) ν_{max}: 3403, 2965, 2834, 1514, 1248, 1172, 1035 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.05 (s, 3H), 1.22 (s, 3H), 1.30−1.41 (m, 1H), 1.41−1.63 (m, 2H), 1.63−1.76 (m, 1H), 2.47 (s, 3H), 3.22 (ddd, *J* = 9.7, 7.2, 2.3 Hz, 1H), 3.68−4.97 (br, 2H), 5.01 (d, *J* = 1.8 Hz, 1H), 7.19−7.28 (m, 2H), 7.28−7.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.0, 16.6, 18.0, 26.8, 34.3, 63.8, 69.5, 70.3, 126.2, 126.6, 136.7, 138.3; HRMS calcd for $[C_{14}H_{22}NO_2S]^+$ (M +

H)$^+$: 268.1366; found: 268.1367.

(*S*)-2-((*S*)-(4-Fluorophenyl)(hydroxy)methyl)pyrrolidin-1-ol (**2l**)



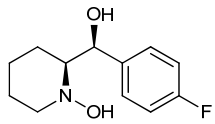
Following the **modified method 1**, the asymmetric reductive coupling of nitrone **1l** (0.30 mmol, 1.0 equiv.) with 4-fluorobenzaldehyde (48 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2l** as the major diastereomer [dr = 1/2.1 (*anti*/*syn*), determined by chiral HPLC analysis]; major diastereomer (*syn*): 97% ee [Lux® Amylose-1 column, Agilent HPLC, 30 ºC, hexane/EtOH = 70/30 (v/v), 1.0 mL/min, 270 nm; t_1 = 10.4 min, t_2 = 13.2 min]; minor diastereomer (*anti*): 4% ee [Lux® Amylose-1 column, Agilent HPLC, 30 ºC, hexane/EtOH = 85/15 (v/v), 1.0 mL/min, 270 nm; t_1 = 10.6 min, t_2 = 18.1 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc; 45.6 mg, 72% combined yield).

Following the **modified method 2**, the desired product **2l** was obtained as the major diastereomer [dr = 1/12 (*anti*/*syn*)] in 64% combined yield (40.6 mg) with 72% ee.

Major diastereomer (**2l**, *syn*, more polar) as a colorless oil: $[\alpha]_D^{20}$ = +6.7 (*c* 1.0, MeOH, 97% ee); IR (film) ν_{max}: 3350, 2966, 2873, 1611, 1505, 1223 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22−1.34 (m, 1H), 1.38−1.56 (m, 1H), 1.61−1.89 (m, 2H), 2.95 (ddd, apparent dt, *J* = 11.0, 8.6 Hz, 1H), 3.09−3.36 (m, 2H), 4.30−4.90 (m, 1H), 6.59−7.23 (br, 2H), 6.94−7.07 (m, 2H), 7.26−7.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 25.7, 58.6 (2C), 74.5, 115.2 (d, *J* = 21.3 Hz), 128.6 (d, *J* = 8.0 Hz), 137.7 (d, *J* = 2.9 Hz), 162.3 (d, *J* = 246.1 Hz); HRMS calcd for $[C_{11}H_{14}FNNaO_2]^+$ $(M + Na)^+$: 234.0901; found: 234.0902.

Minor diastereomer (*anti*, less polar) as a colorless oil: $[\alpha]_D^{25}$ = +1.6 (*c* 1.0, $CHCl_3$, 4% ee); IR (film) ν_{max}: 3372, 2972, 2860, 1611, 1511, 1226 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35−1.48 (m, 1H), 1.57−1.93 (m, 3H), 2.83 (ddd, apparent q, *J* = 9.5 Hz, 1H), 2.99 (ddd, apparent td, *J* = 8.9, 1.6 Hz, 1H), 3.30 (ddd, *J* = 9.5, 7.3, 2.0 Hz, 1H), 5.08−5.23 (m, 1H), 5.51−6.54 (br, 2H), 6.94−7.07 (m, 2H), 7.27−7.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3, 19.4, 57.8, 69.9, 73.8, 115.0 (d, *J* = 21.3 Hz), 127.2 (d, *J* = 7.9 Hz), 137.1 (d, *J* = 3.0 Hz), 161.9 (d, *J* = 245.1 Hz); HRMS calcd for $[C_{11}H_{14}FNNaO_2]^+$ $(M + Na)^+$: 234.0901; found: 234.0902.

(*S*)-2-((*S*)-(4-Fluorophenyl)(hydroxy)methyl)piperidin-1-ol (**2m**)



Following the **modified method 1**, the asymmetric reductive coupling of nitrone **1m** (0.30 mmol, 1.0 equiv.) with 4-fluorobenzaldehyde (48 μL, 0.45 mmol, 1.5 equiv.) gave the desired product **2m** as the major diastereomer [dr = 1/9.9 (*anti*/*syn*), determined by chiral HPLC analysis] with 97% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 270 nm; t_1 = 8.2 min, t_2 = 8.6 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc; 39.0 mg, 58% combined yield).

Following the **modified method 2**, the desired product **2m** was obtained as the major diastereomer [dr = 1/20 (*anti*/*syn*)] in 47% combined yield (31.8 mg) with 57% ee.

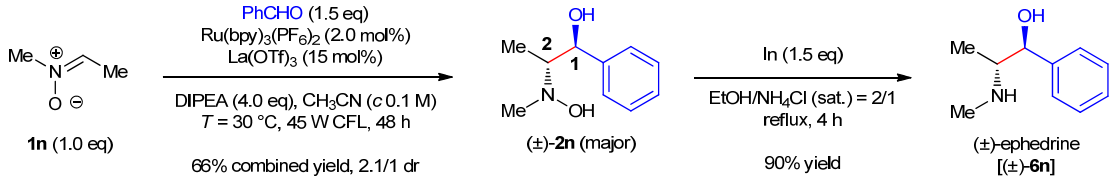
Major diastereomer (*syn*, more polar) as a white solid: mp 122.9−123.6 ºC; $[\alpha]_D^{20}$ = −15.6 (*c* 1.0, MeOH, 97% ee); IR (film) ν_{max}: 3366, 2921, 2850, 1601, 1511, 1223 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d6, 25 ºC) δ 0.31−0.77 (m, 1H), 0.91−1.22 (m, 2H), 1.39−1.67 (m, 3H), 2.34−2.60 (m, 2H), 3.08−3.25 (m, 1H), 4.88−5.52 (m, 2H), 7.02−7.19 (m, 2H), 7.38−7.52 (m, 2H), 7.82−8.17 (br, 1H); ^{13}C NMR (100 MHz, DMSO-d6, 25 ºC) δ 23.0, 24.7, 25.1, 60.0,

70.4, 72.0, 113.6 (d, J = 20.0 Hz), 128.9 (d, J = 7.6 Hz), 138.6 (d, J = 2.3 Hz), 161.0 (d, J = 241.4 Hz); ^{1}H NMR (400 MHz, DMSO-d6, 75 ºC) δ 0.78−0.96 (m, 1H), 1.05−1.17 (m, 1H), 1.34−1.56 (m, 4H), 2.49−2.60 (m, 2H), 3.13−3.24 (m, 1H), 4.68−5.07 (br, 1H), 4.95 (d, J = 4.9 Hz, 1H), 6.99−7.13 (m, 2H), 7.38−7.48 (m, 2H), 7.48−7.80 (br, 1H); ^{13}C NMR (100 MHz, DMSO-d6, 75 ºC) δ 22.5, 23.3, 23.9, 58.6, 71.0, 71.8, 113.2 (d, J = 20.9 Hz), 128.4 (d, J = 7.8 Hz), 138.3 (d, J = 3.0 Hz), 160.7 (d, J = 241.9 Hz); HRMS calcd for $[C_{12}H_{16}FNNaO_2]^+$ $(M + Na)^+$: 248.1057; found: 248.1059.

Supplementary Discussion:

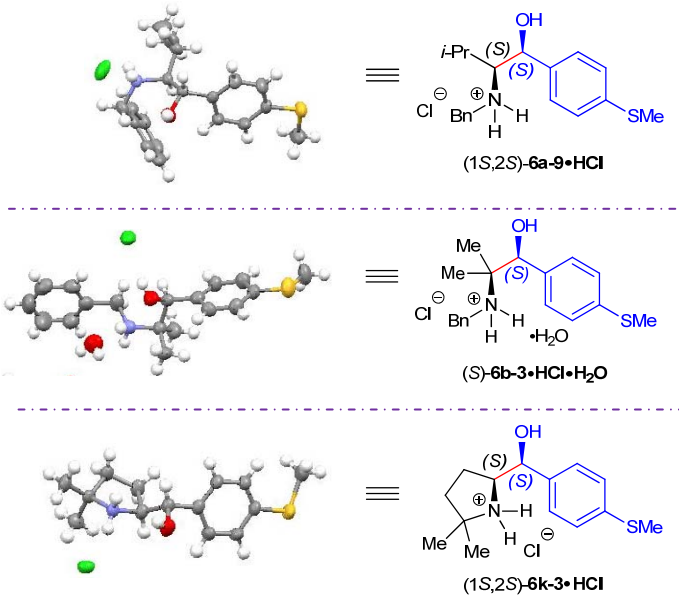
Determination of the Absolute Configuration of Vicinal Amino Alcohols:

In order to determinate the relative stereochemistry of major diastereomers in Table 2, under a general chiral ligand free condition (as demonstrated in Supplementary Table 2, entry 1), reductive coupling of nitrone **1n** with benzaldehyde provided desired vicinal hydroxyamino alcohol as a separable mixture of diastereomers in 66% combined yield with 2.1/1 dr. The stereochemistry of major diastereomer (±)-**2n** was assigned as 1,2-*anti* according to the observed vicinal coupling constant[10] ($J_{1,2}$ = 0 Hz, as to minor diastereomer $J_{1,2}$ = 9.0 Hz). Indium-mediated reduction[11] of (±)-**2n** afforded racemic (±)-ephedrine [(±)-**6n**] in 90% yield and it also confirmed the 1,2-*anti* configuration of (±)-**2n** (Supplementary Fig. 1). However, most of the observed vicinal coupling constants ($J_{1,2}$) of major diastereomers in Table 2 were higher than 7.0 Hz. So, we speculated that the relative stereochemistry of the major diastereomers in Table 2 should be 1,2-*syn* configuration.



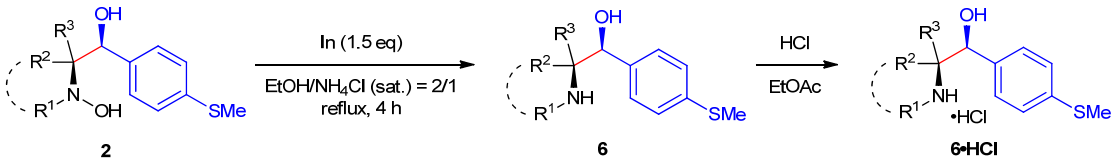
Supplementary Figure 1. **Concise synthesis of (±)-ephedrine [(±)-6n].** Reductive coupling of nitrone **1n** with benzaldehyde under a general chiral ligand free condition gave (±)-**2n** as the major diastereomer (2.1/1 dr). Indium-mediated reduction of (±)-**2n** gave (±)-**6n** in 40% yield for two steps, which also confirmed the 1,2-*anti* configuration of (±)-**2n**.

Furthermore, indium-mediated reduction of vicinal hydroxyamino alcohols **2a-9**, **2b-3** and **2k-3** followed by acidification afforded hydrochlorides of vicinal amino alcohols **6a-9**, **6b-3** and **6k-3**. Their absolute configurations were determined to be (1*S*,2*S*)-**6a-9**, (*S*)-**6b-3** and (1*S*,2*S*)-**6k-3** by single-crystal X-ray diffraction analysis (Supplementary Fig. 2).

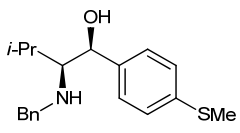


Supplementary Figure 2. **Single X-ray structures of 6a-9•HCl, 6b-3•HCl and 6k-3•HCl.** The absolute configurations of (1*S*,2*S*)-**6a-9•HCl** (CCDC: 1537335), (*S*)-**6b-3•HCl•H_2O** (CCDC: 1537337) and (1*S*,2*S*)-**6k-3•HCl** (CCDC: 1537338) were determined by single-crystal X-ray diffraction analysis.

General procedure for vicinal amino alcohol hydrochlorides[11]: To a solution of vicinal hydroxyamino alcohol **2** in EtOH/NH_4Cl (sat.) = 2/1 (v/v) (*c* 0.05 M) was added indium powder (1.5 equiv.). The mixture was heated to reflux for 4 hours. Upon completion, the reaction mixture was cooled to room temperature, filtered through a thin pad of Celite and washed with EtOAc. Saturated Na_2CO_3 (aq.) was added to the filtrate, the organic layer was separated and the aqueous layer was extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography to afford the vicinal amino alcohol **6**. The amino alcohol **6** was dissolved in HCl solution (2.0 M in EtOAc). The solvent was evaporated under reduced pressure to form the hydrochloride **6•HCl**. Recrystallization of **6•HCl** from ethanol/cyclohexane afforded X-ray quality crystals.



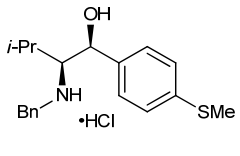
(1*S*,2*S*)-2-(Benzylamino)-3-methyl-1-(4-(methylthio)phenyl)butan-1-ol (**6a-9**)



Following the **general procedure**, the reduction of **2a-9** (200 mg, 0.60 mmol, 90% ee) gave the desired product **6a-9** as a colorless oil (chromatography on silica gel, eluent: MeOH/CH_2Cl_2 = 1/30; 152 mg, 80% yield): $[\alpha]_D^{20}$ = +41.9 (*c* 1.0, $CHCl_3$, 90% ee); IR (film) ν_{max}: 3375, 2959, 2911, 1499, 1450, 1092 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (d, *J* = 6.9 Hz, 3H), 0.97 (d, *J* = 6.9 Hz, 3H), 1.69−1.84 (m, 1H), 2.43 (s, 3H), 2.57 (dd, *J* = 5.3, 4.9 Hz, 1H), 3.56 (d, *J* = 12.8 Hz, 1H), 3.68 (d, *J* = 12.8 Hz, 1H), 4.39 (d, *J* = 5.3 Hz, 1H), 7.11−7.37 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$)

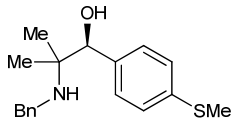
δ 15.8, 17.7, 20.4, 30.0, 54.4, 69.0, 71.8, 126.5, 126.6, 127.0, 128.0, 128.3, 136.6, 139.9, 141.4; HRMS calcd for $[C_{19}H_{26}NOS]^+$ $(M + H)^+$: 316.1730; found: 316.1729.

(1*S*,2*S*)-2-(Benzylamino)-3-methyl-1-(4-(methylthio)phenyl)butan-1-ol hydrochloride (**6a-9•HCl**)



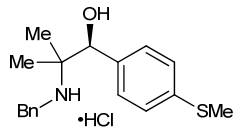
The product **6a-9•HCl** as a white solid: mp 169.0−169.7 ºC; $[\alpha]_D^{20}$ = +14.0 (*c* 1.0, MeOH, 90% ee); IR (film) ν_{max}: 3369, 2959, 2921, 1454, 1335, 1089 cm^{-1}; ^1H NMR (400 MHz, MeOD) δ 0.89 (d, *J* = 7.0 Hz, 3H), 0.93 (d, *J* = 7.0 Hz, 3H), 1.75−1.90 (m, 1H), 2.49 (s, 3H), 3.20 (dd, *J* = 7.6, 3.0 Hz, 1H), 4.31 (d, *J* = 13.0 Hz, 1H), 4.43 (d, *J* = 13.0 Hz, 1H), 4.93 (d, *J* = 7.6 Hz, 1H), 7.26−7.37 (m, 4H), 7.40−7.50 (m, 5H); ^{13}C NMR (100 MHz, MeOD) δ 15.5, 17.6, 18.8, 29.0, 53.3, 68.6, 72.0, 127.7, 128.3, 130.2, 130.8, 131.7, 132.3, 139.5, 140.8; HRMS calcd for $[C_{19}H_{26}NOS]^+$ $(M)^+$: 316.1730; found: 316.1729.

(*S*)-2-(Benzylamino)-2-methyl-1-(4-(methylthio)phenyl)propan-1-ol (**6b-3**)



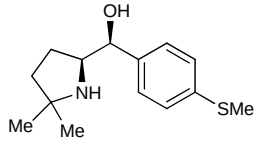
Following the **general procedure**, the reduction of **2b-3** (210 mg, 0.66 mmol, 94% ee) gave the desired product **6b-3** as a colorless oil (chromatography on silica gel, eluent: EtOAc/PE = 1/1; 175 mg, 88% yield): $[\alpha]_D^{20}$ = +10.6 (*c* 0.5, $CHCl_3$, 94% ee); IR (film) ν_{max}: 3356, 2966, 2917, 2853, 1777, 1668, 1457, 1265, 1098 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (s, 3H), 1.12 (s, 3H), 2.42 (s, 3H), 3.73 (s, 2H), 4.43 (s, 1H), 7.14−7.19 (m, 2H), 7.20−7.35 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 21.4, 23.1, 46.1, 57.1, 77.2, 125.6, 126.9, 128.00, 128.04, 128.3, 136.9, 137.3, 140.3; HRMS calcd for $[C_{18}H_{24}NOS]^+$ $(M + H)^+$: 302.1573; found: 302.1576.

(*S*)-2-(Benzylamino)-2-methyl-1-(4-(methylthio)phenyl)propan-1-ol hydrochloride (**6b-3•HCl**)



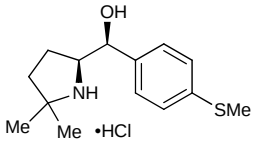
The product **6b-3•HCl** as a white solid: mp 137.6−138.5 ºC; $[\alpha]_D^{20}$ = +31.4 (*c* 1.0, MeOH, 94% ee); IR (film) ν_{max}: 3369, 2917, 1438, 1338, 1092 cm^{-1}; ^1H NMR (400 MHz, MeOD) δ 1.27 (s, 3H), 1.37 (s, 3H), 2.49 (s, 3H), 4.31 (d, *J* = 12.6 Hz, 1H), 4.39 (d, *J* = 12.6 Hz, 1H), 5.06 (s, 1H), 7.26−7.32 (m, 2H), 7.39−7.52 (m, 5H), 7.58−7.67 (m, 2H); ^{13}C NMR (100 MHz, MeOD) δ 15.6, 19.4, 21.1, 46.4, 64.6, 74.5, 126.9, 129.5, 130.1, 130.4, 131.4, 133.2, 137.1, 140.4; HRMS calcd for $[C_{18}H_{24}NOS]^+$ $(M)^+$: 302.1573; found: 302.1576.

(*S*)-((*S*)-5,5-Dimethylpyrrolidin-2-yl)(4-(methylthio)phenyl)methanol (**6k-3**)



Following the **general procedure**, the reduction of **2k-3** (181 mg, 0.68 mmol, 95% ee) gave the desired product **6k-3** as a colorless oil (chromatography on silica gel, eluent: MeOH/CH_2Cl_2 = 1/6; 89.0 mg, 52% yield): $[\alpha]_D^{20}$ = +22.6 (*c* 0.5, $CHCl_3$, 95% ee); IR (film) ν_{max}: 3324, 2956, 2917, 2853, 1265, 1092, 1008 cm^{-1}; ^1H NMR (500 MHz, MeOD) δ 1.16 (s, 3H), 1.23 (s, 3H), 1.55−1.65 (m, 4H), 2.46 (s, 3H), 3.38−3.45 (m, 1H), 4.41 (d, *J* = 7.4 Hz, 1H), 7.22−7.26 (m, 2H), 7.27−7.32 (m, 2H); ^{13}C NMR (125 MHz, MeOD) δ 15.9, 28.6, 29.4, 29.8, 40.0, 60.5, 65.4, 78.0, 127.6, 128.3, 139.2, 141.4; HRMS calcd for $[C_{14}H_{22}NOS]^+$ $(M + H)^+$: 252.1417; found: 252.1418.

(*S*)-((*S*)-5,5-Dimethylpyrrolidin-2-yl)(4-(methylthio)phenyl)methanol hydrochloride (6k-3•HCl)

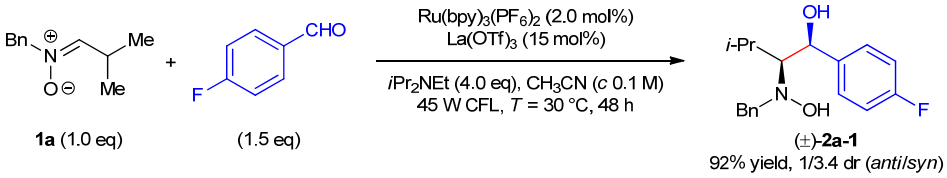


The product **6k-3•HCl** as a white solid: mp > 230 ºC (decomposed); $[\alpha]_D^{20}$ = +46.4 (*c* 1.0, MeOH, 95% ee); IR (film) ν_{max}: 3369, 2972, 2914, 1438, 1380, 1082 cm^{-1}; ^1H NMR (400 MHz, MeOD) δ 1.44 (s, 3H), 1.53 (s, 3H), 1.83−2.00 (m, 4H), 2.47 (s, 3H), 3.85−3.96 (m, 1H), 4.75 (d, *J* = 8.5 Hz, 1H), 7.25−7.31 (m, 2H), 7.38−7.44 (m, 2H); ^{13}C NMR (100 MHz, MeOD) δ 15.6, 25.5, 25.9, 27.0, 38.4, 66.1, 66.2, 74.6, 127.6, 128.4, 139.0, 140.5; HRMS calcd for $[C_{14}H_{22}NOS]^+$ $(M)^+$: 252.1417; found: 252.1418.

Control Experiments for the Photocatalytic Cross-Coupling of Nitrones with Aldehydes:

A series of experimental studies were carried out to gain a better comprehension of this reductive coupling reaction. Control experiments established that photocatalyst, Lewis acid, co-reductant (DIPEA) and light are both essential for this reaction (Supplementary Table 4). Additionally, when 1.0 equivalent of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) was added to the reaction system, the reductive coupling of nitrones with aldehydes did not occur. All of these results implied a free radical process in this reductive coupling reaction.

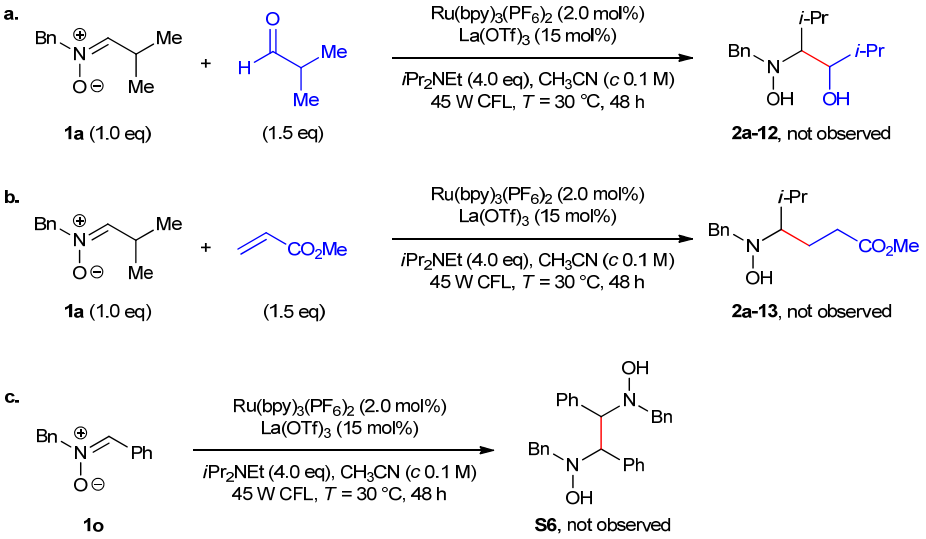
Supplementary Table 4. Control experiments for the mechanism study



Entry	Variation from standard condition	Yield (%)[a]
1	None	92
2	No $Ru(bpy)_3(PF_6)_2$	0
3	No $La(OTf)_3$	0
4	No DIPEA	0
5	No light	0
6	Added TEMPO (1 equiv.)	0

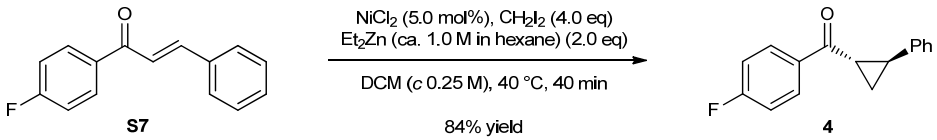
[a] Yields were determined by ^1H NMR analysis using an internal standard.

To compare our photocatalytic reductive coupling reaction with previous SmI_2-mediated reductive coupling of nitrones with aldehydes/ketones[12], some experiments were conducted to examine the role of nitrones under the photocatalytic conditions. Surprisingly, nitrone **1a** reacted with neither aliphatic aldehydes (*e.g.*, isobutyraldehyde, Supplementary Fig. 3-a) nor α,β-unsaturated compounds (*e.g.*, methyl acrylate, Supplementary Fig. 3-b) under the standard condition (as demonstrated in Supplementary Table 4). Moreover, homocoupling product **S6** was not observed when nitrone **1o** was treated under the standard condition in the absence of aldehyde, which could be obtained under SmI_2-mediated condition[12] (Supplementary Fig. 3-c). Combined these results with radical clock reactions (see Fig. 2), we speculated this photocatalytic reductive coupling is initialed by visible-light-exited single electron transfer (SET) reduction of aldehydes rather than that of nitrones.



Supplementary Figure 3. **Examinations of the role of nitrones under the photocatalytic conditions. a,** cross-coupling product **2a-12** was not observed when nitrone **1a** and isobutyraldehyde were treated under the standard condition. **b**, cross-coupling product **2a-13** was not observed when nitrone **1a** and methyl acrylate were treated under the standard condition. **c**, homocoupling product **S6** was not observed when nitrone **1o** was treated under the standard condition in the absence of aldehyde.

Radical Clock Reactions:

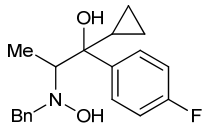


Based on a literature procedure[13], an oven-dried 100 mL round bottom flask equipped with a magnetic stir bar was added **S7** (1.13 g, 5.0 mmol, 1.0 equiv.) and $NiCl_2$ (32.4 mg, 0.25 mmol, 5.0 mol%) in the glove box. When the flask was sealed and removed from the glove box, DCM (20.0 mL) was added, followed by CH_2I_2 (1.61 mL, 20 mmol, 4.0 equiv.). The mixture was heated to 40 ºC, and Et_2Zn (ca. 1.0 M in hexane) (10.0 mL, 10 mmol, 2.0 equiv.) was added slowly (over 30 min). After being stirred at 40 ºC for additional 10 min, the reaction mixture was diluted with 20 mL EtOAc, and quenched with saturated NH_4Cl (aq.) (10 mL). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford **4** as a white solid (eluent: EtOAc/PE = 1/30; 1.01 g, 84% yield): mp 60.1−60.7 ºC; IR (film) ν_{max}: 3062, 3026, 1668, 1595, 1418, 1220, 1159, 1034 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.54 (ddd, J = 7.6, 6.8, 4.2 Hz, 1H), 1.84−1.97 (m, 1H), 2.62−2.76 (m, 1H), 2.77−2.90 (m, 1H), 7.04−7.26 (m, 5H), 7.26−7.38 (m, 2H), 7.95−8.09 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 29.1, 29.9, 115.6 (d, J = 21.8 Hz), 126.1, 126.6, 128.5, 130.6 (d, J = 9.3 Hz), 134.1 (d, J = 2.9 Hz), 140.3, 165.6 (d, J = 254.5 Hz), 196.8; HRMS calcd for $[C_{16}H_{13}FNaO]^+$ $(M + Na)^+$: 263.0843; found: 263.0843.

General procedure for the radical clock reaction: An oven-dried 25 mL Schlenk tube equipped with a

magnetic stir bar was added nitrone **1f** (74.6 mg, 0.50 mmol, 1.0 equiv.), ketone **3** or **4** (0.50 mmol, 1.0 equiv.), $Ru(bpy)_3(PF_6)_2$ (8.6 mg, 0.01 mmol, 2.0 mol%) and $La(OTf)_3$ (44.0 mg, 0.075 mmol, 15 mol%) in the glove box. When the tube was sealed and removed from the glove box, CH_3CN (5.0 mL, *c* 0.1 M) was added, followed by DIPEA (0.35 mL, 2.0 mmol, 4.0 equiv.). The tube was placed approximately 10 cm away from a 45 W CFL. After being stirred at 30 ºC under an argon atmosphere for 48 hours, the reaction mixture was filtered through a thin pad of silica gel (100 to 200 mesh), washed with EtOAc and concentrated under reduced pressure. The residue was purified by flash chromatography to afford the product.

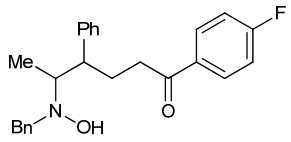
2-(Benzyl(hydroxy)amino)-1-(4-fluorophenyl)propan-1-ol (2f-2)



Following the **general procedure**, the reaction of nitrone **1f** and ketone **3** afforded **2f-2** as a 1/1.6 (dr, minor/major) mixture of inseparable diastereomers (chromatography on silica gel, eluent: EtOAc/PE = 1/8; 42.7 mg, 27% combined yield; recovered 59.0 mg ketone **3**, 72%): IR (film) ν_{max}: 3427, 3004, 2942, 1604, 1502, 1223 cm^{-1}; HRMS calcd for $[C_{19}H_{22}FNNaO_2]^+$ $(M + Na)^+$: 338.1527; found: 338.1525.

Major diastereomer (data read from spectrum of the diastereomeric mixture): ^1H NMR (400 MHz, $CDCl_3$) δ 0.14−0.32 (m, 2H), 0.36−0.58 (m, 2H), 1.11 (d, *J* = 6.8 Hz, 3H), 1.42−1.53 (m, 1H), 3.16 (q, *J* = 6.8 Hz, 1H), 3.76 (d, *J* = 13.3 Hz, 1H), 3.86−4.02 (br, 1H), 3.94 (d, *J* = 13.3 Hz, 1H), 4.28−4.48 (br, 1H), 6.91−7.03 (m, 2H), 7.19−7.45 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.6, 1.9, 6.4, 20.3, 62.0, 68.8, 76.2, 114.4 (d, *J* = 20.9 Hz), 127.2 (d, *J* = 7.7 Hz), 127.5, 128.4, 129.0, 137.7, 141.6 (d, *J* = 3.1 Hz), 161.4 (d, *J* = 244.4 Hz).
Minor diastereomer (data read from spectrum of the diastereomeric mixture): ^1H NMR (400 MHz, $CDCl_3$) δ 0.14−0.32 (m, 1H), 0.36−0.58 (m, 2H), 0.60−0.71 (m, 1H), 1.18 (d, *J* = 6.8 Hz, 3H), 1.30−1.37 (m, 1H), 3.03 (q, *J* = 6.8 Hz, 1H), 3.72 (d, *J* = 13.3 Hz, 1H), 3.86−4.02 (br, 1H), 4.02 (d, *J* = 13.3 Hz, 1H), 4.53−4.68 (br, 1H), 6.91−7.03 (m, 2H), 7.19−7.45 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.1, 2.5, 5.8, 16.4, 62.0, 69.1, 75.4, 114.3 (d, *J* = 21.0 Hz), 127.5, 128.0 (d, *J* = 7.9 Hz), 128.4, 129.1, 137.4, 142.4 (d, *J* = 2.9 Hz), 161.5 (d, *J* = 244.7 Hz).

5-(Benzyl(hydroxy)amino)-1-(4-fluorophenyl)-4-phenylhexan-1-one (5)



Following the **general procedure**, the reaction of nitrone **1f** and ketone **4** afforded **5** as a 1/2.0 (dr, minor/major) mixture of diastereomers (chromatography on silica gel, eluent: EtOAc/PE = 1/8; 104 mg, 53% combined yield; recovered 55.3 mg ketone **4**, 46%).

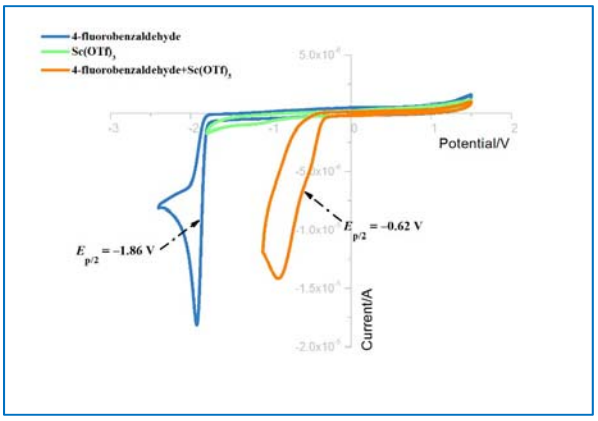
Major diastereomer (more polar) as a white solid: mp 85.0−85.7 ºC; IR (film) ν_{max}: 3462, 3030, 2917, 1688, 1598, 1223, 1150 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.18 (d, *J* = 5.9 Hz, 3H), 1.86−2.00 (m, 1H), 2.34−2.47 (m, 1H), 2.68−2.81 (m, 2H), 2.95−3.08 (m, 2H), 3.64 (d, *J* = 13.4 Hz, 1H), 3.95 (d, *J* = 13.4 Hz, 1H), 4.78−5.05 (br, 1H), 6.97−7.06 (m, 2H), 7.08−7.26 (m, 8H), 7.26−7.36 (m, 2H), 7.73−7.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.5, 24.5, 36.4, 48.5, 60.0, 65.8, 115.4 (d, *J* = 21.8 Hz), 126.2, 126.8, 128.0, 128.3, 128.4, 128.9, 130.5 (d, *J* = 9.4 Hz), 133.3 (d, *J* = 2.8 Hz), 138.6, 142.9, 165.5 (d, *J* = 254.3 Hz), 198.8; HRMS calcd for $[C_{25}H_{26}FNNaO_2]^+$ $(M + Na)^+$: 414.1840; found: 414.1843.

Minor diastereomer (less polar) as a white solid: mp 123.1−124.0 ºC; IR (film) ν_{max}: 3346, 3026, 2975, 2930, 1681, 1595, 1233, 1156 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (d, *J* = 6.3 Hz, 3H), 1.66−1.80 (m, 1H), 2.66−2.81 (m, 3H), 2.93−3.13 (m, 2H), 3.78 (d, *J* = 13.6 Hz, 1H), 4.08 (d, *J* = 13.6 Hz, 1H), 5.44−5.57 (br, 1H), 6.99−7.08 (m,

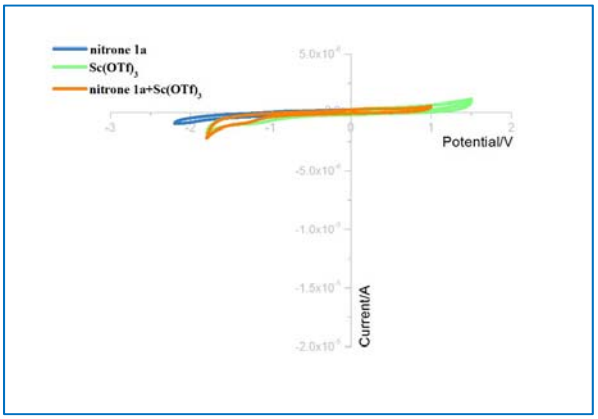
2H), 7.08−7.14 (m, 2H), 7.17−7.37 (m, 6H), 7.40−7.49 (m, 2H), 7.77−7.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.5, 27.1, 35.9, 50.0, 60.3, 64.7, 115.5 (d, J = 21.7 Hz), 126.5, 126.9, 128.2, 128.5, 128.6, 128.9, 130.6 (d, J = 9.3 Hz), 133.4 (d, J = 2.9 Hz), 139.0, 143.4, 165.6 (d, J = 254.6 Hz), 199.4; HRMS calcd for $[C_{25}H_{26}FNNaO_2]^+$ (M + Na)$^+$: 414.1840; found: 414.1840.

Cyclic Voltammetry Experiments:

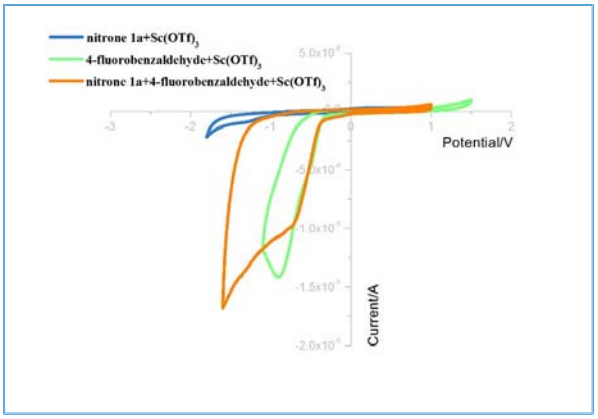
Cyclic voltammetry was performed on a CHI660E electrochemical analyzer. All data were obtained at 10 ºC and 50 mV/s sweep rate using a three electrode setup: Pt wire counter electrode, glassy carbon working electrode and saturated calomel reference electrode (SCE). A 0.01 M CH_3CN solution of nitrone **1a** or 4-fluorobenzaldehyde [with or without $Sc(OTf)_3$] was prepared with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. The solutions were sparged with nitrogen for 10 minutes prior to acquiring all CV data.



Supplementary Figure 4. **CV of 4-fluorobenzaldehyde and $Sc(OTf)_3$.** Addition of $Sc(OTf)_3$ resulted in a significant reduction in 4-fluorobenzaldehyde's half-wave potential which shifted from −1.86 V to −0.62 V (*vs.* SCE) in CH_3CN.



Supplementary Figure 5. **CV of nitrone 1a and $Sc(OTf)_3$.** Addition of $Sc(OTf)_3$ has no significant influence on nitrone **1a**'s half-wave potential in CH_3CN.



Supplementary Figure 6. **CV of nitrone 1a, 4-fluorobenzaldehyde and $Sc(OTf)_3$.** A mixture of nitrone **1a**, 4-fluorobenzaldehyde and $Sc(OTf)_3$ with an onset potential $E_{op} > -0.5$ V (*vs.* SCE) in CH_3CN.

Solubility of Nitrones, Aldehydes and Lewis Acids in Acetonitrile or 1,2-Dichloroethane:

The solubility of nitrone **1a**, 4-fluorobenzaldehyde and Lewis acids with the same stoichiometry as the standard photocatalytic condition demonstrated in Supplementary Table 4 was investigated (Supplementary Fig. 7). Lewis acids, such as $La(OTf)_3$, showed poor solubility in CH_3CN (Supplementary Fig. 7-A, entry I). Addition of 4-fluorobenzaldehyde has no significant influence on $La(OTf)_3$'s solubility (Supplementary Fig. 7-A, entry II). However, nitrones (such as **1a**) can significantly improve the solubility of $La(OTf)_3$ in CH_3CN to give a homogeneous and transparent solution (Supplementary Fig. 7-A, entries III and IV). Similar solubility of nitrone **1a**, 4-fluorobenzaldehyde and $Sc(OTf)_3$ in DCE was observed (Supplementary Fig. 7-B). Taking full account of control experiments, CV experiments and reactants' solubility studies, a complex of nitrone, aldehyde and Lewis acid is a plausible starting point of the photocatalytic reaction.

A:

(**I**) $La(OTf)_3$ (26 mg, 0.045 mmol) in CH_3CN (3.0 mL). (**II**) $La(OTf)_3$ (26 mg, 0.045 mmol) and 4-fluorobenzaldehyde (48 μL, 0.45 mmol) in CH_3CN (3.0 mL). (**III**) $La(OTf)_3$ (26 mg, 0.045 mmol) and nitrone **1a** (53 mg, 0.30 mmol) in CH_3CN (3.0 mL). (**IV**) $La(OTf)_3$ (26 mg, 0.045 mmol), nitrone **1a** (53 mg, 0.30 mmol) and 4-fluorobenzaldehyde (48 μL, 0.45 mmol) in CH_3CN (3.0 mL).

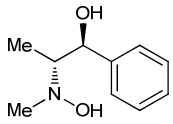
B:

(**I**) $Sc(OTf)_3$ (22 mg, 0.045 mmol) in DCE (3.0 mL). (**II**) $Sc(OTf)_3$ (22 mg, 0.045 mmol) and 4-fluorobenzaldehyde (48 μL, 0.45 mmol) in DCE (3.0 mL). (**III**) $Sc(OTf)_3$ (22 mg, 0.045 mmol) and nitrone **1a** (53 mg, 0.30 mmol) in DCE (3.0 mL). (**IV**) $Sc(OTf)_3$ (22 mg, 0.045 mmol), nitrone **1a** (53 mg, 0.30 mmol) and 4-fluorobenzaldehyde (48 μL, 0.45 mmol) in DCE (3.0 mL).

Supplementary Figure 7. **The solubility of nitrones, aldehydes and Lewis acids in acetonitrile or 1,2-dichloroethane.** Nitrones can improve the solubility of Lewis acids while aldehydes cannot. Thus, Lewis acids have a significantly higher affinity with nitrones than that with aldehydes.

Concise Synthesis of (+)-Ephedrine and (–)-Selegiline:

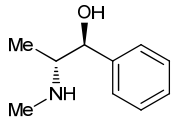
(1*S*,2*R*)-2-(Hydroxy(methyl)amino)-1-phenylpropan-1-ol (**2n**)



Following the **modified method 1**, the asymmetric reductive coupling of nitrone **1n** (110 mg, 1.5 mmol, 5.0 equiv.) with benzaldehyde (31 μL, 0.30 mmol, 1.0 equiv.) gave the desired product **2n** as the major diastereomer [dr = 11/1 (*anti*/*syn*), determined by chiral HPLC analysis] with 94% ee [Lux® Amylose-1 column, Shimadzu HPLC, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 225 nm; t_1 = 7.2 min, t_2 = 8.1 min]. Characterization data was obtained by chromatography on silica gel (eluent: EtOAc; 46.2 mg, 85% combined yield).

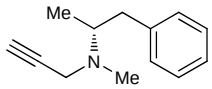
Major diastereomer (*anti*, more polar) as a white solid: mp 69.8−70.4 ºC; $[\alpha]_D^{20}$ = +12.6 (*c* 1.0, MeOH, 94% ee); IR (film) ν_{max}: 3369, 2988, 2850, 1460 cm^{-1}; ^1H NMR (400 MHz, MeOD) δ 0.91 (d, *J* = 6.7 Hz, 3H), 2.68 (s, 3H), 2.73−2.82 (m, 1H), 5.24 (s, 1H), 7.17−7.25 (m, 1H), 7.27−7.42 (m, 4H); ^{13}C NMR (100 MHz, MeOD) δ 9.0, 45.8, 70.5, 73.8, 127.0, 127.8, 129.0, 144.2; HRMS calcd for $[C_{10}H_{15}NNaO_2]^+$ $(M + Na)^+$: 204.0995; found: 204.0995.

(1*S*,2*R*)-Ephedrine (6n)



Following the **general procedure**, the reduction of **2n** (29.8 mg, 0.16 mmol, 94% ee) gave the desired product **6n** as a colorless oil [chromatography on silica gel, eluent: MeOH/CH_2Cl_2 = 1/5 with 1% aqueous NH_3 (sat.); 24.5 mg, 90% yield]: $[\alpha]_D^{20}$ = +30.6 (for **6n•HCl**, *c* 2.0, H_2O, 94% ee), [lit.[14] for (–)-ephedrine•HCl: $[\alpha]_D^{20}$ = –34.7 (*c* 5.0, H_2O)]; IR (film) ν_{max}: 3315, 2927, 2853, 1777, 1668, 1451 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (d, *J* = 6.5 Hz, 3H), 2.47 (s, 3H), 2.76−2.87 (m, 1H), 3.20−3.46 (br, 2H), 4.82 (d, *J* = 3.5 Hz, 1H), 7.21−7.27 (m, 1H), 7.27−7.38 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 33.7, 60.5, 72.9, 126.0, 127.0, 128.0, 141.5; MS (ESI): *m/z* 166 $(M + H)^+$.

(*R*)-Selegiline (8)



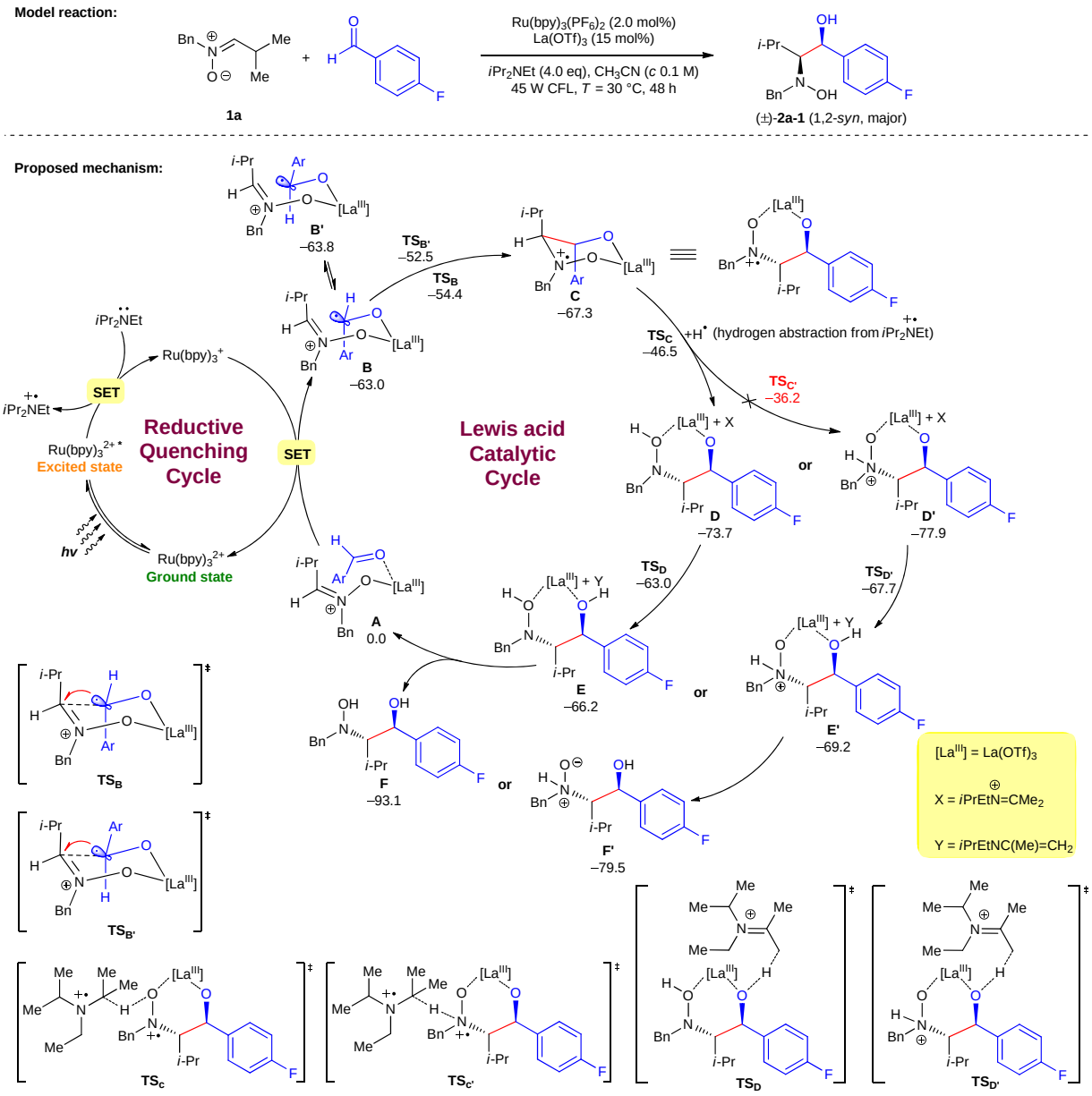
To a 10 mL round bottom flask equipped with a magnetic stir bar was added 10% Pd/C (27.2 mg, 30% wt) and a solution of **2n** (90.6 mg, 0.50 mmol, 1.0 equiv.) in 1 N aqueous HCl (5.0 mL, *c* 0.1 M). The reaction mixture was stirred under hydrogen (1 atmosphere) at 60 ºC for 48 hours. Upon completion, the reaction mixture was cooled to room temperature, filtered through a thin pad of Celite and washed with methanol. The filtrate was concentrated under reduce pressure and then was dried under vacuum to afford crude (*R*)-methamphetamine hydrochloride in quantitative yield, which can be used in next step without further purification.

To a mixture of crude (*R*)-methamphetamine hydrochloride (92.5 mg, ca. 0.50 mmol, 1.0 equiv.) and K_2CO_3 (207 mg, 1.5 mmol, 3.0 equiv.) was added CH_3CN (10.0 mL, *c* 0.05 M) and propargyl bromide (59 μL, ca. 80% wt in toluene, 0.55 mmol, 1.1 equiv.) under an argon atmosphere. The reaction mixture was stirred at 80 ºC for 16 hours. Upon completion, the reaction mixture was cooled to room temperature, filtered, washed with CH_2Cl_2 and concentrated under reduce pressure. The residue was purified by flash chromatography on silica gel to afford the desired product **8** as a yellow oil (eluent: EtOAc/PE = 1/4; 84.4 mg, 90% yield for two steps from **2n**): $[\alpha]_D^{25}$ = –1.02 (*c* 1.0, EtOH, 94% ee), [lit.[15] for **8**: $[\alpha]_D^{20}$ = –1.29 (*c* 6.43, EtOH, > 99% ee)]; IR (film) ν_{max}: 3295, 3026, 2959, 2930, 2786, 1454 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.96 (d, *J* = 6.5 Hz, 3H), 2.23 (t, *J* = 2.3 Hz, 1H), 2.38

(dd, J = 12.8, 9.5 Hz, 1H), 2.41 (s, 3H), 2.92−3.02 (m, 1H), 3.03 (dd, J = 12.8, 4.0 Hz, 1H), 3.41 (d, J = 2.3 Hz, 2H), 7.14−7.21 (m, 3H), 7.23−7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.0, 37.3, 39.7, 43.0, 59.3, 72.4, 80.3, 125.8, 128.2, 129.2, 140.2; MS (ESI): m/z 188 $(M + H)^+$.

DFT Calculations for the Proposed Mechanism Cycle:

To determinate the proposed mechanism of our photocatalytic reductive cross-coupling reaction of nitrones with aldehydes, the detailed density functional theory (DFT) calculations were performed (Supplementary Fig. 8).



Supplementary Figure 8. **DFT calculations of La(OTf)$_3$-promoted photocatalytic reductive cross-coupling reaction of nitrones with aldehydes (ΔG in kcal/mol at 298 K).** The detailed DFT calculations were performed. Note that iPr$_2$NEt (DIPEA) was used as sacrificed reductant and hydrogen-source. Thus, $[i\text{Pr}_2(\text{Et})\text{N}\cdot]^+$ (formed by donating an electron from DIPEA to the photo-excited state of $[\text{Ru(bpy)}_3]^{2+}$) and $[i\text{Pr(Et)N=C(Me)}_2]^+$ were used as hydrogen- and proton-sources in the hydrogen-abstraction and proton-transfer steps, respectively.

Computational methods: All calculations were carried out with the Gaussian 09 programs[16]. The geometries of all the species were fully optimized by using DFT of the B3LYP method[17,18]. This method was proven to be reliable for description of geometrical parameters and electronic structures as well as for studying the substrates and reproducing the ground state geometry of La(III) based systems[19–22]. It has been successfully applied to the mechanistic studies of various catalytic reactions. The 6-31G (d)[23] basis set was used for all atoms except for lanthanum. For all systems the core electrons of lanthanum are described with quasi-relativistic effective core potential (ECP) which were optimized by the Stuttgard-Dresden group[24–26]. The large core ECP (MWB46) that considers the 4f electrons in the core and the 5s, 5p, 5d and 6s electrons in the valence shell (11 valence electrons) is applied to La(III). As it is stated in the literature, the 4f electrons do not take part in the metal-ligand bond because of their contraction in the core[22]. The large core ECP is used in combination with the optimized basis set. All stationary points were verified as minima or first-order saddle points by vibrational frequency analysis. IRC[27] calculations were used to confirm the transition state (TS). The intermediates were characterized by all real frequencies. All discussed energies are Gibbs free energies at 298 K and the solvent effects of acetonitrile solvent (ε = 37.5) for lanthanum catalysis were studied by performing the self-consistent reaction field (SCRF) of the SMD method of Truhlar and Cramer[28] at the same computational level.

Complexes Formed from Nitrones, Aldehydes, $La(OTf)_3$ and Their Anions:

The electron affinity of nitrone **1a**, 4-fluorobenzaldehyde (**FBA**) in acetonitrile solvent is predicted to be 23.4 and 45.1 kcal/mol (in free energy), respectively (see Supplementary Equations 1 and 2).

$$\mathbf{1a} + e \rightarrow [\mathbf{1a}]^- \qquad \Delta G(298K) = -23.4,\ \Delta E = -23.0 \qquad (1)$$

$$\mathbf{FBA} + e \rightarrow [\mathbf{FBA}]^- \qquad \Delta G(298K) = -45.1,\ \Delta E = -44.7 \qquad (2)$$

Ligation of nitrone **1a** to the Lewis acid $La(OTf)_3$ is slightly stronger than that of **FBA**. Thus, both complexes $La(OTf)_3(\mathbf{1a})_2$ and **A** [**A** = $La(OTf)_3(\mathbf{1a})(\mathbf{FBA})$] can be formed within the solution (see Supplementary Equations 3 and 4).

$$La(OTf)_3 + 2\ (\mathbf{1a}) \rightarrow La(OTf)_3(\mathbf{1a})_2 \qquad \Delta G(298K) = 15.7,\ \Delta E = -10.9 \qquad (3)$$

$$La(OTf)_3(\mathbf{1a})_2 + \mathbf{FBA} \rightarrow \mathbf{A} + \mathbf{1a} \qquad \Delta G(298K) = 3.8,\ \Delta E = 6.0 \qquad (4)$$

However, complex **A** is found to be much more electron-withdrawing than $La(OTf)_3(\mathbf{1a})_2$ and, upon SET from the photo-generated $Ru(bpy)_3^+$, the formation of cross-coupling precursor **B** (**B** = $[La(OTf)_3(\mathbf{1a})(\mathbf{FBA})]^-$) is overwhelmingly favored over the formation of homocoupling precursors $[La(OTf)_3(\mathbf{1a})_2]^-$ and $[La(OTf)_3(\mathbf{FBA})_2]^-$ (see Supplementary Equations 5 to 7).

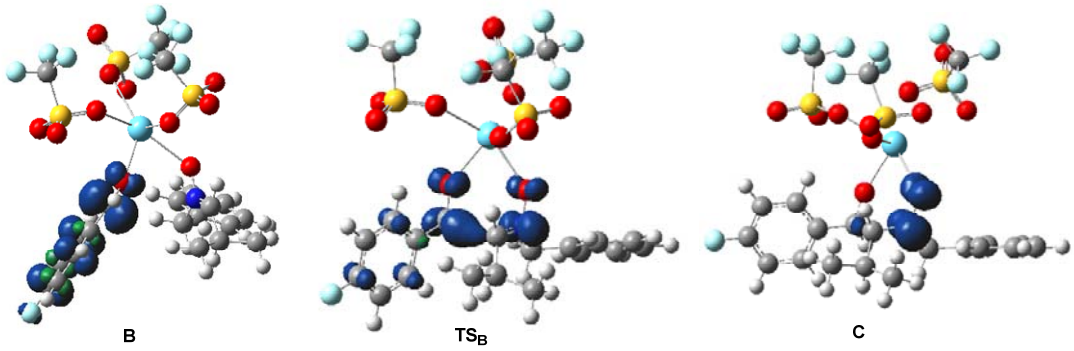
$$La(OTf)_3(\mathbf{1a})_2 + e \rightarrow [La(OTf)_3(\mathbf{1a})_2]^- \qquad \Delta G(298K) = -42.9,\ \Delta E = -41.2 \qquad (5)$$

$$\mathbf{A} + e \rightarrow \mathbf{B} \qquad \Delta G(298K) = -63.0,\ \Delta E = -63.6 \qquad (6)$$

$$\mathbf{B} + \mathbf{FBA} \rightarrow [La(OTf)_3(\mathbf{FBA})_2]^- + \mathbf{1a} \qquad \Delta G(298K) = 3.6,\ \Delta E = 5.0 \qquad (7)$$

It is also clear that complexation to the Lewis acid significantly enhances the electron affinity of **FBA** (by ~18 kcal/mol) and, as a result, promotes the rate of SET from photo-generated $Ru(bpy)_3^+$ to complex **A**. The attached electron in the as-formed cross-coupling precursor **B** is delocalized within the **FBA** moiety (Supplementary Fig. 9). After the cross-coupling carbon-carbon bond formation (via transition state $\mathbf{TS_B}$), the as-formed intermediate **C** has the spin-unpaired electron mostly localized within the *N-O* π*-orbital. This accounts for the preferential addition of

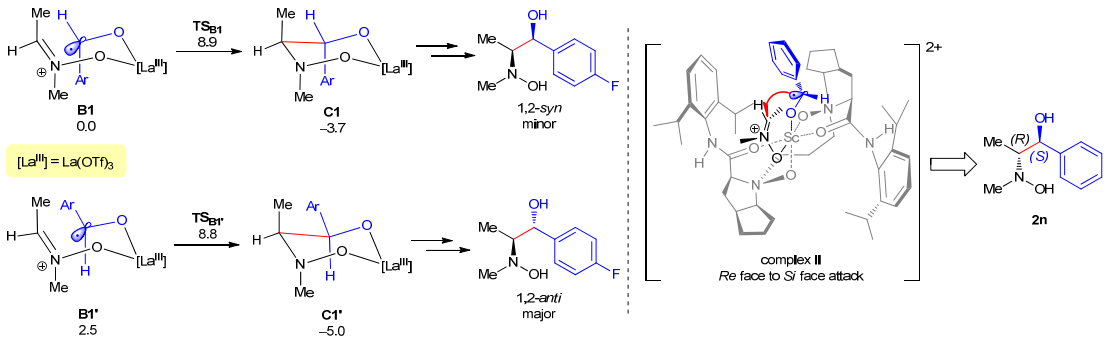
hydrogen (abstracted from the $[(i\text{Pr})_2\text{EtN}\cdot]^+$ radical cation via $\mathbf{TS_C}$) to the nitroxyl *O* atom in the following elementary step.



Supplementary Figure 9. **The spin density distribution within intermediate B, transition State $\mathbf{TS_B}$ and intermediate C.** As shown in the figure, the attached electron in **B** is delocalized within the **FBA** moiety, which agrees well with the mechanism that this photocatalytic reaction is initiated by SET reduction of aldehydes. The as-formed intermediate **C** (via $\mathbf{TS_B}$) has the spin-unpaired electron mostly localized within the *N*-*O* π*-orbital, so the addition of hydrogen to the nitroxyl *O* atom in the following elementary step is preferential.

Understanding the Stereoselectivity of Photocatalytic Cross-Coupling of Nitrone 1n with FBA:

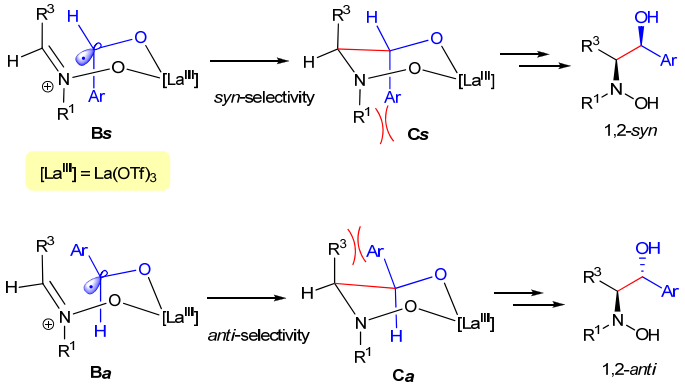
For the photocatalytic reductive cross-coupling of nitrone **1n** with **FBA** catalyzed by $La(OTf)_3$, the *anti*-coupling pathway (via transition state $\mathbf{TS_{B1'}}$, Supplementary Fig. 10) has a smaller barrier height than the *syn*-coupling pathway (via $\mathbf{TS_{B1}}$), which accounts for the stereoselectivity towards *anti*-configuration product. Moreover, the enantioselectivity of cross-coupling product of nitrone **1n** with benzaldehyde is revealed by chiral scandium complex **II**[29] involving a *Re*-to-*Si*-facial attack of the ketyl radical to nitrone **1n**.



Supplementary Figure 10. **DFT-computed relative free energies for precursors, transition states and products of the cross-coupling step between nitrone 1n and FBA ligated to $La(OTf)_3$ (ΔG in kcal/mol at 298 K).** DFT calculations revealed the *anti*-coupling pathway is more favored than *syn*-coupling pathway when nitrone **1n** cross-couples with **FBA**. Moreover, the enantioselectivity is revealed by chiral scandium complex **II** reasonably.

Compare with **2a-1**, **2e~2j** and **2n**, these result suggest *anti*- or *syn*-selectivity of this radical coupling reaction may be determined by interactions between substituent R^1 or R^3 of the aldimine oxide (R^2 = H) and Ar group of the

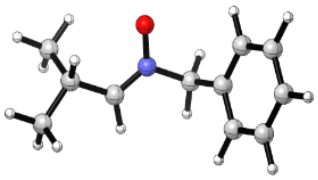
aldehyde. As shown in Supplementary Fig. 11, when R^3 is a bulky group, the interaction between R^3 and Ar will be greater than that between R^1 and Ar, *syn*-vicinal hydroxyamino alcohol will be obtained as a major diastereomer. While R^3 is a small group, the interaction between R^1 and Ar will be greater than that between R^3 and Ar of aldehyde, *anti*-vicinal hydroxyamino alcohol will be obtained as a major diastereomer.



***Supplementary Figure 11*. Understanding the *syn*- or *anti*-stereoselectivity of photocatalytic reductive cross-coupling of nitrones with aromatic aldehydes.** A plausible understanding of diastereomeric selectivity by comparing the relative size of R^3 and R^1.

Molecular Geometries and Energies:

B3LYP/6-31G*/ MWB46 cartesian coordinates and energies in Hartree



1a

Number of imaginary frequencies = 0

0 1

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H	1.91241800	5.66913400	0.73069400
N	2.55279100	4.25467300	-0.59231500
O	3.39873700	3.77800900	-1.43762300
C	3.84854500	6.99837400	-1.47526600
H	3.02007700	7.71723500	-1.46129200
H	4.77739900	7.55466400	-1.65130700
H	3.69723500	6.30791500	-2.31112200
C	4.14616000	7.16244000	1.04870200
H	5.05807100	7.75470500	0.91050500
H	3.30631500	7.86058600	1.15781500
H	4.24466600	6.60503900	1.98794300

H	0.61831200	3.99554400	0.21776000
H	0.92415700	3.23715900	-1.36425300
C	1.67873000	2.11723500	0.32682900
C	1.44506400	1.96873100	1.70060000
C	2.25008600	1.05347400	-0.38647400
C	1.77291900	0.77714100	2.35247300
H	1.00051400	2.78860500	2.26005800
C	2.58134200	-0.13657800	0.26437600
H	2.43626100	1.16476200	-1.45006600
C	2.34342700	-0.27764900	1.63516700
H	1.58127000	0.67319700	3.41729100
H	3.02199300	-0.95523000	-0.29884700
H	2.59677000	-1.20630000	2.14004600
C	3.93189900	6.22129200	-0.14426900
H	4.78400200	5.53225500	-0.22378800

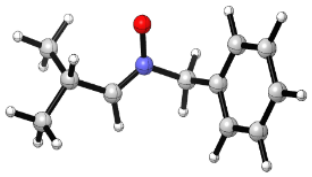
Energies (0K) = -558.122421

Energies (0K) + ZPE = -557.881501

Enthalpies (298K) = -557.867816

Free Energies (298K) = -557.922002

[1a]$^-$



Number of imaginary frequencies = 1

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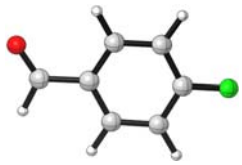
H	1.80353700	5.76072300	0.54008600
N	2.33612600	4.29349300	-0.81725700
O	3.25461100	3.79417800	-1.64901200
C	3.80825200	6.91695400	-1.32546500
H	2.98971200	7.64645400	-1.23829700
H	4.73455700	7.47968300	-1.52199900
H	3.60883500	6.27148600	-2.18708100
C	4.23561200	6.91090000	1.17137600
H	5.14918600	7.50229300	1.02222500
H	3.42014200	7.61877100	1.38005900
H	4.37052400	6.29569500	2.07033600
H	0.40618200	3.96238700	-0.06298500
H	0.81714500	3.10995200	-1.57603300
C	1.57538900	2.17180500	0.20898100

C	1.44836700	2.14299600	1.60902600
C	2.20301500	1.08601200	-0.42643000
C	1.91757800	1.05584700	2.35077400
H	0.96871100	2.97672400	2.11762800
C	2.67456800	-0.00152500	0.31259400
H	2.32259000	1.10585600	-1.50575700
C	2.53371400	-0.02210800	1.70537600
H	1.79937400	1.04741400	3.43213200
H	3.15110600	-0.83626900	-0.19697000
H	2.89692300	-0.87028700	2.28066200
C	3.91127300	6.04161300	-0.05384400
H	4.75769900	5.35830500	-0.22436800

Energies (0K) = -558.1540562
Energies (0K) + ZPE = -557.918175
Enthalpies (298K) = -557.904127
Free Energies (298K) = -557.959253

4-fluorobenzaldehyde = FBA



Number of imaginary frequencies = 0
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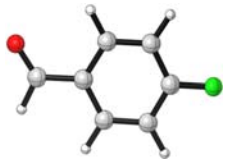
C	-2.16870000	9.96288800	0.34930800
C	-2.88369100	11.15671700	0.34834600
C	-4.27778100	11.20564900	0.34800100
C	-4.97872800	10.00621900	0.34863500
H	-2.35632700	7.81929600	0.35070000
H	-1.08380400	9.98113100	0.34954900
H	-4.78287100	12.16614700	0.34725300
H	-6.06439800	10.00310500	0.34839200
C	-5.02657100	7.50295200	0.35026100
H	-4.38433800	6.59807600	0.35081300
O	-6.24435400	7.40124800	0.34997000
F	-2.19995400	12.32021300	0.34771800

Energies (0K) = -444.8102625
Energies (0K) + ZPE = -444.708281
Enthalpies (298K) = -444.700222
Free Energies (298K) = -444.740139



[FBA]$^-$

Number of imaginary frequencies = 1

-1 2

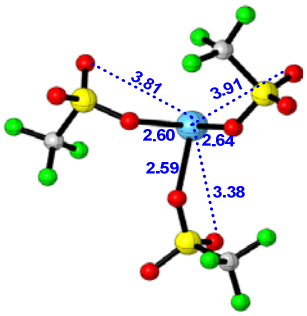
C	-4.30496900	8.73288500	0.34957300
C	-2.86845300	8.76988700	0.34991900
C	-2.16634700	9.96392900	0.34934400
C	-2.87580100	11.17572400	0.34839800
C	-4.27465300	11.20156900	0.34798700
C	-4.97935300	10.00662200	0.34855000
H	-2.31896600	7.82890600	0.35067500
H	-1.07893500	9.97999900	0.34960900
H	-4.78964300	12.16006300	0.34721200
H	-6.06592100	10.00978100	0.34824300
C	-5.03347500	7.50729000	0.35024700
H	-4.39325700	6.59169100	0.35093400
O	-6.29903100	7.38353900	0.34999900
F	-2.17825600	12.36090900	0.34779800

Energies (0K) = -444.8779447

Energies (0K) + ZPE = -444.779533

Enthalpies (298K) = -444.771255

Free Energies (298K) = -444.812089



La(OTf)$_3$

Number of imaginary frequencies = 0

0 1

O	2.40212200	4.24699600	0.95787100
S	1.37545400	5.04051300	1.64659400
O	1.66535500	6.46761600	1.88530600
O	-0.02088900	4.79432100	1.12319200
C	1.28418000	4.31332600	3.35628000
F	0.99082900	3.00943300	3.31053300
F	2.45479700	4.46749600	3.98824200
F	0.33121600	4.93781000	4.08208300

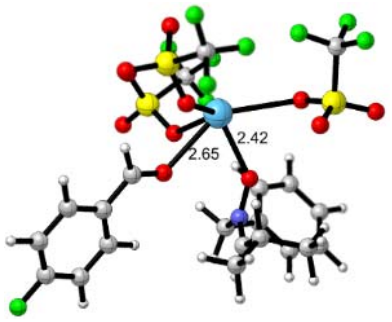
O	-2.95493000	1.74114900	4.22830000
S	-3.20293900	3.14090500	3.86209200
O	-3.24905300	4.13390500	4.95293800
O	-2.40177300	3.60739500	2.66776200
C	-4.92420400	3.16690900	3.16230300
F	-5.06082900	2.26764300	2.18197100
F	-5.18750800	4.39011900	2.64914100
F	-5.82959200	2.91006200	4.11322000
O	-4.46794100	3.77565200	-1.79728800
S	-3.35489400	4.67461100	-1.45849400
O	-3.53078800	6.10899000	-1.75996400
O	-2.77279500	4.42018900	-0.08713400
C	-1.95748200	4.13240600	-2.55454600
F	-1.61523400	2.86471900	-2.29243300
F	-0.88240900	4.91315100	-2.36542800
F	-2.32322100	4.22070100	-3.84118000
La	-2.22038500	6.06637100	1.83647800

Energies (0K) = -2916.21933

Energies (0K) + ZPE = -2916.133254

Enthalpies (298K) = -2916.106048

Free Energies (298K) = -2916.19435



A = La(OTf)$_3$(1a)(FBA)

Number of imaginary frequencies = 0

0 1

O	-4.12668400	2.18959200	1.67919400
O	1.37309300	2.18460500	0.58944000
S	0.28956300	3.12855900	0.29046500
O	0.33034400	3.83417300	-1.00459700
O	-1.08521400	2.59325600	0.63084100
C	0.46405500	4.49058300	1.54351800
F	0.43498600	4.00299400	2.79152600
F	1.61178000	5.15249600	1.36876700
F	-0.55622900	5.36530900	1.41072400
O	-7.04753000	4.63457400	0.83397400
S	-6.28892300	5.49528700	1.76293300

O	-6.88191800	5.74217900	3.08539700
O	-4.81579800	5.17544100	1.81267300
C	-6.27022500	7.15788200	0.93529500
F	-5.69660100	7.06577700	-0.27877900
F	-5.57154900	8.04159300	1.66193200
F	-7.51626700	7.62350300	0.77860200
O	-3.38210500	5.69937700	-3.36843000
S	-4.27760600	4.56709700	-3.67717500
O	-4.03745900	3.84744300	-4.93730400
O	-4.51152500	3.64656300	-2.50129400
C	-5.95566400	5.33665800	-3.88111600
F	-6.32032400	5.97011900	-2.75578200
F	-6.87273500	4.39960300	-4.15668300
F	-5.93596600	6.22604000	-4.88284800
O	-3.19692300	1.31094800	-1.06325700
C	-3.13319700	0.89460200	-2.23073900
H	-3.27623600	1.59777600	-3.06365500
C	-2.88159100	-0.49165200	-2.59079600
C	-2.66889600	-1.48633100	-1.61408000
C	-2.85904900	-0.83192500	-3.95693100
C	-2.43803500	-2.79929300	-1.99645600
H	-2.68537300	-1.21866900	-0.56284800
C	-2.63008300	-2.14482100	-4.35199400
H	-3.02349800	-0.06071900	-4.70448800
C	-2.42509600	-3.10030500	-3.36008100
H	-2.26997500	-3.58765000	-1.27038000
H	-2.60820200	-2.43501200	-5.39687500
La	-3.38124600	3.74303800	-0.02638100
C	-2.94712300	0.38212500	2.65204200
C	-5.14261200	0.12980200	1.60812400
H	-5.04822100	-0.91064400	1.90244000
N	-4.14201000	0.88848900	1.91830200
C	-6.88875900	-0.43856700	-0.06798500
H	-7.11929500	-1.38825700	0.42981500
H	-7.80316900	-0.07907800	-0.55231800
H	-6.14486300	-0.63391100	-0.84834100
C	-7.45678700	0.90690400	2.01847200
H	-8.36938300	1.27310900	1.53520700
H	-7.70870200	0.00240600	2.58428300
H	-7.11080700	1.67058100	2.72275700
H	-3.01776300	-0.70721600	2.66018300
H	-2.08478700	0.68764000	2.05660600
C	-2.87844800	0.94919800	4.05293100
C	-3.72123400	0.45334700	5.05772700

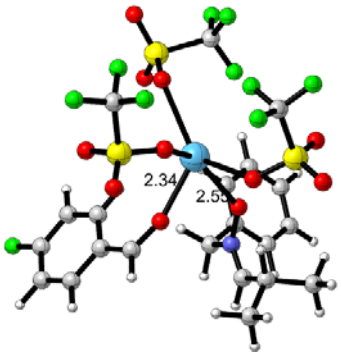
C	-1.97280100	1.97162900	4.36136900
C	-3.66290500	0.97712700	6.35013500
H	-4.42220600	-0.34571000	4.82757000
C	-1.91117400	2.49399800	5.65625600
H	-1.31158500	2.35318800	3.58918800
C	-2.75739900	1.99950100	6.65172300
H	-4.31938400	0.58476500	7.12219900
H	-1.20185600	3.28502200	5.88496400
H	-2.70984200	2.40488400	7.65893700
C	-6.38991900	0.60907100	0.93965000
H	-6.16846000	1.54368700	0.41624100
F	-2.20277600	-4.37404400	-3.73028500

Energies (0K) = -3919.1630476

Energies (0K) + ZPE = -3918.730808

Enthalpies (298K) = -3918.67988

Free Energies (298K) = -3918.82543



B = $[La(OTf)_3(1a)(FBA)]^-$

Number of imaginary frequencies = 0

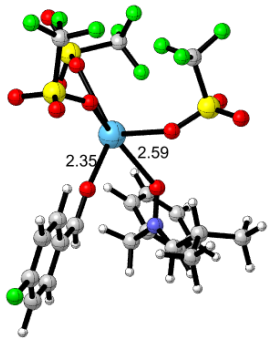
-1 2

C	-1.73786000	-3.81472900	1.30938100
C	-3.64494600	-2.55024000	0.47576300
N	-2.45688600	-2.54809500	0.99075700
O	-1.80756400	-1.44885300	1.31374300
O	4.77538700	1.17491200	0.89524200
S	3.47290700	0.52846200	1.10854700
O	2.39086300	1.01772200	0.18197800
O	3.46642200	-0.93677100	1.29008800
C	2.88822400	1.18073100	2.74906100
F	3.72947100	0.82977400	3.72834100
F	2.78561000	2.51619700	2.72759300
F	1.66829100	0.67496000	3.04292100
O	-3.84872600	3.18066900	0.76219600
S	-2.53781100	2.58322500	1.05156500
O	-2.23965100	2.24642000	2.45557300

O	-2.15031700	1.49771400	0.07454100
C	-1.30065000	3.90904800	0.64773200
F	-1.43000700	4.33448700	-0.61395500
F	-0.05085100	3.42442500	0.80647100
F	-1.45282100	4.95476300	1.47029800
O	0.07033400	1.49965000	-1.94737400
S	0.68419100	1.33229800	-3.31501100
O	1.66550800	0.23573400	-3.40032100
O	-0.28923300	1.44591700	-4.41349100
C	1.69980900	2.88268400	-3.43491800
F	0.92037200	3.96724800	-3.30508800
F	2.31347500	2.94198900	-4.62723200
F	2.63522700	2.91755100	-2.47628600
O	-1.01131000	-1.40252200	-1.59273400
C	-1.09424900	-2.36630400	-2.47754100
C	-0.19775400	-3.46231200	-2.56718000
C	-0.38897400	-4.47120300	-3.56319800
C	0.91880200	-3.62220000	-1.68644400
C	0.46484200	-5.55692600	-3.67139100
H	-1.22691700	-4.37959600	-4.25071100
C	1.77568700	-4.71274000	-1.79504200
H	1.10583600	-2.87853500	-0.91693000
C	1.54041700	-5.66617300	-2.78320500
H	0.31531500	-6.32037400	-4.42959600
H	2.62306200	-4.83223700	-1.12548800
La	-0.07638100	-0.05070700	0.07819300
H	-4.07629900	-3.52956700	0.29447000
H	-1.92223300	-2.31493800	-3.19353500
C	-5.40015000	-1.03485100	1.34986200
H	-6.11305700	-1.85745200	1.48286100
H	-4.85714600	-0.89511600	2.29104300
H	-5.96915900	-0.12070100	1.14483800
C	-5.19191500	-1.47837100	-1.14833000
H	-5.90235700	-2.31319100	-1.10167700
H	-5.75730700	-0.56553800	-1.36715700
H	-4.50595900	-1.66025000	-1.98345100
C	-4.43192800	-1.31549500	0.17808700
H	-3.73768300	-0.47525600	0.09978900
H	-2.34853300	-4.63668600	0.93123500
H	-0.80291300	-3.77730100	0.74533700
C	-1.48005700	-3.94867900	2.79249900
C	-2.50352600	-4.37355900	3.65131300
C	-0.22062100	-3.64949900	3.32702500
C	-2.27306700	-4.48931900	5.02326200

H	-3.48223800	-4.61548700	3.24333800
C	0.01297100	-3.76766200	4.69970900
H	0.58193100	-3.33430500	2.66453200
C	-1.01400300	-4.18519300	5.55024300
H	-3.07340000	-4.82115800	5.67934600
H	0.99559500	-3.53674500	5.10246700
H	-0.83331600	-4.27824400	6.61783200
F	2.37959300	-6.73583600	-2.88979100

Energies (0K) = -3919.2608022
Energies (0K) + ZPE = -3918.832089
Enthalpies (298K) = -3918.780946
Free Energies (298K) = -3918.925805



B′
(another isomer of [La(OTf)$_3$(1a)(FBA)]$^-$)
Number of imaginary frequencies = 0
-1 2

C	-4.28471900	-2.08593300	2.59075700
C	-6.29156100	-0.87496700	1.92897900
N	-5.05292000	-0.83991900	2.30764100
O	-4.38876500	0.27685600	2.52108600
O	2.09611000	3.33878900	1.90877900
S	0.84152200	2.60460200	2.13454300
O	-0.23757900	2.91340400	1.13206500
O	0.95709400	1.16836500	2.46332000
C	0.13371700	3.35019400	3.68182000
F	0.94196400	3.14584600	4.72920300
F	-0.06058300	4.66860900	3.54113100
F	-1.06296000	2.78288300	3.95967700
O	-6.55681200	4.65963100	1.96033800
S	-5.17002200	4.19702900	2.10939200
O	-4.68752800	3.92690700	3.47641500
O	-4.79104000	3.12424400	1.11484600
C	-4.12207500	5.62178300	1.53813000
F	-4.44782900	5.99628700	0.29556700
F	-2.82200800	5.26908700	1.54993700

F	-4.28109600	6.67112100	2.35631300
O	-2.59363200	3.15028700	-0.92028300
S	-1.99695400	3.34169500	-2.28939000
O	-0.84355800	2.47028700	-2.57551300
O	-3.00946100	3.47604800	-3.35120500
C	-1.28064900	5.04767400	-2.12378800
F	-2.23941400	5.92983100	-1.80191800
F	-0.72616100	5.42896900	-3.28590500
F	-0.33759700	5.08358200	-1.17415200
O	-3.64895200	0.23155300	-0.53925500
C	-4.08987700	-0.88808100	-1.06720300
C	-4.61335500	-0.98920400	-2.38269200
C	-5.08587100	-2.24402800	-2.87840800
C	-4.69375300	0.13617400	-3.26139500
C	-5.60120500	-2.36942700	-4.15979400
H	-5.03862600	-3.11876600	-2.23329100
C	-5.20902100	0.00817100	-4.54548000
H	-4.33951000	1.10241700	-2.91735400
C	-5.65672900	-1.23915000	-4.98013000
H	-5.96000100	-3.32402900	-4.53428200
H	-5.26681600	0.86162500	-5.21560600
La	-2.69792900	1.61903700	1.09810900
H	-6.72593800	-1.86489400	1.83198600
H	-4.04626600	-1.79733200	-0.45635300
C	-8.05362700	0.60207000	2.86082300
H	-8.74280900	-0.23610600	3.01927600
H	-7.48429400	0.75768400	3.78385400
H	-8.64944400	1.50234100	2.67151000
C	-7.91792500	0.15484900	0.35842700
H	-8.60822100	-0.69481900	0.43151000
H	-8.50966700	1.05482100	0.15643900
H	-7.25548600	-0.01592500	-0.49743500
C	-7.11834200	0.33992500	1.65958300
H	-6.44463400	1.19347400	1.55266900
H	-4.90714400	-2.92758200	2.28108500
H	-3.40030600	-2.04093900	1.95052500
C	-3.90090900	-2.18399900	4.04935800
C	-4.85153900	-2.57530700	5.00285000
C	-2.59651400	-1.89048500	4.46561700
C	-4.50438500	-2.66389800	6.35186800
H	-5.86522600	-2.81105800	4.68720900
C	-2.24629400	-1.98197200	5.81556100
H	-1.85072500	-1.59995800	3.72940400
C	-3.20035900	-2.36695900	6.76083000

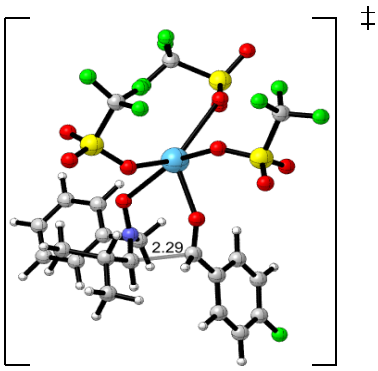
H	-5.24886600	-2.96967600	7.08214900
H	-1.22983200	-1.75543400	6.12624900
H	-2.92925500	-2.43925400	7.81077900
F	-6.16204300	-1.36189600	-6.24127200

Energies (0K) = -3919.2597517

Energies (0K) + ZPE = -3918.831408

Enthalpies (298K) = -3918.779906

Free Energies (298K) = -3918.927138



TS_B

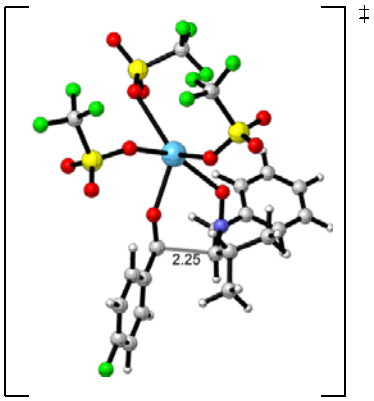
Number of imaginary frequencies = 1

-1 2

C	-3.76672600	-1.95735700	2.65242000
C	-5.49890600	-0.95503300	1.19719300
N	-4.54376100	-0.82225700	2.12538100
O	-4.18493000	0.37948100	2.59237600
O	2.15582400	3.68305100	2.27611000
S	0.89934300	2.94536000	2.48056200
O	-0.15908900	3.24024100	1.45326200
O	1.01449400	1.51221000	2.82327600
C	0.16069100	3.70152900	4.00923500
F	0.95536600	3.51726500	5.07066400
F	-0.04348200	5.01649000	3.84994800
F	-1.03504900	3.12769100	4.27833800
O	-6.84081700	4.63077800	1.75596100
S	-5.47934400	4.23860700	2.14642900
O	-5.23248400	3.97380200	3.57617400
O	-4.86719700	3.20898500	1.22717200
C	-4.42693200	5.72767900	1.78887000
F	-4.55790100	6.12095500	0.51636900
F	-3.12804200	5.43268200	2.00888900
F	-4.76526600	6.74709600	2.58867700
O	-2.48394900	3.43592900	-0.65898400
S	-1.88615000	3.24718000	-2.03023200
O	-0.86418300	2.18658600	-2.09908300

O	-2.87978700	3.28702900	-3.11624300
C	-0.93150500	4.82852800	-2.22651400
F	-1.75008800	5.88784000	-2.12939400
F	-0.34094900	4.86024400	-3.43214200
F	0.01842700	4.94049300	-1.28908400
O	-3.54224700	0.51718900	-0.25836000
C	-4.29932900	-0.45455900	-0.68242900
C	-3.72497700	-1.75161900	-1.05350700
C	-4.50641900	-2.70422900	-1.74379500
C	-2.39371500	-2.08814400	-0.72825400
C	-3.98749900	-3.94771400	-2.09029900
H	-5.53163600	-2.46040000	-2.01162200
C	-1.86223800	-3.33101100	-1.06895200
H	-1.77318800	-1.36213500	-0.21198600
C	-2.67010300	-4.24074000	-1.74283600
H	-4.58133100	-4.68309300	-2.62449200
H	-0.83789100	-3.59672600	-0.82545000
La	-2.62827000	1.92347800	1.41446600
H	-5.73893200	-1.99017500	0.97346700
H	-5.21413600	-0.17660100	-1.21442900
C	-7.31026800	0.23669100	2.46441600
H	-7.77777800	-0.70041200	2.79189800
H	-6.59522100	0.55454600	3.22775500
H	-8.09655400	0.99822600	2.39266900
C	-7.65667600	-0.36416800	0.04257000
H	-8.11050600	-1.32708400	0.31097900
H	-8.46099000	0.37805000	-0.01601200
H	-7.22755100	-0.46488100	-0.95958800
C	-6.62091900	0.06367900	1.09325800
H	-6.19524900	1.03268300	0.81201800
H	-3.99159300	-2.82745200	2.03213600
H	-2.70679100	-1.71003100	2.54040100
C	-4.09989400	-2.23192400	4.10666500
C	-5.26564900	-2.93601800	4.44234400
C	-3.26245200	-1.77656100	5.13248200
C	-5.59120000	-3.17366500	5.77879000
H	-5.91910700	-3.30133600	3.65341900
C	-3.58552300	-2.01430500	6.47179700
H	-2.34985400	-1.24082200	4.88117300
C	-4.75138100	-2.71173200	6.79738300
H	-6.49615500	-3.72318300	6.02492000
H	-2.92616600	-1.65655100	7.25831400
H	-5.00337700	-2.89823700	7.83803900
F	-2.15817100	-5.45253700	-2.07859200

Energies (0K) = -3919.2488226
Energies (0K) + ZPE = -3918.820054
Enthalpies (298K) = -3918.770045
Free Energies (298K) = -3918.912131



$TS_{B'}$
Number of imaginary frequencies = 1
-1 2

C	-3.90130700	-2.04322800	2.45586800
C	-5.57533500	-0.93308200	1.02455500
N	-4.66532800	-0.86712800	2.01558300
O	-4.17137000	0.30816600	2.42729600
O	2.17610400	3.55119000	2.06512200
S	0.92164000	2.81389200	2.28246600
O	-0.15272900	3.12288000	1.27529200
O	1.03794100	1.37675800	2.60677900
C	0.20803200	3.55251200	3.83086400
F	1.01718200	3.34674800	4.87774400
F	0.00982000	4.87037300	3.69549100
F	-0.98606200	2.97929400	4.10722900
O	-6.44998600	5.00269800	1.91986800
S	-5.14330300	4.41195400	2.24105500
O	-4.88269200	4.06990600	3.65137500
O	-4.72089900	3.33614600	1.26865700
C	-3.90628300	5.74883200	1.87594700
F	-4.02850900	6.20017700	0.62210400
F	-2.65593300	5.26515600	2.03142000
F	-4.06661200	6.77730100	2.71858900
O	-2.52630200	3.32984600	-0.80591300
S	-2.15076300	3.28360600	-2.26426500
O	-1.07779500	2.32348900	-2.57968600
O	-3.30971900	3.31448500	-3.17329700
C	-1.36435000	4.95482500	-2.47285200
F	-2.22172400	5.92709400	-2.12750900

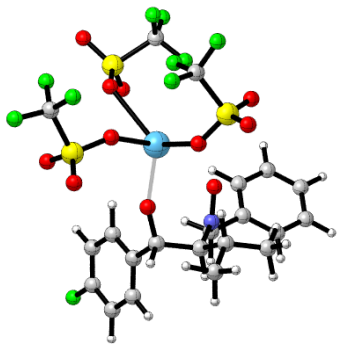
F	-1.00981700	5.13799900	-3.75454500
F	-0.26672500	5.06856800	-1.71142700
O	-3.58251300	0.42901100	-0.44255300
C	-4.13193900	-0.72827800	-0.69125200
C	-4.89960900	-0.92600300	-1.92540200
C	-5.29596800	-2.22364600	-2.31374600
C	-5.25198800	0.16329900	-2.74986000
C	-6.03557900	-2.43199400	-3.47383800
H	-5.01913500	-3.07513200	-1.69632800
C	-5.99106600	-0.03380700	-3.91472500
H	-4.92419300	1.16145500	-2.47897900
C	-6.37522800	-1.32759400	-4.25272800
H	-6.34397900	-3.42612500	-3.78254400
H	-6.26367000	0.79550700	-4.56061900
La	-2.62421800	1.81878700	1.24704200
H	-5.90690100	-1.94903100	0.82867800
H	-3.62130500	-1.62676700	-0.32396600
C	-7.18375400	0.65338200	2.17133300
H	-7.74672700	-0.15656000	2.65278700
H	-6.40604600	0.99280300	2.85792000
H	-7.87702800	1.48502500	1.99561700
C	-7.72366100	-0.28260200	-0.09596100
H	-8.29205700	-1.09620300	0.37342300
H	-8.41900900	0.54439600	-0.28150000
H	-7.36194700	-0.63891000	-1.06292600
C	-6.58642300	0.18303200	0.82801100
H	-6.07713300	1.04069900	0.37100000
H	-4.35679600	-2.91911200	1.98657300
H	-2.87748300	-1.94032500	2.07541600
C	-3.88818100	-2.19095200	3.96400900
C	-5.07416100	-2.47321000	4.65772400
C	-2.69269300	-2.07078300	4.68169300
C	-5.06329700	-2.62786400	6.04447400
H	-6.00758600	-2.57117800	4.10814400
C	-2.67843300	-2.22985800	6.07115700
H	-1.76750500	-1.85965700	4.14977500
C	-3.86379100	-2.50797200	6.75493200
H	-5.98863800	-2.84693200	6.57101100
H	-1.74250200	-2.13614500	6.61573400
H	-3.85518600	-2.63250900	7.83455400
F	-7.09543900	-1.52423800	-5.38620600

Energies (0K) = -3919.247013

Energies (0K) + ZPE = -3918.817904

Enthalpies (298K) = -3918.768102

Free Energies (298K) = -3918.909155



C

Number of imaginary frequencies = 0

-1 2

C	-1.38061900	-3.97521900	1.32233900
C	-2.68335900	-2.61574900	-0.45000200
N	-1.93205800	-2.70233500	0.81129700
O	-1.48471300	-1.61240300	1.34400800
O	5.02772200	1.48830100	0.91703000
S	3.71274300	0.87876800	1.16282400
O	2.67926100	1.20774000	0.11689300
O	3.68896400	-0.53738200	1.58298400
C	3.04174100	1.77421700	2.64499500
F	3.83522100	1.60185900	3.70889700
F	2.91963400	3.08633400	2.40797500
F	1.81738200	1.28772700	2.95195100
O	-3.61346800	3.28590200	0.82606900
S	-2.30568800	2.68536300	1.12377100
O	-2.03082000	2.32357300	2.52690700
O	-1.89967700	1.61835700	0.13474900
C	-1.07020800	4.02545400	0.76012300
F	-1.20627500	4.48951100	-0.48769400
F	0.18338000	3.54384100	0.89775600
F	-1.22393700	5.04498800	1.61477300
O	0.34532400	1.66054600	-1.91897400
S	0.73638800	1.55895700	-3.37089900
O	1.79885900	0.57221800	-3.63848900
O	-0.40805300	1.57421300	-4.29705800
C	1.54975800	3.21086400	-3.61904200
F	0.70507200	4.20334300	-3.30068300
F	1.91370500	3.35911800	-4.90232400
F	2.64506900	3.32585400	-2.85378500
O	-0.96347700	-1.16501900	-1.40606200
C	-1.67738300	-2.31595300	-1.63619000
C	-0.78988300	-3.53259400	-1.94162300
C	-1.35202300	-4.69176800	-2.50078600

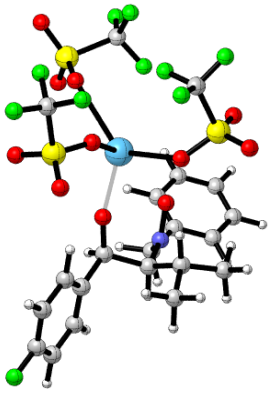
C	0.58994400	-3.51218600	-1.70824000
C	-0.56932000	-5.80634800	-2.80300700
H	-2.41847300	-4.72433600	-2.71265600
C	1.39485600	-4.61718500	-2.00380100
H	1.05020000	-2.61637600	-1.30313700
C	0.79612400	-5.74650800	-2.54453000
H	-0.99954500	-6.70276100	-3.23894000
H	2.46613600	-4.60336400	-1.82704800
La	0.20338000	0.09750900	0.09190200
H	-3.12360300	-3.60509100	-0.60908100
H	-2.33022000	-2.20055000	-2.51741300
C	-4.75296300	-1.93833900	0.85375800
H	-5.22986900	-2.91569700	0.69804700
H	-4.21311200	-1.97337700	1.80571200
H	-5.55115500	-1.19289500	0.95175100
C	-4.64747700	-1.47613000	-1.61693400
H	-5.02117900	-2.45808200	-1.93721300
H	-5.51771600	-0.82971500	-1.45186800
H	-4.07554700	-1.04375300	-2.44417800
C	-3.82800100	-1.57923000	-0.32113000
H	-3.37421200	-0.60336600	-0.12211000
H	-1.92066700	-4.77910100	0.81817900
H	-0.32886100	-4.02599300	1.01577400
C	-1.49288400	-4.10289000	2.82576000
C	-2.69049200	-4.53184600	3.41547900
C	-0.39650800	-3.81128800	3.64754100
C	-2.79093300	-4.66119400	4.80228400
H	-3.54363600	-4.77109300	2.78505500
C	-0.49422300	-3.94037000	5.03556000
H	0.54095000	-3.49365800	3.19686300
C	-1.69245300	-4.36521100	5.61538700
H	-3.72294900	-4.99993600	5.24701600
H	0.36559900	-3.71499600	5.66105600
H	-1.76857000	-4.47120400	6.69435600
F	1.56732600	-6.82407400	-2.83991400

Energies (0K) = -3919.2726993

Energies (0K) + ZPE = -3918.840519

Enthalpies (298K) = -3918.790774

Free Energies (298K) = -3918.932745



C′

Number of imaginary frequencies = 0

-1 2

C	-4.48102300	-2.23154900	2.57018600
C	-5.60208600	-0.80368000	0.75973600
N	-4.90828800	-0.90879400	2.05826200
O	-4.30399700	0.13478600	2.51732400
O	2.25219600	3.44034100	1.61604400
S	1.01272000	2.70847900	1.91985600
O	-0.15735800	3.09924400	1.05979200
O	1.13096000	1.25111700	2.13543000
C	0.48767200	3.35528400	3.58183700
F	1.39445400	3.05877200	4.52096200
F	0.32093300	4.68473200	3.55228700
F	-0.69052600	2.79894000	3.94910600
O	-6.39131300	4.95924400	2.42787700
S	-5.04228100	4.39172300	2.56018800
O	-4.59209400	4.02011000	3.91493400
O	-4.72694200	3.34891400	1.51439600
C	-3.89390500	5.77103300	2.07517100
F	-4.19752500	6.25180000	0.86367200
F	-2.62135600	5.32409600	2.04565000
F	-3.96678000	6.77059500	2.96375600
O	-2.70350300	3.44191100	-0.72946600
S	-2.40456200	3.42926300	-2.20710100
O	-1.31131700	2.51941100	-2.59198000
O	-3.61198600	3.41794800	-3.05127800
C	-1.70396700	5.13539800	-2.43239900
F	-2.58421600	6.06372600	-2.02986700
F	-1.42424400	5.34764100	-3.72760000
F	-0.57452400	5.28659600	-1.72634000
O	-3.85003600	0.57902600	-0.26054300
C	-4.46206000	-0.65379200	-0.33360100
C	-4.94411200	-0.99912600	-1.74831500
C	-5.40733100	-2.28856400	-2.05208300
C	-4.86870900	-0.05453800	-2.77923200

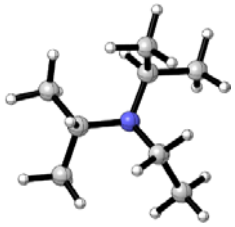
C	-5.80957400	-2.62750700	-3.34511500
H	-5.45117700	-3.04734600	-1.27399600
C	-5.26541800	-0.37470900	-4.08092500
H	-4.49815100	0.94010000	-2.55592900
C	-5.73198100	-1.65706600	-4.33787300
H	-6.16891900	-3.62310200	-3.58694300
H	-5.21161900	0.35337000	-4.88499600
La	-2.63454100	1.83982000	1.21896800
H	-6.09791000	-1.76944200	0.61832200
H	-3.74802100	-1.46070400	-0.07566400
C	-7.54257200	0.17469400	2.08441400
H	-8.06586000	-0.79109000	2.10325700
H	-6.95564200	0.25998400	3.00413700
H	-8.30419600	0.96354000	2.10119700
C	-7.57895900	0.31939200	-0.41822100
H	-8.06579200	-0.65417700	-0.56275600
H	-8.37050000	1.06795500	-0.29027900
H	-7.03797500	0.56506600	-1.33434400
C	-6.67235000	0.31458600	0.82258000
H	-6.14812200	1.27368100	0.87280900
H	-5.29615200	-2.92622300	2.35188900
H	-3.60313400	-2.54754300	1.98925200
C	-4.15402200	-2.21271400	4.04396600
C	-5.17549200	-2.29134600	5.00084800
C	-2.82359300	-2.13034600	4.47484900
C	-4.87192800	-2.27765400	6.36384100
H	-6.21087100	-2.36493100	4.67660900
C	-2.51677100	-2.11807600	5.83806300
H	-2.02442500	-2.08471700	3.73834300
C	-3.54157400	-2.19035600	6.78534700
H	-5.67246900	-2.34069900	7.09629900
H	-1.47991000	-2.05753600	6.15836100
H	-3.30510700	-2.18402900	7.84614000
F	-6.11863000	-1.97840500	-5.60030400

Energies (0K) = -3919.2694203

Energies (0K) + ZPE = -3918.837488

Enthalpies (298K) = -3918.787476

Free Energies (298K) = -3918.930594



***i*Pr$_2$NEt (*i.e.*, DIPEA)**

Number of imaginary frequencies = 0

0 1

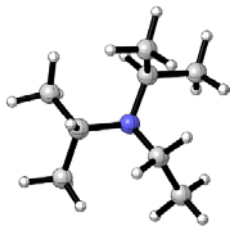
C	1.36283600	-0.23304000	0.27129300
H	1.36971900	-0.30922000	1.37654000
N	0.12243400	0.43565300	-0.18989800
C	2.59729900	0.58782400	-0.13720200
H	2.58126700	1.60440500	0.26689500
H	3.50726800	0.10223000	0.23496400
H	2.66770800	0.65629700	-1.23014800
C	-0.06245900	1.77028300	0.42095300
H	0.63570500	1.90316800	1.25896800
H	-1.06181900	1.84391400	0.86337000
C	-1.10016800	-0.40260900	-0.16247800
H	-0.84633000	-1.32268800	-0.69564400
C	-1.58198800	-0.80876000	1.24548500
H	-2.41719200	-1.51670400	1.17355500
H	-0.78354900	-1.29659100	1.81692100
H	-1.93164100	0.05472800	1.82446600
C	1.51923000	-1.65438100	-0.28836400
H	1.43169300	-1.65769100	-1.38231900
H	2.51452300	-2.03354400	-0.03037000
H	0.78955700	-2.36089400	0.11879000
C	-2.23343900	0.24761800	-0.96913900
H	-1.89430600	0.50022800	-1.98044500
H	-3.07525700	-0.44979500	-1.05720200
H	-2.61499800	1.16097500	-0.49797700
C	0.10858100	2.92294100	-0.57457700
H	1.10607500	2.92070300	-1.02742000
H	-0.62617300	2.85233300	-1.38499200
H	-0.03359100	3.88969200	-0.07296300

Energies (0K) = -371.0378683

Energies (0K) + ZPE = -370.775079

Enthalpies (298K) = -370.76227

Free Energies (298K) = -370.811463



iPr_2NEt radical cation, **[*i*Pr_2(Et)N·]$^+$**

Number of imaginary frequencies = 1

1 2

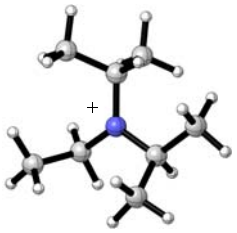
C	1.46025700	-0.20940500	0.32733300
H	1.67090900	-0.09048500	1.40122500
N	0.12402300	0.41238700	0.16635000
C	2.52692800	0.59436600	-0.44701000
H	2.61699800	1.62316500	-0.09266100
H	3.48972300	0.09989100	-0.28726900
H	2.30961400	0.59572700	-1.51959500
C	-0.03834000	1.79372900	0.62879600
H	0.75009000	1.98300800	1.36024600
H	-1.00561300	1.85524900	1.13373700
C	-1.06266500	-0.38213800	-0.18911200
H	-0.69872300	-1.23882500	-0.75496400
C	-1.70889300	-0.90184100	1.12146800
H	-2.51823100	-1.58292800	0.84025200
H	-0.99089700	-1.44753300	1.73940000
H	-2.12997200	-0.07688700	1.70392800
C	1.52574200	-1.69180000	-0.03094100
H	1.37642800	-1.86170100	-1.10248000
H	2.53094400	-2.04131600	0.22393100
H	0.81329000	-2.29790600	0.53434000
C	-2.07693900	0.37699300	-1.04961800
H	-1.62770900	0.72581400	-1.98345600
H	-2.87782400	-0.32649300	-1.29900200
H	-2.52751200	1.22322700	-0.52354500
C	0.02083300	2.85756500	-0.48612800
H	0.97434200	2.83966800	-1.01732100
H	-0.78969500	2.74292100	-1.20734500
H	-0.08612300	3.83262200	0.00050400

Energies (0K) = -370.8656712

Energies (0K) + ZPE = -370.601661

Enthalpies (298K) = -370.588808

Free Energies (298K) = -370.639223



[*i*Pr(Et)N=C(Me)$_2$]$^+$

Number of imaginary frequencies = 0

1 1

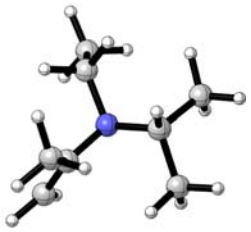
C	0.96828700	-0.74542400	-0.28211700
N	-0.01692200	0.02136500	0.08953900
C	2.38684300	-0.27903200	-0.32981500
H	2.54590200	0.77433800	-0.11272100
H	2.96897700	-0.88431300	0.37720700
H	2.78107700	-0.50825200	-1.32730200
C	0.19956200	1.43539600	0.52517200
H	0.85801600	1.91709100	-0.19898700
H	-0.76591000	1.93441400	0.45720500
C	-1.44652500	-0.45265700	0.06290400
H	-1.40607800	-1.51589700	-0.15694400
C	-2.11974700	-0.28254300	1.42613400
H	-3.11578700	-0.73396400	1.36781200
H	-1.56017400	-0.79666200	2.21397600
H	-2.24759200	0.76762900	1.70559600
C	0.75135400	-2.17319700	-0.69943900
H	0.11865200	-2.22893200	-1.59261800
H	1.71190700	-2.63696000	-0.92891300
H	0.26707800	-2.75033900	0.09523600
C	-2.20352900	0.23923400	-1.07593500
H	-1.69394200	0.09451600	-2.03433900
H	-3.20133200	-0.20602600	-1.14802800
H	-2.32871700	1.31273100	-0.90209800
C	0.74899000	1.54636400	1.94653700
H	0.06285000	1.10709400	2.67598400
H	1.72364100	1.06080200	2.05142400
H	0.87043200	2.60807200	2.18781900

Energies (0K) = -370.3107569

Energies (0K) + ZPE = -370.057366

Enthalpies (298K) = -370.04458

Free Energies (298K) = -370.094016



***i*Pr(Et)N-C(Me)=CH_2**

Number of imaginary frequencies = 0

0 1

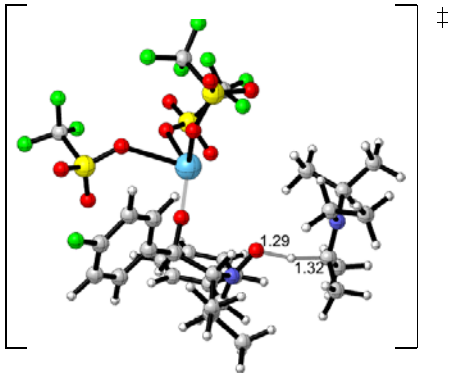
C	1.14983900	-0.03273100	0.10342800
H	1.28283000	-0.15497500	1.19521200
N	-0.15979400	0.59940200	-0.19238700
C	2.30215000	0.84227000	-0.40845800
H	2.32062700	1.83155500	0.05890400
H	3.25976300	0.35733100	-0.18508400
H	2.23198200	0.97696900	-1.49487200
C	-0.33645100	1.94998200	0.40035200
H	0.43580700	2.13912400	1.15888700
H	-1.29385300	1.98395500	0.93364100
C	-1.31028900	-0.23902800	0.06437300
C	-1.50930900	-0.77988700	1.46375200
H	-2.44743500	-1.33797200	1.54521600
H	-0.69062500	-1.44965600	1.75565600
H	-1.52832500	0.03312900	2.20160700
C	1.24265000	-1.41689100	-0.55020800
H	1.12131600	-1.33701900	-1.63765400
H	2.22623600	-1.85556600	-0.34731500
H	0.48526100	-2.11279600	-0.17670200
C	-2.18039400	-0.46968000	-0.92561300
H	-3.08186600	-1.05645100	-0.76422600
H	-2.01080100	-0.07315400	-1.92316300
C	-0.32841200	3.06131300	-0.65092200
H	0.62093300	3.09688300	-1.19607900
H	-1.13068800	2.90455300	-1.38207500
H	-0.48618600	4.03963700	-0.17809400

Energies (0K) = -369.8096337

Energies (0K) + ZPE = -369.570964

Enthalpies (298K) = -369.558477

Free Energies (298K) = -369.607466



TS_C

Number of imaginary frequencies = 1

0 1

C	-2.04057600	-4.53632100	1.88223900
C	-2.69729800	-2.82572000	0.02655300
N	-2.38043600	-3.17931700	1.41866800
O	-2.26512000	-2.22525300	2.27557900
O	5.48589700	-0.62305100	3.79605800
S	4.03357000	-0.66133600	3.56668300
O	3.65328400	-0.76551100	2.11445600
O	3.23511800	-1.52692800	4.45635400
C	3.44902100	1.04797500	3.99860200
F	3.68407800	1.32156700	5.28748400
F	4.05167800	1.97772200	3.24676700
F	2.11447100	1.14193200	3.78933600
O	-0.27409000	3.53922800	-1.24479800
S	0.30921500	2.73186100	-0.16499300
O	-0.06845800	3.07576700	1.21913900
O	0.27350400	1.24713800	-0.44074200
C	2.13403500	3.08610200	-0.24070900
F	2.61556400	2.84976000	-1.46673700
F	2.80257200	2.30129200	0.63225800
F	2.37480800	4.36363600	0.07678500
O	2.61508300	-0.77406000	-1.01665100
S	3.16582300	-1.91756900	-1.84051200
O	2.98657100	-3.23498300	-1.20187700
O	2.84523100	-1.81178000	-3.27125200
C	4.99231600	-1.59011700	-1.74185400
F	5.27183000	-0.34927400	-2.16368200
F	5.65347900	-2.46404200	-2.51478300
F	5.42935700	-1.72193600	-0.48268200
O	-0.46961900	-1.88515100	-0.11611700
C	-1.29270900	-2.79893400	-0.73552000
C	-1.41819000	-2.51886700	-2.22991600
C	-1.44116400	-3.57155500	-3.15485100
C	-1.48001100	-1.20109800	-2.70718300
C	-1.55491300	-3.32736500	-4.52594100

H	-1.36555700	-4.59808700	-2.80497100
C	-1.59377300	-0.93615300	-4.07245000
H	-1.42277600	-0.37677900	-2.00324500
C	-1.63540500	-2.00946800	-4.95661200
H	-1.56989300	-4.13675700	-5.24932800
H	-1.64215900	0.07969800	-4.45272500
La	1.11282700	-0.74771700	1.03438300
H	-3.04300400	-1.78996400	0.09006100
H	-0.90011900	-3.82493300	-0.63712500
C	-4.14293100	-1.40504700	3.85902000
H	-3.29724900	-1.93273000	2.99830100
N	-3.90986800	-0.04236600	3.79801000
C	-5.46729100	-1.91099300	3.28557700
H	-5.69565000	-1.51645900	2.29470800
H	-5.44213200	-3.00142100	3.22629800
H	-6.27957400	-1.62719500	3.96812500
C	-4.33339000	0.71295300	2.60242000
H	-4.32092300	0.03515100	1.74312000
H	-3.57644600	1.47593700	2.40628400
C	-2.93096100	0.61367300	4.70063300
H	-2.91349700	0.02203300	5.61469400
C	-1.51144700	0.61123100	4.10490800
H	-0.81489300	1.05199000	4.82738000
H	-1.18531100	-0.41139000	3.88846700
H	-1.45883600	1.20321300	3.18343300
C	-3.75017800	-2.13066600	5.14258300
H	-4.33035300	-1.74336100	5.99046600
H	-3.98382200	-3.19246300	5.03256800
H	-2.68791400	-2.04019000	5.37999200
C	-3.37827800	2.02675500	5.09762800
H	-4.37597800	2.01392400	5.54755400
H	-2.67502600	2.41448800	5.84258900
H	-3.38082500	2.72311300	4.25300500
C	-5.70812200	1.38017700	2.72437200
H	-6.50193000	0.65016200	2.90619600
H	-5.72602900	2.11641200	3.53271000
H	-5.93283300	1.90045000	1.78568900
C	-4.58005200	-2.88351100	-1.68078600
H	-5.16350900	-2.09677500	-1.18491800
H	-3.93634000	-2.40581200	-2.42065700
H	-5.28319100	-3.53277500	-2.21553800
C	-4.83352900	-4.28885500	0.34903700
H	-5.32295000	-3.49515400	0.92328200
H	-5.61380000	-4.81115200	-0.21731800

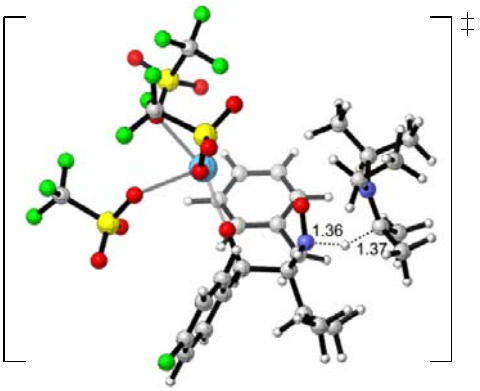
H	-4.41261300	-5.01214200	1.05153400
C	-3.80271200	-3.70760800	-0.63502600
H	-3.31014100	-4.54603800	-1.14526500
H	-2.10827400	-5.19065500	1.01179200
H	-2.81660300	-4.83838400	2.59644600
C	-0.67690400	-4.65706000	2.53775400
C	-0.53905300	-4.47004000	3.92017200
C	0.45152100	-5.01126500	1.78422600
C	0.70484000	-4.62439600	4.53814700
H	-1.41244100	-4.22145000	4.51729900
C	1.69640200	-5.16800200	2.40041400
H	0.35238400	-5.18409700	0.71560500
C	1.82608200	-4.97270100	3.77907700
H	0.79575200	-4.48425700	5.61208800
H	2.55990400	-5.45561300	1.80619300
H	2.79211500	-5.09989100	4.25987400
F	-1.74408700	-1.75954400	-6.28607600

Energies (0K) = -4290.1291412

Energies (0K) + ZPE = -4289.435606

Enthalpies (298K) = -4289.373066

Free Energies (298K) = -4289.538757



$TS_{C'}$

Number of imaginary frequencies = 1

0 1

C	-2.26877100	-3.95442000	2.18041200
C	-2.83782600	-2.44864300	0.11592100
N	-2.63459300	-2.55097800	1.63415900
O	-1.97041400	-1.57758900	2.13726100
O	5.78925900	-0.53923200	3.38782200
S	4.32556900	-0.54451000	3.23707900
O	3.86385200	-0.85742800	1.84066300
O	3.54645000	-1.21909200	4.29342000
C	3.83746800	1.23882600	3.41726400

F	4.15506400	1.70122900	4.63245700
F	4.43912700	2.00558000	2.49749400
F	2.49994200	1.37137900	3.25673600
O	0.04030600	3.36289000	-1.86821100
S	0.71498900	2.58444200	-0.82087400
O	0.53664600	3.02830400	0.57618700
O	0.57494100	1.08927300	-0.99591700
C	2.52994100	2.81492700	-1.13577500
F	2.85627600	2.42697200	-2.37466300
F	3.23781300	2.07075800	-0.26045600
F	2.88181500	4.09637300	-0.97983700
O	2.63744600	-1.26384700	-1.34093000
S	3.14672600	-2.57128000	-1.90564600
O	3.16549800	-3.66266300	-0.91381400
O	2.61024200	-2.88281200	-3.23852800
C	4.93442700	-2.16168100	-2.20453000
F	5.04290100	-1.12176200	-3.04252000
F	5.55769500	-3.21693900	-2.74821300
F	5.54988100	-1.84912000	-1.05615800
O	-0.43273300	-1.92697900	-0.12182600
C	-1.45446600	-2.70836000	-0.61157200
C	-1.60439000	-2.49263400	-2.12351300
C	-1.57987400	-3.57451900	-3.01230900
C	-1.70455700	-1.19476700	-2.64876600
C	-1.67433500	-3.38155200	-4.39409900
H	-1.47957600	-4.58589700	-2.62625100
C	-1.80165800	-0.97999500	-4.02384600
H	-1.68812800	-0.34144000	-1.97829600
C	-1.78839200	-2.08348700	-4.87153700
H	-1.65227000	-4.21619400	-5.08786100
H	-1.88102200	0.01994900	-4.43925200
La	1.27534600	-0.75139400	0.75613700
H	-3.07780900	-1.38956400	0.00327400
H	-1.23288500	-3.78010800	-0.46814700
C	-4.62226700	-1.56202600	3.04311300
H	-3.86351700	-2.29254200	2.16667200
N	-3.72207700	-0.56202400	3.33063000
C	-5.86448100	-1.20243600	2.22514000
H	-5.65967600	-0.66065100	1.30176500
H	-6.40800500	-2.11415800	1.97188200
H	-6.52701300	-0.58590100	2.84510000
C	-3.66051000	0.64376600	2.46726200
H	-3.93851100	0.33959700	1.45981900
H	-2.61736300	0.95243400	2.41713200

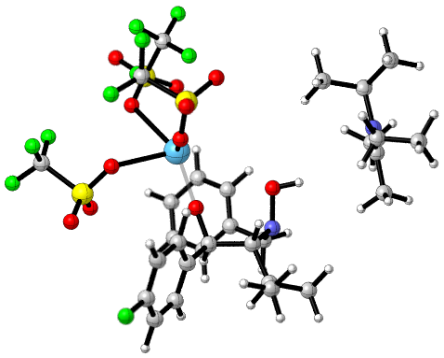
C	-2.99156800	-0.51499900	4.64316200
H	-2.73225600	-1.54737700	4.87017100
C	-1.68145700	0.27295400	4.58098000
H	-1.15883200	0.12488100	5.53245100
H	-1.03204700	-0.08457200	3.77864200
H	-1.84277300	1.34943400	4.46299500
C	-4.94292800	-2.61565100	4.09963300
H	-5.68058600	-2.22409200	4.81013200
H	-5.39809000	-3.47671700	3.60292400
H	-4.07709900	-2.96779600	4.66211100
C	-3.89036600	0.02456100	5.77122000
H	-4.85174900	-0.49168700	5.82752500
H	-3.37458800	-0.12481100	6.72677100
H	-4.08122500	1.09532900	5.65717700
C	-4.53221200	1.81876700	2.92282500
H	-5.57468700	1.52719600	3.08009000
H	-4.15642000	2.27661300	3.84172200
H	-4.50943400	2.58326400	2.13709100
C	-4.92436500	-2.43254600	-1.32855100
H	-5.52393500	-1.78643800	-0.67699400
H	-4.37449400	-1.79041800	-2.02353600
H	-5.61516400	-3.04870300	-1.91613900
C	-4.81711200	-4.25051900	0.40154600
H	-5.32465800	-3.72000400	1.20970400
H	-5.59681100	-4.71150000	-0.21616900
H	-4.23802600	-5.06776800	0.83705700
C	-3.97886400	-3.32995700	-0.50746100
H	-3.48474600	-4.00461800	-1.21461000
H	-2.24288800	-4.61659700	1.31706000
H	-3.09348000	-4.25964100	2.82310500
C	-0.96171200	-4.01783500	2.92630000
C	-0.92824500	-3.86479600	4.31920400
C	0.22933300	-4.32979000	2.25273500
C	0.27068700	-3.99759500	5.02455300
H	-1.84977700	-3.65872000	4.85683700
C	1.42803900	-4.47316000	2.95596300
H	0.21419500	-4.48150200	1.17719200
C	1.45270500	-4.30164400	4.34396000
H	0.27798400	-3.87871300	6.10475500
H	2.33884800	-4.73289000	2.42239800
H	2.38475800	-4.41520500	4.89042600
F	-1.88144800	-1.88167100	-6.21024900

Energies (0K) = -4290.1169505

Energies (0K) + ZPE = -4289.420000

Enthalpies (298K) = -4289.358138

Free Energies (298K) = -4289.522328



D

Number of imaginary frequencies = 0

0 1

C	-2.52706300	-3.60185800	1.03768500
C	-3.04796700	-2.00738400	-0.91019500
N	-3.07476100	-2.33385400	0.53398000
O	-2.55583900	-1.24285100	1.31966700
O	5.28580900	0.01542400	3.03770700
S	3.84159300	-0.00157800	2.75431300
O	3.50472700	-0.22818800	1.30925300
O	2.98890500	-0.75650300	3.69723100
C	3.29821100	1.75760300	3.00448200
F	3.44080500	2.12542900	4.28528000
F	4.00636600	2.59887700	2.24036000
F	1.99241900	1.89096300	2.67648100
O	-0.57705900	3.98995800	-2.00255700
S	0.01155500	3.16535700	-0.93744600
O	-0.36617000	3.48749600	0.45236600
O	-0.01336000	1.68711900	-1.23883500
C	1.83270800	3.53276700	-1.00660600
F	2.31590500	3.32675100	-2.23864600
F	2.50437000	2.73209000	-0.15257300
F	2.06935400	4.80466200	-0.66120300
O	2.38502600	-0.33238300	-1.86834700
S	3.07938500	-1.42184500	-2.65125100
O	3.17391400	-2.69733000	-1.91772100
O	2.66575400	-1.48632900	-4.06097500
C	4.81866100	-0.77206100	-2.70927100
F	4.84703800	0.43644700	-3.28881300
F	5.59268800	-1.60509000	-3.42093200
F	5.33249100	-0.66425500	-1.47680000
O	-0.68308800	-1.44383000	-0.96663700

C	-1.64701300	-2.22768600	-1.58874400
C	-1.63102000	-1.98198900	-3.09835300
C	-1.73505000	-3.04527600	-4.00590200
C	-1.48027400	-0.68264300	-3.60933500
C	-1.72228700	-2.82862300	-5.38713400
H	-1.82258500	-4.06317800	-3.63358100
C	-1.46530600	-0.44367600	-4.98445400
H	-1.35888100	0.14818600	-2.92106000
C	-1.59281000	-1.52586000	-5.84904200
H	-1.79908400	-3.64972000	-6.09340300
H	-1.35041000	0.55856300	-5.38661800
La	0.88244600	-0.35926200	0.19815500
H	-3.24882700	-0.93058300	-0.93027500
H	-1.41664000	-3.29674400	-1.45147100
C	-5.32943400	-0.03096000	3.88689500
H	-3.34204000	-0.94233200	1.81014600
N	-5.19500400	1.24358600	3.65378700
C	-6.19118800	-0.92552000	3.05612900
H	-6.74002600	-0.44445200	2.25061600
H	-5.55097300	-1.71433200	2.63946200
H	-6.90133200	-1.42847400	3.72438800
C	-5.88621500	1.91958900	2.51439000
H	-5.79974400	1.27669200	1.63794000
H	-5.31763100	2.82368600	2.30094800
C	-4.27068900	2.10552000	4.47414400
H	-4.02051900	1.52349600	5.35794200
C	-2.98362100	2.37084700	3.68525900
H	-2.28953800	2.92651800	4.32446600
H	-2.50118100	1.43240000	3.38986800
H	-3.16498200	2.97004700	2.78659200
C	-4.59792200	-0.71346600	5.00822300
H	-4.92525700	-0.32490900	5.97957600
H	-4.80370200	-1.78453300	4.98110900
H	-3.51627500	-0.56213000	4.93145900
C	-4.95826800	3.38677600	4.95027300
H	-5.86856000	3.16391600	5.51530000
H	-4.26437300	3.90685800	5.61895200
H	-5.20347000	4.06933600	4.13103700
C	-7.34448600	2.26834200	2.80972800
H	-7.94375900	1.37783800	3.02172700
H	-7.43246000	2.95342500	3.65696200
H	-7.76627300	2.76071400	1.92667100
C	-4.84352100	-1.81109400	-2.72676900
H	-5.35037700	-0.95919000	-2.25303000

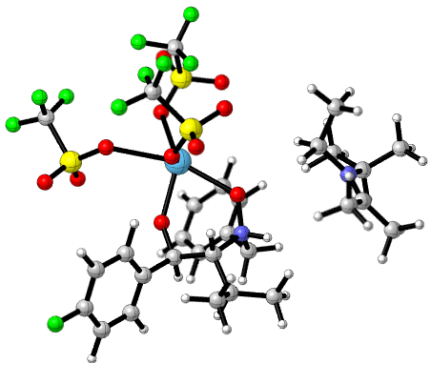
H	-4.10215100	-1.41034600	-3.42111400
H	-5.59320200	-2.35530400	-3.31488600
C	-5.37132900	-3.20057700	-0.73487900
H	-5.81207300	-2.36237800	-0.18171100
H	-6.16534000	-3.64610100	-1.34831800
H	-5.05807400	-3.95326800	-0.00647600
C	-4.22950000	-2.72898100	-1.65229000
H	-3.82518300	-3.61974200	-2.15347300
H	-2.91630500	-4.38024800	0.37374600
H	-2.99750700	-3.76024700	2.01786500
C	-1.02394200	-3.80761500	1.20270500
C	-0.28987500	-3.10270400	2.17156800
C	-0.35798800	-4.78801900	0.45331700
C	1.07906400	-3.33083800	2.34377000
H	-0.79625100	-2.36555400	2.78725800
C	1.00694200	-5.03464100	0.63273000
H	-0.91423900	-5.37055300	-0.27779500
C	1.73314200	-4.29876900	1.57242900
H	1.63425000	-2.76168500	3.08466600
H	1.49884700	-5.80411600	0.04292100
H	2.79401200	-4.48758000	1.71648800
F	-1.57614700	-1.30166100	-7.18914600

Energies (0K) = -4290.1767186

Energies (0K) + ZPE = -4289.477017

Enthalpies (298K) = -4289.414022

Free Energies (298K) = -4289.58207



D′

Number of imaginary frequencies = 0

0 1

C	-1.71590100	-4.25331900	1.64908000
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N	-2.12970800	-2.84109700	1.14336800
O	-1.30032500	-1.82643600	1.57716500
O	5.09531200	-0.30172400	3.40317800

S	3.64379000	-0.30422500	3.16042500
O	3.26486400	-0.66257500	1.75072100
O	2.79560900	-0.92676800	4.19662100
C	3.15216900	1.48482000	3.23296100
F	3.42204200	2.01094800	4.43394400
F	3.78796200	2.20562800	2.29865300
F	1.82115600	1.60269700	3.01400000
O	-1.62948400	3.25267200	-1.39057000
S	-0.64437400	2.59819000	-0.51625600
O	-0.76496700	2.84754600	0.93447200
O	-0.40341500	1.15090500	-0.86022800
C	0.98073300	3.36552900	-0.98192800
F	1.22372300	3.20606300	-2.29004900
F	1.98224800	2.78672100	-0.29500000
F	0.98033600	4.67641200	-0.70431000
O	2.43840300	-0.33860500	-1.20107100
S	3.24099700	-1.12501500	-2.20249600
O	3.54892500	-2.50417700	-1.78005800
O	2.80256300	-0.93682400	-3.59573500
C	4.86939500	-0.23518000	-2.11329700
F	4.69870100	1.07886100	-2.32873700
F	5.71085300	-0.71083700	-3.04516200
F	5.44154700	-0.39514800	-0.91121400
O	-0.22242900	-1.99883200	-1.01827300
C	-1.10098900	-3.05865900	-1.15918600
C	-1.31068600	-3.39655600	-2.63962100
C	-1.52497200	-4.71833400	-3.05448300
C	-1.22456200	-2.39394900	-3.61506700
C	-1.69016300	-5.03687100	-4.40504100
H	-1.55449300	-5.51805300	-2.31823600
C	-1.38609900	-2.68978500	-4.96979000
H	-1.02199100	-1.37470700	-3.30327100
C	-1.62230300	-4.00975500	-5.33780800
H	-1.85315600	-6.05895800	-4.73312900
H	-1.32359300	-1.91943000	-5.73250600
La	0.71694700	-0.73609000	0.64893800
H	-2.67040500	-1.71167500	-0.50356700
H	-0.68417000	-3.98372700	-0.72564700
C	-4.50104300	-0.71026400	3.74062500
H	-3.03064000	-2.66000400	1.60045200
N	-3.34952700	-0.21729800	4.10697500
C	-5.28055700	-0.13368300	2.59308700
H	-4.67302300	-0.00258900	1.69357000
H	-6.12277200	-0.78620200	2.35718500

H	-5.67727900	0.85077300	2.87142100
C	-2.77444400	0.96990200	3.41090100
H	-3.10356100	0.94313600	2.37519300
H	-1.69384900	0.84737800	3.40254900
C	-2.58207900	-0.79752900	5.28177700
H	-2.78919900	-1.86678800	5.25433200
C	-1.07009000	-0.63792400	5.13323500
H	-0.59920600	-1.23980300	5.91721600
H	-0.72436900	-1.01524400	4.16586500
H	-0.73650000	0.39628700	5.26604400
C	-5.16813600	-1.86155600	4.42357100
H	-6.18281800	-1.54408900	4.69537700
H	-5.28670200	-2.66723200	3.68724400
H	-4.67475700	-2.25003600	5.31005300
C	-3.10139200	-0.21202600	6.59851100
H	-4.17514400	-0.38389800	6.72267600
H	-2.57891300	-0.69897600	7.42894600
H	-2.90994000	0.86307000	6.66163300
C	-3.16895600	2.29671400	4.06010100
H	-4.25633400	2.40405900	4.12476700
H	-2.74443500	2.40540900	5.06162700
H	-2.78133200	3.10963900	3.43668800
C	-4.39869500	-3.03177600	-1.95290900
H	-4.83814800	-2.05373400	-1.71755700
H	-3.72803000	-2.90014500	-2.80206900
H	-5.21262500	-3.69708300	-2.26329900
C	-4.75361300	-3.63407400	0.42242500
H	-5.04435300	-2.61605900	0.71663500
H	-5.65711500	-4.13436900	0.05662800
H	-4.43636700	-4.18432200	1.31480900
C	-3.70045600	-3.60894600	-0.70529800
H	-3.39913200	-4.64376600	-0.91137400
H	-1.64113200	-4.89756100	0.77456700
H	-2.55800400	-4.59360100	2.25284100
C	-0.45128000	-4.30787900	2.46299400
C	-0.53045100	-4.41693600	3.85830300
C	0.81226700	-4.36143200	1.85294900
C	0.62444900	-4.56700000	4.63100700
H	-1.50499300	-4.40331800	4.34091100
C	1.96786400	-4.51204600	2.62255900
H	0.89508200	-4.30132700	0.77095500
C	1.87684900	-4.61557700	4.01431600
H	0.54380300	-4.65723800	5.71099500
H	2.93755000	-4.56196600	2.13419900

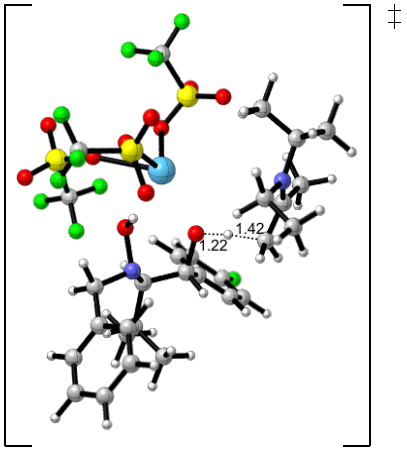
H	2.77608000	-4.74042400	4.61138400
F	-1.77623100	-4.30705900	-6.65401800

Energies (0K) = -4290.1832383

Energies (0K) + ZPE = -4289.481635

Enthalpies (298K) = -4289.419209

Free Energies (298K) = -4289.588726



TS_D

Number of imaginary frequencies = 1

0 1

C	-1.65673800	-4.42229800	0.14840600
C	-2.72517100	-2.85855300	-1.54200200
N	-1.51118000	-3.26409100	-0.77166500
O	-1.23618400	-2.14094500	0.13723500
O	-4.22596600	1.21508800	3.62508900
S	-3.81955700	0.01300300	2.88397100
O	-2.64204100	0.25003100	1.96556600
O	-3.71439900	-1.24625700	3.63511600
C	-5.20086700	-0.28486300	1.67260900
F	-6.36099700	-0.43551700	2.31980500
F	-5.31669400	0.74284400	0.81623400
F	-4.96551900	-1.39848500	0.95434700
O	-1.41416100	4.26145800	-1.11234800
S	-2.54162900	4.18186600	-0.16049700
O	-3.65803100	5.11559400	-0.35929800
O	-2.98124500	2.76503700	0.12939500
C	-1.79324200	4.66242100	1.46940300
F	-0.79338400	3.81481600	1.78282200
F	-2.70645700	4.61363800	2.44627300
F	-1.29132400	5.90186000	1.40917600
O	-1.36770600	-0.89346700	-2.23630400
C	-2.29339400	-1.88892200	-2.68471800
C	-3.45952100	-1.19412400	-3.38488500

C	-3.54816300	-1.21299100	-4.78375700
C	-4.41852600	-0.45799700	-2.66867700
C	-4.55887400	-0.52307400	-5.45954500
H	-2.81768600	-1.77482600	-5.35982600
C	-5.43421300	0.24032200	-3.32245700
H	-4.39948300	-0.44256700	-1.58257100
C	-5.48305700	0.19415800	-4.71187800
H	-4.63026000	-0.53702300	-6.54259600
H	-6.18208500	0.80266200	-2.77195400
La	-1.49590700	0.57531800	-0.22749600
H	-3.39323900	-2.33798100	-0.83940000
H	-1.76134500	-2.49298700	-3.42833900
C	1.14919800	0.54272000	-4.00793200
N	2.33695600	0.59597900	-3.39029300
C	0.40314100	-0.65219400	-4.17365900
H	-0.52587700	-0.71784000	-3.09893100
H	-0.30729800	-0.60809000	-4.99947800
H	0.92199600	-1.60589000	-4.11477100
C	2.98449300	-0.64742600	-2.91556500
H	2.22277700	-1.28050800	-2.45382200
H	3.68025200	-0.37244600	-2.12146100
C	3.02671900	1.88169100	-3.07801600
H	2.51014500	2.65508000	-3.64264200
C	2.89816200	2.22334200	-1.58766600
H	3.34799100	3.20408600	-1.39658200
H	1.84489200	2.27092000	-1.28645700
H	3.40739700	1.49270400	-0.94996800
C	0.50967600	1.82282200	-4.49364900
H	1.12642800	2.30349800	-5.26202300
H	-0.46579000	1.60199100	-4.93094900
H	0.36597600	2.54704700	-3.68432800
C	4.48529000	1.88207400	-3.54990400
H	4.55550800	1.65516700	-4.61878600
H	4.90537300	2.88070400	-3.38735500
H	5.10536500	1.16913400	-2.99659500
C	3.72822100	-1.41391900	-4.01277500
H	3.06862100	-1.67329000	-4.84651500
H	4.56603200	-0.83159600	-4.40714500
H	4.12777500	-2.34490400	-3.59407500
O	1.47569100	-1.98095900	0.53066000
S	1.52907700	-0.94231700	1.59794600
O	2.77177100	-0.16791900	1.69305300
O	0.26054500	-0.13325000	1.64391500
C	1.42235000	-1.90644100	3.18256200

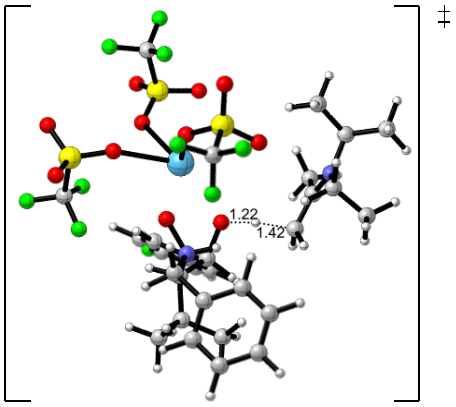
F	0.31412000	-2.65938500	3.19361800
F	2.48876200	-2.70621900	3.29519300
F	1.39059400	-1.07408500	4.22827700
H	-0.25255700	-2.18412900	0.21784800
C	-2.93570400	-4.75075000	-3.34010900
H	-3.10257600	-4.14048100	-4.23480200
H	-1.86035800	-4.93474700	-3.24928500
H	-3.42391300	-5.71768400	-3.51111800
C	-5.02381900	-3.79954700	-2.27810100
H	-5.21896500	-3.15335300	-3.13805900
H	-5.55578800	-4.74392300	-2.44750200
H	-5.46120900	-3.32712500	-1.39020300
H	-2.66462300	-4.49236700	0.58197700
H	-0.97813600	-4.20400700	0.97775900
C	-1.23090100	-5.74514900	-0.46382400
C	-0.01157300	-5.85489800	-1.14974000
C	-2.00580300	-6.89773800	-0.28167900
C	0.41666700	-7.08674300	-1.64808300
H	0.60128700	-4.96904800	-1.29252200
C	-1.57699700	-8.13391700	-0.77494000
H	-2.95154800	-6.82719400	0.25105600
C	-0.36503500	-8.23172500	-1.46199700
H	1.36322500	-7.15433900	-2.17853200
H	-2.19193100	-9.01744500	-0.62368800
H	-0.03091900	-9.19080100	-1.84912600
C	-3.52427600	-4.09262600	-2.08105800
H	-3.49284700	-4.83964900	-1.28637900
F	-6.46708700	0.86929800	-5.35425100

Energies (0K) = -4290.1576008

Energies (0K) + ZPE = -4289.461435

Enthalpies (298K) = -4289.399728

Free Energies (298K) = -4289.564949



$TS_{D'}$

Number of imaginary frequencies = 1

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C	-1.81721500	-4.21662200	0.20315200
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N	-1.91069300	-2.95278500	-0.64046300
O	-2.07398500	-1.90464600	0.26469400
O	-4.57035800	1.30533800	3.68959900
S	-4.10871400	0.07770700	3.02298800
O	-2.87592100	0.28186900	2.18098200
O	-4.06422700	-1.14986900	3.83334500
C	-5.41194600	-0.26621300	1.73861600
F	-6.62832800	-0.26501500	2.29818700
F	-5.38693800	0.67360400	0.77464400
F	-5.21506100	-1.45918600	1.15598300
O	-1.45719400	4.12671000	-0.96625200
S	-2.57615200	4.08472600	-0.00271100
O	-3.67112100	5.04375700	-0.20619700
O	-3.04532900	2.68637900	0.31396600
C	-1.79990000	4.57785200	1.60975400
F	-0.80450200	3.72425600	1.91987100
F	-2.69881600	4.55122500	2.60142000
F	-1.28604200	5.81173300	1.52758300
O	-1.55168600	-0.92056100	-2.22240800
C	-2.58209000	-1.76256100	-2.73536300
C	-3.74235400	-0.93024900	-3.26982700
C	-3.85281800	-0.71638400	-4.65195100
C	-4.66820800	-0.30335800	-2.42204900
C	-4.85395300	0.09925300	-5.18347000
H	-3.14799500	-1.19525700	-5.32701800
C	-5.67481000	0.51859100	-2.93193400
H	-4.62383300	-0.45669000	-1.34867700
C	-5.74698200	0.70408400	-4.30794700
H	-4.94499500	0.26497000	-6.25234100
H	-6.39608000	1.00115800	-2.27977100
La	-1.62699500	0.46132700	-0.00509400

H	-3.85567900	-2.49818600	-1.08700800
H	-2.14730700	-2.29148000	-3.59005200
C	1.12769200	0.16676900	-4.08221100
N	2.31495300	0.18264100	-3.46427900
C	0.27444800	-0.96760500	-4.11574900
H	-0.66810200	-0.85393800	-3.05961600
H	-0.42235400	-0.95151800	-4.95467900
H	0.71251000	-1.95060100	-3.95801800
C	2.81912800	-1.03417700	-2.78928400
H	1.98193600	-1.51290300	-2.27649400
H	3.50637200	-0.71101300	-2.00732000
C	3.12697200	1.42774400	-3.31880700
H	2.74019100	2.13414200	-4.05096600
C	2.94595100	2.03901200	-1.92291200
H	3.51167700	2.97536800	-1.85853000
H	1.89115000	2.26652200	-1.72857800
H	3.30468800	1.37035100	-1.13361100
C	0.60700100	1.43680200	-4.71415500
H	1.23957500	1.74907500	-5.55364400
H	-0.40163300	1.26958700	-5.09648800
H	0.57128200	2.26628600	-3.99980600
C	4.60289500	1.19645900	-3.66118000
H	4.71821000	0.78564100	-4.66942300
H	5.12134700	2.16083900	-3.62641800
H	5.09995500	0.52943600	-2.94934100
C	3.51773500	-2.02313600	-3.72571800
H	2.86021300	-2.35388700	-4.53587000
H	4.41622800	-1.58722900	-4.17194500
H	3.81931400	-2.90773600	-3.15244700
O	2.04269300	-0.60266300	0.47267000
S	1.54016400	-0.45046300	1.85349300
O	2.33085800	0.39306600	2.76310800
O	0.05680400	-0.19703800	1.91846300
C	1.65229600	-2.15604800	2.58137100
F	1.01065800	-3.04561800	1.80332600
F	2.93451200	-2.53329800	2.68043700
F	1.10104900	-2.18629400	3.80094100
C	-2.50190300	-4.75286100	-3.42251600
H	-2.59867500	-4.21444800	-4.37203300
H	-1.45100700	-4.71588700	-3.11789700
H	-2.75198300	-5.80146400	-3.61977500
C	-4.88186700	-4.08059000	-2.91597600
H	-4.93448200	-3.39614200	-3.76889200
H	-5.21562500	-5.06618900	-3.26118500

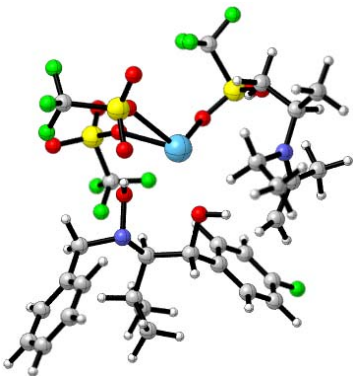
H	-5.59110000	-3.73323200	-2.15563200
H	-2.83663600	-4.49328700	0.47337900
H	-1.31196900	-3.85368000	1.09852900
C	-1.04437000	-5.36853200	-0.39592400
C	0.30743100	-5.21868900	-0.74461000
C	-1.63765700	-6.63210400	-0.51743100
C	1.03867800	-6.30229300	-1.23431900
H	0.79677600	-4.25527800	-0.61794900
C	-0.90284600	-7.72115400	-0.99262800
H	-2.67802200	-6.76551500	-0.23183700
C	0.43475200	-7.55714800	-1.35961800
H	2.08302400	-6.16993300	-1.50392700
H	-1.37716600	-8.69525600	-1.07648200
H	1.00641300	-8.40253300	-1.73295300
C	-3.45330400	-4.19349600	-2.35033800
H	-3.51507700	-4.92463100	-1.53945100
F	-6.72351300	1.49651400	-4.81159600
H	-1.01815400	-2.81322500	-1.13299400

Energies (0K) = -4290.1666532

Energies (0K) + ZPE = -4289.468966

Enthalpies (298K) = -4289.407175

Free Energies (298K) = -4289.572524



E

Number of imaginary frequencies = 0

0 1

C	-0.30094700	-4.12538800	0.68627100
C	-1.19065700	-2.55393700	-1.11575400
N	-0.04385700	-3.03045900	-0.28330300
O	0.31266200	-1.88904700	0.56988100
O	-2.73854000	1.48040400	3.99447500
S	-2.26645800	0.25301300	3.34046000
O	-1.05029300	0.47138600	2.46630000
O	-2.16852000	-0.96154600	4.16132900
C	-3.56195000	-0.13954600	2.06267800

F	-4.78493900	-0.08311500	2.59503200
F	-3.49216900	0.74260000	1.04723500
F	-3.36946000	-1.36814600	1.55528100
O	0.13099900	4.50730400	-0.59888200
S	-0.99921400	4.41244400	0.34773000
O	-2.12576900	5.33353100	0.15024200
O	-1.42619400	2.98792000	0.62622800
C	-0.26209200	4.88974100	1.98402700
F	0.73273800	4.03886800	2.30439600
F	-1.18292600	4.84395700	2.95324100
F	0.24385800	6.12742600	1.92684500
O	0.39252000	-0.83378200	-1.85977600
C	-0.62222000	-1.76291400	-2.32605400
C	-1.65617400	-0.99783000	-3.13985200
C	-1.71636900	-1.16762300	-4.52992700
C	-2.51889200	-0.06411500	-2.54235800
C	-2.61417600	-0.43599800	-5.31183300
H	-1.05455700	-1.88160600	-5.01264500
C	-3.42012500	0.67880600	-3.30451100
H	-2.51743200	0.07568700	-1.46494800
C	-3.44883500	0.47655600	-4.68067000
H	-2.66630700	-0.56553800	-6.38809100
H	-4.09546900	1.39525600	-2.84739200
La	0.06701900	0.81284000	0.26969700
H	-1.79063200	-1.88363600	-0.48257200
H	-0.11113800	-2.47515200	-2.97912200
C	2.62737600	1.16782600	-3.89581000
N	3.85688400	1.27275300	-3.28971100
C	2.03447900	-0.02517500	-4.23121900
H	0.89730700	-0.48667100	-2.64929100
H	1.13143600	-0.00061400	-4.83232200
H	2.53939700	-0.98159400	-4.15993900
C	4.59103000	0.04850000	-2.94517900
H	3.88666800	-0.68658700	-2.53575700
H	5.28611200	0.28687600	-2.13726900
C	4.38144900	2.55390000	-2.76230300
H	3.80015700	3.34634100	-3.23141900
C	4.18545700	2.67062400	-1.24143700
H	4.51600200	3.65548200	-0.89084800
H	3.12737900	2.55685500	-0.97460000
H	4.76059000	1.91367700	-0.69552700
C	1.87983100	2.44635400	-4.21907000
H	2.45825000	3.09383000	-4.88886100
H	0.93870100	2.20462900	-4.71832000

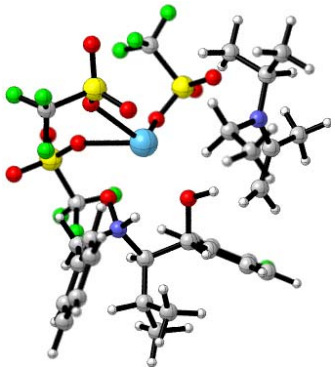
H	1.64540900	3.03254300	-3.32296400
C	5.84455100	2.78644900	-3.16379100
H	5.96607900	2.73513400	-4.25123200
H	6.15671100	3.78417900	-2.83421500
H	6.52413600	2.06100700	-2.70305900
C	5.36748300	-0.56474000	-4.11633000
H	4.71217400	-0.78454300	-4.96501300
H	6.15681000	0.11076600	-4.46268300
H	5.83795100	-1.50341200	-3.79931800
O	3.02234900	-1.75110400	0.99553000
S	3.08386300	-0.72035400	2.06906100
O	4.33218800	0.04325200	2.16924200
O	1.82314300	0.10326100	2.12220500
C	2.96535100	-1.69392800	3.64672500
F	1.84420300	-2.42741200	3.65572600
F	4.01788700	-2.51309000	3.74849700
F	2.95169100	-0.86934800	4.69871800
H	1.29573600	-1.97049100	0.63788500
C	-1.65639200	-4.53801100	-2.76410300
H	-1.74592400	-3.98238600	-3.70411400
H	-0.61562800	-4.85897200	-2.65552900
H	-2.27300700	-5.43958900	-2.85940300
C	-3.59396800	-3.24181600	-1.77892300
H	-3.70827900	-2.62247200	-2.67259700
H	-4.24128600	-4.11878500	-1.90098200
H	-3.96407800	-2.67368600	-0.91728200
H	-1.30854500	-4.07883800	1.12257800
H	0.39998200	-3.93558100	1.50406300
C	-0.00716400	-5.50635200	0.12718700
C	1.19547800	-5.76190000	-0.54944400
C	-0.89748900	-6.56634800	0.34075700
C	1.49441200	-7.04573700	-1.00933700
H	1.89669700	-4.94899200	-0.71741100
C	-0.59826900	-7.85438800	-0.11414700
H	-1.83190600	-6.38262200	0.86645900
C	0.59712400	-8.09713500	-0.79409300
H	2.42914300	-7.22641300	-1.53431300
H	-1.30209600	-8.66444300	0.05922000
H	0.82973900	-9.09642000	-1.15286800
C	-2.14358400	-3.71314300	-1.56056700
H	-2.19906800	-4.39263500	-0.70892300
F	-4.32137000	1.19338800	-5.42715400

Energies (0K) = -4290.1654842

Energies (0K) + ZPE = -4289.465462

Enthalpies (298K) = -4289.403203

Free Energies (298K) = -4289.569986



E′

Number of imaginary frequencies = 0

0 1

C	-0.37861800	-3.86437800	0.58062100
C	-1.47135000	-2.51979600	-1.39499400
N	-0.38081800	-2.62533900	-0.31241600
O	-0.51632700	-1.54032900	0.54739500
O	-2.97366200	1.60574400	4.04100400
S	-2.50884800	0.36999300	3.39320100
O	-1.25707400	0.55926700	2.57178100
O	-2.48201900	-0.85165100	4.21199800
C	-3.78962200	0.02291000	2.08452900
F	-5.01920100	0.10403900	2.60597300
F	-3.69243500	0.91929700	1.08277900
F	-3.62988100	-1.20020400	1.55887900
O	0.06696100	4.47883600	-0.57582200
S	-1.04626200	4.42658400	0.39411800
O	-2.14899400	5.37844400	0.20141500
O	-1.50638000	3.02287800	0.70777400
C	-0.26072800	4.91703600	2.00297200
F	0.74155000	4.06696900	2.30033400
F	-1.15113800	4.88153500	3.00164400
F	0.24600800	6.15365800	1.92131700
O	0.01052600	-0.59670800	-1.91377900
C	-1.01730900	-1.46627700	-2.45423800
C	-2.15972300	-0.64029100	-3.02147900
C	-2.27588500	-0.49270200	-4.41138400
C	-3.07085500	0.03438100	-2.19400300
C	-3.27461200	0.30497100	-4.97268700
H	-1.58092700	-1.01073300	-5.06701800
C	-4.07262100	0.84024100	-2.73602000
H	-3.01645600	-0.06281500	-1.11345900

C	-4.15451800	0.95867500	-4.11930900
H	-3.37306200	0.42054700	-6.04731700
H	-4.78390900	1.36190200	-2.10349300
La	-0.06028000	0.81630000	0.37952600
H	-2.30871900	-2.14409800	-0.80642800
H	-0.54338700	-2.00235700	-3.27800000
C	2.69630100	0.67680500	-3.94505900
N	3.90932700	0.62756400	-3.30942800
C	1.88616200	-0.41917500	-4.14464400
H	0.67030800	-0.40145700	-2.64939900
H	1.03186200	-0.30642800	-4.80491800
H	2.21078700	-1.43522300	-3.95155600
C	4.38550600	-0.65501100	-2.77183700
H	3.54156700	-1.17738900	-2.30721900
H	5.08849600	-0.44396200	-1.96398100
C	4.67942800	1.84590900	-2.96158200
H	4.29625000	2.64834900	-3.59077400
C	4.46368200	2.25680700	-1.49663800
H	5.00485600	3.18566800	-1.28090700
H	3.40004000	2.43269200	-1.29382300
H	4.82269400	1.49055400	-0.80063900
C	2.21117400	2.01641600	-4.46134000
H	2.89565600	2.42876700	-5.21238800
H	1.23240600	1.89531700	-4.93097700
H	2.11360200	2.76171500	-3.66367800
C	6.17002000	1.70073500	-3.29807400
H	6.31183300	1.43056900	-4.35019100
H	6.67338800	2.65871800	-3.12424000
H	6.66909200	0.94990400	-2.67578100
C	5.05751200	-1.55814000	-3.81254300
H	4.39352600	-1.76363600	-4.65818200
H	5.97278700	-1.10077000	-4.20220900
H	5.32699000	-2.51691600	-3.35281300
O	3.38628700	-0.77241500	0.66449900
S	3.10136900	-0.33142200	2.04615500
O	4.10156900	0.53669900	2.68699200
O	1.67797800	0.13063400	2.23881400
C	3.12537000	-1.89058100	3.05688100
F	2.27574600	-2.80086500	2.55286300
F	4.35740400	-2.41759000	3.05143700
F	2.77258800	-1.63541800	4.32284000
C	-0.91759200	-4.46213400	-3.05678600
H	-0.97130200	-3.94480300	-4.02148600
H	0.12116300	-4.43059000	-2.71213200

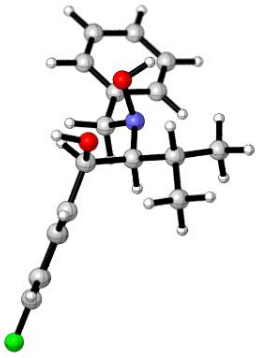
H	-1.17330400	-5.51174200	-3.23954500
C	-3.31073700	-3.75658800	-2.64456600
H	-3.33292800	-3.10684900	-3.52507200
H	-3.64697200	-4.75142200	-2.95894300
H	-4.03517800	-3.37172000	-1.91743500
H	-1.42002400	-4.10703500	0.79320100
H	0.07669400	-3.47937200	1.49277200
C	0.40637900	-5.04737600	0.06635200
C	1.78661700	-4.93341200	-0.16403000
C	-0.20716900	-6.29673900	-0.09439100
C	2.52943000	-6.04009400	-0.57859700
H	2.28646100	-3.98134800	0.00013700
C	0.53826700	-7.40845500	-0.49420700
H	-1.27093300	-6.40185300	0.10335800
C	1.90637900	-7.28076900	-0.74495100
H	3.59645000	-5.93723900	-0.75657300
H	0.04881100	-8.37178200	-0.60939000
H	2.48665700	-8.14418300	-1.05901200
C	-1.90085000	-3.86791200	-2.03425400
H	-1.99690500	-4.57633300	-1.20771500
F	-5.12720500	1.73443300	-4.65155100
H	0.53458500	-2.56292800	-0.77776900

Energies (0K) = -4290.1723782

Energies (0K) + ZPE = -4289.470544

Enthalpies (298K) = -4289.408297

Free Energies (298K) = -4289.57493



F

Number of imaginary frequencies = 0

0 1

C	0.17406400	3.73791600	-0.46835000
C	1.68033600	5.69895700	-0.07835000
H	2.51525800	5.09205700	0.30862200
N	0.91089500	4.87319900	-1.04013200
O	1.91618500	4.28179000	-1.90999300

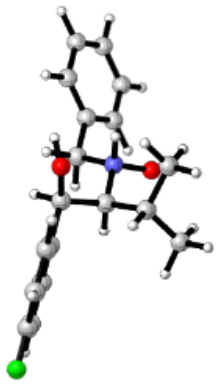
C	3.70654400	6.72364600	-1.30279000
H	3.71685600	5.97884400	-2.10389600
H	4.13146400	7.65743100	-1.69321100
H	4.37062200	6.36668200	-0.50508400
C	1.38237100	7.56126300	-1.86661600
H	1.79554600	8.52122100	-2.20237600
H	1.31538200	6.90820800	-2.74456900
H	0.36838900	7.73644900	-1.49606800
H	0.83166800	3.06828400	0.10961500
H	-0.57271200	4.15529900	0.21357300
C	-0.54604000	2.95044900	-1.54628400
C	-0.34950700	1.57128200	-1.68182800
C	-1.44980800	3.59027600	-2.40842400
C	-1.04277000	0.84133300	-2.65291500
H	0.35228700	1.06457300	-1.02302500
C	-2.13952100	2.86646100	-3.38243300
H	-1.60679400	4.66186200	-2.31362700
C	-1.93921000	1.48724000	-3.50701100
H	-0.87734000	-0.22938100	-2.74336700
H	-2.83668500	3.37690500	-4.04240800
H	-2.47746200	0.92291300	-4.26423300
C	2.28184700	6.96251200	-0.77485100
H	2.37330700	7.72250500	0.00968200
C	1.61439700	6.80331300	2.23464000
C	2.55559100	6.12915700	3.02760200
C	3.28468500	6.80046300	4.00930200
C	3.05100200	8.15869800	4.19553000
C	2.12010700	8.85917800	3.44034300
C	1.40489100	8.17044900	2.45703100
H	2.72052900	5.06425900	2.88199300
H	4.01455900	6.28664100	4.62706200
H	1.96171100	9.91799900	3.62001300
H	0.67312600	8.70263700	1.85777200
C	0.82595700	6.03767200	1.17419200
H	0.53790600	5.08532500	1.63839600
O	-0.34239800	6.73658900	0.74969300
F	3.75132500	8.81807200	5.15231000
H	1.61085800	4.54112500	-2.79690900
H	-0.89610400	6.88274800	1.53743200

Energies (0K) = -1004.127191

Energies (0K) + ZPE = -1003.758574

Enthalpies (298K) = -1003.73614

Free Energies (298K) = -1003.811034



F′

Number of imaginary frequencies = 0

0 1

C	-1.24137000	-0.37380000	-2.79426000
C	-0.43304700	0.68696200	-0.60660000
H	0.56671600	0.67541700	-1.04788900
N	-1.33562400	0.80633300	-1.83719900
O	-1.06505700	1.96432500	-2.51159200
C	0.43112900	3.03547700	-0.04479300
H	0.27153900	3.38526200	-1.06749800
H	0.33849200	3.88318300	0.64660600
H	1.45724400	2.65316800	0.03376800
C	-2.02101500	2.51710900	0.34066600
H	-2.06602700	3.34551300	1.05817600
H	-2.30630100	2.90085900	-0.64457500
H	-2.74775000	1.76309800	0.66123800
H	-0.20190700	-0.37509300	-3.12842700
H	-1.45608900	-1.30094900	-2.25906200
C	-2.21083200	-0.21017700	-3.93537700
C	-1.90499900	0.60689700	-5.03450200
C	-3.44447600	-0.87439900	-3.90632900
C	-2.81583400	0.75311800	-6.08164600
H	-0.95580000	1.13062900	-5.05390000
C	-4.36096100	-0.72506900	-4.95174100
H	-3.68857000	-1.51475000	-3.06133200
C	-4.04689300	0.08898400	-6.04222800
H	-2.56690300	1.38602100	-6.92976800
H	-5.31325500	-1.24769800	-4.91545700
H	-4.75458600	0.20335800	-6.85936800
C	-0.59335400	1.94443300	0.30116200
H	-0.36366100	1.59935900	1.31665100
C	0.48984300	-0.84466500	1.19679600
C	1.80901900	-1.03362400	0.75646000
C	2.84886800	-1.23735500	1.66348200
C	2.55057000	-1.25324100	3.02141400

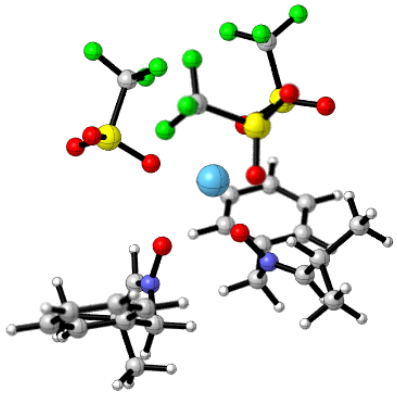
C	1.25766700	-1.07780500	3.49526400
C	0.22799800	-0.87509400	2.57213300
H	2.03210300	-1.02989200	-0.30747900
H	3.87107500	-1.38718800	1.33071000
H	1.06306200	-1.10306900	4.56304700
H	-0.78911200	-0.74857300	2.92468800
C	-0.62653900	-0.64253200	0.17929400
H	-0.56404800	-1.48259900	-0.52132400
O	-1.88146900	-0.68184500	0.86101300
F	3.55642800	-1.45276200	3.90977300
H	-2.31058500	0.81185100	-1.49352900
H	-2.56340200	-0.95361800	0.22318000

Energies (0K) = -1004.109395

Energies (0K) + ZPE = -1003.738422

Enthalpies (298K) = -1003.716544

Free Energies (298K) = -1003.78953



[La(OTf)$_3$(1a)$_2$]

Number of imaginary frequencies = 0

0 1

O	-2.08217700	1.04646900	1.26798800
O	2.02653600	3.86349400	-0.14756300
S	0.62567600	4.19081100	-0.44863900
O	0.27763400	4.46227100	-1.85536400
O	-0.35982400	3.27232400	0.23953100
C	0.30294500	5.79608700	0.42665200
F	0.48952400	5.66683000	1.74643000
F	1.12524400	6.74723100	-0.03258700
F	-0.96523800	6.18803600	0.21306500
O	-5.34574700	4.25575100	2.03879100
S	-4.05200100	4.58387000	2.67140700
O	-3.97601500	4.48775100	4.13654800
O	-2.86846700	3.95357800	1.97241100
C	-3.79227800	6.38398500	2.29042900

F	-3.81818200	6.58395800	0.96131500
F	-2.60965300	6.80056800	2.75908100
F	-4.76081200	7.12027200	2.84947200
O	-4.22005400	5.42163100	-2.70456100
S	-4.84859900	4.19415100	-3.23386500
O	-4.96620700	4.07778100	-4.69471200
O	-4.35916000	2.93576800	-2.56229000
C	-6.60133300	4.28271100	-2.62575600
F	-6.62730900	4.33493200	-1.28191600
F	-7.29716500	3.20525000	-3.01669600
F	-7.20592300	5.37829700	-3.10318700
La	-2.81121600	2.77040500	-0.37423900
C	-2.07236300	1.15221900	3.62483900
C	-0.02072400	1.05330100	2.25268400
H	0.33962000	1.03399500	1.22953800
N	-1.31034700	1.08851100	2.35349200
C	2.07183400	0.01580700	3.07411100
H	2.57896200	0.20651600	2.12066700
H	2.82481300	0.03580500	3.86946200
H	1.64164200	-0.99133600	3.03724300
C	1.61979600	2.49393300	3.43121500
H	2.39123400	2.50791500	4.20963600
H	2.08527300	2.77394000	2.47995100
H	0.86596900	3.24878600	3.67919100
H	-1.36055300	1.25620700	4.44393500
H	-2.66159900	2.06757700	3.56598200
C	-2.96167000	-0.05640000	3.82756100
C	-2.44014000	-1.35741500	3.78846200
C	-4.31877600	0.12480300	4.12179500
C	-3.26524000	-2.45708000	4.02969200
H	-1.38710300	-1.51287000	3.56636500
C	-5.14382400	-0.97559500	4.37436100
H	-4.72812700	1.13112600	4.16466100
C	-4.61966600	-2.26904200	4.32567300
H	-2.84956600	-3.46060400	3.99423700
H	-6.19414000	-0.81945000	4.60558200
H	-5.25944300	-3.12576100	4.51959700
C	0.99642900	1.08218800	3.35417200
H	0.52940400	0.85644800	4.31631300
C	-4.77179200	-0.95091700	0.18489900
C	-2.63112000	-1.61150600	-0.77664100
H	-2.82028800	-2.56096000	-0.28628600
N	-3.54445400	-0.70814500	-0.62458000
C	-0.22089300	-2.18512500	-0.98362400

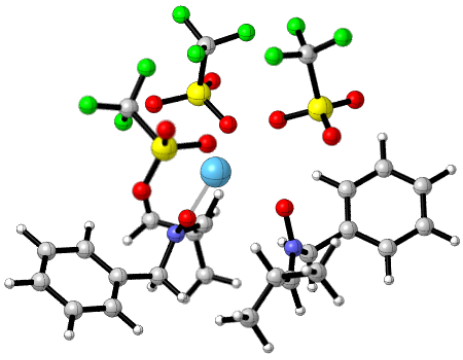
H	-0.42344900	-3.26283400	-0.95614700
H	0.68325600	-2.02629800	-1.58151000
H	-0.01441600	-1.85130100	0.03971900
C	-1.67152500	-1.87056600	-3.05272700
H	-0.77380300	-1.71286000	-3.66111400
H	-1.92693600	-2.93589300	-3.09063000
H	-2.49394800	-1.30192700	-3.49957100
H	-4.64792600	-1.91854100	0.67416100
H	-4.78148900	-0.16653800	0.94455600
C	-6.02128700	-0.90886800	-0.66433000
C	-6.38230900	-2.01566800	-1.44540000
C	-6.83156300	0.23301100	-0.68204500
C	-7.53105400	-1.97670900	-2.23752300
H	-5.76268700	-2.90936500	-1.43148300
C	-7.98086900	0.27504400	-1.47555700
H	-6.56494700	1.08911100	-0.06702700
C	-8.33139400	-0.83002000	-2.25538600
H	-7.80316100	-2.84106700	-2.83744200
H	-8.59555700	1.17065300	-1.48735400
H	-9.22603600	-0.80009200	-2.87165300
C	-1.39921600	-1.41653800	-1.60085600
H	-1.17024100	-0.34587800	-1.61706900
O	-3.49008800	0.47578700	-1.20289900

Energies (0K) = -4032.4850664

Energies (0K) + ZPE = -4031.913582

Enthalpies (298K) = -4031.85723

Free Energies (298K) = -4032.013329



$[La(OTf)_3(1a)_2]^-$

Number of imaginary frequencies = 0

-1 2

O	-2.53793100	1.30747800	1.43716500
O	1.19979400	5.00834600	1.37653600
S	-0.23776900	5.19902100	1.12630000
O	-0.60985900	6.01735400	-0.04474900

O	-1.04399000	3.93231800	1.26560500
C	-0.84082900	6.17296400	2.58910300
F	-0.68149900	5.46956400	3.72168800
F	-0.15083300	7.31805600	2.69933000
F	-2.14041100	6.47451100	2.45811700
O	-6.43381900	2.91207300	2.02352100
S	-5.70432300	4.17965800	2.21698200
O	-5.98134000	4.93683000	3.44590300
O	-4.23521100	4.08852300	1.88678200
C	-6.32233100	5.26324300	0.84030700
F	-6.12340500	4.64950500	-0.34354400
F	-5.66729600	6.43374600	0.81623400
F	-7.63107400	5.50845500	0.97414800
O	-2.39946000	3.92770200	-3.85424900
S	-3.86688800	4.05653100	-3.72152000
O	-4.65531200	3.94905300	-4.96053100
O	-4.43695300	3.29949900	-2.55919300
C	-4.10040400	5.81680200	-3.17779800
F	-3.49297400	6.02016800	-1.98857900
F	-5.40073000	6.10961100	-3.03279800
F	-3.57029800	6.66958100	-4.06591700
La	-3.01858600	2.91060500	-0.12531500
C	-1.46135600	1.38833500	3.52331800
C	-0.49625600	0.18113800	1.56612500
H	-0.79040100	-0.09836600	0.55684300
N	-1.60383800	0.68305100	2.25218600
C	1.68083000	-0.00940700	2.95773900
H	1.34787000	0.47565600	3.88269700
H	2.46737500	-0.72501500	3.23127800
H	2.13104600	0.76124900	2.32089600
C	-0.07864300	-1.83628700	3.11268000
H	0.69380400	-2.54817900	3.43232200
H	-0.53560500	-1.41991500	4.01817500
H	-0.85248700	-2.39867900	2.57603500
H	-0.62451800	0.93010400	4.05719100
H	-1.19891900	2.43781300	3.33313200
C	-2.70085900	1.31654400	4.39779100
C	-3.09727100	2.43885500	5.13699000
C	-3.42970900	0.12687700	4.54108200
C	-4.19534100	2.37751900	6.00101900
H	-2.54433900	3.36973500	5.02884300
C	-4.53031300	0.06322400	5.39848500
H	-3.13484100	-0.74945300	3.97012200
C	-4.91610200	1.18845100	6.13442900

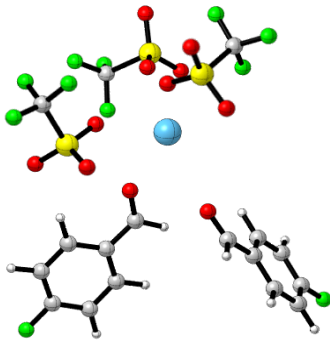
H	-4.49003900	3.26070800	6.56231000
H	-5.08638700	-0.86627500	5.49457400
H	-5.77315700	1.13899500	6.80125500
C	0.53153900	-0.73176000	2.21912900
H	1.00466100	-1.24299500	1.36861100
C	-4.42483000	-1.01310000	0.07667700
C	-2.51771500	-1.25985100	-1.42673100
H	-2.48666500	-2.28099300	-1.06188500
N	-3.45714700	-0.51171600	-0.94057400
C	-0.23460900	-1.58558800	-2.36447400
H	-0.40911700	-2.64987000	-2.56538500
H	0.48641300	-1.21694200	-3.10242800
H	0.22299600	-1.49770900	-1.37221700
C	-2.16601200	-0.88024400	-3.86657900
H	-1.45857100	-0.49714800	-4.61091700
H	-2.40045600	-1.92035600	-4.12176300
H	-3.08638200	-0.29130900	-3.93150700
H	-4.09535800	-2.01105100	0.37357900
H	-4.31818600	-0.33027500	0.92209400
C	-5.83603100	-1.03397100	-0.46447700
C	-6.24747200	-2.06723700	-1.31847100
C	-6.74564400	-0.02430000	-0.12492900
C	-7.54501500	-2.08626700	-1.83289100
H	-5.54852400	-2.85838100	-1.58065300
C	-8.04586000	-0.04375600	-0.63802100
H	-6.44115900	0.77410400	0.54764200
C	-8.44677800	-1.07231900	-1.49443700
H	-7.85315900	-2.89248000	-2.49349000
H	-8.74406200	0.74370600	-0.36640500
H	-9.45775200	-1.08728400	-1.89313600
C	-1.54081000	-0.78368600	-2.45701900
H	-1.33327700	0.27413700	-2.25423100
O	-3.65431700	0.73045800	-1.33097400

Energies (0K) = -4032.5463442

Energies (0K) + ZPE = -4031.979277

Enthalpies (298K) = -4031.922104

Free Energies (298K) = -4032.081724



$La(OTf)_3(FBA)_2$

Number of imaginary frequencies = 0

0 1

O	2.31748100	3.45185900	0.84494000
S	1.64727100	4.53341500	1.57721400
O	2.32633100	5.84097400	1.63823800
O	0.17024200	4.64204700	1.26886200
C	1.59976200	3.96572800	3.34454400
F	0.99831200	2.77656400	3.45542700
F	2.83564500	3.87217100	3.84726300
F	0.90730000	4.85906800	4.08523200
O	-3.37606100	2.39770100	4.15634300
S	-3.33447000	3.82915800	3.83551900
O	-3.28339000	4.78431500	4.95962400
O	-2.35657500	4.16618200	2.72715900
C	-4.95722500	4.19851100	3.01099700
F	-5.12622000	3.44544700	1.91899700
F	-4.99217400	5.49513900	2.64504800
F	-5.97187300	3.96955700	3.85332700
O	-3.98140400	6.35375600	-1.87137000
S	-2.68033400	5.91451600	-1.34217800
O	-1.49488300	6.71051300	-1.71107200
O	-2.72024800	5.54969100	0.12897800
C	-2.40543400	4.24485900	-2.11093500
F	-3.39927000	3.41126600	-1.77822800
F	-1.24657800	3.71779400	-1.69783800
F	-2.37037800	4.36207500	-3.44565500
La	-1.46814700	6.48439800	2.08524800
C	-4.42139000	10.17861800	0.45981400
C	-4.77401800	11.50424900	0.77924300
C	-5.56639300	12.24916500	-0.08608100
C	-5.99545000	11.64361600	-1.26481900
C	-5.66875600	10.33098900	-1.61125500
C	-4.87625700	9.59587900	-0.74238800
H	-4.41994300	11.94655700	1.70631200
H	-5.85138800	13.27288900	0.13176700
H	-6.03476600	9.91465400	-2.54384700

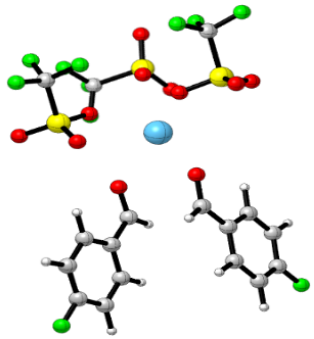
H	-4.60320400	8.57296700	-0.98489900
C	-3.57524200	9.44261900	1.38310900
H	-3.27508700	9.97389300	2.29927600
O	-3.18700200	8.28103200	1.18891700
C	-0.24408400	11.53208900	3.33448900
C	0.36958700	12.79662300	3.31135900
C	0.18838000	13.68844700	4.36406500
C	-0.61203800	13.28939200	5.43061500
C	-1.23498700	12.04171100	5.48855800
C	-1.04565200	11.16197700	4.43164100
H	0.98833100	13.07798500	2.46348000
H	0.64951000	14.67030700	4.37092900
H	-1.84638900	11.78514100	6.34739200
H	-1.51458600	10.18306600	4.44573300
C	-0.03393500	10.62266800	2.20539900
H	0.62175800	11.00578500	1.40253300
O	-0.53208200	9.50295500	2.10308500
F	-0.79432100	14.14387200	6.45533200
F	-6.76069200	12.35539700	-2.11118300

Energies (0K) = -3805.834271

Energies (0K) + ZPE = -3805.540918

Enthalpies (298K) = -3805.496037

Free Energies (298K) = -3805.626039



$[La(OTf)_3(FBA)_2]^-$

Number of imaginary frequencies = 1

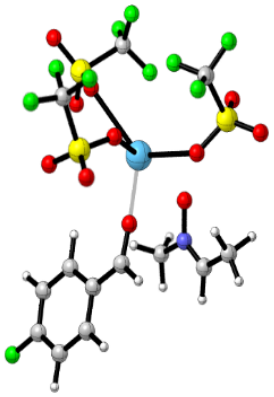
-1 2

O	2.49920200	6.03529600	1.28532300
S	1.44907100	5.46865400	2.14370900
O	1.51452000	5.77299600	3.58567200
O	0.05626700	5.61734000	1.57045000
C	1.68412600	3.62971300	2.02584200
F	1.51820600	3.21925200	0.76124000
F	2.92173400	3.30224900	2.42439700
F	0.80323200	2.98679400	2.80309200

O	-2.97785300	2.33011100	4.86150100
S	-3.16005200	3.74397800	4.50497700
O	-3.13982100	4.72739900	5.60634800
O	-2.36125900	4.18316800	3.30519100
C	-4.88552700	3.85326900	3.82718300
F	-5.07277600	2.96426600	2.84395400
F	-5.09450500	5.08780500	3.32081100
F	-5.79504400	3.63314400	4.78435800
O	-4.56583500	5.70978700	-1.33744900
S	-3.15447800	5.65745700	-0.92727500
O	-2.24322100	6.66253800	-1.50180700
O	-2.97108600	5.44395900	0.55945400
C	-2.53272100	4.03207500	-1.57764600
F	-3.23899500	3.01632100	-1.06185100
F	-1.24203900	3.85646800	-1.26135200
F	-2.65139700	3.99935300	-2.91318400
La	-2.03256400	6.70388500	2.52043400
C	-3.90726400	10.62504600	0.42884300
C	-4.25502400	11.95921900	0.73847800
C	-4.49792700	12.88455300	-0.27130200
C	-4.39136000	12.46380300	-1.59479700
C	-4.05119500	11.15640600	-1.94205800
C	-3.81118600	10.23772400	-0.92801700
H	-4.33639900	12.26342100	1.77864300
H	-4.76825600	13.91234100	-0.05062400
H	-3.98084400	10.88002800	-2.98949700
H	-3.53849800	9.21510400	-1.17000100
C	-3.66038800	9.68125900	1.50333600
H	-3.76522600	10.06659500	2.52696900
O	-3.47057600	8.44294600	1.31953800
C	-1.02332200	11.02015000	2.98979700
C	-1.07391600	12.40697200	2.70176800
C	-1.14150800	13.34902900	3.72144600
C	-1.15264300	12.90310200	5.04224700
C	-1.09529800	11.54983700	5.37242200
C	-1.02926000	10.61328100	4.34762400
H	-1.05667100	12.73655400	1.66628900
H	-1.17905000	14.41338500	3.51072200
H	-1.09553300	11.25095100	6.41622400
H	-0.97006900	9.55609300	4.58898800
C	-0.95418900	10.06638500	1.90719200
H	-0.86501500	10.47134900	0.89156400
O	-0.82594200	8.80318200	2.06692400
F	-1.21419400	13.81748500	6.04137000

F	-4.62884900	13.35776600	-2.58319900

Energies (0K) = -3805.9408495
Energies (0K) + ZPE = -3805.650977
Enthalpies (298K) = -3805.605715
Free Energies (298K) = -3805.738249



B1

Number of imaginary frequencies = 0
-1 2

C	-1.22422200	-4.20628300	1.88427000
C	-3.35799200	-3.27824200	1.19650400
N	-2.15551900	-3.09589700	1.63956400
O	-1.68850600	-1.90019900	1.94340500
O	4.63348500	1.37334300	1.38639000
S	3.37988600	0.63636400	1.60789800
O	2.30752500	0.93437700	0.59414200
O	3.49709100	-0.79741500	1.94632800
C	2.65989000	1.39082200	3.14617700
F	3.46480800	1.19867400	4.19828600
F	2.46029000	2.70704500	2.99365800
F	1.46483400	0.82056400	3.42416600
O	-4.31213600	2.23492100	1.38049500
S	-2.87470100	1.95713000	1.49964400
O	-2.30552700	1.86214200	2.85725300
O	-2.39842600	0.85598100	0.57973900
C	-2.02963400	3.44144100	0.76936000
F	-2.41945700	3.64542000	-0.49452700
F	-0.69499000	3.25627700	0.77949000
F	-2.30749500	4.53859800	1.48559000
O	-0.05433400	1.14588900	-1.50576700
S	0.51632800	0.94181700	-2.88719900
O	1.57168100	-0.08542900	-2.95219100
O	-0.50372900	0.92051100	-3.94873000
C	1.41002500	2.55020300	-3.14358400

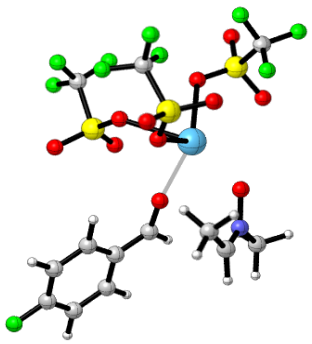
F	0.55426100	3.58068700	-3.06364300
F	1.98188900	2.56775200	-4.35801200
F	2.36827800	2.72307400	-2.22358600
O	-1.08417400	-1.80221100	-1.01950400
C	-1.48404500	-2.75533200	-1.82572800
C	-0.70595000	-3.88942000	-2.17356400
C	-1.23155400	-4.88642900	-3.05334800
C	0.61628800	-4.09574100	-1.66876900
C	-0.49596300	-6.00922000	-3.39896100
H	-2.23318600	-4.75709800	-3.45762800
C	1.35370900	-5.22236600	-2.01527100
H	1.05033600	-3.35434000	-1.00447400
C	0.79073500	-6.16562700	-2.87336400
H	-0.89860500	-6.76530700	-4.06709200
H	2.35843000	-5.37858800	-1.63192900
La	-0.14958200	-0.37375500	0.56564400
H	-3.64674100	-4.30734100	1.01730400
H	-2.48693300	-2.65821300	-2.25655500
C	-4.29672300	-2.15029700	0.97708400
H	-4.63727400	-1.74769700	1.94204800
H	-1.69999500	-5.15628500	1.63985600
H	-0.34053200	-4.05388500	1.26104500
F	1.51307200	-7.27197500	-3.21191500
H	-5.17139000	-2.49261100	0.41947500
H	-3.80868700	-1.32787400	0.44554200
H	-0.94078200	-4.18048500	2.93894300

Energies (0K) = -3609.5816331

Energies (0K) + ZPE = -3609.291669

Enthalpies (298K) = -3609.247311

Free Energies (298K) = -3609.377333



B1′

Number of imaginary frequencies = 0

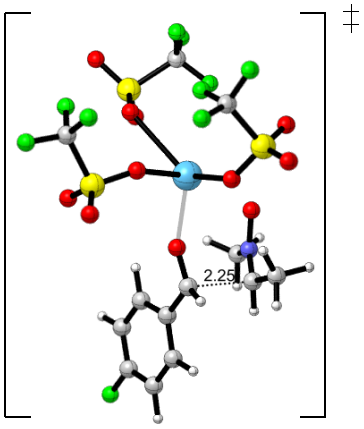
-1 2

C	-0.62909600	-4.56747000	1.57181200

C	-2.85018300	-3.58619000	1.56523700
N	-1.57432400	-3.45500000	1.73897100
O	-1.03029300	-2.31803900	2.12749500
O	5.02218200	1.17757500	1.49718400
S	3.77655400	0.42914500	1.72417300
O	2.69408700	0.72529900	0.71975100
O	3.90663300	-1.00549200	2.05272000
C	3.06054100	1.16860600	3.27099400
F	3.87524000	0.98087600	4.31619000
F	2.84386900	2.48299500	3.12637300
F	1.87468300	0.58230700	3.55374700
O	-3.93612800	1.92223500	1.63085300
S	-2.51325600	1.59127000	1.77726700
O	-2.00803100	1.31122900	3.13415100
O	-2.01921800	0.59772500	0.74691900
C	-1.59716700	3.12561300	1.26614400
F	-1.93315400	3.49813200	0.02595600
F	-0.26869500	2.88934000	1.29313100
F	-1.86132400	4.13419500	2.10486300
O	0.31800900	0.92496100	-1.37400900
S	0.90226500	0.67145800	-2.74317900
O	1.86125800	-0.44762400	-2.77634200
O	-0.08889500	0.73793100	-3.82872300
C	1.94348400	2.19136300	-2.98497200
F	1.18301400	3.29564000	-2.93757300
F	2.54479100	2.14093000	-4.18442700
F	2.88897200	2.28740100	-2.04225600
O	-0.69933500	-2.02841000	-0.89479700
C	-0.72213400	-3.01377200	-1.76378900
C	-1.68509700	-3.13713800	-2.79735500
C	-1.65680200	-4.25909700	-3.68274900
C	-2.71274200	-2.16456700	-3.00569500
C	-2.58520900	-4.40191300	-4.70269100
H	-0.88646500	-5.01608100	-3.55171800
C	-3.64259000	-2.30840000	-4.02823800
H	-2.75534000	-1.29766700	-2.35401000
C	-3.56948500	-3.42252300	-4.86410400
H	-2.56024700	-5.25501100	-5.37481300
H	-4.42116100	-1.56784700	-4.18970900
La	0.25217100	-0.59332800	0.68808500
H	-3.19159100	-4.57296700	1.27522600
H	0.04965200	-3.78809800	-1.67976000
C	-3.79007600	-2.45702400	1.77614100
H	-3.76908200	-2.13287600	2.82559700

H	-1.15914400	-5.46905600	1.26437300
H	0.10235900	-4.27774900	0.81545000
F	-4.48216600	-3.56191300	-5.86866500
H	-4.80742100	-2.76008600	1.51989800
H	-3.50392100	-1.58858800	1.17214900
H	-0.12659000	-4.72652000	2.52890800

Energies (0K) = -3609.5812988
Energies (0K) + ZPE = -3609.29067
Enthalpies (298K) = -3609.246834
Free Energies (298K) = -3609.373379



TS_{B1}
Number of imaginary frequencies = 1
-1 2

C	-5.44052500	-1.02502800	1.34189000
N	-4.48603500	-0.83113600	2.25858800
O	-4.21153300	0.39550600	2.72933300
O	2.10772400	3.66011300	2.34873900
S	0.85339800	2.91320200	2.53203100
O	-0.18951200	3.20120600	1.48784000
O	0.97244300	1.48068800	2.87509200
C	0.08726800	3.66244900	4.05090600
F	0.86798300	3.48270400	5.12351200
F	-0.12411000	4.97631100	3.89058500
F	-1.10768300	3.08020600	4.30312000
O	-6.83636900	4.69386100	1.59075000
S	-5.46926200	4.30215500	1.96159500
O	-5.18436500	4.10315700	3.39576300
O	-4.89547600	3.21824300	1.08094900
C	-4.40993500	5.75895200	1.50544700
F	-4.53664000	6.06896000	0.21005500
F	-3.11426800	5.47489400	1.74929500
F	-4.74848300	6.83028800	2.23563500

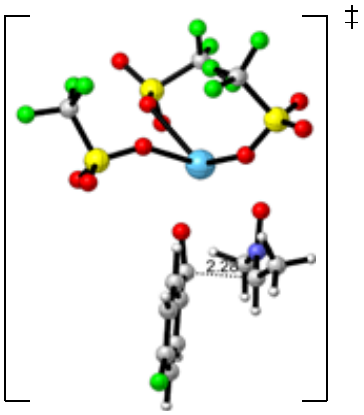
O	-2.47108500	3.40054400	-0.67233500
S	-1.81520400	3.31391400	-2.02551700
O	-0.77914000	2.26922100	-2.12776000
O	-2.76632500	3.41889800	-3.14512600
C	-0.87662300	4.91683000	-2.07184200
F	-1.70947600	5.95304000	-1.88433000
F	-0.27680600	5.06524500	-3.26413300
F	0.06380800	4.95390600	-1.11978500
O	-3.60563300	0.45159200	-0.19892300
C	-4.38293100	-0.52763200	-0.57563000
C	-3.81538400	-1.80377600	-1.02576000
C	-4.63016000	-2.74773800	-1.68767200
C	-2.45774900	-2.12319600	-0.81401400
C	-4.11586600	-3.96683500	-2.11956500
H	-5.67627300	-2.51422000	-1.87146500
C	-1.93039700	-3.34023300	-1.24123200
H	-1.81334900	-1.40271100	-0.32004200
C	-2.77045000	-4.24232100	-1.88616000
H	-4.73449800	-4.69434900	-2.63603600
H	-0.88523700	-3.59168500	-1.08773400
La	-2.66784500	1.89866100	1.41791300
H	-5.64710600	-2.07082200	1.14173100
H	-5.34077500	-0.25782800	-1.03569700
F	-2.26133000	-5.42781100	-2.30821800
C	-3.57426600	-1.87777400	2.69917000
H	-2.55589600	-1.64935000	2.36683300
H	-3.58842000	-1.91406400	3.79361300
H	-3.88765800	-2.84163900	2.29531600
C	-6.56489300	-0.03666300	1.22826200
H	-7.24997700	-0.34599000	0.43416600
H	-7.13035700	-0.00085100	2.17096000
H	-6.20802000	0.97445500	1.01818900

Energies (0K) = -3609.5728815

Energies (0K) + ZPE = -3609.282154

Enthalpies (298K) = -3609.239414

Free Energies (298K) = -3609.363146



$TS_{B1'}$

Number of imaginary frequencies = 1

-1 2

C	-3.34654700	-2.19545300	2.19809400
C	-5.33372300	-1.35219200	1.03571800
N	-4.36130900	-1.18529300	1.93533100
O	-4.10493400	0.02349700	2.46021700
O	2.01322600	3.51181700	2.11678500
S	0.76047700	2.77158700	2.33290600
O	-0.31047400	3.07176500	1.31861400
O	0.87971600	1.33678400	2.66571900
C	0.03742100	3.51816000	3.87361200
F	0.83944400	3.31949700	4.92681400
F	-0.16061000	4.83560000	3.72828700
F	-1.15867200	2.94763700	4.14530800
O	-6.99287900	4.30972800	2.09193500
S	-5.55966900	4.03551000	2.25812500
O	-5.04237600	3.90768000	3.63337800
O	-5.04357300	2.95983300	1.32891900
C	-4.69761800	5.53898300	1.58838300
F	-5.05855400	5.77489500	0.32135800
F	-3.36251000	5.35486900	1.62209100
F	-4.99241600	6.61643700	2.32657100
O	-2.67134800	3.29495200	-0.78486700
S	-2.04630800	3.14667600	-2.14967200
O	-1.02436500	2.08718700	-2.22721900
O	-3.01728900	3.22252800	-3.25370700
C	-1.08734600	4.73256400	-2.27859400
F	-1.90610400	5.78861700	-2.15078400
F	-0.48416000	4.80800100	-3.47599800
F	-0.14725500	4.80877800	-1.32819800
O	-3.69048100	0.40580200	-0.44826000
C	-4.16171000	-0.74978000	-0.82832700
C	-5.13473700	-0.84505500	-1.91333100
C	-5.46158500	-2.10359300	-2.46691400
C	-5.76687000	0.30399300	-2.43850400

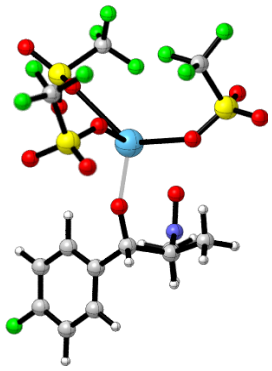
C	-6.38428500	-2.21710100	-3.50201100
H	-4.97745500	-2.99817900	-2.08203400
C	-6.69045000	0.20190600	-3.47628600
H	-5.51396600	1.27758200	-2.03223900
C	-6.98417800	-1.05766800	-3.98978600
H	-6.63570000	-3.17942800	-3.93743500
H	-7.17466100	1.08004500	-3.89302200
La	-2.76919300	1.76805400	1.27916600
H	-5.50319900	-2.38673100	0.75694000
H	-3.52740600	-1.63376200	-0.68946000
C	-6.47440400	-0.38575500	0.98641600
H	-6.99868100	-0.37216700	1.95302500
H	-3.67597100	-3.16374300	1.81690800
H	-2.40365400	-1.90841200	1.71562400
F	-7.88025500	-1.16119700	-5.00516600
H	-7.18694800	-0.69168800	0.21715800
H	-6.14015500	0.63425200	0.78070400
H	-3.18705400	-2.25713400	3.27848100

Energies (0K) = -3609.5736642

Energies (0K) + ZPE = -3609.282913

Enthalpies (298K) = -3609.240224

Free Energies (298K) = -3609.363248



C1

Number of imaginary frequencies = 1

-1 2

C	-1.69172100	-4.52374300	1.71921300
C	-2.71456700	-3.13062100	-0.19043900
N	-2.03044100	-3.24788900	1.10215000
O	-1.54308000	-2.18809200	1.66211200
O	4.80057500	1.07607100	1.17489800
S	3.50091500	0.44606600	1.44890900
O	2.39771900	0.88625800	0.51966600
O	3.49652800	-1.00746100	1.71764700
C	2.94487600	1.19048800	3.05817000

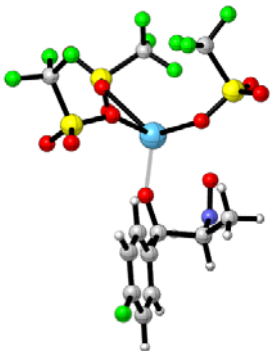
F	3.78678200	0.87319900	4.04880500
F	2.86672400	2.52511000	2.97216200
F	1.71808000	0.72238200	3.38396500
O	-4.25796100	2.36901700	1.33803700
S	-2.86101600	1.99346600	1.59144500
O	-2.46385600	1.74390000	2.98943500
O	-2.33905600	0.94956600	0.62841300
C	-1.86379000	3.48401300	1.09951600
F	-2.12017300	3.84131600	-0.16398000
F	-0.54664000	3.21040000	1.20311600
F	-2.14134800	4.51774000	1.90341800
O	0.03069600	1.31067900	-1.44366200
S	0.20375600	1.27883300	-2.94160500
O	1.25378300	0.35482300	-3.40486100
O	-1.06609100	1.28326000	-3.68638900
C	0.91232600	2.97183200	-3.22702300
F	0.06484400	3.91818400	-2.79639700
F	1.13285700	3.16353800	-4.53670200
F	2.07672400	3.11824700	-2.57695300
O	-0.97163600	-1.64250100	-1.05662400
C	-1.67481100	-2.79077500	-1.33054000
C	-0.77703900	-4.00225000	-1.61548300
C	-1.31420300	-5.15031400	-2.21972200
C	0.58194000	-3.99931400	-1.28313000
C	-0.52633300	-6.27331700	-2.47284100
H	-2.36445400	-5.16869000	-2.50288300
C	1.39132100	-5.11343300	-1.52822900
H	1.01754200	-3.10866000	-0.84144900
C	0.81757600	-6.23233000	-2.11626600
H	-0.93634100	-7.16271500	-2.94153400
H	2.44720000	-5.11604700	-1.27498100
La	-0.08084700	-0.25627100	0.53692000
H	-3.13826400	-4.11708000	-0.39138000
H	-2.31319800	-2.65534300	-2.22440700
C	-3.84434600	-2.10215000	-0.11501400
H	-4.54821400	-2.36373300	0.68320700
H	-2.28336300	-5.31922700	1.26481200
H	-0.62409400	-4.73478600	1.58173000
F	1.59331000	-7.31997400	-2.35982400
H	-4.38981900	-2.10365200	-1.06504500
H	-3.46597500	-1.09464900	0.06683400
H	-1.90854100	-4.46290600	2.79012200

Energies (0K) = -3609.5973772

Energies (0K) + ZPE = -3609.303168

Enthalpies (298K) = -3609.260795

Free Energies (298K) = -3609.383264



C1′

Number of imaginary frequencies = 1

-1 2

C	-3.70187800	-2.32896200	2.51558200
C	-5.28264400	-1.17089500	0.88027000
N	-4.44836500	-1.15116100	2.08988000
O	-4.06119200	-0.01256000	2.57170600
O	2.09266000	3.40366600	1.87047500
S	0.83033400	2.69782400	2.13522800
O	-0.25333500	2.98919100	1.12862200
O	0.92094900	1.27214100	2.50957900
C	0.14833300	3.51059700	3.66191400
F	0.96768100	3.33211600	4.70463900
F	-0.02641400	4.82518500	3.47175300
F	-1.05308500	2.97347800	3.97576800
O	-6.94558200	4.25265600	2.16169200
S	-5.52456900	3.91893500	2.32299300
O	-5.05612800	3.56378100	3.67544100
O	-4.99957800	2.99464800	1.24638400
C	-4.60759600	5.48539500	1.92542400
F	-4.96629700	5.96227700	0.72787400
F	-3.28008500	5.24114900	1.90203900
F	-4.84609000	6.42184000	2.85066300
O	-2.83977900	3.31478200	-0.90703300
S	-2.29774600	3.24653800	-2.31543300
O	-1.18688300	2.29223800	-2.48007000
O	-3.35000100	3.23642300	-3.34415700
C	-1.51288600	4.92371500	-2.47299500
F	-2.42781000	5.88861700	-2.29878000
F	-0.97416500	5.06259800	-3.69387900
F	-0.54413600	5.08901000	-1.56179200
O	-3.65002900	0.26502800	-0.24017200

C	-4.34466500	-0.91674700	-0.37020200
C	-5.16792300	-0.98630900	-1.65871900
C	-5.68255300	-2.20954300	-2.11449000
C	-5.41741100	0.16938400	-2.40900400
C	-6.43878500	-2.28322600	-3.28566500
H	-5.48673200	-3.12179100	-1.55518000
C	-6.16988800	0.11596700	-3.58540900
H	-4.99948500	1.11337600	-2.07690100
C	-6.66972400	-1.11191500	-3.99876500
H	-6.83766900	-3.22570500	-3.64804100
H	-6.36215800	1.00628700	-4.17661800
La	-2.71674700	1.81843400	1.14196900
H	-5.66962600	-2.19110400	0.80801100
H	-3.65129600	-1.77767900	-0.38769800
C	-6.44218200	-0.18618000	1.01149700
H	-6.99394300	-0.37116000	1.93992900
H	-4.25898500	-3.23065500	2.25414700
H	-2.71842500	-2.34996600	2.02669300
F	-7.40004600	-1.17464800	-5.14249600
H	-7.13251900	-0.32725200	0.17497500
H	-6.10131100	0.85058200	1.01089600
H	-3.56081500	-2.27507400	3.59783000

Energies (0K) = -3609.5973621

Energies (0K) + ZPE = -3609.303574

Enthalpies (298K) = -3609.260824

Free Energies (298K) = -3609.385282

Single-Crystal X-Ray Diffraction Analysis of 6a-9•HCl, 6b-3•HCl and 6k-3•HCl:

Supplementary Table 5. Crystal data and structure refinement for **6a-9•HCl**

Identification code	**6a-9•HCl**	
CCDC	1537335	
Empirical formula	$C_{19}H_{26}ClNOS$	
Formula weight	351.92	
Temperature	173.00(10)	
Wavelength	1.54184 Å	
Crystal system, space group	Monoclinic, $P2_1$	
Unit cell dimensions	a = 7.67810(10) Å	alpha = 90 deg.
	b = 7.98550(10) Å	beta = 91.5140(10) deg.
	c = 15.5357(2) Å	gamma = 90 deg.
Volume	952.22(2) Å ^3	
Z, Calculated density	2, 1.227 g/cm^3	
Absorption coefficient	2.817 mm^-1	
F (000)	376.0	

Crystal size	0.3 × 0.1 × 0.05 mm
2 Theta range for data collection	11.396 to 153.66 deg.
Limiting indices	$-9 \le h \le 9$, $-10 \le k \le 10$, $-19 \le l \le 19$
Reflections collected / unique	15866 / 3949 [R_{int} = 0.0589, R_{sigma} = 0.0498]
Completeness to theta = 67.684	0.999
Absorption correction	multi-scan
Max. and min. transmission	1.00000 and 0.36743
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3949/1/212
Goodness-of-fit on F^2	1.102
Final R indices [I>2sigma(I)]	R_1 = 0.0366, wR_2 = 0.0884
R indices (all data)	R_1 = 0.0423, wR_2 = 0.0905
Absolute structure parameter	0.007(11)
Largest diff. peak and hole	0.32 and -0.32 e.Å^-3

Supplementary Table 6. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **6a-9•HCl**. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor

Atom	x	y	z	U(eq)
Cl(1)	10599.7(14)	4558.6(10)	-519.7(5)	44.3(2)
S(1)	3036.4(11)	1351.1(11)	4597.5(5)	36.6(2)
O(1)	9498(3)	2634(3)	1751.1(14)	31.4(5)
N(1)	9192(3)	5860(3)	1182.7(14)	23.5(5)
C(8)	6157(4)	2436(4)	3924(2)	32.6(7)
C(6)	6632(4)	2578(4)	2385.9(19)	25.0(6)
C(14)	10839(4)	6548(4)	2551.6(18)	27.8(6)
C(9)	4522(4)	1781(4)	3774.6(19)	28.0(6)
C(1)	7739(4)	3190(4)	1656.7(18)	24.1(6)
C(2)	7711(4)	5120(3)	1667.5(17)	20.9(6)
C(13)	10955(4)	5962(4)	1633(2)	30.5(7)
C(19)	10212(4)	8125(4)	2746(2)	30.7(7)
C(3)	5957(4)	5833(4)	1327.4(19)	27.3(6)
C(7)	7206(4)	2822(4)	3236(2)	32.2(7)
C(11)	5001(5)	1872(4)	2246.2(19)	31.7(7)
C(10)	3942(4)	1472(4)	2926.1(19)	33.0(7)
C(17)	10571(5)	7557(5)	4258(2)	38.8(8)
C(4)	5631(5)	7598(4)	1675(2)	36.6(7)
C(16)	11204(5)	5992(5)	4072(2)	40.5(9)
C(5)	5762(5)	5791(5)	342(2)	43.8(9)
C(18)	10063(5)	8629(5)	3600(2)	37.9(8)
C(15)	11336(5)	5481(4)	3221(2)	36.4(8)
C(12)	4122(6)	2098(6)	5563(2)	47.0(9)

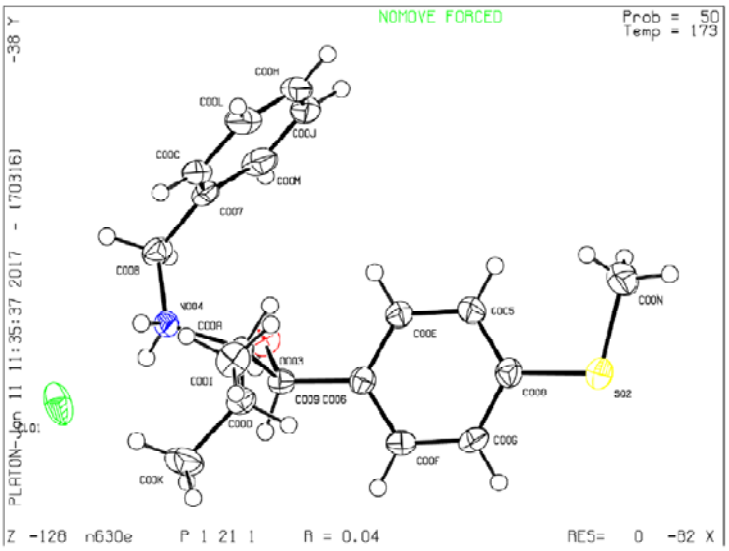
Supplementary Table 7. Bond lengths for **6a-9•HCl**

Atom	Atom	Length/Å
S(1)	C(9)	1.769(3)
S(1)	C(12)	1.798(4)
O(1)	C(1)	1.426(4)
N(1)	C(2)	1.502(4)
N(1)	C(13)	1.510(4)
C(8)	C(9)	1.374(5)
C(8)	C(7)	1.390(5)
C(6)	C(1)	1.515(4)
C(6)	C(7)	1.395(4)
C(6)	C(11)	1.385(5)
C(14)	C(13)	1.507(4)
C(14)	C(19)	1.384(5)
C(14)	C(15)	1.390(4)
C(9)	C(10)	1.402(4)
C(1)	C(2)	1.542(4)
C(2)	C(3)	1.542(4)
C(19)	C(18)	1.394(4)
C(3)	C(4)	1.532(5)
C(3)	C(5)	1.534(4)
C(11)	C(10)	1.387(5)
C(17)	C(16)	1.375(6)
C(17)	C(18)	1.382(5)
C(16)	C(15)	1.391(5)

Supplementary Table 8. Bond angles for **6a-9•HCl**

Atom	Atom	Atom	Angle/deg.
C(9)	S(1)	C(12)	104.17(17)
C(2)	N(1)	C(13)	118.1(2)
C(9)	C(8)	C(7)	119.9(3)
C(7)	C(6)	C(1)	119.6(3)
C(11)	C(6)	C(1)	122.5(3)
C(11)	C(6)	C(7)	117.8(3)
C(19)	C(14)	C(13)	121.3(3)
C(19)	C(14)	C(15)	119.0(3)
C(15)	C(14)	C(13)	119.7(3)
C(8)	C(9)	S(1)	123.7(2)
C(8)	C(9)	C(10)	119.5(3)
C(10)	C(9)	S(1)	116.8(3)
O(1)	C(1)	C(6)	111.8(2)
O(1)	C(1)	C(2)	108.9(2)
C(6)	C(1)	C(2)	107.8(2)

N(1)	C(2)	C(1)	112.2(2)
N(1)	C(2)	C(3)	110.4(2)
C(1)	C(2)	C(3)	112.2(2)
C(14)	C(13)	N(1)	112.4(2)
C(14)	C(19)	C(18)	120.5(3)
C(4)	C(3)	C(2)	111.6(2)
C(4)	C(3)	C(5)	111.0(3)
C(5)	C(3)	C(2)	113.3(3)
C(8)	C(7)	C(6)	121.5(3)
C(6)	C(11)	C(10)	121.3(3)
C(11)	C(10)	C(9)	119.8(3)
C(16)	C(17)	C(18)	120.1(3)
C(17)	C(16)	C(15)	120.1(3)
C(17)	C(18)	C(19)	119.8(3)
C(14)	C(15)	C(16)	120.4(3)



Supplementary Table 9. Crystal data and structure refinement for **6b-3•HCl•H_2O**

Identification code	**6b-3•HCl**	
CCDC	1537337	
Empirical formula	$C_{18}H_{26.33}ClNO_{2.17}S$	
Formula weight	358.88	
Temperature	173.00(10)	
Wavelength	1.54184 Å	
Crystal system, space group	Monoclinic, $P2_1$	
Unit cell dimensions	a = 9.9390(3) Å	alpha = 90 deg.
	b = 15.6514(3) Å	beta = 96.850(2) deg.
	c = 12.5115(2) Å	gamma = 90 deg.

Volume	1932.39(8) Å ^3
Z, Calculated density	4, 1.234 g/cm^3
Absorption coefficient	2.831 mm^-1
F (000)	767.0
Crystal size	0.1 × 0.08 × 0.02 mm
2 Theta range for data collection	7.116 to 129.998 deg.
Limiting indices	$-11 \leq h \leq 11$, $-18 \leq k \leq 18$, $-14 \leq l \leq 14$
Reflections collected / unique	30230 / 6450 [R_{int} = 0.0866, R_{sigma} = 0.0645]
Completeness to theta = 64.999	0.987
Absorption correction	multi-scan
Max. and min. transmission	1.00000 and 0.47199
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6450/7/451
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R_1 = 0.0554, wR_2 = 0.1215
R indices (all data)	R_1 = 0.0623, wR_2 = 0.1247
Absolute structure parameter	0.010(13)
Largest diff. peak and hole	0.35 and -0.22 e.Å^-3

Supplementary Table 10. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **6b-3•HCl•H_2O**. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor

Atom	x	y	z	U(eq)
Cl(2)	-5599.9(14)	4091.2(7)	4412.2(9)	43.6(3)
Cl(1)	-9969.7(14)	901.4(6)	5532.2(9)	45.0(3)
S(003)	-10431.3(15)	1004.9(9)	-1029.8(9)	49.3(3)
S(004)	-4800.8(16)	3969.2(8)	10964.8(10)	50.4(3)
O(21)	-6233(4)	2551(2)	5844(2)	38.6(7)
O(11)	-11292(4)	2281.8(19)	3974(3)	38.1(7)
N(21)	-4937(4)	1121(2)	5332(3)	31.3(8)
O(1)	-2687(4)	3828(3)	5565(3)	55.7(10)
C(113)	-9379(5)	3749(3)	6543(4)	36.7(10)
C(209)	-3756(6)	3363(3)	9226(4)	44.5(12)
C(208)	-4950(5)	3467(3)	9688(4)	36.8(11)
N(11)	-10265(4)	3847(2)	4616(3)	31.3(8)
C(206)	-6177(5)	2846(3)	8099(4)	34.3(10)
C(205)	-4982(5)	2752(3)	7634(4)	31.6(9)
C(202)	-4788(5)	1405(3)	6506(3)	30.5(9)
C(101)	-10218(5)	2595(3)	3427(3)	29.4(9)
C(105)	-10270(5)	2230(3)	2298(3)	32.2(10)
C(204)	-3387(5)	1156(3)	7029(4)	39.8(11)
C(203)	-5900(5)	929(3)	7002(3)	36.5(10)

C(207)	-6158(6)	3199(3)	9122(4)	38.6(11)
C(108)	-10291(5)	1506(3)	243(4)	36.2(10)
C(201)	-5002(5)	2386(3)	6506(3)	31.0(9)
C(102)	-10309(5)	3584(3)	3444(3)	30.9(9)
C(110)	-11481(5)	2066(3)	1658(4)	36.6(10)
C(112)	-9109(6)	3543(3)	5406(4)	42.6(11)
C(210)	-3773(5)	3016(3)	8201(4)	40.3(11)
C(218)	-4914(6)	1887(3)	2761(4)	41.3(12)
C(103)	-9114(5)	3992(3)	2978(3)	37.5(10)
C(107)	-9072(5)	1675(3)	866(4)	38(1)
C(213)	-4378(5)	1276(3)	3469(3)	35.4(10)
C(217)	-5270(6)	1682(4)	1676(4)	49.6(13)
C(106)	-9068(5)	2038(3)	1888(4)	35.8(10)
C(114)	-9854(6)	3125(3)	7185(4)	43.1(12)
C(118)	-9135(7)	4558(3)	6961(4)	53.1(15)
C(214)	-4185(8)	453(3)	3095(4)	57.9(16)
C(109)	-11503(5)	1713(3)	650(4)	38.9(11)
C(212)	-3945(6)	1486(4)	4632(4)	45.6(12)
C(115)	-10055(7)	3308(4)	8239(5)	53.0(14)
C(216)	-5087(7)	871(5)	1325(4)	61.1(16)
C(111)	-8745(6)	1017(4)	-1373(4)	53.4(14)
O(2B)	-7574(7)	720(7)	4071(7)	53(2)
C(104)	-11654(5)	3905(3)	2897(4)	37.4(10)
C(116)	-9803(8)	4118(5)	8650(4)	66.6(18)
C(117)	-9350(9)	4738(4)	7999(5)	72(2)
C(215)	-4555(10)	263(4)	2033(5)	77(2)
C(211)	-6494(8)	4052(5)	11251(5)	70.8(19)
O(3A)	-2482(15)	4942(10)	7300(10)	71(5)
O(2A)	-7560(12)	1199(11)	4311(9)	47(3)

Supplementary Table 11. Bond lengths for **6b-3•HCl•H_2O**

Atom	Atom	Length/Å
S(003)	C(108)	1.765(4)
S(003)	C(111)	1.780(6)
S(004)	C(208)	1.771(5)
S(004)	C(211)	1.766(7)
O(21)	C(201)	1.416(6)
O(11)	C(101)	1.422(5)
N(21)	C(202)	1.524(5)
N(21)	C(212)	1.508(6)

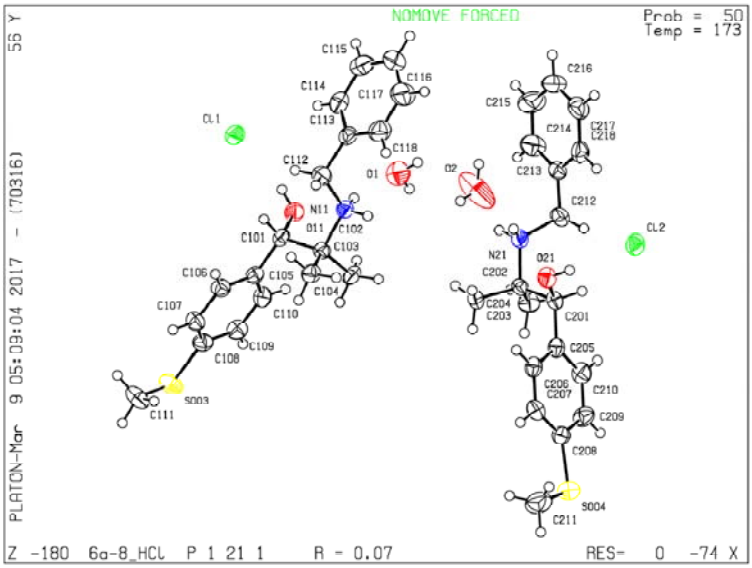
C(113)	C(112)	1.513(6)
C(113)	C(114)	1.382(8)
C(113)	C(118)	1.380(7)
C(209)	C(208)	1.390(8)
C(209)	C(210)	1.391(7)
C(208)	C(207)	1.384(8)
N(11)	C(102)	1.519(5)
N(11)	C(112)	1.500(6)
C(206)	C(205)	1.392(7)
C(206)	C(207)	1.392(7)
C(205)	C(201)	1.521(6)
C(205)	C(210)	1.384(7)
C(202)	C(204)	1.517(7)
C(202)	C(203)	1.525(6)
C(202)	C(201)	1.549(6)
C(101)	C(105)	1.519(6)
C(101)	C(102)	1.551(5)
C(105)	C(110)	1.388(7)
C(105)	C(106)	1.388(7)
C(108)	C(107)	1.386(7)
C(108)	C(109)	1.400(7)
C(102)	C(103)	1.524(7)
C(102)	C(104)	1.513(7)
C(110)	C(109)	1.375(7)
C(218)	C(213)	1.368(7)
C(218)	C(217)	1.398(8)
C(107)	C(106)	1.399(7)
C(213)	C(214)	1.391(7)
C(213)	C(212)	1.505(6)
C(217)	C(216)	1.362(10)
C(114)	C(115)	1.387(8)
C(118)	C(117)	1.371(8)
C(214)	C(215)	1.369(9)
C(115)	C(116)	1.381(10)
C(216)	C(215)	1.363(10)
C(116)	C(117)	1.377(11)

Supplementary Table 12. Bond angles for **6b-3•HCl•H_2O**

Atom	Atom	Atom	Angle/deg.
C(108)	S(003)	C(111)	103.8(3)
C(211)	S(004)	C(208)	103.7(3)
C(212)	N(21)	C(202)	117.0(4)
C(114)	C(113)	C(112)	120.5(4)

C(118)	C(113)	C(112)	120.5(5)
C(118)	C(113)	C(114)	119.0(5)
C(208)	C(209)	C(210)	120.8(5)
C(209)	C(208)	S(004)	116.3(4)
C(207)	C(208)	S(004)	124.7(4)
C(207)	C(208)	C(209)	118.9(5)
C(112)	N(11)	C(102)	118.9(4)
C(205)	C(206)	C(207)	120.5(5)
C(206)	C(205)	C(201)	120.7(4)
C(210)	C(205)	C(206)	119.1(4)
C(210)	C(205)	C(201)	120.2(4)
N(21)	C(202)	C(203)	104.9(4)
N(21)	C(202)	C(201)	106.9(3)
C(204)	C(202)	N(21)	108.6(4)
C(204)	C(202)	C(203)	111.8(4)
C(204)	C(202)	C(201)	112.0(4)
C(203)	C(202)	C(201)	112.2(4)
O(11)	C(101)	C(105)	111.9(4)
O(11)	C(101)	C(102)	106.8(3)
C(105)	C(101)	C(102)	113.1(3)
C(110)	C(105)	C(101)	122.5(4)
C(106)	C(105)	C(101)	119.3(4)
C(106)	C(105)	C(110)	118.2(4)
C(208)	C(207)	C(206)	120.4(5)
C(107)	C(108)	S(003)	124.2(4)
C(107)	C(108)	C(109)	118.9(4)
C(109)	C(108)	S(003)	116.9(4)
O(21)	C(201)	C(205)	112.8(4)
O(21)	C(201)	C(202)	106.9(4)
C(205)	C(201)	C(202)	112.7(3)
N(11)	C(102)	C(101)	106.7(3)
N(11)	C(102)	C(103)	108.8(4)
C(103)	C(102)	C(101)	111.3(4)
C(104)	C(102)	N(11)	105.6(4)
C(104)	C(102)	C(101)	112.0(4)
C(104)	C(102)	C(103)	112.1(4)
C(109)	C(110)	C(105)	121.4(5)
N(11)	C(112)	C(113)	110.1(4)
C(205)	C(210)	C(209)	120.3(5)
C(213)	C(218)	C(217)	120.1(5)
C(108)	C(107)	C(106)	119.9(5)
C(218)	C(213)	C(214)	119.2(4)
C(218)	C(213)	C(212)	121.2(4)
C(214)	C(213)	C(212)	119.5(5)

C(216)	C(217)	C(218)	119.9(5)
C(105)	C(106)	C(107)	121.2(5)
C(113)	C(114)	C(115)	120.3(5)
C(117)	C(118)	C(113)	120.5(5)
C(215)	C(214)	C(213)	119.7(5)
C(110)	C(109)	C(108)	120.4(5)
C(213)	C(212)	N(21)	110.3(4)
C(116)	C(115)	C(114)	120.2(5)
C(217)	C(216)	C(215)	119.8(5)
C(117)	C(116)	C(115)	119.0(5)
C(118)	C(117)	C(116)	120.9(6)
C(216)	C(215)	C(214)	121.2(6)



Supplementary Table 13. Crystal data and structure refinement for **6k-3•HCl**

Identification code	**6k-3•HCl**	
CCDC	1537338	
Empirical formula	$C_{14}H_{22}ClNOS$	
Formula weight	287.83	
Temperature	173.00(10)	
Wavelength	1.54184 Å	
Crystal system, space group	Orthorhombic, $P2_12_12_1$	
Unit cell dimensions	a = 7.23813(6) Å	alpha = 90 deg.
	b = 8.06555(6) Å	beta = 90 deg.
	c = 26.48022(19) Å	gamma = 90 deg.
Volume	1545.90(2) Å ^3	
Z, Calculated density	4, 1.237 g/cm^3	
Absorption coefficient	3.353 mm^-1	

F (000)	616.0
Crystal size	0.3 × 0.11 × 0.08 mm
2 Theta range for data collection	11.468 to 153.734 deg.
Limiting indices	$-9 \le h \le 8$, $-10 \le k \le 10$, $-33 \le l \le 33$
Reflections collected / unique	27152 / 3247 [R_{int} = 0.0571, R_{sigma} = 0.0292]
Completeness to theta = 67.684	0.999
Absorption correction	multi-scan
Max. and min. transmission	1.00000 and 0.58671
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3247/0/167
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R_1 = 0.0284, wR_2 = 0.0710
R indices (all data)	R_1 = 0.0335, wR_2 = 0.0716
Absolute structure parameter	-0.002(6)
Largest diff. peak and hole	0.21/-0.19 e.Å^-3

Supplementary Table 14. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **6k-3•HCl**. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{IJ} tensor

Atom	x	y	z	U(eq)
Cl(1)	-653.8(7)	1768.0(6)	5359.8(2)	32.40(13)
S(1)	8859.6(8)	7200.1(7)	7672.5(2)	38.05(14)
O(1)	3756(2)	4629.9(17)	5727.2(6)	34.4(3)
N(1)	3457(2)	1151.5(18)	5625.2(6)	24.1(3)
C(5)	3712(3)	-712(2)	5657.4(7)	26.8(4)
C(8)	6114(3)	4489(2)	6357.8(7)	25.9(4)
C(12)	8863(3)	5700(2)	6721.7(7)	28.7(4)
C(13)	7990(3)	4845(2)	6334.0(7)	28.2(4)
C(9)	5114(3)	5026(3)	6776.9(8)	31.3(4)
C(10)	5975(3)	5874(3)	7167.3(8)	32.1(4)
C(4)	5633(3)	-818(2)	5889.2(8)	31.4(4)
C(1)	5188(3)	3590(2)	5925.4(7)	25.9(4)
C(11)	7871(3)	6193(2)	7144.2(7)	27.6(4)
C(2)	4345(3)	1932(2)	6083.8(7)	26.5(4)
C(3)	5741(3)	614(2)	6270.2(7)	32.2(4)
C(6)	2225(3)	-1415(3)	6004.4(9)	37.8(5)
C(14)	11294(3)	7049(3)	7555.0(9)	40.2(5)
C(7)	3563(4)	-1421(3)	5125.4(8)	37.2(5)

Supplementary Table 15. Bond lengths for **6k-3•HCl**

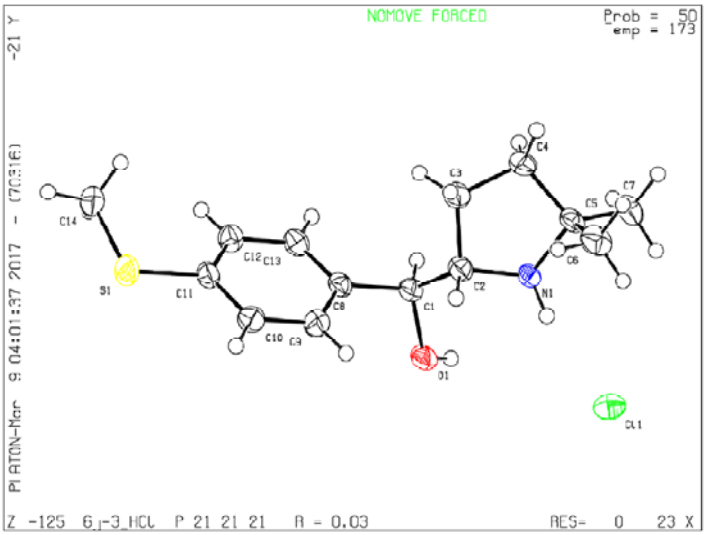
Atom	Atom	Length/Å
S(1)	C(11)	1.769(2)
S(1)	C(14)	1.794(3)

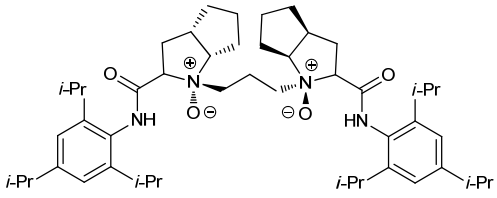
O(1)	C(1)	1.433(2)
N(1)	C(5)	1.517(2)
N(1)	C(2)	1.511(2)
C(5)	C(4)	1.523(3)
C(5)	C(6)	1.524(3)
C(5)	C(7)	1.524(3)
C(8)	C(13)	1.389(3)
C(8)	C(9)	1.394(3)
C(8)	C(1)	1.512(3)
C(12)	C(13)	1.389(3)
C(12)	C(11)	1.388(3)
C(9)	C(10)	1.387(3)
C(10)	C(11)	1.398(3)
C(4)	C(3)	1.535(3)
C(1)	C(2)	1.529(2)
C(2)	C(3)	1.548(3)

Supplementary Table 16. Bond angles for **6k-3•HCl**

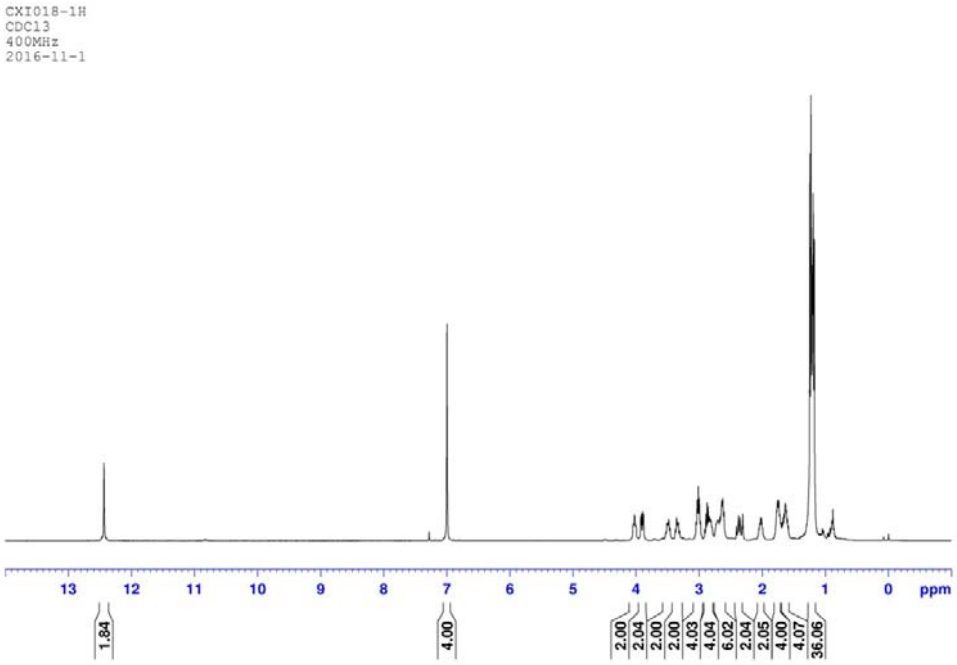
Atom	Atom	Atom	Angle/deg.
C(11)	S(1)	C(14)	103.23(10)
C(2)	N(1)	C(5)	108.40(14)
N(1)	C(5)	C(4)	100.93(15)
N(1)	C(5)	C(6)	108.45(16)
N(1)	C(5)	C(7)	108.14(15)
C(4)	C(5)	C(6)	112.38(18)
C(4)	C(5)	C(7)	114.58(18)
C(6)	C(5)	C(7)	111.57(18)
C(13)	C(8)	C(9)	118.66(18)
C(13)	C(8)	C(1)	119.84(18)
C(9)	C(8)	C(1)	121.46(19)
C(11)	C(12)	C(13)	120.2(2)
C(8)	C(13)	C(12)	120.91(19)
C(10)	C(9)	C(8)	120.9(2)
C(9)	C(10)	C(11)	119.97(19)
C(5)	C(4)	C(3)	105.61(16)
O(1)	C(1)	C(8)	108.51(15)
O(1)	C(1)	C(2)	108.87(16)
C(8)	C(1)	C(2)	112.87(15)
C(12)	C(11)	S(1)	124.05(17)
C(12)	C(11)	C(10)	119.38(18)
C(10)	C(11)	S(1)	116.57(15)
N(1)	C(2)	C(1)	108.27(14)
N(1)	C(2)	C(3)	104.36(14)

C(1)	C(2)	C(3)	115.32(17)
C(4)	C(3)	C(2)	105.89(16)

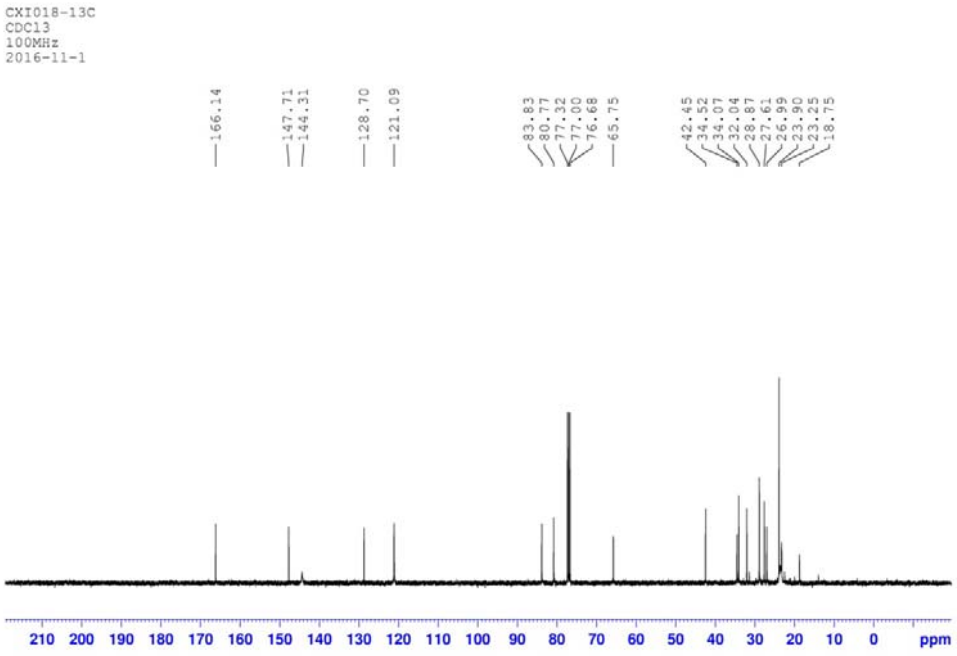




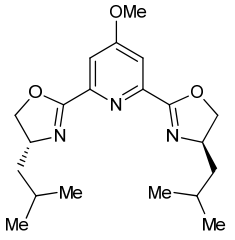
L1-b



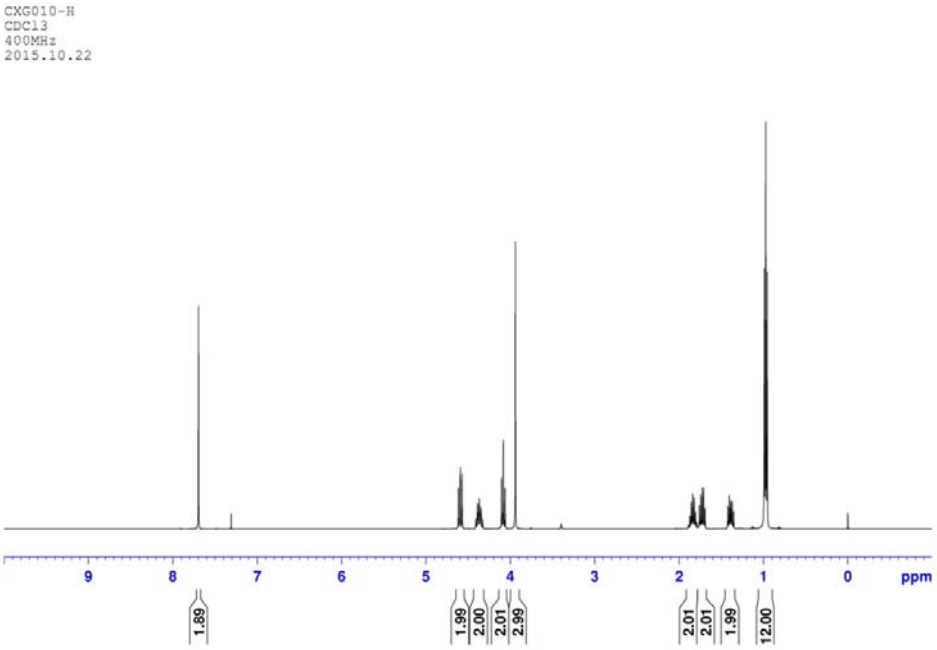
Supplementary Figure 12. ^{1}H NMR ($CDCl_3$) of compound **L1-b**.



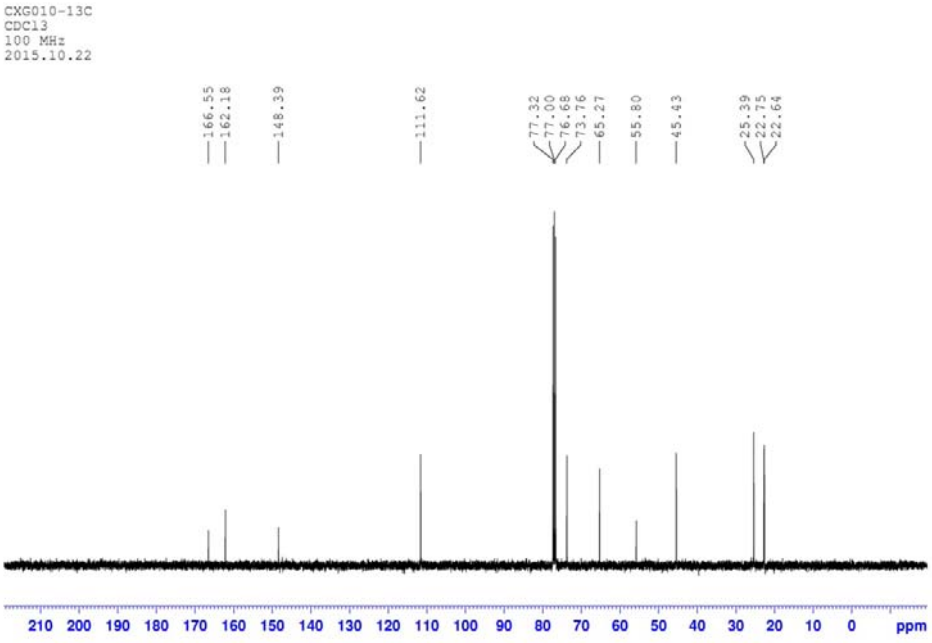
Supplementary Figure 13. ^{13}C NMR ($CDCl_3$) of compound **L1-b**.



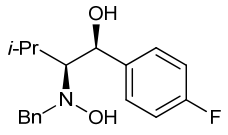
L2-b



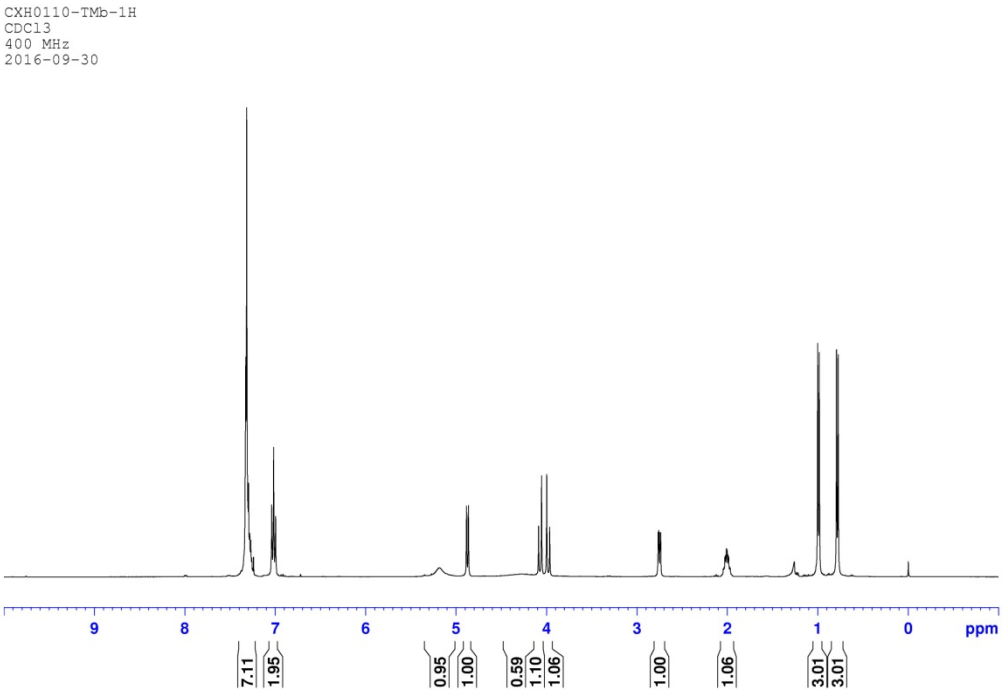
Supplementary Figure 14. ^{1}H NMR ($CDCl_3$) of compound **L2-b**.



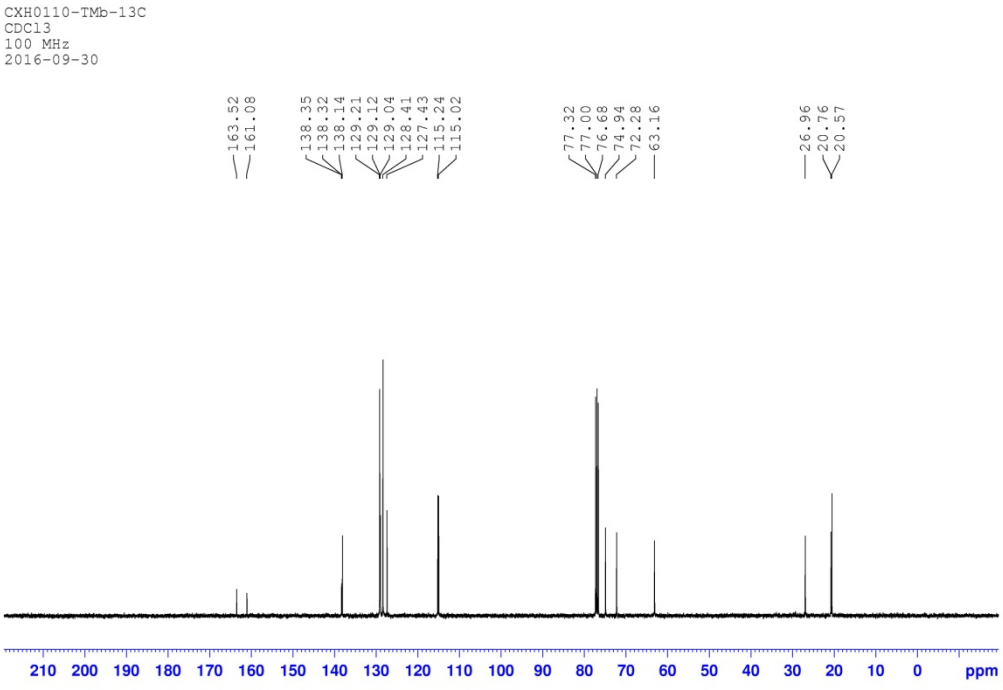
Supplementary Figure 15. ^{13}C NMR ($CDCl_3$) of compound **L2-b**.



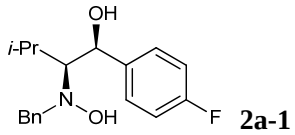
2a-1



Supplementary Figure 16. ^{1}H NMR ($CDCl_3$) of compound **2a-1**.

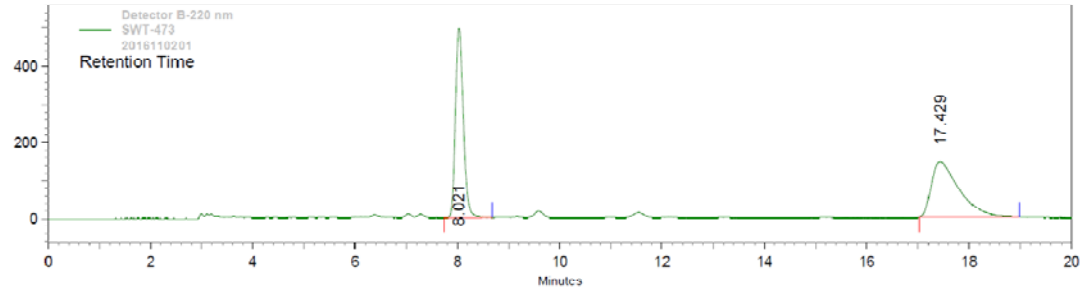


Supplementary Figure 17. ^{13}C NMR ($CDCl_3$) of compound **2a-1**.



2a-1

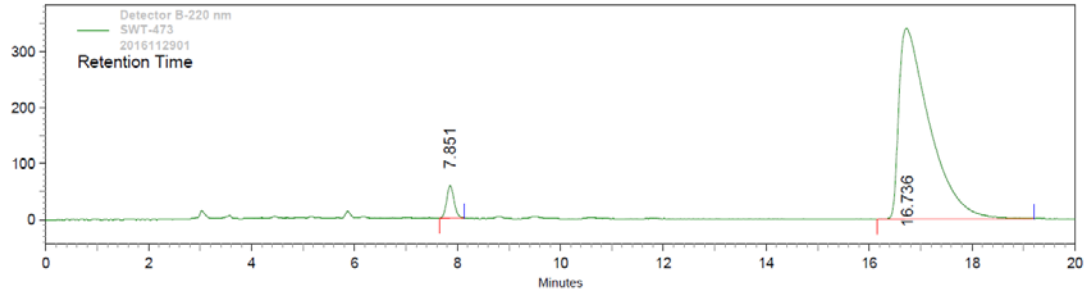
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 85/15 (v/v), 1.0 mL/min, 220 nm]



Detector B-220 nm

Pk #	Retention Time	Area	Area Percent	Height
1	8.021	5453480	49.54	497022
2	17.429	5554977	50.46	145289

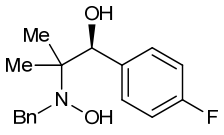
Supplementary Figure 18. Racemate of compound **2a-1**.



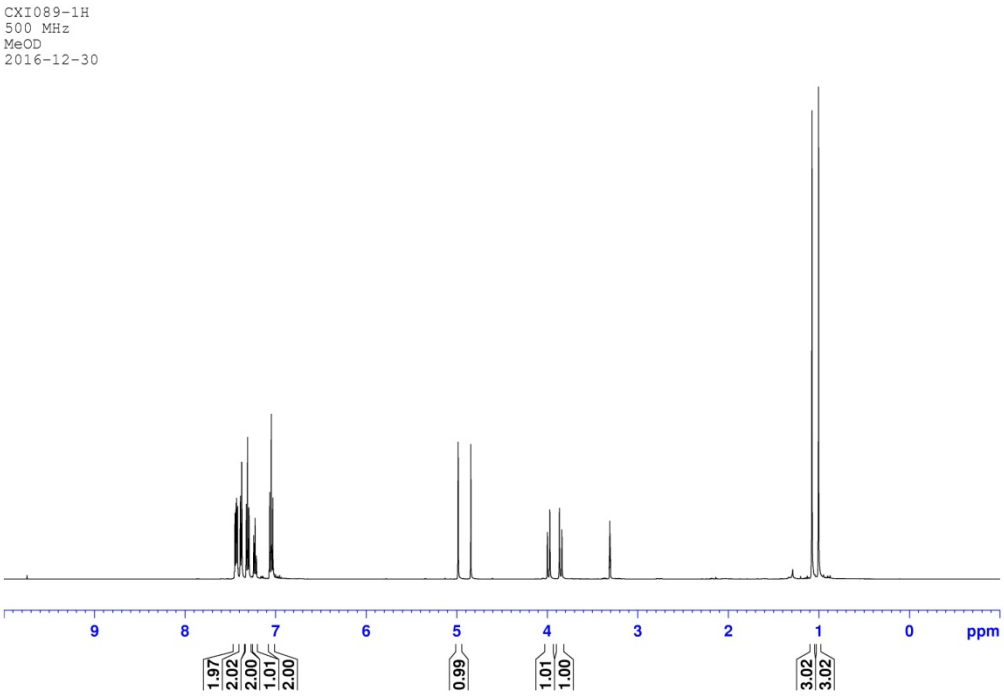
Detector B-220 nm

Pk #	Retention Time	Area	Area Percent	Height
1	7.851	586999	4.00	57895
2	16.736	14077559	96.00	340318

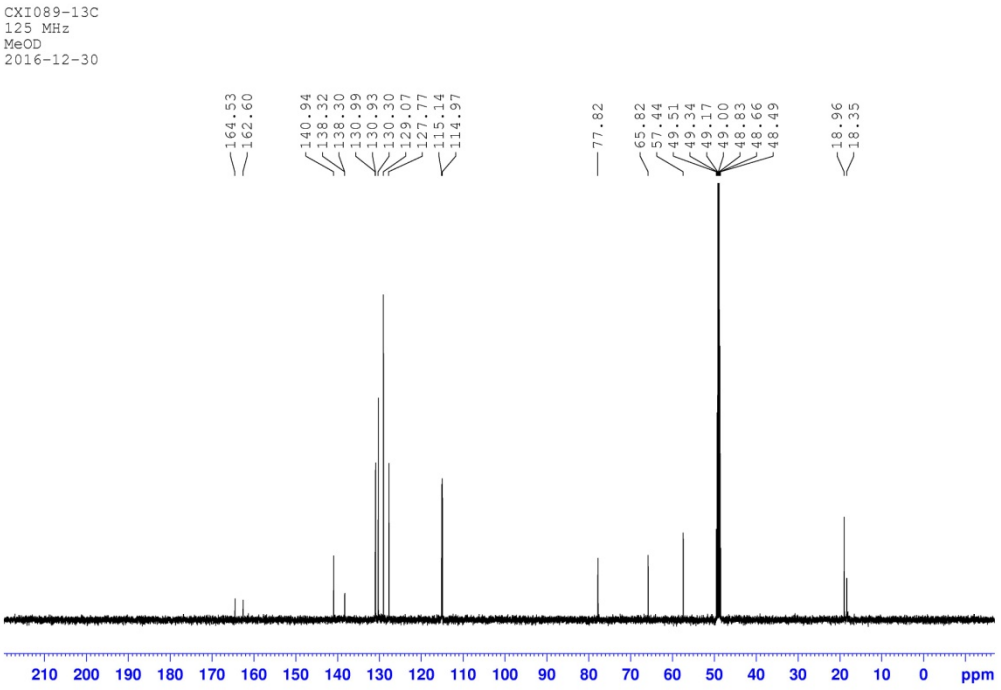
Supplementary Figure 19. Enantioenriched mixture of compound **2a-1**.



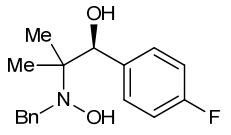
2b-1



Supplementary Figure 20. ^{1}H NMR (MeOD) of compound **2b-1**.

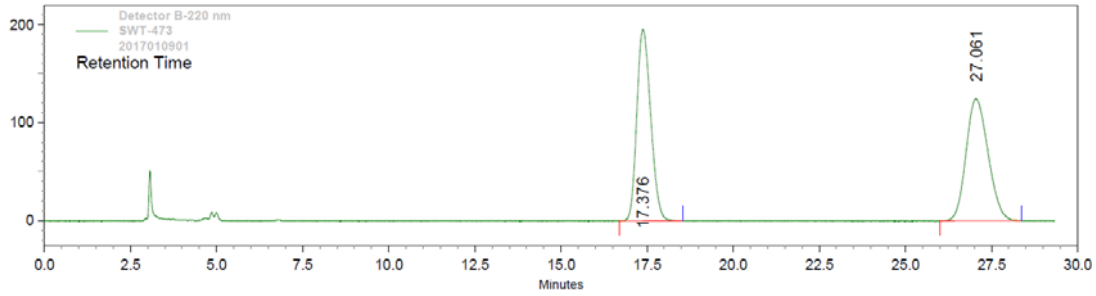


Supplementary Figure 21. ^{13}C NMR (MeOD) of compound **2b-1**.



2b-1

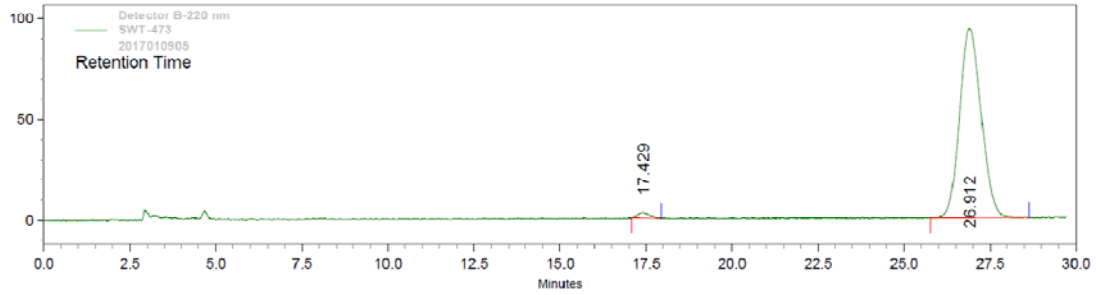
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 60/40 (v/v), 1.0 mL/min, 220 nm]



Detector B-220 nm

Pk #	Retention Time	Area	Area Percent	Height
1	17.376	5467730	49.81	195513
2	27.061	5509160	50.19	124332

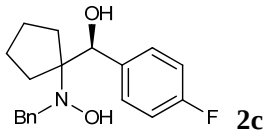
Supplementary Figure 22. Racemate of compound **2b-1**.



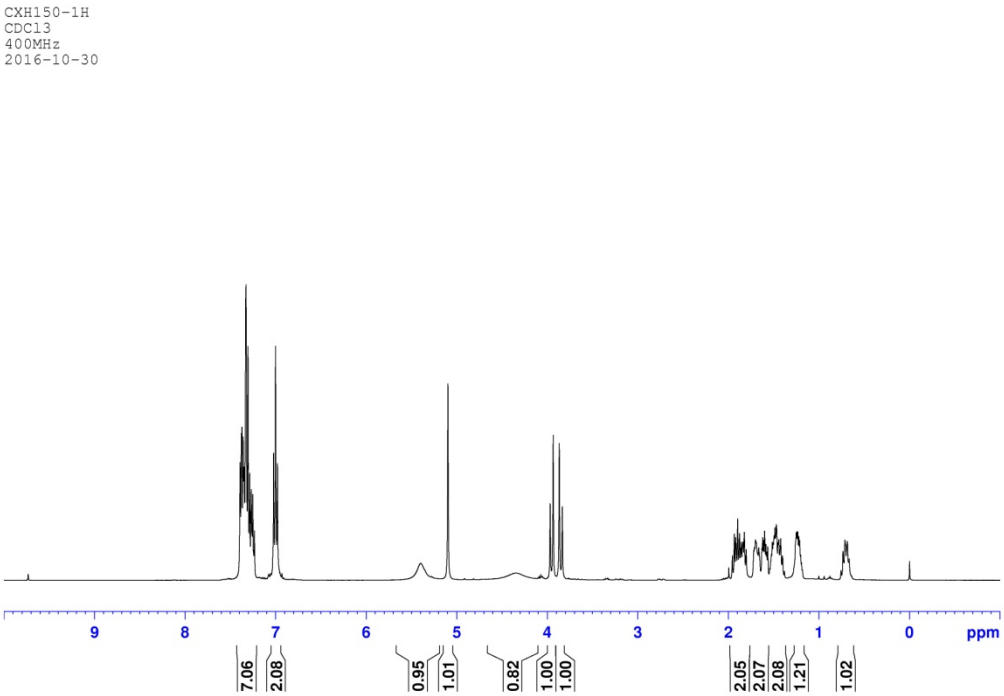
Detector B-220 nm

Pk #	Retention Time	Area	Area Percent	Height
1	17.429	61294	1.48	2833
2	26.912	4076642	98.52	93447

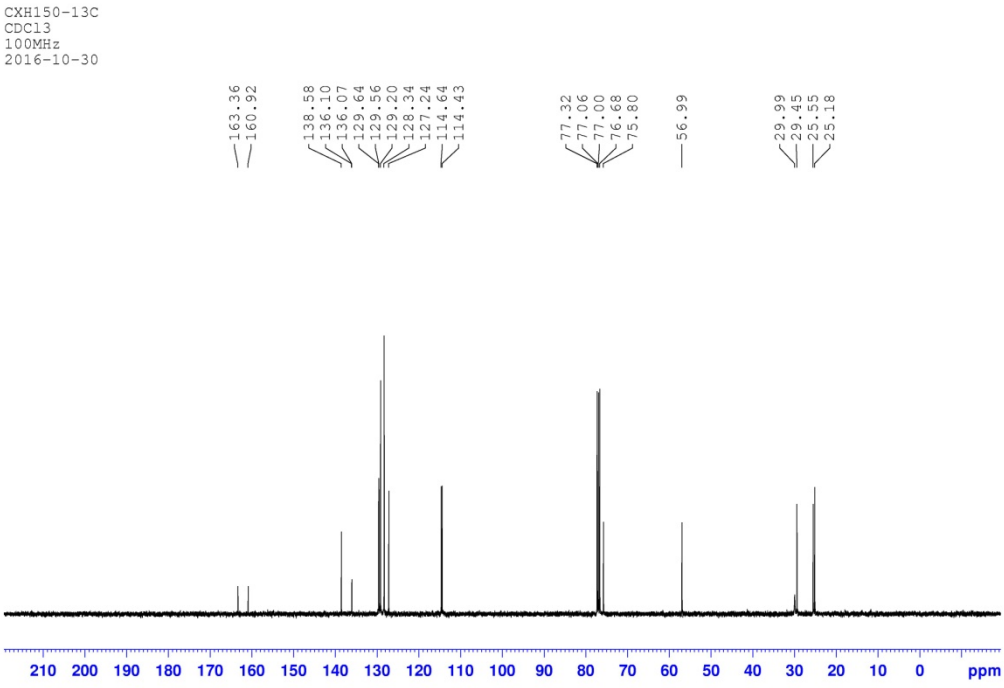
Supplementary Figure 23. Enantioenriched mixture of compound **2b-1**.



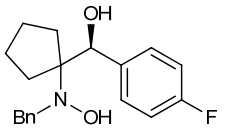
2c



Supplementary Figure 24. ^{1}H NMR ($CDCl_3$) of compound **2c**.

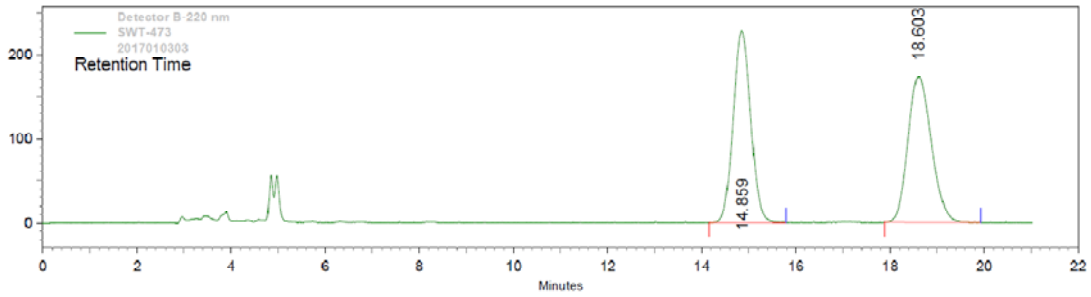


Supplementary Figure 25. ^{13}C NMR ($CDCl_3$) of compound **2c**.



2c

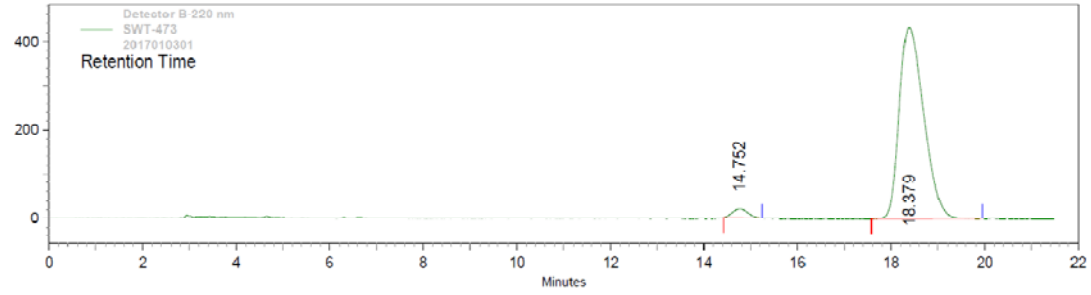
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 60/40 (v/v), 1.0 mL/min, 220 nm]



Detector B-220 nm

Pk #	Retention Time	Area	Area Percent	Height
1	14.859	5917112	49.87	227899
2	18.603	5947977	50.13	172520

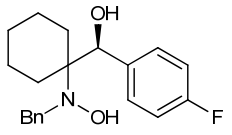
Supplementary Figure 26. Racemate of compound **2c**.



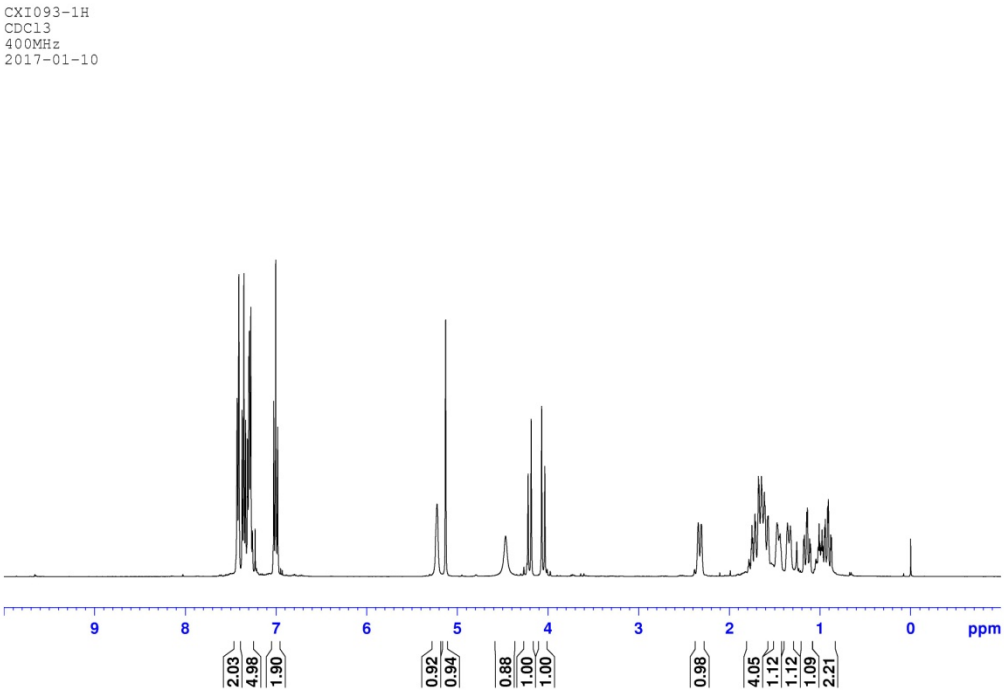
Detector B-220 nm

Pk #	Retention Time	Area	Area Percent	Height
1	14.752	495954	3.07	21489
2	18.379	15684191	96.93	431438

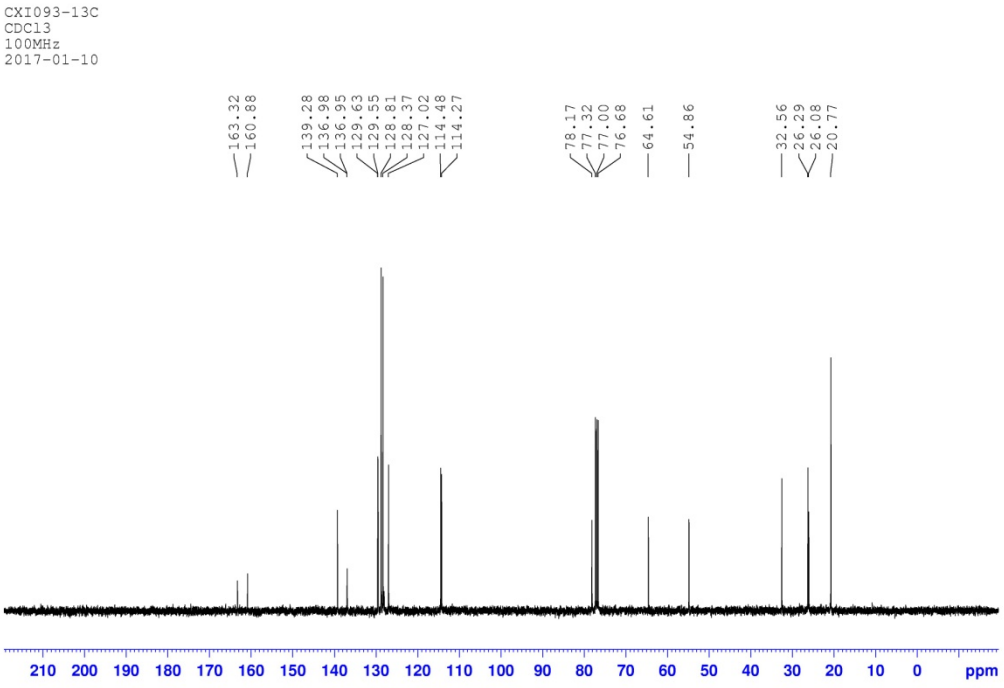
Supplementary Figure 27. Enantioenriched mixture of compound **2c**.



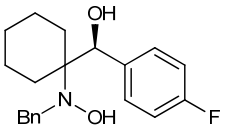
2d



Supplementary Figure 28. ^{1}H NMR ($CDCl_3$) of compound **2d**.

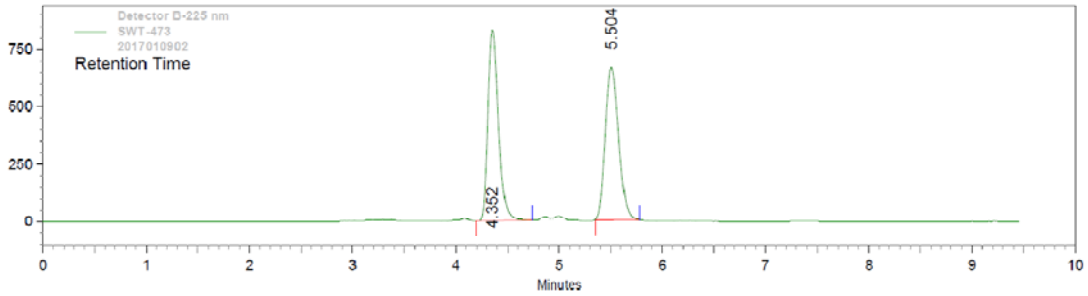


Supplementary Figure 29. ^{13}C NMR ($CDCl_3$) of compound **2d**.



2d

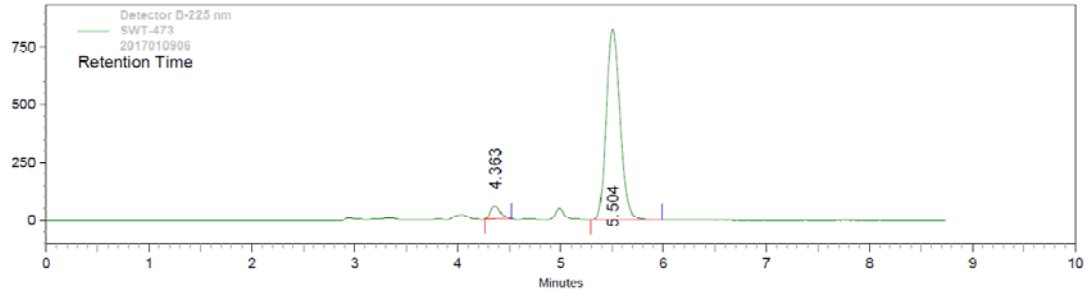
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 60/40 (v/v), 1.0 mL/min, 225 nm]



Detector B-225 nm

Pk #	Retention Time	Area	Area Percent	Height
1	4.352	6023879	49.68	833612
2	5.504	6101631	50.32	668896

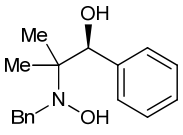
Supplementary Figure 30. Racemate of compound **2d**.



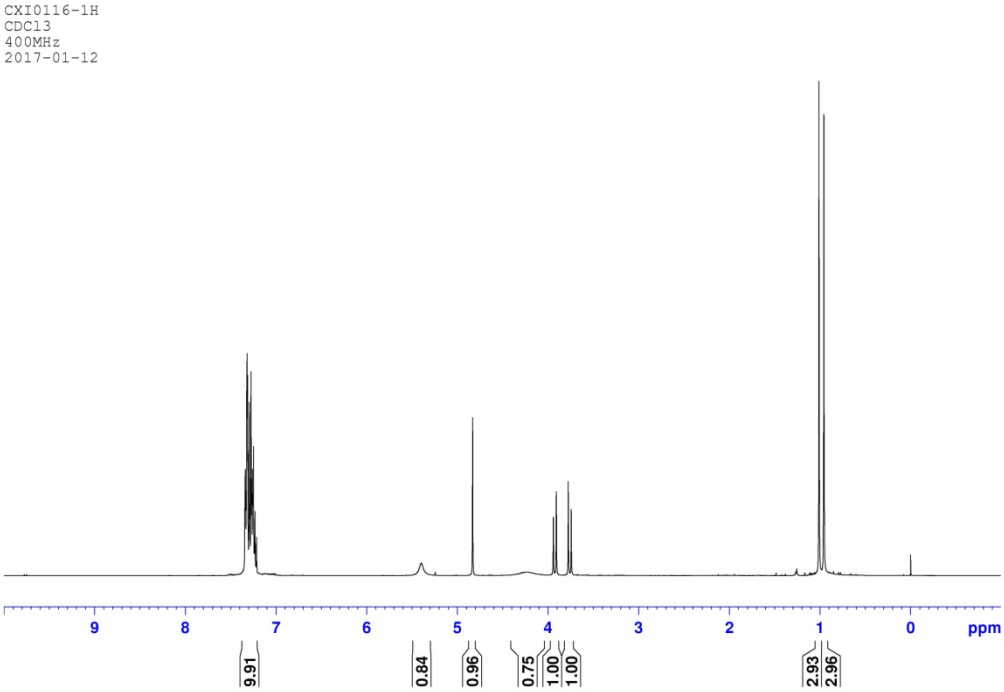
Detector B-225 nm

Pk #	Retention Time	Area	Area Percent	Height
1	4.363	342358	4.22	52792
2	5.504	7760813	95.78	828363

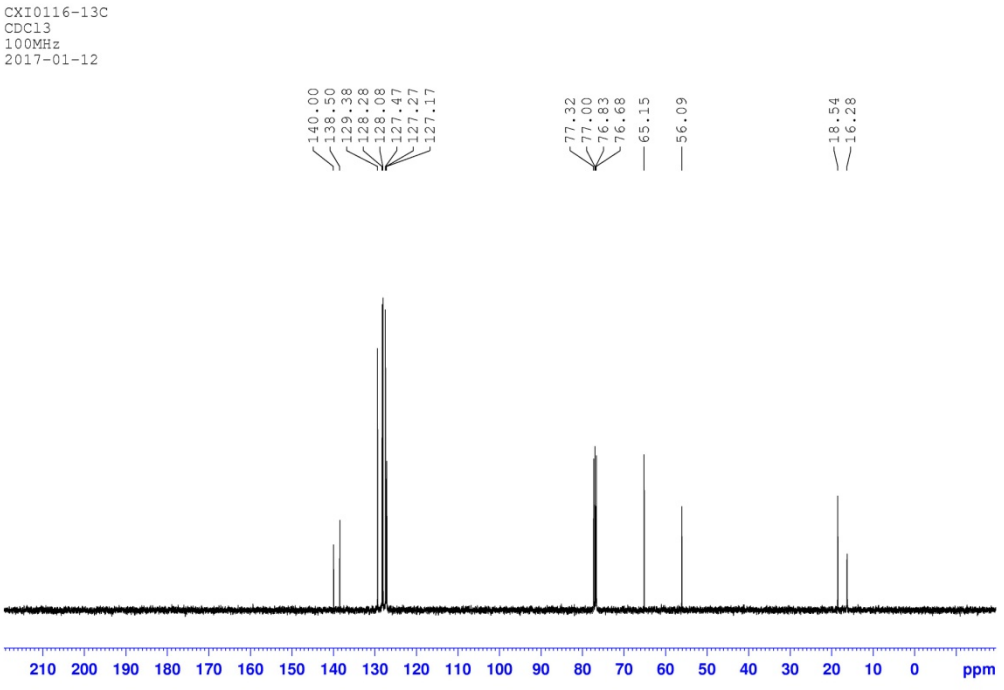
Supplementary Figure 31. Enantioenriched mixture of compound **2d**.



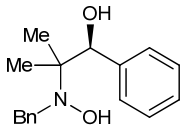
2b-2



Supplementary Figure 32. ^{1}H NMR ($CDCl_3$) of compound **2b-2**.

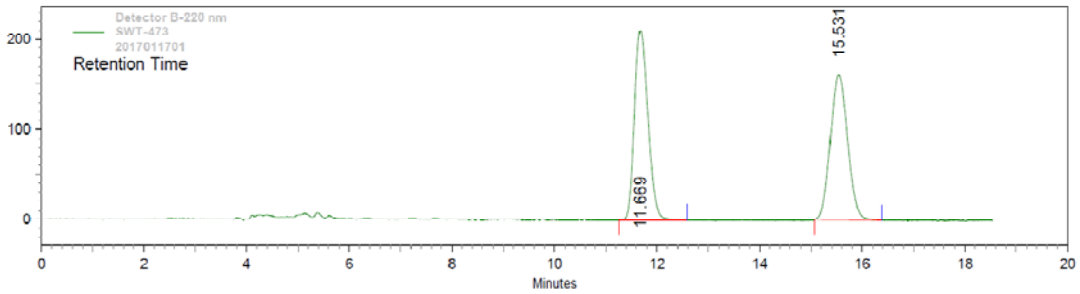


Supplementary Figure 33. ^{13}C NMR ($CDCl_3$) of compound **2b-2**.



2b-2

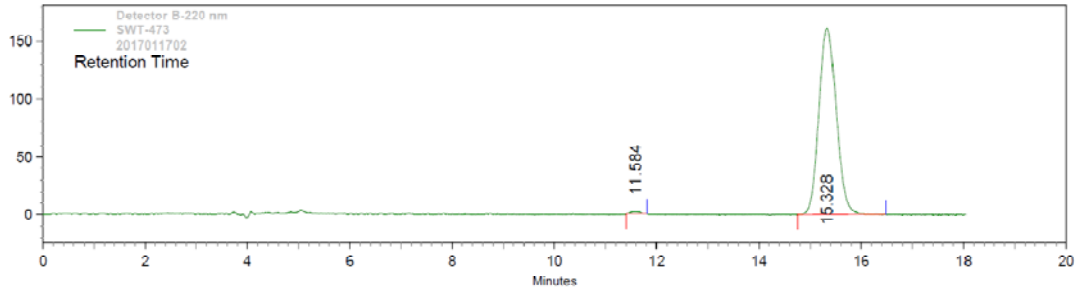
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 60/40 (v/v), 1.0 mL/min, 220 nm]



Detector B-220 nm

Pk #	Retention Time	Area	Area Percent	Height
1	11.669	3768416	49.99	210600
2	15.531	3770031	50.01	161108

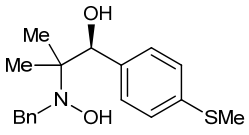
Supplementary Figure 34. Racemate of compound **2b-2**.



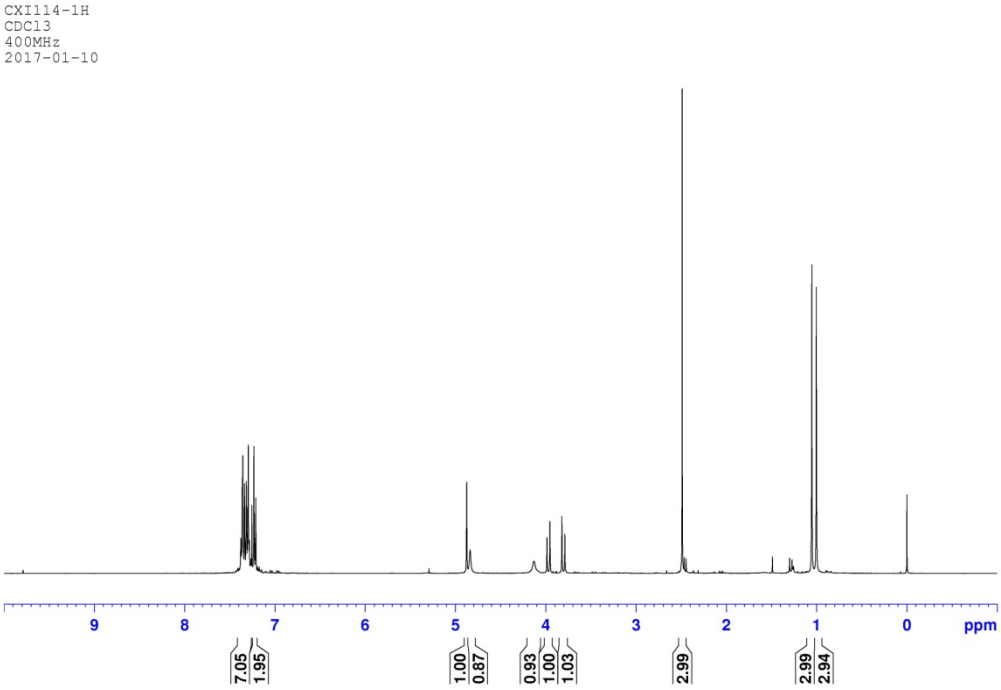
Detector B-220 nm

Pk #	Retention Time	Area	Area Percent	Height
1	11.584	22725	0.60	1961
2	15.328	3766262	99.40	161278

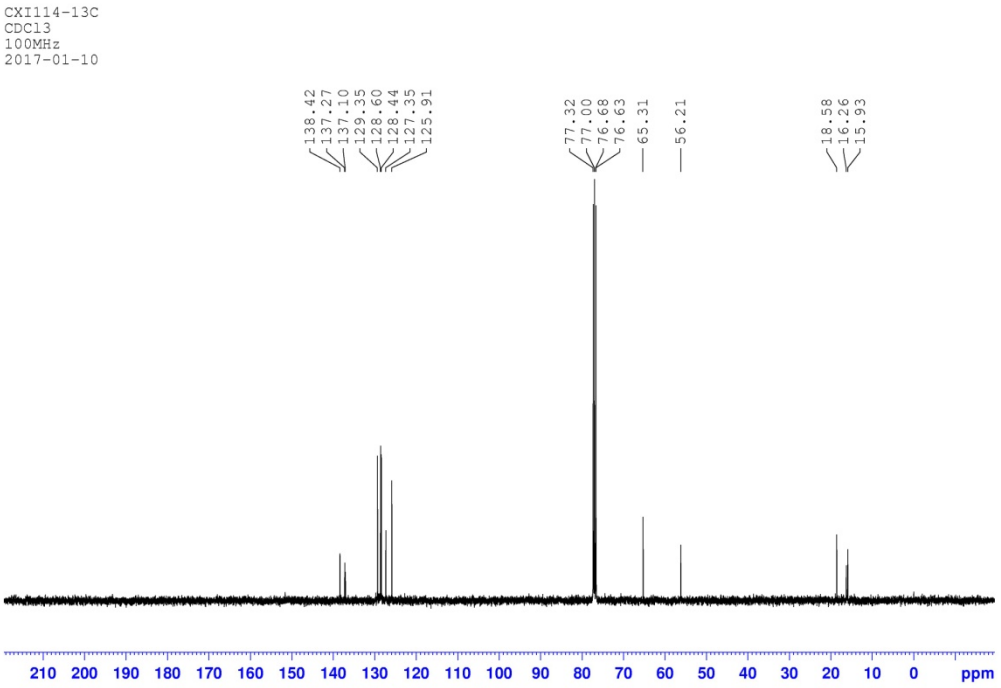
Supplementary Figure 35. Enantioenriched mixture of compound **2b-2**.



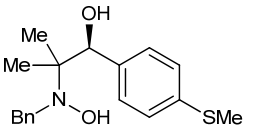
2b-3



Supplementary Figure 36. ^{1}H NMR ($CDCl_3$) of compound **2b-3**.

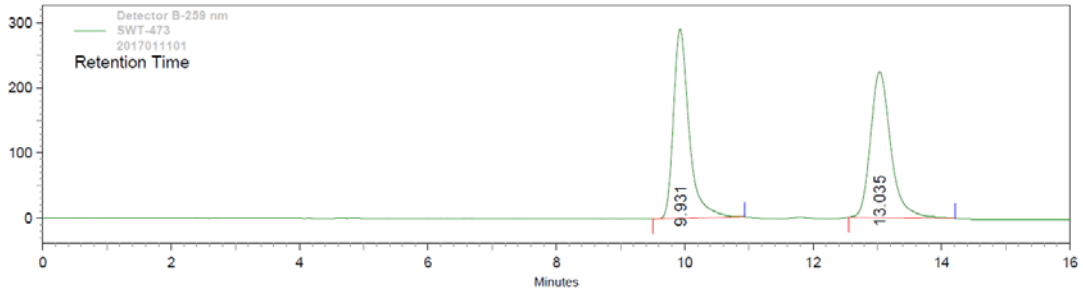


Supplementary Figure 37. ^{13}C NMR ($CDCl_3$) of compound **2b-3**.



2b-3

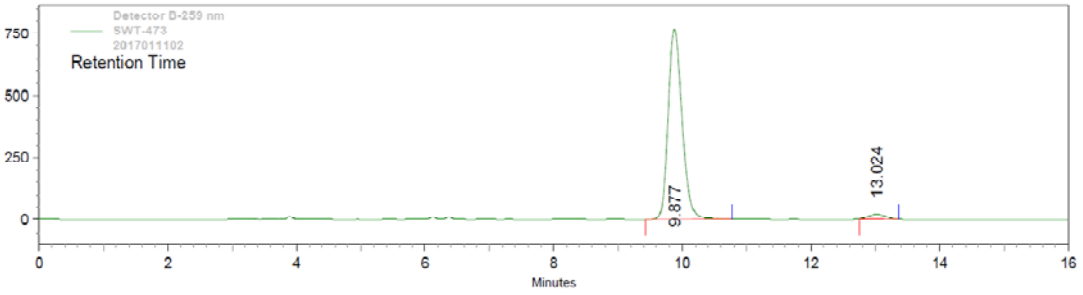
[Lux® Amylose-1 column, 30 ºC, hexane/*i*-PrOH = 85/15 (v/v), 1.0 mL/min, 259 nm]



Detector B-259 nm

Pk #	Retention Time	Area	Area Percent	Height
1	9.931	4940188	50.05	291190
2	13.035	4930906	49.95	224641

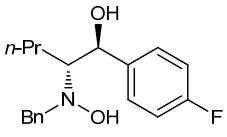
Supplementary Figure 38. Racemate of compound **2b-3**.



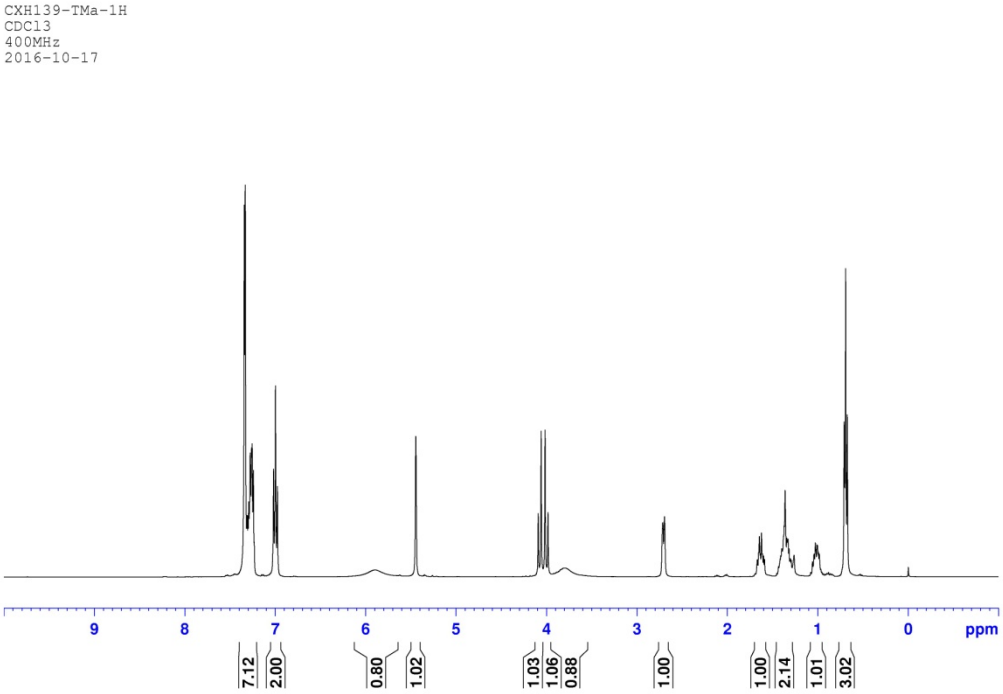
Detector B-259 nm

Pk #	Retention Time	Area	Area Percent	Height
1	9.877	11799465	97.15	768638
2	13.024	346714	2.85	19539

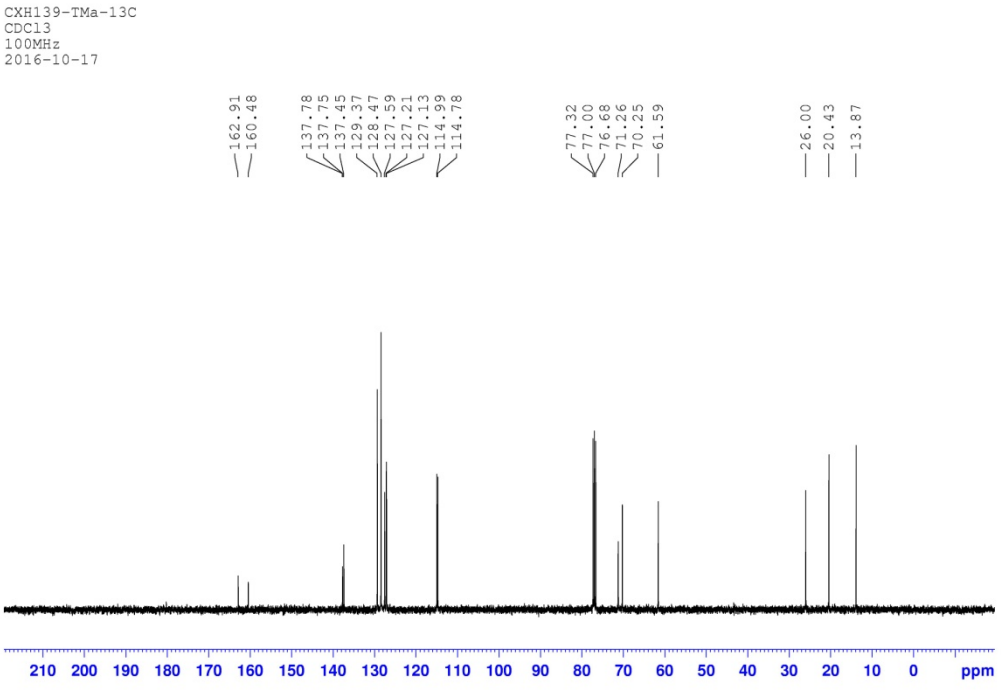
Supplementary Figure 39. Enantioenriched mixture of compound **2b-3**.



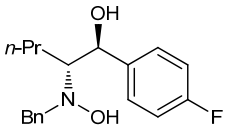
diastereomer of **2e** (major)



Supplementary Figure 40. ^{1}H NMR ($CDCl_3$) of the diastereomer of **2e**.

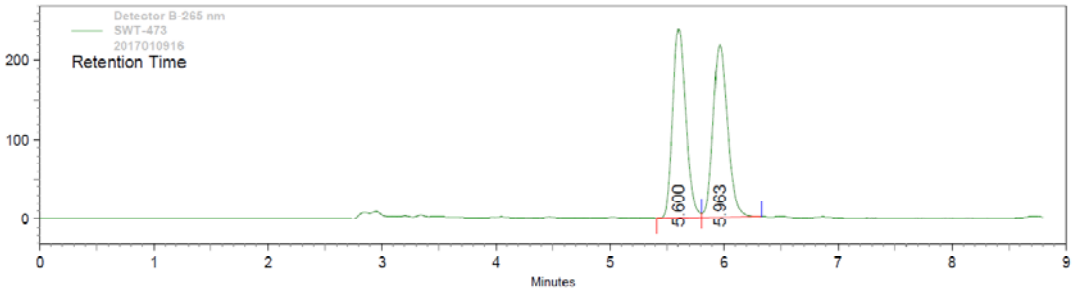


Supplementary Figure 41. ^{13}C NMR ($CDCl_3$) of the diastereomer of **2e**.



diastereomer of **2e** (major)

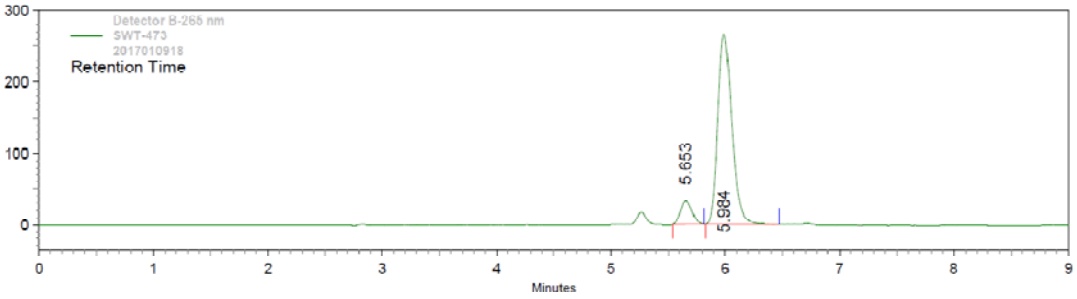
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 265 nm]



Detector B-265 nm

Pk #	Retention Time	Area	Area Percent	Height
1	5.600	1887347	49.62	238912
2	5.963	1916334	50.38	217813

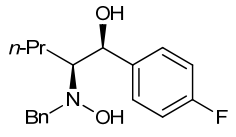
Supplementary Figure 42. Racemate of the diastereomer of **2e**.



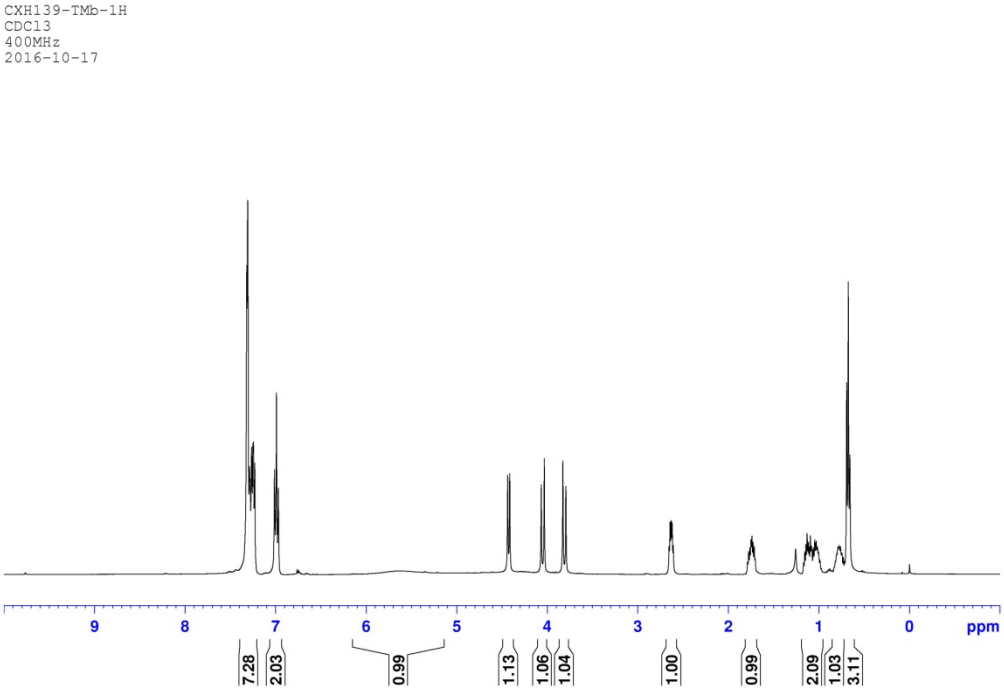
Detector B-265 nm

Pk #	Retention Time	Area	Area Percent	Height
1	5.653	218832	8.94	31100
2	5.984	2229724	91.06	265415

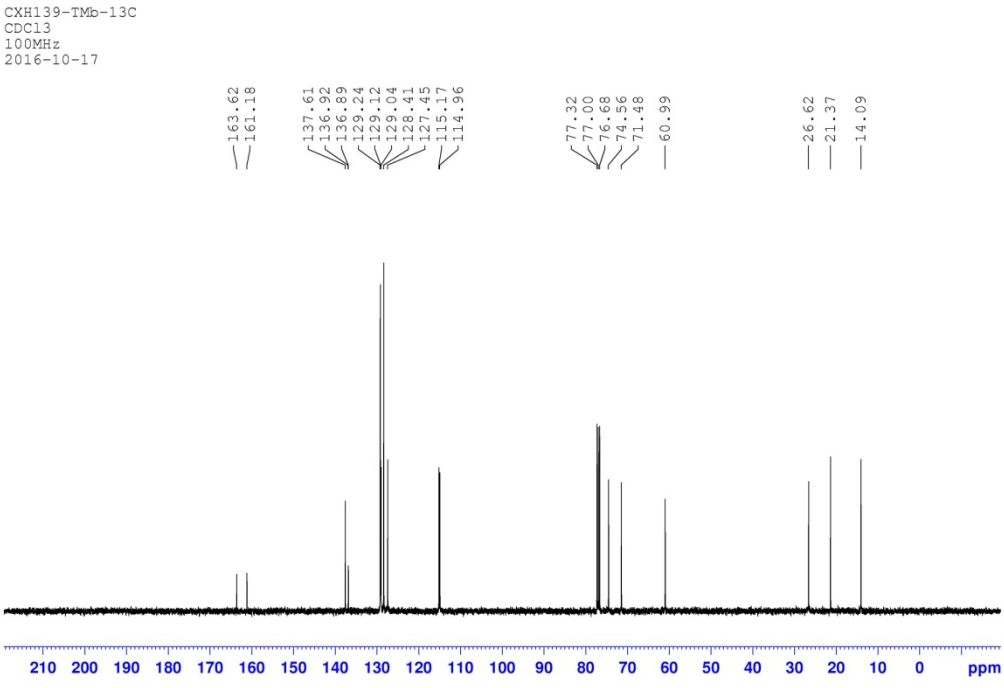
Supplementary Figure 43. Enantioenriched mixture of the diastereomer of **2e**.



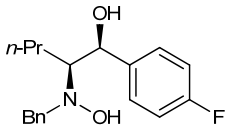
2e (minor)



Supplementary Figure 44. ^{1}H NMR ($CDCl_3$) of compound **2e**.

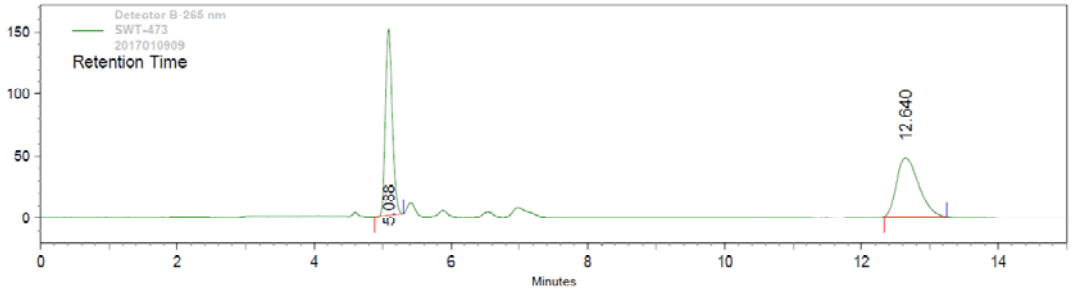


Supplementary Figure 45. ^{13}C NMR ($CDCl_3$) of compound **2e**.



2e (minor)

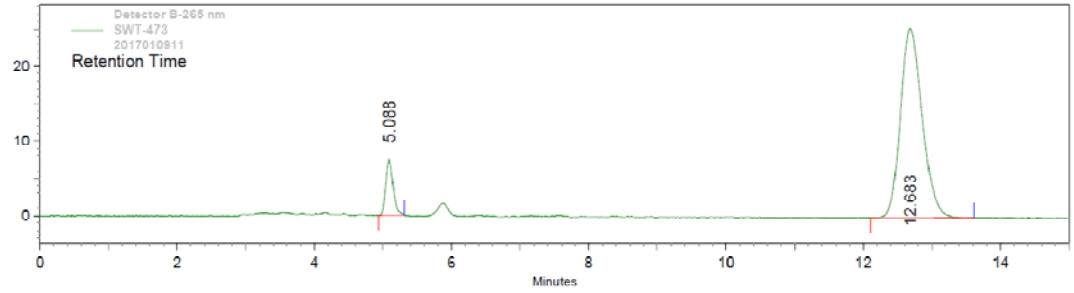
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 60/40 (v/v), 1.0 mL/min, 265 nm]



Detector B-265 nm

Pk #	Retention Time	Area	Area Percent	Height
1	5.088	1067356	49.90	151037
2	12.640	1071474	50.10	47843

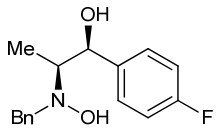
Supplementary Figure 46. Racemate of compound **2e**.



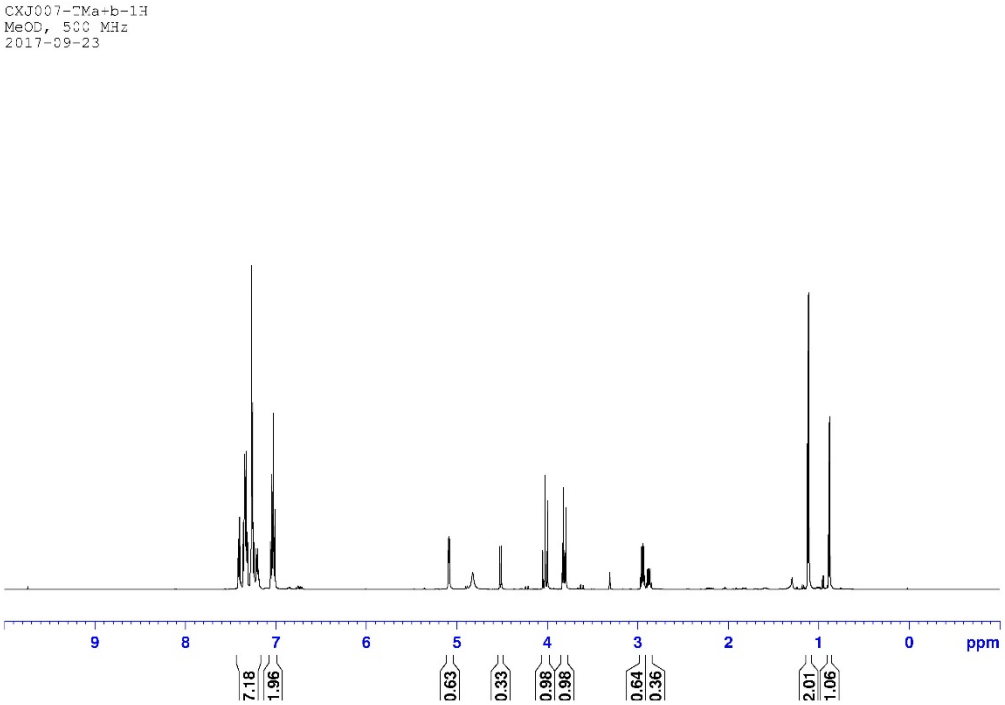
Detector B-265 nm

Pk #	Retention Time	Area	Area Percent	Height
1	5.088	53457	8.66	7487
2	12.683	563763	91.34	25425

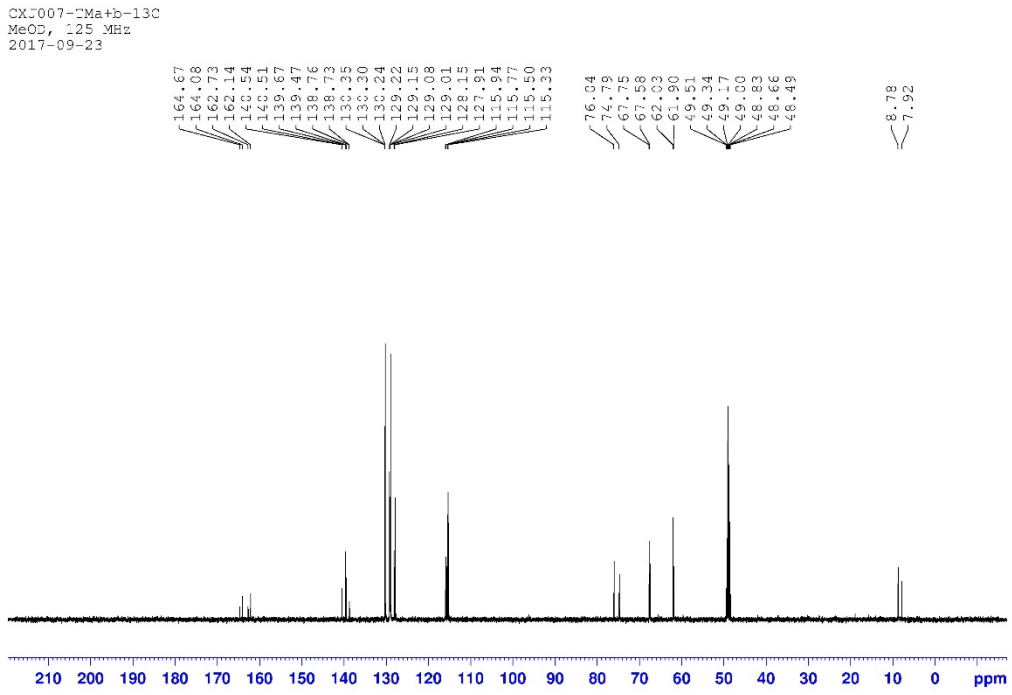
Supplementary Figure 47. Enantioenriched mixture of compound **2e**.



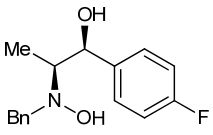
2f-1 [mixture of diastereomers (*anti*/*syn* = 1.8/1)]



Supplementary Figure 48. ^{1}H NMR (MeOD) of the diastereomeric mixture of **2f-1** (*anti*/*syn* = 1.8/1).

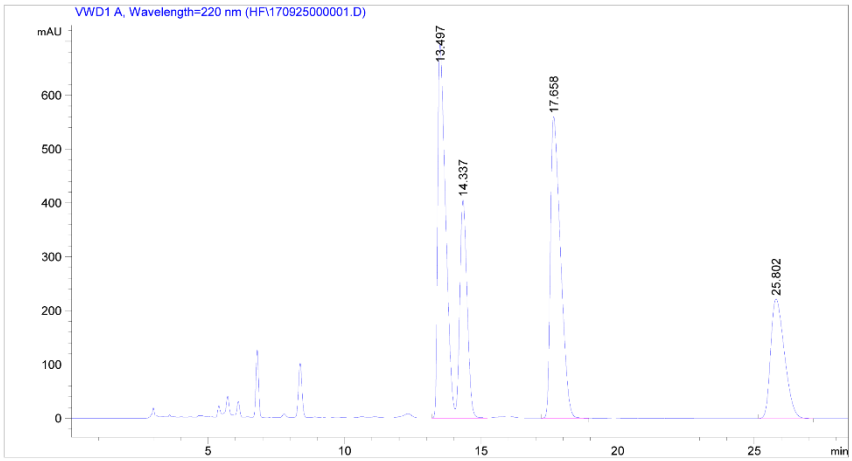


Supplementary Figure 49. ^{13}C NMR (MeOD) of the diastereomeric mixture of **2f-1** (*anti*/*syn* = 1.8/1).



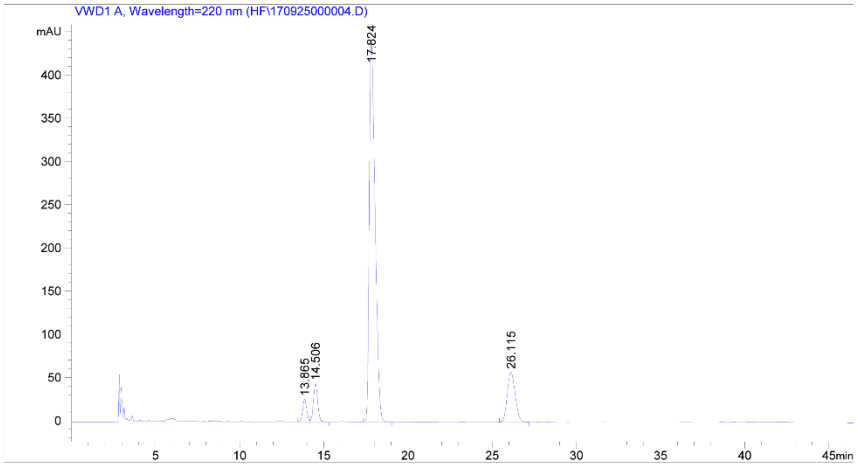
2f-1

[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 90/10 (v/v), 1.0 mL/min, 220 nm]



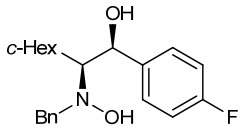
Pk #	Retention Time [min]	Area [mAU*s]	Height [mAU]	Area Percent %
1	13.497	1.39515e4	695.31830	31.9766
2	14.337	7537.83789	404.98318	17.2766
3	17.658	1.43654e4	559.94757	32.9252
4	25.802	7775.60791	221.91034	17.8216
Totals:		4.36304e4	1882.15939	100.0000

Supplementary Figure 50. Racemic diastereomeric mixture of **2f-1** (*anti*/*syn* = 1.8/1).

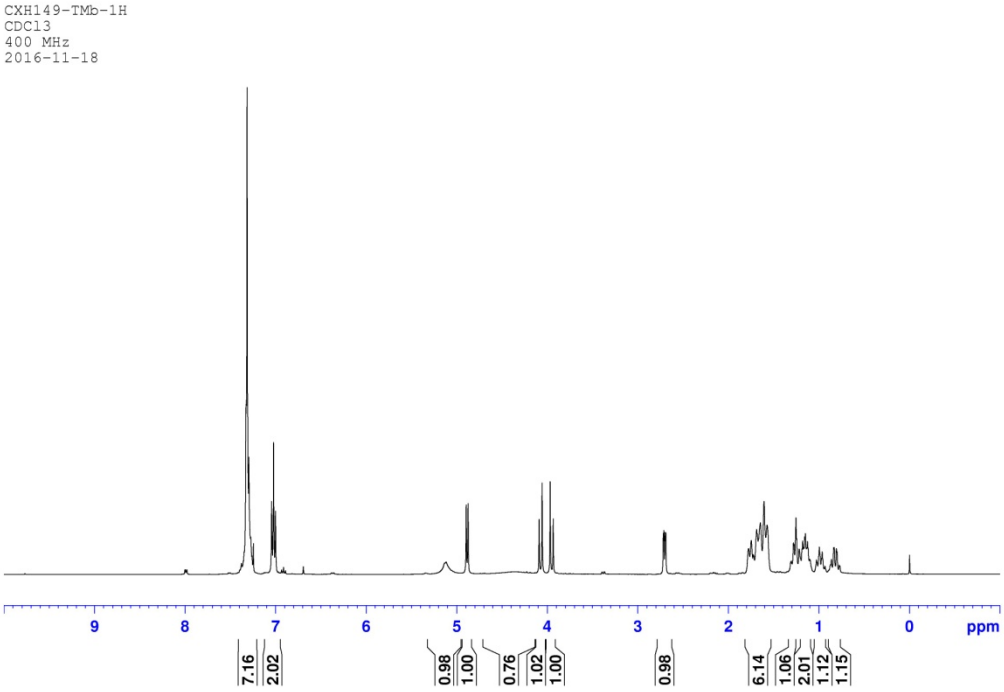


Pk #	Retention Time [min]	Area [mAU*s]	Height [mAU]	Area Percent %
1	13.865	436.49664	25.91280	3.1573
2	14.506	786.12903	44.09354	5.6862
3	17.824	1.06956e4	437.80728	77.3628
4	26.115	1907.00378	57.84807	13.7937
Totals:		1.38252e4	565.66169	100.0000

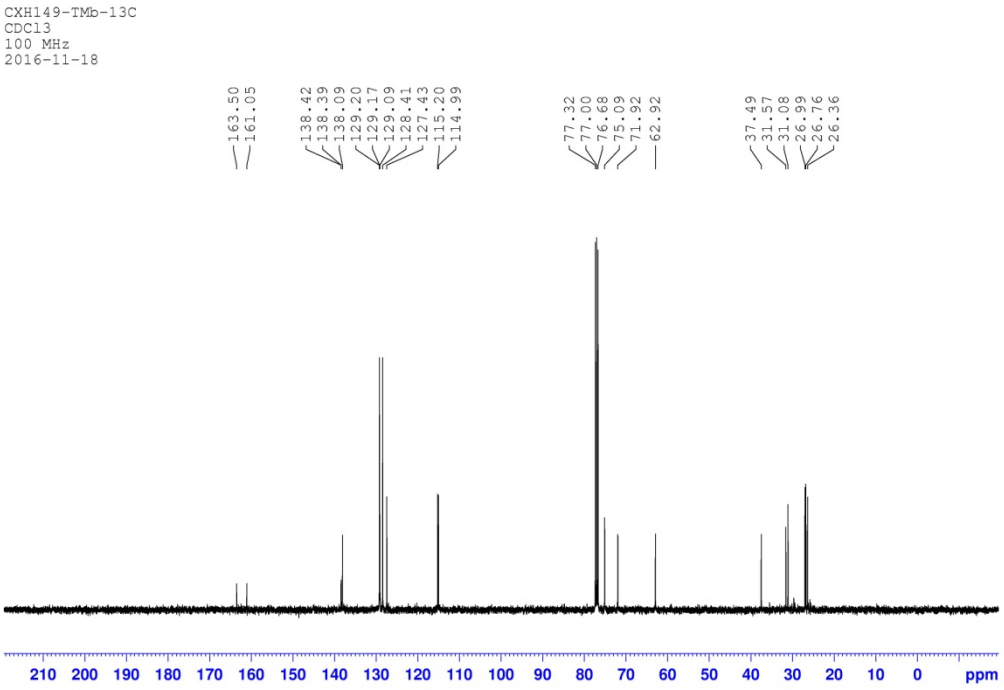
Supplementary Figure 51. Enantioenriched diastereomeric mixture of **2f-1** (*anti*/*syn* = 4.1/1).



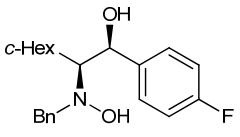
2g (major)



Supplementary Figure 52. ^{1}H NMR ($CDCl_3$) of compound **2g**.

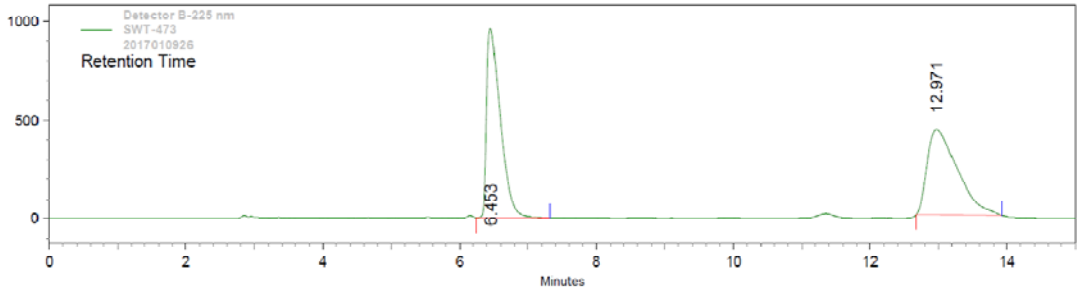


Supplementary Figure 53. ^{13}C NMR ($CDCl_3$) of compound **2g**.



2g (major)

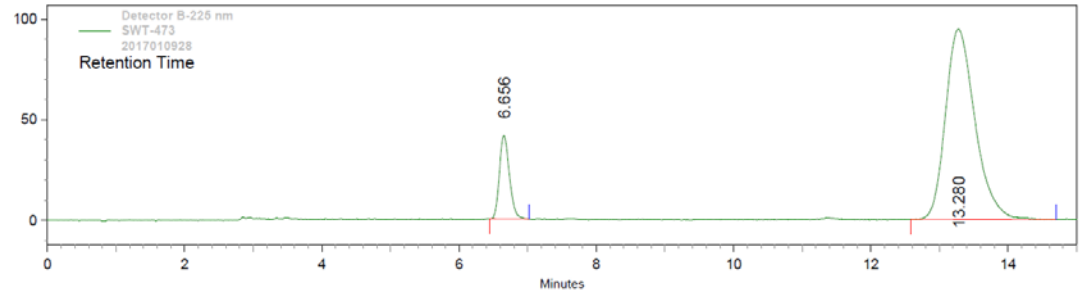
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 225 nm]



Detector B-225 nm

Pk #	Retention Time	Area	Area Percent	Height
1	6.453	13247334	49.79	961082
2	12.971	13358417	50.21	430960

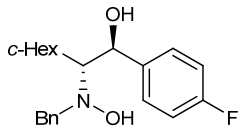
Supplementary Figure 54. Racemate of compound **2g**.



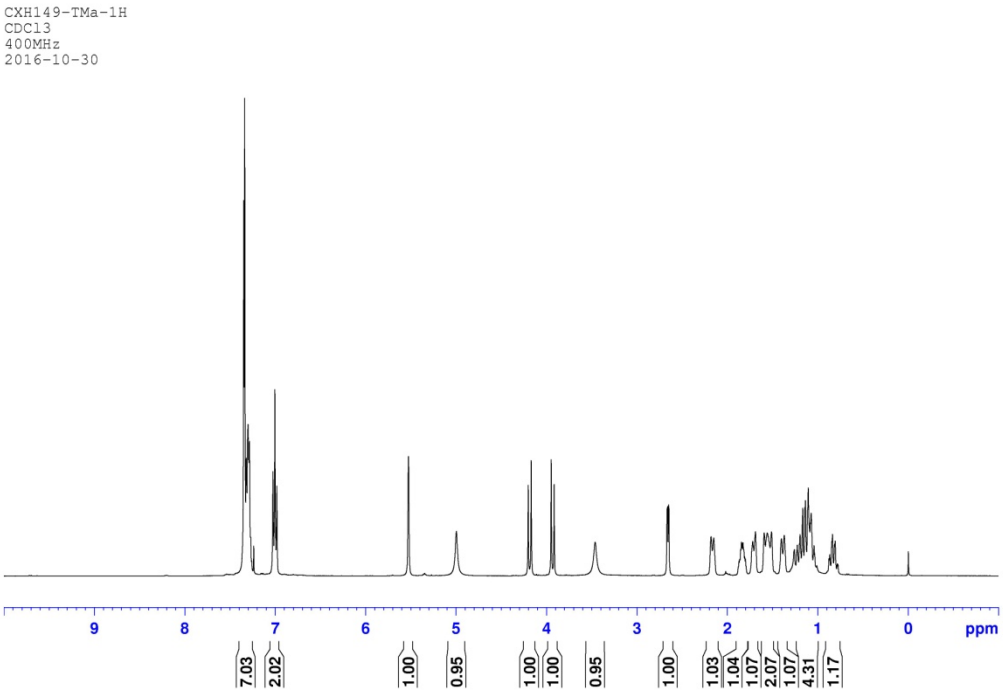
Detector B-225 nm

Pk #	Retention Time	Area	Area Percent	Height
1	6.656	415955	12.82	41321
2	13.280	2829226	87.18	94508

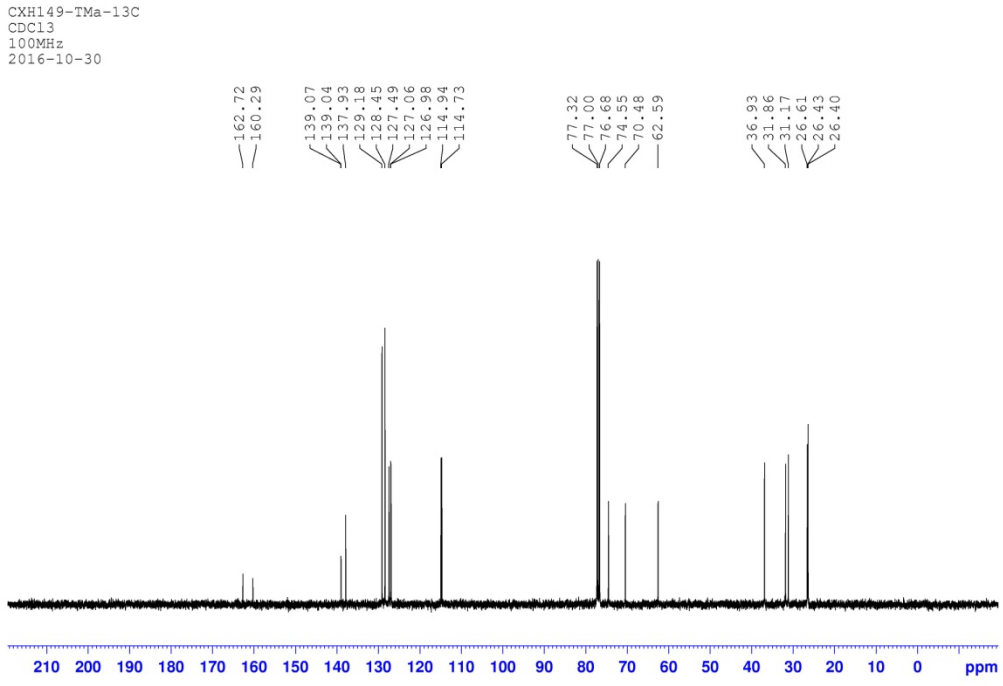
Supplementary Figure 55. Enantioenriched mixture of compound **2g**.



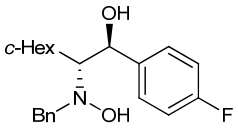
diastereomer of **2g** (minor)



Supplementary Figure 56. ^{1}H NMR ($CDCl_3$) of the diastereomer of **2g**.

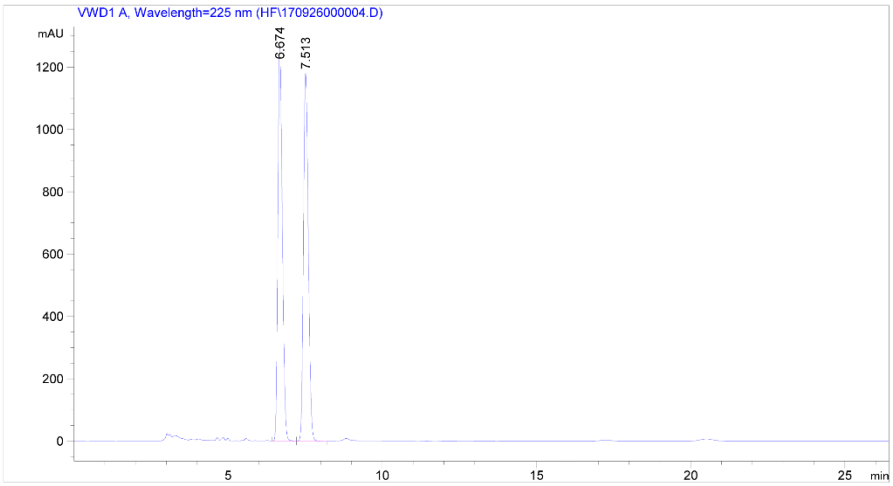


Supplementary Figure 57. ^{13}C NMR ($CDCl_3$) of the diastereomer of **2g**.



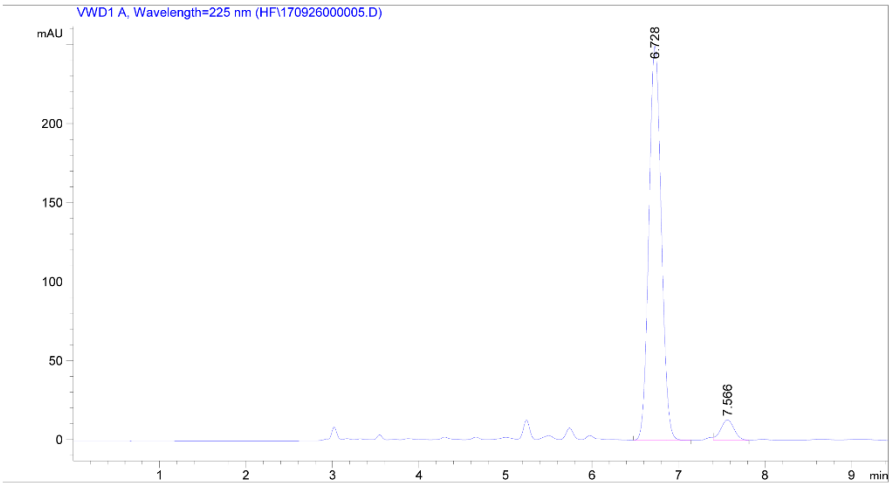
diastereomer of **2g** (minor)

[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 85/15 (v/v), 1.0 mL/min, 225 nm]



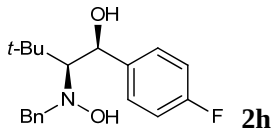
Pk #	Retention Time [min]	Area [mAU*s]	Height [mAU]	Area Percent %
1	6.674	1.29336e4	1266.73926	49.9329
2	7.513	1.29684e4	1181.47131	50.0671
Totals:		2.59020e4	2448.21057	100.0000

Supplementary Figure 58. Racemate of the diastereomer of **2g**.

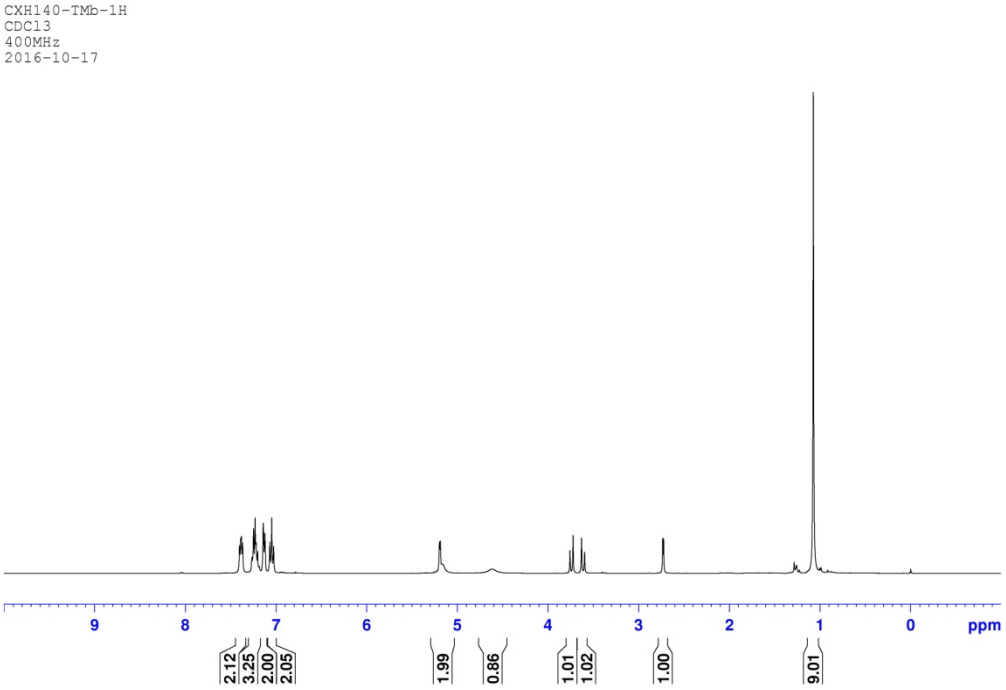


Pk #	Retention Time [min]	Area [mAU*s]	Height [mAU]	Area Percent %
1	6.728	2481.00146	249.51520	94.7077
2	7.566	138.64044	12.95741	5.2923
Totals:		2619.64191	262.47260	100.0000

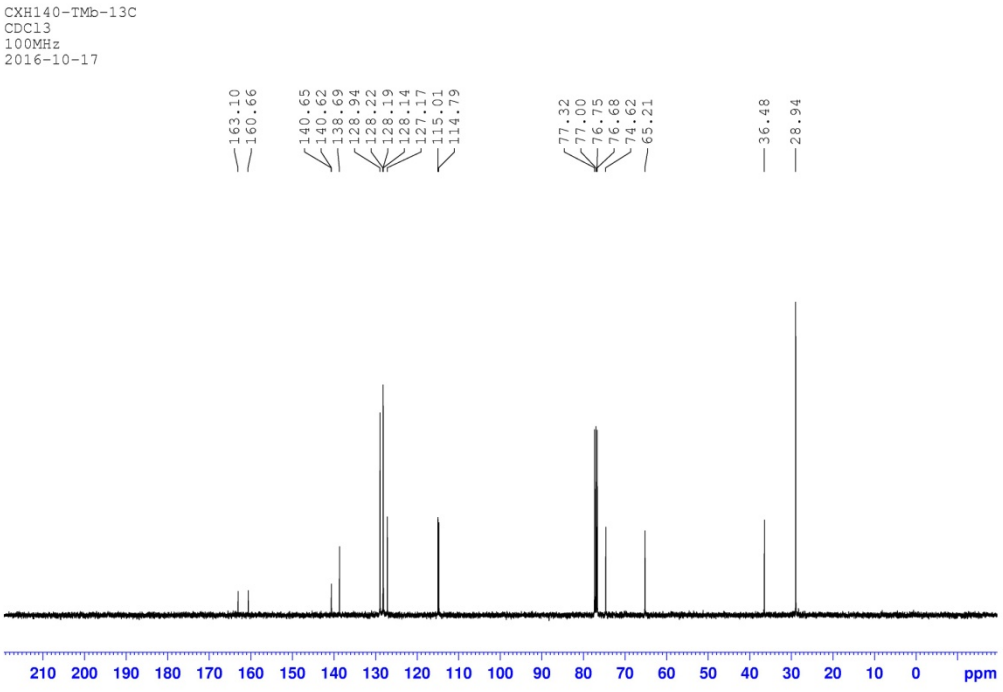
Supplementary Figure 59. Enantioenriched mixture of the diastereomer of **2g**.



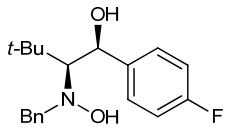
2h



Supplementary Figure 60. ^{1}H NMR ($CDCl_3$) of compound **2h**.

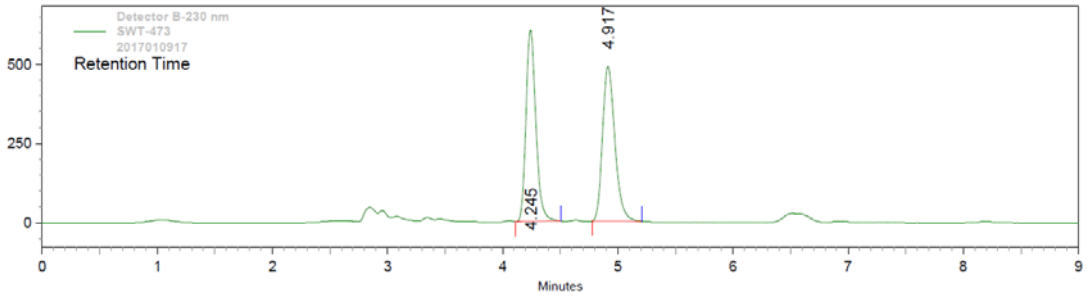


Supplementary Figure 61. ^{13}C NMR ($CDCl_3$) of compound **2h**.



2h

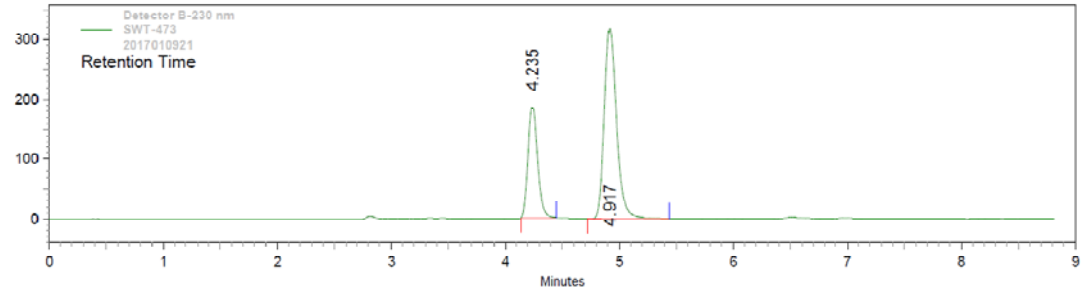
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 230 nm]



Detector B-230 nm

Pk #	Retention Time	Area	Area Percent	Height
1	4.245	3602157	49.89	603004
2	4.917	3617699	50.11	488489

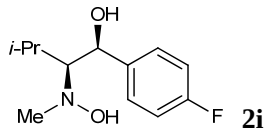
Supplementary Figure 62. Racemate of compound **2h**.



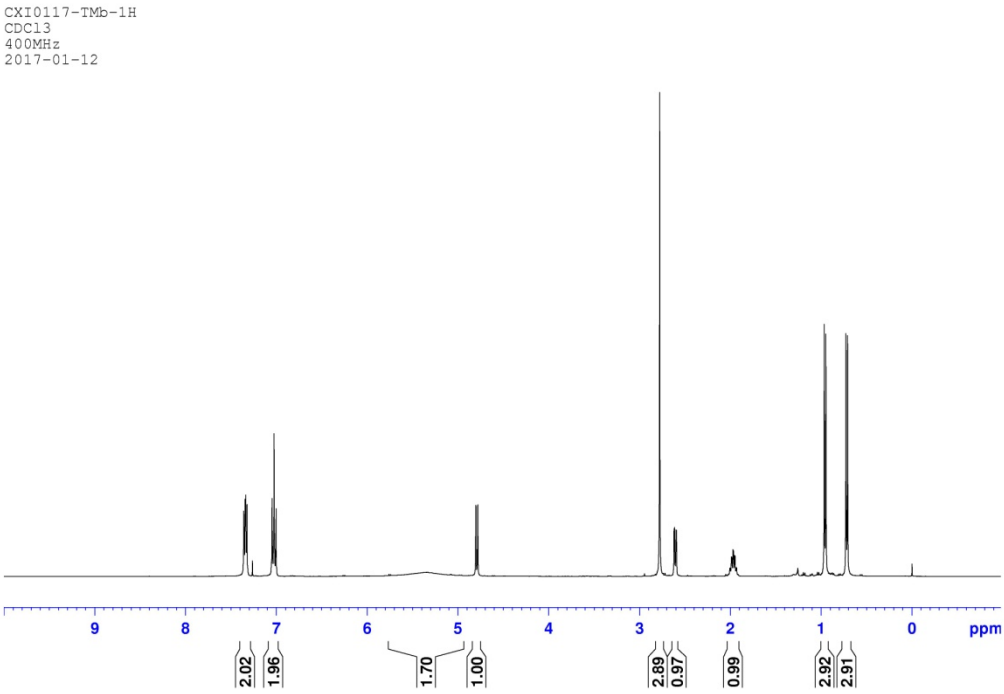
Detector B-230 nm

Pk #	Retention Time	Area	Area Percent	Height
1	4.235	1035087	30.96	185004
2	4.917	2308319	69.04	318433

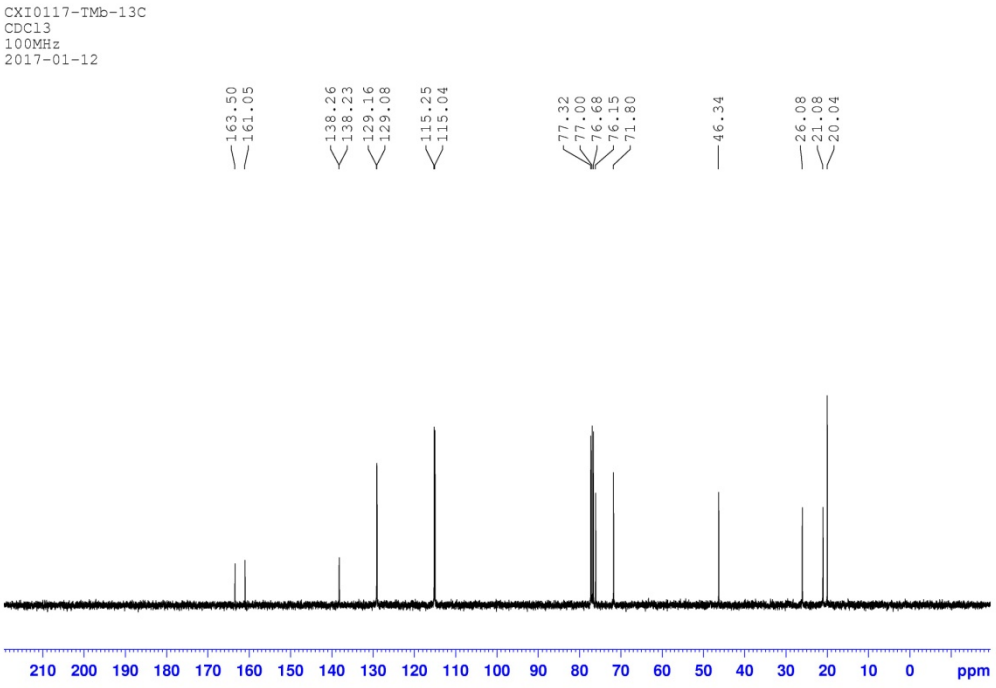
Supplementary Figure 63. Enantioenriched mixture of compound **2h**.



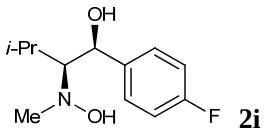
2i



Supplementary Figure 64. ^{1}H NMR ($CDCl_3$) of compound **2i**.

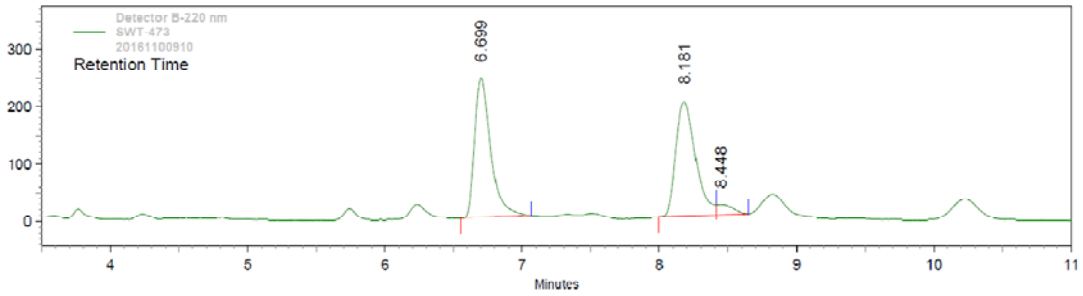


Supplementary Figure 65. ^{13}C NMR ($CDCl_3$) of compound **2i**.



2i

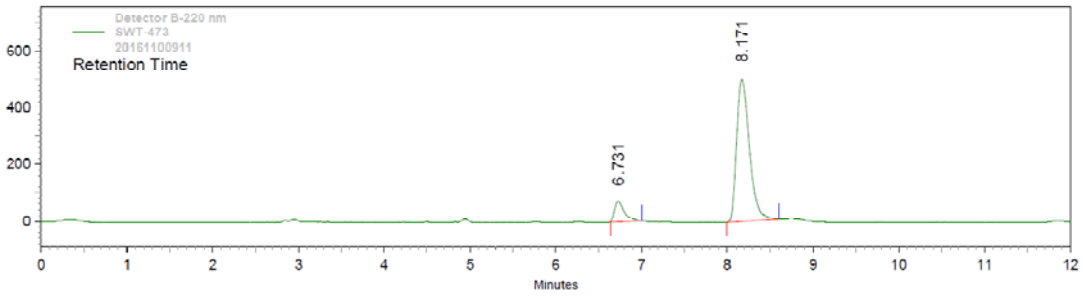
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 90/10 (v/v), 1.0 mL/min, 220 nm]



Detector B-220 nm

Pk #	Retention Time	Area	Area Percent	Height
1	6.699	2034313	48.28	243358
2	8.181	2033228	48.25	200396
3	8.448	146456	3.48	18682

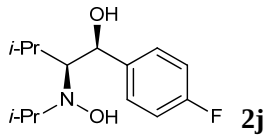
Supplementary Figure 66. Racemate of compound **2i**.



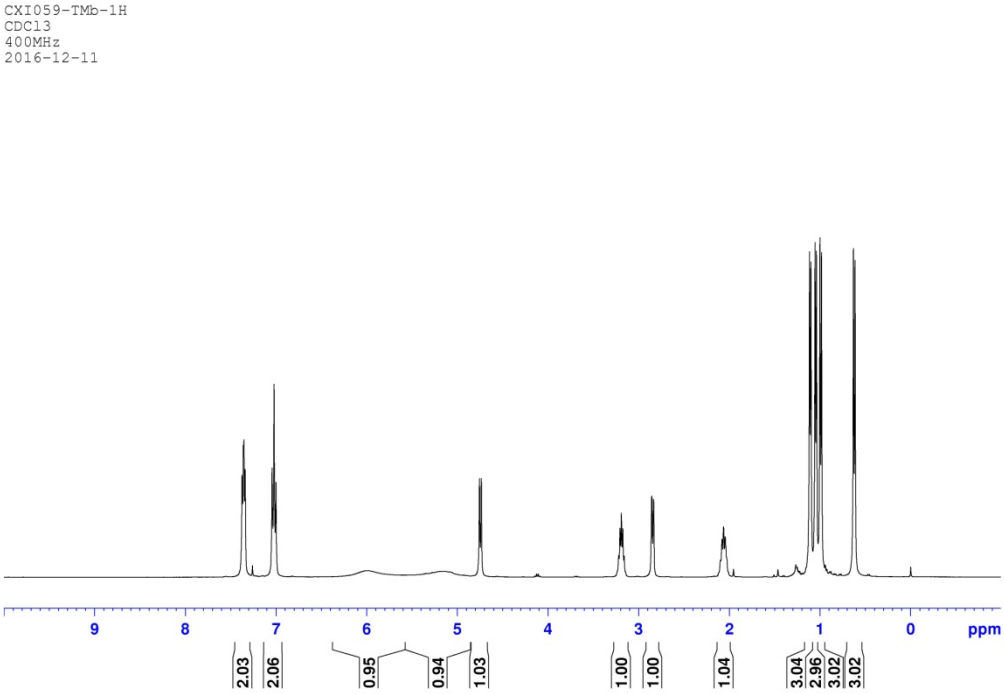
Detector B-220 nm

Pk #	Retention Time	Area	Area Percent	Height
1	6.731	564936	9.66	68421
2	8.171	5284531	90.34	501303

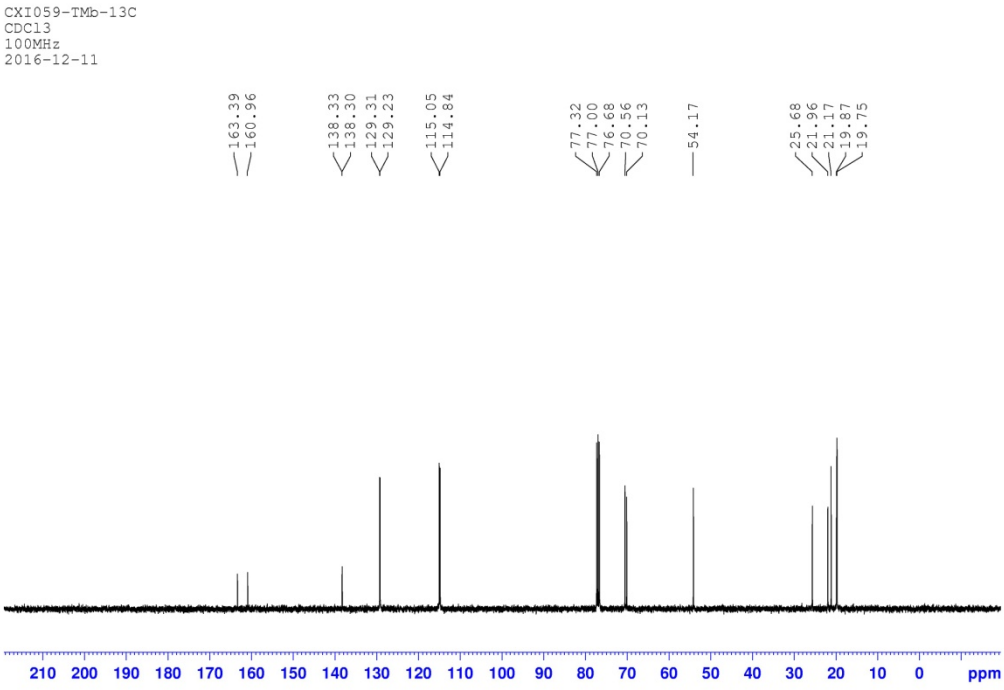
Supplementary Figure 67. Enantioenriched mixture of compound **2i**.



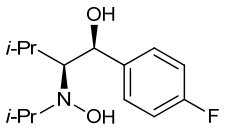
2j



Supplementary Figure 68. ^{1}H NMR ($CDCl_3$) of compound **2j**.

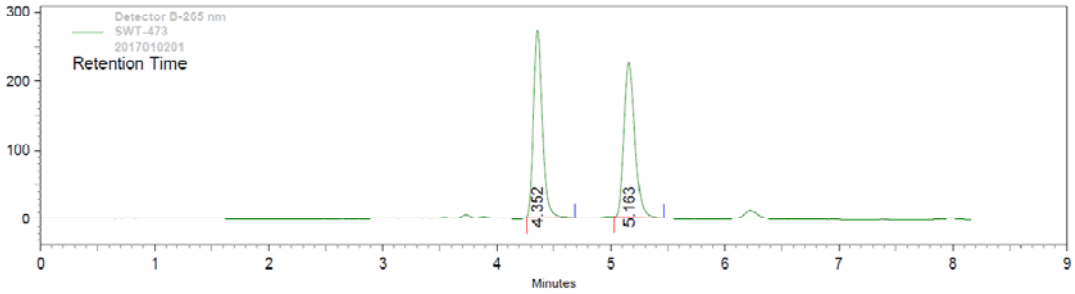


Supplementary Figure 69. ^{13}C NMR ($CDCl_3$) of compound **2j**.



2j

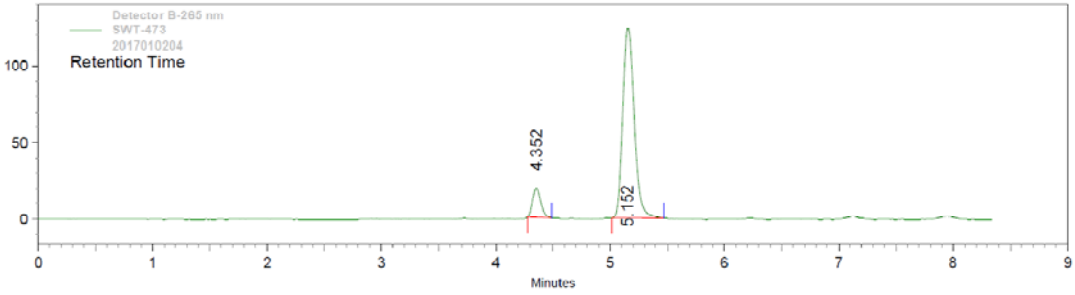
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 265 nm]



Detector B-265 nm

Pk #	Retention Time	Area	Area Percent	Height
1	4.352	1525904	50.07	273356
2	5.163	1521489	49.93	225573

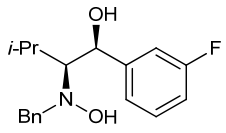
Supplementary Figure 70. Racemate of compound **2j**.



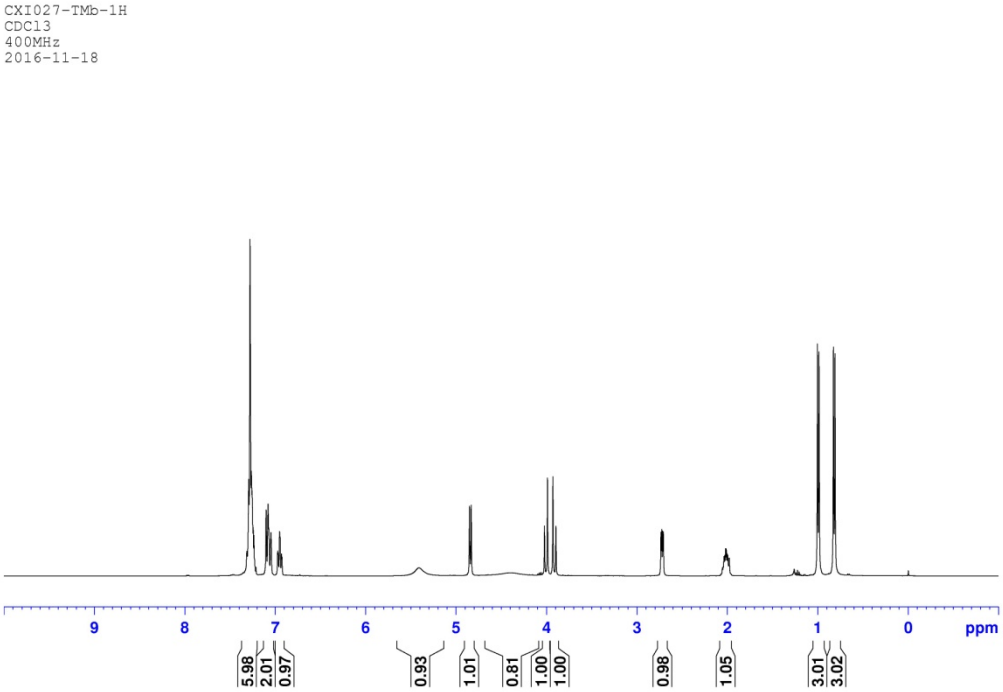
Detector B-265 nm

Pk #	Retention Time	Area	Area Percent	Height
1	4.352	97055	10.38	19320
2	5.152	838037	89.62	123964

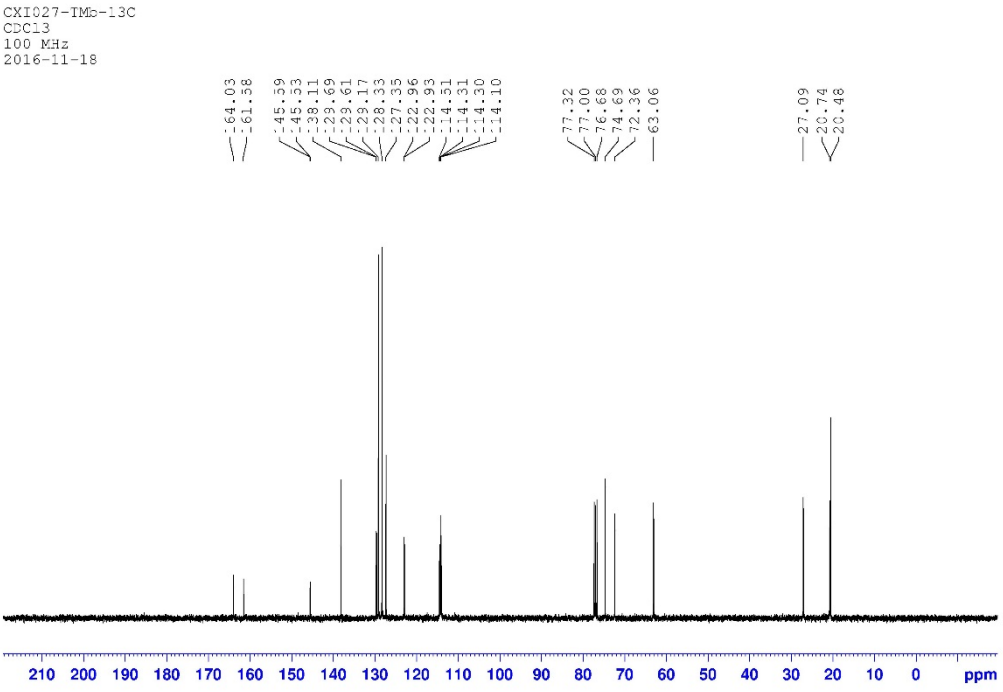
Supplementary Figure 71. Enantioenriched mixture of compound **2j**.



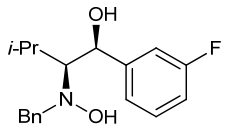
2a-2



Supplementary Figure 72. ^{1}H NMR ($CDCl_3$) of compound **2a-2**.

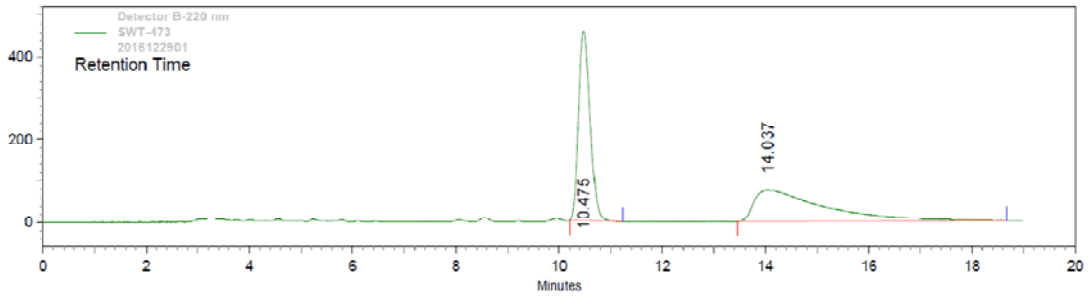


Supplementary Figure 73. ^{13}C NMR ($CDCl_3$) of compound **2a-2**.



2a-2

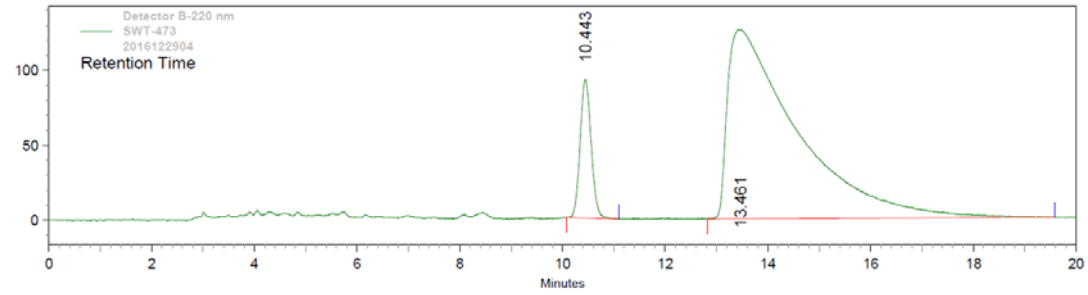
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 220 nm]



Detector B-220 nm

Pk #	Retention Time	Area	Area Percent	Height
1	10.475	7231071	50.17	459938
2	14.037	7182349	49.83	75585

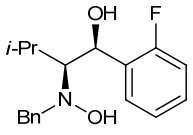
Supplementary Figure 74. Racemate of compound **2a-2**.



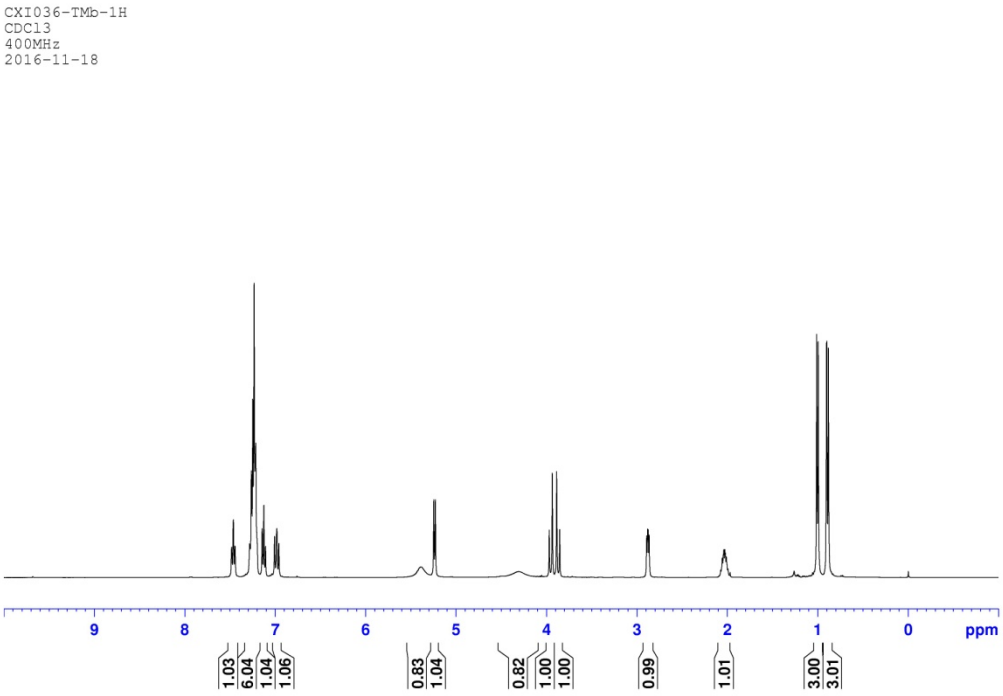
Detector B-220 nm

Pk #	Retention Time	Area	Area Percent	Height
1	10.443	1378338	10.39	92543
2	13.461	11888908	89.61	126400

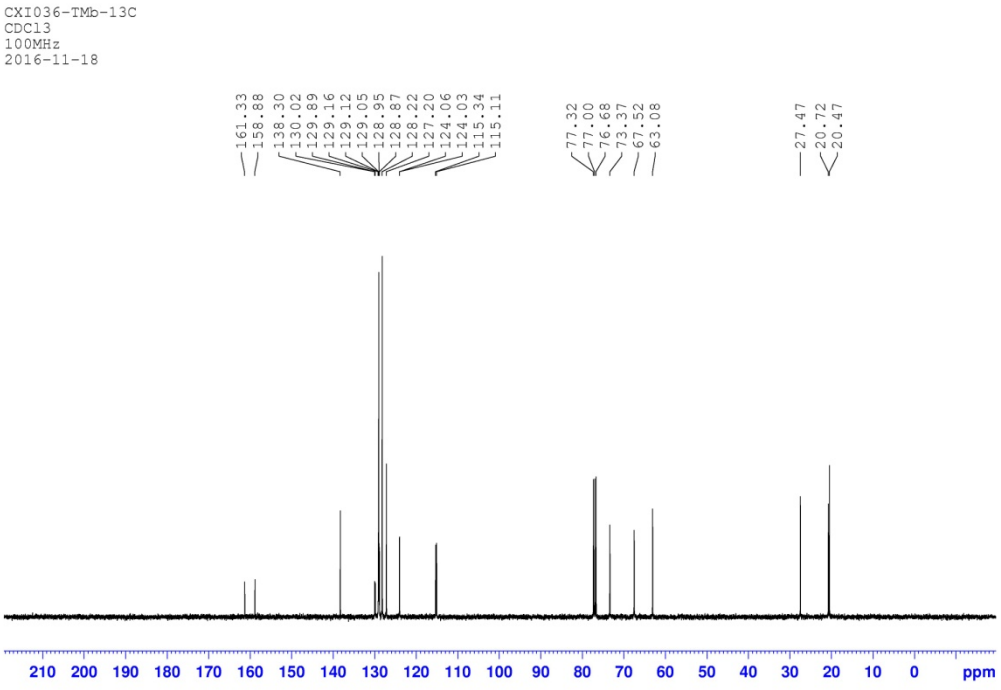
Supplementary Figure 75. Enantioenriched mixture of compound **2a-2**.



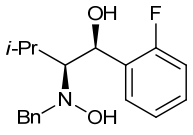
2a-3



Supplementary Figure 76. ^{1}H NMR ($CDCl_3$) of compound **2a-3**.

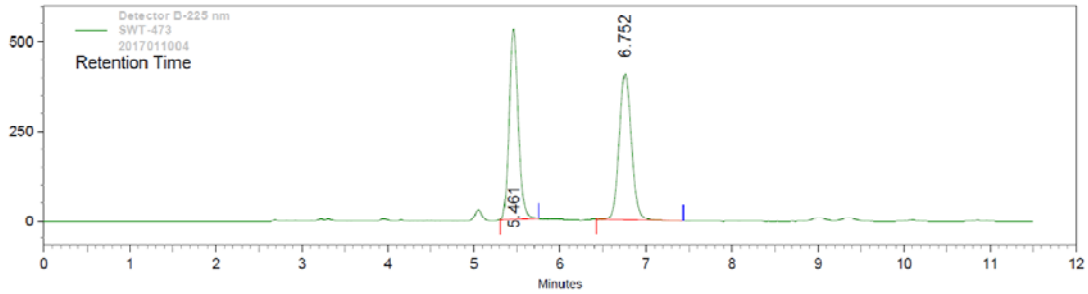


Supplementary Figure 77. ^{13}C NMR ($CDCl_3$) of compound **2a-3**.



2a-3

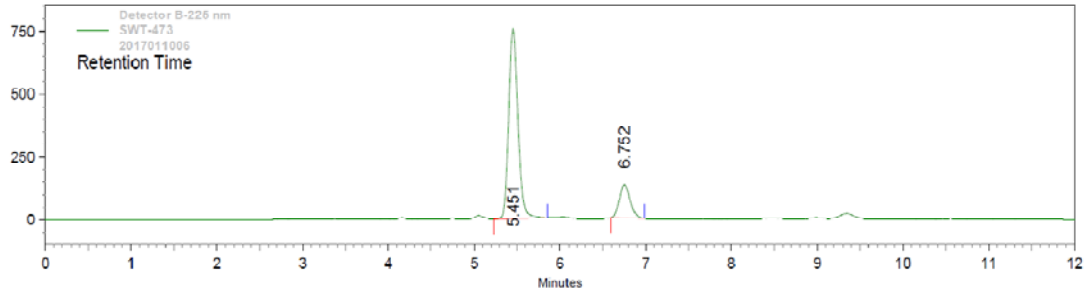
[Lux® Amylose-1 column, 30 ºC, hexane/*i*-PrOH = 85/15 (v/v), 1.0 mL/min, 225 nm]



Detector B-225 nm

Pk #	Retention Time	Area	Area Percent	Height
1	5.461	3945277	50.18	531067
2	6.752	3916467	49.82	405650

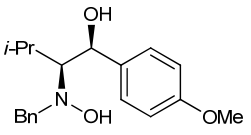
Supplementary Figure 78. Racemate of compound **2a-3**.



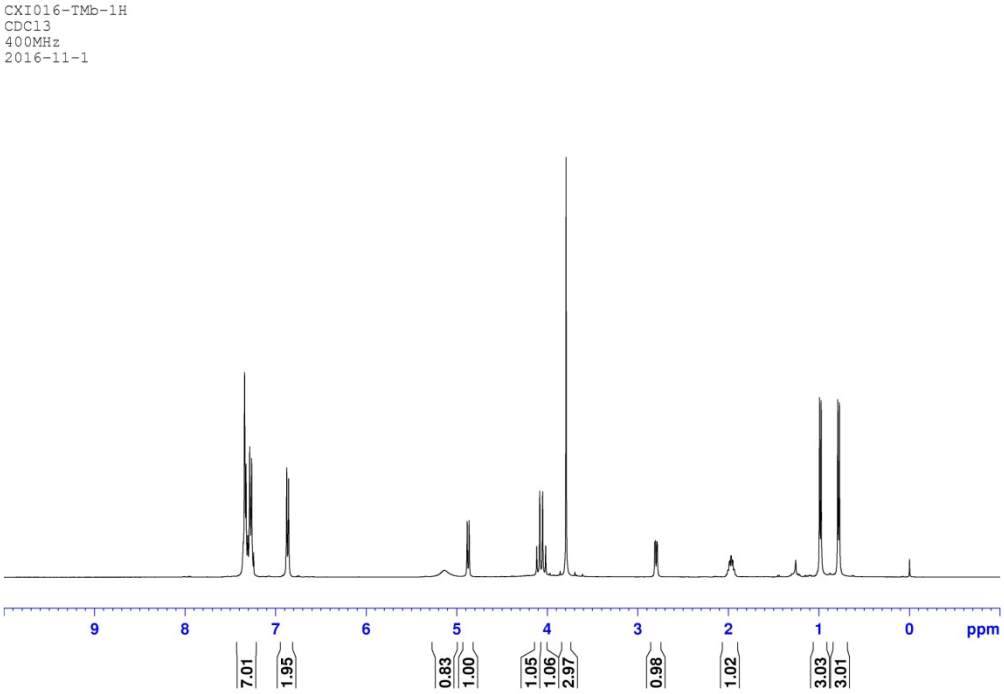
Detector B-225 nm

Pk #	Retention Time	Area	Area Percent	Height
1	5.451	5846144	82.85	757459
2	6.752	1210234	17.15	132003

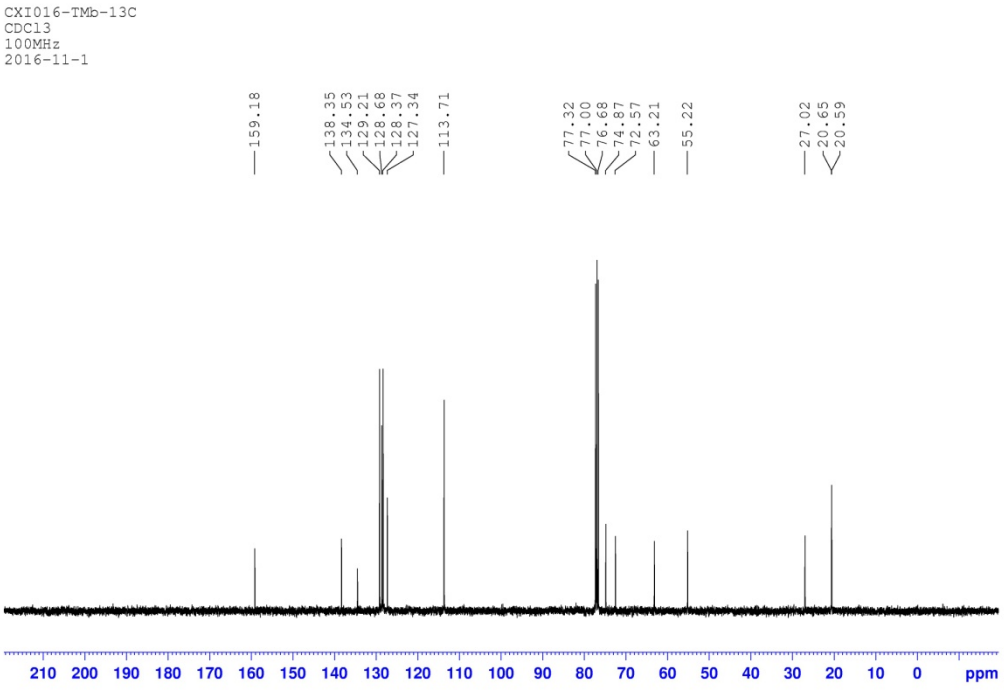
Supplementary Figure 79. Enantioenriched mixture of compound **2a-3**.



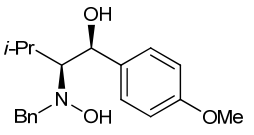
2a-4



Supplementary Figure 80. ^{1}H NMR ($CDCl_3$) of compound **2a-4**.

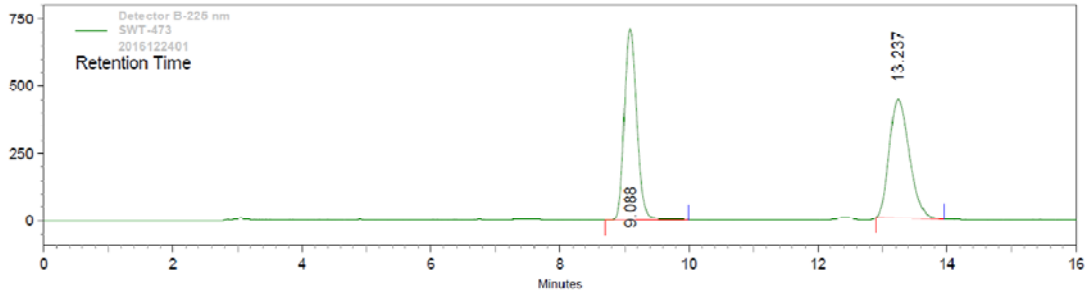


Supplementary Figure 81. ^{13}C NMR ($CDCl_3$) of compound **2a-4**.



2a-4

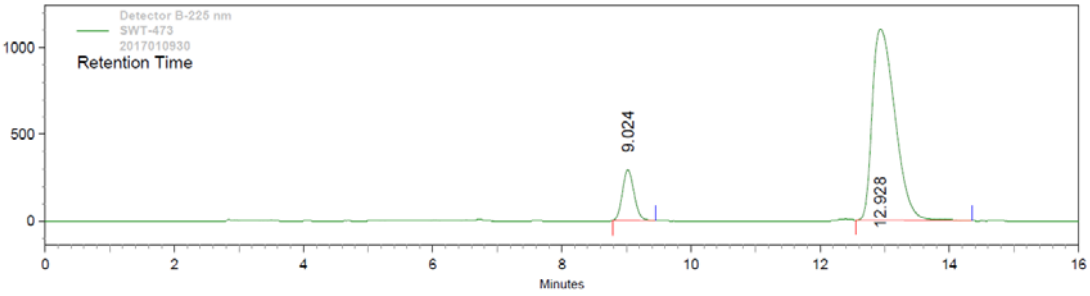
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 225 nm]



Detector B-225 nm

Pk #	Retention Time	Area	Area Percent	Height
1	9.088	9548692	50.00	710501
2	13.237	9549502	50.00	442468

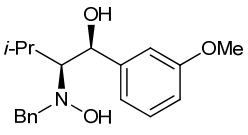
Supplementary Figure 82. Racemate of compound **2a-4**.



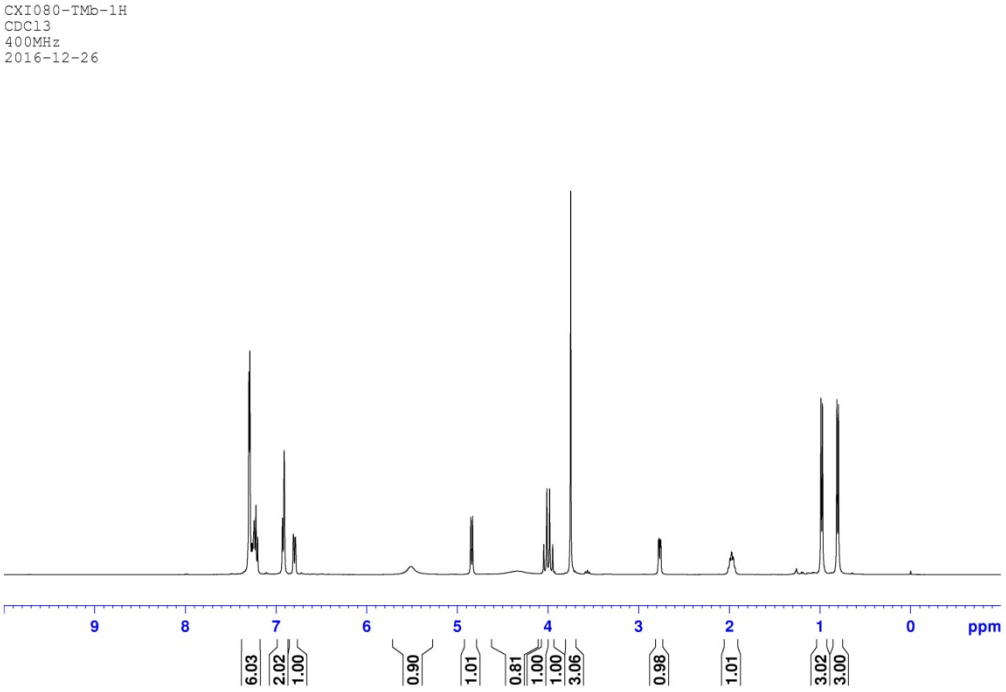
Detector B-225 nm

Pk #	Retention Time	Area	Area Percent	Height
1	9.024	3669867	11.95	293503
2	12.928	27039793	88.05	1104125

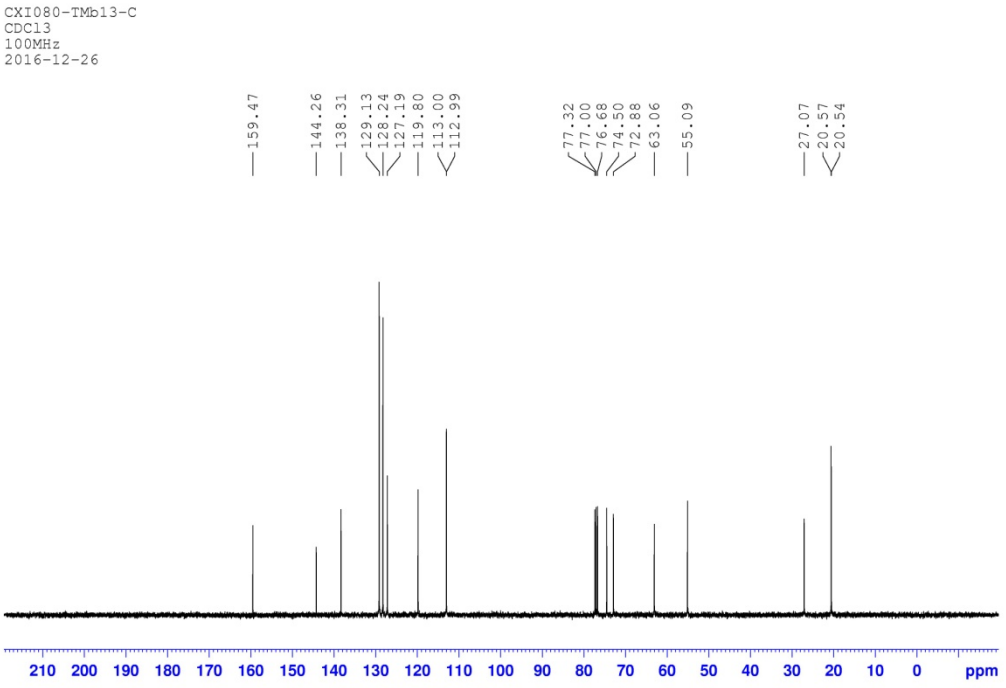
Supplementary Figure 83. Enantioenriched mixture of compound **2a-4**.



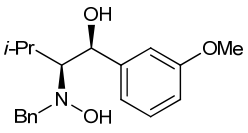
2a-5



Supplementary Figure 84. ^{1}H NMR ($CDCl_3$) of compound **2a-5**.

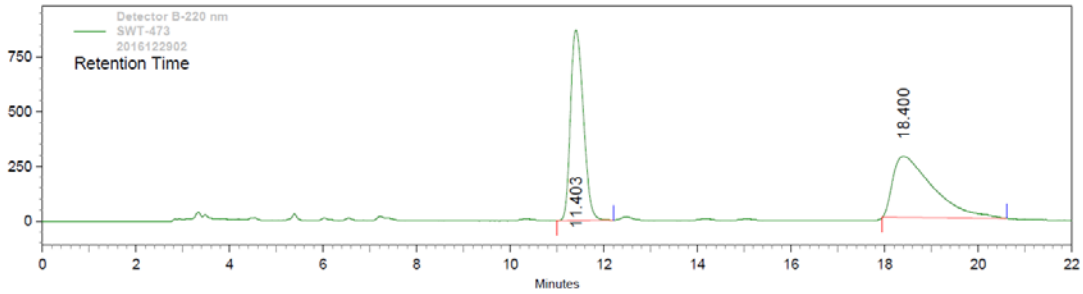


Supplementary Figure 85. ^{13}C NMR ($CDCl_3$) of compound **2a-5**.



2a-5

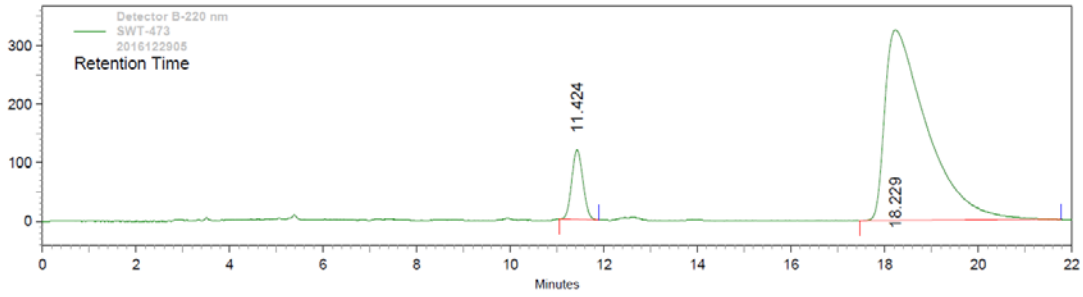
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 220 nm]



Detector B-220 nm

Pk #	Retention Time	Area	Area Percent	Height
1	11.403	16635941	50.00	872103
2	18.400	16639232	50.00	280416

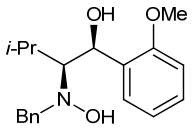
Supplementary Figure 86. Racemate of compound **2a-5**.



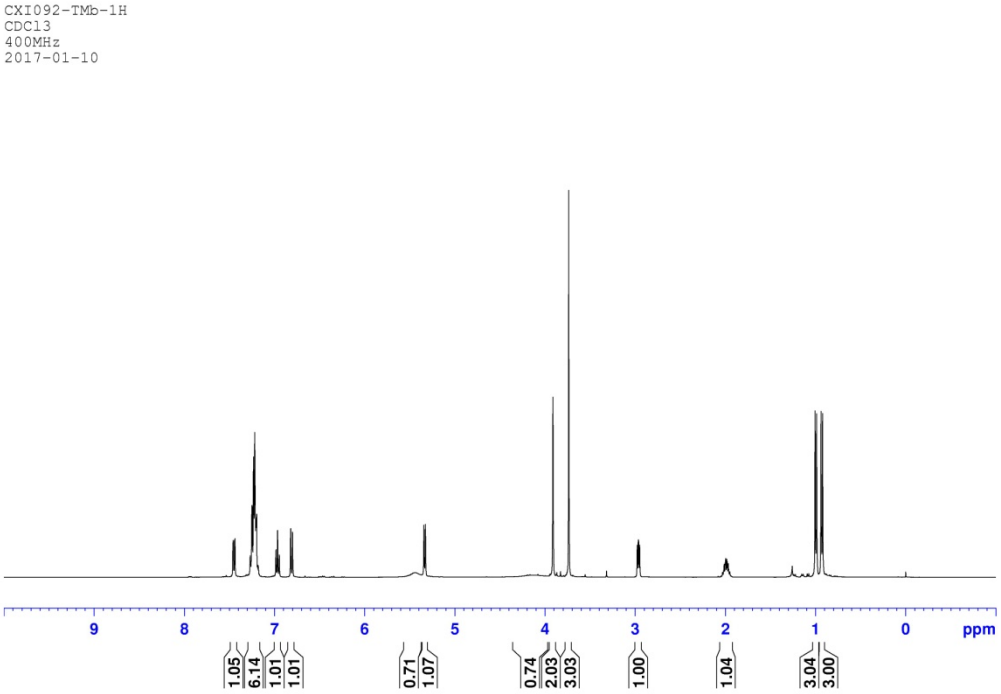
Detector B-220 nm

Pk #	Retention Time	Area	Area Percent	Height
1	11.424	1966910	8.83	118589
2	18.229	20303561	91.17	326219

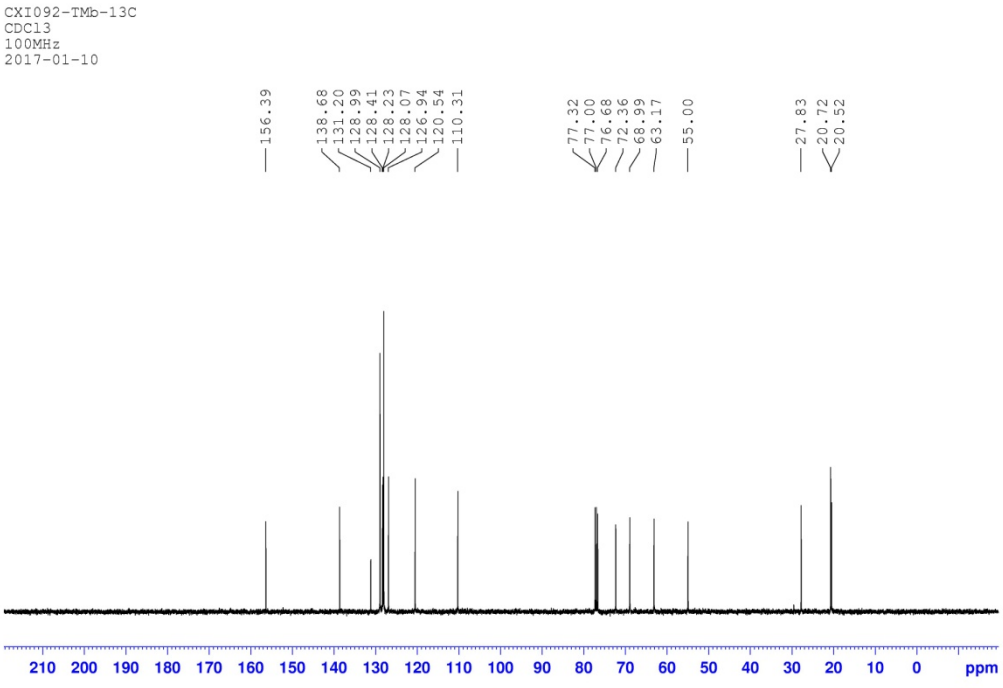
Supplementary Figure 87. Enantioenriched mixture of compound **2a-5**.



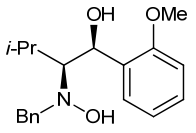
2a-6



Supplementary Figure 88. ^{1}H NMR ($CDCl_3$) of compound **2a-6**.

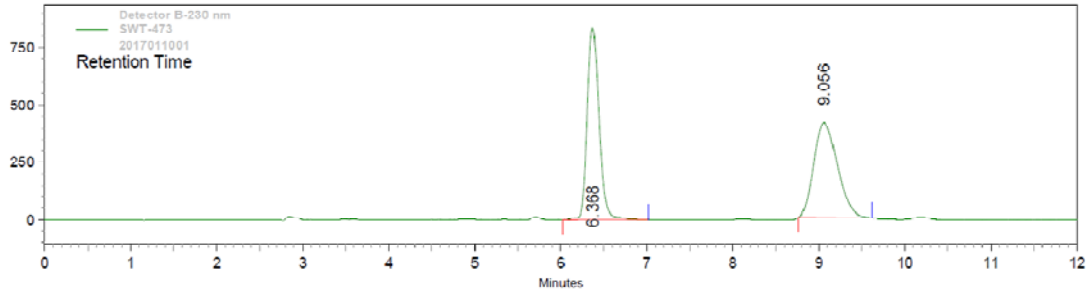


Supplementary Figure 89. ^{13}C NMR ($CDCl_3$) of compound **2a-6**.



2a-6

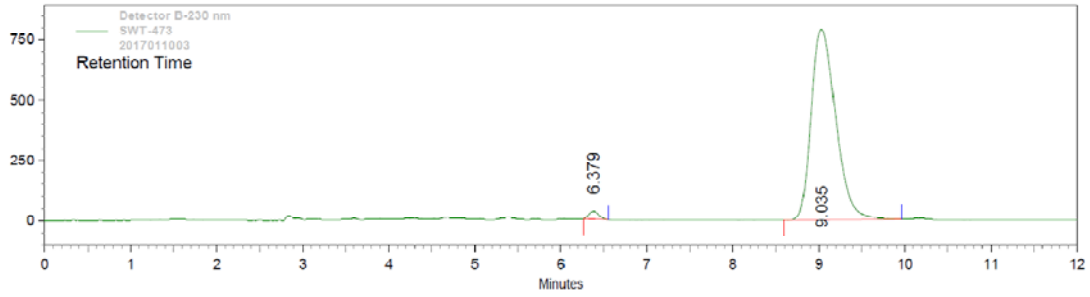
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 85/15 (v/v), 1.0 mL/min, 230 nm]



Detector B-230 nm

Pk #	Retention Time	Area	Area Percent	Height
1	6.368	7826096	49.80	832193
2	9.056	7888798	50.20	412285

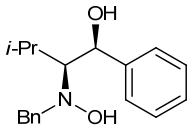
Supplementary Figure 90. Racemate of compound **2a-6**.



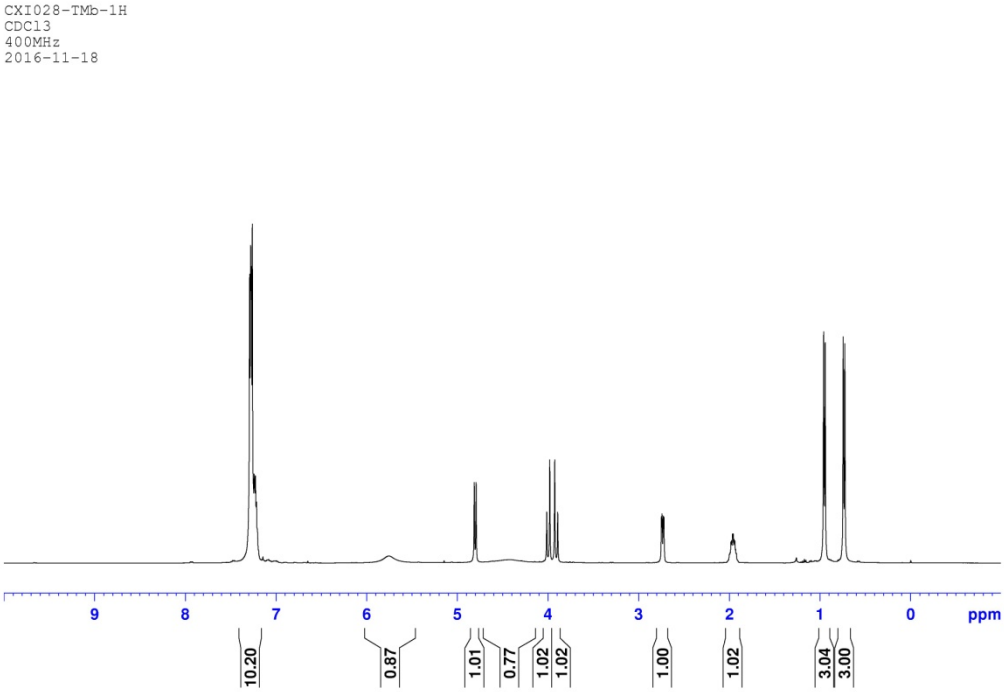
Detector B-230 nm

Pk #	Retention Time	Area	Area Percent	Height
1	6.379	246015	1.53	32516
2	9.035	15809419	98.47	793695

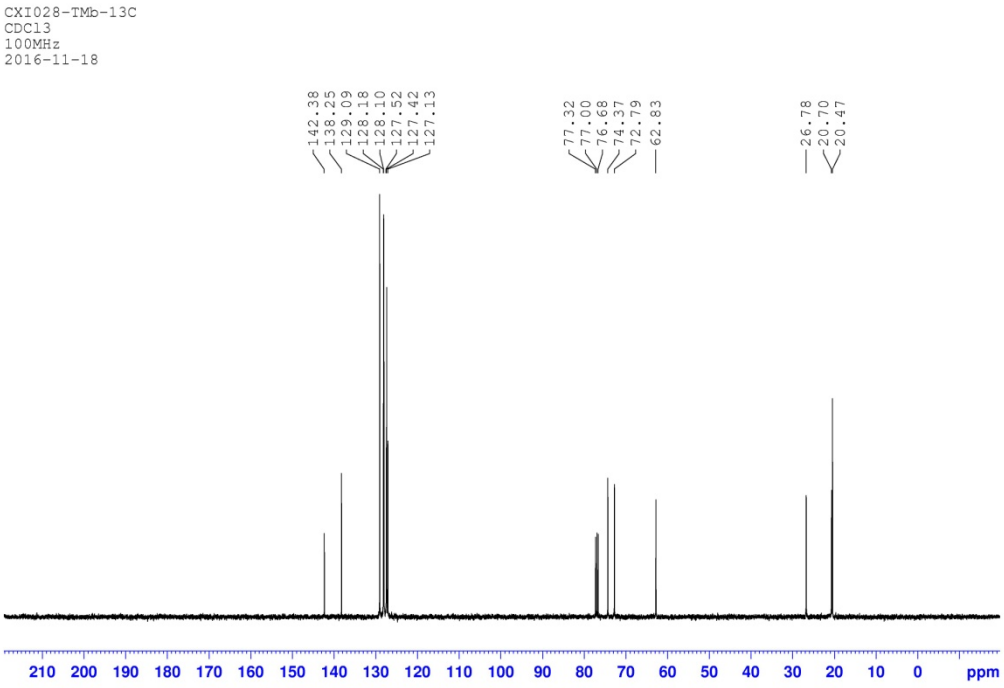
Supplementary Figure 91. Enantioenriched mixture of compound **2a-6**.



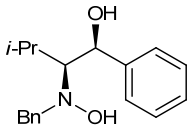
2a-7



Supplementary Figure 92. ^{1}H NMR ($CDCl_3$) of compound **2a-7**.

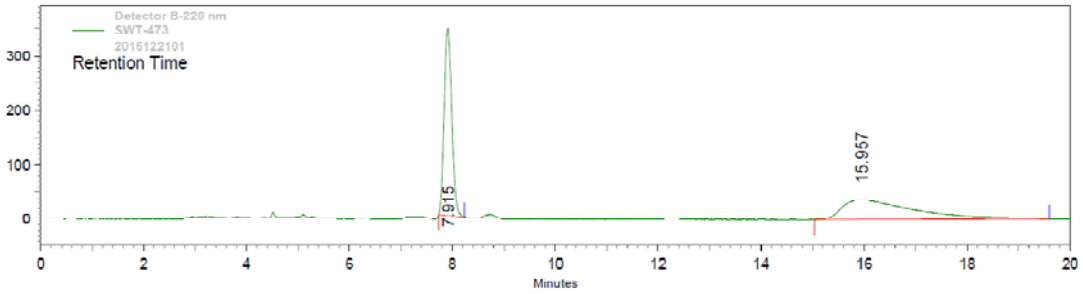


Supplementary Figure 93. ^{13}C NMR ($CDCl_3$) of compound **2a-7**.



2a-7

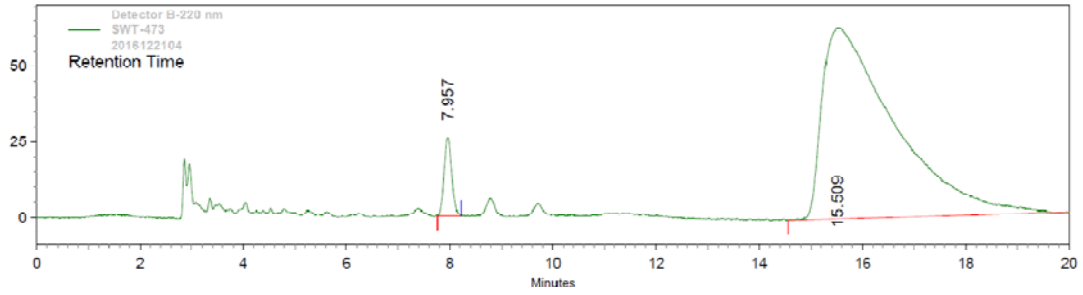
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 220 nm]



Detector B-220 nm

Pk #	Retention Time	Area	Area Percent	Height
1	7.915	3628323	50.05	343632
2	15.957	3620498	49.95	37401

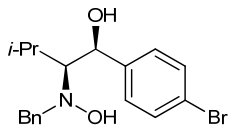
Supplementary Figure 94. Racemate of compound **2a-7**.



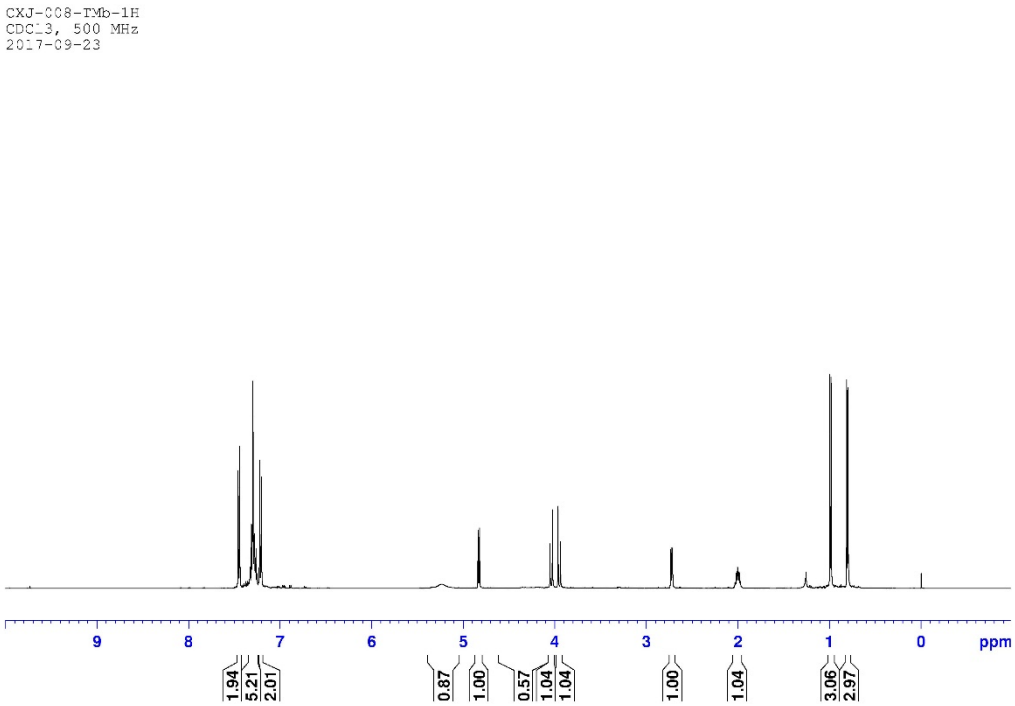
Detector B-220 nm

Pk #	Retention Time	Area	Area Percent	Height
1	7.957	268883	4.21	25726
2	15.509	6120301	95.79	63108

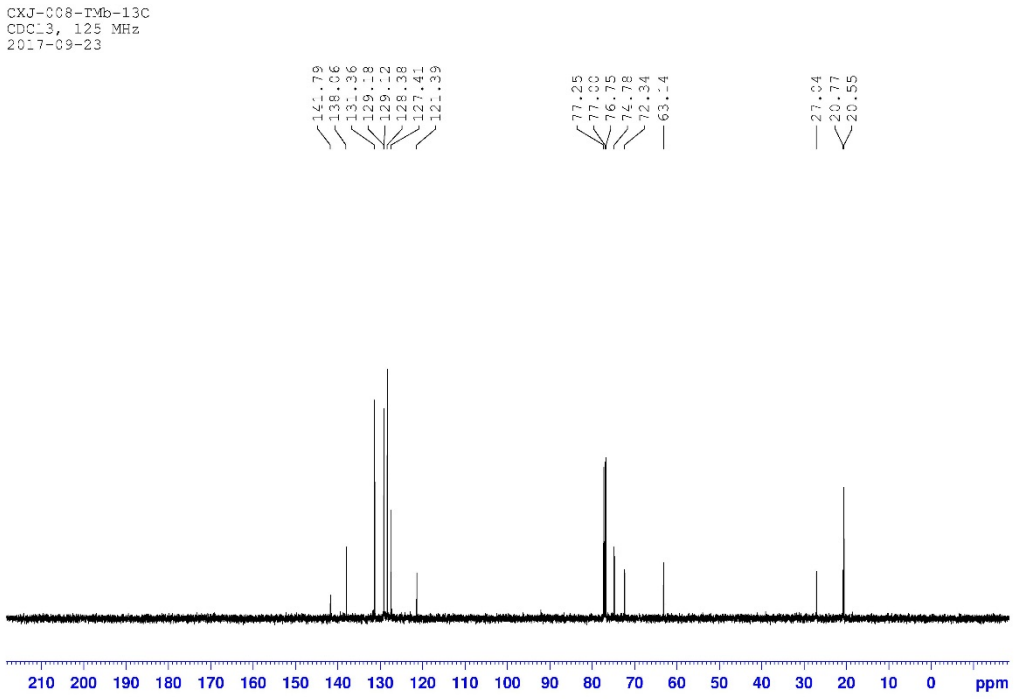
Supplementary Figure 95. Enantioenriched mixture of compound **2a-7**.



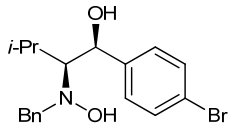
2a-8



Supplementary Figure 96. ^{1}H NMR ($CDCl_3$) of compound **2a-8**.

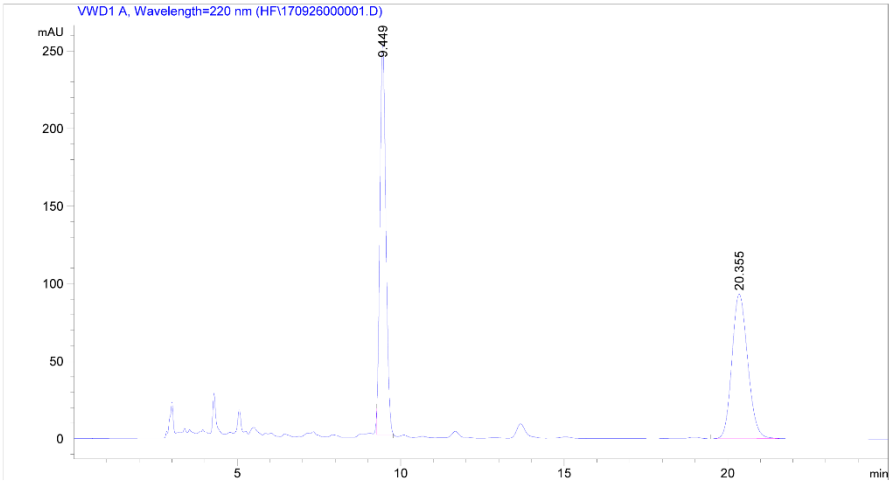


Supplementary Figure 97. ^{13}C NMR ($CDCl_3$) of compound **2a-8**.



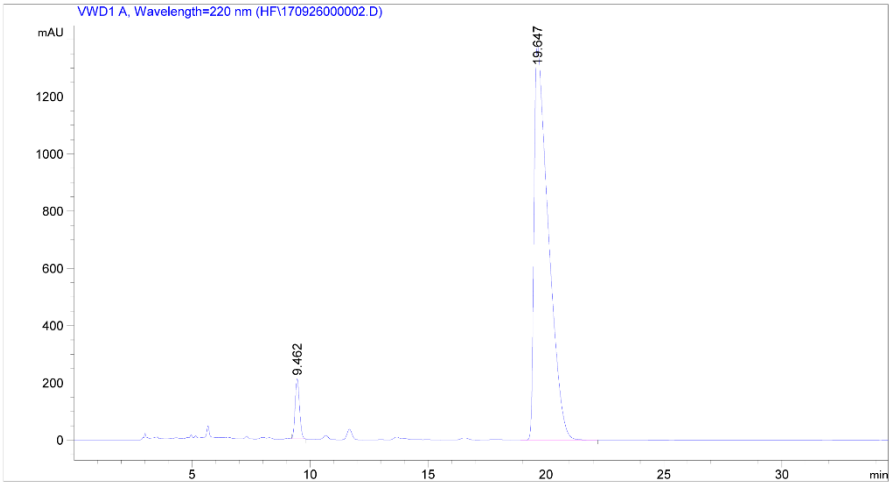
2a-8

[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 85/15 (v/v), 1.0 mL/min, 220 nm]



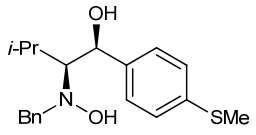
Pk #	Retention Time [min]	Area [mAU*s]	Height [mAU]	Area Percent %
1	9.449	3188.23486	251.30400	50.5575
2	20.355	3117.92554	93.22905	49.4425
Totals:		6306.16040	344.53305	100.0000

Supplementary Figure 98. Racemate of compound **2a-8**.

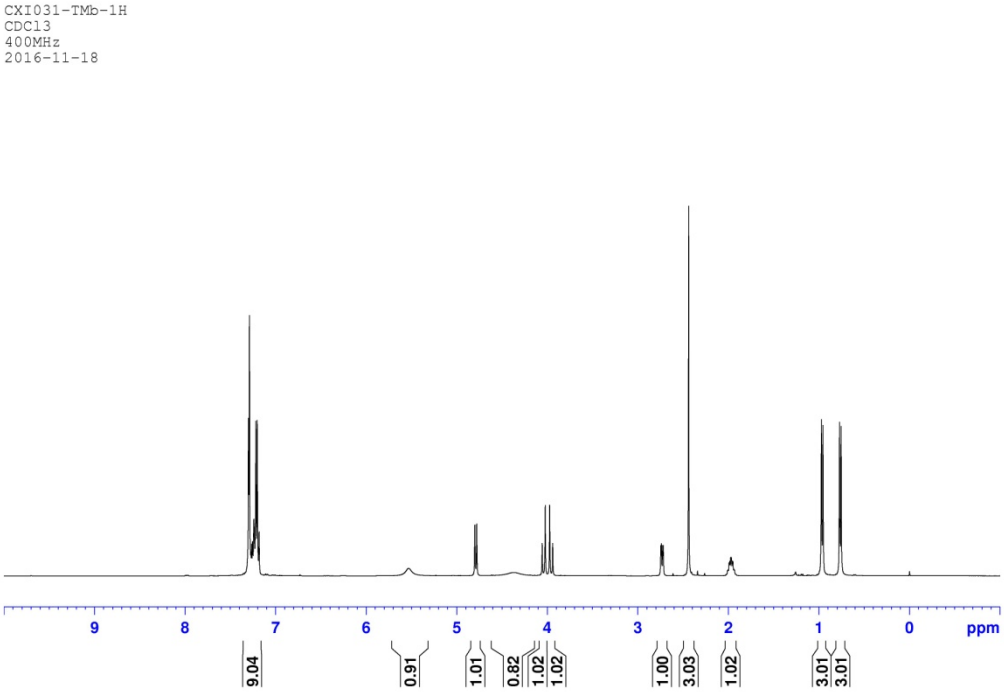


Pk #	Retention Time [min]	Area [mAU*s]	Height [mAU]	Area Percent %
1	9.462	2699.80225	209.19240	4.4457
2	19.647	5.80293e4	1379.35938	95.5543
Totals:		6.07291e4	1588.55177	100.0000

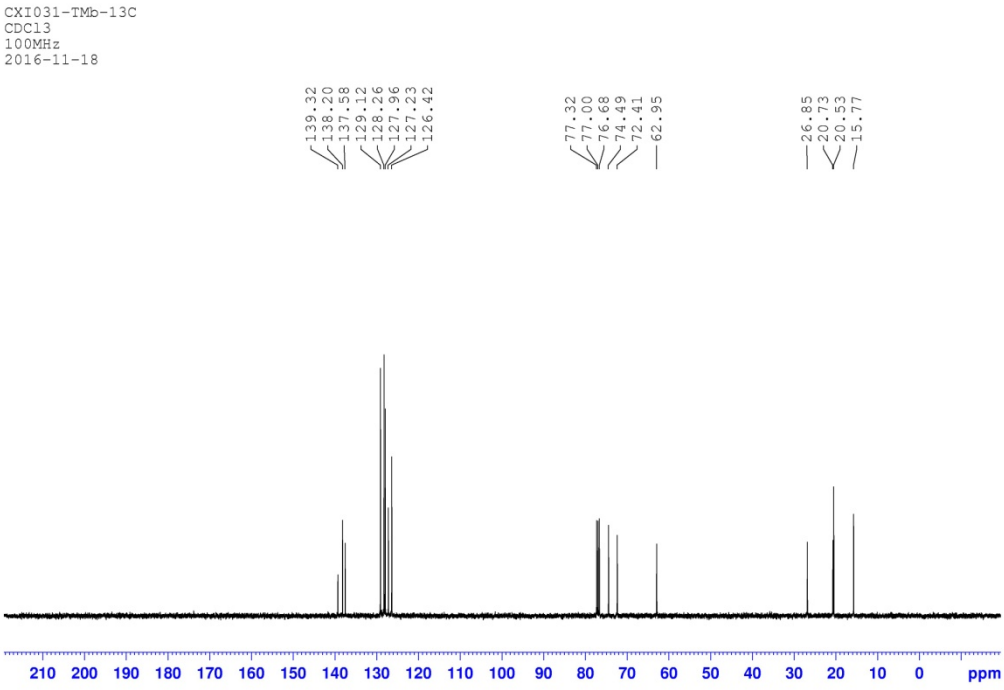
Supplementary Figure 99. Enantioenriched mixture of compound **2a-8**.



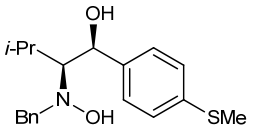
2a-9



Supplementary Figure 100. ^{1}H NMR ($CDCl_3$) of compound **2a-9**.

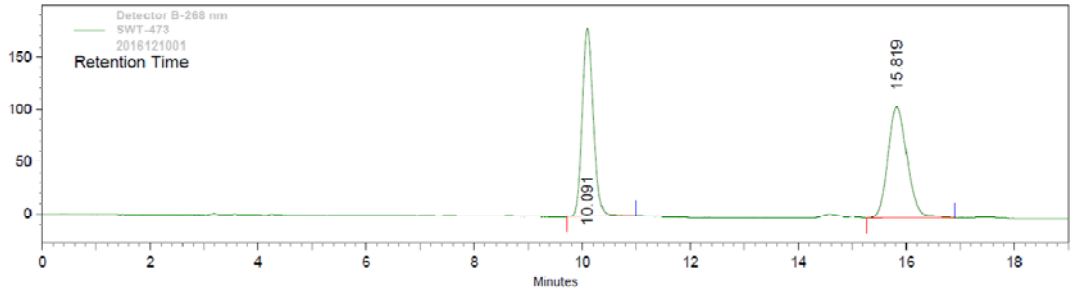


Supplementary Figure 101. ^{13}C NMR ($CDCl_3$) of compound **2a-9**.



2a-9

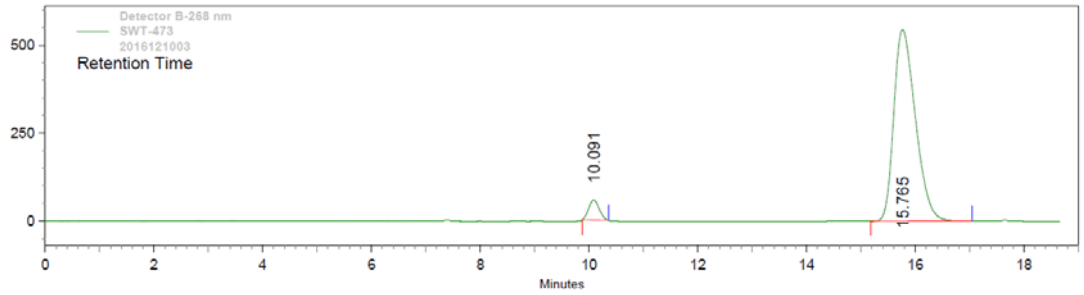
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 268 nm]



Detector B-268 nm

Pk #	Retention Time	Area	Area Percent	Height
1	10.091	2622062	49.96	179697
2	15.819	2626382	50.04	105748

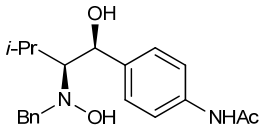
Supplementary Figure 102. Racemate of compound **2a-9**.



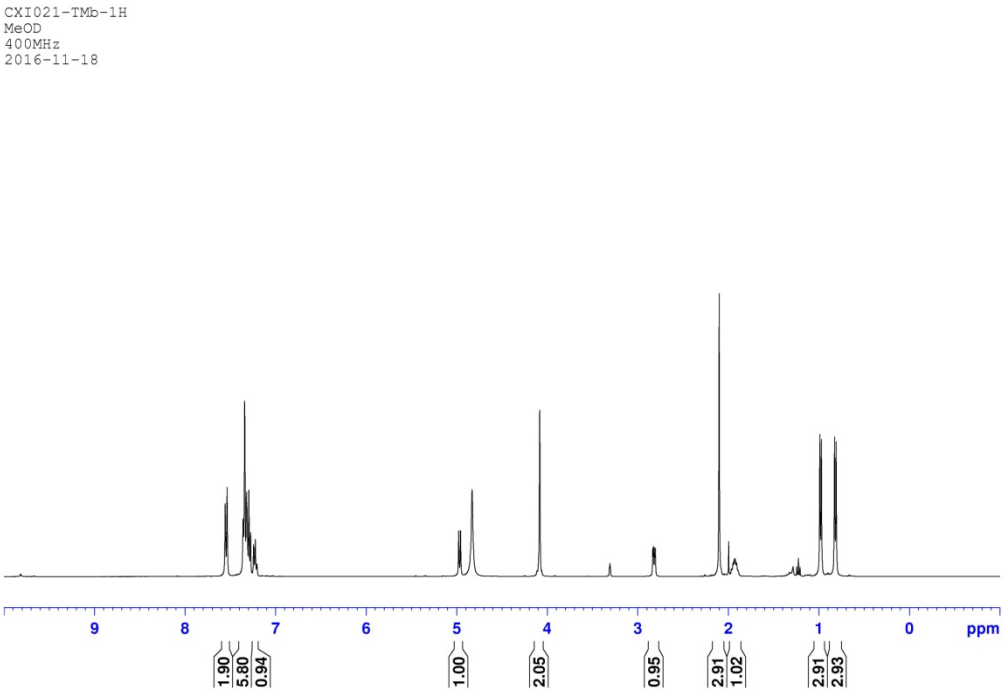
Detector B-268 nm

Pk #	Retention Time	Area	Area Percent	Height
1	10.091	755231	4.79	56414
2	15.765	14998789	95.21	545316

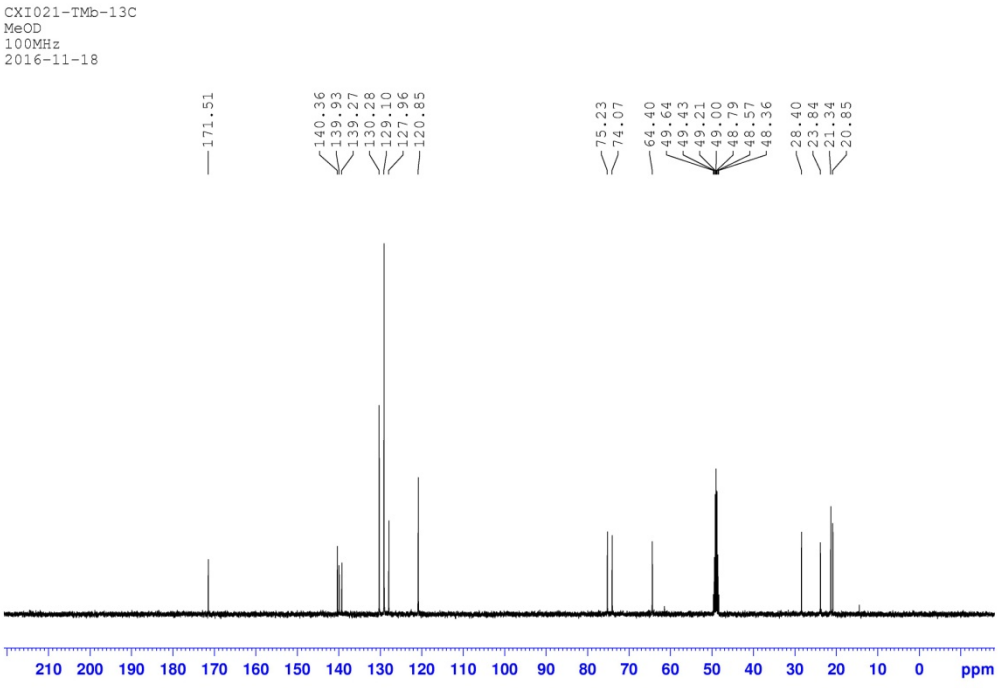
Supplementary Figure 103. Enantioenriched mixture of compound **2a-9**.



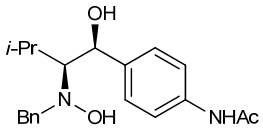
2a-10



Supplementary Figure 104. ^{1}H NMR (MeOD) of compound **2a-10**.

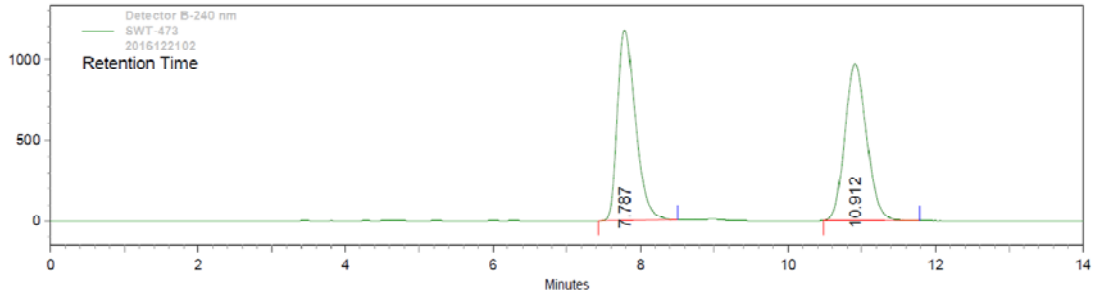


Supplementary Figure 105. ^{13}C NMR (MeOD) of compound **2a-10**.



2a-10

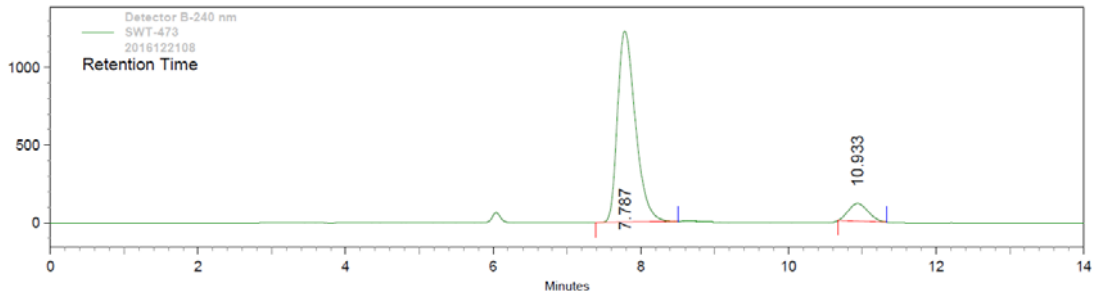
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 240 nm]



Detector B-240 nm

Pk #	Retention Time	Area	Area Percent	Height
1	7.787	20064807	49.95	1181029
2	10.912	20102171	50.05	970316

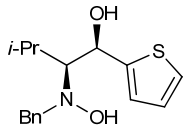
Supplementary Figure 106. Racemate of compound **2a-10**.



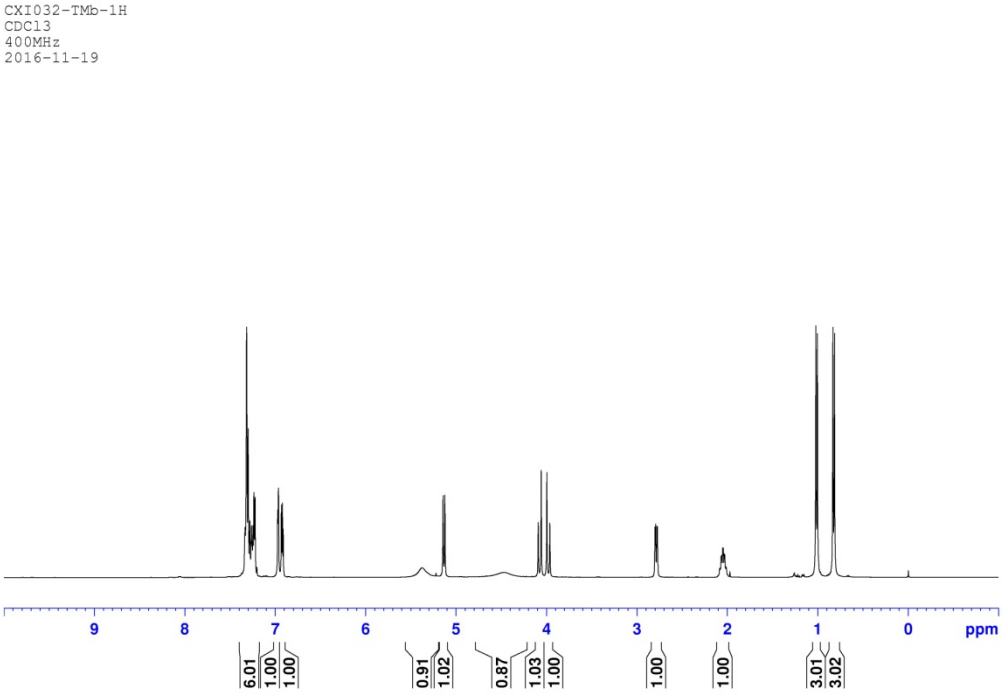
Detector B-240 nm

Pk #	Retention Time	Area	Area Percent	Height
1	7.787	20757686	91.02	1230972
2	10.933	2047304	8.98	111181

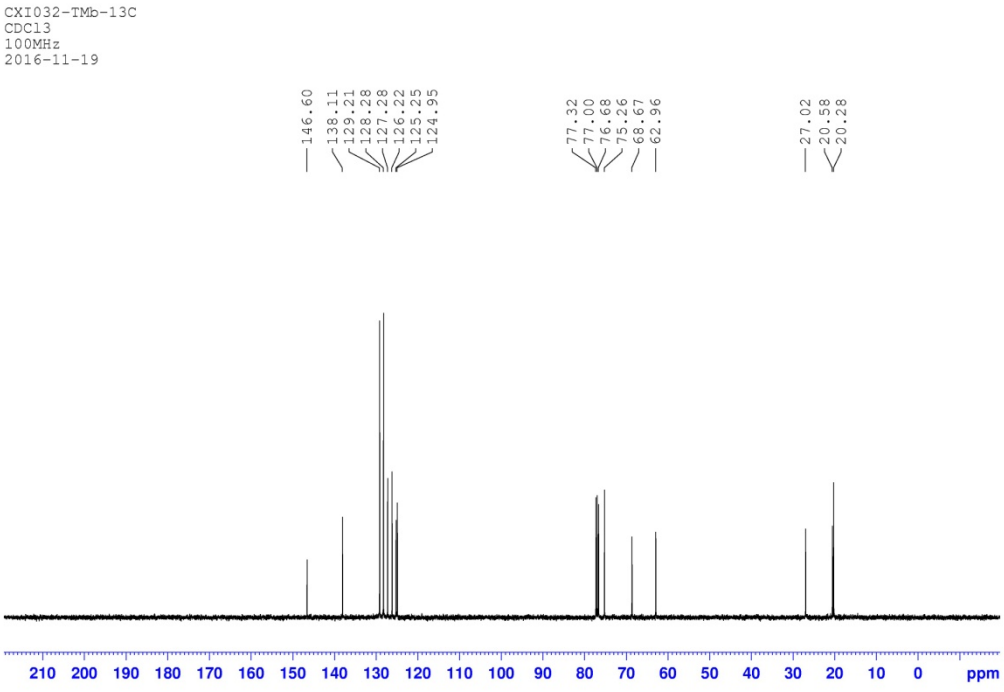
Supplementary Figure 107. Enantioenriched mixture of compound **2a-10**.



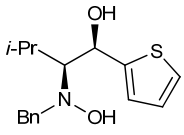
2a-11



Supplementary Figure 108. ^{1}H NMR ($CDCl_3$) of compound **2a-11**.

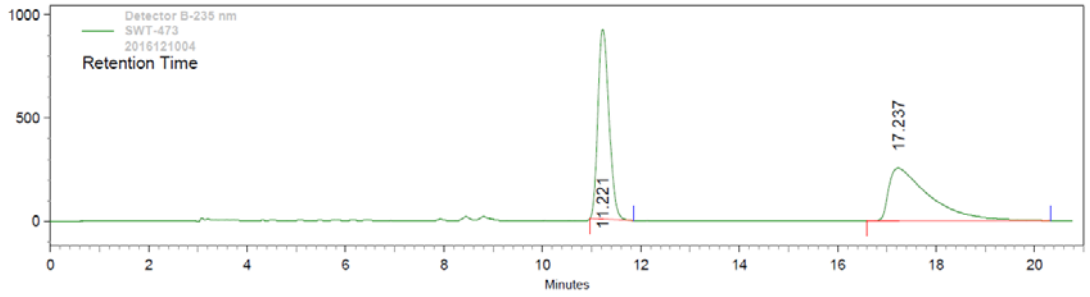


Supplementary Figure 109. ^{13}C NMR ($CDCl_3$) of compound **2a-11**.



2a-11

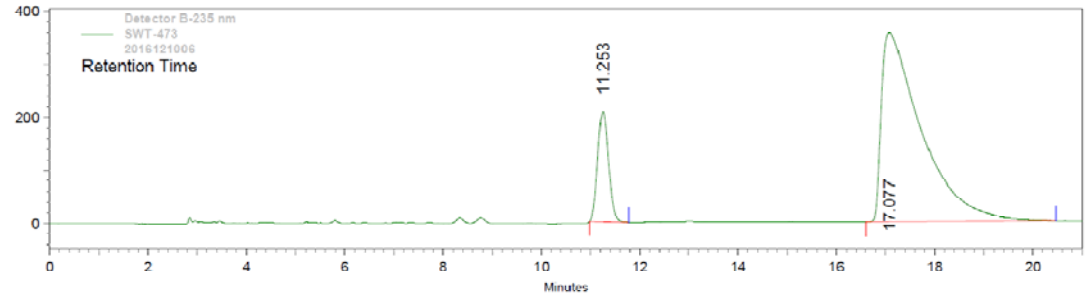
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 235 nm]



Detector B-235 nm

Pk #	Retention Time	Area	Area Percent	Height
1	11.221	14453906	50.16	920646
2	17.237	14361517	49.84	253102

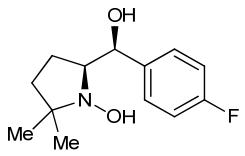
Supplementary Figure 110. Racemate of compound **2a-11**.



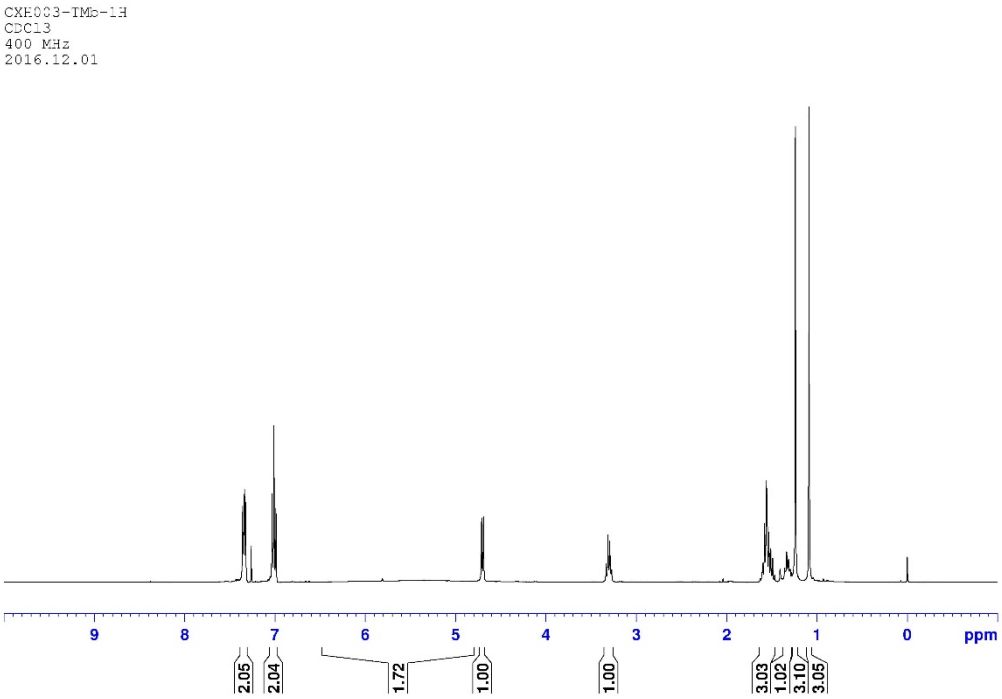
Detector B-235 nm

Pk #	Retention Time	Area	Area Percent	Height
1	11.253	3129608	13.41	207599
2	17.077	20201701	86.59	356242

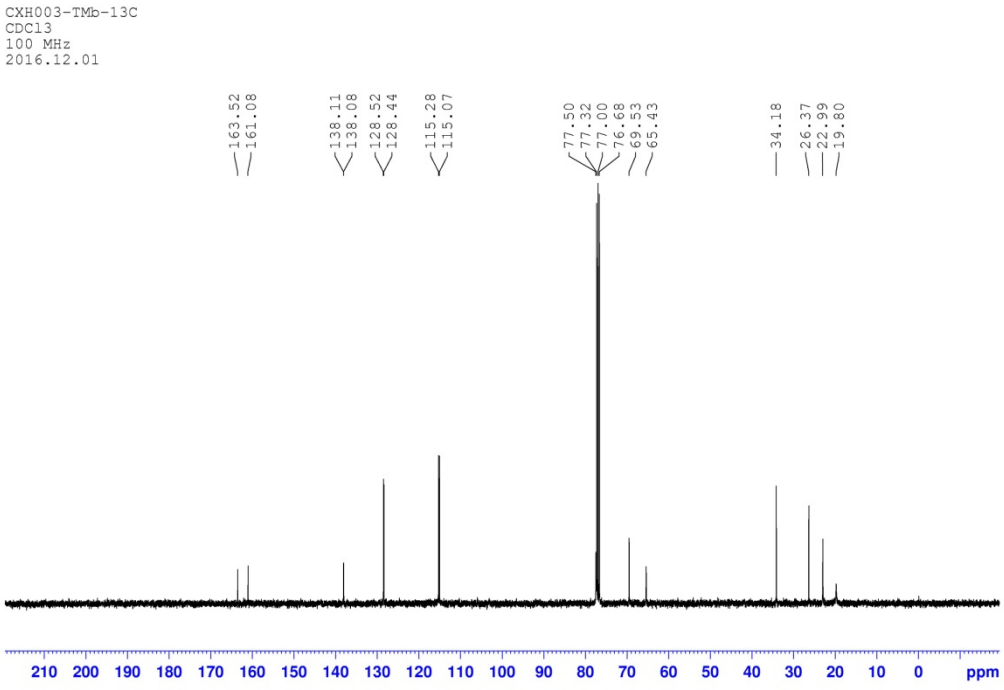
Supplementary Figure 111. Enantioenriched mixture of compound **2a-11**.



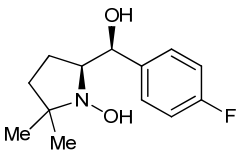
2k-1 (major)



Supplementary Figure 112. ^{1}H NMR ($CDCl_3$) of compound **2k-1**.

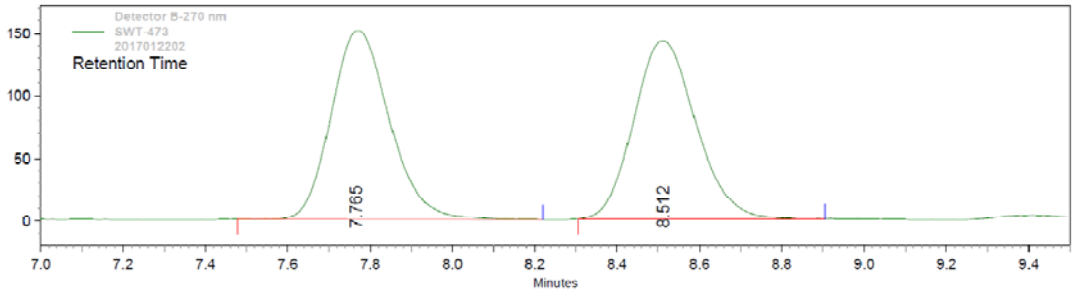


Supplementary Figure 113. ^{13}C NMR ($CDCl_3$) of compound **2k-1**.



2k-1 (major)

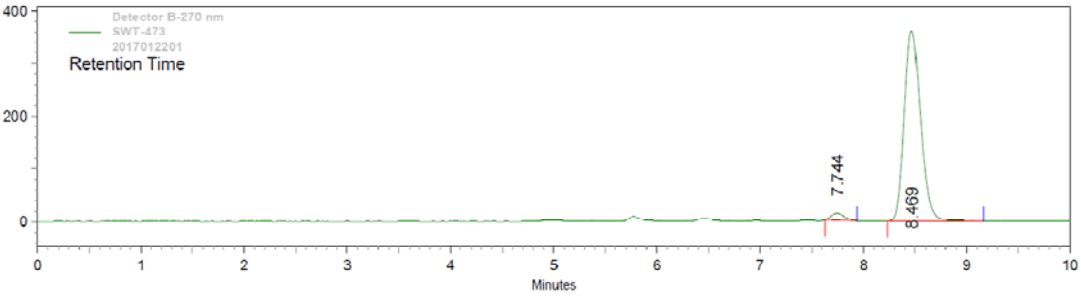
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 270 nm]



Detector B-270 nm

Pk #	Retention Time	Area	Area Percent	Height
1	7.765	1489600	49.97	151484
2	8.512	1491152	50.03	142705

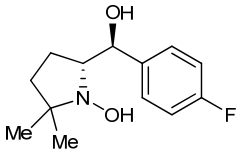
Supplementary Figure 114. Racemate of compound **2k-1**.



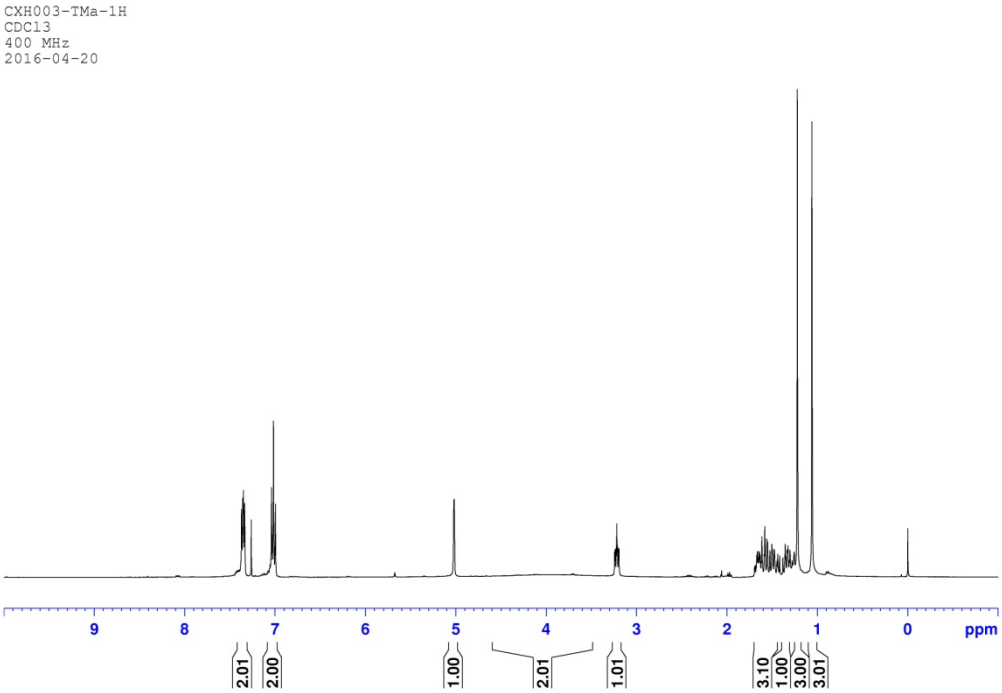
Detector B-270 nm

Pk #	Retention Time	Area	Area Percent	Height
1	7.744	121378	2.97	13982
2	8.469	3970612	97.03	362665

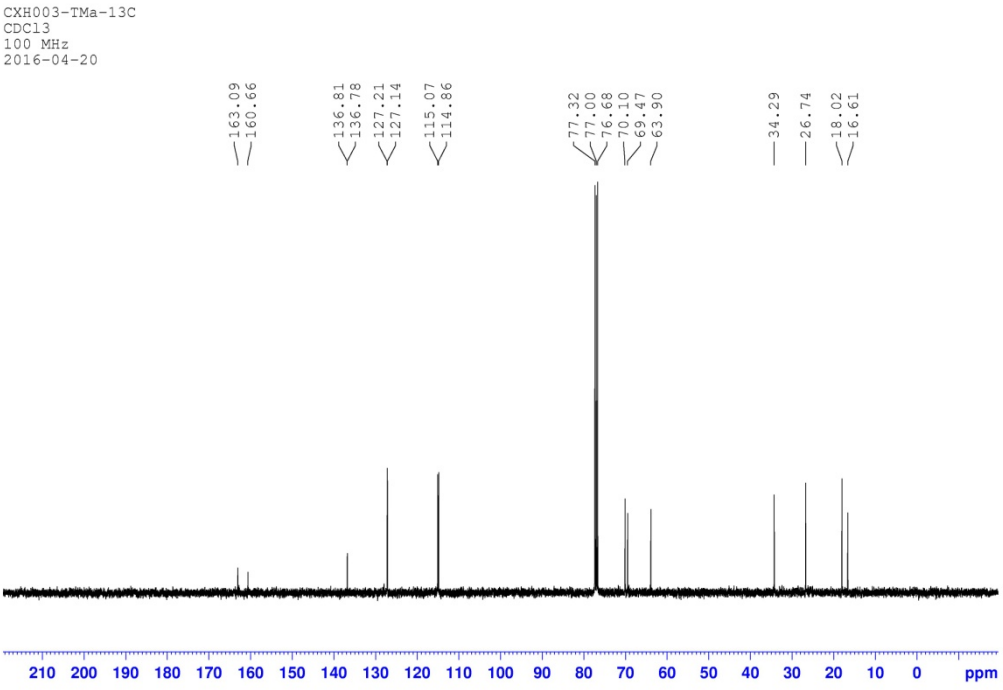
Supplementary Figure 115. Enantioenriched mixture of compound **2k-1**.



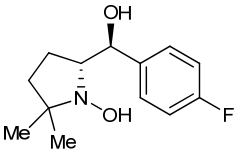
diastereomer of **2k-1** (minor)



Supplementary Figure 116. ^{1}H NMR ($CDCl_3$) of the diastereomer of **2k-1**.

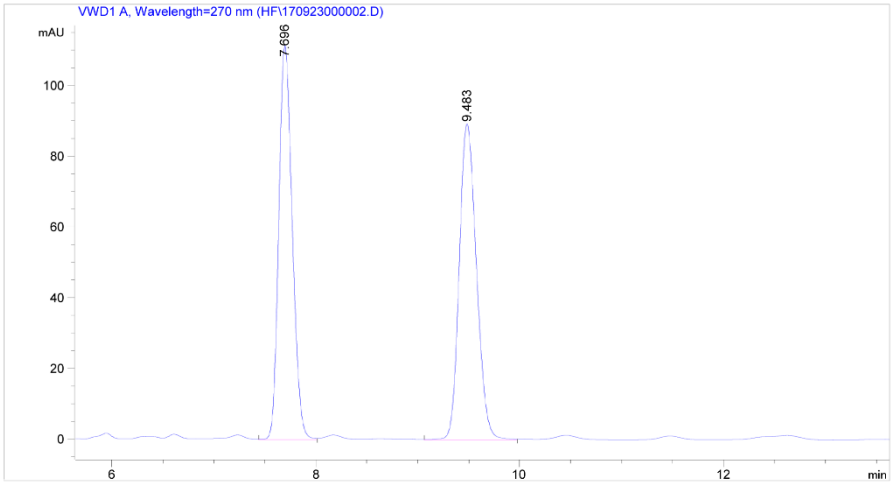


Supplementary Figure 117. ^{13}C NMR ($CDCl_3$) of the diastereomer of **2k-1**.



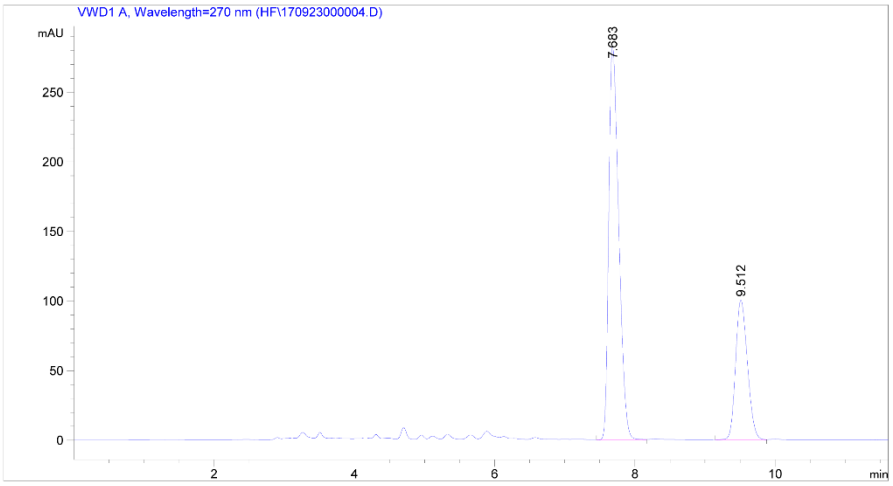
diastereomer of **2k-1** (minor)

[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 85/15 (v/v), 1.0 mL/min, 270 nm]



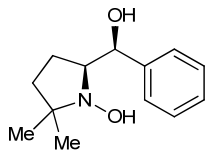
Pk #	Retention Time [min]	Area [mAU*s]	Height [mAU]	Area Percent %
1	7.696	1025.07556	111.50843	49.5229
2	9.483	1044.82837	89.20393	50.4771
Totals:		2069.90393	200.71236	100.0000

Supplementary Figure 118. Racemate of the diastereomer of **2k-1**.

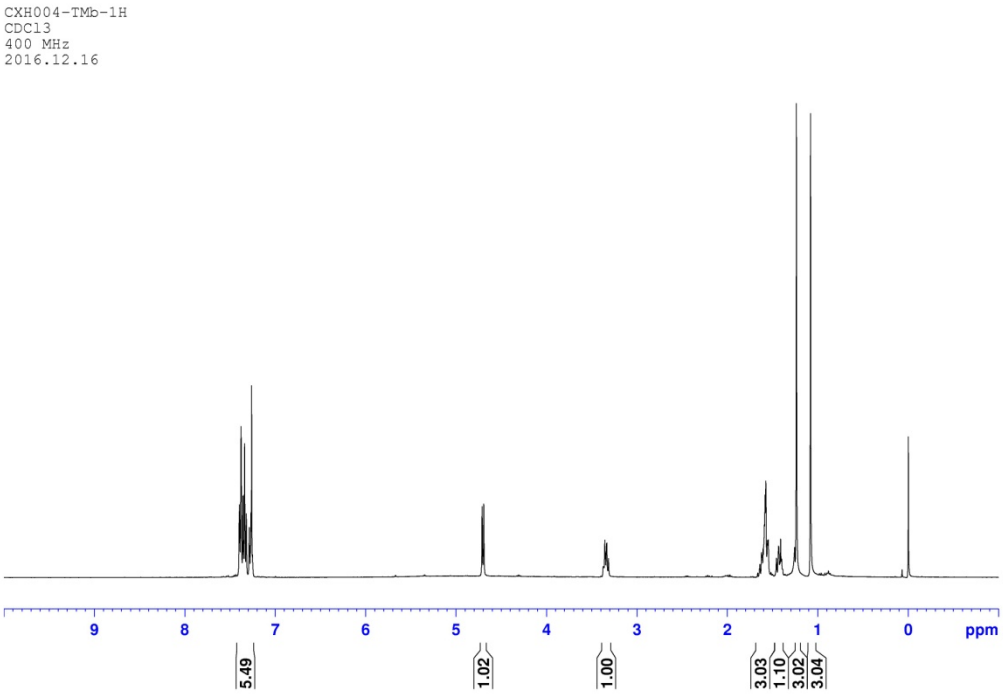


Pk #	Retention Time [min]	Area [mAU*s]	Height [mAU]	Area Percent %
1	7.683	2810.85400	283.10849	70.4526
2	9.512	1178.85583	100.39719	29.5474
Totals:		3989.70984	383.50568	100.0000

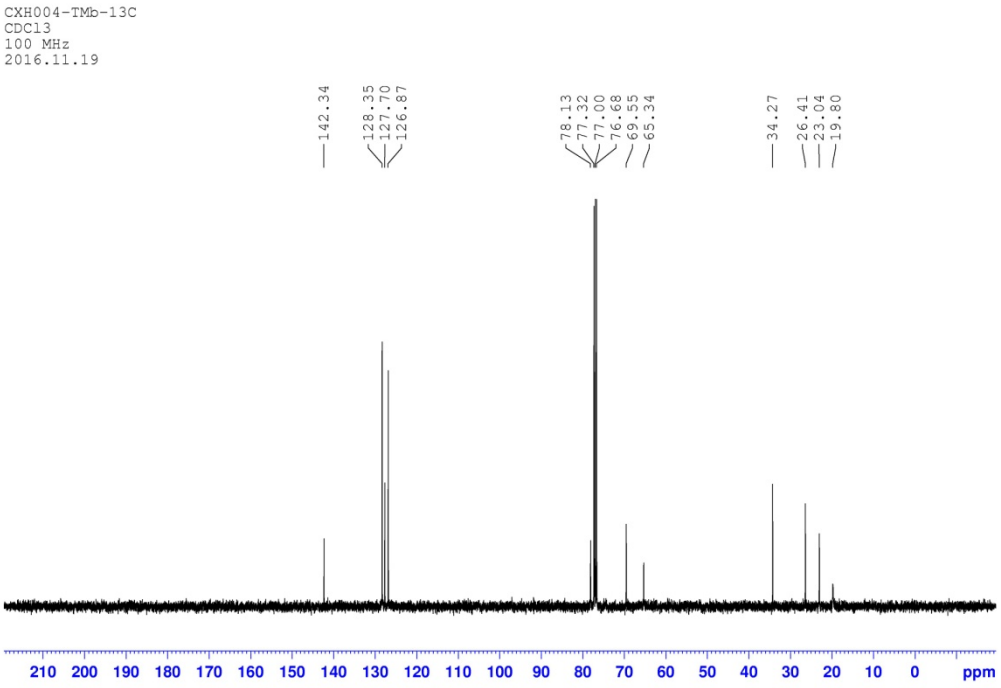
Supplementary Figure 119. Enantioenriched mixture of the diastereomer of **2k-1**.



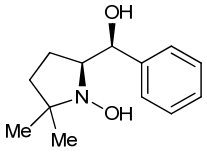
2k-2 (major)



Supplementary Figure 120. ^{1}H NMR ($CDCl_3$) of compound **2k-2**.

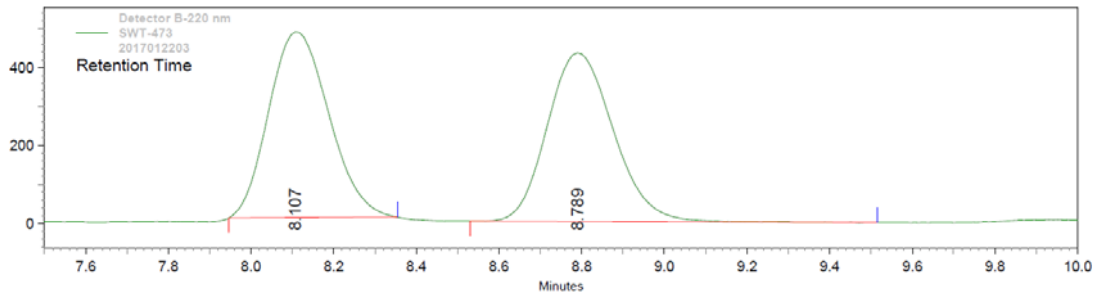


Supplementary Figure 121. ^{13}C NMR ($CDCl_3$) of compound **2k-2**.



2k-2 (major)

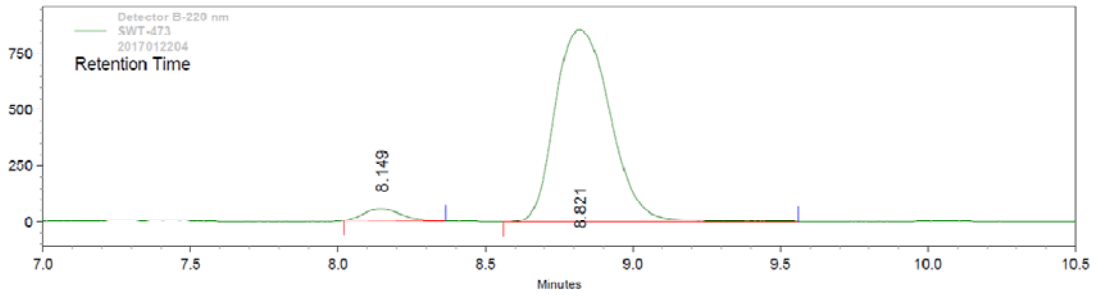
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 220 nm]



Detector B-220 nm

Pk #	Retention Time	Area	Area Percent	Height
1	8.107	4818013	50.00	477288
2	8.789	4817168	50.00	433144

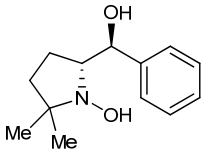
Supplementary Figure 122. Racemate of compound **2k-2**.



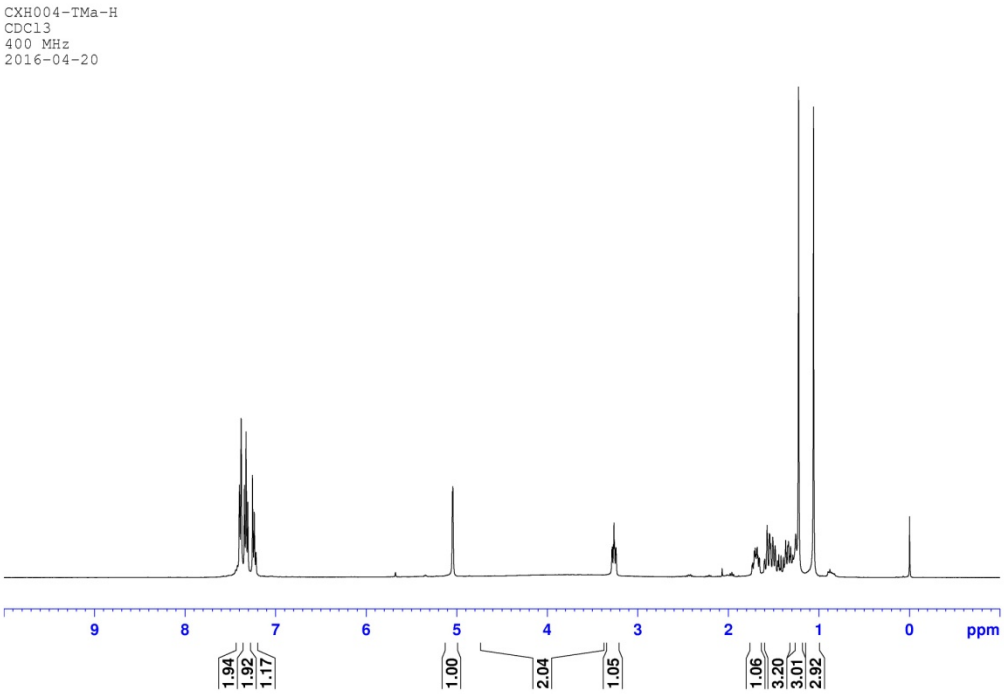
Detector B-220 nm

Pk #	Retention Time	Area	Area Percent	Height
1	8.149	448823	3.90	50046
2	8.821	11073889	96.10	854629

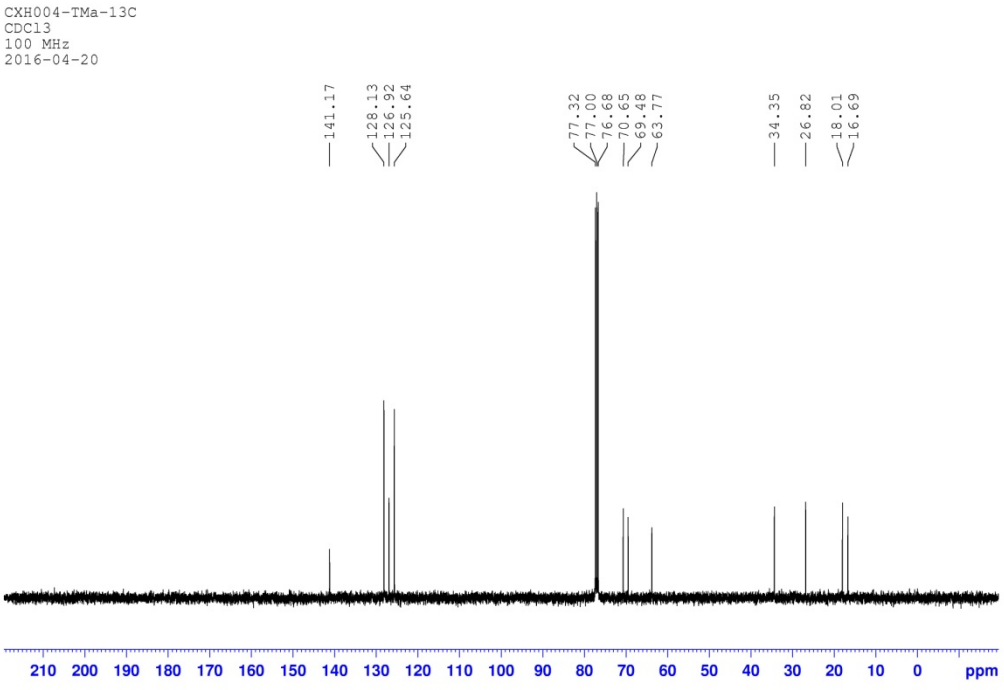
Supplementary Figure 123. Enantioenriched mixture of compound **2k-2**.



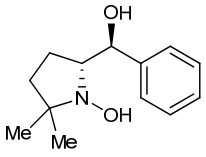
diastereomer of **2k-2** (minor)



Supplementary Figure 124. ^{1}H NMR ($CDCl_3$) of the diastereomer of **2k-2**.

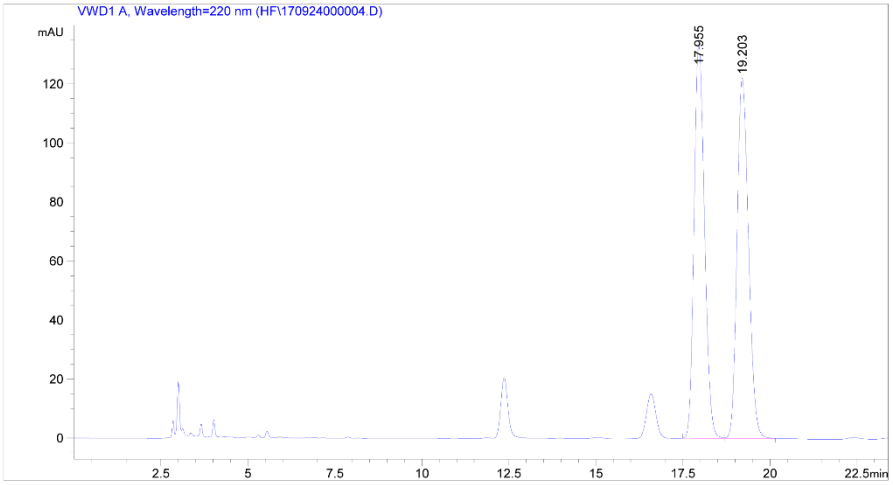


Supplementary Figure 125. ^{13}C NMR ($CDCl_3$) of the diastereomer of **2k-2**.



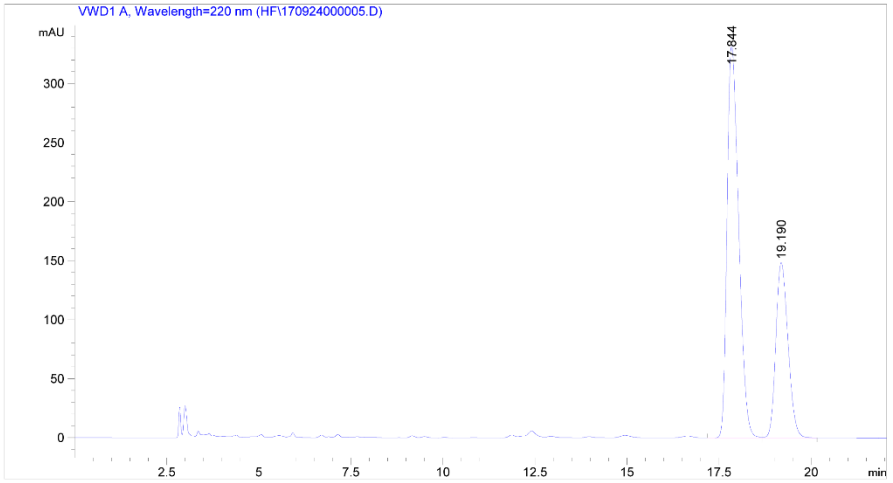
diastereomer of **2k-2** (minor)

[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 95/5 (v/v), 1.0 mL/min, 220 nm]



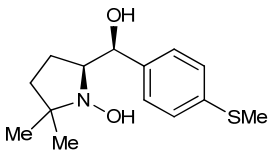
Pk #	Retention Time [min]	Area [mAU*s]	Height [mAU]	Area Percent %
1	17.955	2786.83252	133.47337	49.9584
2	19.203	2791.47876	122.29587	50.0416
Totals:		5578.31128	255.76924	100.0000

Supplementary Figure 126. Racemate of the diastereomer of **2k-2**.

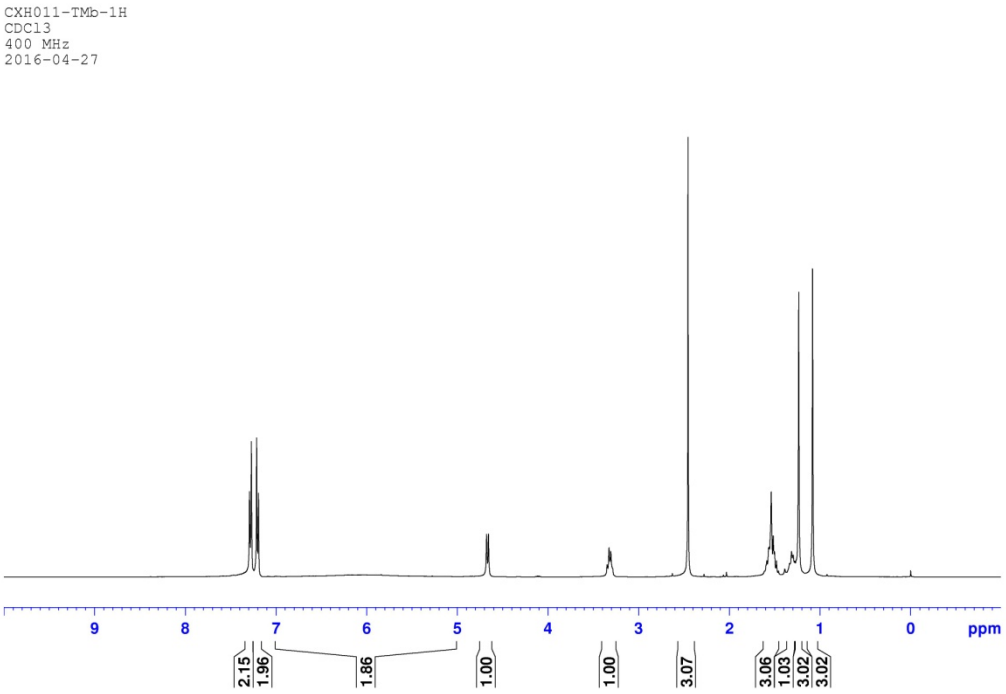


Pk #	Retention Time [min]	Area [mAU*s]	Height [mAU]	Area Percent %
1	17.844	7275.76367	332.85065	68.0117
2	19.190	3422.04175	148.47241	31.9883
Totals:		1.06978e4	481.32306	100.0000

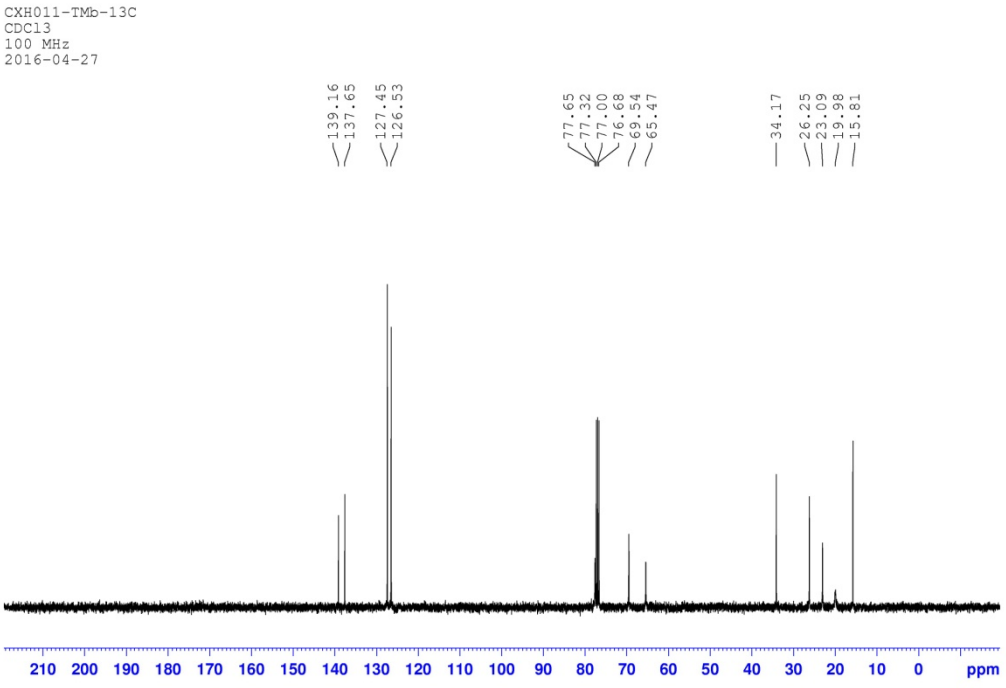
Supplementary Figure 127. Enantioenriched mixture of the diastereomer of **2k-2**.



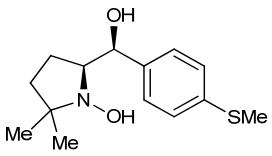
2k-3 (major)



Supplementary Figure 128. ^{1}H NMR ($CDCl_3$) of compound **2k-3**.

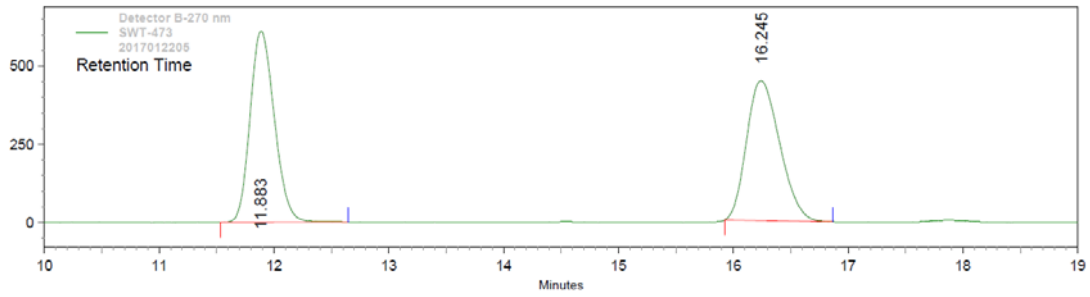


Supplementary Figure 129. ^{13}C NMR ($CDCl_3$) of compound **2k-3**.



2k-3 (major)

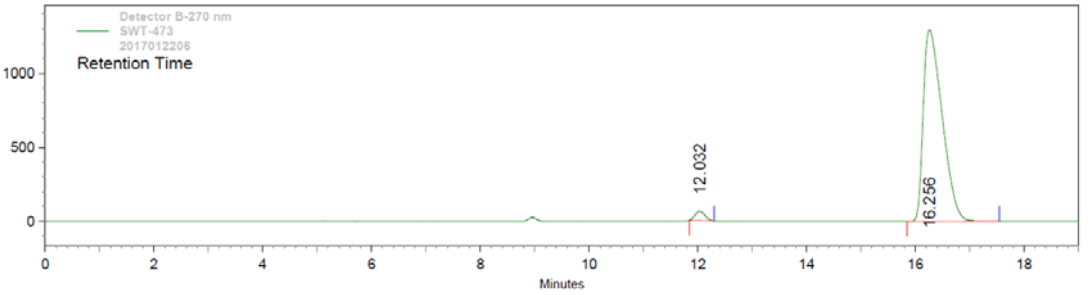
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 270 nm]



Detector B-270 nm

Pk #	Retention Time	Area	Area Percent	Height
1	11.883	8989956	49.99	610083
2	16.245	8994740	50.01	447376

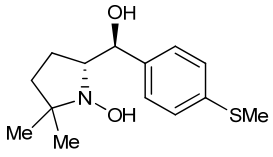
Supplementary Figure 130. Racemate of compound **2k-3**.



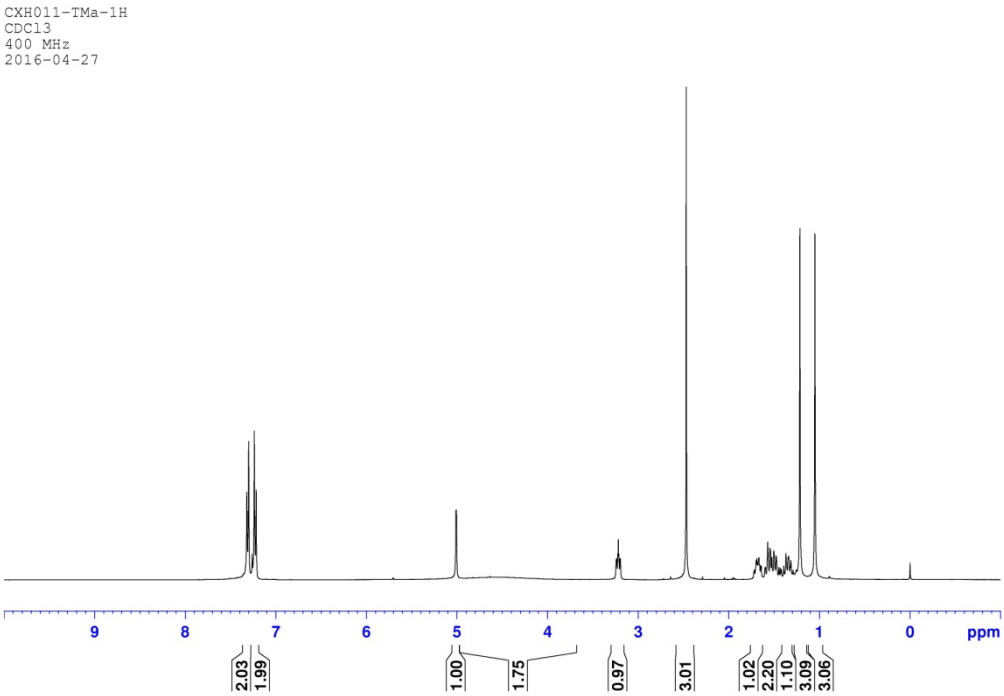
Detector B-270 nm

Pk #	Retention Time	Area	Area Percent	Height
1	12.032	802192	2.51	61774
2	16.256	31219066	97.49	1294447

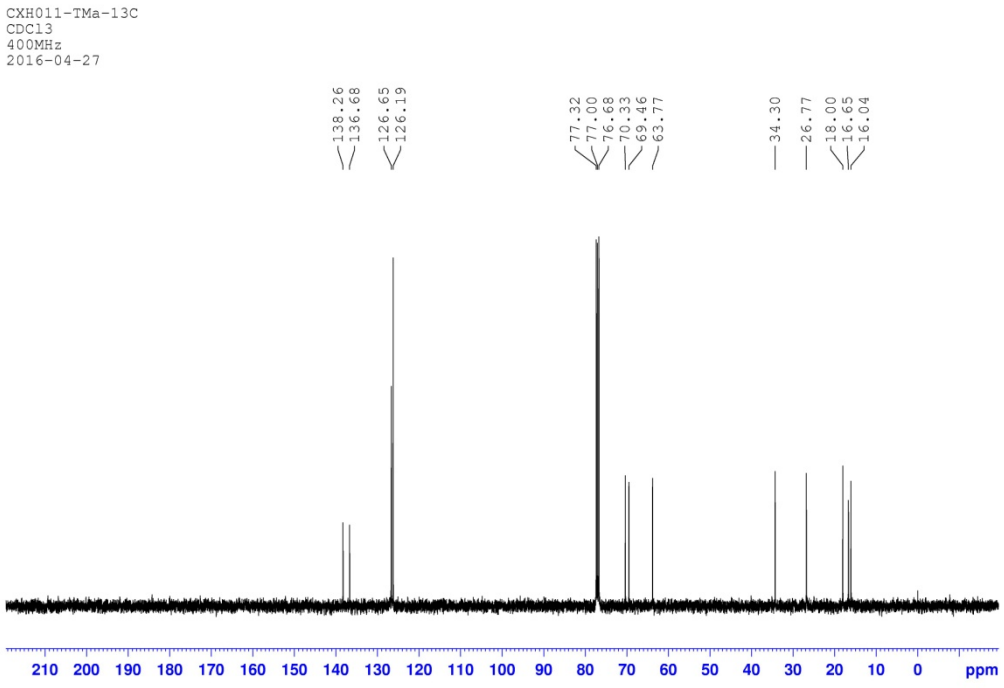
Supplementary Figure 131. Enantioenriched mixture of compound **2k-3**.



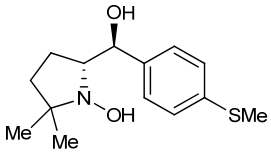
diastereomer of **2k-3** (minor)



Supplementary Figure 132. ^{1}H NMR ($CDCl_3$) of the diastereomer of **2k-3**.

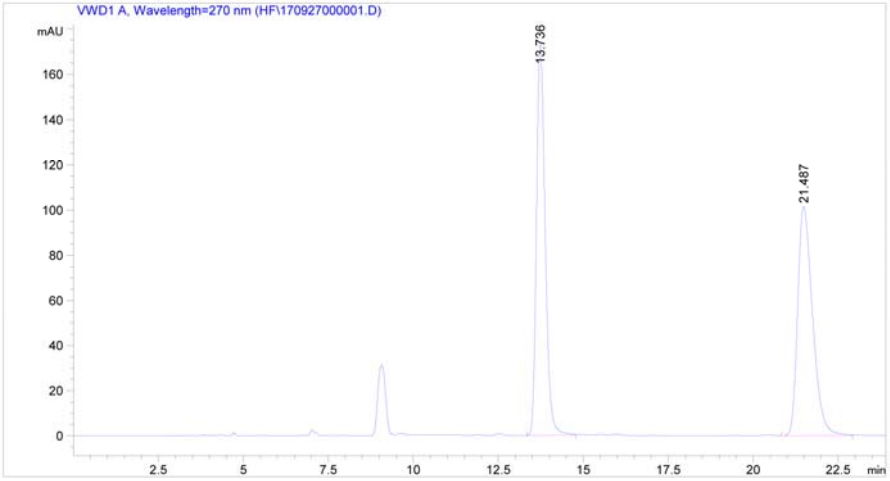


Supplementary Figure 133. ^{13}C NMR ($CDCl_3$) of the diastereomer of **2k-3**.



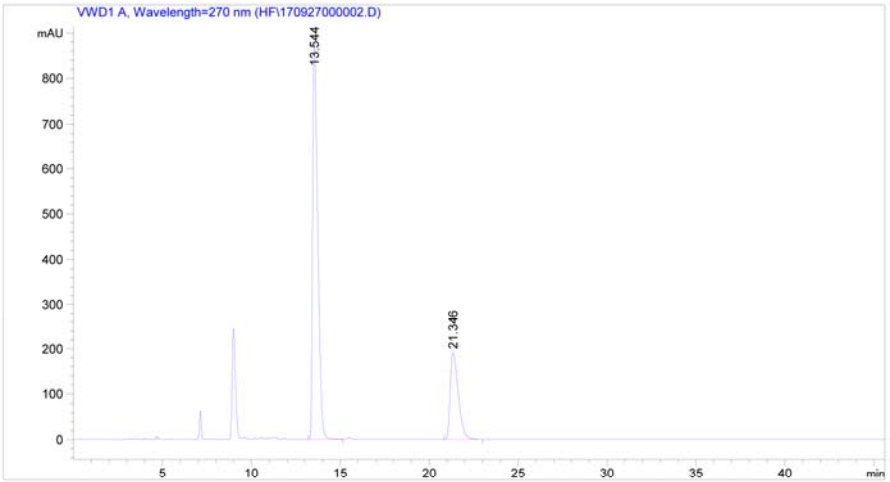
diastereomer of **2k-3** (minor)

[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 85/15 (v/v), 1.0 mL/min, 270 nm]



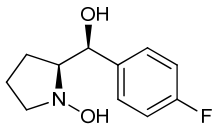
Pk #	Retention Time [min]	Area [mAU*s]	Height [mAU]	Area Percent %
1	13.736	3080.38794	172.95279	50.0224
2	21.487	3077.63428	101.38963	49.9776
Totals:		6158.02222	274.34241	100.0000

Supplementary Figure 134. Racemate of the diastereomer of **2k-3**.

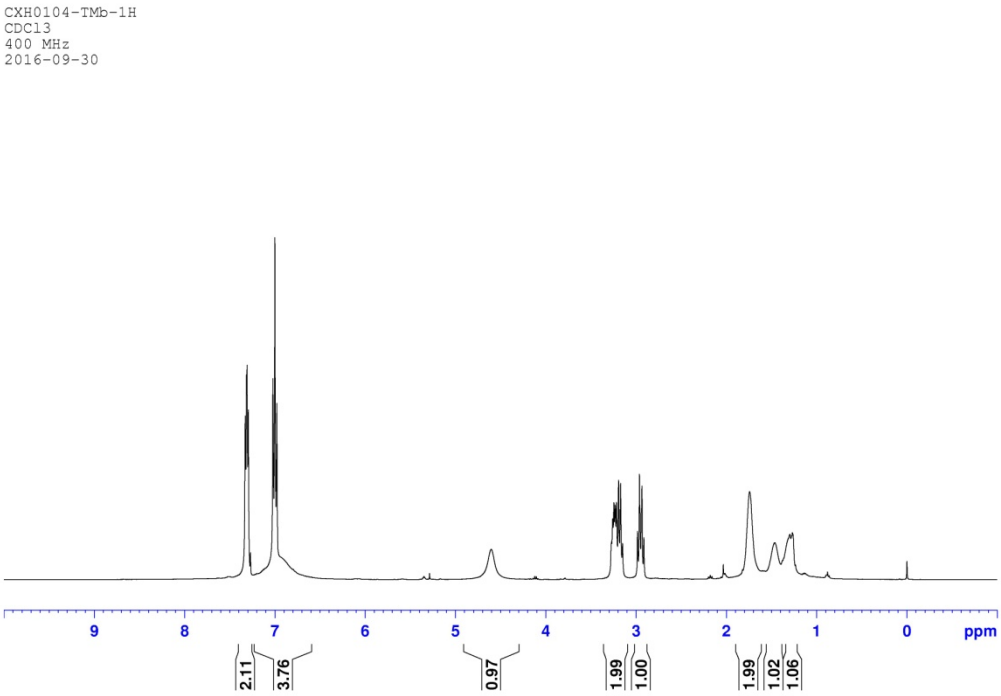


Pk #	Retention Time [min]	Area [mAU*s]	Height [mAU]	Area Percent %
1	13.544	1.76278e4	871.05206	74.4174
2	21.346	6059.94482	191.72087	25.5826
Totals:		2.36877e4	1062.77293	100.0000

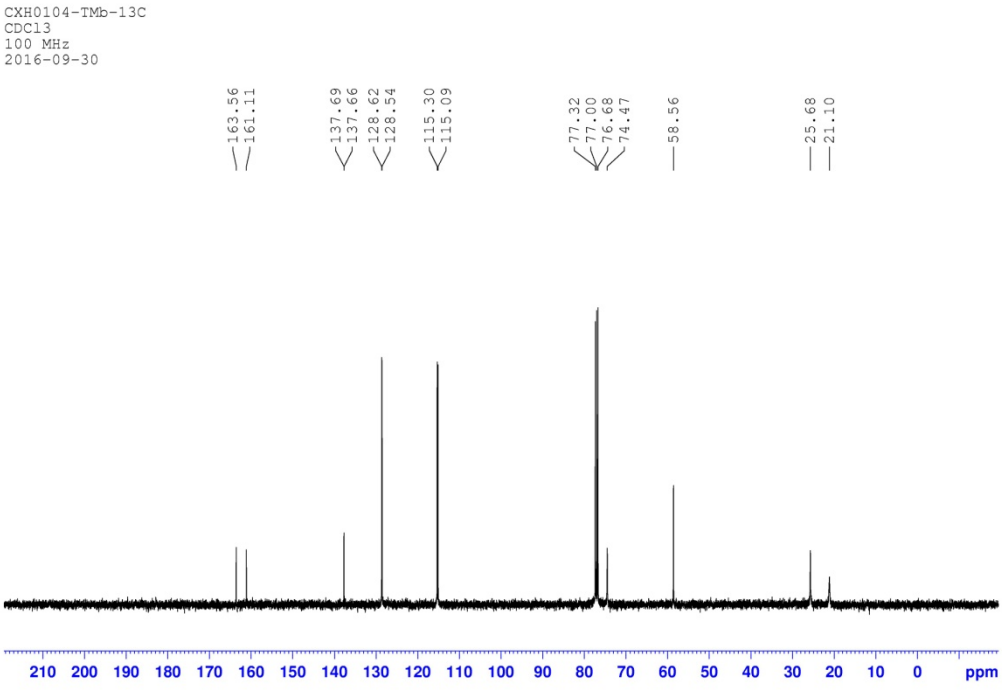
Supplementary Figure 135. Enantioenriched mixture of the diastereomer of **2k-3**.



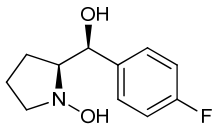
2l (major)



Supplementary Figure 136. ^{1}H NMR ($CDCl_3$) of compound **2l**.

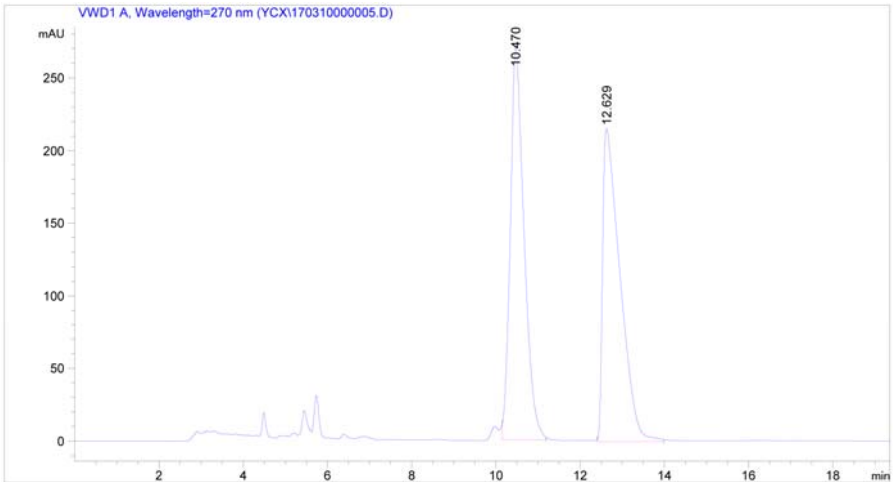


Supplementary Figure 137. ^{13}C NMR ($CDCl_3$) of compound **2l**.



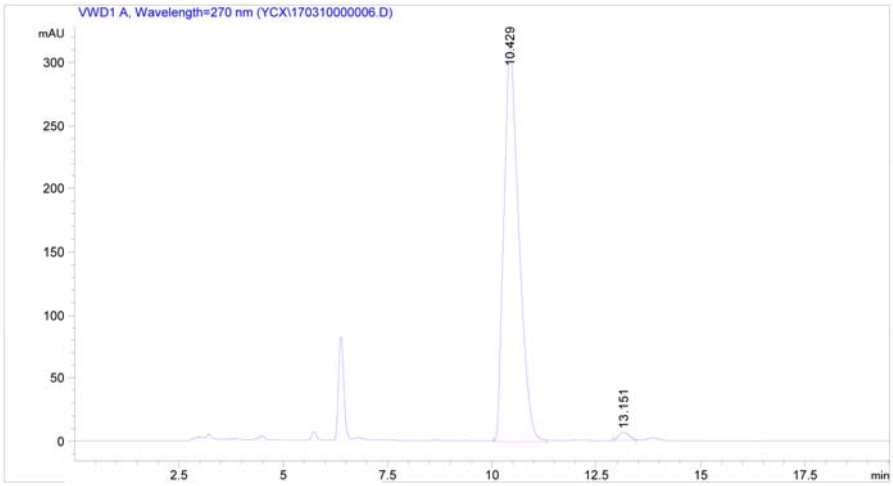
2l (major)

[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 70/30 (v/v), 1.0 mL/min, 270 nm]



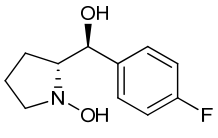
Pk #	Retention Time [min]	Area [mAU*s]	Height [mAU]	Area Percent %
1	10.470	6165.55664	270.67529	50.0106
2	12.629	6162.93604	215.40651	49.9894
Totals:		1.23285e4	486.08180	100.0000

Supplementary Figure 138. Racemate of compound **2l**.

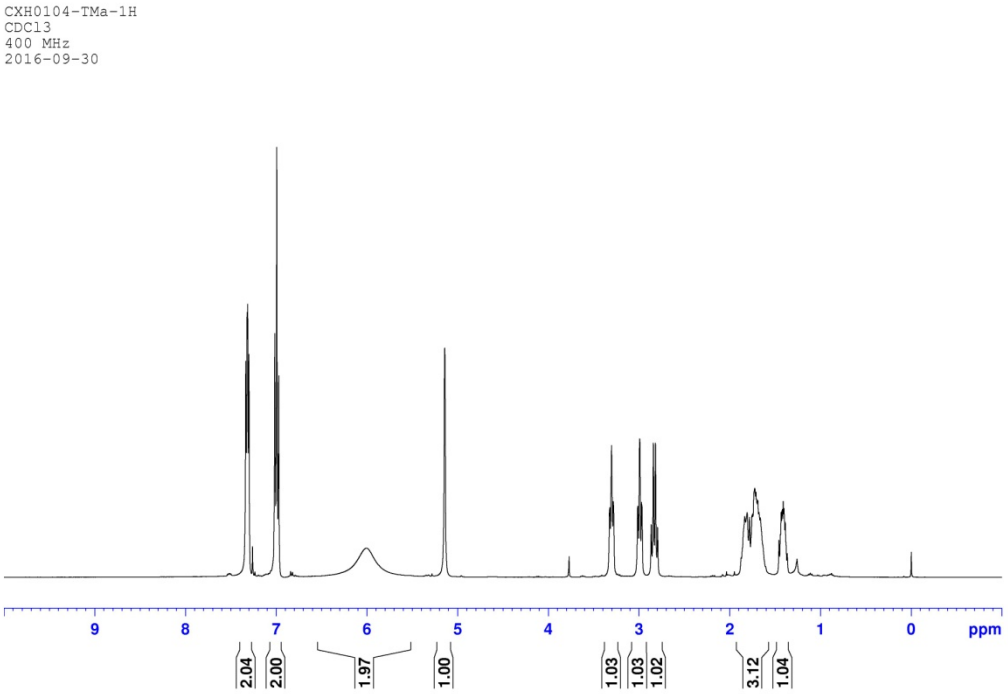


Pk #	Retention Time [min]	Area [mAU*s]	Height [mAU]	Area Percent %
1	10.429	7830.97705	313.14923	98.5951
2	13.151	111.58207	6.43195	1.4049
Totals:		7942.55912	319.58118	100.0000

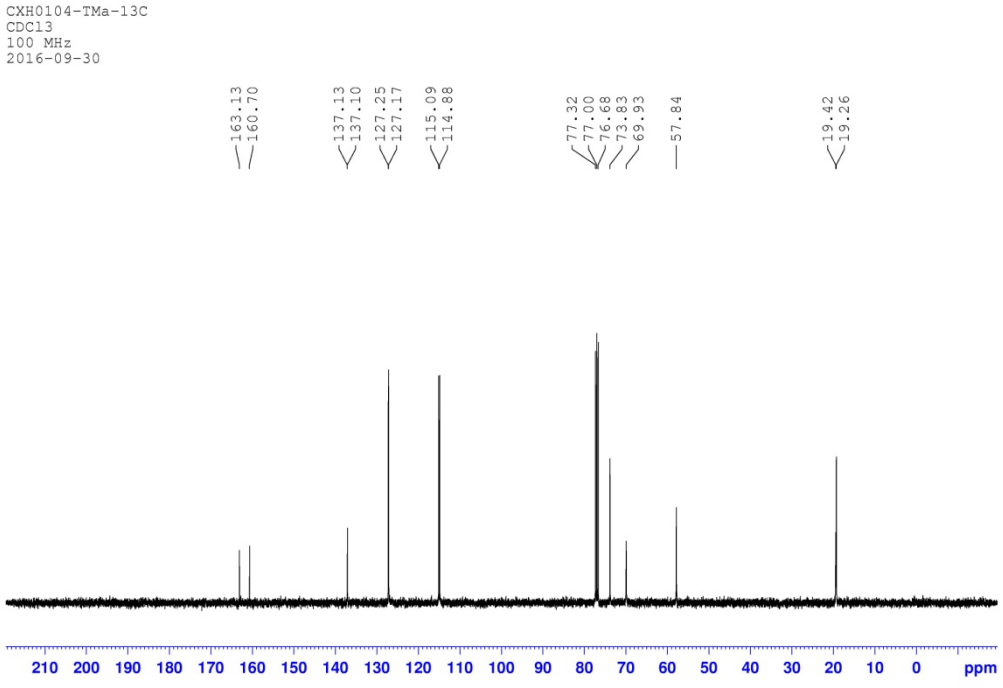
Supplementary Figure 139. Enantioenriched mixture of compound **2l**.



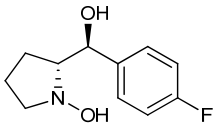
diastereomer of **2l** (minor)



Supplementary Figure 140. ^{1}H NMR ($CDCl_3$) of the diastereomer of **2l**.

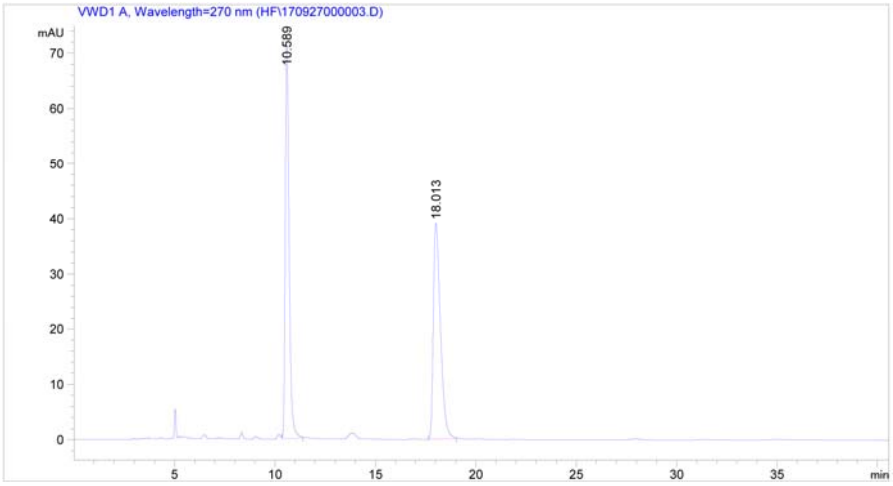


Supplementary Figure 141. ^{13}C NMR ($CDCl_3$) of the diastereomer of **2l**.



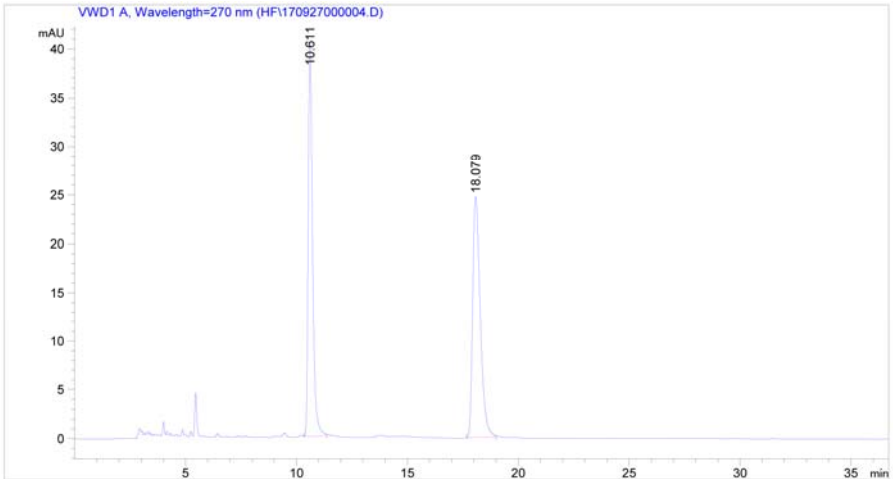
diastereomer of **2l** (minor)

[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 85/15 (v/v), 1.0 mL/min, 270 nm]



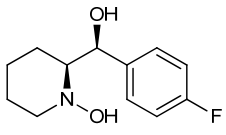
Pk #	Retention Time [min]	Area [mAU*s]	Height [mAU]	Area Percent %
1	10.589	955.67194	71.14536	49.9710
2	18.013	956.78064	39.13541	50.0290
Totals:		1912.45258	110.28077	100.0000

Supplementary Figure 142. Racemate of the diastereomer of **2l**.

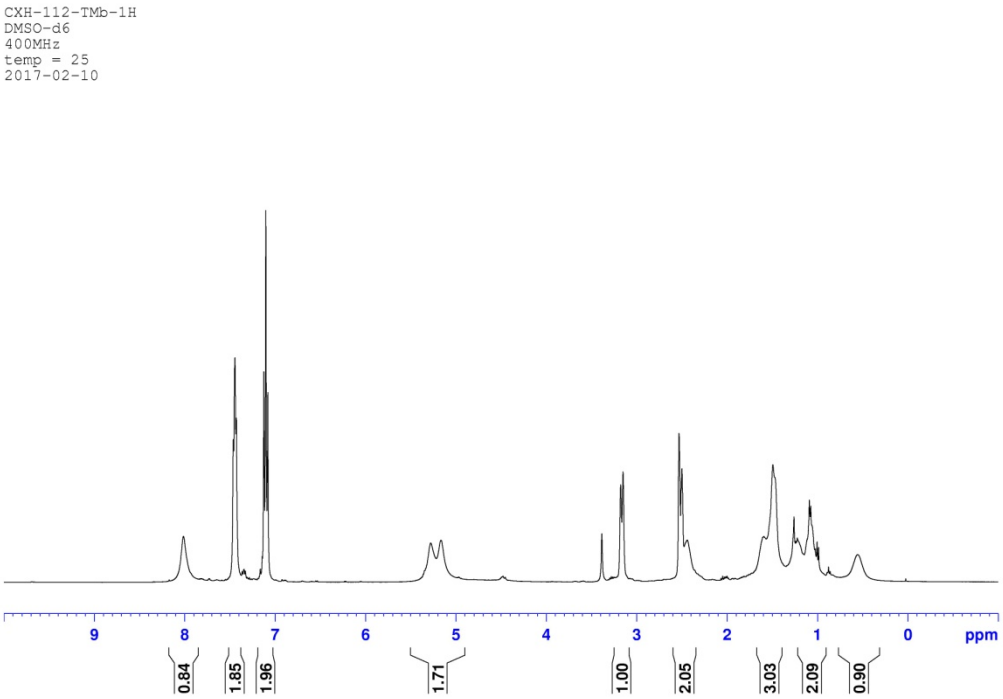


Pk #	Retention Time [min]	Area [mAU*s]	Height [mAU]	Area Percent %
1	10.611	547.21069	40.09608	48.2250
2	18.079	587.49280	24.67539	51.7750
Totals:		1134.70349	64.77147	100.0000

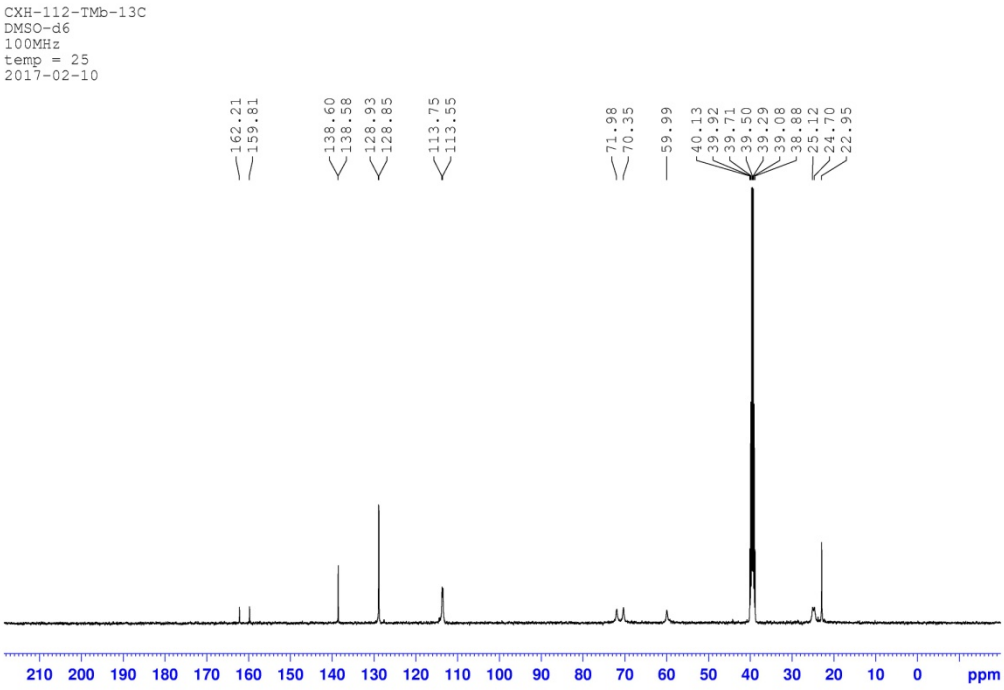
Supplementary Figure 143. Enantioenriched mixture of the diastereomer of **2l**.



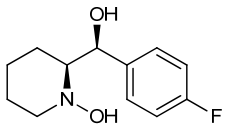
2m (DMSO-d6, 25 ºC)



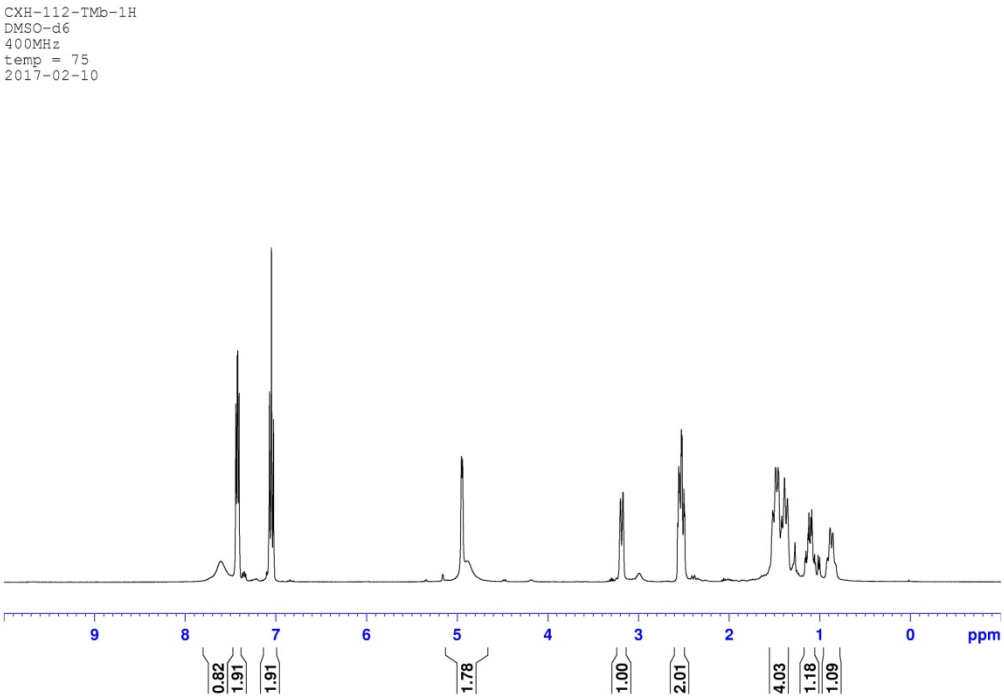
Supplementary Figure 144. ^{1}H NMR (DMSO-d6, 25 ºC) of compound **2m**.



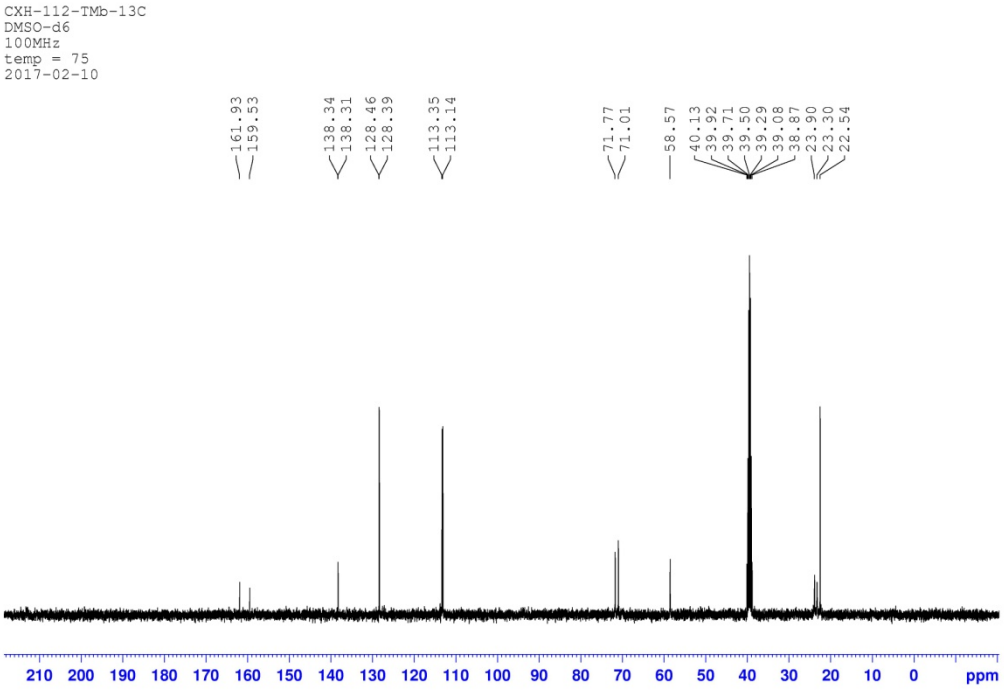
Supplementary Figure 145. ^{13}C NMR (DMSO-d6, 25 ºC) of compound **2m**.



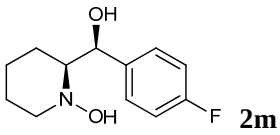
2m (DMSO-d6, 75 ºC)



Supplementary Figure 146. ^{1}H NMR (DMSO-d6, 75 ºC) of compound **2m**.

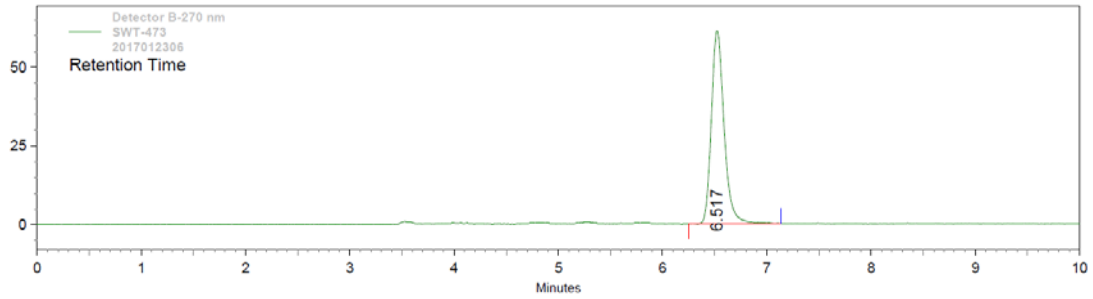


Supplementary Figure 147. ^{13}C NMR (DMSO-d6, 75 ºC) of compound **2m**.

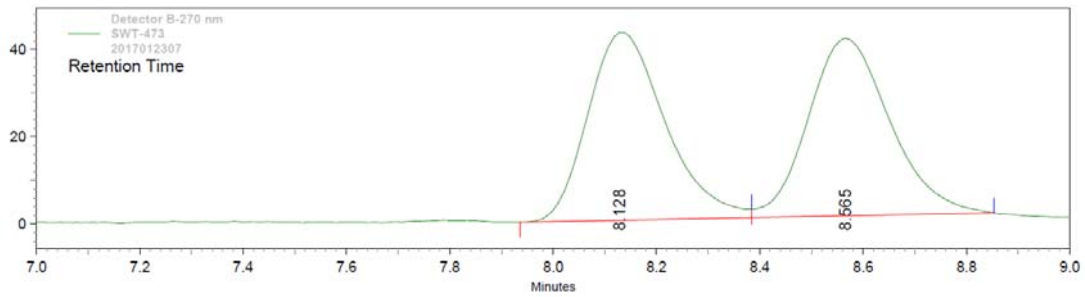


2m

[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 270 nm]



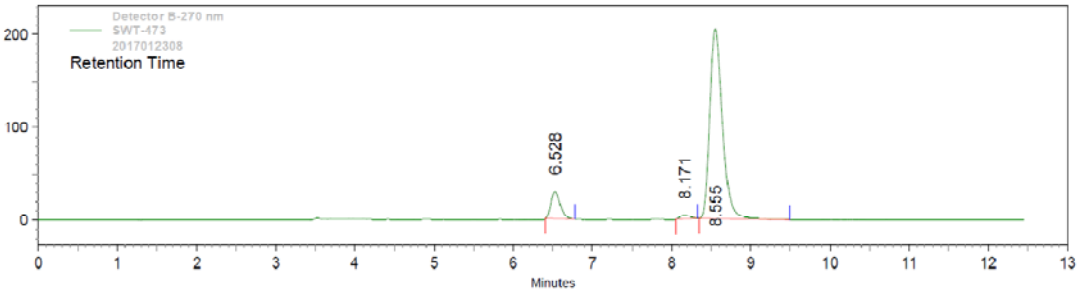
Supplementary Figure 148. Racemate of the diastereomer of **2m**.



Detector B-270 nm

Pk #	Retention Time	Area	Area Percent	Height
1	8.128	446470	50.04	43060
2	8.565	445785	49.96	40691

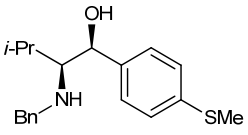
Supplementary Figure 149. Racemate of compound **2m**.



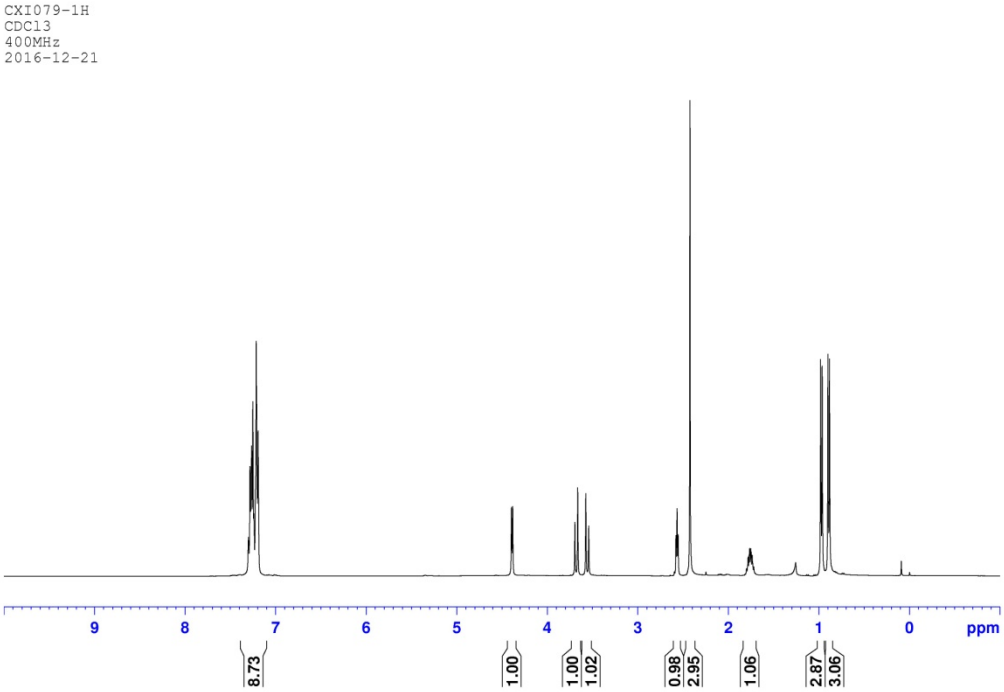
Detector B-270 nm

Pk #	Retention Time	Area	Area Percent	Height
1	6.528	234961	9.17	29771
2	8.171	30985	1.21	3631
3	8.555	2296744	89.62	204445

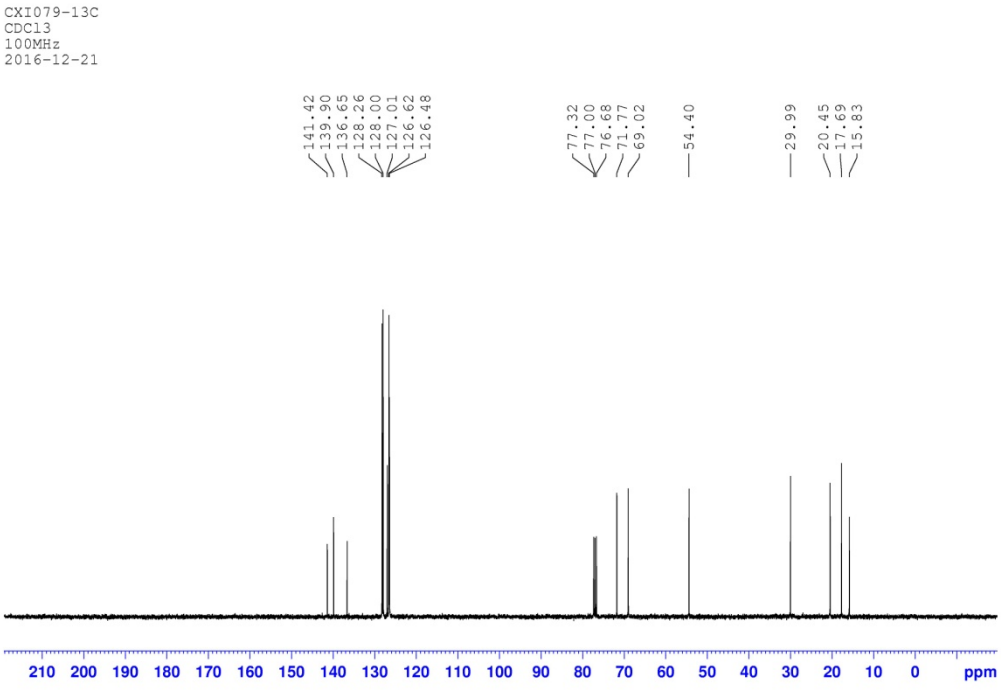
Supplementary Figure 150. Enantioenriched diastereomeric mixture of **2m**.



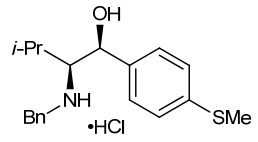
6a-9



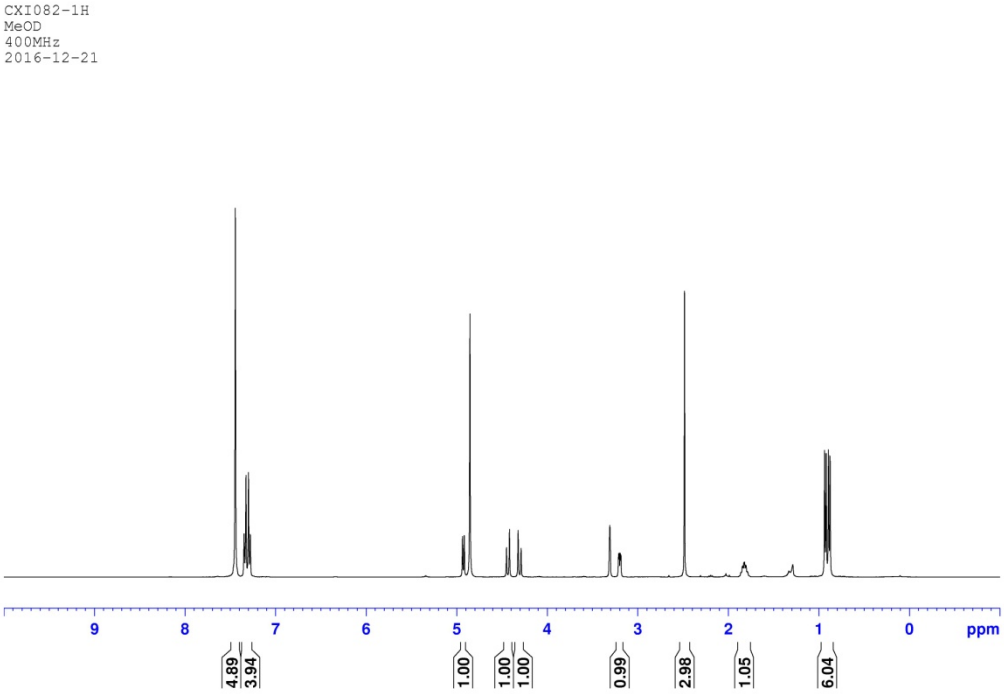
Supplementary Figure 151. ^{1}H NMR ($CDCl_3$) of compound **6a-9**.



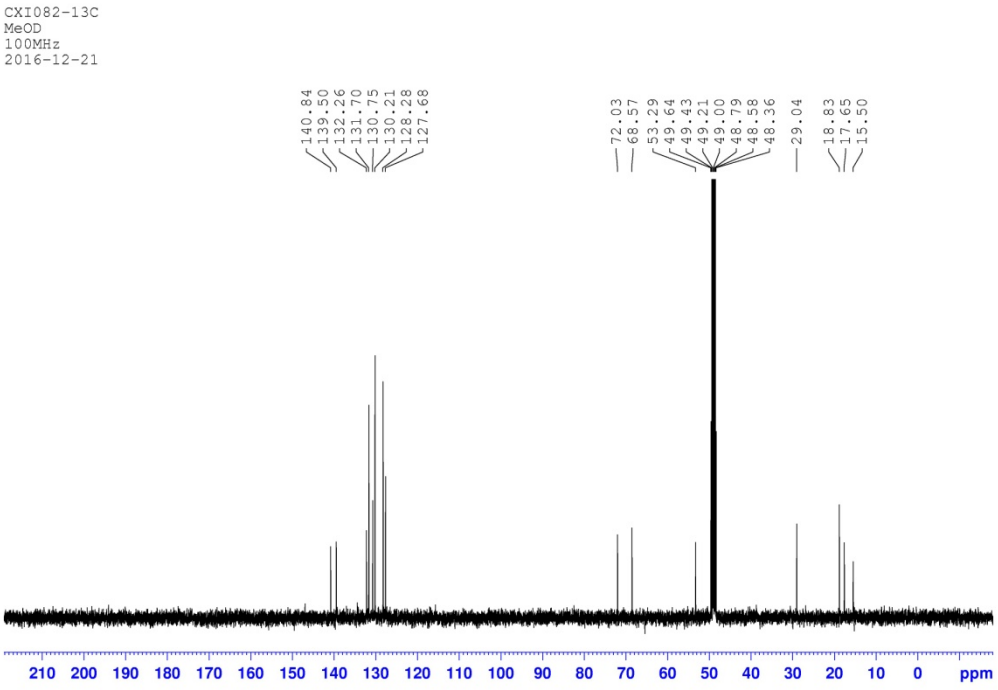
Supplementary Figure 152. ^{13}C NMR ($CDCl_3$) of compound **6a-9**.



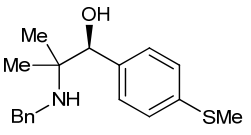
6a-9•HCl



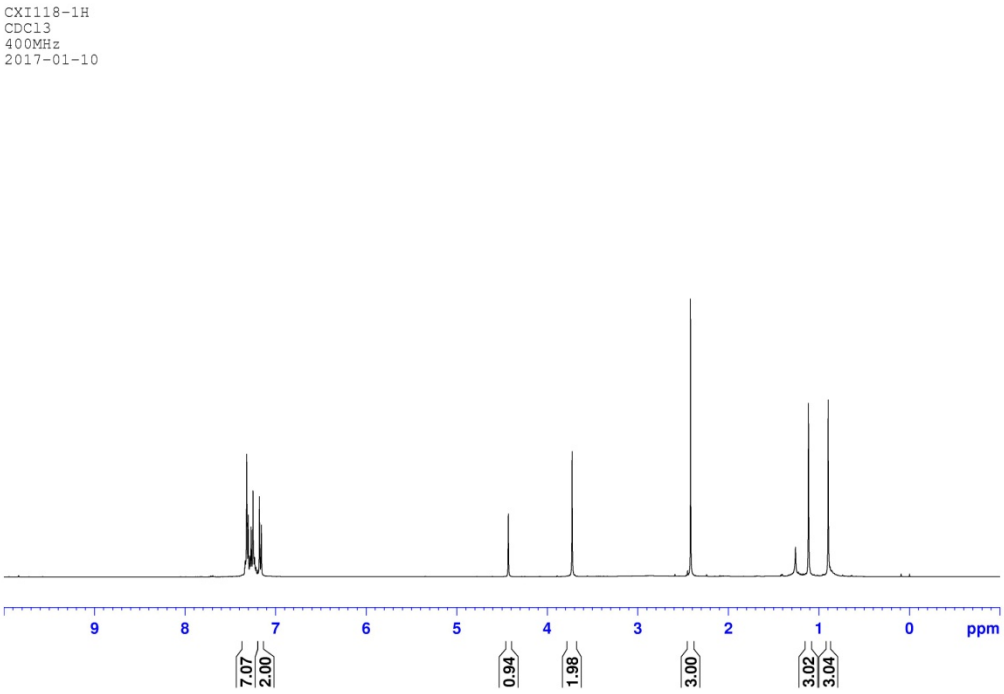
Supplementary Figure 153. ^{1}H NMR (MeOD) of compound **6a-9•HCl**.



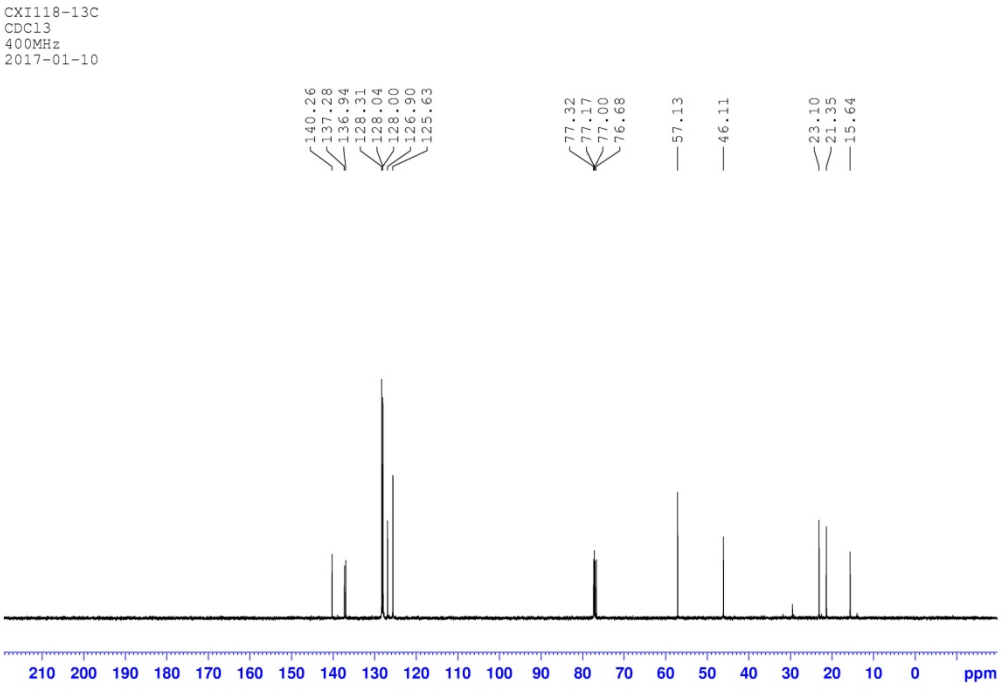
Supplementary Figure 154. ^{13}C NMR (MeOD) of compound **6a-9•HCl**.



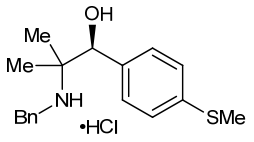
6b-3



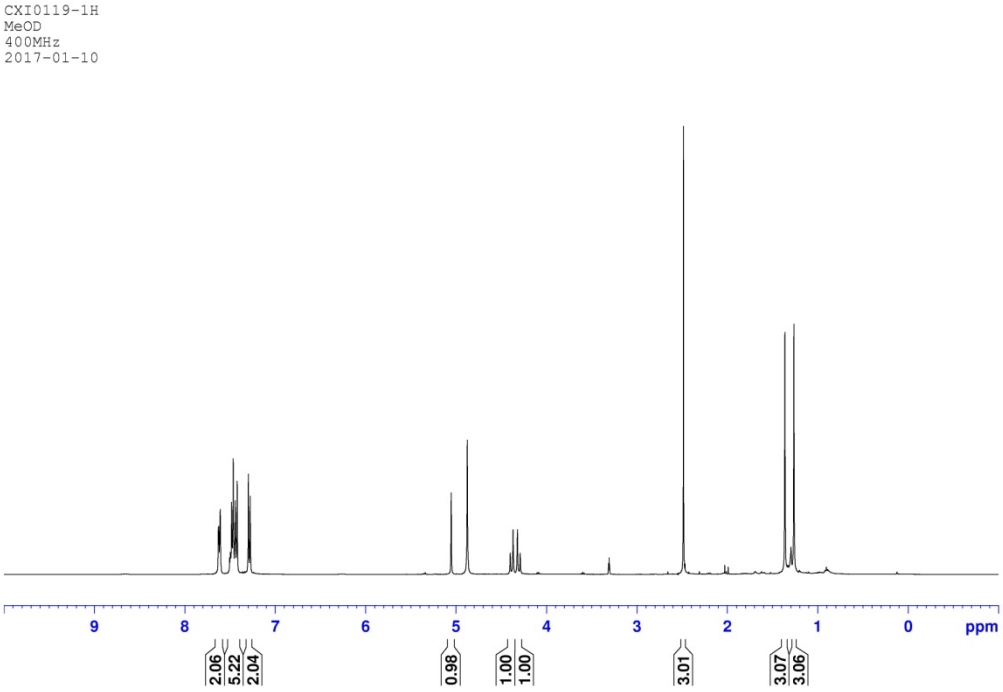
Supplementary Figure 155. ^{1}H NMR ($CDCl_3$) of compound **6b-3**.



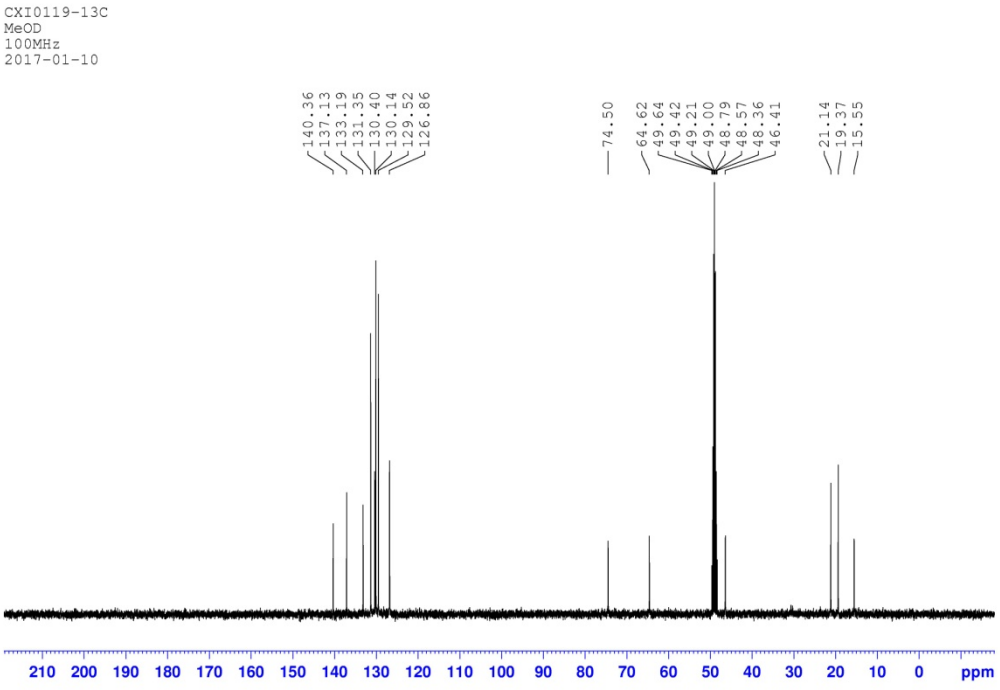
Supplementary Figure 156. ^{13}C NMR ($CDCl_3$) of compound **6b-3**.



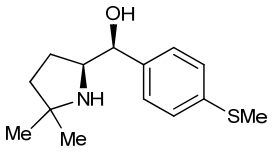
6b-3•HCl



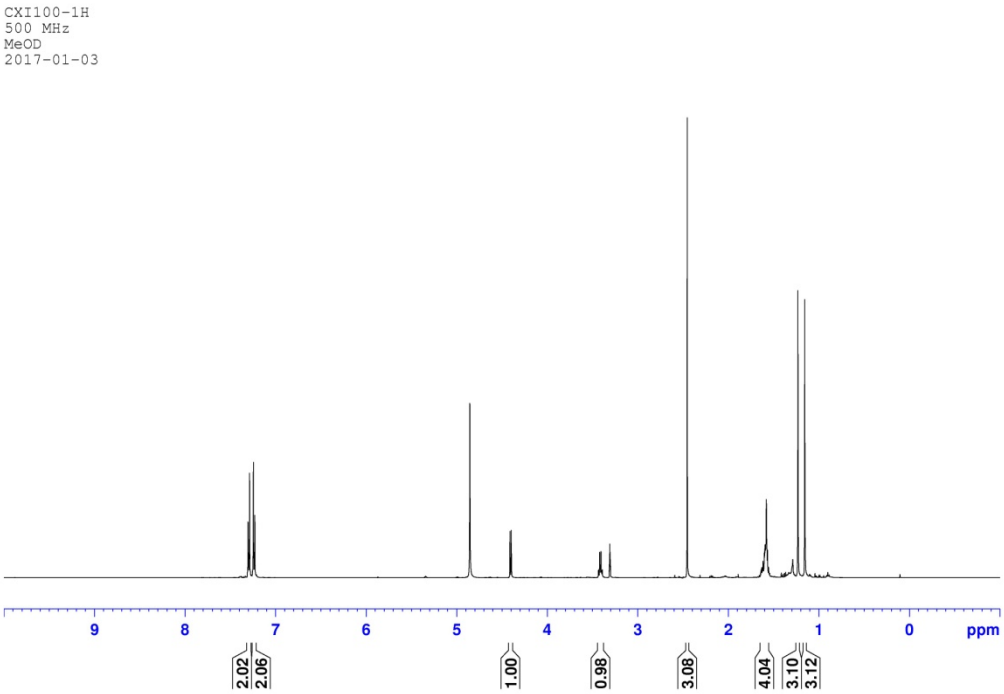
Supplementary Figure 157. ^{1}H NMR (MeOD) of compound **6b-3•HCl**.



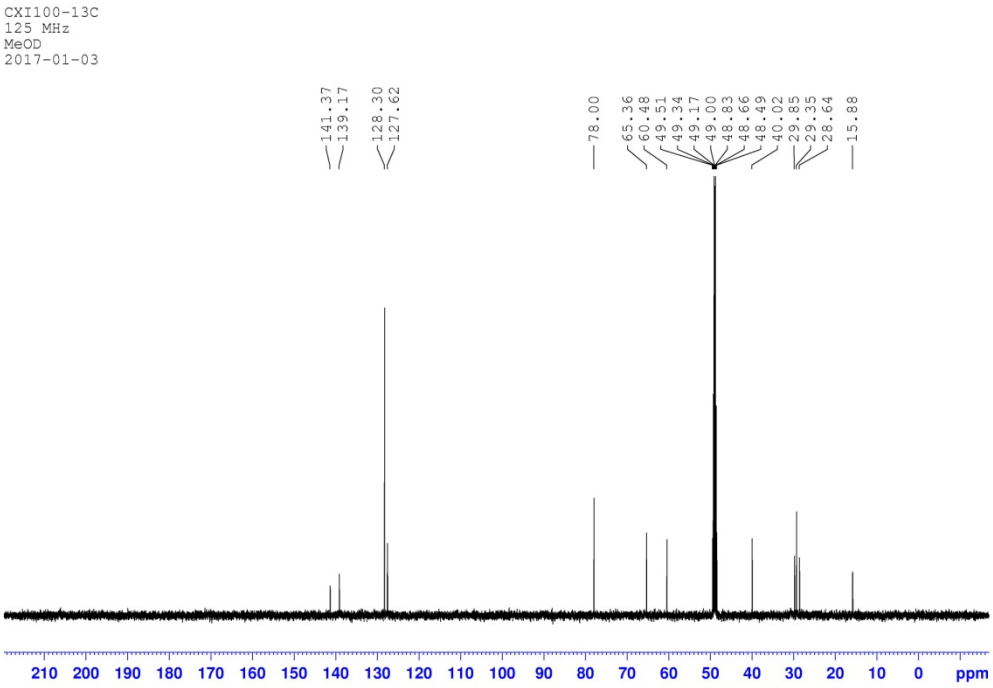
Supplementary Figure 158. ^{13}C NMR (MeOD) of compound **6b-3•HCl**.



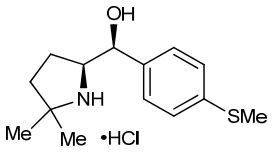
6k-3



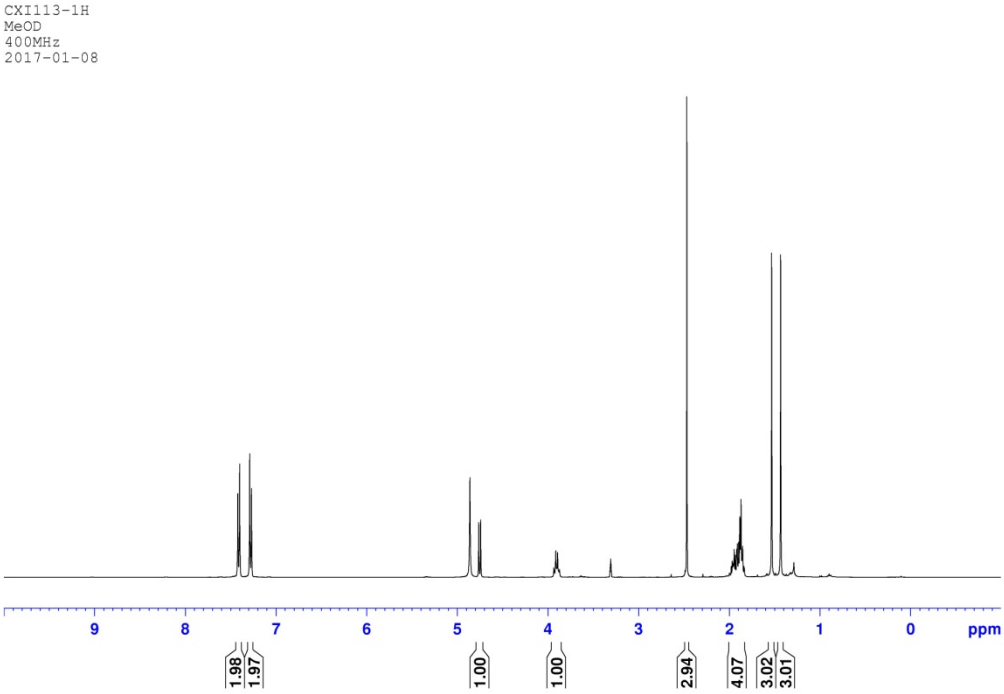
Supplementary Figure 159. ^{1}H NMR (MeOD) of compound **6k-3**.



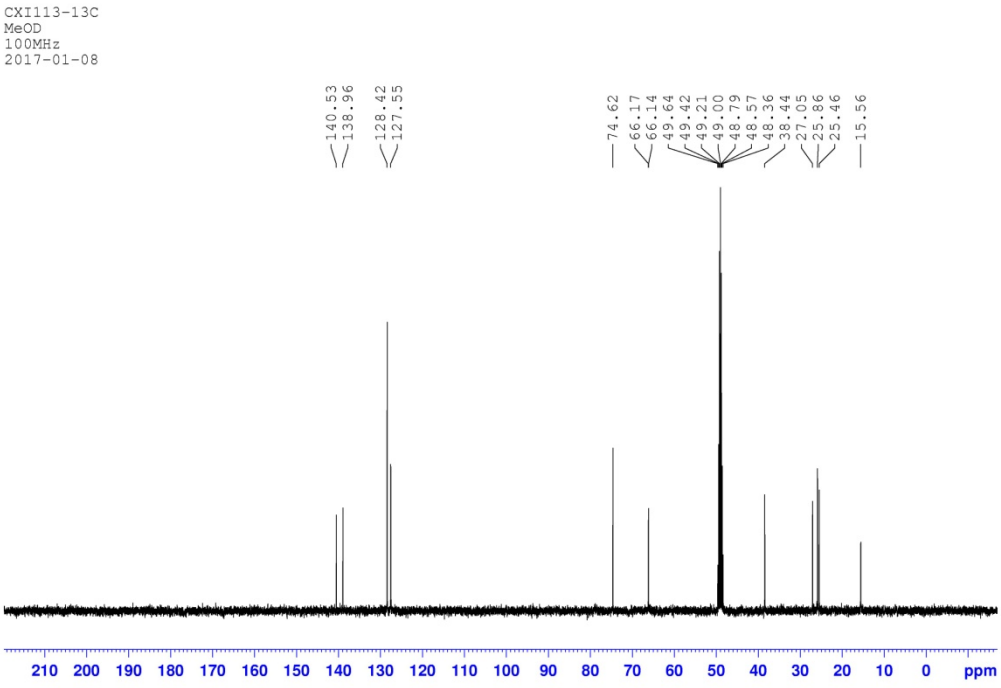
Supplementary Figure 160. ^{13}C NMR (MeOD) of compound **6k-3**.



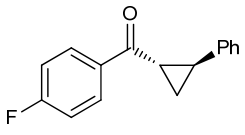
6k-3•HCl



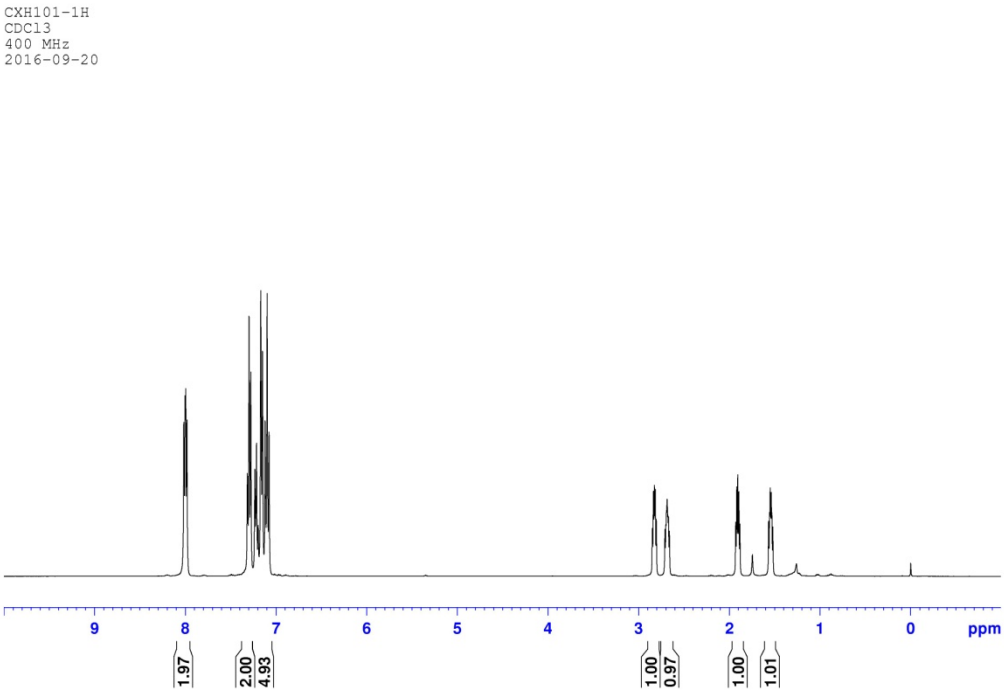
Supplementary Figure 161. ^{1}H NMR (MeOD) of compound **6k-3•HCl**.



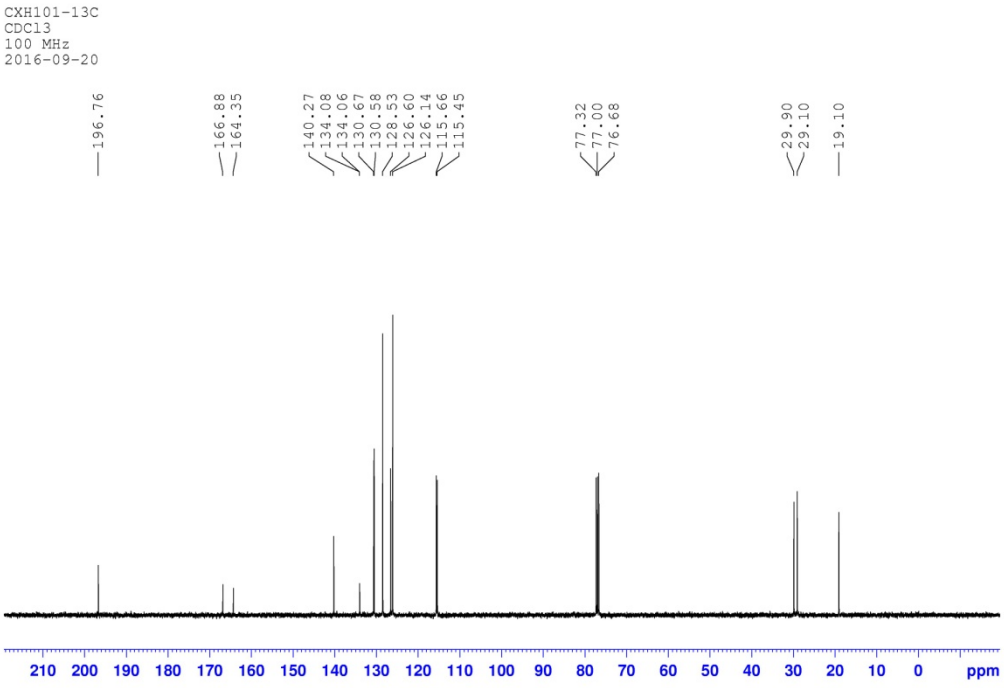
Supplementary Figure 162. ^{13}C NMR (MeOD) of compound **6k-3•HCl**.



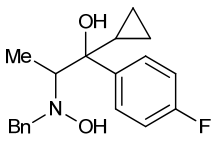
4



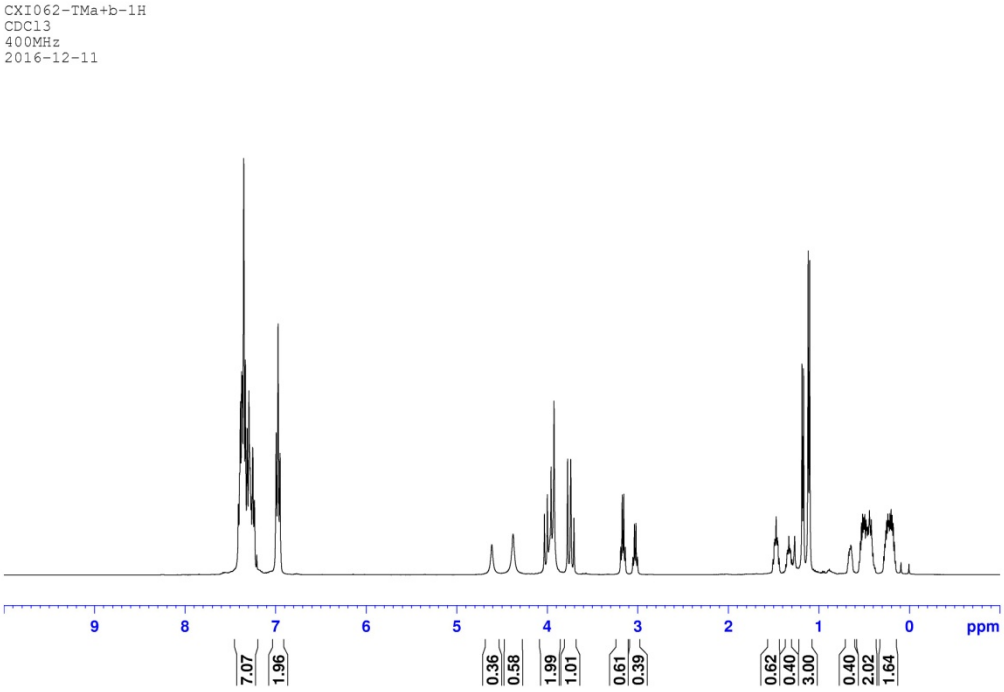
Supplementary Figure 163. ^{1}H NMR ($CDCl_3$) of compound **4**.



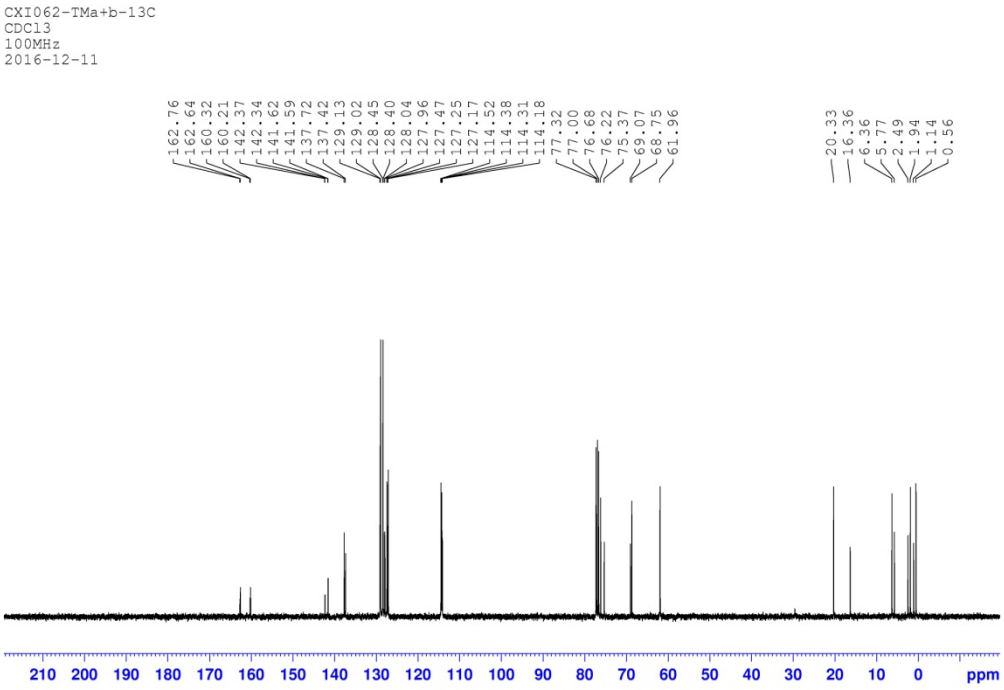
Supplementary Figure 164. ^{13}C NMR ($CDCl_3$) of compound **4**.



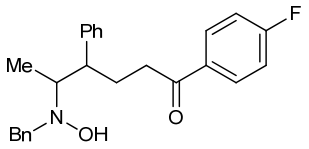
2f-2 (mixture of diastereomers)



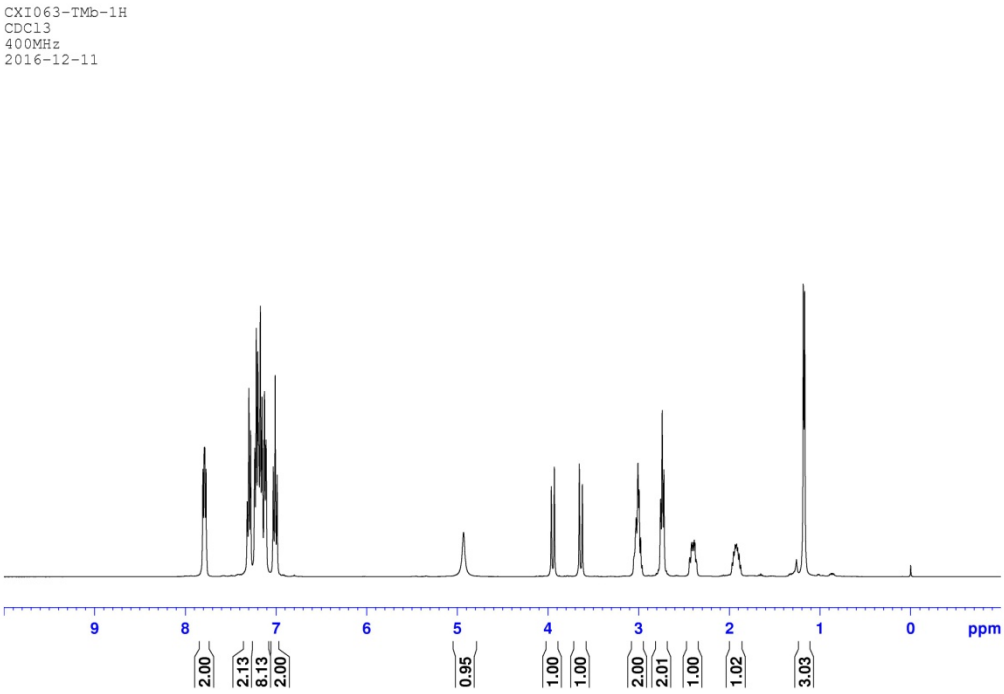
Supplementary Figure 165. ^{1}H NMR ($CDCl_3$) of the diastereomeric mixture of **2f-2**.



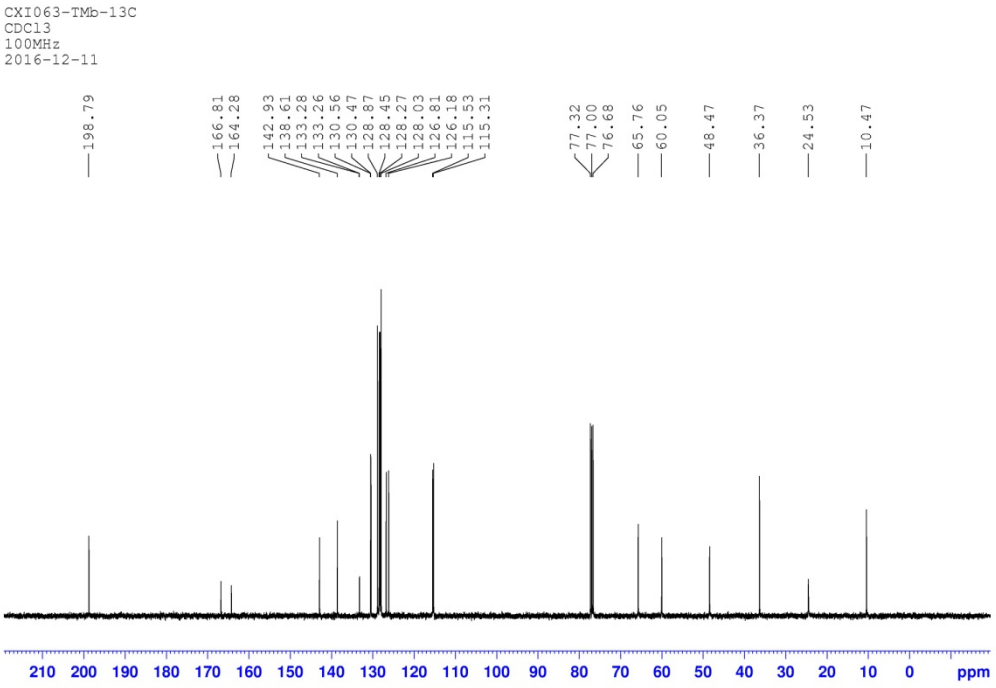
Supplementary Figure 166. ^{13}C NMR ($CDCl_3$) of the diastereomeric mixture of **2f-2**.



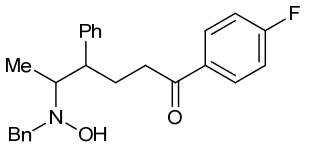
(major diastereomer of **5**)



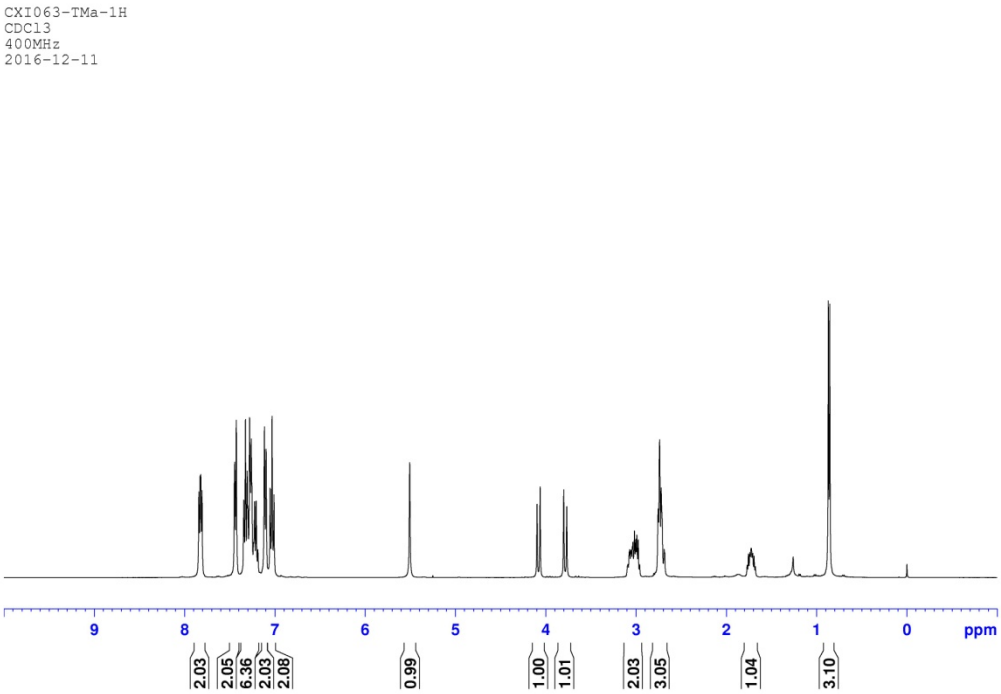
Supplementary Figure 167. ^{1}H NMR ($CDCl_3$) of the major diastereomer of **5**.



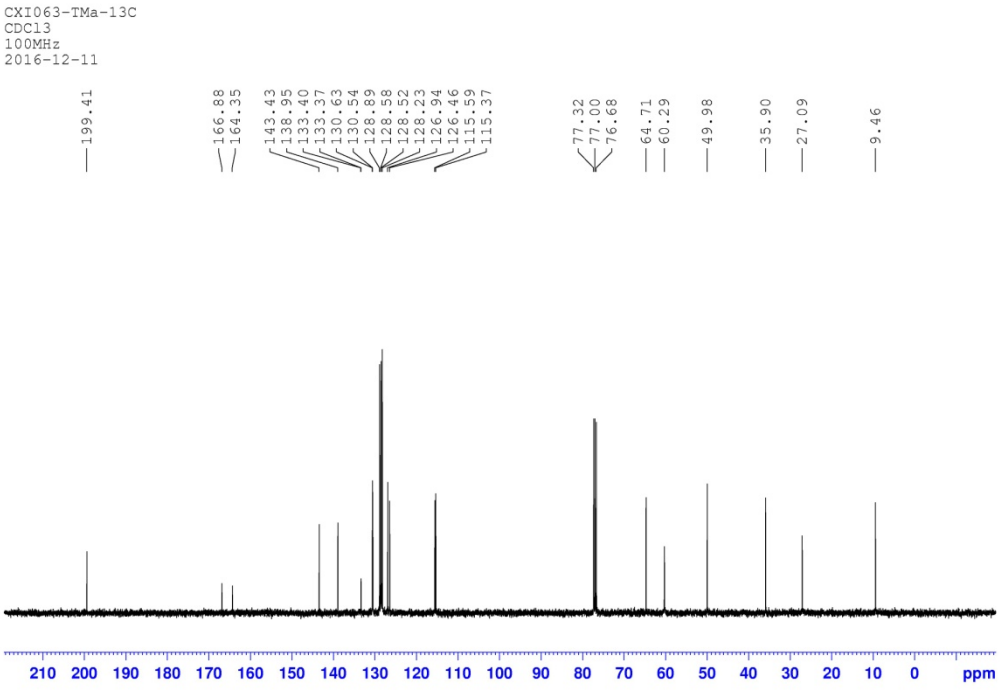
Supplementary Figure 168. ^{13}C NMR ($CDCl_3$) of the major diastereomer of **5**.



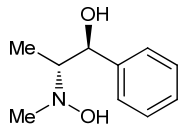
(minor diastereomer of **5**)



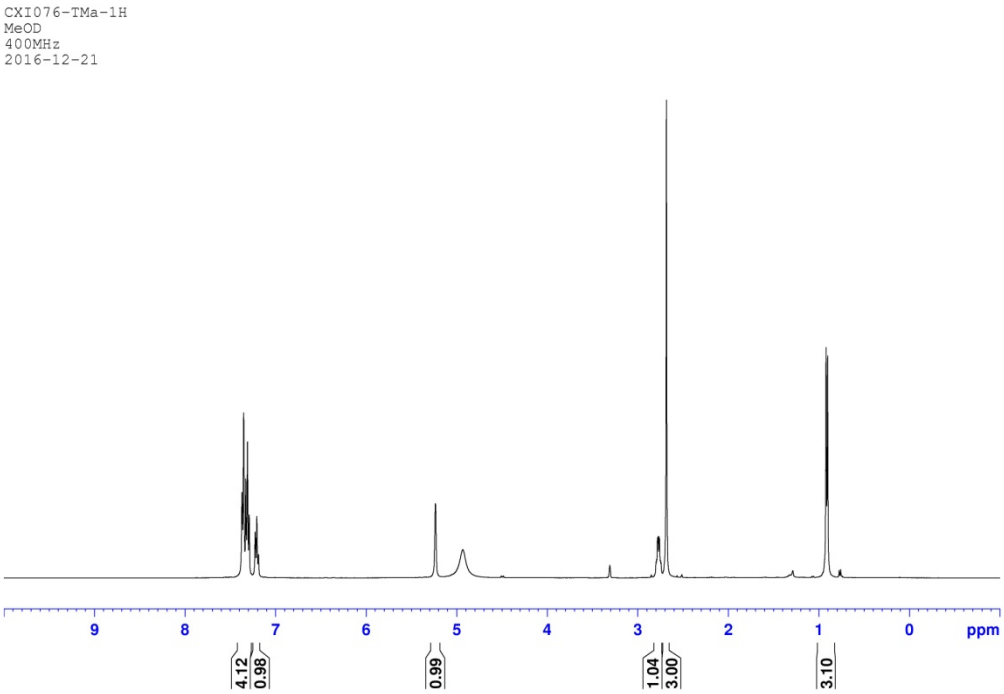
Supplementary Figure 169. ^{1}H NMR ($CDCl_3$) of the minor diastereomer of **5**.



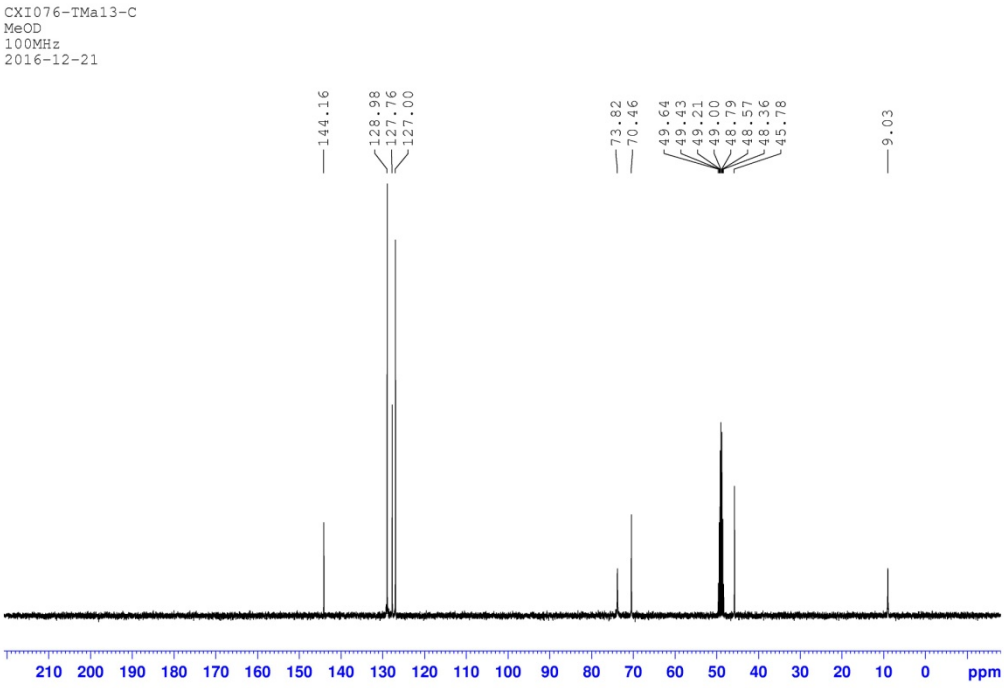
Supplementary Figure 170. ^{13}C NMR ($CDCl_3$) of the minor diastereomer of **5**.



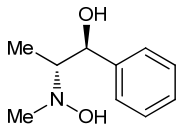
2n



Supplementary Figure 171. ^{1}H NMR (MeOD) of compound **2n**.

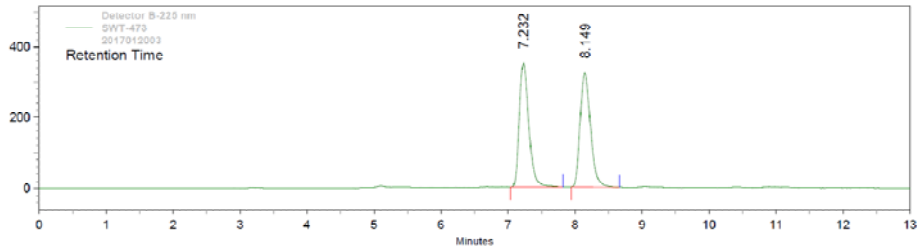


Supplementary Figure 172. ^{13}C NMR (MeOD) of compound **2n**.



2n

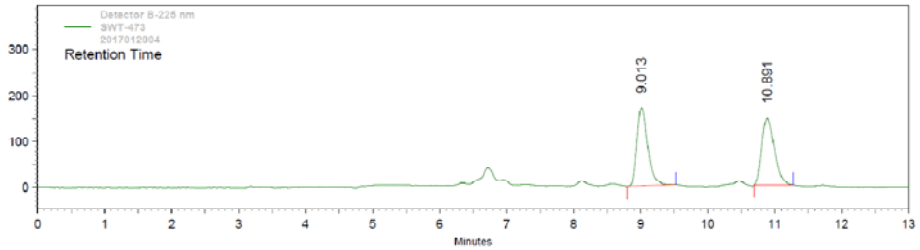
[Lux® Amylose-1 column, 30 ºC, hexane/EtOH = 80/20 (v/v), 1.0 mL/min, 225 nm]



Detector B-225 nm

Pk #	Retention Time	Area	Area Percent	Height
1	7.232	3482321	49.91	351013
2	8.149	3495101	50.09	322859

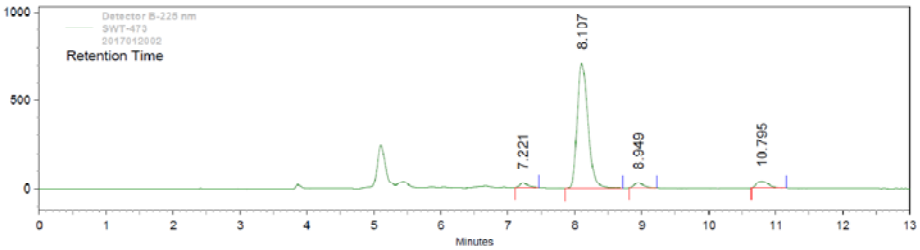
Supplementary Figure 173. Racemate of compound **2n**.



Detector B-225 nm

Pk #	Retention Time	Area	Area Percent	Height
1	9.013	1941403	50.03	171220
2	10.891	1938703	49.97	146651

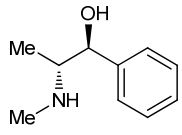
Supplementary Figure 174. Racemate of the diastereomer of **2n**.



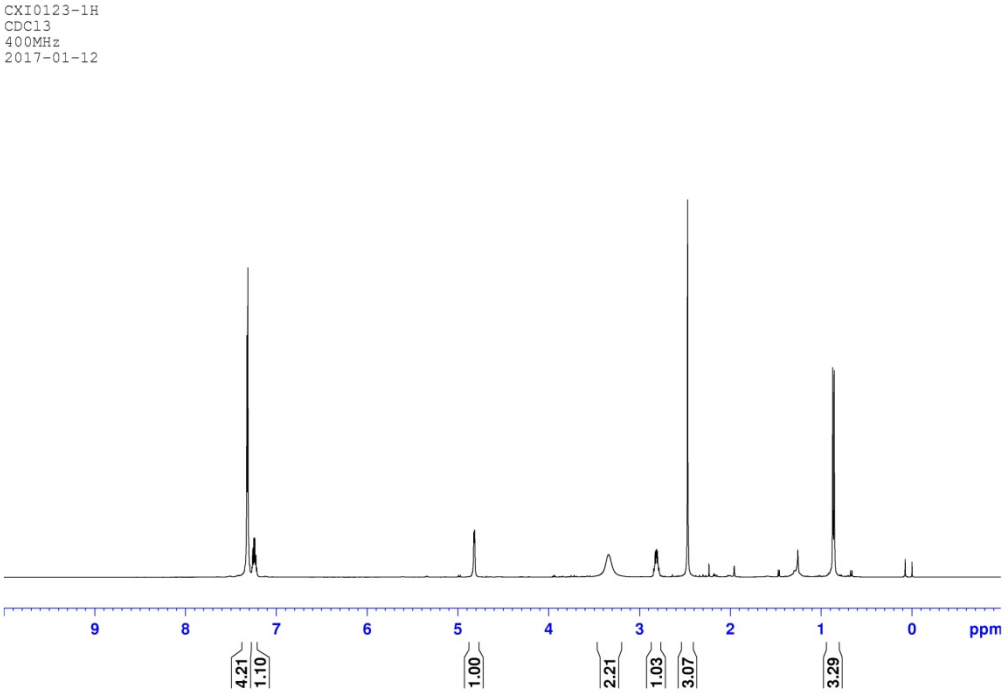
Detector B-225 nm

Pk #	Retention Time	Area	Area Percent	Height
1	7.221	225302	2.53	22680
2	8.107	7928720	89.01	705142
3	8.949	267169	3.00	25805
4	10.795	486012	5.46	39213

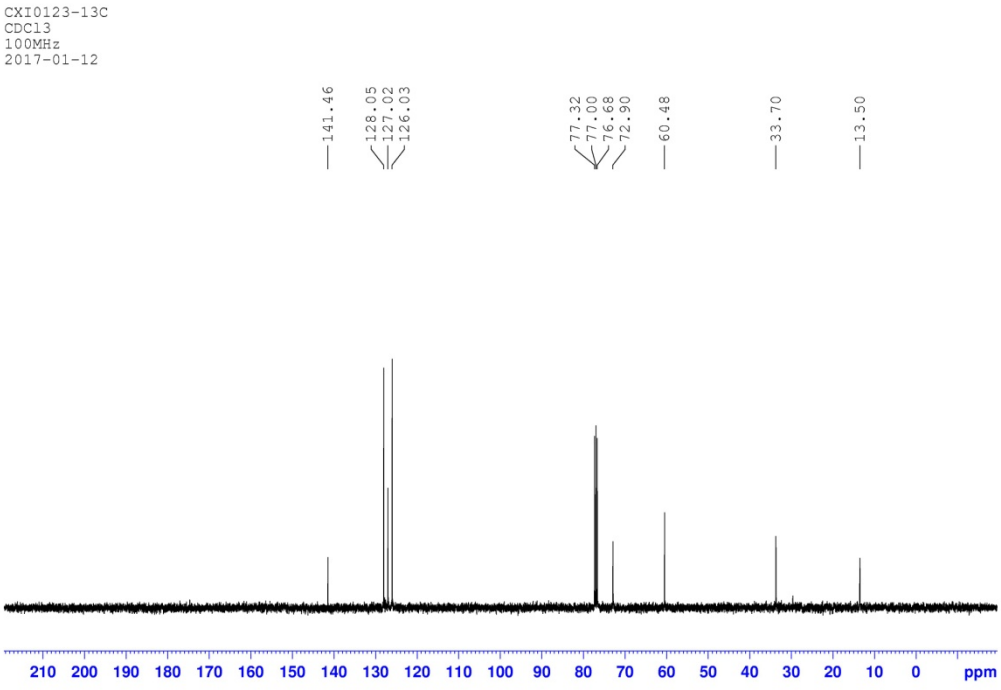
Supplementary Figure 175. Enantioenriched diastereomeric mixture of **2n**.



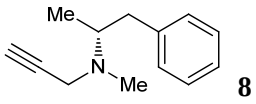
6n



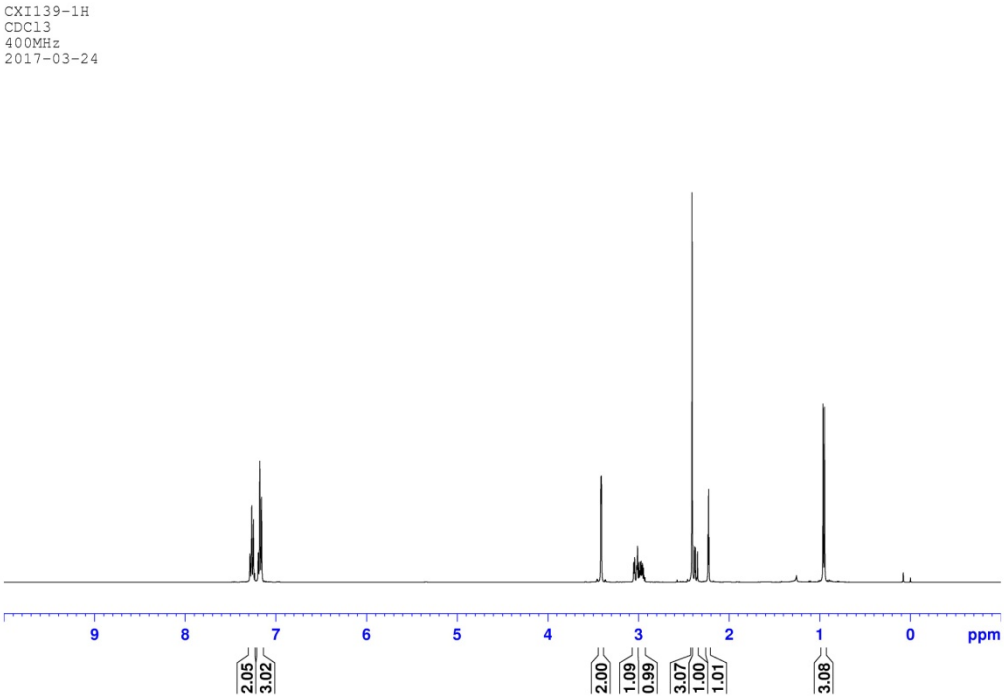
Supplementary Figure 176. ^{1}H NMR ($CDCl_3$) of compound **6n**.



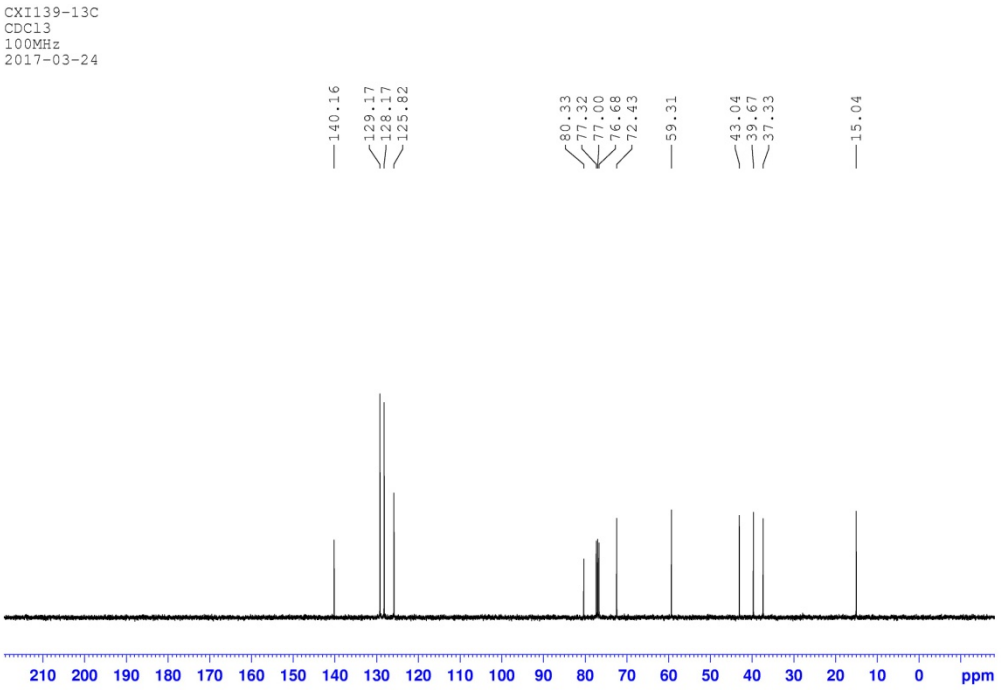
Supplementary Figure 177. ^{13}C NMR ($CDCl_3$) of compound **6n**.



8



Supplementary Figure 178. ^{1}H NMR ($CDCl_3$) of compound **8**.



Supplementary Figure 179. ^{13}C NMR ($CDCl_3$) of compound **8**.

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