

Supporting Information

Asymmetric Transfer Hydrogenation of Heterobicyclic

Alkenes with Water as Hydrogen Source

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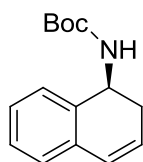
A: General Information

The reactions and manipulations were performed under an atmosphere of argon by using standard Schlenk techniques and Drybox (Mikrouna, Supper 1220/750). Anhydrous 1,4-dioxane was distilled from calcium hydride and stored under argon. ^1H NMR, ^{13}C NMR spectra were recorded on Bruker-Avance 400 MHz spectrometer. CDCl_3 was used as solvent. Chemical shifts (δ) were reported in ppm with tetramethylsilane as internal standard, and J values were given in Hz. The enantioselective excesses were determined by Agilent 1260 Series HPLC using Daicel AD-H, AS-H, OJ-H or OD-H chiral columns eluted with a mixture of isopropyl alcohol and hexane. Column chromatography was performed with silica gel (200-300 mesh) with petroleum ether and ethyl acetate as eluents.

B: Procedure for the reactions

Typical procedure for the asymmetric transfer hydrogenation of azabenzonorbornadiene: $\text{Pd}(\text{OAc})_2$ (11.5 mg, 0.05 mmol), (*R*)-SEGPLHOS (36.5 mg, 0.06 mmol) and 5.0 mL 1,4-dioxane were added to a Schlenk tube under argon atmosphere. The resulting solution was stirred at room temperature for 30 min, then $\text{Zn}(\text{OTf})_2$ (36.5 mg, 0.1 mmol) was added and stirred for additional 10 min. Azabenzonorbornadiene **1a** (243 mg, 1 mmol) in 1,4-dioxane (5.0 mL) was added to the above mixture and stirred for additional 10 min, zinc powder (195 mg, 3 mmol) was added to the above mixture. After the addition of H_2O (90 μL , 5 mmol), the mixture was stirred at 60 $^\circ\text{C}$ under argon atmosphere with TLC monitoring until the complete consumption of **1a**. The residue was purified by chromatography on a silica gel column to afford the desired product **2a** (233 mg, 95% yield).

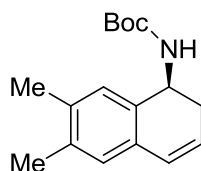
C: Characterization Data of Products



(*S*)-*tert*-butyl (1,2-dihydronaphthalen-1-yl)carbamate (**2a**)^[1]

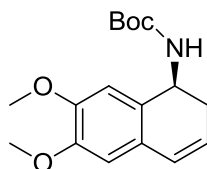
Colorless oil, purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1/10), 46.6 mg, 95% yield, 96% *ee*. $[\alpha]_{\text{D}}^{20} = -54.5$ ($c = 0.88$, CH_2Cl_2). ^1H NMR

(400 MHz, CDCl_3) δ 7.26 – 7.24 (m, 1H), 7.19 – 7.11 (m, 2H), 7.00 (dd, $J = 7.1, 1.5$ Hz, 1H), 6.44 (d, $J = 9.6$ Hz, 1H), 5.92 – 5.87 (m, 1H), 4.82 – 4.60 (m, 2H), 2.53 – 2.38 (m, 2H), 1.36 (s, 9H). The *ee* of **2a** was determined by HPLC analysis using a Daicel Chiralcel OJ-H column (25 cm $\times$ 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 98/2, 1.0 mL/min, 254 nm; $t_{\text{minor}} = 6.6$ min, $t_{\text{major}} = 7.5$ min.



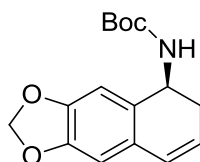
(S)-tert-butyl (6,7-dimethyl-1,2-dihydronaphthalen-1-yl)carbamate (2b)^[1]

Colorless oil, purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1/10), 51.9 mg, 95% yield, 94% *ee*. $[\alpha]_{\text{D}}^{20} = -21.2$ ($c = 0.66$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ 7.10 (s, 1H), 6.87 (s, 1H), 6.47 (d, $J = 9.6$ Hz, 1H), 5.92 – 5.87 (m, 1H), 4.88 – 4.61 (m, 2H), 2.57 – 2.42 (m, 2H), 2.24 (d, $J = 6.3$ Hz, 6H), 1.44 (s, 9H). The *ee* of **2b** was determined by HPLC analysis using Daicel Chiralcel AD-H columns (25 cm $\times$ 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 0.5 mL/min, 254 nm; $t_{\text{minor}} = 11.1$ min, $t_{\text{major}} = 12.3$ min.



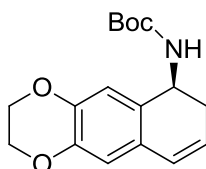
(S)-tert-butyl (6,7-dimethoxy-1,2-dihydronaphthalen-1-yl)carbamate (2c)^[1]

Colorless oil, purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1/5), 55.6 mg, 91% yield, 92% *ee*. $[\alpha]_{\text{D}}^{22} = -44.3$ ($c = 0.70$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ 6.88 (s, 1H), 6.61 (s, 1H), 6.42 (d, $J = 9.6$ Hz, 1H), 5.87 – 5.83 (m, 1H), 4.90 (d, $J = 8.9$ Hz, 1H), 4.80 – 4.75 (m, 1H), 3.87 (d, $J = 6.0$ Hz, 6H), 2.58 – 2.43 (m, 2H), 1.42 (s, 9H). The *ee* of **2c** was determined by HPLC analysis using Daicel Chiralcel OD-H columns (25 cm $\times$ 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 0.5 mL/min, 254 nm; $t_{\text{minor}} = 15.2$ min, $t_{\text{major}} = 17.6$ min.



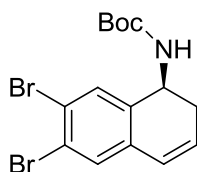
(S)-tert-butyl (5,6-dihydronaphtho[2,3-d][1,3]dioxol-5-yl)carbamate (2d)^[1]

White solid, purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1/8), 54.4 mg, 94% yield, 94% *ee*, mp 86 – 89 °C. $[\alpha]_{\text{D}}^{22} = -34.6$ ($c = 0.78$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ 6.83 (s, 1H), 6.57 (s, 1H), 6.38 (d, $J = 9.6$ Hz, 1H), 5.92 – 5.91 (m, 2H), 5.87 – 5.82 (m, 1H), 4.89 (d, $J = 8.8$ Hz, 1H), 4.77 – 4.71 (m, 1H), 2.54 – 2.40 (m, 2H), 1.42 (s, 9H). The *ee* of **2d** was determined by HPLC analysis using Daicel Chiralcel AS-H columns (25 cm $\times$ 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 0.5 mL/min, 254 nm; $t_{\text{major}} = 21.6$ min, $t_{\text{minor}} = 27.6$ min.



(S)-tert-butyl (2,3,6,7-tetrahydronaphtho[2,3-b][1,4]dioxin-6-yl)carbamate (2e)^[1]

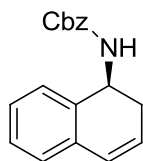
Colorless oil, purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1/8), 55.2 mg, 91% yield, 99% *ee*. $[\alpha]_{\text{D}}^{22} = -14.8$ ($c = 0.54$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ 6.84 (s, 1H), 6.60 (s, 1H), 6.38 (d, $J = 9.7$ Hz, 1H), 5.87 – 5.82 (m, 1H), 4.84 – 4.74 (m, 2H), 4.23 (s, 4H), 2.55 – 2.37 (m, 2H), 1.43 (s, 9H). The *ee* of **2e** was determined by HPLC analysis using Daicel Chiralcel AS-H columns (25 cm $\times$ 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; $t_{\text{major}} = 17.5$ min, $t_{\text{minor}} = 19.6$ min.



(S)-tert-butyl (6,7-dibromo-1,2-dihydronaphthalen-1-yl)carbamate (2f)^[1]

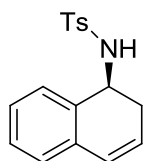
Colorless oil, purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1/10), 61.3 mg, 76% yield, 89% *ee*. $[\alpha]_{\text{D}}^{20} = -17.4$ ($c = 0.46$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ 7.56 (s, 1H), 7.32 (s, 1H), 6.42 (d, $J = 9.7$ Hz, 1H), 6.08 – 6.03 (m, 1H), 4.84 (s, 2H), 2.58 – 2.40 (m, 2H), 1.45 (s, 9H). The *ee* of **2f** was determined by HPLC analysis using Daicel Chiralcel OD-H columns (25 cm $\times$ 0.46 cm ID),

conditions: *n*-hexane/*i*-PrOH = 98/2, 0.8 mL/min, 254 nm; t_{minor} = 40.3 min, t_{major} = 43.0 min.



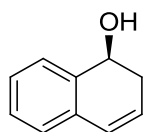
(S)-benzyl (1,2-dihydronaphthalen-1-yl)carbamate (2g)^[2]

White solid, purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1/10), 52.5 mg, 94% yield, 91% *ee*. mp 75 - 77 °C. $[\alpha]_{\text{D}}^{22} = -31.6$ ($c = 0.76$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ 7.41 - 7.34 (m, 6H), 7.32 - 7.23 (m, 2H), 7.13 (dd, $J = 7.2, 1.0$ Hz, 1H), 6.57 (d, $J = 9.6$ Hz, 1H), 6.02 - 5.98 (m, 1H), 5.53 - 5.09 (m, 3H), 5.00 - 4.96 (m, 1H), 2.68 - 2.51 (m, 2H). The *ee* of **2g** was determined by HPLC analysis using Daicel Chiralcel OJ - H columns (25 cm $\times$ 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 23.2 min, t_{major} = 28.6 min.



(S)-N-(1,2-dihydronaphthalen-1-yl)-4-methylbenzenesulfonamide (2h)^[3]

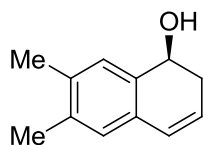
White solid, purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1/5), 35.9 mg, 60% yield, 86% *ee*. mp 163 - 165 °C. $[\alpha]_{\text{D}}^{20} = -97.5$ ($c = 0.4$, CH_2Cl_2). ^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, $J = 8.3$ Hz, 2H), 7.32 - 7.29 (m, 2H), 7.25 - 7.21 (m, 1H), 7.09 (dd, $J = 12.1, 4.5$ Hz, 2H), 6.94 (d, $J = 7.6$ Hz, 1H), 6.53 (d, $J = 9.6$ Hz, 1H), 5.93 - 5.89 (m, 1H), 4.91 (d, $J = 8.6$ Hz, 1H), 4.52 - 4.47 (m, 1H), 2.54 - 2.41 (m, 5H). The *ee* of **2h** was determined by HPLC analysis using Daicel Chiralcel AD - H columns (25 cm $\times$ 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; t_{minor} = 20.0 min, t_{major} = 21.2 min.



(S)-1,2-dihydronaphthalen-1-ol (2i)^[4]

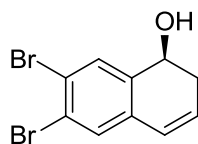
White solid, purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1/5), 21.1 mg, 72% yield, 84% *ee*. mp 52 - 55 °C. $[\alpha]_{\text{D}}^{22} = -42.9$ ($c = +0.42$,

CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.30 (d, *J* = 7.2 Hz, 1H), 7.23 - 7.15 (m, 2H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.48 (d, *J* = 9.6 Hz, 1H), 5.94 - 5.90 (m, 1H), 4.71 (t, *J* = 5.4 Hz, 1H), 2.59 - 2.47 (m, 2H), 1.77 (s, 1H). The *ee* of **2i** was determined by HPLC analysis using Daicel Chiralcel OD-H columns (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm; *t*_{major} = 29.7 min, *t*_{minor} = 33.5 min.



(S)-6,7-dimethyl-1,2-dihydronaphthalen-1-ol (2j)^[4]

White solid, purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1/5), 10.5 mg, 30% yield, 82% *ee*. mp 89 - 92°C. [α]_D²⁰ = -10.9 (*c* = 0.46, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.14 (s, 1H), 6.92 (s, 1H), 6.52 (d, *J* = 9.6 Hz, 1H), 5.93 (t, *J* = 4.8 Hz, 1H), 4.72 (d, *J* = 4.0 Hz, 1H), 2.64 - 2.54 (m, 2H), 2.26 (d, *J* = 6.4 Hz, 6H), 1.70 (d, *J* = 6.0 Hz, 1H). The *ee* of **2j** was determined by HPLC analysis using Daicel Chiralcel As-H columns (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, 254 nm; *t*_{major} = 8.8 min, *t*_{minor} = 12.8 min.



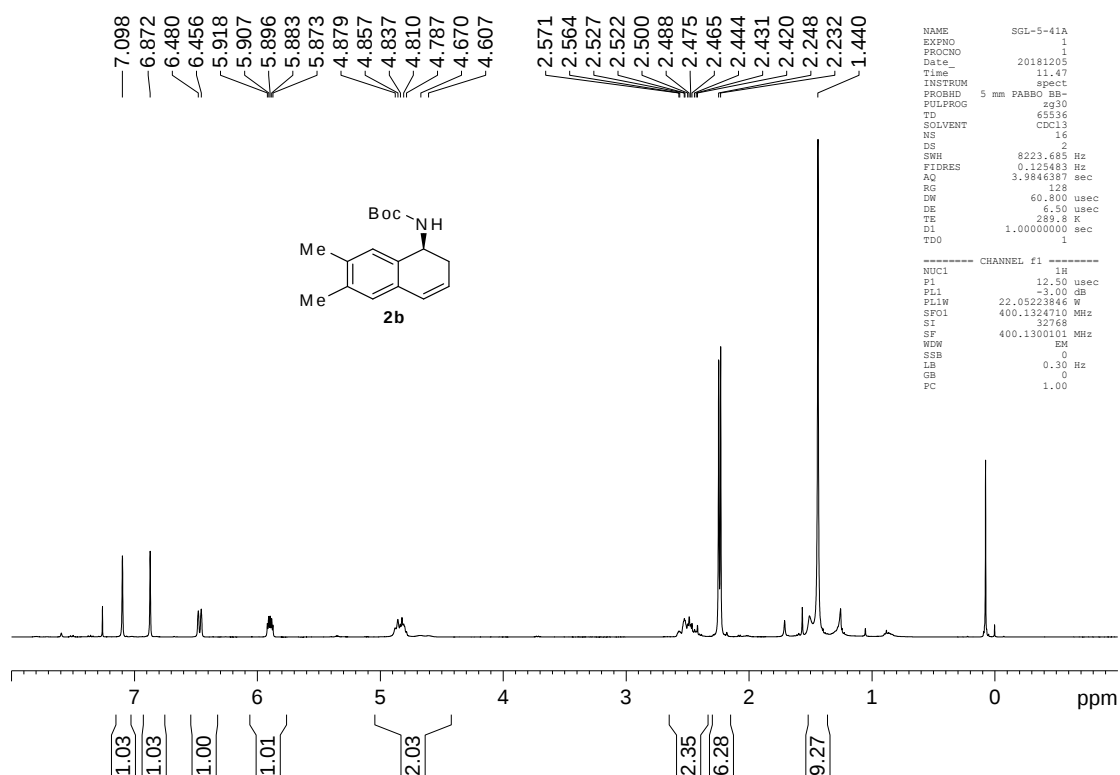
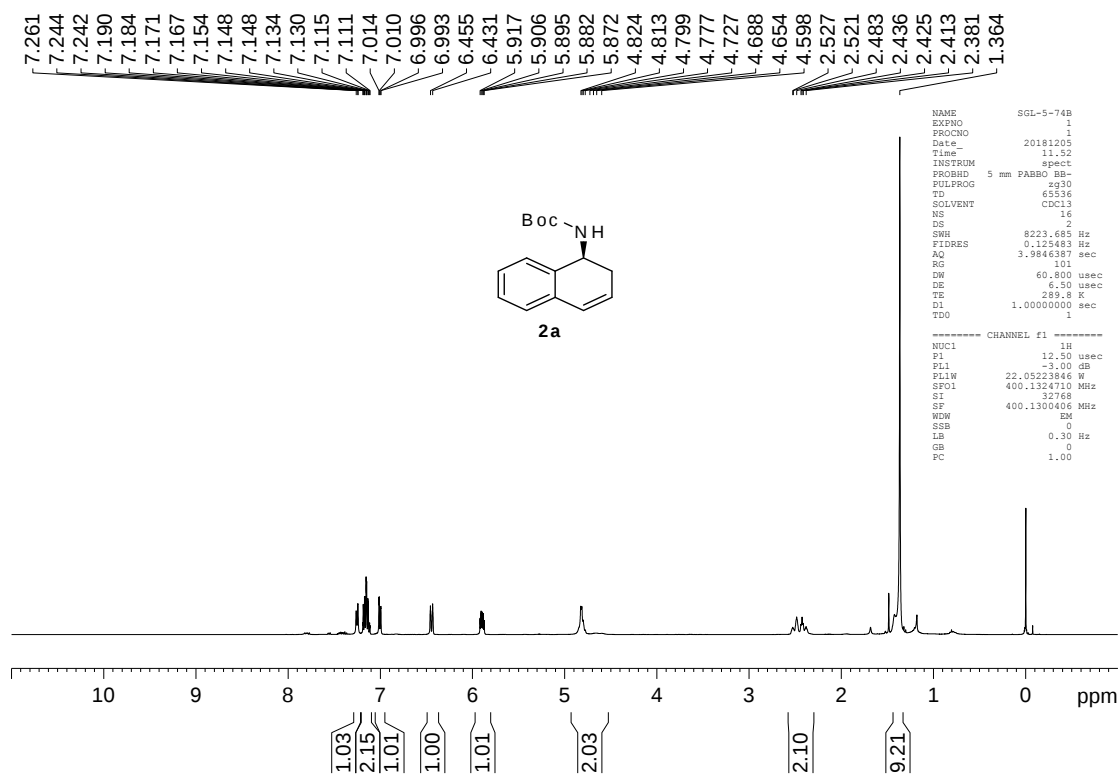
(S)-6,7-dibromo-1,2-dihydronaphthalen-1-ol (2k)^[4]

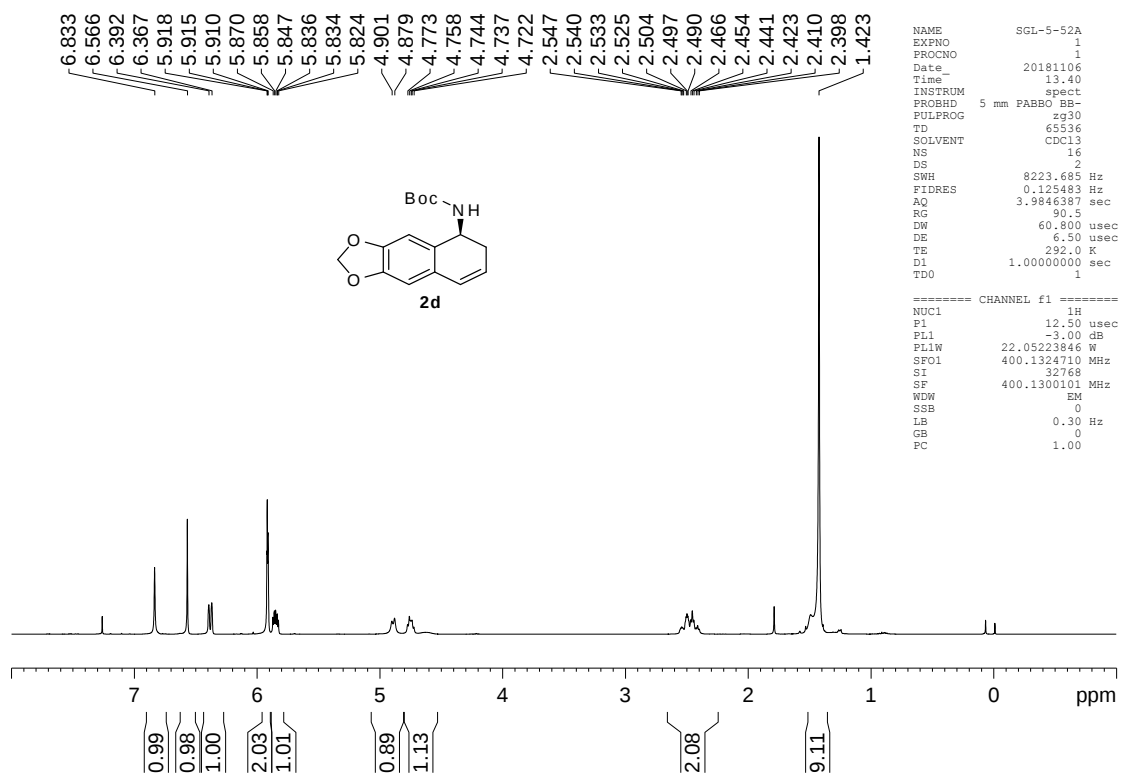
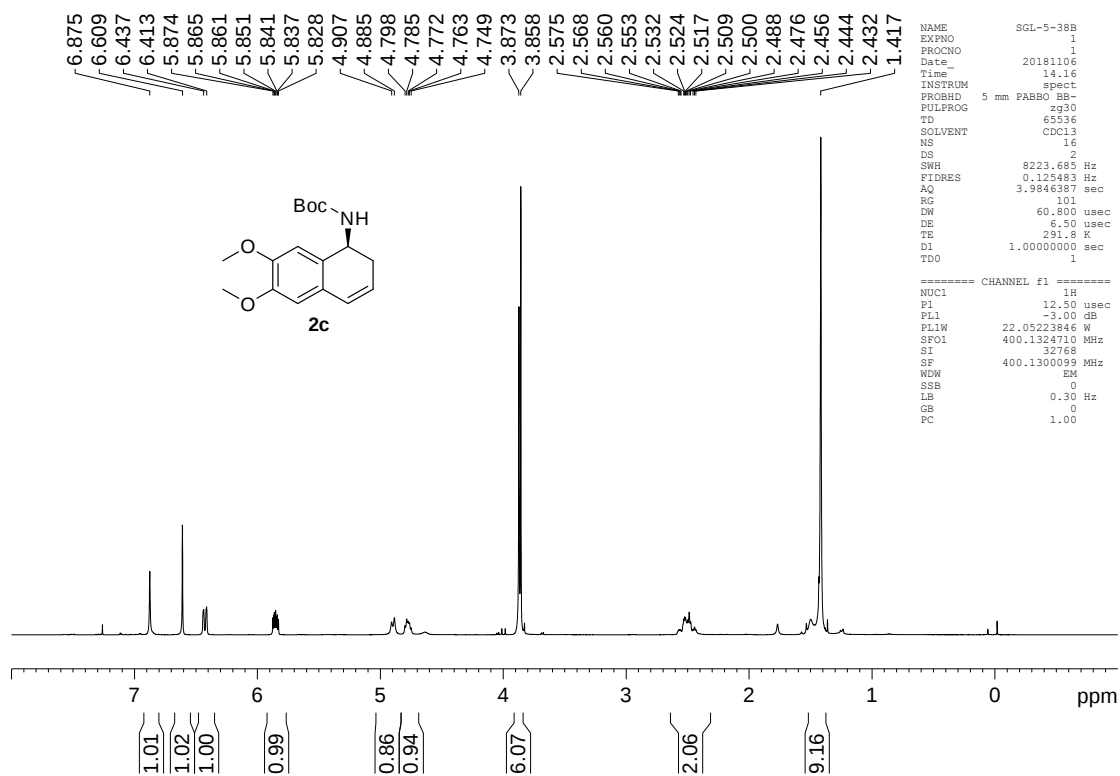
White solid, purified by silica gel column chromatography (ethyl acetate/petroleum ether, 1/5), 51.7 mg, 85% yield, 84% *ee*. mp 83-85°C. [α]_D²² = +28.8 (*c* = 1.04, CH₂Cl₂). ¹H NMR (400 MHz, CDCl₃) δ 7.64 (s, 1H), 7.36 (s, 1H), 6.44 (d, *J* = 9.6 Hz, 1H), 6.09 - 6.05 (m, 1H), 4.76 (q, *J* = 6.0 Hz, 1H), 2.58 - 2.56 (m, 2H), 1.86 (s, 1H). The *ee* of **2k** was determined by HPLC analysis using Daicel Chiralcel OJ-H columns (25 cm × 0.46 cm ID), conditions: *n*-hexane/*i*-PrOH = 95/5, 1.0 mL/min, 254 nm; *t*_{minor} = 15.2 min, *t*_{major} = 20.4 min.

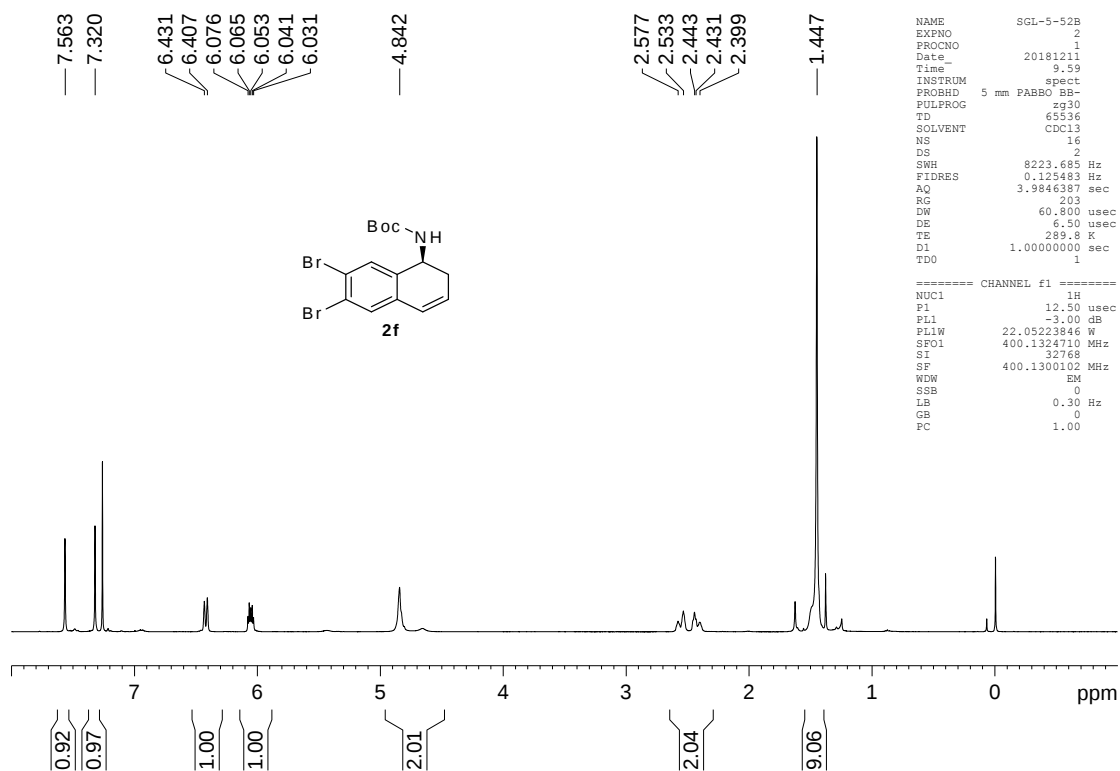
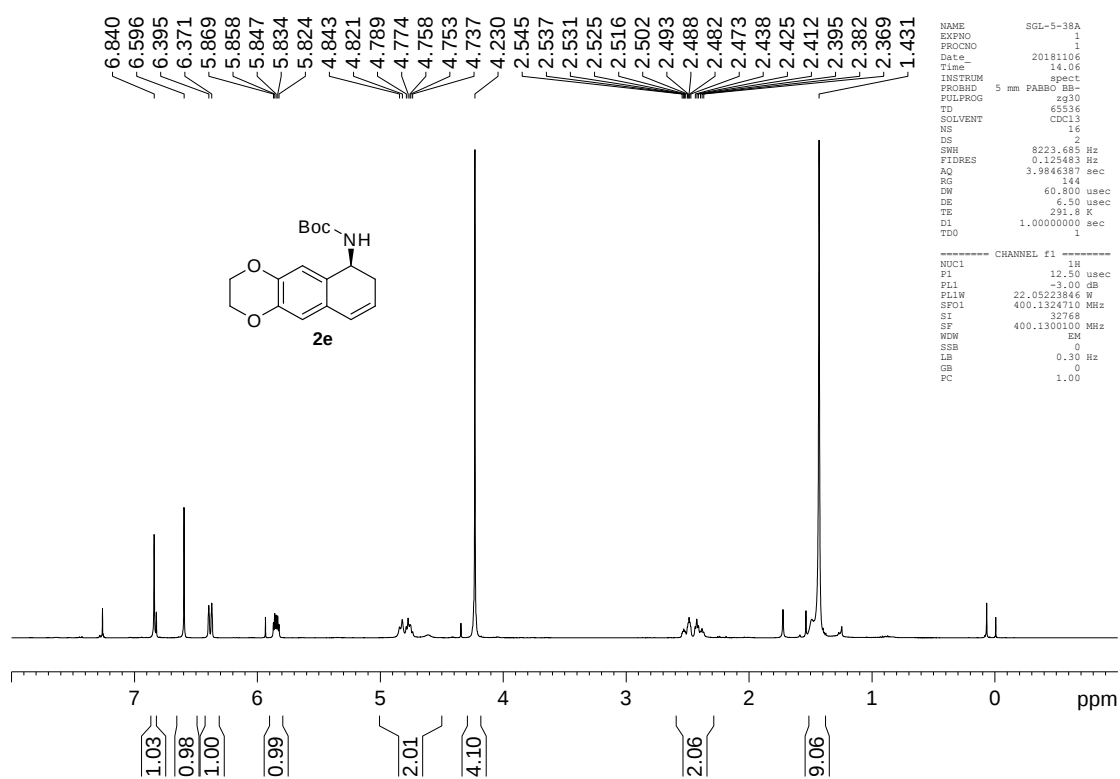
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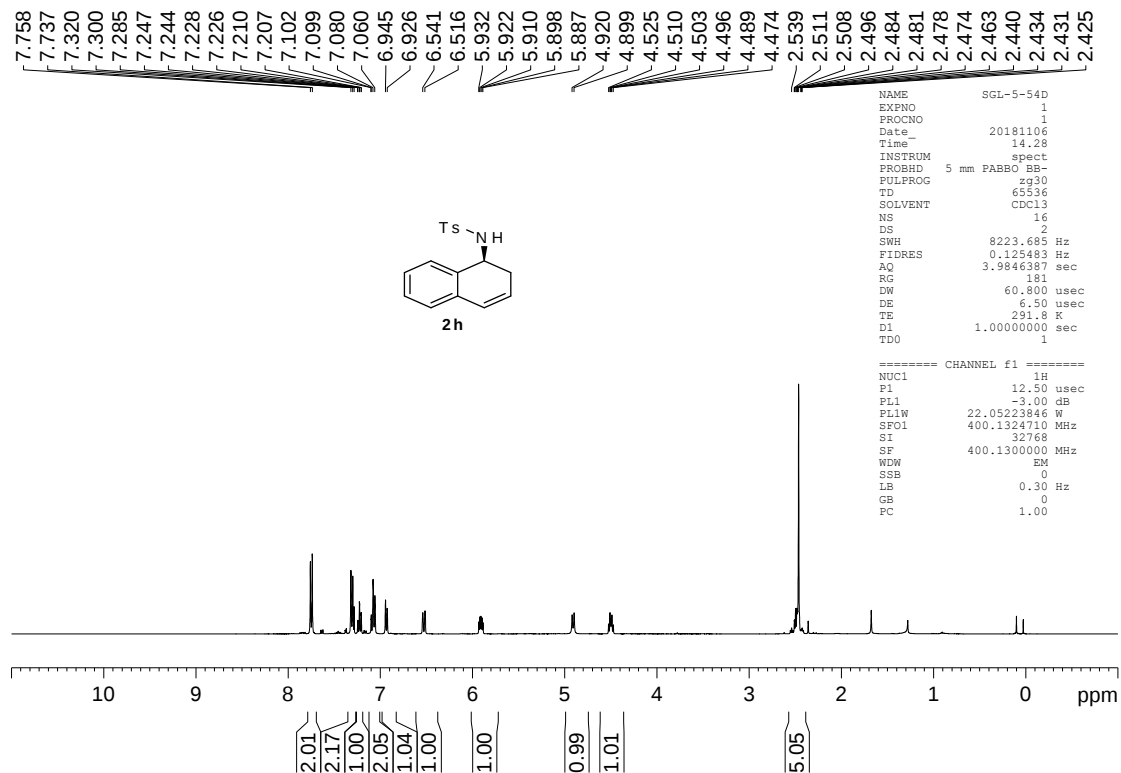
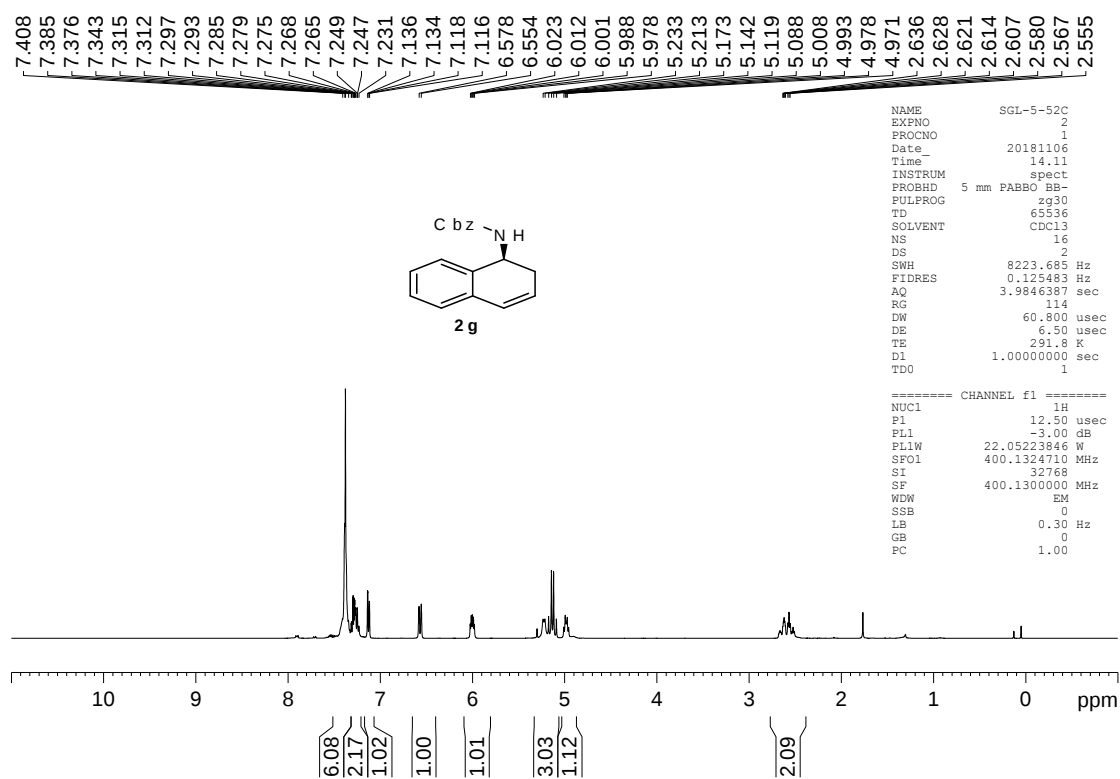
- [1] F. Yang, J.-C. Chen, J.-B. Xu, F.-J. Ma, Y.-Y. Zhou, M. V. Shinde, and B.-M. Fan, *Org. Lett.*, **2016**, *18*, 4832–4835.
- [2] D.-P. Zhang, R. Khan, F. Yang, X.-X. Zhang, G.-L. Shen, Y. Gao, R.-F. Fan, W.-Q. Sun and B.-M. Fan, *Eur. J. Org. Chem.* **2018**, 3464-3470.
- [3] D.-D. Pu, Y.-Y. Zhou, F. Yang, G.-L. Shen, Y. Gao, W.-Q. Sun, R. Khan, B.-M. Fan, *Org. Chem. Front.* **2018**, *5*, 3077–3082.
- [4] F.-J. Ma, J.-C. Chen, F. Yang, M. V. Shinde, Y.-Y. Zhou, B.-M. Fan, *Org. Biomol. Chem.* **2017**, *15*, 2359-2361.

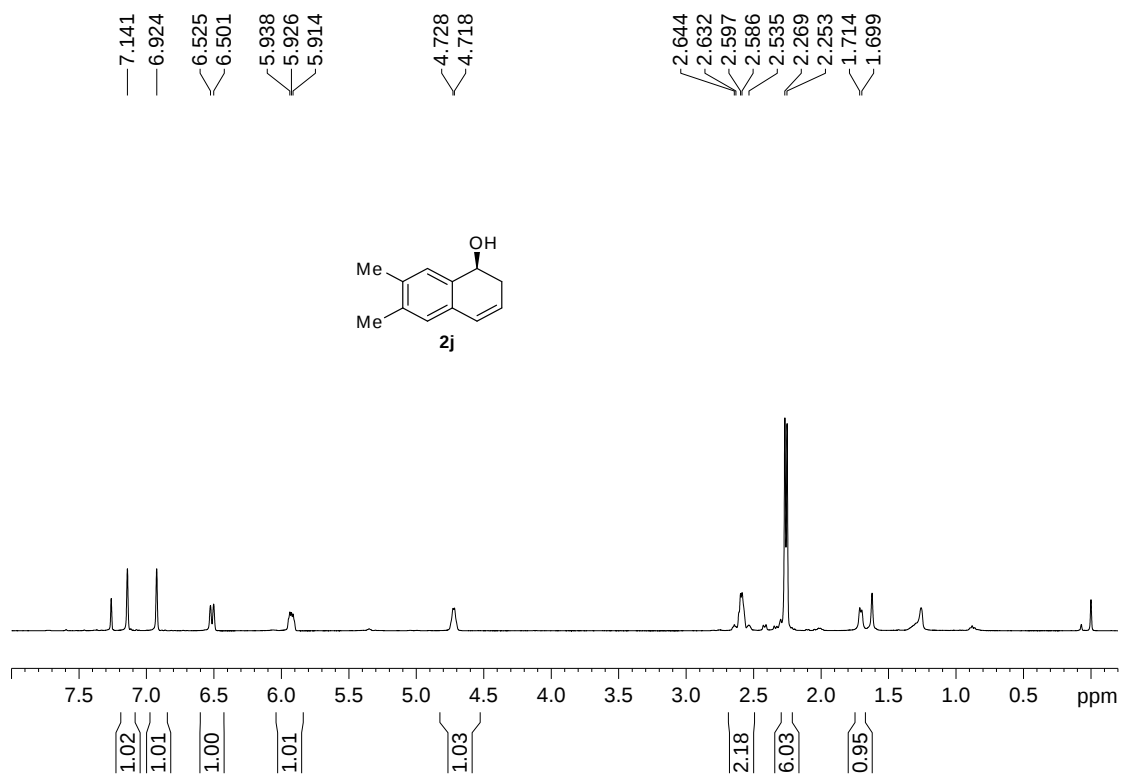
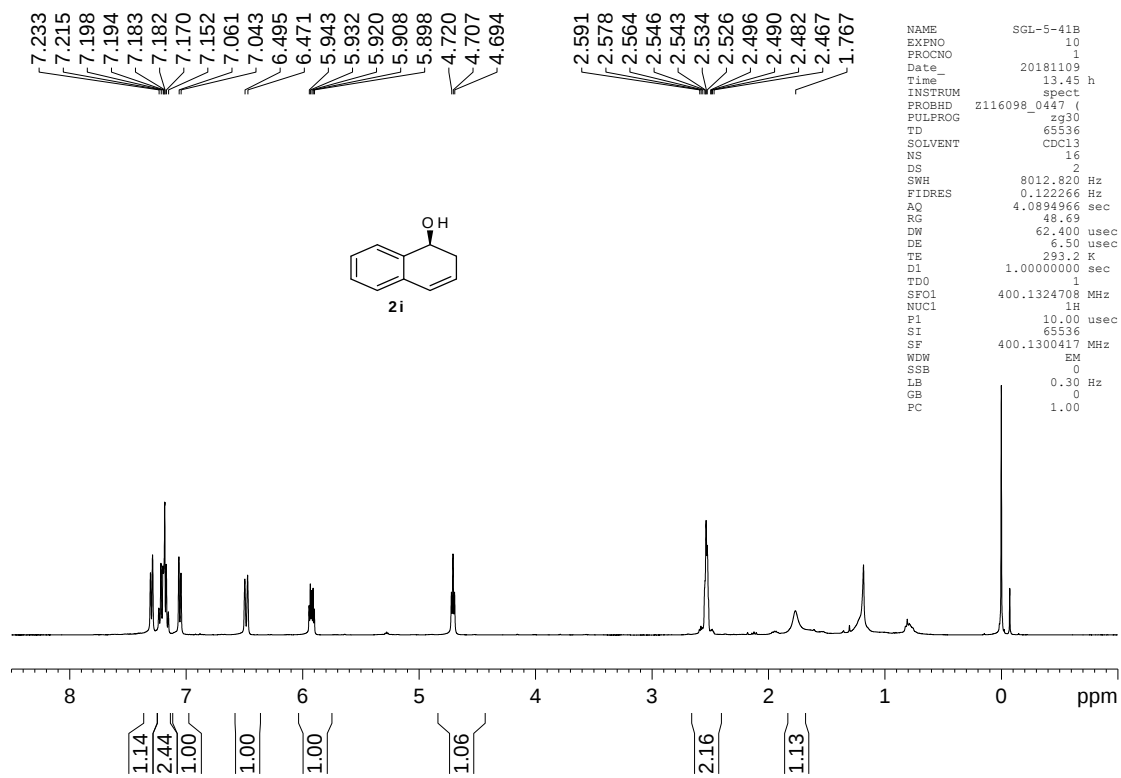
E: NMR Spectra of Products

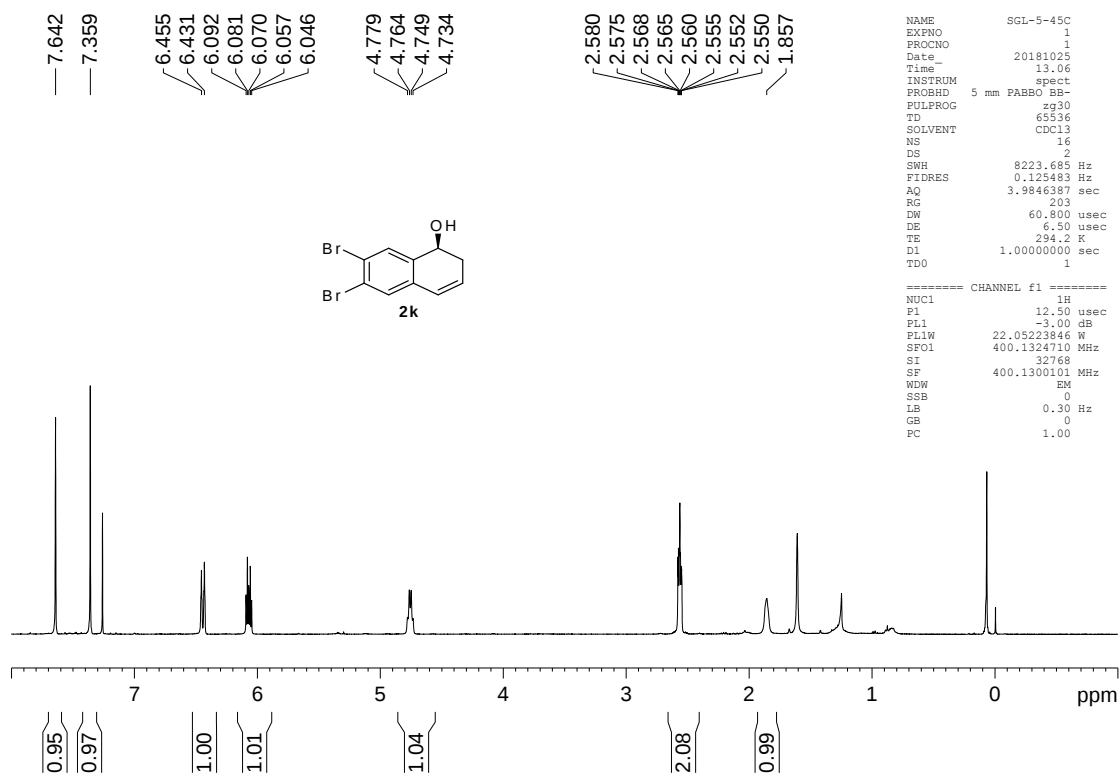




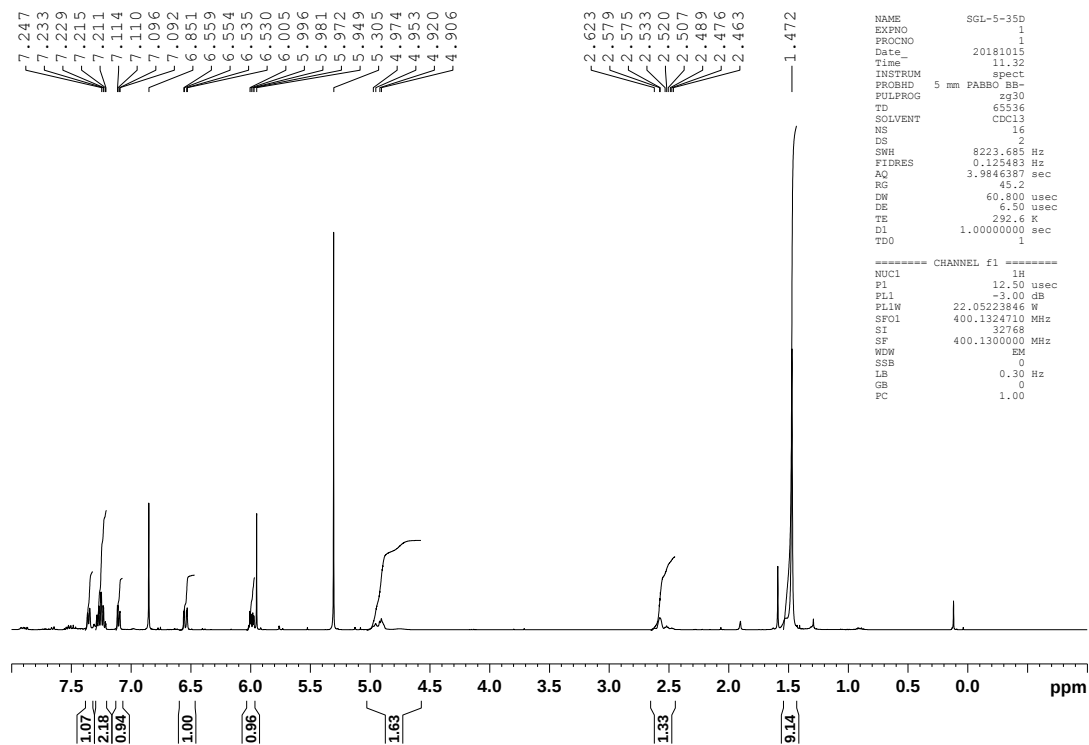




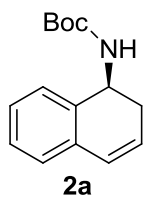




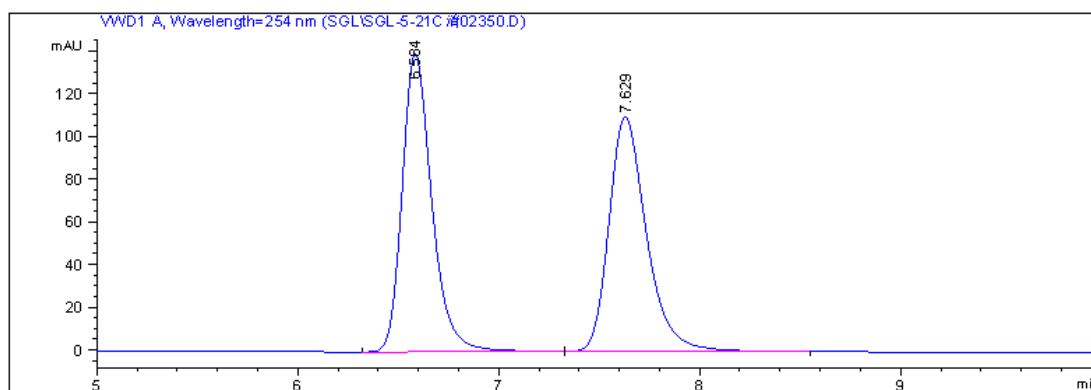
¹H-NMR of 2a-D (67% D) with 1,3-benzodioxole as internal standard:



F: HPLC Spectra of Products

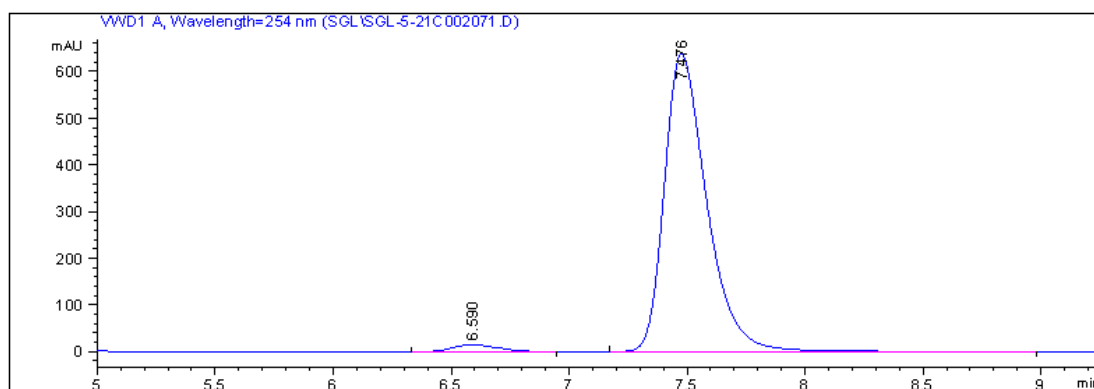


Racemic:

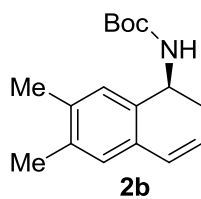
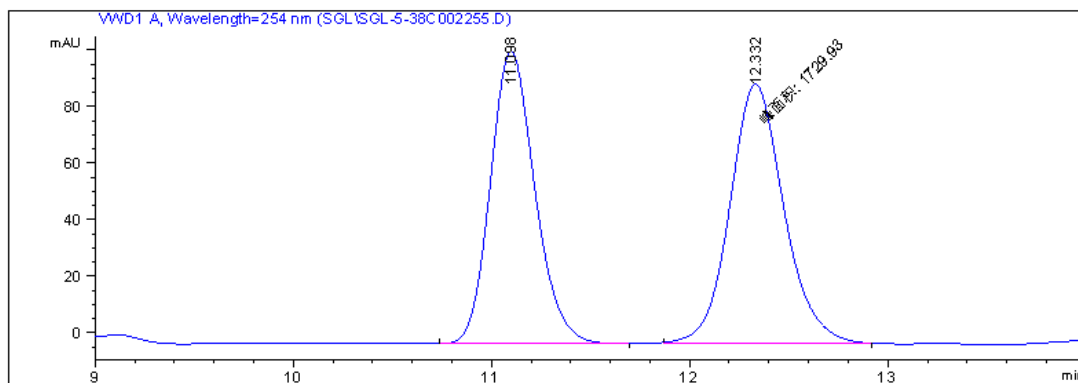


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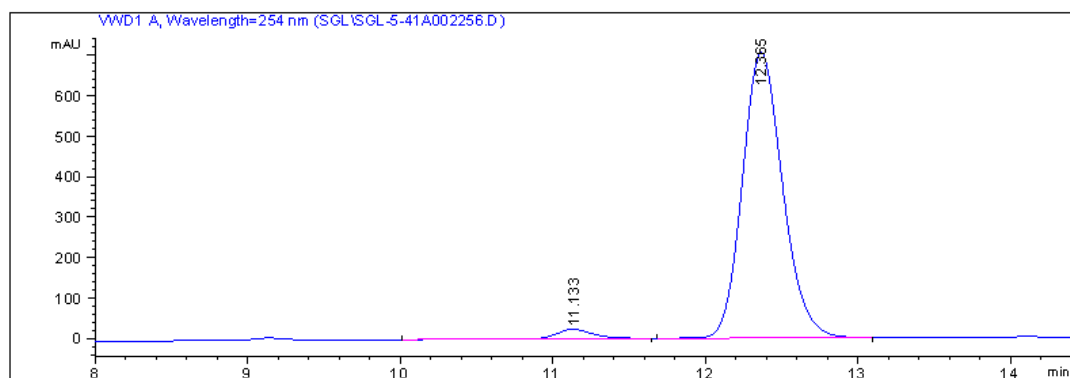
Enantioenriched:



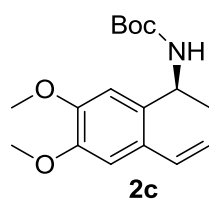
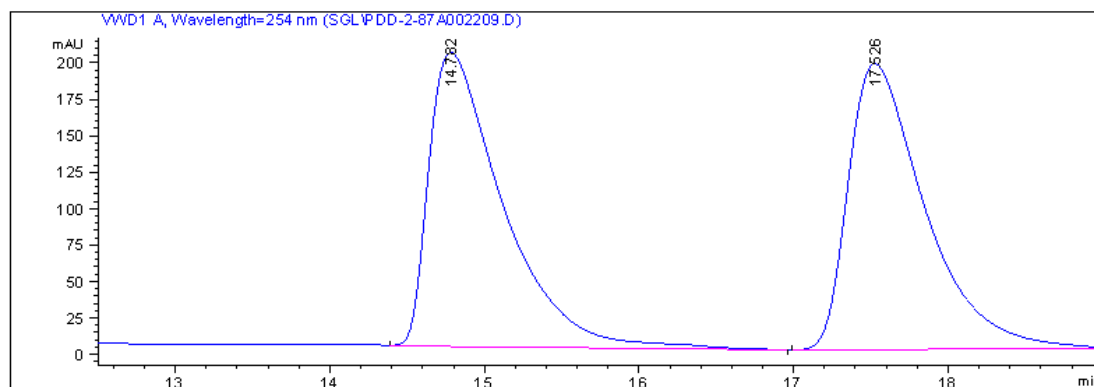
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1	6.590	BB	0.1966	188.17708	14.39014	2.3111
2	7.476	BB	0.1897	7953.96777	636.86334	97.6889

**Racemic:**

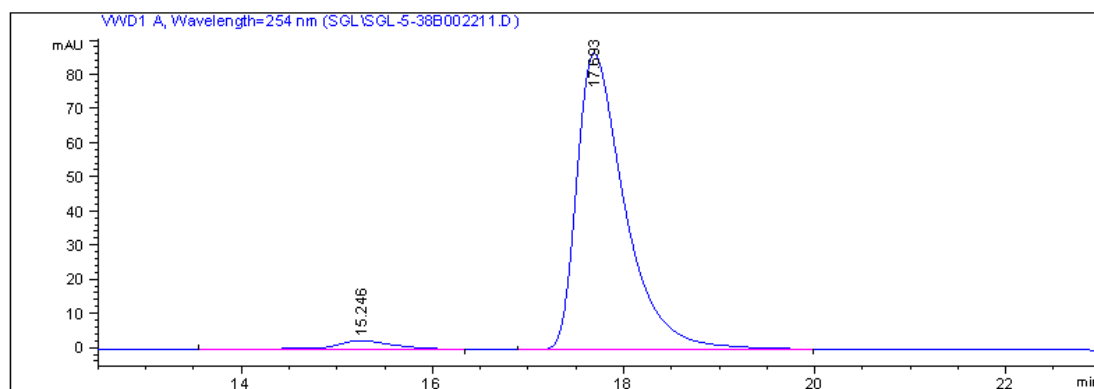
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2	12.332	MM	0.3148	1729.92920	91.57565	51.8355

Enantioenriched:

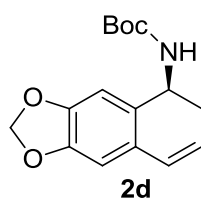
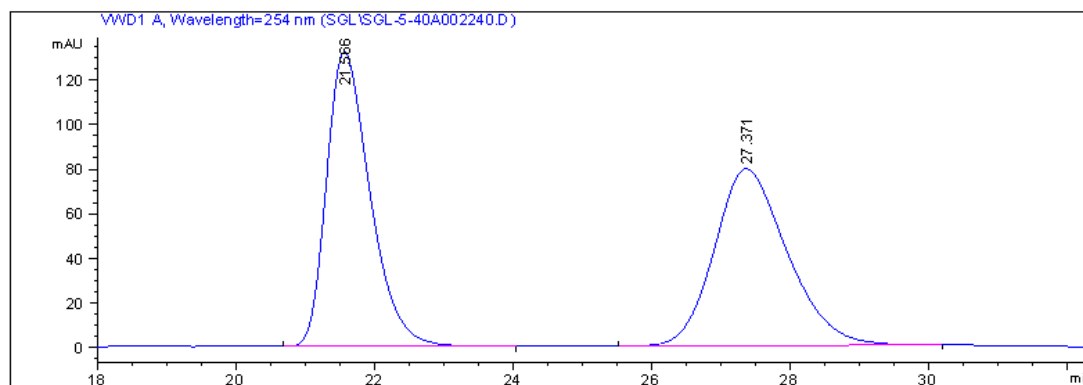
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2	12.365	BV	0.2828	1.29497e4	706.78894	97.1500

**Racemic:**

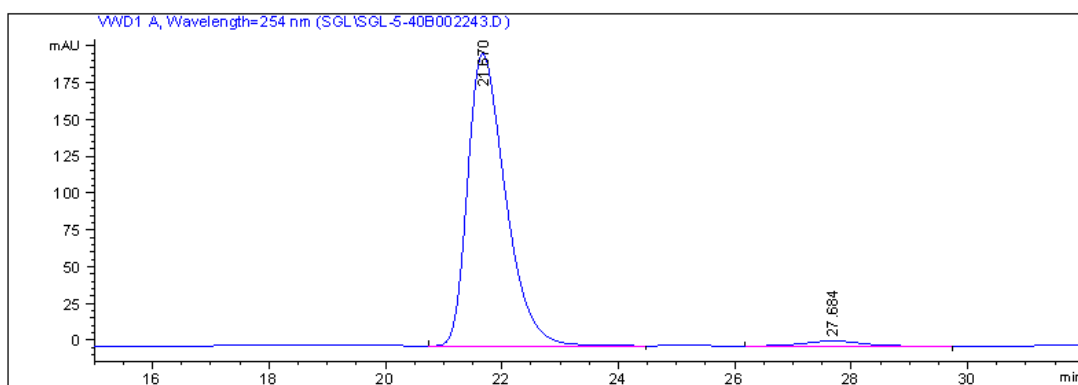
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2	17.526	BB	0.5226	6788.28027	196.24269	50.1458

Enantioenriched:

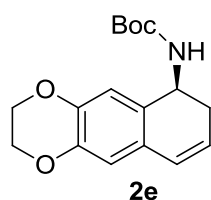
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.246	BB	0.6195	119.41863	2.67681	3.7893
2	17.693	BB	0.5247	3032.05713	86.77206	96.2107

**Racemic:**

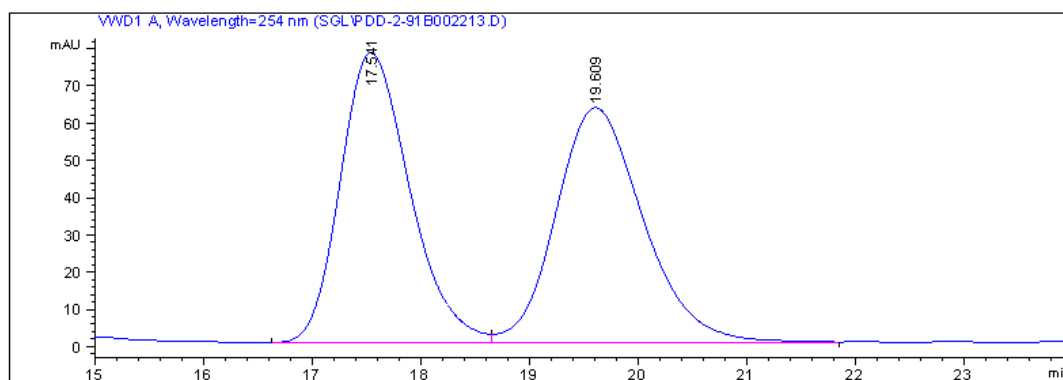
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.566	BB	0.6727	5774.97217	132.17554	49.9010
2	27.371	BB	1.1051	5797.88379	79.38014	50.0990

Enantioenriched:

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.670	BB	0.6931	8951.56543	198.52023	97.3994
2	27.684	BB	0.9687	239.01357	3.34057	2.6006

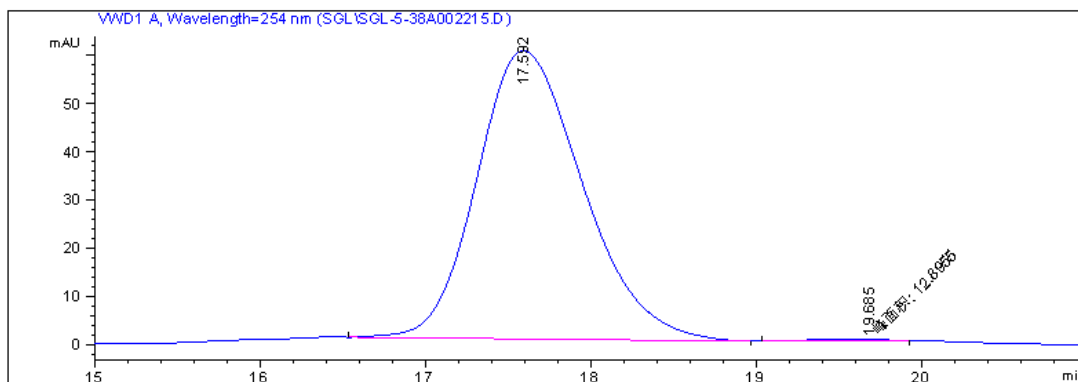


Racemic:

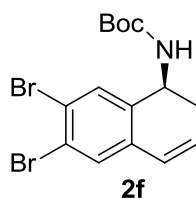


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.541	BV	0.6858	3454.73999	77.84125	49.6307
2	19.609	VB	0.8680	3506.15234	63.03132	50.3693

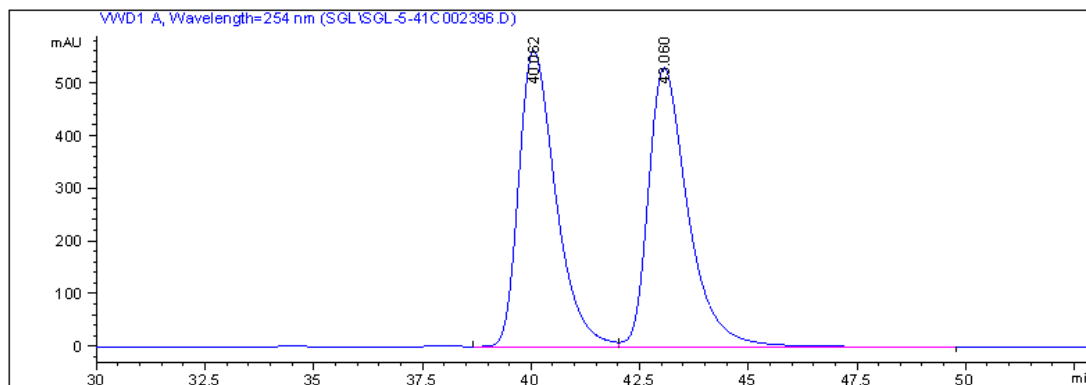
Enantioenriched:



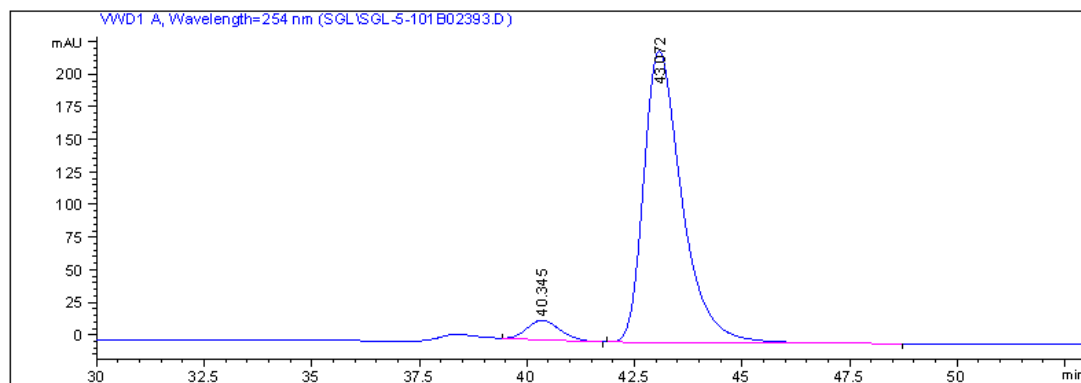
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.592	BB	0.6838	2666.62695	59.73605	99.5187
2	19.685	MM	0.5159	12.89552	4.16599e-1	0.4813



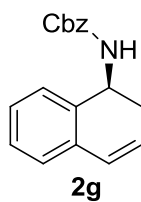
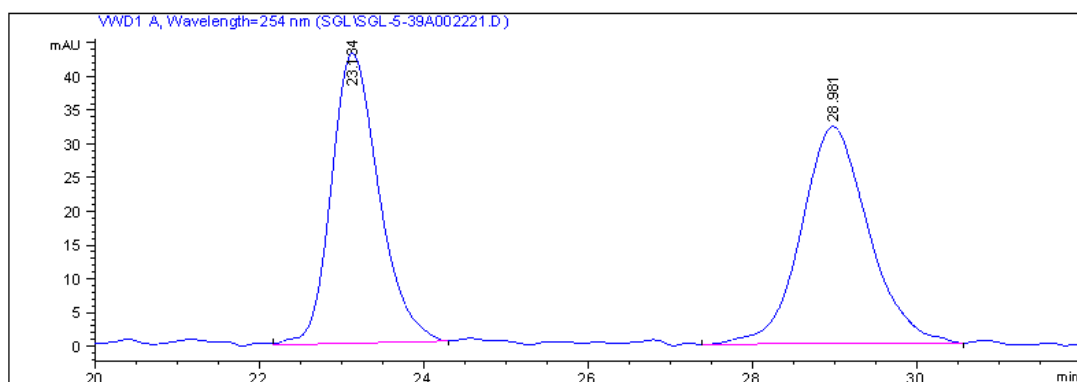
Racemic:



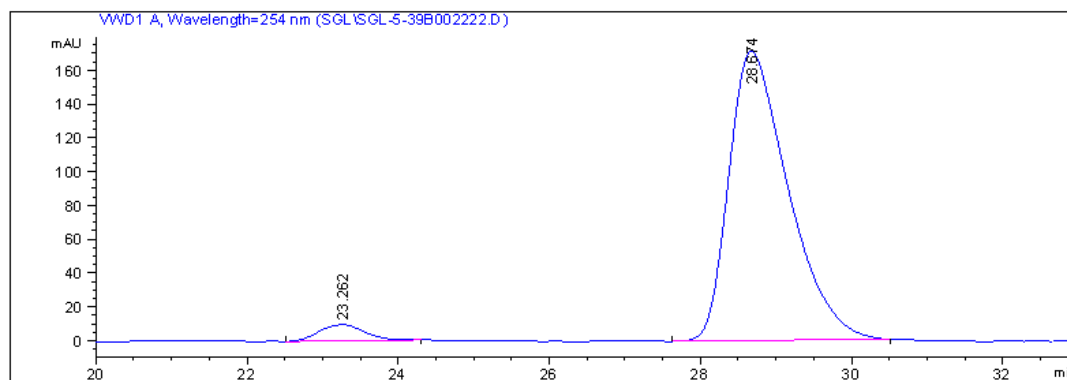
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.062	BV	0.9043	3.31797e4	561.56854	49.7479
2	43.060	VB	0.9570	3.35160e4	529.09784	50.2521

Enantioenriched:

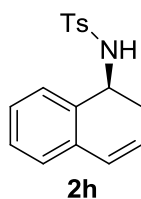
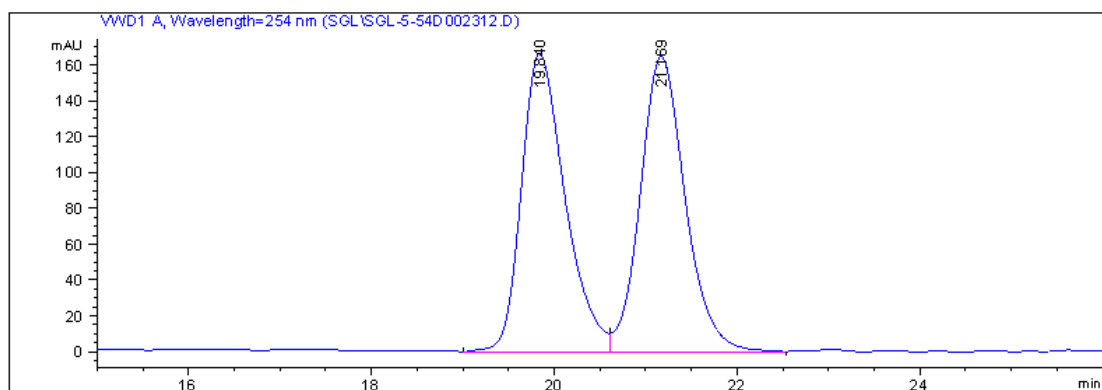
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.345	BB	0.8152	786.18268	14.78988	5.4012
2	43.072	BB	0.9390	1.37696e4	223.43306	94.5988

**Racemic:**

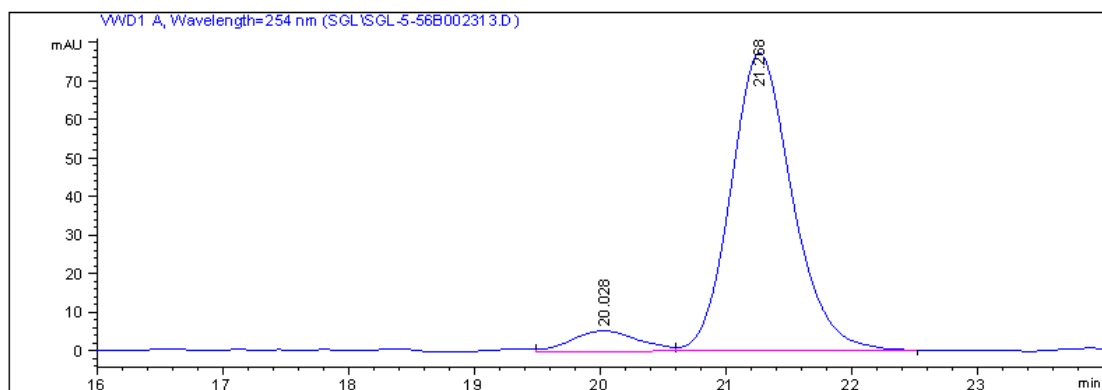
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.134	VB	0.6196	1729.98438	42.98005	48.6459
2	28.981	BB	0.8596	1826.29663	32.15871	51.3541

Enantioenriched:

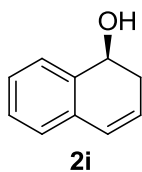
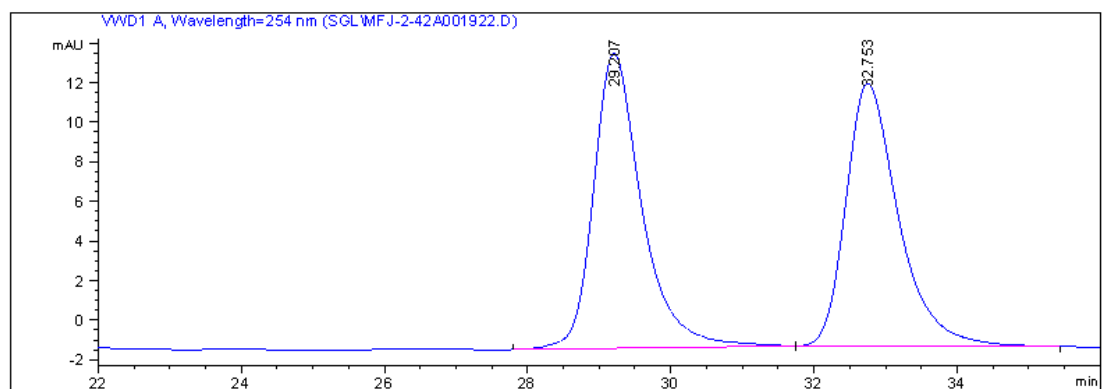
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.262	BB	0.6579	404.39487	9.57250	4.1524
2	28.674	BB	0.8414	9334.42285	171.13115	95.8476

**Racemic:**

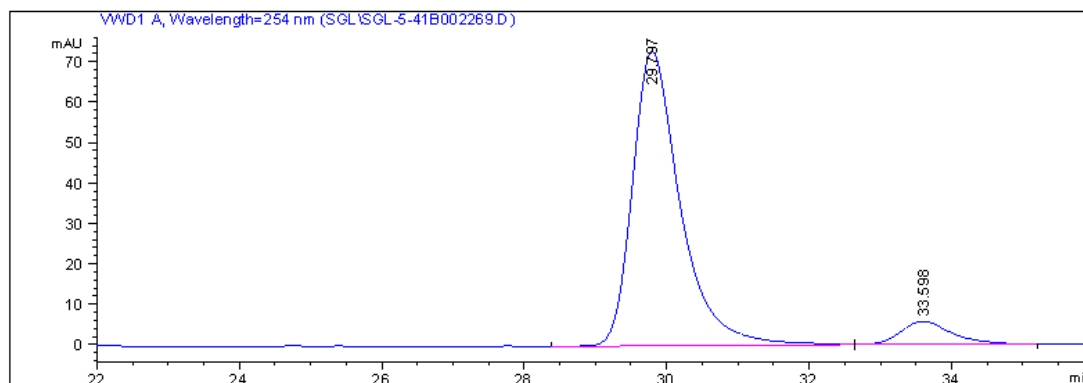
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.840	BV	0.5031	5505.50195	166.34393	49.5449
2	21.169	VB	0.5211	5606.63965	164.70906	50.4551

Enantioenriched:

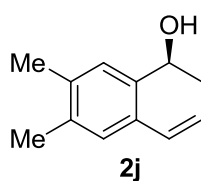
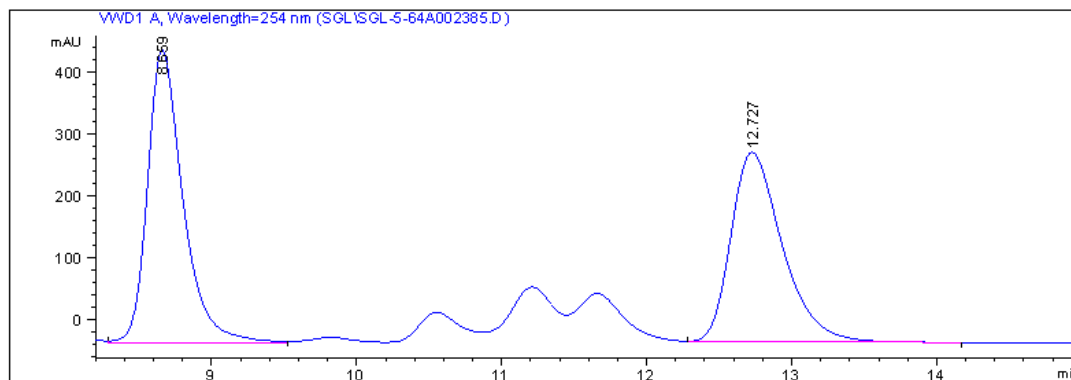
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.028	VV	0.5661	194.11200	5.22937	6.8986
2	21.268	VB	0.5154	2619.69556	77.29933	93.1014

**Racemic:**

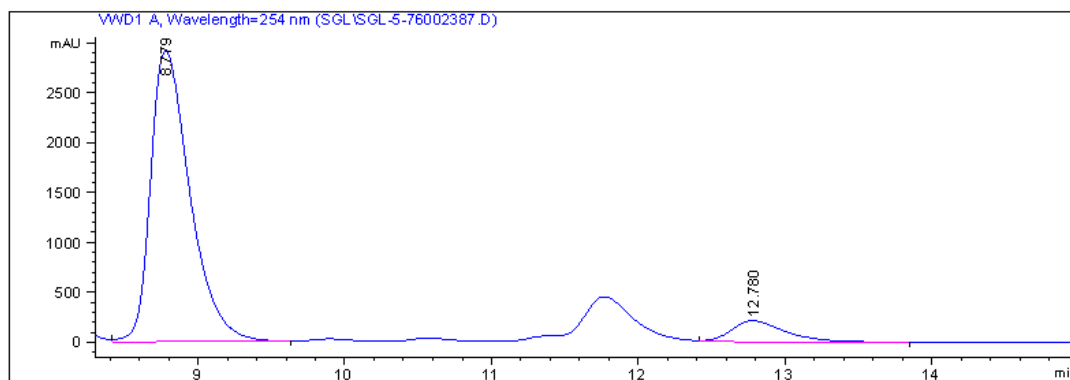
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.207	BB	0.6970	700.06146	14.90322	50.8455
2	32.753	BB	0.7667	676.78015	13.27766	49.1545

Enantioenriched:

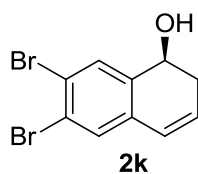
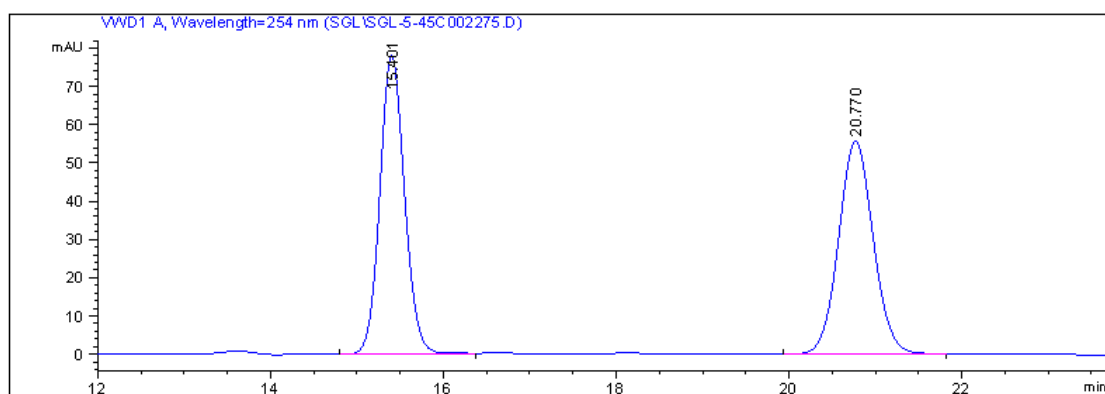
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.797	BB	0.6982	3395.77466	72.80329	92.3033
2	33.598	BB	0.7364	283.15720	5.73087	7.6967

**Racemic:**

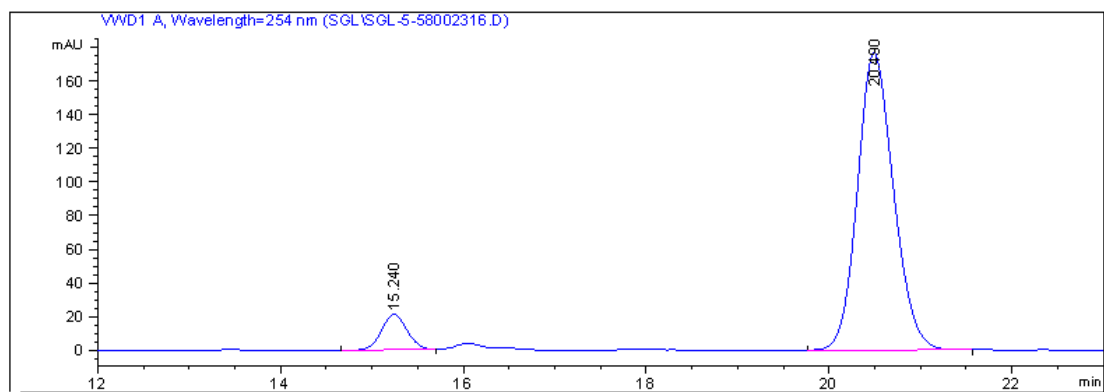
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.659	VV	0.2551	8012.44824	471.93610	51.6386
2	12.727	BB	0.3747	7503.93066	305.38007	48.3614

Enantioenriched:

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.779	VB	0.2824	5.42119e4	2908.65454	91.0010
2	12.780	VB	0.3810	5360.96338	211.26773	8.9990

**Racemic:**

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.401	BB	0.3060	1548.12402	78.18282	49.8839
2	20.770	BB	0.4289	1555.33215	55.85254	50.1161

Enantioenriched:

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.240	BB	0.2993	403.78671	20.90478	7.7033
2	20.490	BB	0.4209	4837.94141	176.41559	92.2967