

## Supporting Information

### Azopyridine-based chiral oxazolines with rare-earth metals for photoswitchable catalysis

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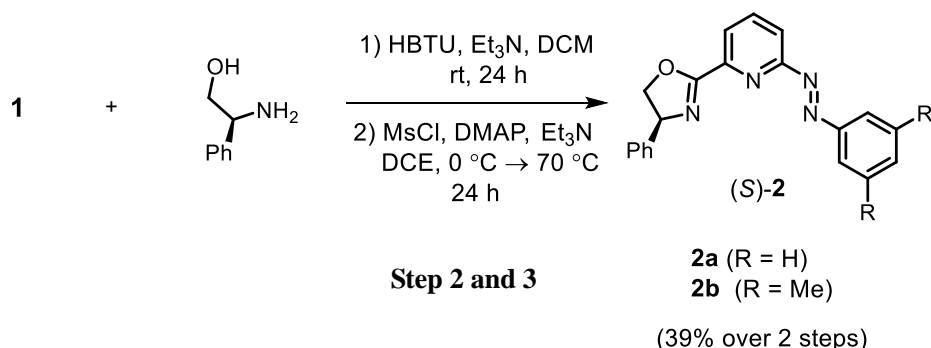
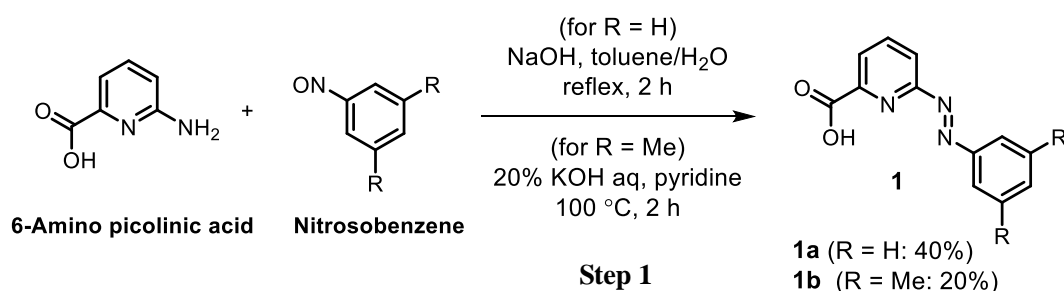
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## General information

<sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded with a JEOL JMN ECS400 FT NMR NMR (<sup>1</sup>H-NMR 400 MHz, <sup>13</sup>C-NMR 100 MHz). <sup>1</sup>H-NMR spectra are reported as follows: chemical shift in ppm relative to the chemical shift of CHCl<sub>3</sub> at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, m = multiplet), and coupling constants (Hz). <sup>13</sup>C-NMR spectra reported in ppm relative to the central line of triplet for CDCl<sub>3</sub> at 77 ppm. ESI- and APCI-MS spectra were obtained with JMS-T100LC (JEOL). HPLC analyses were performed on a JASCO HPLC system (JASCO PU 980 pump and UV-975 UV/Vis detector). UV spectra were recorded on JASCO v-770. FT-IR spectra were recorded on a JASCO FT-IR system (FT/IR4100). Column chromatography on SiO<sub>2</sub> was performed with Kanto Silica Gel 60 (40-100 μm). Commercially available organic and inorganic compounds were used without further purification. Photoirradiation was performed with LED lamp (PER-AMP, Techno Sigma Co., Ltd.).

## General procedure for the preparation of 2.

3,5-Dimethyl nitrosobenzene was prepared according to the reported procedure.<sup>1</sup>



**Step 1 (for R = H)**

To a solution of 6-aminopicolinic acid (829 mg, 6.0 mmol) and NaOH (2880 mg, 12 eq.) in toluene/H<sub>2</sub>O (6 mL/30 mL) was added nitrosobenzene (643 mg, 1.0 eq.) at room temperature. The solution was allowed to warm up to 100 °C. After being refluxed for 2 h, the solution was cooled to room temperature and washed with toluene to remove unreacted nitrosobenzene. Then, the remaining aqueous phase was neutralized with 1 M HCl (20 mL) and extracted with EtOAc (20 mL×2). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give crude mixture. The mixture was purified by silica gel column chromatography using hexane-ethyl acetate as an eluent to provide **1a**.

**Step 1 (for R = Me)**

To a stirred solution of 6-aminopicolinic acid (691 mg, 5.0 mmol) in 20% aq. KOH (25 mL) and pyridine (10 mL) was added a solution of 3,5-dimethylnitrosobenzene (1014 mg, 1.5 eq.) in pyridine (40 mL) at 100 °C. After being refluxed for 2 h at 100 °C, the solution was cooled to room temperature, neutralized with 1 M HCl (20 mL) and extracted with EtOAc (20 mL×2). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give crude mixture. The mixture was purified by silica gel column chromatography using hexane-acetone as an eluent to provide **1b**.

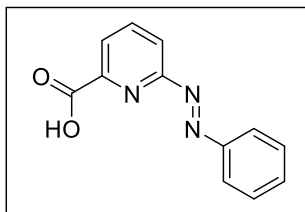
**Step 2 and 3 (two-step procedure)**

To a stirred solution of **1** (0.5 mmol), Et<sub>3</sub>N (0.14 mL, 2.0 eq.) and (*S*)-phenyl glycinol (89 mg, 1.3 eq.) in DCM (7.1 mL) was added HBTU (247 mg, 1.3 eq.) at room temperature. The stirring was continued under nitrogen atmosphere at the same temperature. After being stirred for 24 h, the reaction mixture was washed with sat. NaHCO<sub>3</sub> (15 mL) and the organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> followed by removal of the solvent under reduced pressure to give crude mixture. The mixture was purified by silica gel column chromatography using hexane-ethyl acetate as an eluent to give amide product (contained tetra methyl urea: coproduct generated from HBTU), which was used in the next step without further purification.

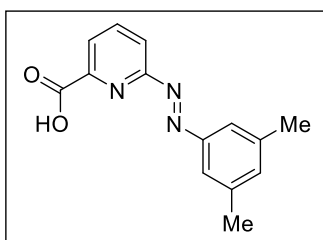
To a solution of the amide (0.25 mmol), DMAP (12 mg, 0.4 eq.) and Et<sub>3</sub>N (0.1 mL, 3.0 eq.) in DCE (2.3 mL) were added methanesulfonyl chloride (25 μL, 1.3 eq.) at 0 °C. The solution was allowed to warm up to 70 °C. After being stirred for 24 h, sat. NaHCO<sub>3</sub> (15 mL) was added to the solution. The resulting mixture was extracted with DCM (10 mL). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure to give crude mixture. The mixture was purified by silica gel column chromatography using hexane-acetone as an eluent to provide pure **2**.

## Analytical data

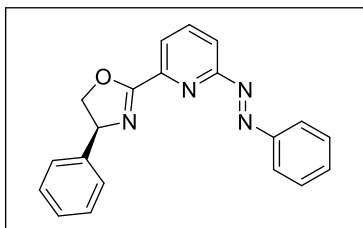
Characterization of new compounds and 5.



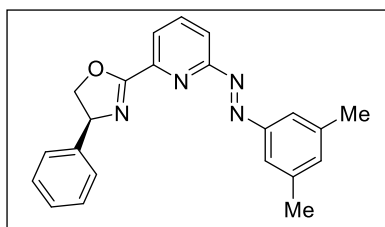
**1a**: 40% yield; dark orange solid;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.37 (dd,  $J = 7.8, 0.9$  Hz, 1H), 8.17 (t,  $J = 7.8$  Hz, 1H), 8.07-8.02 (m, 3H), 7.62-7.57 (m, 3H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.17, 161.41, 152.02, 145.95, 140.65, 133.09, 129.37, 125.32, 123.70, 117.89; HRMS (ESI) calcd for  $\text{C}_{12}\text{H}_9\text{N}_3\text{O}_2\text{Na}$ :  $m/z$  ( $[\text{M}+\text{Na}^+]$ ) 250.0587, found 250.0584; IR (KBr) 3047, 2849, 2592, 1704, 1578, 1452, 1332, 1277, 1146, 778, 680  $\text{cm}^{-1}$



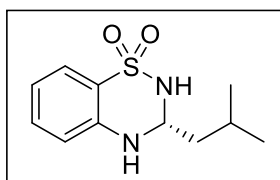
**1b**: 20% yield; orange solid;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.36 (dd,  $J = 7.6, 0.9$  Hz, 1H), 8.15 (t,  $J = 7.6$  Hz, 1H), 8.02 (d,  $J = 7.6$  Hz, 1H), 7.66 (s, 2H), 7.25 (s, 1H), 2.45 (s, 6H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.29, 161.61, 152.30, 146.16, 140.50, 139.12, 134.78, 125.12, 121.50, 117.38, 21.15; HRMS (ESI) calcd for  $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}_2\text{Na}$ :  $m/z$  ( $[\text{M}+\text{Na}^+]$ ) 278.0900, found 278.0897; IR (KBr) 2915, 2504, 1720, 1589, 1452, 1342, 1266, 1162, 1129, 866, 772, 685  $\text{cm}^{-1}$



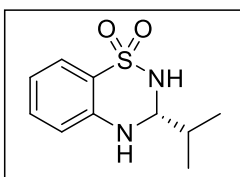
**(S)-2a**: 39% yield (over 2 steps); orange solid;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.32 (dd,  $J = 7.8, 0.9$  Hz, 1H), 8.11-8.06 (m, 2H), 8.00 (t,  $J = 7.8$  Hz, 1H), 7.91 (dd,  $J = 7.8, 0.9$  Hz, 1H), 7.57-7.52 (m, 3H), 7.40-7.29 (m, 5H), 5.50 (dd,  $J = 10.1, 8.5$  Hz, 1H), 4.96 (dd,  $J = 10.1, 8.5$  Hz, 1H), 4.46 (t,  $J = 8.5$  Hz, 1H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.52, 162.91, 152.21, 146.51, 141.71, 139.04, 132.41, 129.12, 128.81, 127.79, 126.84, 125.55, 123.86, 115.36, 75.46, 70.42; HRMS (ESI) calcd for  $\text{C}_{20}\text{H}_{16}\text{N}_4\text{ONa}$ :  $m/z$  ( $[\text{M}+\text{Na}^+]$ ) 351.1216, found 351.1209; IR (KBr) 3052, 2959, 2921, 2893, 1632, 1589, 1573, 1436, 1364, 1150, 1107, 1074, 981, 762, 701  $\text{cm}^{-1}$



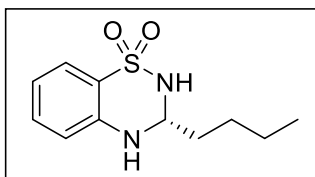
**(S)-2b**: 39% yield (over 2 steps); red oil;  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.30 (d,  $J = 7.3$  Hz, 1H), 7.99 (t,  $J = 7.8$  Hz, 1H), 7.89 (d,  $J = 7.2$  Hz, 1H), 7.73 (s, 2H), 7.40-7.29 (m, 5H), 7.18 (s, 1H), 5.50 (dd,  $J = 10.3, 8.7$  Hz, 1H), 4.95 (dd,  $J = 10.3, 8.7$  Hz, 1H), 4.45 (t,  $J = 8.7$  Hz, 1H), 2.41 (s, 6H);  $^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.56, 162.90, 152.38, 146.41, 141.70, 138.98, 138.77, 134.11, 128.79, 127.76, 126.81, 125.39, 121.69, 114.96, 75.44, 70.35, 21.16; HRMS (ESI) calcd for  $\text{C}_{22}\text{H}_{20}\text{N}_4\text{O}_6\text{Na}$ :  $m/z$  ( $[\text{M}+\text{Na}^+]$ ) 379.1529, found 379.1524; IR (KBr) 3063, 2959, 2915, 2860, 1638, 1567, 1442, 1364, 1277, 1129, 1107, 981, 849, 817, 745  $\text{cm}^{-1}$



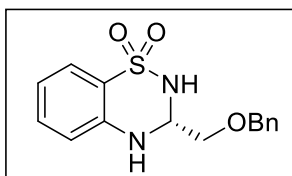
(*R*)-**5a**<sup>2,3,4</sup>: 95% yield (Table 2, entry 6); white solid; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 (t, *J* = 7.8 Hz, 1H), 7.30-7.25 (m, 1H), 6.83 (q, *J* = 7.2 Hz, 1H), 6.69-6.65 (m, 1H), 5.01-4.91 (m, 1H), 4.46 (s, 1H), 4.33 (d, *J* = 12.8 Hz, 1H), 1.97-1.85 (m, *J* = 13.5, 6.7 Hz, 1H), 1.77-1.68 (m, *J* = 14.1, 7.8 Hz, 1H), 1.62-1.54 (m, 1H), 1.01 (d, *J* = 2.4 Hz, 3H), 0.99 (d, *J* = 2.4 Hz, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 142.42, 133.23, 124.73, 118.86, 116.21, 64.80, 43.64, 24.05, 22.57, 22.28; HRMS (ESI) calcd for C<sub>11</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>SNa: *m/z* ([M+Na<sup>+</sup>]) 263.0825, found 263.0824; IR (KBr) 3381, 3222, 2953, 2866, 1605, 1567, 1496, 1326, 1287, 1156, 1085, 926, 745, 559 cm<sup>-1</sup>; HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/<sup>i</sup>PrOH = 80/20, 1.0 mL/min, 250 nm, t<sub>R</sub> = 7.6 min (major) and 16.8 min (minor).



(*R*)-**5b**<sup>3,4</sup>: 76% yield (Scheme 2, under dark); white solid; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64-7.61 (m, 1H), 7.31-7.25 (m, 1H), 6.86-6.81 (m, 1H), 6.69 (m, 1H), 4.76 (dd, *J* = 13.3, 4.6 Hz, 1H), 4.47 (s, 1H), 4.32 (m, 1H), 2.06-1.97 (m, 1H), 1.11 (m, 6H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 142.68, 133.26, 124.75, 122.58, 118.83, 116.24, 70.55, 32.05, 17.64, 16.62; HRMS (ESI) calcd for C<sub>11</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>SNa: *m/z* ([M+Na<sup>+</sup>]) 249.0668 found 249.0666; IR (KBr) 3358, 3326, 2967, 2869, 1602, 1575, 1488, 1326, 1281, 1161, 1080, 905, 748, 569 cm<sup>-1</sup>; HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/<sup>i</sup>PrOH = 80/20, 1.0 mL/min, 250 nm, t<sub>R</sub> = 8.3 min (major) and 30.1 min (minor).



(*R*)-**5c**<sup>4</sup>: 81% yield (Scheme 2, under dark); white solid; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.29-7.25 (m, 1H), 6.85-6.81 (m, 1H), 6.67 (d, *J* = 8.2 Hz, 1H), 4.94-4.88 (m, 1H), 4.52 (s, 1H), 4.36 (d, *J* = 12.8 Hz, 1H), 1.78 (q, *J* = 7.0 Hz, 2H), 1.57-1.36 (m, 4H), 0.94 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 142.49, 133.26, 124.73, 122.54, 118.82, 116.18, 66.18, 34.47, 26.32, 22.21, 13.83; HRMS (ESI) calcd for C<sub>11</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>SNa: *m/z* ([M+Na<sup>+</sup>]) 263.0825, found 263.0826; IR (KBr) 3375, 3225, 2950, 2917, 2858, 1700, 1592, 1483, 1317, 1167, 1142, 742, 558 cm<sup>-1</sup>; HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/<sup>i</sup>PrOH = 80/20, 1.0 mL/min, 250 nm, t<sub>R</sub> = 7.6 min (major) and 17.5 min (minor).



(*R*)-**5d**<sup>4</sup>: 54% yield (Scheme 2, under dark); white solid; <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) δ 7.64 (d, *J* = 7.8 Hz, 1H), 7.41-7.28 (m, 6H), 6.85 (t, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 8.2 Hz, 1H), 5.14-5.08 (m, 1H), 4.80 (s, 1H), 4.68 (d, *J* = 12.8 Hz, 1H), 4.60 (s, 2H), 3.80 (dd, *J* = 10.1, 2.7 Hz, 1H), 3.68 (q, *J* = 5.0 Hz, 1H); <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) δ 142.33, 136.67, 133.31, 128.70, 128.38, 128.05, 124.65, 122.76, 119.08, 116.84, 73.79, 69.98, 64.69; HRMS (ESI) calcd for C<sub>11</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>SNa: *m/z* ([M+Na<sup>+</sup>]) 263.0774, found 263.0767; IR (KBr) 3364, 3239, 3027, 2864, 1607, 1569, 1488, 1389, 1362, 1308, 1281, 1150, 1123, 1064, 738, 693, 580, 547, 514 cm<sup>-1</sup>; HPLC

conditions: Daicel Chiralpak OD-H column, *n*-hexane/*i*PrOH = 80/20, 1.0 mL/min, 240 nm, tR = 18.3 min (major) and 26.1 min (minor).

## Photoisomerization experiments of **2** and **2-La** complexes

### Photoisomerization of **2a**

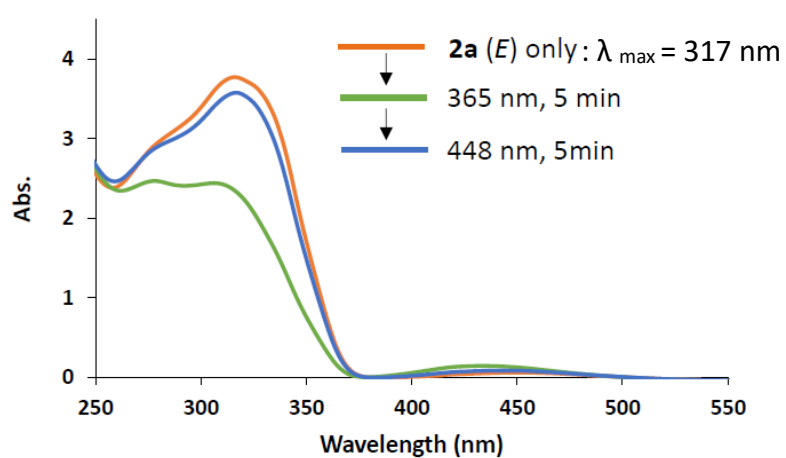
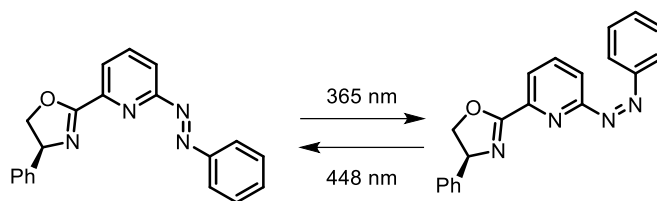


Fig. S1 UV-Vis spectra of **2a** (250  $\mu\text{M}$ ) in MeCN.

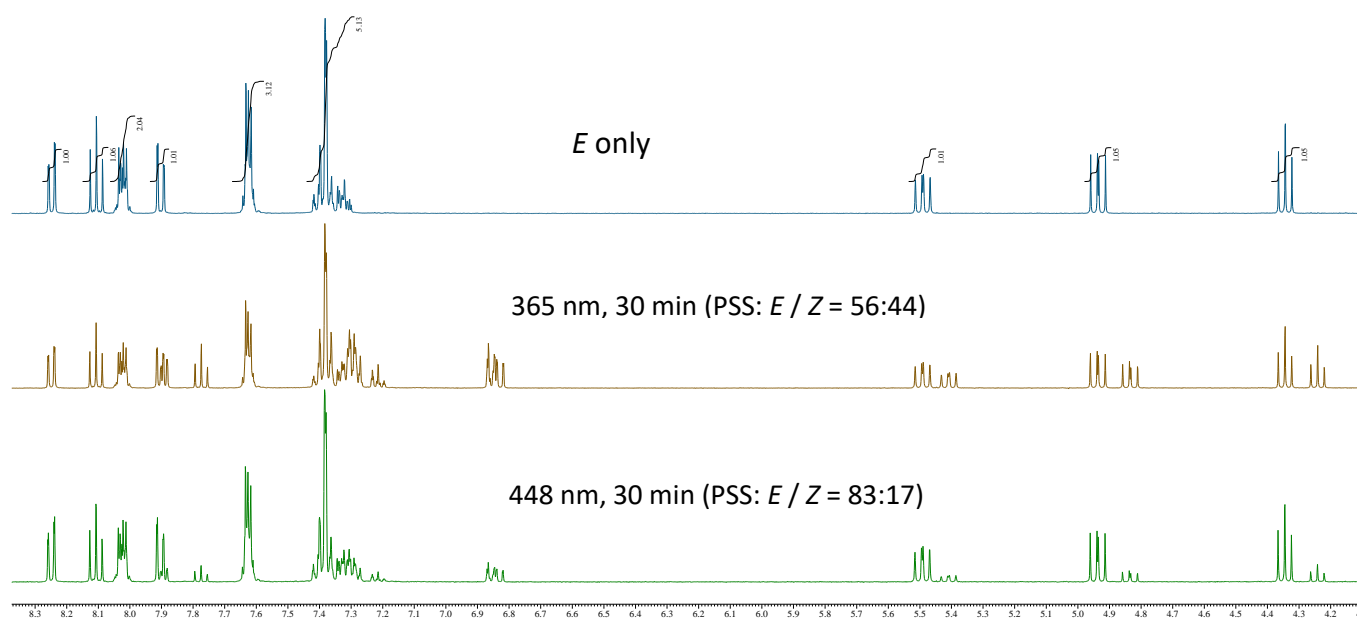


Fig. S2  $^1\text{H-NMR}$  of **2a** (8 mM) in  $\text{CD}_3\text{CN}$ .

## Photoisomerization of **2a**-La(OTf)<sub>3</sub>

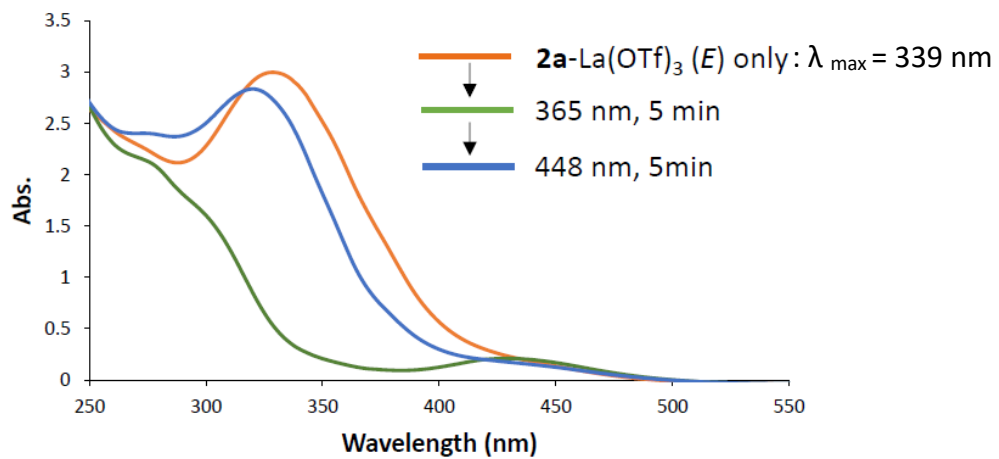


Fig. S3 UV-Vis spectra of **2a**-La(OTf)<sub>3</sub> (250  $\mu$ M) in MeCN.

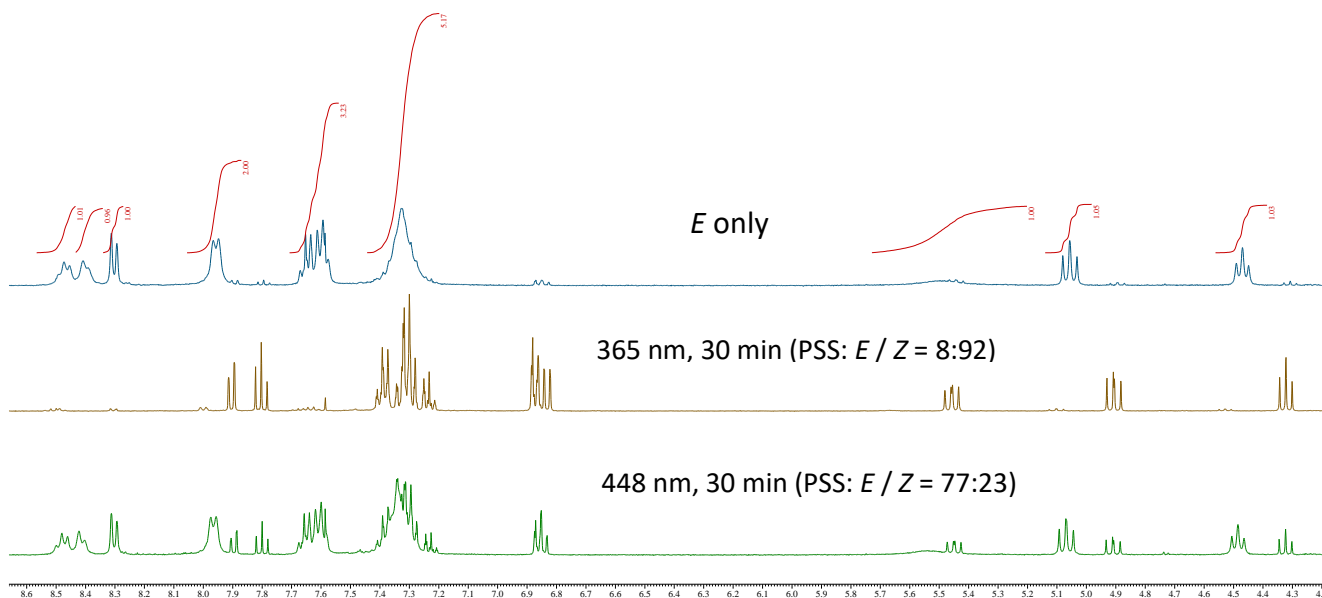


Fig. S4 <sup>1</sup>H-NMR of **2a**-La(OTf)<sub>3</sub> (8 mM) in CD<sub>3</sub>CN.



Peak shifting of (*E*) or (*Z*)-**2a** after coordination to La(OTf)<sub>3</sub>

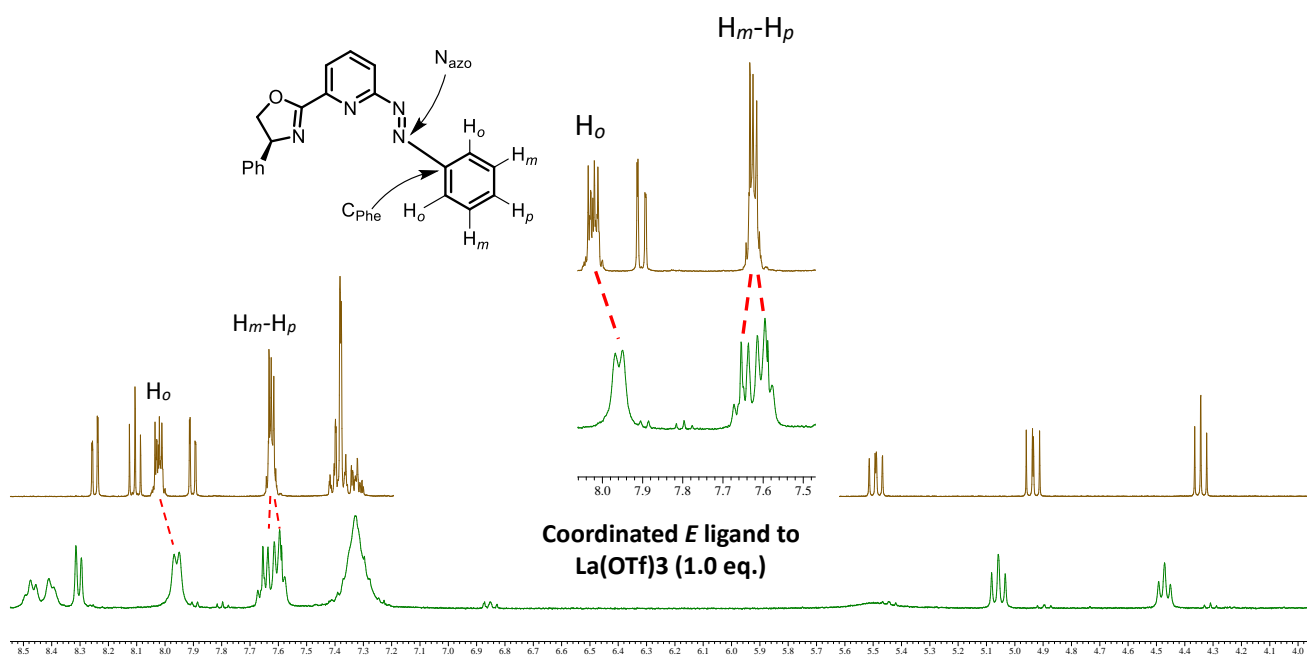


Fig. S5 Comparison of (*E*)-**2a** and (*E*)-**2a**-La(OTf)<sub>3</sub> (8 mM) in CD<sub>3</sub>CN: H<sub>o</sub> was shifted and broadening, and H<sub>m-p</sub> were splitted, supporting coordination of azo group with slow C<sub>Phe</sub>-N<sub>azo</sub> rotation.

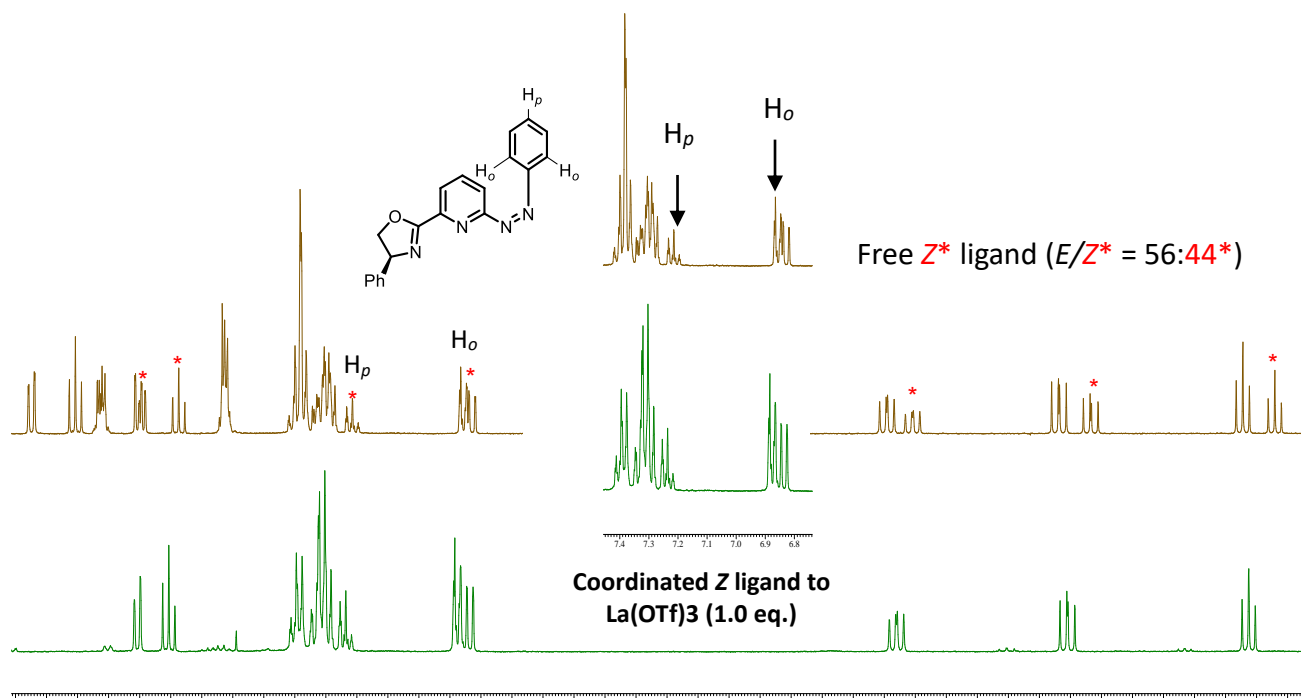


Fig. S6 Comparison of (*Z*)-**2a** and (*Z*)-**2a**-La(OTf)<sub>3</sub> (8 mM) in CD<sub>3</sub>CN: H<sub>o</sub> and H<sub>p</sub> were assigned but there was no apparent peak shift, supporting azo group was not participating into coordination.

## Photoisomerization of **2b**

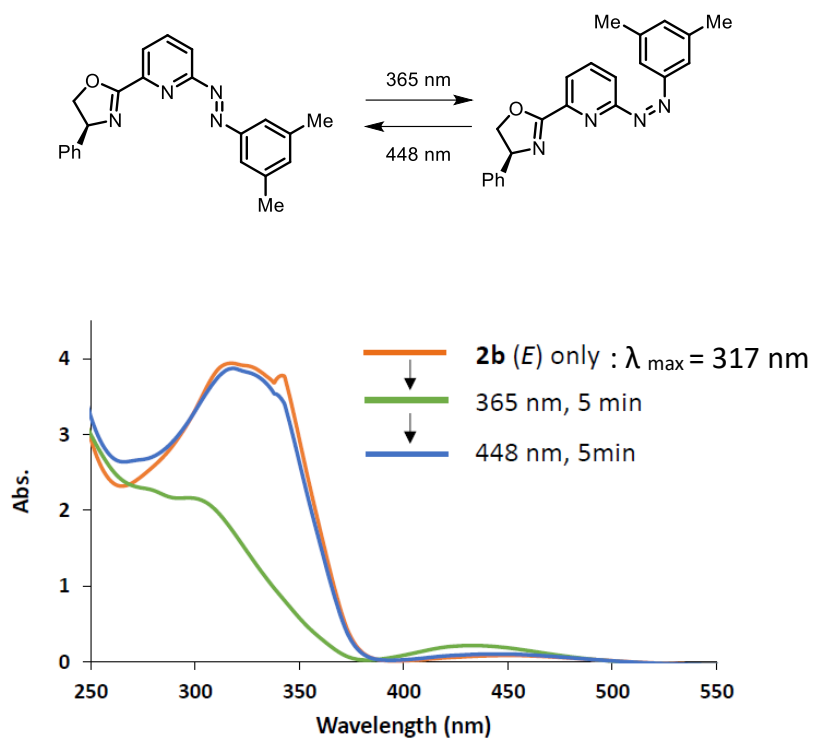


Fig. S7 UV-Vis spectra of **2b** (250 μM) in MeCN.

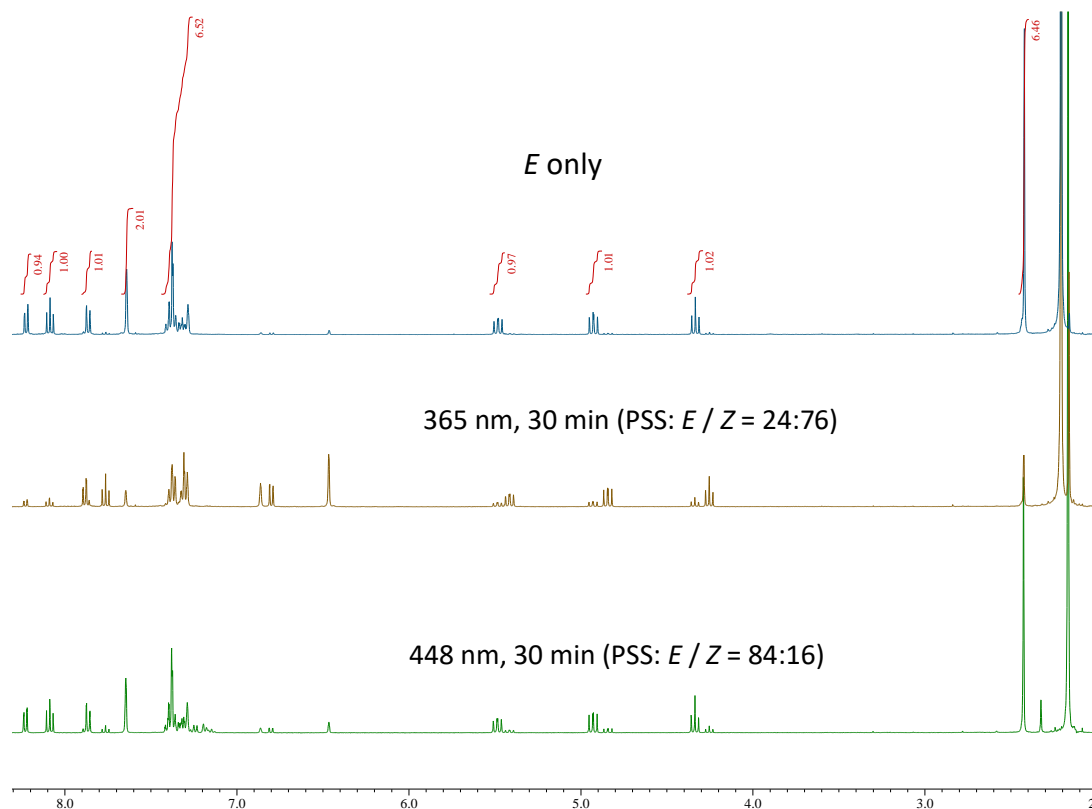


Fig. S8 <sup>1</sup>H-NMR of **2b** (8 mM) in CD<sub>3</sub>CN.

Photoisomerization of **2b**-La(OTf)<sub>3</sub>

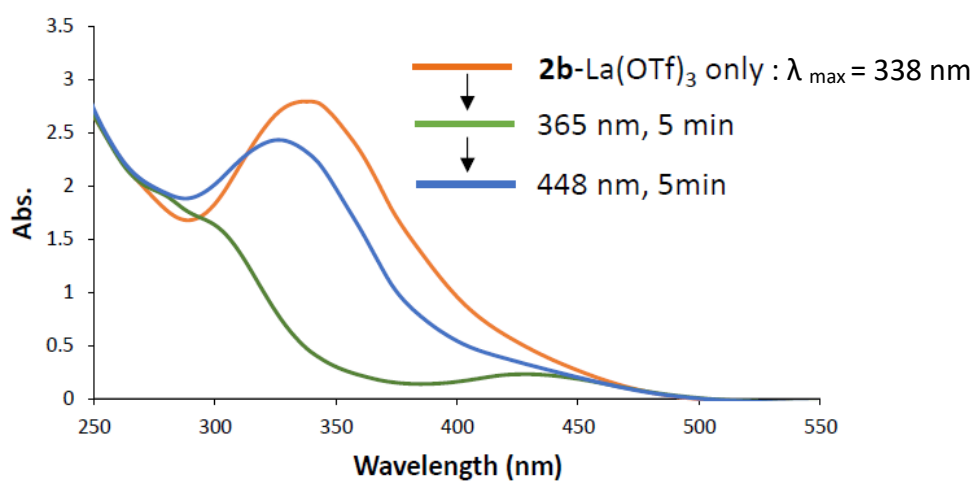


Fig. S9 UV-Vis spectra of **2b**-La(OTf)<sub>3</sub> (250 μM) in MeCN.

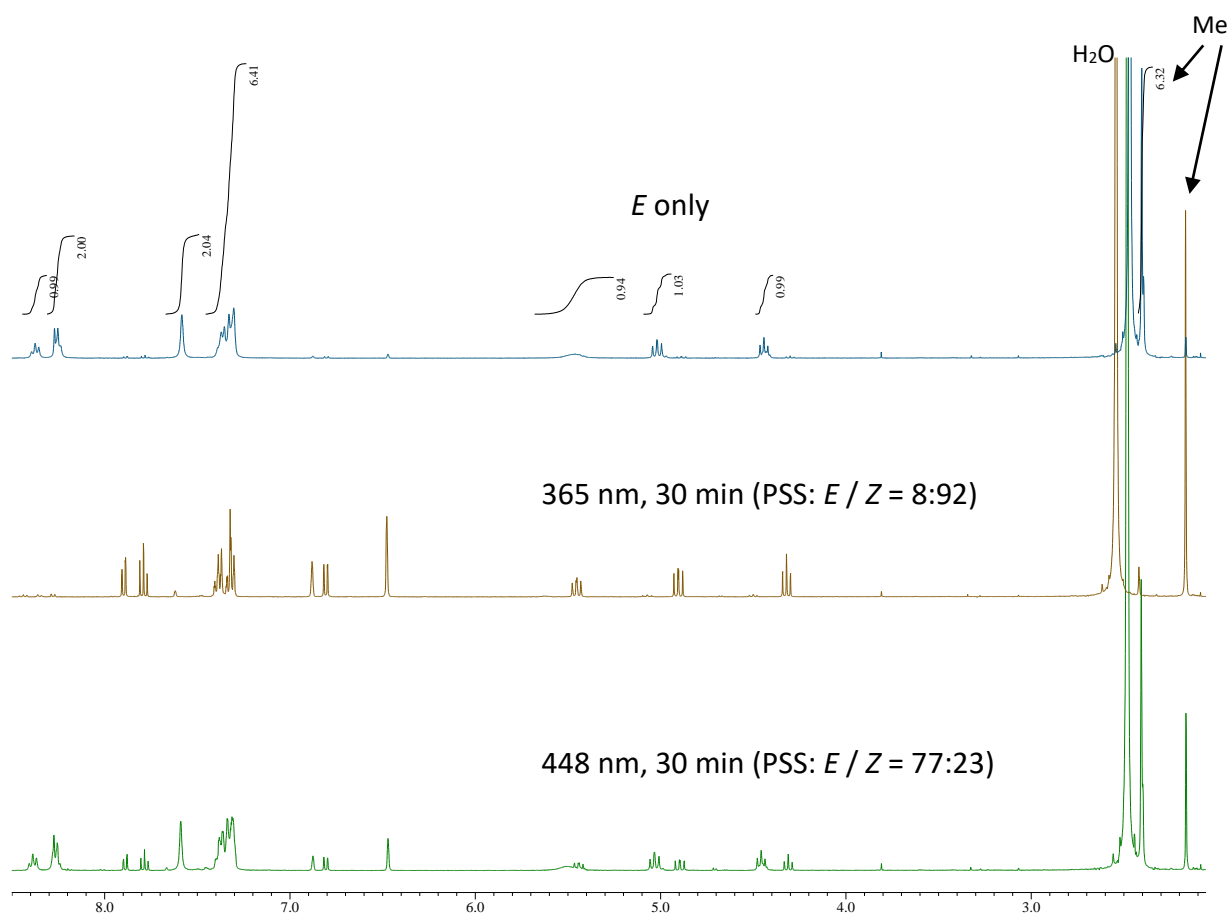


Fig. S10 <sup>1</sup>H-NMR of **2b**-La(OTf)<sub>3</sub> (8 mM) in CD<sub>3</sub>CN.

Peak shifting of (*E*) or (*Z*)-**2b** after coordination to La(OTf)<sub>3</sub>

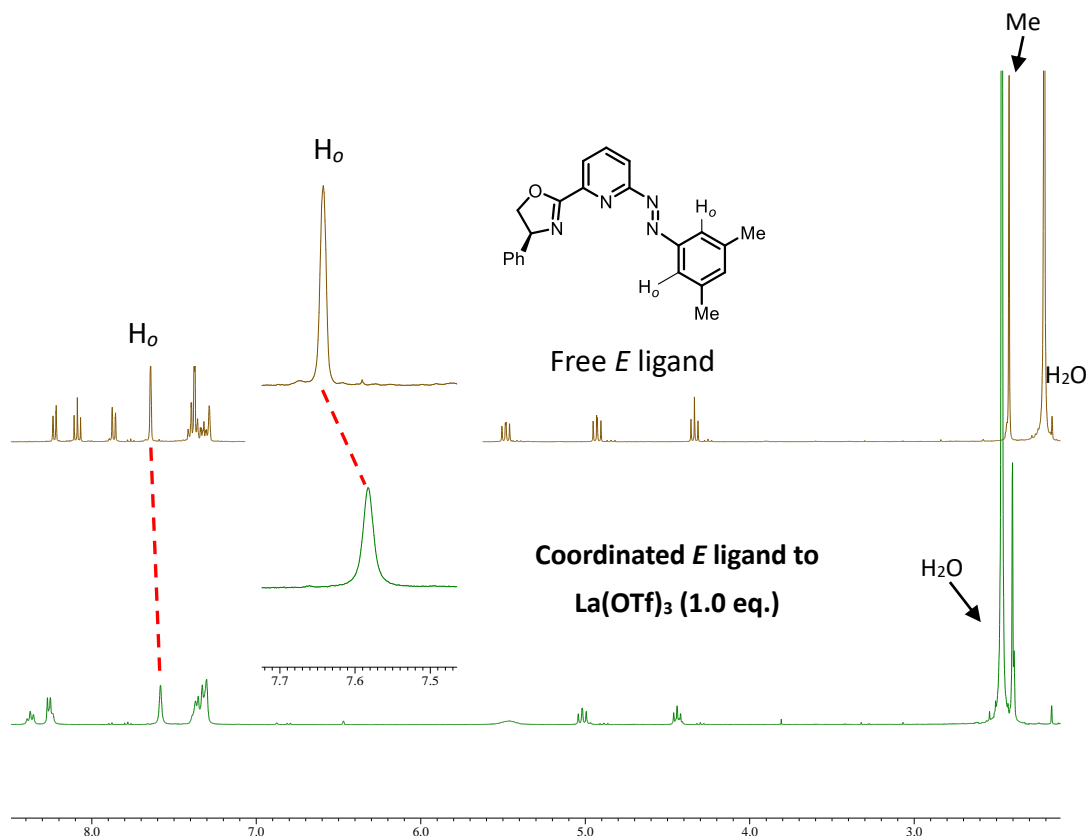


Fig. S11 Comparison of (*E*)-**2b** and (*E*)-**2b**-La(OTf)<sub>3</sub> (8 mM) in CD<sub>3</sub>CN: H<sub>o</sub> was shifted to indicate coordination of azo group.

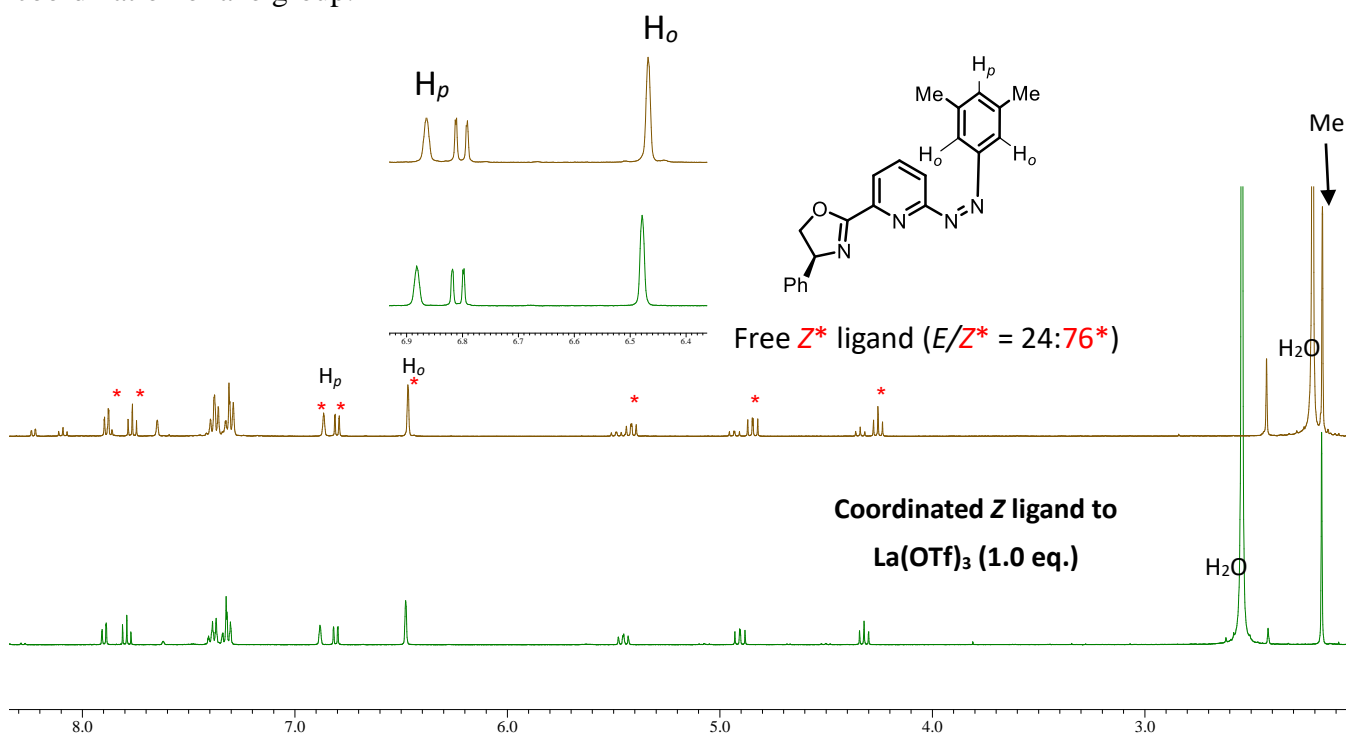
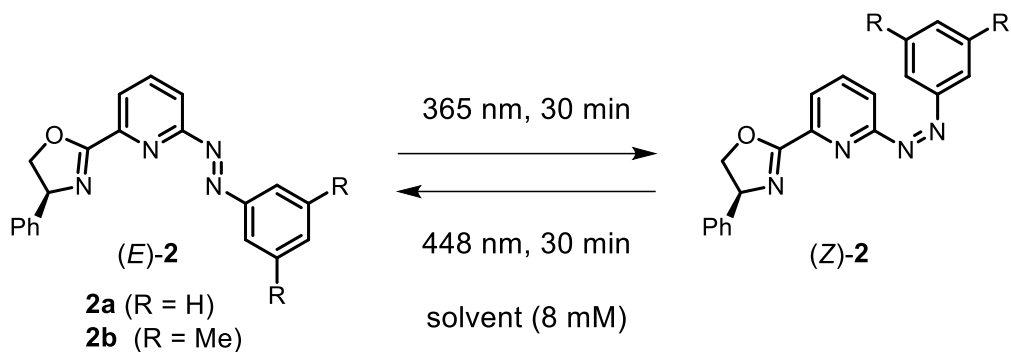


Fig. S12 Comparison of (*Z*)-**2b** and (*Z*)-**2b**-La(OTf)<sub>3</sub> (8 mM) in CD<sub>3</sub>CN: H<sub>o</sub> and H<sub>p</sub> were assigned but there was no apparent peak shift, supporting azo group was not participating into coordination.

Table S1. Solvent effect on the PSS.



entry	<b>2</b>	solvent	365 nm <i>E/Z</i> <sup>a</sup>	448 nm <i>E/Z</i> <sup>a</sup>
1	<b>2a</b>	MeCN- <i>d</i> <sub>3</sub>	56:44	83:17
2	<b>2b</b>		24:76	84:16
3	<b>2a</b>	toluene- <i>d</i> <sub>8</sub>	53:47	88:12
4	<b>2b</b>		23:77	88:12
5	<b>2a</b>	THF- <i>d</i> <sub>8</sub>	63:37	86:14
6	<b>2b</b>		35:65	87:13
7	<b>2a</b>	CDCl <sub>3</sub>	50:50	88:12
8	<b>2b</b>		20:80	88:12

<sup>a</sup> Determined by <sup>1</sup>H-NMR

## Half-life of (Z)-2 and (Z)-2-La complexes

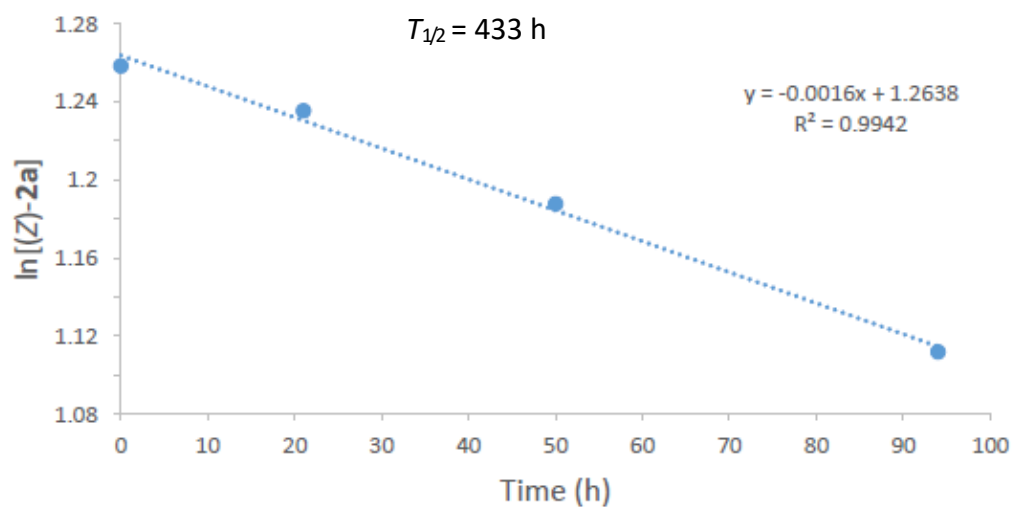


Fig. S13 First order kinetic plot for the thermal reimerization of (Z)-2a at 20 °C in CD<sub>3</sub>CN.

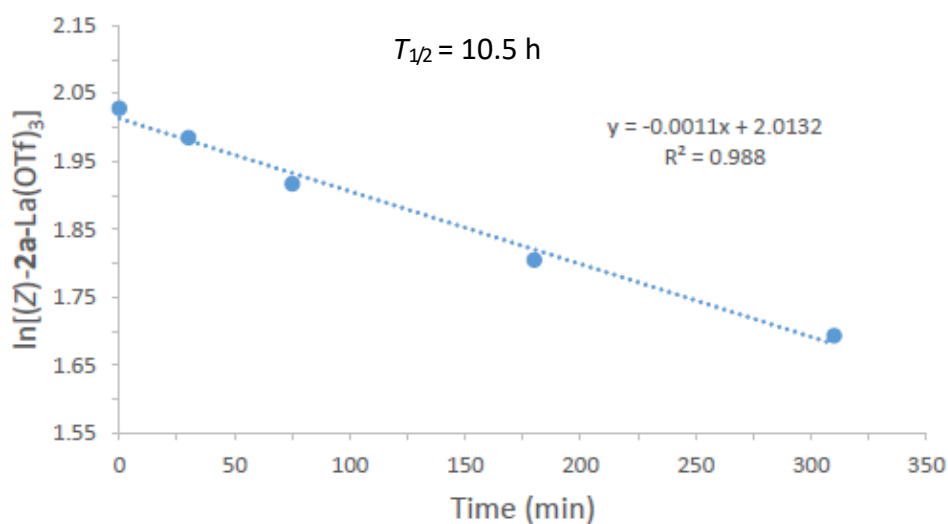


Fig. S14 First order kinetic plot for the thermal reimerization of (Z)-2a-La(OTf)<sub>3</sub> at 20 °C in CD<sub>3</sub>CN.

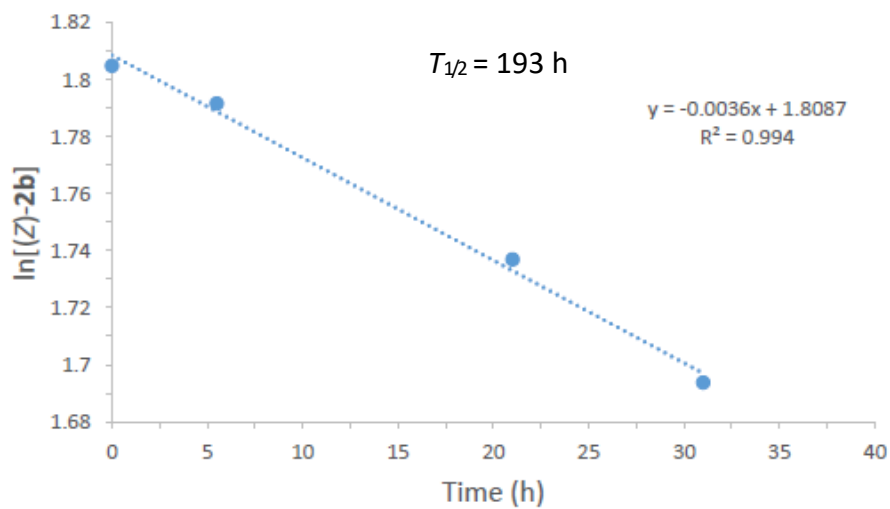


Fig. S15 First order kinetic plot for the thermal reversion of (Z)-**2b** at 20 °C in CD<sub>3</sub>CN.

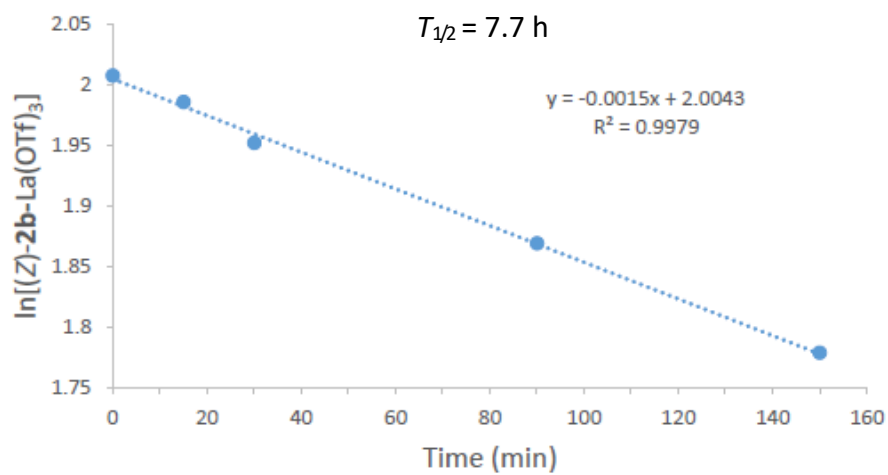
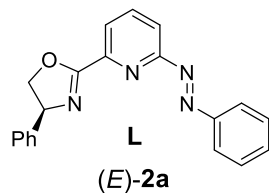


Fig. S16 First order kinetic plot for the thermal reversion of (Z)-**2b**-La(OTf)<sub>3</sub> at 20 °C in CD<sub>3</sub>CN.

### Mass spectra of (*E*)-2a-La complex

A cationic  $L_2\text{-RE}(\text{OTf})_2^+$  ( $L = i\text{Pr-Pybox}$ ) can be observed for the tridentate Pybox, according to the previous report by Aspinall.<sup>5</sup> The observed spectra for (*E*)-2a (Fig. S17) also showed  $L_2\text{-La}(\text{OTf})_2^+$  ( $L = (E)\text{-2a}$ ) and it agrees well with the theoretical spectra (Fig. S18).



Calcd for  $\text{C}_{42}\text{H}_{32}\text{F}_6\text{LaN}_8\text{O}_8\text{S}_2^+$ :  $m/z$  ( $[\text{M}^+]$ ):  
1093.0747 found 1093.0758

MS-166\_APCI\_1223 #20 RT: 0.27 AV: 1 NL: 9.84E5  
T: FTMS + p APCI corona Full ms [500.00-1500.00]

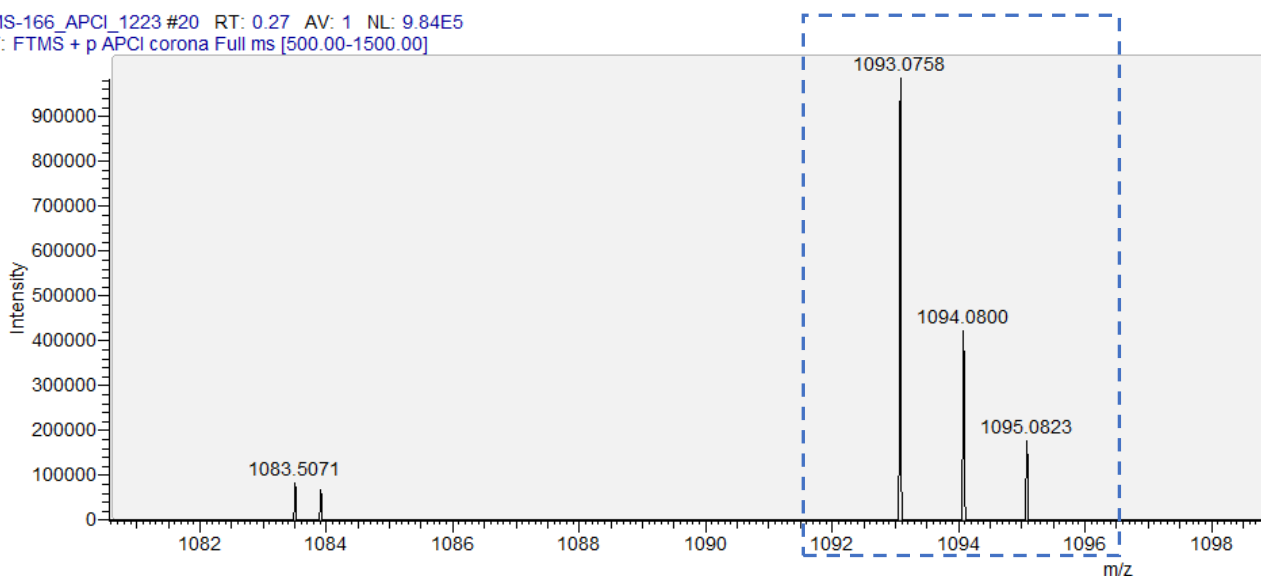


Fig. S17 APCI-MS spectra of  $L_2\text{-La}(\text{OTf})_2^+$  ( $L = (E)\text{-2a}$ )

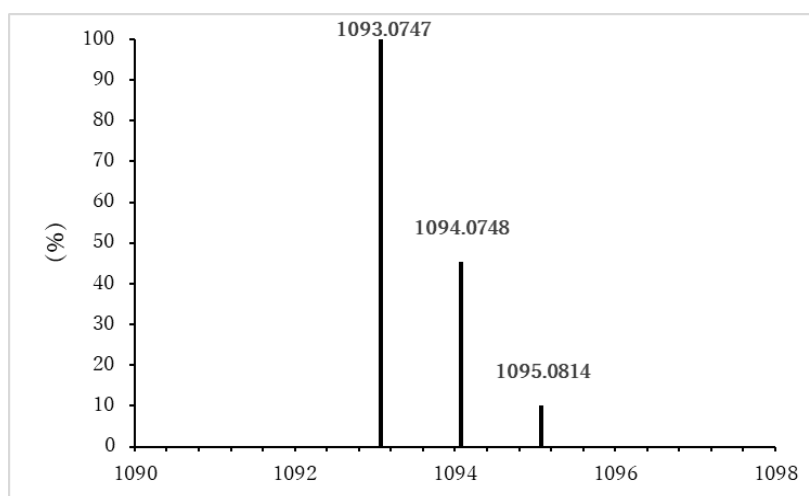


Fig. S18 Theoretical spectra of  $L_2\text{-La}(\text{OTf})_2^+$  ( $L = (E)\text{-2a}$ )



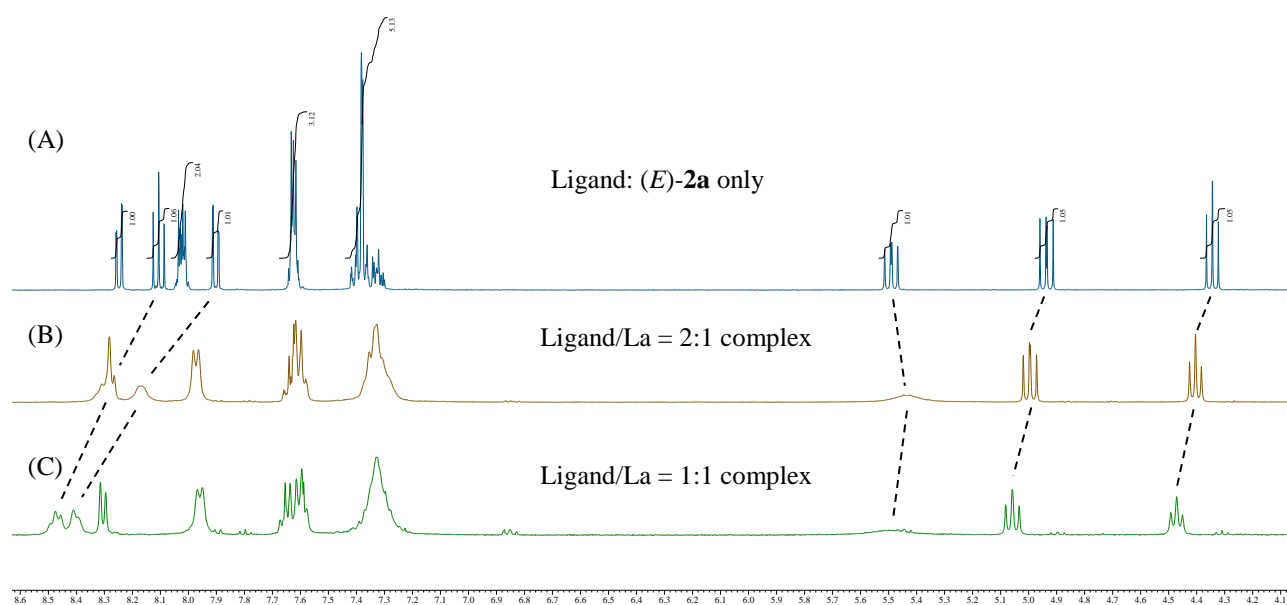
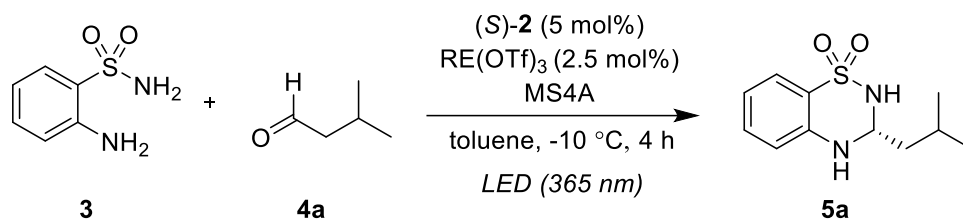


Fig. S19 Comparison of the <sup>1</sup>H-NMR spectra of (A) (*E*)-2a, (B) (*E*)-2a + La(OTf)<sub>3</sub> (0.5 eq.), and (C) (*E*)-2a + La(OTf)<sub>3</sub> (1.0 eq.) (8 mM, CD<sub>3</sub>CN).

**General procedure for the 2-RE(OTf)<sub>3</sub> catalyzed enantioselective intermolecular cyclization of sulfonamide **3** and aldehyde **4** (Table 2).**



The following procedure was conducted under nitrogen atmosphere and photoirradiation with LED (365 nm). To a flame dried test tube equipped with LED were added (S)-**2** (5 mol%) and toluene (0.7 mL). Photoirradiation was started and the solution was stirred for 30 min at 0 °C. After that, RE(OTf)<sub>3</sub> (2.5 mol%) was added to the solution and the stirring was continued for another 30 min at 0 °C, followed by the addition of MS4A (17 mg), **3** (12.1 mg, 0.07 mmol) and **4a** (7.5 μL, 1.0 eq.) at -10 °C. After 4 h, the mixture was pathed through short pad of silica and washed with EtOAc to give crude mixture. A small part of the mixture was taken and purified by preparative TLC (eluent: hexane-ethyl acetate) to immediately complete HPLC analysis in 1 h. The rest of the mixture was purified by silica gel column chromatography using hexane-ethyl ethyl acetate as an eluent to provide **5a**.<sup>2,3,4</sup> The reaction under dark was conducted without LED.

Although **5a** is reported to racemize at room temperature,<sup>2</sup> it did not proceed during the course of reaction and after the immediate purification with preparative TLC (Table. S2). The racemization of HPLC sample in <sup>t</sup>PrOH was sufficiently slow ( $T_{1/2}$  = 6.2 h at 20 °C) to ensure all of the obtained ee value (Fig. S20).

Table S2. Time course measurement of the ee of **5a**

$\text{3} + \text{4a} \xrightarrow[\text{toluene, -10 }^\circ\text{C, time under dark}]{\text{(S)-2a (5 mol\%), La(OTf)}_3 \text{ (2.5 mol\%), MS4A}}$		(R)- <b>5a</b>
entry	time (h)	ee of <b>5a</b> (%)
1	1	66 <sup>a</sup>
2	2	67 <sup>a</sup>
3	3	68 <sup>a</sup>
4	4	67 <sup>a</sup>
5	4	68 <sup>b</sup>

<sup>a</sup> Determined as crude state. <sup>b</sup>After purification with preparative TLC.

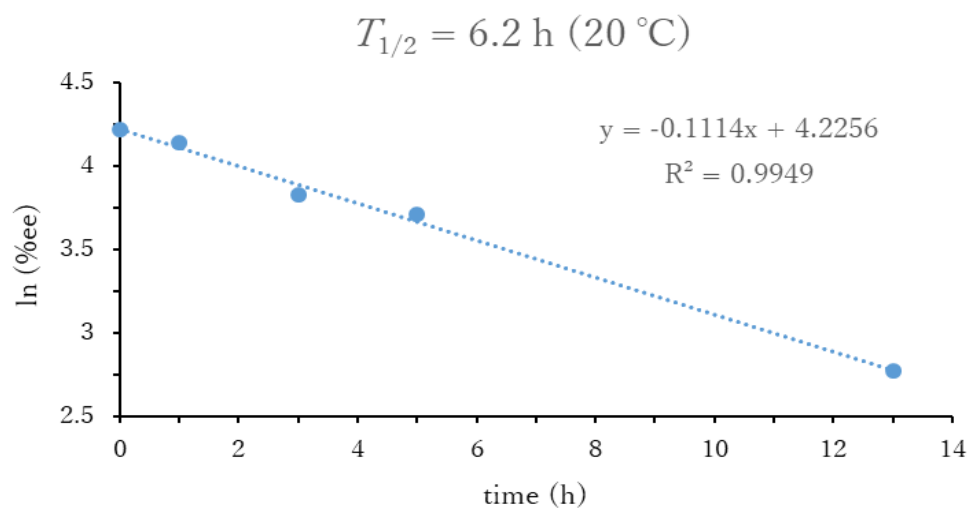


Fig. S20 Racemization rate of (*R*)-**5a** in *i*PrOH monitored by HPLC (20 °C). HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/*i*PrOH = 80/20, 1.0 mL/min, 250 nm.

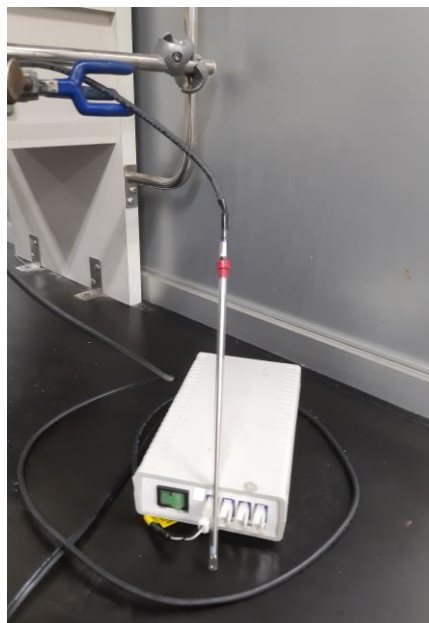
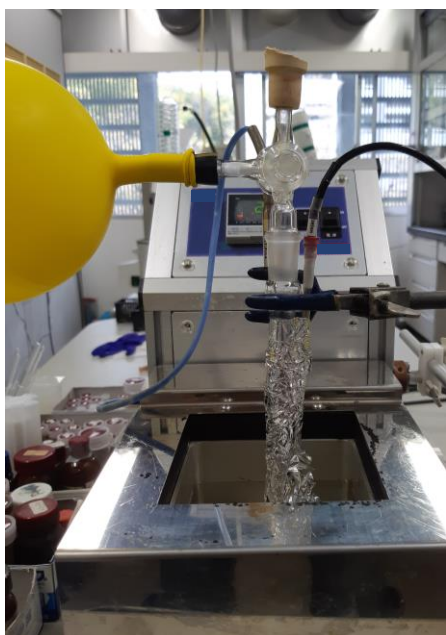
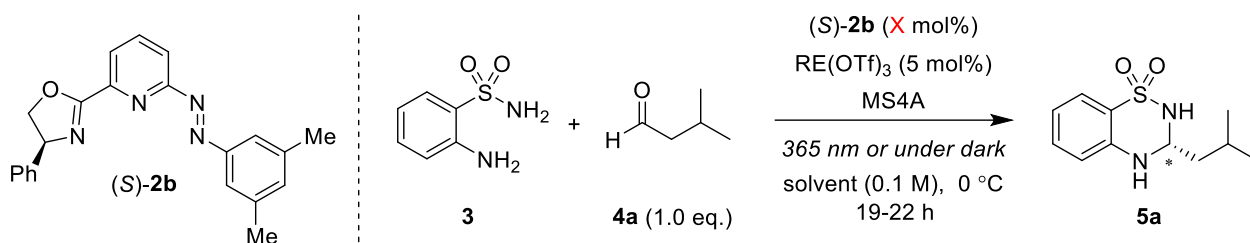


Fig. S21 Reaction setting with LED (left), and LED apparatus (PER-AMP) (right).

## Reaction condition optimization

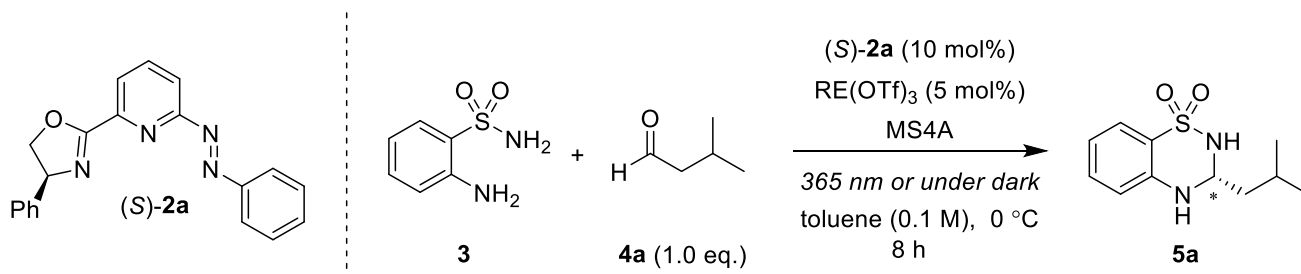
Table S3. Initial condition screening and solvent effect.



entry	LED	X	RE(OTf) <sub>3</sub>	solvent	yield (%) <sup>a</sup>	ee (%)
1	365 nm	5	Sc(OTf) <sub>3</sub>	DCM	87	6
2	under dark					19
3	365 nm	10	Sc(OTf) <sub>3</sub>	DCM	95<	21
4	under dark					38
5	365 nm	10	La(OTf) <sub>3</sub>	DCM	76	26
6	under dark					49
7	365 nm	10	La(OTf) <sub>3</sub>	toluene	88	30
8	under dark					63
9	365 nm	10	La(OTf) <sub>3</sub>	MeCN	78	0
10	under dark					48

<sup>a</sup> Determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as an internal standard.

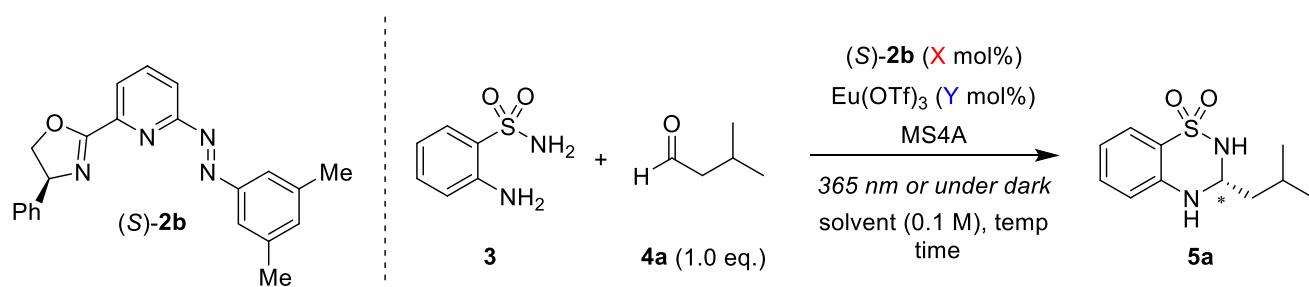
Table S4. Metal screening.



entry	RE(OTf) <sub>3</sub>	LED	yield (%) <sup>a</sup>	ee (%)
1	La(OTf) <sub>3</sub>	365 nm	95<	32
2		under dark	95<	65
-----				
3	Eu(OTf) <sub>3</sub>	365 nm	95<	23
4		under dark	95<	64
-----				
5	Gd(OTf) <sub>3</sub>	365 nm	79	41
6		under dark	77	69
-----				
7	Yb(OTf) <sub>3</sub>	365 nm	95<	30
8		under dark	95<	59

<sup>a</sup> Determined by <sup>1</sup>H-NMR using 1,3,5-trimethoxybenzene as an internal standard.

Table S5. Catalyst loading, metal/ligand ratio, and temperature effect on the Eu catalyzed reaction.



entry	$X / Y$	LED	temp. ( $^{\circ}\text{C}$ )	time (h)	yield (%)	ee (%)
1		$365\text{ nm}$			$31^a$	49
2	20 / 10	<i>under dark</i>	-20	8	$67^a$	75
3		$365\text{ nm}$			$28^a$	49
4	10 / 5	<i>under dark</i>	-20	8	$61^a$	74
5		$365\text{ nm}$			$88^b$	32
6	5 / 2.5	<i>under dark</i>	-10	4	$95^b$	72
7		$365\text{ nm}$			$67^a$	45
8	7.5 / 2.5	<i>under dark</i>	-10	4	$67^a$	77
9		$365\text{ nm}$			$89^a$	40
10	12.5 / 2.5	<i>under dark</i>	-10	4	$88^a$	66

<sup>a</sup> Determined by  $^1\text{H-NMR}$  using 1,3,5-trimethoxybenzene as an internal standard. <sup>b</sup> Isolated yield.

## Plausible stereochemical model

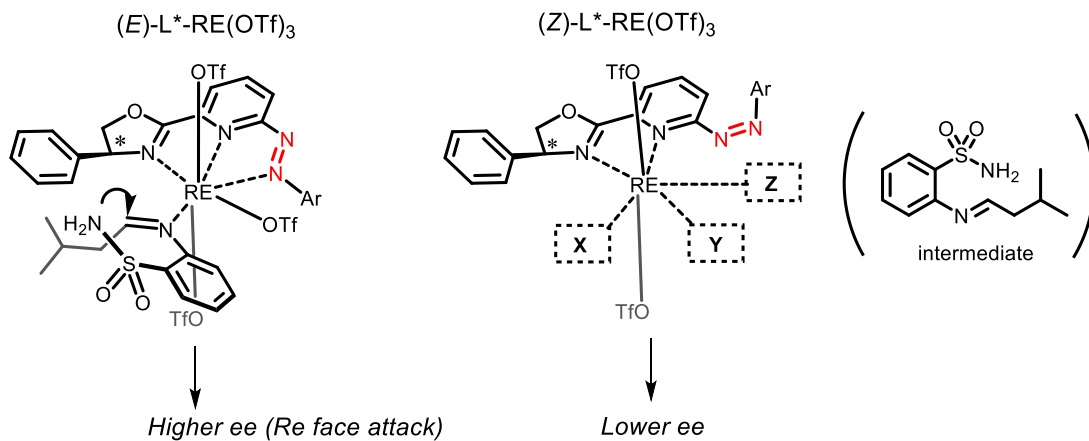


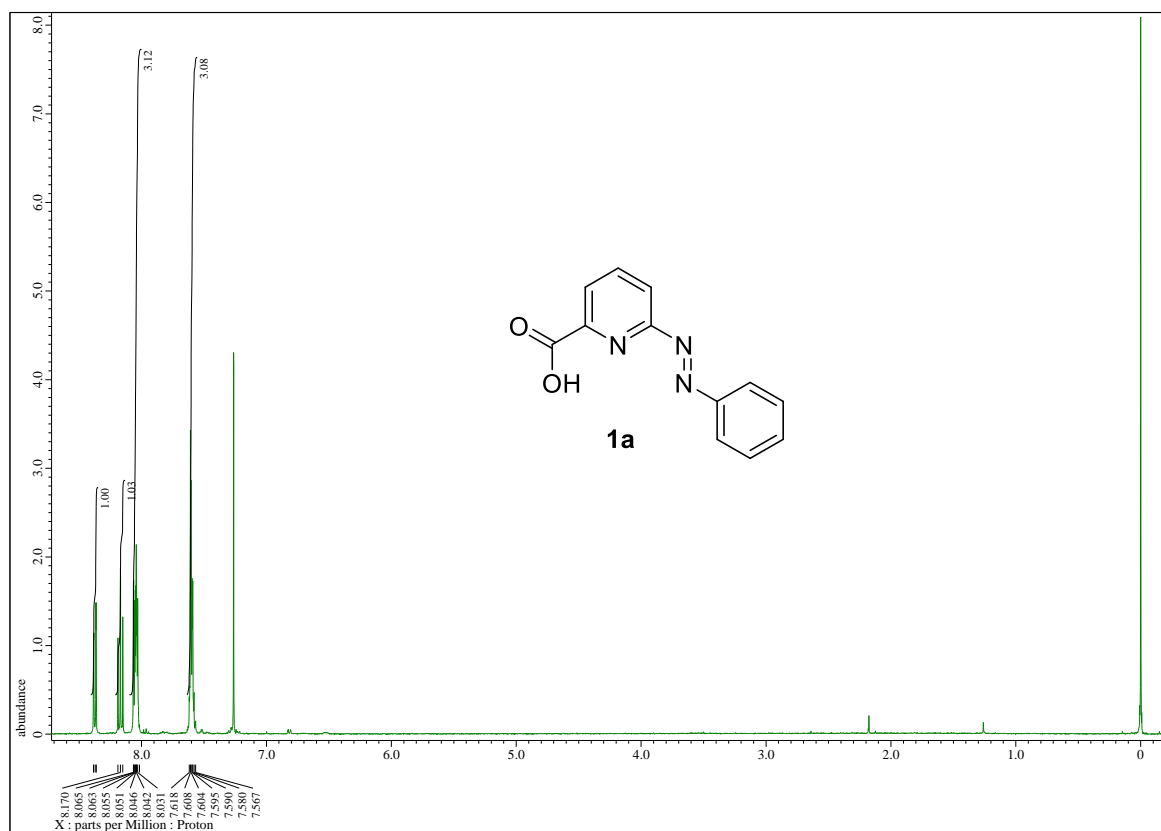
Fig. S22. Plausible stereochemical model for the 1:1 complex: in the  $Z$  state (right), the imine intermediate would be accessible to  $Y$  or  $Z$ , resulting in the cyclization reaction away from the chiral oxazoline.

## References

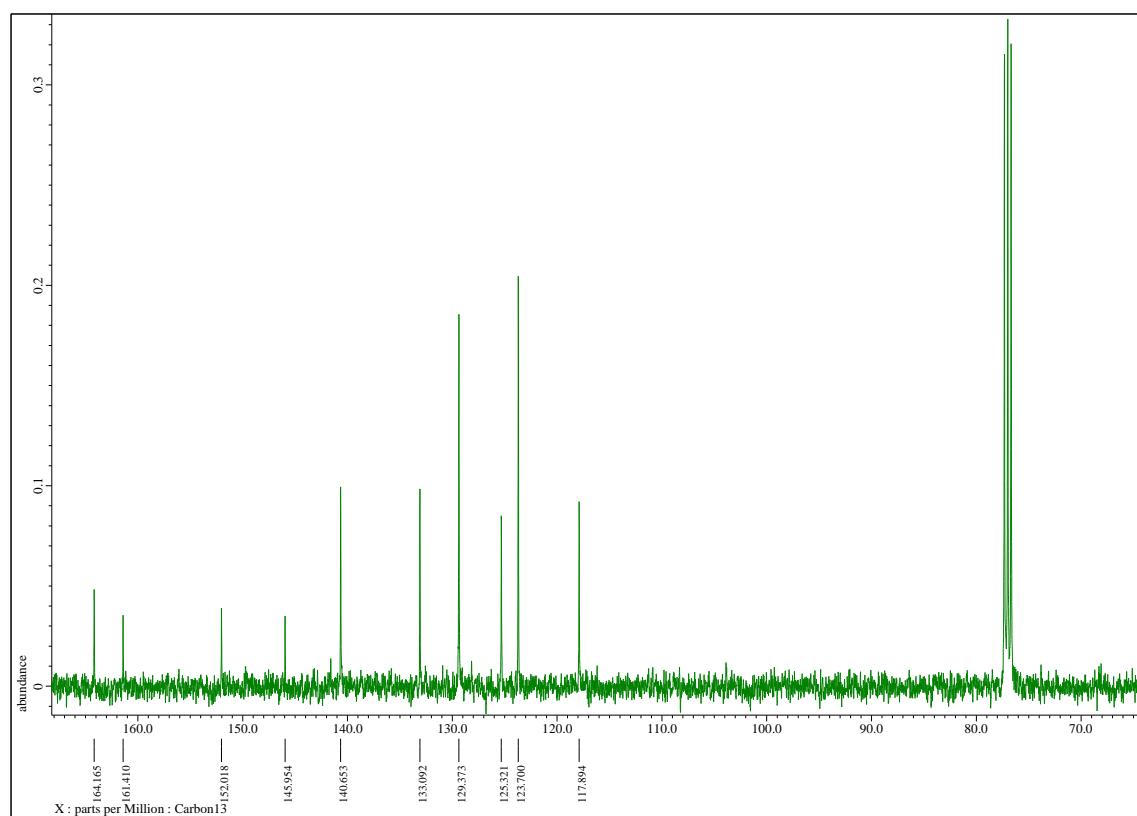
1. Y. Xiao, X. Wu, H. Wang, S. Sun, J.-T. Yu and J. Cheng, *Org. Lett.*, 2019, **21**, 2565–2568.
2. X. Cheng, S. Vellalath, R. Goddard and B. List, *J. Am. Chem. Soc.*, 2008, **130**, 15786–15787.
3. P. Du, H. Zhou, Y. Sui, Q. Liu and K. Zou, *Tetrahedron*, 2016, **72**, 1573–1578.
4. Y. Sui, P. Cui, S. Liu, Y. Zhou, P. Du and H. Zhou, *Eur. J. Org. Chem.*, 2018, 215–218.
5. H. C. Aspinall, J. F. Bickley, N. Greeves, R. V. Kelly and P. M. Smith, *Organometallics*, 2005, **24**, 3458–3467.

# <sup>1</sup>H-, <sup>13</sup>C-NMR charts

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) chart of **1a**

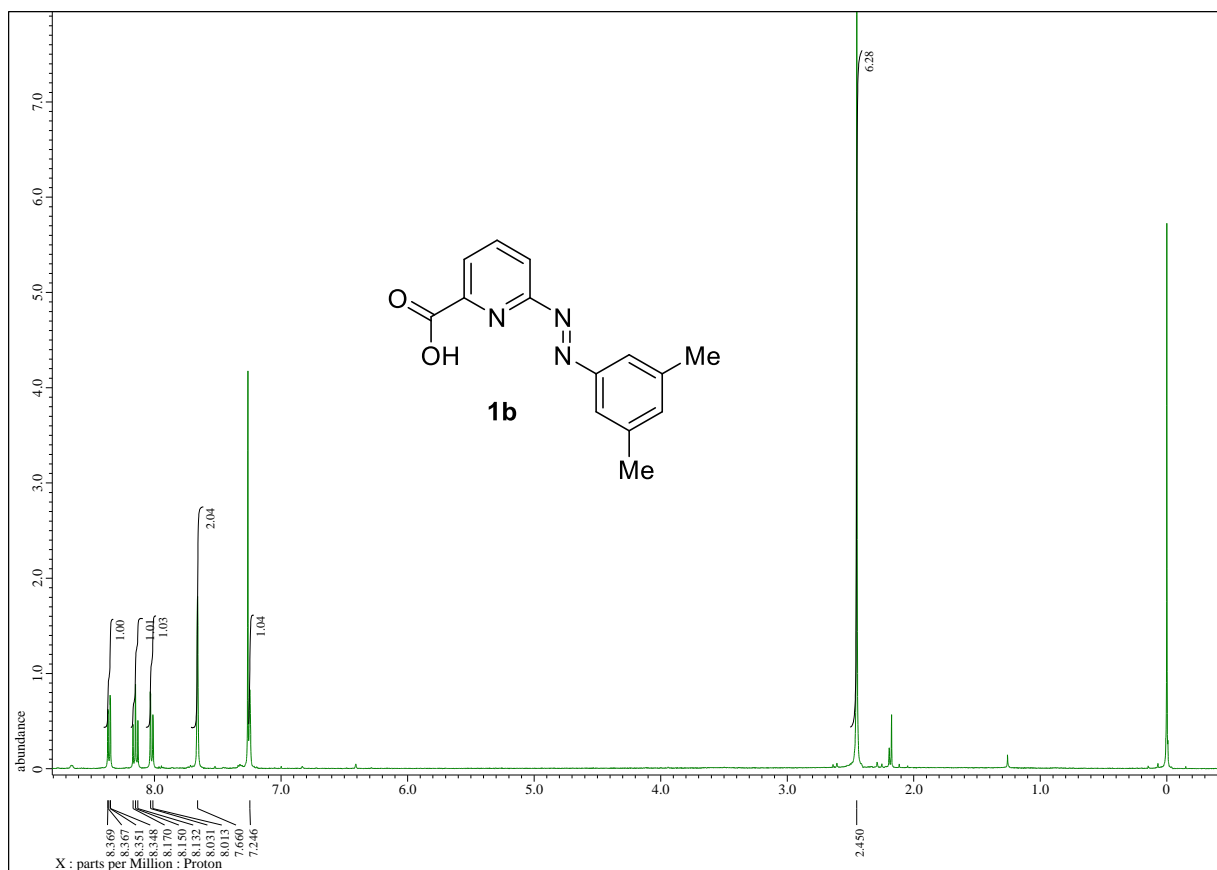


<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) chart of **1a**

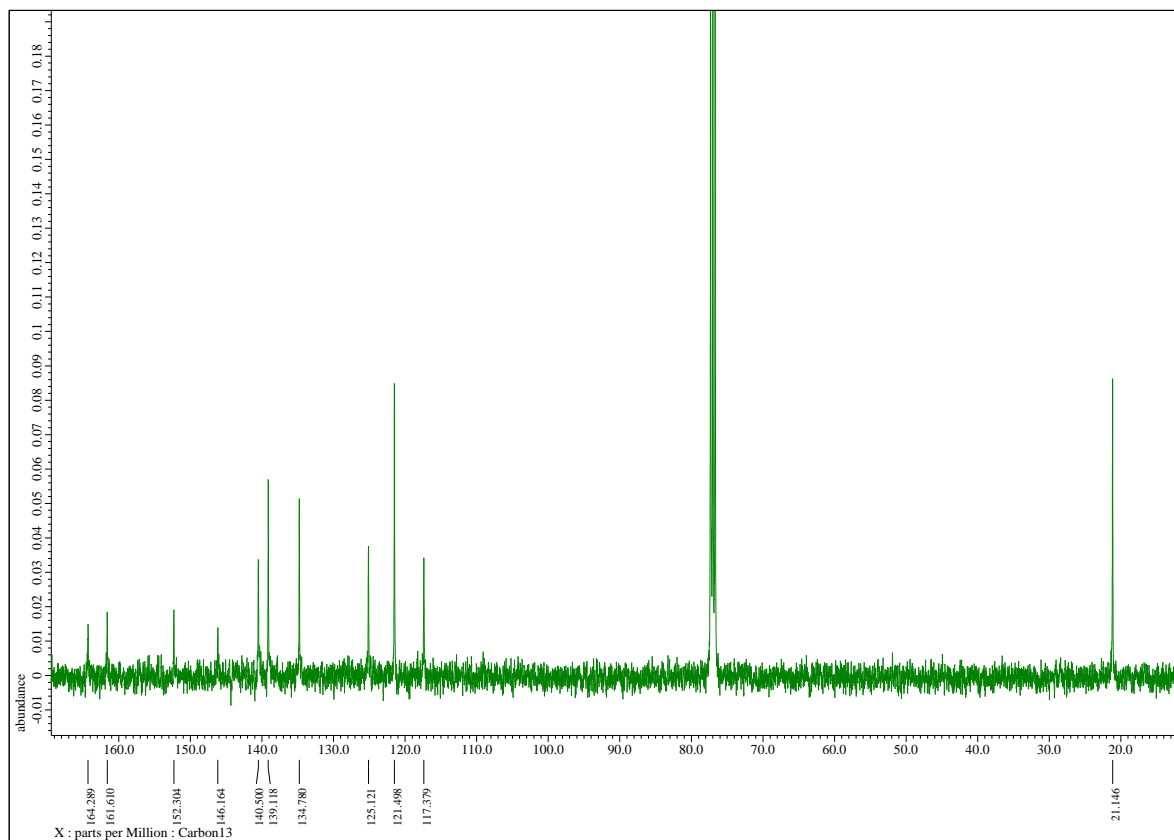




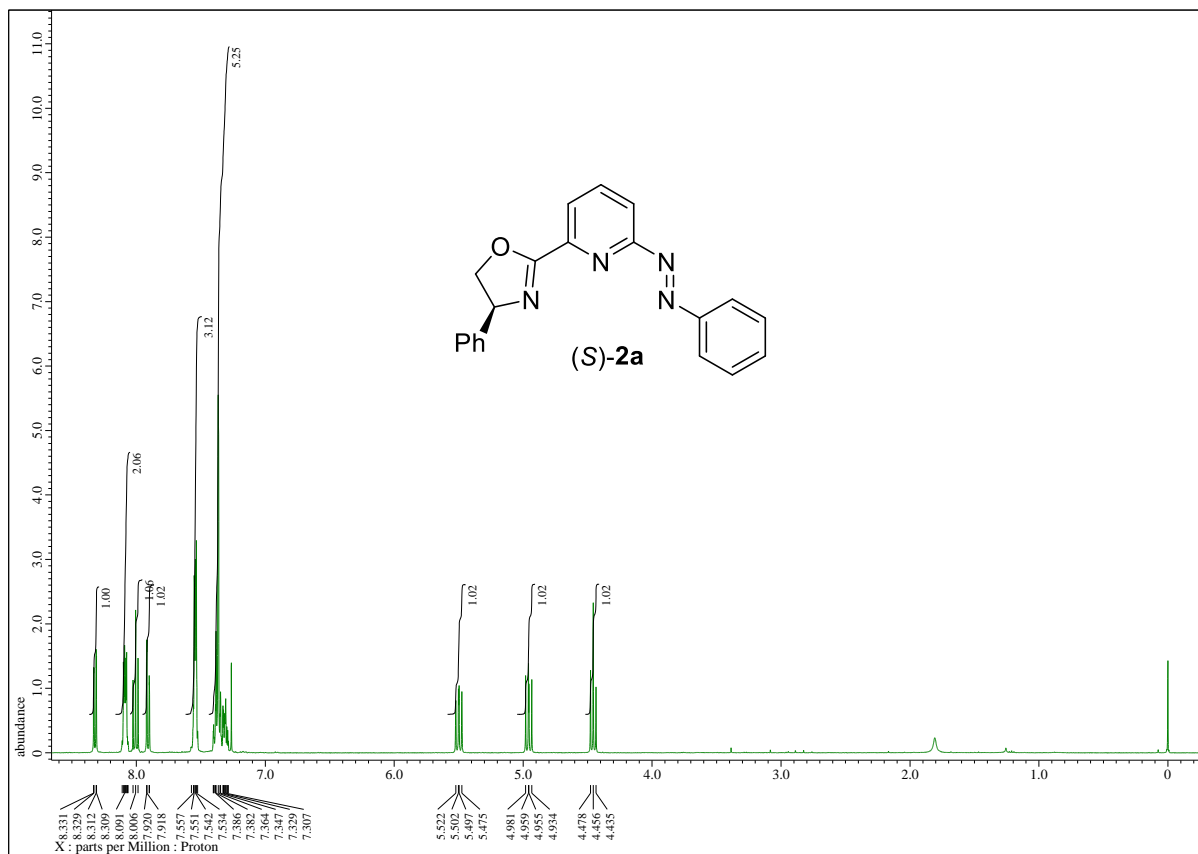
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) chart of **1b**



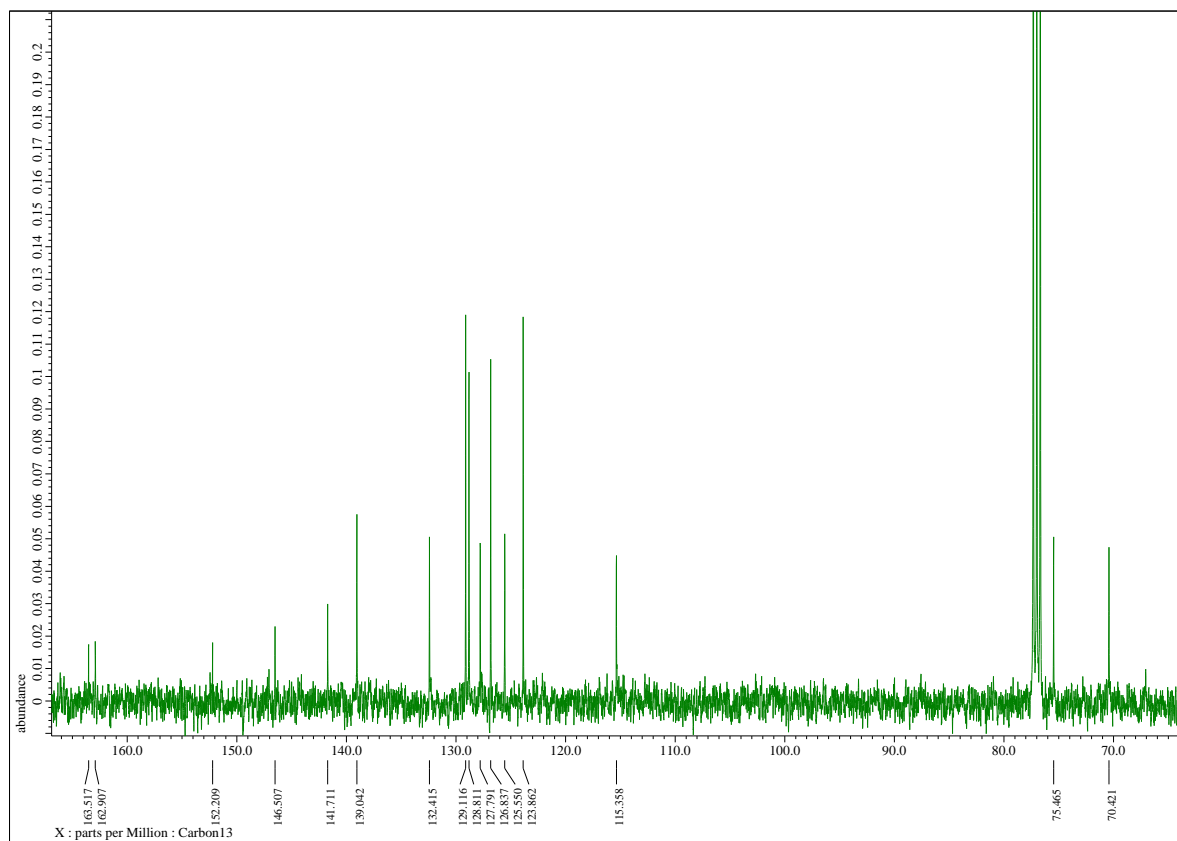
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) chart of **1b**



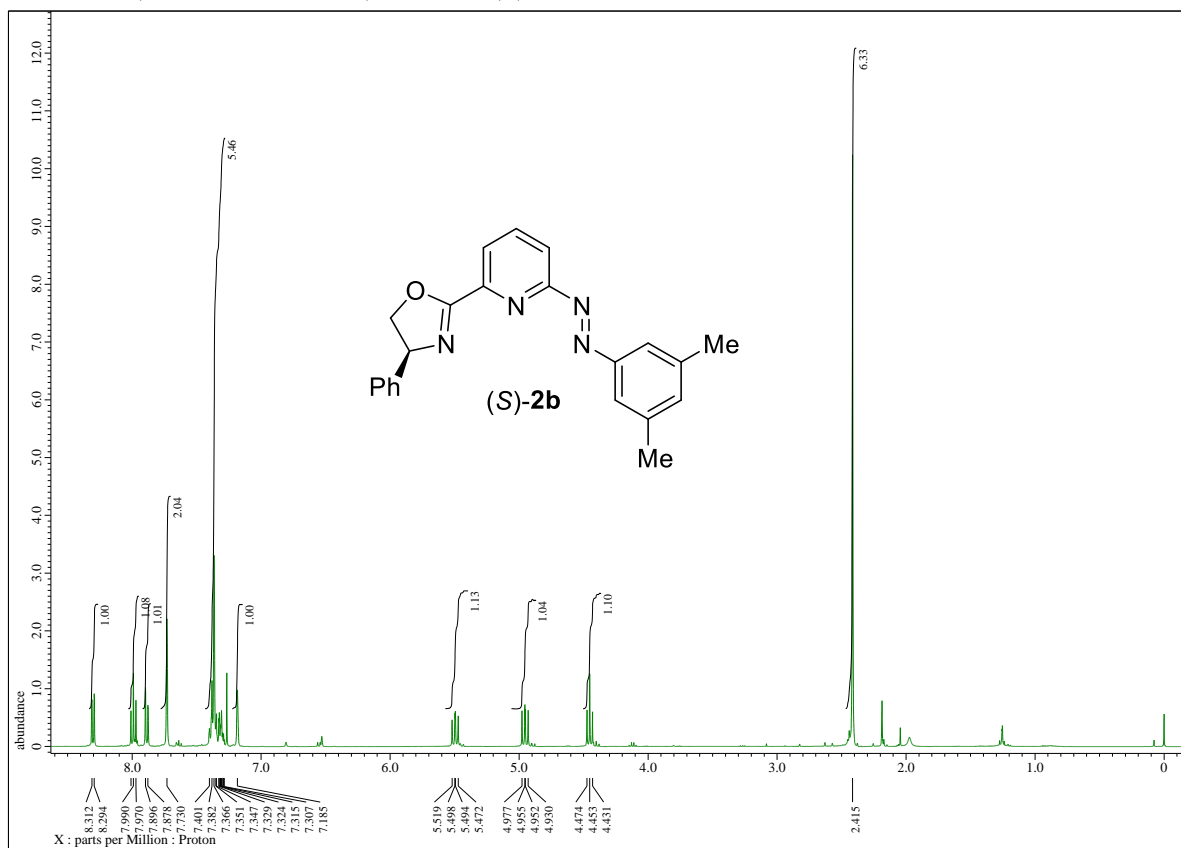
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) chart of (*S*)-**2a**



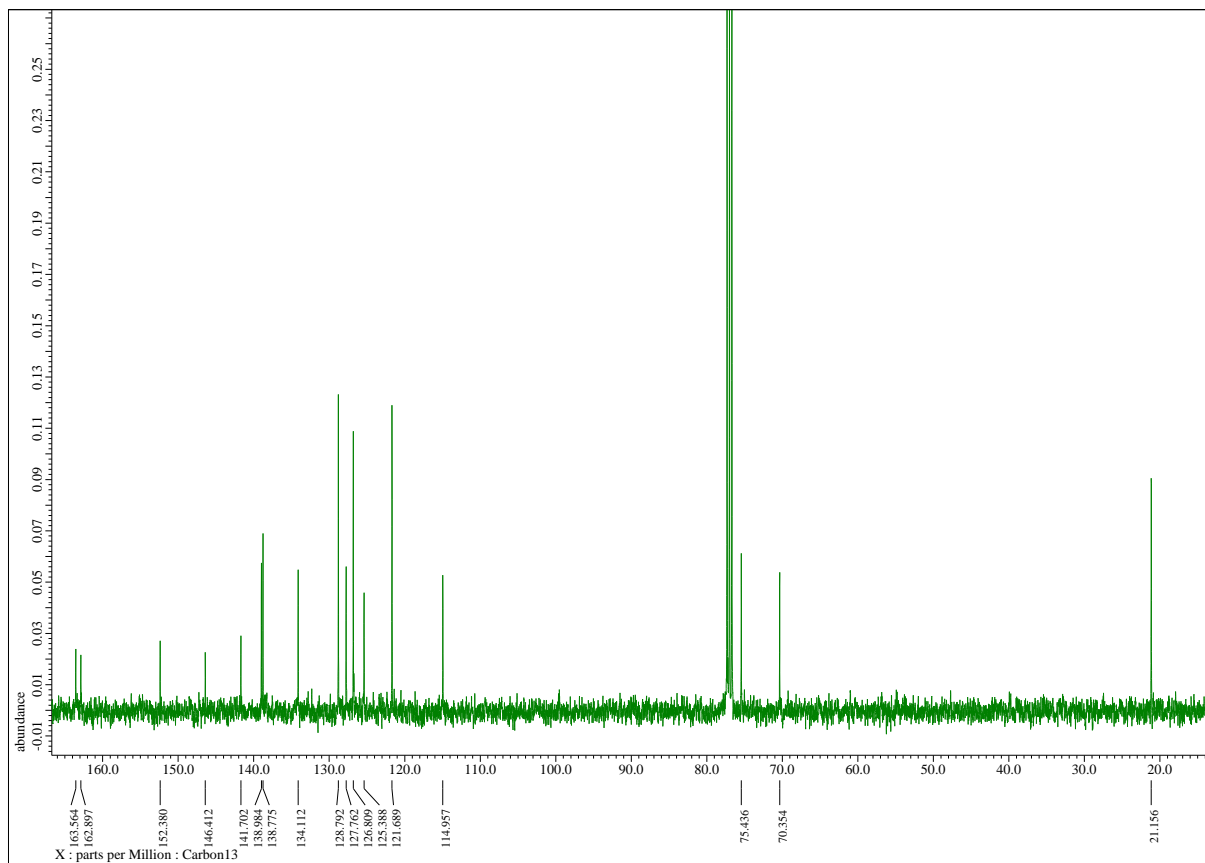
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) chart of (*S*)-**2a**



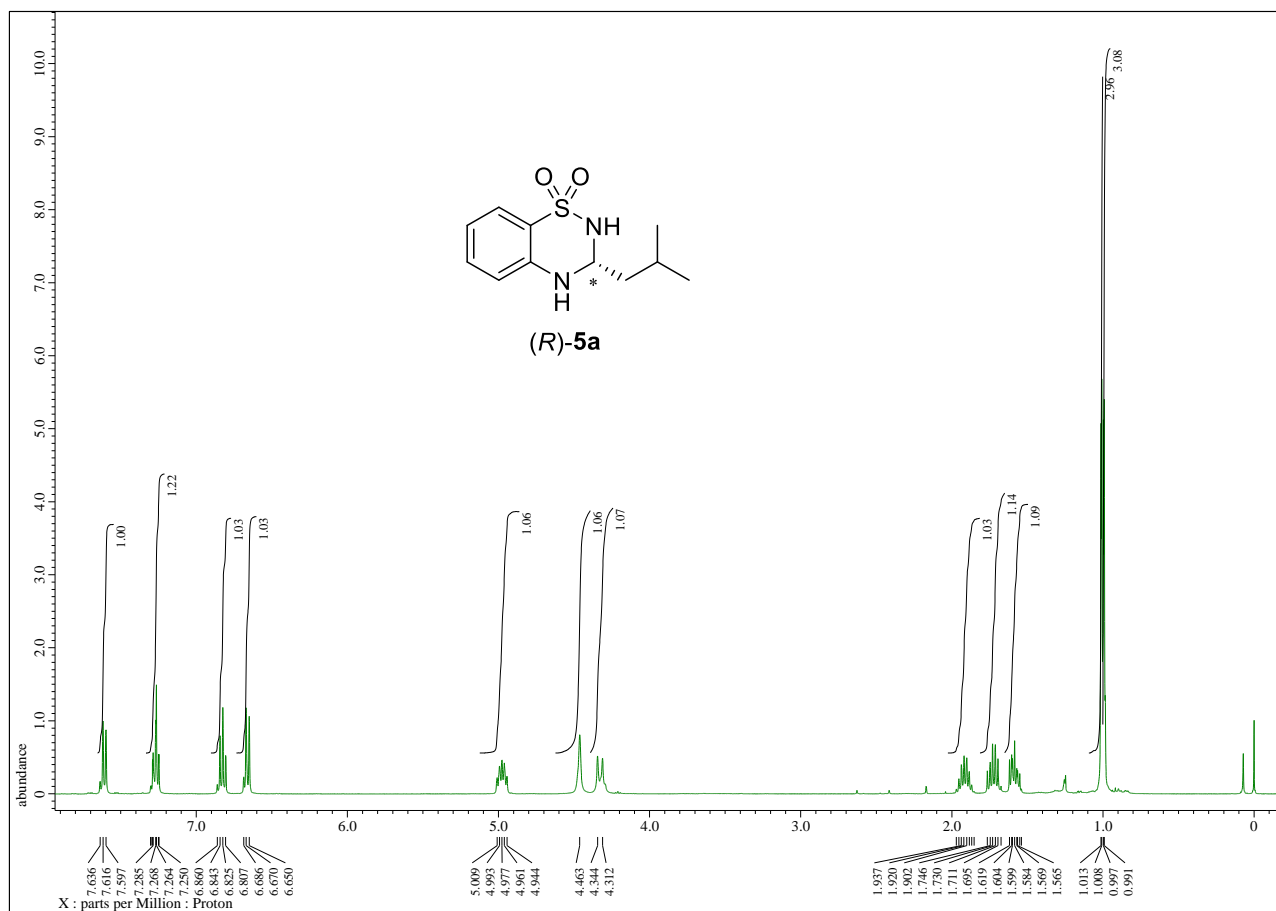
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) chart of (*S*)-**2b**



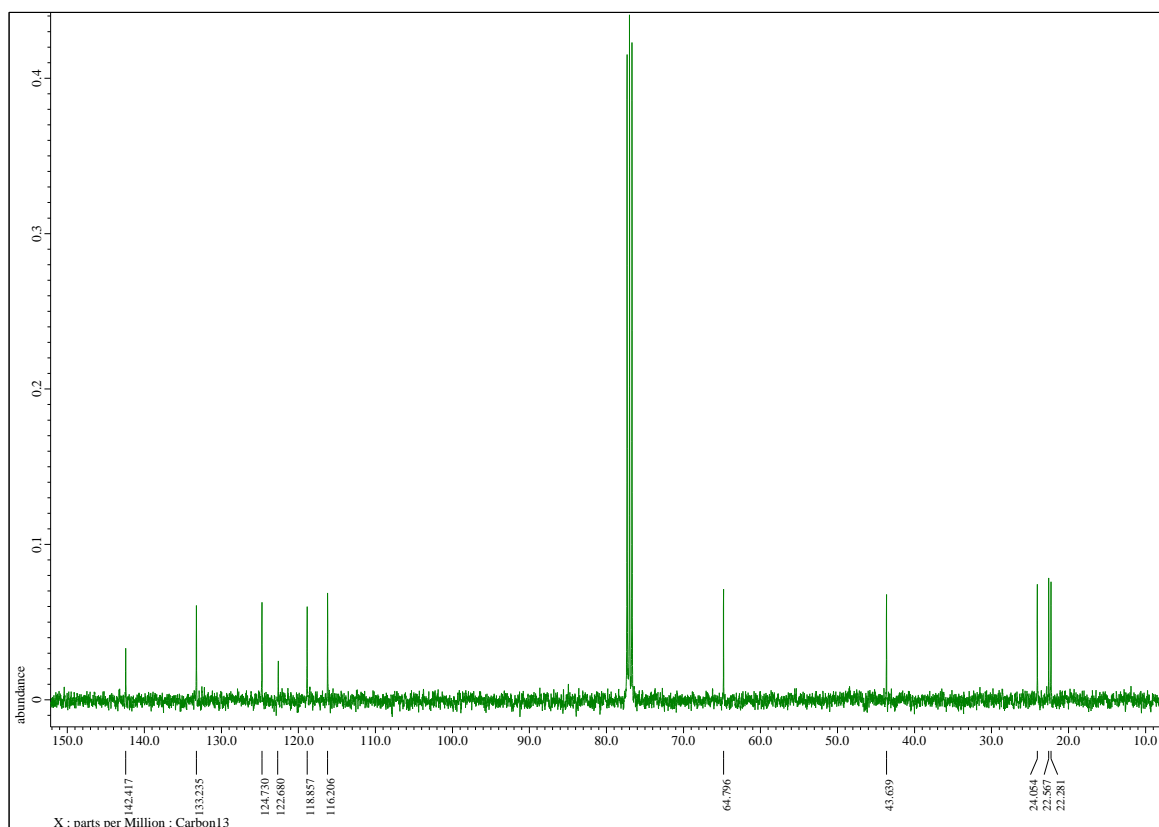
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) chart of (*S*)-**2b**



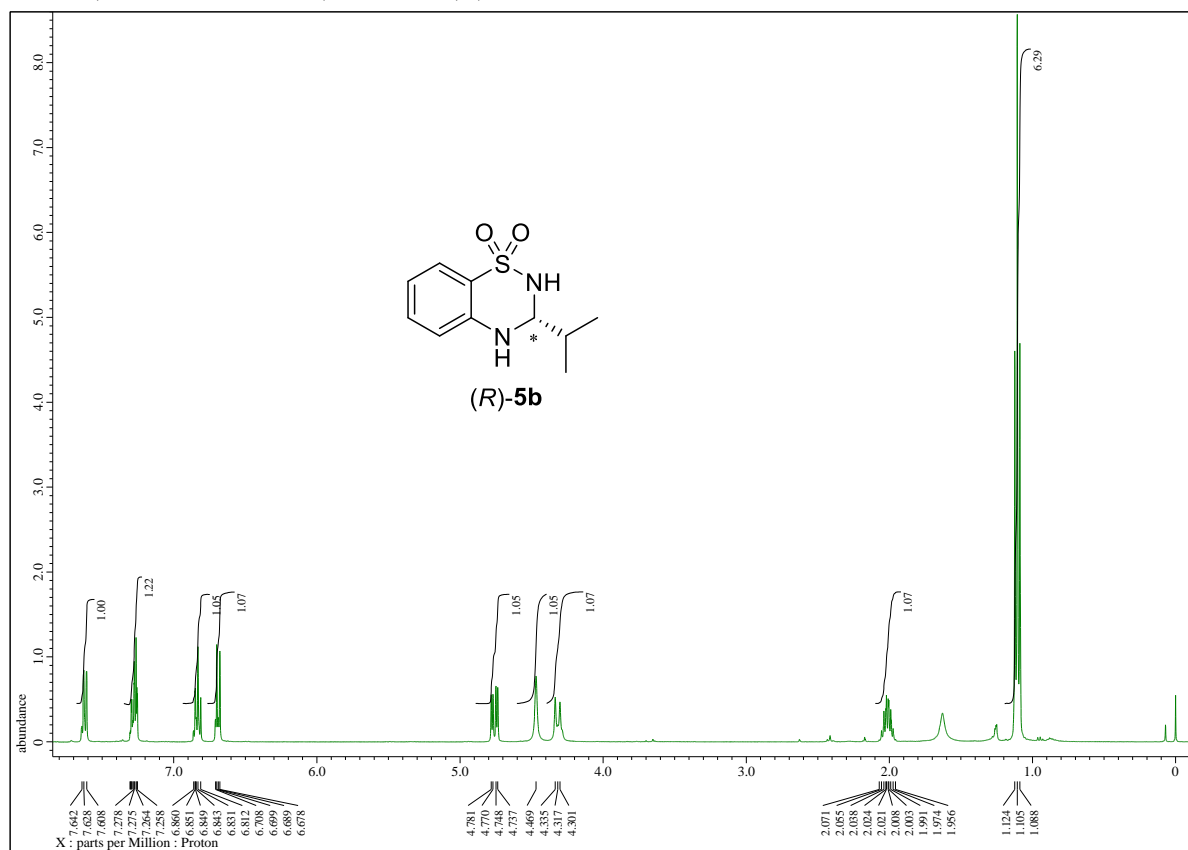
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) chart of (*R*)-**5a**



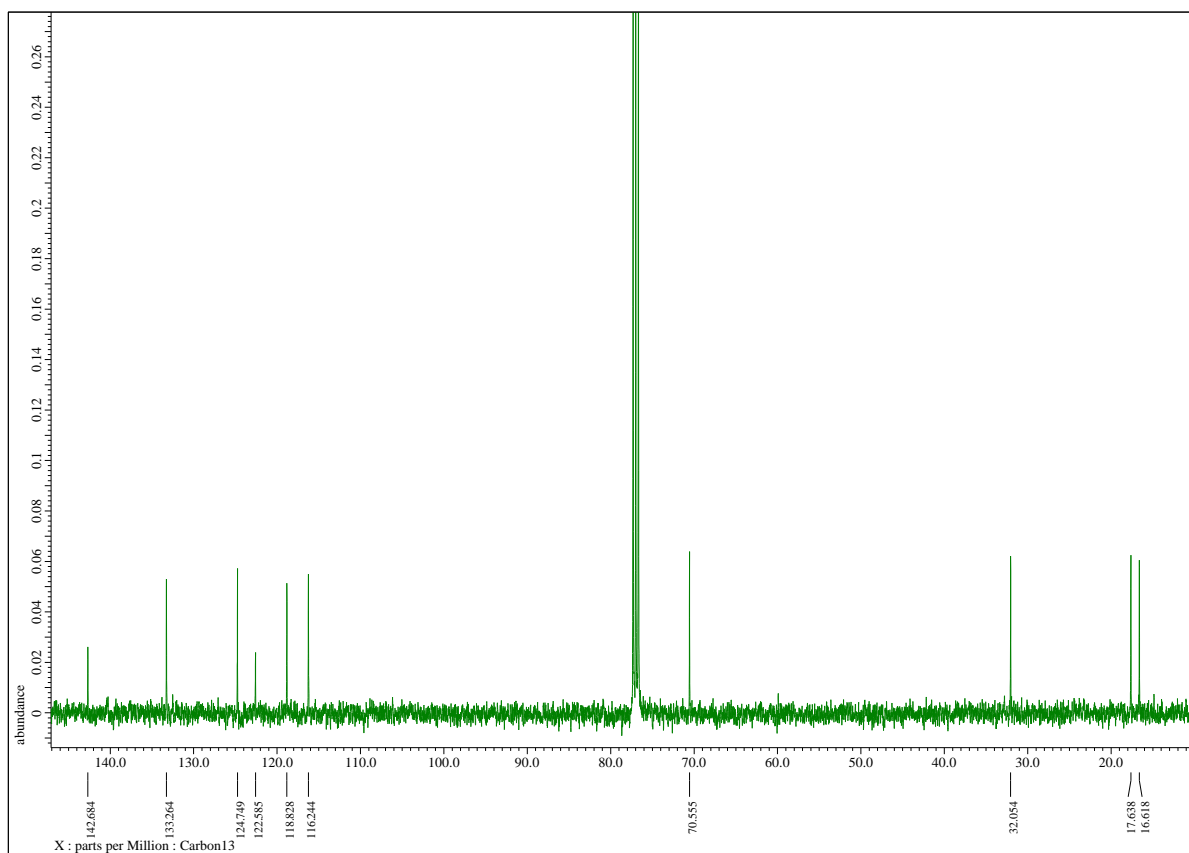
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) chart of (*R*)-**5a**



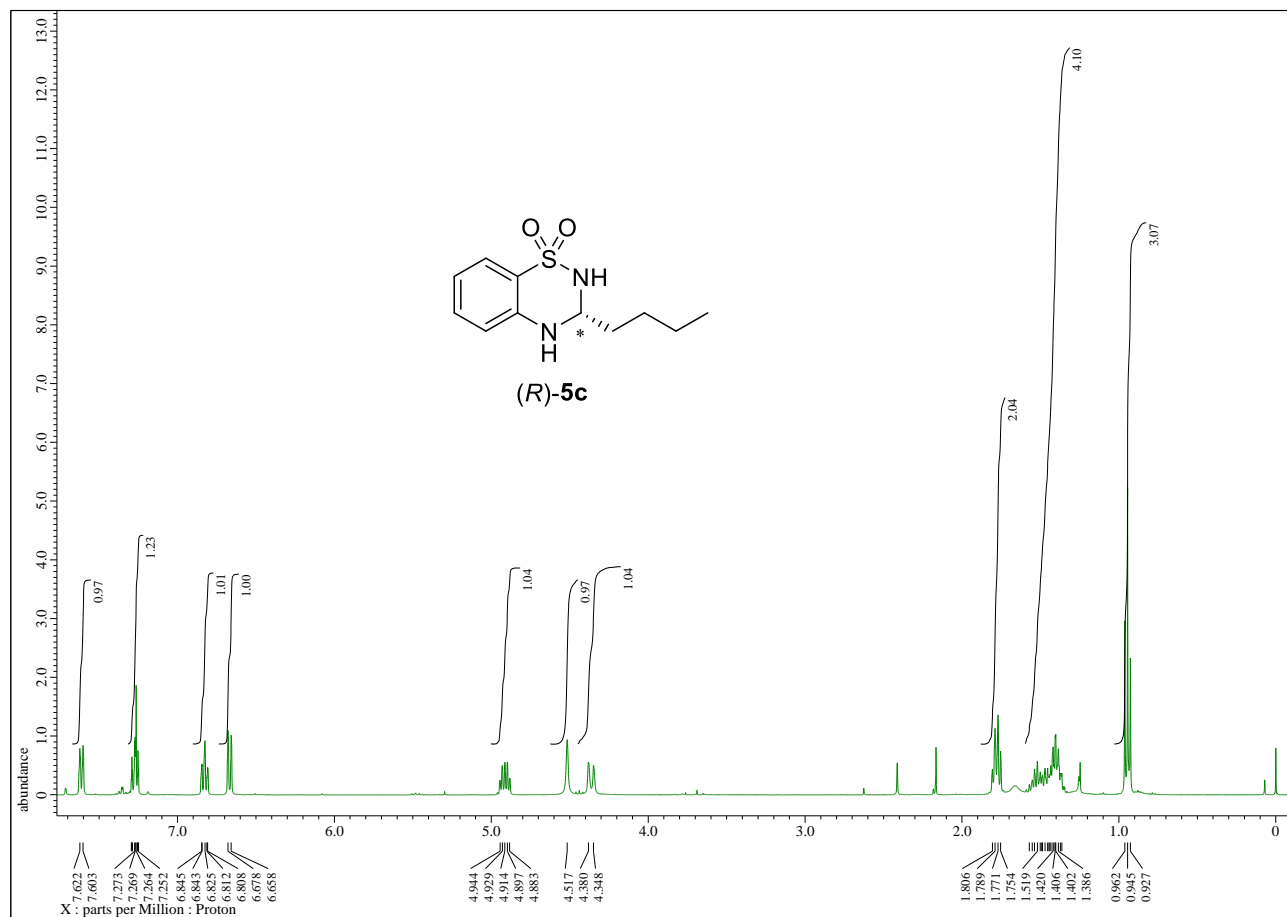
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) chart of (*R*)-**5b**



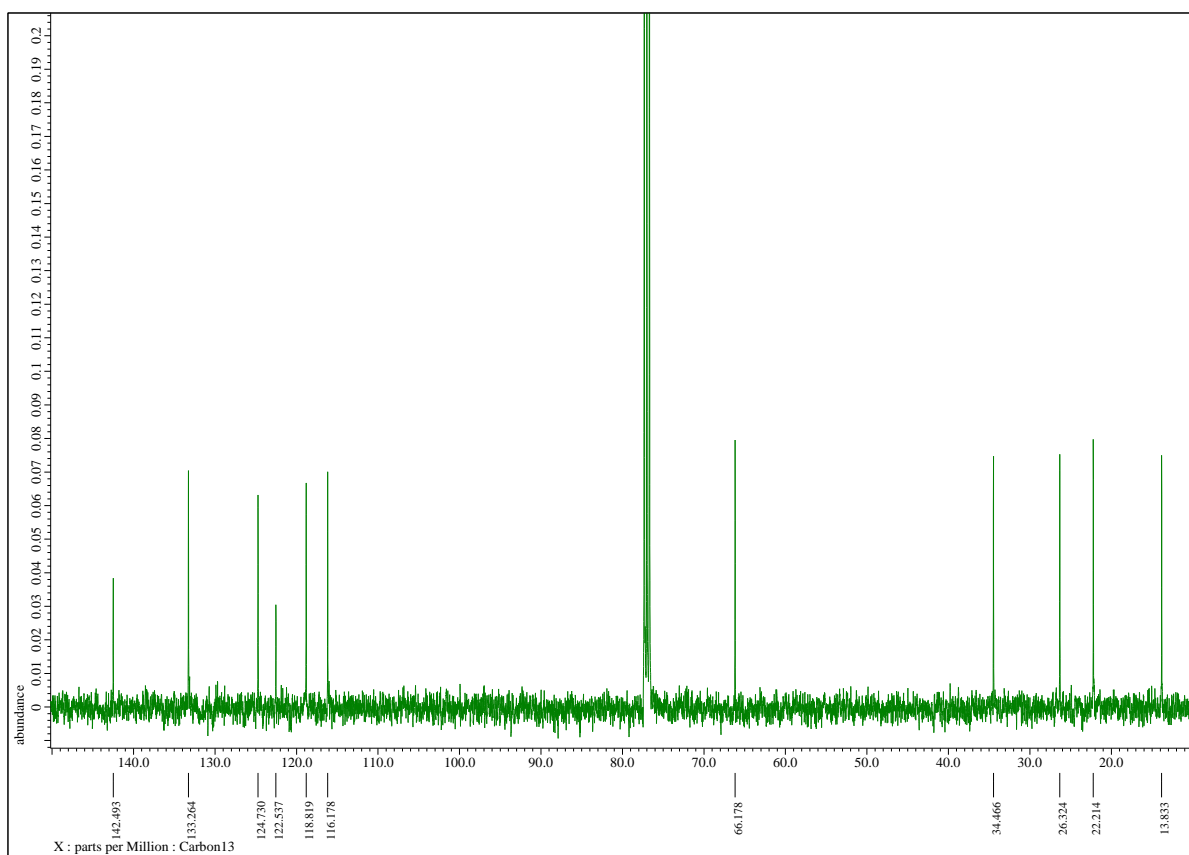
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) chart of (*R*)-**5b**



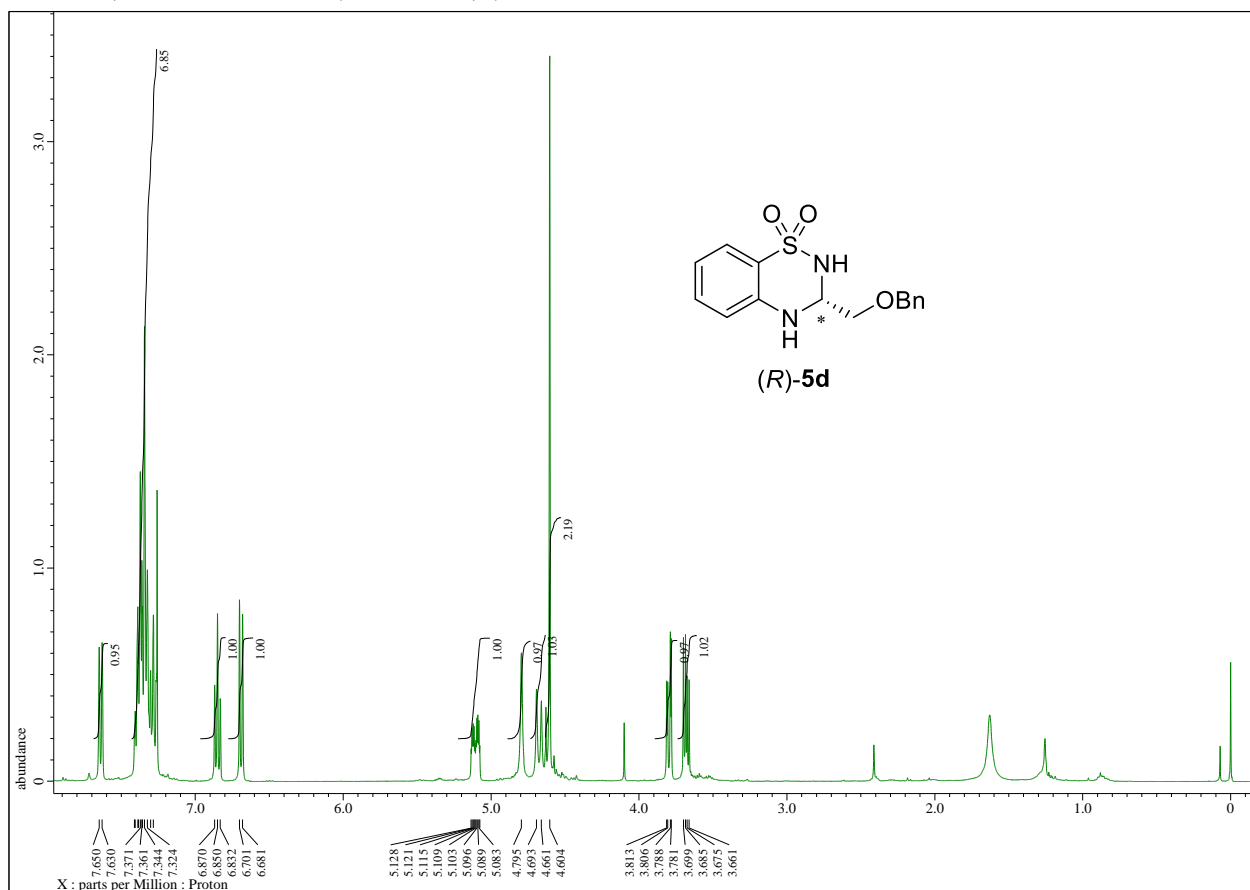
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>) chart of (*R*)-**5c**



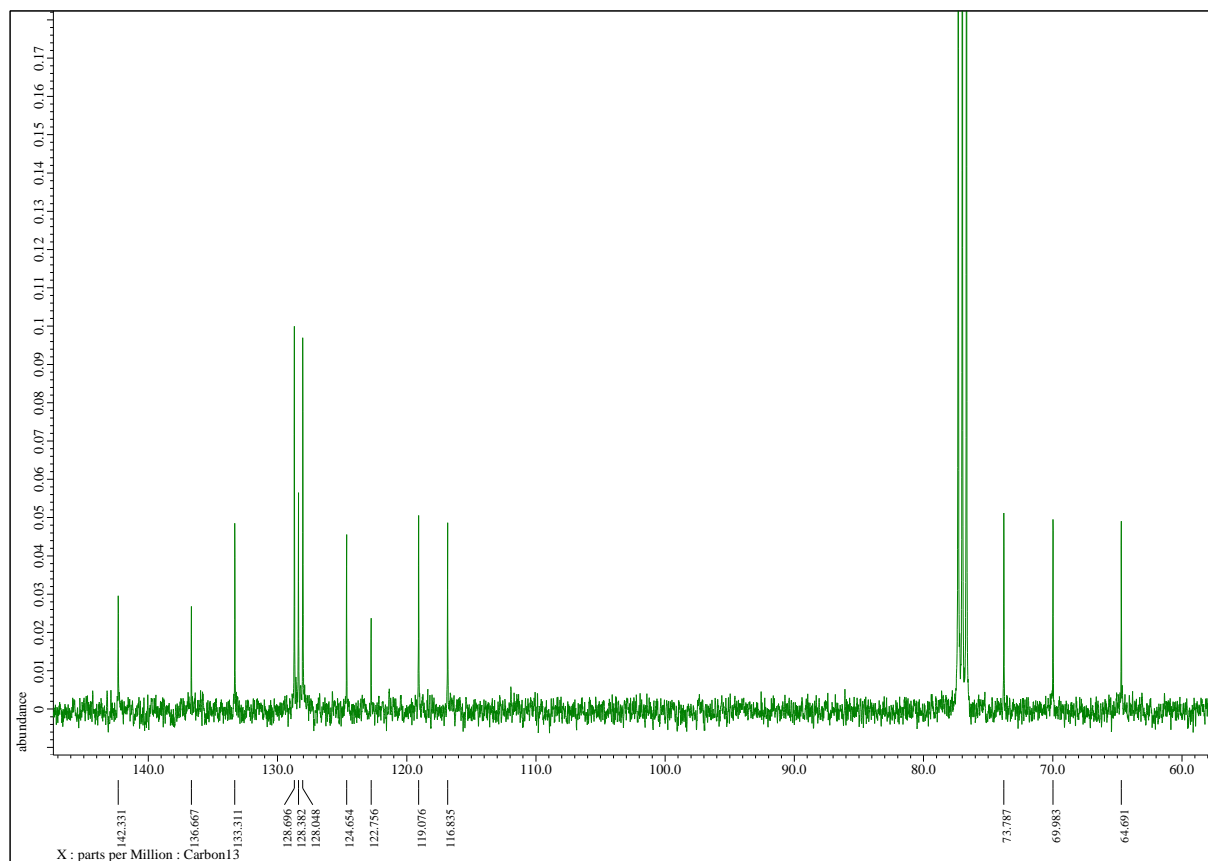
<sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>) chart of (*R*)-**5c**



$^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ) chart of (*R*)-**5d**

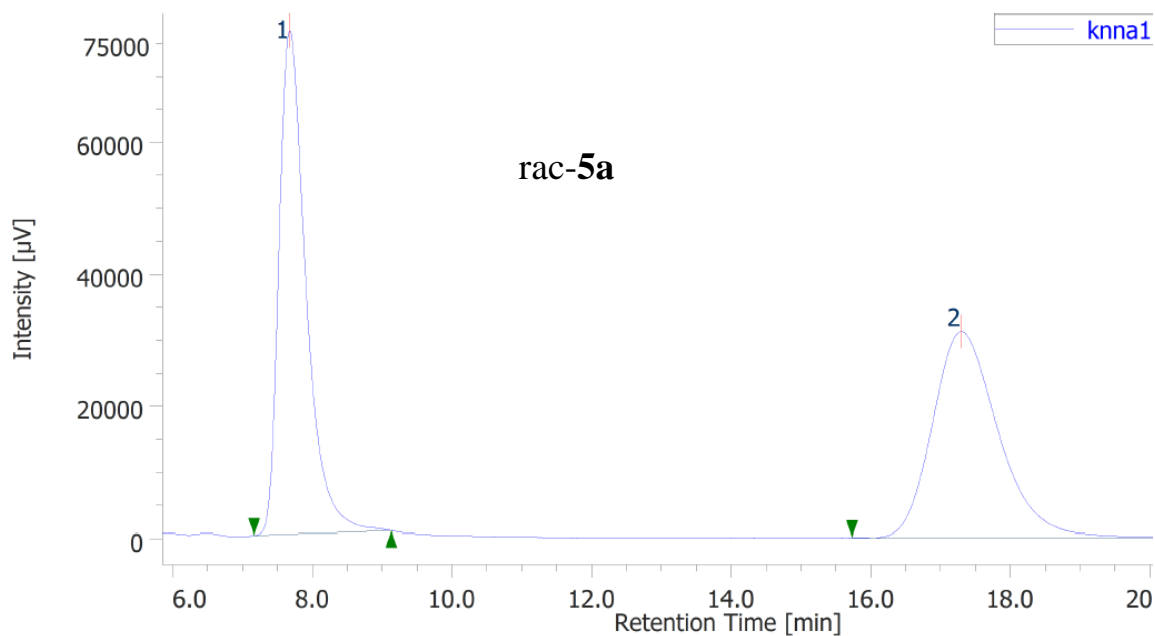


$^{13}\text{C-NMR}$  (100 MHz,  $\text{CDCl}_3$ ) chart of (*R*)-**5d**

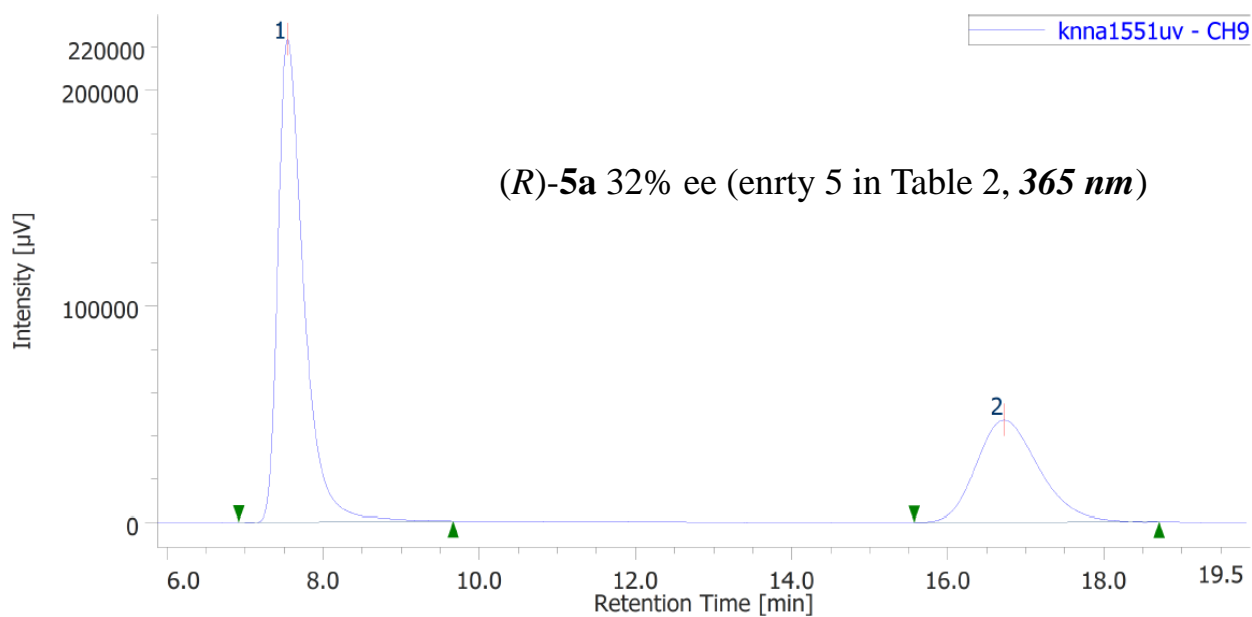


## HPLC charts

HPLC charts of **5a**: HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/*i*PrOH = 80/20, 1.0 mL/min, 250 nm.

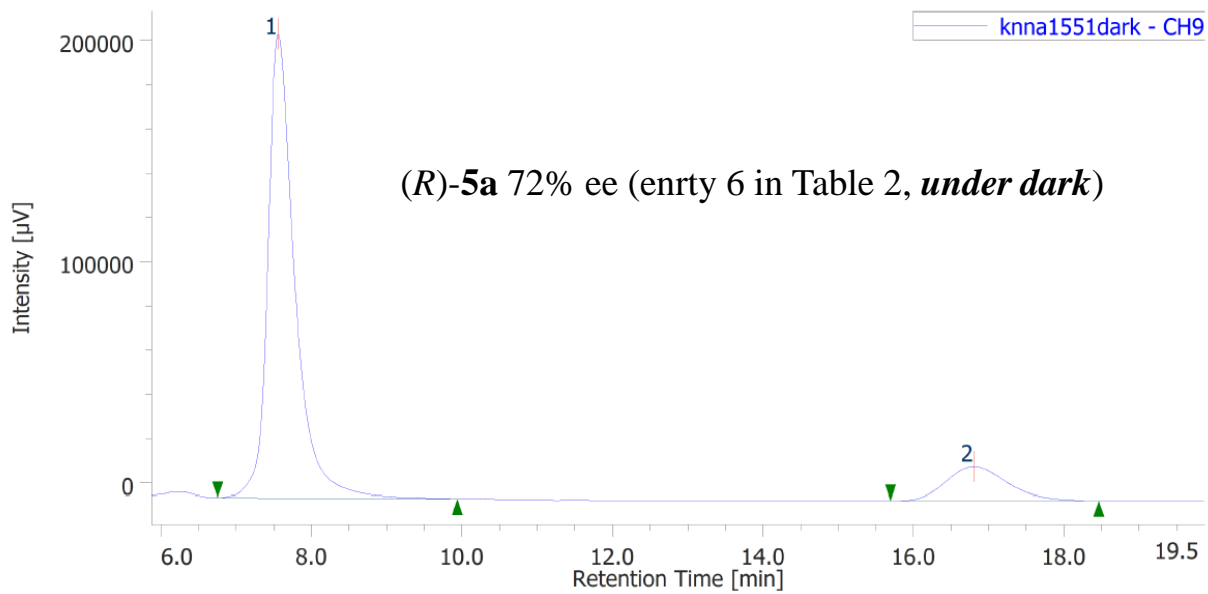


#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	7.680	2050542	76181	50.358	71.012	N/A	2059	8.197	1.521	
2	Unknown	9	17.297	2021368	31097	49.642	28.988	N/A	1705	N/A	1.267	



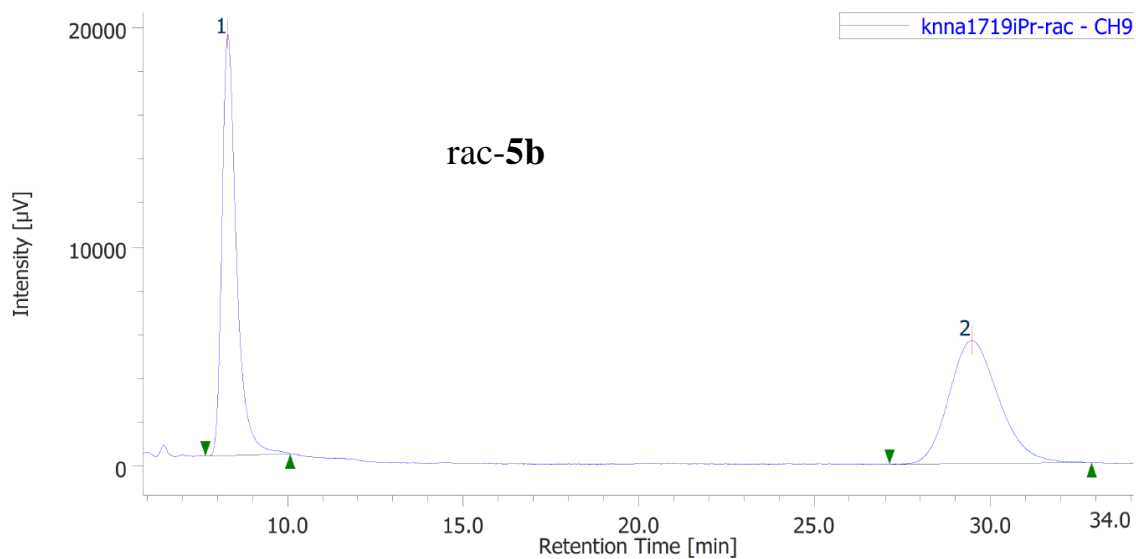
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	7.540	5105706	223259	66.284	82.635	N/A	2848	9.132	1.620	
2	Unknown	9	16.720	2597110	46915	33.716	17.365	N/A	2125	N/A	1.223	



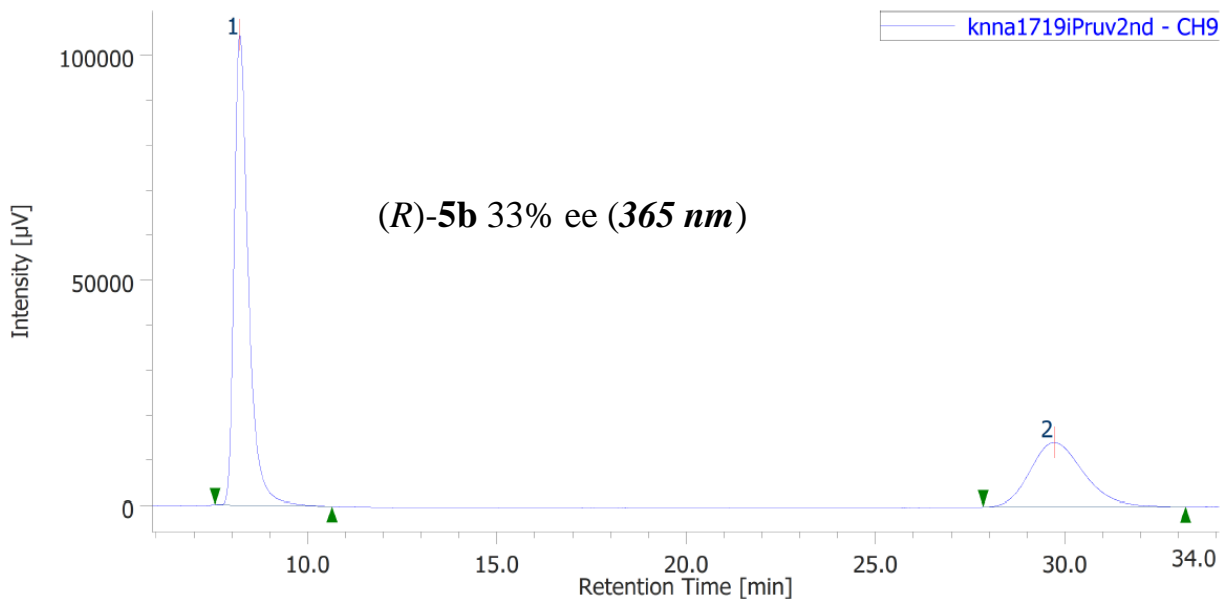


#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	7.557	5222131	209495	86.019	93.260	N/A	2631	8.986	1.415	
2	Unknown	9	16.800	848807	15141	13.981	6.740	N/A	2080	N/A	1.208	

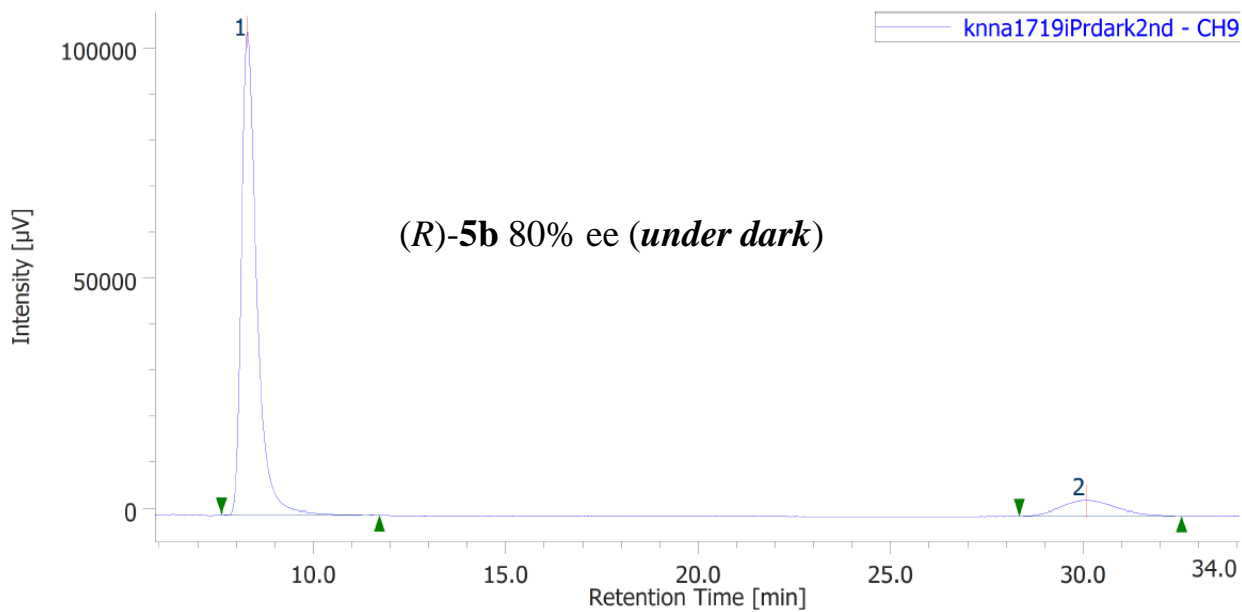
HPLC charts of **5b**: HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/*i*PrOH = 80/20, 1.0 mL/min, 250 nm.



#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	8.300	549930	19194	49.941	77.325	N/A	2212	13.010	1.488	
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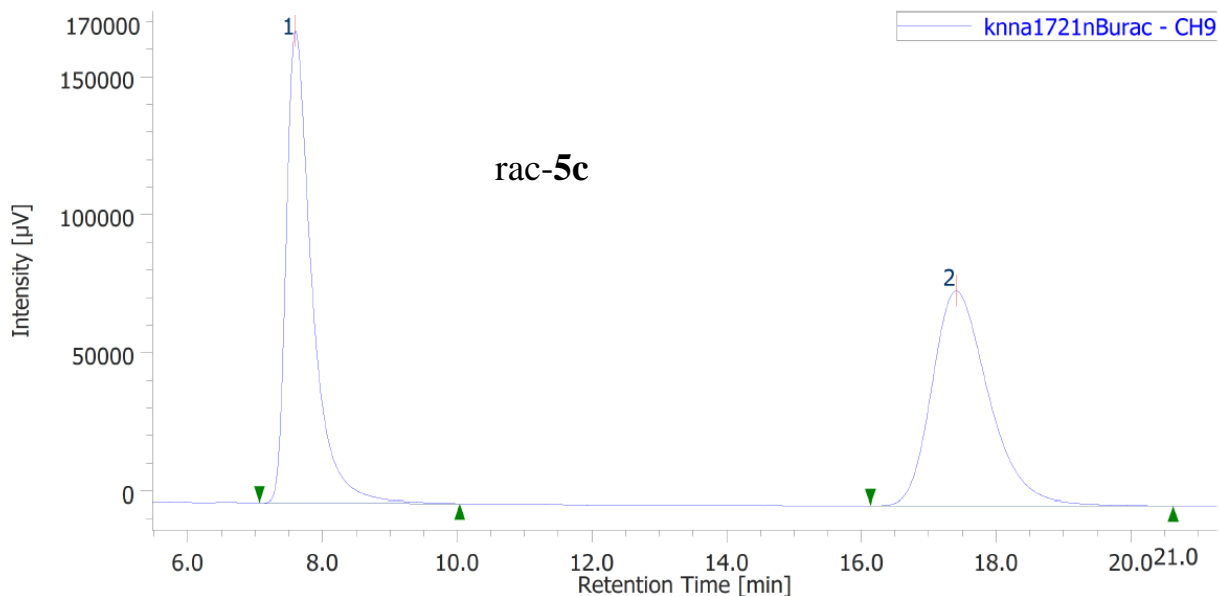


#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	8.210	2704650	104230	66.293	88.051	N/A	2615	13.541	1.514	
2	Unknown	9	29.703	1375197	14145	33.707	11.949	N/A	2187	N/A	1.219	

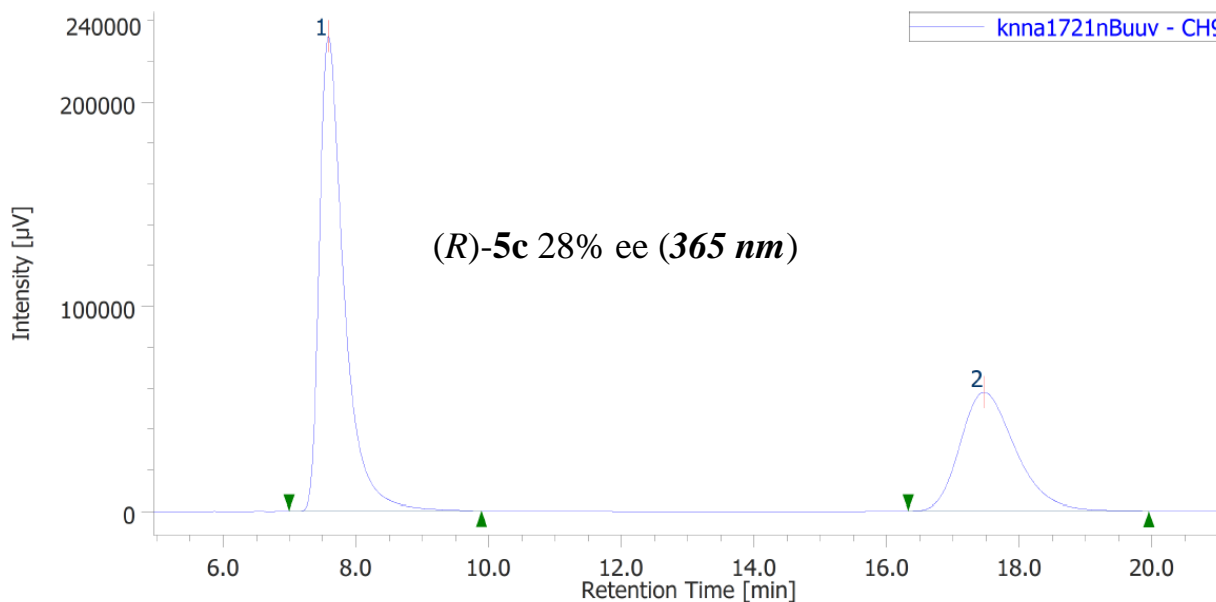


#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	8.290	2868534	104640	90.081	97.030	N/A	2432	13.301	1.549	
2	Unknown	9	30.070	315854	3203	9.919	2.970	N/A	2122	N/A	1.162	

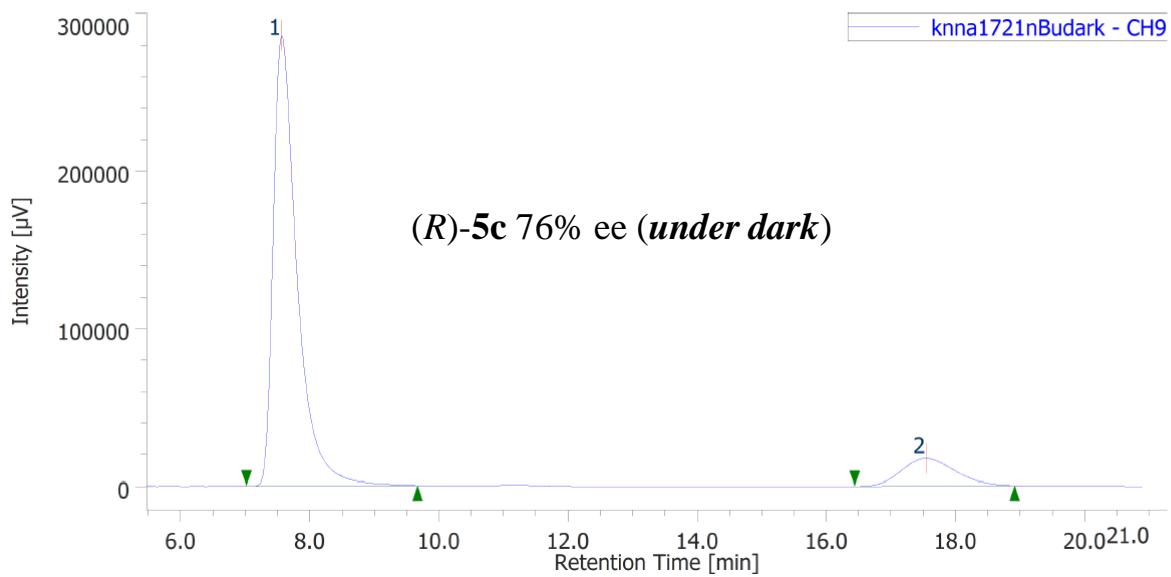
HPLC charts of **5c**: HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/*i*PrOH = 80/20, 1.0 mL/min, 250 nm.



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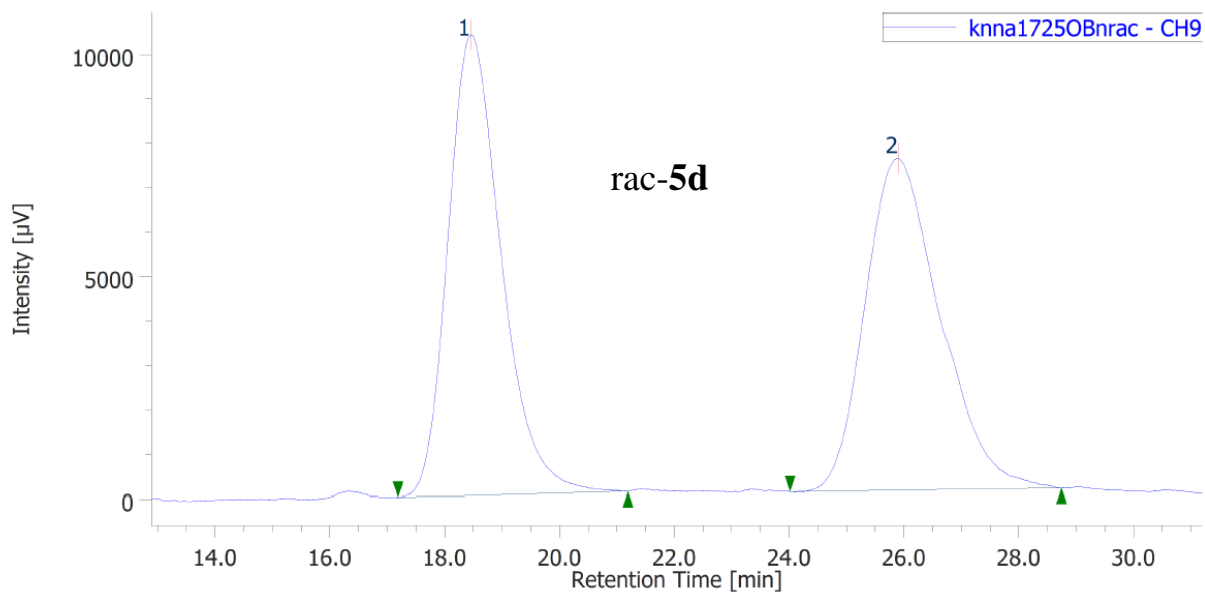


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2	Unknown	9	17.467	3334923	57766	35.895	19.943	N/A	2179	N/A	1.285	

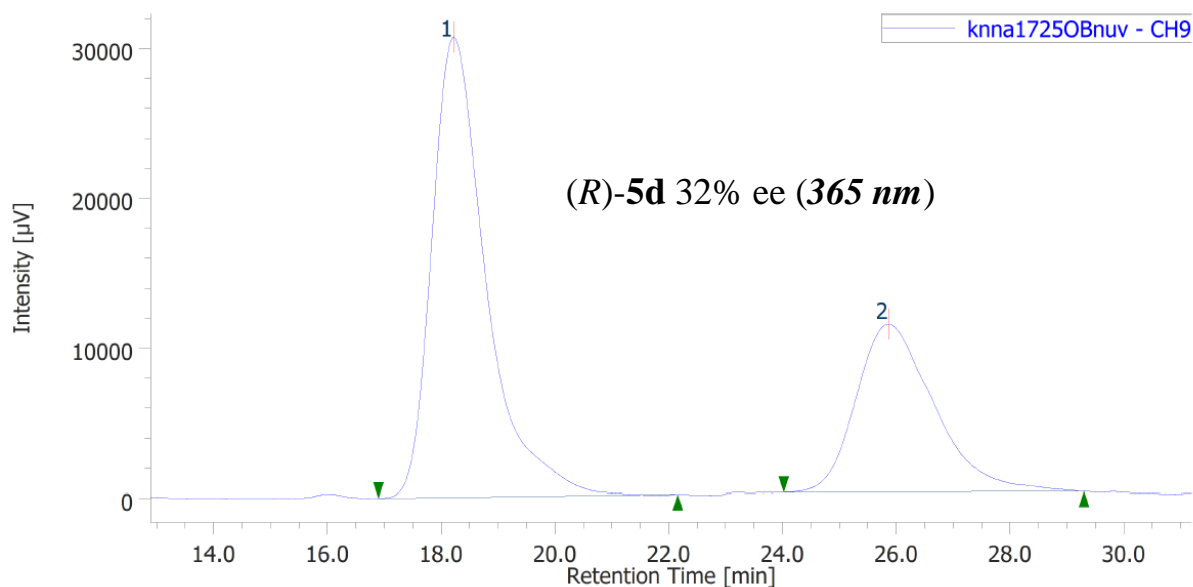


#	Peak Name	CH	tR [min]	Area [ $\mu\text{V}\cdot\text{sec}$ ]	Height [ $\mu\text{V}$ ]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	7.567	7275945	285619	88.185	94.336	N/A	2359	9.372	1.770	
2	Unknown	9	17.537	974863	17149	11.815	5.664	N/A	2158	N/A	1.176	

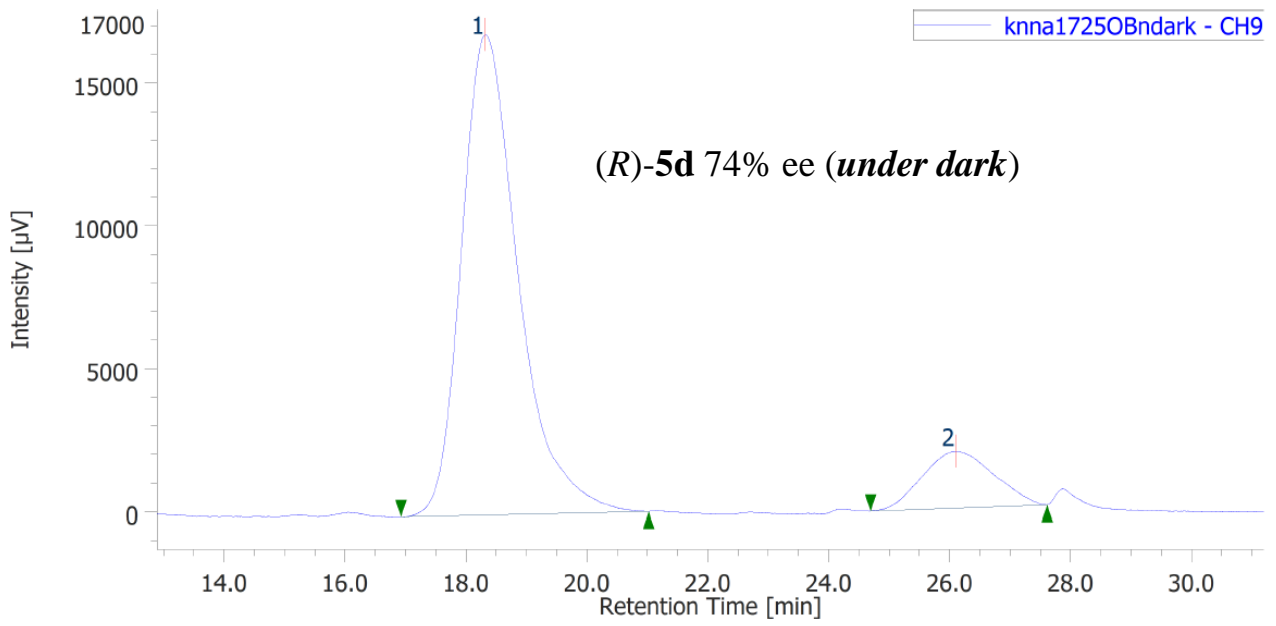
HPLC charts of **5d**: HPLC conditions: Daicel Chiralpak OD-H column, *n*-hexane/*i*PrOH = 80/20, 1.0 mL/min, 240 nm.



#	Peak Name	CH	tR [min]	Area [ $\mu$ V $\cdot$ sec]	Height [ $\mu$ V]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	18.460	666611	10364	49.678	58.140	N/A	1980	3.724	1.297	
2	Unknown	9	25.903	675256	7462	50.322	41.860	N/A	1947	N/A	1.261	



#	Peak Name	CH	tR [min]	Area [ $\mu$ V $\cdot$ sec]	Height [ $\mu$ V]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	18.213	2021251	30633	65.675	73.293	N/A	2017	3.751	1.623	
2	Unknown	9	25.863	1056416	11162	34.325	26.707	N/A	1758	N/A	1.360	



#	Peak Name	CH	tR [min]	Area [µV-sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	18.317	1092514	16799	87.099	89.424	N/A	1991	4.016	1.419	
2	Unknown	9	26.093	161819	1987	12.901	10.576	N/A	2168	N/A	1.090	