

## SUPPORTING INFORMATION

### Efficient Synthesis of Tetrahydrofurans with Chiral Tertiary Allylic Alcohols Catalyzed by Ni/P-Chiral Ligand DI-BIDIME

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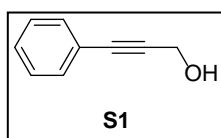
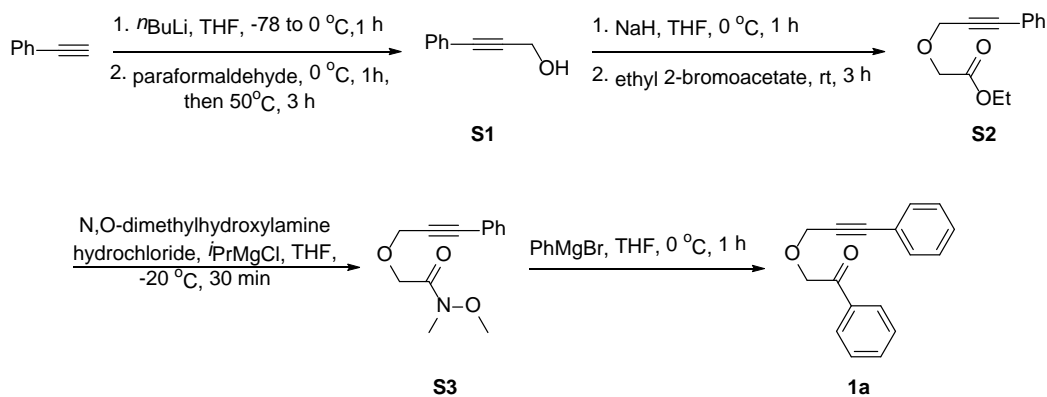
## 1. General Information and Materials

All reactions and manipulations were performed in a nitrogen-filled glove box or using standard Schlenk techniques, unless otherwise noted. All anhydrous solvents were purchased from J & K Chemicals or Alfa Chemicals Inc, or used after standard purification procedures. Ni(cod)<sub>2</sub> was purchased from Strem chemicals. Commercialized reagents were used without further purifications. All air sensitive ligands were stored in a nitrogen-filled glove box before use. Chiral ligand intermediates were prepared according to our reported procedures. cod = 1,5-cyclooctadiene.

<sup>1</sup>H, and <sup>13</sup>C NMR data were recorded on a BrukerDRX500, DRX400, NMR Spectrometer with CDCl<sub>3</sub>, or CD<sub>3</sub>OD as the solvent. <sup>1</sup>H chemical shifts were referenced to CDCl<sub>3</sub> at 7.26 ppm. <sup>13</sup>C chemical shifts were referenced to CDCl<sub>3</sub> at 77.16 ppm and obtained with <sup>1</sup>H decoupling. <sup>31</sup>P shifts were referenced to 85% H<sub>3</sub>PO<sub>4</sub> in D<sub>2</sub>O at 0.0 ppm as external standard and obtained with <sup>1</sup>H decoupling. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), septet (sept), multiplet (m), and broad (br). MS was measured on Agilent 5973N (EI), Agilent 1100 Series LC/MSD (ESI) mass spectrometers. Column chromatography was performed with silica gel (200-300 mesh). X-Ray crystallographic analysis data were collected using a Bruker Smart-APEX instrument (CCD detector) or a Bruker Kappa APEX-II instrument (CCD detector). HPLC analyses and purifications were performed on a Thermo Fisher LC system with UV/VIS detector using chiralcel columns.

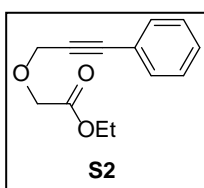
## 2. Substrates Synthesis

### Scheme 1. General procedure for substrate 1a



**Phenylprop-2-yn-1-ol (S1).** To a solution of phenylacetylene (22.0 mL, 200 mmol, 1.00 equiv) in THF (150 mL) at  $-78^\circ\text{C}$  was added dropwise *n*BuLi (84.0 mL, 210 mmol, 1.05 equiv, 2.5 M) in hexanes over 1 h under nitrogen.

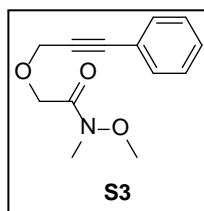
The resulting mixture was warmed to  $0^\circ\text{C}$  and paraformaldehyde (7.87 g, 240 mmol, 1.20 equiv) was added. After stirred at rt for 1 h, the mixture was heated to  $50^\circ\text{C}$  and stirred for 3 h, then cooled to rt, quenched with saturated  $\text{NH}_4\text{Cl}$  solution (500 mL), extracted with EtOAc, washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography (eluent: PE/EA 20/1) to provide compound S1 as light yellow oil (S1, 20.6 g, 78% yield). S1:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47-7.40 (m, 2H), 7.34-7.27 (m, 3H), 4.50 (s, 2H). The  $^1\text{H NMR}$  spectra is in agreement with these reported in the literature.<sup>1,5</sup> S1 was prepared according to literature procedure.<sup>5</sup>



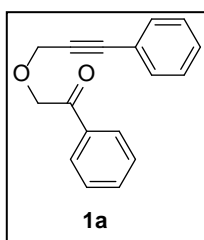
**Ethyl 2-((3-phenylprop-2-yn-1-yl)oxy)acetate (S2).** To a solution of NaH (4.32 g, 108.2 mmol, 1.20 equiv, 60% content) in THF (150 mL) at  $0^\circ\text{C}$  was added 3-phenylprop-2-yn-1-ol (S1, 12.5 g, 94.6 mmol, 1.05 equiv) under nitrogen. Until no gas was generated, the mixture was allowed to warm up to

rt and stirred for 1 h. Then ethyl 2-bromoacetate (10.0 mL, 90.2 mmol, 1.00 equiv) was added at rt under nitrogen. After stirred at rt for 3 h, the reaction was quenched with saturated  $\text{NH}_4\text{Cl}$  solution, extracted with EtOAc, washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography (eluent: PE/EA 15/1) to afford compound S2 as light yellow oil (S2, 14.7 g, 75%). S2:  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (dd,  $J = 7.5, 2.0$  Hz, 2H), 7.33 (t,  $J = 5.9$  Hz, 3H), 4.54 (s, 2H), 4.24 (dd,  $J = 13.3,$

6.2 Hz, 4H), 1.30 (t,  $J = 7.2$  Hz, 3H). The  $^1\text{H}$  NMR spectra is in agreement with these reported in the literature.<sup>2,5</sup> **S2** was prepared according to literature procedure.<sup>5</sup>



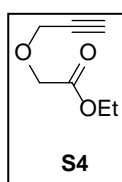
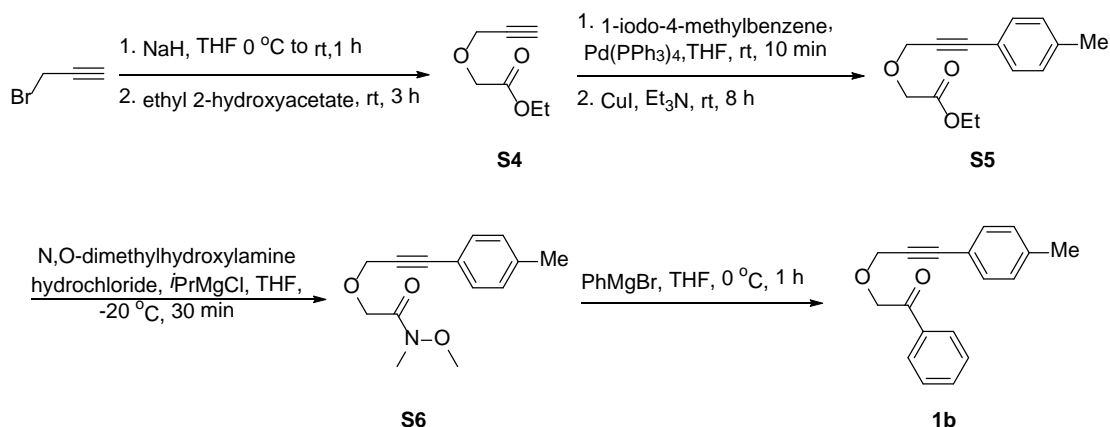
**Methoxy-N-methyl-2-((3-phenylprop-2-yn-1-yl)oxy)acetamide (S3).** To a solution of ethyl 2-((3-phenylprop-2-yn-1-yl)oxy)acetate (**S2**, 8.7 g, 40.0 mmol, 1.00 equiv) and N,O-dimethylhydroxylamine hydrochloride (6.5 g, 60.0 mmol, 1.50 equiv) in THF (150 mL) at  $-20$  °C was added dropwise  $i\text{PrMgCl}$  (90.0 mL, 180 mmol, 3.00 equiv, 2.0 M) in THF over 30 min under nitrogen. The mixture was stirred at  $-20$  °C for 30 min, then quenched with saturated  $\text{NH}_4\text{Cl}$  solution, extracted with EtOAc, washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography (eluent: PE/EA 5/1 to 3/1) to afford **S3** as white solid (**S3**, 6.16 g, 66% yield). **S3**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (dd,  $J = 7.4, 2.3$  Hz, 2H), 7.35 – 7.29 (m, 3H), 4.57 (s, 2H), 4.46 (s, 2H), 3.71 (s, 3H), 3.21 (s, 3H).  $^1\text{H}$  NMR spectra is in agreement with these reported in the literature.<sup>2,5</sup> **S3** was prepared according to literature procedure.<sup>5</sup>



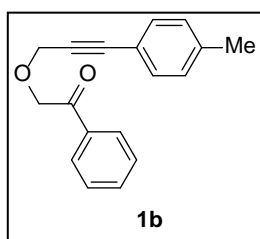
**Phenyl-2-((3-phenylprop-2-yn-1-yl)oxy)ethan-1-one (1a).** To a solution of N-methoxy-N-methyl-2-((3-phenylprop-2-yn-1-yl)oxy)acetamide (**S3**, 500 mg, 2.14 mmol, 1.00 equiv) in THF (10 mL) at  $0$  °C under nitrogen was added  $\text{PhMgBr}$  (3.2 mL, 3.21 mmol, 1.5 equiv, 1.0 M) in THF. After stirred at  $0$  °C for 1 h, the reaction was quenched with 2 M HCl, extracted with EtOAc, washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum.

The residue was purified by column chromatography (eluent: PE/EA 20/1) to afford compound **1a** as white solid (498 mg, 93% yield). **1a**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (m, 2H), 7.59 (t,  $J = 7.4$  Hz, 1H), 7.47 (t,  $J = 7.7$  Hz, 2H), 7.44 (dd,  $J = 7.5, 1.8$  Hz, 2H), 7.35 – 7.27 (m, 3H), 4.94 (s, 2H), 4.60 (s, 2H).  $^1\text{H}$  NMR spectra is in agreement with these reported in the literature.<sup>3,5</sup> **1a** was prepared according to literature procedure.<sup>5</sup>

## Scheme 2. Synthetic Procedures for Substrate 1b

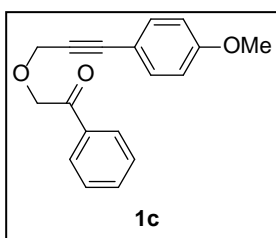


**Ethyl 2-(prop-2-yn-1-yloxy)acetate (S4).** To a solution of NaH (693 mg, 17.4 mmol, 1.00 equiv, 60% content) in THF (60 mL) at 0 °C was added dropwise ethyl 2-hydroxyacetate (1.64 mL, 17.4 mmol, 1.00 equiv) under nitrogen. Until no gas was generated, the mixture was allowed to warm up to rt and stirred for 1 h. Then 3-bromoprop-1-yne (1.80 mL, 20.9 mmol, 1.20 equiv) was added. After stirred at rt for 3 h, the reaction was quenched with saturated NH<sub>4</sub>Cl solution, extracted with EtOAc, washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography (eluent: PE/EA 50/1) to afford colorless oil (**S4**, 1.98 g, 80%). **S4:** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.45 (dd, *J* = 7.4, 2.3 Hz, 2H), 7.35 – 7.29 (m, 3H), 4.57 (s, 2H), 4.46 (s, 2H), 3.71 (s, 3H), 3.21 (s, 3H). The <sup>1</sup>H NMR spectra is in agreement with these reported in the literature.<sup>4,5</sup> **S4, S5, S6** and **1b** was prepared according to literature procedure.<sup>5</sup>



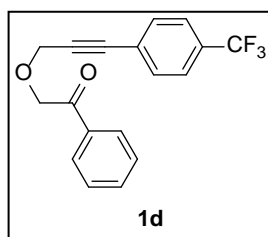
**phenyl-2-((3-(p-tolyl)prop-2-yn-1-yl)oxy)ethan-1-one (1b):** white solid, 95% yield; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 4.94 (s, 2H), 4.59 (s, 2H), 2.35 (s, 3H). The <sup>1</sup>H NMR spectra is in agreement with these reported in the literature.<sup>5</sup>

Preparation of **1c-1s** were carried out according to a procedure similar to that for the synthesis of **1b** from corresponding aryl iodides.

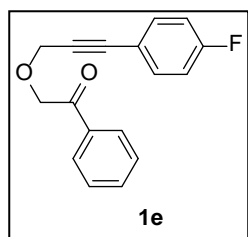


**2-((3-(4-methoxyphenyl)prop-2-yn-1-yl)oxy)-1-phenylethan-1-one (1c):** white solid, 79% yield; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.96 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.62 – 7.55 (m, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.41 – 7.34 (m, 2H), 6.88 – 6.78 (m, 2H), 4.93 (s, 2H), 4.59 (s, 2H), 3.81 (s, 3H). The <sup>1</sup>H NMR spectra is in agreement with these reported in the

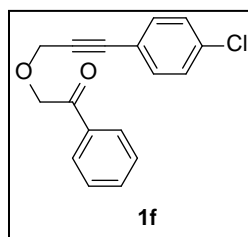
literature.<sup>5</sup>



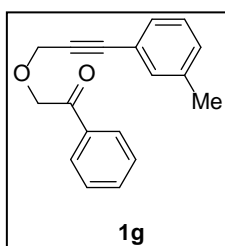
**1-phenyl-2-((3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)oxy)ethan-1-one (1d):** white solid, 74% yield; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.59 – 7.51 (m, 4H), 7.49 (t, *J* = 7.7 Hz, 2H), 4.94 (s, 2H), 4.62 (s, 2H). The <sup>1</sup>H NMR spectra is in agreement with these reported in the literature.<sup>5</sup>



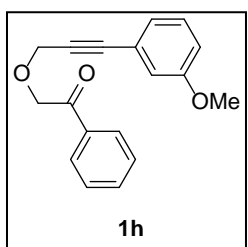
**2-((3-(4-fluorophenyl)prop-2-yn-1-yl)oxy)-1-phenylethan-1-one (1e):** white solid, 93% yield; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.00 – 7.91 (m, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.45 – 7.38 (m, 2H), 7.04 – 6.94 (m, 2H), 4.93 (s, 2H), 4.59 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 195.7, 163.7, 161.7, 134.9, 133.8, 133.7, 133.7, 128.8, 127.9, 118.4, 115.7, 115.5, 86.3, 83.9, 71.8, 59.2. HRMS (ESI) calculated for [M+Na, C<sub>17</sub>H<sub>13</sub>NaFO<sub>2</sub>]<sup>+</sup>: 291.0792; found: 291.0792.



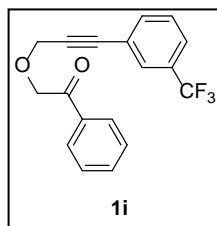
**2-((3-(4-chlorophenyl)prop-2-yn-1-yl)oxy)-1-phenylethan-1-one (1f):** white solid, 76% yield; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.96 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.64 – 7.56 (m, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.40 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 4.92 (s, 2H), 4.59 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 195.6, 134.8, 134.8, 133.7, 133.0, 128.8, 128.7, 127.9, 120.8, 86.2, 85.2, 71.9, 59.2. HRMS (ESI) calculated for [M+Na, C<sub>17</sub>H<sub>13</sub>NaClO<sub>2</sub>]<sup>+</sup>: 307.0496; found: 307.0499.



**1-phenyl-2-((3-(m-tolyl)prop-2-yn-1-yl)oxy)ethan-1-one (1g):** light yellow oil, 84% yield; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.99 – 7.92 (m, 2H), 7.62 – 7.54 (m, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 9.6 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 4.93 (s, 2H), 4.59 (s, 2H), 2.31 (s, 3H). The <sup>1</sup>H NMR spectra is in agreement with these reported in the literature.<sup>5</sup>

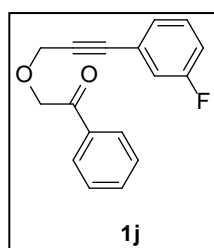


**2-((3-(3-methoxyphenyl)prop-2-yn-1-yl)oxy)-1-phenylethan-1-one (1h):** colorless oil, 76% yield; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.01 – 7.88 (m, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 2.3 Hz, 1H), 6.88 (dd, *J* = 8.3, 2.5 Hz, 1H), 4.94 (s, 2H), 4.60 (s, 2H), 3.78 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 195.7, 159.3, 134.9, 133.6, 129.4, 128.8, 127.9, 124.3, 123.3, 116.7, 115.2, 87.3, 84.0, 71.8, 59.2, 55.3; HRMS (ESI) calculated for [M+Na, C<sub>18</sub>H<sub>16</sub>NaO<sub>3</sub>]<sup>+</sup>: 303.0992; found: 303.1008.



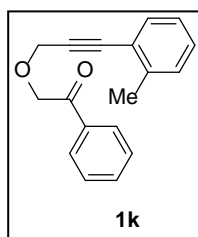
**1-phenyl-2-((3-(3-(trifluoromethyl)phenyl)prop-2-yn-1-yl)oxy)ethan-1-one (1i):** colorless oil, 86% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 – 7.93 (m, 2H), 7.68 (s, 1H), 7.63 – 7.56 (m, 3H), 7.51 – 7.46 (m, 2H), 7.44 (t,  $J = 7.8$  Hz, 1H), 4.94 (s, 2H), 4.61 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  195.6, 134.9, 134.8, 133.7, 131.1, 130.8, 128.9, 128.8,

128.6 (q,  $J = 3.8$  Hz), 127.9, 125.2 (q,  $J = 3.7$  Hz), 123.3, 85.9, 85.8, 72.0, 59.1. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{18}\text{H}_{13}\text{NaF}_3\text{O}_2]^+$ : 341.0760; found: 341.0761.

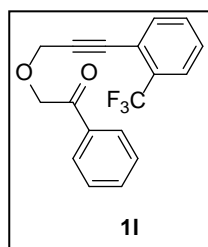


**2-((3-(3-fluorophenyl)prop-2-yn-1-yl)oxy)-1-phenylethan-1-one (1j):** light yellow oil, 78% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (dd,  $J = 8.3, 1.1$  Hz, 2H), 7.64 – 7.54 (m, 1H), 7.47 (t,  $J = 7.8$  Hz, 2H), 7.27 (td,  $J = 7.8, 5.8$  Hz, 1H), 7.21 (dt,  $J = 7.7, 1.1$  Hz, 1H), 7.12 (ddd,  $J = 9.4, 2.4, 1.4$  Hz, 1H), 7.03 (tdd,  $J = 8.5, 2.6, 1.0$  Hz, 1H), 4.93 (s, 2H), 4.59 (s, 2H).  $^{13}\text{C}$  NMR (126

MHz,  $\text{CDCl}_3$ )  $\delta$  195.6, 163.3, 161.3, 134.8, 133.7, 129.9, 128.8, 127.9, 127.7, 124.2, 118.7, 118.5, 116.1, 115.9, 86.1, 85.2, 71.9, 59.1.; HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{17}\text{H}_{13}\text{NaFO}_2]^+$ : 291.0792; found: 291.0796.



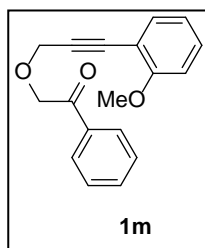
**1-phenyl-2-((3-(o-tolyl)prop-2-yn-1-yl)oxy)ethan-1-one (1k):** light yellow oil, 83% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (m, 2H), 7.59 (t,  $J = 7.4$  Hz, 1H), 7.47 (t,  $J = 7.7$  Hz, 2H), 7.40 (d,  $J = 7.7$  Hz, 1H), 7.24 – 7.17 (m, 2H), 7.13 (t,  $J = 7.3$  Hz, 1H), 4.96 (s, 2H), 4.65 (s, 2H), 2.42 (s, 3H). The  $^1\text{H}$  NMR spectra is in agreement with these reported in the literature.<sup>5</sup>



**1-phenyl-2-((3-(2-(trifluoromethyl)phenyl)prop-2-yn-1-yl)oxy)ethan-1-one (1l):** colorless oil, 81% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 – 7.91 (m, 2H), 7.65 (d,  $J = 7.8$  Hz, 1H), 7.59 (t,  $J = 7.3$  Hz, 2H), 7.52 – 7.45 (m, 3H), 7.42 (t,  $J = 7.7$  Hz, 1H), 4.98 (s, 2H), 4.65 (s, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.6, 134.8, 134.1, 133.7, 131.8, 131.5, 129.6, 128.8, 128.4, 127.9,

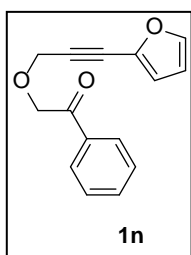
125.85 (q,  $J = 5.1$  Hz), 124.9, 122.2, 120.6, 90.0, 83.4, 71.6, 59.0.; HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{18}\text{H}_{13}\text{NaF}_3\text{O}_2]^+$ : 341.0760; found: 341.0758.





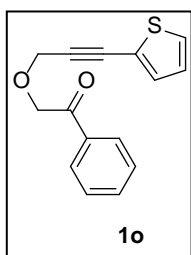
**2-((3-(2-methoxyphenyl)prop-2-yn-1-yl)oxy)-1-phenylethan-1-one (1m):**

white solid, 70% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (dd,  $J = 8.3, 1.2$  Hz, 2H), 7.63 – 7.54 (m, 1H), 7.47 (t,  $J = 7.7$  Hz, 2H), 7.40 (dd,  $J = 7.6, 1.7$  Hz, 1H), 7.30 (td,  $J = 8.4, 1.7$  Hz, 1H), 6.90 (td,  $J = 7.5, 0.8$  Hz, 1H), 6.87 (d,  $J = 8.4$  Hz, 1H), 4.98 (s, 2H), 4.66 (s, 2H), 3.84 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  195.9, 160.2, 135.0, 133.7, 133.5, 130.1, 128.7, 128.0, 120.4, 111.5, 110.6, 88.2, 84.0, 71.6, 59.4, 55.7.; HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{18}\text{H}_{16}\text{NaO}_3]^+$ : 303.0992; found: 303.1009.



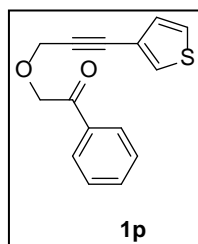
**2-((3-(furan-2-yl)prop-2-yn-1-yl)oxy)-1-phenylethan-1-one (1n):**light yellow

oil, 82% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 – 7.88 (m, 2H), 7.59 (tt, 1H), 7.52 – 7.43 (m, 2H), 7.38 (dd,  $J = 1.8, 0.6$  Hz, 1H), 6.61 (d,  $J = 3.4$  Hz, 1H), 6.38 (dd,  $J = 3.4, 1.9$  Hz, 1H), 4.92 (s, 2H), 4.62 (s, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  195.5, 143.9, 136.2, 134.8, 133.7, 128.8, 127.9, 116.1, 110.9, 88.8, 77.7, 71.7, 59.1. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{15}\text{H}_{12}\text{NaO}_3]^+$ : 263.0679; found: 263.0685.



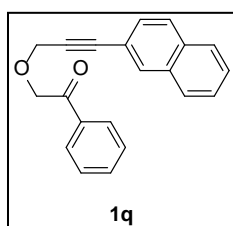
**1-phenyl-2-((3-(thiophen-2-yl)prop-2-yn-1-yl)oxy)ethan-1-one (1o):**light

yellow oil, 77% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 – 7.89 (m, 2H), 7.62 – 7.53 (m, 1H), 7.47 (t,  $J = 7.8$  Hz, 2H), 7.24 (ddd, 2H), 6.97 (dd,  $J = 5.1, 3.7$  Hz, 1H), 4.92 (s, 2H), 4.61 (s, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  195.7, 134.8, 133.7, 132.7, 128.8, 127.9, 127.7, 127.0, 122.2, 88.2, 80.7, 71.8, 59.3. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{15}\text{H}_{12}\text{NaSO}_2]^+$ : 279.0450; found: 279.0470.



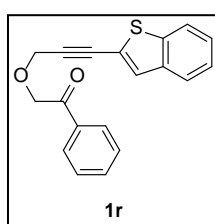
**1-phenyl-2-((3-(thiophen-3-yl)prop-2-yn-1-yl)oxy)ethan-1-one (1p):**light

yellow oil, 71% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (dd,  $J = 8.3, 1.2$  Hz, 2H), 7.65 – 7.54 (m, 1H), 7.52 – 7.42 (m, 3H), 7.25 (dd,  $J = 5.0, 3.0$  Hz, 1H), 7.10 (dd,  $J = 5.0, 1.1$  Hz, 1H), 4.92 (s, 2H), 4.58 (s, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  195.8, 134.8, 133.7, 129.9, 129.5, 128.8, 127.9, 125.4, 121.4, 83.9, 82.5, 71.8, 59.3. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{15}\text{H}_{12}\text{NaSO}_2]^+$ : 279.0450; found: 279.0449.



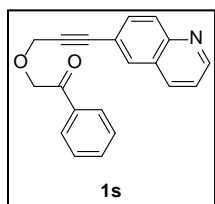
**2-((3-(naphthalen-2-yl)prop-2-yn-1-yl)oxy)-1-phenylethan-1-one (1q):**

white solid, 95% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (dd,  $J = 7.4, 6.2$  Hz, 3H), 7.79 (ddd,  $J = 13.1, 7.1, 3.6$  Hz, 3H), 7.58 (t,  $J = 7.4$  Hz, 1H), 7.53 – 7.41 (m, 5H), 4.97 (s, 2H), 4.65 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  195.8, 134.9, 133.6, 133.0, 133.9, 131.9, 128.8, 128.4, 128.0, 127.9, 127.8, 127.8, 126.9, 126.6, 119.6, 87.7, 84.5, 71.9, 59.4. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{21}\text{H}_{16}\text{NaO}_2]^+$ : 323.1043; found: 323.1053.



**2-((3-(benzo[b]thiophen-2-yl)prop-2-yn-1-yl)oxy)-1-phenylethan-1-one (1r):**

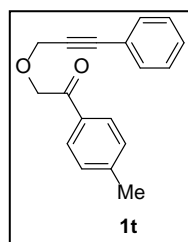
white solid, 73% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 – 7.92 (m, 2H), 7.78 – 7.70 (m, 2H), 7.62 – 7.55 (m, 1H), 7.51 – 7.42 (m, 3H), 7.39 – 7.32 (m, 2H), 4.94 (s, 2H), 4.64 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  195.6, 140.3, 138.9, 134.8, 133.7, 129.6, 128.8, 128.0, 125.7, 124.8, 123.9, 122.1, 122.0, 90.1, 80.9, 71.9, 59.3. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{19}\text{H}_{14}\text{NaSO}_2]^+$ : 329.0607; found: 329.0608.



**1-phenyl-2-((3-(quinolin-6-yl)prop-2-yn-1-yl)oxy)ethan-1-one (1s):**

white solid, 86% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.91 (dd,  $J = 4.2, 1.7$  Hz, 1H), 8.10 (d,  $J = 8.3$  Hz, 1H), 8.04 (d,  $J = 8.7$  Hz, 1H), 7.98 (dd,  $J = 8.3, 1.1$  Hz, 2H), 7.93 (d,  $J = 1.5$  Hz, 1H), 7.71 (dd,  $J = 8.7, 1.8$  Hz, 1H), 7.63 – 7.56 (m, 1H), 7.48 (dd,  $J = 10.8, 4.7$  Hz, 2H), 7.41 (q,  $J = 8.3, 4.2$  Hz, 1H), 4.97 (s, 2H), 4.66 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  195.7, 151.2, 147.9, 135.8, 134.9, 133.7, 132.1, 131.6, 129.7, 128.8, 127.9, 121.8, 120.6, 86.9, 85.5, 71.9, 59.3. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{20}\text{H}_{15}\text{NaNO}_2]^+$ : 324.0995; found: 324.1047.

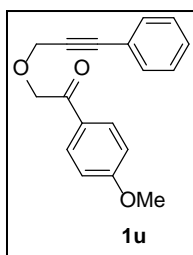
Preparation of **1t-1am** were carried out according to a procedure similar to that for the synthesis of **1a** from corresponding magnesium reagents.



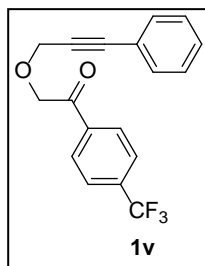
**2-((3-phenylprop-2-yn-1-yl)oxy)-1-(p-tolyl)ethan-1-one (1t):**

white solid, 95% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (dd,  $J = 6.9, 5.5$  Hz, 2H), 7.48 – 7.41 (m, 2H), 7.37 (dd,  $J = 14.6, 7.5$  Hz, 2H), 7.33 – 7.27 (m, 3H), 4.93 (s, 2H),

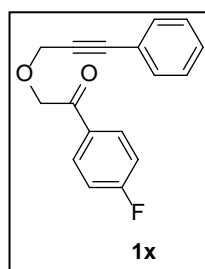
4.60 (s, 2H), 2.40 (s, 3H).  $^1\text{H}$  NMR spectra is in agreement with these reported in the literature.<sup>5</sup>



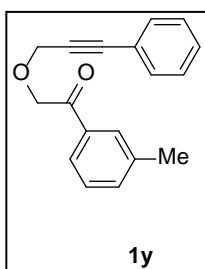
**1-(4-methoxyphenyl)-2-((3-phenylprop-2-yn-1-yl)oxy)ethan-1-one (1u):** white solid, 85% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 – 7.91 (m, 2H), 7.44 (dd,  $J = 7.4, 2.0$  Hz, 2H), 7.36 – 7.27 (m, 3H), 6.99 – 6.89 (m, 2H), 4.88 (s, 2H), 4.59 (s, 2H), 3.86 (s, 3H).  $^1\text{H}$  NMR spectra is in agreement with these reported in the literature.<sup>5</sup>



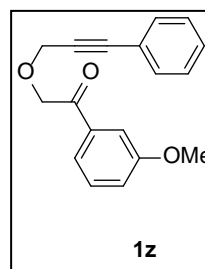
**2-((3-phenylprop-2-yn-1-yl)oxy)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (1v):** white solid, 64% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 (s, 1H), 8.16 (d,  $J = 7.8$  Hz, 1H), 7.84 (d,  $J = 7.8$  Hz, 1H), 7.62 (t,  $J = 7.8$  Hz, 1H), 7.43 (dd,  $J = 7.6, 1.7$  Hz, 2H), 7.38 – 7.28 (m, 3H), 4.92 (s, 2H), 4.60 (s, 2H).  $^1\text{H}$  NMR spectra is in agreement with these reported in the literature.<sup>5</sup>



**1-(4-fluorophenyl)-2-((3-phenylprop-2-yn-1-yl)oxy)ethan-1-one (1x):** white solid, 53% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 – 7.96 (m, 2H), 7.43 (dd,  $J = 7.6, 1.8$  Hz, 2H), 7.38 – 7.27 (m, 3H), 7.18 – 7.11 (m, 2H), 4.88 (s, 2H), 4.59 (s, 2H).  $^1\text{H}$  NMR spectra is in agreement with these reported in the literature.<sup>5</sup>

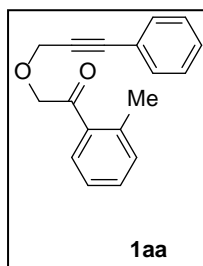


**2-((3-phenylprop-2-yn-1-yl)oxy)-1-(m-tolyl)ethan-1-one (1y):** colorless oil, 73% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J = 8.2$  Hz, 2H), 7.51 – 7.38 (m, 2H), 7.37 – 7.28 (m, 3H), 7.26 (d,  $J = 8.0$  Hz, 2H), 4.91 (s, 2H), 4.59 (s, 2H), 2.41 (s, 3H).  $^1\text{H}$  NMR spectra is in agreement with these reported in the literature.<sup>5</sup>

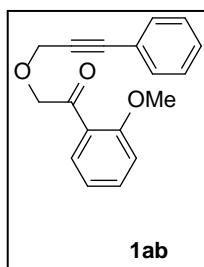


**1-(3-methoxyphenyl)-2-((3-phenylprop-2-yn-1-yl)oxy)ethan-1-one (1z):** white solid, 77% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 (d,  $J = 7.7$  Hz, 1H), 7.50 – 7.48 (m, 1H), 7.44 (dd,  $J = 7.5, 1.9$  Hz, 2H), 7.38 (t,  $J = 7.9$  Hz, 1H), 7.35 – 7.28 (m, 3H), 7.13 (dd,  $J = 8.2, 2.6$  Hz, 1H), 4.92 (s, 2H), 4.60 (s, 2H), 3.85 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  195.6, 160.0, 136.2, 131.8, 129.8, 128.6, 128.3, 122.4, 120.4, 120.2, 112.2, 87.4, 84.1, 71.8, 59.3,

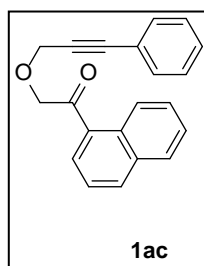
55.5.; HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{18}\text{H}_{16}\text{NaO}_3]^+$ : 303.0992; found:303.1012.



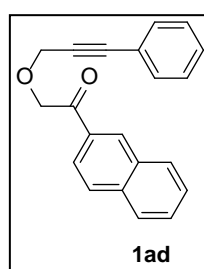
**3-((3-phenylprop-2-yn-1-yl)oxy)-1-(o-tolyl)ethan-1-one (1aa):** colorless oil, 94% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (d,  $J = 7.7$  Hz, 1H), 7.44 (dd,  $J = 7.5, 1.8$  Hz, 2H), 7.39 (t,  $J = 7.5$  Hz, 1H), 7.31 (t,  $J = 6.0$  Hz, 3H), 7.26 (d,  $J = 8.1$  Hz, 2H), 4.79 (s, 2H), 4.58 (s, 2H), 2.52 (s, 3H).  $^1\text{H NMR}$  spectra is in agreement with these reported in the literature.<sup>5</sup>



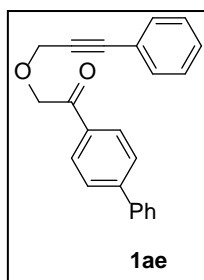
**(2-methoxyphenyl)-2-((3-phenylprop-2-yn-1-yl)oxy)ethan-1-one (1ab):** white solid, 87% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (dd,  $J = 7.7, 0.8$  Hz, 1H), 7.53 – 7.48 (m, 1H), 7.44 (dd,  $J = 6.9, 1.7$  Hz, 2H), 7.38 – 7.27 (m, 3H), 7.04 (t,  $J = 7.5$  Hz, 1H), 6.98 (d,  $J = 8.4$  Hz, 1H), 4.87 (d,  $J = 0.7$  Hz, 2H), 4.59 (s, 2H), 3.92 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  197.2, 159.2, 134.4, 131.8, 130.8, 128.5, 128.3, 125.3, 122.6, 121.0, 111.5, 86.8, 84.8, 75.6, 59.1, 55.6; HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{18}\text{H}_{16}\text{NaO}_3]^+$ :303.0992; found:303.1035.



**1-(naphthalen-1-yl)-2-((3-phenylprop-2-yn-1-yl)oxy)ethan-1-one (1ac):** light yellow oil, 87% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.64 (d,  $J = 8.4$  Hz, 1H), 8.01 (d,  $J = 8.2$  Hz, 1H), 7.92 – 7.81 (m, 2H), 7.61 – 7.51 (m, 2H), 7.49 (dd,  $J = 8.0, 7.4$  Hz, 1H), 7.43 (dd,  $J = 7.6, 1.8$  Hz, 2H), 7.34 – 7.26 (m, 3H), 4.93 (s, 2H), 4.63 (s, 2H).  $^1\text{H NMR}$  spectra is in agreement with these reported in the literature.<sup>5</sup>

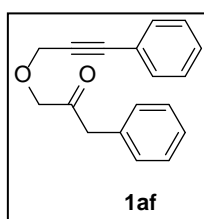


**1-(naphthalen-2-yl)-2-((3-phenylprop-2-yn-1-yl)oxy)ethan-1-one (1ad):** light yellow oil, 90% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.48 (s, 1H), 8.01 (dd,  $J = 8.6, 1.7$  Hz, 1H), 7.94 (d,  $J = 8.1$  Hz, 1H), 7.88 (dd,  $J = 15.2, 8.4$  Hz, 2H), 7.57 (dddd,  $J = 28.0, 8.1, 6.9, 1.2$  Hz, 2H), 7.46 – 7.42 (m, 2H), 7.34 – 7.26 (m, 3H), 5.06 (s, 2H), 4.64 (s, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  195.9, 136.0, 132.6, 132.3, 131.9, 129.8, 128.8, 128.7, 128.5, 128.0, 127.9, 127.0, 125.9, 123.7, 122.5, 87.5, 84.3, 72.1, 59.5. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{21}\text{H}_{16}\text{NaO}_2]^+$ : 323.1045; found: 323.1065.



**1-([1,1'-biphenyl]-4-yl)-2-((3-phenylprop-2-yn-1-yl)oxy)ethan-1-one (1ae):**

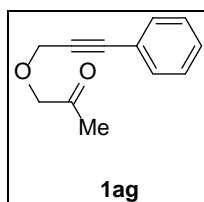
white solid, 86% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J = 8.4$  Hz, 2H), 7.69 (d,  $J = 8.4$  Hz, 2H), 7.62 (dd,  $J = 5.2, 3.4$  Hz, 2H), 7.50 – 7.37 (m, 5H), 7.35 – 7.27 (m, 3H), 4.96 (s, 2H), 4.62 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  195.4, 146.3, 139.8, 133.6, 131.8, 129.0, 128.7, 128.4, 127.4, 127.3, 122.4, 87.4, 84.2, 71.9, 59.3. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{23}\text{H}_{18}\text{NaO}_2]^+$ : 349.1199; found: 349.1197.



**1-phenyl-3-((3-phenylprop-2-yn-1-yl)oxy)propan-2-one (1af):**

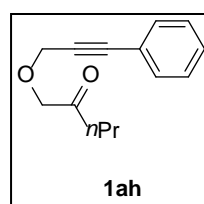
white solid, 84% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (dd,  $J = 7.6, 1.8$  Hz, 2H), 7.32 (dt,  $J = 7.5, 5.3$  Hz, 5H), 7.27 – 7.20 (m, 3H), 4.46 (s, 2H), 4.28 (s, 2H), 3.81 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  205.6, 133.4, 131.8, 129.5, 128.8, 128.7, 128.4, 127.2, 122.2, 87.4, 83.9, 73.7, 59.3, 46.4. HRMS (ESI)

calculated for  $[\text{M}+\text{Na}, \text{C}_{18}\text{H}_{16}\text{NaO}_2]^+$ : 287.1043; found: 287.1057.



**1-((3-phenylprop-2-yn-1-yl)oxy)propan-2-one (1ag):**

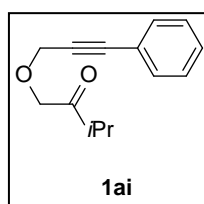
colorless oil, 90% yield;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 – 7.40 (m, 2H), 7.36 – 7.28 (m, 3H), 4.49 (s, 2H), 4.23 (s, 2H), 2.20 (s, 3H).  $^1\text{H}$  NMR spectra is in agreement with these reported in the literature.<sup>5</sup>



**1-((3-phenylprop-2-yn-1-yl)oxy)pentan-2-one (1ah):**

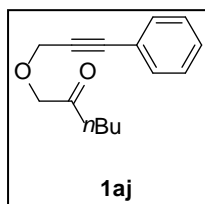
colorless oil, 78% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (dd,  $J = 7.5, 2.1$  Hz, 2H), 7.37 – 7.28 (m, 3H), 4.49 (s, 2H), 4.22 (s, 2H), 2.47 (t,  $J = 7.3$  Hz, 2H), 1.72 – 1.56 (m, 2H), 0.94 (t,  $J = 7.4$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  208.2, 131.8, 128.7, 128.3, 122.3, 87.3, 84.0, 74.3, 59.2, 41.0, 16.8, 13.7. HRMS (ESI)

calculated for  $[\text{M}+\text{Na}, \text{C}_{14}\text{H}_{16}\text{NaO}_2]^+$ : 239.1043; found: 239.1044.

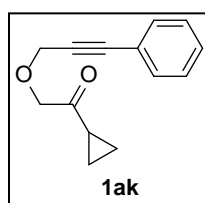


**1-methyl-1-((3-phenylprop-2-yn-1-yl)oxy)butan-2-one (1ai):**

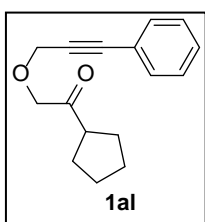
colorless oil, 95% yield;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (dd,  $J = 7.5, 2.1$  Hz, 2H), 7.38 – 7.28 (m, 3H), 4.49 (s, 2H), 4.32 (s, 2H), 2.81 (hept,  $J = 6.9$  Hz, 1H), 1.13 (d,  $J = 7.0$  Hz, 6H).  $^1\text{H}$  NMR spectra is in agreement with these reported in the literature.<sup>5</sup>



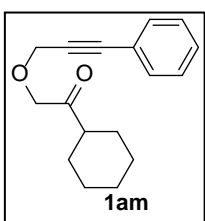
**1-((3-phenylprop-2-yn-1-yl)oxy)hexan-2-one (1aj):** colorless oil, 68% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{cdCl}_3$ )  $\delta$  7.47 – 7.40 (m, 2H), 7.35 – 7.28 (m, 3H), 4.49 (s, 2H), 4.23 (s, 2H), 2.48 (t,  $J = 7.5$  Hz, 2H), 1.63 – 1.54 (m, 2H), 1.38 – 1.28 (m, 2H), 0.90 (t,  $J = 7.4$  Hz, 3H).  $^1\text{H NMR}$  spectra is in agreement with these reported in the literature.<sup>5</sup>



**1-cyclopropyl-2-((3-phenylprop-2-yn-1-yl)oxy)ethan-1-one (1ak):** colorless oil, 79% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (dd,  $J = 7.5, 2.1$  Hz, 2H), 7.36 – 7.27 (m, 3H), 4.51 (s, 2H), 4.38 (s, 2H), 2.20 – 2.10 (m, 1H), 1.15 – 1.08 (m, 2H), 0.95 (dq,  $J = 7.3, 3.6$  Hz, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  208.0, 131.8, 128.7, 128.3, 122.3, 87.2, 84.1, 74.6, 59.2, 17.1, 11.5. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{14}\text{H}_{14}\text{NaO}_2]^+$ : 237.0886; found: 237.0909.

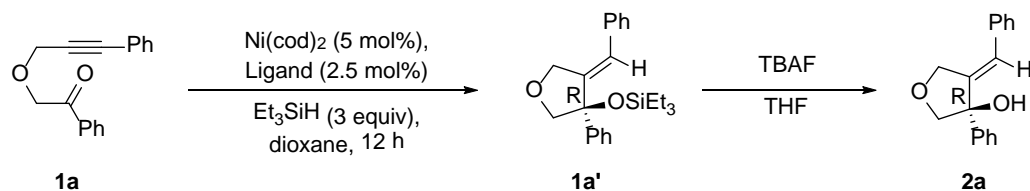


**1-cyclopentyl-2-((3-phenylprop-2-yn-1-yl)oxy)ethan-1-one (1al):** colorless oil, 84% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 – 7.40 (m, 2H), 7.38 – 7.28 (m, 3H), 4.50 (s, 2H), 4.32 (s, 2H), 3.07 – 2.95 (m, 1H), 1.88 – 1.73 (m, 4H), 1.73 – 1.63 (m, 2H), 1.63 – 1.54 (m, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  210.1, 131.8, 128.6, 128.4, 122.4, 87.2, 84.1, 73.5, 59.1, 47.5, 28.9, 26.1. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{16}\text{H}_{18}\text{NaO}_2]^+$ : 265.1199; found: 265.1214.



**1-cyclohexyl-2-((3-phenylprop-2-yn-1-yl)oxy)ethan-1-one (1am):** colorless oil, 88% yield;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 – 7.40 (m, 2H), 7.38 – 7.28 (m, 3H), 4.49 (s, 2H), 4.31 (s, 2H), 2.53 (tt,  $J = 11.5, 3.4$  Hz, 1H), 1.91 – 1.73 (m, 4H), 1.46 – 1.14 (m, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  210.6, 131.8, 128.6, 128.3, 122.4, 87.2, 84.1, 72.8, 59.1, 47.1, 28.2, 25.8, 25.6. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{17}\text{H}_{20}\text{NaO}_2]^+$ : 279.1356; found: 279.1365.

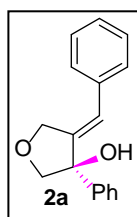
### 3. General Procedure of Nickel-Catalyzed Intramolecular Reductive Coupling of O-Alkynesones



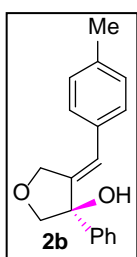
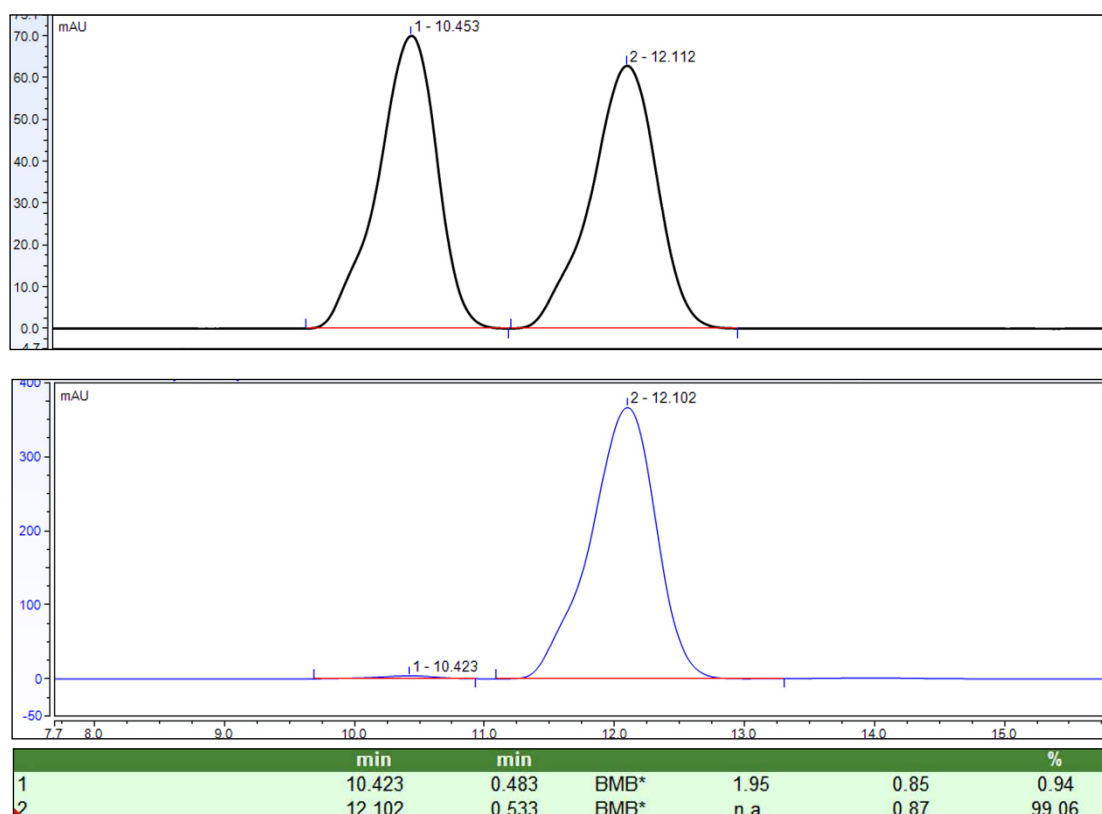
**General procedure for asymmetric synthesis:** Ni(cod)<sub>2</sub> (0.0075 mmol, 5 mol %), (*S,S*)-DI-BIDIME (L13, 0.00375 mmol, 2.5 mol %), and dioxane (0.4 mL) were added to a 4 mL screw-cap vial equipped with a magnetic stirring bar in the glove box. Substrate **1a** (0.15 mmol, 1.0 equiv.) was added to the solution in one portion, stirred for 5 mins, followed by the addition of triethylsilane (Et<sub>3</sub>SiH, 0.072 mL, 0.45 mmol, 3.0 equiv.). The vial was closed with a screw-cap, and the resulting mixture was stirred at 0 °C for 12 h. Quenched with saturated sodium bicarbonate (NaHCO<sub>3</sub>), extracted with ethyl acetate (EtOAc), washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography (eluent: PE/EA 40/1) to afford **1a'**. After **1a'** was desilylated with TBAF in THF, the reaction was quenched with saturated NH<sub>4</sub>Cl solution, extracted with EtOAc, washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography (eluent: PE/EA 4/1) to afford **2a**.

**General procedure for preparing racemic product:** Ni(cod)<sub>2</sub> (0.0075 mmol, 5 mol %), PPh<sub>3</sub> (0.0075 mmol, 5 mol %), and dioxane (0.4 mL) were added to a 4 mL screw-cap vial equipped with a magnetic stirring bar in the glove box. Substrate **1a** (0.15 mmol, 1.0 equiv.) was added to the solution in one portion, stirred for 5 mins, followed by the addition of triethylsilane (Et<sub>3</sub>SiH, 0.072 mL, 0.45 mmol, 3.0 equiv.). The vial was closed with a screw-cap, and the resulting mixture was stirred at rt for 12 h. Quenched with saturated sodium bicarbonate (NaHCO<sub>3</sub>), extracted with ethyl acetate (EtOAc), washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography (eluent: PE/EA 40/1) to afford racemic **1a'**. After racemic **1a'** was desilylated with TBAF in THF, the reaction was quenched with saturated NH<sub>4</sub>Cl solution, extracted with EtOAc, washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography (eluent: PE/EA 4/1) to afford racemic **2a**.

#### 4. Physical Data of Products



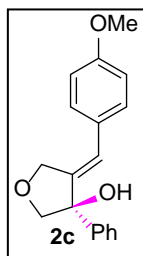
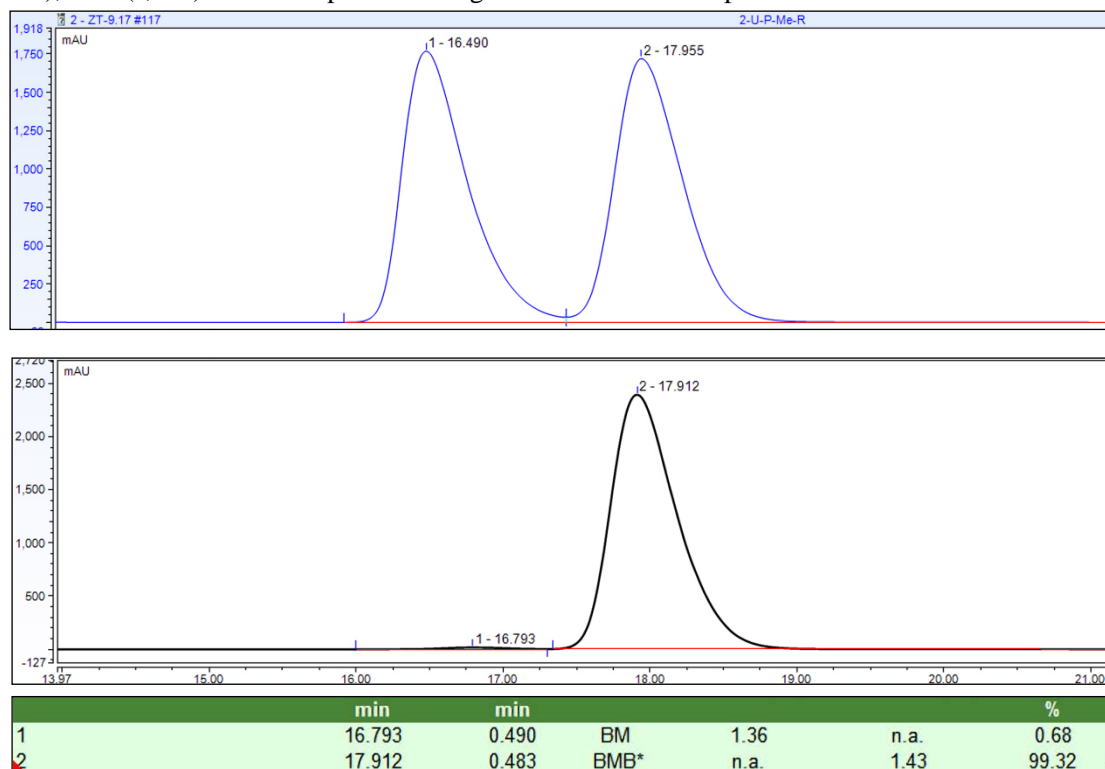
**2a**: white solid, 99% yield, > 99:1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 10.42 min (*S*), 12.10 min (*R*).  $[\alpha]_D^{25} = +4.4$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 (d,  $J = 7.4$  Hz, 2H), 7.40 – 7.31 (m, 5H), 7.27 – 7.24 (m, 1H), 7.13 (d,  $J = 7.5$  Hz, 2H), 6.30 (t,  $J = 2.5$  Hz, 1H), 4.97 (ddd,  $J = 113.1, 14.5, 2.5$  Hz, 2H), 4.04 (dd,  $J = 58.6, 9.6$  Hz, 2H), 2.41 (s, 1H).  $^1\text{H NMR}$  spectra is in agreement with these reported in the literature.<sup>5</sup>



**2b**: white solid, 93% yield, > 99:1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 95/5, 254 nm, 16.80 min (*S*), 17.91 min (*R*).  $[\alpha]_D^{25} = +15.2$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 – 7.51 (m, 2H), 7.38 (dd,  $J = 10.4, 4.7$  Hz, 2H), 7.30 (t,  $J = 7.3$  Hz, 1H), 7.08 (dd,  $J = 64.7, 8.0$  Hz, 4H), 6.25 (t,  $J$

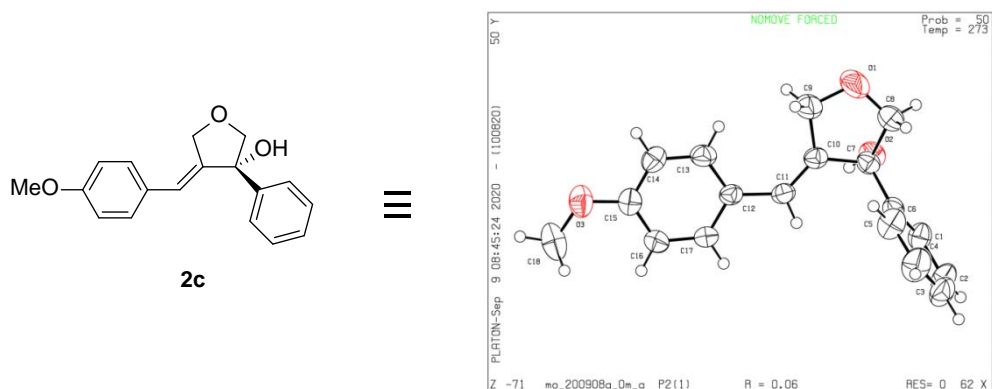


= 2.4 Hz, 1H), 4.94 (ddd,  $J = 114.7, 14.4, 2.4$  Hz, 2H), 4.02 (dd,  $J = 61.4, 9.6$  Hz, 2H), 2.46 (s, 1H), 2.34 (s, 3H).  $^1\text{H}$  NMR spectra is in agreement with these reported in the literature.<sup>5</sup>

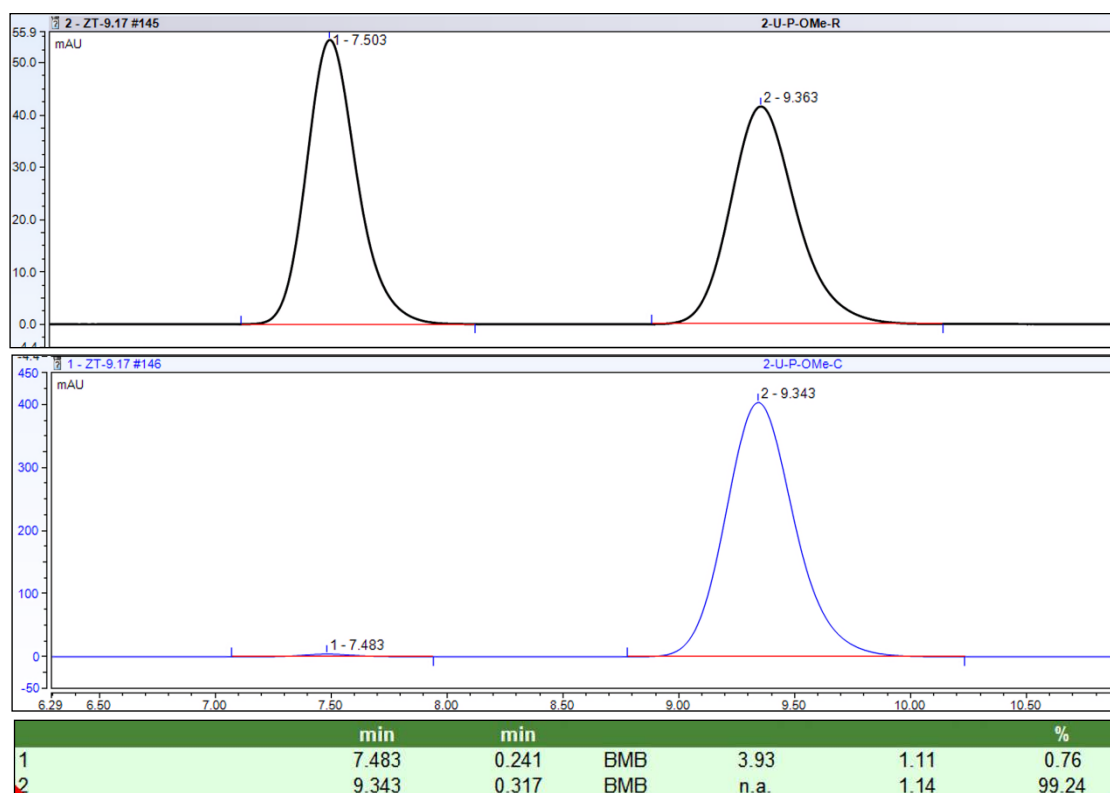


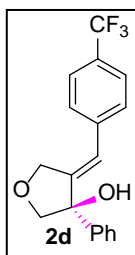
**2c**: white solid, 90% yield, > 99:1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 15/85, 254 nm, 7.48 min (*S*), 9.34 min (*R*).  $[\alpha]_D^{25} = +25.3$  ( $c = 1.0, \text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 – 7.52 (m, 2H), 7.38 (t,  $J = 7.5$  Hz, 2H), 7.31 (t,  $J = 7.3$  Hz, 1H), 6.97 (dd,  $J = 75.4, 8.7$  Hz, 4H), 6.23 (t,  $J = 2.5$  Hz, 1H), 4.94 (ddd,  $J = 92.7, 14.3, 2.4$  Hz, 2H), 4.03 (dd,  $J = 51.6, 9.5$  Hz, 2H), 3.81 (s, 3H), 2.41 (s, 1H).  $^1\text{H}$  NMR spectra is in agreement with these reported in the literature.<sup>5</sup>

Crystallization from n-Pentane/DCM (9:1) gave crystals suitable for X-ray crystallographic analysis, which revealed its absolute configuration for the chiral tertiary alcohol **2c** as shown in **Figure 1**.

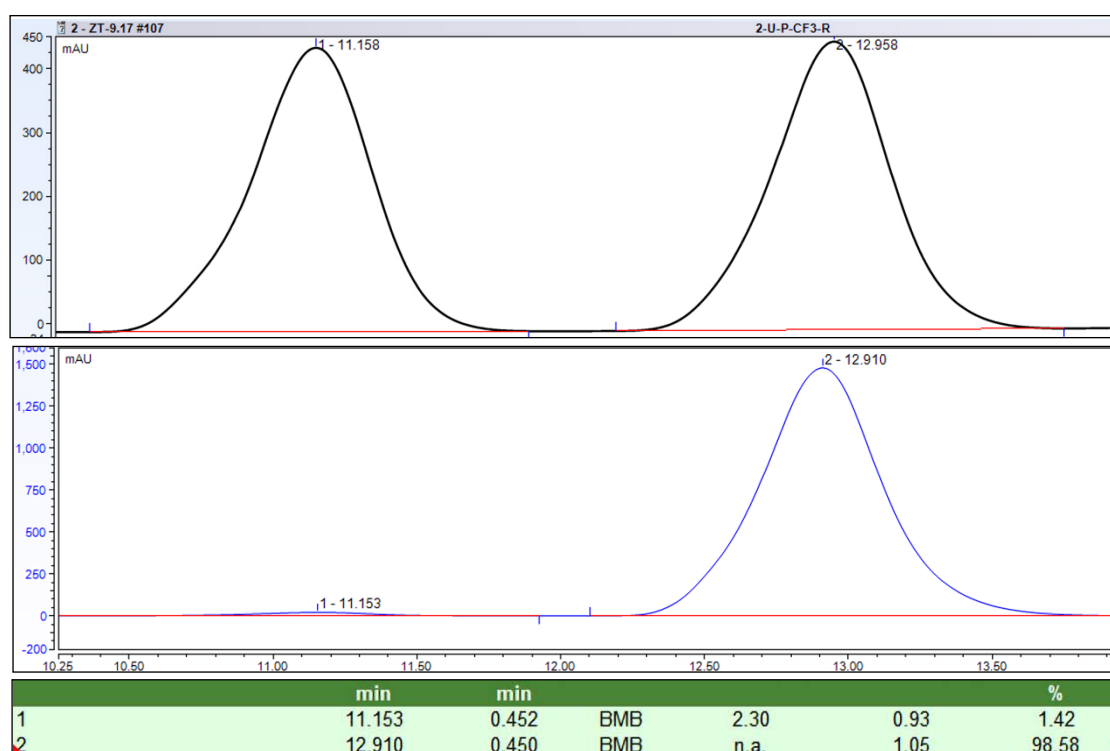


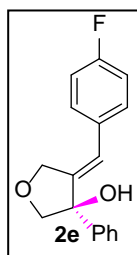
**Figure 1.** X-ray derived ORTEP representation of **2c**. (CCDC Number: 2040946 contains the supplementary crystallographic data of **2c**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre)



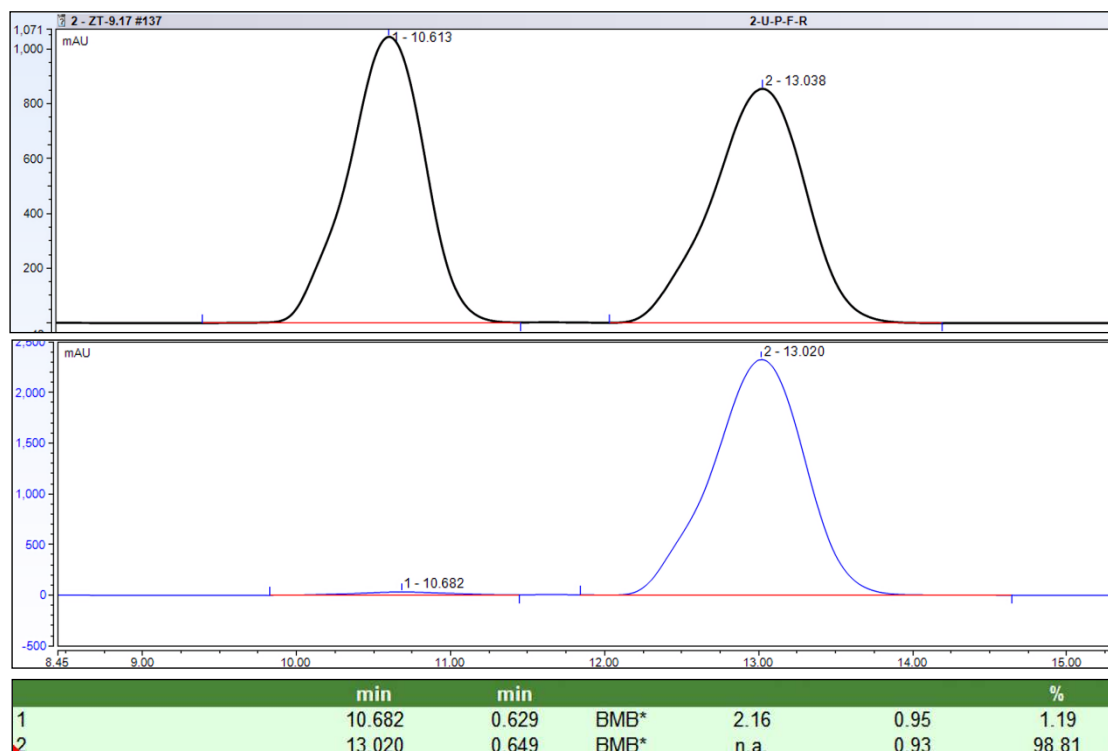


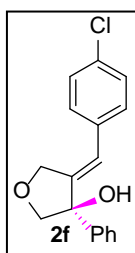
**2d**: white solid, 70% yield, 99:1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 11.16 min (*S*), 12.91 min (*R*).  $[\alpha]_D^{25} = +8.6$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (ddd,  $J = 8.3, 7.1, 5.3$  Hz, 4H), 7.43 – 7.37 (m, 2H), 7.36 – 7.30 (m, 1H), 7.22 (d,  $J = 8.2$  Hz, 2H), 6.34 (t,  $J = 2.5$  Hz, 1H), 4.95 (ddd,  $J = 105.5, 14.7, 2.5$  Hz, 2H), 4.06 (dd,  $J = 40.7, 9.6$  Hz, 2H), 2.52 (s, 1H).  $^1\text{H NMR}$  spectra is in agreement with these reported in the literature.<sup>5</sup>



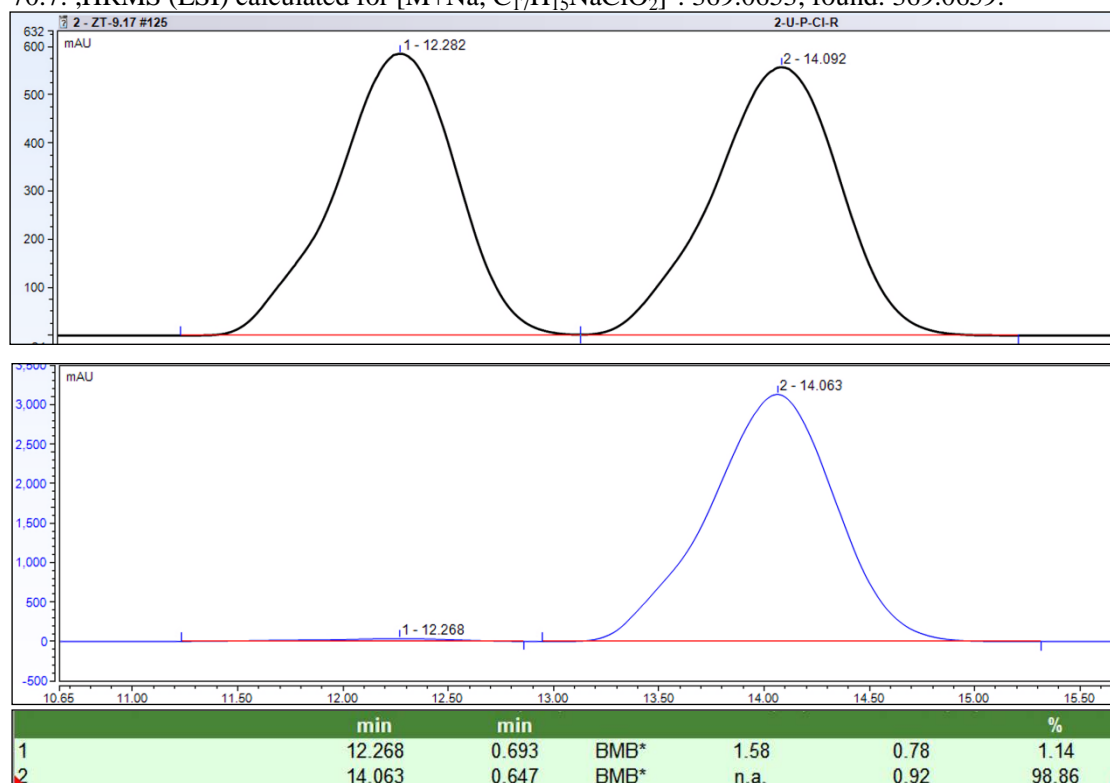


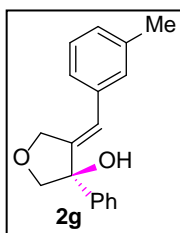
**2e**: colorless oil, 79% yield, 99:1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 10.68 min (*S*), 13.02 min (*R*).  $[\alpha]_D^{25} = +4.3$  ( $c=1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (dt,  $J = 3.1, 1.8$  Hz, 2H), 7.43 – 7.35 (m, 2H), 7.34 – 7.28 (m, 1H), 7.13 – 6.97 (m, 4H), 6.25 (t,  $J = 2.6$  Hz, 1H), 4.91 (ddd,  $J = 108.9, 14.4, 2.5$  Hz, 2H), 4.03 (dd,  $J = 52.3, 9.6$  Hz, 2H), 2.57 (s, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  163.0, 161.0, 147.0, 147.0, 141.5, 132.5, 130.0 (d,  $J = 8.1$  Hz), 128.2, 127.6, 126.3, 123.7, 115.7, 115.6, 82.9, 81.2, 70.6. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{17}\text{H}_{15}\text{NaFO}_2]^+$ : 239.0948; found: 239.0949.





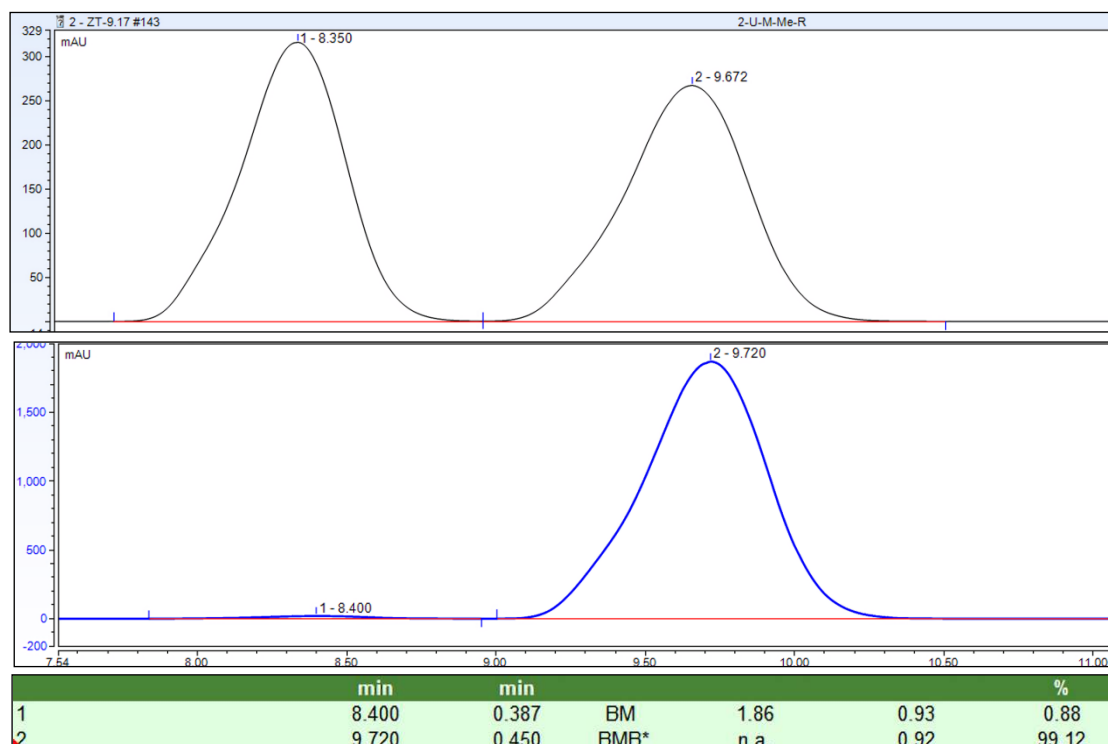
**2f**: colorless oil, 83% yield, 99:1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 12.27 min (*S*), 14.06 min (*R*).  $[\alpha]_D^{25} = +20$  ( $c = 1.0, \text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 – 7.51 (m, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.29 (m, 3H), 7.05 (t,  $J = 5.5$  Hz, 2H), 6.25 (t,  $J = 2.6$  Hz, 1H), 4.92 (ddd,  $J = 109.3, 14.5, 2.5$  Hz, 2H), 4.04 (dd,  $J = 48.4, 9.6$  Hz, 2H), 2.41 (s, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  148.1, 141.3, 134.8, 133.4, 129.7, 128.8, 128.3, 127.6, 126.2, 123.7, 83.0, 81.1, 70.7. ;HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{17}\text{H}_{15}\text{NaClO}_2]^+$ : 369.0653; found: 369.0659.

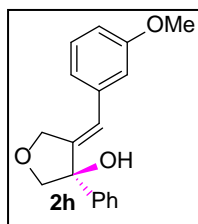




**2g**: white solid, 84% yield, > 99/1 er with **L2** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 8.40 min (*S*), 9.72 min (*R*).  $[\alpha]_D^{25} = +4.7$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (dt,  $J = 3.0, 1.8$  Hz, 2H),

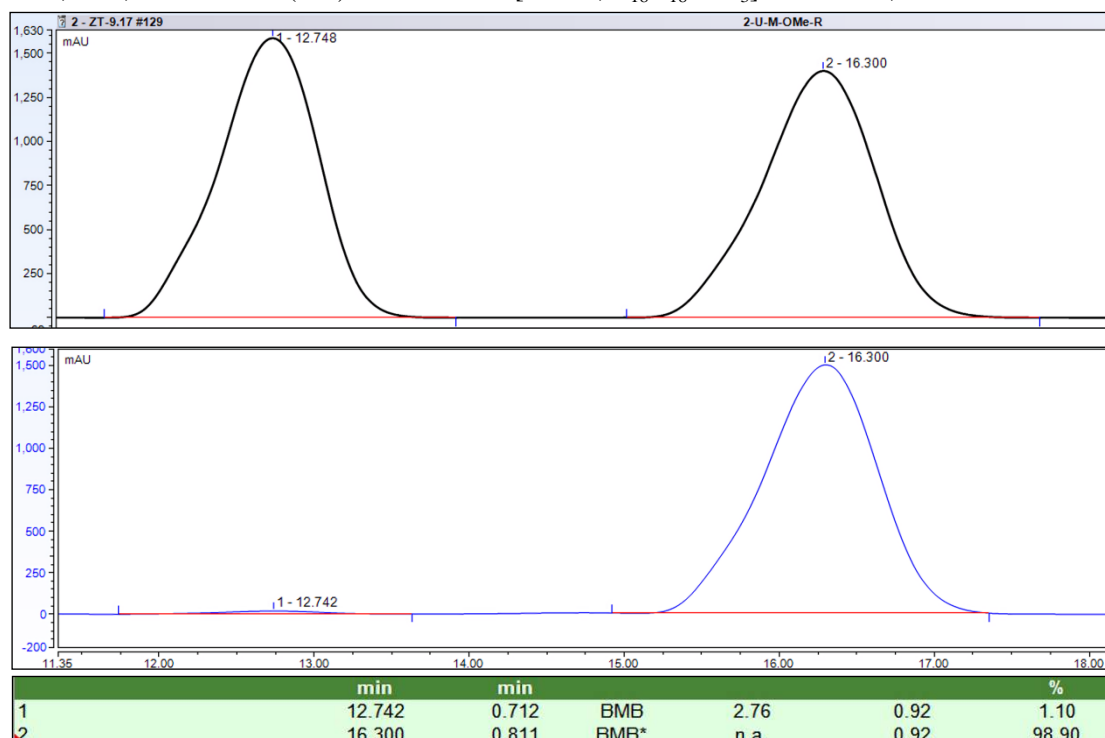
7.41 – 7.34 (m, 2H), 7.33 – 7.26 (m, 1H), 7.23 (dd,  $J = 10.8, 4.8$  Hz, 1H), 7.06 (d,  $J = 7.5$  Hz, 1H), 6.92 (d,  $J = 7.4$  Hz, 2H), 6.25 (t,  $J = 2.6$  Hz, 1H), 4.94 (ddd,  $J = 112.5, 14.5, 2.5$  Hz, 2H), 4.02 (dd,  $J = 59.7, 9.6$  Hz, 2H), 2.58 (s, 1H), 2.32 (s, 3H).  $^1\text{H NMR}$  spectra is in agreement with these reported in the literature.<sup>5</sup>

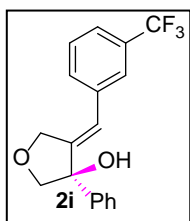




**2h**: colorless oil, 71% yield, 99:1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 12.74 min (*S*), 16.30 min (*R*).  $[\alpha]_D^{25} = +5.3$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 – 7.52 (m,

2H), 7.41 – 7.35 (m, 2H), 7.34 – 7.29 (m, 1H), 7.26 (d,  $J = 8.0$  Hz, 1H), 6.81 (dd,  $J = 8.2, 2.3$  Hz, 1H), 6.72 (d,  $J = 7.7$  Hz, 1H), 6.66 – 6.62 (m, 1H), 6.26 (t,  $J = 2.6$  Hz, 1H), 4.95 (ddd,  $J = 112.2, 14.5, 2.5$  Hz, 2H), 4.03 (dd,  $J = 57.1, 9.6$  Hz, 2H), 3.78 (s, 3H), 2.49 (s, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7, 147.8, 141.6, 137.7, 129.6, 128.2, 127.5, 126.3, 124.8, 120.8, 114.0, 113.2, 83.0, 81.2, 70.8, 55.2. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{18}\text{H}_{18}\text{NaO}_3]^+$ : 305.1148; found: 305.1150.





**2i**: colorless oil, 58% yield, 99:1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 6.39min (*S*), 7.63 min (*R*).  $[\alpha]_D^{25} = +12.0$

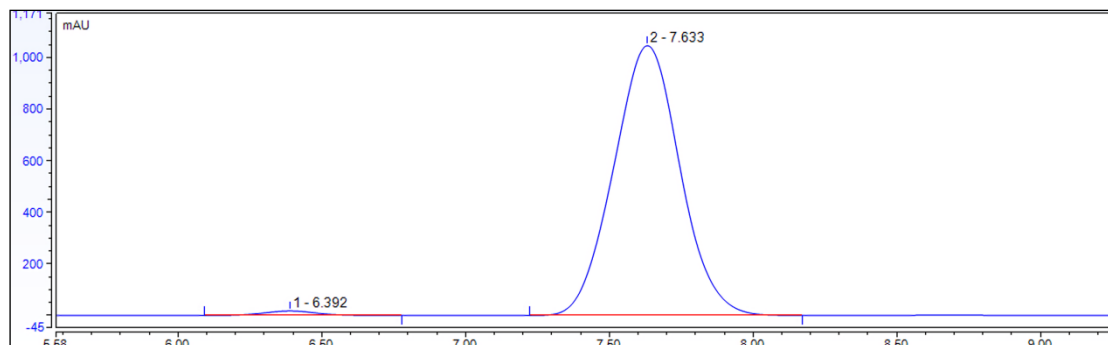
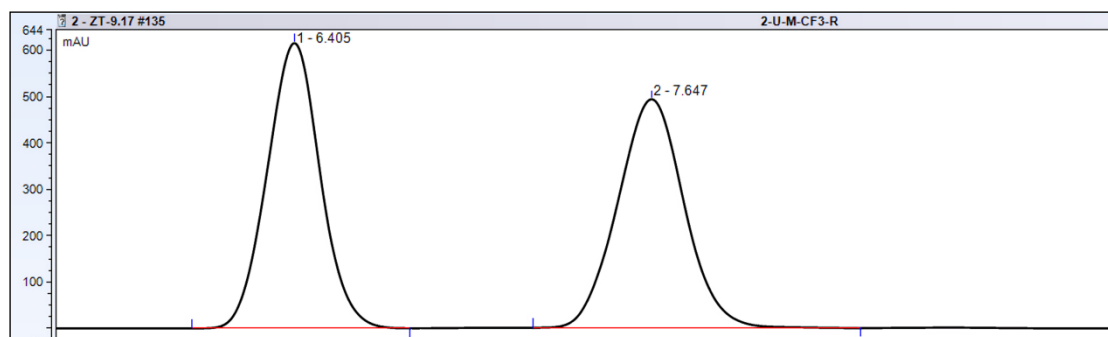
(*c* = 1.0, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.58 (dd, *J* = 5.3, 3.4 Hz, 2H),

7.49 (dt, *J* = 15.3, 7.7 Hz, 2H), 7.43 – 7.36 (m, 3H), 7.36 – 7.29 (m, 2H), 6.33 (t, *J* = 2.6 Hz, 1H),

4.96 (ddd, *J* = 104.8, 14.6, 2.6 Hz, 2H), 4.06 (dd, *J* = 40.8, 9.6 Hz, 2H), 2.38 (s, 1H). <sup>13</sup>C NMR

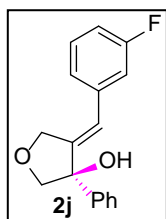
(126 MHz, CDCl<sub>3</sub>) δ 149.6, 141.2, 137.0, 131.2, 129.2, 128.4, 127.7, 126.2, 125.1, 124.1, 123.5,

82.9, 81.1, 70.5. HRMS (ESI) calculated for [M+Na, C<sub>18</sub>H<sub>15</sub>NaF<sub>3</sub>O<sub>2</sub>]<sup>+</sup>: 343.0916; found: 343.0920



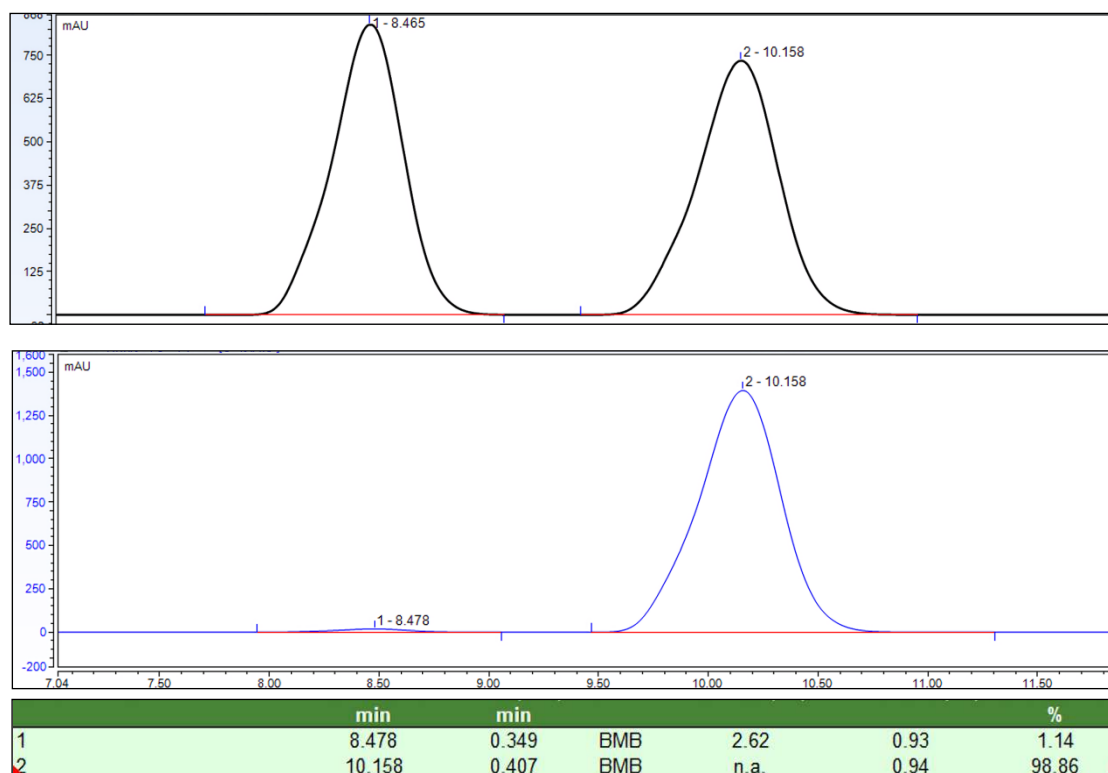
	min	min				%
1	6.392	0.198	BMB	3.28	1.03	1.34
2	7.633	0.249	BMB	n.a	1.03	98.66

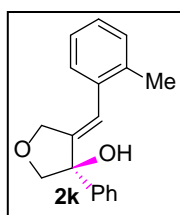




**2j**: colorless oil, 83% yield, 99:1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 8.48 min (*S*), 10.16 min (*R*).  $[\alpha]_D^{25} = +5.0$

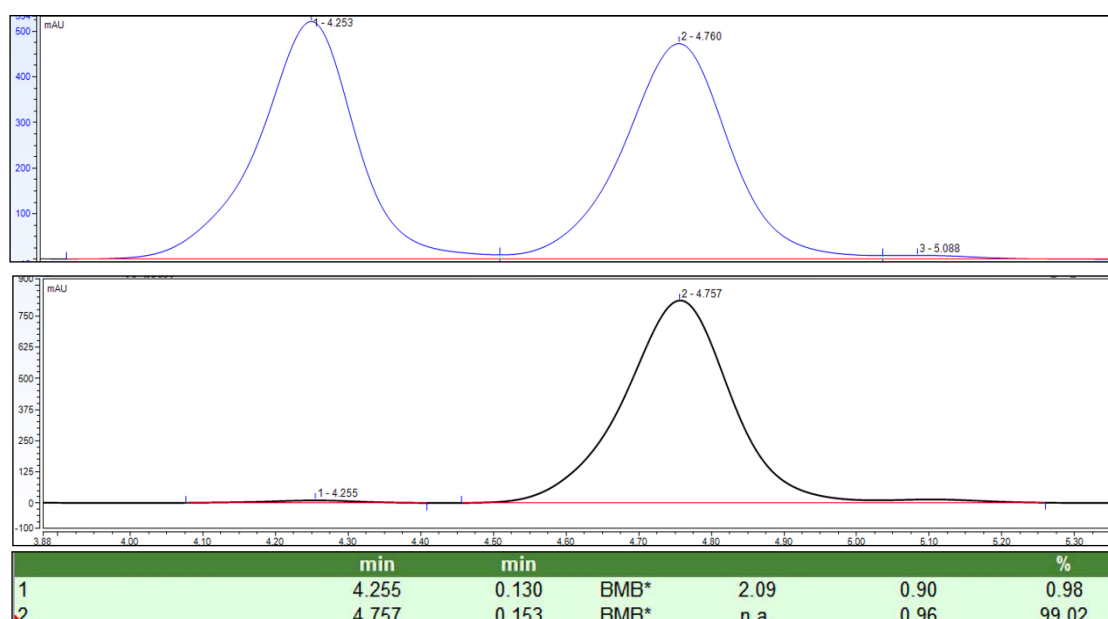
(*c* = 1.0, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.58 – 7.50 (m, 2H), 7.42 – 7.34 (m, 2H), 7.33 – 7.23 (m, 2H), 6.93 (td, *J* = 8.4, 2.4 Hz, 1H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.82 – 6.75 (m, 1H), 6.25 (t, *J* = 2.6 Hz, 1H), 4.90 (ddd, *J* = 105.6, 14.6, 2.5 Hz, 2H), 4.02 (dd, *J* = 48.3, 9.6 Hz, 2H), 2.82 (s, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 163.9, 161.9, 148.82, 141.4, 138.5, 138.5, 128.3, 127.6, 126.3, 124.1, 124.1, 123.8, 123.8, 114.7 (dd, *J* = 67.4, 21.6 Hz), 82.9, 81.0, 70.6. HRMS (ESI) calculated for [M+Na, C<sub>17</sub>H<sub>15</sub>NaFO<sub>2</sub>]<sup>+</sup>: 239.0948; found: 239.0948.

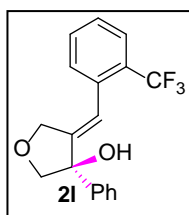




**2k**: white solid, 97% yield, 99:1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 15/85, 254 nm, 4.26 min (*S*), 4.76 min (*R*).  $[\alpha]_D^{25} = -28.7$

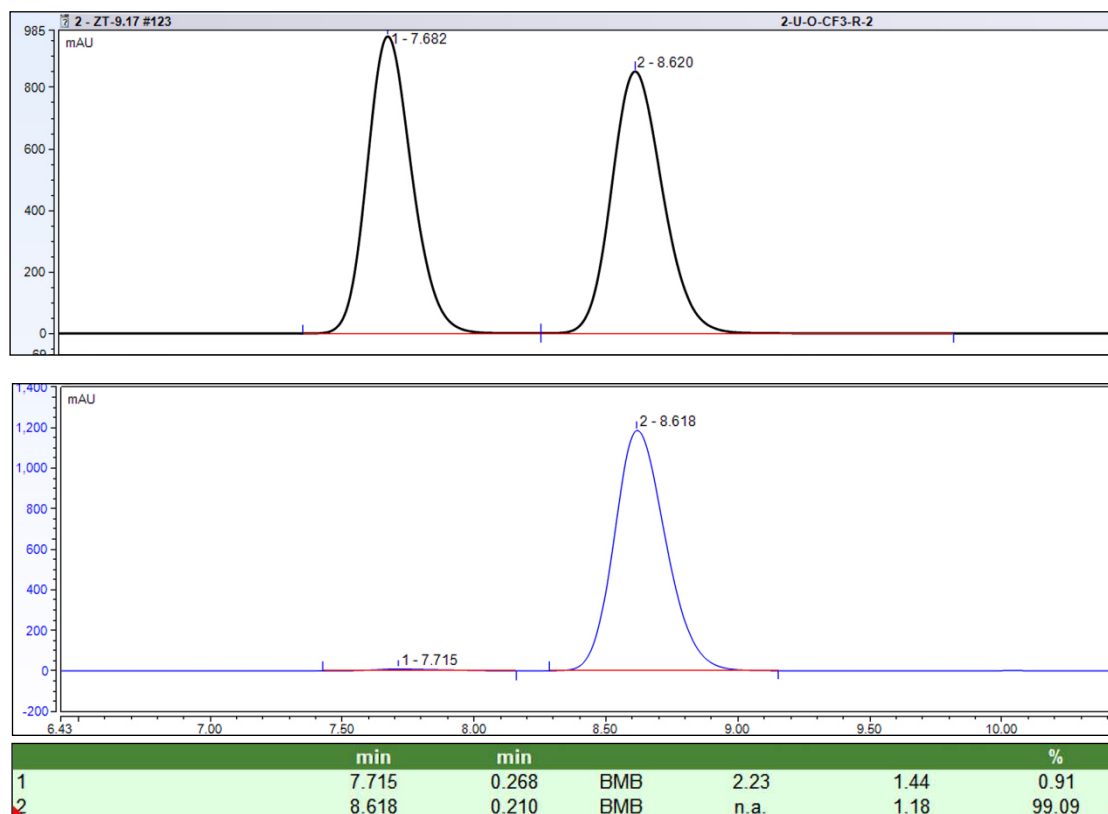
(*c* = 1.0, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.59 (dt, *J* = 3.0, 1.7 Hz, 2H), 7.43 – 7.34 (m, 2H), 7.34 – 7.27 (m, 1H), 7.21 – 7.10 (m, 3H), 7.08 – 7.01 (m, 1H), 6.45 (t, *J* = 2.5 Hz, 1H), 4.82 (ddd, *J* = 131.2, 14.3, 2.5 Hz, 2H), 4.04 (dd, *J* = 63.5, 9.6 Hz, 2H), 2.57 (s, 1H), 2.17 (s, 3H). <sup>1</sup>H NMR spectra is in agreement with these reported in the literature.<sup>5</sup>

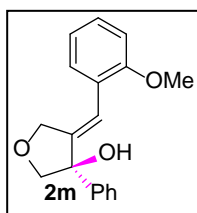




**2l**: colorless oil, 56% yield, > 99/1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 7.72 min (*S*), 8.62 min (*R*).  $[\alpha]_D^{25} = -8.3$

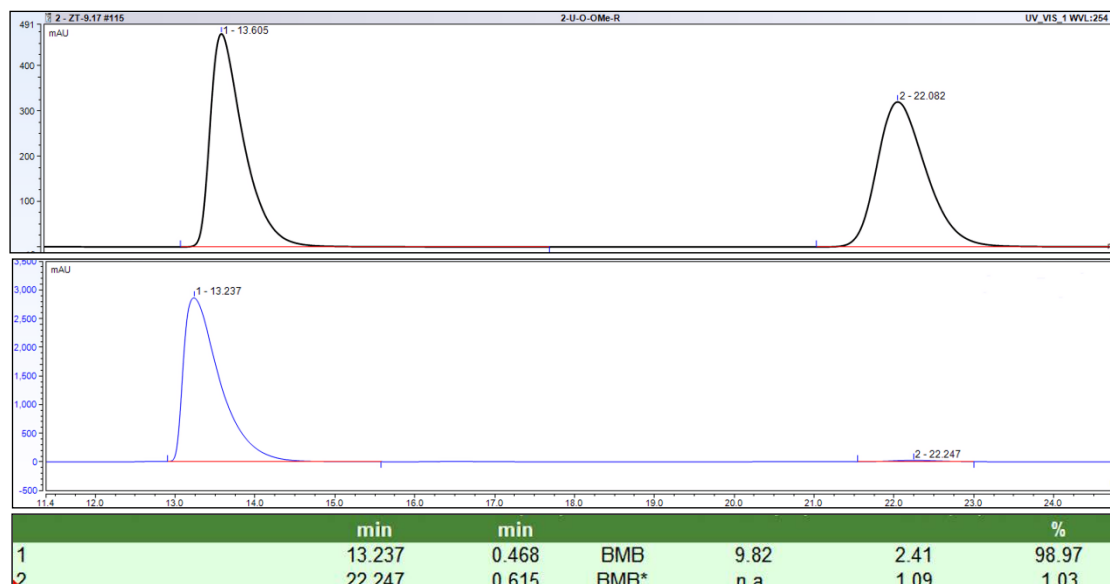
(*c* = 1.0, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.65 (d, *J* = 7.8 Hz, 1H), 7.61 – 7.56 (m, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.45 – 7.31 (m, 4H), 7.25 (d, *J* = 8.1 Hz, 1H), 6.58 (dd, *J* = 4.6, 2.3 Hz, 1H), 4.75 (ddd, *J* = 138.7, 14.5, 2.5 Hz, 2H), 4.06 (dd, *J* = 55.5, 9.7 Hz, 2H), 2.39 (s, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 150.6, 140.8, 135.1, 131.8, 129.3, 128.2, 127.7, 126.2, 126.1 (q, *J* = 5.7 Hz), 121.2, 82.4, 81.3, 70.0. HRMS (ESI) calculated for [M+Na, C<sub>18</sub>H<sub>15</sub>NaF<sub>3</sub>O<sub>2</sub>]<sup>+</sup>: 343.0916; found: 343.0915.

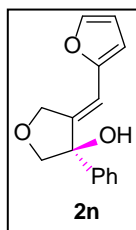




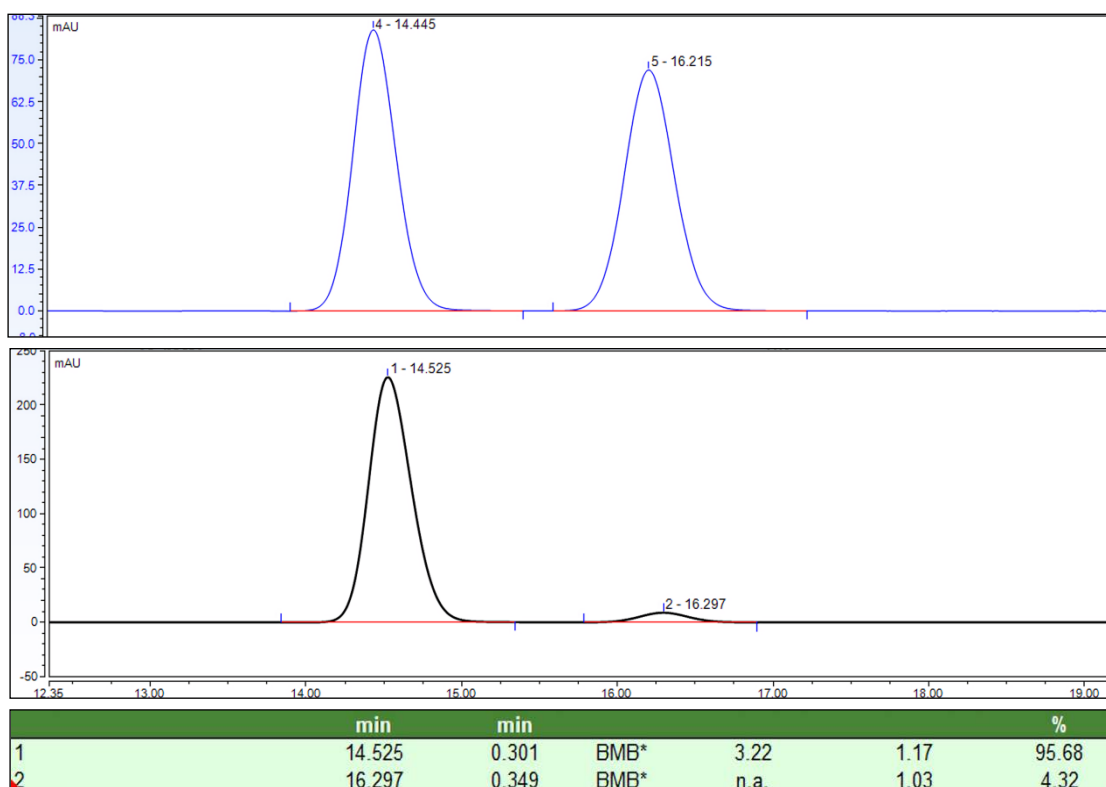
**2m**: white solid, 17% yield, 99:1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 13.24 min (*R*), 22.25 min (*S*).  $[\alpha]_D^{25} = -8.0$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 – 7.54

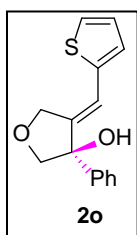
(m, 2H), 7.41 – 7.32 (m, 2H), 7.32 – 7.26 (m, 1H), 7.25 – 7.19 (m, 1H), 7.03 (dd,  $J = 7.6, 1.6$  Hz, 1H), 6.93 (td,  $J = 7.5, 0.7$  Hz, 1H), 6.83 (dd,  $J = 8.2, 0.7$  Hz, 1H), 6.67 (t,  $J = 2.5$  Hz, 1H), 4.86 (ddd,  $J = 84.2, 14.3, 2.6$  Hz, 2H), 4.02 (dd,  $J = 62.3, 9.5$  Hz, 2H), 3.73 (s, 3H), 2.66 (s, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.9, 147.2, 142.2, 129.0, 128.4, 128.1, 127.4, 126.4, 125.4, 120.4, 119.5, 110.7, 82.8, 81.4, 70.9, 55.4. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{18}\text{H}_{18}\text{NaO}_3]^+$ : 305.1148; found: 305.1149.





**2n**: colorless oil, 47% yield, 96:4 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark OJ-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 80/20, 254 nm, 14.53 min (*R*), 16.30 min (*S*).  $[\alpha]_D^{25} = +12.4$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (dq,  $J = 2.6, 1.8$  Hz, 2H), 7.43 (d,  $J = 1.6$  Hz, 1H), 7.41 – 7.34 (m, 2H), 7.33 – 7.28 (m, 1H), 6.39 (dd,  $J = 3.3, 1.8$  Hz, 1H), 6.18 (d,  $J = 3.3$  Hz, 1H), 6.09 (t,  $J = 2.6$  Hz, 1H), 5.00 (ddd,  $J = 141.1, 15.7, 2.5$  Hz, 2H), 4.03 (dd,  $J = 61.8, 9.6$  Hz, 2H), 2.44 (s, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  152.2, 145.3, 143.0, 141.1, 128.2, 127.5, 126.3, 112.3, 111.6, 110.2, 82.6, 81.5, 71.5. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{15}\text{H}_{14}\text{NaO}_3]^+$ : 265.0835; found: 265.0836.

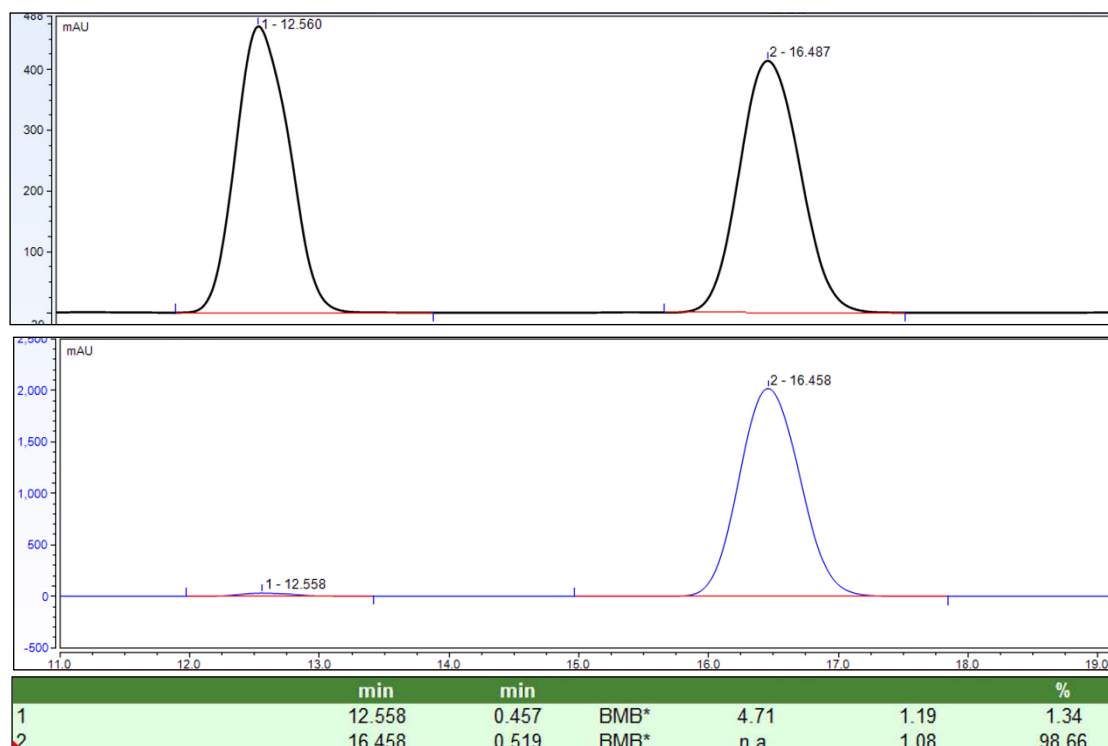


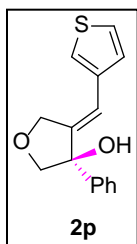


**2o**: light yellow oil, 58% yield, 99:1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 12.56 min (*S*), 16.46 min (*R*).  $[\alpha]_D^{25} = +6.0$

(*c* = 1.0, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.56 (dt, *J* = 3.1, 1.8 Hz, 2H), 7.41 – 7.36 (m, 2H), 7.36 – 7.29 (m, 2H), 7.02 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.88 (d, *J* = 3.5

Hz, 1H), 6.47 (t, *J* = 2.6 Hz, 1H), 4.91 (ddd, *J* = 126.2, 15.0, 2.5 Hz, 2H), 4.05 (dd, *J* = 58.3, 9.6 Hz, 2H), 2.44 (s, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 145.3, 141.2, 140.2, 128.2, 127.6, 126.7, 126.4, 117.6, 82.9, 81.8, 71.1. HRMS (ESI) calculated for [M+Na, C<sub>15</sub>H<sub>14</sub>NaSO<sub>2</sub>]<sup>+</sup>: 281.0607; found: 281.0608.





**2p**: white solid, 60% yield, 99:1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min,

hexanes/isopropanol: 90/10, 254 nm, 15.71 min (*S*), 18.66 min (*R*).  $[\alpha]_D^{25} = +5.4$

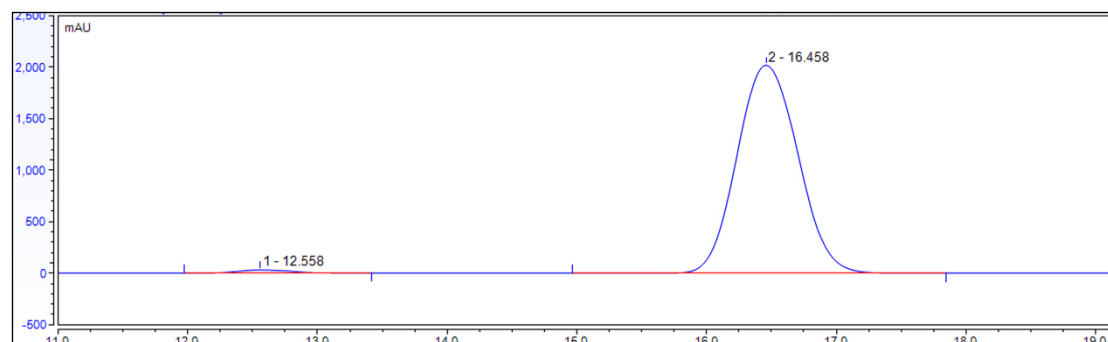
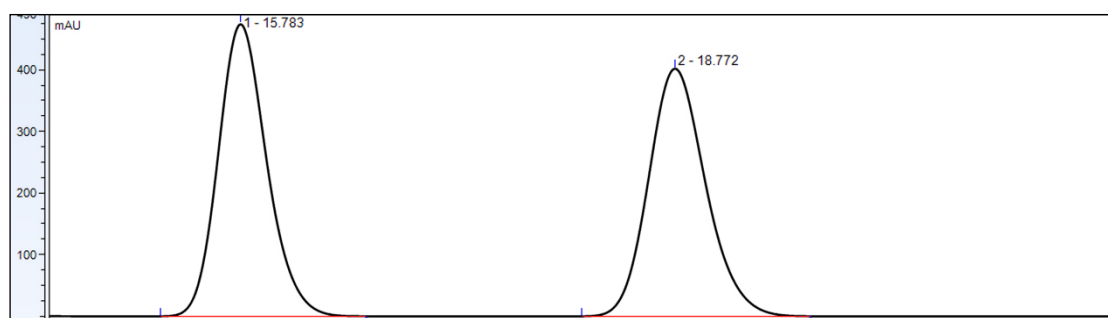
( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 (dt,  $J = 3.1, 1.9$  Hz, 2H), 7.41

– 7.34 (m, 2H), 7.34 – 7.27 (m, 2H), 7.02 (d,  $J = 2.3$  Hz, 1H), 6.95 (dd,  $J = 5.0, 1.2$  Hz, 1H), 6.30 (t,  $J = 2.6$  Hz, 1H), 4.91 (ddd,  $J = 115.3, 14.4, 2.6$  Hz, 2H), 4.03 (dd,  $J = 60.3, 9.6$  Hz, 2H), 2.51 (s, 1H).

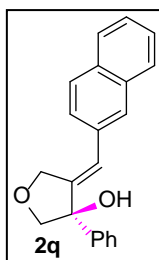
$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  146.1, 141.4, 138.0, 128.2, 127.6, 127.5, 126.4, 126.1, 123.8,

118.5, 82.8, 81.6, 71.1. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{15}\text{H}_{14}\text{NaSO}_2]^+$ : 281.0607; found:

281.0605.



	min	min				%
1	12.558	0.457	BMB*	4.71	1.19	1.34
2	16.458	0.519	BMB*	n a	1.08	98.66



**2q**: colorless oil, 95% yield, 98:2 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min,

hexanes/isopropanol: 90/10, 254 nm, 16.99 min (*S*), 21.39 min (*R*).  $[\alpha]_D^{25} = +43.4$

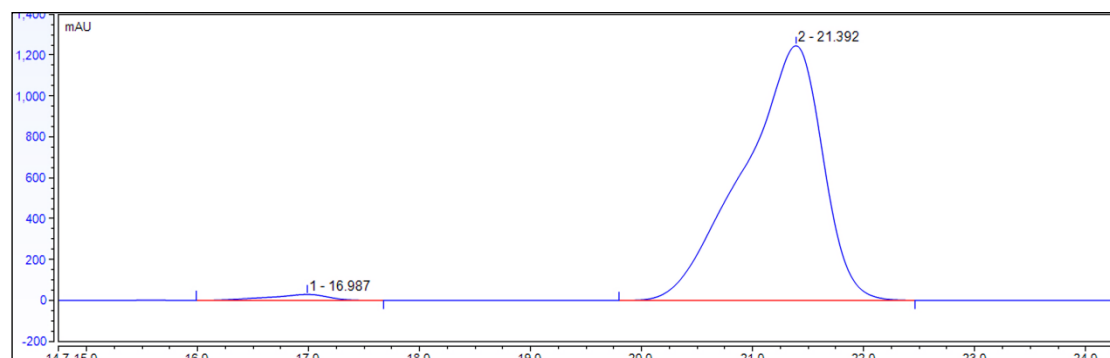
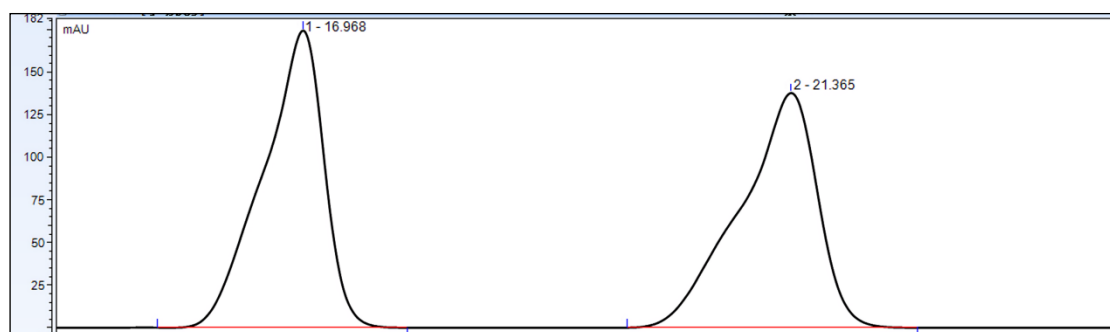
( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 – 7.70 (m, 3H), 7.65 – 7.56 (m, 2H), 7.53 (s, 1H), 7.48 – 7.42 (m, 2H), 7.42 – 7.36 (m, 2H), 7.35 – 7.29 (m,

1H), 7.23 (dd,  $J = 8.6, 1.7$  Hz, 1H), 6.44 (t,  $J = 2.6$  Hz, 1H), 5.05 (ddd,  $J = 111.5, 14.4, 2.5$  Hz,

2H), 4.06 (dd,  $J = 53.8, 9.6$  Hz, 2H), 2.66 (s, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  147.8, 141.7,

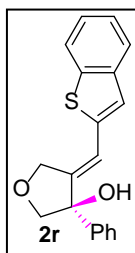
133.9, 133.4, 132.5, 128.3, 128.1, 127.8, 127.6, 126.5, 126.4, 126.4, 126.0, 125.0, 83.1, 81.2, 70.9.

HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{21}\text{H}_{18}\text{NaO}_2]^+$ : 325.1199; found: 325.1212.



	min	min	BMB*			%
1	16.987	0.584	BMB*	3.86	0.77	1.79
2	21.392	0.762	BMB*	n a	0.75	98.21

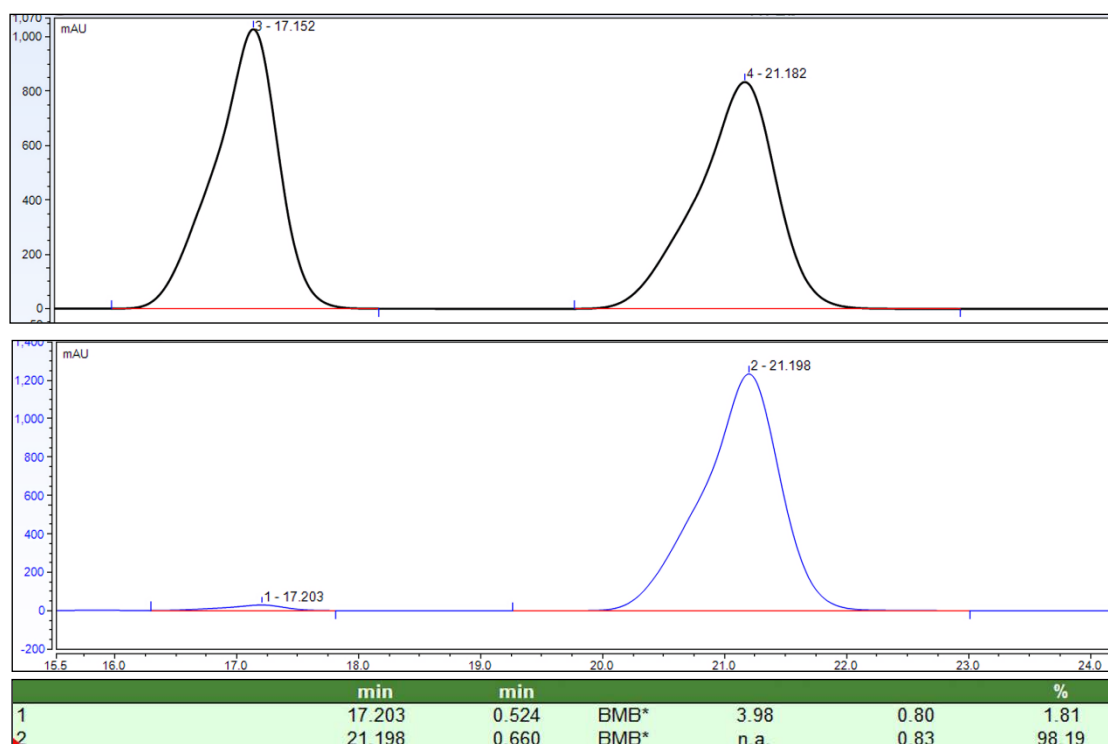


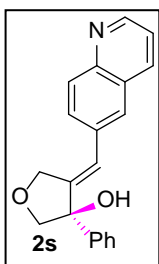


**2r**: white solid, 30% yield, 98:2 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 17.20 min (*S*), 21.20 min (*R*).  $[\alpha]_D^{25} = +3.0$

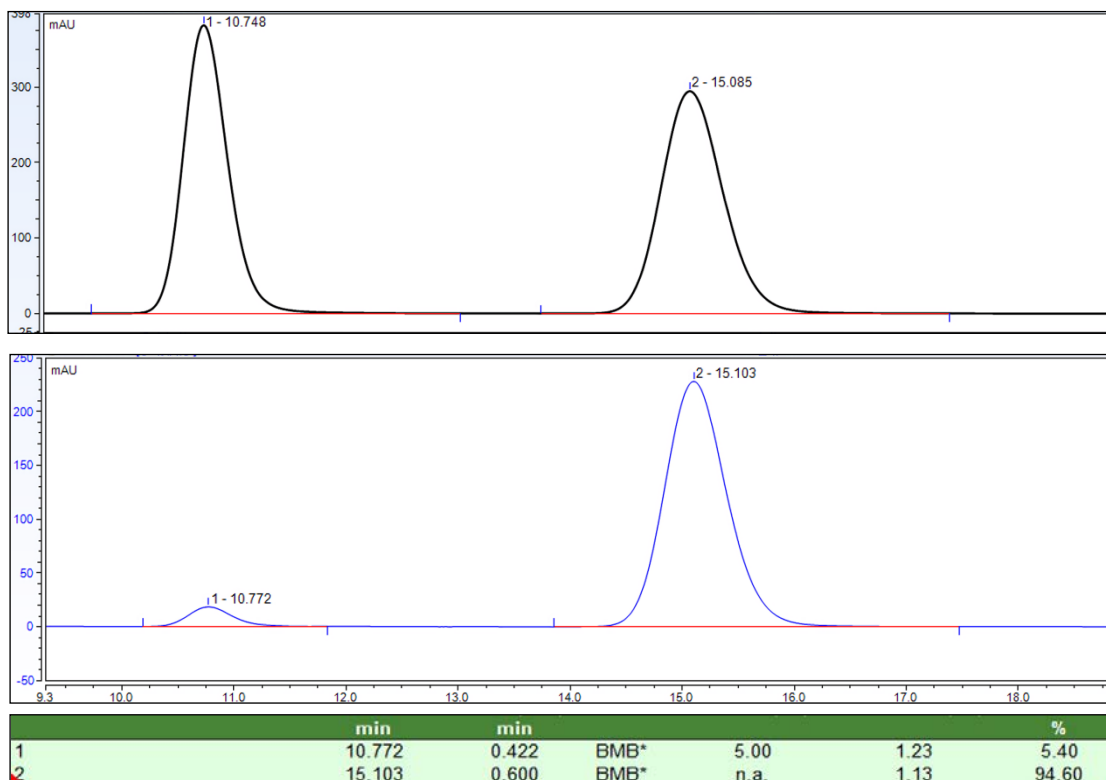
(*c* = 1.0, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.76 (dd, *J* = 42.0, 7.3 Hz, 2H), 7.64 – 7.52 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.38 – 7.27 (m, 3H), 7.09 (s, 1H), 6.54

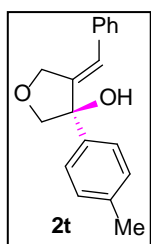
(t, *J* = 2.5 Hz, 1H), 5.03 (ddd, *J* = 133.1, 15.1, 2.5 Hz, 2H), 4.08 (dd, *J* = 51.7, 9.6 Hz, 2H), 2.43 (s, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 148.0, 141.0, 140.4, 140.0, 139.6, 128.3, 127.7, 126.3, 124.7, 124.4, 123.8, 122.7, 118.2, 82.9, 81.6, 70.8. HRMS (ESI) calculated for [M+Na, C<sub>19</sub>H<sub>16</sub>NaSO<sub>2</sub>]<sup>+</sup>: 331.0763; found: 331.0766.



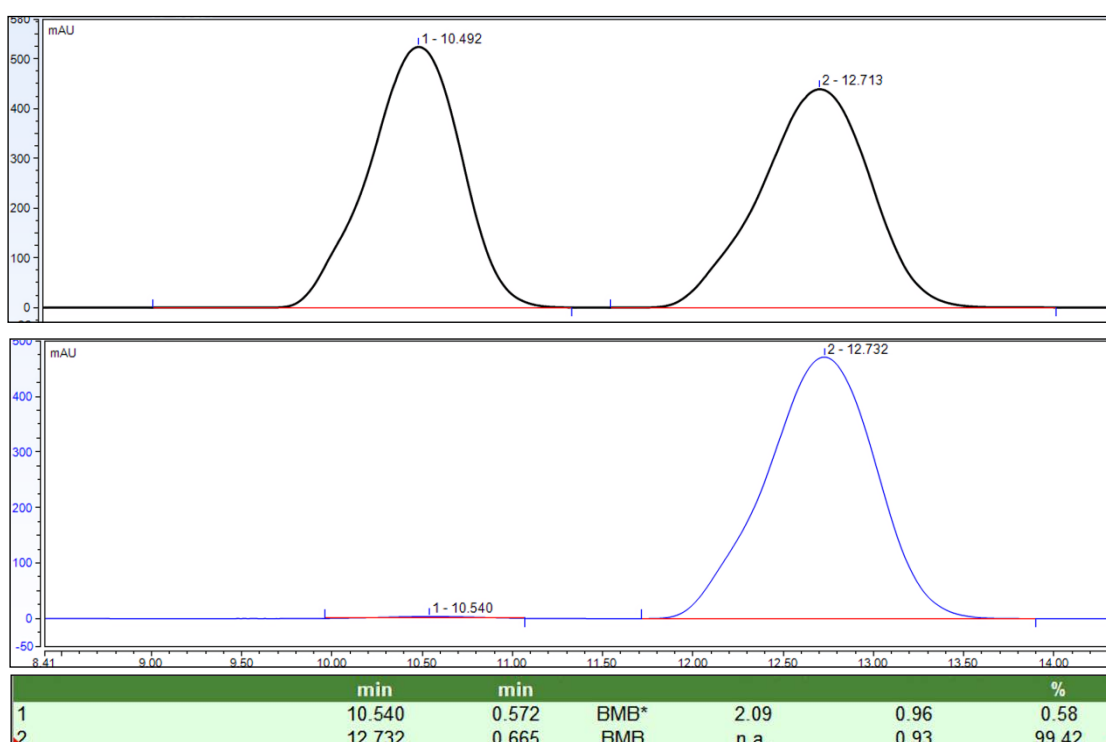


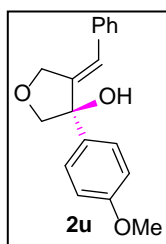
**2s**: white solid, 31% yield, 95:5 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 70/30, 254 nm, 10.77 min (*S*), 15.10 min (*R*).  $[\alpha]_D^{25} = +10.2$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.88 (dd,  $J = 4.2, 1.6$  Hz, 1H), 8.10 (d,  $J = 7.5$  Hz, 1H), 8.06 (d,  $J = 8.7$  Hz, 1H), 7.68 – 7.58 (m, 2H), 7.51 (s, 1H), 7.49 (dd,  $J = 8.8, 2.0$  Hz, 1H), 7.45 – 7.37 (m, 3H), 7.34 (ddd,  $J = 7.3, 3.8, 1.2$  Hz, 1H), 6.46 (t,  $J = 2.6$  Hz, 1H), 5.06 (ddd,  $J = 101.5, 14.5, 2.5$  Hz, 2H), 4.09 (dd,  $J = 45.7, 9.6$  Hz, 2H), 2.75 (s, 1H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  150.7, 149.1, 147.4, 141.5, 136.1, 134.7, 129.8, 129.7, 128.3, 128.2, 127.6, 127.3, 126.3, 124.1, 121.6, 83.0, 81.2, 70.8. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{20}\text{H}_{17}\text{NaNO}_2]^+$ : 326.1151; found: 326.1153.



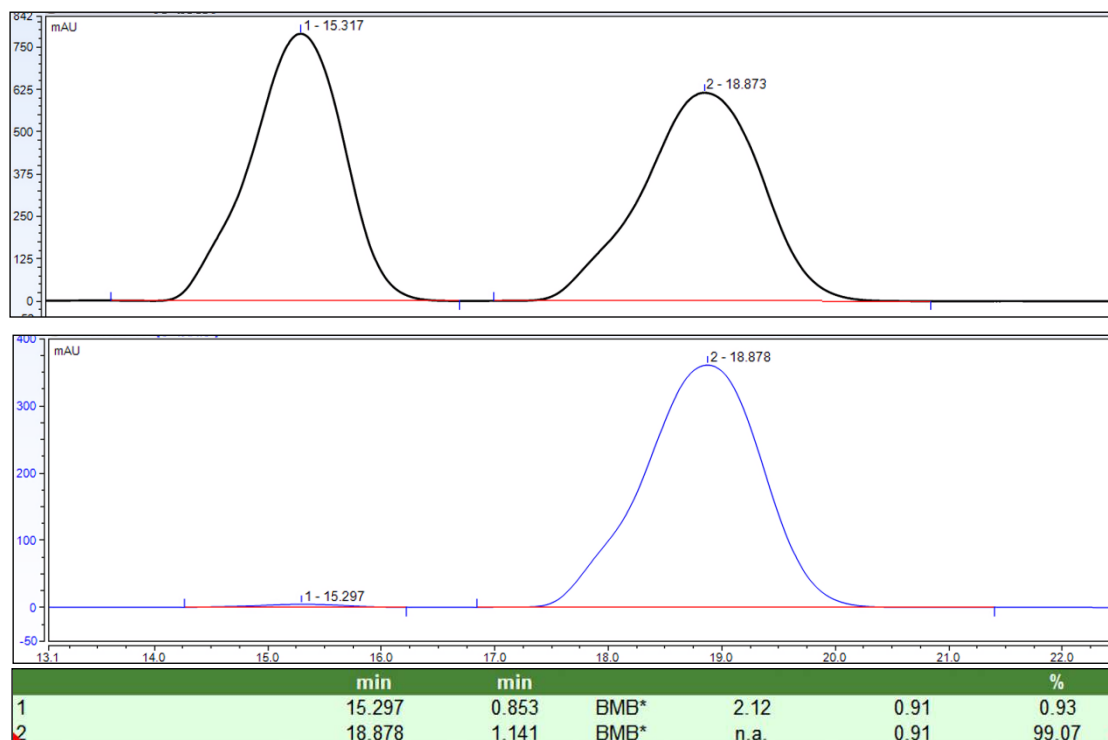


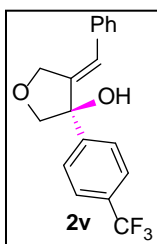
**2t**: light yellow oil, 98% yield, > 99/1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 10.54 min (*S*), 12.73 min (*R*).  $[\alpha]_D^{25} = +24.5$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 (d,  $J = 8.2$  Hz, 2H), 7.33 (t,  $J = 7.6$  Hz, 2H), 7.24 (t,  $J = 7.4$  Hz, 1H), 7.15 (dd,  $J = 33.4, 7.7$  Hz, 4H), 6.29 (t,  $J = 2.5$  Hz, 1H), 4.94 (ddd,  $J = 113.1, 14.5, 2.5$  Hz, 2H), 4.00 (dd,  $J = 60.3, 9.5$  Hz, 2H), 2.52 (s, 1H), 2.36 (s, 3H).  $^1\text{H NMR}$  spectra is in agreement with these reported in the literature.<sup>5</sup>



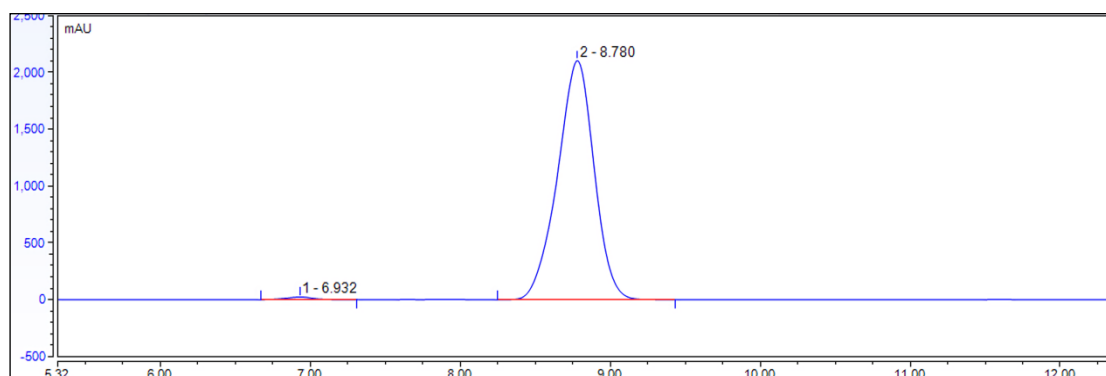
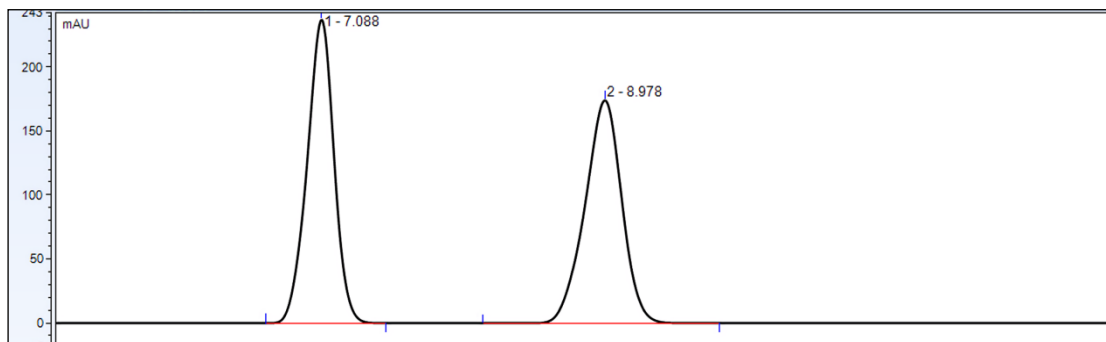


**2u**: white solid, 91% yield, > 99/1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 15.30 min (*S*), 18.88 min (*R*).  $[\alpha]_D^{25} = -2.6$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 – 7.42 (m, 2H), 7.33 (t,  $J = 7.5$  Hz, 2H), 7.24 (dd,  $J = 8.4, 6.3$  Hz, 1H), 7.11 (d,  $J = 7.5$  Hz, 2H), 6.96 – 6.84 (m, 2H), 6.30 (t,  $J = 2.5$  Hz, 1H), 4.92 (ddd,  $J = 89.4, 14.5, 2.4$  Hz, 2H), 3.99 (dd,  $J = 50.1, 9.5$  Hz, 2H), 3.81 (s, 3H), 2.59 (s, 1H).  $^1\text{H NMR}$  spectra is in agreement with these reported in the literature.<sup>5</sup>

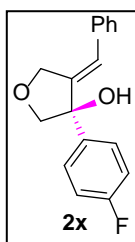




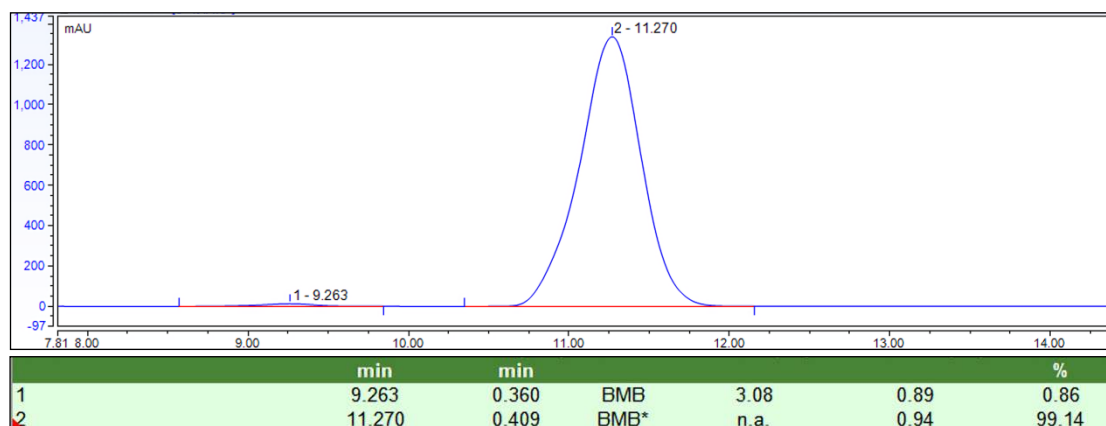
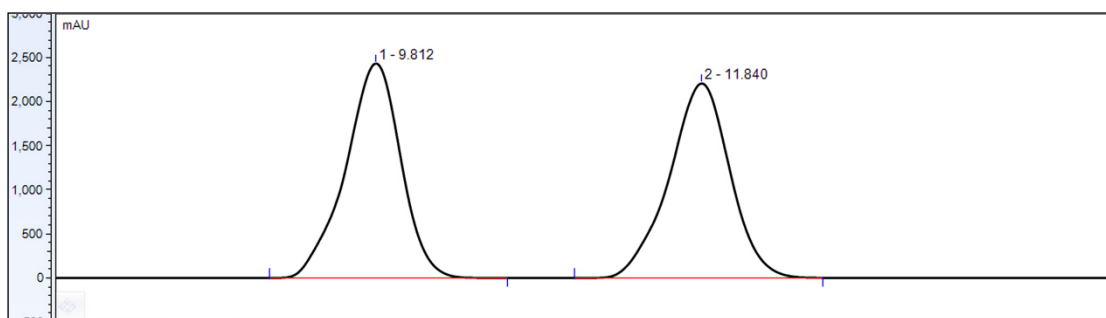
**2v**: white solid, 99% yield, > 99:1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 6.93 min (*S*), 8.78 min (*R*).  $[\alpha]_D^{25} = +5.3$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (s, 1H), 7.71 (d,  $J = 7.9$  Hz, 1H), 7.58 (d,  $J = 7.8$  Hz, 1H), 7.49 (t,  $J = 7.8$  Hz, 1H), 7.35 (t,  $J = 7.6$  Hz, 2H), 7.30 – 7.22 (m, 1H), 7.12 (d,  $J = 7.4$  Hz, 2H), 6.27 (t,  $J = 2.6$  Hz, 1H), 4.97 (ddd,  $J = 105.3, 14.5, 2.5$  Hz, 2H), 4.03 (dd,  $J = 70.1, 9.7$  Hz, 2H), 2.65 (s, 1H).  $^1\text{H NMR}$  spectra is in agreement with these reported in the literature.<sup>5</sup>

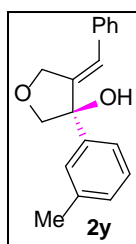


	min	min	BMB*			%
1	6.932	0.186	BMB*	4.90	0.94	0.78
2	8.780	0.259	BMB*	n.a.	0.93	99.22

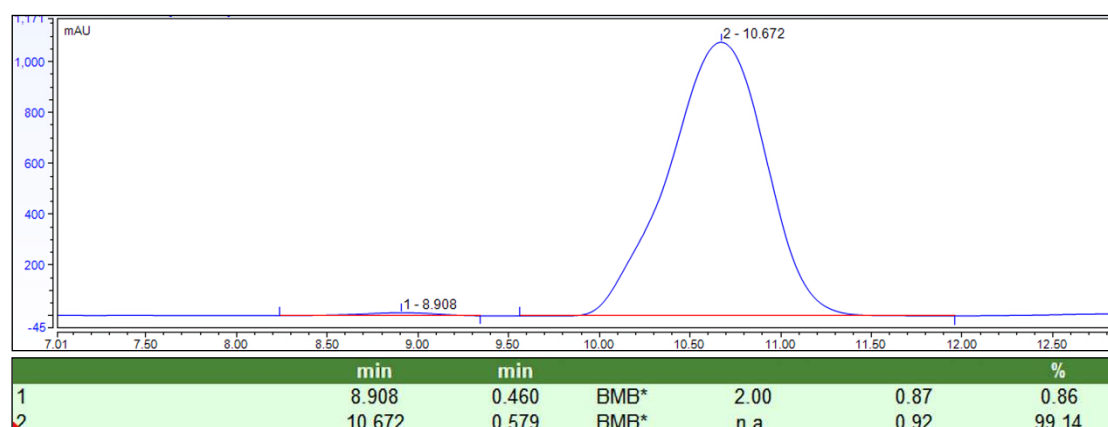
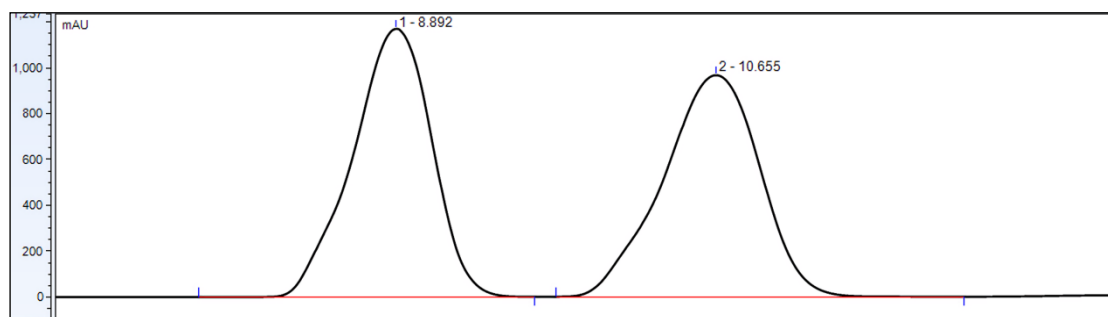


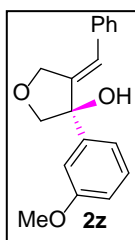
**2x**: white solid, 99% yield, > 99/1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 9.26 min (*S*), 11.27 min (*R*).  $[\alpha]_D^{25} = +4.6$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 – 7.48 (m, 2H), 7.34 (t,  $J = 7.6$  Hz, 2H), 7.25 (dd,  $J = 9.5, 5.1$  Hz, 1H), 7.11 (d,  $J = 7.6$  Hz, 2H), 7.08 – 7.00 (m, 2H), 6.28 (t,  $J = 2.5$  Hz, 1H), 4.93 (ddd,  $J = 111.0, 14.5, 2.4$  Hz, 2H), 3.99 (dd,  $J = 68.2, 9.6$  Hz, 2H), 2.61 (s, 1H).  $^1\text{H NMR}$  spectra is in agreement with these reported in the literature.<sup>5</sup>



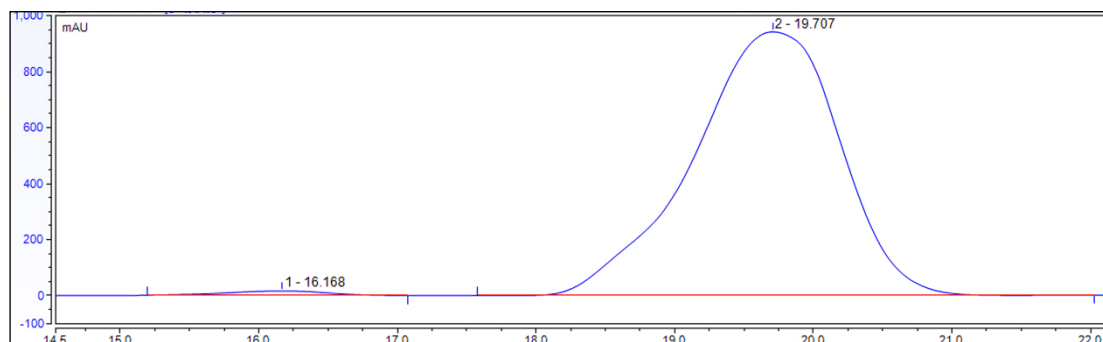
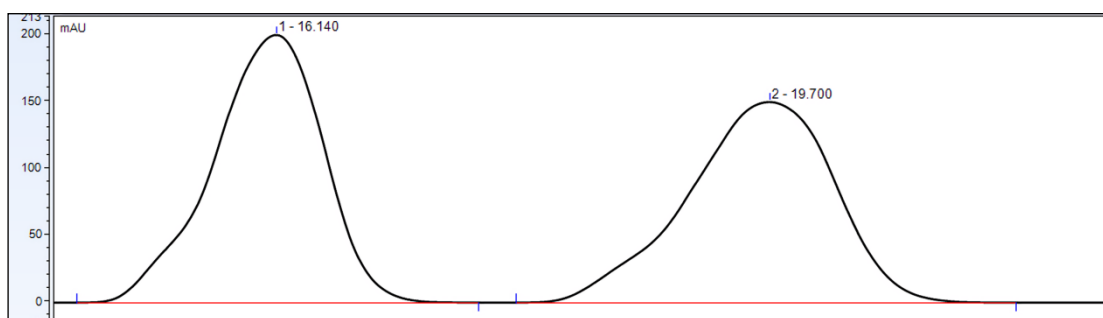


**2y**: light yellow oil, 96% yield, > 99/1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 8.91 min (*S*), 10.67 min (*R*).  $[\alpha]_D^{25} = +7.1$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 (s, 1H), 7.34 (dd,  $J = 10.6, 4.5$  Hz, 3H), 7.29 – 7.21 (m, 2H), 7.12 (d,  $J = 7.6$  Hz, 3H), 6.30 (t,  $J = 2.5$  Hz, 1H), 4.95 (ddd,  $J = 109.5, 14.5, 2.5$  Hz, 2H), 4.02 (dd,  $J = 52.8, 9.5$  Hz, 2H), 2.53 (s, 1H), 2.37 (s, 3H).  $^1\text{H NMR}$  spectra is in agreement with these reported in the literature.<sup>5</sup>



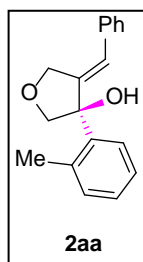


**2z**: colorless oil, 93% yield, 99:1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 16.17 min (*S*), 19.71 min (*R*).  $[\alpha]_D^{25} = +12.7$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (t,  $J = 7.6$  Hz, 2H), 7.28 (t,  $J = 8.0$  Hz, 1H), 7.24 (dd,  $J = 8.0, 6.8$  Hz, 1H), 7.20 – 7.16 (m, 1H), 7.11 (t,  $J = 7.6$  Hz, 3H), 6.89 – 6.79 (m, 1H), 6.31 (t,  $J = 2.5$  Hz, 1H), 4.94 (ddd,  $J = 109.4, 14.5, 2.5$  Hz, 2H), 4.02 (dd,  $J = 54.4, 9.5$  Hz, 2H), 3.82 (s, 3H), 2.60 (s, 1H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  159.6, 147.2, 143.4, 136.3, 129.3, 128.7, 128.4, 127.6, 124.9, 118.8, 112.8, 112.4, 82.9, 81.2, 70.8, 55.3. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{18}\text{H}_{18}\text{NaO}_3]^+$ : 305.1148; found: 305.1149.

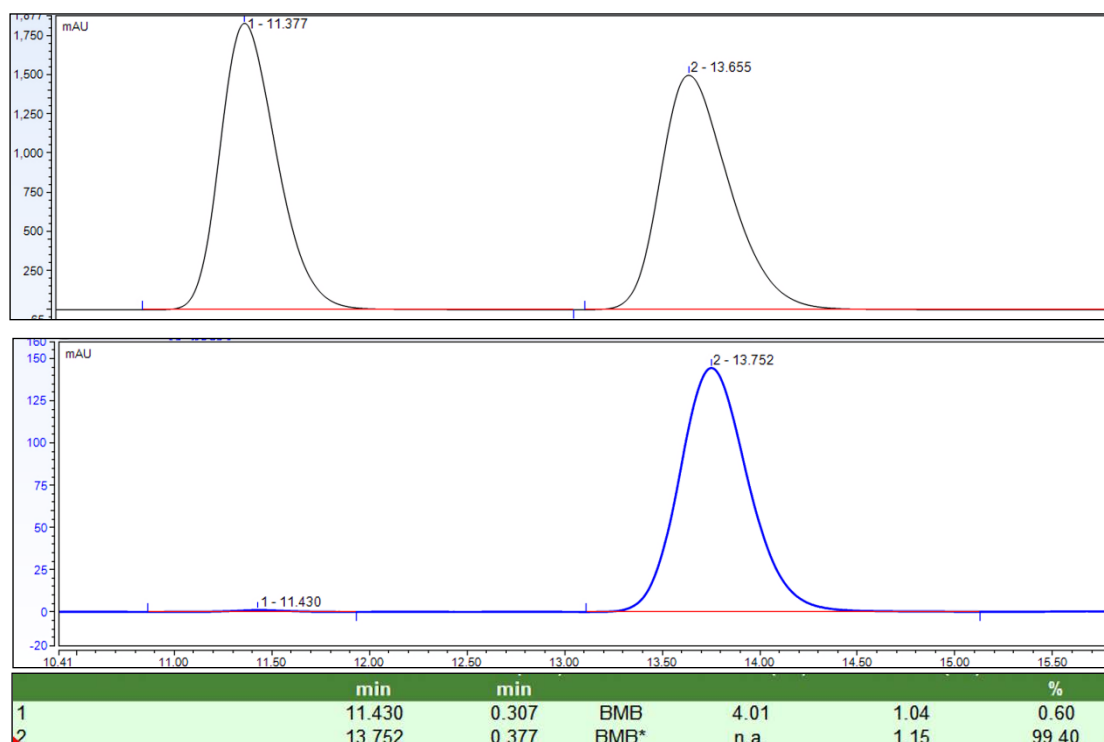


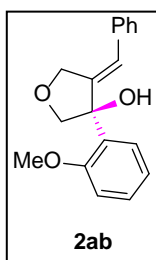
	min	min				%
1	16.168	0.796	BMB*	2.17	0.89	1.14
2	19.707	1.129	BMB*	n.a.	0.87	98.86



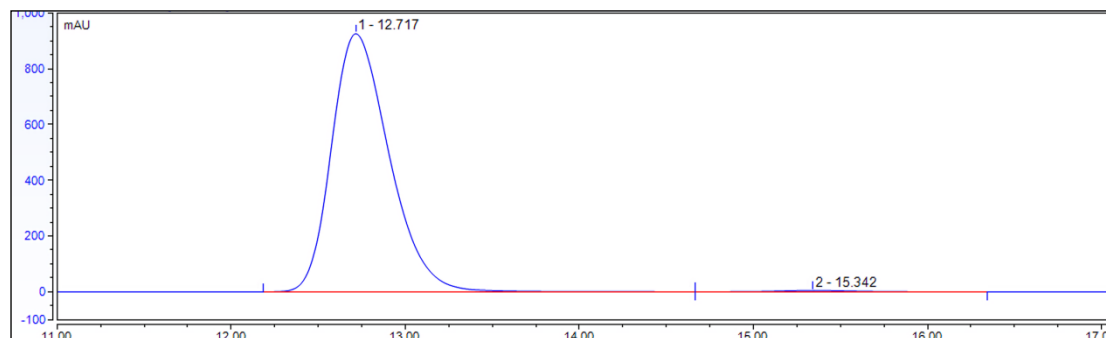
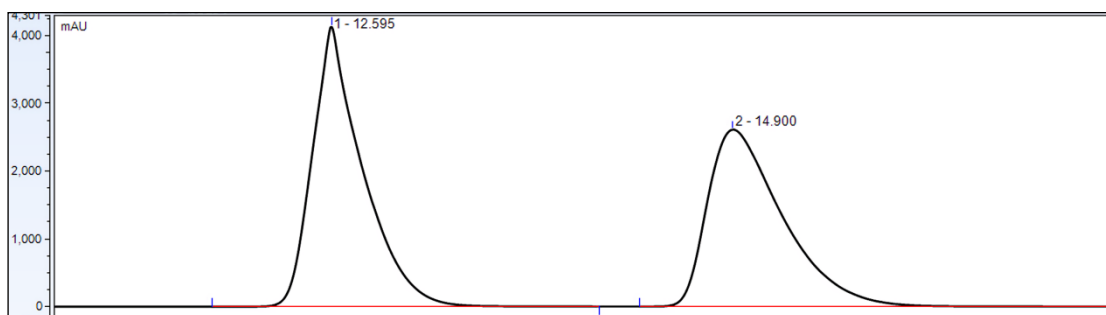


**2aa**: white solid, 98% yield, > 99/1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 11.43 min (*S*), 13.75 min (*R*).  $[\alpha]_D^{25} = +29.3$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 – 7.80 (m, 1H), 7.35 (t,  $J = 7.6$  Hz, 2H), 7.28 – 7.22 (m, 3H), 7.21 – 7.17 (m, 1H), 7.13 (d,  $J = 7.5$  Hz, 2H), 6.31 (t,  $J = 2.4$  Hz, 1H), 4.98 (ddd,  $J = 84.3, 14.4, 2.4$  Hz, 2H), 4.08 (dd,  $J = 61.6, 9.7$  Hz, 2H), 2.39 (d,  $J = 9.9$  Hz, 1H), 2.35 (s, 3H).  $^1\text{H NMR}$  spectra is in agreement with these reported in the literature.<sup>5</sup>

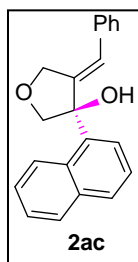




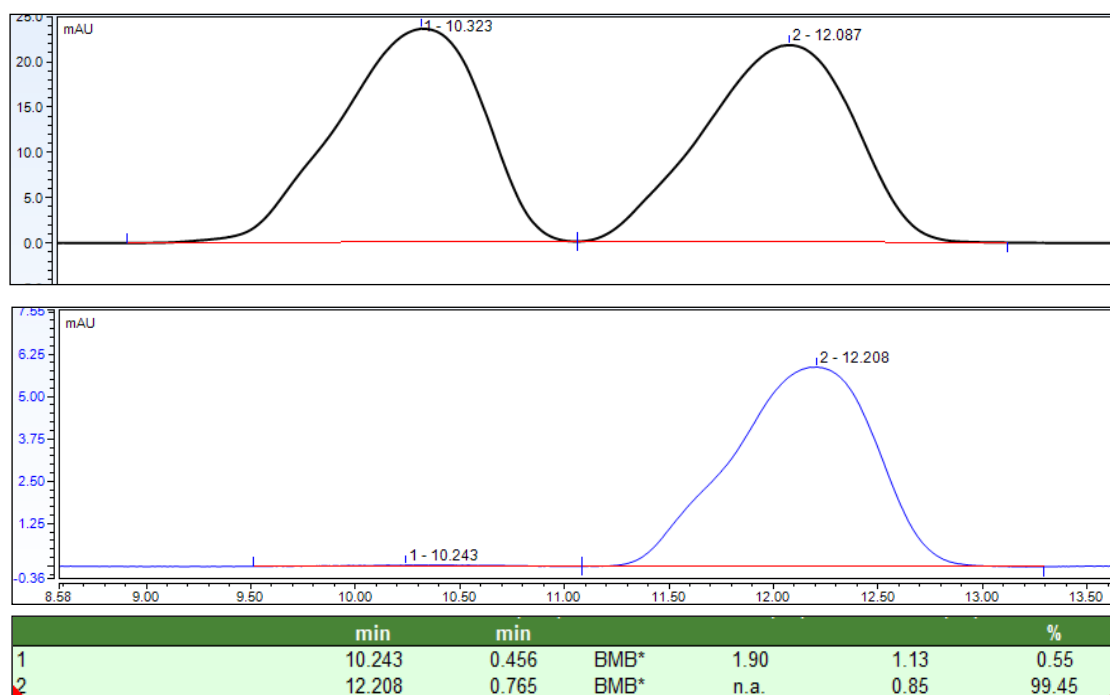
**2ab**: white solid, 99% yield, > 99/1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 12.72 min (*R*), 15.34 min (*S*).  $[\alpha]_D^{25} = +30.2$  ( $c=1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (dd,  $J = 7.7, 1.6$  Hz, 1H), 7.35 (t,  $J = 7.7$  Hz, 2H), 7.30 (td,  $J = 8.0, 1.7$  Hz, 1H), 7.24 (dd,  $J = 8.7, 6.1$  Hz, 1H), 7.18 (d,  $J = 7.4$  Hz, 2H), 6.98 (td,  $J = 7.6, 0.8$  Hz, 1H), 6.93 (d,  $J = 8.2$  Hz, 1H), 6.45 (t,  $J = 2.4$  Hz, 1H), 4.90 (ddd,  $J = 48.4, 14.1, 2.4$  Hz, 2H), 4.10 (dd,  $J = 159.6, 8.9$  Hz, 2H), 3.85 (s, 3H), 3.77 (s, 1H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  156.4, 146.0, 136.9, 130.9, 129.1, 128.6, 128.4, 128.1, 127.2, 123.1, 120.9, 111.4, 81.9, 78.8, 70.6, 55.5. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{18}\text{H}_{18}\text{NaO}_3]^+$ : 305.1148; found: 305.1150.

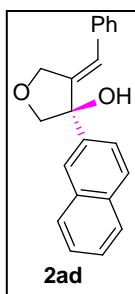


	min	min				%
1	12.717	0.354	BM	3.84	1.30	99.30
2	15.342	0.453	MB	n.a.	1.06	0.70

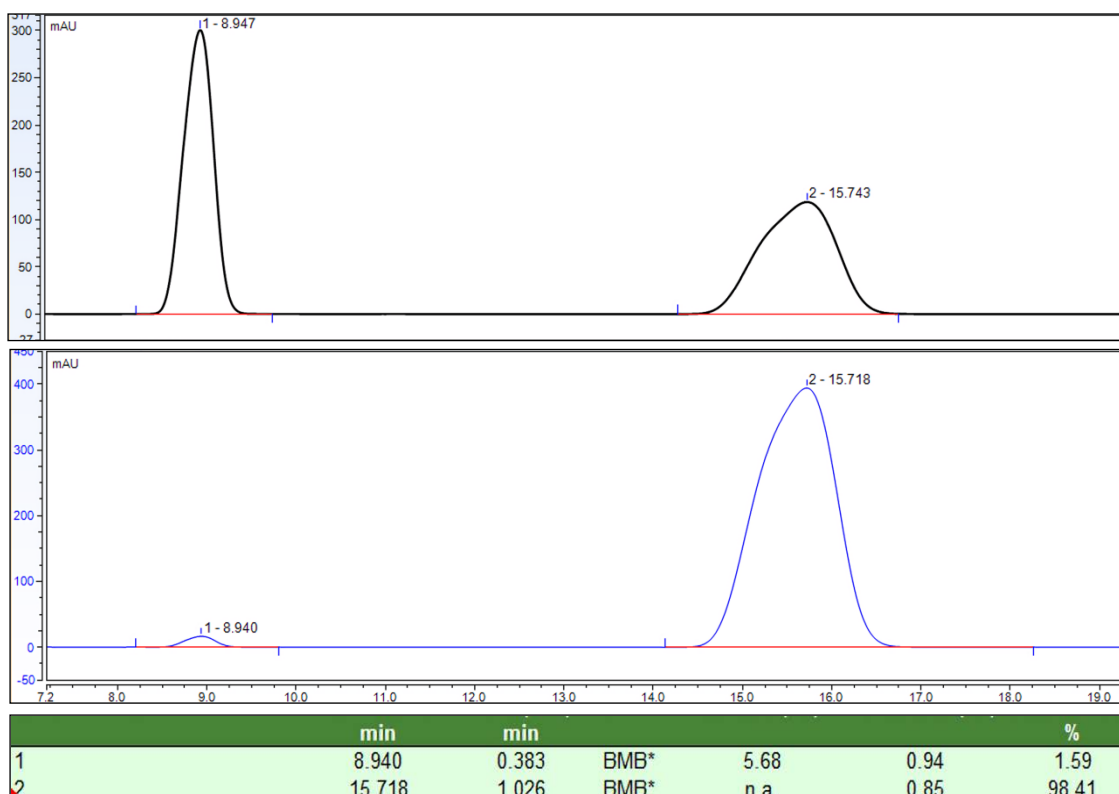


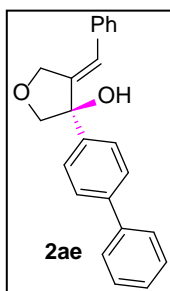
**2ac**: yellow solid, 99% yield, > 99:1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 85/15, 254 nm, 10.24 min (*S*), 12.21 min (*R*).  $[\alpha]_D^{25} = -9.8$  ( $c=1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (dd,  $J = 6.8, 2.7$  Hz, 1H), 7.93 (dd,  $J = 7.3, 1.1$  Hz, 1H), 7.90 – 7.86 (m, 1H), 7.84 (d,  $J = 8.2$  Hz, 1H), 7.50 – 7.41 (m, 3H), 7.38 – 7.31 (m, 2H), 7.28 – 7.24 (m, 1H), 7.13 (d,  $J = 7.3$  Hz, 2H), 6.35 (t,  $J = 2.5$  Hz, 1H), 5.10 (ddd,  $J = 33.1, 14.5, 2.5$  Hz, 2H), 4.32 (dd,  $J = 177.5, 9.5$  Hz, 2H), 2.58 (s, 1H). HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{21}\text{H}_{18}\text{NaO}_2]^+$ : 323.1043; found: 323.1072.  $^1\text{H NMR}$  spectra is in agreement with these reported in the literature.<sup>5</sup>



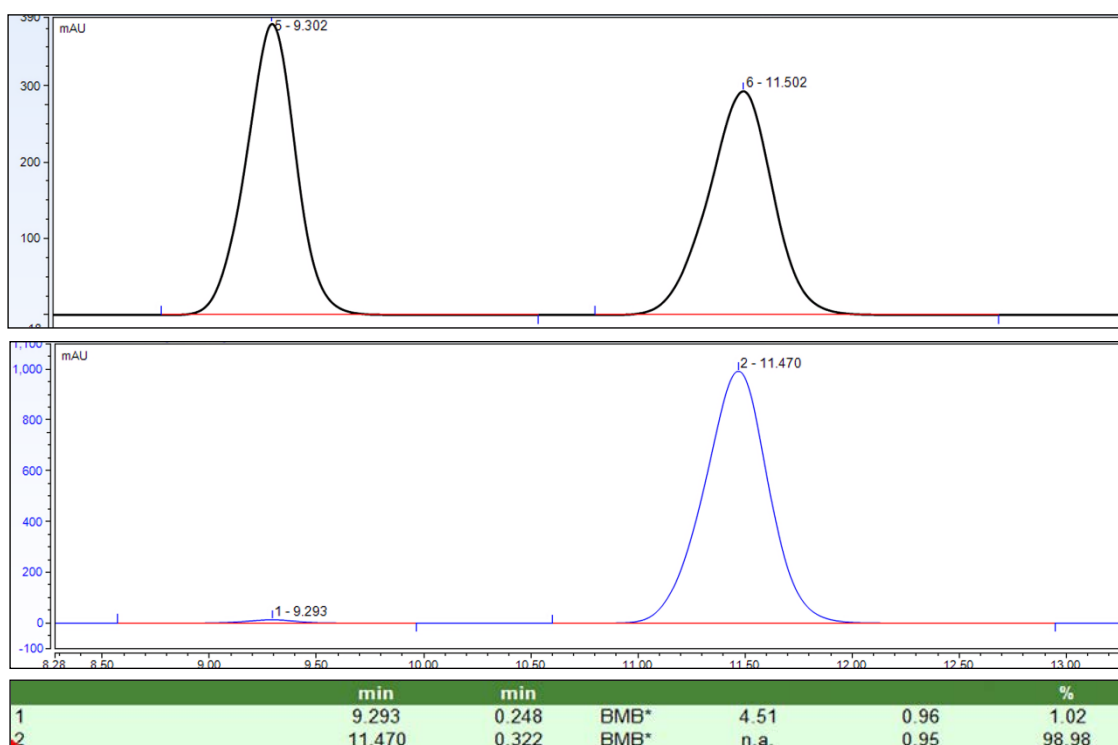


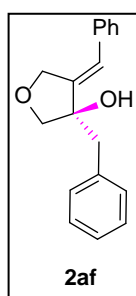
**2ad**: white solid, 80% yield, 98:2 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 8.94 min (*S*), 15.72 min (*R*).  $[\alpha]_D^{25} = +85.9$  ( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 (d,  $J = 1.3$  Hz, 1H), 7.92 – 7.78 (m, 3H), 7.55 – 7.45 (m, 3H), 7.33 (dd,  $J = 10.5, 4.7$  Hz, 2H), 7.24 (t,  $J = 7.4$  Hz, 1H), 7.10 (d,  $J = 7.3$  Hz, 2H), 6.29 (t,  $J = 2.6$  Hz, 1H), 5.01 (ddd,  $J = 107.9, 14.5, 2.5$  Hz, 2H), 4.12 (dd,  $J = 32.2, 9.7$  Hz, 2H), 2.67 (s, 1H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  147.4, 138.9, 136.3, 133.0, 132.7, 128.7, 128.4, 128.0, 127.6, 127.6, 126.3, 126.2, 125.2, 124.5, 83.3, 81.0, 70.9. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{21}\text{H}_{18}\text{NaO}_2]^+$ : 325.1199; found: 325.1201.



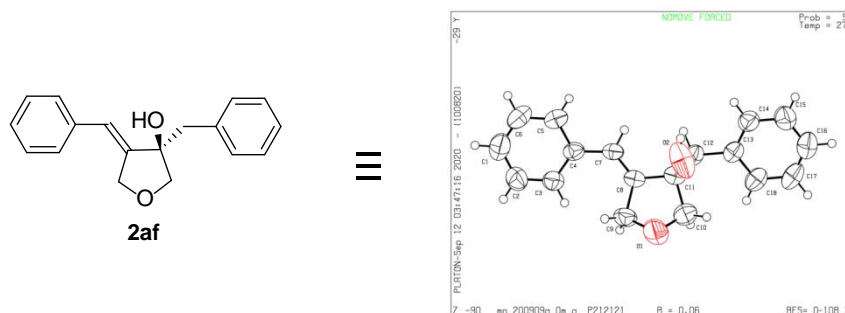


**2ae**: white solid, 98% yield, 99:1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 80/20, 254 nm, 9.29 min (*S*), 11.47 min (*R*). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.68 – 7.57 (m, 6H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 3H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 2H), 6.36 (t, *J* = 2.5 Hz, 1H), 4.99 (ddd, *J* = 108.2, 14.5, 2.5 Hz, 2H), 4.07 (dd, *J* = 51.0, 9.6 Hz, 2H), 2.47 (s, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 147.3, 140.7, 140.6, 140.4, 136.3, 128.8, 128.7, 128.4, 127.6, 127.4, 127.1, 127.0, 126.8, 124.9, 83.0, 81.2, 70.9. HRMS (ESI) calculated for [M+Na, C<sub>23</sub>H<sub>20</sub>NaO<sub>2</sub>]<sup>+</sup>: 351.1356; found: 351.1353.

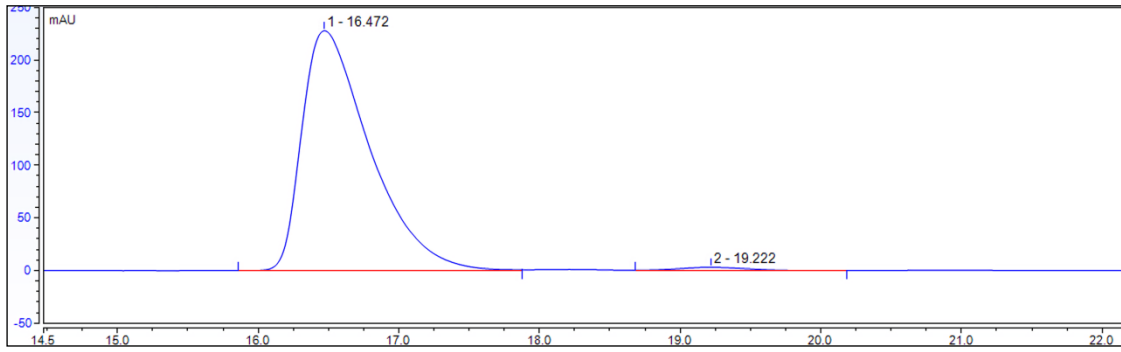
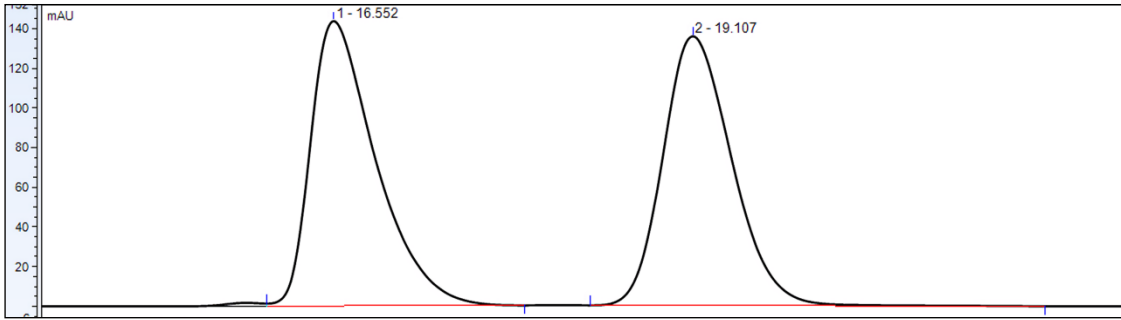




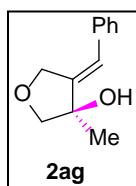
**2af**: white solid, 68% yield, 99:1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 16.47 min (*R*), 19.22 min (*S*). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.36 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.23 (m, 6H), 7.13 (d, *J* = 7.4 Hz, 2H), 6.37 (t, *J* = 2.5 Hz, 1H), 4.76 (ddd, *J* = 57.2, 14.4, 2.5 Hz, 2H), 3.73 (dd, *J* = 184.6, 9.1 Hz, 2H), 3.06 (q, *J* = 13.7 Hz, 2H), 2.04 (s, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 145.0, 136.5, 136.4, 130.5, 128.6, 128.3, 127.3, 126.9, 122.4, 80.2, 70.4, 44.4. HRMS (ESI) calculated for [M+Na, C<sub>18</sub>H<sub>18</sub>NaO<sub>2</sub>]<sup>+</sup>: 289.1199; found: 289.1199. Crystallization from n-Pentane/DCM (9:1) gave crystals suitable for X-ray crystallographic analysis, which revealed its absolute configuration for the chiral tertiary alcohol **2af** as shown in **Figure 2**.



**Figure 2.** X-ray derived ORTEP representation of **2af**. (CCDC Number: 2040947 contains the supplementary crystallographic data of **2af**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre)

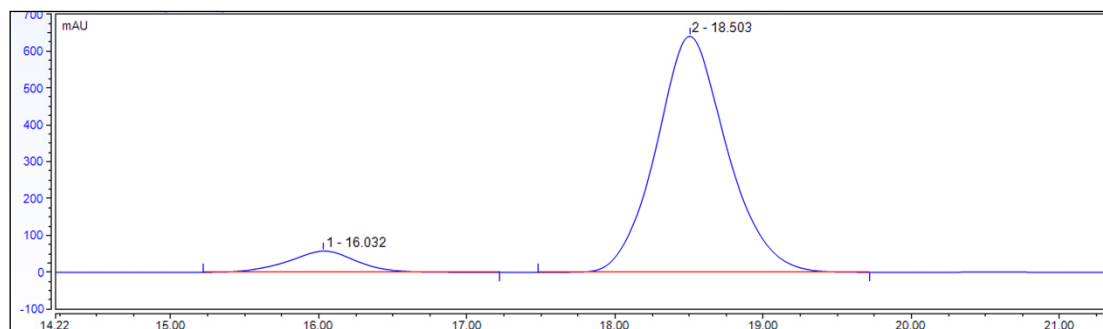
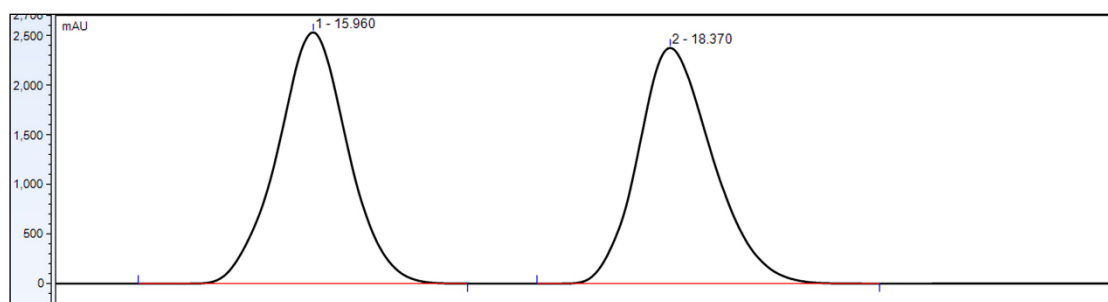


	min	min				%
1	16.472	0.508	BM	3.17	1.84	98.80
2	19.222	0.517	BMB*	n.a.	1.09	1.20



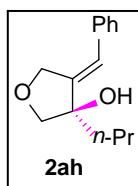
**2ag**: colorless oil, 60% yield, 92:8 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 95/5, 254 nm, 16.03 min (*S*), 18.50 min (*R*).  $[\alpha]_D^{25} = +49.0$

( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (t,  $J = 7.6$  Hz, 2H), 7.27 (d,  $J = 6.1$  Hz, 1H), 7.17 (d,  $J = 7.4$  Hz, 2H), 6.56 (t,  $J = 2.5$  Hz, 1H), 4.77 (ddd,  $J = 78.6, 14.5, 2.5$  Hz, 2H), 3.76 (dd,  $J = 64.4, 9.2$  Hz, 2H), 2.10 (s, 1H), 1.52 (s, 3H).  $^1\text{H NMR}$  spectra is in agreement with these reported in the literature.<sup>5</sup>



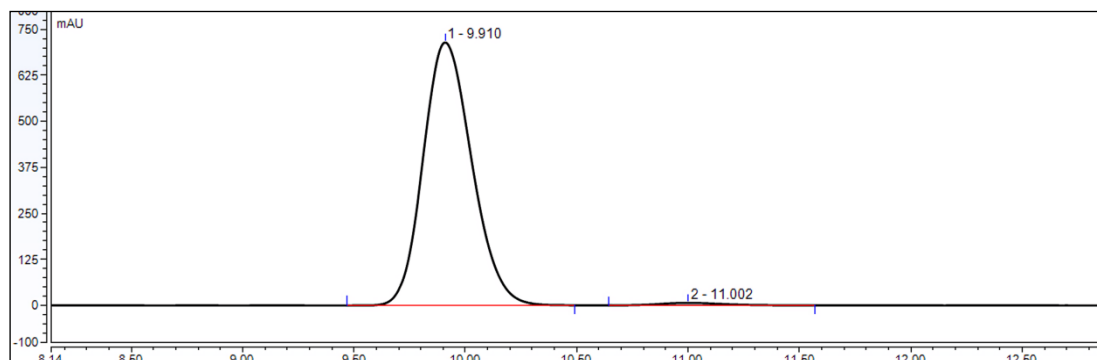
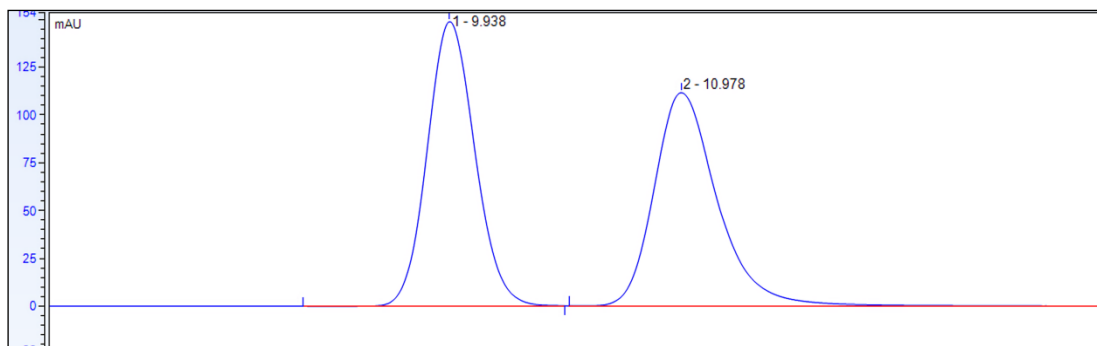
	min	min				%
1	16.032	0.480	BMB	2.97	0.97	7.95
2	18.503	0.500	BMB*	n.a.	1.11	92.05



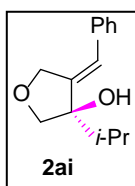


**2ah**: colorless oil, 83% yield, 99:1 er with **L13** (2 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 9.91 min (*R*), 11.00 min (*S*).  $[\alpha]_D^{25} = +43.1$

( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (t,  $J = 7.7$  Hz, 2H), 7.25 (t,  $J = 7.4$  Hz, 1H), 7.16 (d,  $J = 7.4$  Hz, 2H), 6.51 (t,  $J = 2.5$  Hz, 1H), 4.74 (ddd,  $J = 87.1, 14.4, 2.5$  Hz, 2H), 3.78 (dd,  $J = 21.7, 9.2$  Hz, 2H), 1.97 (s, 1H), 1.86 (ddd,  $J = 13.6, 12.2, 4.5$  Hz, 1H), 1.76 – 1.65 (m, 1H), 1.61 – 1.50 (m, 1H), 1.44 – 1.31 (m, 1H), 0.97 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  145.9, 136.5, 128.6, 128.3, 127.3, 121.7, 80.5, 70.3, 40.3, 17.6, 14.6. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{14}\text{H}_{18}\text{NaO}_2]^+$ : 241.1199; found: 241.1199.

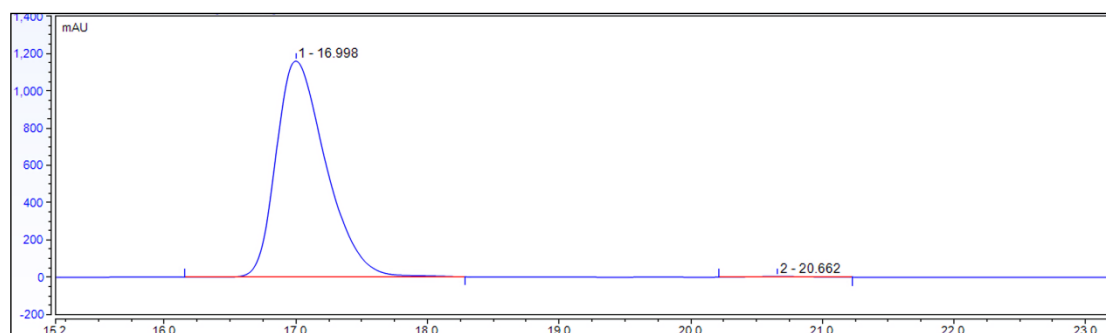
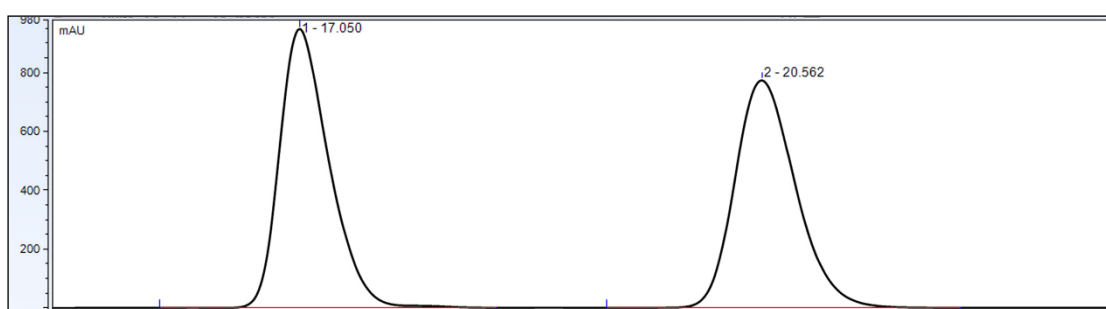


	min	min				%
1	9.910	0.237	BMB*	2.37	1.16	98.80
2	11.002	0.307	BMB*	n.a	1.24	1.20

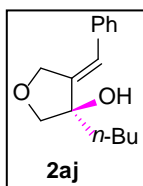


**2ai**: light yellow oil, 40% yield, > 99/1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 17.00 min (*R*), 20.66 min (*S*).  $[\alpha]_D^{25} = +58.0$

(*c* = 1.0, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.37 (dd, *J* = 10.6, 4.7 Hz, 2H), 7.27 (s, 1H), 7.17 (d, *J* = 7.3 Hz, 2H), 4.72 (ddd, *J* = 89.9, 14.4, 2.5 Hz, 2H), 3.84 (dd, *J* = 163.4, 9.4 Hz, 2H), 2.12 (hept, *J* = 6.9 Hz, 1H), 1.85 (s, 1H), 1.04 (dd, *J* = 48.0, 6.9 Hz, 6H). <sup>1</sup>H NMR spectra is in agreement with these reported in the literature.<sup>5</sup>

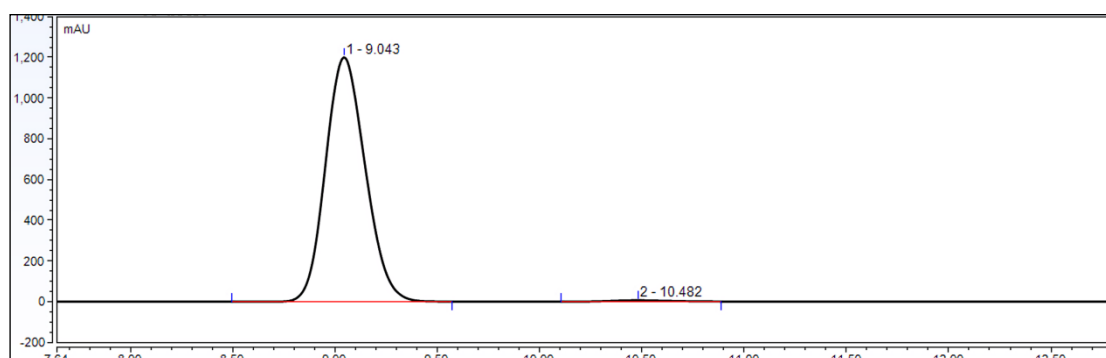
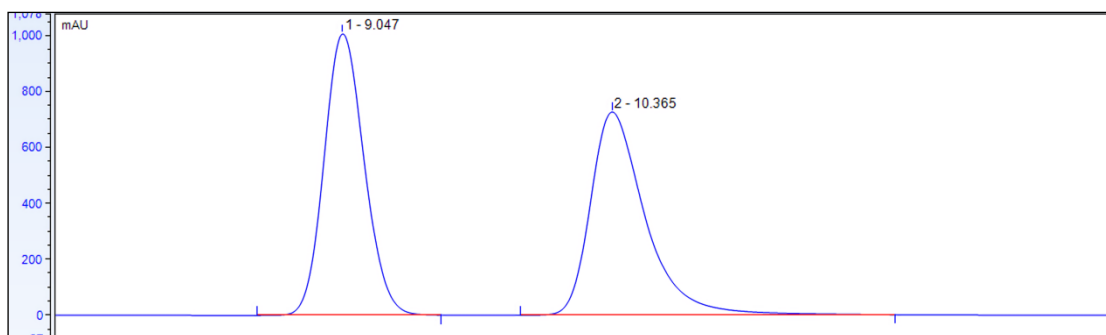


	min	min				%
1	16.998	0.403	BMB*	4.97	1.41	99.67
2	20.662	0.466	BMB*	n.a.	1.10	0.33

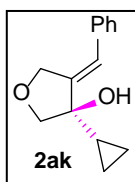


**2aj**: colorless oil, 98% yield, > 99:1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 9.04 min (*R*), 10.48 min (*S*).  $[\alpha]_D^{25} = +47.1$

( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (t,  $J = 7.7$  Hz, 2H), 7.26 (d,  $J = 6.2$  Hz, 1H), 7.17 (d,  $J = 7.4$  Hz, 2H), 6.51 (t,  $J = 2.5$  Hz, 1H), 4.75 (ddd,  $J = 87.4, 14.4, 2.5$  Hz, 2H), 3.79 (dd,  $J = 21.7, 9.2$  Hz, 2H), 1.90 (s, 1H), 1.89 – 1.84 (m, 1H), 1.78 – 1.68 (m, 1H), 1.57 – 1.48 (m, 1H), 1.35 (tt,  $J = 10.0, 6.2$  Hz, 3H), 0.93 (t,  $J = 7.2$  Hz, 3H).  $^1\text{H NMR}$  spectra is in agreement with these reported in the literature.<sup>5</sup>

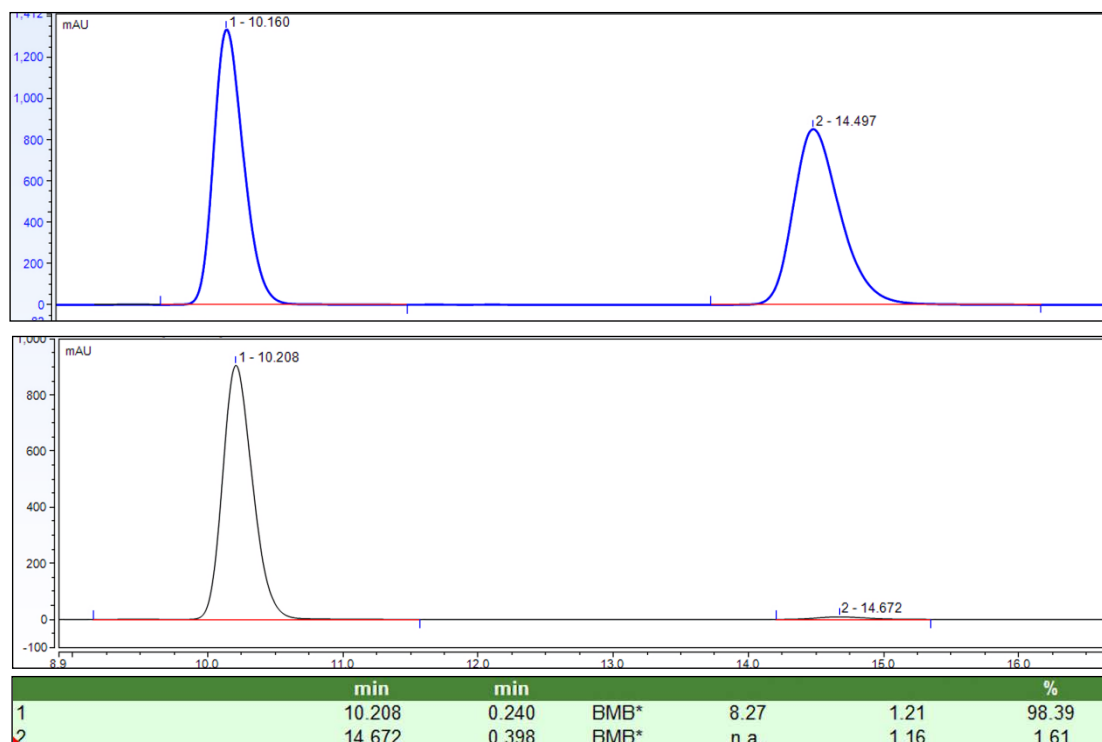


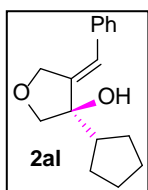
	min	min				%
1	9.043	0.212	BMB*	3.22	1.14	99.20
2	10.482	0.316	BMB*	n.a.	1.16	0.80



**2ak**: white solid, 44% yield, 98:2 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 10.21 min (*R*), 14.67 min (*S*).  $[\alpha]_D^{25} = +48.0$

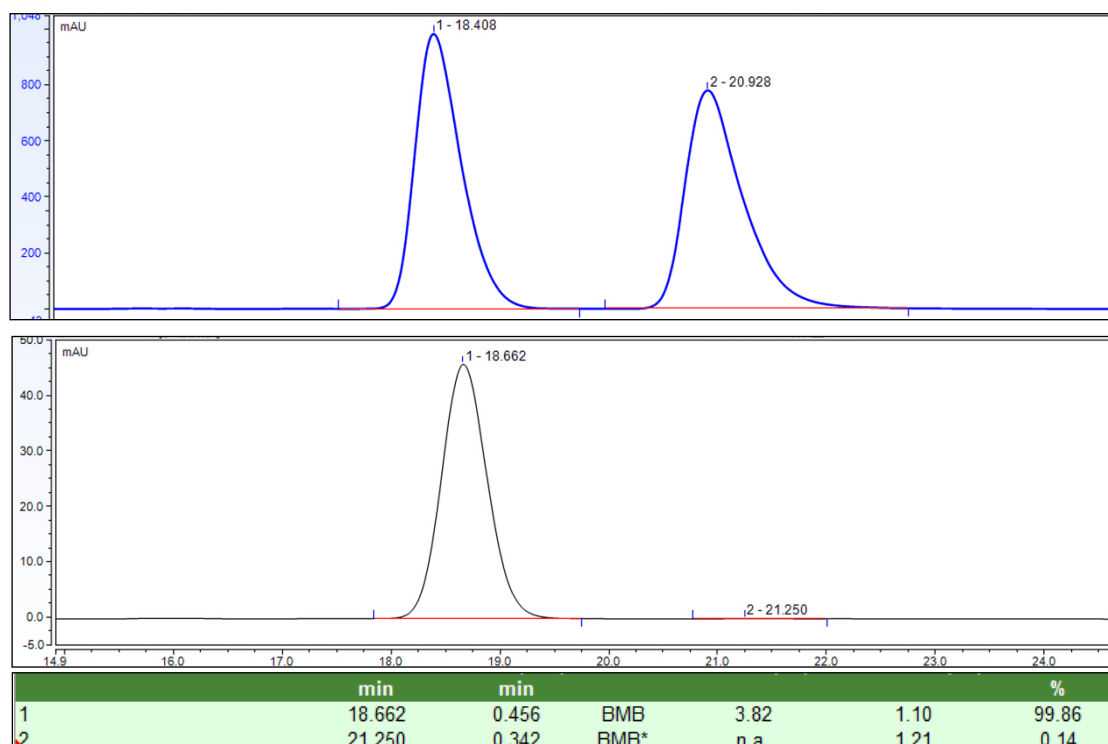
( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (t,  $J = 7.7$  Hz, 2H), 7.27 – 7.24 (m, 1H), 7.17 (d,  $J = 7.3$  Hz, 2H), 6.65 (t,  $J = 2.6$  Hz, 1H), 4.78 (ddd,  $J = 82.3, 14.5, 2.6$  Hz, 2H), 3.80 – 3.72 (m, 2H), 1.74 (s, 1H), 1.12 (tt,  $J = 8.3, 5.4$  Hz, 1H), 0.64 – 0.41 (m, 4H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  145.4, 136.5, 128.6, 128.4, 127.3, 122.4, 78.9, 77.9, 70.6, 16.8, 0.6, 0.5. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{14}\text{H}_{16}\text{NaO}_2]^+$ : 239.1043; found: 239.1044.

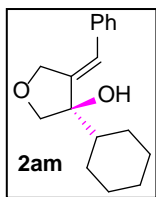




**2al**: white solid, 75% yield, > 99/1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 18.66 min (*R*), 21.25 min (*S*).  $[\alpha]_D^{25} = +54.4$

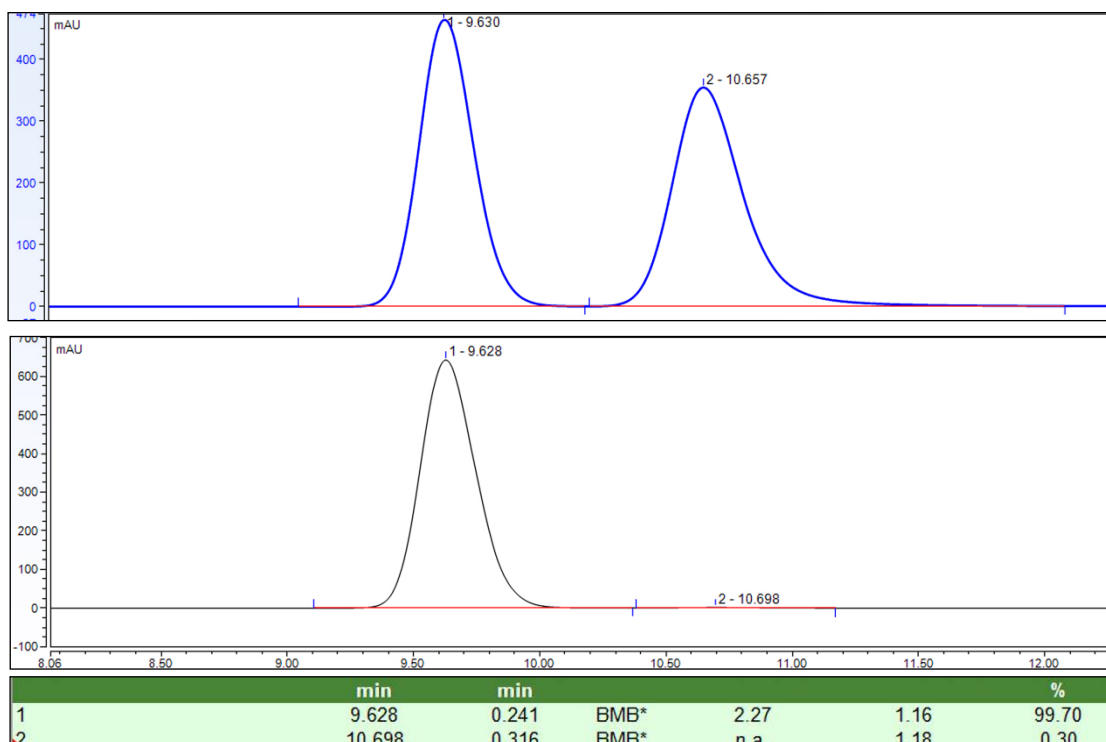
(*c* = 1.0, CH<sub>2</sub>Cl<sub>2</sub>); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.36 (t, *J* = 7.7 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.16 (d, *J* = 7.4 Hz, 2H), 6.54 (t, *J* = 2.5 Hz, 1H), 4.74 (ddd, *J* = 66.2, 14.4, 2.5 Hz, 2H), 3.82 (dd, *J* = 110.4, 9.2 Hz, 2H), 2.38 (p, *J* = 8.8 Hz, 1H), 1.92 (s, 1H), 1.91 – 1.82 (m, 1H), 1.72 – 1.41 (m, 7H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 145.9, 136.6, 128.6, 128.4, 127.2, 122.1, 82.2, 76.2, 70.6, 46.8, 27.6, 27.6, 26.0, 25.8. HRMS (ESI) calculated for [M+Na, C<sub>16</sub>H<sub>20</sub>NaO<sub>2</sub>]<sup>+</sup>: 267.1356; found: 267.1356.



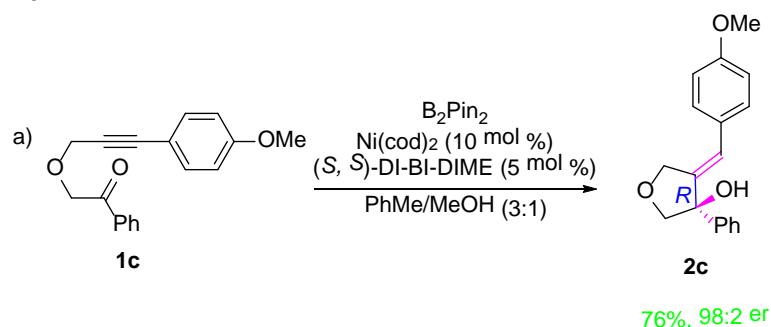


**2am**: white solid, 80% yield, > 99/1 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark OD-H, 25 °C, flow rate: 1 mL/min, hexanes/isopropanol: 90/10, 254 nm, 9.63 min (*R*), 10.70 min (*S*).  $[\alpha]_D^{25} = +70.8$

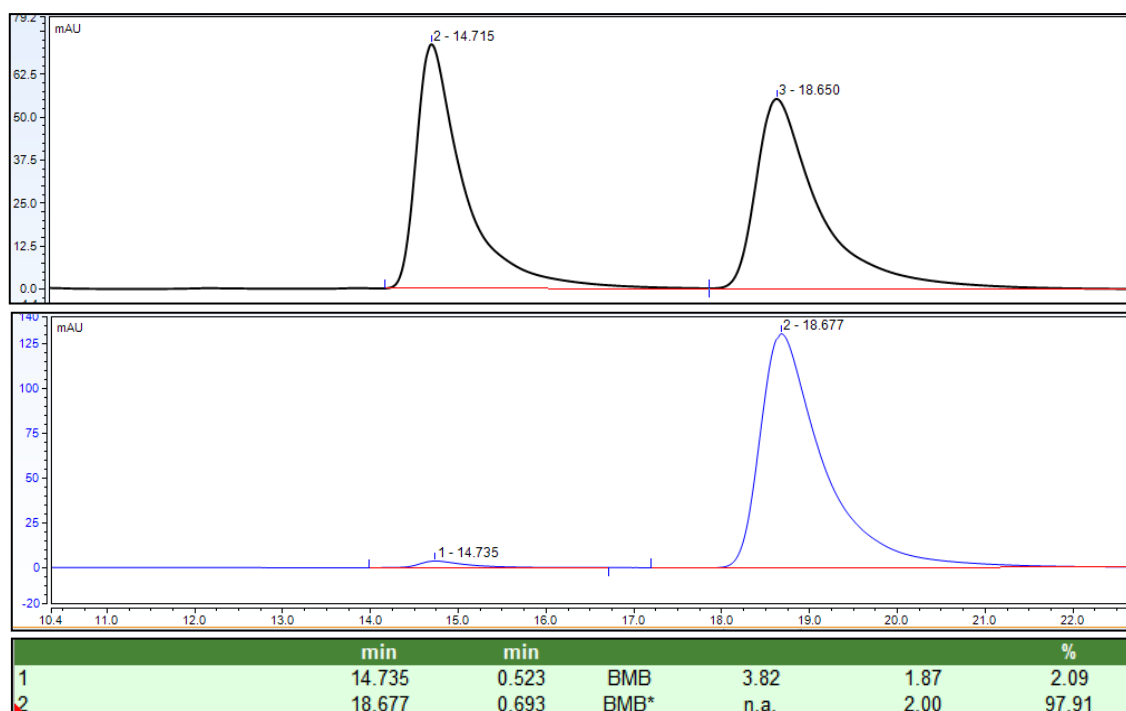
( $c = 1.0$ ,  $\text{CH}_2\text{Cl}_2$ );  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (t,  $J = 7.7$  Hz, 2H), 7.25 (t,  $J = 7.4$  Hz, 1H), 7.17 (d,  $J = 7.4$  Hz, 2H), 6.49 (t,  $J = 2.5$  Hz, 1H), 4.70 (ddd,  $J = 91.9, 14.3, 2.5$  Hz, 2H), 3.83 (dd,  $J = 178.8, 9.4$  Hz, 2H), 2.10 (d,  $J = 12.9$  Hz, 1H), 1.88 (s, 1H), 1.82 (d,  $J = 13.4$  Hz, 1H), 1.79 – 1.65 (m, 4H), 1.33 – 1.20 (m, 2H), 1.18 – 1.07 (m, 2H), 1.03 (ddd,  $J = 24.9, 12.6, 3.6$  Hz, 1H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  145.7, 136.5, 128.6, 128.3, 127.3, 122.3, 82.9, 75.4, 70.8, 45.7, 27.8, 27.4, 26.6, 26.5, 26.4. HRMS (ESI) calculated for  $[\text{M}+\text{Na}, \text{C}_{17}\text{H}_{22}\text{NaO}_2]^+$ : 281.1512; found: 281.1526.

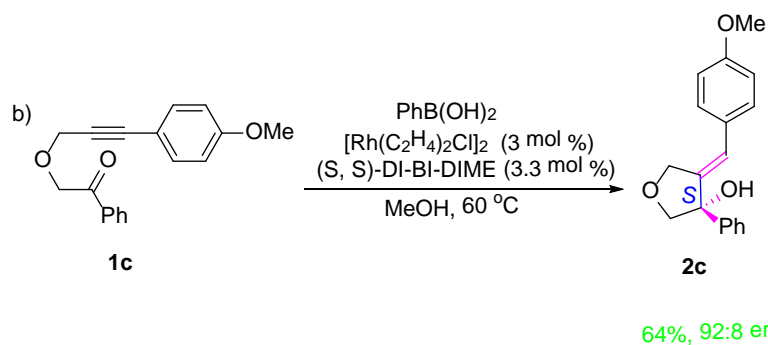


## 5. Discovered New Asymmetric Cyclization Reactions with (*S,S*)-DI-BIDIME and *O*-Alkynone **1c**

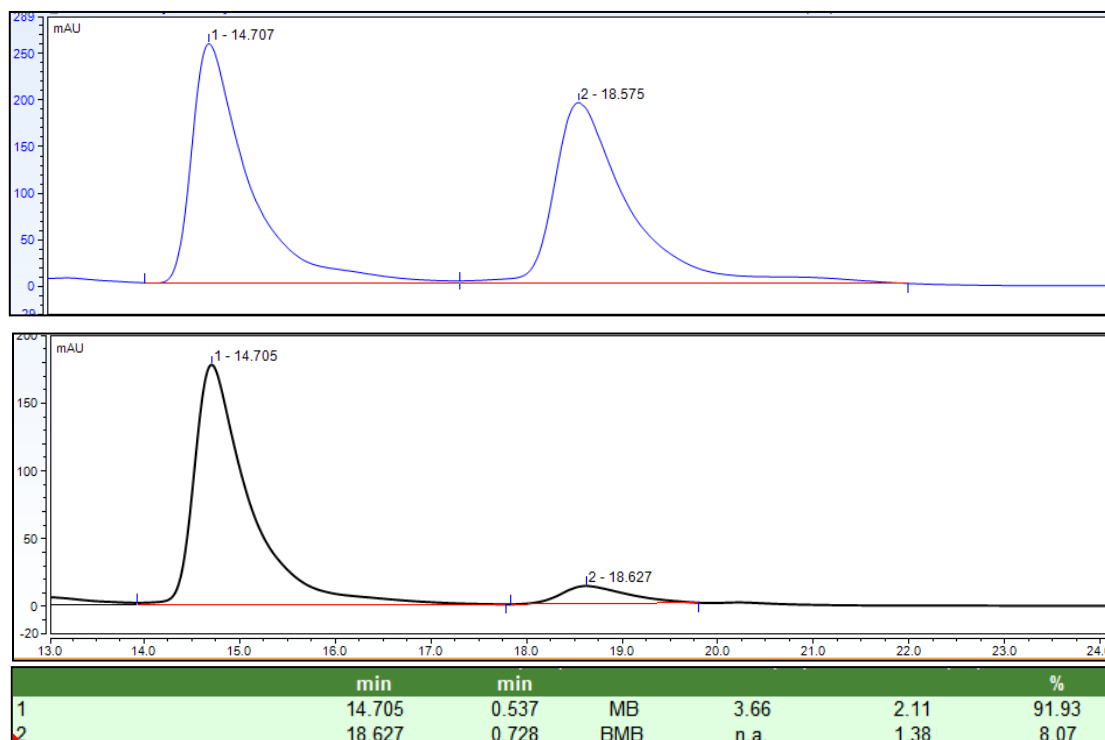


**General Procedure:**  $Ni(cod)_2$  (0.0075 mmol, 10 mol %), (*S,S*)-DI-BIDIME (**L13**, 0.00375 mmol, 5 mol %), toluene (0.3 mL) were added to a 4 mL screw-cap vial equipped with a magnetic stirring bar in the glove box and stirred for 10 min. followed by the addition of  $B_2Pin_2$  (0.375 mmol, 2.5 equiv.) and the mixture was stirred for 30 min. Substrate **1c** (0.1 mmol, 1.0 equiv.) and methanol (0.1 mL) was added to the solution in one portion. The vial was closed with a screw-cap, and the resulting mixture was stirred at rt for 24 h. The mixture was filtered through a Celite pad and concentrated. The residue was purified by column chromatography (eluent: PE/EA 4/1) to afford **2c**. **2c**: white solid, 76% yield, 98:2 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 0.5 mL/min, hexanes/isopropanol: 15/85, 254 nm, 14.74 min (*S*), 18.68 min (*R*).  $^1H$  NMR spectra is in agreement with mentioned above.





**General Procedure:**  $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$  (0.03 mmol, 3 mol%), phenylboric acid (0.2 mmol, 2 equiv),  $(S,S)\text{-DI-BIDIME}$  (**L13**, 0.015 mmol, 1.5 mol %), and degassed methanol (0.5 mL) were added to a 4 mL screw-cap vial equipped with a magnetic stirring bar in the glove box. Substrate **1c** (0.1 mmol, 1.0 equiv.) was added to the solution in one portion. The vial was closed with a screw-cap, and the resulting mixture was stirred at 60 °C until the raw materials are completely consumed. The solvent was removed in vacuo. The residue was purified by column chromatography (eluent: PE/EA 4/1) to afford **2c**. **2c**: white solid, 64% yield, 92:8 er with **L13** (2.5 mol %). Enantiomeric ratio was determined by chiral HPLC. Chiralpark AD-H, 25 °C, flow rate: 0.5 mL/min, hexanes/isopropanol: 15/85, 254 nm, 14.71 min (*S*), 18.57 min (*R*).  $^1\text{H}$  NMR spectra is in agreement with mentioned above.





## 6. References

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- [3] L. Zhao, X. Lu, *Angew. Chem. Int. Ed.* **2002**, *41*, 4343-4345.
- [4] M. Starck, P. Kadjane, E. Bois, B. Darbouret, A. Incamps, R. Ziessel, L. J. Charbonnière, *Chem. Eur. J.* **2011**, *17*, 9164-9179.
- [5] W. Fu, M. Nie, A. Wang, Z. Cao, W. Tang, *Angew. Chem. Int. Ed.* **2015**, *54*, 2520-2524.

## 7. NMR Spectra

