Supporting Information

Enantioselective *trans*-Dihydroxylation of Aryl Olefins by Cascade Biocatalysis with Recombinant *E. coli* Co-Expressing Monooxygenase and Epoxide Hydrolase

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1. Chemicals

All olefin substrates were purchased from commercial suppliers and used without further purification:

(1) Substrates from Sigma Aldrich: styrene **1a** (≥99%), 4-fluorostyrene **2a** (99%), 4-chlorostyrene **3a** (97%), 4-bromostyrene **4a** (97%), 3-chlorostyrene **9a** (98%), 3-bromostyrene **10a** (97%), 3-methylstyrene **11a** (99%), 3-methoxystyrene **12a** (97%), 2-fluorostyrene **13a** (98%), 2-methylstyrene **15a** (≥95%), *trans*-*β*-methylstyrene **16a** (99%), 2-methyl-1-phenyl-1-propene **20a** (99%), *α*-methylstyrene **21a** (99%), 3-trifluoromethylstyrene **22a** (99%);

(2) Substrates from Alfa Aesar: 4-methoxystyrene **6a** (98%), 4-trifluoromethylstyrene **7a** (98%), 3-fluorostyrene **8a** (97%), 2-chlorostyrene **14a** (98%), 1,2-dihydronaphthalene **19a** (96%);

(3) Substrate from Fluka: 4-methylstyrene **5a** (≥99%);

(4) Substrate from Merck: Indene **18a** (≥95%);

(5) Substrate from TCI: *cis*-*β*-methylstyrene **17a** (≥98%).

Some of the epoxides were commercially available or from previous synthesis[S1]:

(1) Epoxide from Fluka: styrene oxide **1b** (97%);

(2) Epoxides from Sigma Aldrich: 2-(4-fluorophenyl)oxirane **2b** (95%), 2-(4-chlorophenyl)oxirane **3b** (96%), 2-(4-bromophenyl)oxirane **4b** (96%);

(3) Epoxides from Amatek Chemical: 2-(3-chlorophenyl)oxirane **9b** (97%), 2-(2-chlorophenyl)oxirane **14b** (97%);

(4) Epoxides from Enamine: 2-(4-trifluoromethylphenyl)oxirane **7b** (95%), 2-(3-trifluoromethylphenyl)oxirane **22b** (95%);

(5) Epoxides from previous synthesis[S1]: 2-(3-fluoro-phenyl)oxirane **8b** (>95%), 2-(3-bromo-phenyl)oxirane **10b** (>95%).

Most of the racemic diols were chemically synthesized (see Section 2 synthesis of racemic diol), but some of racemic diols were obtained commercially or from previous synthesis:

(1) Racemic diols from Sigma Aldrich: 1-phenyl-1,2-ethanediol **1c** (97%), 2-phenyl-1,2-propanediol **21c** (97%);

(2) Racemic diols from Spectra Group: 1-(4-methylphenyl)-1,2-ethandediol **5c**, 1-(3-chlorophenyl)-1,2-ethandediol **9c**;

(3) Racemic diol from TCI: 1,2-dihydroxyindan **18c** (≥98%, mixture of *cis* and *trans*);

(4) Racemic diol from previous synthesis[S2]: *trans*-1,2-dihydroxyindan *trans*-**18c** (>95%).

Some enantiopure diols were purchased from companies:

(1) enantiopure diols from Sigma Aldrich: (*R*)-1-phenyl-1,2-ethanediol (*R*)-**1c** (99%), (*S*)-1-phenyl-1,2-ethanediol (*S*)-**1c** (99%), (*S*)-1-(2-chlorophenyl)-1,2-ethanediol (*S*)-**14c** (96%), (1*R*, 2*R*)-*trans*-1,2,3,4-tetrahydro-1,2-naphthalenediol (1*R*, 2*R*)-**19c** (≥96%), (1*S*, 2*S*)-*trans*-1,2,3,4-tetrahydro-1,2-naphthalenediol (1*S*, 2*S*)-**19c** (≥96%);

(2) enantiopure diol from Maybridge: (1*R*, 2*R*)-indan-1,2-diol (1*R*, 2*R*)-**18c** (97%).

Other enantiopure diols were synthesized by using Sharpless dihydroxylation method (see Section 3).

Other chemicals were obtain commercially, the important ones were listed below:

(1) Reagents and solvent from Sigma Aldrich: *m*-CPBA (≤77%), H_2SO_4 (98%), NaOH (pellets), AD-mix-α, AD-mix-β, Hexadecane (99%), THF (anhydrous, 99.9%), NaCl (≥99.5%), Na_2SO_4 (anhydrous, ≥99%), Na_2CO_3•H_2O (puriss), $NaHCO_3$ (ACS reagent);

(2) Solvents from Fisher: dichloromethane (HPLC), ethyl acetate (HPLC), isopropanol (HPLC);

(3) Solvents from Tedia: acetonitrile (HPLC), *n*-hexane (HPLC);

(4) Reagent from Merck: Silica gel 60 (0.040–0.063 mm).

2. Chemical Synthesis of Racemic Diols as Analytical Standards

2.1 Chemical synthesis method A: direct acid hydrolysis of racemic epoxide

According to previous publication[S3]: 200 mg epoxides were dissolved in the mixture of 10 mL THF and 5 mL water. Then 100 μL concentrated H_2SO_4 (98%) was added into the system. The reaction was magnetically stirred at room temperature and TLC was performed to check the conversion of epoxide and formation of diol. When the majority of epoxide was hydrolyzed (usually take 12–36 h), the reaction system was neutralized by adding saturated $NaHCO_3$ solution, saturated with solid NaCl, followed by extraction by ethyl acetate three times (3×10 mL). The combined organic phase was washed with saturated NaCl solution and dried over Na_2SO_4 overnight. The solvent was then removed by evaporation. The crude product was purified by flash chromatography on a silica gel column (n-hexane: ethyl acetate = 2:1 to 1:1, $R_f \approx 0.3$). The racemic diols produced by method A including: 1-(4-fluorophenyl)-1,2-ethanediol **2c**, 1-(4-chlorophenyl)-1,2-ethanediol **3c**, 1-(4-bromophenyl)-1,2-ethanediol **4c**, 1-(4-trifluoromethyl)-1,2-ethanediol **7c**, 1-(3-fluorophenyl)-1,2-ethanediol **8c**, 1-(3-bromophenyl)-1,2-ethanediol **10c**, 1-(2-chlorophenyl)-1,2-ethanediol **14c**, and 1-(3-trifluoromethyl)-1,2-ethanediol **22c**. All the racemic diols were obtained in 40–80% yield. Only **8c** is colorless oil, and others are white to light yellow solids under 4 °C storage.

2.2 Chemical synthesis method B: *m*-CPBA epoxidation of olefins and followed by acid hydrolysis

According to previous report[S4]: *m*-CPBA (2 mmol) was stepwise added to a stirred solution of olefin (2 mmol) in a CH_2Cl_2: water system (20 mL, 1:1) on ice, and the mixture was stirred at room temperature for 3–12 h. If needed, a second equivalent of *m*-CPBA (2 mmol) was then added to the mixture and stirred for longer time (additional 12 h) to complete the reaction. Na_2CO_3 (10%) was added to adjust pH to 8, and then the mixture was extracted with CH_2Cl_2 three times (3 × 20 mL). The organic phase was separated, washed with saturated NaCl solution, and dried using Na_2SO_4, and the solvent was removed by evaporation. The crude epoxide intermediate was directly used for acid hydrolysis without purification. A mixture of 10 mL THF and 5 mL water was added to the system, followed by addition of 100 μL concentrated H_2SO_4 (98%) to start hydrolysis at room temperature. When the hydrolysis completed (12–36 h), the reaction system was neutralized by $NaHCO_3$ solution, saturated with solid NaCl and then extracted by ethyl acetate three times (3×10 mL). The combined organic phase was washed with saturated NaCl solution and dried over Na_2SO_4 overnight. The solvent was then removed by evaporation. The crude product was purified by flash chromatography on a silica gel column (*n*-hexane: ethyl acetate = 2:1 to 1:1, $R_f \approx 0.3$). The racemic diols produced by method B including: 1-(4-methoxyphenyl)-1,2-ethanediol **6c**, 1-(3-methylphenyl)-1,2-ethanediol **11c**, 1-(3-methoxyphenyl)-1,2-ethanediol **12c**, 1-(2-fluorophenyl)-1,2-ethanediol **13c**, 1-(2-methylphenyl)-1,2-ethanediol **15c**, 1,2,3,4-tetrahydro-1,2-naphthalenediol (*trans*: *cis* ≈ 5: 1) **19c**. Except **6c** was obtained in 10% yield, all the other racemic diols were obtained in 30–70% yield. While **11c** is colorless oil, others are white to light yellow solid under 4 °C storage.

2.3 Chemical synthesis method C: *m*-CPBA epoxidation of olefins and base hydrolysis in one pot

According to previous study[S5]: *m*-CPBA (2 mmol) was stepwise added to a stirred solution of olefin (2 mmol) in CH_2Cl_2 (15 mL) on ice, and the mixture was stirred at room temperature for 3–12 h. If needed, a second equivalent of *m*-CPBA (2 mmol) was then added to the mixture and stirred for longer time (additional 12 h) to complete the reaction. Once the epoxidation finished, high concentrated NaOH (10 M, 100 μL) was added, and the mixture was reflex at 80 °C. The reaction was monitored by TLC, and once

completed, extracted with CH_2Cl_2 three times (3 × 20 mL). The organic phase was separated, washed with saturated NaCl solution, and dried using Na_2SO_4, and the solvent was removed by evaporation. The crude product was purified by flash chromatography on a silica gel column (*n*-hexane: ethyl acetate = 2:1 to 1:1, $R_f \approx 0.3$). The racemic diols produced by method C including: 1-phenyl-1,2-propanediol **16c** (as mixture of four enantiomers), 2-methyl-1-phenyl-1,2-propanediol **20c**, which were obtained in 40–60% yield, and become white solid under 4 °C storage.

3. Synthesis of Enantiopure/enriched Diols by Sharpless Dihydroxylation as Chiral Standards

Many enantiopure/enriched diols were synthesized in 10 mg-scale and used as a standard to for chiral HPLC analysis. The asymmetric synthesis was performed as reported[S6]: 0.1 mmol olefin was added to 1 mL mixture of *tert*-BuOH and water (1:1) with 0.15g AD-mix-α (or AD-mix-β for another enantiomer). The reaction was shaken on a mixing block at room temperature for 3 h, and then 50 mg Na_2SO_3 was added to quench the dihydroxylation. The *tert*-BuOH was removed by evaporation, and the remaining aqueous phase was saturated with NaCl and extracted with ethyl acetate (2 mL). The organic layer was dried by Na_2SO_4 for 5 h, and then the clear upper layer was separated and evaporated. The enantiopure/enriched diols were obtained and directly used in chiral HPLC analysis without further purification. The enantiopure/enriched diols prepared including: (*S*)-**2c**, (*S*)-**3c**, (*S*)-**4c**, (*S*)-**5c**, (*S*)-**6c**, (*S*)-**7c**, (*S*)-**8c**, (*S*)-**9c**, (*S*)-**10c**, (*S*)-**11c**, (*S*)-**12c**, (*S*)-**13c**, (*S*)-**15c**, (1*S*, 2*S*)-**16c**, (1*S*, 2*R*)-**16c**, (*S*)-**20c**, (*S*)-**21c**, (*S*)-**22c**, (*R*)-**2c**, (*R*)-**3c**, (*R*)-**4c**, (*R*)-**5c**, (*R*)-**6c**, (*R*)-**7c**, (*R*)-**8c**, (*R*)-**9c**, (*R*)-**10c**, (*R*)-**11c**, (*R*)-**12c**, (*R*)-**13c**, (*R*)-**15c**, (1*R*, 2*S*)-**16c**, (1*R*, 2*R*)-**16c**, (*R*)-**20c**, (*R*)-**21c**, (*R*)-**22c**.

4. Analytical Methods

The concentrations of diol products (**1c**–**22c**) from biotransformations were determined using a Shimadzu prominence reverse phase HPLC system with an Agilent Poroshell 120 EC-C18 column (150 × 4.6 mm,

2.7 μm) and UV detection at 210 nm. Conditions: 40% water: 60% acetonitrile, flow rate: 0.4 mL min^{-1}. The retention times for most of the diols (**1c–22c**) are from 4 to 5 min. The concentrations of alkene substrates (**1a–22a**) were quantified using a Shimadzu prominence normal phase HPLC system with an Agilent Zorbax Rx-SIL column (150 × 4.6 mm, 5 μm) and UV detection at 210 nm. Condition: 10% IPA: 90% *n*-hexane, flow rate: 1.0 mL min^{-1}. The retention times for most of the alkenes (**1a–22a**) are from 1 to 2 min.

The *ee* and *de* values of diol products (**1c–22c**) were determined by chiral HPLC using a Shimadzu prominence HPLC system (normal phase) with the following 4 methods:

Chiral HPLC method A: Daicel Chiralpak AS-H (250 × 4.6 mm, 5μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm.

Chiral HPLC method B: Daicel Chiralpak OB-H (250 × 4.6 mm, 5μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 0.5 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm.

Chiral HPLC method C: Daicel Chiralpak IA-3 (250 × 4.6 mm, 3μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm.

Chiral HPLC method D: Daicel Chiralpak IA-3 (250 × 4.6 mm, 3μm) column, mobile phase 5% IPA: 95% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm.

Table S1. Analytic chiral HPLC methods and retention times for all diols (**1c–22c**) in this article.

Diol Product	Method	(*S*) Retention Time (min)	(*R*) Retention Time (min)
1c	A	10.9	11.6
2c	A	11.6	12.7
3c	A	10.9	12.4
4c	A	10.9	12.5
5c	A	9.9	11.1

6c	A	18.3	19.7
7c	A	7.3	8.7
8c	A	9.9	10.6
9c	A	10.3	10.7
10c	A	10.7	11.0
11c	A	9.3	9.8
12c	C	12.8	13.8
13c	A	10.9	9.7
14c	A	11.5	9.5
15c	A	9.3	8.9
16c	D	16.8 (1*S*, 2*S*); 18.2 (1*S*, 2*R*)	18.7 (1*R*, 2*S*); 20.5 (1*R*, 2*R*)
18c	B	11.9 (1*S*, 2*S*); 16.0&17.2 (*cis*)	13.4 (1*R*, 2*R*); 16.0&17.2 (*cis*)
19c	B	12.5 (1*S*, 2*S*); 15.2&16.6 (*cis*)	13.7 (1*R*, 2*R*); 15.2&16.6 (*cis*)
20c	C	8.6	10.6
21c	A	8.6	10.2
22c	A	6.9	7.4

5. Strains and Biochemicals

Escherichia coli T7 expression cells, restriction enzymes and Quick DNA Ligase were purchased from New England Biolabs. Oligos (primers) were purchased from 1st BASE. Phusion DNA polymerase was from Thermo Scientific. Medium LB, tryptone, agar, and yeast extract were purchased from Biomed Diagnostics. Antibiotics kanamycin (>99%), glucose, and other salts in culture medium were from Sigma Aldrich or Merck. IPTG (Isopropyl β-D-1-thiogalactopyranoside) from Gold Biotechnology.

6. Culture Media

1 L M9 medium containing: 8.5 g Na_2HPO_4•$2H_2O$, 3.0 g KH_2PO_4, 0.5 g NaCl, 1.0 g NH_4Cl, 2 mL $MgSO_4$ solution (1M), 0.1 mL $CaCl_2$ solution, 1 mL 1000X MT solution (8.3 g/L $FeCl_3$•$6H_2O$, 0.84 g/L $ZnCl_2$, 0.13 g/L $CuCl_2$•$2H_2O$, 0.1 g/L $CoCl_2$•$2H_2O$, 0.1 g/L H_3BO_3, 0.016 g/L $MnCl_2$•$4H_2O$, 1 M HCl). Also usually containing 30 g/L glucose as carbon source and 5 g/L yeast extract in this study.

1 L modified Riesenberg medium[S7] containing: 13.3 g KH_2PO_4, 4.0 g $(NH_4)_2HPO_4$, 1.7 g Citric acid, 1.2 g $MgSO_4$•7H2O, 4.5 mg Thiamin HCl, 15 g Glucose, 10 mL trace metal solution (6 g/L Fe(III) citrate, 1.5 g/L $MnCl_2$•$4H_2O$, 0.8 g/L $Zn(CH_3COO)_2$•$2H_2O$, 0.3 g/L H_3BO_3, 0.25 g/L Na_2MoO_4•$2H_2O$, 0.25 g/L $CoCl_2$•$6H_2O$, 0.15 g/L $CuCl_2$•$2H_2O$, 0.84 g/L EDTA, 0.1 M HCl).

7. Genetic Engineering of Recombinant *E. coli* Strains

PCR primer list for SMO (StyA & StyB), SpEH, and StEH:

StyA-BspHI-F: ACTGTCATGAAAAAGCGTATCGGTATTGTTGG

StyA-EcoRI-R: ACTGGAATTCTCATGCTGCGATAGTTGGTGCGAACTG

StyB-EcoRI-RBS-F: ACTGGAATTCTAAGGAGATTTCAAATGACGCTGAAAAAAGATATGGC

StyB-NdeI-F: ACTGCATATGACGCTGAAAAAAGATATGGC

StyB-HindIII-R: ACTGAAGCTTTCAATTCAGTGGCAACGGGTTGC

StyB-KpnI-R: ACTGGGTACCTCAATTCAGTGGCAACGGGTTGC

SpEH-NdeI-F: ATCGCATATGATGAACGTCGAACATATCCGCCC

SpEH-KpnI-RBS-F: ACTGGGTACCTAAGGAGATATATCATGATGAACGTCGAACATATCCGCC

SpEH-XhoI-R: ATCGCTCGAGTCAAAGATCCATCTGTGCAAAGGCC

StEH-NdeI-F: ACTGCATATGGAGAAAATCGAACACAAGATG

StEH-KpnI-RBS-F: ACTGGGTACCTAAGGAGATATATCATGGAGAAAATCGAACACAAGATG

StEH-XhoI-R: ACTGCTCGAGTTAGAATTTTTGAATAAAATC

Construction of plasmid SSP1: primers StyA-BspHI-F and StyA-EcoRI-R were used to amplify the *styA* from pSPZ10, and primers StyB-EcoRI-RBS-F and StyB-KpnI-R were used to amplify the *styB* from pSPZ10, and primers SpEH-KpnI-RBS-F and SpEH-XhoI-R were used to amplify the *spEH* from the genome of *Sphingomonas* sp. HXN-200[S1]. Phusion DNA polymerase was used for all the PCRs according to the instruction. The PCR products were subjected to double digestion with appropriate restriction enzymes (New England Biolabs), and the parental plasmid pRSFduet (Novagen) was also subjected to digestion. Then ligation of digested PCR product and plasmid was performed, and then the ligation products were used for chemical transformation of competent T7 Express Competent *E. coli* cell (New England Biolabs). The three genes (*styA*, *styB*, and *spEH*) were inserted to pRSFduet one by one (first *styA*, then *styB*, last *spEH*). The final successful construction is SSP1 which was transformed to *E. coli* to give *E. coli* (SSP1).

Similarly, the construction of plasmid SSP2-1 used primers StyA-BspHI-F, StyA-EcoRI-R, StyB-EcoRI-RBS-F, StyB-HindIII-R, SpEH-NdeI-F, and SpEH-XhoI-R. The genetic construction is on the same parental plasmid pRSFduet. The transformation of SSP2-1 gave *E. coli* (SSP2-1).

Similarly, the construction of plasmid SSP2-2 used primers StyA-BspHI-F, StyA-EcoRI-R, StyB-NdeI-F, StyB-KpnI-R, SpEH-KpnI-RBS-F, and SpEH-XhoI-R. The genetic construction is on the same parental plasmid pRSFduet. The transformation of SSP2-2 gave *E. coli* (SSP2-2).

Construction of plasmid SST1 is similar to SSP1, but *stEH* was amplified from the synthesized *stEH* gene (codon optimized for *E. coli*) from Genscript according to the sequence Genbank U02497 using primers StEH-KpnI-RBS-F and StEH-XhoI-R. Other *styA* and *styB* construction is the same to SSP1 by using the intermediate genetic construct in the last step engineering of SSP1. The transformation of SST1 gave *E. coli* (SST1).

Construction of plasmid SST2-1 is similar to SSP2-1, but just the gene of last enzyme *stEH* was amplified using StEH-NdeI-F, and StEH-XhoI-R. And the construction intermediate in the last step of SSP2-1 was used for SST2-1. The transformation of SST2-1 gave *E. coli* (SST2-1).

Construction of plasmid SST2-2 is similar to SSP2-2, but just the gene of last enzyme *stEH* was amplified using StEH-KpnI-RBS-F, and StEH-XhoI-R. And the construction intermediate in the last step of SSP2-2 was used for SST2-2. The transformation of SST2-2 gave *E. coli* (SST2-2).

8. NMR and Optical Rotation of Diols Prepared by Biocatalytic Dihydroxylation

The NMR of prepared diols were determined using a Bruker 400 MHz NMR system. Optical rotations were determined using a Jasco polarimeter DIP-1000.

(*S*)-1-Phenyl-1,2-ethanediol (*S*)-1c: white solid; yield: 85.5%; *ee*: 96%; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.23–7.38 (m, 5H, ArH), 4.79–4.82 (m, 1H), 3.62–3.76 (m, 2H), 2.50–2.78 (br, 2H, OH). $[\alpha]_D^{25}$: +36.8° (*c* 1.0, EtOH), lit.[S8] $[\alpha]_D^{23}$: +38.4° (*c* 4.38, EtOH);

(*R*)-1-Phenyl-1,2-ethanediol (*R*)-1c: white solid; yield: 83.8%; *ee*: 96%; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.26–7.37 (m, 5H, ArH), 4.76–4.79 (dd, *J* = 8.4, 3.2 Hz, 1H), 3.70–3.74 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.60–3.65 (dd, *J* = 11.6, 8.4 Hz, 1H), 3.05–3.20 (br, 2H, OH). $[\alpha]_D^{26}$: -38.2° (*c* 1.0, EtOH), lit.[S9] $[\alpha]_D^{25}$: -37.8° (*c* 1.0, EtOH);

(*S*)-1-(4-Fluorophenyl)-1,2-ethanediol (*S*)-2c: white solid; yield: 76.7%; *ee*: 97%; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.26–7.34 (m, 2H, ArH), 7.01–7.06 (t, *J* = 8.8, 2H, ArH), 4.77–4.80 (dd, *J* = 8.4, 3.2 Hz, 1H), 3.70–3.74 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.58–3.63 (dd, *J* = 11.2, 8.4 Hz, 1H), 2.52–2.75 (br, 2H, OH). $[\alpha]_D^{27}$: +63.6° (*c* 1.0, $CHCl_3$), lit.[S10] $[\alpha]_D^{30}$: +62.8° (*c* 1.0, $CHCl_3$);

(*R*)-1-(4-Fluorophenyl)-1,2-ethanediol (*R*)-2c: white solid; yield: 80.7%; *ee*: 97%; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.26–7.34 (m, 2H, ArH), 7.01–7.06 (t, *J* = 8.4, 2H, ArH), 4.77–4.80 (dd, *J* = 8.4, 3.6 Hz,

1H), 3.70–3.74 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.58–3.63 (dd, *J* = 11.2, 8.4 Hz, 1H), 2.50–2.72 (br, 2H, OH). $[\alpha]_D^{27}$: -62.8° (*c* 1.0, $CHCl_3$), lit.[S9] $[\alpha]_D^{25}$: -58.2° (*c* 1.0, $CHCl_3$);

(*S*)-1-(4-Methylphenyl)-1,2-ethanediol (*S*)-5c: white solid; yield: 73.4%; *ee*: 92%; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.14–7.26 (m, 4H, ArH), 4.74–4.77 (dd, *J* = 8.0, 3.2 Hz, 1H), 3.68–3.72 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.61–3.65 (dd, *J* = 11.6, 8.4 Hz, 1H), 2.95–3.08 (br, 2H, OH), 2.34 (s, 3H). $[\alpha]_D^{27}$: +66.2° (*c* 1.0, $CHCl_3$), lit.[S10] $[\alpha]_D^{30}$: +68.5° (*c* 1.12, $CHCl_3$);

(*S*)-1-(3-Chlorophenyl)-1,2-ethanediol (*S*)-9c: colorless syrup; yield: 75.6%; *ee*: 97%; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.14–7.22 (m, 4H, ArH), 4.71–4.74 (dd, *J* = 8.0, 3.6 Hz, 1H), 3.67–3.71 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.53–3.58 (dd, *J* = 11.2, 8.0 Hz, 1H), 2.36 (s, 2H, OH). $[\alpha]_D^{25}$: +21.8° (*c* 1.0, EtOH), lit.[S8] $[\alpha]_D^{26}$: +21.1° (*c* 1.31, EtOH);

(*R*)-1-(3-Chlorophenyl)-1,2-ethanediol (*R*)-9c: colorless syrup; yield: 70.6%; *ee*: 96%; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.23–7.39 (m, 4H, ArH), 4.79–4.82 (dd, *J* = 8.0, 3.2 Hz, 1H), 3.75–3.79 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.61–3.66 (dd, *J* = 11.2, 8.0 Hz, 1H), 2.67 (s, 2H, OH). $[\alpha]_D^{26}$: -23.6° (*c* 1.0, EtOH), lit.[S9] $[\alpha]_D^{25}$: -22.5° (*c* 1.1, EtOH);

(*S*)-1-(3-Methoxyphenyl)-1,2-ethanediol (*S*)-12c: colorless syrup; yield: 85.3%; *ee*: 97%; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 6.84–7.19 (m, 4H, ArH), 4.69–4.73 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.73 (s, 3H), 3.66–3.70 (dd, *J* = 11.6, 3.6 Hz, 1H), 3.56–3.60 (dd, *J* = 11.6, 8.0 Hz, 1H), 2.43 (s, 2H, OH). $[\alpha]_D^{25}$: +25.6° (*c* 1.0, EtOH), lit.[S8] $[\alpha]_D^{27}$: +26.9° (*c* 1.12, EtOH);

(1*R*,2*S*)-1-Phenyl-1,2-propanediol (1*R*,2*S*)-16c: colorless syrup; yield: 82.3%; *ee*: >98%; *de*: 98%; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.29–7.43 (m, 5H, ArH), 4.69–4.70 (d, *J* = 4.4 Hz, 1H), 4.01–4.07 (m, 1H), 2.17 (s, 2H, OH), 1.10–1.12 (d, *J* = 7.2 Hz, 3H). $[\alpha]_D^{25}$: -16.6° (*c* 1.0, EtOH), lit.[S11] $[\alpha]_D^{20}$: -17.8° (*c* 1.0, EtOH);

(1*R*,2*R*)-1-Phenyl-1,2-propanediol (1*R*,2*R*)-16c: colorless syrup; yield: 78.8%; *ee*: 99%; *de*: >99%; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 7.26–7.38 (m, 5H, ArH), 4.35–4.37 (d, *J* = 7.2 Hz, 1H), 3.82–3.89

(quint, *J* = 6.4 Hz, 1H), 2.52 (s, 2H, OH), 1.04–1.06 (d, *J* = 6.4 Hz, 3H). $[\alpha]_D^{27}$: -51.2° (*c* 1.0, CH_2Cl_2), lit.[S12] $[\alpha]_D^{20}$: -51.3° (*c* 3.5, $CHCl_3$).

9. Experiments with *E. coli* (pSPZ10) and *Pichia pastoris CBS 7435_MutS_PotHis*

Procedure for cell growth and epoxidation activity of *E. coli* JM101 (pSPZ10): *E. coli* JM101 (pSPZ10)[S13] were inoculated (1%) in LB medium with kanamycin (50 mg/L) and the cultures were grown at 30 °C, 250 rpm for 2 h (OD450 ~ 0.4). 0.05% (vol/vol) DCPK was added to induce protein expression, and then cultures were grown at 25 °C and 250 rpm for another 12 h. Aliquots of 0.5–1 mL cell suspension were centrifuged and resuspended with 0.475 mL KP buffer (pH 7.5, 100 mM, containing 1% glucose) to a cell density of 1 g cdw/L. The cell suspension was incubated in a shaker (1000 rpm, 30 °C) for 5 min. 25 μL of a 50 mM styrene solution in ethanol was added to the mixture to form a final concentration of 2.5 mM. The reaction continued for 5 min in the shaker and was stopped by adding 0.5 ml of cold ethyl acetate (containing 0.5 mM dodecane as an internal standard). The aqueous phase was extracted by vigorous shaking for 20 s and the phases were separated by centrifugation. The organic phase was dried over anhydrous magnesium sulfate and analyzed by GC.

Procedure for cell growth and hydrolysis activity of *Pichia pastoris* CBS 7435_MutS_PotHis: Cells were grown at 28 °C in baffled 2 L Erlenmeyer flasks, filled with 135 mL BMD 1% and covered with linen. The *P. pastoris* cells from an overnight culture were inoculated in the flask to an OD_{600} value of 0.1. After approximately 60 h, 15 mL BMM10 were added using a sterile syringe. 10 and 24 h after BMM10 induction, 1.5 mL methanol was added to induce protein expression. Cells are harvested at approximately 24 h after the last induction by centrifugation (4000 rpm, 4 °C, and 10 min). The supernatant was removed and cell pellets were stored at -20 °C until needed. Aliquots of 0.5–1 ml cell suspension were centrifuged and resuspended with 0.475 ml KP buffer (pH 7.5, 100 mM, and containing 1% glucose) to a cell density of 1 g/L cdw. 25 μL of a 200 mM styrene oxide solution in ethanol was added to form a final concentration of 10 mM. The reaction continued for 5 min in the shaker and was finally stopped by adding 0.5 ml of cold

ethanol containing 1 mM benzyl alcohol as an internal standard. The aqueous phase was analyzed by reverse HPLC.

Procedure for enantioselective dihydroxylation of styrene 1a with tandem biocatalysts of *E. coli JM101* (pSPZ10) and *Pichia pastoris* CBS 7435_MutS_PotHis: The frozen *P. pastoris* yeast cells were washed overnight, before lyophilized to powder form for 48 h. 12.5 mg of lyophilized powder was dissolved into 2.5 mL of frozen/thawed cell suspension (10 g cdw/L) of *E. coli* JM101 (pSPZ10). The cell suspension was made up of 100 mM KP Buffer (pH 7.5), with initial 0.5 w/v % glucose. A volume of 2.5 mL hexadecane containing 100 mM styrene **1a** was added to the aqueous phase and incubating at 300 rpm and 30 ºC. After 2 h, 0.5 w/v % glucose and 20 mM sodium carbonate was added simultaneously to the aqueous phase. Subsequently, after additional 6 h, 0.2 w/v % glucose and 8 mM sodium carbonate was added. At different point of time, 20 μL from organic and aqueous phase were extracted. All 20 μL samples were diluted with 480 μL ethanol, and adding another 0.5 mL ethanol containing 2 mM benzyl alcohol as internal standard. The samples were analysed by HPLC to determine styrene, styrene oxide and diols concentration in each phase. For the determination of the *ee* of diols, 100 μL of aqueous phase was saturated with NaCl. The saturated solution was extracted with 200 μL ethyl acetate before centrifugation. The extracted organic layer was dried over magnesium sulphate for chiral HPLC analysis.

10. Experiments with *E. coli* (pSPZ10_pMS470Δ8)

Procedure for engineering *E. coli* (pSPZ10_pMS470Δ8) as a two-plasmid system: The electronic competent cells of *E. coli* JM101 (pSPZ10) were prepared by first cooled down the cell culture of 400 mL LB medium (OD600 = 0.5) on ice, and harvested the cells with centrifugation (4000 rpm, 4 ºC, and 10 minutes), and then washed the pallet with chilled water, and finally resuspended the cell pallet with 40 mL 10% glycerol. 0.4 μL pMS470Δ8 (containing StEH gene) was used to electronically transformed into 60 μL of the competent cells of *E. coli* JM101 (pSPZ10). The transformation was done with Gene Pulser® cuvette and Bio-Rad MicroPulser ™ system according to the protocol from Bio-Rad with pulse time of 5.7

ms. After electronic transformation, the *E. coli* (pSPZ10_pMS470Δ8) was recovered in SOC media at 37 °C for 40 min, and then transferred to LB agar plate with ampicillin (50 mg/L) and kanamycin (25 mg/L). The colonies were inoculated in the LB medium with ampicillin (50 mg/L) and kanamycin (25 mg/L) to test cell growth and expression of SMO and StEH.

Procedure for cell growth of *E. coli* (pSPZ10_pMS470Δ8): *E. coli* (pSPZ10_pMS470Δ8) cells were inoculated in TB medium at an initial cell density of OD450 = 0.1. The cells were grown at 30 °C, 250 rpm for 2 h (OD450 ~ 0.4). 0.05% (vol/vol) DCPK was added to induce SMO expression, and then cultures were grown at 25 °C and 250 rpm for another 12 h. Then, IPTG (0.05 mM) was added to induce the expression of StEH. The cells were still cultured at 25 °C and 250 rpm for another 2 h, and harvested by centrifugation (5000 g, 5 min).

Procedure for enantioselective dihydroxylation of styrene 1a with *E. coli* (pSPZ10_pMS470Δ8): The freshly prepared *E. coli* (pSPZ10_pMS470Δ8) cells were resuspended to a cell density of 20 g cdw/L in KP buffer (100 mM, pH 7.5) containing glucose (0.25%, w/v) to 2.5 mL system. 2.5 mL *n*-hexadecane containing 100 mM styrene **1a** was added to the reaction system to form a second phase. The reaction mixture was shaken at 300 rpm and 30 °C. And glucose and Na_2CO_3 were added to the reaction system at different time. At 1 h reaction time, 0.25% glucose and 20 μL of 1 M Na_2CO_3 were added; at 2 h reaction time, 0.1% glucose and 20 μL of 1 M Na_2CO_3 were added; at 4 h reaction time, 20 μL of 1 M Na_2CO_3 were added; at 8 h reaction time, 10 μL of 1 M Na_2CO_3 were added. At different point of time, 20 μL from organic and aqueous phase were extracted. All 20 μL samples were diluted with 480 μL ethanol, and adding another 0.5 mL ethanol containing 2 mM benzyl alcohol as internal standard. The samples were analysed by HPLC to determine styrene, styrene oxide and diols concentration in each phase. For the determination of the *ee* of diols, 100 μL of aqueous phase was saturated with NaCl. The saturated solution was extracted with 200 μL ethyl acetate before centrifugation. The extracted organic layer was dried over magnesium sulphate for chiral HPLC analysis.

11. Figure S1. Time course of representative dihydroxylation

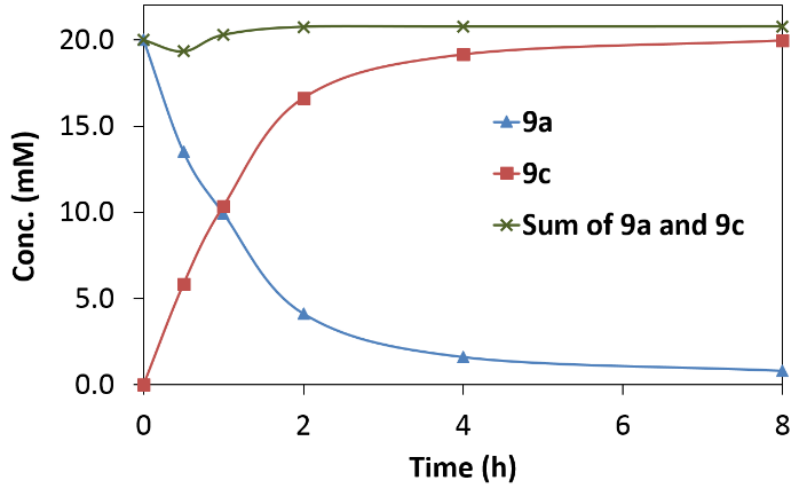

Figure S1. Enantioselective dihydroxylation of 3-chlorostyrene **9a** to (*S*)-1-(3-chlorophenyl)-1,2-ethanediol **9c** with resting cells of *E. coli* (SSP1). The dihydroxylation was performed with resting cells (10 g cdw/L) in a two-liquid phase system (*n*-hexadecane: KP buffer = 1:1).

12. Figure S2-S23. Chiral HPLC Chromatograms

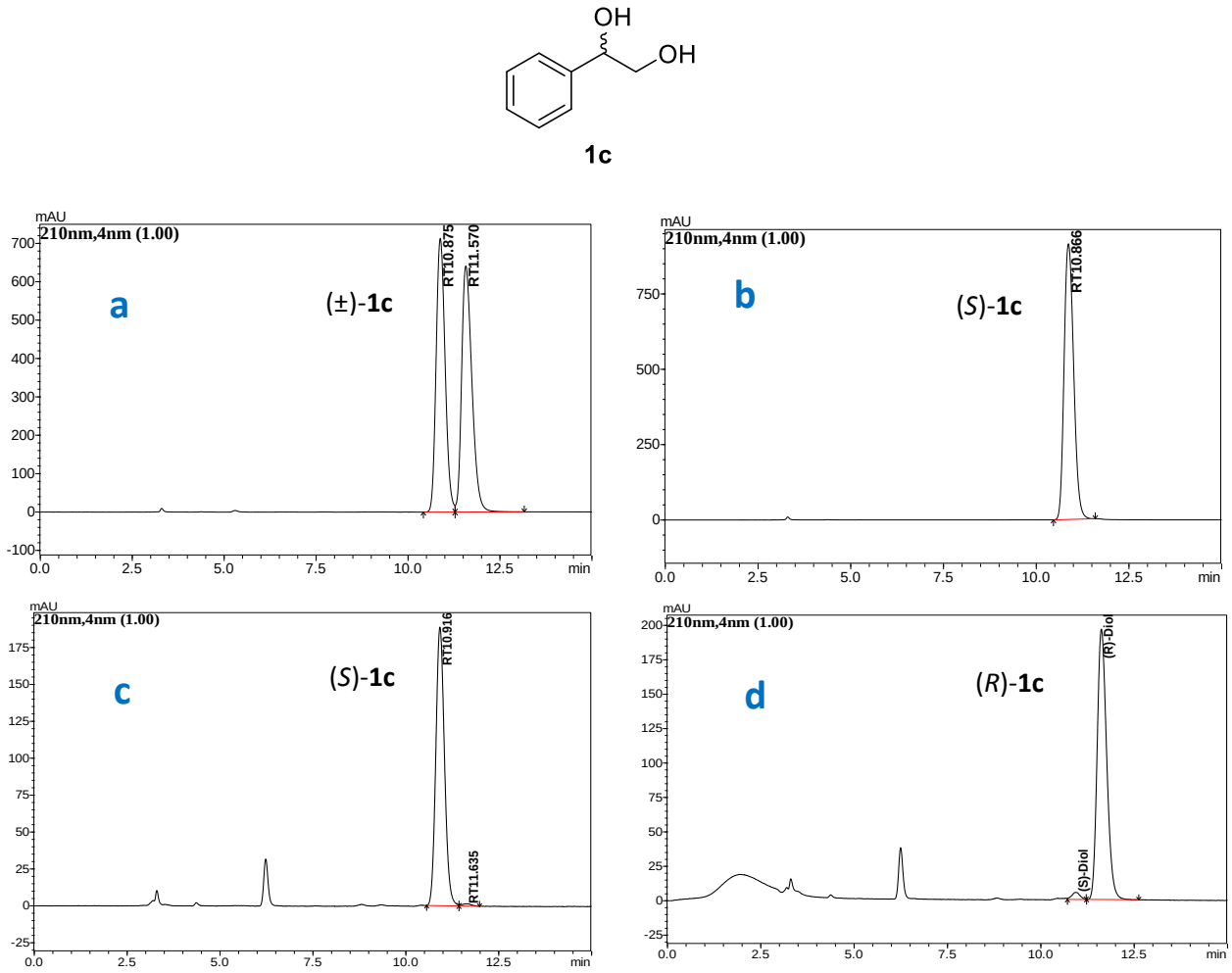

Figure S2. Chiral HPLC chromatograms of diol **1c**. a) racemic **1c**; b) (*S*)-**1c** standard; c) (*S*)-**1c** produced by *E. coli* (SSP1); d) (*R*)-**1c** produced by *E. coli* (SST1). (Daicel Chiralpak AS-H (250 × 4.6 mm, 5µm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm)

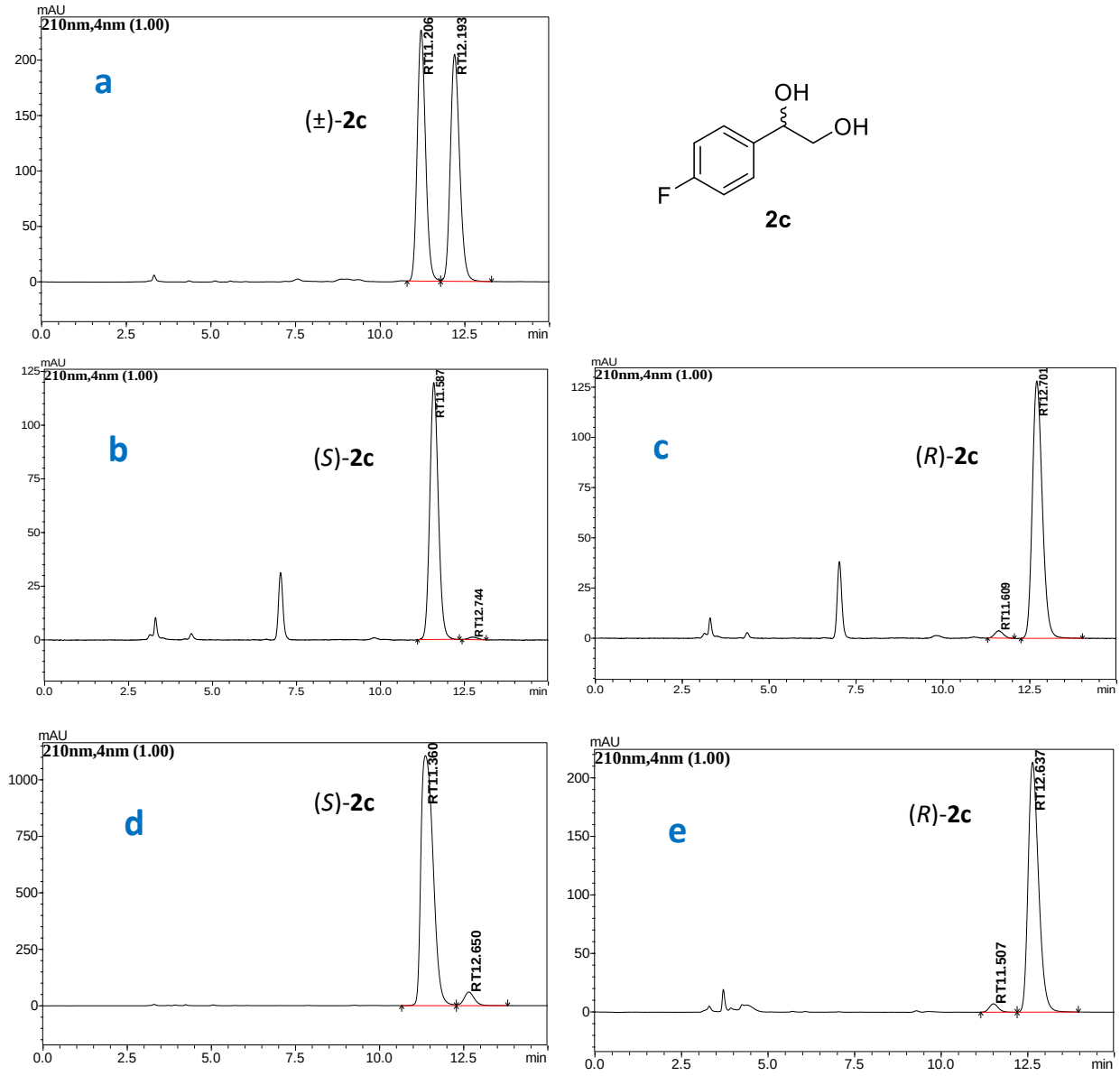

Figure S3. Chiral HPLC chromatograms of diol **2c**. a) racemic **2c**; b) (*S*)-**2c** produced by *E. coli* (SSP1); c) (*R*)-**2c** produced by *E. coli* (SST1); d) (*S*)-**2c** produced by AD-mix-α; e) (*R*)-**2c** produced by AD-mix-β. (Daicel Chiralpak AS-H (250 × 4.6 mm, 5µm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 ^{o}C, UV detection at 210 nm)

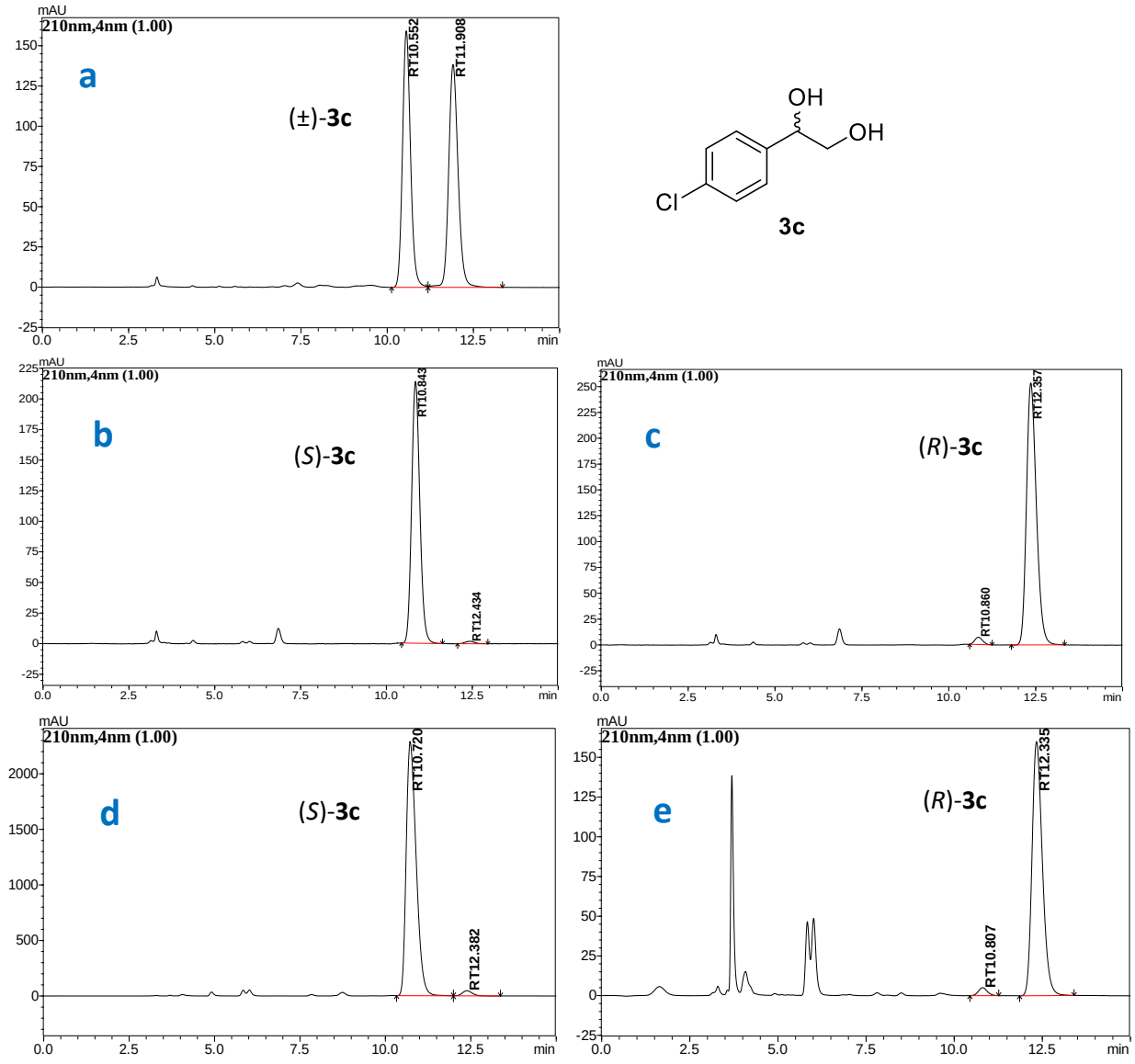

Figure S4. Chiral HPLC chromatograms of diol **3c**. a) racemic **3c**; b) (*S*)-**3c** produced by *E. coli* (SSP1); c) (*R*)-**3c** produced by *E. coli* (SST1); d) (*S*)-**3c** produced by AD-mix-α; e) (*R*)-**3c** produced by AD-mix-β. (Daicel Chiralpak AS-H (250 × 4.6 mm, 5μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm)

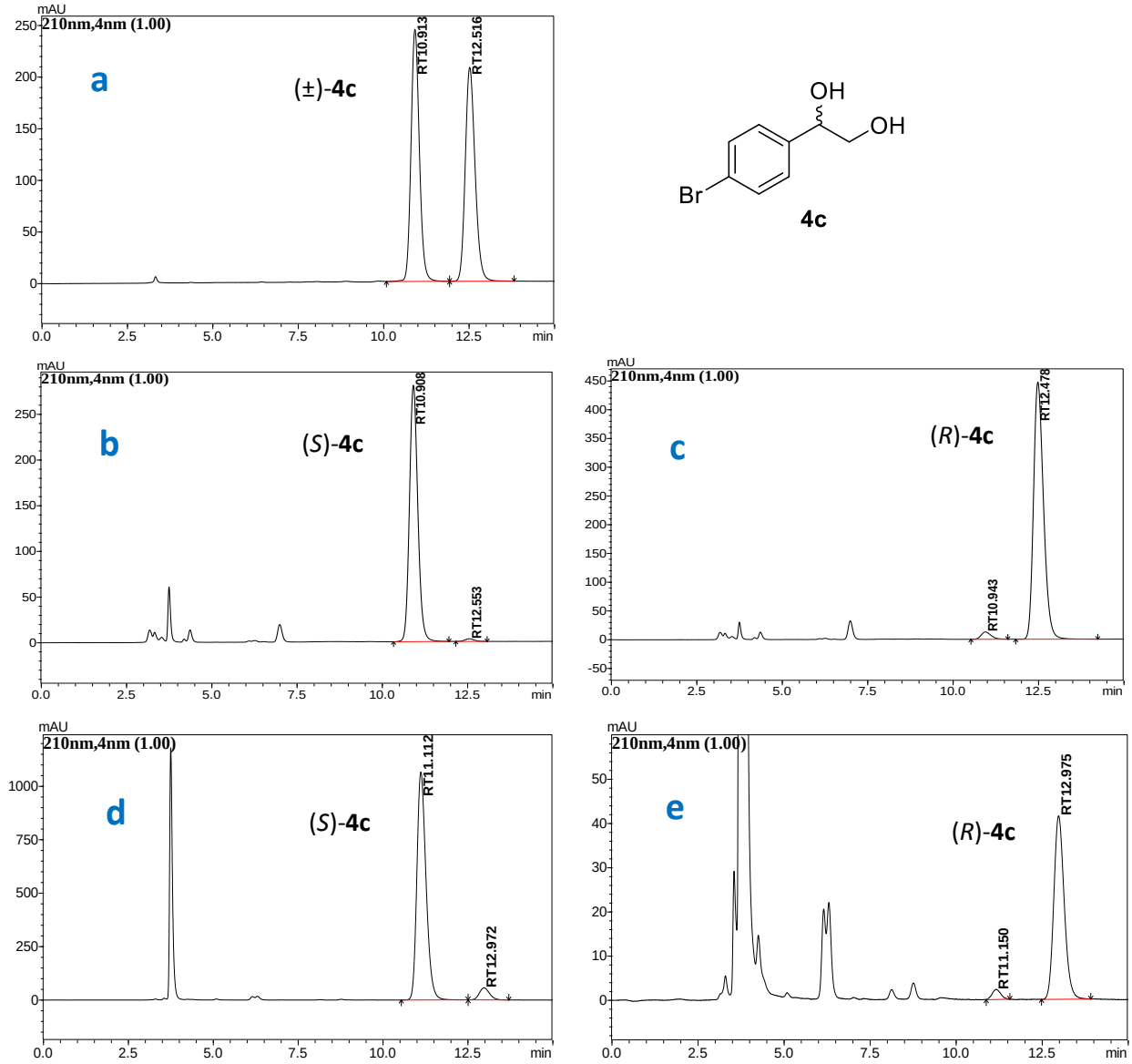

Figure S5. Chiral HPLC chromatograms of diol **4c**. a) racemic **4c**; b) (*S*)-**4c** produced by *E. coli* (SSP1); c) (*R*)-**4c** produced by *E. coli* (SST1); d) (*S*)-**4c** produced by AD-mix-α; e) (*R*)-**4c** produced by AD-mix-β. (Daicel Chiralpak AS-H (250 × 4.6 mm, 5μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 ºC, UV detection at 210 nm)

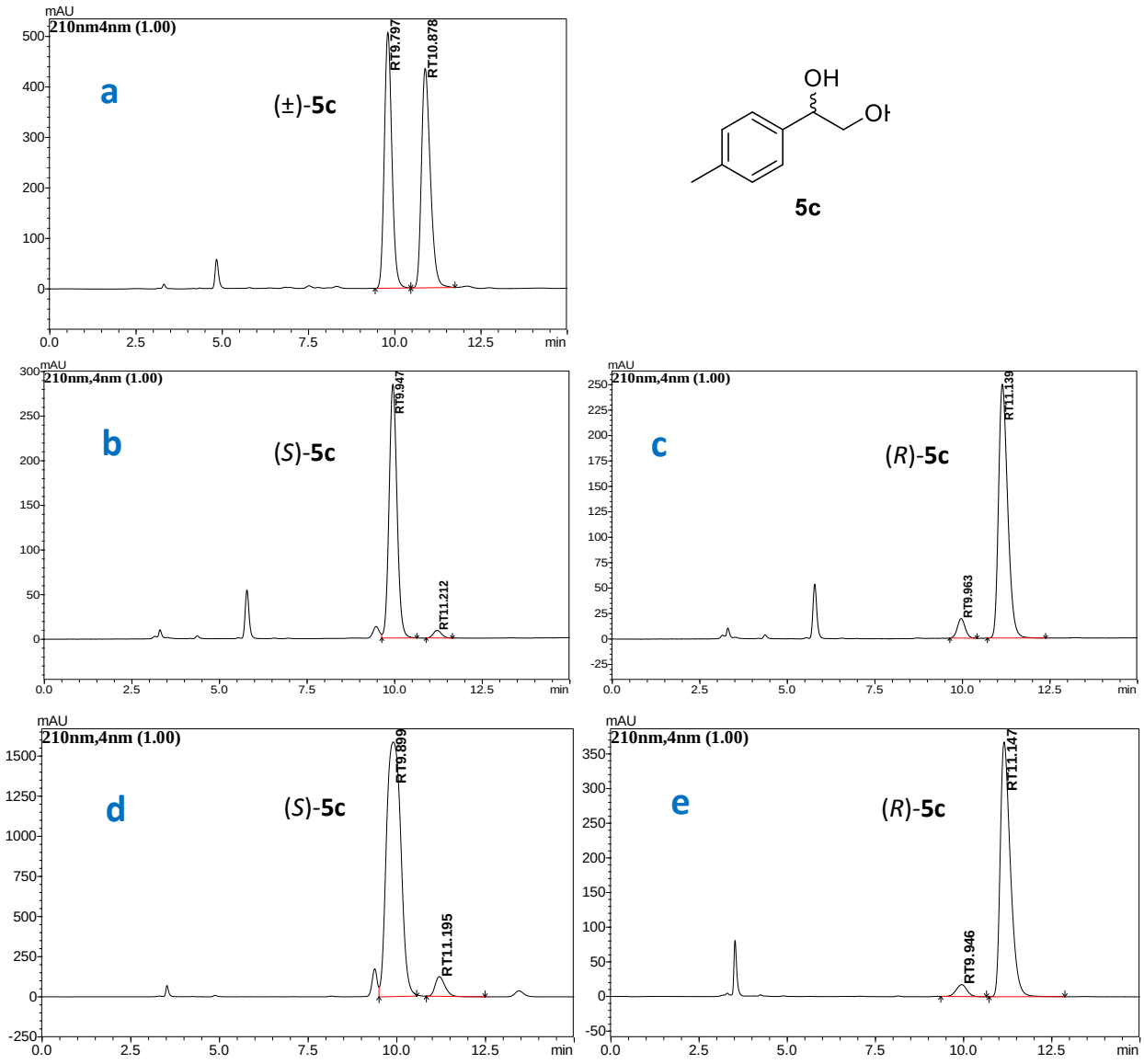

Figure S6. Chiral HPLC chromatograms of diol **5c**. a) racemic **5c**; b) (*S*)-**5c** produced by *E. coli* (SSP1); c) (*R*)-**5c** produced by *E. coli* (SST1); d) (*S*)-**5c** produced by AD-mix-α; e) (*R*)-**5c** produced by AD-mix-β. (Daicel Chiralpak AS-H (250 × 4.6 mm, 5µm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 ^{o}C, UV detection at 210 nm)

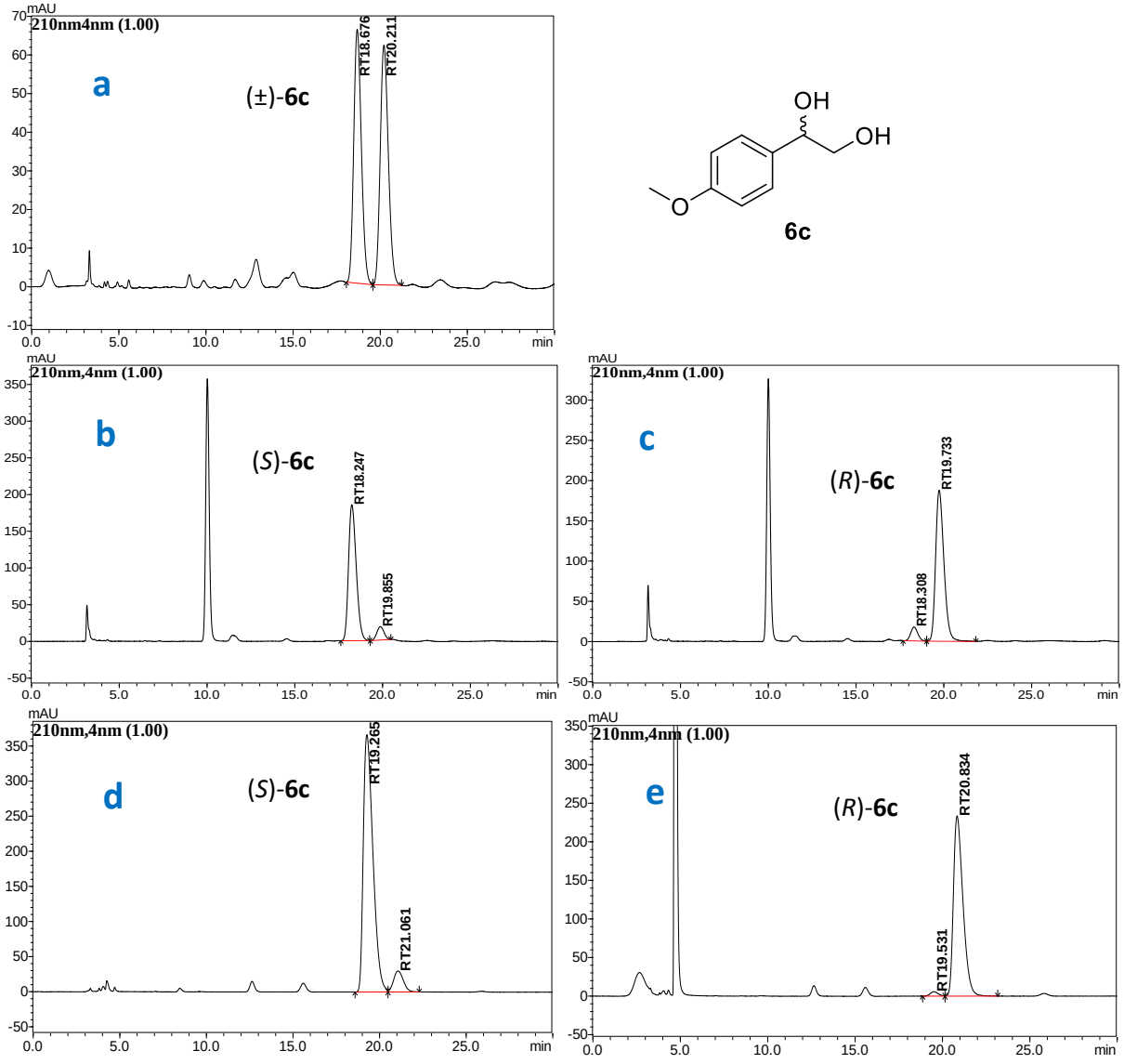

Figure S7. Chiral HPLC chromatograms of diol **6c**. a) racemic **6c**; b) (*S*)-**6c** produced by *E. coli* (SSP1); c) (*R*)-**6c** produced by *E. coli* (SST1); d) (*S*)-**6c** produced by AD-mix-α; e) (*R*)-**6c** produced by AD-mix-β. (Daicel Chiralpak AS-H (250 × 4.6 mm, 5μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 ºC, UV detection at 210 nm)

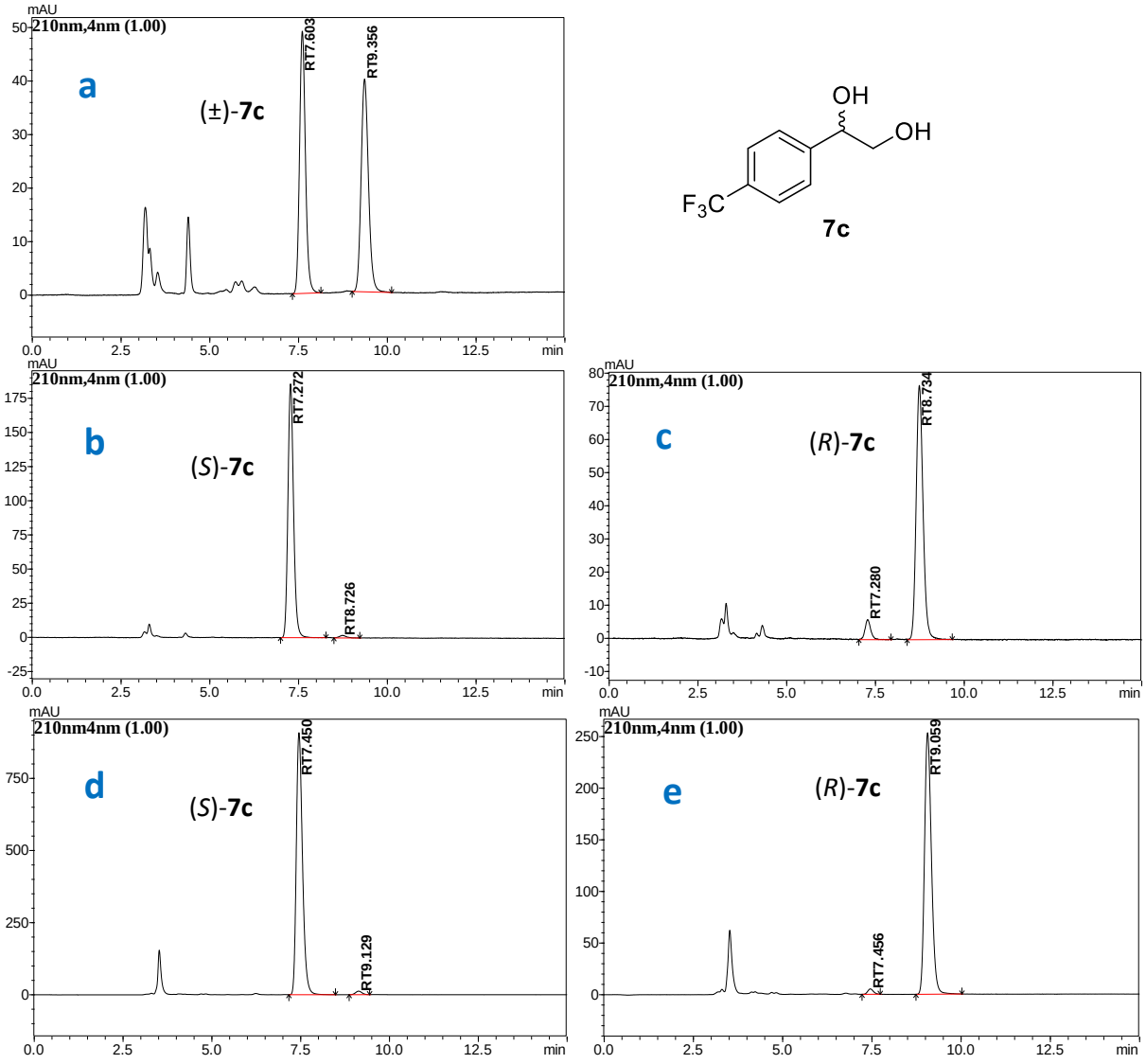

Figure S8. Chiral HPLC chromatograms of diol **7c**. a) racemic **7c**; b) (*S*)-**7c** produced by *E. coli* (SSP1); c) (*R*)-**7c** produced by *E. coli* (SST1); d) (*S*)-**7c** produced by AD-mix-α; e) (*R*)-**7c** produced by AD-mix-β. (Daicel Chiralpak AS-H (250 × 4.6 mm, 5μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm)

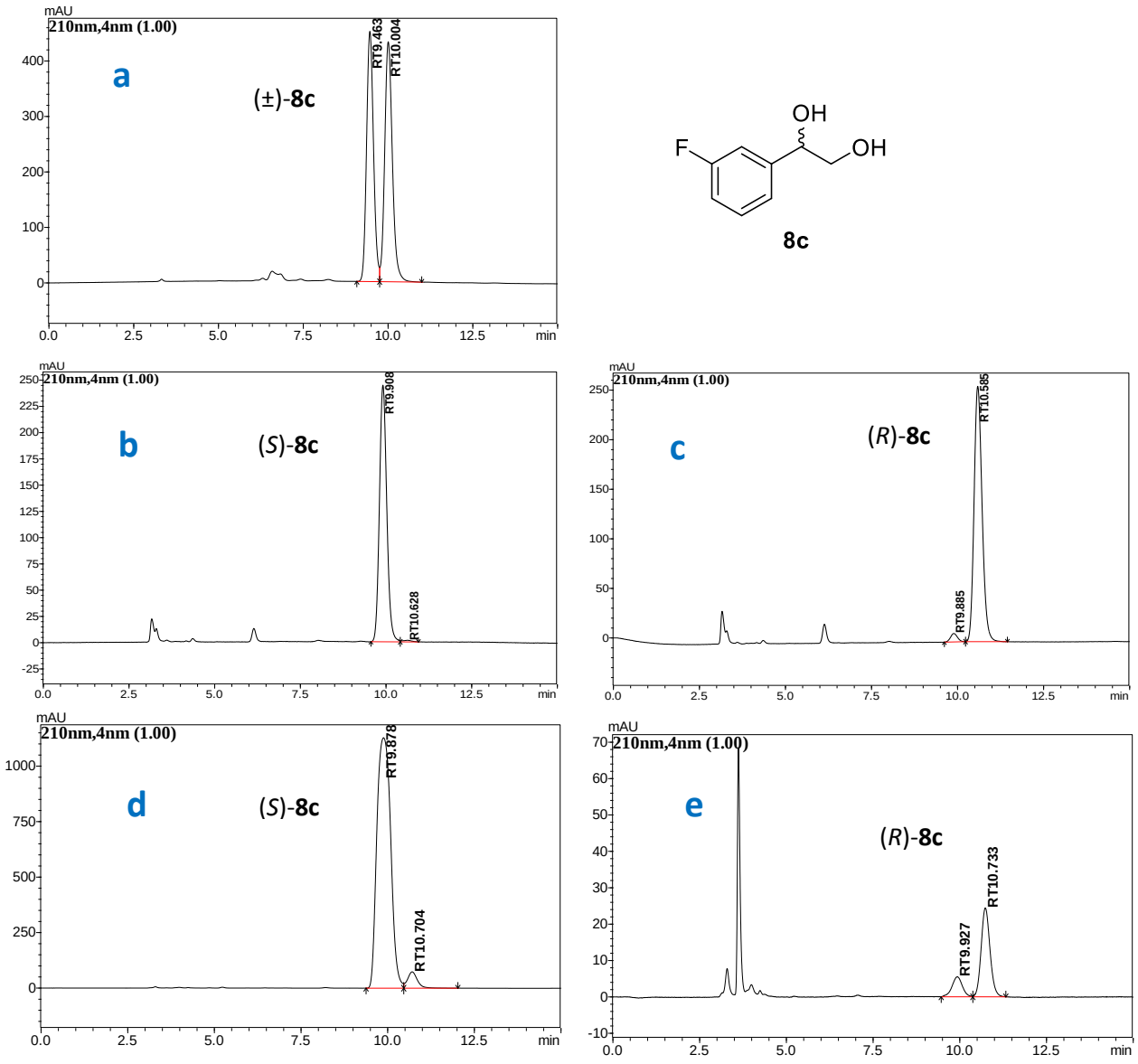

Figure S9. Chiral HPLC chromatograms of diol **8c**. a) racemic **8c**; b) (*S*)-**8c** produced by *E. coli* (SSP1); c) (*R*)-**8c** produced by *E. coli* (SST1); d) (*S*)-**8c** produced by AD-mix-α; e) (*R*)-**8c** produced by AD-mix-β. (Daicel Chiralpak AS-H (250 × 4.6 mm, 5μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm)

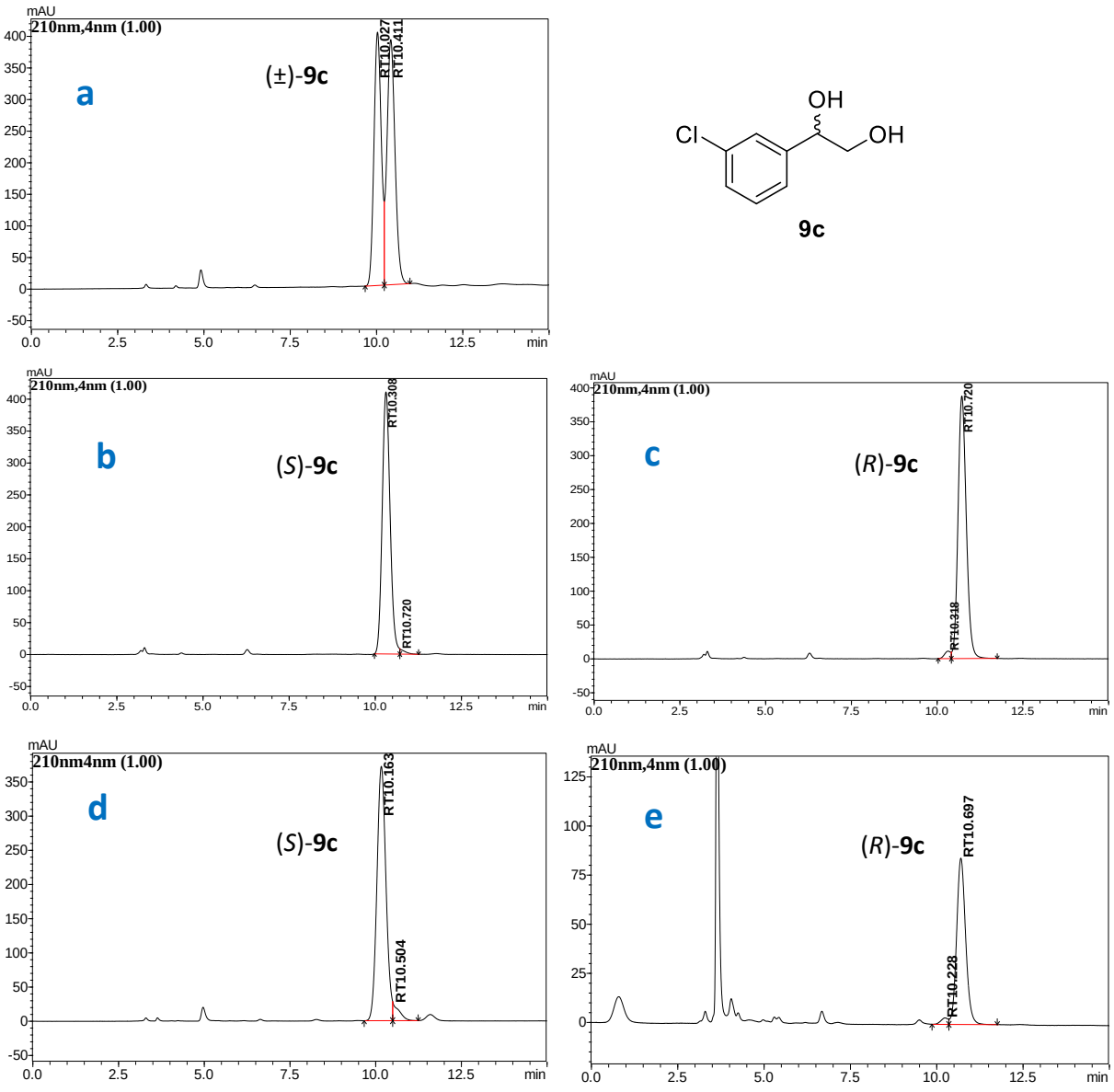

Figure S10. Chiral HPLC chromatograms of diol **9c**. a) racemic **9c**; b) (*S*)-**9c** produced by *E. coli* (SSP1); c) (*R*)-**9c** produced by *E. coli* (SST1); d) (*S*)-**9c** produced by AD-mix-α; e) (*R*)-**9c** produced by AD-mix-β. (Daicel Chiralpak AS-H (250 × 4.6 mm, 5μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 ^{o}C, UV detection at 210 nm)

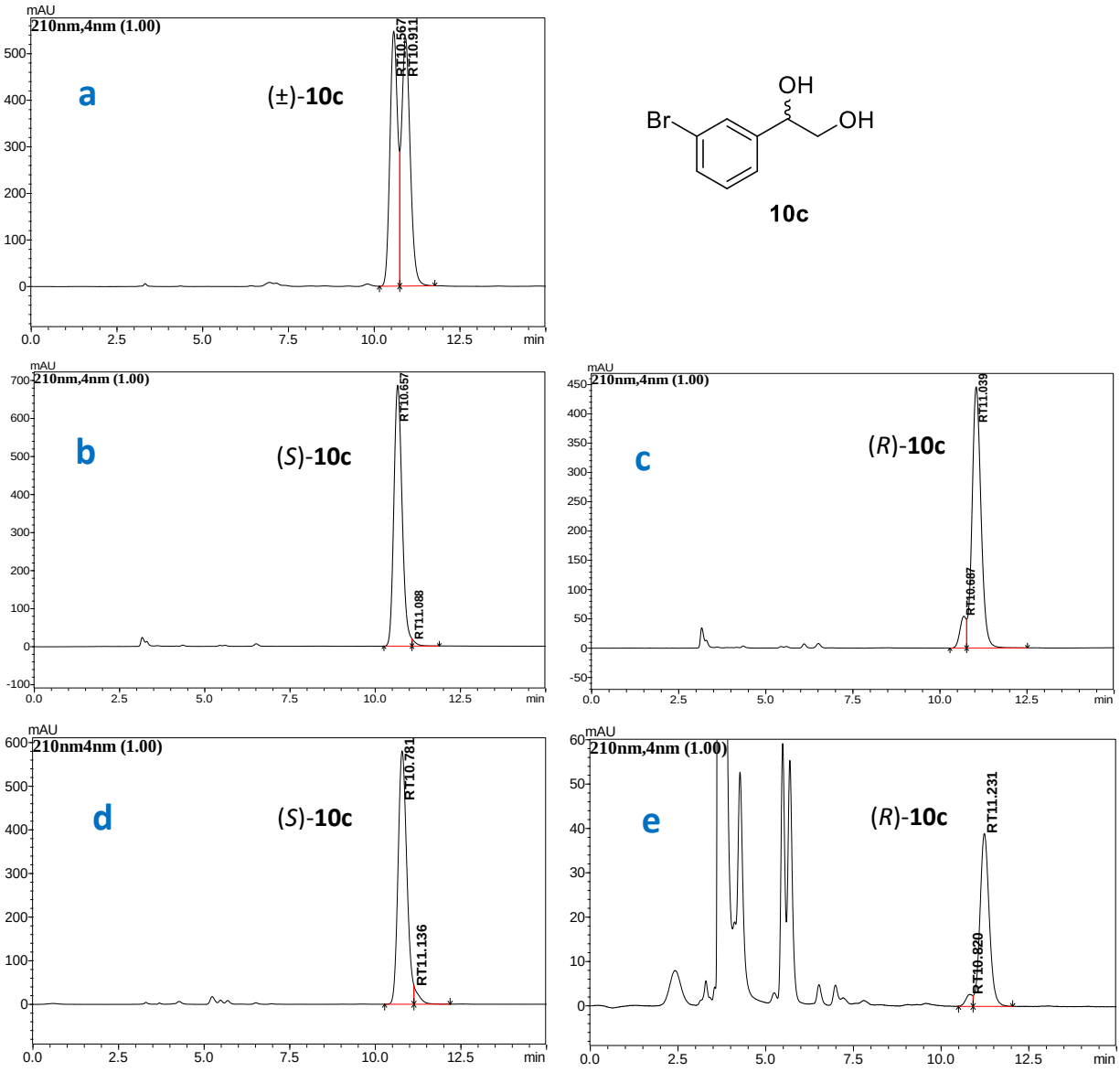

Figure S11. Chiral HPLC chromatograms of diol **10c**. a) racemic **10c**; b) (*S*)-**10c** produced by *E. coli* (SSP1); c) (*R*)-**10c** produced by *E. coli* (SST1); d) (*S*)-**10c** produced by AD-mix-α; e) (*R*)-**10c** produced by AD-mix-β. (Daicel Chiralpak AS-H (250 × 4.6 mm, 5μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm)

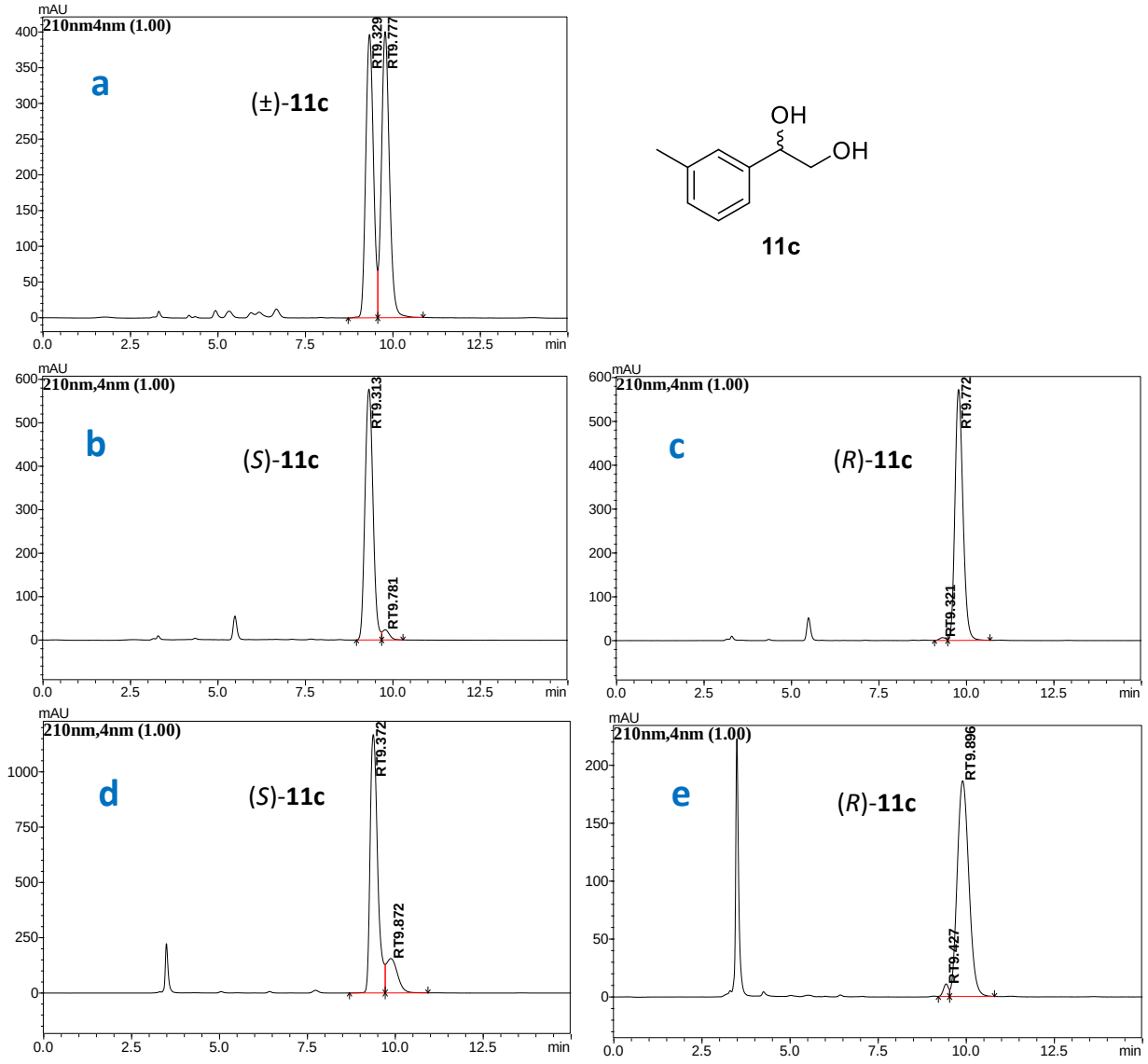

Figure S12. Chiral HPLC chromatograms of diol **11c**. a) racemic **11c**; b) (*S*)-**11c** produced by *E. coli* (SSP1); c) (*R*)-**11c** produced by *E. coli* (SST1); d) (*S*)-**11c** produced by AD-mix-α; e) (*R*)-**11c** produced by AD-mix-β. (Daicel Chiralpak AS-H (250 × 4.6 mm, 5μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm)

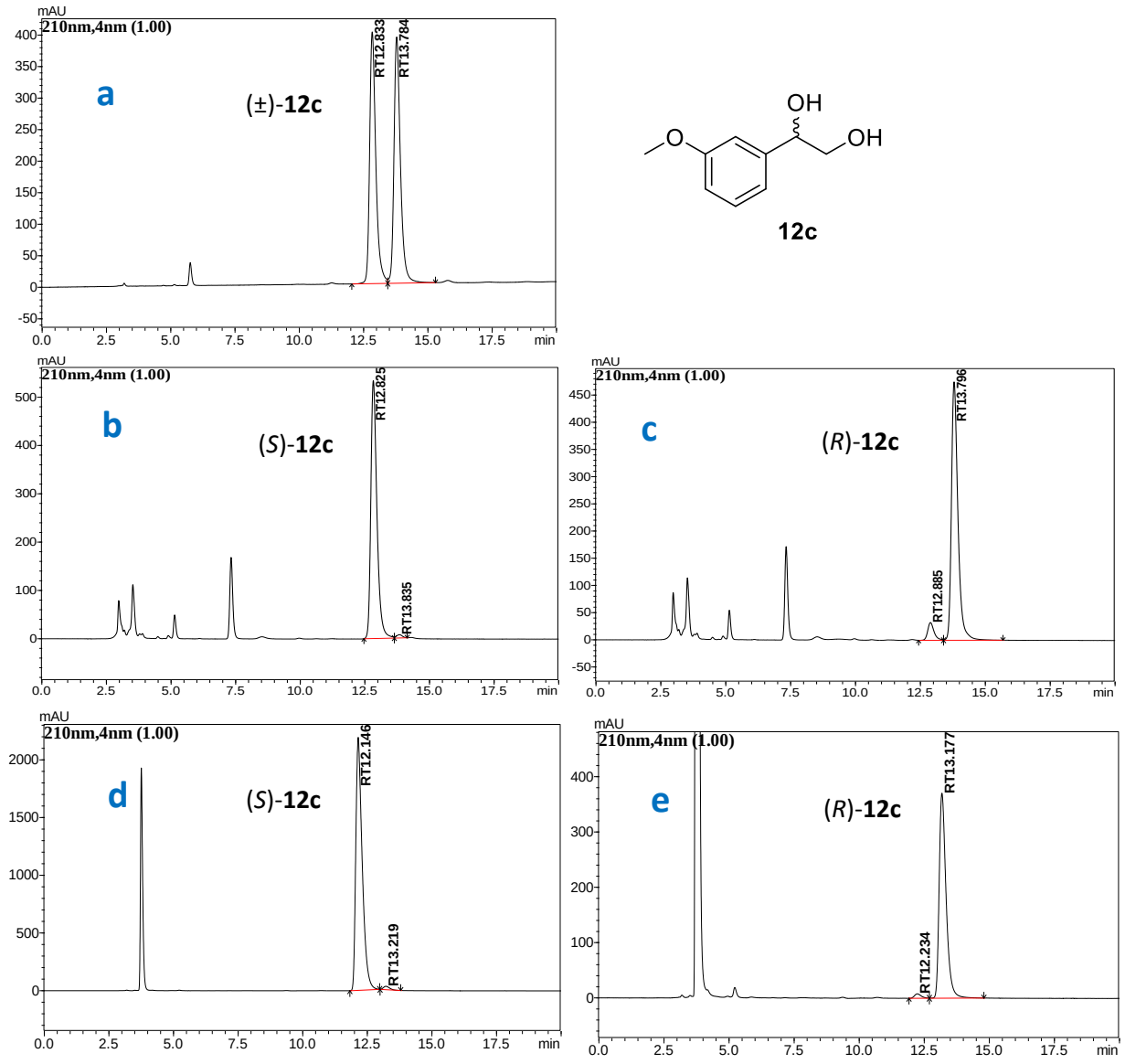

Figure S13. Chiral HPLC chromatograms of diol **12c**. a) racemic **12c**; b) (*S*)-**12c** produced by *E. coli* (SSP1); c) (*R*)-**12c** produced by *E. coli* (SST1); d) (*S*)-**12c** produced by AD-mix-α; e) (*R*)-**12c** produced by AD-mix-β. (Daicel Chiralpak IA-3 (250 × 4.6 mm, 3μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm)

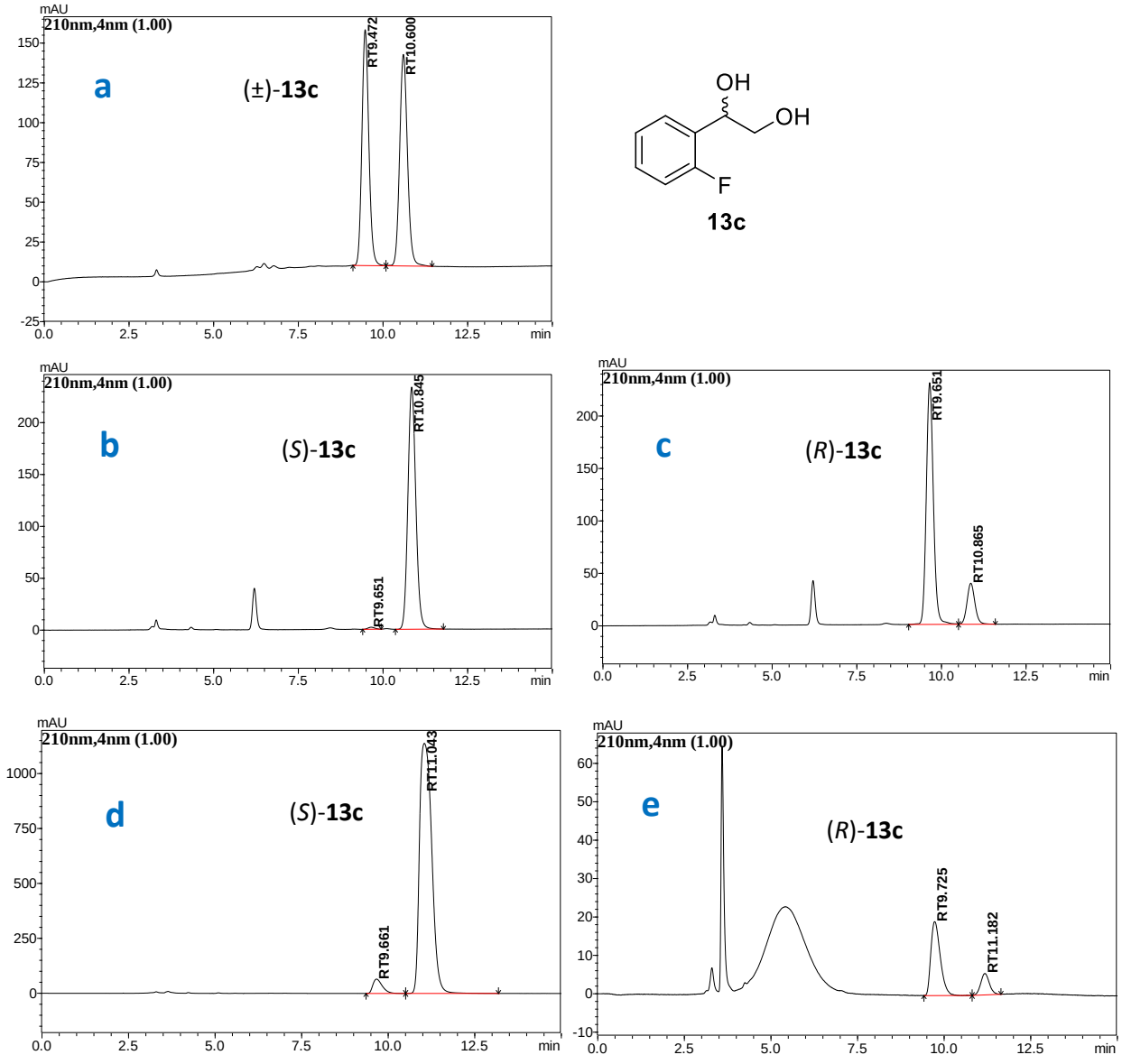

Figure S14. Chiral HPLC chromatograms of diol **13c**. a) racemic **13c**; b) (*S*)-**13c** produced by *E. coli* (SSP1); c) (*R*)-**13c** produced by *E. coli* (SST1); d) (*S*)-**13c** produced by AD-mix-α; e) (*R*)-**13c** produced by AD-mix-β. (Daicel Chiralpak AS-H (250 × 4.6 mm, 5µm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 ºC, UV detection at 210 nm)

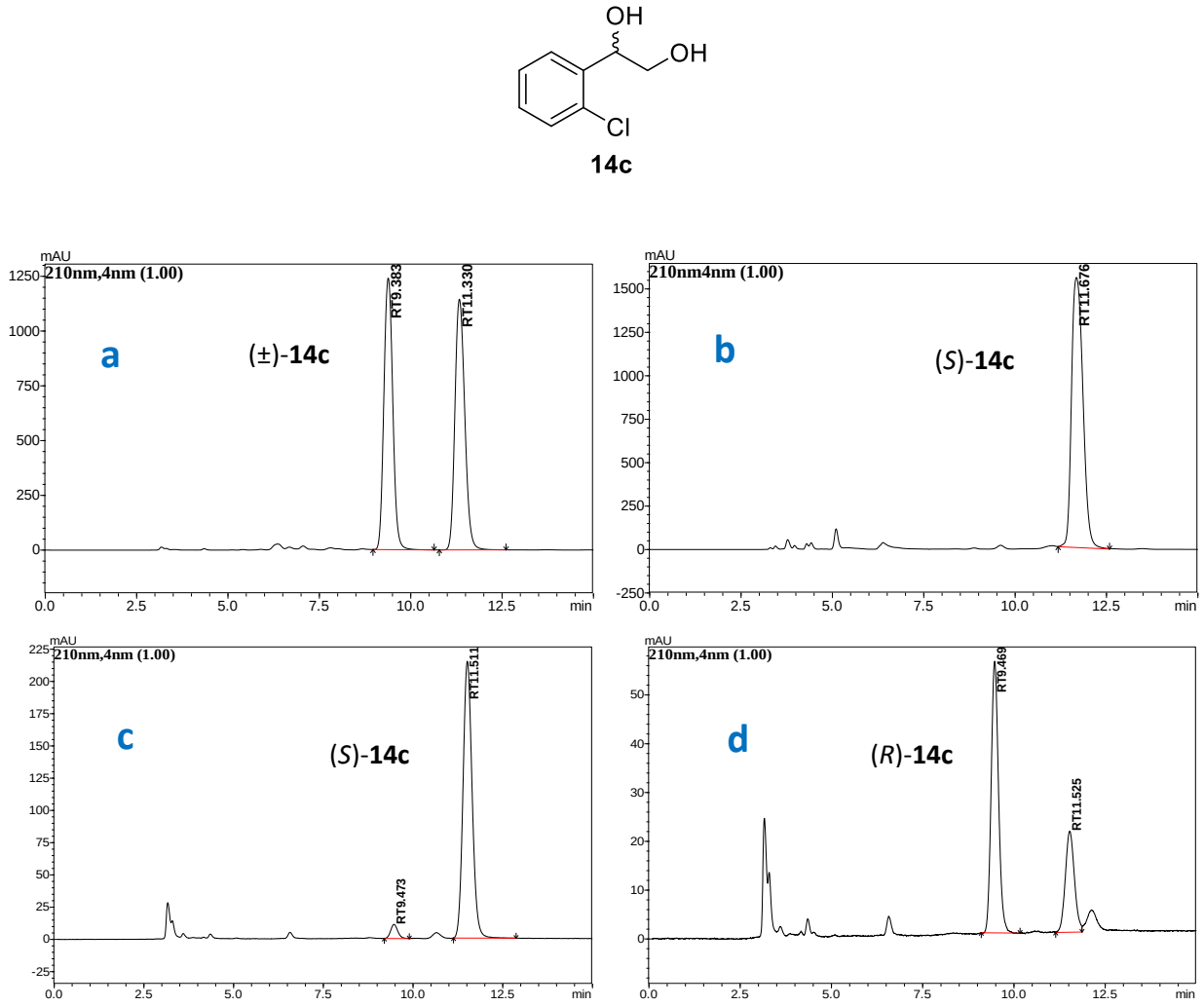

Figure S15. Chiral HPLC chromatograms of diol **14c**. a) racemic **14c**; b) (*S*)-**14c** standard; c) (*S*)-**14c** produced by *E. coli* (SSP1); d) (*R*)-**14c** produced by *E. coli* (SST1). (Daicel Chiralpak AS-H (250 × 4.6 mm, 5µm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 ^{o}C, UV detection at 210 nm)

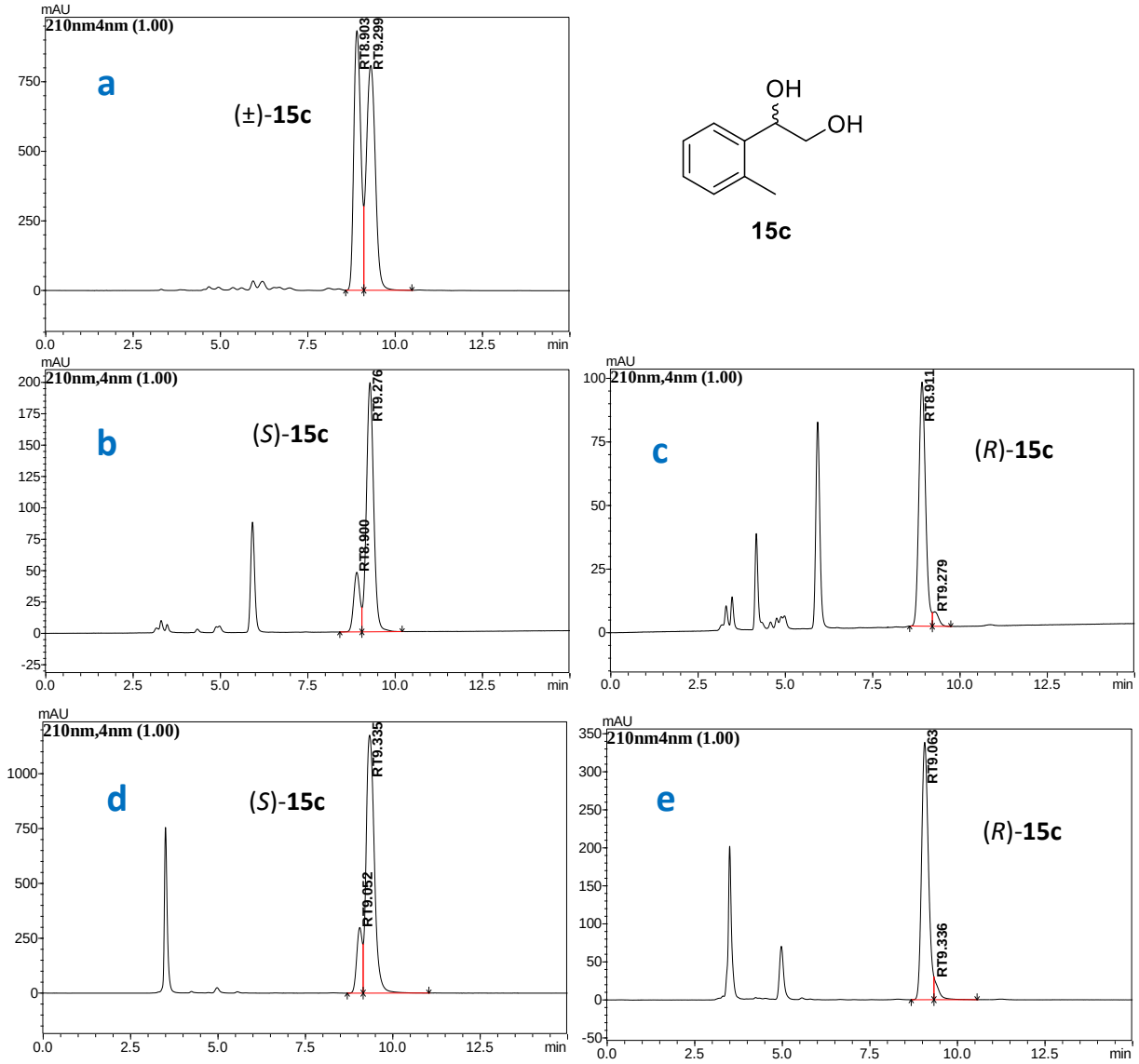

Figure S16. Chiral HPLC chromatograms of diol **15c**. a) racemic **15c**; b) (*S*)-**15c** produced by *E. coli* (SSP1); c) (*R*)-**15c** produced by *E. coli* (SST1); d) (*S*)-**15c** produced by AD-mix-α; e) (*R*)-**15c** produced by AD-mix-β. (Daicel Chiralpak AS-H (250 × 4.6 mm, 5μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm)

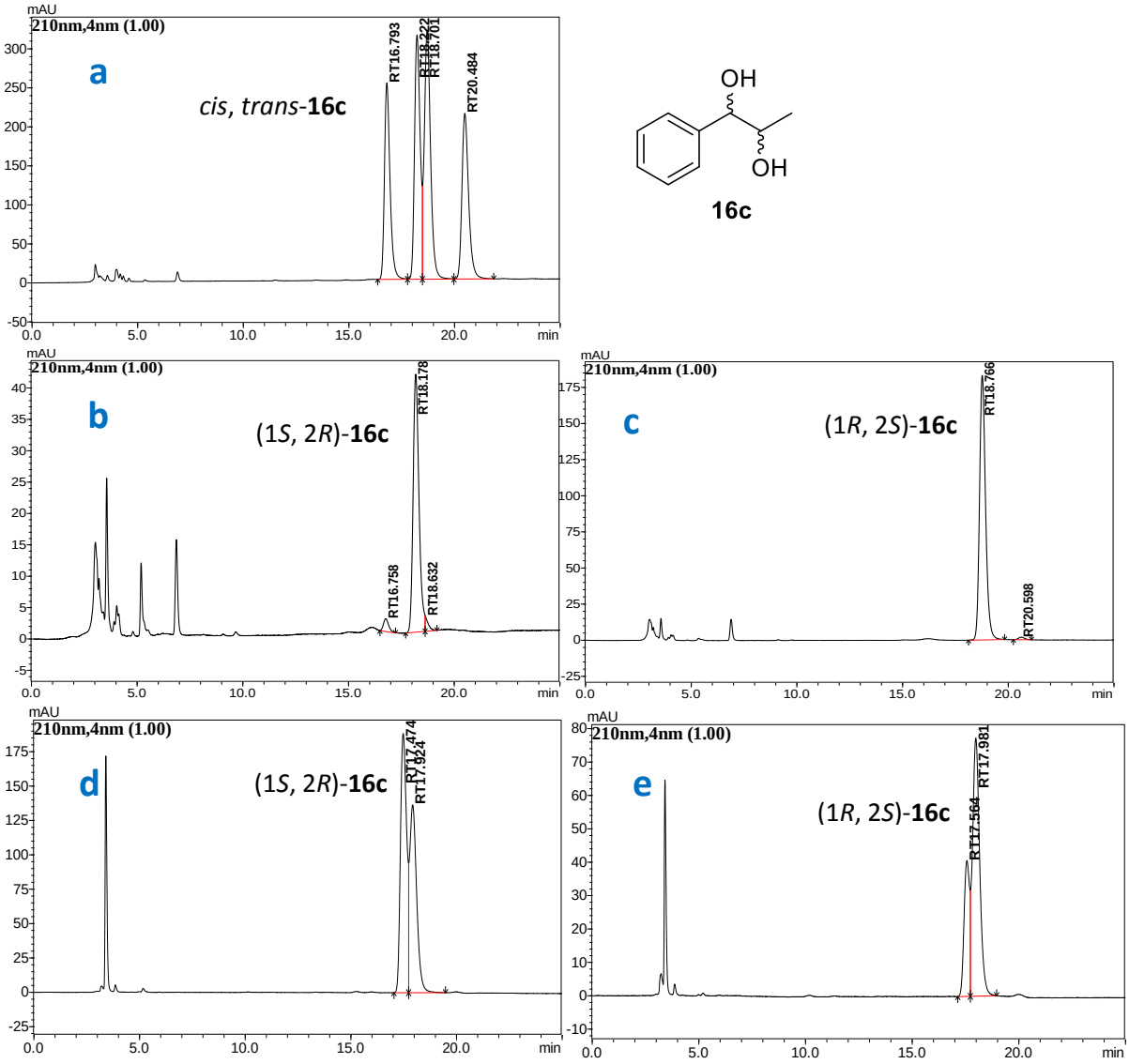

Figure S17. Chiral HPLC chromatograms of diol **16c**. a) racemic **16c** (mixture of *trans* and *cis*); b) (1*S*, 2*R*)-**16c** produced by *E. coli* (SSP1) from **16a**; c) (1*R*, 2*S*)-**16c** produced by *E. coli* (SST1) from **16a**; d) (1*S*, 2*R*)-**16c** produced by AD-mix-α from **17a** (low *ee*); e) (1*R*, 2*S*)-**16c** produced by AD-mix-β from **17a** (low *ee*). (Daicel Chiralpak IA-3 (250 × 4.6 mm, 3µm) column, mobile phase 5% IPA: 95% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm)

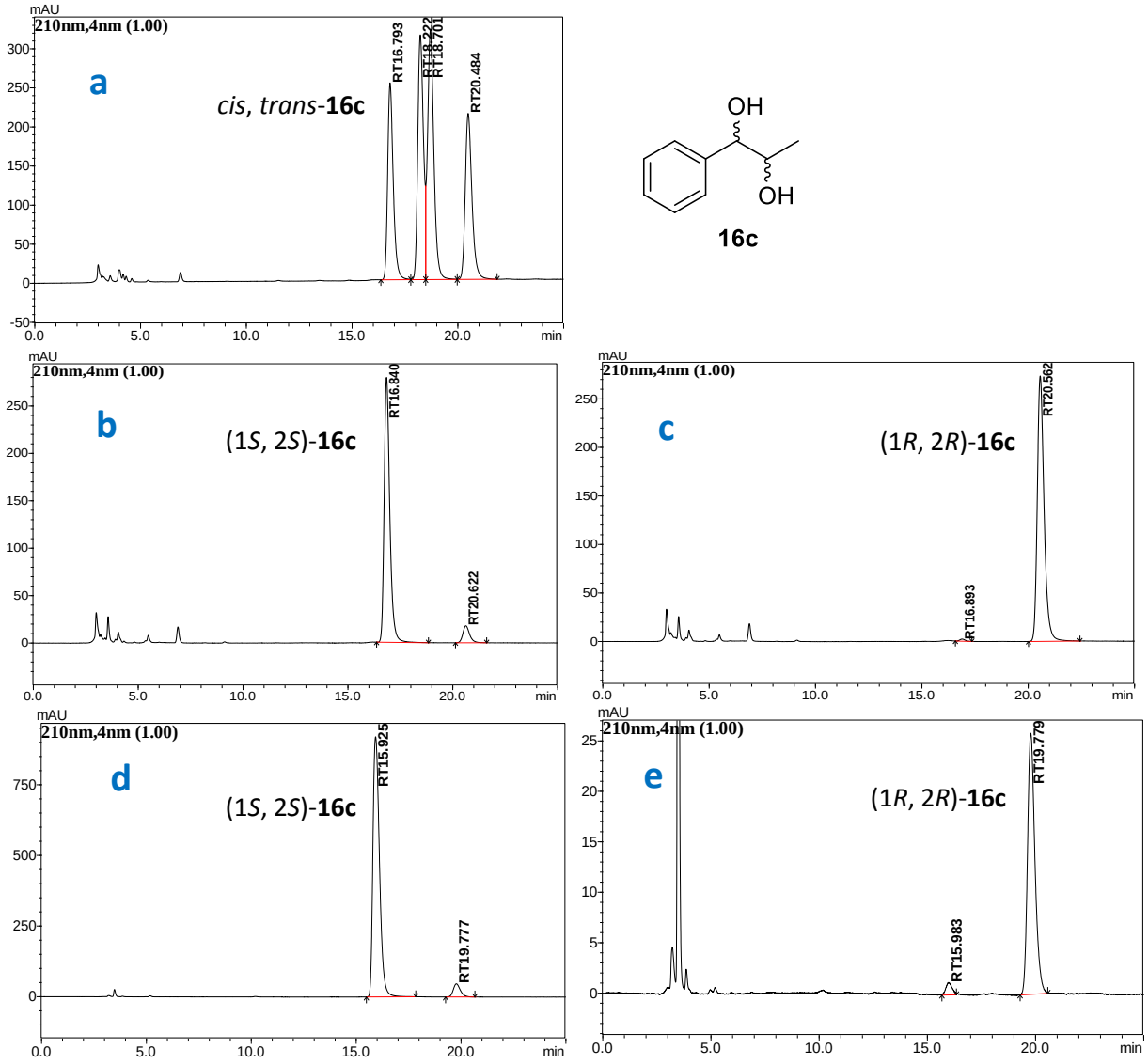

Figure S18. Chiral HPLC chromatograms of diol **16c** (continue). a) racemic **16c** (mixture of *trans* and *cis*); b) (1*S*, 2*S*)-**16c** produced by *E. coli* (SSP1) from **17a**; c) (1*R*, 2*R*)-**16c** produced by *E. coli* (SST1) from **17a**; d) (1*S*, 2*S*)-**16c** produced by AD-mix-α from **16a**; e) (1*R*, 2*R*)-**16c** produced by AD-mix-β from **16a**. (Daicel Chiralpak IA-3 (250 × 4.6 mm, 3µm) column, mobile phase 5% IPA: 95% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 ºC, UV detection at 210 nm)

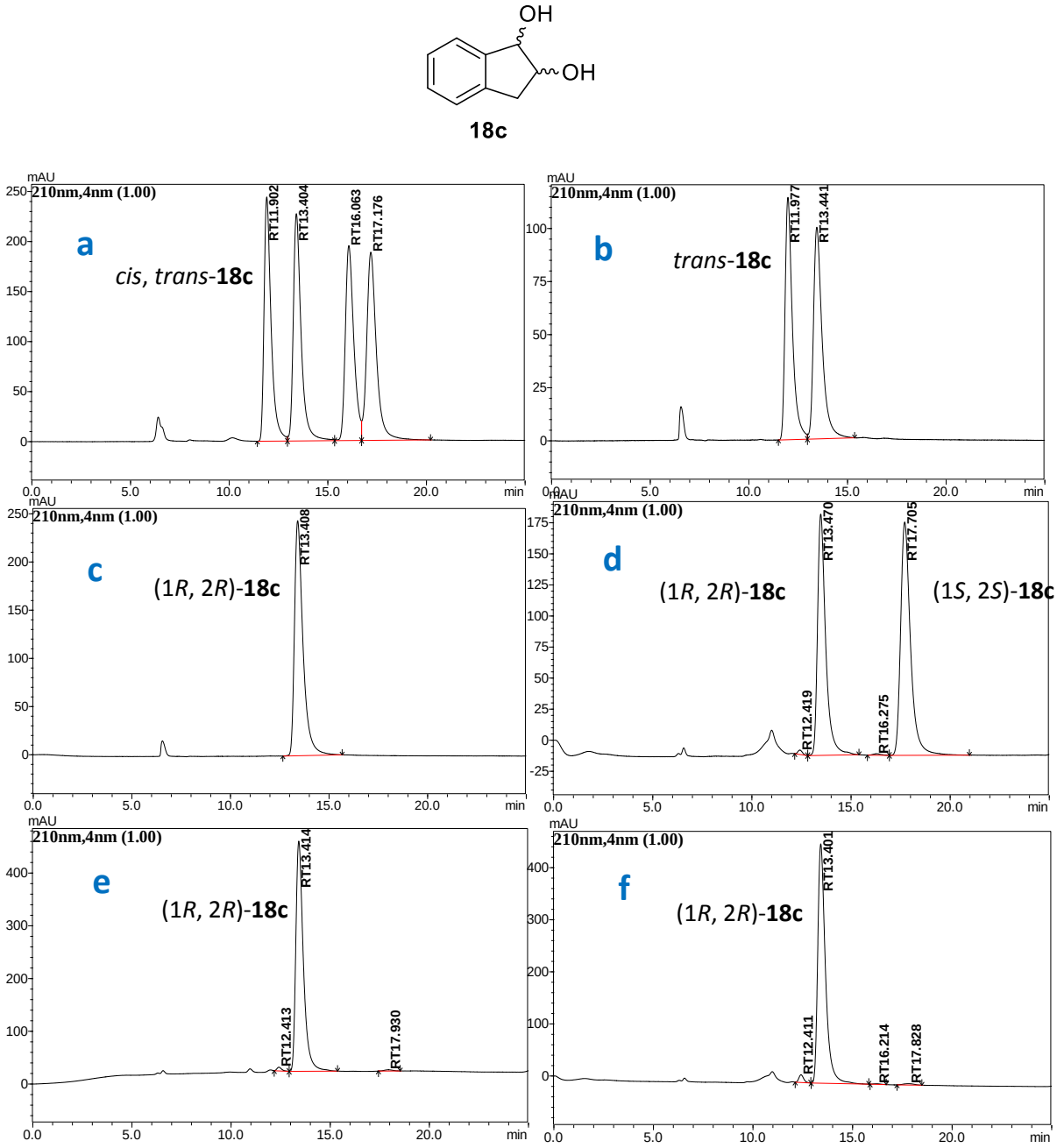

Figure S19. Chiral HPLC chromatograms of diol **18c**. a) racemic **18c** (mixture of *cis* and *trans*); b) *trans*-**18c** strandard; c) (1*R*, 2*R*)-**18c** strandard; d) **18c** (mixture of *cis* and *trans*) produced by styrene monooxygenase and undergo autohydrolysis; e) (1*R*, 2*R*)-**18c** produced by *E. coli* (SSP1); f) (1*R*, 2*R*)-**18c** produced by *E. coli* (SST1). (Daicel Chiralpak OB-H (250 × 4.6 mm, 5μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 0.5 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm)

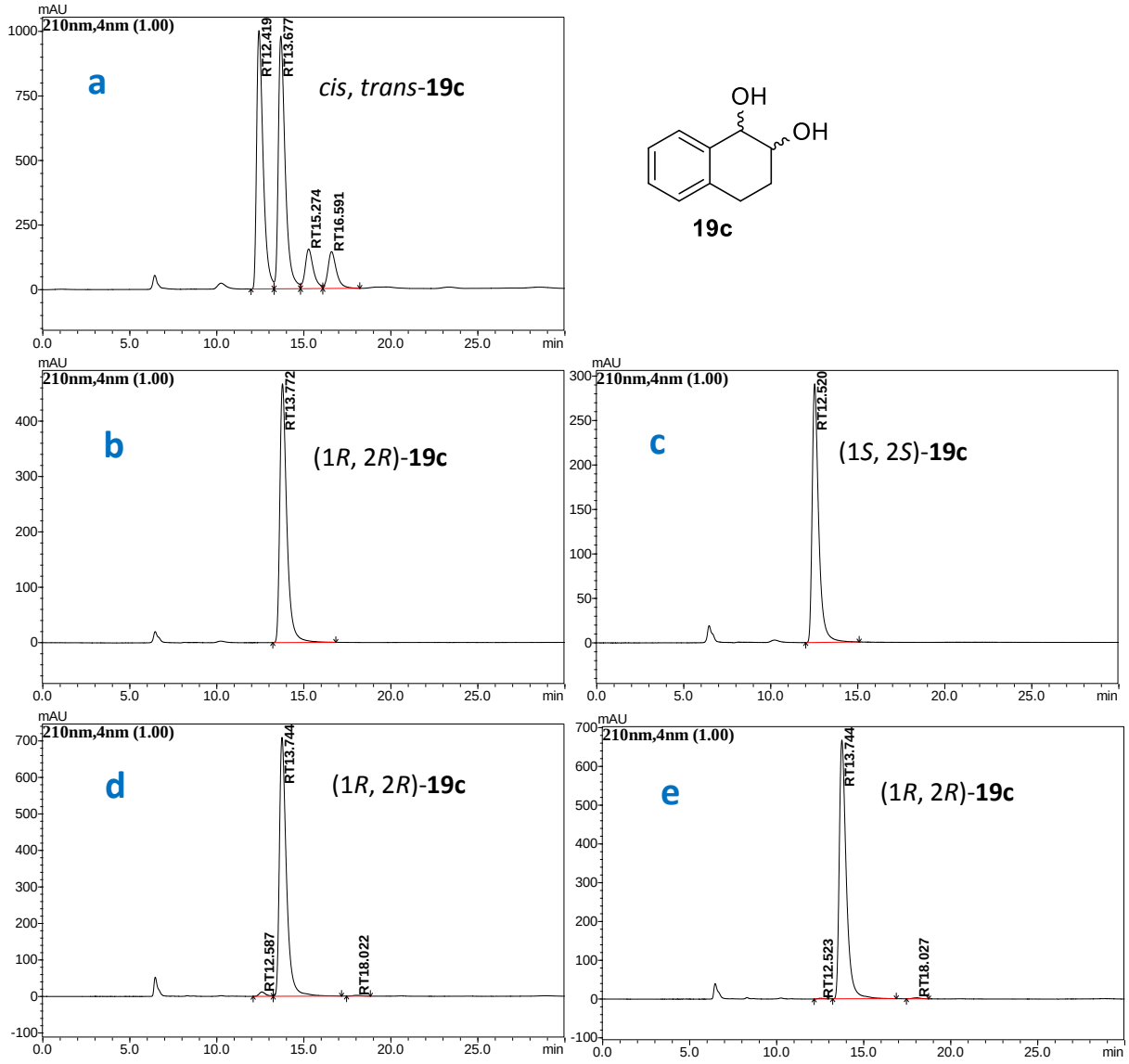

Figure S20. Chiral HPLC chromatograms of diol **19c**. a) racemic **19c** (mainly *trans*, some *cis*); b) (1*R*, 2*R*)-**19c** strandard; c) (1*S*, 2*S*)-**19c** strandard; d) (1*R*, 2*R*)-**19c** produced by *E. coli* (SSP1); e) (1*R*, 2*R*)-**19c** produced by *E. coli* (SST1). (Daicel Chiralpak OB-H (250 × 4.6 mm, 5μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 0.5 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm)

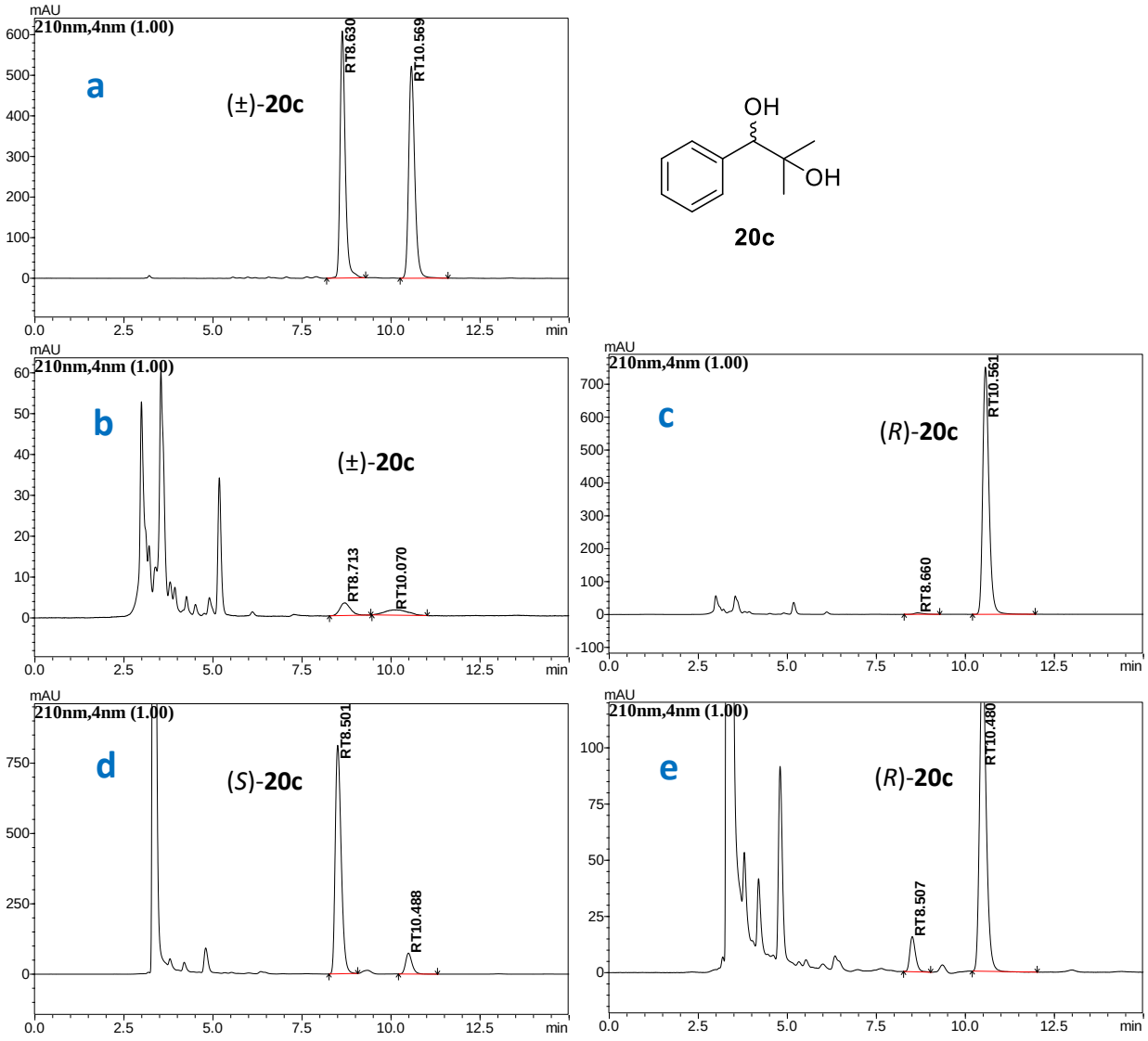

Figure S21. Chiral HPLC chromatograms of diol **20c**. a) racemic **20c**; b) (*S*)-**20c** produced by *E. coli* (SSP1) (low *ee*); c) (*R*)-**20c** produced by *E. coli* (SST1); d) (*S*)-**20c** produced by AD-mix-α; e) (*R*)-**20c** produced by AD-mix-β. (Daicel Chiralpak IA-3 (250 × 4.6 mm, 3μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm)

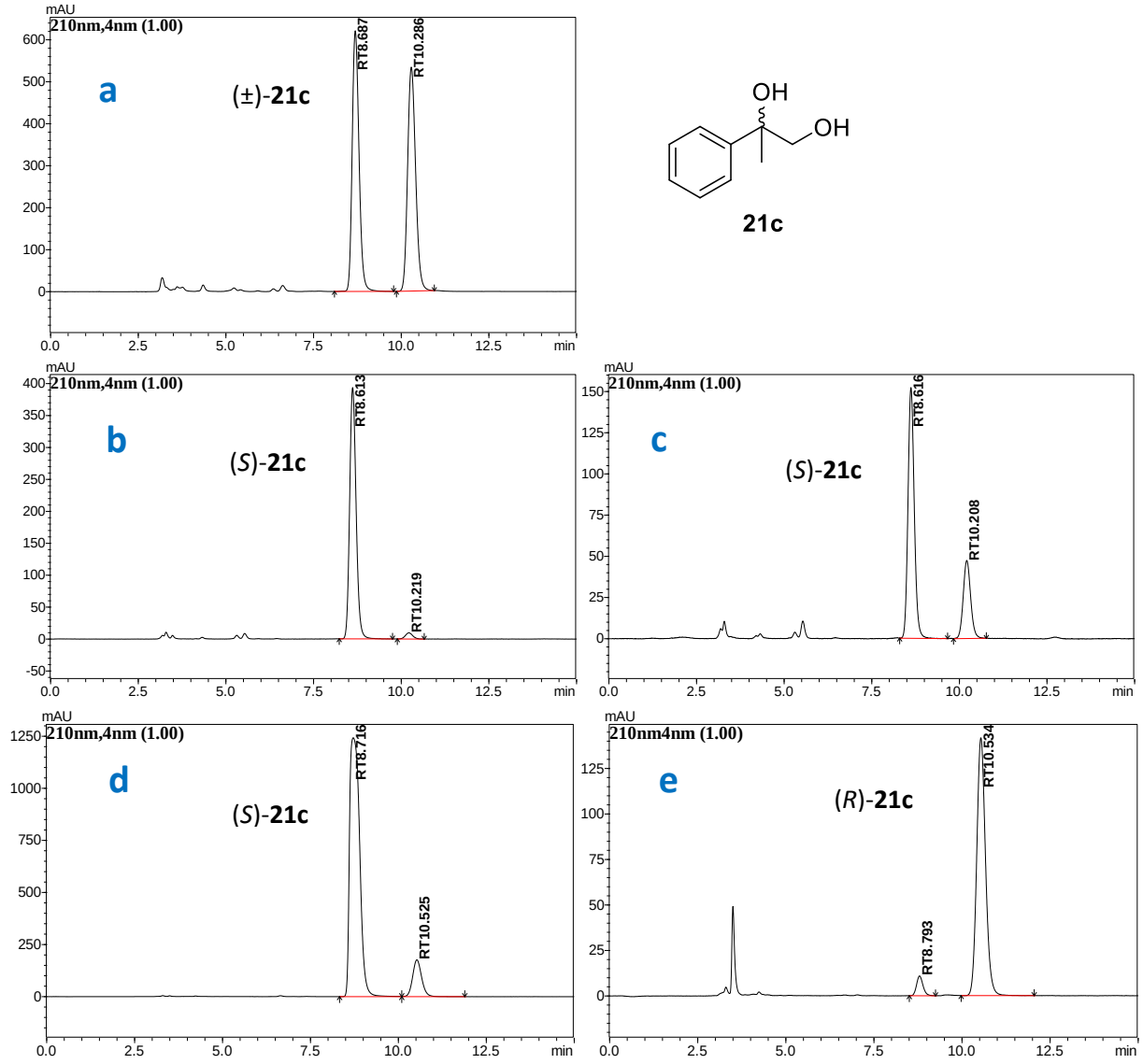

Figure S22. Chiral HPLC chromatograms of diol **21c**. a) racemic **21c**; b) (*S*)-**21c** produced by *E. coli* (SSP1); c) (*S*)-**21c** produced by *E. coli* (SST1); d) (*S*)-**21c** produced by AD-mix-α; e) (*R*)-**21c** produced by AD-mix-β. (Daicel Chiralpak AS-H (250 × 4.6 mm, 5μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm)

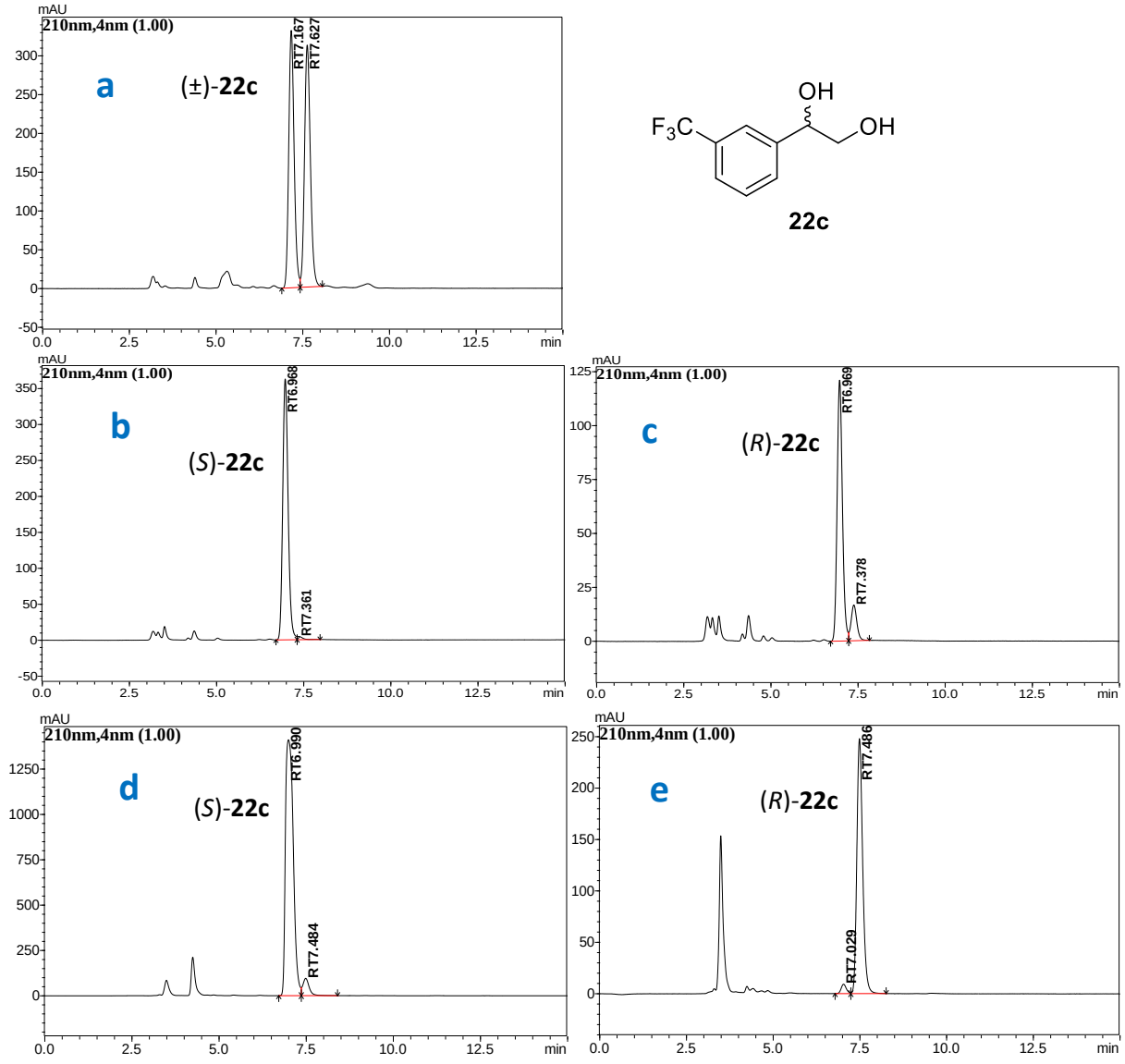

Figure S23. Chiral HPLC chromatograms of diol **22c**. a) racemic **22c**; b) (*S*)-**22c** produced by *E. coli* (SSP1); c) (*S*)-**22c** produced by *E. coli* (SST1); d) (*S*)-**22c** produced by AD-mix-α; e) (*R*)-**22c** produced by AD-mix-β. (Daicel Chiralpak AS-H (250 × 4.6 mm, 5µm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm)

13. Figure S24-S33. ^{1}H NMR Spectra and Chiral HPLC Chromatograms of Prepared Diols

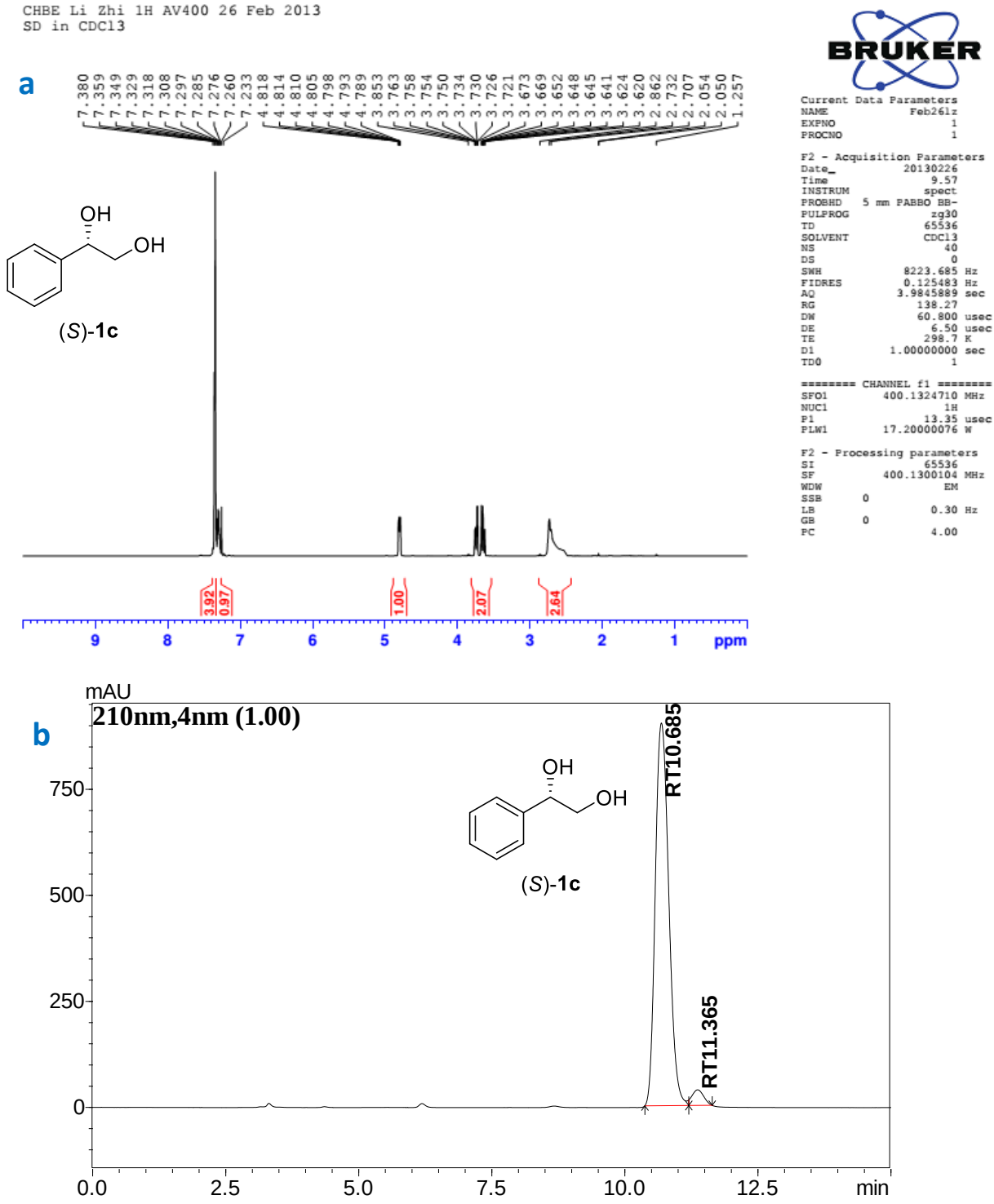

Figure S24. ^{1}H NMR spectrum and Chiral HPLC chromatogram of prepared product (*S*)-**1c**. a) ^{1}H NMR (400 MHz, $CDCl_3$, TMS); b) Chiral HPLC (Daicel Chiralpak AS-H (250 × 4.6 mm, 5μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm).

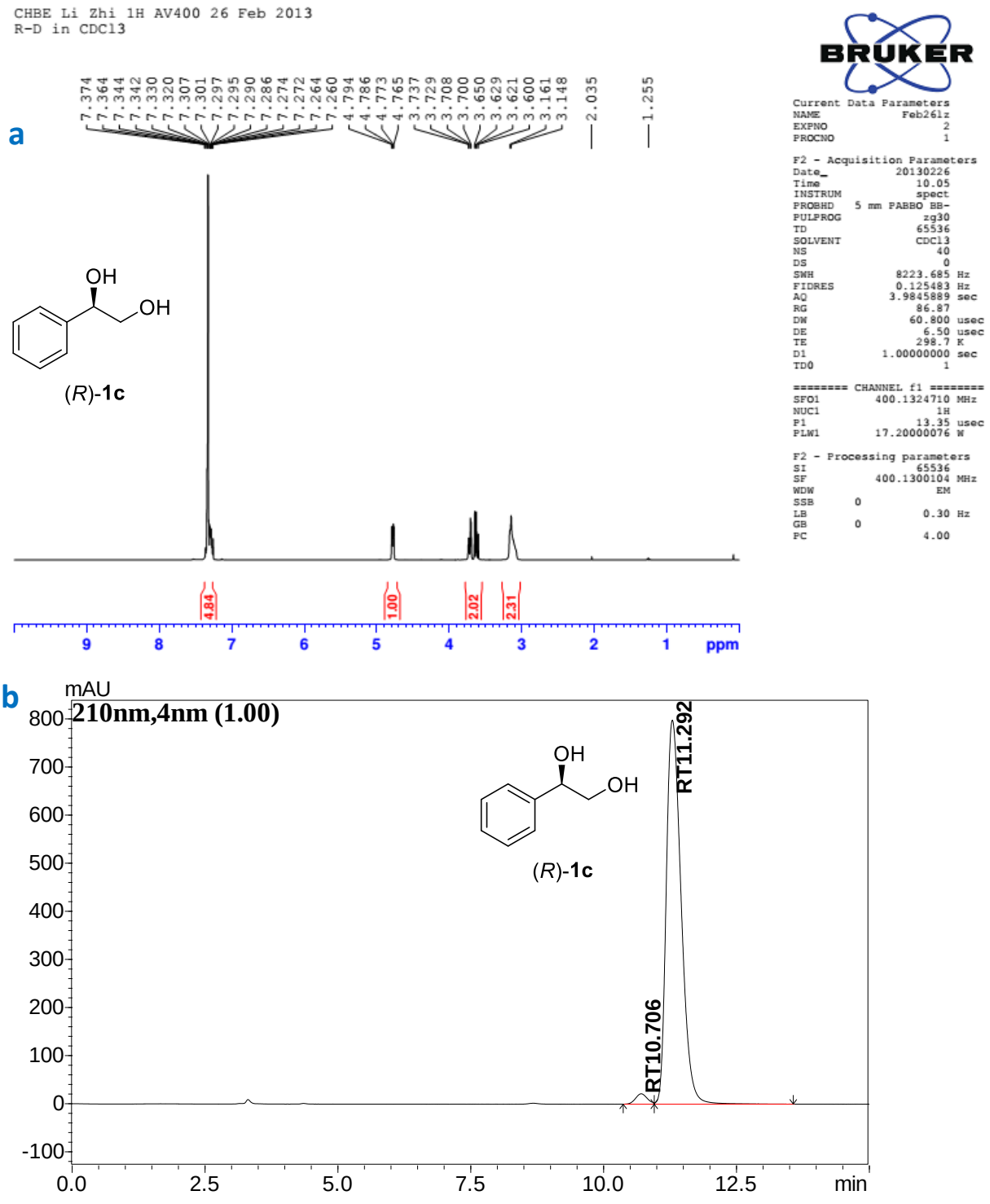

Figure S25. ^{1}H NMR spectrum and Chiral HPLC chromatogram of prepared product (*R*)-**1c**. a) ^{1}H NMR (400 MHz, $CDCl_3$, TMS); b) Chiral HPLC (Daicel Chiralpak AS-H (250 × 4.6 mm, 5μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 ºC, UV detection at 210 nm).

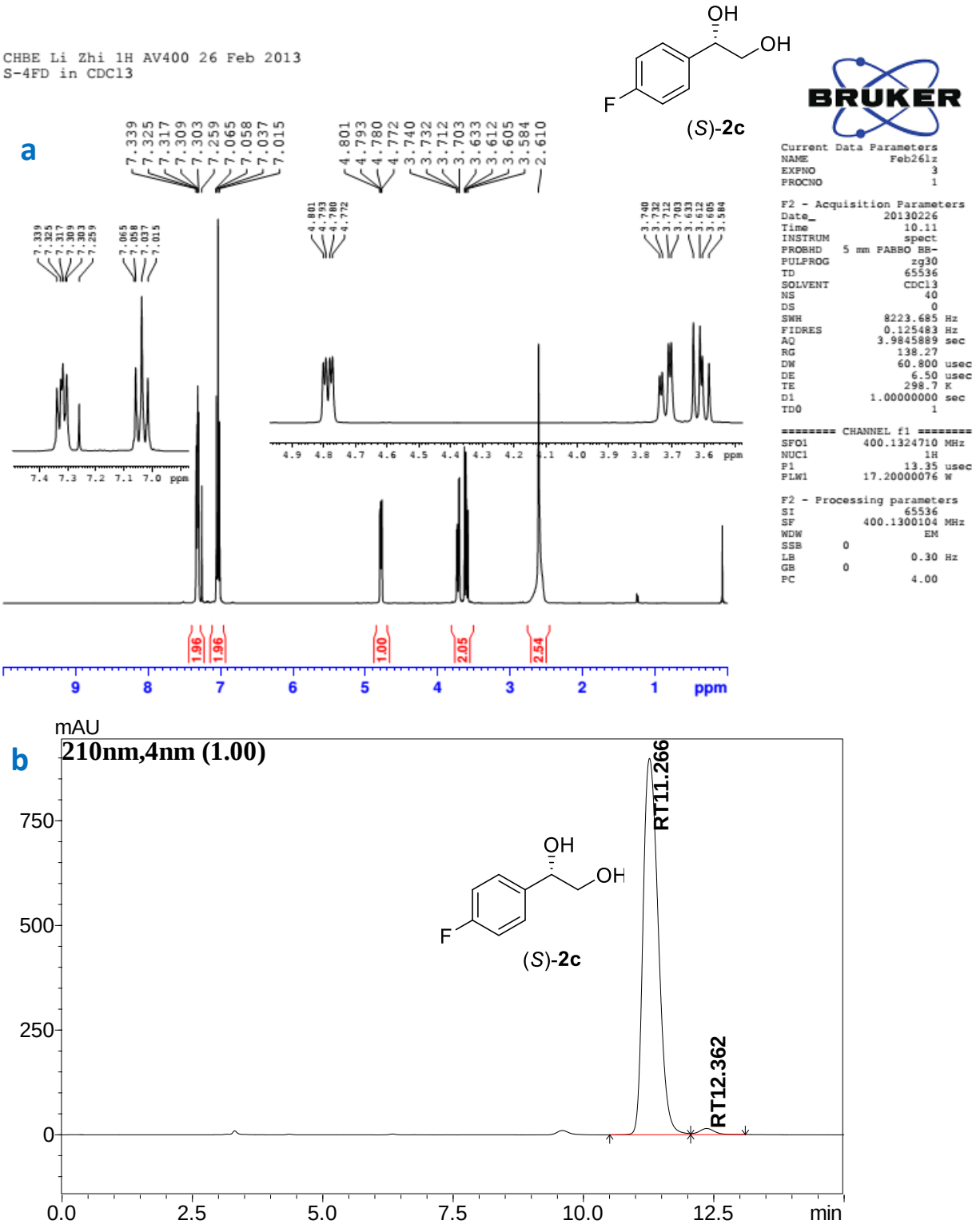

Figure S26. ^{1}H NMR spectrum and Chiral HPLC chromatogram of prepared product (*S*)-**2c**. a) ^{1}H NMR (400 MHz, $CDCl_3$, TMS); b) Chiral HPLC (Daicel Chiralpak AS-H (250 × 4.6 mm, 5μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm).

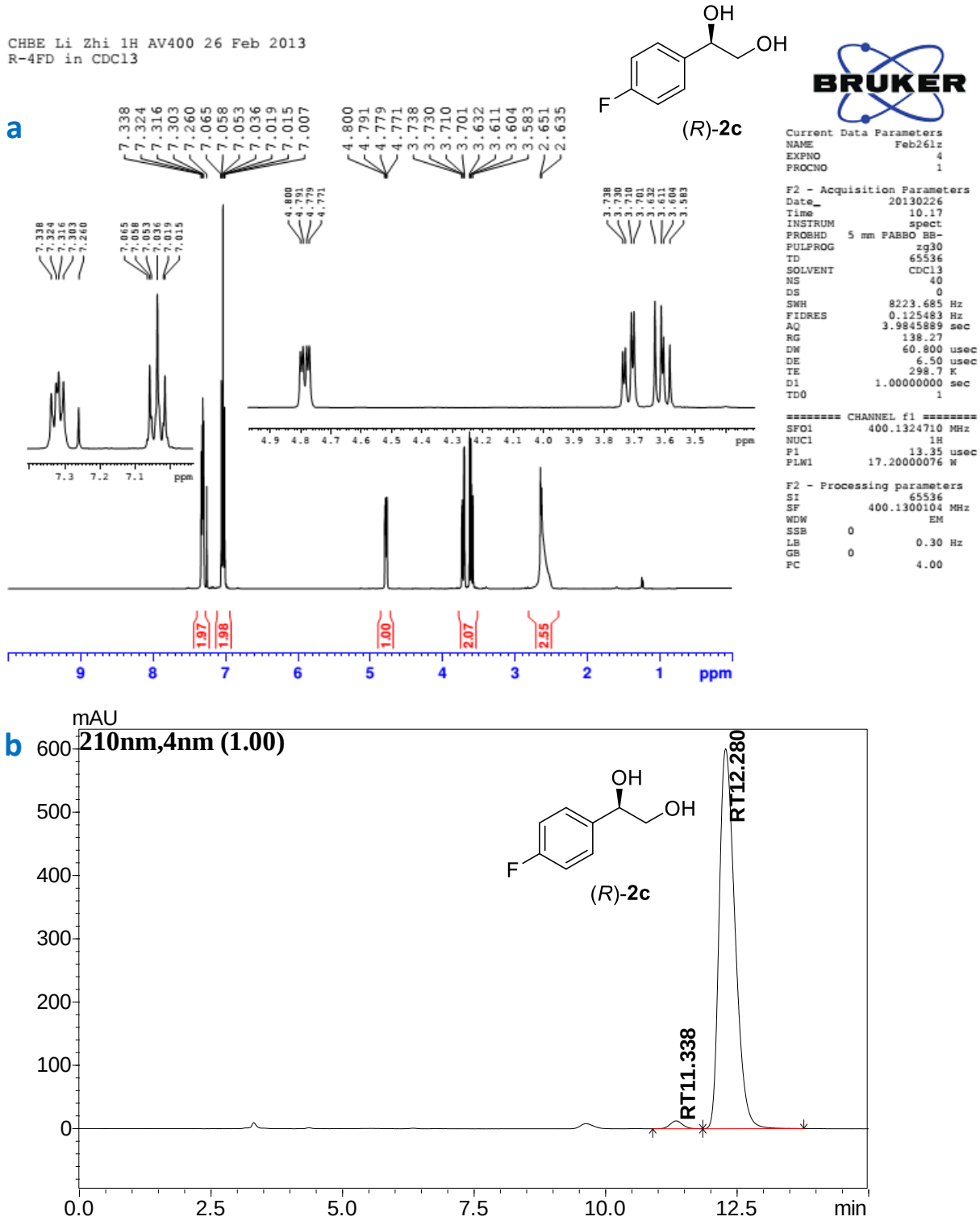

Figure S27. ^{1}H NMR spectrum and Chiral HPLC chromatogram of prepared product (*R*)-**2c**. a) ^{1}H NMR (400 MHz, $CDCl_3$, TMS); b) Chiral HPLC (Daicel Chiralpak AS-H (250 × 4.6 mm, 5μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm).

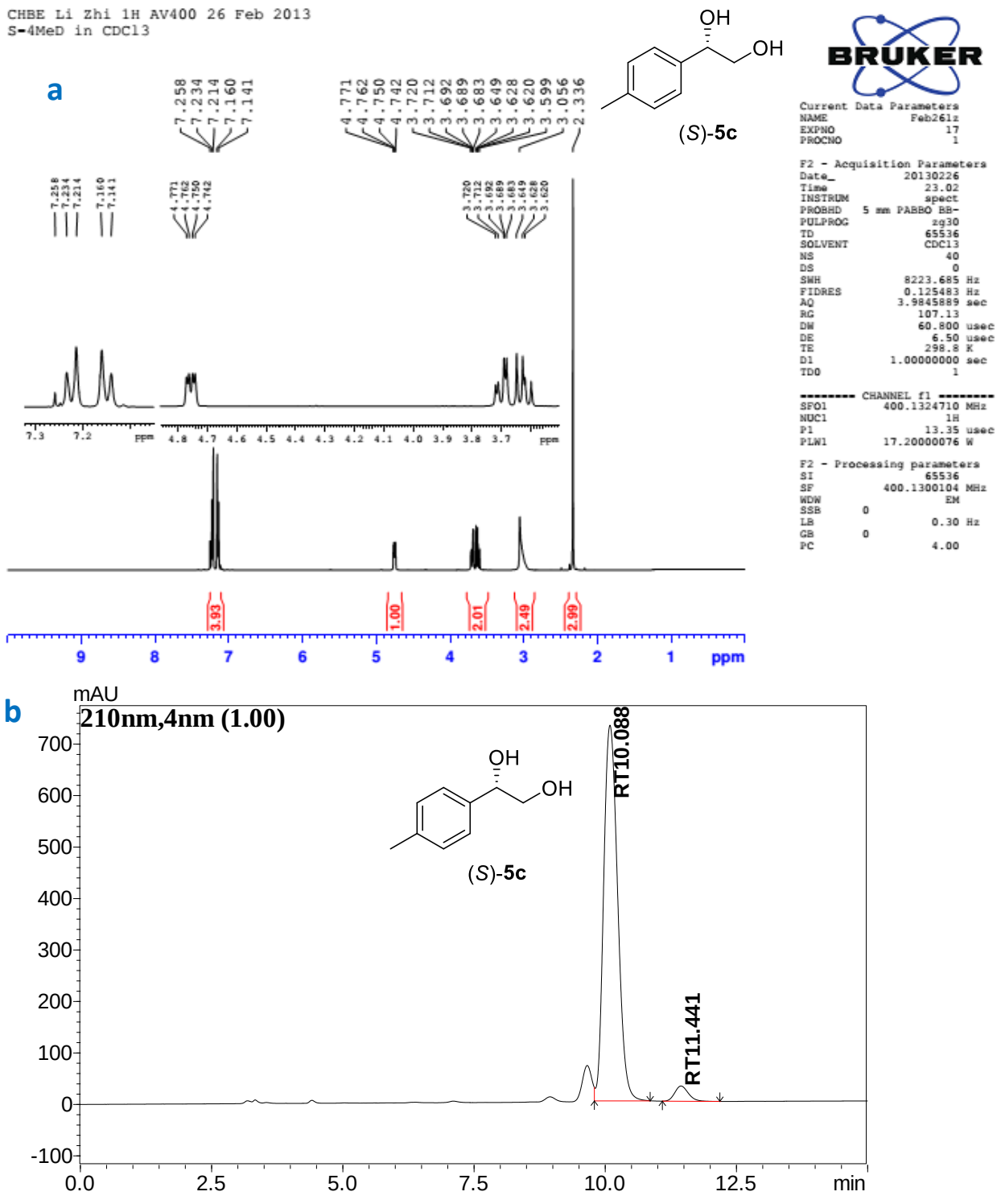

Figure S28. ^{1}H NMR spectrum and Chiral HPLC chromatogram of prepared product (*S*)-**5c**. a) ^{1}H NMR (400 MHz, $CDCl_3$, TMS); b) Chiral HPLC (Daicel Chiralpak AS-H (250 × 4.6 mm, 5μm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm).

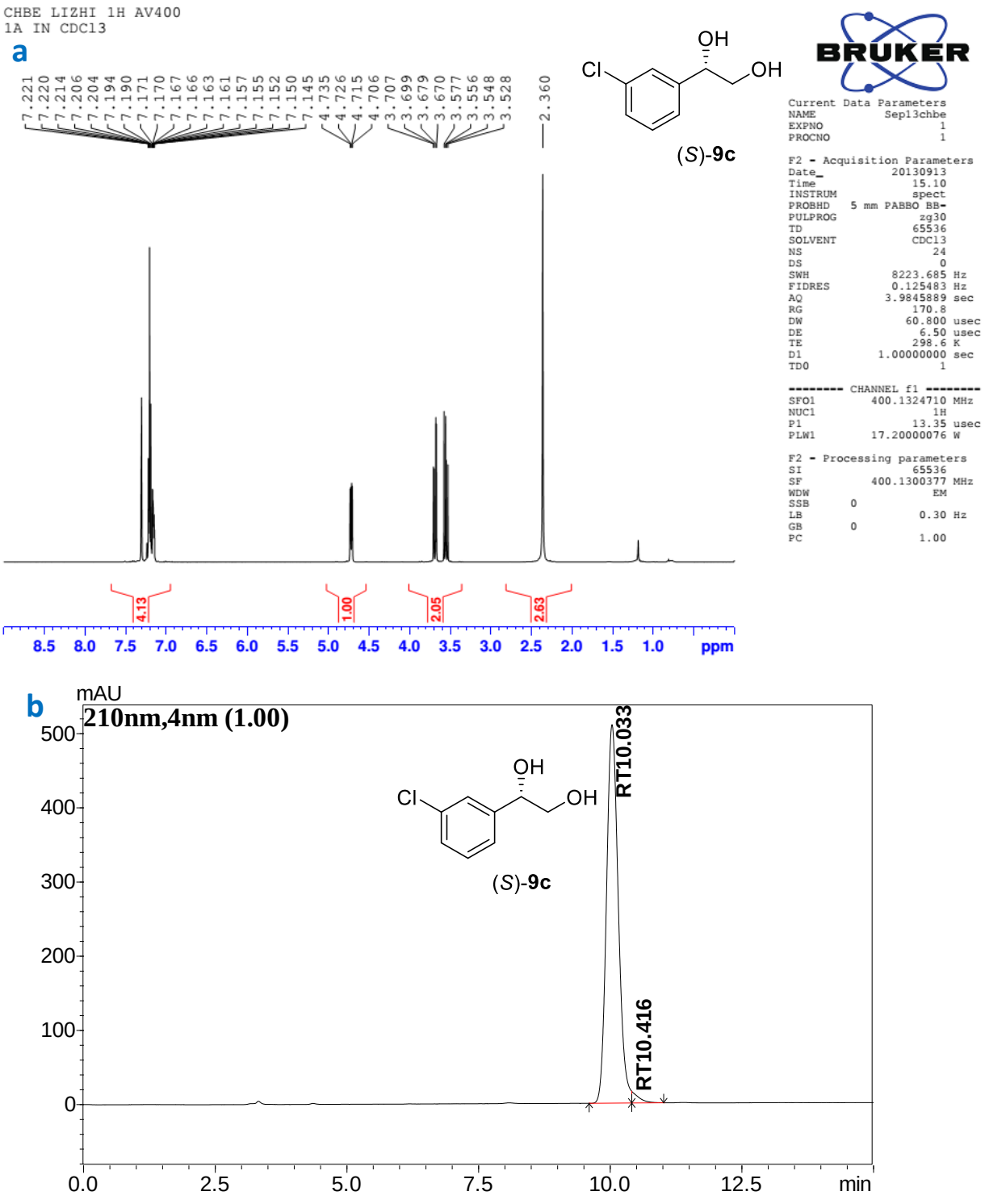

Figure S29. ^{1}H NMR spectrum and Chiral HPLC chromatogram of prepared product (*S*)-**9c**. a) ^{1}H NMR (400 MHz, $CDCl_3$, TMS); b) Chiral HPLC (Daicel Chiralpak AS-H (250 × 4.6 mm, 5µm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 ºC, UV detection at 210 nm).

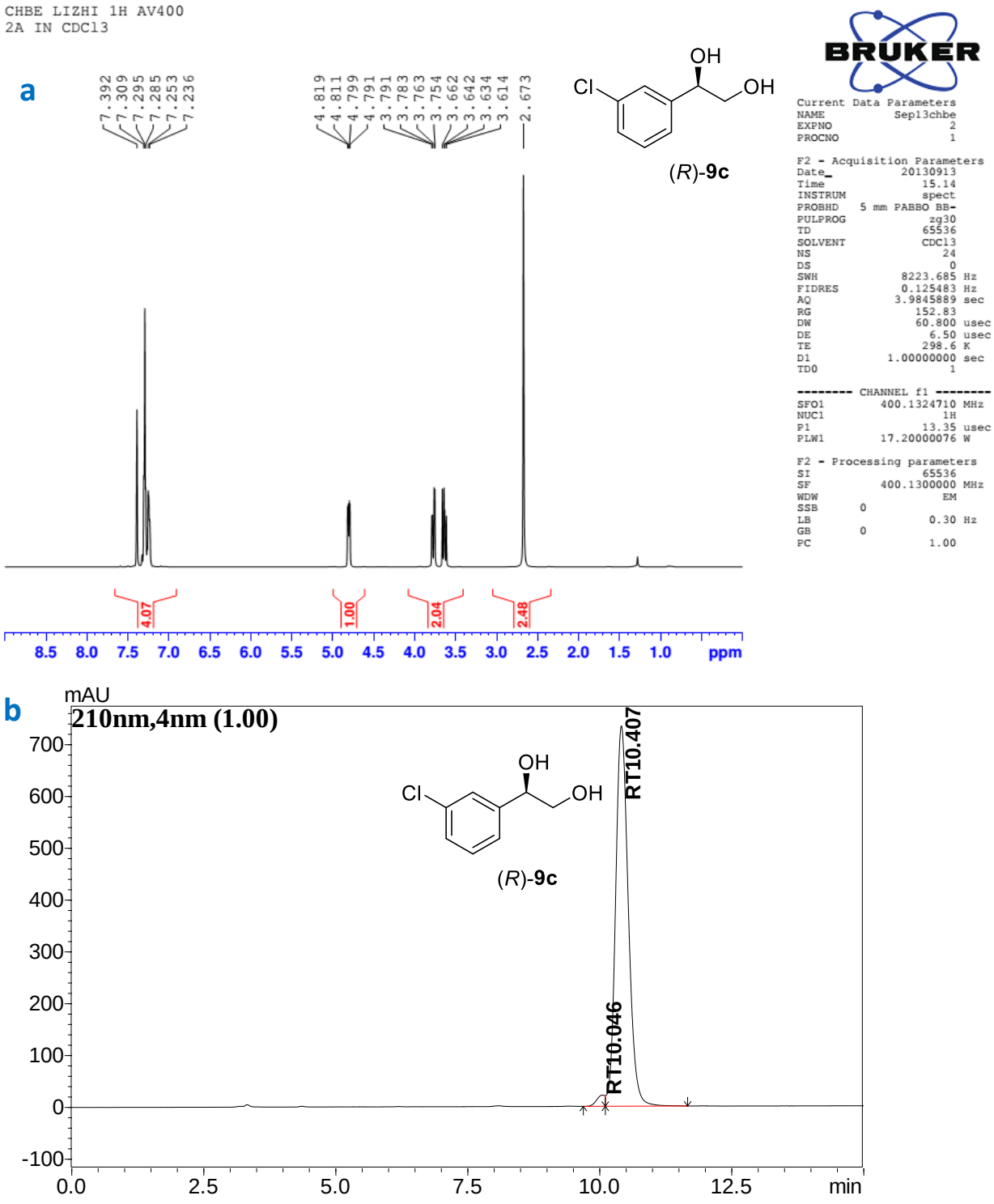

Figure S30. ^{1}H NMR spectrum and Chiral HPLC chromatogram of prepared product (*R*)-**9c**. a) ^{1}H NMR (400 MHz, $CDCl_3$, TMS); b) Chiral HPLC (Daicel Chiralpak AS-H (250 × 4.6 mm, 5µm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm).

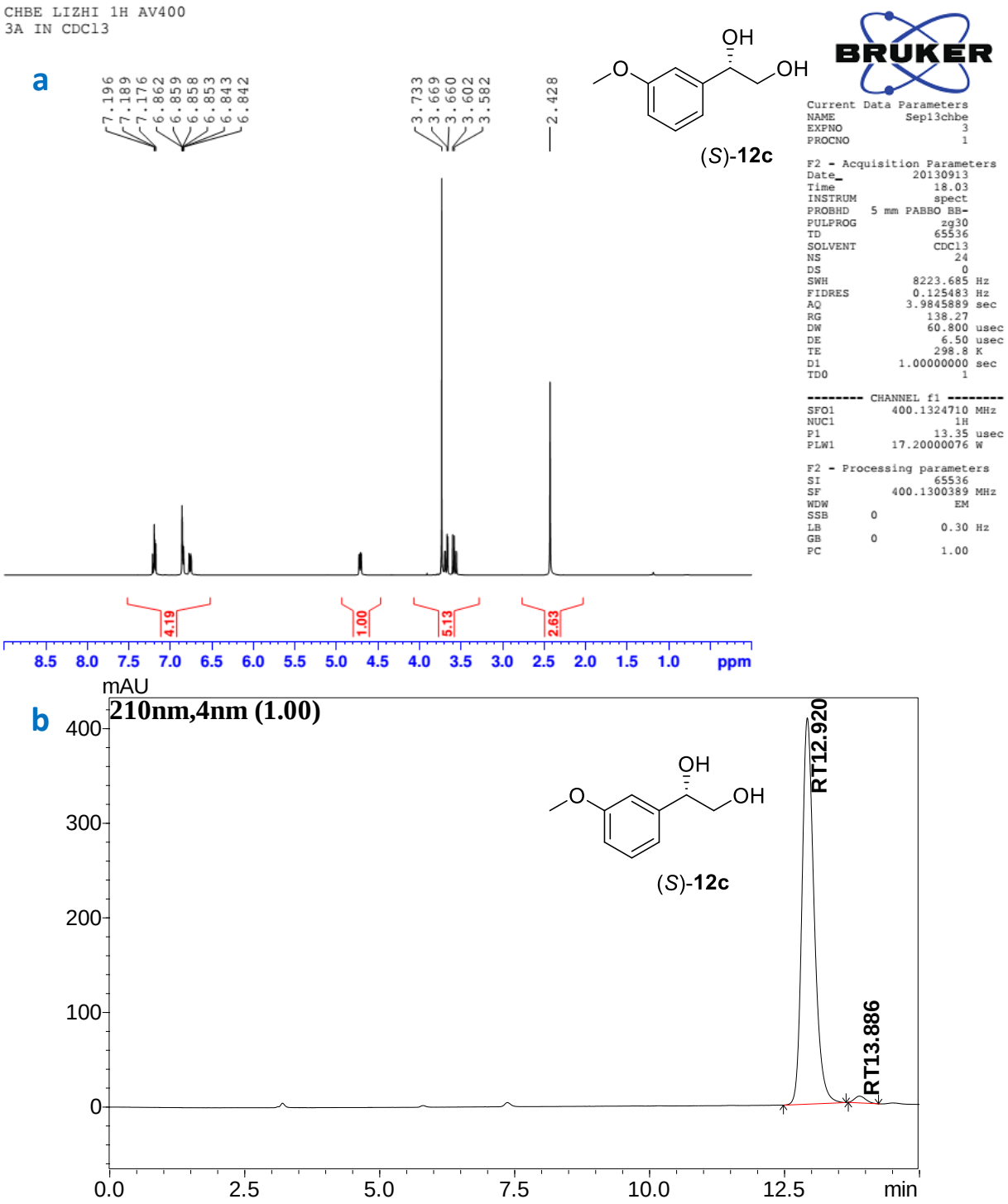

Figure S31. ^{1}H NMR spectrum and Chiral HPLC chromatogram of prepared product (*S*)-**12c**. a) ^{1}H NMR (400 MHz, $CDCl_3$, TMS); b) Chiral HPLC (Daicel Chiralpak IA-3 (250 × 4.6 mm, 3µm) column, mobile phase 10% IPA: 90% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 ^{o}C, UV detection at 210 nm. thod C).

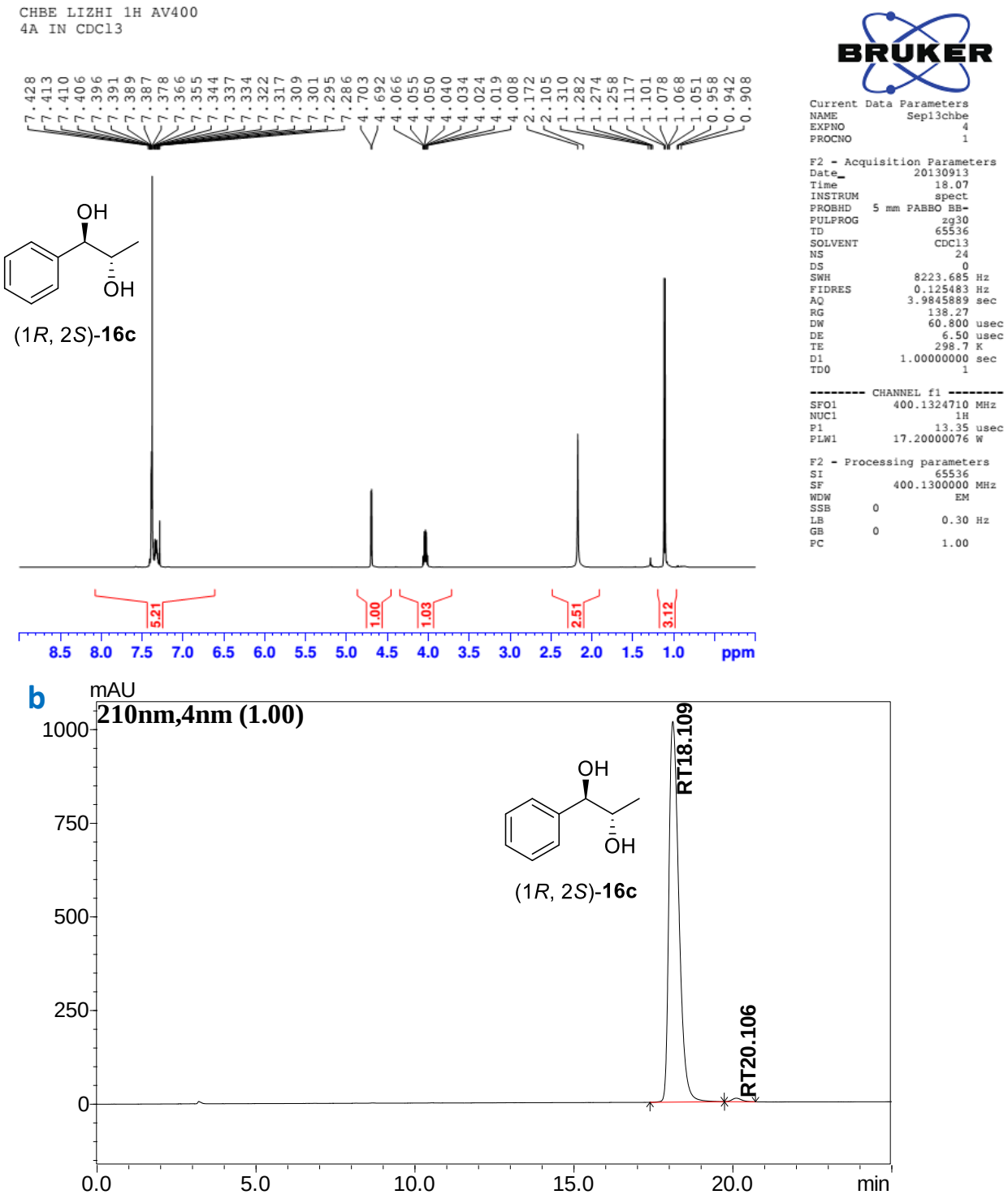

Figure S32. ^{1}H NMR spectrum and Chiral HPLC chromatogram of prepared product (1*R*, 2*S*)-**16c**. a) ^{1}H NMR (400 MHz, $CDCl_3$, TMS); b) Chiral HPLC (Daicel Chiralpak IA-3 (250 × 4.6 mm, 3µm) column, mobile phase 5% IPA: 95% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm).

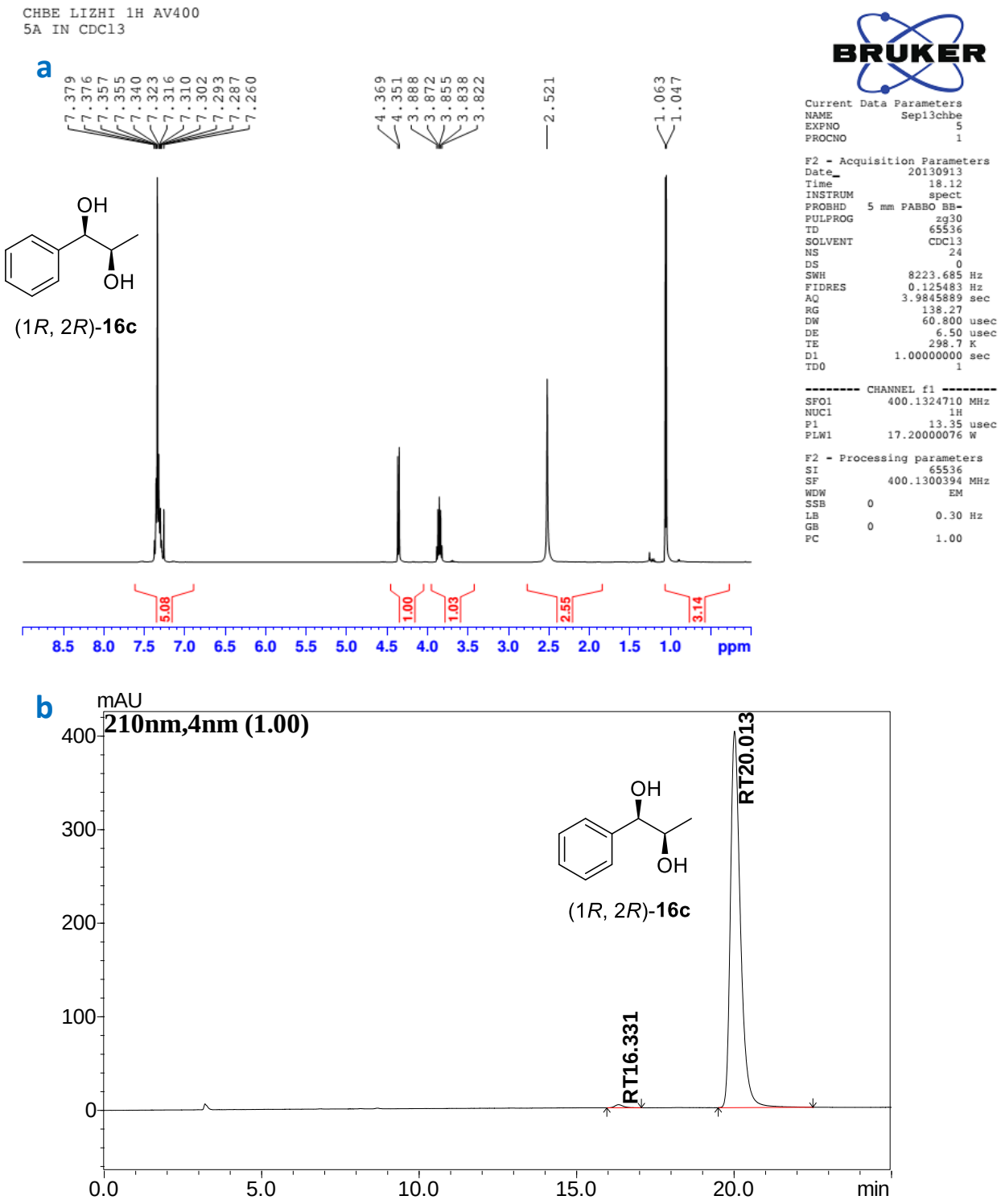

Figure S33. ^{1}H NMR spectrum and Chiral HPLC chromatogram of prepared product (1*R*, 2*R*)-**16c**. a) ^{1}H NMR (400 MHz, $CDCl_3$, TMS); b) Chiral HPLC (Daicel Chiralpak IA-3 (250 × 4.6 mm, 3μm) column, mobile phase 5% IPA: 95% *n*-hexane, flow rate 1.0 mL min^{-1}, oven temperature 25 °C, UV detection at 210 nm).

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