Electronic Supporting Information (ESI)

A new monooxygenase from *Herbaspirillum huttiense* catalyzed highly enantioselective epoxidation of allylbenzenes and allylic alcohols

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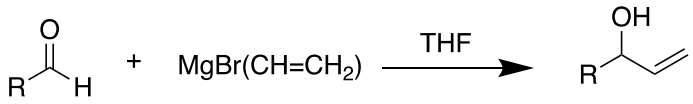
1. Synthesis of secondary allylic alcohols 13a-21a



Secondary allylic alcohols **13a-21a** were prepared from the corresponding aldehydes and vinylmagnesium bromide [1].

1-Phenyl-prop-2-en-1-ol (**13a**): yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.40 (m, 5H), 6.02-6.10 (m, 1H), 5.33-5.39 (m, 1H), 5.19-5.23 (m, 2H).

1-(3-Fluoro-phenyl)-prop-2-en-1-ol (**14a**): colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.34 (m, 1H), 7.09-7.15 (m, 2H), 6.95-7.00 (m, 1H), 5.97-6.05 (m, 1H), 5.33-5.38 (m, 1H), 5.19-5.30 (m, 2H).

1-(4-Fluoro-phenyl)-prop-2-en-1-ol (**15a**): colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.36 (m, 2H), 7.01-7.07 (m, 2H), 5.98-6.06 (m, 1H), 5.31-5.36 (m, 1H), 5.18-5.22 (m, 2H), 1.99 (br, 1H).

1-Naphthalen-1-yl-prop-2-en-1-ol (**16a**): yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-8.21 (m, 1H), 7.80-7.90 (m, 2H), 7.62-7.64 (m, 1H), 7.46-7.56 (m, 3H), 6.22-6.30 (m, 1H), 5.95 (d, J = 5.34 Hz, 1H), 5.44-5.49 (m, 1H), 5.27-5.31 (m, 1H).

1-Naphthalen-2-yl-prop-2-en-1-ol (**17a**): yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.85 (m, 4H), 7.47-7.50 (m, 3H), 6.09-6.17 (m, 1H), 5.37-5.44 (m, 2H), 5.23-5.27 (m, 1H), 2.12 (br, 1H).

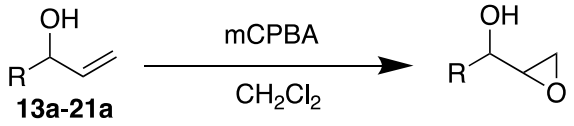
1-Naphthalen-2-yl-prop-2-en-1-ol (**18a**): yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.55 (m, 1H), 7.24-7.27 (m, 2H), 6.36-6.44 (m, 1H), 5.66-5.72 (m, 2H), 5.51-5.56 (m, 1H), 2.50-2.51 (m, 1H).

1-Thiophen-3-yl-prop-2-en-1-ol (**19a**): yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (m, 1H), 7.22-7.23 (m, 1H), 7.07-7.09 (m, 1H), 6.05-6.13 (m, 1H), 5.34-5.39 (m, 1H), 5.27-5.30 (m, 1H), 5.21-5.24 (m, 1H).

1-Phenyl-but-3-en-2-ol (**20a**): yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.34 (m, 2H), 7.23-7.25 (m, 3H), 5.90-5.99 (m, 1H), 5.12-5.28 (m, 2H), 4.33-4.39 (m, 1H), 2.77-2.91 (m, 2H).

1-Cyclohexyl-prop-2-en-1-ol (**21a**): yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82-5.90 (m, 1H), 5.17-5.22 (m, 1H), 5.12-5.16 (m, 1H), 3.83-3.87 (m, 1H), 1.83-1.92 (m, 1H), 1.73-1.77 (m, 2H), 1.65-1.68 (m, 2H), 1.36-1.42 (m, 1H), 1.14-1.26 (m, 5H).

2. Preparation of racemic epoxides



All the racemic epoxides were synthesized from the corresponding alkenes by *meta*-chloroperoxybenzoic acid [2].

Oxiranyl-phenyl-methanol: colorless oil, retention time: t_{R1} 19.80 min, t_{R2} 23.5 min, t_{R3} 24.62 min, t_{R4} 27.48 min (AS-H, *n*-Hexane: *iso*-propanol = 90: 10, 0.5 mL/min), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.43 (m, 10H), 4.93-4.94 (m, 1H), 4.48 (t, J = 4.93, 9.79 Hz 1H), 3.22-3.25 (m, 1H), 2.97 (dd, J = 2.78, 5.05 Hz, 1H), 2.82-2.87 (m, 2H), 2.76-2.78 (m, 1H), 2.51 (m, 1H), 2.32 (m, 1H).

(3-Fluoro-phenyl)-oxiranyl-methanol: colorless oil, retention time: t_{R1} 9.72 min, t_{R2} 11.02 min, t_{R3} 11.90 min (AS-H, *n*-Hexane: *iso*-propanol = 90: 10, 1.0 mL/min), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.37 (m, 2H), 6.99-7.19 (m, 6H),4.93-4.94 (m, 1H), 4.48-4.50 (m, 1H), 3.19-3.24 (m, 1H), 2.93-2.95 (m, 1H), 2.84 (dd, J = 2.72, 4.80 Hz, 1H), 2.76 (dd, J = 2.64, 4.69 Hz, 1H), 2.58 (d, J = 5.10 Hz, 1H), 2.38 (d, J = 2.23 Hz, 1H).

(4-Fluoro-phenyl)-oxiranyl-methanol: yellow oil, retention time: t_{R1} 10.36 min, t_{R2} 13.52 min, t_{R3} 15.51 min (AS-H, *n*-Hexane: *iso*-propanol= 90:10, 1.0 mL/min), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.42 (m, 4H), 7.04-7.09 (m, 4H), 4.92 (d, J = 3.00 Hz, 1H), 4.48 (d, J = 5.38

Hz, 1H), 3.18-3.21 (m, 1H), 2.93-2.95 (m, 1H), 2.86-2.88 (m, 1H), 2.82 (dd, *J* = 2.73, 4.82 Hz, 1H), 2.77 (dd, *J* = 3.99, 4.97 Hz, 1H), 2.49 (br, 1H), 2.32 (br, 1H).

Naphthalen-1-yl-oxiranyl-methanol: white solid, retention time: t_{R1} 13.82 min, t_{R2} 14.88 min, t_{R3} 16.10 min, t_{R4} 17.69 min (AS-H, *n*-Hexane: *iso*-propanol= 90:10, 1.0 mL/min), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.90 (m, 8H), 7.48-7.54 (m, 6H), 5.11-5.12 (m, 1H), 4.65-468 (m, 1H), 3.30-3.34 (m, 1H), 3.01-3.03 (m, 1H), 2.89-2.91 (m, 1H), 2.78-2.81 (m, 1H), 2.53 (br,1H), 2.37 (br,1H).

Naphthalen-2-yl-oxiranyl-methanol: yellow oil, retention time: t_{R1} 12.89 min, t_{R2} 15.26 min, t_{R3} 17.39 min, t_{R4} 20.06 min (AS-H, *n*-Hexane: *iso*-propanol = 90: 10, 1.0 mL/min), ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10-8.17 (m, 2H), 7.70-7.90 (m, 4H), 7.67-7.72 (m, 2H), 7.47-7.57 (m, 6H), 5.76-5.77 (m, 1H), 5.30-5.32 (m, 1H), 4.65-4.68 (m, 1H), 3.46-3.50 (m, 1H), 2.93-3.03 (m, 1H), 2.76-2.88 (m, 1H), 2.52 (br, 1H), 2.48 (br, 1H).

1-Oxiranyl-2-phenyl-ethanol: colorless oil, retention time: t_{R1} 11.34 min, t_{R1} 13.46 min, t_{R2} 19.32 min, t_{R3} 22.21 min (AS-H, *n*-Hexane: *iso*-propanol= 90:10, 1.0 mL/min), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.34 (m, 10H), 3.99-4.03 (m, 1H), 3.69-3.75 (m, 1H), 3.03-3.06 (m, 2H), 2.79-2.99 (m, 6H), 2.76 (dd, *J* = 4.10, 4.95, 1H), 2.62 (dd, *J* = 2.77, 4.93, 1H), 2.03 (br, 1H), 1.92 (br, 1H).

Cyclohexyl-oxiranyl-methanol: yellow oil, retention time: t_{R1} 12.65 min, t_{R2} 12.81 min, t_{R3} 12.90 min, t_{R4} 13.08 min (chiral GC, CHIRASIL-DEX CB column), ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.62 (dd, *J* = 3.22, 5.74 Hz, 1H), 3.14 (dd, *J* = 5.36, 10.90 Hz, 1H), 3.02-3.08 (m, 2H), 2.81-2.83 (m, 2H), 2.74 (dd, *J* = 4.05, 5.15 Hz, 1H), 2.70 (dd, *J* = 2.78, 4.97 Hz, 1H), 1.90-1.95 (m, 2H), 1.65-1.79 (m, 10H), 1.49-1.59 (m, 2H), 1.22-1.30 (m, 8H).

3. The data of the epoxides from the HhMo-catalyzed epoxidation

(*S*)-allylbenzene oxide (**1b**): colorless oil, $[\alpha]_D^{25}$ = +13.6 (c = 0.82 in $CHCl_3$), 99% ee (AS-H, *n*-Hexane: *iso*-propanol = 90: 10, 1.0 mL/min), retention time: t_R (*R*) 4.78 min, t_R (*S*) 5.18

min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.38 (m, 5H), 3.14-3.17 (m, 1H), 2.92 (dd, J = 5.47, 14.4 Hz, 1H), 2.78-2.84 (m, 2H), 2.55 (dd, J = 2.66, 4.97 Hz, 1H).

(*S*)-2-(3-Fluoro-benzyl)-oxirane (**2b**): colorless oil, 91% ee (AS-H, *n*-Hexane: *iso*-propanol = 90: 10, 1.0 mL/min), retention time: t_R (*R*) 5.22 min, t_R (*S*) 5.70 min, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.30 (m, 1H), 6.92-7.04 (m, 3H), 3.13-3.17 (m, 1H), 2.87 (d, J = 5.62 Hz, 2H), 2.80-2.82 (m, 1H), 2.55 (dd, J = 2.63, 4.94 Hz, 1H).

(*S*)-2-(4-Fluoro-benzyl)-oxirane (**3b**): colorless oil, 87% ee (AS-H, *n*-Hexane: *iso*-propanol = 90: 10, 1.0 mL/min), retention time: t_R (*R*) 5.69 min, t_R (*S*) 6.18 min, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.26 (m, 2H), 6.98-7.02 (m, 2H), 3.11-3.15 (m, 1H), 2.85 (d, J = 5.36 Hz, 2H), 2.78-2.81 (m, 1H), 2.52 (dd, J = 2.64, 4.97 Hz, 1H).

(*S*)-2-(2-Methyl-benzyl)-oxirane (**4b**): colorless oil, 71% ee (AS-H, *n*-Hexane: *iso*-propanol = 90: 10, 0.5 mL/min), retention time: t_R (*R*) 4.45 min, t_R (*S*) 4.81 min, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.34 (m, 4H), 3.24-3.28 (m, 1H), 3.05 (dd, J = 5.24, 14.78 Hz, 1H), 2.88-2.94 (m, 2H), 2.62 (dd, J = 2.64, 5.04 Hz, 1H), 2.43 (s, 3H).

(*S*)-2-(3-Methyl-benzyl)-oxirane (**5b**): colorless oil, 95% ee (AS-H, *n*-Hexane: *iso*-propanol = 90: 10, 0.5 mL/min), retention time: t_R (*R*) 8.62 min, t_R (*S*) 9.27 min, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.24 (m, 1H), 7.05-7.08 (m, 3H), 3.14-3.18 (m, 1H), 2.90 (dd, J = 5.64, 14.52 Hz, 1H), 2.76-2.82 (m, 2H), 2.62 (dd, J = 2.64, 4.98 Hz, 1H), 2.36 (s, 3H).

(*S*)-2-(4-Methyl-benzyl)-oxirane (**6b**): colorless oil, 92% ee (AS-H, *n*-Hexane: *iso*-propanol = 90: 10, 0.5 mL/min), retention time: t_R (*R*) 8.88 min, t_R (*S*) 9.49 min, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12-7.17 (m, 4H), 3.12-3.17 (m, 1H), 2.90 (dd, J = 5.59, 14.93 Hz, 1H), 2.25-2.81 (m, 2H), 2.62 (dd, J = 2.64, 5.04 Hz, 1H), 2.35 (s, 3H).

(*S*)-2-(2-Methoxy-benzyl)-oxirane (**7b**): yellow oil, 35% ee (AS-H, *n*-Hexane: *iso*-propanol = 90: 10, 1.0 mL/min), retention time: t_R (*R*) 4.45 min, t_R (*S*) 4.80 min, ^{1}H NMR (400 MHz,

$CDCl_3$): δ 7.19-7.24 (m, 2H), 6.86-6.94 (m, 2H), 3.84 (s, 3H), 2.96 (dd, J = 5.34, 14.22 Hz, 1H), 2.72-2.82 (m, 2H), 2.62 (dd, J = 2.68, 5.05 Hz, 1H).

(*S*)-2-(4-Methoxy-benzyl)-oxirane (**8b**): colorless oil, 70% ee (AS-H, *n*-Hexane: *iso*-propanol = 90: 10, 0.5 mL/min), retention time: t_R (*R*) 14.40 min, t_R (*S*) 15.94 min, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16-7.18 (m, 2H), 6.85-6.87 (m, 2H), 3.80 (s, 3H), 3.10-3.14 (m, 1H), 2.87 (dd, J = 5.64, 14.63 Hz, 1H), 2.74-2.79 (m, 2H), 2.53 (dd, J = 2.64, J = 5.01Hz, 1H).

(*S*)-2-Phenethyl-oxirane (**9b**): colorless oil, 81% ee (AS-H, *n*-Hexane: *iso*-propanol = 90: 10, 1.0 mL/min), retention time: t_R (*R*) 4.74 min, t_R (*S*) 5.35 min, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.32 (m, 2H), 7.19-7.22 (m, 3H), 2.94-2.98 (m, 1H), 2.72-2.87 (m, 3H), 2.48 (dd, J = 2.68, 4.95 Hz, 1H), 1.79-1.93 (m, 2H).

(*S*)-2-Phenoxymethyl-oxirane (**10b**): colorless oil, 46% ee (AS-H, *n*-Hexane: *iso*-propanol = 90: 10, 0.5 mL/min), retention time: t_R (*R*) 15.54 min, t_R (*S*) 16.42 min, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.31 (m, 2H), 6.92-6.99 (m, 2H), 4.22 (dd, J = 3.22, 10.94 Hz, 1H), 3.98 (dd, J = 5.62, 10.94 Hz, 1H), 3.3.4-3.38 (m, 1H), 2.90-2.92 (m, 1H), 2.76 (dd, J = 2.69, 4.98 Hz, 1H).

(1*R*, 2*R*)-Oxiranyl-phenyl-methanol (**13b**): colorless oil, $[\alpha]_D^{25}$ = -19.8 (c = 1.8 in $CHCl_3$), >99% ee, >99% de (AS-H, *n*-Hexane: *iso*-propanol = 90: 10, 0.5 mL/min), retention time: t_R 27.59 min, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.44 (m, 5H), 4.48 (m, 1H), 3.22-3.25 (m, 1H), 2.83-2.88 (m, 2H), 2.34 (m, 1H).

(1*R*, 2*R*)-(3-Fluoro-phenyl)-oxiranyl-methanol (**14b**): colorless oil, >99% ee, 96% de (AS-H, *n*-Hexane: *iso*-propanol = 90: 10, 1.0 mL/min), retention time: t_{R1} 9.72 min, t_{R2} 11.90 min (major), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.38 (m, 1H), 7.15-7.19 (m, 2H), 7.00-7.05 (m, 1H), 4.49 (d, J = 5.37 Hz, 1H), 3.19-3.22 (m, 1H), 2.88-2.90 (m, 1H), 2.84 (dd, J = 2.74, 4.79 Hz, 1H).

(1*R*, 2*R*)-(4-Fluoro-phenyl)-oxiranyl-methanol (**15b**): yellow oil, >99% ee, >99% de (AS-H, *n*-Hexane: *iso*-propanol = 90: 10, 1.0 mL/min), retention time: t_R 15.60 min, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.42 (m, 2H), 7.05-7.09 (m, 2H), 4.48 (d, J = 5.37 Hz, 1H), 3.19-3.22 (m, 1H), 2.86-2.88 (m, 1H), 2.83 (dd, J = 2.69, 4.80 Hz, 1H).

(1*R*, 2*R*)-Naphthalen-1-yl-oxiranyl-methanol (**16b**): white solid, >99% ee, 70% de (AS-H, *n*-Hexane: *iso*-propanol= 90:10, 1.0 mL/min), retention time: t_R 15.19 min.

(1*R*, 2*R*)-Naphthalen-2-yl-oxiranyl-methanol (**17b**): yellow oil, >99% ee, >99% de (AS-H, *n*-Hexane: *iso*-propanol = 90: 10, 1.0 mL/min), retention time: t_{R3} 17.74 min.

(1*R*, 2*R*)-Oxiranyl-thiophen-2-yl-methanol (**18b**): yellow oil, >99% ee, >99% de (AS-H, *n*-Hexane: *iso*-propanol = 90: 10, 1.0 mL/min), retention time: t_{R4} 21.51 min, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.32 (m, 1H), 7.08-7.09 (m, 1H), 7.01-7.03 (m, 1H), 4.78 (d, J = 4.92 Hz, 1H), 3.33-3.36 (m, 1H), 2.86-2.92 (m, 2H), 2.34 (m, 1H).

(2*R*, 3*R*)-Oxiranyl-thiophen-3-yl-methanol (**19b**): yellow oil, >99% ee, >99% de (AS-H, *n*-Hexane: *iso*-propanol = 90: 10, 1.0 mL/min), retention time: t_R 18.2 min, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.36 (m, 2H), 7.13-7.15 (m, 1H), 4.60 (d, J = 5.01 Hz, 1H), 3.26-3.29 (m, 1H), 2.88-2.90 (m, 1H), 2.84-2.86 (dd, J = 2.74, 4.86 Hz, 1H).

(1*R*, 2*R*)-1-Oxiranyl-2-phenyl-ethanol (**20b**): colorless oil, >99% ee, 91% de, (AS-H, *n*-Hexane: *iso*-propanol= 90:10, 1.0 mL/min), retention time: t_R (*R*) 11.34 min, t_{R3} 22.4 min (major).

(1*R*, 2*R*)-Cyclohexyl-oxiranyl-methanol (**21b**): yellow oil, >99% ee, >99% de (chiral GC, CHIRASIL-DEX CB column), retention time: t_R 12.81 min, ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.15 (dd, J = 5.26, 6.65 Hz, 1H), 3.02-3.05 (m, 1H), 2.82 (dd, J = 4.01, 4.94Hz, 1H), 2.70 (dd, J = 2.77, 4.99 Hz, 1H), 1.90-1.95 (m, 1H), 1.65-1.77 (m, 5H), 1.52-1.57 (m, 1H), 1.25-1.28 (m, 4H).

4. Table S1-S2

Table S1. The selected candidates.

Gene ID	Predicted function	Source	Identity (%)	E value
WP_091504755.1	monooxygenase	*A. sacchari*	50	2E-135
WP_039783212.1	alaninephosphoribitol ligase	*H. huttiense*	31	8E-57

Table S2. Polymerase chain reaction primers for the amplification of sequences.

	Oligonucleotides
24a-F	5’-AAG CTT GCG GCC GCA-3’
24a-R	5’-GTC GAC GGA GCT CGA ATT CG-3’
HhMo-F	5’-GAA TTC GAG CTC CGT CGA CAT GCG TAG CAT CGC AAT TG-3’
HhMo-R	5’-CGA GTG CGG CCG CAA GCT TGG CTG CAA CGG CTA AAG-3’
AsMo-F	5’-GAA TTC GAG CTC CGT CGA CAT GGA CGG CAT TGG TAT TG-3’
AsMo-R	5’-CGA GTG CGG CCG CAA GCT TCA CGG CAC CAT GGC GGG C-3’
24HhMo-F	5’-ATC CGC TGC CCC TGA ATT AAA AGC TTG CGG CCG CA-3’
24HhMo-R	5’-TTG GAT CAC CTG CAA ATT TAT CAG GCT GCA ACG GCT AAA GCC TTT-3’
pETB-F	5’-TGA TAA ATT TGC AGG TGA TCC AAA TGA CGC TAA AGA CAG ATG CG-3’
pETB-R	5’-TCC GCT GCC CCT GAA TTA A-3’
24AsMo-F	5’-ATC CGC TGC CCC TGA ATT AAA AGC TTG CGG CCG CA-3’
24AsMo-R	5’-TTG GAT CAC CTG CAA ATT TAT TAC ACG GCA CCA TGG CGG GCC AGA T-3’

Figure S1-S6

MSKRIGIVGAGTAGLHLGLYLRQHDIDVTIYTDRRPDEYADIRLLNTVAH 50
HSVTIEREVDLGVNHWPESGYFGHYYYVGGPQPLRFYGDLKKPSRAVDYR 100
IYLPTLMKAFEARGGKIEYEAVSVEDLESLSEQYDLVVVCTGKYALGQLF 150
DTQEESSPFEKPQRALCVGLFKGIKEAPIRAVTMSFSPGNGELIEIPTLS 200
FDGMCTALVLENHIGGDLEVLANTKYDENPRAFLDLLLEKLHKHHPSVAE 250
RIDPEEFDLVNSSLDILQGAVTPVFRNGHATLKNGKTIIGLGDVQATVDP 300
VLGQGANMASHAAWILGEEIVSNSVFDQRFCEHVERRRQDRVLCATRWTN 350
YMLSNLQALPPEFIQFIGTLSQSRAMADEFTDNFNYPERQWDYFSSPERI 400
MHWCAQYAPGIAA 413

Figure S1. The sequence of AnStyA.

Figure S2. The analysis of motifs in the 6 known styrene monooxygenases. Styrene monooxygenase from *Pseudomonas* sp. LQ26 (PsLQ26StyA, GenBank: ADE62390), *Rhodococcus opacus* 1CP (RoStyA, GenBank: AII82583), *Rhodococcus* sp. ST-5 (RsST5StyA, GenBank: BAL04132), *Rhodococcus* sp. ST-10 (RsST10StyA, GenBank: BAL04129), *Paraglaciecola agarilytica* (PaStyA, GenBank: WP_008305084.1), and *Marinobacterium litorale* (MlStyA, WP_027855270.1).

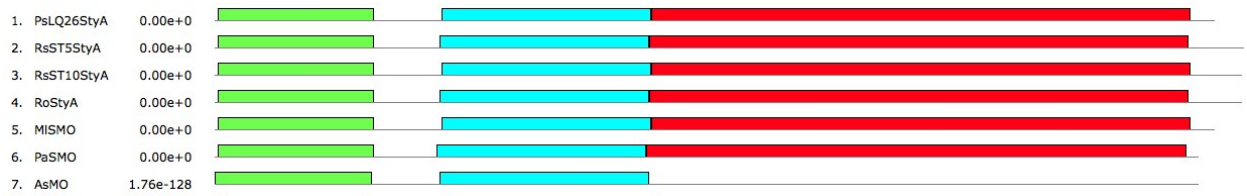


Figure S3. The analysis of motifs in the 6 known styrene monooxygenases and the putative monooxygenase from *A. sacchari* (AsMo, GenBank: WP_091504755).

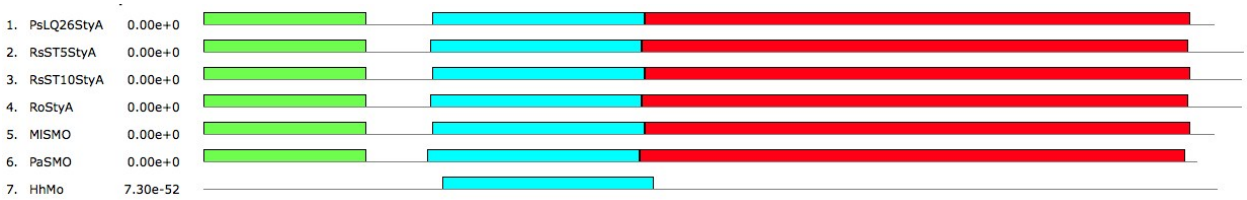


Figure S4. The analysis of motifs in the 6 known styrene monooxygenases and the putative alaninephosphoribitol ligase from *H. huttiense* (HhMo, GenBank: WP_039783212).

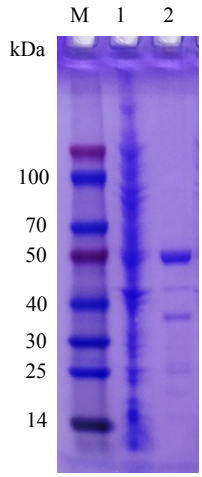


Figure S5. SDS-PAGE analysis of the HhMo expression and purity. Lane M: markers; Lane 1: cell-free extracts of *E. coli* harboring pET-HhMo-StyB; Lane 2: purified HhMo.

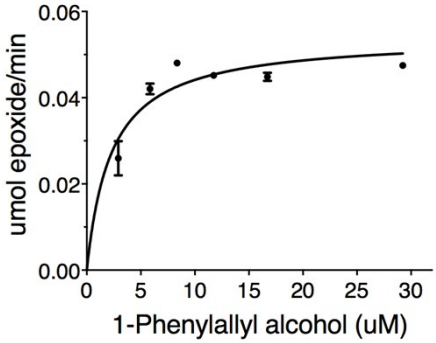
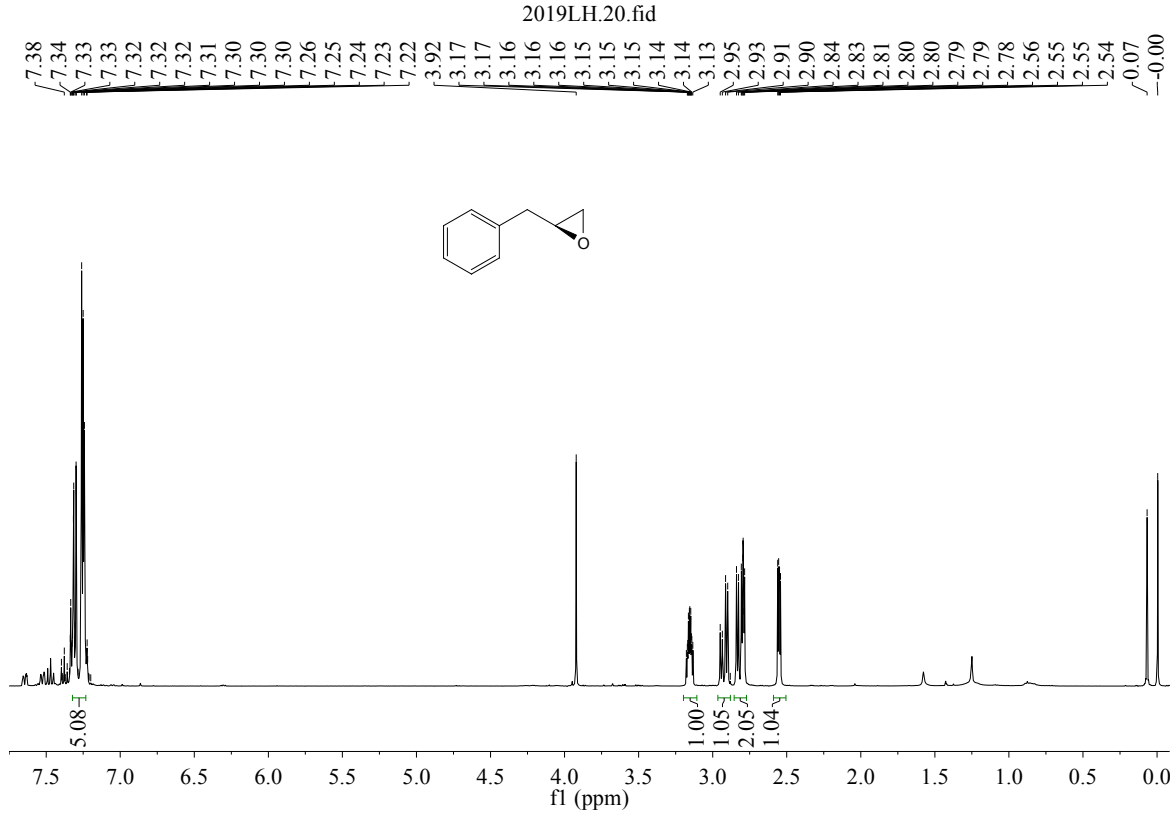


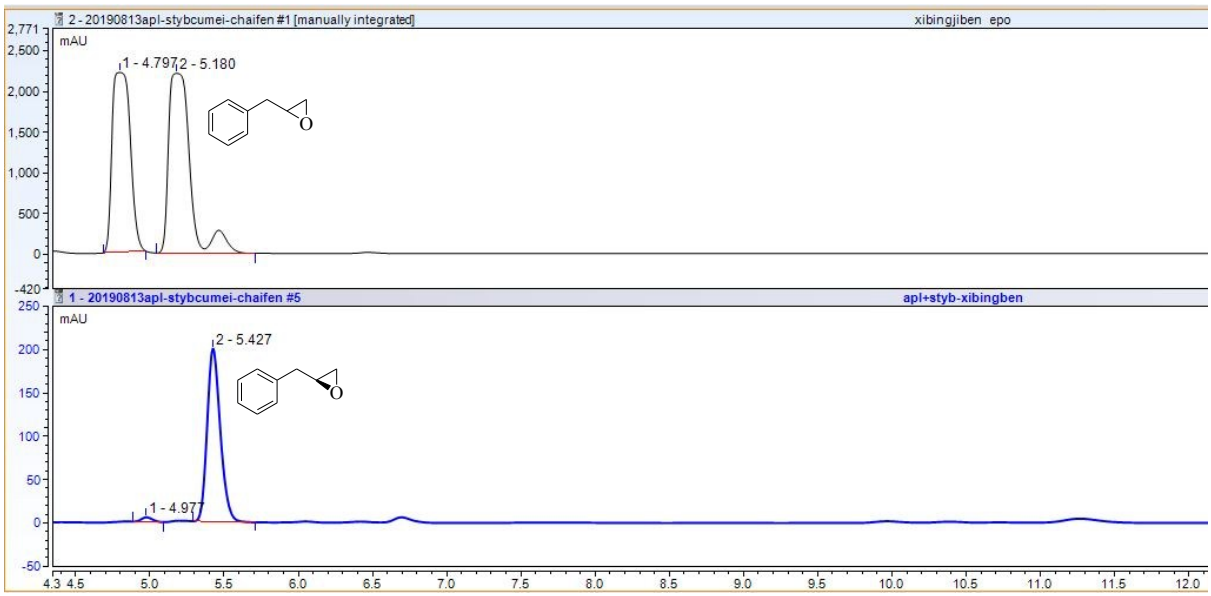
Figure S6. Steady-state kinetics of HhMo-catalyzed the epoxidation of 1-phenylallyl alcohol. Steady state kinetics were measured in triplicates by varying the 1-phenylallyl alcohol concentration from 3 μM to 29 μM and fitting the data to the Michaelis-Menten equation. Errors limits are standard deviations.

6. Selected ^{1}H NMR spectra and HPLC chromatograms

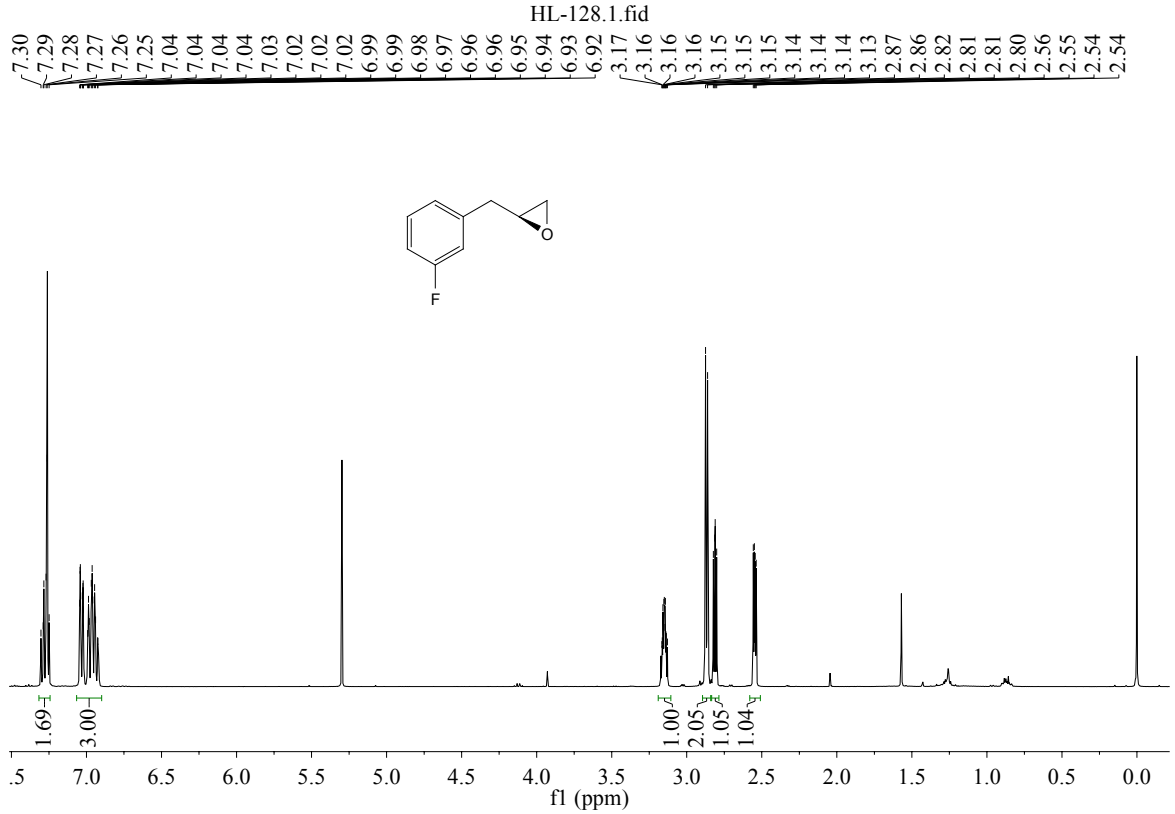
(*S*)-2-benzyloxirane (**1b**)



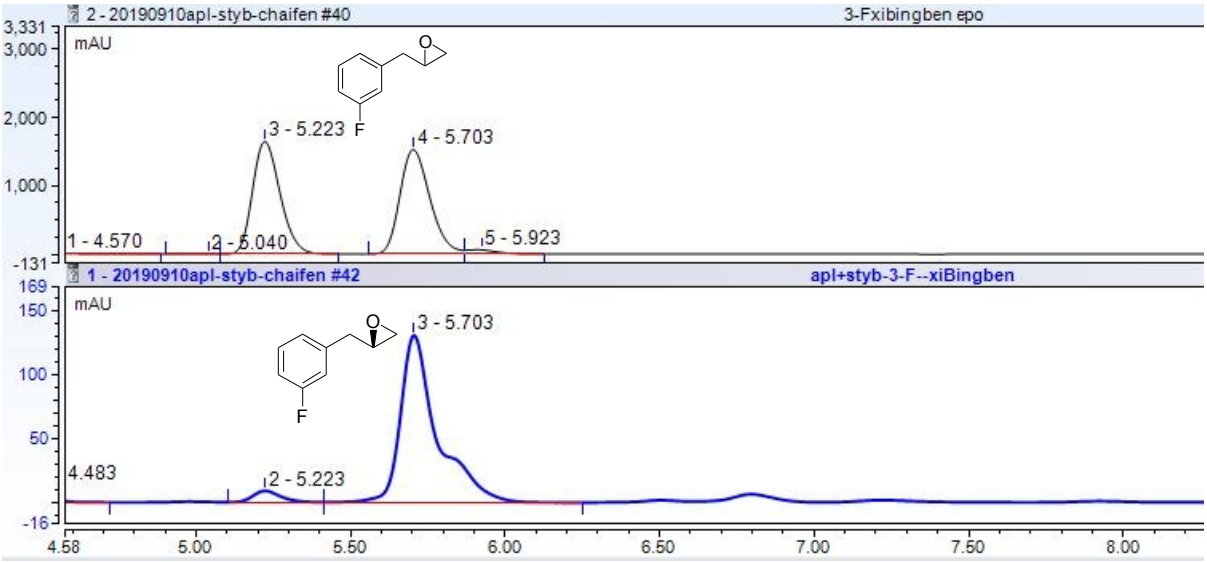
(*S*)-2-benzyloxirane (**1b**)



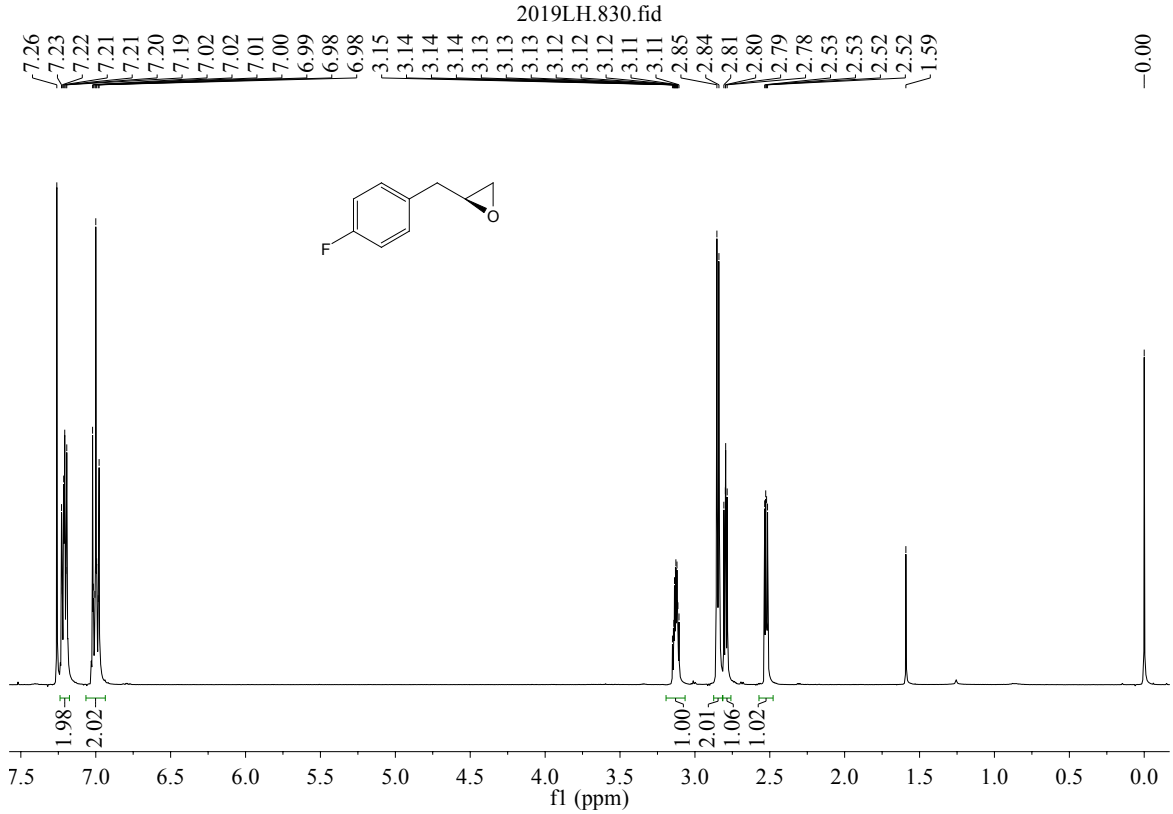
(*S*)-2-(3-fluorobenzyl)oxirane (**2b**)



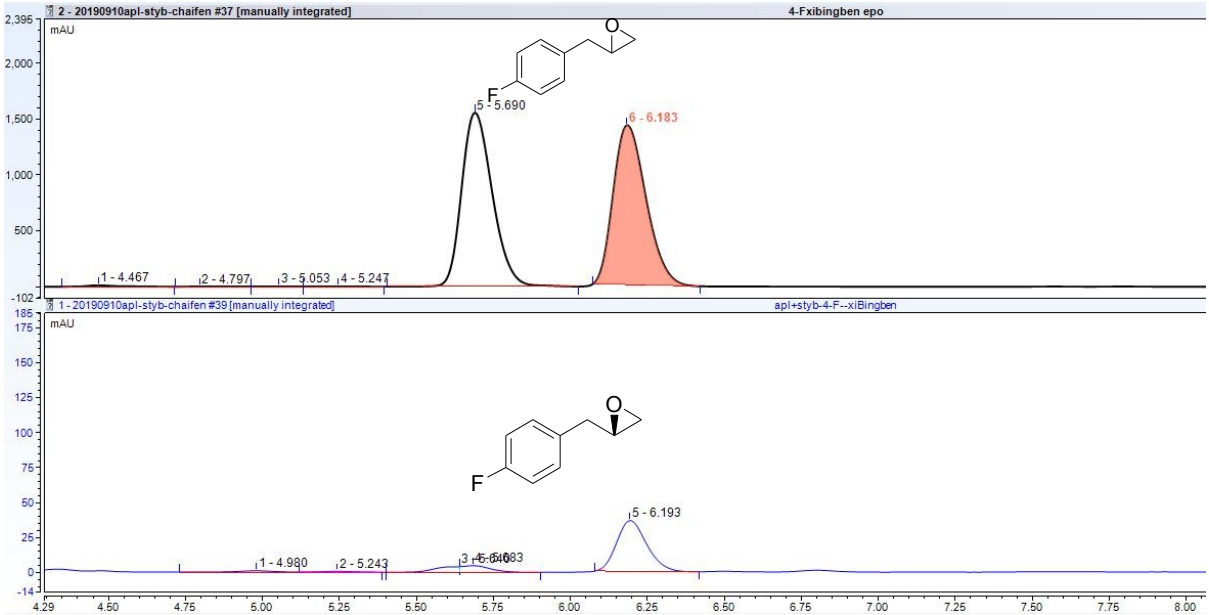
(*S*)-2-(3-fluorobenzyl)oxirane (**2b**)



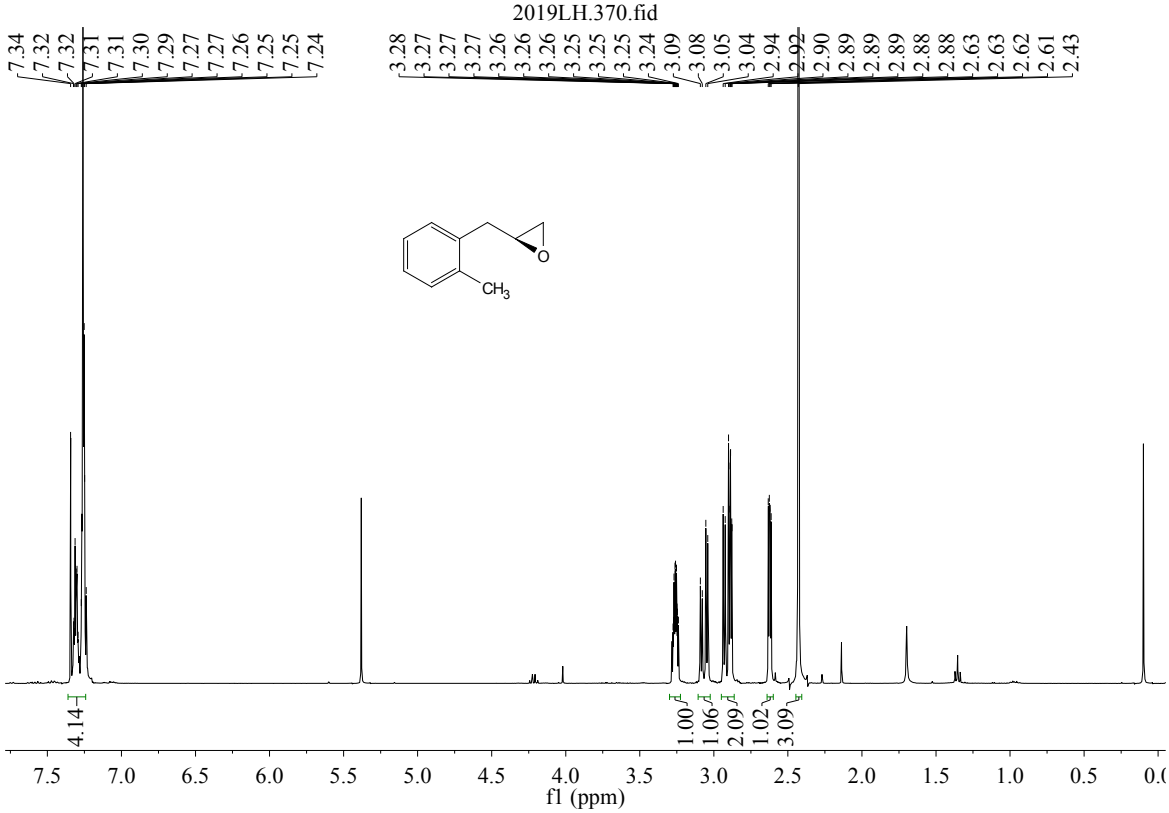
(*S*)-2-(4-fluorobenzyl)oxirane (**3b**)



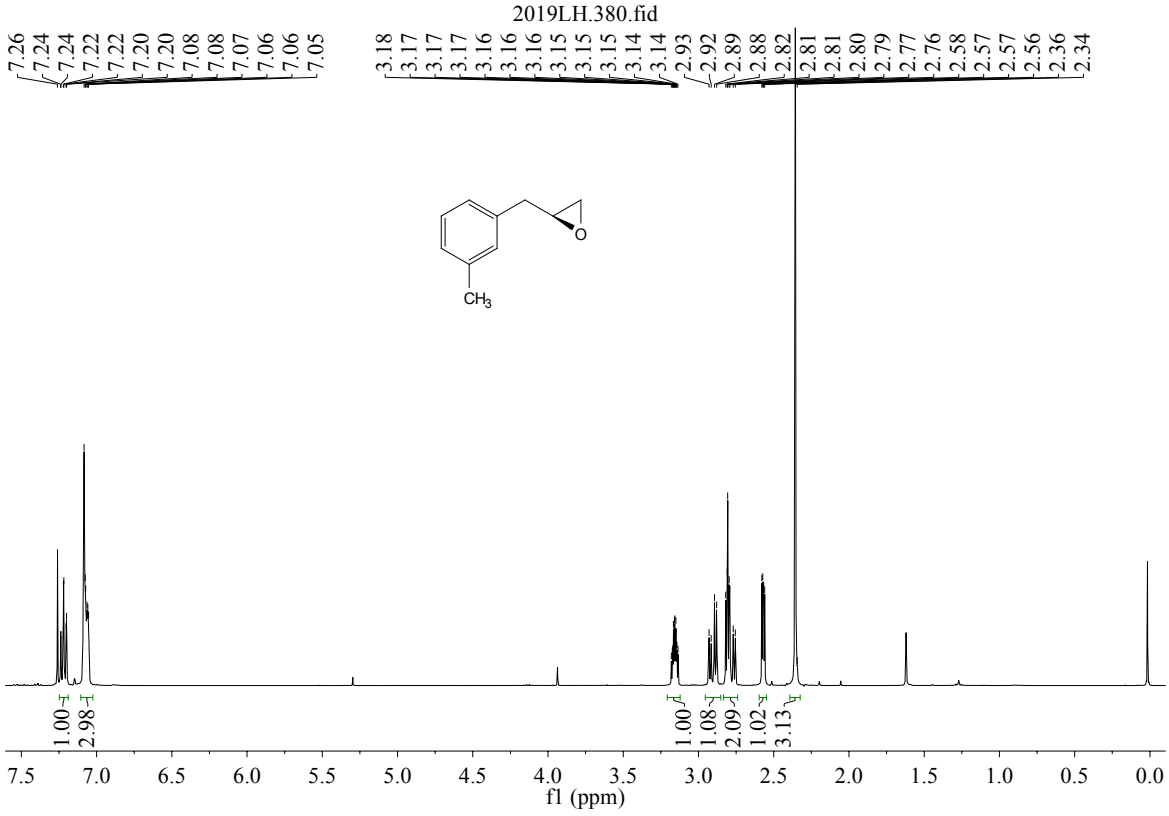
(*S*)-2-(4-fluorobenzyl)oxirane (**3b**)



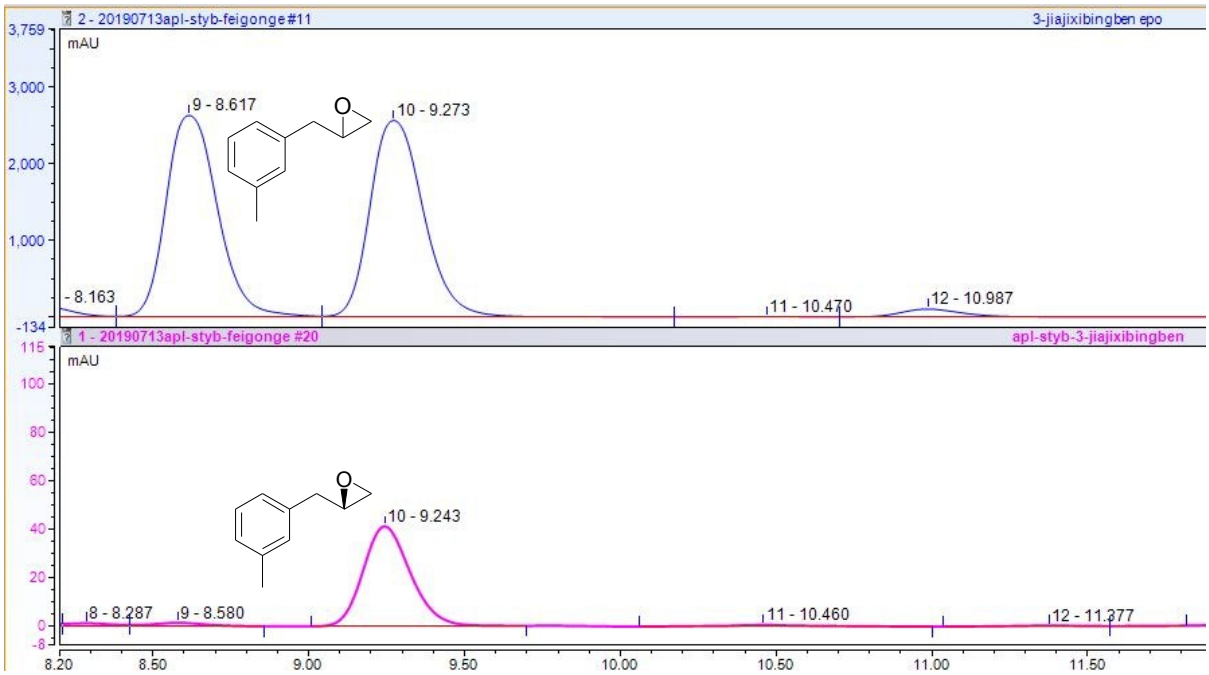
(*S*)-2-(2-methylbenzyl)oxirane (**4b**)



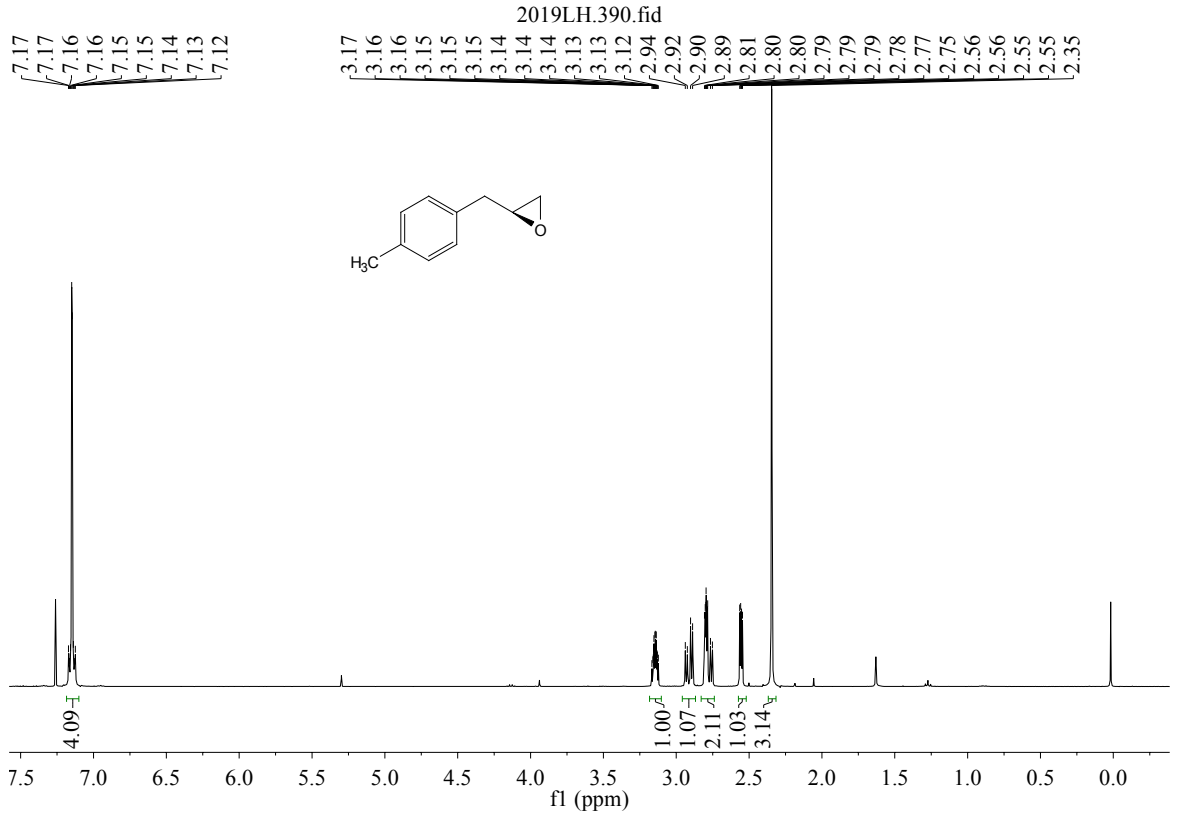
(*S*)-2-(3-methylbenzyl)oxirane (**5b**)



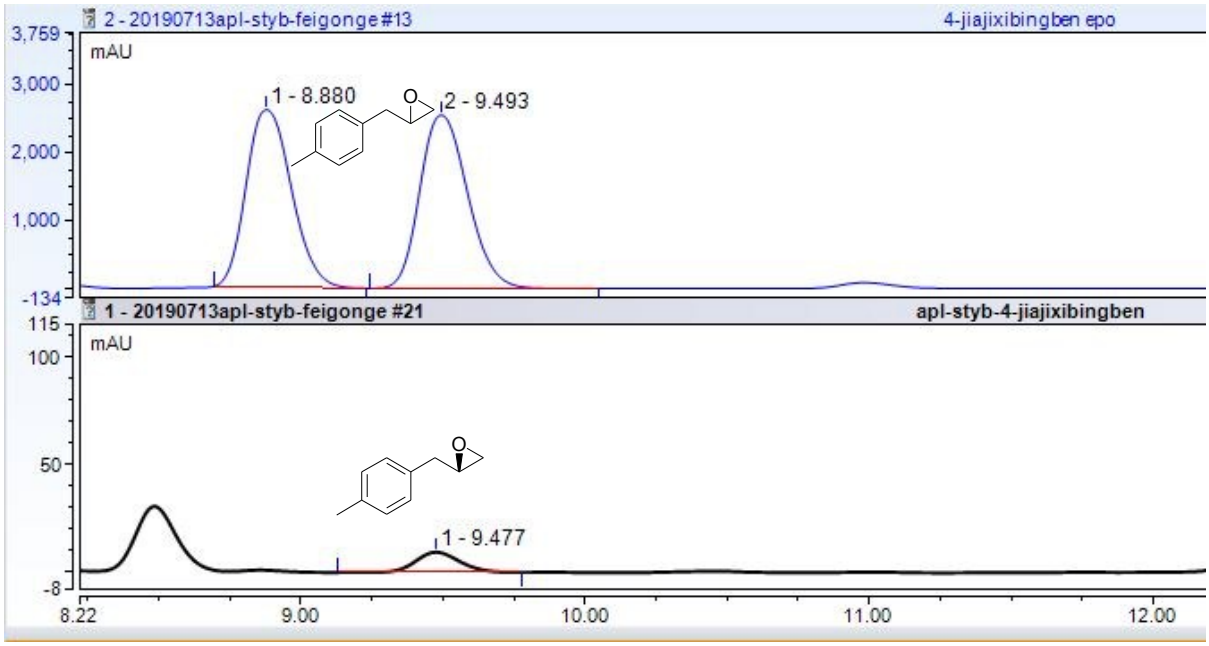
(*S*)-2-(3-methylbenzyl)oxirane (**5b**)



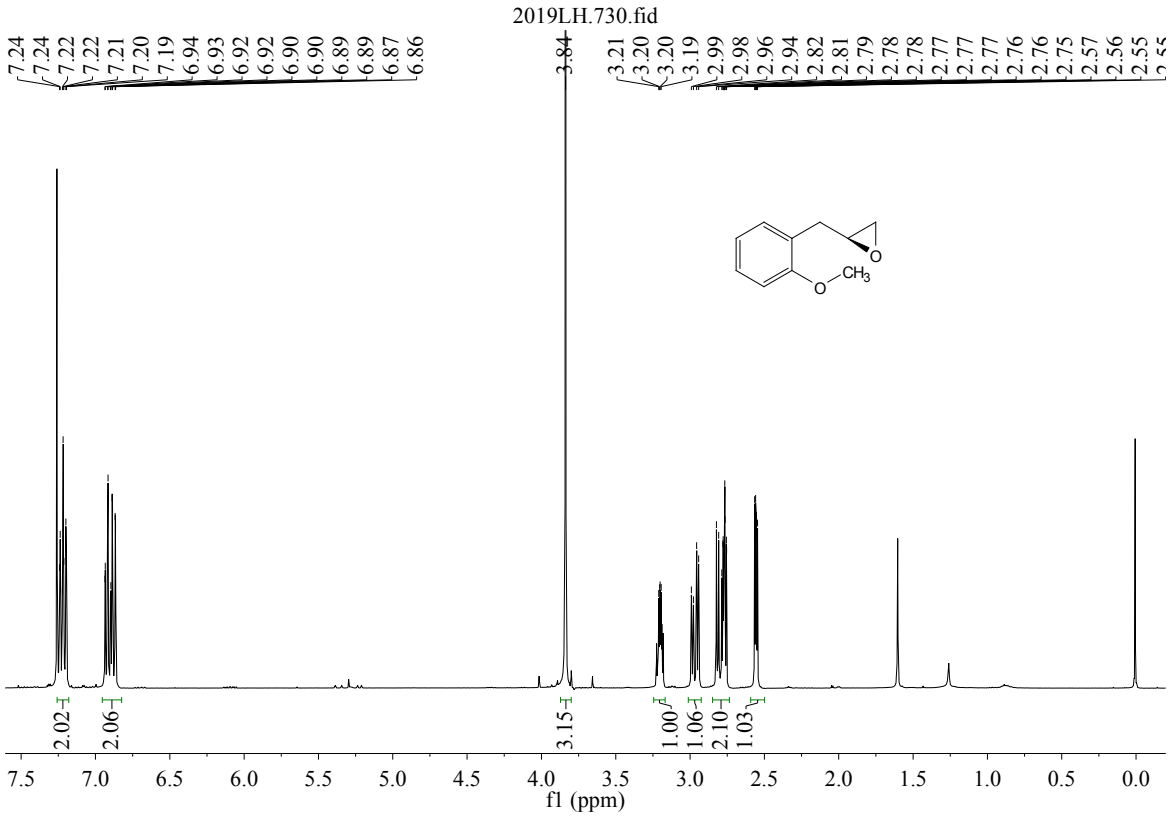
(*S*)-2-(4-methylbenzyl)oxirane (**6b**)



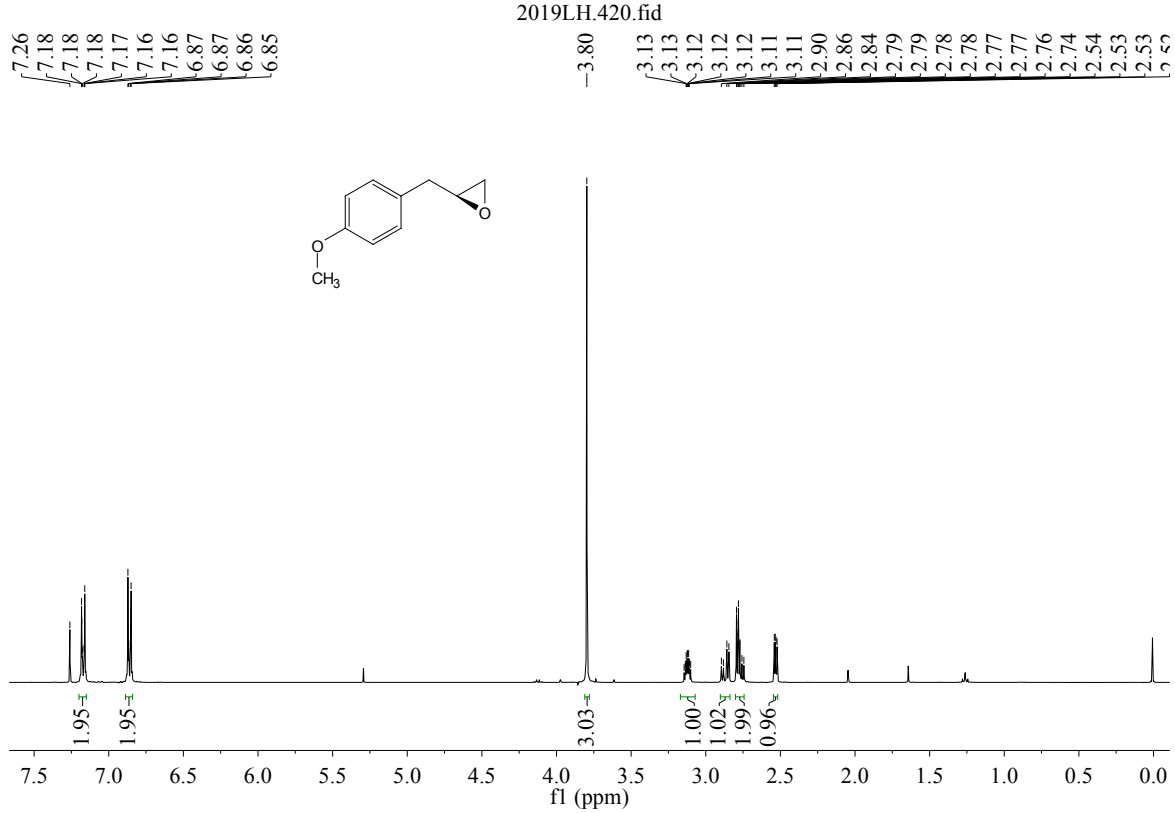
(*S*)-2-(4-methylbenzyl)oxirane (**6b**)



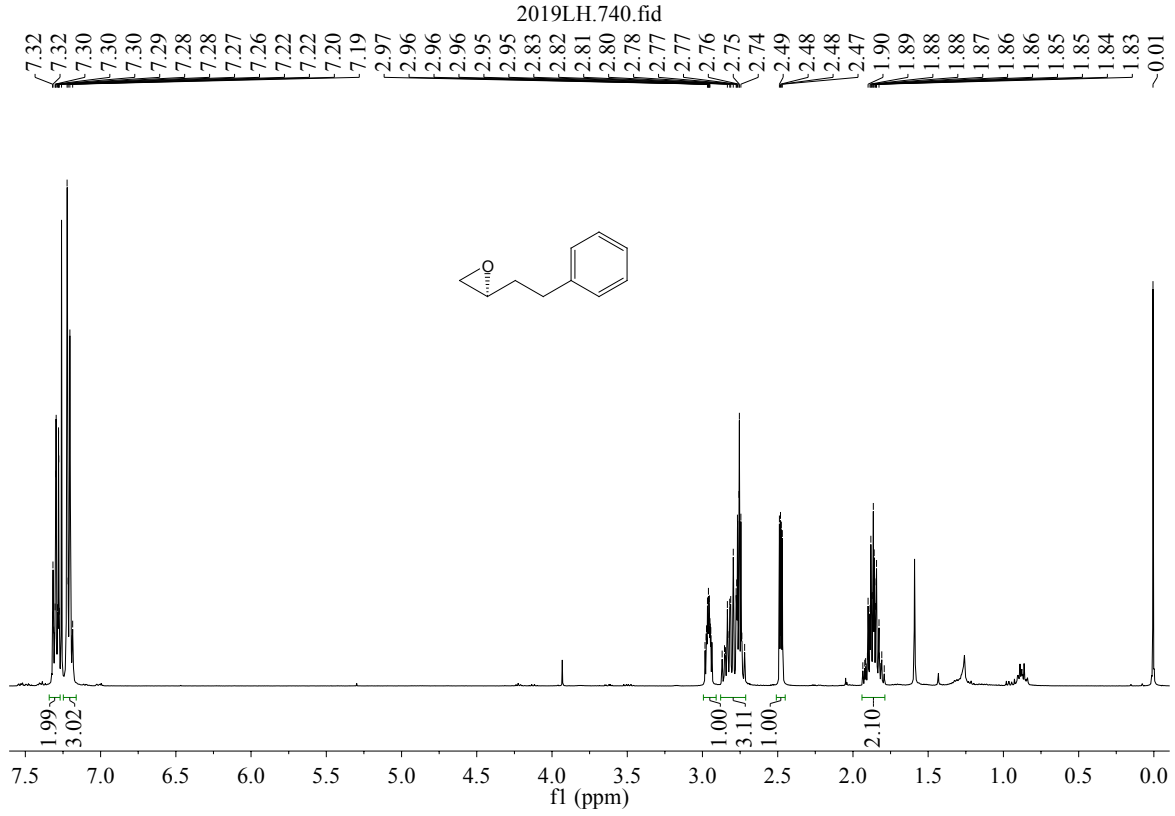
(*S*)-2-(3-methoxybenzyl)oxirane (**7b**)



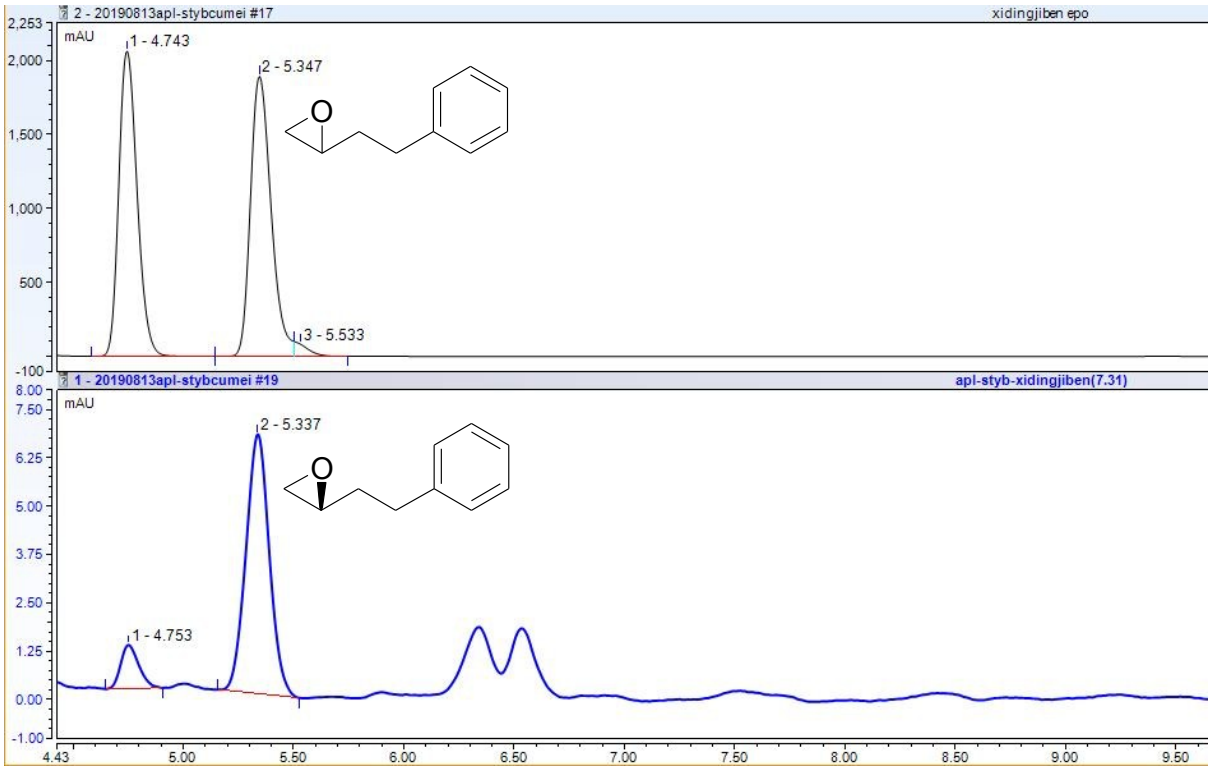
(*S*)-2-(4-methoxybenzyl)oxirane (**8b**)



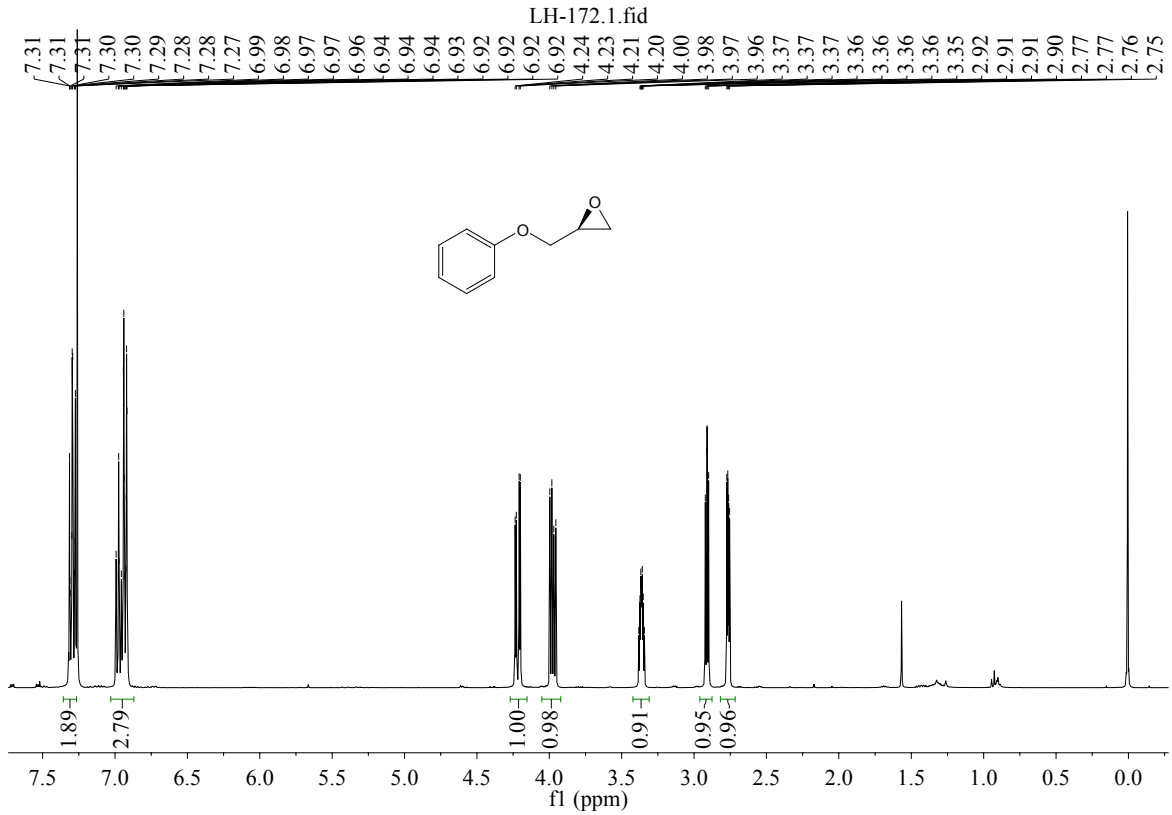
(*S*)-2-(3-methoxybenzyl)oxirane (**9b**)



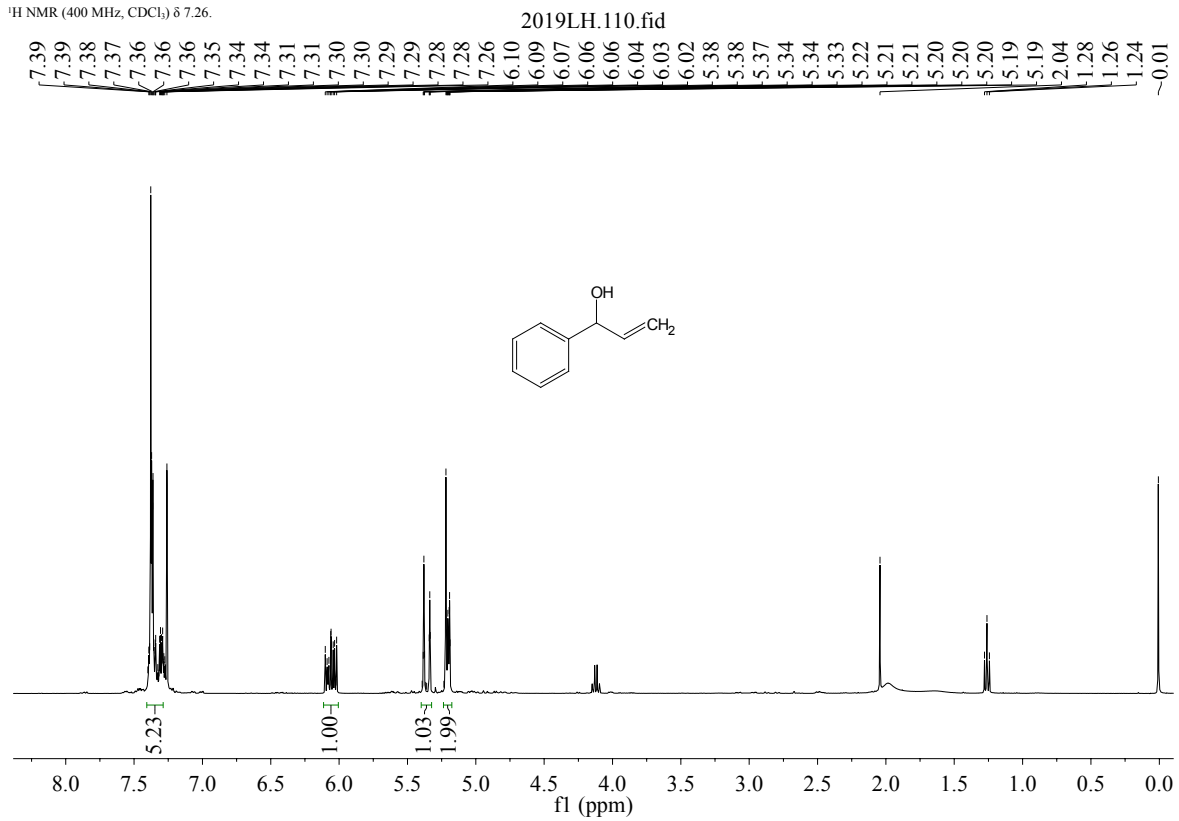
(*S*)-2-(3-methoxybenzyl)oxirane (**9b**)



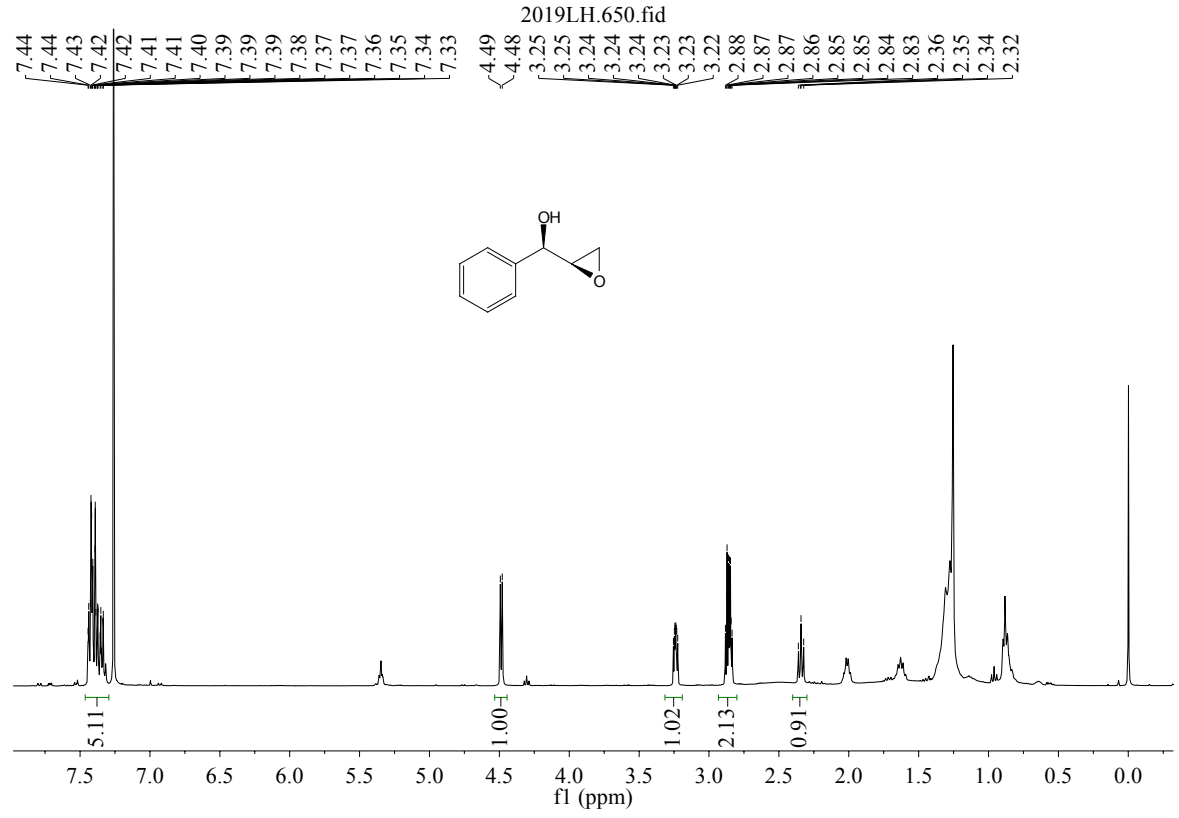
(*S*)-2-(phenoxymethyl)oxirane (**10b**)



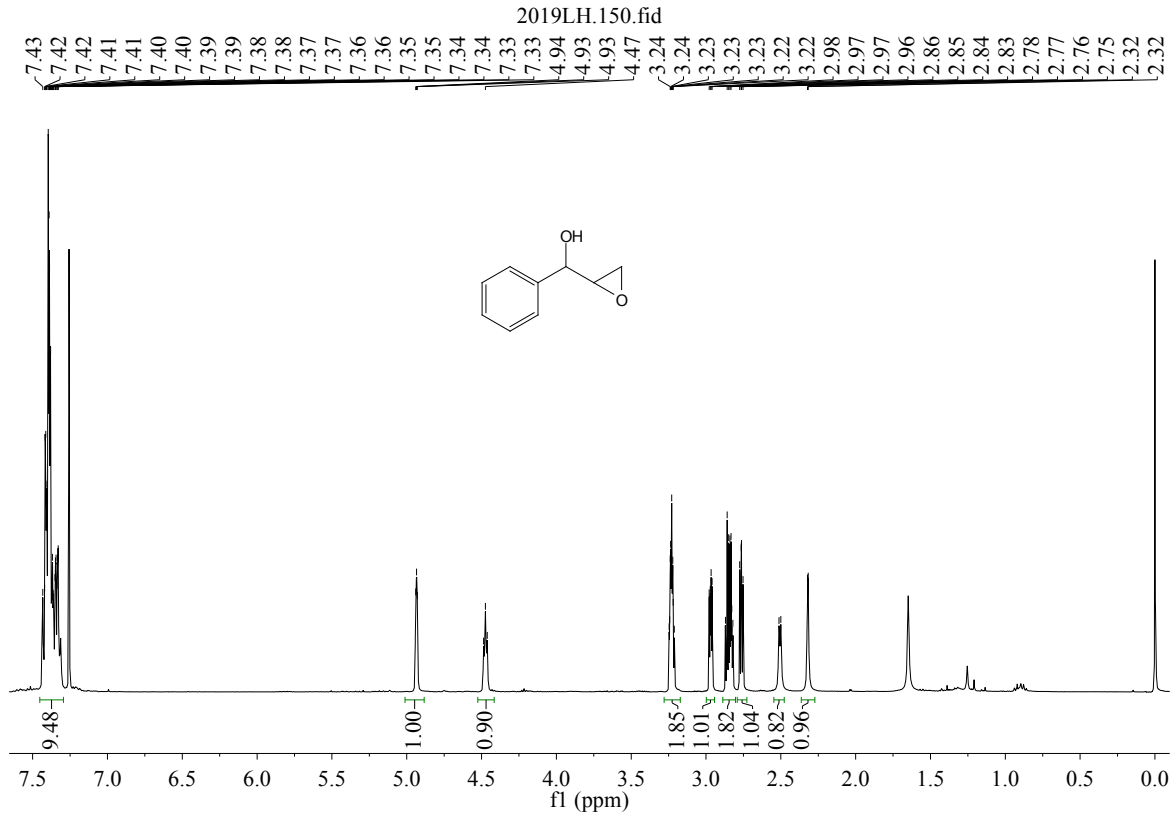
1-phenylprop-2-en-1-ol (**13a**)



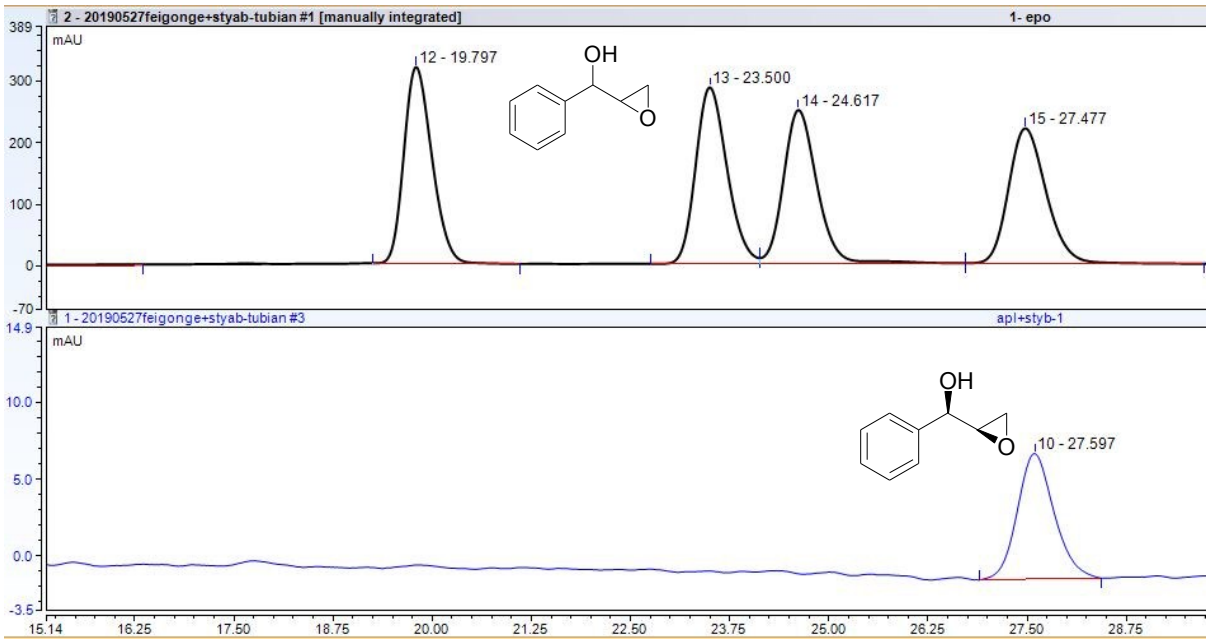
((*R*)-oxiran-2-yl)(phenyl)methanol (**13b**)



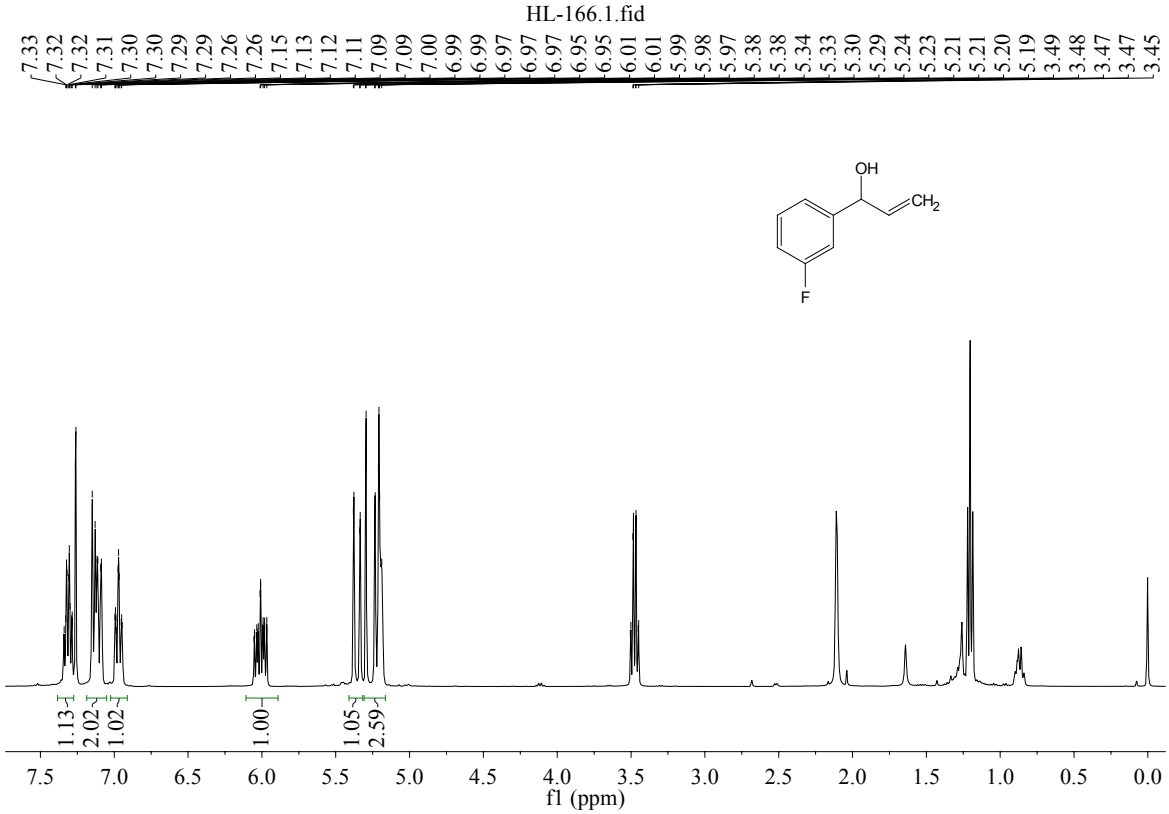
oxiran-2-yl(phenyl)methanol



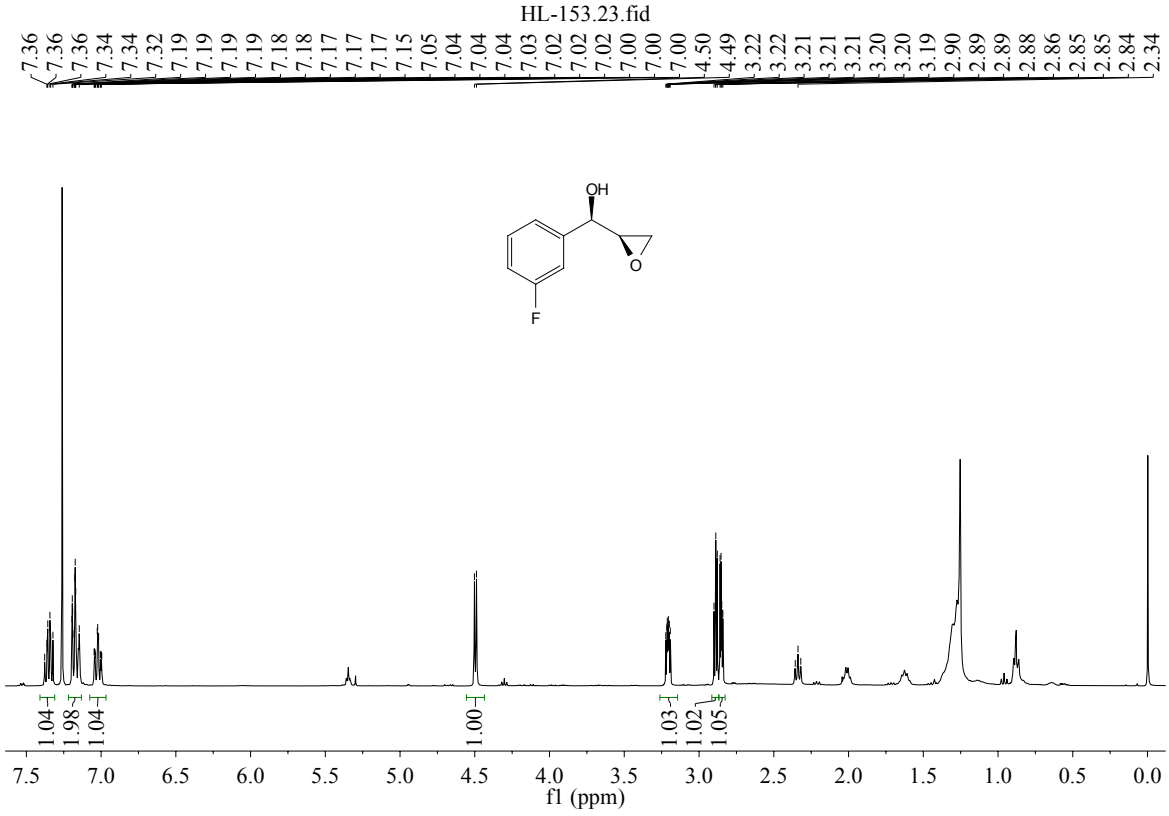
((*R*)-oxiran-2-yl)(phenyl)methanol (**13b**)



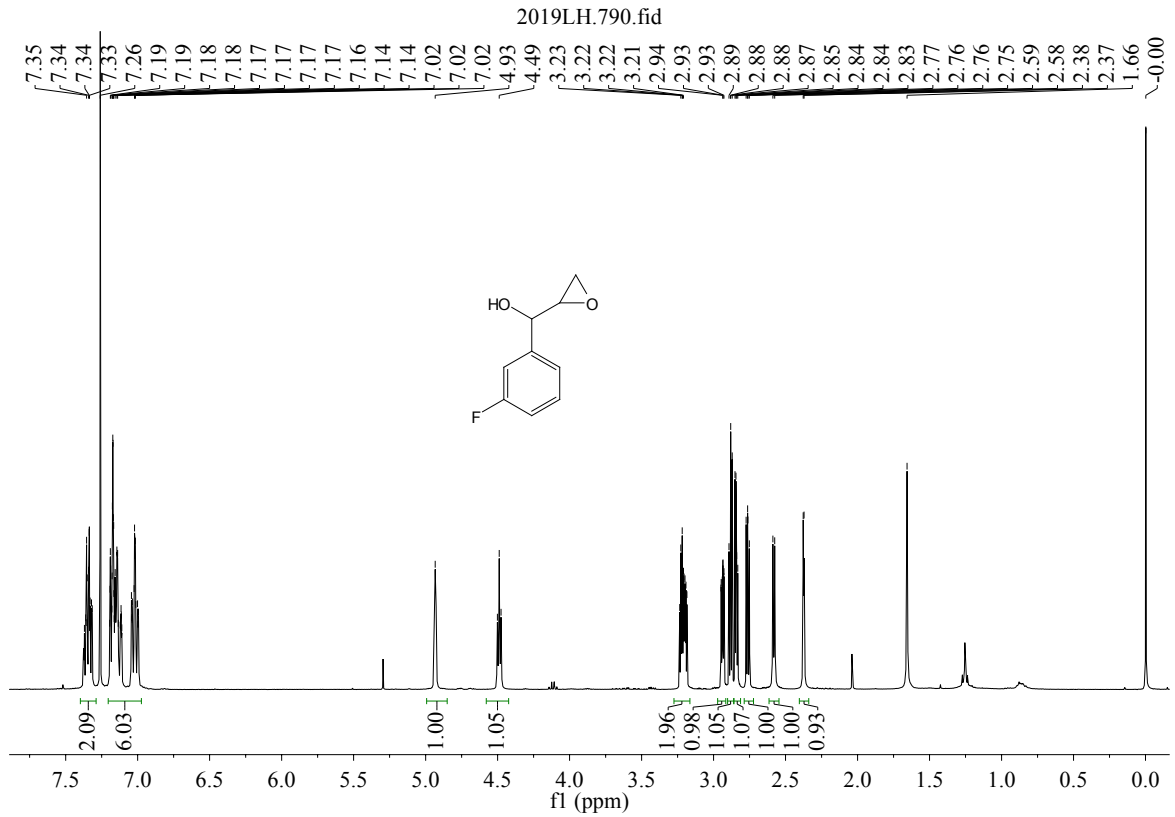
1-(3-fluorophenyl)prop-2-en-1-ol (**14a**)



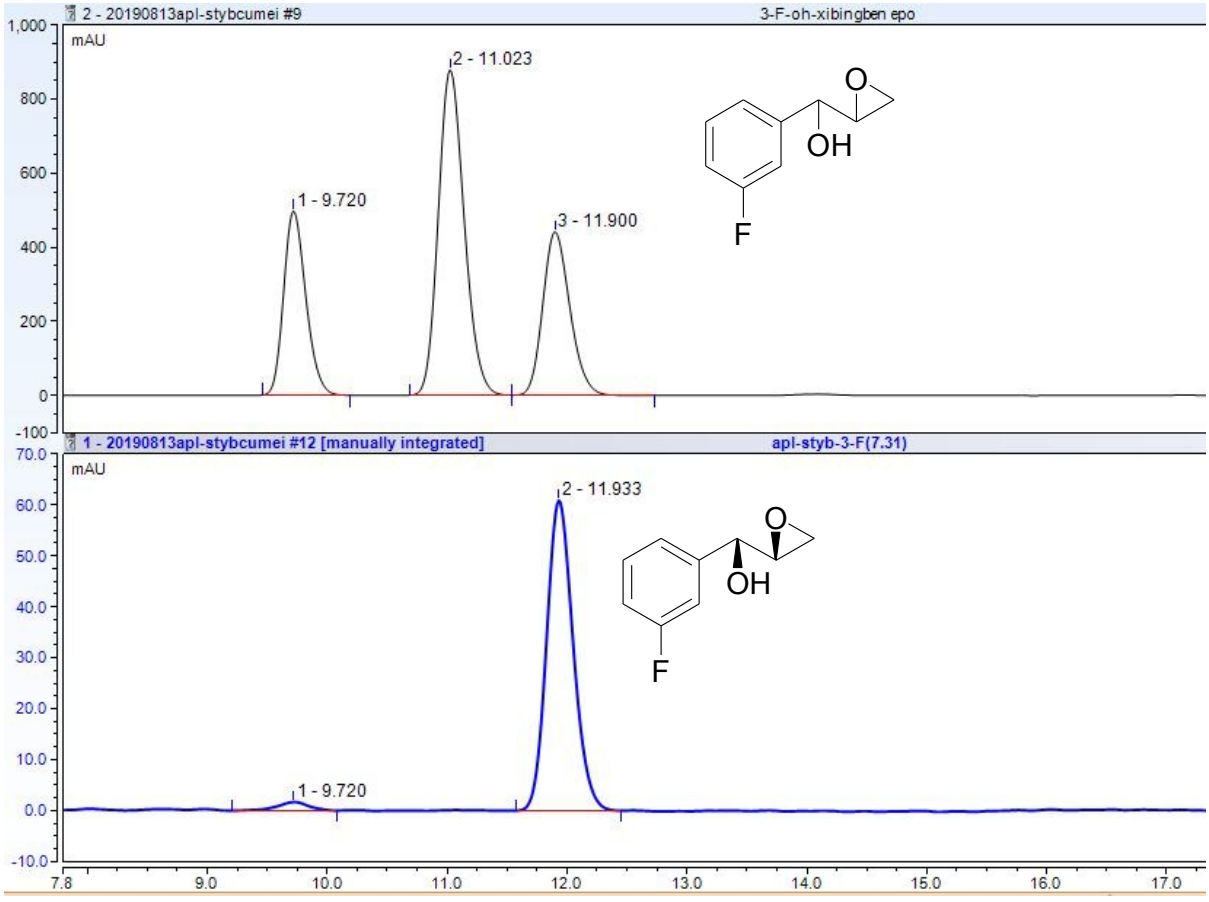
(*R*)-(3-fluorophenyl)((*R*)-oxiran-2-yl)methanol (**14b**)



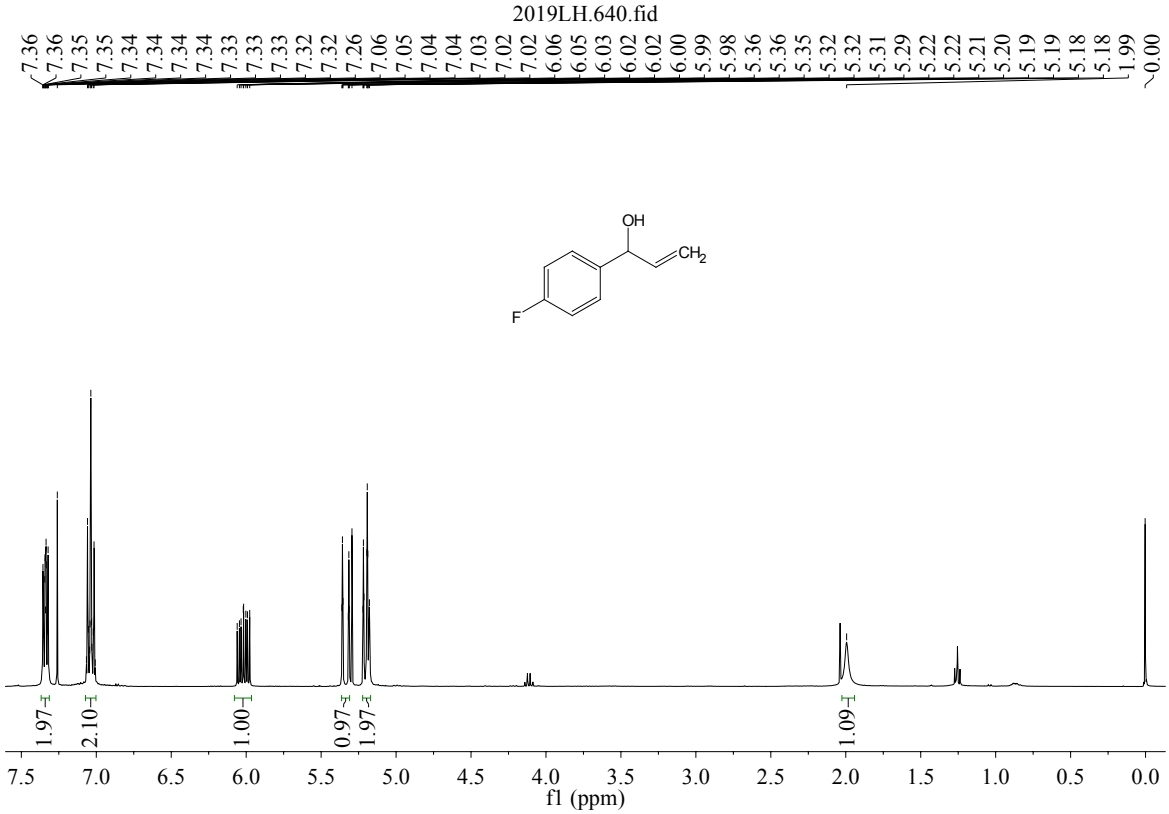
(3-fluorophenyl)(oxiran-2-yl)methanol



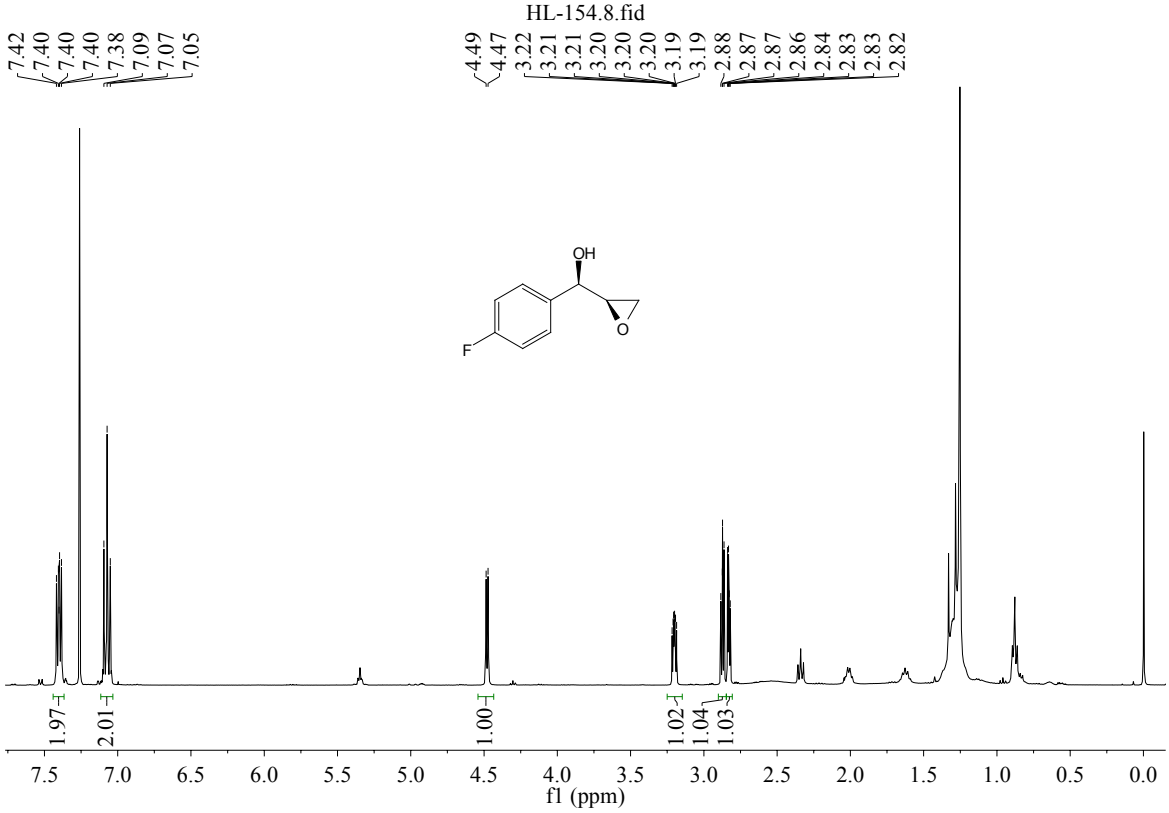
(*R*)-(3-fluorophenyl)((*R*)-oxiran-2-yl)methanol (**14b**)



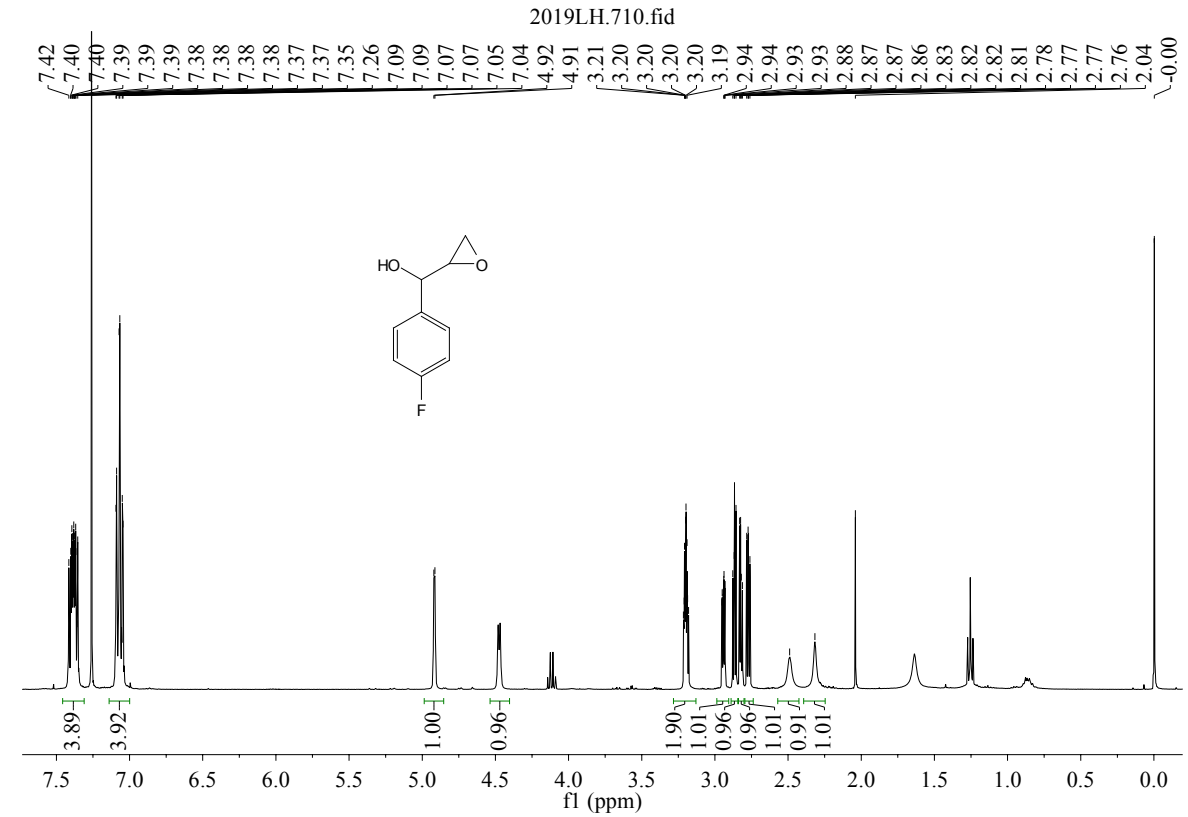
1-(4-fluorophenyl)prop-2-en-1-ol (**15a**)



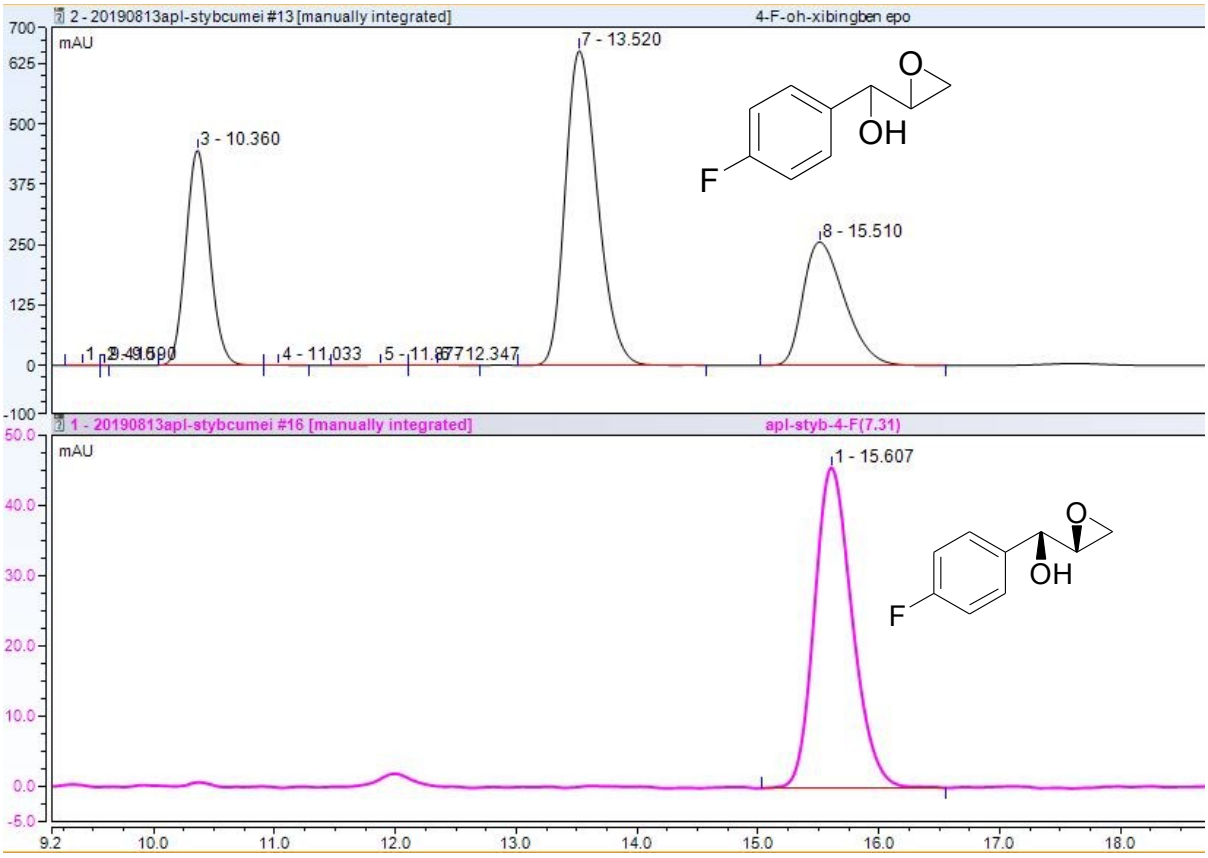
(*R*)-(4-fluorophenyl)((*R*)-oxiran-2-yl)methanol (**15b**)



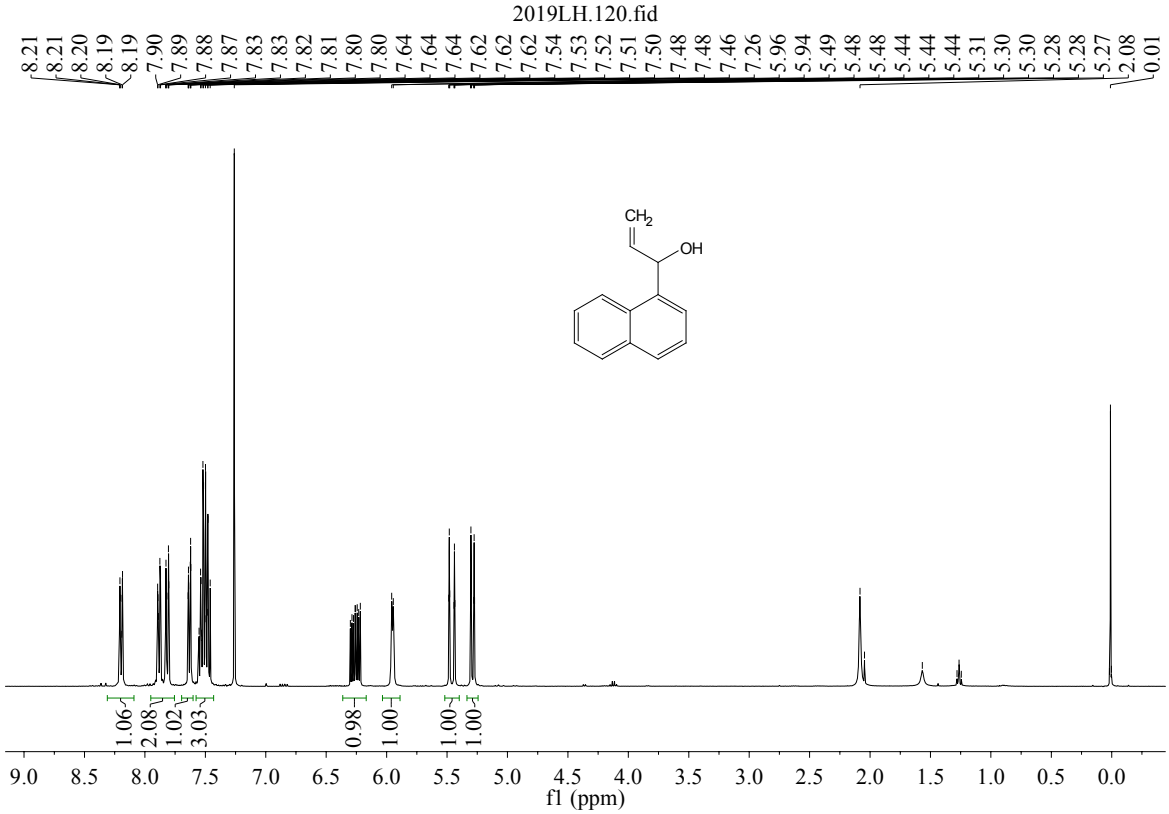
(4-fluorophenyl)(oxiran-2-yl)methanol



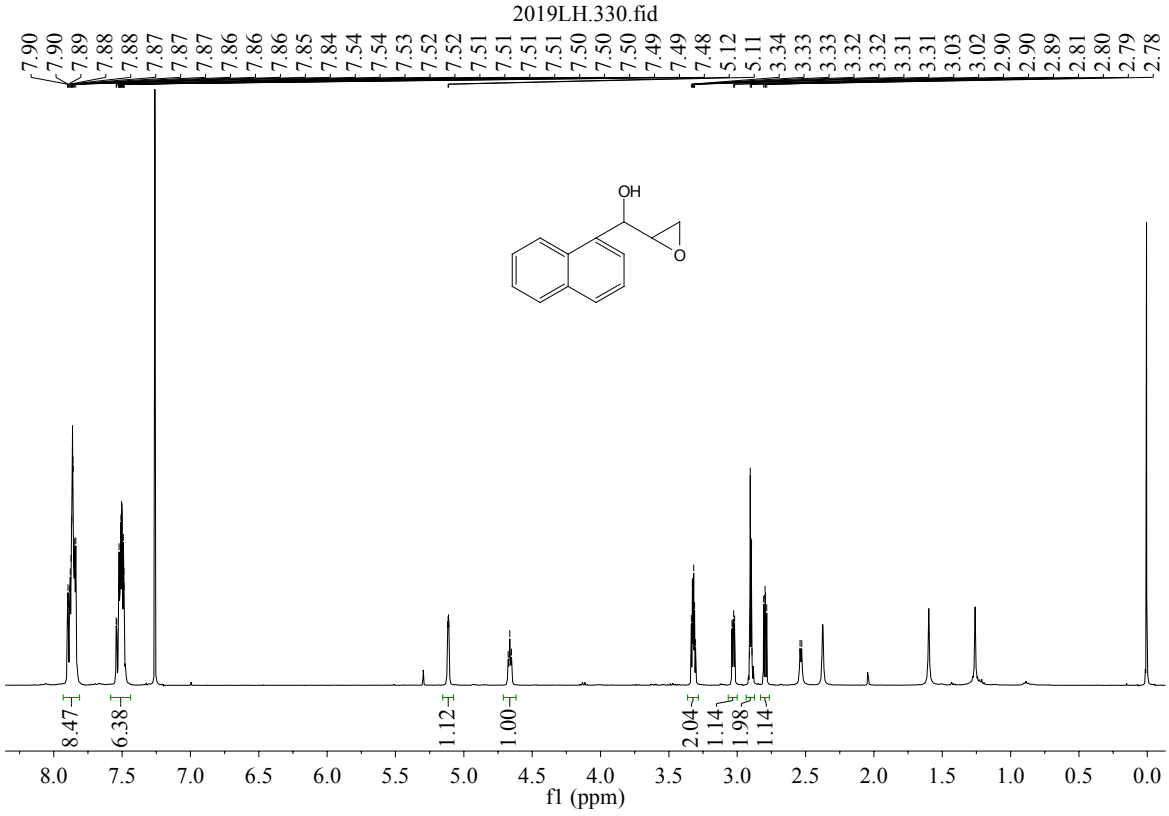
(*R*)-(4-fluorophenyl)((*R*)-oxiran-2-yl)methanol (**15b**)



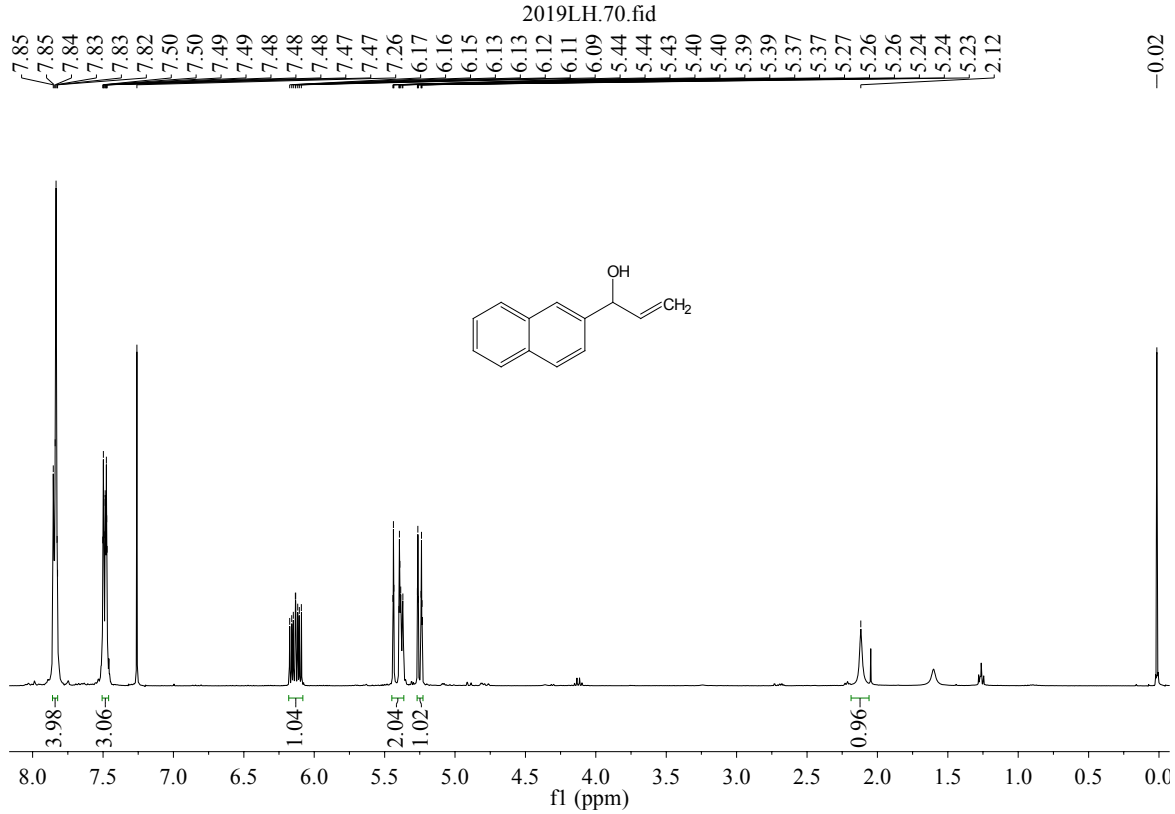
1-(naphthalen-1-yl)prop-2-en-1-ol (**16a**)



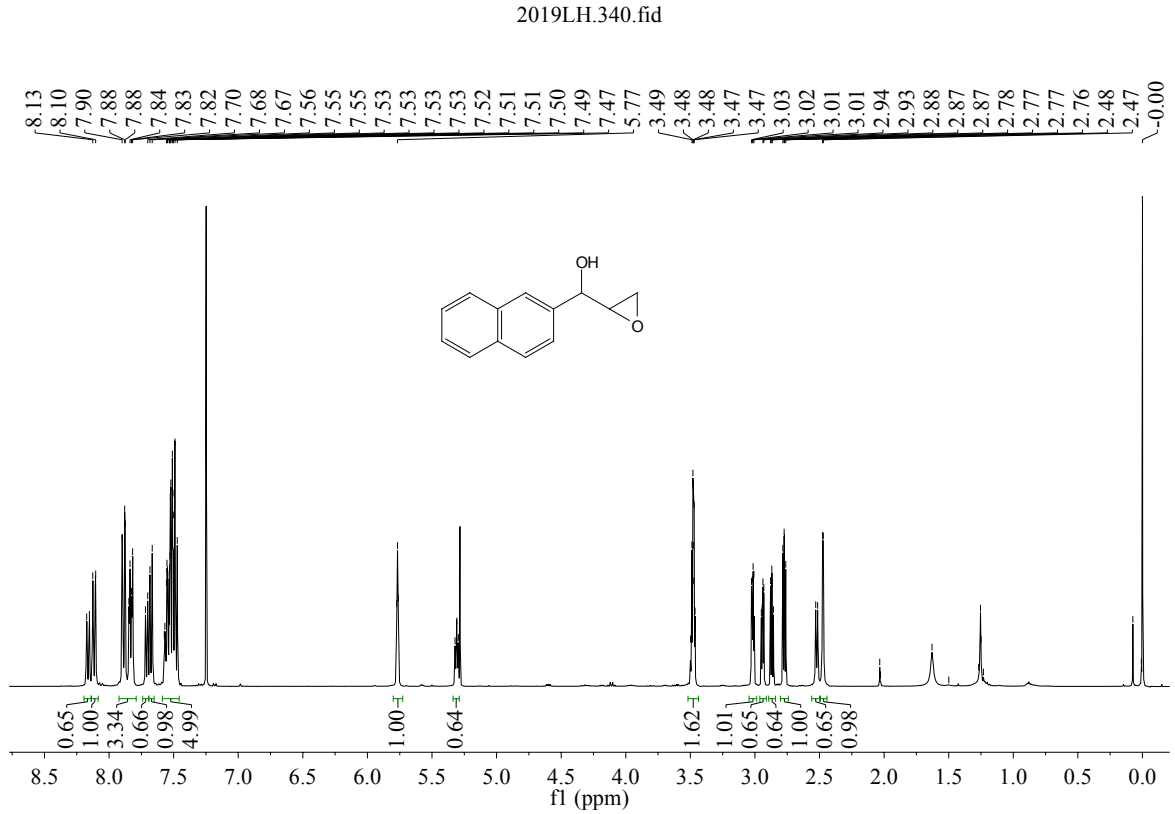
naphthalen-1-yl(oxiran-2-yl)methanol



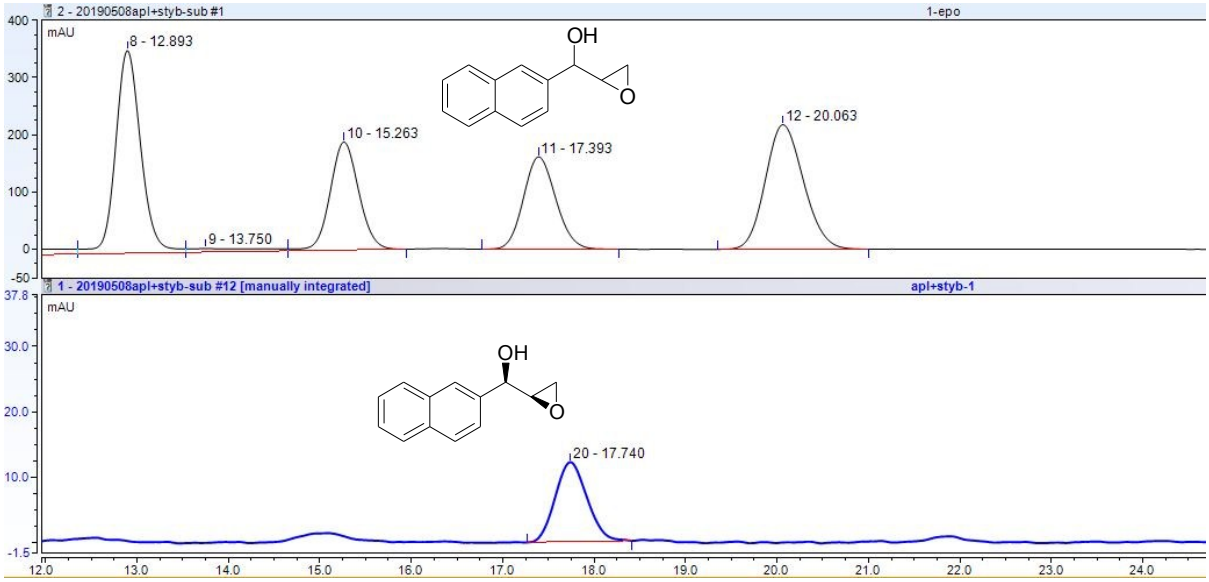
naphthalen-2-yl(oxiran-2-yl)methanol (**17a**)



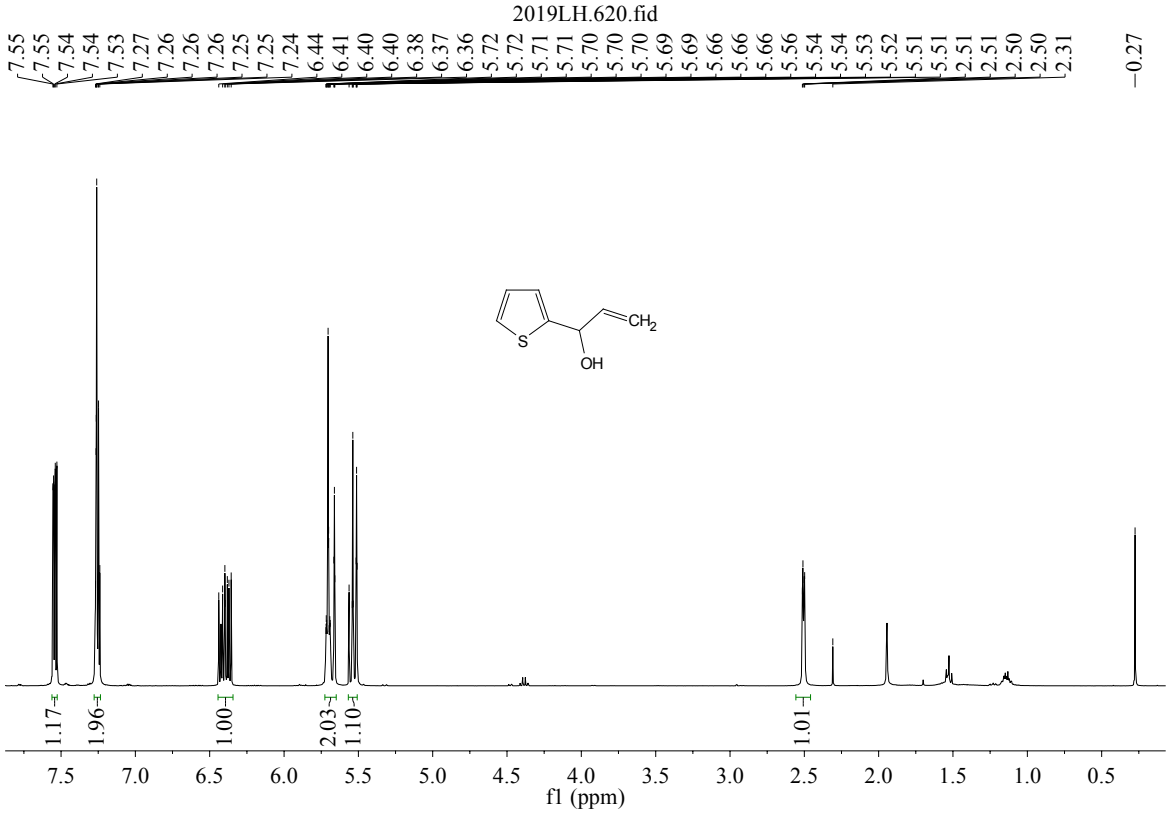
naphthalen-2-yl(oxiran-2-yl)methanol



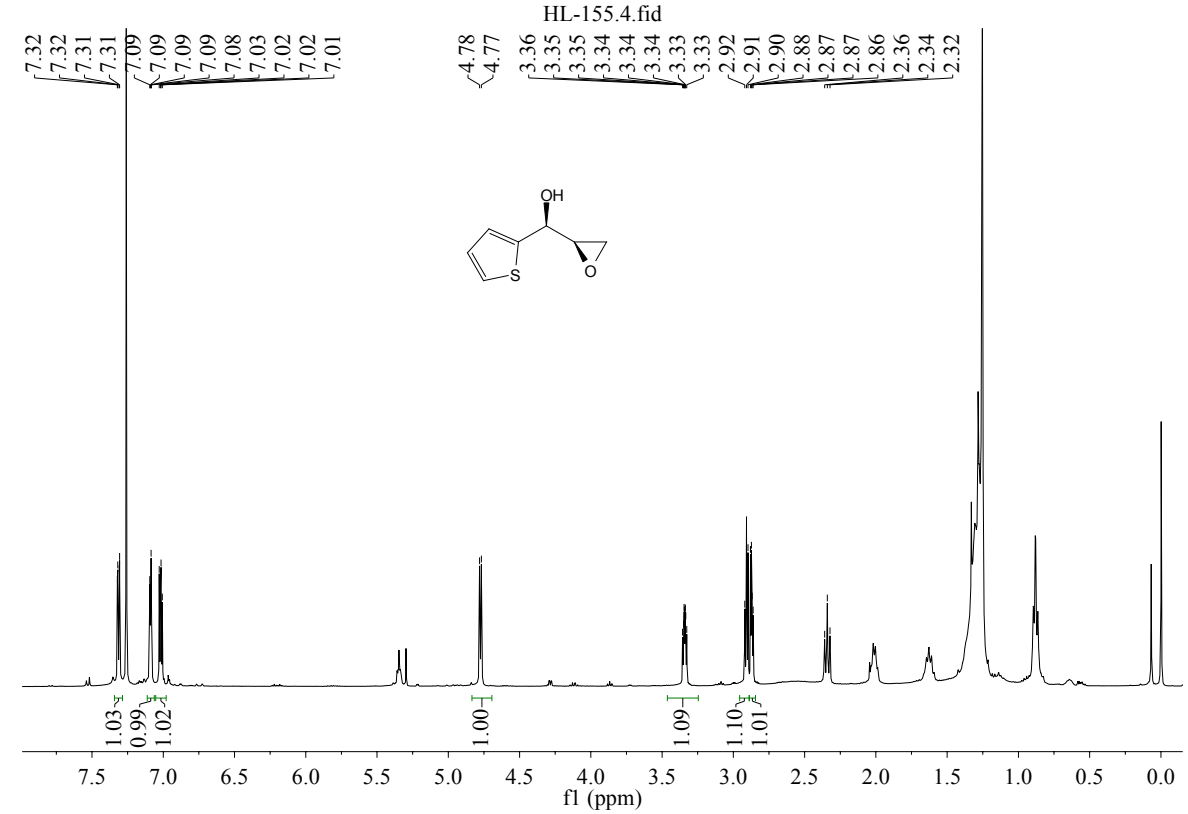
(*R*, *R*)-naphthalen-2-yl(oxiran-2-yl)methanol (**17b**)



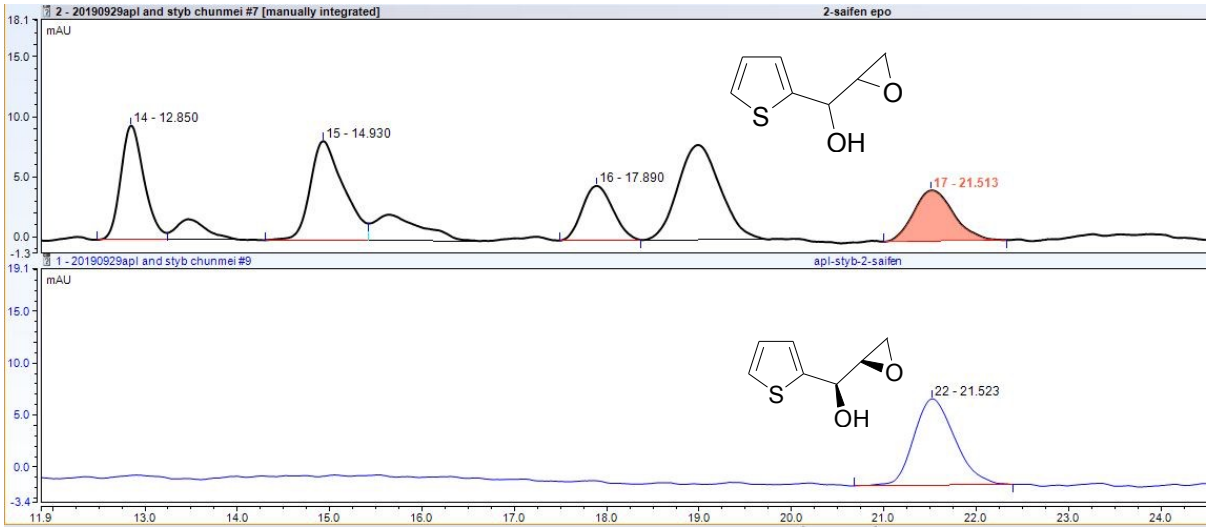
1-(thiophen-2-yl)prop-2-en-1-ol (**18a**)



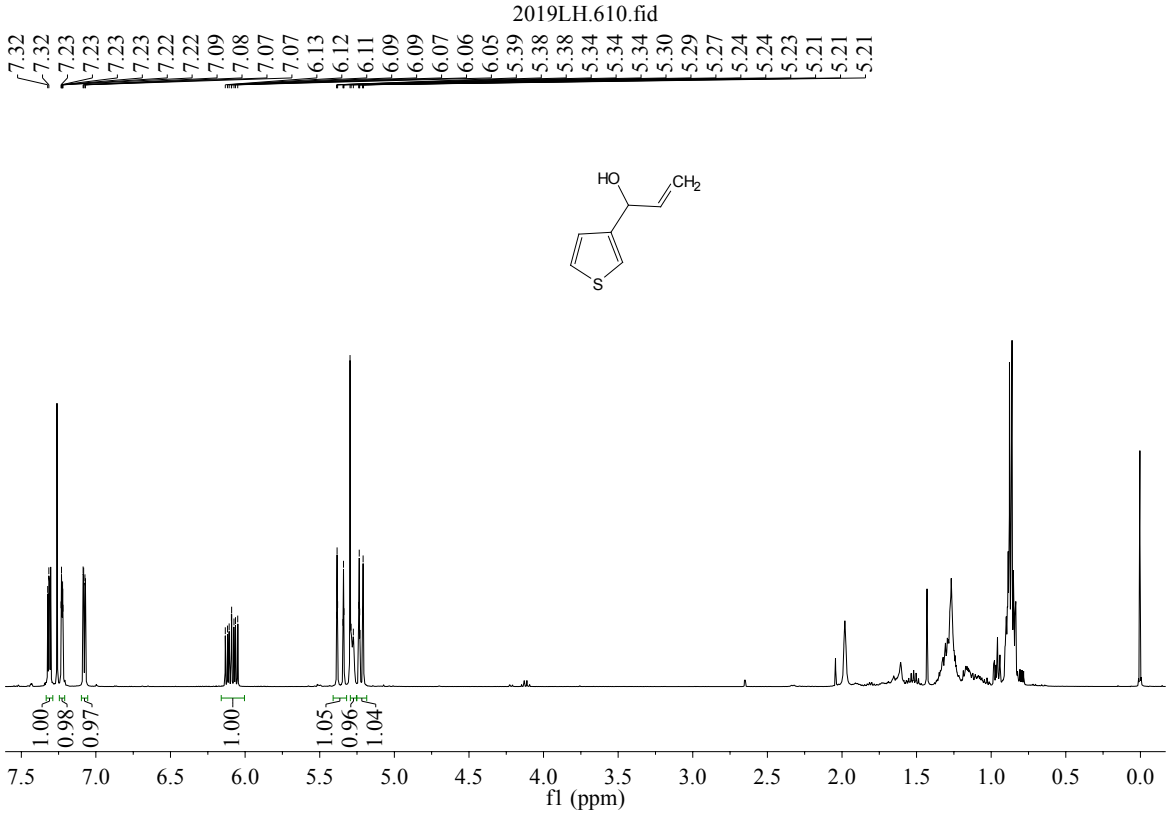
(*S*)-((*R*)-oxiran-2-yl)(thiophen-2-yl)methanol (**18b**)



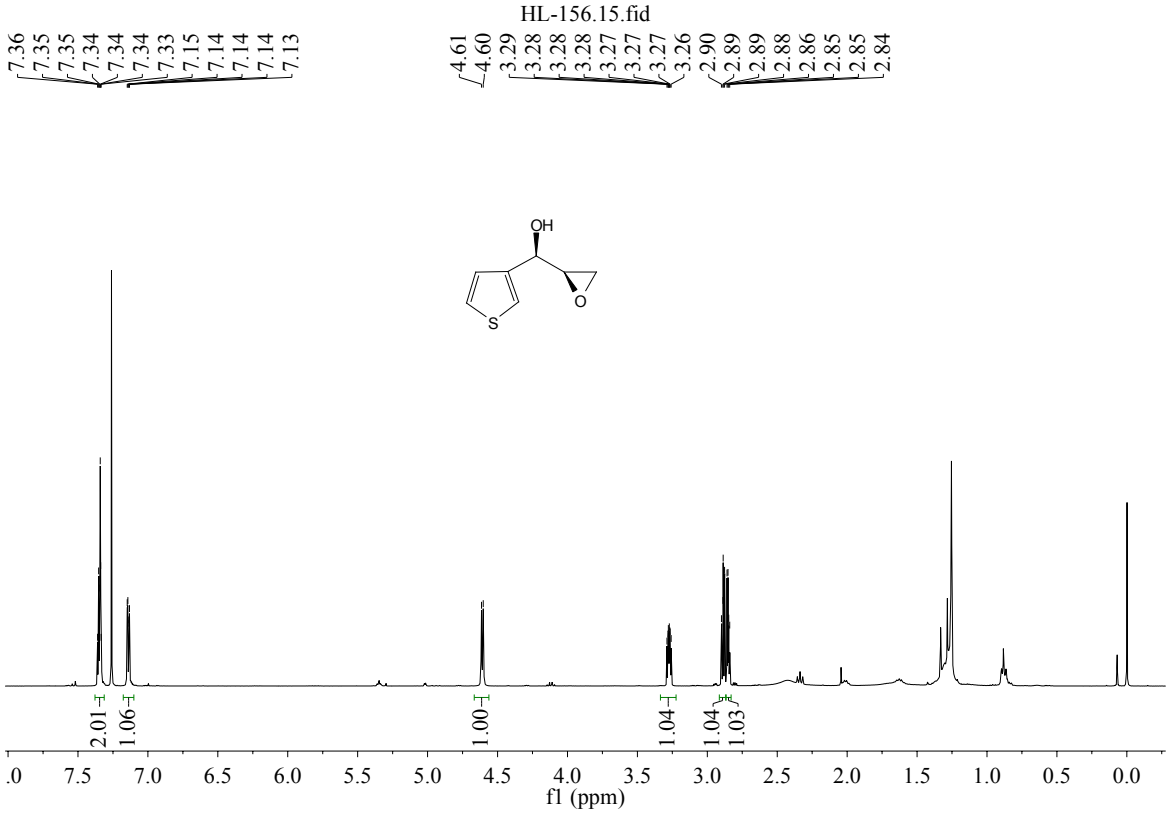
(*S*)-((*R*)-oxiran-2-yl)(thiophen-2-yl)methanol (**18b**)



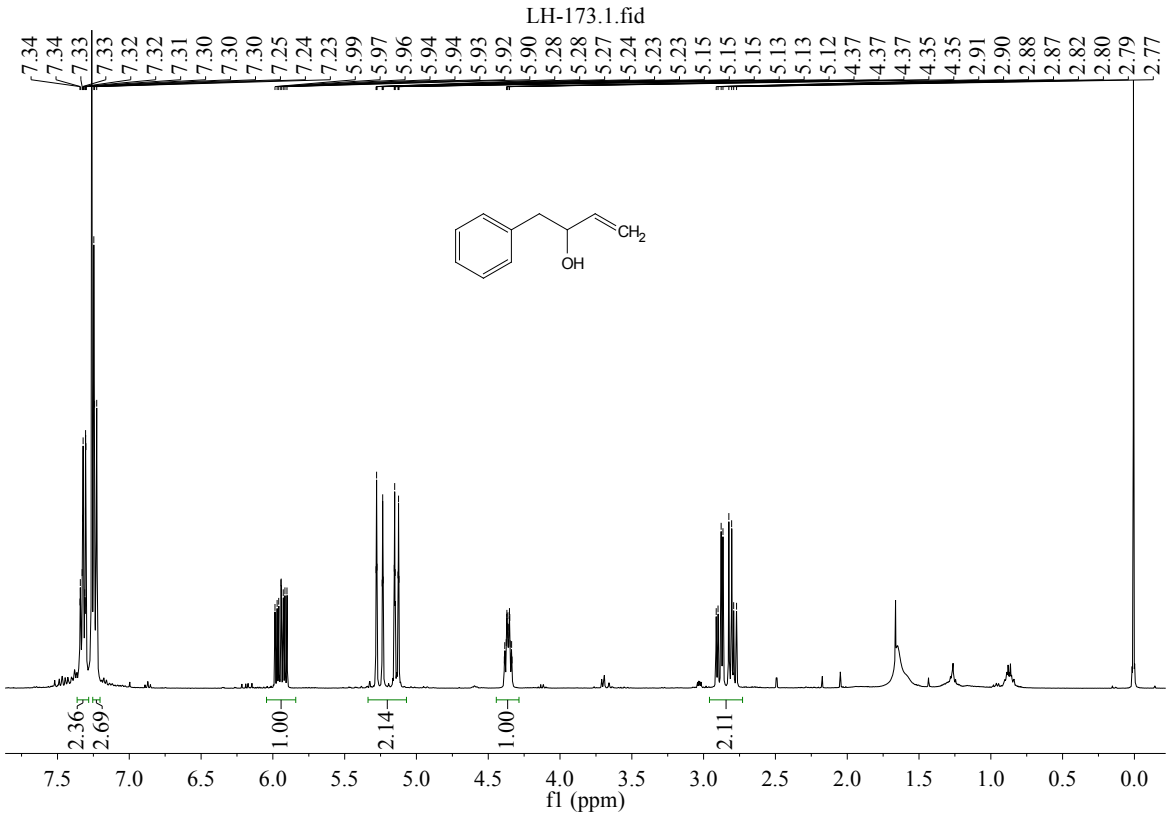
1-(thiophen-3-yl)prop-2-en-1-ol (**19a**)



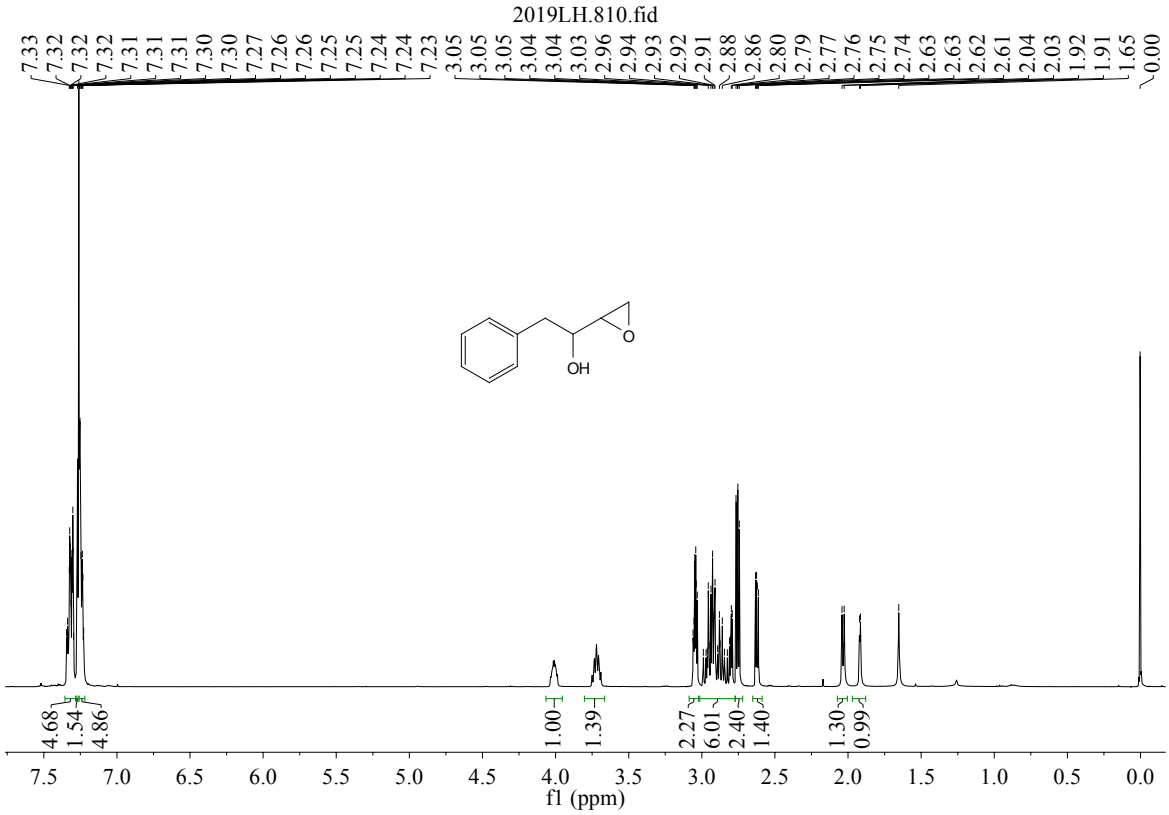
(*S*)-((*R*)-oxiran-3-yl)(thiophen-2-yl)methanol (**19b**)



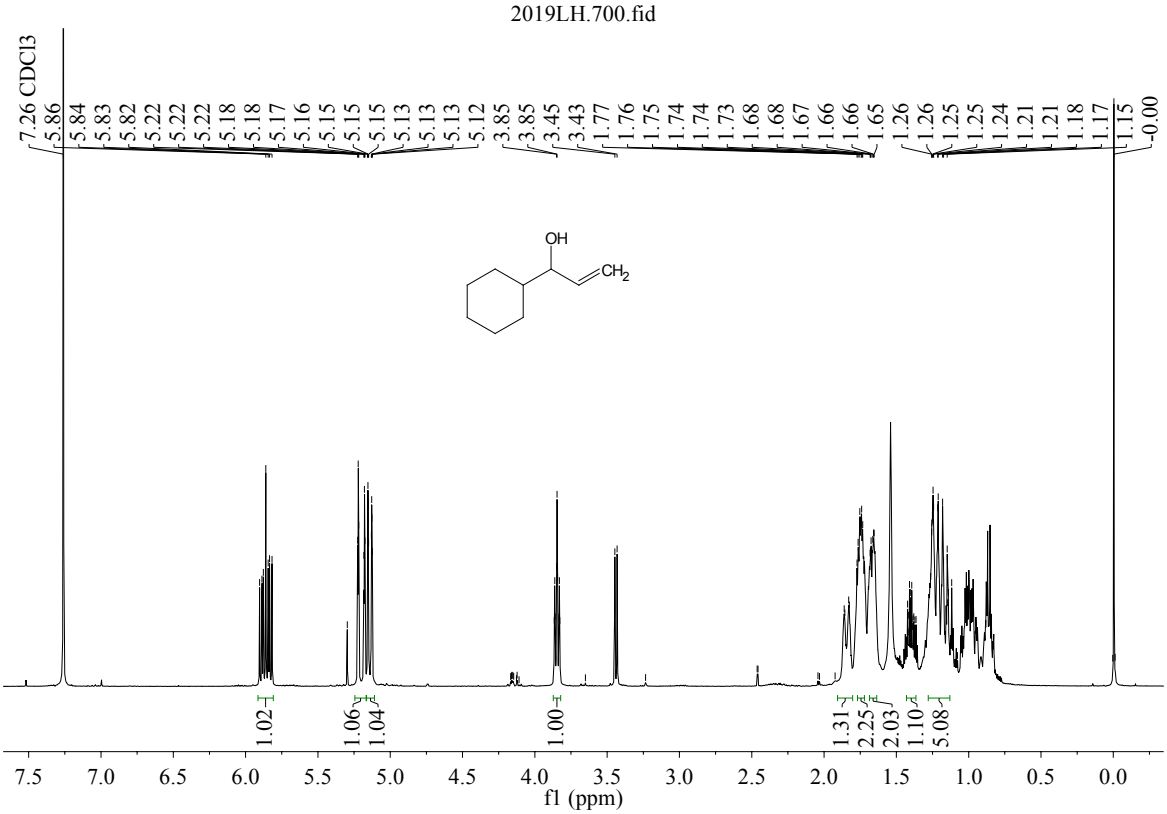
1-(oxiran-2-yl)-2-phenylethan-1-ol (**20a**)



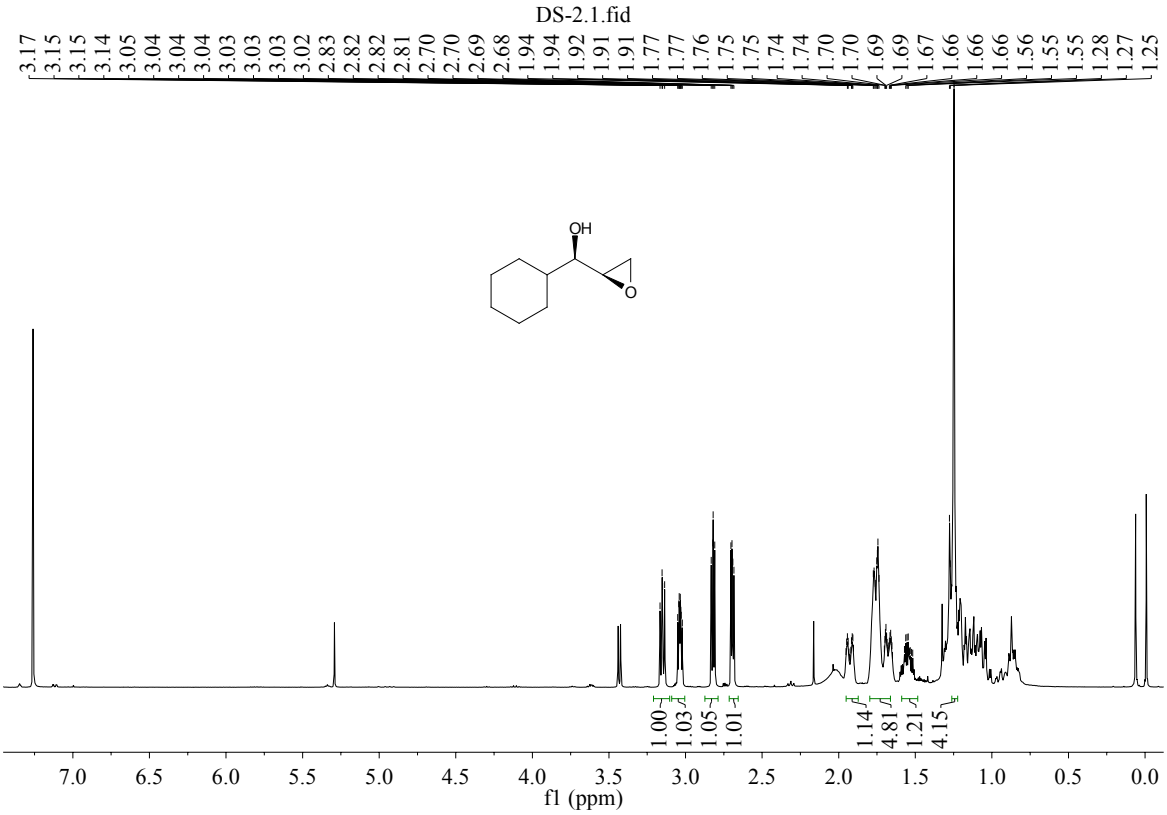
1-(oxiran-2-yl)-2-phenylethan-1-ol



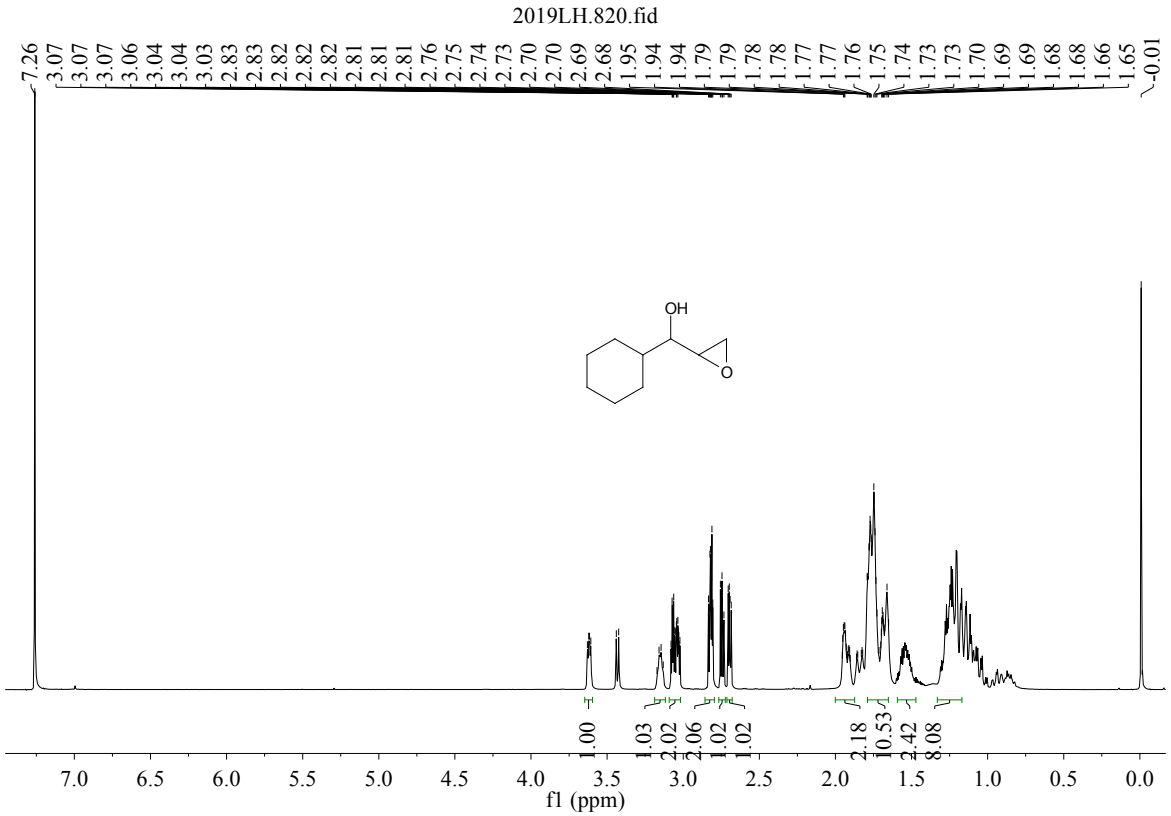
1-cyclohexylprop-2-en-1-ol (**21a**)



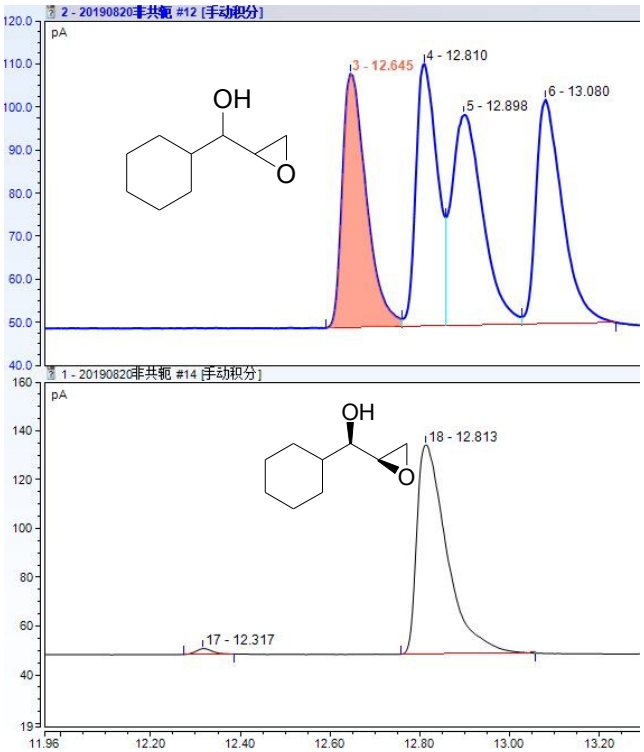
(*R*)-cyclohexyl((*R*)-oxiran-2-yl)methanol (**21b**)



cyclohexyl(oxiran-2-yl)methanol



(*R*)-cyclohexyl((*R*)-oxiran-2-yl)methanol (**21b**)



7. References

1. H. Lin, Y. Liu and Z.-L. Wu, *Chem. Commun.*, 2011, **47**, 2610-2612.

2. H. Lin, J. Qiao, Y. Liu and Z.-L. Wu, *J. Mol. Catal. B Enzym.*, 2010, **67**, 236-241.