

Supporting Information

for

One-pot synthesis of epoxides from benzyl alcohols and aldehydes

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Experimental procedures and characterization for all new compounds described herein

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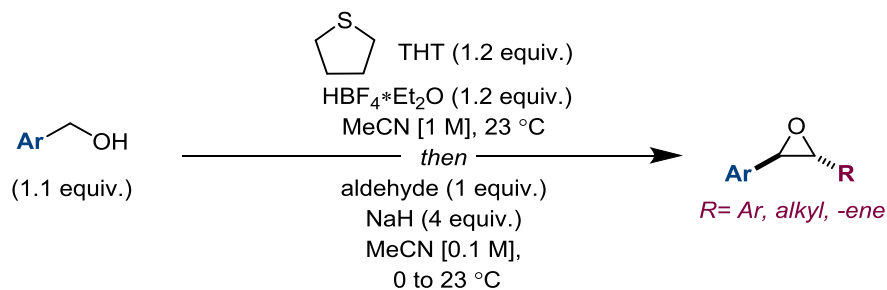
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General information:

¹H NMR and ¹³C NMR spectra were recorded at ambient temperature on a Varian Agilent-500 MHz VNMRs (500 and 126 MHz, respectively), and are internally referenced to the residual protio solvent signal (CDCl₃: δ 7.26 and 77.0 ppm). Data for ¹H NMR are reported as follows: chemical shift, multiplicity (brs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, *overlap* = overlapping peaks), coupling constants in Hz and integration. Data for ¹³C NMR are reported in terms of chemical shift and no special nomenclature is used for equivalent carbons. High-resolution mass spectra were obtained in the Boston University Chemical Instrumentation Center using a Waters Q-TOF APIUS mass spectrometer. Commercial reagents were purified prior to use following the guidelines of Chai and Armarego.¹ All solvents were purified according to the method of Grubbs.² Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. Chromatographic purification of products was accomplished by flash chromatography on Silicycle F60 silica gel or Sorbtech neutral alumina 32–63 μm according to the method of Still.³ All reactions were carried out in well ventilated fume hoods. Reactions were monitored by thin-layer chromatography (TLC) using Silicycle 250 μm silica gel plates or Sorbtech neutral alumina 250 μm. Visualization of the developed chromatogram was performed by irradiation with a 254 nm ultra-violet (UV) light or treatment with aqueous potassium permanganate (KMnO₄) or ethanolic phosphomolybdic acid (PMA) followed by heating. Yields refer to purified compounds unless otherwise noted.

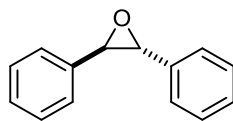
1. Chai, C.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; 6th ed.; Butterworth Heinemann: Oxford, **2009**.
2. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
3. Still, W. C.; Kahn, M.; Mitra, A. J. *Org. Chem.* **1978**, *43*, 2923.

General procedure for Corey–Chaykovsky epoxidation:



A flame-dried round bottom flask (for 3 mmol: 50 mL flask, 5 mmol: 100 mL, 10 mmol: 250 mL) with a magnetic stirring bar was charged with the benzyl alcohol (1.1 equiv), tetrahydrothiophene (THT) (1.2 equiv), and acetonitrile (MeCN) ([1 M] *with respect to (w.r.t.)* the benzyl alcohol). Thereafter, tetrafluoroboric acid diethyl ether complex (HBF₄·OEt₂) (1.2 equiv) was added dropwise and the reaction was left to stir until full consumption of the alcohol was observed by TLC (1:1 hexanes (Hex)/ethyl acetate (EtOAc)) or for a 12 h period. The reaction was then cooled to 0 °C (water/ice bath), diluted with MeCN ([0.1 M] *w.r.t.* aldehyde) and sodium hydride (NaH) (4 equiv) was added in small portions. After stirring for 5 minutes the aldehyde (1 equiv.) was added dropwise or in small portions (solids). The reaction was left to stir until full consumption of the aldehyde was seen by TLC (4:1 Hex/EtOAc) or for a 12 h period. Then, the reaction was cooled to 0 °C and water was added dropwise until no further gas evolution was observed. The mixture was concentrated *in vacuo* and the resultant residue was introduced into a separatory funnel with the assistance of water and EtOAc. The mixture was extracted three times with EtOAc and the combined organic fractions were dried over MgSO₄ and concentrated *in vacuo*. The resultant material was purified by flash chromatography. Diastereoselectivity was determined by crude ¹H NMR prior to purification unless otherwise noted.

Synthesis of **(2R,3R)-2,3-diphenyloxirane (6)** from *phenylmethanol* and *benzaldehyde*:



6

Chemical Formula: C₁₄H₁₂O

Exact Mass: 196.09

Scale: 3 mmol

Flash Chromatography: 10:1 Hex/EtOAc

TLC: R_f = 0.3 in 10:1 Hex/EtOAc, Stain: PMA (color:green)

Physical state: *white solid*

% yield: 91% (535 mg)

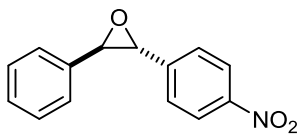
d.r. >20:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.43 – 7.29 (m, 10H), 3.88 (s, 2H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 137.24, 128.70, 128.46, 125.64, 62.99.

Synthesis of **(2R,3R)-2-(4-nitrophenyl)-3-phenyloxirane (7)** from *phenylmethanol* and *4-nitrobenzaldehyde*:



7

Chemical Formula: C₁₆H₁₃NO₂

Exact Mass: 251.09

Scale: 3 mmol

Flash Chromatography: 20:1 Hex/EtOAc → 10:1 Hex/EtOAc

TLC: R_f = 0.6 in 20:1 Hex/EtOAc, Stain: PMA (color: green)

Physical state: *yellow solid*

% yield: 83% (600 mg)

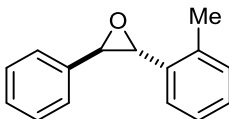
d.r. >20:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.46 – 7.31 (m, 5H), 3.98 (d, *J* = 1.8 Hz, 1H), 3.86 (d, *J* = 1.8 Hz, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 147.99, 144.54, 136.18, 128.96, 128.86, 126.38, 125.67, 124.03, 63.50, 61.81.

Synthesis of **(2R,3R)-2-phenyl-3-(*o*-tolyl)oxirane (8)** from *phenylmethanol* and *2-methylbenzaldehyde*:



8

Chemical Formula: C₁₅H₁₄O

Exact Mass: 210.10

Scale: 3 mmol

Flash Chromatography: 20:1 Hex/EtOAc → 10:1 Hex/EtOAc

TLC: R_f = 0.5 in 20:1 Hex/EtOAc, Stain: PMA (color: green)

Physical state: *white solid*

% yield: 79% (501 mg)

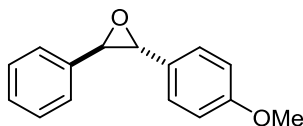
d.r. >20:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.29 (m, 6H), 7.29 – 7.21 (m, 2H), 7.21 – 7.15 (m, 1H), 4.00 (s, 1H), 3.77 (s, 1H), 2.36 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 137.42, 136.03, 135.67, 129.96, 128.73, 128.44, 127.90, 126.34, 125.61, 124.12, 62.06, 61.04, 19.06.

Synthesis of **(2R,3R)-2-(4-methoxyphenyl)-3-phenyloxirane (9)** from *phenylmethanol* and *4-methoxybenzaldehyde*:



9

Chemical Formula: C₁₅H₁₄O₂

Exact Mass: 226.10

Scale: 3 mmol

Flash Chromatography: 10:1 Hex/EtOAc + 3% triethyl amine (TEA) → 10:1 Hex/EtOAc

TLC: R_f = 0.6 in 4:1 Hex/EtOAc, Stain: PMA (color: green)

Physical state: *white solid*

% yield: 74% (502 mg)

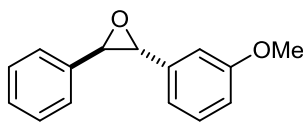
d.r. >20:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.30 (m, 5H), 7.27 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 3.86 (d, *J* = 2.0 Hz, 1H), 3.83 (s, 3H), 3.82 (d, *J* = 2.0 Hz, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 159.89, 137.38, 129.24, 128.67, 128.36, 126.94, 125.59, 114.16, 62.89, 62.80, 55.48.

Synthesis of **(2R,3R)-2-(3-methoxyphenyl)-3-phenyloxirane (10)** from *phenylmethanol* and *3-methoxybenzaldehyde*:



10

Chemical Formula: C₁₅H₁₄O₂

Exact Mass: 226.10

Scale: 3 mmol

Flash Chromatography: 20:1 Hex/Et₂O → 10:1 Hex/Et₂O

TLC: R_f = 0.2 in 20:1 Hex/Et₂O, Stain: PMA (color: green)

Physical state: *clear oil*

% yield: 85% (577 mg)

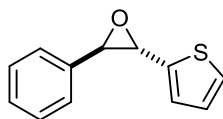
d.r. >20:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.46 – 7.32 (m, 5H), 7.32 – 7.24 (m, 1H), 6.99 – 6.93 (m, 1H), 6.93 – 6.86 (m, 2H), 3.86 (s, 2H), 3.83 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 160.08, 138.91, 137.16, 129.76, 128.69, 128.46, 125.62, 118.10, 114.24, 110.54, 62.88, 55.40, 55.39.

Synthesis of **(2R,3S)-2-phenyl-3-(thiophen-2-yl)oxirane (11)** from *phenylmethanol* and *2-thiophenecarboxaldehyde*:



11

Chemical Formula: C₁₂H₁₀OS

Exact Mass: 202.05

Scale: 3 mmol

Flash Chromatography: 10:1 Hex/EtOAc + 3 % TEA → 10:1 Hex/EtOAc

TLC: R_f = 0.5 in 10:1 Hex/EtOAc, Stain: PMA (color: green)

Physical state: red solid

% yield: 82% (497 mg)

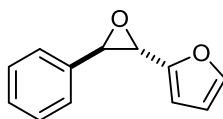
d.r. >20:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.32-7.40 (m, 5H), 7.31 (d, *J* = 4.9 Hz, 1H), 7.15 (d, *J* = 3.6, 1H), 7.00 (dd, *J* = 4.9, 3.6 Hz, 1H), 4.10 (d, *J* = 1.7 Hz, 1H), 4.05 (d, *J* = 1.7 Hz, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 141.20, 136.66, 128.73, 128.61, 127.28, 126.11, 125.62, 125.34, 63.62, 59.68.

Synthesis of **2-((2S,3R)-3-phenyloxiran-2-yl)furan (12)** from *phenylmethanol* and *2-furancarboxaldehyde* as a mixture of separable diastereomer:



12

Chemical Formula: C₁₂H₁₀O₂

Exact Mass: 186.07

Scale: 3 mmol

Flash Chromatography: 20:1 Hex/EtOAc + 3 % TEA → 10:1 Hex/EtOAc

TLC: R_f = 0.3 in 10:1 Hex/EtOAc, Stain: PMA (color: green)

Physical state: yellow oil

% yield: 59% (330 mg)

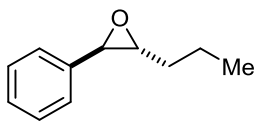
d.r. 7:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) 7.25-7.60 (m, 6H), 6.49 (d, *J* = 3.4 Hz, 1H), 6.39 (dd, *J* = 3.4, 2.0 Hz, 1H), 4.35 (d, *J* = 2.0 Hz, 1H) δ 3.91 (d, *J* = 2.0 Hz, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 149.96, 143.09, 136.58, 128.72, 128.61, 125.72, 110.93, 110.00, 59.72, 56.42.

Synthesis of **(2R,3R)-2-phenyl-3-propyloxirane (13)** from *phenylmethanol* and *propionaldehyde* as a mixture of inseparable diastereomer:



13

Chemical Formula: C₁₁H₁₄O

Exact Mass: 162.10

Scale: 3 mmol

Flash Chromatography: 20:1 Hex/Et₂O+ 3 % TEA → 20:1 Hex/Et₂O

TLC: R_f = 0.2 in 20:1 Hex/Et₂O, Stain: PMA (color: green)

Physical state: *yellow oil*

% yield: 60% (335 mg)

d.r. 1:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.36-7.27 (m, 5H), 3.61 (d, 1H, *J* = 2.0 Hz), 2.95 (dt, 1H, *J* = 2.0, 5.5 Hz), 1.64-1.70 (m, 2H), 1.52-1.58 (m, 2H), 1.00 (t, 3H, *J* = 7.5 Hz).

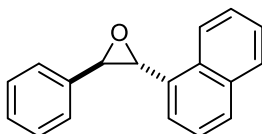
¹³C NMR (126 MHz, Chloroform-*d*) δ 138.05, 128.55, 128.09, 125.62, 63.17, 58.73, 34.49, 19.38, 14.11.

cis:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.20 (m, 5H), 4.08 (d, *J* = 4.2 Hz, 1H), 3.22 (td, *J* = 6.0, 4.2 Hz, 1H), 1.49 – 1.32 (m, 2H), 1.28 – 1.20 (m, 2H), 0.85 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 135.91, 128.55, 127.53, 126.60, 59.52, 57.51, 28.81, 19.50, 14.01.

Synthesis of **(2R,3R)-2-(naphthalen-1-yl)-3-phenyloxirane (14)** from *phenylmethanol* and *1-naphthaldehyde*:



14

Chemical Formula: C₁₈H₁₄O

Exact Mass: 246.10

Scale: 3 mmol

Flash Chromatography: 20:1 Hex/EtOAc

TLC: R_f = 0.6 in 20:1 Hex/EtOAc, Stain: PMA (color: green)

Physical state: *yellow oil*

% yield: 73% (539 mg)

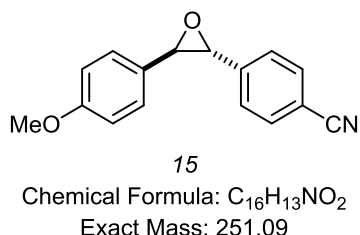
d.r. >20:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 8.03 – 7.95 (m, 1H), 7.93 – 7.88 (m, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.66 – 7.58 (m, 1H), 7.55 – 7.48 (m, 3H), 7.48 – 7.37 (m, 5H), 4.51 (d, *J* = 1.9 Hz, 1H), 3.88 (d, *J* = 1.9 Hz, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 137.31, 133.41, 133.37, 131.32, 128.85, 128.83, 128.59, 128.34, 126.55, 126.09, 125.75, 125.73, 123.02, 122.15, 62.15, 61.28.

Synthesis of **4-((2R,3R)-3-(4-methoxyphenyl)oxiran-2-yl)benzonitrile (15)** from (4-methoxyphenyl)methanol and 4-formylbenzonitrile as a mixture of separable diastereomer:



Scale: 3 mmol

Flash Chromatography: 20:1 Hex/EtOAc + 3 % TEA → 10:1 Hex/EtOAc

TLC: R_f^{trans, cis} = 0.2, 0.1 in 10:1 Hex/EtOAc, Stain: PMA (color: green)

Physical state: *trans*: white solid, *cis*: clear oil

% Yield: 74% (557 mg)

d.r. 2:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 3.90 (d, *J* = 1.7 Hz, 1H), 3.83 (s, 3H), 3.77 (d, *J* = 1.7 Hz, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 160.19, 142.76, 132.51, 128.25, 126.98, 126.21, 118.78, 114.27, 112.01, 63.34, 61.84, 55.49.

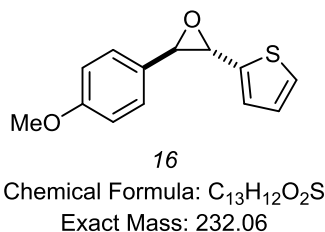
cis:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.72 (d, *J* = 8.7 Hz, 2H), 4.38 (d, *J* = 4.2 Hz, 1H), 4.33 (d, *J* = 4.2 Hz, 1H), 3.72 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 159.32, 140.29, 131.75, 128.02, 127.65, 125.42, 118.79, 113.61, 111.44, 59.89, 59.12, 55.25.

HRMS-ESI (m/z): calculated C₁₆H₁₃NO₂ + H⁺: 252.1025 found 252.1021

Synthesis of **(2R,3S)-2-(4-methoxyphenyl)-3-(thiophen-2-yl)oxirane (16)** from (4-methoxyphenyl)methanol and thiophene-2-carbaldehyde as a mixture of inseparable diastereomer:



Scale: 3 mmol

Flash Chromatography: 20:1 Hex/EtOAc+ 3 % TEA → 20:1 Hex/EtOAc

TLC: R_f = 0.4 in 10:1 Hex/EtOAc, Stain: PMA (color: green)

Physical state: green oil

% Yield: 90% (625 mg)

d.r. 2:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.29 – 7.25 (overlap, 3H), 7.15 (dd, *J* = 3.5, 0.5 Hz, 1H), 7.01 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.92 (d, *J* = 5.0, 2H), 4.10 (d, *J* = 1.9 Hz, 1H), 4.02 (d, *J* = 1.9 Hz, 1H), 3.82 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 160.00, 141.38, 128.37, 127.26, 126.96, 126.39, 125.96, 114.18, 63.53, 59.49, 55.47.

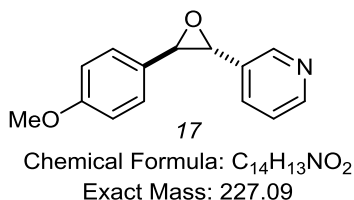
cis:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.5 Hz, 2H), 7.11 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.95 – 6.91 (overlap, 1H), 6.86 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.83 (d, *J* = 8.5 Hz, 2H), 4.44 (d, *J* = 4.0 Hz, 1H), 4.37 (d, *J* = 4.0 Hz, 1H), 3.78 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 159.49, 137.68, 128.64, 127.44, 126.35, 125.86, 125.23, 113.54, 60.18, 56.74, 55.31.

HRMS-ESI (m/z): calculated C₁₃H₁₂O₂S+ H⁺: 233.0636 found 233.0634.

Synthesis of **3-((2*R*,3*R*)-3-(4-methoxyphenyl)oxiran-2-yl)pyridine (17)** from (4-methoxyphenyl)methanol and nicotinaldehyde as a mixture of inseparable diastereomer:



Scale: 3 mmol

Flash Chromatography: 4:1 Hex/EtOAc+ 3 % TEA → 1:1 Hex/EtOAc

TLC: R_f= 0.2 in 4:1 Hex/EtOAc, Stain: PMA (color: green)

Physical state: brown oil

% Yield: 86% (587 mg)

d.r. 2:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 8.62 (d, *J* = 2.0 Hz, 1H), 8.57 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.61 (dt, *J* = 7.8, 2.0 Hz, 1H), 7.30 (dd, *J* = 7.8, 4.8 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 3.89 (d, *J* = 1.8 Hz, 1H), 3.83 (d, *J* = 1.8 Hz, 1H), 3.82 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 160.10, 149.72, 147.90, 134.54, 132.77, 128.09, 126.96, 123.59, 114.24, 62.84, 60.60, 55.48.

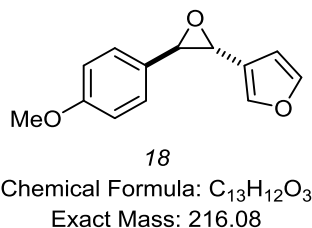
cis:

¹H NMR (500 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 2.1 Hz, 1H), 8.40 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.40 (dt, *J* = 7.9, 2.1 Hz, 1H), 7.11 – 7.08 (overlap, 1H), 7.07 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 8.7 Hz, 2H), 4.37 (d, *J* = 4.1 Hz, 1H), 4.31 (d, *J* = 4.1 Hz, 1H), 3.71 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 159.28, 148.99, 148.75, 133.00, 130.52, 128.47, 125.63, 122.80, 113.64, 59.52, 57.72, 55.25.

LRMS-ESI (m/z): calculated C₁₄H₁₃NO₂+ H⁺: 228.1025 found 228.0972

Synthesis of **3-((2*R*,3*R*)-3-(4-methoxyphenyl)oxiran-2-yl)furan (18)** from (4-methoxyphenyl)methanol and furan-3-carbaldehyde as a mixture of inseparable diastereomer:



Scale: 3 mmol

Flash Chromatography: 20:1 Hex/EtOAc+ 3 % TEA → 10:1 Hex/EtOAc

TLC: R_f= 0.2 in 20:1 Hex/EtOAc, Stain: PMA (color: green)

Physical state: clear oil

% Yield: 82% (529 mg)

d.r. 2:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.55 (s, 1H), 7.42 (t, *J* = 1.7 Hz, 1H), 7.26 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.39 (d, *J* = 1.7 Hz, 1H), 3.92 (d, *J* = 2.0 Hz, 1H), 3.82 (s, 3H), 3.80 (d, *J* = 2.0 Hz, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 159.90, 143.72, 141.25, 128.05, 126.93, 123.03, 114.16, 108.12, 61.16, 56.38, 55.46.

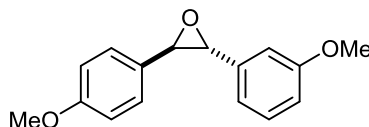
cis:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.23 – 7.18 (*overlap*, 3H), 7.17 (d, *J* = 0.8 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.03 – 5.99 (m, 1H), 4.29 (d, *J* = 4.0 Hz, 1H), 4.11 (d, *J* = 4.0 Hz, 1H), 3.79 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 159.31, 142.75, 141.56, 128.96, 127.02, 119.82, 113.56, 109.89, 58.98, 55.32, 53.72.

LRMS-ESI (*m/z*): calculated C₁₃H₁₂O₃ + H⁺: 217.0865 found 217.0994

Synthesis of **(2*R*,3*R*)-2-(3-methoxyphenyl)-3-(4-methoxyphenyl)oxirane (19)** from (4-methoxyphenyl)methanol and 3-methoxybenzaldehyde as a mixture of inseparable diastereomer:



19

Chemical Formula: C₁₆H₁₆O₃

Exact Mass: 256.11

Scale: 5 mmol

Flash Chromatography: 20:1 Hex/EtOAc + 3 % TEA → 20:1 Hex/EtOAc → 10:1 Hex/EtOAc

TLC: R_f = 0.4 in 10:1 Hex/EtOAc, Stain: PMA (color: green)

% yield: 100% (1.28 g)

Physical state: *clear oil*

d.r. 2:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.33-7.25 (*overlap*, 3H), 6.99 – 6.84 (*overlap*, 5H), 3.85 (d, *J* = 1.9 Hz, 1H), 3.82 (s, 5H), 3.81 (d, *J* = 2.0 Hz, 1H).

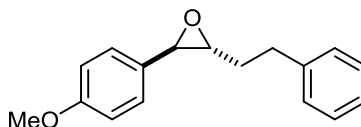
¹³C NMR (126 MHz, Chloroform-*d*) δ 159.94, 159.78, 138.94, 129.60, 128.10, 126.81, 117.94, 114.02, 113.30, 110.35, 62.68, 59.73, 55.27, 55.12.

cis:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.15 – 7.07 (m, 3H), 6.82 – 6.69 (m, 5H), 4.30 (s, 2H), 3.73 (s, 3H), 3.69 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 159.11, 158.97, 136.16, 129.03, 128.87, 126.40, 119.37, 114.03, 113.47, 112.03, 62.59, 59.57, 55.34, 55.10.

Synthesis of **(2*R*,3*R*)-2-(4-methoxyphenyl)-3-phenethyloxirane (20)** from (4-methoxyphenyl)methanol and 3-phenylpropanal as a mixture of inseparable diastereomer:



20

Chemical Formula: C₁₇H₁₈O₂

Exact Mass: 254.13

Scale: 5 mmol

Flash Chromatography: 20:1 Hex/Et₂O + 3 % TEA → 20:1 Hex/Et₂O → 10:1 Hex/Et₂O

TLC: R_f = 0.1 in 20:1 Hex/Et₂O, Stain: PMA (color: green)

% yield: 66% (840 mg)

Physical state: *clear oil*

d.r. 1:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.34 – 6.83 (*overlap*, 9H), 4.04 (d, *J* = 4.1 Hz, 1H), 3.82 (s, 3H), 3.22 (ddd, *J* = 6.6, 6.0, 4.1 Hz, 1H), 2.73 (m, 1H), 2.64 (m, 1H), 1.73 (m, 1H), 1.59 (m, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 159.14, 141.29, 129.66, 128.60, 128.47, 127.65, 126.05, 113.63, 58.95, 57.46, 55.39, 32.37, 28.67.

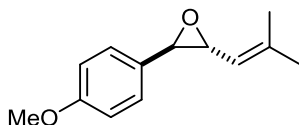
cis:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.34 – 6.83 (*overlap*, 9H), 3.81 (s, 3H), 3.51 (d, *J* = 2.1 Hz, 1H), 3.00 (ddd, *J* = 6.1, 5.5, 2.1 Hz, 1H), 2.90 (m, 1H), 2.79 (m, 1H), 2.09 – 1.93 (*overlap*, 2H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 159.64, 141.33, 129.53, 128.55, 128.43, 126.94, 126.16, 113.97, 62.31, 58.77, 55.41, 34.29, 32.26.

LRMS-ESI (*m/z*): calculated C₁₇H₁₈O₂ + H⁺: 255.1385 found 255.1499

Synthesis of **(2*R*,3*R*)-2-(4-methoxyphenyl)-3-(2-methylprop-1-en-1-yl)oxirane (21)** from (4-methoxyphenyl)methanol and 3-methylbut-2-enal as a mixture of inseparable diastereomer:



21

Chemical Formula: C₁₃H₁₆O₂

Exact Mass: 204.12

Scale: 5 mmol

Flash Chromatography: 20:1 Hex/Et₂O + 3 % TEA → 20:1 Hex/Et₂O → 10:1 Hex/Et₂O

TLC: R_f = 0.1 in 20:1 Hex/Et₂O, Stain: PMA (color: green)

% yield: 67% (689 mg)

Physical state: clear oil

d.r. 2:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.22 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.00 (dp, *J* = 8.7, 1.4 Hz, 1H), 3.81 (s, 3H), 3.72 (d, *J* = 2.1 Hz, 1H), 3.51 (dd, *J* = 8.7, 2.1 Hz, 1H), 1.80 (d, *J* = 1.4 Hz, 3H), 1.79 (d, *J* = 1.4 Hz, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 159.67, 140.59, 129.67, 126.84, 122.09, 114.06, 60.04, 59.86, 55.43, 26.07, 18.54.

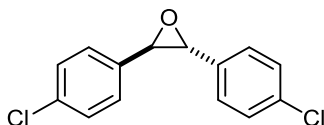
cis:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 8.9 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 2H), δ 4.76 (dp, *J* = 8.7, 1.4 Hz, 1H), 4.18 (d, *J* = 4.2 Hz, 1H), 3.84 (dd, *J* = 8.7, 4.2 Hz, 1H), 3.81 (s, 3H), 1.81 (d, *J* = 1.4 Hz, 3H), 1.66 (d, *J* = 1.4 Hz, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 159.18, 142.36, 127.82, 127.77, 117.84, 113.64, 58.94, 56.19, 55.36, 26.28, 18.62.

LRMS-ESI (*m/z*): calculated C₁₃H₁₆O₂ + H⁺: 205.1229 found 205.1317

Synthesis of **(2*R*,3*R*)-2,3-bis(4-chlorophenyl)oxirane (22)** from (4-chlorophenyl)methanol and 4-chlorobenzaldehyde:



22

Chemical Formula: C₁₄H₁₀Cl₂O

Exact Mass: 264.01

Scale: 10 mmol

Flash Chromatography: 4:1 Hex/DCM

TLC: R_f = 0.3 in 4:1 Hex/DCM, Stain: PMA (color: green)

% yield: 70% (1.85 g)

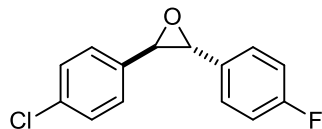
Physical state: white solid

d.r. >20:1

¹H NMR (500 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.7 Hz, 4H), 7.26 (d, *J* = 8.7 Hz, 4H), 3.80 (s, 2H)

¹³C NMR (126 MHz, Chloroform-*d*) δ 135.39, 134.40, 128.97, 126.95, 62.36.

Synthesis of **(2R,3R)-2-(4-chlorophenyl)-3-(4-fluorophenyl)oxirane (23)** from (4-chlorophenyl)methanol and 4-fluorobenzaldehyde:



23

Chemical Formula: C₁₄H₁₀ClFO

Exact Mass: 248.04

Scale: 10 mmol

Flash Chromatography: 20:1 → 10:1 Hex/EtOAc

TLC: R_f = 0.3 in 10:1 Hex/EtOAc, Stain: PMA (color:green)

% yield: 74% (1.85 g)

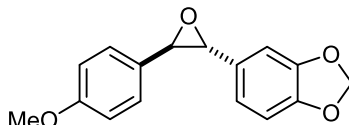
Physical state: white solid

d.r. >20:1

¹H NMR (500 MHz, Chloroform-*d*) δ 7.39 – 7.33 (m, 2H), 7.33 – 7.25 (m, 4H), 7.11 – 7.02 (m, 2H), 3.81 (s, 2H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 163.96, 161.99, 135.53, 134.34, 132.64, 132.61, 128.95, 127.35, 127.29, 126.95, 115.85, 115.68, 62.43, 62.29.

Synthesis of **5-((2R,3R)-3-(4-methoxyphenyl)oxiran-2-yl)benzo[d][1,3]dioxole (29)** from benzo[d][1,3]dioxol-5-ylmethanol and 4-methoxybenzaldehyde as a mixture of inseparable diastereomer:



29

Chemical Formula: C₁₆H₁₄O₄

Exact Mass: 270.09

Scale: 5 mmol

Flash Chromatography: 9:1 Hex/EtOAc + 3 % TEA → 9:1 Hex/EtOAc

TLC: R_f = 0.3 in 9:1 Hex/EtOAc, Stain: PMA (color: green)

% yield: 98% (1.325 g)

Physical state: clear oil

d.r. 5:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.82 – 6.77 (overlap, 2H), 5.97 (s, 2H), 3.82 (s, 3H), 3.78 (d, *J* = 1.9 Hz, 1H), 3.77 (d, *J* = 1.9 Hz, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 159.89, 148.20, 147.80, 131.38, 129.17, 126.90, 119.64, 114.16, 108.44, 105.58, 101.30, 62.78, 62.70, 55.49.

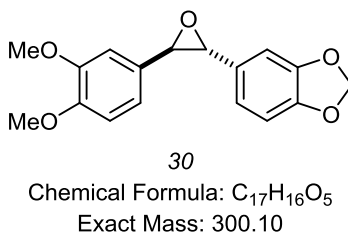
cis:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.09 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.68 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.66 – 6.61 (m, 2H), 5.88 (q, *J* = 1.5 Hz, 2H), 4.24 (q, *J* = 4.2 Hz, 2H), 3.74 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 159.11, 147.35, 147.03, 128.59, 128.23, 126.52, 120.61, 113.48, 107.96, 107.50, 101.03, 59.82, 59.71, 55.28.

HRMS-ESI (*m/z*): calculated C₁₆H₁₄O₄ + H⁺: 271.0970 found 271.0988.

Synthesis of **5-((2R,3R)-3-(3,4-dimethoxyphenyl)oxiran-2-yl)benzo[d][1,3]dioxole (30)** from *benzo[d][1,3]dioxol-5-ylmethanol* and *3,4-dimethoxybenzaldehyde* as a mixture of separable diastereomer but only the major compound was characterized:



Scale: 10 mmol

Flash Chromatography: 4:1 Hex/DCM + 3 % TEA → 4:1 Hex/DCM + 1 % MeOH

TLC: R_f = 0.3 in 4:1 Hex/DCM + 1 % MeOH, Stain: PMA (color: green)

% yield: 95% (2.85 g)

Physical state: white solid

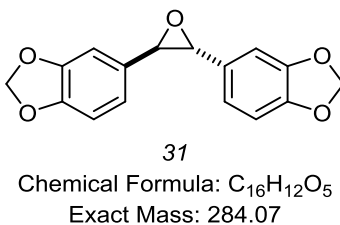
d.r. 6:1

¹H NMR (500 MHz, Chloroform-*d*) δ 6.92 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.84 – 6.77 (overlap, 5H), 5.97 (s, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 3.77 (s, 2H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 149.29, 149.13, 148.06, 147.69, 131.10, 129.53, 119.51, 118.28, 111.07, 108.31, 107.81, 105.42, 101.16, 62.70, 62.68, 55.98, 55.89.

HRMS-ESI (*m/z*): calculated C₁₇H₁₆O₅ + H⁺: 301.1076 found 301.1082.

Synthesis of **(2R,3R)-2,3-bis(benzo[d][1,3]dioxol-5-yl)oxirane (31)** from *benzo[d][1,3]dioxol-5-ylmethanol* and *benzo[d][1,3]dioxole-5-carbaldehyde* as a mixture of separable diastereomer but only the major compound was characterized:



Scale: 6.45 mmol

Flash Chromatography: 4:1 Hex/EtOAc + 3 % TEA → 4:1 Hex/EtOAc

TLC: R_f = 0.3 in 4:1 Hex/EtOAc, Stain: PMA (color: green)

% yield: 100% (1.85 g)

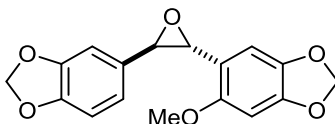
Physical state: white solid

d.r. 5:1

¹H NMR (500 MHz, Chloroform-*d*) δ 6.83 (dd, *J* = 8.0, 1.6 Hz, 2H), 6.80 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 1.6 Hz, 2H), 5.97 (s, 5H), 3.74 (s, 2H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 148.20, 147.85, 131.14, 119.66, 108.44, 105.55, 101.31, 62.77.

Synthesis of **5-((2R,3R)-3-(benzo[d][1,3]dioxol-5-yl)oxiran-2-yl)-6-methoxybenzo[d][1,3]dioxole (32)** from benzo[d][1,3]dioxol-5-ylmethanol and 6-methoxybenzo[d][1,3]dioxole-5-carbaldehyde as a mixture of inseparable diastereomer:



32

Chemical Formula: C₁₇H₁₄O₆

Exact Mass: 314.08

Scale: 3 mmol

Flash Chromatography: 4:1 Hex/EtOAc + 3 % TEA → 4:1 Hex/EtOAc

TLC: R_f = 0.4 in 4:1 Hex/EtOAc, Stain: PMA (color: green)

% yield: 98% (922 mg)

Physical state: yellow solid

d.r. 7:1

¹H NMR (500 MHz, Chloroform-*d*) δ 6.85 – 6.78 (m, 2H), 6.77 (d, *J* = 1.5 Hz, 1H), 6.54 – 6.49 (m, 2H), 5.97 (overlap, 4H), 3.90 (s, 3H), 3.73 (d, *J* = 1.8 Hz, 1H), 3.71 (d, *J* = 1.8 Hz, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 149.24, 148.20, 147.88, 143.97, 135.38, 131.86, 131.00, 119.67, 108.45, 105.53, 104.91, 101.76, 101.32, 99.67, 62.88, 62.83, 56.69.

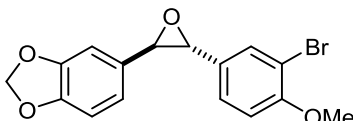
cis:

¹H NMR (500 MHz, Chloroform-*d*) δ 6.73 – 6.64 (m, 2H), 6.63 (d, *J* = 1.6 Hz, 1H), 6.38 – 6.33 (m, 2H), 5.91 – 5.87 (overlap, 4H), 4.22 (d, *J* = 4.1 Hz, 1H), 4.20 (d, *J* = 4.1 Hz, 1H), 3.78 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 148.53, 147.40, 147.14, 143.31, 134.73, 128.98, 128.29, 120.56, 107.98, 107.41, 106.24, 101.56, 101.27, 101.08, 59.89, 59.82, 56.49.

HRMS-ESI (*m/z*): calculated C₁₆H₁₄O₄ + Na⁺: 337.0688 found 337.0702

Synthesis of **5-((2R,3R)-3-(3-bromo-4-methoxyphenyl)oxiran-2-yl)benzo[d][1,3]dioxole (33)** from benzo[d][1,3]dioxol-5-ylmethanol and 3-bromo-4-methoxybenzaldehyde as a mixture of separable diastereomer but only the major compound was characterized:



33

Chemical Formula: C₁₆H₁₃BrO₄

Exact Mass: 348.00

Scale: 3 mmol

Flash Chromatography: 10:1 Hex/EtOAc + 3 % TEA → 10:1 Hex/EtOAc

TLC: R_f = 0.3 in 10:1 Hex/EtOAc, Stain: PMA (color: green)

% yield: 75% (790 mg)

Physical state: off-white solid

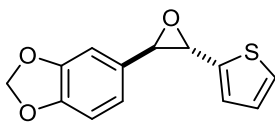
d.r. 6:1

¹H NMR (500 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 2.1 Hz, 1H), 7.24 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.85 – 6.79 (overlap, 2H), 6.77 (d, *J* = 1.4 Hz, 1H), 5.98 (s, 2H), 3.91 (s, 3H), 3.77 – 3.72 (m, 2H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 155.91, 148.09, 147.79, 130.75, 130.62, 130.29, 125.84, 119.57, 111.94, 111.80, 108.33, 105.39, 101.19, 62.71, 61.65, 56.34.

HRMS-ESI (*m/z*): calculated C₁₆H₁₃BrO₄ + H⁺: 350.0075 found 350.0195.

Synthesis of **5-((2R,3S)-3-(thiophen-2-yl)oxiran-2-yl)benzo[d][1,3]dioxole (34)** from *benzo[d][1,3]dioxol-5-ylmethanol* and *thiophene-2-carbaldehyde* as a mixture of separable diastereomer but only the major compound was characterized:



34

Chemical Formula: C₁₃H₁₀O₃S

Exact Mass: 246.04

Scale: 3 mmol

Flash Chromatography: 20:1 Hex/Et₂O + 3 % TEA → 20:1 Hex/Et₂O

TLC: R_f = 0.2 in 20:1 Hex/Et₂O, Stain: PMA (color: green)

% yield: 79% (583 mg)

Physical state: clear oil

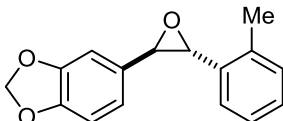
d.r. 4:1

¹H NMR (500 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.14 (dd, *J* = 3.5, 1.1 Hz, 1H), 7.01 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.85 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.78 (d, *J* = 1.6 Hz, 1H), 5.98 (s, 2H), 4.05 (d, *J* = 1.9 Hz, 1H), 3.98 (d, *J* = 1.9 Hz, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 148.23, 147.99, 141.13, 130.60, 127.28, 126.06, 125.32, 119.77, 108.48, 105.56, 101.35, 63.61, 59.51.

HRMS-ESI (*m/z*): calculated C₁₃H₁₀O₃S + H⁺: 247.0429 found 247.0420.

Synthesis of **5-((2R,3R)-3-(*o*-tolyl)oxiran-2-yl)benzo[d][1,3]dioxole (35)** from *benzo[d][1,3]dioxol-5-ylmethanol* 2-methylbenzaldehyde as a mixture of separable diastereomer but only the major compound was characterized:



35

Chemical Formula: C₁₆H₁₄O₃

Exact Mass: 254.09

Scale: 3 mmol

Flash Chromatography: 20:1 Hex/Et₂O + 3 % TEA → 20:1 Hex/Et₂O

TLC: R_f = 0.2 in 20:1 Hex/Et₂O, Stain: PMA (color: green)

% yield: 96% (728 mg)

Physical state: clear oil

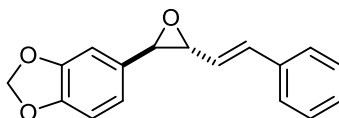
d.r. 8:1

¹H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.29 (m, 1H), 7.28 – 7.21 (m, 2H), 7.21 – 7.14 (m, 1H), 6.88 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.85 – 6.80 (m, 2H), 5.99 (s, 2H), 3.95 (d, *J* = 2.0 Hz, 1H), 3.69 (d, *J* = 2.0 Hz, 1H), 2.36 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 148.22, 147.87, 135.96, 135.60, 131.39, 129.94, 127.87, 126.33, 124.05, 119.65, 108.50, 105.58, 101.32, 62.04, 60.89, 19.04.

HRMS-ESI (*m/z*): calculated C₁₆H₁₄O₃ + H⁺: 255.1021 found 255.1022.

Synthesis of **5-((2R,3R)-3-((E)-styryl)oxiran-2-yl)benzo[d][1,3]dioxole (36)** from *benzo[d][1,3]dioxol-5-ylmethanol* and *cinnamaldehyde* as a mixture of inseparable diastereomer:



36

Chemical Formula: C₁₇H₁₄O₃

Exact Mass: 266.09

Scale: 3 mmol

Flash Chromatography: 20:1 Hex/Et₂O + 3 % TEA → 20:1 Hex/Et₂O

TLC: R_f = 0.3 in 20:1 Hex/Et₂O, Stain: PMA (color: green)

% yield: 90% (715 mg)

Physical state: *clear oil*

d.r. 4:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.40 (m, 2H), 7.34 (m, 2H), 7.30 – 7.25 (*overlap*, 2H), 6.84 – 6.78 (m, 2H), 6.76 (d, *J* = 16.0 Hz, 1H), 6.05 (dd, *J* = 16.0, 7.7 Hz, 1H), 5.97 (s, 2H), 3.82 (d, *J* = 1.9 Hz, 1H), 3.48 (dd, *J* = 7.7, 1.9 Hz, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 148.19, 147.81, 136.15, 134.52, 131.07, 128.80, 128.28, 126.62, 126.20, 119.66, 108.44, 105.57, 101.29, 63.08, 60.87.

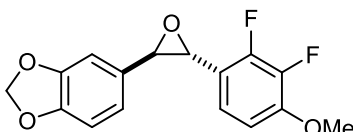
cis:

¹H NMR (500 MHz, Chloroform-*d*) δ 7.40 (m, 2H), 7.34 (m, 2H), 7.30 – 7.25 (*overlap*, 2H), 6.84 – 6.76 (*overlap*, 3H), 5.97 (*overlap*, 2H), 5.76 (dd, *J* = 15.9, 8.7 Hz, 1H), 4.25 (d, *J* = 4.1 Hz, 1H), 3.79 (dd, *J* = 8.7, 4.1 Hz, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 147.79, 147.35, 137.04, 136.26, 129.19, 128.67, 128.23, 126.65, 123.17, 120.00, 108.33, 107.02, 101.23, 60.27, 59.43.

HRMS-ESI (m/z): calculated C₁₇H₁₄O₃ + H⁺: 267.1021 found 267.1022.

Synthesis of **5-((2R,3R)-3-(2,3-difluoro-4-methoxyphenyl)oxiran-2-yl)benzo[d][1,3]dioxole (37)** from *benzo[d][1,3]dioxol-5-ylmethanol* and *2,3-difluoro-4-methoxybenzaldehyde* as a mixture of inseparable diastereomer:



37

Chemical Formula: C₁₆H₁₂F₂O₄

Exact Mass: 306.07

Scale: 4 mmol

Flash Chromatography: 20:1 Hex/EtOAc + 3 % TEA → 10:1 Hex/EtOAc

TLC: R_f = 0.2 in 10:1 Hex/EtOAc, Stain: PMA (color: green)

% yield: 89% (1.09 g)

Physical state: *off-white solid*

d.r. 3:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 6.96 (m, 1H), 6.91 – 6.70 (m, 4H), 5.97 (s, 2H), 4.02 (d, *J* = 1.9 Hz, 1H), 3.91 (s, 3H), 3.78 (d, *J* = 1.9 Hz, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 151.28 (d, *J* = 11.4 Hz), 149.30 (d, *J* = 11.4 Hz), 148.97 (dd, *J* = 8.0, 3.2 Hz), 148.26, 147.26, 142.01 (d, *J* = 13.9 Hz), 140.04 (d, *J* = 14.0 Hz), 130.47, 119.87, 119.52 (t, *J* = 4.5 Hz), 118.33 (d, *J* = 10.6 Hz), 108.49, 108.44 (d, *J* = 3.3 Hz), 105.63, 101.37, 62.20 (d, *J* = 1.3 Hz), 56.81, 56.69 (dd, *J* = 5.0, 3.1 Hz).

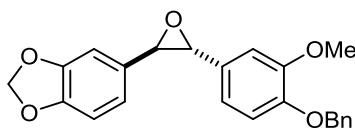
cis:

¹H NMR (500 MHz, Chloroform-*d*) δ 6.92 – 6.84 (m, 1H), 6.71 – 6.56 (m, 4H), 5.88 (s, 2H), 4.33 (d, *J* = 4.2 Hz, 1H), 4.30 (d, *J* = 4.2 Hz, 1H), 3.83 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 150.73 (d, *J* = 11.3 Hz), 148.76 (d, *J* = 11.3 Hz), 148.61 (dd, *J* = 7.9, 3.3 Hz), 147.41, 147.26, 141.66 (d, *J* = 13.6 Hz), 139.69 (d, *J* = 13.8 Hz), 127.90, 122.22 (t, *J* = 4.6 Hz), 120.29, 115.83 (d, *J* = 11.6 Hz), 108.02, 107.47 (d, *J* = 3.3 Hz), 107.04, 101.10, 59.19, 56.58, 55.39 (t, *J* = 3.6 Hz).

HRMS-ESI (*m/z*): calculated C₁₆H₁₂F₂O₄ + H⁺: 307.0782 found 307.0775.

Synthesis of **5-((2*R*,3*R*)-3-(4-(benzyloxy)-3-methoxyphenyl)oxiran-2-yl)benzo[*d*][1,3]dioxole (38)** from benzo[*d*][1,3]dioxol-5-ylmethanol and 4-(benzyloxy)-3-methoxybenzaldehyde as a mixture of separable diastereomer but only the major compound was characterized:



38

Chemical Formula: C₂₃H₂₀O₅

Exact Mass: 376.13

Scale: 5 mmol

Flash Chromatography: 20:1 Hex/EtOAc + 3 % TEA → 4:1 Hex/EtOAc

TLC: R_f = 0.5 in 4:1 Hex/EtOAc, Stain: PMA (color: green)

% yield: 68% (1.32 g)

Physical state: white solid

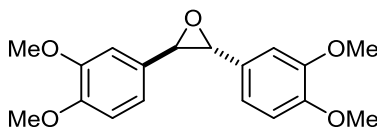
d.r. 6:1

¹H NMR (500 MHz, Chloroform-*d*) δ 7.48 – 7.41 (m, 2H), 7.40 – 7.33 (m, 2H), 7.33 – 7.28 (m, 1H), 6.90 – 6.77 (m, 6H), 5.97 (s, 2H), 5.17 (s, 2H), 3.91 (s, 3H), 3.76 (m, 2H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 150.10, 148.34, 148.18, 147.81, 137.11, 131.22, 130.22, 128.68, 127.98, 127.34, 119.64, 118.31, 114.03, 108.50, 108.43, 105.54, 101.29, 71.18, 62.80, 62.79, 56.13.

HRMS-ESI (*m/z*): calculated C₂₃H₂₀O₅ + Na⁺: 399.1208 found 399.1198.

Synthesis of **(2*R*,3*R*)-2,3-bis(3,4-dimethoxyphenyl)oxirane (39)** from (3,4-dimethoxyphenyl)methanol and 3,4-dimethoxybenzaldehyde as a mixture of separable diastereomer but only the major compound was characterized:



39

Chemical Formula: C₁₈H₂₀O₅

Exact Mass: 316.13

Scale: 6.45 mmol

Flash Chromatography: 4:1 Hex/DCM + 3 % TEA → 1:1 Hex/DCM + 1 % MeOH

TLC: R_f = 0.4 in 4:1 Hex/DCM, Stain: PMA (color: green)

% yield: 86% (1.757 g)

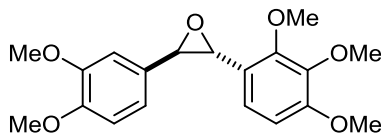
Physical state: white solid

d.r. 7:1

¹H NMR (500 MHz, Chloroform-*d*) δ 6.93 (dd, *J* = 8.2, 1.9 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.84 (d, *J* = 2.0 Hz, 2H), 3.90 (s, 6H), 3.89 (s, 6H), 3.81 (s, 2H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 149.49, 149.31, 129.82, 118.44, 111.30, 108.06, 62.92, 56.17, 56.07.

Synthesis of **(2R,3R)-2-(3,4-dimethoxyphenyl)-3-(2,3,4-trimethoxyphenyl)oxirane (40)** from (3,4-dimethoxyphenyl)methanol and 2,3,4-trimethoxybenzaldehyde as a mixture of inseparable diastereomer:



40

Chemical Formula: C₁₉H₂₂O₆
Exact Mass: 346.14

Scale: 5 mmol

Flash Chromatography: 4:1 Hex/EtOAc + 3 % TEA → 4:1 Hex/EtOAc

TLC: R_f = 0.1 in 4:1 Hex/EtOAc

% yield: 90% (1.55 g)

Physical state: white solid

d.r. 2:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 6.94 (d, *J* = 8.6 Hz, 1H), 6.89 – 6.83 (m, 3H), 6.70 (d, *J* = 8.6 Hz, 1H), 4.09 (d, *J* = 2.0 Hz, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 3.87 (s, 3H), 3.77 (d, *J* = 2.0 Hz, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 153.65, 152.66, 149.38, 149.20, 142.03, 129.89, 123.35, 122.70, 119.65, 111.19, 108.11, 107.64, 62.36, 61.61, 61.04, 58.41, 56.18, 56.09, 56.02.

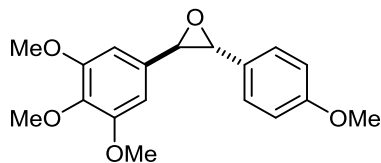
cis:

¹H NMR (500 MHz, Chloroform-*d*) δ 6.93 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.70 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.58 (d, *J* = 2.0 Hz, 1H), 6.53 (d, *J* = 8.5 Hz, 1H), 4.35 (d, *J* = 4.1 Hz, 1H), 4.28 (d, *J* = 4.1 Hz, 1H), 3.79 (s, 3H), 3.79 (s, 3H), 3.77 (s, 3H), 3.68 (s, 6H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 153.42, 152.14, 148.87, 148.30, 141.67, 127.43, 120.84, 119.65, 118.54, 110.53, 109.74, 106.46, 60.93, 60.85, 59.41, 57.69, 56.04, 55.87, 55.73.

HRMS-ESI (*m/z*): calculated C₁₉H₂₂O₆ + H⁺: 347.1495 found 347.1491.

Synthesis of **(2R,3R)-2-(4-methoxyphenyl)-3-(3,4,5-trimethoxyphenyl)oxirane (41)** from (3,4,5-trimethoxyphenyl)methanol and 4-methoxybenzaldehyde as a mixture of separable diastereomer but only the major compound was characterized:



41

Chemical Formula: C₁₈H₂₀O₅
Exact Mass: 316.13

Scale: 10 mmol

Flash Chromatography: 9:1 Hex/EtOAc + 3 % TEA → 4:1 Hex/EtOAc

TLC: R_f = 0.4 in 4:1 Hex/EtOAc, Stain: PMA (color: green)

% yield: 98% (3.24 g)

Physical state: clear oil

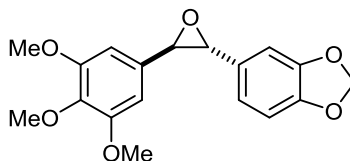
d.r. 9:1

¹H NMR (500 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.57 (s, 2H), 3.87 (s, 6H), 3.85 (s, 3H), 3.82 (overlap, 4H), 3.77 (d, *J* = 1.7 Hz, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 159.94, 153.69, 137.95, 133.07, 129.03, 126.91, 114.18, 102.17, 62.95, 62.83, 61.02, 56.25, 55.49.

HRMS-ESI (*m/z*): calculated C₁₈H₂₀O₅ + H⁺: 317.1389 found 317.1393.

Synthesis of **5-((2R,3R)-3-(3,4,5-trimethoxyphenyl)oxiran-2-yl)benzo[d][1,3]dioxole (42)** from (3,4,5-trimethoxyphenyl)methanol and benzo[d][1,3]dioxole-5-carbaldehyde:



42

Chemical Formula: $C_{18}H_{18}O_6$

Exact Mass: 330.11

Scale: 10 mmol

Flash Chromatography: 9:1 + 3 % TEA $\rightarrow$ 4:1 Hex/EtOAc

TLC: R_f = 0.3 in 4:1 Hex/EtOAc, Stain: PMA (c:green)

% yield: 100% (3.3 g)

Physical state: clear oil

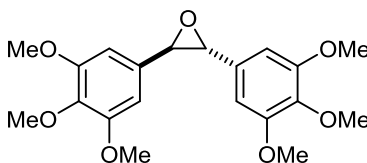
d.r. >20:1

^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.71, 148.24, 147.92, 138.02, 132.85, 131.01, 119.71, 108.48, 105.55, 102.19, 101.34, 62.95, 62.91, 61.04, 56.26.

1H NMR (500 MHz, Chloroform-*d*) δ 6.87 – 6.77 (m, 3H), 6.56 (s, 2H), 5.97 (s, 2H), 3.87 (s, 6H), 3.85 (s, 3H), 3.78 (d, J = 1.9 Hz, 1H), 3.74 (d, J = 1.9 Hz, 1H).

HRMS-ESI (m/z): calculated $C_{18}H_{18}O_6 + H^+$: 331.1182 found 331.1180.

Synthesis of **(2R,3R)-2,3-bis(3,4,5-trimethoxyphenyl)oxirane (43)** from (3,4,5-trimethoxyphenyl)methanol and 3,4,5-trimethoxybenzaldehyde as a mixture of separable diastereomer but only the major compound was characterized:



43

Chemical Formula: $C_{20}H_{24}O_7$

Exact Mass: 376.15

Scale: 5 mmol

Flash Chromatography: 4:1 Hex/DCM + 3% TEA $\rightarrow$ 4:1 Hex/DCM + 1% MeOH $\rightarrow$ 3:1 Hex/DCM + 1% MeOH $\rightarrow$ 3:1 Hex/DCM + 3% MeOH

TLC: R_f = 0.1 in 4:1 Hex/DCM + 3% MeOH

% yield: 60% (1.123 g)

Physical state: white solid

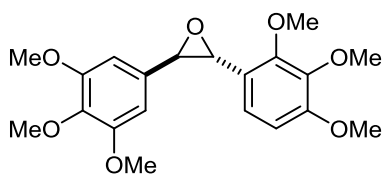
d.r. >20:1 (determined after purification)

1H NMR (500 MHz, Chloroform-*d*) δ 6.57 (s, 4H), 3.87 (s, 12H), 3.85 (s, 6H), 3.78 (s, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.70, 138.05, 132.69, 102.18, 63.08, 61.00, 56.24.

HRMS-ESI (m/z): calculated $C_{20}H_{24}O_7 + Na^+$: 399.1420 found 399.1432

Synthesis of **(2R,3R)-2-(2,3,4-trimethoxyphenyl)-3-(3,4,5-trimethoxyphenyl)oxirane (44)** from (3,4,5-trimethoxyphenyl)methanol and 2,3,4-trimethoxybenzaldehyde as a mixture of inseparable diastereomer:



44

Chemical Formula: C₂₀H₂₄O₇

Exact Mass: 376.15

Scale: 5 mmol

Flash Chromatography: 10:1 Hex/Et₂O + 3 % TEA → 3:1 Hex/Et₂O

TLC: R_f = 0.2 in 4:1 Hex/EtOAc

% yield: 73% (1.38 g)

Physical state: clear oil

d.r. 4:1

trans:

¹H NMR (500 MHz, Chloroform-*d*) δ 6.93 (d, *J* = 8.7 Hz, 1H), 6.69 (d, *J* = 8.7 Hz, 1H), 6.58 (s, 2H), 4.05 (d, *J* = 1.9 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.87 (*overlap*, 9H), 3.85 (s, 3H), 3.77 (d, *J* = 2.0 Hz, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 153.73, 153.64, 152.68, 142.02, 137.94, 133.06, 123.07, 119.69, 107.63, 102.30, 62.44, 61.62, 61.02, 60.98, 58.53, 56.23, 56.18.

cis:

¹H NMR (500 MHz, Chloroform-*d*) δ 6.94 (d, *J* = 8.5 Hz, 1H), 6.53 (d, *J* = 8.5 Hz, 1H), 6.37 (s, 2H), 4.35 (d, *J* = 4.3 Hz, 1H), 4.26 (d, *J* = 4.3 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.75 (s, 3H), 3.70 (*overlap*, 9H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 153.50, 152.76, 152.10, 141.64, 137.36, 130.44, 122.68, 120.62, 106.42, 103.94, 60.92, 60.84, 59.58, 57.69, 56.23, 56.06, 56.04.

HRMS-ESI (m/z): calculated C₂₀H₂₄O₇ + Na⁺: 399.1420 found 399.1411.

