Supporting Information for**Novel Approach to Multifunctionalized Homoallylic Alcohols
via Regioselective Ring Opening of Aryl Oxiranes with 3-Iodo
Allenoates**

Adishesu Kattuboina, Parminder Kaur, Cody Timmons and Guigen Li*

Department of Chemistry & Biochemistry, Texas Tech University, Lubbock, TX-79409-1061.

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General Methods

All solvents used for the reactions were purified and dried by passing via an Alumina column immediately prior to use. All reactions were performed in oven-dried glassware. NMR spectra were recorded at 500 and 125 MHz for ^1H and ^{13}C , respectively. Shifts are reported in ppm shift based on an internal TMS standard (for $^1\text{H}/\text{CDCl}_3$) or on residual solvent peaks (for $^{13}\text{C}/\text{CDCl}_3$). ^{19}F NMR spectra, where applicable, were recorded in CDCl_3 and shifts are reported based on an external TFA reference. Flash chromatography was performed on silica gel (200-300 mesh). FTIR spectra were recorded as methylene chloride deposits on a NaCl disk. Melting points were taken in open capillaries and are reported uncorrected.

Typical Procedure for ring opening reactions of oxiranes:

Into a oven dried glass vial was weighed 0.278 g (1.0 mmol) of MgI_2 . The vial was flushed with N_2 and cooled to $0\text{ }^\circ\text{C}$. To this was added 3.0 mL of dry methylene chloride and 0.090 mL of methyl propiolate (1.0 mmol). The contents were stirred for 2 h at $0\text{ }^\circ\text{C}$ and then 0.75 mmol of aryl oxirane in 1.0 mL of methylene chloride was added. Stirring was continued at $0\text{ }^\circ\text{C}$ for ca. 12 h at which time the ice bath was removed and the reaction was allowed to stir at room temperature for 12 h. To this was added 3.0 mL of 1N HCl and the two layers were separated. The aqueous layer was extracted with two 5 mL portions of methylene chloride. The combined methylene chloride layers were washed with water and dried over anhydrous sodium sulfate. The sodium sulfate was filtered and the remaining solution was evaporated to obtain crude product. This crude product was subjected to flash column chromatography using silica gel (200-300 mesh) and 4% acetone in hexanes as the solvent system.

(Z)-2a:

Pale yellow oil. ^1H NMR (500 MHz, CDCl_3): 7.32 (m, 2H), 7.26-7.23 (m, 1H), 7.20 (m, 2H), 7.12 (d, $J = 1\text{ Hz}$, 1H), 4.65 (m, 1H), 3.85 (s, 3H), 3.03 (dd, $J = 5.0\text{ Hz}$, 13.5 Hz , 1H), 2.81 (dd, $J = 8.0\text{ Hz}$, 13.5 Hz , 1H), 2.35 (d, $J = 5.5\text{ Hz}$, 1H). ^{13}C NMR (125 MHz,

CDCl_3): 166.4, 145.3, 136.8, 129.5, 128.5, 126.9, 85.8, 75.4, 52.0 43.0. FTIR (cm^{-1}): 3449.2, 1719.3. HRMS MNa^+ : expected: 354.9802, found: 354.9810.

(E)-2a:

Pale yellow oil. ^1H NMR (500 MHz, CDCl_3): 7.91 (s, 1H), 7.32-7.28 (m, 2H), 7.25-7.21 (m, 3H), 4.85 (m, 1H), 3.80 (s, 3H), 3.62 (d, $J = 10.5$ Hz, 1H), 3.10 (dd, $J = 8.0$ Hz, 13.5 Hz, 1H), 2.97 (dd, $J = 5.5$ Hz, 13.5 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): 163.7, 142.2, 137.3, 129.6, 128.4, 126.6, 100.3, 76.9, 52.5, 42.7. FTIR (cm^{-1}): 3512.0, 1701.2.

(Z)-2b:

White solid; mp 47-48 $^{\circ}\text{C}$. ^1H NMR (500 MHz, CDCl_3): 7.17-7.14 (m, 2H), 7.10 (d, $J = 1.0$ Hz, 1H), 6.99 (t, $J = 9.0$ Hz, 2H), 4.61 (m, 1H), 3.85 (s, 3H), 2.98 (dd, $J = 5.0$ Hz, 14.0 Hz, 1H), 2.80 (dd, $J = 8.0$ Hz, 14.0 Hz, 1H), 2.41 (d, $J = 5.5$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): 166.4, 161.8 (d, $J = 243.8$ Hz), 145.2, 132.5 (d, $J = 3.0$ Hz), 131.0 (d, $J = 8.0$ Hz), 115.3 (d, $J = 21.25$ Hz), 85.9, 75.4, 52.0, 42.0. ^{19}F NMR (282 MHz, CDCl_3): -116.4 (m). (FTIR (cm^{-1}): 3449.3, 1719.2. HRMS MNa^+ : expected: 372.9707, found: 372.9691.

(Z)-2c:

White solid; mp 54-55 $^{\circ}\text{C}$. ^1H NMR (500 MHz, CDCl_3): 7.29-7.26 (m, 2H), 7.14 (m, 2H), 7.13 (d, $J = 1.0$ Hz, 1H), 4.61 (m, 1H), 3.85 (s, 3H), 2.98 (dd, $J = 5.0$ Hz, 13.5 Hz, 1H), 2.80 (dd, $J = 8.0$ Hz, 13.5 Hz, 1H), 2.35 (bs, 1H). ^{13}C NMR (125 MHz, CDCl_3): 166.4, 145.1, 135.4, 132.7, 130.8, 128.6, 86.1, 75.3, 52.0, 42.2. FTIR (cm^{-1}): 3448.9, 1719.4. HRMS MNa^+ : expected: 388.9412, found: 388.9397.

(Z)-2d:

Pale yellow solid; mp 40-41 °C. ^1H NMR (500 MHz, CDCl_3): 7.12 (d, $J = 8.5$ Hz, 2H), 7.10 (d, $J = 1$ Hz, 1H), 6.85 (d, $J = 9.0$ Hz, 2H), 4.60 (m, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 2.97 (dd, $J = 5.0$ Hz, 14.0 Hz, 1H), 2.75 (dd, $J = 8.0$ Hz, 14.0 Hz, 1H), 2.28 (d, $J = 5.5$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): 166.5, 158.5, 145.3, 130.5, 128.7, 114.0, 85.6, 75.4, 55.2, 52.0, 42.0. FTIR (cm^{-1}): 3470.1, 1724.8. HRMS MNa^+ : expected: 384.9907, found: 384.9913.

(Z)-2e:

Yellow oil. ^1H NMR (500 MHz, CDCl_3): 7.16-7.12 (m, 3H), 7.11-7.08 (m, 2H), 4.63 (m, 1H), 3.86 (s, 3H), 3.00 (dd, $J = 5.0$ Hz, 14.0 Hz, 1H), 2.76 (dd, $J = 8.5$ Hz, 14.0 Hz, 1H), 2.33 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3): 166.4, 145.3, 136.5, 133.6, 129.3, 129.2, 85.7, 75.3, 51.9, 42.5, 21.0. FTIR (cm^{-1}): 3469.2, 1723.9. HRMS MNa^+ : expected: 368.9958, found: 368.9950.

(Z)-2f:

Pale yellow oil. ^1H NMR (500 MHz, CDCl_3): 7.38-7.35 (m, 1H), 7.22-7.26 (m, 1H), 7.22-7.18 (m, 2H), 7.16 (d, $J = 1.0$ Hz, 1H), 4.75 (m, 1H), 3.85 (s, 3H), 3.19 (dd, $J = 5.0$ Hz, 13.5 Hz, 1H), 3.01 (dd, $J = 8.5$ Hz, 13.5 Hz, 1H), 2.46 (d, $J = 6.0$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): 166.3, 145.0, 134.8, 134.3, 132.0, 129.6, 128.4, 126.8, 86.4, 74.3, 52.0, 40.6. FTIR (cm^{-1}): 3449.0, 1719.3.

(Z)-2g:

Pale yellow oil. ^1H NMR (500 MHz, CDCl_3): 7.26-7.21 (td, $J = 2.0$ Hz, 8.5 Hz, 1H), 7.10 (dd, $J = 1.5$ Hz, 7.5 Hz, 1H), 7.07 (d, $J = 1.0$ Hz, 1H), 6.94-6.90 (td, $J = 1.0$ Hz, 7.5 Hz,

1H), 6.89-6.85 (d, $J = 8.5$ Hz, 1H), 4.70 (m, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 3.06 (dd, $J = 4.5$ Hz, 13.5 Hz, 1H), 3.04 (d, $J = 5.5$ Hz, 1H), 2.93 (dd, $J = 7.5$ Hz, 13.5 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): 166.3, 157.3, 145.2, 131.5, 128.3, 125.2, 120.8, 110.4, 85.5, 74.9, 55.4, 51.8, 37.7. FTIR (cm^{-1}): 3466.8, 1722.5.

(Z)-2h:

Yellow oil. ^1H NMR (500 MHz, CDCl_3): 7.18 (d, $J = 1.5$ Hz, 1H), 7.10-7.17 (m, 4H), 4.61 (m, 1H), 3.81 (s, 3H), 3.03 (dd, $J = 4.5$ Hz, 14.0 Hz, 1H), 2.77 (dd, $J = 8.5$ Hz, 14.0 Hz, 1H), 2.45 (d, $J = 5.0$ Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): 166.3, 145.4, 136.6, 135.2, 130.4, 130.3, 126.9, 125.9, 85.8, 74.1, 51.8, 40.4, 19.4. FTIR (cm^{-1}): 3496.9, 1718.3.

(Z)-2i:

Pale yellow oil. ^1H NMR (500 MHz, CDCl_3): 7.23 (d, $J = 1.5$ Hz, 1H), 7.19 (dd, $J = 1.5$ Hz, 5.0 Hz, 1H), 6.95 (dd, $J = 3.5$ Hz, 5.0 Hz, 1H), 6.86 (d, $J = 3.5$ Hz, 1H), 4.65 (m, 1H), 3.86 (s, 3H), 3.25 (dd, $J = 5.0$ Hz, 14.5 Hz, 1H), 3.07 (dd, $J = 8.0$ Hz, 14.5 Hz, 1H), 2.49 (d, $J = 5.5$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): 166.2, 144.6, 138.6, 127.0, 126.7, 124.8, 86.7, 75.0, 52.0, 37.0. FTIR (cm^{-1}): 3468.7, 1717.0.

(Z)-2j:

Yellow oil. ^1H NMR (500 MHz, CDCl_3): 7.21-7.24 (m, 1H), 7.14 (d, $J = 1$ Hz, 1H), 6.77-6.82 (m, 2H), 6.74-6.76 (m, 1H), 4.65 (m, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 3.01 (dd, $J = 5.0$ Hz, 14.0 Hz, 1H), 2.76 (dd, $J = 8.0$ Hz, 14.0 Hz, 1H), 2.32 (d, $J = 5.0$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): 166.4, 159.7, 145.2, 138.3, 129.6, 121.8, 115.0, 112.4, 85.8, 75.2, 55.2, 52.0, 43.0. FTIR (cm^{-1}): 3450.0, 1719.5.

ad1-2-017, major
in CDCl₃
SW Probe
akn071305.1

Pulse Sequence: szpul

S6

ad1-2-017, minor
in CDC13
SW Probe
akh071205.1

Pulse Sequence: s2pul

(E)-2a

57

aid-2-036, major
in CDCl₃
SW Probe
akh091905.1

Pulse Sequence: s2pu1

adt-2-027, major.
in CDCl3
SV Probe
ak0091405.1
Pulse Sequence: szpu1

59

adi-2-043, major
in CDCl₃
SW Probe
akh092905.1

Pulse Sequence: s2pul

(Z)-2d

067

adi-2-methyl, major
in CDCl₃
SW Probe
akh033106.2

Pulse Sequence: s2pu1

(Z)-2e

S11

adi-2-072, major
in CDCl₃
SV probe
akn030606.2
Pulse Sequence: szpu1

S12

adi-2-074, major
in CDCl₃
SV Probe
akn031006.1
Pulse Sequence: szpu1

(Z)-29

di-2-074, major
in CDCl3 with D2O added
Non uniform solution
SV Probe
akb031306.1

Pulse Sequence: szpul

D₂O EXCHANGE

adi-2-063, major
no peak at integral reference (4.5ppm)
in CDCl₃
SW Probe
akh021306.2

Pulse Sequence: s2pu1

(Z)-2h

S15

adt-2-069, major
in CDC13
SV Probe
akh022706.1

Pulse Sequence: szpu1

516

adi-2-076, major
in CDCl3
SV Probe
akn031406.1
Pulse Sequence: szpu1

S17

13, major
probe
6071305.1
Pulse Sequence: szpu1

518

2-017, minor
in CDCl₃
SW Probe
akc071205.1

Pulse Sequence: szpu1

519

ad-2-036, major
in CDCl₃
SV Probe
akc091905.1
Pulse Sequence: szpul

S20

2-027
COC13
SV Probe
AKC091405.1
Pulse Sequence: szpul

521

ad1-2-043, major
1H CDCl3
SW Probe
akc092905.1
Pulse Sequence: szpu1

S22

180
160
140
120
100
80
60
40
20
ppm

067
 1-2-~~XXXXXX~~, Major
 IN CDCl₃
 SW PROBE
 AKC03106.2
 Pulse Sequence: szpul

S23

1-2-072, major
in CDCl₃
SV Probe
AKC030606.2
Pulse Sequence: szpu1

S24

3-074, major
 CCl₃
 SV Probe
 AKC031006.1
 Pulse Sequence: szpu1

S25

180
 160
 140
 120
 100
 80
 60
 40
 20
 ppm

1-2-063, major
in CDCl₃
SV Probe
akc021306.2
Pulse Sequence: szpu1

S26

180
160
140
120
100
80
60
40
20
ppm

166.271

145.416

136.668
135.282
130.543

130.448
130.369
130.235
126.929
126.689
125.942

125.780

85.886

77.253
77.000
76.743
74.113

51.867

39.514

40.458

19.433

2-069, major
CDCl₃
Probe
AKC022706.1

Pulse Sequence: szpu1

527

180
160
140
120
100
80
60
40
20
ppm

4-2-076, major
 in CDCl₃
 SW Probe
 akc031406.1
 Pulse Sequence: szpul

528

180 160 140 120 100 80 60 40 20 ppm

166.433

159.735

145.242

138.374

129.615

121.788

115.062

112.428

85.862

75.254

77.257

77.000

76.747

55.197

52.010

43.045

ad1-2-036-major
in CDC13
SW Probe
Mercury300
akf091905.1

Pulse Sequence: s2pu1

¹⁹F NMR

529