Metalloporphyrin-Catalyzed Diastereoselective Epoxidation of Allyl-Substituted Alkenes

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SUPPORTING INFORMATION

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General Structures of Metalloporphyrin Catalysts

- 1:** $M = Mn^{3+}$; $X=Cl$; $Y=Z=H$; $L = Cl$ $Mn(TDCPP)Cl$
2: $M = Ru^{2+}$; $X=Cl$; $Y=Z=H$; $L = CO$ $Ru(TDCPP)(CO)$
 $M = Mn^{3+}$; $X=Z=CH_3$; $Y=H$; $L = Cl$ $Mn(TMP)Cl$
 $M = Mn^{3+}$; $X=Y=Z=F$; $L = Cl$ $Mn(F_{20}-TPP)Cl$
 $M = Mn^{3+}$; $X=Y=H$; $Z=CH_3$; $L = Cl$ $Mn(TTP)Cl$

Literature References for Alkenes 3a–3e and 5a–5h

<p>3a</p>	Salamonczyk, G. M.; Han, K.; Guo, Z.-W.; Sih, C. J. <i>J. Org. Chem.</i> 1996 , <i>61</i> , 6893.
<p>3b</p>	Charette, A. B.; Lacasse, M.-C. <i>Org. Lett.</i> 2002 , <i>4</i> , 3351.
<p>3c</p>	Goering, H. L.; Seitz, E. P. Jr.; Tseng, C.-C. <i>J. Org. Chem.</i> 1981 , <i>46</i> , 5304.
<p>3d</p>	Cooksey, J.; Gunn, A.; Kocienski, P. J.; Kuhl, A.; Uppal, S.; Christopher, J. A.; Bell, R. <i>Org. Biomol. Chem.</i> 2004 , <i>2</i> , 1719.
<p>3e</p>	Tseng, C.-C.; Paisley, S. D.; Goering, H. L. <i>J. Org. Chem.</i> 1986 , <i>51</i> , 2884.
<p>5a</p>	Houk, K. N.; Moses, Susan R.; Wu, Y. D.; Rondan, Nelson G.; Jager, Volker; Schohe, R.; Fronczek, Frank R. <i>J. Am. Chem. Soc.</i> 1984 , <i>106</i> , 3880.
<p>5b</p>	Bellemin-Laponnaz, S.; Le Ny, J. P.; Osborn, J. A. <i>Tetrahedron Lett.</i> 2000 , <i>41</i> , 1549.
<p>5c</p>	Murai, Y.; Nishikawa, M.; Ueda, Y.; Onomura, O.; Takase, I. PCT Int. Appl. (1995), WO 9523793.

<p>5d</p>	<p>Skowronek, P.; Gawronski, J. <i>Tetrahedron Lett.</i> 2000, 41, 2975.</p>
<p>5e</p>	<p>Luly, J. R.; Dellaria, J. F.; Plattner, J. J.; Soderquist, J. L.; Yi, N. <i>J. Org. Chem.</i> 1987, 52, 1487.</p>
<p>5f</p>	<p>Luly, J. R.; Dellaria, J. F.; Plattner, J. J.; Soderquist, J. L.; Yi, N. <i>J. Org. Chem.</i> 1987, 52, 1487.</p>
<p>5g</p>	<p>Chung, S. J.; Chung, S.; Lee, H. S.; Kim, E.-J.; Oh, K. S.; Choi, H. S.; Kim, K. S.; Kim, Y. J.; Hahn, J. H.; Kim, D. H. <i>J. Org. Chem.</i> 2001, 66, 6462.</p>
<p>5h</p>	<p>Rajendra, G.; Miller, M. J. <i>J. Org. Chem.</i> 1987, 52, 4471.</p>

Literature References for Epoxides **4b**, **6a**, **6c**, **6e–6h** and **8**

<p style="text-align: center;">erythro-4b</p>	<p>Suda, K.; Kikkawa, T.; Nakajima, S.-i.; Takanami, T. <i>J. Am. Chem. Soc.</i> 2004, 126, 9554.</p>
<p style="text-align: center;">erythro-6a + threo-6a</p>	<p>Erythro-6a: Hindupur, R. M.; Panicker, B.; Valluri, M.; Avery, M. A. <i>Tetrahedron Lett.</i> 2001, 42, 7341.</p> <p>Threo-6a: Hatakeyama, S.; Sakurai, K.; Takano, S. <i>Heterocycles</i> 1986, 24, 633.</p>
<p style="text-align: center;">erythro-6c + threo-6c</p>	<p>Erythro-6c: Parkes, K. E. B.; Bushnell, D. J.; Crackett, P. H.; Dunsdon, S. J.; Freeman, A. C.; Gunn, M. P.; Hopkins, R. A.; Lambert, R. W.; Martin, J. A. et al. <i>J. Org. Chem.</i> 1994, 59, 3656.</p> <p>Threo-6c: Sengupta, S.; Sen Sarma, D.; Das, D. <i>Tetrahedron: Asymmetry</i> 1999, 10, 1653.</p>
<p style="text-align: center;">erythro-6e + threo-6e</p>	<p>Luly, J. R.; Dellaria, J. F.; Plattner, J. J.; Soderquist, J. L.; Yi, N. <i>J. Org. Chem.</i> 1987, 52, 1487.</p>
<p style="text-align: center;">erythro-6f + threo-6f</p>	<p>Luly, J. R.; Dellaria, J. F.; Plattner, J. J.; Soderquist, J. L.; Yi, N. <i>J. Org. Chem.</i> 1987, 52, 1487.</p>
<p style="text-align: center;">erythro-6g + threo-6g</p>	<p>Chung, S. J.; Chung, S.; Lee, H. S.; Kim, E.-J.; Oh, K. S.; Choi, H. S.; Kim, K. S.; Kim, Y. J.; Hahn, J. H.; Kim, D. H. <i>J. Org. Chem.</i> 2001, 66, 6462.</p>

<p style="text-align: center;"> erythro-6h threo-6h </p>	<p>Kim, D. H.; Chung, S. J. <i>Bioorg. Med. Chem. Lett.</i> 1995, 5, 1667.</p>
<p style="text-align: center;"> $\alpha\text{-8}$ $\beta\text{-8}$ </p>	<p>Che, C.-M.; Liu, C.-J.; Yu, W.-Y.; Li, S.-G. <i>J. Org. Chem.</i> 1998, 63, 7364.</p>

Characterization Data of Epoxides 4a–4e, 6b and 6d

Colorless oil, analytical TLC (silica gel 60) (10% EA in hexane), *erythro-4a* $R_f = 0.26$, *threo-4a* $R_f = 0.3$; ^1H NMR (400 MHz, CDCl_3) δ 7.35–7.26 (m, 5H), 3.8 (d, $J = 2.0$ Hz, *threo-* 1/3 x 1H), 3.76 (s, *erythro-* 2/3 x 3 H), 3.71 (s, *threo-* 1/3 x 1H), 3.70 (d, $J = 2.0$ Hz, *erythro-* 1/3 x 1H), 3.22 (dd, $J = 7.3, 2.0$ Hz, *erythro-* 2/3 x 3 H), 3.12 (dd, $J = 7.1, 2.0$ Hz, *threo-* 1/3 x 1H), 2.58–2.51 (m, 1H), 1.37 (d, $J = 7.1$ Hz, *threo-* 1/3 x 3H), 1.29 (d, $J = 7.3$ Hz, *erythro-* 2/3 x 3 H); ^{13}C NMR (100.61 MHz, CDCl_3) δ 174.0, 136.8, 128.54, 128.50, 128.3, 128.2, 125.6, 63.1, 62.9, 58.1, 57.2, 52.1, 52.0, 42.5, 13.7, 13.2; IR (KBr) 1735 cm^{-1} ; EIMS m/z 206 (M^+); HRMS (EI) for $\text{C}_{12}\text{H}_{14}\text{O}_3$, calcd 206.0942, found 206.0937.

Colorless oil, analytical TLC (silica gel 60) (2% EA in hexane), *erythro-4b* $R_f = 0.35$, *threo-4b* $R_f = 0.35$; ^1H NMR (400 MHz, CDCl_3) δ 7.35–7.24 (m, 5H), 3.92–3.86 (m, *erythro-* 1/2 x 1H), 3.82 (d, $J = 1.9$ Hz, *erythro-* 1/2 x 1H), 3.78–3.72 (m, *threo-* 1/2 x 1H), 3.73 (d, $J = 2.1$ Hz, *threo-* 1/2 x 1H), 3.00 (dd, $J = 5.7, 2.0$ Hz, *threo-* 1/2 x 1H), 2.91 (dd, $J = 4.2, 2.1$ Hz, *erythro-* 1/2 x 1H), 1.28 (d, $J = 6.4$ Hz, *erythro-* 1/2 x 3H), 1.26 (d, $J = 6.5$ Hz, *threo-* 1/2 x 3H), 0.93 (s, *threo-* 1/2 x 9H), 0.89 (s, *erythro-* 1/2 x 9H),

0.15 (s, 1/2 x 3H), 0.11 (s, 1/2 x 3H), 0.10 (s, 1/2 x 3H), 0.09 (s, 1/2 x 3H); ^{13}C NMR (100.61 MHz, CDCl_3) δ 137.5, 137.2, 128.4, 128.3, 128.0, 127.9, 125.6, 125.5, 69.3, 67.4, 66.7, 66.0, 56.1, 56.0, 25.8, 25.7, 20.8, 20.3, 18.19, 18.16, -4.61, -4.65, -4.8; IR (KBr) 2956, 1463, 836 cm^{-1} EIMS m/z 221 ($\text{M}^+ - \text{C}_4\text{H}_9$); HRMS (EI) for $\text{C}_{12}\text{H}_{17}\text{O}_2\text{Si}$ ($\text{M}^+ - \text{C}_4\text{H}_9$), calcd 221.0998, found 221.0996.

Colorless oil, analytical TLC (silica gel 60) (20% EA in hexane), *erythro-4c* R_f = 0.38, *threo-4c* R_f = 0.44; ^1H NMR (400 MHz, CDCl_3) δ 7.34–7.25 (m, 5H), 4.98–4.91 (m, 1H), 3.86 (d, J = 2.0 Hz, *threo*- 1/2 x 1H), 3.78 (d, J = 2.0 Hz, *erythro*- 1/2 x 1H), 3.13 (dd, J = 5.8, 2.0 Hz, *erythro*- 1/2 x 1H), 3.03 (dd, J = 4.8, 2.0 Hz, *threo*- 1/2 x 1H), 2.09 (s, *erythro*- 1/2 x 3H), 2.05 (s, *threo*- 1/2 x 3H), 1.35 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100.62 MHz, CDCl_3) δ 170.2, 136.7, 136.4, 128.55, 128.49, 128.42, 128.3, 125.66, 125.61, 70.3, 69.2, 63.4, 62.9, 56.9, 56.1, 21.1, 21.0, 16.5, 16.2; IR (KBr) 1720 cm^{-1} ; EIMS m/z 206 (M^+); HRMS (EI) for $\text{C}_{12}\text{H}_{14}\text{O}_3$, calcd 206.0942, found 206.0951.

Colorless oil, analytical TLC (silica gel 60) (20% EA in hexane) *erythro-4d* $R_f = 0.48$, *threo-4d* $R_f = 0.53$; ^1H NMR (400 MHz, CDCl_3) δ 8.10–8.08 (m, 2H), 7.56–7.27 (m, 8H), 5.24–5.20 (m, 1H), 3.96 (d, $J = 2.0$ Hz, *threo-* 2/5 x 1H), 3.86 (d, $J = 2.0$ Hz, *erythro-* 3/5 x 1H), 3.27 (dd, $J = 5.5, 2.0$ Hz, *erythro-* 3/5 x 1H), 3.16 (dd, $J = 4.8, 2.0$ Hz, *threo-* 2/5 x 1H), 1.49 (d, $J = 6.5$ Hz, *erythro-* 3/5 x 1H), 1.48 (d, $J = 6.6$ Hz, *threo-* 2/5 x 1H); ^{13}C NMR (100.62 MHz, CDCl_3) δ 165.66, 165.64, 136.5, 136.3, 133.1, 129.78, 129.74, 128.6, 128.5, 128.48, 128.45, 128.3, 125.7, 125.6, 70.5, 69.8, 63.5, 63.0, 57.0, 56.0, 16.6, 16.2; IR (KBr) 1709 cm^{-1} ; EIMS m/z 268 (M^+); HRMS (EI) for $\text{C}_{17}\text{H}_{16}\text{O}_3$, calcd 268.1099, found 268.1090.

Colorless oil, analytical TLC (silica gel 60) (10% EA in hexane), *erythro-4e* $R_f = 0.44$; ^1H NMR (300 MHz, CDCl_3) δ 7.36–7.25 (m, 5H), 4.97–4.89 (m, 1H), 3.78 (d, $J = 2.0$ Hz, 1H), 3.15 (dd, $J = 5.7, 2.1$ Hz, 1H), 1.34 (d, $J = 6.5$ Hz, 3H), 1.24 (s, 9H); ^{13}C NMR (100.62 MHz, CDCl_3) δ 177.7, 136.5, 128.5, 128.3, 125.6, 69.7, 63.5, 56.0, 38.8, 27.1, 16.4; IR (KBr) 1730 cm^{-1} ; EIMS m/z 248 (M^+); HRMS (EI) for $\text{C}_{15}\text{H}_{20}\text{O}_3$, calcd 248.1412, found 248.1411.

threo-4e

Colorless oil, analytical TLC (silica gel 60) (10% EA in hexane), **threo-4e** $R_f = 0.49$; ^1H NMR (300 MHz, CDCl_3) δ 7.35–7.25 (m, 5H), 5.01–4.97 (m, 1H), 3.85 (d, $J = 2.0$ Hz, 1H), 3.01 (dd, $J = 5.6, 2.0$ Hz, 1H), 1.35 (d, $J = 6.5$ Hz, 3H), 1.21 (s, 9H); ^{13}C NMR (75.47 MHz, CDCl_3) δ 177.7, 136.8, 128.4, 128.2, 125.5, 68.7, 63.1, 56.5, 38.8, 27.1, 16.3; IR (KBr) 1731 cm^{-1} ; EIMS m/z 248 (M^+); HRMS (EI) for $\text{C}_{15}\text{H}_{20}\text{O}_3$, calcd 248.1412, found 248.1413.

Colorless oil; analytical TLC (silica gel 60) (5% EA in hexane), **erythro-6b** $R_f = 0.51$, **threo-6b** $R_f = 0.42$; ^1H NMR (300 MHz, CDCl_3) δ 3.56 (dd, $J = 10.9, 4.9$ Hz, **erythro-** 1/2 x 1H), 3.29–3.23 (m, **threo-** 1/2 x 1H), 2.93–2.88 (m, **threo-** 1/2 x 1H), 2.87–2.84 (m, **erythro-** 1/2 x 1H), 2.78–2.75 (m, **threo-** 1/2 x 1H), 2.69 (dd, $J = 5.4, 3.9$ Hz, **erythro-** 1/2 x 1H), 2.64 (dd, $J = 5.5, 2.7$ Hz, **erythro-** 1/2 x 1H), 2.54 (dd, $J = 4.9, 2.7$ Hz, **threo-** 1/2 x 1H), 1.56–1.32 (m, 4H), 0.95–0.87 (m, 3H), 0.90 (s, **threo-** 1/2 x 9H), 0.88 (s, **erythro-** 1/2 x 9H), 0.10–0.04 (m, 6H); ^{13}C NMR (75.47 MHz, CDCl_3) δ 74.3, 71.0, 55.9, 54.6, 44.76, 44.72, 37.4, 36.8, 25.77, 25.72, 18.4, 18.0, 14.1, 14.0, -4.4, -4.9, -5.1; IR (KBr) 2958, 1463, 836 cm^{-1} ; EIMS m/z 215 ($\text{M}^+ - \text{CH}_3$); HRMS (EI) for $\text{C}_{11}\text{H}_{23}\text{O}_2\text{Si}$ ($\text{M}^+ - \text{CH}_3$), calcd 215.1467, found 215.1445.

Pale yellow oil; analytical TLC (silica gel 60) (20% EA in hexane), *erythro-6d* $R_f = 0.3$, *threo-6d* $R_f = 0.3$; ^1H NMR (300 MHz, CDCl_3) δ 7.87–7.82 (m, 2H), 7.75–7.71 (m, 2H), 3.70–3.66 (m, 1H), 3.44–3.36 (m, 1H), 2.99 (dd, $J = 5.1, 3.9$ Hz, *threo-* 2.5/3.5 x 1H), 2.75 (dd, $J = 5.0, 2.5$, *threo-* 2.5/3.5 x 1H), 2.69–2.61 (m, *erythro-* 1/3.5 x 2H), 2.47 (dd, $J = 5.0, 2.6$ Hz, *erythro-* 1/3.5 x 1H), 1.19 (d, $J = 6.7$ Hz, *erythro-* 1/3.5 x 3H), 1.10 (d, $J = 6.7$ Hz, *threo-* 2.5/3.5 x 3H), 0.89 (d, $J = 6.7$ Hz, *threo-* 2.5/3.5 x 3H), 0.87 (d, $J = 6.7$ Hz, *erythro-* 1/3.5 x 3H); ^{13}C NMR (75.47 MHz, CDCl_3) δ 168.3, 168.1, 134.1, 133.9, 131.7, 131.6, 123.3, 123.2, 61.4, 61.0, 51.9, 51.0, 48.9, 44.6, 30.0, 28.4, 19.9, 19.7, 19.5; IR (KBr) 1777, 1711 cm^{-1} ; EIMS m/z 245 (M^+); HRMS (EI) for $\text{C}_{14}\text{H}_{15}\text{O}_3\text{N}$, calcd 245.1051, found 245.1047.

¹H NMR Spectra of Diastereomeric Mixtures of Epoxides 4

Table 1, entry 1

Table 1, entry 6

Table 3, entry 2

Table 3, entry 4

Table 3, entry 5

Table 3, entry 8

Determination of the α -8/ β -8 Ratio with ^1H NMR

23. **APPLIED AND INTERMEDIATE**

[7-9]	
(6C) (8d)	

16	1991
15	1990
14	1989
13	1988
12	1987
11	1986
10	1985
9	1984
8	1983
7	1982
6	1981
5	1980
4	1979
3	1978
2	1977
1	1976

SOLVENT	CDC 13

0-246532 HC
P. 0447733 680

1000

[illegible]

12 - Processing parameters

0.0001

10 mm disc diameter
C1 70.00 cm

1000

NAME: 4E-12
 CONC: 2
 DMSO-D6: 1

F2 - Acquisition Parameters
 Date_: 06/06/14
 Time: 16:19
 INSTRUM: spect
 PROBHD: 5 mm QNP 1H/13
 PULPROG: zgpg30
 TD: 32768
 SOLVENT: DMSO-D6
 NS: 388
 DS: 4
 SWH: 24517.810 Hz
 F2 (MHS): 500.136000 MHz
 AQ: 0.00000000 sec
 RG: 655.36
 INJ: 10.000 uL
 DE: 0.00 uL/sec
 TE: 300.2 K
 DT: 2.50000000 sec
 dT1: 0.02000000 sec

===== CHANNEL f2 =====
 NUC1: 13C
 P1: 8.10 uSec
 PL1: -5.00 dB
 SFO: 100.6261904 MHz

===== CHANNEL f1 =====
 NUC2: 1H
 P2: 12.00 uSec
 PL2: -19.00 dB
 SFO2: 400.1463600 MHz

===== CHANNEL f2 =====
 CPDPRG2: waltz16
 NUC2: 1H
 P2: 12.00 uSec
 PL2: -19.00 dB
 PL12: 12.00 dB
 SFO2: 400.1463600 MHz

F2 - Processing parameters
 SI: 32768
 SF: 500.136000 MHz
 DSF: 128
 KHZ: 1
 WDW: EM
 SSF: 1.00 Hz
 LB: 0
 GB: 0
 PC: 1.49

10 uM 0.1% 300KHz
 C1: 20.00 sec
 C2: 3.20 sec
 F2 (P): 500.136000 MHz
 F1: 201.264 MHz
 F2P: -10.000 ppm
 F2: -1006.13 Hz
 PPM (M): 9.20000 ppm/cm
 H1CN: 985.82751 Hz/cm

Current Data Parameters
NAME: 100-1001
EXPNO: 2
PROCNO: 1
F2 - Acquisition Parameters
Date_ : 06/01/01
Time: 11:50
INSTRUM: spect
PROBHD: 5 mm QNP 1H/13
PULPROG: zgpg30
TD: 65536
SOLVENT: CDCl3
NS: 2048
DS: 4
SWH: 19150.869 Hz
FIDRES: 0.700773 Hz
AQ: 0.0001302 sec
RG: 1.0000000
RT: 1.0000000 sec
TE: 300.2 K
D1: 2.50000000 sec
d11: 0.00000000 sec
===== CHANNEL f1 =====
NUC1: 13C
P1: 9.70 usec
PL1: -0.00 dB
SFO: 100.626184 MHz
===== CHANNEL f2 =====
CPROG2: zgpg30
NUC2: 1H
PCPD2: 90.00 usec
PL2: -4.00 dB
PL12: 19.00 dB
SFO2: 400.146007 MHz
F2 - Processing parameters
SI: 32768
SF: 500.137700 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 0
PC: 1.00
LO Mode: SFO: 500.137700 MHz
CY: 8.17 usec
FIR: 200.000 usec
FI: 20194.81 Hz
FQ: -16.000 usec
F2 - Acquisition Parameters
NAME: 100-1001
EXPNO: 2
PROCNO: 1