A Cyclodextrin-Modified Ketoester for Stereoselective Epoxidation of Alkenes

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(I) Characterization Data of Terpenes (S)-**3b**–**d**

Terpenes (S)-**3b–d** were prepared from (S)- α -terpineol (**3a**) ($[\alpha]_D^{20}$ 79.1 (c = 20, EtOH)).

^1H NMR (300 MHz, CDCl_3) 5.39 (br s, 1H), 3.18 (s, 3H), 1.67–2.02 (m, 6H), 1.65 (s, 3H), 1.16–1.30 (m, 1H), 1.10 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (75.47 MHz, CDCl_3) 133.99, 120.84, 76.63, 48.69, 41.48, 31.08, 26.84, 23.91, 23.35, 22.33, 21.84. (ref: Crivello, J. V.; Liu, S. *Chem. Mater.* **1998**, *10*, 3724.)

^1H NMR (300 MHz, CDCl_3) 5.37 (br s, 1H), 1.71–2.19 (m, 6H), 1.94 (m, 3H), 1.64 (s, 3H), 1.44 (s, 3H), 1.41 (s, 3H), 1.23–1.36 (m, 1H); ^{13}C NMR (75.47 MHz, CDCl_3) 170.47, 133.94, 120.29, 84.82, 42.55, 30.87, 26.35, 23.84, 23.31, 23.10, 22.47. (ref: Hirata, T.; Izumi, S.; Ekida, T.; Suga, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 289.)

^1H NMR (300 MHz, CDCl_3) 7.97–8.00 (m, 2H), 7.34–7.55 (m, 3H), 5.40 (br s, 1H), 1.87–2.18 (m, 6H), 1.67 (s, 3H), 1.60 (s, 3H), 1.58 (s, 3H), 1.38–1.54 (m, 1H); ^{13}C NMR (75.47 MHz, CDCl_3) 165.30, 133.98, 132.38, 132.09, 129.36, 128.19, 120.35, 85.48, 43.19, 30.94, 26.48, 24.02, 23.45, 23.41, 23.30; $[\alpha]_{\text{D}}^{20}$ 44 (c = 4, EtOAc). (ref: Ravindranath, B.; Srinivas, P. *Tetrahedron* **1984**, 40, 1623.)

(II) References of Epoxides **4a–c** and Limonene epoxides

<p><i>cis-4a</i> + <i>trans-4a</i></p>	<p>Kopperman, H. L.; Hallcher, R. C.; Riehl, A.; Carlson, R. M.; Caple, R. <i>Tetrahedron</i> 1976, 32, 1621.</p>
<p><i>cis-4b</i> + <i>trans-4b</i></p>	<p>Crivello, J. V.; Liu, S. <i>Chem. Mater.</i> 1998, 10, 3724.</p>
<p><i>cis-4c</i> + <i>trans-4c</i></p>	<p>Hirata, T.; Izumi, S.; Ekida, T.; Suga, T. <i>Bull. Chem. Soc. Jpn.</i> 1987, 60, 289.</p>
<p><i>cis-</i> + <i>trans-</i></p>	<p>Asouti, A.; Hadjarapoglou, L. P. <i>Synlett</i> 2001, 1847.</p>
<p><i>trans</i> + <i>cis</i></p>	<p>Battioni, P.; Renaud, J. P.; Bartoli, J. F.; Reina-Artiles, M.; Fort, M.; Mansuy, D. <i>J. Am. Chem. Soc.</i> 1988, 110, 8462.</p>

(III) Characterization Data of 4d

Colorless liquid; analytical TLC (silica gel 60) (10% EtOAc in hexane), $R_f = 0.41$; ^1H NMR (300 MHz, CDCl_3) 7.95–7.99 (m, 2H), 7.39–7.54 (m, 3H), 3.11 (br s, $\frac{1}{2}$ 1H), 3.01 (d, $J = 5$ Hz, $\frac{1}{2}$ 1H), 1.66–2.33 (m, 6H), 1.58 (s, 3H), 1.55 (s, $\frac{1}{2}$ 3H), 1.50 (s, $\frac{1}{2}$ 3H), 1.35 (s, $\frac{1}{2}$ 3H), 1.32 (s, $\frac{1}{2}$ 3H); ^{13}C NMR (75.47 MHz, CDCl_3) 165.61, 165.47, 132.55, 132.45, 132.02, 131.78, 129.38, 129.33, 128.26, 128.22, 85.26, 84.65, 60.99, 59.12, 57.68, 57.52, 41.59, 39.63, 30.76, 29.42, 26.88, 25.53, 24.38, 23.48, 23.42, 23.30, 22.85, 22.82, 20.28; IR (KBr) 1712 cm^{-1} ; FABMS m/z 275 (M^+ , 18); HRMS (EI) for $\text{C}_{10}\text{H}_{16}\text{O}$ (M^+ PhCOOH), calcd 152.1201, found 152.1195.

(IV) ^1H NMR Spectra of Diastereomeric Mixtures of Terpene Epoxides

Table 1, entry 1

Table 1, entry 6

Table 1, entry 9

Table 1, entry 12

Table 2, entry 1

Table 2, entry 4

(V) ^1H NMR Spectra of Enantiomeric Mixtures of Epoxides

Enantiopurities of the chiral epoxides were determined by ^1H NMR spectroscopy using $\text{Eu}(\text{hfc})_3$ (Aldrich Cat. No. 16,474-7) as chiral shift reagent. The percentage of enantiomeric excess (%ee) was evaluated on the basis of the integration ratio of the corresponding resolved peak areas. The spectra of each epoxide in both racemic and enantiomerically enriched forms are provided on the following pages.

Table 3, entry 4

^1H NMR Conditions
Chiral shift reagent: $\text{Eu}(\text{hfc})_3$

Table 3, entry 5

^1H NMR Conditions
Chiral shift reagent: $\text{Eu}(\text{hfc})_3$

Racemic

Chiral

Table 3, entry 6

^1H NMR Conditions
Chiral shift reagent: $\text{Eu}(\text{hfc})_3$

Table 3, entry 7

^1H NMR Conditions
Chiral shift reagent: $\text{Eu}(\text{hfc})_3$

Racemic

Chiral

Table 3, entry 9

^1H NMR Conditions
Chiral shift reagent: $\text{Eu}(\text{hfc})_3$

Racemic

Chiral

Table 3, entry 10

^1H NMR Conditions
Chiral shift reagent: $\text{Eu}(\text{hfc})_3$

References for the determination of enantiomeric excesses of epoxides:

<p>(<i>R,R</i>)-<i>trans</i>-stilbene oxide</p> <p>Wang, Z. X.; Tu, Y.; Frohn, M.; Shi, Y. <i>J. Org. Chem.</i> 1997, 62, 2328.</p>
<p>(<i>R,R</i>)-<i>trans</i>-1-phenyl-2-methyloxirane</p> <p>Wang, Z. X.; Tu, Y.; Frohn, M.; Shi, Y. <i>J. Org. Chem.</i> 1997, 62, 2328.</p>
<p>(<i>R,R</i>)-<i>trans</i>-1-phenyl-2-methyl-2-phenyloxirane</p> <p>The absolute configuration of this epoxide was determined by optical rotation measurement, see: Brandes, B. D.; Jacobsen, E. N. <i>J. Org. Chem.</i> 1994, 59, 4378.</p>
<p>(1<i>R</i>,2<i>S</i>)-3,4-dihydronaphthalene oxide</p> <p>Wang, Z. X.; Tu, Y.; Frohn, M.; Zhang, J. R.; Shi, Y. <i>J. Am. Chem. Soc.</i> 1997, 119, 11224.</p>
<p>(<i>R</i>)-<i>p</i>-chlorostyrene oxide</p> <p>Yang, D.; Yip, Y. C.; Tang, M. W.; Wong, M. K.; Zheng, J. H.; Cheung, K. K. <i>J. Am. Chem. Soc.</i> 1996, 118, 491.</p>
<p>(<i>R</i>)-1-phenyl-2-methyloxirane</p> <p>Yang, D.; Yip, Y. C.; Tang, M. W.; Wong, M. K.; Zheng, J. H.; Cheung, K. K. <i>J. Am. Chem. Soc.</i> 1996, 118, 491.</p> <p>The absolute configuration of this epoxide was determined by optical rotation measurement, see: Fujisawa, T.; Takemura, I.; Ukaji, Y. <i>Tetrahedron Lett.</i> 1990, 31, 5479.</p>

Current Data Parameters
NAME: DC-2-127
EXPNO: 4
PROCNO: 1

F2 - Acquisition Parameters
Date_: 20020614
Time: 9:43
Date_: 20020614
Time: 9:43
PROBHD: 5 mm QNP 1H/13
PULPROG: zgpg30
TD: 65536
SOLVENT: DMSO
NUC1: 13C
NUC2: 1H
FIDRES: 0.182959 Hz
AQ: 2.7232011 sec
RG: 327.68
DE: 83.400 usec
TE: 300.0 K
D1: 1.00000000 sec

===== CHANNEL f1 =====
NUC1: 13C
P1: 10.50 usec
PL1: -4.00 dB
SFO1: 400.126000 MHz

F2 - Processing parameters
SI: 32768
SF: 400.126000 MHz
WDW: EM
SSB: 0
LB: 0.30 Hz
GB: 0
PC: 1.00

10 NMR Data Parameters
CX: 25.00 cm
CY: 61.67 cm
CZ: 10.250 cm
F1: 400.126 MHz
F2: -100.03 MHz
PCPN: 0.42000 cm/sec
WDCN: 100.05400 Hz/cm

2 in D₂O

Current Data Parameters
 Name: DC-2127C
 EXPNO: 1
 PROCNO: 1
 F2 - Acquisition Parameters
 Date_ Time: 2005.09.14 9:42
 INSTRUM: spect
 PULPROG: zgpg30
 PRGDATE: 5 May 1993
 F2 - Processing Parameters
 Date_ Time: 2005.09.14 10:20
 SOLVENT: D2O
 NS: 1691
 DS: 2
 SWH: 25125.629 Hz
 FIDRES: 0.000137 Hz
 AQ: 0.6591372 sec
 RG: 1149.4
 DW: 19.500 usec
 DE: 6.00 usec
 TE: 300.2 K
 D1: 3.0000000 sec
 d11: 0.0300000 sec
 d12: 0.0002000 sec
 ***** CHANNEL f1 *****
 NUC1: 13C
 P1: 6.50 usec
 PL1: -5.00 dB
 SFO1: 100.6270504 MHz
 ***** CHANNEL f2 *****
 NUC2: 1H
 P2: 100.00 usec
 PL2: 19.00 dB
 SFO2: 400.146005 MHz
 F2 - Processing Parameters
 SI: 32768
 SF: 100.617742 MHz
 AQ: 0.6591372 sec
 RG: 1149.4
 DW: 19.500 usec
 DE: 6.00 usec
 TE: 300.2 K
 D1: 3.0000000 sec
 d11: 0.0300000 sec
 d12: 0.0002000 sec
 1D NMR plot parameters
 CX: 25.00 cm
 CY: 12.00 cm
 F1P: 215.000 ppm
 F2P: 2163.120 Hz
 F3P: 15.000 ppm
 F2: -503.06 Hz
 PPMCK: 8.80000 ppm/Hz
 NUCN: 8B5 38240 Hz/Hz

cis-4d + *trans*-4d

 in CDCl₃

Partial contour plot of 500 MHz ROESY spectrum for binding of **3b** (5.9 mM) to **2** (5.1 mM) in D₂O.