

**Asymmetric Epoxidation Catalyzed by α,α -Dimethylmorpholinone Ketone.
Methyl Group Effect on Spiro and Planar Transition States**

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Supporting Information

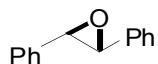
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General Methods. All commercially available reagents were used without further purification. All glassware used for the epoxidation was carefully washed with soap water to remove any trace metals which may catalyze the decomposition of Oxone. Column chromatography was performed with silica gel (230-400 mesh). ^1H NMR spectra were recorded on 300 or 400 MHz NMR spectrometer and ^{13}C NMR spectra were recorded on 75 or 100 MHz NMR spectrometer using CDCl_3 as a solvent. IR spectra were recorded on a FT-IR spectrometer. Melting points were uncorrected.

Characterization Data of Epoxides

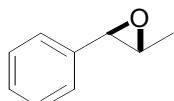
Table 1, Entries 1 and 2



White solid; $[\alpha]_D^{25} = +334.6$ (*c* 0.73, benzene) (97 % ee); ^1H NMR (300 MHz, CDCl_3) δ 7.44-7.34 (m, 10H), 3.90 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 137.3, 128.8, 128.5, 125.7, 63.1.

- (a) Chang, H-T.; Sharpless, K.B. *J. Org. Chem.* **1996**, *61*, 6456.
- (b) Wang, Z-X.; Tu, Y.; Frohn, M.; Zhang, J-R.; Shi, Y. *J. Am. Chem. Soc.* **1997**, *119*, 11224.

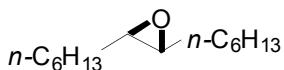
Table 1, Entry 3 and 4



Colorless oil; $[\alpha]_D^{25} = +44.3$ (*c* 0.32, CHCl_3) (90 % ee); ^1H NMR (300 MHz, CDCl_3) δ 7.39-7.26 (m, 5H), 3.60 (d, *J* = 2.1 Hz, 1H), 3.06 (qd, *J* = 5.1, 2.1 Hz, 1H), 1.48 (d, *J* = 5.1 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 138.0, 128.6, 128.2, 125.8, 59.7, 59.2, 18.1.

- (a) Witkop, B.; Foltz, C.M. *J. Am. Chem. Soc.* **1957**, *79*, 197.
- (b) Wang, Z-X.; Tu, Y.; Frohn, M.; Zhang, J-R.; Shi, Y. *J. Am. Chem. Soc.* **1997**, *119*, 11224.

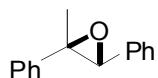
Table 1, Entry 5 and 6



Colorless oil; [α]_D²⁵ = +22.8 (*c* 0.65, CHCl₃) (83% ee); ¹H NMR (300 MHz, CDCl₃) δ 2.65 (t, *J* = 4.5 Hz, 2H), 1.56-1.23 (m, 20H), 0.89 (t, *J* = 6.6 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 59.2, 32.4, 32.0, 29.3, 26.2, 22.8, 14.3

Wang, Z-X.; Tu, Y.; Frohn, M.; Zhang, J-R.; Shi, Y. *J. Am. Chem. Soc.* **1997**, *119*, 11224.

Table 1, Entry 7 and 8

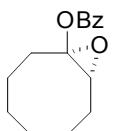


White solid; [α]_D²⁵ = +98.8 (*c* 0.72, EtOH) (89 % ee); ¹H NMR (400 MHz, CDCl₃) δ 7.51-7.34 (m, 10H), 4.02 (s, 1H), 1.51 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 142.5, 136.1, 128.7, 128.4, 127.9, 127.7, 126.7, 125.3, 67.3, 63.3, 16.9.

(a) Brandes, B.D.; Jacobsen, E.N. *J. Org. Chem.* **1994**, *59*, 4378.

(b) Wang, Z-X.; Tu, Y.; Frohn, M.; Zhang, J-R.; Shi, Y. *J. Am. Chem. Soc.* **1997**, *119*, 11224.

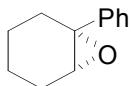
Table 1, Entry 9 and 10



Colorless oil; [α]_D²⁵ = +7.3 (*c* 0.62, CHCl₃) (90% ee); ¹H NMR (300 MHz, CDCl₃) δ 8.03-8.00 (m, 2H), 7.57 (tt, *J* = 7.2, 1.5 Hz, 1H), 7.46-7.41 (m, 2H), 3.21 (dd, *J* = 10.2, 4.5 Hz, 1H), 2.91-2.86 (m, 1H), 2.27 (ddd, *J* = 13.8, 7.8, 4.5 Hz, 1H), 1.88-1.20 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 165.2, 133.5, 130.1, 129.9, 128.6, 85.9, 60.4, 28.0, 26.2, 26.1, 25.2, 24.9.

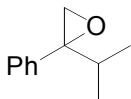
Zhu, Y.; Shu, L.; Tu, Y.; Shi, Y. *J. Org. Chem.* **2001**, *66*, 1818.

Table 1, Entries 11 and 12



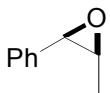
Colorless oil; $[\alpha]_D^{25} = -92.0$ (*c* 0.64, benzene) (80% ee); $[\alpha]_D^{25} = +102.4$ (*c* 0.54, benzene) (87% ee); ^1H NMR (300 MHz, CDCl_3) δ 7.42-7.25 (m, 5H), 3.10 (s, 1H), 2.36-2.26 (m, 1H), 2.12 (dt, *J* = 14.7, 5.1 Hz, 1H), 2.03-1.99 (m, 2H), 1.69-1.46 (m, 3H), 1.41-1.28 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 142.7, 128.4, 127.4, 125.5, 62.1, 60.4, 29.0, 24.9, 20.3, 20.0.
Wang, Z-X.; Tu, Y.; Frohn, M.; Zhang, J-R.; Shi, Y. *J. Am. Chem. Soc.* **1997**, *119*, 11224.

Table 1, Entry 13 and 14



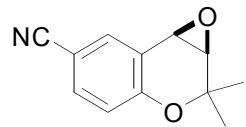
Colorless oil; $[\alpha]_D^{25} = +33.5$ (*c* 1.10, CHCl_3) (84% ee); $[\alpha]_D^{25} = -19.4$ (*c* 0.51, CHCl_3) (45% ee); ^1H NMR (300 MHz, CDCl_3) δ 7.39-7.26 (m, 5H), 3.00 (d, *J* = 5.4 Hz, 1H), 2.73 (d, *J* = 5.4 Hz, 1H), 2.10 (septet, *J* = 6.9 Hz, 1H), 0.96 (d, *J* = 6.9 Hz, 3H), 0.95 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 139.6, 128.1, 127.6, 127.5, 64.7, 53.4, 33.3, 18.7, 18.0.
Wang, B.; Wong, O.A.; Zhao, M.-X.; Shi, Y. *J. Org. Chem.* **2008**, *73*, 9539.

Table 1, Entry 15 and 16



Colorless oil; $[\alpha]_D^{25} = -37.8$ (*c* 0.49, CHCl_3) (85% ee); ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.28 (m, 5H), 4.08 (d, *J* = 4.5 Hz, 1H), 3.36 (qd, *J* = 5.4, 4.5 Hz, 1H), 1.10 (d, *J* = 5.4 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 135.7, 128.2, 127.7, 126.8, 57.7, 55.4, 12.7.
Tian, H.; She, X.; Yu, H.; Shu, L.; Shi, Y. *J. Org. Chem.* **2002**, *67*, 2435.

Table 1, Entry 17 and 18



White solid; $[\alpha]_D^{25} = +59.8$ (c , 1.20, CHCl_3) (81% ee); ^1H NMR (300 MHz, CDCl_3) δ 7.66 (d, J = 2.1 Hz, 1H), 7.53 (dd, J = 8.4, 1.8 Hz, 1H), 6.87 (d, J = 8.4 Hz, 1H), 3.92 (d, J = 4.5 Hz, 1H), 3.55 (d, J = 4.5 Hz, 1H), 1.60, (s, 3H), 1.30 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 156.7, 134.6, 134.0, 121.3, 119.2, 118.9, 104.4, 74.8, 62.5, 50.1, 25.7, 23.2.

Wong, O.A.; Shi, Y. *J. Org. Chem.* **2006**, *71*, 3973.

The X-ray structure of ketone 4

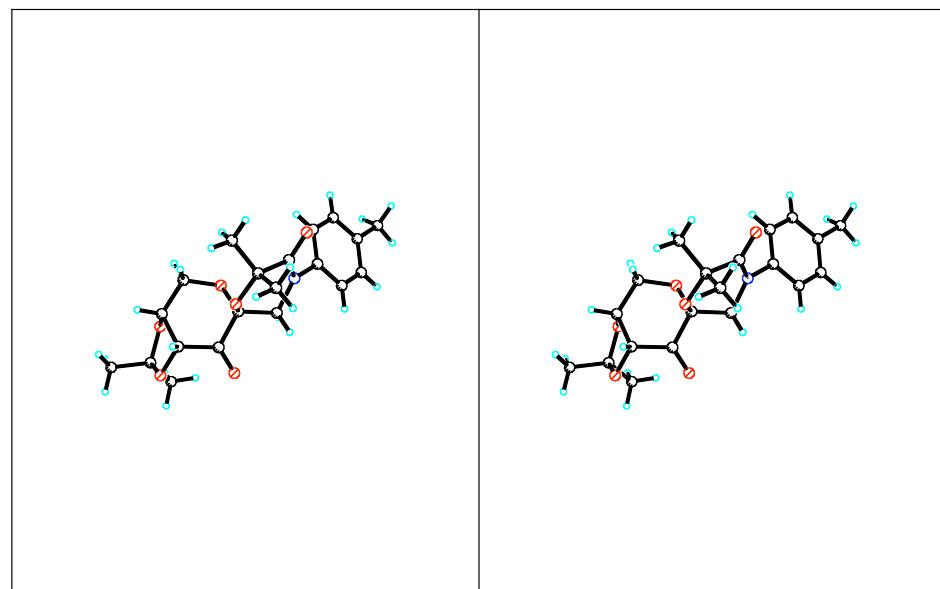
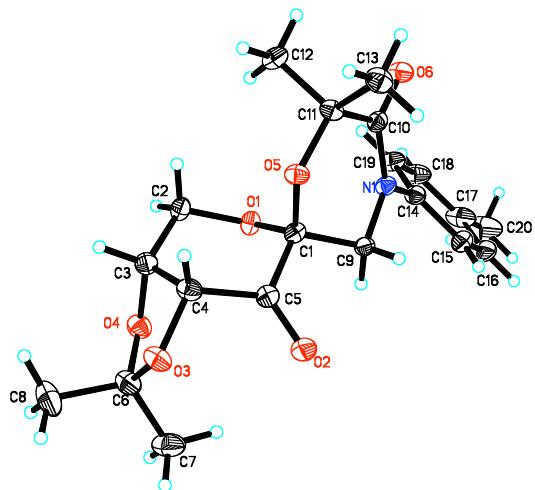


Table 1. Crystal data and structure refinement for ketone **4**.

Identification code	ys140
Empirical formula	C20 H25 N O6
Formula weight	375.41
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 10.4164(3) Å b = 17.5391(5) Å c = 21.0938(6) Å
	α = 90°. β = 90°. γ = 90°.
Volume	3853.72(19) Å ³
Z	8
Density (calculated)	1.294 Mg/m ³
Absorption coefficient	0.096 mm ⁻¹
F(000)	1600
Crystal size	0.38 x 0.28 x 0.07 mm ³
Theta range for data collection	1.51 to 30.47°.
Index ranges	-14<=h<=10, -20<=k<=25, -26<=l<=30
Reflections collected	44539
Independent reflections	11127 [R(int) = 0.0559]
Completeness to theta = 30.47°	99.3 %
Absorption correction	multiscans
Max. and min. transmission	0.9935 and 0.9648
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	11127 / 0 / 488
Goodness-of-fit on F ²	0.752
Final R indices [I>2sigma(I)]	R1 = 0.0529, wR2 = 0.1397
R indices (all data)	R1 = 0.0936, wR2 = 0.1812
Extinction coefficient	0.0011(5)
Largest diff. peak and hole	0.311 and -0.251 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ys140. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	3810(2)	391(1)	1069(1)	16(1)
O(1)	1890(2)	1050(1)	1830(1)	17(1)
O(2)	4269(2)	1608(1)	2770(1)	25(1)
O(3)	2414(2)	2566(1)	3261(1)	23(1)
O(4)	913(2)	1633(1)	3083(1)	22(1)
O(5)	3266(2)	1939(1)	1332(1)	18(1)
O(6)	3490(2)	598(1)	17(1)	21(1)
C(1)	3135(2)	1375(2)	1801(1)	16(1)
C(2)	866(3)	1589(2)	1929(1)	20(1)
C(3)	1044(3)	2069(2)	2513(1)	21(1)
C(4)	2386(3)	2387(2)	2605(1)	20(1)
C(5)	3382(3)	1784(1)	2432(1)	17(1)
C(6)	1515(3)	2061(2)	3576(1)	24(1)
C(7)	2230(4)	1516(2)	4002(1)	34(1)
C(8)	547(4)	2552(2)	3930(2)	37(1)
C(9)	4062(3)	727(1)	1695(1)	16(1)
C(10)	3554(2)	842(2)	558(1)	17(1)
C(11)	3291(3)	1692(2)	669(1)	17(1)
C(12)	1991(3)	1881(2)	374(1)	21(1)
C(13)	4369(3)	2153(2)	362(1)	23(1)
C(14)	3859(3)	-421(2)	1004(1)	18(1)
C(15)	4852(3)	-829(2)	1277(1)	23(1)
C(16)	4853(3)	-1622(2)	1251(1)	29(1)
C(17)	3867(4)	-2016(2)	957(1)	32(1)
C(18)	2870(3)	-1599(2)	693(1)	28(1)
C(19)	2860(3)	-806(2)	712(1)	23(1)
C(20)	3860(5)	-2876(2)	930(2)	48(1)
N(1A)	7244(2)	2829(1)	1808(1)	18(1)
O(1A)	5933(2)	3872(1)	1030(1)	18(1)
O(2A)	3774(2)	3963(1)	2227(1)	23(1)
O(3A)	3693(2)	4683(1)	477(1)	25(1)

O(4A)	2827(2)	5084(1)	1420(1)	21(1)
O(5A)	6715(2)	4404(1)	1978(1)	19(1)
O(6A)	9326(2)	3127(1)	1608(1)	22(1)
C(1A)	5815(2)	3908(1)	1699(1)	16(1)
C(2A)	5932(3)	4607(2)	730(1)	19(1)
C(3A)	4690(2)	5032(2)	833(1)	17(1)
C(4A)	4165(2)	4999(2)	1508(1)	17(1)
C(5A)	4498(3)	4256(2)	1855(1)	16(1)
C(6A)	2497(3)	4766(2)	810(1)	20(1)
C(7A)	1630(3)	5338(2)	478(2)	30(1)
C(8A)	1905(3)	3986(2)	864(2)	28(1)
C(9A)	5945(3)	3102(2)	1946(1)	18(1)
C(10A)	8249(3)	3322(2)	1776(1)	18(1)
C(11A)	8037(3)	4125(2)	2033(1)	19(1)
C(12A)	8900(3)	4694(2)	1703(1)	23(1)
C(13A)	8330(3)	4084(2)	2745(1)	25(1)
C(14A)	7457(3)	2028(1)	1697(1)	16(1)
C(15A)	7767(3)	1769(2)	1093(1)	20(1)
C(16A)	8030(3)	997(2)	1000(1)	23(1)
C(17A)	7967(3)	475(2)	1497(1)	20(1)
C(18A)	7633(3)	744(2)	2095(1)	20(1)
C(19A)	7377(3)	1514(2)	2199(1)	19(1)
C(20A)	8323(3)	-350(2)	1394(2)	29(1)

Table 3. Bond lengths [\AA] and angles [$^\circ$] for ys140.

N(1)-C(10)	1.364(3)
N(1)-C(14)	1.433(3)
N(1)-C(9)	1.468(3)
O(1)-C(1)	1.418(3)
O(1)-C(2)	1.441(3)
O(2)-C(5)	1.207(3)
O(3)-C(4)	1.419(3)
O(3)-C(6)	1.450(4)
O(4)-C(6)	1.426(3)
O(4)-C(3)	1.430(3)
O(5)-C(1)	1.407(3)
O(5)-C(11)	1.465(3)
O(6)-C(10)	1.220(3)
C(1)-C(9)	1.509(4)
C(1)-C(5)	1.535(4)
C(2)-C(3)	1.504(4)
C(3)-C(4)	1.517(4)
C(4)-C(5)	1.525(4)
C(6)-C(7)	1.509(4)
C(6)-C(8)	1.522(4)
C(10)-C(11)	1.535(4)
C(11)-C(12)	1.526(4)
C(11)-C(13)	1.526(4)
C(14)-C(15)	1.382(4)
C(14)-C(19)	1.384(4)
C(15)-C(16)	1.391(4)
C(16)-C(17)	1.386(5)
C(17)-C(18)	1.387(5)
C(17)-C(20)	1.510(4)
C(18)-C(19)	1.392(4)
N(1A)-C(10A)	1.361(3)
N(1A)-C(14A)	1.442(3)
N(1A)-C(9A)	1.464(3)
O(1A)-C(1A)	1.419(3)

O(1A)-C(2A)	1.436(3)
O(2A)-C(5A)	1.202(3)
O(3A)-C(3A)	1.421(3)
O(3A)-C(6A)	1.438(3)
O(4A)-C(4A)	1.413(3)
O(4A)-C(6A)	1.444(3)
O(5A)-C(1A)	1.407(3)
O(5A)-C(11A)	1.465(3)
O(6A)-C(10A)	1.225(3)
C(1A)-C(9A)	1.514(4)
C(1A)-C(5A)	1.537(4)
C(2A)-C(3A)	1.510(4)
C(3A)-C(4A)	1.527(4)
C(4A)-C(5A)	1.535(4)
C(6A)-C(8A)	1.506(4)
C(6A)-C(7A)	1.519(4)
C(10A)-C(11A)	1.525(4)
C(11A)-C(12A)	1.512(4)
C(11A)-C(13A)	1.534(4)
C(14A)-C(15A)	1.390(4)
C(14A)-C(19A)	1.392(4)
C(15A)-C(16A)	1.395(4)
C(16A)-C(17A)	1.395(4)
C(17A)-C(18A)	1.391(4)
C(17A)-C(20A)	1.510(4)
C(18A)-C(19A)	1.394(4)
C(10)-N(1)-C(14)	120.5(2)
C(10)-N(1)-C(9)	120.9(2)
C(14)-N(1)-C(9)	118.6(2)
C(1)-O(1)-C(2)	114.79(19)
C(4)-O(3)-C(6)	107.4(2)
C(6)-O(4)-C(3)	106.8(2)
C(1)-O(5)-C(11)	117.77(19)
O(5)-C(1)-O(1)	113.7(2)
O(5)-C(1)-C(9)	111.3(2)

O(1)-C(1)-C(9)	106.8(2)
O(5)-C(1)-C(5)	105.4(2)
O(1)-C(1)-C(5)	107.7(2)
C(9)-C(1)-C(5)	112.0(2)
O(1)-C(2)-C(3)	113.3(2)
O(4)-C(3)-C(2)	112.2(2)
O(4)-C(3)-C(4)	100.2(2)
C(2)-C(3)-C(4)	115.1(2)
O(3)-C(4)-C(3)	103.0(2)
O(3)-C(4)-C(5)	111.9(2)
C(3)-C(4)-C(5)	110.0(2)
O(2)-C(5)-C(4)	123.9(2)
O(2)-C(5)-C(1)	121.4(2)
C(4)-C(5)-C(1)	114.7(2)
O(4)-C(6)-O(3)	105.7(2)
O(4)-C(6)-C(7)	108.6(2)
O(3)-C(6)-C(7)	110.0(3)
O(4)-C(6)-C(8)	111.3(3)
O(3)-C(6)-C(8)	107.9(2)
C(7)-C(6)-C(8)	113.1(3)
N(1)-C(9)-C(1)	108.8(2)
O(6)-C(10)-N(1)	123.2(2)
O(6)-C(10)-C(11)	118.2(2)
N(1)-C(10)-C(11)	118.5(2)
O(5)-C(11)-C(12)	108.0(2)
O(5)-C(11)-C(13)	105.2(2)
C(12)-C(11)-C(13)	111.4(2)
O(5)-C(11)-C(10)	115.9(2)
C(12)-C(11)-C(10)	107.9(2)
C(13)-C(11)-C(10)	108.6(2)
C(15)-C(14)-C(19)	119.8(2)
C(15)-C(14)-N(1)	120.0(2)
C(19)-C(14)-N(1)	120.0(2)
C(14)-C(15)-C(16)	120.1(3)
C(17)-C(16)-C(15)	121.0(3)
C(16)-C(17)-C(18)	118.2(3)

C(16)-C(17)-C(20)	121.3(3)
C(18)-C(17)-C(20)	120.6(3)
C(17)-C(18)-C(19)	121.4(3)
C(14)-C(19)-C(18)	119.6(3)
C(10A)-N(1A)-C(14A)	119.6(2)
C(10A)-N(1A)-C(9A)	120.9(2)
C(14A)-N(1A)-C(9A)	119.6(2)
C(1A)-O(1A)-C(2A)	113.46(19)
C(3A)-O(3A)-C(6A)	109.32(19)
C(4A)-O(4A)-C(6A)	108.1(2)
C(1A)-O(5A)-C(11A)	116.96(19)
O(5A)-C(1A)-O(1A)	112.7(2)
O(5A)-C(1A)-C(9A)	111.9(2)
O(1A)-C(1A)-C(9A)	107.0(2)
O(5A)-C(1A)-C(5A)	105.08(19)
O(1A)-C(1A)-C(5A)	108.0(2)
C(9A)-C(1A)-C(5A)	112.1(2)
O(1A)-C(2A)-C(3A)	112.4(2)
O(3A)-C(3A)-C(2A)	109.7(2)
O(3A)-C(3A)-C(4A)	102.4(2)
C(2A)-C(3A)-C(4A)	115.0(2)
O(4A)-C(4A)-C(3A)	103.1(2)
O(4A)-C(4A)-C(5A)	112.0(2)
C(3A)-C(4A)-C(5A)	113.4(2)
O(2A)-C(5A)-C(4A)	122.1(2)
O(2A)-C(5A)-C(1A)	122.0(2)
C(4A)-C(5A)-C(1A)	115.9(2)
O(3A)-C(6A)-O(4A)	105.6(2)
O(3A)-C(6A)-C(8A)	107.4(2)
O(4A)-C(6A)-C(8A)	112.4(2)
O(3A)-C(6A)-C(7A)	110.9(2)
O(4A)-C(6A)-C(7A)	107.3(2)
C(8A)-C(6A)-C(7A)	113.1(2)
N(1A)-C(9A)-C(1A)	108.6(2)
O(6A)-C(10A)-N(1A)	122.8(2)
O(6A)-C(10A)-C(11A)	119.5(2)

N(1A)-C(10A)-C(11A)	117.3(2)
O(5A)-C(11A)-C(12A)	107.6(2)
O(5A)-C(11A)-C(10A)	114.6(2)
C(12A)-C(11A)-C(10A)	111.1(2)
O(5A)-C(11A)-C(13A)	106.3(2)
C(12A)-C(11A)-C(13A)	111.3(2)
C(10A)-C(11A)-C(13A)	105.9(2)
C(15A)-C(14A)-C(19A)	120.0(2)
C(15A)-C(14A)-N(1A)	120.2(2)
C(19A)-C(14A)-N(1A)	119.8(2)
C(14A)-C(15A)-C(16A)	119.4(2)
C(17A)-C(16A)-C(15A)	121.5(3)
C(18A)-C(17A)-C(16A)	118.1(2)
C(18A)-C(17A)-C(20A)	121.2(3)
C(16A)-C(17A)-C(20A)	120.7(3)
C(17A)-C(18A)-C(19A)	121.2(2)
C(14A)-C(19A)-C(18A)	119.7(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ys140. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	19(1)	13(1)	17(1)	0(1)	-2(1)	2(1)
O(1)	14(1)	14(1)	23(1)	-2(1)	0(1)	-2(1)
O(2)	21(1)	32(1)	21(1)	-1(1)	-3(1)	0(1)
O(3)	30(1)	21(1)	18(1)	-2(1)	2(1)	-3(1)
O(4)	26(1)	21(1)	20(1)	2(1)	3(1)	-1(1)
O(5)	23(1)	14(1)	16(1)	2(1)	-1(1)	-1(1)
O(6)	29(1)	18(1)	17(1)	0(1)	-2(1)	2(1)
C(1)	15(1)	16(1)	18(1)	2(1)	-2(1)	-2(1)
C(2)	17(1)	21(1)	23(1)	1(1)	0(1)	4(1)
C(3)	24(1)	19(1)	19(1)	5(1)	2(1)	4(1)
C(4)	26(1)	17(1)	17(1)	-1(1)	0(1)	-1(1)
C(5)	19(1)	15(1)	19(1)	1(1)	0(1)	-1(1)
C(6)	31(2)	22(1)	20(1)	-1(1)	2(1)	0(1)
C(7)	47(2)	30(2)	23(1)	4(1)	-7(1)	2(2)
C(8)	43(2)	32(2)	35(2)	-4(1)	16(2)	5(2)
C(9)	18(1)	17(1)	14(1)	-1(1)	-2(1)	2(1)
C(10)	14(1)	18(1)	19(1)	2(1)	-1(1)	0(1)
C(11)	19(1)	16(1)	15(1)	1(1)	1(1)	-5(1)
C(12)	24(1)	17(1)	23(1)	0(1)	-7(1)	1(1)
C(13)	24(2)	24(1)	22(1)	2(1)	2(1)	-6(1)
C(14)	22(1)	16(1)	17(1)	0(1)	-1(1)	2(1)
C(15)	22(1)	24(1)	22(1)	1(1)	-2(1)	5(1)
C(16)	38(2)	23(1)	25(1)	1(1)	-4(1)	12(1)
C(17)	56(2)	18(1)	20(1)	-1(1)	-4(1)	6(1)
C(18)	42(2)	20(1)	21(1)	1(1)	-7(1)	-4(1)
C(19)	29(2)	20(1)	21(1)	2(1)	-6(1)	1(1)
C(20)	97(3)	15(1)	31(2)	-2(1)	-13(2)	6(2)
N(1A)	18(1)	10(1)	27(1)	-2(1)	-1(1)	1(1)
O(1A)	22(1)	14(1)	19(1)	-3(1)	2(1)	1(1)
O(2A)	21(1)	22(1)	27(1)	0(1)	7(1)	2(1)
O(3A)	19(1)	37(1)	20(1)	-8(1)	-1(1)	1(1)

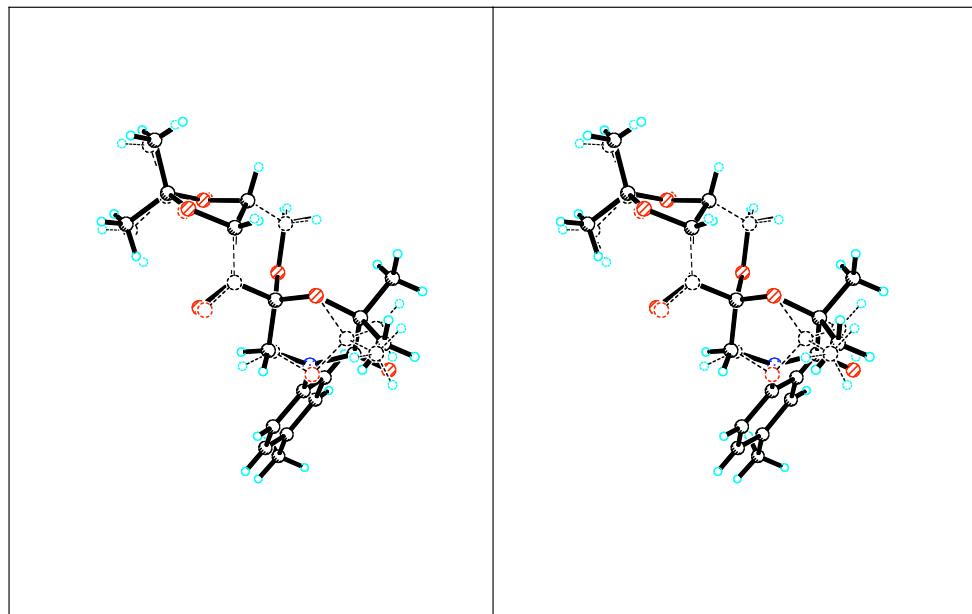
O(4A)	18(1)	22(1)	24(1)	-5(1)	1(1)	5(1)
O(5A)	17(1)	14(1)	27(1)	-5(1)	-3(1)	2(1)
O(6A)	17(1)	18(1)	32(1)	0(1)	1(1)	2(1)
C(1A)	15(1)	16(1)	19(1)	-2(1)	0(1)	1(1)
C(2A)	20(1)	16(1)	20(1)	1(1)	3(1)	0(1)
C(3A)	16(1)	17(1)	20(1)	-2(1)	-1(1)	-1(1)
C(4A)	14(1)	15(1)	21(1)	-3(1)	1(1)	2(1)
C(5A)	19(1)	14(1)	16(1)	-4(1)	-3(1)	2(1)
C(6A)	17(1)	21(1)	23(1)	-4(1)	1(1)	1(1)
C(7A)	26(2)	29(2)	35(2)	2(1)	-7(1)	3(1)
C(8A)	27(2)	24(1)	32(2)	-4(1)	0(1)	-1(1)
C(9A)	16(1)	15(1)	23(1)	-1(1)	3(1)	2(1)
C(10A)	20(1)	14(1)	20(1)	-1(1)	-2(1)	2(1)
C(11A)	17(1)	16(1)	25(1)	-4(1)	-1(1)	4(1)
C(12A)	20(1)	16(1)	34(1)	-1(1)	1(1)	-1(1)
C(13A)	26(2)	24(1)	23(1)	-4(1)	-5(1)	4(1)
C(14A)	15(1)	12(1)	22(1)	0(1)	0(1)	0(1)
C(15A)	25(1)	16(1)	20(1)	2(1)	-5(1)	2(1)
C(16A)	26(2)	21(1)	21(1)	-5(1)	-1(1)	4(1)
C(17A)	17(1)	14(1)	30(1)	-1(1)	-3(1)	-1(1)
C(18A)	17(1)	17(1)	26(1)	7(1)	2(1)	-2(1)
C(19A)	18(1)	20(1)	19(1)	-1(1)	3(1)	1(1)
C(20A)	26(2)	17(1)	43(2)	-3(1)	-1(1)	3(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for ys140.

	x	y	z	U(eq)
H(2A)	61	1314	1963	24
H(2B)	809	1922	1563	24
H(3A)	420	2487	2513	25
H(4A)	2508	2847	2349	24
H(7A)	2826	1223	3754	50
H(7B)	1630	1179	4204	50
H(7C)	2688	1799	4319	50
H(8A)	119	2883	3636	55
H(8B)	985	2852	4243	55
H(8C)	-73	2230	4134	55
H(9A)	4938	914	1713	20
H(9B)	3954	344	2022	20
H(12A)	1806	2412	436	32
H(12B)	1336	1579	572	32
H(12C)	2015	1771	-72	32
H(13A)	4216	2687	427	35
H(13B)	4393	2047	-84	35
H(13C)	5175	2013	550	35
H(15A)	5519	-573	1478	28
H(16A)	5527	-1891	1435	34
H(18A)	2193	-1854	500	33
H(19A)	2186	-535	530	28
H(20A)	4617	-3070	1134	72
H(20B)	3848	-3039	495	72
H(20C)	3112	-3067	1143	72
H(2AA)	6072	4542	278	23
H(2AB)	6637	4907	897	23
H(3AA)	4790	5565	701	21
H(4AA)	4494	5433	1750	20
H(7AA)	2054	5823	457	45

H(7AB)	843	5389	711	45
H(7AC)	1446	5162	57	45
H(8AA)	2491	3650	1077	41
H(8AB)	1727	3791	448	41
H(8AC)	1121	4018	1101	41
H(9AA)	5793	3092	2400	22
H(9AB)	5317	2774	1743	22
H(12D)	8700	4705	1259	35
H(12E)	9781	4546	1759	35
H(12F)	8768	5191	1881	35
H(13D)	8213	4579	2931	37
H(13E)	9201	3922	2806	37
H(13F)	7759	3726	2943	37
H(15B)	7799	2108	754	24
H(16B)	8253	828	597	27
H(18B)	7579	404	2432	24
H(19B)	7153	1685	2601	23
H(20D)	8219	-627	1783	43
H(20E)	9202	-382	1259	43
H(20F)	7777	-566	1075	43

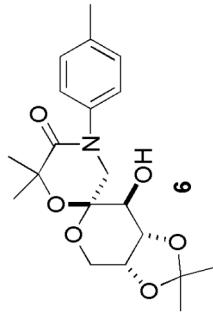
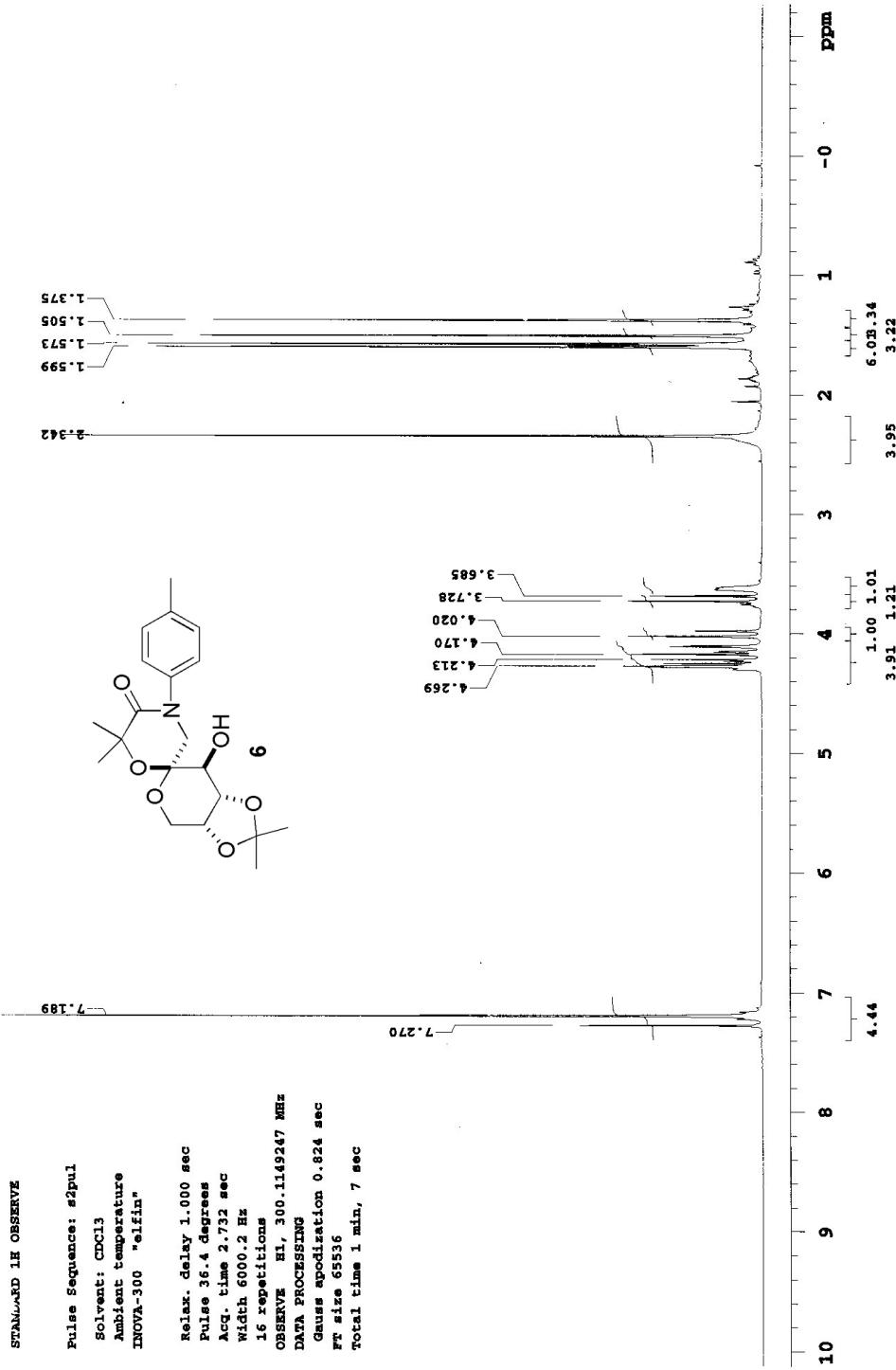
The stereoview of the structure overlay of ketones 1 and 4



STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDCl₃
Ambient temperature
T₁ = 100 Hz 15.1 ms

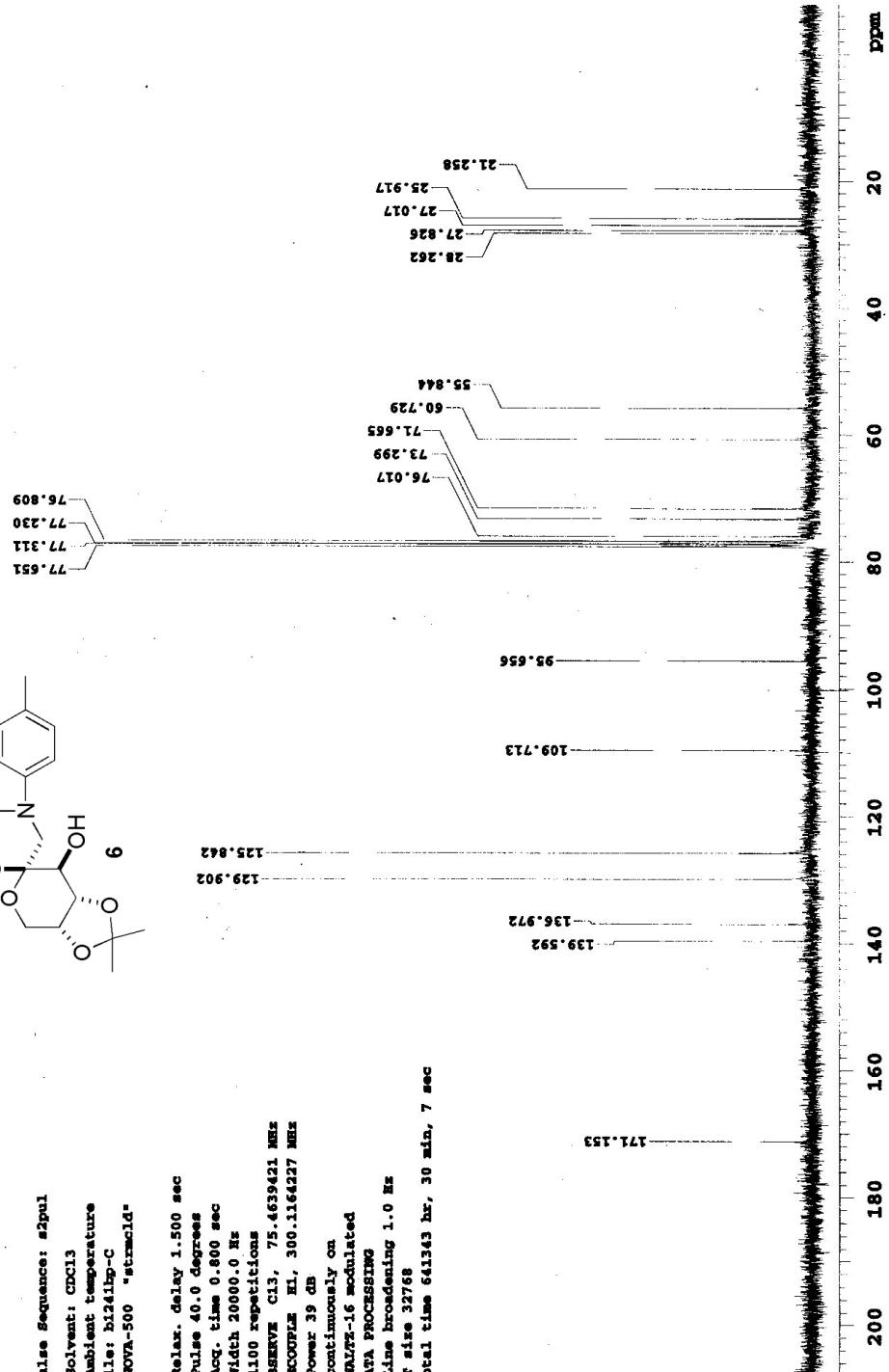
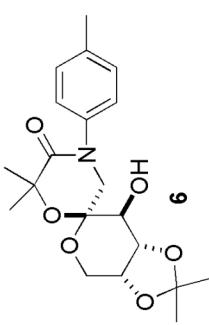
Relax. delay 1.00 sec
 Pulse 36.4 degrees
 Acq. time 2.732 sec
 Width 6000.2 Hz
 16 repetitions
 OBSERVE EII, 300.114947 MHz
 DATA PROCESSING
 Gauss apodization 0.824 sec
 FFT size 65536
 total time 1 min, 7 sec



13C OBSERVE

Pulse Sequence: #2pul
 Solvent: CDCl₃
 Ambient temperature
 File: bx241sp-C
 INNOVA-500 "stcmclid"

Relax. delay 1.500 sec
 Pulse 40.0 degrees
 Acq. time 0.800 sec
 Width 20000.0 Hz
 1100 repetitions
 OBSERVE CH₃, 75.4639421 MHz
 DECOUPLE H1, 300.1164227 MHz
 Power 39 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 32768
 Total time 64.3343 hr, 30 min, 7 sec



STANDARD 1H OBSERVE

Pulse Sequence: s6pul

Solvent: CDCl₃

Ambient temperature

F1: oav-04-06-09-dimethylketone

INOVA-500 "epoxide"

Relax. delay 0.000 sec

Pulse 2.0 degrees

W1: 1.08 ,.16 sec

W2: 1.515 ,.22 Hz

32 FID's 114.0 sec

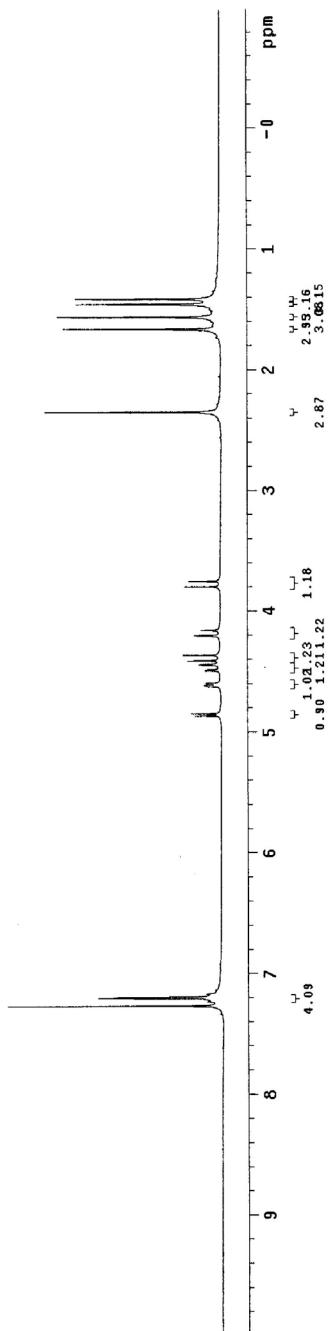
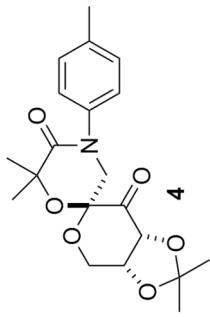
OBSERVE: 411.300-1582159 MHz

DATA PROCESSING

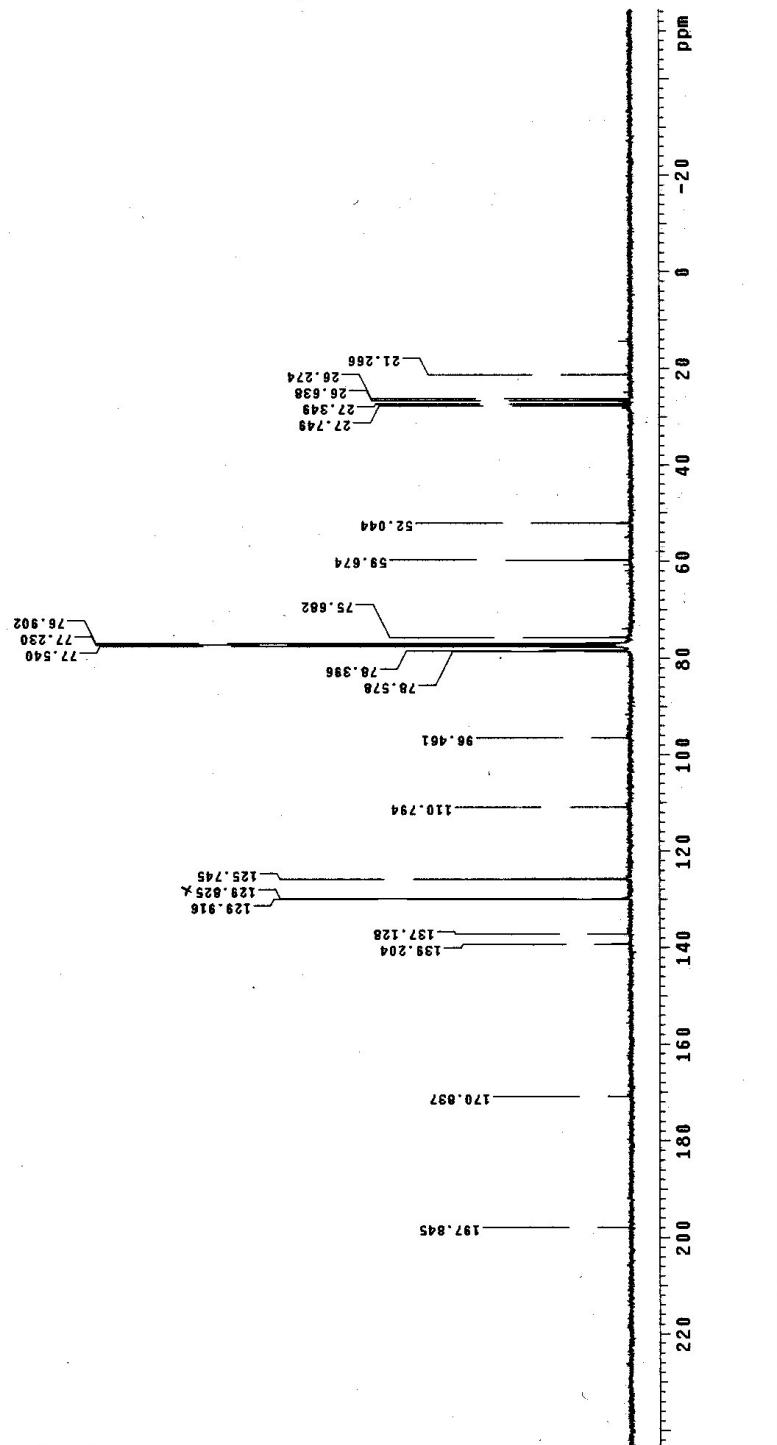
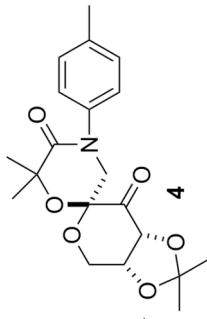
Gauss apodization 0.896 sec

F1 size 32768

Total time 2 min, 56 sec



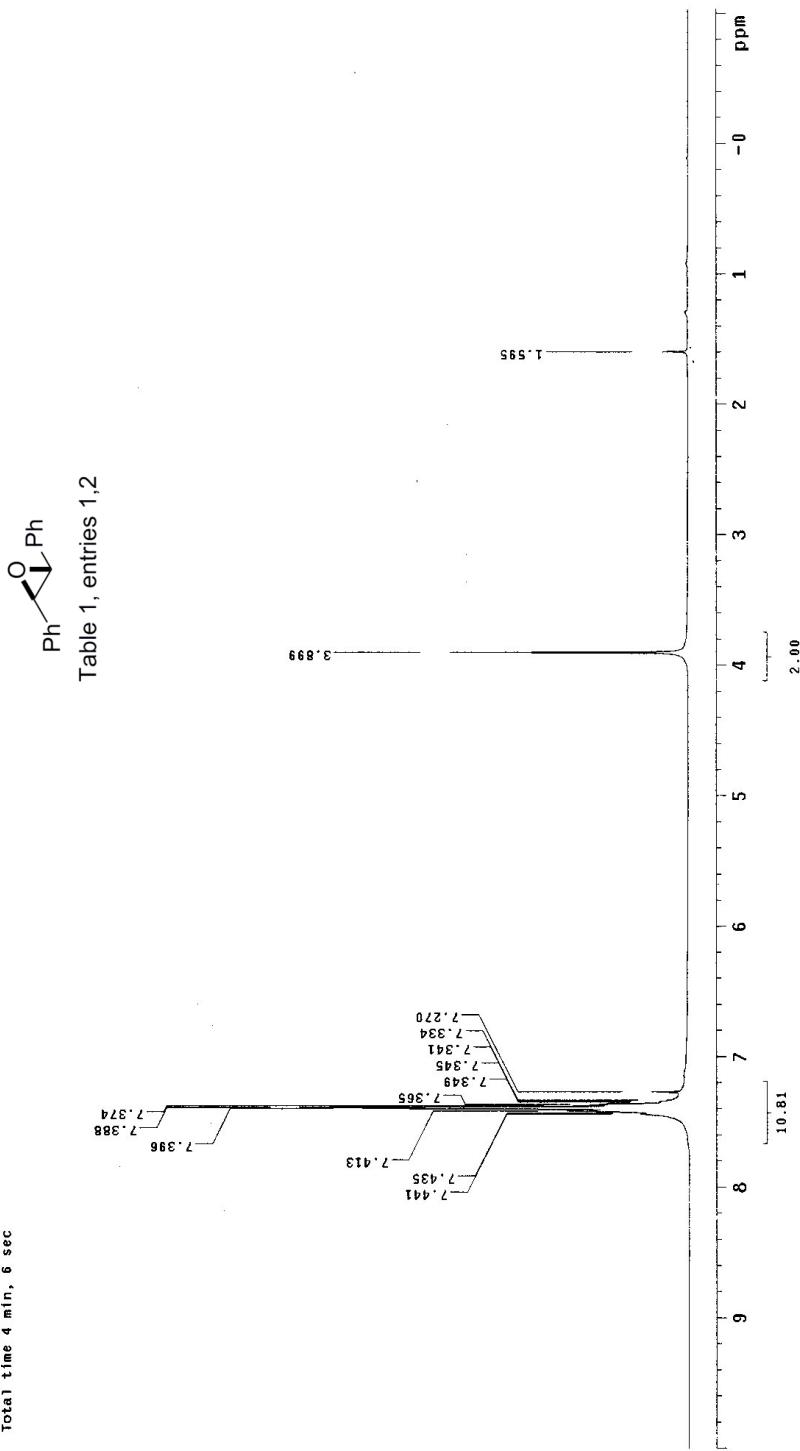
MUSIC OBSERVE



STANDARD 1H OBSERVE

Pulse Sequence: s2pu1
Solvent: C6c13
Ambient temperature
File: caw-09_09_08-H2350-2
INOVA-500 "epoxide"

Relax delay 1.000 sec
Pulse 34.0 degrees
Acq. time 2.792 sec
Wdwidth 60.0 Hz
2048 points
OBSERVE H1/99.9533672 MHz
DATA PROCESSING
Gauss apodization 0.824 sec
FT size 65536
Total time 4 min, 6 sec



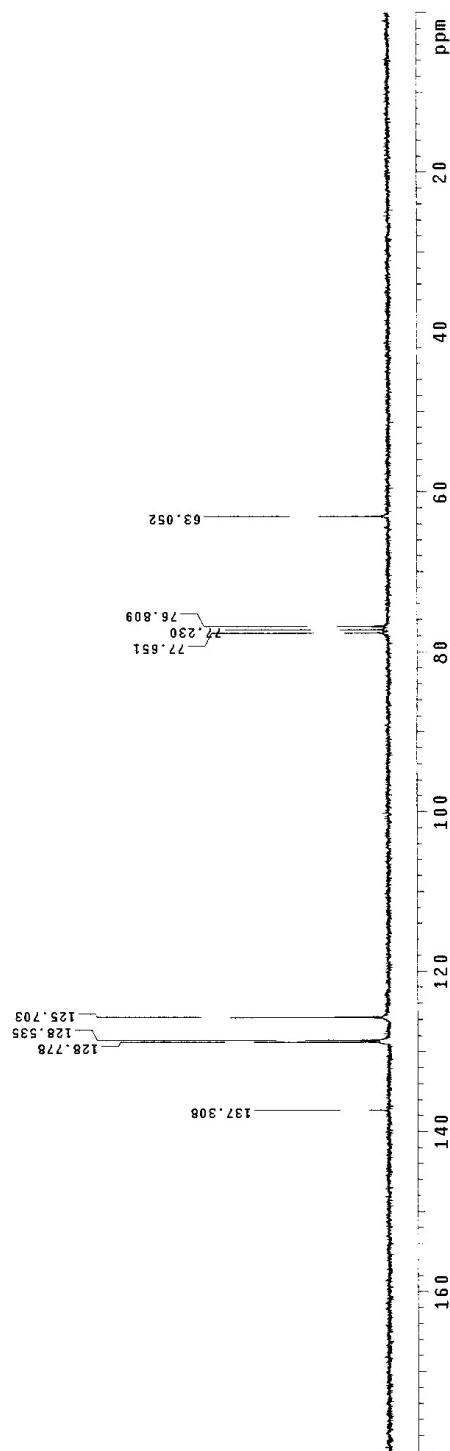
13C OBSERVE

Pulse Sequence: s2pu1
 Solvent: CnC12
 Shmitt, Temperature-
 f116 raw-09 09 08-C-2350-2
 INOVA-500
 "epoxide"

Relax-delay 1.500 sec
 Pulse 39.1 degrees
 Acq. time 0.800 sec
 Width 2000.0 Hz
 32. repeat 1.0 sec
 0.03, 75.4233210 MHz
 0.03, 75.4233210 MHz
 Decouple H, 239.9548659 MHz
 Decouple H, 239.9548659 MHz
 Cover 36 dB
 Gated in 16 ms
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 f1 size 32768
 Total time 61343 hr, 30 min, 7 sec



Table 1, entries 1,2



STANDARD 1H OBSERVE

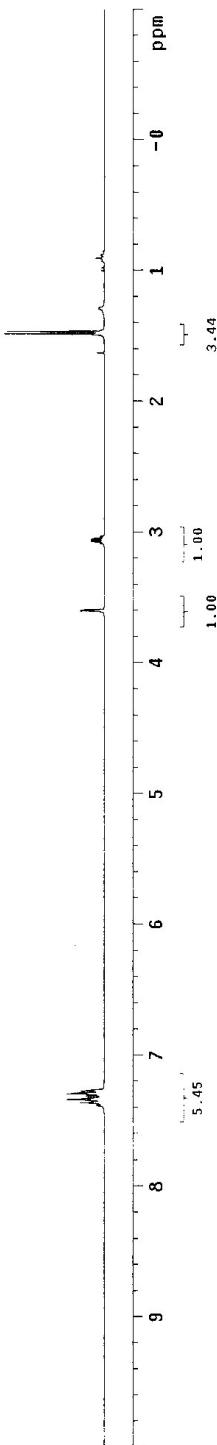
```

Pulse Sequence: s2pu1
Solvent: C6C13
Ambient Temperature
File: cov-09_09_08-H-2350-1
INOVA-500 "epoxide"
PhOCH2CH2CO2Ph
Relax delay 1.000 sec
Pulse 34.0 degrees
90deg pulse
Acq 1.000 sec
Wdft 6000 Hz
12800 t1 points
OBSERVE FID H1 99.9533661 MHz
DATA PROCESSING
Gauss apodization 0.824 sec
FT size 65536
Total time 4 min, 6 sec

```

O
Ph—

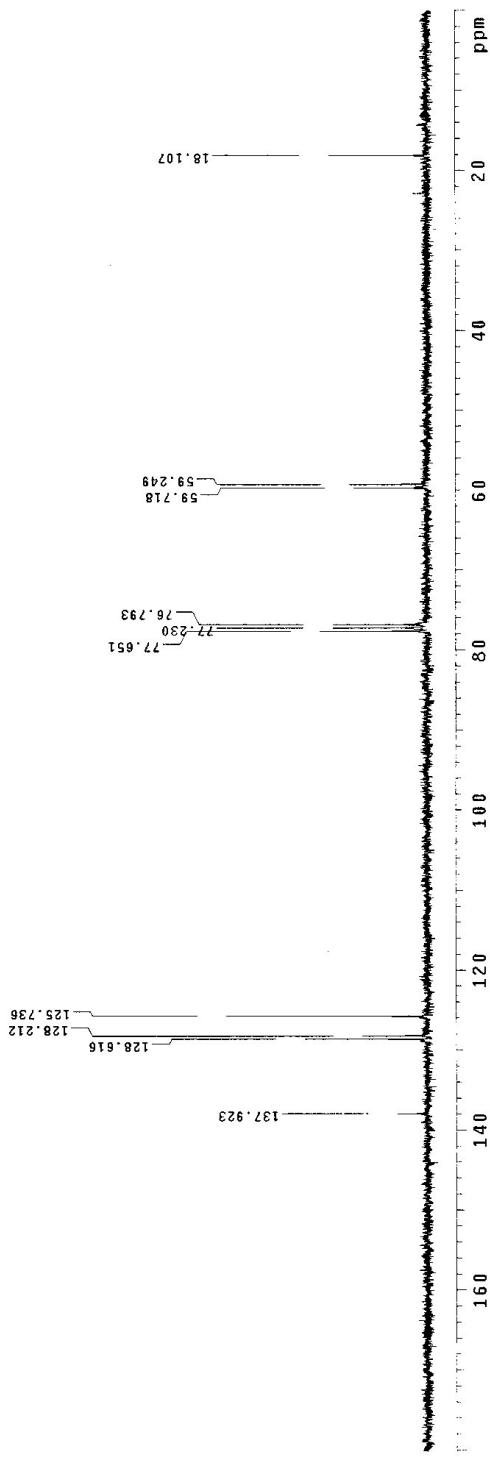
Table 1, entries 3, 4



13C OBSERVE



Table 1, entries 3, 4



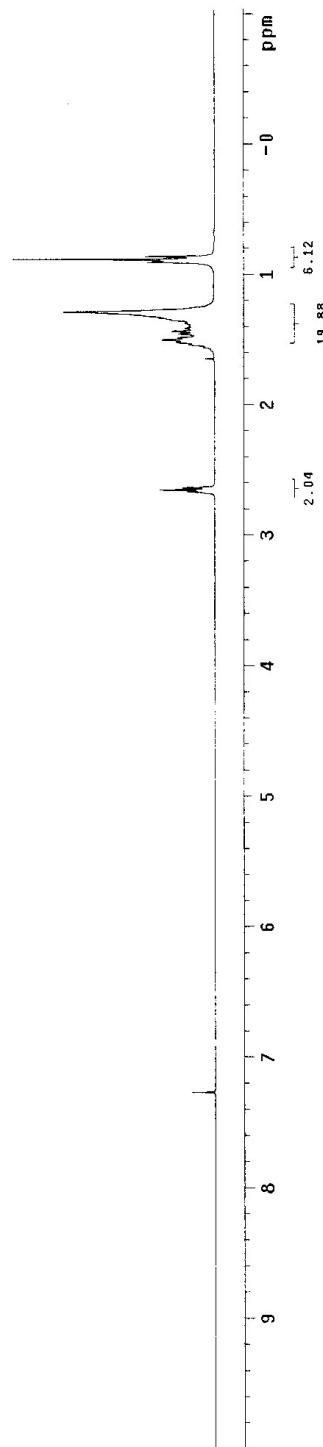
STANDARD 1H OBSERVE

Pulse Sequence: s2pu1
Solvent: CDCl₃
Ambient temperature
File: raw-03_03_00-H-2349-2
INNOVA-500 "epoxide"

Relax. delay 1.000 sec
Pulse 34.0 degrees
Acq. time 2.732 sec
Width 6000.6 Hz
8 repetitions
OBSERVE H1 299.9533681 MHz
DATA PROCESSING
Gauss apodization 0.824 sec
FT size 65536
Total time 4 min, 6 sec



Table 1, entries 5, 6



13C OBSERVE

Pulse Sequence: s2pu1
 Solvent: CDCl₃
 Object: Temperature-C-2349-2
 File name-09_09_08-C-2349-2
 INDAVA-500 "epoxide"

Relax-delay 1.500 sec
 Pulse 39.1 degrees
 Acq. Time 0.800 sec
 Watch 20.0 Hz
 Acquisition 32
 Observations 75
 OBSERVE C13, 75.4223186 MHz
 DECOPLE F1 H, 29.9548659 MHz
 Power 36 dB
 continuosly on
 WAITZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 f1 size 32768
 Total time 641343 hr, 30 min, 7 sec

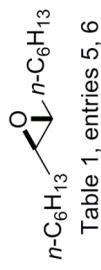
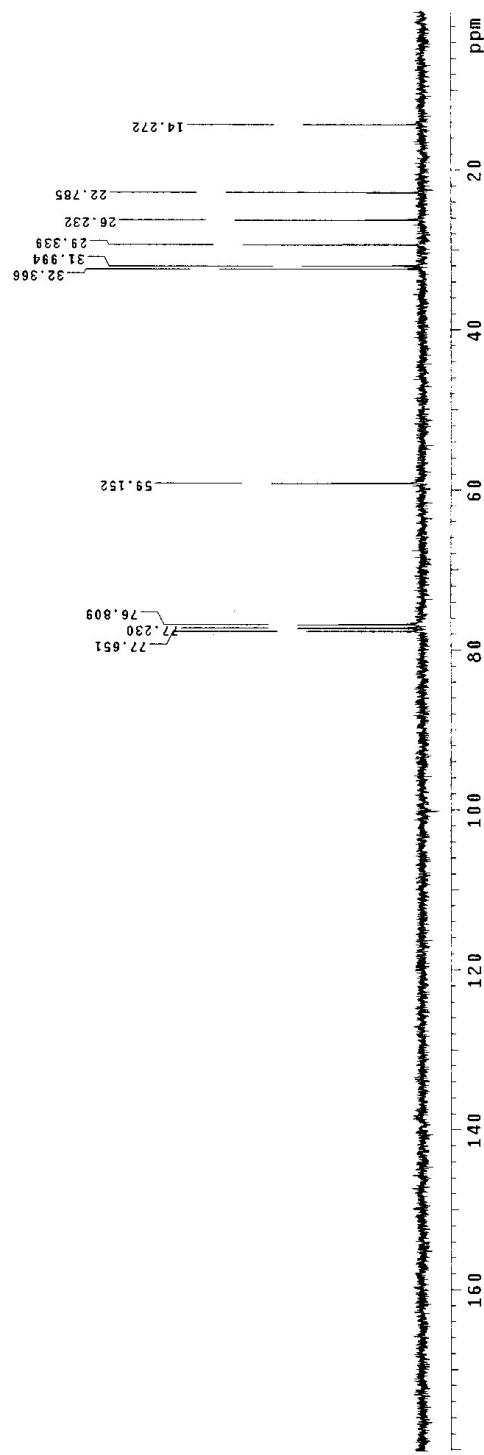


Table 1, entries 5, 6



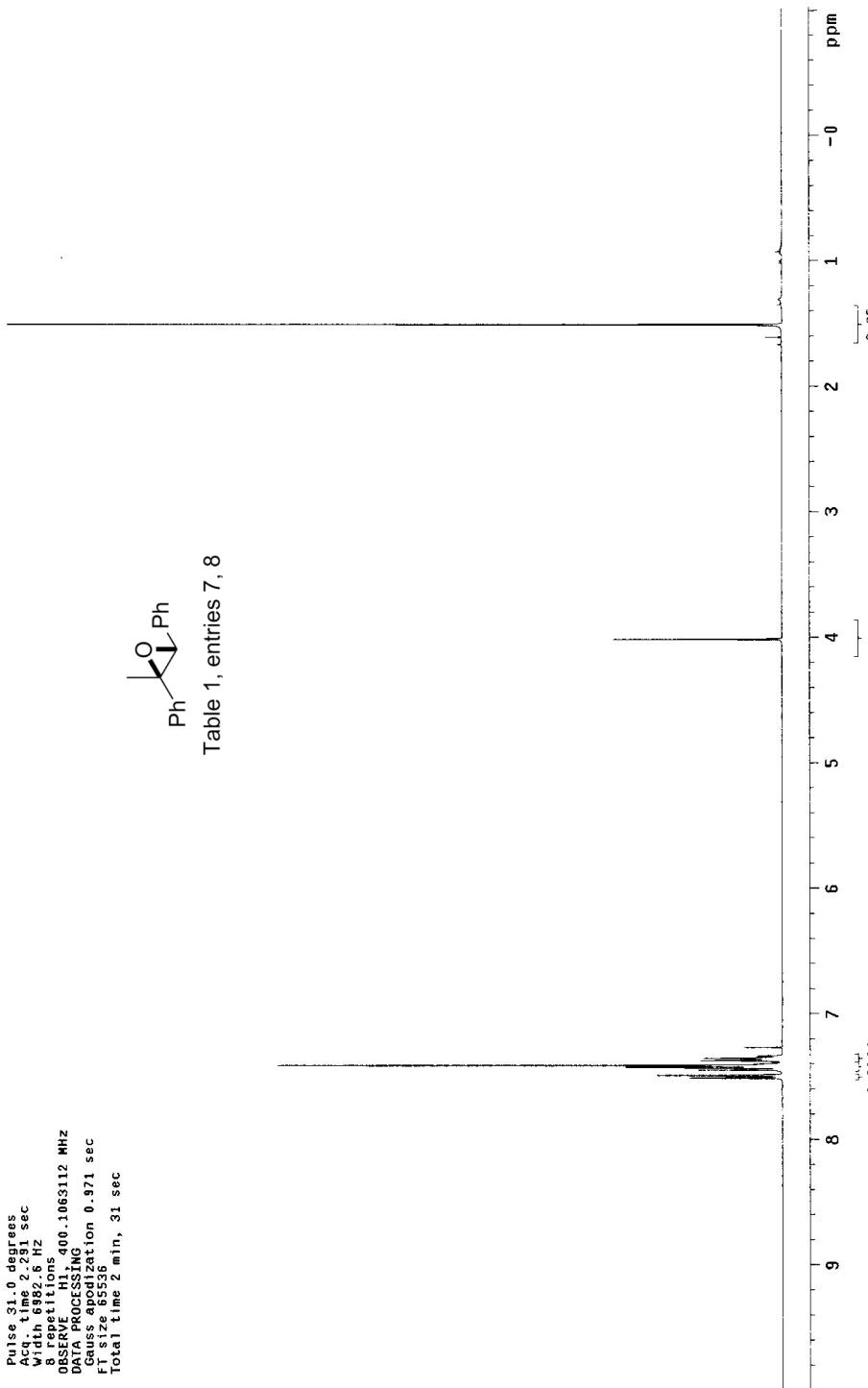
STANDARD 1H OBSERVE

Pulse Sequence: s2pu1
 Solvent: CDCl₃
 Ambient temperature
 File name-01, 15, 01_H-2407-2
 INOVA-510 "epoxide"

Pulse 31.0 degrees
 Acq. time 2.29 sec
 Width 692.6 Hz
 8 repetitions
 OBSERVE H1, 400.1063112 MHz
 DATA PROCESSING
 Gauss apodization 0.971 sec
 Fsize 65536
 total time 2 min, 31 sec



Table 1, entries 7, 8



13C OBSERVE

Pulse Sequence: s2pu1
 Solvent: CDCl₃
 Ambient Temperature
 File: saw-091508-C-2407-2
 INOVA-500 "epoxide"
 Relax-delay 1.200 sec
 Pulse 44.5 degrees
 Acq. time 0.53 sec
 Width 3018.4 Hz
 Decoupling 133, 100, 6067960 MHz
 DCouplF H, 400, 1083268 MHz
 Power 42 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 2.0 Hz
 FT size 32768
 Total time 622735 hr, 34 min, 7 sec

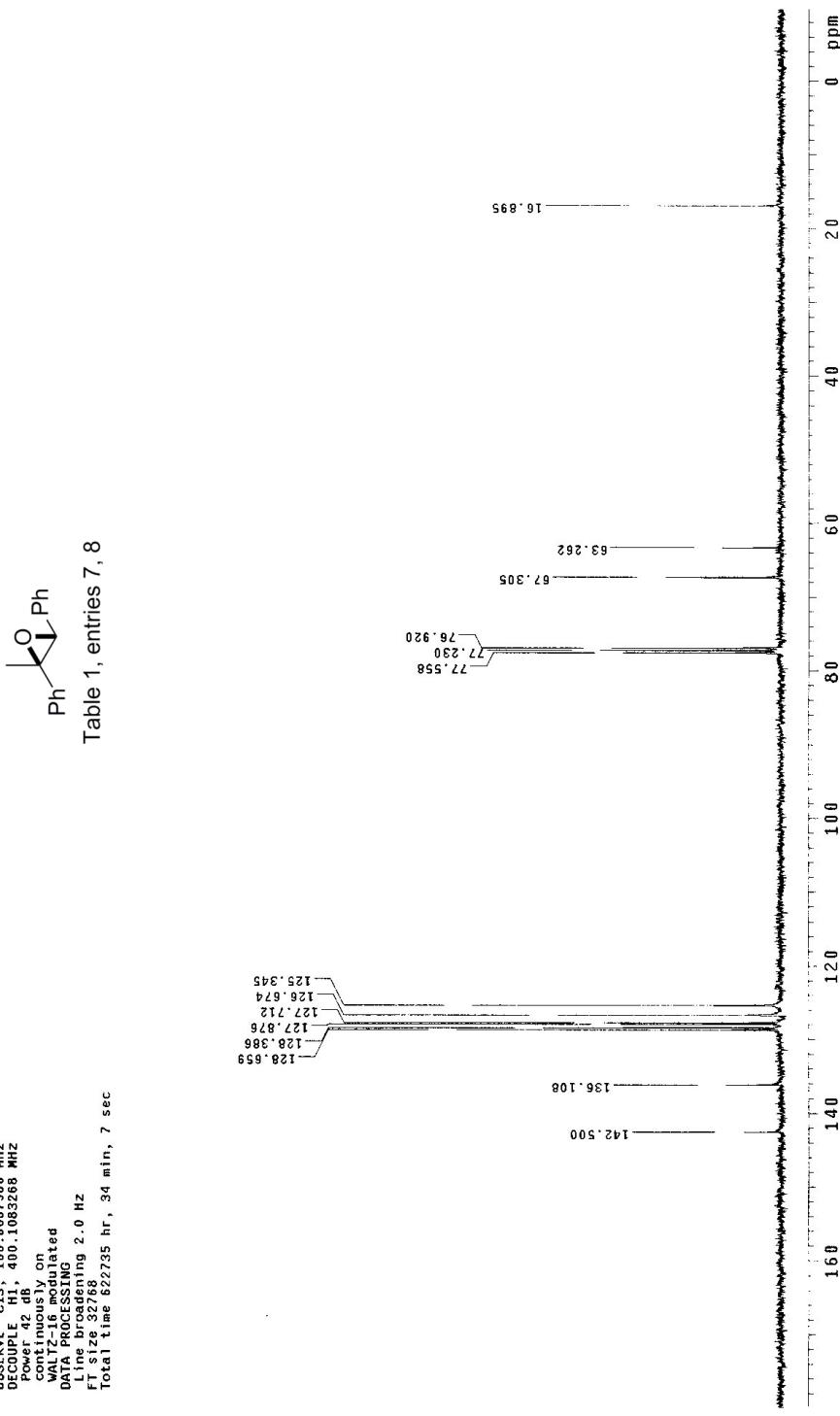


Table 1, entries 7, 8

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: CDC13
Ambient temperature
File: oaw-09.15.08-H-2
TMNOVA-500 "unoptimized"

```

Relax. delay 0.000 sec
Pulse 2.0 degrees
Acq. time 6.668 sec
Width 5.991-2 Hz
d repetitions
OBSERVE H1 300.1592160 MHz
DATA PROCESSING
Gauss apodization 0.896 sec
FT size 32/68
Total time 2 min, 56 sec

```

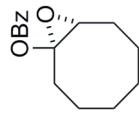
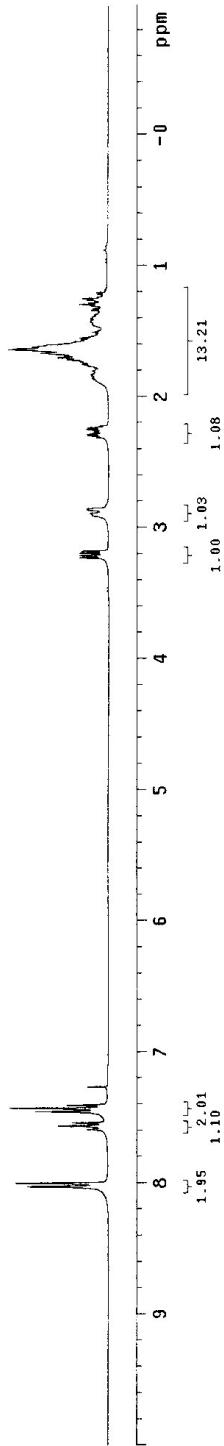


Table 1, entries 9, 10



13C OBSERVE

Pulse Sequence: s2pu1
 Solvent: CDCl₃
 Ambient temperature
 File: oaw-9.15.08-C-2407-1b
 INNOVA-500 "epoxi ide"

Relax. delay 1.000 sec
 Pulse 96.3 degrees
 Acc. time 0.697 sec
 Width 22.955.8 Hz
 44 repetitions
 OBSERVE C13, 75.4750846 MHz
 POWER 40 dB
 DECOPLE H1, 300.1606719 MHz
 CONTINUOUSLY ON
 WALTZ-16 MODULATED
 DATA PROCESSING
 Line broadening 2.0 Hz
 FT size 32768
 Total time 56 min, 52 sec

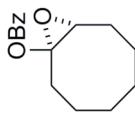
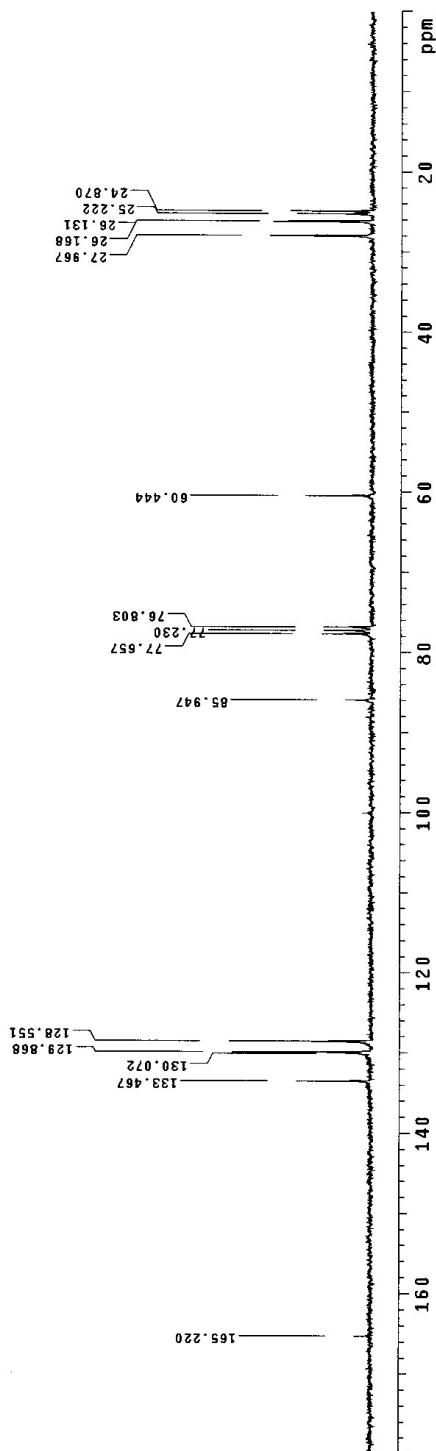


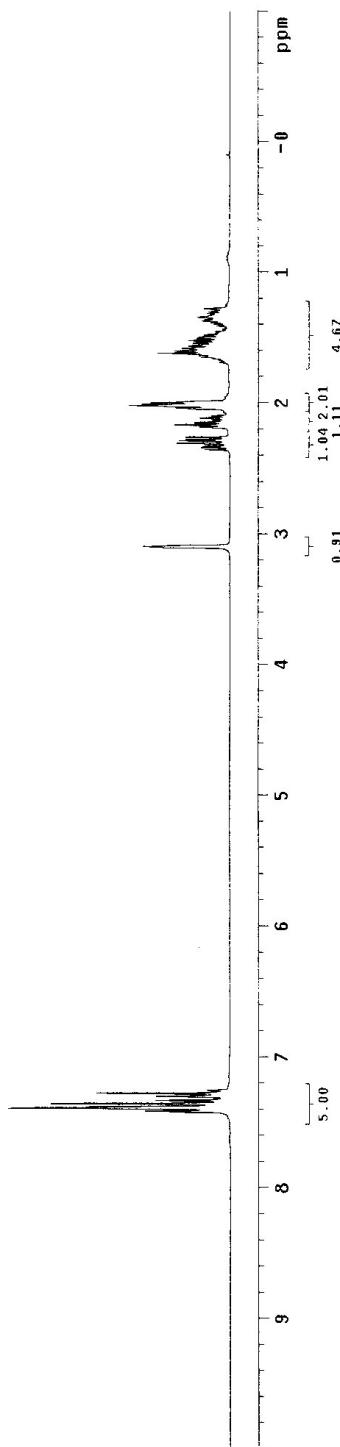
Table 1, entries 9, 10



STANDARD 1H OBSERVE
 Pulse Sequence: s2pu1
 Solvent: CDCl₃
 Solvents mixture-
 Fmoc-Lysine-OBz-H-2349-1
 INOVA-500 "epoxide"
 Relax-delay 1.000 sec
 Pulse 34.0 degrees
 Acq. time 2.732 sec
 Width 600.0 Hz
 24 repeat 1.1ms
 1.299, 9533661 MHz
 DATA PROCESSING
 Gauss apodization 0.824 sec
 FT size 83533
 Total time 4 min, 6 sec



Table 1, entries 11, 12

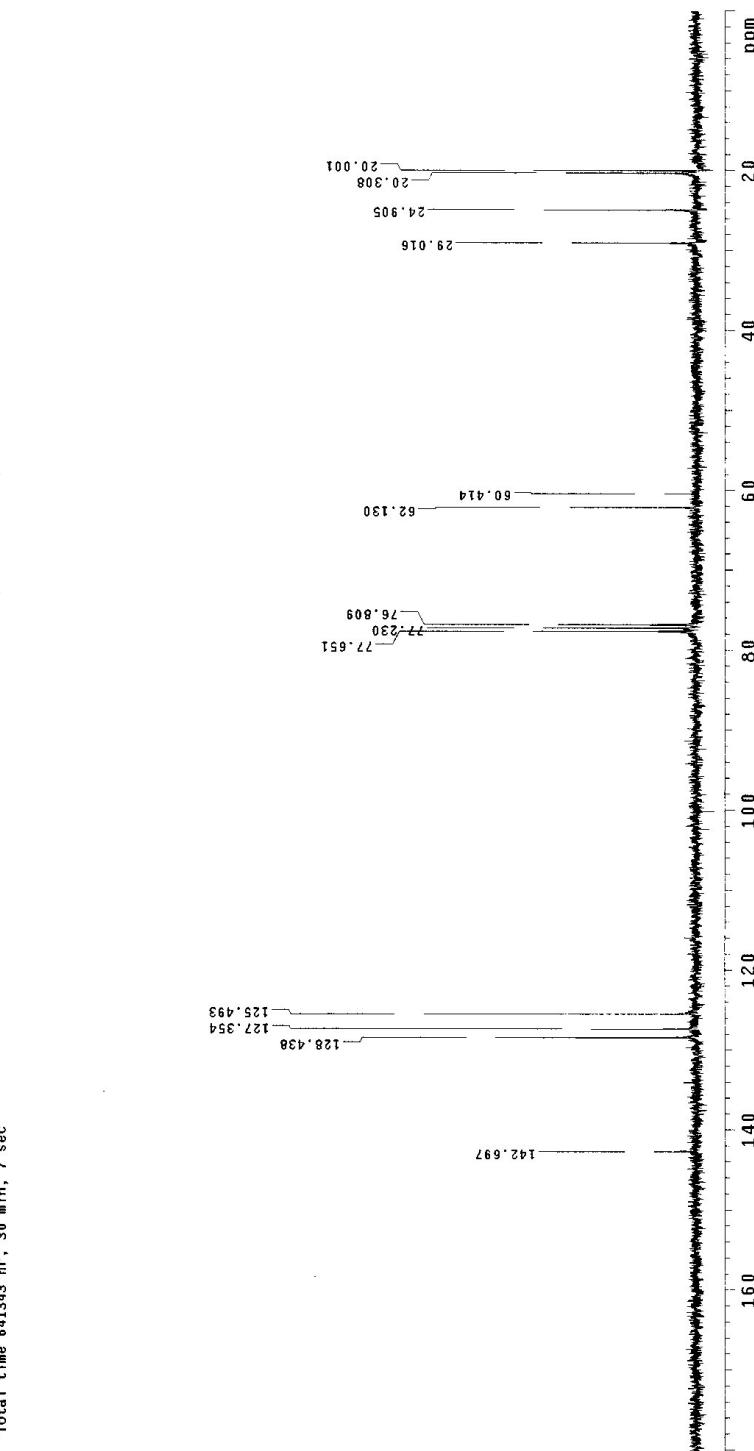


13C OBSERVE
 Pulse Sequence: s2pu1
 Solvent: CDCl₃
 Ambient temperature
 File: Caw-09_09_08-C-2349-1
 INNOVA-500 "Epoxide"

Relax. delay 1.500 sec
 90° 39°
 Acc. time 0.80 sec
 Width 20000 Hz
 92 repetitions
 OBSERVE C13, 75.4233210 MHz
 DECOUPLE H1, 299.9548659 MHz
 Power 36 dB
 Continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 32768
 Total time 641343 hr, 30 min, 7 sec



Table 1, entries 11, 12



STANDARD 1H OBSERVE

Pulse Sequence: s2pu1
Solvent: CDCl₃
Ambient temperature
File: b-oav-08-24-racemic-H
INNOVA-500 "epoxide"

Relax, delay 0.000 sec
Pulse, 26.0 degrees
Acq. time, 2.668 sec
Width 5.9912 Hz
8 repetitions
OBSERVE, H1, 300.1592164 MHz
DATA PROCESSING
Gauss Apodization 0.895 sec
FT size 32768
Total time 2 min., 56 sec

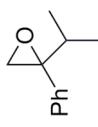
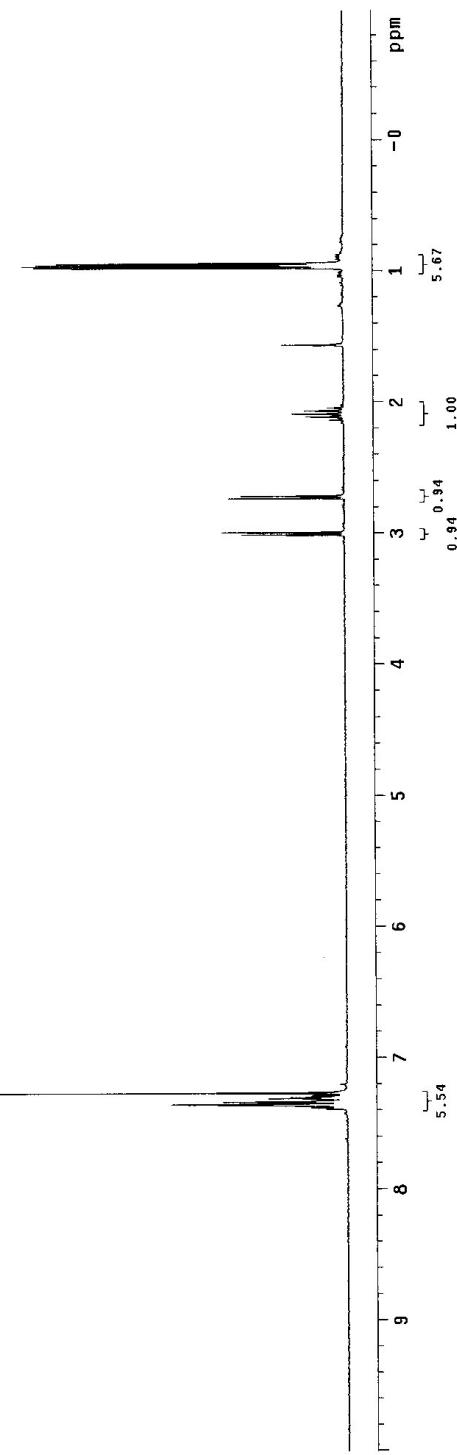


Table 1, entries 13, 14



13C OBSERVE

Pulse Sequence: \$2pu1
 Solvent: CDCl₃
 Ambient temperature
 File: mx2nao-1/-11-4-13C
 INOVA-500 "epoxide"

Relax. delay 1.000 sec
 Pulse 46.3 degrees
 Acq. time 0.637 sec
 Width 2235.8 Hz
 72 repetitions
 OBSERVE C13, 75.4750790 MHz
 DICOUPLER H1, 300.1666739 MHz
 Power 40 dB
 continuously on
 WALTZ16 modulated
 DATA PROCESSING
 Lines broadening 2.0 Hz
 File size 32768
 Total time 11 min, 22 sec

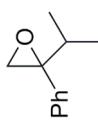
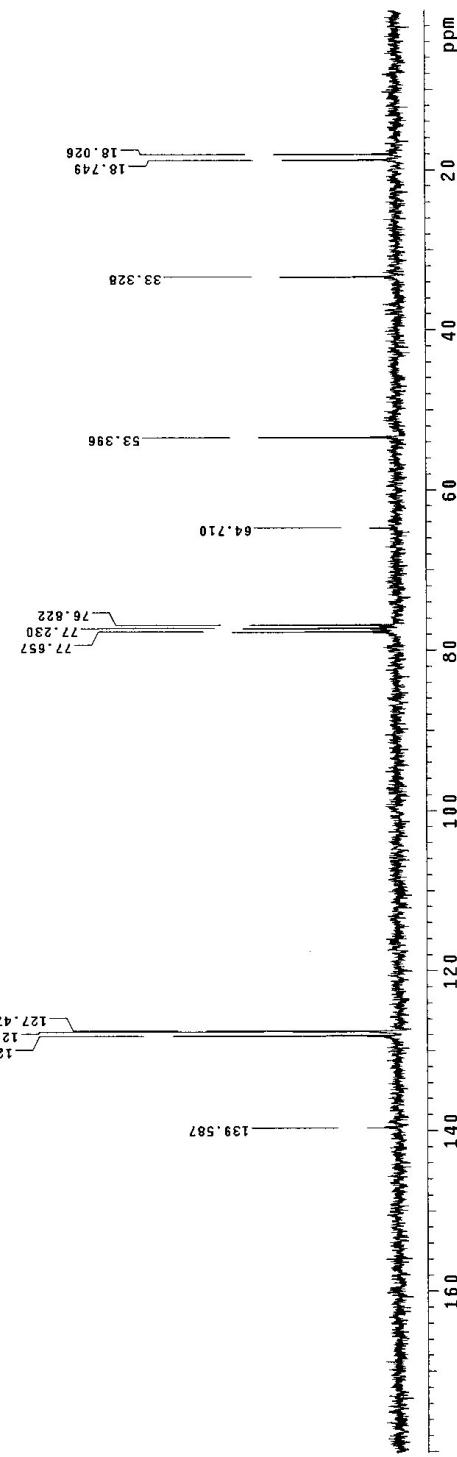


Table 1, entries 13, 14

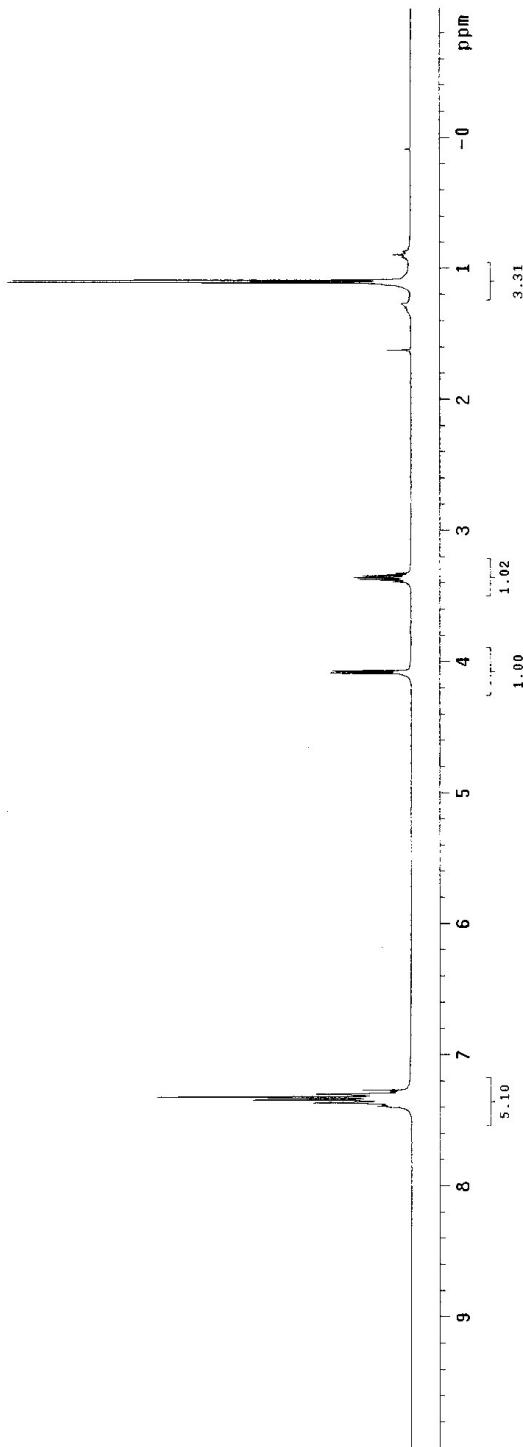


STANDARD 1H OBSERVE

Pulse Sequence: \$2pu1
 Solvent: CDCl₃
 Object: Temperature-10.20.08-H-2437-2
 File: raw-10.20.08-H-2437-2
 INOVA-500 "epoxides"
 Relax - delay 0.000 sec
 Pulse 26.0 degrees
 Acq time 2.605 sec
 Width 3.935 . Hz
 SENSITIVITY 8
 OBSERVE H 300.1592164 MHz
 DATA PROCESSING
 Gauss Apodization 0.896 sec
 FT Size 32768
 Total time 2 min, 56 sec



Table 1, entries 15, 16



13C OBSERVE

Pulse Sequence: \$2pu1

Solvent: CDCl₃

Ambient temperature

File: oaw-0.20.08-C-2437-2

INOVA-500 "spoxide"

Relax. delay 1.000 sec

Pulse 46.3 degrees

Acq. time 0.697 sec

Width 2235.8 Hz

52 repetition

OBSERVE C13, 75.4750818 MHz

DECOUPLE H1, 300.1606799 MHz

Power 40 dB

WALTZ-16 modulated

continuous on

DATA PROCESSING

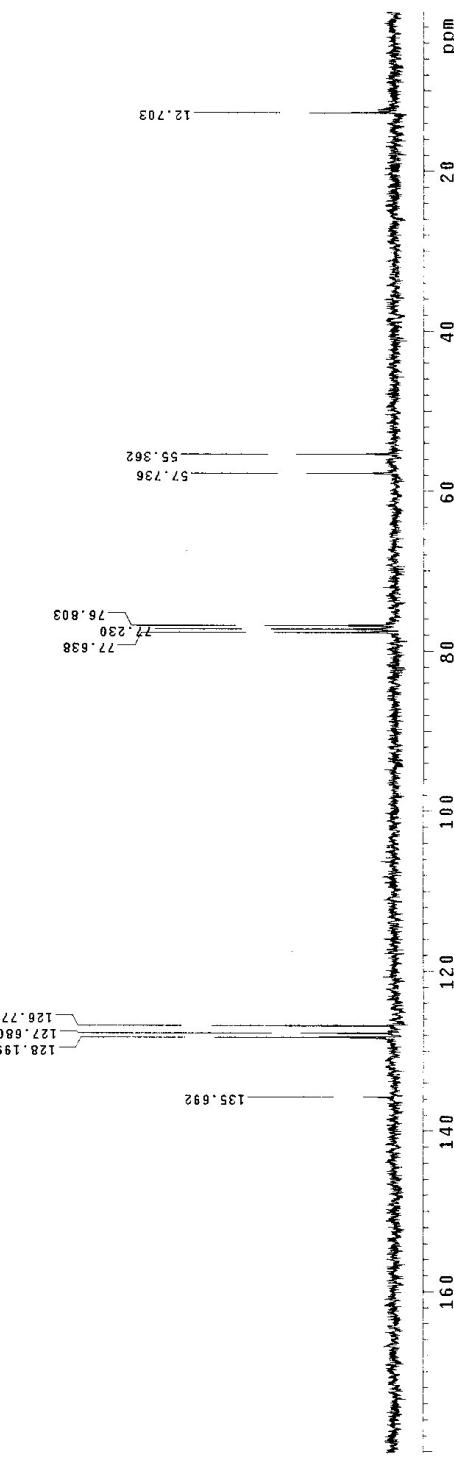
Line broadening 2.0 Hz

FT size 32768

Total time 56 min, 52 sec



Table 1, entries 15, 16



STANDARD 1H OBSERVE

Pulse Sequence: s2pu1
 Solvent: CDCl₃
 Ambient temperature
 File: raw-10_21.08-H-2438
 INOVA-500 "epoxide"
 Relax. delay 0.000 sec
 Pulse 66 degrees
 Acq. time 2.68 sec
 W1fb 196.2 Hz
 Repetition 1.64 MHz
 OBSERVE H1 300.1582164 MHz
 DATA PROCESSING
 Gauss apodization 0.896 sec
 FT size 32768
 Total time 2 min, 56 sec

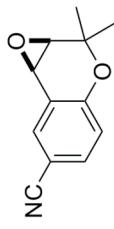
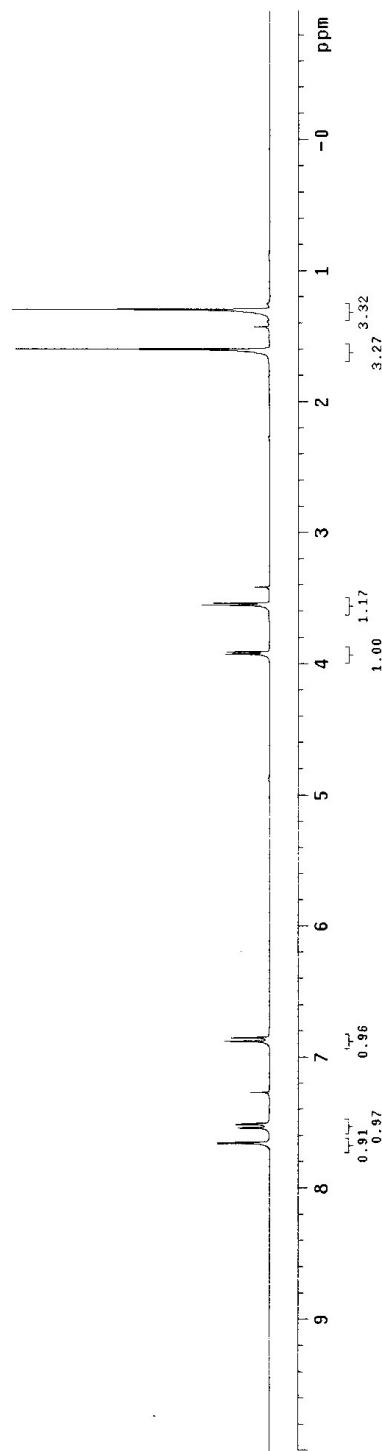


Table 1, entries 17, 18



13C OBSERVE

Pulse Sequence: s2pu1
Solvent: CDCl₃
Ambient temperature
File: Saw-10.21.08-C-2438
INOVA-500 "epoxide"

Relax. delay 1.000 sec
Pulse 90 degrees
Acq. time 0.097 sec
Width 22.953 Hz
156 spectra taken
OBSERVE C13, 155.4750832 MHz
DECOUPLE 1H, 300.1600735 MHz
Power 10 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 32768
Total time 56 min, 52 sec

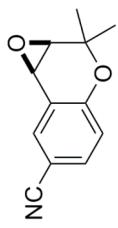
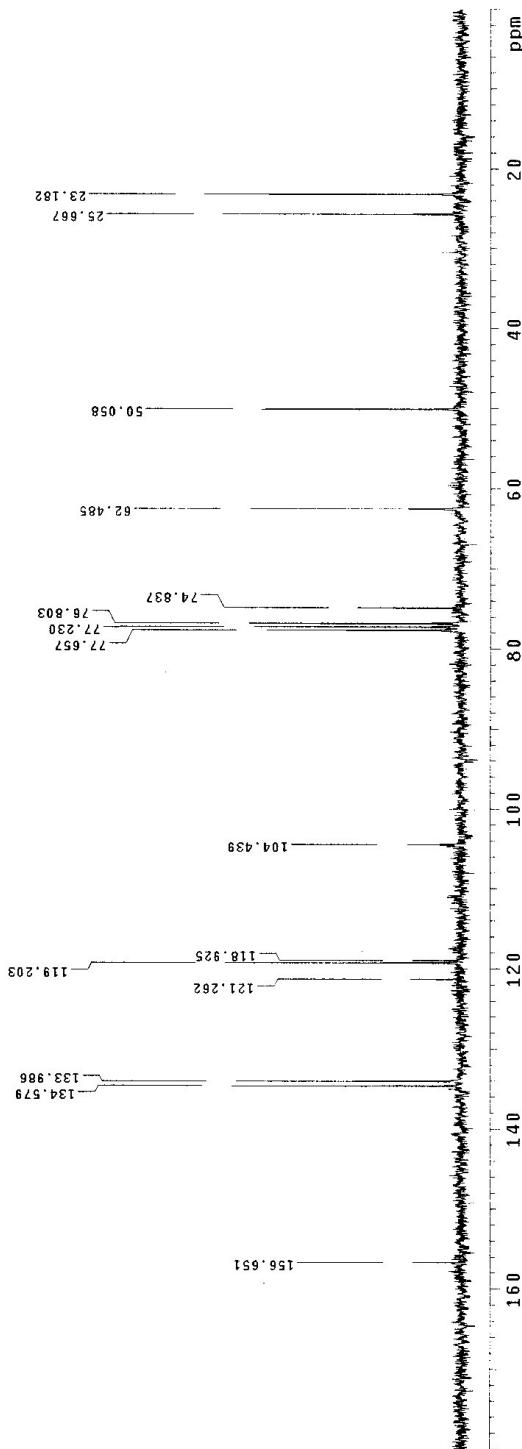
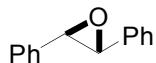


Table 1, entries 17, 18



The chromatograms for the determination of enantioselectivity

Table 1, Entry 2



HPLC Condition: **Column:** Chiralcel OD (Column No. OD00CE-DL010), Daicel Chemical Industries, Ltd.

Eluent: Hexanes/IPA (90/10); **Flow rate:** 1.0 mL/min; **Detection:** UV220 nm.

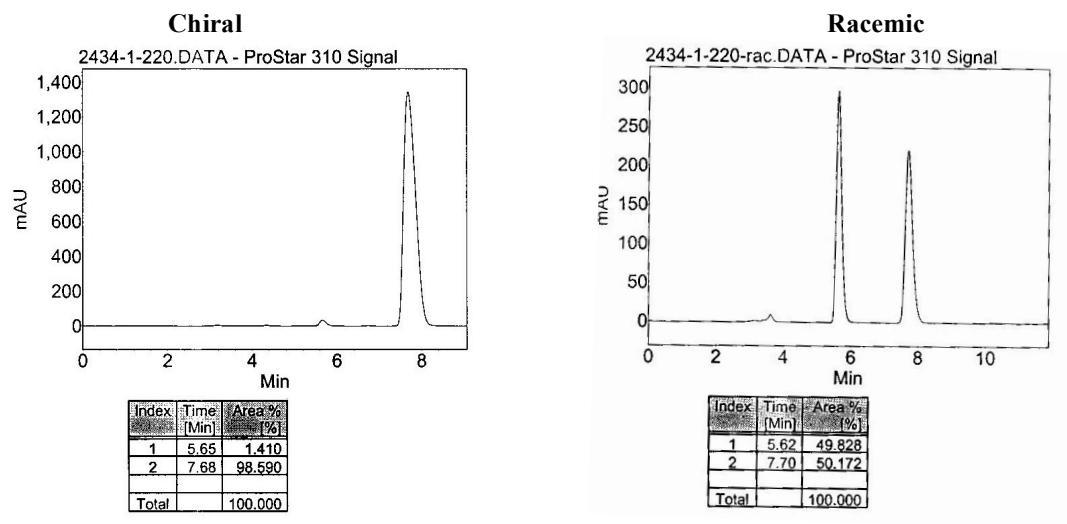
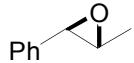


Table 1, Entry 4



GC Condition: **Column:** Chiraldex B-DM (Cat. No. 77023), Adv. Separation Technologies, Inc.

Oven: 80 °C; **Carrier:** Helium, head pressure 20 psi; **Detection:** FID 250 °C.

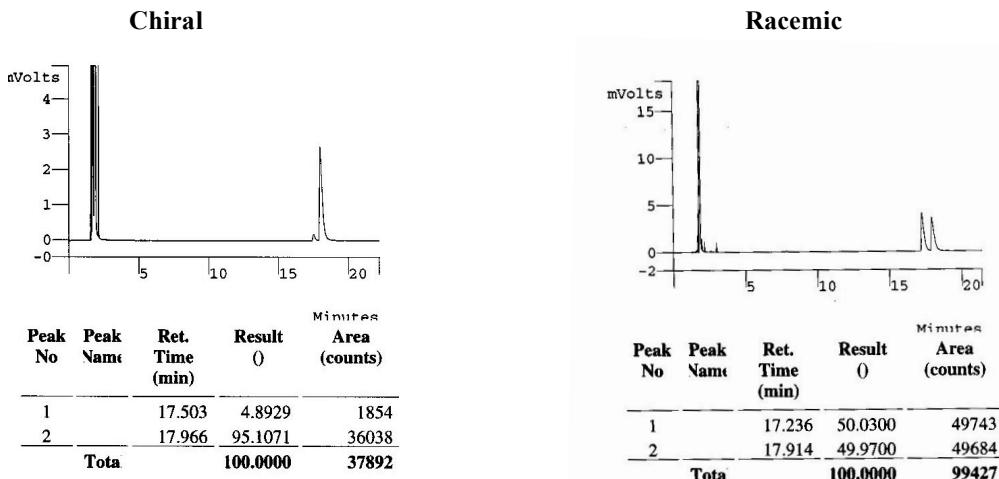
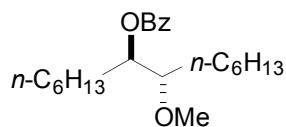
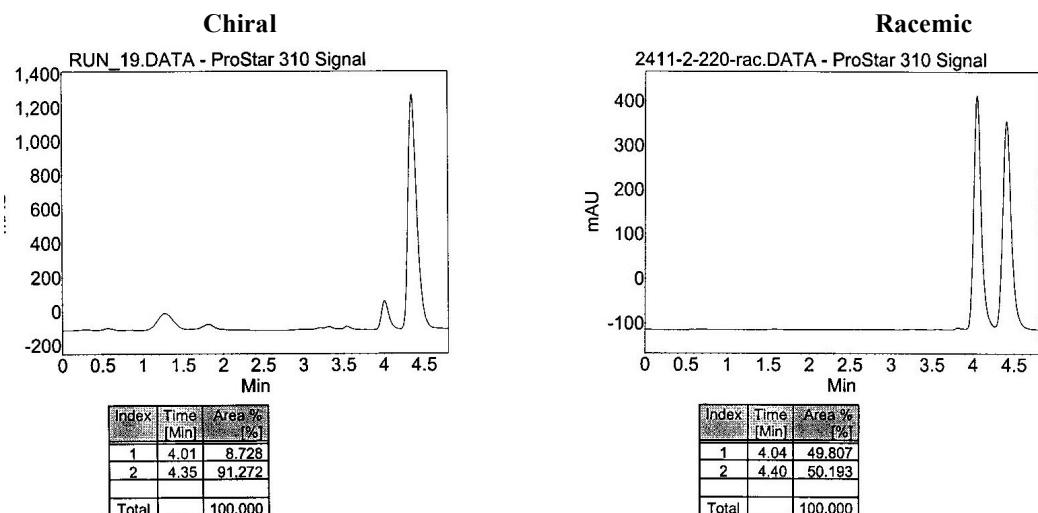
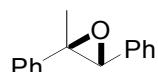


Table 1, Entry 6

HPLC Condition: Column: Chiralcel OD-H (Column No. ODH0CE-ME069), Daicel Chemical Industries, Ltd.

Eluent: Hexanes/IPA (400/01); Flow rate: 1.0 mL/min; Detection: UV220 nm.

**Table 1, Entry 8**

HPLC Condition: Column: Chiralcel OD (Column No. OD00CE-DL010), Daicel Chemical Industries, Ltd.

Eluent: Hexanes/IPA (90/10); Flow rate: 1.0 mL/min; Detection: UV210 nm.

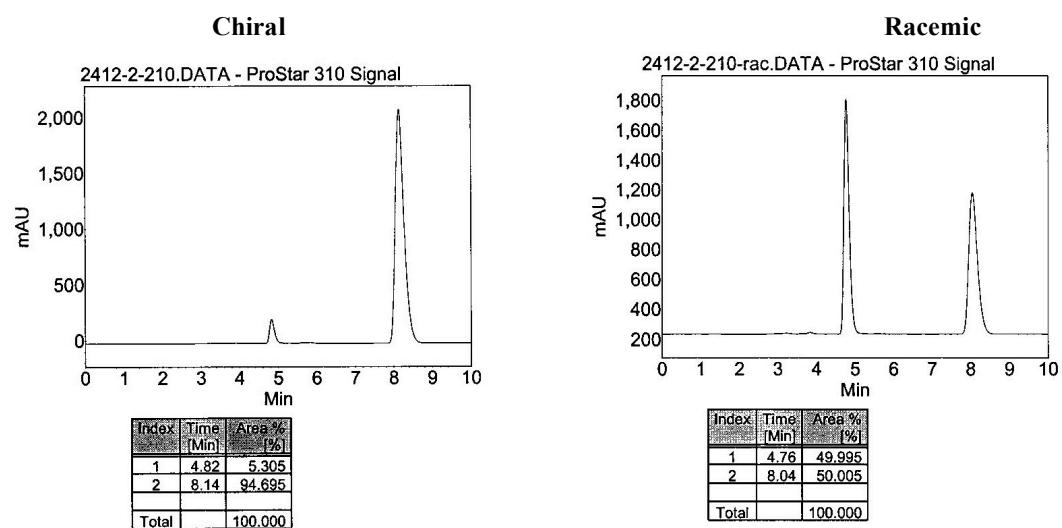
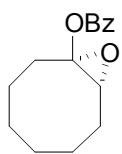
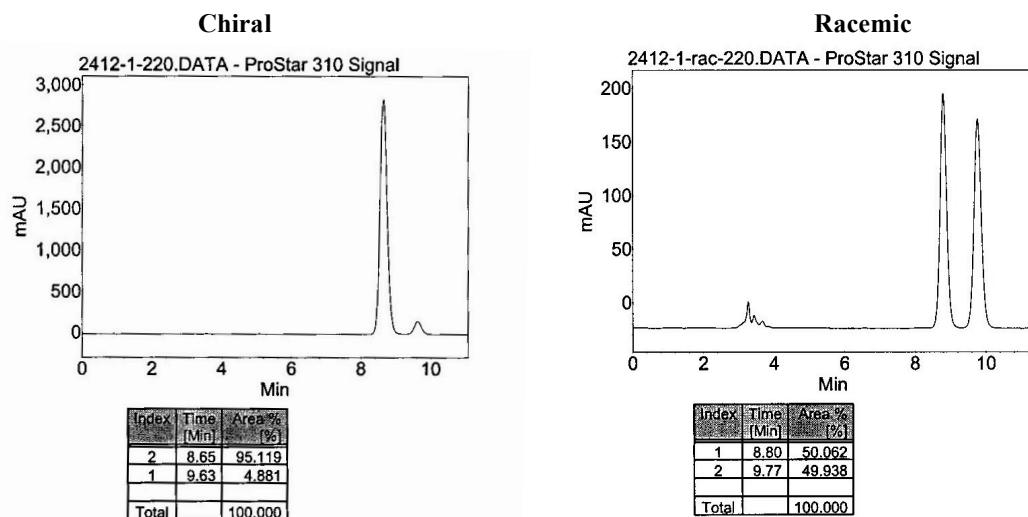
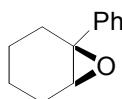


Table 1, Entry 10

HPLC Condition: Column: Chiraldex AD-H (Column No. ADH0CE-FD069), Daicel Chemical Industries, Ltd.

Eluent: Hexanes/IPA (97/03); **Flow rate:** 1.0 mL/min; **Detection:** UV220 nm.

**Table 1, Entry 11**

GC Condition: Column: Chiraldex B-DM (Cat. No. 77023), Adv. Separation Technologies, Inc.

Oven: 110 °C; **Carrier:** Helium, head pressure 30 psi; **Detection:** FID 250 °C.

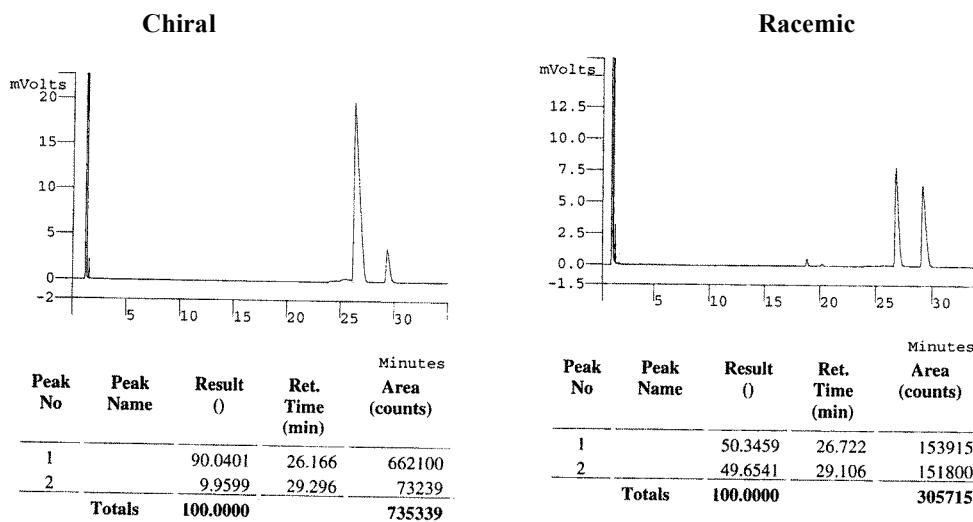
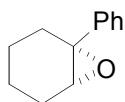
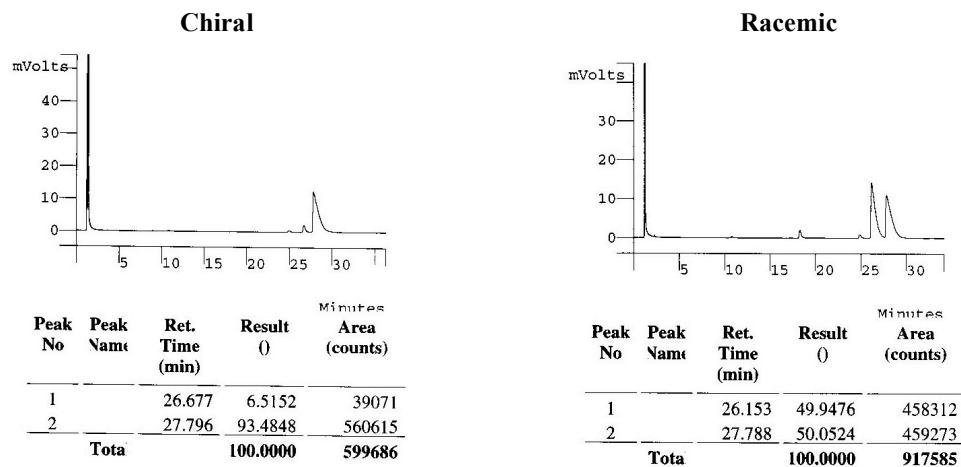
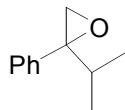


Table 1, Entry 12

GC Condition: Column: Chiraldex B-DM (Cat. No. 77023), Adv. Separation Technologies, Inc.

Oven: 110 °C; Carrier: Helium, head pressure 30 psi; Detection: FID 250 °C.

**Table 1, Entry 13**

GC Condition: Column: Chiraldex B-DM (Cat. No. 77023), Adv. Separation Technologies, Inc.

Oven: 115 °C; Carrier: Helium, head pressure 25 psi; Detection: FID 250 °C.

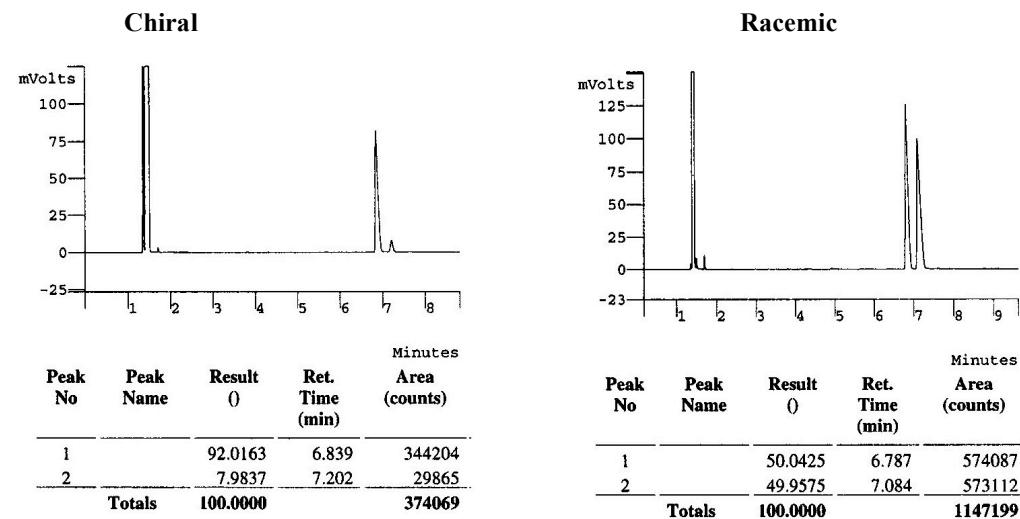
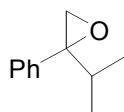
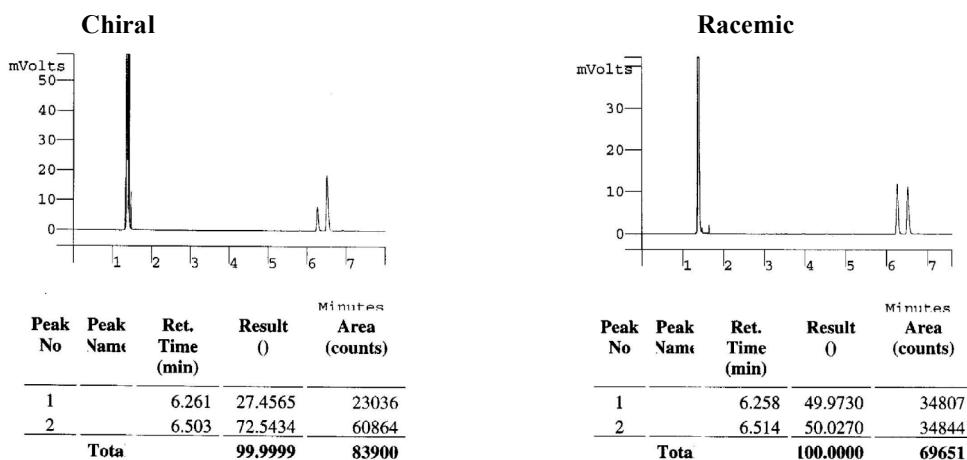
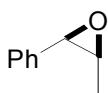


Table 1, Entry 14

GC Condition: Column: Chiraldex B-DM (Cat. No. 77023), Adv. Separation Technologies, Inc.

Oven: 115 °C; Carrier: Helium, head pressure 25 psi; Detection: FID 250 °C.

**Table 1, Entry 16**

GC Condition: Column: Chiraldex B-DM (Cat. No. 77023), Adv. Separation Technologies, Inc.

Oven: 100 °C; Carrier: Helium, head pressure 25 psi; Detection: FID 250 °C.

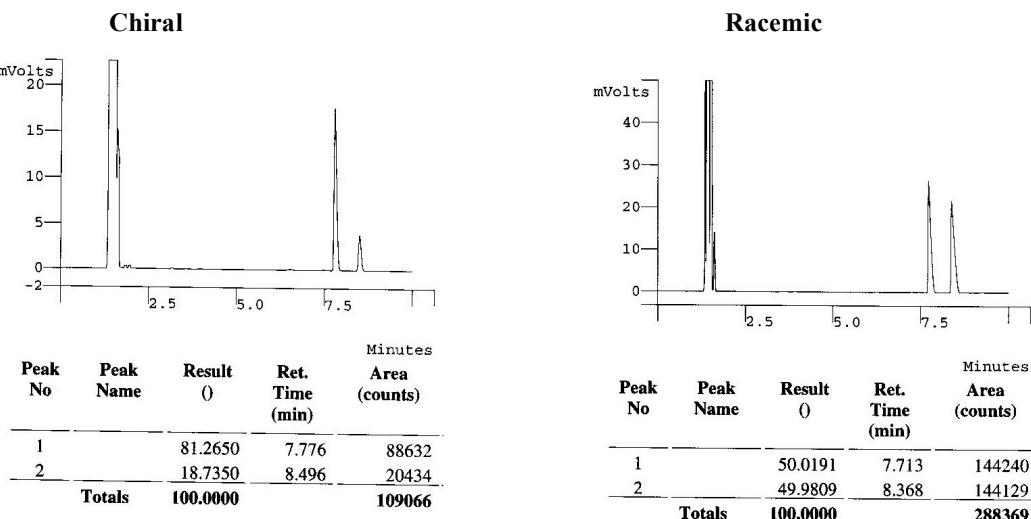
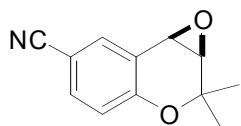


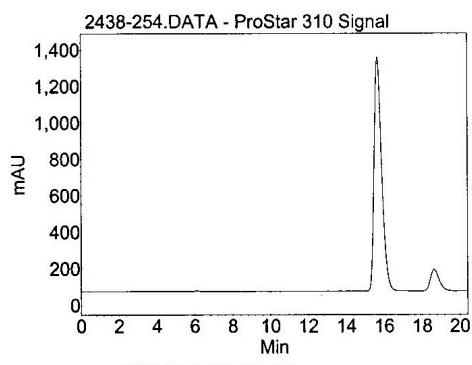
Table 1, Entry 18



HPLC Condition: **Column:** Chiralcel OD (Column No. OD00CE-DL010), Daicel Chemical Industries, Ltd.

Eluent: Hexanes/IPA (90/10); **Flow rate:** 0.6 mL/min; **Detection:** UV254 nm.

Chiral



Racemic

