Supporting Information for

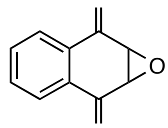
A New Catalytic and Enantioselective Desymmetrization of Symmetrical Methylidene Cycloalkene Oxides.

Fabio Bertozzi, Paolo Crotti, Franco Macchia, Mauro Pineschi*
Dipartimento di Chimica Bioorganica e Biofarmacia, Università di Pisa, Via Bonanno 33, 56126 Pisa, Italy

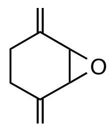
Alexander Arnold and Ben L. Feringa*
Department of Organic and Molecular Inorganic Chemistry, University of Groningen, Nijenborgh 4, NL9747 AG Groningen, The Netherlands.

General. All reactions were conducted in flame dried glassware with magnetic stirring under an atmosphere of argon. Toluene and diethyl ether were distilled from sodium/benzophenone ketyl and stored under argon. THF and Diisopropylamine were distilled from $LiAlH_4$ and CaH_2 respectively and stored under argon. Et_2Zn (1.1 M solution in toluene), EtMgCl (2.0 M solution in THF) and Butyllithium (1.6 M solution in hexanes) were purchased from Aldrich. Methyl-triphenyl-phosphonium-bromide (98%) and 2-Methyl-1,3-cyclopentanedione (99%) were purchased from Aldrich. Analytical TLC were performed on Alugram SIL G/UV254 silica gel sheets (Macherey-Nagel) with detection by 0.5% phosphomolybdic acid solution in 95% EtOH. Silica gel 60 (Macherey-Nagel 230-400 mesh) was used for flash chromatography. Solvents for extraction and chromatography were HPLC grade.

Optical rotation were measured on a Perkin-Elmer 241 digital polarimeter with a 1 dm cell. ^{1}H NMR spectra were recorded on a Bruker AC-200 spectrometer on $CDCl_3$ solution. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: δ 7.26). ^{13}C NMR spectra were recorded on a Bruker AC-200 (50 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm downfield from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: δ 77.7). Gas chromatography was performed on a Perkin-Elmer 8420 apparatus (FI detector) using a Chromopak fused silica 25 m x 0.25 mm column, coated with CP-Cyclodextrin-B-236-M-19). In all cases, the injector and detector temperature was 250°C and a 1.8 mL / min helium flow was employed. Analytical high performance liquid chromatography (HPLC) was performed on a Waters 600E equipped with a Waters 990 photodiode array detector using a Daicel Chiralcel OD-H column.



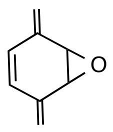
1,4-Dimethylidene-2,3-epoxy-2,3-dihydro-naphthalene (8). Typical Procedure for Wittig Olefination. Accordingly to a previously described procedure,[1] to a stirring suspension of $MePh_3PBr$ (8.21 g, 23 mmol) in anhydrous THF (20 ml) is added by a cannula at 0°C a solution of LDA (23 mmol) in anhydrous THF (10 ml). After the reaction mixture was stirred for 1.5 h at 0°C, 2,3-epoxy-2,3-dihydro-1,4-naphthoquinone[2] (1.0 g, 5.75 mmol) in anhydrous THF (5 ml) was added and the mixture was vigorously stirred for 1.5 h at room temperature. The mixture was quenched with saturated aqueous NH_4Cl and extracted with petroleum ether. Evaporation of the dried ($MgSO_4$) organic phase gave a crude product which was subjected to chromatography (SiO_2) with 20% EtOAc : hexanes to give 0.745 g (77%) of pure **8**, as a solid. M.p.=37-39°C. ^{1}H NMR δ 7.45-7.50 (m, 2H, Ar-**H**), 7.22-7.27 (m, 2H, Ar-**H**), 5.67 (s, 2H, methylidene-**H**), 5.45 (s, 2H, methylidene-**H**), 3.95 (s, 2H, C_2-**H** and C_3-**H**). ^{13}C NMR δ 141.29, 131.81, 129.48, 126.04, 116.02, 57.98. Anal. Calcd. for $C_{12}H_{10}O$: C, 84.67; H, 5.93. Found : C, 84.38; H, 5.96.



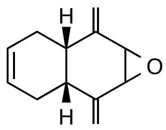
3,6-Dimethylidene-1,2-epoxy-cyclohexane (7). Following the above described typical procedure 2,3-epoxy-cyclohexan-1,4-dione[3] (0.160 g, 1.27 mmol) in anhydrous THF (3 ml) was added dropwise at 0°C to a suspension of $Ph_3P{=}CH_2$ (4.0 eq) in anhydrous THF (8 ml). After 1 h at room temperature the usual work-up afforded a crude product which was subjected to chromatography (SiO_2) with 8% diisopropyl ether: petroleum ether to give 72 mg of pure **7** (47%) as a liquid. ^{1}H NMR δ 5.26 (s, 2H, methylidene-**H**), 5.14 (s, 2H, methylidene-**H**), 3.64 (s, 2H, C_1-**H** and C_2-**H**), 2.32-2.47 (m, 2H, one of C_4-$\mathbf{H}_2$ and one of C_5-$\mathbf{H}_2$), 2.07-2.23 (m, 2H, one of C_4-$\mathbf{H}_2$ and one of C_5-$\mathbf{H}_2$). ^{13}C NMR δ 142.65, 116.63, 58.18, 29.28. Anal. Calcd. for $C_8H_{10}O$: C, 78.64; H, 8.26. Found : C, 78.37; H, 8.39.

---

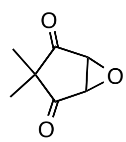
1) Marino, J.P.; Abe, H. *Synthesis*, **1980**, 872.
2) Alder, K.; Flock, F.H.; Beumling, H. *Chem. Ber.* **1960**, *93*, 1896.
3) Abbulut, N.; Balci, M. *J. Org. Chem.* **1988**, *53*, 3338.



3,6-Dimethylidene-1,2-epoxy-4-cyclohexene (6). Following the typical procedure, 2,3-epoxy-1,4-benzoquinone[2] (0.180 g, 1.47 mmol) in anhydrous THF (4 ml) was added dropwise at 0°C to a suspension of $Ph_3P{=}CH_2$ (4.0 eq) in anhydrous THF (10 ml). After 45 min at room temperature the usual work-up afforded a crude product which was subjected to chromatography (SiO_2) with 8% diisopropyl ether: petroleum ether to give 67 mg of pure **6** (39%), as a liquid. ^{1}H NMR δ 6.09 (s, 2H, C_4-**H** and C_5-**H**), 5.49 (s, 2H, methylidene-**H**), 5.38 (s, 2H, methylidene-**H**), 3.79 (s, 2H, C_1-**H** and C_2-**H**). ^{13}C NMR δ 139.09, 127.02, 120.0, 56.01. Anal. Calcd. for C_8H_8O: C, 79.96; H, 6.72. Found : C, 79.77; H, 6.69.

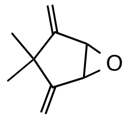


1,4-Dimethylidene-2,3-epoxy-*cis*-2,3,4a,5,8,8a-hexahydronapthalene (9). Following the typical procedure 2,3-epoxy-2,3,4a,5,8,8a-hexahydro-1,4-naphtoquinone[4] (0.712 g, 4.0 mmol) in anhydrous THF (15 ml) was added dropwise at 0°C to a suspension of $Ph_3P{=}CH_2$ (4.0 eq) in anhydrous THF (30 ml). After 1.5 h at room temperature the usual work-up afforded a crude product which was subjected to chromatography (SiO_2) with 8% diisopropyl ether: petroleum ether to give 397 mg of pure **9** (57%) as a liquid. ^{1}H NMR δ 5.52-5.58 (m, 2H, C_6-**H** and C_7-**H**), 5.37 (s, 2H, methylidene-**H**), 5.10 (s, 2H, methylidene-**H**), 3.67 (s, 2H, C_2-**H** and C_3-**H**), 2.66-2.72 (m, 2H, C_{4a}-**H** and C_{8a}-**H**), 1.94-2.04 (m, 4H, C_5-$\mathbf{H_2}$ and C_8-$\mathbf{H_2}$). ^{13}C NMR δ 144.43, 125.46, 117.23, 58.00, 36.08, 28.87. Anal. Calcd. for $C_{12}H_{14}O$: C, 82.71; H, 8.1. Found : C, 82.93; H, 8.26.



2,2-Dimethyl-4,5-epoxy-cyclopentan-1,3-dione (16). Typical Procedure for Alkaline Epoxidation. According to a previously described procedure,[2] to a solution of 2,2-dimethyl-4-cyclopenten-1,3-dione[5] (400 mg, 3.22 mmol) in acetone (10 ml), at 0°C, under vigorous strirring, were added Na_2CO_3 (20%) (120 mg, 1.12 mmol) and H_2O_2 (30%) (1.1 ml, 9.67 mmol). After 1.5 h at room temperature the reaction was quenched with $Na_2S_2O_3$ (10%) and H_2O (reaction kept cold with ice-water bath), and gave 348 mg of pure **16** (78%), as a pale yellow solid. M.p.= 37-39°C. ^{1}H NMR δ 3.94 (s, 2H, C_4-**H** and C_5-**H**), 1.27 (s, 3H, one of C_2-$\mathbf{CH_3}$), 1.11 (s, 3H, one of C_2-$\mathbf{CH_3}$). ^{13}C NMR δ 207.57, 57.52, 48.31, 24.05, 20.53. Anal. Calcd. for $C_7H_8O_3$: C, 59.98; H, 5.76. Found : C, 59.74; H, 5.59.

4) Herz, W.; Iyer, V.S.; Nair, M.G. *J. Org. Chem.* **1975**, *40*, 3519.
5) Agosta, W.C.; Smith, A.B. III. *J. Org. Chem.* **1970**, *35*, 3856.



4,4-Dimethyl-1,2-epoxy-3,5-dimethylidene-cyclopentane (10). Following the typical procedure for Wittig olefination, 5,5-Dimethyl-2,3-epoxy-cyclopentan-1,4-dione **16** (0.348 g, 2.48 mmol) in anhydrous THF (10 ml) was added dropwise at 0°C to a suspension of $Ph_3P=CH_2$ (4.0 eq) in anhydrous THF (20 ml). After 1 h at room temperature the reaction was quenched with H_2O and the usual work-up afforded a crude product which was subjected to chromatography (SiO_2) with petroleum ether:diethyl ether:Et_3N (95:5:1) to give 158 mg of **10** (47%), as an oil (contaminated with 4% PPh_3). ^{1}H NMR δ 5.32 (s, 2H, methylidene-**H**), 5.12 (s, 2H, methylidene-**H**), 3.91 (s, 2H, C_1-**H** and C_2-**H**), 1.17 (s, 3H, one of C_4-**CH_3**), 1.15 (s, 3H, one of C_4-**CH_3**). ^{13}C NMR δ 156.57, 110.71, 61.36, 42.96, 33.66, 28.61. Anal. Calcd. for $C_9H_{12}O$: C, 79.36; H, 8.89. Found : C, 79.55; H, 8.81.

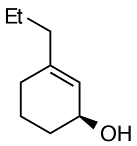
Determination of Absolute Configurations. The absolute configurations of all 1,4-addiction products **4**, **17-20** were determined on compound **4** by means of the known diastereofacial selectivity of 1-substituted allylic alcohols with titanium/tartrate/TBHP (Sharpless kinetic resolution AE).[6] This inherently reliable procedure had been applied quite recently to the related (±)-3-methyl-2-cyclohexen-1-ol to give optically active products with a known absolute configuration.[7] Also the comparison of the optical rotation of optically active seudenol [*R*-(+) and *S*-(-)-3-methyl-2-cyclohexen-1-ol],[8] an aggregation pheromone from *Dendroctonus pseudotsugae*, bearing a methyl instead of propyl in the 3 position of compound **4**, gave us the same indication obtained with the kinetic resolution strategy (see below).

Titanium Tartrate Catalytic Asymmetric Epoxidation of 4. Following the original procedure,[9] an oven-dried 25 mL two-necked round-bottomed flask was charged with 30 mg of 4 Å powdered activated molecular sieves and with 2 mL of dry CH_2Cl_2 under an argon atmosphere. The flask was cooled to -20°C and *D*-(-)-DIPT (10 mg dissolved in a minimum amount of CH_2Cl_2, 6 mol%), Ti(O-*i*-Pr)$_4$ (10.6 μl, 5 mol%) and anhydrous TBHP (0.47 mL of a 3.0 M solution in isooctane, 2 eq.) were added sequentially with stirring. The resulting mixture was stirred at -20°C for 30 min. and (±)-3-propyl-2-cyclohexen-1-ol (**4**) (100 mg, 0.714 mmol) dissolved in 0.5 mL of CH_2Cl_2 was then added dropwise and the reaction temperature was maintained between -20°C and -25°C. The reaction was monitored by GC and quenched (Ferrous sulfate/tartaric acid work-up) after 2 h (60% conversion). The

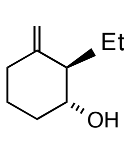
6) Johnson, R.A.; Sharpless, K.B. In *Catalytic Asymmetric Synthesis*; Ojima, I, Ed.; VCH: New York, **1993**; pp 104-108.
7) Brown, S.M.; Davies, S.G.; Sousa, J.A.A. *Tetrahedron: Asymm.* **1991,** *2*, 511.
8) Mori, K.; Tamada, S.; Uchida, M.; Mizumachi, N.; Tachibana, Y.; Matsui, M. *Tetrahedron* **1978**, *34*, 1901.
9) Gao, Y.; Hanson, R.M.; Klunder, J.M.; Ko, S.Y.; Masamune, H.; Sharpless, K.B. *J. Am. Chem. Soc.* **1988**, *109*, 5765.

enantiomeric excess of unreacted **4** (35%) was determined by chiral GC (CP-cyclodex-β-column), programmed temperature rate: 100°C/ 7.0 min + 3°/min up to 120°C, *S*-(-) (major) t_R17.79 min, *R*-(+) (minor) t_R18.36 min. The same reaction was also carried out with enantiomeric *L*-(+)-DIPT, affording *R*-(+) as the major enantiomer of the unreacted substrate **4**.

General Procedure for the Enantioselective Ring-Opening of Vinyloxiranes 3 and 6-10 with Et_2Zn. A solution of $Cu(OTf)_2$ (2.70 mg, 0.0075 mmol) and chiral ligand (*S,S,S*)-**1** or (*S,R,R*)-**2** (8.1 mg, 0.015 mmol) in anhydrous toluene (1.5 mL) was stirred at r.t. for 40 min. The colorless solution was cooled to -70 °C, additioned with a solution of the epoxide (0.5 mmol) in toluene (0.5 mL) and then with 0.68 mL (0.75 mmol) of a 1.1M solution of Et_2Zn in toluene (0.23 mL for the **kinetic resolution protocol**, see Table 1). For all reactions, the temperature was allowed to warm slowly to 0°C (3 h) and the mixture was quenched with saturated aqueous NH_4Cl (3.0 mL). Extraction with Et_2O (2 x 20 mL) and evaporation of the dried ($MgSO_4$) organic phase gave a crude product which was subjected to chromatography (SiO_2).



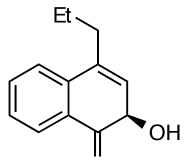
***S*-(-)-3-Propyl-2-cyclohexen-1-ol (4)**. The general procedure was followed, in accordance with a kinetic resolution protocol, employing 55 mg of racemic vinyloxirane **3**[10] (0.5 mmol), $Cu(OTf)_2$ (2.70 mg, 0.0075 mmol), chiral ligand **2** (8.1 mg, 0.015 mmol) and Et_2Zn (0.23 mL). The usual work-up afforded a crude reaction mixture which was subjected to chromatography (SiO_2) with 10% EtOAc: hexanes to give 18 mg of pure **4** (76% based on unreacted **3**), as a liquid. TLC (15% EtOAc/hexanes) R_f=0.14. $[\alpha]_D$=-45.9 (*c*=1.08, $CHCl_3$). ^{1}H NMR δ 5.41-5.49 (m, 1H, C_2-**H**), 4.15-4.22 (m, 1H, C**H**-OH), 1.90-1.98 (m, 4H), 1.37-1.84 (m, 6H), 0.88 (t, 3H, *J*=7.32 Hz, $C_{3'}$-$\mathbf{H}_3$).^{13}C NMR δ 143.15, 124.47, 66.69, 40.41, 32.73, 29.20, 21.35, 19.84, 14.53. Anal. Calcd. for $C_9H_{16}O$: C, 77.08; H, 11.51. Found : C, 77.29; H, 11.62. The enantiomeric excess of **4** (85%) was determined by chiral GC (CP-cyclodex-β-column), programmed temperature rate: 100°C/ 7.0 min + 3°/min up to 120°C, *S*-(-) (major) t_R17.79 min, *R*-(+) (minor) t_R18.36 min.



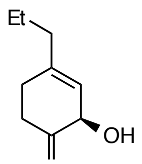
3-Methylidene-2-ethyl-1-cyclohexanol (5). The first eluting fractions of the above flash chromatography afforded 3 mg of pure **5** (9% based on unreacted **3**). TLC (15% EtOAc/hexanes) R_f=0.20. ^{1}H NMR δ 4.83-4.87 (m, 1H, methylidene-**H)**, 4.69-4.74 (m, 1H, methylidene-**H)**, 3.65-3.74 (m, 1H, C**H**-

10) Tanis, S.P.; Herrinton, P.M. *J. Org. Chem.* **1985**, *50*, 3988.

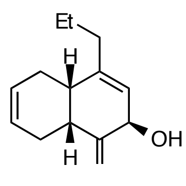
OH), 2.02-2.13 (M, 1H, C_2-**H**), 1.44-1.85 (m, 8H, -C**H**$_2$-), 0.86 (t, 3H, *J*=7.3 Hz, -C**H**$_3$). ^{13}C NMR δ 148.5, 111.6, 73.1, 54.1, 32.5, 30.4, 23.5, 23.3, 12.7.



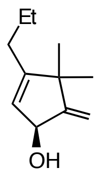
***R*-(-)-4-propyl-1-methylidene-(2*H*)-2-naphthol (17)** The general procedure was followed employing 85 mg of symmetrical vinyloxirane **8** (2.0 mmol), $Cu(OTf)_2$ (10.8 mg, 0.03 mmol), chiral ligand **1** (32.4 mg, 0.06 mmol) and Et_2Zn (2.70 mL). The usual work-up afforded a crude reaction mixture which was subjected to chromatography (SiO_2) with 20% EtOAc: hexanes, to give 366 mg of pure **17** (92%), as a liquid. $[\alpha]_D$=-172.8 (*c*=1.31, $CHCl_3$). ^{1}H NMR δ 7.47-7.51 (m, 1H, Ar-**H**), 7.11-7.21 (m, 3H, Ar-**H**), 5.86 (d, 1H, *J*=4.4 Hz, C_3-**H**), 5.48 (s, 1H, methylidene-**H**), 5.34 (s, 1H, methylidene-**H**), 4.63-4.75 (m, 1H, C**H**-OH), 2.28-2.38 (m, 2H, $C_{1'}$-**H**$_2$), 1.34-1.53 (m, 2H, $C_{2'}$-**H**$_2$), 0.87 (t, 3H, *J*=7.32 Hz, $C_{3'}$-**H**$_3$).^{13}C NMR δ 138.43, 133.40, 129.01, 128.26, 126.79, 125.86, 124.13, 114.80, 107.44, 69.29, 35.25, 21.85, 14.57. Anal. Calcd. for $C_{14}H_{16}O$: C, 83.95; H, 8.06. Found : C, 83.77; H, 8.04. The enantiomeric excess (66%) was determined on the purified product (SiO_2) by chiral HPLC (Daicel Chiralcel OD-H column), hexanes / 2-propanol 97:3, flow rate 0.5 mL/min, *R*--(-) t_R19.98 , *S*-(+) t_R20.94 min.



***R*-(-)-3-propyl-6-methylidene-2-cyclohexen-1-ol (19)** The general procedure was followed employing 56 mg of symmetrical vinyloxirane **7** (0.46 mmol), $Cu(OTf)_2$ (2.49 mg, 0.0069 mmol), chiral ligand **1** (7.5 mg, 0.0138 mmol) and Et_2Zn (0.63 mL). The usual work-up afforded a crude reaction mixture which was subjected to chromatography (SiO_2) with 20% EtOAc: hexanes, to give 63 mg of pure **19** (90%), as a liquid. $[\alpha]_D$=-110 (*c*=0.96, $CHCl_3$). ^{1}H NMR δ 5.47-5.51 (m, 1H, C_2-**H**), 5.01 (s, 1H, methylidene-**H**), 4.89 (s, 1H, methylidene-**H**), 4.48-4.55 (m, 1H, C**H**-OH), 2.40-2.53 (m, 1H), 2.21-2.33 (m, 1H), 1.92-2.17 (m, 4H), 1.34-1.52 (m, 2H, $C_{2'}$-**H**$_2$), 0.88 (t, 3H, *J*=7.32 Hz, $C_{3'}$-**H**$_3$).^{13}C NMR δ 149.41, 143.63, 124.11, 109.06, 69.85, 40.02, 31.76, 29.82, 21.37, 14.52. Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.6. Found : C, 78.56; H, 10.48. The enantiomeric excess (97%) was determined by chiral GC (CP-cyclodex-β-column), programmed temperature rate: 100°C/3.0 min + 3°/ min up to 120°C, *S*(+) t_R17.89, *R*(-) t_R18.09 min.



(4a*S*, 8a*R*, 2*R*)-(+)-4-Propyl-1-methylidene-*cis*-,5,4a,8,8a-tetrahydro-(2*H*)-naphthalen-2-ol (18) The general procedure was followed employing 87 mg of symmetrical vinyloxirane **9** (0.5 mmol), $Cu(OTf)_2$ (2.70 mg, 0.0075 mmol), chiral ligand **1** (8.1 mg, 0.015 mmol) and Et_2Zn (0.68 mL). The usual work-up afforded a crude reaction mixture which was subjected to chromatography (SiO_2) with 20% EtOAc: hexanes, to give 80 mg of pure **18** (78%), a solid. M.p.= 35-38°C. $[\alpha]_D$=+20.96 (*c*=1.04, $CHCl_3$).^{1}H NMR δ 5.52-5.75 (m, 2H, C_6-**H** and C_7-**H**), 5.48 (d, 1H, *J*= 4.0 Hz, C_3-**H**), 5.15 (s, 1H, methylidene-**H**), 4.84 (s, 1H, methylidene-**H**), 4.44 (d, 1H, *J*= 3.9 Hz, C**H**-OH), 2.82-2.92 (m, 1H), 1.93-2.42 (m, 7H), 1.33-1.55 (m, 2H, $C_{2'}$-$\mathbf{H_2}$), 0.91 (t, 3H, *J*= 7.33 Hz, $C_{3'}$-$\mathbf{H_3}$). ^{13}C NMR δ 149.69, 149.08, 125.89, 125.17, 122.08, 111.51, 70.74, 39.14, 37.76, 34.32, 28.37, 27.07, 21.38, 14.48. Anal. Calcd. for $C_{14}H_{20}O$: C, 82.29; H, 9.87. Found : C, 82.12; H, 9.86. The enantiomeric excess of **18** (71%) was determined by chiral HPLC analysis (Daicel Chiralcel OD-H column), hexanes / 2-propanol 99:1, flow rate 0.5 mL/min, t_R 7.14 min (major), t_R 8.89 min (minor) on the corresponding (*R*)-MTPA ester obtained using a three fold excess of the corresponding (*R*)-MTPA chloride in anhydrous pyridine in the presence of catalytic amounts of DMAP.



***R*-(-)-4,4-Dimethyl-3-propyl-5-methylidene-2-cyclopenten-1-ol (20)** The general procedure was followed employing 34 mg of symmetrical vinyloxirane **10** (0.25 mmol), $Cu(OTf)_2$ (1.35 mg, 0.0037 mmol), chiral ligand **1** (4.1 mg, 0.0075 mmol) and Et_2Zn (0.34 mL). Usual work-up afforded a crude reaction mixture which was subjected to chromatography (SiO_2) with 10% EtOAc: hexanes, to give 33 mg of pure **20** (80%), as a liquid. $[\alpha]_D$=-125.9 (*c*=0.52, $CHCl_3$). ^{1}H NMR δ 5.44-5.49 (m, 1H, C_2-**H**), 5.28 (d, 1H, *J*=1.71 Hz, methylidene-**H**), 5.09 (d, 1H, *J*=1.71 Hz, methylidene-**H**), 4.96-5.04 (m, 1H, C**H**-OH), 1.92-2.02 (m, 2H, $C_{1'}$-$\mathbf{H_2}$), 1.47-1.65 (m, 2H, $C_{2'}$-$\mathbf{H_2}$), 1.16 (s, 3H, one of C_4-$\mathbf{CH_3}$), 1.08 (s, 3H, one of C_4-$\mathbf{CH_3}$), 0.96 (t, 3H, *J*=7.32 Hz, $C_{3'}$-$\mathbf{H_3}$).^{13}C NMR δ 164.42, 156.73, 123.96, 107.93, 48.73, 30.39, 29.30, 28.49, 28.35, 21.39, 14.92. Anal. Calcd. for $C_{11}H_{18}O$: C, 79.45; H, 10.92. Found : C, 79.28; H, 10.98. The enantiomeric excess (85%) was determined after chromatography (SiO_2) by chiral GC (CP-cyclodex-β-column), isothermal 110°C, *R*-(-) t_R 33.55, *S*-(+) t_R35.44 min.

Synthesis of Racemic S_N2' (Conjugate) Adducts 4, 17-20. To a stirring suspension of CuCN (9.0 mg, 0.1 mmol) in anhydrous Et_2O (0.5 mL), at -40°C, was added dropwise EtMgCl (2.0 M in THF) (0.38 mL, 0.75 mmol). The heterogeneous mixture was allowed to stir for 30 min at the same temperature and was then cooled up to -65°C. A solution of the vinyloxirane (0.5 mmol) in Et_2O (0.5 mL) was slowly added and the resulting mixture was allowed to warm to 0°C. The reaction was followed with analytical TLC and was quenched at 0°C with saturated aqueous NH_4Cl. Extraction with Et_2O and evaporation of the dried ($MgSO_4$) organic phase gave almost exclusively the corresponding racemic S_N2' adduct **4, 17-20** for all the employed vinyloxiranes.