Enantioselective Epoxidation of Alkenes

Catalyzed by 2-Fluoro-*N*-Carbethoxytropinone

and related Tropinone Derivatives

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Supporting Information

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General experimental details

Diethyl ether and tetrahydrofuran solvents were distilled from sodium-benzophenone ketyl; toluene from sodium; and dichloromethane from calcium hydride. Petrol refers to petroleum ether b.p. 40-60°C which was distilled prior to use. Other solvents and reagents were purified by standard procedures as necessary. Flash chromatography was performed on Merck Kieselgel 60 (230-400 mesh) unless otherwise stated. Analytical thin layer chromatography was performed using pre-coated glass-backed plates (Merck Kieselgel 60 F₂₅₄). Chemical shifts for ¹H and ¹³C NMR are expressed in ppm relative to internal CHCl₃, 7.26 ppm) or CDCl₃ (77.0 ppm, t). J values are measured in Hertz. Multiplicities in ¹³C spectra were determined by DEPT experiments. IR spectra were recorded as thin films on NaCl plates unless otherwise stated.

Preparation of alkenes for epoxidation

The following alkene substrates in Table 2 were not commercially available and were synthesised according to literature methods:

1-*t*-Butyldimethylsiloxy-1-phenylpropene (entry 18): Adam, W.; Fell, R.T.; Stegmann, V.R.; Saha-Moller, R.C. *J. Am. Chem. Soc.* **1998**, *120*, 708.

Benzoic acid cyclohex-1-enyl ester (entries 19, 20): Al Adel, I.; Salami, B.A.; Lavisalles, J.; Rudler, H. *Bull. Soc. Chim. Fr.* **1976**, 903.

Characterisation Data for Product Epoxides in Table 2

The epoxide products are all literature compounds:

Entries 1-2 (*trans*-stilbene oxide): Imuta, M.; Ziffer, H.J. *J. Org. Chem.* **1979**, *44*, 2505-2509. Chang, H.-T.; Sharpless, K.B. *J. Org. Chem.* **1996**, *61*, 6456-6457.

Entry 3 (*trans*- α -methylstyrene oxide): Witkop, B.; Foltz, C.M. *J. Am. Chem. Soc.* **1957**, *79*, 197-210.

Entry 4 (*trans*- β -(hydroxymethyl)styrene oxide): Melloni, P.; Della, T.A.; Lazzari, E.; Mazzini, G.; Meroni, M. *Tetrahedron* **1985**, *41*, 1393.

Entry 5: Gao, Y.; Hanson, R.M.; Klunder, J.M.; Ko, S.Y.; Masamune, H.; Sharpless, K.B. *J. Am. Chem. Soc.* **1987**, *109*, 5765-5780.

Entry 6: Garcia Martinez, A.; Oliver Ruiz, M.; Contelles, J. L. M. *Synthesis* **1986**, 125-128. Sugita, K.; Ohta, A.; Onaka, M.; Izumi, Y. *Chem.Lett.* **1990**, 481-484.

Entry 7 (*trans*-5-decene oxide): Tanner, D.; Birgersson, C.; Gogoll, A.; Luthman, K. *Tetrahedron* **1994**, 50, 9797-9824.

Entries 8-11 (phenylstilbene oxide and 1-phenylcyclohexene oxide): Brandes, B.D.; Jacobsen, E.N. *J. Org. Chem.* **1994**, 59, 4378-4380.

Entry 12 (3,4-dihydronaphthalene oxide): Akhtar, M.N.; Boyd, D.R.; Hamilton, J.G. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2437-2440.

Entry 13 (α -methylstyrene oxide): Fujisawa, T.; Takemura, I.; Ukaji, Y. *Tetrahedron Lett.* **1990**, 31, 5479-5482. Archelas, A.; Furstoss, R. *J. Org. Chem.* **1999**, 64, 6112.

Entry 14-15 (styrene oxide): Robinson, P. L.; Barry, C. N.; Kelly, J. W.; Evans, S. A. *J. Am. Chem. Soc.* **1985**, 107, 5210-5219.

Entry 16: (*trans*-ethyl cinnamate oxide): Adolfsson, H.; Coperet, C.; Chiang, J. P.; Yudin, A. K. *J. Org. Chem.* **2000**, 65, 8651-8658.

Entry 17: (*E*-chalcone oxide) Augustyn, J. A. N.; Bezuidenhoudt, B. C. B.; Ferreira, D. *Tetrahedron* **1990**, 46, 2651-2660.

Entry 18 (α -hydroxypropiophenone): Demir, A. S.; Hamamci, H.; Sesenoglu, O.; Aydogan, F.; Capanoglu, D.; Neslihanoglu, R.. *Tetrahedron: Asymmetry* **2001**, 12, 1953-1956.

Entries 19-20 (1-benzyloxycyclohexene oxide): Zhu, Y.; Shu, L.; Tu, Y.; Shi, Y. *J. Org. Chem.* **2001**, 66, 1818-1826.

Determination of epoxide enantiomeric purity in Table 2

Entries 1 and 2: chiral HPLC on Chiracel OD, 10% *i*PrOH/hexane, 0.8 ml/min, detecting at 254 nm, as detailed by Shi: Tu, Y; Wang, Z-X.; Shi, Y. *J. Am. Chem. Soc.*, **1996**, *118*, 9806. Absolute configuration determined by comparison to Shi's results.

Entries 3-6, 8-12, 14, 15: ee and configuration determined by ¹H NMR in the presence of Eu(hfc)₃ as chiral shift reagent, as detailed by Shi: Tu, Y; Wang, Z-X.; Shi, Y. *J. Am. Chem. Soc.*, **1996**, *118*, 9806. Absolute configuration determined by comparison to Shi's results.

Entry 7: ee determined by ring opening with NaOMe/MeOH followed by formation of the acetate and ¹H NMR analysis in the presence of Eu(hfc)₃ as chiral shift reagent, as detailed by Shi: Tu, Y; Wang, Z-X.; Shi, Y. *J. Am. Chem. Soc.*, **1996**, *118*, 9806. Absolute configuration determined by comparison to Shi's results.

Entry 13: chiral HPLC on Chiracel OD, 5% *i*PrOH/hexane, 0.8 ml/min, detecting at 254 nm, as detailed by Shi: Wang, Z. X.; Tu, Y.; Frohn, M.; Zhang, J. R.; Shi, Y. *J. Am. Chem. Soc.* **1997**, *119*, 11224-11235. Absolute configuration determined by comparison to Shi's results.

Entry 16: chiral HPLC on Chiracel OJ, 10% *i*PrOH/hexane, 1.0 ml/min, detecting at 254 nm, retention times 6.99 min (minor enantiomer), 10.74 min (major enantiomer). Major enantiomer assigned as (2*R*, 3*S*) by comparison of the sign of the product's optical rotation to the literature value of [α]_D +152 for the (2*S*, 3*R*) isomer: Cabon, O.; Larchevêque, M.; Buisson, D.; Azerad, R. *Tetrahedron Lett.* **1992**, *38*, 7337-7340.

Entry 17: chiral HPLC on Chiracel OD, 5% EtOH/hexane, 1.0 ml/min, detecting at 254 nm, retention times 9.45 min (minor enantiomer), 10.87 min (major enantiomer).

Entry 18: chiral HPLC on Chiracel OD: Adam, W.; Diaz, M.T.; Fell, R. T.; Saha-Moller, C. R.. *Tetrahedron: Asymmetry* **1996**, *7*, 2207-2210.

Entries 19-20: chiral HPLC on Chiracel OD, as detailed by Shi: Zhu, Y.; Shu, L.; Tu, Y.; Shi, Y. *J. Org. Chem.* **2001**, *66*, 1818-1826.

ORTEP representation of X-ray crystallographic data for fluoroketone 2

CIF file is also included separately as Supporting Information.