

# Catalytic Asymmetric Alkylations of Ketoimines. Enantioselective Synthesis of *N*-Substituted Quaternary Carbon Stereogenic Centers by Zr-Catalyzed Additions of Dialkylzinc Reagents to Aryl-, Alkyl- and Trifluoroalkyl-Substituted Ketoimines

Peng Fu, Marc L. Snapper,\* and Amir H. Hoveyda\*

*Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467*

## SUPPORTING INFORMATION, Part IV

### The complete citation for *reference 18* of the manuscript:

(18) All structures were minimized according to the following sequence. The promising conformers from conformer distributions, obtained with PM3 semi-empirical method, were optimized at B3LYP level of theory. Conformer distributions were calculated with Spartan '04 suite. Final stationary points on the potential energy surface were calculated with Gaussian 03.D02 suite. Electronic configurations of the molecular systems were described by 6-31G(d,p) double- $\zeta$  basis set on H, C, N, and O; the basis sets for N and O were augmented with a single *sp*-type and a single *d*-type diffuse functions as supplied by Gaussian 03.D02. All basis sets are as supplied by Gaussian 03.D02 suite. The valley nature of stationary points was confirmed by frequency calculation at the same level of theory. (a) Spartan '04: Kong, J.; White, C. A.; Krylov, A. I.; Sherrill, C. D.; Adamson, R. D.; Furlani, T. R.; Lee, M. S.; Lee, A. M.; Gwaltney, S. R.; Adams, T. R.; Ochsenfeld, C.; Gilbert, A. T. B.; Kedziora, G. S.; Rassolov, V. A.; Maurice, D. R.; Nair, N.; Shao, Y.; Besley, N. A.; Maslen, P. E.; Dombroski, J. P.; Daschel, H.; Zhang, W.; Korambath, P. P.; Baker, J.; Byrd, E. F. C.; VanVoorhis, T.; Oumi, M.; Hirata, S.; Hsu, C. -P.; Ishikawa, N.; Florian, J.; Warshel, A.; Johnson, B. G.; Gill, P. M. W.; Head-Gordon, M.; Pople, J. A. *J. Computational Chem.* **2000**, *21*, 1532–1548. (b) Gaussian 03, revision D02: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.;

Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004. (c) 6-31G(d,p): Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257–2261.

**The complete citation for reference 20 of the manuscript:**

For an example of a medically relevant agent with a trifluoromethyl-substituted tertiary carbinol, see: (a) Pierce, M. E.; Parsons, R. L.; Radesca, L. A.; Lo, Y. S.; Silverman, S.; Moore, J. R.; Islam, Q.; Choudhry, A.; Fortunak, J. M. D.; Nguyen, D.; Luo, C.; Morgan, S. J.; Davis, W. P.; Confalone, P. N.; Chen, C.; Tillyer, R. D.; Frey, L.; Tan, L.; Xu, F.; Zhao, D.; Thompson, A. S.; Corley, E. G.; Grabowski, E. J. J.; Reamer, R.; Reider, P. J. *J. Org. Chem.* **1998**, *63*, 8536–8543. For a general discussion regarding the significance of F-containing molecules to modern medicine, see: (b) Muller, K.; Faeh, C.; Diederich, F. *Science* **2007**, *317*, 1881–1886.