Supporting Information

for

A Kinetic Study of the Reaction of *N,N*-Dimethylanilines with 2,2-Diphenyl-1-picrylhydrazyl Radical. A Proton-Coupled Electron Transfer Mechanism?

Enrico Baciocchi, Alessandra Calcagni, Osvaldo Lanzalunga

Instrumentation

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a 300MHz spectrometer in $CDCl_3$ and CD_3CN. GC-MS analyses were performed on a gas chromatograph equipped with a OV1 capillary column (12 m x 0.2 mm) coupled with a mass selective detector. UV-vis measurement was performed on a diode array spectrophotometer.

Materials

CH_3CN (spectrophotometric grade) was distilled over CaH_2. Other solvents were of the highest grade commercially available and were used as received. 2,2-diphenyl-1-picrylhydrazyl radical (dpph) and magnesium perchlorate were commercial products and used as received.

N,N-Dimethylaniline, *N*-methylaniline, *N,N*-dimethyl-*p*-toluidine, *N*-methyl-*p*-toluidine were commercially available and further purified by distillation. 4-Methoxy-*N*-methylaniline and 4-phenoxy-N-methylaniline were prepared according to the literature by treating the corresponding anilines with succinimide and aqueous formaldehyde and then reducing the amminomethylsuccinimide with $NaBH_4$ in DMSO.[S1] 4-methoxy-*N,N*-dimethylaniline, 4-phenoxy-*N,N*-dimethylaniline and *N,N*-di(trideuteriomethyl)anilines were prepared by reaction of the corresponding anilines with CH_3I or CD_3I in the presence of tetra-*n*-butylammonium iodide and potassium hydroxide in benzene/water according to the procedure reported in the literature.[S2,S3] *N*-methyl-*N*-trideuteriomethylanilines were prepared by reaction of the corresponding *N*-methylanilines with CD_3I.[S2] Spectral data of the unknown compounds are the following:

4-Phenoxy-*N,N*-bis(trideuteriomethyl)aniline. ^{1}H NMR δ 6.70-6.77 (m, 2H), 6.91-7.03 (m, 5H), 7.23-7.31 (m, 2H); ^{13}C NMR δ 113.9, 117.2, 121.0, 121.9, 129.5, 147.3, 147.7, 159,2; GC-MS *m/z* (%) M^+ 219 (100), 217 (35), 201 (8), 142 (75), 114 (8), 77 (21), 66 (9), 51 (18).

4-Phenoxy-*N*-methyl-N-trideuteriomethylaniline. ^{1}H NMR δ 2.92 (s, 3H), 6.70-6.77 (m, 2H), 6.91-7.03 (m, 5H), 7.23-7.31 (m, 2H); ^{13}C NMR δ 41.2, 113.9, 117.2, 121.0, 121.9, 129.5, 147.3,

147.7, 159,2; GC-MS *m/z* (%) M^+ 216 (100), 215 (33), 214 (15), 139 (67), 111 (7), 77 (24), 65 (11), 51 (20).

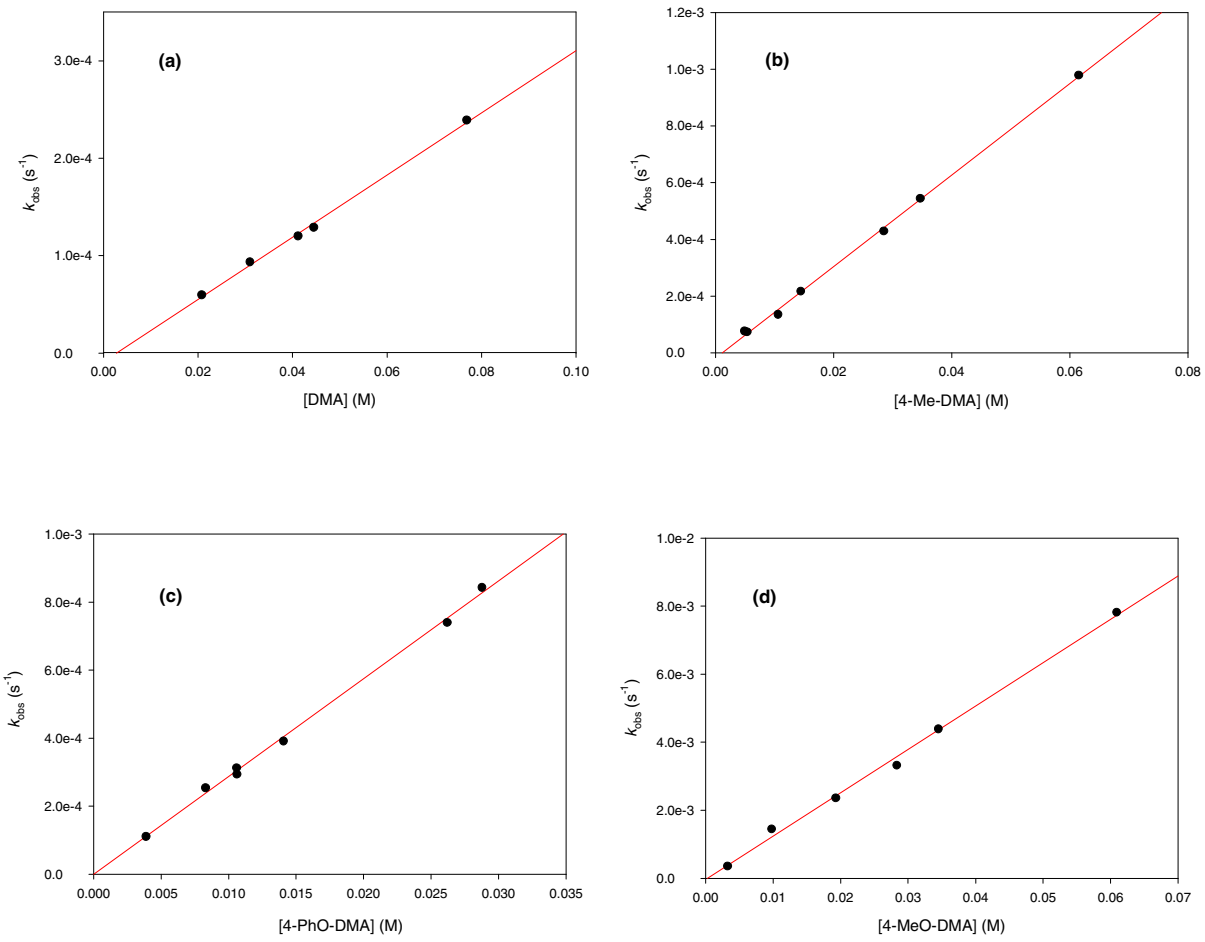

Figure S1: Plots of k_{obs} vs substrate concentration for the reaction of *N,N*-dimethylanilines (DMAs) with dpph$^{\bullet}$ in CH_3CN at 298 K. (a) DMA, (b) 4-Me-DMA, (c) 4-PhO-DMA, (d) 4-MeO-DMA

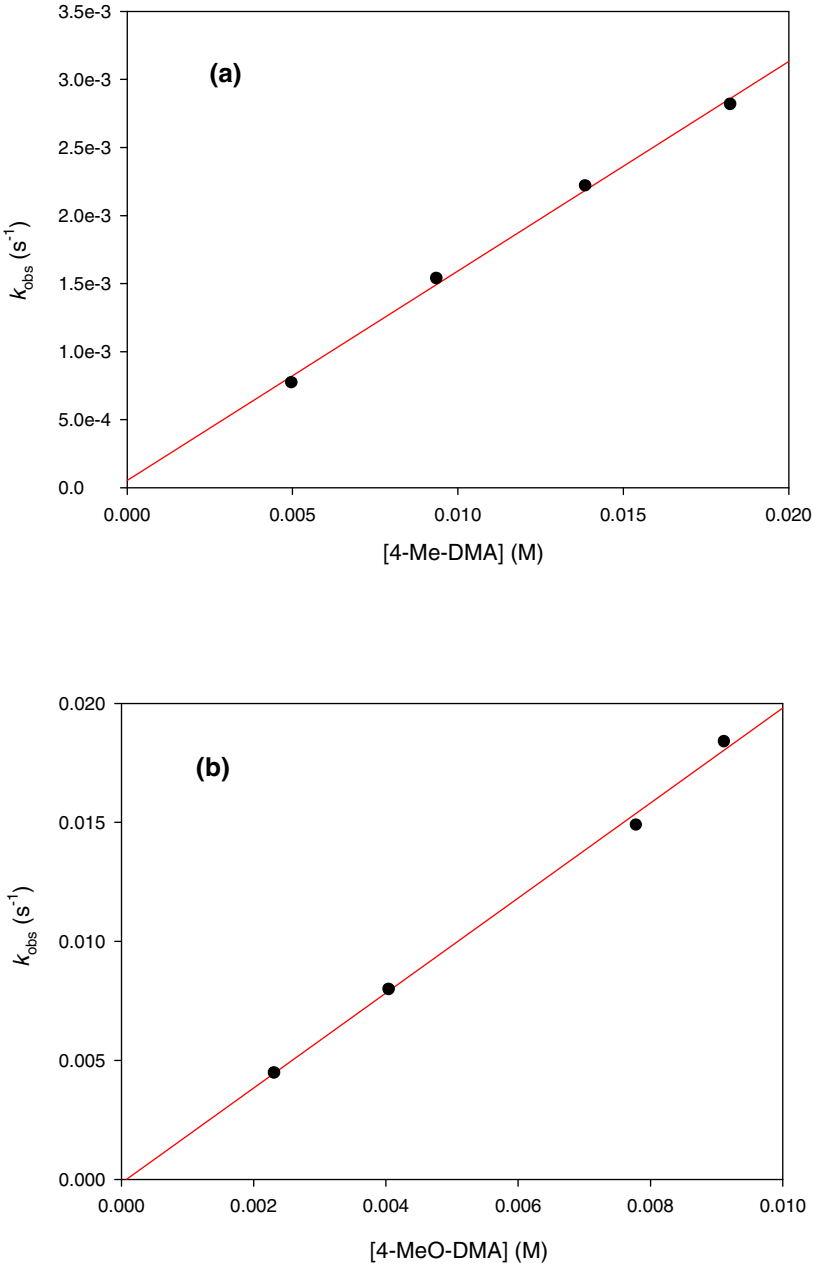

Figure S2: Plots of k_{obs} vs substrate concentration for the reaction of *N,N*-dimethylanilines (DMAs) with dpph$^{\bullet}$ in toluene at 298 K. (a) 4-Me-DMA, (b) 4-MeO-DMA

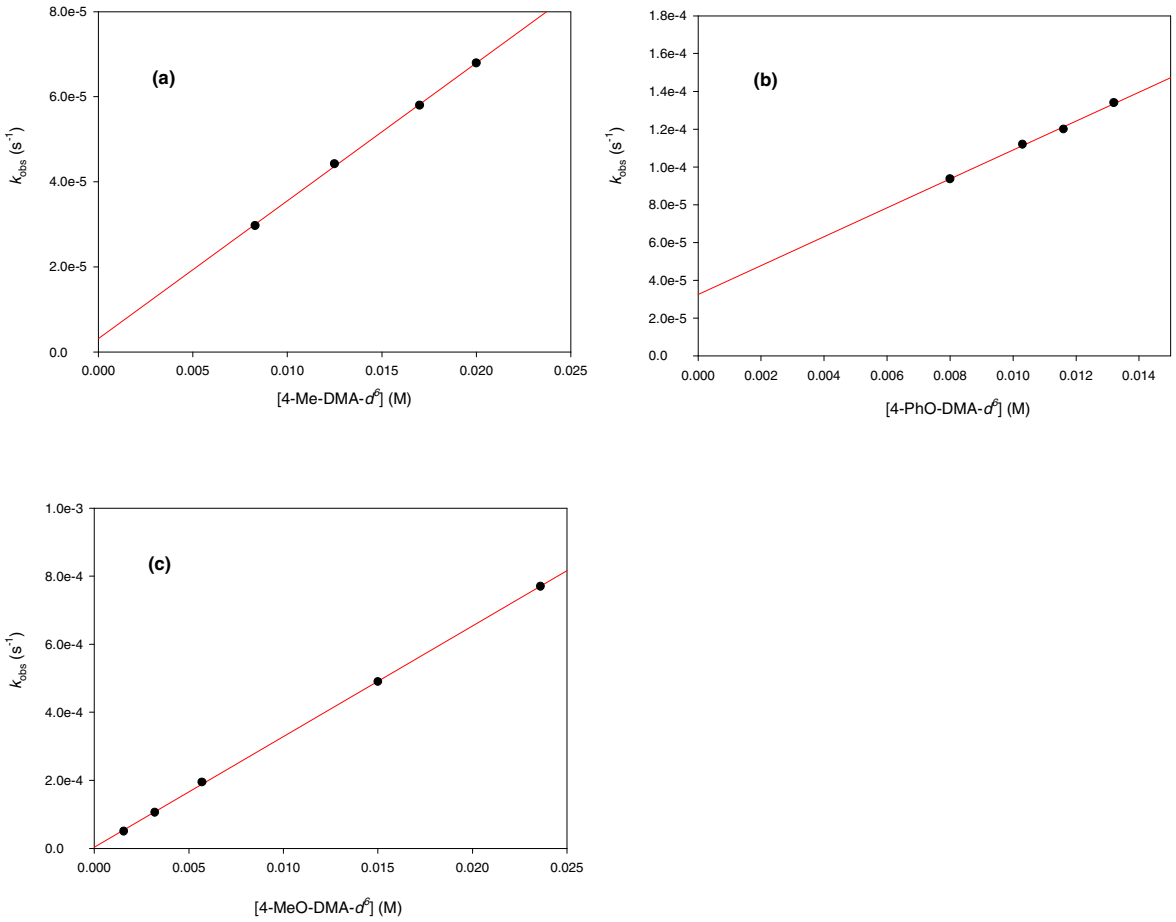

Figure S3: Plots of k_{obs} vs substrate concentration for the reaction of *N*,*N*-di(trideuteriomethyl)-anilines (DMAs-d^6) with dpph$^\bullet$ in CH_3CN at 298 K. (a) 4-Me-DMA-d^6, (b) 4-PhO-DMA-d^6, (c) 4-MeO-DMA-d^6

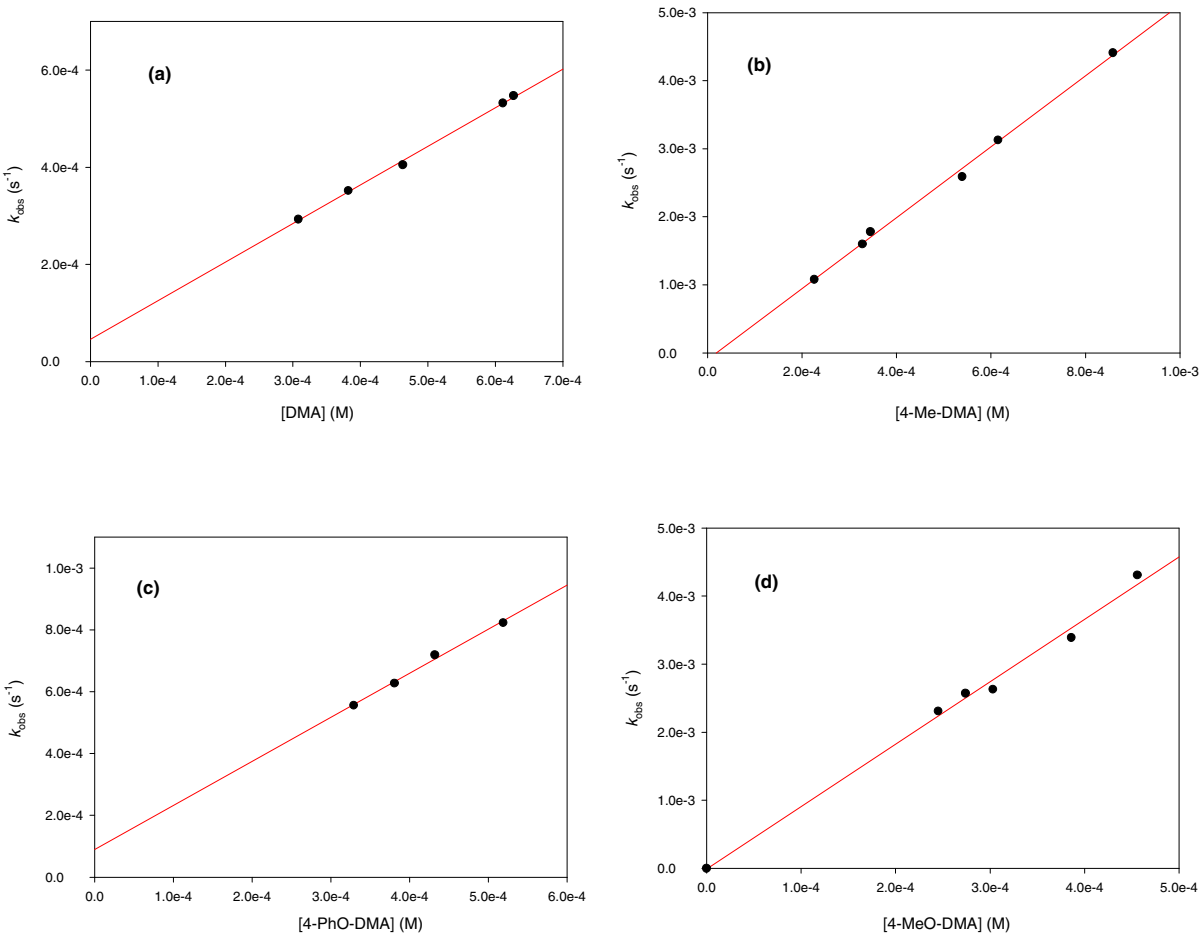

Figure S4: Plots of k_{obs} vs substrate concentration for the reaction of *N,N*-dimethylanilines (DMAs) with dpph$^{\bullet}$ in CH_3CN in the presence of $Mg(ClO_4)_2$ 1×10^{-3} M at 298 K. (a) DMA, (b) 4-Me-DMA, (c) 4-PhO-DMA, (d) 4-MeO-DMA

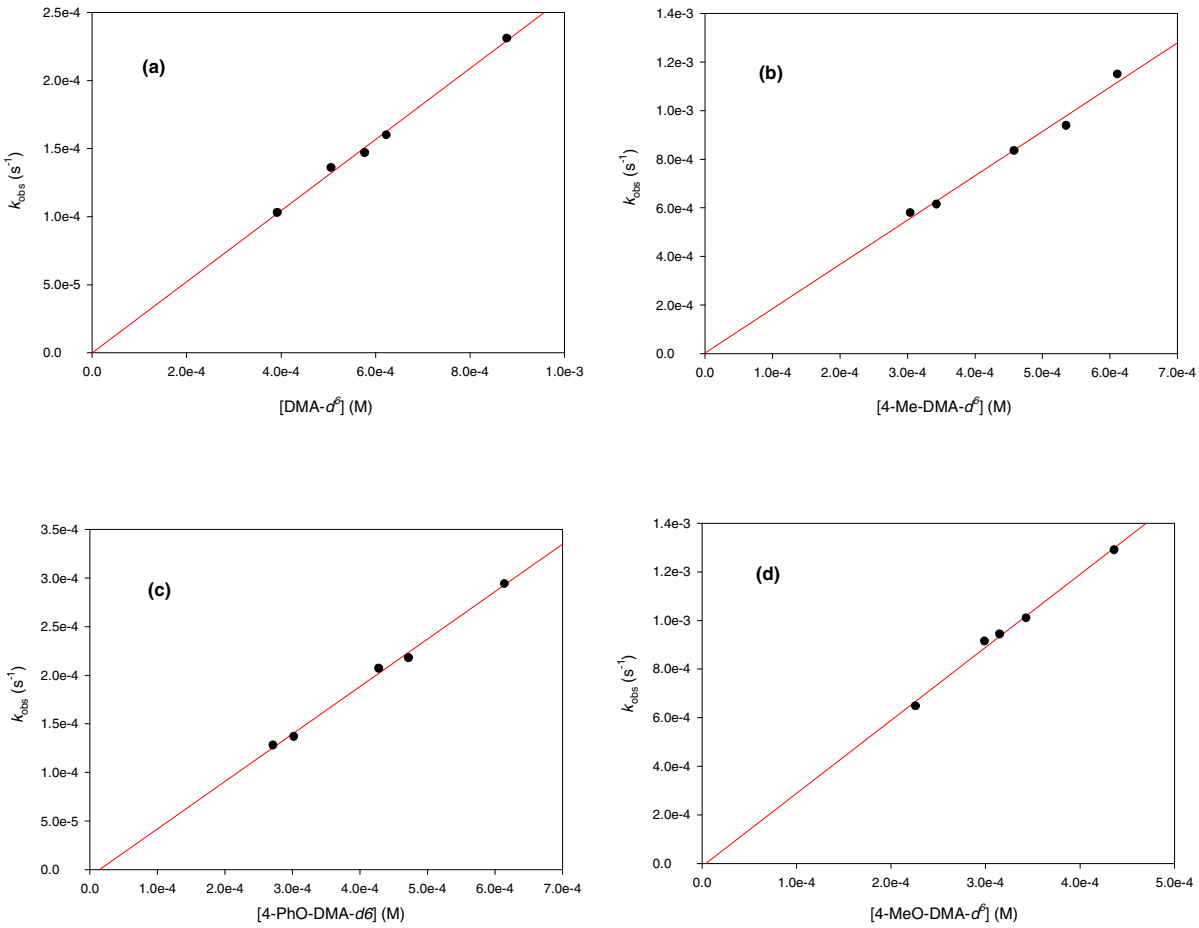

Figure S5: Plots of k_{obs} vs substrate concentration for the reaction of *N,N*-di(trideuteriomethyl)-anilines (DMAs) with dpph$^{\bullet}$ in CH_3CN in the presence of $Mg(ClO_4)_2$ 1×10^{-3} M at 298 K. (a) DMA-d^6, (b) 4-Me-DMA-d^6, (c) 4-PhO-DMA-d^6, (d) 4-MeO-DMA-d^6

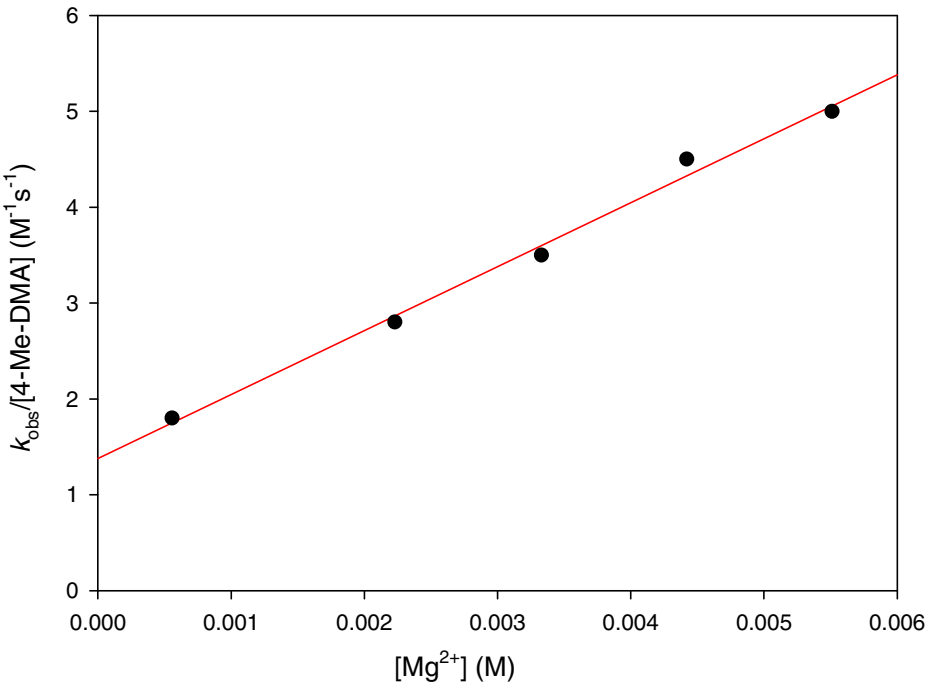

Figure S6: Plots of k_{obs}/[4-Me-DMA] vs Mg^{2+} concentration for the reaction of 4-methyl-*N*,*N*-dimethylaniline (0.6 mM) with dpph$^{\bullet}$ in CH_3CN in the presence of $Mg(ClO_4)_2$ at 298 K.

References for Supporting Information

S1. Kadin, S. B. *J. Org. Chem.* **1973**, *38*, 1348-1350.

S2. Dinnocenzo, J. P.; Karki, S. B.; Jones, J. P. *J. Am. Chem. Soc.* **1993**, *115*, 7111-7116.

S3. E. Baciocchi, M. Bietti, M. F. Gerini, O. Lanzalunga *J. Org. Chem.* **2005**, *70*, 5144-5149.