Supporting Information
for

Fast TiO_2-catalyzed direct Amidation of neat Carboxylic Acids under mild dielectric Heating

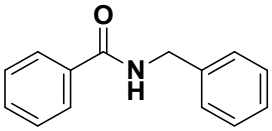
E. Calcio Gaudino,[a] D. Carnaroglio,[a] M.A. Gonçalves Nunes,[b] L. Schmidt,[b] E.M.M. Flores,[b] C. Deiana,[c] Y. Sakhno,[c] G. Martra,[c] G. Cravotto, [a]*

[a] *Dipartimento di Scienza e Tecnologia del Farmaco and Interdepartmental Centre "Nanostructured interfaces and surfaces- NIS", University of Torino, Via P. Giuria 9, 10125 Torino (Italy)*
[b] *Dipartimento de Química, Universidade Federal de Santa Maria, 97105-900, Santa Maria, RS, Brazil*
[c] *Dipartimento di Chimica and Interdepartmental Centre "Nanostructured interfaces and surfaces- NIS", University of Torino, Via P. Giuria 7, 10125 Torino (Italy)*

**Corresponding author. Tel.: +39 011 670 7684; fax: +39 011 670 7687.*
E-mail address: giancarlo.cravotto@unito.it

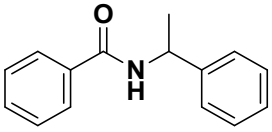
1. Analytical Data

1.1. *N*-benzylbenzamide 3 (Table 3, entry 1):



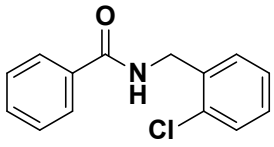
Yield 263 mg (quant.); a white solid.[S1]

1.2. *N*-(1-phenylethyl)benzamide 13 (Table 3, entry 2):



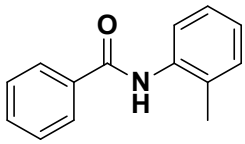
Yield 219 mg (78%); a white solid.[S2]

1.3. *N*-(2-chlorobenzyl)benzamide 14 (Table 3, entry 3):



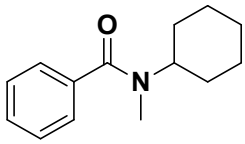
Yield 236 mg (77%); a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.62 – 7.18 (m, 9H), 4.21 (s, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.49, 134.32, 131.73, 128.71, 128.47, 127.29, 127.11, 42.21 ppm. *m/z* (MALDI-TOF MS): calcd for $C_{14}H_{12}ClNO$ $[M + H]^+$: 246.0686, found: 246.0682.

1.4. *N*-(*o*-tolyl)benzamide 15 (Table 3, entry 4):



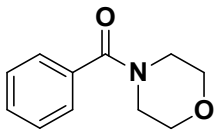
Yield 145 mg (55%); a white solid.[S3]

1.5. *N*-cyclohexyl-*N*-methylbenzamide 16 (Table 3, entry 5):



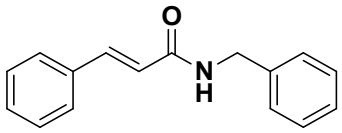
Yield 182 mg (67%); a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, 2H), 7.51 – 7.30 (m, 3H), 3.54 (m, 4H), 1.91 – 1.41 (m, 6H), 1.36 – 1.07 (m, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.22, 134.89, 128.99, 128.45, 128.12, 65.01, 34.87, 28.77, 25.71, 25.05 ppm. *m/z* (MALDI-TOF MS): calcd for $C_{14}H_{19}NO$ $[M + H]^+$: 218.1545, found: 218.1547.

1.6. *N*-benzoylmorpholine 17 (Table 3, entry 6):



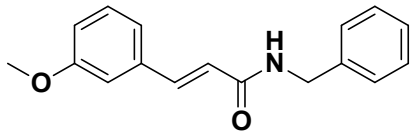
Yield 84 mg (35%); a white solid.[S4]

1.7. *N*-benzylcinnamamide 18 (Table 3, entry 7):



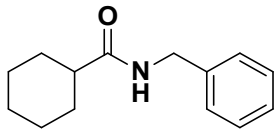
Yield 290 mg (98%); a white solid.[S5]

1.8. *N*-benzyl-3-(3-methoxyphenyl)acrylamide 19 (Table 3, entry 8):



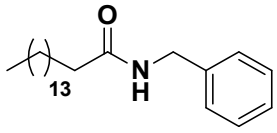
Yield 320 mg (96%); a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.64 (d, 2H), 7.40 – 7.23 (m, 6H), 6.90 (d, 2H), 6.40 (d, 1H), 4.59 (d, 2H) 3.82 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.32, 113.21, 141.66, 138.33, 134.78, 129.13, 128.53, 120.82, 113.87, 53.84, 44.27 ppm. *m/z* (MALDI-TOF MS): calcd for $C_{17}H_{17}NO_2$ $[M + H]^+$: 268.1337, found: 268.1339.

1.9. *N*-benzylcyclohexanecarboxamide 20 (Table 3, entry 9):



Yield 258 mg (95%); a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.47 – 7.13 (m, 5H), 4.11 (s, 2H), 2.12 (m, 1H), 1.92 – 1.71 (m, 4H), 1.34 – 1.12 (m, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.95, 138.64, 128.62, 128.57, 45.42, 43.17, 29.66, 25.81, 25.72 ppm. *m/z* (MALDI-TOF MS): calcd for $C_4H_{19}NO$ $[M + H]^+$: 98.1545, found: 98.1542.

1.10. *N*-benzylpalmitamide 21 (Table 3, entry 10):



Yield 307 mg (92%); a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.41 – 7.21 (m, 5H), 4.44 (s, 2H), 2.20 (t, 2H), 1.64 (m, 2H), 1.37 – 1.16 (m, 24H), 0.87 (t, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.94, 165.97, 1471.31, 138.18, 129.66, 128.67, 127.82, 127.55, 115.42, 55.42, 43.79 ppm. *m/z* (MALDI-TOF MS): calcd for $C_{17}H_{17}NO_2$ $[M + H]^+$: 268.1337, found: 268.1333.

2. IR Spectroscopy Data

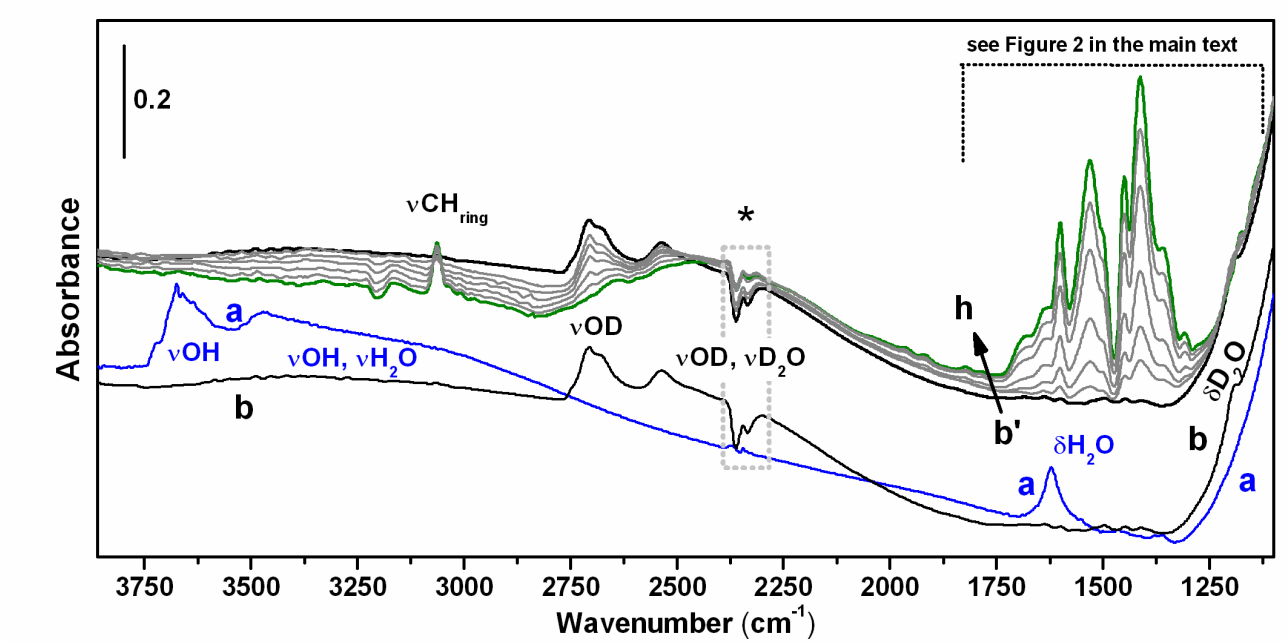


Figure S1. IR spectra, in the 3800-1100 cm^{-1} range, of the TiO_2 powder used as catalyst: a) outgassed at 450 °C, reoxidized with O_2, rehydrated at room temperature by contact with 20 mbar of H_2O vapor and finally outgassed at beam temperature (ca. 50 °C) in the IR cell (see Experimental section in the main text); b) after H/D exchange by contact with 20 mbar of D_2O vapor and outgassed at beam temperature (5 cycles of D_2O admission/outgassing, until invariance of the spectra); b') the same as spectrum b, shifted along the Y axis for the sake of comparison with the following spectra; c-h) after admission in the IR cell of increasing amount of H_5C_6COOD. The negative signals in the grey dotted frame, labelled with the asterisk, resulted due to the antisymmetric stretching mode of CO_2 molecules, the amount of which in the instrument changed with respect to the reference spectrum (empty sample chamber) along the series of measurements.

2.1. Comment to the Figure:

Spectrum (a) of the catalyst exhibits the typical IR features of hydroxy groups and water molecules left adsorbed on the surface after outgassing at beam temperature, constituting a complete first layer of hydration. The low frequency limit of the spectrum corresponds to the inset of the cut-off imposed by the lattice modes of TiO_2. The signals at frequency ≥ 3500 cm^{-1} are due to surface hydroxy groups not experiencing H-bonding. Conversely, the O-H stretching modes of both hydroxy groups and water molecules involved in H-bonding are responsible for the broad pattern spread over the 3500-2750 cm^{-1} range. Finally, the deformation mode of water molecules produces the band at ca. 1620 cm^{-1}.[S6] All these features were substituted by the corresponding signals, shifted to lower frequency, due to –OD groups and D_2O molecules after the accomplishment of the complete H/D exchange (curve b).

The subsequent admission of increasing amounts of H_5C_6COOD resulted in (i) the appearance of the signals due to adsorbed benzoic acid molecules, (ii) the downshift of the stretching mode of surface –OD initially "vibrationally free" because of the interaction with newly adsorbed molecules, and (iii) the depletion of the IR features due to D_2O molecules (unequivocally monitored by the δD_2O band at 1200 cm^{-1}) because of their displacement by the incoming H_5C_6COOD molecules. These latter are responsible for the band at ca. 3060 cm^{-1} , due to the νCH stretching mode of the

aromatic ring [S7,S8] and the series of signals in the 1750-1100 cm^{-1} range, the assignment of which is reported in the comment to Figure 2 in the main text.

References

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