Electronic Supporting Information

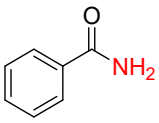
Single-pot tandem oxidative/C-H modification amidation process using ultra small PdNPs encapsulated porous organosilica nanotubes

Behnam Gholipour, [a] Afsaneh Zonouzi, *[,a], Sadegh Rostamnia, *[,b] Xiao Liu, *[,c]

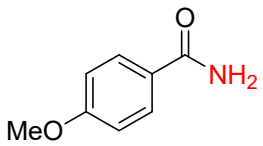
[b] *University of Tehran, Department of Chemistry, P.O. Box 14155-6455, Tehran, Iran*
Email: zonouziafsaneh@ut.ac.ir
[b] *Organic and Nano Group (ONG), Department of Chemistry, Iran University of Science and Technology (IUST), PO Box 16846-13114, Tehran, Iran Email: rostamnia@iust.ac.ir; srostamnia@gmail.com*
[c] *Key Laboratory of Pesticide & Chemical Biology of the Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, P. R. China. Email: liuxiao71@tju.edu.cn*

Data ^{1}H NMR and ^{13}C NMR

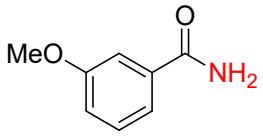
The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE NMR spectrometer at 300 and 100 MHz, respectively.



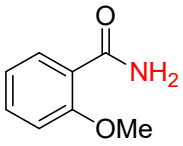
Benzamide (Table 2, 3a): ^{1}H NMR (400 MHz, DMSO-*d6*): δ_H (ppm) = 8.01 (1 H, s, 1H of NH), 7.88 (2 H, m, 2 H of CH aromatic), 7.54 (1 H, m, 1 H of CH aromatic), 7.46 (2 H, m, 2H of CH aromatic), 7.39 (1 H, s,1H of NH); ^{13}C NMR (100 MHz; DMSO-*d6*): δ_C (ppm) = 168.41, 134.65, 131.73, 128.69, 127.91.



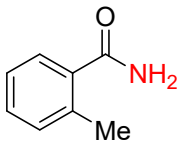
4-methoxybenzamide (Table 2, 3b): ^{1}H NMR (400 MHz, DMSO-*d6*): δ_H (ppm) = 3.80 (3 H, s, 3 H of OCH_3) 7.86 (2 H, d, 2H of CH aromatic,$^{3}J_{HH}$ = 8.8 Hz), 7.20 (1 H, s, 1 H of NH), 6.98 (2 H, d, , 2 H of CH aromatic, $^{3}J_{HH}$ = 9.2 Hz); ^{13}C NMR (100 MHz; DMSO-*d6*): δ_C (ppm) = 162.06, 129.84, 126.86, 113.86, 55.78.



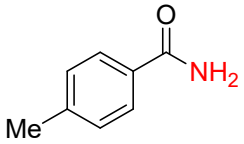
3-Methoxybenzamide (Table 2, 3c): ^{1}H NMR (400 MHz, DMSO-*d6*): δ_H (ppm) = 3.80 (3 H, s, 3 H of OCH_3), 7.99 (1 H, s, 1 H of NH),7.47-7.42 (2 H, m, 2 H of CH aromatic), 7.37 (1 H, t, 1 H of CH, $^{3}J_{HH}$ = 7.6 Hz), 7.09 (1 H,m, 1 H of CH aromatic); ^{13}C NMR (100 MHz; DMSO-*d6*): δ_C (ppm) = 168.04, 159.59, 136.08, 120.14, 117.56, 113.06, 55.68.



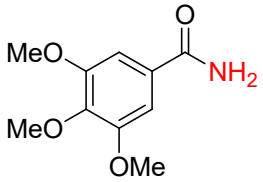
2-Methoxybenzamide (Table 2, 3d): ^{1}H NMR (400 MHz, DMSO-*d6*), δ_H (ppm) = 7.81 (1 H, d, 1 H of CH aromatic, $^{3}J_{HH}$ = 7.6 Hz), 7.66 (1 H,s, 1 H of NH_2), 7.53 (1H, s, 1 H of NH_2), 7.48 (1 H, t, 1 H of CH aromatic), 7.14 (1 H, d, 1 H of CH aromatic, $^{3}J_{HH}$ = 8.4Hz), 7.03 (1 H, t, , 1 H of CH aromatic , $^{3}J_{HH}$ = 8.4 Hz), 3.89 (3 H, s, 3H of OCH_3); ^{13}C NMR (100 MHz, DMSO-*d6*): δ_C (ppm)= 166.76, 157.70, 132.98, 131.19, 123.02, 120.87, 112.43, 56.26.



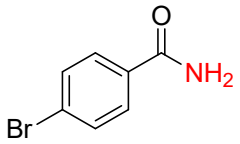
2- Methylbenzamide (Table 2, 3e): ^{1}H NMR (400 MHz, DMSO-*d6*), δ_H (ppm) = 7.93 (1 H, s, 1 H of NH), 7.78 (2 H, dd, 2 H of CH aromatic, $^{3}J_{HH}$ = 6.6 Hz), 7.29 (1 H, s, 1 H of NH), 7.25 (2 H, d, 2 H of CH aromatic, $^{3}J_{HH}$ =8.0 Hz), 2.35 (3 H, s, 3 H of CH_3); ^{13}C NMR (125 MHz, DMSO-*d6*): δ_C (ppm) = 168.26, 141.58, 131.86, 131.83, 129.22, 127.97, 21.41.



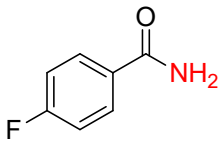
4-methylbenzamide (Table 2, 3f): ^{1}H NMR (400 MHz, DMSO-*d6*), δ_H (ppm) = 7.94 (1 H, s, 1 H of NH), 7.78 (2 H, d, 2 H of CH aromatic, $^{3}J_{HH}$ = 8.4 Hz), 7.28 (1 H, s, 1 H of NH), 7.26 (2 H, d, 2 H of CH aromatic, $^{3}J_{HH}$ = 8.0 Hz), 2.35(3 H, s, 3 H of CH_3); ^{13}C NMR (100 MHz, DMSO-*d6*): δ_C (ppm)= 168.25, 141.57, 131.84, 129.21, 127.97, 21.42.



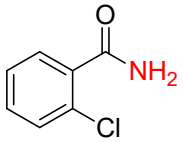
3, 4, 5-trimethoxybenzamide (Table 2, 3g): ^{1}H NMR (400 MHz, DMSO-*d6*), δ_H (ppm) = 7.23 (2 H, s, 2 H of CH aromatic), 3.82 (6 H, s, 6 H of CH aromatic), 3.70 (3 H, s, 3 H of CH aromatic); ^{13}C NMR (100 MHz, DMSO): δ_C (ppm) = 167.76, 140.37, 129.82, 105.50, 60.52, 56.44.



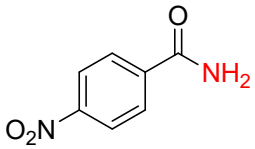
4-Bromobenzamide (Table 2, 3h): ^{1}H NMR (400 MHz, DMSO-*d6*), δ_H (ppm) = 8.02 (1 H s, 1 H of NH), 7.95 (2 H, m, 2 H of CH aromatic), 7.41 (1 H, s, 1 H of NH), 7.28 (2 H, t, 2 H of CH aromatic, $^{3}J_{HH}$ = 9.2 Hz); ^{13}C NMR (100 MHz, DMSO *d6*): δ_C (ppm)= 167.29, 165.63, 163.17, 131.13, 130.58, 115.58.



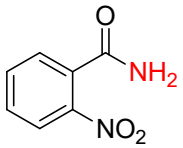
4-Fluorobenzamide (Table 2, 3i): ^{1}H NMR (400 MHz, DMSO-*d6*), δ_H (ppm) = 8.02 (1 H s, 1 H of NH), 7.95 (2 H, m, 2 H of CH aromatic), 7.41 (1 H, s, 1 H of NH), 7.28 (2 H, t, 2 H of CH aromatic, $^{3}J_{HH}$ = 9.2 Hz); ^{13}C NMR (100 MHz, DMSO *d6*): δ_C (ppm) = 167.29, 165.63, 163.17, 131.13, 130.58, 115.58.



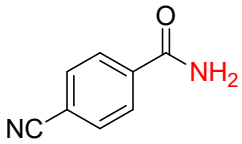
2- Chlorobenzamide (Table 2, 3j): ^{1}H NMR (400 MHz, DMSO-*d6*), δ_H (ppm) = 7.90 (1 H, s, 1 H of NH), 7.61 (1 H, s, 1 H of NH),7.50-7.36 (4 H, m, 4 H of CH aromatic); ^{13}C NMR (100 MHz, DMSO): δ_C (ppm) = 68.60, 137.51, 131.07, 130.08, 129.13, 129.13, 127.5.



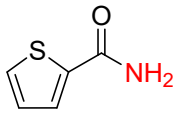
4-Nitrobenzamide (Table 2, 3k): ^{1}H NMR (400 MHz, DMSO-*d6*), δ_H (ppm) = 8.34 (1 H, s, 1 H of NH), 8.30 (2 H, d, 2 H of CH aromatic, $^{3}J_{HH}$ = 8.4 Hz), 8.11 (2 H, d, 2 H of CH aromatic, $^{3}J_{HH}$ = 8.8 Hz), 7.75 (1 H, s, 1 H of NH); ^{13}C NMR (100 MHz, DMSO-*d6*): δ_C (ppm)= 166.70, 149.53, 140.39, 129.4, 123.93.



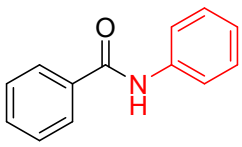
2-Nitrobenzamide (Table 2, 3l): Yield = 43%. ^{1}H NMR (400 MHz, DMSO-*d6*), δ_H (ppm) = 8.20 (1 H, s, 1H of NH), 8.00 (1 H, d, 1 H of CH aromatic, $^{3}J_{HH}$ = 8.0 Hz), 7.78 (1 H, t, 1 H of CH aromatic, $^{3}J_{HH}$ = 7.6 Hz), 7.72 (1 H, s, 1 H of NH), 7.70-7.64 (2 H, m, 2 H of CH aromatic);^{13}C NMR (100 MHz, DMSO-*d6*): δ_C (ppm)= 167.65, 147.7, 133.83, 132.98, 131.12, 129 .32, 124.42.



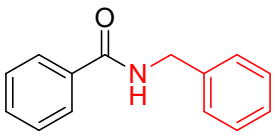
4- Cyanobenzamide (Table 2, 3m): ^{1}H NMR (400 MHz, DMSO-*d6*), δ_H (ppm) = 8.26 (1 H, s, 1 H of NH), 8.03 (1 H, d, 2 H of CH aromatic, $^{3}J_{HH}$ = 8.4), 7.96 (1 H, d, 2 H of CH aromatic, $^{3}J_{HH}$ = 8.4), 7.7 (1 H, s, 1 H of NH); ^{13}C NMR (100 MHz, DMSO-*d6*): δ_C (ppm)= 166.91, 138.70, 133.70, 132.87, 129.84, 128.68.



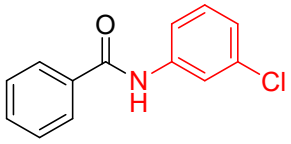
2-Thiophenecarboxamide (Table 2, 3n): Yield = 88%. 1H NMR (400 MHz, DMSO-d6), δH (ppm) = 8.00 (1 H, s, 1 H of NH), 7.75-7.74 (2 H, m, 2 H of CH aromatic), 7.40 (1 H, s, 1H of NH), 7.14 (1 H, t, 1 H of CH aromatic, 3J HH = 4.2 Hz);13C NMR (100 MHz, DMSO-d6): δC (ppm) = 163.3, 140.68, 131.47, 129.19, 128.39.



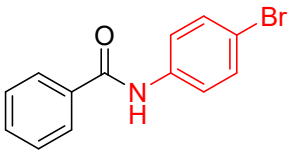
N-Phenylbenzamide (Table 4, 6a): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.98 (s, 1 H), 7.06-7.80 (m, 10 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 165.71, 137.96, 135.09, 131.80, 129.09, 128.78, 127.00, 124.57, 120.21.



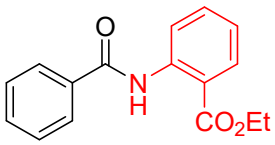
***N*-Benzylbenzamide (Table 4, 6b):** ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.11 (s, 1 H), 7.28-7.82 (m, 10 H), 4.64(d, j= 5.63 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 167.485, 138.28, 134.39, 131.533, 128.758, 128.572, 127.883, 127.565, 127.039, 44.097.



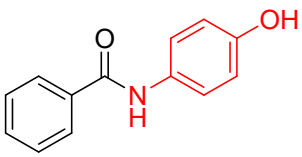
***N*-(3-Chlorophenyl)benzamide (Table 4, 6c):** ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.138 (s, 1 H), 7.13-7.75 (m, 9 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 166.11, 139.11, 134.66, 134.48, 132.07, 130.01, 128.78, 127.11, 124.61, 120.51, 118.40.



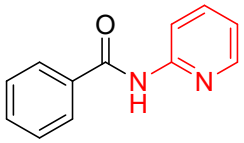
N-(4-Bromophenyl)benzamide (Table 4, 6d): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.97 (s, 1 H), 7.189-7.797 (m, 9 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.14, 137.01, 134.86, 132.08, 128.88, 126.99, 121.69, 114.51.



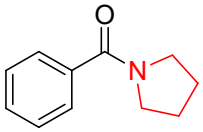
Ethyl 2-(benzamido) benzoate (Table 4, 6e): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 12.10 (s,1 H), 7.14-8.97 (m, 9 H), 4.45 (q, j= 1.8 Hz, 2 H), 1.45 (t, j= 1.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.62, 165.70, 141.93, 135.02, 134.64, 131.84, 130.90, 128.76, 127.39, 122.51, 120.50, 115.54, 61.47, 14.18.



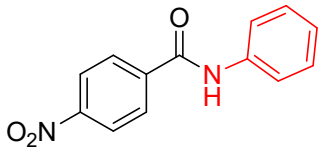
***N*-(4-Hydroxyphenyl) benzamide (Table 4, 6f):** ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.06 (s, 1 H), 7.18-8.04 (m, 9 H), 5.08 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 171.59, 158.62, 133.77, 130.21, 129.26, 129.04, 128.86, 128.59, 128.493.



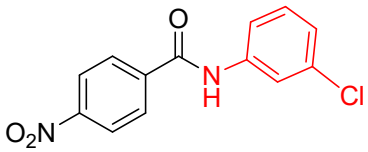
***N*-(Pyridin-2-yl) benzamide (Table 4, 6g):** ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 9.23 (br, 1 H), 7.09-8.47 (m, 9 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 173.04, 151.75, 149.30, 147.36, 138.79, 132.47, 129.31, 127.44, 119.87, 114.60. FT-IR δ: 1458, 1528, 1579, 1598, 3173.



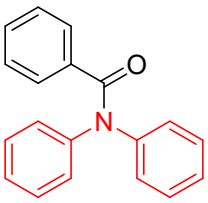
Phenyl(pyrrolidin-1-yl)methanone (Table 4, 6h): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.301-7.44 (m, 5 H), 3.57 (t, j= 6.6 Hz, 2 H), 3.33 (t, j= 6.2 Hz, 2 H), 1.87 (t, j= 6.5 Hz, 2 H), 1.79 (t, j= 6.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.71, 136.30, 128.72, 127.21, 126.07, 45.13, 25.37.



4-Nitro-*N*-phenylbenzamide (Table 4, 6i): ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.109-8.30 (m, 10 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 163.66, 154.68, 140.04, 138.31, 130.24, 128.27, 125.42, 124.12, 120.54.



***N*-(3-Chlorophenyl)-4-nitrobenzamide (Table 4, 6j):** ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.19-8.30 (m, 9 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 161.08, 142.96, 136.803, 129.309, 128.259, 125.369, 124.100, 120.362, 116.894, 116.804, 116.520.



***N,N*-Diphenylbenzamide (Table 4, 6k):** ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.172-7.494 (m, 15 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 170.572, 143.985, 136.227, 130.090, 129.148, 129.059, 127.820, 127.497, 126.291.