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SUPPORTING INFORMATION FOR

Fluorinated Solvent-Assisted Photocatalytic Aerobic Oxidative Amidation of Alcohols via Visible-Light-Mediated MOF-POM Catalysis

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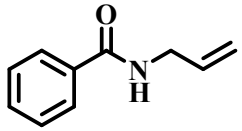
1. General procedure

Oxidative amidation of benzyl alcohol was performed according to the following procedure: benzyl alcohol (1mmol), 0.5 mL and 2 mL of HFB (hexaflourobenzene) and acetonitrile, and catalyst (15 mg) were mixed together and stirred for 2 h at room temperature under air balloon and visible light illumination. During the reaction, the temprature was kept constant via a cooling fan under visible light illumination of a 500-W Hg lamp with high pressure. After such a period, amine (1.2 mmol) was also added, and the reaction advancement was checked to utilize TLC after 5h. After assuring the reaction completion, the dilution of the mixture was accomplished with ethyl acetate, and the solid catalyst was also centrifuged and rinsed four times with ethanol. The final mixture was extracted by adding water, and the organic layer was separated by column chromatography.

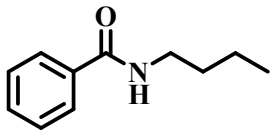
2. Analytical Data

N-allylbenzamide (1a)



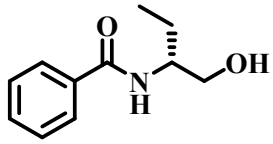
Compound **1a** was prepared according to the general procedure and purified by column chromatography (*n*-Hexane: EtOAc= 4:1) to give 51 % yield. Colorless oil.
Colorless oil.
^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.80–7.78 (m, 2H), 7.44 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.6 Hz, 2H), 6.92 (br, 1H), 5.92–5.85 (m, 1H), 5.23 (dd, J1 = 17.2 Hz, J2 = 0.8 Hz, 1H), 5.14 (d, J = 10.3 Hz, 1H), 4.00 (t, J = 5.6 Hz, 2H);
^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.3, 132.5, 133.3, 131.3, 127.2, 126.2, 115.1, 41.5.
Analytical data was similar to those previously reported.[1]

N-butylbenzamide (1b)



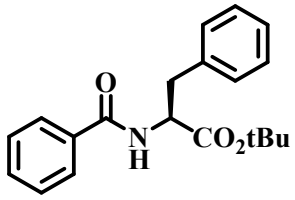
Compound **1b** was prepared according to the general procedure and purified by column chromatography (*n*-Hexane: EtOAc= 4:1) to give 68 % yield. Yellow oil.
^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 7.98-8.01 (m, 2H), 7.42-7.18 (m, 3H), 6.31 (br s, 1H), 3.39-3.41 (q, 2H, J = 6.8 Hz), 1.55-1.47 (m, 2H), 1.35-1.27 (m, 2H), 0.92-0.85 (t, 3H, J = 7.0 Hz).
Analytical data was similar to those previously reported.[2]

(*R*)-*N*-(1-hydroxybutan-2-yl)benzamide (1c)



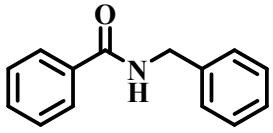
Compound **1c** was prepared according to the general procedure and purified by column chromatography (*n*-Hexane: EtOAc= 4:1) to give 72 % yield. M.p. 72-74 °C (lit. 76 °C)
^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 7.73-7.66 (m, 2H), 7.41-7.29 (m, 3H), 6.33 (s, 1H), 4.01 (br s, 1H), 3.72-3.59 (dd, 2H, *J* = 10.8, 2.6 Hz), 2.97-3.00 (br s, 1H), 1.52-1.67 (m, 2H), 0.95-0.93 (t, 3H, *J*=7.0Hz).
^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 168.3, 134.4, 131.6, 128.6, 127.0, 65.2, 53.7, 24.3, 10.7.
Analytical data was similar to those previously reported.[3]

***tert*-butyl benzoyl-*L*-phenylalaninate (1d)**



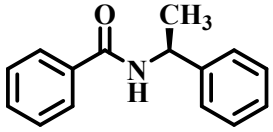
Compound **1d** was prepared according to the general procedure and purified by column chromatography (*n*-Hexane: EtOAc= 4:1) to give 82 % yield. M.p. 75–79 °C (lit. 60 °C).
^{1}H NMR (CDCl$_3$, 200 MHz): δ (ppm) = 7.70-7.54 (m, 2H), 7.43-7.22 (m, 3H), 7.22-7.05 (m, 5H), 6.64 (d, 1H, *J* = 7.3 Hz), 4.90 (dt, 1H, *J* = 7.4, 5.8 Hz), 3.12 (d, 2H, *J* = 5.7 Hz), 1.32 (s, 9H).
^{13}C NMR (CDCl$_3$, 75 MHz): δ (ppm) = 172.9, 165.6, 133.1, 132.7, 130.9, 128.8, 127.6, 127.1, 126.0, 81.4, 53.2, 36.7, 27.5.
Analytical data was similar to those previously reported.[4]

***N*-benzylbenzamide (1e)**



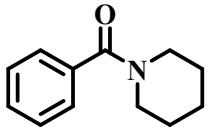
Compound **1e** was prepared according to the general procedure and purified by column chromatography (*n*-Hexane: EtOAc= 4:1) to give 91 % yield. M.p. 103–106 °C (lit. 104 °C).
^{1}H NMR (CDCl3, 200 MHz): δ (ppm) = 7.80-7.63 (m, 2H), 7.50-7.23 (m, 8H), 6.36 (br s, 1H), 4.65-4.62 (d, 2H, *J* = 5.5 Hz).
Analytical data was similar to those previously reported.[5]

(*S*)-*N*-(1-phenylethyl)benzamide (1f)



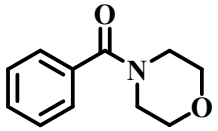
Compound **1f** was prepared according to the general procedure and purified by column chromatography (*n*-Hexane: EtOAc= 4:1) to give 93 % yield. M.p. 120–123 °C (lit. 123 °C).
^{1}H NMR (CDCl$_3$, 200 MHz): δ (ppm) 7.82-7.80 (m, 2H), 7.58-7.33 (m, 8H), 6.31 (d, *J* = 7.0 Hz, 1H), 5.30 (q, *J* = 7.2 Hz, 1H), 1.61 (d, *J* = 7.1 Hz, 3H).
^{13}C NMR (CDCl$_3$, 75 MHz): δ (ppm) = 163.5, 141.1, 132.5, 129.7, 126.6, 126.1, 125.5, 125.1, 124.7, 50.2, 20.9.
Analytical data was similar to those previously reported.[6]

phenyl(piperidin-1-yl)methanone (1g)



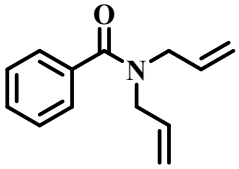
Compound **1g** was prepared according to the general procedure and purified by column chromatography (*n*-Hexane: EtOAc= 4:1) to give 75 % yield. Colorless oil.
^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 7.41 (s, 5H), 3.74 (s, 2H), 3.50 (s, 2H), 1.42-1.65 (m, 6H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 171.5, 137.4, 130.3, 128.9, 126.2, 47.1, 42.3, 25.5, 24.6, 23.9.
Analytical data was similar to those previously reported. [7]

morpholino(phenyl)methanone (1h)



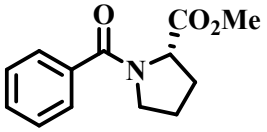
Compound **1h** was prepared according to the general procedure and purified by column chromatography (*n*-Hexane: EtOAc= 4:1) to give 67 % yield. Colorless oil.
^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 7.42 (s, 5H), 3.68 (br s, 2H), 3.48 (br s, 2H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 171.7, 134.9, 131.7, 129.0, 128.1, 65.0.
Analytical data was similar to those previously reported.[7]

***N,N*-diallylbenzamide (1i)**



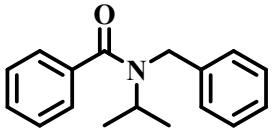
Compound **1i** was prepared according to the general procedure and purified by column chromatography (*n*-Hexane: EtOAc= 4:1) to give 53 % yield. Yellow oil.
^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 7.42-7.39 (s, 5H), 5.91 (br s, 1H), 5.76 (br s, 1H), 5.24-5.20 (s, 4H), 4.17 (s, 2H), 3.86 (s, 2H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 172.9, 137.2, 134.1, 133.1, 130.0, 129.1, 127.8, 118.0, 50.9, 47.7.
Analytical data was similar to those previously reported.[3]

methyl benzoyl-*L*-prolinate (1j)



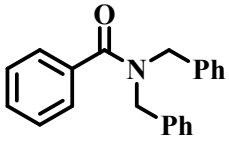
Compound **1j** was prepared according to the general procedure and purified by column chromatography (*n*-Hexane: EtOAc= 4:1) to give 70 % yield. M.p. 87-90 °C (Lit. 91 °C).
^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 7.59-7.56 (m, 2H), 7.46-7.36 (m, 3H), 4.70-4.55 (dd, 1H (79%), *J* = 7.5, 4.4 Hz), 4.35 (d, 1H (21%), *J* = 8.5 Hz), 3.82-3.70 (s, 3H (78%)), 3.56-3.55 (s, 3H (20%)), 3.70-3.42 (m, 2H), 2.33-2.28 (m,1H), 2.07-1.87 (m, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 173.9, 170.9, 134.2, 131.2, 129.1, 128.5, 60.1, 51.7, 51.0, 30.2, 27.6.
Analytical data was similar to those previously reported.[8]

***N*-benzyl-*N*-isopropylbenzamide (1k)**



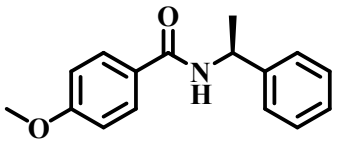
Compound **1k** was prepared according to the general procedure and purified by column chromatography (*n*-Hexane: EtOAc= 4:1) to give a 59 % yield. Yellow oil.
^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 7.46 (m, 5H), 7.38-7.26 (m, 5H), 4.81 (br s, 2H), 4.18 (br s, 1H), 1.22 (s, 6H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 168.9, 142.2, 136.5, 131.8, 127.6, 126.4, 126.0, 125.5, 125.0, 47.1, 20.7.
Analytical data was similar to those previously reported.[3]

***N,N*-dibenzylbenzamide (1l)**



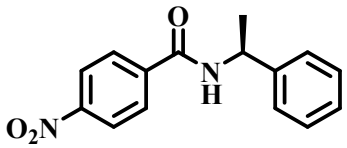
Compound **1l** was prepared according to the general procedure and purified by column chromatography (*n*-Hexane: EtOAc= 4:1) to give 60 % yield. M.p. 93-97 °C (Lit. 96-97 °C)
^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 7.55-7.29 (m, 7H), 7.18 (s, 1H), 4.72 (s, 2H), 4.44 (s, 2H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) = 173.5, 137.8, 137.1, 135.8, 130.1, 127.1, 126.7, 125.9, 125.2, 124.8, 54.3, 45.4.
Analytical data was similar to those previously reported.[9]

(*S*)-4-methoxy-*N*-(1-phenylethyl)benzamide (1m)



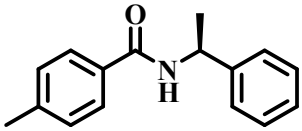
Compound **1m** was prepared according to the general procedure and purified by column chromatography (*n*-Hexane: EtOAc= 4:1) to give 66 % yield. M.p. 130-134 °C.
^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 7.81-7.77 (d, 2H, *J* = 8.3 Hz), 7.46-7.24 (m, 9H), 6.28 (d, 1H, *J* = 6.8 Hz), 5.40-5.33 (m, 1H), 2.42 (s, 3H), 1.66-1.62 (d, 3H, *J* = 7.1 Hz).
Analytical data was similar to those previously reported. [10]

(*S*)-4-nitro-*N*-(1-phenylethyl)benzamide (1n)



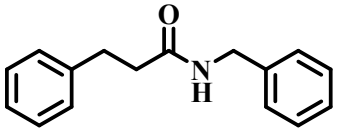
Compound **1n** was prepared according to the general procedure and purified by column chromatography (*n*-Hexane: EtOAc= 4:1) to give 83 % yield. M.p. 134-136 °C (Lit. 136-138 °C).
^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 8.33-8.15 (m, 2H), 8.00-7.85 (m, 2H), 7.45-7.29 (m, 5H), 6.72 (d, 1H, J = 7.3 Hz), 5.33 (p, 1H, J = 7.0 Hz), 1.59 (d, 3H, J = 6.9 Hz).
Analytical data was similar to those previously reported.[11]

(*S*)-4-methyl-*N*-(1-phenylethyl)benzamide (1o)



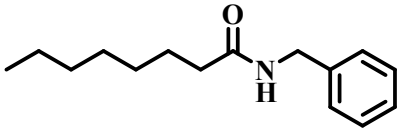
Compound 1o was prepared according to the general procedure and purified by column chromatography (*n*-Hexane: EtOAc= 4:1) to give 65 % yield. M.p. 131-134 °C.
^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) = 7.76-7.73 (d, 2H, J = 9 Hz), 7.36-7.23 (m, 6H), 6.95-6.90 (m, 2H), 6.27 (d, 1H, J = 7.3 Hz), 5.34-5.28 (p, 1H, J = 6.9 Hz), 3.82 (s, 3H), 1.64-1.64 (d, 3H, J = 6.8 Hz).
Analytical data was similar to those previously reported.[10]

***N*-benzyl-3-phenylpropanamide (1p)**



Compound **1p** was prepared according to the general procedure and purified by column chromatography (*n*-Hexane: EtOAc= 4:1) to give 41 % yield. M.p. 77–81 °C (lit. 80 °C).
^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.40–7.15 (m, 10 H), 5.57 (br s, 1 H), 4.40 (d, J = 5.7 Hz, 2 H), 3.05 (t, J = 7.6 Hz, 2 H), 2.52 (t, J = 7.6 Hz, 2 H) ppm;
Analytical data was similar to those previously reported.[12]

***N*-benzyloctanamide (1q)**



Compound **1q** was prepared according to the general procedure and purified by column chromatography (*n*-Hexane: EtOAc= 4:1) to give 32 % yield. Yellow oil.
^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.33–7.24 (m, 6 H), 5.76 (br s, 1 H), 4.40 (d, J = 5.5 Hz, 2 H), 3.21 (td, J = 7.2, 5.9 Hz, 2H, 3), 1.95 (s, 3H, 1), 1.50 – 1.44 (m, 2H, 4), 1.32 – 1.25 (m, 6H, 5-7), 0.86 (t, J = 6.7 Hz, 3H, 8)
Analytical data was similar to those previously reported.[13]

3. References

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