

Supplementary Information

Direct Oxidative Esterification of Alcohols and Hydration of Nitriles Catalyzed By A Reusable Silver Nanoparticle Grafted Mesoporous Polymelamine Formaldehyde (AgNPs@mPMF)

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1. NMR datas of the substrates for the oxidative esterification reaction

Methyl benzoate (Table 3, entry 1)¹:

¹H NMR (400 MHz, CDCl₃, 25 °C) δ = 3.92 (3H, s), 7.42 (2H, t, J = 7.6 Hz), 7.56 (1H, t, J = 8.0 Hz), 8.05 (2H, d, J = 7.6 Hz); ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 167.2, 132.8, 130.1, 129.7, 128.4, 52.1.

Methyl 4-chlorobenzoate (Table 3, entry 2)²:

¹H NMR (400 MHz, CDCl₃, 25 °C) δ = 3.87 (3H, s), 7.36 (2H, d, J = 8.4 Hz), 7.92 (2H, d, J = 8.0 Hz); ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 166.2, 139.3, 130.8, 128.6, 128.5, 52.3.

Methyl 3-chlorobenzoate (Table 3, entry 3)³:

¹H NMR (400 MHz, CDCl₃, 25 °C) δ = 3.92 (3H, s), 7.38 (1H, t, J = 8.0 Hz), 7.53 (1H, d, J = 8.0 Hz), 7.92 (1H, d, J = 7.6 Hz), 8.03 (1H, s); ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 165.8, 134.7, 133.0, 131.9, 129.7, 127.9, 122.0, 52.6.

Methyl 2-chlorobenzoate (Table 3, entry 4)⁴:

¹H NMR (400 MHz, CDCl₃, 25 °C) δ = 3.92 (3H, s), 7.30-7.32 (1H, m), 7.38-7.45 (2H, m), 7.80-7.82 (1H, m); ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 166.2, 133.8, 132.7, 131.5, 131.2, 130.2, 126.7, 52.5.

Methyl 4-bromobenzoate (Table 3, entry 5)³:

¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ = 3.84 (3H, s), 7.72 (2H, d, J = 8.8 Hz), 7.86 (2H, d, J = 8.4 Hz); ¹³C NMR (100 MHz, DMSO-d₆, 25 °C): δ = 166.7, 133.0, 132.2, 129.8, 128.4, 51.5.

Methyl 4-fluorobenzoate (Table 3, entry 6)⁵:

¹H NMR (300 MHz, CDCl₃, 25 °C) δ = 3.90 (s, 3H), 7.11 (2H, dd, J₁ = J₂ = 8.7), 8.06 (2H, dd, J₁ = 5.7, J₂ = 8.7); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ = 166.4, 166.0 (d), 132.3 (d), 126.6, 115.7 (d), 52.4.

Methyl 4-(trifluoromethyl) benzoate (Table 3 entry 7)¹:

¹H NMR (300 MHz, CDCl₃, 25 °C) δ = 3.95 (3H, s), 7.68 (2H, d, J = 8.1 Hz), 8.15 (2H, d, J = 8.1 Hz); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ = 166.2, 134.8, 133.6, 130.2, 125.6, 125.6, 52.8.

Methyl 3-(trifluoromethyl) benzoate (Table 3 entry 8)¹:

¹H NMR (300 MHz, CDCl₃, 25 °C) δ = 3.96 (3H, s), 7.58 (1H, dd, J₁ = J₂ = 7.8 Hz), 7.80 (1H, d, J = 7.8 Hz), 8.23 (1H, d, J = 7.8 Hz), 8.30 (1H, s); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ = 166.0, 133.6, 133.0, 131.3, 129.8, 129.3, 126.8, 52.8.

Methyl 4-nitrobenzoate (Table 3 entry 9)⁶:

¹H NMR (400 MHz, CDCl₃, 25 °C) δ = 2.38 (3H, s), 3.88 (3H, s), 7.29-7.36 (2H, m), 7.83-7.86 (2H, m); ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 167.2, 143.6, 129.5, 129.0, 127.5, 51.8, 21.8.

Methyl 3-nitrobenzoate (Table 3 entry 10)⁷:

¹H NMR (300 MHz, CDCl₃, 25 °C) δ = 3.98 (3H, s), 7.61-7.69 (1H, m), 8.35-8.45 (2H, m), 8.82-8.88 (1H, m); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ = 52.7, 124.5, 127.3, 129.5, 131.8, 135.1, 148.2, 164.8.

Dimethyl terephthalate (Table 3 entry 11)¹:

¹H NMR (300 MHz, CDCl₃, 25 °C) δ = 3.95 (6H, s), 8.08 (4H, s); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ = 166.7, 134.3, 129.8, 52.8.

Methyl biphenyl-4-carboxylate (Table 3 entry 12)⁸:

¹H NMR (300 MHz, CDCl₃, 25 °C) δ = 3.83 (3H, s), 7.25-7.38 (3H, m), 7.53 (2H, d, *J* = 9.9 Hz), 7.58 (2H, d, *J* = 8.7 Hz), 8.00 (2H, d, *J* = 8.1 Hz); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ = 167.6, 146.2, 140.6, 131.3, 130.7, 129.4, 128.6, 127.8, 127.6, 52.7.

Methyl 4-methylbenzoate (Table 3 entry 13)¹:

¹H NMR (400 MHz, CDCl₃, 25 °C) δ = 2.39 (3H, s), 3.88 (3H, s), 7.29-7.36 (2H, m), 7.83-7.86 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ ppm: 167.1, 143.5, 129.6, 129.0, 127.4, 51.8, 21.6.

Methyl 3-methylbenzoate (Table 3 entry 14)¹:

¹H NMR (400 MHz, CDCl₃, 25 °C) δ = 2.39 (3H, s), 3.88 (3H, s), 7.29-7.36 (2H, m), 7.83-7.86 (2H, m); ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 167.3, 138.2, 133.7, 130.2, 128.3, 126.8, 52.0, 21.3.

Methyl 2-methylbenzoate (Table 3 entry 15)⁹:

¹H NMR (400 MHz, CDCl₃, 25 °C) δ = 2.60 (3H, s), 3.89 (3H, s), 7.22-7.25 (2H, m), 7.36-7.40 (1H, m), 7.89-7.91 (1H, m); ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 168.2, 140.3, 132.0, 131.8, 130.7, 129.7, 125.8, 51.9, 21.8.

Methyl 3,4-dimethylbenzoate (Table 3 entry 16)¹⁰:

¹H NMR (400 MHz, CDCl₃, 25 °C) δ = 2.28 (6H, s), 3.88 (3H, s), 7.17 (1H, d, *J* = 8.0 Hz), 7.75 (1H, d, *J* = 8.8 Hz), 7.80 (3H, s); ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 167.8, 142.8, 137.3, 131.3, 130.3, 128.2, 127.8, 52.3, 20.6, 20.3.

Methyl 4-methoxybenzoate (Table 3 entry 17)¹:

¹H NMR (400 MHz, CDCl₃, 25 °C) δ = 3.86 (3H, s), 3.89 (3H, s), 6.92 (2H, d, *J* = 8.8 Hz), 7.98 (2H, d, *J* = 8.8 Hz); ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 166.8, 163.5, 131.7, 122.7, 113.7, 55.5, 51.8.

Methyl 3-methoxybenzoate (Table 3 entry 18)¹:

¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ = 3.78 (3H, s), 3.82 (3H, s), 7.17-7.20 (1H, m), 7.37-7.41 (2H, m), 7.52 (d, J = 7.6 Hz, 1H); ¹³C NMR (100 MHz, DMSO-d₆, 25 °C): δ = 166.2, 159.4, 131.1, 129.8, 121.5, 119.4, 113.9, 55.4, 52.3.

Methyl 3,4-dimethoxybenzoate (Table 3 entry 19)¹¹:

¹H NMR (400 MHz, CDCl₃, 25 °C) δ = 3.89 (3H, s), 3.93 (6H, s), 6.89 (1H, d, J = 8.4 Hz), 7.54 (1H, d, J = 1.6), 7.68 (1H, dd, J₁ = J₂ = 1.6 Hz); ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 167.5, 153.6, 149.3, 124.2, 123.3, 112.6, 110.9, 56.7, 52.7.

Methyl 3,4,5-trimethoxybenzoate (Table 3 entry 20)⁶:

¹H NMR (400 MHz, CDCl₃, 25 °C) δ = 3.88 (12H, s), 7.28 (2H, s); ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 166.9, 153.1, 142.3, 125.3, 106.9, 103.2, 61.1, 56.4, 52.4.

Methyl 1-naphthoate (Table 3 entry 21)³:

¹H NMR (400 MHz, CDCl₃, 25 °C) δ = 4.02 (1H, s), 7.48-7.56 (m, 1H), 7.60-7.64 (1H, m), 7.88 (1H, d, J = 8.4 Hz), 8.03 (1H, d, J = 8.4 Hz), 8.20 (1H, d, J = 7.2 Hz), 8.93 (1H, d, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃, 25 °C) δ = 168.2, 133.8, 133.5, 131.5, 130.4, 128.7, 127.9, 127.3, 126.4, 125.8, 124.7, 52.3.

Methyl furan-2-carboxylate (Table 3 entry 22)¹:

¹H NMR (300 MHz, CDCl₃, 25 °C) δ = 3.8 (3H, s), 6.48 (1H, dd, J₁ = 1.8 Hz, J₂ = 3.3 Hz), 7.16 (1H, d, J = 3.3 Hz), 7.55 (1H, d, J = 0.6 Hz); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ = 159.5, 146.6, 144.9, 118.3, 112.2, 52.2.

Methyl thiophene-2-carboxylate (Table 3 entry 23)¹:

¹H NMR (300 MHz, CDCl₃, 25 °C) δ = 3.88 (3H, s), 7.09 (1H, dd, J₁ = 3.9 Hz, J₂ = 4.5 Hz), 7.54 (1H, d, J = 4.5 Hz), 7.80 (1H, d, J = 3.0 Hz); ¹³C NMR (75 MHz, CDCl₃, 25 °C) δ = 163.2, 134.2, 134.0, 132.8, 128.2, 52.5.

2. NMR datas of the substrates for the hydration of nitriles**Benzamide (Table 4, entry 1)¹²:**

¹H NMR (400MHz, DMSO-d₆, 25 °C): δ = 7.84 (2H, m), 7.48 (3H, m), 5.86 (2H, br. s). ¹³C NMR (100MHz, DMSO-d₆, 25 °C): δ = 168.8, 134.2, 131.2, 128.2, 127.5.

4-Chlorobenzamide (Table 4, entry 2)¹³:

¹H NMR (300MHz, DMSO-d₆, 25 °C) δ = 8.09 (1H, s), 7.91-7.95 (2H, m), 7.55-7.59 (2H, m); ¹³C NMR (75MHz, DMSO-d₆, 25 °C): δ = 167.7, 137.2, 134.0, 130.5, 129.3.

3-Chlorobenzamide (Table 4, entry 3)¹³:

¹H NMR (300MHz, DMSO-d₆, 25 °C) δ = 8.12 (1H, s), 7.94-7.96 (1H, m), 7.85-7.89 (1H, m), 7.60-7.64 (1H, m), 7.58 (1H, s), 7.50-7.55 (1H, m). ¹³C NMR (75MHz, DMSO-d₆, 25 °C): δ = 167.4, 137.2, 134.0, 132.0, 131.2, 128.2, 127.0.

2-Chlorobenzamide (Table 4, entry 4)¹³:

¹H NMR (300MHz, DMSO-d₆, 25 °C) δ = 8.14-6.84 (6H, m). ¹³C NMR (75MHz, DMSO-d₆, 25 °C): δ = 169.4, 138.0, 130.8, 130.5, 129.7, 127.9.

4-Bromobenzamide (Table 4, entry 5)¹²:

¹H NMR ((400 MHz, DMSO-d₆, 25 °C) δ = 7.66 (2H, m), 7.57 (2H, m), 5.88 (2H, br. s). ¹³C NMR (100MHz, DMSO-d₆, 25 °C): δ = 165.2, 135.4, 132.0, 131.1, 126.6.

4-Fluorobenzamide (Table 4, entry 6)¹³:

¹H NMR (300MHz, DMSO-d₆, 25 °C) δ = 8.04 (1H, s), 7.96-8.00 (2H, m), 7.43 (1H, s), 7.29-7.35 (2H, m); ¹³C NMR (75 MHz, DMSO-d₆, 25 °C): δ = 167.7, 164.8, 131.7, 130.9, 115.8.

3-Fluorobenzamide (Table 4, entry 7)¹³:

¹H NMR (300MHz, DMSO-d₆, 25 °C) δ = 8.10 (1H, s), 7.74-7.77 (1H, m), 7.67-7.71 (1H, m), 7.51-7.57 (2H, m), 7.38-7.42 (1H, m). ¹³C NMR (75 MHz, DMSO-d₆, 25 °C): δ = 166.5, 162.0, 136.8, 130.4, 123.8, 118.1.

4-Nitrobenzamide (Table 4, entry 8)¹²:

¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ = 8.37-8.21 (3H, m), 8.11 (2H, d), 7.73 (1H, br. s). ¹³C NMR (100 MHz, DMSO-d₆, 25 °C): δ = 166.3, 149.1, 140.0, 128.9, 123.9.

2-Nitrobenzamide (Table 4, entry 9)¹⁴:

¹H NMR (300MHz, CDCl₃, 25 °C): δ = 8.10–8.00 (1H, m), 7.73–7.55 (3H, m), 5.84 (2H, s, br); ¹³C NMR (75MHz, CDCl₃, 25 °C): δ = 133.6, 131.0, 130.9, 129.0, 128.8, 124.7.

4-(Trifluoromethyl)benzamide (Table 4, entry 10)¹³:

¹H NMR (300MHz, DMSO-d₆, 25 °C): δ = 8.26 (1H, s), 8.10-8.13 (2H, m), 7.85-7.89 (2H, m), 7.69 (1H, s); ¹³C NMR (75MHz, DMSO-d₆, 25 °C): δ = 167.6, 139.1, 132.2, 129.4, 126.4, 124.7.

4-Methoxybenzamide (Table 4, entry 11)¹²:

¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ = 7.73 (2H, d), 7.23 (2H, d), 5.93 (2H, br. s), 3.73 (3H, s); ¹³C NMR (100 MHz, DMSO-d₆, 25 °C): δ = 166.0, 145.0, 133.9, 129.6, 129.5, 54.2.

3, 4-Dimethoxybenzamide (Table 4, entry 12)¹³:

¹H NMR (300 MHz, DMSO-d₆, 25 °C): δ = 7.91 (1H, s), 7.47-7.56 (2H, m), 7.23 (1H, s), 6.99-7.05 (2H, m), 3.84 (3H, s) 3.82 (3H, s). ¹³C NMR (75 MHz, DMSO-d₆, 25 °C): δ = 164.9, 152.3, 149.1, 127.7, 121.6, 111.7, 56.4, 56.2.

4-Thiomethylbenzamide (Table 4, entry 13)¹³:

¹H NMR (300 MHz, DMSO-d₆, 25 °C): δ = 8.26 (1H, s), 8.11-8.17 (2H, m), 8.01-8.09 (2H, m), 7.70 (1H, s) 3.32 (3H, s). ¹³C NMR (75 MHz, DMSO-d₆, 25 °C): δ = 169.5, 143.9, 139.8, 129.7, 127.5, 44.2.

4-Methylbenzamide (Table 4, entry 14)¹²:

¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ = 7.74 (2H, d), 7.23 (2H, d), 5.94 (2H, br. s), 2.38 (3H, s); ¹³C NMR (100 MHz, DMSO-d₆, 25 °C): δ = 166.1, 145.1, 134.0, 129.6, 129.5, 21.3.

2-Methylbenzamide (Table 4, entry 15)¹³:

¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ = 8.33-8.45 (2H, m), 7.64-7.65 (2H, m), 7.33-7.53 (2H, m), 2.67 (3H, s); ¹³C NMR (100 MHz, DMSO-d₆, 25 °C): δ = 169.7, 135.8, 133.6, 132.2, 131.7, 131.5, 126.6, 22.2.

3-Methylbenzamide (Table 4, entry 16)¹³:

¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ = 8.01-8.05 (1H, m), 7.95 (1H, s), 7.67-7.73 (2H, m), 7.32-7.39 (2H, m), 2.36 (3H, s). ¹³C NMR (100 MHz, DMSO-d₆): δ = 169.7, 135.7, 133.6, 132.3, 131.7, 131.5, 126.6, 22.2.

Pyridine-3-carboxamide (Table 4, entry 17)¹³:

¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ = 8.72-8.77 (2H, m), 8.24-8.30 (2H, m), 7.69 (1H, s), 7.48-7.53 (1H, m); ¹³C NMR (100 MHz, DMSO-d₆, 25 °C): δ = 167.5, 152.9, 149.7, 136.2, 130.7, 124.5.

Pyridine-4-carboxamide (Table 4, entry 18)¹³:

¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ = 8.43 (2H, d), 7.93 (2H, d), 5.95 (2H, br. s); ¹³C NMR (100 MHz, DMSO-d₆, 25 °C): δ = 171.2, 151.0, 122.1.

Pyridine-2-carboxamide (Table 4, entry 19)¹³:

¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ = 8.79 (1H, d), 8.01 (1H, t), 7.89 (1H, t), 7.67 (1H, d), 5.96 (2H, br. s); ¹³C NMR (100 MHz, DMSO-d₆, 25 °C): δ = 166.0, 150.3, 148.4, 137.6, 126.4, 121.9.

2-Furamide (Table 4, entry 20)¹⁴:

¹H NMR (300MHz, CDCl₃, 25 °C): δ = 7.49–7.44 (1H, m), 7.14 (1H, d), 6.50 (1H, dd), 6.37 (2H, s, br); ¹³C NMR (75MHz, CDCl₃, 25 °C): δ = 160.5, 147.7, 144.4, 115.0, 112.2.

Thiophene-2-carboxamide (Table 4, entry 21)¹²:

¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ = 7.12 (1H, t), 7.35 (1H, br. s), 7.73 (2H, m), 7.93 (1H, br. s, NH); ¹³C-NMR (100 MHz, DMSO-d₆, 25 °C): δ = 163.2, 143.4, 137.8, 136.7, 128.6.

3-Methyl thiophene-2-carboxamide (Table 2, entry 22)¹²:

¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ = 7.36 (1H, d), 7.03 (1H, d), 5.95 (2H, br. s), 2.37 (3H, s). ¹³C NMR (100 MHz, DMSO-d₆, 25 °C): δ = 164.6, 144.3, 138.8, 137.7, 129.9, 13.6.

Indole-3-carboxamide (Table 4, entry 23)¹¹:

¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ = 9.94 (1H, s), 8.19 (1H, d), 8.08 (1H, m), 7.51 (1H, d), 7.25 (2H, m), 5.99 (2H, br. s, NH₂). ¹³C NMR (100 MHz, DMSO-d₆, 25 °C): δ = 167.3, 138.4, 137.3, 124.1, 123.4, 122.1, 120.8, 118.2, 112.1.

2-Naphthamide (Table 4, entry 24)¹³:

¹H NMR (300 MHz, DMSO-d₆, 25 °C): δ = 8.65 (1H, s), 8.13-8.17 (1H, m), 7.77-8.02 (4H, m), 7.60-7.77 (3H, m). ¹³C NMR (100 MHz, DMSO-d₆, 25 °C): δ = 169.3, 135.0, 132.6, 130.5, 129.0, 128.6, 128.1, 127.9, 127.8, 126.9, 123.7.

Acetamide (Table 4, entry 25)¹³:

¹H NMR (300 MHz, DMSO-d₆, 25 °C): δ = 7.32 (1H, s), 6.72 (1H, s), 1.79 (3H, s); ¹³C NMR (100 MHz, DMSO-d₆, 25 °C): δ = 160.7, 23.5.

Propionamide (Table 4, entry 26)¹⁵:

¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 2.18-2.26 (2H, q), 1.12-1.17 (3H, t); ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 180.55, 30.08, 10.83.

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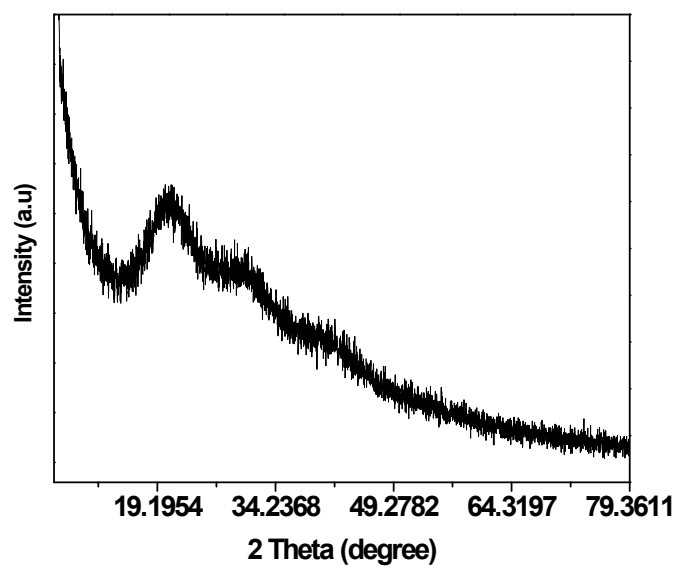


Figure S1. Powder XRD pattern of mPMF material.

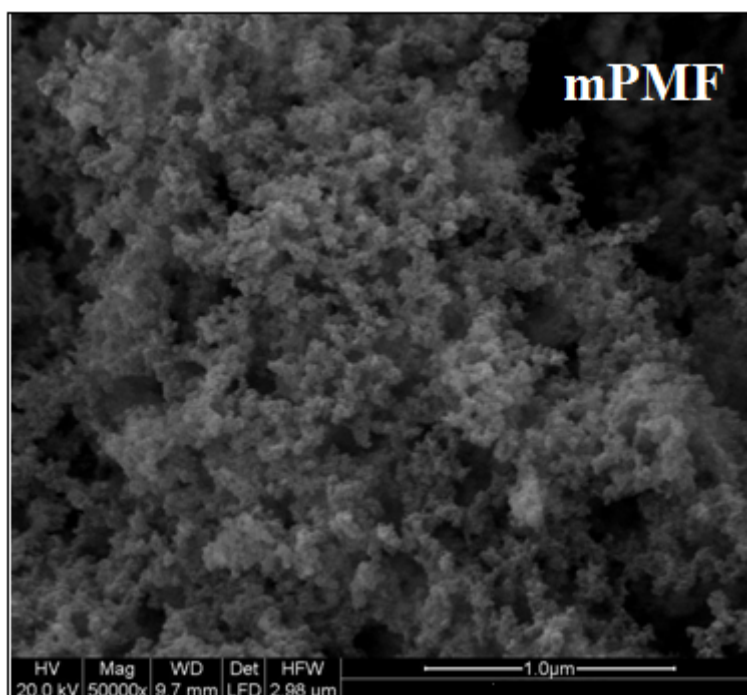


Figure S2. FE-SEM image of mPMF material

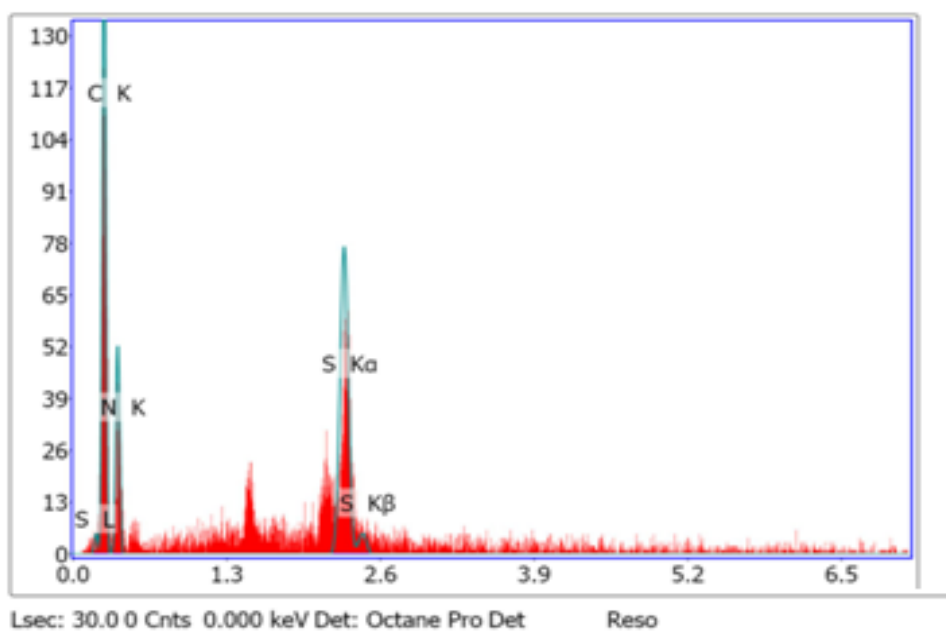


Figure S3. EDX image of mPMF material

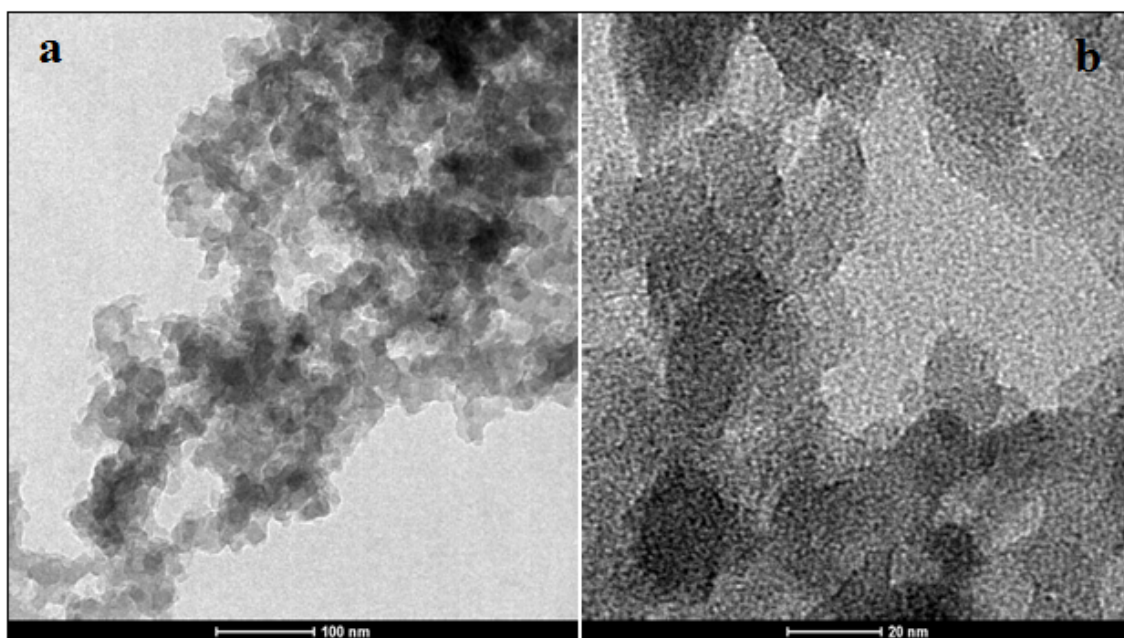


Figure S4. HR-TEM images of mPMF material

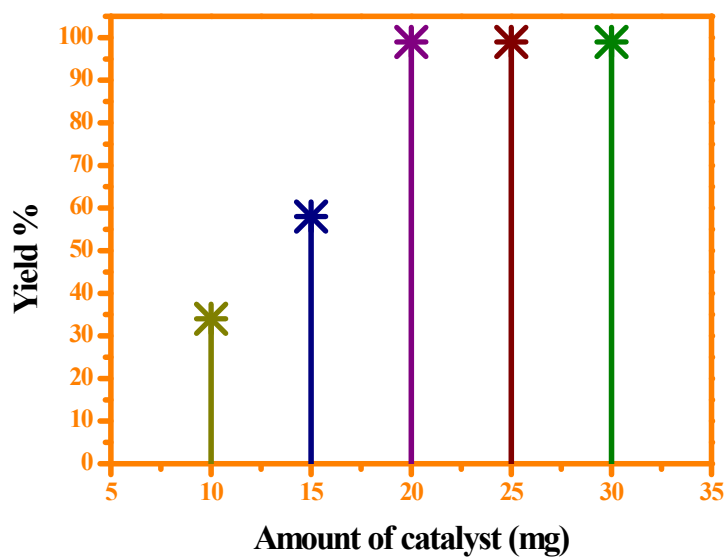


Figure S5. Effect of catalyst amount on aerobic oxidative esterification of benzyl alcohol

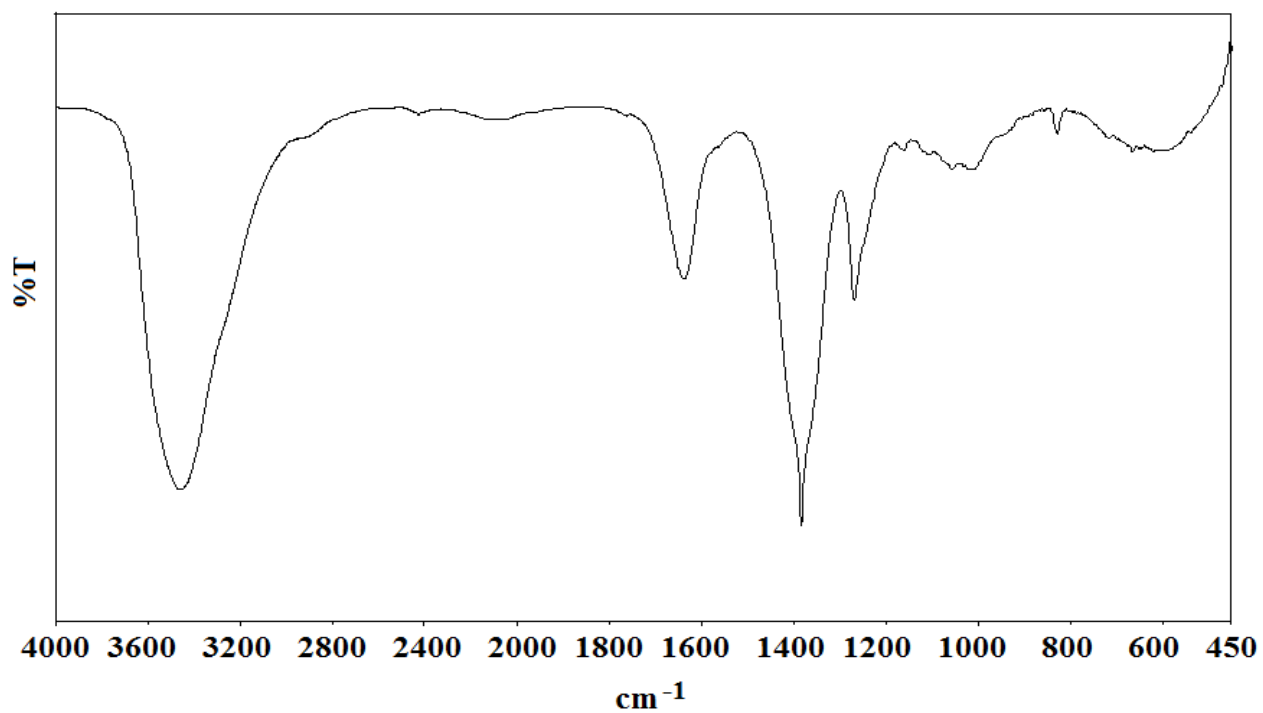


Figure S6. FT-IR spectra of homogeneous Ag NPs

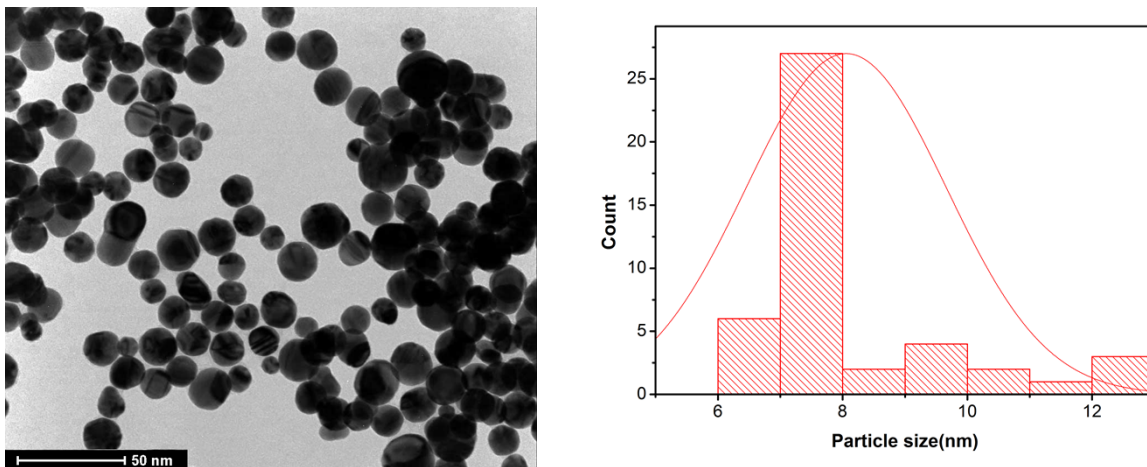


Figure S7. TEM image and distribution plot of homogeneous Ag NPs

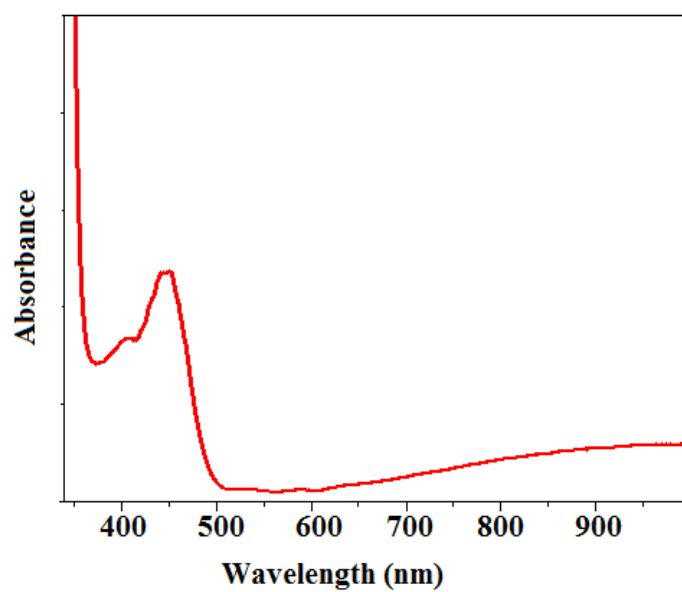


Figure S8. Uv-vis spectra of homogeneous Ag NPs

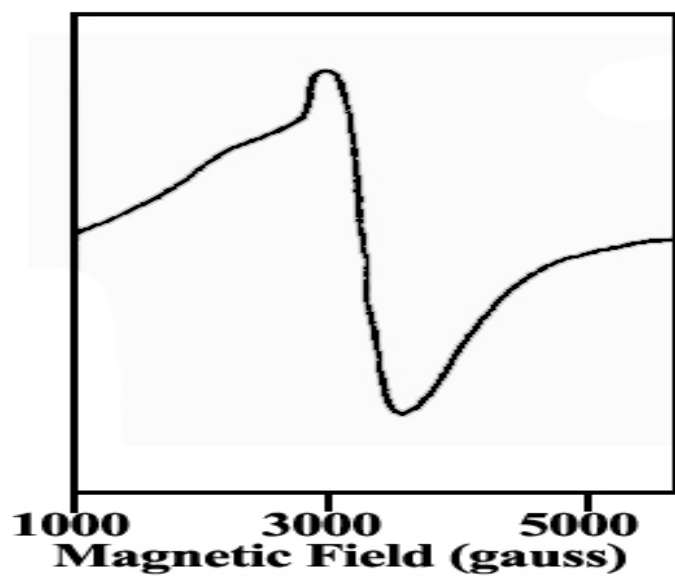


Figure S9. EPR spectrum of homogeneous Ag NPs