Nano-Fe₃O₄@walnut shell/Cu(II) as a highly effective environmental friendly catalyst for one-pot *pseudo* three-component synthesis of 1,3-oxazine derivatives under solvent-free condition

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2-Phenyl-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazine (4a) (Table 2, entry 1):

White solid, m.p. 45-47 °C; FT-IR (ATR) \bar{v} (cm⁻¹): 3060, 1600, 1496, 1231, 1057; ¹H NMR (Acetone-d₆, 400 MHz) / δ ppm: 7.89 (d, 1H, ³*J*= 8.4 Hz, Ar-H), 7.85 (d, 1H, ³*J*= 8 Hz, Ar-H), 7.73 (d, 1H, ³*J*= 9.2 Hz, Ar-H), 7.53-7.57 (m, 1H, Ar-H), 7.38-7.42 (m, 1H, Ar-H), 7.23-7.28 (m, 4H, Ar-H), 7.04 (d, 1H, ³*J*= 8.8 Hz, Ar-H), 6.87-6.91 (m, 1H, Ar-H), 5.54 (s, 2H, O-CH₂-N), 5.06 (s, 2H, -Ar-CH₂-N).



The FT-IR spectrum of product (4a)



The ¹H NMR (400 MHz) spectrum of product (4a)

2,3-Dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazine(4b) (Table 2, entry 2):

Yellow solid, m.p. 87-89 °C; FT-IR (ATR) $\bar{\upsilon}$ (cm⁻¹): 1597, 1470, 1226, 1096; ¹H NMR (Acetoned₆, 400 MHz) / δ ppm: 7.82 (t, 2H, ³*J*= 8.8 Hz, Ar-H), 7.69 (d, 1H, ³*J*= 9.2 Hz, Ar-H), 7.51 (t, 1H, ³*J*= 8 Hz, Ar-H), 7.36 (t, 1H, ³*J*= 8 Hz, Ar-H), 6.99-7.04 (m, 3H, Ar-H), 7.09-7.11 (m, 2H, Ar-H), 5.52 (s, 2H, O-CH₂-N), 5.02 (s, 2H, -Ar-CH₂-N), 2.24 (s, 3H, CH₃-Ar).



The FT-IR spectrum of product (4b)



The ¹H NMR (400 MHz) spectrum of product (4b)

2-(4-Ethylphenyl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazine (4c) (Table 2, entry 3):

Off-white solid, m.p. 44-46 °C; FT-IR (ATR) \bar{v} (cm⁻¹): 1597, 1467, 1226, 1056; ¹H NMR (Acetone-d₆, 400 MHz) / δ ppm: 7.80-7.85 (m, 2H, Ar-H), 7.69-7.71 (m, 1H, Ar-H), 7.50-7.55 (m, 1H, Ar-H), 7.35-7.40 (m, 1H, Ar-H), 6.99-7.14 (m, 5H, Ar-H), 5.49 (s, 2H, O-CH₂-N), 5.00 (s, 2H, -Ar-CH₂-N), 2.49-2.54 (m, 2H, <u>-CH₂-CH₃</u>), 1.15 (t, 3H, ³*J*= 7 Hz, -CH₂-CH₃).



The ¹H NMR (400 MHz) spectrum of product (4c)

2-(4-Chlorophenyl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazine(4d) (Table 2, entry 4):

White solid, m.p. 100-103 °C; FT-IR (ATR) \bar{v} (cm⁻¹): 1593, 1492, 1225, 1092; ¹H NMR (Acetone-d₆, 400 MHz) / δ ppm: 7.84 (t, 2H, ³*J*= 9.2 Hz, Ar-H), 7.71 (d, 1H, ³*J*= 8.8 Hz, Ar-H), 7.53 (t, 1H, ³*J*= 7.2 Hz, Ar-H), 7.38 (t, 1H, ³*J*= 7.6 Hz, Ar-H), 7.24-7.29 (m, 4H, Ar-H), 7.02 (d, 1H, ³*J*= 8.8 Hz, Ar-H), 5.51 (s, 2H, O-CH₂-N), 5.03(s, 2H, -Ar-CH₂-N).





2-(4-Bromophenyl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazine(4e) (Table 2, entry 5):

White solid, m.p. 116-119 °C; FT-IR (ATR) \bar{v} (cm⁻¹): 1588, 1489, 1223, 1092; ¹H NMR (Acetone-d₆, 400 MHz) / δ ppm: 7.84 (t, 2H, ³*J*= 9.2 Hz, Ar-H), 7.71 (d, 1H, ³*J*= 9.2 Hz, Ar-H), 7.52 (t, 1H, ³*J*= 8.4 Hz, Ar-H), 7.37-7.40 (m, 3H, Ar-H), 7.20 (d, 2H, ³*J*= 9.2 Hz, Ar-H), 7.01 (d, 1H, ³*J*= 9.2 Hz, Ar-H), 5.51 (s, 2H, O-CH₂-N), 5.03(s, 2H, -Ar-CH₂-N).



The ¹H NMR (400 MHz) spectrum of product (4e)

2-Benzyl-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazine(4f) (*Table 2, entry 6*):

Off-white, m.p. 123-125 °C; FT-IR (ATR) ῡ (cm⁻¹): 1623, 1597, 1461, 1223, 1058, 738. ¹H NMR (DMSO-d₆, 500 MHz) /δ ppm: 7.05-7.71 (m, 11H, Ar-H), 4.89 (s, 2H, O-CH₂-N), 4.22 (s, 2H, -Ar-CH₂-N), 3.89 (s, 2H, -Ar-CH₂-N); ¹³C NMR (DMSO-d₆, 100 MHz) /δ ppm: 46.55, 55.17, 81.55, 111.67, 118.32, 121.15, 123.37, 126.57, 127.19, 127.76, 128.34, 128.39, 128.49, 128.59, 131.53, 138.33, 151.41.



The FT-IR spectrum of product (4f)



The ¹H NMR (500 MHz) spectrum of product (4f)



The ¹³C-NMR (100 MHz) spectrum of product (**4f**)

2-(2-Chlorobenzyl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazine (4g) (Table 2, entry 7):

Yellow soid, m.p. 70-73 °C; FT-IR (ATR) $\bar{\nu}$ (cm⁻¹): 1594, 1468, 1226, 1057; ¹H NMR (DMSO-d₆, 500 MHz) /δ ppm: 7.07-7.82 (m, 10H, Ar-H), 4.95 (s, 2H, O-CH₂-N), 4.27 (s, 2H, -Ar-CH₂-N), 4.00 (s, 2H, -Ar-CH₂-N); ¹³C NMR (DMSO-d₆, 100 MHz) /δ ppm: 46.82, 52.56, 81.94, 111.73, 118.33, 121.26, 123.42, 126.46, 127.23, 127.85, 128.39, 128.50, 128.90, 129.35, 130.61, 131.54, 133.23, 135.81, 151.41.



The ¹H NMR (500 MHz) spectrum of product (4g)



The ¹³C-NMR (100 MHz) spectrum of product (4g)



The ¹³C-NMR (100 MHz) spectrum of product (4g)

2-(4-Methoxyphenyl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazine(4h) (Table 2, entry 8):

Off-white solid, m.p. 75-77 °C; FT-IR (ATR) \bar{v} (cm⁻¹): 1596, 1467, 1246, 1230, 1031; ¹H NMR (Acetone-d₆, 400 MHz) / δ ppm: 7.80-7.82 (m, 2H, Ar-H), 7.70 (d, 1H, ³*J*= 8.8 Hz, Ar-H), 7.51 (m, 1H, Ar-H), 7.36 (m, 1H, Ar-H), 7.13 (d, 2H, ³*J*= 7.2 Hz, Ar-H), 7.00 (d, 1H, ³*J*= 8.8 Hz, Ar-H), 6.80 (d, 2H, ³*J*= 7.2 Hz, Ar-H), 5.42 (s, 2H, O-CH₂-N), 4.93(s, 2H, -Ar-CH₂-N), 3.68 (s, 3H, O-CH₃).



The FT-IR spectrum of product (4h)



The ¹H NMR (400 MHz) spectrum of product (4h)

2-Phenethyl-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazine(4i) (*Table 2, entry 9*):

White solid, m.p. 232 °C (d); FT-IR (ATR) \bar{v} (cm⁻¹): 1597, 1469, 1225, 1060; ¹H NMR (DMSO-d₆, 500 MHz) / δ ppm: 7.81 (m, 1H, Ar-H), 7.69 (m, 2H, Ar-H), 7.49 (m, 1H, Ar-H), 7.35 (m, 1H, Ar-H), 7.24 (m, 5H, Ar-H), 7.02 (m, 1H, Ar-H), 4.92 (s, 2H, O-CH₂-N), 4.32 (s, 2H, -Ar-CH₂-N), 2.96 (m, 2H, Ar-CH₂-CH₂-N), 2.88 (m, 2H, Ar-<u>CH₂</u>-CH₂-N); ¹³C NMR (DMSO-d₆, 125 MHz) / δ ppm: 34.86, 47.95, 53.92, 82.69, 113.08, 119.18, 122.26, 124.19, 126.74, 127.33, 128.51, 129.05, 129.22, 129.31, 129.54, 132.43, 140.88, 152.43.



The FT-IR spectrum of product (4i)



The ¹H NMR (500 MHz) spectrum of product (4i)



The ¹³C-NMR (100 MHz) spectrum of product (4i)

2-Cyclohexyl-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazine(4j) (*Table 2, entry 10*):

Off-white solid, m.p. 248 °C (d); FT-IR (ATR) $\bar{\upsilon}$ (cm⁻¹): 2926, 2852, 1597, 1467, 1227, 1058; ¹H NMR (DMSO-d₆, 500 MHz) / δ ppm: 7.66-7.81 (m, 3H, Ar-H), 7.48 (m, 1H, Ar-H), 7.35 (m, 1H, Ar-H), 6.98 (m, 1H, Ar-H), 4.99 (s, 2H, O-CH₂-N), 4.33 (s, 2H, -Ar-CH₂-N), 2.70 (m, 1H, CH-N), 1.08-1.86 (m, 10H, 5CH₂).



The FT-IR spectrum of product (4j)



The ¹H NMR (500 MHz) spectrum of product (4j)

2-Hexyl-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazine(4k) (*Table 2, entry 11*):

Brown solid, m.p. 177 °C (d); FT-IR (ATR) \bar{v} (cm⁻¹): 2927, 2854, 1597, 1467, 1225, 1057; ¹H NMR (DMSO-d₆, 500 MHz) /δ ppm: 7.80 (m, 1H, Ar-H), 7.68 (m, 2H, Ar-H), 7.47 (m, 1H, Ar-H), 7.34 (m, 1H, Ar-H), 7.00 (m, 1H, Ar-H), 4.87 (s, 2H, O-CH₂-N), 4.25 (s, 2H, -Ar-CH₂-N), 2.68 (m, 2H, -CH₂-N), 1.53 (m, 2H, CH₂), 1.25 (m, 6H, 3CH₂), 0.84 (m, 3H, CH₃). ¹³C NMR (DMSO-d₆, 125 MHz) /δ ppm: 14.77, 22.98, 27.23, 28.38, 32.02, 47.87, 52.09, 82.71, 112.97, 119.14, 122.18, 124.13, 127.32, 128.46, 129.21, 129.28, 132.44, 152.42.



The ¹H NMR (500 MHz) spectrum of product (4k)



The ¹³C-NMR (100 MHz) spectrum of product (4k)

2-(Furan-2-ylmethyl)-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazine(4l) (*Table 2, entry 12*):

Pale-pink, m.p. 98-100 °C; FT-IR (ATR) \bar{v} (cm⁻¹): 1597, 1467, 1226, 1060; ¹H NMR (DMSO-d₆, 500 MHz) / δ ppm: 7.71-8.02 (m, 4H, Ar-H), 7.36-7.61 (m, 2H, Ar-H), 7.04 (s, 1H, Ar-H), 6.32-6.52 (m, 2H, Ar-H), 4.89 (s, 2H, O-CH₂-N), 4.26 (s, 2H, -Ar-CH₂-N), 3.90 (s, 2H, furan-CH₂-N); ¹³C NMR (DMSO-d₆, 125 MHz) / δ ppm: 46.37, 47.86, 81.22, 108.76, 110.42, 111.52, 118.27, 121.19, 123.43, 126.60, 127.80, 128.39, 128.50, 131.48, 142.70, 151.29, 151.79.



The ¹H NMR (500 MHz) spectrum of product (41)



The ¹³C-NMR (100 MHz) spectrum of product (41)

2-Butyl-2,3-dihydro-1*H*-naphtho[1,2-*e*][1,3]oxazine(4m) (Table 2, entry 13):

White solid, m.p. 170 °C (d); FT-IR (ATR) \bar{v} (cm⁻¹): 2954, 2864, 1597, 1433, 1225, 1056. ¹H NMR (DMSO-d₆, 500 MHz) / δ ppm: 7.81 (m, 1H, Ar-H), 7.69 (m, 2H, Ar-H), 7.47 (m, 1H, Ar-H), 7.35 (m, 1H, Ar-H), 7.00 (m, 1H, Ar-H), 4.88 (s, 2H, O-CH₂-N), 4.25 (s, 2H, -Ar-CH₂-N), 2.69 (m, 2H, -CH₂-N), 1.53 (m, 2H, CH₂), 1.31 (m, 2H, CH₂), 0.87 (m, 3H, CH₃). ¹³C NMR (DMSO-d₆, 100 MHz) / δ ppm: 13.80, 19.80, 29.64, 46.94, 50.84, 81.81, 112.08, 118.25, 121.31, 123.26, 126.45, 127.57, 128.32, 128.37, 131.54, 151.51.



The ¹H NMR (500 MHz) spectrum of product (4m)



The ¹³C-NMR (100 MHz) spectrum of product (4m)

3-Phenyl-3,4-dihydro-2*H*-benzo[e][1,3]oxazine (9a) (Table 2, entry 14):

Light yellow solid, m.p. 59-62 °C.

FT-IR (ATR) \bar{v} (cm⁻¹): 1595, 1555, 1455, 1203, 1042, 782.

¹H NMR (400 MHz, CDCl₃)/δ ppm: 7.76 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.38 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.27 (d, 1H, *J* = 8 Hz, Ar-H), 6.96-6.95 (m, 1H, Ar-H), 6.85-6.84 (m, 1H, Ar-H), 6.27-6.52 (m, 4H, Ar-H), 5.40 (s, 2H, CH₂), 4.89 (s, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) /δ ppm: 55.17, 97.55, 109.15, 111.67, 115.45, 118.32, 120.65,

122.37, 126.57, 128.19, 148.33, 152.41.









The ¹³C NMR (125 MHz) spectrum of product (9a)

3-(4-Chlorophenyl)-3,4-dihydro-2*H*-benzo[e][1,3]oxazine (9b) (Table 2, entry 15):

Pale yellow solid, m.p. 67-69 °C. FT-IR (ATR) ῡ (cm⁻¹): 1623, 1594, 1492, 1225, 1054, 809. ¹H NMR (400 MHz, CDCl₃)/δ ppm: 7.46 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.18 (m, 1H, Ar-H), 6.78-6.92 (m, 3H, Ar-H), 6.43 (d, 2H, *J* = 8.3 Hz, Ar-H), 5.82 (s, 2H, CH₂), 4.46 (s, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) /δ ppm: 55.92, 98.96, 110, 112.18, 116.74, 120.03, 125.29, 125.74, 127.33, 146.68, 155.43.



The FT-IR spectrum of product (9b)



The ¹H NMR (500 MHz) spectrum of product (9b)



The ¹³C NMR (125 MHz) spectrum of product (9b)

3-Phenyl-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-ol (9c) (Table 2, entry 16):

White solid, m.p. 75-76 °C. FT-IR (ATR) ῡ (cm⁻¹): 3258, 1599, 1510, 1469, 1228, 1058, 809. ¹H NMR (400 MHz, CDCl₃)/δ ppm: 7.42-7.65 (m, 4H, Ar-H), 7.02 (m, 1H, Ar-H), 6.93 (m, 1H, Ar-H), 6.96 (d, 2H, *J* = 8.2 Hz, ArH), 6.76 (d, 2H, Ar-H), 6.12 (s, 2H, CH₂), 5.54 (s, 1H, OH), 4.97 (s, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) /δ ppm: 56.82, 90.04, 112.73, 116.33, 121.26, 122.42, 126.46, 129.91, 129.97, 131.54, 152.23, 152.61.









3,4-Dihydro-3-phenyl-2H-naphtho[2,1-e][1,3]oxazine (11a) (Table 2, entry 17):

White solid, m.p. 57-60 °C

FT-IR (ATR) v (cm⁻¹): 3056, 1596, 1502, 1232, 1066.

¹H NMR (DMSO-d₆, 500 MHz) /δ ppm: 7.75-7.78 (m, 4H, Ar-H), 7.68 (d, 2H, *J*= 8.5 Hz, Ar-H), 7.39 (t, 1H, *J*= 7 Hz, Ar-H), 7.24 (t, 1H, *J*= 7 Hz, Ar-H), 7.08-7.12 (m, 3H, Ar-H), 5.45 (s, 2H, CH₂), 4.97 (s, 2H, CH₂).

¹³C NMR (DMSO-d₆, 100 MHz) /δ ppm: 55.23, 88.42, 108.65, 118.61, 122.63, 123.48, 125.98, 126.10, 127.53, 127.73, 129.28, 131.75, 134.60, 136.25, 150.85, 155.28.



The FT-IR spectrum of product (11a)



The ¹H NMR (500 MHz) spectrum of product (11a)



The ¹³C NMR (125 MHz) spectrum of product (11a)

3-(4-chlorophenyl)-3,4-dihydro-2H-naphtho[2,1-e][1,3]oxazine (11b) (Table 2, entry 18):

Yellow solid, m.p. 107-109 °C

FT-IR (ATR) $\bar{\upsilon}$ (cm⁻¹): 3057, 1591, 1496, 1224, 1060. ¹H NMR (DMSO-d₆, 500 MHz) / δ ppm: 7.88 (d, 1H, *J*= 8 Hz, Ar-H), 7.84 (d, 1H, *J*= 8 Hz, Ar-H), 7.73 (d, 1H, *J*= 8 Hz, Ar-H), 7.54 (t, 1H, *J*= 7.2 Hz, Ar-H), 7.39 (t, 1H, *J*= 7.6 Hz, Ar-H), 7.20-7.27 (m, 4H, Ar-H), 7.03 (d, 1H, *J*= 8 Hz, Ar-H), 5.51 (s, 2H, CH₂), 4.97(s, 2H, CH₂). ¹³C NMR (DMSO-d₆, 100 MHz) / δ ppm: 46.83, 78.35, 112.69, 118.28, 118.94, 121.47, 123.64, 126.70, 128.07, 128.35, 128.45, 128.79, 130.91, 146.90, 151.55.



The FT-IR spectrum of product (11b)



The ¹H NMR (500 MHz) spectrum of product (11b)



The ¹³C NMR (125 MHz) spectrum of product (11b)

3-(4-methoxyphenyl)-3,4-dihydro-2H-naphtho[2,1-e][1,3]oxazine (11c) (Table 2, entry 19):

White solid, m.p. 300 °C (d) FT-IR (ATR) ῡ (cm⁻¹): 1623, 1593, 1490, 1223, 1094. ¹H NMR (DMSO-d₆, 400 MHz) /δ ppm: 7.85-7.84(m, 2H, Ar-H), 7.72 (d, 1H, *J*= 7.2 Hz, Ar-H), 7.54 (t, 1H, *J*= 8 Hz Ar-H), 7.39 (t, 1H, *J*= 7.6 Hz, Ar-H), 7.12 (d, 2H, *J*= 7.2 Hz, Ar-H), 7.02 (d, 1H, *J*= 7.2 Hz, Ar-H), 6.82 (d, 2H, *J*= 7.2 Hz, Ar-H), 5.44 (s, 2H, CH₂), 4.90 (s, 2H, CH₂), 3.66 (s, 3H, O-CH₃). ¹³C NMR (DMSO-d₆, 100 MHz) /δ ppm: 47.48, 55.22, 79.80, 112.82, 114.41, 118.39, 119.62,

121.43, 123.55, 126.70, 127.96, 128.42, 128.44, 131.02, 141.94, 151.72, 154.03, 155.46.



The FT-IR spectrum of product (11c)



The ¹H NMR (500 MHz) spectrum of product (11c)



The ¹³C NMR (125 MHz) spectrum of product (11c)

3-(p-tolyl)-3,4-dihydro-2H-naphtho[2,1-e][1,3]oxazine (11d) (Table 2, entry 20):

Yellow solid, m.p. 195-198 °C FT-IR (ATR) ῡ (cm⁻¹): 1598, 1509, 1467, 1223, 1059, 938. ¹H NMR (DMSO-d₆, 500 MHz) /δ ppm: 7.76 (t, 2H, *J*= 7.7 Hz, Ar-H), 7.68 (d, 1H, *J*= 8 Hz, Ar-H), 7.39 (t, 1H, *J*= 7 Hz, Ar-H), 7.26 (t, 1H, *J*= 7 Hz, Ar-H), 6.94-7.06 (m, 3H, Ar-H), 6.85 (d, *J*= 8.5 Hz, 2H, Ar-H), 5.48 (s, 2H, CH₂), 4.87 (s, 2H, CH₂), 2.63 (s, 3H, CH₃). ¹³C NMR (DMSO-d₆, 100 MHz) /δ ppm: 26.58, 52.17, 86.87, 112.82, 114.41, 116.54, 118.39, 119.62, 121.43, 123.55, 126.70, 127.96, 129.47, 130.27, 131.02, 141.94, 150.02, 153.14.



The FT-IR spectrum of product (11d)



The ¹H NMR (500 MHz) spectrum of product (11c)



The ¹³C NMR (125 MHz) spectrum of product (11d)