

Supporting Information

Oxidative Amidation by Cu(II)-Guanidine Acetic Acid Immobilized on the Magnetized Sawdust and Eggshell as a Natural Base

Atefeh Darvishi,^[a] Maryam Kazemi Miraki,^[a] Marzban Arefi ^[a] and Akbar Heydari*^[a]

^[a] Chemistry Department, Tarbiat Modares University, P.O. Box 14155-4838, Tehran, Iran
Email: heydari_a@modares.ac.ir

Table of contents

Spectra information of oxidative amidation	S2
Copy of ¹ H NMR, ¹³ C NMR and mass spectra of amide derivatives	S4

Characterization of products

Spectra information of oxidative amidation

***N*-ethylbenzamide** (Table 2, entry 3a): white solid; mp: 70-72 °C; FTIR (KBr) ν (cm⁻¹): 3318, 3074, 2977, 1637, 1546, 1430, 1308; ¹H NMR (CDCl₃, 250 MHz) δ (ppm): 7.39-7.78 (m, 5H), 6.12 (br s, 1H), 3.45-3.57 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H); MS (EI, 70 ev) m/z (%): 149 (M⁺, 60), 134 (3), 105 (100), 77 (42).

***N*-buthylbenzamide** (Table 2, entry 3b): yellow oil; FTIR (KBr) ν (cm⁻¹): 3302, 3081, 2958, 2870, 1635, 1548, 1488, 1315; ¹H NMR (CDCl₃, 250 MHz) δ (ppm): 7.29-8.00 (m, 5H), 6.32 (br s, 1H), 3.32-3.40 (m, 2H), 1.18-1.57 (m, 4H), 0.87 (t, J = 7.5 Hz, 3H).

***N*-(1-hydroxybutan-2-yl)benzamide** (Table 2, entry 3c): white solid; mp: 74-75 °C; FTIR (KBr) ν (cm⁻¹): 3301, 3067, 2958, 2930, 2868, 1636, 1539, 1454, 1048; ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 7.70 (d, J = 7.6 Hz, 2H), 7.42 (t, J = 7.2 Hz, 1H), 7.34 (dd, J = 7.6 Hz, J = 7.2 Hz, 2H), 6.36 (s, 1H), 4.0 (brs, 1H), 3.71 (dd, J = 10.7 Hz, J = 2.8 Hz, 1H), 3.62 (dd, J = 10.7 Hz, J = 5.2 Hz, 1H), 2.96 (br s, 1H), 1.51-1.67 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 168.3, 134.4, 131.6, 128.6, 127.0, 65.2, 53.7, 24.3, 10.7; MS (EI, 70 ev) m/z (%): 193 (M⁺, 3), 175 (6), 162 (98), 150 (10), 122 (48), 105 (100), 77 (50).

***N*-tert-butylbenzamide** (Table 2, entry 3d): colorless solid; mp: 134-136 °C. FTIR (KBr) ν (cm⁻¹): 3323, 3061, 2970, 1638, 1537, 1450, 1310, 1219; ¹H NMR (CDCl₃, 250 MHz) δ (ppm): 7.74 (d, J = 8.0 Hz, 2H), 6.97 - 7.12 (m, 3H), 5.92 (br s, 1H), 1.48 (s, 9H); ¹³C NMR (CDCl₃, 62.9 MHz) δ (ppm): 167.0, 136.1, 131.2, 128.6, 126.8, 51.7, 29.0; MS (EI, 70 ev) m/z (%): 177 (M⁺, 60), 162 (60), 122 (50), 105 (100), 77 (88), 57 (10).

***N*-benzylbenzamide** (Table 2, entry 3e): white solid; mp: 105-107 °C; FTIR (KBr) ν (cm⁻¹): 3295, 3060, 2978, 1644, 1540, 1488, 1260; ¹H NMR (CDCl₃, 250 MHz) δ (ppm): 7.79-7.81 (m, 2H), 7.31-7.79 (m, 8H), 6.40 (br s, 1H), 4.66 (d, J = 4.7 Hz, 2H); MS (EI, 70 ev) m/z (%): 211 (M⁺, 61), 121 (4), 105 (100), 91 (12), 77 (65).

***N*-(1-phenylethyl)benzamide** (Table 2, entry 3f): white solid; mp: 97-98 °C; FTIR (KBr) ν (cm⁻¹): 3329, 3030, 2967, 1635, 1525, 1449, 1080; ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 7.79-7.81 (m, 2H), 7.30-7.54 (m, 8H), 6.34 (d, J = 5.2 Hz, 1H), 5.32-5.41 (m, 2H), 1.64 (d, J = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 166.6, 143.1, 134.6, 131.5, 128.8, 128.6, 127.5, 126.9, 126.3, 49.2, 21.7; MS (EI, 70 ev) m/z (%): 225 (M⁺, 40), 210 (12), 120 (10), 105 (100), 91 (3), 77 (80).

4-methoxy-*N*-(1-phenyl)benzamide (Table 2, entry 3g): white solid; mp: 131-132 °C; FTIR (KBr) ν (cm⁻¹): 3434, 3337, 2818, 2849, 1622, 1526, 1502, 1257; ¹H NMR (CDCl₃, 250 MHz) δ (ppm): 7.74 (d, J = 8.7 Hz, 2H), 7.30-7.39 (m, 5H), 6.89-6.93 (m, 2H), 6.23 (br s, 1H), 5.31-5.36 (m, 1H), 3.84 (s, 3H), 1.60 (d, J = 6.7 Hz, 3H).

4-chloro-*N*-(1-phenyl)benzamide (Table 2, entry 3h): white solid; mp: 136-139 °C; FTIR (KBr) ν (cm⁻¹): 3421, 3338, 2980, 1636, 1529, 1485, 1268; ¹H NMR (CDCl₃, 250 MHz) δ (ppm): 7.71 (d, J = 8.2 Hz, 2H), 7.30-7.40 (m, 7H), 6.39 (br s, 1H), 5.28-5.34 (m, 1H), 1.60 (d, J = 7.0, 3H).

***N,N*-dibutylbenzamide** (Table 2, entry 3i): yellow oil; FTIR (KBr) ν (cm⁻¹): 3070, 2952, 2869, 1635, 1523, 1438, 1349; ¹H NMR (CDCl₃, 250 MHz) δ (ppm): 7.28-7.39 (m, 5H), 3.18-3.49 (m, 4H), 1.11-1.64 (m, 8H), 0.77-1.00 (m, 6H).

***N*-piperidylbenzamide** (Table 2, entry 3j): colorless oil; FTIR (KBr) ν (cm⁻¹): 3059, 2931, 2858, 1625, 1565, 1433, 1277; ¹H NMR (CDCl₃, 250 MHz) δ (ppm): 7.39 (s, 5H), 3.72 (s, 2H), 3.35 (s, 2H), 1.42-1.68 (m, 6H); ¹³C NMR (CDCl₃, 62.9 MHz) δ (ppm): 170.4, 136.6, 129.5, 128.5, 126.9, 48.8, 43.2, 26.8, 25.8, 24.7; MS (EI, 70 ev) m/z (%): 189 (M⁺, 18), 160 (4), 133 (4), 111 (46), 105 (86), 84 (18), 77 (100).

***N*-morpholinebenzamide** (Table 2, entry 3k): colorless oil; FTIR (KBr) ν (cm⁻¹): 3058, 2925, 2862, 1630, 1436, 1259; ¹H NMR (CDCl₃, 250 MHz) δ (ppm) : 7.37-7.43 (m, 5H), 3.46-3.71 (m, 8H); ¹³C NMR (CDCl₃, 62.9 MHz) δ (ppm): 170.6, 135.4, 130.0, 128.7, 127.2, 67.0, 48.2, 42.7; MS (EI, 70 ev): m/z (%): 191 (M⁺, 8), 176 (5), 148 (5), 114 (5), 105 (100), 86 (11), 77 (87).

***N,N*-diallylbenzamide** (Table 2, entry 3l): yellow oil; FTIR (KBr) ν (cm⁻¹): 3074, 2924, 2800, 1637, 1416, 1261; ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 7.43 (d, J=7.2, 2H), 7.27-7.43 (m, 3H), 5.89 (br s, 1H), 5.74 (br s, 1H), 5.18-5.26 (m, 4H), 4.15 (br s, 2H), 3.84 (br s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 171.8, 136.3, 133.2, 132.8, 129.6, 128.4, 126.6, 117.6, 50.7, 46.9; MS (EI, 70 ev): m/z (%): 201 (M⁺, 18), 160 (34), 105 (100), 96 (14), 77 (50).

***N*-benzyl-*N*-isopropylbenzamide** (Table 2, entry 3m): yellow oil; FTIR (KBr) ν (cm⁻¹): 3061, 2978, 2850, 1633, 1421, 1344, 1179; ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 7.42-7.45 (m, 5H), 7.33-7.36 (m, 5H), 4.70 (s, 2H), 4.15 (br s, 1H), 1.12 (br s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 168.9, 137.3, 133.2, 129.9, 129.2, 128.6, 128.4, 127.0, 126.2, 50.8, 43.4, 21.5; MS (EI, 70 ev): m/z (%): 253 (M⁺, 15), 210 (24), 162 (20), 105 (100), 91 (68), 77 (80).

***N,N*-dibenzylbenzamide** (Table 2, entry 3n): white solid; mp: 93-96 °C; FTIR (KBr) ν (cm⁻¹): 3059, 2927, 1622, 1489, 1429, 1251; ¹H NMR (CDCl₃, 400 MHz) δ (ppm): 7.51 (dd, J=5.2 Hz, J=1.6 Hz, 2H), 7.39 (dd, J=6.8 Hz, J=5.2 Hz, 2H), 7.35-7.40 (m, 7H), 7.31 (t, J=6.8 Hz, 2H), 7.16 (d, J=7.2 Hz, 2H), 4.72 (s, 2H), 4.42 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 172.35, 136.93, 136.45, 136.24, 129.74, 128.92, 128.75, 128.62, 128.53, 127.75, 127.62, 127.14, 126.71, 51.53, 46.93; MS (EI, 70 ev): m/z (%): 301 (M⁺, 10), 210 (86), 105 (100), 91 (88), 77 (90).

Copy of ¹H NMR, ¹³C NMR and mass spectra of amide derivatives































