SUPPLEMENTARY MATERIAL TO

K-10 clay as a reusable catalyst for the solvent-free, MW-induced synthesis of enaminones

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PHYSICAL AND SPECTRAL DATA FOR THE SYNTHESIZED ENAMINONES

3-Phenylamino-but-2-enoic acid ethyl ester (1). Oil, IR (neat, cm⁻¹): 3429, 3018, 2959, 1630, 1508, 1293, 1128, 1085, 921, 796; 1H-NMR (500 MHz, CDCl₃, δ / ppm): 1.22 (3H, t, J = 7.3 Hz), 1.92 (3H, s), 4.12 (2H, q, J = 7.3 Hz), 4.61 (1H, s), 6.68–7.35 (5H, aromatic), 11.38 (1H, s, NH); 13C-NMR (125 MHz, CDCl₃, δ / ppm): 15.8 (CH₂C₃H₃), 18.7 (CH₃), 57.6 (CH₂), 92.7 (=CH), 123.9 (CH), 125.3 (CH), 128.4 (CH), 138.8 (qC), 158.0 (N–C=), 189.2 (O=C).

3-Benzylamino-but-2-enoic acid ethyl ester (2). Oil, IR (neat, cm⁻¹): 3292, 3074, 2951, 1655, 1608, 1512, 1229, 1173, 1151, 1068, 928, 756; 1H-NMR (500 MHz, CDCl₃, δ / ppm): 1.20 (3H, t, J = 7.3 Hz), 1.89 (3H, s), 4.15 (2H, q, J = 7.3 Hz), 4.33 (2H, d, J = 6.4 Hz), 4.54 (1H, s), 7.08–7.29 (5H, aromatic), 11.21 (1H, s, NH); 13C-NMR (125 MHz, CDCl₃, δ / ppm): 14.2 (CH₂C₃H₃), 18.6 (CH₃), 46.3 (PhCH₂), 57.6 (CH₂), 82.8 (=CH), 126.2 (CH), 126.4 (CH), 128.4 (CH), 138.4 (qC), 161.5 (N–C=), 171.2 (O=C).

3-(1-Phenylethanamino)-but-2-enoic acid ethyl ester (3). Oil, IR (neat, cm⁻¹): 3298, 3019, 2996, 1686, 1616, 1541, 1229, 1182, 1163, 1055, 980, 745; 1H-NMR (500 MHz, CDCl₃, δ / ppm): 1.27 (3H, s), 1.32 (3H, t, J = 7.3 Hz), 2.04 (3H, d, J = 4.7 Hz), 4.09 (1H, m), 4.29 (2H, q, J = 7.3 Hz), 4.68 (1H, s), 7.15–7.41 (5H, aromatic), 11.06 (1H, s, NH); 13C-NMR (125 MHz, CDCl₃, δ / ppm): 14.3 (CH₂C₃H₃), 18.5 (CH₃), 22.3 (CH₃CH), 56.0 (CH₂C₃H₃), 61.4 (CHCH₃), 82.3 (=CH), 116.9 (CH), 126.7 (CH), 128.5 (CH), 129.9 (qC), 162.2 (N–C=), 170.4 (O=C).

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3-Allylamino-but-2-enoic acid ethyl ester (4). Oil, IR (neat, cm⁻¹): 3297, 3064, 2975, 1668, 1611, 1508, 1284, 1169, 1058, 949, 766; ¹H-NMR (500 MHz, CDCl₃, δ / ppm): 1.23 (3H, t, J = 7.3 Hz), 3.61 (3H, s), 3.81–3.86 (2H, m), 4.14 (2H, q, J = 7.3 Hz), 4.83 (1H, s), 5.16–5.24 (2H, m), 5.82–5.90 (1H, m), 8.64 (1H, s, NH); ¹³C-NMR (125 MHz, CDCl₃, δ / ppm): 14.2 (CH₂C₂H₃), 24.5 (CH₃), 49.7 (C₃H₂C=), 61.4 (CH₂CH₃), 82.3 (=CH), 116.9 (=CH₂), 134.4 (=CH–CH₂), 161.8 (N–C=), 170.5 (O=C).

3-Methylamino-but-2-enoic acid ethyl ester (5). Oil, IR (neat, cm⁻¹): 3288, 3046, 2989, 1645, 1602, 1529, 1274, 1154, 1138, 1072, 943, 792; ¹H-NMR (500 MHz, CDCl₃, δ / ppm): 1.21 (3H, t, J = 7.3 Hz), 1.93 (3H, s), 2.81 (3H, d, J = 7.4 Hz), 4.11 (2H, q, J = 7.3 Hz), 4.52 (1H, s), 11.82 (1H, s, NH); ¹³C-NMR (125 MHz, CDCl₃, δ / ppm): 14.2 (CH₂C₂H₃), 18.7 (CH₃), 46.3 (NCH₃), 57.3 (CH₂CH₃), 80.3 (=CH), 162.3 (N–C=), 171.3 (O=C).

3-Phenylamino-but-2-enoic acid methyl ester (6). Oil, IR (neat, cm⁻¹): 3454, 3092, 2940, 1639, 1524, 1291, 1274, 1154, 1138, 1072, 943, 792; ¹H-NMR (500 MHz, CDCl₃, δ / ppm): 1.42 (3H, s), 2.19 (3H, s), 4.70 (1H, s), 7.02–7.48 (5H, m, aromatic), 11.19 (1H, s, NH); ¹³C-NMR (125 MHz, CDCl₃, δ / ppm): 14.6 (CH₂C₂H₃), 54.3 (OCH₃), 91.2 (=CH), 122.4 (CH), 129.1 (CH), 139.1 (qC), 160.2 (N–C=), 179.9 (O=C).

3-(2-Methyl-phenylamino)-but-2-enoic acid methyl ester (7). M.p. 65–67 °C; IR (KBr, cm⁻¹): 3435, 2692, 1648, 1590, 1442, 1284, 1141, 880, 791; ¹H-NMR (500 MHz, CDCl₃, δ / ppm): 1.38 (3H, s), 1.80 (3H, s), 3.43 (3H, s), 4.61 (1H, s, aromatic), 7.02–7.48 (4H, m, aromatic), 10.48 (1H, s, NH); ¹³C-NMR (125 MHz, CDCl₃, δ / ppm): 14.0 (CH₂C₂H₃), 18.5 (CH₃), 51.9 (PhCH₃), 84.4 (=CH), 123.8 (CH), 126.5 (CH), 127.2 (CH), 131.3 (CH), 135.0 (qC), 136.1 (CH₃–C aromatic), 160.4 (N–C=), 170.8 (O=C).

3-(4-Ethoxy-phenylamino)-but-2-enoic acid methyl ester (8). M.p. 60–62 °C; IR (KBr, cm⁻¹): 3445, 2681, 1635, 1587, 1429, 1248, 1159, 869, 776; ¹H-NMR (500 MHz, CDCl₃, δ / ppm): 1.44 (3H, t, J = 7.2 Hz), 1.92 (3H, s), 3.65 (3H, s), 4.1 (2H, q, J = 7.2 Hz), 4.68 (1H, s), 6.81 (2H, d, J = 8.7 Hz), 7.09 (2H, d, J = 8.7 Hz), 10.12 (1H, s, NH); ¹³C-NMR (125 MHz, CDCl₃, δ / ppm): 14.8 (OCH₂CH₃), 20.1 (CH₃), 50.1 (OCH₃), 62.3 (OCH₂CH₃), 84.3 (=CH), 115.2 (CH), 127.1 (CH), 131.8 (qC), 156.9 (O–C aromatic), 160.1 (N–C=), 170.5 (O=C).

4-(1-Phenylethanamino)-3-penten-2-one (9). M.p. 58–61 °C; IR (KBr, cm⁻¹): 3438, 3016, 1657, 1593, 1242, 1179, 1025, 941, 883; ¹H-NMR (500 MHz, CDCl₃, δ / ppm): 1.26 (3H, s), 1.97 (3H, s), 4.23 (1H, m), 5.11 (1H, s), 7.24–7.45 (5H, aromatic), 10.56 (1H, s, NH); ¹³C-NMR (125 MHz, CDCl₃, δ / ppm): 22.4 (CH₃), 24.6 (CH₂CH₃), 27.4 (COCH₃), 56.2 (CH₂CH₃), 95.0 (=CH), 126.4 (CH), 126.5 (CH), 128.3 (CH), 141.5 (qC), 160.1 (N–C=), 195.7 (O=C).
**4-Methylamino-3-penten-2-one (10).** M.p. 36–38 °C; IR (KBr, cm⁻¹): 3269, 3082, 2988, 1651, 1560, 1281, 1154, 1063, 974, 787; ¹H-NMR (500 MHz, CDCl₃, δ / ppm): 1.94 (3H, s), 1.98 (3H, s), 2.85 (3H, d, J = 5.6 Hz), 11.86 (1H, s, NH); ¹³C-NMR (125 MHz, CDCl₃, δ / ppm): 18.1 (CH₃), 28.3 (NCH₃), 29.1 (OCCH₃), 94.8 (=CH), 163.7 (N–C=), 192.8 (O=C).

**4-phenylamino-3-penten-2-one (11).** M.p. 47–49 °C; IR (KBr, cm⁻¹): 3432, 3058, 1629, 1587, 1255, 1194, 1068, 859; ¹H-NMR (500 MHz, CDCl₃, δ / ppm): 1.95 (3H, s), 2.28 (3H, s), 5.19 (1H, s), 7.12–7.49 (5H, m, aromatic), 12.45 (1H, s, NH); ¹³C-NMR (125 MHz, CDCl₃, δ / ppm): 19.5 (CH₃), 28.7 (OC₃C₆H₃), 96.9 (=CH), 124.5 (CH), 125.3 (CH), 128.7 (CH), 139.0 (qC), 159.8 (N–C=), 195.2 (O=C).

**4-(2-Ethoxy-phenylamino)-3-penten-2-one (12).** M.p. 56–58 °C; IR (KBr, cm⁻¹): 3448, 3071, 1627, 1564, 1249, 1173, 1028, 872, 747; ¹H-NMR (500 MHz, CDCl₃, δ / ppm): 1.36 (3H, t, J = 7.2 Hz), 1.93 (3H, s), 2.56 (3H, s), 4.09 (2H, q, J = 7.2 Hz), 4.68 (1H, m, aromatic), 10.18 (1H, s, NH); ¹³C-NMR (125 MHz, CDCl₃, δ / ppm): 14.8 (CH₂C₆H₃), 19.8 (CH₃), 27.8 (CO₃C₆H₃), 63.5 (CH₂CH₃), 96.4 (=CH), 113.5 (CH), 121.1 (CH), 122.3 (CH), 123.8 (CH), 130.4 (qC), 154.2 (O–C aromatic), 159.6 (N–C=), 195.6 (O=C).

**4-(2-Methyl-phenylamino)-3-penten-2-one (13).** M.p. 52–55 °C. IR (KBr, cm⁻¹): 3435, 3042, 1624, 1571, 1239, 1187, 1058, 854, 762; ¹H-NMR (500 MHz, CDCl₃, δ / ppm): 1.96 (3H, s), 2.16 (3H, s), 2.26 (3H, s), 5.21 (1H, s), 6.29–7.32 (4H, m, aromatic), 10.79 (1H, s, NH); ¹³C-NMR (125 MHz, CDCl₃, δ / ppm): 17.8 (PhC₆H₃), 19.6 (CH₃), 27.5 (COCH₃), 97.6 (=CH), 123.5 (CH), 126.4 (CH), 127.4 (CH), 131.3 (CH₃–C aromatic), 135.8 (CH), 136.6 (qC), 159.7 (N–C=), 196.1 (O=C).

**4-(3-Chloro-phenylamino)-3-penten-2-one (14).** M.p. 75–78 °C; IR (KBr, cm⁻¹): 3424, 3156, 1691, 1621, 1524, 1486, 1264, 1145, 1039, 894; ¹H-NMR (500 MHz, CDCl₃, δ / ppm): 1.97 (3H, s), 2.21 (3H, s), 5.20 (1H, s), 6.31–7.14 (4H, m, aromatic), 11.99 (1H, s, NH); ¹³C-NMR (125 MHz, CDCl₃, δ / ppm): 18.5 (CH₃), 23.4 (COCH₃), 96.8 (=CH), 122.3 (CH), 124.7 (CH), 134.7 (CH), 135.6 (C–Cl), 141.1 (qC), 158.2 (N–C=), 195.9 (O=C).

**4-Benzylamino-3-penten-2-one (15).** Oil, IR (neat, cm⁻¹): 3288, 3046, 2989, 1645, 1602, 1529, 1274, 1138, 1154, 1072, 943, 792; ¹H-NMR (500 MHz, CDCl₃, δ / ppm): 1.81 (3H, s), 2.07 (3H, s), 4.38 (2H, d), 4.93 (1H, s), 6.81–7.29 (5H, m, aromatic), 11.19 (1H, s, NH); ¹³C-NMR (125 MHz, CDCl₃, δ / ppm): 18.7 (CH₃), 22.6 (COCH₃), 57.3 (CH₂), 80.3 (=CH), 123.9 (CH), 125.3 (CH), 127.2 (CH), 136.8 (qC), 162.3 (N–C=), 191.3 (O=C).