



SUPPLEMENTARY MATERIAL TO
**K-10 clay as a reusable catalyst for the solvent-free,
MW-induced synthesis of enamines**

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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, m, aromatic), 11.38 (1H, s, NH); ¹³C-NMR (125 MHz, CDCl₃, δ / ppm): 15.8 (CH₂CH₃), 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, m, aromatic), 11.21 (1H, s, NH); ¹³C-NMR (125 MHz, CDCl₃, δ / ppm): 14.2 (CH₂CH₃), 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, m, aromatic), 11.06 (1H, s, NH); ¹³C-NMR (125 MHz, CDCl₃, δ / ppm): 14.3 (CH₂CH₃), 18.5 (CH₃), 22.3 (CH₃CH), 56.0 (CH₂CH₃), 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; $^1\text{H-NMR}$ (500 MHz, CDCl_3 , 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); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ / ppm): 14.2 (CH_2CH_3), 24.5 (CH_3), 49.7 ($\text{CH}_2\text{C}=\text{}$), 61.4 (CH_2CH_3), 82.3 ($=\text{CH}$), 116.9 ($=\text{CH}_2$), 134.4 ($=\text{CH}-\text{CH}_2$), 161.8 ($\text{N}-\text{C}=\text{}$), 170.5 ($\text{O}=\text{C}$).

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; $^1\text{H-NMR}$ (500 MHz, CDCl_3 , 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); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ / ppm): 14.2 (CH_2CH_3), 18.7 (CH_3), 46.3 (NCH_3), 57.3 (CH_2CH_3), 80.3 ($=\text{CH}$), 162.3 ($\text{N}-\text{C}=\text{}$), 171.3 ($\text{O}=\text{C}$).

3-Phenylamino-but-2-enoic acid methyl ester (6). Oil, IR (neat, cm^{-1}): 3454, 3092, 2940, 1639, 1524, 1252, 1149, 1125, 1078, 912, 737; $^1\text{H-NMR}$ (500 MHz, CDCl_3 , 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); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ / ppm): 14.6 (CH_2CH_3), 54.3 (OCH_3), 91.2 ($=\text{CH}$), 122.4 (CH), 129.1 (CH), 129.6 (CH), 139.1 (qC), 160.2 ($\text{N}-\text{C}=\text{}$), 179.9 ($\text{O}=\text{C}$).

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; $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ / ppm): 1.38 (3H, s), 1.80 (3H, s), 3.43 (3H, s), 4.61 (1H, s), 6.75–7.19 (4H, m, aromatic), 10.48 (1H, s, NH); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ / ppm): 14.0 (CH_2CH_3), 18.5 (CH_3), 51.9 (PhCH_3), 84.4 ($=\text{CH}$), 123.8 (CH), 126.5 (CH), 127.2 (CH), 131.3 (CH), 135.0 (qC), 136.1 (CH_3-C aromatic), 160.4 ($\text{N}-\text{C}=\text{}$), 170.8 ($\text{O}=\text{C}$).

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; $^1\text{H-NMR}$ (500 MHz, CDCl_3 , 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); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ / ppm): 14.8 (OCH_2CH_3), 20.1 (CH_3), 50.1 (OCH_3), 62.3 (OCH_2CH_3), 84.3 ($=\text{CH}$), 115.2 (CH), 127.1 (CH), 131.8 (qC), 156.9 ($\text{O}-\text{C}$ aromatic), 160.1 ($\text{N}-\text{C}=\text{}$), 170.5 ($\text{O}=\text{C}$).

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; $^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ / ppm): 1.26 (3H, s), 1.97 (3H, d, $J = 4.7$ Hz), 2.25 (3H, s), 4.23 (1H, m), 5.11 (1H, s), 7.24–7.45 (5H, m aromatic), 10.56 (1H, s, NH); $^{13}\text{C-NMR}$ (125 MHz, CDCl_3 , δ / ppm): 22.4 (CH_3), 24.6 (CHCH_3), 27.4 (COCH_3), 56.2 (CHCH_3), 95.0 ($=\text{CH}$), 126.4 (CH), 126.5 (CH), 128.3 (CH), 141.5 (qC), 160.1 ($\text{N}-\text{C}=\text{}$), 195.7 ($\text{O}=\text{C}$).

4-Methylamino-3-penten-2-one (10). M.p. 36–38 °C; IR (KBr, cm^{-1}): 3269, 3082, 2988, 1651, 1639, 1560, 1281, 1154, 1063, 974, 787; ^1H -NMR (500 MHz, CDCl_3 , δ / ppm): 1.94 (3H, s), 1.98 (3H, s), 2.85 (3H, d, J = 5.6 Hz), 11.86 (1H, s, NH); ^{13}C -NMR (125 MHz, CDCl_3 , δ / ppm): 18.1 (CH_3), 28.3 (NCH_3), 29.1 (OCCCH_3), 94.8 ($=\text{CH}$), 163.7 ($\text{N}-\text{C}=\text{}$), 192.8 ($\text{O}=\text{C}$).

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, CDCl_3 , 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); ^{13}C -NMR (125 MHz, CDCl_3 , δ / ppm): 19.5 (CH_3), 28.7 (OCCCH_3), 96.9 ($=\text{CH}$), 124.5 (CH), 125.3 (CH), 128.7 (CH), 139.0 (qC), 159.8 ($\text{N}-\text{C}=\text{}$), 195.2 ($\text{O}=\text{C}$).

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, CDCl_3 , 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, s), 6.61–6.98 (4H, m, aromatic), 10.18 (1H, s, NH); ^{13}C -NMR (125 MHz, CDCl_3 , δ / ppm): 14.8 (CH_2CH_3), 19.8 (CH_3), 27.8 (COCH_3), 63.5 (CH_2CH_3), 96.4 ($=\text{CH}$), 113.5 (CH), 121.1 (CH), 122.3 (CH), 123.8 (CH), 130.4 (qC), 154.2 ($\text{O}-\text{C}$ aromatic), 159.6 ($\text{N}-\text{C}=\text{}$), 195.6 ($\text{O}=\text{C}$).

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, CDCl_3 , 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); ^{13}C -NMR (125 MHz, CDCl_3 , δ / ppm): 17.8 (PhCH_3), 19.6 (CH_3), 27.5 (COCH_3), 97.6 ($=\text{CH}$), 123.5 (CH), 126.4 (CH), 127.4 (CH), 131.3 (CH_3-C aromatic), 135.8 (CH), 136.6 (qC), 159.7 ($\text{N}-\text{C}=\text{}$), 196.1 ($\text{O}=\text{C}$).

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, CDCl_3 , δ / ppm): 1.97 (3H, s), 2.21 (3H, s), 5.20 (1H, s), 6.31–7.14 (4H, m, aromatic), 11.68 (1H, s, NH); ^{13}C -NMR (125 MHz, CDCl_3 , δ / ppm): 18.5 (CH_3), 23.4 (COCH_3), 96.8 ($=\text{CH}$), 122.3 (CH), 124.7 (CH), 125.6 (CH), 134.7 (CH), 135.6 ($\text{C}-\text{Cl}$), 141.1 (qC), 158.2 ($\text{N}-\text{C}=\text{}$), 195.9 ($\text{O}=\text{C}$).

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, CDCl_3 , 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); ^{13}C -NMR (125 MHz, CDCl_3 , δ / ppm): 18.7 (CH_3), 22.6 (COCH_3), 57.3 (CH_2), 80.3 ($=\text{CH}$), 123.9 (CH), 125.3 (CH), 127.2 (CH), 136.8 (qC), 162.3 ($\text{N}-\text{C}=\text{}$), 191.3 ($\text{O}=\text{C}$).