

Supporting Information

Bimetallic Ag-Cu Alloy Nanoparticles as Highly Active Catalyst for Enamination of 1, 3 dicarbonyl Compounds

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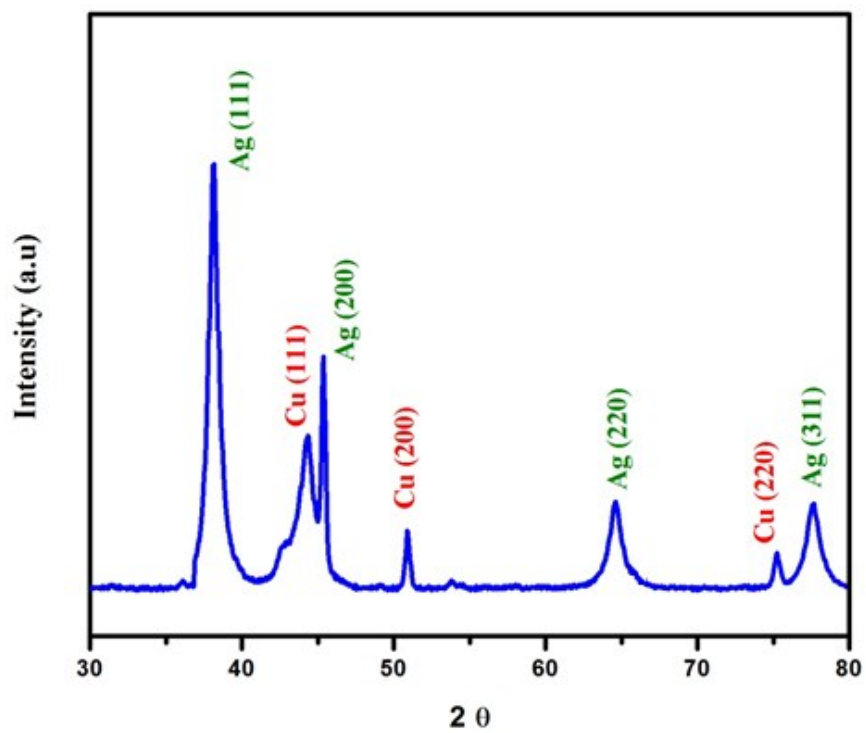


Fig. S1. XRD pattern of $\text{Ag}_1\text{-Cu}_3$ after 4 cycles of catalytic reaction.

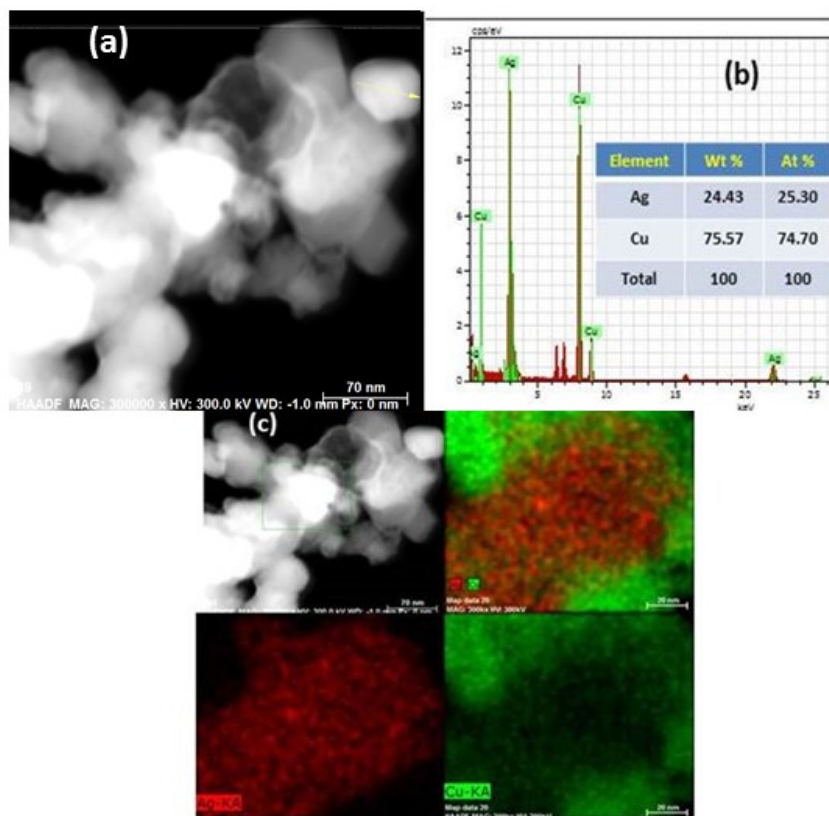
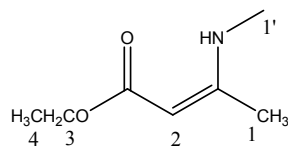


Fig. S2. (a) TEM micrograph (b) EDX and (c) EDS mapping of Ag_1-Cu_3 after 4th cycle of catalytic reaction.

^1H and ^{13}C of some selected compounds

(Z)-Ethyl 3-(methyl amino) but-2-enoate (Table 6, Entry 1)



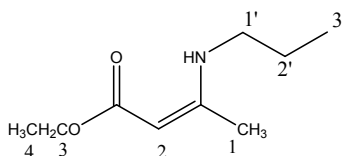
Yellow oil

% purity: 88

^1H NMR (400MHz, CDCl_3) δ (ppm): 8.47 (brs, 1H, NH), 4.42 (s, 1H, 2-CH), 4.04 (q, 2H, 3- CH_2), 2.85 (d, 3H, 1'- CH_3), 1.82 (s, 3H, 1- CH_3), 1.21 (t, 3H, 4- CH_3)

^{13}C NMR (100MHz, CDCl_3) δ (ppm): 14.2, 19.1, 29.2, 5.2, 81.7, 162.5, 170.4.

(Z)-Ethyl 3-(propyl amino)but-2-enoate (Table 6, Entry 2)



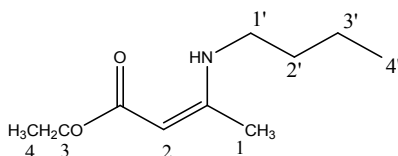
Yellow oil

% purity: 85

^1H NMR (400 MHz, TMS, CDCl_3) δ (ppm): 8.59 (s, 1H, NH), 4.45 (s, 1H, 2-CH), 4.07-4.11 (m, 2H, 3- CH_2), 3.10-3.15 (m, 2H, 1'- CH_2), 1.87 (s, 3H, 1- CH_3), 1.52-1.58 (m, 2H, 2'- CH_2), 1.19-1.22 (t, 3H, 4- CH_3), 0.92-0.95 (t, 3H, 3'- CH_3).

^{13}C NMR (100 MHz, TMS, CDCl_3) δ (ppm): 11.2, 14.5, 19.2, 23.5, 44.4, 58.1, 83.5, 161.8, 170.53.

Ethyl 3-(butyl amino) but-2-enoate (Table 6, Entry 3)



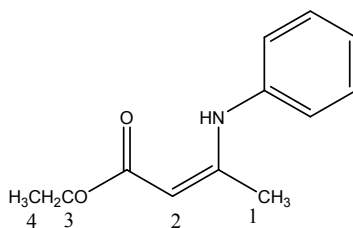
Yellow oil

% purity: 90

^1H NMR (400 MHz, TMS, CDCl_3) δ (ppm): 9.12 (s, 1H, NH), 4.61 (s, 1H, 2-CH), 4.18 (m, 2H, 3- CH_2), 3.25 (t, 2H, 1'- CH_2), 1.94 (s, 3H, 1- CH_3), 1.39-1.61 (m, 4H, 2', 3'- CH_2), 1.28 (t, 3H, 4- CH_3), 0.96 (t, 3H, 4'- CH_3).

^{13}C NMR (100 MHz, TMS, CDCl_3) δ (ppm): 13.4, 18.4, 20.2, 28.3, 32.4, 42.6, 59.1, 95.0, 163.1, 194.1.

Ethyl 3-(phenyl amino)but-2-enoate (Table 6, Entry 4)



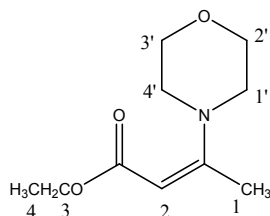
Yellow oily liquid

% purity: 95

^1H NMR (400 MHz, TMS, CDCl_3) δ (ppm): 10.39 (s, 1H, NH), 7.32–7.36 (m, 2H, 2 x ArH), 7.09–7.17 (m, 3H, 3 x ArH), 4.71 (s, 1H, 2-CH), 4.14–4.20 (m, 2H, 3- CH_2), 2.01 (s, 3H, 1- CH_3), 1.27 (m, 3H, 4- CH_3).

^{13}C NMR (100 MHz, TMS, CDCl_3) δ (ppm): 170.4, 158.97, 139.35, 129.05, 124.92, 124.44, 86.01, 58.76, 20.32, 14.59.

Ethyl 3-morpholinobut-2-enoate (Table 6, Entry 5)



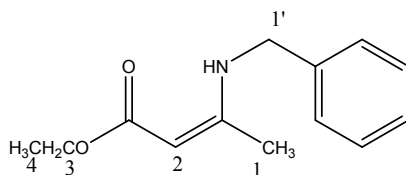
Yellow solid

m.p-55-56 °C

^1H NMR (400 MHz, TMS, CDCl_3) δ (ppm): 4.77 (s, 1H, 2-CH), 4.05-4.10 (m, 2H, 3- CH_2), 3.66-3.71 (m, 4H, 2', 3'- CH_2), 3.19-3.23 (m, 4H, 1', 4'- CH_2), 2.40 (s, 3H, 1- CH_3), 1.22-1.27 (m, 3H, 4- CH_3).

^{13}C NMR (100 MHz, TMS, CDCl_3) δ (ppm): 168.6, 160.9, 88.1, 66.0, 58.4, 46.1, 15.0, 14.2.

Ethyl 3-(benzyl amino)but-2-enoate (Table 6, Entry 6)



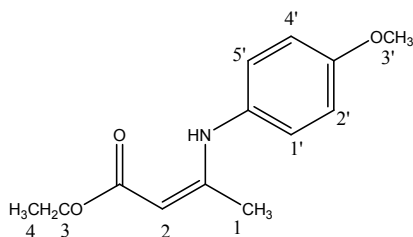
Yellow oily liquid

% purity: 90

^1H NMR (400 MHz, CDCl_3) δ (ppm): 1.2 (t, 3H, 4- CH_3), 1.90 (s, 3H, 1- CH_3), 4.10 (q, 2H, 3- CH_2), 4.42 (d, 2H, 1'- CH_2), 4.55 (s, 1H, 2-CH), 7.22–7.40 (m, 5H, ArH), 8.94 (br s, 1H, NH).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 14.7, 19.5, 24.1, 46.8, 58.5, 83.2, 126.8, 127.4, 128.8, 138.8, 161.0, 170.6.

Ethyl 3-(4-methoxyphenylamino)but-2-enoate (Table 6, Entry 8)



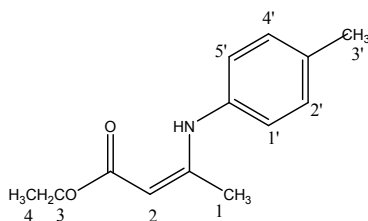
Yellow oil

% purity: 85

¹H NMR (CDCl₃, 400 MHz) δ (ppm): 1.29(t, 3H, 4-CH₃), 1.84 (s, 3H, 1-CH₃), 3.76 (s, 3H, b3'-CH₃), 4.10(q, 2H, 3-CH₂), 4.58 (s, 1H, 2-CH), 6.81 (d, 2H, 1'-4' CH, CH), 7.08 (d, 2H, 2'-5' CH, CH), 10.35 (brs, 1H, NH).

¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 14.4, 19.4, 55.3, 58.4, 84.6, 113.3, 126.8, 131.6, 157.3, 159.5, 170.3.

Ethyl 3-(p-Tolylamino)but-2-enoate (Table 6, Entry 9)



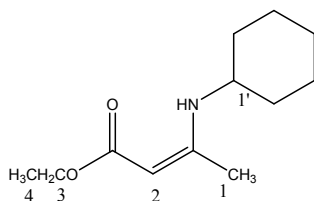
Yellow oil

% purity: 82

¹H NMR (400MHz, CDCl₃) δ (ppm): 10.36 (s, 1H, NH), 7.11–7.14 (m, 2H, 1'-4'- CH,CH), 6.92–6.96 (m, 2H, 2'-5'- CH,CH), 4.68 (s, 1H, 2-CH), 4.15 (q, 2H, 3-CH₂), 2.33 (s, 3H, 3'-CH₃), 1.91 (s, 3H, 1-CH₃), 1.26 (t, 3H, 4-CH₃).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 14.5, 20.1, 20.8, 58.6, 85.3, 124.6, 129.5, 134.6, 137.0, 159.3, 170.3.

Ethyl 3-(cyclohexylamino) but-2-enoate (Table 6, Entry 10)



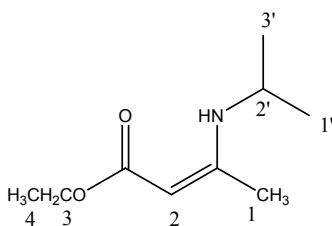
Yellow oily liquid

% purity: 94

¹H NMR (400MHz, CDCl₃) δ (ppm): 1.22 (t, 3H, 4-CH₃), 1.25–1.88 (m, 10H, cyclohexyl), 1.93 (s, 3H, 1-CH₃), 3.29–3.33 (m, 1H, 1'-CH), 4.07 (q, 2H, 3-CH₂), 4.38 (s, 1H, 2-CH), 8.63 (br, s, 1H).

¹³C NMR (100 MHz, CDCl₃) δ (ppm): 14.73, 19.21, 24.71, 25.47, 34.56, 51.41, 58.23, 60.36, 81.78, 160.79, 170.63.

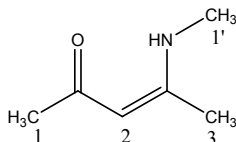
Ethyl 3-(isopropyl amino) but-2-enoate (Table 6, Entry 12)



% purity: 84

^1H NMR (400MHz, CDCl_3) δ (ppm): 1.24-1.31 (m, 9H, 4-1'-3'- CH_3), 1.98 (s, 3H, 1-CH), 3.64-3.78 (m, 1H, 2'-CH), 4.12 (q, 2H, 3- CH_2), 4.41 (s, 1H, 2-CH), 8.54 (brs, 1H, NH).

4-(methylamino) pent-3-en-2-one (Table 6, Entry 13)



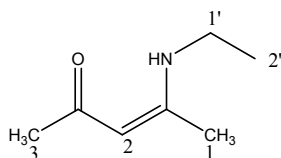
Yellowish oily liquid

% purity: 83

^1H NMR (400MHz, CDCl_3) δ (ppm): 5.13 (s, 1H, 2-CH), 2.12 (s, 3H, 1- CH_3), 3.1 (d, 3H, 1'- CH_3), 10.73 (s, 1H, NH), 1.98 (s, 3H, 3- CH_3).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 17.6, 25.9, 28.1, 94.4, 167.6, 193.2.

4-(ethyl amino)pent-3-en-2-one (Table 6, Entry 14)



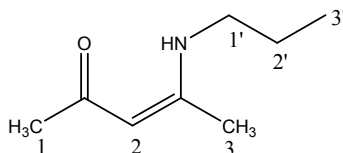
Yellowish oily liquid

% purity: 88

^1H NMR (400MHz, CDCl_3) δ (ppm): 5.12 (s, 1H, 2-CH), 4.23 (q, 2H, 1'- CH_2), 3.45 (t, 3H, 2'- CH_3), 2.12 (s, 3H, 3- CH_3), 1.92 (s, 3H, 1- CH_3), 10.83 (s, 1H, NH).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 15.3, 24.1, 28.1, 40.4, 100.3, 159.5, 196.2.

4-(propyl amino)pent-3-en-2-one (Table 6, Entry 15)



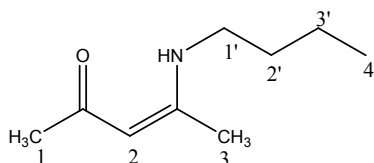
Yellow liquid

% purity: 82

^1H NMR (400MHz, CDCl_3) δ (ppm): 10.83 (brs, 1H, NH), 4.93 (s, 1H, 2-CH), 3.12-3.18 (m, 2H, 1'- CH_2), 1.94 (s, 3H, 1- CH_3), 1.88 (s, 3H, 3- CH_3), 1.48-1.62 (m, 2H, 2'- CH_2), 0.92-0.98 (m, 3H, 3'- CH_3).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 11.4, 18.2, 23.2, 28.2, 44.4, 94.8, 162.6, 194.1.

4-(butyl amino)pent-3-en-2-one (Table 6, Entry 16)



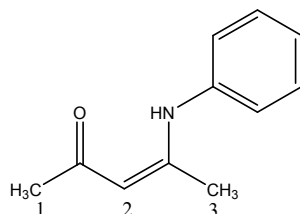
Yellow liquid

% purity: 91

^1H NMR (400MHz, CDCl_3) δ (ppm): 0.96 (t, 3H, CH_3), 1.38-1.42 (m, 2H, CH_2), 1.44-1.61 (m, 2H, CH_2), 1.92 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 3.21 (q, 2H, CH_2), 4.96 (s, 1H, CH), 10.87 (brs, 1H, NH);

^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 13.7, 20.5, 27.4, 27.8, 34.7, 49.4 95.0, 156.6, 194.6.

4-(phenyl amino) pent-3-en-2-one (Table 6, Entry 17)



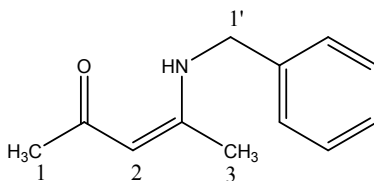
Pale yellow solid

m.p (45-47 °C)

^1H NMR (CDCl_3 , 400 MHz) δ 2.01 (s, 3H, 3- CH_3), 2.12 (s, 3H, 1- CH_3), 5.20 (s, 1H, 2-CH), 7.12-7.38 (m, 5H, Ar-H), 12.49 (brs, 1H, NH).

^{13}C NMR (CDCl_3 , 100 MHz) δ 19.3, 28.6, 97.2, 124.1, 125.0, 128.6, 138.2, 159.7, 195.5.

4-(benzylamino)pent-3-en-2-one (Table 6, Entry 19)



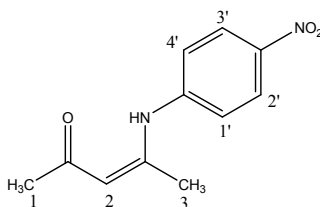
Yellow liquid

% purity: 81

^1H NMR (400MHz, CDCl_3) δ (ppm): 11.25 (br s, 1H, NH), 7.21-7.33 (m, 5H, C_6H_5), 5.05 (s, 1H), 4.31 (d, , 2H) 2.01 (s, 3H), 1.89 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 18.7, 286, 46.5, 95.6, 126.4, 127.1, 128.6, 137.6, 162.7, 195.2.

4-(4-nitrophenylamino) pent-3-en-2-one (Table 6, Entry 20)



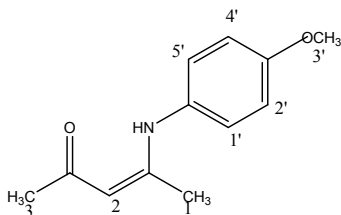
Orange solid

m.p-55-56 °C

^1H NMR (400MHz, CDCl_3) δ (ppm): 7.21 (d, 2H, 2', 4'-CH,CH), 8.22 (d, 2H,1'-3', CH, CH), 5.32 (s, 1H, 2-CH), 4.35 (s, 1H, NH), 2.12 (s, 3H,1- CH_3), 1.96 (s, 3H, 3- CH_3).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 38.7, 39.6, 98.0, 112.9, 126.1, 138.1, 145.8, 153.8, 195.2.

4-(p-methoxy phenyl amino) pent-3-en-2-one (Table 6, Entry 21)



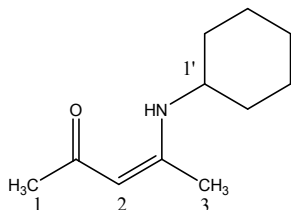
Pale yellow oil

% purity: 85

^1H NMR (400MHz, CDCl_3) δ (ppm): 12.34 (br, 1H, NH), 7.01(d, 2H, 1'-2', CH-CH), 6.84 (d, 2H, 2'-5', CH-CH), 5.13 (s, 1H, 2-CH), 3.81 (s, 3H, 3'-OCH₃), 2.18 (s, 3H, 3-CH₃), 1.93 (s, 3H, 1-CH₃).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 19.3, 28.6, 55.3, 96.3, 114.0, 126.6, 131.1, 157.6, 161.0, 195.7.

4-(cyclohexylamino) pent-3-en-2-one (Table 6, Entry 23)



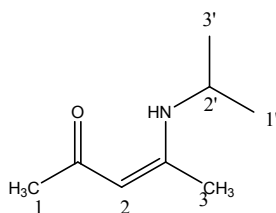
Yellow oil

% purity: 90

^1H NMR (400MHz, CDCl_3) δ (ppm): 1.22–1.77 (m, 10H, cyclohexyl), 1.79 (s, 3H, 3-CH₃), 1.85 (s, 3H, 1-CH₃), 3.24–3.29 (m, 1H, 1'-CH), 4.82 (s, 1H, 2-CH), 10.89 (br, s, 1H, NH).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 19.2, 24.07, 24.99, 29.54, 31.46, 51.13, 94.59, 161.56, 206.1.

4-(isopropyl amino) pent-3-en-2-one (Table 6, Entry 25)

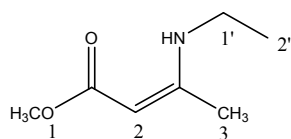


Yellowish oil

% purity: 83

^1H NMR (400MHz, CDCl_3) δ (ppm): δ 10.83 (br, 1H, NH), 4.91 (s, 1H, 2-CH), 3.71 (m, 1H, 2'-CH), 2.1 (s, 3H, 1-CH₃), 1.94 (s, 3H, 3-CH₃), 1.23 (d, 6H, 1'-3'-CH₃).

Methyl 3-(ethyl amino)but-2-enoate (Table 6, Entry 26)



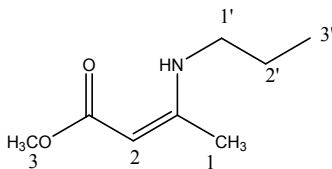
Yellowish oily liquid

% purity: 82

^1H NMR (400MHz, CDCl_3) δ (ppm): 10.82 (s, 1H, NH), 5.12 (s, 1H, 2-CH), 4.31 (m, 2H, 1'-CH), 3.41 (t, 3H, 2'- CH_3), 2.13 (s, 3H, 1- OCH_3) 1.81 (s, 3H, 3- CH_3).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 15.2, 24.1, 28.2, 40.4, 100.2, 159.2, 170.2.

Methyl 3-(propyl amino) but-2-enoate (Table 6, Entry 27)



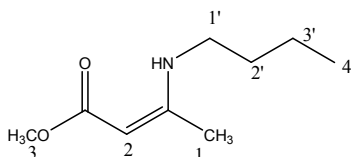
Orange solid

m.p- 46-48 °C

^1H NMR (400MHz, CDCl_3) δ (ppm): 8.21 (s, 1H, NH), 4.63 (s, 1H, 2-CH), 3.62 (s, 3H, 3- CH_3), 2.28 (m, 2H, 1'- CH_2), 1.53 (s, 3H, 1- CH_3), 1.23 (m, 2H, 2'- CH_2), 0.94 (t, 3H, 3'- CH_3).

^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 11.1, 18.6, 23.1, 28.4, 44.6, 94.8, 162.8, 171.2.

Methyl 3-(butyl amino) but-2-enoate (Table 6, Entry 28)



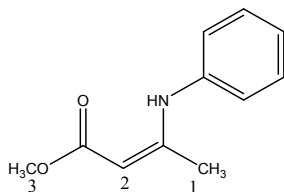
Yellowish oily liquid

% purity: 93

^1H NMR (400 MHz, TMS, CDCl_3) δ (ppm): 8.56 (s, 1H, NH), 4.40 (s, 1H, 2-CH), 3.19 (m, 2H, 1'- CH_2), 1.91 (s, 3H, 3- OCH_3), 1.89 (s, 3H, 1- CH_3), 1.46–1.57(m, 2H, 2'- CH_2), 1.29–1.38 (m, 2H, 3'- CH_2), 0.86 (m, 3H, 4'- CH_3).

^{13}C NMR (100 MHz, TMS, CDCl_3) δ (ppm): 13.5, 19.6, 22.7, 28.4, 31.8, 42.2, 94.6, 162.9, 173.2.

Methyl 3-(phenyl amino)but-2-enoate (Table 6, Entry 29)



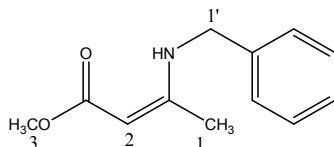
Yellowish oily liquid

% purity: 88

^1H NMR (400 MHz, TMS, CDCl_3) δ (ppm): 2.01 (s, 3H, 1- CH_3), 3.70(s, 3H, 3- OCH_3), 4.71 (s, 1H, 2-CH), 7.18 (m, 3H, Ar-H), 7.20-7.34 (m, 2H, Ar-H), 10.37 (br s, 1H, NH).

^{13}C NMR (100 MHz, TMS, CDCl_3) δ (ppm): 24.1, 28.0, 96.8, 114.2, 117.1, 128.2, 136.8, 160.1, 170.5.

Methyl 3-(benzyl amino) but-2-enoate (Table 6, Entry 31)



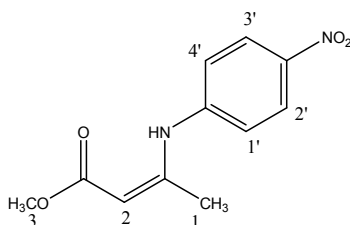
Yellowish oily liquid

% purity: 86

^1H NMR (400 MHz, TMS, CDCl_3) δ (ppm): 1.92 (s, 3H, 1- CH_3), 3.63 (s, 3H, 3-O CH_3), 4.43 (d, 2H, 1'- CH_2), 4.53 (s, 1H, 2-CH), 7.24-7.28 (m, 3H, Ar-H), 7.32-7.36 (m, 2H, Ar-H), 8.95 (br s, 1H, NH).

^{13}C NMR (100 MHz, TMS, CDCl_3) δ (ppm): 19.4, 46.8, 50.1, 82.6, 126.4, 127.2, 128.6, 138.5, 162.1, 170.6.

Methyl 3-(4-nitrophenylamino)but-2-enoate (Table 6, Entry 32)



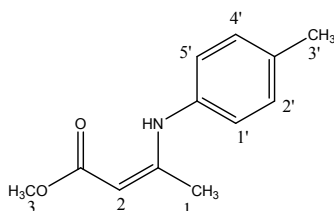
Yellowish oily liquid

% purity: 84

^1H NMR (400 MHz, TMS, CDCl_3) δ (ppm): 1.31 (s, 3H, 1- CH_3), 2.22 (s, 3H, 3-O CH_3), 4.86 (s, 1H, 2-CH), 7.11 (d, 2H, Ar-H), 8.17 (d, 2H, Ar-H), 11.1 (br s, 1H, NH).

^{13}C NMR (100 MHz, TMS, CDCl_3) δ (ppm): 20.8, 50.6, 91.0, 120.5, 125.2, 145.6, 155.7, 159.1, 170.1.

Methyl 3-(p-tolyl amino) but-2-enoate (Table 6, Entry 34)



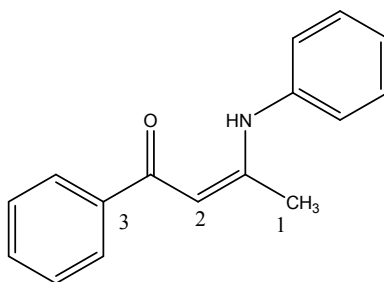
Yellow Oily liquid

% purity: 81

^1H NMR (400 MHz, TMS, CDCl_3) δ (ppm): 1.95 (s, 3H, 1- CH_3), 2.33 (s, 3H, 3-O CH_3), 3.66 (s, 3H, 3'- CH_3), 4.65 (s, 1H, 2-CH), 6.95 (d, 2H, ArH), 7.12 (d, 2H, ArH), 10.32 (br s, 1H, NH).

^{13}C NMR (100 MHz, TMS, CDCl_3) δ (ppm): 20.1, 20.7, 50.1, 85.1, 124.5, 129.4, 130.6, 136.5, 159.4, 170.7.

1-phenyl-3-(phenyl amino)but-2-en-1-one (Table 6, Entry 39)



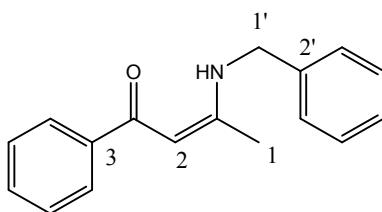
Yellow Oil

% purity: 90

^1H NMR (400 MHz, TMS, CDCl_3) δ (ppm): 2.11 (s, 3H, 1- CH_3), 5.84 (s, 1H, 2-CH), 7.13–7.24 (m, 3H, ArH), 7.31–7.43 (m, 3-ArXH), 7.90–7.95 (m, 2H, ArH), 11.8 (brs, 1H, NH).

^{13}C NMR (100 MHz, TMS, CDCl_3) δ (ppm): 20.4, 93.3, 122.8, 126.8, 127.8, 128.6, 129.1, 131.1, 138.5, 140.2, 162.2, 188.5.

3-(benzyl amino)-1-phenylbut-2-en-1-one (Table 6, Entry 40)



Yellow Oily liquid

% purity: 92

^1H NMR (400 MHz, TMS, CDCl_3) δ (ppm): 2.07 (s, 3H, 1- CH_3), 4.52 (d, 2H, 1'- CH_2), 5.73 (s, 1H, 2-CH), 7.20–7.42 (m, 8H, ArH), 7.85–7.82 (m, 2H, Ar-H), 12.31 (bs, 1H, NH).

^{13}C NMR (100 MHz, TMS, CDCl_3) δ (ppm): 9.5, 47.3, 92.6, 126.8, 127.1, 127.6, 128.2, 128.9, 130.6, 137.8, 140.3, 165.0.