Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Graphene Oxide-SnO_2 Nanocomposite as an Efficient Catalyst for Synthesis of *β*-enaminones and *β*-enaminoesters

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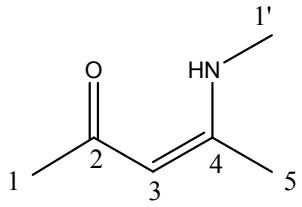
Spectral analysis data of some selected compound

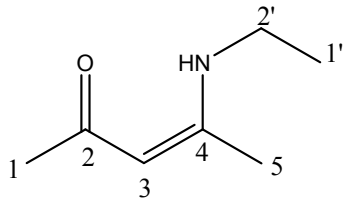
(Z)-4-(methylamino) pent-3-en-2-one (Table 2, entry 1)



Yellowish Oily liquid

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 10.78 (s, 1H, NH), 5.12 (s, 1H, 3-CH), 3.1 (d, 3H, 1'-CH_3), 2.91 (s, 3H, 1-CH_3), 1.38 (s, 3H, 5-CH_3)
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 193.20 (C-2), 167.72 (C-4), 94.42 (C-3), 28.10 (C-1'), 25.86 (C-1), 17.70 (C-5).

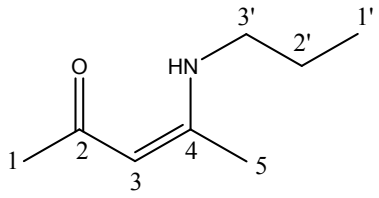
(Z)-4-(ethylamino) pent-3-en-2-one (Table 2, entry 2)



Yellowish oily liquid

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 10.82 (s, 1H, NH), 5.12 (s, 1H, 3-CH), 4.3 (m, 2H, 2'-CH), 3.42 (t, 3H, 1'-CH_3), 2.38 (s, 3H, 1-CH_3), 2.12 (s, 3H, 5-CH_3).
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 196.30(C-2), 159.45(C-4), 100.24(C-3), 40.51(C-2'), 28.10(C-1), 24.16(C-5), 15.30(C-1').

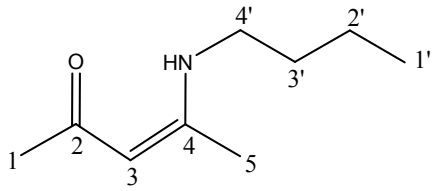
(Z)-4-(propylamino) pent-3-en-2-one (Table 2, entry 3)



Yellow liquid

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 10.82 (brs, 1H, NH), 4.91 (s, 1H, 3-CH), 3.12-3.18 (m, 2H, 2'-CH_2), 1.94 (s, 3H, 1-CH_3), 1.88 (s, 3H, 5-CH_3), 1.48-1.62 (m, 2H, 3'-CH_2), 0.92-0.98 (m, 3H, 1'-CH_3).
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 194.2(C-2), 162.8(C-4), 94.8(C-3), 44.6(C-3'), 28.4(C-1), 23.1(C-2'), 18.6(C-5), 11.1(C-1').

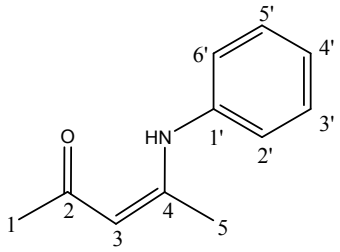
(Z)-4-(butylamino) pent-3-en-2-one (Table 2, entry 4)



Yellow liquid

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 10.82 (s, 1H, NH), 4.89 (s, 1H), 3.19 (m, 2H), 1.96 (s, 3H), 1.89 (s, 3H), 1.46–1.57(m, 2H), 1.29–1.38 (m, 2H), 0.86 (m, 3H)
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 194.3(C-2), 162.9(C-4), 94.7(C-3), 42.4(C-4'), 31.9(C-3'), 28.5(C-1), 22.8(C-5), 19.7(C-2'), 13.5(C-1').

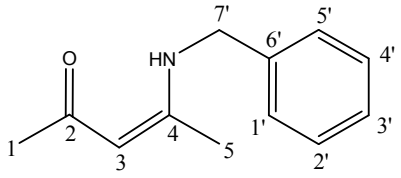
(Z)-4-(phenylamino) pent-3-en-2-one (Table 2, entry 5)



Yellow liquid

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 12.49 (brs, 1H, NH), 7.12–7.38 (m, 5H, 5 x ArH), 5.21 (s, 1H, 3-CH), 2.12 (s, 3H, 1-CH_3), 2.01 (s, 3H, 5-CH_3).
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 195.11(C-2), 159.60 (C-4), 137.81(C-1'), 128.32(C-3', C-5'), 117.08(C-4'), 114.19(C-2', C-6'), 96.92(C-3), 28.18(C-1), 24.21(C-5).

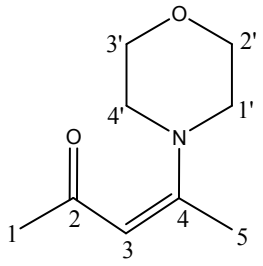
(Z)-4-(benzylamino) pent-3-en-2-one (Table 2, entry 6)



Yellow liquid

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 11.17 (s, 1H, NH), 7.22–7.34 (m, 5H, 5 x ArH), 5.03 (s, 1H, 3-CH), 4.44 (d, 2H, 7'-CH_2), 2.02 (s, 3H, 1-CH_3), 1.88 (s, 3H, 5-CH_3).
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 195.1(C-2), 162.9(C-4), 138.02(C-6'), 128.6(C-2',C-4'), 127.2(C-3'), 126.5(C-1',C-5'), 95.92(C-3), 46.72(C-7'), 28.91(C-1), 22.92(C-5).

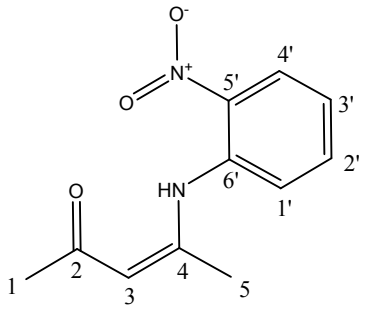
(Z)-4-morpholinopent-3-en-2-one (Table, entry 7)



Yellow oily liquid

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 5.24 (s, 1H), 3.68-3.75 (m, 4H, 2', 3'-CH_2), 3.30-3.36 (m, 4H. 1', 4'-CH_2), 2.47 (s, 3H, 1-CH_3), 2.01 (s, 3H, 5-CH_3)
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 197.5(C-2), 162.6(C-4), 96.9(C-3), 68.5(C-2', C-3'), 45.8(C-1', C-4'), 30.7(C-1), 15.1(C-5).

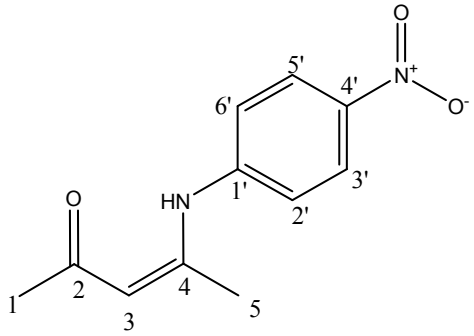
(Z)-4-(2-nitrophenylamino) pent-3-en-2-one (Table, entry 8)



Orange solid

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 10.38 (s, 1H, NH), 7.32-7.02 (m, 4H, 4 x ArH), 2.01 (s, 3H, 1-CH_3), 1.46 (s, 3H, 5-CH_3).
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 197.01(C-2), 157.80(C-4), 141.80(C-6'), 138.13(C-2'), 136.21(C-5'), 126.10(C-4'), 121.67(C-3'), 117.92(C-1'), 97.06(C-3), 39.76(C-1), 29.41(C-5).

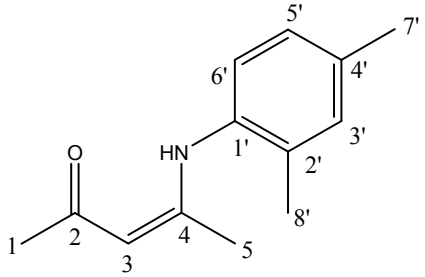
(Z)-4-(4-nitrophenylamino) pent-3-en-2-one (Table 2, entry 9)



Yellow solid

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 12.76 (s, 1H, NH), 8.20–8.20 (m, 2H, 2 x ArH), 7.22-7.20 (m, 2H, 2 x ArH), 5.36 (s, 1H, 3-CH), 2.21 (s, 3H, 1-CH_3), 2.11 (s, 3H, 5-CH_3).
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 198.10(C-2), 157.14(C-4), 145.40(C-1'), 143.52(C-4'), 125.26(C-3', C-5'), 122.22(C-2', C-6'), 102.11(C-3), 29.68(C-1), 20.64(C-5).

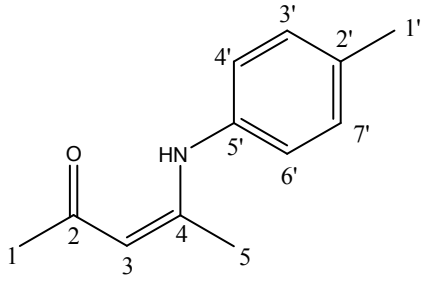
(Z)-4-(2, 4-dimethylphenylamino) pent-3-en-2-one (Table 2, entry 10)



Yellow solid

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 11.92 (1H, s, NH), 7.13-7.06 (m, 3H, ArH), 5.21(s, 1H), 2.19 (s, 6H, 7', 8'-CH_3), 2.11 (s, 3H, 1-CH_3)1.62 (s, 3H, 5-CH_3).
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 195.87(C-2), 162.82(C-4), 137.92(C-1'), 128.09(C-2',C-4'), 127.32(C-3'), 126.41(C-5'), 118.22(C-6'), 95.68(C-3), 28.91(C-1), 24.81(C-7'), 21.79(C-5'), 18.12(C-8').

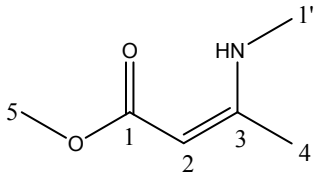
(Z)-4-(p-tolylamino) pent-3-en-2-one (Table 2, entry 11)



Yellow solid

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 12.40 (s, 1H, NH), 7.22–7.04 (m, ArH), 5.18 (s, 1H, 3-CH), 2.36 (s, 3H, 1'-CH_3), 2.13 (s, 3H, 1- CH_3), 1.96 (s, 3H, 5- CH_3).
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 195.94(C-2), 160.68(C-4), 136.12(C-5'), 135.56(C-3', C-7'), 129.66(C-2'), 124.88(C-4', C-6'), 97.09(C-3), 29.19(C-1), 20.95(C-1'), 19.78(C-5).

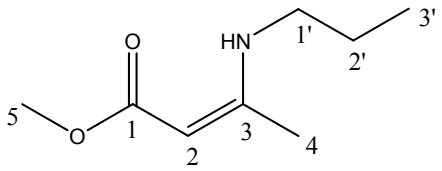
(Z)-methyl 3-(methylamino)but-2-enoate (Table 2, entry 12)



Yellow oil

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 8.48 (s, 1H, NH), 4.48(s, 1H, 3-CH), 3.63 (s, 3H, 5-CH_3), 2.91 (d, 3H, 1'-CH_3), 1.93 (s, 3H, 4-CH_3).
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 170.71 (C-1), 162.12 (C-2), 82.02 (C-2), 49.7 (C-5), 29.86 (C-1'), 19.02 (C-4).

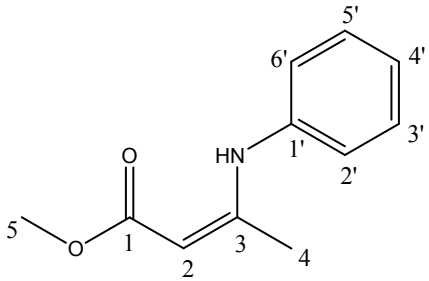
(Z)-methyl 3-(propylamino)but-2-enoate (Table 2, entry 14)



Orange solid

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 8.24 (s, 1H, NH), 4.06 (s, 1H, 2-CH), 3.21 (s, 3H, 5-CH_3), 2.28 (m, 2H, 1'-CH_2), 1.53 (s, 3H, 4-CH_3), 1.23 (m, 2H, 2'-CH_2), 0.94 (t, 3H, 3'-CH_3).
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 173.2(C-1), 163.1(C-3), 89.4(C-2), 68.8(C-5), 60.1(C-1'), 53.6(C-2'), 18.8(C-4), 12.2 (C-3').

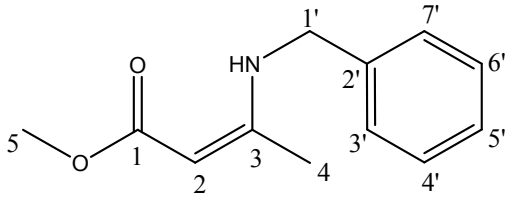
(Z)-methyl 3-(phenylamino)but-2-enoate (Table 2, entry 16)



Yellow liquid

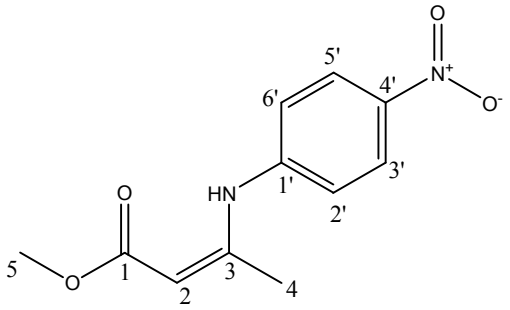
^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 10.37 (s, 1H, NH), 7.34 (m, 2H, 2 x ArH), 7.12 (m, 3H, 3 x 3H), 4.66 (s, 1H, 3-CH), 3.64 (s, 3H, 1-CH_3), 1.98 (s, 3H, 5-CH).
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 170.02(C-1), 159.04(C-3), 139.31(C-1'), 128.98 (C-3', C-5'), 125.03 (C-4'), 124.44(C-2', C-6'), 85.63(C-2), 50.19(C-5), 20.20(C-4).

(Z)-methyl 3-(benzylamino)but-2-enoate (Table 2, entry 17)



Yellow liquid
^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 8.94 (s, 1H, NH), 7.32–7.26 (m, 2H, 2 x ArH), 7.23 (m, 3H, 3 x ArH), 4.53 (s, 1H, 3-CH), 4.42 (m, 2H, 1'-CH_2), 3.63 (s, 3H, 1-CH_3), 1.93 (s, 3H, 5-CH_3).
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 170.61(C-1), 161.71(C-3), 138.48(C-2'), 128.62(C-4', C-8'), 127.21(C-5'), 126.53(C-3', C-7'), 82.72(C-2), 50.12(C-5), 46.82(C-1'), 19.46(C-4).

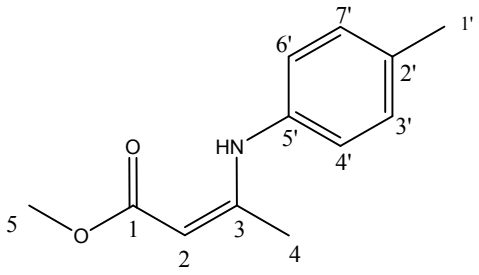
(Z)-methyl 3-(4-nitrophenylamino)but-2-enoate (Table 2, entry 20)



Yellow liquid

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 10.86 (s, 1H, NH), 8.14 (m, 2H, 2 x ArH), 7.12–7.09 (m, 2H, 2x ArH), 4.87 (s, 1H, 2-CH), 3.70 (s, 3H, 5-CH_3), 2.18 (s, 3H, 4-CH_3).
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 170.30(C-1), 159.22(C-3), 155.86(C-1'), 145.72(C-4'), 125.30(C-3', C-5'), 120.74(C-2',C-6'), 91.11(C-2), 50.74(C-5), 20.91(C-4).

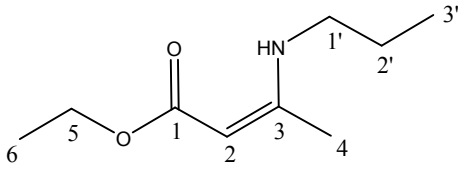
(Z)-methyl 3-(p-tolylamino)but-2-enoate (Table 2, entry 22)



Yellow Oily liquid

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 10.12(s, 1H, NH), 7.23–7.02 (m, 4H, 4 x ArH), 4.70 (s, 1H), 3.68 (s, 3H, 1'-CH_3), 2.28 (s, 3H, 1- CH_3), 1.86 (s, 3H, 5-CH_3).
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 170.93(C-1), 159.91(C-3), 137.94(C-5'), 130.81 (C-3', C-7'), 126.34(C-2'), 123.02(C-4', C-6'), 84.82(C-2), 50.03(C-1'), 19.97(C-5), 18.01(C-4).

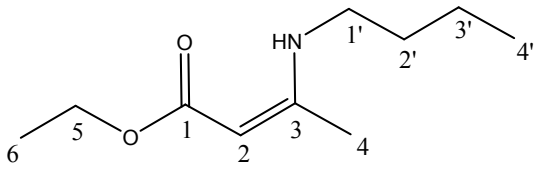
(Z)-ethyl 3-(propylamino)but-2-enoate (Table 2, entry 25)



Yellow liquid

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 8.54 (s, 1H, NH), 4.39 (s, 1H, 2-CH), 4.01-4.07 (m, 2H,5-CH_2), 3.10-3.15 (m, 2H,1'-CH_2), 1.87 (s, 3H,4-CH_3), 1.52-1.58 (m, 2H,2'-CH_2), 1.19-1.22 (m, 3H,6-CH_3), 0.92-0.95 (m, 3H,3'-CH_3).
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 170.52(C-1), 161.81(C-3), 83.47(C-2), 58.01(C-5), 44.52(C-1'), 23.58(C-2'), 19.23(C-4), 14.57(C-6), 11.21(C-3').

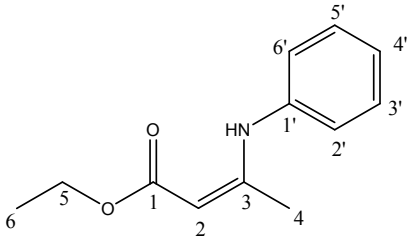
(Z)-ethyl 3-(butylamino)but-2-enoate (Table, entry 26)



Yellow liquid

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 9.14 (s, 1H, NH), 4.60 (s, 1H,2-CH), 4.18 (m, 2H,5-CH_2), 3.26 (m, 2H,1'-CH_2), 1.94 (s, 3H,4-CH_3), 1.38-1.62 (m, 4H,2',3'-CH_2), 1.29 (t, 3H,6-CH_3), 0.97 (t, 3H,4'-CH_3).
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 194.16(C-1), 163.12(C-3), 95.01(C-2), 59.02(C-5), 42.57(C-1'), 32.38(C-2'), 28.30(C-4), 20.26(C-3'), 18.38(C-6), 13.42(C-4').

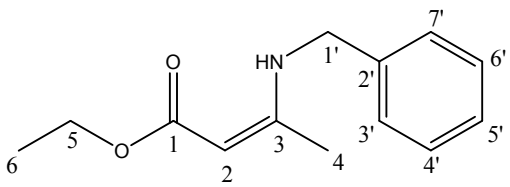
(Z)-ethyl 3-(phenylamino)but-2-enoate (Table, entry 27)



Yellow oily liquid
^{1}H 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), 4.14–4.19 (m, 2H, 5-CH_2), 2.01 (s, 3H, 4-CH_3), 1.27 (m, 3H,6-CH_3).

^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 170.25(C-1), 158.81(C-3), 139.23(C-1'), 128.93(C-3',C-5'), 124.78(C-4'), 124.26(C-2',C-6'), 85.94(C-2), 58.63(C-5), 20.16(C-4), 14.48(C-6).

(Z)-ethyl 3-(benzylamino)but-2-enoate (Table, entry 28)

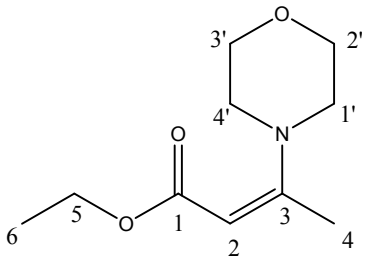


Yellow liquid

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 10.31 (s, 1H, NH), 7.13 (m, 2H,2 x ArH), 6.98 (m, 3H,3 x ArH), 4.69 (s, 1H,2-CH), 4.18 (m, 4H,5 and 1'-CH_2), 1.93 (s, 3H,4-CH_3), 1.27 (m, 3H,6-CH_3).

^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 170.66(C-1), 162.82(C-3), 138.85(C-2'), 128.81(C-4',C-6'), 127.46(C-3',C-7'), 126.82(C-5'), 83.21(C-2), 58.51(C-5), 46.86(C-1'), 24.15(C-4), 14.73(C-6).

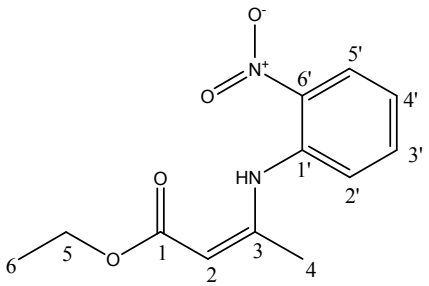
(Z)-ethyl 3-morpholinobut-2-enoate (Table, entry 29)



Yellow solid

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 4.78 (s, 1H, 2-CH), 4.06-4.12 (m, 2H, 5-CH_2), 3.69-3.73 (m, 4H, 2', 3'-CH_2), 3.19-3.23 (m, 4H,1', 4'-CH_2), 2.40 (s, 3H,4-CH_3), 1.22-1.27 (m, 3H,6-CH_3)
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 168.6(C-1), 160.9(C-3), 88.1(C-2), 66.0(C-2', C-3'), 58.4(C-1', C-4'), 46.1(C-5), 15.0(C-4), 14.2(C-6).

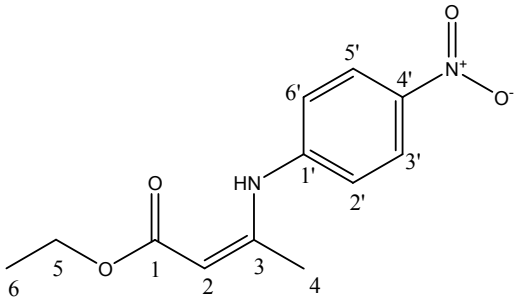
(Z)-ethyl 3-(2-nitrophenylamino)but-2-enoate (Table, entry 30)



Orange solid

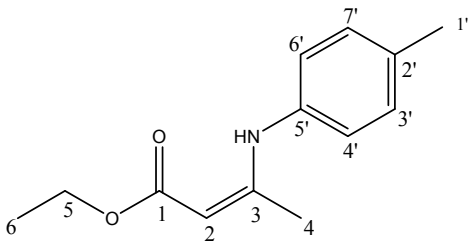
^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 9.79 (s, 1H, NH), 7.27 (m, 1H,5'-CH), 7.08 (m, 1H,3'-CH), 6.92 (d, 1H,4'-CH), 6.58 (m, 1H,2'-CH), 4.75 (s, 1H,2-CH), 4.17 (m, 2H,5-CH_2), 1.65 (s, 3H,CH_3), 1.29 (m, 3H,6-CH_3).
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 170.45(C-1), 160.59(C-3), 141.08(C-1'), 128.55(C-3'), 127.92(C-6'), 126.90(C-5'), 123.36(C-4'), 118.11(C-2'), 84.86(C-2), 61.74(C-5), 18.43(C-4), 14.45(C-6).

(Z)-ethyl 3-(4-nitrophenylamino)but-2-enoate (Table, entry 31)



Yellow solid
^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 10.96 (s, 1H, NH), 8.24 (d, 2H, 2H, 2 x ArH), 7.15 (d, 2H, 2H, 2 x ArH), 4.90 (s, 1H,2-CH), 4.25 (m, 2H,5-CH_2), 2.26 (s, 3H,4-CH_3), 1.34 (m, 3H,6-CH_3).
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 167.23(C-1), 162.04(C-3), 152.25(C-1'), 139.05(C-4'), 122.65(C-3', C-5'), 119.14(C-2', C-6'), 84.46(C-2), 61.57(C-5), 21.26(C-4), 14.45(C-6).

(Z)-ethyl 3-(p-tolylamino)but-2-enoate (Table, entry 33)



Yellow solid

^{1}H NMR (400 MHz, TMS, $CDCl_3$) δ (ppm): 10.28 (s, 1H, NH), 7.16–6.98 (m, 4H, 4 x ArH), 4.69 (s, 1H, 2-CH), 4.16–4.13 (m, 2H, 5-CH_2), 2.34 (s, 3H, 1'-CH_3), 1.98 (s, 3H,4-CH_3), 1.30 (m, 3H,6-CH_3).
^{13}C NMR (100 MHz, TMS, $CDCl_3$) δ (ppm): 170.43(C-1), 159.28(C-3), 136.71(C-5'), 134.83(C-3', C-7'), 129.58(C-2'), 124.69(C-4', C-6'), 85.29(C-2), 58.56(C-5), 20.81(C-1'), 20.14(C-4), 14.76(C-6).