

Supplementary data

Penicillin G acylase catalyzed Markovnikov addition of allopurinol to vinyl ester

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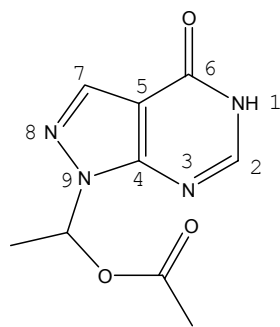
3a: A solution of 0.50g (3.68mmol) allopurinol and 0.50g immobilized penicillin G acylase from *Escherichia. coli* (3.5.1.11, 100U/g) in 10ml DMSO was incubated at 50 °C and 200 r.p.m. (orbitally shaken) for 5 minutes. Then, the vinyl acetate (0.63g, 7.36mmol) was added in order to initiate the reaction. After 96h, the reaction was terminated by filtering off the enzyme. The DMSO was removed by evaporation under reduced pressure (80 mmHg, 0.5mmHg). The crude product was purified by chromatography on silica gel by eluting with petroleum/ethyl acetate (1:8, by vol) (0.39 g, 47.7% yield). ¹H NMR (DMSO-*d*₆, 500 MHz, δ, ppm): 11.76(s, 1H, O=CNH), 8.70 (s, 1H, N=CH-NH), 7.97 (s, 1H, N=CH-), 6.91 (q, 1H, *J*=6.00Hz, N-CH-O-C=O), 2.05 (s, 3H, O=C-CH₃), 1.79 (d, 3H, *J*=6.05Hz, -CH-CH₃). ¹³C NMR (DMSO-*d*₆, 125 MHz, δ, ppm): 169.71 (-O-C=O), 159.30 (-NH-C=O), 159.14(C4), 148.13 (C2), 129.88 (C7), 107.62 (C5), 80.81 (-N-CH-O-), 21.14 (O=C-CH₃), 19.83 (CH₃ of -CH-CH₃). IR (cm⁻¹): 3435 (ν_{N-H}), 3179, 3068 (ν_{N=C-H}), 1746 (ν_{O-C=O}), 1677 (ν_{N-C=O}), 1277, 1231, 1181, 1140 (ν_{C-O} and ν_{C-N}). ESI-MS: *m/z*=222.7(M+1). [α]_D²⁰/MeOH: -24.43°.

3b: This was prepared from allopurinol (0.5g, 3.68mmol), immobilized penicillin G acylase (0.5g) and vinyl pentanoate (0.94g, 7.36mmol) by the same method as **3a**. (0.31g, 31.9%). ¹H NMR (DMSO-*d*₆, 500 MHz, δ, ppm): 11.82(s, 1H, O=CNH), 8.71 (s, 1H, N=CH-N), 7.98 (s, 1H, N=CH-), 6.92 (q, 1H, *J*=6.00Hz, N-CH-O-C=O), 2.32 (t, 2H, O=C-CH₂-), 1.78 (d, 3H, *J*=5.89Hz, -CH-CH₃), 1.46, 1.23 (m, 4H, -CH₂-CH₂-), 0.81 (t, 3H, -CH₂-CH₃). ¹³C NMR (DMSO-*d*₆, 125 MHz, δ, ppm): 172.35 (-O-C=O), 159.33 (-NH-C=O), 159.24 (C4), 148.21 (C2), 129.92 (C7), 107.62 (C5), 80.78 (-N-CH-O-), 33.48 (O=C-CH₂), 26.77, 21.97 (-CH₂-CH₂-), 19.88 (CH₃ of -CH-CH₃), 14.08 (CH₃ of -CH₂-CH₃). IR (cm⁻¹): 3433 (ν_{N-H}), 3192, 3072 (ν_{N=C-H}), 1735 (ν_{O-C=O}), 1686 (ν_{N-C=O}), 1277, 1241, 1175, 1110 (ν_{C-O} and ν_{C-N}). ESI-MS: *m/z*=264.8(M+1). [α]_D²⁰/MeOH: -9.74°

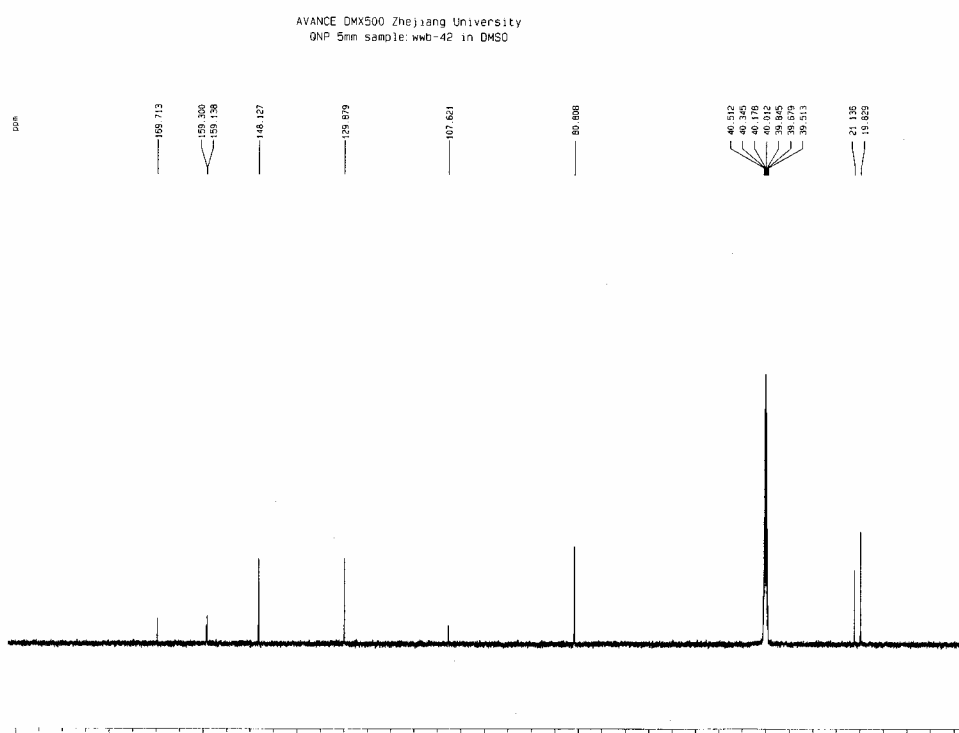
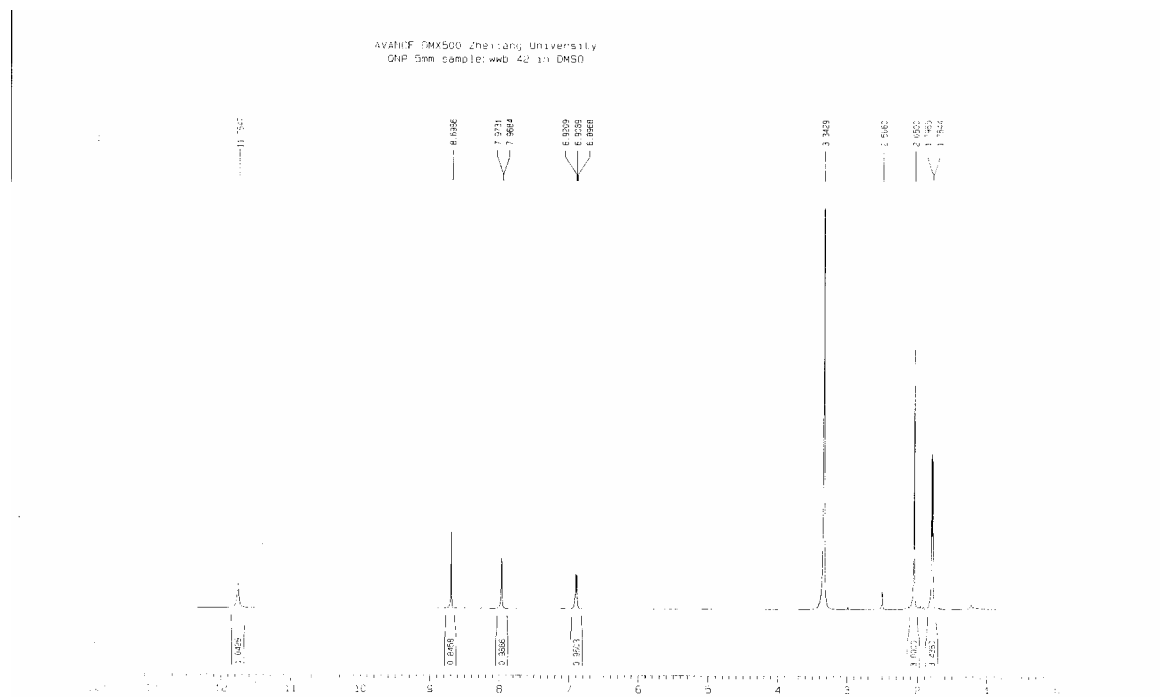
3c: This was prepared from allopurino (0.5g , 3.68mmol), immobilized penicillin G acylase (0.5g) and vinyl decanoate (1.46g, 7.36mmol) by the same method as **3a**. (0.26 g, 21.2%). ¹H NMR (DMSO-*d*₆, 500 MHz, δ, ppm): 11.85 (s, 1H, O=CNH), 8.69 (s, 1H, N=CH-N), 7.96 (s, 1H, N=CH-), 6.92 (q, 1H, *J*=6.12Hz, N-CH-O-C=O), 2.31 (t, 2H, O=C-CH₂-), 1.78 (d, 3H, *J*=6.09Hz , -CH-CH₃), 1.47, 1.23, 1.16 (m, 14H, -(CH₂)₇-), 0.84 (t, 3H, -CH₂-CH₃). ¹³C NMR (DMSO-*d*₆, 125 MHz, δ, ppm): 172.22 (-O-C=O), 159.25 (-NH-C=O), 159.08 (C4), 148.02 (C2), 129.80 (C7), 107.57 (C5), 80.62 (-N-CH-O-), 33.70 (CH₂ of O=C-CH₂), 31.70, 29.25, 29.03, 29.01, 28.64, 24.64, 22.52 (-(CH₂)₇-), 19.75 (CH₃ of -CH-CH₃), 14.41 (CH₃ of -CH₂-CH₃). IR (cm⁻¹): 3448 (ν_{N-H}), 3190, 3071 (ν_{N=C-H}), 1736 (ν_{O-C=O}), 1675 (ν_{N-C=O}), 1272, 1241, 1171, 1142 (ν_{C-O} and ν_{C-N}). ESI-MS: *m/z*=335.0(M+1). [α]_D²⁰/MeOH: +7.58°

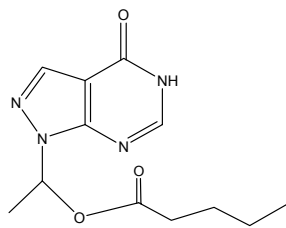
3d: This was prepared from allopurino (0.5g , 3.68mmol), immobilized penicillin G acylase (0.5g) and divinyl sebacate (1.87g, 7.36mmol) by the same method as **3a**. (0.35 g, 24.4%). ¹H NMR (DMSO-*d*₆, 500 MHz, δ, ppm): 11.80 (s, 1H, O=CNH), 8.70 (s, 1H, N=CH-N), 7.97 (s, 1H, N=CH-), 7.22 (m, 1H, -CH=CH₂), 6.92 (q, 1H, *J*=6.10Hz, N-CH-O-C=O), 4.87 (d, 1H, -CH=CH₂), 4.64 (d, 1H, -CH=CH₂), 2.39 (t, 2H, O=C-CH₂-), 2.31 (t, 2H, O=C-CH₂-), 1.78 (d, 3H, *J*=6.10Hz , -CH-CH₃), 1.50, 1.20 (m, 12H, -(CH₂)₆-). ¹³C NMR (DMSO-*d*₆, 125 MHz, δ, ppm): 172.50 (-O-C=O), 171.17 (-O-C=O), 159.41 (-NH-C=O), 159.37 (C4), 148.26 (C2), 141.89 (CH of -CH=CH₂), 130.09 (C7), 107.69 (C5), 98.72 (CH₂ of -CH=CH₂), 80.83 (-N-CH-O-), 33.88 (O=C-CH₂), 33.66 (O=C-CH₂), 29.09, 29.05, 28.86, 28.76, 24.79, 24.66, (-(CH₂)₆-), 19.39 (CH₃ of -CH-CH₃). IR (cm⁻¹): 3319 (ν_{N-H}), 3189, 3070 (ν_{N=C-H}), 1755 (ν_{O-C=O}), 1690 (ν_{N-C=O}), 1272, 1215, 1169, 1087 (ν_{C-O} and ν_{C-N}). ESI-MS: *m/z*=390.9(M+1). [α]_D²⁰/MeOH: +5.85°

3e: This was prepared from allopurino (0.5g , 3.68mmol), immobilized penicillin G acylase (0.5g) and vinyl benzoate (1.09g, 7.36mmol) by the same method as **3a**. (0.014 g, 1.3%). ¹H NMR (DMSO-*d*₆, 500 MHz, δ, ppm): 11.83 (s, 1H, O=CNH), 8.85 (s, 1H, N=CH-N), 7.97 (m, 3H, N=CH- and 2H of phenyl), 7.70, 7.54 (m, 3H, 3H of phenyl), 7.18 (q, 1H, *J*=6.05Hz, N-CH-O-C=O), 1.94 (d, 3H, *J*=6.06Hz , -CH-CH₃). IR (cm⁻¹): 3435 (ν_{N-H}), 3265, 3079 (ν_{N=C-H}, ν_{Ar-H}), 1730 (ν_{O-C=O}), 1660 (ν_{N-C=O}), 1603, 1486 (δ_{Ar}), 1272, 1235, 1178, 1099 (ν_{C-O} and ν_{C-N}). ESI-MS: *m/z*=284.8(M+1).

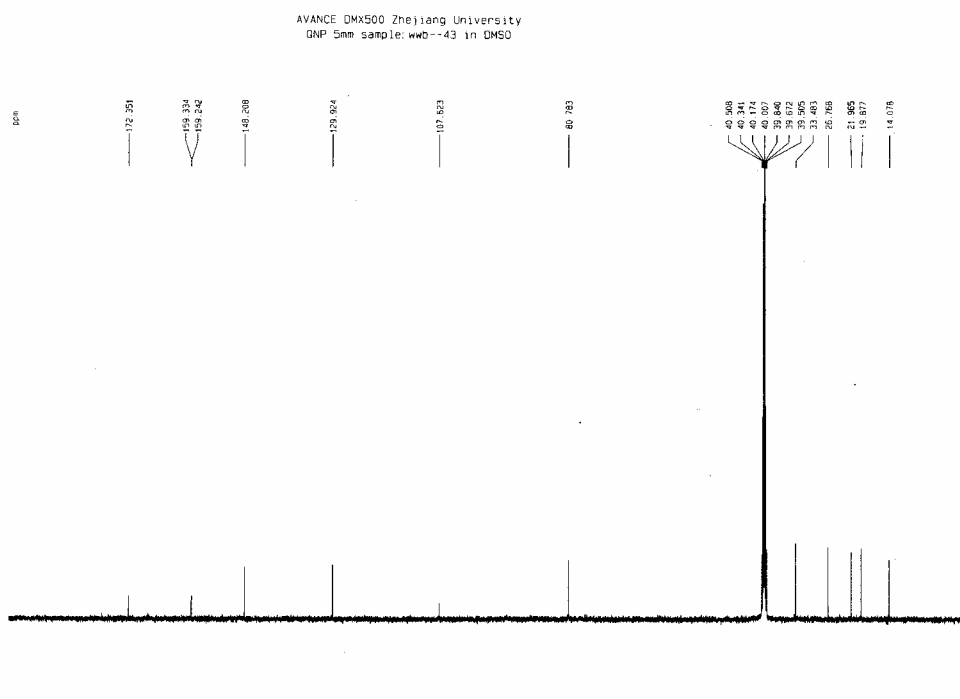
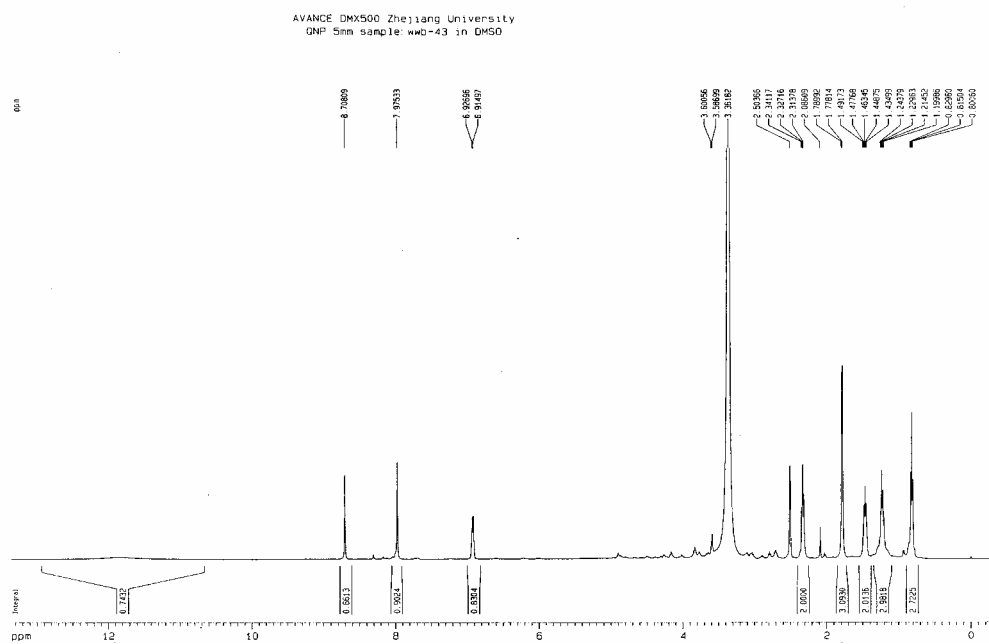


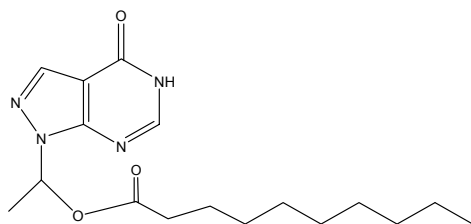
3a



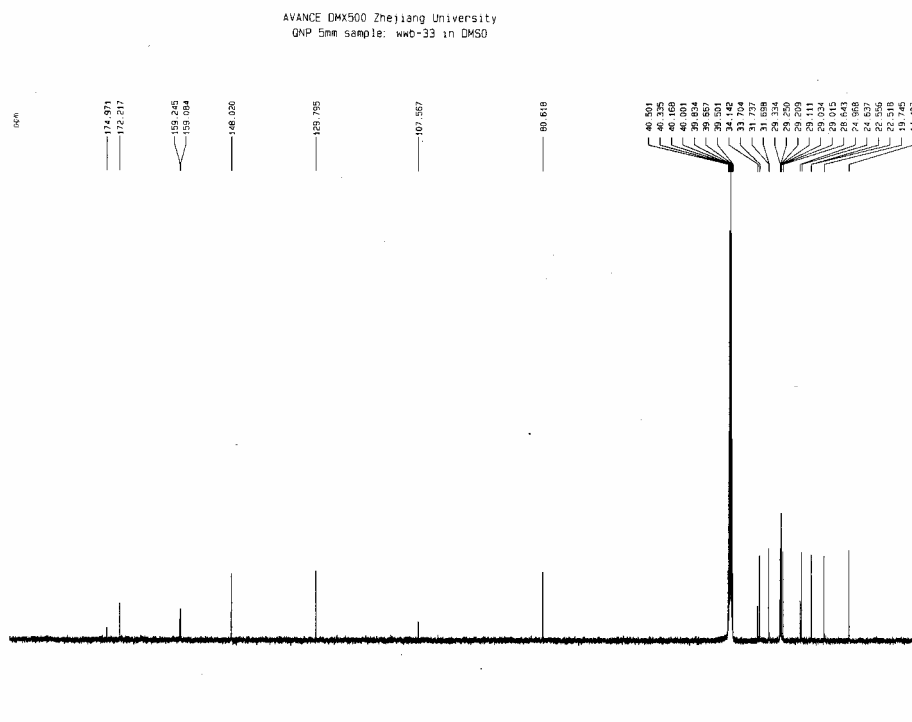
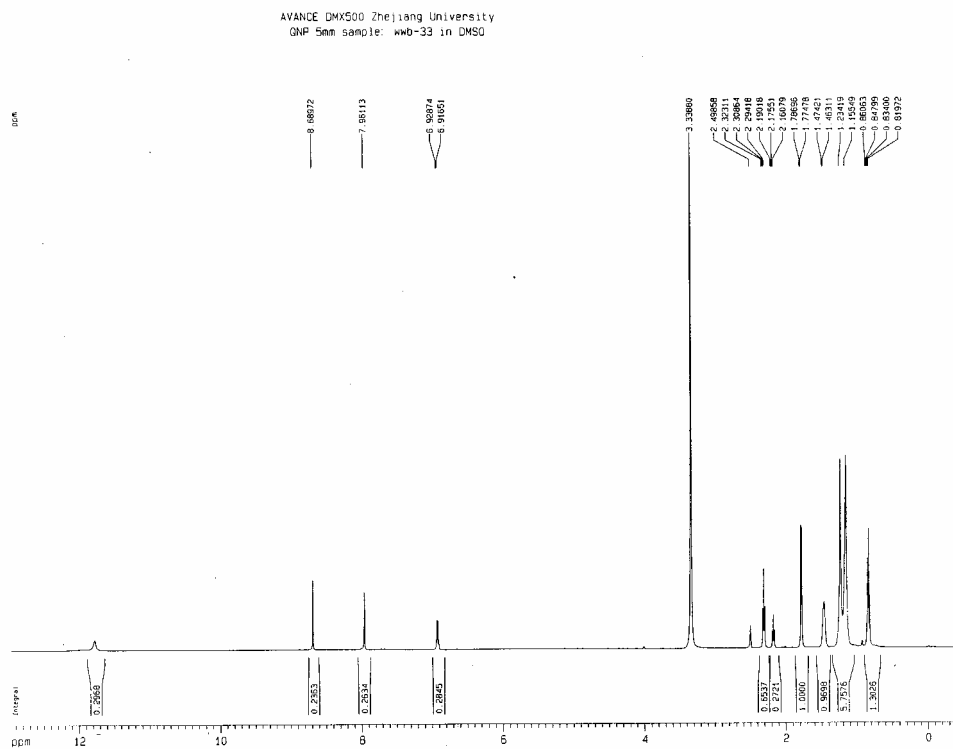


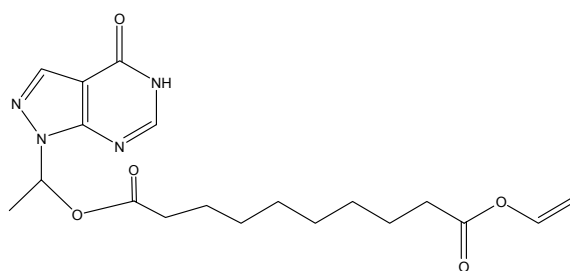
3b





3c





3d

