Supplementary Information for:

Microwave-assisted [3+2]-cycloadditions of azomethine ylides

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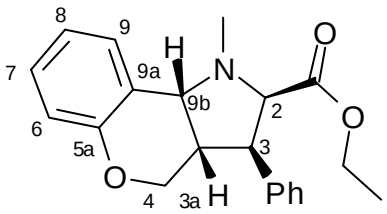
Compound 7b:

(2R, 3S, 3aS, 9bR ; 2S, 3aR, 9bS)-2-Ethoxycarbonyl-1-methyl-3-phenyl-4*H*-[1]benzopyrano[4,3-*b*]pyrrolidine

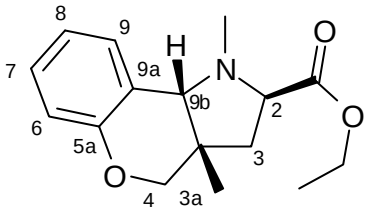


In a pyrex test tube (2x15), *O*-(3-phenyl)-allylsalicylaldehyde **4b** (1mmol), ethyl sarcosinate **6a** (2mmol) and xylene (0.5 mL) were submitted to microwave irradiation (CEM *Discover* apparatus. Settings: 130°C, 100W) during 5 minutes. After cooling, the crude reaction mixture was purified by flash column chromatography on silica gel (CH_2Cl_2, Rf: 0.32) to provide product **7b** in 89% yield as a viscous oil.

IR (ν cm^{-1}): 3077vw, 3056vw, 3028vw, 1606vw, 1581 w, 759s, 700s (C_6H_5, 1,2-disub.-C_6H_4); 1721vs (C=O); 1191vs (C-O), **^{1}H NMR** ($CDCl_3$, 300MHz): 7.40-7.16 (m, 7H, H_7, H_9, C_6H_5); 7.04-6.92 (m, 2H, H_8, H_6); 4.40 (d, 1H, $H_{9b\beta}$, J 9.6Hz); 4.10-3.82 (m, 6H, $2H_4$, CH_2O, H_2, H_3); 3.50-3.42 (m, 1H, $H_{3a\beta}$); 2.54 (s, 3H, CH_3N); 0.90 (t, 3H, CH_3CH_2), **^{13}C NMR** ($CDCl_3$, 75MHz): 171.8 (C=O); 156.8 (C_{5a}); 137.1 ($C_{1'}$); 129.8 (C_9); 128.6, 128.5 ($C_{2'}$, $C_{6'}$, $C_{3'}$, $C_{5'}$); 128.4, 127.4 ($C_{4'}$, C_7); 126.1 (C_{9a}); 121.5, 118.0 (C_8, C_6); 72.3 (C_2); 68.5 (C_4); 60.2 (C_{9b}); 58.9 (CH_2O); 48.5 (C_3); 43.2 (C_{3a}); 36.0 (CH_3N), 13.9 (CH_3CH_2); **MS (EI) m/z(%):** 337 ($M^{+\cdot}$, 3); 265 [($M^{+\cdot}$-$C_3H_4O_2$), 42]; 264 [($M^{+\cdot}$-$C_3H_5O_2$), 100]; 131 [$C_9H_7O^+$, 70], 91 [$C_7H_7^+$,48]; 77 [$C_6H_5^+$,23]; 42 [$C_2H_4N^+$, 45].

Compound 7d:

(2R, 3aR, 9bR ; 2S, 3aS, 9bS)-2-Ethoxycarbonyl-1,3a-dimethyl-4*H*-[1]benzopyrano[4,3-*b*]pyrrolidine

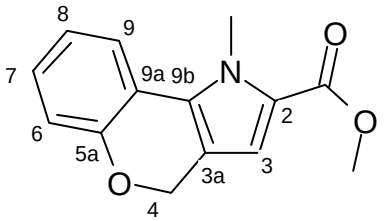


In a pyrex test tube (2x15), *O*-methallylsalicylaldehyde **4d** (1mmol), ethyl sarcosinate **6a** (1mmol) and xylene (0.5 mL) were submitted to microwave irradiation (Settings: 130°C, 100W) during 20min. After a few minutes of cooling, a further half equivalent of ethyl sarcosinate **6a** (0.5mmol) was added and the mixture was heated under irradiation again for 10min. After cooling and column chromatography on silica gel (CH_2Cl_2, Rf: 0.39), the product **7d** was isolated as a colorless viscous oil in 98% yield.

IR (ν cm^{-1}): 3070w, 3035w, 1609s, 1583s, 758vs (1,2-disub.C_6H_4); 1729vs (C=O); 1227vs, 1180vs (C-O); **^{1}H NMR** ($CDCl_3$, 300MHz): 7.24-7.19 (m, 2H, H_7, H_9); 6.92-6.86 (m, 2H, H_6, H_8); 4.22 and 4.20 (AB of ABX_3 system, 2H, CH_2O, J 10.8, 7.2Hz); 3.96 (A of ABX system, 1H, $H_{4\alpha}$, J 10.3Hz); 3.79 (dd, 1H, $H_{2\alpha}$, J 8.1, 4.7Hz); 3.69 (B of ABX system, 1H, $H_{4\beta}$, J 10.3 , 1.2Hz); 3.6 (s, 1H, $H_{9b\beta}$); 2.43 (s, 3H, CH_3N); 1.92 (A of ABX system, 1H, $H_{3\alpha}$, J 13.6, 8.1Hz); 1.88 (B of ABX system, 1H, $H_{3\beta}$, J 13.6, 4.8Hz); 1.31 (t, 3H, CH_3CH_2, J 7.2Hz); 1.10 (s, 3H, CH_3C);**^{13}C NMR**: ($CDCl_3$, 75MHz): 174.2 (C=O); 154.2 (C_{5a}); 132.5 and 132.0 (C_9, C_7); 120.0 (C_{9a}); 119.8 and 116.9 (C_6, C_8); 71.9 (C_4); 64.7 (C_{9b}); 63.4 (C_2); 60.3 (CH_2O); 38.0 (C_3, C_{3a}); 34.8 (CH_3N); 20.8 (CH_3C); 14.4 (CH_3CH_2); **MS (EI) m/z(%):** 275 ($M^{+\cdot}$, 3); 203 [($M^{+\cdot}$-$C_3H_4O_2$), 39]; 202 [($M^{+\cdot}$-$C_3H_5O_2$), 100]; 145 [($M^{+\cdot}$-$C_6H_{13}NO_2$), 59], 131 [$C_9H_7O^+$, 29], 77 [$C_6H_5^+$, 9]; 42 [$C_2H_4N^+$, 57]; 29 [$C_2H_5^+$, 15].

Compound 8a:

2-Carbomethoxy-N-methyl-1*H*,4*H*-[1]benzopyrano[4,3-*b*]pyrrole



O-Propargylsalicylaldehyde **5a** (1.5mmol) and methyl sarcosinate **6b** (3mmol) in xylene 0.5 mL, were irradiated in the presence of sulphur (7.25mmol) at a constant temperature setting of 130°C with a maximal

power output of 100W. After cooling, the reaction crude was filtered and the mixture was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (Ethyl acetate / pentane: 2/8, Rf: 0.54) to provide 8a in 70% yield.

IR : 3030w, 1605w, 1582w, 760m (1,2-disub.-C_6H_4) ; 1702s (C=O) ; 1230s and 1048w (C-O).
^{1}H NMR ($CDCl_3$, 300MHz): 7.55 (dd, 1H, H_9, *J* 7.6, 2.0 Hz) ; 7.26-6.90 (m, 3H, H_6, H_7 and H_8) ; 6.78 (s, 1H, H_3) ; 5.10 (s, 2H, $2H_4$) ; 4.18 (s, 3H, CH_3N) ; 3.82 (s, 3H, CH_3O);
^{13}C NMR ($CDCl_3$, 75MHz): 161.6 and 154.6 (C=O, C_{5a}) ; 131.0 and 123.8 (C_2, C_{9b}) ; 128.5 , 122.2 and 121.7 (C_7, C_8, C_9) ; 118.4 and 116.2 (C_{9a}, C_{3a}) ; 117.8 (C_6) ; 112.7 (C_3) ; 65.3 (C_4) ; 51.0 (CH_3O) ; 34.8 (CH_3N); **SM (IE) : m/z(%)** : 244 ($[M+H]^+$,15) ; 243 ($[M]^+$, 79) ; 242 ($[M-H]^+$, 100) ; 228 ($[M-CH_3]^+$, 2) ; 212 ($[M-OCH_3]^+$, 8) ; 184 ($[M-COOCH_3]^+$, 12) ; 170 ($[C_{11}H_8NO]^+$, 2) ; 169 ($[C_{11}H_7NO]^+$, 13).