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 (CH₂Cl₂, 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 (C₆H₅, 1,2-disub.-C₆H₄); 1721vs (C=O); 1191vs (C-O), **¹H NMR** (CDCl₃, 300MHz): 7.40-7.16 (m, 7H, H₇, H₉, C₆H₅); 7.04-6.92 (m, 2H, H₈, H₆); 4.40 (d, 1H, H_{9bβ}, J 9.6Hz); 4.10-3.82 (m, 6H, 2H₄, CH₂O, H₂, H₃); 3.50-3.42 (m, 1H, H_{3aβ}); 2.54 (s, 3H, CH₃N); 0.90 (t, 3H, CH₃CH₂), **¹³C NMR** (CDCl₃, 75MHz): 171.8 (C=O); 156.8 (C_{5a}); 137.1 (C_{1'}); 129.8 (C₉); 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 (C₈, C₆); 72.3 (C₂); 68.5 (C₄); 60.2 (C_{9b}); 58.9 (CH₂O); 48.5 (C₃); 43.2 (C_{3a}); 36.0 (CH₃N), 13.9 (CH₃CH₂); **MS (EI)** **m/z**(%): 337 (M⁺, 3); 265 [(M⁺-C₃H₄O₂), 42]; 264 [(M⁺-C₃H₅O₂), 100]; 131 [C₉H₇O⁺, 70], 91 [C₇H₇⁺, 48]; 77 [C₆H₅⁺, 23]; 42 [C₂H₄N⁺, 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 (CH₂Cl₂, 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.C₆H₄); 1729vs (C=O); 1227vs, 1180vs (C-O); **¹H NMR** (CDCl₃, 300MHz): 7.24-7.19 (m, 2H, H₇, H₉); 6.92-6.86 (m, 2H, H₆, H₈); 4.22 and 4.20 (AB of ABX₃ system, 2H, CH₂O, J 10.8, 7.2Hz); 3.96 (A of ABX system, 1H, H_{4 α} , J 10.3Hz); 3.79 (dd, 1H, H_{2 α} , J 8.1, 4.7Hz); 3.69 (B of ABX system, 1H, H_{4 β} , J 10.3, 1.2Hz); 3.6 (s, 1H, H_{9b β}); 2.43 (s, 3H, CH₃N); 1.92 (A of ABX system, 1H, H_{3 α} , J 13.6, 8.1Hz); 1.88 (B of ABX system, 1H, H_{3 β} , J 13.6, 4.8Hz); 1.31 (t, 3H, CH₃CH₂, J 7.2Hz); 1.10 (s, 3H, CH₃C); **¹³C NMR**: (CDCl₃, 75MHz): 174.2 (C=O); 154.2 (C_{5a}); 132.5 and 132.0 (C₉, C₇); 120.0 (C_{9a}); 119.8 and 116.9 (C₆, C₈); 71.9 (C₄); 64.7 (C_{9b}); 63.4 (C₂); 60.3 (CH₂O); 38.0 (C₃, C_{3a}); 34.8 (CH₃N); 20.8 (CH₃C); 14.4 (CH₃CH₂); **MS (EI) m/z(%)**: 275 (M⁺, 3); 203 [(M⁺-C₃H₄O₂), 39]; 202 [(M⁺-C₃H₅O₂), 100]; 145 [(M⁺-C₆H₁₃NO₂), 59], 131 [C₉H₇O⁺, 29], 77 [C₆H₅⁺, 9]; 42 [C₂H₄N⁺, 57]; 29 [C₂H₅⁺, 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.-C₆H₄) ; 1702s (C=O) ; 1230s and 1048w (C-O).

¹H NMR (CDCl₃, 300MHz): 7.55 (dd, 1H, H_b, *J* 7.6, 2.0 Hz) ; 7.26-6.90 (m, 3H, H₆, H₇ and H₈) ; 6.78 (s, 1H, H₃) ; 5.10 (s, 2H, 2H₄) ; 4.18 (s, 3H, CH₃N) ; 3.82 (s, 3H, CH₃O);

¹³C NMR (CDCl₃, 75MHz): 161.6 and 154.6 (C=O, C_{5a}) ; 131.0 and 123.8 (C₂, C_{9b}) ; 128.5 , 122.2 and 121.7 (C₇, C₈, C₉) ; 118.4 and 116.2 (C_{9a}, C_{3a}) ; 117.8 (C₆) ; 112.7 (C₃) ; 65.3 (C₄) ; 51.0 (CH₃O) ; 34.8 (CH₃N); **SM (IE) : m/z(%)** : 244 ([M+H]⁺, 15) ; 243 ([M]⁺, 79) ; 242 ([M-H]⁺, 100) ; 228 ([M-CH₃]⁺, 2) ; 212 ([M-OCH₃]⁺, 8) ; 184 ([M-COOCH₃]⁺, 12) ; 170 ([C₁₁H₈NO]⁺, 2) ; 169 ([C₁₁H₇NO]⁺, 13).