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Synthesis of nitrogen-containing benzoannulated eight- and nine-membered heterocycles from methyl 4-amino-3-iodobenzoate

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Methyl 4-amino-3-vinylbenzoate (2a) Tributyl(vinyl)stannane (5.30 ml, 18.0 mmol) and K_2CO_3 (10.0 g, 72.4 mmol) were added to solution of methyl 4-amino-3-iodobenzoate (5.00 g, 18.0 mmol) in mixture of toluene:ethanol (140 ml, 1:1) under argon atmosphere. Then, tetrakis(triphenylphosphine) palladium (0.500 g, 0.433 mmol) was added and the reaction mixture was heated at 90 ^oC for 8 h. The reaction mass was filtered, the filtrate was concentrated, dissolved in ethyl acetate and washed with 6% HCl, water and brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Column chromatography was done using (hexane/EtOAc, 80:20) as eluent to obtain 2.23 g of compound **2a** (69%). ^1H NMR (400 Mhz, $CDCl_3$) δ: 3.83 (s, 3H), 4.24 (bs, 2H), 5.31 (dd, J = 10.8, 1.2 Hz, 1H), 5.65 (dd, J = 17.2, 1.2 Hz, 1H), 6.60 (d, J = 8.3 Hz, 1H), 6.66 (dd, J = 17.2, 10.8 Hz, 1H), 7.73 (dd, J = 8.3, 2.0 Hz, 1H), 7.95 (d, J = 2.0Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 51.3, 114.6, 116.2, 119.1, 122.4, 129.1, 130.2, 131.6, 148.4, 167.1.

Methyl 3-allyl-4-aminobenzoate (2b) Yield 2.70 g (80%). ^1H NMR (400 MHz, $CDCl_3$) δ: 3.28 (d, J = 6.4 Hz, 2H), 3.83 (s, 3H), 4.14 (bs, 2H), 5.06–5.14 (m, 2H), 5.86–5.95 (m, 1H), 6.61 (d, J = 9.2 Hz, 1H), 7.74–7.75 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 36.2, 51.6, 114.6, 116.7, 119.7, 122.7, 129.8, 132.1, 135.2, 149.2, 167.4.

Methyl 3-vinyl-4-(2-vinylbenzoylamino)benzoate (4a) Freshly distilled thionyl chloride (10.0 ml, 137 mmol) and DMF (2 drops) were added to 2-vinylbenzoic acid (2.00 g, 14.3 mmol) and stirred at 85 ^oC for 2 h. Excess thionyl chloride was removed under vacuum to obtain compound **3**. Compound **2a** (2.00 g, 11.3 mmol) was dissolved in dry DCM in another flask under nitrogen and cooled to 0 ^oC, pyridine (5.50 ml, 68.3 mmol) was added and stirred for 10 min. Then, solution of compound **3** dissolved in DCM was added dropwise. The reaction mixture was stirred at 0 ^oC to room temperature for 12 h. The reaction mass was concentrated, the obtained slurry was dissolved in DCM and washed with 6% HCl, water and brine. The organic layer was dried

over Na_2SO_4 and concentrated under reduced pressure. Column chromatography was performed using (hexane/EA, 80:20) to obtain 1.81 g of compound **4a** (50%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.85 (s, 3H), 5.33 (dd, *J* = 11.0, 0.8 Hz, 1H), 5.38 (dd, *J* = 11.0, 0.8 Hz, 1H), 5.66 (dd, *J* = 7.0, 0.8 Hz, 1H), 5.72 (dd, *J* = 7.0, 0.8 Hz, 1H), 6.72 (dd, *J* = 17.4, 11.0 Hz, 1H), 7.05 (dd, *J* = 17.4, 11.0 Hz, 1H), 7.25 (td, *J* = 7.5, 0.8 Hz, 1H), 7.39 (td, *J* = 7.5, 0.8 Hz, 1H), 7.47 (s, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.87 (dd, *J* = 8.4, 1.8 Hz, 1H), 8.05 (d, *J* = 1.8 Hz, 1H), 8.12 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 51.9, 117.4, 119.3, 122.3, 126.4, 126.5, 127.5, 127.7, 128.4, 129. 5, 129.7, 130.7, 131.1, 134.2, 134.6, 136.1, 138.5, 166.4, 167.5.

Methyl 3-allyl-4-(2-vinylbenzoylamino)benzoate (4b) Yield 2.18 g (52%) ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.32 (d, *J* = 5.9 Hz, 2H), 3.77 (s, 3H), 4.90 (d, *J* = 17.1, Hz, 1H), 5.04 (t, *J* = 10.4, Hz, 1H),5.26 (d, *J* = 10.4 Hz, 1H), 5.64 (d, *J* = 17.1, Hz, 1H), 5.75–5.86 (m, 1H), 7.08 (dd, *J* = 11.1, 8.6 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.80–7.86 (m, 2H), 8.05 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 35.9, 51.7, 116.8, 117.0, 122.1, 126.2, 127.1, 127.5, 128.6, 130.4, 131.3, 133.9, 134.5, 134.8, 135.8, 138.2, 140.1, 166.2, 172.1.

Methyl 4-[*N*-(*tert*-butoxycarbonyl)-2-vinylbenzoylamino]-3-vinylbenzoate (5a) Triethylamine (0.900 ml, 6.50 mmol) was added to a solution of compound **4a** (1.00 g, 3.25 mmol) in dried DCM at 0 ^{o}C and stirred for 10 min. Di-*tert*-butyl-dicarbonate (1.42 g, 6.50 mmol) was added followed by addition of DMAP (0.120 g, 0.980 mmol) and the reaction mixture was stirred at 0 ^{o}C to room temperature for 12 h. The reaction mass was concentrated, the obtained slurry was dissolved in DCM and washed with 6% HCl, water and brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. Column chromatography was done using (hexane/EA, 70:30) to obtain 1.12 g, compound **5a** (85%). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.13 (s, 9H), 3.90 (s, 3H), 5.39 (dd, *J* = 11.1, 0.8 Hz, 1H), 5.47 (dd, *J* = 11.1, 0.8 Hz, 1H), 5.76 (dd, *J* = 17.5, 0.8 Hz, 1H), 5.89 (dd, *J* = 17.5, 0.8 Hz, 1H), 6.82 (dd, *J* = 17.5, 11.0 Hz, 1H), 7.03 (dd, *J* = 17.5, 11.0 Hz, 1H), 7.32 (d, *J* = 1.3 Hz, 1H), 7.35 (s, 1H), 7.39 (d, *J* = 1.3 Hz, 1H), 7.43 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.59 (d, *J* = 7.4 Hz, 1H), 8.02 (dd, *J* = 8.3, 1.9 Hz, 1H), 8.33 (d, *J* = 1.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 27.1, 52.1, 83.9, 117.0, 118.5, 125.8, 126.2, 127.2, 127.9, 129.1, 129.4, 129.9, 130.3, 130.9, 133.6, 135.5, 136.1, 136.4, 140.1, 151.5, 166.1, 171.2.

Methyl 3-allyl-4-[*N*-(*tert*-butoxycarbonyl)-2-vinylbenzoylamino]benzoate (5b) Yield 1.87 g (68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.14 (s, 9H), 3.43 (d, *J* = 6.5 Hz, 2H), 3.92 (s, 3H), 5.15–5.20 (m, 2H), 5.40 (dd, *J* = 11.1, 0.9 Hz, 1H), 5.78 (dd, *J* = 17.4, 0.9 Hz, 1H), 5.92–6.02 (m, 1H), 7.00 (dd, *J* = 17.4, 11.1 Hz, 1H), 7.31–7.35 (m, 2H), 7.41–7.45 (m, 2H), 7.61 (d, *J* = 7.7 Hz, 1H),

7.80 (dd, J = 8.1, 1.4 Hz, 1H), 8.04 (d, J = 1.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 27.4, 35.7, 52.3, 84.2, 117.2, 117.6, 126.0, 126.2, 127.4, 128.8, 129.2, 130.0, 130.6, 131.7, 133.8, 135.1, 135.7, 136.7, 138.6, 141.3, 151.8, 166.5, 171.4.