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Ionic liquid-promoted stereoselective [3+2] cycloaddition of 1-hetaryl-2-nitroethenes to azomethine imines generated *in situ*

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General procedure for the synthesis of compounds **2b-d.** Bu^{t}OCl (0.022 mol) solution in 3 ml MeOH was added dropwise to 1,3-diaminopropane (0.04 mol) solution in 30 ml MeOH at vigorous stirring and at temperature –5–0 ºC. Then 0.02 mol of corresponding aldehyde in 4-6 ml MeOH was added and the reaction mixture was kept for 24 h at 0-5ºC. The precipitate was filtered through a thin layer (1,5-2,0 cm) of SiO_2, the solvent was evacuated and water (50 ml) was added. The prepared solution was saturated with NaCl, extracted with CH_2Cl_2 (3×30 ml), dried with K_2CO_3, the solvent was evaporated, and the residue was crystallized from ether.

6-(2,4-Dimethoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane **2b.** Mp 65-67ºC. ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C) δ: 1.85 (m, 1 H, H_{ax}(3)); 1.90 (m, 1 H, H_{eq}(3)); 3.25 (m, 2 H, H_{ax}(2), H_{ax}(4)); 3.55 (s, 1 H, $HC_{diaz.ring}$(6)); 3.52 (m, 2 H, H_{eq}(2), H_{eq}(4)); 3.80 (s, 3 H, (MeO)); 3.85 (s, 3 H, (CH_3O)); 6.40 (s, 1 H, HC_{Ar}(3)); 6.49 (d, 1 H, HC_{Ar}(5), *J* 9,8 Hz); 7.25 (d, 1 H, HC_{Ar}(6)). ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C) δ: 22.0 ($C_{.ring}$(3)); 51.1 (MeO); 52.1 (C_{ring}(2(4))); 55.3 (C_{ring}(6), MeO); 98.0 (C_{Ar}(3)); 104.5 (C_{Ar}(5)); 117.8 (C_{Ar}(1)); 128.4 (C_{Ar}(5)); 159.3 (C_{Ar}(2); 160.7 (C_{Ar}(4)); HRMS (ESI): *m/z* $[M + H]^+$ calc. for $C_{12}H_{16}N_2O_2$: 221.1285. Found: 221.1281.

6-(3,5-Dimethoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane **2c.** Mp 154-155ºC. ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C) δ: 1.88 (m, 1 H, H_{ax}(3)); 1.92 (m, 1 H, H_{eq}(3)); 3.17 (m, 2 H, H_{ax}(2), H_{ax}(4)); 3.58 (m, 2 H, H_{eq}(2), H_{eq}(4)); 3.78 (s, 6 H, 2(MeO)); 3.80 (s, 1 H, $HC_{diaz.ring}$(6)); 6.41 (s, 1 H, HC_{Ar}(4)); 6.52 (s, 2 H, HC_{Ar}(2), HC_{Ar}(6)). ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C) δ: 21.7 (C_{ring}(3)); 52.3 (C_{ring}(2(4))); 55.4 2(MeO); 56.9 (C_{ring}(6)); 101.4 (C_{Ar}(4)); 104.9 (C_{Ar} (2,6)); 139.4 (C_{Ar}(1); 160.8 (C_{Ar}(3,5)); HRMS (ESI): *m/z* $[M + H]^+$ calc. for $C_{12}H_{16}N_2O_2$: 221.1285. Found: 221.1280.

6-(2,4,6-Trimethoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane **2d.** Mp 123-125ºC. ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C) *δ*: 1.82 (m, 2 H, $H_{ax}(3)$); 3.11 (m, 2 H, $H_{ax}(2)$, $H_{ax}(4)$); 3,15 (c, 1 H, $HC_{diaz.ring}(6)$); 3.56 (m, 2 H, $H_{eq}(2)$, $H_{eq}(4)$); 3.75 (s, 3 H, (MeO)); 3,79 (s, 6 H, 2(MeO)); 6.06 (s, 2 H, $C_{Ar}(3,5)$). ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C) *δ*: 21.4 ($C_{ring}(3)$); 51.5 (MeO); 52.0 ($C_{ring}(2(4))$; 55.2 ($C_{ring}(6)$, 55.9 (2(MeO)); 90.7 ($C_{Ar}(3,5)$); 106,0 ($C_{Ar}(1)$); 160,1 ($C_{Ar}(2,6)$); 160,8 ($C_{Ar}(4)$). HRMS (ESI): *m/z* $[M + H]^+$ calc. for $C_{13}H_{18}N_2O_3$: 251.1390. Found: 251.1387.

4-(Furan-2-yl)-2-(2,4-dimethoxyphenyl)-3-nitro-1,5-diazabicyclo[3.3.0]octane (trans-trans-adduct) **4b**. ^{1}H NMR (600 MHz, $CDCl_3$, 30 °C) *δ*: 7.66 (d, 1H, H-6_{Ar}, *J* 8.5 Hz), 7.40 (s, 1H, H-5_{furan}), 6.54 (dd, 1H, H-5_{Ar}, *J* 8.5, 2.2 Hz), 6.46 (d, 1H, H-3_{Ar}, *J* 2.2 Hz), 6.34 (dd, 2H, H-$3,4_{furan}$, *J* 6.6, 2.3 Hz,), 5.25 (dd, 1H, H-3, *J* 7.0, 5.1 Hz), 5.10 (d, 1H, H-2, *J* = 5.0 Hz,), 4.60 (d, 1H, H-4, *J* 7.1 Hz), 3.83 (s, 3H, 2-MeO), 3.74 (s, 3H, 4-MeO), 3.48 – 3.41 (m, 1H, H-8a), 3.40 – 3.35 (m, 1H, H-8b), 3.30 (m, 2H, H-6), 2.40 (m, 1H, H-7a), 2.25 – 2.08 (m, 1H, H-7b). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 160.73 (C-4_{Ar}), 157.34 (C-2_{Ar}), 150.39 (C-2_{furan}), 143.30 (C-5_{furan}), 127.94 (), 120.84 (C-1_{Ar}), 110.41 (C-4_{furan}), 108.91 (C-3_{furan}), 104.53 (C-5_{Ar}), 100.15 (C-3), 98.14 (C-3_{Ar}), 66.61 (C-4), 66.28 (C-2), 55.43 (2-MeO), 55.06 (4-MeO), 50.89 (C-8), 50.24 (C-6), 23.79 (C-7). MS, *m/z* (%): 359 (6) [M^+], 243 (100), 149 (40), 81 (39). Found (%): C, 60.33; H, 5.75; N, 11.81. Calc. for $C_{18}H_{21}N_3O_5$ (%): C, 60.16; H, 5.89; N, 11.69.

*4-(Furan-2-yl)-2-(2,4-dimethoxyphenyl)-3-nitro-1,5-diazabicyclo[3.3.0]octane (cis-trans-*adduct*)* **4'b**. ^{1}H NMR (600 MHz, $CDCl_3$, 30 °C) *δ*: 7.52 (d, 1H, H-6_{Ar}, *J* 8.5 Hz), 7.47 (d, 1H, H-5_{furan}, *J* 2.8 Hz), 6.51 (dd, 1H, H-5_{Ar}, *J* 8.5, 2.3 Hz), 6.45 (dd, 2H, H-$3,4_{furan}$, *J* 6.1, 2.8 Hz), 6.40 (d, 1H, H-3_{Ar}, *J* 2.3 Hz), 5.87 (dd, 1H, H-3, *J* 8.7, 7.0 Hz), 5.14 (br s, 1H, H-4), 4.61 (d, 1H, H-2, *J* 8.7 Hz), 3.85, 3.81 (both s, 6H, 2-OMe, 4-OMe), 3.28 – 3.21 (m, 1H, H-8a), 3.03 – 2.95 (m, 1H, H-6a), 2.76 – 2.69 (m, 1H, H-6b), 2.68 – 2.59 (m, 1H, H-8b), 2.34 – 2.18 (m, 2H, H-7). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 160.84 (C-4_{Ar}), 158.19 (C-2_{Ar}), 148.84 (C-2_{furan}), 143.19 (C-5_{furan}), 129.12 (C-6_{Ar}), 114.87 (C-1_{Ar}), 110.53 (C-3_{Ar}), 109.48 (C-4_{furan}), 104.20 (C-5_{Ar}), 98.18 (C-3_{furan}), 94.46 (C-3), 63.69 (C-4), 63.44 (C-2), 55.38, 55.22 (2-OMe, 4-OMe), 49.02 (C-8), 47.23 (C-6), 26.44 (C-7). MS, *m/z* (%): 359 (96) [M^+], 243 (83), 220 (79), 151 (100), 80 (92). Found (%):C, 60.21; H, 5.96; N, 11.53. Calc. for $C_{18}H_{21}N_3O_5$ (%): C, 60.16; H, 5.89; N, 11.69.

4-(Thiophen-2-yl)-2-(4-methoxyphenyl)-3-nitro-1,5-diazabicyclo[3.3.0]octane **4c**. ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C) *δ*: 7.43 (d, 2H, H-$2,6_{Ar}$, *J* 8.5 Hz), 7.29 (d, 1H, H-$5_{thienyl}$, *J* 5.0 Hz), 7.05 (d, 1H, H-$3_{thienyl}$, *J* 2.9 Hz), 7.01 – 6.95 (m, 1H, H-4 $_{thienyl}$), 6.91 (d, 2H, H-$3,5_{Ar}$, *J* 8.5

Hz), 5.11 (t, 1H, H-3, *J* 5.8 Hz), 5.04 (d, 1H, H-2, *J* 5.8 Hz), 4.65 (d, 1H, H-4, *J* 5.8 Hz), 3.81 (s, 3H, OMe), 3.42 – 3.08 (m, 4H, H-8,6), 2.45 – 2.27 (m, 1H, H-7a), 2.22 – 2.07 (m, 1H, H-7b). ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C) *δ*: 159.61 (C-4_{Ar}), 143.01 (C-$2_{thienyl}$), 131.21 (C-1_{Ar}), 128.51 (C-2,6_{Ar}), 126.98 (C-$5_{thienyl}$), 125.96(C-$4_{thienyl}$), 125.44 (C-$3_{thienyl}$), 114.31 (C-3,5_{Ar}), 103.04 (C-3), 71.70 (C-4), 67.81 (C-2), 55.30 (OMe), 50.92 (C-8), 50.70 (C-6), 24.04 (C-7). MS, *m/z* (%): 345 (96) [M^+], 297 (35), 230 (100), 145 (83). Found (%): C, 59.20; H, 5.41; N, 12.11. Calc. for $C_{17}H_{19}N_3O_3S$ (%): C, 59.11; H, 5.54; N, 12.17.

4-(Thiophen-2-yl)-2-(2,4-dimethoxyphenyl)-3-nitro-1,5-diazabicyclo[3.3.0]octane **4d** *(trans-trans*-adduct*).* ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C) *δ*: 7.67 (d, 1H, H-6_{Ar}, *J* 8.5 Hz), 7.32 – 7.21 (dd, 1H, H-$5_{thiophene}$), 7.05 – 6.90 (m, 2H, H-3,$4_{thiophene}$), 6.53 (dd, 1H, H-5_{Ar}, *J* 8.5, 2.2 Hz), 6.42 (d, 1H, H-3_{Ar}, *J* 2.2 Hz), 5.10 (d, 1H, H-2, *J* 4.8 Hz), 4.95 (dd, , 1H, H-3, *J* 6.7, 4.8 Hz), 4.79 (d, 1H, H-4, *J* 6.7 Hz), 3.81 (s, 3H, OMe), 3.70 (s, 3H, OMe), 3.54 – 3.11 (m, 4H, H-6,8), 2.46 – 2.28 (m, 1H, H-7a), 2.24 – 2.08 (m, 1H, H-7b). ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C) *δ*: 160.43 (C-4_{Ar}), 157.18 (C-2_{Ar}), 142.26 (C-$2_{thiophene}$), 127.93 (C-$5_{thiophene}$), 126.88 (C-6_{Ar}), 125.97 (C-$4_{thiophene}$), 125.79 (C-$3_{thiophene}$), 121.01 (C-1_{Ar}), 104.47 (C-5_{Ar}), 103.75 (C-3), 98.03 (C-3_{Ar}), 69.07 (C-4), 66.23 (C-2), 55.40 (OMe), 55.03 (OMe), 51.20 (C-8), 50.14 (C-6), 23.92 (C-7). MS, *m/z* (%): 375 (63) [M^+], 328 (3), 259 (100). Found (%): C, 57.65; H, 5.72; N, 11.12; S, 8.50. Calc. for $C_{18}H_{21}N_3O_4S$ (%): C, 57.58; H, 5.64; N, 11.19; S, 8.54.

4-(Thiophen-2-yl)-2-(2,4-dimethoxyphenyl)-3-nitro-1,5-diazabicyclo[3.3.0]octane **4'd** *(cis-trans*-adduct*).* ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C) *δ*: 7.47 (d, 1H, H-6_{Ar}, *J* = 8.5 Hz), 7.33 (d, 1H, H-$5_{thiophene}$, *J* 4.9 Hz), 7.09 (d, 1H, H-$3_{thiophene}$, *J* 3.1 Hz), 7.00 (dd, 1H, H-$4_{thiophene}$, *J* 4.9, 3.1 Hz), 6.49 (dd, 1H, H-5_{Ar}, *J* = 8.5, 2.1 Hz), 6.43 (d, 1H, H-3_{Ar}, *J* = 2.1 Hz), 5.69 – 5.57 (m, 1H, H-3), 5.06 (d, 1H, H-4, *J* 6.7 Hz), 4.51 (d, 1H, H-4, *J* 8.5 Hz), 3.82, 3.80 (both s, 6H, OMe), 3.27 – 3.14 (m, 1H, H-8a), 3.05 – 2.92 (m, 1H, H-6a), 2.73 – 2.61 (m, 1H, H-6b), 2.55 – 2.41 (m, 1H, H-8b), 2.40 – 2.24 (m, 2H, H-7). ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C) *δ*: 160.88 (C-4Ar), 158.13 (C-2Ar), 139.95 (C-2 $_{thiophene}$), 129.06 (C-$5_{thiophene}$), 126.95 (C-6_{Ar}), 126.02 (C-$4_{thiophene}$), 125.77 (C-$3_{thiophene}$), 114.96 (C-1_{Ar}), 104.33 (C-5_{Ar}), 98.87 (C-3), 98.27 (C-3_{Ar}), 65.90 (C-4), 63.57 (C-2), 55.40 (OMe), 55.26 (OMe), 48.73 (C-8), 47.34 (C-6), 27.70 (C-7). Found (%): C, 57.69; H, 5.60; N, 11.23; S, 8.47. Calc. for $C_{18}H_{21}N_3O_4S$ (%): C, 57.58; H, 5.64; N, 11.19; S, 8.54.

4-(5-Nitrofuran-2-yl)-2-(4-methoxyphenyl)-3-nitro-1,5-diazabicyclo[3.3.0]octane **4e**. ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C) δ: 7.38 – 7.30 (m, 3H, H-4_{furan}, H-$2,6_{Ar}$), 6.91 (d, 2H, H-$3,5_{Ar}$, *J* 8.6 Hz), 6.71 (d, 1H, H-3_{furan}, *J* 3.6 Hz,), 5.36 – 5.22 (m, 1H, H-3), 5.03 (d, 1H, H-2, *J* 4.4 Hz), 4.51 (d, 1H, H-4, *J* = 6.7 Hz), 3.82 (s, 3H, OMe), 3.45 – 3.28 (m, 2H, H-8), 3.25 – 3.15 (m, 1H, H-6a), 3.07 – 2.92 (m, 1H, H-6b), 2.48 – 2.30 (m, 1H, H-7a), 2.21 – 2.12 (m, 1H, H-7b). ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C) δ: 160.05 (C-4_{Ar}), 155.91 (C-2_{furan}), 152.05 (C-5_{furan}), 129.23 (C-1_{Ar}), 128.81 (C-$2,6_{Ar}$), 114.47 (C-$3,5_{Ar}$), 112.39 (C-4_{furan}), 111.08 (C-3_{furan}), 99.12 (C-3), 71.84 (C-4), 64.66 (C-2), 55.31 (OMe), 51.07 (C-8), 49.95 (C-6), 24.07 (C-7). MS, *m/z* (%): 374 (5) [M^+], 326 (10), 258 (100), 220 (16), 189 (20), 121 (23). Found (%): C, 54.60; H, 4.91; N, 14.93. Calc. for $C_{17}H_{18}N_4O_6$ (%): C, 54.54; H, 4.85; N, 14.97.

4-(5-Methylfuran-2-yl)-2-(4-methoxyphenyl)-3-nitro-1,5-diazabicyclo[3.3.0]octane **4f**. ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C) δ: 7.44 (d, 2H, H-$2,6_{Ar}$, *J* 8.4 Hz), 6.91 (d, 2H, H-$3,5_{Ar}$, *J* 8.4 Hz), 6.26 (d, 1H, H-4furan, *J* 2.5 Hz), 5.93 (br s, 1H, H-3furan), 5.34 (t, 1H, H-3, *J* 6.1 Hz), 4.76 (d, 1H, H-2, *J* 6.1 Hz), 4.59 (d, 1H, H-4, *J* 6.1 Hz,), 3.81 (s, 3H, OMe), 3.40 – 3.20 (m, 3H, H-8, H-6a), 3.19 – 3.04 (m, 1H, H-6b), 2.44 – 2.24 (m, 4H, H-7a, Me), 2.20 – 2.02 (m, 1H, H-7b). ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C) δ: 159.73 (C-4Ar), 153.14 (C-2furan), 149.03 (C-5furan), 131.18 (C-1Ar), 128.61 (C-2,6Ar), 114.36 (C-3,5Ar), 109.42 (C-4furan), 106.53 (C-3furan), 99.55 (C-3), 71.67 (C-4), 65.73 (C-2), 55.35 (OMe), 50.95, 50.69 (C-6,8), 24.01 (C-7), 13.68 (Me). MS, *m/z* (%): 343 (30) [M^+], 295 (42), 228 (100), 189 (57), 145 (63), 121 (77). Found (%): C, 63.05; H, 6.10; N, 12.33. Calc. for (%) $C_{18}H_{21}N_3O_4$: C, 62.96; H, 6.16; N, 12.24.

4-(5-Nitrothiophen-2-yl)-2-(4-methoxyphenyl)-3-nitro-1,5-diazabicyclo[3.3.0]octane **4h**. ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C) δ: 7.83 (d, 1H, H-$4_{thiophene}$, *J* 4.1 Hz), 7.35 (d, H-$2,6_{Ar}$, 2H, *J* 8.4 Hz), 6.99 (d, 1H, H-$3_{thiophene}$, *J* 4.1 Hz,), 6.91 (d, 2H, H-$3,5_{Ar}$, *J* 8.4 Hz), 5.05 (s, 2H, H-3,2), 4.74 – 4.57 (m, 1H, H-4), 3.81 (s, 3H, OMe), 3.54 – 3.37 (m, 1H, H-8a), 3.28 (m, 2H, H-8b, H-6a), 3.12 – 2.94 (m, 1H, H-6b), 2.54 – 2.29 (m, 1H, H-7a), 2.28 – 2.09 (m, 1H, H-7b). ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C) δ: 159.96 (C-4_{Ar}), 153.64 (C-$2_{thiophene}$), 151.64 (C-$5_{thiophene}$), 129.46 (C-1_{Ar}), 128.77 (C-$3_{thiophene}$), 128.59 (C-$2,6_{Ar}$), 123.57 (C-$4_{thiophene}$), 114.47 (C-$3,5_{Ar}$), 102.10 (C-3), 71.69 (C-4), 67.20 (C-2), 55.30 (OMe), 51.02 (C-8), 50.24 (C-6), 24.14 (C-7). MS, *m/z* (%): 390 (7) [M^+], 274 (100), 211 (17), 155 (17), 97 (34), 86 (92). Found (%): C, 52.21; H, 4.72; N, 14.30; S, 8.28. Calc. for $C_{17}H_{18}N_4O_5S$ (%): C, 52.30; H, 4.65; N, 14.35; S, 8.21.

4-(1H-Indol-3-yl)-2-(4-Methoxyphenyl)-3-nitro-1,5-diazabicyclo[3.3.0]octane 3 **4i**. ^{1}H NMR (300 MHz, $CDCl_3$, 30 °C) δ: 8.39 (br s, 1H, NH), 7.76 (d, 1H, H-4_{indole}, *J* 7.9 Hz), 7.46 (d, 2H, H-$2,6_{Ar}$, *J* 8.5 Hz), 7.39 – 7.04 (m, 4H, H-$2,5,6,7_{indole}$), 6.92 (d, 2H, H-$3,5_{Ar}$, *J* 8.5 Hz), 5.36 – 5.24 (m, 1H, H-3), 5.08 (d, 1H, H-2, *J* 6.4 Hz), 4.76 (d, 1H, H-4, *J* 6.0 Hz), 3.82 (s, 3H, OMe), 3.44 – 3.19 (m, 4H, H-6,8), 2.53 – 2.35 (m, 1H, H-7a), 2.24 – 2.10 (m, 1H, H-7b). ^{13}C NMR (75 MHz, $CDCl_3$, 30 °C) δ: 159.53 (C-4Ar), 136.77 (C_{indole}), 131.67 (C_{indole}), 128.49 (C-2,6Ar), 123.32 (HC_{indole}), 122.60 (HC_{indole}), 120.14 (HC_{indole}), 119.52 (HC_{indole}), 114.39 (C-3,5Ar)113.68 (C_{indole}), 111.50 (HC_{indole}), 102.04 (C-3), 71.76 (C-4), 66.32 (C-2), 55.38 (OMe), 50.97, 50.92 (C-6,8), 24.13 (C-7). MS, *m/z* (%): 378 (11) [M^+], 330 (13), 263 (44), 228 (35), 199 (40), 130 (100). Found (%): C, 66.58; H, 5.79; N, 14.90. Calc. for $C_{21}H_{22}N_4O_3$ (%): C, 66.65; H, 5.86; N, 14.81.