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A new approach to incorporate the carboranyl fragment into 2,5-diazabicyclo[2.2.2]oct-2-enes

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5-Ethyl-6-oxo-3-(thiophen-2-yl)-7-(1,2-dicarba-closo-*dodecarboran-9-ylmethyl-2,5-diazabicyclo[2.2.2]oct-2-ene-1-carbonitrile* **7b**. Beige crystal powder, mp 229–241 °C. HPLC, t_R 4.0–5.5 min. In the ^{1}H NMR spectrum two sets of signals corresponding to major (**A**) and minor (**B**) diastereomers of **7b** were observed. ^{1}H NMR ($CDCl_3$) δ: isomer **A**: 0.61 (m, 1H, CH), 1.11 (t, 3H, Me, *J* 7.2 Hz), 1.21–2.80 (m, 15H, BH, CH, $2CH_2$, C^8H), 3.28–3.39 (m, 1H, NCH_A), 3.54–3.64 (m, 1H, NCH_B), 4.68 (dd, 1H, C^4H, *J* 3.7 Hz, *J* 1.9 Hz), 7.14–7.16 (m, 1H, thiophene), 7.54– 7.55 (m, 1H, thiophene), 7.59–7.60 (m, 1H, thiophene); isomer **B**: 0.61 (m, 1H, CH), 1.12 (t, 3H, Me, *J* 7.2 Hz), 1.21–2.80 (m, 15H, BH, CH, $2CH_2$, C^8H), 3.28–3.39 (m, 1H, NCH_A), 3.54–3.64 (m, 1H, NCH_B), 4.70 (dd, 1H, C^4H, *J* 2.3 Hz, *J* 3.3 Hz), 7.14–7.16 (m, 1H, thiophene), 7.51–7.53 (m, 1H, thiophene), 7.58–7.59 (m, 1H, thiophene). LC/MS (APCI, in MeOH, Q-array scan): *m*/*z* [*I*(%), positive region]: 416 $[M]^+$ (92), 417 $[M + H]^+$ (100); *m*/*z* [*I*(%), negative region]: –414 [M – 2H]– (86), –415 [M – H]– (42), –416 [M]– (17). Found (%): C, 46.30; H, 5.94; N, 9.84. Calc. for $C_{16}H_{25}N_3OB_{10}S$ (%): C, 46.24; H, 6.06; N, 10.11.

5-Ethyl-6-oxo-3-(thiophen-3-yl)-7-(1,2-dicarba-closo-*dodecarboran-9-ylmethyl-2,5-diazabicyclo[2.2.2]oct-2-ene-1-carbonitrile* **7c**. Yellow crystal powder, mp 217–228 °C. HPLC, t_R 3.5–5.5 min. In the ^{1}H NMR spectrum two sets of signals corresponding to major (**A**) and minor (**B**) diastereomers of **7c** were observed. ^{1}H NMR ($CDCl_3$) δ: isomer **A**: 0.59 (m, 1H, CH), 1.11 (t, 3H, Me, *J* 7.2 Hz), 1.20–2.80 (m, 15H, BH, CH, $2CH_2$, C^8H), 3.28–3.40 (m, 1H, NCH_A), 3.52–3.62 (m, 1H, NCH_B), 4.65 (dd, 1H, C^4H, *J* 3.5 Hz, *J* 2.0 Hz), 7.43 (dd, 1H, $H^{5'}$-thiophene, *J* 5.1 Hz, *J* 2.8 Hz), 7.61 (dd, 1H, $H^{4'}$-thiophene, *J* 5.1 Hz, *J* 1.3 Hz), 7.83 (dd, 1H, $H^{2'}$-thiophene, *J* 2.8 Hz, *J* 1.3 Hz);

isomer **B**: 0.58 (m, 1H, CH), 1.11 (t, 3H, Me, *J* 7.2 Hz), 1.20–2.80 (m, 15H, BH, CH, $2CH_2$, C^8H), 3.28–3.40 (m, 1H, NCH_A), 3.52–3.62 (m, 1H, NCH_B), 4.68 (dd, 1H, C^4H, *J* 2.5 Hz, *J* 3.2 Hz), 7.43 (dd, 1H, $H^{5'}$-thiophene, *J* 5.1 Hz, *J* 2.8 Hz), 7.61 (dd, 1H, $H^{4'}$-thiophene, *J* 5.1 Hz, *J* 1.3 Hz), 7.83 (dd, 1H, $H^{2'}$-thiophene, *J* 2.8 Hz, *J* 1.3 Hz). LC/MS (APCI, in MeCN, Q-array scan), *m*/*z* [*I*(%), positive region]: 416 $[M]^+$ (9), 417 $[M + H]^+$ (14), 457 $[M + MeCN]^+$ (100), 458 $[M + H + MeCN]^+$ (92); *m*/*z* [*I*(%), negative region]: –414 [M – 2H]– (10), –415 [M – H]– (8), –416 [M]– (11). Found (%): C, 46.47; H, 6.29; N, 9.94. Calc. for $C_{16}H_{25}N_3OB_{10}S$ (%): C, 46.24; H, 6.06; N, 10.11.

5-Ethyl-6-oxo-3-(thiophen-2-yl)-7-(1,7-dicarba-closo-*dodecarboran-9-ylmethyl-2,5-diazabicyclo[2.2.2]oct-2-ene-1-carbonitrile* **8b**. Yellow crystal powder, mp 235–238 °C. HPLC, t_R 5.0–6.5 min. In the ^1H NMR spectrum two sets of signals corresponding to major (**A**) and minor (**B**) diastereomers of **8b** were observed. ^1H NMR ($CDCl_3$) δ: isomer **A**: 0.75 (m, 1H, CH), 1.13 (t, 3H, Me, *J* 7.2 Hz), 1.25–2.90 (m, 15H, BH, CH, $2CH_2$, C^8H), 3.33–3.38 (m, 1H, NCH_A), 3.59–3.64 (m, 1H, NCH_B), 4.71 (dd, 1H, C^4H, *J* 3.6 Hz, *J* 2.0 Hz), 7.15–7.17 (m, 1H, thiophene), 7.56–7.57 (m, 1H, thiophene), 7.60–7.62 (m, 1H, thiophene); isomer **B**: 0.75 (m, 1H, CH), 1.16 (t, 3H, Me, *J* 7.2 Hz), 1.25–2.90 (m, 15H, BH, CH, $2CH_2$, C^8H), 3.33–3.38 (m, 1H, NCH_A), 3.59–3.64 (m, 1H, NCH_B), 4.74 (dd, 1H, C^4H, *J* 2.3 Hz, *J* 3.3 Hz), 7.13–7.14 (m, 1H, thiophene), 7.52–7.54 (m, 1H, thiophene), 7.59 (m, 1H, thiophene). LC/MS (ESI, in MeCN, Q-array scan), *m*/*z* [*I*(%), positive region]: 416 $[M]^+$ (29), 417 $[M + H]^+$ (29). Found (%): C, 46.08; H, 6.06; N, 9.98. Calc. for $C_{16}H_{25}N_3OB_{10}S$ (%): C, 46.24; H, 6.06; N, 10.11.

5-Ethyl-6-oxo-3-(thiophen-3-yl)-7-(1,7-dicarba-closo-*dodecarboran-9-ylmethyl-2,5-diazabicyclo[2.2.2]oct-2-en-1-carbonitrile* **8c**. Yellow crystal powder, mp 218–243 °C. HPLC, t_R 5.0–7.0 min. In the ^1H NMR spectrum two sets of signals corresponding to major (**A**) and minor (**B**) diastereomers of **8c** were observed. ^1H NMR ($CDCl_3$) δ: isomer **A**: 0.72 (m, 1H, CH), 1.11 (t, 3H, Me, *J* 7.2 Hz), 1.26–2.90 (m, 15H, BH, CH, $2CH_2$, C^8H), 3.30–3.45 (m, 1H, NCH_A), 3.55–3.64 (m, 1H, NCH_B), 4.69 (dd, 1H, C^4H, *J* 3.6 Hz, *J* 1.9 Hz), 7.44 (dd, 1H, $H^{5'}$-thiophene, *J* 5.1 Hz, *J* 2.8 Hz), 7.63 (dd, 1H, $H^{4'}$-thiophene, *J* 5.1 Hz, *J* 1.2 Hz), 7.85 (dd, 1H, $H^{2'}$-thiophene, *J* 2.8 Hz, *J* 1.3 Hz); isomer **B**: 0.72 (m, 1H, CH), 1.13 (t, 3H, Me, *J* 7.2 Hz), 1.26–2.90 (m, 15H, BH, CH, $2CH_2$, C^8H), 3.30–3.45 (m, 1H, NCH_A), 3.55–3.64 (m, 1H, NCH_B), 4.71 (dd, 1H, C^4H, *J*

2.3 Hz, *J* 3.2 Hz), 7.42 (dd, 1H, $H^{5'}$-thiophene, *J* 5.1 Hz, *J* 2.8 Hz), 7.61 (dd, 1H, $H^{4'}$-thiophene, *J* 5.1 Hz, *J* 1.2 Hz), 7.82 (dd, 1H, $H^{2'}$-thiophene, *J* 2.8 Hz, *J* 1.2 Hz). LC/MS (ESI, in MeCN, Q-array scan), *m*/*z* [*I*(%), positive region]: 416 $[M]^+$ (94), 417 $[M + H]^+$ (87); *m*/*z* [*I*(%), negative region]: –414 [M – 2H]– (86), –415 [M – H]– (42), –416 [M]– (17). Found (%): C, 46.34; H, 5.88; N, 9.95. Calc. for $C_{16}H_{25}N_3OB_{10}S$ (%): C, 46.24; H, 6.06; N, 10.11.

4-Ethyl-3-oxo-6-phenyl-3,4-dihydropyrazine-2-carbonitrile **11a**. Yellow crystal powder, yield 51%, mp 191–193 °C. ^{1}H NMR (CD_3CN) δ: 1.39 (t, 3H, Me, *J* 7.2 Hz), 4.08 (dd, 2H, NCH_2, *J* 14.4 Hz, *J* 7.2 Hz), 7.40–7.42 (m, 1H, Ph), 7.46–7.50 (m, 2H, Ph), 7.78–7.81 (m, 2H, Ph), 8.23 (s, 1H, C^5H). IR (Nujol, ν/cm^{-1}): 1653 (C=O), 2227 (C≡N). Found (%): C, 69.29; H, 5.02; N, 18.68. Calc. for $C_{13}H_{11}N_3O$ (%): C, 69.32; H, 4.92; N, 18.66.

4-Ethyl-3-oxo-6-(thiophen-3-yl)-3,4-dihydropyrazine-2-carbonitrile **11c**. Yellow crystal powder, yield 42%, mp 191–193 °C. ^{1}H NMR (CD_3CN) δ: 1.38 (t, 3H, Me, *J* 7.2 Hz), 4.05 (dd, 2H, NCH_2, *J* 14.4 Hz, *J* 7.2 Hz), 7.46 (dd, 1H, $H^{4'}$-thiophene, *J* 5.2 Hz, *J* 1.2 Hz), 7.52 (dd, 1H, $H^{5'}$-thiophene, *J* 5.2 Hz, *J* 3.2 Hz), 7.73 (dd, 1H, $H^{2'}$-thiophene, *J* 2.8 Hz, *J* 1.2 Hz), 8.16 (s, 1H, C^5H). IR (Nujol, ν/cm^{-1}): 1652 (C=O), 2232 (C≡N). Found (%): C, 57.31; H, 4.12; N, 18.43. Calc. for $C_{11}H_9N_3OS$ (%): C, 57.13; H, 3.92; N, 18.17.