

## Zwitterionic borane adducts of N-heterocyclic carbenes from mesomeric betaines of uracil†

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We prepared a series of imidazolium-substituted uracil-anions which are members of the class of cross-conjugated heterocyclic mesomeric betaines. They are in tautomeric equilibrium with their N-heterocyclic carbenes, uracil-6-yl-imidazol-2-ylidenes. These carbenes can be trapped by reaction with sulfur, selenium, as well as by triethylborane and triphenylborane, respectively. The latter trapping reaction yielded the first representatives of a new heterocyclic zwitterionic ring system, imidazo[2',1':3,4][1,4,2]diazaborolo[1,5-c]pyrimidin-10-ide. Results of two single crystal X-ray structure analyses are presented.

### Introduction

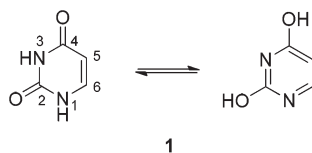
Uracil **1** is one of the four nucleobases of RNA and its derivatives display a broad variety of biological activities.<sup>1</sup> Due to lactim–lactam tautomerism uracil can exist in six tautomeric forms, two of which are shown in Scheme 1. Spectroscopic examinations as well as calculations reveal that the diketo tautomer is the predominant form in the solid state and in solution.<sup>2</sup> The two oxygen atoms of uracil were calculated to be the most susceptible sites of attachment of complex formations,<sup>3</sup> and numerous complexes through the O4 site<sup>4</sup> or through the N3/O4<sup>5</sup> and O4/N3/O2<sup>6</sup> sites have been described. Some uracil metal complexes through the deprotonated N1 site are known as well.<sup>7</sup> To our surprise, only very little information is available concerning the interaction of uracils with boranes.<sup>8</sup>

In view of the current interest in the area of overlap between the chemistry of N-heterocyclic carbenes (NHC) and

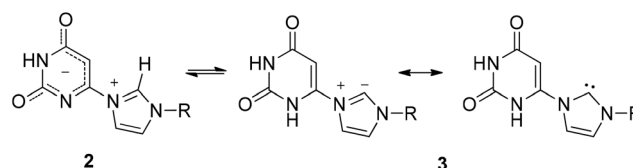
the chemistry of heterocyclic mesomeric betaines (MB),<sup>9</sup> we aimed at mesomeric betaines of uracil-6-yl-imidazolium betaines **2** which give rise to betaine 2–N-heterocyclic carbene **3** tautomerism. Borane adduct formation from N-heterocyclic carbenes is a rapidly growing field of chemistry<sup>10</sup> so that we intended to explore the behavior of our target compounds toward boranes (Scheme 2).

Mesomeric betaines such as **2** are defined as neutral compounds which can exclusively be represented by dipolar resonance forms in which the positive and negative charges are delocalized within a common  $\pi$ -electron system. Four distinct main classes are distinguished: (i) conjugated mesomeric betaines (CMB), (ii) ylides, (iii) cross-conjugated (CCMB) mesomeric betaines, and (iv) pseudo-cross-conjugated mesomeric betaines (PCCMB).<sup>11,12</sup> The relationships to normal (NHC), abnormal (aNHC)<sup>13</sup> [sometimes called mesoionic carbenes (MIC)<sup>14</sup>] and remote N-heterocyclic carbenes (rNHC)<sup>15</sup> are summarized in reviews on betaine–carbene interconversions,<sup>9</sup> betaine and carbene chemistry of pyrazoles and indazoles,<sup>16</sup> or complex chemistry.<sup>17</sup>

Betaine–carbene interconversions can be achieved by decarboxylations, deprotonations, and tautomerisms starting from suitable betaines. Members of the class of PCCMBs<sup>11,12</sup> such as imidazolium-2-carboxylates **3**<sup>18</sup> and pyrazolium-3-carboxylates<sup>19</sup> are convenient precursors of normal N-heterocyclic



Scheme 1



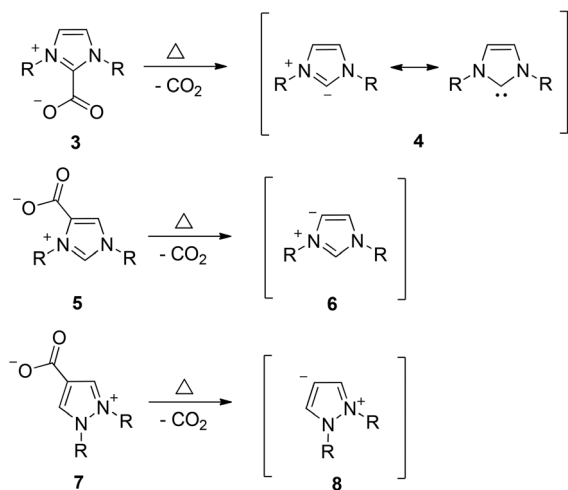
Scheme 2

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Scheme 3

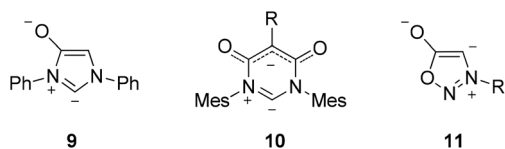
carbenes such as **4** (Scheme 3). On the other hand, PCCMBs can be formed by trapping reactions of NHCs with heterocumulenes.<sup>9,20</sup> Decarboxylations of CCMBs such as imidazolium-4-carboxylate **5** and pyrazolium-4-carboxylate **7** to yield the aNHC **6** or the rNHC **8** require harsh conditions, and as a consequence, only a few examples of successful conversions exist.<sup>21</sup> The latter molecule **8** has been described as a dipolar structure as shown and as a cyclic bent allene, and has been studied intensively.<sup>22</sup>

Deprotonations of mesomeric betaines result in the formation of anionic N-heterocyclic carbenes. Examples are the anions of the CMB imidazolium-4-olate **9**,<sup>23</sup> the CCMB pyrimidin-4-olate **10**,<sup>24</sup> and the CMB sydnone **11**<sup>9,25</sup> (Scheme 4).

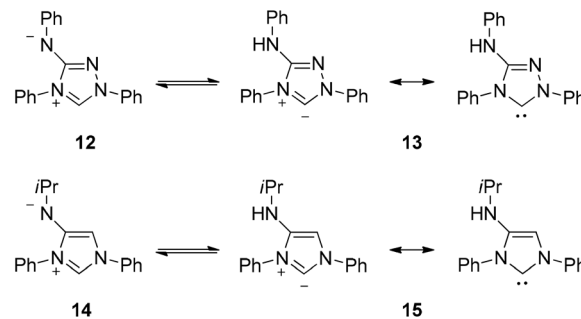
Tautomerism of a mesomeric betaine to an N-heterocyclic carbene has surprisingly been observed on examination of the mesoionic compound **12** (Busch's reagent, nitron) which is in equilibrium with **13** (Scheme 5).<sup>26</sup> Correspondingly imidazolium-4-aminide **14** is in tautomeric equilibrium with carbene **15**.<sup>27</sup>

We investigated tautomeric equilibria of the ylides imidazolium-indolates **16** with their N-heterocyclic carbenes **17** (Scheme 6). We also investigated conversions into the anionic N-heterocyclic carbenes **18** and reported on borane adduct formations to **19**.<sup>28</sup>

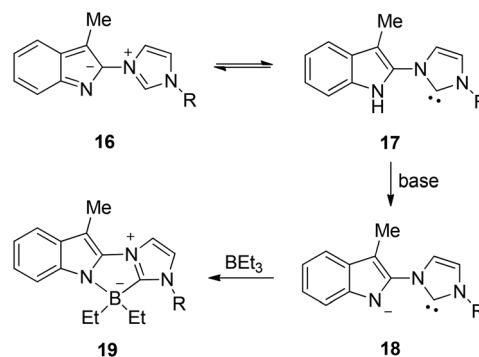
We describe here the first equilibria of imidazolium-substituted uracils with their corresponding N-heterocyclic carbenes. The carbenes can be trapped with boranes to yield first representatives of a new heterocyclic ring system, a zwitterionic imidazo[2',1':3,4][1,4,2]diazaborolo[1,5-c]pyrimidin-10-ide.



Scheme 4



Scheme 5



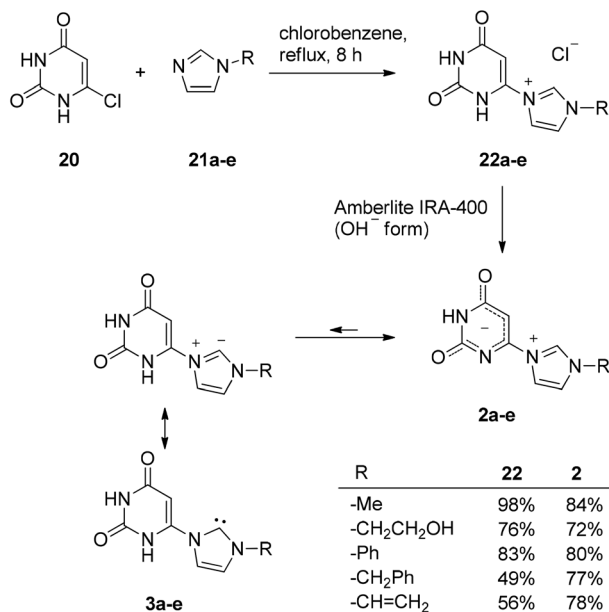
Scheme 6

## Results and discussion

In continuation of our earlier work on uracils,<sup>29</sup> we reacted 6-chlorouracil **20** (6-chloropyrimidine-2,4(1*H*,3*H*)-dione) with the imidazoles **21a–e** and obtained the imidazolium salts **22a–e** in moderate to excellent yields. The anion exchange resin Amberlite IRA-400 in its hydroxy form deprotonated the salts **22a–e** to the target mesomeric betaines **2a–e** in good yields (Scheme 7).

The resonance frequency of 5-*H* of the uracil ring is diagnostic of the success of the deprotonation, as it shifts upfield by 0.15–0.54 ppm in the <sup>1</sup>H NMR spectra, depending on the substitution pattern. The betaines **2a–e** are soluble in water and other highly polar solvents such as DMSO and methanol, but almost insoluble in acetonitrile or chloroform. In the spectra of NMR measurements taken in DMSO-*d*<sub>6</sub> only the betaine tautomer of **2a–e** can be seen. No traces of the N-heterocyclic carbenes **3a–e** are visible under these conditions. At least in part this can be explained by the solubility of **2a–e** which compelled us to use highly polar solvents for the characterization. The betaines **2a–e** belong to the class of cross-conjugated heterocyclic mesomeric betaines (CCMB). Characteristically, the charges are restricted to separate parts of the common  $\pi$ -electron system in the resonance forms (**I**). The anionic part of the molecule is joined to the cationic part through a union bond which starts from an unstarred position of the isoconjugated equivalent of the  $\pi$ -electron system which delocalizes the negative charge (**II**). This is a nodal (inactive)





Scheme 7

position of the highest occupied molecular orbital (HOMO) (III) which induces the charge separation in the ground state in cross-conjugated mesomeric betaines (Fig. 1).<sup>11,12,30</sup>

In the presence of trapping reagents, the equilibrium can be shifted toward the N-heterocyclic carbene tautomer 3a. Thus, in the presence of sulfur and selenium, respectively, the thione 23 and the selenone 24 were formed in high yields (Scheme 8).

Similarly, triethylborane in dioxane converted the betaine-NHC equilibrium into the new ring system of imidazo[2,1'-[1,4,2]diazaborolo[1,5-c]pyrimidin-10-ides 25a-d as fluorescent crystalline solids (Scheme 9). A similar series of

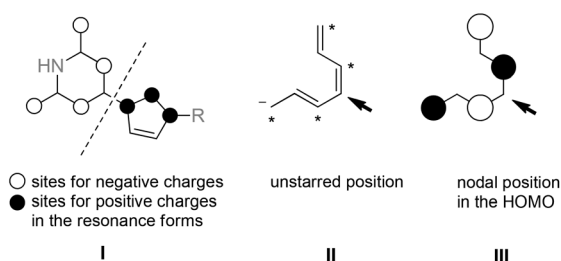
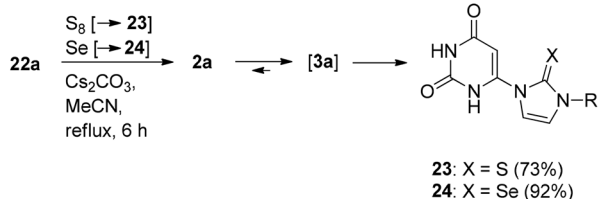
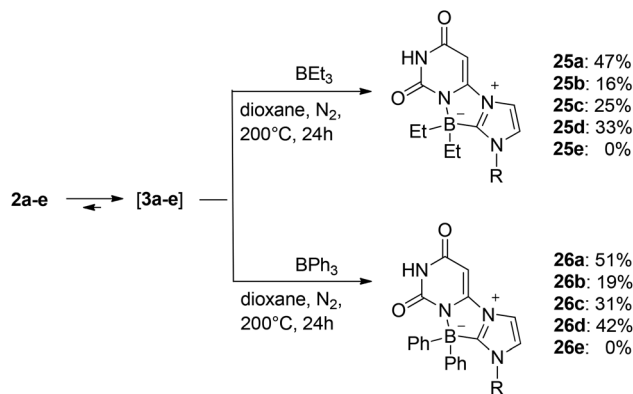


Fig. 1 Characteristic features of cross-conjugated mesomeric betaines.



Scheme 8



Scheme 9

reactions was performed with triphenylborane so that 2a-d were converted into 26a-d which were also obtained as crystalline compounds. Betaine 2e, however, did not react under these conditions. The resonance frequency of 5-H of the uracil moiety was detected between 5.96 ppm and 6.01 ppm (25) and between 6.20 ppm and 6.32 ppm (26), and the <sup>11</sup>B NMR signals appear between -1.6 ppm and 1.4 ppm depending on the solvent and the substitution pattern of the borane adduct, respectively. Thermogravimetric analyses show that decomposition of 25a, 25c, and 25d occurs above 270 °C in the solid state. The borane adducts proved to be stable towards acids. Thus, after treatment of 25a with trifluoroacetic acid in methanol at reflux temperature we were able to recover the material unchanged.

Single crystals of the boron adducts 25b and 25d were obtained by slow evaporation of concentrated solutions in ethanol. Results of single crystal X-ray analyses are as follows. The zwitterions 25b (Fig. 2) and 25d (Fig. 3 and 4) crystallized monoclinic and orthorhombic, respectively. In 25b the ethyl-hydroxy group is disordered. The B-C<sub>carbene</sub> bond lengths [B-C11; crystallographic numbering] were determined to be 161.8(4) pm (25b) and 160.7(5) pm (25d), and the B-N<sub>uracil</sub> bonds 162.3(3) pm and 162.8(4) pm, respectively. The corresponding bond angles N1-B1-C11 were determined to be 92.37(19)° (25b) and 92.2(3)° (25d). The three rings uracil, diazaborole, and imidazole are almost planar and dihedral angles

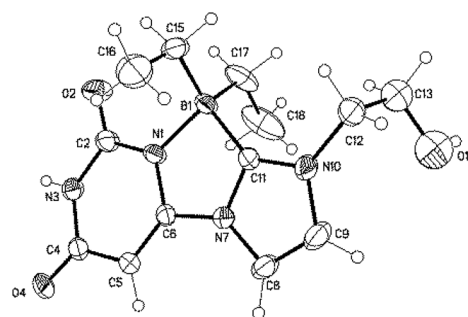


Fig. 2 Molecular structure of 25b (minor disordered part is omitted for clarity; displacement parameters are drawn at the 50% probability level).

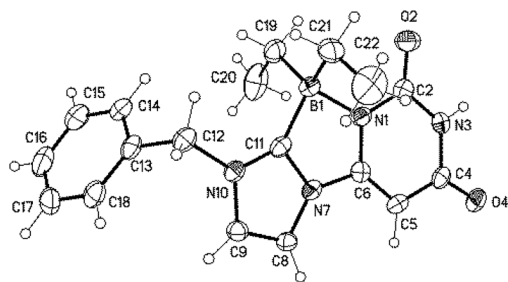


Fig. 3 Molecular structure of **25d** (one of the crystallographically independent molecules is shown; displacement parameters are drawn at the 50% probability level).

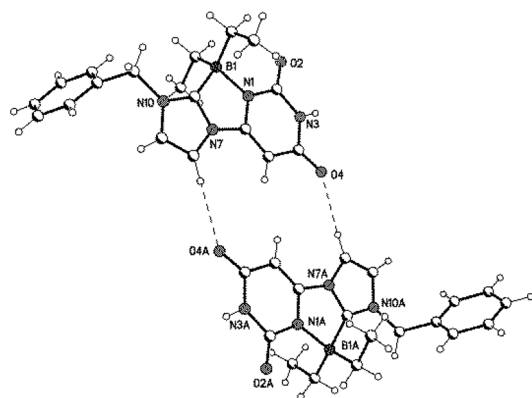


Fig. 4 Asymmetric unit of **25d** showing the dimer.

$\text{N1-C2-N3-C4} = 1.8(5)^\circ/0.0(4)^\circ$ ,  $\text{C11-B1-N1-C6} = -1.0(3)^\circ/-1.2(3)^\circ$  and  $\text{N7-C8-C9-N10} = -0.3(4)^\circ/-0.2(3)^\circ$  were measured in **25b** and **25d**, respectively. In **25b** hydrogen bonds were found between O2 and the ethyl-hydroxy group with N3-H and O4 of a neighbouring molecule, respectively.

The zwitterion **25d** dimerizes through hydrogen bonds between O4 and C8-H (264 pm,  $164^\circ$ ; crystallographic numbering).

## Conclusions

We present first examples of cross-conjugated heterocyclic mesomeric betaines which are in tautomeric equilibrium with their N-heterocyclic carbenes. Thus imidazolium-uracilates undergo tautomerism to uracil-6-yl-imidazol-2-ylidenes. Trapping reactions were performed with sulfur and selenium to give an imidazole-thione and -selenone, respectively. Triethylborane and triphenylborane yield the first representatives of a new heterocyclic zwitterionic ring system, imidazo[2',1':3,4][1,4,2]-diazaborolo[1,5-c]pyrimidinium-10-ide. These results supplement our knowledge about the interesting area of overlap between mesomeric betaines and N-heterocyclic carbenes.

## Experimental

### General considerations

Flash-chromatography was performed using silica gel 60 (0.040–0.063 mm). Nuclear magnetic resonance (NMR) spectra were obtained using Bruker Avance 400 and Bruker Avance III 600 MHz instruments.  $^1\text{H}$  NMR spectra were recorded at 400 MHz or 600 MHz.  $^{13}\text{C}$  NMR spectra were recorded at 100 MHz or 150 MHz, with the solvent peak or tetramethylsilane used as the internal reference.  $^{11}\text{B}$  NMR spectra were recorded at 128 MHz or 192 MHz. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. FT-IR spectra were recorded on a Bruker Vector 22 in the range of 400 to  $4000\text{ cm}^{-1}$ . ATR-IR spectra were recorded on a Bruker Alpha in the range of 400 to  $4000\text{ cm}^{-1}$ . The mass spectra were measured with a Varian 320 MS Triple Quad GC/MS/MS with a Varian 450-GC. The electrospray ionization mass spectra (ESIMS) were measured with an Agilent LCMSD series HP 1100 with APIES. Melting points are uncorrected and were determined in an apparatus according to Dr Tottoli (Büchi). Yields are not optimized. The compounds **22a** and **2a** have been reported in one of our earlier publications.<sup>29</sup>

**3-(2,6-Dioxo-1,2,3,6-tetrahydropyrimidin-4-yl)-1-methyl-1H-imidazolium chloride 22a.** A solution of 147 mg (1.0 mmol) of **20** and 164 mg (2.0 mmol) of **21a** in 15 mL of chlorobenzene was heated under reflux for 8 h. After cooling, a fine, nearly white precipitate was deposited, which was filtered off and thoroughly washed with diethyl ether. Recrystallization from water yielded 224 mg (98%) of a white solid. All spectroscopic data are in agreement with those reported earlier.<sup>29</sup>

**3-(2,6-Dioxo-1,2,3,6-tetrahydropyrimidin-4-yl)-1-(2-hydroxyethyl)-1H-imidazolium chloride 22b.** A solution of 147 mg (1.0 mmol) of **20** and 224 mg (2.0 mmol) of **21b** in 15 mL of chlorobenzene was heated under reflux for 8 h. After cooling, a fine, gray green precipitate was deposited, which was filtered off and thoroughly washed with diethyl ether. Recrystallization from water yielded 197 mg (76%) of a gray green solid: dec  $> 243^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta = 11.54$  (s, 1H), 9.95 (s, 1H), 8.03 (m, 1H), 8.22 (m, 1H), 6.15 (s, 1H), 4.33 (t,  $J = 5.1$  Hz, 2H), 3.79 (t,  $J = 5.1$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ):  $\delta = 163.4, 150.7, 144.3, 136.9, 123.7, 120.6, 93.6, 58.9, 52.5$  ppm; IR (ATR): 3348, 3133, 3064, 3026, 2833, 1718, 1675, 1415, 1161, 1057, 832, 583, 533  $\text{cm}^{-1}$ ; HR-ESI-MS for  $\text{C}_9\text{H}_{11}\text{N}_4\text{O}_3$  required 223.0831. Found 223.0833.

**3-(2,6-Dioxo-1,2,3,6-tetrahydropyrimidin-4-yl)-1-phenyl-1H-imidazolium chloride 22c.** A solution of 147 mg (1.0 mmol) of **20** and 288 mg (2.0 mmol) of **21c** in 15 mL of chlorobenzene was heated under reflux for 8 h. After cooling, a fine, light yellow precipitate formed, which was filtered off and thoroughly washed with diethyl ether. Recrystallization from water yielded 242 mg (83%) of a light yellow solid: dec  $> 243^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta = 11.47$  (s, 1H), 10.56 (s, 1H), 8.60 (m, 1H), 8.49 (m, 1H), 7.94–7.92 (m, 2H), 7.73–7.69 (m, 2H), 7.66–7.63 (m, 1H), 6.26 (s, 1H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ):  $\delta = 163.5, 151.1, 144.8, 135.9,$





134.3, 130.4, 130.2, 122.1, 121.7, 121.5, 93.1 ppm; IR (ATR): 3451, 3305, 2940, 2732, 1733, 1668, 1635, 1412, 1391, 1320, 1235, 823, 754, 685, 511, 430 cm<sup>-1</sup>; HR-ESI-MS for C<sub>13</sub>H<sub>11</sub>N<sub>4</sub>O<sub>2</sub> required 255.0882. Found 255.0884.

**1-Benzyl-3-(2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-yl)-1H-imidazolium chloride 22d.** A solution of 147 mg (1.0 mmol) of **20** and 316 mg (2.0 mmol) of **21d** in 15 mL of chlorobenzene was heated under reflux for 8 h. After cooling, a fine, light yellow precipitate formed, which was filtered off and thoroughly washed with diethyl ether. Recrystallization from water yielded 149 mg (49%) of a light yellow solid: dec > 258 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ = 11.58 (s, 1H), 10.19 (s, 1H), 8.24 (m, 1H), 8.09 (m, 1H), 7.55–7.53 (m, 2H), 7.47–7.71 (m, 3H), 6.16 (s, 1H), 5.56 (s, 2H) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ = 163.3, 150.6, 144.1, 137.0, 133.9, 128.9, 128.7, 128.2, 123.0, 121.5, 93.9, 52.6 ppm; IR (ATR): 3028, 2973, 2844, 1639, 1548, 1528, 1356, 1206, 974, 699, 438 cm<sup>-1</sup>; HR-ESI-MS for C<sub>14</sub>H<sub>13</sub>N<sub>4</sub>O<sub>2</sub> required 269.1039. Found 269.1039.

**3-(2,6-Dioxo-1,2,3,6-tetrahydropyrimidin-4-yl)-1-vinyl-1H-imidazolium chloride 22e.** A solution of 147 mg (1.0 mmol) of **20** and 188 mg (2.0 mmol) of **21e** in 15 mL of chlorobenzene was heated under reflux for 8 h. After cooling, a fine, light yellow precipitate formed which was filtered off and thoroughly washed with diethyl ether. Recrystallization from water yielded 135 mg (56%) of a light yellow solid: dec > 194 °C; <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ = 9.79 (s, 1H), 8.08 (m, 1H), 8.02 (m, 1H), 7.25 (dd, *J* = 15.5/8.6 Hz, 1H), 6.11 (s, 1H), 5.98 (dd, *J* = 15.5/3.1 Hz, 1H), 5.60 (dd, *J* = 8.6/3.1 Hz, 1H) ppm; <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O): δ = 165.8, 152.0, 144.5, 135.0, 127.9, 121.6, 121.2, 112.5, 95.5 ppm; IR (ATR): 3101, 3061, 2923, 2832, 1727, 1681, 1571, 1547, 1160, 1096, 1041, 579, 526 cm<sup>-1</sup>; HR-ESI-MS for C<sub>9</sub>H<sub>9</sub>N<sub>4</sub>O<sub>2</sub> required 205.0726. Found 205.0726.

### General procedure for the synthesis of the cross-conjugated mesomeric betaines 2a–2e

A 150 mL portion of the anion-exchange resin Amberlite IRA-400 was filled into a column (height: 16 cm, diameter: 3 cm) and washed with 2 L of water. Then 100 mL of a 5% hydrochloric acid solution was added and remained in the column for 2 h. The hydrochloric acid was then rinsed out with water until pH 7 was reached. 100 mL of a 5% aqueous solution of sodium hydroxide was added and remained in the column for 2 h. Then the base was rinsed out with water until pH = 7 was reached. Then, samples of 2 mmol of uracyl/hetarenum salts **22a–22e** in 100 mL of water, respectively, were added on the resin. A flow rate of one drop per second was adjusted. The eluates were evaporated to dryness *in vacuo*.

**6-(3-Methylimidazolio)-2,4(1H,3H)-pyrimidinedionate 2a.** 458 mg (2 mmol) of **22a** was used. The general procedure yielded 323 mg (84%) of a white solid. All spectroscopic data are in agreement with those reported earlier.<sup>29</sup>

**6-(3-(2-Hydroxyethyl)-imidazolio)-2,4(1H,3H)-pyrimidinedionate 2b.** 518 mg (2 mmol) of **22b** was used. The general procedure yielded 320 mg (72%) of a gray solid: dec > 230 °C; <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ = 8.05 (d, *J* = 2.2 Hz, 1H), 7.71 (d, *J* = 2.2 Hz, 1H), 5.97 (s, 1H), 4.45 (t, *J* = 4.8, 2H), 4.01 (t, *J* = 4.8,

2H) ppm; <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O): δ = 169.5, 160.5, 156.0, 132.4, 119.5, 87.0, 59.6, 52.3 ppm; IR (ATR): 3381, 3079, 3044, 2955, 1608, 1535, 1476, 1439, 1373, 1101, 1071, 788, 585, 546 cm<sup>-1</sup>; HR-ESI-MS for C<sub>9</sub>H<sub>11</sub>N<sub>4</sub>O<sub>3</sub> required 223.0831. Found 223.0831.

**6-(3-Phenylimidazolio)-2,4(1H,3H)-pyrimidinedionate 2c.** 582 mg (2 mmol) of **22c** was used. The general procedure yielded 406 mg (80%) of a light yellow solid: dec > 267 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ = 10.28 (s, 1H), 10.20 (s, 1H), 8.48 (m, 1H), 8.46 (m, 1H), 7.92–7.90 (m, 2H), 7.69–7.65 (m, 2H), 7.63–7.59 (m, 1H), 5.90 (s, 1H) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ = 166.2, 157.1, 152.7, 134.6, 133.9, 130.0, 122.2, 121.8, 119.9, 85.5 ppm; IR (ATR): 3394, 3116, 3050, 2970, 1726, 1676, 1618, 1545, 1217, 1109, 1081, 972, 764, 601, 528, 421 cm<sup>-1</sup>; HR-ESI-MS for C<sub>13</sub>H<sub>11</sub>N<sub>4</sub>O<sub>2</sub> required 255.0882. Found 255.0884.

**6-(3-Benzylimidazolio)-2,4(1H,3H)-pyrimidinedionate 2d.** 610 mg (2 mmol) of **22d** was used. The general procedure yielded 413 mg (77%) of a light yellow solid: dec > 278 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ = 9.97 (s, 1H), 9.74 (s, 1H), 8.28 (m, 1H), 7.88 (m, 1H), 7.49–7.47 (m, 2H), 7.44–7.41 (m, 2H), 7.40–7.38 (m, 1H), 5.62 (s, 1H), 5.45 (s, 2H) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ = 167.4, 159.0, 155.3, 135.1, 129.5, 129.3, 128.9, 123.5, 119.7, 83.3, 52.8 ppm; IR (ATR): 3152, 3061, 2948, 2775, 1610, 1544, 1475, 1395, 1376, 1185, 1110, 908, 851, 768, 716, 701, 543, 447 cm<sup>-1</sup>; HR-ESI-MS for C<sub>14</sub>H<sub>13</sub>N<sub>4</sub>O<sub>2</sub> required 269.1039. Found 269.1039.

**6-(3-Vinylimidazolio)-2,4(1H,3H)-pyrimidinedionate 2e.** 482 mg (2 mmol) of **22e** was used. The general procedure yielded 318 mg (78%) of a light yellow solid: dec > 226 °C; <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O): δ = 8.08 (d, *J* = 2.3 Hz, 1H), 7.94 (d, *J* = 2.3 Hz, 1H), 7.23 (dd, *J* = 15.5/8.6 Hz, 1H), 5.96 (s, 1H), 5.95 (dd, *J* = 15.5/3.0 Hz, 1H), 5.56 (dd, *J* = 8.6/3.0 Hz, 1H) ppm; <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O): δ = 169.4, 160.5, 155.8, 128.1, 120.2, 119.8, 111.1, 87.0 ppm; IR (ATR): 3372, 3110, 2966, 1676, 1623, 1490, 1085, 975, 781, 612, 448 cm<sup>-1</sup>; HR-ESI-MS for C<sub>9</sub>H<sub>9</sub>N<sub>4</sub>O<sub>2</sub> required 205.0726. Found 205.0727.

**6-(3-Methyl-2-thioxo-2,3-dihydro-1H-imidazol-1-yl)pyrimidine-2,4(1H,3H)-dione 23.** 326 mg (1 mmol) of caesium carbonate was added to a suspension of 96 mg (0.5 mmol) of **22a** and 38 mg (0.6 mmol) of sulfur in 15 mL of dry acetonitrile. The mixture was heated under a nitrogen atmosphere under reflux for 7 h. After cooling, the solvent was evaporated *in vacuo*. The product was separated with column chromatography (pure ethyl acetate). Evaporating to dryness *in vacuo* formed a light yellow solid: yield 82 mg (73%); dec > 320 °C; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ = 9.77 (s, 1H), 7.62 (d, *J* = 2.6 Hz, 1H), 7.22 (d, *J* = 2.6 Hz, 1H), 6.78 (s, 1H), 3.48 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>): δ = 167.0, 160.9, 158.7, 157.0, 118.4, 115.5, 88.0, 34.4 ppm; IR (ATR): 3114, 2915, 2812, 1683, 1617, 1564, 1399, 1366, 1268, 1233, 811, 541, 531, 431 cm<sup>-1</sup>; HR-ESI-MS for C<sub>8</sub>H<sub>7</sub>N<sub>4</sub>O<sub>2</sub>S required 223.0290. Found 223.0285.

**6-(3-Methyl-2-selenoxo-2,3-dihydro-1H-imidazol-1-yl)pyrimidine-2,4(1H,3H)-dione 24.** 326 mg (1 mmol) of caesium carbonate was added to a suspension of 96 mg (0.5 mmol) of **22a** and 47 mg (0.6 mmol) of selenium in 15 mL of dry



acetonitrile. The mixture was heated under a nitrogen atmosphere under reflux for 7 h. After cooling, the solvent was evaporated *in vacuo*. The product was separated with column chromatography (pure ethyl acetate). Evaporating to dryness *in vacuo* formed a yellow solid: yield 125 mg (92%); dec > 312 °C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  = 9.80 (s, 1H), 7.69 (d,  $J$  = 2.4 Hz, 1H), 7.41 (d,  $J$  = 2.4 Hz, 1H), 6.58 (s, 1H), 3.58 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  = 166.7, 158.4, 157.2, 153.7, 120.5, 118.4, 89.6, 36.5 ppm; IR (ATR): 3115, 2916, 1612, 1563, 1486, 1446, 1365, 1227, 862, 783, 459  $\text{cm}^{-1}$ ; HR-ESI-MS for  $\text{C}_8\text{H}_7\text{N}_4\text{O}_2\text{Se}$  required 270.9734. Found 270.9736.

**10,10-Diethyl-1-methyl-6,8-dioxo-6,7,8,10-tetrahydro-1H-imidazo[2',1':3,4][1,4,2]diazaborolo[1,5-c]pyrimidin-10-ide 25a.** A solution of 460 mg (5 mmol) of  $\text{BeT}_3$  in 2 mL of dioxane was added to a suspension of 96 mg (0.5 mmol) of **2a** in 5 mL of dioxane. The mixture was then stirred at 200 °C under a nitrogen atmosphere in a Schlenk-tube for 24 h. After cooling, the solvent was evaporated *in vacuo*. The product was separated by column chromatography (ethyl acetate–ethanol = 2 : 1). After evaporating to dryness *in vacuo*, recrystallization from ethanol formed a colorless solid: yield 61 mg (47%); dec > 251 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  = 8.00 (d,  $J$  = 2.0 Hz, 1H), 7.56 (d,  $J$  = 2.0 Hz, 1H), 5.96 (s, 1H), 3.89 (s, 1H), 1.07–0.98 (m, 2H), 0.74–0.65 (m, 2H), 0.51 (t,  $J$  = 7.7 Hz, 6H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  = 168.5, 153.8, 153.5, 128.4, 115.2, 83.4, 35.8, 12.4, 10.9 ppm;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  = 1.3 ppm; IR (ATR): 3118, 2942, 2864, 1704, 1634, 1482, 1398, 1317, 796, 769, 599, 451  $\text{cm}^{-1}$ ; HR-ESI-MS for  $\text{C}_{12}\text{H}_{18}\text{N}_4\text{O}_2\text{B}$  required 261.1523. Found 261.1525.

**10,10-Diethyl-1-(hydroxymethyl)-6,8-dioxo-6,7,8,10-tetrahydro-1H-imidazo[2',1':3,4][1,4,2]diazaborolo[1,5-c]pyrimidin-10-ide 25b.** A solution of 460 mg (5 mmol) of  $\text{BeT}_3$  in 2 mL of dioxane was added to a suspension of 111 mg (0.5 mmol) of **2b** in 5 mL of dioxane. The mixture was stirred at 200 °C under a nitrogen atmosphere in a Schlenk-tube for 24 h. After cooling, the solvent was evaporated *in vacuo*. The product was separated by column chromatography (ethyl acetate–ethanol = 2 : 1). After evaporating to dryness *in vacuo*, recrystallization from ethanol formed a colorless solid: yield 30 mg (16%); dec > 185 °C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  = 10.60 (s, 1H), 8.22 (d,  $J$  = 2.0 Hz, 1H), 7.77 (d,  $J$  = 2.0 Hz, 1H), 6.00 (s, 1H), 4.12 (t,  $J$  = 5.3 Hz, 2H), 3.75 (t,  $J$  = 5.3 Hz, 2H), 0.92–0.83 (m, 2H), 0.54–0.45 (m, 2H), 0.40 (t,  $J$  = 7.6 Hz, 6H) ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  = 165.0, 151.2, 150.7, 136.0, 129.9, 129.8, 127.0, 123.7, 115.0, 82.5, 12.0, 10.4 ppm;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  = –0.4 ppm; IR (ATR): 3386, 3158, 3136, 3022, 2935, 2900, 2659, 1668, 1641, 1563, 1452, 1402, 1079, 787, 724, 595, 446  $\text{cm}^{-1}$ ; HR-ESI-MS for  $\text{C}_{13}\text{H}_{19}\text{N}_4\text{O}_3\text{BNa}$  required 313.1448. Found 313.1448.

**10,10-Diethyl-6,8-dioxo-1-phenyl-6,7,8,10-tetrahydro-1H-imidazo[2',1':3,4][1,4,2]diazaborolo[1,5-c]pyrimidin-10-ide 25c.** A solution of 460 mg (5 mmol) of  $\text{BeT}_3$  in 2 mL of dioxane was added to a suspension of 127 mg (0.5 mmol) of **2c** in 5 mL of dioxane. The mixture was stirred at 200 °C under a nitrogen atmosphere in a Schlenk-tube for 24 h. After cooling, the solvent was evaporated *in vacuo*. The product was separated by

column chromatography (ethyl acetate–ethanol = 2 : 1). After evaporating to dryness *in vacuo*, recrystallization from ethanol formed a yellow solid: yield 40 mg (25%); dec > 204 °C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  = 10.70 (s, 1H), 8.49 (d,  $J$  = 2.1 Hz, 1H), 8.20 (d,  $J$  = 2.1 Hz, 1H), 7.69–7.64 (m, 2H), 7.62–7.58 (m, 3H), 6.13 (s, 1H), 0.91–0.82 (m, 2H), 0.37 (t,  $J$  = 7.5 Hz, 6H), 0.33–0.24 (m, 2H) ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  = 165.2, 151.3, 151.0, 126.7, 114.0, 81.9, 59.6, 50.8, 11.7, 10.5 ppm;  $^{11}\text{B}$  NMR (128 MHz, DMSO- $d_6$ ):  $\delta$  = 0.0 ppm; IR (ATR): 3135, 2917, 2858, 1694, 1637, 1593, 1471, 1451, 1395, 1258, 793, 763, 750, 735, 690  $\text{cm}^{-1}$ ; HR-ESI-MS for  $\text{C}_{17}\text{H}_{19}\text{N}_4\text{O}_2\text{BNa}$  required 345.1499. Found 345.1500.

**1-Benzyl-10,10-diethyl-6,8-dioxo-6,7,8,10-tetrahydro-1H-imidazo[2',1':3,4][1,4,2]diazaborolo[1,5-c]pyrimidin-10-ide 25d.** A solution of 460 mg (5 mmol) of  $\text{BeT}_3$  in 2 mL of dioxane was added to a suspension of 134 mg (0.5 mmol) of **2d** in 5 mL of dioxane. The mixture was stirred at 200 °C under a nitrogen atmosphere in a Schlenk-tube for 24 h. After cooling, the solvent was evaporated *in vacuo*. The product was separated by column chromatography (ethyl acetate–ethanol = 2 : 1). After evaporating to dryness *in vacuo*, recrystallization from ethanol formed a yellow solid: yield 56 mg (33%); dec > 262 °C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  = 10.62 (s, 1H), 8.27 (d,  $J$  = 1.4 Hz, 1H), 7.81 (d,  $J$  = 1.4 Hz, 1H), 7.43–7.40 (m, 2H), 7.38–7.35 (m, 1H), 7.32–7.31 (m, 2H), 6.01 (s, 1H), 5.34 (s, 2H), 0.89–0.83 (m, 2H), 0.50–0.43 (m, 2H), 0.33 (t,  $J$  = 5.1 Hz, 6H) ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  = 165.6, 151.8, 151.4, 135.6, 129.3, 128.9, 128.1, 127.0, 115.3, 82.6, 52.1, 12.1, 10.9 ppm;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  = –0.2 ppm; IR (ATR): 3173, 2928, 2896, 2855, 2814, 1706, 1661, 1560, 1475, 1367, 1238, 794, 758, 706, 694, 446, 419  $\text{cm}^{-1}$ ; HR-ESI-MS for  $\text{C}_{18}\text{H}_{21}\text{N}_4\text{O}_2\text{BNa}$  required 359.1655. Found 359.1658.

**1-Methyl-6,8-dioxo-10,10-diphenyl-6,7,8,10-tetrahydro-1H-imidazo[2',1':3,4][1,4,2]diazaborolo[1,5-c]pyrimidin-10-ide 26a.** A solution of 242 mg (1 mmol) of  $\text{BPh}_3$  in 2 mL of dichloromethane was added to a suspension of 96 mg (0.5 mmol) of **2a** in 5 mL of dioxane. The mixture was stirred at 200 °C under a nitrogen atmosphere in a Schlenk-tube for 24 h. After cooling, the solvent was evaporated *in vacuo*. The product was separated by column chromatography (ethyl acetate–ethanol = 2 : 1). After evaporating to dryness *in vacuo*, recrystallization from ethanol formed a white solid: yield 91 mg (51%); dec > 352 °C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  = 10.73 (s, 1H), 8.32 (d,  $J$  = 2.0 Hz, 1H), 7.76 (d,  $J$  = 2.0 Hz, 1H), 7.23–7.12 (m, 10H), 6.20 (s, 1H), 3.29 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  = 164.9, 150.9, 150.3, 144.3, 133.5, 128.0, 127.1, 126.0, 114.6, 83.4, 35.4 ppm;  $^{11}\text{B}$  NMR (192 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  = –1.3 ppm; IR (ATR): 3154, 3115, 3041, 1683, 1661, 1460, 1398, 1240, 989, 876, 714, 700, 592, 582, 435  $\text{cm}^{-1}$ . HR-ESI-MS for  $\text{C}_{20}\text{H}_{17}\text{N}_4\text{O}_2\text{BNa}$  required 379.1342. Found 379.1343.

**1-(2-Hydroxyethyl)-6,8-dioxo-10,10-diphenyl-6,7,8,10-tetrahydro-1H-imidazo[2',1':3,4][1,4,2]diazaborolo[1,5-c]pyrimidin-10-ide 26b.** A solution of 242 mg (1 mmol) of  $\text{BPh}_3$  in 2 mL of dichloromethane was added to a suspension of 111 mg (0.5 mmol) of **2b** in 5 mL of dioxane. The mixture was



stirred at 200 °C under a nitrogen atmosphere in a Schlenk-tube for 24 h. After cooling, the solvent was evaporated *in vacuo*. The product was separated with column chromatography (ethyl acetate–ethanol = 2 : 1). After evaporating to dryness *in vacuo*, recrystallization from ethanol formed a light brown solid: yield 37 mg (19%); dec > 255 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 10.71 (s, 1H), 8.34 (d, *J* = 2.0 Hz, 1H), 7.74 (d, *J* = 2.0 Hz, 1H), 7.23–7.15 (m, 10H), 6.21 (s, 1H), 5.01 (t, *J* = 5.0 Hz, 1H), 3.95 (t, *J* = 5.0 Hz, 2H), 3.23 (q, *J* = 5.0 Hz, 2H) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 164.9, 150.7, 150.3, 144.3, 133.5, 127.7, 127.1, 126.0, 114.3, 83.4, 58.8, 50.8 ppm; <sup>11</sup>B NMR (128 MHz, DMSO-*d*<sub>6</sub>): δ = –1.2 ppm; IR (ATR): 3156, 3091, 3004, 1699, 1645, 1478, 1079, 996, 810, 752, 717, 701, 590, 433 cm<sup>–1</sup>; HR-ESI-MS for C<sub>21</sub>H<sub>19</sub>N<sub>4</sub>O<sub>3</sub>BNA required 409.1448. Found 409.1447.

**6,8-Dioxo-1,10,10-triphenyl-6,7,8,10-tetrahydro-1*H*-imidazo[2',1':3,4][1,4,2]diazaborolo[1,5-*c*]pyrimidin-10-ide 26c.** A solution of 242 mg (1 mmol) of BPh<sub>3</sub> in 2 mL of dichloromethane was added to a suspension of 127 mg (0.5 mmol) of **2c** in 5 mL of dioxane. The mixture was stirred at 200 °C under a nitrogen atmosphere in a Schlenk-tube for 24 h. After cooling, the solvent was evaporated *in vacuo*. The product was separated by column chromatography (ethyl acetate–ethanol = 2 : 1). After evaporating to dryness *in vacuo*, recrystallization from ethanol formed a light yellow solid: yield 65 mg (31%); dec > 339 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 10.79 (s, 1H), 8.62 (d, *J* = 2.0 Hz, 1H), 8.22 (d, *J* = 2.0 Hz, 1H), 7.47–7.42 (m, 1H), 7.36–7.32 (m, 2H), 7.20–7.17 (m, 2H), 7.10 (s, 10H), 6.32 (s, 1H) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 164.9, 150.7, 150.0, 144.4, 135.7, 133.5, 129.7, 129.4, 127.4, 126.9, 125.9, 123.9, 115.5, 83.9 ppm; <sup>11</sup>B NMR (128 MHz, DMSO-*d*<sub>6</sub>): δ = –1.0 ppm; IR (ATR): 3161, 3135, 2999, 2823, 1711, 1662, 1480, 1428, 1392, 1251, 804, 762, 720, 689, 598, 546, 443 cm<sup>–1</sup>; HR-ESI-MS for C<sub>25</sub>H<sub>19</sub>N<sub>4</sub>O<sub>2</sub>BNA required 441.1499. Found 441.1501.

**1-Benzyl-6,8-dioxo-10,10-diphenyl-6,7,8,10-tetrahydro-1*H*-imidazo[2',1':3,4][1,4,2]diazaborolo[1,5-*c*]pyrimidin-10-ide 26d.** A solution of 242 mg (1 mmol) of BPh<sub>3</sub> in 2 mL of dichloromethane was added to a suspension of 134 mg (0.5 mmol) of **2d** in 5 mL of dioxane. The mixture was stirred at 200 °C under a nitrogen atmosphere in a Schlenk-tube for 24 h. After cooling, the solvent was evaporated *in vacuo*. The product was separated by column chromatography (ethyl acetate–ethanol = 2 : 1). After evaporating to dryness *in vacuo*, recrystallization from ethanol formed a light yellow solid: yield 90 mg (42%); dec > 346 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 10.75 (s, 1H), 8.36 (d, *J* = 2.1 Hz, 1H), 7.68 (d, *J* = 2.1 Hz, 1H), 7.30–7.27 (m, 4H), 7.22–7.17 (m, 7H), 7.14–7.10 (m, 2H), 6.64–6.61 (m, 2H), 6.20 (s, 1H), 5.11 (s, 2H) ppm; <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 164.9, 150.8, 150.2, 144.4, 134.0, 133.5, 128.5, 128.4, 128.1, 127.3, 126.2, 126.1, 115.6, 83.6, 51.6 ppm; <sup>11</sup>B NMR (128 MHz, DMSO-*d*<sub>6</sub>): δ = –1.5 ppm; IR (ATR): 3169, 3148, 3024, 3002, 1712, 1662, 1567, 1472, 1363, 1339, 993, 807, 752, 707, 588, 570, 433 cm<sup>–1</sup>. HR-ESI-MS for C<sub>26</sub>H<sub>21</sub>N<sub>4</sub>O<sub>2</sub>BNA required 455.1655. Found 455.1652.

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## Notes and references

- 1 M. S. Novikov and A. N. Geisman, *Chem. Heterocycl. Compd.*, 2014, **49**, 1426; S. A. Grabovskiy, Y. I. Murinov and N. N. Kabal'nova, *Curr. Org. Chem.*, 2012, **16**, 2389; A. O. Dolinkin and M. S. Chernov'yants, *Pharm. Chem. J.*, 2010, **44**, 99; D. Lecca and S. Ceruti, *Biochem. Pharmacol.*, 2008, **75**, 1869.
- 2 M. Goodgame and D. A. Jakubovic, *Coord. Chem. Rev.*, 1987, **79**, 97.
- 3 R. Parajuli, *Int. J. Chem. Sci.*, 2012, **10**, 1477.
- 4 W. Zhu, X. Luo, C. M. Puah, X. Tan, J. Shen, J. Gu, K. Chen and H. Jiang, *J. Phys. Chem. A*, 2004, **108**, 4008; M. Goodgame and K. W. Johns, *J. Chem. Soc., Dalton Trans.*, 1977, **2**, 1680; J. A. Carrabine and M. Sundaralingham, *Biochemistry*, 1971, **10**, 292.
- 5 B. Lippert, W. Micklitz, O. Renn, G. Trötscher, I. Dieter and G. Frommer, *Pure Appl. Chem.*, 1990, **62**, 1075; B. Lippert, *Inorg. Chim. Acta*, 1981, **55**, 5.
- 6 T. Matsubara and K. Hirao, *J. Mol. Struct. (THEOCHEM)*, 2002, **581**, 203.
- 7 K. K. Narang, V. P. Singh and D. Bhattacharya, *Transition Met. Chem.*, 1997, **22**, 333; Md. Abdus Salam, H. Q. Yuan, T. Kikuchi, N. Anand Prasad, I. Fujisawa and K. Aoki, *Inorg. Chim. Acta*, 2009, **362**, 1158.
- 8 M. E. Kletskii, E. B. Tsupak and D. A. Nazarov, *Chem. Heterocycl. Compd.*, 2002, **38**, 965.
- 9 A. Schmidt, S. Wiechmann and T. Freese, *ARKIVOC*, 2013, **i**, 424.
- 10 D. P. Curran, A. Solov'yev, M. M. Brahmi, L. Fensterbank, M. Malacria and E. Lacôte, *Angew. Chem., Int. Ed.*, 2011, **50**, 10294.
- 11 W. D. Ollis, S. P. Stanforth and C. A. Ramsden, *Tetrahedron*, 1985, **41**, 2239.
- 12 A. Schmidt, *Curr. Org. Chem.*, 2004, **8**, 653; A. Schmidt, *Adv. Heterocycl. Chem.*, 2003, **85**, 67; H. Wamhoff and A. Schmidt, *J. Org. Chem.*, 1993, **58**, 6976.
- 13 S. Grundemann, A. Kovacevic, M. Albrecht, J. W. Faller and R. H. Crabtree, *Chem. Commun.*, 2001, 2274.
- 14 G. Guisado-Barrios, J. Bouffard, B. Donnadiou and G. Bertrand, *Angew. Chem.*, 2010, **122**, 4869, (*Angew. Chem. Int. Ed.*, 2010, **49**, 4759).
- 15 O. Schuster, L. Yang, H. G. Raubenheimer and M. Albrecht, *Chem. Rev.*, 2009, **109**, 3445; H. G. Raubenheimer and S. Cronje, *Dalton Trans.*, 2008, 1265; C. E. Strasser, E. Stander-Grobler, O. Schuster, S. Cronje and H. G. Raubenheimer, *Eur. J. Inorg. Chem.*, 2009, 1905.
- 16 A. Schmidt and Z. Guan, *Synthesis*, 2012, 3251; A. Schmidt and A. Dreger, *Curr. Org. Chem.*, 2011, **15**, 2897; A. Schmidt





- and A. Dreger, *Curr. Org. Chem.*, 2011, **15**, 1423; A. Schmidt, A. Beutler and B. Snovydyovych, *Eur. J. Org. Chem.*, 2008, 4073.
- 17 R. H. Crabtree, *Coord. Chem. Rev.*, 2013, **257**, 755.
- 18 B. R. van Ausdall, B. R. J. L. Glass, K. M. Wiggins, A. M. Aarif and J. Louie, *J. Org. Chem.*, 2009, **74**, 7935; H. Zhou, W.-Z. Zhang, C.-H. Liu, J.-P. Qu and X.-B. Lu, *J. Org. Chem.*, 2008, **73**, 8039; A. M. Magill, K. G. Cavell and B. F. Yates, *J. Am. Chem. Soc.*, 2004, **126**, 8717; M. Fèvre, J. Pinaud, A. Leteneur, Y. Gnanou, J. Vignolle, D. Taton, K. Miqueu and J.-M. Sotiropoulos, *J. Am. Chem. Soc.*, 2012, **134**, 6776; J. Li, J. Peng, G. Zhang, Y. Bai, G. Lai and X. Li, *New J. Chem.*, 2010, **34**, 1330; T. Le Gall, S. Baltatu and S. K. Collins, *Synthesis*, 2011, 3687; T. K. Olszewski and D. E. Jaskólska, *Heteroat. Chem.*, 2012, **23**, 605; W. Wyer, G. Gucciardo, V. Leigh, H. Müller-Bunz and M. Albrecht, *J. Organomet. Chem.*, 2011, **696**, 2882.
- 19 A. Schmidt and T. Habeck, *Lett. Org. Chem.*, 2005, **2**, 37; A. Schmidt, T. Habeck, L. Merkel, M. Mäkinen and P. Vainiotalo, *Rapid Commun. Mass Spectrom.*, 2005, **19**, 2211; A. Schmidt, N. Münster and A. Dreger, *Angew. Chem.*, 2010, **122**, 2851, (*Angew. Chem. Int. Ed.*, 2010, **49**, 2790); A. Dreger, R. Cisneros Camuña, N. Münster, T. A. Rokob, I. Pápai and A. Schmidt, *Eur. J. Org. Chem.*, 2010, 4296.
- 20 L. Delaude, *Eur. J. Inorg. Chem.*, 2009, 1681; S.-i. Matsuoka, Y. Tochigi, K. Takagi and M. Suzuki, *Tetrahedron*, 2012, **68**, 9836; L. M. Yagupol'skii, Yu. P. Kokhanovskii and K. I. Petko, *Russ. J. Org. Chem.*, 2010, **46**, 903; M. Hans, Q. Willem, J. Wouters, A. Demonceau and L. Delaude, *Organometallics*, 2011, **30**, 6133; Z. Guo, N. R. Song, J. H. Moon, M. Kim, E. J. Jun, J. Choi, J. Y. Lee, C. W. Bielawski, J. L. Sessler and J. Yoon, *J. Am. Chem. Soc.*, 2012, **134**, 17846.
- 21 A. Dreger, M. Nieger, M. H. H. Drafz and A. Schmidt, *Z. Naturforsch.*, 2012, **67b**, 359; A. Schmidt, A. Beutler, M. Albrecht and F. J. Ramírez, *Org. Biomol. Chem.*, 2008, **6**, 287.
- 22 V. Lavallo, C. A. Dyker, B. Donnadieu and G. Bertrand, *Angew. Chem.*, 2008, **120**, 5491, (*Angew. Chem., Int. Ed.*, 2008, **47**, 5411); V. Lavallo, C. A. Dyker, B. Donnadieu and G. Bertrand, *Angew. Chem.*, 2009, **121**, 1568, (*Angew. Chem., Int. Ed.*, 2009, **48**, 1540); M. Christl and B. Engels, *Angew. Chem.*, 2009, **121**, 1566, (*Angew. Chem., Int. Ed.*, 2009, **48**, 1538); Y. Han and H. V. Huynh, *Dalton Trans.*, 2011, **40**, 2141; M. M. Hänninen, A. Peuronen and H. M. Tuononen, *Chem. – Eur. J.*, 2009, **15**, 7287.
- 23 L. Benhamou, N. Vujkovic, V. César, H. Gornitzka, N. Lugan and G. Lavigne, *Organometallics*, 2010, **29**, 2616; L. Benhamou, V. César, H. Gornitzka, N. Lugan and G. Lavigne, *Chem. Commun.*, 2009, 4720; A. T. Biju, K. Hirano, R. Fröhlich and F. Glorius, *Chem.–Asian J.*, 2009, **4**, 1786.
- 24 G. Lavigne, V. César and N. Lugan, *Chem.–Eur. J.*, 2010, **16**, 11432; V. César, N. Lugan and G. Lavigne, *J. Am. Chem. Soc.*, 2008, **130**, 11286.
- 25 S. Wiechmann and T. Freese, manuscript in preparation.
- 26 C. Färber, M. Leibold, C. Bruhn, M. Maurer and U. Siemeling, *Chem. Commun.*, 2012, **48**, 227.
- 27 V. César, J.-C. Tourneux, N. Vujkovic, R. Brousses, N. Lugan and G. Lavigne, *Chem. Commun.*, 2012, **48**, 2349; A. A. Danopoulos, K. Yu. Monakhov and P. Braunstein, *Chem.–Eur. J.*, 2013, **19**, 450.
- 28 N. Pidlypnyi, J. C. Namyslo, M. H. H. Drafz, M. Nieger and A. Schmidt, *J. Org. Chem.*, 2013, **78**, 1070; N. Pidlypnyi, F. Uhrner, M. Nieger, M. H. H. Drafz, E. G. Hübner, J. C. Namyslo and A. Schmidt, *Eur. J. Org. Chem.*, 2013, 7739.
- 29 A. Schmidt, M. K. Kindermann, P. Vainiotalo and M. Nieger, *J. Org. Chem.*, 1999, **64**, 9499.
- 30 K. T. Potts, P. M. Murphy and W. R. Kuehnling, *J. Org. Chem.*, 1988, **53**, 2889; K. T. Potts, P. M. Murphy, M. R. DeLuca and W. R. Kuehnling, *J. Org. Chem.*, 1988, **53**, 2898.

