Influence of Guanidinium Salts and Other Ionic Liquids on the Three-Component Aza-*Diels–Alder* Reaction

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The three-component reaction of aniline, benzaldehyde, and dienophiles such as 2,3-dihydrofuran, ethyl vinyl ether, 2,3-dihydropyran, and cyclopentadiene can be promoted by ionic liquids like imidazolium salts and guanidinium salts under thermal as well as microwave conditions. The chemical yield as well as the diastereoselectivity of the *Povarov* reaction strongly depend on the ionic liquid employed. The guanidinium salts can be recycled and reused several times without loss of reactivity.

Introduction. – The inverse electron-demand aza-*Diels–Alder* reaction of an electron-poor, positively charged, or neutral 2-azabutadiene with an electron-rich alkene, the so-called *Povarov* reaction, is one of the most efficient and flexible routes for the synthesis of tetrahydroquinolines [1]. Two methods, *i.e.*, the use of preformed 2-azabutadienes and the *in situ* preparation of 2-azabutadienes, have been developed to supply the required 2-azabutadienes. Many aza-*Diels–Alder* reactions reported so far make use of a preformed *N*-arylimine as the heterodiene, which can be generated by condensation of an aromatic amine with a carbonyl compound [2]. However, the use of preformed imines as heterodienes is often hampered by their instability. In fact, many imines are unstable at higher temperatures and rapidly hydrolyze upon contact to H_2O. Their purification by distillation or chromatography can sometimes be difficult [3]. The *in situ* generation of 2-azabutadienes by reaction of an amine with a CO compound in the presence of a dienophile not only circumvents the problems encountered with the instability of preformed 2-azabutadienes, it also allows the synthesis of tetrahydroquinolines and related heterocycles in one pot [4]. This type of three-component reaction can be promoted by numerous reagents such as SmI_2 [4a], $SbCl_3$ [4b], phosphomolybdic acid [4c], TMSCl [4d], I_2 [4e], sulfamic acid [4f], $InCl_3$ [4g][4j], $Sc(OTf)_3$ [4g], *Selectfluor*™ [4h], fluorinated alcohols [4i], $Dy(OTf)_3$ [4k][4m], $GdCl_3$ [4l], $Ln(OTf)_3$ [4n], and CF_3CO_2H [4o][4p].

Recently, the application of ionic liquids as solvents and catalysts in organic transformations has become very popular [5]. Ionic liquids have negligible vapor pressure, are thermally and chemically stable, have a wide operating temperature range, and can be reused. This is why they represent a more sustainable, environmentally safe alternative to volatile traditional organic solvents. However, the attention which ionic liquids have received in organic synthesis is not only due to their solvent properties but also to their catalytic effects. It has been demonstrated that ionic liquids

exert a strong influence on the kinetics or the stereoselectivity of reactions [5c][5f][6]. These effects probably can be attributed to polar interactions between the ionic liquids, and the substrates, the transition states, or the intermediates. Apart from the well-studied imidazolium salts, there are a number of other ionic liquids such as pyridinium, phosphonium, and ammonium salts [5]. Recently, guanidinium salt-based ionic liquids have received considerable attention. Guanidinium salts can easily be synthesized by a number of efficient and reliable methods [7]. They have been used as solvents or catalysts for a number of transformations such as the aldol reaction [8], the condensation of indoles with aldehydes to produce bis(indolyl)methanes [9], the *Knoevenagel* reaction [10], the *Mannich* reaction [11], the asymmetric α-aminoxylation of CO compounds [12], the *Henry* reaction [13], the fixation of CO_2 by epoxides [14], the *Heck* reaction [15], the hydrogenation [16], the hydroformylation [17], the oxidation of benzylic alcohols [18], and the *Sharpless* dihydroxylation [19].

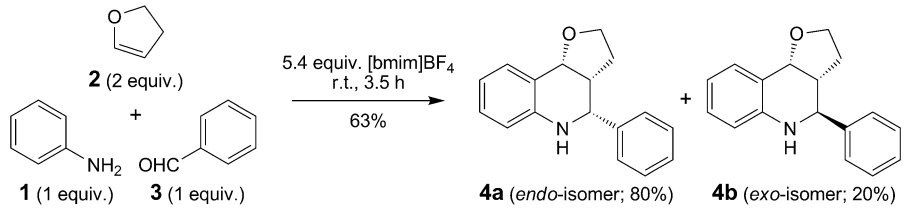
Ionic liquids have also been employed to promote aza-*Diels–Alder* reactions [20][21]. *Yadav et al.* reported the three-component synthesis of pyrano- and furoquinolines using [bmim]BF_4 as ionic liquid [20d]. *Jurčík* and *Wilhelm* have shown that aza-*Diels–Alder* reactions between preformed 2-azabutadienes and alkenes can be catalyzed by an imidazolinium hexafluorophosphate as the ionic liquid [20c]. *Li et al.* reported the synthesis of pyrano- and furoquinolines *via* the three-component reaction between an imidazolium tetrafluoroborate bound benzaldehyde, an aniline, and a cyclic enol ether [20b]. In addition, it has been established that aza-*Diels–Alder* reactions with imines as the dienophile can be performed in the presence of ionic liquids [20c][21].

Results and Discussion. – Close inspection of the results published led to the assumption that yields and stereoselectivities of the aza-*Diels–Alder* reaction for the synthesis of furoquinolines depend on the ionic liquid and the reaction conditions. This prompted us to study the influence of different ionic liquids on the outcome of a typical aza-*Diels–Alder* reaction under different reaction conditions. As part of a program devoted to the development of new ionic liquids for application in organic synthesis, we were particularly interested whether guanidinium salts can be used as solvents and/or catalysts for the aza-*Diels–Alder* reaction.

The three-component reaction between aniline (**1**), 2,3-dihydrofuran (**2**), and benzaldehyde (**3**) was studied first. For comparison, this reaction was performed initially in the presence of an imidazolium salt. When 1 equiv. of **1**, 2 equiv. of **2**, and 1 equiv. of **3** were reacted in [bmim]BF_4 (=1-butyl-3-methylimidazolium tetrafluoroborate) under *Yadav*'s conditions [20d], *i.e.*, at room temperature for 3.5 h, 63% of a 4:1 mixture of the *endo*- and the *exo*-furoquinolines, **4a** and **4b**, respectively, was formed (*Scheme 1*). The *endo*/*exo* ratio was determined by ^{1}H-NMR analysis of the mixture after column filtration on SiO_2. This result is in contrast to the findings of *Yadav et al.* who reported the exclusive formation of the *endo*-isomer **4a** in 92% yield.

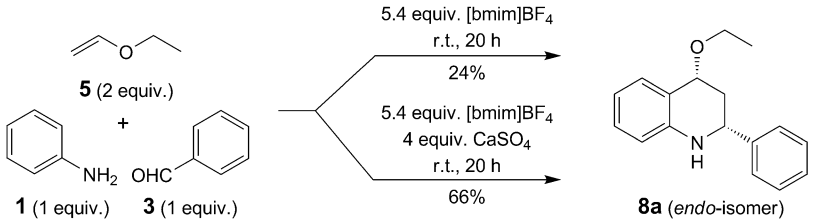
Apart from 2,3-dihydrofuran (**2**) as the dienophile, the *Povarov* reaction in [bmim]BF_4 was also performed with ethyl vinyl ether (**5**), 2,3-dihydropyran (**6**) and cyclopentadiene (**7**) as dienophiles. When 1 equiv. of **1**, 2 equiv. of ethyl vinyl ether (**5**), and 1 equiv. of **3** were reacted in 5.4 equiv. of [bmim]BF_4 for 20 h at room temperature, 24% of the *endo*-4-ethoxy-1,2,3,4-tetrahydro-2-phenylquinoline (**8a**) were isolated

Scheme 1. *[bmim]BF$_4$-Promoted Reaction between* **1**, **2**, *and* **3**



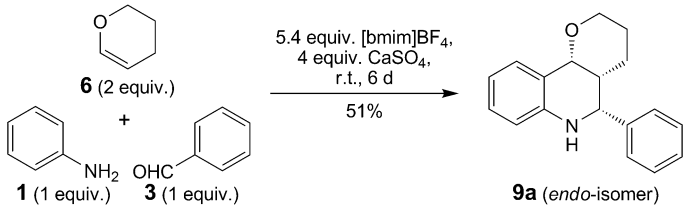
(*Scheme 2*). It should be noted that the yield of **8a** could be improved to 66%, when the experiment was repeated in the presence of $CaSO_4$ to remove H_2O formed during the condensation of aniline (**1**) and benzaldehyde (**3**).

Scheme 2. *[bmim]BF$_4$-Promoted Reaction between* **1**, **3**, *and Ethyl Vinyl Ether* (**5**)



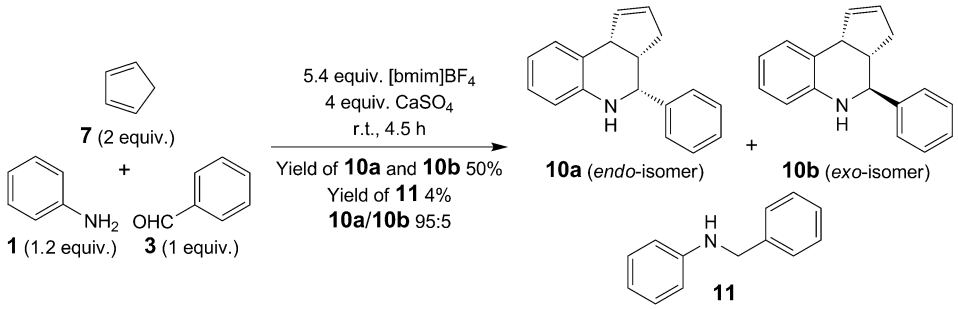
The highly diastereoselective *Povarov* reaction between 1 equiv. of **1**, 2 equiv. of 2,3-dihydropyran (**6**), and 1 equiv. of **3**, in the presence of 5.4 equiv. of [bmim]BF_4 and 4 equiv. of $CaSO_4$, delivered 51% of the *endo*-isomer **9a** after 6 d at room temperature (*Scheme 3*).

Scheme 3. *[bmim]BF$_4$-Promoted Reaction between* **1**, **3**, *and 2,3-Dihydropyran* (**6**)



The *Povarov* reaction was also performed with cyclopentadiene (**7**) as the dienophile. When 1.2 equiv. of **1**, 2 equiv. of **7**, and 1 equiv. of **3** were reacted with 5.4 equiv. of [bmim]BF_4 and 4 equiv. of $CaSO_4$, 50% of a 95 : 5 *endo*/*exo* mixture, **10a**/**b**, were formed (*Scheme 4*). In addition to the cycloadducts **10a** and **10b**, 4% of *N*-benzylaniline (**11**) were obtained. First, the *endo*-isomer **10a** could be separated by recrystallization of the product mixture. *N*-Benzylaniline (**11**) and the *exo*-isomer **10b** were volatile enough to be separated *via* bulb-to-bulb distillation. The *exo*-isomer **10b** could be obtained in pure form by flash chromatography of the distillate.

Scheme 4. *[bmim]BF$_4$-Promoted Reaction between* **1**, **3**, *and Cyclopentadiene* (**7**)



The three-component reaction between aniline (**1**), 2,3-dihydrofuran (**2**), and benzaldehyde (**3**) was selected as a model reaction to study the influence of different ionic liquids and microwave irradiation on the outcome of the *Povarov* reaction. First, the [bmim]BF$_4$-promoted reaction was studied under microwave conditions (*Table 1*) [22]. It was found that the reaction with 5.4 equiv. of the ionic liquid could be brought to completion within 7 min to yield 69% of **4a**/**4b** (*endo*/*exo* 75:25; *Table 1, Entry 1*). Reduction of the amount of [bmim]BF$_4$ was associated with longer reaction times and decreasing yields, but an improved *endo*/*exo* ratio, **4a**/**4b** (*Table 1*, *Entries 2* and *3*). When the reaction was performed in the absence of any ionic liquid under microwave conditions (150 W, 70°, 5 min), not a trace of the aza-*Diels–Alder* product was formed. This control experiment clearly underlined the importance of the ionic liquid for this transformation.

Table 1. *Influence of the Amount of [bmim]BF$_4$ on Yield and Selectivity of the Synthesis of* **4a**/**4b** *under Microwave Conditions*[a])

Entry	[bmim]BF$_4$ [equiv.]	*t* [min]	Yield [%]	**4a** (*endo*)/**4b** (*exo*)
1	5.4	7	69	75:25
2	1.0	10	57	83:17
3	0.1	15	51	84:16

[a]) The reactions were performed in sealed vials. Conditions: **1** (1 equiv.) + **2** (2 equiv.) + **3** (1 equiv.), in the presence of [bmim]BF$_4$, at 70°; microwave, 10 W.

To determine the influence of the microwave irradiation on the outcome of this reaction, it was also studied under thermal conditions in a sealed vial at 70° (*Table 2*). Interestingly, in terms of diastereoselectivity there was no difference between the reactions under thermal and microwave conditions (*Table 1*, *Entries 1* and *3*, and *Table 2*, *Entries 1–3*). However, the yield of **4a**/**4b** under thermal conditions was slightly better than under microwave conditions (*Table 1*, *Entry 1*, and *Table 2*, *Entry 1*). This is why all further experiments were performed in sealed vials in oil bath. Variation of the amounts of the substrates revealed that best yields were obtained when 1.2 equiv. of **1**, 2 equiv. of **2** and 1 equiv. of **3** were reacted in 5.4 equiv. of [bmim]BF$_4$ under the conditions indicated in *Table 2*, *Entry 5*.

Table 2. *[bmim]BF_4-Promoted Synthesis of* **4a**/**4b** *under Thermal Conditions*[a])

Entry	**1** [equiv.]	**2** [equiv.]	**3** [equiv.]	[bmim]BF_4 [equiv.]	*t* [min]	Yield [%]	**4a** (*endo*)/**4b** (*exo*)
1	1	2	1	5.4	5	76	75:25
2	1	2	1	0.1	14	44	84:16
3	1	2	1	0.1	60	43	84:16
4	1.2	2	1	5.4	5	78	75:25
5	1.2	2	1	5.4	7	81	78:22
6	1.2	2.2	1	5.4	7	75	76:24
7	1.2	2.4	1	5.4	7	76	75:25

[a]) The reactions were performed in sealed vials. Conditions: **1** + **2** + **3**, in the presence of [bmim]BF_4, at 70°, in an oil bath.

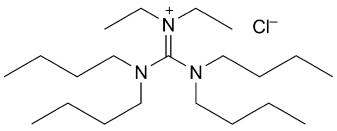
In further experiments, the influence of the reaction temperature on the reaction time, the chemical yield, and the *endo*/*exo* selectivity was studied by reacting **1**, **2**, and **3** in [bmim]BF_4 as the ionic liquid in a sealed vial under thermal conditions (*Table 3*). It was found that the reaction time could be substantially reduced when the reaction temperature was changed from 0° to 160°. Simultaneously, the amount of the *exo*-isomer **4b** increased. At 160°, it took only 3 min to obtain a 67:33 mixture **4a**/**4b** in quantitative yield (*Table 3*, *Entry 4*). To summarize, using [bmim]BF_4 as the ionic liquid led under all reaction conditions to *endo*/*exo* mixtures **4a**/**4b**. Interesting to note is that lower reaction temperatures favored the formation of the *endo*-isomer. The influence of microwave irradiation on yield and selectivity seems to be negligible.

Table 3. *Influence of the Reaction Temperature on the Formation of* **4a**/**4b** *in the Presence of [bmim]BF_4*[a])

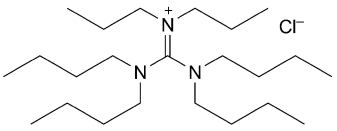
Entry	*T* [°]	*t* [min]	Yield [%]	**4a** (*endo*)/**4b** (*exo*)
1	0	1140	79	85:15
2	r.t.	210	90	81:19
3	70	7	81	78:22
4	160	3	quant.	67:33

[a]) The reactions were performed in sealed vials. Conditions: **1** (1.2 equiv.) + **2** (2 equiv.) + **3** (1 equiv.), in the presence of 5.4 equiv. [bmim]BF_4, in an oil bath.

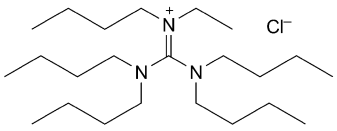
During the search for ionic liquids favoring the formation of either the *endo*-isomer **4a** or the *exo*-isomer **4b**, we came across the guanidinium salts. These ionic liquids are easily available as they can be prepared efficiently by well-elaborated synthetic protocols [7]. Another advantage is that guanidinium salts are known to be highly stable [7]. Therefore, the synthesis of **4a**/**4b** was studied in different guanidinium salts **12**, starting with the reaction between 1.2 equiv. of **1**, 2 equiv. of **2**, and 1 equiv. of **3** with 5.4 equiv. of the guanidinium salts **12a** – **12r** under thermal conditions (160°, 3 min; *Table 4*). It was found that the yield as well as the *endo*/*exo* ratio, **4a**/**4b**, strongly depend on the structure of the guanidinium cation, as well as that of the counter ion. With the guanidinium chlorides the *exo*-product **4b** was formed preferentially, while the guanidinium tetrafluoroborates delivered the *endo*-isomer **4a** in excess. A particularly



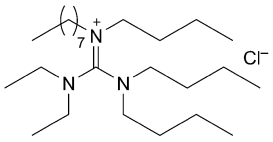
12a



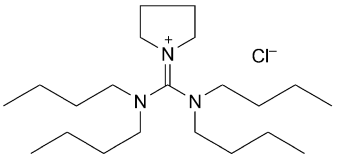
12b



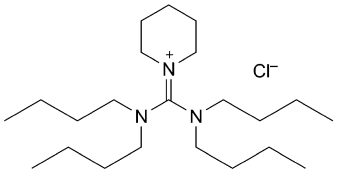
12c



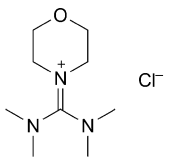
12d



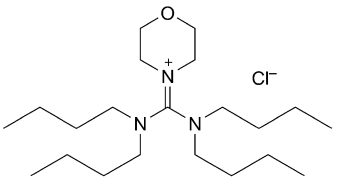
12e



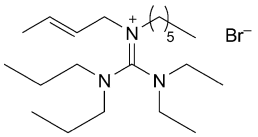
12f



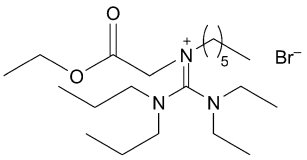
12g



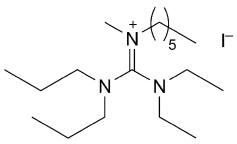
12h



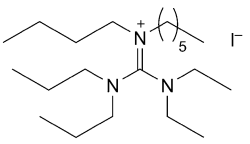
12i



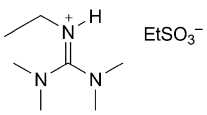
12j



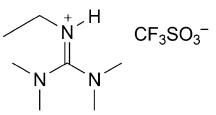
12k



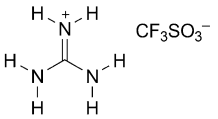
12l



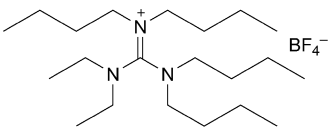
12m



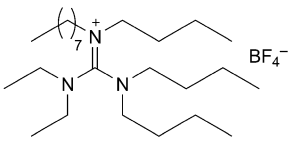
12n



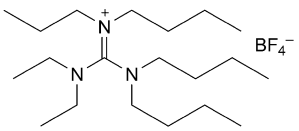
12o



12p



12q



12r

striking example was the reaction in **12g**, which resulted in the exclusive formation of the *exo*-isomer **4b**, albeit at low yields (*Table 4*).

Using the guanidinium salts **12g** and **12p** as examples, it could be demonstrated that the chemical yield as well as the *endo*/*exo* ratio depend on the concentration of the guanidinium salt (*Table 5*). It was particularly interesting to note that the trans-

Table 4. *Influence of Different Guanidinium Salts on the Synthesis of* **4a/4b**[a])

Compound **12**	Yield [%]	**4a** (*endo*)/**4b** (*exo*)	Compound **12**	Yield [%]	**4a** (*endo*)/**4b** (*exo*)
12a	7	36 : 64	**12j**	20	41 : 59
12b	14	32 : 68	**12k**	47	77 : 23
12c	5	32 : 68	**12l**	45	78 : 22
12d	no reaction		**12m**	37	40 : 60
12e	5	44 : 56	**12n**	67	68 : 32
12f	12	41 : 59	**12o**	43	53 : 47
12g	21	0 : 100	**12p**	74	83 : 17
12h	12	49 : 51	**12q**	81	88 : 12
12i	25	71 : 29	**12r**	74	83 : 17

[a]) The reactions were performed in sealed vials. Conditions: **1** (1.2 equiv.) + **2** (2 equiv.) + **3** (1 equiv.), in the presence of 5.4 equiv. **12**, at 160°, 3 min.

formation could be performed with catalytic amounts of the guanidinium salts (0.1 equiv.) in the absence of any solvent (*Table 5*, *Entries 1–5*). It turned out that the reactions could be run under thermal (*Table 5*, *Entries 1*, *4*, and *5*) as well as microwave conditions (*Table 5*, *Entries 2* and *3*). In addition, the chemical yields as well as the *endo*/*exo* ratios depend on the reaction temperature. It should also be emphasized that no cycloadducts **4** were formed, when the microwave-assisted reaction between **1**, **2**, und **3** was run in the absence of an ionic liquid (*Table 5*, *Entry 6*). These results underline that ionic liquids cannot only be used as solvents but can also be employed as catalysts for this chemical transformation.

Table 5. *Influence of Catalytic Amounts* (0.1 equiv.) *of* **12g** *and* **12p** *on the Synthesis of* **4a/4b**[a])

Entry	Ionic liquid	Reaction conditions	Yield **4** [%]	**4a** (*endo*)/**4b** (*exo*)
1	**12g**	160°, 3 min	36	35 : 65
2	**12g**	Microwave, 70°, 40 min	64	79 : 21
3	**12p**	Microwave, 70°, 40 min	86	79 : 21
4	**12g**	70°, 40 min	72	81 : 19
5	**12p**	70°, 40 min	97	88 : 12
6	–	Microwave, 70°, 5 min	–	–

[a]) The reactions were performed in sealed vials. Conditions: **1** (1.2 equiv.) + **2** (2 equiv.) + **3** (1 equiv.), in the presence of 0.1 equiv. **12g** or **12p**.

And finally, it was demonstrated that guanidinium salts can be used for several successive cycles with comparable yields and diastereoselectivities, and without significant loss of catalytic activity (*Table 6*). The results presented here clearly demonstrate the potential of guanidinium salts as solvents and catalysts for the aza-*Diels–Alder* reaction.

The structures of isomers **4a** and **4b** were elucidated by mass spectrometry and NMR-spectroscopic methods, including ^{1}H,^{13}C-COSY, HSQC, and HMBC experiments. The relative configurations of the products were established based on the

Table 6. *Recycling and Reuse of Guanidinium Salt* **12p**[a])

No. of runs	1st	2nd	3rd	4th
Yield [%]	70	65	75	74
endo/*exo*	82 : 18	80 : 20	83 : 17	81 : 19

[a]) The reactions were performed in sealed vials. Conditions: **1** (1.2 equiv.) + **2** (2 equiv.) + **3** (1 equiv.), in the presence of 5.4 equiv. **12p**, at 160°, 3 min.

coupling constants between H–C(3a) and H–C(4). In **4a** (*endo*), the vicinal coupling constant *J*(3a,4) amounts to 3.2 Hz and is significantly smaller than the corresponding coupling constant in **4b** (*exo*), which amounts to 10.9 Hz (*Fig.*).

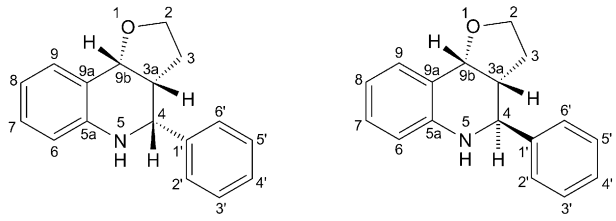


Figure. *Structures of the* endo-*Isomer* **4a** *and the* exo-*Isomer* **4b**

Conclusions. – In summary, it has been demonstrated that the three-component reaction between aniline, benzaldehyde, and 2,3-dihydrofuran can be catalyzed by ionic liquids such as imidazolium and guanidinium salts under thermal as well as under microwave conditions. The chemical yield as well as the diastereoselectivity of the one-pot aza-*Diels–Alder* reaction strongly depend on the ionic liquid employed. The guanidinium salts can be used for several successive cycles without significant loss of yield, diastereoselectivity, and loss of activity.

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Experimental Part

General. Aniline was distilled from KOH, benzaldehyde from $MgSO_4$, and 2,3-dihydrofuran from CaH_2. Cyclopentadiene was obtained by heating dicyclopentadiene. Reactions were performed using a *Discover*™ *Explorer* microwave synthesizer (*CEM Corp.*), producing continuous irradiation at 2450 MHz. All experiments were conducted under Ar. TLC: TLC aluminum roll silica gel *60* F_{254} (*Merck*); visualization with UV light (λ 254 nm). M.p.: *Kofler* apparatus (*Reichert*, Austria); uncorrected. UV Spectra: *Varian Cary 50*; λ in nm (log ε). IR Spectra: *Spectrum One FT-IR Spectrometer* (*Perkin Elmer*); $\tilde{\nu}$ in cm^{-1}. NMR Spectra: in $CDCl_3$ on 300- and 500-MHz spectrometers; the chemical shifts referenced to residual solvent signals at δ(H) 7.26 and δ(C) 77 ppm relative to TMS; δ in ppm, *J* in Hz. MS: *MAT95* at 70 eV; *m*/*z*.

General Procedure for the Three-Component Reaction between Aniline (**1**)*, 2,3-Dihydrofuran* (**2**)*, and Benzaldehyde* (**3**). 1.2 Equiv. of **1** (0.6 mmol), 2.0 equiv. of **2** (1 mmol), 1.0 equiv. of **3** (0.5 mmol), and 5.4 equiv. of a guanidinium salt **12** (2.7 mmol) were placed in a 10-ml microwave reaction vial that had been heated and cooled under Ar. The vial was sealed with a septum and heated in an oil bath at 160° for 3 min. After completion of the reaction (TLC), the mixture was allowed to cool to r.t. and extracted with Et_2O (5 × 5 ml). The combined extracts were concentrated *in vacuo* and the resulting crude product was purified by flash chromatography (FC; SiO_2; CH_2Cl_2/petroleum ether (PE) 10 : 3) to afford a mixture of the furoquinolines, **4a**/**4b**, in anal. pure form (for the ratio of **4a**/**4b**, see *Table 4*).

*(3a*RS*,4*RS*,9b*RS*)-2,3,3a,4,5,9b-Hexahydro-4-phenylfuro[3,2-*c*]quinoline* (**4a**). R_f (PE/AcOEt 8 : 2) 0.48. M.p. 98–100°. ^{1}H-NMR (500 MHz): 1.53 (*dd*, *J* = 11.7, 6.8, 1 H–C(3)); 2.22 (*dd*, *J* = 11.8, 9.5, 1 H–C(3)); 2.80 (*dddd*, *J* = 9.4, 8.0, 7.0, 3.2, H–C(3a)); 3.70–3.75 (*m*, 1 H–C(2)); 3.80–3.86 (*m*, 1 H–C(2)); 3.84 (br. *s*, NH); 4.71 (*d*, *J* = 3.2, H–C(4)); 5.29 (*d*, *J* = 8.0, H–C(9b)); 6.61 (*dd*, *J* = 7.9, 0.7, H–C(6)); 6.82 (*ddd*, *J* = 7.5, 7.5, 1.0, H–C(8)); 7.10 (*ddd*, *J* = 7.6, 6.9, 1.5, H–C(7)); 7.30–7.34 (*m*, H–C(4′)); 7.36 (*d*, *J* = 7.4, H–C(9)); 7.38–7.42 (*m*, H–C(3′), H–C(5′)); 7.46–7.49 (*m*, H–C(2′), H–C(6′)). ^{13}C-NMR (125 MHz): 24.6 (C(3)); 45.8 (C(3a)); 57.5 (C(4)); 66.8 (C(2)); 75.9 (C(9b)); 114.9 (C(6)); 119.2 (C(8)); 122.7 (C(9a)); 126.5 (C(2′), C(6′)); 127.6 (C(4′)); 128.3 (C(7)); 128.6 (C(3′), C(5′)); 130.1 (C(9)); 142.2 (C(1′)); 144.9 (C(5a)). EI-MS: 251 (75, M^+), 232 (36), 218 (82), 206 (100), 174 (31), 146 (19), 130 (29), 115 (30), 91 (45), 77 (42), 65 (17), 51 (26).

*(3a*RS*,4*SR*,9b*RS*)-2,3,3a,4,5,9b-Hexahydro-4-phenylfuro[3,2-*c*]quinoline* (**4b**). R_f (PE/AcOEt 8 : 2) 0.41. ^{1}H-NMR (500 MHz): 1.73 (*dd*, *J* = 13.5, 1.0, 1 H–C(3)); 2.02 (*dd*, *J* = 13.1, 7.5, 1 H–C(3)); 2.47 (*dddd*, *J* = 10.9, 7.6, 5.1, 1.0, H–C(3a)); 3.81 (*d*, *J* = 10.9, H–C(4)); 3.82–3.87 (*m*, 1 H–C(2)); 4.01–4.07 (*m*, 1 H–C(2)); 4.14 (br. *s*, NH); 4.61 (*d*, *J* = 5.1, H–C(9b)); 6.63 (*dd*, *J* = 8.1, 0.7, H–C(6)); 6.81 (*ddd*, *J* = 7.5, 7.5, 1.1, H–C(8)); 7.13 (*ddd*, *J* = 7.8, 7.8, 1.5, H–C(7)); 7.33–7.37 (*m*, H–C(4′)); 7.38–7.41 (*m*, H–C(3′), H–C(5′)); 7.39–7.42 (*m*, H–C(9)); 7.44–7.46 (*m*, H–C(2′), H–C(6′)). ^{13}C-NMR (125 MHz): 28.8 (C(3)); 43.4 (C(3a)); 57.8 (C(4)); 65.2 (C(2)); 76.2 (C(9b)); 114.7 (C(6)); 118.4 (C(8)); 120.0 (C(9a)); 128.1 (C(4′)); 128.3 (C(2′), C(6′)); 128.7 (C(3′), C(5′)); 128.9 (C(7)); 131.2 (C(9)); 141.7 (C(1′)); 145.4 (C(5a)). EI-MS: 251 (85, M^+), 220 (17), 206 (100), 182 (27), 174 (18), 144 (16), 130 (18), 115 (15), 91 (29), 77 (16).

Three-Component Reaction between **1***, Ethyl Vinyl Ether* (**5**)*, and* **3**. A mixture of 1 equiv. of **1** (1 mmol), 2 equiv. of **5** (2 mmol), and 1 equiv. of **3** (1 mmol) in 5.4 equiv. of [bmim]BF_4 (5.4 mmol) was stirred under Ar at r.t. for 20 h. After completion of the reaction (TLC), the mixture was extracted with ^{t}BuOMe (6 × 7 ml). The combined org. phases were washed with NaCl soln. (3 × 10 ml), dried (Na_2SO_4), and concentrated *in vacuo*. The resulting crude product was purified by prep. layer chromatography (SiO_2; PE/acetone 100 : 1) to afford **8a**.

*(2*RS*,4*RS*)-4-Ethoxy-1,2,3,4-tetrahydro-2-phenylquinoline* (**8a**). R_f (PE/TBME 10 : 1) 0.51. M.p. 76–78°. UV (MeCN): 207 (4.15), 255 (4.20), 322 (3.49). IR (ATR): 2923, 1597, 1553, 1507, 1489, 1446, 1422, 1319, 1283, 1124, 1023, 828, 792, 730, 689. ^{1}H-NMR (300 MHz): 1.26 (*t*, *J* = 6.9, Me); 2.08 (*ddd*, *J* = 11.5, 11.5, 11.5, H_{ax}–C(3)); 2.42 (*ddd*, *J* = 12.3, 5.6, 5.6, H_{eq}–C(3)); 3.58 (*dq*, *J* = 9.2, 7.0, OCH_2); 3.94 (br. *s*, NH); 4.54 (*dd*, *J* = 11.5, 2.5, H–C(2)); 4.82 (*dd*, *J* = 10.5, 5.6, H–C(4)); 6.50–6.55 (*m*, H–C(8)); 6.72–6.79 (*m*, H–C(6)); 7.03–7.10 (*m*, H–C(7)); 7.27–7.49 (*m*, H–C(5), 5 arom. H). ^{13}C-NMR (75 MHz): 15.6 (Me); 37.1 (C(3)); 55.9 (C(2)); 63.5 (OCH_2); 74.0 (C(4)); 114.0 (C(8)); 117.8 (C(6)); 122.6 (C(4a)); 126.6 (C(2′), C(6′)); 127.2 (C(5)); 127.8 (C(4′)); 128.2 (C(7)); 128.7 (C(3′), C(5′)); 143.7 (C(2′)); 144.6 (C(8a)). EI-MS: 253 (< 1, M^+), 205 (100), 176 (7), 149 (6), 128 (2), 102.5 (10), 102 (18), 88 (5), 57 (3), 28 (24).

Three-Component Reaction between **1***, 2,3-Dihydropyran* (**6**)*, and* **3**. A mixture of 1 equiv. of **1** (1 mmol), 2 equiv. of **6** (2 mmol), 1 equiv. of **3** (1 mmol), and 4 equiv. anh. $CaSO_4$ (4 mmol) in 5.4 equiv. of [bmim]BF_4 (5.4 mmol) was stirred under Ar at r.t. for 6 d. After completion of the reaction (TLC), the mixture was extracted with ^{t}BuOMe (7 × 7 ml). The combined org. phases were washed with NaCl soln. (3 × 10 ml), dried (Na_2SO_4), and concentrated *in vacuo*. The resulting crude product was purified by FC (SiO_2; PE/AcOEt 40 : 1) to afford **9a**.

*(4a*RS*,5*RS*,10b*RS*)-3,4,4a,5,6,10b-Hexahydro-5-phenyl-2*H*-pyrano[3,2-*c*]quinoline* (**9a**). R_f (PE/AcOEt 8 : 2) 0.48. M.p. 126–128°. UV (MeCN): 214 (4.33), 249 (4.00), 304 (3.34). IR (ATR): 3330, 2942, 1606, 1482, 1352, 1317, 1273, 1144, 1084, 1071, 1033, 970, 929, 840, 774, 700, 704. ^{1}H-NMR

(500 MHz): 1.29–1.34 (*m*, H–C(4)); 1.40–1.49 (*m*, H–C(3)); 1.50–1.60 (*m*, H–C(4)); 1.50–1.60 (*m*, H–C(3)); 2.13–2.22 (*m*, H–C(4a)); 3.44 (*dt*, *J* = 11.4, 2.1, H_{ax}–C(1)); 3.60 (*ddt*, *J* = 11.4, 4.0, 1.5, H_{eq}–C(2)); 3.88 (br. *s*, NH); 4.70 (*d*, *J* = 2.3, H–C(5)); 5.34 (*d*, *J* = 5.6, H–C(10b)); 6.61 (*dd*, *J* = 7.7, 1.2, H–C(7)); 6.80 (*ddd*, *J* = 7.4, 7.4, 1.2, H–C(9)); 7.10 (*dddd*, *J* = 8.0, 7.4, 1.6, 0.8, H–C(8)); 7.31 (br. *t*, *J* = 7.2, H–C(4′)); 7.39 (br. *t*, *J* = 7.8, H–C(3′), H–C(5′)); 7.42 (br. *d*, *J* = 7.2, H–C(2′), H–C(6′)); 7.44 (*ddd*, *J* = 7.5, 1.6, 0.8, H–C(10)). ^{13}C-NMR (125 MHz): 18.0 (C(4)); 25.4 (C(3)); 38.9 (C(4a)); 59.3 (C(5)); 60.6 (C(2)); 72.8 (C(10b)); 114.4 (C(7)); 118.3 (C(9)); 119.9 (C(10a)); 126.8 (C(2′), C(6′)); 127.5 (C(4′)); 127.6 (C(10)); 128.1 (C(8)); 128.4 (C(3′), C(5′)); 141.1 (C(1′)); 145.2 (C(6a)). HR-EI-MS: 265.1481 (M^+, $C_{18}H_{19}NO^+$; calc. 265.1461).

Three-Component Reaction between **1***, Cyclopentadiene* (**7**)*, and* **3**. A mixture of 1.2 equiv. of **1** (1.2 mmol), 2 equiv. of **7** (2 mmol), 1 equiv. of **3** (1 mmol), and 4 equiv. of anh. $CaSO_4$ (4 mmol) in 5.4 equiv. of [bmim]BF_4 (5.4 mmol) was stirred under Ar at r.t. for 4.5 h. After completion of the reaction (TLC), the mixture was extracted with ^{t}BuOMe (7 × 7 ml). The combined org. phases were washed with NaCl soln., dried (Na_2SO_4), and concentrated *in vacuo*. First, *endo*-isomer **10a** was separated by recrystallization of the mixture from MeOH. N-*benzylaniline* (**11**) and the *exo*-isomer **10b** were volatile enough to be separated *via* bulb-to-bulb distillation. The *exo*-isomer **10b** was obtained in pure form by FC (SiO_2; PE/AcOEt 19:1) of the distillate.

*(3a*SR*,4*RS*,9b*RS*)-3a,4,5,9b-Tetrahydro-4-phenyl-3*H*-cyclopenta[*c*]quinoline* (**10a**). R_f (PE/AcOEt 8:2) 0.60. M.p. 123–125°. UV (MeCN): 209 (4.57), 251 (3.85), 298 (3.38). IR (ATR): 3355, 3025, 1605, 1587, 1498, 1474, 1449, 1361, 1286, 1260, 1137, 1110, 1026, 1005, 929, 844, 778, 745, 700. ^{1}H-NMR (500 MHz): 1.83 (*dddd*, *J* = 16.3, 8.7, 2.6, 1.5, H–C(3)); 2.66 (*dddd*, *J* = 16.4, 9.2, 2.4, 2.4, H–C(3)); 3.03 (*dddd*, *J* = 9.0, 9.0, 9.0, 3.3, H–C(3a)); 3.76 (*s*, NH); 4.13 (br. *d*, *J* = 8.6, H–C(9b)); 4.66 (*d*, *J* = 3.1, H–C(4)); 5.64–5.68 (*m*, H–C(2)); 5.84–5.88 (*m*, H–C(1)); 6.64 (*d*, *J* = 7.4, H–C(6)); 6.77 (*ddd*, *J* = 7.3, 7.3, 1.4, H–C(8)); 7.00 (*ddd*, *J* = 7.7, 7.7, 1.8, H–C(7)); 7.08 (*ddd*, *J* = 7.6, 1.6, 1.0, H–C(9)); 7.29 (*t*, *J* = 7.4, H–C(4′)); 7.39 (*t*, *J* = 7.4, H–C(3′), H–C(5′)); 7.45 (*d*, *J* = 7.4, H–C(2′), H–C(6′)). ^{13}C-NMR (125 MHz): 31.5 (C(3)); 46.0 (C(3a)); 46.4 (C(9b)); 58.1 (C(4)); 115.9 (C(6)); 119.2 (C(8)); 126.1 (C(9a)); 126.3 (C(7)); 126.5 (C(2′), C(6′)); 127.2 (C(4′)); 128.5 (C(3′), C(5′)); 129.0 (C(9)); 130.4 (C(2)); 134.0 (C(1)); 142.8 (C(1′)); 145.6 (C(5a)). EI-MS: 247 (100, M^+), 218 (10), 206 (15), 193 (7), 170 (21), 156 (36), 129 (10), 115 (7), 91 (4), 77 (5), 44 (8), 28 (26).

*(3a*SR*,4*SR*,9b*RS*)-3a,4,5,9b-Tetrahydro-4-phenyl-3*H*-cyclopenta[*c*]quinoline* (**10b**). R_f (PE/AcOEt 8:2) 0.60. UV (MeCN): 209 (4.50), 251 (3.92), 299 (3.41). IR (ATR): 3368, 3052, 2929, 2847, 1608, 1588, 1495, 1474, 1454, 1421, 1346, 1315, 1296, 1264, 1252, 1173, 1109, 1064, 1029, 923, 871, 807, 747, 717, 701, 669. ^{1}H-NMR (500 MHz): 2.11 (br. *d*, *J* = 16.8, H–C(3)); 2.46 (*dm*, *J* = 16.8, H–C(3)); 2.75 (br. *ddd*, *J* = 10.5, 7.2, 7.2, H–C(3a)); 3.73 (*d*, *J* = 10.5, H–C(4)); 3.90 (br. *s*, NH); 4.02 (br. *d*, *J* = 7.5, H–C(9b)); 5.68–5.72 (*m*, H–C(2)); 5.93–5.96 (*m*, H–C(1)); 6.58 (*dd*, *J* = 8.0, 1.2, H–C(6)); 6.79 (*ddd*, *J* = 7.4, 7.4, 1.2, H–C(8)); 7.02 (*dddd*, *J* = 8.1, 7.3, 1.6, 0.8, H–C(7)); 7.26 (br. *d*, *J* = 7.5, H–C(9)); 7.31–7.35 (*m*, H–C(4′)); 7.36–7.40 (*m*, H–C(3′), H–C(5′)); 7.41–7.44 (*m*, H–C(2′), H–C(6′)). ^{13}C-NMR (125 MHz): 35.8 (C(3)); 43.1 (C(3a)); 46.8 (C(9b)); 58.4 (C(4)); 114.8 (C(6)); 118.4 (C(8)); 124.1 (C(9a)); 126.5 (C(7)); 127.8 (C(4′)); 128.1 (C(1)); 128.5 (C(2′), C(6′), C(3′), C(5′)); 129.4 (C(9)); 136.1 (C(2)); 142.9 (C(1′)); 145.7 (C(5a)).

N-*Benzylaniline* (**11**). R_f (PE/AcOEt 8:2) 0.60. M.p. 36–38°. UV (MeCN): 202 (4.48), 248 (4.12), 297 (3.29). IR (ATR): 3417, 3027, 1600, 1508, 1492, 1449, 1429, 1328, 1276, 1180, 1118, 1065, 1027, 984, 858, 735, 688. ^{1}H-NMR (500 MHz): 4.04 (br. *s*, NH); 4.34 (*s*, CH_2); 6.64 (*d*, *J* = 8.6, H–C(2), H–C(6)); 6.70–6.74 (*m*, H–C(4)); 7.18 (*dd*, *J* = 8.5, 7.4, H–C(3), H–C(5)); 7.28 (*t*, *J* = 7.3, H–C(4′)); 7.35 (*t*, *J* = 7.4, H–C(3′), H–C(5′)); 7.38 (br. *d*, *J* = 7.5, H–C(2′), H–C(6′)). ^{13}C-NMR (125 MHz): 48.3 (C(7′)); 112.8 (C(2), C(6)); 117.6 (C(4)); 127.2 (C(4′)); 127.5 (C(2′), C(6′)); 128.6 (C(3′), C(5′)); 129.3 (C(3), C(5)); 139.4 (C(1′)); 148.1 (C(1)).

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