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Imidazolinium salts as catalysts for the aza-Diels–Alder reaction

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Received 28th September 2004, Accepted 3rd November 2004
First published as an Advance Article on the web 9th December 2004

Various easily accessible imidazolinium salts have been found to be capable of catalysing an aza-Diels–Alder reaction with a range of imines and Danishefsky's diene, giving the desired products in good to excellent yields. The influence of the counter-anions on the reactivity has been explored. These salts could contribute to the field of metal-free catalysis/organocatalysis.

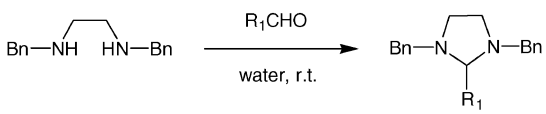
Introduction

Imidazolinium salts are important precursors for N–C–N carbene ligands, which have found widespread application in various metal-catalysed reactions.[1] However, these salts, which possess weak Lewis acidity in the imidazolinium unit, have been rarely used as catalysts. In fact, to the best of our knowledge, there has been only one report of an imidazolinium salt being used as a catalyst, in which the salt catalysed the opening of an epoxide.[2] Depending which mesomeric structure is used to describe imidazolinium cations, they can also be described as imidazolidinium[3] cation. In addition, they are also known as 4,5-dihydroimidazolium.

Since imidazolinium salts do not contain any metals, they could contribute to the field of organocatalysis,[4] which has attracted much interest in recent years. This research area is part of the larger field of homogeneous catalysis, that has so far been mainly dominated by metal–ligand systems.[5,6] In addition to covalent-based organocatalytic systems,[7–13] catalysts that activate carbonyl compounds *via* hydrogen bonds have been found.[14] In addition, metal-free Lewis bases,[15] Lewis acids[2,16–21] and Brønsted acids[22,23] have been used as catalysts. However, the number of examples of organocatalysts in the literature remains small, compared to metal-based systems.[4] This prompted us to present here our investigation of imidazolinium salts as metal-free Lewis acid catalysts for the aza-Diels–Alder reaction, which is an important method for the preparation of nitrogen-containing six-membered rings,[24] and has been catalysed by various catalytic systems, either achiral[25–35] or chiral.[36]

Results and discussion

Initially, various imidazolidines were prepared from secondary diamines and aldehydes in water following a literature procedure, as shown in Scheme 1.[37]



Scheme 1

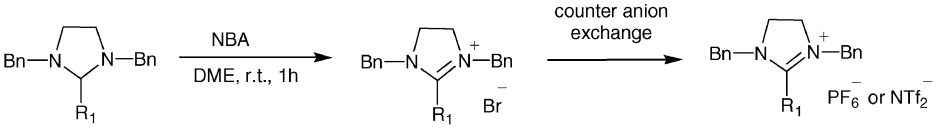
The imidazolidenes were then transformed into imidazolinium bromide salts by treating them with *N*-bromoacetamide (Scheme 2), using a modified literature procedure.[38] After stirring in DME for 1 h, the salts precipitated and were isolated by filtration. In cases where no precipitate was formed, diethyl ether was added in order to isolate the salts as solids or oils, which were washed with diethyl ether after decanting the solvent from the reaction mixture. The results are presented in Table 1. All salts have various aryl groups in the 2-position. Although the aryl groups in these salts are nearly perpendicular to the imidazolinium ring,[39] it may be still possible to slightly tune the positive charge of the imidazolinium unit through the σ-bond framework. All bromide salts were obtained in very good yields (88–99%). As well as substituted (runs 3, 6 and 9, Table 1) and polyfluorinated aryls (run 11, Table 1), the reaction also tolerated the electron-deficient heteroaromatic pyridinyl substituent (run 13, Table 1) and the electron-rich thiophenyl substituent (run 15, Table 1).

Table 1 Preparation of imidazolinium salts[a]

Run	Imidazolidines		Imidazolinium salts		Yield (%)[b]
		R_1		Anion	
1	**1**	C_6H_5	**2a**	Br	95
2	**1**	C_6H_5	**2b**	PF_6	86
3	**3**	1-(2-Cl–C_6H_4)	**4a**	Br	93
4	**3**	1-(2-Cl–C_6H_4)	**4b**	PF_6	95
5	**3**	1-(2-Cl–C_6H_4)	**4c**	NTf_2	71
6	**5**	1-(4-Cl–C_6H_4)	**6a**	Br	88
7	**5**	1-(4-Cl–C_6H_4)	**6a**	PF_6	89
8	**5**	1-(4-Cl–C_6H_4)	**6c**	NTf_2	90
9	**7**	1-(2,4-Cl_2–C_6H_3)	**8a**	Br	91
10	**7**	1-(2,4-Cl_2–C_6H_3)	**8b**	PF_6	90
11	**9**	C_6F_5	**10a**	Br	90
12	**9**	C_6F_5	**10b**	PF_6	90
13	**11**	2-(C_5H_4N)	**12a**	Br	99
14	**11**	2-(C_5H_4N)	**12b**	PF_6	71
15	**13**	2-(C_4H_3S)	**14a**	Br	90
16	**13**	2-(C_4H_3S)	**14b**	PF_6	92

[a] See Experimental for details. [b] Isolated yields.

All bromide salts were highly hygroscopic and difficult to handle, and therefore CHN-analyses were carried out after changing the bromide anion into a hexafluorophosphate and/or bis(trifluoromethylsulfonyl)imide anion. For the anion exchange the bromide salts were dissolved in DCM and stirred with 1.5 equiv. of either KPF_6 or $LiNTf_2$ (Scheme 2). The mixture was washed with water for 1 h. This was repeated two times. The



Scheme 2

DOI: 10.1039/b415023f

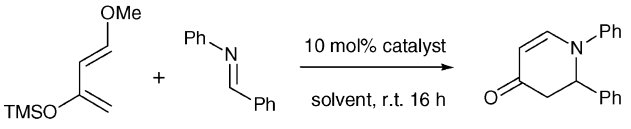
Table 2 Aza-Diels–Alder reactions with 10 mol% catalyst at r.t.[a]

Run	Catalyst	Solvent	Yield (%)[b]
1	—	MeCN	10
2	—	DCM	0
3	—	Toluene	0
4	**2a**	MeCN	14
5	**2b**	MeCN	46
6	**4b**	MeCN	63
7	**4c**	MeCN	98
8[c]	**4c**	Toluene	41
9[d]	**4c**	DCM	79
10	**6a**	MeCN	56
11	**6b**	MeCN	76
12	**6c**	MeCN	82
13	**8b**	MeCN	72
14	**10b**	MeCN	95
15	**10b**	DCM	40
16[e]	**10b**	MeCN	94
17[f]	**10b**	MeCN	76
18[g]	**10b**	MeCN	73
19	**12b**	MeCN	73
20	**12b**	DCM	24
21	**14b**	MeCN	47

[a] See Experimental for details. [b] Isolated yields. [c] Reaction time 48 h [d] Reaction time 6 days. [e] 5 mol% **10b**. [f] 2.5 mol% **10b**. [g] 1 mol% **10b**.

solvent was evaporated and the salts dried under high vacuum. The results are presented in Table 1. All PF_6 and NTf_2 salts were isolated in very good yields between 71 and 95% (runs 2, 4, 5, 7, 8, 10, 12, 14 and 16, Table 1). All salts gave a correct CHN-analysis, indicating that the corresponding bromide salts were also obtained in high purity. The hexafluorophosphate salt **6b** and the two bis(trifluoromethylsulfonyl)imides **4c** and **6c** have melting points of 71, 83 and 80 °C, respectively. Since their melting points are lower than 100 °C, these three salts belong by definition to the family of ionic liquids.[40,41]

The salts were tested as catalysts in the aza-Diels–Alder reaction of *N*-benzylideneaniline (**16**) and Danishefsky's diene (**15**). The reaction was performed for 16 h at room temperature in various solvents (Scheme 3, Table 2). First, control reactions were carried out in acetonitrile, DCM and toluene. The reaction with the last two solvents gave no product at all (runs 2 and 3, Table 2). In acetonitrile the expected product **17** was isolated in 10% yield (run 1, Table 2).



15 **16** **17**

Scheme 3

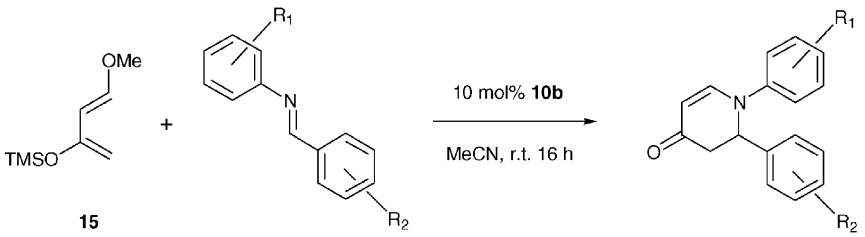
The first compound tested was the bromide salt **2a** bearing a phenyl group at the C-2 position, which led to a yield of 14%, using acetonitrile as the solvent (run 4, Table 2). By changing the counter-anion to PF_6, the yield increased to 46% (run 5, Table 2). This increase could be expected, since the PF_6 anion is a weaker coordinating anion[42,43] than the bromide, which explains the higher reactivity of salt **2b**. When the salt **4b** was tested, the yield increased to 63% (run 6, Table 2), which may be related to the more electron-withdrawing 2-chlorophenyl substituent of the salt. The catalyst **4c** gave the desired product in a yield of 98% (run 7, Table 2). This increase in yield can be attributed to the NTf_2 anion, which is even less coordinating than the PF_6 anion. Catalyst **4c** was then used in different solvents. In toluene a yield of 41% was found, however, the reaction time was extended to 48 h (run 8, Table 2), while in DCM a yield of 79% was obtained after 6 days (run 9, Table 2). The lower yields in these two solvents and the longer reaction times can be rationalised by their lower capability to dissociate salts compared to acetonitrile. Next, the salts **6a**, **6b** and **6c** with a 4-chlorophenyl substituent were tested. As expected, the yields increased from the bromide **6a** to the hexafluorophosphate **6b** to the bis(trifluoromethylsulfonyl)imide **6c**, giving 56, 76 and 82%, respectively (runs 10, 11 and 12, Table 2). The yields for the 4-chlorophenyl and 2-chlorophenyl substituents were quite similar. When salt **8b** with a 2,4-dichlorophenyl substituent was applied, the yield obtained was nearly the same as for **6b** (run 13, Table 2). Attention was then directed to the salt **10b**, which has a pentafluorophenyl substituent at the 2-position. The polyfluorinated substituent may have two positive effects: first, it can increase the positive charge of the imidazolinium unit, due to the strong electron-withdrawing capability of the fluorine atoms; second, the fluorine atoms are lipophilic and can help to increase the solubility of the salt. Under standard reaction conditions, salt **10b** gave a yield of 95% in acetonitrile (run 14, Table 2). When DCM was used as the solvent, the desired product was isolated in 40% yield (run 15, Table 2). In addition, three more reactions in acetonitrile were carried out with **10b**, using a catalyst loading of 5, 2.5 and 1 mol%, which gave the product in 94, 76 and 73% yield, respectively (runs 16, 17 and 18, Table 2). In acetonitrile, the salt **12b** gave a yield of 73% (run 19, Table 2), which is comparable with salts **4b**, **6b** and **8b** (runs 6, 11 and 13, Table 2). When **12b** was evaluated in DCM, a poor yield of 24% was obtained (run 20, Table 2), which is nearly half that obtained with the more lipophilic salt **10b** (run 15, Table 2). Finally, in acetonitrile, salt **14b** gave a moderate yield of 47% (run 21, Table 2). Clearly, the electron-rich thiophenyl substituent reduces the Lewis acidity of the imidazolinium cation.

With the standard conditions using 10 mol% of salt **10b**, various imines were tested in the aza-Diels–Alder reaction with Danishefsky's diene (**15**) (Scheme 4). The results are summarised in Table 3. It was possible to observe that neither an electron-withdrawing, nor an electron-donating substituent on the aryl ring of the nitrogen atom of the imine had an influence on the reaction. All three imines **16**, **18** and **20** gave similar good yields (runs 1, 2 and 3, Table 3). The scope of the reaction was then explored by using different aryls attached to the carbon atom of the imine. When an electron-withdrawing chlorine atom was placed in the *para*-position of the aryl, the yield dropped slightly to 72% (run 4, Table 3). When an electron-donating methoxy group was present at the *ortho* position, the yield decreased to 57% (run 5, Table 3), while at the *para*-position an even lower yield of 45% was found (run 7, Table 3). Finally, the imines **26** and **30** furnished the desired products in 50 and 93% yield, respectively (runs 6 and 8, Table 3). Interestingly, the 4-nitrophenyl group of imine **30** had a significance influence on the yield, while the 2-pyridinyl group of imine **26** did not, although both groups are electron-deficient.

At the end, the salt **10b** was tested as a catalyst in an aza-Diels–Alder reaction with imine **16** and 3,4-dihydro-2*H*-pyran (**35**) or 2,3-dihydrofuran (**32**) (Scheme 5). In this reaction, imine **16** is the diene and with **35** gave the product **36** in 16% yield. Only the *trans*-diastereomer **36** was found. The yield increased to 70% when **32** was used as the dienophile. However, both possible diasteremomers **33** and **34** were formed in a ratio of 1 : 1 as determined by ^{1}H NMR spectroscopy.

The mechanism of the reaction can be considered similar to metal Lewis acid catalysed reactions. The imidazolinium cations, which are Lewis acids, are activating the imines, which react with Danishefsky's diene (**15**) in a [4 + 2] reaction. Intermediates, which can be observed in a Mannich-type condensation mechanism, were not detected during the course of the reaction.

In conclusion, we have demonstrated for the first time that imidazolinium salts are good catalysts for an aza-Diels–Alder reaction with Danishefsky's diene (**15**). The salts are metal-free Lewis acids, which can contribute to the field of organocatalysis. In addition, new imidazolinium salts have been prepared, of

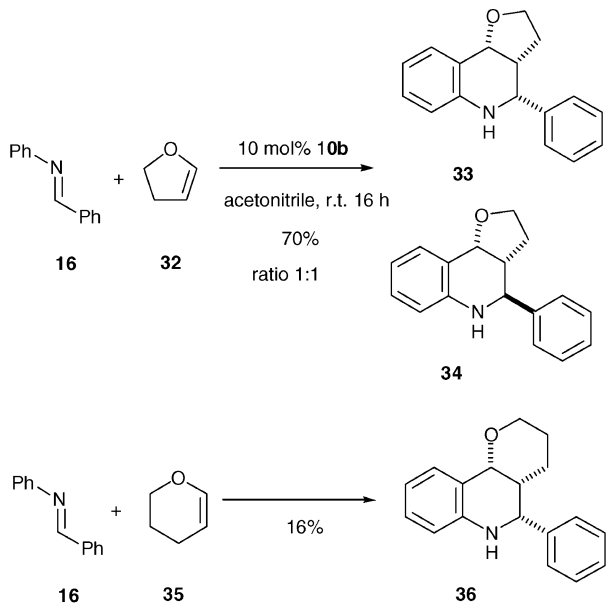


Scheme 4

Table 3 Aza-Diels–Alder reaction with various imines[a]

Run	Imine	R_1	R_2	Product	Yield (%)[b]
1	**16**	C_6H_5	C_6H_5	**17**	95
2	**18**	4-Cl–C_6H_4	C_6H_5	**19**	84
3	**20**	4-MeO–C_6H_4	C_6H_5	**21**	92
4	**22**	C_6H_5	4-Cl–C_6H_4	**23**	72
5	**24**	C_6H_5	2-MeO–C_6H_4	**25**	57
6	**26**	C_6H_5	2-C_5H_4N	**27**	93
7	**28**	C_6H_5	4-MeO–C_6H_4	**29**	45
8	**30**	C_6H_5	4-NO_2–C_6H_4	**31**	50

[a] See Experimental for details. [b] Isolated yields.



Scheme 5

which a few are ionic liquids. Present investigations within the group concern the behaviour of chiral analogues of these salts.

Experimental

General

Imidazolidines **1**, **3**, **5**, **7**, **9**, **11** and **13** were prepared according to a literature procedure.[37] Imines **16**, **18**, **20**, **22**, **24**, **26**, **28** and **30** were prepared according to a literature procedure.[44] 3,4-Dihydro-2*H*-pyran (**35**) and Danishefsky's diene (**15**) were purchased from Merck. 2,3-Dihydrofuran (**32**), anhydrous DME and $LiN(CF_3SO_2)_2$ were purchased from Aldrich. KPF_6 was purchased from Fluka and *N*-bromoacetamide was purchased from Lancaster. Reactions were carried out under nitrogen and were performed using standard Schlenk line techniques.[45] Acetonitrile and DCM were distilled from calcium hydride. Toluene was distilled from sodium.

Flash column chromatography[46] was performed on Sorbisil C-60. All reactions were monitored by TLC with Merck Silica gel 60 F_{254} plates. Elemental analyses were carried out by the Microanalytical Laboratory of the Institut für Pharmazeutische Chemie der Universität Braunschweig. Infrared spectra were recorded on a Perkin–Elmer 2000 FT-IR System. NMR spectra were taken in $CDCl_3$ at ambient temperature on Bruker AMX 400 and a Bruker AC 200F instruments. Mass spectra were recorded on Hewlett Packard 5898B instrument (at 70 eV). Melting points were taken with an apparatus from Dr Tottoli and are uncorrected.

General procedure for the preparation of imidazolinium bromide salts

Imidazolidine (1 mmol) was dissolved in a minimal amount of 1,2-dimethoxyethane. *N*-Bromacetamide (1 mmol) was added in two portions (0.5 mmol each) with an interval of 15 min. After addition of the second portion, the reaction mixture was stirred for an additional hour. The salt precipitated and was isolated by filtration. In cases where no precipitate was formed, diethyl ether was added and an oily solid formed. The solvent was decanted and the residue was washed with diethyl ether and dried under high vacuum to give the corresponding bromide salt. This procedure is a modification of a literature procedure.[38]

1,3-Dibenzyl-2-(phenyl)imidazolinium bromide (2a). From **1** in 95% yield as a white hygroscopic solid, m.p. 167 °C. MS (EI), *m/e* 326 (cation $M^+ - H$, 75%), 249 (45), 234 (50), 132 (25), 91 (100); IR (KBr) 3442s, 1601vs, 1581s, 1569s 1253s, 726s, 699s cm^{-1}; ^1H NMR (400 MHz) δ 8.04–8.02 (m, 2 H, H-14,18), 7.71–7.66 (m, 3 H, H-15,16,17), 7.42–7.23 (m, 10 H, H–Ar), 4.57 (s, 4 H, H-6,19), 4.13 (s, 4 H, H-4,5); ^{13}C NMR (100 MHz) δ 167.4, 133.4, 133.2, 130.5, 129.7, 129.32, 129.28, 128.6, 122.6, 52.7, 48.7.

1,3-Dibenzyl-2-(2-chlorophenyl)imidazolinium bromide (4a). From **3** in 93% yield as a yellow hygroscopic oil. MS (EI), *m/e* 360 (cation $M^+ - H$, 30%), 269 (50), 151 (30), 91 (100); IR (neat) 3355s, 3177s, 1664vs, 1598vs, 1291s, 1254s, 759s, 703s cm^{-1}; ^1H NMR (400 MHz) δ 8.95–8.92 (m, 1 H, H-15), 7.69–7.61 (m, 3 H, H–Ar), 7.43–7.35 (m, 10 H, H–Ar), 4.64 (d, $J = 15.1$ Hz, 2 H, H-6,19), 4.52–4.47 (m, 2 H, H-4,5), 4.42 (d, $J = 14.8$ Hz, 2 H, H-6,19), 3.77–3.72 (m, 2 H, H-4,5); ^{13}C NMR (100 MHz) δ 164.1, 134.7, 133.6, 132.4, 132.0, 130.6, 129.7, 126.44, 129.36, 129.1, 122.2, 52.7, 48.6.

1,3-Dibenzyl-2-(4-chlorophenyl)imidazolinium bromide (6a). From **5** in 88% yield as a white hygroscopic solid, m.p. 155 °C. MS (EI), *m/e* 360 (cation $M^+ - H$, 15%), 269 (40), 151 (40), 91 (100); IR (KBr) 3026m, 2996m, 1605vs, 1581s, 1565s, 1482s, 1253s, 834s, 707vs cm^{-1}; ^1H NMR (400 MHz) δ 8.05–8.02 (m, 2 H, H-15,17), 7.65–7.63 (m, 2 H, H-14,18), 7.39–7.35 (m, 6 H, H–Ar), 7.25–7.22 (m, 4 H, H–Ar), 4.56 (s, 4 H, H-6,19), 4.12 (s, 4 H, H-4,5); ^{13}C NMR (100 MHz) δ 166.6, 140.1, 132.9, 130.9, 129.8, 129.4, 128.5, 120.9, 77.7, 52.7, 48.8.

1,3-Dibenzyl-2-(2,4-dichlorophenyl)imidazolinium bromide (8a). From **7** in 91% yield as a yellow hygroscopic oil. MS (EI), *m/e* 394 (cation $M^+ - H$, 10%), 304 (10), 185 (15), 91 (100), 65 (20); IR ($CDCl_3$) 2360s, 1600vs, 1455m, 910vs, 730vs cm^{-1}; ^1H NMR (400 MHz) δ 9.10 (d, $J = 8.4$ Hz, 1 H, H-15), 7.68–7.62 (m, 2 H, H-17,18), 7.47–7.35 (m, 10 H, H–Ar), 4.65 (d, $J = 14.8$ Hz, 2 H, H-6,19), 4.52–4.47 (m, 2 H, H-4,5), 4.41 (d, $J = 14.8$ Hz,

2 H, H-6,19), 3.75–3.70 (m, 2 H, H-4,5); ^{13}C NMR (100 MHz) δ 163.4, 140.7, 134.9, 132.9, 132.3, 130.6, 130.0, 129.7, 129.4, 129.1, 120.7, 52.8, 48.7.

1,3-Dibenzyl-2-(pentafluorophenyl)imidazolinium bromide (10a). From **9** in 90% yield as a yellow hygroscopic oil. MS (EI), *m/e* 417 (cation M^+, 1%), 326 (5), 235 (5), 207 (5), 91 (100); IR (neat) 1665vs, 1605vs, 1518s, 1365s, 12995s, 998s cm^{-1}; ^{1}H NMR (200 MHz) δ 7.41–7.19 (m, 10 H, H–Ar), 4.71 (s, 4 H, H-16,19), 4.37 (s, 4 H, H-4,5); ^{13}C NMR (50 MHz) δ 172.9, 131.0, 129.5, 128.4, 52.6, 49.4.

1,3-Dibenzyl-2-(2-pyridinyl)imidazolinium bromide (12a). From **11** in 99% yield as a colorless hygroscopic oil. MS (EI), *m/e* 328 (cation M^+, 20%), 237 (30), 105 (35), 91 (100), 78 (35), 65 (35), 51 (35); IR ($CDCl_3$) 1668m, 1601s, 910vs, 732vs, 650s cm^{-1}; ^{1}H NMR (400 MHz) δ 8.97 (d, J = 8.3 Hz, 1 H, H-15,), 7.63–7.59 (m, 2 H, H-17,18), 7.38–7.27 (m, 11 H, H–Ar), 4.50 (d, J = 14.9 Hz, 2 H, H-6,19), 4.44–4.35 (m, 4 H, H-4,5,6,19), 3.73–3.68 (m, 2 H, H-4,5); ^{13}C NMR (100 MHz) δ 163.4, 140.8, 134.6, 132.9, 132.2, 130.7, 129.9, 129.7, 129.4, 129.1, 52.8, 48.7.

1,3-Dibenzyl-2-(2-thiophenyl)imidazolinium bromide (14a). From **13** in 90% yield as a white solid, m.p. 157 °C. MS (EI), *m/e* 332 (cation $M^+ - H$, 10%), 241 (30), 123 (30), 91 (100), 65 (20); IR (KBr) 1593s, 1577s, 1287m, 761m, 733m cm^{-1}; ^{1}H NMR (400 MHz) δ 8.17–8.15 (m, 1 H, H-2), 7.81 (dd, J = 6.8 Hz, J = 1.24 Hz), 7.40–7.28 (m, 11 H, H–Ar), 4.69 (s, 4 H, H-11,18), 4.08 (s, 4 H, H-8,9); ^{13}C NMR (100 MHz) δ 162.9, 135.9, 133.1, 132.9, 129.7, 129.5, 129.3, 128.6, 119.7, 53.1, 48.7.

General procedure for counter-anion exchange with potassium hexafluorophosphate

Imidazolinium bromide (1 mmol) was dissolved in DCM (3 ml) and stirred vigorously with 1.5 equiv. of KPF_6 in water (3 ml) for 30 minutes. The organic phase was separated, washed with water (3 × 3 ml) and dried with 3 Å molecular sieves. The solvent was evaporated and the product was further dried overnight under high vacuum to give the corresponding imidazolinium hexafluorophosphate.

1,3-Dibenzyl-2-(2-phenyl)imidazolinium hexafluorophosphate (2b). From **2a** in 86% yield as a yellow solid, m.p. 118 °C. MS (EI), *m/e* 326 (cation $M^+ - H$, 75%), 249 (45), 234 (50), 132 (25), 91 (100); IR (KBr) 1598vs, 1441m, 1355m, 1301m 1252s, 839vs, 774s, 763s, 703s cm^{-1}; ^{1}H NMR (400 MHz) δ 7.75–7.65 (m, 5 H, H–Ar), 7.43–7.16 (m, 10 H, H–Ar), 4.48 (s, 4 H, H-6,19), 3.98 (s, 4 H, H-4,5); ^{13}C NMR (100 MHz) δ 167.0, 133.6, 132.8, 130.8, 129.8, 129.4, 128.7, 128.4, 122.2, 52.2, 48.0; Anal. calculated for $C_{23}H_{23}N_2PF_6$: C, 58.48; H, 4.91; N, 5.93, found: C, 58.48; H, 4.91; N, 5.78.

1,3-Dibenzyl-2-(2-chlorophenyl)imidazolinium hexafluorophosphate (4b). From **4a** in 95% yield as a yellow solid, m.p. 144 °C. MS (EI), *m/e* 360 (cation $M^+ - H$, 70%), 324 (40), 283 (20), 91 (100); IR (KBr) 1598vs, 1441m, 1355m, 1301m 1252s, 839vs, 774s, 763s, 703s cm^{-1}; ^{1}H NMR (400 MHz) δ 8.09–8.07 (m, 1 H, H-15), 7.76–7.68 (m, 3 H, H–Ar), 7.44–7.27 (m, 10 H, H–Ar), 4.49–4.39 (m, 4 H, H-6,19), 4.22–4.17 (m, 2 H, H-4,5), 3.84–3.79 (m, 2 H, H-4,5); ^{13}C NMR (100 MHz) δ 163.9, 135.0, 132.3, 132.0, 131.8, 131.0, 129.8, 129.63, 129.59, 129.0, 121.0, 52.3, 48.1. Anal. calculated for $C_{23}H_{22}ClN_2PF_6$: C, 54.50; H, 4.37; N, 5.53, found: C, 54.57; H, 4.22; N, 5.40.

1,3-Dibenzyl-2-(4-chlorophenyl)imidazolinium hexafluorophosphate (6b). From **6a** in 89% yield as a white solid, m.p. 71 °C. MS (EI), *m/e* 361 (cation M^+, 5%), 270 (10), 151 (15), 107 (15), 91 (100), 55 (60); IR (KBr) 1602vs, 1565s, 1456s, 1360s, 1288s, 1095s, 834vs, 749s, 702s cm^{-1}; ^{1}H NMR (400 MHz) δ 8.05–8.02 (m, 2 H, H-15,17), 7.65–7.63 (m, 2 H, H-14,18), 7.39–7.35 (m, 6 H, H–Ar), 7.25–7.22 (m, 4 H, H–Ar), 4.56 (s, 4 H, H-6,19), 4.12 (s, 4 H, H-4,5); ^{13}C NMR (100 MHz) δ 166.6, 140.1, 132.9, 130.9, 129.8, 129.4, 128.5, 120.9, 77.7, 52.7, 48.8. Anal. calculated for $C_{23}H_{22}ClF_6N_2P$: C, 54.50; H, 4.37; N, 5.53, found: C, 54.31; H, 4.09; N, 5.37.

1,3-Dibenzyl-2-(2,4-dichlorophenyl)imidazolinium hexafluorophosphate (8b). From **8a** in 90% yield as a yellow solid, m.p. 130 °C. MS (EI), *m/e* 394 (cation $M^+ - H$, 50%), 358 (40), 317 (20), 282 (20), 91 (100), 65; IR (KBr) 3095m, 1599vs, 1254s, 840vs, 702s, 557s cm^{-1}; ^{1}H NMR (400 MHz) δ 8.01 (d, 1 H, J = 8.4 Hz, H-15), 7.70–7.69 (m, 1 H, H-17), 7.65–7.22 (m, 1 H, H-18), 7.42–7.36 (m, 6 H, H–Ar), 7.28–7.24 (m, 4 H, H–Ar), 4.46–4.37 (m, 4 H, H-6,19), 4.17–4.12 (m, 2 H, H-4,5), 3.85–3.80 (m, 2 H, H-4,5); ^{13}C NMR (100 MHz) δ 163.1, 141.1, 133.3, 132.6, 131.8, 131.1, 130.1, 129.8, 129.6, 129.0, 120.3, 52.3, 48.2. Anal. calculated for $C_{23}H_{21}Cl_2N_2PF_6$: C, 51.03; H, 3.91; N, 5.18, found: C, 50.73; H, 3.81; N, 4.86.

1,3-Dibenzyl-2-(pentafluorophenyl)imidazolinium hexafluorophosphate (10b). From **10a** in 90% yield as a white solid, m.p. 161 °C. MS (ESI), *m/e* 417.1 (cation M^+, 100%); IR (KBr) 1610m, 1520m, 840s cm^{-1}; ^{1}H NMR (400 MHz) δ 7.40–7.18 (m, 10 H, H–Ar), 4.54 (s, 4 H, H-6,19), 4.08 (s, 4 H, H-4,5); ^{13}C NMR (100 MHz) δ 155.1, 131.3, 129.9, 128.7, 52.7, 48.9. Anal. Calcd for $C_{23}H_{18}N_2PF_{11}$ C, 49.12; H, 3.23; N, 4.98. Found: C, 49.07; H, 3.51; N, 4.81.

1,3-Dibenzyl-2-(2-pyridinyl)imidazolinium hexafluorophosphate (12b). From **12a** in 71% yield as white solid, m.p. 120 °C. MS (EI), *m/e* 327 (cation $M^+ - H$, 30%), 236 (30), 105 (20), 91 (100), 65 (20); IR (KBr) 1619m, 1599m, 839s, 557m cm^{-1}; ^{1}H NMR (400 MHz) δ 8.94 (d, J = 4.7 Hz, 1 H, H-15), 8.21 (d, J = 7.6 Hz, 1 H, H-17), 8.14–8.10 (m, 1 H, H-18), 7.71–7.68 (m, 1 H, H-16), 7.44–7.32 (m, 10 H, H–Ar), 4.50 (s, 4 H, H-6,19), 4.00 (s, 4 H, H-4,5); ^{13}C NMR (100 MHz) δ 163.8, 151.6, 142.2, 139.2, 132.6, 129.7, 129.5, 128.8, 127.8, 126.9, 52.9, 48.8. Anal. calculated for $C_{22}H_{22}F_6N_3P$: C, 55.82; H, 4.68; N, 8.88, found: C, 55.97; H, 4.63; N, 8.57.

1,3-Dibenzyl-2-(2-thiophenyl)imidazolinium hexafluorophosphate (14b). From **14a** in 92% yield as a white solid, m.p. 110–112 °C. MS (EI), *m/e* 332 (cation $M^+ - H$, 20%), 240 (30), 132 (20), 91 (100), 65 (20); IR (KBr) 1596s, 1580s, 1283m, 836vs, 731m, 698m cm^{-1}; ^{1}H NMR (400 MHz) δ 7.86–7.82 (m, 2 H, H-2,3), 7.44–7.34 (m, 7 H, H–Ar), 7.28–7.25 (m, 4 H, H–Ar), 4.61 (s, 4 H, H-11,18), 3.98 (s, 4 H, H-8,9); ^{13}C NMR (100 MHz) δ 162.3, 135.2, 133.3, 132.8, 129.83, 129.80, 129.4, 128.4, 119.1, 52.6, 48.1. Anal. calculated for $C_{21}H_{21}N_2SPF_6$: C, 52.72; H, 4.42; N, 5.86, found: C, 52.36; H, 4.39; N, 5.68.

General procedure for counter-anion exchange with lithium bis-(trifluoromethylsulfonyl)imide

Imidazolinium bromide (1 mmol) was dissolved in DCM (3 ml) and vigorously stirred with a solution of $LiN(CF_3SO_2)_2$ (1.5 mmol) in water (3 ml) for 30 minutes. The organic phase was separated, washed with water (3 × 3 ml) and dried with molecular 3 Å sieves. The solvent was evaporated and the product was further dried under high vacuum overnight to give the corresponding imidazolinium bis(trifluromethylsulfonyl)imide.

1,3-Dibenzyl-2-(2-chlorophenyl)imidazolinium bis(trifluoromethylsulfonyl)imide (4c). From **4a** in 71% yield as a white solid, m.p. 83 °C. MS (EI), *m/e* 360 (cation $M^+ - H$, 100%), 151 (5), 91 (60); IR (KBr) 1604vs, 1471m, 1458m, 1441m, 1355vs, 1304s, 1192vs, 1135s, 1056s, 772s, 702s, 616s cm^{-1}; ^{1}H NMR (400 MHz) δ 8.09–8.07 (m, 1 H, H-15), 7.76–7.70 (m, 3 H, H–Ar), 7.45–7.40 (m, 4 H, H–Ar), 7.30–7.27 (m, 6 H, H–Ar), 4.50–4.39 (m, 4 H, H-6,19), 4.24–4.19 (m, 2 H, H-4,5), 3.80–3.75 (m, 2 H, H-4,5); ^{13}C NMR (100 MHz) δ 163.8, 135.0, 132.2, 131.9, 131.0, 129.8, 129.69, 129.66, 129.1, 121.9, 77.7, 52.3, 47.9. Anal. calculated for $C_{25}H_{22}ClF_6N_3O_4S_2$: C, 46.77; H, 3.45; N, 6.54, found: C, 46.45; H, 3.34; N, 6.57.

1,3-Dibenzyl-2-(4-chlorophenyl)imidazolinium bis(trifluoromethylsulfonyl)imide (6c). From **6a** in 90% yield as a white solid, m.p. 80 °C. MS (EI), *m/e* 360 (cation $M^+ - H$, 100%), 227 (70), 152 (70), 89 (70), 77 (40); IR (KBr) 1596s, 1563m, 1354s, 1289m, 1289m, 1227s, 1203vs, 1182m, 1063s, 703m, 614s cm^{-1}; ^1H NMR (400 MHz) δ 7.76–7.68 (m, 4 H, H-14,15,17,18), 7.46–7.38 (m, 6 H, H–Ar), 7.23–7.21 (m, 4 H, H–Ar), 4.50 (s, 4 H, H-6,19), 4.00 (s, 4 H, H-4,5); ^{13}C NMR (100 MHz) δ 166.3, 140.5, 132.5, 131.2, 130.3, 129.9, 129.5, 128.4, 121.0, 120.4, 118.8, 52.3, 48.1. Anal. calculated for $C_{25}H_{22}ClF_6N_3O_4S_2$: C, 46.77; H, 3.45; N, 6.54, found: C, 46.46; H, 3.42; N, 6.38.

General procedure for the catalysed aza-Diels–Alder reaction in acetonitrile

The imine (0.2 mmol) and the catalyst (0.02 mmol, 10 mol%) were placed into a dry Schlenk flask under nitrogen. The reaction mixture was dissolved in dry acetonitrile (2 ml) and Danishefsky's diene (**15**) (0.22 mmol, 42.8 µl) was added. After 16 h stirring at room temperature, the mixture was quenched by addition of a saturated solution of potassium hydrogencarbonate (2 ml) and extracted with ethyl acetate (3 × 5 ml). Organic phases were combined, dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. Flash column chromatography (PE–EtOAc, 1 : 1) gave the desired product.

2,3-Dihydro-1,2-diphenylpyridin-4(1*H*)-one (17). From **15** and **16** in 95% yield as a yellow solid, m.p. 53 °C (lit.[47] m.p. 54–55 °C). Spectral data were consistent with literature values.[35]

1-(4-Chlorophenyl)-2,3-dihydro-2-phenylpyridin-4(1*H*)-one (19). From **15** and **18** in 84% yield as a yellow solid, m.p. 148 °C (lit.[33] m.p. 150 °C). Spectral data were consistent with literature values.[33]

1-(4-Methoxyphenyl)-2,3-dihydro-2-phenylpyridin-4(1*H*)-one (21). From **15** and **20** in 92% yield as a yellow oil. Spectral data were consistent with literature values.[33]

2,3-Dihydro-2-(4-chlorophenyl)-1-phenylpyridin-4(1*H*)-one (23). From **15** and **22** in 72% yield as an oil. Spectral data were consistent with literature values.[35]

2,3-Dihydro-2-(2-methoxyphenyl)-1-phenylpyridin-4(1*H*)-one (25). From **15** and **24** in 57% yield as an oil. Spectral data were consistent with literature values.[30]

2,3-Dihydro-2-(2-pyridinyl)-1-phenylpyridin-4(1*H*)-one (27). From **15** and **26** in 93% yield as a yellow oil. Spectral data were consistent with literature values.[35]

2,3-Dihydro-2-(4-methoxyphenyl)-1-phenylpyridin-4(1*H*)-one (29). From **15** and **28** in 45% yield as a yellow oil. Spectral data were consistent with literature values.[35]

2,3-Dihydro-2-(4-nitrophenyl)-1-phenylpyridin-4(1*H*)-one (31). From **15** and **30** in 50% yield as a yellow solid, m.p. 155 °C. Spectral data were consistent with literature values.[35]

General procedure for the reversed aza-Diels–Alder reaction

The imine **16** (0.2 mmol) and catalyst **10b** (0.02 mmol, 10 mol%) were placed into a dry Schlenk flask under nitrogen. The reaction mixture was dissolved in dry acetonitrile (2 ml) and the dienophile (2,3-dihydrofuran (**32**) (0.4 mmol, 30.27 µl) or 3,4-dihydro-2*H*-pyran (**34**) (0.4 mmol, 36.18 µl)) was added. After 16 h stirring at room temperature, the solvent was evaporated under reduced pressure. Flash column chromatography (PE–EtOAc, 8 : 2) gave the desired product.

2,3,3a,4,5,9b-Hexahydro-4-phenylfuro[3,2-*c*]quinoline (33) and (34). From **16** and **32** in 70% yield as a 1 : 1 mixture of the diastereomers **33** and **34**. Spectral data were consistent with literature values.[48]

***Trans*-3,4,4a,5,6,10b-hexahydro-5-phenyl-2*H*-pyrano[3,2-*c*]-quinoline (36).** From **16** and **35** in 16% yield as a yellow oil. Spectral data were consistent with literature values.[26]

Acknowledgements

Financial support by Fonds der Chemischen Industrie, BMBF, DFG (WI 2147/1–1) and Nieders. Vorab der Volkswagen Stiftung is gratefully acknowledged.

References

1 For a review, see: W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290.
2 H. Y. Zhou, E. J. Campbell and S. T. Nguyen, *Org. Lett.*, 2001, **3**, 2229.
3 For an example, see: J. Pytkowicz, S. Roland, P. Mangeney, G. Meyer and A. Jutand, *J. Organomet. Chem.*, 2003, **678**, 166.
4 For a review, see: P. I. Dalko and L. Moisan, *Angew. Chem., Int. Ed.*, 2001, **40**, 3726.
5 E. N. Jacobsen, A. Pfaltz, and H. Yamamoto, *Comprehensive Asymmetric Catalysis*, Springer, Heidelberg, 1999.
6 D. Schinzer, *Selectivities in Lewis Acid Promoted Reactions*, Kluwer Academic Publishers, Dordrecht, 1989.
7 B. List, R. A. Lerner and C. F. Barbas, *J. Am. Chem. Soc.*, 2000, **122**, 2395.
8 For a brief review of proline-catalysed reactions, see: R. O. Duthaler, *Angew. Chem., Int. Ed.*, 2003, **42**, 975.
9 A. B. Northrup and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2002, **124**, 2458.
10 W. Zhuang, S. Saaby and K. A. Jørgensen, *Angew. Chem., Int. Ed.*, 2004, **43**, 4476.
11 A. J. A. Cobb, D. M. Shaw and S. V. Ley, *Synlett*, 2004, 558.
12 For a brief review on acyl anion equivalents, see: J. S. Johnson, *Angew. Chem., Int. Ed.*, 2004, **43**, 1326.
13 For a review on the Stetter and benzoin reactions, see: D. Enders and T. Balensiefer, *Acc. Chem. Res.*, 2004, **37**, 534.
14 For a brief review see:P. M. Pihko, *Angew. Chem. Int. Ed.*, 2004, **43**, 2062.
15 For a review see: S. E. Denmark and R. A. Stavenger, *Acc. Chem. Res.*, 2000, **33**, 432.
16 T. Mukaiyama, M. Yanagisawa, D. Iida and I. Hachiya, *Chem. Lett.*, 2000, 606.
17 C.-T. Chen, S.-D. Chao, K.-C. Yen, C. H. Chen, I.-C. Chou and S.-W. Hon, *J. Am. Chem. Soc.*, 1997, **119**, 11341.
18 K. Miura, K. Ootsuka, S. Suda, H. Nishikori and A. Hosomi, *Synlett*, 2002, 313.
19 C.-T. Chen, S.-D. Chao and K.-C. Yen, *Synlett*, 1998, 924.
20 J. Howarth, K. Hanlon, D. Fayne and P. McCormac, *Tetrahedron Lett.*, 1997, **38**, 3097.
21 T. Ooi and K. Maruoka, *Acc. Chem. Res.*, 2004, **37**, 526.
22 T. Akiyama, J. Ithoh, K. Yokota and K. Fuchibe, *Angew. Chem., Int. Ed.*, 2004, **43**, 1566.
23 D. Uraguchi and M. Terada, *J. Am. Chem. Soc.*, 2004, **126**, 5356.
24 S. M. Weinreb, 'Hetero Dienophile Additions to Dienes', in *Comprehensive Organic Synthesis, Vol. 5*, ed. B. M. Trost and I. Fleming, Pergamon, Oxford, 1991.
25 C. Loncaric, K. Manabe and S. Kobayashi, *Chem. Commun.*, 2003, 574.
26 Inverse electron demand aza-Diels–Alder reaction in ionic liquids: J. S. Yadav, B. V. S. Reddy, J. S. S. Reddy and R. S. Rao, *Tetrahedron*, 2003, **59**, 1599.
27 J. S. Yadav, B. V. S. Reddy, V. Sunitha and K. S. Reddy, *Adv. Synth. Catal.*, 2003, **345**, 1203.
28 N. Prabagaran and B. Varghese, *Org. Lett.*, 2001, **3**, 1973.
29 N. J. Patmore, C. Hague, J. H. Cotgreave, M. F. Mahon, C. G. Frost and A. S. Weller, *Chem. Eur. J.*, 2002, **8**, 2088.
30 J. Collin, N. Jaber and M. I. Lannou, *Tetrahedron Lett.*, 2001, **42**, 7405.
31 H. Laurent-Robert, B. Garrigues and J. Dubac, *Synlett*, 2000, 1160.
32 T. Ali, K. K. Chauhan and C. G. Frost, *Tetrahedron Lett.*, 1999, **40**, 5621.
33 S. Kobayashi, H. Ishitani and S. Nagayama, *Synthesis*, 1995, 1195.
34 R. Kumareswaran, B. G. Reddy and Y. D. Vankar, *Tetrahedron Lett.*, 2001, **42**, 7493.
35 (*a*) Aza-Diels–Alder reaction in alcoholic solvents without catalyst: Y. Yuan, X. Li and K. L. Ding, *Org. Lett.*, 2002, **4**, 3309; (*b*) M. V. Spanedda, V. D. Hoang, B. Crousse, D. Bonnet-Delpon and J.-P. Bégué, *Tetrahedron Lett.*, 2003, **44**, 217.

36 For a review on asymmetric hetero-Diels–Alder reactions, see: K. A. Jørgensen, *Angew. Chem., Int. Ed.*, 2000, **39**, 3558.
37 V. Jurčík and R. Wilhelm, *Tetrahedron*, 2004, **60**, 3205.
38 A. Salerno, C. Caterina and I. A. Perillo, *Synth. Commun.*, 2000, **30**, 3369.
39 V. Jurčík, B. Blaschkowski, A. Adam and R. Wilhelm, unpublished X-ray data, 2004.
40 T. Welton, *Chem. Rev.*, 1999, **99**, 2071.
41 P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, 2003.
42 I. Krossing and I. Raabe, *Angew. Chem., Int. Ed.*, 2004, **43**, 2066.
43 S. H. Strauss, *Chem. Rev.*, 1993, **93**, 927.
44 A. Simion, C. Simion, T. Kanda, S. Nagashima, Y. Mitoma, T. Yamada, K. Mimura and M. Tashiro, *J. Chem. Soc., Perkin Trans. 1*, 2001, 2071.
45 D. F. Shriver and M. A. Drezdon, *The Manipulation of Air-Sensitive Compounds*, Wiley, Chichester, 1986.
46 W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923.
47 A. Bolognese, M. V. Diurno, O. Mazzoni and F. Giordano, *Tetrahedron*, 1991, **47**, 7417.
48 J. S. Yadav, B. V. S. Reddy, C. R. Madhuri and G. Sabitha, *Synthesis*, 2001, 1065.