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Enantioselective addition of alkynes to imines in ionic liquids

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Abstract

The enantioselective alkyne–imine addition catalysed by copper(I)–bis(oxazoline) (box) can be efficiently performed in the ionic liquid 1-*n*-butyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide [bmim][NTf_2]. Several substrates were tested and the reuse of the catalytic CuOTf/(box) was carried out for six cycles allowing high overall yield (87%) and enantioselectivity (first cycle 94%, sixth cycle 89%).

Keywords: Ionic liquids; Reuse; Recycling; Enantioselective catalysis; Imines; Propargylamines

1. Introduction

Propargylamines are important synthetic intermediates for the synthesis of various amino derivatives, including biologically active compounds [1]. Apart the continuous interest in the development of synthetic methods for racemic propargylamines [1,2], the non-catalytic [1,3] and catalytic [1] enantioselective synthesis of propargylamines have been recently published [4,5]. Both reported catalytic systems are based on the copper(I)-catalysed addition of alkynes to imines [4] and enamines [5] using copper(I)–bis(oxazoline) (box) [6] and copper(I)–aminophosphane (Quinap) [7] complexes, respectively.

The possibility to recycle and reuse the chiral catalytic system is an important issue for asymmetric synthetic transformations [8]. Apart from other different solutions, the approach based on the immobilisation of the catalyst in homogenous or heterogeneous supports is the most common [9]. However, these methods frequently require prior functionalization of the catalyst. In opposition, the possibility to develop a recoverable system based on the use of a non-functionalized catalyst is more appealing. This approach is mainly based on the separation of the catalyst from the reaction products by retention of the catalyst by microencapsulation [8], using membrane assisted filtration [10] or ion-exchange entrapment [8]. Another efficient approach is based on solvent extraction due to large different affinities of the catalyst system and the reaction products for each liquid phase, as for example, supercritical CO_2 ($scCO_2$) [11] or fluorinated solvents [12]. Room temperature ionic liquids (RTILs) are more recently studied media which also fulfil the above requirements, mainly due to their special solubility properties, in which, depending of the structure of the cation and of the anion, they can be miscible in $scCO_2$, water and common organic solvents [13]. The ongoing development of new types of RTILs also demonstrates that it is possible to tune the RTIL structure in order to achieve more specific solvent solubility and substrate affinity properties [14]. It has also been demonstrated that RTILs are an efficient medium for the reuse and recycling of a large range of organometallic, organic and biocatalysts in a remarkable number of diverse synthetic transformations [15]. In line with our effort to use of RTILs in a range of applications [16], including their use as an alternative reaction media [17] and the reported efficient immobilisation of Cu(II)–bis(oxazoline) complexes in RTILs [18], we were prompted to study the enantioselective preparation of propargylamines **4** in RTILs by using the recently reported method based on the enantioselective Cu(I)–bis(oxazoline) catalysed addition of alkynes to imines [4] (Scheme 1).

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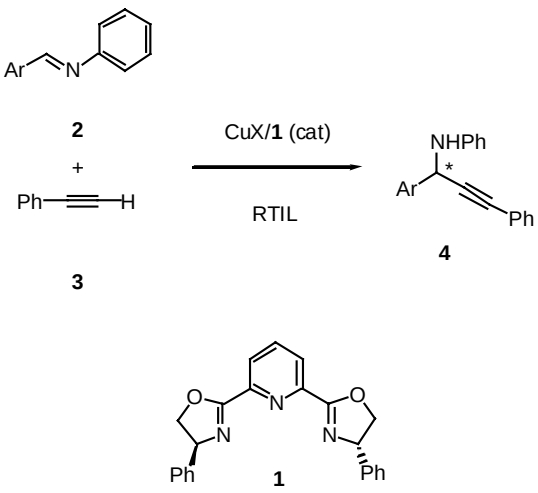

Scheme 1.

2. Experimental

2.1. General remarks

Toluene was freshly distilled over calcium hydride. All reactions were performed in oven-dried glassware under an atmosphere of argon. The room temperature ionic liquids 1-*n*-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6], 1-*n*-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][NTf_2], 1-*n*-octyl-3-methylimidazolium hexafluorophosphate [C_8mim][PF_6], 1-*n*-butyl-2,3-dimethylimidazolium tetrafluoroborate [bdmim][BF_4], 1-*n*-butyl-2,3-dimethylimidazolium hexafluorophosphate [bdmim][PF_6] and 1-*n*-butyl-2,3-dimethylimidazolium bis-(trifluoromethylsulfonyl)imide were prepared following general reported procedures [19]. The bis(oxazolinyl)pyridine (pybox) **1**, CuBr and CuOTf were purchased from Aldrich. Flash chromatography and preparative thin layer chromatography (TLC) were carried out on silica gel 60 M from MN (Ref. 815381) and silica G-UV_{254} from MN (Ref. 816320), respectively. Reaction mixtures were analysed by TLC using ALUGRAM® SIL G/UV_{254} from MN (Ref. 818133, silica gel 60). Visualisation of TLC spots was effected using UV and solution of phosphomolybdic acid or I_2. Melting points (uncorrected) were determined on a Electrothermal Mod. IA 6304 capillary melting point apparatus. Infrared spectra (IR) spectra were recorded on a Mattson Instruments model Satellite FTIR as thinly dispersed films. High and low resolution mass spectra (EI, FAB) were carried out by mass spectrometry service of University of Santiago de Compostela (Spain). NMR spectra were recorded in a Brucker AMX 400 using $CDCl_3$ as solvent and $(CH_3)_4Si$ (^1H) as internal standard. All coupling constants are expressed in Hz. The enantiomer excess was determined by HPLC analysis using Merck & Hitachi components L-600A, L-4250, T-6300, D-6000 on a Chiralcel O D column (0.46 cm × 25 cm) at 25 °C following reported conditions [4] for each product **4**. The copper content in the organic phases and in the ionic liquid was measured by flame atomic absorption spectrometry analysis (AAS) using Varian Spectra AA-300 at a wavelength of 324.7 nm, air/acetylene mixture, standards: 0.25, 0.50, 1.00, 2.50 and 5.00 ppm. Each sample residue was decomposed at 600 °C and dissolved in aqueous HNO_3 solution (0.5 M, 10 ml).

2.2. General procedure for the synthesis of imines (*2a–f*)

A solution of the adequate aldehyde and aniline in toluene was refluxed for 2 h, after which the toluene and water formed in the reaction were distilled out as an azeotropic mixture. The residual toluene was removed under reduced pressure, affording the crude product as a solid, which was further purified by crystallisation from ethanol/water.

2.2.1. *N*-benzylidene-aniline (*2a*)

Pale yellow plates, 68%, mp, 49–50 °C, lit. [20] 51.5–52 °C; identical spectral data to those previously reported [21].

2.2.2. *N*-(*p*-methylbenzylidene)-aniline (*2b*)

Pale yellow plates, 63%, mp 44–45 °C, lit. [20] 44–45 °C; identical spectral data to those previously reported [21].

2.2.3. *N*-(*p*-trifluoromethylbenzylidene)-aniline (*2c*)

White needles, 83%, mp 79–81 °C, lit. [20] 77.5–78 °C; ν_{max} 3086, 3059, 3033, 2993, 2885, 1622, 1577, 1485, 1361, 1328, 1256, 1171, 1153, 1121, 1069 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.51 (s, 1H), 8.03 (d, J = 8.1 Hz, 2H), 7.74 (d, J = 8.1 Hz, 2H), 7.43 (t, J = 7.8 Hz, 2H), 7.26 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.5, 151.3, 139.3, 129.2, 128.9, 126.5, 125.7, 120.8.

2.2.4. *N*-(*p*-chlorobenzylidene)-aniline (*2d*)

White needles, 77%, mp 63–64 °C, lit. [20] 63.5–64 °C; ν_{max} 3081, 3063, 3048, 2875, 1622, 1589, 1489, 1449, 1402, 1353, 1099, 1087, 1074 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.42 (s, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.41 (t, J = 7.7 Hz, 2H), 7.24 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.7, 151.6, 137.3, 134.7, 129.9, 129.2, 129.0, 126.2, 120.8.

2.2.5. *N*-(*p*-bromobenzylidene)-aniline (*2e*)

White needles, 75%, mp 73–75 °C, lit. [20] 72–72.5 °C; ν_{max} 3078, 3058, 3048, 2873, 2850, 1623, 1582, 1486, 1448, 1398, 1361, 1069 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.41 (s, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.40 (t, J = 7.7 Hz 2H), 7.24 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.9, 135.1, 132.0, 130.1, 129.2, 126.2, 125.9, 120.8.

2.2.6. *N*-(2-naphthylmethylene)-aniline (*2f*)

Light brown crystalline powder, 71%, mp 113–116 °C; ν_{max} 3057, 3033, 2872, 1619, 1588, 1486, 1397, 1335, 1204,

1168, 1120 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.63 (s, 1H), 8.20 (m, 2H), 7.92 (m, 3H), 7.56 (m, 2H), 7.43 (m, 2H), 7.28 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.3, 134.9, 133.8, 133.1, 132.2, 131.3, 129.2, 128.8, 128.6, 127.9, 127.5, 126.6, 126.0, 123.9, 120.9.

2.3. General procedure for the synthesis of propargylamines (*4a–f*)

To a mixture of imine **2** (0.28 mmol), copper(I) triflate toluene complex (5 mol%), pybox **1** (5 mol%) and solvent (250 μl), was added phenylacetylene **3** (33 μl, 0.31 mmol). The mixture was stirred for 4 days at room temperature, becoming homogeneous, then applied directly on a silica gel column for flash chromatography (a drop of ethyl acetate may be needed to reduce viscosity), using 1:20 ethyl acetate/hexane as eluent. The products were obtained as pale yellow to orange oils, crystallising upon removal of residual solvents in vacuo. The enantiomeric excess was determined of the homogeneous solid by HPLC, using a Chiralcel OD column and 1:20 isopropanol/hexane as eluent. Identical spectral data and similar chromatographic to those reported [4].

2.4. Procedure for the reuse of the catalytic system

To a mixture of the imine **2a** (0.28 mmol), copper(I) triflate toluene complex (10 mol%), pybox **1** (5 mol%) and [bmim][Tf_2N] (500 μl), was added phenylacetylene **3** (33 μl, 0.31 mmol). The mixture was stirred for 4 days at room temperature, becoming homogeneous, then extracted with hexane (4× 5 ml). The organic phase was concentrated under reduced pressure and applied on a silica gel TLC, using 1:10 ethyl acetate/hexane as eluent. Enantiomeric excess of **4a** was determined as previously described, and the recovered ionic liquid containing the catalyst was loaded with a new batch of **2a** and phenylacetylene. The process was repeated for six cycles, after which the residual **4a** was extracted with diethyl ether (4× 5 ml) and purified as described before.

3. Results and discussion

Using the best reported tridentate chiral ligand bis(oxazolinyl)pyridine (pybox) **1** in water or in toluene [4], we first optimised the reaction conditions using the imine **2a**, mainly by screening different ionic liquids (Table 1). When the reaction temperature was increased to 40 °C higher yields of **4a** were observed (entry 15, 88% at 40 °C versus entry 14, 74% at rt) but some erosion on the enantioselectivity also occurred (e.e. 88% at 40 °C versus e.e. 94% at rt) which is in line with reported results by Wei and Li [4] using water or toluene as reaction solvent.

The authors also found that in water, the copper catalyst CuBr gave considerably lower enantioselectivity than CuOTf. When using the ionic liquids [bmim][NTf_2] (entry 5 versus entry 14), [bdmim][NTf_2] (entry 6 versus entry 9) or [bdmim][BF_4] (entry 7 versus entry 10) higher yields of the propargylamine **4a** were obtained using CuBr but a drastic reduction of the e.e.s also occurred. Using only CuOTf at room temperature, the dependence of the transformation on the structure of the ionic liquid was further studied. Several combinations of the common imidazolium cations ([bmim], [C_8mim] and [bdmim]) and anions ([BF_4], [PF_6] and [NTf_2]) were tested. By keeping the nonpolar anion [PF_6] and changing the cation structure, similar yields were obtained (entries 11–13, 75–76%). However, a considerable effect on the e.e was observed; [C_8mim] 27% (entry 13), [bdmim] 76% (entry 11) and [bmim] of 86% (entry 12), which suggests that a good balance between the overall hydrophibility of the cation ([C_8mim] versus [bmim]) and the presence or absence ([bmim] versus [bdmim]) of the more acidic C(2)−H plays an important role on the enantioselectivity. This observation is in line with reported examples of strong dependence of the reactivity on the ionic liquid structure [22], including side reactions [17a,23]. Regarding the anion structure, no appreciable change on the enantioselectivity was observed for [NTf_2] (entry 9, 79%), [BF_4] (entry 10, 78%) or [PF_6] (entry 11, 76%), although the [BF4] anion gave considerably lower yield (51% versus 75% for [PF_6] and 82% for [NTf_2]). The ionic liquid resulting from the combination of the cation [bmim] and the anion [NTf_2] gave the best results (entry 14, 74%, e.e. 94%) which are very similar to the ones in toluene (entry 3, 74%, e.e. 95%, reported [4] entry 2, 78%, e.e. 96%) and considerably better than in water (reported [4] entry 1, 71%, e.e. 84%).

Table 1
Optimisation of the reaction conditions using **2a** (Ar = Ph)[a]

Entry	Temperature (°C)[b]	Solvent	CuX	Yield (%)[c]	e.e. (%)[d]
1	(22)	(water)	(CuOTf)	(71)	(84)
2	(22)	(toluene)	(CuOTf)	(78)	(96)
3	rt	toluene	CuOTf	74	95
4	40 °C	[bmim][NTf_2]	CuBr	76	12
5	rt	[bmim][NTf_2]	CuBr	85	20
6	rt	[bdmim][NTf_2]	CuBr	83	0.8
7	rt	[bdmim][BF_4]	CuBr	60	23
8	rt	[bmim][PF_6]	CuBr	55	10
9	rt	[bdmim][NTf_2]	CuOTf	82	79
10	rt	[bdmim][BF_4]	CuOTf	51	78
11	rt	[bdmim][PF_6]	CuOTf	75	76
12	rt	[bmim][PF_6]	CuOTf	75	86
13	rt	[C_8mim][PF_6]	CuOTf	76	27
14	rt	[bmim][NTf_2]	CuOTf	74	94
15	40 °C	[bmim][NTf_2]	CuOTf	88	88

[a] **2a** (50 mg, 0.28 mmol), **3** (1.1 eq.), CuX (5 mol%), **1** (5 mol%), solvent (250 μl), 4 days. In brackets are presented reported results [4].
[b] Room temperature refers to an average temperature of 20 °C.
[c] Isolated yield after purification by flash chromatography.
[d] The enantiomeric excess of **4a** (e.e.) is referred to the (+) enantiomer [4].

Table 2
Scope of the reaction for different imines **2a–f** in [bmim][NTf_2][a]

Entry	Substrate	Ar	Yield (%)[b]	e.e. (%)
1	**a**	Ph	74	94
2	**b**	4-MeC_6H_4	91	86
3	**c**	4-$CF_3C_6H_4$	76	96
4	**d**	4-ClC_6H_4	92	94
5	**e**	4-BrC_6H_4	90	99
6	**f**	2-Naphthyl	91	86

[a] **2** (0.28 mmol), **3** (1.1 eq.), CuOTf (5 mol%), **1** (5 mol%), [bmim][NTf_2] (250 μl), room temperature, 4 days.
[b] Isolated yield after purification by flash chromatography.

Under the prior optimised conditions, the scope of this transformation was examined for a variety of substrates as presented in Table 2. In all cases high yields and enantioselectivites were observed. It should also be mentioned that using only 5 mol% of CuOTf/**1** gave similar results to that reported using 10 mol% in toluene [4].

Furthermore, we explored the possibility to reuse the precious CuOTf (10 mol%)/**1** (5 mol%) catalytic system using the substrate **2a** as a representative example (Table 3). After the first run, the ionic liquid [bmim][NTf_2] (0.5 ml) was extracted with hexane (4× 5 ml) and more reactants **2a** and **3** were added to the ionic liquid for the next cycle. The following cycle gave higher yield than the prior one, which is due to incomplete extraction of the product **4a** from the previous cycle. In fact, after the last cycle, the ionic liquid was further extracted with diethyl ether and more product **4a** (34%) was isolated. The reuse experiment was performed in duplicate in order to obtain additional information about the Cu content in the organic layer and in the final reused ionic liquid. For the first cycle, the Cu content in the hexane was only 0.3% of initial amount of catalyst CuOTf and for the cycles 2–6 of 0.1%. In contrast, the remaining [bmim][NTf_2] after all six cycles retained 96 and 69% of CuOTf, respectively after extraction with hexane and with diethyl ether. These results clearly show that the CuOTf is efficiently immobilised in the ionic liquid if the product is removed using hexane. In spite of diethyl ether or *tert*-butyl methyl ether being more efficient for product extraction, these solvents are not appropriate for the reuse experiments due to the occurrence of extraction of the catalytic system. Additionally, if a lower amount of CuOTf (5 mol%) was used, a considerable erosion of the isolated yield was also observed (first cycle 58%, second cycle 25%, third cycle 5%). Using CuOTf in 10 mol% and **1** in 5 mol% high isolated overall yield (89%), TON (105) and enantioselectivities (88–94%) were observed for all six cycles tested, which demonstrates the occurrence of efficient immobilisation and stability of the catalytic system in the ionic liquid. It should also be mentioned that the recovered ionic liquid from the last cycle presents identical spectral data to that of the initial sample, which demonstrates that no decomposition of the ionic liquid occurs during the reaction [17a,23].

Table 3
Reuse of the catalytic system CuOTf/**1**

Cycle[a]	Yield (%)[b]	e.e (%)	Cu in hexane (%)[c]	Cu in [bmim][NTf_2] (%)[c]
1	51	94	0.3[d]	–
2	70	93	0.1[d]	–
3	82	90	0.1[d]	–
4	91	89	0.1[d]	–
5	102	88	0.1[d]	–
6	94	89	0.1[d]	96[d]
	34[e]			69

[a] **2a** (50 mg, 0.28 mmol), **3** (1.1 eq.), CuOTf (10 mol%), **1** (5 mol%), [bmim][NTf_2] (0.5 ml), room temperature, 4 days followed by extraction with hexane (4× 5 ml).
[b] Isolated yield after purification by TLC chromatography.
[c] Percentage of Cu relative to initial amount detected by flame atomic absorption spectrometry in the hexane phase and in the remained reused ionic liquid phase.
[d] Results obtained for the parallel experiment.
[e] Isolated product by further extraction of the ionic liquid with diethyl ether (4× 5 ml).

4. Conclusion

The recently reported catalytic enantioselective formation of propargylamines by CuOTf/**1** catalysed alkyne–imine addition [4] can be efficiently performed in the ionic liquid [bmim][NTf_2], allowing the reuse of the catalytic system.

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