Universiteit
Leiden
The Netherlands

Nickel N-heterocyclic carbene complexes in homogeneous catalysis

Berding, J.

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Appendix A

Synthesis of diimidazolium salts

Abstract. *The syntheses of a number of diimidazolium salts using conventional heating in THF or 1,4-dioxane, as well as using microwave-assisted reactions in toluene are described and evaluated. In total, the synthesis and characterization of nineteen novel (di)imidazolium salts is presented.*

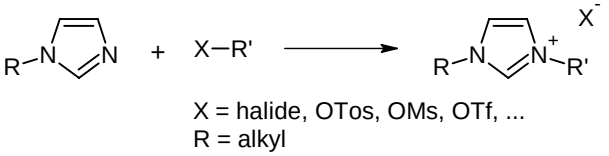
A.1 Introduction

Imidazolium salts have been under investigation for a number of applications. Small N,N′-dialkyl imidazolium salts are a well known class of ionic liquids, and have as such found use as highly versatile solvents in synthesis and catalysis.[1] Polyimidazolium salts, on the other hand, have been studied for their anion receptor properties.[2, 3] Recent interest in imidazolium salts is mainly due the fact that they are excellent precursors for N-heterocyclic carbenes (see Chapter 1).

Generally, imidazolium salts are prepared by a quaternization reaction between an N-substituted imidazole with an alkyl halide or an alkyl chain with another suitable leaving group (Scheme A.1). Often, the reaction is performed in an apolar solvent, such as THF, toluene, or diethyl ether, in which the reagents dissolve and from which the product salt separates. Only in the case of N,N′-diaryl imidazolium salts this synthetic route cannot be followed, as aryl halides are unreactive towards nucleophilic substitution. Usually, these salts are obtained following a ring-closing pathway, in which the imidazole ring is formed *in situ*.[4]

The quaternization reaction, depending on the leaving group, often requires refluxing conditions to proceed at an appreciable rate. In principle, the rate of the reaction may be increased by refluxing in a higher boiling solvent. Alternatively, a lower boiling solvent may be used when performing the reaction in a pressure tube, at temperatures well above the boiling point of the solvent.[5] In addition, the reaction may be heated using microwave radiation. The use of household or laboratory microwave ovens is one of the latest advances in organic synthesis,[6] although there is an ongoing debate whether the success of its use is due to the high temperatures employed, or if there is an added enhancement due to the radiation.[7] In 2001 Varma *et al.* reported the use of a household microwave oven in the solvent-free synthesis of mono- and diimidazolium salts.[8] Later, the method was improved and extended to a scale up to 2 mol, using an open-vessel microwave setup.[9]

In this appendix the synthetic procedures leading toward various imidazolium salts are described. These products were obtained during the research described in Chapters 2-5, however, attempts to synthesize their corresponding nickel N-heterocyclic carbene complexes failed, or were ultimately not attempted. Still, a number of these novel imidazolium salts have not been reported in the literature.



Scheme A.1. General synthetic route toward imidazolium salts.

A.2 Results and discussion

A number of N-substituted imidazoles that could not be obtained commercially were synthesized following various literature procedures or adaptations thereof. In total, eleven different N-substituted imidazoles and benzimidazoles were obtained, shown in Figure A.1. The various products obtained from these N-substituted imidazoles are depicted in Figure A.2 (N.B. Product numbering is as follows: the numeral denotes the type of imidazole or diimidazole; the letter suffix is unique for the N-sidegroup). In principle, diimidazolium salts may be obtained either by reaction of an N-substituted imidazole with a suitable alkyl dihalide,[10] or by reaction of a bridged bisimidazole with two equivalents of an alkyl halide or another alkylating reagent.[11] With the exception of [**6k**]Br_2, all diimidazolium salts were obtained following the first route.

A small survey was undertaken to determine the optimal conditions for the quaternization reaction of these N-substituted imidazoles with 1,2-dibromoethane. The details of the synthetic procedures leading to diimidazolium salts *via* three different methods are summarized in Table A.1. The yield of the different products is given for each method. Method A consists of refluxing a solution of the reagents in THF for 2 – 3 days, as developed by Lee *et al*.[10] In Method B the reagents are dissolved in toluene in a pressure tube and heated in a laboratory microwave to 125 to 140 °C for five to ten minutes. In Method C the reagents are heated in 1,4-dioxane at 100 °C for 16 hours.

Method A gave the salts in relatively high yields in most cases. However, of the three methods, Method A has the lengthiest reaction time and some products contained colored impurities, and therefore the mixture had to be recrystallized. Moreover, imidazoles **1c** and **2a** appeared to be quite unreactive, leading to an inseparable mixture of mono- and dicondensates. It should be noted, however, that products [**5c**]Br_2 and [**7a**]Br_2 have been prepared before and more efficiently, by heating the reagents for 2 days in THF at 130 °C in a pressure tube.[5] Method B, which has the shortest reaction time and fair to good yields, gave colored products which needed recrystallization, as well. Presumably, the coloration is caused by

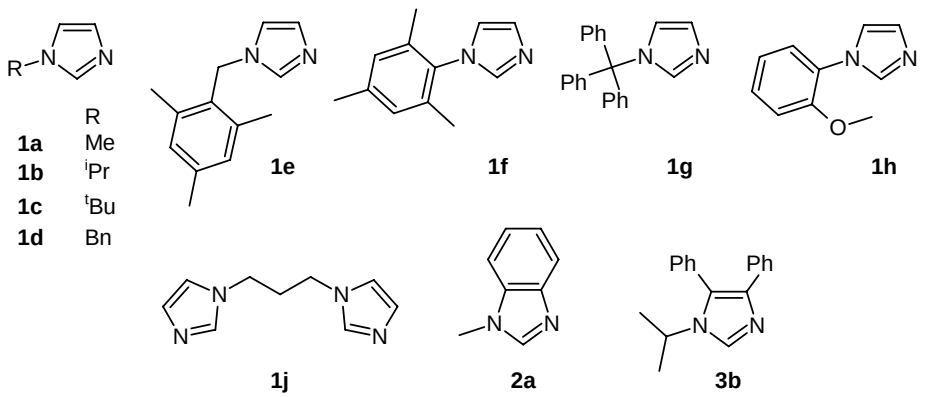


Figure A.1. N-substituted imidazoles used in this study.

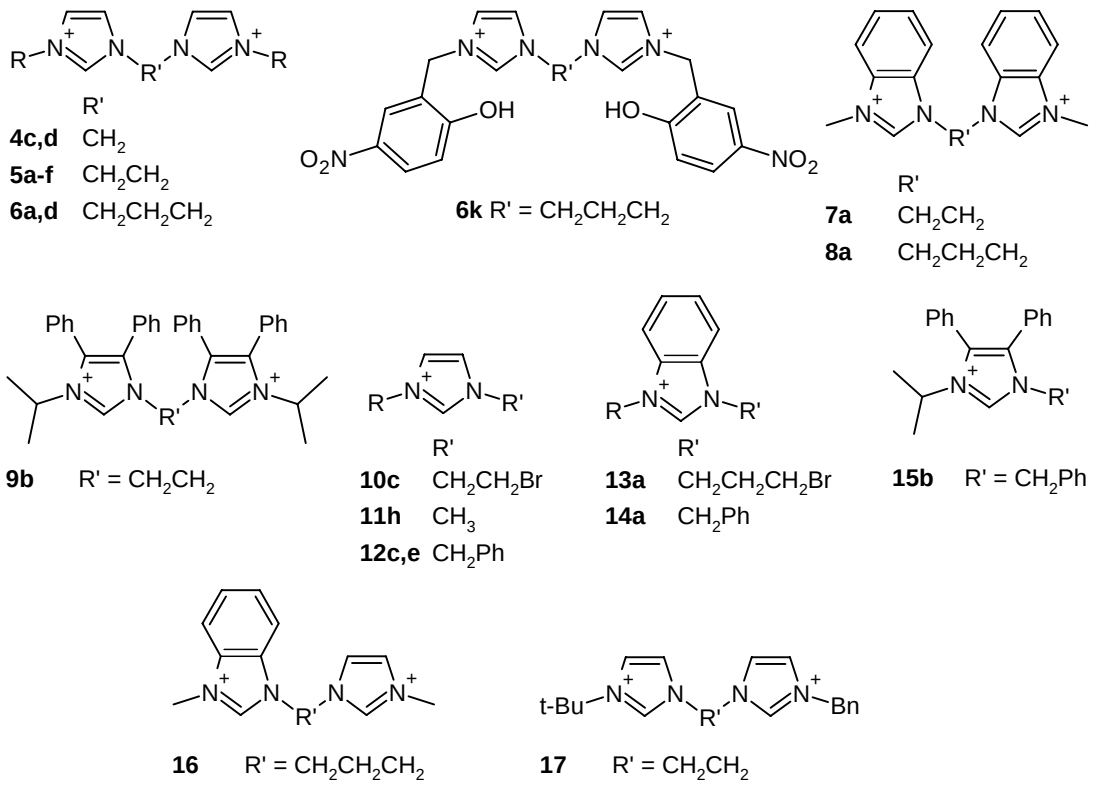


Figure A.2. All imidazolium cations prepared in this study.

decomposition due to the high temperatures employed in the microwave assisted synthesis. Method C gave most products in good to high yields, and in high purity (>99%, judging from the NMR spectra), without further purification being required.

The initial survey included the use of leaving groups other than bromides, i.e. tosylates and mesylates. These leaving groups gave the corresponding products in high yields, except for the microwave assisted synthesis with 1,2-di-O-mesylethane which lead to a mixture of mono- and di-condensates.

Table A.1. Imidazolium salts synthesized and the yield depending on the method used.

Dication	R-Im	X-R'-X R'	X	THF, 80 °C, 2-3 d [a]	Toluene, μW [a]	1,4-Dioxane, 100 °C, 16 h [a]
5a	**1a**	CH_2CH_2	OTos		86	95
5c	**1c**	CH_2CH_2	Br	0 [b] (85) [c]	35	78
5d	**1d**	CH_2CH_2	Br	65 (52) [10]	43	
5d	**1d**	CH_2CH_2	OMs	75	0 [b]	
5e	**1e**	CH_2CH_2	Br		27	66
5f	**1f**	CH_2CH_2	Br	39 (45) [10]	21	70
7a	**2a**	CH_2CH_2	Br	0[b] (68) [c]	37	55

[a] X-R'-X : R-Im = 1 : 2.1-2.5; isolated yield (%), literature values in parentheses; [b] A mixture of inseparable products was obtained; [c] THF, pressure tube, 130 °C, 2 d, ref. 5.

In summary, it is clear from Table A.1 that, even though the microwave-assisted synthesis yields the products in moderate amounts in a very short time, the conventional heating in 1,4-dioxane is the superior synthesis method in terms of isolated yields and, moreover, in terms of product purity. Therefore, the remaining syntheses were performed by conventional heating.

The conditions and yields of the synthesis of an additional variety of diimidazolium salts by conventional heating are summarized in Table A.2. Variations are made in the N-substituent, the length of the bridge and the leaving group. The bromide salts of **4c**, **4d** and **5b** have been reported before in higher yielding reactions, either by heating in a pressure tube to 130 °C in THF,[5] or following a solvent-free method.[10]

In the case of the trityl-substituted imidazolium salts, only a mixture of the mono- and dicondensates could be obtained, probably due to the poor solubility of the starting material, or the low reactivity. Unfortunately, the mixture could not be separated.

Table A.2. Overview of diimidazolium salts obtained by conventional heating.

Dication	R-Im	R'	X	Yield (%) [a]	Solvent and conditions [b]
4c	**1c**	CH_2	Br	42	1,4-dioxane
				79 [5]	THF, 130 °C, 2 d
4d	**1d**	CH_2	Br	30	1,4-dioxane
				81 [10]	Neat, 80 °C, 16 h
5b	**1b**	CH_2CH_2	Br	75	THF
				90 [5]	THF, 130 °C, 2 d
5d	**1d**	CH_2CH_2	OTos	95	THF
5g	**1g**	CH_2CH_2	Br	0 [c]	1,4-dioxane
5h	**1h**	CH_2CH_2	Br	42	THF
6a	**1a**	$(CH_2)_3$	OTos	93	THF
6d	**1d**	$(CH_2)_3$	Br	60	1,4-dioxane
6d	**1d**	$(CH_2)_3$	OTos	93	THF
6k	**1j**	3-(NO_2)-6-(OH)Bn	Br	86	3 : 1 1,4-dioxane-acetonitrile, R-Im : R'-X = 1 : 2.4
8a	**2a**	$(CH_2)_3$	OTos	94	1,4-dioxane
9b	**3b**	CH_2CH_2	Br	53	1,4-dioxane
16	**1a**	**13a**	Br	58	1,4-dioxane, R'-X : R-Im = 1 : 1.7
17	**1d**	**10c**	Br	87	1,4-dioxane, R'-X : R-Im = 1 : 1

[a] Isolated yield (%); [b] Standard conditions: X-R'-X : R-Im = 1 : 2.0-2.5; with THF: 80 °C, 2-3 d; with 1,4-dioxane: 100 °C, 16 h; [c] A mixture of inseparable products was obtained.

Asymmetric diimidazolium salts **16** and **17** were obtained by first reacting a N-substituted imidazole with a large excess of 1,2-dibromoethane or 1,3-dibromopropane to yield monocondensates **10c** and **13a** (see below), which were then reacted further with another N-substituted imidazole. Asymmetric

diimidazolium salts with a methylene bridge could not be obtained following this synthetic route, as even in a large excess of dibromomethane the dicondensate is synthesized.[10]

An overview of various monoimidazolium salts synthesized by conventional heating is presented in Table A.3. Monocondensates [**10c**]Br and [**13a**]Br were obtained by using an excess of alkyl dihalide and stirring at 35 – 40 °C, in order to avoid the formation of an inseparable mixture of mono- and dicondensate. Compound [**11h**]I could be obtained in good yields by stirring at room temperature, as iodomethane is highly reactive towards substitution reactions. Imidazolium salt [**14a**]Br has been synthesized before by stirring the reagents in dimethylacetamide (DMA), although column chromatography was necessary to obtain the pure compound.[12]

Table A.3. Overview of imidazolium salts obtained in this study.

Cation	R-Im	R'	X	Yield (%) [a]	Solvent and conditions [b]
10c	**1c**	CH_2CH_2Br	Br	86	THF, R-Im : R'-X = 1 : 5, 40 °C
11h	**1h**	Me	I	84	THF, RT
12c	**1c**	Bn	Br	82	1,4-dioxane
12e	**1e**	Bn	Br	63	THF
13a	**2a**	$(CH_2)_3Br$	Br	33	THF, R-Im : R'-X = 1 : 6, 35 °C
14a	**2a**	Bn	Br	97	THF, 16 h
				96 [12]	DMA, 50 °C, 16 h
15b	**3b**	Bn	Br	95	1,4-dioxane

[a] Isolated yield (%); [b] Standard conditions: R-Im : R'-X = 1 : 1.1–3.0; with THF: 80 °C, 2-3 d; with 1,4-dioxane: 100 °C, 16 h.

All (di)imidazolium salts are insoluble in 1,4-dioxane, THF, diethyl ether and hydrocarbons, sparingly soluble in dichloromethane and soluble in methanol, DMSO and water, except for the highly substituted imidazolium bromide [**15b**]Br, which was found also soluble in 1,4-dioxane, and was isolated only after precipitation by the addition of diethyl ether. The (di)imidazolium salts were analyzed by ^{1}H and ^{13}C NMR spectrometry, infrared spectroscopy, mass spectrometry and elemental analysis. The characteristic NCHN resonances in the ^{1}H and ^{13}C NMR spectra were present around 9 – 10 and 135 ppm, respectively, with the resonances of the benzimidazolium and 4,5-diphenylimidazolium salts shifted more downfield. Interestingly, the mass spectra of benzyl and *tert*-butyl substituted imidazolium salts showed a defragmentation pattern consistent with partial loss of these substituents.

A.3 Conclusion

In conclusion, three methods for the synthesis of (di)imidazolium salts are discussed and evaluated. Microwave-assisted synthesis of a number of salts was shown to be a fast method; however, the products obtained are often not pure. The

most efficient synthetic route is heating the reagents in 1,4-dioxane at elevated temperatures, leading to high yields and pure products. In total, nineteen novel imidazolium salts were synthesized and characterized.

A.4 Experimental Section

General Procedures. All quaternization reactions were performed under an atmosphere of dry argon, using standard Schlenk techniques, except for the microwave-assisted syntheses, which were performed in a closed pressure tube, which was loaded in air. THF and 1,4-dioxane were distilled from CaH_2 and stored on molecular sieves under argon. The compounds 1-(bromomethyl)-2,4,6-trimethylbenzene,[13] **1b**,[14] **1c**,[15] **1f**,[15] **1g**,[16] **1h**,[17] **3b**,[18] 1,3-di-O-tosylpropane,[19] 1,2-di-O-tosylethane,[20] and 1,2-di-O-mesylethane[21] were prepared according to literature procedures. Compounds **1e**[22] and **1j**[23] are known compounds, but were prepared following different synthetic routes. NMR data of these compounds, however, match those reported in literature. Other chemicals were obtained commercially and used as received. Microwave-assisted syntheses were performed on an Emrys Optimizer laboratory microwave. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX300 spectrometer. Chemical shifts are reported as referenced against the residual solvent signals and quoted in ppm relative to tetramethylsilane (TMS). IR spectra were recorded with a Perkin-Elmer FT-IR Paragon 1000 spectrophotometer equipped with a golden-gate ATR device, using the reflectance technique (4000-300 cm^{-1}; resolution 4 cm^{-1}). Electrospray mass spectra were recorded on a Finnigan TSQ-quantum instrument using an electrospray ionization technique (ESI-MS), using a water/acetonitrile or water/methanol mixture as solvent. C,H,N,S elemental analyses were carried out with a Perkin-Elmer series II CHNS/O analyzer 2400.

1-(2,4,6-trimethylbenzyl)imidazole (1e). To a solution of imidazole (1.36 g, 20 mmol) in 40 mL DMSO was added powdered potassium hydroxide (1.68 g, 30 mmol) and the mixture was stirred at room temperature for 45 min. Then 1-(bromomethyl)-2,4,6-trimethylbenzene (4.24 g, 20 mmol) was added and the solution was stirred vigorously for 3 h, while cooling with a water bath at room temperature. The resulting solution was diluted with 350 mL water and extracted six times with 50 mL chloroform. The combined extracts were washed with water, dried with magnesium sulfate and the solvent was evaporated. The remaining oil was vacuum distilled at 170 °C to yield the product as a pale yellow oil. Yield: 3.40 g (84%). ^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ 7.48 (s, 1H, NCHN), 6.89 (s, 2H, Ar-H), 6.86 (s, 1H, NCH), 6.83 (s, 1H, NCH), 5.14 (s, 2H, NCH_2), 2.22 (s, 3H, CH_3), 2.21 (s, 6H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ 137.3 (2 × C_q), 136.9 (NCHN), 129.5 (C_q), 129.1 (C_{Ar}), 128.3 (NCH), 118.8 (NCH), 43.9 (NCH_2), 20.5 (CH_3), 19.2 (CH_3). IR (neat): 2918 (w), 1613 (w), 1507 (m), 1464 (m), 1225 (m), 1108 (m), 1073 (s), 1024 (s), 906 (m), 853 (m), 733 (m), 686 (s), 662 (s), 617 (m) cm^{-1}.

1,3-bis(1-imidazolyl)propane (1j). To a solution of imidazole (5.72 g, 84 mmol) and 1,3-dibromopropane (4.25 mL, 42 mmol) in 60 mL acetonitrile was added 30 mL 25% aqueous sodium hydroxide solution and the mixture was vigorously stirred for 3 days. After evaporation of all solvents, the remaining solids were extracted into chloroform, dried with magnesium sulfate, and filtered. Evaporation of the solvent yielded the product as a pale yellow oil. Yield: 4.23 g (57%). ^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ 7.45 (s, 2H, NCHN), 7.10

(s, 2H, NCH), 6.89 (s, 2H, NCH), 3.91 (t, 4H, *J* = 7 Hz, NCH_2), 2.29 (pent, 2H, *J* = 7 Hz, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 300 K): δ 137.0 (NCHN), 130.2 (NCH), 118.5 (NCH), 43.3 (NCH_2), 31.9 (CH_2).

General synthesis of diimidazolium salts by conventional heating in THF (method A). A solution of alkyl dihalide, alkyl ditosylate, or alkyl dimesylate and 2.0 – 2.5 equivalents of N-substituted imidazole or N-substituted imidazole derivative in dry THF was stirred and refluxed using an oil bath under an argon atmosphere for 2-3 days. The resulting white to off-white precipitate was isolated by filtration, washed with THF and diethyl ether and dried *in vacuo*. In the case that the reaction resulted in a two-phase mixture, the two layers were separated. The product layer was washed with THF and diethyl ether and the product crystallized upon drying *in vacuo*.

General microwave-assisted synthesis of diimidazolium salts (method B). To a 5 mL pressure tube were added N-substituted imidazole, 1,2-dibromoethane, 1.5 mL toluene and a stir bar. The tube was capped and heated with stirring in the microwave cavity, while keeping the solution at a preset temperature. After cooling, the cap was removed and the off-white to yellow solid product was isolated by filtration and washed with toluene. The product was recrystallized from methanol/diethyl ether and obtained as off-white to white solids.

General synthesis of diimidazolium salts by conventional heating in 1,4-dioxane (method C). As method A, using dry 1,4-dioxane as solvent for the reaction and stirring at 100 °C for 16 h. The product was washed with THF and diethyl ether.

1,1′-tert-butyl-3,3′-(1,1-methylene)diimidazolium dibromide ([4c]Br_2). Following method C, the compound was obtained as a white solid from **1c** (3.97 g, 32.0 mmol) and dibromomethane (2.61 g, 15.0 mmol) in 30 mL 1,4-dioxane. Yield: 2.65 g (42%). NMR spectra are identical to those reported.[5]

1,1′-dibenzyl-3,3′-(1,1-methylene)diimidazolium dibromide ([4d]Br_2). Following method C, the compound was obtained as a white solid from **1d** (5.06 g, 32.0 mmol) and dibromomethane (2.61 g, 15.0 mmol) in 30 mL 1,4-dioxane. Yield: 2.50 g (30%). NMR spectra are identical to those reported.[10]

1,1′-dimethyl-3,3′-(1,2-ethanediyl)diimidazolium ditosylate ([5a][OTos]$_2$). Method B: **1a** (0.36 g, 4.4 mmol) and 1,2-di-O-tosylethane (0.74 g, 2.0 mmol) in 1.5 mL toluene at 125 °C for 250 sec. The compound was further purified by recrystallization from methanol/diethyl ether. Yield: 0.95 g (86%). Method C: **1a** (0.41 g, 5.0 mmol) and 1,2-di-O-tosylethane (0.74 g, 2.0 mmol) in 15 mL 1,4-dioxane. Yield: 1.02 g (95%). ^1H NMR (300 MHz, DMSO-d_6, 300 K): δ 9.01 (s, 2H, NCHN), 7.69 (s, 2H, NCH), 7.58 (s, 2H, NCH), 7.48 (d, 4H, *J* = 8 Hz, Ar-H), 7.09 (d, 4H, *J* = 8 Hz, Ar-H), 4.66 (s, 4H, NCH_2), 3.81 (s, 6H, NCH_3), 2.27 (s, 6H, $ArCH_3$). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ 137.7 (C_q), 137.2 (NCHN), 128.1 (C_{Ar}), 125.5 (C_{Ar}), 123.9 (NCH), 122.4 (NCH), 48.4 (NCH_2), 35.9 (NCH_3), 20.8 (CH_3). IR (neat): 3088 (m), 1559 (m), 1188 (s), 1163 (s), 1121 (s), 1030 (s), 1008 (s), 819 (s), 747 (m), 680 (s), 619 (s), 554 (s) cm^{-1}. ESI-MS: *m*/*z* 191 ($[M - 2\ OTos - H]^+$), 363 ($[M - OTos]^+$, 100%). Anal. Calcd for $C_{24}H_{30}N_4O_6S_2$: C, 53.92; H, 5.66; N, 10.48; S, 11.99. Found: C, 54.02; H, 5.65; N, 10.39; S, 11.86.

1,1′-diisopropyl-3,3′-(1,2-ethanediyl)diimidazolium dibromide ([5b]Br_2). Following method A, the compound was isolated as an off-white solid from **1b** (2.42 g, 22.0 mmol) and

1,2-dibromoethane (1.97 g, 10.5 mmol) in 30 mL THF. Yield: 3.30 g (75%). NMR spectra are identical to those reported.[5]

1,1′-di-tert-butyl-3,3′-(1,2-ethanediyl)diimidazolium dibromide ([5c]Br$_2$). Method A: **1c** (2.60 g, 20.9 mmol) and 1,2-dibromoethane (1.95 g, 10.4 mmol) in 25 mL THF yielded a mixture of the mono- and dicondensate, according to the NMR spectra. Method B: **1c** (0.55 g, 4.4 mmol) and 1,2-dibromoethane (0.38 g, 2.0 mmol) in 1.5 mL toluene, 250 s at 130 °C. Yield: 0.35 g (35%). Method C: **1c** (5.50 g, 44.3 mmol) and 1,2-dibromoethane (4.13 g, 22.0 mmol) in 45 mL 1,4-dioxane. Yield: 7.49 g (78%). NMR spectra are identical to those reported.[5]

1,1′-dibenzyl-3,3′-(1,3-ethanediyl)diimidazolium dibromide ([5d]Br$_2$). Method A: **1d** (8.22 g, 52.0 mmol) and 1,2-dibromoethane (4.70 g, 25.0 mmol) in 40 mL THF. Yield: 8.20 g (65%). Method B: **1d** (0.70 g, 4.4 mmol), and 1,2-dibromoethane (0.38g, 2.0 mmol) in 1.5 mL toluene, 250 s at 125 °C. Yield: 0.44 g (43%). NMR spectra are identical to those reported.[10]

1,1′-dibenzyl-3,3′-(1,2-ethanediyl)diimidazolium ditosylate ([5d][OTos]$_2$). Following method A, the product was obtained as a white solid from **1d** (1.27 g, 8.0 mmol) and 1,2-di-O-tosylethane (1.48 g, 4.0 mmol) in 12 mL dry THF. Yield: 2.60 g (95%). ^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ 9.20 (s, 2H, NCHN), 7.79 (s, 2H, NCH), 7.65 (s, 2H, NCH), 7.48 (d, 4H, J = 8 Hz, Ar-H), 7.38 (m, 10H, Ar-H), 7.10 (d, 4H, J = 8 Hz, Ar-H), 5.37 (s, 4H, NCH$_2$), 4.70 (s, 4H, NCH$_2$), 2.27 (s, 6H, ArCH$_3$). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ 145.5 (C$_q$), 137.8 (C$_q$), 136.9 (NCHN), 134.6 (C$_q$), 129.0 (C$_{Ar}$), 128.8 (C$_{Ar}$), 128.3 (C$_{Ar}$), 128.1 (C$_{Ar}$), 125.5 (C$_{Ar}$), 122.9 (2 × NCH), 52.1 (NCH$_2$), 48.5 (NCH$_2$), 20.8 (CH$_3$). IR (neat): 3090 (m), 1567 (w), 1453 (w), 1219 (s), 1183 (s), 1121 (s), 1035 (m), 1011 (m), 813 (s), 684 (s), 562 (s) cm^{-1}. ESI-MS: m/z 253 ([M – 2 OTos – Bn]$^+$), 342 ([M – 2 OTos – H]$^+$), 515 ([M – OTos]$^+$), 100%). Anal. Calcd for $C_{36}H_{38}N_4O_6S_2$: C, 62.95; H, 5.58; N, 8.16; S, 9.34. Found: C, 62.82; H, 5.56; N, 8.19; S, 9.17.

1,1′-dibenzyl-3,3′-(1,2-ethanediyl)diimidazolium dimesylate ([5d][OMs]$_2$). Method A: **1d** (1.27 g, 8.0 mmol) and 1,2-di-O-mesylethane (0.87 g, 4.0 mmol) in 12 mL dry THF. Yield: 1.60 g (75%). Method B: **1d** (0.70 g, 4.4 mmol) and 1,2-di-O-mesylethane (0.44g, 2.0 mmol) in 1.5 mL toluene, 250 s at 150 °C. Yield: mixture of mono- and dicondensates. Analytical sample obtained from method A: ^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ 9.21 (s, 2H, NCHN), 7.80 (s, 2H, NCH), 7.65 (s, 2H, NCH), 7.40 (m, 10H, Ar-H), 5.39 (NCH$_2$), 4.69 (NCH$_2$), 2.20 (s, 6H, CH$_3$). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ 137.0 (NCHN), 134.6 (C$_q$), 129.0 (C$_{Ar}$), 128.8 (C$_{Ar}$), 128.3 (C$_{Ar}$), 123.2 (NCH), 122.9 (NCH), 52.0 (NCH$_2$), 48.4 (NCH$_2$), 39.3 (SCH$_3$). IR (neat): 3090 (m), 3034 (m), 1558 (m), 1456 (w), 1337 (w), 1557 (s), 1040 (s), 774 (s), 715 (s), 639 (m), 551 (s), 521 (s) cm^{-1}. ESI-MS: m/z 253 ([M – 2 OMs – Bn]$^+$), 343 ([M – 2 OMs – H]$^+$), 439 ([M – OMs]$^+$, 100%). Anal. Calcd for $C_{24}H_{30}N_4O_6S_2 \cdot H_2O$: C, 52.16; H, 5.84; N, 10.14. Found: C, 52.23; H, 5.71; N, 9.98.

1,1′-(1,2-ethanediyl)-3,3′-(2,4,6-trimethylbenzyl)diimidazolium dibromide ([5e]Br$_2$). Method B: **1e** (0.88 g, 4.4 mmol) and 1,2-dibromoethane (0.38 g, 2.0 mmol) in 1.5 mL toluene at 130 °C for 400 s. Yield: 0.32 g (27%). Method C: **1e** (2.0 g, 10.0 mmol) and 1,2-dibromoethane (0.84 g, 4.5 mmol) in 15 mL dry 1,4-dioxane. Yield: 1.75 g (66%). ^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ 8.81 (s, 2H, NCHN), 7.63 (2 × s, 4H, NCH), 6.96 (s, 4H, Ar-H), 5.33 (s, 4H, NCH$_2$), 4.64 (s, 4H, NCH$_2$), 2.24 (s, 6H, CH$_3$), 2.19 (s, 12H, CH$_3$). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ 142.0 (NCHN), 138.6 (C$_q$), 138.1 (C$_q$), 129.4 (C$_{Ar}$), 126.5 (C$_q$), 122.7 (NCH), 48.3 (NCH$_2$), 47.1 (NCH$_2$), 20.6 (CH$_3$), 19.3 (CH$_3$). IR (neat): 3059 (m), 1612 (w), 1559 (m), 1447 (w), 1337 (w), 1156 (s), 850 (m), 758 (m), 634 (s) cm^{-1}. ESI-MS: m/z 295 ([M + 2H]$^{2+}$,

100%), 427 ([M – 2Br – H]$^+$), 509 ([M – Br]$^+$). Anal. Calcd for $C_{28}H_{36}Br_2N_4 \cdot 0.9H_2O$: C, 55.62; H, 6.30; N, 9.27. Found: C, 55.63; H, 6.29; N, 9.36.

1,1′-dimesityl-3,3′-(1,2-ethanediyl)diimidazolium dibromide ([5f]Br$_2$). Method A: **1f** (4.10 g, 22.0 mmol) and 1,2-dibromoethane (1.88 g, 10.0 mmol) in 30 mL THF. Yield: 2.20 g (39%). Method B: **1f** (0.82 g, 4.4 mmol) and 1,2-dibromoethane (0.38 g, 2.0 mmol) in 1.5 mL toluene, 600 s at 130 °C, followed by 300 s at 145 °C. Yield 0.24 g (21%). Method C: **1f** (3.17 g, 17.0 mmol) and 1,2-dibromoethane (1.41 g, 7.5 mmol) in 20 mL 1,4-dioxane. Yield: 2.95 g (70%). NMR spectra are identical to those reported.[10]

1,1′-(1,2-ethanediyl)-3,3′-ditrityldiimidazolium dibromide ([5g]Br2). Following method C, from **1g** (3.41 g, 11.0 mmol) and 1,2-dibromoethane (0.94 g, 5.0 mmol) in 20 mL 1,4-dioxane a mixture of mono- and dicondensate was obtained, which could not be separated.

1,1′-(1,2-ethanediyl)-3,3′-(2-methoxyphenyl)diimidazolium dibromide ([5h]Br$_2$). Following method A, **1h** (1.74 g, 10.0 mmol) and 1,2-dibromoethane (0.94 g, 5.0 mmol) in 20 mL dry THF yielded the product as an off-white solid, which was recrystallized from methanol/diethyl ether and dried *in vacuo*. Yield: 1.14 g (42%). ^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ 9.67 (s, 2H, NCHN), 8.14 (s, 2H, NCH). 7.96 (s, 2H, NCH), 7.61 (m, 4H, Ar-H), 7.36 (d, 2H, J = 8 Hz, Ar-H), 7.16 (t, 2H, 8 Hz, Ar-H), 4.94 (s, 4H, NCH_2), 3.81 (s, 6H, OCH_3). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ 152.0 (C_q), 137.8 (NHCN), 131.8 (C_{Ar}), 126.0 (C_{Ar}), 123.9 (NCH), 123.2 (C_q), 122.4 (NCH), 121.0 (C_{Ar}), 113.3 (C_{Ar}), 56.4 (OCH_3), 48.6 (NCH_2). IR (neat): 3055 (m), 1604 (w), 1557 (s), 1502 (s), 1446 (m), 1254 (s), 1206 (m), 1129 (m), 1067 (m), 1022 (m), 868 (w), 757 (s), 634 (s) cm^{-1}. ESI-MS: m/z 188 ([M – 2Br]$^{2+}$, 100%), 375 ([M – 2Br – H]$^+$). Anal. Calcd for $C_{22}H_{24}Br_2N_4O_2$: C, 49.27, H, 4.51; N, 10.45. Found: C, 49.42; H, 4.42; N, 10.35.

1,1-dimethyl-3,3′-(1,3-propanediyl)diimidazolium ditosylate ([6a][OTos]$_2$). Following method A, the product was obtained as a hygroscopic white solid from **1a** (0.66 g, 8.0 mmol) and 1,3-di-O-tosylpropane (1.54 g, 4.0 mmol) in 12 mL dry THF. Yield: 2.05 g (93%). ^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ 9.11 (s, 2H, NCHN), 7.74 (s, 2H, NCH), 7.71 (s, 2H, NCH), 7.47 (d, 4H, J = 8 Hz, Ar-H), 7.10 (d, 4H, J = 8 Hz, Ar-H), 4.20 (t, 4H, J = 7 Hz, NCH_2), 3.82 (s, NCH_3), 2.36 (pent, 2H, J = 7 Hz, CH_2), 2.27 (s, 6H, $ArCH_3$). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ 145.5 (C_q), 137.8 (C_q), 136.9 (NCHN), 128.0 (C_{Ar}), 125.4 (C_{Ar}), 123.7 (NCH), 122.1 (NCH), 45.7 (NCH_2), 35.7 (NCH_3), 29.4 (CH_2), 20.7 ($ArCH_3$). IR (neat): 3094 (w), 1575 (w), 1191 (s), 1118 (s), 1029 (s), 1008 (s), 812 (m), 678 (s), 617 (m), 559 (s) cm^{-1}. ESI-MS: m/z 205 ([M – 2 OTos – H]$^+$), 377 ([M – OTos]$^+$, 100%). Anal. Calcd for $C_{25}H_{32}N_4O_6S_2 \cdot 0.5H_2O$: C, 53.84; H, 5.96; N, 10.05; S, 11.50. Found: C, 53.39; H, 6.28; N, 10.03; S, 11.30.

1,1′-dibenzyl-3,3′-(1,3-propanediyl)diimidazolium dibromide ([6d]Br$_2$). Following method C, a reaction between **5d** (0.95 g, 6.0 mmol) and 1,3-dibromopropane (0.50 g, 2.5 mmol) in 10 mL 1,4-dioxane yielded the compound as a white solid. Yield: 0.78 g (60%). ^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ 9.49 (s, 2H, NCHN), 7.87 (t, 2H, J = 2 Hz, NCH), 7.82 (t, 2H, J = 2 Hz, NCH), 7.43 (m, 10H, Ar-H), 5.45 (s, 4H, NCH_2Ph), 4.28 (t, 4H, J = 7 Hz, NCH_2), 2.43 (pent, 2H, J = 7 Hz, CH_2). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ 136.4 (NCHN), 134.7 (C_q), 129.0 (C_{Ar}), 128.8 (C_{Ar}), 128.4 (C_{Ar}), 122.8 (NCH), 122.6 (NCH), 51.9 (NCH_2), 46.0 (NCH_2), 29.3 (CH_2). IR (neat): 3068 (w), 2969 (m), 1549 (m), 1447 (m), 1213 (w), 1180 (m), 1149 (s), 846 (m), 748 (m), 718 (s), 702 (s), 636 (s) cm^{-1}. ESI-MS: m/z 267 ([M – 2 Br – Bn]$^+$, 100%), 357 ([M – 2 Br – H]$^+$), 437 ([M – Br]$^+$). Anal. Calcd for $C_{23}H_{26}Br_2N_4$: C, 53.30; H, 5.06; N, 10.81. Found: C, 53.09; H, 5.07; N, 10.80.

1,1-dibenzyl-3,3′-(1,3-propanediyl)diimidazolium ditosylate ([6d][OTos]$_2$). Following method A the product was obtained as a white solid from **5d** (1.27 g, 8.0 mmol) and 1,3-di-O-tosylpropane (1.54 g, 4.0 mmol) in 15 mL dry THF. Yield: 2.61 g (93%). ^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ 9.31 (s, 2H, NCHN), 7.78 (2 × s, 4H, NCH), 7.48 (d, 4H, J = 8 Hz, Ar-H), 7.42 (m, 10H, Ar-H), 7.10 (d, 4H, J = 8 Hz, Ar-H), 5.40 (NCH_2Ar), 4.23 (t, 4H, J = 7 Hz, NCH_2), 2.39 (t, 2H, J = 7 Hz, CH_2), 2.27 (s, 6H, $ArCH_3$). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ 145.5 (C_q), 137.8 (C_q), 136.5 (NCHN), 134.7 (C_q), 129.0 (C_{Ar}), 128.8 (C_{Ar}), 128.4 (C_{Ar}), 128.2 (C_{Ar}), 125.5 (C_{Ar}), 122.8 (NCH), 122.6 (NCH), 51.9 (NCH_2), 46.1 (NCH_2), 29.4 (CH_2), 20.8 (CH_3). IR (neat): 3096 (m), 1567 (m), 1455 (m), 1192 (s), 1120 (s), 1033 (s), 1011 (s), 875 (w), 810 (m), 679 (s), 561 (s) cm^{-1}. ESI-MS: m/z 267 ([M – 2 OTos – Bn]$^+$), 357 ([M – 2 OTos – H]$^+$), 529 ([M – OTos]$^+$, 100%). Anal. Calcd for $C_{37}H_{40}N_4O_6S_2$: C, 63.41; H, 5.75; N, 7.99. Found: C, 63.01; H, 5.61; N, 8.01.

1,1′-(3-nitro-6-hydroxyphenylmethyl)-3,3′-(1,3-propanediyl)diimidazolium dibromide ([6k]Br$_2$). To a solution of α-bromo-4-nitro-o-cresol (2.78 g, 12.0 mmol) in 15 mL dry 1,4-dioxane and 5 mL acetonitrile was added **1j** (0.88 g, 5.0 mmol) and the mixture was stirred 3 days at 100 °C. The resulting two layers were separated and the product layer was washed with THF and dissolved in methanol. Addition of diethyl ether yielded again a two-phase system. After separation, the product layer slowly crystallized *in vacuo* and the product was isolated as a pale yellow solid. Yield: 2.75 g (86%). ^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ 11.7 (s, 2H, OH), 9.31 (s, 2H, NCHN), 8.40 (d, 2H, J = 3 Hz, Ar-H), 8.18 (dd, 2H, J = 9 Hz, J = 3 Hz, Ar-H), 7.81 (s, 4H, NCH), 7.11 (d, 2H, J = 9 Hz, Ar-H), 5.42 (s, 4H, NCH_2), 4.24 (t, 4H, J = 7 Hz, NCH_2), 2.37 (m, 2H, CH_2). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ 163.5 (C_q), 143.0 (NCHN), 140.7 (C_q), 128.5 (C_{Ar}), 128.2 (C_{Ar}), 124.1 (NCH), 123.7 (NCH), 122.8 (C_q), 117.2 (C_{Ar}), 48.7 (NCH_2), 47.2 (NCH_2), 30.8 (CH_2). IR (neat): 3030 (m), 1594 (m), 1557 (m), 1520 (m), 1495 (m), 1435 (m), 1336 (s), 1281 (s), 1151 (m), 1088 (s), 932 (m), 747 (m), 639 (m) cm^{-1}. ESI-MS: m/z 328 ([M – 2Br – $O_2NC_7H_5OH$]$^+$, 100%), 479 ([M – 2Br – H]$^+$), 561 ([M – Br]$^+$). Anal. Calcd for $C_{23}H_{24}Br_2N_6O_6 \cdot 1.7CH_3OH$: C, 42.70; H, 4.47; N, 12.10. Found: C, 42.44; H, 4.35; N, 12.31.

1,1′-dimethyl-3,3′-(1,2-ethanediyl)dibenzimidazolium dibromide ([7a]Br$_2$). Method A: **2a** (4.22 g, 32.0 mmol) and 1,2-dibromoethane (2.81 g, 15.0 mmol) in 35 mL THF yielded 2.0 g of a mixture of mono- and dicondensates. Method B: **2a** (0.58 g, 4.4 mmol) and 1,2-dibromoethane (0.38 g, 2.0 mmol) in 1.5 mL toluene, 250 s at 150 °C. Yield: 0.33 g (37%). Method C: **2a** (4.22 g, 32.0 mmol) and 1,2-dibromoethane (2.81 g, 15.0 mmol) in 35 mL 1,4-dioxane. Yield: 3.70 g (55%). NMR spectra are identical to those reported.[5]

1,1′-dimethyl-3,3′-(1,3-propanediyl)dibenzimidazolium ditosylate ([8a][OTos]$_2$). Following method C, the product was isolated as a white, hygroscopic solid from **2a** (1.59 g, 12.0 mmol) and 1,3-di-O-tosylpropane (1.92g, 5.0 mmol) in 10 mL 1,4-dioxane. Yield: 2.94 g (94%). ^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ 9.71 (s, 2H, NCHN), 8.03 (m, 4H, Ar-H), 7.69 (m, 4H, Ar-H), 7.45 (d, 4H, J = 8 Hz, Ar-H), 7.09 (d, 4H, J = 8 Hz, Ar-H), 4.65 (t, 4H, J = 7Hz, NCH_2), 4.05 (s, 6H, NCH_3), 2.57 (pent, 2H, J = 7 Hz, CH_2), 2.26 (s, 6H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ 146.8 (C_q), 144.3 (NCHN), 139.0 (C_q), 133.0 (C_q), 132.1 (C_q), 129.3 (C_{Ar}), 127.7 (2 × C_{Ar}), 126.7 (C_{Ar}), 114.8 (C_{Ar}), 144.7 (C_{Ar}), 45.0 (NCH_2), 34.5 (NCH_3), 29.4 (CH_2), 22.0 (CH_3). IR (neat): 3054 (w), 1570 (m), 1463 (w), 1429 (w), 1183 (s), 1121 (s), 1031 (s), 1009 (s), 811 (m), 762 (s), 681 (s), 559 (s) cm^{-1}. ESI-MS: m/z 153 ([M – 2 OTos]$^{2+}$, 100%), 305 ([M – 2 OTos – H]$^+$), 477 ([M – OTos]$^+$). Anal. Calcd for $C_{31}H_{36}N_4O_6S_2 \cdot 0.25C_6H_5CH_3$: C, 60.72; H, 5.91; N, 8.65; S, 9.90. Found: C, 60.86; H, 5.61; N, 8.59; S, 9.45.

1,1′-diisopropyl-3,3′-(1,2-ethanediyl)bis-4,5-diphenylimidazolium dibromide ([9b]Br$_2$). The product was obtained as a white solid from a mixture of **3b** (2.10 g, 8.0 mmol) and 1,2-dibromoethane (0.75 g, 4.0 mmol) in 20 mL 1,4-dioxane following method C. Yield: 1.50 g (53%). ^{1}H NMR (300 MHz, DMSO-*d*$_6$, 300 K): δ 10.18 (s, 2H, NCHN), 7.48 (m, 8H, Ar-H), 7.41 (m, 8H, Ar-H), 7.07 (m, 4H, Ar-H), 4.54 (s, 4H, NCH$_2$), 4.41 (sept, 2H, *J* = 7 Hz, NCH), 1.46 (d, 12H, *J* = 7 Hz, CH$_3$). ^{13}C NMR (75 MHz, DMSO-*d*$_6$, 300 K): δ 135.0 (NCHN), 131.1 (C$_q$), 131.0 (C$_q$), 130.7 (2 × C$_{Ar}$), 130.4 (C$_{Ar}$), 130.2 (C$_{Ar}$), 129.1 (C$_{Ar}$), 129.0 (C$_{Ar}$), 124.9 (C$_q$), 124.1 (C$_q$), 50.9 (NCH), 46.4 (NCH$_2$), 22.4 (CH$_3$). IR (neat): 2930 (w), 2882 (w), 1557 (m), 1443 (w), 1357 (w), 1210 (m), 1110 (w), 1022 (w), 771 (m), 701 (s), 667 (m) cm^{-1}. ESI-MS: *m*/*z* 276 ([M – 2Br]$^{2+}$, 100%), 551 ([M – 2Br – H]$^+$), 633 ([M – Br]$^+$). Anal. Calcd for C$_{38}$H$_{40}$Br$_2$N$_4$: C, 64.05; H, 5.66; N, 7.86. Found: C, 64.34; H, 5.79; N, 7.92.

1-(2-bromoethyl)-3-tert-butylimidazolium bromide ([10c]Br). A mixture of **1c** (2.48 g, 20.0 mmol) and 1,2-dibromoethane (8.66 mL, 100 mmol) in 40 mL dry THF was stirred 3 days at 40 °C. The resulting colorless oil was isolated after decantation, washing with THF and diethyl ether and drying *in vacuo*. Yield: 5.40 g (86%). ^{1}H NMR (300 MHz, DMSO-*d*$_6$, 300 K): δ 9.45 (s, 1H, NCHN), 8.08 (s, 1H, NCH), 7.91 (s, 1H, NCH), 4.59 (t, 2H, *J* = 6 Hz, CH$_2$), 3.98 (t, 2H, *J* = 6 Hz, CH$_2$), 1.58 (s, 9H, CH$_3$). ^{13}C NMR (75 MHz, DMSO-*d*$_6$, 300 K): δ 135.0 (NCHN), 122.7 (NCH), 120.2 (NCH), 59.6 (C$_q$), 50.0 (CH$_2$), 31.2 (CH$_2$), 29.0 (CH$_3$). IR (neat): 3028 (m), 1560 (s), 1382 (s), 1293 (m), 1203 (s), 1134 (s), 870 (w), 700 (s), 658 (s), 628 (s), 583 (m) cm^{-1}. ESI-MS: *m*/*z* 175 ([M – Br – ^{t}Bu]$^+$), 231 ([M – Br]$^+$, 100%).

1-(2-methoxyphenyl)-3-methylimidazolium iodide ([11h]I). A solution of **1h** (1.74 g, 10.0 mmol) and methyl iodide (1.56 g, 11.0 mmol) in 15 mL dry THF was stirred for 16 h at room temperature. The resulting pale yellow suspension was filtered, washed with THF and dried *in vacuo* to yield a white solid. Yield: 2.65 g (84%). ^{1}H NMR (300 MHz, DMSO-*d*$_6$, 300 K): δ 9.49 (s, 1H, NCHN), 8.03 (s, 1H, NCH), 7.90 (s, 1H, NCH), 7.59 (m, 2H, Ar-H), 7.35 (d, 1H, *J* = 8 Hz, Ar-H), 7.17 (t, 1H, *J* = 8 Hz, Ar-H), 3.95 (s, 3H, CH$_3$), 3.87 (s, 3H, CH$_3$). ^{13}C NMR (75 MHz, DMSO-*d*$_6$, 300 K): δ 152.1 (C$_q$), 137.6 (NCHN), 131.6 (C$_{Ar}$), 126.2 (C$_{Ar}$), 123.6 (NCH), 123.4 (NCH), 123.3 (C$_q$), 121.1 (C$_{Ar}$), 113.2 (C$_{Ar}$), 56.4 (CH$_3$), 36.1 (CH$_3$). IR (neat): 2973 (m), 1576 (m), 1557 (m), 1500 (s), 1438 (m), 1339 (w), 1268 (s), 1159 (m), 1121 (m), 1016 (s), 880 (m), 768 (s), 748 (s), 694 (m), 651 (m), 620 (s) cm^{-1}. ESI-MS: *m*/*z* 189 ([M – I]$^+$, 100%). Anal. Calcd for C$_{11}$H$_{13}$IN$_2$O: C, 41.79; H, 4.14; N, 8.86. Found: C, 41.85; H, 4.16; N, 8.85.

1-tert-butyl-3-benzylimidazolium bromide ([12c]Br). Following method C, the product was obtained from **1c** (1.88 g, 15.1 mmol) and benzyl bromide (3.42 g, 20 mmol) in 20 mL dry 1,4-dioxane. Yield: 3.65 g (82%). ^{1}H NMR (300 MHz, DMSO-*d*$_6$, 300 K): δ 9.54 (s, 1H NCHN), 8.04 (s, 1H, NCH), 7.84 (s, 1H, NCH), 7.42 (m, 5H, Ar-H), 5.40 (s, 2H, NCH$_2$), 1.59 (s, 9H, CH$_3$). ^{13}C NMR (75 MHz, DMSO-*d*$_6$, 300 K): δ 134.9 (C$_q$), 134.6 (NCHN), 128.9 (C$_{Ar}$), 128.6 (C$_{Ar}$), 128.2 (C$_{Ar}$), 122.5 (NCH), 120.7 (NCH), 59.6 (C$_q$), 51.9 (NCH$_2$), 28.9 (CH$_3$). IR (neat): 3048 (m), 3012 (m), 1557 (m), 1451 (w), 1380 (m), 1201 (m), 1136 (m), 772 (m), 760 (s), 723 (s), 662 (s), 632 (m) cm^{-1}. ESI-MS: *m*/*z* 159 ([M – Br – ^{t}Bu + H]$^+$), 215 ([M – Br]$^+$, 100%). Anal. Calcd for C$_{14}$H$_{19}$BrN$_2$: C, 56.96; H, 6.49; N, 9.49. Found: C, 56.76; H, 6.44; N, 9.55.

1-benzyl-3-(2,4,6-trimethylbenzyl)imidazolium bromide ([12e]Br). The white product was prepared according to method A from **1e** (0.80 g, 4.0 mmol) and benzyl bromide (0.75 g, 4.4 mmol) in 10 mL dry THF. However, the reaction mixture was refluxed for only 16 h. Yield: 0.93 g (63%). ^{1}H NMR (300 MHz, DMSO-*d*$_6$, 300 K): δ 9.23 (s, 1H, NCHN), 7.84 (s, 1H, NCH), 7.58 (s, 1H, NCH), 7.40 (m, 5H, Ar-H), 6.95 (s, 2H, Ar-H), 5.39 (s, 2H, NCH$_2$), 5.36 (s, 2H,

NCH_2), 2.23 (s, 3H, CH_3), 2.22 (s, 6H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ 138.5 (C_q), 138.0 (C_q), 135.7 (NCHN), 135.0 (C_q), 129.4 (C_{Ar}), 128.9 (C_{Ar}), 128.6 (C_{Ar}), 128.1 (C_{Ar}), 126.8 (C_q), 122.7 (NCH), 122.6 (NCH), 51.8 (NCH_2), 47.0 (NCH_2), 20.6 (CH_3), 19.3 (CH_3). IR (neat): 3033 (w), 1558 (m), 1452 (m), 1158 (s), 1031 (w), 849 (w), 799 (w), 749 (s), 732 (s), 696 (m), 641 (s) cm^{-1}. ESI-MS: *m*/*z* 133 ($[M - Br - BnIm + H]^+$), 159 ($[BnIm + H]^+$), 291 ($[M - Br]^+$, 100%). Anal. Calcd for $C_{20}H_{23}BrN_2 \cdot 0.1H_2O$: C, 64.38; H, 6.27; N, 7.51. Found: C, 64.36; H, 6.52; N, 7.51.

1-(3-bromopropyl)-3-methylbenzimidazolium bromide ([13a]Br). A mixture of **2a** (1.32 g, 10.0 mmol) and 1,3-dibromopropane (12.1 g, 60.0 mmol) in 10 mL dry THF was stirred 2 days at 35 °C. The resulting white precipitate was isolated by filtration and washed with THF and diethyl ether. Yield: 1.0 g (33%). ^1H NMR (300 MHz, DMSO-d_6, 300 K): δ 9.78 (s, 1H, NCHN), 8.09 (m, 1H, Ar-H), 8.02 (m, 1H, Ar-H), 7.69 (m, 2H, Ar-H), 4.61 (t, 2H, *J* = 7 Hz, NCH_2), 4.06 (s, 3H, CH_3), 3.61 (t, 2H, *J* = 7 Hz, $BrCH_2$), 2.42 (m, 2H, CH_2). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ 143.0 (NCHN), 131.8 (C_q), 130.9 (C_q), 126.6 (C_{Ar}), 126.5 (C_{Ar}), 113.6 (C_{Ar}), 113.4 (C_{Ar}), 45.1 (CH_2), 33.3 (CH_3), 31.5 (CH_2), 30.7 (CH_2). IR (neat): 3001 (w), 1570 (m), 1464 (w), 1426 (w), 1258 (m), 1225 (m), 1124 (w), 823 (w), 760 (s), 591 (s), 554 (s) cm^{-1}. ESI-MS: *m*/*z* 253 ($[M - Br]^+$, 100%). Anal. Calcd for $C_{11}H_{14}Br_2N_2$: C, 39.55; H, 4.22; N, 8.39. Found: C, 39.89; H, 4.27; N, 8.54.

1-benzyl-3-methylbenzimidazolium bromide ([14a]Br). The compound was obtained as a white solid following method A, starting from **2a** (1.32 g, 10.0 mmol) and benzylbromide (1.88 g, 11.0 mmol) in 20 mL THF. Yield: 2.95 g (97%). NMR spectra are identical to those reported.[12]

1-benzyl-3-isopropyl-4,5-diphenylimidazolium bromide ([15b]Br). The product was obtained following method C from **3b** (0.26 g, 1.0 mmol) and benzyl bromide (0.51 g, 3.0 mmol) in 10 mL dry 1,4-dioxane. In this case, however, the product was precipitated from the reaction mixture by the addition of diethyl ether and filtered to yield an off-white solid. Yield: 0.41 g (95%). ^1H NMR (300 MHz, DMSO-d_6, 300 K): δ 9.98 (s, 1H, NCHN), 7.46 (m, 5H, Ar-H), 7.40 – 7.20 (m, 8H, Ar-H), 7.02 (m, 2H, Ar-H), 5.40 (s, 2H, CH_2), 4.41 (sept, 1H, *J* = 7 Hz, NCH), 1.48 (d, 6H, *J* = 7 Hz, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ 134.6 (NCHN), 134.2 (C_q), 131.5 (C_q), 131.3 (C_q), 131.0 (C_{Ar}), 130.7 (C_{Ar}), 130.2 (C_{Ar}), 130.0 (C_{Ar}), 129.0 (C_{Ar}), 128.7 (2 × C_{Ar}), 128.3 (C_{Ar}), 127.6 (C_{Ar}), 125.3 (C_q), 125.0 (C_q), 50.7 (NCH), 50.4 (NCH_2), 22.4 (CH_3). IR (neat): 2927 (m), 2850 (m), 1554 (m), 1446 (m), 1248 (m), 1210 (m), 1116 (s), 889 (w), 871 (s), 774 (s), 700 (s), 612 (m) cm^{-1}. ESI-MS: *m*/*z* 353 ($[M - Br]^+$, 100%). Anal. Calcd for $C_{25}H_{25}BrN_2$: C, 69.29; H, 5.81; N, 6.46. Found: C, 69.05; H, 6.01; N, 6.46.

1-(1-(3-methylbenzimidazolium))-3-(1-(3-methylimidazolium))propanediyl dibromide ([16]Br_2). A suspension of **[13a]Br** (1.0 g, 3.0 mmol) and **1a** (0.41 g, 5.0 mmol) in 15 mL 1,4-dioxane was stirred for 3 days at 100 °C. The resulting white precipitate was isolated by filtration, washed with 1,4-dioxane and diethyl ether, recrystallized from methanol/diethylether and dried *in vacuo*. Yield: 0.72 g (58%). ^1H NMR (300 MHz, DMSO-d_6, 300 K): δ 9.92 (s, 1H, NCHN), 9.26 (s, 1H, NCHN), 8.12 (m, 1H, Ar-H), 8.05 (m, 1H, Ar-H), 7.83 (s, 1H, NCH), 7.71 (m, 2H, Ar-H), 7.69 (s, 1H, NCH), 4.59 (t, 2H, *J* = 7 Hz, NCH_2), 4.36 (t, 2H, *J* = 7 Hz, NCH_2), 4.10 (s, 3H, NCH_3), 3.84 (s, 3H, NCH_3), 2.55 (m, 2H, CH_2). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ 142.9 (NCHN), 136.8 (NCHN), 131.8 (C_q), 130.8 (C_q), 126.5 (2 × C_{Ar}), 123.7 (NCH), 122.2 (NCH), 113.6 (2 × C_{Ar}), 45.8 (NCH_2), 43.6 (NCH_2), 35.8 (CH_3), 33.3 (CH_3), 28.8 (CH_2). IR (neat): 2954 (m), 1573 (m), 1463 (w), 1423 (w), 1162 (m), 1027 (w), 808 (m), 760

(s), 618 (s) cm^{-1}. ESI-MS: *m*/*z* 128 ($[M - 2Br]^{2+}$, 100%), 255 ($[M - 2Br - H]^{+}$). Anal. Calcd for $C_{15}H_{20}Br_2N_4 \cdot 0.5CH_3OH$: C, 43.08; H, 5.13; N, 12.96. Found: C, 43.08; H, 5.44; N, 13.25.

1-benzyl-1′-tert-butyl-3,3′-(1,2-ethanediyl)diimidazolium dibromide ([17]Br$_2$). To a suspension of **[10c]Br** (1.56 g, 5.0 mmol) in 25 mL 1,4-dioxane was added **1d** (0.79 g, 5.0 mmol) and the mixture was stirred for 16 h at 100 °C. The resulting hygroscopic white solid was isolated by filtration and washed with 1,4-dioxane and diethyl ether and dried *in vacuo*. Yield: 2.06 g (87%). ^{1}H NMR (300 MHz, DMSO-d_6, 300 K): δ 9.33 (s, 1H, NCHN), 9.29 (s, 1H, NCHN), 8.01 (s, 1H, NCH), 7.81 (s, 1H, NCH), 7.68 (s, 1H, NCH), 7.66 (s, 1H, NCH), 7.40 (m, 5H, Ar-H), 5.42 (s, 2H, NCH_2Ar), 4.74 (m, 2H, NCH_2), 4.68 (m, 2H, NCH_2), 1.55 (s, 9H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6, 300 K): δ 136.8 (NCHN), 135.2 (NCHN), 134.5 (C_q), 129.0 (C_{Ar}), 128.7 (C_{Ar}), 128.3 (C_{Ar}), 122.9 (NCH), 122.8 (2 × NCH), 120.4 (NCH), 59.7 (C_q), 51.9 (NCH_2), 48.4 (NCH_2), 48.3 (NCH_2), 28.9 (CH_3). IR (neat): 3051 (s), 1557 (s), 1447 (m), 1379 (m), 1322 (w), 1210 (s), 1157 (s), 1134 (s), 778 (m), 716 (s), 634 (s) cm^{-1}. ESI-MS: *m*/*z* 253 ($[M - 2Br - {}^tBu]^+$, 100%), 309 ($[M - 2Br - H]^+$), 389 ($[M - Br]$). Anal. Calcd for $C_{19}H_{26}Br_2N_4 \cdot 0.7H_2O$: C, 47.46, H, 5.72; N, 11.60. Found: C, 47.26; H, 5.45; N, 11.71.

A.5 References

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