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Benzylic Imidazolidinium, 3,4,5,6-Tetrahydropyrimidinium and Benzimidazolium Salts: Applications in Ruthenium-Catalyzed Allylic Substitution Reactions

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Imidazolidinium, tetrahydropyrimidinium and benzimidazolium salts were prepared. Upon reaction with *t*BuOK, they generate carbene ligands, which were associated in situ to $[RuCp^*(MeCN)_3]PF_6$ to produce ruthenium catalysts that are active for the substitution of allylic substrates by dimethyl malonate as a carbonucleophile and phenol. The influences of the N-heterocyclic structures, as well as that of the benzylic *N*-substituents, on the reactivity and regioselectivity were examined.

Introduction

The substitution of allylic substrates via π-allyl or σ-allyl metal intermediates is recognized as a powerful reaction in organic synthesis for C–C and C-heteroatom bond formation in a controlled manner.[1] Several transition metals including palladium,[2] molybdenum,[3] iridium,[4] rhodium,[5] tungsten,[6] nickel,[7] iron[8] and ruthenium,[9] which exhibit different specificities in terms of regioselectivity properties, have been used for this purpose. In this context, the regioselectivity control is of crucial importance when unsymmetrical allylic derivatives are involved. We reported that cationic Cp*-containing ruthenium(II) complexes provided easy activation of allylic halides and carbonates to form allylic ruthenium(IV) complexes. They were also excellent catalysts for nucleophilic substitution with a large scope of nucleophiles, which led to highly regioselective formation of branched allylic products from unsymmetrical allylic substrates.[10] The nature of the other ancillary ligands associated to Cp* had a determining influence on the activity and regioselectivity of the catalyst. $[RuCp^*(MeCN)_3]PF_6$ (**I**),[11] $[RuCp^*(bipyridine)(MeCN)]PF_6$[12] and $[RuCp^*(phosphane)(MeCN)_2]PF_6$[13] have shown remarkable regioselectivities.

Recently, N-heterocyclic carbene-containing metal complexes have revealed excellent catalytic properties in a wide range of metal-catalyzed transformations.[14] As far as ruthenium is concerned, the main applications are in the field of olefin and enyne metathesis,[15] but a few examples have appeared in other catalytic reactions such as enyne cycloisomerization,[16] hydrogen transfer reduction of ketones,[17] oxidative cleavage of alkenes[18] or Friedlaender quinoline synthesis.[19]

In a previous communication, we showed that *N*-alkyl-substituted benzimidazolylidene–ruthenium complexes were also efficient catalysts to perform regioselective alkylation of cinnamyl carbonate by dimethyl malonate and 1,3-diketones, as well as etherification of allylic halides by phenols, respectively.[20] It is noteworthy that only a few examples of the use of N-heterocyclic carbene complexes have been reported in allylic substitution reactions.[21]

With the objective of understanding the influence of their steric and electronic effects, we prepared a variety of new N-heterocyclic carbene precursors such as imidazolidinium **A**, tetrahydropyrimidinium **B** and benzimidazolium **C** halides (Figure 1), and we studied the catalytic efficiencies of in situ generated ruthenium systems on the basis of the association of the corresponding carbenes with the RuCp* motif.

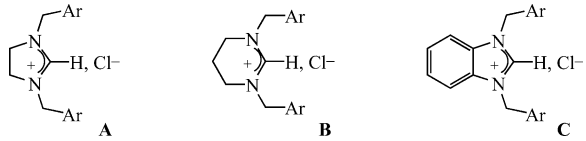

Figure 1. N-Heterocyclic carbene precursors: imidazolidinium **A**, tetrahydropyrimidinium **B** and benzimidazolium **C** chlorides.

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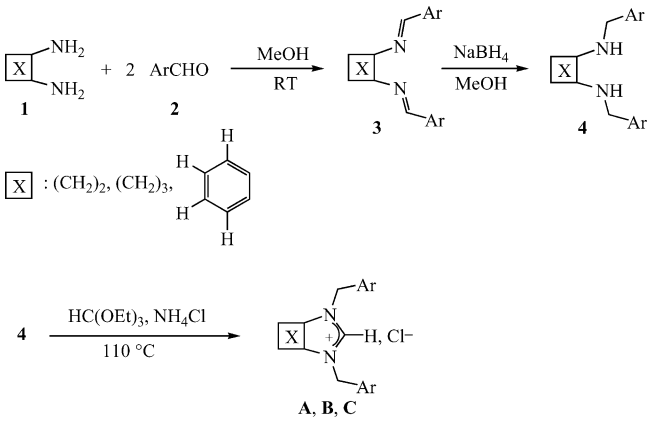
Results and Discussion

Synthesis of Imidazolinium, Tetrahydropyrimidinium and Benzimidazolium Salts

A series of symmetrical and unsymmetrical 1,3-N,N-heterocyclic azolium salts were prepared according to known methods.[22] The symmetrical N-heterocyclic carbene precursors **A6**–**9**, **B1**–**7** and **C1**–**4** were prepared according to the general reaction pathway depicted in Scheme 1. Treatment of 1,2-ethylenediamine, 1,3-propylenediamine and 1,2-diaminobenzene with an aromatic aldehyde (2 equiv.) in methanol at room temperature led to the formation of the corresponding diimine. Their reduction with sodium borohydride in methanol, followed by treatment with triethylorthoformate in the presence of ammonium chloride with continuous elimination of ethanol led to the formation of the expected imidazolidinium, tetrahydropyrimidinium and benzimidazolium chlorides in excellent yields.

The nonsymmetrical imidazolidinium salts **A1**–**5** were also synthesized. They were obtained upon reaction of a benzyl halide (chloride or bromide) with 1-(2,4,6-trimethylbenzyl)imidazoline in dimethylformamide at room temperature.[23] All these salts (Figures 2, 3 and 4) were isolated as solids in very good yields and fully characterized by ^{1}H NMR, ^{13}C NMR and IR spectroscopy, elemental analyses, and their melting points were determined.



Scheme 1. Preparation of symmetrical N-heterocyclic salts.

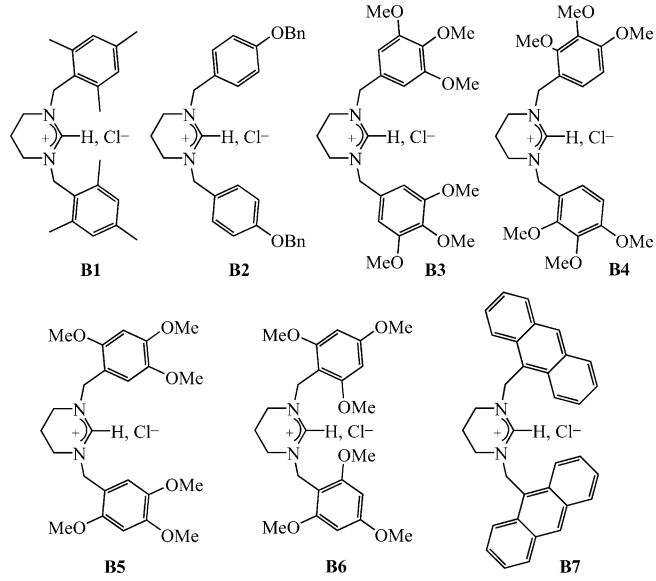


Figure 3. Tetrahydropyrimidinium salts.

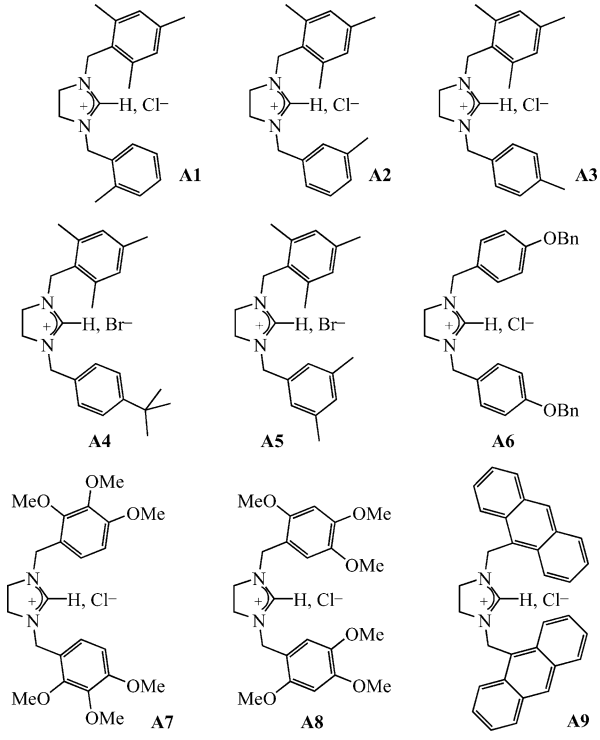


Figure 2. Imidazolidinium salts.

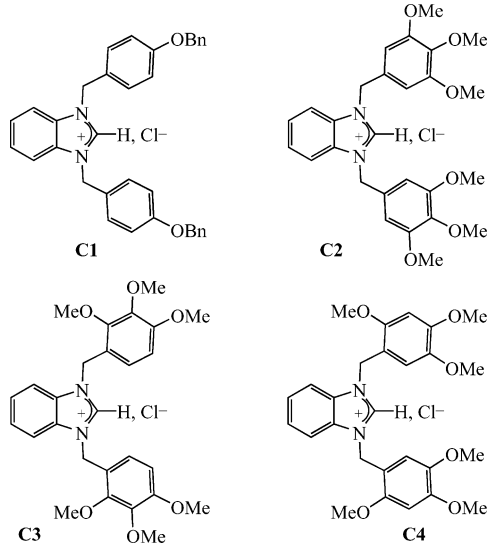


Figure 4. Benzimidazolium salts.

A fine study of the chemical shifts of the acidic C(2) protons shows that they are located in the range 7.82–11.70 ppm, which indicates a significant difference in the acidity of these protons (Table 1). Comparison of the chemical shifts in the three series where the aromatic substituents

Table 1. ^{1}H NMR spectroscopic data for the C(2)–H proton (δ, ppm); ν(CN) [cm^{-1}] of the NHC salts.

A1	10.38; 1658	**A2**	10.39; 1658	**A3**	10.41; 1662	**A4**	9.88; 1664
A5	9.94; 1660	**A6**	10.96; 1611	**A7**	10.18; 1660	**A8**	9.77; 1642
A9	11.40; 1685						
B1	8.56; 1688	**B2**	9.32; 1690	**B3**	10.43; 1701	**B4**	10.00; 1685
B5	8.68; 1670	**B6**	7.82; 1682	**B7**	10.80; 1685		
C1	10.37; 1609	**C2**	10.44; 1603	**C3**	11.62; 1615	**C4**	11.70; 1617

are identical as in (**A7**, **B4**, **C3**), (**A8**, **B5**, **C4**) and (**A9**, **B7**) reveals the order δ(**B**) < δ(**A**) < δ(**C**), which is an indication of the influence of the core structure of the properties of these salts. The position of the three methoxy groups on the phenyl rings also have a strong influence on the acidity of the proton, as a chemical shift of 7.82 ppm is observed in the case of the 2,4,6-substitution in **B6**, whereas the 3,4,5-substitution pattern in **B3** leads to 10.43 ppm.

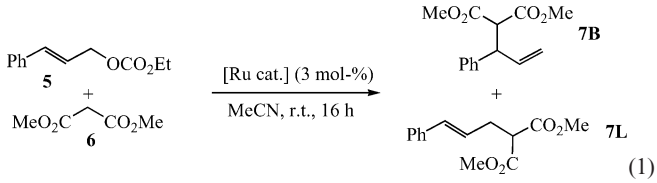
There is also a noticeable influence of the aromatic substituents on the infrared C–N vibration, as the observed wavelengths vary from 1611 to 1701 cm^{-1}. The lowest frequencies located in the narrow range (1609–1617 cm^{-1}) correspond to the benzimidazolium salts, which is an indication of the strong influence of the benzimidazole structure (due to higher electron delocalization) relative to the aromatic substituents at the periphery of the molecule. In contrast, salts **A** and **B** exhibit vibration frequencies centred around 1670–1680 cm^{-1}; a more pronounced influence of the substituents and a slight tendency to higher frequencies for six-membered rings **B** can be seen from comparison of (**A6**, **B2**), (**A7**, **B4**), (**A8**, **B5**) and (**A9**, **B7**).

Generation of Ruthenium Catalysts

The characterization of complexes arising from coordination of the carbenes resulting from deprotonation of salts **A**, **B** and **C** to a [RuCp*] centre could not be achieved. Thus, the carbene was generated first by treatment of the azolium salt with a stoichiometric amount of *t*BuOK in THF at 50 °C for 2 h.[24] [RuCp*(MeCN)$_3$]PF$_6$ (**I**) (0.5 equiv. with respect to the carbene), which contains labile acetonitrile able to exchange with more coordinating ligands such as phosphane or bipyridine, was then added to the solution, and the mixture was heated at 50 °C for 2 h. After removal of the solvent, an air-sensitive solid was collected. Even if we were not able to fully characterize an organometallic complex, it is assumed on the basis of previous work[25] that coordination of one carbene moiety is involved in the formation of [RuCp*(carbene)] species. This solid was directly used in catalytic nucleophilic substitution reactions from allylic substrates.

Allylic Alkylation of Cinnamyl Carbonate in the Presence of Ruthenium Catalysts

The substitution starting from carbonate **5** and carbonucleophile precursor **6** was investigated in the presence of the previously generated catalytic systems. In a typical experiment, cinnamyl carbonate (**5**; 1 mmol) and dimethyl malonate (**6**; 1.2 mmol) were successively added to the catalytic material (0.03 mmol based on ruthenium) dissolved in acetonitrile (6 mL), and the resulting mixture was stirred for 16 h at room temperature [Equation (1)].



(1)

After concentration under vacuum and flash chromatography over silica gel, the crude product was analyzed by ^{1}H NMR spectroscopy, which provided both the conversion and the branched-to-linear ratio (**7B/7L**). The results are gathered in Table 2. A blank experiment carried out without the ruthenium source led to no conversion of the starting substrates. Similarly, the reaction performed with [RuCp*(MeCN)$_3$]PF$_6$ gave no products without prior deprotonation of malonate. These observations provide clear evidence of the crucial role of the carbene ligands in these new catalytic systems. All the catalytic systems resulting from coordination of imidazolinylidene, tetrahydropyrimidinylidene and benzimidazolylidene ligands show good regioselectivity in favour of branched isomer **7B**. However,

Table 2. Ruthenium-catalyzed allylic alkylation of cinnamyl carbonate **5**.[a]

Entry	NHC precursor	Conversion [%]	**7B/7L** ratio
1	**A1**	13	89:11
2	**A2**	10	90:10
3	**A3**	36	93:7
4	**A4**	51	94:6
5	**A5**	18	74:16
6	**A6**	14[b]	66:34
7	**A7**	17	87:13
8	**A8**	17[b]	82:18
9	**A9**	72	97:3
10	**B1**	26	84:16
11	**B2**	26[b]	88:12
12	**B4**	10	89:11
13	**B5**	12	82:18
14	**B6**	94	81:19
15	**B7**	8	81:19
16	**C1**	19	89:11
17	**C2**	60	91:9
18	**C3**	11	90:10
19	**C4**	10	86:14

[a] Conditions: dimethyl malonate (**6**; 1.2 mmol), allylic carbonate (**5**; 1 mmol), (**A**–**C**)-based catalyst (0.03 mmol based on ruthenium) in MeCN (6 mL) at r.t. for 16 h. [b] 50 °C for 16 h.

these catalytic systems have limited application due to their relatively low activities. The most efficient systems combining a good compromise in terms of reactivity and regioselectivity appear to be the catalysts resulting from **A9** and **B6**. It is worth mentioning that relative to **C1**–**4**, benzimidazolium salts **C5**–**8** containing 2-methoxyethyl, 2-diethylaminoethyl or homobenzyl *N*-substituents (Figure 5) led to more reactive catalytic systems, which provides complete conversion of the substrates within 16 h, but with slightly lower regioselectivity (**B/L** ratios in the range 71–88:29–12 as compared to Entries 16–19 in Table 2).[20]

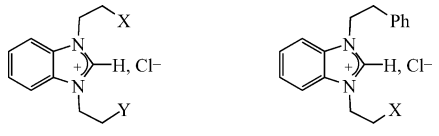
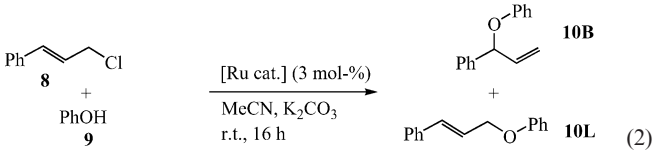


Figure 5. Benzimidazolium salts with alkyl and homobenzyl *N*-substituents.

Allylic Etherification of Cinnamyl Chloride in the Presence of Ruthenium Catalysts

We previously reported that $[RuCp^*(MeCN)_3]PF_6$ (**I**) as a catalyst led to outstanding regioselectivity in the substitution of allylic chlorides by phenoxides. To evaluate the influence of our new catalytic systems based on ruthenium carbene active species, we studied the reaction of cinnamyl chloride with phenol in the presence of a base [Equation (2)].



(2)

Thus, phenol **9** (1.2 mmol), cinnamyl chloride (**8**; 1 mmol), potassium carbonate (1.2 mmol), ruthenium catalyst (0.03 mmol) and K_2CO_3 (1.2 mmol) were stirred in acetonitrile at room temperature for 16 h. The results are collected in Table 3. In this reaction, the blank experiment carried out without ruthenium catalyst during the same reaction time led to a very low yield of linear ether **10L**, exclusively. In acetonitrile, all imidazolidinium salts **A** led to complete conversion with preferred formation of the linear cinnamyl phenyl ether, except **A7**, which gave a **10B/10L** ratio of 92:8.

With tetrahydropyrimidinium salts **B3** and **B6**, the conversions were modest, but with **B4** and **B5** they were good and satisfactory regioselectivities in favour of the branched isomer were observed (**10B/10L**, 86:14, 87:13; Table 3, Entries 13, 16). Benzimidazolium salts **C1**–**3** produced catalytic systems with lower activities and formation of the linear ethers as major products. These results are in contrast to the complete conversion and the regioselective formation of the branched product observed with benzimidazolium salts **C5**–**8** (Figure 5) under similar conditions.[20]

Table 3. Ruthenium-catalyzed allylic etherification of cinnamyl chloride by phenolate.[a]

Entry	NHC precursor	Conversion [%]	**10B/10L** ratio
1	**A1**	100	9:91
2	**A2**	100	–:100
3	**A2**	100[c]	–:100
4	**A3**	100	–:100
5	**A4**	100	–:100
6	**A5**	100	–:100
7	**A7**	90	92:8
8	**A7**	100[c]	–:100
9	**A8**	37	–:100
10	**A9**	50[b]	67:33
11	**A9**	90	9:91
12	**B3**	20	56:44
13	**B4**	95	86:14
14	**B4**	100[c]	83:17
15	**B5**	9[b]	76:24
16	**B5**	95	87:13
17	**B5**	100[c]	32:68
18	**B6**	32	2:98
19	**C1**	50	22:78
20	**C2**	60	41:59
21	**C3**	10	5:95

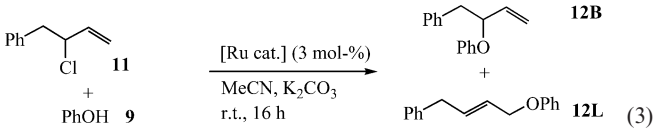
[a] Conditions: phenol **9** (1.2 mmol), K_2CO_3 (1.2 mmol), cinnamyl chloride (**8**; 1 mmol), (**A**–**C**)-based catalyst (0.03 mmol based on ruthenium) in MeCN (6 mL) at r.t. for 16 h. [b] Dichloromethane as solvent. [c] THF as solvent.

With these carbene-containing catalysts, the solvent also showed a drastic influence on both activity and regioselectivity. For instance, with ligand **A7**, similar conversions were observed but regioselectivities were reversed in acetonitrile and tetrahydrofuran (**10B/10L**, 92:8 and 0:100, respectively; Table 3, Entries 7, 8). It is worth noting that in the presence of catalyst **I** without any other ligand, a regioselectivity of 50:1 was obtained in acetonitrile.[12] This selectivity in favour of the branched isomer is much higher than the results presented in Table 3 and reveals the strong influence of the carbene ligands in this catalytic reaction. The ligands themselves show a general tendency to lower the regioselectivity in favour of the branched product but can also lead to the linear ether with perfect regioselectivity.

Allylic Etherification of 3-Chloro-4-phenylbut-1-ene in the Presence of Ruthenium Catalysts

We already experienced that the formation of branched isomers from aliphatic allylic substrates was more challenging than starting from cinnamyl derivatives. The best of our ruthenium catalysts to perform the regioselective substitution of 3-chloro-4-phenylbut-1-ene (**11**) by phenol [Equation (3)] is the phosphane-containing catalyst $[RuCp^*(MeCN)_2(MeOPPh_2)]PF_6$, which leads to a branched/linear ratio of 92/8. However, catalytic ruthenium systems generated from benzimidazolium salts **C5**–**8** produced **12B/12L** ratios up to 85:15, whereas ruthenium precursor **I** led to only a 60:40 ratio. From the new salts where the N-atoms are substituted by benzylic groups, the reac-

tions were not complete within 16 h at room temperature and some reactions required heating to 50 °C (Table 4, Entries 5–8, 10, 12, 13) to give satisfactory conversion, which reveals a decrease in activity relative to N-heterocyclic salts **C5**–**8** with aliphatic *N*-substituents. In all cases, except from **A8** (Table 4, Entry 7), branched compound **12B** is formed as the major isomer, but the regioselectivities are modest (54:46 to 79/21). In this allylic substitution example, there is no important influence of the nature of the benzylic carbene precursors **A**, **B** or **C** on the fate of the reaction.



(3)

Table 4. Ruthenium-catalyzed allylic etherification of **11** by aryloxide anions.[a]

Entry	NHC precursor	Conversion [%]	**12B/12L** ratio
1	**A1**	93	66:34
2	**A2**	80	60:40
3	**A3**	90	70:30
4	**A5**	87	73:27
5	**A6**	91[b]	70:30
6	**A7**	93	63:37
7	**A8**	79[b]	36:64
8	**A9**	88	79:21
9	**B1**	60	60:40
10	**B2**	86[b]	54:46
11	**B3**	88	65:35
12	**B4**	93[b]	68:32
13	**B5**	90[b]	72:28
14	**B6**	7	58:42
15	**B7**	80	60:40
16	**C1**	70	74:26
17	**C3**	65	69:31
18	**C4**	80	60:40

[a] Conditions: phenol **9** (1.2 mmol), K_2CO_3 (1.2 mmol), allylic chloride **11** (1 mmol), (**A**–**C**)-based catalyst (0.03 mmol based on ruthenium) in MeCN (6 mL) at r.t. for 16 h. [b] 50 °C for 16 h.

Conclusions

New imidazolidinium, 3,4,5,6-tetrahydropyrimidinium and benzimidazolium salts, precursors of N-heterocyclic carbenes upon deprotonation, were prepared. They were associated to $[RuCp^*(MeCN)_3]PF_6$ to generate new catalytic species, which are active in the nucleophilic substitution of allylic carbonates and chlorides by malonate and phenol. The observed regioselectivities differ from those obtained with $[RuCp^*(MeCN)_3]PF_6$, which reveals that the active catalytic species are different. However, the regioselectivities strongly depend on the type of substrates and carbene precursors, without any obvious rule, and even perfect selectivity in favour of the undesired linear product is sometimes obtained. It is worth noting that the activities and regioselectivities in favour of the branched isomers obtained with these new benzylic salts are lower than those obtained with benzimidazolium salts that are *N*-substituted by an alkyl chain featuring a coordinating heteroatom (**C5**–**7**) or a homobenzylic group (**C7** and **C8**).

Experimental Section

General Preparation of Nonsymmetrical N-Heterocyclic Salts (A1–5)

***N*-(2,4,6-Trimethylbenzyl)ethylenediamine:** Li (0.34 g, 48.02 mmol) was added to $H_2NCH_2CH_2NH_2$ (1.2 mol, 80 mL), and the mixture was heated on a sand bath (ca. 110 °C) for 1 h. After gas evolution, 2,4,6-trimethylbenzyl chloride (8.0 g, 47.42 mmol) was slowly added at room temperature. Toluene (50 mL) was then added, and the resulting mixture was heated at 110 °C for 2 h. After cooling, the mixture was filtered and the volatiles were removed under vacuum. The residue was distilled to give a colourless liquid (b.p. 98–100 °C/0.01 Torr). Yield: 7.63 g (83%).

1-(2,4,6-Trimethylbenzyl)imidazoline: A mixture of *N*-(2,4,6-trimethylbenzyl) ethylenediamine (7.63 g, 39.74 mmol) and *N*,*N*-dimethylformamide dimethylacetal (5.8 mL, 43.07 mmol) was heated on a steam bath (90–95 °C) for 2 h to remove MeOH and $HNMe_2$. The residue was then heated to 120 °C for 1 h. The volatiles were removed under vacuum, and the remaining yellow viscous liquid was distilled under vacuum (108–109 °C/0.01 Torr) to give a colourless liquid, which solidified on standing, and was then crystallized from hexane (10 mL). White hygroscopic crystals were collected and dried. Yield: 7.39 g (93%).

Preparation of A1 as a Typical Procedure: To a solution of 1-(2,4,6-trimethylbenzyl)imidazoline (2.02 g, 10 mmol) in DMF (5 mL) was slowly added 2-methylbenzyl chloride (1.41 g, 10.1 mmol) at 25 °C, and the resulting mixture was stirred at room temperature for 8 h. Diethyl ether (15 mL) was added to obtain a white crystalline solid, which was filtered off. The solid was washed with diethyl ether (3×10 mL) and dried under vacuum, and the crude product was recrystallized from ethanol/diethyl ether (2:1).

1-(2,4,6-Trimethylbenzyl)-3-(2-methylbenzyl)imidazolinium Chloride (A1): Yield: 3.08 g (90%). M.p. 241–242 °C. IR: IR: $\tilde{\nu}$ = 1658 ν(CN) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.09 [s, 3 H, $CH_2C_6H_2(CH_3)_3$-4], 2.18 [s, 6 H, $CH_2C_6H_2(CH_3)_3$-2,6], 2.39 [s, 3 H, $CH_2C_6H_4(CH_3)$-2], 3.63 and 3.6 9 (m, 4 H, NCH_2CH_2N), 4.80 [s, 2 H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 4.84 [s, 2 H, $CH_2C_6H_4(CH_3)$-2], 6.68 [s, 2 H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 7.01–7.24 [m, 4 H, $CH_2C_6H_4(CH_3)$-3], 10.38 (s, 1 H, NCHN) ppm. $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$): δ = 19.52 [$CH_2C_6H_4(CH_3)$-2], 20.3 [$CH_2C_6H_2(CH_3)_3$-2,6], 21.1 [$CH_2C_6H_2(CH_3)_3$-6], 46.2 [$CH_2C_6H_2(CH_3)_3$-2,4,6], 47.6 and 47.9 (NCH_2CH_2N), 50.0 [$CH_2C_6H_4(CH_3)$-6], 129.9, 131.2, 137.1 and 138.0 [$CH_2C_6H_2(CH_3)_3$-2,4,6], 125.8, 126.7, 129.0, 129.9, 131.1 and 138.6 [$CH_2C_6H_4(CH_3)$-2], 158.9 (NCHN) ppm. $C_{21}H_{27}ClN_2$ (342.91): calcd. C 73.56, H 7.94, N 8.17; found C 73.57, H 7.93, N 8.16.

1-(2,4,6-Trimethylbenzyl)-3-(3-methylbenzyl)imidazolinium Chloride (A2): Yield: 3.02 g (88%). M.p. 246–247 °C. IR: $\tilde{\nu}$ = 1658 ν(CN) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.19 [s, 3 H, $CH_2C_6H_4(CH_3)$-4], 2.22 [s, 6 H, $CH_2C_6H_2(CH_3)_3$-2,6], 2.27 [s, 3 H, $CH_2C_6H_2(CH_3)_3$-2,6], 3.57 and 3.74 (m, 4 H, NCH_2CH_2N), 4.78 [s, 2 H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 4.84 [s, 2 H, $CH_2C_6H_4(CH_3)$-4], 6.78 [s, 2 H, $CH_2C_6H_2(CH_3)_3$-2,4,6], 7.05–7.26 [m, 4 H, $CH_2C_6H_4(CH_3)$-4], 10.39 (s, 1 H, NCHN) ppm. $^{13}C\{H\}$NMR (100 MHz, $CDCl_3$): δ = 21.1 [$CH_2C_6H_4(CH_3)$-4], 20.3 [$CH_2C_6H_2(CH_3)_3$-2,6], 21.5 [$CH_2C_6H_2(CH_3)_3$-6], 46.4 [$CH_2C_6H_2(CH_3)_3$-

2,4,6], 47.6 and 47.7 (NCH$_2$CH$_2$N), 52.3 [CH$_2$C$_6$H$_4$(CH$_3$)-4], 125.9, 132.8, 138.0 and 139.2 [CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6], 125.5, 129.3, 129.9, and 139.3 [CH$_2$C$_6$H$_4$(CH$_3$)-4], 158.8 (NCHN) ppm. $C_{21}H_{27}ClN_2$ (342.91): calcd. C 73.56, H 7.94, N 8.17; found C 73.52, H 7.95, N 8.14.

1-(2,4,6-Trimethylbenzyl)-3-(4-methylbenzyl)imidazolinium Chloride (A3): Yield: 2.91 g (85%). M.p. 279–280 °C. IR: $\tilde{\nu}$ = 1662 ν(CN) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.07 [s, 3 H, CH$_2$C$_6$H$_4$(CH$_3$)-4], 2.16 [s, 6 H, CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,6], 2.19 [s, 6 H, CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,6], 3.55 and 3.71 (m, 4 H, NCH$_2$CH$_2$N), 4.73 [s, 2 H, CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6], 4.74 [s, 2 H, CH$_2$C$_6$H$_4$(CH$_3$)-4], 6.78 [s, 2 H, CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6], 6.94–7.17 [m, 4 H, CH$_2$C$_6$H$_4$(CH$_3$)-4], 10.41 (s, 1 H, NCHN) ppm. ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ = 21.0 [CH$_2$C$_6$H$_4$(CH$_3$)-2], 20.3 [CH$_2$C$_6$H$_2$-(CH$_3$)$_3$-2,6], 21.3 [CH$_2$C$_6$H$_2$(CH$_3$)$_3$-6], 46.2 [CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6], 47.5 and 47.6 (NCH$_2$CH$_2$N), 51.7 [CH$_2$C$_6$H$_4$(CH$_3$)-6], 128.8, 130.3, 137.9 and 138.5 [CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6], 125.8, 129.8, 139.6 [CH$_2$C$_6$H$_4$(CH$_3$)-2], 158.7 (NCHN) ppm. $C_{21}H_{27}ClN_2$ (342.91): calcd. C 73.56, H 7.94, N 8.17; found C 73.51, H 7.97, N 8.21.

1-(2,4,6-Trimethylbenzyl)-3-(4-*tert*-butylbenzyl)imidazolinium Bromide (A4): Yield: 3.74 g (87%). M.p. 290–291 °C. IR: $\tilde{\nu}$ = 1664 ν(CN) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 {s, 9 H, CH$_2$C$_6$H$_4$[C(CH$_3$)$_3$]-4}, 2.18 [s, 6 H, CH$_2$C$_6$H$_2$(CH$_3$)$_3$-4], 2.30 [s, 6 H, CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,6], 3.66 and 3.82 (m, 4 H, NCH$_2$CH$_2$N), 4.78 [s, 2 H, CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6], 4.84 {s, 2 H, CH$_2$C$_6$H$_4$-[C(CH$_3$)$_3$-4]}, 6.79 [s, 2 H, CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6], 7.25–7.32 {m, 4 H, CH$_2$C$_6$H$_4$[C(CH$_3$)$_3$-4]}, 9.88 (s, 1 H, NCHN) ppm. ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ = 20.4 [CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,6], 21.1 [CH$_2$C$_6$H$_2$(CH$_3$)$_3$-6], 31.4 {CH$_2$C$_6$H$_4$[C(CH$_3$)$_3$-3,5]}, 34.8 {CH$_2$C$_6$H$_4$[C(CH$_3$)$_3$-3,5]}, 46.5 [CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6], 47.9 and 48.0 (NCH$_2$CH$_2$N), 52.0 [CH$_2$C$_6$H$_4$(CH$_3$)$_2$-3,5], 126.3, 129.8, 138.1, and 139.2 [CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6], 125.5, 128.8, 130.1, and 152.3 {CH$_2$C$_6$H$_4$[C(CH$_3$)$_3$-4]}, 157.8 (NCHN) ppm. $C_{24}H_{33}BrN_2$ (429.44): calcd. C 67.12, H 7.75, N 6.52; found C 67.19, H 7.77, N 6.51.

1-(2,4,6-Trimethylbenzyl)-3-(3,5-dimethylbenzyl)imidazolinium Bromide (A5): Yield: 3.65 g (91%). M.p. 285–286 °C. IR: $\tilde{\nu}$ = 1660 ν(CN) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18 [s, 6 H, CH$_2$C$_6$H$_2$(CH$_3$)$_3$-4], 2.22 [s, 6 H, CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,6], 2.29 [s, 6 H, CH$_2$C$_6$H$_4$(CH$_3$)$_2$-3,5], 3.65 and 3.79 (m, 4 H, NCH$_2$CH$_2$N), 4.71 [s, 2 H, CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6], 4.84 [s, 2 H, CH$_2$C$_6$H$_3$(CH$_3$)$_2$-3,5], 6.79 [s, 2 H, CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6], 6.89 [s, 3 H, CH$_2$C$_6$H$_3$-(CH$_3$)$_2$-3,5], 9.94 (s, 1 H, NCHN) ppm. ^{13}C{H}NMR (100 MHz, $CDCl_3$): δ = 20.4 [CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,6], 21.1 [CH$_2$C$_6$H$_2$(CH$_3$)$_3$-6], 21.4 [CH$_2$C$_6$H$_3$(CH$_3$)$_2$-3,5], 46.5 [CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6], 47.9 and 48.0 (NCH$_2$CH$_2$N), 52.4 [CH$_2$C$_6$H$_4$(CH$_3$)$_2$-3,5], 126.6, 130.8, 132.6 and 139.1 [CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6], 125.5, 130.0, 138.1 and 139.2 [CH$_2$C$_6$H$_4$(CH$_3$)$_2$-3,5], 157.9 (NCHN) ppm. $C_{22}H_{29}BrN_2$ (401.39): calcd. C 65.83, H 7.28, N 6.98; found C 65.90, H 7.22, N 6.99.

General Preparation of Symmetrical N-Heterocyclic Salts A6–9, B1–7 and C1–4: Aromatic aldehyde **2** (20 mmol) and diamine **1** (10 mmol) were stirred overnight in methanol. The diimine was collected as a white solid, filtered and recrystallized from an alcohol/ether mixture. Diimine **3** (10 mmol) was subsequently reduced by $NaBH_4$ (30 mmol) in CH_3OH (30 mL). The solution was then treated with 1 N HCl, and the organic phase was extracted with CH_2Cl_2 (3 × 30 mL). After drying over $MgSO_4$ and evaporation, diamine **4** was isolated as a solid. Diamine **4** was then treated with a large excess of triethylorthoformate (50 mL) in the presence of NH_4Cl (10 mmol) at 110 °C in a distillation apparatus until removal of ethanol ceased. Upon cooling to room temperature, a colourless solid precipitated, which was collected by filtration and dried under vacuum. Crude product **A**, **B** or **C** was recrystallized from absolute ethanol to give colourless needles, and the solid was washed with diethyl ether (2 × 10 mL) and dried under vacuum.

1,3-Bis(4-benzyloxybenzyl)imidazolinium Chloride (A6): Yield: 4.49 g (90%). M.p. 224–225 °C. IR: $\tilde{\nu}$ = 1611 ν(CN) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.62 (s, 4 H, NCH$_2$CH$_2$N), 4.65 [s, 4 H, CH$_2$C$_6$H$_4$(OCH$_2$)C$_6$H$_5$], 5.02 [s, 4 H, CH$_2$C$_6$H$_4$(OCH$_2$)C$_6$H$_5$], 7.34–6.75 [m, 18 H CH$_2$C$_6$H$_4$(OCH$_2$)C$_6$H$_5$], 10.96 (s, 1 H, NCHN) ppm. ^{13}C{H}NMR (50 MHz, $CDCl_3$): δ = 47.6 (NCH$_2$CH$_2$N), 56.7 [CH$_2$C$_6$H$_4$(OCH$_2$)C$_6$H$_5$], 71.2 [CH$_2$C$_6$H$_4$(OCH$_2$)C$_6$H$_5$], 112.9, 114.2, 121.6, 125.6, 127.4, 128.1; 128.7; 136.9; 148.9; 150.5 [CH$_2$C$_6$H$_4$(OCH$_2$)C$_6$H$_5$], 159.4 (NCHN) ppm. $C_{31}H_{31}ClN_2O_2$ (499.05): calcd. C 74.61, H 6.26, N 5.61; found C 74.65, H 6.29, N 5.60.

1,3-Bis(2,3,4-trimethoxybenzyl)imidazolinium Chloride (A7): Yield: 4.44 g (95%). M.p. 193–194 °C. IR: $\tilde{\nu}$ = 1660 ν(CN) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.72 [s, 6 H, CH$_2$C$_6$H$_2$(OCH$_3$)$_3$-2], 3.85 [s, 6 H, CH$_2$C$_6$H$_2$(OCH$_3$)$_3$-3], 3.96 [s, 6 H, CH$_2$C$_6$H$_2$(OCH$_3$)$_3$-4], 4.77 [s, 4 H, CH$_2$C$_6$H$_2$(OCH$_3$)$_3$], 3.86 (s, 4 H, NCH$_2$CH$_2$N), 6.63; 6.68; 7.17 and 7.21 [m, 4 H, CH$_2$C$_6$H$_2$(OCH$_3$)$_3$], 10.18 (s, 1 H, NCHN) ppm. ^{13}C{H}NMR (50 MHz, $CDCl_3$): δ = 48. 10 (NCH$_2$CH$_2$N), 56.5 [CH$_2$C$_6$H$_2$(OCH$_3$)$_3$-2], 61.24 [CH$_2$C$_6$H$_2$(OCH$_3$)$_3$-3], 61.79 [CH$_2$C$_6$H$_2$(OCH$_3$)$_3$-4], 47.71 [CH$_2$C$_6$H$_2$(OCH$_3$)$_3$], 107.71; 118.8; 126.09; 142.20; 152.56 and 155.24 [CH$_2$C$_6$H$_2$(OCH$_3$)$_3$], 159.21 (NCHN) ppm. $C_{23}H_{31}ClN_2O_6$ (466.96): calcd. C 59.16, H 6.69, N 6.00; found C 59.15, H 6.72, N 6.02.

1,3-Bis(2,4,5-trimethoxybenzyl)imidazolinium Chloride (A8): Yield: 4.20 g (90%). M.p. 169–170 °C. IR: $\tilde{\nu}$ = 1642 ν(CN) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.70 [s, 6 H, CH$_2$C$_6$H$_2$(OCH$_3$)$_3$-2], 3.74 [s, 6 H, CH$_2$C$_6$H$_2$(OCH$_3$)$_3$-5], 3.77 [s, 6 H, CH$_2$C$_6$H$_2$(OCH$_3$)$_3$-4], 4.68 [s, 4 H, CH$_2$C$_6$H$_2$(OCH$_3$)$_3$], 3.81 (s, 2 H, NCH$_2$CH$_2$N), 3.82 (s, 2 H, NCH$_2$CH$_2$N), 6.45 and 7.11 [m, 4 H, CH$_2$C$_6$H$_2$(OCH$_3$)$_3$], 9.77 (s, 1 H, NCHN) ppm. ^{13}C{H}NMR (50 MHz, $CDCl_3$): δ = 47.2 (NCH$_2$CH$_2$N), 56.6 [CH$_2$C$_6$H$_2$(OCH$_3$)$_3$-2], 56.7 [CH$_2$C$_6$H$_2$-(OCH$_3$)$_3$-5], 57.4 [CH$_2$C$_6$H$_2$(OCH$_3$)$_3$-4], 48.1 [CH$_2$C$_6$H$_2$(OCH$_3$)$_3$], 97.41; 112.5; 115.4; 143.7; 150.9 and 152.6 [CH$_2$C$_6$H$_2$(OCH$_3$)$_3$], 159.1 (NCHN) ppm. $C_{23}H_{31}ClN_2O_6$ (466.96): calcd. C 59.16, H 6.69, N 6.00; found C 59.12, H 6.73, N 5.98.

For 1,3-Bis(9-anthracenomethyl)imidazolidinium Chloride (A9): Yield: 3.90 g (80%). M.p. 224–225 °C. IR: $\tilde{\nu}$ = 1685 ν(CN) cm^{-1}. ^{1}H NMR (200 MHz, DMSO): δ = 3.60 (s, 4 H, NCH$_2$CH$_2$N), 5.80 (s, 4 H, CH$_2$C$_{14}$H$_{14}$), 7.20–8.10 (m, 28 H, CH$_2$C$_9$H$_{14}$), 11.4 (s, 1 H, NCHN) ppm. ^{13}C{H}NMR (50 MHz, DMSO): δ = 47.5 (NCH$_2$CH$_2$N), 50.4 (NCH$_2$CH$_2$CH$_2$N), 56.4 (CH$_2$C$_9$H$_{14}$), 123.1, 125.8, 126.4, 127.8, 128.4, 128.9, 129.6, 130.2, 130.7, 131.3, 134.0 (CH$_2$C$_{14}$H$_{14}$), 157.2 (NCHN) ppm. $C_{33}H_{27}ClN_2$ (487.04): calcd. C 81.38, H 5.59, N 5.75; found C 81.39, H 5.62, N 5.72.

1,3-Bis(2,4,6-trimethylbenzyl)-3,4,5,6-tetrahydropyrimidinium Chloride (B1)[26]: Yield: 3.77 g (98%). M.p. 288–289 °C. IR: $\tilde{\nu}$ = 1688 ν(CN) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.56 (s, 1 H, NCHN), 6.73 [s, 4 H, CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6], 4.74 [s, 4 H, CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6], 3.36 (t, J = 5.7 Hz, 4 H, NCH$_2$CH$_2$CH$_2$N), 2.16 and 2.20 [s, 18 H, CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6], 2.01 (quint., J = 5.3 Hz, 2 H, NCH$_2$CH$_2$CH$_2$N) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 151.9 (NCHN), 125.3, 130.0, 137.9 and 138.9 [CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6], 52.1 [CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6], 42.6 (NCH$_2$CH$_2$CH$_2$N), 19.8 and 20.9 [CH$_2$C$_6$H$_2$(CH$_3$)$_3$-2,4,6], 19.1 (NCH$_2$CH$_2$CH$_2$N) ppm. $C_{24}H_{33}ClN_2$ (384.99): calcd. C 74.87, H 8.64, N 7.27; found C 74.83, H 8.66, N 7.30.

1,3-Bis(4-benzyloxybenzyl)-3,4,5,6-tetrahydropyrimidinium Chloride (B2): Yield: 4.36 g (85%). M.p. 238–239 °C. IR: $\tilde{\nu}$ = 1690 ν(CN)

cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.64 [s, 4 H, $CH_2C_6H_4(OCH_2)C_6H_5$], 5.13 [s, 4 H, $CH_2C_6H_4(OCH_2)C_6H_5$], 3.17 (t, J = 4.6 Hz, 4 H, $NCH_2CH_2CH_2N$), 1.96 (quint., J = 4.2 Hz, 2 H, $NCH_2CH_2CH_2N$), 7.06, 7.32, 7.34, 7.38, 7.40, 7.41, 7.44 and 7.46 [m, 18 H, $CH_2C_6H_4(OCH_2)C_6H_5$], 9.32 (s, 1 H, NCHN) ppm. ^{13}C{H}NMR (50 MHz, $CDCl_3$): δ = 19.2 ($NCH_2CH_2CH_2N$), 57.7 ($NCH_2CH_2CH_2N$), 70.13 [$CH_2C_6H_4(OCH_2)C_6H_5$], 115.93 [$CH_2C_6H_4(OCH_2)C_6H_5$], 127.27, 128.67, 128.79, 129.35, 130.83, 137.81 [$CH_2C_6H_4(OCH_2)C_6H_5$], 159.4 (NCHN) ppm. $C_{32}H_{33}ClN_2O_2$ (513.08): calcd. C 74.91, H 6.48, N 5.46; found C 74.96, H 6.44, N 5.47.

1,3-Bis(3,4,5-trimethoxybenzyl)-3,4,5,6-tetrahydropyrimidinium Chloride (B3)[26]: Yield: 4.52 g (94%). M.p. 266–267 °C. IR: $\tilde{\nu}$ = 1701 ν(CN) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.43 (s, 1 H, NCHN), 6.72 [s, 4 H, $CH_2C_6H_2(OCH_3)_3$-3,4,5], 4.75 [s, 4 H, $CH_2C_6H_2(OCH_3)_3$-3,4,5], 3.76 and 3.81 [s, 18 H, $CH_2C_6H_2$-$(OCH_3)_3$-3,4,5], 3.21 (t, J = 5.2 Hz, 4 H, $NCH_2CH_2CH_2N$), 1.93 (quint., J = 5.2 Hz, 2 H, $NCH_2CH_2CH_2N$) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 154.7 (NCHN), 106.6, 129.0, 138.7 and 153.9 [$CH_2C_6H_2(OCH_3)_3$-3,4,5], 61.0 [$CH_2C_6H_2(OCH_3)_3$-3,4,5], 56.8 and 59.0 [$CH_2C_6H_2(OCH_3)_3$-3,4,5], 42.0 ($NCH_2CH_2CH_2N$), 19.3 ($NCH_2CH_2CH_2N$) ppm. $C_{24}H_{33}ClN_2O_6$ (480.99): calcd. C 59.93, H 6.91, N 5.82; found C 59.95, H 6.90, N 5.84.

1,3-Bis(2,3,4-trimethoxybenzyl)-3,4,5,6-tetrahydropyrimidinium Chloride (B4): Yield: 4.28 g (89%). M.p. 184–185 °C. IR: $\tilde{\nu}$ = 1685 ν(CN) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.85 [s, 6 H, $CH_2C_6H_2(OCH_3)_3$-2], 3.90 [s, 6 H, $CH_2C_6H_2(OCH_3)_3$-3], 3.94 [s, 6 H, $CH_2C_6H_2(OCH_3)_3$-4], 4.81 [s, 4 H, $CH_2C_6H_2(OCH_3)_3$], 3.23 (t, J = 5.6 Hz, 4 H, $NCH_2CH_2CH_2N$), 2.03 (quint., J = 4.8 Hz, 2 H, $NCH_2CH_2CH_2N$), 6.64; 6.70; 7.22; 7.26 [m, 4 H, $CH_2C_6H_2$-$(OCH_3)_3$], 10.00 (s, 1 H, NCHN) ppm. ^{13}C{H}NMR (50 MHz, $CDCl_3$): δ = 19.5 ($NCH_2CH_2CH_2N$), 42.4 ($NCH_2CH_2CH_2N$), 56.4 [$CH_2C_6H_2(OCH_3)_3$-2], 61.2 [$CH_2C_6H_2(OCH_3)_3$-3], 61.9 [$CH_2C_6H_2(OCH_3)_3$-4], 54.2 [$CH_2C_6H_2(OCH_3)_3$], 107.8, 119.4, 126.2, 142.3, 152.780 and 154.9 [$CH_2C_6H_2(OCH_3)_3$], 155.2 (NCHN) ppm. $C_{24}H_{33}ClN_2O_6$ (480.99): calcd. C 59.93, H 6.92, N 5.82; found C 59.89, H 6.94, N 5.81.

1,3-Bis(2,4,5-trimethoxybenzyl)-3,4,5,6-tetrahydropyrimidinium Chloride (B5): Yield: 4.09 g (85%). M.p. 129–130 °C. IR: $\tilde{\nu}$ = 1670.3 ν(CN) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.70 [s, 6 H, $CH_2C_6H_2(OCH_3)_3$-2], 3.77 [s, 6 H, $CH_2C_6H_2(OCH_3)_3$-5], 3.79 [s, 6 H, $CH_2C_6H_2(OCH_3)_3$-4], 4.54 [s, 4 H, $CH_2C_6H_2(OCH_3)_3$], 3.18 (t, J = 4.2 Hz, 4 H, $NCH_2CH_2CH_2N$), 1.80 (quint., J = 4.4 Hz, 2 H, $NCH_2CH_2CH_2N$), 6.73 and 7.01 [m, 4 H, $CH_2C_6H_2(OCH_3)_3$], 8.68 (s, 1 H, NCHN) ppm. ^{13}C{H}NMR (50 MHz, $CDCl_3$): δ = 19.2 ($NCH_2CH_2CH_2N$), 42.7 ($NCH_2CH_2CH_2N$), 56.6 [$CH_2C_6H_2(OCH_3)_3$-2], 57.0 [$CH_2C_6H_2(OCH_3)_3$-3], 57.2 [$CH_2C_6H_2(OCH_3)_3$-4], 53.45 [$CH_2C_6H_2(OCH_3)_3$],99.02; 113.3; 116.1; 143.3; 151.0 and 153.1 [$CH_2C_6H_2(OCH_3)_3$], 153.6 (NCHN) ppm. $C_{24}H_{33}ClN_2O_6$ (480.99): calcd. C 59.93, H 6.92, N 5.82; found C 59.92, H 6.95, N 5.83.

1,3-Bis(2,4,6-trimethoxybenzyl)-3,4,5,6-tetrahydropyrimidinium Chloride (B6)[26]: Yield: 4.28 g (89%). M.p. 233–234 °C. IR: $\tilde{\nu}$ = 1682 ν(CN) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (s, 1 H, NCHN), 6.03 [s, 4 H, $CH_2C_6H_2(OCH_3)_3$-2,4,6], 4.46 [s, 4 H, $CH_2C_6H_2(OCH_3)_3$-2,4,6], 3.69 and 3.75 [s, 18 H, $CH_2C_6H_2$-$(OCH_3)_3$-2,4,6], 3.32 (t, J = 5.6 Hz, 4 H, $NCH_2CH_2CH_2N$), 1.96 (quint., J = 5.2 Hz, 2 H, $NCH_2CH_2CH_2N$) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 162.7 (NCHN), 90.8, 101.7, 151.8 and 159.9 [$CH_2C_6H_2(OCH_3)_3$-2,4,6], 58.1 [$CH_2C_6H_2(OCH_3)_3$-2,4,6], 55.7 and 56.1 [$CH_2C_6H_2(OCH_3)_3$-2,4,6], 43.3 ($NCH_2CH_2CH_2N$), 19.4 ($NCH_2CH_2CH_2N$) ppm. $C_{24}H_{33}ClN_2O_6$ (480.99): calcd. C 59.93, H 6.91, N 5.82; found C 59.89, H 6.94, N 5.80.

1,3-Bis(9-anthracenomethyl)-3,4,5,6-tetrahydropyrimidinium Chloride (B7): Yield: 4.26 g (85%). M.p. 198–199 °C. IR: $\tilde{\nu}$ = 1685 ν(CN) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.90 (m, 2 H, $NCH_2CH_2CH_2N$), 3.2 (t, J = 5.6 Hz, 4 H, $NCH_2CH_2CH_2N$), 5.5 (s, 4 H, $CH_2C_{14}H_{14}$), 7.3–8.4 (m, 28 H, $CH_2C_9H_{14}$), 10.8 (s, 1 H, NCHN) ppm. ^{13}C{H}NMR (50 MHz, $CDCl_3$): δ = 18.7 ($NCH_2CH_2CH_2N$), 42.1 ($NCH_2CH_2CH_2N$), 60.1 ($CH_2C_9H_{14}$), 123.2, 125.6, 126.2, 127.5, 128.4, 128.7, 129.3, 130.2, 131.9, 133.9, 140.2 ($CH_2C_{14}H_{14}$), 156.3 (NCHN) ppm. $C_{34}H_{29}ClN_2$ (501.07): calcd. C 81.50, H 5.83, N 5.59; found C 81.49, H 5.85, N 5.58.

1,3-Bis(4-benzyloxybenzyl)benzimidazolium Chloride (C1): Yield: 4.37 g (80%). M.p. 135–136 °C. IR: $\tilde{\nu}$ = 1609 ν(CN) cm^{-1}. ^{1}H NMR (200 MHz, DMSO): δ = 5.11 [s, 4 H, $CH_2C_6H_4(OCH_2)C_6H_5$], 5.74 [s, 4 H, $CH_2C_6H_4(OCH_2)C_6H_5$], 8.05–7.046 [m, 22 H, $C_6H_4N_2CH$ and $CH_2C_6H_4(OCH_2)C_6H_5$], 10.37 (s, 1 H, NCHN) ppm. ^{13}C{H}NMR (50 MHz, DMSO): δ = 50.38 [$CH_2C_6H_4(OCH_2)$-C_6H_5], 70.14 [$CH_2C_6H_4(OCH_2)C_6H_5$], 143.28, 137.70, 131.86, 131.1, 129.4, 128.78, 128.6, 127.54, 126.96, 116.05, 114.97 $C_6H_4N_2CH$ and [$CH_2C_6H_4(OCH_2)C_6H_5$], 159.48 (NCHN) ppm. $C_{35}H_{31}ClN_2O_2$ (547.10): calcd. C 76.84, H 5.71, N 5.12; found C 76.83, H 5.75, N 5.10.

1,3-Bis(3,4,5-trimethoxybenzyl)benzimidazolium Chloride (C2): Yield: 4.63 g (90%). M.p. 248–249 °C. IR: $\tilde{\nu}$ = 1603 ν(CN) cm^{-1}. ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 3.75 and 3.61 [s, 18 H, $CH_2C_6H_2(OCH_3)_3$-3,4,5], 5.66 [s, 4 H, $CH_2C_6H_2(OCH_3)_3$-3,4,5], 7.00 [s, 4 H, $CH_2C_6H_2(OCH_3)_3$-3,4,5], 8.14 and 7.64 [m, 4 H, NC_6H_4N], 10.44 [s, 1 H, NCHN] ppm. ^{13}C NMR (50 MHz, [D$_6$]-DMSO): δ = 56.8 and 50.9 [$CH_2C_6H_2(OCH_3)_3$-3,4,5], 60.6 [$CH_2C_6H_2(OCH_3)_3$-3,4,5], 107.3, 131.7, 138.4 and 151.9 [$CH_2C_6H_2(OCH_3)_3$-3,4,5], 114.7,127.4, 129.9 and 143.2 [NC_6H_4N], 153.8 (NCHN) ppm. $C_{27}H_{31}ClN_2O_6$ (515.01): calcd. C 62.97, H 6.07, N 5.44; found C 63.00, H 6.04, N 5.49.

1,3-Bis(2,3,4-trimethoxybenzyl)benzimidazolium Chloride (C3): Yield: 4.12 g (80%). M.p. 187–188 °C. IR: $\tilde{\nu}$ = 1615 ν(CN) cm^{-1}. ^{1}H NMR (200 MHz, DMSO): δ = 3.76 [s, 6 H, $CH_2C_6H_2$-$(OCH_3)_3$-2], 3.78 [s, 6 H, $CH_2C_6H_2(OCH_3)_3$-3], 3.91 [s, 6 H, $CH_2C_6H_2(OCH_3)_3$-4], 5.72 [s, 4 H, $CH_2C_6H_2(OCH_3)_3$], 7.72–6.62 [m, 8 H, $C_6H_4N_2CH$ and $CH_2C_6H_2(OCH_3)_3$], 11.62 (s, 1 H, NCHN) ppm. ^{13}C{H}NMR (50 MHz, DMSO): δ = 56.19 [$CH_2C_6H_2(OCH_3)_3$-2], 60.98 [$CH_2C_6H_2(OCH_3)_3$-3], 61.69 [$CH_2C_6H_2(OCH_3)_3$-4], 46.69 [$CH_2C_6H_2(OCH_3)_3$], 144.34, 142.02, 131.42, 126.80, 125.717, 118.73, 113.82 $C_6H_4N_2CH$ and [$CH_2C_6H_2(OCH_3)_3$], 155.18 (NCHN) ppm. $C_{27}H_{31}ClN_2O_6$ (515.01): calcd. C 62.97, H 6.07, N 5.44; found C 62.92, H 6.09, N 5.41.

1,3-Bis(2,4,5-trimethoxybenzyl)benzimidazolium Chloride (C4): 4.48 g (87%). M.p. 166–167 °C. IR: $\tilde{\nu}$ = 1617 ν(CN) cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.75 [s, 6 H, $CH_2C_6H_2(OCH_3)_3$-2], 3.79 [s, 6 H, $CH_2C_6H_2(OCH_3)_3$-5], 3.83 [s, 6 H, $CH_2C_6H_2(OCH_3)_3$-4], 4.73 [s, 4 H, $CH_2C_6H_2(OCH_3)_3$], 7.82–6.85 [m, 8 H, $C_6H_4N_2CH$ and $CH_2C_6H_2(OCH_3)_3$], 11.70 (s, 1 H, NCHN) ppm. ^{13}C{H}NMR (50 MHz, $CDCl_3$): δ = 57.2 [$CH_2C_6H_2(OCH_3)_3$-2], 57.8 [$CH_2C_6H_2$-$(OCH_3)_3$-5], 58.2 [$CH_2C_6H_2(OCH_3)_3$-4], 48.1 [$CH_2C_6H_2(OCH_3)_3$], 145.6, 143.08, 132.48, 127.2, 126.9, 119.3, 114.5 $C_6H_4N_2CH$ and [$CH_2C_6H_2(OCH_3)_3$], 158.42 (NCHN) ppm. $C_{27}H_{31}ClN_2O_6$ (515.01): calcd. C 62.97, H 6.07, N 5.44; found C 62.93, H 6.08, N 5.42.

Representative Procedure for Etherification of Cinnamyl Chloride by Phenol: To a degassed THF (5 mL) suspension of imidazolium salt

(0.030 mmol, 6 mol-%) was added *t*BuOK (3.4 mg, 0.030 mmol, 6 mol-%), and the mixture was heated at 50 °C for 2 h and then cooled to room temperature. $[Cp^*Ru(CH_3CN)_3][PF_6]$ (7.6 mg, 0.015 mmol, 3 mol-%) was added, and the solution was heated at 50 °C for 2 h. After cooling to room temperature, THF was removed under vacuum. To the crude ruthenium–carbene catalyst was successively added acetonitrile (3 mL), cinnamyl chloride 15 (166 mg, 1 mmol, 1 equiv.), potassium carbonate (166 mg, 1.2 mmol, 1.2 equiv.) and phenol (113 mg, 1.2 mmol, 1.2 equiv.). The resulting solution was stirred overnight at room temperature. The mixture was filtered through Celite, and after concentration under vacuum, the crude mixture was analyzed by ^{1}H NMR spectroscopy. The product was then purified by column chromatography on silica gel by using heptane as the eluant.

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