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Modular Synthesis of Heterocyclic Carbene Precursors

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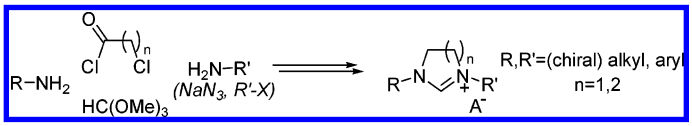

A series of *N*-heterocyclic carbene precursors, containing an imidazoline or tetrahydropyrimidine framework, were prepared from *ω*-chloroalkanoyl chlorides. The sequential attachment of nitrogen nucleophiles and subsequent ring closure gave, depending on the reagents used, either the desired dihydroimidazolium and tetrahydropyrimidinium salts or their parent heterocycles. In this latter case, the second substituent was introduced in an alkylation step. The preparation of carbene precursors bearing chiral or bulky substituents was acieved with comparable efficiency.

Introduction

Following the original reports of Öfele[1] and Wanzlick[2] on the existence of N-heterocyclic carbene (NHC)−metal complexes in 1968 and the seminal paper of Arduengo[3] describing stable NHCs, N-heterocyclic carbenes have had a spectacular career in synthetic chemistry,[4] principally as supporting ligands in transition-metal complexes. Such NHC−metal complexes have been successfully utilized in cross-coupling reactions[5] and related processes, including hydrogenation,[6] hydrosilylation,[7] hydroformylation,[8] oxidation,[9] and Pauson−Khand reactions[10] and olefin metathesis, both achiral[11] and enantioselective.[12] Some of the chiral NHC ligands were also successful in other catalytic asymmetric transformations,[13] and besides their role as ligands in metal complexes, certain NHCs also act as efficient organocatalysts.[14]

It is thus probably not surprising that the preparation of N-heterocyclic carbene precursors[15,16] and their metal complexes[17] has been extensively studied recently. The chemistry of the parent imidazole system and its analogues (oxazoles, triazoles, pyrimidines, and annulated derivatives) is well

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(4) The rapid expansion of the field was greatly facilitated by earlier contributions on stable nonheterocyclic carbenes and their metal complexes. For a comprehensive review of the related literature, see: Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39−91.
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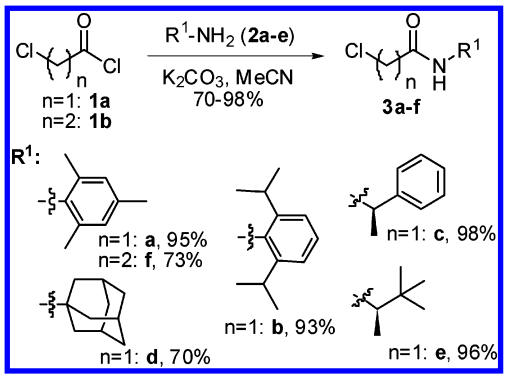
established, the preparation of tailor-made NHC precursors bearing less common substituent combinations, however, is still a challenge attracting much attention.

The aim of our research was the establishment of a modular synthetic protocol, which enables the preparation of a wide range of dihydroimidazolium salts, since this compound class gives very effective ligands both in ruthenium and palladium catalyzed transformations. Besides being carbene precursors themselves, the dihydroimidazolium salts might also be oxidized, providing access to the corresponding imidazolium salts.[18] Substituents attached to the ring nitrogen atoms included chiral groups, bulky alkyl and aryl moieties, or substituents offering additional centers for attachment or coordination of transition metals.

SCHEME 1



Results and Discussion

Our synthetic strategy was based on the construction of the heterocyclic core from readily available building blocks. Our choice for the introduction of the carbon backbone of the imidazole ring was chloroacetyl chloride (**1a**). This approach was expected to offer some advantages over reported routes utilizing the alkylation of ethylenediamine,[19] starting from oxallyl chloride and amines, as described recently by Dinger,[20] or glyoxal and amines,[21] which are biased by mediocre selectivity in the opening step. The acylation of different amines (**2a**−**e**) with **1a** under standard conditions,[22] as expected, led to the isolation of the desired amides in good yield (Scheme 1) and complete chemoselectivity. Using 3-chloropropionyl chloride (**1b**), which opens up the way to tetrahydropyrimidinium salts, amide **3f** was also prepared in somewhat lower yield.

Our first approach to NHC precursors relied on the use of *N*,*N*′-disubstituted ethylenediamine derivatives as key intermediates, since their well-established ring closure with trialkyl orthoformates was expected to give the desired dihydroimidazolium salts efficiently. The preparation of the selected diamines (**5a**−**c**) followed a two-step nucleophilic substitution-reduction sequence (Scheme 2). Amine-chloroamide combinations were chosen to provide diamines with one chiral substituent. The reaction of chloroacetamide derivatives (**3a**,**c**,**e**) with the enantiomer-enriched α-phenylethylamine (**2c**) or *O*-benzylethanolamine (**2f**) gave the desired α-aminoacetamides (**4a**−**c**) in good yield. The reduction of the resulting aminoamides (**4a**−**c**) to the corresponding ethylenediamine derivatives (**5a**−**c**) was achieved using lithium aluminum hydride: the diamines were obtained in analytical purity. Treatment of the diamines (**5a**−

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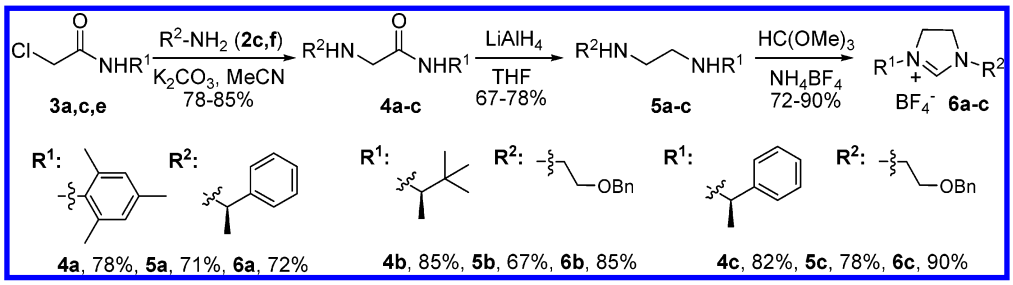
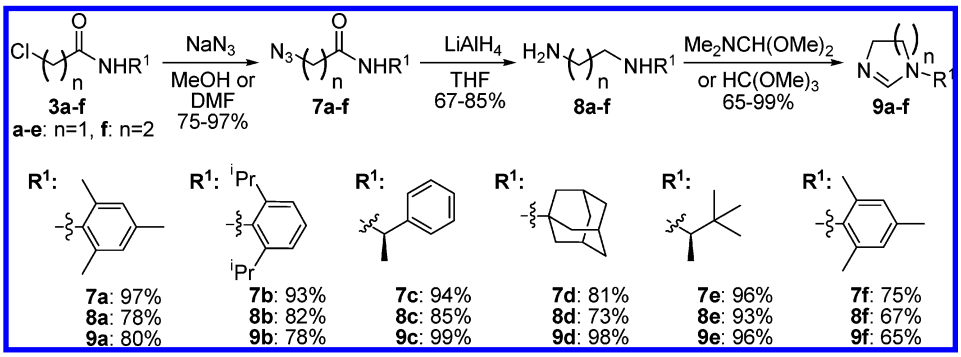
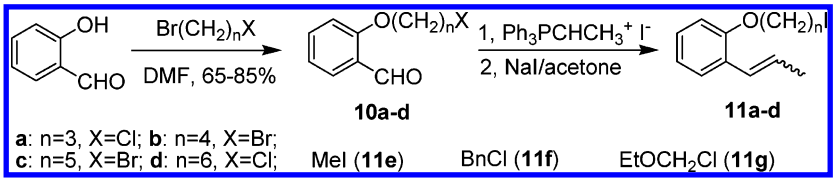
SCHEME 2



SCHEME 3



SCHEME 4. Alkylating Agents Used in the Synthesis of NHC Precursors



c) with trimethyl orthoformate in the presence of ammonium tetrafluoroborate gave the expected dihydroimidazolium salts (**6a**−**c**) in good to excellent yield; these were isolated as tetrafluoroborates. It is interesting to note that **6b** and **6c** are both chiral room-temperature ionic liquids.[23]

In our second approach preparation of the appropriate monosubstituted dihydroimidazoles was followed by the attachment of the desired side chain in the concluding alkylation step. Transformation of the *ω*-chloroacetamide (**3a**−**e**) and propionamide (**3f**) derivatives to dihydroimidazoles started (Scheme 3) by their conversion to the appropriate azides (**7a**−**f**) which in most cases proceeded in excellent yield. Concomitant reduction of the azide and amide groups by lithium aluminum hydride led to the formation of the *N*-substituted ethylenediamine derivatives (**8a**−**f**) in good yield. An alternative route to **8a**−**f** is offered by the direct amination of the chloroamides (**3a**−**f**) but our attempts in this direction gave only low yields. The conversion of the monosubstituted ethylenediamines **8a**−**f** to the desired dihydroimidazoles (**9a**−**f**) was attempted by using *N*,*N*-dimethylformamide dimethyl acetal,[24] which worked very efficiently for the alkylimidazolines **8c**−**e** and furnished the desired ring closed products **9c**−**e** in excellent yield; however in the case of the aryl-substituted amines **8a**,**b** and **8f** substantial amounts of the ring closure intermediate were present in the crude product. In these reactions complete conversion of the diamines to the ring-closed products was achieved using triethyl orthoformate[25] in the presence of catalytic amounts of concentrated hydroiodic acid. The ethylenediamine derivatives gave the arylimidazolines (**9a**,**b**) in good yield, while the analogous ring closure of **8f** was somewhat less efficient, giving the desired *N*-mesityl-1,2,3,4-tetrahydropyrimidine (**9f**) in acceptable yield.

In the final step the heterocycles (**9a**−**f**) were alkylated. Some of the alkylating agents of our choice (Scheme 4) were commercially available (**11e**−**g**), while others (**11a**−**d**) were prepared by us. These latter reagents, bearing a pendant olefin moiety, were selected on the basis of their inherent potential to act as weakly coordinating ligands or alkylidene sources in transition metal complexes. Besides its ability to be attached to a metal center, the unsaturated bond in ligands derived from **11a**−**d** also offers the possibility of further functionalization. The preparation of **11a**−**d** followed a straightforward strategy: alkylation of salicylaldehide with α,*ω*-dihalogenoalkanes gave the *O*-alkylated aldehydes (**10a**−**d**), whose carbonyl group was converted to the olefin moiety (**11a**−**d**) in a classical Wittig reaction.[26] During the Wittig reaction, which gave a 60:40 mixture of *E*- and *Z*-isomers in all cases,[27] we also observed the partial exchange of the pendant halogen by iodine, so in

(23) On the basis of chemical precedent, we presume that the utilized transformations do not erode the *R*/*S* enantiomer ratio introduced with the commercial amines (97:3 for **2c** and >99.5:0.5 for **2e**), but so far we were unable to prove this hypothesis by measuring the enantiomer ratio of the formed salts.

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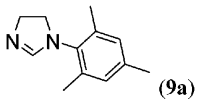
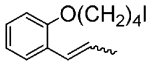
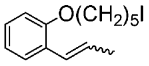
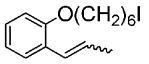
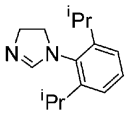
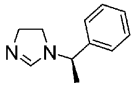
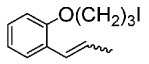
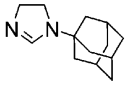
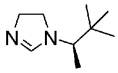
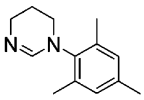
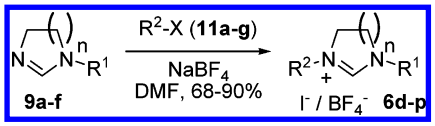
TABLE 1. 1,3-Disubstituted 4,5-Dihydroimidazolium (6d−m) and 3,4,5,6-Tetrahydropyrimidinium (6n−p) Salts Prepared by the Alkylation of the Appropriate Heterocycles (9a−f)

starting heterocycle	alkylating agent	product	Yield
 (**9a**)	 (**11b**)	**6d**	78%
	 (**11c**)	**6e**	85%
	 (**11d**)	**6f**	82%
	BnCl (**11f**)	**6g**	75%
	$EtOCH_2Cl$ (**11g**)	**6h**	88%
 (**9b**)	**11c**	**6i**	68%
	11f	**6j**	73%
 (**9c**)	 (**11a**)	**6k**	82%
 (**9d**)	MeI (**11e**)	**6l**	76%
 (**9e**)	**11f**	**6m**	85%
 (**9f**)	**11c**	**6n**	90%
	11d	**6o**	80%
	11f	**6p**	87%

SCHEME 5



order to complete the process, the crude product was converted to the iodo derivative in a Finkelstein reaction using NaI as reagent.

Alkylation of the heterocycles **9a**−**f** proceeded smoothly in DMF at elevated temperatures and the desired dihydroimidazolium (**6d**−**m**) and tetrahydropyrimidinium salts (**6n**−**p**) were isolated in good yield (Scheme 5, Table 1). The chiral dihydroimidazolium salts **6k** and **6m** are by definition also ionic liquids, having their melting points below 100 °C. The structure of the products was verified unambiguously by ^1H and ^{13}C NMR measurements, and in the case of **6o**, we observed the formation of "cubic" crystals, which were suitable for X-ray analysis. The ORTEP diagram of the unit cell of the crystal and its packing diagram are placed in the Supporting Information.

Search of the Cambridge Structural Database (Version 5.26 update Aug. 2005)[28] revealed that X-ray structure of 1,3-disubstituted 3,4,5,6-tetrahydropyrimidinium salts has been reported only for a few symmetrical systems: diisopropyl,[29] diethyl,[30] and dimesityl[31] tetrahydropyrimidinium salts were investigated and the anion (BF_4^- or PF_6^-) was often disordered. The more interesting structural features of **6o** are the proximity of C2 and I1 (3.251(4) Å) resulting in a weak C2−H2−I1 hydrogen bond, as well as the repulsion between the allylic methyl group of C39 and the disordered methylene group of C5 resulting a short C38−C39 bond (1.297(12) Å). A strong electrostatic interaction between the iodide anion and tetrahydropyrimidinium cation stabilizes the structure and the iodide ion is also close to the neighboring tetrahydropyrimidinium rings. Solution NMR results show that the compound is a mixture of *E* and *Z* isomers and it was also supported by the X-ray analysis. Based on the X-ray data and large atomic displacement parameters, the amount of the E isomer is estimated to be less than 10% in the single crystalline solid phase.

Besides their conversion to the neutral heterocycles, the *N*-substituted diamines (**8a**−**f**) might also be utilized in the preparation of such systems where the two nitrogen atoms bear different aryl moieties (Scheme 6). Buchwald−Hartwig coupling

(27) Since the envisaged application of NHCs prepared from **11a**−**d** was not influenced by the geometry of the olefin side chain, no further attempts were made to improve the *E*/*Z* selectivity of the Wittig reaction.

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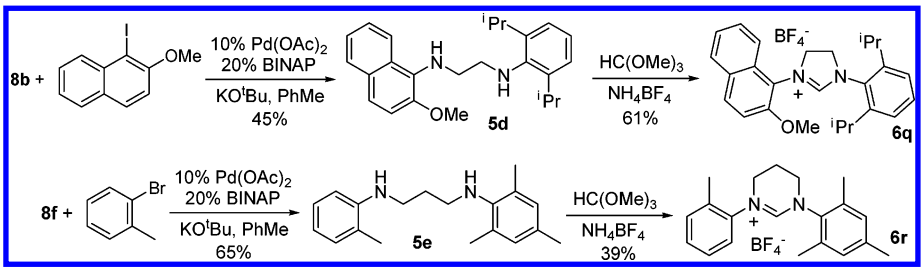
(29) Alder, R. W.; Blake, M. E.; Bortolotti, C.; Bufali, S.; Butts, C. P.; Linehan, E.; Oliva, J. M.; Orpen, G. A.; Quayle, M. J. *Chem. Commun.* **1999**, 241−242.

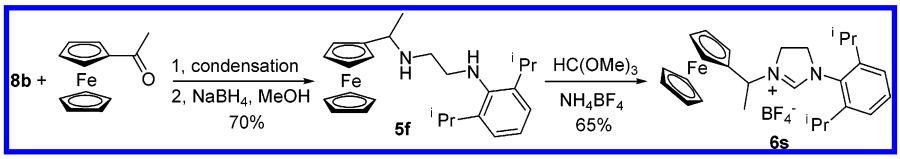
(30) Alder, R. W.; Blake, M. E.; Bufali, S.; Butts, C. P.; Orpen, G. A.; Schutz, J.; Williams, S. J. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1586−1593.

(31) (a) Hermann, W. A.; Schneider, S. K.; Ofele, K.; Sakamoto, M.; Herdtweck, E. *J. Organomet. Chem.* **2004**, *689*, 2441−2449. (b) Paulsen, A. L.; Madsen, R. *Heterocycles* **2004**, *63*, 2051−2056.

SCHEME 6



SCHEME 7



of **8b** with 1-iodo 2-methoxynaphthalene gave the *N*,*N*′-diarylethylenediamine derivative **5d**, while the coupling of the analogous **8f** with 2-bromotoluene also proceeded readily to give the appropriate propylenediamine derivative **5e**.[32] The moderate yields are due to the fact that these reaction conditions were not optimized.[33] Ring closure of the diamines (**5d**,**e**) with trimethyl orthoformate gave the desired *N*,*N*′-diaryldihydroimidazolium (**6q**) and tetrahydropyrimidinium (**6r**) salts in varying yields, the formation of the six-membered ring proceeding less efficiently, as previously observed in other cases.

The monoarylated ethylenediamine **8b** was also used to prepare a ferrocenylmethyl substituted NHC precursor (Scheme 7). Condensation of **8b** with acetylferrocene, followed by the reduction of the crude imine gave the diamine **5f** in good yield. Attempts to isolate the ferrocenylimine in pure form were unsuccessful, due to the instability of this compound, while the diamine was stable and easy to purify by column chromatography. Treatment of **5f** with trimethyl orthoformate gave the desired ferrocenylmethyldihydroimidazolium salt (**6s**) as a brownish yellow solid in acceptable yield.

Conclusion

In summary, we elaborated a series of synthetic protocols that enable the preparation of dihydromidazolium and tetrahydropyrimidinium salts bearing different substituents in positions 1 and 3. These routes rely on the use of easily available starting materials and allow for the efficient preparation of the target systems with different substituent combinations, which include chiral and achiral alkyl groups, as well as different aryl moieties; the introduction of bulky substituents, e.g., 2,6-diisopropylphenyl, posed no difficulty either. Some of the new chiral dihydroimidazolium salts were found to be ionic liquids. Study of the prepared carbene precursors as supporting ligands in metal complexes or as organocatalysts is in progress in our laboratories.

Experimental Section

General Procedure for the Preparation of Amides 3a−f. The acylating agent (**1a** or **1b**) was added dropwise with vigorous stirring to the mixture of the corresponding amine and K_2CO_3 in the appropriate solvent. Reactions were monitored by GC and TLC and were run until completion. In the cases of **3a**−**d**,**f**, the K_2CO_3 was removed by filtration, the MeCN was evaporated under reduced pressure, and the crude products were recrystallized from DCM−hexane. In the case of **3e**, the volume of the solvent was reduced to half, and following the addition of DCM the organic layer was washed with water and brine and dried over $MgSO_4$. Following the evaporation of the solvent, **3e** was obtained as white crystals.

***N*-Chloroacetylmesitylamine (3a).**[34] Starting from **2a** (10 mL, 9.63 g, 71.2 mmol), K_2CO_3 (19,6 g, 142.4 mmol), and **1a** (6.8 mL, 85.4 mmol) in 200 mL of MeCN, **3a** was obtained (14.31 g, 67.61 mmol, 95%) as a white solid: mp 178−178.5 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.83 (s, 1H), 6.9 (s, 2H), 4.21 (s, 2H), 2.27 (s, 3H), 2.18 (s, 6H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 164.5, 137.5, 134.9, 129.9, 128.9, 42.6, 20.8, 18.1. IR (KBr) 3228, 2921, 2104, 1669, 1536, 1240 cm^{-1}. Anal. Calcd for $C_{11}H_{14}ClNO$: C, 62.41; H, 6.67; N, 6.62. Found: C, 62.15; H, 6.42; N, 6.72.

***N*-Chloroacetyl-2,6-diisopropylaniline (3b).**[35] Starting from **2b** (10 mL, 9.39 g, 52.9 mmol), K_2CO_3 (14,6 g, 105.8 mmol), and **1a** (4.21 mL, 52.9 mmol) in 200 mL of MeCN, **3b** was obtained (12.48 g, 49.18 mmol, 93%) as a white solid: mp 148−149 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.83 (s, 1H), 7.36−7.19 (m, 3H), 4.26 (s, 2H), 3.11−2.94 (m, 2H), 1.22 (d, 12H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 165.3, 145.9, 129.9, 128.8, 123.6, 42.7, 28.8, 23.5. IR (KBr) 3251, 2960, 2105, 1680, 1658, 1530 cm^{-1}. Anal. Calcd for $C_{14}H_{20}ClNO$: C, 66.26; H, 7.94; N, 5.52. Found: C, 66.73; H, 7.66; N, 5.28.

***N*-Chloroacetyl-(1*R*)-(+)-1-phenylethylamine (3c).**[22] Starting from **2c** (9.65 g, 10 mL, 77.5 mmol), K_2CO_3 (21.39 g, 155 mmol), and **1a** (6.14 mL, 77.5 mmol) in 200 mL of MeCN, **3c** was obtained (15.01 g, 75.95 mmol, 98%) as a white solid: mp 101−102 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.38−7.25 (m, 5H), 6.85 (s, 1H), 5.12 (quint., 1H, J = 7.0 Hz), 4.02 (dd, 2H, J = 15.2 Hz, J = 2.5 Hz), 1.52 (d, 3H, J = 6.9); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 164.9, 142.2, 128.7, 127.5, 126.0, 49.2, 42.5, 21.6; $[\alpha]_{546}$ = +64.8 (*c* 5.09, CH_2Cl_2); IR (KBr) 3261, 2978, 1650, 1548, 1233 cm^{-1}. Anal. Calcd for $C_{10}H_{12}ClNO$: C, 60.76; H, 6.12; N, 7.09. Found: C, 60.96; H, 5.98; N, 6.92.

***N*-Chloroacetyl-1-aminoadamantane (3d).**[36] Starting from **2d** (10.0 g, 66.1 mmol), K_2CO_3 (18.24 g, 132 mmol), and **1a** (5.26 mL, 66.1 mmol) in 200 mL of MeCN, **3d** was obtained (10.53 g, 46.24 mmol, 70%) as an off-white solid: mp 119−120 °C; ^{1}H NMR

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(33) The same *N*,*N*′-disubstituted diamines might also be prepared in comparable yields in the reaction of the chloroacetamide **3b** or chloropropionamide **3f** and the appropriate aromatic amines. Paczal, A.; Kotschy, A. Unpublished results.

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(35) Phillips, G. B.; Morgan, T. K.; Nickisch, K.; Lind, J. M.; Gomez, R. P.; et al. *J. Med. Chem.* **1990**, *33*, 627−633.

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($CDCl_3$, 250 MHz) δ 6.22 (s, 1H), 3.90 (s, 2H), 2.12−2.03 (m, 3H), 2.03−1.95 (m, 6H), 1.66 (t, 6H, J = 2.8 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 164.5, 52.3, 42.8, 41.1, 36.1, 29.3; IR (KBr) 3238, 3082, 2905, 2105, 1661, 1567, 1236 cm^{-1}. Anal. Calcd for $C_{12}H_{18}ClNO$: C, 63.29; H, 7.97; N, 6.15. Found: C, 63.12; H, 7.85; N, 6.32.

***N*-Chloroacetyl-(2*R*)-(−)-3,3-dimethyl-2-aminobutane (3e).**[37] Starting from **2e** (5 mL, 3.62 g, 35.8 mmol), K_2CO_3 (9.88 g, 71.4 mmol), and **1a** (2.84 mL, 35.8 mmol) in 100 mL of MeCN and 25 mL of H_2O, **3e** was obtained (6.10 g, 34.36 mmol, 96%) as a white solid: mp 71−71.5 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.46 (s, 1H), 4.03 (s, 2H), 3.90−3.78 (m, 1H), 1.07 (d, 3H, J = 6.8 Hz), 0.89 (s, 9H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 164.9, 53.3, 42.8, 34.1, 26.0, 15.8; $[\alpha]_{546}$ = −33 (*c* 5.00, CH_2Cl_2); IR (KBr) 3292, 2966, 1649, 1554 cm^{-1}. Anal. Calcd for $C_8H_{16}ClNO$: C, 54.08; H, 9.08; N, 7.88. Found: C, 54.34; H, 9.22; N, 7.81.

***N*-(3′-Chloropropionyl)mesitylamine (3f).**[38] Starting from **2a** (10 mL, 9.63 g, 71.2 mmol), K_2CO_3 (19,6 g, 142.4 mmol), and **1b** (6.8 mL, 71.2 mmol) in 200 mL of MeCN, **3f** was obtained (11.73 g, 51.97 mmol, 73%) as a light yellow solid: mp 130−131 °C; obtained as a 9:1 mixture of syn/anti amide rotamers; ^{1}H NMR ($CDCl_3$, 250 MHz) syn δ 7.64 (s, 1H), 6.76 (s, 2H), 3.76 (t, 2H, J = 6.2 Hz), 2.67 (t, 2H, J = 6.2 Hz), 2.22 (s, 3H), 2.05 (s, 6H); anti δ 7.64 (s, 1H), 6.93 (s, 2H), 3.72 (t, 2H, J = 6.4 Hz), 2.35 (t, 2H, J = 6.4 Hz), 2.30 (s, 3H), 2.20 (s, 6H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) syn δ 168.5, 136.6, 134.9, 130.9, 128.6, 40.3, 39.1, 20.8, 18.1; anti δ 172.1 138.2, 136.2, 131.1, 129.3, 38.9, 34.9, 20.8, 18.3. Anal. Calcd for $C_{12}H_{16}ClNO$: C, 63.85; H, 7.14; N, 6.21. Found: C, 64.02; H, 6.94; N, 6.33.

General Procedure for the Preparation of Aminoamides 4a−c. A mixture of the chloroamide (**3a**,**c**,**f**), 2 equiv of the corresponding amine (**2c**,**f**), and 2 equiv K_2CO_3 were refluxed in MeCN until the reaction was judged complete by GC or TLC. Following removal of K_2CO_3 by filtration, the solvent was evaporated under reduced pressure. The crude products were purified by column chromatography (**4a**) or by short path distillation at 190−200 °C, 0.2 mbar (**4b** and **4c**).

***N*-Mesityl-2-((1′*R*)-1′-phenylethylamino)acetamide (4a).** Starting from **3a** (1.20 g, 6 mmol), **2c** (1.45 g, 12 mmol), and K_2CO_3 (1.65 g, 12 mmol) in 50 mL of MeCN, **4a** was obtained (1.37 g, 4.62 mmol, 82%) as a white solid: mp 68 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.63 (s, 1H), 7.36−7.21 (m, 5H), 6.86 (s, 2H), 3.82 (q, 1H, J = 6.6 Hz), 3.29 (s, 2H), 2.24 (s, 3H), 2.12 (s, 6H), 2.01 (s, 1H), 1.41 (d, 3H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 170.2, 144.2, 136.5, 134.6, 131.0, 128.7, 128.5, 127.3, 126.4, 58.3, 50.2, 23.8, 20.7, 18.2; $[\alpha]_{546}$ = +48.7 (*c* 5.17, CH_2Cl_2); IR (KBr) 3324, 3285, 2973, 2911, 1674, 1497 cm^{-1}. Anal. Calcd for $C_{19}H_{24}N_2O$: C, 76.99; H, 8.16; N, 9.45. Found: C, 76.61; H, 8.18; N, 9.37.

2-(2′-Benzyloxyethylamino)-*N*-((2*R*)-3,3-dimethylbut-2-yl)-acetamide (4b). Starting from **3e** (1.20 g, 6.7 mmol), 2-benzyloxyethylamine (2.04 g, 13.4 mmol), and K_2CO_3 (1.85 g, 13.4 mmol) in 50 mL of MeCN, **4b** was obtained (1.61 g, 5.49 mmol, 82%) as yellow oil: ^{1}H NMR (DMSO-d_6, 250 MHz) δ 7.50 (d, 1H, J = 9.6 Hz), 7.37−7.23 (m, 5H), 4.47 (s, 2H), 3.74−3.62 (m, 1H), 3.47 (t, 2H, J = 5.6 Hz), 4.4−3.12 (br s, 1H), 2.65 (t, 2H, J = 5.6 Hz), 0.94 (d, 3H), 0.81 (s, 9H); ^{13}C NMR (DMSO-d_6, 62.5 MHz) δ 170.1, 138.4, 128.4, 128.1, 127.4, 127.3, 71.9, 69.4, 51.9, 51.3, 48.6, 33.8, 26.0, 15.7; $[\alpha]_{546}$ = −10.4 (*c* 2.5, CH_2Cl_2); IR (KBr) 3316, 2962, 2868, 1655, 1521, 1096, 736, 698 cm^{-1}. Anal. Calcd for $C_{17}H_{28}N_2O_2$: C, 69.83; H, 9.65; N, 9.58. Found: C, 69.65; H, 9.88; N, 9.32.

2-(2′-Benzyloxyethylamino)-*N*-((1*R*)-1-phenylethyl)acetamide (4c). Starting from **3c** (1.20 g, 6 mmol), 2-benzyloxyethylamine (1.82 g, 12 mmol), and K_2CO_3 (1.65 g, 12 mmol) in 50 mL of MeCN, **4c** was obtained (1.58 g, 5.05 mmol, 85%) as a yellow oil: ^{1}H NMR (DMSO-d_6, 250 MHz) δ 8.2 (d, 1H, J = 8.2 Hz), 7.34−7.16 (m, 10H), 4.95 (quint., 1H, J = 7.0 Hz), 4.46 (s, 2H), 3.48 (t, 2H, J = 5.4 Hz), 3.13 (s, 2H), 2.67 (t, 2H, J = 5.4 Hz) 2.4−2.2 (br s, 1H), 1.34 (d, 3H, J = 7.0 Hz); ^{13}C NMR (DMSO-d_6, 62.5 MHz) δ 170.2, 144.4, 138.4, 128.2, 128.1, 127.4, 127.3, 126.5, 125.8, 71.8, 69.3, 51.9, 48.5, 47.4, 22.3; $[\alpha]_{546}$ = +38.9 (*c* 1.98, CH_2Cl_2); IR (KBr) 3313, 2862, 1655, 1603, 1095, 738, 697 cm^{-1}. Anal. Calcd for $C_{19}H_{24}N_2O_2$: C, 73.05; H, 7.74; N, 8.97. Found: C, 72.92; H, 7.59; N, 8.78.

General Procedures for the Preparation of Ethylenediamine Derivatives. By Reduction of Aminoacetamides (5a−c). The mixture of the aminoamide (**4a−c**) and 4 equiv of $LiAlH_4$ was refluxed in freshly distilled THF under Ar until the reaction was judged complete by GC or TLC. The compounds were used in the next steps without purification.

In Buchwald−Hartwig Coupling (5d,e). A mixture of the monosubstituted ethylenediamine (**8b**,**f**), 1 equiv of aryl halide, 4 equiv of KO^{t}Bu, 10 mol % of $Pd(OAc)_2$, and 20 mol % of (±)-BINAP in 10 mL of toluene/mmol substrate was heated under Ar atmosphere at 100 °C until the reaction was judged complete by GC. The reaction mixtures were filtered trough Celite, and after evaporation of the volatiles in vacuo the crude product was purified by column chromatography (Hex/EtOAc as eluent).

***N*-Mesityl-*N*′-((1*R*)-1-phenylethyl)ethylenediamine (5a).** Starting from **4a** (1.5 g, 7.08 mmol) and $LiAlH_4$ (1.07 g, 28.32 mmol) in 100 mL of THF, **5a** was obtained (1.01 g, 3.6 mmol, 71%) as yellow oil: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.32−7.19 (m, 5H), 6.79 (s, 2H), 3.77 (q, 1H, J = 6.6 Hz), 3.00−2.95 (m, 2H), 2.75−2.58 (m, 2H), 2.24 (s, 6H), 2.21 (s, 3H), 1.37 (d, 3H, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 145.7, 143.8, 129.4, 128.4, 126.8, 126.5, 58.2, 48.6, 47.9, 24.3, 20.5, 18.4; $[\alpha]_{546}$ = +26.8 (*c* 3.06, CH_2Cl_2); IR (KBr) 3359, 2971, 2922, 2848, 1484, 1434, 1242, 1119, 762, 700 cm^{-1} Anal. Calcd for $C_{19}H_{26}N_2$: C, 80.80; H, 9.28; N, 9.92. Found: C, 80.68; H, 9.46; N, 9.69.

***N*-(2-Benzyloxyethyl)-*N*′-(2*R*-3,3-dimethylbut-2-yl)ethylenediamine (5b).** Starting from **4b** (1 g, 3.42 mmol) and $LiAlH_4$ (389 mg, 10.26 mmol) in 50 mL of THF, **5b** was obtained (790 mg, 2.84 mmol, 83%) as a yellow oil: ^{1}H NMR (DMSO-d_6, 250 MHz) δ 7.33−7.23 (m, 5H), 4.46 (s, 2H), 3.48 (t, 2H, J = 5.6 Hz), 2.76−2.66 (m, 3H), 2.58−2.53 (m, 2H), 2.46−2.37 (m, 1H), 2.10 (q, 1H, J = 6.5 Hz), 1.8−1.2 (br s, 2H), 0.89 (d, 3H, J = 6.5 Hz), 0.82 (s, 9H); ^{13}C NMR (DMSO-d_6, 62.5 MHz) δ 138.5, 128.0, 127.2, 127.1, 71.8, 69.5, 61.4, 49.2, 48.6, 47.8, 34.1, 26.2, 14.6; $[\alpha]_{546}$ = −40.36 (*c* 5.5, CH_2Cl_2); IR (KBr) 3324, 3030, 2866, 1665, 1453, 1362, 1097, 735, 697 cm^{-1}. Anal. Calcd for $C_{17}H_{30}N_2O$: C, 73.33; H, 10.86; N, 10.06. Found: C, 73.11; H, 10.81; N, 9.98.

***N*-(2-Benziloxyethyl)-*N*′-((1*R*)-1-phenylethyl)ethylenediamine (5c).** Starting from **4c** (1.00 g, 3.2 mmol) and $LiAlH_4$ (364 mg, 9.6 mmol) in 50 mL of THF, **5c** was obtained (740 mg, 2.49 mmol, 78%) as a yellow oil: ^{1}H NMR (DMSO-d_6, 250 MHz) δ 7.37−7.14 (m, 10H), 4.45 (s, 2H), 3.64 (q, 1H, J = 6.8 Hz), 3.45 (t, 2H, J = 5.6 Hz), 2.63 (t, 2H, J = 5.6 Hz), 2.56−2.46 (m, 3H), 2.44−2.28 (m, 3H), 1.20 (d, 3H, J = 6.8 Hz); ^{13}C NMR (DMSO-d_6, 62.5 MHz) δ 146.3, 138.5, 128.1, 128.0, 127.3, 127.2, 126.3, 71.8, 69.4, 57.5, 49.0, 48.5, 46.8, 24.5; $[\alpha]_{546}$ = +23.4 (*c* 4.99, CH_2Cl_2); IR (KBr) 3313, 2862, 1655, 1516, 1452, 1095, 738, 697 cm^{-1}. Anal. Calcd for $C_{19}H_{26}N_2$: C, 76.47; H, 8.78; N, 9.39. Found: C, 76.22; H, 9.05; N, 9.33.

***N*-(2,6-Diisopropylphenyl)-*N*′-(2-methoxynaphth-1-yl)ethylenediamine (5d).** Starting from **8b** (220 mg, 1 mmol) and 1-iodo-2-methoxynaphthalene (284 mg, 1 mmol), **5d** was obtained (169 mg, 0.45 mmol, 45%) as a brown oil: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.17 (d, 1H, J = 9.0 Hz), 7.75 (d, 1H, J = 8.7 Hz), 7.51−7.39 (m, 2H), 7.34−7.21 (m, 2H), 7.14−7.00 (m, 3H), 4.4−3.4 (br s, 2H), 3.92 (s, 3H), 3.53 (t, 2H, J = 5.4 Hz), 3.30 (hept, 2H, J = 6.8 Hz), 3.04 (t, 2H, J = 5.98 Hz), 1.20 (d, 12H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 147.7, 143.3, 142.5, 131.7, 129.9,

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128.3, 128.4, 123.7, 123.6, 123.5, 122.7, 122.6, 113.3, 56.7, 51.9, 50.3, 27.6, 24.2; IR (KBr) 3360, 2959, 1594, 1512, 1460, 1263, 799, 736 cm^{-1}. Anal. Calcd for $C_{25}H_{32}N_2O$: C, 79.75; H, 8.57; N, 7.44. Found: C, 79.98; H, 8.85; N, 7.35.

***N*-Mesityl-*N*′-(*o*-tolyl)propylenediamine (5e).** Starting from **8e** (385 mg, 2 mmol) and 2-bromotoluene (342 mg, 2 mmol), **5e** was obtained (366 mg, 1.3 mmol, 65%) as a brown oil: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.14−7.01 (m, 2H), 6.80 (s, 2H), 6.67−6.58 (m, 2H), 3.4 (br s, 2H), 3.28 (t, 2H, J = 6.6 Hz), 3.05 (t, 2H, J = 6.6 Hz), 2.23 (s, 6H), 2.21 (s, 3H), 2.09 (s, 3H), 1.91 (quint, 2H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 146.2, 143.3, 131.4, 129.9, 129.7, 129.4, 127.0, 121.8, 116.7, 109.4, 47.2, 42.4, 30.6, 20.5, 18.2, 17.4; IR (KBr) 1666, 1313, 1051, 986 cm^{-1}. Anal. Calcd for $C_{19}H_{26}N_2$: C, 80.80; H, 9.28; N, 9.92. Found: C, 80.56; H, 9.56; N, 9.90.

***N*-(2,6-Diisopropylphenyl)-*N*′-(1-ferrocenylethyl)ethylenediamine (5f).** Compound **8b** (0.965 g, 4.4 mmol), acetylferrocene (1.00 g, 4.4 mmol), and a catalytic amount of *p*-TsOH were dissolved in 50 mL of toluene and refluxed in a vessel equipped with a Dean−Stark distillation head for 5 h. The solvent was removed under reduced pressure to give 1.57 g of the crude product, which was used without further purification. The reduction of the Schiff base was carried out in 50 mL of methanol by stirring with 690 mg (18 mmol, 5 equiv) of $NaBH_4$ at room temperature for 2 h. The crude product was purified by flash chromatography using hexanes−ethyl acetate as eluent. Compound **5f** was obtained (1.39 g, 3.22 mmol, 70%) as a brown oil: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.16−7.05 (m, 3H), 4.24−4.15 (m, 9H), 3.62 (q, 1H, J = 6.6 Hz), 3.58 (hept, 2H, J = 6.8 Hz), 3.09−2.83 (m, 4H), 1,47 (d, 3H, J = 6.6 Hz), 1.58 (d, 12H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 143.6, 142.2, 123.4, 93.8, 68.3, 67.3, 67.2, 67.0, 65.7, 52.1, 51.7, 47.5, 27.5, 24.3, 21.6; IR (KBr) 2965, 1639, 1263, 1145, 1073 cm^{-1}. Anal. Calcd for $C_{26}H_{36}FeN_2$: C, 72.22; H, 8.39; N, 6.48. Found: C, 72.09; H, 8.25; N, 6.42.

General Procedure for the Preparation of Dihydroimidazolium and Tetrahydropyrimidinium Salts. By the Ring Closure of Diamines(6a−c,q−s). The appropriate diamine was refluxed in 20 equiv of trimethyl orthoformate in the presence of 1.1 equiv of NH_4BF_4 under argon atmosphere until its consumption. The volatiles were removed under reduced pressure, and the residue was dissolved in a little DCM and precipitated by the addition of diethyl ether. The precipitate was filtered and recrystallized from toluene/butanol except for **6b** and **6c**, which are liquid at ambient temperature, and purified by column chromatography using ethyl acetate−methanol as eluent.

By the Alkylation of Dihydroimidazoles or Tetrahydropyrimidines (6d−p). A solution of the parent heterocycle and 1 equiv of the alkylating agent was heated in DMF at 100 °C under argon until the reaction was judged complete by TLC. After the solution was cooled to room temperature, the solvent was removed in a vacuum, and the residue was dissolved in MeCN and stirred with 10 equiv of $NaBF_4$ overnight. After evaporation of the solvent, the solid was dissolved in DCM. Following removal of the inorganics by filtration, the products were precipitated by the addition of diethyl ether and purified by crystallization from DCM−ether.

3-Mesityl-1-((1′*R*)-1′-phenylethyl)-4,5-dihydroimidazolium Tetrafluoroborate (6a). Starting from **5a** (500 mg, 1.77 mmol) and NH_4BF_4 (185 mg, 1.77 mmol) in 5 mL of trimethyl orthoformate, **6a** was obtained (484 mg, 1.27 mmol, 72%) as a white solid: mp 119−120 °C; 1H NMR ($CDCl_3$, 250 MHz) δ 8.02 (s, 1H), 7.39−7.35 (m, 5H), 6.88 (s, 2H), 5.15 (q, 1H, J = 6.8 Hz), 4.17−3.99 (m, 4H), 2.24 (s, 3H), 2.22 (s, 6H), 1.75 (d, 3H, J = 6,8 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 156.8, 140.2, 137.2, 135.3, 130.6, 129.9, 129.4, 129.1, 127.0, 58.1, 50.8, 46.8, 20.9, 18.6, 17.4; $[\alpha]_{546}$ = +16.2 (*c* 2.02, CH_2Cl_2); IR (KBr) 3415, 2978, 1634, 1455, 1057, 703 cm^{-1}. Anal. Calcd for $C_{20}H_{25}N_2BF_4$: C, 63.18; H, 6.63; N, 7.37. Found: C, 62.85; H, 6.66; N, 7.32.

3-(2′-Benzyloxyethyl)-1-((2′*R*)-3′,3′-dimethylbut-2′-yl)-4,5-dihydroimidazolium Tetrafluoroborate (6b). Starting from **5b** (210 mg, 0.75 mmol) and NH_4BF_4 (86.6 mg, 0.82 mmol) in 2 mL of trimethyl orthoformate, **6b** was obtained (241 mg, 0.64 mmol, 85%) as a colorless liquid: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.00 (s, 1H), 7.35−7.23 (m, 5H), 4.50 (s, 2H), 4.00−3.90 (m, 4H), 3.75−3.62 (m, 4H), 3.49 (q, 1H, J = 7.0 Hz), 1.26 (d, 3H, J = 7.0 Hz), 0.90 (s, 9H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 157.9, 137.3, 128.2, 127.7, 72.7, 65.9, 63.2, 48.4, 48.1, 47.5, 34.9, 26.3, 13.2; $[\alpha]_{546}$ = −21 (*c* 6.2, CH_2Cl_2); IR (KBr) 2971, 2876, 1645, 1057, 909, 727 cm^{-1}. Anal. Calcd for $C_{18}H_{29}BF_4N_2O$: C, 57.46; H, 7.77; N, 7.45. Found: C, 57.26; H, 7.84; N, 7.32.

3-(2′-Benzyloxyethyl)-1-((1′*R*)-1′-phenylethyl)-4,5-dihydroimidazolium Tetrafluoroborate (6c). Starting from **5c** (500 mg, 1.67 mmol) and NH_4BF_4 (175 mg, 1.67 mmol) in 5 mL of trimethyl orthoformate, **6c** was obtained (595 mg, 1.5 mmol, 90%) as a colorless liquid: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.19 (s, 1H), 7.41−7.24 (m, 10H), 4.74 (q, 1H, J = 7.00 Hz), 4.51 (s, 2H), 3.98−3.83 (m, 2H), 3.76−3.63 (m, 6H), 1.69 (d, 3H, J = 7 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 156.5, 137.5, 137.5, 129.3, 128.9, 128.5, 127.9, 127.8, 126.7, 73.0, 66.6, 58.2, 49.0, 48.1, 47.0, 19.3; $[\alpha]_{546}$ = +6.64 (*c* 4.02, CH_2Cl_2); IR (KBr) 3030, 2925, 1646, 1051, 1034, 748, 701 cm^{-1}. Anal. Calcd for $C_{20}H_{25}BF_4N_2O$: C, 60.62; H, 6.36; N, 7.07. Found: C, 60.89; H, 6.36; N, 6.82.

1-Mesityl-3-(4′-[2″-propenylphenyl]butyl)-4,5-dihydroimidazolium Iodide (6d). Starting from **9a** (250 mg, 1.32 mmol) and **11b** (417 mg, 1.32 mmol) in 10 mL of DMF, **6d** was obtained (514 mg, 1.02 mmol, 78%) as a white solid: mp 132−133 °C; a 7:3 mixture of *Z* and *E* isomers; ^{1}H NMR ($CDCl_3$, 250 MHz) *E*: δ 8.95 (s, 1H), 7.37−7.09 (m, 2H), 6.90−6.79 (m, 4H), 6.67 (dd, 1H, J = 15.7 Hz, J = 1.4 Hz), 6.18 (dq, 1H, J = 15.7 Hz, J = 6.4 Hz), 4.33−4.08 (m, 4H), 4.02−3.89 (m, 4H), 2.23 (s, 6H), 2.22 (s, 3H), 2.00−1.72 (m, 7H); *Z*: δ 8.90 (s, 1H), 7.37−7.09 (m, 2H), 6.90−6.79 (m, 4H), 6.48 (dd, 1H, J = 11.8 Hz, J = 1.5 Hz), 5.72 (dq, 1H, J = 11.8 Hz, J = 7.1 Hz), 4.33−4.08 (m, 4H), 4.02−3.89 (m, 4H), 2.23 (s, 6H), 2.22 (s, 3H), 2.00−1.72 (m, 7H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 157.8, 155.8, 154.9, 140.1, 140.0, 135.1, 130.2, 129.9, 129.7, 127.9, 127.7, 126.8, 126.6, 126.2, 126.1, 125.9, 125.3, 125.0, 120.6, 120.0, 111.9, 111.6, 67.2, 67.1, 50.8, 49.0, 48.2, 25.8, 25.7, 23.9, 23.8, 20.9, 20,8, 18.9, 18.2, 14.5; IR (KBr) 3032, 2970, 1642, 1486, 1448, 1243, 1229 cm^{-1}. Anal. Calcd for $C_{25}H_{33}IN_2O$: C, 59.52; H, 6.59; N, 5.55. Found: C, 59.44; H, 6.42; N, 5.25.

1-Mesityl-3-(5′-[2″-propenylphenyl]pentyl)-4,5-dihydroimidazolium Iodide (6e). Starting from **9a** (500 mg, 2.64 mmol) and **11c** (872 mg, 2.64 mmol) in 10 mL of DMF, **6e** was obtained (1.16 g, 2.24 mmol) as white solid: mp 153−154 °C; a 90:10 mixture of *Z* and *E* isomers; ^{1}H NMR ($CDCl_3$, 250 MHz) *E*: δ 8.44 (s, 1H), 7.34 (d, 1H, J = 7.6 Hz), 7.10 (t, 1H, J = 7.3 Hz), 6.87−6.78 (m, 4H), 6.66 (d, 1H, J = 15.9 Hz), 6.24−6.10 (m, 1H), 4.25−4.09 (m, 4H), 3.93 (t, 2H, J = 5.8 Hz), 3.75 (t, 2H, 6.4 Hz), 2.22 (s, 3H), 2.20 (6H), 1.89−1.78 (m, 7H), 1.70−1.52 (m, 2H); *Z*: 8.44 (s, 1H), 7.34 (d, 1H, J = 7.6 Hz), 7.10 (t, 1H, J = 7.3 Hz), 6.87−6.78 (m, 4H), 6.51 (d, 1H, J = 10.7 Hz), 5.82−5.69 (m, 1H), 4.25−4.09 (m, 4H), 3.93 (t, 2H, J = 5.8 Hz), 3.75 (t, 2H, 6.4 Hz), 2.22 (s, 3H), 2.20 (6H), 1.89−1.78 (m, 7H), 1.70−1.52 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 157.7, 156.0, 155.2, 139.9, 135.1, 130.2, 129.7, 129.6, 127.7, 127.6, 126.7, 126.6, 126.2, 125.9, 125.8, 125.3, 124.9, 120.4, 119.7, 111.8, 111.5, 67.5, 65.5, 50.7, 48.7, 48.2, 28.4, 26.6, 22.6, 20.7, 18.7, 17.6, 15.0, 14.5; IR (KBr) 3015, 2866, 1643, 1488, 1444, 1244, 1055, 763 cm^{-1}. Anal. Calcd for $C_{26}H_{35}IN_2O$: C, 60.23; H, 6.80; N, 5.40. Found: C, 60.13; H, 6.89; N, 5.35%.

1-Mesityl-3-(6′-[2″-propenylphenyl]hexyl)-4,5-dihydroimidazolium Iodide (6f). Starting from **9a** (250 mg, 1.32 mmol) and **11d** (454 mg, 1.32 mmol) in 10 mL of DMF, **6f** was obtained (575 mg, 1.08 mmol, 82%) as a white solid: mp 114−115 °C; a 7:3 mixture of *Z* and *E* isomers; ^{1}H NMR ($CDCl_3$, 250 MHz) *E*: δ 8.81 (s, 1H), 7.37−7.09 (m, 2H), 6.92−6.80 (m, 4H), 6.69 (d, 1H, J = 15.6 Hz), 6.27−6.13 (m, 1H), 4.33−4.12 (m, 4H), 3.94 (t, 2H, J = 5.8 Hz), 3.83 (t, 2H, J = 6.3 Hz), 2.25 (s, 9H), 1.89−1.76

(m, 7H), 1.59−1.43 (m, 4H); *Z*: δ 8.81 (s, 1H), 7.37−7.09 (m, 2H), 6.92−6.80 (m, 4H), 6.54 (d, 1H, *J* = 11.5 Hz), 5.85−5.72 (m, 1H), 4.33−4.12 (m, 4H), 3.94 (t, 2H, *J* = 5.8 Hz), 3.83 (t, 2H, *J* = 6.3 Hz), 2.25 (s, 9H), 1.89−1.76 (m, 7H), 1.59−1.43 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 157.6, 156.1, 155.3, 139.9, 135.0, 130.2, 129.7, 129.6, 127.7, 127.5, 126.7, 126.2, 126.1, 126.0, 125.9, 125.4, 124.9, 120.3, 119.6, 111.8, 111.4, 67.7, 67.6, 50.8, 49.0, 48.3, 28.8, 26.8, 25.7, 25.6, 25.3, 20.7, 18.8, 18.0, 14.5; IR (KBr) 3033, 2862, 1645, 1489, 1449, 1239, 1051, 750 cm^{-1}. Anal. Calcd for $C_{27}H_{37}IN_2O$: C, 60.90; H, 7.00; N, 5.26. Found: C, 60.95; H, 7.09; N, 5.31.

3-Benzyl-1-mesityl-4,5-dihydroimidazolium Tetrafluoroborate (6g). Starting from **9a** (1.00 g, 5.3 mmol) and **11f** (672 mg, 5.3 mmol, 0.61 mL) in 25 mL of DMF, **6g** was obtained (1.45 g, 3.98 mmol, 75%) as a white solid: mp 142−143 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.14 (s, 1H), 7.44−7.30 (m, 5H), 6.85 (s, 2H), 4.76 (s, 2H), 4.18−3.82 (m, 4H), 2.22 (s, 3H), 2.19 (s, 6H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 157.8, 140.1, 135.3, 132.4, 130.5, 129.8, 129.3, 129.1, 129.0, 52.1, 50.1, 48.2, 20.9, 17.3; IR (KBr) 3019, 1643, 1488, 1218, 1050 cm^{-1}. Anal. Calcd for $C_{19}H_{23}BF_4N_2O$: C, 62.32; H, 6.33; N, 7.65. Found: C, 62.41; H, 6.19; N, 7.56.

3-Ethoxymethyl-1-mesityl-4,5-dihydroimidazolium Tetrafluoroborate (6h). Starting from **9a** (200 mg, 1.06 mmol) and **11g** (100 mg, 1.06 mmol, 49.3 μL) in 5 mL of DMF, **6h** was obtained (311 mg, 0.93 mmol, 88%) as a white solid: mp 120−121 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.27 (s, 1H), 6.91 (s, 2H), 5.03 (s, 2H), 4.31−4.12 (m, 4H), 3.58 (q, 2H, *J* = 7.0 Hz), 2.28 (s, 3H), 2.23 (s, 6H), 1.23 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 158.8, 140.4, 135.2, 130.1, 129.9, 78.0, 64.9, 51.3, 47.0, 21.0, 17.3, 14.8; IR (KBr) 3080, 2981, 1643, 1115, 1070 cm^{-1}. Anal. Calcd for $C_{15}H_{23}BF_4N_2O$: C, 53.91; H, 6.94; N, 8.38. Found: C, 53.83; H, 6.89; N, 8.52.

1-(2′,6′-Diisopropylphenyl)-3-(5′-[2"-propenylphenyl]pentyl)-4,5-dihydroimidazolium Iodide (6i). Starting from **9b** (200 mg, 0.87 mmol) and **11c** (275 mg, 0.87 mmol) in 5 mL of DMF, **6i** was obtained (307 mg, 0.59 mmol, 68%) as a white solid: mp 117−118 °C; a 60:40 mixture of *Z* and *E* isomers; ^{1}H NMR ($CDCl_3$, 250 MHz) *E*: δ 8.96 (s, 1H), 7.42−7.10 (m, 5H), 6.94−6.81 (m, 2H), 6.70 (dd, 1H, *J* = 15.9 Hz, *J* = 1.7 Hz), 6.20 (dq, 1H, *J* = 15.9 Hz, *J* = 6.6 Hz), 4.40−4.15 (m, 4H), 3.99−3.90 (m, 4H), 2.88 (hept, 2H, *J* = 6.7 Hz), 1.95−1.79 (m, 7H), 1.63−1.54 (m, 2H), 1.21 (dd, 12H, *J* = 6.6 Hz, *J* = 4.8 Hz); *Z*: δ 8.94 (s, 1H), 7.42−7.10 (m, 5H), 6.94−6.81 (m, 2H), 6.53 (dd, 1H, *J* = 11.8 Hz, *J* = 1.7 Hz), 5.77 (dq, 1H, *J* = 11.8 Hz, *J* = 6.5 Hz), 4.40−4.15 (m, 4H), 3.99−3.90 (m, 4H), 2.88 (hept, 2H, *J* = 6.7 Hz), 1.95−1.79 (m, 7H), 1.63−1.54 (m, 2H), 1.21 (dd, 12H, *J* = 6.6 Hz, *J* = 4.8 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 157.6, 156.2, 155.3, 146.4, 130.9, 129.9, 129.6, 127.8, 127.7, 126.8, 126.3, 126.1, 125.9, 125.5, 125.1, 124.7, 120.5, 119.8, 111.9, 111.6, 67.7, 67.6, 53.3, 49.3, 48.4, 28.6, 28.5, 26.8, 26.7, 25.0, 23.9, 22.7, 18.9, 14.6; IR (KBr) 2958, 1645, 1447, 1239, 1054, 751 cm^{-1}. Anal. Calcd for $C_{29}H_{41}IN_2O$: C, 61.53; H, 7.19; N, 5.13. Found: C, 61.61; H, 7.23; N, 5.18.

1-Benzyl-3-(2′,6′-diisopropylphenyl)-4,5-dihydroimidazolium Tetrafluoroborate (6j). Starting from **9b** (500 mg, 2.17 mmol) and **11f** (249 μL, 274 mg, 2.17 mmol) in 10 mL of DMF, **6j** was obtained (647 mg, 1.58 mmol, 73%) as a white solid: mp 182−183 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.21 (s, 1H), 7.43−7.26 (m, 6H), 7.19−7.16 (m, 2H), 4.82 (s, 2H), 4.18−4.07 (m, 4H), 2.84 (hept, 2H, *J* = 6.6 Hz), 1.18 (dd, 12H, *J* = 12.1 Hz, *J* = 7.0 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 157.6, 146.7, 132.4, 131.1, 129.8, 129.4, 129.2, 129.2, 124.8, 53.4, 52.2, 48.6, 28.6, 24.7, 23.9; IR (KBr) 2964, 1643, 1452, 1269, 1056 cm^{-1}. Anal. Calcd for $C_{22}H_{29}BF_4N_2$: C, 64.72; H, 7.16; N, 6.86. Found: C, 64.81; H, 7.19; N, 6.72.

1-((1′*R*)-1′-Phenylethyl)-3-(3′-[2″-propenylphenyl]propyl)-4,5-dihydroimidazolium Iodide (6k). Starting from **9c** (500 mg, 2.87 mmol) and **11a** (867 mg, 2.87 mg) in 10 mL of DMF, **6k** was obtained (998 mg, 2.35 mmol, 82%) as a white solid: mp 91−92 °C; a 4:6 mixture of *Z* and *E* isomers; ^{1}H NMR ($CDCl_3$, 250 MHz) *E*: δ 8.30 (s, 1H), 7.37−7.11 (m, 7H), 6.96−6.86 (m, 2H), 6.63 (dd, 1H, *J* = 15.9 Hz, *J* = 1.6 Hz), 6.13 (dq, 1H, *J* = 15.9 Hz, *J* = 6.6 Hz), 4.72−4.63 (m, 1H), 4.13−3.59 (m, 8H), 2.24−2.11 (m, 2H), 1.84 (dd, 3H, *J* = 6.6 Hz, *J* = 1.8 Hz), 1.60 (d, 3H, *J* = 7.0 Hz); *Z*: δ 8.33 (s, 1H), 7.37−7.11 (m, 7H), 6.96−6.86 (m, 2H), 6.45 (dd, 1H, *J* = 11.7 Hz, *J* = 1.7 Hz), 5.74 (dq, 1H, *J* = 11.7 Hz, *J* = 7.1 Hz), 4.72−4.63 (m, 1H), 4.13−3.59 (m, 8H), 2.24−2.11 (m, 2H), 1.74 (dd, 3H, *J* = 7.0 Hz, *J* = 1.9 Hz), 1.61 (d, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 155.9, 155.7, 154.8, 137.4, 130.0, 129.1, 128.7, 128.1, 128.0, 126.7, 126.5, 126.2, 126.0, 125.1, 124.8, 121.1, 120.4, 112.1, 111.8, 65.2, 65.1, 58.1, 58.1, 48.1, 47.1, 46.0, 26.6, 26.6, 19.3, 19.3, 18.8, 14.5; $[\alpha]_{546}$ = +8.64 (*c* 1.00, CH_2Cl_2); IR (KBr) 2972, 2874, 1645, 1450, 1233, 1054, 746 cm^{-1}. Anal. Calcd for $C_{23}H_{29}IN_2O$: C, 57.99; H, 6.14; N, 5.88. Found: C, 57.65; H, 6.25; N, 5.75.

1-Adamantyl-3-methyl-4,5-dihydroimidazolium Iodide (6l). Starting from **9d** (204 mg, 1 mmol) and **11e** (142 mg, 65 μL, 1 mmol) in 5 mL of MeCN, **6l** was obtained (263 mg, 0.76 mmol, 76%) as a white solid: mp 225−226 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 9.00 (s, 1H), 4.08 (s, 4H), 3.41 (s, 3H), 2.21 (s, 3H), 2.01 (s, 6H), 1.69 (s, 6H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 154.7, 56.4, 50.0, 43.9, 40.3, 35.0, 34.8, 28.3; IR (KBr) 3020, 2904, 2846, 1648, 1304, 1139 cm^{-1}. Anal. Calcd for $C_{14}H_{23}IN_2$: C, 48.56; H, 6.70; N, 8.09. Found: C, 48.41; H, 6.65; N, 8.11.

1-Benzyl-3-((2′*R*)-3′,3′-dimethylbut-2′-yl)-4,5-dihydroimidazolium Tetrafluoroborate (6m). Starting from **9e** (462 mg, 3 mmol) and **11f** (344 μL, 380 mg, 3 mmol) in 10 mL of DMF, **6m** was obtained (847 mg, 2.55 mmol, 85%) as a white solid: mp 80−82 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.33 (s, 1H), 7.35−7.28 (m, 5H), 4.67 (dd, 2H, *J* = 14.7 Hz, *J* = 3.0 Hz), 4.08−3.72 (m, 4H), 3.58 (q, 1H, *J* = 7.0 Hz), 1.29 (d, 3H, *J* = 7.0 Hz), 0.95 (s, 9H); ^{13}C NMR ($CDCl_3$, 250 MHz) δ 157.5, 132.6, 129.2, 128.9, 128.8, 63.6, 51.9, 48.0, 47.2, 35.1, 26.6, 13.3; $[\alpha]_{546}$ = −10.2 (*c* 5.01, CH_2Cl_2); IR (KBr) 3089, 2978, 1647, 1446, 1210, 1134, 1049 cm^{-1}. Anal. Calcd for $C_{16}H_{25}BF_4N_2$: C, 57.85; H, 7.59; N, 8.43. Found: C, 57.81; H, 7.60; N, 8.29.

1-Mesityl-3-(5′-[2′-propenylphenyl]pentyl)-3,4,5,6-tetrahydropyrimidinium Iodide (6n). Starting from **9f** (596 mg, 2.95 mmol) and **11c** (974 mg, 2.95 mmol) in 10 mL of DMF, **6n** was obtained (1.42 g, 2.65 mmol, 90%) as a white solid: mp 126−127 °C; a 60:40 mixture of *Z* and *E* isomers; ^{1}H NMR ($CDCl_3$, 250 MHz) *E*: δ 8.18 (s, 1H), 7.35−7.09 (m, 2H), 6.92−6.80 (m, 4H), 6.66 (d, 1H, *J* = 15.8 Hz), 6.17 (dq, 1H, *J* = 15.8 Hz, *J* = 6.8 Hz), 3.96 (t, 2H, *J* = 6.0 Hz), 3.80 (t, 2H, *J* = 6.6 Hz), 3.70 (s, 2H), 3.60 (t, 2H, *J* = 5.0 Hz), 2.35 (t, 2H, *J* = 5.0 Hz), 2.25 (s, 3H), 2.21 (s, 6H), 1.87−1.80 (m, 7H), 1.60−1.41 (m, 2H); *Z*: δ 8.18 (s, 1H), 7.35−7.09 (m, 2H), 6.92−6.80 (m, 4H), 6.50 (d, 1H, *J* = 11.7 Hz), 5.76 (dq, 1H, *J* = 11.7 Hz, *J* = 7.0 Hz), 3.96 (t, 2H, *J* = 6.0 Hz), 3.80 (t, 2H, *J* = 6.6 Hz), 3.70 (s, 2H), 3.60 (t, 2H, *J* = 5.0 Hz), 2.35 (t, 2H, *J* = 5.0 Hz), 2.25 (s, 3H), 2.21 (s, 6H), 1.87−1.80 (m, 7H), 1.60−1.41 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 155.9, 155.0, 152.8, 139.5, 136.0, 134.2, 129.6, 127.6, 127.5, 126.5, 126.0, 125.8, 125.7, 125.2, 124.8, 120.3, 119.6, 111.7, 111.4, 67.5, 67.3, 55.6, 45.6, 43.4, 28.3, 26.9, 22.5, 20.6, 18.9, 18.7, 17.8, 14.4; IR (KBr) 2907, 1669, 1487, 1318, 1243, 748 cm^{-1}. Anal. Calcd for $C_{27}H_{37}IN_2O$: C, 60.90; H, 7.00; N, 5.26. Found: C, 60.81; H, 7.11; N, 5.38.

1-Mesityl-3-(6′-[2″-propenylphenyl]hexyl)-3,4,5,6-tetrahydropyrimidinium Iodide (6o). Starting from **9f** (404 mg, 2 mmol) and **11d** (688 mg, 2 mmol) in 10 mL of DMF, **6o** was obtained (799 mg, 1.6 mmol, yield 80%) as a white solid: mp 123−124 °C; a 60:40 mixture of *Z* and *E* isomers; ^{1}H NMR ($CDCl_3$, 250 MHz) *E*: δ 8.22 (s, 1H), 7.36−7.09 (m, 2H), 6.90−6.80 (m, 4H), 6.68 (d, 1H, *J* = 15.8 Hz), 6.14 (dq, 1H, *J* = 15.8 Hz, *J* = 6.7 Hz), 3.95 (t, 2H, *J* = 4.4 Hz), 3.81 (t, 2H, *J* = 6.7 Hz), 3.71 (t, 2H, *J* = 5.0 Hz), 3.62 (s, 2H), 2.37 (t, 2H, *J* = 4.6 Hz), 2.26 (s, 3H), 2.24 (s, 6H), 1.90−1.74 (m, 7H), 1.6−1.35 (m, 4H); *Z*: δ

8.22 (s, 1H), 7.36−7.09 (m, 2H), 6.90−6.80 (m, 4H), 6.52 (d, 1H, J = 11.6 Hz), 5.78 (dq, 1H, J = 11.6 Hz, J = 7.2 Hz), 3.95 (t, 2H, J = 4.4 Hz), 3.81 (t, 2H, J = 6.7 Hz), 3.71 (t, 2H, J = 5.0 Hz), 3.62 (s, 2H), 2.37 (t, 2H, J = 4.6 Hz), 2.26 (s, 3H), 2.24 (s, 6H), 1.90−1.74 (m, 7H), 1.6−1.35 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 156.1, 155.2, 152.8, 139.6, 136.0, 134.3, 129.7, 127.6, 127.4, 126.6, 126.1, 126.0, 125.9, 125.7, 125.3, 124.8, 120.2, 119.5, 111.7, 111.4, 67.7, 67.6, 55.7, 45.7, 43.5, 28.7, 28.7, 27.2, 25.5, 25.5, 25.3, 20.7, 19.0, 18.7, 17.9, 14.4; IR (KBr) 2940, 1674, 1488, 1451, 1242, 753 cm^{-1}. Anal. Calcd for $C_{28}H_{39}IN_2O$: C, 61.53; H, 7.19; N, 5.13. Found: C, 61.42; H, 7.23; N, 5.28.

3-Benzyl-1-mesityl-3,4,5,6-tetrahydropyrimidinium Tetrafluoroborate (6p). Starting from **9f** (404 mg, 2 mmol) and **11f** (253 mg, 2 mmol) in 10 mL of DMF, **6p** was obtained (608 mg, 1.6 mmol, 80%) as a white solid: mp 135−136 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.89 (s, 1H), 7.35−7.27 (m, 5H); 6.89 (s, 2H), 4.74 (s, 2H), 3.50 (q, 4H, J = 5.0 Hz), 2.24−2.19 (m, 11H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 153.3, 139.8, 136.5, 134.5, 132.5, 129.8, 129.2, 129.0, 128.7, 58.8, 45.8, 43.0, 20.84, 18.8, 17.3; IR (KBr) 3040, 1574, 1488, 1451, 1241, 754 cm^{-1}. Anal. Calcd for $C_{20}H_{25}BF_4N_2$: C, 63.18; H, 6.63; N, 7.37. Found: C, 63.19; H, 6.67; N, 7.42.

1-(2′,6′-Diisopropylphenyl)-3-(2′-methoxynaphth-1′-yl)-4,5-dihydroimidazolium Tetrafluoroborate (6q). Starting from **4d** (376 mg, 1 mmol) and NH_4BF_4 (115 mg, 1.1 mmol) in 4 mL of trimethyl orthoformate, **6q** was obtained (289 mg, 0.61 mmol, 61%) as a white solid: mp 211−212 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.00 (s, 1H), 7.91 (t, 1H, J = 8.7 Hz), 7.86 (d, 1H, J = 8.0 Hz), 7.59 (t, 1H, J = 7.4 Hz), 7.44−7.14 (m, 6H), 4.51 (br s, 4H), 3.97 (s, 3H), 3.07 (hept, 2H, J = 6.2 Hz), 1.26 (dd, 12H, J = 21.9 Hz, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 160.7, 152.4, 146.2, 132.3, 131.2, 129.8, 129.4, 129.0, 128.6, 128.4, 124.8, 120.3, 116.7, 112.6, 56.8, 54.2, 52.4, 28.6, 24.7, 23.8; IR (KBr) 3054, 2973, 1671, 1280, 1066, 1051, 1038 cm^{-1}. Anal. Calcd for $C_{26}H_{31}BF_4N_2O$: C, 65.83; H, 6.59; N, 5.91. Found: C, 65.89; H, 6.46; N, 5.82.

1-Mesityl-3-(*o*-tolyl)-3,4,5,6-tetrahydropyrimidinium Tetrafluoroborate (6r). Starting from **4e** (200 mg, 0.71 mmol) and NH_4BF_4 (82 mg, 0.78 mmol) in 2 mL of trimethyl orthoformate, **6r** was obtained (105 mg, 0.27 mmol, 39%) as a white solid: mp 209−210 °C; ^{1}H NMR (CDCl3, 250 MHz) δ 7.55 (s, 2H), 7.38−7.26 (m, 3H), 6.94 (s, 2H), 4.02 (t, 2H, J = 5.2 Hz), 3.87 (t, 2H, J = 5.2 Hz), 2.54 (quint., 2H, J = 5.5 Hz), 2.36 (s, 3H), 2.32 (s, 6H), 2.28 (s, 3H); ^{13}C NMR (CDCl3, 62.5 MHz) δ 153.5, 140.4, 139.9, 136.5, 134.6, 133.3, 131.8, 130.5, 130.1, 128.3, 127.3, 47.2, 46.3, 20.9, 19.4, 17.6, 17.4; IR (KBr) 3072, 1666, 1352, 1094, 1051 cm^{-1}. Anal. Calcd for $C_{20}H_{25}BF_4N_2$: C, 63.18; H, 6.63; N, 7.37. Found: C, 63.25; H, 6.56; N, 7.81.

1-(2′,6′-Diisopropylphenyl)-3-(1′-ferrocenylethyl)-4,5-dihydroimidazolium Tetrafluoroborate (6s). Starting from **4f** (1.00 g, 2.31 mmol) and NH_4BF_4 (267 mg, 2.54 mmol) in 10 mL of trimethyl orthoformate, **6s** was obtained (796 mg, 1.5 mmol, 65%) as a yellow-brown solid: mp 182−184 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 8.00 (s, 1H), 7.36 (t, 1H, J = 7.28 Hz), 7.16 (d, 2H, J = 6.6 Hz), 5.29 (q, 1H, J = 6.5 Hz),4.38 (s, 1H), 4.26−3.87 (m, 12H), 2.75 (dt, 2H, J = 34.4 Hz, J = 6.1 Hz), 1.73 (d, 3H, J = 6.3 Hz), 1.22−1.12 (m, 12H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 156.6, 146.6, 146.2, 130.8, 129.9, 124.7, 124.5, 84.8, 69.5, 69.2, 68.6, 68.1, 65.8, 54.3, 53.0, 45.2, 28.5, 28.4, 24.6, 24.6, 23.8, 23.6, 17.2; IR (KBr) 3361, 3093, 2961, 2867, 1672, 1457, 1254, 1106, 818, 755, 484 cm^{-1}. Anal. Calcd for $C_{27}H_{36}BF_4FeN_2$: C, 61.16; H, 6.65; N, 5.28. Found: C, 61.06; H, 6.68; N, 5.15.

General Procedure for the Preparation of Azidoamides 7a−f. The mixture of the chloroamide (**3a**−**f**) and 2 equiv of sodium azide was heated in MeOH (at reflux for **3a**−**e**) or DMF (at 80 °C for **3f**) until complete conversion as judged by GC. The solvent was removed under reduced pressure, the residue was dissolved in DCM, and the inorganic compounds were removed by filtration. Hexane was added to the filtrate, and the solvent was removed until the product started to precipitate from the warm solution. After being cooled to ambient temperature, the product was collected by filtration (except for **7e** which after removal of the solvents was purified by Kugelrohr distillation at 0.2 Torr at 80 °C).

***2*-Azido-*N*-mesitylacetamide (7a).** Starting from **3a** (10.0 g, 47.2 mmol) and NaN_3 (6.14 g, 94.5 mmol) in 250 mL of MeOH, **7a** was obtained (9.48 g, 43.45 mmol, 92%) as a white solid: mp 178−178.5 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.61 (s, 1H), 6.89 (s, 2H), 4.12 (s, 2H), 2.27 (s, 3H), 2.16 (s, 6H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 165.2, 137.4, 134.9, 130.0, 128.9, 52.6, 20.9, 18.1; IR (KBr) 3235, 3040, 2102, 1666, 1539, 1485, 1245 cm^{-1}. Anal. Calcd for $C_{11}H_{14}N_4O$: C, 60.53; H, 6.47; N, 25.67. Found: C, 60.54; H, 6.44; N, 25.74.

***2*-Azido-*N*-(2′,6′-diisopropylphenyl)acetamide (7b).** Starting from **3b** (10.00 g, 39.4 mmol) and NaN_3 (5.12 g, 78.8 mmol) in 250 mL of MeOH, **7b** was obtained (9.74 g, 37.4 mmol, 95%) as a white solid: mp 129.5−130 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.62 (s, 1H), 7.35−7.18 (m, 3H), 4.18 (s, 2H), 3.00 (hept, 2H, J = 6.9 Hz), 1.21 (d, 12H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 165.9, 145.9, 129.9, 128.69, 123.6, 52.7, 28.8, 23.5; IR (KBr) 3281, 2963, 2100, 1658, 1515, 1221 cm^{-1}. Anal. Calcd for $C_{14}H_{20}N_4O$: C, 64.59; H, 7.74; N, 21.52. Found: C, 64.85; H, 7.78; N, 21.58.

***2*-Azido-*N*-((1′*R*)-1′-phenylethyl)acetamide (7c).** Starting from **3c** (5.00 g, 25.3 mmol) and NaN_3 (3.28 g, 50.6 mmol) in 125 mL of MeOH, **7c** was obtained (4.85 g, 23.7 mmol, 94%) as a white solid: mp 52.5−53.0 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.38−7.23 (m, 5H), 6.65 (s, 1H), 5.12 (quint, 1H, J = 6.9 Hz), 3.93 (dd, 2H, J = 16.4 Hz, J = 2.4 Hz), 1.50 (d, 3H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 165.6, 142.4, 128.7, 127.5, 126.0, 52.5, 48.7, 21.6; $[\alpha]_{546}$ = +78.64 (*c* 5.15, CH_2Cl_2); IR (KBr) 3291, 2976, 2095, 1647, 1543, 1282, 1254, 694 cm^{-1}. Anal. Calcd for $C_{10}H_{12}N_4O$: C, 58.81; H, 5.92; N, 27.43. Found: C, 58.91; H, 5.75; N, 27.28.

***2*-Azido-*N*-adamantylacetamide (7d).** Starting from **3d** (10.00 g, 43.9 mmol) and NaN_3 (5.70 g, 87.8 mmol) in 250 mL of MeOH, **7d** was obtained (8.33 g, 35.6 mmol, 81%) as a white solid: mp 86−86.5 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 5.96 (s, 1H), 3.79 (s, 2H), 2.08−1.98 (m, 3H), 1.97−1.91 (m, 6H), 1.63 (t, 6H, J = 2.8 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 165.2, 52.8, 52.0, 41.2, 36.0, 29.2; IR (KBr) 3236, 2906, 2852, 2100, 1661, 1537, 1242 cm^{-1}. Anal. Calcd for $C_{10}H_{12}N_4O$: C, 58.81; H, 5.92; N, 27.43. Found: C, 58.91; H, 5.75; N, 27.28.

***2*-Azido-*N*-((2′*R*)-3′,3′-dimethylbut-2′-yl)acetamide (7e).** Starting from **3e** (5.00 g, 28.1 mmol) and NaN_3 (3.65 g, 56.3 mmol) in 125 mL of MeOH, **7e** was obtained (4.82 g, 26.2 mmol, 93% yield) as a white solid: mp 54−55 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.20 (s, 1H), 3.93 (d, 2H, J = 3.0 Hz), 3.89−3.76 (m, 1H), 1.03 (d, 3H, J = 6.8 Hz), 0.85 (s, 9H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 165.6, 52.8, 52.6, 33.9, 25.9, 15.8; $[\alpha]_{546}$ = −15.33 (*c* 5.1, CH_2Cl_2); IR (KBr) 3298, 2964, 2096, 1647, 1550, 1284 cm^{-1}. Anal. Calcd for $C_{10}H_{12}N_4O$: C, 58.81; H, 5.92; N, 27.43. Found: C, 58.91; H, 5.75; N, 27.28.

***3*-Azido-*N*-mesitylpropionamide (7f).** Starting from **3f** (5.00 g, 22.2 mmol) and NaN_3 (2.88 g, 44.3 mmol) in 100 mL of DMF, **7f** was obtained (3.86 g, 16.6 mmol, yield 75%) as a light yellow solid: mp 110−112 °C; a 9:1 mixture of syn/anti amide rotamers; ^{1}H NMR ($CDCl_3$, 250 MHz) syn: δ 7.38 (s, 1H), 6.81 (s, 2H), 3.62 (t, 2H, J = 6.4 Hz), 2.52 (t, 2H, J = 6.4 Hz), 2.23 (s, 3H), 2.10 (s, 6H); anti: δ 7.38 (s, 1H), 6.93 (s, 2H), 3.53 (t, 2H, J = 6.3 Hz), 2.29 (s, 3H), 2.20 (s, 6H), 2.12 (t, 2H, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) syn: δ 168.8, 136.9, 135.0, 130.9, 128.7, 47.6, 35.5, 20.9, 18.0; anti: δ 172.6, 138.2, 136.3, 131.3, 129.3, 46.6, 31.5, 20.8, 18.2. Anal. Calcd for $C_{12}H_{16}ClNO$: C, 63.85; H, 7.14; N, 6.21. Found: C, 64.02; H, 6.94; N, 6.33.

General Procedure for the Preparation of *N*-Substituted Ethylenediamines 8a−f. The mixture of the appropriate azidoamide (**7a**−**f**) and 5 equiv of $LiAlH_4$ was refluxed in freshly distilled THF (for **7a**−**d**,**f**) or diethyl ether (for **7e**) under Ar atmosphere until consumption of the starting material as judged by GC. After the reaction mixture was cooled to −10 °C, 1 mL of water, 2 mL of 2

N NaOH, and another 2 mL of water were added slowly to the mixture, and it was allowed to warm to room temperature. Following the addition of some diethyl ether and stirring for a further 1 h, the white inorganics were removed by filtration. After evaporation of the combined solvents, all of the diamines were purified by short path distillation at 0.2 mbar.

***N*-Mesitylethylenediamine (8a).**[39] Starting from **7a** (5.00 g, 22.9 mmol) and $LiAlH_4$ (4.35 g, 114.5 mmol) in 125 mL of THF, **8a** was obtained (3.18 g, 17.86 mmol, 78%) as a pale yellow oil: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.83 (s, 2H), 3.01−2.87 (m, 4H), 2.29 (s, 6H), 2.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 143.5, 131.2, 129.7, 129.3, 51.2, 42.5, 20.5, 18.3; IR (KBr) 3360, 2946, 2861, 2836, 1484, 1230, 853 cm^{-1}. Anal. Calcd for $C_{11}H_{18}N_2$: C, 74.11; H, 10.18; N, 15.71. Found: C, 74.13; H, 10.21; N, 15.59.

***N*-(2′,6′-Diisopropylphenyl)ethylenediamine (8b).** Starting from **7b** (5.00 g, 19.2 mmol) and $LiAlH_4$ (3.64 g, 96 mmol) in 125 mL of THF, **8b** was obtained (3.45 g, 15.7 mmol, 82%) as a pale yellow oil: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.14−7.03 (m, 3H), 3.33 (hept, 2H, J = 6.8 Hz), 3.00−2.90 (m, 4H), 2.6−1.4 (br s, 3H), 1.26 (d, 12H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 143.1, 142.3, 123.5, 123.3, 54.2, 42.4, 27.4, 24.1; IR (KBr) 3362, 2960, 2867, 1444, 754 cm^{-1}. Anal. Calcd for $C_{14}H_{24}N_2$: C, 76.31; H, 10.98; N, 12.71. Found: C, 76.13; H, 10.94; N, 12.57.

***N*-((1′*R*)-1′-Phenylethyl)ethylenediamine (8c).**[40] Starting from **7c** (5.00 g, 24.5 mmol) and $LiAlH_4$ (3.72 g, 98 mmol) in 125 mL of THF, **8c** was obtained (3.41 g, 20.8 mmol, 85%) as a pale yellow oil: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.35−7.18 (m, 5H), 3.75 (q, 1H, J = 6.7 Hz), 2.77−2.72 (m, 2H), 2.61−2.41 (m, 2H), 1.38 (s, 3H), 1.36 (d, 3H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 145.1, 128.3, 126.7, 126.4, 58.2, 50.3, 41.9, 24.4; $[\alpha]_{546}$ = +57.2 (*c* 5.4, CH_2Cl_2); IR (KBr) 3287, 2972, 2829, 1657, 1568, 1492, 1450, 761, 700 cm^{-1}. Anal. Calcd for $C_{10}H_{16}N_2$: C, 73.13; H, 9.82; N, 17.06. Found: C, 73.14; H, 9.94; N, 17.09.

***N*-Adamantylethylenediamine (8d).**[41] Starting from **7d** (5.00 g, 21.3 mmol) and $LiAlH_4$ (3.24 g, 85.36 mmol) in 125 mL of THF, **8d** was obtained (3.02 g, 15.56 mmol, 73%) as a pale yellow oil: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.65−2.60 (m, 2H), 2.51−2.46 (m, 2H), 1.92 (s, 3H), 1.55−1.43 (m, 12H), 1.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 49.8, 42.9, 42.7, 42.6, 36.5, 29.3; IR (KBr) 2900, 2845 cm^{-1}. Anal. Calcd for $C_{12}H_{22}N_2$: C, 74.17; H, 11.41; N, 14.42. Found: C, 74.05; H, 11.55; N, 14.25.

***N*-((2′*R*)-3′,3′-Dimethylbut-2′-yl)ethylenediamine (8e).** Starting from **7e** (5.00 g, 27.13 mmol) and $LiAlH_4$ (4.12 g, 108 mmol) in 125 mL of diethyl ether, **8e** was obtained (3.05 g, 21.2 mmol, 78%) as a colorless oil: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.85−2.66 (m, 3H), 2.57−2.45 (m, 1H), 2.18 (q, 1H, J = 6.5 Hz), 1.28 (s, 3H), 0.97 (d, 3H, J = 6.5 Hz), 0.88 (s, 9H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 61.75, 51.05, 41.81, 34.10, 26.17, 14.70; $[\alpha]_{546}$ = −66.5 (*c* 5.5, CH_2Cl_2); IR (KBr) 2955, 2868, 2827, 1487, 1120 cm^{-1}. Anal. Calcd for $C_8H_{20}N_2$: C, 66.61; H, 13.97; N, 19.42. Found: C, 66.54; H, 13.76; N, 19.29.

***N*-Mesitylpropylenediamine (8f).**[42] Starting from **7f** (5.00 g, 21.5 mmol) and $LiAlH_4$ (3.27 g, 86.1 mmol) in 125 mL of THF, **8f** was obtained (2.77 g, 14.4 mmol, 67%) as a pale yellow oil: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.83 (s, 2H), 3.00 (t, 2H, J = 6.7 Hz), 2.85 (t, 2H, J = 6.8 Hz), 2.27 (s, 6H), 2.24 (s, 3H), 1.9 (br s, 3H), 1.74 (quint., 2H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 143.5, 130.9, 129.4, 129.2, 46.7, 40.3, 34.5, 20.3, 18.1; IR (KBr) 3360, 2942, 2860, 2839, 1483, 1230, 852 cm^{-1}. Anal. Calcd for $C_{12}H_{20}N_2$: C, 74.95; H, 10.48; N, 14.57. Found: C, 74.88; H, 10.52; N, 14.33.

General Procedure for the Preparation of N-Substituted 4,5-Dihydroimidazoles and 3,4,5,6-Tetrahydropyrimidines 9a−f. Ring Closure of Alkylamines 8c−e. The mixture of the appropriate amine and 1 equiv of $Me_2NHC(OCH_3)_2$ in cyclohexane was stirred at 80 °C under Ar atmosphere until consumption of the starting material as judged by GC. In the cases of **8c**,**d**, the reaction proceeded faster (20−25 min), whereas in case of **8e** a longer reaction period was needed. In the latter case, a GC-detectable intermediate could be observed during the reaction.

Ring Closure of Arylamines 8a,b,f. The solution of the appropriate amine in 20 equiv of trimethyl orthoformate was refluxed in the presence of a catalytic amount of concd HI under Ar atmosphere. All of the reactions were followed by GC.

After evaporation of the solvent, all products were purified by short path distillation at 0.2 bar.

1-Mesityl-4,5-dihydro-1*H*-imidazole (9a).[39] Starting from **8a** (3.00 g, 16.8 mmol) and 30 mL of trimethyl orthoformate, **9a** was obtained (2.53 g, 13.5 mmol, 80%) as a white solid: mp 62−63 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.9 (s, 2H), 6.83 (s, 1H), 4.04 (t, 2H, J = 10.0 Hz), 3.54 (t, 2H, J = 10.2 Hz), 2.28 (s, 3H), 2.22 (s, 6H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 155.8, 137.2, 136.8, 134.7, 129.3, 55.2, 48.7, 20.8, 18.0; IR (KBr) 2943, 2858, 1590, 1486, 1261, 1205 cm^{-1}. Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.42; H, 8.75; N, 14.94.

1-(2′,6′-Diisopropylphenyl)-4,5-dihydro-1*H*-imidazole (9b). Starting from **8b** (3.00 g, 13.6 mmol) and 30 mL of trimethyl orthoformate, **9b** was obtained (2.44 g, 10.6 mmol, 78%) as a white solid: mp 67−68 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.32−7.15 (m, 3H), 6.8 (s, 1H), 4.05 (t, 2H, J = 10.0 Hz), 3.56 (t, 2H, J = 10.2 Hz), 3.09 (hept, 2H, J = 6.9 Hz), 1.19 (dd, 12H, J = 11.9 Hz, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 156.1, 148.3, 134.2, 128.5, 124.1, 55.1, 51.5, 28.4, 24.8, 24.0; IR (KBr) 2962, 2926, 2866, 1678, 1598, 1585, 1456, 1203 cm^{-1}. Anal. Calcd for $C_{15}H_{22}N_2$: C, 78.21; H, 9.63; N, 12.16. Found: C, 78.10; H, 9.63; N, 12.16.

1-((1′*R*)-1′-Phenylethyl)-4,5-dihydro-1*H*-imidazole (9c).[18] Starting from **8c** (2.00 g. 12.2 mmol) and $(CH_3)_2NCH(OCH_3)_2$ (1.46 g, 1.63 mL, 12.2 mmol) in 10 mL of cyclohexane, **9c** was obtained (2.10 g, 12.0 mmol, 99%) as a light yellow oil: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.38−7.24 (m, 5H), 7.01 (s, 1H), 4.32 (q, 1H, J = 6.9 Hz), 3.77 (dt, 2H, J = 9.8 Hz, J = 1.7 Hz), 3.10 (t, 2H, J = 9.8 Hz), 1.56 (d, 3H, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 155.3, 141.9, 128.5, 127.3, 126.4, 56.4, 54.3, 46.5, 20.7; $[\alpha]_{546}$ = +48.7 (*c* 3.1, CH_2Cl_2); IR (KBr) 3287, 2972, 2872, 2829, 1657, 1568, 1492, 1450, 761, 700 cm^{-1}. Anal. Calcd for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.63; H, 8.15; N, 16.21.

1-Adamantyl-4,5-dihydro-1*H*-imidazole (9d). Starting from **8d** (3.00 g, 15.4 mmol) and $(CH_3)_2NCH(OCH_3)_2$ (1.84 g, 2.06 mL, 15.4 mmol) in 15 mL of cyclohexane, **9d** was obtained (3.08 g, 15.1 mmol, 98%) as a light brown solid: mp 40−41 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.94 (t, 1H, J = 1.6 Hz), 3.6 (t, 2H, J = 9.5 Hz), 3.14 (t, 2H, J = 9.6 Hz), 1.98 (s, 3), 1.72−1.65 (m, 6H), 1.62−1.45 (m, 6H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 153.0, 53.5, 51.9, 42.4, 41.4, 35.9, 28.9; IR (KBr) 2904, 2849, 1591 cm^{-1}. Anal. Calcd for $C_{13}H_{20}N_2$: C, 76.42; H, 9.87; N, 13.71. Found: C, 76.34; H, 9.73; N, 13.68.

1-((2′*R*)-3′,3′-Dimethylbut-2′-yl)-4,5-dihydro-1*H*-imidazole (9e). Starting from **8e** (2.00 g, 13.9 mmol) and $(CH_3)_2NCH(OCH_3)_2$ (1.66 g, 1.86 mL, 13.9 mmol) in 10 mL of cyclohexane, **9e** was obtained (2.09 g, 13.58 mmol, 98%) as a pale yellow oil: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.73 (s, 1H), 3.75−3.66 (m, 2H), 3.35−3.17 (m, 2H), 3.02 (q, 1H J = 7.1 Hz), 1.07 (d, 3H, J = 7.1 Hz), 0.86 (s,9H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 157.2, 60.7, 54.0, 47.0, 35.6, 26.9, 13.2; $[\alpha]_{546}$ = −38.6 (*c* 2.5, CH_2Cl_2); IR (KBr) 2955, 2869, 2832, 1658, 1599, 1192 cm^{-1}. Anal. Calcd for $C_9H_{18}N_2$: C, 70.08; H, 11.76; N, 18.16. Found: C, 70.04; H, 11.73; N, 18.21.

3-Mesityl-3,4,5,6-tetrahydropyrimidine (9f).[39] Starting from **8f** (3.00 g, 15.6 mmol) and 30 mL of trimethyl orthoformate, **9f** was obtained (2.05 g, 10.1 mmol, 65% yield) as a white solid: mp 80−

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80.5 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 6.86 (s, 3H), 3.40 (t, 2H, J = 5.1 Hz), 3.28 (t, 2H, J = 6.0 Hz), 2.23 (s, 3H), 2.18 (s, 6H), 1.96 (quint., 2H, J = 5.7 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 149.0, 139.6, 137.0, 136.3, 129.0, 45.2, 42.9, 21.2, 20.7, 17.5; IR (KBr) 3230, 2955, 2922, 2851, 2730, 2102, 1627, 1483, 1289, 1029 cm^{-1}. Anal. Calcd for $C_{13}H_{18}N_2$: C, 77.18; H, 8.97; N, 13.85. Found: C, 77.03; H, 8.75; N, 13.57.

2-(6′-Chlorohexyloxy)benzaldehyde (10d). The mixture of salicylic aldehyde (1.22 g, 1.05 mL, 10 mmol), 1-bromo-6-chlorohexane (1.99 g, 1.49 mL, 10 mmol), and potassium carbonate (2.76 g, 20 mmol) was stirred in 50 mL of DMF at ambient temperature until completion. The K_2CO_3 was filtered off, and after evaporation of the DMF under reduced pressure, the product was purified by column chromatography using hexane/ethyl acetate mixtures as eluent. Compound **10d** (2.03 g, 8.4 mmol, 84%) was obtained as a colorless oil: ^{1}H NMR ($CDCl_3$, 250 MHz) δ 10.49 (d, 1H, J = 0.8 Hz), 7.81 (dd, 1H, J = 6.2 Hz, J = 1.8 Hz), 7.55 (ddd, 1H, J = 8.4 Hz, J = 7.5 Hz, J = 1.9 Hz), 7.02−6.94 (m, 2H), 4.06 (t, 2H, J = 6.3 Hz), 3.54 (t, 2H, J = 6.6 Hz), 1.91−1.74 (m, 4H), 1.59−1.46 (m, 4H); ^{13}C NMR ($CDCl_3$, 250 MHz) δ 189.6, 161.3, 135.8, 128.1, 124.8, 120.5, 112.4, 68.2, 44.8, 32.3, 28.9, 26.5, 25.3; IR (KBr) 2939, 2860, 1686, 1598, 1457, 1387, 1285, 1241, 757 cm^{-1}. Anal. Calcd for $C_{13}H_{17}ClO_2$: C, 64.86; H, 7.12. Found: C, 64.85; H, 7.20.

General Procedure for the Preparation of the Alkylating Agents 11a−d. To the suspension of ethyltriphenylphosphonium iodide in freshly distilled THF was added *n*-BuLi at room temperature under Ar atmosphere. After completion of the addition, the reaction mixture turned into a homogeneous red solution. Further stirring for 1 h was followed by the addition of the appropriate aldehyde. The reaction was monitored by GC and TLC. After the starting materials had disappeared, the reaction mixture was poured onto aq NH_4Cl solution, which was followed by extraction with diethyl ether. The combined organic extracts were dried over $MgSO_4$ and then concentrated in vacuo. The crude products were further purified by column chromatography using hexane as eluent. Due to partial exchange of the pendant halogens, all products were converted to their iodo derivatives using NaI in acetone.

***O*-(3′-Iodopropyl)-2-propenylphenol (11a).** Starting from **10a** (3.00 g, 15.1 mmol), ethyltriphenylphosphonium iodide (6.31 g, 15.1 mmol), and 10.4 mL of *n*-BuLi (1.6 M in hexane, 16.6 mmol) in 50 mL of THF, **11a** (2.55 g, 11.0 mmol, 73%) was obtained as a yellow oil: 60:40 mixture of *Z* and *E* isomers; ^{1}H NMR ($CDCl_3$, 250 MHz) *E*: δ 7.39 (dd, 1H, J = 7.5 Hz, J = 1.5 Hz), 7.22−7.10 (m, 1H), 6.95−6.80 (m, 2H), 6.68 (dd, 1H, J = 15.9 Hz, J = 1,7 Hz), 6.20 (dq, 1H, J = 15.9 Hz, J = 6.6 Hz), 4.00 (t, 2H, J = 5.7 Hz), 3.35 (t, 2H, J = 6.8 Hz), 2.32−2.19 (m, 2H), 1.89 (dd, 3H, J = 6.6 Hz, J = 1,7 Hz); *Z*: 7.26 (dd, 1H, J = 7.4 Hz, J = 1.5 Hz), 7.22−7.10 (m, 1H), 6.95−6.80 (m, 2H), 6.52 (dd, 1H, J = 11.5 Hz, J = 1,6 Hz), 5.80 (dq, 1H, J = 11.5 Hz, J = 7.1 Hz), 3.99 (t, 2H, J = 5.7 Hz), 3.33 (t, 2H, J = 6.8 Hz), 2.32−2.19 (m, 2H), 1.82 (dd, 3H, J = 7.1 Hz, J = 1,9 Hz); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 155.9, 155.0, 130.1, 127.8, 127.6, 127.1, 126.6, 126.4, 126.3, 125.3, 124.9, 120.8, 120.2, 111.9, 111.6, 67.5, 67.4, 32.9, 18.9, 14.6, 2.7, 2.6; IR (KBr) 3030, 2934, 2878, 1597, 1488, 1448, 1238, 748 cm^{-1}. Anal. Calcd for $C_{12}H_{15}IO$: C, 47.70; H, 5.00. Found: C, 47.84; H, 5.01.

***O*-(4′-Iodobutyl)-2-propenylphenol (11b).** Starting from **10b** (10 g, 38.9 mmol), ethyltriphenylphosphonium iodide (16.26 g, 38.9 mmol), and 29 mL of *n*-BuLi (1.6 M in hexane, 46.4 mmol) in 100 mL of THF, **11c** (8.6 g, 27.22 mmol, 70%) was obtained as a yellow oil: 60:40 mixture of *Z* and *E* isomers; ^{1}H NMR ($CDCl_3$, 250 MHz) *E*: δ 7.37 (dd, 1H, J = 7.5 Hz, J = 1.5 Hz), 7.20−7.08 (m, 1H), 6.93−6.75 (m, 2H), 6.69 (dd, 1H, J = 15.8 Hz, J = 1 Hz), 6.20 (dq, 1H, J = 15.8 Hz, J = 6.6 Hz), 3.93 (t, 2H, J = 6.0 Hz), 3.23 (t, 2H, J = 6.7 Hz), 2.06−1.80 (m, 7H); *Z*: 7.26 (dd, 1H, J = 7.4 Hz, J = 1.5 Hz), 7.20−7.08 (m, 1H), 6.93−6.75 (m, 2H), 6.53 (dd, 1H, J = 11.4 Hz, J = 1.6 Hz), 5.80 (dq, 1H, J = 11.4 Hz, J = 7.1 Hz), 3.93 (t, 2H, J = 6.0 Hz), 3.21 (dt, 2H, J = 6.3 Hz, J = 4.4 Hz), 2.06−1.80 (m, 7H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 156.1, 155.2, 129.9, 127.7, 127.5, 126.9, 126.4, 126.3, 126.2, 126.1, 125.4, 125.0, 120.6, 119.9, 111.6, 111.3, 66.8, 66.7, 30.2, 30.1, 29.9, 18.9, 14.6, 6.57; IR (KBr) 3030, 2937, 2871, 1596, 1488, 1448, 1237, 747 cm^{-1}. Anal. Calcd for $C_{13}H_{17}IO$: C, 49.38; H, 5.42. Found: C, 49.43; H, 5.41.

***O*-(5′-Iodopentyl)-2-propenylphenol (11c).** Starting from **10c** (5 g, 18.4 mmol), ethyltriphenylphosphonium iodide (7.68 g, 18.4 mmol), and 12.6 mL of *n*-BuLi (1.6 M in hexane, 20.2 mmol) in 50 mL of THF, **11c** (4.74 g, 14.35 mmol, 78%) was obtained as a yellow oil: 60:40 mixture of *Z* and *E* isomers; ^{1}H NMR ($CDCl_3$, 250 MHz) *E*: δ 7.38 (dd, 1H, J = 7.8 Hz, J = 1.7 Hz), 7.21−7.09 (m, 1H), 6.93−6.78 (m, 2H), 6.72 (dd, 1H, J = 15.9 Hz, J = 1,7 Hz), 6.22 (dq, 1H, J = 15.9 Hz, J = 6.6 Hz), 3.94 (t, 2H, J = 6.2 Hz), 3.19 (t, 2H, J = 6.9 Hz), 1.94−1.73 (m, 7H), 1.64−1.49 (m, 2H); *Z*: 7.27 (dd, 1H, J = 7.4 Hz, J = 1.5 Hz), 7.21−7.09 (m, 1H), 6.93−6.78 (m, 2H), 6.55 (dd, 1H, J = 11.6 Hz, J = 1,9 Hz), 5.81 (dq, 1H, J = 11.7 Hz, J = 7 Hz), 3.94 (t, 2H, J = 6.2 Hz), 3.18 (t, 2H, J = 6.9 Hz), 1.94−1.73 (m, 7H), 1.64−1.49 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 156.3, 155.4, 130.0, 127.7, 127.5, 126.9, 126.4, 126.3, 126.2, 126.1, 125.5, 125.1, 120.5, 119.8, 111.7, 111.4, 67.7, 67.6, 33.1, 33.0, 28.2, 28.1, 27.2, 27.1, 18.9, 14.7, 6.8, 6.7; IR (KBr) 3029, 2938, 2866, 1688, 1597, 1449, 1239, 748 cm^{-1}. Anal. Calcd for $C_{14}H_{19}IO$: C, 50.92; H, 5.80. Found: C, 50.84; H, 5.71.

***O*-(6′-Iodohexyl)-2-propenylphenol (11d).** Starting from **10d** (1.50 g, 6.2 mmol), ethyltriphenylphosphonium iodide (2.6 g, 6.2 mmol), and 4.3 mL of *n*-BuLi (1.6 M in hexane, 6.9 mmol) in 25 mL of THF, **11a** (1.72 g, 5.1 mmol, 82%) was obtained as a yellow oil: 60:40 mixture of *E* and *Z* isomers; ^{1}H NMR ($CDCl_3$, 250 MHz) *E*: δ 7.39 (dd, 1H, J = 7.6 Hz, J = 1.8 Hz), 7.23−7.11 (m, 1H), 6.94−6.80 (m, 2H), 6.71 (dd, 1H, J = 15.8 Hz, J = 1,5 Hz), 6.23 (dq, 1H, J = 15.8 Hz, J = 6.7 Hz), 3.96 (t, 2H, J = 6.2 Hz), 3.20 (t, 2H, J = 7.1 Hz), 1.92−1.75 (m, 7H), 1.51−1.46 (m, 4H); *Z*: 7.28 (dd, 1H, J = 7.4 Hz, J = 1.5 Hz), 7.23−7.11 (m, 1H), 6.94−6.80 (m, 2H), 6.55 (dd, 1H, J = 11.6 Hz, J = 1,7 Hz), 5.81 (dq, 1H, J = 11.6 Hz, J = 7.1 Hz), 3.96 (t, 2H, J = 6.4 Hz), 3.19 (t, 2H, J = 7.0 Hz), 1.92−1.75 (m, 7H), 1.51−1.46 (m, 4H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 156.4, 155.5, 130.0, 127.8, 127.6, 127.0, 126.5, 126.4, 126.3, 126.2, 125.6, 125.2, 120.5, 119.8, 111.8, 111.5, 68.0, 67.9, 33.3, 30.2, 29.1, 29.0, 25.1, 25.0, 19.0, 14.7, 7.0, 6.9; IR (KBr) 3031, 2860, 1599, 1490, 1451, 1241, 751 cm^{-1}. Anal. Calcd for $C_{15}H_{21}IO$: C, 52.34; H, 6.15. Found: C, 52.42; H, 6.01.

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Supporting Information Available: Crystal data, structure refinement data, and crystal packing of **6o**; NMR spectra of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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