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PLANAR-CHIRAL IONIC LIQUIDS. CYCLOPHANE-TYPE IMIDAZOLIUM SALTS WITH A C(2)-C(4) BRIDGE

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Abstract – Novel chiral ionic liquids with planar chirality was synthesized, which were based on cyclophane-type imidazolium salts with a dodecamethylene bridge connecting the imidazolium C(2) and C(4) positions. Their potential utility as chiral solvents was demonstrated by ^{1}H NMR spectroscopy and DSC measurement.

INTRODUCTION

Ionic liquids have attracted considerable attentions as a novel class of media, because of their characteristic properties, such as little volatility, inflammability, ion conductivity, and dissolvability of various substrates.[1] Among such ionic liquids, chiral ionic liquids are of special interest, owing to their potential utility in a wide range of scientific fields related to chiral recognition, including asymmetric synthesis, chiral separation, *etc.*[1f,g] Several chiral ionic liquids have been reported to date, and some of them were successfully proved to possess a chiral recognition ability.[2] At the present time, however, there exists a serious problem for the development of further sophisticated chiral ionic liquids; in order to improve the molecular recognition ability of these chiral ionic liquids, the introduction of rigid/polar substituents seems to be advantageous, but at the same time, the substituents might bring unfavorable effects on the properties of ionic liquids, such as melting point, viscosity, and chemical and thermal stabilities.

Recently we have reported a simple and reliable synthesis of chiral ionic liquids, cyclophane-type imidazolium salts with planar chirality.[3–5] The planar-chiral imidazolium salts could be easily prepared

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This paper is dedicated to the memory of the Emeritus Professor Kenji Koga of Tokyo University.

from 2,4-dimethylimidazole by connecting the N(1) and N(3) of the five-membered ring with a bridge with a proper length. The resultant imidazolium salts were promising chiral ionic liquids, which realized low melting point, chemical stability, and chiral recognition ability at the same time.[3] Considering the geometry of the bridge unit with respect to the imidazolium ring, two other classes of planar-chiral cyclophane-type imidazolium salts might be possible; the C(2)–C(4) bridged and the N(1)–C(4) bridged types (Figure 1). Although our previous model, the N(1)–N(3) bridged type, has an advantage in its easy accessibility, the latter two types are expected to possess attractive properties owing to their dissymmetric structure. Furthermore, synthesis and application of imidazoles/imidazolium salts with such characteristic skeletons are of great interest from the viewpoints of heterocycles chemistry and cyclophane chemistry. Here we report the synthesis, characterization, and application of planar-chiral ionic liquids based on a C(2)–C(5) bridged imidazole.

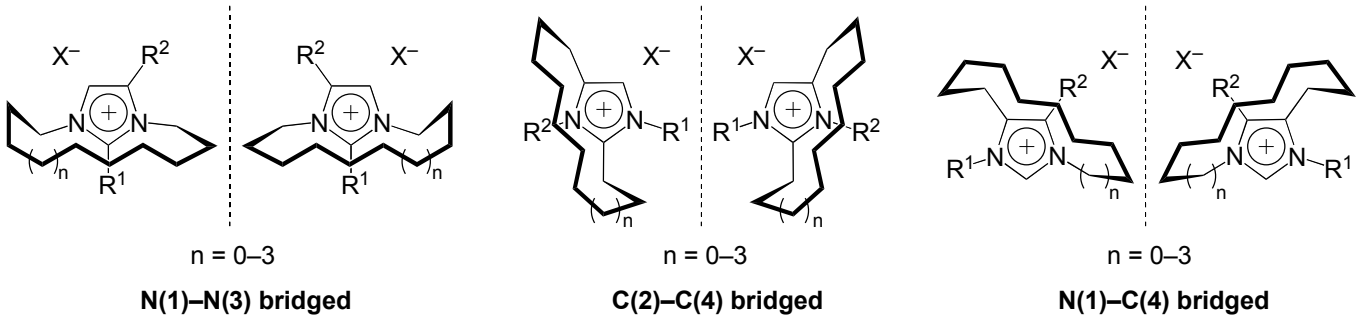
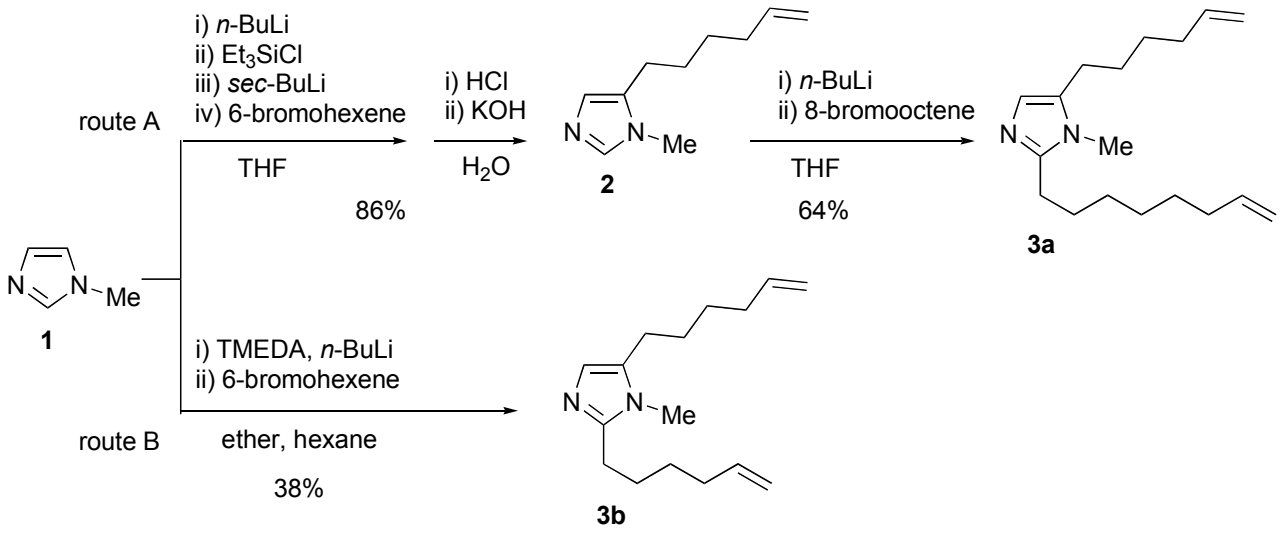


Figure 1. Three classes of cyclophane-type imidazolium salts with planar chirality.

RESULTS AND DISCUSSION

For the synthesis of C(2)–C(4) bridged cyclophane-type imidazolium salts with a bicyclic system, the formation of a macrocyclic ring is a key step. Because the ring-closing metathesis (RCM) using a Grubbs' catalyst is well known to be one of the most reliable reactions to construct a cyclic structure with a relatively large size, we envisaged a synthetic route outlined in Schemes 1–3.[6] The imidazole (**3a**) was synthesized by the stepwise alkylation of 1-methylimidazole (**1**) at the C(5) and C(2) positions (Scheme 1, route A). The introduction of a 5-hexenyl group at the C(5) was conducted according to the reported method with some modifications; the C(2)-protected derivative, generated by treatment of **1** with butyllithium and then chlorotriethylsilane, was allowed to successively react with *sec*-butyllithium and 6-bromohexene and to subject to the acid-induced removal of the silyl group to afford 5-(5-hexenyl)-1-methylimidazole (**2**) in 86 % yield.[7] This reaction predominantly proceeded at the C(5) position rather than the C(4) position, which is in good agreement with the result reported in the literature.[5] The second alkylation, the introduction of 7-octenyl group at the C(2) position, was

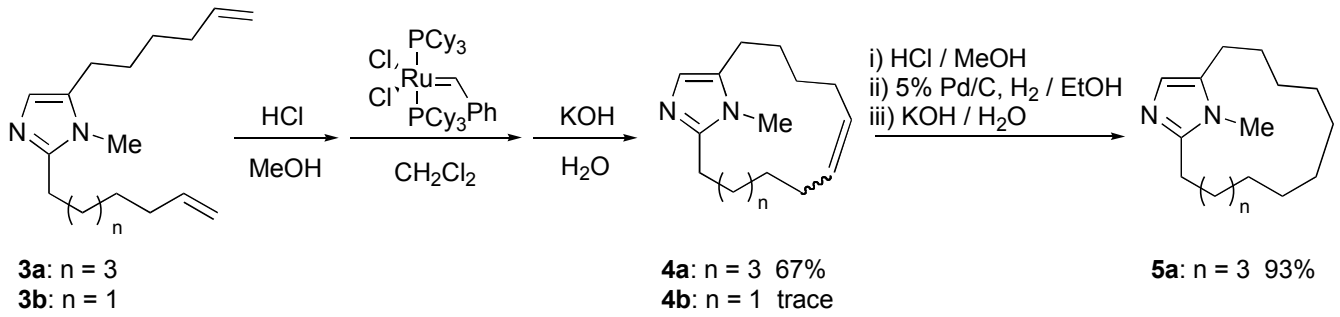
conducted by treating **2** with butyllithium and then with 8-bromohexene to afford 5-(5-hexenyl)-1-methyl-2-(7-octenyl)imidazole (**3a**) in 64% yield. In the case of the synthesis of the imidazole (**3b**) with two identical substituents at the C(2) and C(5) positions, these substituents could be introduced by a one-pot reaction (Scheme 1, route B); **1** was treated with butyllithium in the presence of *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TMEDA) to generate the 2,5-dilithiated derivative, which was subsequently subjected to the nucleophilic attacks to 6-bromohexene at both of the C(2) and C(5) positions to give 2,5-bis(5-hexenyl)-1-methylimidazole (**3b**) in 38% yield.[8]



Scheme 1. Synthesis of imidazoles possessing ω-alkenyl substituents at the C(2) and C(5) positions.

We next attempted to convert the imidazoles thus obtained to the corresponding cyclophane-type imidazoles by using benzylidenebis(tricyclohexylphosphine)dichlororuthenium (a Grubbs' catalyst) as a catalyst for the RCM reaction (Scheme 2).[6] Substrates (**3a** and **3b**) were pretreated with an acid before subjecting them to the RCM reaction in order to prevent their coordination to the ruthenium complex.[9] Unfortunately, the olefin metathesis reaction of **3b** proceeded exclusively in an intermolecular manner to afford a mixture of undesired oligomers. Even under highly diluted conditions (the initial concentration of **3b**: 1.0 mM), only a trace amount of the target cyclic monomer was generated. Contrary to this, in the case of **3a**, the olefin metathesis reaction efficiently proceeded in an intramolecular manner to afford the corresponding cyclophane-type imidazole (**4a**) in 67% yield as a mixture of *E* and *Z* isomers (the *E*/*Z* ratio was not determined). The dramatic change in the efficiency of the intra/intermolecular reactions most likely due to the stability of the intermediate bisolefin/Ru complex and/or the ring-strain of the resultant cyclophane. These observations are in good agreement with the recent report concerning the

synthesis of cyclophane-type thiazoles and furans *via* the RCM reaction.[10] Finally, **4a** was treated with HCl and then subjected to catalytic hydrogenation (5% Pd/C, H_2 [1 atm]) to afford the saturated species (**5a**) in 93% yield.



3a: n = 3
3b: n = 1

4a: n = 3 67%
4b: n = 1 trace

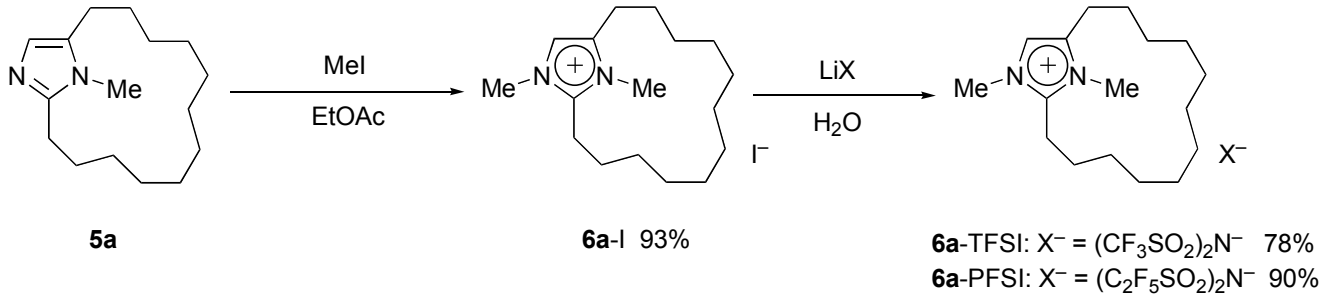
5a: n = 3 93%

Scheme 2. Synthesis of cyclophane-type imidazoles with a C(2)–C(5) bridge.

In the next stage, the dynamic profile of the cyclophane-type imidazole (**5a**) thus obtained was investigated. Because the rope-skipping process of the dodecamethylene bridge through the imidazole ring corresponds to the racemization of planar-chiral **5a**, it is quite important to investigate the kinetics of this process. This motion could be detected by monitoring the ^{1}H NMR resonances attributable to the methylene protons adjacent to the imidazole core as a probe. In $CDCl_3$ at 20 ˚C, the two couples of the geminal protons were unequivalently observed to give complicatedly split signals instead of two sets of triplets. Therefore, the decamethylene chain was likely to be fixed on either of the two faces of the imidazolium plane, at least within an NMR time-scale. The rope-skipping seems to be a hard process to occur, because such unequivalence of the geminal protons were observed even at elevated temperatures up to 180 ˚C in DMSO-d_6. These observations indicate that the methyl group placed at the N(1) position efficiently suppresses the rope-skipping process, which is in good agreement with our previous study.[3] Thus, the planar chirality of **5a** was confirmed to be tolerant to the racemization, which is advantageous for the enanatioseparation of **5a**. Enantiopure **5a** may be converted to the corresponding imidazolium salt as an enantiopure form. Furthermore, enantiopure **5a** itself might be applicable in various fields involving chiral recognition, such as chiral selector, resolving reagent, and asymmetric catalyst.

For the access to an enantiopure cyclophane-type imidazolium salt, the following two routes might be possible: (i) The enantioseparation of racemic **5a** followed by the quaternization of the enantiopure **5a**. (ii) The quaternization of racemic **5a** followed by the enantioseparation of the resultant cyclophane-type imidazolium salt. Considering the fact that the enantioseparation of charged substrates such as onium salts is generally difficult, the former route seems to be advantageous. However, at the preliminary

stage of our ongoing project, we decided to use racemic **5a** for the following study in order to check whether the imidazolium salts derived from **5a** meet the criteria for the application as chiral ionic liquids. By using racemic **5a** as a precursor, imidazolium salts with cyclophane-type planer chirality could be prepared by a quaternization reaction (Scheme 3). Although various electrophiles were applicable for the quaternization of **5a**, we selected methyl iodide for the initial model of this system, because the resultant imidazolium salt would possess a simple structure. The cyclophane-type imidazole **5a** was allowed to react with methyl iodide in AcOEt to give the corresponding imidazolium iodide **6a**–I in excellent yield (93%). The dynamic profile of the dodecamethylene chain, in terms of the rope-skipping process through the five-membered ring, was not influenced by the introduction of the N(3) methyl group, which was confirmed by variable-temperature ^{1}H NMR; the unequivalence of the geminal methylene protons adjacent to the imidazolium core was observed up to 180 ˚C in DMSO-d_6.



Scheme 3. Synthesis of ionic liquids from a cyclophane-type imidazole.

In order to lower the melting point of the salt of **6a**, we then conducted an anion-exchanging reaction (Scheme 3). As the counter anions, bis(trifluoromethylsulfonyl)imide (TFSI) and bis(pentafluoroethylsulfonyl)imide (PFSI) were chosen, because these anions have been most widely used in the study of ionic liquids.[11] According to a usual procedure, iodide anion of **6a**-I was exchanged with the imide anions to afford the corresponding salts (**6a**-TFSI and **6a**-PFSI) in good yields (78 and 90%, respectively), of which the purities were confirmed by their elementary analyses.[11a] Unfortunately, slow evaporation of the solvent from CH_2Cl_2 solutions of **6a**-TFSI and **6a**-PFSI gave solids, indicating that the melting points of these salts were higher than room temperature. However, DSC measurements showed that the melting points of these solids were relatively low (48 and 42 ˚C, respectively). Once melted, furthermore, these salts only displayed glass transitions (–43 and –36 ˚C, respectively) during repetitive cooling/warming cycles. These observations indicate that the crystallinity of the salts of **6a** is not so high most likely due to the dissymmetric skeleton of the imidazolium cation. Therefore, ionic liquids with satisfactorily low melting points might be obtained by further optimization of the anionic part and/or the imidazolium N(3) substituent.

As an initial study of the chiral recognition ability of planar-chiral ionic liquids (**6a**-X), we attempted to detect diastereomeric interaction between the cationic part (**6a**) and chiral anions.[3] For example, **6a**-I and silver(I) (1*S*)-10-camphorsulfonate (**7**) were mixed in $CDCl_3$, and the ^1H NMR spectrum of the resultant diastereomeric mixture was monitored. As a result, the mixture presented two sets of three singlets for the imidazolium C(5)-H, N(1)-CH_3, and N(3)-CH_3 signals (Figure 2a). In contrast, the salts with achiral anions, such as **6a**-I, gave a singlet for each signal. Therefore, splitting observed in the C(5)-H, N(1)-CH_3, and N(3)-CH_3 signals were likely because of both diastereomers being distinctly observed. This assignment was also confirmed by a control experiment using 2,4-dihexyl-1,3-dimethylimidazolium iodide (**8**-I) in the place of **6a**-I; no splitting of the corresponding signals was observed upon interacting with (1*S*)-**7** (Figure 2b). Worth to note is the fact that signal splittings due to the diaseteromeric interaction were observed even for the N(1)-CH_3 and N(3)-CH_3 signals. In the case of our previous model, planar-chiral imidazolium salt with a bridge connecting the N(1) and N(3) positions, such a signal split owing to diastereomeric interaction was detected only for the C(5)-H signal.[3] Thus observed differences between the two types of cyclophane-type imidazolium salts, the N(1)–N(3) bridged and the C(2)–C(4) bridged imidazolium salts, in terms of diastereomeric interaction with a chiral anion, is most likely attributed to the shape of the cationic part; the C(2)–C(4) bridged imidazolium cation is of lower symmetry, compared with the N(1)–N(3) bridged type, which might reflect on the difference in the chemical shift values of the signals for the diastereomeric ion pairs.

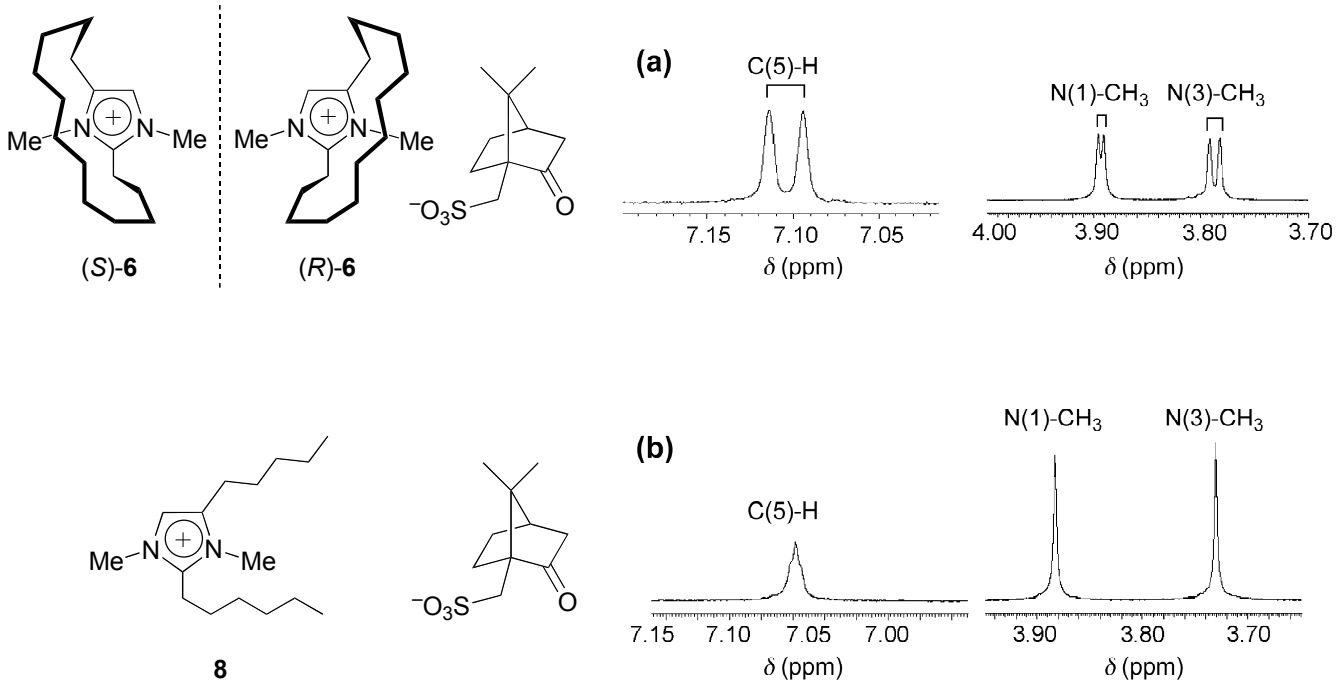


Figure 2. ^1H NMR resonances for the imidazolium C(5)-H, N(1)-CH_3, and N(3)-CH_3 of a mixture of (a) racemic **6a**-I with (1*S*)-**7** and (b) **8**-I with (1*S*)-**7** in $CDCl_3$.

In conclusion, a novel planer-chiral cyclophane-type imidazolium salt was synthesized, of which the bridge unit connected the C(2) and C(4) positions of the imidazolium ring. The resultant imidazolium salt showed a potential utility as a chiral ionic liquid. ^{1}H NMR spectroscopic experiment indicated that C(2)–C(4) bridged cyclophane-type imidazolium salts were expected to possess a chiral recognition ability superior to that of our previous model, the N(1)–N(3) bridged cyclophane-type imidazolium salts. The preparation and application of the enantiopure ionic liquids based on this structure is currently studied in our laboratory.

EXPERIMENTAL

General

^{1}H NMR spectra were recorded on a Varian Mercury 300 operating at 300 MHz, where the chemical shifts were given in ppm downfield from internal tetramethylsilane. IR spectra were recorded on a JASCO model IR-810. FAB-MS spectra were recorded on a JEOL JMS-HX110 spectrometer using a 3-nitrobenzyl alcohol matrix. Melting points were determined on a Mettler model DSC 30.

5-(5-Hexenyl)-1-methylimidazole (**2**)

To a THF solution (40 mL) of 1-methylimidazole (**1**, 620 mg, 0.60 mL, 7.5 mmol) was added dropwise a hexane solution of butyllithium (1.57 M, 5.25 mL, 8.25 mmol) at –78 ˚C under argon atmosphere. After the reaction mixture was stirred at the temperature for 30 min, chlorotriethylsilane (2.3 g, 2.5 mL, 8.25 mmol) was added. The reaction mixture was allowed to warm to rt and stirred for 16 h. From the resultant mixture, the solvent and unreacted chlorotriethylsilane was removed under reduced pressure, and the residue was dissoleved in THF (40 mL). To the THF solution thus obtained was added dropwise a hexane/cyclohexane solution of *sec*-butyllithium (purchased from Kanto Chemical, 0.99 M, 15.2 mL, 15 mmol) at –78 ˚C under argon atmosphere. After being stirred at the temperature for 30 min, 6-bromo-1-hexene (4.9 g, 4.0 mL, 30 mmol) was added to the reaction mixture. The reaction mixture was allowed to warm to rt and stirred overnight. The reaction mixture was concentrated under reduced pressure, diluted with aqueous HCl (2 M, 75 mL), and stirred at rt overnight. After being washed with hexane (3 x 20 mL), the aqueous layer was treated with aqueous KOH (5%) until the pH reached to 10, and the mixture was extracted with AcOEt (5 x 50 mL). The organic layers combined was dried over anhydrous $MgSO_4$, concentrated under reduced pressure, and subjected to silica gel column chromatography ($CHCl_3$:MeOH = 100:0 to 96:4, v/v) to afford **2** as a yellow oil (1.06 g, 86%). IR (KBr) 3045, 2930, 2855, 1640, 1505, 1460, 1110, 910, 810, 665 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 1.44–1.54 (2H, m), 1.59–1.71 (2H, m), 2.06–2.14 (2H, m), 2.53 (2H, t, J = 7.5 Hz), 3.54 (3H, s), 4.94–5.05 (2H, m), 5.74–5.87 (1H, m), 6.77 (1H, s), 7.36 (1H, s).

5-(5-Hexenyl)-1-methyl-2-(7-octenyl)imidazole (**3a**)

To a THF solution (5 mL) of **2** (82.1 mg, 0.50 mmol) was added dropwise a hexane solution of butyllithium (1.57 M, 0.35 mL, 0.55 mmol) at –78 ˚C under argon atmosphere. After being stirred at the temperature for 30 min, 8-bromo-1-octene (380 mg, 0.354 mL, 2.0 mmol) was added to the reaction mixture. The reaction mixture was allowed to warm to rt and stirred overnight. The reaction mixture was concentrated under reduced pressure, diluted with aqueous HCl (2 M, 5 mL), and washed with hexane (5 x 2 mL). Aqueous KOH (5%) was added to the aqueous layer until the pH reached to 10, and the mixture was extracted with AcOEt (5 x 5 mL). The organic layers combined were dried over anhydrous $MgSO_4$, concentrated under reduced pressure, and subjected to silica gel column chromatography ($CHCl_3$:AcOEt = 95:5 to 85:15) to afford **3a** as a pale yellow oil (87.4 mg, 64%). IR (KBr) 2930, 2855, 1640, 1500, 1460, 1435, 1410, 995, 910 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.34–1.78 (12H, m), 2.00–2.14 (4H, m), 2.49 (2H, t, J = 7.5 Hz), 2.62 (2H, t, J = 7.8 Hz), 3.41 (3H, s), 4.90–5.05 (4H, m), 5.73–5.88 (2H, m), 6.65 (1H, s).

2,5-Bis(5-hexenyl)-1-methylimidazole (**3b**)

To an etheral solution (12 mL) of **1** (245 mg, 2.98 mmol) and *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TMEDA) (1.7 g, 2.3 mL, 15 mmol) was added dropwise a hexane solution of butyllithium (1.57 M, 9.6 mL, 15 mmol) at –78 ˚C under argon atmosphere. The reaction mixture was allowed to warm to rt and stirred for 1 h. After the mixture was cooled to –78 ˚C, 6-bromo-1-hexene (4.9 g, 4.0 mL, 30 mmol) was added. The reaction mixture was allowed to warm to rt and stirred overnight. The reaction mixture was treated with aqueous HCl (2.0 M, 20 mL), and the organic phase was extracted with aqueous HCl (2 M, 5 x 10 mL). Aqueous KOH (5%) was added to the combined aqueous layers until the pH reached to 10, and the mixture was extracted with AcOEt (5 x 10 mL). The organic layers combined were dried over anhydrous $MgSO_4$, concentrated under reduced pressure, and subjected to silica gel column chromatography ($CHCl_3$:AcOEt = 95:5 to 90:10) to afford **3b** (280 mg, 38%) as a yellow oil. IR (KBr) 3075, 2930, 2855, 1640, 1500, 1460, 1430, 1415, 995, 910, 810, 670, 635 cm^{-1}. ^1H NMR ($CDCl_3$) δ 1.44–1.81 (8H, m), 2.06–2.14 (4H, m), 2.49 (2H, t, J = 7.4 Hz), 2.64 (2H, t, J = 7.7 Hz), 3.41 (3H, s), 4.91–5.05 (4H, m), 5.74–5.88 (2H, m), 6.65 (1H, s).

17-Methyl-15,17-diazabicyclo[12.2.1]heptadeca-1(16),6,14-triene (**4a**)

A solution of **3a** (47.5 mg, 0.173 mmol) in methanolic HCl (0.5 M, 18 mL) was stirred at rt for 30 min, and the mixture was concentrated under reduced pressure to afford a crude salt of **3a** with HCl. Volatile impurities were removed from the residue by azeotropic evaporation with toluene (3 x 1 mL) and then with CH_2Cl_2 (1 mL). To a solution of the resultant residue in CH_2Cl_2 (173 mL) was added a Grubbs' catalyst, benzylidenebis(tricyclohexylphosphine)dichlororuthenium, (14.2 mg, 0.0173 mmol) under argon

atmosphere, and the mixture was refluxed for 8 h. After addition of water (5 mL), the reaction mixture was concentrated under reduced pressure. The resultant residue was treated with aqueous HCl (2 M, 10 mL) and washed with toluene (5 x 5 mL). Aqueous KOH (5%) was added to the aqueous layer until the pH reached to 10, and the mixture was extracted with AcOEt (5 x 3 mL). The organic layers combined were dried over anhydrous $MgSO_4$, concentrated under reduced pressure, and subjected to silica gel column chromatography ($CHCl_3$:AcOEt = 100:0 to 50:50) to afford **4a** (a mixture of the *E* and *Z* isomers, 28.6 mg, 68%) as a slightly yellow oil. IR (KBr) 2930, 2855, 1500, 1460, 1405, 1275, 970, 805 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.64–2.15 (16H, m), 2.35–2.91 (4H, m), 3.44, 3.45 (3H, s x 2), 5.04-5.43 (2H, m), 6.66, 6.67 (1H, s x 2). ^{13}C NMR ($CDCl_3$) δ 23.88, 24.03, 25.96, 26.54, 27.14, 27.16, 27.33, 27.53, 27.69, 27.71, 27.82, 28.49, 28.52, 28.60, 28.71, 29.44, 29.50, 30.16, 30.50, 30.97, 32.90, 125.23, 125.33, 129.45, 130.07, 130.89, 131.39, 131.49, 148.62, 148.70. EI-MS Calcd for $C_{16}H_{26}N_2$: $[M]^+$ = 246. Found: 246.

17-Methyl-15,17-diazabicyclo[12.2.1]heptadeca-1(16),14-diene (**5a**)

A solution of **4a** (100 mg, 0.407 mmol) in methanolic HCl (0.5 M, 40 mL) was stirred at rt for 30 min, and the mixture was concentrated under reduced pressure to afford a crude salt of **4a**. Volatile impurities were removed from the residue by azeotropic evaporation with EtOH (5 x 5 mL). To an EtOH solution (10 mL) of the resultant residue, which was degassed with argon, was added Pd/C (5%, 30 mg) in one portion, and the resultant suspension was stirred at rt under H_2 atmosphere (1 atm). After being stirred for 2 days, Pd/C was filtered off through Cerite 545. The filtrate was concentrated under reduced pressure and diluted with water (1 mL). Aqueous KOH (2 M, 1 mL) was added to the aqueous solution, and the mixture was extracted with AcOEt (5 x 4 mL). The organic layers combined were dried over $MgSO_4$, concentrated under reduced pressure, and subjected to silica gel column chromatography ($CHCl_3$:MeOH = 100:0 to 97:3) to afford **5a** (94.2 mg, 93%) as a slightly yellow oil, which gradually solidified after several days. IR (KBr) 2940, 2870, 1490, 1460, 1400, 1270, 800, 660 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.96–1.35 (16H, m), 1.49–1.59 (2H, m), 1.68–1.78 (2H, m), 2.53–2.89 (4H, m), 3.47 (3H, s), 6.68 (1H, s). ^{13}C NMR ($CDCl_3$) δ 23.99, 25.35, 25.62, 26.20, 26.39, 26.98, 27.13, 27.19, 27.24, 27.53, 28.42, 28.46, 30.94, 125.61, 131.54, 148.86.

15,17-Dimethyl-17-aza-15-azoniabicyclo[12.2.1]heptadeca-1(16),14-diene iodide (**6a**-I)

To an AcOEt solution (1 mL) of **5a** (54.9 mg, 0.221 mmol) was dropwise added methyl iodide (157 mg, 70 μL, 1.11 mmol) at rt under argon atmosphere. The resultant mixture was stirred at 50 °C for 5 h to gradually generate a white solid. The solid was corrected by filtration and dried in *vacuo* to afford **6a**-I as a white solid (80.2 mg, 93%). IR (KBr) 3080, 2940, 2865, 1630, 1525, 1450, 1180 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.95–1.37 (16H, m), 1.60–1.72 (3H, m), 1.83–2.00 (1H, m), 2.79 (2H, t, J = 6.2 Hz), 3.24–3.42

(2H, m), 3.81 (3H, s), 3.94 (3H, s), 7.24 (1H, s). ^{13}C NMR ($CDCl_3$) δ 23.64, 25.33, 25.44, 25.82, 25.88, 26.33, 26.67, 26.73, 26.91, 27.09, 27.35, 34.26, 36.72, 120.74, 134.47, 148.43.

15,17-Dimethyl-17-aza-15-azoniabicyclo[12.2.1]heptadeca-1(16),14-diene bis(trifluoromethanesulfonyl)imide (**6a**-TFSI)

To an aqueous solution (1 mL) of **6a**-I (29.3 mg, 0.075 mmol) was added lithium bis(trifluoromethylsulfonyl)imide (21.5 mg, 0.075 mmol) at 70 ˚C, and the mixture was stirred for 30 min at the temperature. The reaction mixture was extracted with CH_2Cl_2 (1 mL), and the organic phase was washed with water (5 x 5 mL), then concentrated under reduced pressure. The resultant residue was dried in *vacuo* at 55 ˚C overnight to afford **6a**-TFSI (238 mg, 78%) as a white solid. IR (KBr) 2940, 2870, 1530, 1450, 1345, 1320, 1220, 1185, 1130, 1050, 615, 595, 565, 510 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.96–1.36 (16H, m), 1.60–1.69 (3H, m), 1.84–1.98 (1H, m), 2.77 (2H, t, J = 6.5 Hz), 3.03–3.20 (2H, m), 3.72 (3H, s), 3.80 (3H, s), 6.95 (1H, s). Anal. Calcd for $C_{19}H_{31}N_3O_4F_6S_2$: C 41.98, H 5.75, N 7.73. Found: C 41.76, H 5.71, N 7.61. Melting point: T_m = 48 ˚C (first heating), T_g = –43 ˚C (second heating).

15,17-Dimethyl-17-aza-15-azoniabicyclo[12.2.1]heptadeca-1(16),14-diene bis(pentafluoroethanesulfonyl)imide (**6a**-PFSI)

6a-PFSI was prepared from **6a**-I and lithium bis(pentafluoroethylsulfonyl)imide in the same procedure as that for the synthesis of **6a**-TFSI (90% yield). IR (KBr) 3160, 2945, 2870, 1610, 1530, 1450, 1350, 1320, 1210, 1160, 1080, 970, 635, 610, 520 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.97–1.35 (16H, m), 1.60–1.69 (3H, m), 1.82–1.98 (1H, m), 2.76 (2H, t, J = 6.3 Hz), 3.01–3.19 (2H, m), 3.71 (3H, s), 3.79 (3H, s), 6.94 (1H, s). Anal. Calcd for $C_{21}H_{31}N_3O_4F_{10}S_2$: C 39.19, H 4.85, N 6.53. Found: C 39.04, H 4.85, N 6.39. Melting point: T_m = 42 ˚C (first heating), T_g = –36 ˚C (second heating).

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