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Evaluation, synthesis and structural properties of stable bisbenzimidazolium tetrafluoroborates derived from unstable benzotetraazafulvalenes

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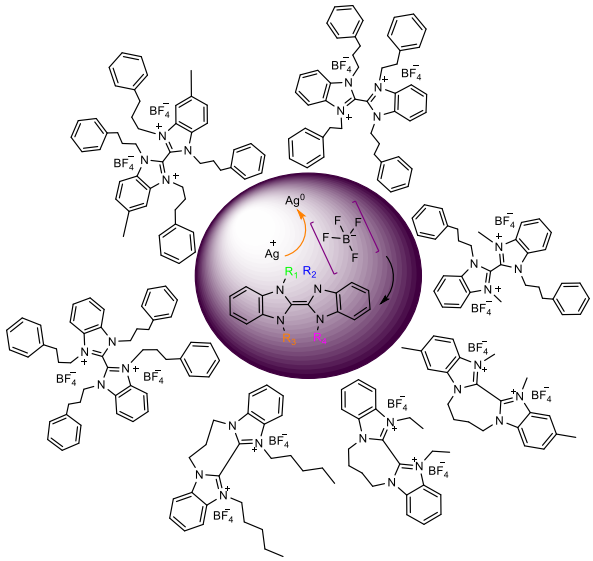
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Abstract

The stable dicationic tetrafluoroborate salts of tetraazafulvalenes were synthesized with unstable N-heterocyclic carbenes or enetetramines derived from benzimidazolium and bridged-bisbenzimidazolium halides. The structural characterizations of all the compounds were determined via spectroscopic methods ^{1}H-NMR, ^{13}C-NMR, IR, and MS and by elemental analysis respectively. Also, the effect of compound **1** as a ligand on the catalytic system was evaluated in the Suzuki-Miyaura reaction.



Keywords: Benzimidazole, N-heterocyclic carbene, tetraazafulvalene, enetetramine, dicationic salt, ligand

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Introduction

Benzimidazole derivatives are pharmacophores that have an important place in medicinal chemistry. They have therapeutic activities for many diseases.[1-3] Besides, they are important N heterocyclic carbene precursors and are used in organic-organometallic compound synthesis and especially in catalysis studies.[4-7]

N-heterocyclic carbenes (NHCs) are a class of compounds in which the carbene is in a nitrogen-containing ring structure and has many uses. NHCs are frequently observed in work areas such as the synthesis of organic or organometallic catalysts, bioactive materials, and metal-organic framework preparation. [7, 8-13] The synthesis of NHCs is generally carried out in two pathways. The first method is the deprotonation of azolium salts in the presence of a strong base, and the second method is the reduction of urea derivatives.[14-17]

The NHCs tend to dimerize in the reaction medium. These compounds containing an exocyclic carbon-carbon double bond are called electron-rich olefin (ERO), dibenzotetraazafulvalene (TAF) N-heterocyclic olefin (NHO), or organic electron-donor (OED).[18-24] The NHCs or NHOs are used as catalysts in many organic reactions such as benzoin condensation, acylation reaction, ring-opening reactions, and isocyanurate synthesis.[25-29] OEDs in other words NHOs with negative redox potentials form radical cations or dicationic products with the loss of one or two electrons. These redox reactions have interesting applications. Examples are redox switches, greenhouse gas reduction agents, polymerization initiators, solar cells, organic field-effect transistors, fluorescent material, and the synthesis of new compounds.[30-39]

The synthesis of dicationic tetraazafulvalenes is also important because of the interest in using fields described above. In this study, a group of new dicationic benzotetraazafulvalene tetrafluoroborates (**1**-**7**) was synthesized and their structural properties were evaluated. The synthesis of stable NHC precursors is important, as N-heterocyclic carbenes (NHCs) or electron-rich olefins (EROs) have many applications such as catalysts and the synthesis of organometallic compounds. These new compounds can be used as stable NHC or electron-rich olefin precursors.[7,31]

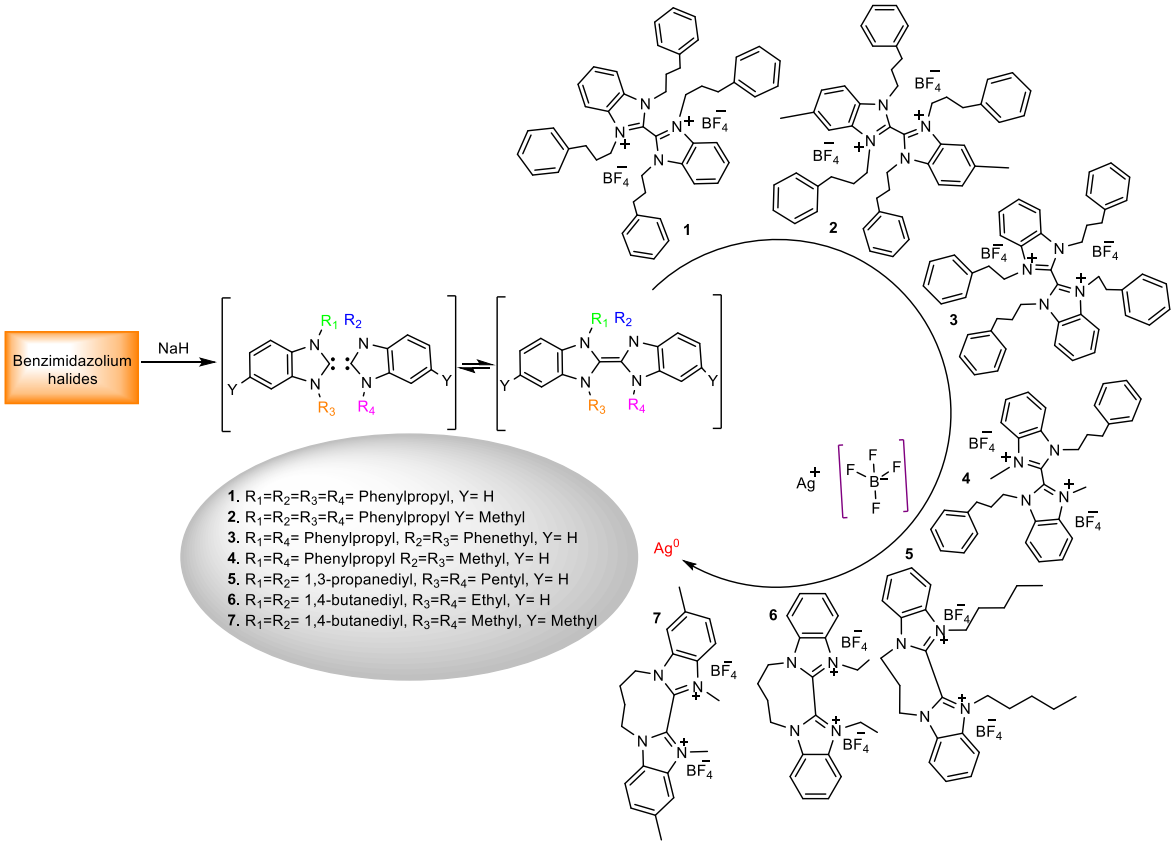
Results and Discussion

N-heterocyclic carbenes (NHCs) are known to be enormously strong reducing agents.[7] Therefore, they have been used as active intermediates for the synthesis of many useful new compounds in organic chemistry for decades.[6,8] Dicationic dibenzotetraazafulvalens have been used as they exhibit a large Stokes shift. Therefore, they can be used in solar cells and laser applications.[40]

The benzimidazolium halides were synthesized according to the literature sources.[14,41] The NHCs were synthesized by mixing benzimidazolium halides as a N-heterocyclic carbene precursor with NaH in dry tetrahydrofuran (THF) for 6h at room temperature (rt) in an argon atmosphere. The unstable carbenes were extracted with toluene and the yellow-colored solid was obtained. The yellow-colored products were washed with hexane and dried. The mixture of yellow solid, $AgBF_4$, and THF was stirred in rt for 30 min. The silver mirror formation was observed along with the precipitated gray solid in the reaction media. The products were crystallized in ethanol. The compounds were obtained with good yields between 67-87%. The structural evaluations of all new compounds were carried out by spectroscopic techniques and elemental analysis. The ^{1}H NMR spectra of all compounds were examined and it was observed that the chemical shift (δ) values of the aromatic peaks were in the range of 8.442-7.090 ppm. The chemical shifts of the methylene groups of the 3-phenylpropyl of compounds **1**, **2**, **3**, and **4** were observed for N-CH_2 at 4.60, 4.43, 4.41, and 4.49; for the Ph-CH_2 group at 2.68, 2.80, 2.62, and 2.78; for the CH_2 group at 2.14, 2.36, 2.23, and 2.37 ppm in the ^{1}H NMR

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spectra. In the ^{13}C NMR spectra of compounds **1**, **3**, and **4**, the peaks of N-CH_2, Ph-CH_2, and CH_2 methylene carbons were also observed at 47.6, 46.9, 47.1; 31.9, 32.3, 32.5; 31.3, 30.2, and 30.0 ppm respectively. It was observed 5(6)-tautomerism[41] with two different chemical shift values, due to the methyl groups present in the 5 position in compounds **2** and **7**. In the ^{13}C NMR spectrum of compound **2**, the carbon peaks of the N-CH_2, Ph-CH_2, and CH_2 groups were recognized at 47.0 and 46.8, 32.5 and 32.4, 30.2 and 30.1 ppm, respectively. Also, the chemical shift values of the N-CH_3 group of compound **7** in the ^{1}H NMR spectrum were observed at 4.26 and 4.24 ppm, which are two values. Similarly, carbon peaks of the N-CH_3 group were observed at 34.7 and 34.6 ppm in the ^{13}C NMR spectrum. Another remarkable situation in the ^{1}H NMR spectra is that each of the bridging methylene groups of the diazocine derivatives (compounds **6** and **7**) has different chemical shift values. The bridging NCH_2 groups of compound **6** were observed at 4.89 and 4.61 ppm. The CH_2 peaks were also identified at 2.25 and 1.98 ppm. In the ^{1}H NMR of compound **7**, four different chemical shift values were observed for bridge methylene groups at 5.04, 4.43, 2.27, and 1.91 ppm, similarly.



Scheme. Synthesis pathway of dicationic tetraazafulvalene ditetrafluoroborates

This situation is thought to be due to the distortion of symmetry as a result of the stereochemical configuration of the bulky groups of the eight-membered ring. So, when the dihedral angles of the methylene groups in the bridge position of the compounds were calculated theoretically, slightly different values were obtained. The data supports the different chemical shift values of the methylene group (Table 1).

Table 1. The dihedral angles of bridge-methylene carbon and hydrogen atoms of compounds **6** and **7**

Entry	Compound **6** atoms	Angle (°)	Compound **7** atoms	Angle (°)

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1	C(31)-C(33)-C(34)-C(32)	-81.811	C(33)-C(35)-C(36)-C(34)	-81.779
2	C(31)-C(33)-C(34)-H(55)	158.264	C(33)-C(35)-C(36)-H(61)	158.264
3	C(31)-C(33)-C(34)-H(56)	38.232	C(33)-C(35)-C(36)-H(62)	38.238
4	H(53)-C(33)-C(34)-C(32)	158.218	H(59)-C(35)-C(36)-C(34)	158.269
5	H(53)-C(33)-C(34)-H(55)	38.293	H(59)-C(35)-C(36)-H(61)	38.311
6	H(53)-C(33)-C(34)-H(56)	-81.739	H(59)-C(35)-C(36)-H(62)	-81.714
7	H(54)-C(33)-C(34)-C(32)	38.223	H(60)-C(35)-C(36)-C(34)	38.256
8	H(54)-C(33)-C(34)-H(55)	-81.702	H(60)-C(35)-C(36)-H(61)	-81.702
9	H(54)-C(33)-C(34)-H(56)	158.265	H(60)-C(35)-C(36)-H(62)	158.273
10	N(24)-C(32)-C(34)-C(33)	2.477	N(24)-C(34)-C(36)-C(35)	2.435
11	N(24)-C(32)-C(34)-H(55)	122.406	N(24)-C(34)-C(36)-H(61)	122.393
12	N(24)-C(32)-C(34)-H(56)	-117.551	N(24)-C(34)-C(36)-H(62)	-117.582
13	H(51)-C(32)-C(34)-C(33)	-117.736	H(57)-C(34)-C(36)-C(35)	-117.716
14	H(51)-C(32)-C(34)-H(55)	2.192	H(57)-C(34)-C(36)-H(61)	2.242
15	H(51)-C(32)-C(34)-H(56)	122.236	H(57)-C(34)-C(36)-H(62)	122.267
16	H(52)-C(32)-C(34)-C(33)	121.872	H(58)-C(34)-C(36)-C(35)	121.852
17	H(52)-C(32)-C(34)-H(55)	-118.200	H(58)-C(34)-C(36)-H(61)	-118.189
18	H(52)-C(32)-C(34)-H(56)	1.844	H(58)-C(34)-C(36)-H(62)	1.836
19	N(19)-C(31)-C(33)-C(34)	3.860	N(19)-C(33)-C(35)-C(36)	3.846
20	N(19)-C(31)-C(33)-H(53)	123.831	N(19)-C(33)-C(35)-H(59)	123.798
21	N(19)-C(31)-C(33)-H(54)	-116.177	N(19)-C(33)-C(35)-H(60)	-116.188
22	H(49)-C(31)-C(33)-C(34)	-116.288	H(55)-C(33)-C(35)-C(36)	-116.305
23	H(49)-C(31)-C(33)-H(53)	3.684	H(55)-C(33)-C(35)-H(59)	3.647
24	H(49)-C(31)-C(33)-H(54)	123.675	H(55)-C(33)-C(35)-H(60)	123.660
25	H(50)-C(31)-C(33)-C(34)	123.275	H(56)-C(33)-C(35)-C(36)	123.265
26	H(50)-C(31)-C(33)-H(53)	-116.754	H(56)-C(33)-C(35)-H(59)	-116.783
27	H(50)-C(31)-C(33)-H(54)	3.238	H(56)-C(33)-C(35)-H(60)	3.230

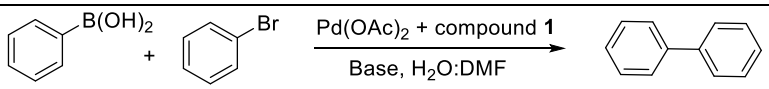
The chemical shift (δ) values of NCN carbons were observed at 140.99, 141.03, 141.55, 142.34, 142.64, 133.51, 140.17, and 140.12 ppm, respectively in the ^{13}C NMR spectra of the compounds. In the IR spectra, peaks of the C=N bonds of imidazole cycles were observed at 1521.52, 1562.77, 1571.79, 1563.93, 1567.00 and 1546.21 cm^{-1}, and peaks of the $BF4^-$ group were observed at 1032.41, 1028.03, 1031.00, 1023.98, 1031.63, 1030.90 and 1027.86 cm^{-1}. In addition, the mass spectra of the compounds were evaluated. In the spectrum of compound **1**, the molecular peak of the cation after the salt compound lost its two BF_4^- anions are 708.4, and the peak value of 354.3, which is the mass value of half of the dicationic compound. The mass spectrum values of compound **2** were determined as $[M^{+2}2BF_4^- - 2BF_4^-]$ = 736.3 and $[M^{+2}2BF_4^- - 2BF_4^-]/2$ = 368.8. Similarly, the mass spectra of compounds **3**-**7** show 769.4, 589.3, 505.2, 433.2, and 433.2 values belonging to the dicationic structures formed by the separation of a trifluoroborate anions from the molecule. These data are consistent with the literature.[6, 14, 42] After, the structural characterization of the compounds, the activity of a catalytic system was investigated that consists of compound **1** as a ligand in presence of $Pd(OAc)_2$ in the Suzuki Miyaura C-C coupling reaction. The Suzuki-Miyaura cross-coupling reaction provides the formation of new C-C bonded compounds. This reaction is performed with organoboron compounds and organic electrophiles such as aryl

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halides in presence of a suitable catalytic system. The most effective catalysts used in the Suzuki-Miyaura reaction are bearing Pd and Ni.[43,44] One of the most preferred in situ catalytic reactions contains a catalytic system consisting of a base, NHC precursor, and $Pd(OAc)_2$ due to their stability. In our previous work, in situ C-C coupling reactions were also carried out with high activities with NHC precursors/$Pd(OAc)_2$ catalytic systems.[14,45]

Here, its catalytic contribution to C-C bond formation was evaluated when compound **1** was used in the presence of palladium acetate as the ligand (Table 2). To observe the changing in the reaction yield were used different bases like K_2CO_3, KOH, and NaOH. K_2CO_3 was the most active (Table 2, entry 3). It was observed that the yield decreased from 80% to 55% when the ligand (compound **1**) was not used in the reaction at 80 °C. It was noticed that increasing the temperature from 80 to 100 °C did not cause a remarkable increase in yield (Table 2, entries 3 and 6).

Table 2. The ligand activity of compound **1** in the Suzuki-Miyaura cross-coupling reaction



Entry	Base	Heat (°C)	Time (h)	Yield (%)[a]
1	NaOH	80	1	27
2	KOH	80	1	43
3	K_2CO_3	80	1	80
4	K_2CO_3	80	1	55[b]
5	K_2CO_3	80	2	80
6	K_2CO_3	100	1	83

Conditions: bromobenzene (1 mmol), phenylboronic acid (1 mmol), solvent (4 mL), base (2 mmol), $Pd(OAc)_2$ (0.01 mmol), and compound **1** (0.01 mmol). [a]Isolated yield, [b]without compound **1**.

Conclusions

In this study new dicationic benzimidazolium ditetrafluoroborates (**1**-**7**) were synthesized with N-heterocyclic carbenes or their dimer electron-rich olefins in other ways electron donor olefins. The structural differences of dicationic benzotetraazafulvalenes were evaluated. Benzimidazole compounds contain alkyl groups such as phenylpropyl, phenylethyl, methyl, ethyl, pentyl, 1,3-propanediyl, and 1,4-butanediyl in the 1 and 3 positions. Moreover, It was observed that compound **1**, which was used as a ligand in the presence of palladium acetate increased the yield of biphenyl formation in the Suzuki-Miyaura C-C coupling reaction between phenylboronic acid and bromobenzene. Structural characterization of the new compounds was performed via spectroscopic methods such as ^1H, ^{13}C NMR, IR, and MS.

Experimental Section

General. The starting materials were purchased from Acros, Aldrich, and Fluka Chemical Co. All ^1H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra were recorded using Bruker Avance 300 UltraShield high-performance digital FT NMR spectrometer. Infrared spectra of prepared compounds were measured as KBr pellets in the range 4000-400 cm^{-1} on a Perkin-Elmer Spectrum One FT-IR spectrometer. MS spectra belong to seven

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benzimidazolium tetrafloroborates were performing by Agilent 1100 Series LC/MSD SL (Mass column ACE5 C18 S/N-A20826 250 4.6 mm, ACE-121-2546). Elemental analyses were performed by LECO CHNS-932 elemental analyzer. Melting points were measured using an electrothermal melting point apparatus, Electrothermal 9200. The dihedral angles of bridge-methylene carbon and hydrogen atoms of compounds **6** and **7**. were calculated by the program of ChemDraw professional 2016 (page of launch Chem 3D calculations).

Synthesis. The mixture of benzimidazolium halides (2.30 mmol), NaH (2.50 mmol), and tetrahydrofuran (10 mL) was stirred in room temperature for 6h. After the reaction, the solvent was removed by vacuum and the crude product was extracted with toluene (10 mL). The solvent was removed again in yellow colored solution. The yellow solid was washed with hexane and dried. The mixture of yellow solid, $AgBF_4$ (2.46 mmol), and THF (10 mL) was stirred in rt for 30 min. The silver mirror formation was observed along with the precipitated gray solid. The product was crystallized in ethanol (30 mL).

1,1',3,3'-Tetrakis(3-phenylpropyl)-1*H*,1'*H*-[2,2'-bibenzo[*d*]imidazole]-3,3'-diium ditetrafluoroborate (1). Yield: 0.80 g, 74 %; mp 232-234 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.40-8.37 (*m*, 4H, Ar-$H_{benzimidazole}$), 8.05-8.01 (*m*, 4H, Ar-$H_{benzimidazole}$), 7.23-7.10 (*m*, 20H, Ar-H_{Ph}), 4.60 (*t*, 8H, N-CH_2, *J* 7,5 Hz), 2.68 (t, 8H, CH_2-Ph, *J* 7,5 Hz), 2.14 (*quint*, 8H, CH_2, *J* 7,5 Hz) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 140.8 (NCN), 133.7, 129.6, 129.0, 128.9, 128.4, 126.6, 115.9 (Ar-C), 47.6 (N-CH_2), 31.9 (*C*H_2-Ph), 31.3 (CH_2) ppm. IR(ν, cm^{-1}): 1521.52 (C=N), 1032.41 (BF_4^-). MS (ES-API) *m/z* (%): 708.4 (10, [$M^{+2}2BF_4^-$-$2BF_4^-$]), 354.3 (80, [$M^{+2}2BF_4^-$-$2BF_4^-$]/2). Analysis Calcd. for $C_{50}H_{52}B_2F_8N_4$ (882.4): C, 68.04; H, 5.94; N, 6.35; found: C, 67.91; H, 5.78; N, 6.25.

5(6),5(6)'-Dimethyl-1,1',3,3'-tetrakis(3-phenylpropyl)-1*H*,1'*H*-[2,2'-bibenzo[*d*]imidazole]-3,3'-diium ditetrafluoroborate (2). Yield: 67 %; mp 241-242 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.42-7.34 (*m*, 6H, Ar-$H_{benzimidazole}$), 7.30-7.15 (*m*, 20H, Ar-H_{Ph}), 4.43 (*t*, 8H, NCH_2, *J* 6.9 Hz), 2.80 (*t*, 8H, Ph-CH_2, *J* 7.2 Hz), 2.55 (*s*, 6H, Ar-CH_3), 2.36 (*quint*, 8H, CH_2, J 7.2 Hz) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 141.0 (NCN), 139.8, 139.8, 138.0, 131.5, 129.4, 128.8, 128.6, 128.4, 128.3, 126.4, 126.4, 112.6 (Ar-C), 47.0 and 46.8 (N-CH_2), 32.5 and 32.4 (Ph-CH_2), 30.2 and 30.1 (CH_2), 21.8 (CH_3) ppm. IR(ν, cm^{-1}): 1562.77 (C=N), 1028.03 (BF_4^-). MS (ES-API) *m/z* (%): 736.3 (3, [$M^{+2}2BF_4^-$-$2BF_4^-$]), 368.8 (100, [$M^{+2}2BF_4^-$-$2BF_4^-$]/2). Analysis Calcd. for $C_{52}H_{56}B_2F_8N_4$ (910.5): C, 68.58; H, 6.20; N, 6.15; found: C, 68.30; H, 6.11; N, 6.04.

3,3'-Diphenethyl-1,1'-bis(3-phenylpropyl)-1*H*,1'*H*-[2,2'-bibenzo[*d*]imidazole]-3,3'-diium ditetrafluoroborate (3). Yield: 87 %; mp 94-95 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.59-7.52 (*m*, 8H, Ar-$H_{benzimidazole}$), 7.28-7.16 (*m*, 20H, Ar-H_{Ph}), 4.70 (*t*, 4H, N-C$H_{2Phenetyl}$, *J* 7,2 Hz), 4.41 (*t*, 4H, N-C$H_{2Phenylpropyl}$, *J* 7,2 Hz), 3.26 (*t*, 4H, CH_2-$Ph_{Phenetyl}$, J 7,2 Hz), 2.62 (*t*, 8H, CH_2-$Ph_{Phenylpropyl}$, *J* 7,2 Hz), 2.23 (*quint*, 4H, $CH_{2Phenylpropyl}$, *J* 7,2 Hz) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 141.6 (NCN), 139.7, 136.0, 131.2, 131.0, 128.8, 128.7, 128.6, 128.3, 127.4, 127.2, 127.1, 126.4, 113.1, 113.0 (Ar-C), 48.7 (N-$CH_{2Phenetyl}$), 46.9 (N-$CH_{2Phenylpropyl}$), 35.3 (*C*H_2-Ph $_{Phenetyl}$), 32.3 (*C*H_2-$Ph_{Phenylpropyl}$), 30.2 ($CH_{2Phenylpropyl}$) ppm. IR(ν, cm^{-1}): 1562.64 (C=N), 1031.00 (BF_4^-). MS (ES-API) *m/z* (%): 769.4 (40, [$M^{+2}2BF_4^{-1}$-BF_4^{-1}]), 341.2 (100, [$M^{+2}2BF_4^-$-$2BF_4^-$]/2). Analysis Calcd. for $C_{48}H_{48}B_2F_8N_4$ (854.4): C, 67.47; H, 5.66; N, 6.56; found: C, 67.24; H, 5.40; N, 6.50.

3,3'-Dimethyl-1,1'-bis(3-phenylpropyl)-1*H*,1'*H*-[2,2'-bibenzo[*d*]imidazole]-3,3'-diium ditetrafluoroborate (4). Yield: 78 %; mp 98-99 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.71-7.53 (*m*, 4H, Ar-$H_{benzimidazole}$), 7.21-7.13 (*m*, 10H, Ar-H_{phenyl}), 4.49 (*t*, 4H, N-CH_2, *J* 7,2 Hz), 4.08 (*s*, 6H, CH_3), 2.78 (t, 4H, CH_2-Ph, *J* 7,2 Hz), 2.37 (*quint*, 4H, CH_2, *J* 7,2 Hz) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 142.3 (NCN), 139.8, 132.0, 131.1, 128.5, 128.3, 127.2, 127.1, 126.3, 113.0, 112.9 (Ar-C), 47.1 (N-CH_2), 33.4 (CH_3), 32.5 (*C*H_2-Ph), 30.0 (CH_2) ppm. IR(ν, cm^{-1}): 1571.79 (C=N), 1023.98 (BF_4^-). MS (ES-API) *m/z* (%): 589.3 (100, [$M^{+2}2BF_4^-$-BF_4^-]), 251.1 (20, [$M^{+2}2BF_4^-$-$2BF_4^-$]/2). Analysis Calcd. for $C_{34}H_{36}B_2F_8N_4$ (674.3): C, 60.56; H, 5.38; N, 8.31; found: C, 60.32; H, 5.20; N, 8.07.

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14,15-Dipentyl-7,8-dihydro-6*H*-benzo[4,5]imidazo[1,2-*a*]benzo[4,5]imidazo[2,1-*c*][1,4]-diazepine-14,15-diium ditetrafluoroborate (5). Yield: 76 %; mp 172-173 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.16-8.08 (*m*, 4H, Ar-H), 7.76-7.70 (*m*, 4H, Ar-H), 4.68 (*t*, 4H, N-C$H_{2bridge}$, *J* 7,2 Hz), 4.49 (*t*, 4H, N-C$H_{2phentyl}$, *J* 7,2 Hz), 2.65 (*quint*, 2H, $CH_{2bridge}$, *J* 7,2 Hz), 1.93 (*quint*, 4H, $CH_{2phentyl}$, *J* 6,9 Hz), 1.38-1.33 (m, 8H, CH_2-$CH_{2phentyl}$), 0.89 (t, 6H, $CH_{3phentyl}$, J 6,6 Hz) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 142.6 (NCN), 131.7, 131.6, 127.1, 127.1, 114.2, 114.0 (Ar-C), 47.2 (N-$CH_{2bridge}$), 44.4 (N-$CH_{2phentyl}$), 28.7 (C$H_{2bridge}$), 28.5 ($CH_{2phentyl}$), 28.4 ($CH_{2phentyl}$), 22.1 (CH_2-$CH_{2phentyl}$), 14.2 ($CH_{3phentyl}$) ppm. IR(ν, cm^{-1}): 1563.93 (C=N), 1031.63 (BF_4^-). MS (ES-API) *m/z* (%): 505.2 (100, [$M^{+2}2BF_4^{-1}$-BF_4^{-1}]), 417.3 (5, [$M^{+2}2BF_4^{-1}$-$2BF_4^{-1}$]). Analysis Calcd. for $C_{27}H_{36}B_2F_8N_4$ (590.3): C, 54.95; H, 6.15; N, 9.49; found: C, 54.78; H, 6.14; N, 9.33.

15,16-Diethyl-6,7,8,9-tetrahydrobenzo[4,5]imidazo[1,2-*a*]benzo[4,5]imidazo[2,1-*c*][1,4]diazocine-15,16-diium ditetrafluoroborate (6). Yield: 80 %; mp 139-140 °C. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.44-8.40 (*m*, 4H, Ar-H), 8.03-7.97 (*m*, 4H, Ar-H), 5.12 (*dd*, 2H, NC$H_2$$CH_3$, *J* 8,7, 6.1 Hz), 4.89 (*sextet*, 2H, N-CH_2, *J* 6,9 Hz), 4.61 (*sextet*, 2H, N-CH_2, *J* 6,9 Hz), 4.50 (*quart*, 2H, NC$H_2$$CH_3$, *J* 7.2 Hz), 2.25 (*quint*, 2H, CH_2, J 6 Hz), 1.98 (*quint*, 2H, CH_2, *J* 7.2 Hz), 1.50 (*t*, 6H, CH_3, *J* 7,2 Hz) ppm. ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 133.5 (NCN), 130.6, 129.4, 129.3, 115.8, 114.9 (Ar-C), 56.5 (CH_2CH_3), 46.3 (N-$CH_{2bridge}$), 44.2 (N-$CH_{2bridge}$), 26.2 (CH_2CH_3), 19.0 (CH_2), 15.1 (CH_2) ppm. IR(ν, cm^{-1}): 1567.00 (C=N), 1030.90 (BF_4^-). MS (ES-API) *m/z* (%): 433.2 (10, [$M^{+2}2BF_4^{-1}$-BF_4^{-1}]), 173.1 (100, [$M^{+2}2BF_4^{-1}$-$2BF_4^{-1}$]/2). Analysis Calcd. for $C_{22}H_{26}B_2F_8N_4$ (520.09): C, 50.81; H, 5.04; N, 10.77; found: C, 50.54; H, 4.98; N, 10.52.

2,12,15,16-Tetramethyl-6,7,8,9-tetrahydrobenzo[4,5]imidazo[1,2-*a*]benzo[4,5]imidazo[2,1-*c*][1,4]diazocine-15,16-diium ditetrafluoroborate (7). Yield: 70 %; mp 178-179 °C. ^{1}H-NMR ($DMSOd_6$, 300 MHz): δ 8.33-8.15 (*m*, 4H, Ar-H), 7.84 (*d*, 2H, Ar-H, *J* 8.7 Hz), 5.04 (*t*, 2H, NCH_2, *J* 13.1 Hz), 4.43 (*t*, 2H, NCH_2, *J* 13.1 Hz), 4.26 and 4.24 (*s*, 6H, N-CH_3), 2.67 (*s*, 6H, Ar-CH_3), 2.27 (*m*, 2H, CH_2), 1.91 (*m*, 2H, CH_2) ppm. ^{13}C-NMR ($DMSOd_6$, 75 MHz): δ 140.2 and 140.1 (NCN), 134.7, 133.2, 1323, 131.3, 131.2, 131.0, 114.8, 114.2, 114.1, 113.5 (Ar-C), 46.8 and 46.6 (NCH_2), 34.7 and 34.6 (NCH_3), 26.4 (Ar-CH_3), 21.9 and 21.8 (CH_2) ppm. IR(ν, cm^{-1}): 1546.21 (C=N), 1027.86 (BF_4^-). MS (ES-API) *m/z* (%): 433.2 (40, [$M^{+2}2BF_4^{-1}$-BF_4^{-1}]), 173.2 (100, [$M^{+2}2BF_4^{-1}$-$2BF_4^{-1}$]/2). Analysis Calcd. for $C_{22}H_{26}B_2F_8N_4$ (520.09): C, 50.81; H, 5.04; N, 10.77; found: C, 50.67; H, 5.02; N, 10.70.

Biphenyl ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.57-7.52 (m, 4H, Ar-H), 7.39-7.31 (m, 4H, Ar-H), 7.30-7.22 (m, 2H, A-H) ppm.

General process for catalytic reactions

The mixture of benzyl bromide (1 mmol), phenylboronic acid (1 mmol), base (2 mmol), $Pd(OAc)_2$ (0.01 mmol), compound **1** as a ligand (0.01 mmol), and solvent (DMF:H_2O (1:1), 4 mL) was stirred and conventionally heated at 80 °C for 1h. Then, it was cooled and extracted with ethyl acetate. The purification was done by crystallization from ethyl acetate/n-hexane (1:1). The isolated yield was calculated. The biphenyl structure was determined by ^{1}H-NMR spectroscopy.

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Supplementary Material

^{1}H, ^{13}C NMR, MS, and FT-IR spectra of compounds are accessible via the “Supplementary Material” section of this article’s web page.

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