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Synthesis of novel C_2-symmetric 1,3-bis{(1*S*,2*R*,3*S*,4*R*)-1,7,7-trimethyl-3′*H*-spiro[bicyclo[2.2.1]heptane-2,2′-furan]-3-yl}-benzoimidazolium tetrafluoroborates

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Abstract—Two new C_2-symmetric benzoimidazolium tetrafluoroborates **19** and **20** were prepared from (1*S*)-(+)-camphorquinone **1** in seven and eight steps, respectively. Thus, N^1-((1*S*,2*R*,3*S*,4*R*)-1,7,7-trimethyl-4′-methylenedihydro-3′*H*-spiro[bicyclo[2.2.1]heptane-2,2′-furan]-3-yl)benzene-1,2-diamine **11**, available in three steps from **1**, was first condensed with **1** to afford amino imines **12** and **13**/**13**′. [3 + 2] Cycloaddition of trimethylenemethane (TMM) to **12** or **13**/**13**′ gave cycloadduct **17**, which was successfully reduced to diamine **4** using $NaCNBH_3$. Catalytic hydrogenation of methylene groups of **4** gave the methyl analogue **18**. Finally, cyclization of diamines **4** and **18** with triethyl orthoformate furnished the desired C_2-symmetric benzoimidazolium tetrafluoroborates **19** and **20**, respectively. The structures were determined by NMR techniques, NOESY spectroscopy, and X-ray diffraction.

1. Introduction

Camphor and its derivatives belong among the most frequently employed types of chiral starting materials, building blocks, resolving agents, shift reagents in NMR spectroscopy, and ligands in various asymmetric reagents and/or catalysts.[1–4]

Another group of interesting compounds are enantiomerically pure 1,2-diamines, which have attracted considerable attention as chiral ligands in a variety of transition metal-catalyzed asymmetric processes.[5–19] Chiral and achiral diamines are also frequently used as starting materials for the synthesis of (benz)imidazolium salts, the precursors for the corresponding N-heterocyclic carbenes.[20–22] Ever since the pioneering report by Herrmann et al.[23] on the first application of N-heterocyclic carbene (NHC) palladium complexes as catalysts in 1995, the use of NHC ligands as phosphine mimetics has been found in all areas of transition metal catalysis.[20] Currently, the field of stereoselective catalysis based on N-heterocyclic carbenes is in the process of rapid expansion.[20,23–26] Surprisingly, there are, to the best of our knowledge, only a few reports of NHC ligands with N-substituents containing terpene based centers of chirality. (−)-Isopinocamphenylamine and (+)-bornylamine based imidazolium salts were tested as stereodirecting ligands in the palladium-catalyzed asymmetric oxindole reaction with ee's up to 76%.[27,28] Some examples of chiral NHC ligands are depicted in Figure 1.

Over the last decade, our studies on the preparation and synthetic applications of 3-(dimethylamino)propenoates and related enaminones[29–31] have been extended to chiral non-racemic enaminones, available from α-aminoacids[29–35] and (+)-camphor.[31,36–45] Within this context, (+)-camphor derived enaminones have been used as key-intermediates in the synthesis of various terpene functionalized heterocycles.[36–45] Recently, our attention was focused on (1*S*)-(+)-camphorquinone **1** derived imines as valuable chiral building blocks. Thus, 3-aryliminocamphors were used as dipolarophiles in stereospecific [3 + 2] cycloadditions to trimethylenemethane (TMM) leading to spiro[bicyclo[2.2.1]heptane-2,2′-furans] and spiro[bicyclo[2.2.1]heptane-3,2′-pyrrolidines],[46] which underwent stereoselective [4 + 2] cycloadditions to 1,2,4,5-tetrazines to furnish 11:14-isopropylidene-2,3-diaza-8-oxadispiro[5.1.5.2]pentadeca-1,4-dienes and 11:14-isopropylidene-2,3,8-triazadispiro[5.1.5.2]pentadeca-1,4-dienes as novel dispiro (hetero)cyclic systems.[47] Reductions of spiro[bicyclo[2.2.1]heptane-2,2′-furans] and spiro[bicyclo[2.2.1]heptane-3,2′-pyr-

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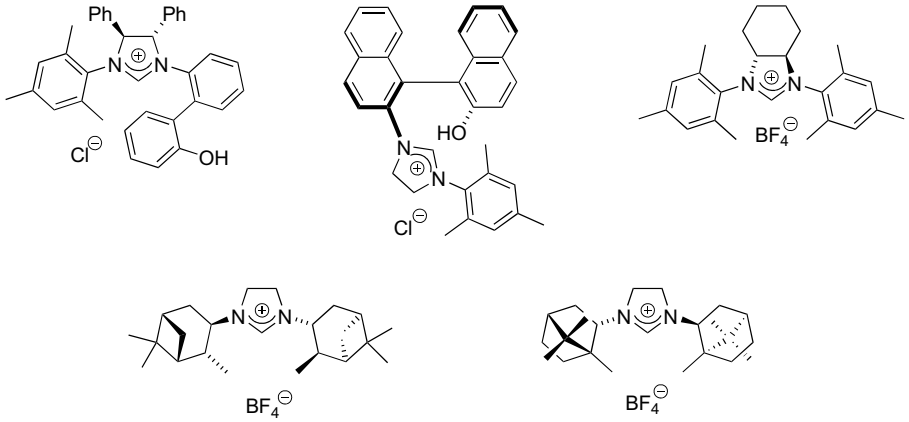


Figure 1. Some examples of chiral NHC ligands.

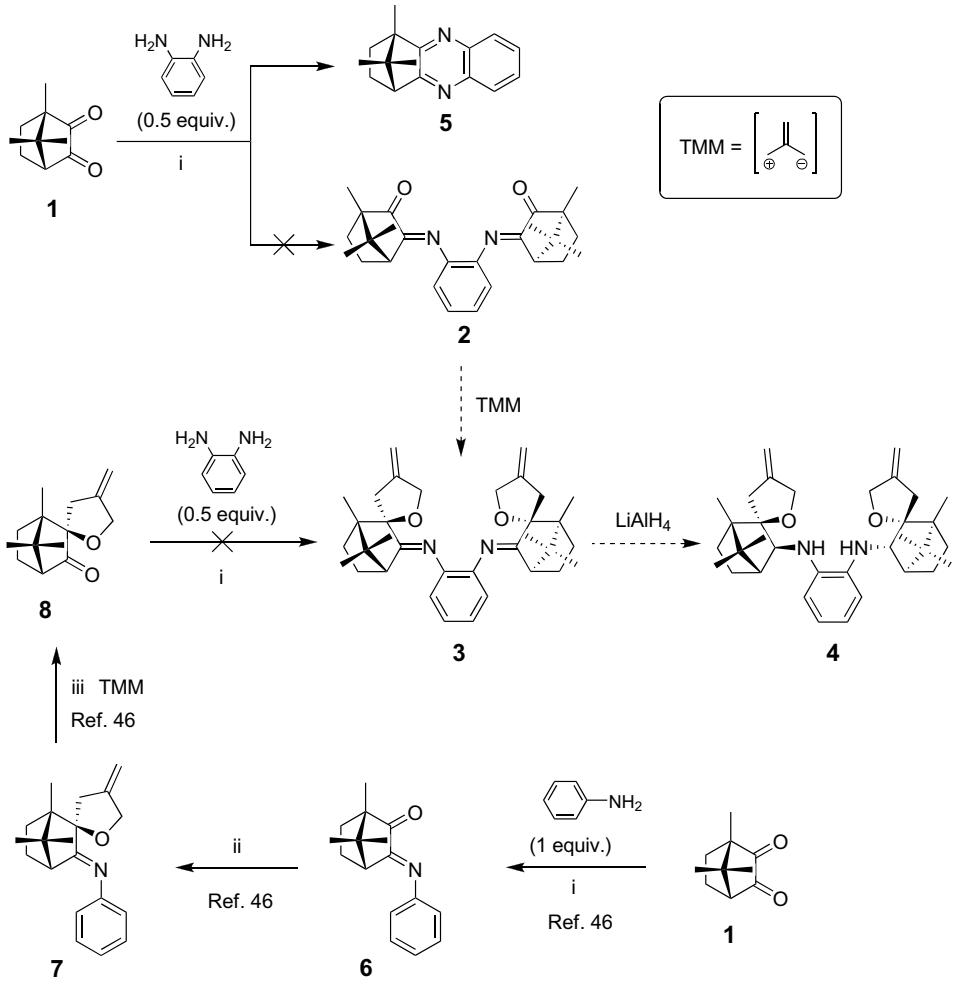
rolidines] afforded novel non-racemic amines, diamines, and amino alcohols.[46] In continuation of our work on stereoselective transformations of 3-iminocamphor derivatives, we herein report the synthesis of novel C_2-symmetric benzimidazolium tetrafluoroborates **19** and **20**, the precursors for the corresponding N-heterocyclic carbenes as ligands in transition metal catalysis. The synthetic route to benzimidazolium tetrafluoroborates **19** and **20** produced a number of new chiral non-racemic diamines and aminoimines, as potential ligands in asymmetric processes.

2. Results and discussion

Our primary goal was to synthesize N^1,N^2-bis{(1*S*,2*R*,3*S*,4*R*)-1,7,7-trimethyl-4′-methylenedihydro-3′*H*-spiro[bicyclo[2.2.1]heptane-2,2′-furan]-3-yl}benzene-1,2-diamine **4**, a novel bulky C_2-symmetric chiral diamine, as a precursor for the corresponding benzoimidazolium tetrafluoroborate. The original synthetic approach was based on a recently developed method for the preparation of closely analogous amines[46] comprising of a three step transformation of (1*S*)-(+)-camphorquinone **1** into **4** via acid-catalyzed condensation with benzene-1,2-diamine **1**→**2**, [3 + 2] cycloaddition of trimethylenemethane (TMM) **2**→**3**, and reduction with $LiAlH_4$ **3**→**4**. Unfortunately, this strategy failed at the very beginning, since condensation of **1** with 0.5 equiv of benzene-1,2-diamine yielded a quinoxaline derivative **5** instead of the desired diimine **2**. An alternative synthetic approach starting from spirofuran **8** followed by condensation of **8** with benzene-1,2-diamine **8**→**3**, and *endo*-stereoselective reduction of diimine **3** (**3**→**4**) was then envisaged. The starting spirofuran **8** was prepared in three steps from (1*S*)-(+)-camphorquinone **1** according to literature procedures.[46] Condensation of spirofuran **8** with 0.5 equiv of benzene-1,2-diamine in refluxing toluene in the presence of catalytic amounts of *p*-toluenesulfonic acid failed to give the expected diimine **3** (Scheme 1, Table 1).

On the other hand, acid-catalyzed condensation of diaminofuran **11**, available in three steps from (1*S*)-(+)-camphorquinone **1**,[46] did take place when treated with (1*S*)-(+)-camphorquinone **1** in refluxing toluene. However, the reaction was not selective and afforded three condensation products **12**, **13**, and **13′** in a ratio of 26:44:30, respectively. Using chromatographic techniques, this mixture was partially separated into the pure compound **12** and a mixture of epimeric compounds **13** and **13′** in a ratio of 60:40, respectively. Further reduction of α-iminoketone **12** with $NaCNBH_3$ was chemo- and stereoselective and furnished the α-amino ketone **14** in 70% yield and in 100% de. Isolation of epimeric compounds **13** and **13′** was somewhat surprising, yet explainable by the initial formation of a deeply orange-red α-iminoketone **12**, which undergoes either a double [1,5] sigmatropic hydrogen shift via the intermediate **15**, or an intramolecular hydride shift to give colorless *C*-3 epimeric α-aminoketones **13** and **13′**. Equilibration between epimers **13** and **13′** is feasible via the enol form **16** (Scheme 2, Table 1).

Treatment of **12** with a large excess (5 equiv) of TMM gave the desired cycloadduct **17** in 69% yield. Similarly, the reaction of a mixture of α-aminoketone epimers **13** and **13′** with a slight excess (1.4 equiv) of TMM followed by chromatographic workup yielded isomerically pure cycloadduct **17** in 32% yield and the unreacted mixture of starting compounds **13** and **13′** in a ratio of 2:98, respectively, in 22% yield. Crystallization of **13′**/**13** from dichloromethane–*n*-heptane gave isomerically pure epimer **13′**. The lower reactivity of epimer **13′** in the cycloaddition to trimethylenemethane (TMM) could be attributed to steric hindrance from both faces of **13′** imposed by the secondary amine (*endo*-face) and the two methyl groups (*exo*-face). Attempt to reduce imine **17** with $LiAlH_4$ resulted in a disappointingly low conversion into the desired ligand **4**, which was isolated in only 10% yield. Reduction of **17** with $NaCNBH_3$, however, proceeded smoothly to give the desired C_2-symmetric diamine **4** in quantitative yield. Additions of TMM and $NaCNBH_3$ or $LiAlH_4$ to the exocyclic C=N double bond of **12**, **13**, and **17** afforded kinetically controlled *exo*-isomers **4** and **17**, exclusively. No *endo*-epimers of compounds **4** and **17** were observed in the ^1H NMR spectra of the crude reaction mixtures. The predominant attack of both reagents from the less hindered *endo*-face of the bicyclic system was in accordance with the previously reported results (Scheme 3, Table 1).[46,47]



Scheme 1. Reagents and conditions: (i) *p*-toluenesulfonic acid (cat.), toluene, reflux; (ii) [2-(acetoxymethyl)allyl]trimethylsilane (1.4 equiv), $Pd(OAc)_2$, $(i\text{-PrO})_3P$, toluene, reflux; HCl–H_2O, MeOH, rt.

Table 1. Selected experimental data for compounds **4**, **5**, **12**–**14**, **17**–**20**, **13′**, and **18′**

Reaction	Product	Yield (%)	de[a] (%)
1→5	**5**	81	100
11→12 + 13/13′	**12**	31	100
	13	36	34
12→14	**14**	70	100
12→17	**17**	69	100
13/13′→17 + 13′	**17**	32	100
	13′	22	96
17→4	**4**	10 (Procedure A)	100
	4	88 (Procedure B)	100
4→18/18′	**18**	100	70
	18[b]	44[b]	100[b]
4→19	**19**	61	100
18→20	**20**	42	100

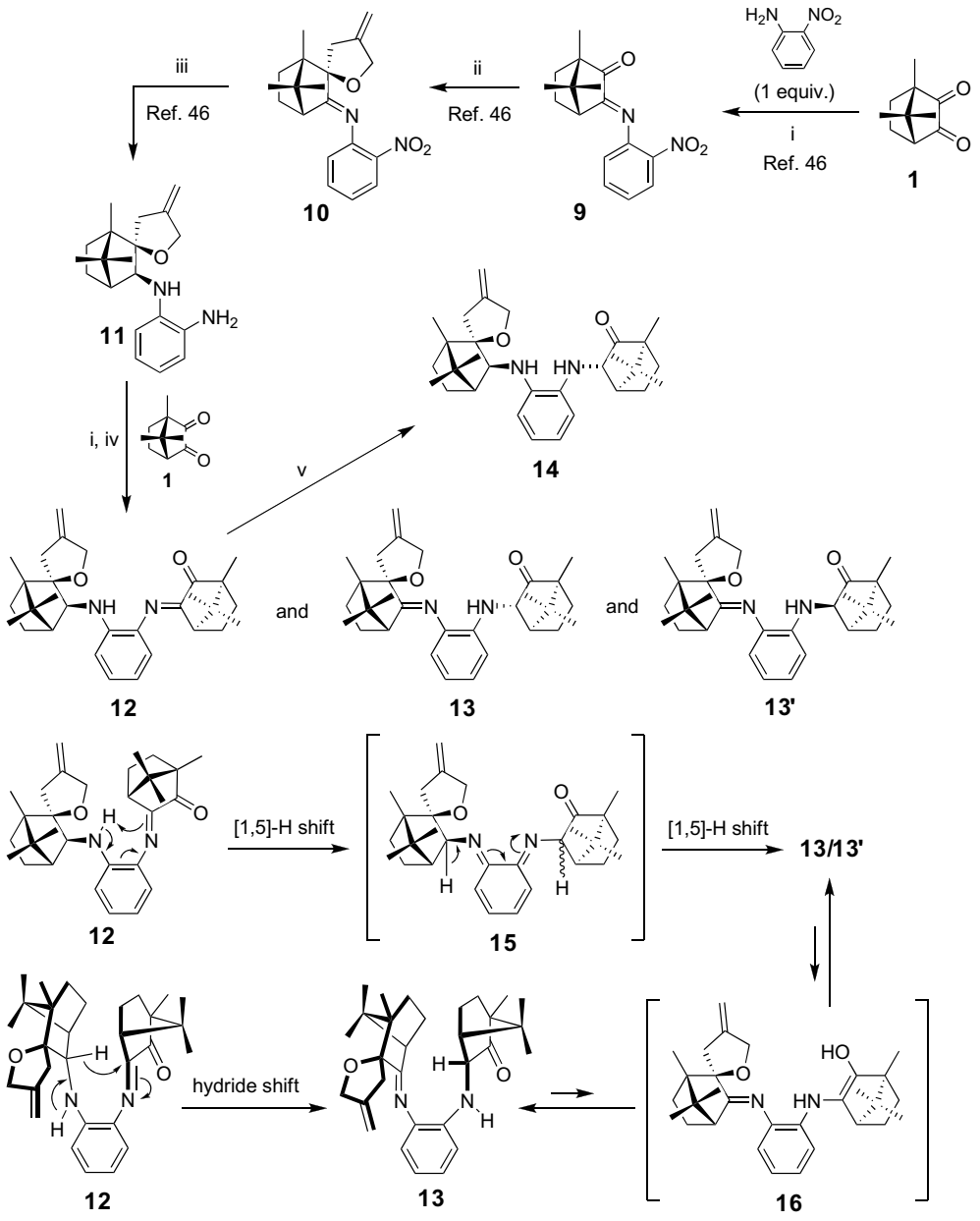
[a] Determined by ^{1}H NMR.
[b] After chromatographic separation.

Catalytic hydrogenation of diamine **4** gave a mixture of fully saturated 1,2-diaminobenzenes **18** and **18′** in a ratio of 85:15 in quantitative yield. Further chromatographic purification afforded isomerically pure compound **18** in 44% yield. Diamines **4** and **18** were then successfully cyclized into the corresponding benzoimidazolium tetrafluoroborates **19** and **20**, respectively, using triethyl orthoformate and ammonium tetrafluoroborate in the presence of a catalytic amount of formic acid (Scheme 4, Table 1).

3. Structure determination

The structures of compounds **4**, **5**, **12**, **13**, **13′**, **14**, **17**, **18**, **18′**, **19**, and **20** were determined by spectroscopic methods (IR, ^{1}H and ^{13}C NMR, NOESY spectroscopy, MS) and by elemental analyses for C, H, and N. Compounds **5**, **12**, **13′**, and **17**–**20** were prepared in isomerically pure form. Compound **13** could not be prepared in isomerically pure form and was characterized by ^{1}H NMR, ^{13}C NMR, and by EI-HRMS as a mixture of epimers **13** and **13′**. The minor isomer **18′** was characterized only by ^{1}H NMR. Compounds **4**, **5**, **13′**, **19**, and **20** were not prepared in analytically pure form; their identities were confirmed by ^{13}C NMR and EI-HRMS.

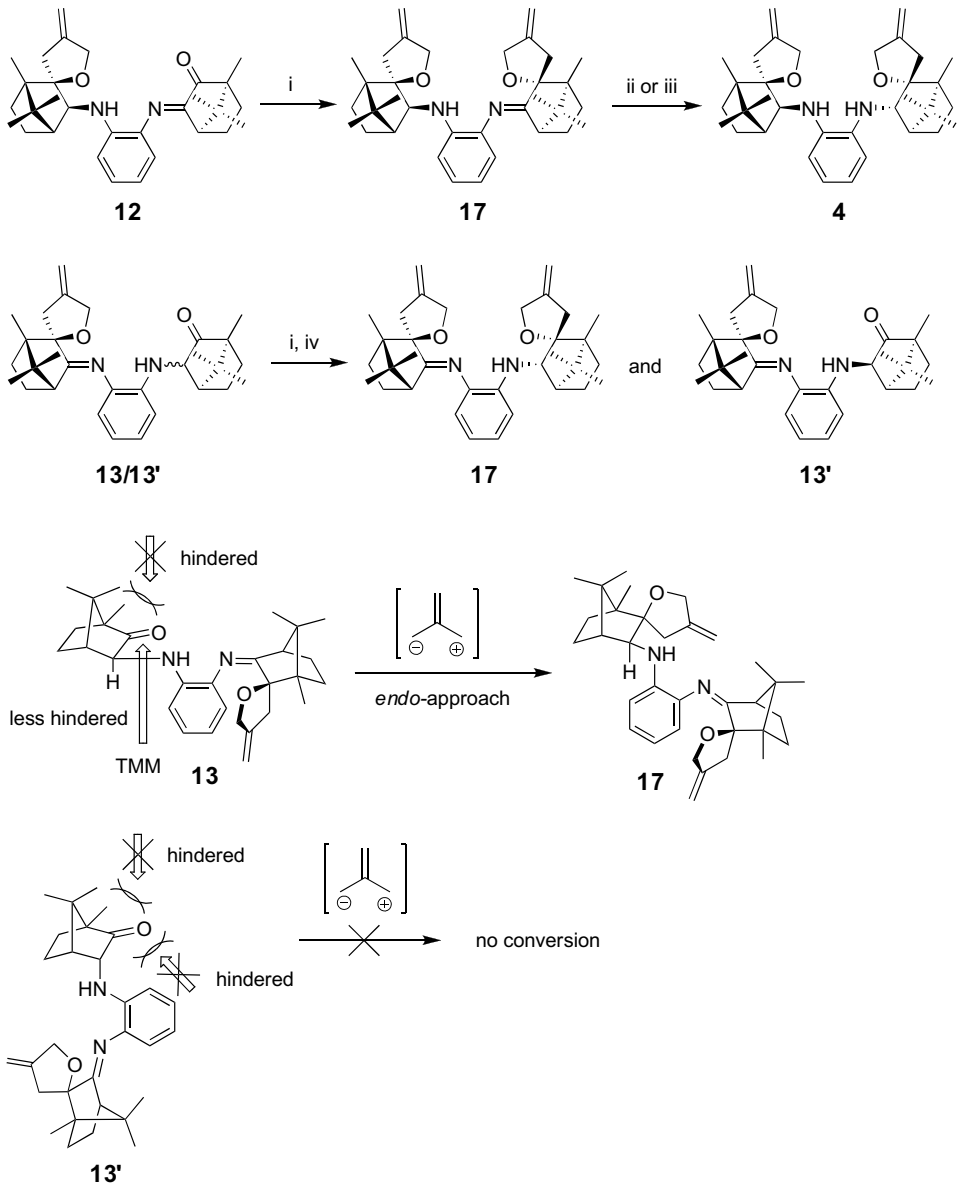
The configuration at the 3-position in secondary amines **4**, **12**, **13**, **13′**, **14**, **17**, **18**, and **18′** was determined by ^{1}H NMR on the basis of vicinal coupling constants ($^3J_{H(3)–H(4)}$) and



Scheme 2. Reagents and conditions: (i) *p*-toluenesulfonic acid (cat.), toluene, reflux; (ii) [2-(acetoxymethyl)allyl]trimethylsilane, $Pd(OAc)_2$, $(i\text{-PrO})_3P$, toluene, reflux; (iii) $LiAlH_4$, Et_2O–THF, 55 °C; (iv) chromatographic separation; (v) $NaCNBH_3$, MeOH, AcOH, rt.

multiplicities for proton *H*–C(3). The dihedral angles between *H*–C(3) and *H*–C(4) in the secondary *exo*-amines **4**, **12**, **13**, **14**, **17**, **18**, and **18′** are close to 90° and, following the Karplus equation,[48] no appreciable coupling between these protons would be expected. Accordingly, negligible coupling constants, $^3J_{H(3)-H(4)} \sim 0$ Hz, were observed in ^{1}H NMR spectra of the secondary *exo*-amines **4**, **12**, **13**, **14**, **17**, **18**, and **18′**. Signals for *H*–C(3) appeared either as doublets (coupled with *H*–N protons) or singlets (lack of coupling with *H*–N protons). Similarly, the *H*–C(3) in *endo*-benzoimidazolium tetrafluoroborates **19** and **20** does not couple with *H*–C(4) and, therefore, appears as a singlet. In *endo*-amine **13′**, however, the dihedral angle between *H*–C(3) and *H*–C(4) is smaller (~30°) and proton *H*–C(3) couples with *H*–C(4) as well as with *H*–N proton, therefore appearing as a triplet ($J = 3.7$ Hz). Similar patterns of multiplicities for *H*–C(3) and magnitudes of coupling constants, $^3J_{H(3)-H(4)}$, have also been reported in the literature for analogous compounds.[36,39,40,42–44,46,47,49,50] The configuration at 3-position in secondary amines **4**, **12**, **14**, and **17** was additionally confirmed by NOESY spectroscopy. The NOE between *H*–C(3) and *H*a–C(4′) and NOE between *H*–N and the bridge methyl group in compounds **4**, **12**, **14**, and **17** supported the proposed *exo*-configuration (Fig. 2).

The structures of compounds **12**, **13′**, and **20** were determined by X-ray diffraction analysis (Figs. 3–5). On the basis of X-ray diffraction data, the (*E*)-configuration around the exocyclic C=N double bond in compounds **12** and

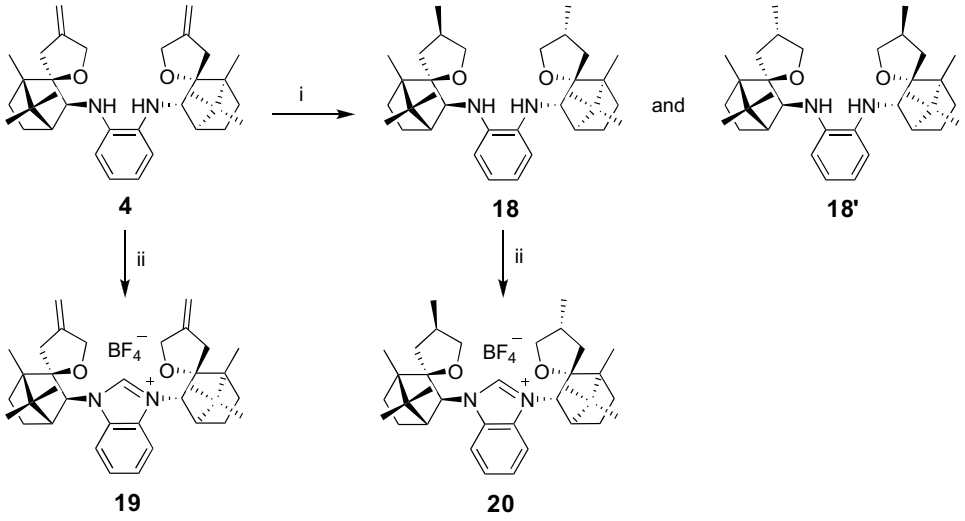


Scheme 3. Reagents and conditions: (i) [2-(acetoxymethyl)allyl]trimethylsilane, $Pd(OAc)_2$, $(i\text{-PrO})_3P$, toluene, reflux; (ii) $NaCNBH_3$, MeOH, AcOH, rt; (iii) $LiAlH_4$, THF, 55 °C (Ref. 36); (iv) chromatographic separation.

13′ was established (cf. Figs. 3 and 4). Since the (*E*)-configuration imposes lesser steric strain than the (*Z*)-configuration around the exocyclic C=N double bond, it is safe to assume the (*E*)-configuration also for the other imines **13** and **17**.

4. Conclusion

Two novel chiral non-racemic C_2-symmetric benzoimidazolium tetrafluoroborates **19** and **20** were prepared in several steps from commercially available (1*S*)-(+)-camphorquinone **1** in 3.8% and 1.1% overall yields, respectively. The synthetic approach comprises of (a) a three step preparation of N^1-{(1*S*,2*R*,3*S*,4*R*)-1,7,7-trimethyl-4′-methylenedihydro-3′*H*-spiro[bicyclo[2.2.1]heptane-2,2′-furan]-3-yl}benzene-1,2-diamine **11** from **1** and 2-nitroaniline, (b) an acid-catalyzed condensation of **11** with **1** to give isomeric imino ketones **12** and **13/13′**, (c) a stereoselective [3 + 2] cycloaddition of trimethylenemethane (TMM) to the C=O bonds of **12** or **13** leading to cycloadduct **17**, (d) a stereoselective reduction of the C=N bond of **17** to give diamine **4**, and (e) a cyclization of N^1,N^2-disubstituted benzene-1,2-diamine **4** with $HC(OEt)_3$–NH_4BF_4 in the presence of a catalytic amount of formic acid into benzoimidazolium tetrafluoroborate **19.** Catalytic hydrogenation of **4** furnished the saturated diamine **18**, which was then cyclized into the corresponding benzoimidazolium salt **20**. The initially intended synthesis of **19** from **1** or **8** via bis-condensation of benzene-1,2-diamine failed. In contrast to their simpler analogues,[46] the C=N double bond in imine **12** was quite resistant for reduction with $LiAlH_4$ in THF, yet it reacted smoothly with $NaCNBH_3$ in MeOH–AcOH to give the corresponding diamine **4** as a single diastereomer.



Scheme 4. Reagents and conditions: (i) H_2, 10% Pd–C, EtOH, then chromatographic separation; (ii) $HC(OEt)_3$, HCOOH, NH_4BF_4, 120 °C.

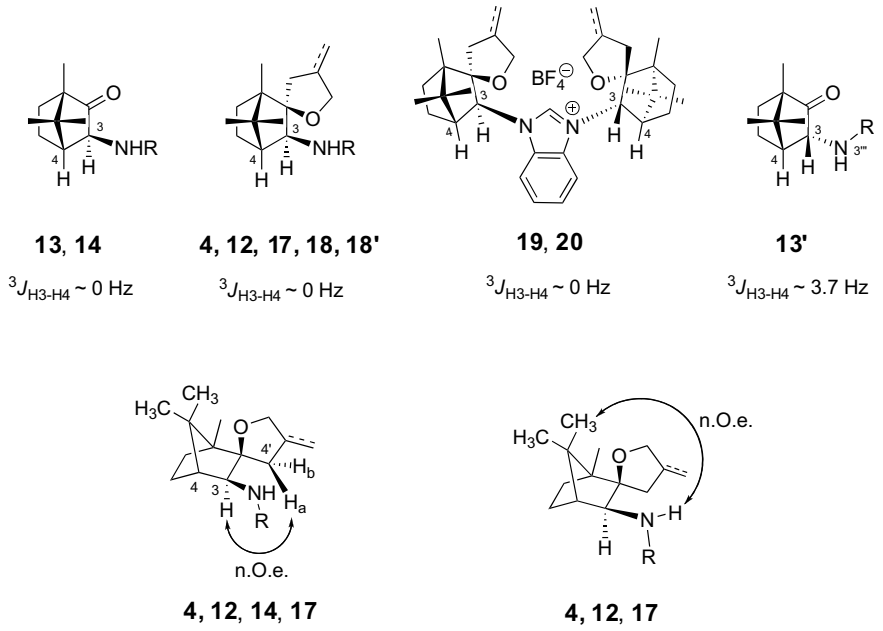


Figure 2. Structure determination by ^1H NMR and NOESY spectroscopy.

In conclusion, we have developed the synthesis of novel chiral non-racemic C_2-symmetric diamines **4** and **18** and their respective benzoimidazolium tetrafluoroborates **19** and **20**, which might be useful ligands in asymmetric processes. Our current studies are focused on possible applications of these chiral compounds.

5. Experimental

5.1. General methods

Melting points were determined on a Kofler micro hot stage. The ^1H NMR spectra were obtained on a Bruker Avance DPX 300 at 300 MHz for ^1H and 75.5 MHz for ^{13}C nucleus, using DMSO-d_6 and $CDCl_3$, with TMS as the internal standard, as solvents. All NMR experiments were carried out at 23 °C. Optical rotations were measured on a Perkin–Elmer 241MC Polarimeter. Mass spectra were recorded on an AutoSpecQ spectrometer, IR spectra on a Perkin–Elmer Spectrum BX FTIR spectrophotometer. Microanalyses were performed on a Perkin–Elmer CHN Analyzer 2400. Column chromatography (CC) was performed on silica gel (Fluka, Silica Gel 60, 0.04–0.06 mm). The ratio of the isomers and de were determined by ^1H NMR.

(1*S*)-(+)-Camphorquinone **1**, benzene-1,2-diamine, *p*-toluenesulfonic acid monohydrate, [2-(acetoxymethyl)allyl]-trimethylsilane, $Pd(OAc)_2$, $(i\text{-PrO})_3P$, $LiAlH_4$, and

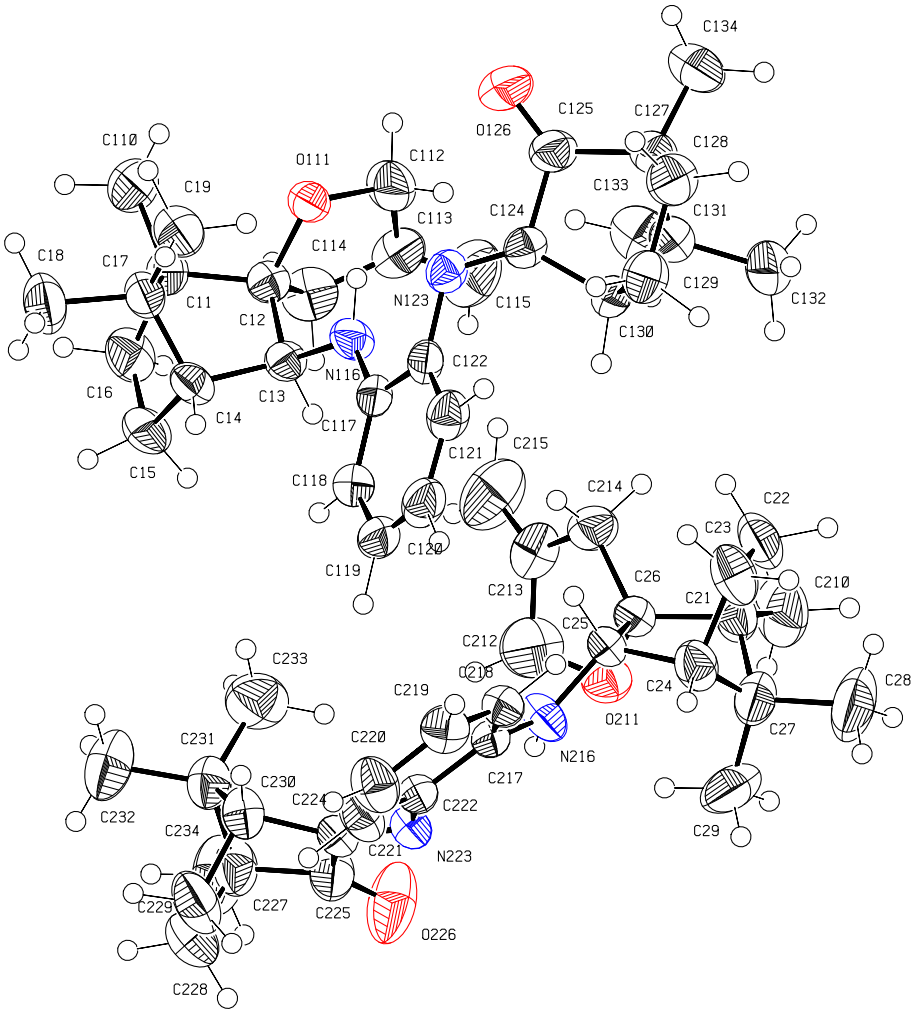


Figure 3. The asymmetric unit of compound **12**. Ellipsoids are plotted at 50% probability level. H atoms are drawn as circles of arbitrary radii.

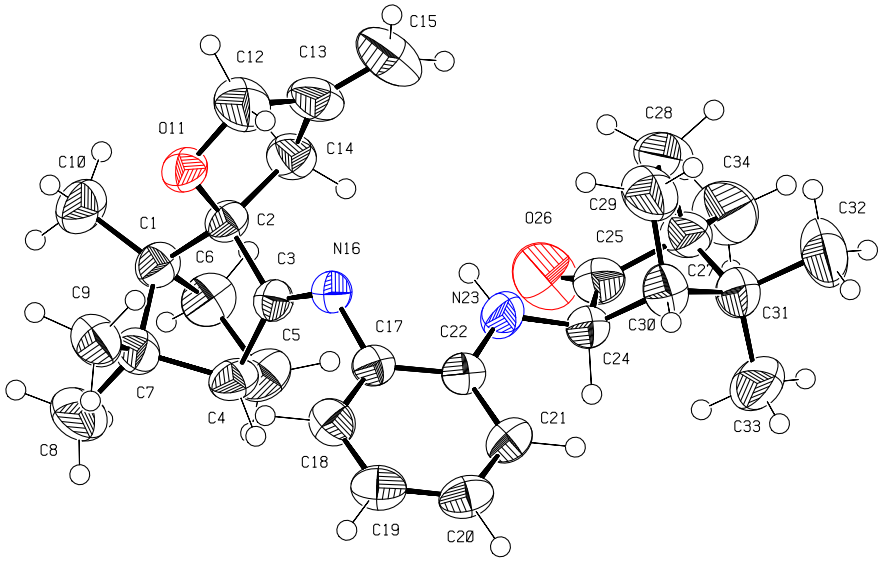


Figure 4. The asymmetric unit of compound **13′**. Ellipsoids are plotted at 50% probability level. H atoms are drawn as circles of arbitrary radii.

$NaCNBH_3$ are commercially available (Fluka AG). (1*S*,2*R*,4*R*)-1,7,7-Trimethyl-4′-methylenedihydro-3′*H*-spiro-[bicyclo[2.2.1]heptane-2,2′-furan]-3-one **8** and N^1-((1*S*,2*R*,3*S*,4*R*)-1,7,7-trimethyl-4′-methylenedihydro-3′*H*-spiro[bi-

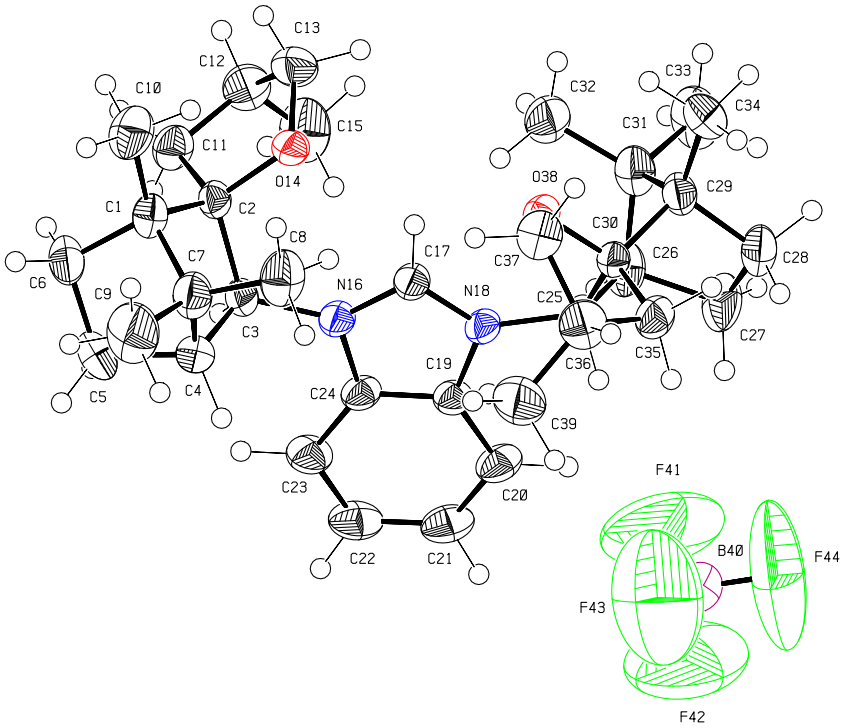


Figure 5. The asymmetric unit of compound **20**. Ellipsoids are plotted at 50% probability level. H atoms are drawn as circles of arbitrary radii.

cyclo-[2.2.1]heptane-2,2′-furan]-3-yl)benzene-1,2-diamine **11** were prepared according to literature procedures.[46]

Source of chirality: (1*S*)-(+)-camphorquinone **1**, 99%, (Fluka AG), product number 27,207-8, $[\alpha]_D^{20} = +100$ (*c* 1.9, toluene), mp 200–202 °C.

5.2. Synthesis of (1*S*,4*R*)-1,11,11-trimethyl-1,2,3,4-tetrahydro-1,4-methanophenazine 5

A mixture of (1*S*)-(+)-camphorquinone **1** (3 mmol, 499 mg), benzene-1,2-diamine (1.5 mmol, 163 mg), and *p*-toluenesulfonic acid monohydrate (0.3 mmol, 58 mg) in anhydrous toluene (35 mL) was heated at reflux for 6 h. A Dean–Stark water trap was used to remove water during the reaction. The reaction mixture was cooled to 5 °C, poured into a cooled saturated aq $NaHCO_3$ (150 mL, 5 °C) and the product was extracted with EtOAc (2 × 100 mL). The organic phases were combined, dried over anhydrous Na_2SO_4, filtered, and the filtrate was evaporated in vacuo. The residue was purified by CC (EtOAc–hexanes, 1:80). Fractions containing the product were combined and evaporated in vacuo to give **5**. Yield: 0.290 g (81%) of a yellow oil; $[\alpha]_{589}^{21} = -29.0$ (*c* 0.30, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.63, 1.12, 1.44 (9H, 3s, 1:1:1, 3 × Me); 1.37–1.47, 1.99–2.13, 2.23–2.38 (4H, 3m, 2:1:1, 2 × CH_2); 3.07 (1H, d, $J = 4.5$ Hz, H–C(4)); 7.62–7.68, 7.96–8.08 (4H, 2m, 1:1, 4H of Ar). ^{13}C NMR ($CDCl_3$): δ 10.1, 18.6, 20.4, 24.7, 31.9, 53.4, 53.8, 54.3, 128.09, 128.11, 128.7, 128.8, 141.4, 141.6, 163.8, 165.5. *m*/*z* (EI) = 238 (M^+); *m*/*z* (HRMS) found: 238.146320 (M^+); $C_{16}H_{18}N_2$ requires: *m*/*z* = 238.146999. ($C_{16}H_{18}N_2$ requires: C, 80.63; H, 7.61; N, 11.75. Found: C, 79.67; H, 8.06; N, 11.55.); ν_{max} (NaCl) 3064, 2961, 2929, 2872, 1580, 1513, 1472, 1453, 1405, 1391, 1380, 1371, 1362, 1334, 1267, 1173, 1134, 1118, 1109, 1073, 1053, 1018, 999, 914, 868, 829, 762 cm^{-1}.

5.3. Synthesis of N^1-[(1*S*,3*E*,4*R*)-2-oxo-1,7,7-trimethylbicyclo[2.2.1]hept-3-ylidene]-N^2-{(1*S*,2*R*,3*S*,4*R*)-1,7,7-trimethyl-4′-methylenedihydro-3′*H*-spiro[bicyclo[2.2.1]- heptane-2,2′-furan]-3-yl}benzene-1,2-diamine 12, N^1-[(1*S*,3*S*,4*R*)-2-oxo-1,7,7-trimethylbicyclo[2.2.1]hept-3-yl]-N^2-{(1*S*,2*R*,4*R*)-1,7,7-trimethyl-4′-methylenedihydro-3′*H*-spiro[bicyclo[2.2.1]heptane-2,2′-furan]-3-ylidene}benzene-1,2-diamine 13, and N^1-[(1*S*,3*R*,4*R*)-2-oxo-1,7,7-trimethylbicyclo[2.2.1]hept-3-yl]-N^2-{(1*S*,2*R*,4*R*)-1,7,7-trimethyl-4′-methylenedihydro-3′*H*-spiro[bicyclo[2.2.1]heptane-2,2′-furan]-3-ylidene}benzene-1,2-diamine 13′

A mixture of N^1-((1*S*,2*R*,3*S*,4*R*)-1,7,7-trimethyl-4′-methylenedihydro-3′*H*-spiro[bicyclo[2.2.1]heptane-2,2′-furan]-3-yl)benzene-1,2-diamine **11** (6.33 mmol, 1978 mg), (1*S*)-(+)-camphorquinone **1** (6.33 mmol, 1053 mg), and *p*-toluenesulfonic acid monohydrate (0.32 mmol, 61 mg) in anhydrous toluene (60 mL) was heated at reflux for 4 h. A Dean–Stark water trap was used to remove water during the reaction. The reaction mixture was cooled to room temperature, poured into ethyl acetate (300 mL), and the resulting mixture was washed with saturated aq $NaHCO_3$ (100 mL) and water (100 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered, and the filtrate was evaporated in vacuo to give a mixture of compounds **12**, **13**, and **13′** in a ratio of 26:44:30, respectively, which was separated by CC (EtOAc–hexanes, 1:20). A mixture of compounds **13** and **13′** was eluted first, followed by

the elution of compound **12**. Fractions containing the products were combined and evaporated in vacuo to give pure compound **12** and a mixture of compounds **13** and **13′** in a ratio of 60:40. Crystallization of **13/13′** from ethanol afforded a mixture of compounds **13** and **13′** in a ratio of 67:33.

5.3.1. Data for compound 12. Yield: 0.904 g (31%) of an orange red solid; mp 168–175 °C; $[\alpha]_{589}^{18} = -854.4$ (*c* 0.09, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.80, 0.88, 0.99, 1.10, 1.15 (18H, 5s, 1:2:1:1:1, 6 × Me); 1.11–1.21, 1.30–1.39, 1.42–1.53 (3H, 3m, 3H of CH_2); 1.56–1.89 (5H, m, 4H of CH_2, H–C(4^1)); 2.04–2.18 (1H, m, 1H of CH_2); 2.37 (1H, dd, $J = 1.1$; 15.9 Hz, Ha–C(4′)); 2.85 (1H, br d, $J = 15.4$ Hz, Hb–C(4′)); 3.06 (1H, d, $J = 4.5$ Hz, H–C(4^2)); 3.11 (1H, d, $J = 6.8$ Hz, H–C(3)); 4.28–4.35 (1H, m, Ha–C(2′)); 4.42 (1H, br d, $J = 12.8$ Hz, Hb–C(2′)); 4.70 (1H, d, $J = 1.5$ Hz, Ha–C(3″)); 4.87 (1H, d, $J = 1.5$ Hz, Hb–C(3″)); 5.27 (1H, d, $J = 6.8$ Hz, NH); 6.43–6.47, 6.51–6.57 (2H, 2m, 1:1, 2H of Ar); 6.64 (1H, dd, $J = 1.5$; 7.5 Hz, 1H of Ar); 7.04–7.10 (1H, m, 1H of Ar). ^{13}C NMR ($CDCl_3$): δ 9.2, 9.9, 17.7, 20.9, 21.7, 22.3, 24.4, 26.1, 30.3, 31.7, 43.1, 44.7, 49.1, 49.3, 50.1, 52.1, 57.8, 68.7, 72.9, 93.8, 104.2, 110.3, 114.3, 119.2, 127.9, 133.7, 142.6, 146.9, 169.6, 205.8. *m/z* (EI) = 460 (M^+); *m/z* (HRMS) found: 460.310320 (M^+); $C_{30}H_{40}N_2O_2$ requires: *m/z* = 460.308979. ($C_{30}H_{40}N_2O_2$ requires: C, 78.22; H, 8.75; N, 6.08. Found: C, 78.03; H, 8.95; N, 6.01.); ν_{max} (KBr) 3409, 2953, 2882, 1749 (C=O), 1653, 1647, 1595, 1504, 1484, 1456, 1425, 1400, 1390, 1371, 1330, 1320, 1295, 1257, 1194, 1157, 1073, 1060, 1040, 1012, 971, 882, 743 cm^{-1}.

5.3.2. Data for a mixture of compounds 13 and 13′. Yield: 1.060 g (36%) of a grayish-white solid; **13**:**13′** = 67:33; mp 185–193 °C; $[\alpha]_{589}^{18} = -11.3$ (*c* 0.20, **13**:**13′** = 73:27, $CHCl_3$). ^{13}C NMR ($CDCl_3$): δ 9.4, 9.5, 18.9, 19.5, 19.9, 20.6, 20.8, 22.2, 22.4, 23.97, 24.04, 26.4, 28.8, 31.6, 31.7, 32.8, 39.9, 40.0, 44.2, 46.7, 47.57, 47.60, 48.3, 48.7, 51.0, 51.2, 51.8, 51.9, 56.7, 58.4, 62.3, 64.8, 72.5, 72.6, 90.1, 90.2, 103.5, 104.1, 110.3, 110.5, 116.96, 117.04, 118.5, 118.6, 124.9, 125.0, 137.09, 137.12, 140.46, 140.48, 147.4, 148.1, 187.0, 187.5, 217.0, 218.1. *m/z* (EI) = 460 (M^+); *m/z* (HRMS) found: 460.310120 (M^+); $C_{30}H_{40}N_2O_2$ requires: *m/z* = 460.308979. ($C_{30}H_{40}N_2O_2$ requires: C, 78.22; H, 8.75; N, 6.08. Found: C, 78.48; H, 9.08; N, 6.03.); ν_{max} (KBr) 3448, 2960, 2870, 1751 (C=O), 1686 (C=N), 1595, 1504, 1483, 1456, 1390, 1372, 1324, 1296, 1263, 1191, 1156, 1065, 1040, 1019, 884, 740 cm^{-1}.

5.3.3. ^{1}H NMR data for compound 13. ^{1}H NMR ($CDCl_3$): δ 0.87, 0.93, 0.94, 0.95, 0.97, 1.16 (18H, 6s, 1:1:1:1:1:1, 6Me); 1.18–1.31 (1H, m, 1H of CH_2); 1.35–1.51 (1H, m, 1H of CH_2); 1.56–1.87 (5H, m, 5H of CH_2); 1.99–2.14 (1H, m, 1H of CH_2); 2.19 (1H, d, $J = 4.5$ Hz, H–C(4^1)); 2.45–2.50 (1H, m); 2.64 (1H, $J = 4.9$ Hz, H–C(4^2)); 2.71–2.83 (1H, m); 3.36 (1H, d, $J = 2.6$ Hz, H–C(3)); 4.46–4.58 (2H, m); 4.77–4.84 (1H, m); 4.87–5.01 (2H, m); 5.08–5.11 (1H, m); 6.50–6.59, 6.63–6.69, 6.94–7.01 (4H, 3m, 2:1:1, 4H of Ar).

5.4. Synthesis of N^1-{(1*S*,2*R*,3*S*,4*R*)-1,7,7-trimethyl-4′-methylenedihydro-3′*H*-spiro[bicyclo[2.2.1]-heptane-2,2′-furan]-3-yl}-N^2-{(1*S*,2*R*,3*E*,4*R*)-1,7,7-trimethyl-4′-methylenedihydro-3′*H*-spiro[bicyclo-[2.2.1]heptane-2,2′-furan]-3-ylidene}benzene-1,2-diamine 17

Procedure A: Compound **12** (0.1 mmol, 46 mg) and [2-(acetoxymethyl)allyl]trimethylsilane (0.5 mmol, 94 mg) were dissolved in anhydrous toluene (2 mL) under argon and heated at reflux. Then, a solution of $Pd(OAc)_2$ (0.036 mmol, 8 mg) and (*i*-PrO)$_3$P (0.215 mmol, 0.05 mL, $d_4^{20} = 0.905$ g/L) in anhydrous THF (0.5 mL) was added and the reaction mixture was heated at reflux for 3 h. Volatile components were evaporated in vacuo and the residue was purified by CC (EtOAc–hexanes, 1:30). Fractions containing the product were combined and evaporated in vacuo to give **17**.

Procedure B: A mixture of compounds **13** and **13′** in a ratio of 67:33 (2 mmol, 922 mg) and [2-(acetoxymethyl)allyl]trimethylsilane (2.8 mmol, 522 mg) was dissolved in anhydrous toluene (6 mL) under argon and heated at reflux. Then, a solution of $Pd(OAc)_2$ (0.2 mmol, 46 mg) and (*i*-PrO)$_3$P (1.3 mmol, 0.3 mL, $d_4^{20} = 0.905$ g/L) in anhydrous THF (2 mL) was added and the reaction mixture was heated at reflux for 2 h. Volatile components were evaporated in vacuo and the residue was purified by CC. Product **17** was eluted with EtOAc–hexanes (1:40), followed by the elution of a mixture of the unreacted **13/13′** with EtOAc–hexanes (1:10). Fractions containing the product were combined and evaporated in vacuo to give **17** and a mixture of unreacted **13** and **13′** (**13**:**13′** = 98:2), respectively. Further recrystallization of the mixture of compounds **13** and **13′** from *n*-heptane/CH_2Cl_2 gave pure compound **13′**.

5.4.1. Data for compound 17. Yield: 0.029 g (69%, Procedure A) or 0.334 g (32%, Procedure B) of a yellowish solid; mp 123–126 °C; $[\alpha]_{589}^{18} = -115.0$ (*c* 0.21, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.79, 0.86, 0.90, 0.95, 1.07, 1.13 (18H, 6s, 1:1:1:1:1:1, 6 × Me); 1.15–1.21, 1.32–1.57, 1.59–1.79, 1.82–1.93 (8H, 4m, 1:4:2:1, 4 × CH_2); 1.86 (1H, d, $J = 4.5$ Hz, H–C(4^1)); 2.39 (1H, d, $J = 15.1$ Hz, Ha–C($4^{1\prime}$)); 2.59 (1H, d, $J = 15.8$ Hz, Ha–C($4^{2\prime}$)); 2.69 (1H, d, $J = 5.1$ Hz, H–C(4^2)); 2.76 (1H, br dd, $J = 1.1$; 15.9 Hz, Hb–C($4^{1\prime}$)); 2.86 (1H, br d, $J = 15.3$ Hz, H_β–C($4^{2\prime}$)); 3.13 (1H, d, $J = 7.0$ Hz, H–C(3)); 4.41 (1H, br d, $J = 12.8$ Hz, Ha–C($2^{1\prime}$)); 4.46–4.54 (2H, m); 4.69 (1H, d, $J = 0.9$ Hz, Ha–C($3^{1\prime\prime}$)); 4.85 (2H, br s, Hb–C($3^{1\prime\prime}$), Ha–C($3^{2\prime\prime}$)); 4.94–4.99 (2H, m); 5.07 (1H, br d, $J = 7.0$ Hz, NH); 6.35 (1H, d, $J = 7.9$ Hz, 1H of Ar); 6.47–6.53 (2H, m, 2H of Ar); 6.91–7.00 (1H, m, 1H of Ar). ^{13}C NMR ($CDCl_3$): δ 9.5, 10.0, 19.1, 21.5, 22.3, 22.5, 24.3, 26.1, 31.71, 31.74, 39.5, 43.2, 47.6, 48.3, 49.1, 51.4, 51.8, 52.2, 68.4, 72.8, 73.3, 90.6, 93.7, 103.5, 104.1, 109.5, 114.2, 119.2, 125.4, 135.8, 140.8, 147.0, 147.9, 185.9. *m/z* (EI) = 514 (M^+); *m/z* (HRMS) found: 514.357320 (M^+); $C_{34}H_{46}N_2O_2$ requires: *m/z* = 514.355929. ($C_{34}H_{46}N_2O_2$ requires: C, 79.33; H, 9.01; N, 5.44. Found: C, 79.35; H, 9.23; N, 5.39.); ν_{max} (KBr) 3425, 2988, 2950, 1668 (C=N), 1592, 1503, 1482, 1454, 1423, 1389, 1371, 1326, 1293, 1262, 1239, 1192, 1155, 1065, 1044, 1018, 884, 737 cm^{-1}.

5.4.2. Data for compound 13′. Procedure B, 0.207 g (22%) of a white solid; **13**:**13′** = 98:2. Crystallization from *n*-heptane/CH_2Cl_2 gave pure compound **13′**; mp 203–205 °C; $[\alpha]_{589}^{18} = -71.9$ (*c* 0.21, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.87, 0.94, 0.98, 1.01, 1.04, 1.10 (18H, 6s, 1:1:1:1:1.1, 6 × Me); 1.23–1.31, 1.34–1.44, 1.52–1.87 (8H, 3m, 1:1:6, 4 × CH_2); 2.49 (1H, t, $J = 4.2$ Hz, H–C(4^1)); 2.60 (1H, d, $J = 4.9$ Hz, H–C(4^2)); 2.61 (1H, d, $J = 15.1$ Hz, Ha–C(4′)); 2.78 (1H, br d, $J = 15.5$ Hz, Hb–C(4′)); 3.95 (1H, t, $J = 3.7$ Hz, H–C(3)); 4.50 (1H, d, $J = 4.0$ Hz, NH); 4.54 (1H, br d, $J = 13.0$ Hz, Ha–C(2′)); 4.88–4.99 (3H, m, Hb–C(2′), $H_2C(3'')$); 6.53–6.59 (2H, m, 2H of Ar); 6.65, 6.96 (2H, 2dt, 1:1, $J = 1.1$; 7.5 Hz, 2H of Ar). ^{13}C NMR ($CDCl_3$): δ 9.4, 9.5, 18.96, 18.99, 19.5, 19.9, 22.3, 24.0, 31.8, 32.8, 39.9, 44.3, 47.6, 48.7, 51.2, 51.8, 58.4, 62.3, 72.6, 90.2, 103.6, 110.5, 117.0, 118.7, 124.9, 137.1, 140.5, 148.1, 187.5, 218.2. *m*/*z* (EI) = 460 (M^+); *m*/*z* (HRMS) found: 460.309560 (M^+); $C_{30}H_{40}N_2O_2$ requires: *m*/*z* = 460.308979. ($C_{30}H_{40}N_2O_2$ requires: C, 78.22; H, 8.75; N, 6.08. Found: C, 78.64; H, 8.97; N, 6.06.); ν_{max} (KBr) 3400, 2988, 2961, 2870, 1737 (C=O), 1690 (C=N), 1597, 1509, 1482, 1459, 1441, 1389, 1374, 1326, 1294, 1277, 1265, 1190, 1154, 1066, 1058, 1038, 1018, 1004, 878, 747 cm^{-1}.

5.5. Synthesis of N^1-[(1*S*,3*S*,4*R*)-2-oxo-1,7,7-trimethylbicyclo[2.2.1]hept-3-yl]-N^2-{(1*S*,2*R*,3*S*,4*R*)-1,7,7-trimethyl-4′-methylenedihydro- 3′*H*-spiro[bicyclo[2.2.1]heptane-2,2′-furan]-3-yl}benzene-1,2-diamine 14

$NaCNBH_3$ (1.71 mmol, 108 mg) was added to a solution of compound **12** (0.57 mmol, 263 mg) in anhydrous MeOH (70 mL) under argon followed by the addition of glacial acetic acid (0.2 mL) and the reaction mixture was stirred at room temperature for 3 h. Afterwards, water (30 mL) was added and the reaction mixture was stirred at room temperature for 1 h. MeOH was evaporated in vacuo from the reaction mixture, water (70 mL) was added to the residue, and the resulting mixture was extracted twice with CH_2Cl_2 (100 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and the filtrate was evaporated in vacuo. The residue was purified by CC (EtOAc–hexanes, 1:20). Fractions containing the product were combined and evaporated in vacuo to give **14**. Yield: 0.185 g (70%) of a grayish-white solid; mp 117–120 °C; $[\alpha]_{589}^{21} = +42.2$ (*c* 0.06, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.82, 0.89, 0.94, 0.99, 1.02, 1.23 (18H, 6s, 1:1:1:1:1:1, 6 × Me); 1.14–1.27 (1H, m, 1H of CH_2); 1.32–1.49, 1.59–1.65 (4H, 2m, 1:1, 2 × CH_2); 1.68–1.81 (3H, m, 2H of CH_2, H–C(4^1)); 2.03–2.15 (1H, m, 1H of CH_2); 2.20 (1H, d, $J = 4.2$ Hz, H–C(4^2)); 2.39 (1H, dd, $J = 1.2$; 15.3 Hz, Ha–C(4′)); 2.89 (1H, br d, $J = 15.3$ Hz, Hb–C(4′)); 3.08 (1H, d, $J = 4.2$ Hz, H–C(3^1)); 3.38 (1H, s, H–C(3^2)); 3.58 (1H, s, H–N^1); 4.22–4.28 (2H, m, Ha–C(2′), H–N^2); 4.40 (1H, br d, $J = 12.6$ Hz, Hb–C(2′)); 4.74 (1H, d, $J = 1.2$ Hz, Ha–C(3″)); 4.88 (1H, s, Hb–C(3″)); 6.44 (1H, d, $J = 7.8$ Hz, 1H of Ar); 6.50 (1H, d, $J = 7.5$ Hz, 1H of Ar); 6.66 (1H, dt, $J = 1.2$; 7.5 Hz, 1H of Ar); 6.82 (1H, dt, $J = 1.2$; 7.5 Hz, 1H of Ar). ^{13}C NMR ($CDCl_3$): δ 9.4, 10.1, 20.8, 20.9, 21.9, 22.4, 25.9, 26.4, 29.0, 31.7, 43.1, 46.9, 47.0, 49.2, 49.5, 52.6, 56.9, 64.3, 69.0, 73.1, 94.1, 104.7, 110.3, 112.1, 116.7, 120.5, 135.0, 137.9, 146.5, 217.7. *m*/*z* (EI) = 463 (MH^+); *m*/*z* (HRMS) found: 463.3308 (MH^+); $C_{30}H_{43}N_2O_2$ requires: *m*/*z* = 463.3325. ($C_{30}H_{42}N_2O_2$ requires: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.75; H, 9.39; N, 5.97.); ν_{max} (KBr) 3404, 2957, 2875, 1749 (C=O), 1599, 1515, 1481, 1446, 1430, 1390, 1371, 1329, 1312, 1264, 1242, 1074, 1040, 1027, 886, 733 cm^{-1}.

5.6. Synthesis of N^1,N^2-bis{(1*S*,2*R*,3*S*,4*R*)-1,7,7-trimethyl-4′-methylenedihydro-3′*H*-spiro[bicyclo-[2.2.1]heptane-2,2′-furan]-3-yl}benzene-1,2-diamine 4

Procedure A: To a solution of compound **17** (0.5 mmol, 258 mg) in anhydrous THF (15 mL) under argon was added a solution of $LiAlH_4$ (5 mmol, 5 mL, 1 M in THF) and the reaction mixture was heated at 55 °C for 7 h. The reaction mixture was cooled to 0 °C and the unreacted $LiAlH_4$ was carefully quenched with saturated aq Na_2SO_4 (just enough to quench all $LiAlH_4$). The reaction mixture was filtered, the solid residue thoroughly washed with CH_2Cl_2 (100 mL), the filtrate evaporated in vacuo, and the residue was purified by CC (PhMe–hexanes, 1:1). Fractions containing the products were combined and evaporated in vacuo to give **4**. Further elution with EtOAc–hexanes (1:1) followed by evaporation afforded the unreacted compound **17**.

Procedure B: $NaCNBH_3$ (2 mmol, 126 mg) was added to a solution of compound **17** (0.5 mmol, 258 mg) in anhydrous MeOH (70 mL) under argon followed by the addition of glacial acetic acid (0.2 mL) and the reaction mixture was stirred at room temperature for 20 h. Volatile components were evaporated in vacuo and the residue was purified by CC (PhMe–hexanes, 2:1). Fractions containing the product were combined and evaporated in vacuo to give **4**.

Yield: 0.026 g (10%, Procedure A) or 0.228 g (88%, Procedure B) of a grayish-white solid; mp 70–76 °C; $[\alpha]_{589}^{22} = +189.0$ (*c* 0.17, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.80, 0.91, 1.19 (18H, 3s, 1:1:1, 6 × Me); 1.15–1.27, 1.33–1.54, 1.70–1.81 (8H, 3m, 2:4:2, 4 × CH_2); 1.89 (2H, d, $J = 4.5$ Hz, 2 × H–C(4)); 2.41, 2.89 (4H, 2br d, 1:1, $J = 15.2$ Hz, 2 × $H_2C(4')$); 3.14 (2H, d, $J = 5.7$ Hz, 2 × H–C(3)); 3.95 (2H, br d, $J = 5.7$ Hz, 2 × NH); 4.40–4.50 (4H, m, 2 × $H_2C(2')$); 4.74, 4.88 (4H, 2br s, 1:1, 2 × $H_2C(3'')$); 6.35–6.41, 6.63–6.69 (4H, 2m, 1:1, 4H of Ar). ^{13}C NMR ($CDCl_3$): δ 10.1, 21.8, 22.5, 26.1, 31.7, 43.1, 48.4, 49.4, 52.4, 69.0, 73.3, 94.3, 104.6, 110.1, 117.2, 135.7, 146.8. *m*/*z* (EI) = 516 (M^+); *m*/*z* (HRMS) found: 516.373050 (M^+); $C_{34}H_{48}N_2O_2$ requires: *m*/*z* = 516.371579. ($C_{34}H_{48}N_2O_2$ requires: C, 79.02; H, 9.36; N, 5.42. Found: C, 79.57; H, 10.43; N, 4.88.); ν_{max} (KBr) 3406, 2953, 2886, 1670, 1596, 1517, 1481, 1446, 1430, 1401, 1389, 1371, 1330, 1310, 1268, 1245, 1194, 1152, 1073, 1040, 996, 885, 730 cm^{-1}.

5.7. Synthesis of N^1,N^2-bis{(1*S*,2*R*,3*S*,4*R*,4′*R*)-1,4′,7,7-tetramethyldihydro-3′*H*-spiro[bicyclo[2.2.1]-heptane-2,2′-furan]-3-yl}benzene-1,2-diamine 18 and its (1*S*,2*R*,3*S*,4*R*,4′*S*)-epimer 18′

A mixture of compound **4** (0.63 mmol, 326 mg), ethanol (50 mL), and 10% Pd–C (100 mg) was hydrogenated (3

bar of H_2) at room temperature for 10 h. The reaction mixture was filtered through a short pad of Celite®, washed with dichloromethane (100 mL), and the filtrate evaporated in vacuo to give a mixture of epimers **18** and **18′** in a ratio of 85:15, which was purified by CC (PhMe–hexanes, 1:2). Fractions containing the product were combined and evaporated in vacuo to give compound **18**.

5.7.1. Data for compound 18. Yield: 0.145 g (44%) of a greenish-white solid; mp 163–173 °C; $[\alpha]_{589}^{21} = +93.1$ (*c* 0.12, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.79, 0.84, 1.18 (18H, 3s, 1:1:1, 6 × Me); 0.84 (6H, d, $J = 6.9$ Hz, 2 × H_3C–C(3′)); 1.20–1.27, 1.42–1.47 (6H, 2m, 1:2, 3 × CH_2); 1.58 (2H, dd, $J = 3.6$; 12.9 Hz, 2 × Ha–C(4′)); 1.67–1.78 (2H, m, CH_2); 1.84 (2H, d, $J = 4.5$ Hz, 2 × H–C(4)); 2.12–2.26 (2H, m, 2 × H–C(3′)); 2.42 (2H, dd, $J = 7.8$; 12.9 Hz, 2 × Hb–C(4′)); 3.15 (2H, d, $J = 3.3$ Hz, 2 × H–C(3)); 3.58 (2H, dd, $J = 3.6$; 8.1 Hz, 2 × Ha–C(2′)); 3.93 (2H, dd, $J = 6.0$; 8.1 Hz, 2 × Hb–C(2′)); 4.43 (2H, br s, 2 × NH); 6.33–6.39, 6.62–6.68 (4H, 2m, 1:1, 4H of Ar). ^{13}C NMR ($CDCl_3$): δ 10.3, 18.4, 21.9, 22.7, 25.8, 31.4, 33.5, 44.3, 48.7, 49.4, 52.8, 68.9, 77.1, 93.2, 109.0, 116.8, 135.5. *m*/*z* (EI) = 520 (M^+); *m*/*z* (HRMS) found: 520.404120 (M^+); $C_{34}H_{52}N_2O_2$ requires: $m/z = 520.402879$. ($C_{34}H_{52}N_2O_2$ requires: C, 78.41; H, 10.06; N, 5.38. Found: C, 78.63; H, 10.34; N, 5.38.); ν_{max} (KBr) 3385, 2963, 2937, 2873, 1595, 1518, 1481, 1455, 1445, 1426, 1387, 1366, 1352, 1312, 1274, 1261, 1247, 1150, 1116, 1072, 1047, 1042, 1024, 1013, 994, 967, 936, 738 cm^{-1}.

5.7.2. Data for compound 18′. ^{1}H NMR ($CDCl_3$): δ 0.88 (6H, s, 2 × Me); 0.92 (6H, d, $J = 6.3$ Hz, 2 × H_3C–C(3′)); 1.16 (6H, s, 2 × Me); 2.03–2.13 (2H, m, 2 × H–C(3′)); 3.04 (2H, s, 2 × H–C(3)); 3.24 (2H, dd, $J = 7.8$; 10.8 Hz); 4.05 (2H, t, $J = 7.5$ Hz); 4.20 (2H, br s, 2 × NH).

5.8. General procedure for the preparation of benzo[*d*]-imidazolium tetrafluoroborates 19 and 20

Two drops of formic acid were added to a mixture of diamine **4** (0.218 g, 0.42 mmol) or **18** (0.220 g, 0.42 mmol) and NH_4BF_4 (0.42 mmol, 45 mg) in triethyl orthoformate (3 mL) under argon. The reaction mixture was heated at 120 °C for 3 h. Upon cooling to room temperature, Et_2O (10 mL) was added, and the resulting precipitate was collected by filtration, and washed with Et_2O (10 mL) to give product **19** or **20**, respectively. Compounds **19** and **20** were prepared in this manner.

5.8.1. 1,3-Bis{(1*S*,2*R*,3*S*,4*R*)-1,7,7-trimethyl-4′-methylenedihydro-3′*H*-spiro[bicyclo[2.2.1]heptane-2,2′-furan]-3-yl}-1*H*-benzo[*d*]imidazol-3-ium tetrafluoroborate 19. Prepared from **4**; 0.158 g (61%) of a dirty-white solid; mp 219–225 °C; $[\alpha]_{589}^{23} = +64.8$ (*c* 0.23, $CHCl_3$). ^{1}H NMR (DMSO-d_6): δ 0.90, 0.95, 1.23 (18H, 3s, 1:1:1, 6 × Me); 1.53–1.69, 1.86–1.98 (8H, 2m, 3:1, 4 × CH_2); 2.32 (2H, d, $J = 4.5$ Hz, 2 × H–C(4)); 3.08, 3.23 (4H, 2br d, 1:1, $J = 17.0$ Hz, 2 × H_2C(4′)); 3.66 (2H, dd, $J = 0.9$; 12.9 Hz, 2 × Ha–C(2′)); 4.25 (2H, d, $J = 12.9$ Hz, 2 × Hb–C(2′)); 4.74 (2H, s, 2 × Ha–C(3″)); 4.88 (2H, s, 2 × H–(3)); 5.04 (2H, br s, 2 × Hb–C(3″)); 7.64–7.70, 7.93–7.98 (4H, 2m, 1:1, 4H of Ar); 9.31 (1H, s, 1H of Ar). ^{13}C NMR ($CDCl_3$): δ 9.8, 22.3, 23.7, 28.2, 30.2, 41.7, 49.7, 51.0, 54.5, 72.5, 73.4, 95.9, 106.4, 114.5, 127.2, 131.7, 139.1, 144.5. *m*/*z* (EI) = 527 (M-87$^+$); *m*/*z* (HRMS) found: 527.364900 (M-87$^+$); $C_{35}H_{47}N_2O_2$ requires: $m/z = 527.363754$. ($C_{35}H_{47}BF_4N_2O_2$ requires: C, 68.40; H, 7.71; N, 4.56. Found: C, 67.77; H, 7.86; N, 4.65.); ν_{max} (KBr) 3422, 3210, 2952, 2930, 2872, 1636, 1617, 1549, 1481, 1458, 1449, 1394, 1373, 1320, 1244, 1235, 1196, 1168, 1123, 1083, 1063, 1032, 899, 765, 752 cm^{-1}.

5.8.2. 1,3-Bis{(1*S*,2*R*,3*S*,4*R*,4′*R*)-1,4′,7,7-tetramethyldihydro-3′*H*-spiro[bicyclo[2.2.1]heptane-2,2′-furan]-3-yl}-1*H*-benzo[*d*]imidazol-3-ium tetrafluoroborate 20. Prepared from compound **16**; 0.110 g (42%) of a dirty-white solid; mp 333–337 °C; $[\alpha]_{589}^{22} = +54.7$ (*c* 0.09 $CHCl_3$). ^{1}H NMR (DMSO-d_6): δ 0.68 (6H, d, $J = 6.9$ Hz, 2 × H_3C–C(3′)); 0.89, 0.90, 1.19 (18H, 3s, 1:1:1, 6 × Me); 1.50–1.76, 1.82–1.93 (8H, 2m, 3:1, 4 × CH_2); 2.04 (2H, dd, $J = 6.3$; 13.5 Hz, 2 × Ha–C(4′)); 2.12 (2H, d, $J = 4.2$ Hz, 2 × H–C(4)); 2.18–2.29 (2H, m, 2 × H–C(3′)); 2.62 (2H, dd, $J = 7.5$; 13.5 Hz, 2 × Hb–C(4′)); 3.11 (2H, dd, $J = 6.0$; 7.8 Hz, 2 × Ha–C(2′)); 3.88 (2H, dd, $J = 6.3$; 7.8 Hz, 2 × Hb–C(2′)); 4.91 (2H, s, 2 × H–C(3)); 7.76–7.82, 8.00–8.06 (4H, 2m, 1:1, 4H of Ar); 10.05 (1H, s, 1H of Ar). ^{13}C NMR (DMSO-d_6): δ 10.0, 17.0, 21.7, 22.2, 27.0, 30.1, 32.5, 42.8, 49.4, 51.3, 53.9, 71.6, 76.5, 95.2, 114.5, 127.1, 131.6, 141.0. *m*/*z* (EI) = 531 (M−87$^+$); *m*/*z* (HRMS) found: 531.3944 (M−87$^+$); $C_{35}H_{51}N_2O_2$ requires: $m/z = 531.3951$. ($C_{35}H_{51}BF_4N_2O_2$ requires: C, 67.96; H, 8.31; N, 4.53. Found: C, 67.41; H, 8.45; N, 4.61.); ν_{max} (KBr) 3447, 3227, 2977, 2964, 2940, 2891, 1636, 1534, 1489, 1459, 1391, 1323, 1313, 1237, 1168, 1123, 1081, 1053, 1032, 989, 980, 942, 779, 766 cm^{-1}.

5.9. X-ray structure analysis for compounds 12, 13′, and 20

Single crystal X-ray diffraction data of compounds **12**, **13′**, and **20** were collected at room temperature on a Nonius Kappa CCD diffractometer using the Nonius Collect Software.[51] DENZO and SCALEPACK[52] were used for indexing and scaling of the data and the structures were solved by means of SIR97.[53] Refinement was done using XTAL3.4[54] program package and the crystallographic plots were prepared by ORTEP III.[55] Crystal structures were refined on *F* values using the full-matrix least-squares procedure. The non-hydrogen atoms were refined anisotropically in all cases, while the positions of hydrogen atoms were geometrically calculated and their positional and isotropic atomic displacement parameters were not refined. Absorption correction was not necessary. Regina[56] weighting scheme was used in all cases.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 668594–668596. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

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