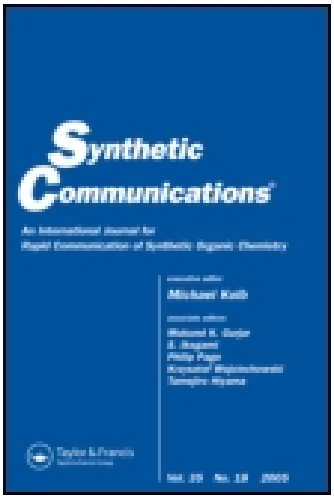

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Intramolecular Cyclization of 1-Benzyl-2-(nitromethylene)pyrrolidines in Triflic Acid

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INTRAMOLECULAR CYCLIZATION OF 1-BENZYL-2-(NITROMETHYLENE)PYRROLIDINES IN TRIFLIC ACID

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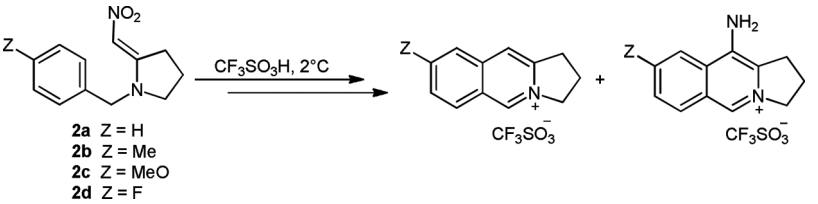
[3]*Laboratoire IC2MP-UMR 7285 CNRS, Poitiers, France*

GRAPHICAL ABSTRACT



Abstract *1-Benzyl-2-(nitromethylene)pyrrolidines in triflic acid undergo intramolecular cyclization to afford the corresponding 2,3-dihydro-1H-pyrrolo[1,2-b]isoquinolinium triflates and/or 10-amino-2,3-dihydro-1H-pyrrolo[1,2-b]isoquinolinium triflates, depending on the nature of the aromatic substituent. Structures of products and reaction mechanisms are discussed.*

Keywords Intramolecular cyclization; isoquinolinium triflates; 2-(nitromethylene) pyrrolidines; protonation; triflic acid

INTRODUCTION

In previous articles, we reported the behaviour and reactivity in superacidic media (HF-SbF_5 or triflic acid) of 1-heterosubstituted-1-methylthio-2-nitroethene derivatives,[1,2] acyclic nitroketene S,S-acetals,[3] and nitroketene aminals.[4]

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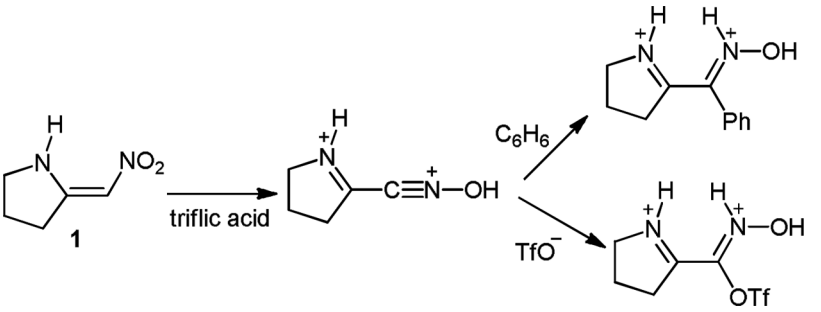
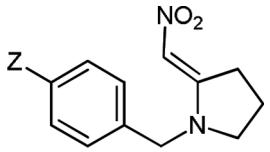
This publication is dedicated in memory of Professor Jean-Marie Coustard, who supervised this work but passed away at the end of August 2013.



Scheme 1. Reactivity of 2-(nitromethylene)pyrrolidine in triflic acid.



2a Z = H
2b Z = Me
2c Z = MeO
2d Z = F

Figure 1. 1-Benzyl-2-(nitromethylene)pyrrolidine derivatives **2a–d** used in this study.

For instance, nonaromatic 1-methyl-2-(nitromethylene)pyrrolidine **1** in triflic acid formed hydroxynitrilium ions that can be trapped in situ either with triflate anion or benzene[1] (Scheme 1).

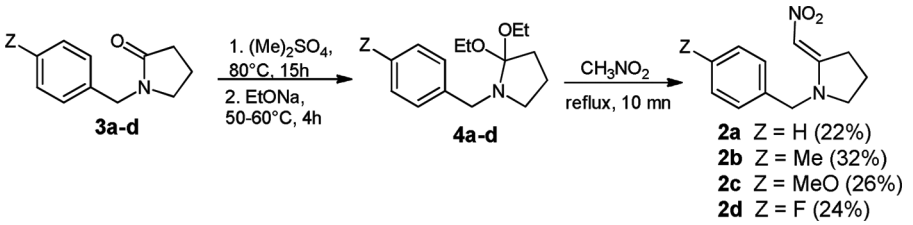
To widen the scope of these reactions in triflic acid and to synthesize new pyrrolidines that may have some physiological interest, intramolecular reactions were undertaken on 2-(nitromethylene)pyrrolidines with different *para*-substituted *N*-benzyl groups **2a–d** (Fig. 1).

RESULTS AND DISCUSSION

Starting Material

1-Benzylpyrrolidin-2-one derivatives **3** were prepared conventionally by alkylation[5] of pyrrolidin-2-one with the appropriate *para*-substituted bromobenzyle derivative. Further treatment with dimethylsulfate followed by sodium ethoxide led to the corresponding 1-benzyl-2,2-diethoxypyrrolidines **4,**[6] which upon reaction with nitromethane[7] afforded the expected 1-benzyl-2-(nitromethylene)pyrrolidine derivatives **2** (Scheme 2). Column chromatography and crystallization from CH_2Cl_2/hexanes afforded the expected products **2a–d.** Yields are reported in Scheme 2 without optimization.

Starting materials **2a–d** were characterized from their NMR spectra, with the vinylic protons in the range δ_H 6.69–6.87 ppm, the carbons bearing the nitromethylene group =CH-NO_2 at δ_C 109.7–109.9 ppm, and the other ethylenic carbons >C=C at



Scheme 2. 1-Benzyl-2-(nitromethylene)pyrrolidines **2a–d** from **3a–d** with yields (%) not optimized after crystallization.

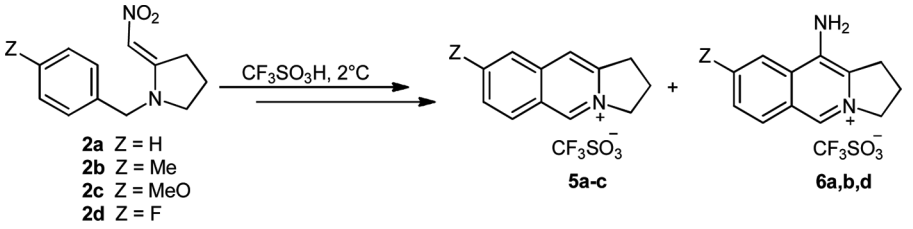
164.5–164.7 ppm. A single set of signals was observed by NMR, indicating the presence of a sole stereoisomer in solution, presumably the (*E*)-isomer, as previously reported for 1-methyl-2-(nitromethylene)pyrrolidine by Rajappa et al.[8]

Reactions in Triflic Acid

Triflic acid (5 mL, 56.2 mmol) was placed under nitrogen in a 10-mL round-bottomed flask equipped with a three-way valve and a Teflon-coated magnetic stirrer. *Caution*: Triflic acid is a strong corrosive acid that may react violently with water. The system was cooled to ice-water bath temperature, and then the 1-benzyl-2-(nitromethylene)pyrrolidine **2** (1 mmol) was added. Compounds **2a–d** dissolved easily under stirring. The reaction proceeded under nitrogen (Scheme 3) for 3 to 6 h, depending on the *para*-substituent. At the end of the reaction, the acidic medium was quenched over CH_2Cl_2/MeOH (97/3) at −60 to −40 °C and let warm to about 0 °C when brine (10 mL) and anhydrous Na_2CO_3 (6 g) were added. The extraction was carried out promptly with CH_2Cl_2/MeOH (95/5).

The solvent was evaporated in vacuo to obtain crude product, which was purified using silica-gel column chromatography. The isolated products **5** and **6** were crystallized from dichloromethane–petroleum ether. The yields were in the range of 15 to 69% depending on the *para*-substituent as indicated in Table 1. The methoxy compound gave the lowest yield, probably because of other intermolecular reactions occurring in triflic acid, as previously observed in situ with 1-amino-2-nitroethylene derivatives.[1] Compounds **5c** and **6d** were the sole products isolated from the reactions with **2c** and **2d** respectively.

The products **5** and **6** were isolated as triflate salts. The triflate anion was characterized from its CF_3 group that resonates at δ_F −75 to −72 ppm and as a



Scheme 3. Intramolecular cyclization of 1-benzyl-2-(nitromethylene)pyrrolidines **2a–d** in triflic acid.

Table 1. Yields of isolated products after reaction in triflic acid

Starting compounds	Z	Products **5a–d** yield (%)	Products **6a–d** yield (%)
2a	H	39	27
2b	Me	62	31
2c	MeO	15	0
2d	F	0	69

Note. After crystallization.

quadruplet (J_{CF} Hz) at δ_C 120–122 ppm. Molecular and formula weights of the cationic part were determined by high-resolution mass spectrometric (HR-MS) analysis. NMR analysis of compounds **5** and **6** are characterized by a highly deshielded proton that resonates as singlet at δ_H 9–10 ppm. Chemical shifts with the same magnitude were previously reported on the aromatic carbon adjacent to the quaternary nitrogen.[9]

For example, with compound **5a** (Z=H), the ^{13}C NMR spectrum showed the presence of six sp^2 CH, at δ_C 147.62 (δ_H 10.02), 137.63 (δ_H 8.17), 131.54 (δ_H 8.49), 131.21 (δ_H 7.97), 128.43 (δ_H 8.27), and 122.60 ppm (δ_H 8.47 ppm), and two quaternary sp^2 carbons, at 140.09 and 150.16 ppm. The signal at δ_C 147.62 ppm is broad and weak because of ^{15}N coupling (triplet) and because of the fast relaxation effect caused by the quadripolar moment of ^{14}N nucleus, the most abundant isotope.[10] Chemical shifts are also close to values reported for vasconine **7** (Fig. 2).[9]

Compounds **6** are characterized with a broad singlet of 2H intensity at δ_H 6.6 ppm. These protons are easily exchangeable with D_2O. Two-dimensional (2D) NMR indicated that the hydrogens are not bonded to a carbon. This broad singlet was attributed to the NH_2 group, in agreement with the formula weight of the cationic part. Compound **6a** (Z=H) was also characterized by the presence of five sp^2 CH at δ_C 134.5 (δ_H 7.9), 132.3 (δ_H 9.16), 131.2 (δ_H 8.05), 130.6 (δ_H 8.28), and 122.9 ppm (δ_H 8.47 ppm) and three quaternary carbons at 129.3, 131.6, and 141.3 ppm. The signal at 132.3 ppm (δ_H 9.16) is broad and weak because of the proximity of the ammonium nitrogen, as previously indicated for compound **5a**.

NMR Study and Reaction Mechanism

To have a better understanding of the reaction mechanism, 1-(4-methylbenzyl)-2-(nitromethylene)pyrrolidine **2b** in triflic acid was examined by NMR spectroscopy

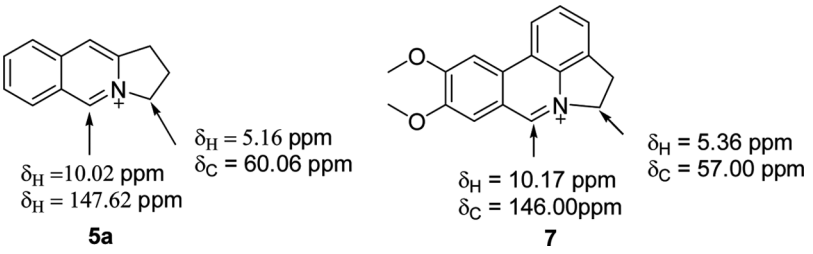
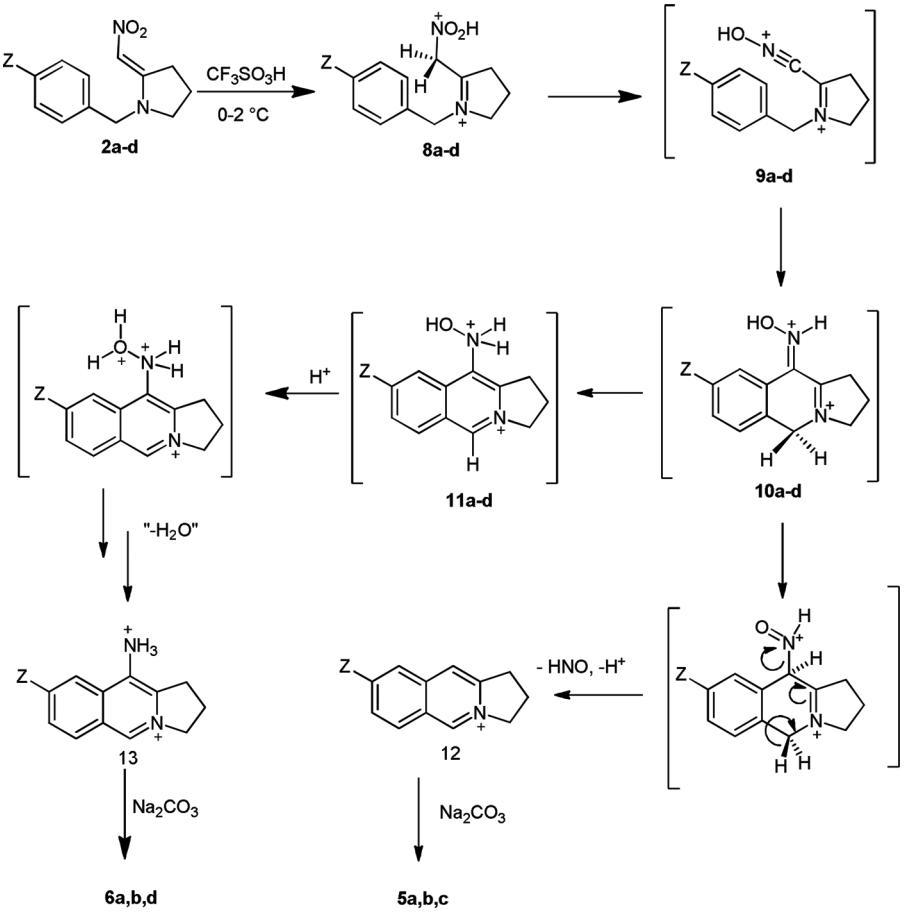


Figure 2. Chemical shifts of compound **5a** and vasconine **7**.

at 255 K. The starting material quickly disappeared to afford the observable cation **8b** with a deshielded methylene (δ_C 71.6 and δ_H 5.37 ppm) next to the protonated nitro group. These values are close to those previously observed for *C,O*-diprotonated nitroethylene derivatives in triflic acid.[1,11,12] After the disappearance of kinetic cation **8b**, cation **12b** was observed as the main cation in this experiment. The reference spectrum for cation **12b** was prepared by dissolving **5b** in triflic acid (see the supplementary material). The mechanism for the formation of cation **8b** is probably similar to the one previously reported for nitroketene aminals.[4] At the beginning of the reaction, 1-benzyl-2-(nitromethylene)pyrrolidines **2a–d** undergo double protonation: a *C*-protonation on the carbon bearing the nitro group and an *O*-protonation of the nitro group. The *O*-protonation occurs through a fast proton exchange process with the acidic medium, as observed in fluorosulfonic acid at −80 °C.[13] Prototropic exchanges and the formal loss of a molecule of water lead to the formation of the conjugated hydroxynitrilium ion **9**.[2,3] As soon as it is formed, as indicated in Scheme 4, **9** reacts with the tethered phenyl ring to afford



Scheme 4. Plausible mechanism for the formation of **5** and **6**.

the kinetic transient tricyclic cation **10.** In the final step, cation **10** undergoes aromatization either with the loss of the oxime group, or the formation of the amino group, as indicated in Scheme 4. The driving force of the reaction is probably the aromatization of the heteroaromatic ring.

The addition of triflate anion on the hydroxynitrilium ion **9** should not be excluded, as previously observed,[1] and might explained the poor yield observed with the methoxy derivative.

On neutralizing the reaction, compounds **5** and **6** were isolated as triflate salts because of the presence of quaternary nitrogen in the isoquinolinium structure.

CONCLUSION

The current study is an application of the use of triflic acid and 2-(nitromethylene)pyrrolidine derivatives in the field of heterocyclic synthesis to afford 2,3-dihydro-1H-pyrrolo[1,2-b] isoquinolinium triflates and/or 10-amino-2,3-dihydro-1H-pyrrolo[1,2-b] isoquinolinium triflates, depending on the nature of the substituent on the phenyl ring. The formed cations were studied by NMR in situ and a mechanism was postulated for the observed reaction.

From a practical point of view, this reaction is a new, easy route to isoquinolinium derivatives. These derivatives occurred as natural products, with some of them having inhibitor enzyme activities and anti-inflammatory[14,15] or anticancer properties.[16,17] Simpler isoquinolinium are also known to form ionic liquid crystals.[18,19]

EXPERIMENTAL

Melting points were determined with a Büchi melting-point B545 apparatus using capillary tubes (temperature rate 2 °C/min) and were not corrected. A Bruker DPX 300 spectrometer, equipped with a low-temperature probe, was used for ^{1}H, ^{19}F, and ^{13}C NMR spectra, which were recorded at 300.13, 282.37, and 75.47 MHz, respectively. NMR spectra of cations were recorded in neat triflic acid at low temperature in the presence of CD_3OD contained in a sealed capillary tube placed inside the NMR tube. NMR spectra of starting compounds and products were recorded at room temperature and chemical shifts reported relative to Me_4Si or $CFCl_3$ for fluorine. The reproducibility of ^{13}C NMR shift was about ± 0.05 ppm, depending on cell and concentration. Chemical assignments were made using DEPT 135, 2D, and usual chemical shift assignments rules. Electron-impact ionization (70 eV) mass spectra were obtained with a Finnigan Incos 500 instrument. HR-MS was performed by the Faculty of Sciences-University of Picardie/Jules Verne, France. Column chromatography was carried out on flash silica gel (20 to 45 μm particle size). Triflic acid was purchased from Acros. No attempt was made to optimize the yields.

(*E*)-1-Benzyl-2-(nitromethylene)pyrrolidine (2a)

1-Benzylpyrrolidin-2-one (4.63 g, 26.46 mmol) and dimethylsulfate (2.60 mL, 27.40 mmol) were heated at 80 °C for 15 h under nitrogen atmosphere. The reaction mixture was then cooled at 50/60 °C and a solution of sodium ethoxide (0.742 g of

sodium in ethanol, 14 mL) was added dropwise. The resulting mixture was stirred under nitrogen for 4 h at 50/60 °C. Then nitromethane dried over $CaCl_2$ (3 mL, 55.0 mmol) was added, and the resulting solution was refluxed for 10 min. After cooling, the solvent was evaporated under reduced pressure. The residue was dissolved in CH_2Cl_2 and filtered, and the solvent was evaporated in vacuo. The resulting oil was purified by column chromatography on silica gel (CH_2Cl_2/AcOEt, 99/1). Further crystallization from CH_2Cl_2/petroleum ether afforded compound **2a** as white crystals (0.424 g, 28%).

Mp 94.9 °C (CH_2Cl_2/petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.10$ (m, 2H, CH_2-CH_2-CH_2), 3.56 (m, 4H, CH_2-CH_2-CH_2), 4.40 (s, 2H, CH_2-Ph), 6.86 (s, 1H, =CH-NO_2), 7.08 (d, $J = 7.3$ Hz, 2H, *o*-H), 7.37 (m, 3H, *p*-H, *m*-H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 20.85$ (*C*H_2-C=), 35.04 (CH_2-*C*H_2-CH_2), 51.37 (CH_2-Ph), 54.56 (N-*C*H_2-CH_2), 109.88 (=CH-NO_2), 127.60 (2 × ar-CH), 128.68 (ar-CH), 129.54 (2 × ar-CH), 134.24 (*ipso*-C), 164.72 (>C=CH-; C-2). HRMS (ESI): *m/z* $[M+Na]^+$ calcd. for $C_{12}H_{14}N_2O_2Na$: 218.0953; found: 241.0959.

2,3-Dihydro-1H-pyrrolo[1,2-b]isoquinolin-4-ium Trifluoromethanesulfonate (5a)

(*E*)-1-Benzyl-2-(nitromethylene)pyrrolidine **2a** (218 mg, 1 mmol) was dissolved in triflic acid (5 mL, 56.2 mmol) at 2 °C under nitrogen atmosphere. The reaction was monitored by thin-layer chromatography (TLC; CH_2Cl_2/MeOH, 97/3). After the disappearance of the starting compound, the acidic solution was poured into 50 mL of a mixture of CH_2Cl_2/MeOH (90:10) at −60 to −40 °C and let warm. When the temperature was close to 0 °C, brine (10 mL) and anhydrous Na_2CO_3 (6 g) were added. The extraction was carried out promptly with CH_2Cl_2/MeOH, 95/5 (4 × 20 mL). The organic phase was dried over $MgSO_4$ and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using CH_2Cl_2/MeOH (95/5) as eluent, followed by precipitation from a mixture of dichloromethane/petroleum ether, to yield **5a** (124 mg, 39%) as white powder.

Mp 73–74 °C (CH_2Cl_2/petroleum ether). ^{1}H NMR (300 MHz, acetone-d_6): $\delta = 2.66$ (m, 2H, CH_2-CH_2-CH_2), 3.67 (t, *J* 7.5 Hz, 2H, CH_2-C=), 5.16 (t, *J* 7.4 Hz, 2H, CH_2-N), 7.98 (t, *J* 7.2 Hz, 1H, H-9), 8.18 (t, *J* 7.3 Hz, 1H, H-8), 8.26 (d, *J* 8.4 Hz, 1H, H-7), 8.47 (d, *J* 9.5 Hz, 1H, H-10), 8.49 (s, 1H, H-6), 10.02 (s, 1H, H-5). ^{13}C NMR (75 MHz, CD_3COCD_3): $\delta = 23.90$ (CH_2-*C*H_2-CH_2), 31.99 (*C*H_2-C=), 60.06 (CH_2-N), 122.61 (qd, J_{CF} 321.6 Hz, *C*$F_3SO_3^-$), 122.60 (C-6), 128.25 (C-5a), 128.43 (C-7), 131.21 (C-9), 131.54 (C-10), 137.63 (C-8), 140.09 (C-9a), 147.62 (C-5), 150.16 (C-10a). ^{19}F NMR (282 MHz, CD_3COCD_3): $\delta = -73.9$ ($CF_3SO_3^-$). HRMS (EI): *m/z* [M-($CF_3SO_3^-$)] calcd. for $C_{12}H_{12}N$: 170.0969; found 170.0961.

10-Amino-2,3-dihydro-1h-pyrrolo[1,2-b]isoquinolin-4-ium Trifluoromethanesulfonate (6a)

From **2a,** the second product **6a** (91 mg, 27%) was obtained as powder.

Mp 153–154 °C (CH_2Cl_2/petroleum ether). ^{1}H NMR (300 MHz, CD_3COCD_3): $\delta = 2.66$ (m, 2H, CH_2-CH_2-CH_2), 3.67 (m, 2H, CH_2-C=), 5.16 (m, 2H, CH_2-N), 6.65

(broad s, 2H, NH_2), 7.92 (dt, *J* 7.2 Hz; 1.2 Hz, 1H, H-8), 8.05 (dt, *J* 7.0 Hz; 1.0 Hz, 1H, H-7), 8.28 (d, *J* 8.3 Hz, 1H, H-9), 8.48 (d, *J* 8.6 Hz, 1H, H-6), 9.17 (s, 1H, H-5). ^{13}C NMR (75 MHz, CD_3COCD_3): $\delta = 22.99$ (CH_2-*C*H_2-CH_2), 29.88 (*C*H_2-C=), 60.74 (CH_2-N^+≤), 122.54 (qd, J_{CF} 321.6 Hz, *C*$F_3SO_3^-$), 122.98 (≥CH, C-6), 127.21 (C-5a), 129.35 (C-9a), 130.63 (≥CH, C-9), 131.18 (≥CH, C-7), 131.58 (C-10a), 132.32 (bs,>N^+=CH-; C-5), 134.49 (CH, C-8), 141.32 (C-NH_2). ^{19}F NMR (282 MHz, CD_3COCD_3): $\delta = -74.1$ ($CF_3SO_3^-$). HRMS (EI): *m*/*z* [M-(CF_3SO_3-)] calcd. for $C_{12}H_{13}N_2$: 185.1074; found 185.1074.

Cation in Triflic Acid 12b

^{1}H NMR (300 MHz, 298 K, CD_3OD): $\delta = 1.98$ (t, *J* 7,5 Hz, 2H, H-2), 2,04 (s, 3H, CH_3), 2.92 (t, *J* 7.5 Hz, 2H, H-1), 4.26 (t, *J* 7.5 Hz, 2H, H-3), 7.16 (d, *J* 8,6 Hz, 1H, H-6), 7.27 (s, 1H, H-9), 7.45 (s, 1H, H-10), 7.47 (d, *J* 8,6 Hz, 1H, H-7), 8.58 (s, 1H, H-5). ^{13}C NMR (75 MHz, 298 K, CD_3OD): $\delta = 21.72$ (CH_3), 22.71 C-2), 30.80 (C-1), 58.77 (C-3), 121.29 (C-6), 126.14 (C-5a), 126.29 (C-10), 129.32 (C-7), 133.75 (C-9), 140.21 (C-8), 144.12 (C-5), 148.66 (C-9a), 150.40 (C-10a).

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SUPPORTING INFORMATION

Full experimental details and ^{1}H and ^{13}C NMR spectra for this article can be accessed on the publisher's website.

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