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Stabilization of γ-lactam and lactone ring-fused norcaradienes by protonation: DFT calculations of norcaradiene and the corresponding cycloheptatriene structures

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ABSTRACT

Stabilization of norcaradiene structures of γ-lactone and lactam ring-fused 7-vinylnorcaradienes **1a**–**1e** in their norcaradiene – cycloheptatriene valence isomerization was achieved by protonation. Induced ^{13}C NMR chemical shifts caused by protonation were monitored for the cyclopropane ring carbons (C1, C6 and C7) of the norcaradiene structures as indices of their stabilities. DFT calculations (B3LYP/6-311+G(d) level) of norcaradienes, the corresponding cycloheptatrienes, and their protonated structures supported the experimental results.

1. Introduction

Norcaradines are usually unstable valence isomers and the corresponding cycloheptatrines exist predominantly [1–3]. They are proposed as intermediates in some rearrangements [4–6]. Certain structural devices are required to prepare stable norcaradienes. In the past, great efforts have been devoted to prepare stable norcaradienes either by structural restrictions (an incorporation of fused ring system [7–9], steric hindrance [10,11], or resonance stabilization [12–14]) or electronic effects (an introduction of π-acceptors at 7-position [15–17] or π-donors at 3- and 4-positions [18,19]). However, almost no effort has been made to control the stability of norcaradienes not by these factors but by changing some external conditions using the same molecules. We are interested in this stability tunable norcaradienes. Since an introduction of an electron withdrawing group at the 7-position is known to stabilize the norcaradiene structure, we have planned to furnish a proton acceptor as a substituent at this position. Depending on the degree of protonation, an electron withdrawing character of the substituent varies. Thus the stability of norcardiene can be tuned externally by the degree of protonation of the proton acceptor at the 7-position.

In our previous study, we reported the synthesis of unusually stable 7-vinylnorcaradienes fused with a γ-lactone ring at the 1,7-position [20–22] and their thermal [23], photochemical [24], and acid-catalyzed rearrangements [25]. We have chosen this γ-lactone moiety as a proton acceptor. Since the γ-lactone ring-fused system could provide norcaradienes of moderate stabilities depending on their substituents, they are an appropriate candidate for stability study. Therefore, we chose the 1,7-γ-lactone ring-fused norcaradiene together with γ-lactam ring-fused one as a model system. Herein, we report on our approach to the control of the norcaradiene – cycloheptatriene valence isomerization by protonation which increases the π-acceptor character of the substituents at the 7-position. This kind of approach to stabilize norcaradiene structures by heteroatom-stabilized carbocations as substituents at the 7-position has been reported by Daub et al. [26,27].

2. Results and discussion

The stability of norcaradienes could be roughly estimated from their ^{13}C NMR chemical shifts of cyclopropane carbons, C1, C6, and C7 [28]. If the nocaradiene structure exists predominantly in the valence isomerization, these carbons possess an sp^3 character. However, C1 and C6 should be sp^2 carbons if the cycloheptatriene structure predominates completely in the valence isomerization (Scheme 1). In equilibrium, chemical shifts of these carbons appear as their weight average depending on their ratios. Norcaradienes examined, **1a**, **1b** [21], **1c** [24], **1d** [20], and **1e,** were prepared according to our reported method (Scheme 2). Thermolysis of cyclopropenes generated vinylcarbenes whose intramolecular cycloaddition to a benzene or a naphthalene ring afforded the corresponding 7-vinylnorcaradienes. Table 1 shows the chemical shifts of cyclopropane carbons (C1, C6, and C7) of **1a**–**1e** and their

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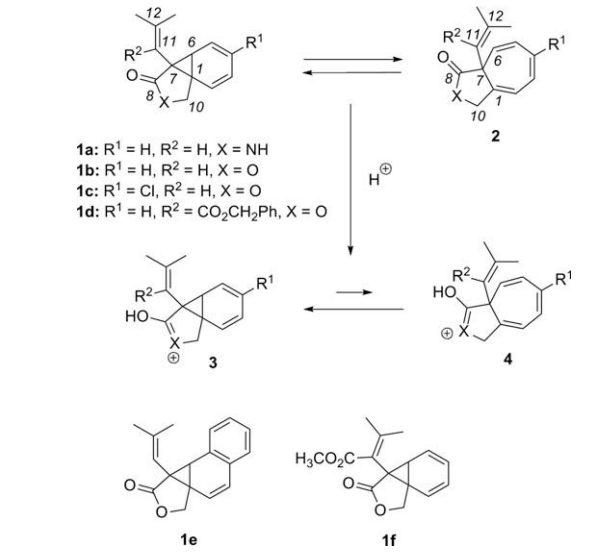
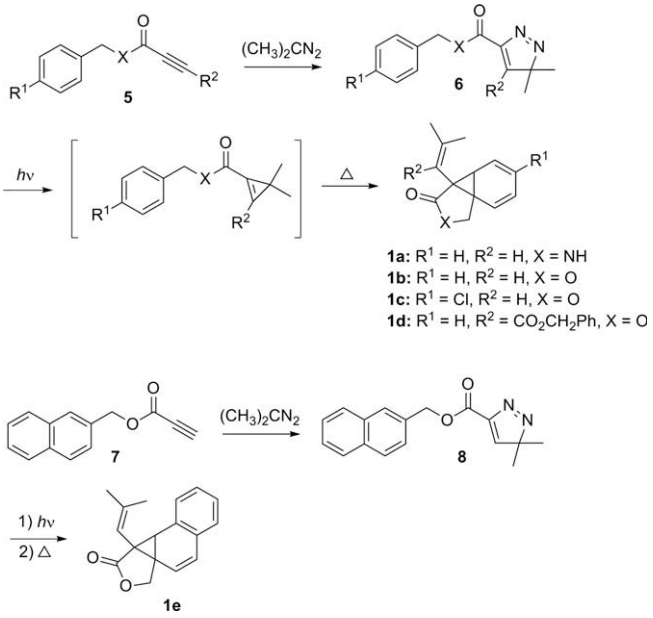


Scheme 1. Norcaradience – cycloheptatriene valence isomerization.



Scheme 2. Synthesis of 7-vinylnorcaradienes.

Table 1
Chemical shifts (δ) for C1, C6 and C7 of **1a**–**1e** and their induced chemical shifts ($\Delta\delta$) caused by the addition of TFA[a].

Carbon		**1a**[b]	**1b**[b]	**1c**[b]	**1d**[c]	**1e**[b]
C1	δ	72.1	52.4	56.2	41.4	39.4
	$\Delta\delta$[d]	−21.5	−5.8	−8.7	+1.3	+2.0
C6	δ	67.9	47.9	52.5	39.6	37.8
	$\Delta\delta$[d]	−19.2	−5.3	−7.9	+1.6	+1.5
C7	δ	31.9	23.0	26.1	21.6	24.3
	$\Delta\delta$[d]	−5.3	−0.3	−1.2	+1.2	+1.5

[a] Measurements were carried out on ca. 0.5 M solution of **1a**–**1e** in $CDCl_3$ at ambient temperature (ca. 300 K).
[b] With 8 eq. amount of TFA.
[c] With 10 eq. amount of TFA.
[d] Plus and minus signs designate downfield and upfield shifts, respectively.

induced chemical shifts ($\Delta\delta$) data after the addition of TFA at ambient temperature (ca. 300 K). Judging from these data, **1a**–**1c** exist as an equilibrium mixture with their cycloheptatriene structures **2a**–**2c**. The γ-lactam ring-fused norcaradiene **1a** shows the lowest shift values in $CDCl_3$ for C1(δ 72.1), C6(δ 67.9), and C7(δ 31.9) among them. In contrast, the stable norcaradienes **1d** and **1e** showed reasonable chemical shift values for C1, C6, and C7 as sp^3 carbons. In comparison to them, C1 and C6 of **1b** and **1c** appeared at considerably lower field than those of **1d** and **1e**. This indicates that these compounds exist as equilibrium mixtures and their C1 and C6 bears some sp^2 character. Therefore, **1a** is the least stable norcaradiene among them. Norcaradiene **1d** was reported to be stable from its X-ray analysis [19]. Due to the resonance stabilization, it is hard to take the cycloheptatriene structure in **1e**.

Fig. 1a and b shows the induced ^{13}C NMR chemical shifts of C1, C6, C7, C8, C10, C11, and C12 for **1a** and **1d** with increasing amount of TFA, respectively. Induced ^{13}C NMR chemical shifts ($\Delta\delta$ are obtained as $\Delta\delta = \delta_{TFA} - \delta_0$, where δ_{TFA} and δ_0 are the chemical shifts of **1a** and **1d** with and without TFA, respectively. Negative and positive signs of $\Delta\delta$ indicate upfield and downfield induced shifts, respectively. Large upfield shifts, −21.5 and −19.2 ppm after addition of 8 eq. of TFA, were observed for C1 and C6 of **1a**, respectively. An upfield shift of −5.3 ppm was observed for C7 (Fig. 1a). A relatively small shift value for C7 is reasonable since it remains as an sp^3 carbon in both norcaradiene and cycloheptatriene structures. On the contrary, C8 and C10 showed downfield shifts due to the protonation of the carbonyl group. These results indicated that the norcaradiene structure of **1a** was stabilized significantly by the addition of TFA in the valence isomerization. The acid-catalyzed thermal acetylene–allene rearrangement of 2-ethynylcycloheptatriene has been reported in which protonation of an acetylene moiety initiated the rearrangement of the corresponding norcaradiene structure [29,30]. In contrast to this, no rearrangement had occurred for **1a** under the reaction conditions. Similar tendency of the induced shifts by the addition of TFA was observed for the γ-lactone ring-fused 7-vinylnorcaradienes **1b** and **1c**. However, the upfield shift values for the C1 and C6 were smaller compared to those of **1a**. The γ-lactone ring fusion stabilizes the norcaradiene structure more than by the ring fusion with the γ-lactam.

In contrast to the upfield shifts observed for **1a**, **1b**, and **1c**, the stable norcaradienes **1d** and **1e** showed slight downfield shifts for their C1, C6 and C7 carbons after the addition of TFA. Fig. 1b shows the induced chemical shifts for **1d**. These downfield shifts are the normal tendency caused by protonation in a static system if no valence isomerization exists. Protonation strengthen the electron withdrawing ability of the lactone moiety resulting in the downfield shifts of the contiguous carbons. The degree of downfield shifts for C8 and C10 is nearly the same for all norcaradienes, which indicates the protonation takes place in the similar manner. The results proved the fact that **1d** and **1e** exist almost completely as the norcaradiene structures.

In order to evaluate the experimental results, DFT calculations were carried out. DFT calculations of some norcaradienes were reported previously [31]. Norcardienes, **1a** and **1b**, the corresponding cycloheptatrienes, **2a** and **2b**, and their protonated structures were calculated using Gaussian 03 program package [32] and B3LYP [33,34] method in conjunction with 6-311+G(d) basis set. Depending on direction of the vinyl substituents, two conformations are possible to be taken for norcaradiene, **1a** and **1b**, and cycloheptatriene, **2a** and **2b**. Four possible conformations could be existed for their protonated structures because of the direction of protonation. Geometry optimizations were carried out for all these possible conformations to find out their most stable conformations. Fig. 2 shows the most stable conformations of **1a**, **1b**, **2a**, **2b**, and their protonated forms together with **1f** and **2f**. Stabilities

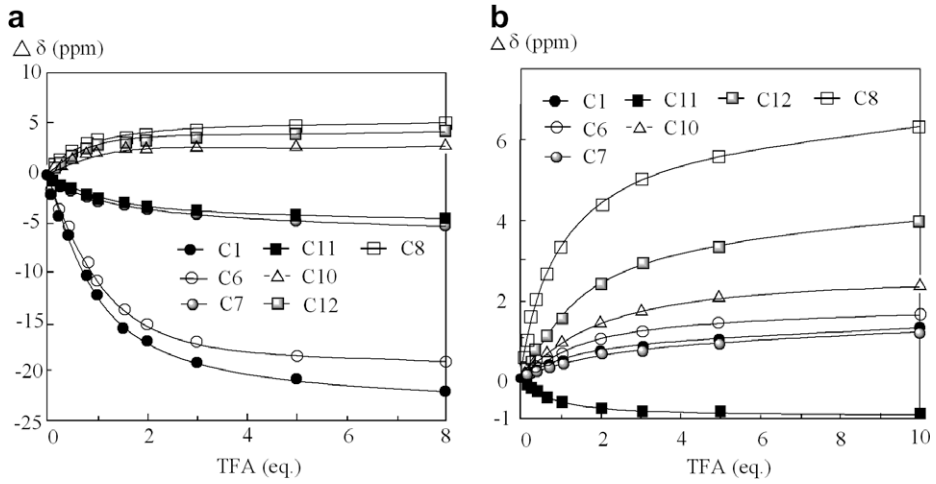


Fig. 1. Induced ^{13}C NMR chemical shifts of **1a** (a) and **1d** (b) with addition of TFA.

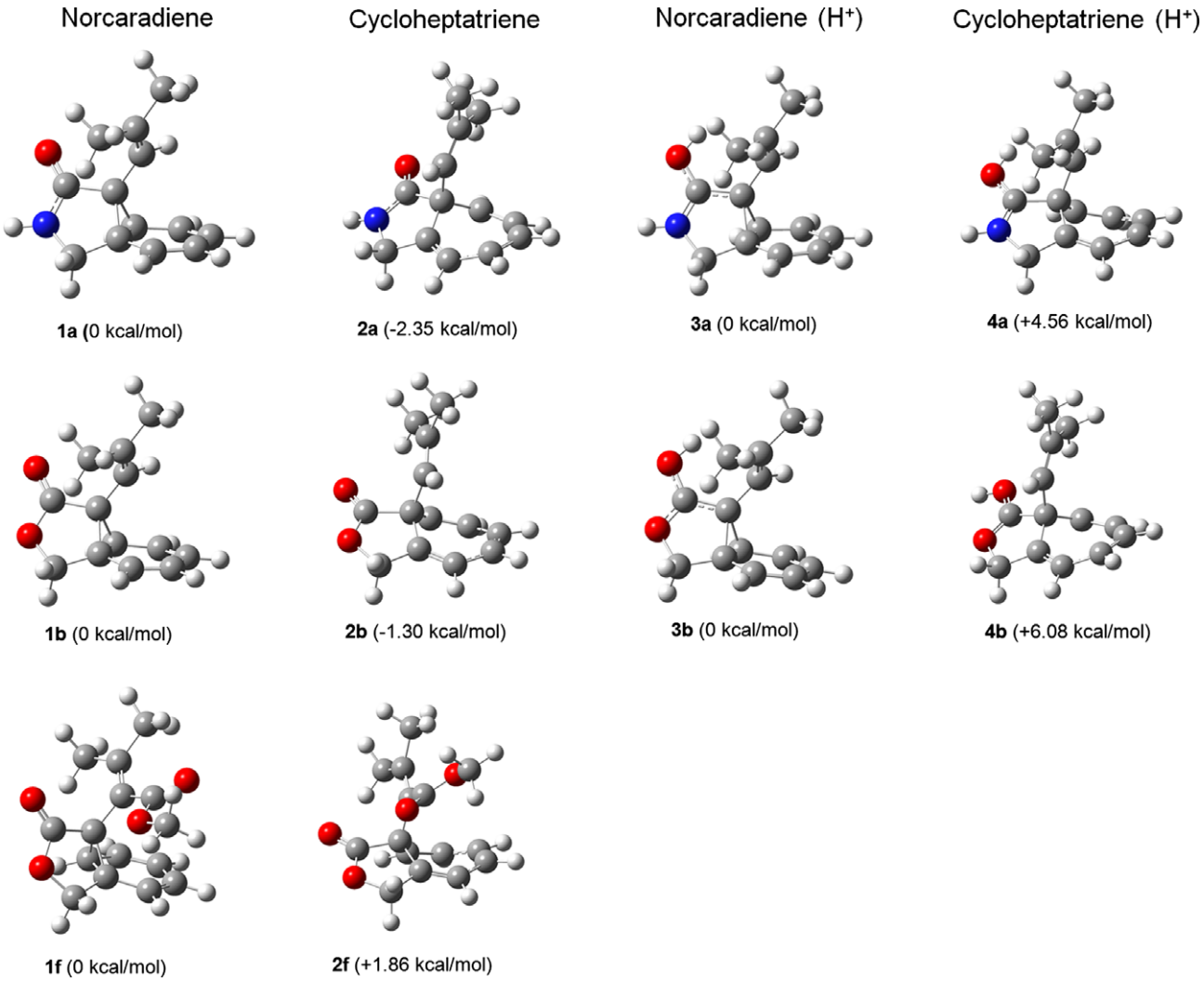


Fig. 2. Stable conformations of norcaradienes and cycloheptatrienes of **1a**, **1b**, and **1f**, and the corresponding protonated structures calculated by B3LYP/6-311+G(d). Stability of cycloheptatriene structures relative to the corresponding norcaradine structures are presented in kcal/mol in parentheses.

of cycloheptatrienes relative to the most stable corresponding norcaradiene conformers are presented in kcal/mol in parentheses. Relative energies of all possible conformers can be found in Supplementary data. Comparison between the norcaradiene and the corresponding cycloheptatrines shows that the lactam ring-fused norcaradiene **1a** is less stable than that of the lactone

ring-fused one **1b**. This agrees with experimental results in which the chemical shifts of C1 and C6 of **1a** appeared in lower fields than those of **1b**. Calculations show that cycloheptatriene structures are more stable than the corresponding norcaradiene structures in 2.35 and 1.30 kcal/mol for **1a** and **1b**, respectively. However, they seem to have a similar stability judging from their observed chemical shifts. Protonation resulted in the stabilization of norcaradine structures in both cases as observed in upfield shifts of cyclopropane carbons C1 and C6. Calculations also predicted that protonation stabilized the norcaradiene structure. The results indicate that the protonated forms of norcaradienes **3a** and **3b** are more stable than those of the corresponding protonated cycloheptatrienes **4a** and **4b** in 4.56 and 6.08 kcal/mol, respectively. Protonation causes an increase of electron withdrawing ability of substituents at the C7 position, which results in the stabilization of the norcaradiene structures. We reported that **1d** was the very stable norcaradiene in our previous study because of the electron withdrawing nature of an ester substituent [20]. In order to evaluate the stability of **1d**, the calculation was carried out on the simplified structure, the corresponding methyl ester **1f**. In contrast to **1a** and **1b**, it was calculated that the norcaradiene structure of **1f** is more stable than the corresponding cycloheptatriene structure **2f** in 1.86 kcal/mol. An introduction of an ester group to the vinyl moiety stabilizes the norcaradiene structure.

3. Conclusion

As we demonstrated, stability tunable norcaradienes could be attained by protonation of γ-lactam and lactone ring-fused 7-vinylnorcaradienes. Protonation increases electron withdrawing nature of substituents which stabilize the norcaradiene structure significantly in the norcaradiene – cycloheptatriene valence isomerization. The degree of stability was monitored by ^{13}C NMR spectroscopy. Geometry optimizations (B3LYP/6-311+G(d) level) on all possible conformers of norcaradienes, cycloheptatrienes, and the corresponding protonated forms were carried out to support these experimental results.

4. Experimental

4.1. General

Mps were determined on a Yanaco MP-S3 apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on JEOL FX-270 and EX-90 spectrometers in $CDCl_3$ with Me_4Si as an internal standard; *J* values are given in Hz. Mass spectra were measured with a Hitachi RMU-7M mass spectrometer. Elemental analyses were performed on a Perkin-Elmer 240 analyser. Reaction mixtures were concentrated on a rotary evaporator at 10–15 mm Hg. Chromatographic separations were accomplished by flash column chromatography on silica gel (Fuji gel BW 200; 150-350 mesh). All solvents were distilled and stored over 4 Å molecular sieves.

4.2. Synthesis

Previously reported norcaradienes **1b**, **1c**, and **1d** were prepared according to the reported method by us. Norcaradies **1a** and **1e** were synthesized in a similar manner from 3*H*-pyrazoles as described below.

4.2.1. Synthesis of 3H-pyrazoles

4.2.1.1. Benzyl 3,3-dimethyl-3H-pyrazole-5-carboxylate 6a. To a solution of *N*-benzyl-propiolamide **5a** (0.666 g, 4.19 mmol) in ether (45 mL) was added dropwisely a cold solution of dimethyldiazomethane in THF at −78 °C until the orange color of dimethyldiazomethane disappeared. After the removal of solvent by evaporation, the residue was purified by flash column chromatography on silica gel with hexane/ethyl acetate as an eluent to give 0.680 g (68%) of **6a** as white crystals. Mp. 115.5–116.5 °C; ^1H NMR ($CDCl_3$) δ 8.15 (br. s, 1H), 7.62 (s, 1H), 7.33 (s, 5H), 4.68 (d, *J* = 11.2 Hz, 2H), 1.45 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 159.6 (s), 150.4 (d), 149.1 (s), 137.6 (s), 128.2 (d), 127.5 (d), 127.1 (d), 95.0 (s), 42.9 (t), 19.5 (q); HRMS (FAB) calcd for $C_{13}H_{16}ON_3$ (MH^+) 230.1293, found 230.1296; Anal. Calcd for $C_{13}H_{15}N_3O$: C, 68.10; H, 6.59; N, 18.33. Found: C, 67.81; H, 6.37; N, 18.52.

4.2.1.2. Naphthalen-2-ylmethyl 3,3-dimethyl-3H-pyrazole-5-carboxylate 8. In a similar manner as for the synthesis of **6a**, **8** was prepared from naphthalene-2-ylmethyl propiolate **7** in 75% yield as white crystals. Mp. 99.5–101.0 °C; ^1H NMR ($CDCl_3$) δ 8.0–7.7 (m, 4H), 7.65 (s, 1H), 7.6–7.4 (m, 3H), 5.54 (s, 2H), 1.45 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 160.6 (s), 154.2 (d), 146.5 (s), 133.0 (s), 132.9 (s), 132.4 (s), 128.3 (d), 127.8 (d), 127.7 (d), 127. 5 (d), 126.2 (d), 126.1 (d), 125.9 (d), 94.9 (s), 67.1 (t), 19.5 (q); MS (EI) 280 (M^+, 10), 142 (13), 141 (100), 115 (15), 83 (26); Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.64; H, 5.58; N, 9.77.

4.2.2. Synthesis of norcaradienes

4.2.2.1. Norcaradiene 1a. A benzene solution (20 mL) of **6a** (0.213 g, 0.929 mmol) was irradiated for 40 min with a high pressure mercury lamp (USHIO UM452) at 0 °C. After removal of benzene by evaporation, the residue was dissolved in toluene (40 mL) and then refluxed for 15 h. After evaporation of solvent, the residue was chromatographed on silica gel to give norcaradiene **1a** (0.099 g, 53%) as white crystals. Mp. 188–189 °C; ^1H NMR ($CDCl_3$); 6.28 (t, *J* = 7.8 Hz, 1H), 6.23 (br. s, 1H), 6.18 (t, *J* = 7.8 Hz, 1H), 6.10 (dd, *J* = 7.8, 6.3 Hz, 1H), 5.97 (d, *J* = 7.8 Hz, 1H), 4.52 (sept, *J* = 1.3 Hz, 1H), 3.91 (d, *J* = 12.0 Hz, 1H), 3.66 (d, *J* = 12.0 Hz, 1H), 3.48 (d, *J* = 6.3 Hz, 1H), 1.63 (d, *J* = 1.3 Hz, 3H), 1.50 (d, *J* = 1.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) 180.1 (s), 140.4 (s), 126.4 (d), 124.9 (d), 123.6 (d), 121.8 (d), 116.7 (d), 71.7 (s), 67.5 (d), 47.0 (t), 31.8 (s), 25.5 (q), 18.7 (q). HRMS (FAB): calcd for $C_{13}H_{16}NO$ (MH^+) 202.1232, found 202.1225. Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.50; H, 7.31; N, 6.77.

*4.2.2.2. Norcaradiene **1e**.* In a similar manner, norcaradiene **1e** is prepared from **8** in 74% as colorless oil, ^1H NMR ($CDCl_3$) δ 7.49–7.18 (m, 4H), 6.63 (d, *J* = 10.0 Hz, 1H), 6.11 (dd, *J* = 10.0, 5.0 Hz, 1H), 5.12 (d, *J* = 9.6 Hz, 1H), 4.50 (qq, *J* = 1.4, 1.3 Hz, 1H), 4.38 (d, *J* = 9.6 Hz, 1H), 2.67 (d, *J* = 5.0 Hz, 1H), 1.51 (d, *J* = 1.3 Hz, 3H), 1.41 (d, *J* = 1.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 177.6 (s), 144.1 (s), 131.7 (s), 129.4 (d), 128.5 (d), 127.8 (d), 127.3 (d), 127.1 (d), 125.2 (d), 120.8 (d), 110.6 (d), 68.1 (t), 39.0 (s), 35.1 (d), 24.7 (q), 24.3 (s), 19.3 (q); HRMS (FAB): calcd for $C_{17}H_{17}O_2$ (MH^+) 253.1231, found 253.1233.

Appendix A. Supplementary data

The results of full geometry optimization (B3LYP/6-311+G(d) level) of **1a**, **2a**, **1b**, **2b**, and their protonated forms, **1f** and **2f** (PDF, 63 pages) is available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2009.10.049.

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