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1,3-Dipolar Cycloaddition of Azomethine Ylides Generated from Schiff Bases and Difluorocarbene to Symmetric Olefins*

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Abstract—Difluoro(iminio)methanides generated by the action of difluorocarbene on Schiff bases react with derivatives of maleic and fumaric acids, following the 1,3-dipolar cycloaddition pattern to give 2,2-difluoropyrrolidines which were detected by gas chromatography–mass spectrometry. The final products are stereoisomeric substituted 2-pyrrolidinones formed by hydrolysis of difluoropyrrolidines and their dehydrofluorination products, 2-fluoro-4,5-dihydropyrroles. The observed stereoselectivity of the cycloaddition suggests *Z* configuration of intermediate ylide and both *endo*- and *exo*-approach to the dipolarophile in the transition state corresponding to cycloaddition.

Tandem processes involving nonstabilized ylides generated from heteroelement-containing compounds and carbenes (including dihalocarbenes) constitute now a promising synthetic line in the chemistry of heterocyclic compounds [1]. For example, 1,3-dipolar cycloaddition of geminal dichloro-substituted azomethine ylides, formed by reaction of dichlorocarbene with compounds possessing a C=N bond, to electron-deficient alkenes and alkynes opens the way to a wide series of heterocyclic systems with unusual combinations of heteroatoms and functional groups. Among these, derivatives of pyrrole [2–6], pyridine [2, 4, 5], indolizine [7–9], pyrrolodiazines [9, 10], and other heterocycles [11, 12] have been reported. Geminal difluoro-substituted iminium ylides constitute a new almost unknown class of reactive intermediates. The presence of two strongly electronegative fluorine atoms in such ylides essentially affects its geometry and electronic structure, so that considerable variation of its reactivity should be expected, as compared to chloro-substituted analogs [13].

We previously reported a convenient procedure for generation of geminal difluoro-substituted azomethine ylides **Ia**–**Ic** via reaction of Schiff bases **IIa**–**IIc** with difluorocarbene, and their formation was proved by trapping them with some alkenes [14]. In the present work we performed a detailed study of the reaction of *N*-alkyl and *N*-aryl Schiff bases with difluorocarbene and examined 1,3-dipolar cycloaddition of difluoro(iminio)methanides to symmetric alkenes. Difluorocarbene was generated by reduction of dibromodifluoromethane with lead turnings (method *a*) [14–16] and activated lead (method *b*) [17] in the presence of tetrabutylammonium bromide. Traditional methods for generation of dihalocarbenes in alkaline medium, which are used to obtain dichloro- and chlorofluoro-substituted ylides [16], turned out to be inapplicable, presumably because of relatively fast hydrolysis of both difluorocarbene and dipolarophiles.

Our preliminary experiments showed that *N*-benzylidenebenzylamine (**IIa**) is inert under conditions of difluorocarbene generation by method *a*. With *N*-benzylidene(trimethylsilylmethyl)amine (**IIc**) and *N*-benzylideneglycine methyl ester (**IIb**) we observed only a small conversion of the Schiff bases with formation of tarry products. However, in the presence of dimethyl fumarate or dimethyl maleate the

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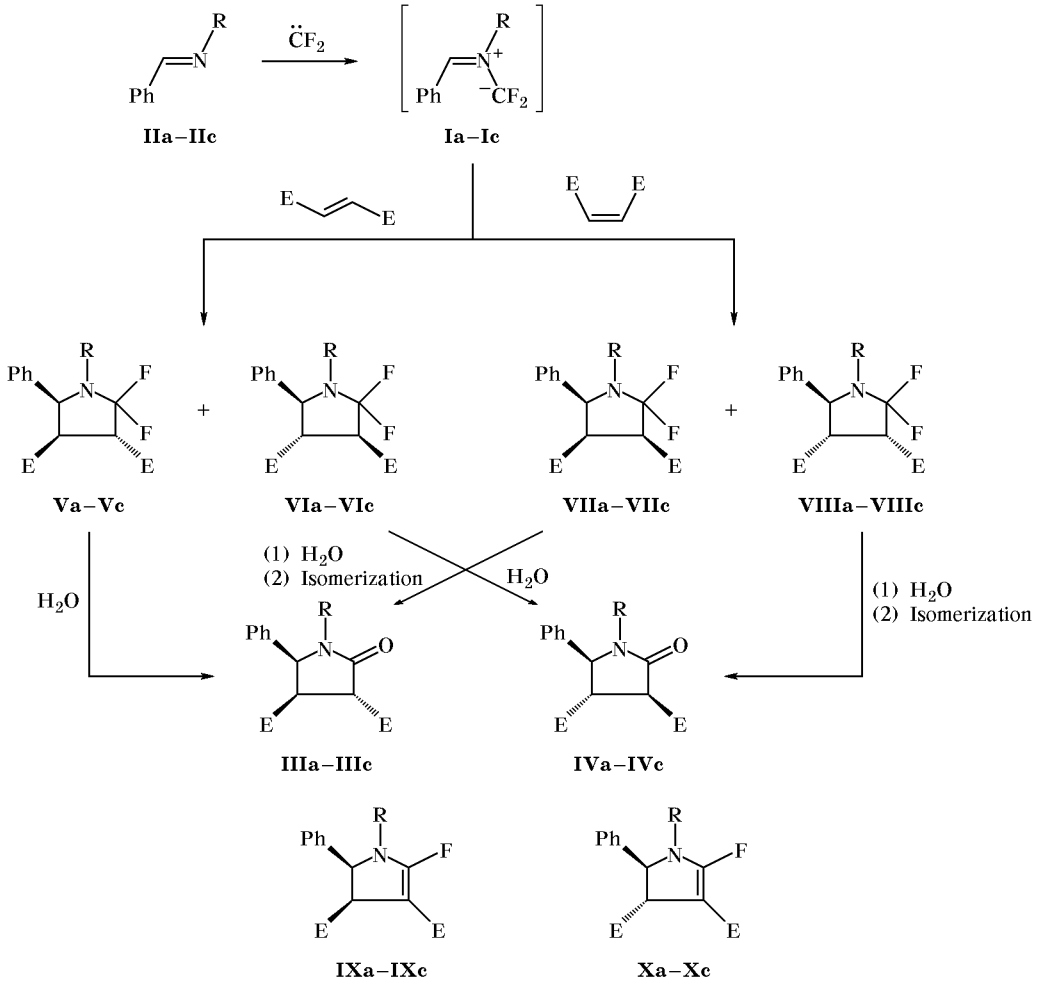
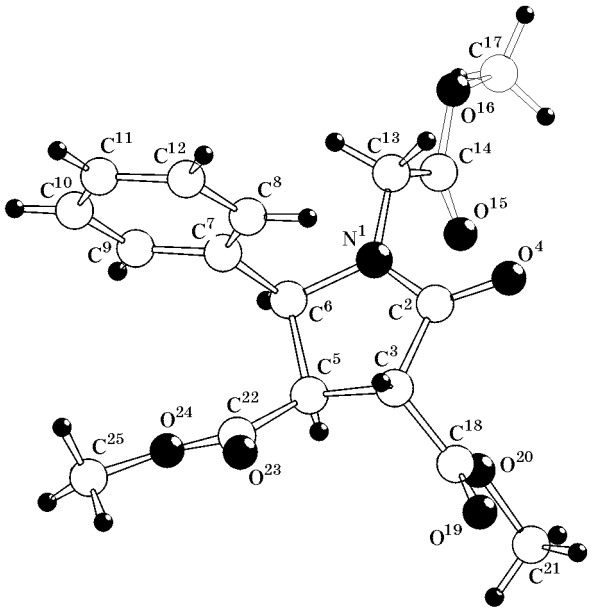
Scheme 1.



R = CH_2Ph (**a**), CH_2CO_2Me (**b**), CH_2SiMe_3 (**c**); E = CO_2Me.

conversion of Schiff bases **IIa**–**IIc** (method *a*) was complete, and by chromatographic treatment of the reaction mixture we isolated stereoisomeric pyrrolidinones **IIIa**–**IIIc** and **IVa**–**IVc** in an overall yield of 28–60% (Scheme 1). By special experiment we showed that dimethyl fumarate does not react with difluorocarbene in the absence of Schiff base under conditions of method *a*.

The structure of compounds **IIIa**–**IIIc** and **IVa**–**IVc** was established on the basis of their IR, ^1H and ^{13}C NMR, and mass spectra. The mass spectra of **IIIa** and **IVa** contain the molecular ion peaks and fragment ion peaks: $[M-31]^+ = [M-MeO]^+$, $[M-59]^+ = [M-CO_2Me]^+$, $[M-91]^+ = [M-CO_2Me-MeOH]^+$. In the IR spectra we observed bands corresponding to vibrations of the ester and amide carbonyl groups. All the products, except for pyrrolidines **IIIb**, **IIIc**, and **IVc**, show in the ^1H NMR spectra ($CDCl_3$) signals from methyl and aromatic protons, nonequivalent protons of the methylene group (J = 14–17 Hz), and three protons of the pyrrolidine ring. The latter appear as two doublets of doublets with coupling constants of 9.0–10.3 and 7.1–9.3 Hz. In the ^1H NMR spectra of **IIIb**, **IIIc**, and **IVc**, signals from heterocyclic protons form an *ABX* system. However, in deuterated benzene these signals are converted into two doublets of doublets with coupling constants of 9.0–10.3 and 7.1–9.0 Hz. The *cis* arrangement of the phenyl and methoxycarbonyl groups in major stereoisomers **IIIa**–**IIIc** and *trans* arrangement of the same groups in isomers **IVa**–**IVc** follow from the chemical shifts of the methoxy protons, δ 3.1–3.3 and 3.7–3.8 ppm, respectively. According to published data [5, 18–21], protons of methoxycarbonyl group in the *cis* position with respect to phenyl should appear in the region 3.1–3.3 ppm, whereas *trans*-methoxycarbonyl group



Structure of the molecule of dimethyl (3*R*,4*R*,5*S*)-(±)-1-methoxycarbonylmethyl-2-oxo-5-phenylpyrrolidine-3,4-dicarboxylate (**IIIb**).

should give a signal at δ 3.6–3.8 ppm. This difference is explained by almost orthogonal orientation of the benzene ring on C^5 with respect to the pyrrolidine ring plane; as a result, protons of the *cis*-methoxycarbonyl group fall into the area shielded by the benzene ring. Simultaneously, the 3-H proton, which is located *cis* with respect to the phenyl group, should be deshielded by the latter, so that its signal should appear in a weaker field relative to the corresponding *trans*-proton signal. In fact, the 3-H signal in the spectra of **IIIa**–**IIIc** shows a downfield shift by 0.3–0.4 ppm relative to the signal of the same proton in compounds **IVa**–**IVc**. These data confirm *trans*-arrangement of the methoxycarbonyl groups in pyrrolidinones **IIIa**–**IIIc** and **IVa**–**IVc**. Our assignments made for structures **III** and **IV** are also supported by the results of ^1H–^1H NOESY experiment performed for the major product of the reaction of Schiff base **IIc** with difluorocarbene in the presence of dimethyl fumarate. According to the ^1H–^1H NOESY data for compound **IIIc**, the 4-H proton is strongly coupled with 5-H but its interaction with aromatic protons and 3-H is very weak. The 3-H proton in turn shows a strong coupling with the aromatic protons. This means that the major product (**IIIc**) has (3*R**,4*R**,5*S**) configuration. The structure of compound **IIIb** was proved by X-ray analysis (Fig. 1, Tables 1–3).

Scheme 1 shows a series of transformations leading to pyrrolidinones **III** and **IV**. Difluorocarbene reacts with Schiff bases **IIa**–**IIc** to give intermediate ylide **Ia**–**Ic**. 1,3-Dipolar cycloaddition of difluoro(iminio)-methanides **Ia**–**Ic** to dimethyl fumarate or dimethyl maleate yields, respectively, pyrrolidines **V** and **VI** or **VII** and **VIII**. These compounds are very readily hydrolyzed on treatment of the reaction mixtures, and we failed to isolate them. Nevertheless, they were detected by gas chromatography–mass spectrometry. GC–MS analysis of the reaction mixtures obtained from *N*-benzylidenebenzylamine (**IIa**) and difluorocarbene in the presence of dimethyl maleate and dimethyl fumarate was performed using an HP-1 capillary column (25 m). The chromatograms of both reaction mixtures contained 6 peaks whose MS fragmentation patterns were identical in pairs. Analysis of the mass spectra allowed us to assign chromatographic peaks in the order of increasing retention indices: isomeric 2,2-difluoropyrrolidines **Va**, **VIa** and **VIIa**, **VIIIa**, isomeric 2-fluorodihydropyrroles **IXa** and **Xa**, and isomeric pyrrolidinones **IIIa** and **IVa**. Compounds **Va**–**VIIIa** turned out to be unstable under chromatographic conditions. We failed to detect them when 5% of SE-30 on Chromaton N-AW-DMCS was used as stationary phase. Presumably, these products readily lose HF molecule to form dihydropyrroles **IXa** and **Xa**, and just the latter are detected. The mass spectra of **Va**–**VIIIa** contain no molecular ion peaks, and the most characteristic are the fragment ion peaks $[M-OMe]^+$, $[M-CO_2Me]^+$, and $[M-PhCH_2]^+$. By contrast, compounds **IXa**, **Xa** and **IXb**, **Xb** show in the spectra (apart from the above peaks) the molecular ion peaks $[M]^+$ with *m*/*z* 369 and 351, respectively.

Isomeric pyrrolidines **Va**–**Vc** and **VIa**–**VIc** formed by addition of ylides **Ia**–**Ic** to dimethyl fumarate undergo hydrolysis to pyrrolidinones **IIIa**–**IIIc** and **IVa**–**IVc** during isolation by column chromatography. In the reaction with dimethyl maleate, initially formed pyrrolidinones **VIIa**–**VIIc** and **VIIIa**–**VIIIc** with *cis* orientation of the ester groups readily undergo isomerization into the same *trans* isomers **IIIa**–**IIIc** and **IVa**–**IVc** on treatment of the reaction mixture.

Reactions of Schiff bases **IIa** and **IId**–**IIj** with difluorocarbene in the presence of N-substituted maleimides lead to formation of mixtures of stereoisomeric products, derivatives of pyrrolo[3,4-*c*]pyrroles **XI** and **XII** (Scheme 2). In these reactions difluorocarbene was also generated by reduction of dibromodifluoromethane with activated lead, which was obtained by treatment of lead acetate with sodium tetrahydridoborate [17]. This procedure allowed us to shorten the reaction time and often to raise the yield of the final products. The steric structure of the products was determined by comparing the 6-H–6a-H coupling

Table 1. Principal bond lengths (*d*, Å) in the molecule of dimethyl (3*R*,4*R*,5*S*)-(±)-1-methoxycarbonylmethyl-2-oxo-5-phenylpyrrolidine-3,4-dicarboxylate (**IIIb**)

Bond	*d*	Bond	*d*	Bond	*d*
O^4-C^2	1.221 (4)	$O^{24}-C^{25}$	1.441 (7)	C^6-C^7	1.518 (3)
$O^{15}-C^{14}$	1.191 (5)	N^1-C^2	1.349 (2)	C^7-C^9	1.384 (4)
$O^{16}-C^{14}$	1.332 (2)	N^1-C^{13}	1.444 (3)	C^7-C^8	1.392 (5)
$O^{16}-C^{17}$	1.435 (4)	N^1-C^6	1.458 (6)	C^8-C^{12}	1.389 (3)
$O^{19}-C^{18}$	1.197 (2)	C^2-C^3	1.514 (4)	C^9-C^{10}	1.390 (3)
$O^{20}-C^{18}$	1.325 (3)	C^3-C^{18}	1.506 (3)	$C^{10}-C^{11}$	1.369 (6)
$O^{20}-C^{21}$	1.442 (4)	C^3-C^5	1.529 (3)	$C^{11}-C^{12}$	1.372 (5)
$O^{23}-C^{22}$	1.201 (2)	C^5-C^{22}	1.502 (7)	$C^{13}-C^{14}$	1.502 (2)
$O^{24}-C^{22}$	1.331 (2)	C^5-C^6	1.571 (2)		

Table 2. Principal bond angles (ω, deg) in the molecule of dimethyl (3*R*,4*R*,5*S*)-(±)-1-methoxycarbonylmethyl-2-oxo-5-phenylpyrrolidine-3,4-dicarboxylate (**IIIb**)

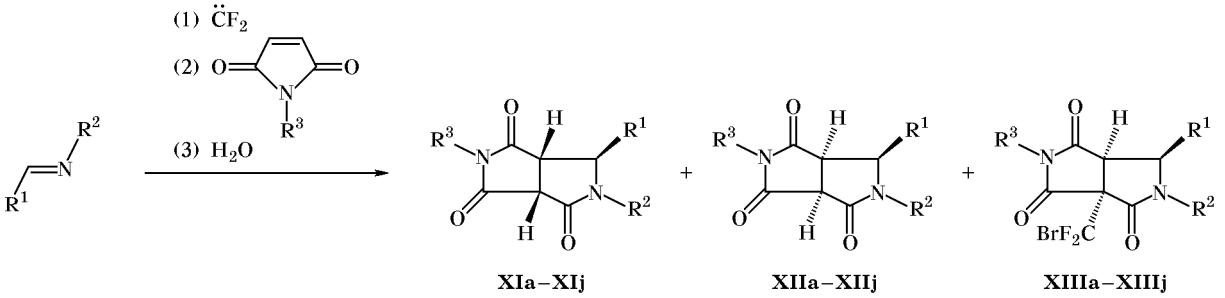
Angle	ω	Angle	ω	Angle	ω
$C^{14}O^{16}C^{17}$	117.96 (19)	$C^{22}C^5C^3$	112.83 (12)	$C^{10}C^{11}C^{12}$	119.38 (28)
$C^{18}O^{20}C^{21}$	116.22 (15)	$C^{22}C^5C^6$	113.24 (12)	$C^{11}C^{12}C^8$	120.66 (20)
$C^{22}O^{24}C^{25}$	116.56 (13)	$C^3C^5C^6$	104.77 (12)	$N^1C^{13}C^{14}$	113.55 (13)
$C^2N^1C^{13}$	121.37 (13)	$N^1C^6C^7$	112.41 (12)	$O^{15}C^{14}O^{16}$	124.74 (17)
$C^2N^1C^6$	115.30 (12)	$N^1C^6C^5$	101.55 (11)	$O^{15}C^{14}C^{13}$	126.93 (16)
$C^{13}N^1C^6$	122.64 (12)	$C^7C^6C^5$	114.05 (12)	$O^{16}C^{14}C^{13}$	108.31 (14)
$O^4C^2N^1$	125.47 (15)	$C^9C^7C^8$	118.56 (17)	$O^{19}C^{18}O^{20}$	124.79 (16)
$O^4C^2C^3$	126.05 (14)	$C^9C^7C^6$	120.21 (15)	$O^{19}C^{18}C^3$	124.87 (15)
$N^1C^2C^3$	108.45 (13)	$C^8C^7C^6$	121.17 (15)	$O^{20}C^{18}C^3$	110.34 (14)
$C^{18}C^3C^2$	111.80 (12)	$C^{12}C^8C^7$	120.27 (18)	$O^{23}C^{22}O^{24}$	123.80 (15)
$C^{18}C^3C^5$	113.99 (12)	$C^7C^9C^{10}$	120.36 (19)	$O^{23}C^{22}C^5$	125.44 (15)
$C^2C^3C^5$	104.49 (12)	$C^{11}C^{10}C^9$	120.75 (21)	$O^{24}C^{22}C^5$	110.75 (12)

constants with those given in [22, 23]. These were equal to 0–1.8 Hz for imides **XI** (*trans*) and 9.7–10.2 Hz for imides **XII** (*cis*). According to the ^{1}H NMR data, the reaction mixtures also contained a small amount of compounds **XIII** which can formally be regarded as bromodifluoromethylation products of *cis*-adducts **XII**. In some cases (runs nos. 9 and 11; Table 3), compounds **XIII** were isolated and identified by the ^{1}H and ^{13}C NMR spectra. These products are formed neither directly from compounds **XI** and **XII** nor by cycloaddition of Schiff bases to *N*-bromodifluoromethylmaleimide (both maleimides and pyrrolo[3,4-*c*]pyrroles **XI** and **XII** are inert under the given conditions). Presumably, by-products **XIII** are formed as a result of reaction of dibromodifluoromethane with intermediate bicyclic fluorodihydropyrroles which are more reactive than monocyclic fluorodihydropyrroles **IX** and **X** due to angular strain.

The data in Table 3 show that the stereoselectivity of cycloaddition strongly depends on the substituents R^1 and R^2 in the initial Schiff base. Theoretically, the cycloaddition of Schiff bases **IIa**–**IIj** can involve either of the four possible transition states: *Z-endo*, *Z-exo*, *E-endo*, and *E-exo* (Scheme 3). The first two of these correspond to the *exo* and *endo* approach of N-substituted maleimide to *Z*-ylide formed under conditions of kinetic control by addition of difluorocarbene to the most termodynamically stable *E* isomer of Schiff base. The two other transition states can appear as a result of isomerization of *E*-ylide into *Z*-ylide. Such isomerization was observed, e.g., for azomethine ylides generated from substituted aziridinecarboxylates [24].

The ratio (**XII** + **XIII**) : **XI** increases as the size of the R^2 substituent grows (runs nos. 6 and 8–12; Table 3) and as the size of the R^1 substituent decreases (runs nos. 12 and 14). In other words, products

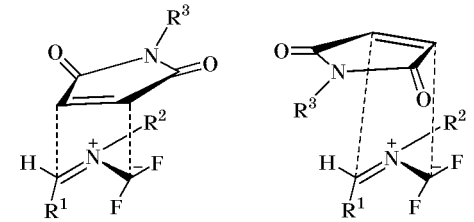
Scheme 2.



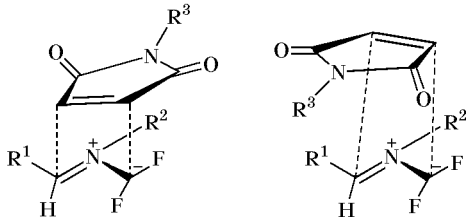
XI–**XIII**, $R^1 = R^3 = Ph$, $R^2 = PhCH_2$ (**a**); $R^1 = Ph$, $R^2 = Me$, $R^3 = Et$ (**b**); $R^1 = R^3 = Ph$, $R^2 = Me$ (**c**); $R^1 = Ph$, $R^2 = R^3 = Et$ (**d**); $R^1 = Ph$, $R^2 = i$-Pr, $R^3 = Et$ (**e**); $R^1 = Ph$, R^2 = cyclohexyl, $R^3 = Et$ (**f**); $R^1 = Ph$, $R^2 = t$-Bu, $R^3 = Et$ (**g**); $R^1 = R^2 = Ph$, R^3 =Et (**h**); $R^1 = R^2 = R^3 = Ph$ (**i**); $R^1 = PhC{\equiv}C$, $R^2 = Ph$, $R^3 = Et$ (**j**).

in which the phenyl substituent on C^6 is located *cis* with respect to the imide ring are formed in higher yield. These data are consistent with the assumption that no isomerization of the kinetically controlled *Z*-ylide occurs; therefore, the cycloaddition involves only *Z-endo* and *Z-exo* transition states. In these cases the above variation of the size of the R^1 and R^2 substituents should favor formation of *Z-exo* transition state and hence increase the yield of compounds **XII** and **XIII**.

Scheme 3.



Z-endo *Z-exo*



E-endo *E-exo*

Thus the reaction of difluorocarbene with *N*-alkyl and *N*-aryl Schiff bases yields *Z*-difluoro(iminio)-methanides as primary intermediates which are readily trapped by 2-butenedioic acid esters and imides to give difluoropyrrolidine derivatives. The latter are very reactive compounds which readily undergo hydrolysis to substituted pyrrolidinones, presumably via intermediate formation of fluorodihydropyrroles.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from solutions, layer thickness 400 μm. The NMR spectra were obtained on a Bruker DPX-300 instrument at 300 MHz for ^1H and 75 MHz for ^{13}C. The elemental compositions were determined on an HP-185B CHN analyzer. The progress of reactions was monitored by TLC on Silufol-254 plates and by GLC on an LKhM-80 chromatograph (glass columns, 1.8 and 2.5 m in length; stationary phase 5% of SE-30 on Chromaton-N-Super). GC–MS analysis was performed on an HP-59970C system using HP-5 capillary column, 25 m × 0.32 mm × 0.52 μm (5% of cross-linked phenylmethylsilicone); electron impact, 70 eV. The products were isolated by column chromatography on silica gel LS 5/40 μm (Chemapol).

N-Benzylideneglycine methyl ester (**IIb**) [25], *N*-benzylidene(trimethylsilylmethyl)amine (**IIc**) [26], *N*-benzylidenemethylamine (**IId**), *N*-benzylideneethylamine (**IIe**), *N*-benzylideneisopropylamine (**IIf**), *N*-benzylidenecyclohexylamine (**IIg**), and *N*-benzylidene-*tert*-butylamine (**IIh**) [27] were synthesized by known methods. *N*-Benzylidene(phenylethynyl)amine (**IIj**) was prepared by condensation of 3-phenyl-2-propynal with aniline in ethanol.

Preparation of activated lead. A solution of 1.66 g (0.04 mol) of sodium tetrahydridoborate in 5 ml of water was added dropwise with stirring to a solution of 6.5 g (0.02 mol) of lead acetate in 20 ml of 2 M acetic acid, while cooling with ice water. The mixture was diluted with 20 ml of 2 M acetic acid, and an additional portion of sodium tetrahydrido-

Table 3. Reactions of difluorocarbene with Schiff bases $R^1CH{=}NR^2$ (**IIa**–**IIj**) in the presence of dipolarophiles

Run no.	Schiff base no.	R^1	R^2	Dipolarophile	Method	Yield of **IV**, **XI**, %	Yield of **III**, **XII**, %	Ratio **XI** : **XII** : **XIII**[a]
1	**IIa**	Ph	CH_2Ph	Dimethyl fumarate	*a*	13	25	
2	**IIa**	Ph	CH_2Ph	Dimethyl maleate	*a*	54	6	
3	**IIa**	Ph	CH_2Ph	*N*-Phenylmaleimide	*a*	27	9	1 : 0.9 : 0
4	**IIb**	Ph	CH_2CO_2Me	Dimethyl fumarate	*a*	21	29	
					b	20	26	
5	**IIc**	Ph	CH_2SiMe_3	Dimethyl fumarate	*a*	9	19	
6	**IId**	Ph	Me	*N*-Ethylmaleimide	*b*	32	32	1 : 0.3 : 0.1
7	**IId**	Ph	Me	*N*-Phenylmaleimide	*b*	18		1 : 0.2 : 0.7
8	**IIe**	Ph	Et	*N*-Ethylmaleimide	*b*	18	26	1 : 0.3 : 0.1
9	**IIf**	Ph	*i*-Pr	*N*-Ethylmaleimide	*b*	30	7[b]	1 : 0.6 : 0.3
10	**IIg**	Ph	Cyclohexyl	*N*-Ethylmaleimide	*b*	22	17	1 : 0.6 : 0.3
11	**IIh**	Ph	*t*-Bu	*N*-Ethylmaleimide	*b*	15	0[c]	1 : 0.3 : 0.4
12	**IIi**	Ph	Ph	*N*-Ethylmaleimide	*b*	48	21	1 : 0.3 : 0.3
13	**IIi**	Ph	Ph	*N*-Phenylmaleimide	*b*	50	15	1 : 0.6 : 0.2
14	**IIj**	PhC≡C	Ph	*N*-Ethylmaleimide	*b*	33	47	1 : 0.6 : 0.6

[a] The isomer ratio was determined by ^{1}H NMR spectroscopy from the 6-H signal intensities.
[b] Compound **XIIIf** was isolated in 11% yield.
[c] Compound **XIIIh** was isolated in 9% yield.

borate, 1.66 g (0.04 mol), in 5 ml of water was added dropwise while stirring and cooling. The black precipitate was washed in succession with 1 M acetic acid (3 × 30 ml), water (3 × 20 ml), ethanol (3 × 5 ml), and methylene chloride (3 × 5 ml). Each time, the precipitate was separated by decanting. It was then dried under reduced pressure (10 mm) at 60–70°C and was immediately used in syntheses.

Reactions of Schiff bases with difluorocarbene in the presence of fumaric and maleic acid derivatives. *a* (*general procedure*). A 50-ml flask was filled with argon and charged in succession with 1.2 g (5.8 mmol) of freshly prepared lead turnings, 1.9 g (6.0 mmol) of tetrabutylammonium bromide, 7 ml of dry methylene chloride, 0.55 g (2.8 mmol) of Schiff base **IIa**, 1 g (6.9 mmol) of dimethyl fumarate, and 1.92 g (9.2 mmol) of dibromodifluoromethane. The flask was tightly capped, and the mixture was stirred at 45°C using a magnetic stirrer until the lead disappeared completely. The mixture was cooled, 2 g of silica gel (LS 40/100 μm, Chemapol) was added, the solvent was distilled off under reduced pressure to dryness, and the resulting powder was transferred to a chromatographic column charged with silica gel (LS 5/40 μm, Chemapol). The products were eluted with a hexane–ethyl acetate mixture. Recrystallization from hexane–Et_2O gave 0.26 g (25%) of dimethyl (3*R*,4*R*,5*S*)-(±)-1-benzyl-2-oxo-5-phenylpyrrolidine-3,4-dicarboxylate (**IIIa**) and 0.134 g (13%) of dimethyl (3*R*,4*R*,5*R*)-(±)-1-benzyl-2-oxo-5-phenylpyrrolidine-3,4-dicarboxylate (**IVa**).

Compound **IIIa**. mp 137–139°C (from Et_2O). IR spectrum (CCl_4), ν, cm^{-1}: 3090 w, 3070 w, 3030, 3000 w, 2955, 2930, 2850 w, 1740 s, 1705 s, 1495 w, 1455, 1440, 1420, 1365, 1320, 1240, 1220, 1170, 1020 w. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.24 s (3H, 4-CO_2CH_3), 3.48 d (1H, CH_2, *J* = 14.5 Hz), 3.84 s (3H, 3-CO_2CH_3), 4.01 d.d (1H, 4-H, *J* = 9.0, 10.5 Hz), 4.24 d (1H, 3-H, *J* = 10.5 Hz), 4.72 d (1H, 5-H, *J* = 9.0 Hz), 5.12 d.d (1H, CH_2, *J* = 14.5 Hz), 7.0–7.4 m (10H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 44.8 (CH_2); 46.5, 48.5 (C^3, C^4); 51.5, 52.7 (CH_3); 60.2 (C^5); 127.0, 127.5, 128.0, 128.4, 128.5, 128.6, 134.7, 134.9 (C_{arom}); 167.8, 168.8, 168.9 (CO). Found, %: C 68.57; H 5.64; N 3.63. $C_{21}H_{21}NO_5$. Calculated, %: C 68.65; H 5.76; N 3.81.

Compound **IVa**. mp 92–94°C (from hexane–Et_2O). For spectral parameters, see [11].

b (*general procedure*). A 50-ml flask was charged with 2.45 g (11.8 mmol) of activated lead under argon, and 14 ml of dry methylene chloride, 3.9 g (12.2 mmol) of tetrabutylammonium bromide, 0.72 g (5.4 mmol) of Schiff base **IIe**, and 1.75 g (14 mmol) of *N*-ethylmaleimide were added in succession. The mixture was cooled to 10–15°C with cold water,

3.36 g (16 mmol) of dibromodifluoromethane was added, the flask was tightly capped, and the mixture was stirred at 45°C with a magnetic stirrer until the lead disappeared completely. The mixture was then treated as described above in *a*. Recrystallization from Et_2O–CH_2Cl_2 gave 0.27 g (18%) of (3a*R*,6*S*,6a*S*)-(±)-2,5-diethyl-6-phenylperhydropyrrolo[3,4-*c*]pyrrole-1,3,4-trione (**XId**) and 0.4 g (26%) of (3a*R*,6*R*,6a*S*)-(±)-2,5-diethyl-6-phenylperhydropyrrolo[3,4-*c*]pyrrole-1,3,4-trione (**XIId**).

Compound **XId**. mp 107–109°C (from EtOH–Et_2O–hexane). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3040, 2985, 2940 w, 2880 w, 1780, 1720 s, 1460, 1430, 1400, 1380, 1350, 1320 w, 1270, 1130, 1085 w, 1070 w, 1005 w, 960 w. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.00 t (3H, CH_3, *J* = 7.1 Hz), 1.18 t (3H, CH_3, *J* = 7.5 Hz), 2.74 m (1H, CH_2), 3.30 d.d (1H, 6a-H, *J* = 1.8, 8.4 Hz), 3.60 q (2H, CH_2, *J* = 7.1 Hz), 3.72 m (1H, CH_2), 3.87 d (1H, 3a-H, *J* = 8.4 Hz), 4.95 d (1H, 6-H, *J* = 1.8 Hz), 7.2–7.4 m (5H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 11.9, 12.6 (CH_3); 34.1, 36.1 (CH_2); 47.2, 48.2 (C^{3a}, C^{6a}); 61.6 (C^6); 125.6, 128.6, 129.2, 138.9 (C_{arom}); 165.2, 170.3, 175.9 (CO). Found, %: C 66.90; H 6.50; N 9.71. $C_{16}H_{18}N_2O_3$. Calculated, %: C 67.12; H 6.34; N 9.78.

Compound **XIId**. mp 162–164°C (from Et_2O–CH_2Cl_2). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3040, 2985 w, 2945 w, 2885 w, 1780 w, 1720 s, 1460, 1440, 1400, 1395, 1380, 1350, 1320 w, 1280, 1130, 1080 w, 1050 w, 1005 w, 965 w. ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 0.88 t (3H, CH_3, *J* = 7.1 Hz), 1.01 t (3H, CH_3, *J* = 7.1 Hz), 2.59 m (1H, CH_2), 3.23 m (2H, CH_2), 3.67 m (1H, CH_2), 3.83 d (1H, 3a-H, *J* = 9.3 Hz), 3.97 d.d (1H, 6a-H, *J* = 9.3, 10.6 Hz), 5.29 d (1H, 6-H, *J* = 10.6 Hz), 7.1–7.4 m (5H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 11.5, 12.2 (CH_3); 33.8, 36.1 (CH_2); 42.9, 49.0 (C^{3a}, C^{6a}); 61.1 (C^6); 128.6, 128.8, 134.7 (C_{arom}); 165.6, 170.5, 173.2 (CO). Found, %: C 67.19; H 6.32; N 9.88. $C_{16}H_{18}N_2O_3$. Calculated, %: C 67.12; H 6.34; N 9.78. The yields of compounds **XId** and **XIId** are given in Table 3.

Dimethyl (3*R*,4*R*,5*S*)-(±)-1-methoxycarbonylmethyl-2-oxo-5-phenylpyrrolidine-3,4-dicarboxylate (IIIb) [11]. Found, %: C 58.20; H 5.36; N 3.71. $C_{17}H_{19}NO_7$. Calculated, %: C 58.45; H 5.48; N 4.01. X-Ray diffraction data: $C_{17}H_{19}NO_7$. *M* 349.33. Unit cell parameters: *a* = 19.529(2), *b* = 7.7305(10), *c* = 11.3818(12) Å; β = 91.70(1)°; *V* = 1717.54(40) $Å^3$; d_{calc} = 1.351 g/cm^3; monoclinic; space group $P2_1/c$; *Z* = 4. Enraf–Nonius CAD4 diffractometer, CuK_α irradiation, λ = 1.54178 Å, graphite monochromator, θ_{max} = 42.61°, temperature –100°C, crystal habit 0.5 × 0.4 × 0.3 mm.

Dimethyl (3*R*,4*R*,5*R*)-(±)-1-methoxycarbonylmethyl-2-oxo-5-phenylpyrrolidine-3,4-dicarboxylate (IVb). For spectral parameters, see [11].

Dimethyl (3*R*,4*R*,5*S*)-(±)-2-oxo-5-phenyl-1-trimethylsilylmethylpyrrolidine-3,4-dicarboxylate (IIIc). mp 123–125°C (Et_2O). IR spectrum (CCl_4), ν, cm^{-1}: 3070 w, 3030 w, 3000 w, 2950, 2900, 2850 w, 1755 s, 1710 s, 1495 w, 1435, 1360, 1320, 1255, 1220, 1170, 1030, 1020. ^{1}H NMR spectrum (C_6D_6), δ, ppm: –0.4 s (9H, CH_3Si), 1.87 d (1H, CH_2, *J* = 15.2 Hz), 2.87 s (3H, 4-CO_2CH_3), 3.07 d (1H, CH_2, *J* = 15.2 Hz), 3.39 s (3H, 3-CO_2CH_3), 4.33 d.d (1H, 4-H, *J* = 9.0, 10.3 Hz), 4.48 d (1H, 3-H, *J* = 10.3 Hz), 4.63 d (1H, 5-H, *J* = 9.0 Hz), 6.8–7.2 m (5H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: –1.9 (CH_3Si); 33.2 (CH_2); 46.7, 48.1, 51.6, 52.7 (C^3, C^4, $2CH_3O$); 63.5 (C^5); 126.9, 128.4, 128.6, 134.9 (C_{arom}); 167.1, 169.0, 169.3 (CO). Found, %: C 59.38; H 6.78; N 3.71. $C_{18}H_{25}NO_5Si$. Calculated, %: C 59.48; H 6.93; N 3.71.

Dimethyl (3*R*,4*R*,5*R*)-(±)-2-oxo-5-phenyl-1-trimethylsilylmethylpyrrolidine-3,4-dicarboxylate (IVc). Oily substance. IR spectrum (CCl_4), ν, cm^{-1}: 3065 w, 3030, 3000 w, 2955, 2930 w, 2900 w, 2855 w, 1740 s, 1705 s, 1695, 1615 w, 1495 w, 1455, 1435, 1255 s, 1240 s, 1175, 1035 w, 1020 w. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.02 s (9H, CH_3Si), 2.07 d (1H, CH_2, *J* = 15.3 Hz), 3.05 d (1H, CH_2, *J* = 15.3 Hz), 3.63 d.d (1H, 4-H, *J* = 6.9, 8.0 Hz), 3.71 s (3H, CH_3O), 3.85 s (3H, 3-CO_2CH_3), 3.85 d (1H, 3-H, *J* = 8.0 Hz), 6.81 d (1H, 5-H, *J* = 6.9 Hz), 7.2–7.5 m (5H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: –1.6 (CH_3Si); 33.1 (CH_2); 49.1, 50.6, 52.4, 52.8 (C^3, C^4, CH_3O); 60.5 (C^5); 127.3, 128.2, 128.5, 128.8, 129.4, 138.3 (C_{arom}); 166.3, 169.1, 171.4 (CO).

(3a*R*,6*S*,6a*S*)-(±)-5-Benzyl-2,6-diphenylperhydropyrrolo[3,4-*c*]pyrrole-1,3,4-trione (XIa). Oily substance. IR spectrum ($CHCl_3$), ν, cm^{-1}: 3065 br.w, 3010 w, 2930 w, 1785 w, 1725 s, 1695, 1600 w, 1505 w, 1425 w, 1380, 1085 w, 1035 w, 940 w. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.48 d.d (1H, 6a-H, *J* = 1.7, 8.3 Hz), 3.59 d (1H, CH_2, *J* = 14.7 Hz), 4.11 d (1H, 3a-H, *J* = 8.3 Hz), 4.80 d (1H, 6-H, *J* = 1.7 Hz), 5.17 d (1H, CH_2, *J* = 14.7 Hz), 7.0–7.6 m (15H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 44.8 (CH_2); 47.0, 48.3 (C^{3a}, C^{6a}); 61.7 (C^6); 125.9, 127.6, 127.8, 128.6, 128.8, 128.9, 129.3, 131.0, 134.8, 138.2 (C_{arom}); 165.5, 169.5, 174.9 (CO).

(3a*R*,6*R*,6a*S*)-(±)-5-Benzyl-2,6-diphenylperhydropyrrolo[3,4-*c*]pyrrole-1,3,4-trione (XIIa). mp 278–280°C (from Et_2O–CH_2Cl_2). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3070 br.w, 2935 w, 1785 w, 1725 s, 1700, 1600 w, 1505, 1460 w, 1430, 1375, 1090 w, 1035 w. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.55 d (1H, CH_2, *J* = 14.5 Hz), 3.88 d.d (1H, 6a-H, *J* = 9.4, 10.2 Hz), 4.02 d (1H, 3a-H, *J* = 9.4 Hz), 4.89 d (1H, 6-H, *J* = 10.2 Hz), 5.24 d (1H, CH_2, *J* = 14.5 Hz), 6.8–7.5 m (15H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 41.1 (C^{6a}); 45.1 (CH_2); 49.0 (C^{3a}); 61.0 (C^6); 125.6, 127.9, 128.3, 128.6, 128.7, 129.0, 129.1, 130.9, 134.3, 134.5 (C_{arom}); 165.5, 169.4, 172.2 (CO). Found, %: C 75.85; H 5.16; N 7.18. $C_{25}H_{20}N_2O_3$. Calculated, %: C 75.74; H 5.08; N 7.07.

(3a*R*,6*S*,6a*S*)-(±)-2-Ethyl-5-methyl-6-phenylperhydropyrrolo[3,4-*c*]pyrrole-1,3,4-trione (XIb). mp 143–144°C (from Et_2O). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3040 w, 2985 w, 2940 w, 2885 w, 1780, 1720 s, 1460 w, 1390, 1380, 1350, 1250 w, 1135 w. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.18 t (3H, CH_3C, *J* = 7.3 Hz), 2.74 s (3H, CH_3N), 3.31 d.d (1H, 6a-H, *J* = 1.3, 8.4 Hz), 3.59 q (2H, CH_2, *J* = 7.3 Hz), 3.88 d (1H, 3a-H, *J* = 8.4 Hz), 4.83 d (1H, 6-H, *J* = 1.3 Hz), 7.2–7.5 m (5H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.6 (**C**H_3C); 28.5 (CH_3N); 34.1 (CH_2); 47.0, 47.8 (C^{3a}, C^{6a}); 64.1 (C^6); 125.5, 128.6, 129.2, 138.4 (C_{arom}); 165.6, 170.2, 175.8 (CO). Found, %: 66.23; H 5.97; N 10.13. $C_{15}H_{16}N_2O_3$. Calculated, %: C 66.16; H 5.92; N 10.29.

(3a*R*,6*R*,6a*S*)-(±)-2-Ethyl-5-methyl-6-phenylperhydropyrrolo[3,4-*c*]pyrrole-1,3,4-trione (XIIb). mp 162–163°C (from Et_2O). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3035 w, 2985 w, 2940 w, 2880 w, 1780, 1720 s, 1460 w, 1395, 1380, 1350, 1280 w, 1140 w, 1120 w, 1105 w, 1075 w. ^1H NMR spectrum (acetone-d_6), δ, ppm: 0.87 t (3H, CH_3, *J* = 7.1 Hz), 2.59 m (1H, CH_2), 2.64 s (3H, CH_3), 3.23 m (2H, CH_2), 3.82 d (1H, 3a-H, *J* = 9.3 Hz), 3.98 d.d (1H, 6a-H, *J* = 9.3, 10.6 Hz), 5.12 d (1H, 6-H, *J* = 10.6 Hz), 7.1–7.4 m (5H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.2 (**C**H_3C); 28.9 (CH_3N); 33.8 (CH_2); 43.0, 48.8 (C^{3a}, C^{6a}); 63.9 (C^6); 126.7, 128.7, 128.9, 134.6 (C_{arom}); 166.1, 170.4, 173.1 (CO). Found, %: C 66.11; H 5.89; N 10.49. $C_{15}H_{16}N_2O_3$. Calculated, %: C 66.16; H 5.92; N 10.29.

(3a*R*,6*S*,6a*S*)-(±)-5-Methyl-2,6-diphenylperhydropyrrolo[3,4-*c*]pyrrole-1,3,4-trione (XIc). mp 163–167°C (from Et_2O). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3050 w, 2980 w, 2930 w, 1785 w, 1725 s, 1600 w, 1505 w, 1460 w, 1380, 1105 w, 1085 w, 1050 w, 1045 w. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.79 s (3H, CH_3), 3.49 d (1H, 6a-H, *J* = 7.7 Hz), 4.04 d (1H, 3a-H, *J* = 7.7 Hz), 4.94 s (1H, 6-H), 7.2–7.5 m (5H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 28.7 (CH_3); 47.2, 47.9 (C^{3a}, C^{6a}); 64.3 (C^6); 125.6, 125.9, 128.5, 128.7, 128.8, 129.3, 131.0, 138.3 (C_{arom}); 165.4, 169.4, 175.1 (CO). Found, %: C 71.40; H 4.97; N 8.78. $C_{19}H_{16}N_2O_3$. Calculated, %: C 71.24; H 5.03; N 8.74.

(3a*R*,6*S*,6a*S*)-(±)-2-Ethyl-5-isopropyl-6-phenylperhydropyrrolo[3,4-*c*]pyrrole-1,3,4-trione (XIe). mp 136–138°C (from Et_2O). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3040 br.w, 2985 w, 2940 w, 2880 w, 1780, 1710 s, 1600 w, 1460 w, 1445 w, 1420, 1400, 1380, 1350, 1280 w, 1255 w, 1135. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.83 d (3H, CH_3, *J* = 6.6 Hz), 1.15 d (3H, CH_3, *J* = 6.6 Hz), 1.15 t (3H, CH_3, *J* = 7.1 Hz), 3.22 d (1H, 6a-H, *J* = 7.9 Hz), 3.57 q (2H, CH_2, *J* = 7.1 Hz), 3.91 d (1H, 3a-H, *J* = 7.9 Hz), 4.12 quint (1H, CH, *J* = 6.6 Hz), 4.98 s (1H, 6-H), 7.2–7.5 m (5H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 12.5, 19.5, 20.3 (CH_3); 33.9 (CH_2); 45.6, 48.1, 48.5 (C^{3a}, C^{6a}, CHN); 60.5 (C^6); 125.6, 128.4, 128.9, 141.0 (C_{arom}); 165.3, 170.4, 175.9 (CO). Found, %: C 67.91; H 6.77; N 9.37. $C_{17}H_{20}N_2O_3$. Calculated, %: C 67.98; H 6.71; N 9.33.

(3a*R*,6*R*,6a*S*)-(±)-2-Ethyl-5-isopropyl-6-phenylperhydropyrrolo[3,4-*c*]pyrrole-1,3,4-trione (XIIe). mp 154–155°C (from Et_2O–CH_2Cl_2). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3040 br, 2985, 2945 w, 2880 w, 1780, 1715 s, 1460, 1445, 1425, 1395, 1380, 1345, 1280, 1130, 1080 w, 1040 w, 940 w. ^1H NMR spectrum (acetone-d_6), δ, ppm: 0.90 t (3H, CH_3, *J* = 7.1 Hz), 0.99 d (3H, CH_3, *J* = 7.1 Hz), 1.24 d (3H, CH_3, *J* = 6.6 Hz), 3.22 m (2H, CH_2), 3.74 d.q (1H, CH, *J* = 6.6, 7.1 Hz), 3.78 d (1H, 3a-H, *J* = 9.3 Hz), 3.95 d.d (1H, 6a-H, *J* = 9.3, 10.6 Hz), 5.27 d (1H, 6-H, *J* = 10.6 Hz), 7.0–7.4 m (5H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.1, 19.0, 20.1 (CH_3); 33.7 (CH_2); 43.4, 46.6, 49.4 (C^{3a}, C^{6a}, CHN); 61.3 (C^6); 125.1, 128.1, 128.4, 128.7, 136.7 (C_{arom}); 165.7, 170.7, 173.2 (CO). Found, %: C 67.73; H 6.99; N 9.21. $C_{17}H_{20}N_2O_3$. Calculated, %: C 67.98; H 6.71; N 9.33.

(3a*R*,6*S*,6a*R*)-(±)-3a-Bromodifluoromethyl-2-ethyl-5-isopropyl-6-phenylperhydropyrrolo[3,4-*c*]-pyrrole-1,3,4-trione (XIIIe). mp 111–113°C (from Et_2O–hexane). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3040 br, 2985, 2940 w, 2885 w, 1790, 1730 s, 1460, 1445, 1425, 1395, 1380, 1350, 1340, 1280, 1240, 1160, 1120, 1080, 1060, 960 w. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.03 t (3H, CH_3, *J* = 7.0 Hz), 1.11 d

(3H, CH_3, J = 7.0 Hz), 1.34 d (3H, CH_3, J = 7.0 Hz), 3.39 m (2H, CH_2), 3.80 quint (1H, CH, J = 7.0 Hz), 3.90 d (1H, 6a-H, J = 10.5 Hz), 5.11 d (1H, 6-H, J = 10.5 Hz), 6.9–7.5 m (5H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.0, 19.0, 19.2 (CH_3); 34.6 (CH_2); 48.0, 48.1 (C^{6a}, CHN); 60.3 (C^6); 66.2 t (C^{3a}, $^2J_{C,F}$ = 20.7 Hz), 118.2 d.d (CF_2Br, $^1J_{C,F}$ = 312.9, 317.3 Hz); 124.7, 128.3, 128.8, 129.2, 135.3 (C_{arom}); 160.9, 165.1, 170.5 (CO). Found, %: C 50.66; H 4.50; N 6.63. $C_{18}H_{19}BrF_2N_2O_3$. Calculated, %: C 50.37; H 4.46; N 6.53.

(3a*R*,6*S*,6a*S*)-(±)-5-Cyclohexyl-2-ethyl-6-phenylperhydropyrrolo[3,4-*c*]pyrrole-1,3,4-trione (XIf). mp 179–180°C (from Et_2O). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3040 br.w, 2985 w, 2945, 2865 w, 1805, 1780 w, 1720 s, 1600 w, 1455 w, 1420 w, 1400, 1380, 1355, 1280 w, 1255, 1135. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.7–1.9 m (10H, cyclohexyl), 1.16 t (3H, CH_3, J = 7.1 Hz), 3.19 d.d (1H, 6a-H, J = 0.9, 7.9 Hz), 3.59 q (2H, CH_2, J = 7.1 Hz), 3.82 m (1H, CHN), 3.89 d (1H, 3a-H, J = 7.9 Hz), 5.02 d (1H, 6-H, J = 0.9 Hz), 7.2–7.5 m (5H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.6 (CH_3); 24.7, 25.2, 25.2, 30.0, 30.8, 34.0 (CH_2); 48.3, 48.5 (C^{3a}, C^{6a}); 53.6 (CHN); 60.6 (C^6); 125.4, 128.3, 129.0, 141.3 (C_{arom}); 165.4, 170.5, 175.9 (CO). Found, %: C 70.78; H 7.25; N 8.17. $C_{20}H_{24}N_2O_3$. Calculated, %: C 70.57; H 7.11; N 8.23.

(3a*R*,6*R*,6a*S*)-(±)-5-Cyclohexyl-2-ethyl-6-phenylperhydropyrrolo[3,4-*c*]pyrrole-1,3,4-trione (XIIf). mp 184–185°C (from Et_2O–CH_2Cl_2). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3050 br.w, 2945, 2865 w, 1800, 1780, 1715 s, 1605 w, 1455 w, 1420, 1400, 1380, 1350, 1280 w, 1250, 1135. ^1H NMR spectrum (acetone-d_6), δ, ppm: 0.9–1.9 m (10H, cyclohexyl), 0.88 t (3H, CH_3, J = 7.3 Hz), 3.20 m (2H, CH_2, J = 7.3 Hz), 3.45 m (1H, CHN), 3.78 d (1H, 3a-H, J = 9.3 Hz), 3.95 d.d (1H, 6a-H, J = 9.3, 10.6 Hz), 5.29 d (1H, 6-H, J = 10.6 Hz), 5.9–7.3 m (5H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.1 (CH_3); 24.7, 25.4, 25.4, 29.4, 30.5, 33.8 (CH_2); 43.6, 49.4 (C^{3a}, C^{6a}); 54.7 (CHN); 61.3 (C^6); 125.2, 128.1, 128.5, 128.8, 136.9 (C_{arom}); 165.8, 170.8, 173.3 (CO). Found, %: C 70.68; H 7.09; N 8.27. $C_{20}H_{24}N_2O_3$. Calculated, %: C 70.57; H 7.11; N 8.23.

(3a*R*,6*S*,6a*S*)-(±)-5-(*tert*-Butyl)-2-ethyl-6-phenylperhydropyrrolo[3,4-*c*]pyrrole-1,3,4-trione (XIg). mp 145.5–146.5°C (from Et_2O–CH_2Cl_2). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3040 br, 2985, 2945 w, 2880 w, 1780, 1715 s, 1600 w, 1455 w, 1400, 1380, 1350, 1290 w, 1255 w, 1130, 1070 w. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.16 t (3H, CH_3, J = 7.1 Hz), 1.29 s (9H, *t*-Bu), 3.06 d (1H, 6a-H, J = 7.7 Hz), 3.59 q (2H, CH_2, J = 7.1 Hz), 3.80 d (1H, 3a-H, J = 7.7 Hz), 5.20 s (1H, 6-H), 7.2–7.4 m (5H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.6 (**C**H_3CH_2); 27.4 (CH_3**C**); 33.9 (CH_2); 47.9, 49.1 (C^{3a}, C^{6a}); 55.9 (CH_3**C**); 61.9 (C^6); 125.1, 128.2, 129.1, 141.8 (C_{arom}); 165.8, 170.7, 176.0 (CO). Found, %: C 68.72; H 7.01; N 8.81. $C_{18}H_{22}N_2O_3$. Calculated, %: C 68.77; H 7.05; N 8.91.

(3a*R*,6*S*,6a*R*)-(±)-3a-Bromodifluoromethyl-5-*tert*-butyl-2-ethyl-6-phenylperhydropyrrolo[3,4-*c*]-pyrrole-1,3,4-trione (XIIIg). mp 189–190°C (from Et_2O–CH_2Cl_2). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3040 br.w, 2985 w, 2945 w, 2880 w, 1785 w, 1725 s, 1600 w, 1460 w, 1400, 1380, 1345, 1280 w, 1155, 1085 w, 1040 w. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.87 t (3H, CH_3, J = 7.1 Hz), 1.36 s (9H, *t*-Bu), 3.21 m (2H, CH_2), 3.89 d (1H, 6a-H, J = 10.4 Hz), 5.30 d (1H, 6-H, J = 10.4 Hz), 6.9–7.4 m (5H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 11.6 (**C**H_3CH_2); 27.2 (CH_3**C**); 34.3 (CH_2); 48.0, 57.4, 59.8 (CH_3**C**, C^6, C^{6a}); 66.2 d.d (C^{3a}, $^2J_{C,F}$ = 20.5, 21.0 Hz); 118.8 d.d (CF_2Br, $^1J_{C,F}$ = 312.9, 316.8 Hz); 124.4, 128.2, 128.4, 128.9, 128.9, 137.1 (C_{arom}); 161.0 d (J = 3.3 Hz); 165.4, 170.6 (CO). Found, %: C 51.61; H 4.87; N 6.24. $C_{19}H_{21}BrF_2N_2O_3$. Calculated, %: C 51.48; H 4.77; N 6.32.

(3a*R*,6*S*,6a*S*)-(±)-2-Ethyl-5,6-diphenylperhydropyrrolo[3,4-*c*]pyrrole-1,3,4-trione (XIIh). mp 188–190°C (Et_2O–CH_2Cl_2). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3045 w, 2990 w, 2940 w, 2880 w, 1780, 1720 s, 1600 w, 1500, 1460 w, 1400, 1380, 1350, 1285, 1145. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.21 t (3H, CH_3, J = 7.1 Hz), 3.39 d (1H, 6a-H, J = 8.2 Hz), 3.64 q (2H, CH_2, J = 7.1 Hz), 4.05 d (1H, 3a-H, J = 8.2 Hz), 5.60 s (1H, 6-H), 7.1–7.5 m (10H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.6 (CH_3); 34.3 (CH_2); 47.1, 48.8 (C^{3a}, C^{6a}); 63.4 (C^6); 121.8, 125.1, 125.6, 128.3, 128.6, 129.2, 136.8, 139.4 (C_{arom}); 164.8, 169.9, 175.6 (CO). Found, %: C 71.92; H 5.35; N 8.37. $C_{20}H_{18}N_2O_3$. Calculated, %: C 71.84; H 5.43; N 8.38.

(3a*R*,6*R*,6a*S*)-(±)-2-Ethyl-5,6-diphenylperhydropyrrolo[3,4-*c*]pyrrole-1,3,4-trione (XIIh). mp 193–195°C (from Et_2O–CH_2Cl_2). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3045, 2990 w, 2950 w, 2880 w, 1780, 1720 s, 1600 w, 1505, 1450 w, 1405, 1380, 1350, 1295, 1250, 1140. ^1H NMR spectrum (acetone-d_6), δ, ppm: 0.85 t (3H, CH_3, J = 7.1 Hz), 3.25 m (2H, CH_2), 4.06 d (1H, 3a-H, J = 9.3 Hz), 4.18 d.d (1H, 6a-H, J = 9.3, 10.6 Hz), 6.03 d (1H, 6-H, J = 10.6 Hz), 7.0–7.6 m (10H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm:

12.1 (CH_3); 33.9 (CH_2); 42.6, 49.7 (C^{3a}, C^{6a}); 63.1 (C^6); 122.4, 125.7, 126.6, 128.5, 128.5, 135.0, 136.5 (C_{arom}); 165.2, 170.4, 173.0 (CO). Found, %: C 71.53; H 5.42; N 8.16. $C_{20}H_{18}N_2O_3$. Calculated, %: C 71.84; H 5.43; N 8.38.

(3a*R*,6*S*,6a*S*)-(±)-2,5,6-Triphenylperhydropyrrolo[3,4-*c*]pyrrole-1,3,4-trione (XIi). mp 201–203°C (from Et_2O–$CHCl_3$). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3040 w, 2990 w, 2940 w, 2910 w, 2885 w, 1790 w, 1725 s, 1600 w, 1505, 1460 w, 1375, 1255, 1120 w, 1050. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.58 d (1H, 6a-H, *J* = 8.4 Hz), 4.21 d (1H, 3a-H, *J* = 8.4 Hz), 5.71 s (1H, 6-H), 7.1–7.9 m (10H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 47.3, 48.9 (C^{3a}, C^{6a}); 63.6 (C^6); 121.8, 125.2, 125.7, 125.9, 128.4, 128.6, 128.7, 128.9, 129.3, 131.0, 136.7, 139.1 (C_{arom}); 164.6, 169.0, 174.9 (CO). Found, %: C 75.44; H 4.75; N 7.28. $C_{24}H_{18}N_2O_3$. Calculated, %: C 75.38; H 4.74; N 7.33.

(3a*R*,6*R*,6a*S*)-(±)-2,5,6-Triphenylperhydropyrrolo[3,4-*c*]pyrrole-1,3,4-trione (XIIi). mp 263–265°C (from Et_2O–CH_2Cl_2). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3050 w, 1790 w, 1730 s, 1600 w, 1505, 1460 w, 1370, 1350, 1295, 1240, 1125 w, 1050 w. ^1H NMR spectrum ($CDCl_3$), δ_C, ppm: 4.28 d (1H, 3a-H, *J* = 9.3 Hz), 4.37 d.d (1H, 6a-H, *J* = 9.3, 10.2 Hz), 6.14 d (1H, 6-H, *J* = 10.2 Hz), 6.9–7.7 m (15H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 47.9, 51.4 (C^{3a}, C^{6a}); 63.5 (C^6); 124.4, 126.7, 127.5, 129.2, 129.4, 129.5, 129.6, 129.7, 132.7, 137.3, 138.0 (C_{arom}); 166.6, 171.6, 174.1 (CO). Found, %: C 75.36; H 4.84; N 7.26. $C_{24}H_{18}N_2O_3$. Calculated, %: C 75.38; H 4.74; N 7.33.

(3a*R*,6*S*,6a*S*)-(±)-2-Ethyl-5-phenyl-6-(phenylethynyl)perhydropyrrolo[3,4-*c*]pyrrole-1,3,4-trione (XIj). Glassy material. IR spectrum ($CHCl_3$), ν, cm^{-1}: 3050 w, 2990 w, 2955 w, 2885 w, 2235 w, 1785, 1725 s, 1600 w, 1500, 1450, 1405, 1380, 1350, 1280 w, 1250 w, 1130, 1040 w. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.22 t (3H, CH_3, *J* = 7.1 Hz), 3.64 m (2H, CH_2), 3.79 d (1H, 6a-H, *J* = 7.9 Hz), 4.10 d (1H, 3a-H, *J* = 7.9 Hz), 5.39 s (1H, 6-H), 7.21–7.4 m (10H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.6 (CH_3); 34.4 (CH_2); 45.4, 48.8 (C^{3a}, C^{6a}); 52.1 (C^6); 84.7, 86.6 (C≡C); 120.8, 121.3, 122.2, 126.3, 128.1, 128.8, 129.2, 130.2, 131.4, 131.7, 136.5 (C_{arom}); 164.0, 169.6, 174.6 (CO). Found, %: C 73.66; H 5.03; N 7.77. $C_{22}H_{18}N_2O_3$. Calculated, %: C 73.73; H 5.06; N 7.82.

(3a*R*,6*R*,6a*S*)-(±)-2-Ethyl-5-phenyl-6-(phenylethynyl)perhydropyrrolo[3,4-*c*]pyrrole-1,3,4-trione (XIIj). mp 193–195°C (from CH_2Cl_2–Et_2O–hexane). IR spectrum ($CHCl_3$), ν, cm^{-1}: 3045, 2990 w, 2960 w, 2885 w, 2240 w, 1790, 1725 s, 1600 w, 1505, 1445 w, 1405, 1375, 1350, 1270, 1250 w, 1140, 1075 w, 1035 w. ^1H NMR spectrum (acetone-d_6), δ, ppm: 1.11 t (3H, CH_3, *J* = 7.1 Hz), 3.56 m (2H, CH_2), 4.05 d (1H, 3a-H, *J* = 9.3 Hz), 4.16 d.d (1H, 6a-H, *J* = 9.3, 9.7 Hz), 5.79 d (1H, 6-H, *J* = 9.7 Hz), 7.2–7.7 m (10H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.6 (CH_3); 34.3 (CH_2); 41.3, 49.3 (C^{3a}, C^{6a}); 51.9 (C^6); 81.8, 89.2 (C≡C); 120.8, 123.5, 126.6, 128.0, 128.7, 128.8, 131.3, 136.1 (C_{arom}); 164.0, 169.8, 173.0 (CO). Found, %: C 73.66; H 5.07; N 7.79. $C_{22}H_{18}N_2O_3$. Calculated, %: C 73.73; H 5.06; N 7.82.

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