1,3-Dipolar cycloaddition of azomethine ylides derived from imines and difluorocarbene to alkynes: a new active Pb-mediated approach to 2-fluoropyrrole derivatives

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Domino reactions of imines with difluorocarbene in the presence of electron-deficient alkynes lead to 2-fluoropyrrole derivatives. The process involves intermediate azomethine ylide formation, its 1,3-dipolar cycloaddition to alkyne, followed by dehydrofluorination. A modified difluorocarbene generation method using active lead for dibromodifluoromethane reduction is proposed, providing shorter reaction time and improved yields of fluoropyrroles. The reactions with monoactivated acetylenes occur regioselectively. The cycloaddition of ylides to dipolarophiles such as phenylpropynal, whose carbonyl group is more active than the triple bond, gives rise to oxazolidine derivatives, implying a change in the reaction site.

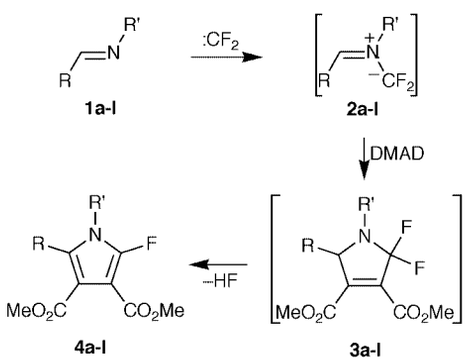
Introduction

Halogen-substituted pyrroles have attracted the attention of synthetic chemists for a long time due to their potential biological activity.[1,2] In particular, fluoropyrroles proved to be attractive targets for porphyrin design[3] and preparation of substances of agricultural and medicinal value. There are a few known synthetic approaches to fluorine-containing pyrroles: a) construction of a pyrrole ring followed by introduction of the fluorine either by direct fluorination[4,5] or by substitution of a functional group (*e.g.* fluorodecarboxylation of pyrrole-2-carboxylic acids[6] used in α-fluoropyrrole synthesis or the Schiemann reaction in β-fluoropyrrole synthesis[7]); b) preparation of an acyclic precursor and its subsequent cyclisation, used in β-fluoropyrrole synthesis;[8] c) a one-step synthesis of fluorinated pyrroles by 1,3-dipolar cycloaddition of fluorine-containing compounds. The latter approach is exemplified by the thermolysis of aziridine-2-carboxylates in the presence of chlorotrifluoroethylene, resulting in 3,4-difluoropyrroles.[9,10] However, the known fluoropyrrole syntheses generally involve many stages and have limited utility. In this connection domino processes, which occur *via* halogenocarbene-derived azomethine ylides[11] and lead to halogenopyrrole derivatives, are of particular interest.

Recently we published preliminary results on the application of another version of the third of the above-mentioned strategies, based on the reaction of fluorinated azomethine ylides derived from *N*-arylimines and difluorocarbene with dimethyl acetylenedicarboxylate (DMAD).[12] The present paper summarises the results of our investigations on the scope and limitations of the reaction. The chemo- and regioselectivity of cycloaddition of fluorinated azomethine ylides to various acetylenes are considered as well.

Results and discussion

As we showed previously, imines **1a**–**e** react with difluorocarbene in the presence of DMAD to give the α-fluoropyrroles **4a**–**e** in 15–68% yield (Scheme 1).[12] This domino process was assumed to occur *via* difluorocarbene attack on the nitrogen lone pair resulting in formation of unstable azomethine ylides **2a**–**e**; 1,3-dipolar cycloaddition of the latter to DMAD gave pyrrolines **3a**–**e**, followed by dehydrofluorination to **4a**–**e**.



Scheme 1

Difluorocarbene was generated by reduction of dibromodifluoromethane with lead powder in the presence of tetrabutylammonium bromide (Method A).

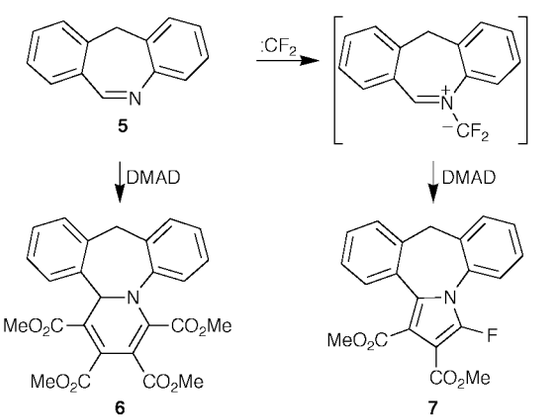
To elucidate the scope and limitations of the reaction, we reacted difluorocarbene with imines in different configurations of the C=N bond (*E* and *Z*) and containing functionalities with different electronic and steric characteristics, in the presence of symmetrical and unsymmetrical dipolarophiles. Moreover, attempts were made to improve the method of difluorocarbene generation in order to reduce the reaction time and obtain higher yields of the target products.

The pyrrole **4a** was obtained in 58% yield from (*E*)-*N*-benzylideneaniline by the above scheme. The reaction of the cyclic imine **5**, a (*Z*) analogue of *N*-benzylideneaniline, with lead-mediated difluorocarbene (Method A) in the presence of DMAD provided fluoropyrrole **7** in a yield as low as 5% (Scheme 2). This disappointing result can be rationalised in terms of increased nucleophilicity of the imine **5** in comparison with the imine **1a**, which leads to direct reaction of the imine **5** with DMAD, which competes with difluorocarbene-mediated ylide formation. This assumption is confirmed by the isolation of product **6** (11%). Evidence in favour of structure **6** comes from a comparison of its ^{13}C NMR spectrum with those reported for analogous products obtained by reactions of acyclic arylimines with DMAD.[13] Further increase in the nucleophilicity of the starting imine results in complete suppression of its reaction with difluorocarbene in favour of the

Table 1 Preparation of pyrroles **4**

Compound	R	R′	Method A		Method C	
			Yield (%)	Reaction time/h	Yield (%)	Reaction time/h
4a	Ph	Ph	58[a]	100		
4b	Ph	4-$MeOC_6H_4$	30[a]	150	70	1
4c	Ph	4-ClC_6H_4	61[a]	63		
4d	2,4-$Cl_2C_6H_3$	Ph	68[a]	35		
4e	2-Furyl	Ph	30[a]	85	69	1
4f	4-BrC_6H_4	Ph			78	0.75
4g	4-$MeOC_6H_4$	Ph			57	1.5
4h	3-$NO_2C_6H_4$	Ph	0		32	15
4i	4-ClC_6H_4	4-ClC_6H_4			70	4
4j	PhC≡C	Ph	11	25	42	1.5
4k	(*E*)-PhCH=CH	Ph			41	3
4l	9-Anthryl	Ph			30 (62)[b]	1

[a] See ref. 12. [b] Per reacted azomethine.



Scheme 2

competitive reaction: attempted synthesis of the corresponding fluoropyrrole from *N*-benzylidenebenzylamine was unsuccessful. On the contrary, the too low nucleophilicity of imines bearing strong electron-withdrawing groups makes them unsuitable substrates as well due to a decrease in the rate of reaction with electrophilic difluorocarbene.

Besides, this protocol (Method A) fails with dipolarophiles less active than DMAD containing only one electron-withdrawing group, *e.g.* tetrolic (methylpropiolic), phenylpropiolic esters. These limitations are largely attributable to the low rate of the difluorocarbene generation step, which allows undesirable reactions with the starting imine to occur. Thus, we had to search for a more efficient method for difluorocarbene generation in order to reduce the reaction time and improve the yields of target pyrroles. The reduction of dibromodifluoromethane with activated zinc dust under ultrasound irradiation (Method B) gave unsatisfactory results.[12] Though the reaction time was reduced considerably, the fluoropyrroles **4** were obtained in lower yields, on account of the known difluorocarbene reaction with THF which was used as a solvent.[14] In the reactions in solvents other than THF (diethyl ether or dimethoxyethane) only traces of the fluoropyrrole **4a** were found.

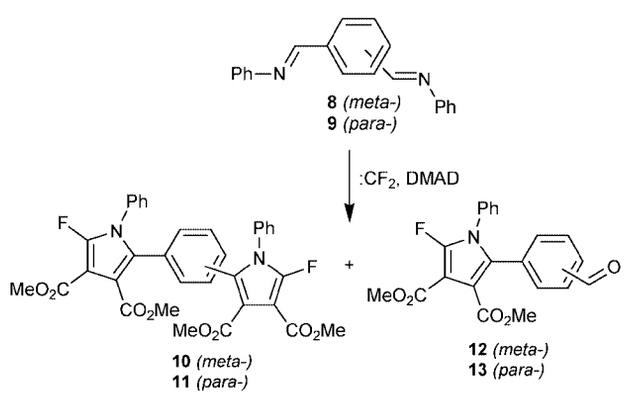
A new modification of the difluorocarbene generation protocol, using active lead obtained by reduction of aqueous lead acetate with sodium borohydride instead of lead powder, was devised (Method C). By this method, pyrrole **7** is available in a remarkably shorter time in 20% yield, while the yield of compound **6** is only 4%.

The application of Method C results in substantial improvement of yields and the reaction speeding up (Table 1, the compounds **4b**,**e**,**j**). Pyrroles from methoxy- and halogen-substituted benzylideneanilines were obtained in 57–78% yields. Considering that the process leading to fluoropyrrole occurs in four steps (Scheme 1) the yields are fairly good. Moreover, this protocol allows us to prepare fluoropyrrole **4h** from azomethine containing a nitro group.

Difluorocarbene is known to add onto double and triple carbon–carbon bonds.[15] However, the reactions of the imines **1j**,**k** with difluorocarbene occur chemoselectively with retention of the carbon–carbon multiple bonds to give finally the pyrroles **4j**,**k**. Pyrroline **3k**, a precursor of compound **4k**, proved to be stable enough to withstand chromatographic purification. It was identified in a mixture with pyrrole **4k** by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum shows signals of three protons at 5.51 (d, $^3J_{HH}$ 5.6 Hz), 6.33 (dd, $^3J_{HH}$ 5.6, $^3J_{HH\ trans}$ 16 Hz) and 6.80 (d, $^3J_{HH\ trans}$ 16 Hz) ppm, assignable to compound **3k**.

The sterically congested ylide **2l** also adds to DMAD to give pyrrole **4l**. Together with the target product, anthraldehyde produced by hydrolysis of the starting imine on silica gel was isolated. The yield of the pyrrole **4l** with respect to imine taken was 30%, while the yield with respect to imine reacted was 62%.

The bispyrrole **10** can be obtained from dianil of isophthalaldehyde **8**, with active lead used in a 4-fold excess (Scheme 3).

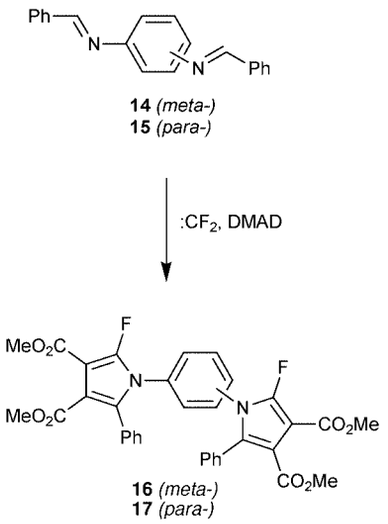


Scheme 3

The formation of the by-product **12** suggests that the used excess of the difluorocarbene source is not enough to convert all the imine into the corresponding bispyrrole. In the reaction of the terephthalaldehyde dianil **9** with difluorocarbene in the presence of DMAD, however, only traces of **11** were found, **13** being the major product.

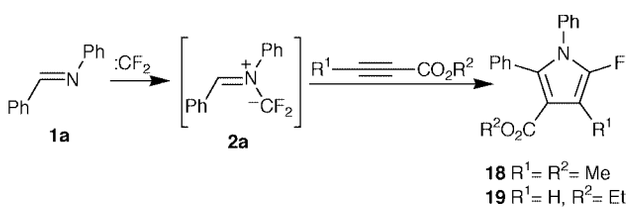
Attempts to synthesise the corresponding bispyrroles from phenylenediamine-derived imines gave unsatisfactory results. The reaction of the imine **14** with DMAD produced no pyrrole **16** at all, while the pyrrole **17** was obtained from the imine **15** in 9% yield (Scheme 4).

The utility of the new protocol was demonstrated for reactions with dipolarophiles less active than DMAD: propiolic,



Scheme 4

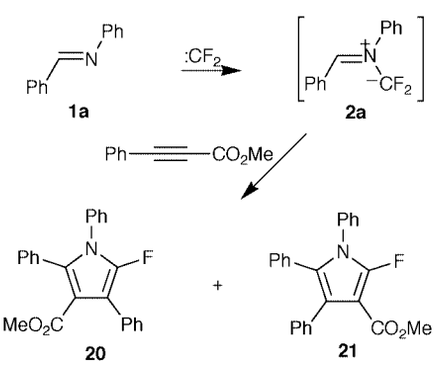
tetrolic, and phenylpropiolic esters. Starting from *N*-benzylideneaniline, we prepared the corresponding α-fluoropyrroles, though in rather low yields. The cycloaddition of the ylide **2a** to methyl ester of tetrolic acid and ethyl ester of propiolic acid occurs completely regioselectively to give the regioisomers **18** or **19**, respectively (Scheme 5).



Scheme 5

Evidence in favour of the structure **18** comes from the ^{13}C NMR spectrum containing a doubled quartet of C4 ($^{2}J_{CH}$ 6.5 Hz, $^{2}J_{CF}$ 9.5 Hz). The structure **19** is confirmed by the observation of a characteristic doublet of C4 ($^{2}J_{CF}$ 10.5 Hz) in the ^{13}C NMR spectrum.

However, the reaction of ylide **2a** with phenylpropiolic ester resulted in formation of both regioisomers **20**, **21** in a *ca.* 3:1 ratio (Scheme 6). Their configuration was assessed on the basis



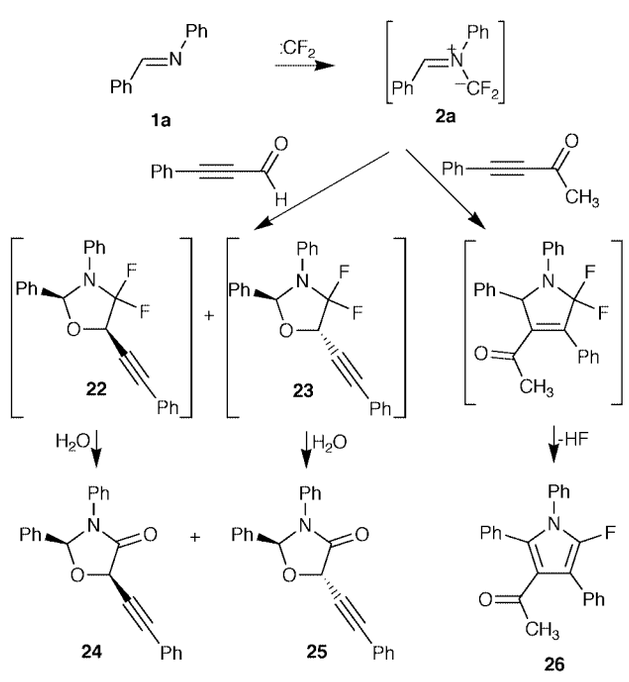
Scheme 6

of the ^{1}H and ^{13}C NMR spectra. The downfield shift of the signal of the carbon atom bearing the fluorine substituent in compound **21** compared with that for the compound **20** proves the "*ortho* arrangement" of the methoxycarbonyl group and the fluorine atom in the former. Such arrangement of substituents in compound **21** is confirmed by the $^{1}J_{CF}$ value of 278 Hz, coincident with the corresponding values for compounds **4a–l** and published data for fluoropyrroles.[4] On the contrary, the $^{1}J_{CF}$ value for the pyrrole **20** is only 263 Hz, which is close to that for pyrroles **18** and **19**.

Thus, the outcome of the reaction depends markedly on the dipolarophilic activity of the alkyne. A decrease in the number of electron-withdrawing substituents at the triple bond dramatically reduces the yields of pyrrole derivatives. In the case of esters of tetrolic and phenylpropiolic acids, the postreaction mixtures contain, along with the corresponding pyrroles, the starting imine **1a** as a major component; the latter is readily hydrolysed under chromatographic work-up to give benzaldehyde and aniline. As neither *N*-benzylideneaniline nor acetylenic dipolarophiles used separately give any products under the difluorocarbene generation conditions and the *N*-benzylideneaniline conversion directly depends on the dipolarophile activity, we assumed that the ylide generation step is reversible. The recovered difluorocarbene oligomerises, affording tetrafluoroethylene and polyfluoroethylene.[17] Hence, to improve the yields of the cycloaddition products it is necessary to employ in the reactions with low-active dipolarophiles and imines a significant excess of difluorocarbene source (see Experimental section).

It is known that ylides derived from *N*-alkylimines and difluorocarbene undergo 1,3-dipolar cycloaddition to the carbonyl group of aldehydes and ketones.[17] This fact prompted us to study the reactions of ylide **2a** in the presence of C=O and C≡C dipolarophile moieties incorporated either into different molecules or into the same one. The carbonyl group of phenylpropynal was found to be more active in 1,3-dipolar cycloadditions with the ylide **2a** than the C≡C bond.

The oxazolidinones **24** and **25** are formed by hydrolysis of *gem*-difluoropyrrolidines **22** and **23**, which readily occurs if the reaction mixture is exposed to air or under column chromatography on silica. The isomer ratio is *ca.* 5:1, the *trans* isomer prevailing (Scheme 7). The structure of the products was



Scheme 7

assigned on the basis of spectral data and comparison of their ^{1}H NMR spectra with those reported in the literature.[17,18]

The reaction of *N*-benzylideneaniline with difluorocarbene in the presence of two dipolarophiles, DMAD and phenylpropynal, taken in an equimolar ratio, gave a mixture of fluoropyrrole **4a** and both stereoisomeric oxazolidinones **24** and **25** (**4a**:(**24** + **25**) 5.5:1). This suggests the C≡C bond of DMAD to be substantially more active than the aldehydic carbonyl in reactions with the ylide **2a**.

Replacement of phenylpropynal by 4-phenylbut-3-yn-2-one results in a change in the reaction site. Here the C≡C bond appears to be more active, and the reaction follows the path of 1,3-dipolar cycloaddition of the ylide **2a** to give the fluoropyrrole **26** as a single regioisomer. The assignment of structure **26** is based on the comparison of the ^{13}C NMR spectrum with the corresponding spectra for the compounds **20** and **21**.

In conclusion, we have developed a one-pot synthesis of 2-fluoropyrrole derivatives, starting from readily available imines, alkynes and dibromodifluoromethane as the fluorine-containing synthon. The domino reaction leading to these compounds involves consecutive difluorocarbene generation, *gem*-difluorosubstituted azomethine ylide formation, its 1,3-dipolar cycloaddition to alkyne followed by aromatisation by means of dehydrofluorination. The reaction conditions used are compatible with the presence in imines of such functionalities as halogens, alkoxy and nitro groups, as well as multiple carbon–carbon bonds and heterocyclic moieties. With unsymmetrical alkynes activated by only one electron-withdrawing group, the reaction provides fewer pyrrole derivatives, the cycloaddition step being either completely or partially regioselective. The reactivity of the dipolarophiles toward the fluorinated ylides **2** was found to decrease in the following order: C≡C bond activated by two electron-withdrawing groups > aldehydic C=O bond > C≡C bond activated by one electron-withdrawing group > ketonic C=O bond.

Experimental

General

Melting points were determined on a hot stage microscope (Boetius) and are uncorrected. IR spectra were recorded on a Carl-Zeiss UR 20 spectrometer. ^1H NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300 MHz with internal standard TMS ($\delta = 0$) and ^{13}C NMR spectra at 62.9 MHz with internal standard $CHCl_3$ ($\delta = 76.7$). Elemental analysis was performed on a Hewlett-Packard 185B CHN-analyser. Methylene chloride was dried by distillation over phosphorus pentoxide. Silica gel LS 5/40 (Chemapol) was used for column chromatography. Sodium borohydride, lead acetate, dibromodifluoromethane, tetrabutylammonium bromide were obtained commercially. DMAD, phenylpropynal, ethyl propiolate, methylbut-2-ynoate, 4-phenylbut-3-yn-2-one, methyl phenylpropiolate were freshly distilled.

The reagent ratios used were the same as those in the typical procedure, unless otherwise specified.

Preparation of active lead

A solution of sodium borohydride (1.66 g, 0.04 mol) in water (5 cm^3) was added dropwise to a magnetically stirred solution of lead acetate (6.5 g, 0.02 mol) in 2 M acetic acid (20 cm^3) cooled with ice–water. Another portion of 2 M acetic acid (20 cm^3) was added to the reaction mixture, and the solution of $NaBH_4$ (1.66 g, 0.04 mol) in water (5 cm^3) was added dropwise. The black precipitate of lead was washed in succession with 1 M acetic acid (3 × 30 cm^3), water (3 × 20 cm^3), ethanol (3 × 5 cm^3) and methylene chloride (3 × 5 cm^3), dried *in vacuo* at 60–70 °C for *ca*. 20 min, and then the flask was filled with argon, and the active lead used at once.

Reactions of imines with difluorocarbene in the presence of alkynes

Typical procedure (Method C). A flask containing active lead (1.2 g, 5.8 mmol) and methylene chloride (7 cm^3) was charged with Bu_4NBr (2.0 g, 6.0 mmol), the imine **1j** (0.55 g, 2.7 mmol), DMAD (0.98 g, 6.9 mmol) and CBr_2F_2 (1.95 g, 9.3 mmol). The flask was tightly stoppered and the mixture was stirred with a magnetic stirrer at 45 °C until the lead was consumed completely. Column chromatography (hexane–ethyl acetate, 4 : 1) followed by recrystallisation from methylene chloride–diethyl ether–hexane provided dimethyl 2-fluoro-1-phenyl-5-(phenylethynyl)pyrrole-3,4-dicarboxylate **4j** (0.425 g, 42%) as a colourless solid; mp 105–107 °C (Found: C, 70.0; H, 4.3; N, 3.5. Calc. for $C_{22}H_{16}FNO_4$: C, 70.0; H, 4.3; N, 3.7%); ν_{max} ($CHCl_3$)/cm^{-1} 2230 (C≡C), 1740 (C=O); δ_H ($CDCl_3$) 3.89 (3 H, s, CH_3), 3.96 (3 H, s, CH_3), 7.3–7.6 (10 H, m, PhH); δ_C ($CDCl_3$) 51.8 (CH_3), 52.1 (CH_3), 78.2 (C=C), 95.6 (d, $^2J_{CF}$ 5.0, C3), 96.8 (C=C), 112.2 (C4), 117.8 (C5), 121.9, 126.9, 128.2, 128.8, 129.2, 129.5, 131.2, 132.9 (Ph), 146.9 (d, $^1J_{CF}$ 280, C2), 161.6 (d, $^3J_{CF}$ 4.5, CH_3CO_2-C3), 163.4 (d, $^4J_{CF}$ 1.5, CH_3CO_2-C4).

Method A. The compound **4j** (11%) was obtained from imine **1j** and DMAD in 25 h according to the typical procedure using lead powder instead of active lead.

The compounds **4b**,**e** were obtained according to the typical procedure (Method C). Yields and reaction times for compounds **4** are presented in Table 1. Compound **4b**, mp 119–121 °C (lit.[12] mp 113–116 °C); **4e**, mp 145–147 °C (lit.[12] mp 145–147 °C). Spectral data for compounds **4b**,**e** are identical to those published earlier.[12]

Dimethyl 2-(4-bromophenyl)-5-fluoro-1-phenylpyrrole-3,4-dicarboxylate 4f

Compound **4f** was obtained from imine **1f** and DMAD as a colourless solid according to the typical procedure, mp 143–145 °C (diethyl ether–hexane) (Found: C, 55.6; H, 3.7; N, 3.2. Calc. for $C_{20}H_{15}FNO_4$: C, 55.6; H, 3.5; N, 3.2%); ν_{max} ($CHCl_3$)/cm^{-1} 1730 (C=O); δ_H ($CDCl_3$) 3.77 (3 H, s, CH_3), 3.88 (3 H, s, CH_3), 7.02–7.11 (4 H, m, PhH), 7.28–7.40 (4 H, m, PhH); δ_C ($CDCl_3$) 51.4 (CH_3), 51.9 (CH_3), 94.3 (d, $^2J_{CF}$ 9.0, C4), 112.9 (C3), 122.5 (Ph), 126.1 (d, $^2J_{CF}$ 2.6, C2), 122.5, 127.1, 127.4, 128.8, 129.1, 130.9, 131.6, 132.6 (Ph), 147.2 (d, $^1J_{CF}$ 278, C5), 161.7 (d, $^3J_{CF}$ 5.2, CH_3CO_2-C4), 164.6 (d, $^3J_{CF}$ 2.6, CH_3CO_2-C3).

Dimethyl 2-fluoro-5-(4-methoxyphenyl)-1-phenylpyrrole-3,4-dicarboxylate 4g

The compound **4g** was obtained from imine **1g** and DMAD as a colourless solid according to the typical procedure, mp 132–134 °C (methylene chloride–diethyl ether) (Found: C, 65.8; H, 4.7; N, 3.7. Calc. for $C_{21}H_{18}FNO_5$: C, 65.8; H, 4.7; N, 3.7%); ν_{max} ($CHCl_3$)/cm^{-1} 1730 (C=O); δ_H ($CDCl_3$) 3.76 (3 H, s, CH_3), 3.77 (3 H, s, CH_3), 3.88 (3 H, s, CH_3), 6.72–6.76 (2 H, m, PhH), 7.06–7.11 (4 H, m, PhH), 7.34–7.37 (3 H, m, PhH); δ_C ($CDCl_3$) 51.3 (CH_3), 51.8 (CH_3), 54.8 (CH_3), 94.0 (d, $^2J_{CF}$ 5.5, C3), 112.0 (C4), 113.1, 120.6, 127.1 (Ph), 127.5 (d, $^3J_{CF}$ 3.8, C5), 128.5, 128.9, 131.5, 133.0 (Ph), 147.0 (d, $^1J_{CF}$ 278, C2), 159.2 (Ph), 162.0 (d, $^3J_{CF}$ 4.5, CH_3CO_2-C3), 164.9 (CH_3CO_2-C4).

Dimethyl 2-fluoro-5-(3-nitrophenyl)-1-phenylpyrrole-3,4-dicarboxylate 4h

The compound **4h** was obtained from imine **1h** and DMAD as a colourless solid according to the typical procedure, mp 153–155 °C (methylene chloride–diethyl ether–hexane) (Found: C, 60.4; H, 4.2; N, 6.8. Calc. for $C_{20}H_{15}FN_2O_6$: C, 60.3; H, 3.8; N, 7.0%); ν_{max} ($CHCl_3$)/cm^{-1} 1730 (C=O); δ_H ($CDCl_3$) 3.79 (3 H, s, CH_3), 3.90 (3 H, s, CH_3), 7.1–8.1 (9 H, m, PhH); δ_C ($CDCl_3$) 51.5 (CH_3), 52.0 (CH_3), 94.9 (d, $^2J_{CF}$ 6.1, C3), 113.9 (C4), 122.8 (Ph), 124.8 (C5), 125.0, 127.1, 128.7, 129.2, 129.4, 130.2, 132.3, 135.9, 147.4 (Ph), 147.5 (d, $^1J_{CF}$ 279, C2), 161.6 (d, $^3J_{CF}$ 5.0, CH_3CO_2-C3), 164.2 (CH_3CO_2-C4).

Dimethyl 1,2-bis(4-chlorophenyl)-5-fluoropyrrole-3,4-dicarboxylate 4i

Compound **4i** was obtained from imine **1i** and DMAD as a colourless solid according to the typical procedure, mp 134–

136 °C (methylene chloride–diethyl ether–hexane) (Found: C, 56.9; H, 3.6; N, 3.2. Calc. for $C_{20}H_{14}Cl_2FNO_4$: C, 56.9; H, 3.3; N, 3.3%); ν_{max} ($CHCl_3$)/cm^{-1} 1730 (C=O); δ_H ($CDCl_3$) 3.76 (3 H, s, CH_3), 3.90 (3 H, s, CH_3), 7.0–7.4 (9 H, m, PhH); δ_C ($CDCl_3$) 51.5 (CH_3), 52.0 (CH_3), 94.7 (d, $^2J_{CF}$ 5.0, C4), 113.2 (C3), 126.0 (d, $^3J_{CF}$ 2.8, C2), 126.6, 128.2, 128.3, 129.4, 131.2, 131.4, 134.5, 134.9 (Ph), 147.1 (d, $^1J_{CF}$ 279, C5), 161.6 (d, $^3J_{CF}$ 5.0, CH_3CO_2-C4), 164.4 (d, $^4J_{CF}$ 2.2, CH_3CO_2-C3).

Dimethyl (*E*)-2-fluoro-1-phenyl-5-(2-phenylethenyl)pyrrole-3,4-dicarboxylate 4k

Compound **4k** was obtained from imine **1k** and DMAD as a colourless solid according to the typical procedure, mp 142–144 °C (methylene chloride–diethyl ether–hexane) (Found: C, 69.9; H, 4.9; N, 3.7. Calc. for $C_{22}H_{18}FNO_4$: C, 69.7; H, 4.8; N, 3.7%); ν_{max} ($CHCl_3$)/cm^{-1} 1730 (C=O); δ_H ($CDCl_3$) 3.88 (3 H, s, CH_3), 3.94 (3 H, s, CH_3), 6.50 (1 H, d, $^3J_{HH}$ 16.8, C=C), 6.87 (1 H, d, $^3J_{HH}$ 16.8, C=C), 7.2–7.6 (10 H, m, PhH); δ_C ($CDCl_3$) 51.4 (CH_3), 52.0 (CH_3), 94.8 (d, $^2J_{CF}$ 5.1, C3), 111.9 (C4), 114.5 (C=C), 125.3 (d, $^3J_{CF}$ 2.2, C5), 126.1, 127.4, 127.8, 128.3, 129.4, 129.5 (Ph), 132.4 (C=C), 133.07, 136.2 (Ph), 147.6 (d, $^1J_{CF}$ 279, C2), 161.8 (d, $^3J_{CF}$ 5, CH_3CO_2-C3), 165.1 (CH_3CO_2-C4).

Dimethyl 2-(9-anthryl)-5-fluoro-1-phenylpyrrole-3,4-dicarboxylate 4l

The compound **4l** (30%) along with 9-anthraldehyde (51%) was obtained from the imine **1l** and DMAD as a pale yellow solid according to the typical procedure (Method C), mp 199–201 °C (methylene chloride–diethyl ether–hexane) (Found: C, 74.4; H, 4.6; N, 2.9. Calc. for $C_{28}H_{20}FNO_4$: C, 74.2; H, 4.5; N, 3.1%); ν_{max} ($CHCl_3$)/cm^{-1} 1740 (C=O); δ_H ($CDCl_3$) 3.34 (3 H, s, CH_3), 3.97 (3 H, s, CH_3), 6.9–7.1 (5 H, m, PhH), 7.4–8.4 (9 H, m, anthryl); δ_C ($CDCl_3$) 51.2 (CH_3), 51.5 (CH_3), 94.8 (d, $^2J_{CF}$ 5.0, C4), 114.5 (C3), 122.7, 124.8, 125.3 (Ph, anthryl), 125.8 (d, $^3J_{CF}$ 3.3, C2), 126.0, 126.2, 128.2, 128.3, 128.4, 128.7, 130.4, 132.0, 132.5 (Ph, anthryl), 147.4 (d, $^1J_{CF}$ 278, C5), 162.2 (d, $^3J_{CF}$ 4.4, CH_3CO_2-C4), 163.6 (CH_3CO_2-C3).

Reaction of imine 5 with difluorocarbene in the presence of DMAD

Dimethyl 3-fluoro-9*H*-dibenzo[*c*,*f*]pyrrolo[1,2-*a*]azepine-1,2-dicarboxylate **7** (20%) and tetramethyl 10,14b-dihydrodibenzo-[*c*,*f*]pyrido[1,2-*a*]azepine-1,2,3,4-tetracarboxylate **6** (4%) were obtained from imine **5** and DMAD in 3 h. The products were isolated by column chromatography (eluent hexane–diethyl ether, 1:1). Compound **7**: colourless solid, mp 149–151 °C (methylene chloride–diethyl ether–hexane) (Found: C, 69.2; H, 4.5; N, 3.7. Calc. for $C_{21}H_{16}NFO_4$: C, 69.0; H, 4.4; N, 3.8%); ν_{max} ($CHCl_3$)/cm^{-1} 1735 (C=O); δ_H ($CDCl_3$) 3.66 (1 H, d, *J* 13.7, CH_2), 3.65 (3 H, s, CH_3), 3.85 (3 H, s, CH_3), 3.91 (3 H, s, CH_3), 4.00 (1 H, d, *J* 13.7, CH_2), 7.2–7.5 (8 H, m, PhH); δ_C ($CDCl_3$) 38.3 (CH_2), 51.4 (CH_3), 52.1 (CH_3), 94.9 (d, $^2J_{CF}$ 5.5, C2), 112.0 (C1), 124.8, 124.8 (Ph), 125.7 (C13b), 126.6, 126.8, 127.2, 128.1, 128.3, 129.0, 129.6, 131.2, 137.0, 140.3 (Ph), 146.2 (d, $^1J_{CF}$ 280, C3), 161.8 (d, $^3J_{CF}$ 5, CO_2CH_3-C2), 165.5 (d, $^4J_{CF}$ 1.6, CO_2CH_3-C1). Compound **6**: yellow solid, mp 217–219 °C (diethyl ether–hexane) (Found: C, 65.3; H, 4.9; N, 2.5. Calc. for $C_{26}H_{23}NO_8$: C, 65.5; H, 4.9; N, 2.9%); ν_{max} ($CHCl_3$)/cm^{-1} 1755, 1720 (C=O); δ_H ($CDCl_3$) 3.50 (3 H, s, CH_3), 3.65 (3 H, s, CH_3), 3.73 (3 H, s, CH_3), 4.03 (3 H, s, CH_3), 4.38 (1 H, d, *J* 18.5, CH_2), 4.77 (1 H, d, *J* 18.5, CH_2), 6.27 (1 H, s, H-C14b), 7.1–7.4 (8 H, m, PhH); δ_C ($CDCl_3$) 40.9 (CH_2), 51.5, 52.0, 52.4, 52.4 (CH_3), 58.1 (C14b), 101.6 (C3), 106.3 (C1), 125.0, 125.6, 126.4, 126.5, 128.1, 128.3, 130.2, 130.9, 134.4, 135.9, 136.1, 140.3, 141.0 (Ph, C2), 147.9 (C4), 162.9, 163.6, 163.8, 167.6 (C=O).

Method A. The compounds **7** (5%) and **6** (11%) were obtained from imine **5** and DMAD in 20 h according to the typical procedure using lead powder instead of active lead.

Reaction of imine 8 with difluorocarbene in the presence of DMAD

Dimethyl 2-fluoro-5-{3-[5-fluoro-3,4-bis(methoxycarbonyl)-1-phenylpyrrol-2-yl]phenyl}-1-phenylpyrrole-3,4-dicarboxylate **10** (0.28 g, 28%) and dimethyl 2-fluoro-5-(3-formylphenyl)-1-phenylpyrrole-3,4-dicarboxylate **12** (0.03 g, 6%) were obtained from imine **8** (0.51 g, 1.8 mmol) and DMAD according to the typical procedure in 4 h. The products were isolated by column chromatography (eluent hexane–ethyl acetate, 5:1). Compound **10**: colourless solid, mp 188–190 °C (methylene chloride–diethyl ether–hexane) (Found: C, 64.8; H, 4.3; N, 4.3. Calc. for $C_{34}H_{26}F_2N_2O_8$: C, 65.0; H, 4.2; N, 4.5%); ν_{max} ($CHCl_3$)/cm^{-1} 1730 (C=O); δ_H ($CDCl_3$) 3.69 (6 H, s, 2 × CH_3), 3.88 (6 H, s, 2 × CH_3), 6.9–7.4 (14 H, m, PhH); δ_C ($CDCl_3$) 51.4 (CH_3), 51.7 (CH_3), 94.3 (d, $^2J_{CF}$ 5.0, C3), 112.7 (C4), 126.9 (d, $^3J_{CF}$ 2.2, C2), 127.1, 127.3, 128.5, 128.7, 128.9, 130.4, 132.7, 133.0 (Ph), 147.1 (d, $^1J_{CF}$ 278, C2), 161.8 (d, $^3J_{CF}$ 5.0 CH_3CO_2-C3), 164.2 (CH_3CO_2-C4). Compound **12**: colourless solid, mp 127–129 °C (methylene chloride–diethyl ether–hexane) (Found: C, 66.2; H, 4.3; N, 3.5. Calc. for $C_{21}H_{16}FNO_5$: C, 66.1; H, 4.2; N, 3.7%); ν_{max} ($CHCl_3$)/cm^{-1} 1720 (C=O); δ_H ($CDCl_3$) 3.76 (3 H, s, CH_3), 3.90 (3 H, s, CH_3), 7.1–7.8 (9 H, m, PhH), 9.87 (1 H, s, CHO); δ_C ($CDCl_3$) 51.5 (CH_3), 51.9 (CH_3), 94.6 (d, $^2J_{CF}$ 5.5, C3), 113.3 (C4), 125.9 (d, $^3J_{CF}$ 2.7, C5), 127.1, 128.4, 128.8, 128.9, 129.1, 129.6, 131.6, 132.5, 135.8, 135.9 (Ph), 147.3 (d, $^1J_{CF}$ 279, C2), 161.7 (d, $^3J_{CF}$ 5.0, CH_3CO_2-C3), 164.4 (CH_3CO_2-C4), 191.1 (CHO).

Reaction of imine 9 with difluorocarbene in the presence of DMAD

Dimethyl 2-fluoro-5-{4-[5-fluoro-3,4-bis(methoxycarbonyl)-1-phenylpyrrol-2-yl]phenyl}-1-phenylpyrrole-3,4-dicarboxylate **11** (0.010 g, 0.5%) and dimethyl 2-fluoro-5-(4-formylphenyl)-1-phenylpyrrole-3,4-dicarboxylate **13** (0.13 g, 20%) were obtained from imine **9** (0.47 g, 1.7 mmol) and DMAD according to the typical procedure in 16 h. The products were isolated by column chromatography (eluent hexane–ethyl acetate, 5:1). Compound **11**: colourless solid, mp 259–261 °C (Found: C, 65.1; H, 4.2; N, 4.3. Calc. for $C_{34}H_{26}F_2N_2O_8$: C, 65.0; H, 4.2; N, 4.5%); ν_{max} ($CHCl_3$)/cm^{-1} 1730 (C=O); δ_H ($CDCl_3$) 3.68 (6 H, s, 2 × CH_3), 3.87 (6 H, s, 2 × CH_3), 6.9–7.4 (14 H, m, PhH); δ_C ($CDCl_3$) 51.4 (CH_3), 51.8 (CH_3), 94.3 (d, $^2J_{CF}$ 5.0, C3), 113.0 (C4), 126.3 (d, $^3J_{CF}$ 2.8, C2), 127.1, 128.5, 128.6, 128.9, 129.6, 132.8 (Ph), 147.3 (d, $^1J_{CF}$ 279, C5), 161.7 (d, $^3J_{CF}$ 4.0, CH_3CO_2-C3), 164.5 (CH_3CO_2-C4). Compound **13**: colourless solid, mp 158–160 °C (ethyl acetate–hexane) (Found: C, 66.1; H, 4.4; N, 3.4. Calc. for $C_{21}H_{16}FNO_5$: C, 66.1; H, 4.2; N, 3.7%); ν_{max} ($CHCl_3$)/cm^{-1} 1720 (C=O); δ_H ($CDCl_3$) 3.77 (3 H, s, CH_3), 3.89 (3 H, s, CH_3), 7.1–7.8 (9 H, m, PhH), 9.95 (1 H, s, CHO); δ_C ($CDCl_3$) 51.5 (CH_3), 52.0 (CH_3), 94.8 (d, $^2J_{CF}$ 5.5, C3), 113.9 (C4), 125.5 (d, $^3J_{CF}$ 2.2, C5), 126.9, 127.0, 127.1, 128.8, 128.9, 129.0, 129.1, 129.2, 130.4, 132.6, 134.5, 135.2 (Ph), 147.6 (d, $^1J_{CF}$ 279, C2), 161.6 (d, $^3J_{CF}$ 5.1, CH_3CO_2-C4), 164.5 (CH_3CO_2-C3), 191.1 (CHO).

Dimethyl 2-fluoro-5-{4-[5-fluoro-3,4-bis(methoxycarbonyl)-1-phenylpyrrol-2-yl]phenyl}-1-phenylpyrrole-3,4-dicarboxylate **11** (0.03 g, 5%) and dimethyl 2-fluoro-5-(4-formylphenyl)-1-phenylpyrrole-3,4-dicarboxylate **13** (0.13 g, 37%) were obtained from imine **9** (0.26 g, 0.9 mmol) and DMAD according to the typical procedure in 16 h, difluorocarbene source (active lead, Bu_4NBr, CBr_2F_2) taken in 11-fold excess. The products were isolated by column chromatography (eluent hexane–ethyl acetate, 5:1).

Reaction of imine 15 with difluorocarbene in the presence of DMAD

Dimethyl 2-fluoro-1-{4-[2-fluoro-3,4-bis(methoxycarbonyl)-5-phenylpyrrol-1-yl]phenyl}-5-phenylpyrrole-3,4-dicarboxylate

17 (0.05 g, 9%) was obtained from the imine **15** (0.25 g, 0.9 mmol) and DMAD in 6 h according to the typical procedure. The product was isolated by column chromatography (eluent hexane–ethyl acetate, 5:1) as a colourless solid, mp 246–250 °C (methylene chloride–diethyl ether–hexane) (Found: C, 64.7; H, 4.3; N, 4.7. Calc. for $C_{34}H_{26}F_2N_2O_8$: C, 65.0; H, 4.2; N, 4.5%); ν_{max} ($CHCl_3$)/cm^{-1} 1740 (C=O); δ_H ($CDCl_3$) 3.75 (6 H, s, 2 × CH_3), 3.90 (6 H, s, 2 × CH_3), 7.1–7.3 (14 H, m, PhH); δ_C ($CDCl_3$) 51.5 (CH_3), 51.9 (CH_3), 94.7 (d, $^2J_{CF}$ 4.4, C3), 113.1 (C4), 127.1 (C5), 127.8, 127.9, 128.3, 130.0, 133.2 (Ph), 146.9 (d, $^1J_{CF}$ 279, C2), 161.7 (d, $^3J_{CF}$ 5, CH_3CO_2-C4), 164.5 (d, $^4J_{CF}$ 2.2, CH_3CO_2-C3).

Methyl 5-fluoro-4-methyl-1,2-diphenylpyrrole-3-carboxylate 18

Compound **18** (13%) was obtained from imine **1a** and methyl but-2-ynoate in 25 h according to the typical procedure. The product was isolated by column chromatography (eluent hexane–diethyl ether, 2:1) as a colourless solid, mp 144–147 °C (methylene chloride–diethyl ether–hexane) (Found: C, 73.8; H, 5.3; N, 4.5. Calc. for $C_{19}H_{16}FNO_2$: C, 73.8; H, 5.2; N, 4.5%); ν_{max} ($CHCl_3$)/cm^{-1} 1715 (C=O); δ_H ($CDCl_3$) 2.28 (3 H, d, $^4J_{HF}$ 1.3, CH_3), 3.68 (3 H, s, OCH_3), 7.0–7.3 (10 H, m, PhH); δ_C ($CDCl_3$) 8.1 (CH_3), 50.3 (OCH_3), 96.1 (d, $^2J_{CF}$ 9.5, C4), 110.1 (d, $^3J_{CF}$ 3.5, C3), 127.1, 127.3, 127.4, 127.6, 128.5 (Ph), 130.0 s (C2), 130.6, 130.9, 134.2 (Ph), 144.1 (d, $^1J_{CF}$ 260, C5), 165.2 (d, $^4J_{CF}$ 3.0, C=O). The following J_{CH} values are taken from the spectrum recorded without proton decoupling: 8.1 (q, $^1J_{CH}$ 127.5, CH_3), 50.3 (q, $^1J_{CH}$ 150, OCH_3), 96.1 (dq, $^2J_{CF}$ 9.5, $^2J_{CH}$ 6.5, C4), 110.1 (d, $^3J_{CF}$ 3.5, C3), 144.1 (dq, $^1J_{CF}$ 260, $^3J_{CH}$ 5.8, C5), 165.2 (d, $^4J_{CF}$ 3.0, C=O).

Ethyl 5-fluoro-1,2-diphenylpyrrole-3-carboxylate 19

Compound **19** (10%) was obtained from imine **1a** and ethyl propiolate in 15 h according to the typical procedure. The product was isolated by column chromatography (eluent hexane–diethyl ether, 4:1) as a colourless solid, mp 85–87 °C (diethyl ether–hexane) (Found: C, 74.0; H, 5.3; N, 4.5. Calc. for $C_{19}H_{16}FNO_2$: C, 73.8; H, 5.2; N, 4.5%); ν_{max} ($CHCl_3$)/cm^{-1} 1715 (C=O); δ_H ($CDCl_3$) 1.20 (3 H, t, *J* 7.0, CH_3), 4.19 (2 H, q, *J* 7.0, CH_2), 6.19 (1 H, d, $^3J_{HF}$ 4.0, H-C4), 7.1–7.3 (10 H, m, PhH); δ_C ($CDCl_3$) 13.8 (CH_3), 59.4 (CH_2), 86.9 (d, $^2J_{CF}$ 10.5, C4), 110.3 (d, $^3J_{CF}$ 4.4, C3), 127.1, 127.3, 127.6, 127.8, 128.6, 130.0 (Ph), 130.7 (d, $^3J_{CF}$ 3.3, C2), 131.0, 134.0 (Ph), 145.9 (d, $^1J_{CF}$ 263, C5), 163.9 (d, $^4J_{CF}$ 3.3, C=O).

Reaction of imine 1a with difluorocarbene in the presence of methyl phenylpropiolate

Methyl 5-fluoro-1,2,4-triphenylpyrrole-3-carboxylate **20** (4%) and methyl 2-fluoro-1,4,5-triphenylpyrrole-3-carboxylate **21** (2%) were obtained from imine **1a** and methyl phenylpropiolate in 3 h according to the typical procedure. The products were isolated by column chromatography (eluent hexane–diethyl ether, 10:1). Compound **20**: colourless solid, mp 132–134 °C (diethyl ether–hexane) (Found: C, 77.8; H, 5.0; N, 3.6. Calc. for $C_{24}H_{18}FNO_2$: C, 77.6; H, 4.9; N, 3.8%); ν_{max} ($CHCl_3$)/cm^{-1} 1720 (C=O); δ_H ($CDCl_3$) 3.56 (3 H, s, CH_3), 7.1–7.4 (15 H, m, PhH); δ_C ($CDCl_3$) 50.7 (CH_3), 102.4 (d, $^2J_{CF}$ 7.2, C4), 110.1 (d, $^3J_{CF}$ 2.2, C3), 126.3, 127.3, 127.6, 127.9, 128.6, 129.1 (Ph), 129.7 (d, $^3J_{CF}$ 2.2, C2), 130.0, 130.8, 131.1 (d, $^3J_{CF}$ 3.3), 133.9 (Ph), 143.4 (d, $^1J_{CF}$ 263, C5), 165.0 (d, $^4J_{CF}$ 3.3, C=O). Compound **21**: colourless solid, mp 138–140 °C (diethyl ether–hexane) (Found: C, 77.7; H, 4.8; N, 3.6. Calc. for $C_{24}H_{18}FNO_2$: C, 77.6; H, 4.9; N, 3.8%); ν_{max} ($CHCl_3$)/cm^{-1} 1720 (C=O); δ_H ($CDCl_3$) 3.76 (3 H, s, CH_3), 6.8–7.2 (15 H, m, PhH); δ_C ($CDCl_3$) 50.7 (CH_3), 93.7 (d, $^3J_{CF}$ 2.8, C4), 121.3 (Ph), 124.0 (d, $^2J_{CF}$ 3.9, C3), 126.6, 127.0, 127.4, 127.5, 127.7, 128.3, 129.0, 129.9, 130.9, 131.1 (Ph), 133.7 (d, $^3J_{CF}$ 1.7, C5), 134.1 (Ph), 148.8 (d, $^1J_{CF}$ 278, C2), 163.3 (d, $^3J_{CF}$ 5.0, CO_2CH_3).

(2*R*,5*S*)- and (2*R*,5*R*)-(±)-2,3-Diphenyl-5-(phenylethynyl)-oxazolidin-4-ones 24 and 25

Compounds **24** (0.050 g, 5%) and **25** (0.230 g, 21%) were obtained from imine **1a** (0.60 g, 3.3 mmol) and phenylpropynal (1.02 g, 8.3 mmol) in 7.5 h according to the typical procedure. The products were isolated by column chromatography (eluent hexane–diethyl ether, 3:1). Compound **24**: colourless solid, mp 137–139 °C (diethyl ether–hexane) (Found: C, 80.9; H, 5.2; N, 4.1. Calc. for $C_{23}H_{17}NO_2$: C, 81.4; H, 5.1; N, 4.1%); ν_{max} ($CHCl_3$)/cm^{-1} 2240 (C≡C), 1735 (C=O); δ_H ($CDCl_3$) 5.51 (1 H, s, H-C5), 6.56 (1 H, s, H-C2), 7.1–7.6 (15 H, m, PhH); δ_C ($CDCl_3$) 69.2 (C5), 82.5, 87.7 (C≡C), 92.1 (C2), 121.4, 122.7, 126.2, 127.4, 127.9, 128.5, 128.7, 128.8, 129.8, 131.7, 134.8, 136.1 (Ph), 166.0 (C4). Compound **25**: colourless solid, mp 147–149 °C (diethyl ether–hexane) (Found: C, 81.5; H, 5.1; N, 4.0. Calc. for $C_{23}H_{17}NO_2$: C, 81.4; H, 5.1; N, 4.1%); ν_{max} ($CHCl_3$)/cm^{-1} 2245 (C≡C), 1735 (C=O); δ_H ($CDCl_3$) 5.57 (1 H, s, H-C5), 6.70 (1 H, s H-C2), 7.1–7.6 (15 H, m, PhH); δ_C ($CDCl_3$) 68.8 (C5), 81.5, 87.7 (C≡C), 91.5 (C2), 121.3, 122.3, 126.0, 127.1, 128.0, 128.6, 128.7, 128.8, 129.9, 131.8, 135.0, 135.5 (Ph), 166.3 (C4).

1-(5-Fluoro-1,2,4-triphenylpyrrol-3-yl)ethanone 26

Compound **26** (0.050 g, 3%) was obtained from imine **1a** (0.98 g, 5.4 mmol) and 4-phenylbut-3-yn-2-one (1.98 g, 14 mmol) in 19 h according to the typical procedure. The product was isolated by column chromatography (eluent hexane–diethyl ether, 3:1) as a colourless solid, mp 159–162 °C (diethyl ether–hexane) (Found: C, 80.9; H, 5.2; N, 3.8. Calc. for $C_{24}H_{18}FNO$: C, 81.1; H, 5.1; N, 3.9%); ν_{max} ($CHCl_3$)/cm^{-1} 1680 (C=O); δ_H ($CDCl_3$) 2.05 (3 H, s, CH_3), 7.1–7.5 (15H, m, PhH); δ_C ($CDCl_3$) 31.1 (CH_3), 101.8 (d, $^2J_{CF}$ 7.7, C4), 120.7 (C3), 126.5, 127.4, 127.7, 128.0, 128.0 (Ph), 128.1 (d, $^3J_{CF}$ 5.0, C2), 128.6, 128.7, 129.2, 130.1, 131.0, 131.1 (d, $^3J_{CF}$ 4.5, Ph), 133.9 (Ph), 143.5 (d, $^1J_{CF}$ 267, C5), 196.7 (C=O).

Reaction of imine 1a with difluorocarbene in the presence of DMAD and phenylpropynal

Compounds **24** (0.030 g, 2%), **25** (0.032 g, 2%) and **4a** (0.322 g, 21%) were obtained from imine **1a** (0.78 g, 4.3 mmol), phenylpropynal (1.33 g, 11 mmol) and DMAD (1.34 g, 11 mmol) in 1.5 h according to the typical procedure. The products were isolated by column chromatography (eluent hexane–diethyl ether, 3:1).

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