Reactions of polyfluorinated chalcones with hydrazine hydrate and phenylhydrazine

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Polyfluorinated di- and triarylpyrazolines were synthesized by the reactions of polyfluorinated chalcones with hydrazine hydrate and phenylhydrazine, respectively. Reactions of benzylidenepolyfluoroacetophenones with phenylhydrazine resulted in the mixtures of isomeric 1,5-diphenyl-3-polyfluoroaryl- and 1,3-diphenyl-5-polyfluoroarylpyrazolines. Fluorescence properties of the synthesized triarylpyrazolines were studied.

Key words: polyfluorinated chalcones, polyfluorinated 1-acetyl-3,5-diaryl-4,5-dihydro-1*H*-pyrazoles, polyfluorinated 1,3,5-triaryl-4,5-dihydro-1*H*-pyrazoles, fluorescence spectra.

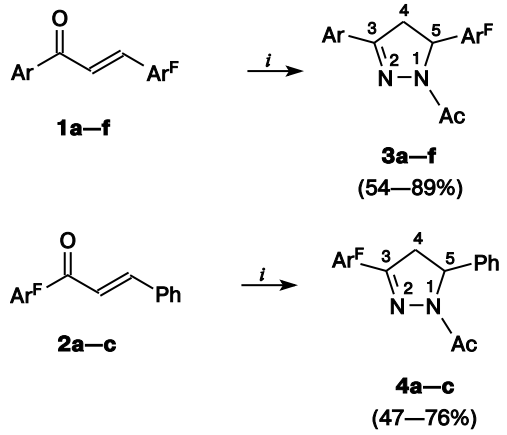
Chalcones (1,3-diphenyl-1-propen-2-ones, benzylideneacetophenones) possess high reactivity due to the presence of the carbonyl group conjugated with the double bond.[1] This instance suggests that the nucleophiles can react with chalcones at both the carbonyl group and the double bond. The reactions with binucleophiles leading to the broad range of heterocyclic compounds are of particular interest. Thus, the reactions of chalcones with phenylhydrazine gave common fluorophores, triarylpyrazolines.[2] Different pyrazoline derivatives, for example, mono- and dihalogen-substituted, possess a wide range of biological activities.[3—5]

Polyfluorinated chalcones contain additional reactive centers due to the presence of mobile nucleophilic fluorine atoms in the aromatic rings, which allow introduction of different substituents in the fluorinated ring. Penta- and decafluoro-substituted chalcones, pentafluorobenzylideneacetophenone, benzylidenepentafluoroacetophenone, and decafluorobenzylideneacetophenone were documented for the first time in Ref. 6. Later, we synthesized a series of polyfluorinated chalcone derivatives by nucleophilic substitution of the fluorine atoms at *para*- and/or *ortho*-positions of the perfluorophenyl ring with the amino, azido, arylalkoxy groups.[7]

The reactions of chalcone and its mono- and disubstituted derivatives with hydrazines under acidic conditions were extensively studied.[4,5,8,9] It was shown that the initial products of the reactions of these compounds with phenylhydrazine are arylhydrazones, which, in acetic acid, readily underwent ring closure to give 1,3,5-triaryl-2-pyrazolines. Under the similar conditions, the reactions with hydrazine hydrate afforded 1-acetyl-3,5-diaryl-2-pyrazolines.[5]

A number of hitherto unknown polyfluorinated triarylpyrazolines were synthesized by the reactions of polyfluorinated chalcones **1a** and **2a** with phenylhydrazine and pentafluorophenylhydrazine (Scheme 1); their spectral properties were studied.[10] However, conditions of the syntheses were described insufficiently. Besides, it was important to extend the range of the polyfluorinated triarylpyrazolines by introduction of different substituents affecting the positions of the maxima of electronic absorption and fluorescence in the perfluorinated ring.

Scheme 1



1, **3**: Ar = Ph, Ar^F = C_6F_5 (**a**), C_6F_4OPh (**b**), $C_6H_4N(CH_2)_5$ (**c**);
Ar = Ar^F = C_6F_5 (**d**), C_6F_4OPh (**e**), $C_6F_4N(CH_2)_5$ (**f**)
2, **4**: Ar^F = C_6F_5 (**a**), C_6F_4OPh (**b**), $C_6F_4N(CH_2)_5$ (**c**)

Reagent and conditions: $NH_2NH_2 \cdot H_2O$, AcOH, reflux, 6 h.

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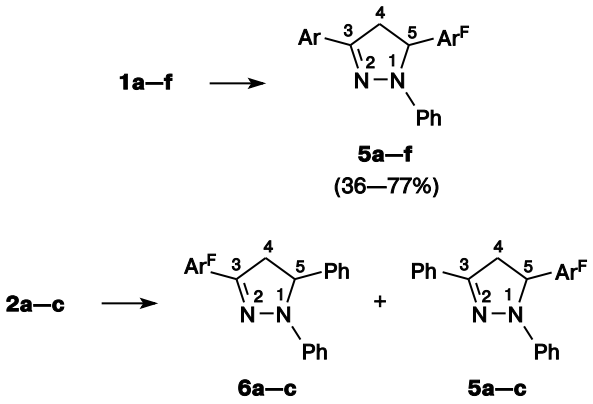
The aim of this work was to study the reaction of polyfluorinated chalcones **1a—f** and **2a—c** with hydrazine hydrate and phenylhydrazine.

Results and Discussion

Boiling of chalcones **1a—f** and **2a—c** with hydrazine hydrate in acetic acid resulted in polyfluorinated 1-acetyl-3,5-diarylpyrazolines **3a—f** and **4a—c** (see Scheme 1).

Under similar conditions, reactions of polyfluorinated chalcones with phenylhydrazine proceed ambiguously: chalcones **1a—f** gave expected triarylpyrazolines **5a—f**, while chalcones **2a—c** led to mixtures of two regioisomeric pyrazolines (in comparable amounts) differing in the substituents at the positions 3 and 5 (Scheme 2).

Scheme 2



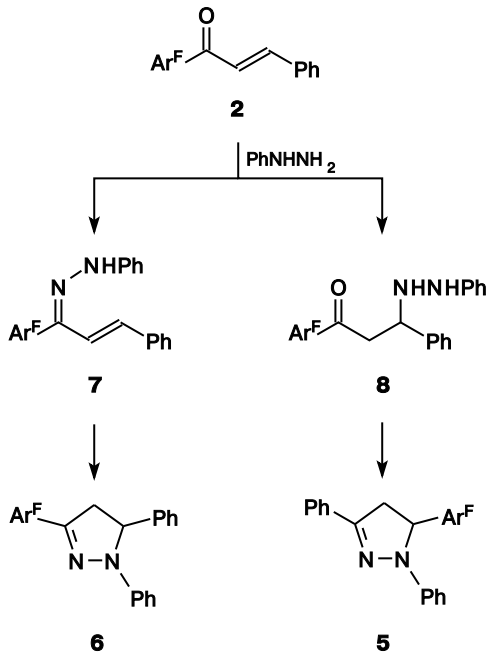
5: Ar = Ph, Ar^F = C_6F_5 (**a**), C_6F_4OPh (**b**), $C_6F_4N(CH_2)_5$ (**c**);
Ar = Ar^F = C_6F_5 (**d**), C_6F_4OPh (**e**), $C_6F_4N(CH_2)_5$ (**f**)
6: Ar^F = C_6F_5 (**a**), C_6F_4OPh (**b**), $C_6F_4N(CH_2)_5$ (**c**)

Reagent and conditions: PhNH—NH_2, AcOH, reflux, 6 h.

We suggested that the formation of pyrazolines **5a—c** along with expected compounds **6a—c** from chalcones **2a—c** bearing the polyfluorobenzoyl groups can result from the initial formation of both the corresponding phenylhydrazones **7** and compounds **8**, which are the products of nucleophilic addition of phenylhydrazine at the β-C atom (Scheme 3). The appearance of an electrophilic center at the β-C atom in chalcones **2** competitive to the carbonyl group can be explained by significant difference in the inductive constants σ* of the substituents at vinylene fragment, which affect the polarization of the latter (σ* = 2.58 for the C_6F_5CO group and σ* = 0.6 for the Ph group).[11] Thus, phenylhydrazine attacks both electrophilic centers and, as a result, two regioisomeric pyrazolines formed.

Pyrazolines **6a,b** were isolated from the isomeric mixtures by preparative TLC on Al_2O_3. Isolation of piperidine-substituted isomer **6c** from its mixture with compound **5c** failed.

Scheme 3



Structures of pyrazolines **3—6** were established based on ^1H, ^{19}F, and ^{13}C NMR spectroscopy and confirmed by elemental analysis. Yields and physicochemical data of the compounds synthesized are given in Tables 1 and 2, the ^1H NMR spectroscopy data are listed in Table 3.

The choice between structures **5a** and **6a** was done based on the following NMR data for isomer **5a**: 1) in the ^{19}F NMR spectrum, the broadening of the signals for the fluorine atoms at the *o*- and *m*-positions of the perfluorophenyl ring was observed, which is due probably to the steric hindrance impeding free rotation of the C_6F_5 group; 2) in the ^1H NMR spectrum, the down-field shift of the signal for the proton at the C(5) atom by 0.45 ppm as compared with that of the corresponding proton of isomer **6a** was observed, this fact is attributed to the electron-withdrawing effect of the C_6F_5 group; 3) in the ^{13}C NMR spectra, the signal for the C(5) atom shifted up-field (δ 53.16 as compared with δ 63.93 for the isomer **6a**).

Electronic absorption spectra and fluorescence spectra of triarylpyrazolines **5a—f** and **6a**,**b** were studied (Table 4). Fluorescence spectra of these compounds contained the typical bands with maxima at 434—472 nm symmetrical to the excitation spectra. The chromophoric system of triarylpyrazolines included the nitrogen atom with a lone electron pair, which interacted with the phenyl group at the position 1, the azomethyne bond, and the aryl residue at the position 3 of the heterocycle conjugated with the above-mentioned bond. In this regard, the structure of the

Table 1. Yields and physicochemical characteristics of polyfluorinated 1-acetylpyrazolines **3a—f** and **4a—c**

Compound	Ar	Ar^F	Yield (%)	m.p./°C (solvent)	Found / Calculated (%)				Molecular formula
					C	H	F	N	
3a	Ph	C_6F_5	89	110—113 (hexane)	57.70 / 57.63	2.98 / 3.13	26.76 / 26.81	7.78 / 7.91	$C_{17}H_{11}N_2OF_5$
3b	Ph	C_6F_4OPh-*p*	88	146—149 (ethanol)	64.58 / 64.49	4.09 / 3.76	17.73 / 17.74	6.45 / 6.54	$C_{23}H_{16}N_2O_2F_4$
3c	Ph	$C_6F_4NC_5H_{10}$-*p*	66	163—165 (hexane—benzene, 1 : 1)	62.91 / 62.99	5.05 / 5.05	17.98 / 18.12	9.99 / 10.01	$C_{22}H_{21}N_3OF_4$
3d	C_6F_5	C_6F_5	89	104—106 (hexane—ethanol)	46.02 / 45.96	1.34 / 1.36	43.14 / 42.77	6.46 / 6.31	$C_{17}H_6N_2OF_{10}$
3e	C_6F_4OPh-*p*	C_6F_4OPh-*p*	86	179—181 (ethanol)	58.67 / 58.79	2.75 / 2.72	25.35 / 25.66	4.64 / 4.73	$C_{29}H_{16}N_2O_3F_8$
3f	$C_6F_4NC_5H_{10}$-*p*	$C_6F_4NC_5H_{10}$-*p*	54	160—162 (ethanol)	56.69 / 56.45	4.55 / 4.56	26.5 / 26.46	9.87 / 9.75	$C_{24}H_{26}N_4OF_8$
4a	Ph	C_6F_5	69	90—92 (ethanol)	58.01 / 57.63	3.19 / 3.13	26.72 / 26.81	7.97 / 7.91	$C_{17}H_{11}N_2OF_5$
4b	Ph	C_6F_4OPh-*p*	47	73—76 (hexane)	64.99 / 64.49	3.71 / 3.76	17.95 / 17.74	6.74 / 6.54	$C_{23}H_{16}N_2O_2F_4$
4c	Ph	$C_6F_4NC_5H_{10}$-*p*	76	100—102 (ethanol)	62.92 / 62.99	5.30 / 5.05	17.98 / 18.12	10.07 / 10.01	$C_{22}H_{21}N_3OF_4$

aryl fragments in the positions 1 and 3 as well as the character of the substituents at these rings strongly affected the spectral fluorescent properties of triarylpyrazolines.[2] Thus, electron-withdrawing groups in the aryl fragment at the position 1 result in the bathochromic shifts of the bands in the absorption and fluorescence spectra, while electron-withdrawing groups in the aryl fragment at the position 3 give rise to the opposite effect. It has been shown that replacement of the phenyl ring by strong acceptor, the C_6F_5 group, resulted in the bathochromic shift of the maximum of the fluorescence in chloroform by 31 nm. This is in good agreement with the data given in Ref. 10, where it was found that the bathochromic shift in toluene is 17 nm. We found that 1,3,5-triphenyl-4,5-dihydro-1*H*-pyrazoline is chemically unstable in chloroform in contrast to polyfluorinated derivatives; this fact is consistent with the data on increase in photostability of dyes due to introduction of the fluorine atoms.[2] No effect on the optical properties of pyrazoline **6b** was found, when the *para*-fluorine atom of the pentafluorophenyl ring at the position 3 was displaced by the phenoxy group (Fig. 1). The C_6F_5 group at the position 5 is not included in the conjugation and, therefore, does not significantly affect the positions of the maxima of absorption and fluorescence. Besides, the fluorescence intensity of 5-C_6F_5-substituted triarylpyrazolines is one order of magnitude lower than that of 3-substituted derivatives. Triarylpyrazoline bearing two perfluorophenyl groups **5d** and its substituted derivatives **5e** and **5f** exhibited almost identical positions of the maxima of the fluorescence shifted bathochromically by ~15—20 nm as compared with the fluorescence maximum of triphenylpyrazoline.

In summary, novel polyfluorinated derivatives of di- and triarylpyrazolines were synthesized by the reaction of polyfluorinated chalcones with hydrazine hydrate and phenylhydrazine. It was found that chalcone **2a** bearing perfluorobenzoyl group and its derivatives **2b** and **2c** containing substituents at the perfluorinated ring react with phenylhydrazine simultaneously on two directions: at the carbonyl group and at the β-C atoms giving different regio-

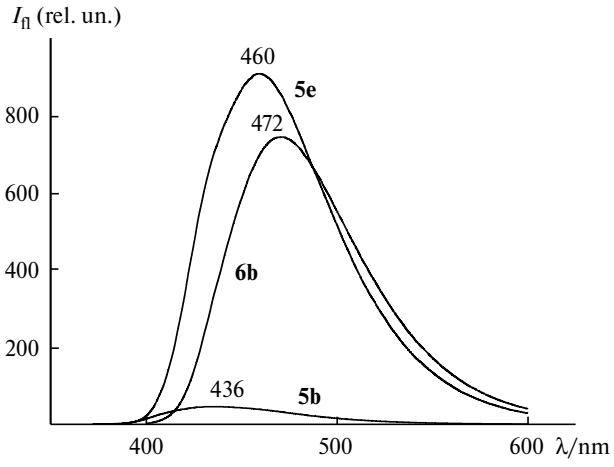


Fig. 1. Fluorescence spectra of compounds **5b**, **5e**, and **6b**.

Table 2. Yields and physicochemical characteristics of polyfluorinated triarylpyrazolines **5a—f** and **6a—c**

Starting chalcone	Product	Ar	Ar^F	Yield (%)	m.p./°C (solvent)	Found / Calculated (%)				Molecular formula
						C	H	F	N	
1a	**5a**	Ph	C_6F_5	36[a]	171—174[b] (hexane)	—	—	—	—	
1b	**5b**	Ph	C_6F_4OPh-*p*	64	150—152[c]	70.02 70.12	3.94 3.92	16.44 16.43	3.94 6.06	$C_{27}H_{18}N_2OF_4$
1c	**5c**	Ph	$C_6F_4NC_5H_{10}$-*p*	64	182—184 (benzene)	69.34 68.86	5.24 5.11	16.64 16.76	9.29 9.27	$C_{26}H_{23}N_3F_4$
1d	**5d**	C_6F_5	C_6F_5	51	163—166 (hexane)	52.81 52.73	1.54 1.69	39.91 39.72	5.87 5.86	$C_{21}H_8N_2F_{10}$
1e	**5e**	C_6F_4OPh-*p*	C_6F_4OPh-*p*	77[a]	155—158 (50% EtOH)	63.39 63.26	2.99 2.90	24.58 24.26	4.45 4.47	$C_{33}H_{18}N_2O_2F_8$
1f	**5f**	$C_6F_4NC_5H_{10}$-*p*	$C_6F_4NC_5H_{10}$-*p*	40[a]	170—172[c]	61.25 61.18	4.67 4.64	24.82 24.97	9.27 9.21	$C_{31}H_{28}N_4F_8$
2a	**5a**	Ph	C_6F_5	30[a]	—	—	—	—	—	—
	6a	Ph	C_6F_5	21[a]	130—132[b] (hexane)	—	—	—	—	—
2b	**5b**	Ph	C_6F_5	27[a]	—	70.57[d] 70.12	4.01 3.92	16.8 16.43	6.13 6.06	$C_{27}H_{18}N_2OF_4$
	6b	Ph	C_6F_4OPh-*p*	28[a]	110—112 (EtOH)					
2c	**5c**	Ph	$C_6F_4NC_5H_{10}$-*p*	35[a]	—	69.09[d] 68.86	5.03 5.11	16.79 16.76	9.31 9.27	$C_{26}H_{23}N_3F_4$
	6c	Ph	$C_6F_4NC_5H_{10}$-*p*	35[a]	—					

[a] Yields were calculated based on the data from the ^{19}F NMR spectra of the reaction mixtures.
[b] Compounds were previously documented;[10] m.p. and elemental analysis data are coincided with published data.
[c] Pure compound was isolated by column chromatography on Al_2O_3 using benzene as eluent.
[d] Elemental analysis is given for the mixture of isomers.

Table 3. ^1H and ^{19}F NMR spectra of pyrazolines **3a—f**, **4a—c**, **5a—f**, and **6a—c** in $CDCl_3$

Compound	^1H NMR, δ (*J*/Hz)	^{19}F NMR, δ (intensity ratio)
3a	2.35 (s, 3 H, MeCO); 3.25 (dd, 1 H, H_a(4), J_1 = 18.0, J_2 = 6.0); 3.77 (dd, 1 H, H_b(4), J_1 = 18.0, J_2 = 12.5); 5.81 (dd, 1 H, H(5), J_1 = 12.5, J_2 = 6.0); 7.38—7.76 (m, 5 H, Ph)	0.07, 7.10, 18.49 (2 : 1 : 2)
3b	2.42 (s, 3 H, MeCO); 3.34 (dd, 1 H, H_a(4), J_1 = 18.0, J_2 = 6.5); 3.82 (dd, 1 H, H_b(4), J_1 = 18.0, J_2 = 12.5); 5.90 (dd, 1 H, H(5), J_1 = 12.5, J_2 = 6.5); 6.90—7.82 (m, 10 H, 2 Ph)	10.53, 20.82 (1 : 1)
3c	1.59 (m, 6 H); 3.13 (m, 4 H, $C_6F_4N(CH_2)_5$); 2.33 (s, 3 H, MeCO); 3.24 (dd, 1 H, H_a(4), J_1 = 18.0, J_2 = 6.0); 3.70 (dd, 1 H, H_b(4), J_1 = 18.0, J_2 = 12.0); 6.25 (dd, 1 H, H(5), J_1 = 12.0, J_2 = 6.0); 7.24—7.73 (m, 5 H, Ph)	10.20, 15.43 (1 : 1)
3d	2.31 (s, 3 H, MeCO); 3.29 (dd, 1 H, H_a(4), J_1 = 19.0, J_2 = 6.0); 3.82 (dd, 1 H, H_b(4), J_1 = 19.0, J_2 = 13.0); 5.81 (dd, 1 H, H(5), J_1 = 13.0, J_2 = 6.0)	0.42, 1.03, 7.77, 11.22, 18.45, 23.85 (2 : 2 : 1 : 1 : 2 : 2)
3e	2.36 (s, 3 H, MeCO); 3.38 (dd, 1 H, H_a(4), J_1 = 18.0, J_2 = 6.5); 3.86 (dd, 1 H, H_b(4), J_1 = 18.0, J_2 = 13.0); 5.87 (dd, 1 H, H(5), J_1 = 13.0, J_2 = 6.5); 6.98—7.37 (m, 10 H, 2 Ph)	7.87, 8.42, 17.95, 23.23 (1 : 1 : 1 : 1)
3f	1.58 (m, 12 H); 3.15 (m, 8 H, 2 $C_6F_4N(CH_2)_5$); 2.31 (s, 3 H, MeCO); 3.30 (dd, 1 H, H_a(4), J_1 = 18.5, J_2 = 6.0); 3.74 (dd, 1 H, H_b(4), J_1 = 18.5, J_2 = 12.6); 5.73 (dd, 1 H, H(5), J_1 = 12.7, J_2 = 6.0)	10.11, 10.31, 15.48, 21.15 (1 : 1 : 1 : 1)
4a	2.37 (s, 3 H, MeCO); 3.18 (dd, 1 H, H_a(4), J_1 = 8.0, J_2 = 5.0); 3.82 (dd, 1 H, H_b(4), J_1 = 18.0, J_2 = 12.0); 5.55 (dd, 1 H, H(5), J_1 = 12.0, J_2 = 5.0); 7.16—7.35 (m, 5 H, Ph)	0.71, 10.51, 23.80 (2 : 1 : 2)

(*to be continued*)

Table 3 (*continued*)

Compound	^{1}H NMR, δ (*J*/Hz)	^{19}F NMR, δ (intensity ratio)
4b	2.42 (s, 3 H, MeCO); 3.25 (dd, 1 H, H_a(4), J_1 = 18.5, J_2 = 5.0); 3.88 (dd, 1H, H_b(4), J_1 = 18.5, J_2 = 12.0); 5.60 (dd, 1 H, H(5), J_1 = 12.0, J_2 = 5.0); 6.85—7.45 (m, 10 H, 2 Ph)	8.22, 23.09 (1 : 1)
4c	1.62 (m, 6 H); 3.19 (m, 4 H, $C_6F_4N(CH_2)_5$); 2.39 (s, 3 H, MeCO); 3.27 (dd, 1 H, H_a(4), J_1 = 17.5, J_2 = 6.0); 3.75 (dd, 1 H, H_b(4), J_1 = 17.0, J_2 = 12.5); 5.82 (dd, 1 H, H(5), J_1 = 12.5, J_2 = 6.0); 7.44—7.77 (m, 5 H, Ph)	10.17, 15.42 (1 : 1)
5a	3.33 (dd, 1 H, H_a(4), J_1 = 18.0, J_2 = 6.5); 3.89 (dd, 1 H, H_b(4), J_1 = 18.0, J_2 = 13.0); 5.75 (dd, 1 H, H(5), J_1 = 13.0, J_2 = 6.5); 6.80—7.79 (m, 10 H, 2 Ph)	0.87, 7.96 (br), 19.58 (br) (2 : 1 : 2)
5b	3.36 (dd, 1 H, H_a(4), J_1 = 17.5, J_2 = 6.0); 3.88 (dd, 1 H, H_b(4), J_1 = 17.5, J_2 = 12.5); 5.76 (dd, 1 H, H(5), J_1 =12.5, J_2 = 6.0); 6.79—7.77 (m, 15 H, 3 Ph)	8.37, 18.96 (1 : 1)
5c	1.62 (m, 6 H); 3.17 (m, 4 H, $C_6F_4N(CH_2)_5$); 3.31 (dd, 1 H, H_a(4), J_1 = 17.0, J_2 = 6.0); 3.83 (dd, 1 H, H_b(4), J_1 = 17.0, J_2 = 13.0); 5.68 (dd, 1 H, H(5), J_1 = 13.0, J_2 = 6.0); 6.78—7.80 (m, 10 H, 2 Ph)	10.82, 16.38 (1 : 1)
5d	3.36 (dd, 1 H, H_a(4), J_1 = 18.0, J_2 = 6.0); 3.93 (dd, 1 H, H_b(4), J_1 = 18.0, J_2 = 13.0); 5.80 (dd, 1 H, H(5), J_1 = 13.0, J_2 = 6.0); 6.85—7.31 (m, 10 H, 2 Ph)	–0.22, 1.35, 7.80, 22.59, 8.87, 19.56, (2 : 2 : 1 : 1 : 2 : 2)
5e	3.47 (dd, 1 H, H_a(4), J_1 = 18.0, J_2 = 6.0); 3.99 (dd, 1 H, H_b(4), J_1 = 18.0, J_2 = 13.5); 5.84 (dd, 1 H, H(5), J_1 = 13.5, J_2 = 6.0); 6.86—7.40 (m, 15 H, 3 Ph)	7.39, 8.72, 19.01, 22.05 (1 : 1 : 1 : 1)
5f	1.62 (m, 12 H); 3.19 (m, 8 H, 2 $C_6F_4N(CH_2)_5$); 3.35 (dd, 1 H, H_a(4), J_1 = 17.0, J_2 = 7.0); 3.76 (dd, 1 H, H_b(4), J_1 = 17.0, J_2 = 13.0); 5.65 (dd, 1 H, H(5), J_1 = 13.0, J_2 = 7.0); 6.76—7.26 (m, 5 H, Ph)	9.71, 10.90, 16.50, 20.05 (1 : 1 : 1 : 1)
6a	3.21 (dd, 1 H, H_a(4), J_1 = 18.0, J_2 = 8.0); 3.90 (dd, 1 H, H_b(4), J_1 = 18.0, J_2 = 13.0); 5.30 (dd, 1 H, H(5), J_1 = 13.0, J_2 = 8.0); 6.78—7.40 (m, 10 H, 2 Ph)	–0.50, 6.99, 22.45 (2 : 1 : 2)
6b	3.25 (dd, 1 H, H_a(4), J_1 = 17.0, J_2 = 7.0); 3.94 (dd, 1 H, H_b(4), J_1 = 17.0, J_2 = 13.0); 5.32 (dd, 1 H, H(5), J_1 = 13.0, J_2 = 7.0); 6.78—7.38 (m, 15 H, 3 Ph)	7.09, 21.91 (1 : 1)
6c	1.66 (m, 6 H); 3.22 (m, 4 H, 2 $C_6F_4N(CH_2)_5$); 3.20 (dd, 1 H, H_a(4), J_2 = 9.0); 3.88 (dd, 1 H, H_b(4), J_2 = 13.0); 5.23 (dd, 1 H, H(5), J_1 = 13.0, J_2 = 9.0); 6.75—7.74 (m, 10 H, 2 Ph)	9.69, 19.90 (1 : 1)

isomers of triarylpyrazolines. Spectral and fluorescent properties of the synthesized polyfluorinated triarylpyrazolines were studied.

Table 4. Absorption (*A*) and fluorescence* (fl) spectra of compounds **5a—f** and **6a—b**

Compound	$\lambda_{max}(A)$/nm (lgε)	λ_{max}^{fl}/nm (I_{fl})
5a	354 (4.28)	433 (36)
6a	356 (4.07)	471 (666)
5d	357 (4.46)	458 (724)
5b	355 (4.25)	436 (46)
6b	362 (4.22)	472 (744)
5e	363 (4.19)	460 (908)
5c	357 (4.59)	436 (423)
5f	367 (4.37)	452 (107)
**	—	439

* The fluorescence spectra were recorded using excitation at 362 nm.

** 1,3,5-Triphenyl-4,5-dihydro-1*H*-pyrazoline.

Experimental

The NMR spectra were recorded on Bruker AC-200 (200.13 MHz for ^{1}H and 188.2 MHz for ^{19}F) and Bruker AV-600 (600.30 MHz for ^{1}H, 150.94 MHz for ^{13}C, and 564.76 MHz for ^{19}F) in $CDCl_3$. Chemical shifts are given in the δ scale relative to C_6F_6 (^{19}F NMR) and residual signal of the protons of $CDCl_3$ (^{1}H and ^{13}C NMR). Electron absorption spectra were recorded on a Hewlett Packard 8453 spectrophotometer; excitation and fluorescence spectra were obtained on a Varian Cary Eclipse spectrofluorimeter in chloroform.

Starting chalcones **1a**, **1d**, and **2a** were synthesized by the known procedures,[6] *para*-substituted chalcones were prepared according to the known method[7].

Reactions of chalcones 1a—f, 2a—c with hydrazine hydrate and phenylhydrazine (general procedure). Acetic acid (10 mL) was added to a mixture of chalcone (1 mmol) and hydrazine hydrate or phenylhydrazine (5 mmol), and the reaction mixture was refluxed for 6 h. After cooling to room temperature, the reaction mixture was poured onto ice, the precipitate that formed was filtered off, washed with water until neutral, and air-dried. The products were analyzed by ^{1}H and ^{19}F NMR spectroscopy. The products were purified by recrystallization or column chro-

matography (see Tables 1 and 2). The mixtures of isomers **5a** and **6a**, **5b** and **6b** were separated by TLC on Al_2O_3, elution with a hexane—benzene mixture (3 : 1)—(5 : 1).

5-Perfluorophenyl-1,3-diphenyl-4,5-dihydro-1*H*-pyrazole (5a). ^{13}C NMR, δ: 40.70 C(4), 53.18 C(5), 113.07, 119.86, 125.70, 128.54, 128.84, 129.12, 132.01, 143.77, 146.61 C(3).

3-Perfluorophenyl-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole (6a). ^{13}C NMR, δ: 45.93 C(4), 63.91 C(5), 113.77, 120.23, 125.73, 127.79, 128.91, 129.19, 141.49, 143.68 C(3).

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