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Formyl Derivatives of Amino-Substituted Polyfluorotriphenyl-4,5-dihydro-1*H*-pyrazoles: Synthesis and Use as Donor Blocks of Nonlinear Optical Chromophores

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Abstract—A series of new formyl derivatives of polyfluorinated triphenyl-4,5-dihydro-1*H*-pyrazoles containing various amine residues in the fluorinated benzene ring have been synthesized and used as donor building blocks in the synthesis of donor–acceptor dyes as potential chromophores for nonlinear electro-optics. Effects of substituents in the donor and acceptor moieties of the obtained chromophores on their spectral characteristics have been studied.

Keywords: formylation, polyfluorotriarylpyrazolines, donor–acceptor structures, nonlinear optical chromophores, electronic absorption spectra.

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Dipolar chromophores with a high molecular polarizability are promising for the design of nonlinear optical (NLO) materials used in electro-optical modulators [1–3]. Such properties are intrinsic to unsymmetrical polymethine dyes containing strong electron-withdrawing and electron-donating groups as terminal fragments [4–6]. Donor fragments of these dyes are commonly obtained from dialkylamino-substituted aromatic aldehydes as starting materials. We propose to build up donor fragments from aldehydes of the polyfluorinated triaryldihydropyrazole series, which can be regarded as heterocyclic analogs of dialkylaminobenzaldehydes. Pyrazole derivatives have already been reported as donor moieties of NLO chromophores [7]; in these cases, the aldehyde group was directly linked to the pyrazole ring.

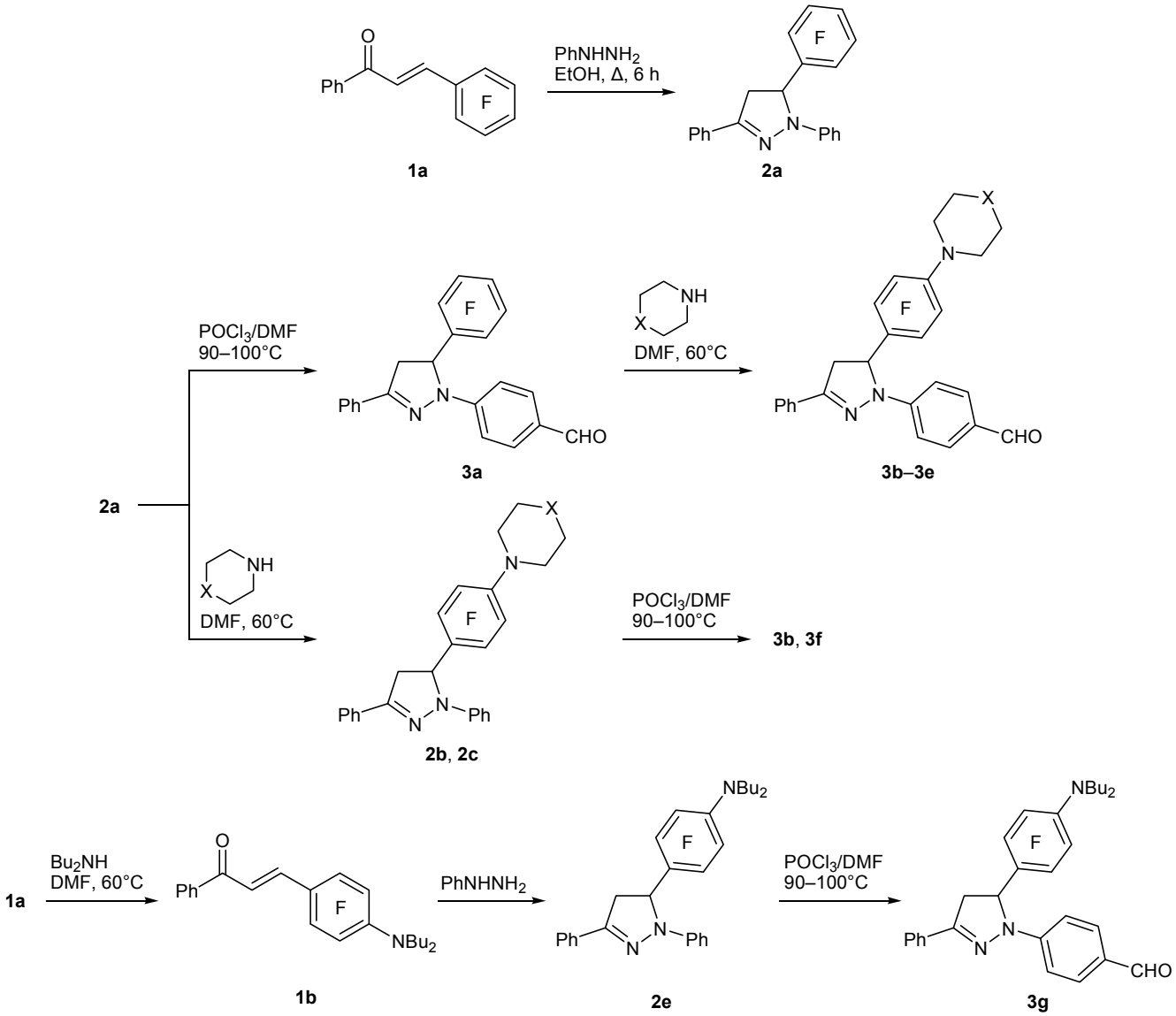
We previously synthesized polyfluorinated triaryldihydropyrazoles [8] which showed strong fluorescence and enhanced photostability in comparison to fluorine-free analogs. The presence of perfluorophenyl substituents provides the possibility of further functionalization via replacement of fluorine atoms by various nucleophilic groups [9, 10]. Formyl derivatives of perfluorophenyl-substituted dihydropyrazoles were used by us to obtain styryl type chromophores containing thioflavylium groups as acceptor moieties [11]. In this work we synthesized new aldehydes on the basis of polyfluorinated triaryldihydropyrazoles containing various amino groups in the fluorinated phenyl ring and used them in the synthesis of NLO chromophores. The amine residues were derived from piperidine, dibutylamine, and piperazine. Replacement of the *para*-fluorine atom in pentafluorophenyl ring by an electron-donating group reduces its acceptor power, and the donor substituent nature affects such important properties of the resulting chromophore as solubility, thermal stability, film-forming ability, and spectral characteristic. A spirocyclic fragment usually improves film-forming properties, whereas dibutylamino group increases the solubility and makes it possible to com-

pare nonlinear optical and electro-optical properties of the chromophore with those of analogous dye derived from 4-(dibutylamino)benzaldehyde [12]. The presence of functional groups in the substituent gives rise to additional ways of further modification. For instance, 4-hydroxypiperidine and piperazine fragments can be subjected to acylation, in particular with a branched reagent to obtain a dendritic structure.

In the general case, the synthesis of aldehydes based on polyfluorinated triaryldihydropyrazoles included three stages: (1) condensation of pentafluorobenzylideneacetophenone **1a** with phenylhydrazine to give dihydropyrazole **2a**, (2) Vilsmeier formylation of **2a** to aldehyde **3a**, and (3) nucleophilic substitution of the *para*-fluroine atom in the fluorinated benzene ring of **3a** by secondary amine. We thus obtained aldehydes **3b**–**3e** (Scheme 1). When the formylation was preceded by substitution of fluorine in **2a** by 4-hydroxypiperidine residue, the subsequent reaction of **2c** with $POCl_3$/DMF was accompanied by replacement of the hydroxy group by chlorine to give aldehyde **3f**. The fluorine atom in both **2a** and **3a** was readily replaced by piperidine residue; however, we succeeded in introducing dibutylamino group only into the initial chalcone **1a** molecule (Scheme 1).

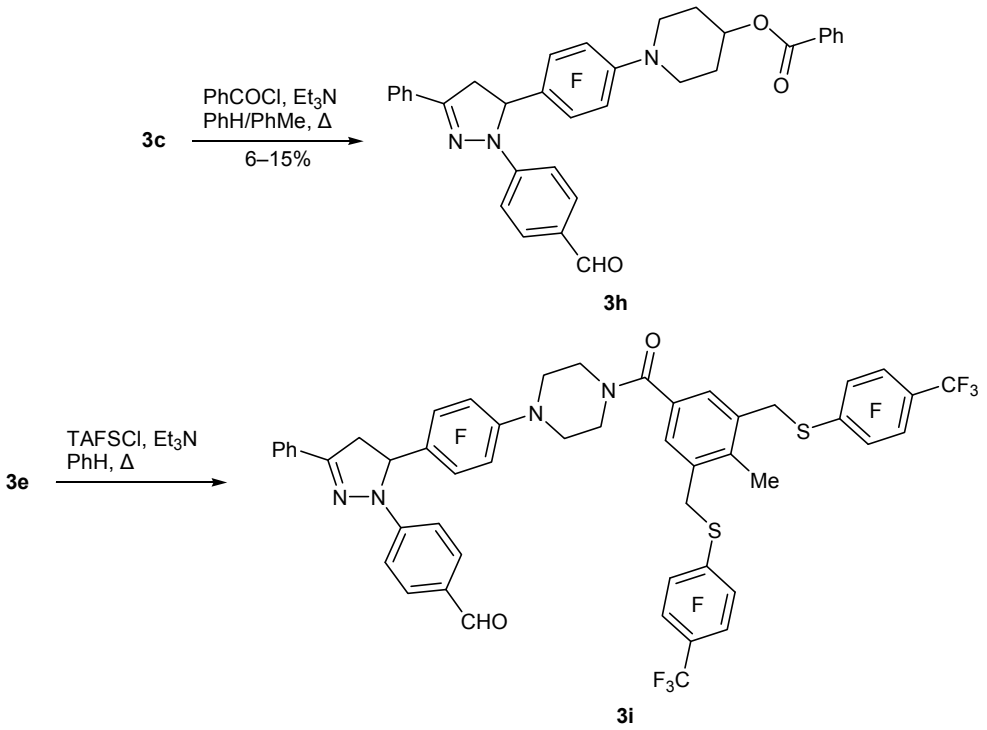
It is known that electro-optical properties of chromophores are largely determined by the presence of bulky spacers, including those with a branched

Scheme 1.



2, **3**, X = CH_2 (**b**), CHOH (**c**), 1,3-dioxolane-2,2-diyl (**d**), NH (**e**), CHCl (**f**).

Scheme 2.

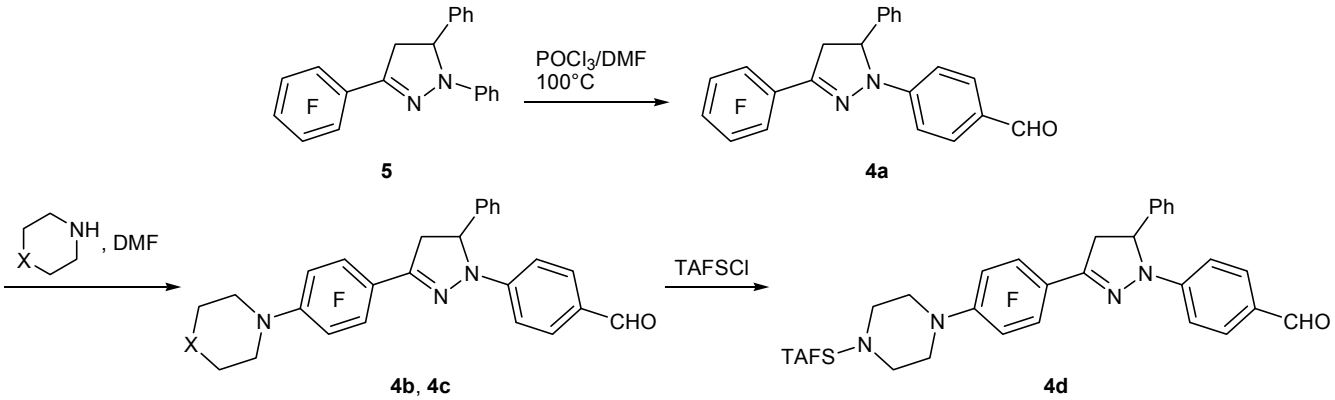


(dendritic) structure, in both donor and acceptor moieties [12]. We modified the donor moiety by acylation of the hydroxypiperidine fragment of **3c** with benzoyl chloride in boiling benzene or toluene in the presence of triethylamine. However, the yield of **3h** was poor (6% in benzene and 15% in toluene), and the most part of initial aldehyde **3c** remained unchanged. The acylation of piperazine derivative **3e** with a dendritic agent, 4-methyl-3,5-bis{[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenylsulfanyl]methyl}benzoyl chloride (TAFSCl, **T**oluic **A**cid, **F**luorinated **S**ulfide, **C**hloride) in benzene in the presence of Et_3N afforded amide **3i** (Scheme 2).

In order to compare the reactivities of regioisomeric aldehydes containing a polyfluorinated phenyl ring in position *3* or *5* of the dihydropyrazole heterocycle and spectral characteristics of chromophores obtained therefrom, we synthesized aldehydes **4a**–**4c** according to a similar scheme starting from dihydropyrazole **5** (Scheme 3).

Aldehydes **3b**–**3i**, **4b**, and **4d** were then used as donor blocks in the synthesis of chromophores. The acceptor moieties of NLO chromophores are generally obtained from furan or pyrrole derivatives with electron-withdrawing substituents such as cyano and/or trifluoromethyl groups. As shown previously [12],

Scheme 3.



4, X = CH_2 (**b**), NH (**c**).

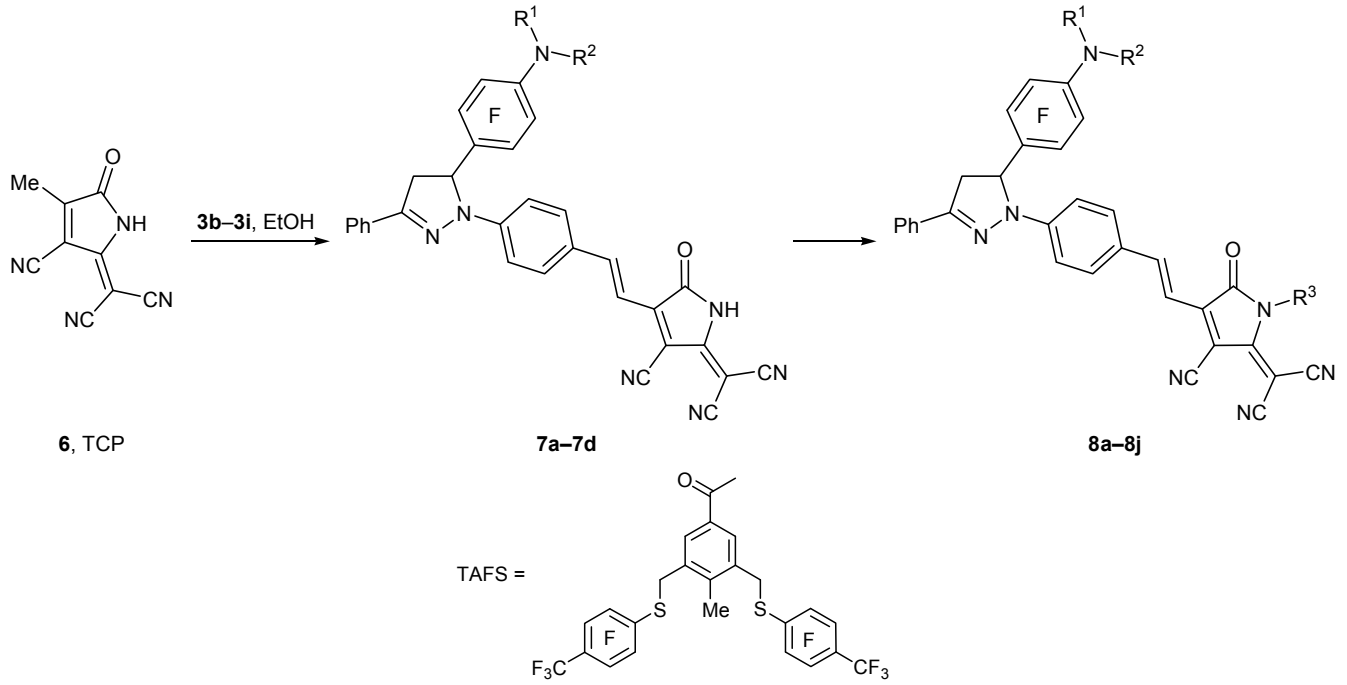
chromophores with pyrrole-based acceptor moieties are characterized by a considerable red shift (up to 100 nm) of the long-wavelength absorption maximum in comparison to furan derivatives. Therefore, we used 2-(3-cyano-4-methyl-5-oxo-1,5-dihydro-2*H*-pyrrol-2-ylidene)propanedinitrile (**6**, TCP) [12] to build up the acceptor moiety. By condensation of **3b**–**3i** with TCP we obtained dyes **7a**–**7d** which were further modified at the pyrrole NH group by treatment with diethyl sulfate, benzyl chloride, benzoyl chloride, and TAFSCl. As a result, chromophores **8a**–**8j** were synthesized (Scheme 4). We failed to introduce two TAFS fragments into molecule **3c** by simultaneous acylation of the hydroxy group in the piperidine residue and nitrogen atom of the dihydropyrrole ring, and the product contained only one TAFS residue on the nitrogen atom. However, the acylation of piperazine derivative **7c** with TAFSCl gave dye **8g** containing two dendritic fragments in the donor and acceptor moieties. Likewise, from aldehydes **4b** and **4d** we obtained dyes **9a**, **9b**, **10a**, and **10b** (Scheme 5).

The yields of **7** and **9** did not exceed 50%, and in all cases the reaction mixtures contained a bright orange impurity. The latter was isolated in the synthesis of **7a** from **3b** and TCP and was identified as 2-amino-4-(4-{5-[4-(piperidin-1-yl)-2,3,5,6-tetrafluorophenyl]-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl}phenyl)buta-1,3-diene-1,1,3-tricarbonitrile (**11**). Obviously, compound **11** is the condensation product of aldehyde **3b** and malononitrile dimer (2-aminoprop-1-ene-1,1,3-tricarbonitrile) which is likely to remain in the reaction mixture in the synthesis of TCP despite twofold excess of ethyl pyruvate or exist in equilibrium with TCP (Scheme 6).

The optimal conditions for the reaction of most aldehydes **3** with TCP were stirring of the reaction mixture at 50–55°C for 4–5 h; the highest yield of **7** was thus attained. For instance, the yield of **7a** was only 22% when the reaction mixture was refluxed for 1 h [12], and it increased to 42% at 55°C. Regardless of the conditions, only traces of the target dye were detected in the reaction with aldehyde **3d** containing a 1,4-dioxa-8-azaspiro[4.5]decane residue, whereas the initial aldehyde remained mostly unchanged. Compounds **4b** and **4d** in which the fluorinated benzene ring is attached to C^3 of the pyrazole ring and is conjugated to the aldehyde group also exhibited low reactivity toward TCP.

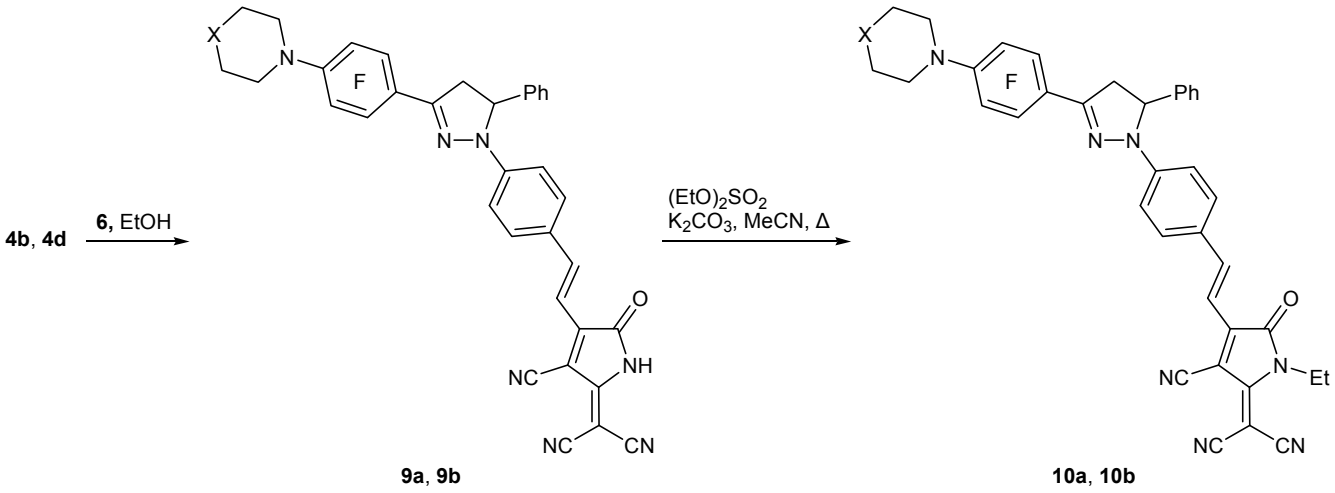
The structure of the synthesized dyes and their precursors was determined on the basis of their ^{1}H and ^{19}F NMR and mass spectra. The ^{1}H NMR spectra of all compounds displayed signals of three protons of the

Scheme 4.



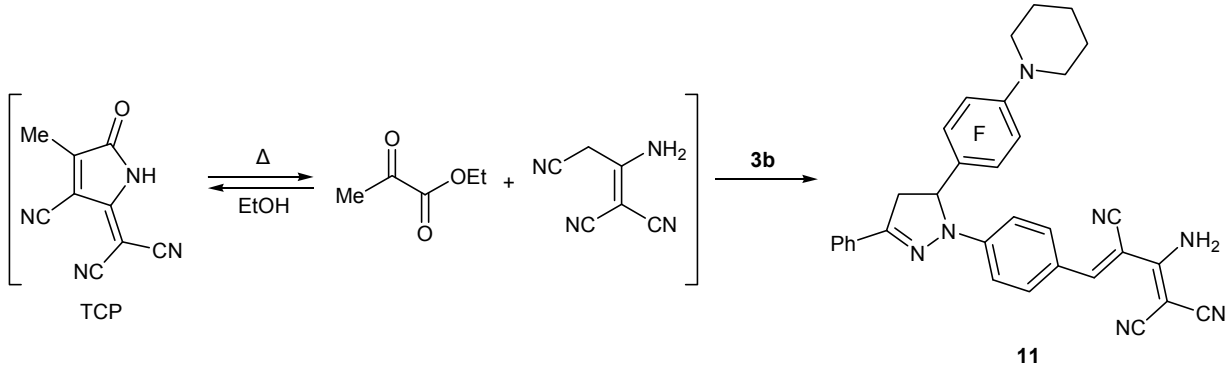
7, R^1R^2N = piperidin-1-yl (**a**), 4-hydroxypiperidin-1-yl (**b**), 4-TAFS-piperazin-1-yl (**c**); R^1 = R^2 = *n*-Bu (**d**); **8**, R^1R^2N = piperidin-1-yl, R^3 = Et (**a**), $PhCH_2$ (**b**), PhCO (**c**), TAFS (**d**); R^1R^2N = 4-hydroxypiperidin-1-yl, R^3 = TAFS (**e**); R^1R^2N = 4-TAFS-piperazin-1-yl, R^3 = Et (**f**), TAFS (**g**); R^1 = R^2 = *n*-Bu, R^3 = Et (**h**), PhCO (**i**), TAFS (**j**).

Scheme 5.



X = CH_2 (**a**), N-TAFS (**b**).

Scheme 6.



dihydropyrazole ring as an *ABX* spin system characterized by one geminal and two vicinal ^1H–^1H coupling constants, as well as signals of aromatic protons and protons of aliphatic and alicyclic fragments present in their molecules. Protons at the exocyclic double C=C bond gave rise to an *AB* system with a coupling constant ^3J of ~16 Hz corresponding to *E* configuration of the double bond. In the ^1H NMR spectra of **7** in DMSO-d_6, the NH proton resonated as a broadened downfield signal at about 12.7 ppm. The ^{19}F NMR spectra contained two signals from four pairwise equivalent fluorine atoms in the *para*-substituted tetrafluorophenyl ring. The *ortho*-fluorine signals of compounds with the fluorinated benzene ring on C^5 were strongly broadened, presumably due to steric hindrances created by the phenyl substituent on N^1; no such broadening was observed in the spectra of 3-(tetrafluorophenyl) isomers. The ^{19}F NMR spectra of compounds with TAFS substituents showed additional triplets of CF_3 groups (δ_F > 100 ppm) and signals of aromatic fluorines.

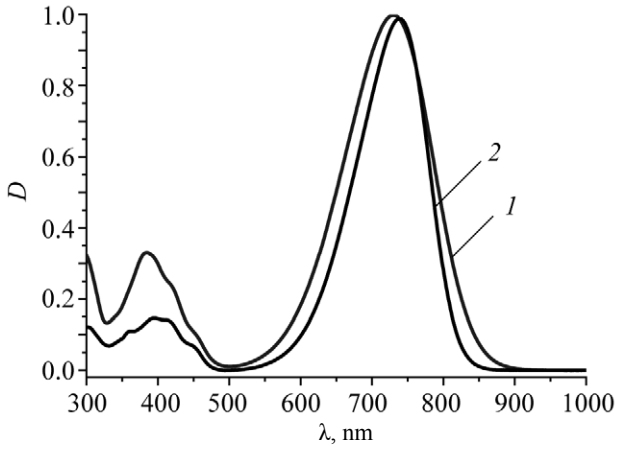
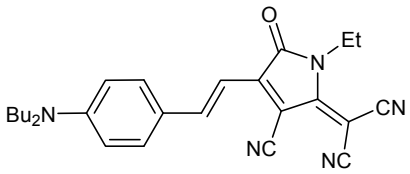


Fig. 1. Normalized electronic absorption spectra of compounds (*1*) **8h** and (*2*) **12** in chloroform.

Figure 1 shows the electronic absorption spectra of **8h** in chloroform at a concentration of about 10^{-4} M and of its analog **12** [12] with a dibutylaminophenyl



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substituent as donor fragment. It is seen that the absorption spectra of **8h** and **12** are almost identical to each other. The most intense long-wavelength band originates from intramolecular charge transfer involving orbitals of the donor and acceptor fragments. Taking into account that the acceptor moieties of **8h** and **12** are similar, the donor power of the dihydropyrazole fragment in the D–A chromophore is similar to that of the 4-(dibutylamino)phenyl fragment of **12**; therefore, polyfluorinated triaryldihydropyrazole derivatives can be used as efficient donors in the design of NLO chromophores.

The long-wavelength absorption maxima and molar absorption coefficients of compounds **7**–**10** are collected in Table 1. It is seen that the nature of amino group in the fluorinated ring of **7a**–**7d** (piperidine, piperazine, 4-hydroxypiperidine, dibutylamine) almost does not affect the position of the absorption maximum which is located in the region λ 725–735 nm; the effect of the 4-hydroxypiperidino group is most appreciable. On the other hand, the effect of the substituent on the pyrrole nitrogen atom in the acceptor TCP moiety was more significant. The absorption maximum of **7a** (NH group) is located at λ 728 nm, while replacement of the NH hydrogen by ethyl, benzyl, benzoyl, and TAFS groups leads to red shift of the absorption maximum to λ 738, 743, 756, and 768 nm, respectively, in keeping with the acceptor power of the N-substituent. The effect of substituents in the donor moiety of chromophores on their spectral characteristics depended on the position of the polyfluorophenyl group in the dihydropyrazole ring (C^3 or C^5), as well as on the substituent in the fluorinated ring. The positions of the absorption maxima of regioisomeric piperidine derivatives are similar (cf. **7a** and **9a**, **8a** and **10a**), whereas the 3-isomers containing a TAFS-piperazine residue showed a small blue shift of the absorption maximum relative to that of the corresponding 5-isomers (cf. **7c** and **9b**, **8f** and **10b**). Obviously, introduction of an acceptor dendritic TAFS fragment into the donor moiety through an alicyclic spacer insignificantly influences the absorption spectrum. In particular, compound **8g** containing TAFS substituents in both donor and acceptor moieties absorbs at λ_{max} 760 nm, i.e., almost in the same region as dye **8j**

Table 1. Electronic absorption spectra of compounds **7a**–**7d**, **8a**–**8j**, **9a**, **9b**, **10a**, and **10b** in chloroform

Compound no.	R^1R^2N	R^3	λ_{max}, nm	log ε
7a	Piperidin-1-yl	H	728	4.84
7b	4-Hydroxypiperidin-1-yl	H	735	–[a]
7c	4-TAFS-piperazin-1-yl	H	726	4.86
7d	Bu_2N	H	725	4.81
8a	Piperidin-1-yl	Et	731	4.85
8b	Piperidin-1-yl	$PhCH_2$	743	4.87
8c	Piperidin-1-yl	PhCO	754	4.87
8d	Piperidin-1-yl	TAFS	769	4.91
8e	4-Hydroxypiperidin-1-yl	TAFS	765	4.89
8f	4-TAFS-piperazin-1-yl	Et	724	4.80
8g	4-TAFS-piperazin-1-yl	TAFS	760	4.82
8h	Bu_2N	Et	730	4.81
8i	Bu_2N	PhCO	757	4.91
8j	Bu_2N	TAFS	763	4.88
9a	Piperidin-1-yl	H	728	4.80
9b	4-TAFS-piperazin-1-yl	H	714	4.83
10a	Piperidin-1-yl	Et	733	4.82
10b	4-TAFS-piperazin-1-yl	Et	716	–[a]

[a] Not determined.

(λ_{max} 763 nm) with only one TAFS fragment in the acceptor moiety.

The NLO parameters of materials for electro-optical modulators are commonly measured at λ 1310 nm, i.e., in the transparency region of optical fiber. Shift of absorption spectrum toward that wavelength can be achieved as a result of extension of conjugation chain or/and increase of electron-withdrawing power of the acceptor moiety. Enhancement of the acceptor properties of the TCP fragment by introduction of additional electron-withdrawing substituents increases charge separation upon excitation of donor–acceptor chromophore and increases its hyperpolarizability at the molecular level. A relation between large nonlinear susceptibility values and intramolecular charge transfer was found in a large number of examples [13].

In summary, we have synthesized a series of new aldehydes on the basis of polyfluorinated triaryldihydropyrazoles and shown that these compounds are promising as donor blocks of donor–acceptor NLO chromophores with a wide possibility of further modification.

EXPERIMENTAL

The spectral and analytical data were obtained at the Joint Chemical Research Center, Siberian Branch, Russian Academy of Sciences. The ^{1}H and ^{19}F NMR spectra were recorded on a Bruker AV-300 instrument (Germany) at 300.13 and 282.37 MHz, respectively, using $CDCl_3$ as solvent and reference ($CHCl_3$, δ 7.24 ppm); the ^{19}F chemical shifts were determined relative to C_6F_6. The electronic absorption spectra were measured on a Hewlett Packard 8453 spectrophotometer (USA) from solutions in chloroform. The high-resolution mass spectra (electron impact, 70 eV) of compounds with a molecular weight lower than 800 were recorded on a Thermo Electron DFS GC/MS instrument (USA) with direct sample admission into the ion source. The mass spectra of compounds with a molecular weight higher than 1000 were obtained with a Bruker Daltonic Autoflex Speed MALDI-TOF spectrometer (Germany) (positive reflectron mode, laser frequency 1000 Hz, accelerating voltage 19 kV) at the Mass Spectrometric Analysis Center of the Institute of Chemical Biology and Fundamental Medicine, Siberian Branch, Russian Academy of Sciences.

Commercial acryloyl chloride (97%, Aldrich), 4-hydroxypiperidine (97%, Alfa Aesar), dibutylamine (99.5%, Aldrich), 1,4-dioxa-8-azaspiro[4.5]decane (98%, Aldrich), diethyl sulfate (>99%, Fluka), piperazine (99%, Aldrich), piperidine (reagent-grade, *Reakhim*), triethylamine (99.5%, AppliChem), phenylhydrazine (97%, Acros Organics), and ethyl pyruvate (98%, Alfa Aesar) were used.

5-(Pentafluorophenyl)-1,3-diphenyl-4,5-dihydro-1*H*-pyrazole (**2a**) [9] and 3-(pentafluorophenyl)-1,5-diphenyl-4,5-dihydro-1*H*-pyrazole (**5**) [11] were synthesized according to reported procedures.

4-Methyl-3,5-bis{[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenylsulfanyl]methyl}benzoyl chloride (TAFSCl). A suspension of 0.23 g (0.35 mmol) of 4-methyl-3,5-bis{[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenylsulfanyl]methyl}benzoic acid [14] in 10.1 g (84.7 mmol) of thionyl chloride was refluxed for 5 h and left overnight; the mixture became transparent. Excess thionyl chloride and volatile products were removed on a rotary evaporator, and the residue was evacuated with an oil pump at 30–40°C; the product crystallized. Yield 0.22 g (93%), colorless crystals decomposing at 74°C. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 2.58 s (3H, CH_3), 4.30 s (4H, CH_2), 7.55 s (2H, H_{arom}). ^{19}F NMR spectrum (CD_3CN), δ_F, ppm: 22.1, 32.0, 107.1 (2:2:3). Mass spectrum: *m*/*z* 677.9543 $[M]^+$. $C_{24}H_9ClF_{14}OS_2$. Calculated: *M* 677.9554.

3-[4-(Dibutylamino)-2,3,5,6-tetrafluorophenyl]-1-phenylprop-2-en-1-one (1b). Dibutylamine, 5.93 mL (4.52 g, 35.0 mmol), was added to a solution of 5.22 g (17.5 mmol) of 3-(pentafluorophenyl)-1-phenylprop-2-en-1-one (**1a**) in 30 mL of DMF, and the mixture was stirred for 5 h at 50–55°C. The mixture was cooled and extracted with diethyl ether, and the extract was washed with aqueous ammonium chloride and water, dried over Na_2SO_4, and evaporated under reduced pressure (water-jet pump). Yield 6.35 g (89%), cream-colored oil. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.87 t (6H, CH_3, *J* = 7.3 Hz), 1.20–1.35 m (4H, CH_2), 1.42–1.55 m (4H, CH_2), 3.24 t (4H, NCH_2, *J* = 7.3 Hz), 7.44–7.59 m (3H, H_{arom}), 7.74 d and 7.81 d (1H each, CH=CH, *J* = 16.1 Hz), 7.96–8.03 m (2H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: 10.75, 20.08 (1:1). Mass spectrum: *m*/*z* 407.1873 $[M]^+$. $C_{23}H_{25}F_5NO$. Calculated: *M* 407.1867.

Reaction of 5-(pentafluorophenyl)-1,3-diphenyl-4,5-dihydro-1*H*-pyrazole (2a) with piperidine derivatives (*general procedure*). The corresponding piperidine derivative, 10.30 mmol, was added to a suspension of 2.0 g (5.15 mmol) of compound **2a** in 5 mL of DMF, and the mixture was stirred for 4 h at a bath temperature of 60°C. The mixture was cooled in

a refrigerator or poured onto ice, and the precipitate was filtered off, washed with water and a small amount of hexane, and dried in air.

1-[4-(1,3-Diphenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-2,3,5,6-tetrafluorophenyl]piperidine (2b). Yield 69%, mp 182–183°C; published data [8]: mp 182–184°C. The ^{1}H and ^{19}F NMR spectra were identical to those reported in [8].

1-[4-(1,3-Diphenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-2,3,5,6-tetrafluorophenyl]piperidin-4-ol (2c). Yield 41%, mp 140–143°C; published data [10]: mp 142–145°C. The ^{1}H and ^{19}F NMR spectra were identical to those reported in [10].

8-[4-(1,3-Diphenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-2,3,5,6-tetrafluorophenyl]-1,4-dioxa-8-azaspiro[4.5]-decane (2d). Yield 60%, yellow powder, mp 204–206°C (from benzene–hexane, 1:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.81–1.88 m (4H, $CH_{2,\,pip}$),[1] 3.29–3.40 m (5H, $CH_{2,\,pip}$, H_{pyr}), 3.86 d.d (1H, H_{pyr}, J = 17.0, 13.2 Hz), 4.02 s (4H, OCH_2), 5.72 d.d (1H, H_{pyr}, J = 13.2, 6.6 Hz), 6.85 t (1H, H_{arom}, J = 7.3 Hz), 7.11–7.16 m (2H, H_{arom}), 7.23–7.31 m (2H, H_{arom}), 7.34–7.49 m (3H, H_{arom}), 7.74–7.82 m (2H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 11.19, 16.79 (1:1). Mass spectrum: m/z 511.1879 $[M]^+$. $C_{28}H_{25}F_4N_3O_2$. Calcu-lat-ed: M 511.1877.

***N*,*N*-Dibutyl-4-(1,3-diphenyl-4,5-dihydro-1*H*-pyrazol-5-yl)-2,3,5,6-tetrafluoroaniline (2e).** Phenylhydrazine, 2.95 mL (3.24 g, 30 mmol), was added to 2.04 g (5.0 mmol) of chalcone **1b** in 70 mL of acetic acid, and the mixture was refluxed for 6 h. The mixture was cooled in a refrigerator, and the precipitate was filtered off, washed with water, and dried in air. Yield 1.74 g. An additional portion of the product containing 80% of **2e** (according to the NMR data), 0.54 g, was isolated from the filtrate. Overall yield 2.17 g (87%), colorless powder, mp 127–129°C. ^{1}H NMR spectrum ($CDCl_3$) δ, ppm: 0.85 t (6H, CH_3, J = 7.3 Hz), 1.18–1.32 m (4H, CH_2), 1.33–1.46 m (4H, CH_2), 3.11 t (4H, NCH_2, J = 7.2 Hz); 3.33 d.d, 3.82 d.d, and 5.67d.d (1H each, *ABX*, H_{pyr}, J = 17.3, 13.1, 6.6 Hz); 6.77–6.84 m (1H, H_{arom}), 7.06–7.42 m (7H, H_{arom}), 7.70–7.76 m (2H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 12.67, 16.43 (1:1). Mass spectrum: m/z 497.2444 $[M]^+$. $C_{29}H_{31}F_4N_3$. Calculated: M 497.2449.

The Vilsmeier formylation of dihydropyrazoles **2a**–**2e** and **5** was carried out according to the procedure described in [11]; the products were purified by silica gel column chromatography.

4-{3-Phenyl-5-[2,3,5,6-tetrafluoro-4-(piperidin-1-yl)phenyl]-4,5-dihydro-1*H*-pyrazol-1-yl}benzaldehyde (3b). Yield 74%, cream-colored powder, mp 203–205°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.51–1.72 m (6H, $CH_{2,\,pip}$), 3.11–3.20 m (4H, $CH_{2,\,pip}$); 3.33 d.d, 3.87 d.d, and 5.74 d.d (1H each, *ABX*, H_{pyr}, J = 17.4, 12.9, 5.8 Hz); 7.12 d (2H, H_{arom}, J = 8.7 Hz), 7.36–7.45 m (3H, H_{arom}), 7.68–7.78 m (4H, H_{arom}), 9.76 s (1H, CHO). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 11.30, 16.21 (1:1). Mass spectrum: m/z 481.1770 $[M]^+$. $C_{27}H_{23}F_4N_3O$. Calculated: M 481.1772.

4-{5-[4-(4-Chloropiperidin-1-yl)-2,3,5,6-tetrafluorophenyl]-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl}benzaldehyde (3f). Yield 62%, light yellow needles, mp 190–192°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.88–2.01 m (2H, H_{pip}), 2.09–2.20 m (2H, H_{pip}), 3.06–3.18 (2H, H_{pip}); 3.35 d.d, 3.90 d.d, and 5.76 d.d (1H each, *ABX*, H_{pyr}, J = 17.9, 13.0, 5.6 Hz); 3.40–3.51 m (2H, H_{pip}), 4.14–4.24 m (1H, CHCl), 7.10–7.15 m (2H, H_{arom}), 7.37–7.46 m (3H, H_{arom}), 7.69–7.78 m (4H, H_{arom}), 9.76 s (1H, CHO). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 11.76, 16.89 (1:1). Mass spectrum: m/z 515.1377 $[M]^+$. $C_{27}H_{22}ClF_4N_3O$. Calculated: M 515.1382.

4-{5-[4-(Dibutylamino)-2,3,5,6-tetrafluorophenyl]-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl}-benzaldehyde (3g). Yield 66%, colorless powder, mp 175–178°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.84 t (6H, CH_3, J = 7.2 Hz), 1.17–1.31 m (4H, CH_2), 1.34–1.46 m (4H, CH_2), 3.11 t (4H, NCH_2, J = 7.3 Hz); 3.37 d.d, 3.88 d.d, and 5.75 d.d (1H each, *ABX*, H_{pyr}, J = 17.4, 12.8, 5.7 Hz); 7.11–7.16 m (2H, H_{arom}), 7.35–7.46 m (3H, H_{arom}), 7.70–7.78 m (4H, H_{arom}), 9.75 s (1H, CHO). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 13.07, 16.29 (1:1). Mass spectrum: m/z 525.2402 $[M]^+$. $C_{30}H_{31}F_4N_3O$. Calculated: M 525.2398.

4-[3-(Pentafluorophenyl)-5-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl]benzaldehyde (4a). Yield 56%, yellow powder, mp 124–127°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.28 d.d, 3.99 d.d, and 5.43 d.d (1H each, *ABX*, H_{pyr}, J = 18.0, 12.4, 5.8 Hz); 7.10 d (2H, H_{arom}, J = 8.6 Hz), 7.22–7.34 m (5H, H_{arom}), 7.68 d (2H, H_{arom}, J = 8.6 Hz), 9.74 s (1H, CHO). ^{19}F NMR spectrum ($CHCl_3$), δ_F, ppm: 0.21, 8.86, 23.24 (2:1:2). Mass spectrum: m/z 416.0954 $[M]^+$. $C_{22}H_{13}F_5N_2O$. Calculated: M 416.0943.

Reaction of aldehydes 3a and 4a with alicyclic amines (*general procedure*). Aldehyde **3a** or **4a**,

[1] Hereinafter, the subscripts "pip," "pyr," and "pz" refer to the piperidine, dihydropyrazole, and piperazine protons, respectively.

0.42 g (1 mmol), was dispersed in 5 mL of DMF, 2 mmol of the corresponding amine was added, and the mixture was stirred for 6 h at 60°C. The mixture was poured onto ice, and the precipitate was filtered off and washed with water and a small amount of hexane. The product was purified by column chromatography on silica gel using methylene chloride as eluent.

4-{3-Phenyl-5-[2,3,5,6-tetrafluoro-4-(piperidin-1-yl)phenyl]-4,5-dihydro-1*H*-pyrazol-1-yl}benzaldehyde (3b) was synthesized from aldehyde **3a** and piperidine. Yield 67%. The product was identical in the melting point and NMR spectra to a sample obtained as described above by formylation of **2b**.

4-{3-Phenyl-5-[2,3,5,6-tetrafluoro-4-(4-hydroxypiperidin-1-yl)phenyl]-4,5-dihydro-1*H*-pyrazol-1-yl}benzaldehyde (3c) was synthesized from aldehyde **3a** and 4-hydroxypiperidine. Yield 65%, yellow powder, mp 217–220°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.37–1.52 m (2H, H_{pip}), 1.73–1.84 m (2H, H_{pip}), 2.97–3.09 m (2H, H_{pip}), 3.25–3.32 m (2H, H_{pip}); 3.53 d.d, 4.00 d.d, and 5.97 d.d (1H each, *ABX*, H_{pyr}, J = 17.8, 12.8, 5.2 Hz); 3.57–3.67 m (1H, H_{pip}), 4.71 d (1H, OH, J = 4.2 Hz), 7.09 d (2H, H_{arom}, J = 8.7 Hz), 7.41–7.53 m (3H, H_{arom}), 7.75 d (2H, H_{arom}, J = 8.7 Hz), 7.78–7.84 m (2H, H_{arom}), 9.71 s (1H, CHO). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 11.8, 17.24 (1:1). Mass spectrum: *m*/*z* 497.1719. $C_{27}H_{23}F_4N_3O_2$. Calculated: M 497.1721.

4-{5-[4-(1,4-Dioxa-8-azaspiro[4.5]dec-8-yl)-2,3,5,6-tetrafluorophenyl]-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl}benzaldehyde (3d) was synthesized from aldehyde **3a** and 1,4-dioxa-8-azaspiro[4.5]-decane. Yield 0.32 g (39%), colorless powder, mp 222–225°C. ^{1}H NMR spectrum ($CDCl_3$) δ, ppm: 1.70–1.85 m (4H, H_{pip}), 3.23–3.41 m (5H, H_{pip}, H_{pyr}), 3.87 d.d (1H, H_{pyr}, J = 17.6, 13.0 Hz), 3.97 s (4H, OCH_2), 5.75 d.d (1H, H_{pyr}, J = 13.0, 5.6 Hz), 7.13 d (2H, H_{arom}, J = 8.0 Hz), 7.37–7.45 m (3H, H_{arom}), 7.68–7.78 m (4H, H_{arom}), 9.74 s (1H, CHO). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 11.55, 16.54 (1:1). Mass spectrum: *m*/*z* 539.1825 $[M]^+$. $C_{29}H_{25}F_4N_3O_3$. Calculated: M 539.1827.

4-{3-Phenyl-5-[2,3,5,6-tetrafluoro-4-(piperazin-1-yl)phenyl]-4,5-dihydro-1*H*-pyrazol-1-yl}benzaldehyde (3e) was synthesized from aldehyde **3a** and piperazine. Yield 0.35 g (72%), cream-colored powder, mp 215–218°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.68–2.81 m (4H, $CH_{2,\,pz}$), 3.04–3.14 m (4H, $CH_{2,\,pz}$); 3.52 d.d, 4.02 d.d, and 5.98 d.d (1H each, *ABX*, H_{pyr}, J = 18.0, 12.8, 5.2 Hz), 7.11 d (2H, H_{arom}, J = 8.6 Hz), 7.41–7.52 m (3H, H_{arom}), 7.75 d (2H, H_{arom}, J = 8.6 Hz), 7.78–7.83 m (2H, H_{arom}), 9.71 s (1H, CHO). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: 11.51, 17.28 (1:1). Mass spectrum: *m*/*z* 482.1730 $[M]^+$. $C_{26}H_{22}F_4N_4O$. Calculated: M 482.1724.

4-{5-Phenyl-3-[2,3,5,6-tetrafluoro-4-(piperidin-1-yl)phenyl]-4,5-dihydro-1*H*-pyrazol-1-yl}benzaldehyde (4b) was synthesized from aldehyde **4a** and piperidine. Yield 83%, yellow crystals, mp 135–137°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.57–1.71 m (6H, $CH_{2,\,pip}$), 3.20–3.31 m (5H, $CH_{2,\,pip}$, H_{pyr}), 3.96 d.d (1H, H_{pyr}, J = 18.2, 12.3 Hz), 5.35 d.d (1H, H_{pyr}, J = 12.3, 5.7 Hz), 7.08 d (2H, H_{arom}, J = 8.8 Hz), 7.20–7.37 m (5H, H_{arom}), 7.66 d (2H, H_{arom}, J = 8.8 Hz), 9.73 s (1H, CHO). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 9.92, 20.73 (1:1). Mass spectrum: *m*/*z* 481.1766 $[M]^+$. $C_{27}H_{23}F_4N_3O$. Calculated: M 481.1772.

4-{5-Phenyl-3-[2,3,5,6-tetrafluoro-4-(piperazin-1-yl)phenyl]-4,5-dihydro-1*H*-pyrazol-1-yl}benzaldehyde (4c) was synthesized from aldehyde **4a** and piperazine. Yield 57%, yellow powder, mp 70–72°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.90–3.10 m (4H, H_{pz}), 3.17–3.43 m (6H, H_{pz}, H_{pyr}, NH), 3.94 d.d (1H, H_{pyr}, J = 18.4, 12.4 Hz), 5.35 d.d (1H, H_{pyr}, J = 12.4, 5.4 Hz), 6.97–7.12 m (2H, H_{arom}), 7.17–7.38 m (5H, H_{arom}), 7.61–7.70 m (2H, H_{arom}), 9.72 s (1H, CHO). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 10.12, 21.19 (1:1). Mass spectrum: *m*/*z* 482.1716 $[M]^+$. $C_{26}H_{22}F_4N_4O$. M 482.1724.

Acylation of aldehydes 3c, 3e, and 4c (*general procedure*). Triethylamine, 0.8 mmol (0.11 mL), was added to a suspension of 0.4 mmol of aldehyde **3c**, **3e**, or **4c** in 10 mL of anhydrous benzene. The mixture was heated until it became homogeneous (~40°C), and a solution of 0.5 mmol of benzoyl chloride or TAFSCl in 5 mL of benzene was added. The mixture was refluxed for 5 h, cooled, and treated with benzene, the benzene solution was washed with water and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was dissolved in chloroform and subjected to column chromatography on SiO_2 or Al_2O_3; a bright yellow fraction was collected.

1-{2,3,5,6-Tetrafluoro-4-[1-(4-formylphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazol-5-yl]phenyl}-piperidine-4-yl benzoate (3h) was synthesized from aldehyde **3c** and benzoyl chloride in benzene or toluene under reflux. Yield 6% (in benzene), 15% (in toluene); light yellow powder, mp 179–181°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.85–1.99 m (2H, H_{pip}), 2.02–2.14 m (2H, H_{pip}), 3.17–3.29 m (2H, H_{pip});

3.34 d.d, 3.89 d.d, and 5.75 d.d (1H each, *ABX*, H_{pyr}, J = 17.8, 13.1, 5.7 Hz), 3.40–3.52 m (2H, H_{pip}), 5.15–5.24 m (1H, CHOCO), 7.0–7.17 m (2H, H_{arom}), 7.38–7.47 m (5H, H_{arom}), 7.52–7.59 m (1H, H_{arom}), 7.69–7.79 m (4H, H_{arom}), 8.00–8.07 m (2H, H_{arom}), 9.75 s (1H, CHO). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 11.73, 16.80 (1:1). Mass spectrum: *m*/*z* 601.1984 $[M]^+$. $C_{34}H_{27}F_4N_3O_3$. Calculated: *M* 601.1983.

4-(3-Phenyl-5-{2,3,5,6-tetrafluoro-4-[4-(4-methyl-3,5-bis{[2,3,5,6-tetrafluoro-4-(trifluoromethyl)-phenylsulfanyl]methyl}benzoyl)piperazin-1-yl]-phenyl}-4,5-dihydro-1*H*-pyrazol-1-yl)benzaldehyde (3i) was synthesized from aldehyde **3e** and TAFSCl. Yield 51%, light yellow powder, mp 120–123°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.54 s (3H, CH_3), 3.05–4.03 m (10H, H_{pz}, H_{pyr}), 4.23 s (4H, SCH_2), 5.78 d.d (1H, H_{pyr}, J = 12.8, 5.5 Hz), 7.09–7.17 m (4H, H_{arom}), 7.38–7.46 m (3H, H_{arom}), 7.69–7.79 m (4H, H_{arom}), 9.76 s (1H, CHO). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 11.75, 17.54, 21.98, 30.35, 105.39 (1:1:2:2:3). Mass spectrum (MALDI-TOF): *m*/*z* 1123.03 $[M - H]^+$. $C_{50}H_{30}F_{18}N_4O_2S_2$. *M* 1124.15.

4-(5-Phenyl-3-{2,3,5,6-tetrafluoro-4-[4-(4-methyl-3,5-bis{[2,3,5,6-tetrafluoro-4-(trifluoromethyl)-phenylsulfanyl]methyl}benzoyl)piperazin-1-yl]-phenyl}-4,5-dihydro-1*H*-pyrazol-1-yl)benzaldehyde (4d) was synthesized from aldehyde **4c** and TAFSCl. Yield 77%, yellow powder, mp 190–193°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.54 s (3H, CH_3), 3.15–3.60 m (7H, H_{pz}, H_{pyr}), 3.68–3.92 m (2H, H_{pz}), 3.99 d.d (1H, H_{pyr}, J = 17.6, 12.4 Hz), 5.38 d.d (1H, H_{pyr}, J = 12.4, 5.6 Hz), 7.08–7.36 m (9H, H_{arom}), 7.62–7.70 m (2H, H_{arom}), 9.74 s (1H, CHO). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 10.69, 21.70, 21.95, 30.57, 105.37 (1:1:2:2:3). Mass spectrum (MALDI-TOF): *m*/*z* 1124.21 $[M]^+$. $C_{50}H_{30}F_{18}N_4O_2S_2$. *M* 1124.15.

Compounds 7a–7e, 9a, and 9b (*general procedure*). A solution of TCP was prepared as described in [12] by heating a mixture of 0.15 mL (1.38 mmol) of ethyl pyruvate and 0.09 g (0.68 mmol) of 2-amino-prop-1-ene-1,1,3-tricarbonitrile in 5 mL of anhydrous ethanol under reflux. It was cooled to 50–55°C, 0.48 mmol of aldehyde **3b–3h** or **4c** was added, and the mixture was stirred for 3–5 h at that temperature under argon, the progress of the reaction being monitored by TLC on Sorbfil plates. The mixture was cooled, and the product was precipitated with diethyl ether, filtered off (green solid), washed with diethyl ether, and dried in air.

2-{3-Cyano-5-oxo-4-[(*E*)-2-(4-{3-phenyl-5-[2,3,5,6-tetrafluoro-4-(piperidin-1-yl)phenyl]-4,5-dihydro-1*H*-pyrazol-1-yl}phenyl)ethenyl]-1*H*-pyrrol-2(5*H*)-ylidene}propanedinitrile (7a) was synthesized by reaction of aldehyde **3b** with TCP. Yield 42%, blue–green powder, decomposition point ~300°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.51–1.62 m (6H, H_{pip}), 3.11–3.18 m (4H, H_{pip}); 3.57 d.d, 4.03 d.d, and 6.03 d.d (1H each, *ABX*, H_{pyr}, J = 17.4, 12.7, 4.4 Hz); 9.96–7.14 m (3H, H_{arom}, CH=), 7.42–7.55 m (3H, H_{arom}), 7.70–7.87 m (4H, H_{arom}), 8.35 d (1H, CH=, J = 16.0 Hz), 12.65 br.s (1H, NH). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: 11.72, 17.28 (1:1). Mass spectrum: *m*/*z* 647.2048 $[M]^+$. $C_{36}H_{25}F_4N_7O$. Calculated: *M* 647.2051.

The ether washings were evaporated under reduced pressure, and the residue was subjected to chromatography on silica gel using chloroform as eluent. From the bright orange fraction we isolated 0.09 g (30%) of **2-amino-4-(4-{3-phenyl-5-[2,3,5,6-tetrafluoro-4-(piperidin-1-yl)phenyl]-4,5-dihydro-1*H*-pyrazol-1-yl}-phenyl)buta-1,3-diene-1,1,3-tricarbonitrile (11)** as orange powder with mp 179–182°C. Electronic absorption spectrum: λ_{max} 486 nm (log ε 4.64). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.51–1.72 m (6H, $CH_{2,\,pip}$), 3.14–3.24 m (4H, $CH_{2,\,pip}$); 3.60 d.d, 4.15 d.d, and 6.03 d.d (1H each, *ABX*, H_{pyr}, J = 18.2, 12.7, 5.3 Hz); 7.22 d (2H, H_{arom}, J = 8.9 Hz), 7.40–7.53 m (3H, H_{arom}), 7.80–7.92 m (3H, H_{arom}, CH=), 7.92–8.05 m (2H, H_{arom}). ^{19}F NMR spectrum (acetone-d_6), δ_F, ppm: 12.55, 17.89 (1:1). Mass spectrum: *m*/*z* 595.2111 $[M]^+$. $C_{33}H_{25}F_4N_7$. Calculated: *M* 595.2102.

When a mixture of **3b** and TCP in ethanol was refluxed for 1 h, the yield of **7a** was 22%, and the yield of **11**, 26%.

2-{3-Cyano-5-oxo-4-[(*E*)-2-(4-{3-phenyl-5-[2,3,5,6-tetrafluoro-4-(4-hydroxypiperidin-1-yl)-phenyl]-4,5-dihydro-1*H*-pyrazol-1-yl}phenyl)-ethenyl]-1*H*-pyrrol-2(5*H*)-ylidene}propanedinitrile (7b) was synthesized by reaction of **3c** with TCP. Yield 42%, blue–green powder, mp > 300°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.37–1.53 m (2H, H_{pip}), 1.72–1.85 m (2H, H_{pip}), 2.97–3.10 m (2H, H_{pip}), 3.50–3.67 m (2H, H_{pip}, H_{pyr}), 4.03 d.d (1H, H_{pyr}, J = 17.6, 12.4 Hz), 6.01 d.d (1H, H_{pyr}, J = 12.4, 5.0 Hz), 6.98–7.14 m (3H, H_{arom}, CH=), 7.43–7.56 m (3H, H_{arom}), 7.72–7.88 m (4H, H_{arom}), 8.33 d (1H, CH=, J = 15.2 Hz), 12.65 br.s (1H, NH). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: 11.88, 17.29 (1:1). Mass spectrum: *m*/*z* 663.2004 $[M]^+$. $C_{36}H_{25}F_4N_7O_2$. Calculated: *M* 663.2000.

2-(3-Cyano-5-oxo-4-{(*E*)-2-[4-(3-phenyl-5-{2,3,5,6-tetrafluoro-4-[4-(4-methyl-3,5-bis{[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenylsulfanyl]-methyl}benzoyl)piperazin-1-yl]phenyl}-4,5-dihydro-1*H*-pyrazol-1-yl)phenyl]ethenyl}-1*H*-pyrrol-2(5*H*)-ylidene)propanedinitrile (7c) was synthesized by reaction of aldehyde **3i** with TCP. Yield 31%, blue–green powder, mp 262–265°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.51 s (3H, CH_3), 3.12–3.53 m (6H, $H_{pz,}$ H_{pyr}), 3.72–3.99 m (2H, H_{pz}, H_{pyr}), 4.34 s (4H, CH_2), 6.06 d.d (1H, H_{pyr}, J = 12.6, 5.2 Hz), 6.98–7.11 m (5H, H_{arom}, CH=), 7.46–7.54 m (3H, H_{arom}), 7.72–7.86 m (4H, H_{arom}), 8.32 d (1H, CH=, J = 15.4 Hz). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: 11.98, 17.65, 20.93, 31.34, 106.93 (1:1:2:2:3). Mass spectrum (MALDI-TOF): m/z 1290.15 $[M]^+$. $C_{59}H_{32}F_{18}N_8O_2S_2$. Calculated: M 1290.18.

2-{3-Cyano-4-[(*E*)-2-(4-{5-[4-(dibutylamino)-2,3,5,6-tetrafluorophenyl]-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl}phenyl)ethenyl]-5-oxo-1*H*-pyrrol-2(5*H*)-ylidene}propanedinitrile (7d) was synthesized by reaction of aldehyde **3g** with TCP under reflux for 1.5 h. Yield 18%, blue–green powder, decomposition point ~290°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 0.81 t (6H, CH_3, J = 7.3 Hz), 1.16–1.26 m (4H, CH_2), 1.32–1.41 m (4H, CH_2), 3.07–3.15 m (4H, CH_2); 3.65 d.d, 4.03 d.d, and 6.04 d.d (1H each, *ABX*, H_{pyr}, J = 17.6, 12.5, 2.8 Hz); 7.00–7.11 m (2H, H_{arom}, CH=), 7.45–7.54 m (3H, H_{arom}), 7.74–7.86 m (4H, H_{arom}), 8.3 d (1H, CH=, J = 15.4 Hz), 12.67 br.s (1H, NH). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: 13.20, 17.35 (1:1). Mass spectrum: m/z 691.2668 $[M]^+$. $C_{39}H_{33}F_4N_7O$. Calculated: M 691.2627.

2-{3-Cyano-5-oxo-4-[(*E*)-2-(4-{5-phenyl-3-[2,3,5,6-tetrafluoro-4-(piperidin-1-yl)phenyl]-4,5-dihydro-1*H*-pyrazol-1-yl}phenyl)ethenyl]-1*H*-pyrrol-2(5*H*)-ylidene}propanedinitrile (9a) was synthesized by reaction of aldehyde **4b** with TCP (50–52°C, 12 h). Yield 23%, green powder, decomposition point ~260°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.52–1.69 m (6H, $CH_{2,\,pip}$), 3.14–3.32 m (5H, $CH_{2,\,pip}$, H_{pyr}), 4.10 d.d (1H, H_{pyr}, J = 18.2, 12.0 Hz), 5.78 d.d (1H, H_{pyr}, J = 12.0, 5.0 Hz), 6.98–7.45 m (8H, H_{arom}), 7.70–7.88 m (3H, H_{arom}), 12.72 br.s (NH). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: 10.80, 21.90 (1:1). Mass spectrum: m/z 647.2049 $[M]^+$. $C_{36}H_{25}F_4N_7O$. Calculated: M 647.2051.

2-(3-Cyano-5-oxo-4-{(*E*)-2-[4-(5-phenyl-3-{2,3,5,6-tetrafluoro-4-[4-(4-methyl-3,5-bis{[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenylsulfanyl]-methyl}benzoyl)piperazin-1-yl]phenyl}-4,5-dihydro-1*H*-pyrazol-1-yl)phenyl]ethenyl}-1*H*-pyrrol-2(5*H*)-ylidene)propanedinitrile (9b) was synthesized by reaction of aldehyde **4c** with TCP (45–50°C, 22 h). Yield 11%, blue–green powder, mp 238–241°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.55 s (3H, CH_3), 3.20–3.94 m (9H, H_{pz}, H_{pyr}), 4.04 d.d (1H, H_{pyr}, J = 15.4, 11.8 Hz), 4.24 s (4H, CH_2), 5.46 d.d (1H, H_{pyr}, J = 11.8, 4.8 Hz), 7.00 d (1H, CH=, J = 15.5 Hz), 7.06–7.42 m (7H, H_{arom}), 7.48–7.60 m (2H, H_{arom}), 8.40–8.52 m (2H, CH=, NH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 10.77, 22.09, 22.63, 30.54, 105.53 (1:2:1:2:3). Mass spectrum (MALDI-TOF): m/z 1290.14 $[M]^+$. $C_{59}H_{32}F_{18}N_8O_2S_2$. Calculated: M 1290.18.

Modification of chromophores 7 and 9 (*general procedure*). A suspension of 0.11 mmol of **7a**–**7d** or **9a** and 0.31 mmol of freshly calcined potassium carbonate in 3 mL of anhydrous acetonitrile was refluxed for 10 min with stirring in a stream of argon; the mixture turned dark violet. The corresponding alkylating or acylating agent, 0.21 mmol, was added (the mixture changed its color to dark green), and the mixture was refluxed for 1 h. When the green color disappeared, an additional 0.21 mmol of the reagent was added, and the mixture was refluxed for 30 min. It was then cooled, and the product was precipitated with diethyl ether, filtered off, washed with water to remove potassium carbonate, dried in air, and purified by silica gel column chromatography using methylene chloride as eluent; the first bright green fraction was collected.

2-{3-Cyano-1-ethyl-5-oxo-4-[(*E*)-2-(4-{3-phenyl-5-[2,3,5,6-tetrafluoro-4-(piperidin-1-yl)phenyl]-4,5-dihydro-1*H*-pyrazol-1-yl}phenyl)ethenyl]-1*H*-pyrrol-2(5*H*)-ylidene}propanedinitrile (8a) was synthesized from **7a** and diethyl sulfate. Yield 62%, green powder, mp 297–299°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.31 t (3H, $CH_2C\mathbf{H}_3$, J = 7.0 Hz), 1.54–1.68 m (6H, $CH_{2,\,pip}$), 3.12–3.21 m (4H, $CH_{2,\,pip}$); 3.37 d.d, 3.92 d.d, and 5.79 d.d (1H each, *ABX*, H_{pyr}, J = 17.3, 12.6, 5.3 Hz); 4.10 q (2H, $C\mathbf{H}_2CH_3$, J = 7 Hz), 7.02 d and 8.45 d (1H each, *AB*, CH=CH, J = 15.4 Hz), 7.11 d and 7.57 d (2H each, *AB*, H_{arom}, J = 8.3 Hz), 7.37–7.48 m (3H, H_{arom}), 7.71–7.83 m (2H, H_{arom}). ^{19}F NMR spectrum (DMSO-d_6), δ_F, ppm: 11.6, 16.4 (1:1). Mass spectrum: m/z 675.2358 $[M]^+$. $C_{38}H_{29}F_4N_7O$. Calculated: M 675.2364.

2-{1-Benzyl-3-cyano-5-oxo-4-[(*E*)-2-(4-{3-phenyl-5-[2,3,5,6-tetrafluoro-4-(piperidin-1-yl)phenyl]-4,5-dihydro-1*H*-pyrazol-1-yl}phenyl)ethenyl]-1*H*-pyr-

rol-2(5*H*)-ylidene}propanedinitrile (8b) was synthesized from **7a** and benzyl chloride. Yield 11%, green powder, decomposition point ~270°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.56–1.68 m (6H, $CH_{2,\,pip}$), 3.17–3.21 m (4H, $CH_{2,\,pip}$); 3.38 d.d, 3.93 d.d, and 5.80 d.d (1H each, *ABX*, H_{pyr}, J = 17.4, 12.6, 5.3 Hz); 5.31 s (2H, C**H**$_2$Ph), 7.05–7.20 m (5H, 4H, H_{arom}, CH=), 7.29–7.39 m (3H, H_{arom}), 7.40–7.48 m (3H, H_{arom}), 7.60 d (2H, H_{arom}, J = 8.8 Hz), 7.72–7.80 m (2H, H_{arom}), 8.51 d (1H, CH=, J = 15.6 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 11.64, 16.37 (1:1). Mass spectrum: m/z 737.2538 $[M]^+$. $C_{43}H_{31}F_4N_7O$. Calculated: M 737.2521.

2-{1-Benzoyl-3-cyano-5-oxo-4-[(*E*)-2-(4-{3-phenyl-5-[2,3,5,6-tetrafluoro-4-(piperidin-1-yl)-phenyl]-4,5-dihydro-1*H*-pyrazol-1-yl}phenyl)-ethenyl]-1*H*-pyrrol-2(5*H*)-ylidene}propanedinitrile (8c) was synthesized from **7a** and benzoyl chloride. Yield 72%, green powder, decomposition point ~270°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.52–1.62 m (6H, $CH_{2,\,pip}$), 3.12–3.20 m (4H, $CH_{2,\,pip}$); 3.38 d.d, 3.93 d.d, and 5.79 d.d (1H each, *ABX*, H_{pyr}, J = 17.5, 12.7, 5.1 Hz); 7.01–7.15 m (3H, H_{arom}, CH=), 7.40–7.47 m (3H, H_{arom}), 7.50–7.60 m (4H, H_{arom}), 7.68–7.81 m (3H, H_{arom}), 7.90–7.97 m (2H, H_{arom}), 8.39 d (1H, CH=, J = 15.4 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 11.34, 16.37 (1:1). Mass spectrum: m/z 751.2297 $[M]^+$. $C_{43}H_{29}F_4N_7O_2$. Calculated: M 751.2313.

2-{3-Cyano-1-(4-methyl-3,5-bis{[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenylsulfanyl]methyl}-benzoyl)-4-[(*E*)-2-(4-{3-phenyl-5-[2,3,5,6-tetrafluoro-4-(piperidin-1-yl)phenyl]-4,5-dihydro-1*H*-pyrazol-1-yl}phenyl)ethenyl]-5-oxo-1*H*-pyrrol-2(5*H*)-ylidene}propanedinitrile (8d) was synthesized from **7a** and TAFSCl. Yield 33%, green powder, mp 225–228°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.55–1.67 m (6H, $CH_{2,\,pip}$), 2.67 s (3H, CH_3), 3.14–3.21 m (4H, $CH_{2,\,pip}$); 3.40 d.d, 3.94 d.d, and 5.82 d.d (1H each, *ABX*, H_{pyr}, J = 17.5, 12.5, 5.3 Hz); 4.27 s (4H, CH_2), 7.02 d and 8.37 d (1H each, *AB*, CH=CH, J = 15.4 Hz), 7.13 d and 7.59 d (2H each, *AB*, H_{arom}, J = 9.0 Hz), 7.41–7.47 m (3H, H_{arom}), 7.55 s (2H, H_{arom}), 7.76–7.81 m (2H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 11.56, 16.23, 22.16, 30.10, 105.29 (1:1:2:2:3). Mass spectrum (MALDI-TOF): m/z 1289.26 $[M]^+$. $C_{60}H_{33}F_{18}N_7O_2S_2$. Calculated: M 1289.18.

2-{3-Cyano-1-(4-methyl-3,5-bis{[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenylsulfanyl]methyl}-benzoyl)-4-[(*E*)-2-(4-{3-phenyl-5-[2,3,5,6-tetrafluoro-4-(4-hydroxypiperidin-1-yl)phenyl]-4,5-dihydro-1*H*-pyrazol-1-yl}phenyl)ethenyl]-5-oxo-1*H*-pyrrol-2(5*H*)-ylidene}propanedinitrile (8e) was synthesized from **7b** and TAFSCl. Yield 33%, black powder, mp 244–246°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.57–1.70 m (2H, $CH_{2\,pip}$), 1.89–2.00 m (2H, $CH_{2,\,pip}$), 2.67 s (3H, CH_3), 3.04–3.16 m (2H, $CH_{2,\,pip}$), 3.34–3.46 m (3H, $CH_{2,\,pip}$, H_{pyr}), 3.78–3.88 m (1H, CH_{pip}), 3.94 d.d (1H, H_{pyr}, J = 18.0, 12.4 Hz), 4.26 s (4H, SCH_2), 5.82 d.d (1H, H_{pyr}, J = 12.4, 5.1 Hz), 7.04 d and 8.39 d (1H each, *AB*, CH=CH, J = 15.4 Hz), 7.09–7.17 m (2H, H_{arom}), 7.41–7.47 m (3H, H_{arom}), 7.54 s (2H, H_{arom}), 7.60 d (2H, H_{arom}, J = 8.9 Hz), 7.74–7.81 m (2H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 12.01, 16.77, 22.30, 30.22, 105.42 (1:1:2:2:3). Mass spectrum (MALDI-TOF): m/z 1305.19 $[M]^+$. $C_{60}H_{33}F_{18}N_7O_3S_2$. Calculated: M 1305.18.

2-(3-Cyano-1-ethyl-5-oxo-4-{(*E*)-2-[4-(3-phenyl-5-{2,3,5,6-tetrafluoro-4-[4-(4-methyl-3,5-bis-{[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenylsulfanyl]methyl}benzoyl)piperazin-1-yl]phenyl}-4,5-dihydro-1*H*-pyrazol-1-yl)phenyl]ethenyl}-1*H*-pyrrol-2(5*H*)-ylidene)propanedinitrile (8f) was synthesized from **7c** and diethyl sulfate. Yield 15%, green powder, mp 240–242°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.31 t (3H, CH_2C**H**$_3$, J = 7.2 Hz), 2.52 s (3H, CH_3), 3.22 br.s (6H, $CH_{2,pz}$); 3.39 d.d, 3.97 d.d, and 5.83 d.d (1H each, *ABX*, H_{pyr}, J = 18.0, 12.8, 5.0 Hz); 3.51–3.88 m (2H, $CH_{2,\,pz}$), 4.10 q (2H, C**H**$_2$CH$_3$, J = 7.2 Hz), 4.23 s (4H, CH_2), 6.95 d and 8.42 d (1H each, *AB*, CH=CH, J = 15.4 Hz), 7.05–7.15 m (4H, H_{arom}), 7.41–7.48 m (3H, H_{arom}), 7.57 d (2H, H_{arom}, J = 8.7 Hz), 7.74–7.80 m (2H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 12.30, 17.63, 33.07, 30.44, 105.54 (1:1:2:2:3). Mass spectrum (MALDI-TOF): m/z 1318.13 $[M]^+$. $C_{61}H_{36}F_{18}N_8O_2S_2$. Calculated: M 1318.21.

2-(3-Cyano-1-(4-methyl-3,5-bis{[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenylsulfanyl]methyl}-benzoyl)-5-oxo-4-{(*E*)-2-[4-(3-phenyl-5-{2,3,5,6-tetrafluoro-4-[4-(4-methyl-3,5-bis{[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenylsulfanyl]methyl}-benzoyl)piperazin-1-yl]phenyl}-4,5-dihydro-1*H*-pyrazol-1-yl)phenyl]ethenyl}-1*H*-pyrrol-2(5*H*)-ylidene)propanedinitrile (8g) was synthesized from **7c** and TAFSCl. Yield 10%, dark green powder, mp 140–142°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.53 s (3H, CH_3), 2.69 s (3H, CH_3), 3.04–3.86 m (9H, $CH_{2,\,pz}$, H_{pyr}), 3.97 d.d (1H, H_{pyr}, J = 18.2, 13.3 Hz), 4.22 s and 4.26 s (4H each, SCH_2), 5.85 d.d (1H, H_{pyr}, J = 13.3, 5.2 Hz), 7.05 d and 8.38 d (1H, *AB*, CH=CH,

J = 15.6 Hz), 7.13 br.s (4H, H_{arom}), 7.37–7.67 m (7H, H_{arom}), 7.73–7.82 m (2H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 12.42, 17.78, 21.96, 22.26, 30.18, 30.38, 105.50 (1:1:2:2:2:2:6). Mass spectrum (MALDI-TOF): m/z 1932.30 $[M]^+$. $C_{83}H_{40}F_{32}N_8O_3S_4$. Calculated: M 1932.16.

2-{3-Cyano-4-[(*E*)-2-(4-{5-[4-(dibutylamino)-2,3,5,6-tetrafluorophenyl]-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl}phenyl)ethenyl]-1-ethyl-5-oxo-1*H*-pyrrol-2(5*H*)-ylidene}propanedinitrile (8h) was synthesized from **7d** and diethyl sulfate. Yield 73%, dark green powder with metallic lustre, mp 274–278°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.84 t [6H, $(CH_2)_3C\mathbf{H}_3$, J = 7.3 Hz], 1.17–1.46 m [11H, $NCH_2(C\mathbf{H}_2)_2$, $NCH_2C\mathbf{H}_3$], 3.13 t (4H, $NC\mathbf{H}_2CH_2$, J = 7.4 Hz); 3.41 d.d, 3.95 d.d, and 5.82 d.d (1H each, *ABX*, H_{pyr}, J = 18.0, 12.5, 5.3 Hz); 4.09 q (2H, $NC\mathbf{H}_2CH_3$, J = 7.1 Hz), 6.98 d and 8.42 d (1H each, *AB*, CH=CH, J = 15.4 Hz), 7.07–7.13 m (2H, H_{arom}), 7.41–7.46 m (3H, H_{arom}), 7.56 d (2H, H_{arom}, J = 9.0 Hz), 7.75–7.80 m (2H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 13.28, 16.42 (1:1). Mass spectrum: m/z 719.2883 $[M]^+$. $C_{41}H_{37}F_4N_7O$. Calculated: M 719.2990.

2-{1-Benzoyl-3-cyano-4-[(*E*)-2-(4-{5-[4-(dibutylamino)-2,3,5,6-tetrafluorophenyl]-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl}phenyl)ethenyl]-5-oxo-1*H*-pyrrol-2(5*H*)-ylidene}propanedinitrile (8i) was synthesized from **7d** and benzoyl chloride. Yield 65%, dark green powder with metallic lustre, decomposition point 255–257°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.84 t (6H, CH_3, J = 7.3 Hz), 1.17–1.31 m (4H, CH_2), 1.34–1.46 m (4H, CH_2), 3.13 t (4H, NCH_2, J = 7.3 Hz); 3.42 d.d, 3.96 d.d, and 5.82 d.d (1H each, *ABX*, H_{pyr}, J = 17.5, 12.5, 5.2 Hz); 7.02 d and 8.37 d (1H each, *AB*, CH=CH, J = 15.4 Hz), 7.08–7.15 m (2H, H_{arom}), 7.40–7.47 m (3H, H_{arom}), 7.51–7.59 m (4H, H_{arom}), 7.69–7.82 m (3H, H_{arom}), 7.91–7.96 m (2H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 13.35, 16.42 (1:1). Mass spectrum: m/z 795.2943 $[M]^+$. $C_{46}H_{37}F_4N_7O_2$. Calculated: M 795.2939.

2-{3-Cyano-4-[(*E*)-2-(4-{5-[4-(dibutylamino)-2,3,5,6-tetrafluorophenyl]-3-phenyl-4,5-dihydro-1*H*-pyrazol-1-yl}phenyl)ethenyl]-1-(4-methyl-3,5-bis{[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenylsulfanyl]methyl}benzoyl)-5-oxo-1*H*-pyrrol-2(5*H*)-ylidene}propanedinitrile (8j) was synthesized from **7d** and TAFSCl. Yield 20%, dark green powder, decomposition point 236–237°C. ^1H NMR spectrum (acetone-d_6), δ, ppm: 0.83 t (6H, CH_3, J = 7.0 Hz), 1.18–1.31 m (4H, CH_2), 1.37–1.48 m (4H, CH_2), 2.78 s (3H, CH_3), 3.19 t (4H, NCH_2, J = 7.5 Hz); 3.67 d.d, 4.20 d.d, and 6.12 d.d (1H each, *ABX*, $1H_{pyr}$, J = 18.0, 12.8, 5.4 Hz); 4.52 s (4H, SCH_2), 7.16 d and 8.38 d (1H each, *AB*, CH=CH, J = 15.6 Hz), 7.23 d (2H, H_{arom}, J = 8.6 Hz), 7.46–7.52 m (3H, H_{arom}), 7.78–7.83 m (4H, H_{arom}), 7.88–7.92 m (2H, H_{arom}). ^{19}F NMR spectrum (acetone-d_6), δ_F, ppm: 14.64, 18.16, 22.42, 32.05, 107.64 (1:1:2:2:3). Mass spectrum (MALDI-TOF): m/z 1040.14 $[M - 1]^+$. $C_{48}H_{33}F_{14}N_5O_2S_2$. Calculated :$M$ 1041.19.

2-{3-Cyano-1-ethyl-5-oxo-4-[(*E*)-2-(4-{5-phenyl-3-[2,3,5,6-tetrafluoro-4-(piperidin-1-yl)phenyl]-4,5-dihydro-1*H*-pyrazol-1-yl}phenyl)ethenyl]-1*H*-pyrrol-2(5*H*)-ylidene}propanedinitrile (10a) was synthesized from **9a** and diethyl sulfate. Yield 58%, bright green powder, mp ~260°C (decomp.). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.31 t (3H, $C\mathbf{H}_3CH_2$, J = 7.0 Hz), 1.57–1.73 m (6H, $CH_{2,\,pip}$), 3.23–3.31 m (5H, $CH_{2,\,pip}$, H_{pyr}), 4.01 d.d (1H, H_{pyr}, J = 18.0, 11.8 Hz), 4.11 q (2H, $CH_3C\mathbf{H}_2$, J = 7.0 Hz), 5.41 d.d (1H, H_{pyr}, J = 11.8, 5.2 Hz), 6.99 d (1H, CH=, J = 15.6 Hz), 7.07 d (2H, H_{arom}, J = 8.6 Hz), 7.18–7.38 m (5H, H_{arom}), 7.51 d (2H, H_{arom}, J = 8.9 Hz), 8.42 d (1H, CH=, J = 15.6 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 10.01, 21.31 (1:1). Mass spectrum: m/z 675.2360 $[M]^+$. $C_{38}H_{29}F_4N_7O$. Calculated: M 675.2364.

2-(3-Cyano-1-ethyl-5-oxo-4-{(*E*)-2-[4-(5-phenyl-3-{2,3,5,6-tetrafluoro-4-[4-(4-methyl-3,5-bis{[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenylsulfanyl]methyl}benzoyl)piperazin-1-yl]phenyl}-4,5-dihydro-1*H*-pyrazol-1-yl)phenyl]ethenyl}-1*H*-pyrrol-2(5*H*)-ylidene)propanedinitrile (10b) was isolated as a minor product in the reaction of **9a** with diethyl sulfate. Green powder. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.32 t ($NCH_2C\mathbf{H}_3$, J = 6.8 Hz), 2.55 s (3H, CH_3), 3.17–3.95 m (9H, H_{pz}, H_{pyr}), 3.96–4.20 m (3H, $NC\mathbf{H}_2CH_3$, H_{pyr}), 4.24 s (4H, CH_2), 5.46 d.d (1H, H_{pyr}, J = 12.5, 5.0 Hz), 7.00 d and 8.42 d (1H each, *AB*, CH=CH, J = 15.8 Hz), 7.03–7.40 m (11H, H_{arom}). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 10.74, 22.11, 30.46, 105.52 (1:3:2:3).

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CONFLICT OF INTERESTS

The authors declare the absence of conflict of interests.

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