# Synthesis of 1-hetaryl-5,6-dihydropyrrolo[2,1-*a*]isoquinolines from 1-hetarylmethyl-3,4-dihydroisoquinolines and 1,1,1-trifluoro-3-nitrobut-2-ene

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1-Hetarylmethyl-3,4-dihydroisoquinolines and their crown-containing derivatives reacted with 1,1,1-trifluoro-3-nitrobut-2-ene upon reflux in isobutanol or in toluene at room temperature to form 1-hetaryl-5,6-dihydropyrrolo[2,1-*a*]isoquinolines, including those with the benzocrown ether fragments.

**Key words:** 3,4-dihydroisoquinolines, 1,1,1-trifluoro-3-nitrobut-2-ene, benzocrown ethers, 1-hetaryl-5,6-dihydropyrrolo[2,1-*a*]isoquinolines.

In the last years, much attention is paid to the development of new methods for the synthesis of $CF_3$-containing heterocyclic compounds, since due to their unique physicochemical and biological properties they are widely used in different branches of industry, medicine, and agriculture.[1,2] Besides, the introduction of a $CF_3$ group substantially influences the electron density distribution in organic molecules, that makes some partially fluorinated compound valuable synthons for the preparation of new fluorine-containing heterocycles.[3—6] Thus, trifluoromethylated nitroalkenes readily react with 1,3-dicarbonyl compounds with the formation of tetrasubstituted furans[7] and pyrroles,[8] as well as serve as heterodienes in Diels—Alder reaction with the reverse electron requirements, giving 1,2-oxazine *N*-oxides as the products.[9,10]

Recently, we have shown[11] that the reaction of 1,1,1-trifluoro-3-nitrobut-2-ene with 1-methyl- and 1-benzyl-3,4-dihydroisoquinolines leads to the preparation of 5,6-dihydropyrrolo[2,1-*a*]isoquinolines, the structural skeleton of which lies in the basis of alkaloid crispin, which possesses a high cytotoxic activity.[12] In the present work, we studied the reaction of 1,1,1-trifluoro-3-nitrobut-2-ene with 1-hetarylmethyl-3,4-dihydroisoquinolines and showed that this reaction constitutes a simple and convenient method for the preparation of 1-hetaryl-5,6-dihydropyrrolo[2,1-*a*]isoquinolines, including those with the benzocrown ether fragments.

## Results and Discussion

We found that the reaction of 1,1,1-trifluoro-3-nitrobut-2-ene (**1**) with 3,4-dihydroisoquinolines **2a**,**b**, which, in contrast to benzyl derivatives, exist in the enamine tautomeric form due to the intramolecular hydrogen bonding (IMHB), upon reflux in isobutanol for 1 h (procedure ***A***) or in toluene at room temperature for 24 h (procedure ***B***) led to the formation of 1-benzothiazolyl-5,6-dihydropyrrolo[2,1-*a*]isoquinolines **3a**,**b** in 45—63% yields. The mechanism of this noncatalytic reaction includes a nucleophilic attack on nitroalkene **1** by the enamine tautomer of dihydroisoquinoline **2** (intermediate **I**) with subsequent cyclization at the carbon atom of the *aci* form (intermediate **II**), which is accompanied by the elimination of water and hyponitrous acid molecules (Grob cyclization,[8] Scheme 1).

Note that this transformation is characteristic of only 1,1,1-trifluoro-3-nitrobut-2-ene (**1**) and does not take place when a trifluoromethyl group is replaced with the trichloromethyl one. The presence of the methyl group in alkene **1** also plays an important role, since 1-nitro-3,3,3-trifluoropropene does not give this reaction. Though all this reduces a synthetic importance of the reaction under consideration, it remains still high enough because of a wide range of very different 1-methyl-3,4-dihydroisoquinoline derivatives.[13]

Taking into account the fact that the introduction of a heterocycle in the benzocrown ether molecule can lead

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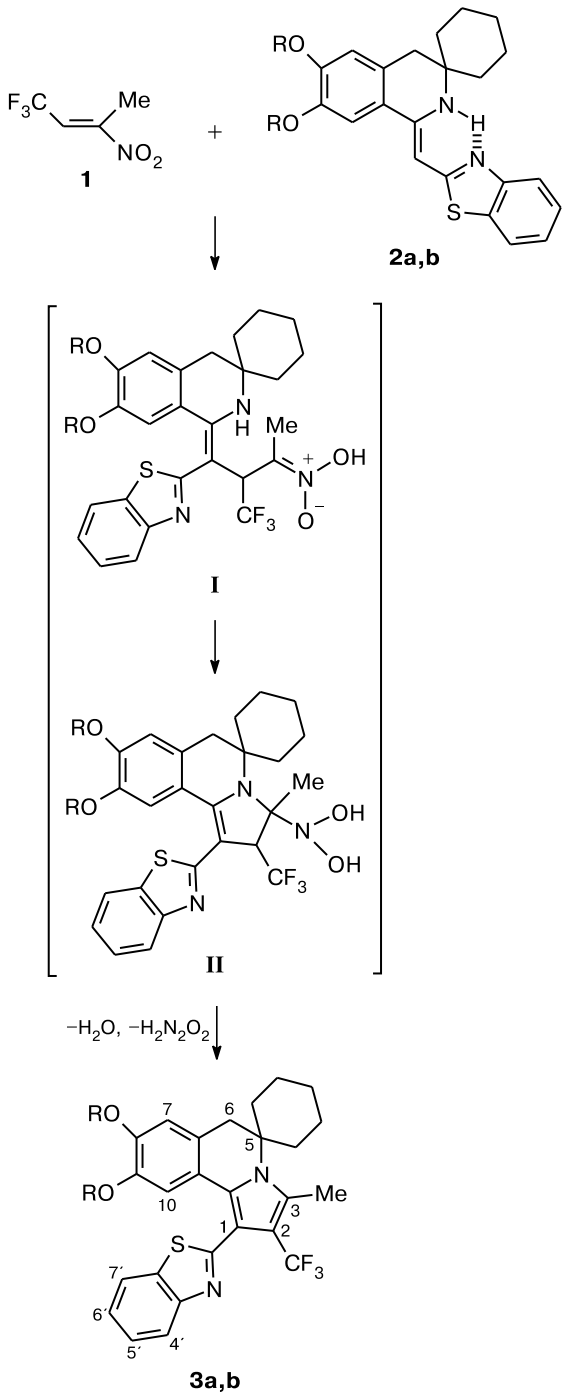
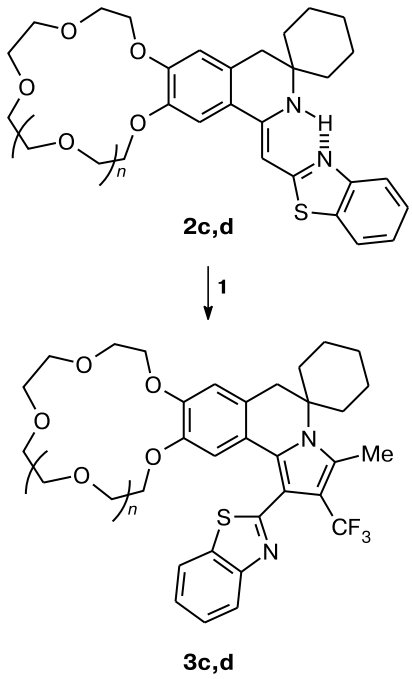
**Scheme 1**




R = Me (**a**), Et (**b**)

to considerable changes in its complexation and biological properties,[14] we used the reaction described above for the preparation of benzocrown ethers bound to the substituted 5,6-dihydropyrrolo[2,1-*a*]isoquinoline system. The synthesis of the crown-containing dihydroisoquinolines **2c**,**d** was accomplished using a three-component version of Ritter reaction from benzo-18-crown-6 and benzo-15-crown-5, as well as cyclohexylcarbaldehyde and benzothiazolylacetonitrile, in the presence of concentrated $H_2SO_4$ according to the procedure described earlier.[15] It was found that the reaction of nitroalkene **1** with compounds **2c**,**d** gave crown-containing 5,6-dihydropyrrolo[2,1-*a*]isoquinolines **3c**,**d** in 35—47% yields in isobutanol (method ***A***) and in 49—66% yields in toluene (method ***B***) (Scheme 2).

**Scheme 2**




n = 1 (**c**), 2 (**d**)

The products **3a**—**d** are colorless crystalline compounds, the structure of which was confirmed by elemental analysis, IR spectra, $^1H$, $^{19}F$, and $^{13}C$ NMR spectroscopy, as well as by X-ray diffraction study of compound **3d**. A general view of the molecule is shown in Fig. 1. According to the X-ray diffraction data, compound **3d** crystallizes in the form of crystal hydrate with the localization of the water molecule in the crown ether cavity. In this case, all six oxygen atoms of the crown ether fragment lie virtually in one plane (the deviation from the mean-square plane passed through the oxygen atoms lies within 0.07 Å), the water oxygen atom deviates from this plane by 1.56 Å, whereas the water protons form two bifurcated hydrogen bonds involving four crown ether oxygen atoms, thus fixing the saddle-like conformation of the crown ether chain (Table 1).

The carbon atoms of the ethylene fragments of the crown ether and the cyclohexane ring are remote from the spiro atom and demonstrate a strong anisotropy of ther-

**Table 1.** Hydrogen bonds O—H···O(*d*)*

| $O_{H_2O}$—$H_{H_2O}$ | $d$(O—H)$_{H_2O}$ | $d$($H_{H_2O}$···$O_{crown}$) | Angle $O_{H_2O}$—$H_{H_2O}$—$O_{crown}$ | $d$($O_{H_2O}$···$O_{crown}$) | $O_{crown}$** |
|---|---|---|---|---|---|
| O(7)—H(7A) | 1.080 | 2.197 | 139 | 3.094(3) | O(6) |
| | | 2.221 | 140 | 3.128(3) | O(1) |
| O(7)—H(7B) | 0.925 | 2.320 | 127 | 2.971(4) | O(3) |
| | | 2.375 | 164 | 3.274(4) | O(4) |

* $d$(H···O) < $r$(O) + 2.0 Å; the $O_{H_2O}$—$H_{H_2O}$—$O_{crown}$ angle > 110 deg.
** The O atoms of the crown ether fragment.

mal vibrations reflected in the shape of ellipsoids, that indicates the presence of structural disorder of these fragments. It seems impossible to resolve the components of this disorder without the introduction of additional limitations in the model because of a strong overlap of thermal ellipsoids. A similar character of ellipsoids is observed also for the conformationally labile $CF_3$ group. The dihydroazine ring has a *pseudo-twist* conformation; a virtually planar pyrrole ring of this tricyclic system is turned by 17.5° relative to the plane of the phenylene fragment. The benzothiazole substituent of the pyrrole ring is turned relative to its plane by 73.0° and is disordered in the plane over two positions with the occupancies 0.6/0.4. Because of the partial overlap of the atomic thermal ellipsoids, the limitations on the interatomic bond lengths were introduced for the corresponding components of the disorder (the DFIX 1.35 commands in the SHELXL refinement program), whereas the atomic thermal parameters were refined partially isotropically (the ISOR 0.01 command in the SHELXL refinement program). Apart from this, because of the almost entirely identical coordinates of the nitrogen and the sulfur atoms, for the components of the disorder the thermal parameters of the corresponding pairs of atoms were positively leveled (the EADP command).

It should be noted that the phenomenon of structural disorder of the conformationally labile groups at room temperature and the disorder of the thiazole ring in the plane are quite expected. The introduction of the corre-

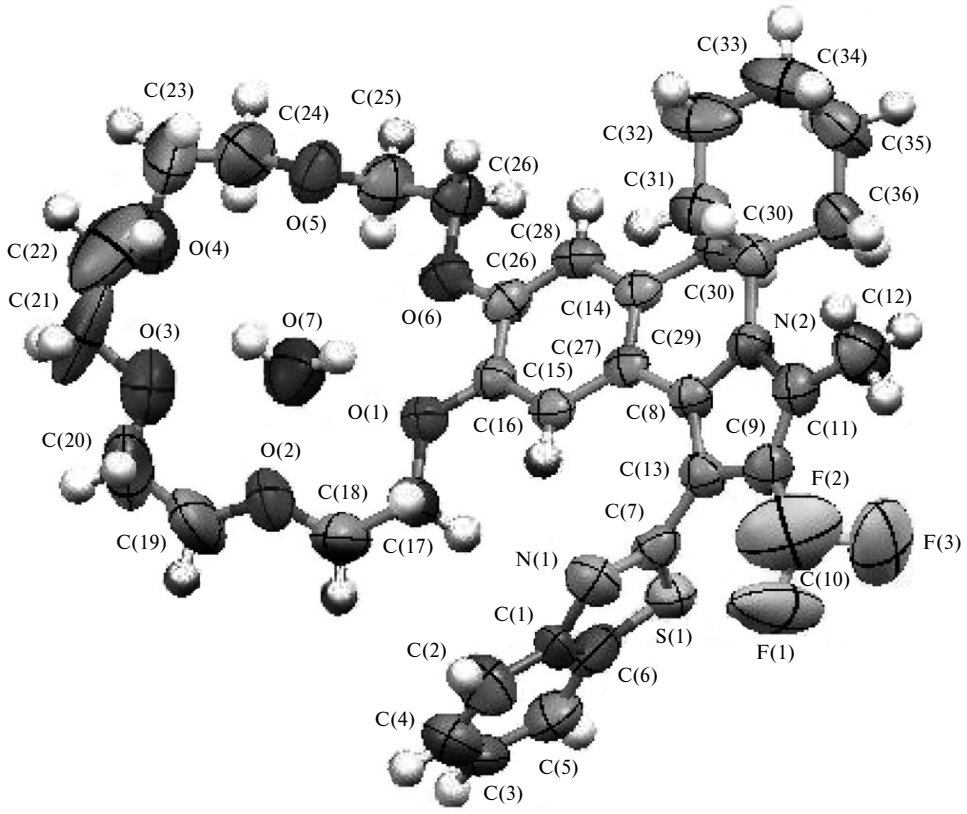


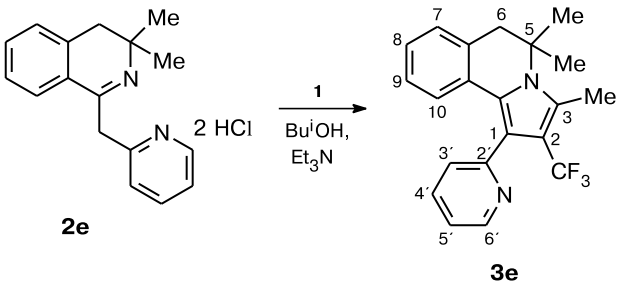

**Fig. 1**. Molecular structure of compound **3d**. Disordering of the benzothiazole ring is not shown.

sponding limitations and assumptions in the structural model suggested leads, of course, to certain deviations from the real atomic coordinates and, as a consequence, to the distortions of bond lengths and bond angles, but, as we see it, does not abolish the in general correct confirmation of the structure. The development of more accurate structural model is possible when the low-temperature experimental data will be used in future studies.

The turn of the benzothiazole ring relative to the pyrrole one exerts a shielding effect on proton H(10), which, as a result, is observed more upfield in the $^1$H NMR spectra of compounds **3a—d** as compared to proton H(7) ($\delta_{H(10)}$ = 6.16—6.25, $\delta_{H(7)}$ = 6.62—6.63). In the $^{19}$F NMR spectra of these compounds, the trifluoromethyl group is found at δ 110.1—110.2 as a slightly broad singlet or a partially unresolved quartet with $^5J_{F,H}$ = 0.8 Hz due to the splitting on the neighboring methyl group.

It should be noted that 3,3-dimethyl-1-(pyridin-2-ylmethyl)-3,4-dihydroisoquinoline dihydrochloride (**2e**) (obtained by the Ritter reaction from dimethyl benzyl carbinol and pyridin-2-ylacetonitrile[16]) also reacts with nitroalkene **1** under conditions of method ***A***, giving rise to 3,5,5-trimethyl-1-(pyridin-2-yl)-2-trifluoromethyl-5,6-dihydropyrrolo[2,1-*a*]isoquinoline (**3e**) in 62% yield, that makes it possible to introduce a pyridine ring to position 1 of the 5,6-dihydropyrrolo[2,1-*a*]isoquinoline system (Scheme 3).

**Scheme 3**




The structure of pyrroloisoquinoline **3e** was confirmed by X-ray diffraction study (Fig. 2). In general, the structure does not demonstrate any substantial deviations from the standard values of bond lengths or bond angles; essentially shortened intermolecular contacts in the crystal are absent, too. The X-ray diffraction study showed that the central fragment of the tricyclic system is in the *pseudo-twist* conformation, whereas the pyrrole ring is turned relative to the benzene ring by 23.7°. The planes of the pyrrole and the pyridine rings are turned with respect to each other by 56.3°, with the rotation of the latter around the C(1)—C(2′) bond being retarded by the bulky $CF_3$ group and the structurally rigid phenylene fragment, that leads to the formation of rotamers and the appearance in the

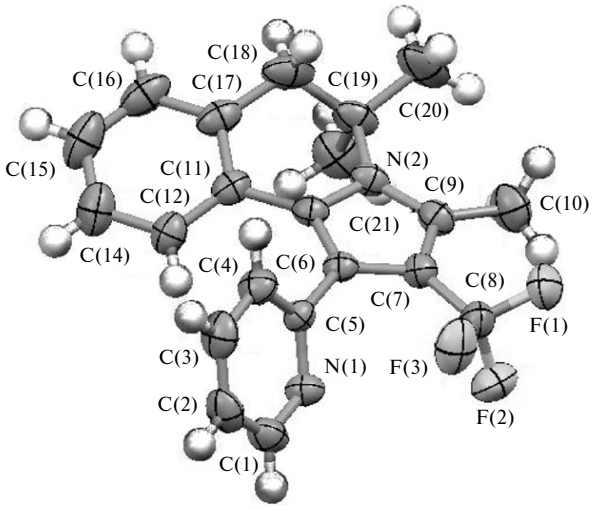



**Fig. 2.** Molecular structure of compound **3e**.

$^1$H NMR spectrum of this compound of three strongly broadened singlets of the pyridine protons H(3′), H(4′), and H(5′).

In conclusion, 1-hetarylmethyl-3,4-dihydroisoquinolines and their crown-containing derivatives involved in the reactions with 1,1,1-trifluoro-3-nitrobut-2-ene behave similarly to 1-benzyl-3,4-dihydroisoquinolines studied earlier, giving a number of new 1-hetaryl-5,6-dihydropyrrolo[2,1-*a*]isoquinolines in good yields, which are of interest for medicinal and analytical chemistry.

## Experimental

$^1$H and $^{19}$F NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 and 376 MHz, respectively), $^{13}$C NMR spectra were recorded on a Bruker Avance-500 spectrometer (126 MHz) in $CDCl_3$, using $Me_4Si$ and $C_6F_6$ as internal standards. IR spectra were obtained on a Perkin-Elmer Spectrum BX-II spectrometer in KBr pellets. Elemental analysis was performed on a PE 2400 automated analyzer. Dihydroisoquinolines **2** were obtained according to the known procedures.[13,16]

**Synthesis of compounds 3a—d (general procedure).** ***A.*** A mixture of nitrobutene **1** (0.16 g, 1.0 mmol) and the corresponding dihydroisoquinoline **2** (1.0 mmol) was refluxed in isobutanol (2 mL) for 1 h. Then, the solvent was evaporated at reduced pressure, a precipitate formed was filtered, washed with water, dried, and recrystallized from isobutanol or a mixture of dichloromethane—hexane.

***B.*** A solution of nitrobutene **1** (0.16 g, 1.0 mmol) and the corresponding dihydroisoquinoline **2** (1.0 mmol) in toluene (2 mL) was allowed to stand at ~25 °C for 24 h, the solvent was evaporated at reduced pressure, the residue was subjected to chromatography on silica gel (eluent chloroform) and recrystallized from isobutanol or a mixture of dichloromethane—hexane.

**1-(1,3-Benzothiazol-2-yl)-8,9-dimethoxy-3-methyl-5,5-pentamethylene-2-trifluoromethyl-5,6-dihydropyrrolo[2,1-*a*]isoquinoline (3a).** The yield was 46% (method ***A***), 63% (method ***B***), a white powder, m.p. 236—237 °C (dichloromethane—hexane,

1 : 2). Found (%): C, 65.35; H, 5.26; N, 5.22. $C_{28}H_{27}F_3N_2O_2S$. Calculated (%): C, 65.61; H, 5.31; N, 5.46. IR, ν/cm$^{-1}$: 1662, 1610, 1570, 1549, 1524, 1486, 1466, 1454, 1442, 1429. $^1$H NMR, δ: 1.24—2.27 (m, 10 H, 5 $CH_2$); 2.68 (s, 3 H, Me); 2.96 (s, 3 H, MeO); 3.16 (s, 2 H, $CH_2$); 3.83 (s, 3 H, MeO); 6.25 (s, 1 H, H(10)); 6.63 (s, 1 H, H(7)); 7.41 (t, 1 H, H(5′/6′), $J$ = 7.5 Hz); 7.50 (t, 1 H, H(6′/5′), $J$ = 7.6 Hz); 7.88 (d, 1 H, H(4′/7′), $J$ = 7.9 Hz); 8.11 (d, 1 H, H(7′/4′), $J$ = 7.9 Hz). $^{19}$F NMR, δ: 110.2 (s, $CF_3$).

**1-(1,3-Benzothiazol-2-yl)-8,9-diethoxy-3-methyl-5,5-pentamethylene-2-trifluoromethyl-5,6-dihydropyrrolo[2,1-*a*]isoquinoline (3b).** The yield was 47% (method ***A***), 45% (method ***B***), a white powder, m.p. 192—193 °C (dichloromethane—hexane, 1 : 3). Found (%): C, 66.79; H, 5.75; N, 5.13. $C_{30}H_{31}F_3N_2O_2S$. Calculated (%): C, 66.65; H, 5.78; N, 5.18. IR, ν/cm$^{-1}$: 1608, 1572, 1547, 1525, 1489, 1472, 1449, 1432, 1392. $^1$H NMR, δ: 0.78 (t, 3 H, Me, $J$ = 7.0 Hz); 1.22—2.25 (m, 10 H, 5 $CH_2$); 1.39 (t, 3 H, Me, $J$ = 7.0 Hz); 2.67 (q, 3 H, Me, $^5J_{H,F}$ = 0.8 Hz); 3.12 (s, 2 H, $CH_2$); 3.15 (q, 2 H, $CH_2O$, $J$ = 7.0 Hz); 4.04 (q, 2 H, $CH_2O$, $J$ = 7.0 Hz); 6.24 (s, 1 H, H(10)); 6.62 (s, 1 H, H(7)); 7.40 (ddd, 1 H, H(5′/6′), $J$ = 7.9 Hz, $J$ = 7.5 Hz, $J$ = 1.2 Hz); 7.49 (ddd, 1 H, H(6′/5′), $J$ = 7.9 Hz, $J$ = 7.5 Hz, $J$ = 1.2 Hz); 7.88 (d, 1 H, H(4′/7′), $J$ = 7.9 Hz); 8.09 (d, 1 H, H(7′/4′), $J$ = 7.9 Hz). $^{19}$F NMR, δ: 110.2 (q, $CF_3$, $^5J_{F,H}$ = 0.8 Hz). $^{13}$C NMR, δ: 14.0, 14.8, 15.6 (q, MeC(3), $^4J_{C,F}$ = 1.8 Hz); 23.0, 25.3, 34.5, 37.0, 63.0, 63.3, 64.5, 109.3, 109.6 (q, C(1), $^3J_{C,F}$ = 1.9 Hz); 112.6, 112.8 (q, C(2), $^2J_{C,F}$ = 33.2 Hz); 120.6, 121.3, 122.7, 123.4, 124.9 (q, $CF_3$, $^1J_{C,F}$ = 268.7 Hz); 125.2, 125.9, 129.4 (q, C(3), $^3J_{C,F}$ = 3.5 Hz); 130.0, 136.9, 147.1, 147.4, 153.4, 163.8.

**1-(1,3-Benzothiazol-2-yl)-3-methyl-5,5-pentamethylene-8,9-(1′,4′,7′,10′,13′-pentaoxatridecylene)-2-trifluoromethyl-5,6-dihydro[2,3-*g*]pyrrolo[2,1-*a*]isoquinoline (3c).** The yield was 47% (method ***A***), 49% (method ***B***), a white powder, m.p. 231—232 °C (isobutanol). Found (%): C, 63.23; H, 5.74; N, 4.23. $C_{34}H_{37}F_3N_2O_5S$. Calculated (%): C, 63.54; H, 5.80; N, 4.36. IR, ν/cm$^{-1}$: 1664, 1610, 1549, 1521, 1486, 1445, 1423. $^1$H NMR, δ: 1.22—2.25 (m, 10 H, 5 $CH_2$); 2.67 (s, 3 H, Me); 3.07—4.10 (m, 16 H, crown); 3.12 (s, 2 H, $CH_2$); 6.16 (s, 1 H, H(10)); 6.62 (s, 1 H, H(7)); 7.40 (t, 1 H, H(5′/6′), $J$ = 7.6 Hz); 7.49 (t, 1 H, H(6′/5′), $J$ = 7.6 Hz); 7.88 (d, 1 H, H(4′/7′), $J$ = 7.9 Hz); 8.09 (d, 1 H, H(7′/4′), $J$ = 8.0 Hz). $^{19}$F NMR, δ: 110.1 (s, $CF_3$). $^{13}$C NMR, δ: 15.6 (q, MeC(3), $^4J_{C,F}$ = 1.6 Hz); 23.0, 25.2, 34.5, 36.9, 63.0, 67.3, 68.9, 69.2, 69.6, 70.3, 70.5, 70.9, 71.2, 109.5, 109.8 (q, C(1), $^3J_{C,F}$ = 1.9 Hz); 112.8 (q, C(2), $^2J_{C,F}$ = 33.2 Hz); 113.5, 121.1, 121.4, 123.2, 123.4, 124.3 (q, $CF_3$, $^1J_{C,F}$ = 268.6 Hz); 125.2, 125.9, 129.5 (q, C(3), $^3J_{C,F}$ = 3.5 Hz); 129.9, 136.9, 147.5, 147.7, 153.3, 163.8.

**1-(1,3-Benzothiazol-2-yl)-3-methyl-5,5-pentamethylene-8,9-(1′,4′,7′,10′,13′,16′-hexaoxahexadecylene)-2-trifluoromethyl-5,6-dihydro[2,3-*g*]pyrrolo[2,1-*a*]isoquinoline (3d).** The yield was 35% (method ***A***), 66% (method ***B***), colorless prisms, m.p. 166—167 °C (isobutanol). Found (%): C, 61.81; H, 6.16; N, 4.03. $C_{36}H_{41}F_3N_2O_6S \cdot H_2O$. Calculated (%): C, 61.35; H, 6.15; N, 3.97. IR, ν/cm$^{-1}$: 1641, 1611, 1549, 1524, 1484, 1447, 1429. $^1$H NMR, δ: 1.22—2.25 (m, 10 H, 5 $CH_2$); 2.66 (br.s, 3 H, Me); 3.11 (s, 2 H, $CH_2$); 3.13—4.12 (m, 20 H, crown); 6.17 (s, 1 H, H(10)); 6.62 (s, 1 H, H(7)); 7.40 (ddd, 1 H, H(5′/6′), $J$ = 7.9 Hz, $J$ = 7.3 Hz, $J$ = 1.2 Hz); 7.49 (ddd, 1 H, H(6′/5′), $J$ = 8.0 Hz, $J$ = 7.3 Hz, $J$ = 1.2 Hz); 7.88 (d, 1 H, H(4′/7′), $J$ = 7.9 Hz); 8.09 (d, 1 H, H(7′/4′), $J$ = 8.0 Hz). $^{19}$F NMR, δ: 110.1 (q, $CF_3$, $^5J_{F,H}$ = 0.8 Hz).

**3,5,5-Trimethyl-1-(2-pyridyl)-2-trifluoromethyl-5,6-dihydropyrrolo[2,1-*a*]isoquinoline (3e).** A mixture of nitrobutene **1** (0.16 g, 1.0 mmol), dihydrochloride **2e** (0.32 g, 1.0 mmol), and triethylamine (0.24 g, 2.2 mmol) was refluxed in isobutanol (2 mL) for 1 h. Then, the solvent was evaporated at reduced pressure, a precipitate formed was filtered, washed with water, dried, and recrystallized from a mixture of dichloromethane—hexane. The yield was 62%, colorless prisms, m.p. 167—168 °C. Found (%): C, 68.99; H, 5.80; N, 5.13. $C_{21}H_{19}F_3N_2$. Calculated (%): C, 70.77; H, 5.37; N, 7.86. IR, ν/cm$^{-1}$: 1595, 1565, 1537, 1490, 1450, 1423, 1385. $^1$H NMR, δ: 1.60 (s, 6 H, 2 Me); 2.59 (q, 3 H, Me(3), $^5J_{H,F}$ = 1.3 Hz); 3.02 (s, 2 H, $CH_2$); 6.35 (d, 1 H, H(10), $J$ = 7.9 Hz); 6.86 (td, 1 H, H(9), $J$ = 7.5 Hz, $J$ = 1.0 Hz); 7.03 (t, 1 H, H(8), $J$ = 7.5 Hz); 7.11 (d, 1 H, H(7), $J$ = 7.5 Hz); 7.34 (br.s, 1 H, H(3′/5ь′); 7.45 (br.s, 1 H, H(5′/3′); 7.79 (br.s, 1 H, H(4′)); 8.70 (d, 1 H, H(6′), $J$ = 4.1 Hz). $^{19}$F NMR, δ: 110.4 (br.s, $CF_3$).

**Table 2.** Principal parameters of X-ray diffraction experiment

| Parameter | **3d** | **3e** |
|---|---|---|
| Elemental composition | $C_{36}H_{41}F_3N_2O_6S \cdot H_2O$ | $C_{21}H_{19}F_3N_2$ |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ |
| Unit cell parameters | | |
| $a$/Å | 15.3025(17) | 9.1505(8) |
| $b$/Å | 18.8731(18) | 11.3720(5) |
| $c$/Å | 14.5600(7) | 17.4820(11) |
| β/deg | 104.609(7) | 104.092(5) |
| $V$/Å$^3$ | 4069.1(6) | 1764.4(2) |
| $Z$ | 4 | 4 |
| $d_{calc}$/g cm$^{-3}$ | 1.150 | 1.342 |
| μ/mm$^{-1}$ | 0.137 | 0.101 |
| $F$(000) | 1488 | 744 |
| θ/deg | 2.60—26.48 | 2.91—26.37 |
| Index intervals | $-19 < h < 19$, $-16 < k < 23$ $-16 < l < 18$ | $-11 < h < 11$ $-6 < k < 14$ $-11 < l < 21$ |
| Reflections | | |
| measured | 18072 | 6594 |
| independent ($R_{int}$) | 7955 (0.0411) | 3431 (0.0172) |
| collected with $I > 2\sigma(I)$ | 2440 | 2196 |
| Completeness of data collection (%) | 95.6 for θ ≤ 25.50° | 95.4 for θ ≤ 26.37° |
| Adjustment factor $S$ on $F^2$ | 0.991 | 1.000 |
| Convergence factor ($R$-factor) for ($I > 2\sigma(I)$) | | |
| $R_1$ | 0.0504 | 0.0369 |
| $wR_2$ | 0.1074 | 0.0855 |
| on all the reflections | | |
| $R_1$ | 0.1701 | 0.0664 |
| $wR_2$ | 0.1171 | 0.0923 |
| Residual peaks of electron density, $\Delta\rho_e$/eÅ$^{-3}$ (max/min) | 0.224/−0.157 | 0.037/−0.217 |

**X-ray diffraction study of compounds 3d** and **3e.** Single crystals of compounds **3d** and **3e** were obtained by crystallization from the reaction mixtures. X-ray diffraction experiments were carried out on a Xcalibur 3 diffractometer with a CCD detector according to the standard procedure ($T$ = 295(2) K, Mo-K$\alpha$ radiation, graphite monochromator, $\omega$-scan technique). The crystalographic data and principal parameters of refinement for compounds **3d** and **3e** are given in Table 2. Absorption was included using the experimental curves of azimuthal scanning ($T_{min}/T_{max}$). All the nonhydrogen atoms were refined independently in anisotropic approximation, hydrogen atoms were placed in geometrically calculated positions and included in the refinement using a riding model with dependent thermal parameters. The hydrogen atoms of water molecule in the structure **3d** were found based on the peaks of electron density and included in the refinement with the fixed coordinates and thermal parameters dependent on the parent oxygen. All the calculations were performed using the SHELX97 software package.[17] The details of the X-ray diffraction studies of compounds **3d** (CCDC 1029081) and **3e** (CCDC 1029080) were deposited with the Cambridge Crystallographic Data Center.

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