2-(Polyfluoroalkyl)chromones
15.* Transformation of 3-chloro-2-(polyfluoroalkyl)chromones into benzofuran derivatives by hydroxylamine

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The reactions of 3-chloro-2-(polyfluoroalkyl)chromones with hydroxylamine in the presence of sodium acetate proceed with ring contraction to form benzofuran derivatives.

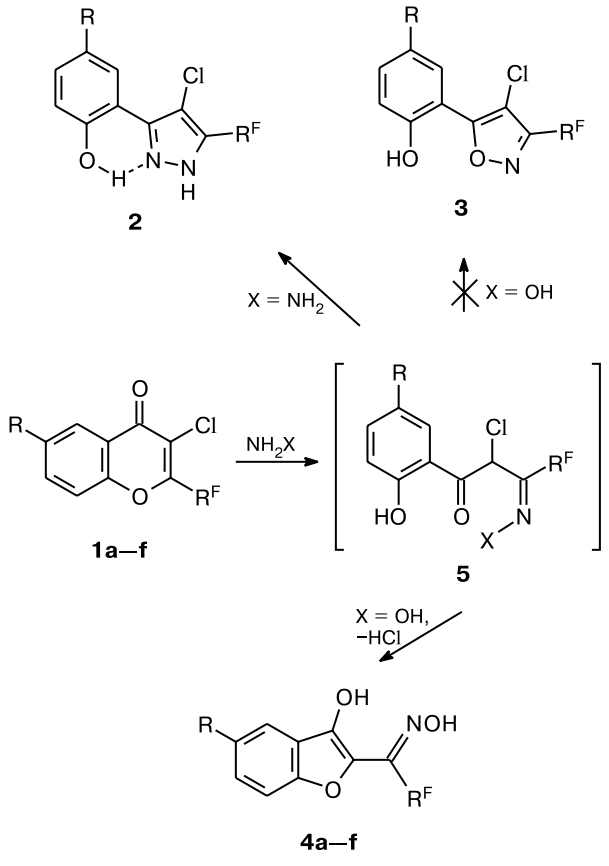
Key words: 3-chloro-2-(polyfluoroalkyl)chromones, hydroxylamine, benzofuran derivatives.

The chromone system, being the benzannelated γ-pyrone ring, is the structural basis of flavonoids, *viz.*, flower and fruit pigments, which are widely abundant in the vegetable kingdom. Many chromone derivatives are biologically active substances and valuable substrates in the organic synthesis.[2] Although chromones can be considered as a well-studied class of organic compounds, data on the reactions of 3-halosubstituted chromones with hydrazines and hydroxylamine are restricted. The present study is aimed at compensating this deficiency.

Results and Discussion

We have previously shown that 2-(polyfluoroalkyl)chromones react with hydrazine hydrate and hydroxylamine to form 3(5)-(2-hydroxyaryl)-5(3)-(polyfluoroalkyl)pyrazoles[3] and 5-(2-hydroxyaryl)-3-(polyfluoroalkyl)isoxazoles,[4] respectively. The radical chlorination of 2-R^F-chromones afforded[1,5] 2-R^F-3-chlorochromones **1a—f**, which are resinified by hydrazine hydrate but, being boiled in ethanol with $N_2H_4 \cdot 2HCl$, produce[1] 4-chloro-3(5)-(2-hydroxyaryl)-5(3)-(polyfluoroalkyl)pyrazoles **2**. Based on these data, we could expect that the reaction of 3-chlorochromones **1a—f** with hydroxylamine affords 4-chloro-5-(2-hydroxyaryl)-3-(polyfluoroalkyl)isoxazoles **3**. However, it turned out that the reactions of these compounds with $NH_2OH \cdot HCl$ in the presence of AcONa in boiling ethanol for 0.5—1 h produce benzofuran derivatives **4a—f** in high yields (58—91%) instead of isoxazoles **3** (Scheme 1). The introduction of the 6-NO_2 group enhances the reactivity of chromones toward hydroxylamine, which is manifested as shortening of the reaction duration and an increase in the yield of the target products.

Scheme 1



1—4	a	b	c	d	e	f
R	H	H	H	NO_2	NO_2	NO_2
R^F	CF_3	CF_2H	$(CF_2)_2H$	CF_3	CF_2H	$(CF_2)_2H$

Similar γ-pyrone ring contraction in 3-halochromones to form 2-aroyl-1-benzofuran-3-ones has previously[6] been observed for the interaction of 3-chloroflavones with an

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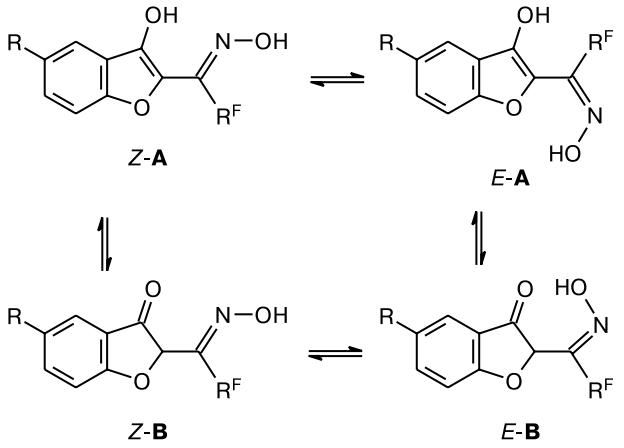
ethanol solution of KOH. It is also known that the reactions of 3-bromochromone with primary amines, 6-bromonorkhellin with primary and secondary amines in MeCN in the presence of K_2CO_3,[7] and 3-chloro-, 3-bromo-, and 3-iodochromones with secondary amines in DMF in the presence of K_2CO_3 [8] afford 2-aminomethylene-1-benzofuran-3-ones. The transformation of the chromone system into benzofuran by hydroxylamine was described only for 3-bromochromone from which 3-hydroxy-1-benzofuran-2-carbaldehyde oxime was synthesized.[7] The structure of this product was proved by X-ray diffraction analysis. However, the procedure of its synthesis and spectroscopic and physicochemical characteristics were not presented. Our results show that the reaction of 3-halochromones with hydroxylamine is general and makes it possible to synthesize new functionalized benzofuran derivatives **4**, which are of interest for further transformations into various R^F-containing compounds.

We believe that the reactions of chromones **1a—f** with hydrazine and hydroxylamine proceed through intermediate **5** formed by the attack of the NH_2 group at the C(2) atom with pyrone ring opening. Further, in the case of X = NH_2, the intramolecular Ad_N reaction occurs between the C=O and NH_2 groups to produce pyrazoles **2**. In the case of X = OH, the nucleophilic substitution of the Cl atom by phenolic hydroxyl resulting in benzofuran derivatives **4a—f** are more preferable.

The structure of products **4a—f**, which can theoretically exist in two tautomeric forms **A** and **B**, each of which is capable of *Z*/*E* isomerism (Scheme 2), was confirmed by elemental analysis, IR spectroscopic, and ^1H and ^{19}F NMR spectroscopic data (Table 1). The ^1H NMR spectra of compounds **4a,d,f** in solutions of $CDCl_3$ and DMSO-d_6 contains one set of signals (in these cases, the content of minor tautomers and isomers did not exceed 2—3%) corresponding to aromatic and two acidic protons. These data allow us to exclude tautomeric form **B** and ascribe the enolized structure **A** with the *Z* configuration of the C=N bond in the *s-cis*-conformation to these compounds. In the case of this conformation, the

Scheme 2



4a—f

Table 1. ^1H NMR and IR spectroscopic data for benzofurans **4a—f**

Compound	^1H NMR, δ (*J*/Hz)							IR, ν/cm^{-1}
	H(4)	H(5)	H(6)	H(7)	OH/CH	NOH	R^F	
4a[a,b], *Z*-**A** (72%)	7.73 (d, J_o = 7.9)	7.29 (ddd, J_o = 7.9, 6.7, J_m = 1.3)	7.47 (ddd, J_o = 8.1, 6.7, J_m = 1.2)	7.44 (d, J_o = 8.1)	7.90 (br.s)	9.70 (br.s)	−66.0 (s)[c]	2900—3400, 1620, 1605, 1560[d]
4a[a,b], *E*-**B** (28%)	7.73 (d)[e]	7.17 (t, J_o = 7.5)	7.67 (t, J_o ≈ 7.5)	7.20 (d, J_o ≈ 8.0)	5.80 (s); 5.26 (s, *Z*-**B**) (*E* : *Z* = 95 : 5)	9.20 (br.s)	−67.7 (s,[c] *E*-**B**); −65.2 (s,[c] *Z*-**B**)	2900—3400, 1705, 1645, 1610, 1560[f]
4a[b,g], *Z*-**A** (90%)	7.77 (d, J_o = 7.8)	7.31 (ddd, J_o = 7.8, 7.1, J_m = 0.7)	7.45 (ddd, J_o = 8.4, 7.1, J_m = 1.3)	7.54 (d, J_o = 8.4)	9.80 (br.s)	13.30 (br.s)	—	—
4a[b,g], *E*-**B** (10%)	7.71 (d, J_o = 7.7)	7.22 (t, J_o = 7.4)	7.78 (t)[e]	7.35 (d, J_o ≈ 8.0)	6.01 (s)	13.51 (s)	—	—
4b[a], *Z*-**A** (65%)	7.72 (d, J_o = 7.8)	7.29 (ddd, J_o = 7.8, 6.7, J_m = 1.3)	7.45 (ddd, J_o = 8.4, 6.7, J_m = 1.1)	7.42 (d, J_o = 8.1)	7.80—9.70 (br.s)		6.81 (t, $^2J_{H,F}$ = 53.5)	2900—3400, 1660, 1610, 1570
4b[a], *E*-**B** (35%)	7.71 (d)[e]	7.15 (t, J_o = 7.5)	7.66 (t, J_o ≈ 7.5)	7.20 (d, J_o = 8.4)	5.76 (s); 5.27 (s, *Z*-**B**) (*E* : *Z* = 87 : 13)	—[h]	6.23 (t, $^2J_{H,F}$ = 54.2)	—

(*to be continued*)

Table 1 (*continued*)

Compound	^{1}H NMR, δ (*J*/Hz)							IR, ν/cm^{-1}
	H(4)	H(5)	H(6)	H(7)	OH/CH	NOH	R^F	
4b[g], *Z*-**A** (85%)	7.74 (d, J_o = 7.6)	7.30 (ddd, J_o = 7.9, 7.1, J_m = 0.8)	7.44 (ddd, J_o = 8.4, 7.1, J_m = 1.3)	7.54 (d, J_o = 8.4)	9.60 (br.s); 10.07 (s, *E*-**A**) (*Z* : *E* ≈ 10 : 1)	13.00 (br.s); 12.56 (s, *E*-**A**)	6.84 (t, $^2J_{H,F}$ = 53.3)	—
4b[g], *E*-**B** (15%)	7.67 (d, J_o = 7.7)	7.19 (t, J_o = 7.6)	7.73 (t)[e]	7.30 (d, J_o = 8.4)	5.76 (s); 5.63 (s, *Z*-**B**) (*E* : *Z* = 88 : 12)	12.82 (s); 12.92 (s, *Z*-**B**)	6.67 (t, $^2J_{H,F}$ = 53.3)	—
4c[a], *Z*-**A** (14%)	7.73 (d, J_o = 7.8)	7.29 (ddd, J_o = 7.8, 6.8, J_m = 1.3)	7.47 (ddd, J_o = 8.3, 6.8, J_m = 1.2)	7.43 (d, J_o = 8.3)	7.90 (br.s)	9.30 (br.s)	6.37 (tt, $^2J_{H,F}$ = 53.0, $^3J_{H,F}$ = 5.4)	—
4c[a], *E*-**B** (86%)	7.71 (d, J_o = 7.5)	7.16 (t, J_o = 7.5)	7.67 (t, J_o ≈ 7.5)	7.19 (d, J_o = 8.4)	5.79 (s); 5.28 (s, *Z*-**B**) (*E* : *Z* = 96 : 4)	9.30 (br.s)	6.12 (tdd, $^2J_{H,F}$ = 52.8, $^3J_{H,F}$ = 6.8, 3.5)	3280, 1715, 1615
4c[g], *Z*-**A** (75%)	7.75 (d, J_o = 7.9)	7.28 (ddd, J_o = 7.9, 7.2, J_m = 0.9)	7.42 (ddd, J_o = 8.4, 7.2, J_m = 1.3)	7.52 (d, J_o = 8.4)	9.70 (br.s)	13.20 (br.s)	6.88 (tt, $^2J_{H,F}$ = 51.8, $^3J_{H,F}$ = 5.6)	—
4c[g], *E*-**B** (25%)	7.67 (d, J_o = 7.7)	7.18 (t, J_o = 7.8)	7.73 (t)[e]	7.30 (d, J_o = 8.4)	5.83 (s); 5.72 (s, *Z*-**B**) (*E* : *Z* = 82 : 18)	13.34 (s); 13.57 (s, *Z*-**B**)	6.86 (tt, $^2J_{H,F}$ = 51.8, $^3J_{H,F}$ = 6.0)	—
4d[a], *Z*-**A**	8.69 (dd, J_m = 2.4, J_p = 0.5)	—	8.37 (dd, J_o = 9.2, J_m = 2.4)	7.56 (dd, J_o = 9.2, J_p = 0.5)	7.90 (br.s)	9.50 (br.s)	−66.1 (s)[c]	2900—3400, 1635, 1610, 1570, 1540
4d[g,i], *Z*-**A**	8.74 (d, J_m = 2.4)	—	8.30 (dd, J_o = 9.1, J_m = 2.4)	7.81 (d, J_o = 9.1)	10.8 (br.s)	13.6 (br.s)	—	—
4e[g], *Z*-**A** (84%)	8.72 (d, J_m = 2.4)	—	8.29 (dd, J_o = 9.2, J_m = 2.4)	7.80 (d, J_o = 9.2)	10.4 (br.s)	13.0 (br.s)	6.86 (t, $^2J_{H,F}$ = 53.3)	2900—3400, 1630, 1610, 1570, 1530
4e[g], *E*-**A** (16%)	8.81 (d, J_m = 2.4)	—	8.26 (dd, J_o = 9.2, J_m = 2.4)	7.77 (d, J_o = 9.2)	10.71 (s)	12.84 (s)	7.31 (t, $^2J_{H,F}$ = 52.7)	—
4f[g,j], *Z*-**A**	8.75 (d, J_m = 2.4)	—	8.29 (dd, J_o = 9.1, J_m = 2.4)	7.80 (d, J_o = 9.1)	10.60 (br.s)	13.40 (br.s)	6.91 (tt, $^2J_{H,F}$ = 51.8, $^3J_{H,F}$ = 5.5)	3400, 3290, 1635, 1620, 1580, 1540

[a] In $CDCl_3$.
[b] The ^{1}H NMR spectrum recorded 3 months after **4a** was synthesized.
[c] The ^{19}F NMR spectrum relatively to $CFCl_3$.
[d] The IR spectrum of the freshly prepared sample of **4a**.
[e] The signal is disguised by a doublet of the H(4) proton of the **A** form.
[f] The IR spectrum recorded 3 months after **4a** was synthesized.
[g] In DMSO-d_6.
[h] No signal is detected.
[i] The spectrum exhibits the *E*-**A** isomer (2—3%).
[j] The *E*-**A** and *E*-**B** forms (2—3% each) are observed in the spectrum.

molecule can be stabilized due to the formation of an intramolecular hydrogen bond between the enolic hydroxyl and the oxime N atom. The *Z* configuration of the C=N bond was suggested from the chemical shift (CS) of the CF_3 group of oxime **4a** in the ^{19}F NMR spectrum (δ −66.0). According to the published data,[4,9—11] the signal of this group in the spectra of *Z* isomers of trifluoromethylated oximes and hydrazones appears at δ −64 to −66, whereas for the *E* isomers it appears at δ −67 to −71. 3-Hydroxy-1-benzofuran-2-carbaldehyde oxime (R = R^F = H) in the crystalline state has a similar structure.[7]

The IR spectra of nitro derivatives **4d—f** (in Nujol) agree well with the proposed enolic form **A**: the ν(C=O) band is absent but a broad band of absorption of hydroxyl groups is observed at 2900—3400 cm^{-1}. The IR spectrum of the sample of compound **4a** directly after preparation had a similar shape. However, after storage for 3 months,

its spectrum contained an additional ν(C=O) peak at 1705 cm^{-1}, indicating the partial isomerization of tautomer **A** to keto form **B** upon prolonged storage of the sample at ~20 °C. The ^1H NMR spectrum of the same sample in a $CDCl_3$ solution contained two sets of signals, one of which belonged to tautomer **A** (72%) and another set exhibited the signals from aromatic protons and a singlet at δ 5.80, which did not disappear when CD_3CO_2D was added and was attributed to the methine proton of tautomeric form **B** (28%). After 22 h, this solution contained 38% tautomer **B**, *i.e.*, in a solution of oxime **4a** in $CDCl_3$ the tautomeric equilibrium shifts toward form **B**. In more polar DMSO-d_6, the prototropism rate increases sharply and the equilibrium shifts rapidly toward tautomer **A**. For example, in the spectrum of sample **4a** with the composition **A** : **B** = 72 : 28 immediately after dissolution in DMSO-d_6, the ratio of tautomers **A** : **B** was 90 : 10. The higher stability of tautomer **A** compared to **B** in DMSO-d_6 is related, most likely, to the presence of two acidic protons, which can participate in the formation of an intermolecular hydrogen bond with basic solvent molecules.

Tautomers **A** and **B** exhibit a substantial difference in CS of the H(5), H(6), and H(7) protons. In both $CDCl_3$ and DMSO-d_6 solutions, the signals of the H(5) and H(7) protons of form **B** demonstrate the upfield shift by 0.10—0.25 ppm, and the H(6) proton is characterized by the downfield shift by 0.20—0.35 ppm (see Table 1). This agrees well with the structural changes that occur in the furan ring during keto-enol tautomerism.

Note that in the ^1H NMR spectra of benzofurans **4a—c** in solutions of $CDCl_3$ and DMSO-d_6 the singlet at δ ~5.8 is always accompanied by a low-intensity singlet at δ 5.3—5.7, which also does not disappear upon deuteration and is assigned to the proton of the CH group of one of the geometric isomers of tautomers **B** (*E*-**B** or *Z*-**B**). The ^{19}F NMR spectrum of benzofuran **4a** in a solution of $CDCl_3$, which was recorded 3 months after its preparation, contains the singlet of the CF_3 group of enol **A** and, in addition, singlets at δ −67.7 and −65.2, which should be assigned on the basis of the published data[9—11] to the *E* and *Z* tautomers of form **B**. The calculation based on the relative integral intensities (RII) of signals from the protons of the CH and CF_3 groups shows that the ratio of isomers *E*-**B** and *Z*-**B** for **4a** is 95 : 5. The higher stability of isomer *E*-**B** compared to that of *Z*-**B** can be referred, most likely, to the possibility of formation of an intramolecular hydrogen bond between the oxime hydroxyl and the O atom of the carbonyl group, as it was observed[4,9] in monooximes of β-diketones with the oxime function at the C atom bound to the R^F group.

Nitro derivative **4e**, as **4d,f**, exists only in the enolic form **A**. However, the ^1H NMR spectrum of this compound in DMSO-d_6 (it is insoluble in $CDCl_3$) contains two sets of signals with RII = 84 : 16, among which, as we assume, the major set belongs to isomer *Z*-**A** and the minor set belongs to *E*-**A**. This conclusion can be made from the absence of the singlet of the methine proton in the spectrum and the presence of two triplets of the CF_2H groups, among which the minor triplet exhibits the downfield shift by 0.45 ppm compared to the major triplet. Probably, in the case of the *E*-**A** form, the *s-trans*-conformation, in which the proton of the CF_2H group lies in the region of hydroxyl deshielding, is more favorable.

Unlike benzofuran **4a**, which was obtained in the form of tautomer *Z*-**A** and partially isomerized to form *E*-**B** only upon prolonged storage, benzofurans **4b,c** are immediately formed as a mixture of tautomers **A** and **B**. For example, according to the ^1H NMR spectroscopic data, in a freshly prepared solution of **4b** in $CDCl_3$ tautomers **A** and **B** exist in a ratio of 65 : 35, whereas in DMSO-d_6, which stabilizes form **A** and accelerates prototropism, they are found in the 85 : 15 ratio. More thorough analysis of the spectra of benzofuran **4b** shows that each of tautomeric forms **A** and **B** in these solvents is presented by the isomers with the ratios *Z*-**A** : *E*-**A** ≈ 10 : 1 (calculation from RII of aromatic protons) and *E*-**B** : *Z*-**B** ≈ 7 : 1 (calculation from RII of methine protons). The ^1H NMR spectra in $CDCl_3$ show that sample **4c** after two recrystallizations from a hexane—chloroform mixture consists of keto form **B** by 60—70% and enol **A** by 40—30% and the additional filtration of an ethyl acetate solution of **4c** through the silica gel layer increases the content of form **B** to 86% (the IR spectrum contained absorption bands of ν(C=O) at 1715 cm^{-1} and ν(C=N) at 1615 cm^{-1}). During the dissolution of the latter sample in DMSO-d_6, tautomer **B** is immediately transformed into form **A**, and their ratio becomes equal to **A** : **B** = 75 : 25. Note that, in the case of benzofuran **4c**, only keto form **B** was represented by isomers *E*-**B** and *Z*-**B** in ratios of 96 : 4 in $CDCl_3$ and 82 : 18 in DMSO-d_6, respectively (see Table 1).

Thus, the reactions of 3-chloro-2-(polyfluoroalkyl)chromones with hydroxylamine occur with the substitution of the Cl atom and transformation of the chromone system into the R^F-containing benzofuran derivatives, whose isomeric and tautomeric composition depends on the solvent nature, the number of F atoms in the polyfluoroalkyl substituent, and the presence of the nitro group in the benzene ring.

Experimental

IR spectra were recorded on an IKS-29 instrument in Nujol. ^1H NMR spectra were obtained on a Bruker DRX-400 spectrometer in $CDCl_3$ or DMSO-d_6 with a working frequency of 400.13 MHz using Me_4Si as an internal standard. ^{19}F NMR spectra were recorded on a Tesla BS-587A instrument in $CDCl_3$ with a working frequency of 75.3 MHz using $CFCl_3$ as an inter-

Table 2. Main physicochemical characteristics of compounds **4a—f**

Compound	Yield (%)	M.p. /°C	Found / Calculated (%)			Molecular formula
			C	H	N	
4a	88	148—150 (PhMe)	48.92 / 48.99	2.28 / 2.47	5.74 / 5.71	$C_{10}H_6F_3NO_3$
4b[a]	58	121—125 (C_6H_{14}—PhMe)	52.95 / 52.87	3.10 / 3.11	6.09 / 6.17	$C_{10}H_7F_2NO_3$
4c[b]	60	96—99 (C_6H_{14}—$CHCl_3$)	47.62 / 47.67	2.47 / 2.55	4.99 / 5.05	$C_{11}H_7F_4NO_3$
4d	91	>190 (decomp.) (PhMe)	41.44 / 41.40	1.81 / 1.74	9.75 / 9.65	$C_{10}H_5F_3N_2O_5$
4e	67	>215 (decomp.) (AcOEt)	44.30 / 44.13	1.91 / 2.22	10.25 / 10.29	$C_{10}H_6F_2N_2O_5$
4f	79	165—168 (PhMe)	41.15 / 41.01	1.63 / 1.88	8.66 / 8.70	$C_{11}H_6F_4N_2O_5$

[a] **A** : **B** = 65 : 35.
[b] **A** : **B** = 28 : 72, at **A** : **B** = 14 : 86 the mixture had m.p. 102—104 °C.

nal standard. The synthesis of initial 3-chlorochromones **1a—f** has been described previously.[1,5] The ^1H, ^{19}F NMR and IR spectroscopic data for compounds **4a—f** are presented in Table 1.

1-(3-Hydroxybenzofuran-2-yl)-2,2,2-trifluoroethanone oxime (4a). 3-Chlorochromone **1a** (0.50 g, 2.0 mmol), hydroxylamine hydrochloride (0.21 g, 3.0 mmol), and anhydrous sodium acetate (0.37 g, 4.5 mmol) were dissolved on heating in an EtOH—H_2O (1 : 1.5) mixture (10 mL). The resulting solution was refluxed for 1 h, cooled, and diluted with water (10 mL). The precipitate that formed was filtered off, washed with water, dried, and recrystallized from toluene.

Compounds **4b,c** were synthesized using a similar procedure. Nitro derivatives **4d—f** to synthesize required only boiling for 15—30 min. All resulting products had good elemental analysis data but melted in a wide temperature interval (2—4 °C). The yields, melting points, and elemental analysis data for compounds **4a—f** are presented in Table 2.

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