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Synthesis and some chemical properties of 1-aryloxy-2-chloro-1,2-difluoroethenes

Alexei I. Mushta, Mikhail M. Kremlev *

Department of Fluorine Chemistry, Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanskaya st. 5, UA-02094 Kiev, Ukraine

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Abstract

A convenient method of synthesis of 1-aryloxy-2-chloro-1,2-difluoroethenes **1a–h** and 1,2-di(aryloxy)-1,2-difluoroethenes **2a–d** by the reaction of 1,2-dichloro-1,2-difluoroethene with substituted phenols was developed. Compounds **1a–c** treated with *n*-C_4H_9Li and then with CO_2 and I_2 formed 3-aryloxy-2,3-difluoroacrylic acids **3a–e** or 1-aryloxy-2-iodo-1,2-difluoroethenes **4a,c**, respectively. Reaction of lithium derivative of 1-(4-methylphenoxy)-2-chloro-1,2-difluroethene **1c** with DMF or *N*-formylpiperidine gave 3-(4-methylphenoxy)-3-(dimethylamino or piperidin-1-yl)-2-fluoropropenal **5c**, **6c**.

Keywords: Phenols; 1,2-Dichloro-1,2-difluoroethene; 1-(Aryloxy)-2-chloro-1,2-difluoroethenes; 1,2-Di(aryloxy)-1,2-difluoroethenes

1. Introduction

The synthetic methods for the addition of substituted phenols to chlorotrifluoroethene are well established [1,2], and these compounds are used for the synthesis of herbicides and pesticides [3]. However, the general procedures for the substitution of fluorine atom in chlorotrifluoroethene by an aryloxy fragment with the formation of the corresponding olefins of general formula ArOCF = CFCl are limited so far to very few examples. The only synthetic procedure described in literature was the preparation of 1-(phenyloxy)-2-chloro-1,2-difluoroethene by the reaction of sodium phenolate with chlorotrifluoroethene in anhydrous diethyl ether [4].

We decided to develop a simpler method for the synthesis of such types of compounds by the reactions of substituted phenols with a industrial example of 1,2-dichloro-1,2-difluoroethene.

Previously, we showed that 4-methoxycarbonylaminothiophenol easily reacted with 1,2-dichloro-1,2-difluoroethene in acetone in the presence of potassium hydroxide with the formation of 4-methoxycarbonylaminophenyl(1,2-difluoro-2-chloroethenyl)sulfide. The reaction apparently occurred in two stages: the addition of substituted thiophenol to 1,2-dichloro-1,2-fluoroethene, followed by the dehydrochlorination process [5].

2. Results and discussion

It was found that substituted phenols containing electron donating or electron withdrawing groups in para-position of benzene ring did not react with 1,2-dichloro-1,2-difluoroethene in the presence of potassium hydroxide in acetone as a solvent even under reflux. In spite of its low boiling point 1,2-dichloro-1,2-difluoroethene has good solubility in acetone and is present in a boiling mixture.

However, the reaction of substituted phenols with 1,2-dichloro-1,2-difluoroethene in *N*,*N*-dimethylformamide (DMF) or *N*,*N*-dimethylacetamide (DMA) in the presence of potassium hydroxide in a 1.25:1 molar ratio to phenol at 75–80 °C allows the preparation of compounds **1a–h** in good yields (Scheme 1).

* Corresponding author. Tel.: +38 44 5510652; fax: +38 44 5732643.
E-mail address: kremlyov1@yandex.ru (M.M. Kremlev).

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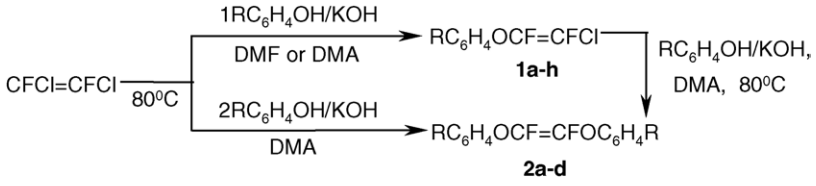


R=H (**a**), 3-CH_3 (**b**), 4-CH_3 (**c**), 4-OCH_3 (**d**), 3-$NHCOCH_3$ (**e**), 4-Br (**f**), 3-F (**g**), 4-F (**h**)

Scheme 1.

The use of excess of KOH is necessary because it takes part in the addition of 1,2-dichloro-1,2-difluoroethene to phenol as a catalyst and in the elimination of HCl from the intermediate product. Decrease in the amount of KOH does not raise the yields of the desired compounds; this was shown by a special experiment.

Similarly to the reactivity of 4-methoxycarbonylaminothiophenols [5], this reaction apparently occurs in two stages: first by the addition of substituted phenol to 1,2-dichloro-1,2-difluoroethene, followed by the elimination of hydrogen chloride.

Treatment of the compounds **1a–d** with the substituted phenols in DMA in the presence of potassium hydroxide leads to the formation of 1,2-di(aryloxy)-1,2-difluoroethene **2a–d** in 50–60% yield (Scheme 1). 1,2-Di(aryloxy)-1,2-difluoroethenes **2a–d** could be obtained by the reaction of two moles of the corresponding phenol with one mole of 1,2-dichloro-1,2-difluoroethene (Scheme 1).

Technical 1,2-dichloro-1,2-difluoroethene exists as a 1:1 mixture of E- and Z-isomers [6]. The same E- and Z-isomer ratio was determined for the compounds **1a–h**. In contrast to the compounds **1a–h**, compounds **2a–d** are single isomers as determined by ^{19}F NMR spectroscopy. Due to the symmetry of compounds **2a–d**, we may assume that they are E-isomers according to the chemical shifts of signals in ^{19}F NMR spectra, compared with the chemical shifts in the ^{19}F NMR spectra of Z-isomers **1a–h**.

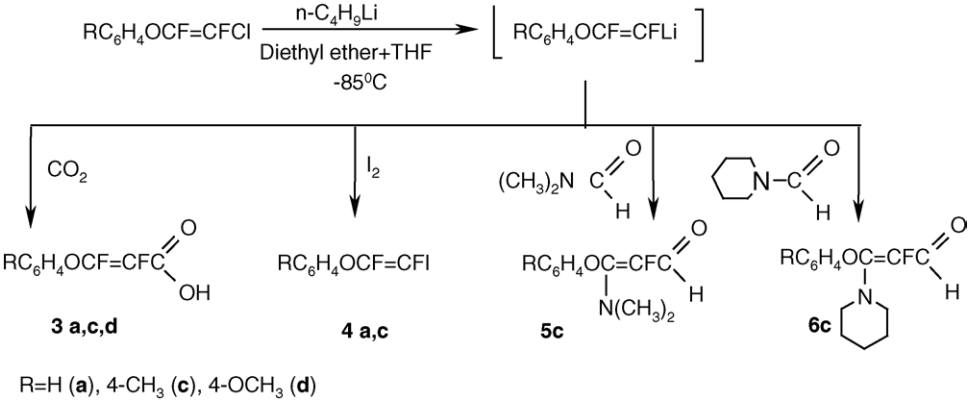
We prepared meta- and para-fluorosubstituted 1-(fluorophenoxy)-2-chloro-1,2-difluoroethenes **1g,h** for the determination of σ-constants of the ClCF = CFO-group. σ-Constants were determined by ^{19}F NMR spectroscopy and calculated by equations described in [7]. It appears, that σ-constants of E- and Z- –OCF = CFCl groups are equivalent for the both fragments: σ_I 0.52, σ_R −0.28, σ_P 0.24. It is seen from these data that E- and Z-isomers of ClCF = CFO-group possess acceptor properties, compared with E- (σ_I 0.1, σ_R 0.1,σ_P 0.20) and Z-1, 2-difluoro-2-chlorovinyl (σ_I 0.2, σ_R 0.06, σ_P 0.26) groups [8].

The chlorine atom in the ClCF = CFO-series of compounds **1a,c,d** can be substituted with lithium using *n*-butyllithium. Treatment of lithium derivatives with carbon dioxide or iodine leads to the formation of 3-aryloxy-2,3-difluoroacrylic acids **3a,c,d** or 1-(aryloxy)-2-iodo-1,2-difluoroethenes **4a,c** (Scheme 2).

Compounds **3a,c,d** and **4a,c** are a 1:1 mixture of E- and Z-isomers according to ^{19}F NMR spectroscopy. In contrast to the compounds **1a,c,d** para-substituted derivatives of α,β-difluoro-β-chlorostyrene which are a 1:3 mixture of E- and Z-isomers form only stable E-difluorostyryllithium derivatives on the interaction of *n*-butyllithium, and their products of reaction with various substrates contain only E-difluorovinylene links [9].

The reactions of lithium derivative of compound **1c** with DMF or *N*-formylpiperidine lead to the formation of products **5c**, **6c** with the aldehyde function and dimethylamino- **5c** or piperidine fragment **6c** bonded to the β-carbon atom of the vinylene link (Scheme 2).

These reactions showed the difference of lithium derivative of compound **1c** from difluorostyryllithium



R=H (**a**), 4-CH_3 (**c**), 4-OCH_3 (**d**)

Scheme 2.

derivatives, which have formed substituted E-α,β-difluorocinnamaldehydes under similar reaction conditions. The products of substitution of β-fluorine atom by piperidine fragment were obtained only by the reaction of E-α,β-difluorocinnamaldehyde derivatives with excess of piperidine. The aldehyde group in the last case shows no reactivity [10].

Coupling constants of aldehyde group hydrogen atom and fluorine in the compounds **5c** and **6c** (J_{FH} = 19.5 Hz) are similar to the J_{FH} in derivatives of E-α,β-difluorocinnamaldehydes [10].

3. Experimental

3.1. General

All chemicals were of reagent grade or were purified by standard methods before use. ^1H, ^{19}F NMR spectra were recorded at 299.95 and 282.2 MHz respectively with a Varian VXR-300 spectrometer. Chemical shifts are given in ppm relative to Me_4Si and $CFCl_3$, respectively as internal standard. Coupling constants are given in Hz. Melting point were determined in open capillaries and are uncorrected. Reactions of lithium derivatives were carried out in anhydrous solvents and under inert (Ar) atmosphere.

3.2. Preparative procedures

3.2.1. 1-(aryloxy)-2-chloro-1,2-difluoroethenes (*1a–h*)

A mixture of 40 mmol of the corresponding substituted phenol, 50 mmol of potassium hydroxide, 50 mmol of 1,2-dichloro-1,2-difluoroethene and 30 ml of DMF or DMA was stirred for 10 h at 75–80 °C. Reaction mixture was cooled to room temperature and poured into water. Organic layer was extracted with diethyl ether, the extract was washed with 4% aqueous potassium hydroxide, water, dried over magnesium sulfate and distilled (see Tables 1 and 2).

3.2.2. 1.2-Di(aryloxy)-1,2-difluoroethenes (*2a–d*)

A. A mixture of 10 mmol of corresponding compounds (**1a–d**), 25 mmol of potassium hydroxide, 10 mmol of substituted phenol and 30 ml of fresh distilled DMA was stirred for 10 h at 75–80 °C. Reaction mixture was cooled to room temperature and poured into water. Organic layer was extracted with diethyl ether, extract was washed with 4% aqueous potassium hydroxide, water, dried over magnesium sulfate and distilled or crystallised for **2d** (see Tables 1 and 2).

B. A mixture of 20 mmol of the corresponding substituted phenol, 25 mmol of potassium hydroxide, 10 mmol of 1,2-dichloro-1,2-difluoroethene and 30 ml of fresh

Table 1
Yields, physicals constants and analysis of compounds **1–6**

Sample number	Yield (%)	B.p. (°C) (mm Hg)	M.p. (°C)	n_D^t	Analysis		
					Found	Formula	Calcd.
1a	47	21–23 (0.4)		1.4800^{18}	C 50.50; H 2.60; Cl 18.60; F 19.85	$C_8H_5ClF_2O$	C 50.40; H 2.60; Cl 18.60; F 19.90.
1b	54	27–29 (0.07)		1.4840^{12}	C 53.10; H 3.70; Cl 17.40	$C_9H_7ClF_2O$	C 52.80; H 3.40; Cl 17.40.
1c	49	27–29 (0.07)		1.4813^{18}	C 52.60; H 3.50; Cl 17.20	$C_9H_7ClF_2O$	C 52.80; H 3.40; Cl 17.40.
1d	56	40–41 (0.4)		1.4950^{15}	C 48.80; H 3.20; Cl 16.40	$C_9H_7ClF_2O_2$	C 49.00; H 3.20; Cl 16.10.
1e	99		49–50		C 48.70; H 3.50 Cl 14.20	$C_{10}H_8ClF_2NO_2$	C 48.50; H 3.20; Cl 14.30.
1f	19	44–46 (0.4)		1.5200^{19}	C 35.35; H 1.30; F 14.00	$C_8H_4BrClF_2O$	C 35.60; H 1.50; F 14.10
1g	19	48–50 (20)			C 45.75; H 2.00; Cl 17.00; F 26.80	$C_8H_4ClF_3O$	C 46.00; H 1.90; Cl 17.00; F 27.00
1h	19	28–30 (0.7)			C 45.70; H 1.80; Cl 16.70; F 26.90	$C_8H_4ClF_3O$	C 46.00; H 1.90; Cl 17.00; F 27.00
2a	A. 45 B. 30	94–95 (0.4)			C 67.80; H 4.00	$C_{14}H_{10}F_2O_2$	C 67.70; H 4.00.
2b	A. 40 B. 19	112–114 (0.4)			C 69.40; H 5.10	$C_{16}H_{14}F_2O_2$	C 69.60; H 5.10
2c	A. 45 B. 18	116–118 (0.4)			C 69.50; H 5.10	$C_{16}H_{14}F_2O_2$	C 69.60; H 5.10
2d	A. 35 B. 14		29–30		C 62.30; H 4.40	$C_{16}H_{14}F_2O_4$	C 62.30; H 4.55
3a	50		62–63		C 53.90; H 2.95; F 19.00	$C_9H_6F_2O_3$	C 54.00; H 3.00; F 19.00
3c	31		72–73		C 55.85; H 3.70; F 17.55	$C_{10}H_8F_2O_3$	C 56.10; H 3.70; F 17.75
3d	40		110–111		C 52.10; H 3.70; F 16.35	$C_{10}H_8F_2O_4$	C 52.20; H 3.50; F 16.50
4a	75	43–45 (0.4)			C 33.75; H 1.50; I 44.70; F 13.40	$C_8H_5IF_2O$	C 34.00; H 1.80; I 45.00; F 13.50
4c	50	53–55 (0.35)			C 36.20; H 2.20; I 42.80; F 12.50	$C_9H_7IF_2O$	C 36.50; H 2.40; I 42.90; F 12.80
5c	41		98–100		C 64.30; H 6.30; N 6.50	$C_{12}H_{14}FNO_2$	C 64.60; H 6.30; N 6.30
6c	32		90–92		C 68.40; H 6.60; N 5.40	$C_{15}H_{18}FNO_2$	C 68.40; H 6.80; N 5.30

Table 2
^{1}H and ^{19}F NMR data of compounds **1–6**

Number	Nucleus	δ	Splitting	J (Hz)
1a	^{1}H	7.1	d	J_{HH} = 8.4 Hz, 2H, arom., ortho-H
		7.2	t	J_{HH} = 7.84 Hz,1H, arom., para-H
		7.4	d	J_{HH} = 7.8, 2H, arom., meta-H
	^{19}F	−102.2	d	E-isomer: J_{FF} = 41 Hz F^2
		−127.9	d	J_{FF} = 41 Hz F^1
		−117.8	d	Z-isomer: J_{FF} = 120 Hz, F^2
		−134.2	d	J_{FF} = 120 Hz, F^1
1b	^{1}H	2.4	s	3H (CH_3)
		6.9	d	J_{HH} = 6.3 Hz, 2H, arom., $H^{2,6}$
		7.02	d	J_{HH} = 7.5 Hz, 1H, arom., H^4
		7.29	t	J_{HH} = 6.3 Hz, 1H, arom., H^5
	^{19}F	−102.0	d	E-isomer: J_{FF} = 41 Hz, F^2
		−128.0	d	J_{FF} = 41 Hz, F^1
		−117.5	d	Z-isomer: J_{FF} = 120 Hz, F^2
		−134.4	d	J_{FF} = 120 Hz, F^1
1c	^{1}H	2.34	s	3H (CH_3)
		7.00	d	J_{HH} = 8.0 Hz, 2H, arom., $H^{2,6}$
		7.16	d	J_{HH} = 8.0 Hz, 2H, arom., $H^{3,5}$
	^{19}F	−102.0	d	E-isomer: J_{FF} = 41 Hz, F^2
		−128.4	d	J_{FF} = 41 Hz, F^1
		−117.6	d	Z-isomer: J_{FF} = 120 Hz, F^2
		−134.8	d	J_{FF} = 120 Hz, F^1
1d	^{1}H	3.79	s	3H (OCH_3)
		6.90	d	J_{HH} = 9.0 Hz, 2H, arom., $H^{2,6}$
		7.16	d	J_{HH} = 9.0 Hz, 2H, arom., $H^{3,5}$
	^{19}F	−102.0	d	E-isomer: J_{FF} = 38 Hz, F^2
		−128.7	d	J_{FF} = 38 Hz, F^1
		−117.5	d	Z-isomer: J_{FF} = 120 Hz, F^2
		−135.1	d	J_{FF} = 120 Hz, F^1
1e	^{1}H	2.10	s	3H (CH_3)
		6.90	t	1H, arom., H^5
		7.40	d	J_{HH} = 5.4 Hz, 2H, arom., $H^{2,6}$
		7.60	s	1H, H arom.
		10.2	s	1H, NH
	^{19}F	−102.0	d	E-isomer: J_{FF} = 41 Hz, F^2
		−128.4	d	J_{FF} = 41 Hz, F^1
		−117.4	d	Z-isomer: J_{FF} = 120 Hz, F^2
		−134.5	d	J_{FF} = 120 Hz, F^1
1f	^{1}H	7.20	d	J_{HH} = 8.7 Hz, 2H, arom., $H^{2,6}$
		7.60	d	J_{HH} = 8.7 Hz, 2H, arom., $H^{3,5}$
	^{19}F	−102.8	d	E-isomer: J_{FF} = 41 Hz, F^2
		−127.5	d	J_{FF} = 41 Hz, F^1
		−118.3	d	Z-isomer: J_{FF} = 120 Hz, F^2
		−133.6	d	J_{FF} = 120 Hz, F^1
1g	^{1}H	7.10	m	2H, H arom.
		7.28	m	2H, H arom.
	^{19}F	−102.8	d	E-isomer: J_{FF} = 41 Hz, F^2.
		−127.3	d	J_{FF} = 41 Hz, F^1
		−110.4	m	1F, F arom.
		−118.5	d	Z-isomer: J_{FF} = 119 Hz, F^2
		−133.6	d	J_{FF} = 119 Hz, F
		−110.4	m	1F, F arom.
1h	^{19}F	−102.5	d	E-isomer: J_{FF} = 41 Hz, F^2
		−127.7	d	J_{FF} = 41 Hz, F^1
		−118.4	m	1F, F arom.
		−118.1	d	Z-isomer: J_{FF} = 120 Hz, F^2
		−133.6	d	J_{FF} = 120 Hz, F^1
		−118.1	m	1F, F arom.
2a	^{1}H	7.00	d	J_{HH} = 8.3 Hz, 2H, arom., ortho-H
		7.10	t	J_{HH} = 7.4 Hz, 1H, arom., para-H
		7.30	d	J_{HH} = 7.4 Hz,2H, arom., meta-H
	^{19}F	−120.5	s	2F
2b	^{1}H	2.30	s	3H (CH_3)
		6.80	m	2H, H arom.
		6.90	d	1H, H arom.
		7.19	t	J_{HH} = 7.51 Hz, 1H, arom., H^5)
	^{19}F	−120.7	s	2F
2c	^{1}H	2.30	s	3H(CH_3)
		7.00	d	J_{HH} = 8.2 Hz, 2H, arom., $H^{2,6}$
		7.10	d	J_{HH} = 8.2 Hz, 2H, arom., $H^{3,5}$
	^{19}F	−121.0	s	2F
2d	^{1}H	3.70	s	3H(OCH_3)
		6.80	d	J_{HH} = 8.0 Hz, 2H, arom., $H^{2,6}$
		6.90	d	J_{HH} = 8.0 Hz, 2H, arom., $H^{3,5}$
	^{19}F	−122.5	s	2F
3a	^{1}H	7.40	m	2H, H arom.
		7.50	m	1H, H arom.
		7.70	m	2H, H arom.
		11.7	broad-s	1H, COOH
	^{19}F	−77.0	d	E-isomer: J_{FF} = 19.8 Hz, F^1
		−173.5	d	J_{FF} = 19.8 Hz, F^2
		−92.0	d	Z-isomer: J_{FF} = 120 Hz, F^1
		−180.8	d	J_{FF} = 120 Hz, F^2
3c	^{1}H	2.30	s	3H (CH_3)
		7.50	d	J_{HH} = 8.0 Hz, 2H, arom., $H^{2,6}$
		7.70	d	J_{HH} = 8.0 Hz, 2H, arom., $H^{3,5}$
		8.10	broad-s	1H, COOH
	^{19}F	−84.0	d	E-isomer: J_{FF} = 19.8 Hz, F^1
		−169.0	d	J_{FF} = 19.8 Hz, F^2
		−97.2	d	Z-isomer: J_{FF} = 120 Hz, F^1
		−176.5	d	J_{FF} = 120 Hz, F^2
3d	^{1}H	3.80	s	3H (OCH_3)
		6.90	d	J_{HH} = 8.0 Hz, 2H, arom., $H^{2,6}$
		7.80	d	J_{HH} = 8.0 Hz, 2H, arom., $H^{3,5}$
		10.5	broad s	1H, COOH
	^{19}F	−77.5	d	E-isomer: J_{FF} = 19.8 Hz, F^1
		−175.0	d	J_{FF} = 19.8 Hz, F^2
		−92.3	d	Z-isomer: J_{FF} = 120 Hz, F^1
		−182.6	d	J_{FF} = 120 Hz, F^2
4a	^{1}H	7.1	d	J_{HH} = 7.5 Hz, 2H, arom., ortho-H
		7.2	t	J_{HH} = 7.5 Hz, 1H, arom., para-H
		7.3	d	J_{HH} = 7.8 Hz, 2H, 2arom., meta-H
	^{19}F	−90.2	d	E-isomer: J_{FF} = 33 Hz F^2
		−132.3	d	J_{FF} = 33 Hz F^1
		−111.5	d	Z-isomer: J_{FF} = 130 Hz, F^2
		−138.4	d	J_{FF} = 130 Hz, F^1
4c	^{1}H	2.30	s	3H (CH_3)
		7.00	d	J_{HH} = 8.7 Hz, 2H, arom., $H^{2,6}$
		7.20	d	J_{HH} = 8.7 Hz, 2H, arom., $H^{3,5}$
	^{19}F	−90.3	d	E-isomer: J_{FF} = 36 Hz, F^2
		−132.2	d	J_{FF} = 36 Hz, F^1
		−111.7	d	Z-isomer: J_{FF} = 130 Hz, F^2
		−138.5	d	J_{FF} = 130 Hz, F^1
5c	^{1}H	2.30	s	3H (CH_3)
		3.00	m	6H (2-CH_3)
		7.00	d	J_{HH} = 8.9 Hz, 2H, arom., $H^{2,6}$
		7.50	d	J_{HH} = 8.9 Hz, 2H, arom., $H^{3,5}$
		9.20	d	J_{HF} = 19.5 Hz, CO<u>H</u>
	^{19}F	−179.7	d	J_{FH} = 19.5 Hz, 1F

Table 2 (*Continued*)

Number	Nucleus	δ	Splitting	J (Hz)
6c	^{1}H	0.60	m	4H
		0.70	m	4H
		1.70	m	2H
		1.50	s	3H (CH_3)
		6.20	d	J_{HH} = 8.4 Hz, 2H, arom., $H^{2,6}$
		6.40	d	J_{HH} = 8.4 Hz, 2H, arom., $H^{3,5}$
		8.20	d	J_{HF} = 19.6 Hz, COH
	^{19}F	−111.7	d	J_{FH} = 19.6 Hz, 1F

$ArOCF^1=CF^2Cl$ (**1**); $ArOCF=CFOAr$ (**2**); $ArOCF^2=CF^1COOH$ (**3**); $ArOCF^1=CF^2I$ (**4**); $ArOC(N(CH_3)_2)=CFCOH$ (**5**); $ArOC(N(CH_2)_4CH_2)=CFCOH)$ (**6**).

distilled DMA was stirred for 30 h at 75–80 °C. Reaction mixture was cooled to room temperature and poured into water. Organic layer was extracted with diethyl ether, extract was washed with 4% aqueous potassium hydroxide, water, dried over magnesium sulfate and distilled or crystallised for **2d** (see Tables 1 and 2).

3.2.3. 3-Aryloxy-2,3-difluoroacrylic acids (*3a,c,d*)

To the mixture of 21 mmol of corresponding substituted arene (**1a,c,d**), 10 ml diethyl ether, 20 ml THF under stirring at −85 °C was added dropwise 14 ml 1.4 N *n*-butyllithium in hexane for 30 min. The reaction mixture was stirred at −85 °C for 1 h and poured into dry ice. A mixture was warmed to ambient temperature and extracted with 5% aqueous sodium carbonate. Aqueous solution was acidified with aqueous hydrogen chloride, extracted with diethyl ether dried over magnesium sulfate. Solvent was removed in vacuum, residue crystallised from diethyl ether: hexane in ratio 1:1 (see Tables 1 and 2).

3.2.4. 1-(aryloxy)-2-iodo-1,2-difluoroethenes (*4a,c*)

To the mixture of 21 mmol of a corresponding substituted arene **1a,c**, 10 ml diethyl ether, 20 ml THF under stirring at −85 °C was added dropwise 14 ml 1.4 N *n*-butyllithium in hexane for 30 min. After stirring at −85 °C for 1 h was added dropwise the solution of 21 mmol of iodine in a mixture of 10 ml diethyl ether and 10 ml THF at −85 °C. The reaction mixture was stirred at −75 °C 1.5 h warmed to ambient temperature and poured into aqueous hydrogen chloride with ice. Organic layer was extracted with diethyl ether, washed with water, dried over magnesium sulfate and distilled (see Tables 1 and 2).

3.2.5. Reactions of compound *1c* with DMF or *N*-formylpiperidine

To the mixture of 21 mmol of a substituted arene **1c**, 10 ml diethyl ether, 20 ml THF under stirring at −85 °C was added dropwise 14 ml 1.4 N *n*-butyl lithium in hexane for 30 min. After stirring at −85 °C for 1 h was added dropwise 21 mmol of DMF or *N*-formylpiperidine in a mixture of 5 ml diethyl ether and 5 ml THF at −85 °C. The reaction mixture was stirred at −75 °C 2.5 h warmed to ambient temperature and poured into 5% aqueous ammonium chloride with ice. Organic layer was extracted with diethyl ether, washed with water, dried over magnesium sulfate. Solvent was removed in vacuum and residue crystallised from diethyl ether: hexane in a ratio 1:1 (see Tables 1 and 2).

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