Fe and Ni-catalyzed electrochemical perfluoroalkylation of C—H bonds of coumarins*

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A new method for the preparation of perfluoroalkylcoumarins in a single step is developed. The compounds are prepared *via* electrocatalytic reduction of a 1 : 1 mixture of an aromatic compound (coumarin, 6-methylcoumarin, and 7-methylcoumarin) and a fluoroalkylating reagent under mild conditions (room temperature, normal pressure) using [bipyFe^{II}] or [bipyNi^{II}] complexes as catalysts. The developed method makes it possible to obtain perfluoroalkylcoumarins in high yields and 100% conversion of the fluoroalkylating reagent.

Key words: coumarins, perfluoroalkylation, catalysis.

Nowadays, fluorine and fluoroalkyl-substituted aromatic compounds attract the attention of the researchers in the pharmacy, agrochemistry, and other areas.[1—12] Among these classes of compounds, fluoroalkylated coumarins occupy a particular place.[12,13] It is known that coumarin and its derivatives belong to the most important heterocyclic compounds and are found in a variety of natural substances and pharmaceutically active molecules.[3] Many of coumarin derivatives exhibit anticoagulant, antitumor, antiviral, anti-inflammatory, antioxidant, antimicrobial, and inhibitory properties.[4,5] Besides, they are useful synthetic building blocks in organic and medicinal chemistry. It is known that the introduction of fluorine or fluorine-containing fragments into organic molecules can lead to appreciable changes in their biological properties.[1,2] Thus, it was found[6,7] that fluorinated heterocycles show more pronounced antibacterial activity in a comparison with their non-fluorinated analogs. The fluorinated compounds often have specific biological activity, good solubility, and lipophilicity. These lead to an increase in the permeability of cell membranes and better bioavailability of fluorinated compounds compared to their non-fluorinated analogs. In addition, fluorinated compounds are stable in the course of metabolism, since they are more resistant to the oxidation.[8—10] The introduction of a perfluoroalkyl group into potentially useful organic molecules can significantly improve physical, chemical, and their biological properties.[10,11] Coumarins containing the perfluoroalkyl group can be used as anticancer agents, fluorescent markers, and optical molecular sensors.[12,13]

Despite considerable progress in the investigation of the fluoroalkylation reactions, catalytic fluoroalkylation reactions have been little studied as yet.[14—18] The reactions of direct fluoroalkylation of C—H bonds are even less known,[19—22] although the latter approach is interesting because of its atom-economy level is high and it is connected with low-waste technologies.[23]

Among the catalysts used for CH-fluoroalkylation, copper,[24,25] iridium or ruthenium,[26] palladium,[27] ytterbium[28] are most used, and nickel[29] and iron[30] are used less often. Taking into account the trend to introduce inexpensive catalysts, it is important to develop catalytic systems for the functionalization of C—H bonds based on more affordable and cheap metals such as Fe, Ni, and Co.[23]

Metal complexes both in high (Ni^{III}/Ni^{II} and Pd^{III}/Pd^{II}),[21,31—33] and in low (Fe^{II},[30] Ni^{I},[22] Ni^{0} (see Refs 18, 34)) oxidation states are used for the electrochemical fluoroalkylation.

Note that there is practically no description of the methods for obtaining fluoroalkyl coumarins by electrocatalytic reactions. Synthesis of 3-trifluoroalkylated coumarin from bis(trifluoroacetyl) peroxide was reported in 1991 by Matsui and co-workers.[35] Despite the relatively short reaction time (4 h), the preparative yield was 33%. Sometime later the reaction of Langlois reagent (R_FSO_2Na) with unsubstituted coumarins in the presence of Mn^{III} was described.[36] The reaction resulted in the formation of 3-perfluoroalkyl-2*H*-chromen-2-ones in moderate yields (60—65%). However, for the reaction to proceed successfully a high temperature (80 °C) and a twofold excess of the fluoroalkylating reagent were required.

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In the 21 century the baton to study the fluoroalkylation reaction of coumarins was passed on the Domowski group. They reported the preparation of 3-(trifluoromethyl)-coumarin and 3-(trifluoromethyl)-6-nitrocoumarin by treating the corresponding commercially available coumarin-3-carboxylic acid with sulfur tetrafluoride.[37] The reaction proceeded within 3—6 h at high temperatures giving the product yield not exceeding 36%. Quite recently, in 2014, Zu and co-workers[38] proposed modification of the reaction described in Ref. 36: *i.e.*, introduction of the trifluoromethyl group by direct radical C_{sp^2}—H substitution in coumarins. The reaction proceeds under mild conditions to give 3-(trifluoromethyl)coumarins in moderate yields (up to 56% in the presence of excess $Mn(OAc)_3$ in acetic acid).[38] In the same year Ding and co-workers presented the reaction of alkynes with Togni and Umemoto reagents, catalyzed by copper salts (acetates, oxides, and halides) leading to 3-(trifluoromethyl)-coumarins in moderate yields (up to 60%).[39] The reaction proceeds in the presence of excess K_2CO_3 upon heating.

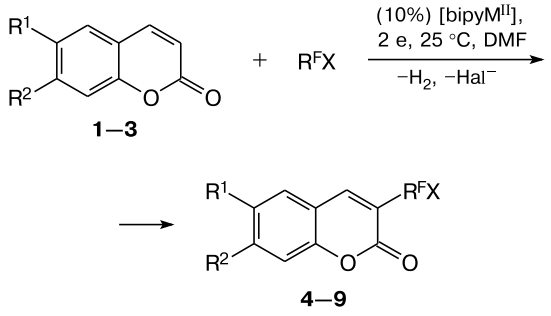
Taking into account the method of metal-induced perfluoroalkylation of benzene and caffeine that we proposed earlier, we attempted to realize a single step electrocatalytic fluoroalkylation of the C—H bonds of coumarins under mild conditions at room temperature.

Results and Discussion

The complexes of iron [bipy$Fe^{II}Cl_2$] and nickel [bipy$Ni^{I}(BF_4)_2$] were selected as catalysts for the fluoroalkylation of coumarins. The choice of these complexes is due to the values of their redox potentials and availability. In addition, we have previously found that these complexes in a mixture with fluoroorganic reagents are reduced at lower negative potentials (in average by 300 mV to the anodic side) compared with the fluoroalkylating agents. Distinctive features of the reaction are the equimolar ratio of coumarin : fluoroalkylating agent and room temperature of the reaction (Scheme 1, Table 1). In the absence of a catalyst, the fluoroalkylation proceeds very slowly and unselectively. As a result different isomeric coumarin derivatives were isolated in the yield not exceeding 25%.

It should be noted that under conditions of electrocatalysis, after passing 2 F of electricity, a 100% conver-

Scheme 1



1—3: $R^1 = R^2 = H$ (**1**), $R^1 = Me$, $R^2 = H$ (**2**); $R^1 = H$, $R^2 = Me$ (**3**)
X = I, SO_2Cl, M = Fe, Ni

Compound	R^1	R^2	R^F	Compound	R^1	R^2	R^F
4	H	H	C_6F_{13}	**7**	Me	H	CF_3
5	H	H	CF_3	**8**	H	Me	C_6F_{13}
6	Me	H	C_6F_{13}	**9**	H	Me	CF_3

Table 1. Electrocatalytic fluoroalkylation of coumarins **1—3**[a]

Coumarin	R^FX	Catalyst	$-E$/V[b]	Product	Yield[c] (%)	Isomer ratio[d]		
						$C(3)R^F$	$C(6)R^F$	$C(7)R^F$
1	$C_6F_{13}I$	[(bipy)Fe^{II}]	0.9	**4**	73 (61)	25	1	2
1	$C_6F_{13}I$	[(bipy)Ni^{II}]	1.0	**4**	65 (55)	35	1	2
1	CF_3SO_2Cl	[(bipy)Fe^{II}]	0.3	**5**	67 (56)	22	1	1
1	CF_3SO_2Cl	[(bipy)Ni^{II}]	0.5	**5**	45 (34)	30	1	1
2	$C_6F_{13}I$	[(bipy)Fe^{II}]	0.9	**6**	78 (64)	25	—	1
2	$C_6F_{13}I$	[(bipy)Ni^{II}]	1.0	**6**	66 (54)	30	—	1
2	CF_3SO_2Cl	[(bipy)Fe^{II}]	0.3	**7**	63 (53)	30	—	1
2	CF_3SO_2Cl	[(bipy)Ni^{II}]	0.5	**7**	57 (45)	1	—	0
3	$C_6F_{13}I$	[(bipy)Fe^{II}]	0.9	**8**	67 (52)	20	1	—
3	$C_6F_{13}I$	[(bipy)Ni^{II}]	1.0	**8**	62 (52)	30	1	—
3	CF_3SO_2Cl	[(bipy)Fe^{II}]	0.3	**9**	65 (54)	35	1	—
3	CF_3SO_2Cl	[(bipy)Ni^{II}]	0.5	**9**	59 (49)	1	0	—

[a] Reaction conditions: coumarin : R^F = 1 : 1, DMF, argon, 23 °C, galvanostatic mode, Q = 2 F per 1 mole R^FX, Zn-anode, Pt-cathode.
[b] In respect to Ag/AgCl.
[c] The yield was determined from the integrated intensity of the signals in the ^{19}F NMR spectra of the reaction mixture. The preparative yield of the products is indicated in parenthesis. The current output coincides with the preparative yield with accuracy of ±0.3%.
[d] The ratio of isomers was determined from the intensity of the signals in the ^{19}F NMR spectra.

sion of the fluoroalkylating reagent is achieved. It should be emphasized that electrochemistry allows one to avoid the use of any additional chemical reagents (bases, oxidants or reducing agents). This is especially important from the point of view of possible upscaling of the developed method.

An analysis of the isomer ratio of fluoroalkylcoumarins formed in the presence of different metals (see Table 1) shows that the reactions in each case probably follows its own specific mechanism. This is in good agreement with the previously published experimental data obtained by our group.[21,30] The mechanisms of the observed transformations will be discussed in detail in our next publications.

Thus, the electrocatalytic synthesis of fluoroalkylcoumarins proceeds under mild conditions (room temperature, normal pressure) with an equimolar ratio of the reagents and allows the preparation of products in high yield (up to 78%) and 100% conversion of the fluoroalkylating reagent by using [(bipy)Ni^{I}] or [(bipy)Fe^{II}] as the catalysts.

Experimental

Preparative electrosynthesis was carried out using a direct current source B5-49 in a 40 mL three-electrode cell. The value of the potential of the working Pt electrode ($S = 48$ cm^2) was fixed using a DC voltmeter B7-27 relative to the Ag/AgCl reference electrode ($C = 0.01$ *M*) in MeCN. The anode was a zinc rod with a diameter of 1 cm. During electrolysis, the electrolyte was constantly stirred by means of a magnetic stirrer at a constant flow of an inert gas that passed through a purification system (to remove oxygen and other impurity gases).

Coumarin (99%), 6-methylcoumarin (99%), 7-methylcoumarin (98%), CF_3SO_2Cl (all Sigma-Aldrich), and $C_6F_{13}I$ (P&M Invest, Russia) were used as received.

Dimethylformamide (extra pure, Acros Organics) served as a solvent in the synthesis; DMF was distilled over calcium hydride under argon atmosphere before experiment.

Tetraethylammonium tetrafluoroborate (Et_4NBF_4) was prepared by mixing a 30—35% aqueous solution of tetraethylammonium hydroxide, Et_4NOH, and HBF_4 until neutral pH was reached. Precipitated white crystalline solid was filtrated and dried. Obtained powder salt was recrystallized from ethanol and dried 2—3 days in vacuum oven at 55 °C.

NMR spectra were recorded using Bruker AVANCE-400 multinuclear spectrometer (400.1 MHz (^{1}H) and 162.0 MHz (^{31}P)). Chemical shifts are represented against internal standard, deuterated solvent (^{1}H) and C_6F_6 (^{19}F).

Mass spectra were recorded using AmazonX spectrometer (Bruker Daltonik GmbH, Germany). Electrospray was used as ionization method. Nitrogen at 22 °C was used as nebulizer gas in the source. Source voltage was 4.5 κV. The solutions of the samples were diluted with acetonitrile to ~10^{-3} mg mL^{-1}. The introduction of the samples was performed using autosampler of the liquid chromatograph Agilent 1260 Infinity (Agilent Technologies, USA).

Synthesis of metal complex (general procedure). To the solution of metal salt MX_2 (1.83 mol) in ethanol (100 mL), 2,2′-bipyridine ($1.83 \cdot 10^{-2}$ mol) in ethanol (30—50 mL) was added slowly under stirring. Reaction mixture was stirred at constant temperature (25 °C) for 3—24 h till formation of crystalline precipitate. The precipitate was filtered under an argon atmosphere and washed with cold (0 °C) ethanol. The obtained complexes [bipy$FeCl_2$][31] and [bipy$Ni(BF_4)_2$][22] were dried for 2—3 days in vacuum oven at 25—55 °C. Physicochemical characteristics of complexes correspond to the literature data.

Electrocatalytic fluoroalkylation of coumarins (general procedure). Fluoroalkylating reagent (1.2 mmol), heterocyclic compound **1**—**3** (1.2 mmol), metal complex MX_2L (0.12 mmol), and DMF (40 mL) were placed in the electrochemical cell. The electrolysis was carried out in the electrochemical cell with separated anodic and cathodic compartments at 23 °C under the atmosphere of dry argon in a galvanostatic mode. The potentials of the working electrode are indicated in Table 1. The amount of electricity transmitted was 2 F per 1 mol of the fluoroalkylating agent. After completion of the electrolysis, the reaction mixture was washed with a saturated solution of ammonium chloride (3×50 mL) and extracted with chloroform (3×70 mL). After separation, the organic layer was dried over magnesium sulfate and the solvent was evaporated. The residue was purified by column chromatography on silica gel (eluent was ethyl acetate—hexane, 10 : 1). The yields of products **4**—**9** are shown in Table 1.

3-(Perfluorohexyl)-2*H*-chromen-2-one (4). Light crystals, m.p. 115—118 °C. IR, ν/cm^{-1}: 3063, 1740, 1629, 1611, 1515, 1461, 1201. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 8.15 (s, 1 H, H(4)); 7.71—7.23 (m, 3 H). ^{13}C (100.6 MHz, $CDCl_3$), δ: 156.1, 154.6, 146.2, 143.1, 129.1, 126.4, 121.5, 117.6, 116.4, 114.4, 22.0. ^{19}F NMR (376 MHz, $CDCl_3$), δ: −81.03 (t, 3 F); −111.32 (t, 2 F); −120.8 (br.s, 2 F); −121.3 (br.s, 2 F); −122.47 (br.s, 2 F); −126.35 (br.s, 2 F). MS, *m/z*: 464 $[M]^+$. Found (%): C, 38.71; H, 1.03. $C_{15}H_5F_{13}O_2$. Calculated (%): C, 38.81; H, 1.09. Physicochemical characteristics of complexes correspond to the literature data.[36]

3-(Trifluoromethyl)-2*H*-chromen-2-one (5). White crystals, m.p. 130—133 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 8.17 (s, 1 H, C(4)H); 7.69 (t, 1 H, ArH, J = 7.9 Hz); 7.63 (d, 1 H, ArH, J = 7.9 Hz); 7.42—7.37 (m, 2 H, ArH). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 155.9, 154.6, 143.4, 134.4, 129.5, 125.3, 121.3, 117.6, 116.7, 115.9. ^{19}F NMR (376.5 MHz, $CDCl_3$), δ: −66.3 (s, 3 F). MS, *m/z*: 214.56 $[M]^+$. Found (%): C, 56.12; H, 2.31. $C_{10}H_5F_3O_2$. Calculated (%): C, 56.09; H, 2.35. Physicochemical characteristics of complexes correspond to the literature data.[38]

6-Methyl-3-(perfluorohexyl)-2*H*-chromen-2-one (6). Light-beige crystals, m.p. 144—146 °C. IR, ν/cm^{-1}: 3063, 1608, 1505, 1461, 1199. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 8.54 (br.s, 1 H, H(4)); 7.61—7.21 (m, 3 H); 2.41 (s, 3 H). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 156.4, 152.7, 143.3, 135.5, 135.1, 129.2, 121.6, 117.4, 116.8, 116.5, 20.7. ^{19}F NMR (376 MHz, $CDCl_3$), δ: −82.00 (t, 3 F, J = 9.8 Hz); −106.01 (t, 2 F, J = 14.5 Hz); −120.53 (br.s, 2 F); −122.03 (br.s, 2 F); −122.72 (br.s, 2 F); −126.05 (br.s, 2 F). MS, *m/z*: 478 $[M]^+$. Found (%): C, 40.16; H, 1.40. $C_{16}H_7F_{13}O_2$. Calculated (%) C, 40.19; H, 1.48.

6-Methyl-3-(trifluoromethyl)-2*H*-chromen-2-one (7). White crystals, m.p. 140—143 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 8.09 (s, 1 H, C(4)H); 7.48 (d, 1 H, ArH, J = 8.5 Hz); 7.39 (s, 1 H, ArH); 7.29 (d, 1 H, ArH, J = 8.5 Hz); 2.44 (s, 3 H, C(6)Me). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 156.2, 152.8, 143.3, 135.5, 135.2, 129.1, 121.4, 117.5, 116.8, 116.5, 20.7. ^{19}F NMR (376 MHz, $CDCl_3$), δ: −65.3 (s, 3 F). MS, *m/z*: 228.98 $[M]^+$.

Found (%): C, 57.93; H, 3.02. $C_{11}H_8F_3O_2$. Calculated (%): C, 57.90; H, 3.09. Physicochemical characteristics of complexes correspond to the literature data.[38]

7-Methyl-3-(perfluorohexyl)-2*H*-chromen-2-one (8). White crystals with a pink tint, m.p. 123—125 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 8.34 (s, 1 H, H(4)); 7.74—7.20 (m, 3 H); 2.43 (s, 3 H). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 156.3, 154.8, 146.3, 143.2, 129.1, 126.5, 121.5, 117.2, 116.4, 114.4, 22.2. ^{19}F NMR (376 MHz, $CDCl_3$), δ: −81.33 (t, 3 F, J = 9.8 Hz); −105.32 (t, 2 F, J = 14.5 Hz); −120.19 (br.s, 2 F); −121.93 (br.s, 2 F); −122.47 (br.s, 2 F); −126.05 (br.s, 2 F). IR, ν/cm^{-1}: 3072, 1604, 1510, 1462, 1195. MS, m/z: 478 $[M]^+$. Found (%): C, 40.17; H, 1.41. $C_{16}H_7F_{13}O_2$. Calculated (%): C, 40.19; H, 1.48.

7-Methyl-3-(trifluoromethyl)-2*H*-chromen-2-one (9). White crystals, m.p. 120—122 °C. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 8.11 (s, 1 H, C(4)H); 7.49 (d, 1 H, ArH, J = 8.0 Hz); 7.18 (d, 2 H, ArH, J = 7.6 Hz); 2.5 (s, 3 H, C(7)Me). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 156.2, 154.8, 146.4, 143.2, 129.1, 126.5, 121.5, 117.5, 116.4, 114.4, 22.0. ^{19}F NMR (376 MHz, $CDCl_3$), δ: −65.5 (s, 3 F). MS, m/z: 229.05 $[M]^+$. Found (%): C, 57.95; H, 3.00. $C_{11}H_8F_3O_2$. Calculated (%): C, 57.90; H, 3.09. Physicochemical characteristics of complexes correspond to the literature data.[38]

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References

1. K. L. Kirk, *J. Fluorine Chem.*, 2006, **127**, 1013.
2. D. Yu. Mikhaylov, Yu. H. Budnikova, *Russ. Chem. Rev.*, 2013, **82**, 835.
3. F. Borges, F. Roleira, N. Milhazes, L. Santana, E. Uriarte, *Curr. Med. Chem.*, 2005, **12**, 887.
4. D. A. Horton, G. T. Bourne, M. L. Smythe, *Chem Rev.*, 2003, **103**, 893.
5. M. E. Riveir, N. De Kimpe, A. Moglioni, R. Vázquez, F. Monczor, C. Shayo, C. Davio *Curr. Med. Chem.*, 2010, **17**, 1325,
6. M. S. Karthikeyan, B. S. M. Holla, N. S. Kumari, *Eur. J. Med. Chem.*, 2007, **42**, 30.
7. G. F. Xu, B. A. Song, P. S. Bhadury, S. Yong, P. Q. Zhang, *Bioorg. Med. Chem. Lett.*, 2007, **15**, 3768.
8. N. A. Meanwell, *J. Med. Chem.*, 2011, **54**, 2529.
9. E. P. Gillis, K. J. Eastman, M. D. Hill, D. J. Donnelly, N. A. Meanwell, *J. Med. Chem.*, 2015, **58**, 8315.
10. T. Yamazaki, T. Taguchi, I. Ojima, *Unique Properties of Fluorine and Their Relevance to Medicinal Chemistry and Chemical Biology*, Wiley-Blackwell, Chichester, 2009, 3.
11. K. Müller, C. Faeh, F. Diederich, *Science*, 2007, **317**, 1881.
12. H. Schill, S. Nizamov, F. Bottanelli, J. Bierwagen, V. N. Belov, S. W. Hell, *Chem. Eur. J.*, 2013, **19**, 16556.
13. M. Matsui, K. Shibata, H. Muramatsu, H. Sawada, M. Nakayama, *Chem. Ber.*, 1992, **125**, 467.
14. Y. Li, G. Qiu, Q. Ding, *Org. Lett.*, 2014, **16**, 4240.
15. M. Oishi, H. Kondo, H. Amii, *Chem. Commun.*, 2009, **14**, 1909.
16. M. Khrizanforov, V. Khrizanforova, V. Mamedov, N. Zhukova, S. Strekalova, V. Grinenko, T. Gryaznova, O. Sinyashin, Y. Budnikova, *J. Organomet. Chem.*, 2016, **820**, 82.
17. M. Khrizanforov, T. Gryaznova, O. Sinyashin, Y. Budnikova, *J. Organomet. Chem.*, 2012, **718**, 101.
18. M. N. Khrizanforov, T. V. Gryaznova, D. Yu. Mikhailov, Yu. H. Budnikova, O. G. Sinyashin, *Russ. Chem. Bull.*, 2012, **61**, 1560.
19. G. Landelle, A. Panossian, S. Pazenok, J. P. Vors, F. R. Leroux, *Beilstein J. Org. Chem.*, 2013, **9**, 2476
20. T. V. Gryaznova, V. V. Khrizanforova, K. V. Kholin, M. N. Khrizanforov, Yu. H. Budnikova, *Russ. Chem. Bull.*, 2016, **65**, 1798.
21. M. N. Khrizanforov, S. V. Fedorenko, S. O. Strekalova, K. V. Kholin, A. R. Mustafina, M. Ye. Zhilkin, V. V. Khrizanforova, Y. N. Osin, V. V. Salnikov, T. V. Gryaznova, Y. H. Budnikova, *Dalton Trans.*, 2016, **45**, 11976.
22. D. Y. Mikhaylov, T. V. Gryaznova, Y. Dudkina, M. N. Khrizanphorov, Sh. Latypov, O. Kataeva, D. A. Vicic, O. G. Sinyashin, Yu. H. Budnikova, *Dalton Trans.*, 2012, **41**, 165.
23. Y. B. Dudkina, M. N. Khrizanforov, T. V. Gryaznova, Y. H. Budnikova, *J. Organomet. Chem.*, 2014, **751**, 301.
24. Z. He, T. Luo, M. Hu, Y. Cao, J. Hu, *Angew. Chem.*, *Int. Ed.*, 2012, **51**, 3944.
25. K. Fujikawa, Y. Fujioka, A. Kobayashi, H. Amii, *Org. Lett.*, 2011, **13**, 5560.
26. N. Iqbal, J. Jung, S. Park, E. J. Cho, *Angew. Chem.*, 2014, **126**, 549.
27. E. J. Cho, T. D. Senecal, T. Kinzel, Y. Zhang, D. A. Watson, S. L. Buchwald, *Science*, 2010, **328**, 1679.
28. D. Yu, Z. Gang, H. Weiyuan, *Tetrahedron Lett.*, 1993, **34**, 1321.
29. Y. Wu, H. R. Zhang, R. X. Jin, Q. Lan, X. S. Wang, *Adv. Synth. Catal.*, 2016, **358**, 3528.
30. M. Khrizanforov, S. Strekalova, V. Khrizanforova, V. Grinenko, K. Kholin, M. Kadirov, T. Burganov, A. Gubaidullin, T. Gryaznova, O. Sinyashin, L. Xu, D. A. Vicic, Y. Budnikova, *Dalton Trans.*, 2015, **44**, 19674.
31. Y. B. Dudkina, D. Y. Mikhaylov, T. V. Gryaznova, O. G. Sinyashin, D. A. Vicic, Y. H. Budnikova, *Eur. J. Org. Chem.*, 2012, **11**, 2114.
32. Y. B. Dudkina, D. Y. Mikhaylov, T. V. Gryaznova, A. I. Tufatullin, O. N. Kataeva, D. A. Vicic, Y. H. Budnikova, *Organometallics*, 2013, **32**, 4785.
33. S. Yu, Y. Dudkina, H. Wang, K. V. Kholin, M. K. Kadirov, Y. H. Budnikova, D. A. Vicic, *Dalton Trans.*, 2015, **44**, 19443.
34. Y. B. Dudkina, T. V. Gryaznova, Y. N. Osin, V. V. Salnikov, N. A. Davydov, S. V. Fedorenko, A. R. Mustafina, D. A. Vicic, O. G. Sinyashin, Y. H. Budnikova, *Dalton Trans.*, 2015, **44**, 8833.
35. M. Matsui, K. Shibata, H. Muramatsu, H. Sawada, M. Nakayama, *Synlett*, 1991, 113.
36. J. T. Liu, W. Y. Huang, *J. Fluorine Chem.*, 1999, **95**, 131.
37. W. Dmowski, K. Piasecka-Maciejewska, *Org. Prep. Proced. Int.*, 2002, **34**, 514.
38. X. H. Cao, X. Pan, P.-J. Zhou, J.-P. Zou, O. T. Asekun, *Chem. Commun.*, 2014, **50**, 3359.
39. Y. Li, Y. Lu, G. Qiu, Q. Ding, *Org. lett.*, 2014, **16**, 4240.

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