Activation of C—F bonds in ionic liquids catalyzed by nickel complex compounds

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A nickel complex-catalyzed hydrodefluorination of acet(pentafluoroanilide) with zinc in ionic liquids resulted in the corresponding 2,3,4,5-tetrafluoro, 3,4,5-trifluoro, and 3,4-difluoro derivatives. The influence of the ionic liquid nature and the reaction conditions on its selectivity were studied, a possibility of the multiple reuse of the ionic liquids as the reaction media was demonstrated.

Key words: metal complex catalysis, activation of C—F bond, ionic liquids, acet-(pentafluoroanilide), nickel complexes, 2,2'-bipyridine, 1,10-phenanthroline, hydrodefluorination, 3,4,5-trifluoroaniline, organofluorine compounds.

Ionic liquids (IL), organic salts with low melting points, are a comparably new class of solvents, which are used in fine organic synthesis and catalysis.¹ The large interest to IL as the reaction media to a considerable extent is due to a number of useful properties of these materials, such as a good ability to dissolve organic, inorganic, and complex compounds and a high thermal and chemical stability. In addition, the zero density of the IL vapors is an important factor determining the eco-friendly technologies in which they are used.

Despite the active studies, to the present moment a comparably few examples of activation of the C_{Ar}-Hal bonds assisted by the transition metal complex compounds in IL are known.²⁻⁶ The majority of the indicated works dealt with the palladium-catalyzed reactions of aryl halides with olefins (the Heck reaction). $^{7-17}$ Several examples of the aryl halides coupling with organoboron compounds (the Suzuki reaction),^{11,14,15,18,19} carbonylation reactions of aryl halides,^{20,21} and homocoupling of aryl halides catalyzed by nickel complexes are also described.^{22,23} A number of works²⁴⁻²⁶ are devoted to the catalytic hydrodehalogenation of aryl halides (chloro and bromo derivatives) in IL. In no one of the works indicated we found examples of activation of the C-F bonds. At the same time, polyfluoroaromatic compounds containing several fluorine atoms in the aromatic ring are the valuable intermediate products in different sectors of fine organic synthesis,²⁷ but are the poorly available compounds.

Earlier,²⁸ we have shown a possibility of the use of 1-butyl-3-methylimidazolium bromide (BMIMBr) as the medium for zinc hydrodefluorination of polyfluoroarenes, which were catalyzed by nickel complexes with 2,2'-bi-pyridine (Bpy) or 1,10-phenanthroline (Phen).

In the present work, taking the hydrodefluorination of acet(pentafluoroanilide) (1) as an example we carried out the systematic studies of the influence of the IL cation and anion nature on the catalytic properties of nickel complex compounds and the selectivity of the process.

Results and Discussion

To study the influence of the nature of IL on the hydrodefluorination of acet(pentafluoroanilide) (1), we conducted the experiments with the use of IL based on the 1-alkyl-3-methylimidazolium salts containing different anions and cations: BMIMBr, 1-butyl-3-methylimidazolium chloride (BMIMCl), 1-butyl-3-methylimidazolium acetate (BMIMOAc), 3-ethyl-1-methylimidazolium bromide (EMIMBr), 1-hexyl-3-methylimidazolium bromide (C₆MIMBr), 1-methyl-3-octylimidazolium bromide (C₈MIMBr), and 1-decyl-3-methylimidazolium bromide (C₁₀MIMBr).

The experiments on the hydrodefluorination of compound 1 (Scheme 1) in a mixture of water and BMIMBr in the presence of a catalytic amount of NiCl₂ (5 mol.% with respect to the substrate) showed that a low conversion of substrate 1 was observed under the conditions described (Table 1, entry 1). Note that in common aprotic solvents, nickel chloride without ligands does not exhibit catalytic activity in the hydrodehalogenation of polyhaloarenes.^{29–35} The *in situ* formation of the carbene complexes similarly to the examples described earlier⁹ seems unlikely in this case, since the hydrodefluorination proceeds under mild enough conditions (70 °C) and in the absence of a strong base which is required for the generation of the free carbene.³⁶ Therefore, it can be

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suggested that nickel halide complexes formed in the presence of the excess of Br^- anions are the good catalysts for hydrodefluorination of compound **1**. In the absence of Bpy or Phen, the hydrodefluorination was nonselective: the formation of a mixture of acet(2,3,4,5-tetrafluoroanilide) (**2**) and acet(2,3,5,6-tetrafluoroanilide) (**3**) was observed.

Scheme 1



The use of the nickel complexes with Bpy or Phen as the catalysts provides to the selective activation of the C—F bonds at *ortho*-positions with respect to the functional group of the substrate. This result agrees with the behavior of nickel complexes in the hydrodefluorination of different substrates in aprotic dipolar solvents.^{29,33–35} In this case, 2,3,4,5-tetrafluoroanilide (2) and 3,4,5-trifluoroanilide (4) are the reaction products. With the high content of product 4 in the reaction mixture, its further defluorination leading to acet(3,4-difluoroanilide) 5 also occured (see Scheme 1).

Like in the reactions in common solvents, nickel complexes with one ligand exhibit the decreased catalytic activity when the reaction is carried out in aqueous BMIMBr (see Table 1, entries 2, 6), though the catalytic activity of these complexes in BMIMBr is higher than in N-methylpyrrolidone.³⁵

A somewhat higher activity was characteristic of the complex $NiCl_2 \cdot 2Bpy$: the 57% selectivity on product 4 with the virtually complete conversion of substrate 1 was reached within 6 h (entry 3). The phenanthroline analog gave the optimal results under these conditions: the complete conversion of compounds 1 and 2 was observed in the reaction catalyzed by $NiCl_2 \cdot 2Phen$ already after 2 h, together with the high selectivity on product 4 (entry 7). Note that the hydrodefluorination in aqueous *N*-methylpyrrolidone assisted by this complex also gave a good result,

 Table 1. Hydrodefluorination of compound 1 upon the action of nickel complexes with Bpy and Phen in IL based on 1-butyl-3-methylimidazolium with different anions

Entry	Complex	Ionic liquid	Reaction time/h	Conversion (%)	Composition of product (%)			TON*
					2	4	5	
1	NiCl ₂	BMIMBr	6	29	48	0	0	5.8
2	NiCl ₂ ·Bpy	BMIMBr	6	86	87	13	0	19.4
3	$NiCl_2 \cdot 2Bpy$	BMIMBr	6	99	43	57	0	29.8
4	$NiCl_2 \cdot 3Bpy$	BMIMBr	0.5	100	0	65	35	40.0
5	$NiCl_2 \cdot 3Bpy$	BMIMBr	2	100	0	60	40	40.0
6	$NiCl_2 \cdot Phen$	BMIMBr	6	100	68	31	1	26.4
7	$NiCl_2 \cdot 2Phen$	BMIMBr	2	100	0	99	1	40.0
8	$NiCl_2 \cdot 3Phen$	BMIMBr	6	100	35	62	3	33.0
9	NiCl ₂	BMIMCl	6	52	69	0	0	10.4
10	$NiCl_2 \cdot Bpy$	BMIMCl	6	100	3	87	11	39.5
11	$NiCl_2 \cdot 2Bpy$	BMIMCl	6	100	0	78	22	40.0
12	NiCl ₂ • 3Bpy	BMIMCl	6	100	0	90	10	40.0
13	NiCl ₂ · Phen	BMIMCl	6	82	90	10	0	17.9
14	$NiCl_2 \cdot 2Phen$	BMIMCl	6	100	69	31	0	26.3
15	$NiCl_2 \cdot 3Phen$	BMIMCl	6	100	36	63	2	32.8
16	NiCl ₂ • Bpy	BMIMOAc	6	15	87	13	0	3.4
17	$NiCl_2 \cdot 2Bpy$	BMIMOAc	6	45	91	9	0	9.8
18	$NiCl_2 \cdot 3Bpy$	BMIMOAc	6	9	100	0	0	1.8
19	NiCl ₂ · Phen	BMIMOAc	6	7	100	0	0	1.4
20	NiCl ₂ •2Phen	BMIMOAc	6	39	92	8	0	8.4
21	$NiCl_2 \cdot 3Phen$	BMIMOAc	6	100	68	32	0	26.4

* For the clarification, see the text.

however, the complete conversion of compounds 1 and 2 was reached in this case later than 6 $h^{.35}$

The catalytic activities of nickel complexes with three ligands significantly differ. The complex NiCl₂ · 3Phen did not exhibit high catalytic activity under the reaction conditions: only 62% conversion of compounds 2 in 4 was observed after 6 h (see Table 1, entry ϑ). The complex NiCl₂ · 3Bpy under these conditions exhibited the maximal activity: the complete conversion of compounds 1 and 2 was achieved already within 30 min, along with 35% conversion of compound 4 to 3,4-difluoroanilide 5 (entry 4). The longer reaction time led to a slight increase in the content of the side product (entry 5). The experimental data obtained are in agreement with the results of hydrodefluorination in *N*-methylpyrrolidone, where the complex NiCl₂ · 3Bpy also demonstrated the higher activity than the phenanthroline analog.³⁵

The experiments on hydrodefluorination of compound 1 in IL with other anion, viz., BMIMCl and BMIMOAc, showed that the nature of the IL anion was the determining factor of the catalytic activity of nickel complexes. The catalytic hydrodefluorination of compound 1 in a mixture of water and BMIMCl in the presence of the nickel complexes with Bpy resulted in the high conversion of the starting substrate 1 and the intermediate product 2 independent of the amount of Bpy in the composition of the nickel complex (see Table 1, entries 10-12). When Bpy was absent (entry 9), the result similar to that in the reaction in the presence of NiCl₂ in aqueous BMIMBr was observed: the 52% conversion of compound 1 was reached within 6 h, whereas tetrafluoroanilides 2 and 3 were the reaction products. The data obtained allowed us to suggest that the nickel complex with one Bpy molecule and Cl⁻ anions were catalytically active in aqueous BMIMCl. When NiCl₂ • 2Bpy and NiCl₂ • 3Bpy were used as the starting complexes in the presence of a large excess of Clanions, it is probable that the substitution for the Bpy molecules with the latter in coordination sphere of nickel took place (Scheme 2). For the phenanthroline nickel complexes (entries 13-15), no similar effect was observed, that, apparently, was due to the higher stability of such nickel complexes as compared to the bipyridine analogs.

Scheme 2

 $Ni(Bpy)_n Cl_2 \xrightarrow{2 Cl} Ni(Bpy)Cl_4^{2-} + (n-1) Bpy$ n = 1-3

The use of a mixture of water and BMIMOAc as the reaction medium led to a sharp decrease in the catalytic activity of the nickel complexes with Bpy (see Table 1, entries 16-18). In this case, the conversion of compound 1 did not exceed 45% within 6 h. A possible reason for the

decrease in the catalytic activity is a partial substitution for the Bpy molecules in the coordination sphere of nickel with acetate ions similarly to the behavior of bipyridine complexes in aqueous BMIMCl (Scheme 3).

Scheme 3

Ni(L)_nCl₂
$$\xrightarrow{OAc^{-}}$$
 Ni(L)_m(OAc)_k^{(k-2)-} + (n-m) L
L = Bpy, Phen; n = 1-3, m = 0-2, k = 2-4

For the phenanthroline nickel complexes in aqueous BMIMOAc, a decreased catalytic activity was also observed as compared to the reactions in other IL. In the presence of the complexes with one and two Phen molecules, the conversion of the substrate **1** did not reach 100% within 6 h (see Table 1, entries *19*, *20*). The complex NiCl₂· 3Phen under these conditions exhibited a higher activity, which, however, was lower than that in other IL (entry *21*).

The experiments carried out with the use of IL with different alkyl substituents in the structure of the imidazolium cation showed that the structure of the IL cation had an insignificant effect on the catalytic properties of nickel complexes. Thus, when the reaction was carried out in EMIMBr, a small increase in the catalytic activity of most nickel complexes was observed as compared to that for the reactions in aqueous BMIMBr (Table 2). In all the cases, the conversion of the starting compound 1 reached 100% within 6 h. The complex NiCl₂·2Phen, conversely, exhibited a decreased activity as compared to the reactions in BMIMBr: the selectivity on product 4 after 6 h was 77% (see Table 2, entry 5). An increase in the length of the alkyl chain of the IL cation produced no considerable changes in the catalytic properties of the system, either. When the reaction was carried out in IL C₆MIMBr and C_8 MIMBr, no noticeable changes in the activity of the nickel complexes (entries 7-18) as compared to their catalytic properties in aqueous BMIMBr were observed. When the reaction was conducted in C₁₀MIMBr, virtually all the nickel complexes exhibited the decreased catalytic activity (entries 19-24), that, most likely, was due to the increase in the density of the reaction medium and, as a consequence, to the worsening the mass transfer and the decrease in the reaction rate observed.

One of the important positive properties of IL is a possibility of their multiple reuse due to the easiness of separation of the reaction products from the IL.^{14,15,37} We studied a possibility of the reuse of IL or the catalytic system (nickel complex + IL) under the condition of hydrodefluorination reaction of compound 1 (Table 3). The studies were performed using the catalytic system NiCl₂·2Phen—BMIMBr as an example, which gave the optimal results for the synthesis of acet(3,4,5-trifluoro-

Entry	Complex	Ionic liquid	Conversion* (%)	Compos	TON		
				2	4	5	
1	NiCl ₂ •Bpy	EMIMBr	100	74	23	3	25.4
2	NiCl ₂ •2Bpy	EMIMBr	100	23	70	7	35.4
3	NiCl ₂ •3Bpy	EMIMBr	100	0	69	31	40.0
4	$NiCl_2 \cdot Phen$	EMIMBr	100	37	58	5	30.8
5	$NiCl_2 \cdot 2Phen$	EMIMBr	100	18	77	5	36.4
6	$NiCl_2 \cdot 3Phen$	EMIMBr	100	13	82	5	37.4
7	$NiCl_2 \cdot Bpy$	C ₆ MIMBr	89	74	26	0	22.4
8	NiCl ₂ •2Bpy	C ₆ MIMBr	95	63	37	0	26.0
9	NiCl ₂ •3Bpy	C ₆ MIMBr	100	8	91	1	38.4
10	$NiCl_2 \cdot Phen$	C ₆ MIMBr	93	77	23	0	22.8
11	$NiCl_2 \cdot 2Phen$	C ₆ MIMBr	93	55	45	0	27.0
12	$NiCl_2 \cdot 3Phen$	C ₆ MIMBr	100	35	65	0	33.0
13	$NiCl_2 \cdot Bpy$	C ₈ MIMBr	91	86	14	0	20.8
14	$NiCl_2 \cdot 2Bpy$	C ₈ MIMBr	91	32	68	0	30.6
15	$NiCl_2 \cdot 3Bpy$	C ₈ MIMBr	100	10	86	4	38.0
16	$NiCl_2 \cdot Phen$	C ₈ MIMBr	94	65	35	0	25.4
17	$NiCl_2 \cdot 2Phen$	C ₈ MIMBr	98	70	30	0	25.2
18	$NiCl_2 \cdot 3Phen$	C ₈ MIMBr	99	21	77	2	35.4
19	$NiCl_2 \cdot Bpy$	C ₁₀ MIMBr	85	92	8	0	18.4
20	NiCl ₂ •2Bpy	$C_{10}MIMBr$	99	65	35	0	26.8
21	$NiCl_2 \cdot 3Bpy$	C_{10}^{10} MIMBr	100	46	54	0	30.8
22	$NiCl_2 \cdot Phen$	C ₁₀ MIMBr	83	87	13	0	18.8
23	$NiCl_2 \cdot 2Phen$	C ₁₀ MIMBr	98	66	34	0	26.2
24	$NiCl_2 \cdot 3Phen$	C ₁₀ MIMBr	96	88	13	0	21.6

Table 2. Hydrodefluorination of compound **1** upon the action of nickel complexes with Bpy and Phen in IL with different length of the alkyl chain of the imidazolium cation

* The reaction time of 6 h.

anilide) **4**. After the first reaction cycle, the product was extracted from the reaction medium with hot ethyl acetate, the completeness of extraction was 96-98%. In the second cycle when the system was used without addition of the catalyst, the considerable decrease in the catalytic activity was observed: the conversion of the starting compound **1** reached only 57% (see Table 3, entry 2). This effect can be attributed to the partial extraction of the nickel complex or the ligand from the reaction mixture along with the hydrodefluorination products. The introduction of an additional portion of the nickel complex in each the subsequent reaction cycle allowed us to reuse the IL, at least for three cycles, without considerable de-

crease in the selectivity on the hydrodefluorination product of compound 4 (entries 3-5).

In conclusion, we found the effect of a considerable increase in the catalytic activity of nickel complexes in the hydrodefluorination reaction of substrate **1** when IL were used as the reaction medium. The nature of the IL anion was shown to considerably influence the catalytic activity of the nickel complexes, that, probably, was due to the partial or complete substitution for the ligands of the nickel complex with the anions of IL provided that an excess of the latter was present in the reaction mixture.

At the same time, the length of the hydrocarbon chain of the substituent in the imidazolium cation of IL does not

Table 3. Experiments on the multiple reuse of IL in the hydrodefluorination reactions of substrate 1

Entry	Cycle number	Amount of catalyst /mg/mmol/mol.%	Reaction time/h	Conversion (%)	Composition of product (%)		
					2	4	5
1	Ι	11/0.025/5	2	100	0	89	11
2	II	_	6	57	95	5	0
3	Ι	11/0.025/5	2	100	1	80	19
4	II	11/0.025/5	2	100	0	75	25
5	III	11/0.025/5	2	100	16	76	8

considerably affect the catalytic properties of the nickel complexes. The easiness of the isolation of hydrodefluorination products from the reaction mixtures by extraction allowed us to multiply reuse IL in the hydrodefluorination reaction of compound **1**.

Based on the results obtained, we developed a procedure for the preparative synthesis of 3,4,5-trifluoroaniline (6) (after deacetylation of product 4) in the process including the multiple reuse of BMIMBr in the step of catalytic hydrodefluorination.

Experimental

¹⁹F NMR spectra were recorded on a Bruker AVANCE 300 spectrometer (282.40 MHz). Chemical shifts were measured relative to CCl₃F (using C₆F₆ as a secondary internal standard, $\delta = -162.9$). α,α,α-Trifluorotoluene (benzotrifluoride) was used as a quantitative internal standard.

HPLC patterns were measured on a Milikhrom A-02 (a 2×75 mm column filled with the ProntoSIL 120-5C18AQ reverse phase sorbent, particle size of 5 μ m, detection at $\lambda = 226$ nm) in the gradient of solvents water—methanol.

Compositions of the reaction mixtures, conversion of the starting compound 1, and yields of the products were determined by HPLC. The TON parameter was calculated as the ratio of the number of moles of the substrate consumed to the number of the catalyst used and taking into account that acet-(3,4,5-trifluoroanilide) 4 resulted from the subsequent hydrodefluorination reaction of product 2.

2,2'-Bipyridine (Bpy) (analytical grade) was purified by recrystallization from hexane. Ethyl acetate (analytical grade), Zn (a powder, GOST 12601-76E), NiCl₂ · $6H_2O$ (pure grade), and 1,10-phenanthroline hydrate (Phen · H_2O , analytical grade) were used without additional purification. IL containing bromide- and chloride ions were synthesized similarly to the procedures described earlier^{38,39} from 1-methylimidazole and the corresponding alkyl halides. Preparation of acet(pentafluoroanilide) **1** is described in the work.⁴⁰ Nickel complex compounds were prepared similarly to the known procedures^{41–43} or were obtained *in situ* from nickel chloride and the corresponding ligands.

1-Butyl-3-methylimidazolium acetate (BMIMOAc). Potassium acetate (5.6 g, 57 mmol) was dissolved in hot glacial acetic acid (55 mL) in a flask, followed by the addition of BMIMBr (11.4 g, 52 mmol) with stirring. The mixture obtained was stirred for 2 h without heating. A precipitate formed was filtered off, acetic acid was evaporated from the filtrate under high vacuum to obtain BMIMOAc (10.3 g, ~100%). The residual content of Br⁻ was 6.6% (data of electrochemical analysis).

Hydrodefluorination of acet(pentafluoroanilide) (1) in IL (general procedure). A corresponding nickel complex with Bpy or Phen (in the case when the complex was prepared *in situ*, $NiCl_2 \cdot 6H_2O$ (0.025 mol) and an appropriate amount of the ligand were stirred for 1 h at 70 °C in IL), zinc dust (0.025 mmol), 327 mg, 5 mmol), a melt of the corresponding IL (0.5 mL), and water (0.1 mL) were placed in a three-neck flask equipped with a thermometer, a magnetic stirrer, and a heating bath. The mixture was stirred for 10 min at 70 °C, followed by the addition of compound 1 (113 mg, 0.5 mmol). The reaction mixture was stirred for the required time. The reaction progress was moni-

tored by HPLC, the samples were collected every hour. The qualitative composition of the reaction products were determined by ¹⁹F NMR.

Multiple reuse of BMIMBr in hydrodefluorination reaction of acet(pentafluoroanilide) (1). The complex NiCl₂ · 2Phen (300 mg, 0.6 mmol), zinc dust (8.01 g, 122.4 mmol), the BMIMBr melt (13 mL), and water ((2.5 mL) were placed in a 25-mL flask equipped with a thermometer, a gas discharge tube, magnetic stirrer, and an oil bath with a thermoregulator. The reaction of mixture was stirred for 10 min at 70 °C, followed by the addition of compound 1 (2.76 g, 12.3 mmol). The mixture obtained was stirred for another 2 h at 70 °C, then diluted with acetonitrile (10 mL), the solid part was filtered off, additionally washed with acetonitrile (10 mL). Acetonitrile was extracted from the reaction mixture with hot ethyl acetate (5×10 mL). The IL left after the extraction of the product was dried in the high vacuum and reused in the second cycle of the reaction.

All the conditions for the carrying out the subsequent cycles were similar to the first reaction cycle.

Ethyl acetate was evaporated *in vacuo* on a rotary evaporator, water (50 mL) and sodium hydroxide (to pH 13—14) were added to the residue, the mixture obtained was stirred for 1 h at ~20 °C. Polyfluoroanilines formed upon hydrolysis were steam distilled, extracted with diethyl ether, the extract was dried with magnesium sulfate, the solvent was evaporated.

After the first reaction cycle, the yield of the product was 1251 mg (70% calculated on the starting compound 1), the selectivity on 3,4,5-trifluoroaniline was 90%.

After the second reaction cycle, the yield of the product was 1375 mg (76% calculated on the starting compound 1), the selectivity on 3,4,5-trifluoroaniline was 82%.

After the third reaction cycle, the yield of the product was 1148 mg (64% calculated on the starting compound 1), the selectivity on 3,4,5-trifluoroaniline was 84%.

Spectroscopic characteristics of the reaction products. Acet-(2,3,4,5-tetrafluoroanilide) (2). ¹⁹F NMR (DMF), δ : -140.3 (m, 1 F, F(5), ³J_{FF} = 22.5 Hz, ³J_{HF} = 10 Hz); -52.0 (m, 1 F, F(2), ³J_{FF} = 17.7 Hz); -158.1 (m, 1 F, F(3), ³J_{FF} = 20 Hz, ³J_{FF} = 20 Hz); -164.4 (m, 1 F, F(4), ³J_{FF} = 21 Hz, ³J_{FF} = 21 Hz).

Acet(2,3,5,6-tetrafluoroanilide) (3). ¹⁹F NMR (MeCN), δ: -140.9 (m, 2 F, F(3), F(5)); -145.5 (m, 2 F, F(2), F(6)).

Acet(3,4,5-trifluoroanilide) (4). ¹⁹F NMR (DMF), δ : -135.0 (dd, 2 F, F(3), F(5), ³*J*_{FF} = 21.3 Hz, ³*J*_{HF} = 10.5 Hz); -169.2 (tt, 1 F, F(4), ³*J*_{FF} = 21.5 Hz, ⁴*J*_{HF} = 6.5 Hz).

(tt, 1 F, F(4), ${}^{3}J_{FF} = 21.5$ Hz, ${}^{4}J_{HF} = 6.5$ Hz). Acet(3,4-difluoroanilide) (5). 19 F NMR (*N*-methylpyrrolidone), δ : -137.4 (m, 1 F, F(3), ${}^{3}J_{FF} = 21.3$ Hz); -145.5 (m, 1 F, F(4), ${}^{3}J_{FF} = 22.2$ Hz).

3,4,5-Trifluoroaniline (6). ¹⁹F NMR (acetone), δ : -136.6 (dd, 2 F, F(3), F(5), ${}^{3}J_{FF} = 21.3$ Hz, ${}^{3}J_{HF} = 10.5$ Hz); -178.9 (tt, 1 F, F(4), ${}^{3}J_{FF} = 21.3$ Hz, ${}^{4}J_{HF} = 6.0$ Hz).

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