Heteroaryl-*N*-difluoromethyltrimethylsilanes – Versatile Sources of Heteroaryl-*N*-difluoromethyl Anions in Reactions with Carbonyl Compounds

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Abstract: An efficient procedure for synthesizing heteroaryl-*N*-difluoromethyltrimethylsilanes - new nucleophilic difluoromethylene synthons - from easily available *N*-bromodifluoromethylated heterocycles, chlorotrimethylsilane and aluminium powder in triglyme or *N*-methylpyrrolidinone on a preparative scale in 71-75% isolated yield is described. Heteroaryl-*N*-difluoromethyltrimethylsilanes and benzaldehyde react under fluoride ion catalysis to give 1-(1,1-difluor-2-hydroxy-2-phenyl-ethyl)heteroaryls, whereas for anionic heteroaryl-*N*-difluoromethylation of cyclohexanone a stoichiometrical mixture of heteroaryl-*N*-difluoromethyltrimethylsilanes and tetramethylammonium fluoride has to be used.

Key words: heteroaryl-*N*-difluoromethyltrimethylsilanes, carbanion trapping, anionic heteroaryl-*N*-difluoromethylation, tetramethylammonium fluoride

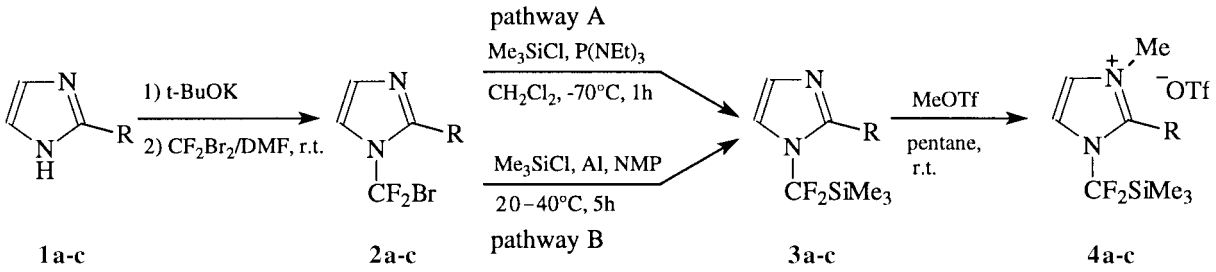
Recently, the introduction of the difluoromethylene moiety into organic compounds has attracted much attention due to the biological properties exhibited by *gem*-difluoro compounds as compared to their non-fluorinated analogs.[1] Along with the traditional fluorination methods, the transformations of nucleophilic difluoromethylene synthons, i.e. 1,1-difluoroalkylsilanes, difluoroenoxysilanes, carbalkoxydifluoromethylene and dialkoxy phosphinyldifluoromethylene zinc, copper and silicon derivatives play a rising role in the synthesis of geminal difluoromethylene compounds.[1-7] In contrast to the extensively investigated chemistry of the aforementioned derivatives, few is known about heteroaryl-*N*-difluoromethyl anions, heteroarylium-*N*-difluoromethylides or their trimethylsilyl derivatives. Meanwhile, the introduction of the heteroaryl-*N*-difluoromethyl moiety, i.e. imidazole-N-CF_2- or benzimidazole-N-CF_2-anions, into organic or organoelement compounds can induce new interesting biological properties. Recently, tetrakis(dimethylamino)ethylene (TDAE) was applied for the generation of heteroaryl-C-difluoromethyl anions, which were trapped by a fivefold excess of the carbonyl compounds.[5,6] Moreover, it was shown, that 2-alkyl-1-bromodifluoromethylbenzimidazoles reacted with TDAE and aromatic aldehydes used in a threefold excess to give 2-alkyl-1-(2-aryl-1,1-difluoro-2-hydroxyethyl)-benzimidazoles, versatile precursors in the synthesis of the potential nonpeptide angiotensin II receptor antagonists.[8]

2-Alkyl-1-bromodifluoromethylbenzimidazoles[8] were prepared by a catalytic method recently disclosed by us for the synthesis of *N*-bromodifluoro-and *N*-trifluoromethylated, nitrogen containing heterocycles (CH_3CN as a solvent and activated Zn or Cu for generating a chain reaction).[9] The above mentioned heteroaryldifluoromethylation reactions, where a two- to fivefold excess of the electrophile was used, gave only low to moderate yields of the corresponding carbinols, limiting these protocols only to aldehydes and preventing therefore a broad application.[5,6,8]

Perfluoroalkyltrimethylsilanes are already well recognized in organic synthesis as versatile anionic perfluoroalkylating reagents.[4] Heteroaryl- and heteroarylium-*N*-difluoromethyltrimethylsilanes were synthesized and studied as stable and easy to handle precursors for the corresponding *N*-difluoromethyl anionic species for the following reasons: To simplify the synthetic protocol for generating the unstable heteroaryl-*N*-difluoromethyl anions, to generate the hitherto unknown heteroarylium-*N*-difluoromethylides as well as to find facile reagents giving high yield in heteroaryl-*N*-difluoromethylating aldehydes or ketones.

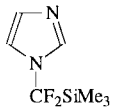
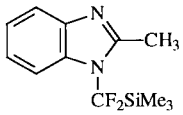
We describe herein our results in the synthesis of the novel heteroaryl-*N*-difluoromethyltrimethylsilanes **3a-c**, of heteroarylium-*N*-difluoromethyltrimethylsilanes **4a-c** and their application for high yield anionic heteroaryl- and heteroarylium-*N*-difluoromethylation of benzaldehyde and cyclohexanone.[10] The key precursors in the synthesis, namely the *N*-bromodifluoromethylated imidazole and benzimidazole derivatives **2a-c**,[11] were prepared by modifying the previously published protocol.[9] We have found conditions for the reactions of dibromodifluoromethane with imidazolyl-and benzimidazolyl- anions in CH_3CN or DMF not requiring any catalytical activation by Zn or Cu powder. Thus, the reaction of imidazolyl potassium generated from **1a** and t-BuOK with CF_2Br_2 in DMF at room temperature without a catalyst led to compound **2a** in 85% isolated yield, whereas, imidazolyl sodium under similar reaction conditions or even upon addition of Zn powder gave 1-bromodifluoromethylimidazole **2a** in only 12% isolated yield.

Trimethylsilylation[12] of 1-bromodifluoromethyl imidazole and benzimidazole derivatives **2a-c** (**a** = imidazolyl, **b** = 2-phenylimidazolyl, **c** = 2-methylbenzimidazolyl) with Me_3SiCl was found to proceed similarly as for the synthesis of Me_3SiCF_3. Both pathways, the one using hexaethyltriamido phoshite in CH_2Cl_2 at −70 °C (pathway **A**)[13] and the "Grobe method" (Al or Zn powder in triglyme or *N*-methylpyrrolidinone at 20-40 °C (pathway **B**)[14] led to corresponding *N*-bromodifluoromethyltrime-



Scheme 1

Table 1 Synthesis of heteroaryl-*N*-difluoromethyltrimethylsilanes **3a-c**[14]

	Product	Method	Yield[a](%)
3a		A	85
		B	71
3b		A	75
		B	75
3c		A	82
		B	73

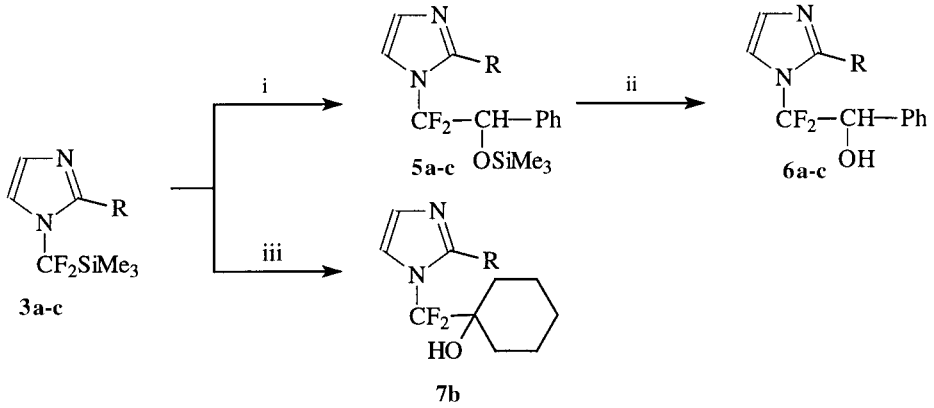
[a]Isolated yield (%) based on 1-bromodifluoromethylimidazole and benzimidazole derivatives **2a-c**.

thylsilanes **3a-c** in 71-85% isolated yields (Scheme 1, Table 1).

The heteroaryl-*N*-difluoromethyltrimethylsilanes **3a-c** were quantitatively converted into heteroarylium-*N*-difluoromethyltrimethylsilanes **4a-c** by treatment with methyl triflate in pentane at ambient temperature.

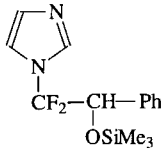
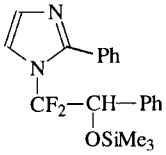
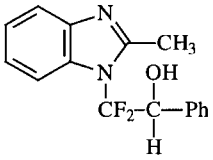
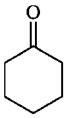
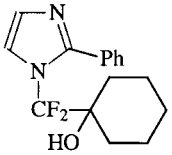
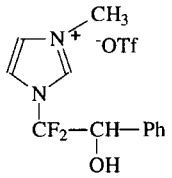
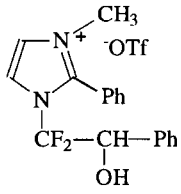
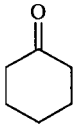
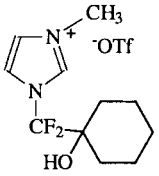
The anionic heteroaryl-*N*-difluoromethylation[15] of benzaldehyde with **3a-c** proceeds smoothly upon adding catalytic quantity (0.02 mol%) of fluoride (Me_4NF, TASF or spray dried KF) to an equimolar mixture of silanes, **3a-c** in THF or monoglyme at 0 °C, warming up to ambient temperature and stirring for 10 h at 20 °C to yield the trimethylsilylated difluorinated carbinols **5a-c.** Desilylation of **5a-c** with aqueous HCl (15%) at ambient temperature affords difluorinated carbinols **6a-c**. The heteroarylium-*N*-difluoromethyltrimethylsilanes **4a,b** were used to generate the previously unknown fluorinated species, namely heteroarylium-*N*-difluoromethylides. The fluoride catalysed reaction of the charged silanes **4a,b** with benzaldehyde is much faster than for neutral silanes **3a-c.** The heteroarylium-*N*-difluoromethylation of benzaldehyde with compounds **4a,b** proceeds upon adding 0.02 mol% of Me_4NF to an equimolar mixture of **4a,b** in monoglyme at 0 °C, warming up to ambient temperature and stirring for 0.5 h at 20 °C yielding the trimethylsilylated difluorinated carbinols **8a,b** (Table 2).

There is a striking difference in reactivity between CF_3SiMe_3 and silanes **3**, **4a-c** in reactions with ketones. If only a catalytic amount (0.02 mol%) of Me_4NF or KF was added to the monoglyme solution of silane **3b** and cyclohexanone at either 0 °C or at ambient temperature, the main reaction product formed was 1-difluoromethyl-2-phenyl-imidazole (99%). The target fluorinated carbinol was observed only as an impurity (1%) in the ^{19}F NMR spectrum. Whereas equimolar amounts of Me_4NF favor the formation of the target carbanion addition product **7b** in 64% (70% ^{19}F NMR) yield. Applying a onefold excess



Scheme 2 i: PhCHO, $Me_4N^+F^-$ cat., THF or monoglyme, 0 °C-r.t., 10 h; ii: HCl (15%), r.t.; iii: 1) cyclohexanone, $Me_4N^+F^-$ equiv 2) H_2O

Table 2 Reactions of heteroaryl-*N*-difluoromethyltrimethylsilanes with benzaldehyde and cyclohexanone[15]

Reagent	Substrate	Product		Reaction Time (h)	Method, Workup	Yield (%)[a]
3a			**5a**	10	$Me_4N^+F^-$ cat.	80(89) 85(95)[b]
3b			**5b**	10	a) $Me_4N^+F^-$ cat. b) K^+F^- cat.	88(95) 85(93)
3c			**6c**	10	1) $Me_4N^+F^-$ cat equiv 2) HCl	81(93)
3b			**7b**	0.5	1) $Me_4N^+F^-$ 2) H_2O	64(70) 77(83)[c]
4a			**8a**	1	1) $Me_4N^+F^-$ cat 2) HCl	76(87)
4b			**8b**	1	1) $Me_4N^+F^-$ cat 2) HCl	81(90)
4a			**9a**	0.5	1) $Me_4N^+F^-$ equiv. 2) H_2O	76(86)

[a] Yield of isolated product (^{19}F NMR yield). [b] With 2 equiv of benzaldehyde. [c] With 2 equiv of cyclohexanone.

of cyclohexanone improved the yield of **7b** to 77% (83% ^{19}F NMR) (Scheme 2, Table 2).

These results are in contrast to the reactivity of trimethylsilyl derivatives CF_2=$CFSiMe_3$, $C_6F_5SiMe_3$ and $(EtO)_2(O)PCF_2SiMe_3$, which give carbanion addition products only with aldehydes but not with enolizable ketones.[16-18] Compounds containing the Alk_2NCF_2 fragment are soft fluorinating agents for alcohols.[19] In contrast, due to the electron withdrawing effect of the heterocycle, the heteroaryl-*N*-CF_2-substituted carbinols **6a-c, 7b, 8a,b, 9a** proved to be stable to hydrolysis.

In conclusion, we have found a simple method for synthesizing new nucleophilic difluoromethylene synthons, i.e. imidazole- and benzimidazole-1-yl-difluoromethyl trimethylsilanes, on a preparative scale. Depending on the reaction conditions, anionic heteroaryl- and heteroarylium-*N*-difluoromethylation of aldehydes or enolizable ketones can be achieved in high yields. The key-point in the heteroaryl-*N*-difluoromethylation of ketones is the use of stoichiometric amounts of anhydrous tetramethylammonium fluoride. Further studies of the scope and applicability of these new nucleophilic synthons for heteroaryl-*N*-difluoromethylation of carboxylic acid halides, esters and

lactones are presently under investigation in our laboratories.

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(11) **Typical procedure for bromodifluoromethylation of imidazole and benzimidazole derivatives** (all reactions were performed under nitrogen in carefully dried solvents): 1-Bromodifluoromethyl-imidazole **2a**. To a solution of 5.0 g (47.2 mmol) imidazolyl-potassium (synthetized from 3.2 g (47.2 mmol) imidazole and 5.3 g (47.2 mmol) t-BuOK in THF) in dried DMF (50 ml) under nitrogen dibromodifluoromethane 29.7g (141.5 mmol) was added. The reaction mixture was stirred for 48 h at ambient temperature. The excess of dibromodifluoromethane was recycled by distilling it into a cooled (−20 °C) trap. The residue was diluted with 100 mL water. The product was extracted with petroleum ether, the organic phase was washed three times with water and dried over sodium sulfate. The product was isolated by distillation at reduced pressure. **2a**: bp 62 °C/30 Torr, yield 8.0 g (85%). ^{1}H NMR δ = 7.1 (dd, $^3J_{HH}$ = 2.2 Hz, $^4J_{HH}$ = 1.0 Hz, CH), 7.3 (m, CH), 7.9 (brs, CH); ^{19}F NMR δ = −28.9 (CF_2); ^{13}C NMR δ = 107.6 (t, J_{CF} 306.7 Hz, CF_2Br), 116.0 (CH), 130.9 (CH), 133.9 (CH); HRMS calcd for $C_4H_3N_2F_2$ ^{79}Br 195.9448, found 195.9450.
1-Bromodifluoromethyl-2-phenyl-imidazole **2b**: bp 64 °C/ 0.005 Torr, yield (83%); ^{1}H NMR δ = 7.1 (d, $^3J_{HH}$ = 2.0 Hz, CH), 7.3 (m, CH), 7.4−7.6 (m, 5H); ^{19}F NMR δ = -25.4 (s, CF_3); ^{13}C NMR δ = 107.9 (t, J_{CF} = 308.9 Hz, CF_2Br), 115.4 (s, C), 117.7 (s, CH), 128.0 (s, CH), 128.7-130.0 (m, Ar); Calcd for $C_{10}H_7N_2F_2Br$: C 43.98, H 2.58, F 13.91; Found: C 44.51, H 2.69, F 13.8.

(12) **Typical procedure for heteroaryl-*N*-difluoromethyltrimethylsilanes preparation.** 2-Phenyl-imidazole-1-yl-difluoromethyltrimethylsilane **3b**, method **A**: To a stirred suspension of 0.2 g (7.4 mmol) aluminium powder (Fluka, purity >98%, 160 μm) in 25 mL NMP were added in one portion 2.7 g (10 mmol) of **2b** and 2.0 g (18.4 mmol) of Me_3SiCl. At the end of the exothermic (40 °C) reaction, the mixture was heated at 40 °C for 5 h. After removal of NMP and the excess of Me_3SiCl at reduced pressure till dryness, the residue was extracted with boiling hexane (3 × 20 mL). The combined hexane solutions of **3b** were concentrated to 10 mL and the product was recrystallized from hexane under cooling till -30 °C. **3b**: colorless crystals, yield 2.0 g (75%) (relative to compound **2b**); mp 95-96°C; ^{1}H NMR δ = 0.1 (s, CH_3), 7.2−7.7 (m, 7 H); ^{19}F NMR δ = -80.6 (CF_2); ^{13}C NMR δ = -3.7 (CH_3), 118.1 (CH), 124.4 (t, J_{CF} = 287.1 Hz), 128.3-147.9 (m, Ar); Calcd for $C_{13}H_{16}N_2F_2Si$: C 58.62, H 6.05, F 14.27; Found: C 58.72, H 5.98, F 14.3.
Imidazole-1-yl-difluoromethyltrimethylsilane **3a**, yield 85%, bp 25°C/ 0.005 Torr; ^{1}H NMR δ = 0.1 (CH_3), 6.9 (dd, $^3J_{HH}$ = 2.2, $^4J_{HH}$ = 1.0 Hz, CH), 6.9 (brs, CH), 7.6 (brs, CH); ^{19}F NMR δ = -88.1 (CF_2); ^{13}C NMR δ = −5.2 (CH_3), 108.2 (t, J_{CF} = 250.6 Hz, CF_2), 114.9 (CH), 129.8 (CH), 133.4 (CH); HRMS calcd for $C_7H_{12}N_2F_2Si$ 190.0738; Found 190.0738.
2-Methyl-benzimidazole-1-yl-difluoromethyltrimethylsilane **3c**: yield 82%, ^{1}H NMR δ = 2.6 (t, $^5J_{FH}$ = 2.5 Hz, CH_3), 7.2-7.7 (m, Ar); ^{19}F NMR δ = −86.5 (s, CF_2); ^{13}C NMR δ = -1.4 (s, CH_3), 16.5 (t, $^4J_{CF}$ = 4.4 Hz, CH_3), 113.9 (t, J_{CF} = 326.1 Hz, CF_2Br), 115.0 (t, $^3J_{CF}$ = 5.3 Hz, C-CH_3), 116.7-147.2 (m, Ar); HRMS calcd for $C_{12}H_{16}N_2F_2Si$: 254.1051; Found: 254.1055

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(15) **(a) Typical procedure for anionic heteroaryl-*N*-difluoromethylation of cyclohexanone:** 1-(1,1-difluoro-1-cyclohexanol-1-yl-methyl)-2-phenyl-imidazole **7b**: To a stirred mixture of 3.0 g (11.3 mmol) **3b** and 2.2 g (22.6 mmol) cyclohexanone in 7 mL monoglyme was added 1.0 g (11.3 mmol) anhydrous tetramethylammonium fluoride at 0 °C. The mixture was stirred for 10 min at 0 °C and then allowed to warm up to ambient temperature within 10 min. After stirring for 1 h at 20 °C, the mixture was poured into 20 mL water. The product was extracted with 3 × 30 mL $CHCl_3$, the combined organic phases were washed once with water (30 mL) and dried over magnesium sulfate and recrystallized. **7b**: yield 2.54 g (77%); mp 115−117 °C (from $CHCl_3$/hexane); ^{1}H NMR δ ($CDCl_3$) = 1.0−1.4 (m, CH_2), 7.0 (brs, OH), 5.6−7.7 (m, Ar); ^{19}F NMR δ ($CDCl_3$) = - 89.3 (s, CF_2); ^{13}C NMR δ ($CDCl_3$) = 21.0−30.6 (m, CH_2), 74.4 (t, $^2J_{CF}$ 28.6 Hz, C(OH)), 122.2 (t, J_{CF} 269.8 Hz, CF_2), 118.4−147.7 (m, Ar); HRMS calcd for $C_{16}H_{18}ON_2F_2$: 292.1389; Found: 292.1387.
1-(1,1-difluoro-1-cyclohexanol-1-yl-methyl)-3-methyl-imidazolium triflate **9a**: yield 47%; mp 212 − 214 °C; ^{1}H NMR δ ($CDCl_3$) = 3.9 (s, CH_3), 4.8 (brs, CH), 5.4 (brs, OH), 7.4 (brs, CH), 7.6 (brs, CH), 9.2 (brs, CH); ^{19}F NMR δ ($CDCl_3$) = -80.4 (s, CF_3), −93.6 (s, CF_2); ^{13}C NMR δ ($CDCl_3$) = 27.2 − 36.1 (m, CH_2), 85.4 (t, $^2J_{CF}$ 29.5 Hz, C(OH)), 131.6 (t, J_{CF} = 258.2Hz, CF_2), 119.0 (CH), 137.1 (CH), 143.8 (CH); HRMS calcd for $C_{11}H_{17}ON_2F_2^+$ 231.1317; Found: 231.1315.
(b) Typical procedure for anionic heteroaryl-N-difluoromethylation of benzaldehyde: 1-(1,1-difluoro-2-phenyl-2-trimethylsiloxy-ethyl)-imidazole **5a**: To a stirred mixture of 3.1 g (16.3 mmol) **3a** and 1.73 g (16.3mmol) benzaldehyde in monoglyme (20 mL) was added ca. 2 mg of anhydrous tetramethylammonium fluoride at 0 °C. The mixture was stirred for 10 min at 0 °C and then allowed within 0.5 h to warm up to ambient temperature. After stirring for 10 h at 20 °C, the solvent was evaporated under reduced pressure. The residue was distilled in vacuo. **5a:** yield 3.9 g (80%); bp 84−86 °C/ 0.005 Torr; ^{1}H NMR δ ($CDCl_3$) = 0.0 (s,CH_3), 5.0 (brs, CH), 6.8 (brs, CH), 7.0 (brs, CH), 7.1−7.3

(m, 5H, CH), 7.5 (brs, CH); ^{19}F NMR δ ($CDCl_3$) = - 86.0 (dd, J_{FF} 210.3 Hz, $^3J_{FH}$ 3.4 Hz), -94.4 (dd, J_{FF} = 210.3, $^3J_{FH}$ = 6.9 Hz); ^{13}C NMR δ ($CDCl_3$) = 0.0 (s, CH_3), 76.2 (t, $^2J_{CF}$ = 33.2 Hz, CH), 118.3 (t, J_{CF} = 259.1 Hz), 126.5−135.6 (m, Ar); HRMS calcd for $C_{14}H_{18}N_2F_2OSi$: 296.1157; Found 296.1153.
1-(1,1-Difluoro-2-phenyl-2-trimethylsiloxy-ethyl)-2-phenyl-imidazole **5b**: yield 88%; bp 97−98°C/0.005 Torr ^{1}H NMR δ ($CDCl_3$) = 0.0 (s, CH_3), 5.0 (dd,CH), 7.0 − 7.7 (m, 5H, CH); ^{19}F NMR δ ($CDCl_3$) = - 83.1 (dd, J_{FF} = 208.6, $^3J_{FH}$ = 3.1 Hz), −94.4 (dd, J_{FF} = 208.6, $^3J_{FH}$ = 8.2 Hz); ^{13}C NMR δ ($CDCl_3$) = - 0.1 (s, CH_3), 72.2, 72.8 (AB-System, J_{AB} = 32.2 Hz, CH), 119.8 (t, J_{CF} = 264.3 Hz), 127.3-139.0 (m, Ar); HRMS calcd for $C_{20}H_{23}N_2F_2OSi$: 373.2128, Found: 373.2123.
2-Phenyl-imidazole-1-yl-2,2-difluoro-1-phenyl-ethanol **6b**: yield 86%; mp 194−196 °C; ^{1}H NMR δ ($CDCl_3$) = 5.2 (dd, CH), 6.9 (brs, OH), 7.1−7.5 (m, Ar); ^{19}F NMR δ ($CDCl_3$) = - 80.2 (d, J_{FF} = 206.9 Hz, CF_2), - 90.7 (dd, J_{FF} = 206.9, $^3J_{FH}$ = 13.8 Hz, CF_2); ^{13}C NMR δ ($CDCl_3$) = 73.6, 74.0 (AB-system, J_{AB} = 27.1 Hz, CH), 119.7 (t, J_{CF} = 261.5 Hz, CF_2), 118.8-147.2 (m, Ar); HRMS calcd for $C_{17}H_{14}ON_2F_2$: 300.1081; Found: 300.1074.

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