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Synthesis of monofluoroalkenes via Julia–Kocienski reaction

G.K. Surya Prakash *, Anton Shakhmin, Mikhail Zibinsky, Istvan Ledneczki, Sujith Chacko, George A. Olah

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, 837 Bloom Walk, Los Angeles, CA 90089-1661, USA

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ABSTRACT

Monofluoromethyl 3,5-bis(trifluoromethyl)phenyl sulfone **1** was synthesized and employed in Julia–Kocienski fluoroolefination reaction with various ketones and aldehydes. Optimal reaction conditions were found to be the treatment of substrates with KOH or CsF in DMSO at room temperature. Mixtures of (*E*) and (*Z*) isomers of monofluoroalkenes **4** were obtained in moderate to excellent yields.

1. Introduction

Only few versatile methods for the preparation of terminal monofluoroalkenes are known. These methods include Wittig type fluoroolefination [1], reduction of terminal difluoroalkenes [2], alkylation/hydroxyalkylation of fluoromethyl sulfones/sulfoximines/sulfoxides with subsequent elimination of sulfenate/sulfinamide/sulfinate moities [3], electrophilic fluorination of olefins [4] and phosphonate based fluoroolefination [5]. The latter can also be considered as a variation of a Wittig type olefination. Fluoroalkenes are often viewed as biomimetics of a peptide bond [6] and have recently been extensively studied for this purpose. Very recently, difluoromethyl-2-pyridyl sulfone was employed as an efficient reagent for *gem*-difluoroolefination of carbonyl compounds [7]. In addition, a general fluoroalkene synthesis protocol has been reported using fluorinated 1-phenyl-1-H-tetrazol-5-sulfonyl derivatives [8].

Also, fluoroolefination of nitrones via the reaction with α-fluorosulfoximines [9] and synthesis of α-fluoro-α,β-unsaturated esters employing Julia–Kocienski-type reaction [10] have been disclosed in the recent literature. In addition synthesis of fluoro enynes can be accomplished by using a novel α-fluoro-1,3-benzothiazol-2-yl propargyl sulfone [11]. A recent comprehensive article covers various aspects of Julia–Kocienski reaction for the synthesis of fluorooelfins [12].

Herein, we report a synthesis of previously unknown monofluoromethyl arylsulfone **1** as a convenient reagent for the direct monofluoroolefination of carbonyl compounds. Reaction of **1** with various aldehydes and ketones gave access to a simple and efficient way for the preparation of monofluoroalkenes in one step [13].

2. Results and discussion

Synthesis of sulfone **1** was performed in 3 steps starting from 3,5-bis(trifluoromethyl)benzenethiol **2** as depicted in Scheme 1. Oxidation of intermediate monofluoromethyl 3,5-bis(trifluoromethyl)phenyl sulfide was carried out in glacial acetic acid with 30% hydrogen peroxide solution at 80 °C. The overall yield of compound **1** was 61%.

Taking into account the acidity and reactivity of monofluoromethyl 3,5-bis(trifluoromethyl)phenyl sulfone **1** compared to the recently reported analogs [14], we tested several solvents and bases in order to find appropriate conditions for this particular reagent system. After brief screening of conditions (Table 1), we found that DMSO is the most suitable solvent, and KOH or CsF is the most efficient base for the protocol.

When KOH/DMSO system is used, the reaction proceeds smoothly. However, the conditions did not work very well for aromatic carbonyl compounds with electron-withdrawing substituents on the aryl ring. On the other hand, CsF reacts

* Corresponding author. Tel.: +1 213 740 5984.
E-mail address: gprakash@usc.edu (G.K. Surya Prakash).

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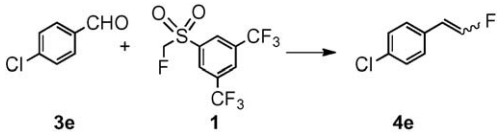
Table 1
Screening of solvents and bases and reaction optimization[a].



3e 1 4e

.

Entry	Solvent	Base	Yield of **4e** (%)	Time
1	THF	KOH/n-Bu_4N^+Br	30	12 h
2		CsOH/n-Bu_4N^+Br	36	12 h
3		LDA	–	5 h
4		CsF	3	12 h
5		Py	–	12 h
6	DMF	NaH (2 equiv.)	–	12 h
7		CsF	–	12 h
8	DMSO	NaH (2 equiv.)	15	12 h
9		NaH (5 equiv.)	5	12 h
10		NaOH	–	12 h
11		KOH	26[b]	2 h
12		CsOH	25	2 h
13		Py	–	12 h
14		Et_3N	–	12 h
15		DBU	31	72 h
16		n-$Bu_4N^+OH^-$	–	5 min
17		KF	–	12 h
18		CsF	95	48 h
19	MeCN	NaH	5	12 h
20		KOH/n-Bu_4N^+Br	20	12 h
21		CsF	2	12 h

[a] All reactions were carried out at ambient temperature except entry 3 where the temperature was gradually raised from −78 °C to ambient within 5 h.
[b] These reaction conditions showed much better performance compared to other base/solvent pairs in reaction with electron-rich carbonyl compounds.

significantly slower but provides products in good to excellent yields in case of both electron-rich and electron-deficient carbonyl compounds. Enolizable ketones and aldehydes gave poor yields in this reaction (5–20%) mainly due to side condensation processes and also due to their significant volatility.

A variety of aromatic ketones and aldehydes **3a–t** were explored in the fluoroolefination reaction with **1** (Table 2). Yields of fluoroolefins **4** were in the range of 8–96%. Most of the alkenes obtained by this method were a mixture of (*E*) and (*Z*) isomers in various ratios.

Ratios of *E*/*Z* isomers were determined by integration of the appropriate peaks in the ^{19}F and ^{1}H NMR spectra of fluoroolefins. Majority of the ketones gave close to 1:1 mixture of *E*/*Z* isomers, and for a number of the cases, we were unable to assign NMR peaks for individual isomers. On the contrary, aldehydes gave a wide range of *E*/*Z* ratios (from 1:1 up to 15:1 for compound **3d**) and assignment of the isomers was carried out based on the NMR data. As was recently proposed by Najera and co-workers [14], the plausible intermediates for similar type of olefination would be structures **A–D** (Scheme 2). Due to the small Van-der-Waals radius of the fluorine atom and no significant energy difference between Newman projection structures **A**, **B** and **C**, **D** for R = Ar, a mixture of *E*/*Z* isomers close to 1:1 is anticipated. As mentioned above, this was experimentally found for all ketones **3k–t**.

On the other hand, aldehydes can give different ratios of isomers, with R = H, intermediates **A** and **C** become somewhat more energetically advantageous. Surprising selectivites towards (*E*)-alkenes for entries **4–7** in Table 2 (15:1, 10:1, 6:1, and 3:1, respectively) could be due to the electronic effect of the fluorine atom in the transition state. Another explanation for the observed selectivities could be a change in the mechanism, which would also explain significantly lower yields (entries **4–6**).

Analysis of the ^{19}F NMR spectra of the fluoroalkenes **4** showed that the fluorine atoms appear as a dd at −115 to −130 ppm with geminal J_{HF} values from 82 to 86 Hz. Vicinal J_{HF} values for *Z* isomers were in the 18–23 Hz range, and vicinal J_{HF} values for *E*-isomers were in the 40–48 Hz range. Values of $^{1}J_{CF}$ were obtained from ^{13}C NMR data and they usually lay in the range of 240–290 Hz, which is consistent with the literature data [5].

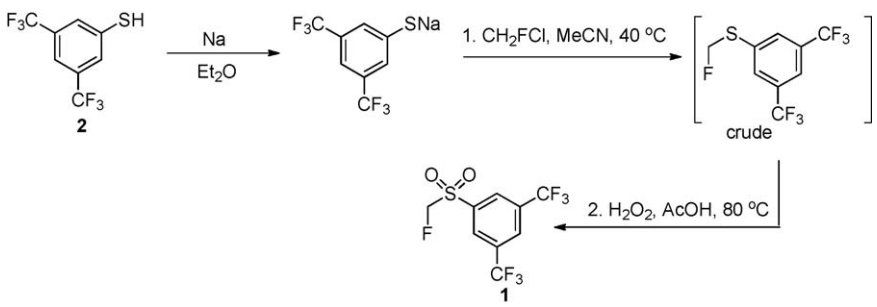
To confirm the molecular weight of all compounds **4** GC–MS analysis was performed after all the necessary work up and purification operations. Unfortunately, due to low stability and propensity of fluoroalkenes to polymerize [15,16], most of them (**4a–4e**, **4h**, **4n**, **4o**, **4q–4t**) were not analyzed by HRMS. All compounds were characterized by ^{1}H, ^{13}C and ^{19}F NMR. For compounds **4m**, **4r–t** (Table 2) (*E*)- and (*Z*)-isomers were separated and fully characterized. However, we were unable to distinguish between two isomers for entry **13** due to the similarity of their NMR spectra.

In conclusion, an efficient method of synthesis of terminal fluoroalkenes was developed. Mixtures of *E*/*Z* isomers can be obtained by this method in good yields. Mild conditions and reasonable reaction time makes this protocol advantageous compared to few other known methods of fluoroolefination.

3. Experimental

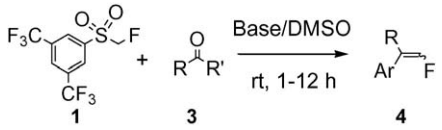
3.1. General

Unless otherwise mentioned, all reagents were purchased from commercial sources. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Varian Inova 400 MHz NMR spectrometer. ^{1}H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) standard at 0.00 ppm. ^{13}C NMR chemical shifts were determined relative to the ^{13}C signal of the solvent: $CDCl_3$ (77.16 ppm). $CFCl_3$ was used as internal standard for ^{19}F NMR. High resolution mass spectra were recorded in EI+ or FAB+ mode on a high resolution mass spectrometer at the Mass Spectrometry facility, University of Arizona.



Scheme 1. Synthesis of sulfone 1.

Table 2
Fluoroolefination of carbonyl compounds with **1**.



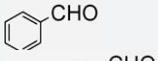
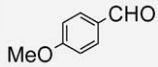
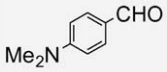
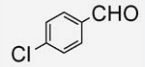
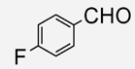
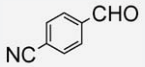
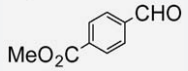
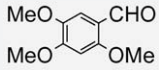
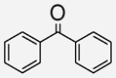
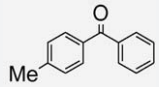
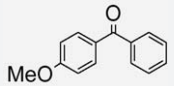
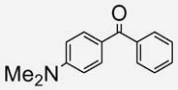
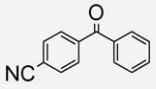
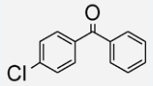
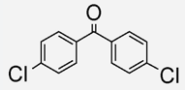
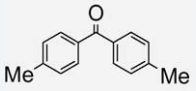
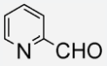
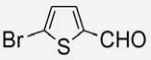
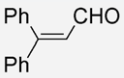
Entry	Carbonyl compound	Base	Yield of **4** (%)	*E*/*Z*
1		KOH	35 (**4a**)	1.8:1
		CsF	78 (**4a**)	1.7:1
2		KOH	82 (**4b**)	2.0:1
		CsF	73 (**4b**)	1.6:1
3		KOH	93 (**4c**)	1.3:1
4		KOH	24 (**4d**)	15.0:1
		CsF	92 (**4d**)	1.3:1
5		KOH	8 (**4e**)	10.0:1
		CsF	68 (**4e**)	1.5:1
6		CsF	25 (**4f**)	6.0:1
7		CsF	55 (**4g**)	3.0:1
8		KOH	96 (**4h**)	1.3:1
9		KOH	75 (**4i**)	n/a
10		KOH	67 (**4j**)	1:1
11		KOH	70 (**4k**)	1:1
12		KOH	62 (**4l**)	1:1
13		CsF	58 (**4m**)	1:1
14		CsF	62 (**4n**)	1:1
15		CsF	68 (**4o**)	n/a
16		KOH	96 (**4p**)	n/a
17	n-$C_9H_{19}CHO$	CsF	17 (**4q**)	2.9:1
18		CsF	83 (**4r**)	1.9:1

Table 2 (*Continued*)

Entry	Carbonyl compound	Base	Yield of **4** (%)	*E*/*Z*
19		CsF	52 (**4s**)	1:1
20		CsF	67 (**4t**)	1:1

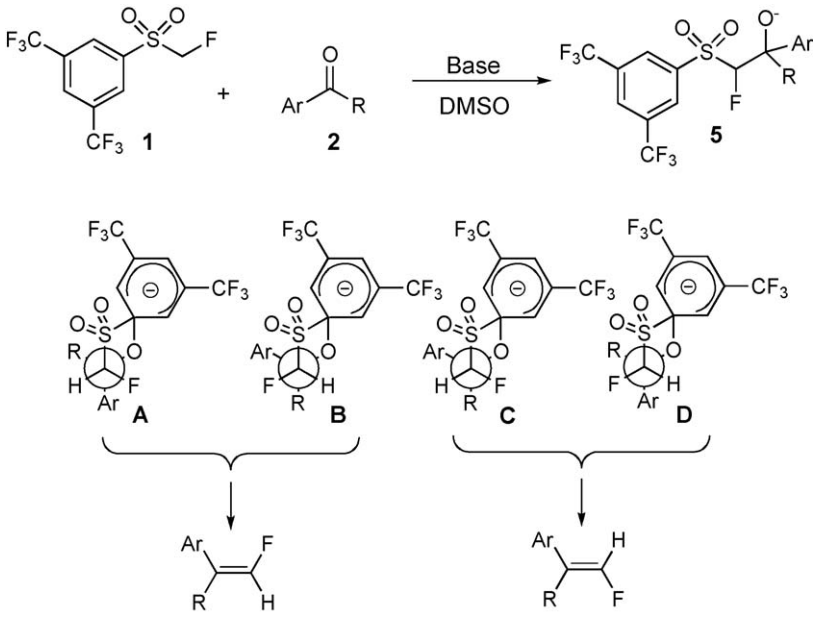
3.2. Preparation of 3,5-bis(trifluoromethyl)phenyl monofluoromethyl sulfone

1.0 g of sodium metal (43.48 mmol) and 40 mL diethyl ether were placed in a three-necked flask equipped with a dropping funnel, reflux condenser, and a stir bar. The solution of 10 g (40.62 mmol) of 3,5-bis(trifluoromethyl)benzenethiol in 50 mL of Et_2O was added to sodium in Et_2O dropwise; the stirred mixture was heated to reflux and was kept under reflux overnight. Subsequently, the remaining sodium was filtered off, most of the Et_2O was removed under reduced pressure, and large amount of hexane (~100 mL) was added to the remaining concentrated ethereal solution. Precipitated white solid was filtered off and air dried. 10.02 g (92%) of sodium salt of 3,5-bis(trifluoromethyl)thiophenol was obtained and used for the next step without additional purification.

Sodium 3,5-bis(trifluoromethyl)thiophenolate (18.65 mmol), 5 g, was placed in a pressure tube, dissolved in 60 mL acetonitrile, and the solution was rapidly cooled down to −78 °C. 6 mL (68.94 mmol) of condensed CH_2ClF was added to the thiophenolate solution at −78 °C. The reaction mixture was allowed to warm up to 40 °C and was stirred overnight. Subsequently, the reaction mixture was cooled down to room temperature and all the remaining volatile products were vented. 100 mL water was added to the residual solution. The mixture was extracted with chloroform (4 × 25 mL) and the combined organic phase was dried over anhydrous magnesium sulfate. Solvents were evaporated under reduced pressure, the residue (crude 3,5-bis(trifluoromethyl)phenyl monofluoromethyl sulfide) was dissolved in 60 mL glacial acetic acid, and 8.46 g of 30% hydrogen peroxide was added to the solution. The reaction mixture was heated to 80 °C and stirred overnight at this temperature. The resulting solution was poured onto the ice and precipitated white crystals of 3,5-bis(trifluoromethyl)phenyl monofluoromethyl sulfone were collected by suction filtration, washed with water and air dried. The yield of 3,5-bis(trifluoromethyl)phenyl monofluoromethyl sulfone was 3.7 g (64%). ^{1}H NMR (400 MHz, $CDCl_3$): 5.23 (d, J_{HF} = 47 Hz), 8.24 (s), 8.43 (s) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): −63.4 (s), −210.9 (t, J_{HF} = 47 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 91.8 (d, J_{CF} = 220 Hz), 122.3 (q, J_{CF} = 272 Hz), 128.7 (t, J_{CF} = 4 Hz), 129.6, 133.7 (q, J_{CF} = 34 Hz), 138.8 ppm.

3.3. Typical procedure for the monofluoroolefination of carbonyl compounds with 3,5-bis(trifluoromethyl)phenyl monofluoromethyl sulfone in the presence of KOH and TBAF

1.5 mmol of aldehyde or ketone and 1.5 mmol (1 equiv.) of 3,5-bis(trifluoromethyl)phenyl monofluoromethyl sulfone are placed in a 50 mL round bottom flask and 15 mL of DMSO was added. A solution of 9 equiv. of KOH in 10 mL DMSO is added dropwise to the reaction mixture over a period of 2 h. The reaction mixture was left at room temperature and monitored by ^{19}F NMR until completion (1–12 h). After completion of the reaction, the solution is poured into cold saturated solution of



Scheme 2. Mechanism of the reaction and plausible reaction intermediates.

ammonium chloride, extracted ethyl acetate (4 × 25 mL), and the organic layer dried over anhydrous sodium sulfate. The solvent was evaporated in a rotavap and the resulting crude product was purified by column chromatography (EtOAc/Hex = 1/10). 1 M solution of TBAF in THF can also be used for this procedure.

3.4. Typical procedure of monofluoroolefination of carbonyl compounds with 3,5-bis(trifluoromethyl)phenyl monofluoromethyl sulfone in the presence of CsF

9 equiv. of CsF under inert atmosphere was placed in a 50 mL round bottom flask and 20 mL of DMSO was introduced. Subsequently, the mixture of 1.5 mmol of aldehyde or ketone and 1.5 mmol of 3,5-bis(trifluoromethyl)phenylmonofluoromethyl sulfone was dissolved in 10 mL of DMSO, and were added simultaneously to the solution of CsF. The reaction mixture was stirred overnight, poured into the cold saturated solution of ammonium chloride, extracted with ethyl acetate (4 × 15 mL), and the organic layer was dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure and the resulting crude product was purified by column chromatography (EtOAc/Hex = 1/10).

3.5. Spectral data of products

*3.5.1. 1-(2-Fluorovinyl)benzene (**4a**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63(dd, J_{HF} = 45 Hz, J_{HH} = 5.2 Hz, 0.9H), 6.42 (dd, J_{HF} = 19 Hz, J_{HH} = 12 Hz, 1H), 6.67 (dd, J_{HF} = 83 Hz, J_{HH} = 5.2 Hz, 0.9H), 7,19 (dd, J_{HF} = 83 Hz, J_{HH} = 12 Hz, 1H), 7.25–7.38 (m, 5.7), 7.17 (d, J_{HH} = 9.8 Hz, 2H), 7.54 (d, J_{HH} = 9.2 Hz, 1.8H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −122.7 (dd, J_{HF} = 83 Hz, J_{HF} = 45 Hz), −130.5 (dd, J_{HF} = 83 Hz, J_{HF} = 19 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.47, 40.57, 110.69, 112.28, 112.74, 113.68 (d, J_{CF} = 16 Hz), 120.59 (d, J_{CF} = 12 Hz), 121.1, 127.9 (d, J_{CF} = 3 Hz), 129.93 (d, J_{CF} = 7 Hz), 146.15 (d, J_{CF} = 264 Hz), 148.13 (d, J_{CF} = 252 Hz), 149.77 (d, J_{CF} = 3 Hz), 150.05 (d, J_{CF} = 1 Hz) ppm.

*3.5.2. 1-(2-Fluorovinyl)-4-methoxybenzene (**4b**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 3.85 (s, 2.5), 5.6 (dd, J_{HF} = 46 Hz, J_{HH} = 5.2 Hz, 0.8H), 6.4 (dd, J_{HF} = 20 Hz, J_{HH} = 11.2 Hz, 1H), 6.64 (dd, J_{HF} = 84 Hz, J_{HH} = 5.2 Hz, 0.8H), 6.88–6.94 (m, 3.6H), 7.15 (dd, J_{HF} = 84 Hz, J_{HH} = 11.2 Hz, 1H), 7.22 (d, J_{HH} = 9.2 Hz, 2H), 7.51 (d, J_{HH} = 8.4 Hz, 1.6H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −125.8 (dd, J_{HF} = 84 Hz, J_{HF} = 46 Hz), −133.15 (dd, J_{HF} = 84 Hz, J_{HF} = 20 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.27, 55.31, 110.30, 113.37 (d, J_{CF} = 16 Hz), 113.98, 114.32 125.10 (d, J_{CF} = 11 Hz), 125.44 (d, J_{CF} = 2 Hz), 127.37 (d, J_{CF} = 3 Hz), 130.22 (d, J_{CF} = 7 Hz), 148.09 (d, J_{CF} = 266 Hz), 149.08 (d, J_{CF} = 256 Hz), 158.94 (d, J_{CF} = 3 Hz), 159.16 (d, J_{CF} = 1 Hz) ppm.

*3.5.3. 4-(2-Fluorovinyl)-N,N-dimethylbenzenamine (**4c**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94 (s, 6H), 3.00 (s, 5.4H), 5.54 (dd, J_{HF} = 46 Hz, J_{HH} = 5.2 Hz, 0.9H), 6.37 (dd, J_{HF} = 20 Hz, J_{HH} = 11.2 Hz, 1H), 6.59 (dd, J_{HF} = 84 Hz, J_{HH} = 5.2 Hz, 0.9H), 6.69–6.74 (m, 3.8H), 7.11 (dd, J_{HF} = 84 Hz, J_{HH} = 11.2 Hz, 1H), 7.17 (d, J_{HH} = 9.8 Hz, 2H), 7.46 (d, J_{HH} = 10 Hz, 1.8H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −127.7 (dd, J_{HF} = 84 Hz, J_{HF} = 46 Hz), −135.9 (dd, J_{HF} = 84 Hz, J_{HF} = 20 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.47, 40.57, 110.69, 112.28, 112.74, 113.68 (d, J_{CF} = 16 Hz), 120.59 (d, J_{CF} = 12 Hz), 121.1, 127.9 (d, J_{CF} = 3 Hz), 129.93 (d, J_{CF} = 7 Hz), 146.15 (d, J_{CF} = 264 Hz), 148.13 (d, J_{CF} = 252 Hz), 149.77 (d, J_{CF} = 3 Hz), 150.05 (d, J_{CF} = 1 Hz) ppm.

*3.5.4. 1-Chloro-4-(2-fluorovinyl)benzene (**4d**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58 (dd, J_{HF} = 44 Hz, J_{HH} = 5.4 Hz, 1H), 6.36 (dd, J_{HF} = 18.8 Hz, J_{HH} = 11.2 Hz, 1H), 6.66 (dd, J_{HF} = 82 Hz, J_{HH} = 5.4 Hz, 1H), 7.14 (dd, J_{HF} = 82 Hz, J_{HH} = 11.2 Hz, 1H), 7.17 (d, J_{HH} = 11.2 Hz, 2H), 7.26–7.33 (m, 4H), 7.44 (d, J_{HH} = 8.4 Hz, 2H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −121.9 (dd, J_{HF} = 82 Hz, J_{HF} = 44 Hz), −129 (dd, J_{HF} = 82 Hz, J_{HF} = 18.8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.90, 113.6 (d, J_{CF} = 17 Hz), 127.45 (d, J_{CF} = 3 Hz), 128.77 129.05, 130.16 (d, J_{CF} = 7 Hz), 131.08 (d, J_{CF} = 13 Hz), 131.24 (d, J_{CF} = 12 Hz), 133.25, 133.27, 148.68 (d, J_{CF} = 270 Hz), 150.5 (d, J_{CF} = 259 Hz) ppm.

*3.5.5. 1-Fluoro-4-(2-fluorovinyl)benzene (**4e**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.58 (dd, J_{HF} = 44 Hz, J_{HH} = 5.4 Hz, 0.9H), 6.36 (dd, J_{HF} = 19.2 Hz, J_{HH} = 11.6 Hz, 1H), 6.63 (dd, J_{HF} = 83 Hz, J_{HH} = 5.4 Hz, 0.9H), 6.98–7.05 (m, 4.8H), 7.19–7.26 (m, 4.8H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −114.2 (m), −114.9 (m), −124 (dd, J_{HF} = 83 Hz, J_{HF} = 44 Hz), −130.6 (dd, J_{HF} = 83 Hz,

J_{HF} = 19.2 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.88, 113.5 (d, J_{CF} = 17 Hz), 115.7, 116.0, 127.8 (d, J_{CF} = 3 Hz), 127.9 (d, J_{CF} = 3 Hz), 130.6 (d, J_{CF} = 7 Hz), 130.7 (d, J_{CF} = 7 Hz), 131.24 (d, J_{CF} = 12 Hz), 148.0 (d, J_{CF} = 267 Hz), 150.0 (d, J_{CF} = 258 Hz), 161.1, 163.53 ppm.

*3.5.6. 4-(2-Fluorovinyl)benzonitrile (**4f**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.66 (dd, J_{HF} = 43 Hz, J_{HH} = 5.4 Hz, 1H), 6.4 (dd, J_{HF} = 18.4 Hz, J_{HH} = 11.2 Hz, 1H), 6.75 (dd, J_{HF} = 82 Hz, J_{HH} = 5.4 Hz, 1H), 7.25 (dd, J_{HF} = 82 Hz, J_{HH} = 11.2 Hz, 1H), 7.32–7.35 (m, 2H), 7.57–763 (m, 6H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −117.2 (dd, J_{HF} = 82 Hz, J_{HF} = 44 Hz), −124.0 (dd, J_{HF} = 82 Hz, J_{HF} = 18.4 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.8, 110.9, 111.05, 113.1 (d, J_{CF} = 17 Hz), 118.8, 118.9, 126.7 (d, J_{CF} = 3 Hz), 128.7 (d, J_{CF} = 4 Hz), 132.4, 132.7, 137.2, 137.7 (d, J_{CF} = 13 Hz), 150.5 (d, J_{CF} = 275 Hz), 152.3 (d, J_{CF} = 264 Hz) ppm. HRMS: calculated: 147.0484, found: 147.0490.

*3.5.7. Methyl 4-(2-fluorovinyl)benzoate (**4g**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (s, 3H), 3.88 (s,), 5.64 (dd, J_{HF} = 44 Hz, J_{HH} = 5.4 Hz, 0.8H), 6.38 (dd, J_{HF} = 18.8 Hz, J_{HH} = 11.2 Hz, 1H), 6.68 (dd, J_{HF} = 82 Hz, J_{HH} = 5.4 Hz, 0.8H), 7.22 (dd, J_{HF} = 82 Hz, J_{HH} = 11.2 Hz, 1H), 7.13–7.28 (d, J_{HH} = 8.4 Hz, 2H), 7.53 (d, J_{HH} = 8.8 Hz, 1.6H), 7.93–798 (m, 4H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −118.8 (dd, J_{HF} = 82 Hz, J_{HF} = 44 Hz), −126.2 (dd, J_{HF} = 82 Hz, J_{HF} = 18.8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.2, 110.3, 113.5 (d, J_{CF} = 16.8 Hz), 126.1 (d, J_{CF} = 3 Hz), 128.8 (d, J_{CF} = 7 Hz), 129.8, 130.2, 137.2 (d, J_{CF} = 2 Hz), 137.5 (d, J_{CF} = 12 Hz), 149.8 (d, J_{CF} = 273 Hz), 151.6 (d, J_{CF} = 262 Hz), 166.8, 166.9 ppm. HRMS: calculated: 180.0587, found: 180.0589.

*3.5.8. 1-((E)-2-fluorovinyl)-2,4,5-trimethoxybenzene (**4h**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 3.81 (s, 3H), 3.86 (s, 3H), 6.4 (dd, J_{HF} = 22 Hz, J_{HH} = 11.2 Hz, 1H), 6.48 (s, 1H), 6.67 (s, 1H), 7.29 (dd, J_{HF} = 86 Hz, J_{HH} = 11.2 Hz, 1H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −128.4 (dd, J_{HF} = 86 Hz, J_{HF} = 22 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.3, 56.5, 56.8, 97.8, 110.2 (d, J_{CF} = 18 Hz), 112.0, 113.2 (d, J_{CF} = 11 Hz), 143.3, 149.4, 150.4 (d, J_{CF} = 231 Hz), 151.9.

*3.5.9. 1-((Z)-2-fluorovinyl)-2,4,5-trimethoxybenzene (**4h**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 3.82 (s, 3H), 3.87 (s, 3H), 5.95 (dd, J_{HF} = 47 Hz, J_{HH} = 5.4 Hz, 1H), 6.58 (dd, J_{HF} = 84 Hz, J_{HH} = 5.4 Hz, 1H), 7.23 (s, 1H), 7.36 (s, 1H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −126.8 (dd, J_{HF} = 84 Hz, J_{HF} = 47 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.2, 56.6, 56.9, 97.4, 110.1 (d, J_{CF} = 2.3 Hz), 113.6 (d, J_{CF} = 12 Hz), 143.1, 147.2 (d, J_{CF} = 266 Hz), 149.4, 151.1 ppm.

*3.5.10. 2-Fluoro-1,1-diphenylethene (**4i**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, J_{HF} = 82.5 Hz, 1H), 7.27–7.29 (m, 2H), 7.35–7.38 (m, 4H), 7.39–7.41(m, 4H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ –128.5 (d, J_{HF} = 82.5 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.35 (d, J_{CF} = 6 Hz), 127.89, 127.92, 128.34, 128.64, 128.79 (d, J_{CF} = 3 Hz), 129.88 (d, J_{CF} = 5 Hz), 137.08, 137.15, 145.90 (d, J_{CF} = 267 Hz) ppm. HRMS: calculated: 198.0845, found: 198.0852.

*3.5.11. 1-(2-Fluoro-1-phenylvinyl)-4-methyl-4-methylbenzene (**4j**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 2.45 (s, 2.55H), 7.00 (d, J_{HF} = 84 Hz, 0.85H), 7.02 (d, J_{HF} = 84 Hz, 1H), 7.25–7.27 (m, 3.65H), 7.31–7.36 (m, 4.5H), 7.38–7.42 (m, 4.5H), 743–7.45 (m, 4H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −128.8 (d, J_{HF} = 84 Hz), δ −129.25 (d, J_{HF} = 84 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.25, 21.36, 126.18 (t, J_{CF} = 5 Hz), 127.80, 127.84, 128.28, 128.57, 128.67 (d, J_{CF} = 3 Hz), 128.80 (d, J_{CF} = 3 Hz), 129.05, 129.34, 129.76 (d, J_{CF} = 4 Hz), 129.87 (d, J_{CF} = 4 Hz), 134.13, 134.21, 137.25, 137.33, 137.68, 137.73, 145.55 (d, J_{CF} = 266 Hz), 145.66 (d, J_{CF} = 266 Hz) ppm. HRMS: calculated: 196.0888, found: 196.0896.

*3.5.12. 1-(2-Fluoro-1-phenylvinyl)-4-methoxybenzene (**4k**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 2.7H), 3.85 (s, 3H), 6.9–6.95 (m, 3.8H), 6.94 (d, J_{HF} = 84 Hz, 1H), 6.96 (d, J_{HF} = 84 Hz, 0.9H), 7.19–7.22 (m), 7.26–7.30 (m, 1.8H), 7.33–7.4 (m, 11.5H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −129.6 (d, J_{HF} = 84 Hz), δ −129.9 (d, J_{HF} = 84 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.35, 55.30, 113.71, 114.03, 125.79 (d, J_{CF} = 5 Hz), 125.80 (d, J_{CF} = 5 Hz), 127.80, 127.85, 128.28, 128.57, 128.86 (d, J_{CF} = 3 Hz), 129.83 (d, J_{CF} = 5 Hz), 129.90 (d, J_{CF} = 3 Hz), 131.58 (d, J_{CF} = 5 Hz), 137.31, 137.39, 145.19 (d, J_{CF} = 266 Hz), 145.33 (d, J_{CF} = 265 Hz), 159.13, 159.48 ppm. HRMS: calculated: 228.0950, found: 228.0953.

*3.5.13. 4-(2-Fluoro-1-phenylvinyl)-N,N-dimethylbenzenamine (**4l**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.01 (s, 4.8H), 3.02 (s, 6H), 6.72–6.77(m, 3.6H), 6.91 (d, J_{HF} = 84 Hz, 1H), 6.98 (d, J_{HF} = 84 Hz, 0.8H) 7.14–7.18 (m, 1.6H), 7.3–7.35 (m, 4H), 7.36–7.45 (m, 6H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −130.8 (d, J_{HF} = 84 Hz), δ −131.9 (d, J_{HF} = 84 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.46, 40.55, 111.91, 112.38, 124.73, 124.80, 126.23 (d, J_{CF} = 5 Hz), 126.08 (d, J_{CF} = 5 Hz), 127.60, 127.67, 128.19, 128.44, 129.09 (d, J_{CF} = 3 Hz), 129.45 (d, J_{CF} = 3 Hz), 129.92 (d, J_{CF} = 4 Hz), 130.68 (d, J_{CF} = 3 Hz), 137.71, 137.80, 144.60 (d, J_{CF} = 264 Hz), 144.74 (d, J_{CF} = 265 Hz), 149.92, 150.26 ppm. HRMS: calculated: 241.1267, found: 241.1265.

*3.5.14. 4-(2-Fluoro-1-phenyl)benzonitrile (**4m-a**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, J_{HF} = 82 Hz, 1H), 7.35–7.42 (m, 4H), 7.63–7.65 (m, 5H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −127.8 (d, J_{HF} = 82 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.6, 118.8, 125.7 (d, J_{CF} = 7.6 Hz), 128.5, 128.6, 129.2 (d, J_{CF} = 3 Hz), 129.8 (d, J_{CF} = 4 Hz), 132.5, 133.9, 142.8 (d, J_{CF} = 8 Hz), 147.1 (d, J_{CF} = 270 Hz) ppm. HRMS: calculated: 223.0797, found: 223.0789.

*3.5.15. 4-(2-Fluoro-1-phenyl)benzonitrile (**4m–b**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.975 (d, J_{HF} = 82 Hz, 1H), 7.15–7.18 (m, 2H), 7.33–7.37 (m, 3H), 7.42–7.49 (m, 2H), 7.6–7.64 (m, 2H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −128.1 (d, J_{HF} = 82 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 111.5, 118.9, 125.1 (d, J_{CF} = 4 Hz), 128.5, 128.9 (d, J_{CF} = 3 Hz), 130.5 (d, J_{CF} = 4 Hz), 120.5, 132.2, 135.7 (d, J_{CF} = 8 Hz), 140.0, 147.2 (d, J_{CF} = 272 Hz) ppm.

*3.5.16. 1-Chloro-4-(2-fluoro-1-phenylvinyl)benzene (**4n**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (d, J_{HF} = 83 Hz, 1H), 6.97 (d, J_{HF} = 83 Hz, 0.8H), 7.17–7.20 (m, 2H), 7.21–7.26 (m, 2H), 7.28–7.42 (m, 12.2H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −127.4 (d, J_{HF} = 83 Hz), δ −127.5 (d, J_{HF} = 83 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.35 (d, J_{CF} = 5 Hz), 125.50 (d, J_{CF} = 7 Hz), 128.11, 128.15, 128.44, 128.56, 128.75, 128.79, 128.85, 129.78 (d, J_{CF} = 4 Hz), 130.03 (t, J_{CF} = 3 Hz), 131.16, 131.21, 135.57, 135.65, 136.54, 136.62, 145.95 (d, J_{CF} = 268 Hz), 146.16 (d, J_{CF} = 268 Hz) ppm.

*3.5.17. 1,1-Bis(4-chlorophenyl)-2-fluoroethene (**4o**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.9 (d, J_{HF} = 83 Hz, 1H), 7.14–7.16 (m, 2H), 7.24–7.27 (m, 2H), 7.31–7.35(m, 4H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −126.7 (d, J_{HF} = 83 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.56 (d, J_{CF} = 6 Hz), 128.72, 129.018, 130.04 (d, J_{CF} = 3 Hz), 131.12 (d, J_{CF} = 4 Hz), 134.00, 134.22, 135.08, 135.16, 146.25 (d, J_{CF} = 269 Hz) ppm.

*3.5.18. 2-Fluoro-1,1-dip-tolylethene (**4p**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 2.44 (s, 3H), 6.98 (d, J_{HF} = 84 Hz, 1H), 7.20–7.25 (m, 4H), 7.32–7.34 (m, 4H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −129.7 (d, J_{HF} = 84 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.26, 21.37, 126.02 (d, J_{CF} = 4 Hz), 128.69 (d, J_{CF} = 3 Hz), 129.02, 129.30, 129.75 (d, J_{CF} = 5 Hz), 134.30, 134.38, 137.60, 137.65, 145.33 (d, J_{CF} = 266 Hz) ppm. HRMS: calculated: 226.1158, found: 226.1160.

*3.5.19. 1-Fluoroundec-1-ene (**4q**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J_{HH} = 7.2 Hz, 4.35H), 1.26–1.36 (m, 20.3H), 1.86–1.9(m, 2H), 2.07–2.13 (m, 0.9H), 4.64–4.79 (m, 0.45H), 5.28–5.39 (m, 1H), 6.43(ddt, J_{HF} = 88 Hz, J_{HH} = 4 Hz, J_{HH} = 1.6 Hz 0.45H), 6.48(ddt, J_{HF} = 88 Hz, J_{HH} = 12 Hz, J_{HH} = 1.2 Hz 1H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −131.64 (dd, J_{HF} = 86.8 Hz, J_{HF} = 19 Hz), −132.02 (dd, J_{HF} = 86 Hz, J_{HF} = 43 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.7, 22.8, 25.0, 25.1, 25.2, 29.1, 29.2, 29.3, 29.5, 29.6, 29.7, 29.8, 32.0, 11.3 (d, J_{CF} = 5.3 Hz), 111.8 (d, J_{CF} = 8.4 Hz), 147.6 (d, J_{CF} = 254 Hz), 148.6 (d, J_{CF} = 252 Hz) ppm.

*3.5.20. 2-((E)-2-fluorovinyl)pyridine (**4r**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36(dd, J_{HF} = 17.6 Hz, J_{HH} = 11.2 Hz, 1H), 7.06–7.1 (m, 2H), 7.53–7.58 (m, 1H), 7.58 (dd, J_{HF} = 83 Hz, J_{HH} = 11.2 Hz, 1H), 8.43–8.45 (m, 1H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −127.92 (dd, J_{HF} = 83 Hz, J_{HF} = 17.6 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.9 (d, J_{CF} = 16 Hz), 121.8 (d, J_{CF} = 5 Hz), 122.3 (d, J_{CF} = 3 Hz), 136.8, 149.5, 152.7 (d, J_{CF} = 4 Hz), 154.4 (d, J_{CF} = 264 Hz) ppm.

*3.5.21. 2-((Z)-2-fluorovinyl)pyridine (**4r**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (dd, J_{HF} = 44 Hz, J_{HH} = 5.4 Hz, 1H), 6.75 (dd, J_{HF} = 82 Hz, J_{HH} = 5.4 Hz, 1H), 7.07–7.1(m, 1H), 7.59–7.63 (m, 1H), 7.7 (d, J_{HH} = 8 Hz, 1H), 8.49–8.51 (m, 1H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −118.31 (dd, J_{HF} = 82 Hz, J_{HF} = 44 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.3 (d, J_{CF} = 2 Hz), 122.1 (d, J_{CF} = 2 Hz), 124.5 (d, J_{CF} = 2 Hz), 136.5, 149.2, 150.6 (d, J_{CF} = 262 Hz), 152.2 (d, J_{CF} = 2 Hz) ppm.

*3.5.22. 2-Bromo-5-((E)-2-fluorovinyl)thiophene (**4s**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.44 (dd, J_{HF} = 17.2 Hz, J_{HH} = 11.6 Hz, 1H), 6.79 (dd, J_{HF} = 88 Hz, J_{HH} = 4 Hz, 1H), 6.96 (d, J_{HH} = 11.4 Hz, 1H), 7.16 (d, J_{HH} = 11.4 Hz, 1H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −128.3 (dd, J_{HF} = 88 Hz, J_{HF} = 17.2 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 107.84 (d, J_{CF} = 20.6 Hz), 110.5 (d, J_{CF} = 4 Hz), 126.3 (d, J_{CF} = 6 Hz), 130.3, 136.6 (d, J_{CF} = 12.2 Hz), 149.9 (d, J_{CF} = 262 Hz) ppm.

*3.5.23. 2-Bromo-5-((Z)-2-fluorovinyl)thiophene (**4s**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (dd, J_{HF} = 44 Hz, J_{HH} = 4.8 Hz, 1H), 6.64 (dd, J_{HF} = 82 Hz, J_{HH} = 5.2 Hz, 1H), 6.8 (d, J_{HH} = 4 Hz, 1H), 7.16 (d, J_{HH} = 6 Hz, 1H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −120.4 (dd, J_{HF} = 82 Hz, J_{HF} = 44 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 105.2 (d, J_{CF} = 3 Hz), 113.4 (d, J_{CF} = 10 Hz), 127.1 (d, J_{CF} = 3 Hz), 129.5, 136.2 (d, J_{CF} = 2 Hz), 147.2 (d, J_{CF} = 268 Hz) ppm.

*3.5.24. (Z)-4-fluoro-1,1-diphenylbuta-1,3-diene (**4t**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.51 (ddd, J_{HF} = 41.8 Hz, J_{HH} = 4.8 Hz, J_{HH} = 11.2 Hz 1H), 6.45 (ddd, J_{HF} = 88 Hz, J_{HH} = 4.8 Hz, J_{HH} = 1.2 Hz 1H), 6.94 (d, J_{HH} = 11.2 Hz, 1H), 7.19–7.28(m, 7H), 7.32–7.39(m, 3H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −125.6 (dd, J_{HF} = 88.6 Hz, J_{HF} = 41.8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 109.6, 117.5 (d, J_{CF} = 5 Hz), 127.7, 127.8, 128.3, 128.4, 130.4, 139.4, 141.9, 143.2 (d, J_{CF} = 5 Hz), 149.3 (d, J_{CF} = 268 Hz) ppm.

*3.5.25. (E)-4-fluoro-1,1-diphenylbuta-1,3-diene (**4t**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.11 (ddd, J_{HF} = 17.6 Hz, J_{HH} = 11.6 Hz, J_{HH} = 11.2 Hz 1H), 6.49 (d, J_{HH} = 11.6 Hz, 1H), 6.95 (dd, J_{HF} = 83.6 Hz, J_{HH} = 10.8 Hz, 1H), 7.17–7.28 (m, 7H), 7.32–7.40 (m, 3H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ −124.51 (dd, J_{HF} = 83.6 Hz, J_{HF} = 17.6 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.7 (d, J_{CF} = 17 Hz), 119.7 (d, J_{CF} = 11 Hz), 127.5, 127.6, 127.7, 128.3, 128.5, 130.32, 139.3, 142.1, 143.2 (d, J_{CF} = 13 Hz), 153.3 (d, J_{CF} = 262 Hz) ppm.

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References

[1] (a) M. Schlosser, M. Zimmermann, Synthesis (1969) 75;
(b) D.G. Cox, N. Gurusamy, D.J. Burton, J. Am. Chem. Soc. 107 (1985) 2811;
(c) K. Kataoka, S. Tsuboi, Synthesis (1999) 452.
[2] S.I. Hayashi, T. Nakai, N. Ishikawa, D.J. Burton, D.J. Naae, H.S. Kesling, Chem. Lett. (1979) 983.
[3] (a) V. Reutrakul, V. Rukachaisirikul, Tetrahedron Lett. 24 (1983) 725;
(b) M. Inbasekaran, N.P. Peet, J.R. McCarthy, M.E. LeTourneau, J. Chem. Soc. Chem. Commun. (1985) 678;
(c) M.L. Boys, E.W. Collington, H. Finch, S. Swanson, J.F. Whitehead, Tetrahedron Lett. 29 (1988) 3365;
(d) J.R. McCarthy, D.P. Matthews, M.L. Edwards, D.M. Stemerick, E.T. Jarvi, Tetrahedron Lett. 31 (1990) 5449.
[4] (a) S.H. Lee, J. Schwartz, J. Am. Chem. Soc. 108 (1986) 2445;
(b) N.A. Petasis, A.K. Yudin, I.A. Zavialov, G.K.S. Prakash, G.A. Olah, SYNLETT (1997) 606;
(c) B. Greedy, V. Gouverneur, J. Chem. Soc. Chem. Commun. (2001) 233.
[5] J.H. van Steenis, A. van der Gen, Eur. J. Org. Chem. (2001) 897.
[6] S. Couve-Bonnaire, D. Chachard, X. Pannecoucke, Org. Biomol. Chem. 5 (2007) 1151, and references therein..
[7] Y. Zhao, W. Huang, L. Zhu, J. Hu, Org. Lett. 12 (7) (2010) 1444.
[8] A.K. Ghosh, B. Zajc, J. Org. Chem. 74 (22) (2009) 8531.
[9] W. Zhang, W. Huang, J. Hu, Angew. Chem. Int. Ed. 48 (2009) 1.
[10] D.A. Alonso, M. Fuensanta, E. Gomez-Bengoa, C. Najera, Adv. Synth. Catal. 350 (2008) 1823.
[11] Preliminary accounts of this work R. Kumar, B. Zajc, ORGN-673, 236th ACS National Meeting, Philadelphia, PA, United States, August 17–21, 2008.
[12] B. Zajc, R. Kumar, Synthesis (2010) 1822.
[13] Preliminary accounts of this work G.K.S. Prakash, A. Shakhmin, M. Zibinsky, S. Chacko, I. Ledneczki, G.A. Olah, ORGN-549, 237th ACS National Meeting, Salt Lake City, UT, United States, March 22–26, 2009.
[14] D.A. Alonso, M. Fuensanta, C. Njera, M. Varea, J. Org. Chem. 70 (2005) 6404.
[15] A. Wayne, K.S. Vinson, P. Bojana Spahic, P.R. Ortiz de Montellano, J. Org. Chem. 48 (24) (1983).
[16] F. Bergmann, A. Kalmus, E. Breuer, J. Am. Chem. Soc. 80 (1958) 4540.