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Electrolytic partial fluorination of organic compounds 84 Anodic mono- and difluorination of benzylphosphonate derivatives

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Abstract

Anodic fluorination of benzylphosphonate derivatives was carried out under various electrolytic conditions to provide the corresponding α-mono- and/or α,α-difluoro-products in moderate to good yields. It was found that the selectivity of fluorinated products was depending on the molecular structures of the starting substrates and the electrolytic conditions.

Keywords: Benzylphosphonate derivative; Electrochemical fluorination; Partial fluorination; Fluorinated benzylphosphonate; PTP inhibitor

1. Introduction

Recently, many studies have indicated that the presence of the fluorine atoms at the α-position of phosphorus in phosphonate increases both the structural and electronic similarities to the parent phosphate groups [1]. Moreover, several analogues of phosphates encompassing the difluoromethylene-phosphonate moiety have been shown to exhibit better bioactivity than the corresponding nonfluorinated phosphonates [2]. It has also been suggested that the α-monofluorophosphonates gave superior results to α,α-difluorination in phosphonate mimics of biological phosphates [3]. Therefore, in recent years, many efforts have been devoted to construct phosphonate mimics with α-fluoro- and α,α-difluoromethylene groups as an isoelectronic and isosteric replacement for oxygen in phosphate groups. These mimics are known to be useful as protein tyrosine phosphatase (PTP) inhibitors [4].

N,*N*-diethylaminosulfurtrifluoride (DAST), selectfluor, and *N*-fluoro-benzene-sulfonimide have been mainly used for the preparation of α-mono- and α,α-difluorophosphonates [3,5]. However, their serious drawback is that it is expensive and sometimes explosive. On the other hand, we have shown that selective electrochemical fluorination is a highly efficient tool for the synthesis of various fluorinated organic compounds [6] with the advantage of mild conditions and avoidance of hazardous and explosive reagents.

Laurent et al. [7] found that anodic benzylic fluorination proceeded selectively in Et_3N-3HF/MeCN when the benzylic position is substituted by electron-withdrawing groups (EWG). α-Monofluorinated and α,α-difluorinated products were obtained respectively depending on electricity passed as shown in Scheme 1. We also studied systematically anodic benylic fluorination of various aromatic compounds [8]. Moreover, quite recently we have successfully prepared cyclic α-monofluorophosphonate esters by using anodic fluorination and ring-closing olefin methathesis as shown in Scheme 2 [9].

With these facts in mind, this electrochemical approach was applied to the synthesis of α-fluoro- and α,α-difluorinated benzylic compounds substituted by phosphonates as an EWG group in this work.

2. Results and discussion

2.1. Oxidation potentials of benzylphosphonates

The oxidation potentials (anodic peak potentials) of benzylphosphonates **1–5** were determined by cyclic voltammetry using a platinum disc electrode in 0.1 M Bu_4NFBF_4/MeCN and a SSCE reference electrode. These phosphonates exhibited irreversible oxidation waves. The first oxidation peak potentials (E_p^{ox}) are shown in Table 1.

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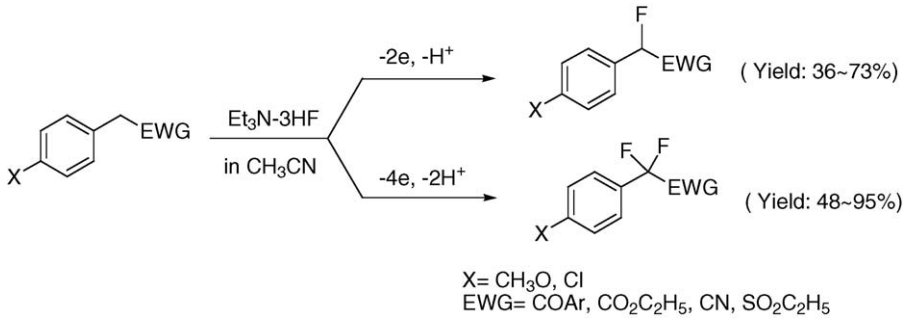
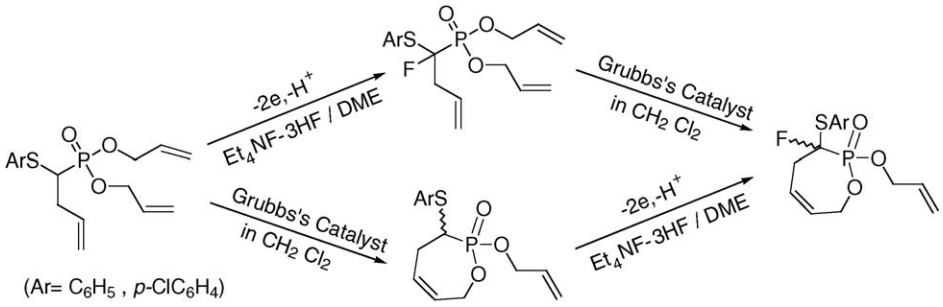


Scheme 1.



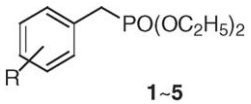
Scheme 2.

Unsubstituted benzylphosphonate **4** exhibited the highest oxidation potential. An electron-donating methoxy group greatly decreased the oxidation potentials. Interestingly, *m*-methoxybenzylphosphonate **3** exhibited a lower oxidation potential compared with *o*- and *p*-methoxy derivatives **1** and **2**. This trend cannot be explained by substituent effects of a methoxy group. Initial electron-transfer seems to take place at the methoxy group instead of benzene ring, similarly to the case of *p*-methoxy isopropylbenzene [8]. Moreover, a *p*-iodo substituent also decreased the oxidation potentials appreciably.

2.2. Anodic fluorination of benzylphosphonate derivatives

Anodic fluorination of *p*-methoxybenzylphosphonate **1** as a model compound was carried out at ambient temperature in several solvents containing various fluorides as a supporting electrolyte and fluorine source, using an undivided cell equipped with platinum plate electrodes under constant current conditions (2.5 mA/cm^2). The results are summarized in Table 2.

Table 1
Oxidation potentials (peak potentials, E_p^{ox}) of benzylphosphonates[a]



1~5

Substrate	R	E_p^{ox} V vs. SSCE[b]
1	*p*-OCH_3	1.69
2	*o*-OCH_3	1.57
3	*m*-OCH_3	1.49
4	H	2.39
5	*p*-I	2.10

[a] Pt disk electrodes (φ = 1 mm), 0.1 M Bu_4NBF_4/MeCN, and sweep rate 100 mV/s.
[b] SSCE: 1 M NaCl calomel electrode.

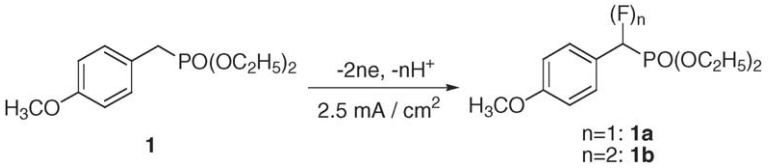
As shown in Table 2, the anodic fluorination greatly depended on both the electrolytic solvents and supporting fluoride salts. The desired α-mono- and α,α-difluorinated products **1a** and **1b** were not obtained in Et_3N-3HF/MeCN (Run 1). This is in sharp contrast to the successful α-fluorination of α-(*p*-methoxybenzyl)acetate under the same conditions as shown in Scheme 1 [7]. When Et_4NF-3HF/MeCN was employed, the corresponding fluorinated products **1a** and **1b** were obtained in low yield (Run 2). On the other hand, the use of Et_4NF-4HF/CH_2Cl_2 provided the desired fluorinated products as a mixture in 64% yield (Run 4). Furthermore, Et_4NF-3HF/DME was found to be the most suitable for the fluorination and expected products were obtained in excellent total yield 91% (Run 5). As reported previously, DME seems to enhance the nucleophilicity of a fluoride ion, which increases the fluorination yield [10].

Since **1a** and **1b** were always formed, the correlation between the yields of fluorinated products **1a** and **1b,** and charge passed was investigated. The correlation is illustrated in Fig. 1.

The yield of **1a** increased to 43% with an increase of electricity up to 3 F/mol and then the yield decreased. On the other hand, α,α-difluorinated product **1b** was formed even at the early stage of the electrolysis and the yield of **1b** increased with an increase of electricity, and finally **1b** was obtained in 78% yield exclusively at 9 F/mol.

Then, this electrolytic system was extended to the fluorination of *o*- and *m*-methoxybenzylphosphonates **2** and **3** (Table 3). The electrolysis of **2** at 4 F/mol provided the

Table 2
Anodic fluorination of diethyl *p*-methoxybenzylphosphonate[a]



Run	Solvent	Supporting electrolyte (1 M)	Electricity (F/mol)	Ratio (**1a**:**1b**)	Total yield[b] (%)
1	CH_3CN	Et_3N-3HF	2	–	0
2	CH_3CN	Et_4NF-3HF	3	4:1	16
3	CH_2CI_2	Et_4NF-3HF	3	2:1	47
4	CH_2CI_2	Et_4NF-4HF	3	1:1	64
5	DME	Et_4NF-3HF	3	1:1	91 (83)[c]
6	DME	Et_4NF-4HF	4	3:1	60
7	DME	Et_4NF-5HF	3	2:1	21

[a] All reactions were performed at platinum plate electrodes under constant current conditions using an undivided cell.
[b] Determined by ^{19}F NMR.
[c] Isolated yield (**1a**: 43% and **1b**: 40%).

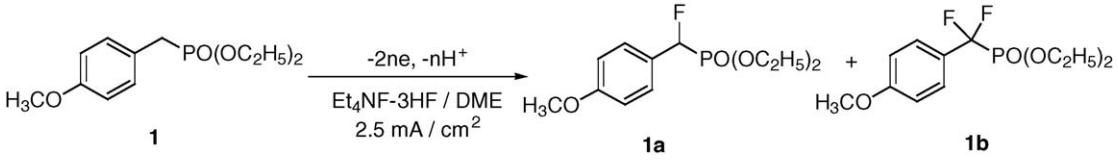
corresponding α-monofluorinated product **2a** exclusively although the yield was unsatisfactory (Run 3). In this case, starting **2** remained considerably. Further electrolysis of **2** resulted in the formation of a mixture of α-mono, and α,α-difluoro-products **2a** and **2b** (Run 4). Anodic fluorination of *m*-methoxybenylphosphonate **3** also provided mainly monofluoroproduct **3a** and the total yield of **3a** and **3b** was moderate (Run 5).

As shown in Table 3, the reactivity toward the fluorination of starting phosphonates decreases in the order of *p*- > *m*- > *o*-methoxy derivatives, and the highest yield was obtained in case of *p*-methoxybenzylphosphonate **1**.

Next, the anodic fluorination of diethyl benzylphosphonate **4** was attempted. It was found that fluorination proceeded selectively and α-monofluorinated benzylphosphonate **4a** was obtained exlusively in moderate yield (Run 6). In this case, a large excess amount of electricity was required because of the rather high oxidation potential of **4** (2.39 V versus SSCE).

Anodic fluorination of diethyl *p*-iodobenzylphosphonate (**5**) was also successfully carried out and the corresponding monofluoro product **5a** was obtained in 50% isolated yield (Run 7). Previously, Yoneda et al. and we found that anodic fluorination of *p*-methyl-, *p*-nitro-, *p*-methoxyiodobenzenes afforded the corresponding iodobenzene difluoride derivatives in moderate to good yields, as shown in Scheme 3 [11,12].

Thus, it was found that the phosphonate ester group greatly change the selectivity of fluorination products. The selective formation of **5a** and **5b** can be accounted in terms with



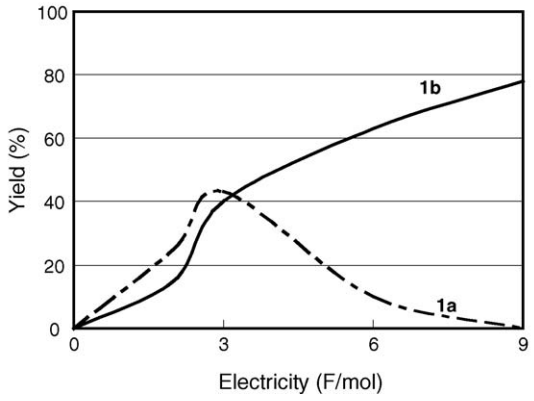
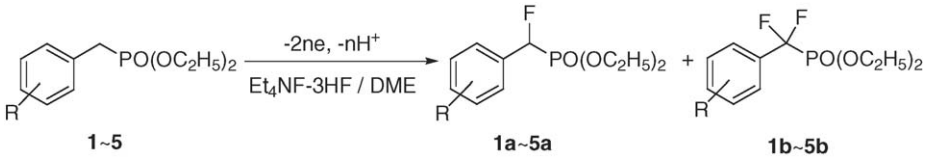


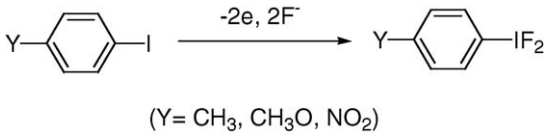
Fig. 1. Correlation between the yields of products **1a** and **1b**, and electricity.

Table 3
Anodic fluorination of benzylphosphonate derivatives[a]



Run	Substrate		Electricity (F/mol)	Ratio (**a**:**b**)	Total yield[b] (%)
	No.	R			
1	**1**	*p*-OCH_3	3	1:1	91 (43)[c]
2	**1**	*p*-OCH_3	9	0:1	78 (70)
3	**2**	*o*-OCH_3	4	1:0	35 (30)
4	**2**	*o*-OCH_3	6	6:1	45
5	**3**	*m*-OCH_3	7	4:1	62 (45)[c]
6	**4**	H	28	1:0	57 (55)
7	**5**	*p*-I	7	3:1	74 (50)[c]

[a] Constant current (2.5 mA/cm^2) electrolysis.
[b] Determined by ^{19}F NMR. Values in parentheses are isolated yields.
[c] Isolated yield of monofluorinated product.



Scheme 3.

facilitation of deprotonation of the radical cation intermediate **A** by the electron-withdrawing phosphonate ester group as shown in Scheme 4.

The products **5a** and **5b** are useful since they are easily converted into phosphonylated tyrosin moieties as shown in Scheme 5 [13].

3. Experimental

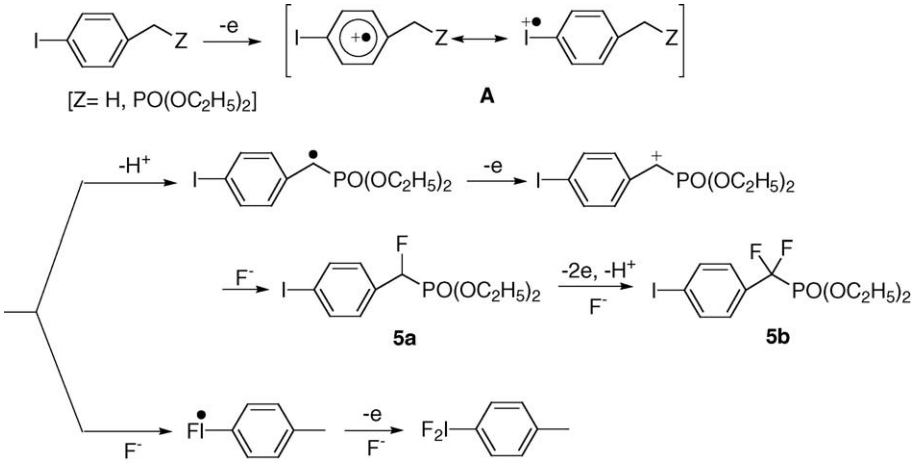
3.1. General

^1H NMR (270 MHz), ^{13}C NMR (68 MHz) and ^{19}F NMR (254 MHz) spectra were determined using $CDCl_3$ as a solvent. The chemical shift for ^{19}F NMR is given in δ (ppm) upfield from the peak for external trifluoroacetic acid. The product yields were determined by ^{19}F NMR using monofluorobenzene as an internal standard material. Mass spectra were obtained with SHIMADZU GC-MS QP5050A spectrometer. Cyclic voltammetry was performed using a BAS ALS/HCH Instruments Model 600A, and preparative electrolysis experiments were carried out using a METRONIX constant current power supply 5944 and Coulomb/Amperehour meter HF-201.

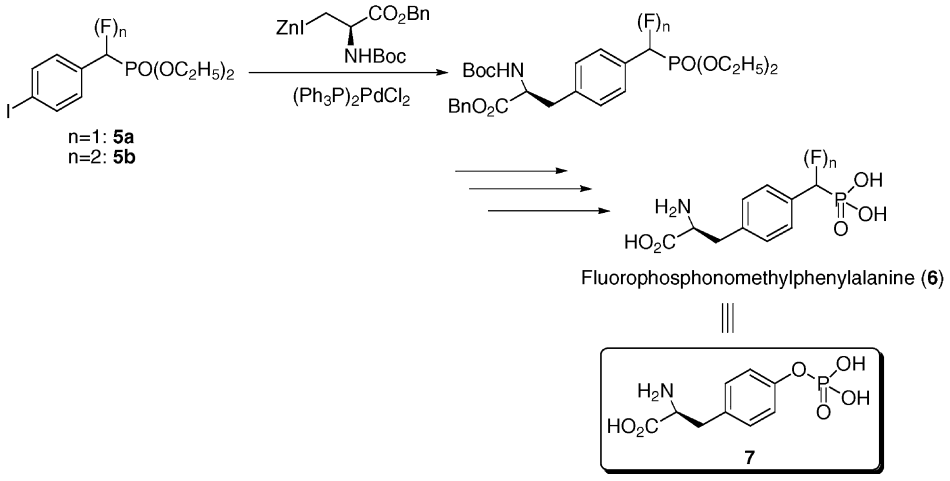
3.2. Materials

Fluoride salts were obtained from Morita Chemical Industries Co. Ltd. (Japan).

Diethyl benzylphosphonate (**4**) was purchased from Aldrich Chemical Co. Diethyl 4-methoxybenzylphosphonate (**1**) [14], diethyl 2-methoxybenzylphosphonate (**2**) [15], diethyl 3-methoxybenzylphosphonate (**3**) [16], and diethyl 4-iodobenzylphosphonate (**5**) [17] were prepared according to the literature [18].



Scheme 4.



Scheme 5.

3.3. Electrolytic procedures for fluorination

A typical procedure is as follows. Anodic oxidation of **1** (0.5 mmol) was carried out in an undivided cell equipped with platinum plate electrodes (2 cm × 2 cm) in 5 ml of 1 M Et_4NF-3HF/dimethoxyethane (DME) at room temperature. Constant current (2.5 mA/cm^2) was passed until the starting material **1** was almost consumed (checked by TLC). After electrolysis, the electrolytic solution was passed through a short column filled with silica gel using ethyl acetate as an eluent to remove fluoride salts. The eluent was evaporated under reduced pressure and the residue was further purified by column chromatography on silica gel using ethyl acetate to give pure fluorinated products. The products were identified by spectroscopic data.

Diethyl α-fluoro-4-methoxybenzylphosphonate (**1a**) [14], diethyl α,α-difluoro-4-methoxybenzylphosphonate (**1b**) [19], diethyl α,α-difluoro-2-methoxybenzylphosphonate (**2b**) [19], diethyl α-fluorobenzylphosphonate (**4a**) [14], and diethyl α,α-difluoro-4-iodobenzylphosphonate (**5b**) [20] were identified by spectroscopic data in the references.

*Diethyl α fluoro-2-methoxybenzylphosphonate (**2a**).* ^{1}H NMR δ 1.24 (t, CH_3CH_2O, $^3J_{HH}$ = 7.02 Hz, 3H), 1.32 (t, CH_3CH_2O, $^3J_{HH}$ = 7.02 Hz, 3H), 3.85 (s, OCH_3, 3H,), 3.88–4.21 (m, CH_3CH_2O, 4H), 6.23 (dd, CHF, $^2J_{PH}$ = 7.29, 44.01 Hz, 1H), 6.88–7.62 (m, C_6H_4); ^{13}C NMR 16.44 (dd, CH_3CH_2O, $^5J_{FC}$ = 8.90, 6.10 Hz,), 55.63 (s, OCH_3), 63.29 (dd, CH_3CH_2O, $^2J_{PC}$ = 6.70 Hz, $^4J_{FC}$ = 14.50 Hz), 83.31 (dd, $^1J_{PC}$ = 174.04 Hz, $^1J_{FC}$ = 179.05 Hz), 110.46 (d, C_6H_4, $^4J_{FC}$ = 1.08 Hz), 119.63 (s, C_6H_4), 120.66 (d, C_6H_4, $^5J_{FC}$ = 1.15 Hz), 128.47 (d, C_6H_4, $^2J_{PC}$ = 4.47 Hz), 128.59 (d, C_6H_4, $^4J_{FC}$ = 3.93 Hz), 130.43 (d, C_6H_4, $^3J_{FC}$ = 4.51 Hz); ^{19}F NMR δ-124.01 (dd, $^2J_{PF}$ = 46.23 Hz, $^2J_{FH}$ = 44.20 Hz); MS: 276 (9), 139 (59), 121 (14), 109 (23) and 91(100); HRMS *m/z* Calcd. for $C_{12}H_{18}FO_4P$ 276.0927 and found: 276.0934.

*Diethyl α-fluoro-3-methoxybenzylphosphonate (**3a**).* ^{1}H NMR δ 1.23 (t, $^3J_{HH}$ = 7.02 Hz, 3H, CH_3CH_2O), 1.32 (t, $^3J_{HH}$ = 7.02 Hz, 3H, CH_3CH_2O), 3.85 (s, OCH_3), 4.08–4.19 (m, 4H, CH_3CH_2O), 6.23 (dd, $^2J_{PH}$ = 7.29 Hz, $^2J_{FH}$ = 44.01 Hz, 1H, CHF), 6.87–7.62 (m, 4H, C_6H_4); ^{13}C NMR 16.49 (dd, $^5J_{FC}$ = 8.88 Hz, $^3J_{PC}$ = 6.01 Hz, CH_3CH_2O), 55.68 (s, OCH_3), 63.35 (dd, $^4J_{FC}$ = 14.50 Hz, $^2J_{PC}$ = 7.25 Hz, CH_3CH_2O), 83.37 (dd, $^1J_{PC}$ = 173.50 Hz, $^1J_{FC}$ = 177.9 Hz, CHF), 110.52 (d, $^5J_{FC}$ = 1.71 Hz, C_6H_4), 115.25 (d, $^2J_{FC}$ = 20.67 Hz, C_6H_4), 120.72 (s, C_6H_4), 123.90 (d, $^3J_{FC}$ = 3.32 Hz, C_6H_4), 128.58 (d, $^4J_{FC}$ = 6.60 Hz, C_6H_4), 129.86 (d, $^3J_{FC}$ = 7.79 Hz, C_6H_4); ^{19}F NMR δ 125.59 (dd, $^2J_{PF}$ = 44.20 Hz, $^2J_{FH}$ = 90.69 Hz); MS: 276 (63), 245 (30), 139 (100), 121 (26), 109 (60) and 91 (75); HRMS *m/z* Calcd. for $C_{12}H_{18}FO_4P$ 276.0927 and found: 276.0933.

*Diethyl α,α-difluoro-3-methoxybenzylphosphonate (**3b**).* ^{1}H NMR δ 1.32 (t, $^3J_{HH}$ = 7.02 Hz, 6H, CH_3CH_2O), 3.87 (s, OCH_3), 4.15–4.29 (m, 4H, CH_3CH_2O), 6.96–7.53 (m, C_6H_4); ^{13}C NMR 16.44 (d, $^3J_{PC}$ = 5.56 Hz, CH_3CH_2O), 55.93 (s, OCH_3), 64.52 (d, $^2J_{PC}$ = 6.71 Hz, CH_3CH_2O), 112.13 (s, CF_2), 115.23 (d, $^2J_{FC}$ = 20.67 Hz, C_6H_4), 120.28 (s), 123.87 (d, $^3J_{FC}$ = 3.30 Hz), 128.06 (s), 129.83 (d, $^4J_{FC}$ = 7.25 Hz), 152.82 (d, $^3J_{FC}$ = 16.5 Hz); ^{19}F NMR δ-27.99 (d, $^2J_{PF}$ = 116.61 Hz); MS: 294 (69), 263 (1), 157 (88), 127 (14), 109 (100); HRMS *m/z* Calcd. for $C_{12}H_{17}F_2O_4P$ 294.0830 and found: 294.0822.

*Diethyl α-fluoro-4-iodobenzylphosphonate (**5a**).* Yellow oil; ^{1}H NMR ($CDCl_3$) δ 7.74 (d, J = 8.08 Hz, 2H), 7.21 (d, J = 8.08 Hz, 2H), 5.63 (dd, J_{FH} = 44.82 Hz, J_{PH} = 8.10 Hz, 1H, CHF), 4.16–4.05 (m, 4H, 2 × $MeCH_2O$), 1.30 (t, J = 6.48 Hz, 3H, CH_3CH_2O), 1.27 (t, J = 6.48 Hz, 3H, CH_3CH_2O); ^{13}C NMR ($CDCl_3$) 137.5 (t, J_{PC} = J_{FC} = 2.24 Hz), 132.6 (d, J_{FC} = 18.90 Hz), 128.2 (t, J_{PC} = J_{FC} = 6.71 Hz), 95.0, 88.9 (dd, J_{PC} = 169.0 Hz, J_{FC} = 184.1 Hz, CHF), 63.7 (dd, J_{PC} = 6.64 Hz, J_{FC} = 27.90 Hz, CH_3CH_2O), 16.5 (d, J_{PC} = 5.56 Hz, CH_3CH_2O); ^{19}F NMR ($CDCl_3$) δ-125.39 (dd, J_{PF} = 83.15 Hz, J_{HF} = 44.45 Hz); MS, *m/z* (%), 372 (M^+, 20), 245 (33), 235 (59), 109 (100) and 81 (65); HRMS, *m/z* Calcd. for $C_{11}H_{15}FIO_3P$ 371.9788 and found: 371.9772.

4. Conclusions

Anodic fluorination reaction of *o-*, *m-* and *p*-methoxybenzylphosphonates resulted in the formation of α-fluoro- and/or α,α-difluoro-methoxybenzylphosphonates in moderate to good

yields. The increase of electricity to 9 F/mol in the anodic fluorination of *p*-methoxybenzylphophonate resulted in the formation of α,α-difluoro-*p*-methoxybenzylphosphonate exclusively in good yield. It was found that anodic fluorination strongly depended on the position of a methoxy substituent on the benzene ring and anodic fluorination of *p*-MeO-substituted benzylphosphonate gave the best yield. The anodic fluorination of diethyl benzylphosphnate and *p*-iodobenzylphosphonate also provided the desired α-fluoroproduts in moderate yields. The fluoroproducts derived from *p*-iodobenzylphosphonate are useful since they are easily converted into phosphonylated tyrosin moieties.

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