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Fluoro-lactonization of 4-alkenoic acid derivatives with *N*-fluoropentachloropyridinium triflate

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Abstract

Fluoro-lactonization of 4-alkenoic acid derivatives containing an aryl substituent at the 4- or 5-position with *N*-fluoropentachloropyridinium triflate proceeds smoothly in a regioselective manner with little or no diastereoselectivity. These reactions possibly involve aryl-stabilized α-fluorocarbocation intermediates formed via single electron transfer from the pyridinium salt to the olefin as the first step. © 1997 Elsevier Science S.A. All rights reserved.

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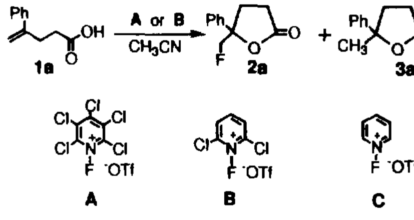
1. Introduction

The halo-lactonization reaction, in particular iodo- or bromo-lactonization, is one of the most useful reactions which can introduce functional groups to alkenes [1,2]. The substrate structure, nature of the substituent in the substrate, electrophilic halogenating reagent employed and reaction conditions, such as kinetic or thermodynamic control, strongly influence both the regiochemistry and diastereoselectivity. The high stereospecificity in these reactions is one of the characteristic features: possibly, the reaction involves the formation of a bridged halonium intermediate, followed by the intramolecular attack of carboxylate by trans-addition. Contrary to the well-documented iodo- or bromo-lactonization, there have been no attempts to study the fluoro-lactonization reaction, in spite of the importance of organic fluorine compounds in the fields of medicinal and materials science [3]; this is probably due to the lack of availability of suitable electrophilic fluorinating reagents as well as procedures for their safe and convenient use. Several electrophilic fluorinating reagents having an *N*–F structure have been developed and some of these are now commercially available [4–10]. In this paper, we report the fluoro-lactonization reaction of 4-alkenoic acids using *N*-fluoropyridinium triflates as electrophilic fluorinating reagents.

2. Results and discussion

Initially, fluoro-lactonization of 4-phenyl-4-pentenoic acid (**1a**) was conducted using a series of *N*-fluoropyridinium triflates (**A**–**C**) [4,5] (Scheme 1). The results are summarized in Table 1. As reported in Ref. [4,5], the reactivity of the *N*-fluoropyridinium salt increases as the electron density of the positive nitrogen site decreases. With the most electron-poor pentachloro derivative **A**, the reaction proceeds at room temperature in CH_3CN to give fluorolactone **2a** (runs 1–3). The salts with higher electron density show lower efficacy; with the 2,6-dichloro derivative **B**, **2a** is formed in good yield at 80 °C (run 4), but the pyridinium salt **C** does not lead to the fluoro-lactonization of **1a**. It should be noted that the addition of a base is needed in this reaction; in the absence of a base, competitive formation of the proton-mediated lactonization product **3a** occurs (runs 2 and 3 vs. run 1). With these results in hand, we examined further fluoro-lactonization reactions using the pentachloro derivative **A** as fluorinating reagent and $NaHCO_3$ as a base.



Scheme 1.

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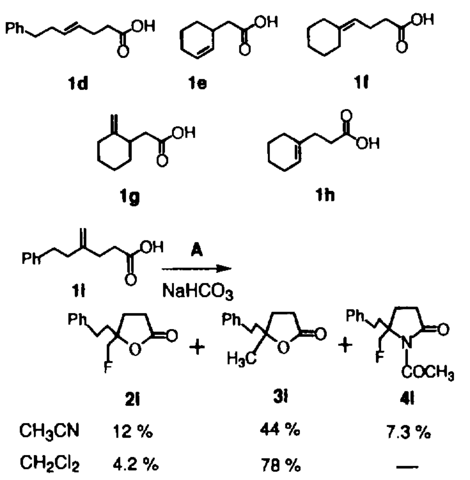
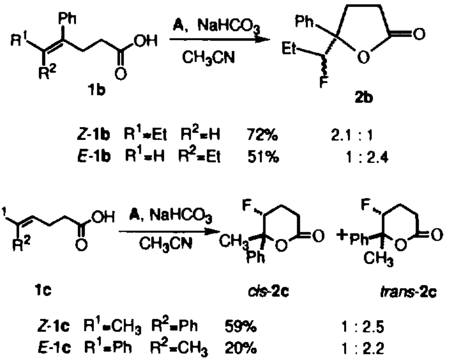
Table 1
Reaction of **1a** with *N*-F-Py salt[a]

Run	Reagent	Additive	Conditions	**2a** (%)[b]	**3a** (%)[b]
1	**A**		Room temperature (rt), 1 h	45	45
2	**A**	$NaHCO_3$	rt, 1 h	69	
3	**A**	2,6-Lutidine	rt, 1 h	55	8
4	**B**	$NaHCO_3$	80 °C, 2 h	74	
5	**C**	$NaHCO_3$	80 °C, 0.5 h[c]		

[a] Molar ratio: **1a** (1 eq.), *N*-F-Py salt (1.2 eq.), additive (1.5 eq.).
[b] Isolated yield.
[c] Decomposition of C.



Scheme 2.



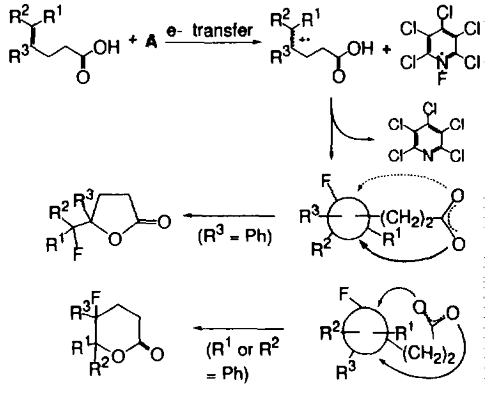
Scheme 3.

Only limited fluoro-lactonization is achieved with alkyl-substituted 4-pentenoic acids. For example, fluoro-lactonized products cannot be obtained with the substrates **1d**–**1h** [5]. In the case of **1i**, which should form a tertiary carbocation intermediate by fluorination of the olefinic part with the salt **A** or by direct protonation of the olefin, fluorolactone **2i**, fluorolactam **4i**, derived from acetonitrile (solvent) incorporation, and non-fluorinated lactone **3i** are obtained under the conditions mentioned above. A similar reaction in CH_2Cl_2 gives **2i** in poor yield together with **3i** as the major product (Scheme 2). In both cases, the proton-mediated lactonized compound **3i** is the major product even in the presence of $NaHCO_3$. These results indicate that reagent **A** has limited ability to transfer electrons to these alkyl-substituted double bonds [5,7].

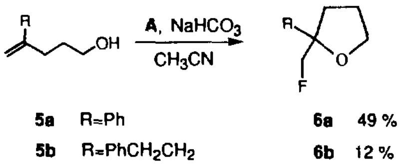
With 4-alkenoic acids containing a phenyl group on the double bond, fluoro-lactonization proceeds smoothly in a regioselective manner, namely by the 5-exo mode in the case of a phenyl group at the 4-position giving rise to the γ-lactone and by a 6-endo mode in the case of a phenyl group at the 5-position giving rise to the δ-lactone (Scheme 3). With regard to the diastereoselectivity, we examined the reaction using the geometrically pure substrates (E or Z isomer of **1b** and **1c**). Under the reaction conditions mentioned above (1.2 eq. of **A**, 1.5 eq. of $NaHCO_3$, CH_3CN, room temperature), *Z*-**1b** gives the fluoro-γ-lactone **2b** in 72% yield in a diastereomeric ratio of 2.1 : 1, while *E*-**1b** gives **2b** in 51% yield in a diastereomeric ratio of 1 : 2.4. The major isomer derived from *Z*-**1b** is the same as the minor isomer derived from *E*-**1b**. Therefore some stereospecificity is observed in the case of **1b**. In the case of **1c**, both *Z*- and *E*-**1c** give the fluoro-δ-lactone **2c** in a similar diastereomeric ratio: *cis*-**2c** : *trans*-**2c** = 1 : 2.5 from *Z*-**1c** and 1 : 2.2 from *E*-**1c**. The structure of **2c** was determined by ^1H and ^{19}F nuclear magnetic resonance (NMR) spectra and nuclear Overhauser effect (NOE) experiments to reveal that both *cis*- and *trans*-**2c** contain preferentially axial fluorine.

It is known that iodo-lactonization proceeds in a highly stereospecific manner through trans-addition of iodine and carboxylic oxygen across the double bond [1]. For example, we confirmed that the iodo-lactonization of *Z*-**1b** under kinetic control (*N*–iodosuccinimide in $CHCl_3$ or I_2–KI, $NaHCO_3$ in tetrahydrofuran–H_2O) gave the corresponding iodo-γ-lactone as a single diastereomer, and nearly the same diastereoselectivity was realized under thermodynamic control (I_2 in CH_3CN). From these results, the fluoro-lactonization reactions examined here probably proceed in a stepwise process involving the generation of a carbocation followed by nucleophilic ring closure.

The electrophilic fluorination of olefins in the presence of weak nucleophiles has been investigated with several fluorinating reagents, e.g. XeF_2 [11], $CsSO_4F$ [12], CF_3COOF [13], *N*-fluoropyridinium salt **A** [5], *N*-fluorobis-[(perfluoroalkyl)sulphonyl]imide [7] and (1-(chloromethyl)-4-fluoro-1,4-diazabicyclo[2.2.2]octane bis(tetrafluoroborate) (F-TEDA-BF_4) [9,10]. Like our fluoro-lactonization, phenyl-substituted olefins react with these reagents to give the fluorinated product in reasonable yield and no stereospecificity is observed with 1,2-disubstituted olefins. For the reaction mechanism, single electron transfer (SET) from the fluorinating reagent to the double bond, followed by F radical capture to form the carbocation intermediate, has been proposed [5,7]. Thus a lower oxidation potential of the double bond and the stabilization of the cationic intermediate by the substituent should be crucial factors in obtaining the fluorinated product. In our fluoro-lactonization (intramolecular reaction), the partial partici-



Scheme 4.



Scheme 5.

pation of the carboxyl group in the intermediate carbon cation is possibly considerable in the case of 5-exo ring closure (**1b** to **2b** in Scheme 3), since opposite diastereoselectivity was realized between the Z and E isomers of **1b**. Such participation may be negligible in the case of the 6-endo reaction (**1c** to **2c**). The formation of a non-fluorinated lactone, such as **3a**, may be derived from a competitive proton-mediated reaction. This is summarized in Scheme 4. A similar tendency was also found in the etherification reaction of **5** with the fluoropyridinium salt **A** (Scheme 5).

In conclusion, the fluoro-lactonization of 4-alkenoic acids and the fluoro-etherification of 4-alkenols with *N*-fluoropentachloropyridinium triflate proceed smoothly in a regioselective manner when the substrates contain an aryl substituent on the double bond. Some stereospecificity is observed in the case of 5-exo ring closure, possibly due to the participation of the oxygen atom in the aryl-stabilized cationic intermediate.

3. Experimental details

3.1. General

IR spectra were recorded on a Hitachi 270-30 IR spectrophotometer. NMR spectra were measured in $CDCl_3$. ^1H and ^{13}C NMR spectra were recorded on a Brucker AM400 or a Varian Gemini 300 spectrometer and chemical shifts were expressed in δ (ppm) downfield from $CHCl_3$ (7.26 ppm) and $CDCl_3$ (77.0 ppm) respectively. ^{19}F NMR spectra were taken on a Brucker AM400 spectrometer using benzotrifluoride ($\delta = -63$ ppm relative to CCl_3F) as a standard. Mass spectra (MS) were recorded by electron impact. Column chromatography was performed on silica gel (Wakogel C-200, 75–150 μm). Medium-pressure liquid chromatography (MPLC) was performed on a 30 cm×4 cm i.d. prepacked column (silica gel, 50 μm) with a UV detector.

3.2. General procedure of fluoro-lactonization reaction

To a mixture of *N*-fluoropyridinium salt (1.2 mmol) and $NaHCO_3$ (1.5 mmol) in CH_3CN was added unsaturated carboxylic acid (1 mmol) under an argon atmosphere. After stirring at room temperature for 1 h, 1 N $Na_2S_2O_3$ solution (5 ml) and AcOEt (20 ml) were added to the reaction mixture. The organic layer was separated and the aqueous layer was extracted with AcOEt (10 ml). The combined organic layer was washed with brine, dried over $MgSO_4$ and evaporated. The residue was purified by silica gel column chromatography (hexane–AcOEt), and further purification was performed by MPLC, if needed, to give the product(s).

3.2.1. 5-Fluoromethyl-5-phenyl-tetrahydro-2-furanone (2a)

Colourless oil. IR ($CHCl_3$) (cm^{-1}): 1782, 1450, 1232. ^1H NMR δ: 2.39–2.64 (2H, m), 2.71–2.93 (2H, m), 4.47 (1H, dd, $J_{HF}=47.5$ Hz, $J_{HH}=10.4$ Hz, CH_2F), 4.54 (1H, dd, $J_{HF}=47.5$ Hz, $J_{HH}=10.4$ Hz, CH_2F), 7.31–7.46 (5H, m, Ph). ^{13}C NMR δ: 28.9, 30.4, 87.1 (d, $J_{CF}=13.4$ Hz), 87.4 (d, $J_{CF}=138$ Hz), 125.1, 128.7, 128.9, 138.4 (d, $J_{CF}=4.3$ Hz), 175.8. ^{19}F NMR δ: -158.5 (t, $J_{HF}=47.5$ Hz). MS *m*/*z*: 194 (M^+), 161 (M^+-CH_2F), 133, 115, 105, 91, 77. Analysis: calculated for $C_{11}H_{11}FO_2$: C, 68.03%; H, 5.71%; found: C, 67.80%; H, 5.76%.

3.2.2. 5-Fluoromethyl-5-(2′-phenylethyl)-tetrahydro-2-furanone (2i)

Colourless oil. IR ($CHCl_3$) (cm^{-1}): 1776, 1604, 1494, 1454. ^1H NMR δ: 1.90–2.20 (3H, m), 2.28–2.41 (1H, m), 2.52–2.82 (4H, m), 4.39 (1H, dd, $J_{HF}=47.0$ Hz, $J_{HH}=9.9$ Hz), 4.51 (1H, dd, $J_{HF}=47.0$ Hz, $J_{HH}=9.9$ Hz), 7.14–7.34 (5H, m). ^{13}C NMR δ: 27.8 (d, $J_{CF}=4.2$ Hz), 29.0 (d, $J_{CF}=2.3$ Hz), 29.3, 37.6 (d, $J_{CF}=4.2$ Hz), 85.8 (d, $J_{CF}=17.4$ Hz), 86.3 (d, $J_{CF}=178$ Hz), 126.3, 128.2, 128.6, 140.5, 176.2. ^{19}F NMR δ: -123.4 (d, $J_{HF}=47.0$ Hz). MS *m*/*z*: 222 (M^+), 202 (M^+-HF), 189 (M^+-CH_2F), 161, 142, 129, 117, 91. Analysis: calculated for $C_{13}H_{15}FO_2$: C, 70.25%; H, 6.80%; found: C, 70.11%; H, 6.70%.

3.2.3. 1-Acetyl-5-fluoromethyl-5-(2′-phenylethyl)-pyrrolidin-2-one (4i)

Colourless oil. IR ($CHCl_3$) (cm^{-1}): 1744, 1700. ^1H NMR δ: 1.73–1.84 (1H, m), 2.02–2.28 (2H, m), 2.53 (3H, s, acetyl), 2.38–2.78 (5H, m), 4.33 (1H, dd, $J_{HF}=46$ Hz, $J_{HH}=9.3$ Hz, CHF), 5.00 (1H, dd, $J_{HF}=48$ Hz, $J_{HH}=9.3$ Hz, CHF), 7.11–7.32 (5H, m, Ph). ^{13}C NMR δ: 26.1 (d, $J_{CF}=3.8$ Hz), 26.7, 29.3, 31.0, 34.8 (d, $J_{CF}=4.4$ Hz), 67.5 (d, $J_{CF}=17.1$ Hz), 85.9 (d, $J_{CF}=174$ Hz), 126.2, 128.2, 128.5, 140.5, 172.5, 176.7. ^{19}F NMR δ: -125.2 (t, $J_{FH}=48$ Hz). MS *m*/*z*: 263 (M^+), 221, 188, 117, 91, 77. Analysis: calculated for $C_{15}H_{18}FNO$: C, 68.42%; H, 6.89%; N, 5.32%; found: C, 68.30%; H, 6.89%; N, 5.32%.

*3.2.4. 5-(1′-Fluoropropyl)-5-phenyl-tetrahydro-2-furanone (**2b**)*

The reaction of Z-**1b** with fluoropyridinium salt **A** in accord with the general procedure provided a diastereomeric mixture of **2b**, which was further separated by MPLC (hexane–AcOEt = 5 : 1) to give less polar **2b** (**2b-LP**) and more polar **2b** (**2b-MP**) in a ratio of 2.1 : 1. **2b-LP**: colourless oil. IR ($CHCl_3$) (cm^{-1}): 1768, 1518, 1496, 1228. ^1H NMR δ: 0.89 (3H, t, J = 7.4 Hz), 1.28 (1H, dddd, J_{HF} = 41 Hz, J_{HH} = 14.9, 7.5, 2.3 Hz), 1.70–1.86 (1H, m), 2.36 (1H, dddd, J_{HH} = 12.3, 10.0, 7.5 Hz, J_{HF} = 2.1 Hz), 2.49 (1H, dddd, J_{HH} = 17.5, 10.0, 4.9 Hz, J_{HF} = 2.7 Hz), 2.77 (1H, dddd, J_{HH} = 17.5, 10.0, 7.5 Hz, J_{HF} = 2.3 Hz), 2.93 (1H, dddd, J_{HH} = 12.3, 10.0, 4.9 Hz, J_{HF} = 1.1 Hz), 4.55 (1H, ddd, J_{HF} = 47 Hz, J_{HH} = 10.4, 2.3 Hz, CHF), 7.30–7.45 (5H, m, Ph). ^{13}C NMR δ: 9.93 (d, J_{CF} = 3.7 Hz), 21.8 (d, J_{CF} = 22.3 Hz), 28.6 (d, J_{CF} = 3.9 Hz), 32.6 (d, J_{CF} = 3.4 Hz), 88.8 (d, J_{CF} = 19.5 Hz), 99.7 (d, J_{CF} = 182.1 Hz), 124.6, 128.1, 128.8, 140.4, 176.3. ^{19}F NMR δ: −131.2 (ddd, J_{HF} = 47, 41, 13 Hz). MS *m/z*: 222 (M^+), 161, 133, 115, 105, 91, 77. Analysis: calculated for $C_{13}H_{15}FO_2$: C, 70.25%; H, 6.80%; found: C, 69.94%; H, 6.83%. **2b-MP**: colourless oil. IR (neat) (cm^{-1}): 1781, 1496, 1385. ^1H NMR δ: 0.93 (3H, t, J = 7.4 Hz), 1.24–1.42 (1H, m), 1.42 (1H, ddqd, J_{HF} = 48 Hz, J_{HH} = 14.6, 7.4, 2.8 Hz), 2.43–2.60 (2H, m), 2.64–2.83 (2H, m), 4.50 (1H, ddd, J_{HF} = 48 Hz, J_{HH} = 10.0, 2.8 Hz, CHF), 7.30–7.45 (5H, m, Ph). ^{13}C NMR δ: 9.77 (d, J_{CF} = 4.1 Hz), 23.2 (d, J_{CF} = 20.7 Hz), 28.4, 29.9, 88.6 (d, J_{CF} = 22.5 Hz), 98.3 (d, J_{CF} = 180.7 Hz), 125.9, 128.4, 138.6 (d, J_{CF} = 2.3 Hz), 175.9. ^{19}F NMR δ: −129.2 (ddd, J_{HF} = 48, 48, 15.6 Hz). MS *m/z*: 222 (M^+), 161, 133, 115, 105, 91, 77. Analysis: calculated for $C_{13}H_{15}FO_2$: C, 70.25%; H, 6.80%; found: C, 70.18%; H, 6.68%.

*3.2.5. 5-Fluoro-6-methyl-6-phenyl-tetrahydro-2-pyrone (**2c**)*

A diastereomeric mixture of **2c**, obtained by reaction of Z-**1c** with fluoropyridinium salt **A** in accord with the general procedure, was separated by silica gel column chromatography (hexane–AcOEt = 5 : 1, then AcOEt) to give *trans*-**2c** and *cis*-**2c** in the order of elution. *trans*-**2c**: colourless oil. IR ($CHCl_3$) (cm^{-1}): 1738, 1446, 1380, 1262. ^1H NMR δ: 1.77 (3H, d, J = 2.4 Hz), 1.77 (1H, ddddd, J_{HF} = 43 Hz, J_{HH} = 14.9, 11.4, 7.8, 2.1 Hz), 2.03–2.12 (1H, m), 2.46 (1H, dddd, J = 18.5, 7.8, 2.2, 0.8 Hz), 2.71 (1H, ddd, J = 18.5, 11.4, 7.9 Hz), 5.02 (1H, ddd, J_{HF} = 47 Hz, J_{HH} = 4.1, 2.1 Hz, CHF), 7.25–7.43 (5H, m, Ph). ^{13}C NMR δ: 21.8 (d, J_{CF} = 21.6 Hz), 23.9 (d, J_{CF} = 3.9 Hz), 25.9 (d, J_{CF} = 5.7 Hz), 86.5 (d, J_{CF} = 19.5 Hz), 89.0 (d, J_{CF} = 182 Hz), 124.2, 128.1, 129.0, 142.0 (d, J_{CF} = 5.1 Hz), 169.7. ^{19}F NMR δ: −132.2 (ddd, J_{HF} = 47, 43, 5.7 Hz). MS *m/z*: 208 (M^+), 180, 165, 121, 105, 77. Analysis: calculated for $C_{12}H_{13}FO_2$: C, 69.22%; H, 6.29%; found: C, 69.13%; H, 6.33%. *cis*-**2c**: colourless oil. IR ($CHCl_3$) (cm^{-1}): 1740, 1234, 1222. ^1H NMR δ: 1.73 (3H, d, J = 1.4 Hz), 2.19–2.28 (1H, m), 2.19–2.38 (1H, m), 2.62–2.83 (2H, m), 4.95 (1H, ddd, J_{HF} = 46.7 Hz, J_{HH} = 5.5, 3.0 Hz, CHF), 7.30–7.47 (5H, m, Ph). ^{13}C NMR δ: 22.37 (d, J_{CF} = 22 Hz), 24.5 (d, J_{CF} = 5.7 Hz), 27.8 (d, J_{CF} = 3.3 Hz), 85.2 (d, J_{CF} = 20 Hz), 89.0 (d, J_{CF} = 180 Hz), 124.8, 127.8, 128.4, 140.4, 169.2. ^{19}F NMR δ: −126.1 (ddd, J_{HF} = 47, 36, 5.5 Hz). MS *m/z*: 208 (M^+), 180, 165, 121, 105, 77. Analysis: calculated for $C_{12}H_{13}FO_2$: C, 69.22%; H, 6.29%; found: C, 69.25%; H, 6.28%.

*3.2.6. 2-Fluoromethyl-2-phenyl-tetrahydrofuran (**6a**)*

Colourless oil. IR ($CHCl_3$) (cm^{-1}): 1216, 1068, 1030. ^1H NMR δ: 1.79–1.95 (1H, m), 1.96–2.21 (2H, m), 2.35–2.48 (1H, m), 3.95 (1H, q, J = 7.2 Hz), 4.08 (1H, q, J = 7.2 Hz), 4.40 (2H, d, J_{HF} = 48 Hz), 7.23–7.48 (5H, m, Ph). ^{13}C NMR δ: 26.0, 33.9 (d, J_{CF} = 3.0 Hz), 67.5, 85.5 (d, J_{CF} = 17.8 Hz), 87.5 (d, J_{CF} = 181 Hz), 125.6, 127.3, 128.2, 142.6 (d, J_{CF} = 4.7 Hz). ^{19}F NMR δ: −131.7 (t, J_{HF} = 48 Hz). MS *m/z*: 161 ($M^+ - F$), 147 ($M^+ - CH_2F$), 129, 117, 105, 91, 77. High resolution MS: $C_{10}H_{11}O$ ($M^+ - CH_2F$) requires 147.0810. Found: 147.0788.

*3.2.7. 2-Fluoromethyl-2-(2′-phenylethyl)-tetrahydrofuran (**6b**)*

Colourless oil. IR ($CHCl_3$) (cm^{-1}): 1220, 1202. ^1H NMR δ: 1.76–2.02 (6H, m), 2.70 (2H, t, J = 8.7 Hz), 3.91 (2H, t, J = 5.9 Hz), 4.26 (1H, dd, J_{HF} = 47.7 Hz, J_{HH} = 9.3 Hz), 4.31 (1H, dd, J_{HF} = 47.7 Hz, J_{HH} = 9.3 Hz), 7.15–7.36 (5H, m, Ph). ^{13}C NMR δ: 26.3, 30.1, 31.9 (d, J_{CF} = 3.0 Hz), 38.2, 68.7, 82.0 (d, J_{CF} = 15.0 Hz), 86.4 (d, J_{CF} = 175.0 Hz), 125.8, 128.3, 128.4, 142.1. ^{19}F NMR δ: −127.4 (t, J_{FH} = 47.8 Hz). MS *m/z*: 208 (M^+), 175, 144, 129, 117, 103, 91.

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