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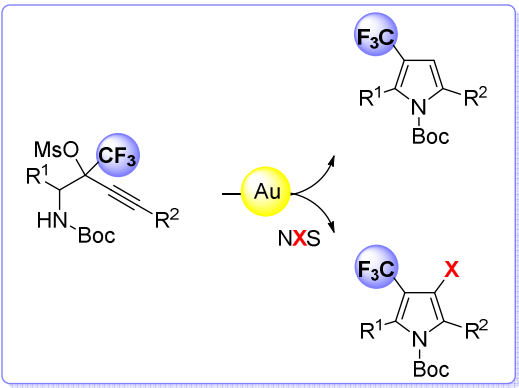
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Gold-Catalyzed Synthesis of Substituted 3-Trifluoromethylpyrroles from Mesylated Amino Trifluoromethylpropargylic Alcohols

Benjamin Guieu, Myriam Le Roch, Michèle David and Nicolas Gouault*

Equipe CORINT, UMR 6226, Université de Rennes 1, 2 avenue du Pr. Léon Bernard 35043 Rennes Cedex, France.
E-mail : nicolas.gouault@univ-rennes1.fr

ABSTRACT: A series of substituted 3-trifluoromethylpyrroles was obtained from trifluoromethyl-amino-ynol derivatives *via* a gold-catalyzed cyclization. These fluorinated starting materials, after mesylation allowed for the obtention of the desired compounds in good yields under mild conditions.

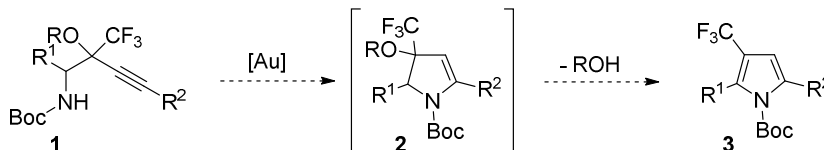


Pyrrole represents a ubiquitous structural motif that occurs in a broad range of biologically active compounds and pharmaceuticals.¹ At the same time, given the unique physicochemical properties engendered by the trifluoromethyl (CF₃) group,² incorporation of this substituent on organic molecules is one of the most important strategies for modulating their properties.³ In particular, the high lipophilicity, the better bioavailability and metabolic characteristics provided by this group offers important opportunities in the field of heterocycles and drug discovery.⁴ So, many preparative methods to obtain trifluoromethylated pyrrole derivatives were developed. Nevertheless, although the 2-trifluoromethylpyrroles are easily accessible *via* electrophilic aromatic substitution using fluorinating reagents,⁵ their 3-trifluoromethylated analogs need others strategies that involve multistep synthetic approaches. These methodologies generally rely on the use of readily available trifluoromethylated compounds as building blocks like trifluoromethylated dipolarophiles in 1,3-dipolar cycloadditions,⁶ α,β -unsaturated trifluoromethylketones,⁷ trifluoromethylated 1,3-diketones,⁸ or trifluoromethylated 1,4-dicarbonyl precursors.⁹ In some instances, these starting materials are not

easily available and may require many synthetic steps, limiting the scope of these reactions. So the search for efficient, convenient alternative strategies is still desirable.

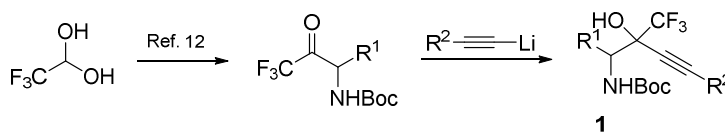
In the past few years, the use of fluorinated starting materials combined with homogeneous gold-catalysis has emerged as a “fruitful partnership” for generating a variety of new fluorinated derivatives.¹⁰ In this context, and on the basis of our previous works dedicated to the development of gold-catalyzed¹¹ strategies to obtain nitrogen-containing heterocycles from amino-ynones intermediates,¹² we decided to explore the reactivity of amino propargylic alcohols bearing a trifluoromethyl group **1** in the presence of a gold-catalyst to obtain substituted 3-trifluoromethylpyrrole derivatives **3** (Scheme 1). To our knowledge, no method using these trifluoromethylated building blocks to access trifluoromethylpyrroles has been explored to date. Our strategy is based on a one pot gold-catalyzed tandem reaction consisting of heterocyclization and elimination. The results of our study are disclosed in this note.

Scheme 1. Gold-Catalyzed Strategy for the Synthesis of Substituted 3-Trifluoromethylated Pyrroles.



Initially, a series of trifluoromethylated amino propargylic alcohols **1** was prepared from commercially available trifluoroacetaldehyde *via* N-protected α -amino trifluoromethylketones intermediates formation¹³ and subsequent addition of various lithium acetylides (Table 1). Thus, trifluoromethylated amino propargylic alcohols **1a-h** were produced in 4 steps with moderate to good overall yield from trifluoroacetaldehyde.

Table 1. Synthesis of Trifluoromethylated Amino Propargylic Alcohols **1**.

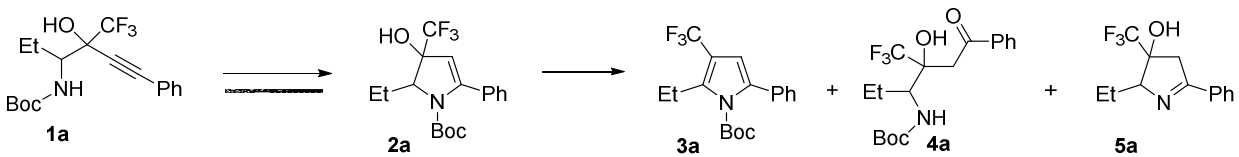


R ¹	R ²	Product	Yield (%) ^a	dr	R ¹	R ²	Product	Yield (%)	dr
Et	Ph	1a	76	80/20	Pent	Ph	1e	74	70/30
Et	<i>n</i> -Pr	1b	57	55/45	Pent	<i>n</i> -Pr	1f	77	75/25
Me	Ph	1c	65	75/25	Ph	Ph	1g	27	100/0
Me	<i>n</i> -Pr	1d	41	60/40	Ph	<i>n</i> -Pr	1h	65	100/0

^a Isolated yield.

With these starting materials in hand, efforts were then made to establish the optimized conditions for the formation of 3-trifluoromethylpyrrole **3a** from **1a** (Table 2).

Table 2. Optimization of the Reaction Conditions^a for the Cyclization of **1a**.



Entry	Substrate	Catalyst	Additive	2a/3a/4a/5a ^b	Yield (%) ^c
1	1a	AuCl	-	18/27/55/0	-
2	1a	Ph ₃ PAuSbF ₆ ^d	-	26/30/44/0	24
3	1a	Ph ₃ PAuOTf ^e	-	9/36/55/0	-
4	1a	AuCl ₃	-	10/35/55/0	-
5	1a	AgNO ₃ /Silica	-	100/0/0/0	86 ^f
6	2a	-	MSA (0.2 equiv)	0/67/0/33	57
7	1a	AuCl	MSA (0.2 equiv)	3/44/37/16	-
8	1a	AgNO ₃	MSA (0.2 equiv)	No conv	-
9	2a	-	MsCl (1.2 equiv) / TEA (2.4 equiv)	17/83/0/0	74

^a Unless indicated otherwise, a mixture of **1** (0.25 mmol), a catalyst (10 mol%) in DCM (2.0 mL) was stirred at room temp. overnight under argon. ^b Ratio determined by ¹H NMR on the crude material. ^c Isolated yield of **3a**. ^d The Ph₃PAuSbF₆ was *in situ* generated from 10 mol% of Ph₃PAuCl and 10 mol% of AgSbF₆. Reaction was performed in 1,2-DCE at 50°C overnight. ^e The Ph₃PAuOTf was *in situ* generated from 10 mol% of Ph₃PAuCl and 10 mol% of AgOTf. ^f Isolated yield of **2a**.

In this way, substrate **1a** was subjected to various conditions. The reaction was initially carried out with a catalytic amount of three commonly used gold(I) catalysts, AuCl, (Ph₃P)AuSbF₆ and (Ph₃P)AuOTf respectively (Table 1, entries 1-3). Notably, the reactions were completed within 18 h under these conditions but afforded at most small amounts of the desired trifluoromethylpyrrole **3a** along with others compounds. Examination of the crude material by ¹H NMR revealed in fact the

1 presence of hydroxypyrroline **2a** and aminoketone **4a** resulting from the isomerization of **2a** to the
2 corresponding iminium followed by its hydrolysis. The use of a gold(III) catalyst gave a similar result
3 (entry 4). The catalytic conditions using silver salts developed by Knight¹⁴ to obtain pyrrole
4 derivatives were then investigated as an alternative. Disappointingly, upon exposure to 10 mol% w/w
5 silver nitrate on silica gel in DCM at room temperature overnight in the dark, pyrrolinol **2a** was
6 obtained as the unique product (entry 5). From a synthetic point of view, this result is interesting, as
7 reduction to pyrrolidines may be envisioned from this intermediate.
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10 We hypothesized that an acidic medium may promote the transformation of this intermediate **2a** to
11 **3a** (elimination reaction).¹⁵ To support this, an attempt was realized by treating alcohol **2a** with 0.2
12 equivalent of methanesulfonic acid (MSA) in dichloromethane. It revealed that, the acidic conditions
13 allowed for the conversion of intermediate **2a** to pyrrole **3a**, along with, nevertheless, formation of
14 cyclic imine **5**, resulting from the deprotection of **2a** (entry 6). We next evaluated the use of MSA as
15 an additive in the catalytic cyclization process (entries 7-8). In the conditions using AuCl as the
16 catalyst, a positive effect was observed with a ratio of **2a/3a** obviously increased in favour of **3a** (entry
17 7 vs entry 1). However, this was accompanied with the formation of **4a** and **5a**. On the other hand, a
18 loss of catalytic activity was observed with the silver salt (entry 8).
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37 We also speculated that increasing the leaving group ability of hydroxyle function might facilitate
38 the elimination. So, intermediate **2a**, resulting from reaction of **1a** with silver nitrate, was treated with
39 mesyl chloride in the presence of triethylamine and allowed for the formation of the desired pyrrole **3a**
40 with a good isolated yield (74%) (entry 9). This positive result prompted us to mesylate substrate **1a** to
41 **1b** and evaluate its reactivity in the cyclization process. Alcohol **1a** was then quantitatively mesylated
42 to the corresponding **6a** by employing MsCl in the presence of TEA in DCM.
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51 The reactivity of **6a** in the presence of gold and silver catalysts was next examined (Table 3). The
52 reaction was first conducted in the presence of AuCl and provided the desired pyrrole **3a** in satisfying
53 isolated yield (entry 1). However, deprotected pyrrole **7a** was also observed, presumably favored by
54 methanesulfonic acid removed in the reaction medium. To limit formation of this by-product,
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potassium carbonate was added to neutralize MSA leading to pyrrole **3a** with an improved yield, nevertheless, still contaminated by **7a** (entry 2). Finally, potassium carbonate was replaced with an organic base (DIPEA). Unfortunately, these conditions proved inefficient since starting material could be recovered quantitatively. This loss of catalytic activity was presumably due to a coordination of the amine to the metal center (entries 3-4). From a kinetic point of view, reaction was much faster when performed starting from mesylated alcohol **6a** (1h instead of several hours with **1a**). Furthermore, reaction was cleaner with **6a**, since only one by-product was detected (deprotected pyrrole **7a**).

Table 3. Optimization of the Reaction Conditions^a for the heterocyclization of **6a**.



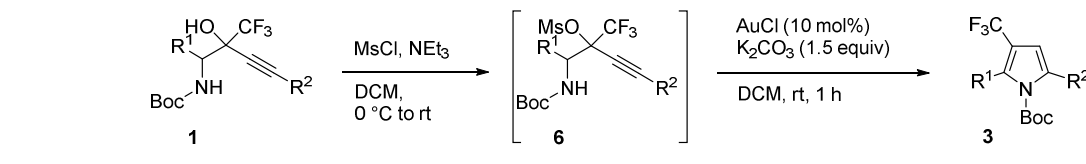
Entry	Substrate	Catalyst	Additive	2a/3a/7a ^b	Yield (%) ^c
1	6a	AuCl	-	0/80/20	69
2	6a	AuCl	K ₂ CO ₃ (1.5 equiv)	0/92/8	78
3	6a	AuCl	DIPEA (1.1 equiv)	0% conv	-
4	6a	AgNO ₃ /Silice	TEA (1.1 equiv)	0% conv	-

^a Unless indicated otherwise, a mixture of **6a** (0.25 mmol), a catalyst (10 mol%) in DCM (2.0 mL) was stirred at room temp. for 1 h under argon. ^b Ratio determined by ¹H NMR on the crude material. ^c Isolated yield of **3a** over two steps.

Based on the optimized reaction conditions (Table 3, entry 2), the substrate scope of this gold-mediated cyclization reaction was examined with a variety of mesylated and trifluoromethylated amino propargylalcohols **6**.

As depicted in Table 4, several structural variations were tolerated under these mild conditions, including alkyl and aryl substituents and a series of 3-trifluoromethylpyrrole derivatives **3a-h** could be successfully obtained with good yields.

Table 4. Substrate Scope of the Reaction.^a



Entry	R ¹	R ²	Product	Yield (%) ^b
Entry	R ¹	R ²	Product	Yield (%)

1	Et	Ph	3a	77	5	Pent	Ph	3e	76
2	Et	<i>n</i> -Pr	3b	71	6	Pent	<i>n</i> -Pr	3f	62
3	Me	Ph	3c	74	7	Ph	Ph	3g	68
4	Me	<i>n</i> -Pr	3d	74	8	Ph	<i>n</i> -Pr	3h	71

^a Reaction conditions: substrate **6** (0.25 mmol), AuCl (10 mol%), K₂CO₃ (1.5 equiv.), DCM (2 mL), r.t., 1 h. ^b Isolated yield over two steps.

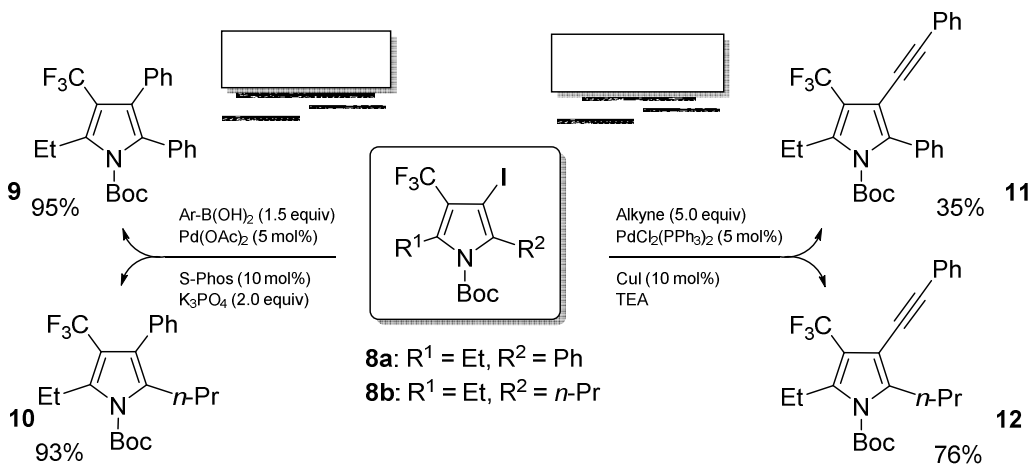
We next extended this protocol to iodocyclization. These methodologies, which typically lead to the incorporation halogen into the heterocyclic structure, allow for the creation of molecular diversity and complexity postcyclization. For this purpose, catalytic iodocyclization under conditions previously developed with NIS (1.1 equiv) as electrophilic halogen source,¹⁶ allowed for the obtaining of iodopyrroles **8** with moderate to good yields (Scheme 2). This reaction was also examined in the presence of NIS and without any catalyst. Notably, the starting amino alkynes **6a-b** were majoritary recovered after 24 h.

Scheme 2. Gold-Catalyzed Iodocyclization to 3-trifluoromethyl-4-Iodopyrroles **8**.



These two halogenated pyrroles **8a-b** were further functionalized by applying palladium-catalyzed processes such as Suzuki-Miyaura, or Sonogashira cross-coupling reactions (Scheme 3).

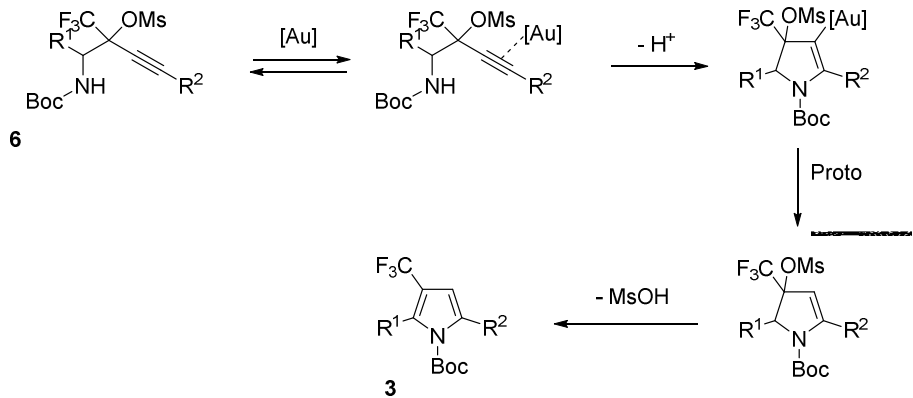
Scheme 3. Pd-Catalyzed Modifications of 4-Iodopyrroles **8**.



For instance, compounds **9** and **10** have been successfully obtained in 95% and 93% isolated yield respectively by the Suzuki cross-coupling reaction of **8a** and **8b** with phenylboronic acid. Concerning the Sonogashira coupling reaction, a first attempt realized starting from **8a** with phenylacetylene at 50°C afforded **11** with a small yield (35%). For the second Sonogashira coupling reaction performed with **8b**, temperature was increased to 80°C and allowed for the obtaining of **12** with a much better yield (76%).

The plausible mechanism for the formation of pyrroles **3** starting from substrates **6** is shown in Scheme 4. The heterocyclization-aromatization proceeds through the intramolecular 5-*endo-dig* nucleophilic attack of the protected amino group to the triple bond coordinated to the metal center, followed by protodeauration and elimination of MSA.

Scheme 4. Plausible Reaction Mechanism.



In conclusion, we have developed a convenient gold-catalyzed approach for the synthesis of substituted 3-trifluoromethylpyrrole derivatives from easily accessible trifluoromethylated α -amino propargylic alcohols as key intermediates. We demonstrated that after mesylation, these starting fluorinated building-blocks allowed for the obtention of the pyrrole products in good yields under mild conditions. The scope of this method was successfully extended to iodocyclizations and subsequent palladium-catalyzed cross-coupling reactions providing fully substituted pyrrole derivatives.

■ EXPERIMENTAL SECTION

General Methods. Unless otherwise specified, all commercially available reagents were used as received. Analytical thin layer chromatography (TLC) was carried out on silica gel 60 F₂₅₄ plates with visualization by ultraviolet light or potassium permanganate dip. Column chromatography was carried out using silica gel 60 (70-200 μ m). ¹H, ¹⁹F and ¹³C NMR spectra were recorded on 300 or 400 MHz instruments. The chemical shifts are given in part per million (ppm) on the delta scale. The solvent peak was used as reference value: for ¹H NMR, CHCl₃ = 7.26 ppm; for ¹³C NMR, CHCl₃ = 77.16 ppm. Infrared spectra were recorded neat. Wavelengths of maximum absorbance (ν_{max}) are quoted in wave numbers (cm⁻¹). ESI-HRMS were carried out on a Agilent 6510 Q-TOF spectrometer at the CRMPO (Centre Régional de Mesures Physiques de l'Ouest), University of Rennes 1.

Typical procedure for the synthesis of trifluoromethylated amino propargylic alcohols 1

To a stirred solution of alkyne (10.0 mmol, 4.0 equiv) in THF (10 mL) at -78 °C, a solution of BuLi 2.5 M in hexane (9.5 mmol, 3.8 equiv) was added dropwise. The solution was stirred for 1h. Then, a solution of trifluoromethyl aminoketone (2.5 mmol, 1.0 equiv) in THF (10 mL) was dropwise added at -78 °C and stirred for 1 h at the same temperature. The mixture was then allowed to warm to -10 °C and, after 5 h, the reaction was quenched by addition of a saturated NH₄Cl solution (40 mL) then

extracted with diethylether (3 x 30 mL). The combined organic layers were washed with brine, then dried over MgSO_4 and evaporated in vacuo. Purification by column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O} = 95/5$ as eluent) provided the expected product.

(1a) Yield: 76% (679 mg). Mixture of diastereoisomers ratio: 80/20. Data for the maj. diastereoisomer (rotamers): White solid. Mp: 110-111 °C. ^1H NMR (300 MHz, CDCl_3) δ 7.49-7.46 (m, 2H), 7.41-7.30 (m, 3H), 4.65 (bd, $J = 9.8$ Hz, 0.82H), 4.39 (bd, $J = 10.5$ Hz, 0.18H), 4.23 (bs, 0.82H), 4.05 (t, $J = 9.6$ Hz, 1H), 3.47 (bs, 0.18H), 2.19-2.06 (m, 1H), 1.62-1.40 (m, 1H), 1.44 (s, 9H), 1.02 (t, $J = 7.4$ Hz, 3H).); ^{13}C NMR (75 MHz, CDCl_3) δ 156.8, 132.2, 129.6, 128.5, 124.0 (q, $^1J_{\text{C-F}} = 286.5\text{Hz}$), 121.1, 88.0, 82.9, 80.6, 74.7 (q, $^2J_{\text{C-F}} = 29.4\text{Hz}$), 57.1, 28.4, 23.5, 11.0; ^{19}F NMR (376 MHz, CDCl_3) δ -77.39, -76.46; IR (UATR) 3420, 3354, 2236, 1688 cm^{-1} ; HRMS (ESI) m/z calcd for $[\text{M}+\text{Na}]^+$ ($[\text{C}_{18}\text{H}_{22}\text{NO}_3\text{F}_3+\text{Na}]^+$) 380.1444, found 380.1445.

(1b): Yield: 57% (461 mg). Mixture of diastereoisomers, ratio: 55/45. Data for the diastereoisomer 1: White solid. Mp: 60-61 °C. ^1H NMR (300 MHz, CDCl_3) δ 4.73 (bd, $J = 8.1$ Hz, 1H), 4.36 (bs, 1H), 3.84-3.76 (m, 1H), 2.22 (t, $J = 7.0$ Hz, 2H), 2.02-1.89 (m, 1H), 1.66-1.50 (m, 3H), 1.45 (s, 9H), 0.99 (t, $J = 7.4$ Hz, 3H), 0.98 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 157.5, 123.9 (q, $^1J_{\text{C-F}} = 286.3$ Hz), 89.3, 80.8, 75.0 (q, $^2J_{\text{C-F}} = 29.6$ Hz), 74.2, 57.0, 28.4, 22.9, 21.7, 20.7, 13.5, 10.7; ^{19}F NMR (282 MHz, CDCl_3) δ -77,76; IR (UATR) 3372, 2237, 1662 cm^{-1} ; HRMS (ESI) m/z calcd for $[\text{M}+\text{Na}]^+$ ($[\text{C}_{15}\text{H}_{24}\text{NO}_3\text{F}_3 + \text{Na}]^+$) 346.1601, found 346.1601. Data for the diastereoisomer 2 (rotamers): White solid. Mp: 80-81 °C. ^1H NMR (300 MHz, CD_2Cl_2) δ 4.61 (bd, $J = 9.6$ Hz, 0.84H), 4.24 (bd, $J = 8.3$ Hz, 0.16H), 3.89-3.86 (m, 1.84H), 3.16 (bs, 0.16H) 2.24 (t, $J = 7.0$ Hz, 2H), 2.05-1.98 (m, 1H), 1.56 (sex, $J = 7.2$ Hz, 2H), 1.48-1.38 (m, 1H) 1.43 (s, 9H), 1.00-0.96 (m, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 156.7, 124.5 (q, $^1J_{\text{C-F}} = 286.3$ Hz), 89.9, 80.3, 74.5, 74.3 (q, $^2J_{\text{C-F}} = 28.8\text{Hz}$), 56.8, 28.4, 23.7, 22.0, 20.8, 13.5, 10.8; ^{19}F NMR (282 MHz, CD_2Cl_2) δ -78.18, -77,45; IR (UATR) 3434, 3349, 2243, 1697 cm^{-1} ; HRMS (ESI) m/z calcd for $[\text{M}+\text{Na}]^+$ ($[\text{C}_{15}\text{H}_{24}\text{NO}_3\text{F}_3 + \text{Na}]^+$) 346.1601, found 346.1601.

(1c): Yield: 65% (558 mg). Mixture of diastereoisomers, ratio: 75/25. Data for the maj. diastereoisomer: White solid. Mp: 108-109 °C. ^1H NMR (300 MHz, CDCl_3) δ 7.51-7.47 (m, 2H),

7.41-7.30 (m, 3H), 5.06 (bs, 1H), 4.91 (bd, $J = 6.7$ Hz, 1H), 4.25-4.15 (m, 1H), 1.46 (s, 9H), 1.44 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 157.5, 132.2, 129.5, 128.5, 123.8 (q, $^1J_{\text{C-F}} = 286.2$ Hz), 121.2, 87.9, 82.0, 81.4, 76.3 (q, $^2J_{\text{C-F}} = 30.5$ Hz), 51.4, 28.4, 16.9; ^{19}F NMR (376 MHz, CDCl_3) δ -77.56; IR (UATR) 3422, 3275, 2236, 1683 cm^{-1} ; HRMS (ESI) m/z calcd for $[\text{M}+\text{Na}]^+$ ($[\text{C}_{17}\text{H}_{20}\text{NO}_3\text{F}_3+\text{Na}]^+$) 366.1288, found 366.1291.

(1d) Yield: 41% (317 mg). Mixture of diastereoisomers, ratio: 60/40. Data for the diastereoisomer 1: Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 4.79 (bs, 1H), 4.57 (bs, 1H), 4.13-4.03 (m, 1H), 2.24 (t, $J = 7.0$ Hz, 2H), 1.57 (sex, $J = 7.2$ Hz, 2H), 1.45 (s, 9H), 1.34 (d, $J = 6.6$ Hz, 3H), 0.99 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 157.1, 123.7 (q, $^1J_{\text{C-F}} = 286.0$ Hz), 89.2, 80.9, 75.5 (q, $^2J_{\text{C-F}} = 29.6$ Hz), 73.5, 50.9, 28.2, 21.6, 20.5, 16.7, 13.3; ^{19}F NMR (376 MHz, CDCl_3) δ -77.97; IR (UATR) 3348, 2248, 1692 cm^{-1} ; HRMS (ESI) m/z calcd for $[\text{M}+\text{Na}]^+$ ($[\text{C}_{14}\text{H}_{22}\text{NO}_3\text{F}_3 + \text{Na}]^+$) 332.1444 found 332.1446. Data for the diastereoisomer 2 (rotamers): White solid. Mp: 72-73 °C. NMR (300 MHz, CD_2Cl_2) δ 4.76 (bs, 1H), 4.17-4.07 (m, 2H), 2.25 (t, $J = 7.0$ Hz, 2H), 1.57 (sex, $J = 7.2$ Hz, 2H), 1.43 (s, 9H), 1.34 (d, $J = 6.9$ Hz, 3H), 1.00 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 156.2, 124.5 (q, $^1J_{\text{C-F}} = 286.3$ Hz), 90.0, 80.5, 74.5 (q, $^2J_{\text{C-F}} = 28.6$ Hz), 74.4, 51.0, 28.4, 22.0, 20.8, 16.9, 13.5; ^{19}F NMR (282 MHz, CD_2Cl_2) δ -78.06, -77.37; IR (UATR) 3357, 2248, 1691 cm^{-1} ; HRMS (ESI) m/z calcd for $[\text{M}+\text{Na}]^+$ ($[\text{C}_{14}\text{H}_{22}\text{NO}_3\text{F}_3 + \text{Na}]^+$) 332.1444 found 332.1446.

(1e): Yield: 74% (739 mg). Pale yellow oil. Mixture of diastereoisomers, ratio: 70/30 Data for the maj. diastereoisomer (rotamers). ^1H NMR (300 MHz, CDCl_3) δ 7.56-7.28 (m, 5H), 4.83 (bd, $J = 9.3$ Hz, 0.29 H), 4.64 (bd, $J = 9.7$ Hz, 0.52H), 4.19-3.92 (m, 1H); 2.13-1.88 (m, 2H); 1.65 (bs, 1H), 1.46 (s, 3H), 1.45 (s, 6H), 1.42-1.21 (m, 6H), 0.90 (t, $J = 6.3$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 156.6, 132.1, 132.0, 130.0, 129.4, 128.4, 128.4, 123.9 (q, $^1J_{\text{C-F}} = 286.7$ Hz), 121.0, 87.9, 82.9, 80.9, 80.5, 74.6 (q, $^2J_{\text{C-F}} = 29.3$ Hz), 55.4, 31.3, 31.3, 30.1, 28.3, 28.2, 25.8, 25.6, 22.5, 22.3, 14.0, 13.9; ^{19}F NMR (282 MHz, CDCl_3) δ -76.31, -75.75; IR (UATR) 3342, 2235, 1689 cm^{-1} ; HRMS (ESI) m/z calcd for $[\text{M}+\text{Na}]^+$ ($[\text{C}_{21}\text{H}_{28}\text{NO}_3\text{F}_3 + \text{Na}]^+$) 422.1919 found 422.1914.

(**1f**): Yield: 77% (703 mg). Pale yellow oil. Mixture of diastereoisomers, ratio: 75/25. Data for the maj. diastereoisomer: ^1H NMR (300 MHz, CDCl_3) δ 4.53 (bd, $J = 9.9$ Hz, 1H), 3.99 (bd, $J = 9.9$ Hz, 1H), 2.23 (t, $J = 7.0$ Hz, 2H), 2.05-1.78 (m, 2H), 1.65(bs, 1H), 1.62-1.48 (m, 2H), 1.44 (s, 9H), 1.40-1.19 (m, 6H), 0.99 (t, $J = 7.4$ Hz, 3H), 0.89 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 156.5, 124.1(q, $^1J_{\text{C-F}} = 286.5$ Hz), 89.5, 80.8, 80.3, 74.5(q, $^2J_{\text{C-F}} = 29.4$ Hz), 55.2, 31.5, 30.3, 28.4, 25.9, 25.7, 22.6, 21.8, 20.7, 14.1, 13.5; ^{19}F NMR (282 MHz, CDCl_3) δ -76.86; IR (UATR) 3354, 2246, 1692 cm^{-1} ; HRMS (ESI) m/z calcd for $[\text{M}+\text{Na}]^+$ ($[\text{C}_{18}\text{H}_{30}\text{F}_3\text{NO}_3 + \text{Na}]^+$) 388.2070, found 388.2070.

(**1g**): Yield: 27% (274 mg). Yellow solid. Mp: 126-127 $^\circ\text{C}$. One diastereoisomer. ^1H NMR (300 MHz, CDCl_3) δ 7.57-7.31 (m, 10H), 5.50 (d, $J = 9.8$ Hz, 1H), 5.33(d, $J = 9.8$ Hz, 1H), 3.20 (bs, 1H), 1.43 (s, 9H); ; ^{13}C NMR (75 MHz, CDCl_3) δ 154.7, 136.5, 132.0, 129.8, 128.7, 128.6, 128.5, 128.3, 123.5 (q, $^1J_{\text{C-F}} = 286.3$ Hz), 120.6, 89.4, 81.8, 80.5, 74.0 (q, $^2J_{\text{C-F}} = 30.4$ Hz), 57.2, 28.3; ^{19}F NMR (376 MHz, CDCl_3) δ -76.87; IR (UATR) 3382, 2236, 1695 cm^{-1} ; HRMS (ESI) m/z calcd for $[\text{M}+\text{Na}]^+$ ($[\text{C}_{22}\text{H}_{22}\text{NO}_3\text{F}_3 + \text{Na}]^+$) 428.1444, found 428.1441.

(**1h**): Yield: 65% (603 mg). White solid. Mp: 112-113 $^\circ\text{C}$. One diastereoisomer. ^1H NMR (300 MHz, CDCl_3) δ 7.46-7.31 (m, 5H), 5.38 (bd, $J = 9.8$ Hz, 1H), 5.17 (bd, $J = 9.8$ Hz, 1H), 2.67 (bs, 1H), 2.26 (t, $J = 7.0$ Hz, 2H), 1.58 (sex, $J = 7.2$ Hz, 2H), 1.42 (s, 9H), 0.99 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 154.5, 136.7, 128.6, 128.4, 128.2, 128.0, 123.6 (q, $^1J_{\text{C-F}} = 286.3$ Hz), 80.6, 80.3, 73.9 (q, $^2J_{\text{C-F}} = 30.4$ Hz), 56.8, 28.3, 21.5, 20.6, 13.4; ^{19}F NMR (282 MHz, CDCl_3) δ -77.60; IR (UATR) 3252, 2226, 1667 cm^{-1} ; HRMS (ESI) m/z calcd for $[\text{M}+\text{Na}]^+$ ($[\text{C}_{19}\text{H}_{24}\text{NO}_3\text{F}_3 + \text{Na}]^+$) 394.1601, found 394.1603.

General Procedure for the Sequential Mesylation/Cyclization Reaction. To the alcohols **1** (0.81 mmol) in dichloromethane (8.5 mL) cooled to 0 $^\circ\text{C}$ was added under an argon atmosphere triethylamine (270 μL , 1.94 mmol) and dropwise methanesulfonyl chloride (75 μL , 0.97 mmol). The reaction mixture was stirred at 0 $^\circ\text{C}$ for 15 min then for 2.5 h at room temperature. The reaction mixture was diluted with diethylether (30 mL), washed with NaHCO_3 10% and brine then dried over

magnesium sulfate. Removal of the solvents afforded the mesylated derivatives as a mixture of diastereomers used in the next step without purification.

To a degassed solution of mesylated derivatives **6** (0.25 mmol) in dichloromethane (2 mL) were added under an argon atmosphere K_2CO_3 (51.8 mg, 0.375 mmol) and AuCl (5.8 mg, 0.025 mmol). After stirring for 30 min to 1 h at room temperature, the reaction mixture was diluted with diethylether (10 mL), washed with $NaHCO_3$ 10% and brine then dried over magnesium sulfate. Removal of the solvents gave a residue that was purified by column chromatography (silica gel, cyclohexane/ CH_2Cl_2 = 70/30 as eluent) to give the desired product.

(3a): Yield: 77% (65.3 mg). White solid. Mp: 56-57 °C. 1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.27 (m, 5H), 6.28 (s, 1H), 2.98 (qq, $J = 7.4$ Hz, $^5J_{H-F} = 0.8$ Hz, 2H), 1.25 (s, 9H), 1.25 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4, 138.4 (q, $^3J_{C-F} = 4.0$ Hz), 134.2, 134.0, 128.4, 128.2, 127.6, 124.1 (q, $^1J_{C-F} = 267.4$ Hz), 113.4 (q, $^2J_{C-F} = 35.6$ Hz), 109.0 (q, $^3J_{C-F} = 3.2$ Hz), 85.0, 27.3, 19.5, 15.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.48; IR (UATR) 1752 cm^{-1} ; HRMS (ESI) m/z calcd for $[M+Na]^+$ ($[C_{18}H_{20}NO_2F_3 + Na]^+$) 362.1338, found 362.1341

(3b): Yield: 76% (58.0 mg). Colorless oil. 1H NMR (300 MHz, $CDCl_3$) δ 6.01 (s, 1H), 2.92 (qq, $J = 7.4$ Hz, $^5J_{H-F} = 0.8$ Hz, 2H), 2.70 (td, $J = 7.6$ Hz, $J = 0.6$ Hz, 2H), 1.66-1.53 (m, 2H), 1.62 (s, 9H), 1.17 (t, $J = 7.4$ Hz, 3H), 0.97 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.8, 137.0 (q, $^3J_{C-F} = 4.1$ Hz), 135.3, 124.3 (q, $^1J_{C-F} = 267.3$ Hz), 113.2 (q, $^2J_{C-F} = 35.1$ Hz), 106.8 (q, $^3J_{C-F} = 3.2$ Hz), 85.0, 31.2, 28.0, 22.3, 20.1, 15.2, 14.1; ^{19}F NMR (282 MHz, $CDCl_3$) δ -56.45; IR (UATR) 1749 cm^{-1} ; HRMS (ESI) m/z calcd for $[M+Na]^+$ ($[C_{15}H_{22}NO_2F_3+Na]^+$) 328.1495, found 328.1495.

(3c): Yield: 74% (60.2 mg). Colorless oil. 1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.26 (m, 5H), 6.27 (s, 1H), 2.54 (q, $^5J_{H-F} = 1.4$ Hz, 3H), 1.25 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.5, 134.3, 134.1, 132.6 (q, $^3J_{C-F} = 4.0$ Hz), 128.6, 128.2, 127.6, 124.0 (q, $^1J_{C-F} = 267.3$ Hz), 114.2 (q, $^2J_{C-F} = 35.5$ Hz), 109.2 (q, $^3J_{C-F} = 3.1$ Hz), 85.0, 27.3, 12.7; ^{19}F NMR (282 MHz, $CDCl_3$) δ -56.60; IR (UATR) 1751 cm^{-1} ; HRMS (ESI) m/z calcd for $[M+Na]^+$ ($[C_{17}H_{18}NO_2F_3+Na]^+$) 348.1182, found 348.1185.

(**3d**): Yield: 75% (54.6 mg). Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 6.02 (s, 1H), 2.71 (t, J = 7.6 Hz, 2H), 1.62 (s, 9H), 2.45 (q, $^5J_{\text{H-F}}$ = 1.4 Hz, 3H), 1.66-1.53 (m, 2H), 1.61 (s, 9H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.9, 135.3, 131.1 (q, $^3J_{\text{C-F}}$ = 4.2 Hz), 124.2 (q, $^1J_{\text{C-F}}$ = 267.2 Hz), 113.9 (q, $^2J_{\text{C-F}}$ = 35.0 Hz), 106.8 (q, $^3J_{\text{C-F}}$ = 3.1 Hz), 84.9, 31.2, 28.1, 22.4, 14.0, 13.7; ^{19}F NMR (282 MHz, CDCl_3) δ -56.55; IR (UATR) 1749 cm^{-1} ; HRMS (ESI) m/z calcd for $[\text{M-H}]^-$ ($[\text{C}_{14}\text{H}_{20}\text{NO}_2\text{F}_3\text{-H}]^-$) 290.1373, found 290.1373.

(**3e**): Yield: 77% (73.4mg). Colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 7.39-7.26 (m, 5H), 6.27 (s, 1H), 2.97-2.88 (m, 2H), 1.67-1.57 (m, 2H), 1.40-1.31, (m, 4H), 1.24 (s, 9H), 0.90 (t, J = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.5, 137.3 (q, $^3J_{\text{C-F}}$ = 4.0 Hz), 134.2, 134.0, 128.4, 128.2, 124.2 (q, $^1J_{\text{C-F}}$ = 267.2 Hz), 113.6 (q, $^2J_{\text{C-F}}$ = 35.4 Hz), 108.9 (q, $^3J_{\text{C-F}}$ = 3.2 Hz), 85.0, 31.9, 30.5, 29.9, 27.2, 26.0, 22.5, 14.1; ^{19}F NMR (282 MHz, CDCl_3) δ -56.29; IR (UATR) 1752 cm^{-1} ; HRMS (ESI) m/z calcd for $[\text{M+Na}]^+$ ($[\text{C}_{21}\text{H}_{26}\text{NO}_2\text{F}_3+\text{Na}]^+$) 404.1813, found 404.1808.

(**3f**): Yield: 71% (61.7 mg). Pale yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 6.01 (s, 1H), 2.87 (t, J = 7.8 Hz, 2H), 2.68 (t, J = 7.8 Hz, 2H), 1.61 (s, 9H), 1.59-1.45 (m, 4H), 1.40-1.23 (m, 4H), 0.97 (t, J = 7.3 Hz, 3H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.9, 135.8, (q, $^3J_{\text{C-F}}$ = 4.1 Hz), 135.2, 124.3 (q, $^1J_{\text{C-F}}$ = 267.3 Hz), 113.4 (q, $^2J_{\text{C-F}}$ = 34.9 Hz), 106.7 (q, $^3J_{\text{C-F}}$ = 3.2 Hz), 84.9, 31.9, 31.1, 30.5, 28.0, 26.6, 22.4, 14.1, 14.0; ^{19}F NMR (282 MHz, CDCl_3) δ -56.23; IR (UATR) 1749 cm^{-1} ; HRMS (ESI) m/z calcd for $[\text{M+Na}]^+$ ($[(\text{C}_{18}\text{H}_{28}\text{NO}_2\text{F}_3+\text{Na})]^+$) 370,1964, found 370,1963.

(**3g**): Yield: 68% (68.8 mg). Pale yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 7.52-7.34 (m, 10H), 6.49 (s, 1H), 1.14 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.8, 134.8, 134.1, 132.5, 131.0, 130.1, 128.7, 128.5, 128.2, 127.9, 127.8, 123.3 (q, $^1J_{\text{C-F}}$ = 267.7 Hz), 115.1 (q, $^2J_{\text{C-F}}$ = 35.8 Hz), 108.8 (q, $^3J_{\text{C-F}}$ = 3.1 Hz), 85.2, 26.9; ^{19}F NMR (282 MHz, CDCl_3) δ -55.35; IR (UATR) 1758 cm^{-1} ; HRMS (ESI) m/z calcd for $[\text{M+Na}]^+$ ($[\text{C}_{22}\text{H}_{20}\text{NO}_2\text{F}_3+\text{Na}]^+$) 410.1338, found 410.1334.

(**3h**): Yield: 71% (62.7 mg). Yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 7.46-7.26 (m, 5H), 6.19 (s, 1H), 2.79 (t, J = 7.8 Hz, 2H), 1.77-1.58 (m, 2H), 1.16 (s, 9H), 1.02 (t, J = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.5, 136.6, 133.0 (q, $^3J_{\text{C-F}}$ = 4.1 Hz), 132.6, 130.0, 128.3, 127.9, 123.5 (q, $^1J_{\text{C-F}}$ =

267.7 Hz), 115.0 (q, $^2J_{C-F} = 35.3$ Hz), 106.7, 84.7, 30.3, 27.2, 22.2, 14.1; ^{19}F NMR (282 MHz, CDCl_3) δ -55.27; IR (UATR) 1751 cm^{-1} ; HRMS (ESI) m/z calcd for $[\text{M}+\text{Na}]^+$ ($\text{C}_{19}\text{H}_{21}\text{NO}_2\text{F}_3+\text{Na}$) $^+$ 376,1495, found 376,1494.

General Procedure for the Iodocyclization Reaction. To a degassed solution of mesylated derivatives **6** (0,5mmol) in dichloromethane (**6a**) or in 1,2-dichloroethane (**6b**) (3mL) were added successively under argon atmosphere NIS (123.7 mg, 0,55 mmol), K_2CO_3 (104.0 mg, 0.75 mmol) and AuCl (11.6 mg, 0.05 mmol). After stirring for 2 h at room temperature (**6a**) or at 60 °C (**6b**), the mixture was diluted with diethylether (20 mL) and was washed with NaHCO_3 10% and brine, dried over magnesium sulfate and concentrated. The residue was purified by column chromatography on silica gel (cyclohexane/ CH_2Cl_2 =70/30) to give the desired product **8**.

(**8a**): Yield: 74% (172.1 mg). Pale yellow solid. Mp: 60-61 °C. ^1H NMR (300 MHz, CDCl_3) δ 7.46 - 7.37 (m, 3H), 7.34 - 7.28 (m, 2H), 3.00 (qq, $J = 7.4$ Hz, $^5J_{H-F} = 1.1$ Hz, 2H), 1.24 (t, $J = 7.4$ Hz, 3H), 1.16 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.5, 139.5 (q, $^3J_{C-F} = 3.3$ Hz), 136.2, 133.7, 130.4, 128.5, 128.3, 123.3 (q, $^1J_{C-F} = 269.0$ Hz), 114.8 (q, $^2J_{C-F} = 34.0$ Hz), 85.6, 65.3, 27.1, 19.6 (q, $^4J_{C-F} = 2.0$ Hz), 15.1; ^{19}F NMR (282 MHz, CDCl_3) δ -55.14; IR (UATR) 1754 cm^{-1} ; HRMS (ESI) m/z calcd for $[\text{M}+\text{Na}]^+$ ($[\text{C}_{18}\text{H}_{19}\text{NO}_2\text{F}_3\text{I}+\text{Na}]^+$) 488.0305, found 488.0305.

(**8b**): Yield: 50% (107.8 mg). Pale yellow solid. Mp: 59-60 °C. ^1H NMR (300 MHz, CDCl_3) δ 2.90 (qq, $J = 7.4$ Hz, $^5J_{H-F} = 1.2$ Hz, 2H), 2.83-2.77 (m, 2H), 1.62 (s, 9H), 1.59-1.46 (m, 2H), 1.17 (t, $J = 7.4$ Hz, 3H), 0.96 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.9, 138.3 (q, $^3J_{C-F} = 3.4$ Hz), 136.7, 123.3 (q, $^1J_{C-F} = 268.9$ Hz), 114.2 (q, $^2J_{C-F} = 33.7$ Hz), 86.0, 64.7 (q, $^3J_{C-F} = 1.9$ Hz), 31.0, 27.9, 23.0, 20.0 (q, $^4J_{C-F} = 2.0$ Hz), 15.2, 14.0; ^{19}F NMR (282 MHz, CDCl_3) δ -55.15; IR (UATR) 1753 cm^{-1} ; HRMS (ESI) m/z calcd for $[\text{M}+\text{Na}]^+$ ($[\text{C}_{15}\text{H}_{21}\text{NO}_2\text{F}_3\text{I}+\text{Na}]^+$) 454.0461, found 454.0457.

Typical procedure for the Suzuki-Miyaura coupling of 4-iodopyrrole with 4- phenylboronic acid

To a degassed solution of 4-iodopyrrole **8** (0.2 mmol) and phenylboronic acid (36.6 mg, 0.3 mmol) in toluene (2 mL) were added successively under argon atmosphere K_3PO_4 (85.0 mg, 0.4 mmol), S-Phos (8.2 mg, 0.02 mmol, 10 mol%) and $Pd(OAc)_2$ (2.3 mg, 0.01 mmol, 5 mol%). The resulting mixture was heated to 80 °C for 2 h. After cooling, the mixture was diluted with ether, filtered over a Celite[®] plug. After removal of solvents in vacuo, the crude product was purified by silica gel chromatography eluting with cyclohexane/ CH_2Cl_2 = 90/10.

(**9**): Yield: 95% (78.9 mg). White solid. Mp: 89-90 °C. 1H NMR (300 MHz, $CDCl_3$) δ 7.21-7.17 (m, 6H), 7.15-7.06 (m, 4H), 3.03 (qq, $J = 7.4$ Hz, $^5J_{H-F} = 0.9$ Hz, 2H), 1.32 (t, $J = 7.4$ Hz, 3H), 1.20 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.5, 137.7 (q, $^3J_{C-F} = 3.7$ Hz), 133.5, 132.9, 131.3, 130.8, 130.1, 127.9, 127.6, 127.4, 126.9, 124.3 (q, $^1J_{C-F} = 269.1$ Hz), 123.3 (q, $^3J_{C-F} = 1.9$ Hz), 112.5 (q, $^2J_{C-F} = 33.3$ Hz), 85.1, 27.2, 19.5, 15.3; ^{19}F NMR (282 MHz, $CDCl_3$) δ -52.80; IR (UATR) 1750 cm^{-1} ; HRMS (ESI) m/z calcd for $[M+Na]^+$ ($[C_{24}H_{24}NO_2F_3+Na]^+$) 438.1651, found 438.1647.

(**10**): Yield: 93% (70.9 mg). colorless oil. 1H NMR (300 MHz, $CDCl_3$) δ 7.39-7.28 (m, 3H), 7.24-7.20 (m, 2H), 2.97 (qq, $J = 7.4$ Hz, $^5J_{H-F} = 1.1$ Hz, 2H), 2.57-2.52 (m, 2H), 1.64 (s, 9H), 1.49-1.36 (m, 2H), 1.23 (t, $J = 7.4$ Hz, 3H), 0.77 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 136.5 (q, $^3J_{C-F} = 3.8$ Hz), 134.4, 132.3, 130.6, 127.9, 127.2, 124.4 (q, $^1J_{C-F} = 269.0$ Hz), 122.5 (q, $^3J_{C-F} = 1.9$ Hz), 112.4 (q, $^2J_{C-F} = 32.9$ Hz), 85.2, 27.9, 27.9, 24.0, 19.7, 15.3, 14.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -52.90; IR (UATR) 1749 cm^{-1} ; HRMS (ESI) m/z calcd for $[M+Na]^+$ ($[C_{21}H_{26}NO_2F_3+Na]^+$) 404.1808, found 404.1806.

Typical procedure for the Sonogashira coupling of 4-iodopyrrole with phenylacetylene

To a degassed solution of 4-iodopyrrole **8** (0.2 mmol) in triethylamine (2 mL) were added under argon atmosphere $PdCl_2(PPh_3)_2$ (7.0 mg, 0.01 mmol, 5 mol%) and CuI (3.8 mg, 0.02 mmol, 10 mol%). The reaction mixture was stirred for 5 min at room temperature. Then a solution of phenylacetylene (110 μ L, 1.0 mmol) in triethylamine (200 μ L) was added dropwise and the mixture was stirred for 2 h at

50 °C for **8a** and 80 °C for **8b**. After cooling, the mixture was diluted with diethylether (10 mL) and washed with brine. The organic extract was separated, dried over magnesium sulfate and concentrated. Chromatography on silica gel eluting with (cyclohexane/CH₂Cl₂ = 80/20 (**11**) and cyclohexane/CH₂Cl₂ = 90/10 (**12**)) afforded the desired product.

(**11**): Yield: 35% (30.8 mg). Yellow solid. Mp: 99-100 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.49-7.24 (m, 10H), 3.00 (qq, *J* = 7.4 Hz, ⁵*J*_{H-F} = 1.0 Hz, 2H), 1.27 (t, *J* = 7.4 Hz, 3H), 1.25 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 148.9, 138.4 (q, ³*J*_{C-F} = 3.5 Hz), 137.3, 132.2, 131.4, 129.2, 128.3, 128.1, 128.1, 128.0, 123.7, 123.7 (q, ¹*J*_{C-F} = 269.0 Hz), 113.4 (q, ²*J*_{C-F} = 34.0 Hz), 104.4 (q, ³*J*_{C-F} = 2.2 Hz), 92.5, 85.7, 81.5, 27.2, 19.3, 15.1; ¹⁹F NMR (282 MHz, CDCl₃) δ -55.72; IR (UATR) 1751 cm⁻¹, 2217 cm⁻¹; HRMS (ESI) *m/z* calcd for [M+Na]⁺ ([C₂₆H₂₄NO₂F₃+Na]⁺) 462.1651, found 462.1652

(**12**): Yield: 76% (61.6 mg). Cream-colored solid. Mp: 54-55 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.50-7.45 (m, 2H), 7.36-7.29 (m, 3H), 2.96-2.89 (m, 4H), 1.69-1.57 (m, 2H), 1.64 (s, 9H), 1.19 (t, *J* = 7.4 Hz, 3H), 0.99 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 149.1, 139.7, 137.2 (q, ³*J*_{C-F} = 3.7 Hz), 131.4, 128.4, 128.0, 124.0, 123.8 (q, ¹*J*_{C-F} = 268.8 Hz), 113.1 (q, ²*J*_{C-F} = 33.7 Hz), 103.8 (q, ³*J*_{C-F} = 2.2 Hz), 93.4, 85.8, 81.4, 29.3, 27.9, 23.3, 19.8, 15.1, 14.1; ¹⁹F NMR (282 MHz, CDCl₃) δ -55.65; IR (UATR) 1751 cm⁻¹, 2216 cm⁻¹; HRMS (ESI) *m/z* calcd for [M+Na]⁺ ([C₂₃H₂₆NO₂F₃+Na]⁺) 428.1808, found 428.1806.

■ ASSOCIATED CONTENT

Supporting Information

Copies of NMR spectra of all compounds. This material is available free of charge via the internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

E-mail : nicolas.gouault@univ-rennes1.fr

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