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Gold-Catalyzed Povarov-Type Reaction of Fluorinated Imino Esters and Furans

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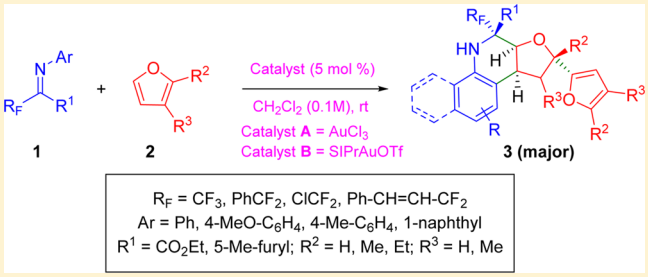
Supporting Information

ABSTRACT: A gold-catalyzed Povarov-type reaction of fluorinated imino esters and furans is described. The process, which takes place in dichoromethane at room temperature, gives rise to novel fluorinated tetrahydrofuran-fused tetrahydroquinolines in good yields and moderate levels of diastereoselectivity in a very simple manner. The reported examples expand the versatility of the Povarov reaction to unprecedented fluorinated substrates, generating scaffolds that contain quaternary α-amino acid units.



INTRODUCTION

The reaction of *N*-arylimines with electron-rich alkenes under Lewis or Brønsted acid catalysis, the so-called Povarov reaction, leads to the formation of tetrahydroquinoline derivatives in a very simple and efficient manner.[1] This family of compounds consists of extremely valuable scaffolds, being widespread in nature and having interesting biological properties.[2] For that reason, the Povarov reaction has gained a lot of interest, and significant advances have been made during the past several decades. Among them, tetrahydrofuran-fused tetrahydroquinolines have recently been disclosed as inhibitors of methionyl amino peptidase and as glucocorticoid receptor modulators, being potential therapeutic agents for the treatment of liver disorders and obesity (Figure 1).[3]

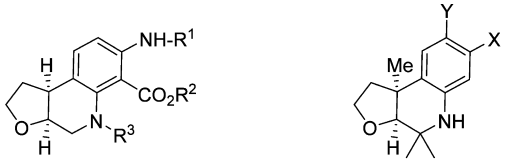


Figure 1. Biologically active tetrahydrofuran-fused tetrahydroquinolines.

On the other hand, it is well-known that the introduction of fluorine atoms into organic molecules is a powerful strategy to modify their physicochemical and biological properties.[4] Specifically, the replacement of one or more hydrogen atoms by fluorine in the vicinity of an amine function often results in a lower basicity, a higher metabolic stability, and a decrease in acute toxicity. For this reason, its introduction into potential drug candidates is a commonly employed approach in drug discovery programs.[5] Also, from an academic point of view, the generation of new fluorinated chemical entities is always of high interest. Despite the importance of tetrahydroquinolines in medicinal chemistry and the unquestionable utility of the Povarov reaction for their construction, the examples reported in the literature involving fluorinated substrates are quite limited.[6]

During an ongoing project in our laboratory directed toward the synthesis of new fluorinated chemical entities, we decided to explore the reactivity of fluorinated imino esters with electron-rich aromatic and heteroaromatic rings as nucleophilic partners in an aza-Friedel–Crafts reaction. This transformation would render valuable fluorinated quaternary α-amino acids. To the best of our knowledge, only one example of the participation of fluorinated imino esters in this type of process has been reported, employing indoles as nucleophiles.[7,8]

Initial attempts were performed with trifluoropyruvate-derived imino esters and substituted furans, in the presence of gold(I) complexes as Lewis acid catalysts. However, instead of the expected addition to the imine functionality, a Povarov-type reaction occurred, thus generating highly substituted fluorinated tetrahydrofuran-fused tetrahydroquinoline derivatives. As far as we know, this is the first example of a Povarov-type reaction involving furans as dienophiles. Here, we present the results, scope, and limitations of this unprecedented transformation.

RESULTS AND DISCUSSION

The reaction of trifluoromethyl imino ester **1a** with 2-methylfuran (**2a**) was selected as a model reaction to find the optimal conditions to carry out the desired tandem process. Several catalysts were tested, and the results obtained are shown in Table 1.

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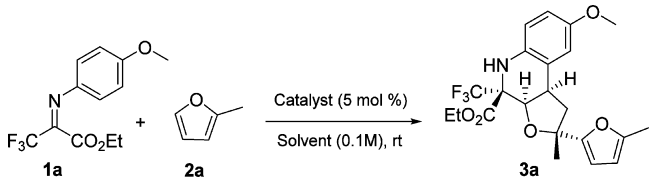
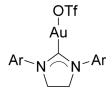
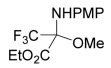
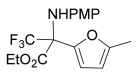
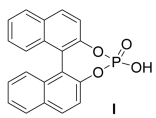
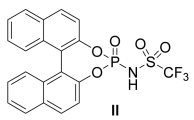
Table 1. Optimization of the Reaction Conditions for the Synthesis of Tricycle 3a



Entry	Catalyst	Solvent	Conversion	Product (isolated yield)[a]
1	$AuCl_3$	CH_2Cl_2	44	**3a** (37%)[b]
2	$AuCl_3$	CH_2Cl_2	>95	**3a** (81%)
3	PPh_3AuOTf	CH_2Cl_2	>95	**3a** (71%)
4	$[Au(P(4\text{-}CF_3C_6H_4)_3)]OTf$	CH_2Cl_2	>95	**3a** (75%)
5	 Ar = 2,6-(*i*-Pr)$_2$C$_6$H$_3$ SIPrAuOTf	CH_2Cl_2	>95	**3a** (86%)
6	$AuCl_3$	Toluene	<10	-
7	$AuCl_3$	THF	0	-
8	$AuCl_3$	MeCN	0	-
9	$AuCl_3$	MeOH		**5a** (82%)
10	$BF_3{\cdot}OEt_2$	CH_2Cl_2	>95	**3a** (67%)
11	TfOH	CH_2Cl_2	>95	**3a** (20%)
12	TFA	CH_2Cl_2	>95	 **4a** (86%)
13	 I	CH_2Cl_2	0	-
14	 II	CH_2Cl_2	0	-

[a]Reactions were performed with **1a** (0.2 mmol) and 2 equiv of **2a** (0.4 mmol) in the presence of the corresponding catalyst (5 mol %) at rt for 12 h. [b]In this case, only 1 equiv of furan **2a** (0.2 mmol) was employed.

According to previous reports regarding the reaction of furans with highly electrophilic imines in the presence of gold salts,[9] and considering the activation of our imine carbon in **1a** by the presence of two electron-withdrawing substituents, the reaction was initially performed with 1 equiv of furan **2a** and $AuCl_3$ as the catalyst in dichloromethane at room temperature. After 12 h, together with some unreacted starting material, the formation of a new product was observed (44% conversion). After isolation of this product by flash chromatography, the tricyclic tetrahydroquinoline **3a** was identified in 37% yield (Table 1, entry 1). The formation of **3a** would entail a Povarov-type process between the *N*-aromatic imine functionality in **1a** and one of the double bonds in the furan ring **2a**, followed by the addition of a second molecule of furan **2a** in a Friedel–Crafts-type reaction.[10]

In view of the incorporation of two molecules of furan into the final product, the reaction was then performed with 2 equiv of **2a**, giving compound **3a** in 81% isolated yield with complete conversion (Table 1, entry 2).[11] It is important to note that four stereocenters were created in only one reaction step and final tetrahydroquinoline products were obtained as mixtures of diastereoisomers, the major one being compound **3a** with the stereochemistry shown in the scheme in Table 1 (also see below).

Other gold(I) complexes were also tested. Hence, PPh_3AuOTf, in situ generated by combination of PPh_3AuCl and AgOTf,

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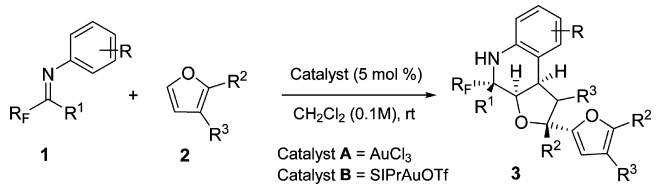
Table 2. Scope of the Tandem Povarov-Type/Friedel–Crafts Reaction



Entry	1, 2	R	R_F	R^1	R^2	R^3	Product Yield	dr-(catalyst)[a]
1	**1a, 2a**	4-OMe	CF_3	CO_2Et	Me	H	**3a**, 81%	63:37 (**A**)
2	**1b, 2a**	4-Me	CF_3	CO_2Et	Me	H	**3b**, 81%	48:52 (**A**)
3	**1c, 2a**	H	CF_3	CO_2Et	Me	H	**3c**, 82%	52:48 (**A**)
4	**1d, 2a**	$-C_4H_4-$[b]	CF_3	CO_2Et	Me	H	**3d**, 81%	48:52 (**A**)[c]
5	**1e, 2a**	4-CF_3	CF_3	CO_2Et	Me	H	-[d]	- (**A**)
6	**1f, 2a**	4-OMe	$PhCF_2$	CO_2Et	Me	H	**3f**, 84%	55:45 (**B**)
7	**1g, 2a**	4-OMe	$PhCH{=}CHCF_2$	CO_2Et	Me	H	**3g**, 79%	45:55 (**A**)
8	**1h, 2a**	4-OMe	$ClCF_2$	CO_2Et	Me	H	**3h**, 75%	59:41 (**B**)
9	**1i, 2a**	4-OMe	CF_3	5-Me-furyl	Me	H	**3i**, 78%	79:21 (**B**)
10	**1a, 2b**	4-OMe	CF_3	CO_2Et	Et	H	**3j**, 85%	45:55 (**A**)
11	**1b, 2b**	4-Me	CF_3	CO_2Et	Et	H	**3k**, 82%	46:54 (**A**)
12	**1c, 2b**	H	CF_3	CO_2Et	Et	H	**3l**, 75%	42:58 (**A**)
13	**1a, 2c**	4-OMe	CF_3	CO_2Et	Me	Me	**3m**, 85%	45:55 (**B**)[e]
14	**1a, 2e**	4-OMe	CF_3	CO_2Et	Ph	H	**3n**, 56%	71:29 (**B**)[e,f]
15	**1a, 2f**	4-OMe	CF_3	CO_2Et	2-thienyl	H	**3o**, 51%	57:43 (**B**)[g]
16	**1a, 2d**	4-OMe	CF_3	CO_2Et	OMe	H	-[h]	- (**A**)
17	**1a, 2e**	4-OMe	CF_3	CO_2Et	Benzyl	H	 **4b**, 65%	(**A**)
18	**1j, 2a**	4-OMe	CF_3	H	Me	H	 **4c**, 86%	(**A**)

[a]Diastereoisomeric ratio = major compound **3**/mixture of other diastereoisomers formed in the tandem process. [b]Starting imino ester **1d** contains a 1-naphthyl unit attached to the nitrogen. [c]Compound **3d** was isolated as a 3:1 mixture of unseparable diastereoisomers. [d]A complex mixture of unidentified products was observed. [e]Compound **3m** was obtained as a 1:1 mixture of diastereoisomers at the stereocenter bearing R^3. [f]Conversion of the process was 65%. [g]Conversion of the process was 68%. [h]Starting material was recovered unaltered.

afforded tricycle **3a** in slightly lower yield (Table 1, entry 3). The use of electronically deficient phosphines such as $P(4\text{-}CF_3C_6H_4)_3$ in the starting gold salt did not lead to better yields, giving rise to compound **3a** in 75% yield (Table 1, entry 4), whereas the NHC-derived gold(I) complex [[1,3-bis(2,6-diisopropylphenyl)-imidazolin-2-ylidene]gold triflate, SIPrAuOTf][12] provided the best results, leading to **3a** in 86% yield (Table 1, entry 5).

When solvent screening was performed subsequently, the reaction in toluene resulted in very poor conversion (<10%), and when more polar solvents such as THF or CH_3CN were used, the reactions did not proceed at all (Table 1, entries 6–8). Finally, when the reaction was carried out in MeOH, fluorinated hemiaminal **5a**, arising from the addition of the solvent to the starting iminoester **1a**, was the only identified product (Table 1, entry 9).

The tandem protocol could also be carried out with $BF_3{\cdot}OEt_2$ as the Lewis acid, although in a less efficient manner (Table 1, entry 10).[13] Additionally, Brønsted acids were also evaluated as catalysts in the synthesis of the tricyclic tetrahydroquinoline **3a**. In this context, the use of triflic acid led us to obtain compound **3a**, albeit in a low 20% yield (Table 1, entry 11), while TFA rendered the aza-Friedel–Crafts product **4a** in excellent yield (Table 1, entry 12). BINOL-derived phosphoric acids were examined next, either the acid **I** itself or the more acidic triflimide **II**. Unfortunately, the starting imino ester **1a** remained unaltered in either case (Table 1, entries 13 and 14).[14]

At this point, the optimal reaction conditions were established when imino ester **1a** and 2 equiv of furan **2a** were treated with either $AuCl_3$ or SIPrAuOTf as the catalysts in dichloromethane at room temperature. These conditions were applied to other fluorinated α-imino esters **1** and furans **2**. Thus, the evaluation of the scope of this tandem process produced the results displayed in Table 2.[15]

As indicated in Table 1, trifluoromethyl imino ester **1a** reacted with furan **2a** in the presence of $AuCl_3$ to render the corresponding tricyclic tetrahydroquinoline as a mixture of four diastereoisomers in 81% overall yield (Table 2, entry 1). Fortunately, the major diastereoisomer **3a**, which represented 63% of the product mixture, had a clearly different chromatographic behavior, and it could be isolated in 51% yield and fully characterized (see the Supporting Information). The rest of the diastereoisomers (30% of the product mixture) appeared together from the column, and it was not possible to separate them. Analogous performance was observed for other substrates **1**.

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The next step of our study was directed at the evaluation of the influence of the substituents on the aromatic ring of the starting imino esters **1**. Substrates **1b** (with a *p*-tolyl), **1c** (with a phenyl ring), and **1d** (with a 1-naphthyl) attached to the nitrogen underwent the tandem protocol efficiently, affording final products in 81%, 82%, and 81% overall yield, respectively (Table 2, entries 2−4). Remarkably, substrate **1d** gave access to a fluorinated steroid-type skeleton. On the other hand, imino ester **1e** bearing an electron-withdrawing group (CF_3) yielded a complex mixture of nonidentified products (Table 2, entry 5). The reaction was also compatible with other fluorinated moieties such as $PhCF_2$, $PhCH{=}CHCF_2$, or CF_2Cl. Tricycles **3f**, **3g**, and **3h** were, therefore, obtained as the major diastereoisomers in good overall yields (Table 2, entries 6−8). Trifluoromethyl ketimine **1i** was found to be a good partner in the tandem reaction with 2-methylfuran (**2a**), giving rise to tetrahydroquinoline **3i** as the major product from a mixture of diastereoisomers with 78% overall yield (Table 2, entry 9).

The scope of the furan counterpart **2** was also explored. Accordingly, 2-ethylfuran (**2b**) took part efficiently in the tandem process with trifluoromethyl imino esters **1a−c**, leading to the corresponding tricyclic derivatives **3j−l** in good yields (Table 2, entries 10−12). The introduction of a methyl substituent at position 3 of the furan ring (R^3) generated an additional stereocenter in the final products. An equimolecular mixture of diastereoisomers at the tetrahydrofuran ring in compound **3m** was observed in this case (Table 2, entry 13). Aryl and heteroaryl substituents were also suitable partners for the tandem protocol, although in those cases the conversion was not complete and some starting material was recovered (Table 2, entries 14 and 15).

Surprisingly, the more activated furan **2d**, bearing a methoxy group at position 2, did not react with imino ester **1a** under the reaction conditions (Table 2, entry 16), whereas other alkyl substituents at that position, such as the benzyl group in furan **2e**, gave the aza-Friedel−Crafts product **4b** in 65% yield (Table 2, entry 17).

Finally, fluorinated aldimine **1j** was also tested in its reaction with furan **2a**. Trifluoromethyl amine **4c**, arising from the aza-Friedel−Crafts reaction, was isolated in 86% yield (Table 2, entry 18).

The relative stereochemistry of the major diastereoisomer **3** was determined by means of NMR experiments on compound **3c**. Specifically, the combination of HOESY and NOESY studies led us to identify the arrangement of the protons and the trifluoromethyl group in the tricyclic structure. Initially, the relative disposition of the trifluoromethyl group and the tetrahydrofuran ring was elucidated by an HOESY experiment. The heteronuclear correlation between fluorine nuclei and protons H^a and H^b (Figure 2) allowed us to assign the relative *cis* stereochemistry at those positions. The *cis* relationship between those protons and the furan ring was determined by means of an NOESY experiment, which showed the correlation between proton H^a and protons H^c and H^d of the furan ring (Figure 2). The same stereochemical assignment was assumed for all tetrahydroquinolines **3**.

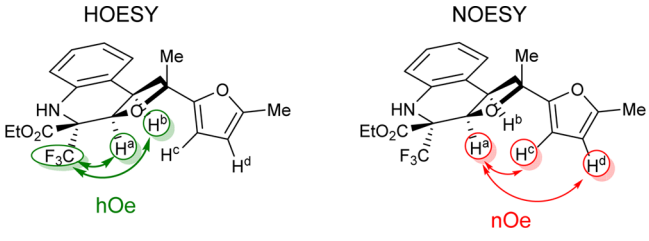

Figure 2. NMR experiments on compound **3a**.

A plausible mechanistic rationale for the transformation presented herein is depicted in Scheme 1. In the first step, imino ester **1** would be activated by the gold salt (acting as a σ-Lewis acid) for the attack of the furan ring through its position 5. This attack would generate intermediate **A**, which would evolve through the nucleophilic attack by the *ortho* position of the aromatic ring, giving rise to tricyclic intermediate **B** (aza-Diels−Alder product in a Povarov reaction).[16] Upon [1,3]-proton shift and coordination of the gold salt with the enol ether moiety (intermediate **C**), the nucleophilic addition of a second molecule of furan **2** would take place in a formal Friedel−Crafts-type process, consequently releasing the final product **3** and regenerating the gold catalytic species (Scheme 1). It is noteworthy to mention that this tandem protocol constitutes another example of the dual σ- and π-Lewis role imparted by gold salts.[17]

Considering this reaction pathway, it is possible to rationalize the results shown in Table 2. On one hand, the introduction of electron-withdrawing substituents into the aromatic ring (imino ester **1e**; R = CF_3) would decrease the nucleophilicity of the *ortho* position, avoiding the formation of intermediate **B** and, therefore, the whole process. On the other hand, the formation of intermediate **D** is most likely to play an important role in the success of the tandem protocol: after the activation of the enol ether functionality in intermediate **C** by the gold salt, the addition of the second molecule of furan would render final products **3** in an irreversible way. With more activated furans such as **2d** (R = CF_3), intermediate **B** would contain an acetal functionality instead of an enol ether. The activation of the acetal moiety would not take place in this case, and the equilibrium would be shifted to the starting material, which indeed remained unaltered. Alternatively, when steric hindrance at the 2-position of the furan increases, which is the case for 2-benzylfuran (**2e**), complexation of the gold salt is disfavored, thus rendering the aza-Friedel−Crafts products **4**. More difficult to explain is the behavior observed with fluorinated aldimine **1j**.

SUMMARY

In summary, we have developed a new tandem protocol that involves a Povarov-type reaction followed by a formal Friedel−Crafts reaction, which rendered furoquinoline derivatives **3** in good yields and moderate levels of diastereoselectivity. The process was efficiently catalyzed by gold complexes, either $AuCl_3$ or SIPrAuOTf, generating complex fluorinated scaffolds in a very simple manner. Additionally, major diastereoisomers could be separated from the rest in most cases, allowing their isolation and characterization. A wide variety of imino esters **1** were compatible with the process, in the aromatic moiety as well as in the fluorinated alkyl chain. However, the scope regarding the starting furans **2** is more limited. It is noteworthy that this is the first reported Povarov-type protocol involving furans as dienophiles.

EXPERIMENTAL SECTION

Reactions were carried out under an argon atmosphere unless otherwise indicated. The solvents were purified prior to use: THF, diethyl ether, and toluene were distilled from sodium/benzophenone, and dichloromethane and acetonitrile were distilled from calcium hydride. The reactions were monitored with the aid of thin-layer chromatography (TLC) on 0.25 mm precoated silica gel plates. Visualization was carried

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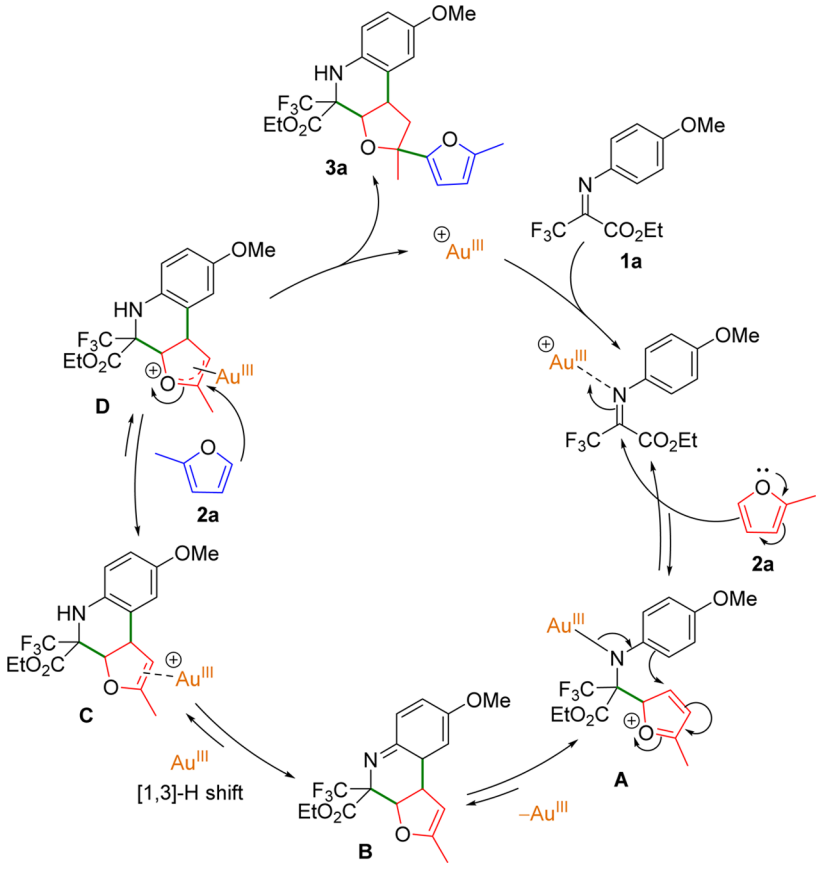
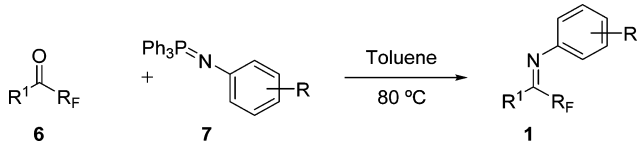
Scheme 1. Mechanistic Proposal for the Synthesis of Tricyclic Tetrahydroquinolines 3



out with UV light and ethanolic phosphomolybdic acid solution or potassium permanganate stain. Flash column chromatography was performed with the indicated solvents on silica gel 60 (particle size 0.040−0.063 mm). ^{1}H and ^{13}C NMR spectra were recorded on 300 and 500 MHz spectrometers, respectively. Chemical shifts are given in parts per million (δ), with reference to the residual proton resonances of the solvents. Coupling constants (J) are given in hertz. The letters m, s, d, t, and q stand for multiplet, singlet, doublet, triplet, and quartet, respectively. The letters br indicate that the signal is broad.

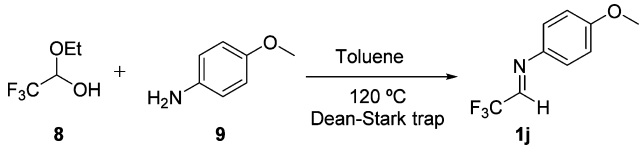
Preparation of the Starting Imines 1a–j. *Procedure A: Ketone or Ketoester Condensation.*



6 **7** **1**

To a solution of the iminophosphorane **7** (5 mmol) in dry toluene (20 mL) was added dropwise the corresponding fluorinated ketone (R^1 = 5-methylfuryl) or keto ester (R^1 = CO_2Et) **6** (5 mmol), and the reaction mixture was stirred at 80 °C for 18 h. Then the reaction mixture was cooled to room temperature, and the solvents were eliminated under reduced pressure. Et_2O (20 mL) was added and the reaction mixture cooled to 0 °C. The white precipitate was filtered through a pad of Celite and washed with cold Et_2O (3 × 10 mL). The filtrate was concentrated under reduced pressure and purified by flash column chromatography.

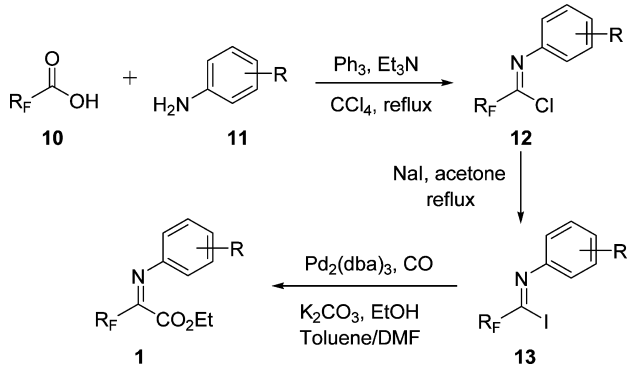
Procedure B: Aldehyde Condensation. Synthesis of ***1j****.*



8 **9** **1j**

To a solution of the trifluoroacetaldehyde ethyl hemiacetal (**8**) (5 mmol) and *p*-anisidine (**9**) (5 mmol) in dry toluene (15 mL) was added *p*-toluenesulfonic acid (5 mg), and the reaction mixture was stirred at reflux under an Ar atmosphere for 1.5 h with a Dean−Stark trap. The mixture was washed with a saturated solution of $NaHCO_3$ (3 × 15 mL) and brine (20 mL). The organic phase was then dried over Na_2SO_4, and the solvents were eliminated under reduced pressure. The crude product was purified by Kugelrohr distillation.

Procedure C: Alkoxycarbonylation.



10 **11** **12** **13** **1**

To a solution of triphenylphosphine (33 mmol) and triethylamine (13.2 mmol) in CCl_4 (20 mL) was added the corresponding carboxylic acid **10** (11 mmol), and the reaction mixture was stirred for 5 min at room temperature. Then the arylamine **11** (13.2 mmol) dissolved in more CCl_4 (10 mL) was added and the reaction mixture refluxed overnight. After cooling to room temperature and evaporation of the solvents, triphenylphosphine oxide precipitate was eliminated by filtration with hexane and the crude product purified by column chromatography.

NaI (11.6 mmol) was added to a solution of the corresponding imidoyl chloride **12** (7.1 mmol) in dry acetone (20 mL), and the mixture

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was stirred at room temperature protected from light for 48 h. The reaction mixture was then quenched with a saturated aqueous solution of $Na_2S_2O_3$, and the aqueous layer was extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with brine (3 × 15 mL) and dried over anhydrous Na_2SO_4. Filtration and evaporation of the solvents quantitatively gave the corresponding crude imidoyl iodides **13** as yellow oils; these were subsequently used in the next step of the synthesis with no further purification.

Under a CO atmosphere (1 atm), a solution of the previously obtained imidoyl iodide **13** in a toluene/DMF mixture (10 mL:1 mL) and ethanol (8.5 mmol) were both added to a two-necked flask containing K_2CO_3 (14.2 mmol) and palladium catalyst $Pd_2(dba)_3{\cdot}CHCl_3$ (0.28 mmol). The reaction mixture was stirred at room temperature until the starting material was totally consumed, as confirmed by means of TLC. The crude reaction mixture was then filtered through a silica pad and washed with CH_2Cl_2. The solvents were eliminated under reduced pressure, and the mixture was purified by means of flash column chromatography.

*Ethyl 3,3,3-Trifluoro-2-[(4-methoxyphenyl)imino]propanoate (**1a**).* Following general procedure A, from 5 mmol of the corresponding iminophosphorane and 5 mmol of trifluoropyruvate, 4.6 mmol (92%) of the desired imine was obtained after purification by column chromatography (hexanes:EtOAc = 10:1) as an orange oil.

Spectroscopic data for the title compound are consistent with the literature.[18]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.01 (d, J = 9.0 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 4.25 (q, J = 7.1 Hz, 2H), 3.82 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H).

*Ethyl 3,3,3-Trifluoro-2-(p-tolylimino)propanoate (**1b**).* Following general procedure A, from 5 mmol of the corresponding iminophosphorane and 5 mmol of trifluoropyruvate, 4.55 mmol (91%) of the desired imine was obtained after purification by column chromatography (hexanes:EtOAc = 10:1) as a pale yellow oil.

Spectroscopic data for the title compound are consistent with the literature.[18]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.09 (d, J = 7.9 Hz, 2H), 6.81 (d, J = 8.3 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 2.28 (s, 3H), 1.05 (t, J = 7.1 Hz, 3H).

*Ethyl 3,3,3-Trifluoro-2-(phenylimino)propanoate (**1c**).* Following general procedure A, from 5 mmol of the corresponding iminophosphorane and 5 mmol of trifluoropyruvate, 4.75 mmol (95%) of the desired imine was obtained after purification by column chromatography (hexanes:EtOAc = 10:1) as a pale yellow oil.

Spectroscopic data for the title compound are consistent with the literature.[18]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.24−7.31 (m, 1H), 7.10−7.20 (m, 1H), 7.02−7.09 (m, 1H), 6.83−6.89 (m, 2H), 4.08 (q, J = 7.2 Hz, 2H), 0.97 (t, J = 7.2 Hz, 3H).

*Ethyl (E)-3,3,3-Trifluoro-2-[(2-methoxyphenyl)imino]propanoate (**1d**).* Following general procedure A, from 5 mmol of the corresponding iminophosphorane and 5 mmol of trifluoropyruvate, 4.35 mmol (87%) of the desired imine was obtained after purification by column chromatography (hexanes:EtOAc = 10:1) as a brown oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93−7.86 (m, 2H), 7.77 (d, J = 8.4 Hz, 1H), 7.61−7.54 (m, 2H), 7.41 (dd, J = 8.3, 7.3 Hz, 1H), 6.87 (dd, J = 7.3, 0.9 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 0.93 (t, J = 7.1 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −69.92 (s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.8 (s), 149.8 (q, J = 36.9 Hz), 143.6 (s), 134.1 (s), 128.2 (s), 127.8 (s), 127.4 (s), 127.0 (s), 126.6 (s), 125.4 (s), 123.6 (s), 118.6 (q, J = 277.5 Hz), 113.1 (s), 63.1 (s), 13.8 (s). HRMS (ES): calcd for (M + 1) $C_{15}H_{12}F_3NO_2F_3$ 296.0893, found 296.0899.

*Ethyl 3,3,3-Trifluoro-2-{[4-(trifluoromethyl)phenyl]imino}-propanoate (**1e**).* Following general procedure A, from 5 mmol of the corresponding iminophosphorane and 5 mmol of trifluoropyruvate, 4.25 mmol (85%) of the desired imine was obtained after purification by column chromatography (hexanes:EtOAc = 10:1) as a pale yellow oil.

Spectroscopic data for the title compound are consistent with the literature.[19]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (d, J = 8.2 Hz, 2H), 6.94 (d, J = 8.1 Hz, 2H), 4.11 (q, J = 7.1 Hz, 2H), 1.00 (t, J = 7.1 Hz, 3H).

*Ethyl (E)-3,3-Difluoro-2-[(4-methoxyphenyl)imino]-3-phenylpropanoate (**1f**).* Following general procedure C, from 11 mmol of the corresponding carboxylic acid and 13.2 mmol of *p*-anysidine, 8.91 mmol (81%) of the desired imine was obtained after purification by column chromatography (hexanes:EtOAc = 10:1) as an orange oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68−7.65 (m, 2H), 7.50−7.46 (m, 3H), 6.91 (d, J = 9.1 Hz, 2H), 6.83 (d, J = 9.1 Hz, 2H), 4.16 (q, J = 7.1 Hz, 2H), 3.79 (s, 3H), 1.09 (t, J = 7.1 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −97.57 (s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.7 (s), 158.9 (s), 140.9 (s), 135.2 (s), 131.0 (s), 130.9 (s), 129.4 (s), 128.8 (s), 126.4 (t, J = 6.0 Hz), 122.0 (s), 117.3 (t, J = 246.4 Hz), 114.5 (s), 62.5 (s), 55.8 (s), 14.2 (s). HRMS (ES): calcd for (M + 1) $C_{18}H_{17}F_2NO_3$ 334.1249, found 334.1242.

*Ethyl (2E,4E)-3,3-Difluoro-2-[(4-methoxyphenyl)imino]-5-phenylpent-4-enoate (**1g**).* Following general procedure C, from 11 mmol of the corresponding carboxylic acid and 13.2 mmol of *p*-anysidine, 8.69 mmol (79%) of the desired imine was obtained after purification by column chromatography (hexanes:EtOAc = 10:1) as an orange oil.

Spectroscopic data for the title compound are consistent with the literature.[20]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53−7.50 (m, 2H), 7.45−7.35 (m, 2H), 7.15 (dt, J = 4.5, 2.5 Hz, 1H), 6.98 (d, J = 9.0 Hz, 2H), 6.88 (d, J = 9.0 Hz, 2H), 6.56 (dt, J = 16.2, 11.5 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 3.82 (s, 3H), 1.15 (t, J = 7.1 Hz, 3H).

*Ethyl (E)-3-Chloro-3,3-difluoro-2-[(4-methoxyphenyl)imino]-propanoate (**1h**).* Following general procedure C, from 11 mmol of the corresponding carboxylic acid and 13.2 mmol of *p*-anysidine, 9.79 mmol (89%) of the desired imine was obtained after purification by column chromatography (hexanes:EtOAc = 10:1) as a brown oil.

Spectroscopic data for the title compound are consistent with the literature.[18]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.02 (d, J = 9.0 Hz, 2H), 6.89 (d, J = 9.0 Hz, 2H), 4.25 (q, J = 7.2 Hz, 2H), 3.82 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H).

*(E)-2,2,2-Trifluoro-N-(4-methoxyphenyl)-1-(5-methylfuran-2-yl)-ethan-1-imine (**1i**).* Following general procedure A, from 5 mmol of the corresponding iminophosphorane and 5 mmol of the corresponding ketone, 4.45 mmol (89%) of the desired imine was obtained after purification by distillation under reduced pressure as an orange oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.90 (d, J = 9.0 Hz, 2H), 6.78 (d, J = 9.0 Hz, 2H), 6.31 (d, J = 3.5 Hz, 1H), 5.99 (dd, J = 3.6, 0.9 Hz, 1H), 3.82 (s, 3H), 2.21 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −69.20 (d, J = 0.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.5 (s), 156.4 (s), 144.8 (s), 144.4 (s), 142.9 (s), 142.5 (s), 120.7 (s), 120.7 (s), 120.1 (q, J = 278.13), 119.9 (s), 114.8 (s), 108.9 (s), 55.9 (s), 14.0 (s). HRMS (ES): calcd for (M + 1) $C_{14}H_{12}F_3NO_2$ 284.0893, found 284.0898.

*2,2,2-Trifluoro-N-(4-methoxyphenyl)ethan-1-imine (**1j**).* Following general procedure B, from 5 mmol of the corresponding amine **9** and 5 mmol of the corresponding hemiacetal **8**, 3.75 mmol (75%) of the desired imine was obtained after purification by distillation under reduced pressure as a pale yellow oil.

Spectroscopic data for the title compound are consistent with the literature.[21]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85 (q, J = 3.7 Hz, 1H), 7.31 (d, J = 9.0 Hz, 2H), 6.96 (d, J = 9.0 Hz, 2H), 3.86 (s, 3H).

General Procedure for the Gold Catalysis. To a small vial fitted with a screw cap and a magnet was added 0.1 mmol of the corresponding imine with 1 mL of dry DCM, and the vial was purged with nitrogen. Then 0.2 mmol of the corresponding furan was added, 5 mol % of either gold trichloride **A** or carbene gold(I) catalyst **B** was loaded, and the reaction mixture was stirred overnight at room temperature. Once the reaction time was completed, the mixture was filtered through a silica pad and the product purified by flash column chromatography.

Ethyl (2R,3aR*,4S*,9bR*)-8-Methoxy-2-methyl-2-(5-methylfuran-2-yl)-4-(trifluoromethyl)-1,2,3a,4,5,9b-hexahydrofuro[2,3-c]-quinoline-4-carboxylate (**3a**).* Following the general procedure, from 28 mg of imine **1a**, 18 μL of 2-methylfuran, and 1.5 mg of **A**, 35.5 mg (81%) of the desired product was obtained, after purification by column chromatography using as the eluent a mixture of hexanes/DCM/EtOAc (9:0.5:0.1), as a mixture of diastereoisomers (63:18:4:15). **3a** was obtained (22 mg, 51%) as a yellow oil, while the rest of the diastereoisomers eluted together from the column.

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Major Diastereoisomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.69−6.68 (m, 3H), 6.01 (d, J = 3.1 Hz, 1H), 5.87−5.85 (m, 1H), 4.83 (d, J = 4.8 Hz, 1H), 4.43 (dq, J = 10.7, 7.1 Hz, 1H), 4.29 (dq, J = 10.7, 7.1 Hz, 1H), 3.76 (s, 3H), 3.58−3.54 (m, 1H), 2.97 (dd, J = 12.9, 7.5 Hz, 1H), 2.36 (dd, J = 12.9, 1.2 Hz, 1H), 2.28 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H), 1.16 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −74.96 (s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3 (s), 157.3 (s), 153.2 (s), 151.6 (s), 133.8 (s), 124.1 (q, J = 293.5 Hz), 123.1 (s), 116.8 (s), 113.8 (s), 113.4 (s), 105.8 (s), 105.1 (s), 79.5 (s), 74.7 (s), 64.4 (q, J = 26.8 Hz), 63.2 (s), 55.8 (s), 45.4 (s), 39.2 (s), 26.9 (s), 13.9 (s), 13.7 (s). HRMS (ES): calcd for (M + 1) $C_{22}H_{24}F_3NO_5$ 440.1679, found 440.1694.

Ethyl (2R,3aR*,4S*,9bR*)-2,8-Dimethyl-2-(5-methylfuran-2-yl)-4-(trifluoromethyl)-1,2,3a,4,5,9b-hexahydrofuro[2,3-c]quinoline-4-carboxylate (**3b**).* Following the general procedure, from 26 mg of imine **1b**, 18 μL of 2-methylfuran, and 1.5 mg of **A**, 34.3 mg (81%) of the desired product was obtained, after purification by column chromatography using as the eluent a mixture of hexanes/DCM/EtOAc (9:0.5:0.1), as a mixture of diastereoisomers (48:6:12:26:8). **3b** was obtained (16 mg, 39%) as a yellow oil, while the rest of the diastereoisomers eluted together from the column.

Major Diastereoisomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.90−6.86 (m, 2H), 6.63 (d, J = 8.0 Hz, 1H), 6.02 (d, J = 3.1 Hz, 1H), 5.87 (dq, J = 3.0, 1.0 Hz, 1H), 4.85 (sa, 1H), 4.83 (s, 1H), 4.44 (dq, J = 10.6, 7.1 Hz, 1H), 4.29 (dq, J = 10.7, 7.1 Hz, 1H), 3.58−3.54 (m, 1H), 2.96 (dd, J = 12.9, 7.4 Hz, 1H), 2.38 (dd, J = 12.9, 1.3 Hz, 1H), 2.28 (d, J = 0.9 Hz, 3H), 2.25 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H), 1.15 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −75.03 (s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3 (s), 157.5 (s), 151.5 (s), 137.4 (s), 128.9 (s), 128.4 (s), 128.1 (s), 124.2 (q, J = 290.1 Hz), 121.6 (s), 115.5 (s), 105.8 (s), 105.0 (s), 79.6 (s), 74.8 (s), 64.3 (q, J = 26.7 Hz), 63.1 (s), 45.4 (s), 38.9 (s), 26.9 (s), 20.8 (s), 13.9 (s), 13.7 (s). HRMS (ES): calcd for (M + 1) $C_{22}H_{24}F_3NO_4$ 424.1730, found 424.1746.

Ethyl (2R,3aR*,4S*,9bR*)-2-Methyl-2-(5-methylfuran-2-yl)-4-(trifluoromethyl)-1,2,3a,4,5,9b-hexahydrofuro[2,3-c]quinoline-4-carboxylate (**3c**).* Following the general procedure, from 25 mg of imine **1c**, 18 μL of 2-methylfuran, and 1.5 mg of **A**, 33.5 mg (82%) of the desired product was obtained, after purification by column chromatography using as the eluent a mixture of hexanes/DCM/EtOAc (9:0.5:0.1), as a mixture of diastereoisomers (52:9:28:5:6). **3c** was obtained (17 mg, 42%) as a yellow oil, while the rest of the diastereoisomers eluted together from the column.

Major Diastereoisomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.12−7.04 (m, 2H), 6.79 (td, J = 7.5, 1.2 Hz, 1H), 6.71 (dd, J = 8.0, 1.0 Hz, 1H), 6.02 (d, J = 3.0 Hz, 1H), 5.87 (dd, J = 3.0, 1.0 Hz, 1H), 4.96 (s, 1H), 4.86 (dd, J = 4.8, 1 Hz, 1H), 4.44 (dq, J = 10.8, 7.1 Hz, 1H), 4.30 (dq, J = 10.8, 7.1 Hz, 1H), 3.61−3.57 (m, 1H), 2.98 (dd, J = 12.9, 7.4 Hz, 1H), 2.39 (dd, J = 12.9, 1.1 Hz, 1H), 2.28 (d, J = 1 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H), 1.13 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −75.12 (s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.2 (s), 157.4 (s), 151.6 (s), 139.9 (s), 128.6 (s), 127.4 (s), 124.1 (q, J = 295.4 Hz), 121.6 (s), 119.3. (s), 115.4 (s), 105.8 (s), 105.0 (s), 79.6 (s), 74.7 (s), 64.1 (q, J = 26.5 Hz) 63.2 (s), 45.4 (s), 38.9 (s), 26.9 (s), 13.9 (s), 13.7 (s). HRMS (ES): calcd for (M + 1) $C_{21}H_{22}F_3NO_4$ 410.1574, found 410.1585.

Ethyl (3aR,11S*,11aR*)-2-Methyl-2-(5-methylfuran-2-yl)-11-(trifluoromethyl)-2,3,3a,10,11,11a-hexahydrobenzo[h]furo[2,3-c]-quinoline-11-carboxylate (**3d**).* Following the general procedure, from 29.5 mg of imine **1d**, 18 μL of 2-methylfuran, and 3 mg of **B**, 37.4 mg (85%) of the desired product was obtained, after purification by column chromatography using as the eluent a mixture of hexanes/DCM/EtOAc (9:0.5:0.1), as a mixture of diastereoisomers (48:21:13:3:15). **3d** was obtained (18 mg, 40%) as a brown oil together with another unseparable diastereoisomer in a 3:1 ratio, while the rest of the diastereoisomers eluted together from the column.

Major Diastereoisomer Mixture (3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (dd, J = 8.2, 0.9 Hz, 1H), 7.95 (dd, J = 8.2, 1.1 Hz, 0.3H), 7.80−7.77 (m, 1H), 7.72−7.69 (m, 0.3H), 7.55−7.41 (m, 2.6H), 7.37 (d, J = 8.5 Hz, 1H), 7.25 (d, J = 10.3 Hz, 1.3H), 7.13 (d, J = 8.5 Hz, 0.3H), 6.02 (d, J = 3.0 Hz, 1H), 5.87 (dq, J = 3.0, 1.0 Hz, 1H), 5.56 (s, 1H), 5.48 (d, J = 3.0 Hz, 0.3H), 5.44 (s, 0.3H), 5.24 (dq, J = 3.0, 1.0 Hz, 0.3H), 4.96 (d, J = 4.8 Hz, 1.3H), 4.55−4.31 (m, 2.6H), 3.77−3.73 (m, 1.3H), 3.05 (dd, J = 13.0, 7.5 Hz, 1H), 2.87 (dd, J = 13.0, 0.6 Hz, 0.3H), 2.58 (dd, J = 13.0, 7.5 Hz, 0.3H), 2.49 (dd, J = 13.0, 0.6 Hz, 1H), 2.29 (d, J = 0.9 Hz, 3H), 1.64 (d, J = 0.9 Hz, 1H), 1.55 (s, 1H), 1.40 (t, J = 7.1 Hz, 1H), 1.31 (t, J = 7.1 Hz, 3H), 1.05 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −74.91 (s), −75.05 (s). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.3 (s), 166.3 (s), 157.3 (s), 155.6 (s), 151.4 (s), 150.1 (s), 134.6 (s), 134.3 (s), 133.0 (s), 132.9 (s), 128.3 (s), 128.1 (s), 126.3 (s), 126.2 (s), 125.7 (s), 125.5 (s), 125.3 (s), 125.1 (s),123.9 (q, J = 288.2 Hz), 123.8 (s), 120.6 (s), 120.4 (s), 119.7 (s), 119.2 (s), 116.2 (s), 116.0 (s), 105.7 (s), 105.4 (s), 104.9 (s), 104.7 (s), 79.8 (s), 79.6 (s), 74.4 (s), 64.1 (q, J = 27.1 Hz), 63.3 (s), 46.1 (s), 44.8 (s), 39.8 (s), 39.3 (s), 31.6 (s), 27.1 (s), 26.8 (s), 22.7 (s), 14.1 (s), 14.0 (s), 13.8 (s), 13.6 (s), 12.7 (s). HRMS (ES): calcd for (M + MeOH) $C_{25}H_{24}F_3NO_4$ 492.1992, found 492.1999.

Ethyl (2S,3aS*,4R*,9bS*)-4-[Difluorophenylmethyl]-8-methoxy-2-methyl-2-(5-methylfuran-2-yl)-1,2,3a,4,5,9b-hexahydrofuro[2,3-c]quinoline-4-carboxylate (**3f**).* Following the general procedure, from 33 mg of imine **1f**, 18 μL of 2-methylfuran, and 3 mg of **B**, 41.7 mg (84%) of the desired product was obtained, after purification by column chromatography using as the eluent a mixture of hexanes/DCM/EtOAc (9:0.5:0.1), as a mixture of diastereoisomers (55:4:27:14). **3f** was obtained (23 mg, 46%) as a yellow oil, while the rest of the diastereoisomers eluted together from the column.

Major Diastereoisomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45−7.35 (m, 5H), 6.72−6.69 (m, 2H), 6.64 (d, J = 9.4 Hz, 1H), 6.04 (d, J = 3.0 Hz, 1H), 5.89−5.88 (m, 1H), 5.11 (d, J = 4.8 Hz, 1H), 4.50 (br s, 1H), 4.33 (dq, J = 10.7, 7.1 Hz, 1H), 4.12 (dq, J = 10.7, 7.1 Hz, 1H), 3.79 (s, 3H), 3.74−3.72 (m, 1H), 3.01 (dd, J = 12.9, 7.6 Hz, 1H), 2.39 (dd, J = 12.9, 0.8 Hz, 1H), 2.30 (d, J = 0.7 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H), 1.17 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −103.19 (d, J = 37.2 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.0 (s), 156.8 (s), 151.6 (s), 150.2 (s), 133.5 (s), 132.5 (t, J = 26.0 Hz), 129.2 (s), 126.8 (s), 125.4 (t, J = 6.3 Hz), 123.0 (s), 119.9 (t, J = 233.4 Hz), 115.2 (s), 112.8 (s), 111.9 (s), 104.6 (s), 103.6 (s), 77.9 (s), 74.1 (s), 65.4 (t, J = 26.8 Hz), 61.3 (s), 54.7 (s), 44.5 (s), 38.7 (s), 26.0 (s), 12.8 (s), 12.6 (s). HRMS (ES): calcd for (M + 1) $C_{28}H_{29}F_2NO_5$ 498.2087, found 498.2096.

Ethyl (2S,3aS*,4R*,9bS*)-4-[(E)-1,1-Difluoro-3-phenylallyl]-8-methoxy-2-methyl-2-(5-methylfuran-2-yl)-1,2,3a,4,5,9b-hexahydrofuro[2,3-c]quinoline-4-carboxylate (**3g**).* Following the general procedure, from 36 mg of imine **1g**, 18 μL of 2-methylfuran, and 1.5 mg of **A**, 41.3 mg (79%) of the desired product was obtained, after purification by column chromatography using as the eluent a mixture of hexanes/DCM/EtOAc (9:0.5:0.1), as a mixture of diastereoisomers (45:17:15:4:19). **3g** was obtained (23 mg, 36%) as a yellow oil, while the rest of the diastereoisomers eluted together from the column.

Major Diastereoisomer. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24−7.21 (m, 3H), 7.15 (dd, J = 6.9, 2.7 Hz, 2H), 6.83 (dd, J = 16.1, 2.2 Hz, 1H), 6.63 (d, J = 1.5 Hz, 2H), 6.55 (s, 1H), 6.11 (dt, J = 16.1, 12.1 Hz, 1H), 5.93 (d, J = 3.0 Hz, 1H), 5.78−5.77 (m, 1H), 4.79 (d, J = 4.8 Hz, 1H), 4.74 (s, 1H), 4.33 (dq, J = 10.7, 7.1 Hz, 1H), 4.19 (dq, J = 10.7, 7.1 Hz, 1H), 3.67 (s, 3H), 3.45 (dd, J = 6.3, 5.6 Hz, 1H), 2.85 (dd, J = 12.9, 7.6 Hz, 1H), 2.24 (dd, J = 12.9, 1.1 Hz, 1H), 2.19 (d, J = 0.8 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H), 1.08 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −103.00 (ddd, J = 246.1, 11.6, 2.3 Hz, 1F), −105.88 (dd, J = 242.1, 12.4 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.3 (s), 157.7 (s), 152.8 (s), 151.3 (s), 135.1 (t, J = 9.5 Hz), 134.9 (s), 134.8 (s), 129.1 (s), 128.7 (s), 127.3 (s), 123.6 (s), 120.3 (t, J = 254.4 Hz), 120.0 (t, J = 24.4 Hz), 116.6 (s), 113.7 (s), 113.4 (s), 105.6 (s), 104.6 (s), 78.9 (s), 75.2 (s), 66.4 (t, J = 26.2 Hz), 62.4 (s), 55.8 (s), 45.5 (s), 39.3 (s), 27.0 (s), 13.9 (s), 13.6 (s). HRMS (ES): calcd for (M + 1) $C_{30}H_{31}F_2NO_5$ 524.2243, found 524.2246.

Ethyl (2S,3aS*,4R*,9bS*)-4-(Chlorodifluoromethyl)-8-methoxy-2-methyl-2-(5-methylfuran-2-yl)-1,2,3a,4,5,9b-hexahydrofuro[2,3-c]quinoline-4-carboxylate (**3h**).* Following the general procedure, from 29 mg of imine **1h**, 18 μL of 2-methylfuran, and 3 mg of **B**, 34.1 mg (75%) of the desired product was obtained, after purification by column chromatography using as the eluent a mixture of hexanes/DCM/EtOAc (9:0.5:0.2), as a mixture of diastereoisomers (59:22:5:14). **3h** was obtained (20 mg, 44%) as a brown oil, while the rest of the diastereoisomers eluted together from the column.

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Major Diastereoisomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.71−6.69 (m, 3H), 6.03 (d, J = 3.0 Hz, 1H), 5.88 (dd, J = 3.0, 1.0 Hz, 1H), 4.92 (d, J = 3.8 Hz, 2H), 4.45 (dq, J = 10.7, 7.1 Hz, 1H), 4.31 (dq, J = 10.7, 7.1 Hz, 1H), 3.78 (s, 3H), 3.64−3.57 (m, 1H), 2.99 (dd, J = 12.9, 7.5 Hz, 1H), 2.39 (dd, J = 12.9, 0.9 Hz, 1H), 2.30 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H), 1.18 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −58.98 (d, J = 158.8 Hz, 1F), −60.78 (dd, J = 158.8, 2.1 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.5 (s), 157.3 (s), 152.9 (s), 151.4 (s), 133.7 (s), 129.3 (dd, J = 311.1, 305.5 Hz), 122.9 (s), 116.4 (s), 113.7 (s), 113.2 (s), 105.7 (s), 104.9 (s), 79.3 (s), 74.7 (s), 68.5 (t, J = 22.6 Hz), 63.0 (s), 55.7 (s), 45.3 (s), 39.2 (s), 26.8 (s), 13.8 (s), 13.6 (s). HRMS (ES): calcd for (M + 1) $C_{22}H_{24}ClF_2NO_5$ 456.1384, found 456.1390.

(2R,3aR*,4S*,9bR*)-8-Methoxy-2-methyl-2,4-bis(5-methylfuran-2-yl)-4-(trifluoromethyl)-1,2,3a,4,5,9b-hexahydrofuro[2,3-c]quinoline (**3i**).* Following the general procedure, from 28 mg of imine **1k**, 21 μL of 2-ethylfuran, and 1.5 mg of **B**, 34.9 mg (78%) of the desired product was obtained, after purification by column chromatography using as the eluent a mixture of hexanes/DCM/EtOAc (9:0.5:0.2), as a mixture of diastereoisomers (79:4:11:3:3). **3i** was obtained (28 mg, 61%) as a yellow oil, while the rest of the diastereoisomers eluted together from the column.

Major Diastereoisomer. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.67 (d, J = 8.7 Hz, 1H), 6.59 (dd, J = 8.7, 2.4 Hz, 1H), 6.47 (d, J = 2.4 Hz, 1H), 6.10 (d, J = 3.2 Hz, 1H), 6.05 (d, J = 3.0 Hz, 1H), 5.83 (dd, J = 3.0, 1.0 Hz, 1H), 5.78 (dd, J = 3.2, 1.0 Hz, 1H), 4.90 (d, J = 5.8 Hz, 1H), 4.20 (br s, 1H), 3.66 (s, 3H), 3.32−3.28 (m, 1H), 2.85 (dd, J = 12.8, 8.2 Hz, 1H), 2.23 (d, J = 0.8 Hz, 3H), 2.15 (d, J = 0.7 Hz, 3H), 2.07 (dd, J = 12.8, 3.3 Hz, 1H), 1.29 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −74.13 (s). ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.2 (s), 152.8 (s), 151.9 (s), 150.4 (s), 147.0 (s), 133.1 (s), 125.3 (s), 123.5 (q, J = 286.4 Hz), 116.7 (s), 112.7 (s), 111.9 (s), 109.9 (s), 105.5 (s), 104.9 (s), 104.1 (s), 80.0 (s), 60.6 (q, J = 27.7 Hz), 54.5 (s), 43.6 (s), 39.2 (s), 29.9 (s), 25.8 (s), 12.7 (s), 12.6 (s). HRMS (ES): calcd for (M + 1) $C_{24}H_{24}F_3NO_4$ 448.1730, found 448.1740.

Ethyl (2R,3aR*,4S*,9bR*)-2-Ethyl-2-(5-ethylfuran-2-yl)-8-methoxy-4-(trifluoromethyl)-1,2,3a,4,5,9b-hexahydrofuro[2,3-c]quinoline-4-carboxylate (**3j**).* Following the general procedure, from 28 mg of imine **1a**, 21 μL of 2-ethylfuran, and 1.5 mg of **A**, 39.7 mg (85%) of the desired product was obtained, after purification by column chromatography using as the eluent a mixture of hexanes/DCM/EtOAc (9:0.5:0.2), as a mixture of diastereoisomers (45:24:10:12:9). **3j** was obtained (18 mg, 38%) as a yellow oil, while the rest of the diastereoisomers eluted together from the column.

Major Diastereoisomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.67−6.62 (m, 3H), 6.06 (d, J = 3.1 Hz, 1H), 5.89 (dt, J = 3.1, 1.0 Hz, 1H), 4.74 (sa, 1H), 4.73 (s, 1H), 4.42 (ddd, J = 12.6, 8.1, 4.5 Hz, 1H), 4.38−4.30 (m, 1H), 3.75 (s, 3H), 3.55−3.51 (m, 1H), 2.90 (dd, J = 13.0, 8.0 Hz, 1H), 2.62 (q, J = 7.6 Hz, 2H), 2.35 (dd, J = 13.0, 1.7 Hz, 1H), 1.48 (q, J = 7.4 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.6 Hz, 3H), 0.52 (t, J = 7.4 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −74.92 (s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3 (s), 157.3 (s), 155.8 (s), 153.3 (s), 133.7 (s),124.2 (q, J = 290.1 Hz), 123.6 (s), 116.8 (s), 113.8 (s), 113.4 (s), 105.7 (s), 104.1 (s), 83.5 (s), 74.2 (s),64.5 (q, J = 26.7 Hz), 63.2 (s), 55.8 (s), 44.0 (s), 38.9 (s), 32.8 (s), 21.6 (s), 14.0 (s), 12.3 (s), 8.7 (s). HRMS (ES): calcd for (M + 1) $C_{24}H_{28}F_3NO_5$ 468.1992, found 468.2017.

Ethyl (2R,3aR*,4S*,9bR*)-2-Ethyl-2-(5-ethylfuran-2-yl)-8-methyl-4-(trifluoromethyl)-1,2,3a,4,5,9b-hexahydrofuro[2,3-c]quinoline-4-carboxylate (**3k**).* Following the general procedure, from 26 mg of imine **1b**, 21 μL of 2-ethylfuran, and 1.5 mg of **A**, 37.0 mg (82%) of the desired product was obtained, after purification by column chromatography using as the eluent a mixture of hexanes/DCM/EtOAc (9:0.5:0.2), as a mixture of diastereoisomers (46:7:21:10:5:11). **3k** was obtained (17 mg, 38%) as a yellow oil, while the rest of the diastereoisomers eluted together from the column.

Major Diastereoisomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.80−6.77 (m, 2H), 6.53 (d, J = 8.7 Hz, 1H), 5.98 (d, J = 3.1 Hz, 1H), 5.81 (dt, J = 3.1, 1.0 Hz, 1H), 4.73 (sa, 1H), 4.67 (d, J = 5.2 Hz, 1H), 4.36 (dq, J = 10.7, 7.1 Hz, 1H), 4.26 (dq, J = 10.7, 7.1 Hz, 1H), 3.47−3.43 (m, 1H), 2.81 (dd, J = 13.0, 8.0 Hz, 1H), 2.54 (qd, J = 7.5, 0.9 Hz, 1H), 2.28 (dd, J = 13.0, 1.7 Hz, 1H), 2.17 (s, 3H), 1.40 (q, J = 7.4 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H), 1.15 (t, J = 7.6 Hz, 3H), 0.44 (t, J = 7.4 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −74.99 (s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3 (s), 157.3 (s), 155.9 (s), 137.3 (s), 128.9 (s), 128.5 (s), 128.0 (s), 124.2 (q, J = 290.3 Hz), 122.2 (s), 115.5 (s), 105.6 (s), 104.1 (s), 83.5 (s), 74.2 (s), 64.4 (q, J = 26.86 Hz), 63.2 (s), 44.0 (s), 38.5 (s), 32.8 (s), 21.6 (s), 20.8 (s), 14.0 (s), 12.3 (s), 8.7 (s). HRMS (ES): calcd for (M + 1) $C_{24}H_{28}F_3NO_4$ 452.2043, found 452.2067.

Ethyl (2R,3aR*,4S*,9bR*)-2-Ethyl-2-(5-ethylfuran-2-yl)-4-(trifluoromethyl)-1,2,3a,4,5,9b-hexahydrofuro[2,3-c]quinoline-4-carboxylate (**3l**).* Following the general procedure, from 25 mg of imine **1c**, 21 μL of 2-ethylfuran, and 1.5 mg of **A**, 32.7 mg (75%) of the desired product was obtained, after purification by column chromatography using as the eluent a mixture of hexanes/DCM/EtOAc (9:0.5:0.2), as a mixture of diastereoisomers (42:6:13:26:4:9). **3l** was obtained (14 mg, 32%) as a yellow oil, while the rest of the diastereoisomers eluted together from the column.

Major Diastereoisomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.08−7.03 (m, 2H), 6.78 (td, J = 7.5, 1.1 Hz, 1H), 6.69 (d, J = 8.0 Hz, 1H), 6.06 (d, J = 3.1 Hz, 1H), 5.89 (dt, J = 3.1, 0.9 Hz, 1H), 4.92 (s, 1H), 4.76 (d, J = 4.9 Hz, 1H), 4.44 (dq, J = 10.7, 7.1 Hz, 1H), 4.34 (dq, J = 10.7, 7.1 Hz, 1H), 3.58−3.54 (m, 1H), 2.90 (dd, J = 13.0, 7.9 Hz, 1H), 2.62 (qd, J = 7.5, 0.6 Hz, 2H), 2.38 (dd, J = 13.0, 1.5 Hz, 1H), 1.46 (q, J = 7.3 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.5 Hz, 3H), 0.50 (t, J = 7.5 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −75.11 (s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3 (s), 157.3 (s), 155.9 (s), 139.7 (s), 128.6 (s), 127.3 (s), 124.1 (q, J = 290.0 Hz), 121.1 (s), 119.3 (s), 115.3 (s), 105.7 (s), 104.1 (s), 83.5 (s), 74.1 (s), 64.2 (q, J = 27.68 Hz), 63.2 (s), 43.8 (s), 38.5 (s), 32.8 (s), 21.6 (s), 14.0 (s), 12.3 (s), 8.7 (s). HRMS (ES): calcd for (M + 1) $C_{23}H_{26}F_3NO_4$ 438.1887, found 438.1906.

Ethyl (2R,3aR*,4S*,9bS*)-2-(4,5-dimethylfuran-2-yl)-8-methoxy-1,2-dimethyl-4-(trifluoromethyl)-1,2,3a,4,5,9b-hexahydrofuro[2,3-c]quinoline-4-carboxylate (**3m**).* Following the general procedure, from 28 mg of imine **1a**, 21 μL of 2,3-dimethylfuran, and 3 mg of **B**, 38.3 mg (82%) of the desired product was obtained, after purification by column chromatography using as the eluent a mixture of hexanes/DCM/EtOAc (9:0.5:0.1), as a mixture of diastereoisomers (46:25:14:12:3). **3m** was obtained (17 mg, 37%) as a brown oil together with another unseparable diastereoisomer in a 3:1 ratio, while the rest of the diastereoisomers eluted together from the column.

Major Diastereoisomer Mixture (3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.73−6.56 (m, 2.6H), 6.53 (d, J = 2.5 Hz, 1H), 6.49 (d, J = 2.6 Hz, 0.3H), 5.94 (sa, 0.3H), 5.93 (sa, 1H), 5.21 (d, J = 8.4 Hz, 0.3H), 5.16 (d, J = 6.2 Hz, 1H), 4.12−3.92 (m, 2.6H), 3.68 (s, 3H), 3.67 (s, 1H), 3.49−3.40 (m, 1.3H), 3.11−2.95 (m, 1.3H), 2.12 (s, 3H), 2.02 (s, 1H), 1.83 (s, 3H), 1.76 (s, 1H), 1.20−0.90 (m, 13.3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −70.73 (s, 1F), −71.99 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.2 (s), 168.0 (s), 155.3 (s), 154.2 (s), 153.8 (s), 153.3 (s), 146.8 (s), 146.4 (s), 136.5 (s), 135.8 (s), 125.6 (q, J = 245.3 Hz), 122.3 (s), 121.2 (q, J = 268.9 Hz), 118.6 (s), 118.4 (s), 115.5 (s), 114.4 (s), 113.6 (s), 113.6 (s), 112.9 (s), 109.1 (s), 108.7 (s), 83.4 (s), 83.2 (s), 70.2 (q, J = 26.3 Hz), 68.7 (q, J = 27.0 Hz), 62.8 (s), 62.7 (s), 55.7 (s), 55.7 (s), 50.2 (s), 47.9 (s), 44.9 (s), 43.4 (s), 31.7 (s), 31.1 (s), 21.2 (s), 19.1 (s), 14.3 (s), 13.9 (s), 13.9 (s), 13.7 (s), 12.4 (s), 11.6 (s), 11.4 (s), 10.0 (s), 10.0 (s). HRMS (ES): calcd for (M + 1) $C_{24}H_{28}$ F_3NO_5 468.1992, found 468.1991.

Ethyl (2S,3aR*,4S*,9bR*)-8-Methoxy-2-phenyl-2-(5-phenylfuran-2-yl)-4-(trifluoromethyl)-1,2,3a,4,5,9b-hexahydrofuro[2,3-c]quinoline-4-carboxylate (**3n**).* Following the general procedure, from 28 mg of imine **1a**, 24 μL of 2-phenylfuran,[22] and 3 mg of **B**, 28.4 mg (56%) of the desired product was obtained, after purification by column chromatography using as the eluent a mixture of hexanes/DCM/EtOAc (9:0.5:0.2), as a mixture of diastereoisomers (71:22:7). **3n** was obtained (20.2 mg, 40%) as a colorless oil together with another unseparable diastereoisomer in a 1:0.8 ratio, while the rest of the diastereoisomers eluted together from the column.

Major Diastereoisomer Mixture (1:0.8). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69−7.66 (m, 1.8H), 7.52−7.50 (m, 1.8H), 7.43−7.38 (m, 3.6H), 7.35−7.30 (m, 1.6H), 7.27−7.16 (m, 5.6H), 7.11−7.06 (m, 2.6H), 6.74−6.64 (m, 3.6H), 6.59−6.47 (m, 3.6H), 6.25 (d, J = 3.3 Hz, 1H), 6.09 (d, J = 3.3 Hz, 0.8H), 5.71 (d, J = 3.4 Hz, 1H),

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5.09 (d, J = 5.3 Hz, 0.8H), 4.92 (d, J = 4.8 Hz, 1H), 4.82 (br s, 0.8H), 4.80 (br s, 1H), 4.56−4.33 (m, 3.6H), 3.75−3.69 (m, 1.8H), 3.64 (s, 3H), 3.63 (s, 2.6H), 3.52 (dd, J = 12.9, 7.4 Hz, 0.8H), 3.45 (dd, J = 13.0, 0.9 Hz, 1H), 3.07 (dd, J = 13.0, 7.5 Hz, 1H), 2.86 (dd, J = 12.9, 2.1 Hz, 0.8H), 1.49 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 2.6H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −74.68 (s), −74.98 (s). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.4 (s), 166.2 (s), 157.1 (s), 155.8 (s), 154.0 (s), 153.4 (s), 153.3 (s), 153.1 (s), 144.9 (s), 143.2 (s), 133.9 (s), 133.8 (s), 130.9 (s), 130.8 (s), 128.9 (s), 128.8 (s), 128.5 (s), 128.4 (s), 127.6 (s), 127.6 (s), 127.5 (s), 127.1 (s), 127.0 (s), 126.3 (q, J = 226.8 Hz), 125.6 (s), 125.3 (s), 124.2 (q, J = 239.4 Hz), 124.2 (s), 123.8 (s), 123.7 (s), 122.4 (s), 122.1 (s), 116.9 (s), 116.6 (s), 113.9 (s), 113.7 (s), 113.6 (s), 109.7 (s), 109.7 (s), 105.6 (s), 105.4 (s), 83.5 (s), 83.5 (s), 75.4 (s), 75.1 (s), 64.6 (q, J = 27.4 Hz), 64.4 (q, J = 25.9 Hz), 63.5 (s), 63.4 (s), 56.0 (s), 55.7 (s), 47.6 (s), 47.0 (s), 39.9 (s), 39.1 (s), 31.7 (s), 29.9 (s), 22.8 (s), 14.3 (s), 14.2 (s), 14.0 (s). HRMS (ES): calcd for (M + 1) $C_{32}H_{28}F_3NO_5$ 564.1920, found 564.1901.

Ethyl (2R,3aR*,4S*,9bR*)-8-Methoxy-2-(thiophene-2-yl)-2-[5-(thiophene-2-yl)furan-2-yl]-4-(trifluoromethyl)-1,2,3a,4,5,9b-hexahydrofuro[2,3-c]quinoline-4-carboxylate (**3o**).* Following the general procedure, from 28 mg of imine **1a**, 24 μL of 2-(2-thienyl)furan, and 3 mg of **B**, 26.4 mg (51%) of the desired product was obtained, after purification by column chromatography using as the eluent a mixture of hexanes/DCM/EtOAc (9:0.5:0.2), as a mixture of diastereoisomers (57:18:11:14). **3o** was obtained (15 mg, 29%) as a yellow oil, while the rest of the diastereoisomers eluted together from the column.

Major Diastereoisomer. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25−7.23 (m, 1H), 7.13 (dd, J = 4.9, 1.3 Hz, 1H), 6.97−6.90 (m, 4H), 6.60 (br s, 1H), 6.56 (d, J = 1.6 Hz, 2H), 6.05 (d, J = 3.4 Hz, 1H), 5.86 (d, J = 3.4 Hz, 1H), 5.04 (d, J = 5.1 Hz, 1H), 4.75 (br s, 1H), 4.46 (qd, J = 7.1, 0.9 Hz, 1H), 3.71 (t, J = 5.8 Hz, 1H), 3.58 (s, 3H), 3.35 (dd, J = 12.9, 1.2 Hz, 1H), 3.09 (dd, J = 12.9, 7.1 Hz, 1H), 1.41 (t, J = 7.1 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −74.89 (s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.1 (s), 154.4 (s), 153.3 (s), 149.2 (s), 148.6 (s), 133.8 (s), 133.7 (s), 127.5 (s), 127.0 (s), 124.7 (s), 124.3 (s), 124.1 (q, J = 290.5 Hz), 123.9 (s), 122.6 (s), 121.6 (s), 116.7 (s), 113.9 (s), 113.4 (s), 108.8 (s), 105.7 (s), 82.1 (s), 75.7 (s), 64.4 (q, J = 26.9 Hz), 63.5 (s), 55.7 (s), 48.1 (s), 39.7 (s), 14.2 (s). HRMS (ES): calcd for (M + 1) $C_{28}H_{24}F_3NO_5S_2$ 576.1121, found 576.1096.

*Ethyl 3,3,3-Trifluoro-2-[(4-methoxyphenyl)amino]-2-(5-methylfuran-2-yl)propanoate (**4a**).* Following the general procedure, from 28 mg of imine **1a**, 18 μL of 2-methylfuran, and 2 μL of trifuoroacetic acid, 31.1 mg (86%) of the monoaddition product was obtained, after purification by column chromatography using as the eluent a mixture of hexanes/DCM/EtOAc (9:0.5:0.2) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.60−6.55 (m, 2H), 6.52−6.47 (m, 2H), 6.37 (dd, J = 3.0, 0.9 Hz, 1H), 5.87 (dq, J = 3.1, 0.9 Hz, 1H), 4.77 (br s, 1H), 4.30−4.19 (m, 2H), 3.63 (s, 3H), 2.13 (d, J = 0.7 Hz, 3H), 1.16 (t, J = 7.1 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −71.88 (s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.9 (s), 154.9 (s), 153.6 (s), 143.4 (s), 137.1 (s), 124.0 (q, J = 288.4 Hz), 121.3 (s), 121.3 (s), 114.3 (s), 113.2 (s), 113.2 (s), 107.0 (s), 68.8 (q, J = 28.5 Hz), 64.0 (s), 55.8 (s), 14.2 (s), 13.8 (s). HRMS (ES): calcd for (M + 1) $C_{17}H_{18}F_3NO_4$ 358.1261, found 358.1270.

*Ethyl 2-(5-Benzylfuran-2-yl)-3,3,3-trifluoro-2-[(4-methoxyphenyl)-amino]propanoate (**4b**).* Following the general procedure, from 28 mg of imine **1a**, 29 μL of 2-benzylfuran, and 1.5 mg of SIPrAuOTf, 26.4 mg (61%) of the monoaddition product was obtained, after purification by column chromatography using as the eluent a mixture of hexanes/DCM/EtOAc (9:0.5:0.2) as a brown oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25−7.18 (m, 3H), 7.04−7.01 (m, 2H), 6.63−6.55 (m, 4H), 6.49 (dd, J = 3.2, 1.2 Hz, 1H), 5.98 (dt, J = 3.3, 0.8 Hz, 1H), 4.90 (br s, 1H), 4.34−4.22 (m, 2H), 3.85 (s, 2H), 3.71 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −71.99 (s). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.5 (s), 155.5 (s), 154.6 (s), 143.6 (s), 137.7 (s), 136.6 (s), 128.4 (s), 126.4 (s), 123.6 (q, J = 288.0 Hz), 121.1 (s), 113.9 (s), 113.0 (s), 107.3 (s), 68.5 (q, J = 28.7 Hz), 63.7 (s), 55.4 (s), 34.2 (s), 13.7 (s). HRMS (ES): calcd for (M + 1) $C_{23}H_{22}F_3NO_4$ 434.1574, found 434.1580.

*4-Methoxy-N-[2,2,2-trifluoro-1-(5-methylfuran-2-yl)ethyl]aniline (**4c**).* Following the general procedure, from 20 mg of imine **1j**, 18 μL of 2-methylfuran, and 1.5 mg of gold(III) tetrachloride, 24.5 mg (86%) of the monoaddition product was obtained, after purification by column chromatography using as the eluent a mixture of hexanes/DCM/EtOAc (9:0.5:0.2) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.74−6.68 (m, 2H), 6.64−6.58 (m, 2H), 6.21 (d, J = 3.2 Hz, 1H), 5.88−5.86 (m, 1H), 4.77 (q, J = 7.0 Hz, 1H), 3.67 (s, 3H), 2.21 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$): δ −74.99 (d, J = 7.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.0 (s), 153.5 (s), 145.6 (s), 139.8 (s), 124.8 (q, J = 282.6 Hz), 116.4 (s), 116.4 (s), 115.2 (s), 110.7 (s), 107.0 (s), 56.7 (q, J = 32.1 Hz), 56.0 (s), 13.9 (s). HRMS (ES): calcd for (M + 1) $C_{14}H_{14}F_3NO_2$ 286.1049, found 286.1054.

*Ethyl 3,3,3-Trifluoro-2-methoxy-2-[(4-methoxyphenyl)amino]-propanoate (**5a**).* Following the general procedure, from 28 mg of imine **1a**, 18 μL of 2-methylfuran, and 1.5 mg of gold(III) tetrachloride, 25 mg (82%) of the methanol addition product was obtained, after purification by column chromatography using as the eluent a mixture of hexanes/DCM/EtOAc (9:0.5:0.2).

Spectroscopic data for the title compound are consistent with the literature.[23]

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.91 (d, J = 9.0 Hz, 2H), 6.78 (d, J = 9.1 Hz, 2H), 5.02 (br s, 1H), 4.38 (q, J = 7.1 Hz, 2H), 3.76 (s, 3H), 3.40 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01139.

^{1}H, ^{13}C, and ^{19}F NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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