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One-Pot Synthesis of α-Fluoroketones and 3-Fluoro-2,4-diarylfurans from Trifluoromethyl β-Diketones via Decarboxylation

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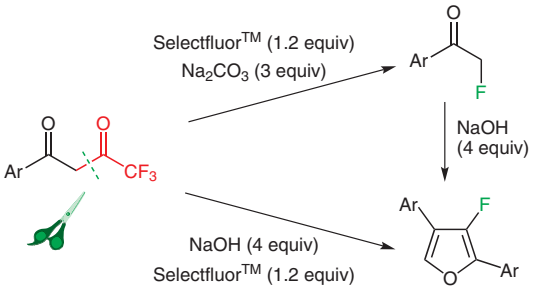

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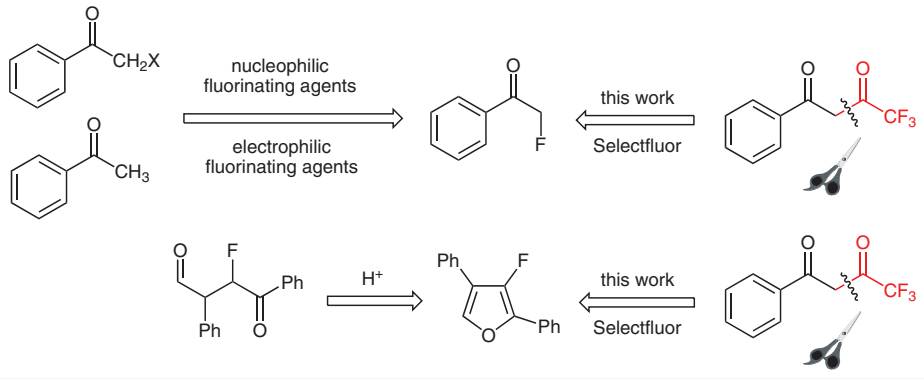
Abstract A facile and mild one-pot protocol via decarboxylation of trifluoromethyl β-diketones has been developed for the construction of α-fluoroketones and 3-fluoro-2,4-diarylfurans which are important units in many biologically active compounds and useful precursors in a variety of functional-group transformations.

Key words fluorine, α-fluoroketones, 3-fluorofurans, one-pot, decarboxylation

It is well recognized that organofluorine compounds have been extensively used as pharmaceuticals, agrochemicals, fine chemicals, and in material science.[1] In particular, 5–15% of the total number of drugs launched worldwide over the past 50 years bear fluorinated substituents.[2] As a consequence, the development of new and efficient methods to synthesize organic fluorides has become a hot topic in organic synthesis.

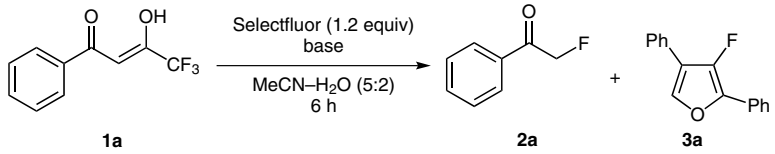
α-Fluoroketones are extremely valuable building blocks in medicinal and biological chemistry and can be easily transformed into chiral α-fluoroethylamines,[3] α-fluoroethylhydroxys,[4] and a large number of interesting molecules.[5] In general, there are mainly two synthetic approaches to α-fluoroketones.[6] One is the introduction of fluorine atom into nonfluorinated substrates with electrophilic fluorinating agents,[7] and the other is the nucleophilic substitution of α-haloketones with fluoride (Scheme 1).[8] However, most of the methods suffer from limitations such as reagent toxicity, low atom economy, and complicated procedures. Therefore, an effective and especially environmentally friendly method is still required.

The furan structure is an ubiquitous unit in a variety of natural products, active pharmaceuticals, agricultural compounds, fragrances, and synthetic precursors.[9] Although two classic methodologies, the Paal–Knorr synthesis[10] and the Feist–Benary synthesis,[11] have proven to be a very useful approach to multisubstituted furans, there exit some limitations, such as difficulty to obtain furans with sensitive functional groups. Also the low reactivity of the furan



Scheme 1 Strategies for synthesis of α-fluoroketone and 3-fluoro-2,4-diphenylfuran

Table 1 Base Screening for the Reaction[a]



1a **2a** **3a**

Entry	Base (equiv)	Temp (°C)	Yield of **2a** (%)[b]	Yield of **3a** (%)[b]
1	DBU (3.0)	30	–	–
2	Na_2CO_3 (3.0)	30	66	–
3	NaOAc (3.0)	30	59	–
4	NaOH (3.0)	30	55	31
5	Na_2CO_3 (3.0)	50	63	–
6	NaOAc (3.0)	50	58	–
7	NaOH (3.0)	50	50	40

[a] Reaction conditions: **1a** (0.5 mmol), Selectfluor (0.6 mmol), base (1.5 mmol), MeCN–H_2O (5:2, 0.7 mL), 6 h.
[b] Isolated yields.

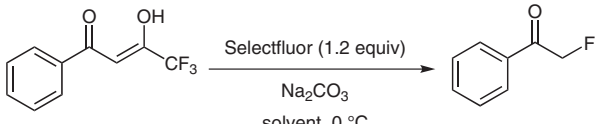
C3-position makes the introduction of functional groups, such as fluorine atom, into this position difficult.[12] In 1965, the first 3-fluoro-2,4-diphenylfuran sample was synthesized from 2-fluoro-1,3-diphenylbutan-1-one (Scheme 1).[13] Recently, Hammond reported the iodocyclization of *gem*-difluorohomopropargyl alcohols with ICl to produce fluorinated 4-iodofurans and continue to prepare multisubstituted 3-fluorofurans using Suzuki cross-coupling reaction.[14]

Our group has reported the decarboxylation of trifluoromethyl α-fluorinated *gem*-diols by cleavage of carbon–carbon bonds through a mild release of the trifluoroacetate unit.[15] Herein we wish to report a one-pot approach for synthesis of α-fluoroketones from trifluoromethyl β-diketones through decarboxylation process. This protocol also provides a facile and mild synthetic approach to 3-fluoro-2,4-diarylfurans.

The starting material trifluoromethyl β-diketones exist exclusively in the enol form.[16] Our initial study started with the reaction of 4,4,4-trifluoro-3-hydroxy-1-phenylbut-2-en-1-one (**1a**), and the results of the base screening are shown in Table 1. With acetonitrile and water as solvent and 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2,2,2]octane bis(tetrafluoroborate) (Selectfluor™) as electrophilic fluorinating agent, the DBU did not work at all (Table 1, entry 1), and weak inorganic bases, such as Na_2CO_3 and NaOAc, gave 2-fluoro-1-phenylethanone (**2a**) in 66% and 59% yields, respectively (Table 1, entries 2 and 3). Relatively low yields of **2a** were obtained at 50 °C (Table 1, entries 5 and 6, 63% and 58%). Surprisingly, using NaOH as base provided **2a** in 55% yield along with 3-fluoro-2,4-diphenylfuran (**3a**) in 31% yield (Table 1, entry 4), and **3a** was isolated in a slightly higher yield of 40% at 50 °C (Table 1, entry 7). Both α-fluoroketone **2a** and 3-fluoro-2,4-diphenylfuran (**3a**) are extremely valuable building blocks, we wished to optimize the reaction conditions to afford **2a** and **3a** using Na_2CO_3 or NaOH as base, respectively.

Subsequently, we found that the ratio of mixed solvents impacts the yield of the model reaction with Na_2CO_3 as base (Table 2). When EtOH–H_2O and MeOH–H_2O were used, moderate yields of **2a** (60% and 62%) were obtained (Table 2, entries 1 and 2). Good yield (73%) was obtained when MeCN–H_2O (5:2) was used as solvent (Table 2, entry 3). To our delight, the yield of **2a** increased significantly with in-

Table 2 Optimization of Solvent for the Synthesis of 2-Fluoro-1-phenylethanone[a]



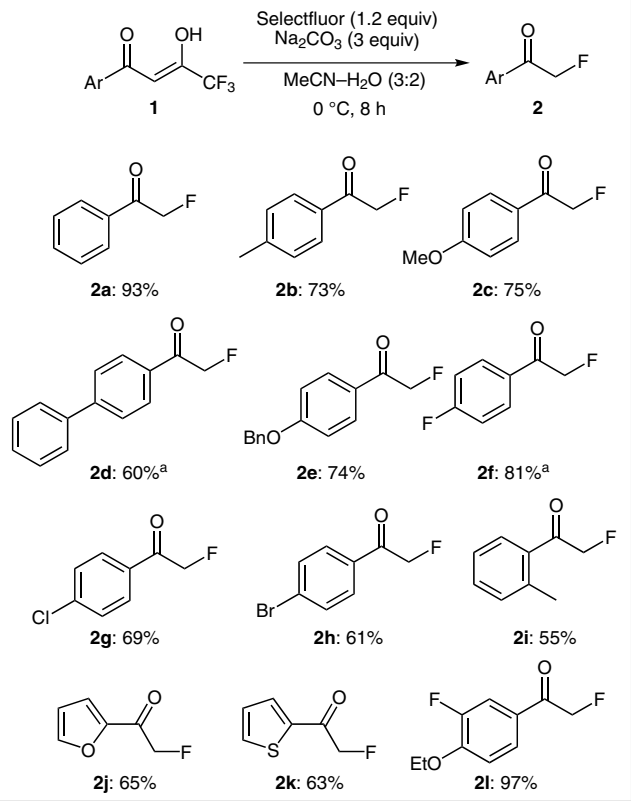
1a **2a**

Entry	Base (equiv)	Solvent (ratio)[b]	Time (h)	Yield (%)[c]
1	Na_2CO_3 (3.0)	EtOH–H_2O (5:2)	8	60
2	Na_2CO_3 (3.0)	MeOH–H_2O (5:2)	8	62
3	Na_2CO_3 (3.0)	MeCN–H_2O (5:2)	8	73
4	Na_2CO_3 (3.0)	MeCN–H_2O (5:3)	8	80
5	Na_2CO_3 (3.0)	MeCN–H_2O (5:4)	8	90
6	Na_2CO_3 (3.0)	MeCN–H_2O (3:2)	8	93
7	Na_2CO_3 (4.0)	MeCN–H_2O (3:2)	8	81
8	Na_2CO_3 (3.0)	MeCN–H_2O (3:2)	10	92

[a] Reaction conditions: **1a** (0.5 mmol), Selectfluor (0.6 mmol), Na_2CO_3, solvent (1.0 mL), 0 °C.
[b] The ratio of mixed solvent was calculated in volume.
[c] Isolated yields.

creasing proportion of H_2O in the mixed solvent (Table 2, entries 4 and 5). But the yield reduced to 81% when the quantity of Na_2CO_3 was elevated to 4.0 equivalents (Table 2, entry 7). This is probably due to the fact that the addition of H_2O is conducive to the solvability of Na_2CO_3 and Selectfluor in the reaction mixture. Screening of different ratios of MeCN–H_2O revealed that 3:2 gave the best result (Table 2, entry 6, 93%). The yield did not increase any further with prolonged reaction time, giving **2a** in 92% yield (Table 2, entry 8).

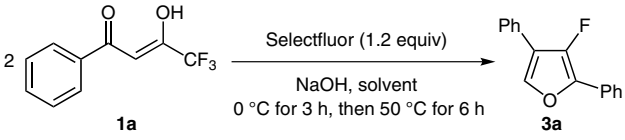
With the optimized conditions in hand, the scope of making α-fluoroketones **2** was investigated (Scheme 2).[17] The protocol was found to tolerate a wide range of functionalities (e.g., methyl, methoxy, phenyl, benzyloxy, fluoro, chloro, and bromo) on the phenyl ring of aryl-substituted trifluoromethyl β-diketones, and good to excellent yields were achieved (**2b**–**i**). Sterically hindered groups, such as phenyl and benzyloxy, at the *para*-position of phenyl ring were also well tolerated, generating the desired products **2d**,**e** in 60% and 74% yield, respectively. And excellent yield of 1-(4-ethoxy-3-fluorophenyl)-2-fluoroethanone (**2l**) was generated when sterically hindered substrate 1-(4-ethoxy-3-fluorophenyl)-4,4,4-trifluoro-3-hydroxybut-2-en-1-one (**1l**) was tested (97%). But the substrate bearing 2-methyl on the phenyl ring showed relatively low reactivity, affording **2i** in a lower yield of 55%. Heterocyclic substituted trifluoromethyl β-diketones were also found to be effective in this protocol, giving the corresponding products **2j** and **2k** in good yields of 65% and 63%, respectively.



Scheme 2 Scope for the synthesis of α-fluoroketones. *Reagents and conditions*: **1** (0.5 mmol), Selectfluor (0.6 mmol), Na_2CO_3 (1.5 mmol), MeCN–H_2O (3:2; 1 mL), 0 °C, 8 h. [a] The reaction was carried out using MeCN–H_2O (7:5; 1.2 mL).

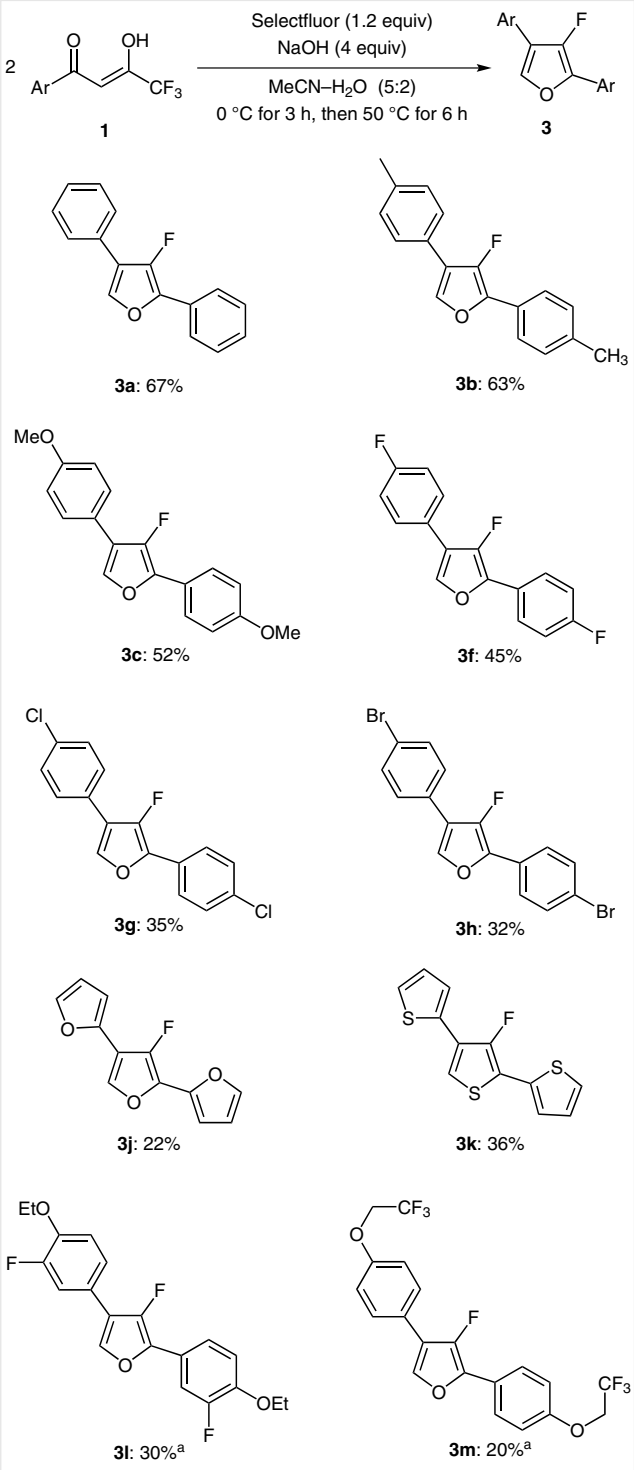
Next, the reaction conditions for the synthesis of 3-fluoro-2,4-diphenylfuran (**3a**) were optimized, and the results are summarized in Table 3. Increasing the amount of NaOH to 4.0 equivalents gave the best result, generating **3a** in 67% yield (Table 3, entry 2). And continuing to add 5.0 equivalents NaOH only got a worse result (Table 3 entry 3, 41%). Then we changed the ratio of the mixed solvent (MeCN–H_2O), but lower yields were obtained (Table 3, entries 4–6). With 4.0 equivalents of NaOH used, various solvents including EtOH, MeOH, $(CH_2OH)_2$, acetone, DMSO, DMF, and EtOH–MeCN–H_2O were screened, unfortunately no good results were obtained (Table 3, entries 7–14). Also, extended reaction time did not lead to an improvement in overall efficiency (Table 3, entry 15). Totally, optimization of the reaction conditions demonstrated that MeCN–H_2O (5:2) to be an optimal solvent in terms of yield (Table 3, entry 2).

Table 3 Optimization of Solvent for the Synthesis of 3-Fluoro-2,4-diphenylfuran[a]



Entry	NaOH (equiv)	Solvent (ratio)[b]	Time (h)	Yield (%)[c]
1	NaOH (3.0)	MeCN–H_2O (5:2)	9	40
2	NaOH (4.0)	MeCN–H_2O (5:2)	9	67
3	NaOH (5.0)	MeCN–H_2O (5:2)	9	41
4	NaOH (5.0)	MeCN–H_2O (5:3)	9	25
5	NaOH (4.0)	MeCN–H_2O (5:3)	9	35
6	NaOH (4.0)	MeCN–H_2O (5:1)	9	37
7	NaOH (4.0)	EtOH–H_2O (5:2)	9	24
8	NaOH (4.0)	MeOH–H_2O (5:2)	9	–
9	NaOH (4.0)	$(CH_2OH)_2$–H_2O (5:2)	9	–
10	NaOH (4.0)	acetone–H_2O (5:2)	9	–
11	NaOH (4.0)	DMSO–H_2O (5:2)	9	–
12	NaOH (4.0)	DMF–H_2O (5:2)	9	–
13	NaOH (4.0)	EtOH–MeCN–H_2O (3:2:2)	9	51
14	NaOH (4.0)	EtOH–MeCN–H_2O (2:3:2)	9	60
15[d]	NaOH (4.0)	MeCN–H_2O (5:2)	12	66

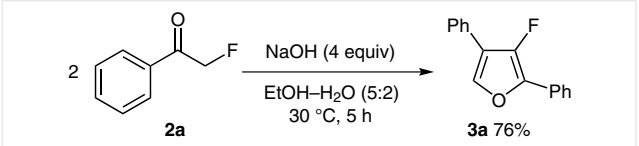
[a] Reaction conditions: **1a** (0.5 mmol), Selectfluor (0.6 mmol), NaOH, solvent (0.7 mL), 0 °C for 3 h, then 50 °C for 6 h.
[b] The ratio of mixed solvent was calculated in volume.
[c] Isolated yield.
[d] The reaction was carried out at 0 °C for 3 h, then at 50 °C for 9 h.



Scheme 3 Scope for the synthesis of 3-fluoro-2,4-diarylfurans. *Reagents and conditions*: **1** (0.5 mmol), selectfluor (0.6 mmol), NaOH (2.0 mmol), MeCN–H_2O (5:2; 0.7 mL), 0 °C for 3 h, then 50 °C for 6 h. [a] The reaction was carried out at 0 °C for 3 h, then 50 °C for 9 h.

The scope of synthesizing 3-fluoro-2,4-diarylfurans is shown in Scheme 3.[18] Aryl substrates with electron-donating or electron-withdrawing groups at the homopropargyl position gave the corresponding 3-fluoro-2,4-diarylfurans **3b**,**c**,**f**–**h** in acceptable to good yields. Sterically hindered substrate 1-(4-ethoxy-3-fluorophenyl)-4,4,4-trifluoro-3-hydroxybut-2-en-1-one was tested, and an acceptable yield of product **3l** was achieved (30%). Lastly, heteroaromatic trifluoromethyl ketones were also suitable substrates in this protocol, delivering the desired furan derivatives **3j**,**k** in relatively low yields, which were attributed to the loss of product during isolation because of their low boiling points (Scheme 3, 22% and 36%).

To further investigate the plausible mechanism of the reaction, the 2-fluoro-1-phenylethanone (**2a**) was put into NaOH solution (4 equiv) of EtOH–H_2O (5:2; 0.7 mL) at 30 °C for five hours. And 3-fluoro-2,4-diphenylfuran (**3a**) was isolated in 76% yield as expected (Scheme 4).



Scheme 4 The reaction of **2a** to **3a** with NaOH as base

According to our previous reports and experimental observations, a possible mechanism for this transformation is proposed in Scheme 5. First, 4,4,4-trifluoro-3-hydroxy-1-phenylbut-2-en-1-one (**1a**) transfers to 2,4,4,4-tetrafluoro-3,3-dihydroxy-1-phenylbutan-1-one with Selectfluor in MeCN–H_2O solution, releasing the trifluoroacetate group to generate the α-fluoroketone product of **2a**. Then the intermolecular condensation reaction occurred to afford the 3-fluoro-2,4-diphenylfuran (**3a**) in strong base.

In conclusion, a one-pot synthesis of α-fluoroketones and 3-fluoro-2,4-diarylfurans through mild release of trifluoroacetate moiety has been developed. This method provides a practical, simple, and mild synthetic approach to α-fluoroketones and 3-fluoro-2,4-diarylfurans, which are important units in biologically active molecules. Further studies to extend the synthetic applications for fluorinated compound are ongoing in our laboratory.

Acknowledgment

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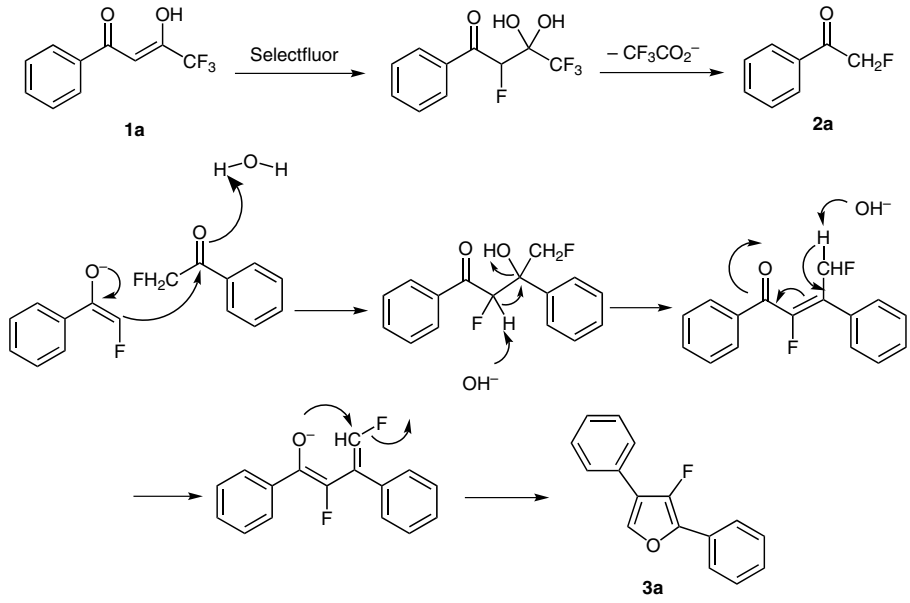
Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1380441.



Scheme 5 Proposed mechanism

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(17) **Typical Experimental Procedure for the Synthesis of 2 from 1**
To a mixture of **1d** (146 mg, 0.5 mmol) and Na_2CO_3 (159 mg, 1.5 mmol) in MeCN (0.3 mL) and H_2O (0.1 mL), a solution of Select-

fluor (212 mg, 0.6 mmol) in MeCN (0.3 mL) and H_2O (0.3 mL) was added over 30 min at 0 °C. The reaction mixture was then stirred for 8 h at 0 °C. When the reaction was complete (monitored by TLC), sat. aq NH_4Cl (4 mL) was added to quench the reaction. After extraction with CH_2Cl_2 and drying with Na_2SO_4, the organic layer was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel using hexane–EtOAc (20:1) as eluent to afford the desired products **2d** (64 mg, 60%).

1-[(1,1′-Biphenyl)-4-yl]-2-fluoroethanone (2d)

White solid; mp 131.5–132.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.0 Hz, 2 H), 7.73–7.71 (m, 2 H), 7.64–7.62 (m, 2 H), 7.51–7.47 (m, 2 H), 7.44–7.40 (m, 1 H), 5.56 (d, *J* = 48.0 Hz, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 193.0 (d, *J* = 15.2 Hz), 146.8, 139.5, 132.3, 129.0, 128.5, 128.4 (d, *J* = 2.0 Hz), 127.4, 127.2, 83.7 (d, *J* = 183.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ = –230.28 (t, *J* = 48.8 Hz, 1 F). IR (KBr): ν = 3380, 2929, 2851, 1700, 1602, 1407, 1241, 1207, 1091, 975, 766, 691 cm^{-1}. MS (EI): *m/z* = 214, 182, 181 (100), 152, 76, 51. HRMS: *m/z* calcd for $[C_{14}H_{11}FO]^+$: 214.0794; found: 214.0795.

(18) **Typical Experimental Procedure for the Synthesis of 3 from 1**

To a mixture of **1a** (108 mg, 0.5 mmol) and NaOH (80 mg, 2.0 mmol) in MeCN (0.2 mL) and H_2O (0.1 mL), a solution of Selectfluor (212 mg, 0.6 mmol) in MeCN (0.3 mL) and H_2O (0.1 mL) was added slowly at 0 °C. The reaction mixture was stirred for 3 h at 0 °C. It was then heated for 6 h at 50 °C. When the reaction was complete (monitored by TLC), sat. aq NH_4Cl (6 mL) was added to quench the reaction. After extraction with EtOAc and drying with Na_2SO_4, the organic layer was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel using hexane–EtOAc (60:1 to 30:1) as eluent to afford the desired products **3a** (40 mg, 67%).

3-Fluoro-2,4-diphenylfuran (3a)

White solid; mp 78.4–79.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 8.0 Hz, 2 H), 7.60 (d, *J* = 8.0 Hz, 2 H), 7.54 (d, *J* = 4.0 Hz, 1 H), 7.46–7.41 (m, 4 H), 7.36–7.29 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.5 (d, *J* = 256.5 Hz), 137.7 (d, *J* = 21.2 Hz), 136.3 (d, *J* = 7.1 Hz), 129.3 (d, *J* = 3.0 Hz), 128.9 (d, *J* = 3.0 Hz), 128.8, 128.7, 127.7, 127.3, 126.5 (d, *J* = 3.0 Hz), 123.5 (d, *J* = 6.0 Hz), 119.4 (d, *J* = 14.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ = –166.91 (d, *J* = 3.7 Hz, 1 F). IR (KBr): ν = 3422, 3151, 2923, 2852, 1948, 1879, 1634, 1496, 1443, 1410, 1066, 908, 759, 747, 690 cm^{-1}. MS (EI): *m/z* = 238 (100), 209, 133, 105, 91, 77, 44. HRMS: *m/z* calcd for $[C_{16}H_{11}FO]^+$: 238.0794; found: 238.0795.