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Palladium-catalyzed direct α-arylation of α-fluoroketones: A straightforward route to α-fluoro-α-arylketones

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ABSTRACT

The palladium-catalyzed direct α-arylation of both open-chain and cyclic α-fluoroketones by using P(*o*-tolyl)$_3$ or RuPhos as ligand and $K_3PO_4 \cdot 3H_2O$ as mild base has been developed. This method allows a variety of quaternary α-aryl-α-fluoroketones to be easily prepared.

1. Introduction

Fluorinated compounds have been widely used as pharmaceuticals and agrochemicals due to the fact that the introduction of fluorine atom into organic molecules can alter their physical and chemical properties and biological activities from structural analogues in a dramatic way [1]. Recently, α-fluorocarbonyl compounds have received a great deal of attention [2], because they have been present as key moieties in many pharmaceutical and bioactive molecules such as Solithromucin (CEM-101) and Flindokalner (BMS 204352) [3]. Direct fluorination of α-aryl-α-ketones was usually used for synthesis of quaternary α-aryl-α-fluoroketones. Direct fluorination includes electrophilic fluorination of tertiary α-aryl-ketones (Scheme 1, path 1) [4] and nucleophilic fluorination of quaternary α-hydroxy (halogen) substituted α-arylketones (Scheme 1, path 2) [5] by fluorinating reagents. These transformations, however, have some practical drawbacks, such as low functionality compatibility or high cost of fluorinating reagents. Recently palladium-catalyzed arylation of monofluorinated silyl enol ethers of cyclic α-fluoroketones in the presence of P(*t*-Bu)$_3$ and TBAT has been found to give quaternary α-aryl-α-fluoroketones in moderate yields (Scheme 1, path 3) [6]. But monofluorinated silyl enol ethers were quite unstable in many reaction conditions and required derivatization from the corresponding α-fluoroketones in advance.

The palladium-catalyzed direct α-arylation of ketones, pioneered by Buchwald, Hartwig and Miura concurrently [7], has become a general methodology for the synthesis of α-arylketones. This direct α-arylation has also been expanded to the arylations of esters, lactones, amides and aldehydes [8]. However, to the best of our knowledge, there are only two papers related to the palladium-catalyzed direct arylation of α-fluorocarbonyl compounds. Shreeve and co-workers described that the cyclic α-fluoroketone could be directly coupled with aryl bromides, however the arylation of open-chain α-fluoroketone failed [6b]. Hartwig group reported the palladium-catalyzed arylation of diethyl α-fluoromalonate [9]. Herein, we describe the efficient and practical palladium-catalyzed direct α-arylation of both open-chain and cyclic α-fluoroketones with aryl halides (Scheme 1, path 4). This is a straightforward route for synthesis of α-aryl-α-fluoroketones with board substrate scope.

2. Results and discussion

Generally the direct α-arylation of ketones required a strong base, such as potassium *tert*-butoxide [7,8,10]. However, we noticed that *α-fluorinated ketones had suffered from the problem of defluorination in harsh basic circumstances* [11]. In consideration of this particular character of α-fluorinated ketones, our initial studies were focused on screening the proper base for the coupling of α-fluoroketone with aryl halides in the presence of Pd(OAc)$_2$ (10 mol%)/PPh$_3$ (20 mol%). As shown in Table 1, when potassium *tert*-butoxide and KHMDS were used as bases, the Pd-catalyzed

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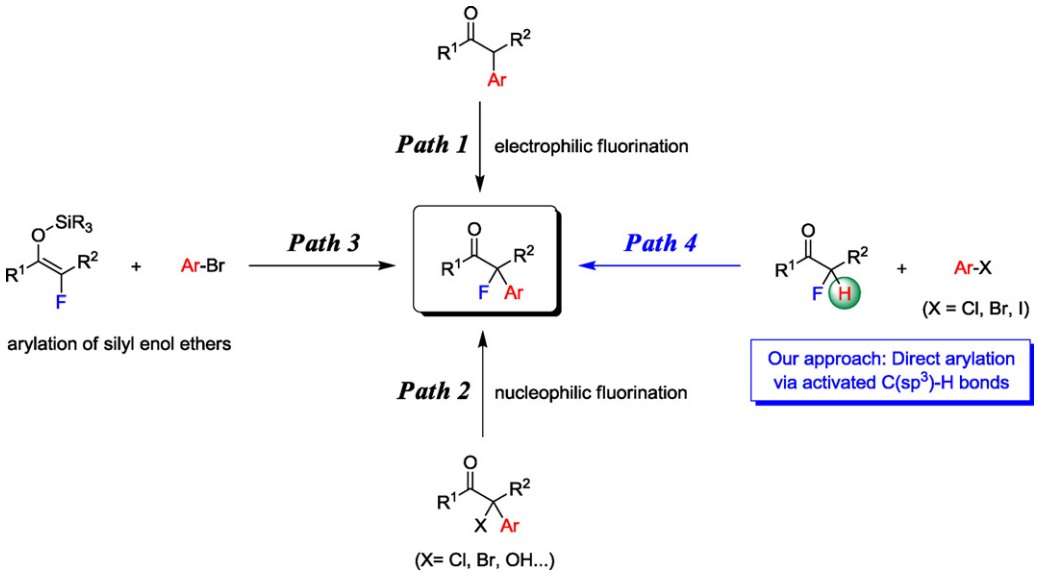


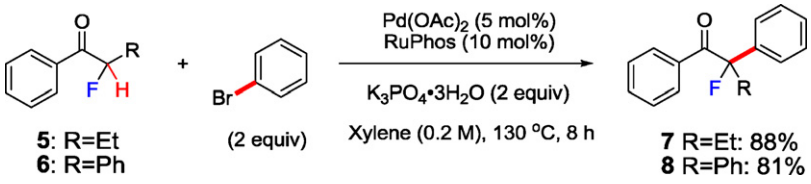
Scheme 1. Synthetic strategies to α-aryl-α-fluoroketones.

reaction of open-chain α-fluoroketone **1** with 4-bromotoluene in toluene at 80 °C led to the complete defluorination of the substrate **1** (Table 1, entries 1–2). **1** remained intact without defluorination in the case of mild base anhydrous K_3PO_4 (entry 3). Gratifyingly, $K_3PO_4{\cdot}3H_2O$ was an effective base for the α-arylation reaction, providing **2a** in 18% yield (entry 4). This result showed that water in potassium phosphate plays an important role in the enhanced reactivity of the catalyst, which has also been illustrated in recent development of a water-mediated catalyst pre-activation protocol [12]. The other advantages of the use of $K_3PO_4{\cdot}3H_2O$ include the easiness of handling because of its less hygroscopic property and the expected good functionality tolerance due to its mild basicity. After $K_3PO_4{\cdot}3H_2O$ was chosen as suitable base, we continued to screen other experimental factors. When xylene was used as solvent instead of toluene and the reaction temperature was elevated to 130 °C, the yield of **2a** was increased to 46% (entry 5). Ligands have been proved to profoundly alter the stability, selectivity and reactivity of the metal complex [13]. Accordingly, a series of phosphine ligands were screened. To our delight, Buchwald's ligands [14], both RuPhos and XPhos, promoted the α-arylation efficiently in xylene and **1** was completely converted to **2a** at 130 °C for 8 h without formation of by-product (Table 1, entries 9–10). It has been reported that the fluorinated silyl enol ethers in palladium-catalyzed arylation and allylation is more active than that of acyclic ones [6b,15]. As expected, the Pd-catalyzed arylation of cyclic α-fluoroketone **3** with 4-bromotoluene by using PPh_3 as ligand occurred with higher conversion (up to 84%) comparing to the open-chain ketone **1**, but the desired product **4a** was formed only in 45% yield (entry 11). Interestingly, when bulky ligand P(*o*-tolyl)$_3$ was used, the reaction of cyclic ketone **3** with 4-bromotoluene in xylene at 130 °C proceeded smoothly to give **4a** in quantitative yield (entry 12), but P(*o*-tolyl)$_3$ was not an effective ligand for the arylation of open-chain ketone **1** (entry 13). Although the cyclic α-aryl-α-fluoroketone **4a** was also formed in quantitative yield in the presence of ligand RuPhos (entry 14), P(*o*-tolyl)$_3$ was chosen as the effective and low-cost ligand for the arylation of cyclic α-fluoroketones. Furthermore, it was found that that the arylations of both **1** and **3** could be proceeded smoothly to give **2a** and **4a** respectively in high yields when the loadings of $Pd(OAc)_2$ and ligand were reduced to 5 mol% and 10 mol%, respectively (entries 15–16).

With the optimized reaction conditions in hand, the scope of the arylation of both open-chain and cyclic α-fluoroketones with aryl halides was investigated. As shown in Table 2, the arylation of open-chain α-fluoroketone **1** encompassed reactions of electron neutral, electron rich, and electron poor aryl bromides. The coupling of **1** with 1,4-dibromobenzene gave the double-arylated compound **2f** selectively in 84% yield without the formation of mono-arylated compound, although the amount of 1,4-dibromobenzene was excess (2.0 equiv). The arylation of **1** with sterically hindered 2-bromotoluene also proceeded smoothly to give product **2k** in 72% yield. Other phenyl halides were also examined as substrates for the arylation of **1**. The coupling of chlorobenzene with **1** gave **2b** in 95% yield. But reaction of iodobenzene with **1** gave **2b** in only 51% yield.

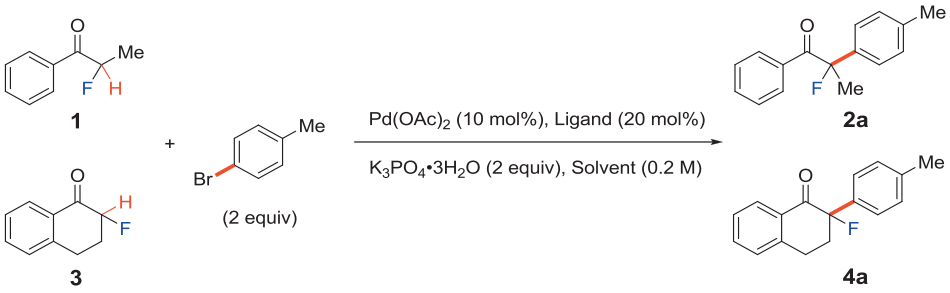
The α-arylation of another two open-chain α-fluoroketones **5** and **6** bearing different substituents on the α-position proceeded smoothly under the optimum conditions for **1** (Scheme 2). The coupling of **5** with bromobenzene provided **7** in 88% yield. Even the sterically hindered substrate **6** went through the process effectively to afford the arylated product **8** in 81% yield.

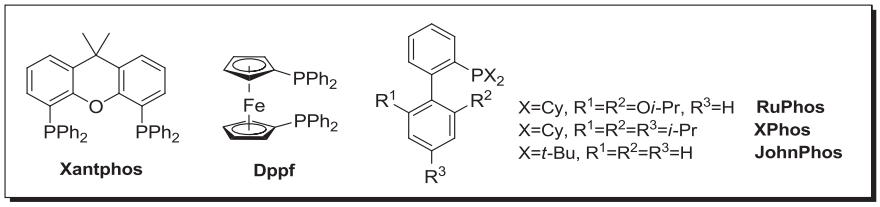
In succession, the scope of the α-arylation of cyclic α-fluoroketones **3** and **9** was summarized in Table 3. In consideration of the higher reactivities of cyclic ketones, the amount of aryl



Scheme 2. Direct α-arylation of **5** and **6** with bromobenzene.

Table 1
Evaluation of bases and supporting ligands for Pd-catalyzed α-arylation of α-fluoroketones **1** and **3** with 4-bromotoluene.[a]

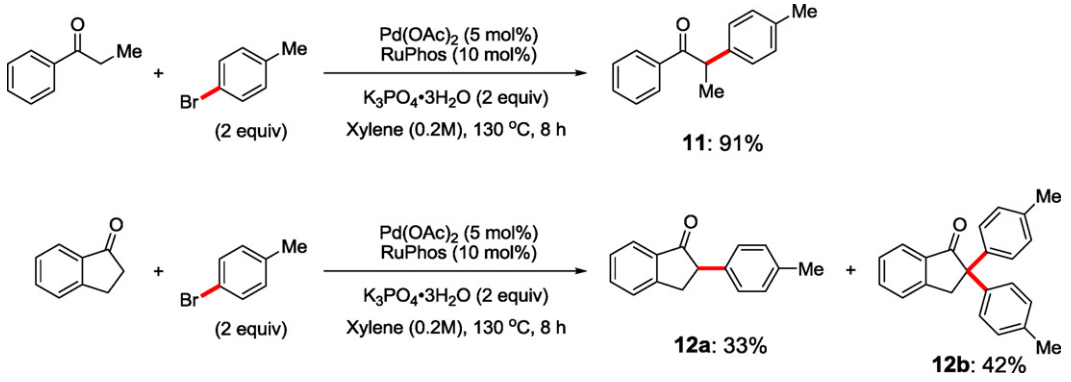




Entry	Ligand	Base	Product	Conversion (%)[b]	Yield (%)[b]
1[c]	PPh_3	*t*-BuOK	**2a**	100[d]	0
2[c]	PPh_3	KHMDS	**2a**	91[d]	0
3[c]	PPh_3	K_3PO_4	**2a**	N.R.[e,f]	0
4[c]	PPh_3	$K_3PO_4{\cdot}3H_2O$	**2a**	18[f]	18
5[g]	PPh_3	$K_3PO_4{\cdot}3H_2O$	**2a**	57[f]	46
6[g]	Dppf	$K_3PO_4{\cdot}3H_2O$	**2a**	44[f]	38
7[g]	JohnPhos	$K_3PO_4{\cdot}3H_2O$	**2a**	59[f]	59
8[g]	Xantphos	$K_3PO_4{\cdot}3H_2O$	**2a**	100	82
9[g]	RuPhos	$K_3PO_4{\cdot}3H_2O$	**2a**	100	100
10[g]	XPhos	$K_3PO_4{\cdot}3H_2O$	**2a**	100	100
11[g]	PPh_3	$K_3PO_4{\cdot}3H_2O$	**4a**	84[f]	45
12[g]	P(*o*-tolyl)$_3$	$K_3PO_4{\cdot}3H_2O$	**4a**	100	100
13[g]	P(*o*-tolyl)$_3$	$K_3PO_4{\cdot}3H_2O$	**2a**	50[f]	50
14[g]	RuPhos	$K_3PO_4{\cdot}3H_2O$	**4a**	100	100
15[g,h]	RuPhos	$K_3PO_4{\cdot}3H_2O$	**2a**	100	100
16[g,h]	P(*o*-tolyl)$_3$	$K_3PO_4{\cdot}3H_2O$	**4a**	100	100

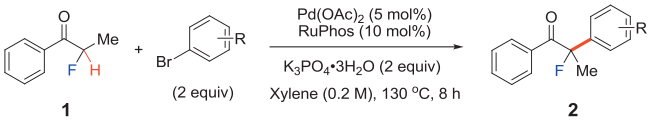
[a] Reaction conditions: 10 mol% $Pd(OAc)_2$, 20 mol% ligand, 2.0 equiv 4-bromotoluene, 2.0 equiv $K_3PO_4{\cdot}3H_2O$, solvent (0.20 mol L^{-1} of **1** or **3**), at 0.2 mmol scale, 8 h.
[b] Determined by ^{19}F NMR using fluorobenzene as internal standard.
[c] Toluene used as solvent at 80 °C.
[d] **1** underwent defluorination.
[e] No reaction.
[f] **1** remained intact.
[g] Xylene used as solvent at 130 °C.
[h] 5 mol% $Pd(OAc)_2$ and 10 mol% ligand were used.
KHMDS = potassium bis(trimethylsilyl)amide.

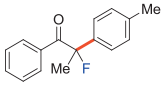
bromide and $K_3PO_4{\cdot}3H_2O$ were reduced to 1.2 equiv and 1.5 equiv, respectively. A number of α-aryl-α-fluoro-1-tetralones **4** were obtained in good to excellent yields by the arylation of α-fluoro-1-tetralone **3** with aryl bromides. Similarly, the direct α-arylations of α-fluoro-1-indanone **9** with diverse aryl bromides provided α-aryl-α-fluoro-1-indalones **10** in moderate to good yields. It should be noteworthy that the α-arylations of **3** or **9** with 1,4-dibromobenzene by using P(*o*-tolyl)$_3$ as ligand gave a mixture of

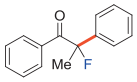


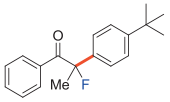
Scheme 3. Direct α-arylation of non-fluorinated ketones.

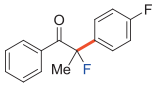
Table 2
Pd-catalyzed α-arylation of **1** with aryl bromides.[a,b]

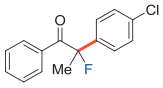



2a: 88%


2b: 94%


2c: 96%


2d: 87%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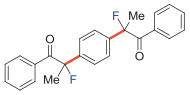
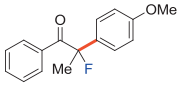
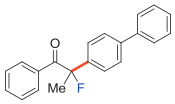
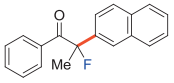
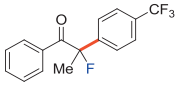
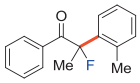

2f: 84%


2g: 93%


2h: 95%

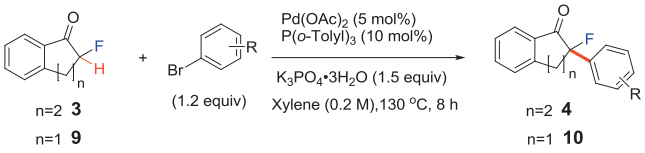

2i: 96%

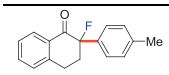

2j: 85%

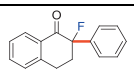

2k: 72%

[a] Reaction conditions: 5 mol% $Pd(OAc)_2$, 10 mol% RuPhos, 2.0 equiv aryl bromide, 2.0 equiv $K_3PO_4 \cdot 3H_2O$, xylene (0.20 mol L^{-1} of **1**), 130 °C, 8 h, at 1.0 mmol scale.
[b] Isolated yield.

Table 3
Substrate scope of palladium catalyzed α-arylation of cyclic α-fluoroketones **3** and **9**.[a,b]




4a: 95%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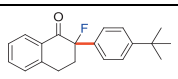
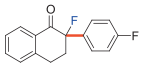
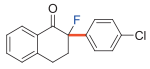
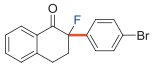
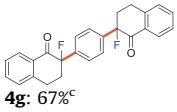
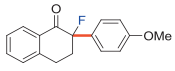

4c: 98%


4d: 75%


4e: 84%


4f: 44%


4g: 67%[c]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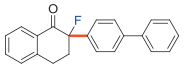
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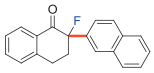
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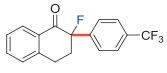
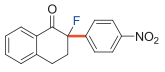

4k: 80%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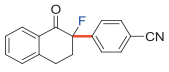
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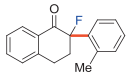
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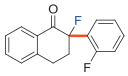
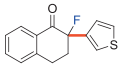

4o: 39%[c]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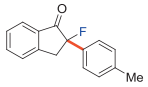
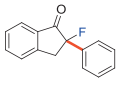

10a: 81%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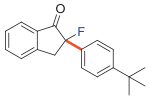
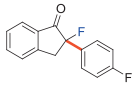
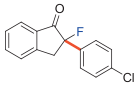
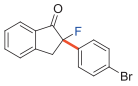






10c: 78%



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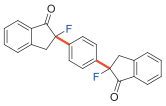
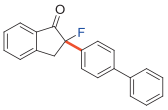
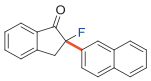


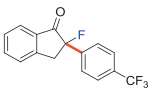
10e: 72%



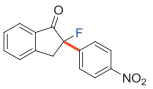
10f: 42%



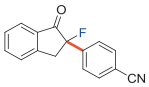
10g: 72%[c]



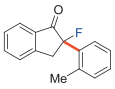
10h: 67%



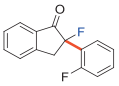
10i: 81%



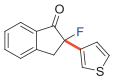
10j: 71%



10k: 69%[c]



10l: 88%[c]



10m: 68%

10n: 48%

10o: 77%

[a] Reaction conditions: 5 mol% $Pd(OAc)_2$, 10 mol% P(*o*-tolyl)$_3$, 1.2 equiv aryl bromide, 1.5 equiv $K_3PO_4{\cdot}3H_2O$, xylene (0.20 mol L^{-1} of **3** or **9**), 130 °C, 8 h.
[b] Isolated yields.
[c] Isolated yields by the use of RuPhos (10 mol%) instead of P(*o*-tolyl)$_3$.

mono-arylated compounds (**4f** and **10f**) and double-arylated compounds (**4g** and **10g**) (**4f**/**4g** = 1.0/0.8, **10f**/**10g** = 1.0/1.1) [16], and the selectivity of the reaction was improved by using RuPhos as ligand instead of P(*o*-tolyl)$_3$ and the double-arylated compounds **4g** and **10g** were isolated as single products. It was found that RuPhos was the more effective ligand than P(*o*-tolyl)$_3$ for the α-arylation of **3** and **9** with aryl bromides bearing NO_2, CN, *ortho*-F groups and 3-bromothiophene and resulted in formation of products **4l**, **10k**, **4m**, **10l**, **4o, 4p** and **10o** in higher yields.

Furthermore, the α-arylation of non-fluorinated ketones in the presence $Pd(OAc)_2$/RuPhos catalytic system and weak base $K_3PO_4{\cdot}3H_2O$ also proceeded smoothly with high efficiency (Scheme 3). The reaction of propiophenone with 4-bromotoluene afford the mono-arylated product **11** exclusively in 91% yield, while the arylation of cyclic substrate 1-indanone gave a mixture of mono-arylated compound **12a** (33%) and double-arylated compound **12b** (42%).

3. Conclusion

In summary, we have developed a versatile method to prepare α-aryl-α-fluoroketones in moderate to excellent yields by palladium-catalyzed direct α-arylation of α-fluoroketones with structurally diverse aryl bromides. In view of all reagents used are readily available and easy to handle, and the mild reaction conditions, we believe that this method will provide a practical and straightforward synthetic route to potentially bioactive α-aryl-α-fluorocarbonyl compounds.

4. Experimental

4.1. General

All reactions were carried out under an argon atmosphere. All commercially available reagents were used without further purification, unless specified otherwise. α-Fluoroketones **1** [4j], **3** [4d], **5** [4j], **6** [4d] and **9** [4d] were prepared according to literature procedures.

All new compounds were characterized by ^{1}H NMR, ^{19}F NMR, ^{13}C NMR, and IR spectroscopy, in addition to high-resolution mass spectroscopy. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer and Varian MR-400, respectively. All ^{1}H NMR experiments are reported in parts per million (ppm) downfield of TMS. All ^{13}C NMR spectra are reported in ppm and were obtained with ^{1}H decoupling. ^{19}F NMR spectra were recorded on a Bruker AM-300 spectrometer ($CFCl_3$ as outside standard and low field is positive). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Infrared spectra were recorded on a Bio-Rad FTS-185 system. LRMS analyses were performed on Agilent 5973N (EI, 70 eV) and HRMS on Waters Micromass GCT Premier.

Ketones **11**, **12a** and **12b** were known compounds and their ^{1}H, ^{13}C NMR spectra were in accordance with those described in the literature [17].

4.2. General procedure for Pd-catalyzed α-arylation of open-chain α-fluoroketone 1 with aryl bromides

An oven-dried Schlenk tube containing a magnetic stirring bar was charged with $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), RuPhos (46.7 mg, 0.10 mmol), and $K_3PO_4{\cdot}3H_2O$ (533 mg, 2.0 mmol). The Schlenk tube was capped with a rubber septum and then evacuated and backfilled with argon for three times. Xylene (5 mL) was added through the septum via syringe and the resulting mixture was stirred at room temperature for 5 min. Then α-fluoroketone **1** (1.0 mmol) and aryl bromide (2.0 mmol) were added. The Schlenk tube was sealed and the reaction mixture was heated at 130 °C with vigorous stirring for 8 h. The reaction mixture was cooled to room temperature and quenched with H_2O (20 mL). The solution was extracted with ether (3 × 10 mL), and the combined organic layers were washed with saturated brine, dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (100/1) as eluent.

4.2.1. 2-Fluoro-1-phenyl-2-p-tolylpropan-1-one (2a) [6c]

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, *J* = 6.9 Hz, 2H), 7.30–7.48 (m, 5H), 7.18 (d, *J* = 8.1 Hz, 2H), 2.32 (s, 3H), 1.90 (d, *J* = 23.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0 (d, *J* = 27.7 Hz), 138.1, 137.5 (d, *J* = 21.9 Hz), 134.5, 133.0, 130.3 (d, *J* = 5.1 Hz), 129.5, 128.2, 123.8 (d, *J* = 8.0 Hz), 101.3 (d, *J* = 183.7 Hz), 26.9 (d, *J* = 25.6 Hz), 21.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ −150.5 (q, *J* = 24.0 Hz, 1F). IR (neat, cm^{-1}): 3059, 2989, 2935, 1688, 1448, 1268, 1105, 979, 725. MS (EI): *m/z* (%) 51 (9), 77 (28), 105 (100), 115 (15), 137 (98), 242 (3, M^+). HRMS: Calcd. for $C_{16}H_{15}FO$: 242.1107; found: 242.1112.

*4.2.2. 2-Fluoro-1,2-diphenylpropan-1-one (**2b**) [6c]*

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, J = 7.8 Hz, 2H), 7.27–7.50 (m, 8H), 1.91 (d, J = 23.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9 (d, J = 27.0 Hz), 140.4 (d, J = 21.8 Hz), 134.4 (d, J = 3.7 Hz), 133.0, 130.3 (d, J = 5.9 Hz), 128.9, 128.3, 128.2, 123.9 (d, J = 8.7 Hz), 101.3 (d, J = 184.5 Hz), 27.0 (d, J = 25.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −150.5 (q, J = 22.8 Hz, 1F). IR (neat, cm^{-1}): 3062, 2990, 1689, 1448, 1269, 980, 698. MS (EI): *m/z* (%) 77 (32), 103 (11), 105 (100), 123 (18), 228 (1, M$^+$). HRMS: Calcd. for $C_{15}H_{13}FO$: 228.0950; found: 228.0946.

*4.2.3. 2-(4-tert-Butylphenyl)-2-fluoro-1-phenylpropan-1-one (**2c**) [6c]*

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (d, J = 7.5 Hz, 2H), 7.32–7.49 (m, 7H), 1.92 (d, J = 22.8 Hz, 3H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2 (d, J = 27.8 Hz), 151.3, 137.3 (d, J = 21.8 Hz), 134.5 (d, J = 3.7 Hz), 132.9, 130.3 (d, J = 5.9 Hz), 128.2, 125.7, 123.7 (d, J = 8.0 Hz), 101.4 (d, J = 183.0 Hz), 34.6, 31.3, 26.9 (d, J = 24.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −150.0 (q, J = 22.8 Hz, 1F). IR (neat, cm^{-1}): 3060, 2964, 2906, 1688, 1269, 1107, 981, 704. MS (EI): *m/z* (%) 77 (20), 105 (62), 149 (18), 164 (20), 179 (100), 284 (1, M$^+$). HRMS: Calcd. for $C_{19}H_{21}FO$: 284.1576; found: 284.1581.

*4.2.4. 2-Fluoro-2-(4-fluorophenyl)-1-phenylpropan-1-one (**2d**)*

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, J = 8.1 Hz, 2H), 7.44–7.50 (m, 3H), 7.35 (t, J = 7.5 Hz, 2H), 7.07 (t, J = 8.7 Hz, 2H), 1.91 (d, J = 23.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8 (d, J = 26.9 Hz), 162.6 (d, J = 246.5 Hz), 136.3 (dd, J = 21.9, 3.0 Hz), 134.3 (d, J = 2.9 Hz), 133.2, 130.2 (d, J = 5.9 Hz), 128.3, 125.9 (t, J = 8.0 Hz), 115.8 (d, J = 21.9 Hz), 100.5 (d, J = 184.5 Hz), 27.0 (d, J = 25.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −113.6 (m, 1F), −149.5 (q, J = 23.7 Hz, 1F). IR (neat, cm^{-1}): 3072, 2991, 2937, 1689, 1509, 1268, 1234, 838. MS (EI): *m/z* (%) 51 (8), 77 (30), 101 (11), 105 (100), 141 (19), 246 (0.6, M$^+$). HRMS: Calcd. for $C_{15}H_{12}F_2O$: 246.0856; found: 246.0853.

*4.2.5. 2-(4-Chlorophenyl)-2-fluoro-1-phenylpropan-1-one (**2e**)*

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, J = 7.8 Hz, 2H), 7.36–7.52 (m, 7H), 1.91 (d, J = 23.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5 (d, J = 26.9 Hz), 139.0 (d, J = 21.9 Hz), 134.4, 134.2 (d, J = 3.6 Hz), 133.2, 130.2 (d, J = 5.8 Hz), 129.1, 128.3, 125.4 (d, J = 8.0 Hz), 101.4 (d, J = 185.2 Hz), 26.8 (d, J = 24.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −150.6 (q, J = 22.6 Hz, 1F). IR (neat, cm^{-1}): 3061, 2991, 2937, 1688, 1491, 1267, 1095, 980, 701. MS (EI): *m/z* (%) 51 (7), 77 (26), 101 (9), 105 (100), 157 (10), 262 (0.6, M$^+$). HRMS: Calcd. for $C_{15}H_{12}ClFO$: 262.0561; found: 262.0567.

*4.2.6. 2,2′-(1,4-Phenylene)bis(2-fluoro-1-phenylpropan-1-one) (**2f**)*

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (d, J = 8.4 Hz, 4H), 7.46–7.53 (m, 6H), 7.34 (t, J = 7.5 Hz, 4H), 1.91 (d, J = 23.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8 (dd, J = 27.0, 5.9 Hz), 140.5 (d, J = 21.9 Hz), 134.3 (d, J = 3.7 Hz), 133.2, 130.2 (d, J = 6.6 Hz), 128.2, 124.5 (d, J = 8.0 Hz), 101.2 (d, J = 185.2 Hz), 26.9 (d, J = 24.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −150.5 (q, J = 23.7 Hz, 1F), −150.8 (q, J = 23.7 Hz, 1F). IR (neat, cm^{-1}): 3068, 2993, 2932, 1685, 1267, 1099, 976, 704. MS (EI): *m/z* (%) 51 (5), 77 (29), 105 (100), 254 (13), 378 (2, M$^+$). HRMS: Calcd. for $C_{24}H_{20}F_2O_2$: 378.1431; found: 378.1441.

*4.2.7. 2-Fluoro-2-(4-methoxyphenyl)-1-phenylpropan-1-one (**2g**)*

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, J = 8.1 Hz, 2H), 7.30–7.48 (m, 5H), 6.90 (d, J = 8.1 Hz, 2H), 3.76 (s, 3H), 1.90 (d, J = 23.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.1 (d, J = 27.7 Hz), 159.6, 134.5 (d, J = 2.9 Hz), 133.0, 132.4 (d, J = 22.6 Hz), 130.2 (d, J = 5.2 Hz), 128.2, 125.4 (d, J = 8.0 Hz), 114.3, 101.1 (d, J = 183.0 Hz), 55.3, 26.8 (d, J = 25.6 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −148.2 (q, J = 22.8 Hz, 1F). IR (neat, cm^{-1}): 3062, 2936, 2837, 1687, 1511, 1253, 1180. MS (EI): *m/z* (%) 77 (14), 105 (14), 153 (100), 258 (2, M$^+$). HRMS: Calcd. for $C_{16}H_{15}FO_2$: 258.1056; found: 258.1055.

*4.2.8. 2-(Biphenyl-4-yl)-2-fluoro-1-phenylpropan-1-one (**2h**)*

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 (d, J = 7.5 Hz, 2H), 7.31–7.61 (m, 12H), 1.95 (d, J = 22.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9 (d, J = 27.7 Hz), 141.3, 140.4, 139.4 (d, J = 21.9 Hz), 134.4 (d, J = 2.9 Hz), 133.1, 130.3 (d, J = 5.8 Hz), 128.9, 128.3, 127.7, 127.6, 127.2, 124.4 (d, J = 8.7 Hz), 101.3 (d, J = 183.7 Hz), 26.9 (d, J = 24.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −150.2 (q, J = 23.7 Hz, 1F). IR (neat, cm^{-1}): 3058, 3031, 2989, 2935, 1687, 1487, 1266, 1104, 980, 699. MS (EI): *m/z* (%) 77 (21), 105 (57), 178 (22), 199 (100), 304 (5, M$^+$). HRMS: Calcd. for $C_{21}H_{17}FO$: 304.1263; found: 304.1265.

*4.2.9. 2-Fluoro-2-(naphthalen-2-yl)-1-phenylpropan-1-one (**2i**)*

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.80–7.97 (m, 6H), 7.59 (dd, J = 8.7, 1.5 Hz, 1H), 7.41–7.49 (m, 3H), 7.30 (d, J = 7.5 Hz, 2H), 1.99 (d, J = 23.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9 (d, J = 27.0 Hz), 137.9 (d, J = 21.8 Hz), 134.4 (d, J = 3.7 Hz), 133.2, 133.1, 133.0, 130.3 (d, J = 5.8 Hz), 128.9, 128.4, 128.3, 127.8, 126.6 (d, J = 3.7 Hz), 123.0 (d, J = 8.7 Hz), 121.6 (d, J = 8.0 Hz), 101.4 (d, J = 184.5 Hz), 27.0 (d, J = 25.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −150.1 (q, J = 22.6 Hz, 1F). IR (neat, cm^{-1}): 3059, 2988, 2932, 1687, 1270, 1119, 981, 709. MS (EI): *m/z* (%) 77 (31), 105 (100), 152 (17), 173 (66), 179 (34), 278 (9, M$^+$). HRMS: Calcd. for $C_{19}H_{15}FO$: 278.1107; found: 278.1108.

*4.2.10. 2-Fluoro-1-phenyl-2-(4-(trifluoromethyl)phenyl)propan-1-one (**2j**) [6c]*

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, J = 8.4 Hz, 2H), 7.61–7.68 (m, 4H), 7.50 (t, J = 7.2 Hz, 1H), 7.36 (t, J = 7.5 Hz, 2H), 1.94 (d, J = 23.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2 (d, J = 27.0 Hz), 144.3 (d, J = 21.8 Hz), 134.0 (d, J = 3.6 Hz), 133.4, 130.6 (d, J = 32.8 Hz), 130.2 (d, J = 5.8 Hz), 128.4, 125.9 (dd, J = 3.6, 1.5 Hz), 124.3 (d, J = 8.7 Hz), 123.9 (q, J = 270.5 Hz), 100.5 (d, J = 186.7 Hz), 26.9 (d, J = 24.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −62.1 (s, 3F), −151.2 (q, J = 22.8 Hz, 1F). IR (neat, cm^{-1}): 3073, 2937, 1690, 1328, 1269, 1129, 708. MS (EI): *m/z* (%) 51 (9), 77 (41), 105 (100), 151 (7), 171 (5), 191 (6). HRMS: Calcd. for $C_{16}H_{12}F_4O$: 296.0824; found: 296.0825.

*4.2.11. 2-Fluoro-1-phenyl-2-o-tolylpropan-1-one (**2k**)*

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (d, J = 8.1 Hz, 2H), 7.13–7.50 (m, 7H), 2.30 (d, J = 1.8 Hz, 3H), 1.96 (d, J = 23.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1 (d, J = 26.3 Hz), 138.6 (d, J = 20.4 Hz), 134.9 (d, J = 2.2 Hz), 134.3, 133.1, 132.4, 130.2 (d, J = 4.4 Hz), 128.6, 128.3, 126.2, 125.1 (d, J = 10.2 Hz), 100.9 (d, J = 179.3 Hz), 24.7 (d, J = 25.5 Hz), 20.8 (d, J = 4.4 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −141.5 (q, J = 23.7 Hz, 1F). IR (neat, cm^{-1}): 3065, 2993, 2937, 1693, 1448, 1265, 1101, 974, 710. MS (EI): *m/z* (%) 51 (8), 77 (27), 105 (100), 115 (15), 137 (34), 242 (5, M$^+$). HRMS: Calcd. for $C_{16}H_{15}FO$: 242.1107; found: 242.1110.

*4.2.12. 2-Fluoro-1,2-diphenylbutan-1-one (**7**)*

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.89 (d, J = 7.8 Hz, 2H), 7.28–7.52 (m, 8H), 2.36–2.56 (m, 1H), 2.10–2.31 (m, 1H), 0.93 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5 (d, J = 27.7 Hz), 138.9 (d, J = 22.6 Hz), 135.2 (d, J = 3.6 Hz), 132.9, 130.0 (d, J = 6.5 Hz), 128.7 (d, J = 1.5 Hz), 128.2, 124.2 (d, J = 9.5 Hz), 103.8 (d, J = 188.1 Hz), 32.8 (d, J = 23.3 Hz), 7.5 (d, J = 4.3 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −164.8 (t, J = 24.8 Hz, 1F). IR (neat, cm^{-1}): 3061, 2978, 2940, 1685, 1448, 1259, 974, 697. MS (EI): *m/z* (%) 51 (7), 77 (27), 105 (100), 137 (13), 242 (1, M$^+$). HRMS: Calcd. for $C_{16}H_{15}FO$: 242.1107; found: 242.1112.

4.2.13. 2-Fluoro-1,2,2-triphenylethanone (8)

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 7.5 Hz, 2H), 7.31–7.49 (m, 13H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5 (d, J = 30.7 Hz), 139.1 (d, J = 22.6 Hz), 135.2 (d, J = 3.7 Hz), 133.0, 130.3 (d, J = 5.1 Hz), 128.7 (d, J = 1.4 Hz), 128.3, 128.1, 126.6 (d, J = 7.3 Hz), 102.9 (d, J = 185.9 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −140.2 (s, 1F). IR (neat, cm^{-1}): 3062, 3029, 1686, 1597, 1494, 1448, 1258, 1182, 848, 750, 696. MS (EI): m/z (%) 51 (6), 77 (24), 105 (100), 165 (33), 185 (57), 290 (0.3, M^+). HRMS: Calcd. for $C_{20}H_{15}FO$: 290.1107; found: 290.1104.

4.3. General procedure for Pd-catalyzed α-arylation of cyclic α-fluoroketones 3 and 9 with aryl bromides

An oven-dried Schlenk tube containing a magnetic stirring bar was charged with $Pd(OAc)_2$ (11.2 mg, 0.05 mmol), P(*o*-tolyl)$_3$ (30.4 mg, 0.10 mmol), α-fluoroketone **3** or **9** (1.0 mmol) and $K_3PO_4{\cdot}3H_2O$ (399 mg, 1.5 mmol). The Schlenk tube was capped with a rubber septum and then evacuated and backfilled with argon for three times. Xylene (5 mL) was added through the septum via syringe and the resulting mixture was stirred at room temperature for 5 min. Then aryl bromide (1.2 mmol) was added. The Schlenk tube was sealed and the reaction mixture was heated at 130 °C with vigorous stirring for 8 h. The reaction mixture was cooled to room temperature and quenched with H_2O (20 mL). The solution was extracted with ether (3 × 10 mL), and the combined organic layers were washed with saturated brine, dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel using petroleum ether/ethyl acetate (40/1) as eluent.

4.3.1. 2-Fluoro-2-p-tolyl-3,4-dihydronaphthalen-1(2H)-one (4a) [6b]

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (d, J = 7.8 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.13–7.26 (m, 5H), 3.02–3.10 (m, 1H), 2.63–2.88 (m, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.2 (d, J = 18.2 Hz), 143.1, 139.2 (d, J = 2.9 Hz), 134.2, 133.5 (d, J = 22.6 Hz), 132.2, 129.4, 128.9, 128.1 (d, J = 1.4 Hz), 127.2, 126.2 (d, J = 5.8 Hz), 96.0 (d, J = 183.0 Hz), 35.3 (d, J = 24.7 Hz), 26.5 (d, J = 8.7 Hz), 21.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ −143.2 (t, 1F) [18]. IR (neat, cm^{-1}): 3061, 3030, 2925, 1701, 1602, 1455, 1308, 1221, 931, 816, 740. MS (EI): m/z (%) 90 (31), 118 (100), 133 (38), 162 (50), 254 (26, M^+). HRMS: Calcd. for $C_{17}H_{15}FO$: 254.1107; found: 254.1105.

4.3.2. 2-Fluoro-2-phenyl-3,4-dihydronaphthalen-1(2H)-one (4b) [6b]

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (d, J = 7.8 Hz, 1H), 7.51 (t, J = 7.2 Hz, 1H), 7.33–7.40 (m, 6H), 7.21 (d, J = 7.5 Hz, 1H), 3.04–3.11 (m, 1H), 2.64–2.86 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.9 (d, J = 18.2 Hz), 143.2, 136.8 (d, J = 22.6 Hz), 134.3, 132.2, 129.2 (d, J = 2.2 Hz), 128.9, 128.7, 128.1, 127.3, 126.1 (d, J = 5.8 Hz), 96.0 (d, J = 183.0 Hz), 35.5 (d, J = 24.8 Hz), 26.4 (d, J = 9.4 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −144.6 (t, J = 12.4 Hz, 1F). IR (neat, cm^{-1}): 3063, 2939, 1698, 1602, 1449, 1307, 1233, 933, 698. MS (EI): m/z (%) 90 (36), 118 (100), 133 (17), 162 (21), 240 (31, M^+). HRMS: Calcd. for $C_{16}H_{13}FO$: 240.0950; found: 240.0949.

4.3.3. 2-(4-tert-Butylphenyl)-2-fluoro-3,4-dihydronaphthalen-1(2H)-one (4c)

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (d, J = 7.5 Hz, 1H), 7.51 (t, J = 7.8 Hz, 1H), 7.20–7.40 (m, 6H), 3.04–3.11 (m, 1H), 2.64–2.91 (m, 3H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.1 (d, J = 18.3 Hz), 152.3 (d, J = 2.2 Hz), 143.2, 134.2, 133.4 (d, J = 22.6 Hz), 132.3, 128.8, 128.1 (d, J = 1.5 Hz), 127.2, 126.0 (d, J = 5.1 Hz), 125.6, 96.0 (d, J = 183.0 Hz), 35.3 (d, J = 25.5 Hz), 34.6, 31.2, 26.5 (d, J = 9.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −143.3 (t, J = 8.7 Hz, 1F). IR (neat, cm^{-1}): 2965, 1692, 1603, 1220, 930, 831, 741. MS (EI): m/z (%) 90 (28), 118 (100), 281 (12), 296 (15, M^+). HRMS: Calcd. for $C_{20}H_{21}FO$: 296.1576; found: 296.1577.

4.3.4. 2-Fluoro-2-(4-fluorophenyl)-3,4-dihydronaphthalen-1(2H)-one (4d)

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15 (d, J = 7.8 Hz, 1H), 7.54 (t, J = 7.5 Hz, 1H), 7.32–7.41 (m, 3H), 7.24 (d, J = 8.1 Hz, 1H), 7.04 (t, J = 8.4 Hz, 2H), 3.08–3.17 (m, 1H), 2.65–2.87 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.4 (d, J = 17.4 Hz), 163.1 (dd, J = 247.2, 2.4 Hz), 143.0, 134.4, 132.7 (d, J = 26.0 Hz), 132.0, 128.9, 128.3 (d, J = 14.2 Hz), 128.2, 127.3, 115.6 (d, J = 21.3 Hz), 95.4 (d, J = 183.3 Hz), 35.4 (d, J = 24.5 Hz), 26.2 (d, J = 8.7 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −112.5 (s, 1F), −144.6 (t, 1F) [18]. IR (neat, cm^{-1}): 3062, 2944, 1699, 1600, 1514, 1190, 1162, 820, 743. MS (EI): m/z (%) 90 (39), 118 (100), 238 (2), 258 (24, M^+). HRMS: Calcd. for $C_{16}H_{12}F_2O$: 258.0856; found: 258.0854.

4.3.5. 2-(4-Chlorophenyl)-2-fluoro-3,4-dihydronaphthalen-1(2H)-one (4e)

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15 (d, J = 7.8 Hz, 1H), 7.55 (td, J = 7.2, 1.2 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.24–7.35 (m, 5H), 3.10–3.19 (m, 1H), 2.65–2.88 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.0 (d, J = 19.0 Hz), 143.0, 135.6 (d, J = 23.3 Hz), 135.2 (d, J = 2.9 Hz), 134.4, 131.9, 128.9, 128.8, 128.3 (d, J = 1.5 Hz), 127.5 (d, J = 6.6 Hz), 127.3, 95.3 (d, J = 183.8 Hz), 35.4 (d, J = 24.8 Hz), 26.1 (d, J = 8.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −147.3 (t, J = 10.4 Hz, 1F). IR (neat, cm^{-1}): 3060, 2944, 1700, 1598, 1496, 1236, 1088, 898, 815, 746. MS (EI): m/z (%) 90 (34), 118 (100), 254 (1), 274 (17, M^+). HRMS: Calcd. for $C_{16}H_{12}ClFO$: 274.0561; found: 274.0568.

4.3.6. 2-(4-Bromophenyl)-2-fluoro-3,4-dihydronaphthalen-1(2H)-one (4f)

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (d, J = 7.8 Hz, 1H), 7.21–7.56 (m, 7H), 3.11–3.17 (m, 1H), 2.64–2.87 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.9 (d, J = 19.0 Hz), 143.1, 136.1 (d, J = 23.4 Hz), 134.5, 131.9, 131.8, 128.9, 128.3, 127.8 (d, J = 5.9 Hz), 127.4, 123.4 (d, J = 3.0 Hz), 95.4 (d, J = 183.0 Hz), 35.4 (d, J = 24.0 Hz), 26.1 (d, J = 8.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −147.1 (t, J = 11.3 Hz, 1F). IR (neat, cm^{-1}): 2928, 1698, 1601, 1488, 1234, 1073, 1010, 932, 741. MS (EI): m/z (%) 90 (34), 118 (100), 234 (9), 240 (12), 318, 320 (6, M^+). HRMS: Calcd. for $C_{16}H_{12}BrFO$: 318.0056; found: 318.0055.

4.3.7. 2,2′-(1,4-Phenylene)bis(2-fluoro-3,4-dihydronaphthalen-1(2H)-one) (4g)

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (dd, J = 7.8, 0.9 Hz, 2H), 7.53 (td, J = 7.8, 1.5 Hz, 2H), 7.33–7.39 (m, 6H), 7.24 (t, J = 7.5 Hz, 2H), 3.07–3.13 (m, 2H), 2.66–2.86 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.3 (d, J = 19.0 Hz), 143.2, 138.0 (d, J = 24.8 Hz), 134.4, 132.0, 129.0, 128.1, 127.3, 126.3 (d, J = 5.8 Hz), 95.6 (d, J = 183.7 Hz), 35.6 (d, J = 24.8 Hz), 26.1 (d, J = 8.7 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −147.6 (t, J = 10.4 Hz, 1F). IR (neat, cm^{-1}): 3064, 2941, 1697, 1602, 1456, 1311, 1235, 1074, 933, 738. MS (EI): m/z (%) 90 (48), 118 (100), 251 (11), 382 (21), 402 (3, M^+). HRMS: Calcd. for $C_{26}H_{20}F_2O_2$: 402.1431; found: 402.1437.

4.3.8. 2-Fluoro-2-(4-methoxyphenyl)-3,4-dihydronaphthalen-1(2H)-one (4h) [6b]

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15 (d, J = 7.8 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.25–7.38 (m, 3H), 7.19 (d, J = 7.5 Hz, 1H), 6.85 (d, J = 8.7 Hz, 2H), 3.75 (s, 3H), 3.01–3.09 (m, 1H), 2.62–2.87 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.3 (d, J = 17.5 Hz), 160.3 (d, J = 2.2 Hz), 143.0, 134.2, 132.2, 128.8, 128.0 (d, J = 1.4 Hz), 127.9 (d, J = 5.1 Hz), 127.2, 114.1, 95.8 (d, J = 183.8 Hz), 55.3, 35.0 (d, J = 25.5 Hz), 26.6 (d, J = 9.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ

−140.1 (t, 1F) [18]. IR (neat, cm^{-1}): 2936, 2839, 1701, 1604, 1515, 1253, 1184, 930, 832, 741. MS (EI): *m/z* (%) 90 (30), 118 (100), 250 (21), 270 (29, M^+). HRMS: Calcd. for $C_{17}H_{15}FO_2$: 270.1056; found: 270.1054.

*4.3.9. 2-(Biphenyl-4-yl)-2-fluoro-3,4-dihydronaphthalen-1(2H)-one (**4i**)*

^1H NMR (300 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.1 Hz, 1H), 7.30–7.56 (m, 11H), 7.21 (d, *J* = 7.5 Hz, 1H), 3.07–3.14 (m, 1H), 2.68–2.92 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.8 (d, *J* = 17.5 Hz), 143.2, 142.1 (d, *J* = 2.2 Hz), 140.3, 135.7 (d, *J* = 22.6 Hz), 134.4, 132.2, 129.0, 128.9, 128.2, 127.8, 127.4, 127.3, 127.2, 126.7 (d, *J* = 5.8 Hz), 95.9 (d, *J* = 183.0 Hz), 35.4 (d, *J* = 24.8 Hz), 26.4 (d, *J* = 9.4 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −145.1 (t, *J* = 10.4 Hz, 1F). IR (neat, cm^{-1}): 3062, 2960, 1693, 1598, 1488, 1238, 928, 766, 736. MS (EI): *m/z* (%) 90 (28), 118 (100), 316 (38, M^+). HRMS: Calcd. for $C_{22}H_{17}FO$: 316.1263; found: 316.1267.

*4.3.10. 2-Fluoro-3,4-dihydro-2,2′-binaphthyl-1(2H)-one (**4j**)*

^1H NMR (300 MHz, $CDCl_3$): δ 8.21 (d, *J* = 7.5 Hz, 1H), 7.69–7.84 (m, 4H), 7.34–7.53 (m, 5H), 7.16 (d, *J* = 7.8 Hz, 1H), 3.03–3.08 (m, 1H), 2.68–2.89 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.9 (d, *J* = 17.5 Hz), 143.1, 134.3, 133.9 (d, *J* = 21.9 Hz), 133.3 (d, *J* = 2.2 Hz), 132.7, 132.1, 128.9, 128.6, 128.4, 128.1, 127.6, 127.2, 126.8, 126.5, 125.9 (d, *J* = 6.5 Hz), 123.3 (d, *J* = 4.4 Hz), 96.1 (d, *J* = 183.8 Hz), 35.3 (d, *J* = 24.8 Hz), 26.3 (d, *J* = 9.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −144.7 (t, 1F) [18]. IR (neat, cm^{-1}): 3059, 2937, 1693, 1601, 1307, 1227, 932, 819, 738. MS (EI): *m/z* (%) 90 (33), 118 (100), 270 (17), 290 (37, M^+). HRMS: Calcd. for $C_{20}H_{15}FO$: 290.1107; found: 290.1104.

*4.3.11. 2-Fluoro-2-(4-(trifluoromethyl)phenyl)-3,4-dihydronaphthalen-1(2H)-one (**4k**) [6b]*

^1H NMR (300 MHz, $CDCl_3$): δ 8.16 (d, *J* = 7.8 Hz, 1H), 7.39–7.64 (m, 6H), 7.28 (d, *J* = 8.1 Hz, 1H), 3.18–3.24 (m, 1H), 2.66–2.90 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.3 (d, *J* = 18.2 Hz), 143.1, 141.5 (d, *J* = 22.6 Hz), 134.5, 131.8, 131.1 (d, *J* = 32.8 Hz), 128.9, 128.4, 127.4, 126.3 (d, *J* = 6.6 Hz), 125.5 (q, *J* = 3.6 Hz), 123.8 (q, *J* = 271.2 Hz), 95.3 (d, *J* = 183.0 Hz), 35.7 (d, *J* = 24.1 Hz), 25.8 (d, *J* = 8.7 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −63.2 (s, 3F), −151.6 (t, *J* = 13.8 Hz, 1F). IR (neat, cm^{-1}): 3061, 2940, 1702, 1333, 1236, 1124, 845. MS (EI): *m/z* (%) 90 (38), 118 (100), 289 (6), 308 (29, M^+). HRMS: Calcd. for $C_{17}H_{12}F_4O$: 308.0824; found: 308.0829.

*4.3.12. 2-Fluoro-2-(4-nitrophenyl)-3,4-dihydronaphthalen-1(2H)-one (**4l**) [6b]*

^1H NMR (300 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.4 Hz, 2H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.52–7.62 (m, 3H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 3.28 (dt, *J* = 17.1, 5.4 Hz, 1H), 2.86–2.94 (m, 1H), 2.65–2.76 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.5 (d, *J* = 19.7 Hz), 148.1, 144.8 (d, *J* = 22.7 Hz), 143.1, 134.7, 131.4, 129.0, 128.6, 127.6, 126.8 (d, *J* = 8.0 Hz), 123.6, 95.1 (d, *J* = 183.0 Hz), 35.8 (d, *J* = 24.0 Hz), 25.5 (d, *J* = 8.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −153.4 (dd, *J* = 18.6, 13.5 Hz, 1F). IR (neat, cm^{-1}): 3077, 2938, 1697, 1602, 1521, 1348, 1237, 935, 853, 741. MS (EI): *m/z* (%) 84 (55), 86 (36), 90 (46), 118 (100), 285 (36, M^+). HRMS: Calcd. for $C_{16}H_{12}NFO_3$: 285.0801; found: 285.0804.

*4.3.13. 4-(2-Fluoro-1-oxo-1,2,3,4-tetrahydronaphthalen-2-yl)benzonitrile (**4m**) [6b]*

^1H NMR (300 MHz, $CDCl_3$): δ 8.13 (d, *J* = 7.8 Hz, 1H), 7.38–7.67 (m, 6H), 7.30 (d, *J* = 7.8 Hz, 1H), 3.24 (dt, *J* = 17.1, 5.7 Hz, 1H), 2.81–2.91 (m, 1H), 2.63–2.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.8 (d, *J* = 19.0 Hz), 143.2, 142.9 (d, *J* = 22.6 Hz), 134.7, 132.3, 131.5, 129.0, 128.5, 127.5, 126.6 (d, *J* = 7.3 Hz), 118.3, 112.8 (d, *J* = 1.4 Hz), 95.1 (d, *J* = 183.0 Hz), 35.6 (d, *J* = 24.0 Hz), 25.5 (d, *J* = 8.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −153.2 (t, *J* = 13.3 Hz, 1F). IR (neat, cm^{-1}): 3066, 2932, 2230, 1697, 1601, 1455, 1307, 1237, 935, 826, 741. MS (EI): *m/z* (%) 84 (100), 86 (66), 90 (20), 118 (51), 265 (12, M^+). HRMS: Calcd. for $C_{17}H_{12}FON$: 265.0903; found: 265.0900.

*4.3.14. 2-Fluoro-2-o-tolyl-3,4-dihydronaphthalen-1(2H)-one (**4n**)*

^1H NMR (300 MHz, $CDCl_3$): δ 8.17 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.07–7.28 (m, 5H), 3.14–3.22 (m, 1H), 2.73–2.91 (m, 2H), 2.51–2.61 (m, 1H), 2.35 (d, *J* = 1.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.8 (d, *J* = 19.7 Hz), 143.4, 136.3 (d, *J* = 21.1 Hz), 135.5 (d, *J* = 2.2 Hz), 134.1, 132.2, 131.9, 128.7, 128.5, 128.3, 127.2, 126.0 (d, *J* = 10.9 Hz), 125.5, 96.8 (d, *J* = 179.3 Hz), 34.8 (d, *J* = 24.8 Hz), 25.7 (d, *J* = 6.5 Hz), 21.2 (d, *J* = 5.1 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −154.8 (dd, *J* = 24.3, 12.1 Hz, 1F). IR (neat, cm^{-1}): 3065, 3024, 2932, 1697, 1602, 1455, 1233, 931, 757. MS (EI): *m/z* (%) 90 (38), 118 (100), 234 (34), 254 (9, M^+). HRMS: Calcd. for $C_{17}H_{15}FO$: 254.1107; found: 254.1105.

*4.3.15. 2-Fluoro-2-(2-fluorophenyl)-3,4-dihydronaphthalen-1(2H)-one (**4o**)*

^1H NMR (300 MHz, $CDCl_3$): δ 8.15 (d, *J* = 7.8 Hz, 1H), 7.47–7.57 (m, 2H), 7.16–7.41 (m, 4H), 7.02–7.09 (m, 1H), 3.26–3.35 (m, 1H), 2.77–2.99 (m, 2H), 2.52–2.63 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6 (d, *J* = 19.0 Hz), 159.1 (dd, *J* = 245.7, 5.1 Hz), 143.5, 134.1, 131.1, 130.4 (d, *J* = 8.0 Hz), 128.7 (d, *J* = 1.5 Hz), 127.4 (d, *J* = 3.6 Hz), 127.3 (d, *J* = 3.7 Hz), 127.2, 126.3 (dd, *J* = 23.3, 13.1 Hz), 124.3 (d, *J* = 3.7 Hz), 115.9 (d, *J* = 21.2 Hz), 94.3 (dd, *J* = 180.1, 2.9 Hz), 35.0 (dd, *J* = 24.0, 3.0 Hz), 25.3 (d, *J* = 5.8 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −111.8 (s, 1F), −162.3 (dd, *J* = 34.7, 12.1 Hz, 1F). IR (neat, cm^{-1}): 3069, 2932, 1693, 1602, 1490, 1454, 1281, 1229, 936, 759, 743. MS (EI): *m/z* (%) 90 (39), 118 (100), 238 (2), 258 (30, M^+). HRMS: Calcd. for $C_{16}H_{12}F_2O$: 258.0856; found: 258.0858.

*4.3.16. 2-Fluoro-2-(thiophen-3-yl)-3,4-dihydronaphthalen-1(2H)-one (**4p**)*

^1H NMR (300 MHz, $CDCl_3$): δ 8.15 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.31–7.39 (m, 2H), 7.15–7.23 (m, 3H), 3.05–3.11 (m, 1H), 2.65–2.95 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.1 (d, *J* = 19.0 Hz), 143.0, 136.8 (d, *J* = 24.1 Hz), 134.3, 131.6, 128.8, 128.2 (d, *J* = 1.5 Hz), 127.2, 126.7, 125.8 (d, *J* = 2.9 Hz), 124.8 (d, *J* = 7.3 Hz), 93.6 (d, *J* = 183.0 Hz), 34.9 (d, *J* = 24.8 Hz), 26.7 (d, *J* = 9.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −138.4 (t, *J* = 9.3 Hz, 1F). IR (neat, cm^{-1}): 3106, 2933, 1698, 1602, 1455, 1303, 1223, 919, 735. MS (EI): *m/z* (%) 90 (38), 118 (100), 226 (20), 246 (13, M^+). HRMS: Calcd. for $C_{14}H_{11}FOS$: 246.0515; found: 246.0523.

*4.3.17. 2-Fluoro-2-p-tolyl-2,3-dihydro-1H-inden-1-one (**10a**)*

^1H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 3.62–3.77 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.4 (d, *J* = 21.1 Hz), 150.3 (d, *J* = 5.8 Hz), 138.5, 136.4, 134.6 (d, *J* = 24.8 Hz), 133.9, 129.4, 128.6, 126.4, 125.6, 124.5 (d, *J* = 8.0 Hz), 97.9 (d, *J* = 188.8 Hz), 41.6 (d, *J* = 24.1 Hz), 21.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ −156.9 (dd, *J* = 20.6, 12.1 Hz, 1F). IR (neat, cm^{-1}): 1733, 1607, 1211, 1090, 916, 738. MS (EI): *m/z* (%) 196 (59), 197 (63), 207 (15), 225 (6), 240 (100, M^+). HRMS: Calcd. for $C_{16}H_{13}FO$: 240.0950; found: 240.0951.

*4.3.18. 2-Fluoro-2-phenyl-2,3-dihydro-1H-inden-1-one (**10b**)*

^1H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.32–7.36 (m, 5H), 3.63–3.78 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2 (d, *J* = 19.7 Hz), 150.3 (d, *J* = 5.1 Hz), 137.8 (d, *J* = 24.1 Hz), 136.5, 133.9, 128.7, 128.6, 128.5, 126.5, 125.6, 124.5 (d, *J* = 8.0 Hz), 97.9 (d, *J* = 188.8 Hz), 41.8 (d, *J* = 24.1 Hz). ^{19}F NMR (282 MHz,

$CDCl_3$): δ −157.9 (dd, 1F) [19]. IR (neat, cm^{-1}): 3063, 1728, 1609, 1212, 1009, 920, 699. MS (EI): *m/z* (%) 178 (40), 179 (43), 196 (44), 197 (41), 206 (20), 226 (100, M^+). HRMS: Calcd. for $C_{15}H_{11}FO$: 226.0794; found: 226.0796.

4.3.19. 2-(4-tert-Butylphenyl)-2-fluoro-2,3-dihydro-1H-inden-1-one (10c)

^1H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 9.0 Hz, 2H), 7.29 (d, *J* = 9.0 Hz, 2H), 3.62–3.82 (m, 2H), 1.28 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.4 (d, *J* = 21.1 Hz), 151.6 (d, *J* = 1.5 Hz), 150.3 (d, *J* = 5.1 Hz), 136.4, 134.5 (d, *J* = 24.1 Hz), 133.9, 128.5, 126.4, 125.6, 124.4 (d, *J* = 8.0 Hz), 98.0 (d, *J* = 188.9 Hz), 41.6 (d, *J* = 24.0 Hz), 34.6, 31.2. ^{19}F NMR (282 MHz, $CDCl_3$): δ −157.0 (dd, *J* = 20.6, 10.4 Hz, 1F). IR (neat, cm^{-1}): 2958, 1722, 1609, 1431, 1302, 1104, 920, 836, 750. MS (EI): *m/z* (%) 91 (17), 196 (34), 197 (23), 267 (100), 268 (20), 282 (34, M^+). HRMS: Calcd. for $C_{19}H_{19}FO$: 282.1420; found: 282.1431.

4.3.20. 2-Fluoro-2-(4-fluorophenyl)-2,3-dihydro-1H-inden-1-one (10d)

^1H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, *J* = 7.8 Hz, 1H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.32–7.37 (m, 2H), 7.01–7.06 (m, 2H), 3.70–3.76 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.9 (d, *J* = 20.4 Hz), 162.8 (d, *J* = 247.9 Hz), 150.1 (d, *J* = 5.1 Hz), 136.6, 133.6, 133.3 (d, *J* = 2.9 Hz), 128.7, 126.6 (t, *J* = 8.0 Hz), 126.5 (d, *J* = 1.5 Hz), 125.7, 115.6 (d, *J* = 21.1 Hz), 97.5 (d, *J* = 189.6 Hz), 41.6 (d, *J* = 24.1 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −113.5 (m, 1F), −155.7 (dd, 1F) [19]. IR (neat, cm^{-1}): 1736, 1507, 1225, 1082, 913, 738. MS (EI): *m/z* (%) 196 (44), 197 (25), 214 (36), 215 (40), 224 (16), 244 (100, M^+). HRMS: Calcd. for $C_{15}H_{10}F_2O$: 244.0700; found: 244.0704.

4.3.21. 2-(4-Chlorophenyl)-2-fluoro-2,3-dihydro-1H-inden-1-one (10e)

^1H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.26–7.34 (m, 4H), 3.70–3.75 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7 (d, *J* = 19.7 Hz), 150.1 (d, *J* = 5.1 Hz), 136.6, 136.2 (d, *J* = 24.8 Hz), 134.7 (d, *J* = 1.4 Hz), 133.6, 128.9, 128.8, 126.5 (d, *J* = 1.5 Hz), 126.0 (d, *J* = 8.0 Hz), 125.8, 97.4 (d, *J* = 190.3 Hz), 41.6 (d, *J* = 24.1 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −157.2 (dd, 1F) [19]. IR (neat, cm^{-1}): 1734, 1490, 1212, 1086, 916, 742. MS (EI): *m/z* (%) 177 (21), 196 (74), 197 (47), 225 (23), 260 (100, M^+), 262 (33). HRMS: Calcd. for $C_{15}H_{10}ClFO$: 260.0404; found: 260.0407.

4.3.22. 2-(4-Bromophenyl)-2-fluoro-2,3-dihydro-1H-inden-1-one (10f)

^1H NMR (300 MHz, $CDCl_3$): δ 7.82 (d, *J* = 7.5 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.45–7.49 (m, 3H), 7.21–7.26 (m, 2H), 3.69–3.75 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6 (d, *J* = 20.5 Hz), 150.1 (d, *J* = 5.1 Hz), 136.9, 136.6, 133.6, 131.8, 128.8, 126.5, 126.3 (d, *J* = 8.8 Hz), 125.8, 122.8 (d, *J* = 1.4 Hz), 97.5 (d, *J* = 189.6 Hz), 41.6 (d, *J* = 24.1 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −157.6 (dd, 1F) [19]. IR (neat, cm^{-1}): 1731, 1211, 1088, 916, 741. MS (EI): *m/z* (%) 98 (34), 178 (35), 196 (100), 197 (50), 304 (66, M^+), 306 (65, M^+). HRMS: Calcd. for $C_{15}H_{10}BrFO$: 303.9899; found: 303.9903.

4.3.23. 2,2′-(1,4-Phenylene)bis(2-fluoro-2,3-dihydro-1H-inden-1-one) (10g)

^1H NMR (300 MHz, $CDCl_3$): δ 7.68–7.81 (m, 4H), 7.43–7.55 (m, 4H), 7.33 (s, 4H), 3.68–3.74 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.8 (dd, *J* = 20.2, 3.7 Hz), 150.1 (dd, *J* = 7.0, 5.3 Hz), 138.0 (ddd, *J* = 24.4, 2.9, 1.6 Hz), 136.5 (d, *J* = 2.5 Hz), 133.6 (d, *J* = 1.7 Hz), 128.6, 126.3 (dd, *J* = 3.3, 1.6 Hz), 125.7 (d, *J* = 1.2 Hz), 124.8 (ddd, *J* = 8.2, 4.1, 1.3 Hz), 97.6 (dd, *J* = 190.2, 0.8 Hz), 41.5 (dd, *J* = 23.9, 3.7 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −157.8 (dd, 1F) [19]. IR (neat, cm^{-1}): 1717, 1605, 1466, 1260, 1211, 1076, 909, 747. MS (EI): *m/z* (%) 196 (45), 197 (36), 296 (13), 297 (13), 374 (100, M^+). HRMS: Calcd. for $C_{24}H_{16}F_2O_2$: 374.1118; found: 374.1119.

4.3.24. 2-(Biphenyl-4-yl)-2-fluoro-2,3-dihydro-1H-inden-1-one (10h)

^1H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.8 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.32–7.59 (m, 11H), 3.68–3.87 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.2 (d, *J* = 20.4 Hz), 150.3 (d, *J* = 5.9 Hz), 141.6, 140.5, 136.7, 136.5, 133.9, 128.9, 128.7, 127.6, 127.5, 127.1, 126.5, 125.8, 125.0 (d, *J* = 8.0 Hz), 97.8 (d, *J* = 188.9 Hz), 41.7 (d, *J* = 24.0 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −157.4 (dd, *J* = 20.6, 10.4 Hz, 1F). IR (neat, cm^{-1}): 3053, 1727, 1429, 1210, 1086, 913, 836, 737, 694. MS (EI): *m/z* (%) 196 (21), 197 (20), 252 (28), 253 (22), 282 (16), 302 (100, M^+). HRMS: Calcd. for $C_{21}H_{15}FO$: 302.1107; found: 302.1111.

4.3.25. 2-Fluoro-2-(naphthalen-2-yl)-2,3-dihydro-1H-inden-1-one (10i)

^1H NMR (300 MHz, $CDCl_3$): δ 7.67–7.86 (m, 6H), 7.37–7.55 (m, 5H), 3.69–3.90 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.3 (d, *J* = 20.5 Hz), 150.4 (d, *J* = 5.1 Hz), 136.6, 135.0 (d, *J* = 24.1 Hz), 133.9, 133.1 (d, *J* = 21.1 Hz), 128.7 (d, *J* = 8.0 Hz), 128.3, 127.7, 126.6 (d, *J* = 6.5 Hz), 126.5 (d, *J* = 1.5 Hz), 125.7, 123.9 (d, *J* = 8.8 Hz), 122.1 (d, *J* = 7.3 Hz), 98.1 (d, *J* = 189.6 Hz), 41.8 (d, *J* = 24.1 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −156.8 (dd, *J* = 20.6, 10.4 Hz, 1F). IR (neat, cm^{-1}): 1727, 1608, 1275, 1214, 1084, 915, 749. MS (EI): *m/z* (%) 226 (25), 228 (28), 246 (41), 247 (49), 256 (19), 276 (100, M^+). HRMS: Calcd. for $C_{19}H_{13}FO$: 276.0950; found: 276.0952.

4.3.26. 2-Fluoro-2-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1H-inden-1-one (10j)

^1H NMR (300 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.45–7.63 (m, 6H), 3.73–3.79 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.3 (d, *J* = 20.4 Hz), 150.2 (d, *J* = 5.1 Hz), 141.8 (d, *J* = 24.0 Hz), 136.8, 133.6, 130.8 (d, *J* = 32.1 Hz), 128.9, 126.5, 125.9, 125.7 (d, *J* = 3.7 Hz), 124.9 (d, *J* = 8.7 Hz), 123.9 (q, *J* = 270.5 Hz), 97.4 (d, *J* = 190.3 Hz), 41.8 (d, *J* = 24.1 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −63.2 (s, 3F), −158.8 (dd, *J* = 17.2, 13.8 Hz, 1F). IR (neat, cm^{-1}): 1722, 1328, 1164, 1121, 1070, 842. MS (EI): *m/z* (%) 69 (27), 77 (23), 196 (57), 197 (33), 275 (14), 294 (100, M^+). HRMS: Calcd. for $C_{16}H_{10}F_4O$: 294.0668; found: 294.0670.

4.3.27. 2-Fluoro-2-(4-nitrophenyl)-2,3-dihydro-1H-inden-1-one (10k)

^1H NMR (300 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.7 Hz, 2H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.50–7.55 (m, 3H), 3.75–3.88 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6 (d, *J* = 19.7 Hz), 150.0 (d, *J* = 5.1 Hz), 148.0, 144.9 (d, *J* = 24.1 Hz), 137.0, 133.4, 129.1, 126.6, 126.0, 125.5 (d, *J* = 8.8 Hz), 123.9, 97.4 (d, *J* = 191.0 Hz), 41.7 (d, *J* = 24.1 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −158.6 (dd, *J* = 20.9, 13.8 Hz, 1F). IR (neat, cm^{-1}): 1722, 1601, 1518, 1349, 1213, 848, 732. MS (EI): *m/z* (%) 176 (24), 178 (22), 196 (53), 271 (100, M^+). HRMS: Calcd. for $C_{15}H_{10}NFO_3$: 271.0645; found: 271.0647.

4.3.28. 4-(2-Fluoro-1-oxo-2,3-dihydro-1H-inden-2-yl)benzonitrile (10l)

^1H NMR (300 MHz, $CDCl_3$): δ 7.74–7.84 (m, 2H), 7.44–7.66 (m, 6H), 3.73–3.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8 (d, *J* = 19.7 Hz), 150.1 (d, *J* = 4.4 Hz), 143.0 (d, *J* = 24.8 Hz), 137.0, 133.4, 132.5, 129.0, 126.6, 125.9, 125.3 (d, *J* = 9.5 Hz), 118.3, 112.5, 97.4 (d, *J* = 191.0 Hz), 41.6 (d, *J* = 24.1 Hz). ^{19}F NMR

(282 MHz, $CDCl_3$): δ −159.1 (dd, 1F) [19]. IR (neat, cm^{-1}): 3066, 2227, 1737, 1606, 1469, 1303, 1213, 1086, 916, 761. MS (EI): *m/z* (%) 196 (19), 203 (29), 204 (35), 221 (28), 222 (28), 251 (100, M^+). HRMS: Calcd. for $C_{16}H_{10}NFO$: 251.0746; found: 251.0750.

*4.3.29. 2-Fluoro-2-o-tolyl-2,3-dihydro-1H-inden-1-one (**10m**)*

^1H NMR (300 MHz, $CDCl_3$): δ 7.91 (d, J = 7.8 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.45–7.50 (m, 2H), 7.36–7.39 (m, 1H), 7.19–7.27 (m, 3H), 3.64–3.79 (m, 2H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.0 (d, J = 19.7 Hz), 150.2, 136.5, 136.4, 136.2, 135.0 (d, J = 3.6 Hz), 134.4, 131.8, 128.5 (d, J = 9.5 Hz), 126.7, 125.9, 125.7, 125.4, 98.5 (d, J = 183.0 Hz), 42.0 (d, J = 26.2 Hz), 20.7 (d, J = 2.9 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −151.6 (dd, J = 24.0, 18.9 Hz, 1F). IR (neat, cm^{-1}): 1720, 1604, 1466, 1244, 1007, 882, 732. MS (EI): *m/z* (%) 178 (39), 191 (42), 196 (67), 197 (46), 219 (40), 240 (100, M^+). HRMS: Calcd. for $C_{16}H_{13}FO$: 240.0950; found: 240.0953.

*4.3.30. 2-Fluoro-2-(2-fluorophenyl)-2,3-dihydro-1H-inden-1-one (**10n**)*

^1H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, J = 7.5 Hz, 1H), 7.68 (t, J = 7.2 Hz, 2H), 7.20–7.48 (m, 4H), 7.00 (t, J = 9.3 Hz, 1H), 3.56–3.77 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5 (d, J = 18.2 Hz), 158.6 (dd, J = 244.3, 6.6 Hz), 150.5, 136.5, 133.5, 130.3 (d, J = 8.0 Hz), 128.3, 127.1 (dd, J = 13.1, 3.7 Hz), 126.6, 126.1 (q, J = 12.4 Hz), 125.5, 124.4, 115.6 (dd, J = 20.4, 1.4 Hz), 95.5 (d, J = 184.4 Hz), 41.8 (dd, J = 26.2, 2.9 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −113.8 (m, 1F), −158.7 (dd, J = 24.3, 20.6 Hz, 1F). IR (neat, cm^{-1}): 1717, 1605, 1488, 1264, 1214, 775. MS (EI): *m/z* (%) 196 (57), 197 (33), 214 (24), 215 (24), 224 (22), 244 (100, M^+). HRMS: Calcd. for $C_{15}H_{10}F_2O$: 244.0700; found: 244.0701.

*4.3.31. 2-Fluoro-2-(thiophen-3-yl)-2,3-dihydro-1H-inden-1-one (**10o**)*

^1H NMR (300 MHz, $CDCl_3$): δ 7.81 (d, J = 7.8 Hz, 1H), 7.68 (t, J = 7.5 Hz, 1H), 7.31–7.51 (m, 4H), 7.11 (d, J = 5.1 Hz, 1H), 3.64–3.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6 (d, J = 19.7 Hz), 149.7 (d, J = 5.1 Hz), 138.1 (d, J = 27.0 Hz), 136.5, 133.5, 128.6, 126.9, 126.6, 125.6, 125.3 (d, J = 4.4 Hz), 123.0 (d, J = 7.3 Hz), 96.0 (d, J = 187.4 Hz), 41.1 (d, J = 24.1 Hz). ^{19}F NMR (282 MHz, $CDCl_3$): δ −147.3 (dd, J = 20.6, 10.4 Hz, 1F). IR (neat, cm^{-1}): 3108, 2927, 1728, 1609, 1303, 1213, 1085, 917, 736. MS (EI): *m/z* (%) 184 (41), 185 (68), 202 (33), 203 (63), 212 (26), 232 (100, M^+). HRMS: Calcd. for $C_{13}H_9FOS$: 232.0358; found: 232.0361.

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