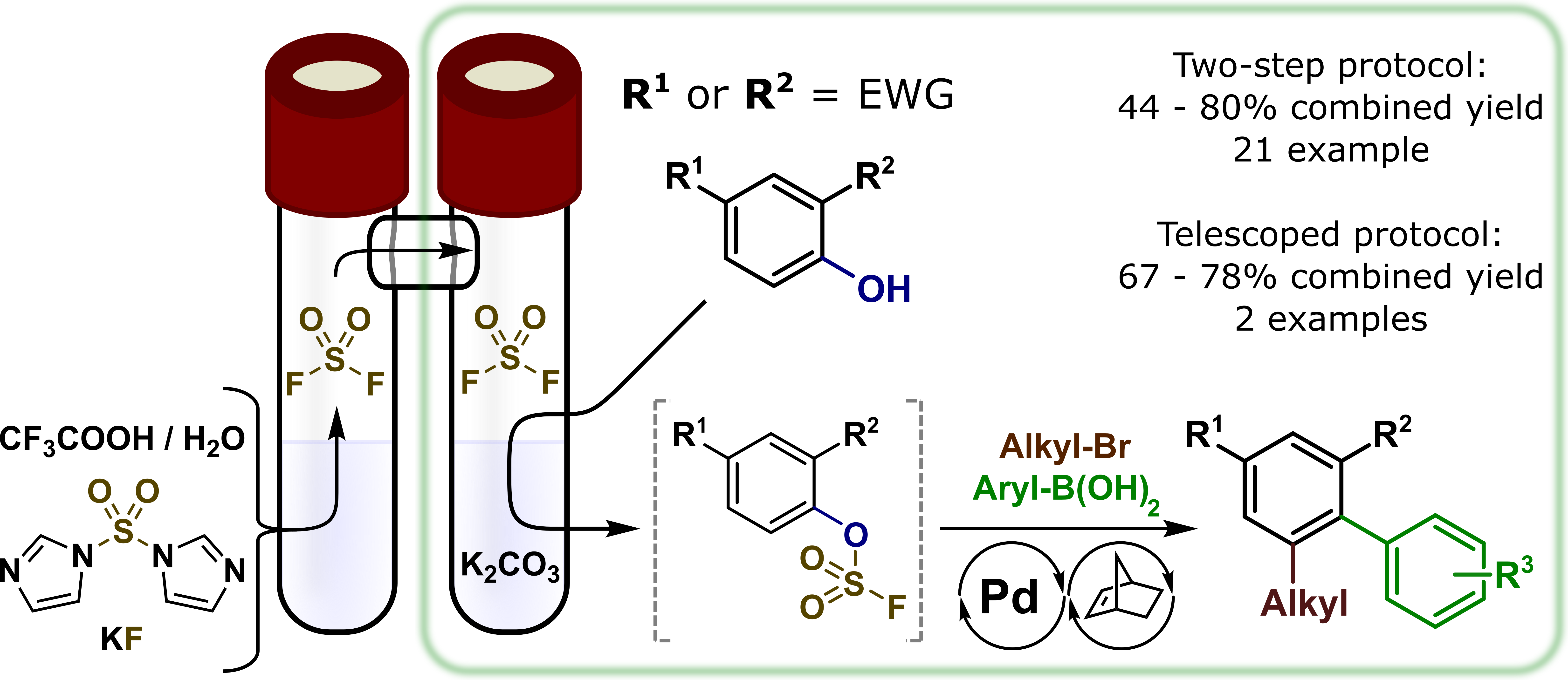
Introduction of Aryl Fluorosulfates into the Realm of Catellani Reaction Substrates

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Supporting Information Placeholder



ABSTRACT: Application of activated phenol fluorosulfates as substrates in a Pd/NBE mediated sequential alkylation-arylation, commonly known as a Catellani reaction, is presented. These substrates provide a level of complementarity to the commonly used aryl halides and, in combination with a plethora of existing Catellani reaction variations, enable even wider application of this powerful synthetic tool.

Two decades ago, Catellani *et al* for the first time described the use of norbornene (NBE) as transient mediator to facilitate aromatic C-H activation *via* palladacycle formation – a discovery that enabled one-pot sequential *ortho*/*ipso* functionalization of iodoarenes.[1](#_ENREF_1) Since then this catalytic system has gathered significant interest and inspired researchers to develop novel variations of the reaction.[2](#_ENREF_2) Even though the range of compatible terminal reagents and introducible functionalities expanded rapidly, the substrate scope remained largely limited to aryl iodides. Indeed, only recent reports detail the application of aryl bromides[3](#_ENREF_7) or arylboronic acids,[4](#_ENREF_9) while only a few sparse accounts of aryl sulfonate application are available to this day.[5](#_ENREF_11)

The introduction of aryl bromides was a tremendous advancement towards broader application of the Catellani reaction. Yet both bromides and iodides are related chemical entities, often sharing common substitution patterns and formal synthesis routes. Furthermore, terrestrial sources are scarce in naturally occurring halogenated aromatic compounds.[6](#_ENREF_13) Phenols, however, are ubiquitous both in biomass and in fossil materials,[7](#_ENREF_14) are susceptible to pre-functionalization owing to their high reactivity, and can be uneventfully transformed into corresponding sulfonates.[8](#_ENREF_15)

Aryl triflates are regarded as the default sulfonates for transition metal-catalyzed reactions, while recent work also demonstrates the application of tosylates and mesylates in combination with complex phosphine ligands.[9](#_ENREF_16) However, the revived interest in aryl fluorosulfate chemistry offers an attractive alternative.[10](#_ENREF_18) Fluorosulfates are efficiently prepared by subjecting phenols to SO2F2 gas – a stable commodity chemical available in pressurized cylinders for large scale applications,[11](#_ENREF_23) or generated from solid reagents in a two-chamber reactor for small scale experiments.[12](#_ENREF_25) When weak bases are used for deprotonation, amino groups and aliphatic hydroxy groups are spared, and the resulting aryl fluorosulfate is endowed with reactivity of a triflate at the low overall cost of a mesylate.[13](#_ENREF_26) Furthermore, low-molecular weight fluorosulfates are thermally stable and more volatile than corresponding phenols or triflates, facilitating purification by vacuum distillation.

With these favorable chemical and physical properties in mind, establishing the compatibility of phenol fluorosulfates with a Catellani-type reaction becomes paramount for advancing their use in organic synthesis. To elucidate the general behavior of aryl fluorosulfates under Pd/NBE catalysis, a phosphine ligand-independent variant of the Catellani reaction was chosen (Scheme 1).[14](#_ENREF_27) It was also an opportunity to expand on this particular transformation as it was explored superficially in terms of tolerable substrate and reactant combinations.

Several 2-substituted fluorosulfates were initially tested and we were pleased by the excellent reactivity of **1a**, even though the two other substrates were recovered nearly quantitatively (Scheme 1). During separate experiments, **1b** provided partial conversion in the presence of X-phos, but a complex mixture was produced. S-phos, PPh3, xantphos and dcype were even less effective.[3a](#_ENREF_7) In addition, substrate **1c** was not transformed into the desired material even in the presence of X-phos. With preliminary results at hand, it was decided to focus on activated fluorosulfates. An extensive optimization was performed on **1a** as the model substrate (SI Table S1) leading to the standard conditions disclosed in the scheme of Table 1.

Scheme 1. Initial substrate scouting



aReagents and conditions: BuBr (1.50 equiv), PhB(OH)2 (1.20 equiv), Pd(OAc)2 (5 mol%), NBE (100 mol%), K2CO3 (6 equiv), DMF ([**1a**] = 0.20M), 80 °C, 5 hours. Isolated yield.

Firstly, it was established that 70 °C offered the best balance between the reaction rate, selectivity and robustness.[15](#_ENREF_28) Increasing the concentration of the fluorosulfate compared to the initial conditions (described under entry 1 of Table 1) further enhanced both the rate and the selectivity, and allowed to reduce the number of equivalents of other reagents, therefore reducing the overall environmental impact and cost of the process. Variations of auxiliary reagents, additives and solvents, however, were poorly tolerated. For example, PPh3 ligand coming from Pd(PPh3)4 suppressed the C-H activation (entry 2), likely by outcompeting NBE before its migratory insertion.[16](#_ENREF_29) X-phos allowed the desired reaction, but failed to provide improvements (entry 3), while norbornene **N2** led to complex mixtures (entry 4).[17](#_ENREF_30) Greener solvents[18](#_ENREF_31) and soluble bases suppressed the reactivity (entries 5-6). The incompatibility of the latter precluded the implementation of this protocol as a telescoped flow fluorosulfation-Catellani process.

Table 1. Optimization of reaction conditions.



|  |  |  |
| --- | --- | --- |
| entry | main deviations from standard conditions | yielda |
| 1 | [**1a**] = 0.20M, 100 mol% NBE, 1.5 equiv **2a** | 74% |
| 2 | Pd(PPh3)4 (5 mol%) as the catalyst | 0% |
| 3 | X-Phos as an additive (6 mol%) | 75% |
| 4 | **N2** instead of **N1** | 49% |
| 5 | MeCN or -valerolactone instead of DMF | <5% |
| 6 | KOAc, TEA or *n*Bu4NOAc as base | <26% |

aIsolated yield.

With the optimal conditions at hand, it was prudent to establish the difference between common leaving groups, especially between halides and sulf(on)ates (Table 2). The reactivity of fluorosulfate **1a** and triflate **5a** was essentially indistinguishable,[13](#_ENREF_26) while most of the mesylate **6a** was recovered unchanged. Good reactivity of the bromide **7a** was also observed, confirming that its transformation can also be accomplished without phosphine ligands. A broad range of activated bromides is expected to exhibit a similar reactivity. Lastly, the iodide **8a** largely favored the alternative reaction path in agreement with literature,[19](#_ENREF_32) demonstrating complementarity to fluorosulfates in the transformation discussed herein. This side-reaction also occurred with the bromide **7a**, but to a much lesser extent.

Table 2. Comparison of leaving groups.



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| substrate | LG | **2aaa**/**9aa**a | **2aaa**b | **9aa**b |
| **1a** | -OSO2F | 100:0 | 82% | n/a |
| **5a** | -OSO2CF3 | 100:0 | 81% | n/a |
| **6a** | -OSO2Me | n/a | 0% | 0% |
| **7a** | -Br | 94:6 | 62% | — |
| **8a** | -I | 26:74 | 9% | 45% |

aGC-MS data. bIsolated yield.

To further the substrate scope, several readily available activated phenols were transformed into corresponding fluorosulfates that were then applied in the Catellani reaction (Table 3). We were pleased to observe, that most of the chosen substrates provided the expected products (entries 2-11) and the outcome was unaffected by a 10-fold scale-up (entry 1). Under these conditions, the symmetrical bis(fluorosulfate) **1p** reacted once, while the second fluorosulfate moiety served as an activating group and remained intact (entry 16). Naturally, in absence of preinstalled *ortho* substituents (R1 = H), C-H activation of both *ortho* positions occurred (entry 17). Presence of aldehyde or nitrile moieties at the 2-position (entries 14, 15) led to complex mixtures devoid of the target material, but aldehyde functionality was well tolerated at the 4-position (entry 13). Unfortunately, compounds bearing weakly electron-withdrawing substituents were insufficiently reactive under the standard conditions. In cases of poor reactivity (Scheme 1, **1b-c** and Table 3, entry 12) rapid and irreversible precipitation of Pd-black occurred within minutes and most of the substrate could be recovered even after prolonged reaction time. These observations suggest the ease of oxidative insertion of Pd0 into the C-O bond to be the primary outcome-determining factor.

Table 3. Carbocyclic substrate scope.



|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| entry | **1** | R1 | R2 | **4** | time | yielda |
| 1b | **1a** | CO2Me | – | **4aaa** | 4 h | 82% |
| 2 | **1d** | CO2Me | 4-Cl | **4daa** | 3 h | 77% |
| 3 | **1e** | NO2 | – | **4eaa** | 2 h | 73% |
| 4 | **1f** | NO2 | 4-OMe | **4faa** | 3 h | 78% |
| 5 | **1g** | CF3 | – | **4gaa** | 4 h | 70% |
| 6 | **1h** | CF3 | 5-F | **4haa** | 4 h | 30% |
| 7c | **1i** | F | – | **4iaa** | 5 h | 52% |
| 8 | **1j** | Me | 4-NO2 | **4jaa** | 5 h | 34% |
| 9c | **1j** | Me | 4-NO2 | **4jaa** | 5 h | 69% |
| 10 | **1k** | Me | 4-COMe | **4kaa** | 5 h | 63% |
| 11c,e | **1k** | Me | 4-COMe | **4kaa** | 5 h | 74% |
| 12 | **1l** | Me | 4-Cl | **4laa** | 4 h | [<5%]g |
| 13 | **1m** | OMe | 4-CHO | **4maa** | 3 h | 74% |
| 14 | **1n** | CHO | – | **4naa** | 4 h | [0%]g |
| 15 | **1o** | CN | – | **4oaa** | 4 h | [0%]g |
| 16c,f | **1p** | Me | 3-Me, 4-OSO2F | **4pab** | 6 h | 55% |
| 17d,h | **1q** | H | 4-CO2Et | **10qaa** | 3 h | 74% |

aIsolated yield. b4.0 mmol scale. c1.4 equiv *n*BuBr. d2.25 equiv *n*BuBr. e100 mol% NBE. fBoronic acid **3b** used. gGC-MS yield. h2,6-dibutylated product is obtained.

Substrates **1i-k** and **1p** were insufficiently active to be fully consumed in 5 hours under the standard conditions and/or produced significant amounts of corresponding non-alkylated Suzuki-Miyaura coupling products. Both issues were solved either by increasing the *n*BuBr loading alone (entries 7, 9 and 16) or by concurrently increasing the amount of norbornene (entry 11). It is worth noting that greater NBE loading reliably suppresses the Suzuki-Miyaura side-reaction but inhibits the migratory de-insertion, leading to increased amounts of NBE-inclusion products (commonly described in literature) that complicate chromatographic purification.[20](#_ENREF_34)

Pleased by the results with the carbocyclic substrates we switched to heterocyclic aromatic fluorosulfates **1r-u** (Scheme 2). The pyridine-2-fluorosulfate (**1t**) was especially interesting as the heterocyclic nitrogen could innately provide the needed electron-withdrawal. Unfortunately, only the thiophene derivative **1r** was in line with the expectations. Fluorosulfate **1s** was susceptible to norbornene inclusion, leading to partial conversion and poor yield, while pyridine-2-fluorosulfate (**1t**) and quinoline-8-fluorosulfate (**1u**) were completely unreactive. It is suspected, that in case of the latter, coordination of Pd to Lewis-basic nitrogen inhibits the target reaction either before the oxidative addition takes place or, more likely, after the migratory insertion of norbornene.[21](#_ENREF_35) Attempts to prepare quinoline-4-fluorosulfate from 4-quinolol were made, but the instability of the obtained compound precluded further investigation.

Scheme 2: Heterocyclic product scope.a



aIsolated yields under standard conditions.

The following alkyl halide trial showed that both straight chain and branched primary alkyl halides should be well tolerated (Scheme 3). Secondary alkyl bromide **2c** was significantly less reactive and required more forcing conditions for a comparable outcome. A switch to a corresponding iodide had an overall negative effect, marked by increased reaction rate and deteriorated selectivity. **2d** and **2e** almost completely shut down the reaction due to even greater steric demand imposed by the rigidity and conformation preference of the corresponding rings. General reactivity of unstrained secondary alkyl halides is expected to lie between **2c** and **2d**.[22](#_ENREF_36) Benzyl chloride (**2f**) provided comparable yield to primary alkyl bromides, whereas benzyl bromide completely failed to provide the target material.[3a](#_ENREF_7) The primary alkyl chloride **2g** also displayed reactivity, but some re-optimization to improve the selectivity towards the target material remains desired.

Scheme 3. Alkyl halide scope.a



aIsolated yields of the corresponding products. b2.0 equiv of **2**, 12h. c100 mol% NBE. d10 mol% Pd(OAc)2. eGC-MS yield.

Typical electron-rich and electron-deficient boronic acids **3b-j** were tested and sterically unhindered acids (Table 4, entries 1-5, 7) displayed largely similar performance. 2-substituted boronic acids **3i** and **3j**, however, failed to provide the desired material in practical quantities even with fluorine as the substituent. Brominated boronic acid **3g** was incompatible as well, largely due to its consumption in side-reactions not involving the substrate.

Table 4. Boronic acid scope.



|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| entry | boronic acid | “Aryl” | product | yielda |
| 1 | **3b** | 4-MeO-C6H4 | **4aab** | 87% |
| 2 | **3c** | 4-F-C6H4 | **4aac** | 79% |
| 3 | **3d** | 3-MeO-C6H4 | **4aad** | 85% |
| 4 | **3e** | 3-F-C6H4 | **4aae** | 74% |
| 5 | **3f** | 3-Cl-C6H4 | **4aaf** | 70% |
| 6 | **3g** | 3-Br-C6H4 | **4aag** | 9% |
| 7 | **3h** | 2-Naphthyl | **4aah** | 78% |
| 8 | **3i** | 2-MeO-C6H4 | **4aai** | [<5%]b,c |
| 9 | **3j** | 2-F-C6H4 | **4aaj** | [<5%]b,c |

aIsolated yields. b12-hour reaction time. cGC-MS yield.

During the early stages of investigation, it was noticed that the K2CO3/DMF system is excellent for the synthesis of the fluorosulfates themselves. This observation prompted an experiment to combine both steps and achieve rapid functionalization of phenols without the isolation of the fluorosulfate intermediate (Scheme 4).[13](#_ENREF_26) It was decided, that the most straightforward way of introducing the remaining Catellani reaction components while maintaining inert atmosphere is to transfer the post-fluorosulfation reaction slurry onto the solid reagents and add the alkyl bromide last. Different approaches to reagent addition are feasible as long as Pd(OAc)2 is not in solution in the absence of the fluorosulfate substrate in order to avoid premature Pd-black precipitation.

Scheme 4. Telescoped fluorosulfation-Catellani reaction.



Despite the additional presence of KF and SO2F2 in the reaction mixture arising from the fluorosulfation step and possible transfer of TFA and H2O vapor from the gas-generating chamber, only the rate of the Catellani reaction was slightly reduced whereas the combined yield was in line with expectations. Naturally, the setup could be further simplified and made even more reliable by using pure SO2F2 from a pressurized cylinder, enabling rapid library generation in multi-well plates. Furthermore, the gaseous nature of the reagent allows it to be flushed out of the fluorosulfation mixture with a stream of inert gas if it hinders the following reaction in any way, leaving only the formed KF as an additional compound, which is known for its compatibility with Pd catalysis.[23](#_ENREF_38)

In conclusion, the presented application of fluorosulfates in a Catellani-type *ortho*-alkylation/*ipso*-arylation reaction paves the way for rapid multi-functionalization of phenols bearing electron-withdrawing groups. By offering an alternative reaction outcome in comparison to corresponding aryl iodides and marginally superior performance to corresponding bromides, it empowers synthetic pathways that might have been previously overlooked. Furthermore, both the Catellani reaction and the preceding fluorosulfation of phenols are inherently compatible, providing a technique for rapid generation of compound libraries.

Experimental Section

**General** **methods**

1H NMR spectra were recorded in CDCl3 on a Bruker Avance™ III HD 400 (400 MHz) spectrometer. Chemical shifts are reported in parts per million using the solvent (7.26 ppm, singlet) as internal reference. First-order multiplets are described as d (doublet), t (triplet), q (quartet), p (pentet), h (hextuplet), hept (heptet) and as combinations thereof, with “br.” indicating a broadened peak(s). When possible, second-order multiplets are described according to their spin system with the corresponding nuclei underlined. Coupling constants were verified with WINDNMR 7.1.14 NMR simulation software.

Proton-decoupled 13C NMR and 13C APT spectra were recorded in CDCl3 on Bruker Avance™ III HD 400 (101 MHz) and Bruker Avance™ II+ 600 (126 MHz) spectrometers. Chemical shifts are reported in parts per million using the solvent (77.00 ppm, triplet) as internal reference. Number of attached protons were deduced by APT experimental data and indicated in parenthesis.

19F NMR spectra (non-decoupled) were recorded in CDCl3 on a Bruker Avance™ III HD 400 (376 MHz) spectrometer. Chemical shifts are reported in parts per million using CFCl3 (0.00 ppm, singlet) as internal reference. Coupling constants were verified with WINDNMR 7.1.14 NMR simulation software.

IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer with ALPHA-P sampling module.

Elemental analyses were performed on a Thermo Scientific Flash 2000 elemental analyzer.

Melting points were measured using Mettler Toledo DSC822e and processed with STARe thermal analysis software.

GC-MS analysis was performed using a ThermoFinnigan Trace GC oven with Restek Rxi-5MS (50 m, 0.20 mm ID, 0.33 μm) capillary column (helium carrier gas, 17:1 split injection) coupled with a Thermo Scientific ITQ900 EI-MS ion trap. A 50 °C (1 min.) – 20 °C/min – 300 °C (5 min.) program was used.

Analytical TLC was performed on pre-coated aluminum-supported silica gel 60 F245 (250 m) TLC plates with the aid of UV (254 nm) visualization. Preparative liquid flash chromatography was conducted on direct phase silica gel (40-60 m, average pore diameter 60 Å) from Acros Organics.

Reagents were obtained from commercial sources (Sigma-Aldrich, Acros Organics, Fluorochem) and were used directly without purification. Petroleum ether (boiling range 40 – 65 °C, VWR) was distilled prior to use. Other chromatography solvents were of analytical grade (Fischer Scientific) and were used as received. Anhydrous solvents over molecular sieves in Acroseal™ bottles and Palladium (II) acetate (99.9% trace metals basis) were purchased from Acros Organics. Deuterated chloroform (99.8% D, 0.1% v/v of TMS as internal standard) was purchased from Sigma-Aldrich.

**1,1’-sulfonyldiimidazole (SDI)**

The material was prepared following a modified literature procedure.[24](#_ENREF_40) SO2Cl2 (24.7 mL, 98.5 wt%, 300 mmol, 1.0 equiv) in DCM (210 mL) was added dropwise (5 mL/min) to a vigorously stirred suspension of imidazole (92.8 g, 99 wt%, 1.35 mol, 4.5 equiv) in DCM (540 mL) maintained at 0 °C. Complete dissolution if imidazole was observed prior to precipitation of imidazolium chloride. Once the addition was completed, the cooling was maintained for 3 hours and then the suspension was left at ambient temperature for 18 hours. Imidazolium chloride was filtered off; the filter cake was washed with DCM (3 × 100 mL) and the combined filtrate was washed with H2O (150 mL), dried with Na2SO4 and evaporated under reduced pressure. The crystalline residue was recrystallized from boiling 2-PrOH (300 mL) to afford the analytically pure target material (53.32 g, 90% yield) as thick colorless plates.

**1H NMR** (400 MHz, CDCl3) δ: 8.04 (dd, *J* = 1.4, 0.8 Hz, 1H), 7.31 (dd, *J* = 1.7, 1.4, 1H), 7.17 (dd, *J* = 1.7, 0.8 Hz, 1H). **13C{1H} NMR** (101 MHz, CDCl3): 136.5, 132.4, 117.3.

**General procedure for synthesis of aryl fluorosulfates 1a-u**

A 10 mL two-chamber reactor (total volume of 10–12 mL) was used for reactions generating up to 2.5 mmol of SO2F2. The 100 mL reactor was used for up to 15 mmol of SO2F2 and the 400 mL reactor was used for up to 50 mmol of SO2F2 respectively (picture of these reactors is provided as SI Figure S1-1). Running the reaction significantly (two times and more) below these indicated thresholds requires raising the excess of SO2F2 to up to 1.50 equiv for reliable full conversion. The gas is highly soluble in organic solvents therefore the actual pressure is lower than theoretical.[12](#_ENREF_25)

Chamber A of a 10 mL two-chamber reactor was charged with 1,1’-sulfonyldiimidazole (496 mg, 2.5 mmol, 1.25 equiv) and potassium fluoride (349 mg, 6.0 mmol, 3.0 equiv). Next, chamber B was charged with the corresponding phenol (2 mmol, 1.0 equiv) or diol (1 mmol, 0.50 equiv), fine dry potassium carbonate (552 mg, 4 mmol, 2.0 equiv) and acetonitrile (4 mL). The reactor was capped and trifluoroacetic acid/water mixture (2 mL, 50:50 v/v) was injected into chamber A through the septa using a syringe. A 15 – 30 s delay followed by gradual gas evolution was observed over the next 30 minutes. Contents of both chambers were vigorously stirred at 20 °C ambient temperature for 18 hours.

Both chambers were uncapped and the SO2F2 was allowed to diffuse out of the reactor over 1 hour. Contents of the chamber B were transferred into a separatory funnel containing EtOAc or PE (20 mL) and water (60 mL). The target material was extracted into the organic phase, which was then washed with water (2 × 20 mL) and brine (20 mL), dried with Na2SO4 and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel, filtration trough a plug of silica gel or vacuum distillation.

**Methyl 2-((fluorosulfonyl)oxy)benzoate (1a)**

General procedure was followed using 1.0 equiv of methyl 2-hydroxybenzoate (1.83 g, 1.56 mL, 12 mmol). The crude material was purified by flash chromatography on silica gel using PE/EtOAc (9:1) to afford analytically pure title compound as a colorless oil (5.265 g, 90%).

Alternatively, general procedure was followed using 1.0 equiv of methyl salicylate (3.80 g, 3.24 mL, 25 mmol). Fractional vacuum distillation of the crude material (110 °C at 1 mbar) provided the analytically pure title compound as a colorless oil (4.100 g, 70%).

**1H NMR** (400 MHz, CDCl3) δ: 8.11 (ddd, *J* = 7.8, 1.8, 0.4 Hz, 1H), 7.66 (ddd, *J* = 8.2, 7.5, 1.8 Hz, 1H), 7.51 (ddd, *J* = 7.8, 7.5, 1.2 Hz, 1H), 7.42 (dddd, *J* = 8.2, 1.6, 1.2, 0.4 Hz, 1H), 3.98 (s, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 163.8 (C=O), 148.5 (d, *J* = 1.3 Hz, C), 134.4 (CH), 132.9 (CH), 128.8 (CH), 123.9 (d, *J* = 1.3 Hz, C), 122.4 (CH), 52.8 (CH3). **19F NMR** (376 MHz, CDCl3) δ: 41.1 (d, *J* = 1.6 Hz). **EI-MS** m/z (calc. 234.0): 234.1 (23%, M+∙), 203.2 (100%), 120.1 (48%). **IR** (neat) cm-1: 1727.3, 1447.1, 1231.2, 911.8, 777.6.

The obtained analytical data is in agreement with literature.[12](#_ENREF_25)

**2-Methylphenyl sulfurofluoridate (1b)**

General procedure was followed using 1.0 equiv of 2-methylphenol (2.70 g, 25 mmol). The crude material was purified by filtration through a short pad of silica gel using PE/EtOAc (95:5) to afford the title compound as a colorless volatile oil (4.51 g, 94%).

**1H NMR** (400 MHz, CDCl3) δ: 7.35 – 7.26 (m, 4H), 2.39 (s, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 149.1 (d, *J* = 1.0 Hz, C), 132.3 (CH), 130.5 (d, *J* = 0.9 Hz, C), 128.5 (CH), 127.7 (CH), 120.9 (d, *J* = 1.1 Hz, CH), 16.0 (d, *J* = 1.4 Hz, CH3). **19F NMR** (376 MHz, CDCl3) δ: 38.6 (p, J = 1.1 Hz). **EI-MS** m/z (calc. 190.0): 190.3 (64%, M+∙), 107.2 (36%), 89.2 (31%), 77.2 (100%). **IR** (neat) cm-1: 1443.4, 1230.8, 915.12, 817.0, 764.4.

The obtained analytical data is in agreement with literature.[10e](#_ENREF_22)

**2-Methoxyphenyl sulfurofluoridate (1c)**

General procedure was followed using 1.0 equiv of 2-methoxyphenol (248 mg, 2.0 mmol). The crude material was purified by flash chromatography on silica gel using PE/EtOAc (95:5) to afford analytically pure title compound as a colorless volatile oil (357 mg, 87%).

**1H NMR** (400 MHz, CDCl3) δ: 7.35 (ddd, *J* = 8.4, 7.5, 1.6 Hz 1H), 7.31 (dddd, *J* = 8.2, 1.6, 1.3, 0.3 Hz, 1H), 7.06 (ddp, *J* = 8.4, 1.5, 0.3 Hz, 1H), 6.99 (ddd, *J* = 8.2, 7.5, 1.5 Hz, 1H), 3.92 (d, *J* = 0.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 151.2 (C), 139.0 (d, *J* = 1.2 Hz, C), 129.6 (CH), 122.4 (d, *J* = 0.9 Hz, CH), 120.9 (CH), 113.5 (CH), 56.1 (CH3). **19F NMR** (376 MHz, CDCl3) δ: 39.1 (d, *J* = 1.3 Hz). **EI-MS** m/z (calc. 206.0): 206.0 (62%, M+∙), 123.0 (59%), 95.7 (55%), 77.1 (100%). **IR** (neat) cm-1: 1499.9, 1440.0, 1230.6, 1101.79, 910.4, 757.1

The obtained analytical data is in agreement with literature.[10b](#_ENREF_19)

**Methyl 5-chloro-2-((fluorosulfonyl)oxy)benzoate (1d)**

General procedure was followed using 1.0 equiv of methyl 5-chloro-2-hydroxybenzoate (1.87 g, 10 mmol). The crude material was purified by flash chromatography on silica gel using PE/EtOAc (9:1) to afford analytically pure title compound as a colorless oil (2.61 g, 97%).

**Anal.** Calcd forC8H6ClFO5S: C, 35.77; H, 2.25; N, 0.00. Found: C, 35.78; H, 2.24; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 8.08 (dd, *J* = 2.7, 0.4 Hz, 1H), 7.62 (dd, *J* = 8.7, 2.7 Hz, 1H), 7.37 (ddd, *J* = 8.7, 1.4, 0.4 Hz, 1H), 3.98 (s, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 162.7 (C=O), 146.8 (d, *J* = 1.2 Hz, C), 134.8 (C), 134.2 (CH), 132.8 (CH), 125.3 (d, *J* = 1.4 Hz, C), 123.9 (CH), 53.1 (CH3). **19F NMR** (376 MHz, CDCl3) δ: 41.2 (d, *J* = 1.4 Hz). **EI-MS** m/z (calc. 268.0): 268.0 (33%, M+∙), 270.0 (11%, M+∙), 237.0 (61%), 154 (100%). **IR** (neat) cm-1: 1730.8, 1451.9, 1436.0, 1170.9, 911.05.

**2-Nitrophenyl sulfurofluoridate (1e)**

General procedure was followed using 1.0 equiv of 2-nitrophenol (1.39 g, 10 mmol). The crude material was purified by flash chromatography on silica gel using PE/EtOAc (8:2) to afford analytically pure title compound as a faintly yellow oil (1.69 g, 77%).

**Anal.** Calcd forC6H4FNO5S: C, 32.59; H, 1.82; N, 6.33. Found: C, 32.73; H, 1.80; N, 6.59. **1H NMR** (400 MHz, CDCl3) δ: 8.20 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.79 (ddd, *J* = 8.2, 7.6, 1.7 Hz, 1H), 7.63 (ddd, *J* = 8.2, 7.6, 1.4 Hz, 1H), 7.58 (dt, *J* = 8.2, 1.4 Hz, 1H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 141.7 (d, *J* = 1.2 Hz, C), 141.3 (br. s, C), 135.4 (CH), 129.6 (CH), 126.9 (CH), 123.8 (d, *J* = 0.7 Hz, CH). **19F NMR** (376 MHz, CDCl3) δ: 42.1 (d, *J* = 1.4 Hz). **EI-MS** m/z (calc. 221.0): 221.1 (100%, M+∙), 191.2 (46%), 108.3 (41%), 80.1 (63%), 63.1 (87%). **IR** (neat) cm-1: 1533.5, 1453.0, 1345.8, 1234.0, 910.2.

**4-Methoxy-2-nitrophenyl sulfurofluoridate (1f)**

General procedure was followed using 1.0 equiv of 4-methoxy-2-nitrophenol (338 mg, 2.0 mmol). The crude material was purified by flash chromatography on silica gel using PE/EtOAc (8:2) to afford analytically pure title compound as a faintly yellow oil (406 mg, 81%).

**Anal.** Calcd forC7H6NFO6S: C, 33.47; H, 2.41; N, 5.58. Found: C, 33.82; H, 2.01; N, 6.07. **1H NMR** (400 MHz, CDCl3) δ: 7.65 (d, *J* = 3.1 Hz, 1H), 7.46 (dd, *J* = 9.1, 1.4 Hz, 1H), 7.23 (dd, *J* = 9.1, 3.1 Hz, 1H), 3.92 (s, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 159.4 (C), 141.7 (br. s, C), 135.0 (d, *J* = 1.2 Hz, C), 124.7 (CH), 120.7 (CH), 111.3 (CH), 56.4 (CH3). **19F NMR** (376 MHz, CDCl3) δ: 41.1 (d, *J* = 1.4 Hz). **EI-MS** m/z (calc. 251.0): 251.2 (99%, M+∙), 168.2 (87%), 110.2 (44%), 69.1 (100%). **IR** (neat) cm-1: 1616.5, 1451.2, 1232.7, 1173.5, 801.1.

**2-(Trifluoromethyl)phenyl sulfurofluoridate (1g)**

General procedure was followed using 1.0 equiv of 2-(trifluoromethyl)phenol (1.62 g, 10 mmol). The crude material was filtered through a short pad of silica using PE/EtOAc (98:2) to afford analytically pure title compound as a volatile colorless oil (2.30 g, 94%).

**Anal.** Calcd forC7H4F4O3S: C, 34.44; H, 1.65; N, 0.00. Found: C, 34.27; H, 1.52; N, 0.00. **1 NMR** (400 MHz, CDCl3) δ: 7.82 – 7.76 (m, 1H), 7.76 – 7.66 (m, 1H), 7.60 – 7.52 (m, 2H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 146.9 (qd, *J* = 1.8, 1.1 Hz, C), 134.0 (q, *J* = 1.1 Hz, CH), 128.6 (CH), 128.1 (q, *J* = 4.8 Hz, CH), 123.0 (qd, *J* = 33.0, 1.4 Hz, C), 122.00 (q, *J* = 273.0 Hz, CF3), 121.95 (d, *J* = 1.3 Hz, CH). **19F NMR** (376 MHz, CDCl3) δ: 41.7 (qd, *J* = 5.6, 1.9 Hz), -61.5 (d, *J* = 5.5 Hz). **EI-MS** m/z (calc. 244.0): 244.0 (100%, M+∙), 161.0 (67%), 133.1 (86%), 113.1 (60%). **IR** (neat) cm-1: 1453.2, 1316.9, 1137.0, 1114.9, 906.3.

**5-Fluoro-2-(trifluoromethyl)phenyl sulfurofluoridate (1h)**

General procedure was followed using 1.0 equiv of 2-(trifluoromethyl)phenol (1.08 g, 6 mmol). The crude material was purified by flash chromatography on silica gel using PE/EtOAc (95:5 – 80:20) to afford two equally sized fractions. The first fraction provided the title compound as a highly volatile colorless oil (690 mg, 44%).

Evaporation more polar fraction and recrystallization of the residue from boiling heptane afforded the corresponding diaryl sulfate (**1h-2**, *vide infra*) as a colorless crystalline solid (700 mg, 55%).

**Anal.** Calcd forC7H3F5O3S: C, 32.07; H, 1.15; N, 0.00. Found: C, 32.60; H, 1.30; N 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.80 (ddqd, *J* = 8.8, 5.7, 0.7, 0.3 Hz, 1H), 7.34 (dm, *J* = 8.1 Hz, 1H), 7.26 (dddq, *J* = 8.8, 7.4, 2.4, 0.7 Hz, 1H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 164.7 (dq, *J* = 258.5, 1.1 Hz, CF), 147.5 (dp, *J* = 11.0, 1.5 Hz, C), 129.7 (dq, *J* = 9.7, 4.8 Hz, CH), 121.7 (q, *J* = 272.7 Hz, CF3), 119.5 (qdd, *J* = 33.6, 4.2, 1.2 Hz, C), 115.9 (d, *J* = 21.7 Hz, CH), 110.7 (dd, *J* = 26.7, 1.3 Hz, CH). **19F NMR** (376 MHz, CDCl3) δ: 41.9 (qd, *J* = 5.5, 1.4 Hz), -61.0 (ddq, *J* = 5.5, 1.6, 0.7 Hz), -101.4 (dddq, *J* = 8.1, 7.4, 5.7, 1.6 Hz). **EI-MS** m/z (calc. 262.0): 262.0 (66%, M+∙), 179.1 (79%), 151.1 (100%), 101.1 (53%). **IR** (neat) cm-1: 1458.7, 1312.3, 1135.1, 1107.2, 814.1.

**Bis(5-fluoro-2-(trifluoromethyl)phenyl) sulfate (1h-2):**

Obtained during **1h** synthesis in 55% yield (*vide supra*).

**Anal.** Calcd forC14H6F8O4S: C, 39.84; H, 1.43; N, 0.00. Found: C, 39.94; H, 1.34; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.76 (ddqd, *J* = 8.8, 5.8, 0.6, 0.3 Hz, 2H), 7.46 (ddqd, *J* = 8.7, 2.4, 0.6, 0.3 Hz, 2H), 7.20 (dddq, *J* = 8.8, 7.4, 2.4, 0.7 Hz, 2H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 164.7 (dq, *J* = 257.4, 1.1 Hz, CF), 148.0 (dq, *J* = 11.2, 1.6 Hz, C), 129.4 (dq, *J* = 10.1, 4.9 Hz, CH), 121.9 (q, *J* = 272.7 Hz, CF3), 119.1 (qd, *J* = 33.3, 4.1 Hz, C), 114.9 (d, *J* = 21.8 Hz, CH), 110.3 (d, *J* = 26.8 Hz, CH). **19F NMR** (376 MHz, CDCl3) δ: -61.0 (dh, *J* = 1.7, 0.7 Hz), -102.1 (dddq, *J* = 8.7, 7.4, 5.8, 1.7 Hz). **EI-MS** m/z (calc. 422.0): 422.0 (100%, M+∙), 243.0 (78%), 179.1 (61%), 151.1 (66%), 101.1 (52%). **IR** (neat) cm-1:1128.3, 1109.0, 825.0.

**2-Fluorophenyl sulfurofluoridate (1i)**

General procedure was followed using 1.0 equiv of 2-fluorophenol (1.12 g, 0.893 mL, 10 mmol). The crude material was purified by flash chromatography on silica gel using PE/EtOAc (95:5) to afford analytically pure title compound as a highly volatile colorless oil (1.64 g, 85%).

**1H NMR** (400 MHz, CDCl3) δ: 7.45 – 7.37 (m, 2H), 7.32 – 7.22 (m, 2H). **13C{1H} NMR** (125 MHz, CDCl3) δ: 153.6 (dd, *J* = 254.6, 0.6 Hz, CF), 137.2 (dd, *J* = 13.1, 0.9 Hz, C), 130.1 (d, *J* = 7.1 Hz, CH), 125.1 (d, *J* = 4.1 Hz, CH), 123.3 (t, *J* = 0.9 Hz, CH), 117.9 (d, *J* = 17.9 Hz, CH). **19F NMR** (376 MHz, CDCl3) δ: 38.6 (dd, *J* = 10.3, 1.2 Hz), -128.3 (ddddd, *J* = 10.3, 9.9, 7.3, 4.7, 1.3 Hz). **EI-MS** m/z (calc. 194.0): 194.0 (80%, M+∙), 111.0 (47%), 83.0 (100%), 57.0 (44%). **IR** (neat) cm-1: 1499.3, 1450.8, 1232.6, 942.1, 761.2.

The obtained analytical data is in agreement with literature.[10e](#_ENREF_22)

**2-Methyl-4-nitrophenyl sulfurofluoridate (1j)**

General procedure was followed using 1.0 equiv of 2-methyl-4-nitrophenol (306 mg, 2.0 mmol). The crude material was purified by flash chromatography on silica gel using PE/EtOAc (85:15) to afford analytically pure title compound as a faintly yellow oil (405 mg, 86%).

**Anal.** Calcd forC7H6FNO5S: C, 35.75; H, 2.57; N, 5.96. Found: C, 35.59; H, 2.39; N, 6.36. **1H NMR** (400 MHz, CDCl3) δ: 8.27 – 8.21 (m, 1H), 8.19 (ddq, *J* = 9.0, 2.8, 0.6 Hz, 1H), 7.52 (ddp, *J* = 9.0, 1.5, 0.4 Hz, 1H), 2.51 (br. s, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 152.2 (d, *J* = 1.0 Hz, C), 147.0 (C), 132.9 (d, *J* = 1.0 Hz, C), 127.5 (CH), 123.3 (CH), 122.1 (d, *J* = 1.3 Hz, CH), 16.3 (d, *J* = 1.2 Hz, CH3). **19F NMR** (376 MHz, CDCl3) δ: 40.3 (dq, *J* = 1.5, 0.7 Hz). **EI-MS** m/z (calc. 235.0): 235.0 (100%, M+∙), 219.0 (15%), 205.0 (49%), 177.0 (38%). **IR** (neat) cm-1: 1530.0, 1449.3, 1349.8, 1233.8, 1222.0, 800.4

**4-Acetyl-2-methylphenyl sulfurofluoridate (1k)**

General procedure was followed using 1.0 equiv of 4-acetyl-2-methylphenol (300 mg, 2.0 mmol). The crude material was purified by flash chromatography on silica gel using PE/EtOAc (85:15) to afford analytically pure title compound as a colorless oil (450 mg, 97%).

**Anal.** Calcd forC9H9FO4S: C, 46.55; H, 3.91; N, 0.00. Found: C, 46.80; H, 3.49; N 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.95 – 7.90 (m, 1H), 7.88 (ddq, *J* = 8.6, 2.3, 0.6 Hz, 1H), 7.42 (ddp, *J* = 8.6, 1.6, 0.4 Hz, 1H), 2.62 (s, 3H), 2.45 (br. s, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 196.4 (C=O), 151.7 (d, *J* = 1.0 Hz, C), 136.9 (C), 132.3 (CH), 131.2 (d, *J* = 0.9 Hz, C), 128.0 (CH), 121.2 (d, *J* = 1.2 Hz, CH), 26.7 (CH3), 16.1 (d, *J* = 1.3 Hz, CH3). **19F NMR** (376 MHz, CDCl3) δ: 39.6 (dq, *J* = 1.6, 0.8 Hz). **EI-MS** m/z (calc. 232.0): 232.0 (4%, M+∙), 217.0 (100%), 134.0 (25%). **IR** (neat) cm-1: 1689.1, 1446.9, 1231.2, 1098.5, 806.2.

**4-Chloro-2-methylphenyl sulfurofluoridate (1l)**

General procedure was followed using 1.0 equiv of 4-chloro-2-methylphenol (285 mg, 2.0 mmol). The intermediate phenolate salt hindered stirring, therefore full conversion was not reached. The crude material was purified by flash chromatography on silica gel using PE/EtOAc (98:2) to afford analytically pure title compound as a colorless oil (256 mg, 57%).

**Anal.** Calcd forC7H6ClFO3S: C, 37.43; H, 2.69; N, 0.00. Found: C, 37.85; H, 2.30; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.34 – 7.29 (m, 1H), 7.29 – 7.24 (m, 2H), 2.37 (s, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 147.3 (d, *J* = 1.0 Hz, C), 134.1 (C), 132.5 (d, *J* = 0.9 Hz, C), 132.1 (CH), 127.8 (CH), 122.3 (d, *J* = 1.1 Hz, CH), 16.0 (d, *J* = 1.3 Hz, CH3). **19F NMR** (376 MHz, CDCl3) δ: 38.7 (br. s). **EI-MS** m/z (calc. 224.0): 224.0 (98%, M+∙), 226.0 (32%, M+∙+2), 141.0 (100%), 143.0 (33%), 77.0 (96%). **IR** (neat) cm-1: 1446.6, 1232.2, 1099.4, 863.8, 805.2.

**4-Formyl-2-methoxyphenyl sulfurofluoridate (1m)**

General procedure was followed using 1.0 equiv of 4-hydroxy-3-methoxybenzaldehyde (304 mg, 2.0 mmol). The crude material was purified by flash chromatography on silica gel using PE/EtOAc (7:3) to afford analytically pure title compound as an oxygen-sensitive colorless oil that solidified on standing (451 mg, 96%).

**Melting point:** 49 – 50 °C. **1H NMR** (400 MHz, CDCl3) δ: 10.00 (s, 1H), 7.59 (br. d, *J* = 1.5 Hz, 1H), 7.55 – 7.49 (m, 2H), 4.01 (s, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 190.3 (CHO), 152.0 (d, *J* = 0.9 Hz, C), 142.8 (d, *J* = 1.3 Hz, C), 137.0 (C), 124.0 (CH), 123.1 (d, *J* = 0.9 Hz, CH), 112.1 (CH), 56.5 (CH3). **19F NMR** (376 MHz, CDCl3) δ: 40.5 (d, *J* = 1.0 Hz). **EI-MS** m/z (calc. 234.0): 234.2 (100%, M+∙), 151.2 (44%), 95.2 (33%), 77.2 (44%). **IR** (neat) cm-1: 1699.7, 1687.5, 1447.6, 1229.4, 904.8.

The obtained analytical data is in agreement with literature.[11a](#_ENREF_23)

**2-Formylphenyl sulfurofluoridate (1n)**

Modified procedure was followed using 1.0 equiv of 2-hydroxybenzaldehyde (244 mg, 212 L 2.0 mmol), DIPEA (775 mg, 1.05 mL, 6 mmol, 3.0 equiv) as base and neat TFA (2.0 mL) as acid. The crude material was purified by flash chromatography on silica gel using PE/EtOAc (8:2) to afford analytically pure title compound as an oxygen sensitive colorless oil (315 mg, 77%).

**1H NMR** (400 MHz, CDCl3) δ: 10.32 (t, *J* = 0.6 Hz, 1H), 8.03 (ddd, *J* = 7.7, 1.9, 0.4 Hz, 1H), 7.76 (ddd, *J* = 8.3, 7.5, 1.9 Hz, 1H), 7.60 (dddd, *J* = 7.7, 7.5, 1.1, 0.6 Hz, 1H), 7.50 (dddd, *J* = 8.3, 1.7, 1.1, 0.4 Hz, 1H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 186.2 (d, *J* = 0.9 Hz, CHO), 150.6 (d, *J* = 0.8 Hz,C), 135.9 (CH), 130.8 (CH), 129.3 (CH), 128.1 (C), 122.1 (d, *J* = 0.9 Hz, CH). **19F NMR** (376 MHz, CDCl3) δ: 38.8 (dd, *J* = 1.7, 0.6 Hz). **EI-MS** m/z (calc. 204.0): 204.0 (2%, M+∙), 203.0 (11%), 120.0 (100%), 92.2 (46%). **IR** (neat) cm-1:1699.6, 1481.8, 1231.5, 911.0, 774.4.

The obtained analytical data is in agreement with literature.[10b](#_ENREF_19)

**2-Cyanophenyl sulfurofluoridate (1o)**

General procedure was followed using 1.0 equiv of 2-hydroxybenzonitrile (1.19 g, 10 mmol). The crude material was purified by flash chromatography on silica gel using PE/EtOAc (8:2) to afford analytically pure title compound as a colorless oil (1.71 g, 85%).

**1H NMR** (400 MHz, CDCl3) δ: 7.81 (ddd, *J* = 7.8, 1.7, 0.4 Hz, 1H), 7.77 (ddd, *J* = 8.5, 7.8, 1.7 Hz, 1H), 7.57 (td, *J* = 7.8, 1.1 Hz, 1H), 7.57 (dddd, *J* = 8.5, 1.3, 1.1 Hz, 0.4 Hz, 1H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 149.9 (d, *J* = 1.0 Hz, C), 135.0 (CH), 134.5 (CH), 129.2 (CH), 122.3 (d, *J* = 1.3 Hz, CH), 113.2 (C), 107.4 (d, *J* = 1.0 Hz, C). **19F NMR** (376 MHz, CDCl3) δ: 40.2 (d, *J* = 1.3 Hz). **EI-MS** m/z (calc. 201.0): 201.1 (88%, M+∙), 118.1 (57%), 90.1 (100%), 63.0 (53%). **IR** (neat) cm-1: 2239.4, 1448.4, 1235.0, 905.9, 819.1.

The obtained analytical data is in agreement with literature.[10b](#_ENREF_19)

**2,3-Dimethyl-1,4-phenylene bis(sulfurofluoridate) (1p)**

General procedure was followed using 0.5 equiv of 2,3-dimethylbenzene-1.4-diol (414 m, 3 mmol). The crude material was purified by flash chromatography on silica gel using PE/MTBE (7:3) to afford analytically pure title compound as a colorless oil (907 mg, 94%).

**Anal.** Calcd forC8H8F2O6S2: C, 31.79; H, 2.67; N, 0.00. Found: C, 31.80; H, 2.70; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.31 (br. s, 2H), 2.36 (s, 6H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 147.8 (d, *J* = 0.8 Hz, C), 133.0 (d, *J* = 0.8 Hz, C), 120.0 (d, *J* = 1.3 Hz, CH), 13.4 (d, *J* = 1.3 Hz, CH3). **19F NMR** (376 MHz, CDCl3) δ: 39.1 (dq, *J* = 1.4, 0.7 Hz). **EI-MS** m/z (calc. 302.0): 302.2 (73%, M+∙), 219.2 (100%), 136.2 (71%), 108.2 (54%). **IR** (neat) cm-1: 1445.8, 1235.0, 1171.4, 912.0, 797.4.

**Ethyl 4-((fluorosulfonyl)oxy)benzoate (1q)**

General procedure was followed using 1.0 equiv of ethyl 4-hydroxybenzoate (166 mg, 1.0 mmol). The crude material was purified by flash chromatography on silica gel using PE/EtOAc (9:1) to afford analytically pure title compound as a colorless oil (234 mg, 94%).

**1H NMR** (400 MHz, CDCl3) δ: 8.18 (AA’MM’X, *J*AM+AA’ = 9.0 Hz, *J*AX = 0 Hz, 2H), 7.42 (AA’MM’X, *J*AM+MM’ = 9.0 Hz, *J*MX = 1.0 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 164.9 (C), 152.7 (d, *J* = 0.8 Hz, C), 132.0 (CH), 131.0 (C), 120.9 (d, *J* = 1.2 Hz, CH), 61.6 (CH2), 14.2 (CH3). **19F NMR** (376 MHz, CDCl3) δ: 38.2 (t, *J* = 1.1 Hz). **EI-MS** m/z (calc. 248.0): 248.2 (4%, M+∙), 220.2 (57%), 203.2 (100%), 120.2 (19%). **IR** (neat) cm-1: 1719.8, 1450.2, 1273.6, 1232.3, 909.3.

The obtained analytical data is in agreement with literature.[10b](#_ENREF_19)

**Methyl 3-((fluorosulfonyl)oxy)thiophene-2-carboxylate (1r)**

General procedure was followed using 1.0 equiv of methyl 3-hydroxythiophene-2-carboxylate (316 mg, 2.0 mmol). The crude material was purified by flash chromatography on silica gel using PE/EtOAc (85:15) to afford analytically pure title compound as a colorless oil (440 mg, 92%).

**1H NMR** (400 MHz, CDCl3) δ: 7.58 (d, *J* = 5.5 Hz, 1H), 7.12 (dd, *J* = 5.5, 1.2 Hz, 1H), 3.94 (s, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 159.7 (C=O), 145.5 (d, *J* = 1.1 Hz, C), 130.7 (CH), 122.4 (d, *J* = 1.1 Hz, C), 121.9 (d, *J* = 0.7 Hz, CH), 52.7 (CH3). **19F NMR** (376 MHz, CDCl3) δ: 39.6 (d, *J* = 1.2 Hz). **EI-MS** m/z (calc. 234.0): 240.2 (100%, M+∙), 209.2 (74%), 126.2 (35%), 101.2 (35%). **IR** (neat) cm-1: 1719.3, 1438.0, 1234.0, 868.2, 773.6.

The obtained analytical data is in agreement with literature.[25](#_ENREF_41)

**Methyl 3-((fluorosulfonyl)oxy)picolinate (1s)**

General procedure was followed using 1.0 equiv of methyl 3-hydroxypicolinate (306 mg, 2.0 mmol). The crude material was purified by flash chromatography on silica gel using PE/EtOAc (6:4) to afford analytically pure title compound as a colorless oil (379 mg, 81%).

**Anal.** Calcd forC7H6FNO5S: C, 35.75; H, 2.57; N, 5.96. Found: C, 36.03; H, 2.64; N, 6.30. **1H NMR** (400 MHz, CDCl3) δ: 8.80 (dd, *J* = 4.6, 1.4 Hz, 1H), 7.84 (dt, *J* = 8.4, 1.4 Hz, 1H), 7.66 (dd, *J* = 8.4, 4.6 Hz, 1H), 4.06 (s, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 162.5 (C=O), 149.4 (CH), 146.4 (d, *J* = 1.3 Hz, C), 141.4 (d, *J* = 0.9 Hz, C), 131.1 (CH), 128.2 (CH), 53.4 (CH3). **19F NMR** (376 MHz, CDCl3) δ: 42.0 (d, *J* = 1.4 Hz). **EI-MS** m/z (calc. 235.0): 232.0 (0%, M+∙), 204.1 (21%), 177.2 (100%), 82.1 (54%). **IR** (neat) cm-1: 1732.7, 1452.1, 1429.8, 1080.3, 906.3.

**Pyridin-2-yl sulfurofluoridate (1t)**

General procedure was followed using 1.0 equiv of 2-pyridone (190 mg, 2.0 mmol). The crude material was purified by flash chromatography on silica gel using pentane/DCM (50:50) to afford analytically pure title compound as a highly volatile colorless oil (265 mg, 75%).

**1H NMR** (400 MHz, CDCl3) δ: 8.43 (ddd, *J* = 4.9, 2.0, 0.8 Hz, 1H), 7.93 (ddd, *J* = 8.3, 7.4, 2.0 Hz, 1H), 7.41 (ddd, *J* = 7.4, 4.9, 0.8 Hz, 1H), 7.20 (dt, *J* = 8.3, 0.8 Hz, 1H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 156.3 (d, *J* = 1.5 Hz, C), 148.6 (CH), 141.2 (CH), 124.2 (CH), 114.1 (d, *J* = 2.6 Hz, CH). **19F NMR** (376 MHz, CDCl3) δ: 43.9 (s). **EI-MS** m/z (calc. 177.0): 177.1 (36%, M+∙), 149.1 (100%). **IR** (neat) cm-1: 1466.1, 1445.7, 1234.3, 1160.5, 910.7.

The obtained analytical data is in agreement with literature.[25](#_ENREF_41)

**Quinolin-8-yl sulfurofluoridate (1u)**

General procedure was followed using 1.0 equiv of quinolin-8-ol (290 mg, 2.0 mmol). The crude material was filtered through silica using PE/EtOAc (6:4) and recrystallized from heptane/MTBE (9:1) to afford analytically pure title compound as a white solid (348 mg, 77%).

**Melting point:** 64 – 65 °C. **1H NMR** (400 MHz, CDCl3) δ: 9.07 (ddd, *J* = 4.3, 1.7, 0.3 Hz, 1H), 8.25 (ddd, *J* = 8.4, 1.7, 0.3 Hz, 1H), 7.90 (ddt, *J* = 8.3, 1.3, 0.3 Hz, 1H), 7.76 (dddd, *J* = 7.7, 1.3, 1.2, 0.3 Hz, 1H), 7.60 (ddd, *J* = 8.2, 7.7, 0.3 Hz, 1H), 7.56 (ddt, *J* = 8.4, 4.3 Hz, 0.3 Hz, 1H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 151.8 (CH), 145.9 (d, *J* = 1.2 Hz, C), 140.4 (C), 135.9 (CH), 129.9 (C), 128.7 (CH), 125.9 (CH), 122.7 (CH), 121.3 (d, *J* = 0.9 Hz, CH). **19F NMR** (376 MHz, CDCl3) δ: 40.1 (d, *J* = 1.2 Hz). **EI-MS** m/z (calc. 227.0): 227.2 (95%, M+∙), 144.2 (47%), 116.2 (100%), 89.16 (42%). **IR** (neat) cm-1: 1941.2, 1442.0, 1427.1, 846.9, 786.8.

The obtained analytical data is in agreement with literature.[25](#_ENREF_41)

**Methyl 2-(((trifluoromethyl)sulfonyl)oxy)benzoate (5a)**

Neat Tf2O (1.693 g, 1.02 mL, 6.0 mmol, 1.2 equiv) was added dropwise to a solution of methyl 2-hydroxybenzoate (761 mg, .650 L, 5 mmol) and pyridine (791 mg, 650 L, 10 mmol, 2.0 equiv) in DCM (10 mL) at 0 °C and the resulting suspension was stirred for 6 hours. It was then diluted with DCM (40 mL), washed with 1N HCl (2 × 50 mL), water (50 mL) and sat. aq NaHCO3 (50 mL), dried with Na2SO4 and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using PE/EtOAc (9:1) to afford the pure target material as a faintly straw-colored oil (1.286 g, 91%).

**1H NMR** (400 MHz, CDCl3) δ: 8.10 (ddd, *J* = 7.8, 1.9, 0.4 Hz, 1H), 7.63 (ddd, *J* = 8.3, 7.5, 1.9 Hz, 1H), 7.48 (ddd, *J* = 7.8, 7.5, 1.1 Hz, 1H), 7.31 (dp, *J* = 8.3, 0.4 Hz, 1H), 3.97 (s, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 164.2 (C=O), 148.3 (C), 134.3 (CH), 132.8 (CH), 128.4 (CH), 124.4 (C), 122.7 (q, *J* = 1.3 Hz, CH), 118.7 (q, *J* = 320.6 Hz, CF3), 52.6 (CH3). **19F NMR** (376 MHz, CDCl3) δ: -74.0 (s). **EI-MS** m/z (calc. 284.0): 284.2 (61%, M+∙), 253.2 (45%), 189.2 (100%), 95.2 (32%). **IR** (neat) cm-1: 1728.7, 1422.4, 1201.6, 1135.4, 888.8.

The obtained analytical data is in agreement with literature.[26](#_ENREF_42)

**Methyl 2-((methylsulfonyl)oxy)benzoate (6a)**

Neat MsCl (550 mg, 374 L, 4.8 mmol, 1.2 equiv) was added dropwise to a solution of methyl 2-hydroxybenzoate (609 mg, .520 L, 4 mmol) and TEA (567 mg, 781 L, 6.4 mmol, 1.4 equiv) in DCM (8 mL) at 0 °C and the resulting suspension was stirred for 6 hours. It was left to stir for 12 hours at ambient temperature and then diluted with DCM (40 mL), washed with 1N HCl (2 × 50 mL), water (50 mL) and sat. aq NaHCO3 (50 mL), dried with Na2SO4 and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using PE/EtOAc (6:4) to afford the pure target material as a viscous colorless oil (850 mg, 92%).

**1H NMR** (400 MHz, CDCl3) δ: 7.98 (ddd, *J* = 7.8, 1.8, 0.4 Hz, 1H), 7.58 (ddd, *J* = 8.3, 7.4, 1.8 Hz, 1H), 7.44 (ddd, *J* = 8.3, 1.2, 0.4 Hz, 1H), 7.39 (ddd, *J* = 7.8, 7.4, 1.2 Hz, 1H), 3.93 (s, 4H), 3.28 (s, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 164.7, 147.7, 133.8, 132.0, 127.2, 124.4, 124.1, 52.4, 38.4. **EI-MS** m/z (calc. 230.0): 230.1 (18%, M+∙), 199.1 (20%), 152.1 (100%), 120.1 (86%), 92.1 (49%). **IR** (neat) cm-1: 1722.2, 1157.2, 1079.2, 867.5.

The obtained analytical data is in agreement with literature.[27](#_ENREF_43)

**Typical small-scale Catellani procedure (0.4 mmol)**

**Methyl 6-butyl-(1,1'-biphenyl)-2-carboxylate (4aaa)**

Palladium acetate (4.5 mg, 0.02 mmol, 5 mol%) and fine dry potassium carbonate (332 mg, 2.4 mmol, 6.0 equiv) was weighed into a 5 mL screw-cap pressure vial which was then capped and subjected to 5 vacuum/argon cycles. Norbornene (18.8 mg, 0.20 mmol, 0.5 equiv), phenylboronic acid (**3a**, 61.0 mg, 0.50 mmol, 1.25 equiv) and methyl 2-((fluorosulfonyl)oxy)benzoate (**1a**, 93.7 mg, 0.40 mmol) were weighed into a 1.5 mL screw-cap vial and briefly flushed with argon. 1-bromobutane (**2a**, 65.8 mg, 51.9 L 0.48 mmol, 1.20 equiv) and DMF (0.8 mL) were then added under inert atmosphere. The obtained solution was transferred *via* 1mLsyringe to the 5 mL screw-cap pressure vial containing the catalyst and the base. The pressure vial was immediately immersed into a pre-heated oil bath (70 °C) and the reaction was conducted for 4 hours under vigorous stirring.

The blackened reaction mixture was poured into water (40 mL) and extracted with PE (20 mL). The organic phase was then washed with water (40 mL) and brine (10 mL), dried with Na2SO4 and concentrated under reduced pressure. The black residue was purified by flash chromatography on silica gel using PE/EtOAc (95:5) as solvent to afford the title compound as a viscous colorless oil (88 mg, 82%). Analytical information provided with the scaled-up procedure (*vide infra*).

**Typical scaled-up Catellani procedure (4.0 mmol)**

**Methyl 6-butyl-(1,1'-biphenyl)-2-carboxylate (4aaa)**

Palladium acetate (45 mg, 0.20 mmol, 5 mol%) and fine dry potassium carbonate (2.76 g, 20 mmol, 5.0 equiv) was weighed into a 25 mL round-bottom flask, which was then capped with a septa and subjected to 5 vacuum/argon cycles. Norbornene (188 mg, 2.0 mmol, 0.5 equiv), phenylboronic acid (**3a**, 610 mg, 5.0 mmol, 1.25 equiv) and methyl 2-((fluorosulfonyl)oxy)benzoate (**1a**, 937 mg, 673 L, 4.0 mmol) were weighed into a 10 mL flask and briefly flushed with argon. 1-bromobutane (**2a**, 658 mg, 519 L, 4.8 mmol, 1.20 equiv) and DMF (8.0 mL) were then added under inert atmosphere. The obtained solution was transferred *via* 10 mL syringe to the 25 mL round-bottom flask containing the catalyst and the base. The flask was immediately immersed into a pre-heated oil bath (70 °C) and the reaction was conducted for 4 hours under vigorous stirring.

The blackened reaction mixture was poured into water (200 mL) and extracted with PE (60 mL). The organic phase was then washed with water (100 mL) and brine (20 mL), dried with Na2SO4 and concentrated under reduced pressure. The black residue was purified by flash chromatography on silica gel using PE/EtOAc (95:5) as solvent to afford the title compound as a viscous colorless oil (879 mg, 82%).

**Anal.** Calcd forC18H20O2: C, 80.56; H, 7.51; N, 0.00. Found: C, 80.56; H, 7.64; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.65 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.42 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.41 – 7.39(m, 4H), 7.17 (AA’BB’C,2H), 3.52 (s, 3H), 2.52 – 2.27 (m, 2H), 1.44 – 1.32 (m, 2H), 1.16 (h, *J* = 7.3 Hz, 2H), 0.75 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 168.9 (C=O), 142.0 (C), 141.3 (C), 139.8 (C), 132.2 (CH), 131.9 (C), 128.9 (CH), 127.6 (CH), 127.1 (CH), 126.8 (CH), 126.7 (CH), 51.7 (CH3), 33.4 (CH2), 32.8 (CH2), 22.4 (CH2), 13.7 (CH3). **EI-MS** m/z (calc. 268.1): 268.1 (77%, M+∙), 236.2 (84%), 207.2 (74%), 193.2 (60%), 165.3 (100%). **IR** (neat) cm-1: 2954.3, 1729.6, 1286.7, 1136.8, 761.3.

**Typical telescoped fluorosulfation – Catellani procedure**

**Methyl 6-butyl-4-chloro-4'-methoxy-(1,1'-biphenyl)-2-carboxylate (4dab)**

Chamber A of a small two-chamber reactor was charged with 1,1’-sulfonyldiimidazole (496 mg, 2.5 mmol, 1.25 equiv) and potassium fluoride (349 mg, 6.0 mmol, 3.0 equiv). Next, chamber B was charged with methyl 5-chloro-2-hydroxybenzoate (**11d**, 187mg, 1 mmol, 1.0 equiv) and fine dry potassium carbonate (276 mg, 2 mmol, 2.0 equiv). The reactor was capped and subjected to 5 vacuum – argon cycles. DMF (2 mL) was injected into chamber B and trifluoroacetic acid/water mixture (2 mL, 50:50 v/v) was injected into chamber A through the corresponding septa using a syringe. A short delay followed by gradual gas evolution was observed over the next 30 minutes. Contents of both chambers were vigorously stirred at ambient temperature (20 °C) for 3 hours.

Palladium acetate (11.2 mg, 0.05 mmol, 5 mol%), fine dry potassium carbonate (553 mg, 4.0 mmol, 4.0 equiv), norbornene (47.1 mg, 0.50 mmol, 0.5 equiv) and 4-methoxyphenylboronic acid (**3b**, 182 mg, 1.20 mmol, 1.20 equiv) were weighed into a 5 mL screw-cap pressure vial and the vial was briefly flushed with argon. The suspension from the chamber B of the actively stirred two-chamber reactor was then transferred to this pressure vial *via* a 3 mL syringe, 1-bromobutane was added (**2a**, 164 mg, 130 L, 1.20 mmol, 1.20 equiv) and the vial was immersed into a pre-heated oil bath (70 °C). The reaction was conducted for 3 hours under vigorous stirring.

The blackened reaction mixture was poured into water (200 mL) and extracted with PE (50 mL). The organic phase was then washed with water (100 mL) and brine (20 mL), dried with Na2SO4 and concentrated under reduced pressure. The black residue was purified by flash chromatography on silica gel using PE/MTBE (9:1) as solvent to afford the title compound as a viscous colorless oil (261 mg, 78%).

**Anal.** Calcd forC19H21ClO3: C, 68.57; H, 6.36; N, 0.00. Found: C, 68.63; H, 6.05; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.60 (d, *J* = 2.3 Hz, 1H), 7.37 (d, *J* = 2.3 Hz, 1H), 7.05 (AA’XX’, *J*AX+AA’ = 8.7 Hz, 2H), 6.92 (AA’XX’, *J*AX+XX’ = 8.7 Hz, 2H), 3.85 (s, 3H), 3.56 (s, 3H), 2.43 – 2.34 (m, 2H), 1.43 – 1.32 (m, 3H), 1.17 (h, *J* = 7.3 Hz, 2H), 0.77 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 167.8 (C=O), 158.7 (C), 144.5 (C), 139.5 (C), 133.6 (C), 132.7 (C), 131.7 (CH), 130.8 (C), 130.0 (CH), 126.5 (CH), 113.3 (CH), 55.2 (CH3), 52.1 (CH3), 33.1 (CH2), 32.8 (CH2), 22.3 (CH2), 13.7 (CH3). **EI-MS** m/z (calc. 332.1): 332.1 (100%, M+∙), 334.1 (33%, M+∙+2), 300.1 (48%), 272.1 (60%). **IR** (neat) cm-1: 2954.8, 1734.2, 1284.2, 1242.2, 1153.0, 830.7.

**Methyl 6-butyl-4-chloro-(1,1'-biphenyl)-2-carboxylate (4daa)**

Typical small-scale procedure was followed using methyl 5-chloro-2-((fluorosulfonyl)oxy)benzoate (**1d**, 107 mg, 0.4 mmol). The reaction was conducted for 3 hours. The crude product was purified by flash chromatography using PE/EtOAc (96:4) as solvent to afford the title compound as a viscous colorless oil (93 mg, 77%).

**Anal.** Calcd forC18H19ClO2: C, 71.40; H, 6.33; N, 0.00. Found: C, 71.36; H, 6.47; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.64 (d, *J* = 2.3 Hz, 1H), 7.39 (d, *J* = 2.3 Hz, 1H), 7.37 (AA’BB’C, 3H), 7.13 (AA’BB’C, 2H), 3.53 (s, 3H), 2.42 – 2.34 (m, 2H), 1.42 – 1.33 (m, 2H), 1.16 (h, *J* = 7.3 Hz, 2H), 0.75 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 167.5 (C=O), 144.1 (C), 139.9 (C), 138.7 (C), 133.2 (C), 132.9 (C), 131.9 (CH), 128.9 (CH), 127.8 (CH), 127.2 (CH), 126.7 (CH), 52.0 (CH3), 33.1 (CH2), 32.8 (CH2), 22.3 (CH2), 13.7 (CH3). **EI-MS** m/z (calc. 302.1): 302.3 (100%, M+∙), 304.3 (100%, M+∙+2), 270.2 (8%), 241.2 (96%), 227.3 (70%), 199.3 (65%). **IR** (neat) cm-1: 2955.2, 1735.2, 1282.2, 1192.7, 700.3.

**2-Butyl-6-nitro-1,1'-biphenyl (4eaa)**

Typical small-scale procedure was followed using 2-nitrophenyl sulfurofluoridate (**1e**, 59.0 L, 88.5 mg, 0.4 mmol). The reaction was conducted for 2 hours. The crude product was purified by flash chromatography using PE/EtOAc (95:5) as solvent to afford the title compound as a viscous faintly yellow oil (74 mg, 73%).

**Anal.** Calcd forC16H17NO2: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.49; H, 6.78; N, 5.93. **1H NMR** (400 MHz, CDCl3) δ: 7.63 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.49 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.45 – 7.35 (m, 4H), 7.20 (AA’BB’C,2H), 2.49 – 2.39 (m, 2H), 1.45 – 1.33 (m, 2H), 1.17 (h, *J* = 7.3 Hz, 2H), 0.76 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 150.6 (C), 143.9 (C), 135.5 (C), 134.9 (C), 132.9 (CH), 128.8 (CH), 128.3 (CH), 127.88 (CH), 127.86 (CH), 120.8 (CH), 33.2 (CH2), 32.8 (CH2), 22.3 (CH2), 13.7 (CH3). **EI-MS** m/z (calc. 255.1): 255.2 (13%, M+∙), 238.3 (100%), 210.3 (35%), 196.3 (59%), 165.3 (91%). **IR** (neat) cm-1: 2957.0, 1524.1, 1358.4, 744.9, 699.7.

**2-Butyl-4-methoxy-6-nitro-1,1'-biphenyl (4faa)**

Typical small-scale procedure was followed using 4-methoxy-2-nitrophenyl sulfurofluoridate (**1f**,100 mg, 0.4 mmol). The reaction was conducted for 3 hours. The crude product was purified by flash chromatography using PE/EtOAc (95:5) as solvent to afford the title compound as a viscous yellow oil (89 mg, 78%).

**Melting point:** 68 – 70 °C. **Anal.** Calcd forC17H19NO3: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.25; H, 6.67; N, 5.26. **1H NMR** (400 MHz, CDCl3) δ: 7.38 (AA’BB’C, 3H), 7.17 (AA’BB’C, 2H), 7.17 (d, *J* = 2.7 Hz, 1H), 7.03 (d, *J* = 2.7 Hz, 1H), 3.88 (s, 3H), 2.46 – 2.30 (m, 2H), 1.45 – 1.32 (m, 2H), 1.16 (h, *J* = 7.3 Hz, 2H), 0.75 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 158.6 (C), 151.1 (C), 145.1 (C), 135.5 (C), 129.3 (CH), 128.2 (CH), 127.7 (CH), 127.6 (C), 119.2 (CH), 105.7 (CH), 55.7 (CH3), 33.08 (CH2), 33.07 (CH2), 22.3 (CH2), 13.7 (CH3). **EI-MS** m/z (calc. 285.1): 285.1 (100%, M+∙), 268.4 (47%), 266.4 (46%), 165.3 (33%), 152.3 (34%). **IR** (neat) cm-1: 2957.3, 1527.4, 1466.6, 766.6, 700.4.

**2-Butyl-6-(trifluoromethyl)-1,1'-biphenyl (4gaa)**

Typical small-scale procedure was followed using 2-(trifluoromethyl)phenyl sulfurofluoridate (**1g**, 67.8 L, 97.7 mg, 0.4 mmol). The reaction was conducted for 4 hours. The crude product was purified by flash chromatography using heptane as solvent to afford the title compound as a colorless oil (78 mg, 70%).

**Anal.** Calcd forC17H17F3: C, 73.35; H, 6.16; N, 0.00. Found: C, 73.60; H, 6.34; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.58 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.45 (br. d, *J* = 7.2 Hz, 1H), 7.42 – 7.34 (m, 4H), 7.22 – 7.16 (m, 2H), 2.34 – 2.26 (m, 2H), 1.44 – 1.32 (m, 2H), 1.15 (h, *J* = 7.3 Hz, 2H), 0.75 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 143.3 (C), 140.1 (q, *J* = 1.6 Hz, C), 137.4 (C), 132.4 (q, *J* = 1.0 Hz, CH), 129.7 (q, *J* = 1.4 Hz, CH), 129.1 (q, *J* = 28.8 Hz, C), 127.44 (CH), 127.36 (CH), 127.2 (CH), 124.2 (q, *J* = 274.2 Hz, CF3), 123.2 (q, *J* = 5.5 Hz, CH), 33.4 (CH2), 32.8 (CH2), 22.4 (CH2), 13.7 (CH3). **19F NMR** (376 MHz, CDCl3) δ: -57.9 (q, *J* = 0.7 Hz). **EI-MS** m/z (calc. 278.1): 278.1 (89%, M+∙), 249.1 (26%), 235.1 (100%), 215.1 (87%), 165.1 (49%). **IR** (neat) cm-1: 2958.7, 1314.3, 1123.2, 653.1.

**2-Butyl-3-fluoro-6-(trifluoromethyl)-1,1'-biphenyl (4haa)**

Typical small-scale procedure was followed using 5-fluoro-2-(trifluoromethyl)phenyl sulfurofluoridate (**1h**, 110 mg, 0.4 mmol). The reaction was conducted for 4 hours. The crude product was purified by flash chromatography using heptane as solvent to afford the title compound as a colorless oil (36 mg, 30%).

**Anal.** Calcd forC17H16F4: C, 68.91; H, 5.44; N, 0.00. Found: C, 69.92; H, 5.82; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.57 (br. dd, *J* = 8.8, 5.3 Hz, 1H), 7.45 – 7.35 (m, 3H), 7.22 – 7.14 (m, 2H), 7.11 (br. t, *J* = 8.9 Hz, 1H), 2.36 – 2.27 (m, 2H), 1.37 – 1.27 (m, 2H), 1.14 (h, *J* = 7.3 Hz, 2H), 0.72 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 163.0 (dq, *J* = 251.0, 1.2 Hz, CF), 143.0 (dq, *J* = 5.9, 1.7 Hz, C), 136.3 (d, *J* = 2.2 Hz, C), 131.1 (d, *J* = 16.0 Hz, C), 129.5 (q, *J* = 1.3 Hz, CH), 127.8 (CH), 127.5 (CH), 125.3 (qd, *J* = 29.5, 3.3 Hz, C), 125.0 (dq, *J* = 10.0, 5.7 Hz, CH), 123.8 (q, *J* = 273.8 Hz, CF3), 114.1 (d, *J* = 24.0 Hz, CH), 32.1 (d, *J* = 1.3 Hz, CH2), 26.1 (d, *J* = 2.4 Hz, CH2), 22.6 (CH2), 13.5 (CH3). **19F NMR** (376 MHz, CDCl3) δ: -57.6 (dp, J = 2.2, 0.7 Hz), -111.7 (ddq, *J* = 9.2, 5.3, 2.2 Hz). **EI-MS** m/z (calc. 296.1): 296.1 (78%, M+∙), 267.1 (30%), 253.1 (82%), 233.1 (100%), 183.2 (39%). **IR** (neat) cm-1: 2960.2, 1314.7, 1126.0, 1099.1, 701.1.

**2-Butyl-6-fluoro-1,1'-biphenyl (4iaa)**

Typical small-scale procedure was followed using 2-fluorophenyl sulfurofluoridate (**1i**,77.7 mg, 0.4 mmol) and 1.4 equiv of 1-bromobutane (**2a**,60.4 L, 76.7 mg, 0.56 mmol) The reaction was conducted for 5 hours. The crude product was purified by flash chromatography using PE/toluene (95:5) as solvent to afford the title compound as a colorless oil (47 mg, 52%).

**Anal.** Calcd forC16H17F: C, 84.17; H, 7.51; N, 0.00. Found: C, 84.29; H, 7.65; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.47 – 7.40 (m, 2H), 7.40 – 7.34 (m, 1H), 7.30 – 7.24 (m, 2H), 7.25 (ddd, *J* = 8.2, 7.7, 5.8 Hz, 1H), 7.07 (ddd, *J* = 7.7, 1.2, 0.6 Hz, 1H), 6.96 (ddd, *J* = 9.3, 8.2, 1.2 Hz, 1H), 2.51 – 2.40 (m, 2H), 1.46 – 1.34 (m, 2H), 1.18 (h, *J* = 7.3 Hz, 2H), 0.76 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 159.9 (d, *J* = 243.8 Hz, CF), 143.5 (d, *J* = 2.3 Hz, C), 134.7 (d, *J* = 1.2 Hz, C), 130.0 (d, *J* = 1.0 Hz, CH), 129.2 (d, *J* = 16.0 Hz, C), 128.3 (d, *J* = 8.9 Hz, CH), 128.1 (CH), 127.4 (CH), 124.5 (d, *J* = 3.1 Hz, CH), 112.6 (d, *J* = 23.2 Hz, CH), 33.3 (CH2), 32.5 (d, *J* = 2.6 Hz, CH2), 22.4 (CH2), 13.7 (CH3). **19F NMR** (376 MHz, CDCl3) δ: -115.2 (dd, *J* = 9.3, 5.8 Hz). **EI-MS** m/z (calc. 228.1): 228.1 (90%, M+∙), 199.1 (21%), 186.1 (57%), 185.1 (90%), 183.1 (49%), 165.1 (100%). **IR** (neat) cm-1: 2956.4, 1456.8, 1241.4, 762.5, 736.6, 699.2.

**2-Butyl-6-methyl-4-nitro-1,1'-biphenyl (4jaa)**

Typical small-scale procedure was followed using 2-methyl-4-nitrophenyl sulfurofluoridate (**1j,** 94.1 mg, 0.4 mmol)and 1-bromobutane (**2a**, 60.4 L, 76.7 mg, 0.56 mmol, 1.4 equiv). The reaction was conducted for 5 hours. The crude product was purified by flash chromatography using heptane/DCM/EtOAc (80:19:1) as solvent to afford the title compound as a colorless oil (74 mg, 69%).

**Anal.** Calcd forC17H19NO2: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.88; H, 7.21; N, 5.59. **1H NMR** (400 MHz, CDCl3) δ: 7.97 (ABq, AB = 11.1 Hz, *J*AB= 2.4 Hz, 2H), 7.46 (AA’BB’C, 2H), 7.40 (AA’BB’C, 1H), 7.10 (AA’BB’C, 2H), 2.49 – 2.27 (m, 2H), 2.09 (t, *J* = 0.6 Hz, 3H), 1.48 – 1.36 (m, 2H), 1.18 (h, *J* = 7.3 Hz, 2H), 0.76 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 148.2 (C), 146.9 (C), 142.9 (C), 138.8 (C), 138.3 (C), 128.6 (CH), 128.4 (CH), 127.5 (CH), 121.8 (CH), 121.2 (CH), 33.3 (CH2), 33.0 (CH2), 22.3 (CH2), 21.2 (CH3), 13.7 (CH3). **EI-MS** m/z (calc. 269.1): 269.1 (92%, M+∙), 266.1 (39%), 210.1 (50%), 180.1 (100%), 165.2 (78%). **IR** (neat) cm-1: 2957.0, 1514.6, 1342.6, 745.1, 702.4.

**2-Butyl-4-acetyl-6-methyl-1,1'-biphenyl (4kaa)**

Modified typical small-scale procedure was followed using 4-acetyl-2-methylphenyl sulfurofluoridate (**1k**, 92.9 mg, 0.4 mmol),1.4 equiv of 1-bromobutane (**2a**, 60.4 L, 76.7 mg, 0.56 mmol) and 1 equiv of norbornene (37.7 mg, 0.4 mmol). The reaction was conducted for 5 hours. The crude product was purified by flash chromatography using PE/EtOAc (95:5) as solvent to afford the title compound as a colorless oil (79 mg, 74%).

**Anal.** Calcd forC19H22O: C, 85.67; H, 8.32; N, 0.00. Found: C, 86.05; H, 8.35; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.72 (d, *J* = 1.9 Hz, 1H), 7.69 (d, *J* = 1.9 Hz, 1H), 7.44 (AA’BB’C, 2H), 7.36 (AA’BB’C, 1H), 7.12 (AA’BB’C, 2H), 2.63 (s, 3H), 2.42 – 2.32 (m, 2H), 2.06 (s, 3H), 1.46 – 1.34 (m, 2H), 1.17 (h, *J* = 7.4 Hz, 2H), 0.75 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 198.4 (C=O), 146.6 (C), 141.5 (C), 139.8 (C), 136.8 (C), 136.0 (C), 128.7 (CH), 128.4 (CH), 127.12 (CH), 127.05 (CH), 126.4 (CH), 33.4 (CH2), 33.3 (CH2), 26.7 (CH3), 22.5 (CH2), 21.1 (CH3), 13.7 (CH3). **EI-MS** m/z (calc. 266.2): 266.1 (38%, M+∙), 251.2 (100%), 181.1 (27%), 165.2 (16%). **IR** (neat) cm-1: 2955.6, 1680.7, 1197.8, 702.6.

**2-butyl-6-methoxy-[1,1'-biphenyl]-4-carbaldehyde (4maa)**

Typical small-scale procedure was followed using 4-formyl-2-methoxyphenyl sulfurofluoridate (**1m**, 93.6 mg, 0.4 mmol). The reaction was conducted for 3 hours. The crude product was purified by flash chromatography using PE/EtOAc (93:7) as solvent to afford the title compound as a colorless oil (79 mg, 74%).

**Anal.** Calcd forC18H20O2: C, 80.56; H, 7.51; N, 0.00. Found: C, 80.73; H, 7.38; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 9.99 (s, 1H), 7.44 (AA’BB’C,2H), 7.43 (d, *J* = 1.6 Hz, 1H), 7.37 (AA’BB’C, 1H), 7.31 (d, *J* = 1.6 Hz, 1H), 7.19 (AA’BB’C,2H), 3.77 (s, 3H), 2.47 – 2.39 (m, 2H), 1.49 – 1.36 (m, 2H), 1.18 (h, *J* = 7.3 Hz, 2H), 0.77 (t, *J* = 7.3 Hz, 1H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 192.3 (CHO), 157.7 (C), 143.5 (C), 137.3 (C), 136.4 (C), 136.3 (C), 129.5 (CH), 128.0 (CH), 127.3 (CH), 125.3 (CH), 106.6 (CH), 55.9 (CH3), 33.1 (CH2), 32.7 (CH2), 22.4 (CH2), 13.7 (CH3). **EI-MS** m/z (calc. 268.1): 268.1 (66%, M+∙), 226.1 (24%), 197.1 (100%), 165.2 (33%). **IR** (neat) cm-1: 2955.8, 1692.9, 1381.0, 1148.4, 699.9.

**6-butyl-4'-methoxy-2,3-dimethyl-[1,1'-biphenyl]-4-yl sulfurofluoridate (4pab)**

Modified typical small-scale procedure was followed using 2,3-dimethyl-1,4-phenylene bis(sulfurofluoridate) (**1p**,121 mg, 0.4 mmol),1.4 equiv of 1-bromobutane (**2a**, 60.4 L, 76.7 mg, 0.56 mmol), 1 equiv of norbornene (37.7 mg, 0.4 mmol) and 4-methoxyphenylboronic acid (**3b**, 76.0 mg, 0.5 mmol, 1.25 eqiuv.) The reaction was conducted for 6 hours. The crude product was purified by flash chromatography using heptane/EtOAc (96:4) as solvent to afford the title compound as a colorless oil (81 mg, 55%).

**Anal.** Calcd forC19H23FO4S: C, 62.28; H, 6.33; N, 0.00. Found: C, 62.49; H, 6.28; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.07 (br. s, 1H), 7.00 (AA’BB’, *J*AB+AA’= 8.9 Hz, 2H), 6.96 (AA’BB’, *J*AB+BB’= 8.9 Hz, 2H), 3.87 (s, 3H), 2.34 – 2.24 (m, 2H), 2.27 (s, 3H) 1.96 (s, 3H), 1.41 – 1.30 (m, 2H), 1.16 (h, *J* = 7.3 Hz, 2H), 0.77 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 158.6 (C), 148.1 (d, *J* = 0.9 Hz, C), 141.7 (C), 141.0 (C), 138.5 (C), 132.2 (C), 130.2 (CH), 125.9 (d, *J* = 0.8 Hz, C), 118.0 (d, *J* = 1.0 Hz, CH), 113.8 (CH), 55.2 (CH3), 33.2 (CH2), 33.0 (CH2), 22.3 (CH2), 18.0 (CH3), 13.8 (CH3), 13.0 (d, *J* = 1.3 Hz, CH3). **19F NMR** (376 MHz, CDCl3) δ: 38.3 (dq, *J* = 1.7, 0.8 Hz). **EI-MS** m/z (calc. 366.1): 366.4 (100%, M+∙), 283.4 (52%), 241.4 (79%), 224.4 (48%), 223.4 (48%). **IR** (neat) cm-1: 2956.7, 1442.3, 1222.4, 1033.2, 792.0.

**Methyl 4-butyl-3-phenylthiophene-2-carboxylate (4raa)**

Typical small-scale procedure was followed using methyl 3-((fluorosulfonyl)oxy)thiophene-2-carboxylate (**1r**, 93.6 mg, 0.4 mmol). The reaction was conducted for 4 hours. The crude product was purified by flash chromatography using PE/EtOAc (95:5) as solvent to afford the title compound as a colorless oil (82 mg, 74%).

**Anal.** Calcd forC16H18O2S: C, 70.04; H, 6.61; N, 0.00. Found: C, 69.95; H, 6.57; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.46 – 7.33 (AA’BB’C, 3H), 7.21 (AA’BB’C, 2H), 7.20 (s, 1H), 3.69 (s, 3H), 2.38 – 2.32 (m, 2H), 1.47 – 1.35 (m, 2H), 1.21 (h, *J* = 7.2 Hz, 2H), 0.80 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 162.4 (C=O), 148.7 (C), 144.3 (C), 136.1 (C), 129.0 (CH), 128.2 (C), 127.9 (CH), 127.5 (CH), 125.9 (CH), 51.7 (CH3), 31.9 (CH2), 28.8 (CH2), 22.2 (CH2), 13.8 (CH3). **EI-MS** m/z (calc. 274.1): 274.2 (31%, M+∙), 232.2 (100%), 200.15 (48%), 172.2 (80%). **IR** (neat) cm-1: 2952.7, 1721.1, 1699.1, 1210.3, 697.8.

**Methyl 4-butyl-3-phenylpicolinate (4saa)**

Typical small-scale procedure was followed using methyl 3-((fluorosulfonyl)oxy)picolinate (**1s**, 94.1 mg, 0.4 mmol). The reaction was conducted for 6 hours. The crude product was purified by flash chromatography using PE/EtOAc (7:3) as solvent to afford the title compound as a colorless oil (20 mg, 19%).

**Anal.** Calcd forC17H19O2N: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.69; H, 7.24; N, 5.66. **1H NMR** (400 MHz, CDCl3) δ: 8.55 (d, *J* = 5.0 Hz, 1H), 7.46 – 7.36 (AA’BB’C, 3H), 7.34 (d, *J* = 5.0 Hz, 1H), 7.20 (AA’BB’C,2H), 3.66 (s, 3H), 2.55 – 2.37 (m, 2H), 1.48 – 1.37 (m, 2H), 1.19 (h, 7.3 Hz, 2H), 0.77 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 167.0 (C=O), 151.7 (C), 149.0 (C), 148.0 (CH), 136.9 (C), 136.4 (C), 128.9 (CH), 128.1 (CH), 127.7 (CH), 125.8 (CH), 52.3 (CH3), 32.25 (CH2), 32.23 (CH2), 22.3 (CH2), 13.6 (CH3). **EI-MS** m/z (calc. 269.1): 269.3 (0.3%, M+∙), 239.2 (33%), 210.3 (20%), 182.3 (100%). **IR** (neat) cm-1: 2955.0, 1736.2, 1299.2, 1152.0, 700.9.

**Methyl 6-(cyclopropylmethyl)-[1,1'-biphenyl]-2-carboxylate (4aba)**

Typical small-scale procedure was followed using methyl 2-((fluorosulfonyl)oxy)benzoate (**1a**,67.3 L, 93.7 mg, 0.4 mmol) and (bromomethyl)cyclopropane (**2b**, 46.6 L, 64.8 mg, 0.48 mmol, 1.20 equiv). The reaction was conducted for 4 hours. The crude product was purified by flash chromatography using PE/EtOAc (94:6) as solvent to afford the title compound as a viscous colorless oil (83 mg, 78%).

**Anal.** Calcd forC18H18O2: C, 81.17; H, 6.81; N, 0.00. Found: C, 81.10; H, 7.01; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.69 (ddt, *J* = 7.7, 1.4, 0.5 Hz, 1H), 7.62 (ddt, *J* = 7.8, 1.4, 0.6 Hz, 1H), 7.42 – 7.30 (m, 4H), 7.16 (AA’BB’C, 2H), 3.52 (s, 3H), 2.32 (d, *J* = 6.9 Hz, 2H), 0.86 – 0.72 (m, 1H), 0.50 – 0.35 (m, 2H), 0.08 – -0.04 (m, 2H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 168.8 (C=O), 141.3 (C), 139.9 (C), 131.9 (CH), 131.7 (C), 128.9 (CH), 127.7 (CH), 127.2 (CH), 126.92 (CH), 126.87 (CH), 51.7 (CH3), 37.6 (CH2), 11.3 (CH), 4.8 (CH2). **EI-MS** m/z (calc. 266.1): 266.3 (6%, M+∙), 234.2 (54%), 206.2 (100%), 205.2 (95%), 178.3 (83%). **IR** (neat) cm-1: 3000.9, 1728.7, 1286.5, 1137.2, 759.5, 700.1.

**Methyl 6-isopropyl-(1,1'-biphenyl)-2-carboxylate (4aca)**

Modified small-scale procedure was followed using methyl 2-((fluorosulfonyl)oxy)benzoate (**1a**,67.3 L, 93.7 mg, 0.4 mmol), 2-bromopropane (**2c**, 75.1 L, 98.4 mg, 0.80 mmol, 2.0 equiv), 1.0 equiv of norbornene (37.7 mg, 0.4 mmol) and 10 mol% of Pd(OAc)2 (9.0 mg). The reaction was conducted for 12 hours. The crude product was purified by flash chromatography using PE/EtOAc (94:6) as solvent to afford the title compound as a viscous colorless oil (61 mg, 60%).

**Anal.** Calcd for C17H18O2: C, 80.28; H, 7.13; N, 0.00. Found: C, 80.05; H, 6.90; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.63 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.52 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.43 – 7.31 (m, 4H), 7.18 (AA’BB’C, 2H), 3.51 (s, 3H), 2.84 (hept, *J* = 7.0 Hz, 1H), 1.10 (d, *J* = 7.0 Hz, 6H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 168.9 (C=O), 147.9 (C), 140.4 (C), 139.8 (C), 131.8 (C), 128.9 (CH), 128.6 (CH), 127.7 (CH), 127.5 (CH), 126.8 (CH), 126.5 (CH), 51.7 (CH3), 29.4 (CH), 24.0 (CH3). **EI-MS** m/z (calc. 254.1): 254.4 (37%, M+∙), 222.4 (57%), 207.4 (100%), 179.4 (58%). **IR** (neat) cm-1: 2962.6, 1729.9, 1720.0, 1286.1, 700.5.

**Methyl 6-benzyl-(1,1'-biphenyl)-2-carboxylate (4afa)**

Small-scale procedure was followed using methyl 2-((fluorosulfonyl)oxy)benzoate (**1a**,67.3 L, 93.7 mg, 0.4 mmol), benzyl chloride (**2f**, 55.2 L, 60.8 mg, 0.48 mmol, 1.2 equiv), The reaction was conducted for 4 hours. The crude product was purified by flash chromatography using PE/EtOAc (92:8) as solvent to afford the title compound as a viscous colorless oil (88 mg, 73%).

**HRMS** (ESI-TOF) m/z: [M+Na] Calcd for C21H18O2Na: 325.1199; found: 325.1199. **1H NMR** (400 MHz, CDCl3) δ: 7.75 – 7.66 (m, 1H), 7.40 – 7.28 (m, 5H), 7.23 – 7.11 (m, 3H), 7.13 – 7.06 (m, 2H), 6.94 – 6.86 (m, 2H), 3.80 (s, 2H), 3.53 (s, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 168.7 (C=O), 141.8 (C), 140.7 (C), 140.1 (C), 139.5 (C), 133.2 (CH), 132.1 (C), 128.90 (CH), 128.85 (CH), 128.2 (CH), 127.8 (CH), 127.4 (CH), 127.3 (CH), 127.0 (CH), 125.9 (CH), 51.8 (CH3), 39.1 (CH2). **EI-MS** m/z (calc. 302.1): 302.3 (30%, M+∙), 270.3 (100%), 242.3 (67%), 241.3 (71%), 165.2 (92%).

**Methyl 6-hexyl-(1,1'-biphenyl)-2-carboxylate (4aga)**

Modified small-scale procedure was followed using methyl 2-((fluorosulfonyl)oxy)benzoate (**1a**,67.3 L, 93.7 mg, 0.4 mmol) and 1-chlorohexane (**2g**, 110 L, 96.5 mg, 0.80 mmol, 2.0 equiv). The reaction was conducted for 12 hours. The crude product was purified by flash chromatography using PE/EtOAc (96:4) as solvent to afford the title compound as a viscous colorless oil (52 mg, 44%).

**Anal.** Calcd forC20H24O2: C, 81.04; H, 8.16; N, 0.00. Found: C, 81.51; H, 8.29; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.65 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.41 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.40 – 7.29 (AA’BB’C, 3H), 7.17 (AA’BB’C, 2H), 3.52 (s, 3H), 2.44 – 2.36 (m, 2H), 1.44 – 1.32 (m, 2H), 1.24 – 1.04 (m, 6H), 0.81 (t, *J* = 7.0 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 168.9 (C=O), 142.0 (C), 141.3 (C), 139.8 (C), 132.2 (CH), 131.9 (C), 128.9 (CH), 127.6 (CH), 127.1 (CH), 126.8 (CH), 126.7 (CH), 51.7 (CH3), 33.1 (CH2), 31.4 (CH2), 31.1 (CH2), 29.0 (CH2), 22.4 (CH2), 14.0 (CH3). **EI-MS** m/z (calc. 296.2): 296.5 (58%, M+∙), 264.4 (60%), 207.4 (72%), 193.4 (67%), 165.4 (100%). **IR** (neat) cm-1: 2926.5, 1730.2, 1287.8, 1136.4, 699.9.

**Methyl 6-butyl-4'-methoxy-(1,1'-biphenyl)-2-carboxylate (4aab)**

Typical small-scale procedure was followed using methyl 2-((fluorosulfonyl)oxy)benzoate (**1a**,67.3 L, 93.7 mg, 0.4 mmol) and 4-methoxyphenylboronic acid (**3b**, 76.0 mg, 0.5 mmol, 1.25 eqiuv.) The reaction was conducted for 4 hours. The crude product was purified by flash chromatography using PE/EtOAc (93:7) as solvent to afford the title compound as a viscous colorless oil (104 mg, 87%).

**Anal.** Calcd forC19H22O3: C, 76.48; H, 7.43; N, 0.00. Found: C, 76.45; H, 7.63; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.61 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.40 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.09 (AA’XX’, *J*AX+AA’ = 8.8 Hz, 2H), 6.92 (AA’XX’, *J*AX+XX’ = 8.8 Hz, 2H), 3.85 (s, 3H), 3.55 (s, 3H), 2.47 – 2.37 (m, 2H), 1.44 – 1.32 (m, 2H), 1.17 (h, *J* = 7.3 Hz, 2H), 0.77 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 169.1 (C=O), 158.4 (C), 142.4 (C), 140.9 (C), 132.3 (C), 132.1 (CH), 132.0 (C), 130.0 (CH), 127.0 (CH), 126.5 (CH), 113.1 (CH), 55.1 (CH3), 51.8 (CH3), 33.4 (CH2), 32.8 (CH2), 22.4 (CH2), 13.8 (CH3). **EI-MS** m/z (calc. 298.2): 298.4 (100%, M+∙), 266.4 (39%), 238.4 (51%), 195.4 (42%). **IR** (neat) cm-1: 2954.1, 1729.5, 1285.7, 1241.5, 1135.7.

**Methyl 6-butyl-4'-fluoro-(1,1'-biphenyl)-2-carboxylate (4aac)**

Typical small-scale procedure was followed using methyl 2-((fluorosulfonyl)oxy)benzoate (**1a**,67.3 L, 93.7 mg, 0.4 mmol) and 4-fluorophenylboronic acid (**3c**, 70.0 mg, 0.5 mmol, 1.25 eqiuv.) The reaction was conducted for 4 hours. The crude product was purified by flash chromatography using PE/EtOAc (95:5) as solvent to afford the title compound as a viscous colorless oil (91 mg, 79%).

**Anal.** Calcd forC18H19FO2: C, 75.50; H, 6.69; N, 0.00. Found: C, 75.50; H, 6.65; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.66 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.42 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.14 (AA’MM’X, *J*AM+AA’ = 8.8 Hz, *J*AX = 5.5 Hz, 2H), 7.08 (AA’MM’X, *J*AM+MM’ = 8.8 Hz, *J*MX = 8.8 Hz, 2H), 3.56 (s, 3H), 2.43 – 2.34 (m, 2H), 1.44 – 1.30 (m, 2H), 1.23 – 1.10 (h, *J* = 7.3 Hz, 2H), 0.76 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 168.7 (C=O), 161.9 (d, *J* = 245.4 Hz, CF), 142.2 (C), 140.3 (C), 135.7 (d, *J* = 3.7 Hz, C), 132.4 (CH), 131.9 (C), 130.5 (d, *J* = 7.9 Hz, CH), 127.4 (CH), 126.9 (CH), 114.7 (d, *J* = 21.3 Hz, CH), 51.8 (CH3), 33.4 (CH2), 32.8 (CH2), 22.4 (CH2), 13.7 (CH3). **19F NMR** (376 MHz, CDCl3) δ: -116.3 (tt, *J* = 8.7, 5.5 Hz). **EI-MS** m/z (calc. 286.1): 286.4 (100%, M+∙), 254.3 (65%), 225.3 (74%), 183.4 (85%). **IR** (neat) cm-1: 2955.3, 1729.1, 1219.8, 1137.1, 761.4.

**Methyl 6-butyl-3'-methoxy-(1,1'-biphenyl)-2-carboxylate (4aad)**

Typical small-scale procedure was followed using methyl 2-((fluorosulfonyl)oxy)benzoate (**1a**,67.3 L, 93.7 mg, 0.4 mmol) and 3-methoxyphenylboronic acid (**3d**, 76.0 mg, 0.5 mmol, 1.25 eqiuv.) The reaction was conducted for 4 hours. The crude product was purified by flash chromatography using PE/EtOAc (93:7) as solvent to afford the title compound as a viscous colorless oil (101 mg, 85%).

**Anal.** Calcd forC19H22O3: C, 76.48; H, 7.43; N, 0.00. Found: C, 76.70; H, 7.34; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.63 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.41 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.29 (ddd, *J* = 8.3, 7.5, 0.4 Hz, 1H), 6.88 (ddd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 6.77 (ddd, *J* = 7.5, 1.5, 1.0 Hz, 1H), 6.73 (ddd, *J* = 2.6, 1.5, 0.4 Hz, 1H), 3.81 (s, 3H), 3.55 (s, 3H), 2.50 – 2.36 (m, 2H), 1.46 – 1.35 (m, 2H), 1.18 (h, *J* = 7.3 Hz, 2H), 0.77 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 168.9 (C=O), 159.0 (C), 141.9 (C), 141.2 (C), 141.0 (C), 132.2 (CH), 131.9 (C), 128.6 (CH), 127.2 (CH), 126.6 (CH), 121.6 (CH), 114.5 (CH), 112.5 (CH), 55.2 (CH3), 51.8 (CH3), 33.5 (CH2), 32.8 (CH2), 22.4 (CH2), 13.8 (CH3). **EI-MS** m/z (calc. 298.2): 298.3 (32%, M+∙), 266.3 (53%), 238.4 (100%), 209.4 (32%). **IR** (neat) cm-1:2953.7, 1730.0, 1285.5, 1136.4, 759.9.

**Methyl 6-butyl-3'-fluoro-(1,1'-biphenyl)-2-carboxylate (4aae)**

Typical small-scale procedure was followed using methyl 2-((fluorosulfonyl)oxy)benzoate (**1a**,67.3 L, 93.7 mg, 0.4 mmol) and 3-fluorophenylboronic acid (**3e**, 70.0 mg, 0.5 mmol, 1.25 eqiuv.) The reaction was conducted for 4 hours. The crude product was purified by flash chromatography using PE/EtOAc (95:5) as solvent to afford the title compound as a viscous colorless oil (85 mg, 74%).

**Anal.** Calcd forC18H19FO2: C, 75.50; H, 6.69; N, 0.00. Found: C, 75.40; H, 6.74; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.69 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.43 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.34 (dddd, *J* = 8.3, 7.6, 6.0, 0.4 Hz, 1H), 7.04 (dddd, *J* = 8.8, 8.3, 2.6, 1.0 Hz, 1H), 6.95 (ddd, *J* = 7.6, 1.5, 1.0 Hz, 1H), 6.91 (dddd, *J* = 9.6, 2.6, 1.5, 0.4 Hz, 1H), 3.56 (s, 3H), 2.43 – 2.36 (m, 2H), 1.44 – 1.33 (m, 2H), 1.17 (h, *J* = 7.3 Hz, 2H), 0.77 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 168.4 (C=O), 162.3 (d, *J* = 245.9 Hz, CF), 142.1 (d, *J* = 7.9 Hz, C), 141.9 (C), 140.1 (d, *J* = 1.9 Hz, C), 132.4 (CH), 131.5 (C), 129.1 (d, *J* = 8.4 Hz, CH), 127.5 (CH), 127.0 (CH), 124.8 (d, *J* = 2.9 Hz, CH), 116.1 (d, *J* = 21.6 Hz, CH), 113.8 (d, *J* = 21.0 Hz, CH), 51.8 (CH3), 33.4 (CH2), 32.7 (CH2), 22.4 (CH2), 13.7 (CH3). **19F NMR** (376 MHz, CDCl3) δ: -114.6 (ddd, *J* = 9.6, 8.8, 6.0 Hz). **EI-MS** m/z (calc. 286.1): 286.2 (32%, M+∙), 254.2 (100%), 225.3 (74%), 183.4 (93%). **IR** (neat) cm-1: 2955.0, 1728.6, 1284.3, 1136.8, 759.7.

**Methyl 6-butyl-3'-chloro-(1,1'-biphenyl)-2-carboxylate (4aaf)**

Typical small-scale procedure was followed using methyl 2-((fluorosulfonyl)oxy)benzoate (**1a**,67.3 L, 93.7 mg, 0.4 mmol) and 3-chlorophenylboronic acid (**3f**, 78.2 mg, 0.5 mmol, 1.25 eqiuv.) The reaction was conducted for 4 hours. The crude product was purified by flash chromatography using PE/EtOAc (95:5) as solvent to afford the title compound as a viscous colorless oil (85 mg, 70%).

**Anal.** Calcd forC18H19ClO2: C, 71.40; H, 6.33; N, 0.00. Found: C, 71.57; H, 6.50; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.69 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.42 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.19 – 7.17 (m, 1H), 7.10 – 7.03 (m, 1H), 3.57 (s, 3H), 2.46 – 2.33 (m, 2H), 1.45 – 1.33 (m, 2H), 1.18 (h, *J* = 7.3 Hz, 2H), 0.77 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 168.4 (C=O), 141.9 (C), 141.8 (C), 140.0 (C), 133.6 (C), 132.5 (CH), 131.4 (C), 129.0 (CH), 128.9 (CH), 127.6 (CH), 127.3 (CH), 127.1 (CH), 127.0 (CH), 51.9 (CH3), 33.4 (CH2), 32.8 (CH2), 22.4 (CH2), 13.7 (CH3). **EI-MS** m/z (calc. 302.1): 302.0 (60%, M+∙), 304.2 (20%, M+∙+2), 270.0 (90%), 235.2 (100%), 199.1 (71%). **IR** (neat) cm-1: 2954.5, 1728.3, 1286.0, 1138.0, 758.4.

**Methyl 3'-bromo-6-butyl- (1,1'-biphenyl)-2-carboxylate (4aag)**

Typical small-scale procedure was followed using methyl 2-((fluorosulfonyl)oxy)benzoate (**1a**,67.3 L, 93.7 mg, 0.4 mmol) and 3-bromophenylboronic acid (**3g**, 100 mg, 0.5 mmol, 1.25 eqiuv.) The reaction was conducted for 4 hours. The crude product was purified by flash chromatography using PE/EtOAc (95:5) as solvent to afford the partially purified title compound as a tan oil (12 mg, 9%).

**HRMS** (ESI-TOF) m/z: [M+Na] C18H19BrO2Na: 369.0460; found: 369.0461. **1H NMR** (400 MHz, CDCl3) δ: 7.69 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.48 (ddd, *J* = 8.0, 2.0, 1.1 Hz, 1H), 7.42 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.34 (ddd, *J* = 2.0, 1.6, 0.4 Hz, 1H), 7.26 (ddd, *J* = 8.0, 7.6, 0.4 Hz, 1H), 7.11 (ddd, *J* = 7.6, 1.6, 1.1 Hz, 1H), 3.57 (s, 3H), 2.43 – 2.34 (m, 2H), 1.44 – 1.34 (m, 2H), 1.18 (h, *J* = 7.3 Hz, 2H), 0.77 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 168.3 (C=O), 142.0 (C), 141.9 (C), 139.9 (C), 132.5 (CH), 131.8 (CH), 131.4 (C), 129.9 (CH), 129.2 (CH), 127.8 (CH), 127.6 (CH), 127.1 (CH), 121.7 (C), 51.9 (CH3), 33.4 (CH2), 32.8 (CH2), 22.4 (CH2), 13.7 (CH3). **EI-MS** m/z (calc. 346.0): 346.2 (26%, M+∙), 348.2 (26%, M+∙+2), 314.3 (30%), 235.3 (100%), 165.3 (78%). **IR** (neat) cm-1: 2952.9, 1728.7, 1285.9, 1138.0, 758.6.

**Methyl 3-butyl-2-(naphthalen-2-yl)benzoate (4aah)**

Typical small-scale procedure was followed using methyl 2-((fluorosulfonyl)oxy)benzoate (**1a**,67.3 L, 93.7 mg, 0.4 mmol) and naphthalen-2-ylboronic acid (**3h**, 86.0 mg, 0.5 mmol, 1.25 eqiuv.) The reaction was conducted for 4 hours. The crude product was purified by flash chromatography using PE/EtOAc (95:5) as solvent to afford the title compound as a viscous colorless oil (99 mg, 78%).

**Anal.** Calcd forC22H22O2: C, 82.99; H, 6.96; N, 0.00. Found: C, 83.01; H, 6.72; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.91 – 7.87 (m, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.84 – 7.78 (m, 1H), 7.69 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.60 (br. s, 1H), 7.53 – 7.46 (m, 2H), 7.45 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.35 (dd, *J* = 8.4, 1.7 Hz, 1H), 3.44 (s, 3H), 2.42 (ABX2, AB = 11.2 Hz, *J*AB = 13.8 Hz, *J*AX = *J*BX = 7.4 Hz, 2H), 1.46 – 1.34 (m, 2H), 1.12 (h, *J* = 7.3 Hz, 2H), 0.71 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 168.9 (C=O), 142.2 (C), 141.2 (C), 137.5 (C), 133.0 (C), 132.3 (C), 132.2 (CH), 132.1 (C), 128.0 (CH), 127.80 (CH), 127.75 (CH), 127.29 (CH), 127.25 (CH), 127.0 (CH), 126.8 (CH), 126.0 (CH), 125.7 (CH), 51.7 (CH3), 33.4 (CH2), 32.9 (CH2), 22.3 (CH2), 13.7 (CH3). **EI-MS** m/z (calc. 318.2): 318.5 (100%, M+∙), 286.5 (62%), 258.5 (65%), 215.5 (95%). **IR** (neat) cm-1: 2953.0, 1728.0, 1285.4, 1136.5, 757.6, 743.7.

**2-Butyl-4'-methoxy-6-nitro-1,1'-biphenyl (4eab)**

Typical telescoped procedure was followed using 2-nitrophenol (**11e**, 139 mg, 1.0 mmol). The Catellani reaction step was conducted for 3 hours. The crude product was purified by flash chromatography using PE/EtOAc (96:4) as solvent to afford the title compound as a viscous yellow oil (191 mg, 67%).

**Anal.** Calcd forC17H19NO3: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.25; H, 6.43; N, 5.32. **1H NMR** (400 MHz, CDCl3) δ: 7.58 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.47 (dd*, J* = 7.8, 1.4 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.12 (AA’XX’, *J*AX+AA’ = 8.8 Hz, 2H), 6.94 (AA’XX’, *J*AX+XX’ = 8.8 Hz, 2H), 3.85 (s, 3H), 2.49 – 2.41 (m, 2H), 1.45 – 1.34 (m, 2H), 1.18 (h, *J* = 7.5 Hz, 2H), 0.77 (t, *J* = 7.3 Hz, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 159.2 (C), 151.1 (C), 144.3 (C), 134.5 (C), 132.6 (CH), 130.0 (CH), 127.7 (CH), 127.4 (C), 120.6 (CH), 113.7 (CH), 55.2 (CH3), 33.2 (CH2), 32.8 (CH2), 22.3 (CH2), 13.7 (CH3). **EI-MS** m/z (calc. 285.1): 285.5 (100%, M+∙), 268.5 (43%), 226.5 (34%), 210.5 (43%). **IR** (neat) cm-1: 2956.7, 1524.9, 1514.3, 1244.2, 831.3.

**Dimethyl (1,1':2',1''-terphenyl)-2,3'-dicarboxylate (9aa)**

Typical small-scale procedure was followed using methyl 2-iodobenzoate (**8a**, 58.8 L, 105 mg, 0.4 mmol). The reaction was conducted for 4 hours. The crude product was purified by flash chromatography using PE/EtOAc (8:2) as solvent to afford the title compound as a viscous colorless oil (31 mg, 45%).

**1H NMR** (400 MHz, CDCl3) δ: 7.83 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.72 (ddd, *J* = 7.7, 1.5, 0.5 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.39 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.33 (td, *J* = 7.6, 1.5 Hz, 1H), 7.23 (td, *J* = 7.7, 1.4 Hz, 1H), 7.14 – 7.07 (m, 3H), 7.07 (ddd, *J* = 7.6, 1.4, 0.5 Hz, 1H), 6.97 (br. s, 2H), 3.61 (s, 3H), 3.55 (s, 3H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 169.1 (C=O), 167.4 (C=O), 142.2 (C), 141.9 (C), 140.0 (C), 139.2 (C), 132.0 (CH), 132.0 (CH), 131.8 (CH), 131.0 (CH), 130.4 (C), 129.7 (CH), 129.4 (CH), 128.5 (CH), 127.2 (br., CH), 126.9 (CH), 126.8 (CH), 126.6 (CH), 51.84 (CH3), 51.80 (CH3). **EI-MS** m/z (calc. 346.1): 346.3 (4%, M+∙), 314.3 (100%), 383.3 (55%), 225.3 (95%). **IR** (neat) cm-1: 2949.7, 1721.1, 1286.3, 1256.1, 701.4.

The obtained analytical data is in agreement with literature.[19a](#_ENREF_32)

**Ethyl 2,6-dibutyl-(1,1'-biphenyl)-4-carboxylate (10qaa)**

Modified small-scale procedure was followed using ethyl 4-((fluorosulfonyl)oxy)benzoate (**1q**, 99.3 mg, 0.4 mmol) and 1-bromobutane (**2a**, 97.3 L, 123 mg, 0.9 mmol, 2.25 equiv). Reaction conducted for 3 hours. The crude product was purified by flash chromatography using PE/MTBE (95:5) as solvent to afford the title compound as a viscous colorless oil (100 mg, 74%).

**Anal.** Calcd forC23H30O2: C, 81.61; H, 8.93; N, 0.00. Found: C, 81.60; H, 8.91; N, 0.00. **1H NMR** (400 MHz, CDCl3) δ: 7.78 (s, 2H), 7.41 (AA’BB’C,2H), 7.35 (AA’BB’C,1H), 7.12 (AA’BB’C,2H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.36 – 2.29 (m, 4H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.44 – 1.33 (m, 4H), 1.15 (h, *J* = 7.4 Hz, 4H), 0.74 (t, *J* = 7.3 Hz, 6H). **13C{1H} NMR** (101 MHz, CDCl3) δ: 167.0 (C=O), 145.8 (C), 141.4 (C), 139.6 (C), 129.18 (C), 129.15 (CH), 128.0 (CH), 127.4 (CH), 126.9 (CH), 60.8 (CH2), 33.39 (CH2), 33.35 (CH2), 22.5 (CH2), 14.4 (CH3), 13.7 (CH3). **EI-MS** m/z (calc. 338.2): 338.1 (45%, M+∙), 295.1 (25%), 223.2 (43%), 167.2 (100%). **IR** (neat) cm-1: 2955.9, 1716.5, 1202.6, 768.8, 703.6.

Supporting information

Picture of the two-chamber reactors, detailed optimization table, and 1H, 13C{1H}, 13C{1H} APT and 19F NMR spectra of the synthesized compounds (PDF).

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