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Electrophilic Triflyl-arylation and Triflyl-pyridylation by Unsymmetrical Aryl/Pyridyl-λ^3-iodonium Salts: Synthesis of Aryl and Pyridyl Triflones

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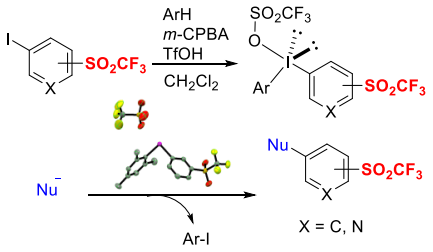


Abstract: Unsymmetrical diaryl-λ^3-iodonium salts containing aryl triflone (Ar-SO_2CF_3) were designed and synthesized. X-ray crystal structure analysis of the salt indicated a T-shaped geometry at the iodine atom. The salts were found to be powerful electrophilic reagents for triflyl-arylation of *C*, *N*, and *O*-centered nucleophiles under mild conditions. Electrophilic transfer of pyridine triflone (Py-SO_2CF_3) to nucleophiles was also realized by the use of corresponding triflylpyridylaryl-λ^3-iodonium salts. Selection of auxiliaries (dummy ligands) of unsymmetrical diaryl-λ^3-iodonium salts is crucial for this transformation.

In the quest for the development of new chemical compounds, the field of fluorine chemistry has always maintained a strong foothold. The powerful influence of fluorine is owed to its unique properties, including its ability to physically and chemically alter a molecule's properties.[1] Fluorinated aromatic compounds such as arylfluorides (Ar-F) and trifluoromethyl aromatics (Ar-CF_3) are two of the most popular fluorinated aromatic motifs as bioactive compounds of pharmaceuticals and agrochemicals,[2] high energy materials,[3] liquid crystals[4] and also as medical diagnostic tools via PET scans.[5] Of the many fluorinated aromatics, we are currently interested in the aryl trifluoromethanesulfonyl compounds (aryl triflones, Ar-SO_2CF_3), which are used as structural units in bioactive compounds,[6] chiral catalysts,[7] and functional materials[8] (Figure 1). The SO_2CF_3 group is highly electronegative (SO_2CF_3, $\sigma_m = 0.79$, $\sigma_p = 0.93$; CF_3, $\sigma_m = 0.43$, $\sigma_p = 0.54$) and mildly lipophilic (SO_2CF_3, $\pi = 0.55$; CF_3, $\pi = 0.88$)[9a] making it an attractive candidate for the aforesaid categories and prompting chemists to develop new methodologies for the synthesis of aryl triflones.

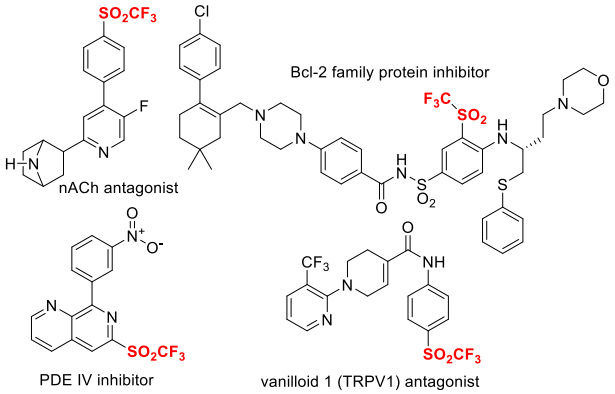
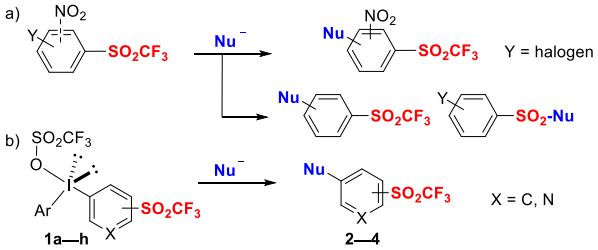


Figure 1: Bioactive compounds consisting of an aryl triflone moiety.

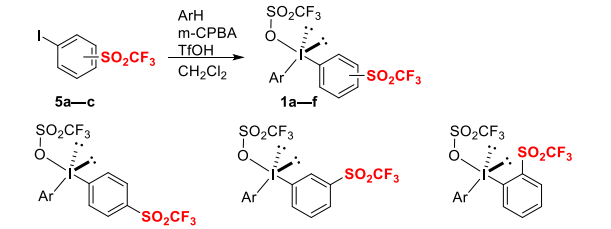
Several methods such as the use of trifluoromethanesulfonylating (triflylating) reagents, oxidation of corresponding trifluoromethylthio aromatic compounds, transformation from SO_2CF_3-containing building blocks, and intramolecular rearrangements have been developed over the years.[9] Despite of all, methods for nucleophilic substitution on an Ar-SO_2CF_3 motif, S_NAr reaction, remain challenging due to the electrophilic nature of sulfone, giving rise to regioselectivity issues. Not many reports are available for nucleophilic substitution on Ar-SO_2CF_3 and a SciFinder® search for the same reveals that a powerful electron-withdrawing group such as nitro (NO_2) on the aryl ring is recommended with a suitable leaving group Y for rendering the required regioselectivity for substitution via the S_NAr reaction.[10a,b] In the case of Ar(F)-SO_2CF_3, both S_NAr and S_N2 reactions are reported depending on the hetero-nucleophiles.[10c-f] The S_N2 substitution reaction by carbon nucleophiles on the sulfonyl center is also anticipated in the absence of a suitable functional group on the aryl ring (Ar)[11] (Scheme 1a). Thus, herein we present a methodology for the direct electrophilic introduction of the Ar-SO_2CF_3 group into *C*, *N* and *O*-centered nucleophiles, i.e., electrophilic triflyl-arylation using unsymmetrical diaryl-λ^3-iodonium salts **1**, providing the corresponding triflyl-arylated products **2**—**4** in good to excellent yields. Moreover, this idea can be extended to another reagent for the direct electrophilic introduction of the pyridine triflone (Py-SO_2CF_3) moiety into nucleophiles by corresponding triflyl-pyridylaryl-λ^3-iodonium salts (Scheme 1b).

Scheme 1. a) Nucleophilic substitution on SO_2CF_3-aromatics with or without a NO_2 group. b) Triflyl-arylation and triflyl-pyridylation of carbon and hetero-centered nucleophiles with diaryl-λ^3-iodonium salts **1**.



Diaryl-λ^3-iodonium salts have been investigated for their various synthetic utilities.[12–16] An extremely electrophilic iodine center induces the attack by the nucleophiles providing the arylation products. With the use of unsymmetrical diaryl-λ^3-iodonium salts, the selective aryl transfer of one of the two aromatic moieties to the nucleophile is of critical importance. This is highly dependent on the electronical and steric properties of each aryl group, and high aryl-selectivity can be achieved by the careful design of each aryl group.[12] Previous investigations showed that electron-rich and sterically demanding aromatics are suitable as auxiliaries, i.e., dummy aryl groups, while electron-deficient aromatics tend to predominately transfer to the nucleophiles. From the viewpoint of electronegativity, fluorinated aromatic groups are ideal for the selective transfer-arylation to nucleophiles from unsymmetrical diaryl-λ^3-iodonium salts.[17] We thus designed trifluoromethylsulfonyl-aryl-λ^3-aryliodonium salts **1a**—**c** and **1d**—**f** which account for the *para*-, *meta*- and *ortho*-SO_2CF_3 on the phenyl ring, respectively (Scheme 2).

Scheme 2: Synthesis of diaryliodonium salts **1** from the corresponding iodides **5**.[a]



[a]Reaction of **5** (1.0 equiv) with the arene ArH (1.1 equiv) was carried out in the presence of *m*CPBA (1.1 equiv) and TfOH (1.7 equiv) in CH_2Cl_2 at rt (see the details for SI).

Two dummy aromatics, mesitylene **1a**—**c** and anisole **1d**—**f**, were selected due to their steric and/or electronic richness, thereby achieving selective transfer-arylation. Reagents **1** were synthesized from iodides **5a**—**c**[18] by the treatment of mesitylene or anisole with *m*-CPBA and trifluoromethanesulfonic acid at room temperature.[13] All the unsymmetrical diaryl-λ^3-iodonium salts were obtained in moderate to high yields (30—91%) and confirmed by spectroscopic analyses. An X-ray crystallographic analysis of **1b** revealed a T-shaped geometry at the iodine atom (Figure 2).

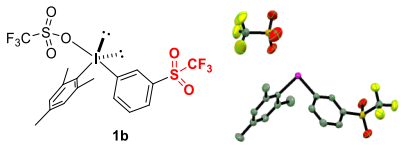
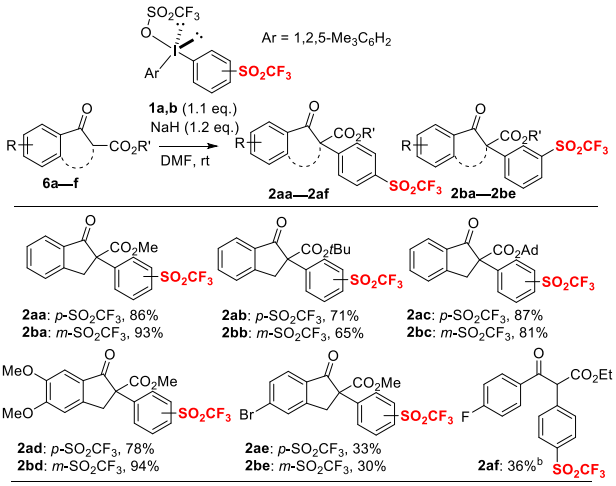


Figure 2: X-ray crystallographic analysis of **1b** (CCDC1560414) drawn at 50% probability.

With the iodonium salts **1** in hand, electrophilic triflyl-arylation was first investigated by the reactions with cyclic β-keto esters **6a**—**e** in the presence of NaH in DMF at room temperature (Scheme 3).[14] Iodonium salts **1a**,**b** proved to be good triflyl-arylating reagents resulting in products having a quaternary carbon center; while **1c** was not reactive. The lack of reactivity of **1c** is presumably due to steric repulsion of the *ortho*-SO_2CF_3 and iodide, which made attack of the nucleophile difficult. The reaction of iodonium salts **1a**,**b** proceeded well for all ester groups providing good yields and was not affected by increasing the size of the esters (Me, *t*Bu, Ad) **2aa**—**2bc**. Substrate **6d**, which has two electron-donating OMe groups on the benzene ring, also provided triflyl-arylated products **2ad** and **2bd** in good yields, but the presence of an electron-withdrawing Br group in **6e** reduced yield to around 30% for **2ae** and **2be**. As an add-on, the triflyl-arylation of an acyclic β-keto ester **6f** with reagent **1a** was also attempted in the presence of *t*BuOK[14a] and it provided the product **2af** in moderate yield.

Scheme 3: Triflyl-arylation of β-keto esters **6** by iodonium salts **1a,b**.[a]

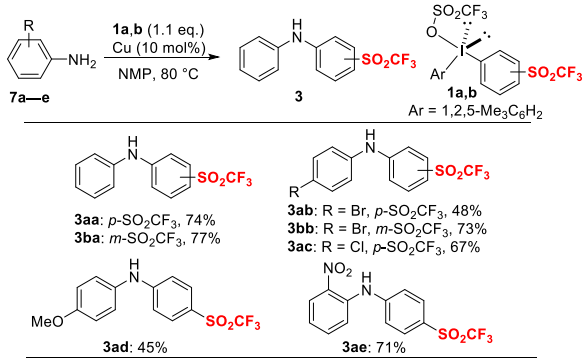


[a]The reaction of **6** (0.10 mmol) with reagent **1a** or **1b** (0.11 mmol) was carried out in the presence of NaH (0.12 mmol) in DMF (1.0 mL) at rt. [b]The reaction of **6f** (0.10 mmol) with reagent **1a** (0.15 mmol) was carried out in the presence of *t*BuOK (0.12 mmol) in THF(1.0 mL) at rt for 24 h.

Next, we investigated the triflyl-arylation reaction of aniline derivatives **7** with **1a**,**b**.[15] Aniline **7a** provided the desired products **3aa** and **3ba** in good yields in the presence of Cu under 80 °C in *N*-Methyl-2-pyrrolidone (NMP).[17b] The presence of a halogen atom (Br, Cl) and an electron-donating group (OMe) on the benzene ring were all effectively sustained to provide the corresponding products **3ab, 3bb**, **3ac** and **3ad** in good yields. The presence of the electron-

withdrawing NO_2 group on the sterically demanding *ortho*-position of aniline **7e** also underwent a reaction to provide the triflyl-phenylated product **3ae** in 71% yield (Scheme 4).

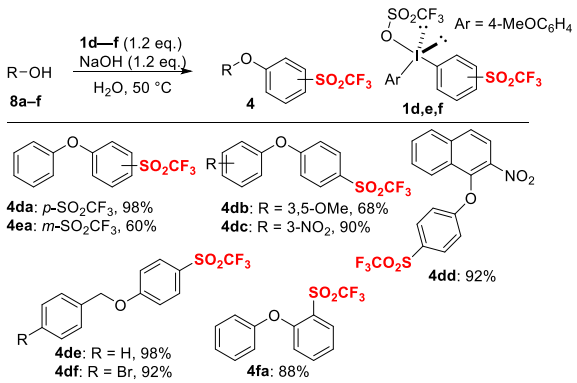
Scheme 4: Triflyl-arylation of anilines **7** with iodonium salts **1a,b**.[a]



[a]The reaction of **7** (0.20 mmol) with reagent **1a** or **1b** (0.22 mmol) was carried out in the presence of Cu (0) (0.02 mmol) in NMP (0.4 mL) at 80 °C.

We further examined *O*-nucleophiles such as phenols and alcohols **8** in the triflyl-arylation reaction (Scheme 5).[16] Proceeding with this investigation, we found that the iodonium salts **1d**,**e** having an anisole dummy ligand reacted with **8** in the presence of NaOH in H_2O at 50°C, to provide better yields than **1a**,**b** with a mesitylene auxiliary. Anisole decreases steric hindrance for the incoming nucleophile while the electronic status on the benzene ring of **1** is not that different from mesitylene, allowing it to attack the electrophilic iodine center more easily in this case.[12a] A wide variety of substrates **8a**—**f** including two electron-rich OMe groups and an electron-withdrawing NO_2 group were found to withstand the reaction to provide the triflyl-arylation products **4da**—**dc** and **4ea** in good to excellent yields. Naphthyl- and benzyl alcohol-derived products **4dd**—**4df** were also obtained in good to excellent yield by iodonium salt **1d**. It should be noted that sterically demanding *ortho*-triflylphenyl-aryliodonium salt **1f** also provided the desired arylation product **4fa** in 88% yield.

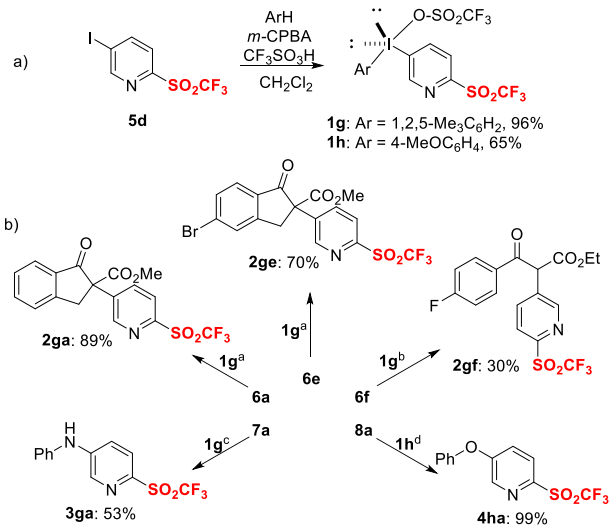
Scheme 5: Triflyl-arylation of phenols and alcohols **8** by iodonium salts **1d**—**f**.[a]



[a]The reaction of **8** (0.10 mmol) with reagent **1d—f** (0.12 mmol) was carried out in the presence of NaOH (0.12 mmol) in H_2O (0.5 mL) at 50 °C.

Considering our approach of electrophilic triflyl-arylation, we finally decided to further extend the design of reagents for the triflyl-pyridylation reaction. It is well known that pyridine is the most commonly occurring heterocycle in bioactive compounds.[19a] Keeping in mind the importance of fluorine for rendering bioactivity, the development of methodologies for the introduction of fluoro-functionalized pyridines is very crucial. Indeed, CF_3-pyridines are one of the most widely occurring fluorinated heterocycles in pharmaceuticals and agrochemicals.[19b] The recent big commercial success of CF_3-pyridines led us to develop pyridine triflones (CF_3SO_2-pyridines). Thus, we designed iodonium salts, trifluoromethylsulfonyl-pyridine-λ^3-aryliodonium salts **1**, which can lead to the introduction of pyridine triflone into various organic compounds. Two types of salts **1** were prepared in the same manner as their aryl counterparts, from the corresponding pyridine iodide **5d** with mesitylene or anisole as a dummy ligand to yield iodonium salts **1g** (96%) and **1h** (65%), respectively (Scheme 6a). We next investigated the reaction for carbon and hetero-centered nucleophiles (Scheme 6b). The reaction of β-keto esters **6a**, **6e** and **6f** with reagent **1g** provided the triflyl-pyridylated products **2ga**, **2ge** and **2gf** in 89%, 70% and 30% yield, respectively. The use of aniline **7a** as an *N*-nucleophile for iodonium salt **1g** provided product **3ga** in 53% yield. For the reaction with phenol **8a**, iodonium salt **1h** was chosen and the desired product **4ha** was obtained in excellent yield (99%).

Scheme 6: a) Synthesis of CF_3SO_2-pyridylaryl-λ^3-iodonium salts **1g**,**h** from pyridine iodide **5d**. b) Triflyl-pyridylation of β-keto esters (**6a,e,f**), aniline (**7a**) and phenol (**8a**).



[a]The reaction of **6a,e** (0.10 mmol) with reagent **1g** (0.11 mmol) was carried out in the presence of NaH (0.12 mmol) in DMF (1.0 mL) at rt. [b]The reaction of **6f** (0.10 mmol) with reagent **1g** (0.15 mmol) was carried out in the presence of *t*BuOK (0.12 mmol) in THF(1.0 mL) at rt for 24 h. [c]The reaction of **7** (0.20 mmol) with reagent **1g** (0.22 mmol) was carried out in the presence of Cu(0) (0.02 mmol) in NMP (0.4 mL) at 80 °C. [d]The reaction of **8** (0.10 mmol) with reagent **1h** (0.12 mmol) was carried out in the presence of *t*BuOK (0.12 mmol) in THF (0.5 mL) at 40 °C.

In conclusion, we have developed triflyl-aryl/pyridyl-aryl-λ^3-iodonium salts **1**, which are excellent reagents for triflyl-arylation and triflyl-pyridylation reactions for *C*- and hetero-

centered nucleophiles. These iodonium salts are stable, easy-to-handle, and useful to synthesize aryl and pyridyl triflones in good to high yields under mild conditions. This methodology paves a way to achieve a variety of SO_2CF_3-arylated/heteroarylated derivatives which can act as building blocks for the synthesis of bioactive compounds and catalysts.

EXPERIMENTAL SECTION

General information: All reactions were performed in oven-dried glassware under positive pressure of nitrogen or argon unless mentioned otherwise. Solvents were transferred via syringe and were introduced into reaction vessels though a rubber septum. All reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel (60-F254). The TLC plates were visualized with UV light and $KMnO_4$ in water/heat. Column chromatography was carried out on columns packed with silica gel (60N spherical neutral size 63-210 μm). The ^{1}H NMR (300 MHz), ^{19}F NMR (282 MHz), and ^{13}C NMR (175 MHz or 125 MHz) spectra for solution in $CDCl_3$ or $(CD_3)_2CO$ were recorded on Varian Mercury 300, Bruker Avance 500 and Joel 700 NMR spectrometers. Chemical shifts (δ) are expressed in ppm downfield from TMS (δ = 0.00) or C_6F_6 [δ = −162.2 ($CDCl_3$) or −163.5 ($(CD_3)_2CO$)] as an internal standard. Mass spectra were recorded on a SHIMADZU GCMS-QP5050A (EI-MS) and SHIMAZU LCMS-2020 (ESI-MS). Solvents CH_3CN, CH_2Cl_2, DMF, THF and NMP were dried and distilled before use.

General Procedure A: Preparation of bromo-((trifluoromethyl)sulfonyl)benzene/pyridine 9[20]: To a stirred solution of phenyl(pyridyl)trifluoromethylsulfide (1.0 eq.) in H_2O: MeCN: CCl_4 (2:1:1) at rt, $RuCl_3 \cdot xH_2O$ (5 mol%) was added in one portion followed by sodium periodate (3.0 eq.) portion wise. The reaction mixture was monitored by TLC and upon completion of the reaction, it was filtered through a celite pad and washed with Et_2O. The organic layer was washed with brine three times and the combined organic layer was concentrated *in vacuo*. The crude was then purified using column chromatography on silica gel to give the desired bromo-((trifluoromethyl)sulfonyl)benzene/pyridine **9**.

1-Bromo-3-((trifluoromethyl)sulfonyl)benzene ***9b****:* Following General Procedure A, (3-bromophenyl)(trifluoromethyl)sulfane (1.54 g, 6.0 mmol), $RuCl_3 \cdot xH_2O$ (62 mg, 0.3 mmol) and $NaIO_4$ (3.9 g, 18 mmol) in H_2O (3.4 mL): MeCN (1.7 mL): CCl_4 (1.7 mL) were used at rt for 1 h. Isolated by column chromatography on silica gel (*n*-hexane/EtOAc, 9/1) to give the desired product **9b** as a colorless oil (1.56 g) in 90% yield. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_7H_4O_2F_3SBr$ 287.9067; Found 287.9085; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.57 (t, *J* = 9 Hz, 1H), 7.95—8.00 (m, 2H), 8.17 (s, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –78.44 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 175 MHz) δ = 119.8 (q, *J* = 323.75 Hz), 124.0, 129.4, 131.5, 133.4, 133.5, 139.8.

1-Bromo-2-((trifluoromethyl)sulfonyl)benzene ***9c****:* Following General Procedure A, (2-bromophenyl)(trifluoromethyl)sulfane (1.56 g, 6.0 mmol), $RuCl_3 \cdot xH_2O$ (62 mg, 0.3 mmol) and $NaIO_4$ (3.9 g, 18 mmol) in H_2O (3.4 mL): MeCN (1.7 mL): CCl_4 (1.7 mL) were used at rt for 1 h. Isolated by column chromatography on silica gel (*n*-hexane/EtOAc, 9/1) to give the desired product **9c** as a white solid (1.5 g) in 86% yield. Mp: 42–44 °C; HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_7H_4O_2F_3SBr$ 287.9067; Found 287.9079; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.62—7.65 (m, 2H), 7.88—7.91 (m, 1H), 8.21—8.24 (m, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –76.18(s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 175 MHz) δ = 119.9 (q, *J* = 325.5 Hz), 123.7, 128.6, 131.7, 135.29, 137.0, 137.3.

5-Bromo-2-((trifluoromethyl)sulfonyl)pyridine ***9d****:* Following General Procedure A, 5-bromo-2-((trifluoromethyl)thio)pyridine (1.85 g, 7.1 mmol), $RuCl_3 \cdot xH_2O$ (73.7 mg, 0.35 mmol) and $NaIO_4$ (4.5 g, 21.3 mmol) in H_2O (3.7 mL): MeCN (1.9 mL): CCl_4 (1.9 mL) were used at rt for 14 h. Isolated by column chromatography on silica gel (*n*-hexane/EtOAc, 9/1) to give the desired product **9d** as a white solid (1.8 g) in 87% yield. Mp: 67–70 °C; HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_6H_3NO_2F_3SBr$ 288.9020; Found 288.9008; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 8.10—8.12 (m, 1H), 8.23—8.26 (m, 1H), 8.95 (s, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –75.92 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 175 MHz) δ = 119.8 (q, *J* = 323.75 Hz), 127.4, 128.6, 141.5, 149.6, 152.9.

General Procedure B: Preparation of iodo-((trifluoromethyl)sulfonyl)benzene/pyridine 5[21]: To a flame-dried Schlenk-tube, CuI (10 mol %), NaI (2.0 equiv) and aryl bromide **9** (1.0 equiv) were added and evacuated and backfilled with Argon. *n*-pentanol (1.0 mL/mmol ArBr) and *N,N′*-dimethylethylenediamine (DMEDA) (20 mol %) were then added and the mixture was stirred at rt for 3 min, followed by 110 °C for 49—72 h. The resulting suspension was cooled to rt, diluted in aqueous NH_3 solution (28 wt%) and H_2O, and extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give the desired product **5**.

1-Iodo-4-((trifluoromethyl)sulfonyl)benzene ***5a****:* Following General Procedure B, 1-bromo-4-((trifluoromethyl)sulfonyl)benzene **9a** (1.9 g, 6.6 mmol), CuI (125 mg, 0.66 mmol), NaI (1.9 g, 13.2 mmol) and DMEDA (.14 mL, 1.32 mmol) in *n*-pentanol (2.5 mL) were used at 130 °C for 72 h. Isolated by a short column chromatography on silica gel (*n*-hexane) to give the desired product **5a** as a white solid (2.0 g) in 88% yield. Mp: 76–79 °C; HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_7H_4O_2F_3SI$ 335.8929; Found 335.8954; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.71—7.84 (m, 2H), 7.88—8.07 (m, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –78.72 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 175 MHz) δ = 106.0, 119.7 (q, *J* = 325.5 Hz), 131.8, 132.2, 133.0, 133.5, 139.5.

1-Iodo-3-((trifluoromethyl)sulfonyl)benzene ***5b****:* Following General Procedure B, 1-bromo-3-((trifluoromethyl)sulfonyl)benzene **9b** (1.56 g, 5.4 mmol), CuI (103 mg, 0.54 mmol), NaI (1.6 g, 10.8 mmol) and DMEDA (0.12 mL, 1.08 mmol) in *n*-pentanol (2 mL) were used at 130 °C for 72 h. Isolated by a short column chromatography on silica gel (*n*-hexane) to give 1.8 g yellow oil which was an inseparable mixture of the **9b** and **5b** (Check SI). HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_7H_4O_2F_3SI$ 335.8929; Found 335.8923.

1-Iodo-2-((trifluoromethyl)sulfonyl)benzene ***5c****:* Following General Procedure B, 1-bromo-2-((trifluoromethyl)sulfonyl)benzene **9c** (1.5 g, 5.2 mmol), CuI (99 mg, 0.52 mmol), NaI (1.54 g, 10.4 mmol) and DMEDA (0.1 mL, 1.0 mmol) in *n*-pentanol (2 mL) were used at 130 °C for 72 h. Isolated by a short column chromatography on silica gel (*n*-hexane) to give 1.5 g yellow oil which was an inseparable mixture of the **9c** and **5c** (Check SI). HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_7H_4O_2F_3SI$ 335.8929; Found 335.8940.

5-Iodo-2-((trifluoromethyl)sulfonyl)pyridine ***5d****:* Following General Procedure B, 5-iodo-2-((trifluoromethyl)sulfonyl)pyridine **9d** (1.5 g, 5.2 mmol), CuI (95.2 mg, 0.5 mmol), NaI (1.53 g, 10.3 mmol) and DMEDA (0.1 mL, 1.0 mmol) in *n*-pentanol (2. mL) were used at 130 °C for 72 h. Isolated by a column chromatography on silica gel

(*n*-hexane/EtOAc 9/1) to give the desired product **5d** as a white solid (1.03 g) in 59% yield. Mp: 72–75 °C; HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_6H_3NO_2F_3SI$ 336.8881; Found 336.8903; ^1H NMR ($CDCl_3$, 300 MHz) δ = 7.97 (d, *J* = 9 Hz, 1H), 8.44 (dd, *J* = 6 Hz, 3 Hz, 1H), 9.10 (s, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –75.94 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 175 MHz) δ = 102.3, 119.8 (q, *J* = 327.25 Hz), 127.3, 147.3, 150.2, 157.8.

General Procedure C: Preparation of diaryliodonium salts 1[13]: *m*CPBA (assume 69 wt%, 1.1 equiv) was dried *in vacuo* at rt for 1 h before the addition of iodo-((trifluoromethyl)sulfonyl)benzene/pyridine **5** (1.0 equiv) and CH_2Cl_2 in a round bottomed flask. The solution was cooled to 0 °C followed by the dropwise addition of TfOH (1.7 equiv), and the resulting mixture was stirred at rt for 2 h. It was then cooled to 0 °C and arene (1.1 equiv) was added dropwise. The mixture was warmed to rt and stirred for 15–20 h. The solvent was then removed under reduced pressure. The resulting crude product was precipitated by adding Et_2O. For reagent **1g** and **1h** the Et_2O solution had to be stored at –20 °C for 12 h for complete precipitation to take place. The precipitate was filtered and dried *in vacuo* to give **1** as a white to grey solid.

*Mesityl(4-((trifluoromethyl)sulfonyl)phenyl)-λ⁶-iodane trifluoromethanesulfonate **1a**:* Following General Procedure C, **5a** (710 mg, 2.1 mmol), *m*CPBA (515.4 mg, 2.3 mmol), TfOH (0.4 mL, 3.6 mmol) and mesitylene (0.3 mL, 2.3 mmol) in CH_2Cl_2 (6 mL) were used from 0 °C to rt for 15 h to give **1a** as a white solid (1.15 g) in 91% yield. Mp: 193–196 °C; HRMS (ESI-TOF) m/z: $[M–OTf]^+$ Calcd for $C_{16}H_{15}O_2F_3SI$ 454.9790; Found 454.9789; ^1H NMR ($(CD_3)_2CO$), 300 MHz) δ = 2.39 (s, 3H), 2.72 (s, 6H), 7.34 (s, 2H), 8.26 (d, *J* = 9 Hz, 2H), 8.45 (d, *J* = 9 Hz, 2H); ^{19}F NMR ($(CD_3)_2CO$), 282 MHz) δ = –80.16 (s, 3F), –79.84 (s, 3F); $^{13}C\{^1H\}$NMR ($(CD_3)_2CO$), 126 MHz) δ = 21.0, 27.1, 120.5 (q, *J* = 323.75 Hz), 121.8, 122 (q, *J* = 320 Hz), 122.6, 131.4, 134.4, 134.9, 136.5, 143.9, 146.0.

*Mesityl(3-((trifluoromethyl)sulfonyl)phenyl)-λ⁶-iodane trifluoromethanesulfonate **1b**:* Following General Procedure C, **5b**[18] (710 mg, 2.1 mmol), *m*CPBA (515.4 mg, 2.3 mmol), TfOH (0.4 mL, 3.6 mmol) and mesitylene (0.3 mL, 2.3 mmol) in CH_2Cl_2 (6 mL) were used from 0 °C to rt for 15 h to give **1b** as a white solid (1.15 g) in 91% yield for overall two steps starting from **9b** (2.1 mmol). Mp: 165–168 °C; HRMS (ESI-TOF) m/z: $[M–OTf]^+$ Calcd for $C_{16}H_{15}O_2F_3SI$ 454.9790; found 454.9792; ^1H NMR ($(CD_3)_2CO$), 300 MHz) δ = 2.37 (s, 3H), 2.73 (s, 6H), 7.32 (s, 2H), 8.02 (t, *J* = 9 Hz, 1H), 8.40 (d, *J* = 6 Hz, 1H), 8.51 (d, *J* = 9 Hz, 1H), 8.76 (s, 1H); ^{19}F NMR ($(CD_3)_2CO$), 282 MHz) δ = –80.09 (s, 3F), –79.89 (s, 3F); $^{13}C\{^1H\}$NMR ($(CD_3)_2CO$), 126 MHz) δ = 21.0, 27.0, 114.2, 120.4 (q, *J* = 323.75 Hz), 121.8 (q, *J* = 318.75 Hz), 122.3, 131.3, 134.3, 134.7, 135.0, 136.4, 142.8, 143.7, 145.8.

*Mesityl(2-((trifluoromethyl)sulfonyl)phenyl)-λ⁶-iodane trifluoromethanesulfonate **1c**:* Following General Procedure C, **5c**[18] (710 mg, 2.1 mmol), *m*CPBA (515.4 mg, 2.3 mmol), TfOH (0.4 mL, 3.6 mmol) and mesitylene (0.3 mL, 2.3 mmol) in CH_2Cl_2 (6 mL) were used from 0 °C to rt for 15 h to give **1c** as a white solid (720 mg) in 57% yield for overall two steps starting from **9c** (2.1 mmol). Mp: 145–147 °C; HRMS (ESI-TOF) m/z: $[M–OTf]^+$ Calcd for $C_{16}H_{15}O_2F_3SI$ 454.9790; Found 454.9782; ^1H NMR ($(CD_3)_2CO$), 300 MHz) δ = 2.47 (s, 3H), 2.66 (s, 6H), 7.40—7.51 (m, 3H), 8.07—8.20 (m, 2H), 8.57 (d, *J* = 6 Hz, 1H); ^{19}F NMR ($(CD_3)_2CO$), 282 MHz) δ = –79.87 (s, 3F), –79.10 (s, 3F); $^{13}C\{^1H\}$NMR ($(CD_3)_2CO$), 126 MHz) δ = 21.3, 26.9, 112.0, 119.53, 120.6 (q, *J* = 323.75 Hz), 121.9 (q, *J* = 320 Hz), 129.9, 131.8, 133.2, 134.3, 137.5, 142.2, 144.9, 147.3.

*Anisole(4-((trifluoromethyl)sulfonyl)phenyl)-λ⁶-iodane trifluoromethanesulfonate **1d**:* Following General Procedure C, **5a** (505 mg, 1.5 mmol), *m*CPBA (406 mg, 1.65 mmol), TfOH (0.3 mL, 2.6 mmol) and anisole (0.2 mL, 1.7 mmol) in CH_2Cl_2 (15 mL) were used from 0 °C to rt for 15 h to give **1d** as a dark grey solid (669 mg) in 75% yield. Mp: 133–136 °C; HRMS (ESI-TOF) m/z: $[M–OTf]^+$ Calcd. for $C_{14}H_{11}O_3F_3SI$ 442.9426; Found 442.9416; ^1H NMR ($(CD_3)_2CO$), 300 MHz) δ = 3.90 (s, 3H), 7.14—7.19 (m, 2H), 8.27 (d, *J* = 9 Hz, 2H), 8.34—8.39 (m, 2H), 8.67—8.71 (m, 2H); ^{19}F NMR ($(CD_3)_2CO$), 282 MHz) δ = –80.16 (s, 3F), –79.86 (s, 3F); $^{13}C\{^1H\}$NMR ($(CD_3)_2CO$), 126 MHz) δ = 56.4, 103.3, 119.0, 120.5 (q, *J* = 323.75 Hz), 121.8 (q, *J* = 320 Hz), 124.8, 134.2, 135.0, 137.5, 139.5, 164.4.

*Anisole(3-((trifluoromethyl)sulfonyl)phenyl)-λ⁶-iodane trifluoromethanesulfonate **1e**:* Following General Procedure C, **5b**[18] (505 mg, 1.5 mmol), *m*CPBA (406 mg, 1.65 mmol), TfOH (0.3 mL, 2.6 mmol) and anisole (0.2 mL, 1.7 mmol) in CH_2Cl_2 (15 mL) were used from 0 °C to rt for 15 h to give **1e** as a dark grey solid (703 mg) in 79% yield for overall two steps starting from **9b** (1.5 mmol). Mp: 178–180 °C; HRMS (ESI-TOF) m/z: $[M–OTf]^+$ Calcd for $C_{14}H_{11}O_3F_3SI$ 442.9426; Found 442.9425; ^1H NMR ($(CD_3)_2CO$), 300 MHz) δ = 3.88 (s, 3H), 7.15 (d, *J* = 9 Hz, 2H), 8.04 (t, *J* = 9 Hz, 1H), 8.37—8.43 (m, 3H), 8.89 (d, *J* = 9 Hz, 1H), 8.99 (s, 1H); ^{19}F NMR ($(CD_3)_2CO$), 282 MHz) δ = –80.10 (s, 3F), –79.90 (s, 3F); $^{13}C\{^1H\}$NMR ($(CD_3)_2CO$), 126 MHz) δ = 56.3, 104.0, 116.7, 118.8, 120.4 (q, *J* = 322.5 Hz), 121.8 (q, *J* = 318.75 Hz), 134.1, 134.6, 134.9, 137.4, 139.1, 144.3, 164.2.

*Anisole(2-((trifluoromethyl)sulfonyl)phenyl)-λ⁶-iodane trifluoromethanesulfonate **1f**:* Following General Procedure C, **5c**[18] (505 mg, 1.5 mmol), *m*CPBA (406 mg, 1.65 mmol), TfOH (0.3 mL, 2.6 mmol) and anisole (0.2 mL, 1.7 mmol) in CH_2Cl_2 (15 mL) were used from 0 °C to rt for 15 h to give **1f** as a dark grey solid (256 mg) in 30% yield for overall two steps starting from **9c** (1.44 mmol). Mp: 125–128 °C; HRMS (ESI-TOF) m/z: $[M–OTf]^+$ Calcd for $C_{14}H_{11}O_3F_3SI$ 442.9426; Found 442.9423; ^1H NMR ($(CD_3)_2CO$), 300 MHz) δ = 3.96 (s, 3H), 7.27 (d, *J* = 9 Hz, 2H), 8.18—8.20 (m, 3H), 8.34 (d, *J* = 9 Hz, 2H), 8.55 (d, *J* = 6 Hz, 1H); ^{19}F NMR ($(CD_3)_2CO$), 282 MHz) δ = –79.82 (s, 3F), –78.85 (s, 3F); $^{13}C\{^1H\}$NMR ($(CD_3)_2CO$), 126 MHz) δ = 56.5, 101.5, 114.3, 119.4, 240.5 (q, *J* = 323.75 Hz), 121.8 (q, *J* = 318.75 Hz), 123.9, 129.8, 134.69, 136. 7, 137.7, 140.6, 141.6, 165.0.

*5-(Mesityl-λ⁶-iodaneyl)-2-((trifluoromethyl)sulfonyl)pyridine trifluoromethanesulfonate **1g**:* Following General Procedure C, **5d** (505 mg, 1.5 mmol), *m*CPBA (406 mg, 1.65 mmol), TfOH (0.3 mL, 2.6 mmol) and mesitylene (0.2 mL, 1.7 mmol) in CH_2Cl_2 (9 mL) were used from 0 °C to rt for 18 h to give **1g** as a white solid (874 mg) in 96% yield. Mp: 132–135 °C; HRMS (ESI-TOF) m/z: $[M–OTf]^+$ Calcd for $C_{15}H_{14}NO_2F_3SI$ 455.9742; Found 455.9749; ^1H NMR ($(CD_3)_2CO$), 300 MHz) δ = 2.39 (s, 3H), 2.75 (s, 6H), 7.33 (s, 2H), 8.48 (d, *J* = 9 Hz, 1H), 8.93 (d, *J* = 9 Hz, 1H) 8.40 (d, *J* = 3 Hz, 1H); ^{19}F NMR ($(CD_3)_2CO$), 282 MHz) δ = –80.16 (s, 3F), –79.86 (s, 3F); $^{13}C\{^1H\}$NMR ($(CD_3)_2CO$), 126 MHz) δ = 21.0, 27.2, 119.1, 120.6 (q, *J* = 325 Hz), 121.7 (q, *J* = 378.75 Hz), 121.8, 129.9, 131.4, 143.9, 146.1, 146.1, 153. 5, 154.9.

*5-(Anisyl-λ⁶-iodaneyl)-2-((trifluoromethyl)sulfonyl)pyridine trifluoromethanesulfonate **1h**:* Following General Procedure C, **5d** (337 mg, 1.0 mmol), *m*CPBA (271 mg, 1.1 mmol), TfOH (0.2 mL,

1.7 mmol) and anisole (0.1 mL, 1.1 mmol) in CH_2Cl_2 (6 mL) were used from 0 °C to rt for 18 h to give **1h** as a dark green solid (384 mg) in 65% yield. Mp: 166–170 °C; HRMS (ESI-TOF) m/z: $[M–OTf]^+$ Calcd for $C_{13}H_{10}NO_3F_3SI$ 443.9378; Found 443.9379; ^1H NMR ($(CD_3)_2CO$), 300 MHz) δ = 3.91 (s, 3H), 7.17 (d, *J* = 9 Hz, 2H), 8.40 (d, *J* = 9 Hz, 2H), 8.52 (d, *J* = 9 Hz, 1H), 9.19 (dd, *J* = 6 Hz, 3 Hz, 1H), 9.63 (d, *J* = 3 Hz, 1H); ^{19}F NMR ($(CD_3)_2CO$), 282 MHz) δ = –79.90 (s, 3F), –77.36 (s, 3F); $^{13}C\{^1H\}$NMR ($(CD_3)_2CO$), 126 MHz) δ = 55.4, 102.3, 118.1, 119.6 (q, *J* = 325 Hz), 120.2 (q, *J* = 318.75 Hz), 120.2, 128.7, 138.5, 145.9, 152.5, 154.7, 163.5.

General Procedure D: Triflyl-arylation/pyridylation of β-keto esters: Method 1[17c]**:** To a suspension of NaH (60% suspension in oil, 1.2 equiv) in DMF (10 mL/mmol β-keto ester), cyclic β-keto ester **6a-e** (1.0 equiv) was added, and the mixture was stirred at rt for 10 min. Diaryliodonium salt **1** (1.1 equiv) was then added to the mixture in one portion at rt. After completion of the reaction, H_2O was slowly added to the reaction mixture and extracted three times with Et_2O. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give α-SO_2CF_3-phenyl/pyridine-β-keto ester **2**.

Method 2[14a]**:** To a suspension of *t*BuOK (1.2 equiv) in THF (10 mL/mmol β-keto ester), acyclic β-keto ester **6f** (1.0 equiv) was added, and the mixture was stirred at rt for 1 h. Diaryliodonium salt **1** (1.5 equiv) was then added to the mixture in one portion at rt. After completion of the reaction, H_2O was slowly added to the reaction mixture and extracted three times with EtOAC. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give α-SO_2CF_3-phenyl/pyridine-β-keto ester **2**.

*Methyl 1-oxo-2-(4-((trifluoromethyl)sulfonyl)phenyl)-2,3-dihydro-1H-indene-2-carboxylate **2aa**:* Following General Procedure D Method 1, cyclic β-ketoester **6a**, (19 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent **1a** (66.5 mg, 0.11 mmol) in DMF (1 mL) were used at room temperature for 3 h. Isolated by column chromatography on silica gel (*n*-hexane/EtOAc, 8/2) to give the desired product **2aa** as white solid (34 mg) in 86% yield. Mp: 127–130 °C; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{13}O_5F_3NaS$ 421.0333; Found 421.0336; ^1H NMR ($CDCl_3$, 300 MHz) δ = 3.58 (d, *J* = 18 Hz, 1H), 3.76 (s, 3H), 4.27 (d, *J* = 18 Hz, 1H), 7.48 (t, *J* = 9 Hz, 1H), 7.55 (d, *J* = 9 Hz, 1H), 7.71 (t, *J* = 6 Hz, 1H), 7.76 (d, *J* = 9 Hz, 2H), 7.87 (d, *J* = 6 Hz, 1H), 8.02 (d, *J* = 9 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –78.74 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 40.5, 53.9, 65.3, 119.9 (q, *J* = 326.34 Hz), 125.6, 126.5, 128.7, 129.4, 130.5, 131.1, 134.6, 136.5, 147.7, 151.8, 169.9, 198.8.

*Methyl 1-oxo-2-(3-((trifluoromethyl)sulfonyl)phenyl)-2,3-dihydro-1H-indene-2-carboxylate **2ba**:* Following General Procedure D Method 1, cyclic β-ketoester **6a**, (19 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent **1b** (66.5 mg, 0.11 mmol) in DMF (1 mL) were used at room temperature for 3 h. Isolated by column chromatography on silica gel (*n*-hexane/EtOAc, 8/2) to give the desired product **2ba** as white solid (37 mg) in 93% yield. Mp: 75–77 °C; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{13}O_5F_3NaS$ 421.0333; Found 421.0322; ^1H NMR ($CDCl_3$, 300 MHz) δ = 3.61 (d, *J* = 18 Hz, 1H), 3.74 (s, 3H), 4.25 (d, *J* = 18 Hz, 1H), 7.47 (t, *J* = 9 Hz, 1H), 7.56 (d, *J* = 9 Hz, 1H), 7.70 (q, *J* = 6 Hz, 1H), 7.87 (d, *J* = 9 Hz, 2H), 7.99 (d, *J* = 9 Hz, 1H), 8.02—8.06 (m, 1H), 8.12 (s, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –78.76 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 40.2, 53.8, 64.6, 119.8 (q, *J* = 326.34 Hz), 125.6, 126.5, 128.6, 130.1 (d, *J* = 13.86 Hz), 130.2, 131.8, 134.6, 136.3 (d, *J* = 22.68 Hz), 140.7, 151.8, 170.1, 198.9.

*Tert-Butyl 1-oxo-2-(4-((trifluoromethyl)sulfonyl)phenyl)-2,3-dihydro-1H-indene-2-carboxylate **2ab**:* Following General Procedure D Method 1, cyclic β-ketoester **6b**, (23.2 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent **1a** (66.5 mg, 0.11 mmol) in DMF (1 mL) were used at room temperature for 3 h. Isolated by column chromatography on silica gel (*n*-hexane/EtOAc, 8/2) to give the desired product **2ab** as white solid (31 mg) in 71% yield. Mp: 76–79 °C; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{21}H_{19}O_5F_3NaS$ 463.0803; Found 463.0809; ^1H NMR ($CDCl_3$, 300 MHz) δ = 1.38 (s, 9H), 3.58 (d, *J* = 15 Hz, 1H), 4.17 (d, *J* = 18 Hz, 1H), 7.46 (t, *J* = 6 Hz, 1H), 7.54 (d, *J* = 9 Hz, 1H), 7.69 (t, *J* = 6 Hz, 1H), 7.81 (d, *J* = 9 Hz, 2H), 7.86 (d, *J* = 9 Hz, 1H), 8.01 (d, *J* = 9 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –78.86 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 27.8, 40.2, 66.1, 83.8, 119.9 (q, *J* = 326.34 Hz), 125.4, 126.3, 128.5, 129.5, 130.2, 130.9, 134.9, 136.1, 148.1, 151.8, 168.4, 199.2.

*Tert-butyl 1-oxo-2-(3-((trifluoromethyl)sulfonyl)phenyl)-2,3-dihydro-1H-indene-2-carboxylate **2bb**:* Following General Procedure D Method 1, cyclic β-ketoester **6b**, (23.2 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent **1b** (66.5 mg, 0.11 mmol) in DMF (1 mL) were used at room temperature for 3 h. Isolated by column chromatography on silica gel (*n*-hexane/EtOAc, 8/2) to give the desired product **2bb** as yellow oil (28 mg) in 65% yield. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{19}O_5F_3NaS$ 463.0803; Found 463.0808; ^1H NMR ($CDCl_3$, 300 MHz) δ = 1.37 (s, 9H), 3.58 (d, *J* = 18 Hz, 1H), 4.18 (d, *J* = 18 Hz, 1H), 7.45 (t, *J* = 6 Hz, 1H), 7.55 (d, *J* = 9 Hz, 1H), 7.68 (q, *J* = 6 Hz, 2H), 7.85 (d, *J* = 9 Hz, 1H), 7.97 (d, *J* = 6 Hz, 1H), 8.05 (d, *J* = 6 Hz, 1H), 8.18 (s, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –78.79 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 27.7, 39.9, 65.5, 83.8, 119.9 (q, *J* = 327.6 Hz), 125.4, 126.5, 128.4, 130.0 (t, *J* = 31.5 Hz), 131.5, 134.8, 136.15 (d, *J* = 15.12), 141.2, 151.8, 168.4, 199.4.

*(3r)-Adamantan-1-yl-1-oxo-2-(4-((trifluoromethyl)sulfonyl)phenyl)-2,3-dihydro-1H-indene-2-carboxylate **2ac**:* Following General Procedure D Method 1, cyclic β-ketoester **6c**, (31 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent **1a** (66.5 mg, 0.11 mmol) in DMF (1 mL) were used at room temperature for 3 h. Isolated by column chromatography on silica gel (*n*-hexane/EtOAc, 8/2) to give the desired product **2ac** as viscous oil (45 mg) in 87% yield. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{25}O_5F_3NaS$ 541.1272; Found 541.1278; ^1H NMR ($CDCl_3$, 300 MHz) δ = 1.61 (s, 7H), 2.00 (s, 6H), 2.13 (s, 3H), 3.57 (d, *J* = 18 Hz, 1H), 4.15 (d, *J* = 18 Hz, 1H), 7.45 (t, *J* = 6 Hz, 1H), 7.54 (d, *J* = 9 Hz, 1H), 7.69 (d, *J* = 9 Hz, 2H), 7.80—7.86 (m, 3H), 8.01 (d, *J* = 9 Hz, 1H), ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –78.81 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 30.9, 36.0, 40.3, 40.9, 66.1, 83.9, 119.9 (q, *J* = 326.34 Hz), 125.4, 126.3, 128.4, 129.5, 130.1, 130.8, 134.9, 136.1, 148.1, 151.9, 167.9, 199.2.

*(3r)-Adamantan-1-yl-1-oxo-2-(3-((trifluoromethyl)sulfonyl)phenyl)-2,3-dihydro-1H-indene-2-carboxylate **2bc**:* Following General Procedure D Method 1, cyclic β-ketoester **6c**, (31 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent **1b** (66.5 mg, 0.11 mmol) in DMF (1 mL) were used at room temperature for 3 h. Isolated by column chromatography on silica gel (*n*-hexane/EtOAc, 8/2) to give the desired product **2bc** as white solid (42

mg) in 81% yield. Mp: 107–110 °C; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{25}O_5F_3NaS$ 541.1272; Found 541.1267; ^1H NMR ($CDCl_3$, 300 MHz) δ = 1.60 (s, 7H), 1.99 (s, 6H), 2.12 (s, 3H), 3.57 (d, *J* = 18 Hz, 1H), 4.18 (d, *J* = 15 Hz, 1H), 7.45 (t, *J* = 9 Hz, 1H), 7.54 (d, *J* = 6 Hz, 1H), 7.67 (q, *J* = 9 Hz, 6 Hz, 2H), 7.84 (d, *J* = 6 Hz, 1H), 7.97 (d, *J* = 9 Hz, 1H), 8.04—8.07 (m, 1H), 8.19 (s, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –78.71 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 30.9, 36.0, 40.0, 40.9, 65.6, 83.8, 119.9 (q, *J* = 326.34 Hz), 125.4, 126.3, 128.4, 129.9 (t, *J* = 32.76 Hz), 131.5, 134.8, 136.0, 136.3, 141.2, 151.9, 168.0, 199.3.

Methyl-5,6-dimethoxy-1-oxo-2-(4-((trifluoromethyl)sulfonyl)phenyl)-2,3-dihydro-1H-indene-2-carboxylate ***2ad****:* Following General Procedure D Method 1, cyclic β-ketoester **6d**, (25 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent **1a** (66.5 mg, 0.11 mmol) in DMF (1 mL) were used at room temperature for 3 h. Isolated by column chromatography on silica gel (*n*-hexane/EtOAc, 5/5) to give the desired product **2ad** as white solid (36 mg) in 78% yield. Mp: 178–181 °C; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{17}O_7F_3NaS$ 481.0545; Found 481.0540; ^1H NMR ($CDCl_3$, 300 MHz) δ = 3.42 (d, *J* = 18 Hz, 1H), 3.77 (s, 3H), 3.94 (s, 3H), 4.00 (s, 3H), 4.18 (d, *J* = 18 Hz, 1H), 6.90 (s, 1H), 7.26 (d, *J* = 6 Hz, 1H), 7.73 (d, *J* = 6 Hz, 2H), 8.01 (d, *J* = 6 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –78.75 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 40.5, 53.9, 56.5 (d, *J* = 31.5 Hz), 65.7, 105.4, 107.1, 119.9 (q, *J* = 326.34 Hz), 127.3, 129.3, 130.4, 131.1, 147.7, 148.4, 150.4, 157.1, 170.2, 197.2.

Methyl-5,6-dimethoxy-1-oxo-2-(3-((trifluoromethyl)sulfonyl)phenyl)-2,3-dihydro-1H-indene-2-carboxylate ***2bd****:* Following General Procedure D Method 1, cyclic β-ketoester **6d**, (25 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent **1b** (66.5 mg, 0.11 mmol) in DMF (1 mL) were used at room temperature for 3 h. Isolated by column chromatography on silica gel (*n*-hexane/EtOAc, 5/5) to give the desired product **2bd** as white solid (43 mg) in 94% yield. Mp: 168–170 °C; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{17}O_7F_3NaS$ 481.0545; Found 481.0555; ^1H NMR ($CDCl_3$, 300 MHz) δ = 3.48 (d, *J* = 15 Hz, 1H), 3.75 (s, 3H), 3.94 (s, 3H), 4.01 (s, 3H), 4.15 (d, *J* = 15 Hz, 1H), 6.94 (s, 1H), 7.25 (s, 1H), 7.67 (t, *J* = 9 Hz, 1H), 7.99 (t, *J* = 9 Hz, 2H), 8.09 (s, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –78.73 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 40.2, 53.8, 56.6 (d, *J* = 34.02 Hz), 64.9, 105.4, 107.1, 119.9 (q, *J* = 326.34 Hz), 127.3, 129.9, 130.1, 130.2, 131.7, 136.2, 141.3, 147.7, 150.4, 156.9, 170.4, 197.4.

Methyl 5-bromo-1-oxo-2-(4-((trifluoromethyl)sulfonyl)phenyl)-2,3-dihydro-1H-indene-2-carboxylate ***2ae****:* Following General Procedure D Method 1, cyclic β-ketoester **6e**, (27 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent **1a** (66.5 mg, 0.11 mmol) in DMF (1 mL) were used at room temperature for 12 h. Isolated by column chromatography on silica gel (*n*-hexane/EtOAc, 7/3) to give the desired product **2ae** as white solid (16 mg) in 33% yield. Mp: 109–101 °C; HRMS (ESI-TOF) m/z: $[M–H]^–$ Calcd for $C_{18}H_{11}O_5F_3SBr$ 474.9463; Found 474.9456; ^1H NMR ($CDCl_3$, 300 MHz) δ = 3.55 (d, *J* = 15 Hz, 1H), 3.77 (s, 3H), 4.26 (d, *J* = 18 Hz, 1H), 7.62 (d, *J* = 6 Hz, 1H), 7.73 (t, *J* = 9 Hz, 4H), 8.03 (d, *J* = 9 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –78.73 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 39.9, 54.1, 65.3, 119.1(q, *J* = 326.34 Hz), 126.7, 129.3, 129.8, 130.7, 131.2, 132.2, 132.4, 133.4, 147.2, 153.2, 169.5, 197.6.

Methyl 5-bromo-1-oxo-2-(3-((trifluoromethyl)sulfonyl)phenyl)-2,3-dihydro-1H-indene-2-carboxylate ***2be****:* Following General Procedure D Method 1, cyclic β-ketoester **6e**, (27 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent **1b** (66.5 mg, 0.11 mmol) in DMF (1 mL) were used at room temperature for 12 h. Isolated by column chromatography on silica gel (*n*-hexane/EtOAc, 7/3) to give the desired product **2be** as white solid (15 mg) in 30% yield. Mp: 97–100 °C; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{12}O_5F_3NaSBr$ 498.9439; Found 498.9434; ^1H NMR ($CDCl_3$, 300 MHz) δ = 3.58 (d, *J* = 15 Hz, 1H), 3.74 (s, 3H), 4.23 (d, *J* = 18 Hz, 1H), 7.60—7.63 (m, 1H), 7.65—7.71 (m, 2H), 7.73 (s, 1H), 7.99—8.03 (m, 2H), 8.11 (s, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –78.70 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 39.7, 53.9, 64.6, 119.8 (q, *J* = 326.34 Hz), 126.7, 129.8, 130.1, 130.2, 130.3, 131.9, 132.1, 132.4, 133.4, 136.1, 140.3, 153.2, 169.7, 197.7.

Ethyl-3-(4-fluorophenyl)-3-oxo-2-(4-((trifluoromethyl)sulfonyl)phenyl)propanoate ***2af****:* Following General Procedure D Method 2, acyclic β-ketoester **6f**, (21 mg, 0.1 mmol), *t*BuOK (13 mg, 0.12 mmol) and reagent **1a** (90 mg, 0.15 mmol) in THF (1 mL) were used at room temperature for 24 h. Isolated by column chromatography on silica gel (*n*-hexane/EtOAc, 9/1) to give the desired product **2af** as colorless oil (15 mg) in 36% yield. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{18}H_{14}O_5F_4S$ 418.0498; Found 418.0492; ^1H NMR ($CDCl_3$, 300 MHz) δ = 1.15 (t, *J* = 9 Hz, 3H), 4.11 (q, *J* = 6 Hz, 2H), 6.28 (s, 1H), 7.07–7.15 (m, 2H), 7.17–7.22 (m, 2H), 7.58–7.63 (m, 2H), 7.95 (d, *J* = 9 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –107.75– –107.65 (m, 1F), –79.06 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 14.1, 60.8, 107.3 (d, *J* = 2.5 Hz), 116.7 (d, *J* = 22.5 Hz), 117.0, 119.9 (q, *J* = 323.75 Hz), 124.2, 128.7 (d, *J* = 3.75 Hz), 128.9 (d, *J* = 8.75 Hz), 133.5, 158.9, 163.70 (d, *J* = 8.75 Hz), 163.71, 165.7.

Methyl 1-oxo-2-(6-((trifluoromethyl)sulfonyl)pyridin-3-yl)-2,3-dihydro-1H-indene-2-carboxylate ***2ga***: Following General Procedure D Method 1, cyclic β-ketoester **6a**, (19 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent **1g** (66 mg, 0.11 mmol) in DMF (1 mL) were used at room temperature for 3 h. Isolated by column chromatography on silica gel (*n*-hexane/EtOAc, 8/2) to give the desired product **2ga** as white solid (31 mg) in 89% yield. Mp: 136–138 °C; HRMS (ESI-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{13}NO_5F_3S$ 400.0467; Found 400.0449; ^1H NMR ($CDCl_3$, 300 MHz) δ = 3.67 (d, *J* = 18 Hz, 1H), 3.77 (s, 3H), 4.27 (d, *J* = 15 Hz, 1H), 7.50 (t, *J* = 6 Hz, 1H), 7.58 (d, *J* = 6 Hz, 1H), 7.71—7.77(m, 1H), 7.88 (d, *J* = 9 Hz, 1H), 8.21 (d, *J* = 9 Hz, 1H), 8.33 (dd, *J* = 3 Hz, 6 Hz, 1H), 8.96 (d, *J* = 3 Hz, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –76.03 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 39.6, 54.1, 63.2, 119.9 (q, *J* = 327.6 Hz), 125.7, 125.9, 126.5, 128.9, 134.2, 136.2, 136.8, 138.2, 140.7, 149.9, 151.1, 151.7, 169.4, 198.1.

Methyl-5-bromo-1-oxo-2-(6-((trifluoromethyl)sulfonyl)pyridin-3-yl)-2,3-dihydro-1H-indene-2-carboxylate ***2ge****:* Following General Procedure D Method 1, cyclic β-ketoester **6e**, (27 mg, 0.1 mmol), NaH (60% suspension in oil, 4.8 mg, 0.12 mmol) and reagent **1g** (66.5 mg, 0.11 mmol) in DMF (1 mL) were used at room temperature for 12 h. Isolated by column chromatography on silica gel (*n*-hexane/EtOAc, 7/3) to give the desired product **2ge** as yellow solid (34 mg) in 70% yield. Mp: 133–135 °C; HRMS (ESI-TOF) m/z: $[M–H]^–$ Calcd for $C_{17}H_{10}NO_5F_3SBr$ 475.9415; Found 475.9412; ^1H NMR ($CDCl_3$, 300 MHz) δ = 3.63 (d, *J* = 18 Hz, 1H), 3.77 (s, 3H), 4.26 (d, *J* = 18 Hz, 1H),7.64 (d, *J* = 9 Hz 1H), 7.72—7.76 (m, 2H), 8.21 (d, *J* = 6 Hz, 1H), 8.29—8.33 (m, 1H), 8.94 (d, *J* = 1.5 Hz, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –75.95 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 39.1, 54.3, 63.3, 119.8 (q, *J* = 326.34 Hz), 125.9, 126.8,

129.9, 132.5, 132.6, 133.0, 138.1, 140.3, 150.2, 151.0, 153.1, 168.9, 196.9.

Ethyl-3-(4-fluorophenyl)-3-oxo-2-(6-((trifluoromethyl)sulfonyl)pyridin-3-yl)propanoate ***2gf****:* Following General Procedure D Method 2, acyclic β-ketoester **6f**, (21 mg, 0.1 mmol), *t*BuOK (13 mg, 0.12 mmol) and reagent **1g** (91 mg, 0.15 mmol) in THF (1 mL) were used at room temperature for 24 h. Isolated by column chromatography on silica gel (*n*-hexane/EtOAc, 8/2) to give the desired product **2gf** as colorless oil (12 mg) in 30% yield. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{13}NO_5F_4NaS$ 442.0348; Found 442.0345; ^1H NMR ($CDCl_3$, 300 MHz) δ = 1.18 (t, *J* = 9 Hz, 3H), 4.12 (q, *J* = 6 Hz, 2H), 6.31 (s, 1H), 7.10–7.16 (m, 2H), 7.47 (dd, *J* = 3 Hz, 6 Hz, 1H), 7.60–7.64 (m, 2H), 8.14 (d, *J* = 9 Hz, 1H), 8.61 (d, *J* = 3 Hz, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –106.98– –106.88 (m, 1F), –76.47 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 14.1, 60.9, 107.4 (d, *J* = 1.25 Hz), 116.9 (d, *J* = 22.5 Hz), 119.9 (q, *J* = 325 Hz), 123.4, 128.1 (d, *J* = 2.5 Hz), 128.5, 128.9 (d, *J* = 8.75 Hz), 140.8, 143.5, 158.3 (d, *J* = 52.5 Hz), 163.4, 163.9, 165.9.

General Procedure E: Triflyl-arylation/pyridylation of Anilines[17b]: To a flame-dried test tube, Cu (0) powder (10 mol %), NMP (2.0 mL/mmol aniline) and aniline **7a–e** (1.0 equiv) were added and the resulting mixture was stirred at rt for 10 min under nitrogen. To the mixture, diaryliodonium salt **1** (1.1 equiv) was added in one portion and the mixture was then stirred at 80 °C. After completion of the reaction, the mixture was cooled to rt, filtered through a pad of silica and the residue was rinsed with Et_2O. The filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give diarylamine **3**.

N-phenyl-4-((trifluoromethyl)sulfonyl)aniline ***3aa****:* Prepared according to the General Procedure E, using aniline **7a** (18.2 µL, 0.2 mmol), Cu (0) powder (1.2 mg, 0.02 mmol) and reagent **1a** (132 mg, 0.22 mmol) in NMP (0.4 mL) at 80 °C for 12 h. Isolated by column chromatography (*n*-hexane/EtOAc, 9/1) to give the desired product **3aa** as yellow solid (45 mg) in 74% yield. Mp: 89–92 °C; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{10}NO_2F_3NaS$ 324.0282; Found 324.0289; ^1H NMR ($CDCl_3$, 300 MHz) δ = 6.39 (s, 1H), 7.01—7.05 (m, 2H), 7.19—7.26 (m, 3H), 7.39—7.44 (m, 2H), 7.80 (d, *J* = 9 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –79.58 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 114.4, 118.3, 120.2 (q, *J* = 326.34 Hz), 122.9, 125.5, 129.9, 133.2, 138.9, 152.0.

N-Phenyl-3-((trifluoromethyl)sulfonyl)aniline ***3ba****:* Prepared according to the General Procedure E, using aniline **7a** (18.2 µL, 0.2 mmol), Cu (0) powder (1.2 mg, 0.02 mmol) and reagent **1b** (132 mg, 0.22 mmol) in NMP (0.4 mL) at 80 °C for 12 h. Isolated by column chromatography (*n*-hexane/EtOAc, 9/1) to give the desired product **3ba** as green oil (46 mg) in 77% yield. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{10}NO_2F_3NaS$ 324.0282; Found 324.0284; ^1H NMR ($CDCl_3$, 300 MHz) δ = 6.02 (bs, 1H), 7.08—7.15 (m, 3H), 7.33—7.42 (m, 3H), 7.42—7.49 (m, 2H), 7.58 (s, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –78.90 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 116.8, 119.9 (q, *J* = 326.34 Hz), 120.3, 121.2, 121.5, 123.3, 123.8, 129.9, 130.9, 132.3, 140.5, 145.7.

N-Phenyl-6-((trifluoromethyl)sulfonyl)pyridin-3-amine ***3ga****:* Prepared according to the General Procedure E, using aniline **7a** (18.2 µL, 0.2 mmol), Cu (0) powder (1.2 mg, 0.02 mmol) and reagent **1g** (132 mg, 0.22 mmol) in NMP (0.4 mL) at 80 °C for 12 h. Isolated by column chromatography (*n*-hexane/EtOAc, 7/3) to give the desired product **3ga** as yellow solid (32 mg) in 53% yield. Mp: 120–122 °C; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{10}N_2O_2F_3S$ 303.0415; Found 303.0412; ^1H NMR ($CDCl_3$, 300 MHz) δ = 6.49 (s, 1H), 7.23—7.29 (m, 3H), 7.37—7.47 (m, 3H), 7.99 (d, *J* = 9 Hz, 1H), 7.41 (d, *J* = 3 Hz, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –77.32 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 118.8, 120.1 (q, *J* = 327.6 Hz), 122.8, 126.2, 128.8, 130.2, 137.9, 138.1, 139.0, 146.3.

4-Bromo-N-(4-((trifluoromethyl)sulfonyl)phenyl)aniline ***3ab****:* Prepared according to the General Procedure E, using aniline **7b** (34.4 mg, 0.2 mmol), Cu (0) powder (1.2 mg, 0.02 mmol) and reagent **1a** (132 mg, 0.22 mmol) in NMP (0.4 mL) at 80 °C for 12 h. Isolated by column chromatography (*n*-hexane/EtOAc, 8/2) to give the desired product **3ab** as white solid (37 mg) in 48% yield. Mp: 131–133 °C; HRMS (ESI-TOF) m/z: $[M–H]^–$ calcd for $C_{13}H_8NO_2F_3SBr$ 377.9411; Found 377.9410; ^1H NMR ($CDCl_3$, 300 MHz) δ = 6.37 (s, 1H), 7.00—7.04 (m, 2H), 7.09—7.13 (m, 2H), 7.49—7.53 (m, 2H), 7.81 (d, *J* = 9 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –79.52 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 114.6, 118.1, 118.9, 120.1 (q, *J* = 326.34 Hz), 124.2, 133.1 (d, *J* = 30.24 Hz), 138.1, 151.5.

N-(4-Bromophenyl)-3-((trifluoromethyl)sulfonyl)aniline ***3bb****:* Prepared according to the General Procedure E, using aniline **7b** (34.4 mg, 0.2 mmol), Cu (0) powder (1.2 mg, 0.02 mmol) and reagent **1b** (132 mg, 0.22 mmol) in NMP (0.4 mL) at 80 °C for 12 h. Isolated by column chromatography (*n*-hexane/EtOAc, 8/2) to give the desired product **3bb** as white solid (55 mg) in 73% yield. Mp: 96–99 °C; HRMS (ESI-TOF) m/z: $[M–H]^–$ calcd for $C_{13}H_8NO_2F_3SBr$ 377.9411; Found 377.9408; ^1H NMR ($CDCl_3$, 300 MHz) δ = 6.01 (bs, 1H), 6.98—7.04 (m, 2H), 7.37—7.42 (m, 1H), 7.43—7.48 (m, 2H), 7.51 (d, *J* = 6 Hz, 2H), 7.57 (s, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –78.86 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 115.9, 117.2, 119.9 (q, *J* = 326.34 Hz), 121.6, 122.1, 123.7, 131.1, 132.5, 132.9, 139.8, 145.1.

4-Chloro-N-(4-((trifluoromethyl)sulfonyl)phenyl)aniline ***3ac****:* Prepared according to the General Procedure E, using aniline **7c** (36 mL, 0.2 mmol), Cu (0) powder (1.2 mg, 0.02 mmol) and reagent **1a** (132 mg, 0.22 mmol) in NMP (0.4 mL) at 80 °C for 12 h. Isolated by column chromatography (*n*-hexane/EtOAc, 7/3) to give the desired product **3ac** as white solid (50 mg) in 67% yield. Mp: 125–128 °C; HRMS (ESI-TOF) m/z: $[M–H]^–$ calcd for $C_{13}H_8NO_2F_3SCl$ 333.9916; Found 333.9917; ^1H NMR ($CDCl_3$, 300 MHz) δ = 6.35 (bs, 1H), 7.00—7.04 (m, 2H), 7.16—7.19 (m, 2H), 7.34—7.38 (m, 2H), 7.81 (d, *J* = 9 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –79.51 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 114.5, 118.9, 120.1 (q, *J* = 326.34 Hz), 124.1, 130.08, 130.6, 133.3, 137.5, 151.6.

4-Methoxy-N-(4-((trifluoromethyl)sulfonyl)phenyl)aniline ***3ad****:* Prepared according to the General Procedure E, using aniline **7d** (24 mg, 0.2 mmol), Cu (0) powder (1.2 mg, 0.02 mmol) and reagent **1a** (132 mg, 0.22 mmol) in NMP (0.4 mL) at 80 °C for 12 h. Isolated by column chromatography (*n*-hexane/EtOAc, 8/2) to give the desired product **3ad** as white solid (30 mg) in 45% yield. Mp: 84–86 °C; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{12}NO_3F_3NaS$ 354.0388; Found 354.0381; ^1H NMR ($CDCl_3$, 300 MHz) δ = 6.22 (s, 1H), 6.84—6.88 (m, 2H), 6.93—6.96 (m, 2H), 7.17 (d, *J* = 9 Hz, 2H), 7.75 (d, *J* = 6 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –79.66 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 55.7, 113.5, 115.2, 117.3, 120.2 (q, *J* = 326.34 Hz), 126.2, 131.4, 133.2, 153.4, 157.9.

2-Nitro-N-(4-((trifluoromethyl)sulfonyl)phenyl)aniline ***3ae****:* Prepared according to the General Procedure E, using aniline **7e** (28 mg, 0.2 mmol), Cu (0) powder (1.2 mg, 0.02 mmol) and reagent **1a** (132 mg, 0.22 mmol) in NMP (0.4 mL) at 80 °C for 12 h. Isolated by column chromatography (*n*-hexane/EtOAc, 7/3) to give the desired

product **3ae** as white solid (49 mg) in 71% yield. Mp: 128–130 °C; HRMS (ESI-TOF) m/z: $[M–H]^-$ Calcd for $C_{13}H_8N_2O_4F_3S$ 345.0157; Found 345.0152; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.09—7.14 (m, 1H), 7.42—7.45 (m, 2H), 7.57—7.65 (m, 2H), 7.99 (d, *J* = 9 Hz, 2H), 8.25 (d, *J* = 6 Hz, 1H), 9.43 (s, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –79.15 (s, 3F); ^{13}C{^{1}H}NMR ($CDCl_3$, 126 MHz) δ = 118.8, 119.6, 121.3, 121.9, 123.7, 127.1, 133.1, 135.7, 137.2, 137.8, 148.0.

General Procedure F: SO_2CF_3-arylation/pyridylation of Alcohols: Method 1[16b]: To a solution of NaOH (2.0 equiv) in H_2O (5.0 mL/mmol alcohol) alcohol **8a–f** (1.0 equiv) was added at rt and the mixture was stirred at rt for 5 min. Diaryliodonium salt **1** (1.2 equiv) was then added to the mixture, which was stirred at 50 °C. After completion of the reaction, the resulting mixture was cooled to rt, H_2O was added and extracted three times with EtOAc. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give SO_2CF_3 phenyl ether **4**.

Method 2[16d]: To a suspension of *t*BuOK (1.2 equiv) in THF (0.5 mL/mmol), phenol **8** (1.0 equiv) was added at 0 °C and the reaction mixture was stirred at this temperature for 10 min. The reagent **1h** (1.2 equiv) was added in one portion and the reaction was stirred in a preheated oil bath at 40 °C until completion. The reaction was quenched by water at 0 °C. The organic phase was separated and the aqueous phase was extracted with dichloromethane three times. The combined organic phases were dried over anhydrous Na_2SO_4, filtered and the solvent was concentrated under reduced pressure. The crude product was isolated by column chromatography over silica gel (*n*-hexane/EtOAc) to give the desired product **4**.

1-Phenoxy-4-((trifluoromethyl)sulfonyl)benzene ***4da****:* Prepared according to the General Procedure F, Method 1, using NaOH (8 mg, 0.2 mmol), phenol **8a** (9.4 mg, 0.1 mmol) and reagent **1d** (71 mg, 0.12 mmol) in H_2O (0.5 mL) at 50 °C for 3 h. Isolated using column chromatography over silica gel (*n*-hexane/EtOAc, 9/1) to give the desired product **4da** as colorless oil (30 mg) in 98% yield. HRMS (ESI-TOF) m/z: $[M–H]^-$ Calcd for $C_{13}H_8O_3F_3S$ 301.0146; Found 301.0151; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.10—7.14 (m, 4H), 7.29 (t, *J* = 9 Hz, 1H), 7.46 (t, *J* = 9 Hz, 2H), 7.96 (d, *J* = 9 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –79.14 (s, 3F); ^{13}C{^{1}H}NMR ($CDCl_3$, 126 MHz) δ = 117.8, 119.9 (q, *J* = 326.34 Hz), 120.9, 123.7, 126.1, 130.6, 133.5, 154.1, 165.4.

1-Phenoxy-3-((trifluoromethyl)sulfonyl)benzene ***4ea****:* Prepared according to the General Procedure F, Method 1, using NaOH (8 mg, 0.2 mmol), phenol **8a** (9.4 mg, 0.1 mmol) and reagent **1e** (71 mg, 0.12 mmol) in H_2O (0.5 mL) at 50 °C for 3 h. Isolated using column chromatography over silica gel (*n*-hexane/EtOAc, 9/1) to give the desired product **4ea** as colorless oil (18 mg) in 60% yield. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{13}H_9O_3F_3S$ 302.0225; Found 302.0221; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.05—7.08 (m, 2H), 7.21—7.26 (m, 1H), 7.40—7.45 (m, 3H), 7.59—7.64 (m, 2H), 7.74 (d, *J* = 9 Hz, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –78.74 (s, 3F); ^{13}C{^{1}H}NMR ($CDCl_3$, 126 MHz) δ = 119.5, 119.9 (q, *J* = 326.34 Hz), 119.9, 124.8, 125.3, 126.0, 130.5, 131.4, 132.8, 155.3, 159.1.

1-Phenoxy-2-((trifluoromethyl)sulfonyl)benzene ***4fa****:* Prepared according to the General Procedure F, Method 1, using NaOH (8 mg, 0.2 mmol), phenol **8a** (9.4 mg, 0.1 mmol) and reagent **1f** (71 mg, 0.12 mmol) in H_2O (0.5 mL) at 50 °C for 3 h. Isolated using column chromatography over silica gel (*n*-hexane/EtOAc, 9/1) to give the desired product **4fa** as colorless oil (27 mg) in 88% yield. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{13}H_9O_3F_3SNa$ 325.0122; Found 325.0116; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 6.94 (d, *J* = 9 Hz, 1H), 7.11 (d, *J* = 9 Hz, 2H), 7.24—7.29 (m, 2H), 7.43 (t, *J* = 9 Hz, 2H), 7.65 (t, *J* = 9 Hz, 1H), 8.09 (d, *J* = 6 Hz, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –77.19 (s, 3F); ^{13}C{^{1}H}NMR ($CDCl_3$, 126 MHz) δ = 118.2, 120.2 (q, *J* = 327.6 Hz), 120.6, 121.5, 122.9, 125.7, 130.4, 130.6, 138.3, 154.6, 158.8.

5-Phenoxy-2-((trifluoromethyl)sulfonyl)pyridine ***4ha****:* Prepared according to the General Procedure F, Method 2, using *t*BuOK (13.5 mg, 0.12 mmol), phenol **8a** (22 mg, 0.1 mmol) and reagent **1h** (72 mg, 0.12 mmol) in THF (0.3 mL) at 40 °C for 4 h. Isolated using column chromatography over silica gel (*n*-hexane/EtOAc, 8/2) to give the desired product **4ha** as white solid (30 mg) in 99% yield. Mp: 151–154 °C; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{12}H_8NO_3F_3SNa$ 326.0075; Found 326.0077; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.13—7.16 (m, 2H), 7.32—7.41 (m, 2H), 7.47—7.53 (m, 2H), 8.15 (d, *J* = 9 Hz, 1H), 8.60 (d, *J* = 3 Hz, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –76.62 (s, 3F); ^{13}C{^{1}H}NMR ($CDCl_3$, 126 MHz) δ = 119.9 (q, *J* = 327.6 Hz), 120.7, 123.7, 126.7, 128.5, 130.9, 142.0, 143.1, 153.5, 159.6.

1,3-Dimethoxy-5-(4-((trifluoromethyl)sulfonyl)phenoxy)benzene ***4db****:* Prepared according to the General Procedure F, Method 1, using NaOH (8 mg, 0.2 mmol), phenol **8b** (15.4 mg, 0.1 mmol) and reagent **1d** (72.5 mg, 0.12 mmol) in H_2O (0.5 mL) at 50 °C for 3 h. Isolated using column chromatography over silica gel (*n*-hexane/EtOAc, 9/1) to give the desired product **4db** as yellow solid (25 mg) in 68% yield. Mp: 59–62 °C; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{13}O_5F_3SNa$ 385.0333; Found 385.0329; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.79 (s, 6H), 6.26 (d, *J* = 1.5 Hz, 2H), 6.38 (t, *J* = 3 Hz, 1H), 7.14—7.19 (m, 2H), 7.97 (d, *J* = 9 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –79.17 (s, 3F); ^{13}C{^{1}H}NMR ($CDCl_3$, 126 MHz) δ = 55.7, 98.0, 99.4, 117.9, 119.9 (q, *J* = 326.34 Hz), 123.8, 133.4, 155.8, 162.2, 165.1.

1-Nitro-3-(4-((trifluoromethyl)sulfonyl)phenoxy)benzene ***4dc****:* Prepared according to the General Procedure F, Method 1, using NaOH (8 mg, 0.2 mmol), phenol **8c** (13.9 mg, 0.1 mmol) and reagent **1d** (72.5 mg, 0.12 mmol) in H_2O (0.5 mL) at 50 °C for 3 h. Isolated using column chromatography over silica gel (*n*-hexane/EtOAc, 9/1) to give the desired product **4dc** as white solid (31 mg) in 90% yield. Mp: 83–85 °C; HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{13}H_8NO_5F_3S$ 347.0075; Found 347.0080; ^{1}H NMR ($CDCl_3$, 300 MHz) δ =7.20—7.23 (m, 2H), 7.49 (d, *J* = 9 Hz, 1H), 7.67 (t, *J* = 9 Hz, 1H), 7.99 (d, *J* = 3 Hz, 1H), 8.05 (d, *J* = 9 Hz, 2H), 8.17 (d, *J* = 9 Hz, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –78.94 (s, 3F); ^{13}C{^{1}H}NMR ($CDCl_3$, 126 MHz) δ = 115.9, 118.6, 120.6, 121.2, 123.8, 125.6, 126.8, 131.4, 133.8, 149.6, 155.0, 163.7.

2-Nitro-1-(4-((trifluoromethyl)sulfonyl)phenoxy)naphthalene ***4dd****:* Prepared according to the General Procedure F, Method 1, using NaOH (8 mg, 0.2 mmol), phenol **8d** (19 mg, 0.1 mmol) and reagent **1d** (72.5 mg, 0.12 mmol) in H_2O (0.5 mL) at 50 °C for 3 h. Isolated using column chromatography over silica gel (*n*-hexane/EtOAc, 9/1) to give the desired product **4dd** as yellow solid (34 mg) in 92% yield. Mp: 125–127 °C; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{10}NO_5F_3SNa$ 420.0129; Found 420.0118; ^{1}H NMR ($CDCl_3$, 300 MHz) δ =7.07—7.11 (m, 2H), 7.62—7.67 (m, 1H), 7.73—7.78 (m, 1H), 7.94—8.04 (m, 5H), 8.12 (d, *J* = 9 Hz, 1H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –78.94 (s, 3F); ^{13}C{^{1}H}NMR ($CDCl_3$, 126 MHz) δ = 116.9, 119.9 (q, *J* = 325.08 Hz), 121.0, 123.8, 124.9, 127.3, 127.5, 128.7, 129.1, 130.4, 133.7, 136.8, 138.9, 143.6, 164.9.

1-(Benzyloxy)-4-((trifluoromethyl)sulfonyl)benzene ***4de****:* Prepared according to the General Procedure F, Method 1, using NaOH (8 mg, 0.2 mmol), phenol **8e** (10.3 µL, 0.1 mmol) and reagent **1d** (72.5 mg, 0.12 mmol) in H_2O (0.5 mL) at 50 °C for 3 h. Isolated using column chromatography over silica gel (*n*-hexane/EtOAc, 9/1) to give the desired product **4de** as white solid (31 mg) in 98% yield. Mp: 77–80 °C; HRMS (EI-TOF) m/z: $[M]^+$ Calcd For $C_{14}H_{11}O_3F_3S$ 316.0381; Found 316.0385; ^1H NMR ($CDCl_3$, 300 MHz) δ =5.18 (s, 2H), 7.16—7.19 (m, 2H), 7.38—7.43 (m, 5H), 7.94—7.97 (m, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –79.27 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 70.9, 116.1, 120.0 (q, *J* = 325.08 Hz), 122.3, 127.7, 128.8, 129.0, 133.4, 135.2, 165.4.

1-Bromo-4-((4-((trifluoromethyl)sulfonyl)phenoxy)methyl)benzene ***4df****:* Prepared according to the General Procedure F, Method 1, using NaOH (8 mg, 0.2 mmol), phenol **8f** (19 mg, 0.1 mmol) and reagent **1d** (72.5 mg, 0.12 mmol) in H_2O (0.5 mL) at 50 °C for 3 h. Isolated using column chromatography over silica gel (*n*-hexane/EtOAc, 9/1) to give the desired product **4df** as white solid (36 mg) in 92% yield. Mp: 101–103 °C; HRMS (ESI-TOF) m/z: $[M–H]^-$ Calcd for $C_{14}H_9O_3F_3SBr$ 392.9408; Found 392.9406; ^1H NMR ($CDCl_3$, 300 MHz) δ =5.13 (s, 2H), 7.15—7.19 (m, 2H), 7.31 (d, *J* = 6 Hz, 2H), 7.56 (d, *J* = 9 Hz, 2H), 7.97 (d, *J* = 9 Hz, 2H); ^{19}F NMR ($CDCl_3$, 282 MHz) δ = –79.29 (s, 3F); $^{13}C\{^1H\}$NMR ($CDCl_3$, 126 MHz) δ = 70.1, 116.1, 119.9 (q, *J* = 326.34 Hz), 122.6, 122.8, 129.3, 132.2, 133.4, 134.2, 165.1.

ASSOCIATED CONTENT

Supporting Information.
ORTEP diagram of **1b** and ^1H NMR, ^{19}F NMR and ^{13}C NMR spectra for all new compounds.

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18. Reagent **5** were prepared from their bromo-analogue **9**. However, **5b** and **5c** could not purified and were used as crude residue for the next step. (See SI)

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