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Synthesis and Reactivity of Aryl(alkynyl)iodonium Salts

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The first practical, yet simple, preparation of aryl(alkynyl)-iodonium trifluoroacetate salts is described. The generic nature of this synthetic method has allowed the production of a range of aryl(alkynyl)iodonium trifluoroacetate salts with independent variation of both the alkynyl and aryliodo groups in yields of 30–85 %. Application of these new reagents to the synthesis of a series of 2-arylfuro[3,2-*c*]pyridines (40–64 %) highlights the potential of this class of materials as precursors to bioactive heterocyclic structures. These experiments have also demonstrated that, in this case, the effect of the aryliodo group on the reaction is negligible.

Introduction

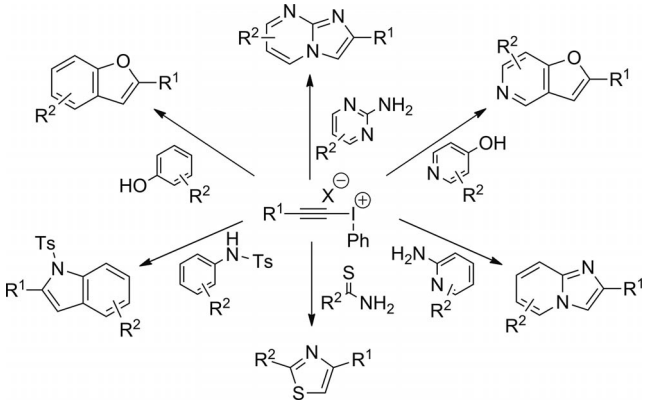
Iodine, like the other halogens, is found typically in its mono-valent form (oxidation state –1). However, due to its large size and polarisability, it is able to form stable multivalent compounds with oxidation states of III, V and VII, termed λ^3-, λ^5- and λ^7-iodanes respectively. Compounds of this type, containing hypervalent iodine, have been known for over a century and continue to receive considerable attention. The ability of these compounds to act as both selective reagents and useful intermediates has formed the basis of this interest.[1]

Of the hypervalent iodanes, the λ^3-class is the most common, with diaryliodonium salts providing the focus of much of these studies. Iodonium salts with alternative functionality, alkyl, alkenyl and alkynyl, have received much less attention despite their rich chemistry. Due to the challenge inherent in their preparation, aryl(alkynyl)iodonium salts, in particular, are an often overlooked member of this group and, as such, the potential of their reactivity profile remains unrealised. The primary mode of reactivity of these materials is based on the Michael addition of soft nucleophiles, generating transient vinyliodonium ylides, which rapidly eliminate aryliodides, resulting in the formation of alkylidene carbenes. These reactive intermediates may then undergo a range of subsequent reactions.[1i–k]

An excellent example of the diverse reactivity associated with alkynyliodonium salts was reported in 1988 by Stang and Kitamura who isolated ten different products through the reaction of alkynyliodonium tosylates with sodium azide.[2] The spectrum of reactivity also demonstrated trapping of both the ylide and the carbene.[2,3] Since then several extensive reviews have highlighted the versatile reactivity of alkynyliodonium salts.[1a,1b,1e,1f,1i,4]

Alkynyliodonium salts have been used in a number of cycloaddition reactions,[1b] including 1,3-dipolar cycloadditions with nitrile oxides,[6] diazoketones[7] and azides,[7] as well as Diels–Alder chemistry.[8]

Further syntheses of cyclopentenes[9] have been reported by 1,5-aliphatic C–H carbene insertions as well as syntheses of dihydropyrroles[5f] and cyclopentenones.[10] Similar alkynyliodonium salt mediated carbene insertions have also provided access to heteroaromatics, such as furopyridines,[5a] imidazopyridines,[5b] thiazoles,[5c–e] indoles,[5f] imidazopyrimidines[5g] and benzofurans[5h–k] (Scheme 1).



Scheme 1. Synthesis of heteroaromatics from alkynyliodonium salts.[5]

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Given the range of organic frameworks that may be accessed by using alkynyliodonium salts, it is surprising that the effects of the "non-participating" aryliodo group, which may be expected to greatly affect reactivity,[11] have yet to be investigated. To date, only one example has been published in which alkynyliodonium salts with a variety of non-participating aryliodo groups have been synthesised. The desired alkynyliodonium salts were isolated in good yields (56–80%), although an excess of the starting acetylene was often required;[12] however, the role of the non-participating group was not established because the subsequent reactivity of these species was not investigated.

Other selected examples have also been reported in which different non-participating groups have been reported; these include *p*-tolyl[13] and fluorous derivatives,[14] and even alkynyl groups, although again these were not comparative studies.[15]

A variety of highly reactive hypervalent iodine reagents have been used in the preparation of alkynyliodonium salts (Figure 1); however, many of these materials are hazardous, are limited to certain functionality, and/or restrict the nature of the counterion.

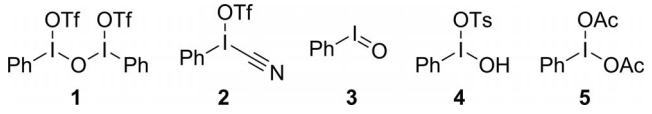


Figure 1. Zefirov's reagent (**1**), Stang's reagent (**2**), iodosylbenzene (**3**), Koser's reagent (**4**) and (diacetoxyiodo)benzene (**5**) (Tf = triflyl).

There is substantial interest in methods for the controlled synthesis of both heteroaromatic and saturated heterocyclic ring systems due to their widespread occurrence in both bioactive natural products and pharmaceuticals. The preparation, from alkynyliodonium salts, of illustrative ring systems utilised in medicinal chemistry has been demonstrated; however, the procedures are not generic and the iodonium salts employed have had limited functionality and counterions. These restrictions are often dictated by the hypervalent iodine starting materials (Figure 1) and their selection is typically as a consequence of desired reactivity rather than structural diversity. As such, the development of a general approach to key heterocyclic scaffolds has been limited.

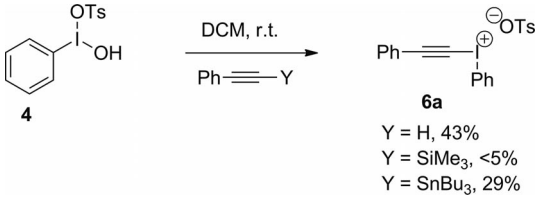
The potential to rapidly access multiple pharmacophores directly from aryl(alkynyl)iodonium salts, and the corresponding benefit to drug discovery and development programmes, suggested that a practical and generic approach to these materials was needed and we now wish to report our initial studies in this area.

Results and Discussion

Synthesis of Aryl(alkynyl)iodonium Salts

To realise our goal of a practical, generic method, which could also be carried out at scale, for the production of aryl(alkynyl)iodonium salts, we decided to restrict the reagents to those that were commercially available/easily prepared and relatively safe. To avoid the hazards associated with some existing methodologies, such as potentially explosive materials (e.g., **3**),[16] air sensitivity (e.g., **1**) or generation of unwanted by-products (e.g., hydrogen cyanide from use of **2**), we identified (diacetoxyiodo)arenes and derivatives of Koser's reagent as suitable precursors. It would also be of benefit to be able to use terminal acetylenes[17] directly, avoiding additional functionalisation prior to iodonium salt formation. This would also eliminate toxicity or instability issues associated with the stannous[18] and boron-based[19] alkyne derivatives, respectively.

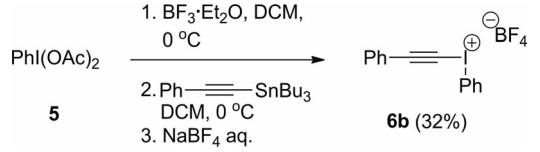
Initially, Koser's reagent was treated with phenylacetylene as well as the trimethylsilyl and tributyltin derivatives thereof (Scheme 2). Despite slightly lower yields, the tin derivative proved the most reliable because reaction of the terminal acetylene itself with Koser's reagent was achieved only once and the analogous silane appeared to be unreactive (although traces of **6a** could be detected by ^{1}H NMR spectroscopy). The product, **6a**, was isolated as a white crystalline solid, which was stable in its solid state; however, decomposition was evident in solution at room temperature.



Scheme 2. Synthesis of alkynyliodonium tosylates from Koser's reagent.

These results suggest that aryl(alkynyl)iodonium tosylates may not display the necessary stability characteristics and simplicity of preparation necessary for their use as versatile precursors to polyfunctional heterocycles. In addition, the use of Koser's reagent pre-determines the counterion (i.e., tosylate) of the resultant aryl(alkynyl)iodonium salt; therefore, alternative syntheses, starting from a (diacetoxyiodo)arene, were used in the preparation of the trifluoroacetate, triflate and tetrafluoroborate aryl(alkynyl)iodonium salts.

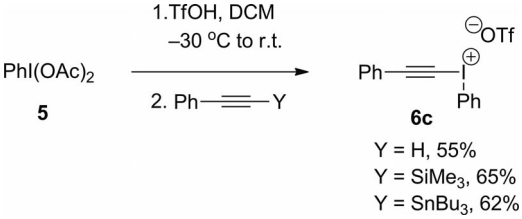
Synthesis of the tetrafluoroborate salt **6b** initially gave low yields (3%) when using the method of Hara et al.[17f] Switching to a slightly modified procedure from Ochiai et al.,[20] however, provided **6b** in a higher yield of 32% (Scheme 3). Analysis of **6b** by ^{1}H and ^{13}C NMR spectroscopy showed that the product was accompanied by an unknown by-product, despite all other spectroscopic analy-



Scheme 3. Synthesis of phenyl(phenylethynyl)iodonium tetrafluoroborate.

sis, including mass spectrometry, elemental composition analysis and IR spectroscopy, suggesting that the desired product was the only material present. The instability of **6b** was in keeping with previous reports.[17d,18,21]

The reaction of $PhI(OAc)_2$·2TfOH with phenylacetylene, under our standard conditions for diaryliodonium salt formation[22] (Scheme 4), showed signs of decomposition on addition of the acid and gave **6c** as a light brown solid; trimethylsilyl and tributylstannyl derivatives produced similar results. Analogous results were also reported by Kitamura et al. who concluded that conditions using triflic acid were too harsh, opting for the use of triflic anhydride instead.[23]



Scheme 4. Attempted route to phenyl(phenylethynyl)iodonium triflate.[23]

A pure sample of **6c** was produced in a yield of 56% by the method outlined by Stang[24] using the Zefirov reagent.[25] The crystal structures of both **6a** and **6c** have also been determined (see the Supporting Information); the dimeric molecule of **6a** is shown in Figure 2. The structure of **6c** is similar.

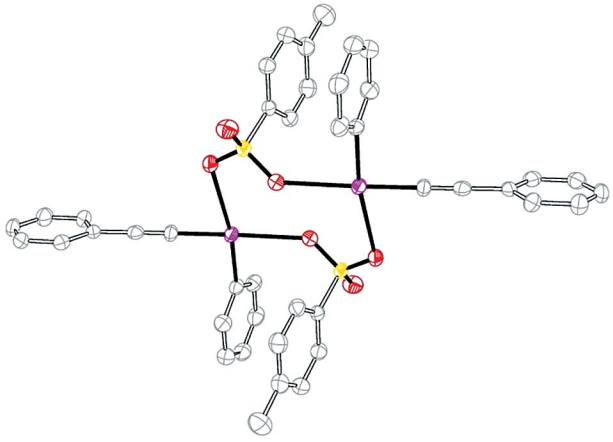
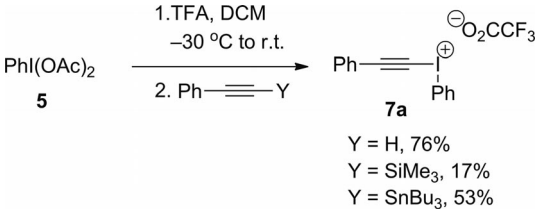


Figure 2. The dimeric structure of **6a**, showing 50% probability displacement ellipsoids. H atoms are omitted.

Analogous synthesis of phenyl(phenylethynyl)iodonium trifluoroacetate (Scheme 5) proved to be much more amenable to successful isolation of the desired product, irrespective of the acetylenic substrate, demonstrating a facile route to this class of materials, which have previously been reported as being unstable and hygroscopic.[1b,26]



Scheme 5. Route to phenyl(phenylethynyl)iodonium trifluoroacetate (TFA = trifluoroacetic acid).

It may be noted here that the highest-yielding preparation of **7a** [from $PhI(OAc)_2$·2TFA] was achieved by using the non-functionalised, terminal acetylene and that isolation of the product, as a white crystalline solid, was also possible directly from the reaction mixture. The highly crystalline nature of **7a** also allowed its crystal structure to be readily determined; this showed that **7a** is dimeric in the solid state (Figure 3), and thus, representative of other compounds in this series (see the Supporting Information).

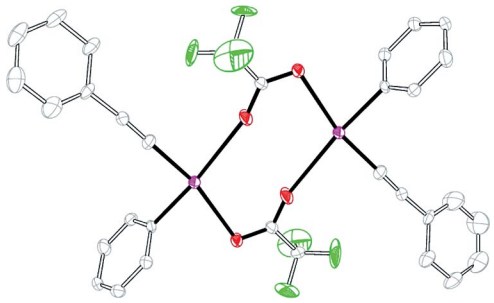


Figure 3. The dimeric structure of **7a**, displayed in the same style as **6a** in Figure 2. Minor disorder components are also omitted.

In summary, phenyl(phenylethynyl)iodonium salts, with a range of counterions, may be prepared, with the direct reaction of $PhI(OAc)_2$·2TFA, phenylacetylene proved to be the most successful.

Before the scope of this approach could be explored further, a degree of optimisation of the process was undertaken, given the known instability of alkynyliodonium salts in solution (cf. **6a**). The reaction was thus performed in an NMR spectrometer with progress monitored at regular intervals by ^{1}H NMR spectroscopy.

Phenylacetylene was injected into a pre-mixed solution of $PhI(OAc)_2$·2TFA at –78 °C to ensure the reaction began slowly enough to be observed. The temperature was then raised to –40 °C then in 10 °C increments to +20 °C; no clear reaction occurred below this temperature. The depletion of phenylacetylene (PhC≡C*H* at ca. δ = 3.1 ppm) was in concurrence with a rise in the signal at about δ = 8.1 ppm, corresponding to the *ortho* protons of the phenyliodo group in **7a**. After 3.5 h (highlighted in a rectangle), phenylacetylene levels remained steady and by-products began to form, most notably a singlet at δ = 5.6 ppm (Figure 4).

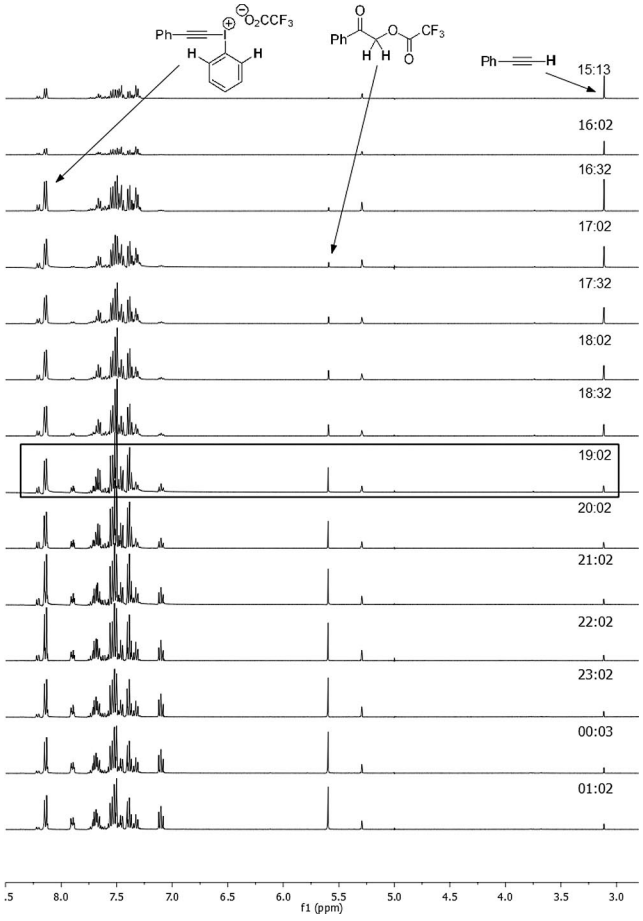


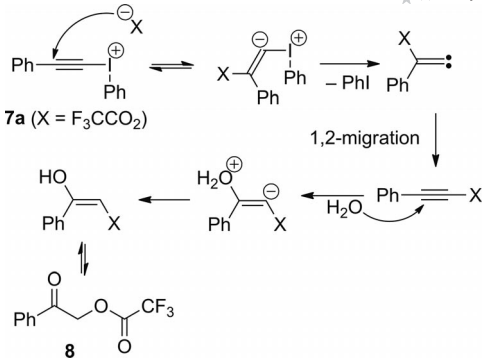
Figure 4. Optimisation of the synthesis of **7a** by ^{1}H NMR spectroscopy.

Two main possibilities were considered for the identity of the by-product: (a) the vinyltrifluoroacetate[2–3] arising from the Michael addition of the counterion and subsequent protonation of the iodonium ylide and (b) decomposition of the ylide to form an alkylidene carbene followed by hydration of the resultant alkyne (Scheme 6).[2] Because α-vinylic protons in iodonium salts are generally observed at δ = 6.8–7.8 ppm,[1b] possibility (b) was deemed to be more likely. Following a literature procedure,[26] an isolated sample of **8** was produced, confirming its identity.

Other α-functionalised ketones, including acetates,[27] chlorides,[28] arylcarboxylates[29] and trifluoroacetates,[30] have been produced in this fashion, often however without isolation of the intermediate alkynyliodonium salt.

Having identified the by-product generated during the synthesis of **7a**, and that reaction time was critical in optimisation of the process, the scope of this approach could then be determined, the results of which are summarised in Table 1.

The alkynyliodonium salts **7a**–**7n** were all isolated as crystalline solids. To meet our criteria for a generic process for the production of aryl(alkynyl)iodonium salts, it was also necessary to demonstrate that the method was sufficiently robust that it could be used reliably to generate appropriate quantities of material. To this end, we also prepared multiple batches (up to 200 mmol) of **7a** without a significant deterioration in yield or quality of product.



Scheme 6. Possible mechanism for the formation of **8**.

Table 1. Synthesis of aryl(arylethynyl)iodonium trifluoroacetates.

Entry	Ar^1	Ar^2	Yield [%][a]
1	C_6H_5	C_6H_5	76 (**7a**)
2	4-$(CH_3)C_6H_4$	C_6H_5	85 (**7b**)
3	4-ClC_6H_4	C_6H_5	76 (**7c**)
4	4-$(CH_3O)C_6H_4$	C_6H_5	71 (**7d**)
5	2-$(CH_3O)C_6H_4$	C_6H_5	56 (**7e**)
6	2-(C_4H_3S)	C_6H_5	30 (**7f**)
7	2,4,6-$(CH_3)_3C_6H_2$	C_6H_5	64 (**7g**)
8	C_6H_5	3-(C_4H_3S)	76 (**7h**)
9	C_6H_5	4-$(C_5H_{11})C_6H_4$	82 (**7i**)
10	C_6H_5	4-BrC_6H_4	66 (**7j**)
11	C_6H_5	2,4,6-$(CH_3)_3C_6H_2$	45 (**7k**)
12	C_6H_5	2,4,5-$(CH_3)_3C_6H_2$	54 (**7l**)
13	C_6H_5	4-$(CH_3O)C_6H_4$	61 (**7m**)[b]
14	C_6H_5	2-$(CH_3O)C_6H_4$	48 (**7n**)

[a] Isolated yields. [b] Only achieved on a single occasion.

The 4-methoxyphenyl derivative **7m** was prepared successfully on only a single occasion, with all subsequent attempts resulting in isolation of the α-trifluoroacetatoketone by-product, **9** (the crystal structure is given in the Supporting Information). The increased rate of counterion addition was attributed to an increased resonance contribution from the methoxy substituent aiding carbene formation.

In contrast, the 2-methoxyphenyl derivative (**7n**) provided a sufficient increase in stability to allow isolation and full characterisation of the aryl(alkynyl)iodonium salt.

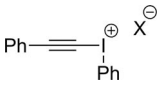
Compounds with alkynyl-terminus substituents (Ar^2) that are more electron withdrawing than 4-bromophenyl, or with reduced steric encumbrance, such as 4′-trifluoromethylphenylethynyl- (**7o**) and 4′-phenylbut-1′-ynyl (**7p**) derivatives, respectively, showed a dramatic decrease in stability and decomposed rapidly to the aforementioned by-products, although these were not isolated, as previously observed for other aliphatic alkynes; the alkynyliodonium salt itself could be crystallised from solution, but could only be

identified by mass spectrometry (see the Supporting Information).

The ^{13}C NMR spectra are characteristic of alkynyliodonium salts; the chemical shifts of the α- (δ = 20–40 ppm) and β-acetylenic carbon atoms (δ = 110–120 ppm) provide diagnostic signals.[1b] Electronic influences of the electron-deficient iodine centre, such as the large upfield shift of the α-acetylenic carbon atoms, are also believed to be accentuated by the "heavy-atom effect" of iodine.[6b]

Table 2 shows the ^{13}C NMR chemical shifts for the acetylenic functional group, compiled from literature data and compounds reported herein. The selected structurally similar alkynyliodonium salts demonstrate an up- and downfield shift of the α- and β-acetylenic carbon atoms, respectively, with reducing coordinative ability of the anion. This effect can be attributed to an increased contribution from the zwitterionic resonance form (Figure 5)[31] of the alkynyliodonium salt with decreasing propensity of the counterion to coordinate to iodine,[5c,13,17c,32a–32c] with the trifluoroacetate salt **7a** at one end of the scale and the hexafluorophosphate derivative **6e** at the other.

Table 2. Acetylenic ^{13}C NMR resonances of alkynyliodonium salts (in $CDCl_3$).



Entry	X	δ (α-^{13}C) [ppm]	δ (β-^{13}C) [ppm]	pK_a of XH
1	F_3CCO_2 (**7a**)	103.70	44.80	–0.25[a]
2	OMs[b] (**6d**)	104.9[5c]	39.3[5c]	–2.6[a]
3	OTs (**6a**)	104.77	38.81	–4.1[32d]
4	OTf (**6c**)	107.49 108.0[32b]	31.82 32.2[32b]	–5.9[32d]
5	PF_6 (**6e**)	107.9[32c]	–	–

[a] Data taken from: http://evans.harvard.edu/pdf/evans_pK_a_Table.pdf. [b] Ms = mesityl.

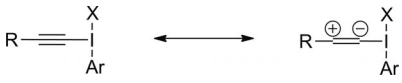


Figure 5. Resonance forms of alkynyliodonium salts.[1b]

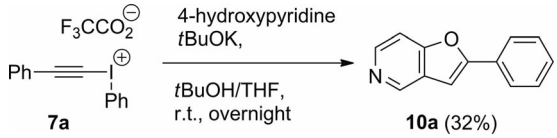
As a means of comparison for the coordinative ability of the anion, the pK_a of the respective conjugate acids are also listed in Table 2.

In addition to the known instability that comes as a result of nucleophillic attack from the counterion on the β-acetylenic position, as reported for tosylate,[17e,33] mesylate[33] and triflate,[34] as well as trifluoroacetate,[26] the data in Table 2 highlight that extremely non-nucleophilic anions also impart instability by increasing reactivity towards external nucleophiles.[32c,35] While the use of hypervalent iodine-containing heterocycles has served to restrain the addition reaction, dramatically increasing alkynyliodonium salt stability, attention must be paid to the possibility that this may restrict coordination of desired nucleophiles to the iodine centre; a step commonly believed to precede many iodonium salt reactions.[5c,5e,17e,31,33,36]

Synthesis of 2-Arylfuro[3,2-*c*]pyridines

With a practical method established for the production of a range of alkynyliodonium salts, the desired application—the synthesis of heteroaromatics—could now be investigated. As an initial study, and to determine the influence of functionality within the series, the synthesis of 2-arylfuro[3,2-*c*]pyridines was carried out.[5a]

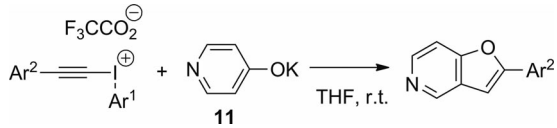
Following a literature procedure,[5a] compound **7a** was added to a solution of potassium *tert*-butoxide (*t*BuOK) and 4-hydroxypyridine in a 1:1 mixture of *t*BuOH/THF (Scheme 7), producing 2-phenylfuro[3,2-*c*]pyridine, **10a**, in an isolated yield of 32%.



Scheme 7. Synthesis of **10a** by using the method reported by Kitamura et al.[5a]

The reaction has been reported to proceed via an alkylidene carbene; these are known to insert intermolecularly into weak bonds, such as O–H.[2] Thus, to improve the process, *t*BuOH was eliminated and *t*BuOK was replaced with potassium hydride. This modification showed an increase in yield from 32 to 52%. Initial application of the modified procedure, using a range of our aryl(alkynyl)iodonium trifluoroacetates, did not, however, demonstrate similar improvements in yield across the series and thus further optimisation was pursued. Screening a range of solvents, stoichiometry and reagent concentrations (for optimisation, see the Supporting Information) highlighted that the best outcome was achieved with 3.5 equiv. of potassium pyridin-4-olate, **11**, in THF using as high a dilution of the aryl(alkynyl)iodonium salt as practicable, given the anhydrous conditions required and the equipment available. Application of the optimised procedure is summarised in Table 3.

Table 3. Formation of 2-arylfuro[3,2-*c*]pyridines, **10**, from alkynyliodonium salts, **7**.

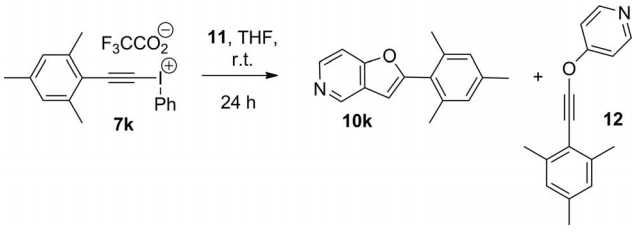


Entry	Ar^1	Ar^2	Yield [%][a]
1	C_6H_5	C_6H_5	62 (**10a**)
2	4-$(CH_3O)C_6H_4$	C_6H_5	64 (**10a**)
3	4-ClC_6H_4	C_6H_5	52 (**10a**)
4	2,4,6-$(CH_3)_3C_6H_2$	C_6H_5	60 (**10a**)
5	C_6H_5	3-C_4H_3S	59 (**10h**)
6	C_6H_5	4-$(C_5H_{11})C_6H_4$	50 (**10i**)
7	C_6H_5	4-BrC_6H_4	40 (**10j**)
8	C_6H_5	2,4,6-$(CH_3)_3C_6H_2$	59 (**10k**)

[a] Isolated yield.

With the yields increased to practical levels, small changes brought about by electronic and steric differences in the aryl(alkynyl)iodonium trifluoroacetates would be more evident. Changing the non-participating phenyl ring to an electron-rich, -deficient or sterically demanding group made little difference to the yield (Table 3, entries 1–4). Substitution of the phenyl group in the arylalkynyl fragment (Table 3, entries 5–8) also had little effect on the yield, affording a range of 2-arylfuro[3,2-*c*]pyridines (**10h**–**k**).

In addition to the desired furopyridines, small amounts of the product of 1,2-migration were observed when using **7k** (Scheme 8). This observation correlates with the mixture of 1,2-migration and 1,5-insertion products reported for similar reactions.[5i,5j]



Scheme 8. Formation of 1,5-insertion and 1,2-migration products from the reaction between **7k** and **11**.

Overall, the furo[3,2-*c*]pyridines, **10**, were formed in good yields of 40–64% (cf. 44–86%).[5a] The structures of **10a** (Figure 6) and **10j** were supported by X-ray crystallography (see the Supporting Information).

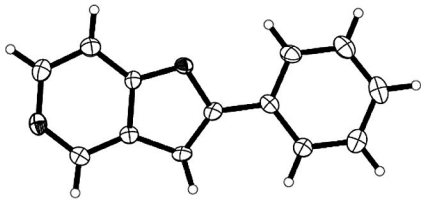


Figure 6. The molecular structure of **10a**.

Conclusions

We have demonstrated the first practical approach to the formation of aryl(alkynyl)iodonium trifluoroacetates from readily available (diacetoxyiodo)arenes and terminal alkynes. Because this approach allows for independent variation of both aromatic substituents, the prospect of increased understanding of the chemistry of these systems has been greatly enhanced through the generation of analogous derivatives that may then be tailored to specific studies.

It should also be noted that the nucleophilicity of the counterion is critical in determining the stability of the aryl(alkynyl)iodonium salt and that trifluoroacetate provides the necessary balance to enable the preparation of a range of materials.

We have demonstrated the application of aryl(alkynyl)iodonium trifluoroacetates in the preparation of a number of 2-arylfuro[3,2-*c*]pyridines using an improved experimental procedure. This study also highlighted that the iodoarene group had a negligible influence on the outcome of this process and that a range of functionality was tolerated in the arylalkynyl fragment.

Experimental Section

General: Reactions requiring anhydrous conditions were performed by using oven- or flame-dried glassware and conducted under a positive pressure of nitrogen. Anhydrous solvents were prepared as follows: CH_2Cl_2 and MeCN were heated at reflux over CaH_2; THF, ethyl ether and hexane were heated at reflux over sodium/benzophenone. IR spectra were recorded on a Varian Scimitar Series 800 FTIR spectrometer with internal calibration. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Advance 300 MHz spectrometer, a Jeol ECS 400 MHz spectrometer or a Jeol Lamda 500 MHz spectrometer with residual tetramethylsilane solvent as the reference for ^1H and ^{13}C spectra. ^{19}F NMR spectra were referenced with $CFCl_3$. Elemental analysis was carried out at London Metropolitan University. Mass spectrometry data was recorded at the EPSRC Mass Spectrometry Service, Swansea, or on a Waters LCT Premier (TOF-MS) instrument operating in "W" mode. Melting points were recorded on a Gallenkamp MF-370 melting point apparatus. Petroleum ether refers to the fractions boiling between 40 and 60 °C. All compound numbering follows that outlined in Figure 7.

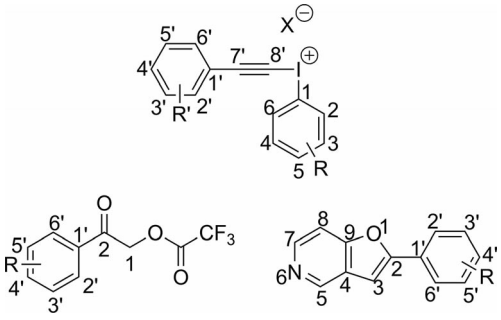


Figure 7. Numbering schemes for compounds **6**, **7**, **8**, **9** and **10**.

Single-crystal X-ray diffraction data were recorded on an Oxford Diffraction (now Agilent Technologies) Gemini A diffractometer (with one exception of a Nonius KappaCCD diffractometer) by using $Mo_{K\alpha}$ and $Cu_{K\alpha}$ radiation (λ = 0.71073 and 1.54180 Å, respectively; see Supporting Information for selected crystallographic data). The structures were solved by direct methods and refined on all unique F^2 values. Minor disorder was resolved in some substituents. CCDC-872886 (for **7a**), -872887 (for **7c**), -872888 (for **7d**), -872889 (for **7e**), -872890 (for **7g**), -872891 (for **7j**), -872892 (for **7l**), -872893 (for **7m**), -872894 (for **7o**), -872895 (for **6a**), -872896 (for **6c**), -872897 (for **5c**), -872898 (for **5b**), -872899 (for **5g**), -872900 (for **5f**), -872901 (for **9**), -872902 (for **10a**), -872903 (for **10j**) contain the supplementary crystallographic data for the 18 structures reported in this paper and its Supporting Information. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Caution! Hypervalent iodine compounds are potentially explosive and should be handled after taking appropriate precautions.[37]

Phenyl(phenylethynyl)iodonium Tosylate (6a).[17c] **Method A:** Phenylacetylene (0.56 mL, 5.01 mmol) was added dropwise to a stirred suspension of hydroxy(tosyloxy)iodosobenzene (1.97 g, 5.03 mmol) in dry CH_2Cl_2 (40 mL) under a positive pressure of nitrogen. The suspension was stirred at room temperature in darkness for 24 h. The solvent was removed from the clear yellow solution in vacuo to give the crude product. Subsequent crystallisation gave the product as a brownish yellow crystalline solid (1.04 g, 2.18 mmol, 43%) with a purity of >95% determined by ^{1}H NMR spectroscopy, although correct elemental analysis could not be obtained.

Method B: Similar to Method A, but by using 1-phenyl-2-(trimethylsilyl)acetylene (0.99 mL, 5.03 mmol). Concentration in vacuo gave the product as a yellow oil with a purity of >95%, as determined by ^{1}H NMR spectroscopy, although correct elemental analysis could not be obtained.

Method C: Similar to Method A, but by using tributyl(phenylethynyl)tin (1.69 mL, 5.00 mmol). Recrystallisation gave the product as a white crystalline solid (0.68 g, 1.43 mmol, 29%) with a purity of >95%, as determined by ^{1}H NMR spectroscopy, although correct elemental analysis could not be obtained.

Method D: Tributyl(phenylethylyl)tin (2.09 g, 5.34 mmol) was added dropwise to a stirred solution of hydroxy(tosyloxy)iodosobenzene (1.94 g, 4.93 mmol) in $CHCl_3$ (50 mL) at reflux. The solution was vigorously heated at reflux for 10 min then dried (Na_2SO_4) and concentrated in vacuo before trituration with diethyl ether (3 × 5 mL) to give the product as a white solid. Subsequent recrystallisation from MeCN/diethyl ether gave the product as a white crystalline solid (0.82 g, 1.69 mmol, 34%), m.p. 101–103 °C (from CH_2Cl_2/diethyl ether–petroleum ether; lit.[17c] m.p. 119–122 °C from diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, J = 8.7 Hz, 2 H, H2/H6), 7.60 (d, J = 7.8 Hz, 2 H), 7.50 (dt, J = 6.9, J = 1.4 Hz, 1 H, H4), 7.39–7.35 (m, 5 H), 7.30–7.24 (m, 2 H), 7.00 (d, J = 8.2 Hz, 2 H), 2.25 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.2, 140.1, 134.0, 132.8, 131.7, 131.6, 130.6, 128.6, 128.3, 125.9, 120.1, 118.7, 104.8 (C7′), 38.8 (C8′), 21.2 (*p*-Me) ppm. IR (neat): $\tilde{\nu}$ = 3058, 2918, 2161, 1446, 1245, 1133, 1116, 1027 cm^{-1}. MS (ESI): *m*/*z* (%): 305 (100) [M – OTs]$^+$, 178 (17). HRMS (ESI): $C_{14}H_{10}I$ calcd. for 304.9822; found 304.9824 [M – OTs]$^+$. $C_{21}H_{17}IO_3S$ (476.33): calcd. C 52.95, H 3.60; found C 53.10, H 3.76.

Phenyl(phenylethynyl)iodonium Tetrafluoroborate (6b). Method A:[17f] Iodosylbenzene (4.19 g, 19.02 mmol) was dispersed in CH_2Cl_2 (63 mL) before the addition of mercuric oxide (red; 0.03 g, 0.12 mmol) followed by aqueous fluoroboric acid (50% w/w; 28 mL, 224 mmol). The solution was stirred vigorously for 5 min before the dropwise addition of phenylacetylene. After a further 30 min of vigorous stirring, the solution was then washed with aqueous sodium tetrafluoroborate (5% w/w; 500 mL) and extracted into $CHCl_3$ (3 × 100 mL). The organic fractions were combined, dried (Na_2SO_4) and concentrated in vacuo to give a brown oil. The oil was then triturated with hexane/diethyl ether and dissolved in a small amount of acetonitrile before the addition of diethyl ether until cloudiness persisted and then it was left in the freezer overnight to crystallise. The product obtained as a white crystalline solid (0.19 g, 0.48 mmol, 3%).

Method B:[20] $BF_3{\cdot}Et_2O$ (0.65 mL, 5.1 mmol) was added dropwise to a solution of tributyl(phenylethynyl)tin (1.72 mL, 5.1 mmol) at 0 °C. The solution was stirred for 10 min before the dropwise addition of (diacetoxyiodo)benzene (1.61 g, 5.0 mmol) in CH_2Cl_2 (20 mL) over 20 min, maintaining the temperature at 0 °C. After a further 25 min, a saturated aqueous solution of $NaBF_4$ (25 mL) was added and the solution was stirred vigorously for 20 min. The solution was then extracted with CH_2Cl_2 (2 × 50 mL), washed with water (50 mL) then brine (50 mL), before being dried ($MgSO_4$) and concentrated in vacuo to afford **6b** as a white solid (0.63 g, 1.6 mmol, 32%) M.p. 78–80 °C (dec., from MeCN/diethyl ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.15 (d, J = 7.2 Hz, 2 H, H2/H6), 7.61–7.58 (m, 3 H), 7.51 (t, J = 7.5 Hz, 1 H, H4), 7.44–7.35 (m, 4 H) ppm. ^{19}F NMR (376 MHz, [D$_7$]DMF): δ = –150.7 ppm. IR (neat): $\tilde{\nu}$ = 2165, 1487, 1464, 1445, 1180, 1069, 1053, 1037, 1024, 1008, 987 cm^{-1}. MS (ESI): *m*/*z* (%): 305 (100) [M – BF_4]$^+$, 178 (16). HRMS (ESI): calcd. for $C_{14}H_{10}I$ 304.9827; found 304.9830 [M – BF_4]$^+$. $C_{14}H_{10}BF_4I$ (391.94): calcd. C 42.90, H 2.58; found C 42.82, H 2.59.

Phenyl(phenylethynyl)iodonium Triflate (6c).[32b] **Method A:** A solution of triflic acid (2.00 mL, 22.6 mmol) in CH_2Cl_2 (15 mL) was added dropwise at –40 °C to a stirred solution of (diacetoxyiodo) benzene (1.67 g, 5.06 mmol) in CH_2Cl_2 (30 mL) over a period of 20 min. After a further 30 min, the solution was warmed to room temperature and stirred for a further hour before being re-cooled and phenylacetylene (0.55 mL, 5.01 mmol) was added over 15 min. The resulting mixture was allowed to reach room temperature over 12 h and the solvent removed was in vacuo to give the crude product. Subsequent recrystallisation gave the product as a pale brown crystalline solid (1.24 g, 2.73 mmol, 55%) with a purity of >95%, as determined by ^{1}H NMR spectroscopy, although correct elemental analysis could not be obtained.

Method B: Using 1-phenyl-2-(trimethylsilyl)acetylene (0.99 mL, 5.03 mmol), (diacetoxyiodo)benzene (1.64 g, 5.09 mmol) and triflic acid (2.00 mL, 22.6 mmol) gave the product as a pale brown crystalline solid (1.48 g, 3.25 mmol, 65%) with a purity of >95%, as determined by ^{1}H NMR spectroscopy, although correct elemental analysis could not be obtained.

Method C: Using tributyl(phenylethynyl)tin (1.69 mL, 5.00 mmol), (diacetoxyiodo)benzene (1.64 g, 5.08 mmol) and triflic acid (2.00 mL, 22.6 mmol) gave the product as a white crystalline solid (1.42 g, 3.12 mmol, 62%) with a purity of >95%, as determined by ^{1}H NMR spectroscopy, although correct elemental analysis could not be obtained.

Method D:[24] Zefirov reagent (4.14 g, 5.88 mmol) was dispersed in dry CH_2Cl_2 (65 mL) and stirred for 10 min at 0 °C under nitrogen before the dropwise addition of tributyl(phenylethynyl)tin (4.14 mL, 11.82 mmol), resulting in a clear yellow solution. The solution was stirred for 40 min at 0 °C and then concentrated in vacuo to give a yellow oil, which was triturated with hexane (3 × 10 mL) then dissolved in CH_2Cl_2 and recrystallised by addition of diethyl ether/hexane to give the product as an off-white crystalline solid (2.83 g, 6.54 mmol, 56%), m.p. 74–76 °C (dec., from CH_2Cl_2/diethyl ether/petroleum ether; lit.[32b] m.p. 83 °C dec. from $CHCl_3$/pentane). ^{1}H NMR (500 MHz, [D$_3$]MeCN): δ = 8.24 (dd, J = 8.5, J = 0.9 Hz, 2 H, H2/H6), 7.78 (t, J = 7.5 Hz, 1 H, H4), 7.64 (dd, J = 9.4, J = 7.8 Hz, 2 H), 7.59–7.54 (m, 3 H), 7.47 (t_{app}, J = 7.4 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, [D$_3$]MeCN): δ = 136.9 (C2/C6), 134.7, 134.5, 134.1, 133.2, 130.5 (C3′/C5′), 122.2 (q, J = 319.5 Hz, CF_3), 120.8, 118.6, 108.2 (C7′), 33.4 (C8′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.3, 133.3, 132.7, 132.6, 132.5, 131.5, 128.8, 120.0 (q, J = 319.7 Hz, CF_3), 119.7, 117.0, 115.2, 107.7 (C7′), 32.0 (C8′) ppm. ^{19}F NMR (471 MHz, [D$_3$]MeCN): δ = –79.2 (CF_3) ppm. IR (neat): $\tilde{\nu}$ = 2173, 1490, 1447, 1291, 1214, 1163, 1021 cm^{-1}. MS (ESI): *m*/*z* (%): 305 (100) [M – OTf]$^+$. HRMS (ESI): calcd. for $C_{14}H_{10}I$ 304.9827; found 304.9828 [M – OTf]$^+$. $C_{15}H_{10}F_3IO_3S$ (454.20): calcd. C 39.67, H 2.22; found C 39.79, H 2.28.

Typical Procedure for the Preparation of Alkynyliodonium Trifluoroacetates

Phenyl(phenylethynyl)iodonium Trifluoroacetate (7a): Trifluoroacetic acid (0.75 mL, 10.10 mmol) was added dropwise at –30 °C to a stirred solution of (diacetoxyiodo)benzene (1.64 g, 5.09 mmol) in CH_2Cl_2 (30 mL) over a period of 10 min. After a further 30 min, the solution was warmed to room temperature and stirred for a further hour before the slow addition of phenylacetylene (0.55 mL, 5.01 mmol). The resulting mixture was stirred at room temperature in darkness for 3.5 h then concentrated in vacuo to around 15 mL. Addition of diethyl ether and petroleum ether initiated crystallisation of the product. After being placed in the freezer (–30 °C) overnight, the product was filtered and dried (in vacuo) as a white crystalline solid (1.60 g, 3.82 mmol, 76%), m.p. 79–81 °C (dec., from CH_2Cl_2/diethyl ether/petroleum ether). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.34 (dd, J = 7.8, J = 0.9 Hz, 2 H, H2/H6), 7.70 (t, J = 7.5 Hz, 1 H, H4), 7.59 (t, J = 7.8 Hz, 2 H), 7.54–7.41 (m, 5 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 159.5 (q, J = 33.6 Hz, C=O), 135.1, 133.1, 132.6, 132.4, 131.5, 129.6, 120.8, 120.4, 117.0 (q, J = 295.6 Hz, CF_3) 102.1 (C7′), 43.3 (C8′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6 (q, J = 36.2 Hz, C=O), 133.6, 132.9, 132.1, 131.9, 130.8, 128.7, 120.6, 120.5, 103.9 (C7′), 45.0 (C8′) ppm. ^{19}F NMR (376 MHz, [D$_6$]DMSO): δ = –73.6 ppm. IR (neat): ṽmax = 3083, 2169, 1665, 1492, 1474, 1442, 1421, 1224, 1185, 1124 cm^{-1}. MS (ESI): m/z (%): 305 (100) [M – TFA]$^+$, 178 (19). HRMS (ESI): calcd. for $C_{14}H_{10}I$ 304.9822; found 304.9821 [M – TFA]$^+$. $C_{16}H_{10}F_3IO_2$ (418.15): calcd. C 45.96, H 2.41; found C 46.01, H 2.30.

Using 1-phenyl-2-(trimethylsilyl)acetylene (1.00 mL, 5.1 mmol), (diacetoxyiodo)benzene (1.62 g, 5.03 mmol) and trifluoroacetic acid (0.75 mL, 10.10 mmol) gave the product as a white crystalline solid (0.38 g, 0.91 mmol, 18%).

Using tributyl(phenylethynyl)tin (1.69 mL, 5.01 mmol), (diacetoxyiodo)benzene (1.62 g, 5.03 mmol) and trifluoroacetic acid (0.68 mL, 9.12 mmol) gave the product as a white crystalline solid (1.12 g, 2.68 mmol, 59%).

4-Methylphenyl(phenylethynyl)iodonium Trifluoroacetate (7b): Using *p*-(diacetoxyiodo)toluene, the product was obtained as a white crystalline solid (1.85 g, 4.27 mmol, 85%), m.p. 68–70 °C (dec., from CH_2Cl_2/diethyl ether/petroleum ether). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.22 (d, J = 8.1 Hz, 2 H, H2/H6), 7.54–7.39 (m, 7 H), 2.38 ppm (s, 3 H, Me) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 158.8 (q, J = 33.6 Hz, C=O), 142.5, 134.6, 132.5, 132.4, 130.9, 129.0, 119.9, 116.5, 116.3 (q, J = 296.2 Hz, CF_3), 101.4 (C7′), 43.8 (C8′), 20.9 (Me) ppm. ^{19}F NMR (376 MHz, [D$_6$]DMSO): δ = –73.7 ppm. IR (neat): ṽ = 2154, 1672, 1654, 1489, 1421, 1190, 1135, 1002 cm^{-1}. MS (ESI): m/z (%): 319 (100) [M – TFA]$^+$, 277 (15). HRMS (ESI): calcd. for $C_{15}H_{12}I$ 318.9984; found 318.9989 [M – TFA]$^+$. $C_{17}H_{12}F_3IO_2$ (432.18): calcd. C 47.25, H 2.80; found C 47.44, H 2.67.

4-Chlorophenyl(phenylethynyl)iodonium Trifluoroacetate (7c): Using *p*-chloro(diacetoxyiodo)benzene, the product was obtained as a white crystalline solid (1.53 g, 3.39 mmol, 76%), m.p. 79–80 °C (dec., from CH_2Cl_2/diethyl ether/petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11 (d, J = 8.7 Hz, 2 H, H2/H6), 7.50–7.35 ppm (m, 7 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5 (q, J = 36.4 Hz, C=O), 138.6, 134.8, 132.8, 132.0, 130.8, 128.6, 120.1, 117.1, 115.4 (q, J = 291.4 Hz; CF_3), 104.0 (C7′), 45.1 (C8′) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 159.6 (q, J = 33.2 Hz, C=O), 137.7, 136.9, 133.0, 132.2, 131.4, 129.5, 120.4, 118.8, 116.7 (q, J = 296.6 Hz, CF_3), 102.0 (C7′), 45.43 (C8′) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –75.0 ppm. IR (neat): ṽ = 3074, 2158, 1661, 1489, 1473, 1423, 1178, 1134, 1089, 1001 cm^{-1}. MS (ESI): m/z (%): 341 (32) [^{37}Cl][M – TFA]$^+$, 339 (100) [^{35}Cl][M – TFA]$^+$. HRMS (ESI): calcd. for $C_{14}H_9{}^{35}ClI$ 338.9438; found 338.9439 [M – TFA]$^+$. $C_{16}H_9ClF_3IO_3$ (468.60): calcd. C 42.46, H 2.00; found C 42.27, H 1.86.

4-Methoxyphenyl(phenylethynyl)iodonium Trifluoroacetate (7d): Using *p*-(diacetoxyiodo)anisole, the product was obtained as a white crystalline solid (5.97 g, 13.3 mmol, 71%), m.p. 74–76 °C (dec., from CH_2Cl_2/diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.20 (d, J = 9.2 Hz, 2 H, H2/H6), 7.48–7.44 (m, 3 H), 7.40 (t, J = 6.9 Hz, 2 H), 7.09 (d, J = 9.2 Hz, 2 H, H2′/H6′), 3.79 ppm (s, 3 H, OMe) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 162.2 (C4′), 160.1 (q, J = 35.2 Hz, C=O), 136.8, 132.8, 131.0, 129.2, 120.6, 118.1, 116.6 (q, J = 295.6 Hz, CF_3), 109.9, 101.3 (C7′), 55.9 (OMe), 45.6 (C8′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.1 (q, J = 35.5 Hz, C=O), 162.0 (C4), 135.3, 132.5, 130.4, 128.4, 120.3, 117.3, 115.4 (q, J = 292.4 Hz, CF_3), 108.9 (C1), 102.8 (C7′), 55.4 (OMe), 44.4 (C8′) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –74.8 ppm. IR (neat): ṽ = 2160, 1666, 1587, 1575, 1489, 1462, 1421, 1298, 1256, 1177, 1129, 1027 cm^{-1}. HRMS (ESI): m/z (%): 335 (100) [M – TFA]$^+$, 324 (23), 304 (20), 281 (21), 277 (48), 236 (11). HRMS (ESI): calcd. for $C_{15}H_{12}OI$ 334.9933. found 334.9930 [M – TFA]$^+$. $C_{17}H_{12}F_3IO_3$ (448.18): calcd. C 45.56, H 2.70; found C 45.59, H 2.63.

2-Methoxyphenyl(phenylethynyl)iodonium Trifluoroacetate (7e): Using *o*-(diacetoxyiodo)anisole, the product was obtained as a white crystalline solid (1.47 g, 3.28 mmol, 56%), m.p. 92–95 °C (dec., from chloroform/diethyl ether/petroleum ether). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.34 (d, J = 8.1 Hz, 1 H, H2), 7.68 (t, J = 7.8 Hz, 1 H), 7.47–7.39 (m, 6 H), 7.11 (t, J = 7.8 Hz, 1 H), 4.02 ppm (s, 3 H, OMe) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 158.8 (q, J = 31.6 Hz, C=O), 155.9 (C2), 136.7, 134.9, 132.5, 130.8, 129.0, 123.4, 120.9, 119.9, 116.5 (q, J = 297.2 Hz, CF_3), 113.3, 110.3 (C1), 99.8 (C7′), 57.3 (OMe), 42.9 (C8′) ppm. ^{19}F NMR (376 MHz, [D$_6$]DMSO): δ = –73.5 ppm. IR (neat): ṽ = 2995, 2951, 2156, 1656, 1593, 1480, 1443, 1422, 1282, 1254, 1187, 1136, 1072, 1048, 1019, 1005 cm^{-1}. MS (ESI): m/z (%): 335 (100) [M – TFA]$^+$, 280 (2). HRMS (ESI): calcd. for $C_{15}H_{12}OI$ 334.9933; found 334.9932 [M – TFA]$^+$. $C_{17}H_{12}F_3IO_3$ (448.18): calcd. C 45.56, H 2.70; found C 45.41, H 2.60.

2-Thienyl(phenylethynyl)iodonium Trifluoroacetate (7f): Using 2-(diacetoxyiodo)thiophene, the product was obtained as a white crystalline solid (0.38 g, 0.90 mmol, 30%), m.p. 89–90 °C (dec., from CH_2Cl_2/diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.09 (d, J = 3.7 Hz, 1 H), 8.01 (d, J = 5.5 Hz, 1 H), 7.54–7.49 (m, 3 H, H2′/H4′/H6′), 7.44 (t, J = 7.3 Hz, 2 H, H3′/H5′), 7.21 (t, J = 4.6 Hz, 1 H, H4) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 158.8 (q, J = 32.6 Hz, C=O), 139.5, 136.6, 132.5, 131.1, 129.2, 129.1, 119.6, 116.4 (q, J = 298.1 Hz, CF_3), 104.0, 101.2 (C7′), 45.4 (C8′) ppm. ^{19}F NMR (376 MHz, [D$_6$]DMSO): δ = –73.6 ppm. IR (neat): ṽ = 3081, 2163, 1660, 1488, 1429, 1389, 1188, 1123, 1085, 1027 cm^{-1}. MS (ESI): m/z (%): 310 (100) [M – TFA]$^+$, 228 (4), 184 (4). HRMS (ESI): calcd. for $C_{12}H_8IS$ 310.9391; found 310.9390 [M – TFA]$^+$. $C_{14}H_8F_3IO_2S$ (424.17): calcd. C 39.64, H 1.90; found C 39.91, H 1.80.

2,4,6-Trimethylphenyl(phenylethynyl)iodonium Trifluoroacetate (7g): Using 1-(diacetoxyiodo)mesitylene, the product was obtained as a white crystalline solid (4.48 g, 9.73 mmol, 64%), m.p. 107–108 °C (from CH_2Cl_2/diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.30 (m, 3 H, H2′/H4′/H6′), 7.28–7.24 (m, 2 H, H3′/H5′), 7.02 (s, 2 H, H3/H5), 2.73 (s, 6 H, *o*-Me), 2.27 (s, 3 H *p*-Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.3 (q, J =

36.4 Hz, C=O), 143.2 (C1), 140.4 (C4′), 132.6, 130.3 (C2/C6), 129.9, 129.4, 128.4, 120.4, 115.4 (q, J = 291.4 Hz, CF_3), 100.7 (C7′), 43.0 (C8′), 26.8 (*o*-Me), 20.8 (*p*-Me) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 159.5 (q, J = 33.2 Hz, C=O), 143.4, 141.0, 133.1, 131.4, 130.1, 129.5, 127.7, 120.3, 116.8 (q, J = 297.6 Hz, CF_3), 99.9 (C7′), 42.6 (C8′), 26.61 (*o*-Me), 21.0 (*p*-Me) ppm. ^{19}F NMR (376 MHz, [D$_6$]DMSO): δ = –73.6 ppm. IR (neat): $\tilde{\nu}$ = 2160, 1662, 1489, 1444, 1417, 1382, 1302, 1180, 1132, 1026 cm^{-1}. MS (ESI): *m*/*z* (%): 347 (100) [M – TFA]$^+$, 220 (49). HRMS (ESI): calcd. for $C_{17}H_{16}I$ 347.0297; found 347.0291 [M – TFA]$^+$. $C_{19}H_{16}F_3IO_2$ (460.23): calcd. C 49.58, H 3.50; found C 49.69, H 3.36.

Phenyl(3′-thienylethynyl)iodonium Trifluoroacetate (7h): Using 3-ethynylthiophene, the product was obtained as a white crystalline solid (2.09 g, 4.92 mmol, 76%), m.p. 94–96 °C (dec., from CH_2Cl_2/diethyl ether/petroleum ether). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.32 (d, J = 7.5 Hz, 2 H, H2/H6), 8.09 (s, 1 H, H2′), 7.73–7.68 (m, 2 H), 7.59 (t, J = 7.5 Hz, 2 H, H3/H5), 7.25 (d, J = 4.5 Hz, 1 H, H5′) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 159.2 (q, J = 32.6 Hz, C=O), 134.7, 134.5, 131.9, 131.8, 129.8, 127.7, 120.4, 118.9, 116.3 (q, J = 296.2 Hz, CF_3), 97.3 (C6′), 40.4 (C7′) ppm. ^{19}F NMR (376 MHz, [D$_6$]DMSO): δ = –73.7 ppm. IR (neat): $\tilde{\nu}$ = 3093, 2161, 1652, 1469, 1444, 1417, 1180, 1133 cm^{-1}. MS (ESI): *m*/*z* (%): 311 (100) [M – TFA]$^+$. HRMS (ESI): calcd. for $C_{12}H_8IS$ 310.9391; found 310.9384 [M – TFA]$^+$. $C_{14}H_8F_3IO_2S$ (424.17): calcd. C 39.64, H 1.90; found C 39.77, H 1.69.

Phenyl(4′-*n*-pentylphenylethynyl)iodonium Trifluoroacetate (7i): Using (4-*n*-pentylphenyl)acetylene, the product was obtained as a white crystalline solid (2.01 g, 4.12 mmol, 82%), m.p. 79–81 °C (dec., from CH_2Cl_2/diethyl ether/petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.18 (dd, J = 7.8, J = 1.2 Hz, 2 H, H2/H6), 7.63 (t, J = 6.8 Hz, 1 H, H4), 7.52 (t, J = 7.2 Hz, 2 H, H3/H5), 7.41 (d, J = 7.8 Hz, 2 H, H2′/H6′), 7.20 (d, J = 8.1 Hz, 2 H, H3′/H5′), 2.64 (t, J = 8.1 Hz, 2 H, H9′), 1.61 (m, 2 H), 1.32 (m, 4 H), 0.90 (t, J = 6.9 Hz, 3 H, H13′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.3 (q, J = 35.5 Hz, C=O), 146.2, 133.3, 132.7, 131.7, 131.5, 128.6, 120.3, 117.4, 115.5 (q, J = 292.4 Hz, CF_3), 104.3 (C7′), 43.8 (C8′), 35.8, 31.2, 30.6, 22.3, 13.8 ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 159.6 (q, J = 33.2 Hz, C=O), 146.3, 134.9, 133.0, 132.3, 132.2, 129.4, 120.9, 117.7, 116.8 (q, J = 296.6 Hz, CF_3), 102.5 (C7′), 44.1 (C8′), 35.6, 31.3, 30.8, 22.4, 14.3 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –74.9 ppm. IR (neat): $\tilde{\nu}$ = 2953, 2926, 2855, 2165, 1666, 1505, 1475, 1443, 1419, 1183, 1130, 1013 cm^{-1}. MS (ESI): *m*/*z* (%): 375 (100) [M – TFA]$^+$. HRMS (ESI): calcd. for $C_{19}H_{20}I$ 375.0610; found 375.0582 [M – TFA]$^+$. $C_{21}H_{20}F_3IO_2$ (488.29): calcd. C 51.66, H 4.13; found C 51.53, H 3.97.

Phenyl(4′-bromophenylethynyl)iodonium Trifluoroacetate (7j): Using (4-bromophenyl)acetylene, the product was obtained as a white crystalline solid (1.65 g, 3.32 mmol, 66%), m.p. 101–103 °C (dec., from CH_2Cl_2/diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 8.32 (dd, J = 8.5, J = 1.2 Hz, 2 H, H2/H6), 7.70 (t, J = 7.3 Hz, 1 H, H4), 7.64 (d, J = 8.7 Hz, 2 H, H2′/H6′), 7.58 (t, J = 7.8 Hz, 2 H, H3/H5), 7.45 (d, J = 8.7 Hz, 2 H, H3′/H5′) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 135.1 (C2′/C6′), 134.9 (C3′/C5′), 132.7 (C2/C6), 132.7 (C4), 132.4 (C3/C5), 125.3 (C4′), 120.7 (C1′), 119.6 (C1), 101.0 (C7′), 46.0 (C8′) ppm. ^{19}F NMR (376 MHz, [D$_6$]DMSO): δ = –73.4 ppm. IR (neat): $\tilde{\nu}$ = 2165, 1662, 1473, 1423, 1186, 1136, 1069, 1011 cm^{-1}. MS (ESI): *m*/*z* (%): 385 (94) [^{81}Br][M – TFA]$^+$, 383 (100) [^{79}Br][M – TFA]$^+$. HRMS (ESI): calcd. for $C_{14}H_9{}^{79}BrI$ 382.8932; found 382.8929 [M – TFA]$^+$. $C_{16}H_9BrF_3IO_2$ (497.05): calcd. C 38.66, H 1.83; found C 38.57, H 1.79.

Phenyl(2′,4′,6′-trimethylphenylethynyl)iodonium Trifluoroacetate (7k): Using (2,4,6-trimethylphenyl)acetylene, the product was obtained as a white crystalline solid (0.95 g, 2.06 mmol, 45%), m.p. 81–84 °C (dec., from CH_2Cl_2/diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (dd, J = 8.7, J = 1.8 Hz, 2 H, H2/H6), 7.57 (t, J = 7.7 Hz, 1 H, H4), 7.46 (t, J = 8.7 Hz, 2 H, H3/H5), 6.86 (s, 2 H, H3′/H5′), 2.31 (s, 6 H, *o*-Me), 2.27 (s, 3 H, *p*-Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.3 (q, J = 35.5 Hz, C=O), 142.1, 140.7, 133.2, 131.9, 131.7, 127.9, 120.9, 117.2, 115.5 (q, J = 290.4 Hz, CF_3), 103.3 (C7′), 50.1 (C8′), 21.3 (*p*-Me), 20.7 (*o*-Me) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 159.2 (q, J = 32.2 Hz, C=O), 141.9, 140.7, 135.1, 132.5, 132.3, 128.4, 121.2, 117.5, 101.0 (C7′), 49.8 (C8′), 21.5 (*p*-Me), 20.7 (*o*-Me) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –75.3 ppm. IR (neat): $\tilde{\nu}$ = 2969, 2917, 2137, 1671, 1569, 1475, 1445, 1424, 1189, 1125 cm^{-1}. MS (ESI): *m*/*z* (%): 347 (100) [M – TFA]$^+$. HRMS (ESI): calcd. for $C_{17}H_{16}I$ 347.0297; found 347.0291 [M – TFA]$^+$. $C_{19}H_{16}F_4IO_2$ (479.23): calcd. C 49.58, H 3.50; found C 49.71, H 3.38.

Phenyl(2′,4′,5′-trimethylphenylethynyl)iodonium Trifluoroacetate (7l): Using (2,4,5-trimethylphenyl)acetylene, the product was obtained as a white crystalline solid (1.24 g, 2.70 mmol, 54%), m.p. 110–111 °C (dec., from CH_2Cl_2/diethyl ether/petroleum ether). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.33 (d, J = 6.0 Hz, 2 H, H2/H6), 7.70 (t, J = 7.5 Hz, 1 H, H4), 7.59 (t, J = 7.5 Hz, 2 H, H3/H5), 7.21 (s, 1 H, H6′) 7.07 (s, 1 H, H3′), 2.22 (s, 2 H, *p*-Me), 2.19 (s, 3 H, *o*-Me), 2.13 (s, 3 H, *m*-Me) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 159.1 (q, J = 32.6 Hz, C=O), 139.8, 138.8, 134.5, 134.2, 133.1, 131.9, 131.7, 131.0, 130.7, 120.7, 117.0, 116.4 (q, J = 297.1 Hz, CF_3), 101.5 (C7′), 46.1 (C8′), 19.4 (*p*-Me), 19.3 (*o*-Me), 18.5 (*m*-Me) ppm. ^{19}F NMR (376 MHz, [D$_6$]DMSO): δ = –73.63 ppm. IR (neat): $\tilde{\nu}$ = 2916, 2160, 1666, 1567, 1495, 1474, 1443, 1421, 1184, 1126, 1070, 1008 cm^{-1}. MS (ESI): *m*/*z* (%): 347 (100) [M – TFA]$^+$. HRMS (ESI): calcd. for $C_{17}H_{16}I$ 347.0297; found 347.0294 [M – TFA]$^+$. $C_{19}H_{16}F_3IO_2$ (460.23): calcd. C 49.58, H 3.50; found C 49.75, H 3.40.

Phenyl(4′-methoxyphenylethynyl)iodonium Trifluoroacetate (7m): Using (4-methoxyphenyl)acetylene, the product was obtained as a pale yellow/white crystalline solid (0.70 g, 1.56 mmol, 61%), m.p. 89–91 °C (dec., from CH_2Cl_2/diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, J = 8.2 Hz, 2 H, H2/H6), 7.57 (t, J = 7.3 Hz, 1 H, H4), 7.46 (t, J = 8.0 Hz, 2 H, H3/H5), 7.41 (d, J = 8.7 Hz, 2 H, H2′/H6′), 6.85 (d, J = 8.7 Hz, 2 H, H3′/H5′), 3.80 (s, 3 H, OMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 134.7, 133.2, 131.9, 131.7 (C4), 120.5, 114.3, 112.0, 105.1, 55.4 (OMe), 42.9 (C8′) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –75.3 ppm. IR (neat): $\tilde{\nu}$ = 2141, 1648, 1600, 1507, 1442, 1420, 1296, 1250, 1138, 1030 cm^{-1}. MS (ESI): *m*/*z* (%): 335 (100) [M – TFA]$^+$. HRMS (ESI): calcd. for $C_{15}H_{12}IO$ 334.9933; found 334.9929 [M – TFA]$^+$.

Subsequent repetition of this reaction yielded only the α-trifluoroacetato ketone, **9**.

Phenyl(2′-methoxyphenylethynyl)iodonium Trifluoroacetate (7n): Using (4-methoxyphenyl)acetylene, the product was obtained as a pale yellow crystalline solid (1.07 g, 2.40 mmol, 48%), m.p. 62–65 °C (dec., from CH_2Cl_2/diethyl ether/petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, J = 8.2 Hz, 2 H, H2/H6), 7.57 (t, J = 7.3 Hz, 1 H, H4), 7.47 (t, J = 8.2 Hz, 2 H, H3/H5), 7.40–7.36 (m, 2 H, H4′/H6′), 6.92 (t, J = 7.8 Hz, 1 H, H5′), 6.89 (d, J = 8.7 Hz, 1 H, H3′), 3.85 (s, 3 H, OMe) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.4 (q, J = 36.4 Hz, C=O), 161.7 (C2′), 134.5 (C6′), 133.2 (C2/C6), 132.4 (C4′), 131.9 (C3/C5), 131.7 (C4), 120.7 (C1′),

120.5 (C5′), 115.4 (q, J = 292.3 Hz, CF_3), 110.8 (C3′), 109.4 (C7′), 101.5 (C1), 55.7 (OMe), 48.2 (C8′) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 161.7 (C2′), 159.3 (q, J = 32.2 Hz, C=O), 134.9, 134.7, 133.3, 132.5, 132.3, 121.2, 120.8, 117.0 (q, J = 298.6 Hz, C=O), 112.2, 109.2, 99.7 (C7′), 56.3 (OMe), 47.0 (C8′) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –75.3 ppm. IR (neat): $\tilde{\nu}$ = 3072, 2950, 2841, 2157, 1652, 1595, 1576, 1493, 1473, 1464, 1423, 1298, 1285, 1259, 1187, 1179, 1133, 1117, 1023 cm^{-1}. MS (ESI): m/z (%) = 335 (100) [M – TFA]$^+$, 208 (17). HRMS (ESI): calcd. for $C_{15}H_{12}IO$ 334.9933.; found 334.9933 [M – TFA]$^+$. $C_{17}H_{12}F_3IO_3$ (448.18): calcd. C 45.56, H 2.70; found C 45.67, H 2.62.

2-Phenyl-2-oxoethyl Trifluoroacetate (8): Compound **7a** (2.07 g, 4.96 mmol) was dissolved in $CHCl_3$ with a few drops of water (*ca* 4 drops) and heated to reflux for 2 h. The solution was then cooled, dried ($MgSO_4$) and concentrated in vacuo. The crude product was then purified by flash chromatography (silica), eluted with dry hexane/dry toluene (1:1), to give the product as a white crystalline solid (0.40 g, 1.71 mmol, 34%), m.p. 54–55 °C (CH_2Cl_2/diethyl ether/petroleum ether). R_f 0.27 (1:1, hexane/toluene). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.92 (dd, J = 8.4, J = 1.2 Hz, 2 H, H2′/H6′), 7.68 (tt, J = 7.5, J = 1.8 Hz, 1 H, H4′), 7.54 (t, J = 7.8 Hz, 2 H, H3′/H5′), 5.60 (s, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.3 (C=O), 157.5 [q, J = 43.0 Hz, (C=O)CF_3], 134.9 (C4′), 133.7 (C1′), 129.5 (C2′/C6′), 128.2 (C3′/C5′), 114.9 (q, J = 285.3 Hz, CF_3), 68.6 (CH_2) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –74.7 ppm. IR (neat): $\tilde{\nu}$ = 1785, 1700, 1600, 1451, 1433, 1384, 1356, 1304, 1287, 1228, 1206, 1154, 1078, 1037, 1027, 1001 cm^{-1}. MS (ACPI): m/z (%): 231 (32) [M – H]$^-$, 227 (100), 203 (14), 183 (5), 134 (20). HRMS (ACPI): calcd. for $C_{10}H_{16}O_3F_3$ 231.0275; found 231.0273 [M – H]$^-$. $C_{10}H_7F_3O_3$ (232.16): calcd. C 51.74, H 3.04; found C 51.66, H 2.98.

2-(4′-Methoxyphenyl)-2-oxoethyl Trifluoroacetate (9): White crystalline solid (0.61 g, 2.32 mmol, 46%), m.p. 68–70 °C (from CH_2Cl_2/diethyl ether/petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (d, J = 9.0 Hz, 2 H, H3′/H5′), 7.00 (d, J = 9.0 Hz, 2 H, H2′/H6′), 5.55 (s, 2 H, CH_2), 3.91 (3 H, s, OMe) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 187.6 (C=O), 165.0 (C4′), 157.3 [q, J = 43.8 Hz, (C=O)CF_3], 130.4 (C2′/C6′), 127.1 (C1′), 115.0 (q, J = 285.3 Hz, CF_3), 114.8 (C3′/C5′), 68.2 (CH_2), 55.8 ppm (OMe). ^{19}F NMR (376 MHz, $CDCl_3$): δ = –74.5 ppm. IR (neat): $\tilde{\nu}$ = 1788, 1686, 1600, 1515, 1468, 1434, 1381, 1354, 1278, 1252, 1214, 1185, 1169, 1141, 1023, 1004 cm^{-1}. MS (EI): m/z (%): 262 (98) [M]$^+$, 135 (100), 121 (8), 107 (12), 92 (29), 77 (23), 69 (14), 64 (15). HRMS (EI): calcd. for $C_{11}H_9F_3O_4$ 262.0447; found 262.0446 [M]$^+$. $C_{11}H_9F_3O_4$ (262.18): calcd. C 50.39, H 3.46; found C 50.51, H 3.44.

Typical Procedure for the Preparation of 2-Arylfuro[3,2-*c*]pyridines

2-Phenylfuro[3,2-*c*]pyridine (10a):[5a] KH (ca. 1.1 mL, 30% dispersion in mineral oil) was added to a dry Schlenk flask and washed with dry, freshly distilled hexane (4 × 50 mL) then dried in vacuo to give dry KH as a greyish-white powder (0.36 g, 8.95 mmol). KH was then re-dispersed in dry, freshly distilled THF (200 mL) before the addition of dry 4-hydroxypyridine (0.88 g, 9.27 mmol) and then stirred for 48 h. Dry **7a** (1.05 g, 2.51 mmol) was then added to the suspension and stirred in darkness at room temp. under nitrogen for 48 h then quenched with water (20 mL). The suspension was added to a mixture of water (500 mL) and brine (100 mL) and the product was extracted with CH_2Cl_2 (3 × 150 mL). The organic layers were dried ($MgSO_4$), concentrated in vacuo onto silica gel and purified by flash chromatography (silica gel) to give the product as a white crystalline solid (0.30 g, 1.56 mmol, 62%), m.p. 115–117 °C (from CH_2Cl_2; lit.[38] m.p. 115–116 °C from ethanol) R_f 0.21 (diethyl ether). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.87 (br. s, 1 H, H5), 8.43 (br. d, J = 2.7 Hz, 1 H, H7), 7.80 (dd, J = 8.1, J = 1.2 Hz, 2 H, H3′/H5′), 7.43–7.31 (m, 4 H, H2′/H4′/H6′/H8), 7.00 (d, J = 0.9 Hz, 1 H, H3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.1 (C2), 156.8 (C9), 144.5 (C7), 143.9 (C5), 129.4 (C1′), 129.3 (C4′), 128.9 (C3′/C5′), 126.6 (C4), 125.2 (C2′/C6′), 106.9 (C8), 99.1 (C3) ppm. IR (neat): $\tilde{\nu}$ = 2981, 1575, 1562, 1491, 1462, 1430, 1329, 1318, 1265, 1218, 1164, 1076, 1037, 1016 cm^{-1}. HRMS (EI): m/z (%): 195 (100) [M]$^+$. HRMS (EI): calcd. for $C_{13}H_9NO$ 195.0679; found 195.0680 [M]$^+$. $C_{13}H_9NO$ (195.22): calcd. C 79.98, H 4.65, N 7.17; found C 80.10, H 4.51, N 7.04.

Using KH [0.36 g (dry), 9.00 mmol], 4-hydroxypyridine (0.90 g, 9.45 mmol) and **7d** (1.14 g, 2.55 mmol), the product was isolated as a white crystalline solid (0.32 g, 1.64 mmol, 64%).

Using KH [0.35 g (dry), 8.60 mmol], 4-hydroxypyridine (0.86 g, 9.02 mmol) and **7c** (1.14 g, 2.51 mmol), the product was isolated as a white crystalline solid (0.26 g, 1.32 mmol, 52%).

Using KH [0.34 g (dry), 8.55 mmol], 4-hydroxypyridine (0.86 g, 8.99 mmol) and **7g** (1.07 g, 2.31 mmol), the product was isolated as a white crystalline solid (0.27 g, 1.39 mmol, 60%).

2-(3′-Thienyl)furo[3,2-*c*]pyridine (10h): Using KH [0.35 g (dry), 8.60 mmol], 4-hydroxypyridine (0.85 g, 8.93 mmol) and **7h** (1.06 g, 2.51 mmol), the product was isolated as a white crystalline solid (0.30 g, 1.49 mmol, 59%), m.p. 150–152 °C (from CH_2Cl_2–diethyl ether). R_f 0.72 (diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.86 (br. s, 1 H, H5), 8.45 (br. d, J = 4.6 Hz, 1 H, H7), 7.73 (m, 1 H, H4′), 7.42–7.38 (m, 3 H, H2′/H5′/H8), 6.82 (s, 1 H, H3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9 (C9), 153.5 (C2), 144.1 (C5), 143.5 (C7), 131.0 (C3′), 126.9 (C5′), 126.5 (C4), 125.0 (C2′), 122.7 (C4′), 106.8 (C8), 98.6 (C3) ppm. IR (neat): $\tilde{\nu}$ = 3126, 3112, 1606, 1571, 1503, 1456, 1438, 1400, 1362, 1318, 1275, 1261, 1217, 1163, 1075, 1037, 1017 cm^{-1}. MS (ESI): m/z (%): 202 (100) [M + H]$^+$. HRMS (ESI): calcd. for $C_{11}H_8NOS$ 202.0327; found 202.0320 [M + H]$^+$. $C_{11}H_7NOS$ (201.24): calcd. C 65.65, H 3.51, N 6.96; found C 65.80, H 3.38, N 6.84.

2-(4′-Pentylphenyl)furo[3,2-*c*]pyridine (10i): Using KH [0.39 g (dry), 9.65 mmol], 4-hydroxypyridine (0.96 g, 10.08 mmol) and **7i** (1.24 g, 2.53 mmol), the product was isolated as a white crystalline solid (0.34 g, 1.27 mmol, 50%), m.p. 65–67 °C (from CH_2Cl_2/diethyl ether). R_f 0.63 (diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.88 (br. s, 1 H, H5), 8.45 (br. s, 1 H, H7), 7.74 (d, J = 8.2 Hz, 2 H, H2′/H6′), 7.42 (d, J = 6.0 Hz, 1 H, H8), 7.25 (d, J = 8.2 Hz, 2 H, H3′/H5′), 7.0 (s, 1 H, H3), 2.64 (t, J = 7.6 Hz, 2 H, H7′), 1.62 (quintet, J = 7.8 Hz, 2 H), 1.33–1.30 (m, 4 H), 0.88 (t, J = 6.9 Hz, 3 H, H11′) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1 (C2), 157.4 (C9), 144.7 (C1′), 143.9 (C7), 143.4 (C5), 129.0 (C3′/C5′), 126.8 (C4′), 125.5 (C4), 125.2 (C2′/C6′), 106.9 (C8), 98.2 (C3), 35.8 (C7′), 31.4, 30.9, 22.5, 14.0 (C11′) ppm. IR (neat): $\tilde{\nu}$ = 2952, 2926, 2870, 1607, 1577, 1503, 1456, 1435, 1377, 1327, 1267, 1221, 1165, 1122, 1029, 1012 cm^{-1}. MS (ESI): m/z (%): 266 (100) [M + H]$^+$. HRMS (ESI): calcd. for $C_{18}H_{20}NO$ 266.1545; found 266.1550 [M + H]$^+$. $C_{18}H_{19}NO$ (265.35): calcd. C 81.47, H 7.22, N 5.28; found C 81.57, H 7.14, N 5.18.

2-(4′-Bromophenyl)furo[3,2-*c*]pyridine (10j): Using KH [0.36 g (dry), 9.00 mmol], 4-hydroxypyridine (0.88 g, 9.25 mmol) and **7j** (1.26 g, 2.54 mmol), the product was isolated as a white crystalline solid (0.28 g, 1.00 mmol, 40%), m.p. 162–165 °C (from CH_2Cl_2/diethyl ether; lit.[38] m.p. 167–168 °C from ethanol). R_f 0.42 (diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.92 (br. s, 1 H, H5), 8.49 (br. d, J = 5.5 Hz, 1 H, H7), 7.71 (d, J = 7.8 Hz, 2 H, H2′/H6′), 7.59 (d, J = 8.2 Hz, 2 H, H3′/H5′), 7.47 (dd, J = 5.5, J = 0.9 Hz, 1 H, H8), 7.06 (s, 1 H, H3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ =

159.4 (C2), 156.2 (C9), 144.1 (C5), 143.5 (C7), 132.2 (C2′/C6′), 128.2 (C4′), 126.7 (C3′/C5′), 126.5 (C4), 123.7 (C1′), 107.1 (C8), 99.7 (C3) ppm. IR (neat): $\tilde{\nu}$ = 2922, 1601, 1577, 1558, 1486, 1454, 1435, 1401, 1323, 1266, 1219, 1167, 1105, 1073, 1027, 1008 cm^{-1}. MS (ESI): *m*/*z* (%): 276 (99) [^{81}Br][M + H]$^+$, 274 (100) [^{79}Br][M + H]$^+$. HRMS (ESI): calcd. for $C_{13}H_9{}^{79}BrNO$ 273.9866; found 273.9862 [M + H]$^+$. $C_{13}H_8BrNO$ (274.12): calcd. C 56.96, H 2.94, N 5.11; found C 57.07, H 3.03, N 4.93.

2-(2′,4′,6′-Trimethylphenyl)furo[3,2-*c*]pyridine (10k): Using KH [0.35 g (dry), 8.60 mmol], 4-hydroxypyridine (0.84 g, 8.84 mmol) and **7k** (0.85 g, 1.85 mmol), the product was isolated as a white crystalline solid (0.26 g, 1.10 mmol, 59%), m.p. 68–71 °C (from CH_2Cl_2/diethyl ether). R_f 0.52 (diethyl ether). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.95 (br. s, 1 H, H5), 8.49 (br. s, 1 H, H7), 7.43 (br. s, 1 H, H8), 6.96 (s, 2 H, H3′/H5′), 6.70 (s, 1 H, H3), 2.33 (3 H, *p*-Me), 2.20 (6 H, *o*-Me) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1 (C2), 156.3 (C9), 143.8 (C5), 143.4 (C7), 139.6 (C1′), 138.3 (C2′/C6′), 128.5 (C3′/C5′), 126.6 (C4′), 126.2 (C4), 107.0 (C8), 104.2 (C3), 21.1 (*p*-Me), 20.4 (*o*-Me) ppm. IR (neat): $\tilde{\nu}$ = 2920, 2855, 1609, 1461, 1438, 1377, 1280, 1266, 1218, 1160, 1043, 1020, 1001 cm^{-1}. MS (ESI): *m*/*z* (%): 238 (100) [M + H]$^+$. HRMS (ESI): calcd. for $C_{16}H_{16}NO$ 238.1232; found 238.1230 [M + H]$^+$. $C_{16}H_{15}NO$ (237.30): calcd. C 80.98, H 6.37, N 5.90; found C 81.05, H 6.41, N 5.97.

Supporting Information (see footnote on the first page of this article): It contains procedures detailing precursor compound synthesis and spectra for all compounds synthesised herein. Crystal structures are also available for compounds **5b**, **5c**, **5f**, **5g**, **6a**, **6c**, **7a**, **7c**, **7d**, **7e**, **7g**, **7j**, **7l**, **7m**, **7o**, **9**, **10a** and **10j**.

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