

Improving alkynyl(aryl)iodonium salts: 2-anisyl as a superior aryl group†

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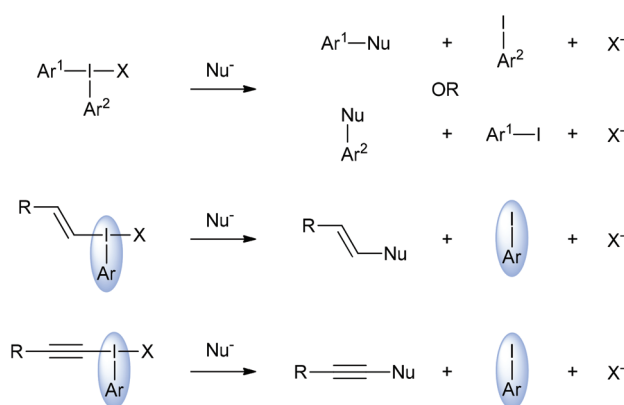
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The majority of alkynyl(aryl)iodonium salts reported in the literature are derived from iodobenzene. This article describes the effects of varying this iodoarene building block on the synthesis, reactivity and stability of these salts. Two procedures to synthesize a variety of known and novel alkynyl(aryl)iodonium tosylates directly from the iodoarene are reported. In the reactions of these salts, those derived from 2-iodoanisole gave superior results than the others tested in every reaction. Isothermal microcalorimetry indicated that these novel salts were significantly more stable and less prone to decomposition than all of the other derivatives.

Introduction

Interest in hypervalent iodine chemistry has surged in recent years with new iodine(III) and iodine(V) compounds being reported regularly alongside novel reactions using these species.¹ There are two main types of hypervalent organoiodine compounds: those with one carbon ligand and those with two. Compounds with one carbon ligand include iodobenzene diacetate (also called diacetoxyiodobenzene or phenyliodide diacetate) and Dess–Martin periodinane. Generally, these types of hypervalent iodine compounds are powerful oxidants. Hypervalent iodine compounds with two carbon ligands are commonly called iodonium salts and these include diaryliodonium salts, alkenyl(aryl)iodonium salts and alkynyl(aryl)iodonium salts. These compounds are not strong oxidants.

Iodonium salts are increasingly popular reagents in organic synthesis because of the range of useful reactivities that they exhibit.² The most investigated iodonium salts are the diaryliodonium salts, which can, in principal, donate either of their aryl groups in reactions with nucleophiles (Scheme 1).³ Whereas, in general, alkynyl(aryl)- and alkenyl(aryl)iodonium salts only donate the alkyne or alkenyl groups respectively. This means that the aryl group is, essentially, a spectator group in these two types of iodonium salts. However, the effect of changing this spectator group on the reactivity of these salts has not been studied. Indeed, the majority of research with these two types of salts has been with those derived from iodobenzene.⁴ Cyclic species such as triisopropylsilyl ethynyl-1,2-



Scheme 1 General reactivities of iodonium salts with nucleophiles highlighting the “spectator” role of the aryl iodide in alkenyl(aryl)- and alkynyl(aryl)iodonium salts.

benziodoxol-3(1*H*)-one (TIPS-EBX) are known, but these have only been reported in alkynylation reactions.⁵

Results and discussion

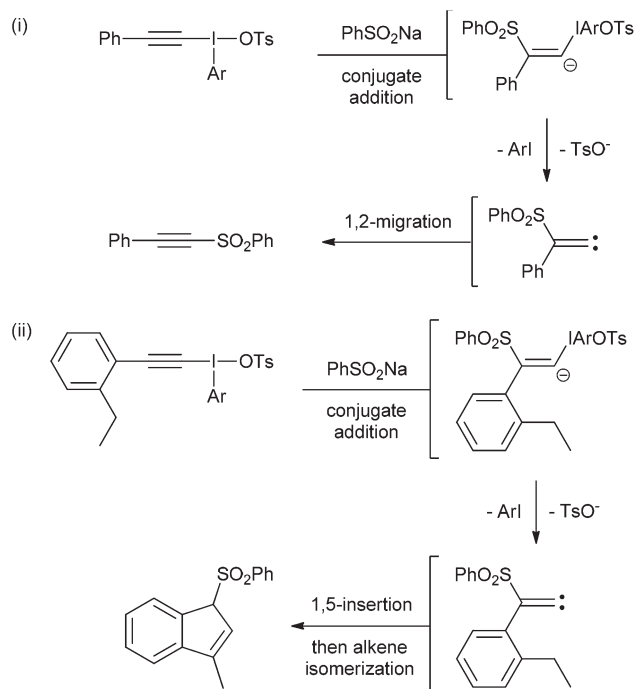
We identified two different reactions from the literature that alkynyl(aryl)iodonium salts undergo and decided to compare and contrast the effect of varying the aryl moiety on the reaction outcomes. The two reactions were (i) conjugate addition of a nucleophile followed by carbene formation and rearrangement to generate a new alkyne⁶ and (ii) conjugate addition of a nucleophile followed by carbene formation and intramolecular 1,5-insertion into a C–H bond (Scheme 2).⁷

Our first challenge was to prepare the requisite alkynyliodonium salts necessary for this study. There are several synthetic

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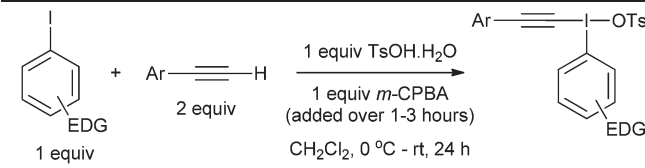


Scheme 2 Two reactions of alkynyl(aryl)iodonium salts.

methods available; however, as alluded to earlier, their effectiveness with regards to preparing salts from different aryl iodides has not been reported. We elected to use the method reported by Merritt and Olofsson for direct formation of the salts from terminal alkynes and aryl iodides using 3-chloroperbenzoic acid and 4-toluenesulfonic acid in dichloromethane.⁸ This procedure was only reported for the preparation of salt **1a** but its simplicity makes it an attractive method. However, our attempts to make pure samples of derivatives by this method failed in most cases, with the major impurity being the hydroxy(tosyloxy)aryliodine(III) compound. In 2012, Bouma and Olofsson published a new protocol using alkynyl boronates instead of terminal alkynes and the authors stated that this was a general route to high purity salts.⁹ Other methods have been reported which also require initial preparation of the corresponding alkynyl silanes,¹⁰ borons¹¹ or stannanes.¹² We wished to develop the method using terminal alkynes as this is more direct and atom efficient.

During our study, we noted that aryl iodides bearing electron-donating substituents behaved differently to those with electron-withdrawing groups; therefore, we optimized reaction conditions for these derivatives separately. For aryl iodides with electron-donating substituents, slow addition of the oxidant over several hours to the reaction mixture at 0 °C provided high purity iodonium salts upon crystallization from the reaction mixture (Table 1). This slow addition of the oxidant to a cold solution of the other components was found to effectively inhibit thermal decomposition of the intermediate iodine(III) species formed during this process. Additionally, by using an excess of the alkyne it was found, as expected, that the amount of the major hydroxy(tosyloxy)aryliodine(III)

Table 1 Synthesis of alkynyl(aryl)iodonium tosylates with electron-donating aryl substituents^a

		
1a 68%	1b 61%	1c 57%
1d 52%	1e 72%	1f 47%
2a 63%	2b 65%	2c 48%

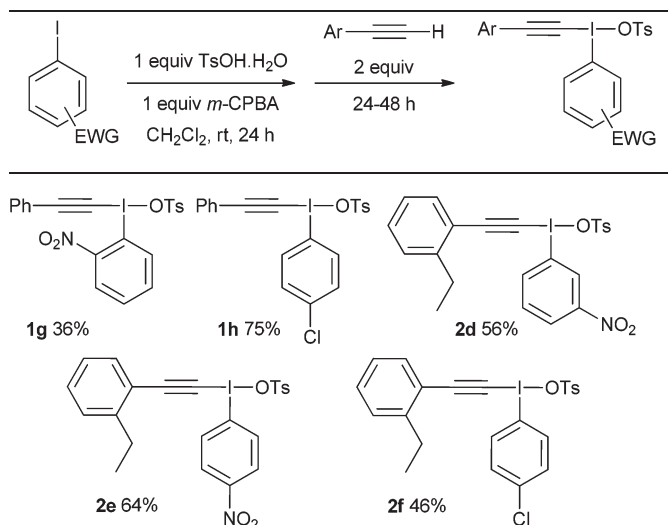
^a Yields are for pure isolated compounds.

impurity was reduced, leading to products of higher purity and in superior yield. If necessary, recrystallization effectively removed any trace impurities.

For aryl iodides with electron-withdrawing substituents, the hydroxy(tosyloxy)iodine(III) species were first prepared *in situ* and then treated with the alkyne to generate the iodonium salts in high purity after crystallization from the reaction mixture (Table 2). Where the conditions reported by Merritt and Olofsson were applied to the synthesis of these aryl iodides it was found that the material obtained was of very low purity; as little as 50%. We assume, therefore, that the presence of electron withdrawing substituents reduces the rate of formation of the alkynyliodonium salts from the corresponding hydroxy(tosyloxy)iodine(III) species and that the low purities were a consequence of incomplete reactions. By forming the hydroxy(tosyloxy)iodine(III) species first, we reduce the amount of time for thermal decomposition of the product alkynyliodonium salts, while an excess of the alkyne results in further gains in both the yield and purity of the product alkynyliodonium salts obtained. Again, any impurities present could be removed by recrystallization, but this was rarely necessary. All of the alkynyliodonium salts synthesised could be stored indefinitely at −20 °C.

With these salts in hand, the addition–rearrangement reaction with sodium phenylsulfinate was investigated (Table 3).⁶



Table 2 Synthesis of alkynyl(aryl)iodonium tosylates with electron-withdrawing aryl substituents^a^a Yields are for pure isolated compounds.**Table 3** Addition–rearrangement reaction

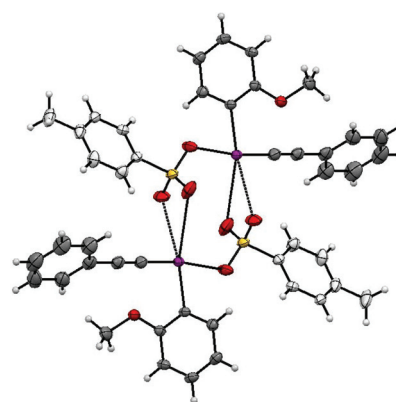
Reaction scheme showing the addition–rearrangement reaction. The starting material is an alkynyl(aryl)iodonium tosylate (**1a-h**). The reaction proceeds with 1.1 equiv PhSO₂Na and 0.1 equiv TEBA in CH₂Cl₂/H₂O at room temperature for 1 h, yielding the product **3**.

Entry	R	Salt	Yield ^a (%)
1	H	1a	81 (74)
2	2-OMe	1b	90 (83)
3	3-OMe	1c	49
4	4-OMe	1d	53
5	2-NO ₂	1e	44
6	3,5-diMe	1f	73
7	4-Me	1g	88
8	4-Cl	1h	79

^a Yields are an average of three runs and were determined by ¹H NMR analysis of the crude reaction mixtures with reference to a standard. Yields of isolated compounds are given in parentheses.

The iodobenzene derived salt **1a** worked well delivering an average of 81% yield over three runs, with 74% yield of isolated compound (entry 1). The 2-methoxy derivative **1b** provided a better yield of 90%, with 83% yield of isolated compound (entry 2) whereas the 3- and 4-methoxy derivatives **1c** and **1d** both led to diminished yields (entries 3 and 4). This suggests that the improvement in yield for **1b** is not due to electronic effects. Indeed, **1b** appeared to show increased solubility compared to **1c** and **1d**. The nitro derivative **1e** was a poor performer (entry 5), whereas *m*-xylyl derivative **1f** delivered 73% product, *p*-tolyl **1g** gave a superior 88% and 4-chloro **1h** was similar to parent **1a** with 79%.

These results suggest that 2-iodoanisole is the best “spectator” group of those tested in this reaction. To get further

**Fig. 1** X-ray crystal structure of **1b**.

insights into salt **1b** a single crystal X-ray structure was obtained (Fig. 1).¹³ This iodonium salt exists as a dimer in the solid state with the bond angles and lengths around the methoxy substituent being distorted somewhat suggesting some coordination to the I(III) center. The C(–I)–C–O bond angle is 116.62° compared to 120.83° for the C(–I)–C–H bond angle. Likewise, the C(–I)–C(–O)–C bond angle is 117.93° and the C(–I)–C(–H)–C bond angle is 118.27°. The distance between the iodine and oxygen atoms is 3.029 Å, which is reasonable for a van der Waals interaction. Recently, Zhdankin and co-workers demonstrated the synthesis and chemistry of iodonium ylides with *ortho*-alkoxy groups bound to the aryl ring.¹⁴ The reported crystal structure shows similar distortions around the I(III) center and the *ortho*-*n*-propoxy oxygen I(III) distance is reported as 2.978 Å. The authors note that these species display superior solubility and reactivity in comparison with their phenyl analogs.

The addition–C–H insertion reaction was investigated next (Table 4).⁷ In our hands, this reaction proved difficult with only 12% yield being achieved with salt **2a** (entry 1). However, the 2-methoxy salt **2b** once again proved to be superior and

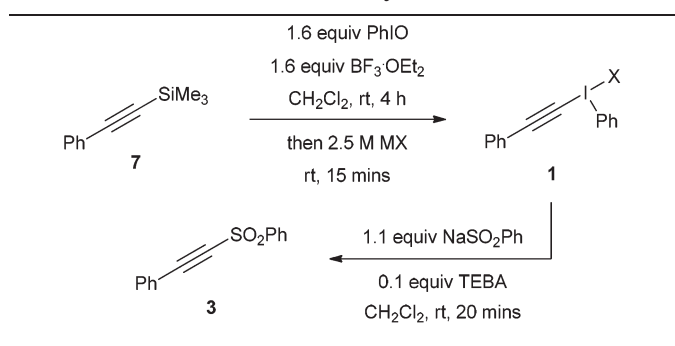
Table 4 Addition/C–H insertion reaction

Reaction scheme showing the addition/C–H insertion reaction. The starting material is an alkynyl(aryl)iodonium tosylate (**2a-j**). The reaction proceeds with 1.1 equiv PhSO₂Na in CH₂Cl₂ at room temperature for 1 h, yielding the product **4**.

Entry	R	Salt	Yield ^a (%)
1	H	2a	12 (5)
2	2-OMe	2b	51 (46)
3	3-NO ₂	2c	32
4	4-NO ₂	2d	10
5	3,5-diMe	2e	<5
6	4-Cl	2f	32

^a Yields are an average of three runs and were determined by ¹H NMR analysis of the crude reaction mixtures with reference to a standard. Yields of isolated compounds are given in parentheses.

Table 5 Effect of counterion on overall yield



Entry	MX	Overall yield ^a (%)
1	NaBF ₄	50 (36)
2	LiOTf	47
3	NaOTs	45
4	NaOMs	37
5	NaNO ₃	46
6	NaPF ₆	48

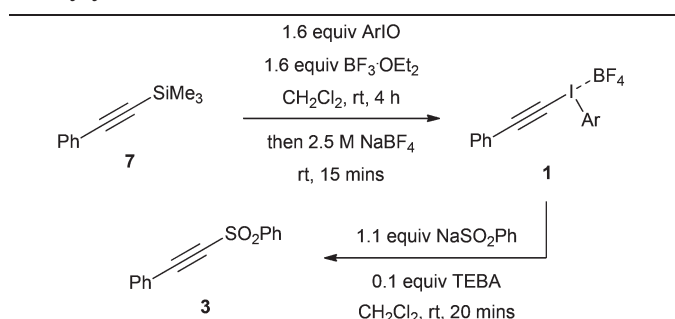
^a Yields are an average of three runs and were determined by ¹H NMR analysis of the crude reaction mixtures with reference to a standard. Yields of isolated compounds are given in parentheses.

51% yield of product was obtained (entry 2). The other salts provided low amounts of products, with xylol derivative **2e** furnishing <5% (entry 5).

In order to investigate the effect of the counterions on reaction yields, alkynyl(phenyl)iodonium salts were prepared from trimethyl(phenylethynyl)silane by reaction with iodosobenzene followed by treatment with aqueous solutions of a variety of lithium or sodium salts. The crude products were directly treated with sodium benzenesulfinate to effect the addition–rearrangement process (Table 5). The product **3** was formed in up to 50% yield from **7** (entry 1). The yields for the different salts were very close, with only a 5% difference, apart from for the mesylate which was 13% lower than the best (entry 4).

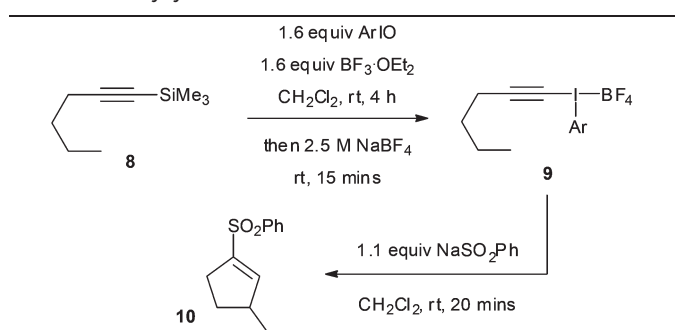
This process was then repeated but with variation of the iodosoarene and the tetrafluoroborate counterion was used (Table 6). The different iodosoarenes required were synthesized by hydrolysis of the corresponding iodoarene diacetates with 3 M NaOH solution.¹⁵ Yields varied from 0–92% for this process and the products were insoluble polymeric solids. Upon running the test reaction, a 50% overall yield of **3** was obtained for the phenyl parent and 36% yield was isolated (entry 1). The 2-iodoanisole appeared to decompose upon addition of the Lewis acid at room temperature, therefore the Lewis acid was added dropwise at –78 °C to the solution of silylalkyne **7** and 2-iodoanisole. The reaction mixture was then warmed to room temperature and the aqueous NaBF₄ solution added. Addition of the NaSO₂Ph to this salt at room temperature led to addition/insertion occurring in a remarkable 96% overall yield (entry 2). The other iodosoarenes tested gave moderate yields.

In a similar fashion, the addition–insertion reaction was investigated starting from the silane **8** but without isolation of the intermediate alkynylidonium salt **9** (Table 7). Upon

Table 6 Conversion of silylalkyne **7** to sulfone **3** without isolation of the alkynylidonium salt **1**

Entry	Ar	Overall yield ^a (%)
1	Ph	50 (36)
2	2-MeOC ₆ H ₄	96 ^b (87)
3	2-NO ₂ C ₆ H ₄	38
4	3,5-diMeC ₆ H ₃	48
5	4-MeC ₆ H ₄	49
6	4-ClC ₆ H ₄	62

^a Yields are an average of three runs and were determined by ¹H NMR analysis of the crude reaction mixtures with reference to a standard. Yields of isolated compounds are given in parentheses. ^b First stage of the iodonium salt formation performed at –78 °C.

Table 7 Conversion of silylalkyne **8** to cyclopentene **10** without isolation of the alkynylidonium salt **9**

Entry	Ar	Overall yield ^a (%)
1	Ph	30 (22)
2	2-MeOC ₆ H ₄	71 ^b (64)
3	2-NO ₂ C ₆ H ₄	35
4	3,5-diMeC ₆ H ₃	57
5	4-MeC ₆ H ₄	54
6	4-ClC ₆ H ₄	46

^a Yields are an average of three runs and were determined by ¹H NMR analysis of the crude reaction mixtures with reference to a standard. Yields of isolated compounds are given in parentheses. ^b First stage of the iodonium salt formation performed at –78 °C.

running the reaction, a 30% overall yield of **10** was obtained for the phenyl parent (entry 1). The 2-iodoanisole derivative gave a superior 71% yield, 64% isolated, which was substantially better than all the other derivatives tested (entry 2). This result is particularly notable for a non-activated aliphatic C–H insertion reaction occurring at room temperature. A small



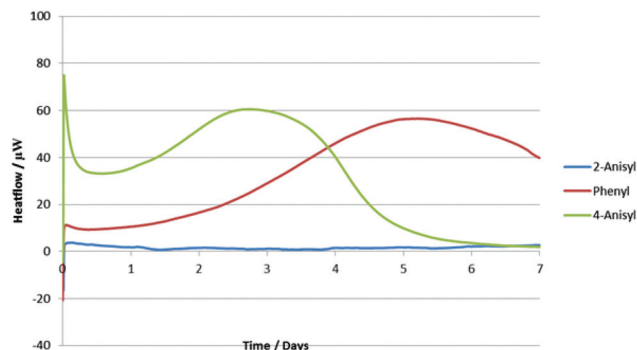


Fig. 2 IMC data for three alkynyl(aryl)iodonium salts in the solid state at 30 °C.

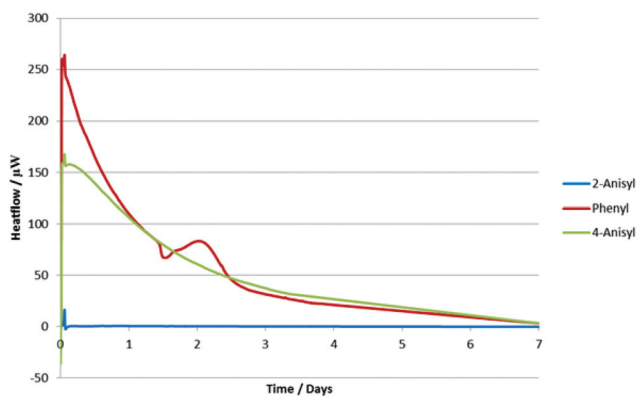


Fig. 3 IMC data for three alkynyl(aryl)iodonium salts in 1,2-dichloroethane at 30 °C.

amount of the 1,2-rearrangement product was also formed in this reaction (<20%).

In order to rationalize these results, we decided to analyze the alkynyl(aryl)iodonium salts by isothermal microcalorimetry (IMC). Holding the samples for seven days at 30 °C under an air atmosphere both as solids (Fig. 2) and in solution (Fig. 3) led to rapid decomposition of all of the salts apart from the 2-iodoanisole derivative. This salt was unchanged after seven days, whereas the others decomposed within minutes. This remarkable stability is postulated to arise from coordination of the oxygen atom to the iodine(III) centre (*vide supra*) as the corresponding 4-iodoanisole derivative rapidly decomposed, suggesting that simple electronic effects are not responsible. Assuming that this effect is also present in the iodonium reaction intermediates, we can rationalize the observed yields in the reactions studied by consideration of the stabilities of the iodine(III) species and the likelihood of their undergoing unproductive decomposition before the desired reaction. These species are not sensitive to water or air and no decompositions have been detected by exposing them to daylight, although storage in the dark is recommended.

Conclusions

We have developed two new modified procedures for the preparation of alkynyl(aryl)iodonium tosylates directly from iodoarenes and terminal acetylenes. We have also demonstrated that the reactivity of alkynyl(aryl)iodonium salts vary considerably depending on which aryl iodide they are derived from.¹⁶ Thus, the aryl iodide is not merely a spectator group but has a profound impact on the reactivity. Importantly, the stability of the iodine(III) species has been shown to be critical for achieving high yields. Of those tested, 2-iodoanisole has been shown to be the optimum choice as it provided augmented yields of products in subsequent reactions compared to other derivatives. It is expected that the use of 2-iodoanisole derived alkynyl(aryl)iodonium salts, and other iodine(III) species, will deliver superior results in other reactions.¹⁴

Experimental

General methods

¹H NMR spectra were recorded at 400 MHz. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl₃: 7.26 ppm). ¹³C NMR were recorded with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal standard (CDCl₃: 77.4 ppm). Mass spectrometry (*m/z*) was performed in ESI mode, with only molecular ions being reported. Infrared (IR) spectra ν_{\max} are reported in cm⁻¹. Petroleum ether refers to the fraction boiling at 40–60 °C. All purchased reagents were used as received without further purification. All reactions were performed under a N₂ atmosphere.

Preparation of alkynyl(aryl)iodonium salts with electron-donating substituents. To a solution of iodoarene (4.90 mmol, 1 equiv.), TsOH·H₂O (0.93 g, 4.90 mmol, 1 equiv.) and an aryl alkyne (9.80 mmol, 2 equiv.) in CH₂Cl₂ (25 mL) at 0 °C, was added *m*-CPBA (70–75% purity, 1.22 g, 4.90 mmol, 1 equiv.) slowly over a period of 1 hour. The resulting solution was slowly warmed to room temperature and stirred for 24 h after which it was reduced to half volume (approx. 12 mL) *in vacuo* at ambient temperature. Diethyl ether (12 mL) was added to this solution in a dropwise manner, with gentle swirling. The resulting homogeneous solution was again reduced to half volume *in vacuo* at ambient temperature, upon which time crystals started to be formed. Over a period of one hour, diethyl ether (75 mL) was added with gentle swirling, and the resulting suspension was allowed to stand for 1 h. The precipitate was filtered, washed with diethyl ether and dried under vacuum, yielding the product as a powder. Analytically pure material was obtained by recrystallization in CH₂Cl₂ and ether.

Preparation of alkynyl(aryl)iodonium salts with electron-donating substituents. To a solution of iodoarene (4.90 mmol, 1 equiv.), TsOH·H₂O (0.93 g, 4.90 mmol, 1 equiv.) in CH₂Cl₂ (25 mL) was added *m*-CPBA (70–75% purity, 1.22 g, 4.90 mmol, 1 equiv.) in one portion. The solution was allowed to stir for



24 hours, upon which time an aryl alkyne (9.80 mmol, 2 equiv.) was added, followed by a further 24 hours stirring. Removal of the volatiles *in vacuo* at ambient temperature yielded a residue, which was dissolved in the minimum amount of CH_2Cl_2 and added dropwise to diethyl ether (75 mL). After 2 h, the precipitate was filtered, washed with diethyl ether and dried under vacuum, yielding the product as a powder. Analytically pure material was obtained by recrystallization in CH_2Cl_2 and ether.

General synthesis of 2-(benzenesulfonyl)ethynylbenzene (3) from trimethyl(phenylethynyl)silane (7). To a suspension of a fine powder of iodosylarene (0.5 mmol) in CH_2Cl_2 (5 mL) under an inert atmosphere was added trimethyl(phenylethynyl)silane 7 (0.052 g, 0.3 mmol), then, over a period of 5 min, boron trifluoride etherate (0.5 mmol). [For 2-(iodosyl)anisole, the suspension was cooled to -78°C and boron trifluoride was added over a period of 1 h.] The reaction was allowed to stir for 4 h, which yielded a bright yellow homogeneous solution. An aqueous solution of a sodium or lithium salt (2.5 M, 1.8 mmol) was added and the resulting emulsion was stirred vigorously for 15 min. The aqueous layer was separated and extracted with CH_2Cl_2 (2×5 mL). The combined organic layers were washed with brine, dried over MgSO_4 , filtered and concentrated *in vacuo* to yield the crude alkynyl(aryl)-iodonium salts as viscous yellow oils. The crude residue was dissolved in CH_2Cl_2 (2 mL) and a solution of benzenesulfinic acid sodium salt (0.019 g, 0.116 mmol) and triethylbenzyl ammonium chloride (TEBA) (0.0024 g, 0.011 mmol) in water (1 mL) was added. The reaction mixture was stirred at room temperature for 1 hour, after which time the aqueous layer was separated and extracted with CH_2Cl_2 (2×5 mL). The combined organic layers were washed with water, then brine, and dried over anhydrous MgSO_4 , filtered and concentrated *in vacuo*, which yielded a viscous yellow oil. Purification by flash column chromatography (9:1 petroleum ether–ethyl acetate) provided a pale yellow solid. Melting point: $70\text{--}71^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3): δ 8.11 (dd, 2H, $J = 7.3$ Hz, $J = 1.3$ Hz), 7.73–7.70 (m, 1H), 7.64–7.61 (m, 2H), 7.55 (dd, 2H, $J = 7.1$ Hz, $J = 1.3$ Hz), 7.52–7.48 (m, 1H), 7.41–7.38 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 141.7, 134.1, 132.7, 131.6, 129.3, 128.7, 127.4, 117.8, 93.5, 85.3. HRMS: calcd for $\text{C}_{14}\text{H}_{10}\text{NaO}_2\text{S}$ $[\text{MNa}]^+$ 265.0294; found 265.0303.

General synthesis of 1-benzenesulfonyl-3-methyl-indene (4) from 1-ethyl-2-ethynylbenzene(aryl)iodonium tosylates (2). To a solution of 1-ethyl-2-ethynylbenzene(aryl)iodonium tosylate 2 (0.099 mmol) in CH_2Cl_2 (2 mL) was added benzenesulfinic acid sodium salt (0.018 g, 0.11 mmol). The suspension was stirred at room temperature for one hour upon which time deionized water (2 mL) was added. After an additional 5 min the aqueous layer was separated and extracted with CH_2Cl_2 (2×5 mL). The combined organic layers were washed with brine, dried over MgSO_4 , filtered and concentrated *in vacuo*, which yielded a yellow oil. Purification by flash column chromatography (9:1 petroleum ether–ethyl acetate) furnished a pale yellow liquid. ^1H NMR (400 MHz, CDCl_3): δ 7.77 (d, 1H, $J = 6.7$ Hz), 7.41–7.35 (m, 3H), 7.26–7.15 (m, 4H), 6.97 (d, 1H, $J =$

6.3 Hz), 6.05 (s, 1H), 4.91 (s, 1H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 146.5, 145.6, 136.0, 135.0, 133.4, 129.1, 128.9, 127.8, 126.3, 125.6, 122.5, 119.5, 72.4, 12.8. HRMS: calcd for $\text{C}_{16}\text{H}_{14}\text{SO}_2\text{Na}$ $[\text{MNa}]^+$ 293.0607; found 293.0609.

General synthesis of (3-methylcyclopenten-1-yl)sulfonylbenzene (10) from alkynylsilane (8). To a suspension of an iodosylarene (0.5 mmol) in CH_2Cl_2 (5 mL) under an inert atmosphere was added hex-1-yn-1-yltrimethylsilane 8 (0.046 g, 0.3 mmol), then, over a period of 5 min, boron trifluoride etherate (0.5 mmol). [For 2-(iodosyl)anisole, the suspension was cooled to -78°C and boron trifluoride was added over a period of 1 h.] The reaction was stirred for 4 h, which yielded a bright yellow homogeneous solution. An aqueous solution of sodium tetrafluoroborate (2.5 M, 1.8 mmol) was added to the mixture and the resultant emulsion was stirred vigorously for 15 min. The aqueous layer was separated and extracted with CH_2Cl_2 (2×5 mL). The combined organic layers were washed with brine, dried over MgSO_4 , filtered and concentrated *in vacuo* at ambient temperature, yielding a viscous yellow oil, which was dissolved in CH_2Cl_2 (3 mL). To this solution was added benzenesulfinic acid sodium salt (0.059 g, 0.36 mmol). The suspension was held at room temperature for 20 minutes upon which time deionized water (3 mL) was added. After an additional five min the aqueous layer was separated and extracted with CH_2Cl_2 (2×5 mL). The combined organic layers were washed with brine, dried over MgSO_4 , filtered and concentrated *in vacuo*, which yielded a yellow oil. Purification by flash column chromatography (9:1 petroleum ether–ethyl acetate) furnished a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.92 (d, 2H, $J = 7.4$ Hz), 7.67–7.55 (m, 3H), 6.66 (d, 1H, $J = 1.8$ Hz), 3.01–2.92 (m, 1H), 2.62–2.56 (m, 1H), 2.54–2.45 (m, 1H), 2.30–2.22 (m, 1H), 1.59–1.53 (m, 1H), 1.11 (d, 3H, $J = 7.0$ Hz). ^{13}C NMR (100 MHz, CDCl_3): δ 148.1, 143.5, 139.6, 133.3, 129.1, 127.9, 40.6, 32.4, 30.4, 19.5. HRMS: calcd for $\text{C}_{12}\text{H}_{14}\text{NaO}_2\text{S}$ $[\text{MNa}]^+$ 245.0607; found 245.0618.

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