Facile synthesis of substituted diaryliodonium tosylates by treatment of aryltributylstannanes with Koser's reagent

Victor W. Pike,†[a] Faisal Butt,[a] Aneela Shah[a] and David A. Widdowson[b]

[a] *Chemistry and Engineering Group, MRC Cyclotron Unit, Imperial College School of Medicine, Hammersmith Hospital, Ducane Road, London, UK W12 ONN*
[b] *Department of Chemistry, Imperial College of Science, Technology and Medicine, London, UK SW7 2AY*

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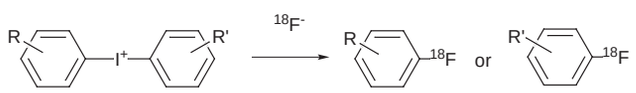
A facile synthesis of substituted diaryliodonium tosylates (toluene-*p*-sulfonates) was developed, based on the treatment of substituted aryltributylstannanes with Koser's reagent [hydroxy(tosyloxy)iodobenzene]. In this manner, several new diaryliodonium salts, bearing one or more substituents on one aryl ring, were prepared in useful yields under mild conditions (dichloromethane, room temperature, 2 h).

Diaryliodonium salts have practical application due to their anti-microbial activity and photochemical properties.[1] They are useful in organic synthesis for the arylation of organic and inorganic bases[2–8] and are suggested as efficient catalysts for radiation-induced polymerisation.[9] Recently, they have been shown to be useful substrates for the introduction of ^{18}F ($t_{1/2}$ = 109.7 min; β^+ = 100%) into arenes[10–12] to provide potential radiopharmaceuticals for positron emission tomography (PET), a powerful imaging technique in clinical research.[13] This process (Scheme 1) is unique in that it allows cyclotron-



Scheme 1

produced [^{18}F]fluoride of high specific radioactivity to be introduced efficiently into electron-rich and electron-deficient aryl rings.[10–12] It is potentially more powerful than former methods of arene radiofluoridation based on the use of the Balz–Schiemann[14,15] or Wallach reactions,[16–18] which are limited by giving low radiochemical yields, especially on complex substrates.

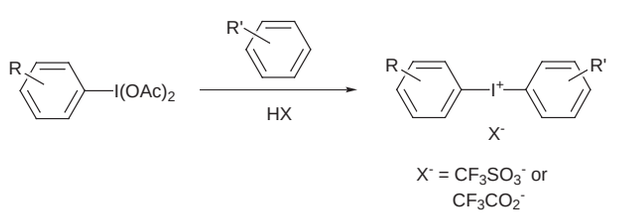
In order to extend our investigations of the mechanism and scope of the new radiofluoridation process, especially the influence of substituents in one or more aryl rings, we have sought to develop more facile syntheses of the required substituted diaryliodonium salts. For example, we have recently demonstrated the preparation of functionalised unsymmetrical diaryliodonium salts by reactions of bis(acetoxy)iodoarenes with arenes in a trifluoromethanesulfonic acid or trifluoroacetic acid medium (Scheme 2).[19] This method has advantages over former procedures,[2–4,6,7,20–22] but still requires acidic conditions and is constrained to high *para*-selectivity.

It has been reported[23] that diaryliodonium salts can be prepared by the reactions of aryltrialkylsilanes with Koser's reagent,[24,25] hydroxy(tosyloxy)iodobenzene. The bond between the iodine and the tosyloxy group in Koser's reagent has significant ionic character[26] and this reagent may be considered as a source of electrophilic $C_6H_5IOH^+$ ion. We therefore considered that Koser's reagent should also react with other metallated arenes, and especially with aryltrialkylstannanes in which the

† E-mail address: vpike@rpms.ac.uk

Table 1 Yields of prepared substituted diphenyliodonium tosylates (Ar–I^+–Ph tosylate)

Cpd.	Ar	Yield (%)
1a	Ph	31
1b	2-MeC_6H_4	50
1c	3-MeC_6H_4	57
1d	2-$MeOC_6H_4$	38
1e	3-$MeOC_6H_4$	51
1f	4-FC_6H_4	18
1g	4-$CF_3C_6H_4$	27
1h	3-F-6-MeC_6H_4	28
1i	3-F-6-$MeOC_6H_4$	25
1j	4-F-3-MeC_6H_4	29
1k	4-(2-F-1-biphenyl)	58
1l	5-(2,3-Dihydrobenzo[*b*]furanyl	19



Scheme 2

strength of the aryl carbon–metal bond is weaker than in aryltrimethylsilanes.[27,28] Moreover, aryltrialkylstannanes are now readily prepared by a variety of methods from haloarenes (*e.g.* by treatment with hexaalkyldistannanes in the presence of palladium complexes[29] or by metallation with *n*-butyllithium and treatment with trimethylchlorostannane[30]). Aryltrialkylstannanes also serve as important precursors for the preparation of structurally elaborate radiopharmaceuticals *via* halodestannylation reactions with radioiodine, radiobromine or radiofluorine (as carrier-added [^{18}F]fluorine or [^{18}F]acetyl hypofluorite).[31] We therefore investigated the reaction of Koser's reagent with a range of commercially available substituted aryltrialkylstannanes.

Treatment of phenyltributylstannane with Koser's reagent in dichloromethane at room temperature for 2 h was found to give a useful yield of diphenyliodonium tosylate (Table 1). By contrast the treatment of phenyltrimethylsilane under the same conditions failed to give this product. It has been reported that harsher conditions (near reflux in acetonitrile for 4 h or even

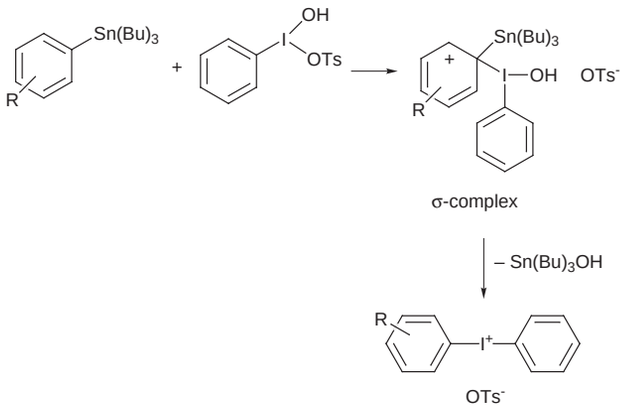
longer in dichloromethane) are needed to prepare diphenyliodonium tosylate **1a** from phenyltrimethylsilane.[23] Thus, the preparation from phenyltributylstannane is more facile. We found that treatment of phenylmercuric acetate with Koser's reagent in dichloromethane at room temperature for 2 h also gave diphenyliodonium tosylate in a similar yield (32%) to the treatment of phenyltributylstannane. Since the known order of C_{aryl}–metal bond strengths is C–Hg < C–Sn < C–Si,[27,28] our findings show that Koser's reagent does indeed react most readily with the weaker bonds.

We were able to prepare a range of substituted diaryliodonium tosylates **1a**–**1l** from commercial aryltributylstannanes in satisfactory yields under the same non-optimised conditions (Table 1), including several previously unknown salts **1d**–**1l**. These compounds were unequivocally characterised by ^{1}H- and ^{13}C-NMR spectroscopy and mass spectrometry. All the ^{1}H-NMR spectra show a signal at $\delta = 2.29$, characteristic of the tosylate anion methyl group. The ^{13}C-NMR spectrum of diphenyliodonium tosylate **1a** usefully provided a substituent chemical shift (SCS) for each carbon in the phenyliodonium (PhI^+) substituent. From the spectrum, SCS values of 120.47, 139.14, 135.72 and 136.00 were assigned to δ_{ipso}, δ_{ortho}, δ_{meta} and δ_{para} respectively, so as to match the order of SCSs in diaryliodonium iodides.[32] The new SCSs were summed with appropriate SCSs for Ph, Me, OMe, F and CF_3 substituents on phenyl rings[33] to predict the chemical shifts for the carbon atoms in each of the substituted diaryliodonium ions in salts **1b**–**k**. This proved an important aid to spectral interpretation. In the spectra of the fluorine-containing iodonium salts (**1f**, **1i**, **1j** and **1k**) long range C–F couplings enabled a doublet to be assigned to the carbon bonded to the iodine. The chemical shifts for carbons in the tosylate anion were virtually constant throughout the spectra.

Aryltributylstannanes bearing electron-donating groups (*e.g.* 2-Me, 3-Me, 2-MeO or 3-MeO) gave the highest yields of the corresponding iodonium salts (**1b**–**e**). Aryltributylstannanes bearing a single electron-withdrawing group (4-F or 4-CF_3) were also converted into iodonium salts (**1f** and **1g**), but in lower yield. Attempts to prepare iodonium salts from (2,5-difluorophenyl)tributylstannane, (2-pyridyl)tributylstannane or (3-pyridyl)tributylstannane were, however, unsuccessful. Salts bearing one electron-withdrawing and one electron-donating substituent (**1h** and **1j**), were obtained in moderate yields. More elaborate polycyclic aryltributylstannanes were also converted successfully into iodonium salts (*e.g.* **1k** and **1l**). The dependence of yield on aryl substitution pattern (Table 1) appears consistent with a reaction mechanism involving electrophilic attack on the arene by Koser's reagent with expulsion of the tosylate anion and formation of a positively charged σ-complex which eliminates trialkyl(hydroxy)stannane (Scheme 3).

The range of substituted aryltributylstannanes converted into diaryliodonium tosylates by this new procedure indicates wide potential utility, except for arenes bearing multiple electron-withdrawing substituents or heteroarenes. The procedure uses a stable commercially available reagent and is simple to perform. Since Koser's reagent reacts with non-metallated arenes only with difficulty,[24] the syntheses are regiospecifically confined to *ipso*-destannylation. It is possible to prepare substituted derivatives of Koser's reagent[25] which are expected to react similarly with the aryltributylstannanes. These have the potential to extend this simple technique to regiospecific preparations of diaryliodonium tosylates substituted in one or both aryl rings. The method we describe also has more versatility than the reported treatment of aryltributylstannanes with the relatively unstable reagent, (dicyano)iodonium triflate, which results in symmetrical diaryliodonium triflates.[34]

We are now continuing to investigate the reactions of the prepared substituted diaryliodonium tosylates with fluoride and no-carrier-added [^{18}F]fluoride, and to extend this procedure to the synthesis of elaborate iodonium salts as precursors to ^{18}F-labelled radiopharmaceuticals.



Scheme 3

Experimental

Koser's reagent [hydroxy(tosyloxy)iodobenzene], trimethyl(phenyl)silane and phenylmercuric acetate were purchased from Aldrich Chemical Co Ltd and used as supplied. The substituted aryltributylstannanes were purchased from Maybridge Chemical Co Ltd. Chemical shifts are reported as δ values relative to tetramethylsilane as an internal standard. ^{1}H- and ^{13}C-NMR were recorded at 360 and 90 MHz, respectively, in DMSO-d_6 on Bruker instruments. Mass spectra were recorded on VG Micromass 7070E and Autospec-Q instruments.

Substituted diaryliodonium tosylates—general procedure

The aryltributylstannane (2.0 mmol) was stirred with Koser's reagent (0.81 g, 2.0 mmol) in dichloromethane (6 mL) at room temperature under nitrogen for 2 h. The solvent was evaporated using a steady stream of nitrogen. The residue was recrystallised from ethanol and diethyl ether to give white crystals. Yields are listed in Table 1.

Diphenyliodonium tosylate[20,23,35] **1a.** Mp 179–180 °C (lit.,[35] mp 178–181 °C). δ_H 8.26–8.24 (4H, d, *J* 7.7, Ar*H*), 7.69–7.65 (2H, t, *J* 7.3, Ar*H*), 7.55–7.51 (4H, t, *J* 7.3, Ar*H*), 7.49–7.46 (2H, d, J_{AB} 7.9, Ar*H* in tosyl), 7.12–7.10 (2H, d, J_{AB} 7.9, Ar*H* in tosyl), 2.29 (3H, s, CH_3) (*cf.* data in ref. 20). δ_C 149.75 (C_{Ar} in tosyl), 141.54 (C_{Ar} in tosyl), 139.14 (C_{Ar}), 136.00 (C_{Ar}), 135.72 (C_{Ar}), 132.01 (C_{Ar} in tosyl), 129.46 (C_{Ar} in tosyl), 120.47 (*C*-I), 24.74 (*C*H$_3$). *m*/*z* (FAB) 281 ($C_{12}H_{10}I^+$, 100%), 91 (19), 81 (21), 77 (18), 69 (30), 55 (38) (Found: 280.9831; $C_{12}H_{10}I^+$ requires: 280.9827).

2-Methylphenyl(phenyl)iodonium tosylate[23] **1b.** Mp 173–175 °C. δ_H 8.40–8.38 (1H, d, *J* 7.8, Ar*H*), 8.21–8.19 (2H, d, *J* 8.0, Ar*H*), 7.66–7.46 (7H, m, 5 × Ar*H* plus 2 × Ar*H* in tosyl), 7.33–7.28 (1H, m, Ar*H*), 7.12–7.10 (2H, d, *J* 8.0, Ar*H* in tosyl), 2.61 (3H, s, CH_3), 2.28 (3H, s, CH_3 in tosyl). δ_C 149.66 (C_{Ar}-Me in tosyl), 144.58 (C_{Ar}-Me), 141.67 (C_{Ar} in tosyl), 141.12, 139.06, 136.83, 135.94, 135.80, 135.42, 133.29, 132.08 (C_{Ar} in tosyl), 129.50 (C_{Ar} in tosyl), 125.47 (*C*-I), 119.91 (*C*-I), 29.01 (*C*H$_3$), 24.79 (*C*H$_3$ in tosyl). *m*/*z* (FAB) 295 ($C_{13}H_{12}I^+$, 100%), 154 (25), 136 (19), 91 (12), 69 (15), 55 (18) (Found: 294.9989; $C_{13}H_{12}I^+$ requires: 294.9984).

3-Methylphenyl(phenyl)iodonium tosylate[23,36] **1c.** Mp 172–175 °C. (lit.,[36] mp 175–180 °C). δ_H 8.25–8.23 (2H, d, *J* 7.4, Ar*H*), 8.11 (1H, s, Ar*H*), 8.06–8.04 (1H, d, *J* 7.8, Ar*H*), 7.67–7.63 (1H, t, *J* 7.2, Ar*H*), 7.59–7.46 (5H, m, 3 × Ar*H* plus 2 × Ar*H* in tosyl), 7.42–7.38 (1H, t, *J* 8.0, Ar*H*), 7.12–7.10 (2H, d, *J* 8.0, Ar*H* in tosyl), 2.32 (3H, s, CH_3), 2.28 (3H, s, CH_3 in

tosyl). δ_C 149.66 (C_{Ar}-Me in tosyl), 145.73 (C_{Ar}-Me), 141.64 (C_{Ar} in tosyl), 139.33, 139.14, 136.65, 136.24, 135.94, 135.68, 135.38, 132.04 (C_{Ar} in tosyl), 129.49 (C_{Ar} in tosyl), 120.38 (*C*-I), 120.27 (*C*-I), 24.75 (CH_3 in tosyl), 24.71 (CH_3). *m*/*z* (FAB) 295 ($C_{13}H_{12}I^+$, 45%), 135 (15), 123 (20), 109 (26), 95 (42), 91 (34), 81 (49), 77 (29), 69 (83), 55 (100) (Found: 294.9992; $C_{13}H_{12}I^+$ requires: 294.9984).

2-Methoxyphenyl(phenyl)iodonium tosylate 1d. Mp 125–130 °C. δ_H 8.30–8.28 (1H, m, Ar*H*), 8.13–8.10 (2H, d, *J* 7.7, Ar*H*), 7.67–7.61 (2H, m, Ar*H*), 7.51–7.46 (4H, m, 2 × Ar*H* plus 2 × Ar*H* in tosyl), 7.31–7.29 (1H, d, *J* 8.1, Ar*H*), 7.12–7.06 (3H, m, 1 × Ar*H* plus 2 × Ar*H* in tosyl), 3.93 (3H, s, OCH_3), 2.28 (3H, s, CH_3 in tosyl). δ_C 160.40 (C_{Ar}-OMe), 149.67 (C_{Ar} in tosyl), 141.68 (C_{Ar} in tosyl), 141.31, 139.08, 138.89, 135.84, 135.61, 132.08 (C_{Ar} in tosyl), 127.43, 119.85, (*C*-I), 117.04, 110.56 (*C*-I), 61.07 (OCH_3), 24.79 (CH_3 in tosyl). *m*/*z* (FAB) 311 ($C_{13}H_{12}OI^+$, 100%), 91 (9), 81 (12), 69 (21), 55 (25) (Found: 310.9945; $C_{13}H_{12}OI^+$ requires: 310.9933).

3-Methoxyphenyl(phenyl)iodonium tosylate 1e. Mp 147–152 °C. δ_H 8.27–8.25 (2H, d, *J* 8.0, Ar*H*), 7.97–7.91 (1H, m, Ar*H*), 7.80–7.77 (1H, d, *J* 8.0, Ar*H*), 7.69–7.64 (1H, t, *J* 7.6, Ar*H*), 7.61–7.42 (5H, m, 3 × Ar*H* plus 2 × Ar*H* in tosyl), 7.23–7.20 (1H, dd, *J* 6.0, *J* 2.3, Ar*H*), 7.12–7.10 (2H, d, *J* 8.0, Ar*H* in tosyl), 3.79 (3H, s, OCH_3), 2.28 (3H, s, CH_3 in tosyl). δ_C 164.40 (C_{Ar}-OMe), 149.70 (C_{Ar} in tosyl), 141.65 (C_{Ar} in tosyl), 139.18, 136.47, 136.02, 135.72, 132.07, (C_{Ar} in tosyl), 131.12, 129.51 (C_{Ar} in tosyl), 121.79, 120.58 (*C*-I), 120.39 (*C*-I), 59.92 (OCH_3), 24.78 (CH_3 in tosyl). *m*/*z* (FAB) 311 ($C_{13}H_{12}OI^+$, 100%), 185 (16) (Found: 310.9932; $C_{13}H_{12}OI^+$ requires: 310.9933).

4-Fluorophenyl(phenyl)iodonium tosylate 1f. Mp 180–181 °C. δ_H 8.34–8.31 (2H, dd, J_{H-H} 8.5, J_{H-F} 5.3, Ar*H*), 8.26–8.24 (2H, d, *J* 7.9, Ar*H*), 7.68–7.64 (1H, t, *J* 7.25, Ar*H*), 7.56–7.47 (4H, m, 2 × Ar*H* plus 2 × A*rH* in tosyl), 7.43–7.38 (2H, t, *J* 8.4, Ar*H*), 7.12–7.09 (2H, d, *J* 7.8, Ar*H*, tosyl), 2.28 (3H, s, CH_3 in tosyl). δ_C 167.90 (d, $^1J_{C-F}$ 251, C_{Ar}-F), 149.71 (C_{Ar} in tosyl), 142.05 (d, $^3J_{C-F}$ 8.8, C_{Ar}), 141.55 (C_{Ar}, tosyl), 139.05, 136.00, 135.70, 132.00 (C_{Ar} in tosyl), 129.46 (C_{Ar} in tosyl), 123.12 (d, $^2J_{C-F}$ 22.5, C_{Ar}), 120.91 (*C*-I), 114.75 (d, $^4J_{C-F}$ 2.5, *C*-I), 24.72 (CH_3 in tosyl). *m*/*z* (FAB) 299 ($C_{12}H_9FI^+$, 100%), 135 (10), 120 (13), 109 (15), 95 (25), 91 (23), 83 (19), 77 (25), 69 (38), 55 (43) (Found: 298.9802; $C_{12}H_9FI^+$ requires: 298.9733).

4-Trifluoromethylphenyl(phenyl)iodonium 1g. Mp 180–184 °C. δ_H 8.47–8.44 (2H, d, *J* 8.3, Ar*H*), 8.32–8.29 (2H, d, *J* 7.9, Ar*H*), 7.92–7.90 (2H, d, *J* 8.5 Ar*H*), 7.71–7.67 (1H, t, *J* 7.4, Ar*H*), 7.59–7.53 (2H, m, Ar*H*), 7.48–7.46 (2H, d, J_{AB} 7.9, Ar*H* in tosyl), 7.12–7.10 (2H, d, J_{AB} 7.9, Ar*H* in tosyl), 2.29 (3H, s, CH_3 in tosyl). δ_C 149.69 (C_{Ar} in tosyl), 141.64 (C_{Ar} in tosyl), 139.99, 139.44, 136.33, 135.84 (d, $^2J_{C-F}$ 33, C_{Ar}), 135.91, 135.47, 132.34 (d, $^3J_{C-F}$ 3.5, C_{Ar}), 132.06 (C_{Ar} in tosyl), 129.50 (C_{Ar} in tosyl), 127.43 (q, $^1J_{C-F}$ 280, CF_3), 124.74 (*C*-I), 120.75 (*C*-I), 24.74 (CH_3). *m*/*z* (FAB) 349 ($C_{13}H_9F_3I^+$, 100%), 222 ($C_{13}H_9F_3^+$, 10), 69 (8), 55 (10) (Found: 348.9715; $C_{13}H_9F_3I^+$ requires: 348.9701).

3-Fluoro-6-methylphenyl(phenyl)iodonium tosylate 1h. Mp 176–178 °C. δ_H 8.46–8.44 (1H, d, J_{H-F} 6.2, Ar*H*), 8.26–8.24 (2H, d, *J* 7.7, Ar*H*), 7.68–7.43 (7H, m, 5 × Ar*H* plus 2 × Ar*H* in tosyl), 7.12–7.10 (2H, d, *J* 7.6, Ar*H* in tosyl), 2.59 (3H, s, CH_3), 2.28 (3H, s, CH_3 in tosyl). δ_C 164.00 (d, $^1J_{C-F}$ 250, C_{Ar}-F) 149.52 (C_{Ar} in tosyl), 141.71 (C_{Ar} in tosyl), 140.85 (d, $^4J_{C-F}$ 2.7, C_{Ar}), 139.10, 136.32 (d, $^3J_{C-F}$ 7.3, C_{Ar}), 136.04, 135.82, 132.05 (C_{Ar} in tosyl), 129.47 (C_{Ar} in tosyl), 127.62 (d, $^2J_{C-F}$ 25, C_{Ar}), 124.47, 124.07 (d, $^2J_{C-F}$ 21, C_{Ar}), 123.52, 120.26 (*C*-I), 27.94 (CH_3), 24.74 (CH_3 in tosyl). *m*/*z* (FAB) 313 ($C_{13}H_{11}FI^+$, 100%), 109 (5), 81 (6), 69 (8), 55 (12) (Found: 312.9914; $C_{13}H_{11}FI^+$ requires: 312.9889).

3-Fluoro-6-methoxyphenyl(phenyl)iodonium tosylate 1i. Mp 149–151 °C. δ_H 8.35–8.34 (1H, d, J_{H-F} 4.8, Ar*H*), 8.16–8.14 (2H, d, *J* 7.7, Ar*H*), 7.67–7.46 (6H, m, 4 × Ar*H*, plus 2 × Ar*H* in tosyl), 7.36–7.32 (1H, m, Ar*H*), 7.12–7.10 (2H, d, *J* 7.4, Ar*H* in tosyl), 3.91 (3H, s, OCH_3), 2.28 (3H, s, CH_3 in tosyl). δ_C 159.91 (d, $^1J_{C-F}$ 244, C_{Ar}-F), 157.28 (d, $^4J_{C-F}$ 1.9, C_{Ar}-OMe), 149.73 (C_{Ar} in tosyl), 141.53 (C_{Ar} in tosyl), 139.09, 135.96, 135.65, 131.99 (C_{Ar} in tosyl), 129.45 (C_{Ar} in tosyl), 127.58 (d, $^2J_{C-F}$ 26, C_{Ar}), 125.12 (d, $^2J_{C-F}$ 23, C_{Ar}), 120.14 (*C*-I), 117.63 (d, $^3J_{C-F}$ 8.1, C_{Ar}), 109.91 (d, $^3J_{C-F}$ 8.7, *C-I)*, 61.59 (O-CH_3), 24.72 (CH_3 in tosyl). *m*/*z* (FAB) 329 ($C_{13}H_{11}OFI^+$, 100%), 135 (10), 123 (14), 109 (15), 97 (14), 91 (27), 81 (28), 69 (39), 55 (56), 43 (37) (Found: 328.9868; $C_{13}H_{11}OFI^+$ requires: 328.9838).

4-Fluoro-3-methylphenyl(phenyl)iodonium tosylate 1j. Mp 158–163 °C. δ_H 8.27–8.22 (2H, m, Ar*H*), 7.98–7.95 (1H, m, Ar*H*), 7.68–7.64 (1H, t, *J* 9.4, Ar*H*), 7.59–7.47 (5H, m, 3 × Ar*H* plus 2 × Ar*H* in tosyl), 7.36–7.31 (1H, t, *J* 9.4, Ar*H*), 7.12–7.10 (2H, d, *J* 7.9, Ar*H*, tosyl), 2.29 (3H, s, CH_3 in tosyl), 2.25 (3H, s, CH_3). δ_C 166.58 (C_{Ar}-F, $^1J_{C-F}$ 251), 149.69, (C_{Ar} in tosyl), 142.66 (d, $^3J_{C-F}$ 6.0, C_{Ar}), 141.66 (C_{Ar} in tosyl), 139.41 (d, $^3J_{C-F}$ 8.8, C_{Ar}), 139.06, 136.04, 135.76, 135.61 (d, $^2J_{C-F}$ 26.9, C_{Ar}-Me), 132.08 (C_{Ar} in tosyl), 129.52 (C_{Ar} in tosyl), 122.54 (d, $^2J_{C-F}$ 23.54, C_{Ar}), 120.85 (*C*-I), 114.32 (d, $^4J_{C-F}$ 3.4, *C-I*), 24.74 (CH_3 in tosyl), 18.06 (CH_3). *m*/*z* (FAB) 313 ($C_{13}H_{11}FI^+$, 100%), 177 (12), 81 (10), 69 (17), 55 (21) (Found: 312.9890; $C_{13}H_{11}FI^+$ requires: 312.9890).

(2-Fluorobiphenyl-4-yl)(phenyl)iodonium tosylate 1k. Mp 207–211 °C. δ_H 8.42–8.39 (1H, dd, J_{H-H} 7.4, J_{H-F} 1.3, Ar*H*), 8.35–8.32 (2H, d, *J* 7.8, Ar*H*), 8.19–8.17 (1H, dd, J_{H-H} 8.2, J_{H-F} 1.2, Ar*H*), 7.72–7.67 (2H, t, *J* 8.0, Ar*H*), 7.59–7.46 (9H, m, 7 × Ar*H* plus 2 × Ar*H* in tosyl), 7.12–7.10 (2H, d, *J* 7.9, Ar*H* in tosyl), 2.28 (3H, s, CH_3 in tosyl). δ_C 162.60 ($^1J_{C-F}$ 254, C_{Ar}-F), 149.65 (C_{Ar} in tosyl), 141.61 (C_{Ar} in tosyl), 139.30, 137.46, 137.43, 137.21, 136.19, 136.04, 135.82, 135.79, 135.74, 135.42, 132.93 (d, $^4J_{C-F}$ 2.5, C_{Ar}), 132.82 (d, $^3J_{C-F}$ 9.2, C_{Ar}), 132.01 (C_{Ar} in tosyl), 130.45, 129.48 (C_{Ar} in tosyl), 127.05 (d, $^2J_{C-F}$ 26.7, C_{Ar}), 120.93 (*C*-I), 118.30 (d, $^3J_{C-F}$ 7.9, *C*-I), 24.72 (CH_3 in tosyl). *m*/*z* (FAB) 375 ($C_{18}H_{13}FI^+$, 100%), 248 ([$C_{18}H_{13}F$]$^+$, 16), 55 (6) (Found: 375.007; $C_{18}H_{13}FI^+$ requires: 375.0046).

(2,3-Dihydrobenzo[*b*]furan-5-yl)(phenyl)iodonium tosylate 1l. Mp 180–182 °C. δ_H 8.20–8.18 (2H, d, *J* 8.0, Ar*H*), 8.12 (1H, s, Ar*H*), 8.01–7.98 (1H, dd, *J* 8.4, *J* 1.6, Ar*H*), 7.66–7.62 (1H, t, *J* 7.6, Ar*H*), 7.53–7.46 (4H, m, 2 × Ar*H* plus 2 × Ar*H* in tosyl), 7.12–7.10 (2H, d, *J* 7.9, Ar*H* in tosyl), 6.92–6.89 (1H, d, *J* 8.7, ArH), 4.62–4.57 (2H, t, J_{AX} 8.8, OCH_2), 3.25–3.20 (2H, t, J_{AX} 8.8, CH_2), 2.28 (3H, s, CH_3 in tosyl). δ_C 166.65 (C_{Ar}-O), 149.75, (C_{Ar} in tosyl), 141.54 (C_{Ar} in tosyl), 140.35, 138.72, 136.48, 135.96, 135.73, 135.56, 132.00 (C_{Ar} in tosyl), 129.46 (C_{Ar} in tosyl), 120.97 (*C*-I), 116.20, 108.42, 76.14 (O-CH_2), 32.60 (CH_2), 24.73 (CH_3 in tosyl). *m*/*z* (FAB) 323 ($C_{14}H_{12}OI^+$, 100%), 246 ($C_8H_7OI^+$, 6), 91 (6), 69 (8), 55 (11) (Found: 322.9959; $C_{14}H_{12}OI^+$ requires 322.9932).

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