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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Synthesis of Alkynyliodonium Salts: Preparation of Phenyl(phenylethynyl)iodonium Trifluoroacetate

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Checked by David M. Guptill and Huw M. L. Davies
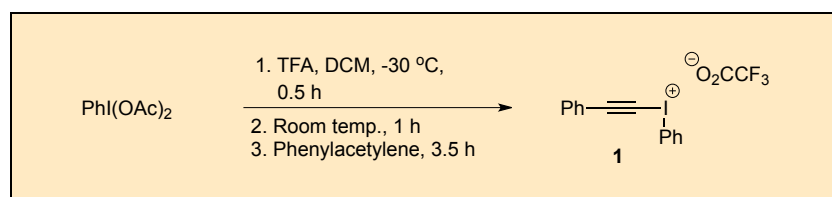
Procedure

> *Caution! Hypervalent iodine compounds are potentially explosive and should be handled taking appropriate precautions.*

Phenyl(phenylethynyl)iodonium trifluoroacetate (1) (Note 1). A 250-mL, two-necked, round-bottomed flask (Note 2), equipped with a 35 × 16 mm, PTFE-coated, oval magnetic stirrer bar, is charged with phenyliodo bis(acetate) (6.44 g, 20 mmol) (Note 3) followed by DCM (120 mL) (Note 4). The suspension is then stirred (Note 5) until dissolution is observed, at which point the solution is then cooled to between −30 °C and −35 °C using an acetone/dry ice bath (Note 6). Trifluoroacetic acid (3.06 mL, 40 mmol, 2.0 equiv) is added drop-wise over a period of 10 min via syringe pump and plastic syringe (Note 7) and stainless steel needle (20 gauge). The solution is then stirred for a further 0.5 h keeping the temperature between −30 °C and −35 °C before the reaction flask is removed from the acetone/dry ice bath

and stirred at room temperature for 1 h. At this point the solution is clear and colorless in appearance. Phenylacetylene (2.20 mL, 20 mmol, 1.0 equiv) is then added to the solution by syringe, as above, over a period of 10 min, and the reaction vessel is wrapped in aluminium foil and stirred in darkness (Note 8) for 3.5 h (Notes 9 and 10) at room temperature. The resulting clear pale yellow solution is then transferred to a 250-mL, single-necked, round-bottomed flask and concentrated to a volume of 30–40 mL (Note 11) *in vacuo* on a rotary evaporator, keeping the water bath at 25 °C. Diethyl ether (40 mL) followed by petroleum ether 40–60 (80 mL) are then added to the solution, mixing by 'swirling' manually, to initiate crystallization of the product, visible by the appearance of a white precipitate. The suspension is then stoppered before being wrapped in foil, placed in the freezer and kept in darkness at −25 °C for 48 h (Note 12). The flask is then removed from the freezer and left for 30 min to warm to room temperature before filtration of the white crystalline solid by suction using a medium-porosity sintered glass funnel and washed with diethyl ether (2 × 15 mL), agitating the crystals quickly with a spatula before the removal of each portion of diethyl ether (Note 13). The solid is then transferred to a pre-weighed vial and dried *in vacuo* for 12–24 h in a vacuum desiccator to give the product as a white crystalline solid 3.98 – 4.59 g, (48 – 55%) (Notes 14 and 15). Purity of the product can be determined by ^{1}H NMR initially, though, due to decomposition in solution (Notes 9 and 10), elemental analysis provides a more accurate indication of purity (Note 16). The described procedure has also been shown to be suitable for larger scale syntheses (Note 17).

Notes

1. Iodonium salts have, in certain cases, been reported to be explosive.[3] In the case of **1**, TGA and DSC data (*vide infra*) suggests that the material is not explosive, but it does experience a little decomposition around its melting point. Caution should, however, be taken in the synthesis and isolation of **1**, conducting all procedures behind a blast shield (e.g. 6 mm Perspex[®]) wherever possible, in addition to the protection afforded by the sash of a fume hood.
2. All reaction glassware was dried in an oven overnight (16 h) at 178 °C (submitters) or flame-dried (checkers) then evacuated under vacuum and back-filled with nitrogen or argon three times while hot, then

maintained under the inert atmosphere during the course of the reaction.

3. Checkers obtained (diacetoxyiodo)benzene (98%), phenylacetylene (98%) and trifluoroacetic acid (ReagentPlus, 99%) from Aldrich Chemical Company, and the reagents were used as received. Submitters obtained phenyliodo bis(acetate) (98+%) and phenylacetylene (98+%) from Alfa Aesar and trifluoroacetic acid (99.5%) was obtained from Apollo Scientific; all chemicals were used as supplied from new, unopened bottles.

4. Checkers obtained dichloromethane (>99.5%), diethyl ether (Laboratory grade) and petroleum ether (Certified ACS) from Fisher Scientific and were used as supplied. Submitters obtained dichloromethane (99+%), diethyl ether (99+%) and petroleum ether (40-60 °C) from Fisher and were used as supplied from new, unopened bottles.

5. Magnetic stirrer hotplates, 'IKAMAG$^{®}$ RCT Classic', stirred at ~633 rpm, setting 6.

6. Acetone/dry ice baths were also equipped with a 15 mm, PTFE-coated, cross-shaped, stir bar to ensure even temperature distribution.

7. Checkers purchased plastic syringes (Norm-ject®, 5 mL) from VWR. Submitters purchased plastic syringes ('BD Discardit™ II', 5 mL) from Fisher Scientific.

8. Alkynyliodonium salts have previously been shown to exhibit photoinitiation behavior under irradiative conditions[4] and should therefore be regarded as photosensitive.

9. Submitters noted that compound (**1**) decomposes in solution to 2-phenyl-2-oxoethyl trifluoroacetate (**2**), the major by-product of the reaction; prolonged reaction times encourage formation of this by-product.

10. Submitters provided the following characterization data and procedure for the preparation of by-product (**2**) (Scheme 1). This method was not repeated by the Checkers. *2-Phenyl-2-oxoethyl trifluoroacetate (2).* Phenyl (phenylethynyl)iodonium trifluoroacetate (**1**) (2.07 g, 4.96 mmol) is added to a 100-mL, single-necked, round-bottomed flask fitted with a water condenser and equipped with a 2 cm, PTFE-coated, oval magnetic stirrer bar. Chloroform (10 mL) and a few drops of water (*ca* 4 drops) are then added. The apparatus was equipped with a Schlenk line and the solution heated to reflux (70 °C, oil bath temperature) for 2 h under an atmosphere of nitrogen with stirring. The solution is then cooled,

dried with MgSO₄, filtered by suction, using a sintered glass funnel, then concentrated *in vacuo*. The crude product is then purified by flash chromatography (silica), eluting with dry hexane/dry toluene (1:1)
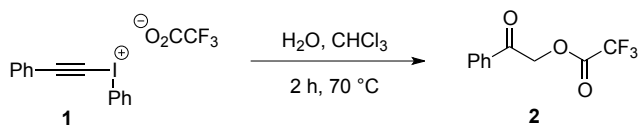
Scheme 1. Preparation of 2-phenyl-2-oxoethyl trifluoroacetate

(both dried by storing over sodium wire), to give the product as a white crystalline solid (0.40 g, 1.71 mmol, 34%). TLC R_f = 0.27 (1:1, hexane: toluene), mp = 54 °C – 55 °C (DCM: diethyl ether: petroleum ether 40 – 60), IR (v[cm⁻¹]) 1785, 1700, 1600, 1451, 1433, 1384, 1356, 1304, 1287, 1228, 1206, 1154, 1078, 1037, 1027, 1001; ¹H NMR (300 MHz, CDCl₃) δ : 5.60 (s, 2 H, CH₂), 7.54 (t, 2 H, *J* = 7.8 Hz, H-3′ , H-5′), 7.68 (tt, 1 H, *J* = 7.5, 1.8 Hz, H-4′), 7.92 (dd, 2 H, *J* = 8.4, 1.2 Hz, H-2′ , H-6′); ¹³C NMR (75 MHz, CDCl₃) δ: 68.6 (CH₂), 114.9 (q, *J* = 285.3 Hz, CF₃), 128.2 (C-3′, C-5′), 129.5 (C-2′, C-6′), 133.7 (C-1′), 134.9 (C-4′), 157.5 (q, *J* = 43.0 Hz, (CO)CF₃); ¹⁹F NMR (376 MHz, CDCl₃) δ: −74.1; ACPI-MS *m/z*: 231(32, [M-H]⁻), 227(100), 203(14), 183(5), 134(20); HRMS (ACPI): [M-H]⁻ calcd. for C₁₀H₆F₃O₃: 231.0275. Found 231.0273; Anal. calcd. for C₁₀H₇F₃O₃: C, 51.74; H, 3.04. Found: C, 51.66; H, 2.98.

11. The volume in the flask was assessed by filling the flask with 35 mL of DCM prior to its use and marking the level with an indelible marker.

12. The total time taken from the end of the 3.5 h stirring period to placing the flask in the freezer was no longer than 30 minutes.

13. The submitters noted that the mother liquor, including all ether washings, can be 'seeded' with a small amount of the pure product and replaced in the freezer (−25 °C) for 7 days to recover a second batch of the product using method outlined above; recovery is 0.55 – 1.47 g.

14. *Phenyl(phenylethynyl)iodonium trifluoroacetate (1)*: mp = 90 – 92 °C (dec.); ¹H NMR (600 MHz, CDCl₃) δ: 7.37 (t, *J* = 7.5 Hz, 2 H), 7.43 (t, *J* = 7.5 Hz, 1 H), 7.46-7.52 (m, 4 H), 7.60 (t, *J* = 7.4 Hz, 1 H), 8.17 (d, *J* = 8.0 Hz, 2 H); ¹³C NMR (100 MHz, CDCl₃) δ: 45.2, 103.9, 115.6 (q, *J* = 292 Hz), 120.5, 120.6, 128.7, 130.8, 131.9, 132.1, 132.9, 133.6, 162.7 (q, *J* = 36.2 Hz); IR (solid): 3077, 2166, 1666, 1185, 1124 cm⁻¹; HRMS (NSI): *m/z* calcd. for

$C_{14}H_{10}I$ ([M - TFA]$^+$): 304.9822. Found: 304.9821; Anal. calcd. for $C_{16}H_{10}F_3IO_2$: C, 45.96; H, 2.41. Found: C, 46.14; H, 2.35.

15. Submitters reported yields of 4.68 – 5.05 g (56 – 60%). Submitters provided the following additional characterization data for product (**1**): ^{19}F NMR (376 MHz, [D$_6$]DMSO) δ: −73.6.

16. Samples (30 mg) were put in small glass vials then wrapped in foil and sent by post for elemental analysis.

17. Submitters also performed the reaction in triplicate on a 100 mmol scale showing some improvements in yield, to provide 22.80 – 24.74 g from first batch followed by 1.08 – 2.30 g (total yield: 23.87 – 26.01 g, 57 – 62%).


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Discussion

Alkynyliodonium salts are highly versatile reactive intermediates[5] and as such, have been used in a number of cycloaddition reactions[6] including 1,3-dipolar cycloadditions with nitrile-oxides,[7] diazoketones[8] and azides[8] as well as Diels-Alder chemistry.[9] Further syntheses of several complex ring systems from alkynyliodonium salts have been reported *via* carbene insertion reactions (Scheme 2).[10]
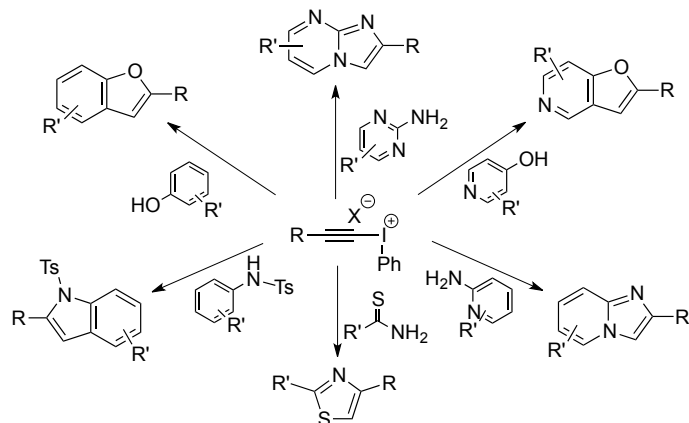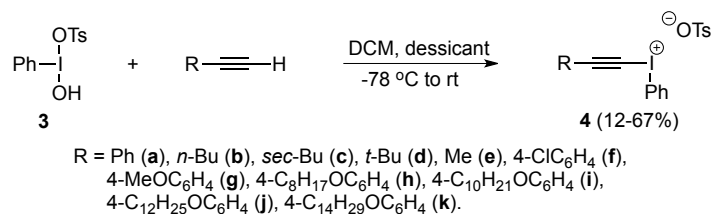
Scheme 2. Synthesis of heteroaromatics from alkynyliodonium salts[10b, 10d-m]

In addition, alkynyliodonium salts have been exploited in terms of their photosensitivity,[4] oxidizing nature and, most commonly, their potential for alkynylation reactions.[5, 11]

The most common methods for the synthesis of alkynyliodonium salts are *via* the use of Koser's Reagent ([hydroxy(tosyloxy)iodo]benzene, **3**)[12] and Stang's Reagent ([cyano(trifloxy)iodo]benzene, **5**).[13]

Koser's reagent is commercially available and non-toxic making it a highly attractive precursor to alkynyliodonium salts, however, it has been shown that the yields can be low due to formation of the corresponding vinylic species as a result of tosylate addition.[14] It was shown that alkynes with bulky groups afforded the desired product in high yields, whereas those with less steric hindrance in the β-acetylenic position afforded high amounts of, or even exclusively, the addition products, phenyl[β-(tosyloxy)vinyl]iodonium tosylates.[14a, 15]

R = Ph (**a**), *n*-Bu (**b**), *sec*-Bu (**c**), *t*-Bu (**d**), Me (**e**), 4-ClC$_6$H$_4$ (**f**),
4-MeOC$_6$H$_4$ (**g**), 4-C$_8$H$_{17}$OC$_6$H$_4$ (**h**), 4-C$_{10}$H$_{21}$OC$_6$H$_4$ (**i**),
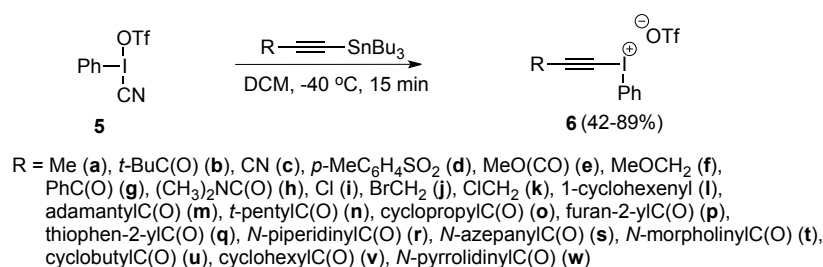4-C$_{12}$H$_{25}$OC$_6$H$_4$ (**j**), 4-C$_{14}$H$_{29}$OC$_6$H$_4$ (**k**).

Scheme 3. Synthesis of alkynyliodonium tosylates from Koser's Reagent[7b, 16]

The addition of a desiccant to the reaction mixture has proven advantageous allowing formation of a range of novel analogues in spite of low steric bulk in the β-acetylenic position (Scheme 3).[16a]

Though triflate anions have also been shown to add,[17] the lower nucleophilicity makes alkynliodonium triflates much less susceptible to decomposition and thus Stang's reagent has found a much wider application in the synthesis of alkynyliodonium salts.[18]

Stang demonstrated the extensive range of functionality possible in the β-alkynyl position of alkynyliodonium salts from the Stang reagent and, although compounds **6b–w** (Scheme 4) had to be isolated at low temperature, the synthetic route proved that alkynyliodonium triflates could be synthesized bearing electron-withdrawing β-alkynyl functionality, without significant triflate addition to the β-alkynyl position.[18a]

R = Me (**a**), t-BuC(O) (**b**), CN (**c**), p-MeC$_6$H$_4$SO$_2$ (**d**), MeO(CO) (**e**), MeOCH$_2$ (**f**),
PhC(O) (**g**), (CH$_3$)$_2$NC(O) (**h**), Cl (**i**), BrCH$_2$ (**j**), ClCH$_2$ (**k**), 1-cyclohexenyl (**l**),
adamantylC(O) (**m**), t-pentylC(O) (**n**), cyclopropylC(O) (**o**), furan-2-ylC(O) (**p**),
thiophen-2-ylC(O) (**q**), N-piperidinylC(O) (**r**), N-azepanylC(O) (**s**), N-morpholinylC(O) (**t**),
cyclobutylC(O) (**u**), cyclohexylC(O) (**v**), N-pyrrolidinylC(O) (**w**)

Scheme 4. Synthesis of alkynyliodonium triflates bearing electron-withdrawing β-alkynyl functionality from Stang's reagent[9b, 10c 18]

It was noted in 1993[9b] that many functionalised alkynyliodonium salts could not be prepared in satisfactory manner from Koser's reagent, Zefirov's reagent, iodosylarenes or related compounds. Stang's reagent, however, has made possible the synthesis of the most comprehensive library of over forty highly functionalized alkynyliodonium salts to date.[9b, 10c, 11a, 18a, 19]

Despite their widespread use, a number of problems remain to be resolved with regard to the synthesis and isolation of alkynyliodonium salts:

- Many procedures require use of the stannous alkynyl-derivatives creating problems with isolation and toxicity issues.

- The most versatile and commonly used of the available precursors, Stang's Reagent,[13] produces the noxious asphyxiant HCN as a by-product.
- Many syntheses require use of iodosylbenzene (PhIO), which is known to disproportionate to the highly explosive iodylbenzene (PhIO$_2$).[20]

Trifluoroacetate analogues have previously been reported as too unstable and hydroscopic to be of practical interest.[21] We have found that not only are they stable isolatable crystalline solids, but they also address many of the problems associated with other syntheses, by the use of un-modified, terminal alkynes and commercially available, non-explosive starting materials with the production of no noxious by-products. The yields of the reaction are also comparable to those of other approaches and the purification is by far the simplest we have experienced.

References

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2. Department of Isotope Chemistry and Metabolite Synthesis, Sanofi-Aventis, Alnwick, NE66 2JH, UK. *Current address*: Department of Isotope Chemistry, Covance Laboratories, Alnwick, Northumberland, UK, NE66 2JH.
3. (a) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991,** *113*, 7277–7287; (b) Tohma, H.; Takizawa, S.; Maegawa, T.; Kita, Y. *Angew. Chem.* **2000,** *112*, 1362–1364; (c) Stang, P. J. *Chem. Eng. News* **1989**; *67*, 4.
4. Hofer, M.; Liska, R. *J. Polym. Sci., Part A: Polym. Chem.* **2009,** *47*, 3419–3430.
5. Wirth, T.; Ochiai, M.; Varvoglis, A.; Zhdankin, V. V.; Koser, G. F.; Tohma, H.; Kita, Y. *Hypervalent Iodine Chemistry.* Springer: London, 2003.
6. Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 274–285.
7. (a) Kitamura, T.; Mansei, Y.; Fujiwara, Y., *J. Organomet. Chem.* **2002**, *646*, 196–199; (b) Kotali, E.; Varvoglis, A.; Bozopoulos, A., *J. Chem. Soc., Perkin Trans. 1* **1989**, 827-832; (c) Stang, P. J.; Murch, P., *Tetrahedron Lett.* **1997**, *38*, 8793–8794.

8. Maas, G.; Regitz, M.; Moll, U.; Rahm, R.; Krebs, F.; Hector, R.; Stang, P. J.; Crittell, C. M.; Williamson, B. L. *Tetrahedron* **1992**, *48*, 3527–3540.

9. (a) Murch, P.; Arif, A. M.; Stang, P. J. *J. Org. Chem.* **1997**, *62*, 5959–5965; (b) Williamson, B. L.; Stang, P. J.; Arif, A. M. *J. Am. Chem. Soc.* **1993**, *115*, 2590-2597; (c) Shimizu, M.; Takeda, Y.; Hiyama, T. *Chem. Lett.* **2008**, *37*, 1304–1305.

10. (a) Ochiai, M.; Kunishima, M.; Tani, S.; Nagao, Y. *J. Am. Chem. Soc.* **1991**, *113*, 3135–3142; (b) Feldman, K. S.; Bruendl, M. M.; Schildknegt, K. *J. Org. Chem.* **1995**, *60*, 7722–7723; (c) Williamson, B. L.; Tykwinski, R. R.; Stang, P. J. *J. Am. Chem. Soc.* **1994**, *116*, 93–98; (d) Kitamura, T.; Tsuda, K.; Fujiwara, Y. *Tetrahedron Lett.* **1998,** *39*, 5375–5376; (e) Liu, Z.; Chen, Z. C.; Zheng, Q. G. *Synth. Commun.* **2004**, *34*, 361–367; (f) Wipf, P.; Venkataraman, S. *J. Org. Chem.* **1996**, *61*, 8004–8005; (g) Zhang, P. F.; Chen, Z. C. *Synthesis* **2001**, 358–360; (h) Miyamoto, K.; Nishi, Y.; Ochiai, M. *Angew. Chem., Int. Ed. Engl.* **2005**, *44*, 6896–6899; (i) Liu, Z.; Chen, Z.-C.; Zheng, Q.-G. *J. Heterocycl. Chem.* **2003**, *40*, 909–912; (j) Kitamura, T.; Zheng, L.; Fukuoka, T.; Fujiwara, Y.; Taniguchi, H.; Sakurai, M.; Tanaka, R. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1511–1515; (k) Kitamura, T.; Zheng, L.; Taniguchi, H.; Sakurai, M.; Tanaka, R. *Tetrahedron Lett.* **1993**, *34*, 4055–4058; (l) Nikas, S.; Rodios, N.; Varvoglis, A. *Molecules* **2000**, *5*, 1182–1186; (m) Feldman, K. S.; Perkins, A. L. *Tetrahedron Lett.* **2001**, *42*, 6031–6033.

11. (a) Stang, P. J.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1990**, *112*, 6437–6438; (b) Stang, P. J.; Crittell, C. M. *Organometallics* **1990**, *9*, 3191–3193; (c) Canty, A. J.; Rodemann, T. *Inorg. Chem. Commun.* **2003**, *6*, 1382–1384; (d) Stang, P. J.; Tykwinski, R. *J. Am. Chem. Soc.* **1992,** *114*, 4411–4412; (e) Ochiai, M.; Kunishima, M.; Nagao, Y.; Fuji, K.; Fujita, E. *J. Chem. Soc., Chem. Commun.* **1987**, 1708–1709; (f) Ochiai, M.; Nagaoka, T.; Sueda, T.; Yan, M.; Chen, D. W.; Miyamoto, K. *Org. Biomol. Chem.* **2003**, *1*, 1517–1521.

12. (a) Koser, G. F.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1981**, *46*, 4324–4326; (b) Zhdankin, V. V.; Tykwinski, R.; Berglund, B.; Mullikin, M.; Caple, R.; Zefirov, N. S.; Kozmin, A. S. *J. Org. Chem.* **1989**, *54*, 2609–2612; (c) Neiland, O. Y.; Karele, B. Y. *Zh. Org. Khim.* **1970**, *6*, 885-886.

13. Zhdankin, V. V.; Crittell, C. M.; Stang, P. J.; Zefirov, N. S. *Tetrahedron Lett.* **1990**, *31*, 4821–4824.

14. (a) Rebrovic, L.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 4700–4702; (b) Lodaya, J. S.; Koser, G. F. *J. Org. Chem.* **1990**, *55*, 1513–1516.

15. Stang, P. J.; Kitamura, T.; Ishihara, K.; Yamamoto, H. *Org. Synth. Coll. Vol.* **1998**, *9*, 477–483.
16. (a) Stang, P. J.; Surber, B. W.; Chen, Z. C.; Roberts, K. A.; Anderson, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 228-235; (b) Kitamura, T.; Lee, C. H.; Taniguchi, H.; Matsumoto, M.; Sano, Y. *J. Org. Chem.* **1994**, *59*, 8053–8057.
17. Kitamura, T.; Furuki, R.; Taniguchi, H.; Stang, P. J. *Tetrahedron* **1992**, *48*, 7149–7156.
18. (a) Stang, P. J.; Williamson, B. L.; Zhdankin, V. V. *J. Am. Chem. Soc.* **1991**, *113*, 5870–5871; (b) Feldman, K. S.; Bruendl, M. M.; Schildknegt, K.; Bohnstedt, A. C. *J. Org. Chem.* **1996**, *61*, 5440–5452.
19. (a) Stang, P. J.; Zhdankin, V. V.; Tykwinski, R.; Zefirov, N. S. *Tetrahedron Lett.* **1992**, *33*, 1419–1422; (b) Stang, P. J.; Tykwinski, R.; Zhdankin, V. V. *J. Org. Chem.* **1992**, *57*, 1861–1864.
20. (a) Lucas, H. J.; Kennedy, E. R., *Org. Synth. Coll. Vol.* **1955**, *3*, 485–487; (b) Bell, R.; Morgan, K. J. *J. Chem. Soc.* **1960**, *245*, 1209–1214; (c) McQuaid, K. M.; Pettus, T. R. R. *Synlett* **2004**, 2403–2405.
21. Merkushev, E. B.; Karpitskaya, L. G.; Novosel'tseva, G. I. *Dokl. Akad. Nauk SSSR* **1979**, *245*, 607–610.

Appendix
Chemical Abstracts Nomenclature (Registry Number)

Phenyliodo bis(acetate): Iodine, bis(acetato-κ*O*)phenyl-; (3240-34-4)
Trifluoroacetic acid: Acetic acid, 2,2,2-trifluoro-; (76-05-1)
Phenylacetylene: Benzene, ethynyl-; (536-74-3)

Luke Dixon was born in Cuckfield, England, in 1984. He obtained his BSc in Chemistry (2005) and MSc in Drug Chemistry (2007) from the Universities of Sheffield and Newcastle respectively. In 2007, he began his PhD with Dr M. A. Carroll in the area of alkynyliodonium salts. Upon completion of his PhD (2011) he moved into the synthesis of complex diaryliodonium salts as precursors to fluorine-18 radiolabelled PET imaging agents.

Michael Carroll gained his BSc and PhD, under the supervision of Dr D. A. Widdowson, from Imperial College London. A number of research positions followed, most notably with Prof. A. B. Holmes FRS at the University of Cambridge. Michael was appointed to the staff at Newcastle University in 2001 where the focus of his research programme is on the development of novel synthetic methodology using hypervalent iodine compounds as reactive intermediates. A key application is the development of diaryliodonium salts as selective precursors to fluorine-18 radiolabelled PET imaging agents.

George Ellames was born in London, UK in 1952 and gained his BSc in Chemistry from the University of Southampton in 1973 and his PhD in Diterpene Biosynthesis under the supervision of Jim Hanson at the University of Sussex in 1976. After 8 years in Medicinal Chemistry with Searle at High Wycombe in the UK, where he led Anti-Infective Chemistry, he moved to Alnwick in Northumberland where he has built up and led Isotope Chemistry and Metabolite Synthesis since 1986 under a succession of site ownerships (Sterling Winthrop, Sanofi, Sanofi-Synthelabo, sanofi-aventis and now Covance Laboratories). He has been heavily involved with the International Isotope Society with a continuing interest in the synthesis and applications of isotopically labelled compounds.

Tom Gregson was born in Sunderland, UK in 1979 and gained his MChem with a Year in Industry, spent with Merck, Sharpe and Dohme, Harlow, from the University of Sheffield in 2001. After achieving his PhD under the supervision of E. J. Thomas at Manchester University in 2005, investigating the total synthesis of the Bryostatins, he moved into industry. He has worked the last six years at Alnwick, Northumberland as part of the Isotope Chemistry and Metabolite Synthesis group, formerly with sanofi-aventis and currently with Covance laboratories.

David M. Guptill was born in Fridley, MN in 1986. He earned his B.A. in ACS Chemistry from Gustavus Adolphus College in Saint Peter, MN in 2005. Currently a fifth-year graduate student in the laboratory of Professor Huw M. L. Davies at Emory University, David's research involves expanding the scope of selective C–H functionalization reactions of donor/acceptor rhodium-carbenoids.