

Scheme 2 Dichotomous reactivity of iodoarenes **1** under photolysis and radical-forming conditions implicates the intermediacy of triplet aryl cation ³[3].

contrast to analogous reactions conducted under radical forming conditions, we saw none of the ring expansion product **20**, suggesting that these reactions also proceed *via* triplet aryl cation **19** rather than aryl radical **18**. Notably, extrusion of carbon monoxide from benzoanthracenones **21** did not occur since the biradical formed by a Norrish type 1 cleavage, ³[24], now gives biradical **23** on decarbonylation rather than a quinodimethane. Nor did the outcome appear unduly influenced by substituents on the tetralone ring, indicating that the lower acidity of the benzylic protons in phenonium ion **22**, compared to **13**, reduces the tendency to form **7a,8**-dihydrobenzofluorenone **25**. The greater propensity for 6-ring closure to tetralones in analogous radical reactions may also be pertinent as it bears testament to the reduction of strain in the tetralone series following *ortho*-cyclisation. Indeed, for substrates lacking mesomeric donor substituents on the iodinated arene, *e.g.* **17d/e**, reactions may proceed, in part, by C-I bond homolysis and radical cyclisation.

Extensions to related heterocyclic analogues **26–29** were next examined and, for the most part, gave good yields of the *ortho*-cyclisation products **30–33** (Scheme 5 and Fig. 1).¹³ Benzo-oxazinone **29** was an outlier, giving **33** in 24% isolated yield. The dichotomy can again be explained by a switch in the favoured mode of collapse of the phenonium ion intermediate **35**, from cation **34** to cation **36**.

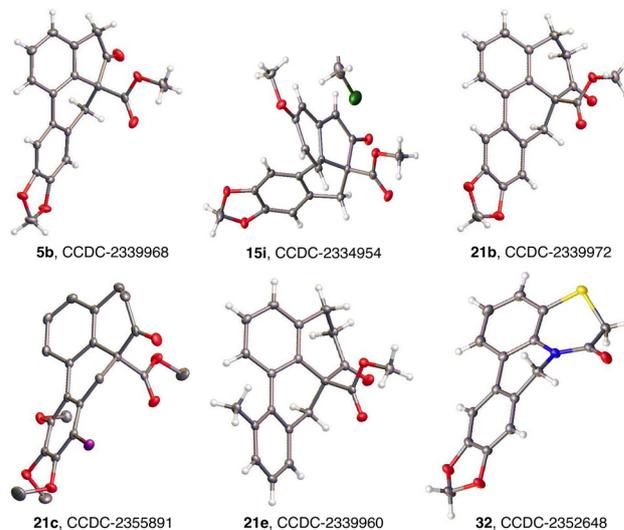
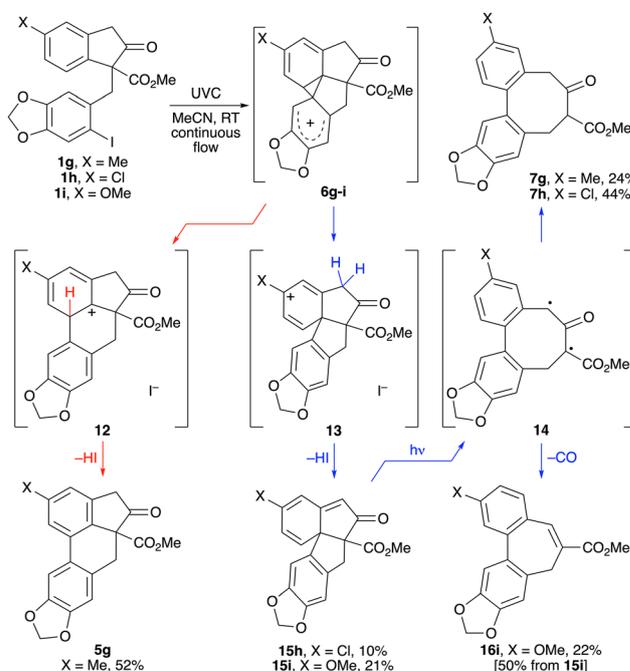


Fig. 1 X-ray crystal structures for **5b** (Scheme 2), **15i** (Scheme 3), **21b**, **c** and **e** (Scheme 4), and **32** (Scheme 5).

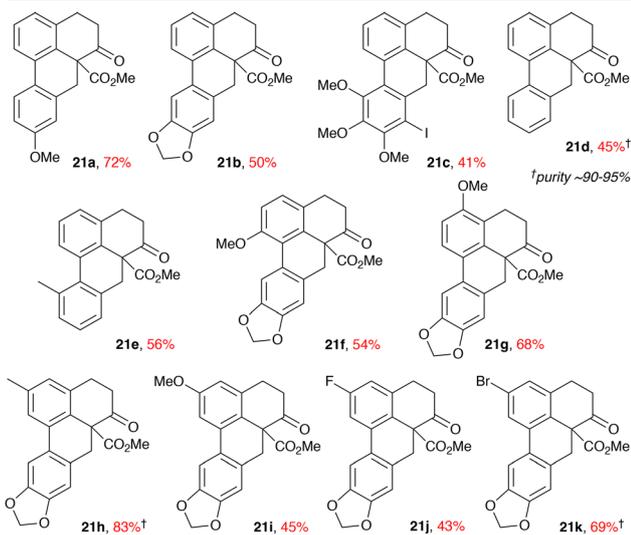
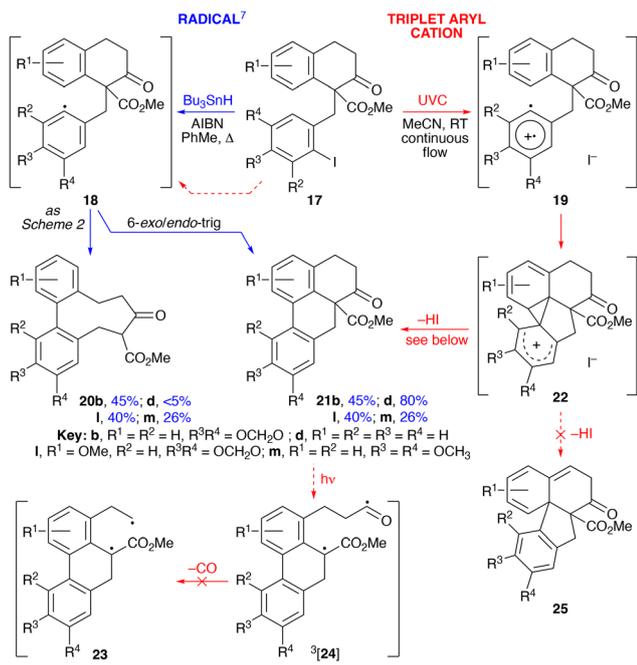
Finally, photolysis of 3,3-*bis*-(*o*-iodobenzyl)indolinone **37** under continuous flow induced sequential 6- and 5-membered ring formation to give azapropellane **38** in a remarkable 72% isolated yield (Scheme 6). The structure of the product was confirmed by X-ray crystallography (CCDC-2334898).

In conclusion, photocyclisations of *o*-iodobenzylindanones and tetralones in acetonitrile give markedly different outcomes to analogous reactions conducted under radical forming conditions. Thus, while radical reactions respectively promote ring expansion to dibenzo-cyclooctanes and cyclononanes *via* a



Scheme 3 The influence of C5 indanone substituents of the course of the reaction.

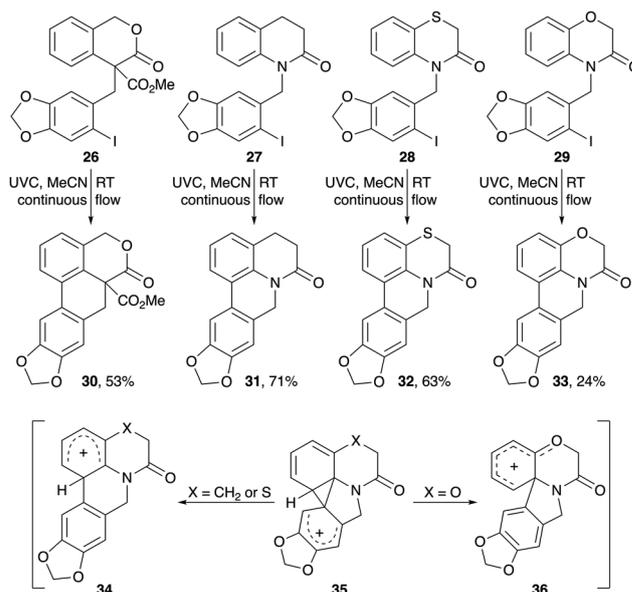




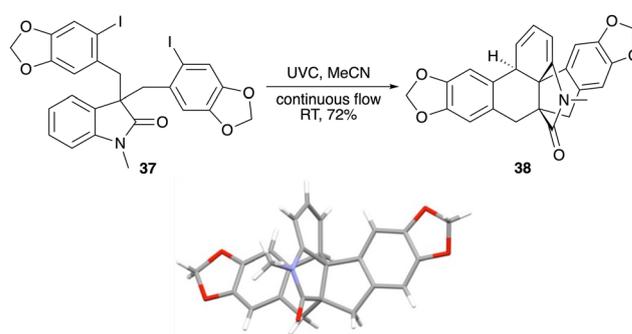
Scheme 4 Photocyclisations of 1-(*o*-iodobenzyl)-2-tetralones give benzanthracenones in moderate to good yield.

5-*exo*-trig *ipso*-cyclisation and ring expansion,⁷ photochemical reactions induce *ortho*-cyclisation implicating the intermediacy of triplet aryl cations. Cyclisations to 2-indanones and 2-tetralones differ in that the former produce acephenanthrylenones that react further by photo-extrusion of carbon monoxide to give dibenzoisochromenones,¹⁰ while the latter produce the homologous benzo[*a*]phenalenones which are not prone to photo-extrusion of carbon monoxide. We are currently examining further intramolecular photocyclisation reactions of aryl iodides to better understand the opportunities triplet aryl cation intermediates present in the context of synthetic chemistry.

Marian Powderly and Toby Lindup conducted the bulk of the experimental work with support from Edward Jackman.



Scheme 5 Extension to related fused heterocycles.



Scheme 6 A tandem cyclisation leading to an azapropellane.

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Conflicts of interest

There are no conflicts of interest to declare.

Data availability

The data supporting this article has been included in the main text and/or the accompanying supplementary information (SI). Supplementary information: full experimental accounts for the preparation of starting materials and products along with characterisation data [where appropriate, MP, IR, UV, LRMS,



HRMS, ^1H NMR, ^{13}C NMR and ^{19}F NMR data]. Copies of NMR spectra accompany each account and include expansions of key regions. X-ray data is provided for 7 representative products. See DOI: <https://doi.org/10.1039/d5cc05185a>.

CCDC 2334898, 2334954, 2339960, 2339968, 2339972, 2352648 and 2355891 contain the supplementary crystallographic data for this paper.¹⁴

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