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An Efficient Synthesis of Substituted Chrysenes

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Abstract: Substituted chrysenes have been swiftly synthesised by the 6-*endo-dig* cyclisation of ethynylnaphthalenes using platinum(II) chloride. Cyclisation precursors were directly prepared from commercially available 2-bromoaldehydes in a telescoped synthetic procedure involving a Cannizzaro triggered cascade and subsequent dehydration and desilylation. This short synthetic procedure allows rapid access to derivatives of biologically active molecules with useful electronic properties.

Introduction

Chrysene (C₁₈H₁₂) is a polycyclic aromatic hydrocarbon (PAH) that is formed during incomplete combustion of carbon rich fuels^[1] and was the first PAH to be discovered in uncontaminated soil samples.^[2] Whilst several studies have shown that chrysene and its metabolites,^[3] *trans*-1,2-dihydroxy-1,2-dihydrochrysene and *trans*-3,4-dihydroxy-3,4-dihydrochrysene (Scheme 1a) are carcinogenic and mutagenic,^[4] it has also been reported that some substituted chrysenes, due to their DNA intercalating nature, show anticancer activity.^[5] Due to their electronic properties chrysenes also have synthetic uses as single electron transfer mediators,^[6] mechanistic probes^[7] and have applications in the field of organic electronics.^[8, 9] The two most common synthetic routes to chrysenes are the photochemical cyclisations of styrylnaphthalenes^[10] and metal catalysed cyclisations of aromatic acetylenes.^[8,11] Our efficient synthesis allows the rapid formation of substituted chrysenes, under simple, benign conditions from readily available commercial materials. As we are able to design chrysene substrates with substitution on both terminal rings and also access substitution patterns that are difficult to control with other synthetic methods^[10] (controlled substitution in the 2- and 4- positions), this work is perfectly complimentary to that which has already been published.

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