NEW GAS-PHASE CYCLISATION REACTIONS LEADING TO BENZOFURANS AND FLAVONES

by

Da Chang

Thesis presented towards the degree of

MASTER OF PHILOSOPHY

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ACKNOWLEDGMENTS

Many people have given me support and encouragement, especially Dr. R. Alan Aitken. Thanks to Alan's patient guidance and help. Without Alan's help I could not have conducted my research so fluently.

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LECTURE COURSES ATTENDED

Organic Research Seminars	1 year attendance
School Colloquia	1 year attendance
Heterocyclic and Pericyclic Chemistry	Dr. R. A. Aitken and Dr. Euan Kay
Chemistry of Sulfur and Related Elements	Dr. R. A. Aitken

ABSTRACT

The main focus of the project was the synthesis of oxo-stabilised phosphonium ylides with an *o*-methoxy functionalised benzene ring, and flash vacuum pyrolysis (FVP) of the ylides leading to cyclisation forming a flavone or ring-fused benzopyranone.

The first class examined were β,γ-dioxo ylides with two carbonyls on the same side. Two compounds of this type were prepared and in one case the structure was determined by X-ray diffraction. Upon FVP, the ylides underwent the desired extrusion of Ph_3PO and a flavone was formed, however a large amount of a benzofuran byproduct was produced regardless of the temperature.

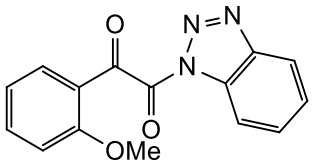
To elucidate the mechanism of the apparently novel heterocyclic reaction by which the flavone was decarbonylated to give the benzofuran, both flavone and 3-iodoflavone were prepared. While flavone was stable to FVP, the 3-iodoflavone readily underwent decarbonylation to give 2-phenylbenzofuran as the main product, thus confirming that decarbonylation occurred via a spiro radical intermediate. In an attempt to overcome this problem, ylides in which one carbonyl was protected as a 1,3-dioxolane were designed but all routes to these failed and the target structures were not accessible, which was mainly attributed to the neopentyl effect.

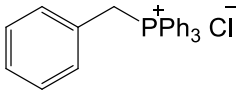
Despite the possibility of Ph_3PO extrusion occurring on either side, leading to mixtures of cyclised products, a range of β,β'-dioxo ylides were prepared and their FVP was examined in one case. As expected, the product mixture was quite complex but three different fused tetracyclic products were tentatively identified.

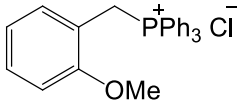
Attempts were made to use ylides with both carbonyl and thiocarbonyl groups present to achieve regioselective extrusion, but surprisingly there was almost equal extrusion of Ph_3PO and Ph_3PS suggesting that no useful selectivity could be achieved in this way.

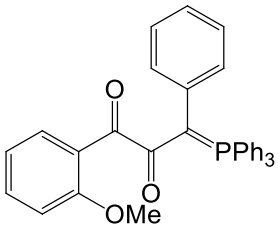
Finally one example of an ylide with stabilising imidoyl and carbonyl groups was prepared and its FVP did result in exclusive elimination of Ph_3PO to give the desired iminobenzopyran, although a higher temperature will apparently be required to bring about a cascade reaction leading to a tetracyclic product.

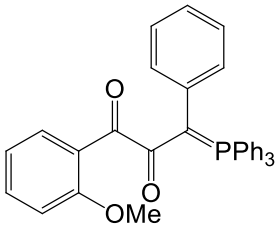
CONTENTS

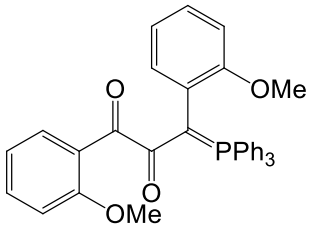


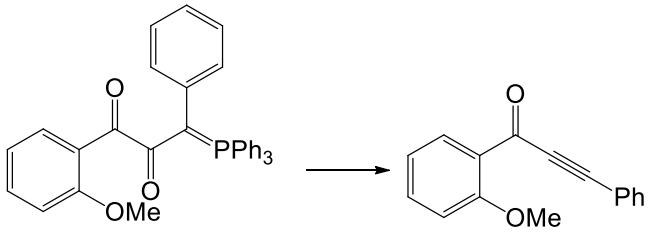


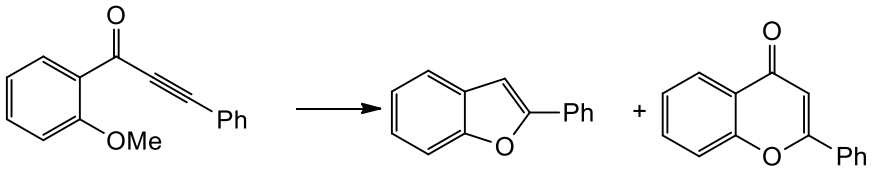


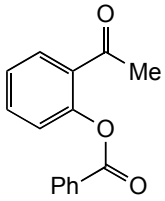


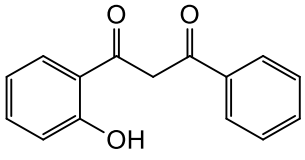


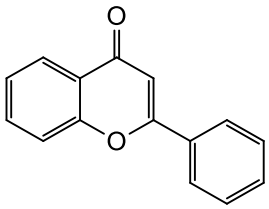


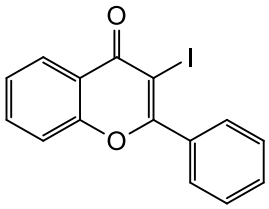


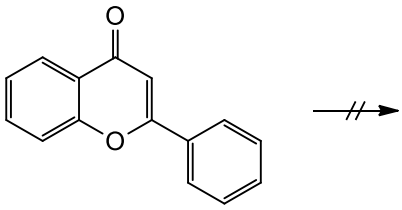


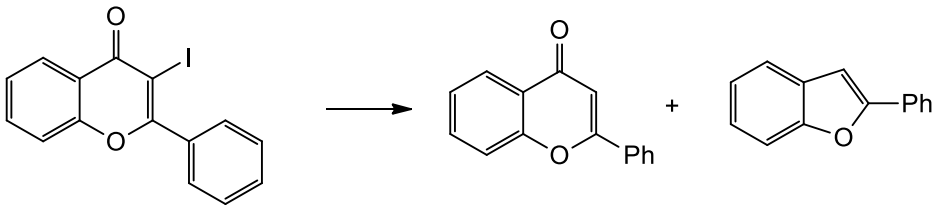


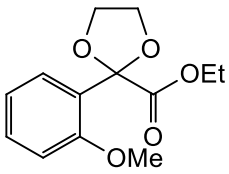


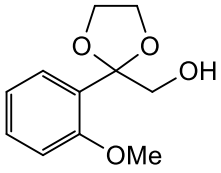


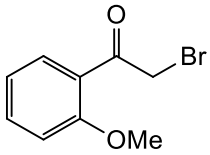


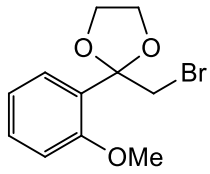


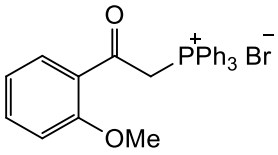


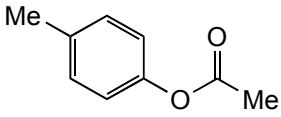


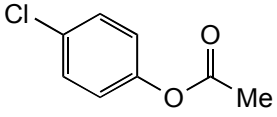


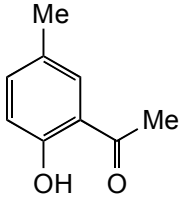


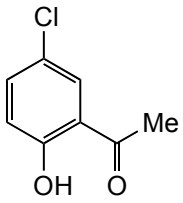












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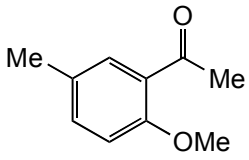

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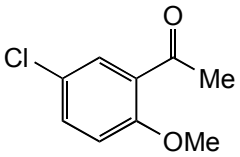

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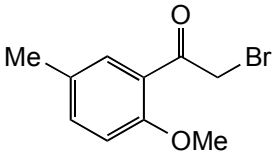

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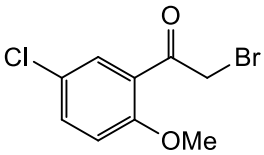

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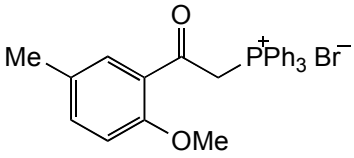

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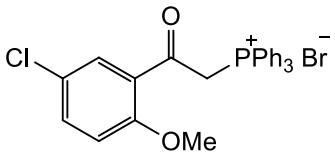
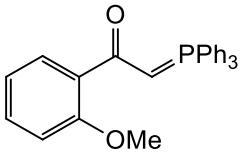
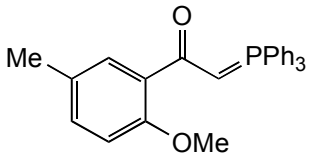
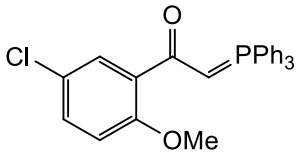
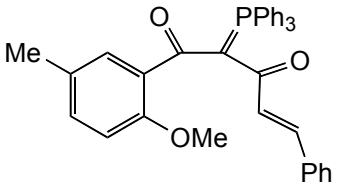


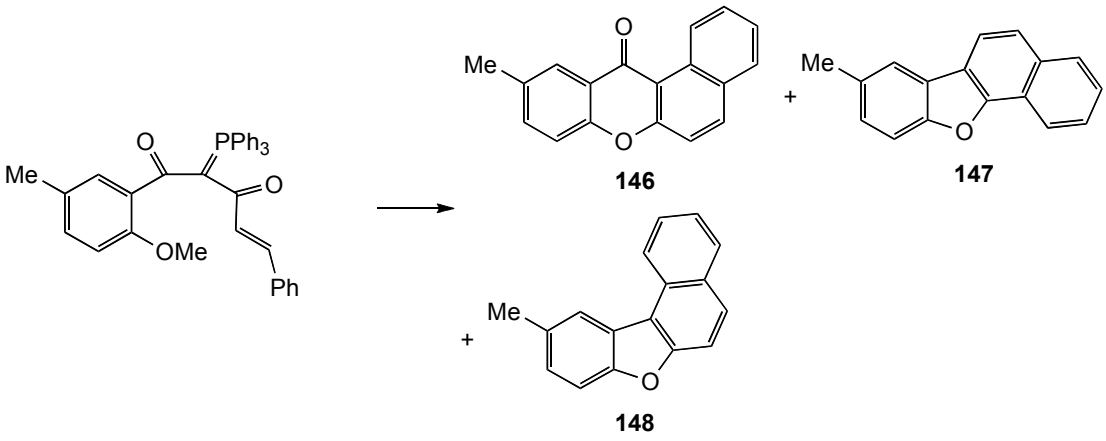
2 Preparation of Ylides

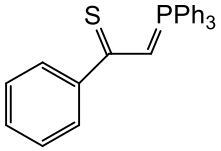


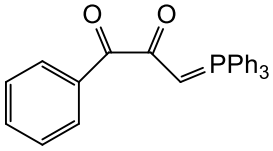


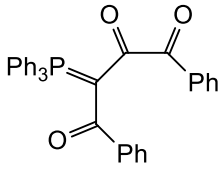


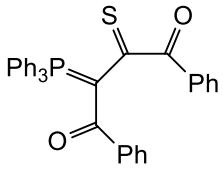


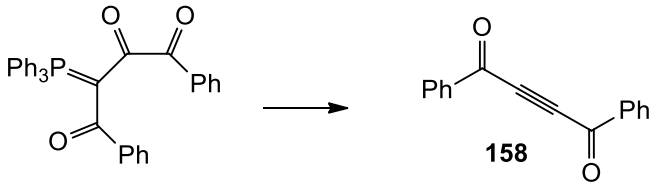


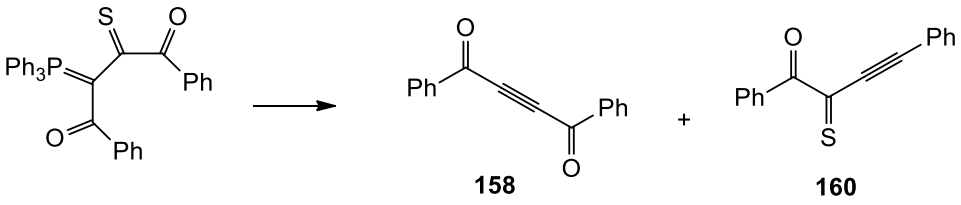


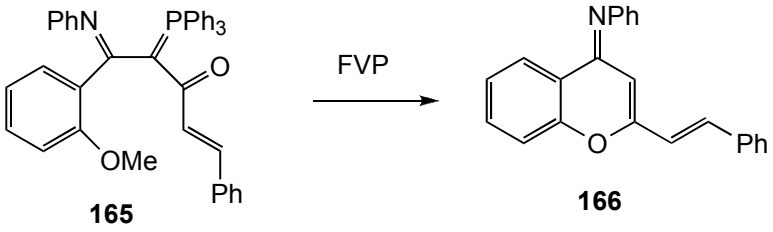












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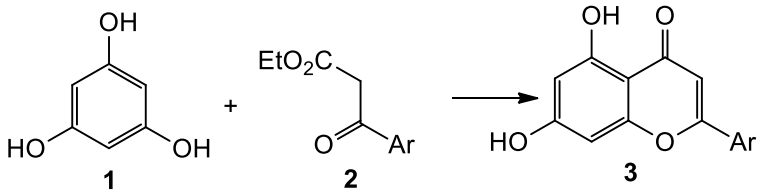
RESULTS AND DISCUSSION

INTRODUCTION

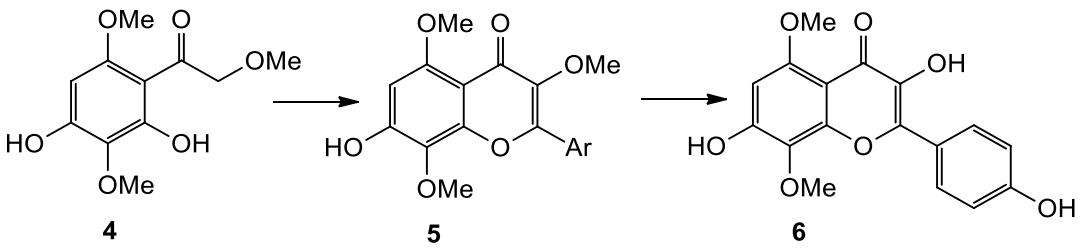
A Synthetic Routes to Flavones using Phosphonium Ylides

1 General Background

Flavones have been discovered largely in plants, especially in herbs and cereals. There is no established record of their being produced in animals. Many members of the family are highly coloured and play a vital role in the ecology of plants.[1] Two standard methods of chromone synthesis have been widely used for the preparation of flavones. In the first of these, a benzenepolyol such as resorcinol **1** is condensed with a substituted benzoylacetic ester **2**. The reaction was carried out without a catalyst by heating the mixture under reduced pressure so that ethanol and water were removed as chromone **3** formed.[2]



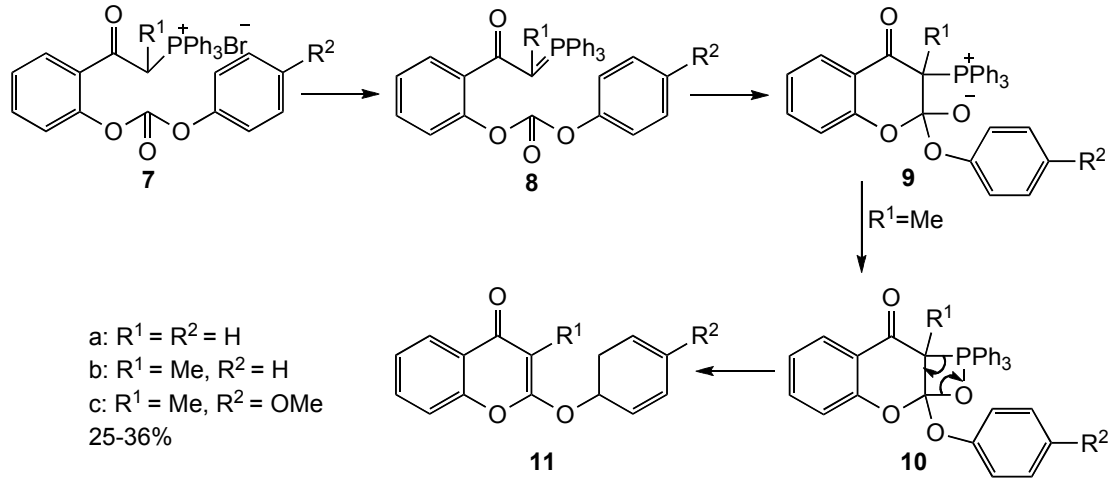
Another chromone synthesis has been more widely used, which was introduced by Allan and Robinson.[3] In this the hydroxyl group of an α-hydroxyketone was protected by methylation to give **4**, which was then heated with the anhydride of the appropriate aromatic carboxylic acid. The resulting aryl benzoate could then cyclise to form **5** and then undergo deprotection to form **6**.



2 Conventional Wittig reaction

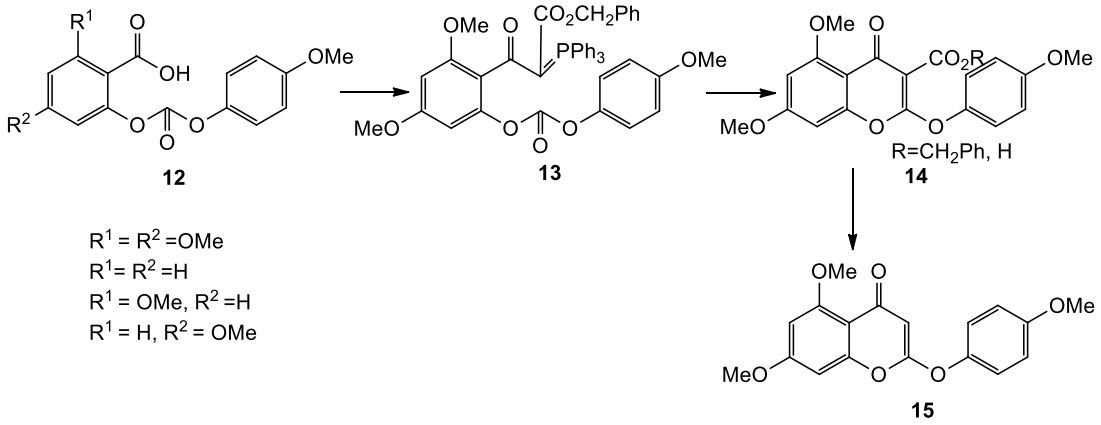
Because of their effective role in pharmacology and physiology, scientific and public interest in flavones has grown enormously. Wittig reactions have been found to provide an important method for construction of various carbon frameworks in synthetic chemistry; this includes the formation of flavones using phosphorus ylides.

This method was first reported by Takeno and Hashimoto.[4] The intramolecular cyclisation of ylide **8** was investigated starting from the corresponding phosphonium salt **7** prepared from the *o*-(phenoxycarbonyloxy)acetophenone. When **8a** was heated under reflux in the presence of *N,N*-diisopropylamine in toluene for 2 h, the sole product isolated was **11**. The process could also be extended to the substituted examples **11b** and **11c**.



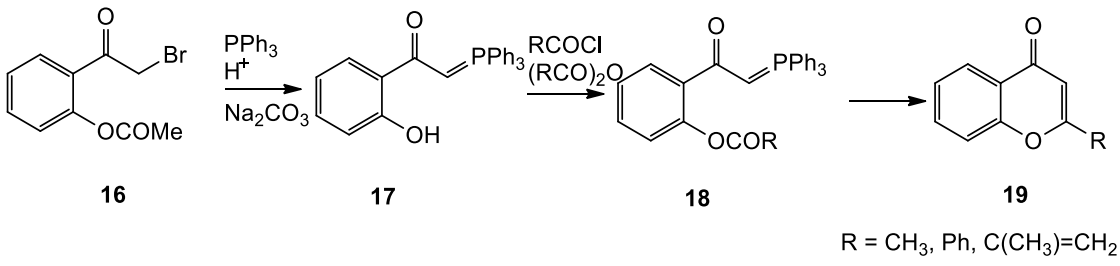
As the Wittig reaction could provide a simple method for access to such ketene acetal structures, some time later the same group reported a new variation which also employed an intramolecular Wittig reaction to produce the ketene acetal function but now with an ester function present which could later be removed. The requisite intermediate ylide **13** was prepared from the benzoic acid **12** which was chlorinated with $SOCl_2$ and subsequently alkylated with benzyl triphenylphosphoranylideneacetate, then the key cyclisation was conducted by heating in toluene to obtain **14**. This was followed by treatment with hydrogen and 10% Pd-C

at atmospheric pressure to remove the benzyl protecting group to give the flavone analogues **15**.[5]

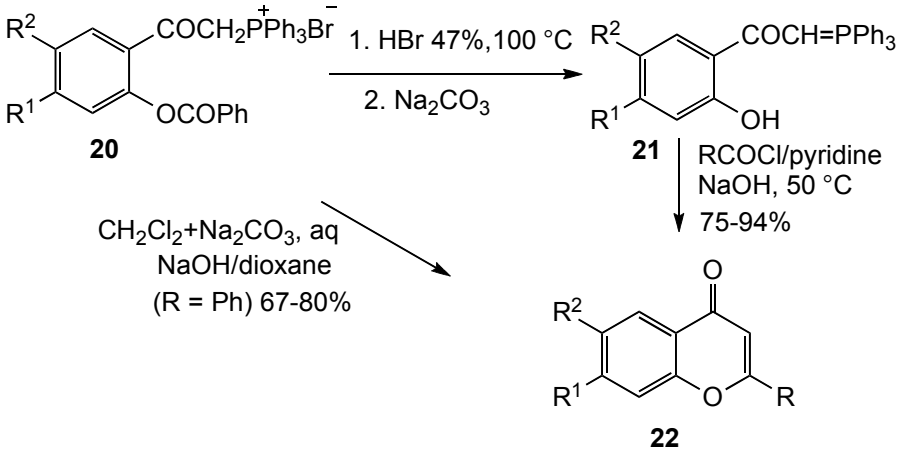


Two groups, those of Hercouet[6] and Floch,[7, 8] both reported similar results for the synthesis of flavone analogues via an intramolecular alkene formation. Hercouet's group obtained benzofurans from *o*-hydroxybenzylidenetriphenylphosphorane by *O*-acylation followed by intramolecular Wittig reaction, and based on this research, they came up with the idea to synthesise chromones from *o*-hydroxyphenacylidenetriphenylphosphorane under mild conditions.

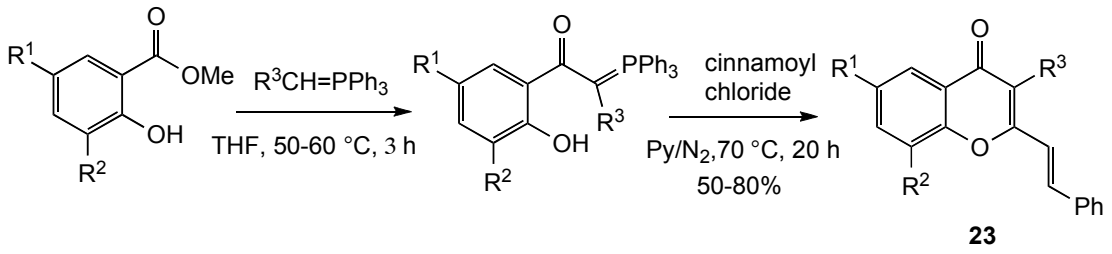
Ylide **17** was prepared in the usual way, namely by reaction of the bromo ketone **16** and triphenylphosphine followed by hydrolysis of the acetoxy group and treatment with Na_2CO_3 to give the target ylide. The reaction of ylide **17** with an acid chloride in boiling toluene with pyridine gave the unstable ylide **18**, which could undergo spontaneous intramolecular olefination of the ester carbonyl group to give chromone **19**. A range of R groups such as methyl and phenyl gave **19** in 65-96% yield.



The group of Floch did almost the same research except for the intramolecular olefination, they used MeONa/MeOH to speed up the reaction.[7] In addition, they also provided a more convenient way to acquire the flavone.[8] In this method the phosphonium salt **20** was heated under reflux in CH_2Cl_2 with sodium carbonate, and then the mixture was treated with NaOH and dioxane to give **22**.

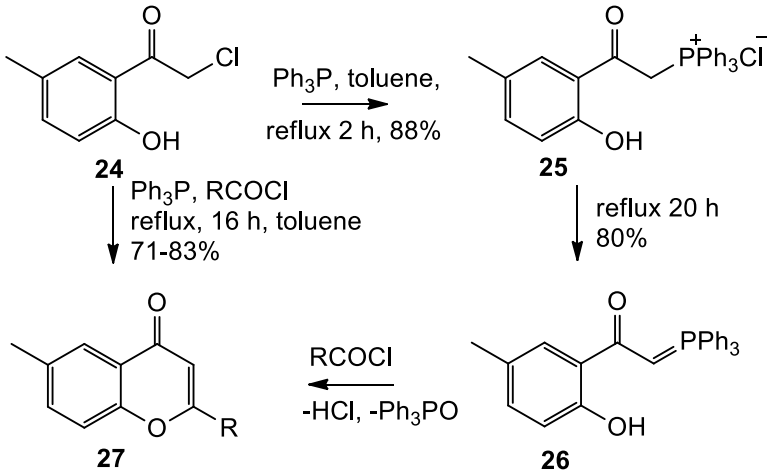


In the recent past, there have been no significant new routes developed for the formation of flavones or flavonoids using phosphorus ylides, with most new papers reporting syntheses using the well described methods already mentioned. However, this method has proved useful for synthesis of the corresponding 2-styrylchromones **23**.[9]

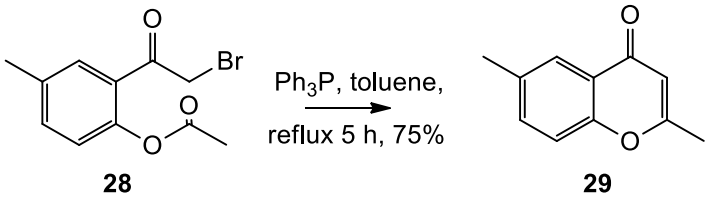


Lee *et al.* reported the special usefulness of the Wittig reaction in the synthesis of flavones. This was achieved by heating *o*-hydroxyphenacyl halide **24** and triphenylphosphine in toluene for 2 h producing **25**, and then heating the

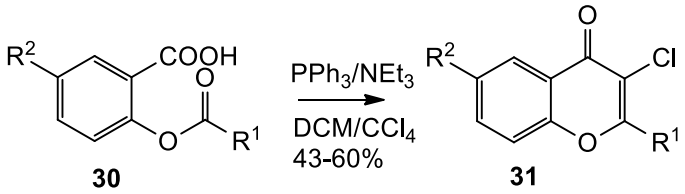
phosphonium salt **25** to form the ylide **26** thermally. The final product **27** was synthesised by reacting **26** with an acid chloride.[10] From this method a shorter one-pot synthesis was devised whereby a mixture of **24**, triphenylphosphine and the acid chloride are heated for 16 h in toluene, producing **27**.



They also observed that by treating the *o*-acetoxyphenacyl bromide **28** with triphenylphosphine in refluxing toluene for 5 h, the final product 2,6-dimethylchromone **29** could be formed directly.[10]

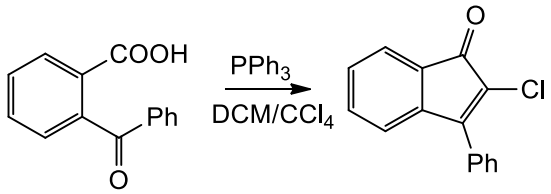


During the studies on the conversion of the carboxylic group of non-steroidal anti-inflammatory agents into the corresponding 1,3-oxazolines with ethanolamine, triphenylphosphine and triethylamine in carbon tetrachloride, Helmut's group found that aspirin **30** could form a small amount flavones. When they just omitted the ethanolamine, they got a 60% yield of flavone **31** as the product. [11]



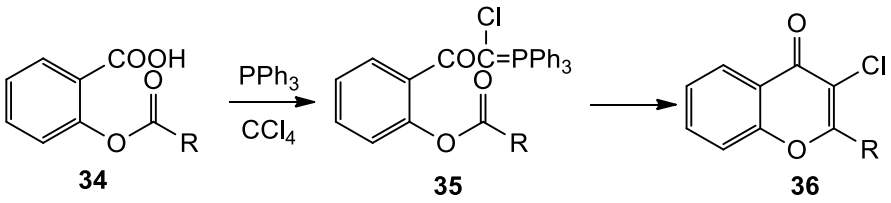
30 31

This method was quite promising; 2-benzoylbenzoic acid **32** gave a 37% yield of 2-chloro-3-phenylindenone **33** under the same conditions.



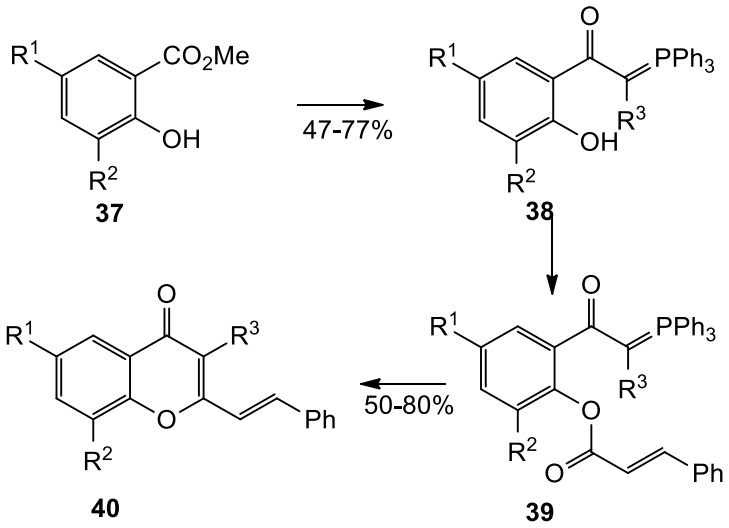
32 33

To elucidate the mechanism, they used the corresponding aromatic acid chlorides. Through a series of experiments and comparisons, it was found that the mechanism involved a similar pre-formed Wittig-type reagent, which reacted with **34** leading to the formation of an ylide **35** that could then undergo the intramolecular olefination to obtain the 3-chloroflavone **36**.

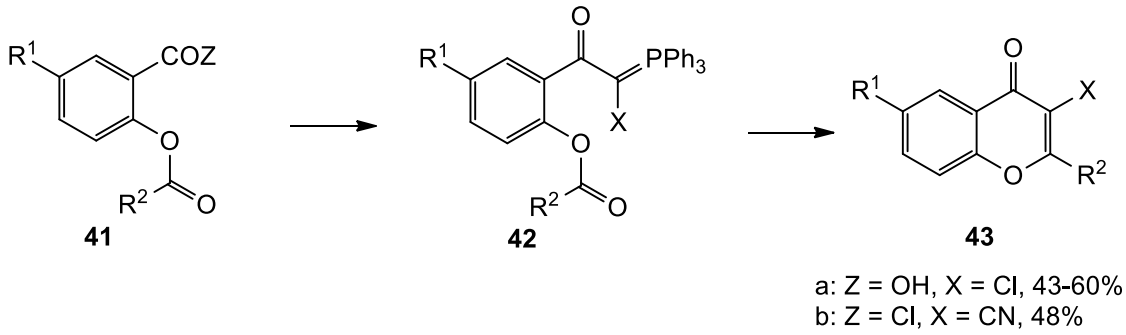


34 35 36

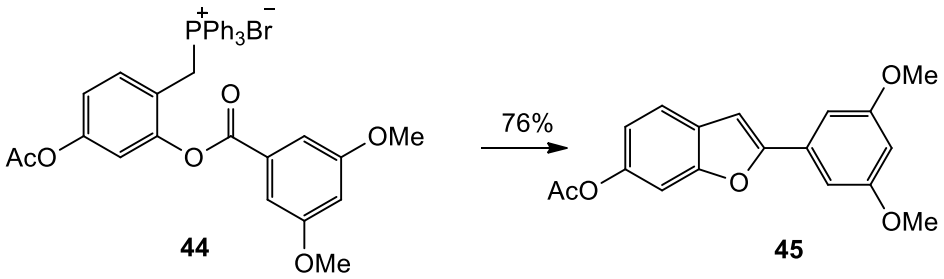
Another useful variation of the Wittig reaction, was to react the ester function of aromatic ester **37** with a non-stabilised ylide leading to the β-ketophosphorane **38**, followed by acylation of the hydroxy group with cinnamoyl chloride to obtain the ester ylide **39**, which then underwent cyclisation on heating to give **40**.[12]



An alternative method could reverse the initial two steps, beginning with acyloxy acid derivatives **41** to be converted into ylides **42** in the presence of carbon tetrachloride, before undergoing cyclisation to obtain compounds **43**.

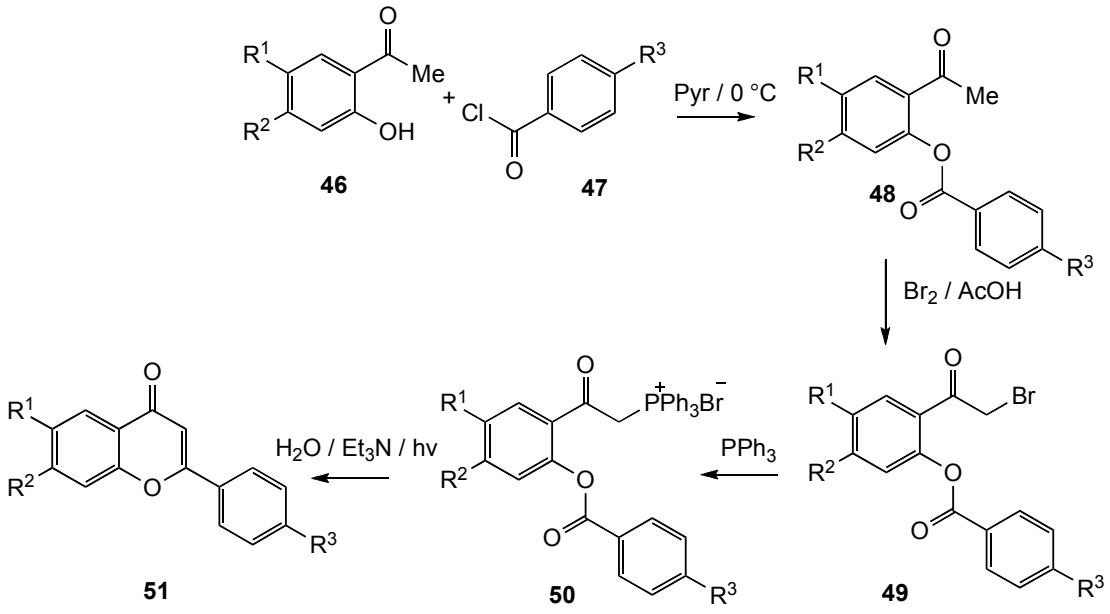


In addition, benzofurans could easily be synthesised by an intramolecular Wittig reaction as exemplified by reaction of **44** to give **45**, which was the key step in a synthesis of the naturally occurring antifungal benzofuran moracin C.[13]



3 Wittig reactions in water

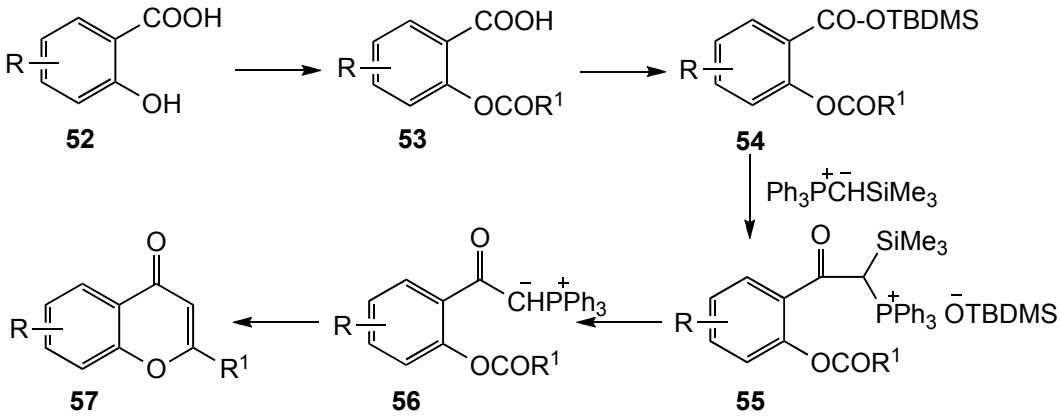
Wittig reactions have been performed in water and were first reported by Märkl in 1973. [14] After the pioneering contribution of Breslow,[15] water could be used in many organic syntheses and reactions to enhance the reactivity and yield. In addition, 'on water' Wittig reactions of stabilised and semi stabilised ylides in aqueous medium leading to enhanced rates and yields have been reported. The usefulness of this reaction was studied by testing with various phosphonium salts **50**, with the products **51** being obtained in high yields (63-91%) and a highly pure state by simple column filtration over silica gel.[16] A mechanism involving radical cations has been suggested.



4 Wittig reaction of silyl esters with silyl ylides

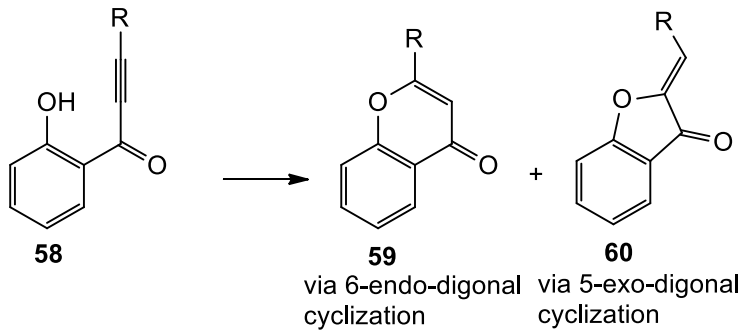
The majority of flavone forming reactions are based on the use of salicylic acid or its substituted derivatives as precursors. When **52** was treated with an acid chloride or anhydride, **53** was formed, which reacted with *tert*-butyldimethylsilyl chloride in the presence of imidazole to give **54**. The mixture of **54** and (trimethylsilyl)methylenetriphenylphosphorane was then heated with THF under

reflux and the desired products **57** were obtained in good yield (55-80%) by sequential reactions.[17]



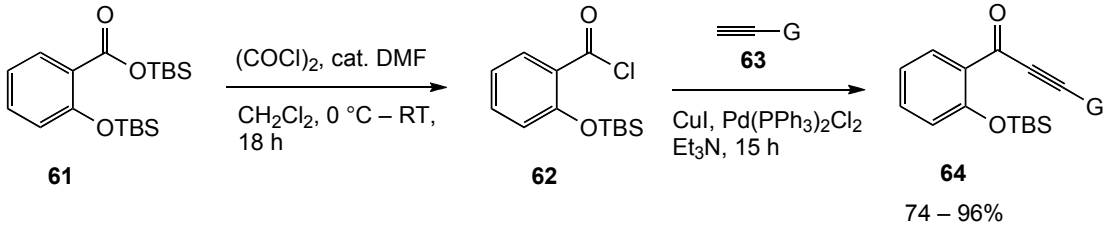
B Flavone Synthesis by Cyclisation of *o*-Silyloxyphenyl Alkynyl Ketones

According to Baldwin's Rules, a conventional route to synthesise the flavone **59** would be to convert alkynone **58** into the desired benzopyrone ring system under basic conditions.[18] However, the benzofuranone **60** could also be formed via 5-*exo-digonal* cyclisation.

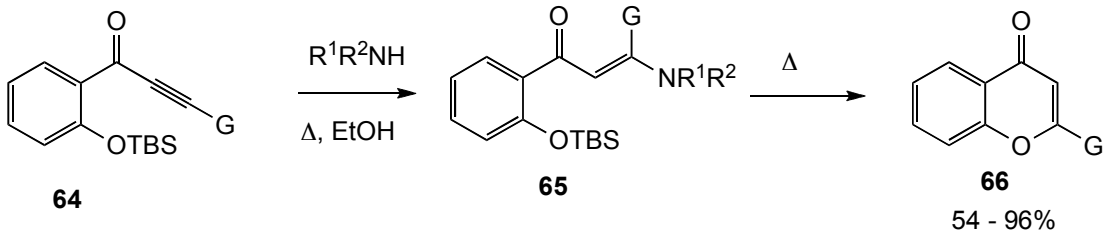


To investigate more efficient ways of synthesising flavones, a recent study has examined the use of suitable protecting groups.[19] This involved reacting salicylic acid with 2.2 equivalent of TBSCl and Et_3N in CH_2Cl_2 to generate the bisTBS protected

acid **61**, which could prevent the mixture of flavone and aurone being formed by oxypalladation reactions. Then the **61** was chlorinated by oxalyl chloride using DMF as a catalyst to get **62**, which underwent Sonogashira coupling with $Pd(PPh_3)_2Cl_2$ and CuI to get the alkynone **64** without any further purification. A lot of different terminal alkynes **63** and salicylic acid derivatives were used to evaluate the effect of the substitutions on the coupling reactions; all of them gave the desired products, even the sensitive NH-Boc function.

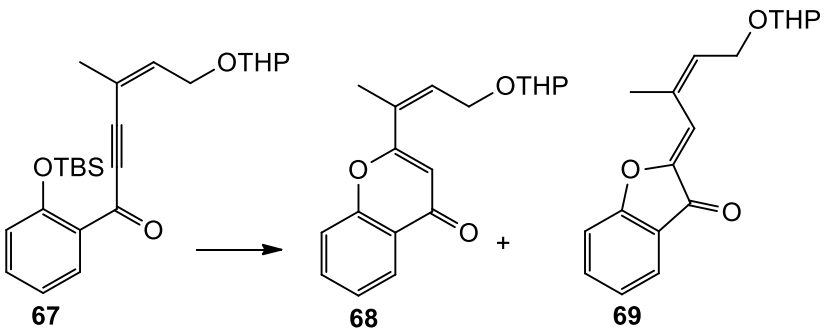


As shown in the scheme below, the alkynones **64** were converted into enaminoketones by treating them in ethanolic solution with 10 equivalents of diethylamine under reflux to form enaminoketones **65**, which could react with excess diethylamine to form flavones **66**.

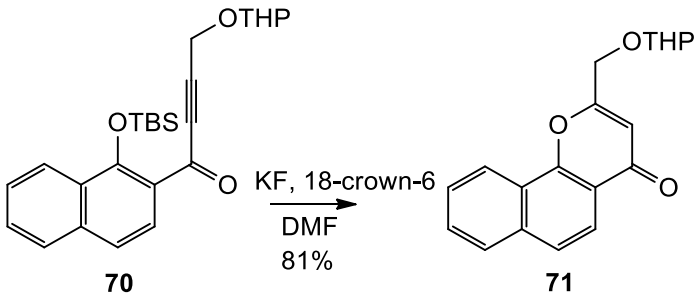


Further investigations of the 6-*endo-digonal* and 5-*exo-digonal* cyclisation of the ethynyl ketone **67** have been performed, combining theoretical and experimental methods.[20] The potential energies for the reactions to form **68** and **69** are +23.60 kcal/mol and +24.22 kcal/mol, respectively. In addition, it was found that the proton donor in the reaction played a critical role in controlling the selectivity of the reaction. If **67** was reacted with TBAF (tetra-*n*-butylammonium fluoride) in THF containing approximately 5% (v/v) of water as a fluoride ion source at 0 °C for 1.5 h, the result

was that both products were produced in 90% yield with very low selectivity (**68**:**69** = 47:53). If the concentration of proton donor (e.g., water) in the reaction system was reduced and spray-dried KF in the presence of 18-crown-6 was used as the fluoride source, the reaction in anhydrous DMF proceeded smoothly giving **68** as the sole product in 97% yield.[20]

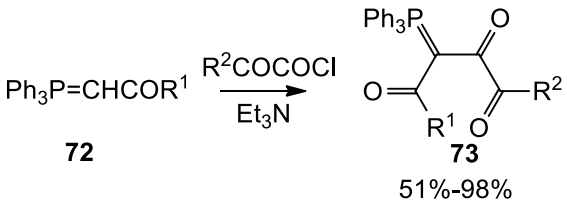


This method was quite useful in the synthesis of kapurimycin A_3. A simple kapurimycin model **70** was tested using KF and 18-crown-6 in DMF at ambient temperature and the reaction proceeded smoothly giving the product **71** in 81% yield.[20]

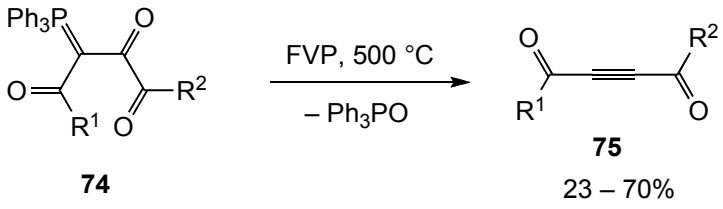


C Previous Synthetic Applications of Ylide Pyrolysis

Previous work in the group has focused on the synthesis and flash vacuum pyrolysis of stabilised ylides. Hundreds of new ylides have been synthesised for these studies. In an early study 16 new trioxo stabilised ylides **73** were produced by acylation of stabilised ylides **72** with 1 equiv. of the α-oxo acid chlorides and triethylamine in toluene at room temperature.[21]



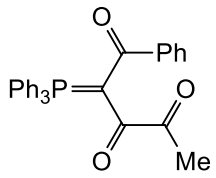
These new ylides were stable crystalline solids; the ^{31}P NMR gave signals at δ_P+15-18 ppm, and the ^{13}C spectra were highly informative. When the ylides **74** were subjected to FVP at 500 °C, the Ph_3PO was extruded to get alkynes **75** in moderate yield in most cases.



The good selectivity was probably a result of the high value of $^2J_{P\text{-}C}$ to the central carbonyl. The ylides with $^2J_{P\text{-}C}$>10 Hz do not generally eliminate Ph_3PO to give alkynes while those with $^2J_{P\text{-}C}$<10 Hz do, however this needs further study.

In addition, the X-ray structures of the new polyoxo phosphorus ylides, such as the trioxo ylide **76**, tetraoxo ylide **77**, and tetraoxo bis ylide **79** and hexaoxo ylide **78** exhibited significant effects of the P=C-C=O unit.[21-23] It was clear that, for effective

delocalisation, the P=C-C=O unit should be planar. From the X-ray structures, the torsion angles and bond lengths were surveyed to justify the theory. [22]



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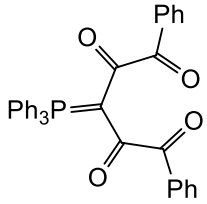

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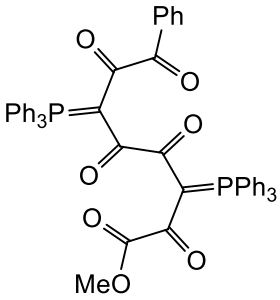

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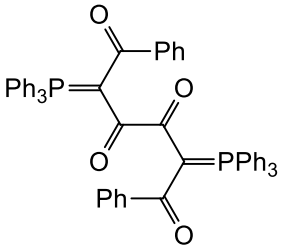
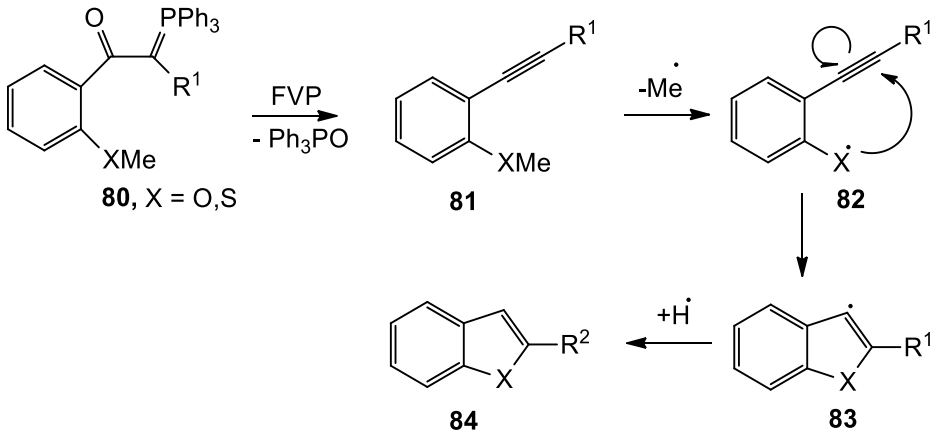


79

In further work it was found that β-oxo stabilised phosphorus ylides **80** with an *ortho*-methoxy or methylthio substituent underwent the normal extrusion of Ph_3PO upon flash vacuum pyrolysis at 700 °C to give alkynes **81**. However at a higher temperature of 850 °C, benzofurans and benzothiophenes were the final products, which were formed by loss of Me· to give **82** followed by intramolecular reactions to give **84**.[24-26]



80, X = O,S

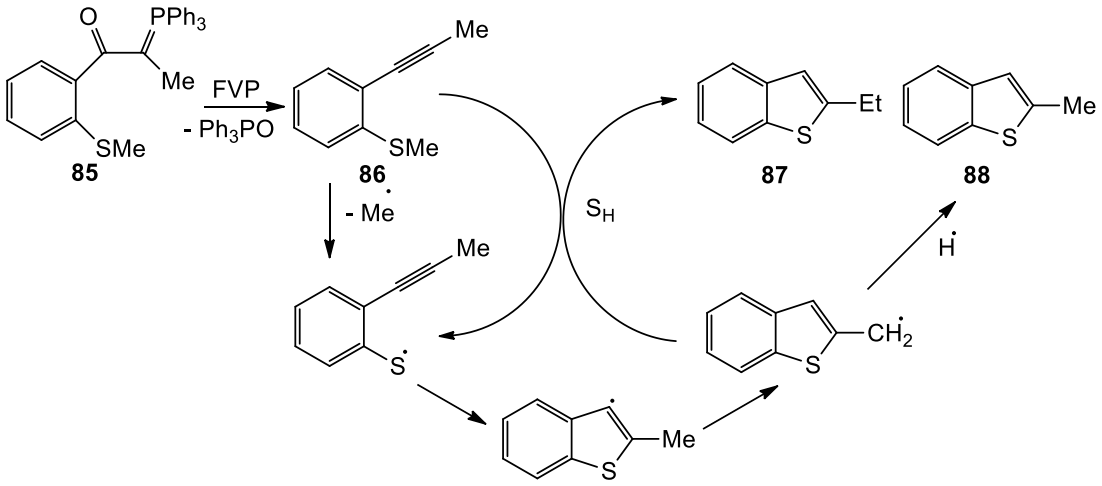
81

82

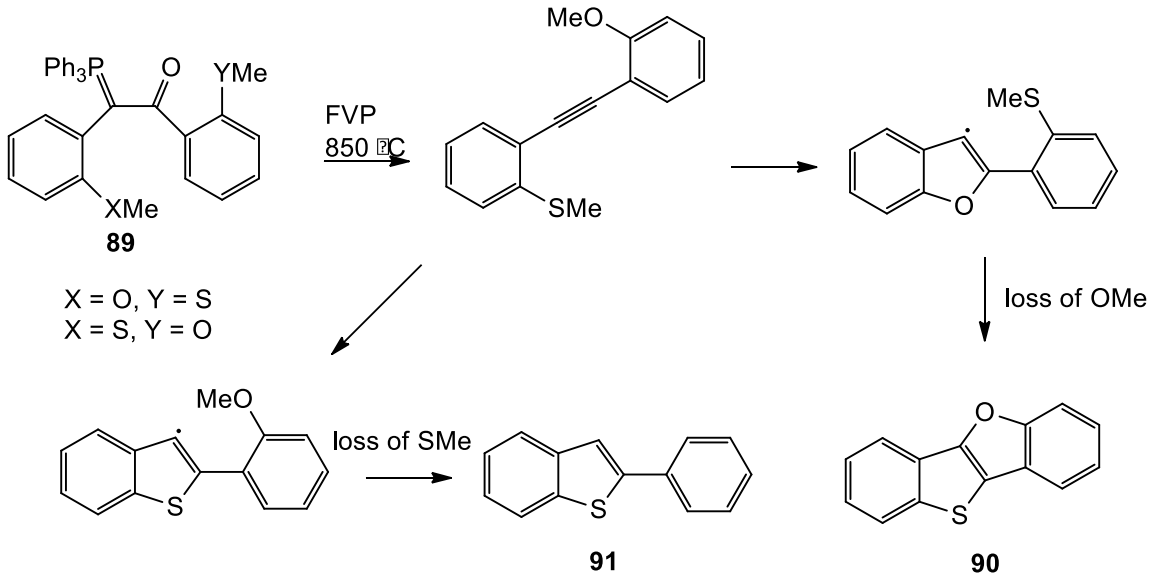
83

84

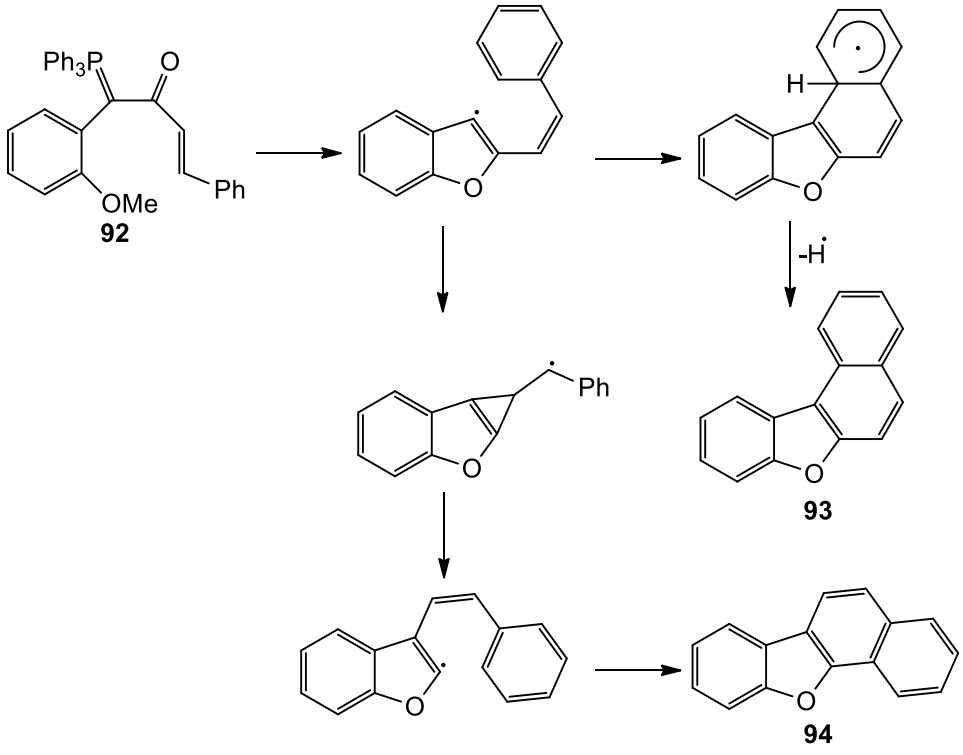
For R^1 = Ph, the product was formed with R^2=R^1 by intermolecular hydrogen atom abstraction, while for simple alkyl substituents, the intermolecular hydrogen atom abstraction allowed the synthesis of **84** where R^2 = Me, Et, vinyl. For example, in the pyrolysis and cyclisation of the ylide **85**, a series of unusual intramolecular hydrogen atom and methyl radical abstractions led to formation of 2-ethylbenzothiophene **87** and 2-methylbenzothiophene **88**. [27]



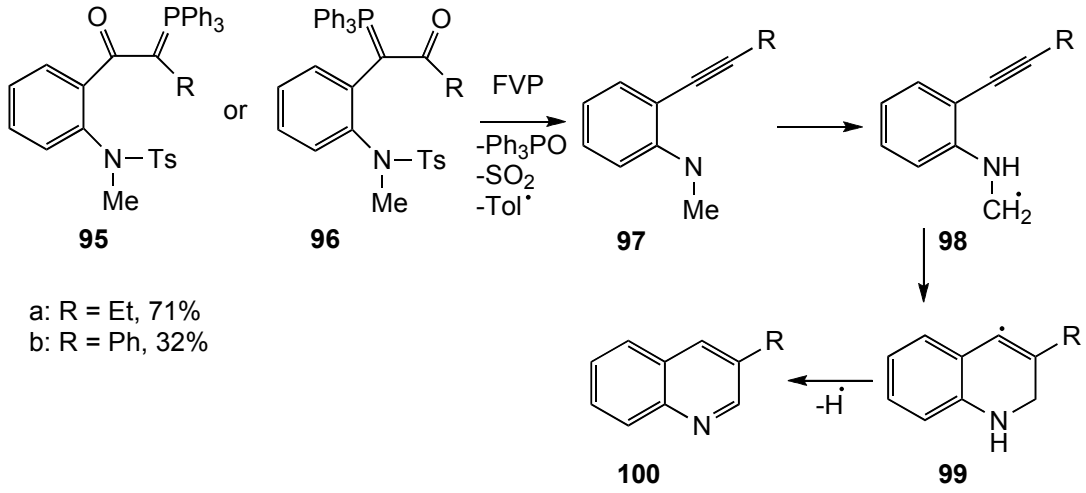
If there was a suitable group in the end of the intermediate alkyne, a cascade reaction could lead to tetracyclic products. If the radical centre in **83** was connected with another radical centre, such as the *ortho*-methoxyphenyl, further cyclisation could take place as shown by FVP of the ylide **89**, with initial loss of either OMe or SMe being followed by further fragmentation to give **90** and **91**, respectively.[28,29]



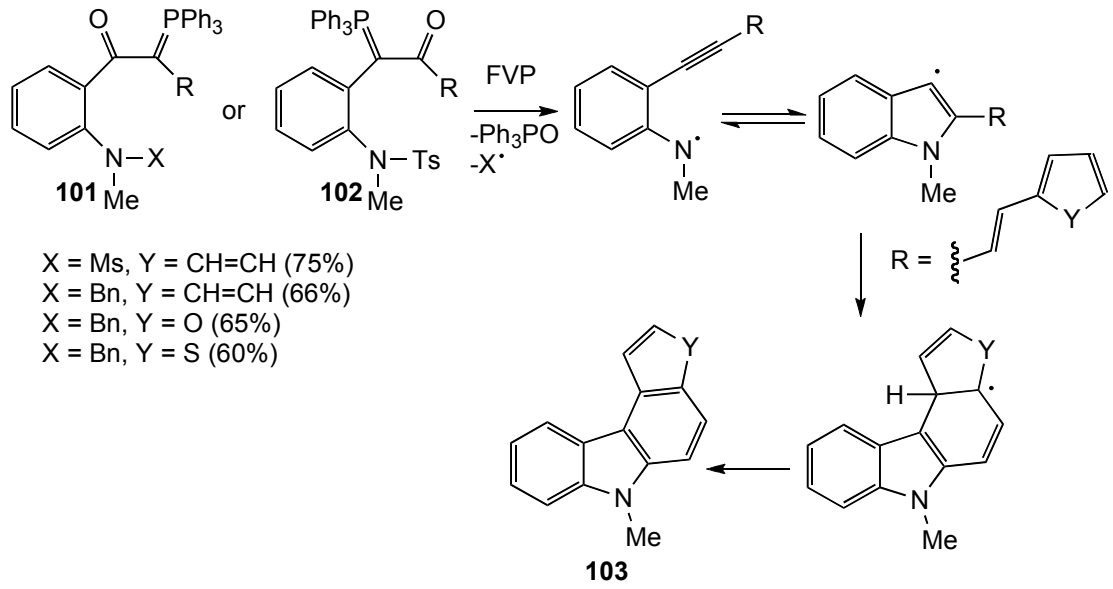
If the 2-position of radical **83** was connected to a styryl group, the resulting product when **92** underwent FVP was mainly the tetracyclic product naphthobenzofuran **93** (44%), accompanied by the side product **94** (14%).[26]



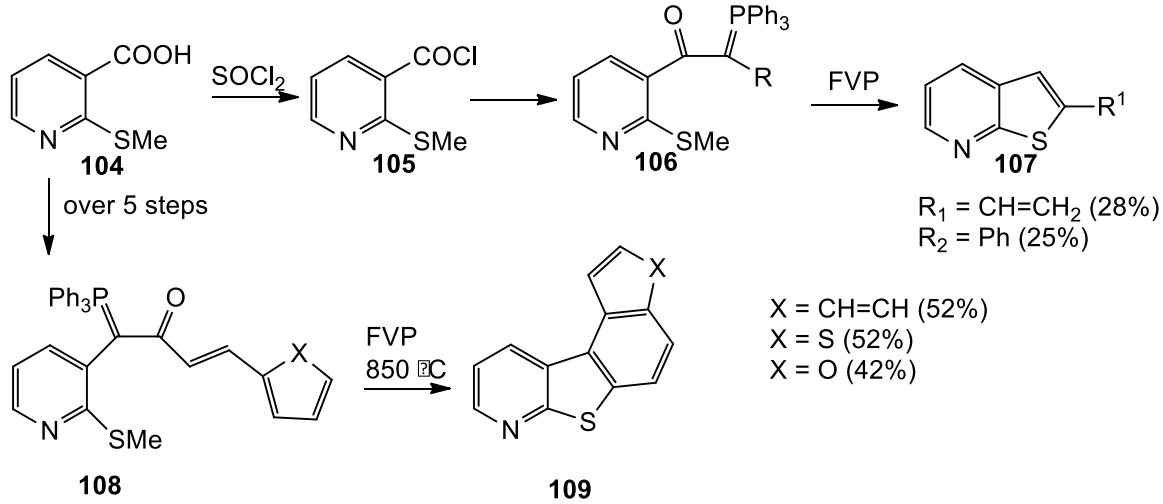
Previous work also extended the use of this approach to *ortho*-aminophenyl ylides to produce tetracyclic ring-fused carbazoles. The ylides **95** or **96** possessed suitable leaving groups on the *ortho* position. When the leaving group was tosyl, and the R = Et or Ph, the products would be 3-ethylquinoline **100a** (71%) and the 3-phenylquinoline **100b** (32%), respectively. When the ylides were exposed to FVP, the Ph_3PO would undergo extrusion first, followed by transfer of the hydrogen atom from the CH_3 to the N in the aminyl radical and cyclisation, followed by losing a hydrogen atom to aromatise to form a quinoline ring.[30]



On the other hand, when ylides **101** or **102** with *N*-methanesulfonyl group or *N*-methyl-*N*-benzyl groups in the *ortho* position were used, FVP of the ylides led to normal cyclisation to give ring-fused carbazoles **103** in good yield.

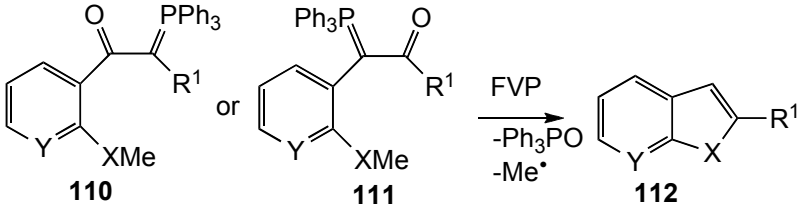


This approach was also successful with a 2,3-disubstituted pyridine as the cyclisation centre, providing convenient access to tetra- and pentacyclic fused ring thieno[2,3-*c*]pyridine heterocyclic systems. Ring-fused thieno[2,3-*c*]pyridine derivatives have been reported to have a range of medicinal applications such as anti-inflammatory agents.[31] The model ylides were prepared in the usual way by conversion of the acid **104** into acid chloride **105** with thionyl chloride, followed by the addition of 2 equiv. of non-stabilised ylides in THF to give the products in excellent yield. The FVP results were just as expected and gave access to some previously unknown fused heterocyclic ring systems.[32]



D Programme of Research

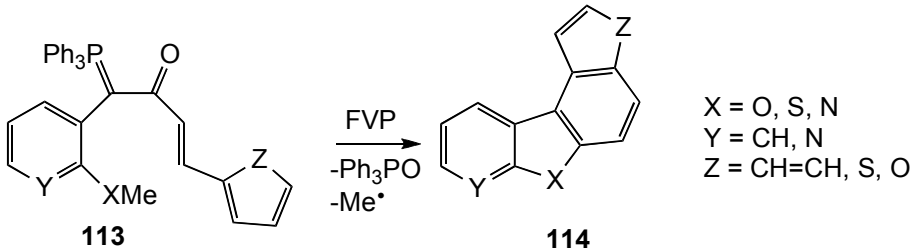
In the course of previous work, synthesis and flash vacuum pyrolysis of oxo stabilised ylides have already been successfully demonstrated. FVP of the oxo stabilised ylides **110** or **111**, results in extrusion of Ph_3PO, accompanied by loss of the $Me^{\cdot}$, resulting in cyclisation to form aromatic ring products, such as the benzofurans and benzothiophenes **112** and quinolines.[26,32]



110 **111** **112**

X = S, O, NH
Y = N, CH

When the R^1 group forms a radical centre under FVP conditions, such as with vinyl benzene, cinnamoyl chloride and the *o*-methoxy or *o*-methylthio phenyl, a cascade reaction would give a tetracyclic product. Using this method, a large range of tetracyclic, pentacyclic and hexacyclic products have already been obtained.



113 **114**

In this project, the aim was to synthesise dioxo stabilised ylides and extend the ring cyclisation approach from five-membered rings to six-membered rings with the extra carbonyl retained. The initial studies would attempt the synthesis of the β,γ-dioxo stabilised ylides, which would then be subjected to FVP to monitor whether the substrates would cyclise to the corresponding benzopyranone. Extension to cascade reactions leading to ring-fused benzopyranones and flavones would then be examined.

EXPERIMENTAL

A Symbols and Abbreviations

bp	boiling point
δ	chemical shift in parts per million
DMF	dimethylformamide
FVP	flash vacuum pyrolysis
h, min	hours, minutes
J	spin-spin coupling constant in Hertz
M	mol dm^{-3}
M^+	molecular ion
mp	melting point
MS	mass spectroscopy
m/z	mass to charge ratio
NMR	nuclear magnetic resonance
RT	room temperature
s, d, t, q, m	singlet, doublet, triplet, quartet, multiplet
THF	tetrahydrofuran
TLC	thin layer chromatography

B Instrumentation and General Techniques

1. NMR Spectroscopy

All ^{1}H NMR ^{13}C NMR and ^{31}P NMR spectra were recorded in $CDCl_3$ on Bruker Avance 300 and Bruker Avance II 400 spectrometers. All chemical shifts are expressed in parts per million to high frequency of internal tetramethylsilane for H and C or external 85% H_3PO_4 for P.

2. Infrared Spectroscopy

All the spectra were obtained on a Perkin-Elmer 1420 instrument. Solids were run as Nujol mulls and liquids as thin films.

3. Mass Spectra

All the mass spectra were obtained on a Micromass GCT mass spectrometer using electrospray (ES) ionisation unless otherwise stated.

4. Melting Points

All melting points were taken using a Gallenkamp melting point apparatus.

5. Thin Layer Chromatography

This was carried out using 0.20 mm layer of silica (Merck, Kieselgel $60F_{254}$) on aluminium sheets. The components were observed under ultraviolet light.

6. Preparative Thin Layer Chromotography

This was carried out by using 1.0 mm layers of silica (Merck, Kieselgel 60-80 mesh), containing 0.5% Woelm fluorescent green indicator, on glass plates. After locating the components with ultraviolet light, the bands were scraped off and the products removed from the support by soaking in CH_2Cl_2 for 20 mins.

7. **Column Chromatography**

This was carried out by using silica gel of 33-70 μm particle sise.

8. **Kugelrohr Distillation**

This was carried out by using a Büchi model GKR-50 apparatus.

9. **Drying and Evaporation of Organic Solutions**

Organic solutions were dried by standing over anhydrous magnesium sulfate unless otherwise stated and were evaporated under reduced pressure on a Büchi rotary evaporator.

10. **Drying and Purification of Solvents**

Commercially available solvents were used without further purification unless otherwise indicated. Dry toluene and THF were prepared by the addition of sodium wire.

11. **Flash Vacuum Pyrolysis**

The apparatus was based on the design of W. D. Crow, Australian National University. The essential features of the apparatus are show below (Figure 1). The samples were volatilised from a horizontal inlet tube, heated via an external heat source, through a

30 × 2.5 cm silica tube. This was heated at the temperature in the range of 500-1000 °C by a furnace. Then the tube was connected to a U-shaped trap cooled by liquid nitrogen, which was connected to the vacuum system. The non-volatile products were collected at the furnace exit and the volatile products were collected in the U-shape trap. The whole system pressure was maintained from 10^{-2} to 10^{-3} Torr by an Edwards Model E2M5 high capacity rotary oil pump, and the pressure was measured on a Pirani gauge situated between the trap and the pump.

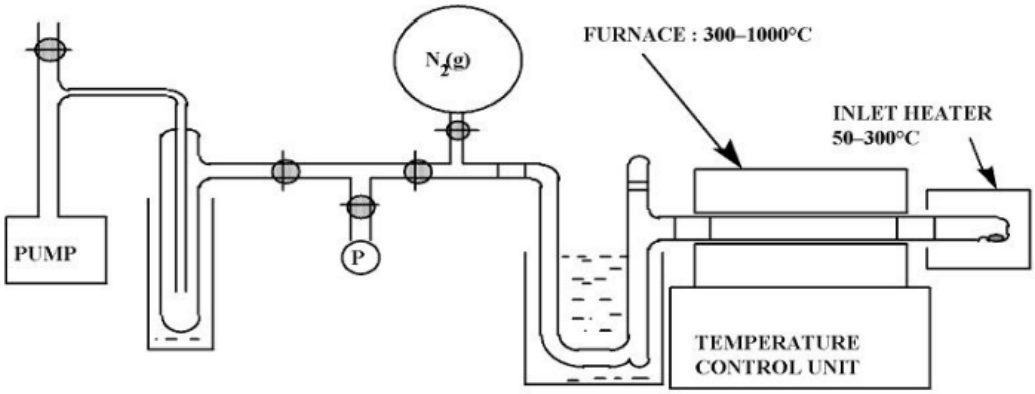


Figure 1: Apparatus used for flash vacuum pyrolysis

After the pyrolysis the whole system was removed from the pump. The products were dissolved in $CDCl_3$ to get out of the trap, unless otherwise stated. For large scale reactions, the products were dissolved in CH_2Cl_2.

C Preparation and Pyrolysis of β, γ-Dioxo Ylides

1 Preparation of Starting Materials

a Preparation of ethyl 2-(2-methoxyphenyl)-2-oxoacetate 115

A solution of the 2-bromoanisole (27.0 g, 144 mmol) in diethyl ether (270 cm^3) was cooled to –70 °C, and 2.5 M butyllithium in hexane (57.6 cm^3, 144 mmol) was added by syringe, and stirred for 45 mins. Diethyl oxalate (78 cm^3, 84.0 g, 576 mmol) was added quickly with stirring and allowing the mixture to warm up to RT. After 1 h, saturated NH_4Cl solution was added and the mixture was extracted with diethyl ether. The combined organic phase was dried over $MgSO_4$ and evaporated and the residue distilled by kugelrohr (170 °C, 0.5 mmHg) to give the product (17.96 g, 60 %) as a deep yellow liquid; δ_H 7.88 (1 H, dd, *J* 7.8, 1.8, H-6), 7.59 (1 H, ddd, *J* 8.7, 7.2, 1.8, H-4), 7.07 (1 H, ddd, *J* 7.8, 7.2, 0.9, H-5), 6.99 (1 H, dd, 8.7, 0.9, H-3), 4.39 (2 H, q, *J* 7.2, CH_2), 3.87 (3 H, s, OMe) and 1.39 (3 H, t, 7.2); δ_C 186.5 (4ry, CO-Ar), 165.2 (4ry, CO-OEt), 160.2 (4ry, C-2), 136.3 (C-4), 130.6 (C-6), 122.6 (4ry, C-1), 121.2 (C-5), 111.9 (C-3), 61.7(CH_2), 55.9 (OMe) and 14.0(CH_3).

b Preparation of 2-(2-methoxyphenyl)-2-oxoacetic acid 116

A solution of the ester **115** (17.0 g, 81.7 mmol) and NaOH (12 g, 300 mmol) in water (200 cm^3) was heated on a steam bath for 1.5 h. Then the solution was washed with diethyl ether, which was discarded, and acidified with dilute HCl leading to precipitation of a yellow oil. The mixture was extracted with diethyl ether again, and the combined ether extracts were dried with $MgSO_4$ and evaporated to give the product (9.5 g, 65%) as deep yellow crystals, mp 96-100 °C (lit.,[33] 102-103 °C), δ_H 10.49 (1 H, OH), 7.89 (1 H, dd, *J* 7.8, 1.8, H-6), 7.62 (1 H, ddd, *J* 9.0, 8.4, 1.8, H-4), 7.07 (1 H, ddd, *J* 8.4, 7.8, 0.9, H-5), 7.02 (1 H, dd, *J* 8.1, 0.9, H-3) and 3.96 (3 H, s, OMe); δ_C 185.7 (4ry, CO-Ar), 169.3 (4ry, CO-OH), 160.5 (4ry, C-2), 136.8 (C-4), 130.7 (C-6), 122.0 (4ry, C-1), 121.4 (C-5), 112.2 (C-3) and 56.0 (OMe).

c Preparation of 2-(2-methoxyphenyl)-2-oxoacetyl chloride 117

To a solution of **116** (2 g, 11 mmol) in CH_2Cl_2 was added oxalyl chloride (1.65 g, 13 mmol) at RT followed by addition of a drop of DMF as catalyst. The mixture was stirred at this temperature until all evolution of gases ceased. After all the volatiles were removed under vacuum this then gave the product as a dark brown liquid (2.04 g, 94%); δ_H 7.92 (1 H, dd, *J* 7.8, 1.8, H-6), 7.67 (1 H, ddd, *J* 9.0, 7.2, 1.8, H-4), 7.12 (1 H, ddd, *J* 8.1, 0.9, H-5), 7.04 (1 H, d, *J* 8.7, H-3) and 3.92 (3 H, s, OMe); δ_C 181.2 (4ry, COAr), 165.6 (4ry, COCl), 160.4 (4ry, C-2), 137.7 (CH, C-4), 131.3 (CH, C-6), 121.8 (CH, C-5), 119.7 (4ry, C-1), 112.2 (CH, C-3) and 56.0 (OMe).

d Preparation of 1-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-2-(2-methoxyphenyl)ethane -1,2-dione 118

To a solution of 1*H*-1,2,3-benzotriazole (11.90 g, 100 mmol) in CH_2Cl_2 (125 cm^3), thionyl chloride (2.97 g, 1.9 cm^3, 25 mmol) was added dropwise. The mixture was stirred at RT for 0.5 h, and the acid **116** (4.5 g, 25 mmol) was added. The mixture was stirred for a further 3 h at RT and the solid was filtered off and washed with CH_2Cl_2. Then the filtrate was washed with 2M aqueous NaOH, water and brine. Drying and evaporation followed by recrystallisation of the residue from hexane and ethyl acetate gave the product (0.75 g, 5.3%) as a yellow solid; mp 145-146 °C; (Found: M^+-N_2 254.0825. $C_{15}H_{12}NO_3$ (M^+-N_2) requires 254.0817); ν_{max}/cm^{-1} 3466, 3004, 1744, 1669, 1598, 1482, 1388, 1251, 1017 and 926; δ_H 8.37 (1 H, dt, *J* 8.4, 1.0), 8.20-8.17 (2 H, m), 7.75 (1 H, ddd, *J* 8.1, 7.2, 0.9), 7.69-7.57 (2 H, m), 7.19 (1 H, ddd, *J* 8.0, 7.0, 0.9, H-5 of ArOMe) and 6.93 (1 H, dd, *J* 7.8, 0.9, H-3 of ArOMe); δ_C 185.1 (4ry, COAr), 164.8 (4ry, CO-N), 160.5 (4ry, C-2 of ArOMe), 145.8 (4ry), 137.5 (C-4 of ArOMe), 130.8 (CH), 130.7 (CH), 130.7 (4ry), 126.7 (C-6 of ArOMe), 122.1 (4ry, C-1 of ArOMe), 121.8 (C-5 of ArOMe), 120.4 (CH), 113.7 (CH), 112.3 (C-3 of ArOMe) and 56.1 (OMe).

e Preparation of benzyltriphenylphosphonium chloride 119

A solution of triphenylphosphine (50.0 g, 190 mmol) and benzyl chloride (26.2 g, 210 mmol) in toluene (500 cm^3) was heated under reflux for 24 h. The white precipitate was filtered off and washed with diethyl ether to give the product (50.53 g, 69 %) as a colourless crystalline solid, mp 328-330 °C (lit.,[34] 325-328 °C); δ_H 7.8-7.7 (9 H, m), 7.65-7.55 (6 H, m), 7.25-7.15 (1 H, m), 7.15-7.1 (4 H, m) and 5.52 (2 H, d, *J* 14.4, CH_2); δ_P +24.6

f Preparation of 2-methoxybenzyltriphenylphosphonium bromide 120

A solution of 2-methoxybenzyl alcohol (18.0 g, 130 mmol) and phosphorus tribromide (4.70 cm^3, 13.56 g, 50 mmol) in toluene (200 cm^3) was stirred at RT for 13 h. The mixture was added to water (500 cm^3), then the organic layer was separated, washed with water and dried with $MgSO_4$. The solution was then heated under reflux for 4h with triphenylphosphine (34.0 g, 130 mmol). The resulting solid was filtered off, washed with diethyl ether and dried in an oven to give a pale yellow product (59.86 g, 99%), mp 240-242 °C (lit.,[35,36] 242-244 °C); δ_H 7.8-7.5 (15 H, m), 7.4-7.0 (2 H, m), 6.79 (1 H, m), 7.59 (1 H, d, *J* 8.4), 5.16 (2 H, d, *J* 15.8, CH_2) and 3.20 (3 H, OMe).

2 Preparation of Ylides

a Preparation of 1-(2-methoxyphenyl)-3-phenyl-3-(triphenylphosphoranyl -idene)propane-1, 2-dione, 121

A solution of phosphonium salt **119** (3.9 g, 10 mmol) in dry THF (30 cm^3) was stirred under nitrogen, while a solution of BuLi in hexanes (4.0 cm^3, 2.5 M, 10 mmol) was added. The resulting solution was stirred for a further 2 h, before adding acid chloride **117** (1.0 g, 5 mmol) in dry THF (10 cm^3). After stirring for another 18 h, the mixture

was added to water and extracted with diethyl ether. The combined solution was dried over $MgSO_4$ and evaporated to give the product (1.37g, 27%) as a yellow crystalline solid, mp 233-235 °C. (Found: C, 77.89; H, 5.16. $C_{34}H_{27}O_3P$ requires C, 79.4; H, 5.3%) (Found: M^++H 515.1777. $C_{34}H_{28}O_3P$ (M^++H) requires 515.1776); ν_{max}/cm^{-1} 2962, 1473, 1655, 1575, 1464, 1289, 1244, 926 and 757; δ_H 7.75-7.62 (7 H, m), 7.55-7.47 (3 H, m), 7.45-7.33 (7 H, m), 7.05-6.95 (2 H, m), 6.93-6.85 (5 H, m) and 3.89 (3 H, s, OMe); δ_C 196.2 (4ry, d, *J* 15, CO-Ar), 184.8 (4ry, d, *J* 7, *C*O-CP), 158.7 (4ry, C-2 of Ar), 135.7 (4ry, d, *J* 10, C-1 of Ph), 136.1 (CH), 136.0 (CH), 134.2 (6 CH, d, *J* 10, C-2 of PPh_3), 133.3 (CH), 131.9 (3 CH, d, *J* 3, C-4 of PPh_3), 131.6 (CH), 128.5 (6 CH, d, *J* 12, C-3 of PPh_3), 127.3 (2 CH, d, *J* 2), 126.8 (4ry, d, *J* 3, C-1 of Ar), 125.7 (4ry, d, *J* 90, C-1 of PPh_3), 125.0 (CH, d, *J* 2), 120.2 (CH), 111.2 (CH), 66.4 (4ry, d, *J* 103, C=PPh_3) and 55.5 (OMe); δ_P +17.02; m/z (ES^+) 536.68 (M^++Na, 100%). The X-Ray structure of this compound was obtained: see Results and Discussion, page 55, and Appendix.

b Alternative preparation of 1-(2-methoxyphenyl)-3-phenyl-3-(triphenyl phosphoranylidene) propane-1, 2-dione 121

A solution of benzyltriphenylphosphonium chloride **119** (0.79 g, 2 mmol) in dry THF (10 cm^3) was stirred under N_2, while a solution of BuLi in hexanes (0.8 cm^3, 2.5 M, 2 mmol) was added. The resulting solution was stirred for a further 2 h, before adding **118** (0.56 g, 2 mmol) in dry THF (10 cm^3). After stirring for another 24 h, the mixture was added to water and extracted with diethyl ether. The combined solution was dried and evaporated to give the product (0.35 g, 35%) as a yellow crystalline solid, mp 233-235 °C; spectra identical to those quoted above.

c Preparation of 1,3-bis(2-methoxyphenyl)-3-triphenylphosphoranylidene propane-1, 2-dione 122

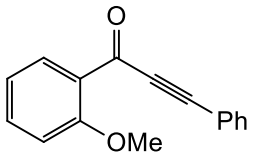
This was prepared as in **C2a**, using salt **120** (4.6 g, 10 mmol) in dry THF (30 cm^3), BuLi in hexanes (4.0 cm^3, 2.5 M, 10 mmol) and acid chloride **117** (1.0 g, 5 mmol) in dry THF (10 cm^3), to give the product (0.50 g, 20%) as yellow crystals, mp 178-182 °C. (Found: M^++H 545.1887. $C_{35}H_{30}O_4P$ (M^++H) requires 545.1882); ν_{max}/cm^{-1} 2926, 1733, 1656 (C=O), 1595, 1460, 1193, 1118, 1022, 993 and 723; δ_H 7.80-7.60 (9 H, m), 7.59-7.42 (5 H, m), 7.42-7.30 (4 H, m), 7.0-6.8 (3 H, m), 6.7-6.6 (1 H, m), 6.23 (1 H, d, *J* 8.4), 3.81 (3 H, s, OMe), and 3.11 (3 H, OMe); δ_C 196.9 (4ry, d, *J* 15, C=O), 183.6 (4ry, d, *J* 7, C=O), 158.6 (4ry, C-2 of Ar), 158.2 (4ry, d, *J* 3, C-2 of P=CAr), 136.2 (d, *J* 6, CH), 133.8 (6 C, d, *J* 10, C-2 of PPh_3), 132.9 (CH), 131.5 (3 C, d, *J* 2, C-4 of PPh_3), 131.4 (CH), 128.1 (6 C, d, *J* 12, C-3 of PPh_3), 127.6 (d, *J* 2, CH), 127.0 (4ry, d, *J* 2, C-1 of Ar), 125.9 (4ry, 3 C, d, *J* 89, C-1 of PPh_3), 125.1 (d, *J* 8, C-1 of P=CAr), 119.9 (2CH), 110.9 (CH), 109.4 (CH), 65.3 (4ry, d, *J* 105, C=P), 55.4 (OMe) and 53.9 (OMe); δ_P +16.3; *m/z* (ES^+) 566.93 (M^++Na, 100%)

3. FVP of Ylides

a FVP of Ylide 121

FVP of the title ylide (55.2 mg) at 700 °C and 2-3 × 10^{-2} Torr gave a yellow solid at the exit of the furnace. The mixture was separated by using column chromatography with ether-hexane (1:9) as eluant to give:

1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one 181 (11.2 mg, 44%) as yellow crystals, mp 98-100 °C; δ_H 8.10 (1 H, dd, *J* 7.8, 1.8, ArH), 7.66-7.63 (2 H, m), 7.55 (1 H, ddd, *J* 9.0, 7.2, 1.8, ArH), 7.49-7.37 (3 H, m), 7.09-7.02 (2 H, m) and 3.98 (3 H, s, OMe); δ_C 176.6 (4ry, CO), 159.8 (4ry, C-2 of Ar), 135.0 (CH), 132.9 (CH), 132.7 (CH), 130.4 (CH), 128.6 (CH), 126.7 (4ry, C-1 of Ar), 120.7 (4ry, C-1 of Ph), 120.3 (CH), 112.2 (CH), 91.6 (4ry, *C*≡C), 89.2 (4ry, C≡*C*) and 55.9 (Me).



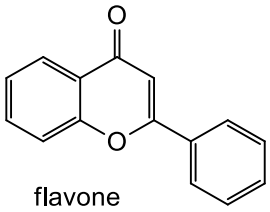
181

b FVP of 181

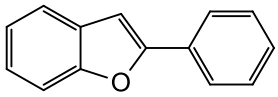
FVP of the title compound **181** (54.2 mg) at 775 °C and 2-3 × 10^{-2} Torr gave a yellow solid at the exit of the furnace. NMR results showed the crude product was a mixture of flavone and 2-phenylbenzofuran:

flavone; δ_H 6.84 (1 H, s); δ_C identical to material prepared in Section D1c (Page 28).

2-phenylbenzofuran; δ_H 7.02 (1 H, d, *J* 0.9); δ_C 155.9, 154.9, 141.3, 128.7 (2 C), 128.7, 126.2, 124.8 (2 C), 124.2, 122.9, 120.8, 111.1 and 101.2.



flavone



benzofuran

D Preparation and Pyrolysis of Flavone and 3-Iodoflavone

1 Preparation of Starting Materials

a Preparation of 2-acetylphenyl benzoate 123

To a 50 cm^3 conical flask were added in order *o*-hydroxyacetophenone (4.5 g, 4 cm^3, 0.03 mol), benzoyl chloride (7 g, 5.8 cm^3, 0.05 mol) and pyridine (7 cm^3). After the heat of reaction had subsided, the mixture was poured into a well stirred mixture of 3% HCl (200 cm^3) and crushed ice (70 g). The resulting solid was filtered off, washed with methanol then water, and dried to give the product (4.62 g, 68%) as a pale yellow crystalline solid, mp 85-87 °C (lit.,[37] 87-88 °C).

b Preparation of 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione 124

A solution of ester **123** (4.5 g, 18 mmol) in pyridine (17.1 cm^3) was warmed to 50 °C, and finely pulverised KOH (1.62 g) was added to the hot solution. The mixture was stirred for 15 min, then cooled to RT and acidified with aq. acetic acid (10%, 22.5 cm^3). The resulting precipitate was filtered off and dried to give the product (3.6 g, 83%) as light brown crystals, mp 117-119 °C (lit.,[38] 118-120 °C).

c Preparation of Flavone 125

To a solution of 1,3-dione **124** (3.6 g, 0.015 mol) in glacial acetic acid (20 cm^3) at room temperature, conc. sulfuric acid (0.8 cm^3) was added. The mixture was heated under reflux for 1h, with occasional shaking and then poured onto crushed ice (110 g) with vigorous stirring. After the ice was melted, the solid product was filtered off and washed with water until free from acid and dried to give the product (3.14 g, 47%) as yellow crystals, mp 97-99 °C (lit.,[39] 96-97 °C); δ_H 8.24 (1 H, dd, *J* 8.1, 1.8), 8.0-7.9 (2 H, m), 7.71 (1 H, m), 7.6-7.5 (4 H, m), 7.43 (1 H, m) and 6.84 (1 H, s); δ_C 178.4 (CO), 163.3 (4ry), 156.2 (4ry), 133.7 (CH), 131.7 (4ry), 131.6 (CH), 129.0 (2CH), 126.2 (2CH), 125.6 (CH), 125.1 (CH), 123.9 (4ry), 118.0 (CH) and 107.5 (CH).

d Preparation of 3-iodoflavone 126

A solution of lithium diisopropylamide was prepared by allowing butyl lithium (2.5 M, 4 cm^3) to react with the diisopropylamine (1.5 cm^3, 10 mmol) in THF (40 cm^3) at -78 °C under N_2. The solution was stirred during the addition of **125** (2.22 g, 10 mmol). After 5 min, a solution of iodine (2.54 g, 10 mmol) in THF (6 cm^3) was added at -78 °C and the colour was observed to fade quickly. The mixture was added to water and extracted with ethyl acetate. The combined extracts were dried and evaporated to give the product (2.92 g, 84%); δ_H 8.29 (1 H, dd, *J* 9, 3), 7.8-7.69 (3 H, m) and 7.6-7.43 (5 H, m); δ_C 174.4 (CO), 164.4 (4ry), 155.7 (4ry), 134.9 (4ry), 134.1

(CH), 130.9 (CH), 129.3 (2CH), 128.2 (2CH), 126.6 (CH), 125.7 (CH), 119.8 (4ry), 117.5 (CH) and 88.2 (C-I).

2 FVP of Flavone and 3-Iodoflavone

a FVP of Flavone

FVP of the title compound **125** (56.4 mg) at 850 °C and 2-3 × 10^{-2} Torr gave a yellow solid at the exit of the furnace. NMR results showed the crude product was unchanged flavone.

b FVP of 3-iodoflavone

FVP of the title compound **126** (71.3 mg) at 750 °C and 2-3 × 10^{-2} Torr gave a yellow solid at the exit of the furnace. NMR results showed the crude products were a mixture of flavone and 2-phenylbenzofuran. The mixture was separated by using column chromatography with ether-hexane (1:5) as eluant. The first fraction was the 2-phenylbenzofuran (10.5 mg, 26%) and the second fraction was flavone (2.0 mg, 4%). For both products the NMR spectra were good agreement with the lit.[58] Further details of pyrolysis at different temperatures are given in the Results and Discussion section.

E Attempted Preparation of Protected Ylides

1 Preparation of Starting Material

a Preparation of ethyl 2-(2-methoxyphenyl)-1,3-dioxolane-2-carboxylate 127

The starting keto ester **115** was added to a stirred solution of ethylene glycol (12.8 g, 200 mmol) and *p*-toluenesulfonic acid (285 mg, 1.5 mmol) in toluene (350 cm^3), then the mixture was heated under reflux for 18 h. After the mixture was cooled, it was washed with saturated aq. $NaHCO_3$ and aq. NaCl, and the organic phase was dried

and evaporated to give the product, which was purified by distillation at 170–175 °C to give a dark coloured liquid (5.45 g, 46%); δ_H 7.63 (1 H, dd, *J* 7.5, 1.8), 7.32 (1 H, td, *J* 7.5, 1.8), 6.97 (1 H, t, *J* 7.0), 6.87 (1 H, d, 8.1), 4.25 (2 H, m), 4.19 (2 H, q, C*H*$_2$CH$_3$), 4.10 (2 H, m), 3.78 (3 H, s, OMe) and 1.19 (3 H, t, CH$_2$C*H*$_3$); δ_C 169.0 (4ry, C=O), 156.6 (4ry, C-2 of Ar), 130.2 (CH of Ar), 126.2 (4ry, O-C-O), 125.5 (CH of Ar), 120.2 (CH of Ar), 110.7 (CH of Ar), 103.9 (4ry, C-1 of Ar), 65.9 (2 C, OCH$_2$CH$_2$O), 61.2 (*C*H$_2$-CH$_3$), 55.4 (OMe) and 13.8 (CH$_2$-*C*H$_3$).

b Preparation of (2-(2-methoxyphenyl)-1,3-dioxolan-2-yl)methanol 128

Under N_2 atmosphere, the starting ester **127** (7.20 g, 30.8 mmol) in dry THF (100 cm^3), was added dropwise to a stirred suspension of $LiAlH_4$ (1.50 g, 39.5 mmol) in dry THF (15 cm^3) and the resulting mixture was heated under reflux for 4 h. To destroy the excess of $LiAlH_4$, water (1.6 cm^3) in THF (10.5 cm^3) was carefully added to the mixture followed by 15% solution sodium hydroxide (1.6 cm^3) and finally water (4.8 cm^3). The mixture was stirred for 0.5 h and extracted with diethyl ether. The organic phase was washed with water, dried, and evaporated to give the crude product. This was recrystallised from hexane and ethyl acetate to give the product (2.21 g, 34%) as white crystals, mp 120-123 °C. (Found: M^++Na 233.0783. $C_{11}H_{14}O_4Na$ (M^++Na) requires 233.0790); ν_{max}/cm^{-1} 3484 (OH), 1600, 1584, 1282, 1242, 1213, 1077, 1039, 865 and 759; δ_H 7.55 (1 H, dd, *J* 8,7, 1.5, H-6 of Ar), 7.33 (1 H, ddd, *J* 8.1, 6.9, 2.1, H-4 of Ar), 6.95 (2 H, m, H-3 and H-5 of Ar), 4.20-4.09 (2 H, m), 4.02-3.94 (2 H, m), 3.99 (2 H, s, C*H*$_2$OH), 3.87 (3 H, s, OMe) and 2.07 (1 H, br s, OH); δ_C 157.3 (4ry, C-2 of Ar), 130.1 (CH), 127.7 (CH), 126.8 (4ry, C-2 of Ar), 120.3 (CH), 111.9 (CH), 109.3 (4ry, O*C*O), 65.5 (2 C, CH$_2$CH$_2$), 65.4 (CH$_2$OH) and 55.8 (OMe); m/z (ES^+) 233.02 (M^++Na, 100%).

c Preparation of 2-bromo-1-(2-methoxyphenyl)ethanone 129

To a stirred solution of 2-methoxyacetophenone (10 g, 67 mmol) in diethyl ether (100 cm^3) was added dropwise liquid bromine (10.6 g, 3.4 cm^3, 67 mmol) while the

temperature was kept below 30 °C. The mixture was stirred at room temperature for 30 minutes, and then was evaporated to dry to give the products, which were purified by distillation at 170 °C to give the product (4.77 g, 31%) as white crystals, mp 41-44 °C (lit.,[40] 40-44 °C). δ_H 7.84-7.81 (1 H, m, H-6), 7.55-7.49 (1 H, m, H-4), 7.06-7.98 (2 H, m, H-3 and 5), 4.61 (2 H, s, CH_2Br) and 3.95 (3 H, s, OMe).

d Preparation of 2-(bromomethyl)-2-(2-methoxyphenyl)-1,3-dioxolane 130

This was prepared as in **E1b**, using bromo ketone **129** (4.77 g, 20.83 mmol), ethylene glycol (1.94 g, 31.25 mmol) and *p*-toluenesulfonic acid (395 mg, 2.08 mmol) in toluene (210 cm^3). The crude product was recrystallised from hexane/ethyl acetate to give the pure product (3.47g, 61%) as white crystals, mp 95-97 °C; (Found: M^++H 273.0120/275.0100. $C_{11}H_{14}O_3{}^{79/81}Br$ (M^++H) requires 273.0126/275.0106); ν_{max}/cm^{-1} 2923, 2853, 1598, 1584.08, 1463, 1280, 1203, 1039, 761 and 617; δ_H 7.57-7.54 (1 H, m, H-6), 7.36-7.31 (1 H, m, H-4), 6.89-6.93 (2 H, m, H-3 and 5), 4.23-4.15 (2 H, m, C_2H_4), 4.02-3.95 (2 H, m, C_2H_4), 3.98 (2 H, s, CH_2Br) and 3.89 (3 H, s, OMe); δ_C 157.1 (4ry, C-2), 130.1 (C-4), 127.6 (C-6), 126.7 (4ry, C-1), 120.3 (C-5), 111.8 (C-3), 107.3 (4ry, O*C*O), 66.0 (2 C, C_2H_4), 55.9 (OMe) and 37.0 (CH_2Br); m/z (ES^+) 273.01 (M^++H, 30%)

e Preparation of (2-methoxybenzoylmethyl)triphenylphosphonium bromide 131

The starting bromo ketone **129** (15.3 g, 67 mmol) and triphenylphosphine (17.6 g, 67 mmol) were stirred in toluene (50 cm^3) at room temperature overnight, then the participate was filtered off and dried to give the product (18.41 g, 74%) as white crystals; δ_H 8.00-6.80 (19 H, m), 6.08 (2 H, *J* 11), 4.04 (3 H, s); δ_H 191.7 (4ry, C=O), 159.8 (4ry, C-2 of Ar), 136.1 (CH), 134.5 (3 C, d, *J* 3, C-4 of PPh_3), 133.9 (6 C, d, *J* 11, C-2 of PPh_3), 131.0 (CH), 130.1 (6 C, d, *J* 13, C-3 of PPh_3), 120.8 (CH), 119.91

(4ry, 3 C, d *J* 89, C-1 of PPh_3), 112.3 (CH), 56.7 (OMe) and 41.8 (d, *J* 59, CH_2); δ_P +21.5

F Preparation and Pyrolysis of β,β'-dioxo ylides

1 Preparation of Starting Material

a Preparation of *p*-tolyl acetate 132

To a solution of *p*-cresol (15 g, 139 mmol) in acetic anhydride (37.5 cm^3) was added pyridine (1.13 cm^3). After 12 h of stirring at 25 °C, the volatiles were evaporated. The resulting oil was taken up in diethyl ether, washed with 10% aqueous sodium bicarbonate twice and brine once, and dried and evaporated to give the acetate (20.85 g, quant. yield) which was used without further purification for **F1c**. δ_H 7.15 (2 H, d, *J* 9, H-3 and 5), 6.95 (2 H, d, *J* 9, H-2 and 6), 2.32 (3 H, s, OMe) and 2.25 (3 H, s, Me)

b Preparation of 4-chlorophenyl acetate 133

This was prepared as in **F1a**, using *p*-chlorophenol (15 g, 116.7 mmol), acetic anhydride (11.96 g, 116.7 mmol) and conc. sulfuric acid (0.05 cm^3) to give the product (19.8 g, quant. yield) which was used without further purification for **F1d**; δ_H 7.32 (2 H, d, *J* 9.3, H-3 and 5), 7.02 (2 H, d, *J* 9.3, H-2 and 6) and 2.27 (3 H, s, Me).

c Preparation of 2-hydroxy-5-methylacetophenone 134

To the crude ester **132** (20.85 g, 0.14 mmol) was added anhydrous aluminum chloride (18.75 g, 0.14 mmol) and the mixture was heated for 1 h at 130 °C. It was then cooled to 25 °C, treated with ice (7.5 g), allowed to stand for 1 h, diluted with CH_2Cl_2 , and stirred overnight. The organic phase phase was separated, dried, and evaporated to

give the product (16.63 g, 80%) as green crystals, mp 48-50 °C, (lit.,[41] 50 °C); δ_H 12.10 (1 H, s, OH), 7.48 (2 H, d, *J* 1.8, H-6), 7.26 (1 H, dd, *J* 8.4, 1.8, H-4), 6.86 (1 H, d, *J* 8.4, H-3), 2.32 (3 H, s, OMe) and 2.25 (2 H, s, Me)

d Preparation of 5-chloro-2-hydroxyacetophenone 135

This was prepared as in **F1c**, using the crude ester **133** (19.8 g, 116.7 mmol) and anhydrous aluminium chloride (15.60 g, 116.7 mmol) to give the product (15.88 g, 80%) as a green liquid; δ_H 12.16 (1 H, s, OH), 7.68 (1 H, d, *J* 2.7, H-6), 7.40 (1 H, dd, *J* 9, 2.7, H-4), 6.93 (1 H, d, *J* 9, H-3) and 2.61 (3 H, s, Me).

e Preparation of 2-methoxy-5-methylacetophenone 136

Methyl iodide (5.02 cm^3, 80 mmol) was added to a stirred mixture of hydroxyacetophenone **134** (10.0 g, 67 mmol) and anhydrous potassium carbonate (9.19 g, 67 mmol) in dry dimethylformamide (120 cm^3), and the mixture was stirred for 18 h at room temperature. The solvent was removed under vacuum, water was added, and the mixture was extracted with diethyl ether. The extracts were washed well with water to remove traces of DMF, dried and evaporated to give the product which was used without further purification for **F1g**; δ_H 7.53 (1 H, d, *J* 1.8, H-6), 7.24 (1 H, dd, *J* 6.3 1.8, H-4), 6.85 (1 H, d, *J* 6.3, H-3), 3.86 (3 H, s, OMe), 2.60 (3 H, s, COMe) and 2.28 (3 H, s, ArMe).

f Preparation of 5-chloro-2-methoxyacetophenone 137

This was prepared as in **F1e**, using hydroxyacetophenone **135** (15.88 g, 93.14 mmol), MeI (7.01 cm^3, 111.8 mmol) and anhydrous K_2CO_3 (12.87 g, 93.14 mmol) in DMF (150 cm^3) to give the crude product which was used without further purification for **F1h**; δ_H 7.69 (1 H, d, *J* 3, H-6), 7.40 (1 H, dd, *J* 9, 3, H-4), 6.91 (1 H, d, *J* 9, H-3), 3.90 (3 H, s, OMe) and 2.60 (3 H, s, Me).

g Preparation of 2-methoxy-5-methylphenacyl bromide 138

This was prepared as in **E1c**, using the crude compound **136** (18.18 g, 111 mmol) and bromine (3.77 cm^3, 73 mmol) in diethyl ether (160 cm^3), with recrystallisation from the ethanol to give the product (11.22 g, 42%) as grey crystals, mp 76-78 °C (lit.,[42] 77 °C); δ_H 7.62 (1 H, m, H-6), 7.31 (1 H, m, H-4), 6.89 (1 H, m, H-3), 4.60 (2 H, s, CH_2Br), 3.92 (3 H, s, OMe), 2.31 (3 H, s, Me of Ph)

h Preparation of 5-chloro-2-methoxyphenacyl bromide 139

This was prepared as in **E1c**, using the crude compound **137** (20.57 g, 112 mmol) and bromine (3.17 cm, 61 mmol) in diethyl ether (150 cm^3), with recrystallisation from ethanol to give the product (10.05 g, 41%) as white crystals, mp 94-96 °C; δ_H 7.78 (1 H, d, *J* 2.7, H-6), 7.46 (1 H, dd, *J* 8.7, 2.7, H-4), 6.95 (1 H, d, *J* 8.7, H-3), 4.57 (2 H, s, CH_2Br) and 3.95 (3 H, s, OMe).

i Preparation of (2-methoxy-5-methylbenzoylmethyl)triphenylphosphonium bromide 140

This was prepared as **E1e**, using starting material **138** (5.86 g, 25.6 mmol) and triphenylphosphine (6.71 g, 25.6 mmol) in toluene (100 cm^3) reacted at room temperature to give the product (8.20 g, 63%) as white crystals, mp 168-170 °C, δ_H 7.93-7.66 (15 H, m), 7.52 (1 H, d, *J* 2, H-4 of Ar), 7.32 (1 H, dd, *J* 8.4, 2, H-6 of Ar), 6.89 (1 H, d, *J* 8.4, H-3 of Ar), 6.07 (2 H, d, *J* 11, CH_2PPh_3), 4.01 (3 H, s, OMe) and 2.25 (3 H, s, ArMe); δ_C 191.7 (4ry, d, *J* 7, CO), 157.9 (4ry, C-2 of Ar), 136.8 (CH of Ar), 134.5 (3 C, d, *J* 3, C-4 of PPh_3), 133.9 (6 C, d, *J* 10, C-2 of PPh_3), 131.0 (CH of Ar), 130.05 (6 C, d, *J* 13, C-3 of PPh_3), 119.0 (3 C, d, *J* 89, C-1 of PPh_3), 112.2 (CH of Ar), 56.7 (OMe), 41.7 (d, *J* 58, CH_2) and 20.1 (ArMe); δ_P +21.4.

j Preparation of (5-chloro-2-methoxybenzoylmethyl)triphenylphosphonium bromide 141

This was prepared as **E1e**, using starting material **139** (10.05 g, 38.14 mmol) and triphenylphosphine (10.00 g, 38.14 mmol) in toluene (150 cm^3) heated under reflux for 3.5 h to give the product (12.0 g, 62%) as white crystals, mp 199-201 °C, δ_H 7.95-7.85 (6 H, m), 7.78-7.70 (3 H, m), 7.70-7.62 (6 H, m), 7.58 (1 H, d, *J* 2.7, H-6 of Ar), 7.46 (1 H, dd, *J* 8.7, 2.7, H-4 of Ar), 6.98 (1 H, d, *J* 8.7, H-3 of Ar), 6.24 (2 H, d, 11, CH_2PPh_3) and 4.11 (3 H, s, OMe); δ_C 190.8 (4ry, d, *J* 7, CO), 158.5 (4ry, C-2 of Ar), 135.6 (CH of Ar), 134.6 (3 C, d, *J* 3, C-4 of PPh_3), 133.9 (6 C, d, *J* 11, C-2 of PPh_3), 132.1 (CH of Ar), 130.1 (CH of Ar), 130.0 (6 C, d, *J* 13, C-3 of PPh_3), 126.2 (4ry, d, *J* 5, C-1 of Ar), 126.0 (4ry, C-5 of Ar), 118.9 (3 C, d, *J* 89, C-1 of PPh_3), 114.0 (CH of Ar), 57.2 (OMe) and 41.9 (d, *J* 59, CH_2); δ_P +21.3.

2 Preparation of Ylides

a Preparation of (2-methoxybenzoyl)methylenetriphenylphosphorane 142

The starting phosphonium salt **131** (10.14 g, 20.65 mmol) was dissolved in a saturated aq. solution of Na_2CO_3, and stirred for a few minutes. The mixture was extracted with CH_2Cl_2 , which was dried and evaporated to give the crude product. This was recrystallised from the ethyl acetate to give the pure product (7.41 g, 87%) as yellow crystals, mp 144-145 °C; δ_H 7.85 (1 H, dd, *J* 1.8, 7.5, H-6 of Ar), 7.80-7.70 (6 H, m), 7.60-7.50 (3 H, m), 7.50-7.40 (6 H, m), 7.26 (1 H, m, H-4 of Ar), 6.91 (2 H, m, H-3 and H-5 of Ar), 4.59 (1 H, d, J, 28.2) and 3.88 (3 H, s, OMe); δ_C 183.9 (4ry, CO), 157.4 (4ry, C-2 of Ar), 133.2 (6 C, d, *J* 10, C-2 of PPh3), 131.8 (3 C, d, *J* 3, C-4 of PPh_3), 129.7 (CH of Ar), 129.6 (CH ofAr), 128.7 (6 C, d, *J* 12, C-3 of PPh_3), 127.3 (3 C, d, *J* 90, C-1 of PPh_3), 120.2 (CH of Ar), 111.4 (CH of Ar), 55.8 (OMe) and 55.1 (d, *J* 110, $CHPPh_3$); δ_p +15.0.

b Preparation of (2-methoxy-5-methylbenzoyl)methylenetriphenylphosphorane 143

This was prepared as **F2a**, using starting material **140** (8.2 g, 16.23 mmol) with recrystallisation from ethyl acetate to give the product (5.64 g, 82%) as white crystals, mp 170-172 °C, (Found: M^++H 425.1658. $C_{28}H_{26}O_2P$ (M^++H) requires 425.1670); ν_{max}/cm^{-1} 1732, 1677, 1602, 1587, 1578, 1266, 1241, 1155, 1103 and 1022; δ_H 7.78-7.70 (7 H, m), 7.57-7.42 (9 H, m), 7.07 (1 H, dd, *J* 9, 3, H-4), 6.81 (1 H, d, *J* 9, H-3), 4.67 (1 H, d, *J* 30, CH=PPh_3), 3.86 (3 H, s, OMe) and 2.27 (3 H, s, ArMe); δ_C 183.6 (4ry, d, *J* 2, CO), 155.4 (4ry, C-2 of Ar), 133.1 (6 C, d, *J* 10, C-2 of PPh_3), 131.7 (3 C, d, C-4 of PPh_3), 131.1 (4ry, d, *J* 13, C-1 of Ar), 130.2 (CH of Ar), 130.0 (CH of Ar), 129.4 (4ry, C-5 of Ar), 128.6 (6 C, d, *J* 12, C-3 of PPh_3), 127.2 (3 C, d, *J* 90, C-1 of PPh_3), 111.6 (CH of Ar), 56.1 (OMe), 55.1 (d, *J* 107, CH=PPh_3) and 20.3 (Me); δ_P +15.0.

c Preparation of (5-chloro-2-methoxybenzoyl)methylenetriphenylphosphorane 144

The was prepared as **F2a**, using starting material **141** (12.36 g, 23.51 mmol) with recrystallisation from ethyl acetate/CH_2Cl_2 to give the product (9.89 g, 95%) as white crystals, mp 191-193 °C; δ_H 7.83 (1 H, d, *J* 2.7, H-6 of Ar), 7.77-7.69 (6 H, m), 7.58-7.52 (3 H, m), 7.49-7.43 (6 H, m), 7.20 (1 H, dd, *J* 8.1, 2.7, H-4 of Ar), 6.82 (1 H, d, *J* 8.1, H-3 of Ar), 4.59 (1 H, d, *J* 27, CH=PPh_3) and 3.84 (3 H, s, OMe); δ_C 182.0 (4ry, CO), 156.0 (4ry, C-2 of Ar), 133.1 (6 C, d, *J* 10, C-2 of PPh_3), 132.0 (3 C, d, *J* 3, C-4 of PPh_3), 129.6 (CH of Ar), 129.1 (CH of Ar), 128.8 (6 C, d, *J* 11, C-3 of PPh_3), 126.89 (3 C, d, *J* 91, C-1 of PPh_3), 125.5 (4ry, C-1 of Ar), 112.8 (CH of Ar), 56.2 (OMe) and 55.8 (d, *J* 104, CH=PPh_3) [C-Cl not apparent]; δ_P +15.2.

d Preparation of (cinnamoyl)(2-methoxy-5-methylbenzoyl)methylenetriphenyl -phosphorane 145

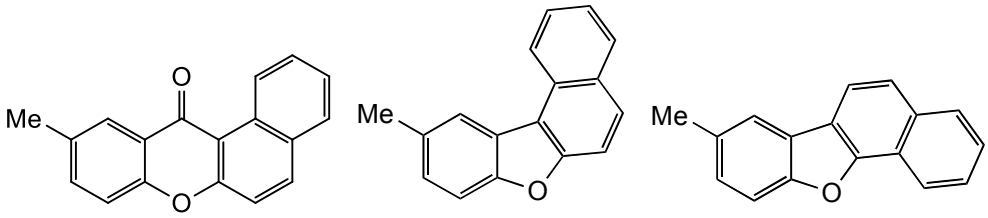
A solution of the stabilised ylide **143** (1.0 g, 2.37 mmol) and triethylamine (0.24 g, 2.37 mmol, 0.33 cm^3) in dry toluene was stirred at room temperature while a solution of the appropriate acid chloride (0.39 g, 2.37 mmol) in dry toluene was added dropwise to it. After the addition, the solution was stirred for 3 h and then poured into water. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 . The combined organic phase was dried and evaporated to give the ylides which were recrystallised from ethyl acetate to give the product (0.5 g, 39%) as yellow crystals, mp 147-148 °C, (Found: M^++Na, 577.1909. $C_{37}H_{31}NaO_3P$ (M+Na) requires 577.1909), ν_{max}/cm^{-1} 2969, 2880, 1630, 1574, 1457, 1312, 1276, 1106 and 978; δ_H 7.82-7.72 (6 H, m), 7.55-7.40 (9 H, m), 7.25-7.12 (5 H, m), 7.12-7.05 (1 H, dd, *J* 8.4, 2), 7.05-6.98 (2 H, m), 6.85 (1 H, d, *J* 15.6), 6.72 (1 H, d, *J* 8.4), 3.77 (3 H, s, OMe) and 2.26 (3 H, s, OMe); δ_C 189.9 (4ry, d, *J* 8, COAr), 185.8 (4ry, d, *J* 6, COCH=), 154.2 (4ry, C-2 of Ar), 136.6 (d, *J* 2, CHPh), 136.1 (4ry, C-1 of Ar), 133.2 (6 C, d, *J* 10, C-2 of PPh_3), 131.4 (3 C, d, *J* 3, C-4 of PPh_3), 130.7 (C-6 of Ar), 129.9 (4ry, C-1 of Ph), 129.6 (C-4 of Ph), 128.4 (6 C, d, *J* 13, C-3 of PPh_3), 128.2 (2 C, C-3 and 5 of Ph), 127.5 (2 C, C-2 and 6 of Ph), 126.9 (d, *J* 10, =CHCO), 126.3 (4ry, 3 C, d, *J* 92, C-1 of PPh_3), 111.0 (C-3 of Ar), 89.8 (4ry, d, *J* 102, C=P), 55.6 (OMe) and 20.3 (Me); δ_P +16.8.

3. FVP of Ylides

a. FVP of Ylide 145

FVP of the title compound **145** (49.9 mg) at 750 °C and 2-3 × 10^{-2} Torr gave a yellow solid at the exit of the furnace. NMR results suggested that the crude product consisted of at least three different heterocyclic compounds such as: 10-methyl-12*H*-benzo[*a*]xanthen-12-one **146**, 10-methylnaphtho[2,1-*b*]benzofuran **147** and 8-methylnaphtho[1,2-*b*]benzofuran **148**. However despite extensive attempts,

the very closely similar properties of these meant that they could not be separated or characterised fully. For further details see the Results and Discussion section.



146 **147** **148**

G Preparation and Pyrolysis of Thiocarbonyl Ylides

1 Preparation of Starting Materials

a Preparation of thiobenzoyl chloride 149

A solution of phenylmagnesium bromide (0.1 mol, 18 g) in dry THF (100 cm^3) under nitrogen atmosphere was cooled to -20 °C and then carbon disulfide (7.6 g, 0.1 mol, 5.9 cm^3) was added dropwise making sure the mixture did not boil. After 30 min the mixture was slowly allowed to reach room temperature and then stirred for 12 h.
Then the mixture was cooled to -20 °C again while ice was added. Both layers were transferred to a separating funnel along with some water washing from the flask. Then the organic layer was removed and discarded and the aqueous layer was washed with diethyl ether, which was also discarded. The aqueous layer was acidified with HCl (aq), which led to the precipitation of the product as violet red, sharp smelling oil. This was extracted with diethyl ether, which was dried over magnesium sulfate. The solution was not fully evaporated but reduced to 100 cm^3 to avoid decomposition and this solution was used directly for the next step.

The solution of the previous part was stirred in a 3-neck flask fitted with a condenser and a dropping funnel under nitrogen atmosphere. Thionyl chloride (31 g, 0.26 mol,

19 cm^3) was added slowly. The mixture was heated under reflux for 7 h, then the excess thionyl chloride and solvent was evaporated off to give a red liquid. This liquid was transferred to a flask for fractional distillation. The liquid was firstly distilled at 50 °C under oil pump to remove $SOCl_2$ and a little S_2Cl_2. Then the temperature was increased to 200 °C to distil over the remainder of the product.

b Preparation of phenylglyoxylyl chloride 150

To a solution of phenylglyoxylic acid (5.0 g, 32.7 mmol) in CH_2Cl_2, was added oxalyl chloride (3.5 cm^3, 4.94 g, 39.2 mmol) at room temperature followed by addition of a drop of DMF as catalyst. The mixture was stirred at this temperature until all gas evolution ceased. The mixture was evaporated to give the crude product which was used directly for the next step; δ_H 8.00-7.97 (2 H, m), 7.75-7.70 (1 H, m) and 7.58-7.52 (2 H, m); δ_C 180.9 (4ry, Ph*C*=O), 166.6 (4ry, ClC=O), 135.9 (C-4 of Ph), 130.4 (2 C, C-3 and 5 of Ph), 129.3 (4ry, C-1 of Ph) and 129.2 (C-2 and 6 of Ph).

c Preparation of 3-bromo-1-phenylpropane-1,2-dione 151

To a stirred solution of 1-phenylpropane-1,2-dione (3.0 g, 20.2 mmol) in diethyl ether (30 cm^3) was added dropwise bromine (3.2 g, 1.04 cm^3, 20.2 mmol) while the temperature was kept below 30 °C. The mixture was stirred at room temperature for 30 min, and then was evaporated to dryness to give the product, which was not purified but used directly for the next reaction; δ_H 8.11-7.98 (2 H, m, Ar), 7.69-7.60 (1 H, m, Ar), 7.53-7.46 (2 H, m, Ar) and 4.41 (2 H, s, CH_2Br).

d Preparation of benzoylmethyltriphenylphosphonium bromide, 152

To a solution of triphenylphosphine (26.2 g, 0.1 mol) in dry toluene (100 cm^3) was added dropwise a solution of phenacyl bromide (20 g, 0.1 mol) in dry toluene (20 cm^3), the mixture was heated under reflux for 2 h and left to stir at RT overnight. The

off-white precipitate was filtered off, washed with ether and dried to furnish the product (40 g, 87%) as a white powder, mp 265-266 °C, δp + 21.9.

2 Preparation of Ylides

a Preparation of (5-chloro-2-methoxythiobenzoyl)methylenetriphenylphosphor -ane, 153

Under an N_2 atmosphere, triflic anhydride (0.65 g, 0.4 cm^3, 2.25 mmol) was added dropwise to the solution of ylide **144** (1 g, 2.25 mmol) in dry CH_2Cl_2 (40 cm^3) with stirring. After complete addition the mixture was left to stir for 1 h under N_2. The solution was evaporated and the residual oil was dissolved in DMF (30 cm^3). This was followed by addition of anhydrous sodium sulfide (0.26 g, 3.4 mmol) and it was left to stir for 24 h. The mixture was added to water and extracted using diethyl ether, which was dried and evaporated to give the product (0.50 g, 48%) as yellow crystals, mp 172-174 °C; (Found: M^++H 461.0901. $C_{27}H_{22}ClOPS$ (M^++H) requires 461.0896); ν_{max}/cm^{-1} 2926, 1463, 1104 (C=S) and 721 (C-Cl) δ_H 7.86-7.79 (6 H, m), 7.62-7.56 (3 H, m), 7.53-7.47 (6 H, m), 7.51 (1 H, d, *J* 3, H-6 of Ar), 7.11 (1 H, dd, *J* 9, 3, H-4 of Ar), 6.78 (1 H, d, *J* 9, H-3 of Ar), 5.46 (1H, d, *J* 33, P=CH) and 3.85 (3 H, s, OMe); δ_C 194.3 (4ry, d, *J* 6, C=S), 152.9 (4ry, C-2 of Ar), 140.6 (4ry, d, *J* 17, C-1 of Ar), 133.4 (6 C, d, *J* 11, C-2 of PPh_3), 132.4 (3 C, d, *J* 2, C-4 of PPh_3), 129.0 (6 C, d, *J* 12, C-3 of PPh_3), 128.8 (C-4 of Ar), 127.4 (C-6 of Ar), 125.4 (4ry, C-5 of Ar), 124.2 (4 ry, 3 C, d, *J* 92, C-1 of PPh_3), 112.7 (C-3 of Ar), 87.1 (d, *J* 109, C=P) and 56.5 (OMe); δ_P +6.4; m/z (ES^+) 461.09 (M^++H, 90%).

b Preparation of benzoylmethylenetriphenylphosphorane 154

The phosphonium salt **152** (15 g, 32.5 mmol) was dissolved in water and the solution extracted with toluene to remove any triphenylphosphine. The aqueous was stirred vigorously as sodium hydroxide (1.3 g, 32.5 mmol) in water was added quickly. The mixture was extracted with CH_2Cl_2 and the combined organic phase was washed with water, dried and evaporated. The resulting solid was recrystallised from ethyl

acetate to give the product (6.8 g, 55%) as white crystals, mp 180-182 °C; δ_H 7.99-7.96 (2 H, m), 7.76-7.68 (6 H, m), 7.60-7.52 (3 H, m), 7.52-7.74 (6 H, m), 7.36-7.34 (3 H, m), and 4.43 (1 H, d, *J* 24, P=CH); δ_P +16.6.

c Preparation of thiobenzoylmethylenetriphenylphosphorane 155

This was prepared as **G2a**, using ylide **154** (3.0 g, 7.9 mmol), triflic anhydride (2.7 g, 1.6 cm^3, 9.5 mmol) and Na_2S (0.95 g, 11.8 mmol) to give the crude product which were recrystallised from ethyl acetate/pet ether to give the product (1.8 g, 58%) as yellow crystals, mp 168-170 °C; δ_H 8.05-7.98 (2 H, m), 7.85-7.75 (6 H, m), 7.62-7.53 (3 H, m), 7.53-7.43 (6 H, m), 7.32-7.25 (3 H, m) and 5.63 (1 H, d, *J* 30.9, P=CH); δ_C 193.9 (4ry, d, *J* 6, C=S), 146.2 (4ry, d, *J* 17, C-1 of Ar), 133.3 (6 C, d, *J* 10, C-2 of PPh_3), 132.2 (3 C, d, *J* 3, C-4 of PPh_3), 128.9 (3 C, d, *J* 13, C-3 of PPh_3), 128.7 (C-4 of Ar), 127.4 (C-2 and 6 of Ar), 126.8 (C-3 and 5 of Ar), 124.6 (3 C, d, *J* 93, C-1 of PPh_3) and 82.8 (d, *J* 116, CH=P); δ_P +7.2.

d Alternative preparation of thiobenzoylmethylenetriphenylphosphorane 155

The ylide **154** (1.5 g, 4.0 mmol) and Lawesson's reagent (0.8 g, 2.3 mmol) were dissolved in the toluene (150 cm^3) and the mixture was heated under reflux for 3 h. The solvent was evaporated off, and the residual crude oil was purified by column chromatograph with diethyl ether/CH_2Cl_2 as eluent to give the product (0.15 g, 9%) as yellow crystals with properties idetical to the product above.

e Preparation of 1-phenyl-3-(triphenylphosphoranylidene)propane-1,2-dione 156

A solution of bromoketone **151** (3.2 g, 13.5 mmol) in dry toluene (10 cm^3) was added dropwise to a solution of triphenylphosphine (3.5 g, 13.5 mmol) in dry toluene (50 cm^3) and the mixture stirred under a nitrogen atmosphere for 3 h. CH_2Cl_2 was added

to dissolve all the precipitated phosphonium salt. Then a solution of NaOH (0.73 g) in water (20 cm_3) was added in one portion. The mixture was stirred rapidly for a few minutes and the organic phase was separated, dried and evaporated to give the product (5.3 g, 94%) as pale yellow crystals, mp 162-164 °C (Lit.,[22] 160-161 °C); δ_H 8.14 (2 H, d, *J* 7, Ph), 7.75-7.68 (6 H, m), 7.60-7.57 (3 H, m), 7.53-7.45 (7 H, m), 7.41-7.36 (2 H, m) and 4.48 (1 H, d, *J* 21, CH=P); δ_C 195.8 (4ry, d, *J* 17, C=O), 183.4 (4ry, d, *J* 3, C=O), 135.0 (4ry, C of Ar), 133.1 (6 C, d, *J* 11, C-2 of PPh_3), 132.6 (CH of Ar), 132.5 (3 C, d, *J* 2, C-4 of PPh_3), 130.4 (2 C, CH of Ar), 129.0 (6 C, d, *J* 13, C-3 of PPh_3), 128.0 (2 C, CH of Ar), 125.6 (4ry, d, *J* 91, C-1 of PPh_3) and 54.8 (d, *J* 105, $CH=PPh_3$); δ_P +17.0.

f Preparation of 1,4-diphenyl-3-(triphenylphosphoranylidene)butane-1,2,4-trione 157

To a stirred solution of ylide **154** (4.2 g, 11 mmol) and triethylamine (1.53 cm^3, 1.11 g, 11 mmol) in dry toluene was added phenylglyoxylyl chloride **150** (1.85 g, 11 mmol, 1 eq.) in dry toluene dropwise. The mixture was stirred at RT for 4 h, washed with water and the organic phase separated. The aqueous phase was extracted with CH_2Cl_2 twice and the combined organic phase dried. The solvent was evaporated to furnish the crude product which was recrystallised from ethyl acetate to give the product (3.83 g, 68%) as yellow crystals, mp 158-160 °C (Lit.,[21] 158-160 °C); δ_H 7.85-6.90 (25 H, m); δ_C 193.4 (4ry, d, *J* 10, CO-*C*O-Ph), 193.3 (4ry, d, *J* 8, P=C*C*O-Ph), 190.1 (4ry, d, *J* 4, *C*O-CO-Ph), 141.8 (4ry, d, *J* 8, C-1 of Ph), 134.1 (4ry, d, *J* 2, C-1 of Ph), 133.3 (6 C, d, *J* 10, C-2 of PPh_3), 132.6 (Ph), 132.2 (3 C, *J* 2, C-4 of PPh_3), 130.5 (Ph), 128.9 (4 C, Ph), 128.7 (6 C, d, *J* 12, C-3 of PPh_3), 127.8 (2 C, Ph), 127.4 (2 C, Ph), 124.2 (3 C, d, *J* 92, C-1 of PPh_3) and 84.1 (d, *J* 97, C=P); δ_P + 16.5.

g Preparation of 1,4-diphenyl-2-thioxo-3-(triphenylphosphoranylidene)butane-1,4-dione 159

Triphenylphosphine (2.36 g, 6.9 mmol) in dry toluene (20 cm^3) was rapidly added with stirring to dibenzoylacetylene **158** (1.05 g, 3.4 mmol) and sulfur (1.42 g, 34 mmol) in dry toluene (20 cm^3). Monitoring by ^{31}P NMR indicated that the mixture contained Ph_3PS and product in the ration of 4:1. The products were separated by chromatography on silica gel with hexane as the eluent to flush off the Ph_3PS and hexane/ether 1:1 to elute the product (0.88 g, 37%) as pale brown crystals, mp 106-108 °C; ν_{max}/cm^{-1} 1730, 1650, 1616, 1463 and 1172 (C=S); δ_H 7.94-7.06 (25 H, m); δ_C 203.6 (4ry, d, *J* 8, C=S), 191.8 (4ry, d, *J* 11, C=O), 191.2 (4ry, d, *J* 15, C=O), 139.2 (4ry, d, *J* 6, C of Ar), 134.7 (4ry, d, *J* 2, C of Ar), 132.8 (6 C, d, *J* 10, C-2 of PPh_3), 132.0 (3 C, d, *J* 3, C-4 of PPh_3), 131.8, 131.5, 129.3, 129.0, 128.4 (6 C, d, *J* 13, C-3 of PPh_3), 127.9 (2 C), 122.3 (4ry, d, *J* 92, C-1 of PPh_3) and 105.8 (4ry, d, *J* 101, C=P); δ_P +10.8.

3. FVP of Ylides

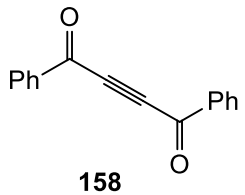
a. **FVP of Ylide 157**

FVP of the title compound 1**57** (3.0 g, 5.86 mmol) at 500 °C and 2-3 × 10-2 Torr gave the dark yellow solid at the exit of the furnace. The product was recrystallised from ethyl acetate/ pet ether to give **dibenzoylacetylene 158** (0.43 g, 31 %) as light green crystals, mp 110-111 °C; δ_H 8.21-8.17 (4 H, m), 7.72-7.62 (2 H, m) and 7.57-7.52 (4 H, m); δ_C 176.5 (4ry, C=O), 135.8 (4ry, C-1 of Ph), 135.2 (2 C, C-4 of Ph), 129.8 (4 C, C-3 and 5 of Ph), 129.0 (4 C, C-2 and 6 of Ph) and 85.8 (4ry, 2 C, C≡C).

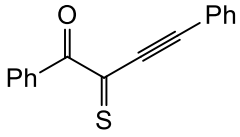
b FVP of Ylide **159**

FVP of the title compound **159** (64.0 mg, 0.12 mmol) at 750 °C and 2-3 × 10-2 Torr gave a dark yellow solid at the exit of the furnace. The ^{31}P NMR results showed the crude product to contain a mixture of Ph_3PO and Ph_3PS with ration of 1:1.2, and the

other pyrolysis products were **dibenzoylacetylene 158** and **1,4-diphenyl-2-thioxobut-3-yn-1-one 160**, respectively.



158



160

H Preparation and Pyrolysis of Imidoyl Ylides

1 Preparation of Starting Materials

a Preparation of 2-methoxybenzoyl chloride 161

To 2-methoxybenzoic acid (30 g, 197 mmol), thionyl chloride (21 cm^3, 300 mmol) was added dropwise with stirring. The mixture was heated for 1 h at 100 °C. Then the mixture was distilled to give the pure liquid product (31.1 g, 93%); δ_H 8.10-8.06 (1 H, m, Ar), 7.59-7.56 (1 H, m, Ar), 7.07-6.99 (2 H, m, Ar) and 3.92 (3 H, s, OMe).

b Preparation of 2-methoxy-*N*-phenylbenzamide 162

To a stirred mixture of aniline (10.9 g, 11 cm^3, 0.12 mol) and NaOH (9.0 g, 0.24 mol) in water (90 cm^3), the acid chloride **161** was added dropwise and the mixture was stirred vigorously for 15 min. The product was extracted with CH_2Cl_2 , which was dried and evaporated to give the crude product. This was recrystallised from ethyl acetate to give the pure product (19.8 g, 73%) as colourless crystals, mp 75-77 °C (lit.,[45] 76-77 °C); δ_H 8.28 (1 H, m, Ar), 7.68 (2 H, m, Ar), 7.50-7.44 (1 H, m, Ar), 7.38-7.32 (2 H, m, Ar), 7.14-7.09 (2 H, m, Ar), 7.01 (1 H, d, *J* 9, Ar) and 4.02 (3 H, s, OMe).

c Preparation of 2-methoxy-*N*-phenylbenzimidoyl chloride 163

A mixture of the starting amide **162** (10 g, 44.1 mmol), PCl_5 (9.1 g, 44.1 mmol) and $POCl_3$ (2 cm^3) was heated under reflux for 5 h. The products were separated by kügelrohr distillation under vacuum. At first the mixture was distilled at RT to remove all the $POCl_3$. When the temperature was raised to 100 °C the mixture became solid, and when the temperature was raised to 170 °C, the product (3.5 g, 32%) was obtained as a yellow liquid; δ_H 7.60-7.55 (1 H, m), 7.38-7.31 (3 H, m), 7.18-7.11 (1 H, m), 7.06-7.00 (2 H, m), 6.95-6.86 (2 H, m) and 3.78 (3 H, OMe); δ_C 159.3 (4ry, C=N), 156.6 (4ry, C-2 of Ar), 147.1 (4ry, C of Ph), 131.8 (CH), 129.9 (CH), 128.6 (2CH), 126.7 (C), 124.8 (CH), 120.1 (2 C, CH), 120.0 (CH), 111.6 (CH) and 55.7 (OMe).

2 Preparation of Ylides

a Preparation of (2-methoxy-*N*-phenylbenzimidoyl)methylenetriphenylphosph -orane 164

To a suspension of methyltriphenylphosphonium bromide (5.3 g, 14.8 mmol) in dry toluene (100 cm^3) at RT and under nitrogen atmosphere was added BuLi (5.9 cm^3, 2.5 M, 14.8 mmol) dropwise. The bright orange solution was stirred for 30 min to form methylenetriphenylphosphorane. To the solution was added imidoyl chloride **163** (1.7 g, 7.4 mmol), then the mixture was stirred overnight. The mixture was added to water and extracted with CH_2Cl_2 . The organic layer was dried and the solvent was removed to furnish a dark red oil, which solidified with time and was recrystallised from ethyl acetate and a little CH_2Cl_2 to give the product (0.77 g, 21%) as yellow crystals, mp 167-169 °C; (Found: M^++H 486.1985. $C_{33}H_{29}NOP$ (M^++H) requires 486.1987); ν_{max}/cm^{-1} 2966, 2945, 1591, 1509, 1460, 1240, 1099, 1022, 890 and 692; δ_H 7.65-7.42 (16 H, m), 7.03-6.84 (6 H, m), 6.53-6.48 (1 H, m), 6.17 (1 H, d, *J* 9) and 3.20 (3 H, s, OMe); δ_C 163.5 (4ry, d, *J* 14, C=N), 155.7 (4ry, C-2 of Ar), 139.4 (4ry, C-1 of Ar), 133.1 (6 C, d, *J* 10, C-2 of PPh3), 133.0 (3 C, d, *J* 2, C-4 of PPh_3), 131.6 (CH), 130.2 (CH), 129.1 (6 C, d, *J* 13, C-3 of PPh_3), 128.1 (CH), 123.6 (CH), 123.3 (4ry, 3 C, d, *J*

92, C-1 of PPh_3), 122.2 (CH), 120.0 (CH), 110.5 (CH), 65.0 (d, *J* 125, *C*H=P) and 54.3 (OMe); δ_P +13.7; m/z (ES^+) 486.08 (M^++H, 100%).

b Preparation of (cinnamoyl)(2-methoxy-*N*-phenylbenzimidoyl)methylenetri -phenylphosphorane 165

A solution of **164** (0.50 g, 1.03 mmol) and triethylamine (0.11 g, 1.03 mmol) in dry toluene (10 cm^3) was stirred at RT while a solution of the cinnamoyl chloride (0.17 g, 1.03 mmol) in dry toluene (5 cm^3) was added dropwise. The mixture was stirred overnight then poured into water. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic extracts were dried and evaporated to give a yellow oil, which solidified and was recrystallised from ethyl acetate to give the product (0.14 g, 22%) as white crystals, mp 215-217 °C; (Found: M^++H 616.2405. $C_{42}H_{35}NO_2P$ (M^++H) requires 616.2405); ν_{max}/cm^{-1} 1634 (C=O), 1274, 1101, 1011, 757 and 722; δ_H 7.63-7.40 (21 H, m), 7.07-6.82 (7 H, m), 6.47-6.42 (1 H, m), 6.07-6.04 (1 H, d, *J* 9), 5.72 (1 H, br s) and 3.54 (3 H, s, OMe); δ_C 190.3 (4ry, d, *J* 4, C=O), 169.7 (4ry, d, *J* 17, C=N), 154.9 (4ry, C-2 of Ar), 141.8 (4ry, C of Ph), 136.0 (4ry, C of Ph), 133.3 (6 C, d, *J* 10, C-2 of PPh_3), 133.0 (3 C, d, *J* 2, C-4 of PPh_3), 132.9 (CH), 130.0 (CH), 129.2 (2 CH), 129.1 (6 C, d, *J* 14, C-3 of PPh_3), 128.8 (CH), 128.5 (CH), 127.9 (CH), 127.6 (2 CH), 126.5 (CH), 121.3 (4ry, 3 C, d, *J* 93, C-1 of PPh_3), 120.7 (4ry, C of Ar), 120.5 (CH), 110.3 (CH), 89.5 (d, *J* 117, *C*H=P) and 55.0 (OMe) [2 CH signals not apparent due to peak overlap]; δ_P +17.0; m/z (ES^+) 616.17 (M^++H, 100%).

3. FVP of Ylides

a. FVP of Ylide 165

FVP of the title compound **165** (50 mg, 0.08 mmol) at 750 °C and 2-3 × 10^{-2} Torr gave a dark yellow solid at the exit of the furnace. The NMR results showed the crude pyrolysis product was a mixture of Ph_3PO and:

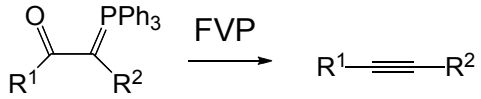
4-phenylimino-2-styryl-4*H*-benzopyran 166 (0.037 mmol, 46%); (Found: M^++H 324.1395. $C_{23}H_{18}NO$ (M^++H) requires 324.1388); δ_H 8.42 (1 H, s), 7.76-7.35 (11 H, m), 7.15-7.10 (1 H, m), 6.97 (2 H, d, *J* 6), 6.58 (1 H, d, *J* 15) and 6.12 (1 H, s); δ_C 167.3 (4ry, C=N), 153.7 (4ry, C-2 of Ar), 135.4 (4ry, C), 132.3 (CH), 131.9 (CH), 131.5 (CH), 129.2 (2 CH), 128.9 (2 CH), 128.4 (CH), 127.2 (CH), 124.9 (CH), 120.9 (CH), 117.4 (CH), 110.1 (CH), 102.1 (CH), 4 C were not apparent; m/z (ES^+) 324.14 (M^++H, 100%).

RESULTS AND DISCUSSION

A Preparation and Pyrolysis of β,γ-Dioxo Ylides

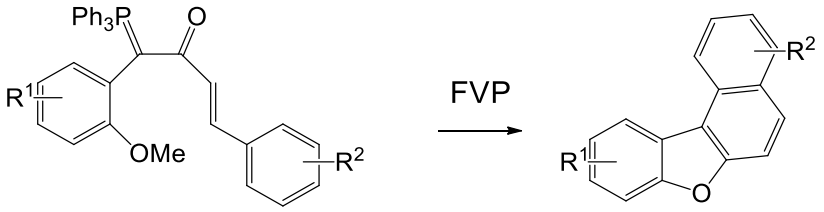
1. Preparation of Starting Materials

As described in the Introduction, previous work in the group focused on the synthesis of a range of oxo stabilised ylides, and after FVP of the ylides at about 500 °C, a wide variety of alkynes were synthesised, which provided a new way to form the alkyne.[46]



167 **168**

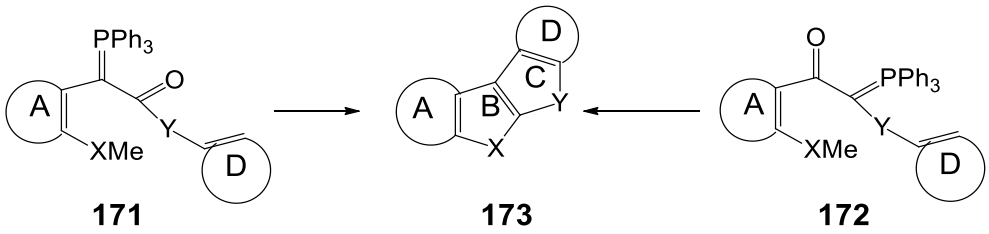
As the pyrolysis temperature was increased, if there was an *o*-methoxy group on the ylide, it was possible to lose it at about 700 °C. Based on this observation, it was possible to get cyclisation products which would contain three, four or five fused aromatic rings.[47]



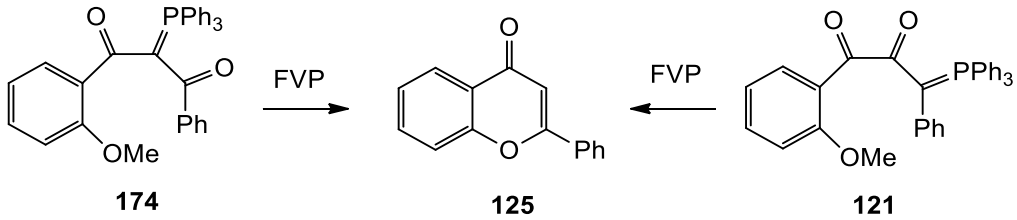
169 **170**

In the course of the previous work, a wide range of different types of ylides were examined, such as the *o*-methoxy phenyl oxo stabilised ylides, the *o*-aminophenyl oxo stabilised ylides and the *o*-methylthio phenyl oxo stabilised ylides. Upon FVP of these ylides, a variety of benzo[*b*]furan, indole and benzo[*b*]thiophene products were

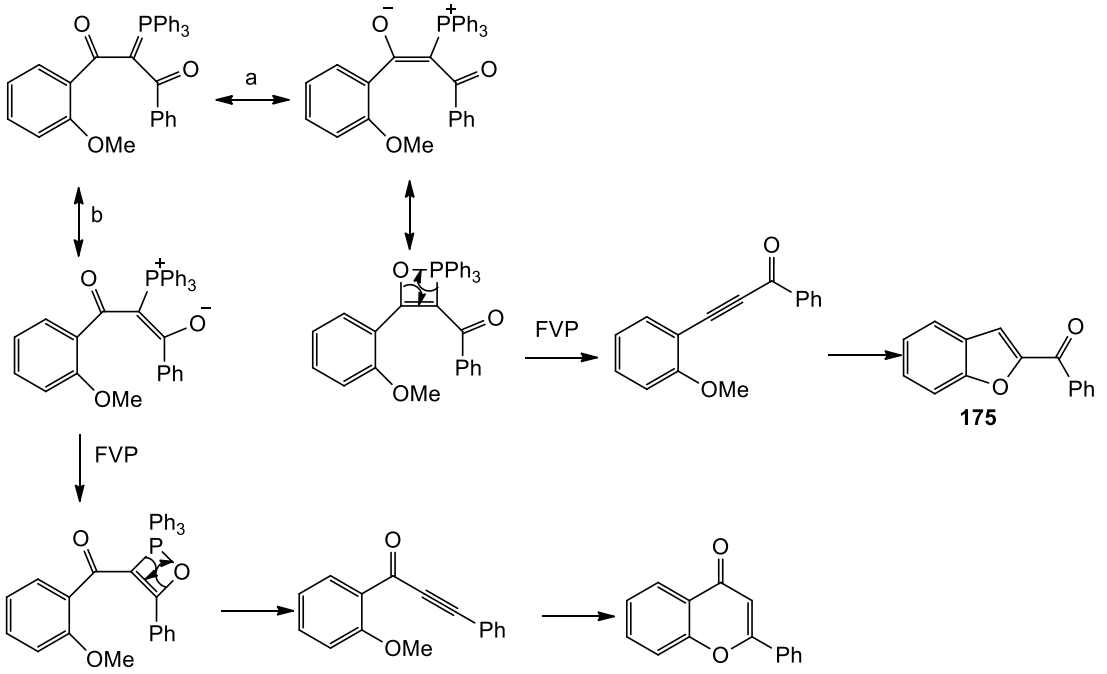
obtained. In its most general form the overall synthesis is as shown below with products **173** being accessible from either of the isomeric ylides **171** or **172**:



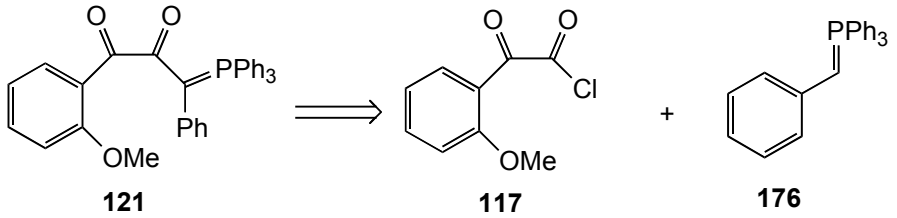
The initial aim of this project was to synthesise the di-oxo stabilised ylides with an *o*-methoxy substituent. After FVP of the ylides, the target was to get the flavonoid products.



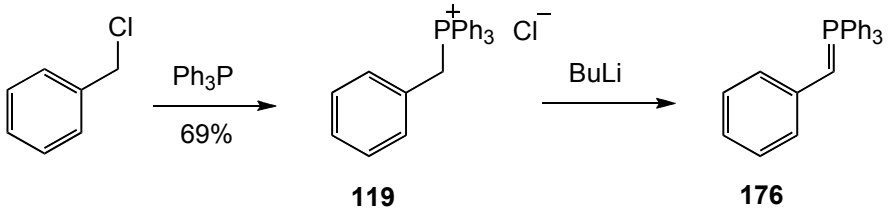
At the beginning, the project was designed to synthesise ylide **121**. Comparing the two ylides **174** and **121**, both of them might undergo FVP to form the desired products. However, the ylide **174** could undergo extrusion Ph_3PO on either side: if it underwent pyrolysis via route **b**, the result would be the desired product, whereas if it chose route **a**, it would instead give the isomeric product **175**. Based on this comparison, ylide **121** had a better chance of selectivity, and that was why ylide **121** was chosen as the initial target.



Based on retrosynthetic analysis, ylide **121** could be divided into two parts, the benzylidene ylide **176** and the phenylglyoxylyl chloride **117**, which were both readily synthesised.

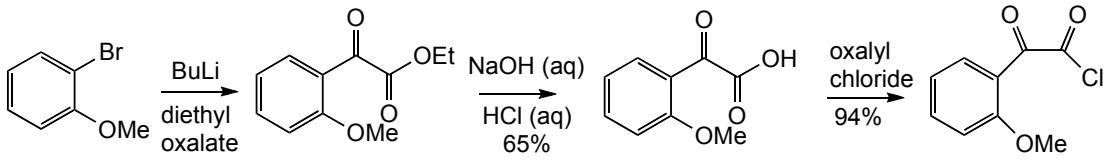


Based on a standard method,[48] the ylide **176** was made from its corresponding phosphonium salt **119**, which was reacted with an equimolar quantity of BuLi under a nitrogen atmosphere. The resulting ylide was used directly without any further purification. The corresponding phosphonium salt **119** was made from the cheap commercially available benzyl chloride and triphenylphosphine in toluene under reflux for 24 h.



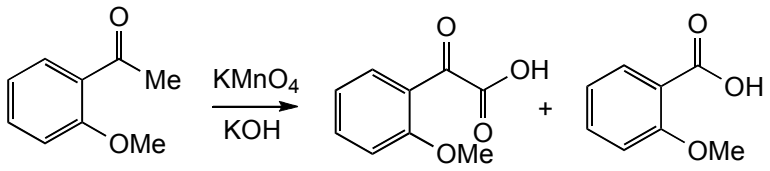
119 **176**

The acid chloride **117** was also readily made from the starting material 2-bromoanisole, according to the literature procedure, which involved lithium-halogen exchange with butyllithium at -70 °C under a nitrogen atmosphere, then the diethyl oxalate was added quickly by syringe and the crude product was distilled by kugelrohr at 170 °C to give **115**.[49,50] The product **115** was treated with a solution of NaOH under reflux and then extracted with diethyl ether, followed by acidifying with HCl aqueous to form the yellow carboxylic acid **116**.[51] The unstable product **117** was obtained by chlorination of **116**, and as the spectra showed that it was almost pure, it was unnecessary to purify it and it was used directly for the next step.[52]



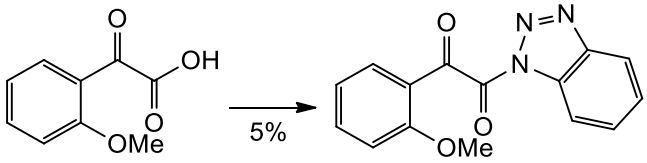
115 **116** **117**

The initial thought was that the acetophenone **177** would be used as the starting material. Based on the literature, **177** could be converted into **116** directly by treatment with potassium permanganate and KOH.[53] However, the spectroscopic results, particularly ^{13}C NMR, showed that the product was a mixture of **116** and the byproduct **178**, and the two were very difficult to separate so this route was not suitable.



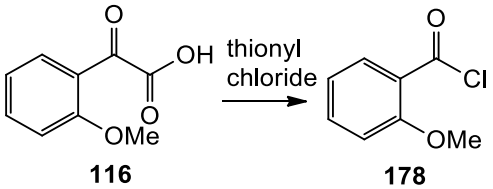
177 **116** **178**

According to previous work, the acylbenzotriazole was quite a good acid chloride equivalent for these reactions.[48] The initial idea was to use acid **116** to react with benzotriazole to give **118**, which could react with ylide **176** to form the desire ylide **121**. However, product **118** proved difficult to separate from the starting material benzotriazole, even through chromatography. The product was obtained in pure form by recrystallisation, however the crystals took a long time to form and a poor yield of 5% was obtained. So the higher yielding and more easily purified acid chloride **117** was used.



116 **118**

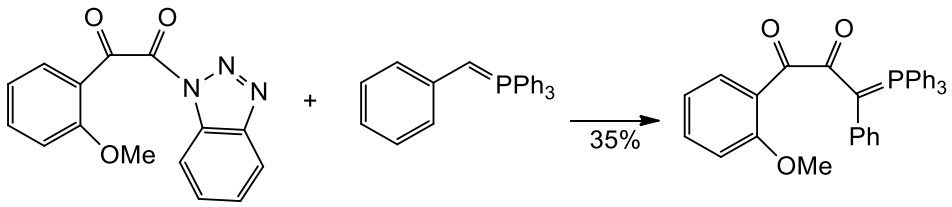
Thionyl chloride is usually a good chlorinating agent, so the chlorination of **116** using it was expected to be straightforward.[48] However after the acid was treated with thionyl chloride under reflux for 5 h and the crude products were distilled by kugelrohr at 85 °C, the NMR specta showed that the only product was 2-methoxybenzoyl chloride **178**. It seemed as if the desired phenylglyoxylyl chloride **117** was not stable and was undergoing spontaneous decarbonylation, so the halogenating agent was changed to oxalyl chloride.



116 **178**

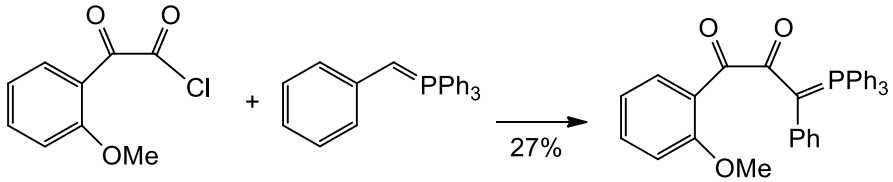
2. Preparation of Ylide

Ylide **176** reacted was reacted with **118** for 24 h, and after recrystallisation the product was obtained in a 35% yield. Due to the large degree of steric hindrance present in the ylide **121**, the 35% yield was acceptable.[47]



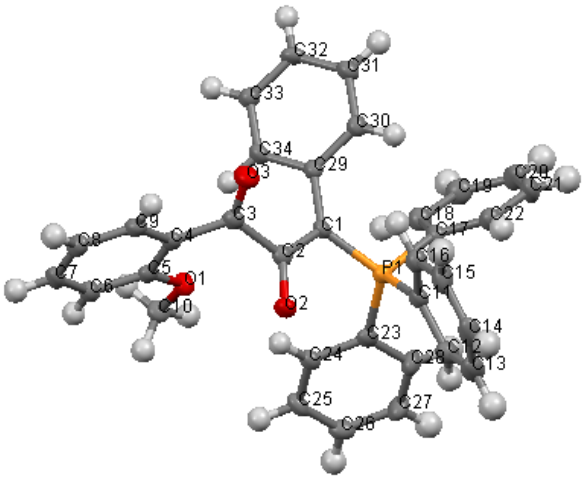
118 **176** **121**

As explained above the acid chloride **117** was perhaps easier to access in pure form and when the ylide **176** reacted with **117** overnight, the desired ylide **121** was obtained in a 27% yield.[47]



117 **176** **121**

Taking into account the steric bulk of the molecule, it seemed worthwhile to examine the structure of the ylide by X-ray crystallography, particularly since it appears that no X-ray structure of a simple β,γ-dioxoylide has so far been determined. Figure **1** shows the resulting structure of the ylide **121**.



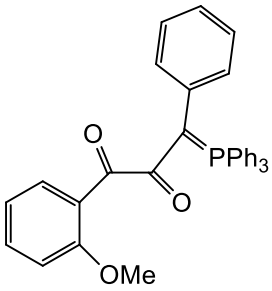
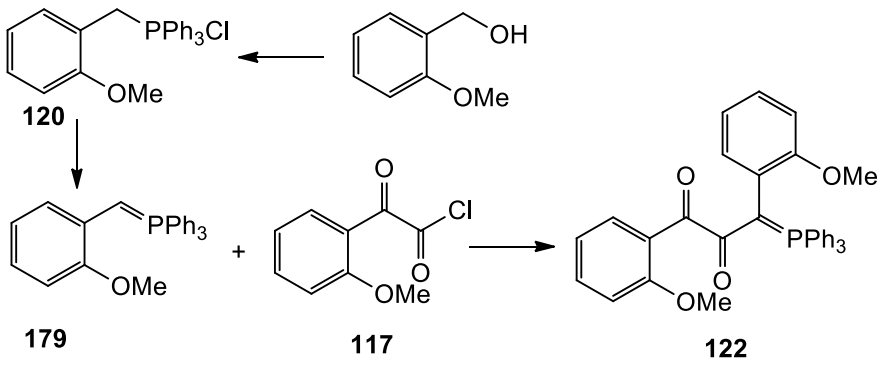


Figure 1: X-ray structure of ylide **121**, selected bond lengths, angles and torsion angles; C(4)-C(3) 1.494(4), C(3)-O(3) 1.227(4), C(3)-C(2) 1.536(5), C(2)-O(2) 1.263(3), C(2)-C(1) 1.392(4), C(1)-P(1) 1.751(4), C(1)-C(29) 1.484(4) Å; C(4)-C(3)-O(3) 120.2(3), C(C)-C(3)-C(2) 120.5 (3), O(3)-C(3)-C(2) 118.5(3), C(3)-C(2)-O(2) 113.0(3), C(3)-C(2)-C(1) 120.8(3), O(2)-C(2)-C(1) 125.8(3), C(2)-C(1)-P(1) 113.0(2), C(2)-C(1)-C(29) 123.4(3), P(1)-C(1)-C(29) 123.5(2)°; O(3)-C(3)-C(2)-O(2) 113.8(3), O(2)-C(2)-C(1)-P(1) -5.8(4) °.

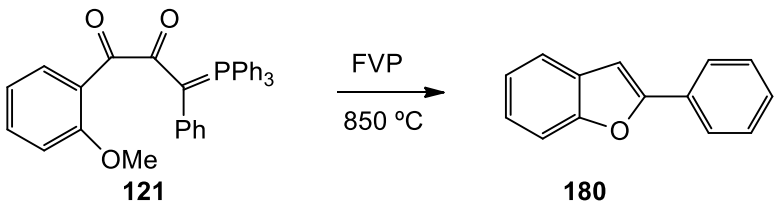
From this structure, it could be concluded that the C=P bond and the β -carbonyl were eclipsing. It was previously found that for β,γ-dioxo ylides the β-carbonyl was *syn* to C=P and the γ-carbonyl was at an odd angle to the β-carbonyl in the X-ray structures have been determined.[54] The C=P and C=O groups are thus in the same plane, which should favour the extrusion Ph_3PO during FVP as initially planned.

Ylide **122** was synthesised using the same method by employing phenylglyoxylyl chloride **117** to react with the non-stabilised ylide **179**, which could be obtained from its corresponding phosphonium salt **120**.[47]

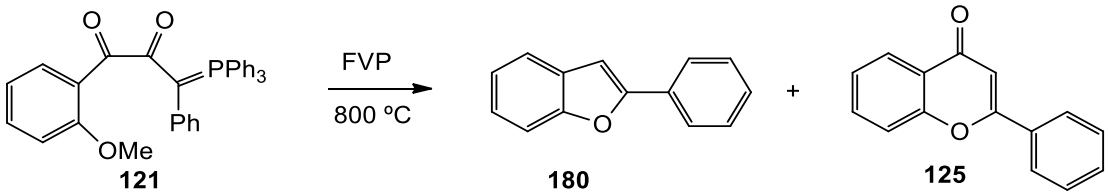


3. FVP of Ylides

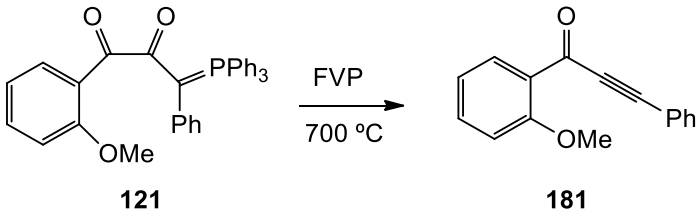
Based on previous work, FVP of the ylide **121** was attempted at a temperature of 850 °C. The ^{31}P NMR spectrum showed a peak at 29.7 ppm confirming formation of Ph_3PO, and the ^{1}H NMR spectrum displayed a distinctive peak at 7.05 ppm, indicating the presence of 2-phenylbenzofuran and the ^{13}C NMR spectrum confirmed the presence of this unexpected product. The NMR results have shown that a mixture of Ph_3PO and 2-phenylbenzofuran but no flavone has formed. It seemed possible that the carbonyl was not stable at the high temperature and that flavone could possible form at a lower temperature.[26,47,56,57]



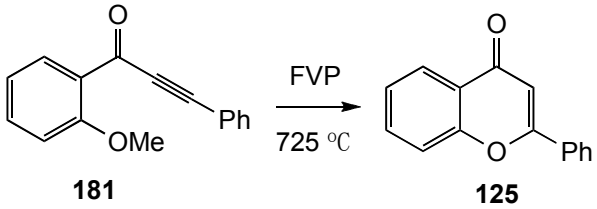
FVP was repeated at 800 °C. This time the ^{1}H NMR spectrum displayed a singlet peak at 6.84 ppm, which indicated the presence of the desired flavone, however, the main product of the pyrolysis was still the benzofuran, the ratio of the benzofuran to the flavone was 73:27. After all, the results demonstrated that flavone could survive at a lower temperature.[58]



The third temperature was 700 °C. This time the ^{1}H NMR spectrum was quite different from before: no peaks representing the benzofuran or flavone could be found, but the peak at about 29.0 ppm was still clear on the ^{31}P NMR spectra, which means the pyrolysis led to extrusion of Ph_3PO without any cyclisation. The crude material was separated by preparative TLC with diethyl ether/hexane (1:9) as the eluent, and the bottom band contained the alkyne 1-(2-methoxyphenyl)-3-phenylprop-2-yn-1-one **181**.[55]



As the *O*-methyl group cannot be removed at a lower temperature, the product **181** was obtained without any cyclisation. In order to minimise the formation of by-products, FVP of the isolated product **181** could be a better choice. Therefore the next step was to subject **181** to FVP at 725 °C. It was very challenging to distinguish the peaks caused by the benzofuran, however obvious NMR signals caused by the flavone and the unreacted **181** were found. Based on these studies, the lowest temperature to achieve cyclisation was found to be around 725 °C.



In the next FVP experiment, the temperature of 750 °C was tried. The ^{1}H NMR results showed that the pyrolysis product contained **181**, flavone and the benzofuran and with the ratio 35:35:30.

At 775 °C, the pyrolysis products only contained flavone and the benzofuran with the ratio 43:57. Table 1 summarises the combined FVP results.

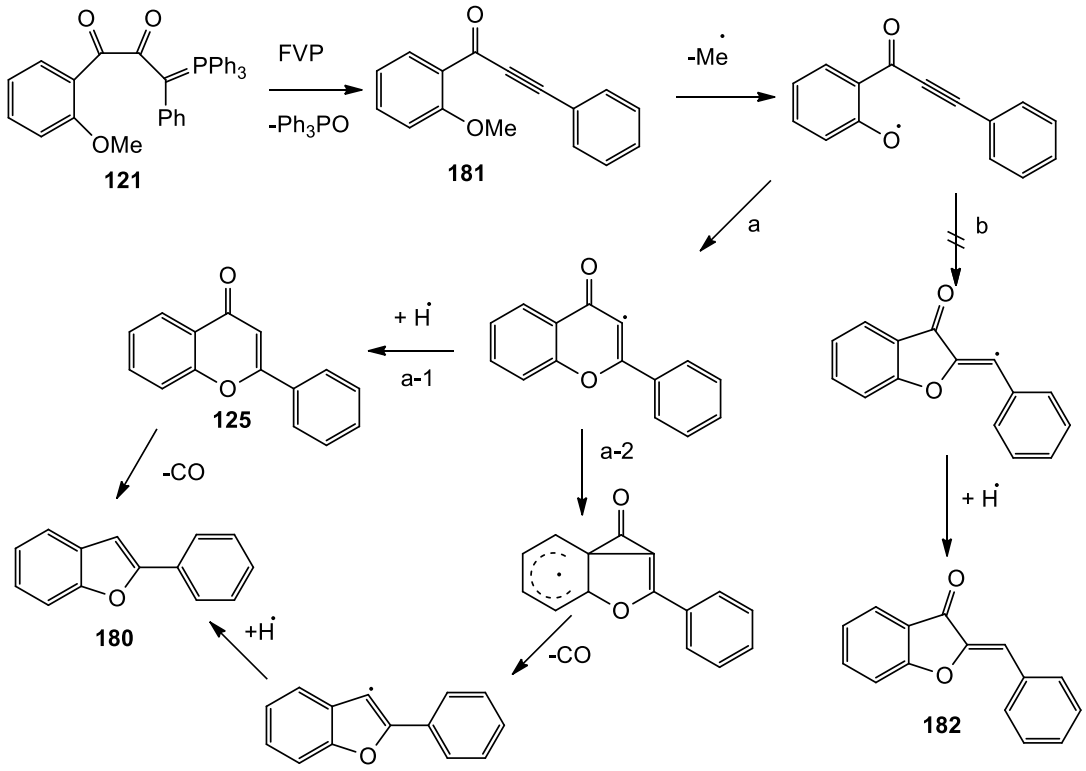
Table 1: Products from FVP of **181** as a function of temperature

FVP temperature (°C)	Composition (**181**:**125**:**180**)
700	100:0:0 (only **181)**
725	65:35:0
750	35:35:30
775	0:43:57
800	0:27:73
850	0:0:100 (only **180**)

In summary, the lowest temperature at which cyclisation was achieved was 725 °C. With increasing temperature, more starting material would cyclise until 775 °C, at which point all of the starting material would have undergone cyclisation. At the temperature of 775 °C, the largest amount of flavone was observed; this temperature could be the best temperature to form the desired flavone. If the temperature kept rising, the final product could be 2-phenylbenzofuran instead of the flavone.

According to the FVP results, the planned route did give the desired flavone but formation of the unexpected 2-phenylbenzofuran was also observed. The possible reaction routes are shown below: the route **b** to get **182** seemed not to occur because none of the spectra displayed a singlet peak at 6.90 ppm. Based on the previous FVP mechanisms, step **a-1** gives a route to obtain the flavone. The only puzzle was how to get to the benzofuran; whether it was obtained through step **a-2** or via loss of CO from

the flavone. To resolve this question it was decided to prepare flavone and 3-iodoflavone and investigate their pyrolysis under the same conditions to shed more light on the mechanism. The following scheme shows the possible mechanisms.[26,56,57]

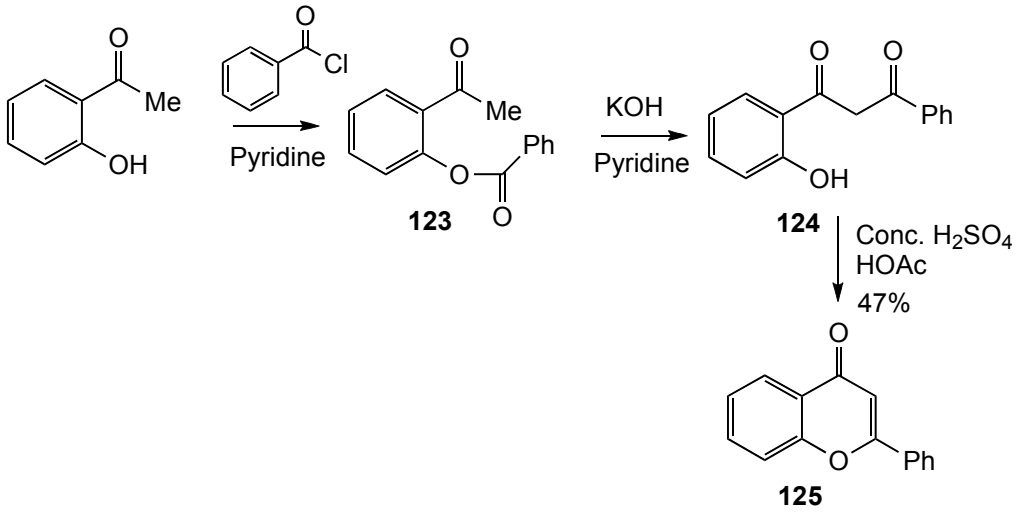


B Preparation and Pyrolysis of Flavone and 3-Iodoflavone

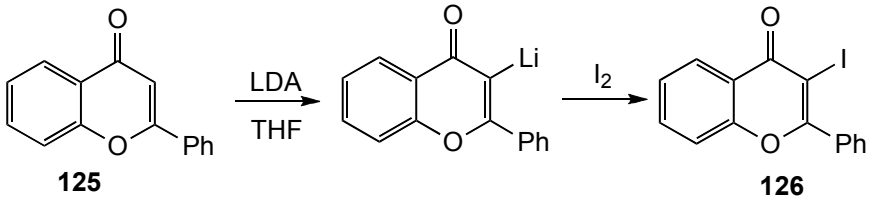
1. Preparation of Starting Material

Since this part of the study was designed to confirm the mechanism, what was required was to find the simplest way to synthesise flavone. Flavone had already been made by many different methods; we selected a very traditional way to obtain it.[59,60] Direct reaction of *o*-hydroxyacetophenone, benzoyl chloride and pyridine gave 2-acetylphenyl benzoate **123**, then this was dissolved in pyridine at 50 °C and treatment with pulverised KOH caused a rearrangement to give 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione **124**. When an acetic acid solution of

124 was reacted with concentrated sulfuric acid with heating for 1 h it gave flavone. During this work, **123** and **124** were only identified by their respective melting points, but the identity of the final flavone **125** was also confirmed by ^{1}H NMR and ^{13}C NMR spectra, which were in agreement with the literature values.[58]



LDA (lithium diisopropylamide) was prepared by allowing butyllithium to react with diisopropylamine in THF at -78 °C under an N_2 atmosphere, followed by allowing the reaction to warm to room temperature and to stir for 15 min to form the LDA. The LDA was cooled down to -78 °C again before adding the solution of flavone and waiting for 5 min to form the lithium derivative. Then a solution of iodine in THF was added and the colour faded quickly to form the iodoflavone **126** in 84% yield.[61] It showed a distinctive ^{13}C NMR signal at 88.2 ppm for the quaternary sp^2 carbon joined to iodine.



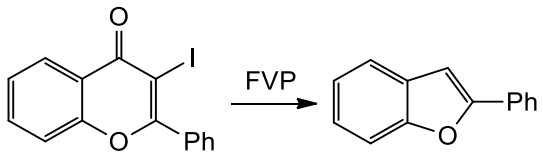
2. FVP of Flavone and 3-Iodoflavone

First of all, to examine the feasibility of route **a-1**, FVP of flavone at temperatures up to 850 °C was examined. Both the ^{1}H NMR and ^{13}C NMR results indicated that the pyrolysis product was unchanged flavone with no sign of 2-phenylbenzofuran, which meant the flavone did not decompose with loss of CO under these conditions. The FVP was also attempted at 800 °C and 700 °C; however, this had no effect upon the flavone. Table **2** summarises the results of the FVP of flavone.

Table **2**: FVP of flavone

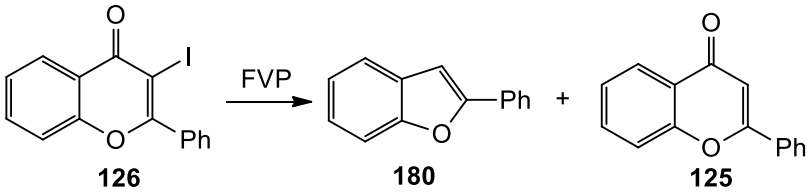
FVP Temperature (°C)	Pyrolysis results
700	No reaction
800	No reaction
850	No reaction

Secondly, the feasibility of route **a-2** was checked by FVP of 3-iodoflavone at different temperatures. The first temperature tried was 800 °C and the crude products were purified by preparative TLC with hexane/diethyl ether (5:1) as eluent. The only product observed from the purified fractions was 2-phenylbenzofuran **180** in 34% yield.[55-58]



126 **180**

The second temperature tried was 750 °C, which is the same conditions as used for FVP of the ylide **121**. After prep TLC with the eluent hexane/diethyl ether, the result was quite interesting because both the benzofuran and flavone were obtained in purified yields of 26% and 4%, respectively.



126 **180** **125**

At 700 °C only benzofuran was found without the flavone, while in the 650 °C FVP experiment, neither of the two products was found; only the unreacted iodoflavone were recovered. Table **3** displays the results of the FVP of 3-iodoflavone.

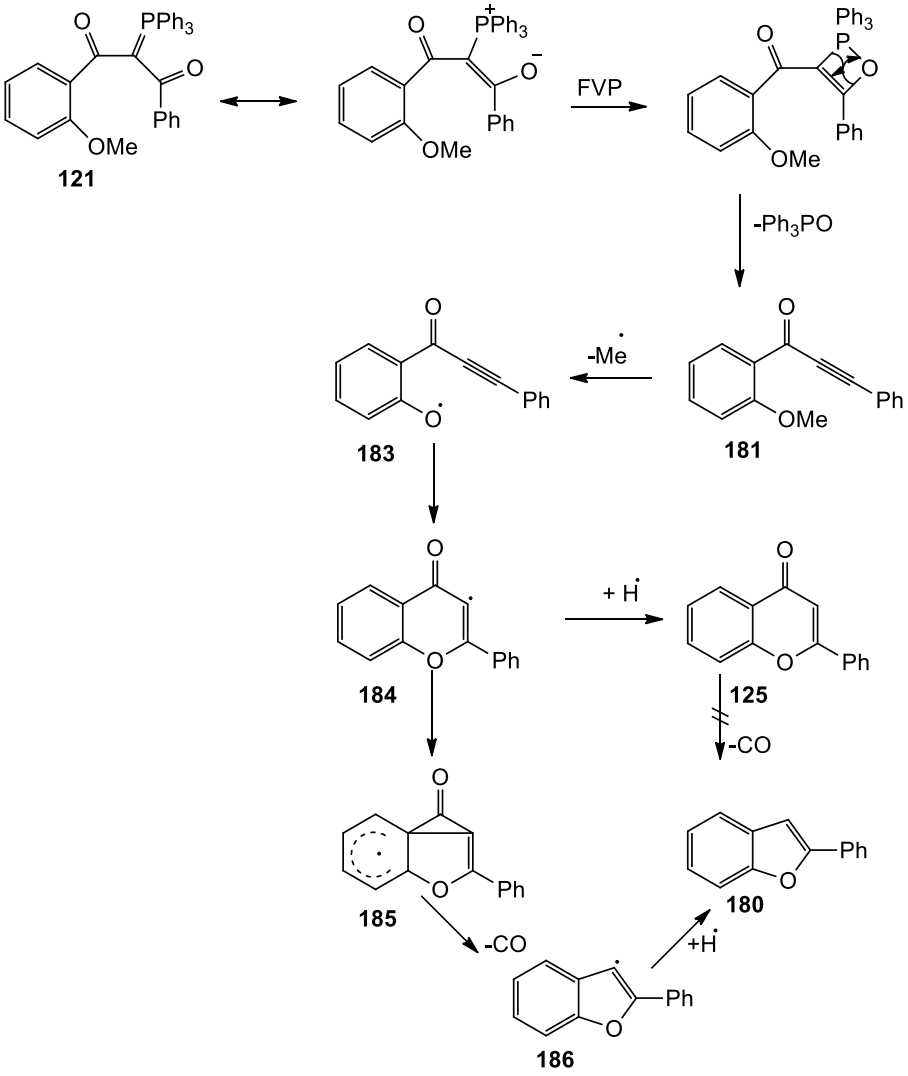
Table **3**: FVP of 3-iodoflavone

FVP temperature (°C)	Pyrolysis Yield (**126:125**:**180**) (%)
650	100:0:0 (only **126)**
700	43:0:16.5
750	31:4:26
800	0:0:34 (only **180**)

In conclusion, while flavone was quite stable to FVP, the 3-iodoflavone was not that stable, and pyrolysis resulted mainly in 2-phenylbenzofuran and some unreacted starting material. When the iodoflavone was exposed to FVP, it would be expected to lose an iodine atom easily to form the flavone radical, then the flavone radical could go two different ways; one was to form the three membered ring and then lose CO to form the benzofuran, another way was to form a tiny amount of the flavone by picking up a hydrogen atom.

Based on the results obtained up to now, the following mechanism can be proposed for the FVP of ylide **121**. The ylide undergoes thermal extrusion of Ph_3PO at lower temperatures to form **181**, but as the temperature is increased, the methyl group is also lost to get the radical **183**, which would cyclise to **184**. Radical **184** could go to two different ways: one is to pick up a hydrogen atom to form the desired flavone **125**; another way is to form the unstable three-membered ring spiro

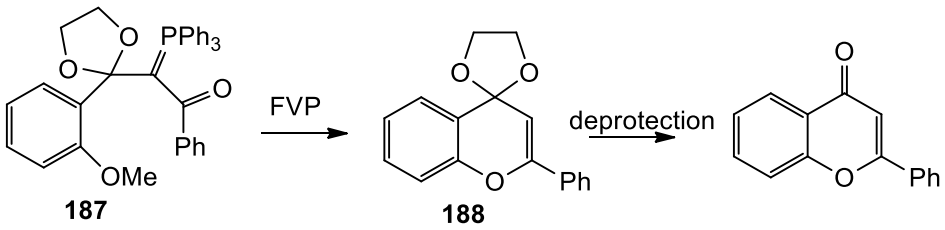
intermediate **185**, followed by loss of the CO to get the radical **186**, which then picks up a hydrogen atom to form the benzofuran **180**. It should be noted that the formation of a benzofuran by thermal extrusion of CO from a flavone derivative has apparently not been previously reported and this method might have some general value for the preparation of substituted benzofurans.



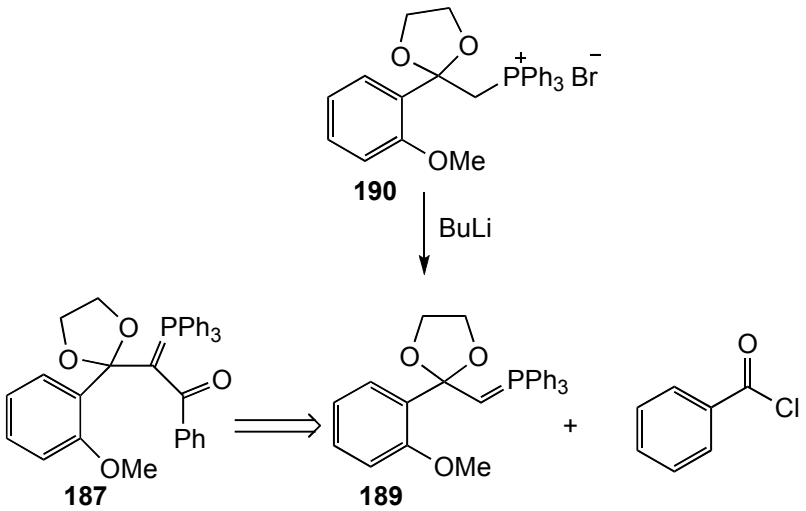
C Attempt preparation of Protected Ylides

1. Preparation of Starting Material

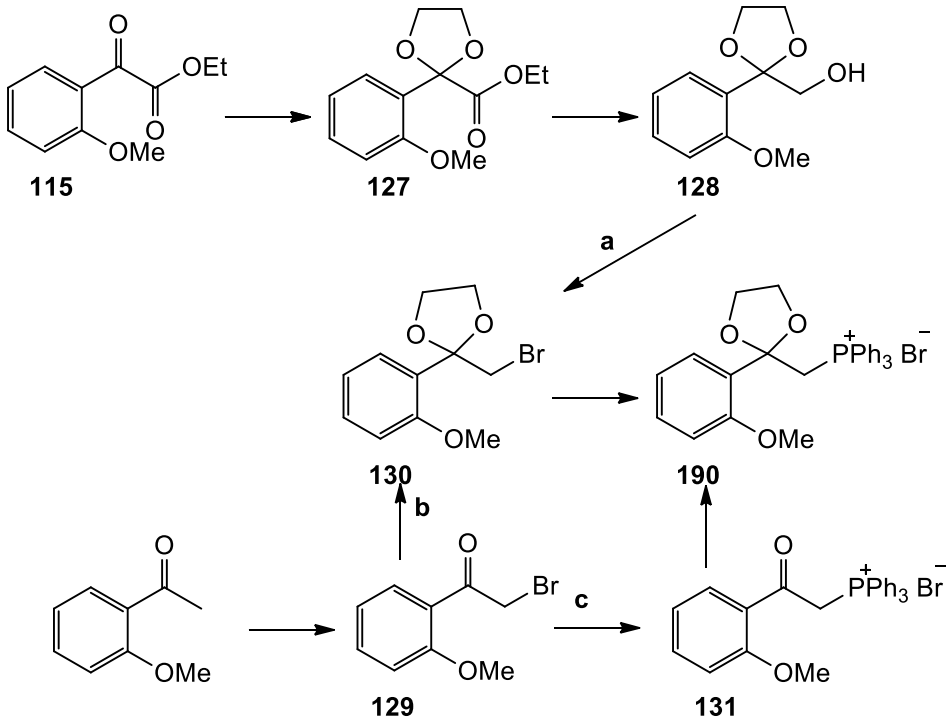
According to previous work, FVP of β,β'-dicarbonyl ylides would not be of great value for the preparation of flavones since the regioselectivity of Ph_3PO extrusion is poor leading to mixtures of isomeric products. However if one carbonyl was protected to stop it reacting during the FVP reaction, for example as the 1,3-dioxolane, and then deprotected to form the carbonyl of the flavone again, this problem could be solved. So in this section of the project the aim was to synthesise protected ylides such as **187** which might form a protected flavone **188** during the FVP.



To get the protected ylide **187**, the most obvious approach was to first prepare the simpler ylide **189**, which could be obtained from the corresponding phosphonium salt **190**, and then subject it to acylation.

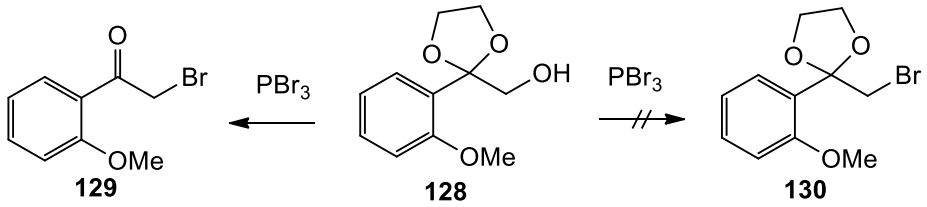


Three different ways were examined to synthesise the phosphonium salt **190**. Path **a** involved first acquiring the protected compound **127** from the previously made α-keto ester **115**, followed by reduction to **128** and then bromination and reaction with Ph_3P leading to synthesis of the phosphonium salt **190**. Both paths **b** and **c** started from bromination of 2-methoxyacetophenone to obtain **129**, then path **b** involved carrying out the protection followed by addition of PPh_3 to get the **190**, while on the other hand path **c** involved obtaining the phosphonium salt **131** first and then protecting the carbonyl to form the target compound **190**.



Path **a** was attempted, whereby **115** was treated with ethylene glycol and *p*-toluenesulfonic acid in toluene to acquire **127** in a yield of 46%.[62] To a suspension of **127** in THF under a nitrogen atmosphere, a solution of $LiAlH_4$ in THF was added dropwise and the resulting mixture was heated under reflux for 4 h to give the desired alcohol **128** in 34% yield. Both the NMR and mass spectra confirmed the product to have the right structure. The next step was to use PBr_3 to brominate **128** to get **130**, which could be followed by the addition of PPh_3 in toluene to form the phosphonium

salt **190**. The NMR spectra of the crude product indicated that the majority of the mixture was **129** and the reason was likely that the PBr_3 or HBr generated during its reaction had deprotected the 1,3-dioxolane.

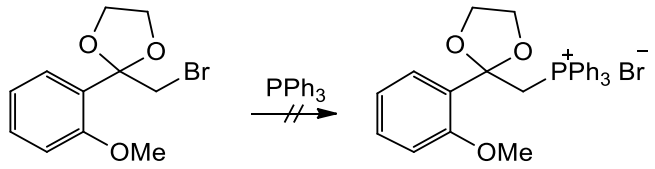


129 **128** **130**

To summarise, path **a** was not practical based on the above results and the protection of the carbonyl should be done after the bromination of the methyl. The originally designed project plan needed some changes to obtain the target, and paths **b** and **c** could possibly make up for the shortcomings of path **a**.

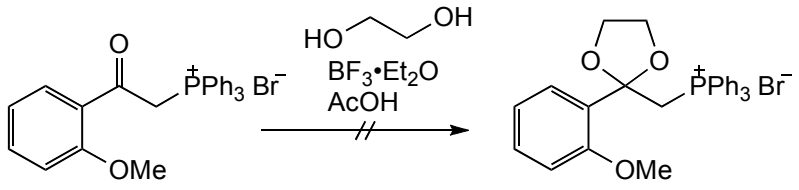
Both path **b** and path **c** started with the bromination of 2-methoxyacetophenone in diethyl ether below 30 °C for 30 min. The crude product was purified by kugelrohr distillation at 140 °C to obtain **129**.[40] Because **129** had already been synthesised, the problem was which one should be done first, the protection of **129** to get the 1,3-dioxolane or the addition the PPh_3 to get the unprotected phosphonium salt **131**. According to the former plan, path **a**, one of the important goals of the whole work was to get **130**, so path **b** was tried first. To a solution of **129** in toluene was added ethylene glycol and *p*-toluenesulfonic acid with a Dean-Stark trap to get the dioxolane **130**, [48] which was recrystallised from hexane and ethyl acetate to obtain white crystals in a yield of 61%.

The next step was to add PPh_3 to the solution of **130** in toluene to give the phosphonium salt **190**. After the reaction was heated under reflux for a whole night, the ^1H NMR result showed that the material in the reaction flask was still unreacted **130**. The main reason which could explain this phenomenon was the neopentyl effect; the 1,3-dioxolane would stop the PPh_3 from reacting with the bromide.



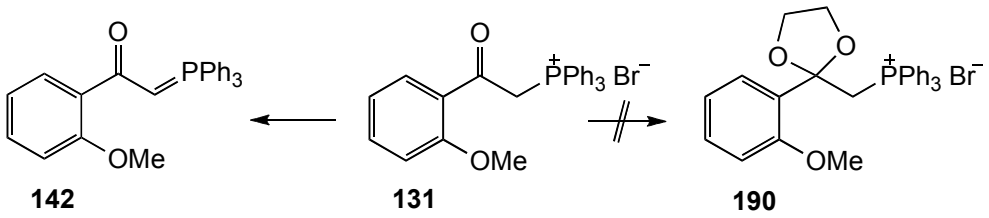
130 **190**

Due to the failure of the previous two paths the only option left to attempt was path **c**. A solution of **129** was reacted with PPh_3 in toluene at RT to synthesise the unprotected phosphonium salt **131** successfully avoiding the neopentyl effect. A solution of **131** and ethylene glycol in acetic acid was heated to 35-40 °C, and boron trifluoride diethyl etherate was added.[63] After 15 mins, the solution was cooled and the white crystals were collected, dissolved in methanol, and then diethyl ether was added to form a white powder. The ^{1}H NMR and ^{31}P NMR spectra indicated that the white powder was still the starting material **131**.



131 **190**

According to the literature, an alternative way to get **190** was available and this was now attempted. It involved adding **131** to a solution of ethylene glycol and dry dichloromethane under a nitrogen atmosphere.[64] To the mixture was added chlorotrimethylsilane and it was then allowed to react overnight. A solution of 5% sodium hydrogen carbonate was added and the mixture was extracted with diethyl ether which was dried and evaporated. Both the ^{1}H NMR and ^{31}P NMR spectra of the product indicated that it was the ylide **142** instead of the protected phosphonium salt.

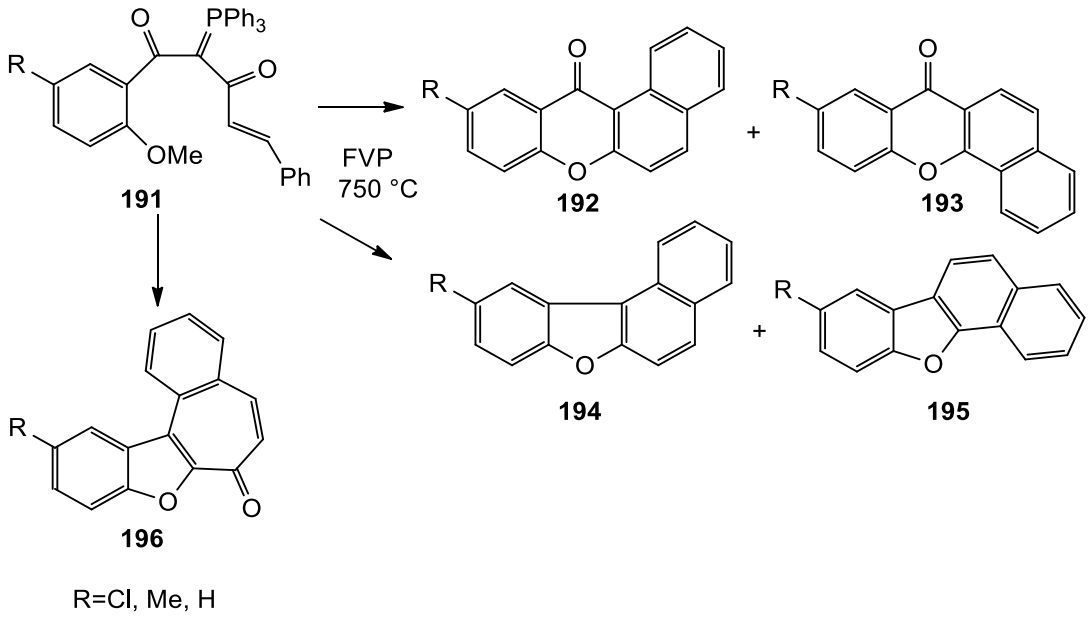


According to the results above, it was not possible to make the protected phosphonium salt **190**. The failure of path **a** occurred at the stage of attempted bromination of **128**, which led to the formation of **129**. Path **b** solved this problem and got the important intermediate **130**, which however could not react with PPh_3 because of the neopentyl effect. Path **c** synthesised the unprotected phosphonium salt **131** first, but no matter what method was tried, it still could not be converted into the protected phosphonium salt **190** so the idea of making the protected ylide had to be abandoned.

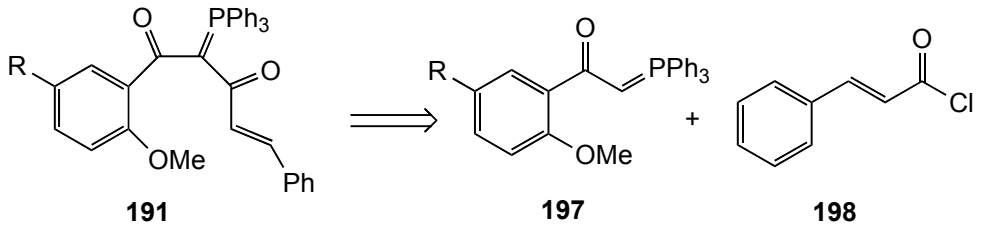
D Preparation and Pyrolysis of β,β'-Dioxo Ylides

1. Preparation of Starting Materials

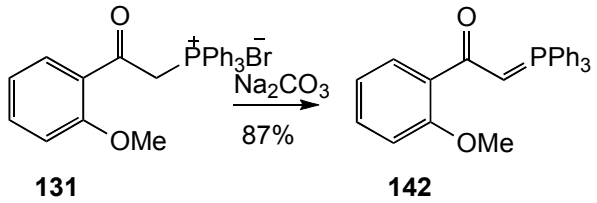
Following the previous successful β,γ-dioxo ylide project and the unsuccessful protected ylide project, attention was now turned to the synthesis of β,β'-dioxo ylides. The overall aim was to obtain ylides **191** which would be capable of forming tetracyclic products during FVP. According to previous FVP experience[26] combined with the novel decarbonylation discovered earlier in this work, the cyclisation could potentially form at least five products **192-196** as shown below.



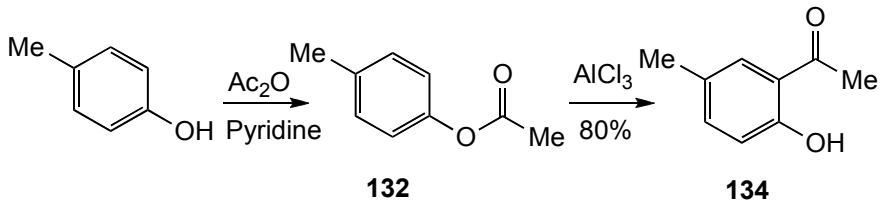
Based on retrosynthetic analysis, ylide **191** could be formed from two parts, the 2-methoxybenzoyl ylide **197** and cinnamoyl chloride **198**.



Ylide **142** (**197**, R = H) had already been formed accidentally in attempts to generate **190**. This time it was obtained from the phosphonium salt **131**, which was dissolved in a saturated solution of Na_2CO_3. The mixture was shaken vigorously for a few minutes and extracted with CH_2Cl_2 to afford the ylide **142**.[65]

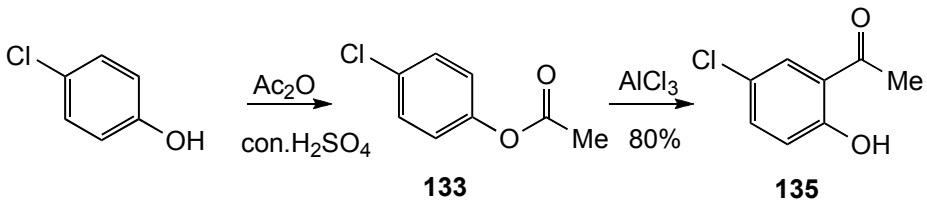


When the R group was methyl, the precursor used was *p*-cresol. To a solution of *p*-cresol in acetic anhydride was added pyridine. After 12 h of stirring at RT, the volatiles were evaporated to form the product **132** as an oil. To the crude **132** was added anhydrous aluminum chloride with heating at 130 °C to perform the Fries rearrangement. During the heating, the whole mixture became a black mass, but after treating with ice, allowing to stand for 1 h, diluting with CH_2Cl_2 and stirring overnight it gave the crude **134**. This was purified by kugelrohr distillation under vacuum at 90-105 °C, and after some time the oil formed green crystals of the pure product.[66]



132 **134**

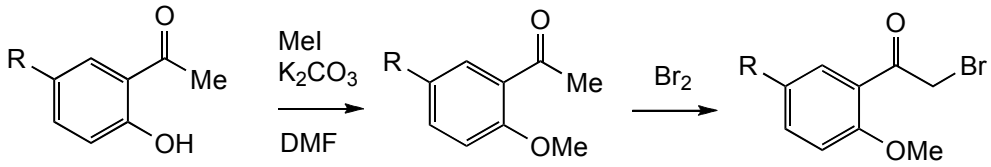
When it came to the synthesis of the chlorine derivative, *p*-chlorophenol and acetic anhydride with a drop of concentrated sulfuric acid were stirred overnight to form *p*-chlorophenyl acetate **133**. The next step was just like the above procedure; to the crude **133** was added anhydrous aluminium chloride to bring about Fries rearrangement to give the crude **135**, which was purified by kugelrohr distillation at 140 °C -160 °C to produce a green liquid.[68-71]



133 **135**

In the next steps, both **134** and **135** underwent the same procedures. Methyl iodide was added to the mixture of the starting material **134** or **135** with K_2CO_3 in dry dimethylformamide, and the mixture was stirred for 18 h at RT. After the usual extraction was done, the *O*-methylated products **136** and **137** were obtained.[72,73] As it

was difficult to purify the crude products, either by recrystallisation or column chromatography, the crude products were used directly for the bromination.[74] After the bromination was done, the crude products could be recrystallised from ethanol to get pure **138** and **139**, both in overall yields of around 40%.

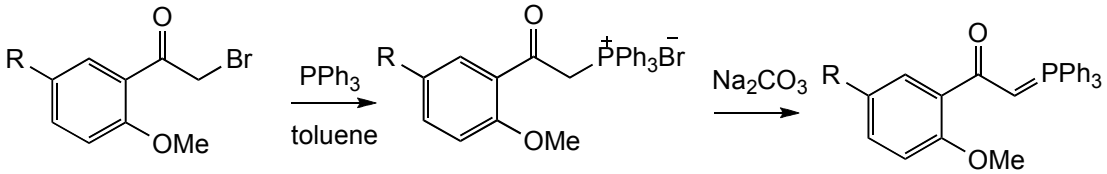


134; R = Me
135; R = Cl

136; R = Me
137; R = Cl

138; R = Me, 40%
139; R = Cl, 40%

The phosphonium salts were synthesised by using the same method detailed earlier: the bromination products **138** and **139** were dissolved in toluene, then Ph_3P was added and the solution heated under reflux overnight to give **140** and **141**, respectively, followed by the treatment with Na_2CO_3 solution in a large separating funnel with vigorous shaking to afford, after extraction the ylides **143** and **144** in yields of 82% and 95% respectively.[48, 65]



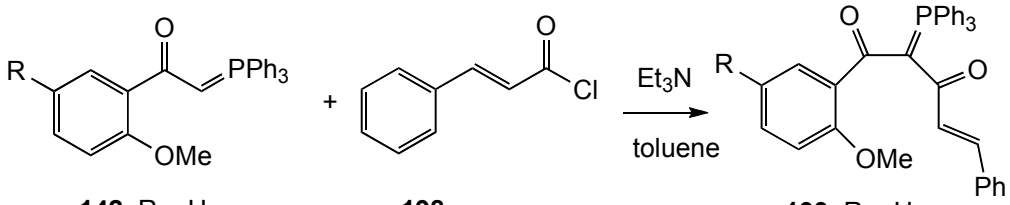
138; R = Me
139; R = Cl

140; R = Me, 63%
141; R = Cl, 62%

143; R = Me, 82%
144; R = Cl, 95%

Based on standard literature methods, the above ylides and triethylamine were dissolved in dry toluene, while a solution of cinnamoyl chloride in dry toluene was added dropwise to the mixture.[21] Before adding the acid chloride into the mixture, the three starting ylides didn't dissolve well in the dry toluene, so the mixtures were heated slightly make sure the starting ylides dissolved fully. After the mixtures were stirred for 3 h, the crude products were obtained. In the ^{31}P NMR spectra, there were

not only the peaks expected for the new ylides, but also major starting ylide peaks, as well as peaks around 29 ppm due to formation of Ph_3PO.



142, R = H
143, R = Me
144, R = Cl

198

199, R = H
145, R = Me
200, R = Cl

The presence of a methyl group on the aromatic ring of the ylide **145** was especially useful, since following the FVP, the methyl could be used as a diagnostic signal to determine the structure and number of products present, so effort was concentrated on this example. After the crude product was recrystallised from ethyl acetate and hexane, the ylide **145** was obtained in a yield of 39%. The remaining two ylides **199** and **200** were also obtained as crystals after recrystallisation, however they took two weeks to form, and the ^{31}P NMR spectra showed that the majority of the solid was Ph_3PO in each case.

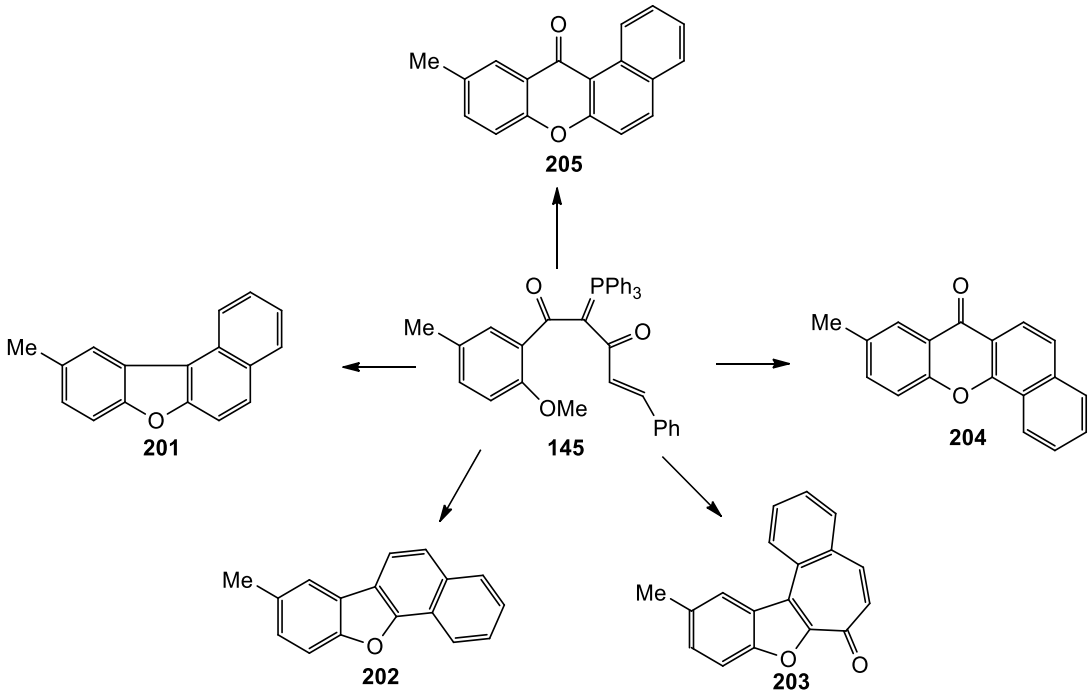
Since a lot of the ylide was unreacted, the reaction conditions were altered so the reaction mixture was heated under reflux instead of being left at room temperature to make sure all the starting ylide reacted. The ^{31}P NMR results showed that the starting ylide had been completely consumed, however the main peak was around 29 ppm, and the products had already extruded the Ph_3PO to form the alkynes. So heating the mixture was not a good idea.

As the ylides would not dissolve in dry toluene at room temperature, the solvent was changed to dry THF and the ylides were found to dissolve well in this solvent. The other steps were the same as before, and after the experiments were done, the ^{31}P NMR indicated that the results were similar to the reactions in dry toluene: in each case the starting ylides, target ylides and Ph_3PO were mixed together.

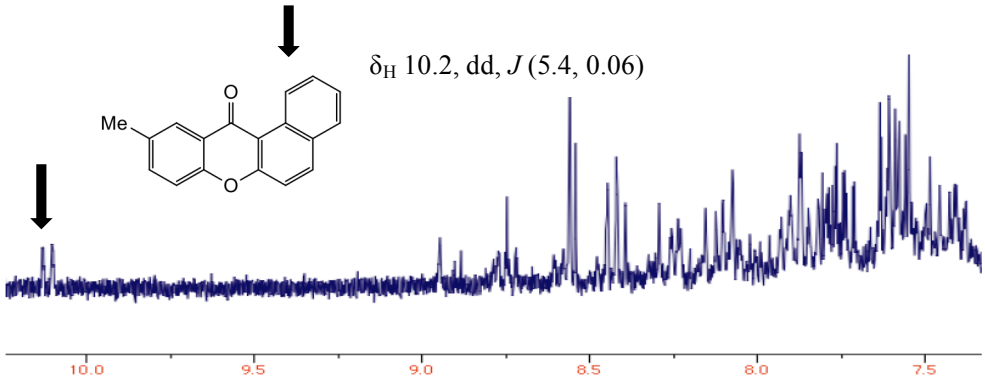
According to the results of the different alternative preparations, the temperature should not be too high to avoid the extrusion of Ph_3PO, and the solvent effect didn't play a vital role in the reactions.

2. FVP of Ylide 145

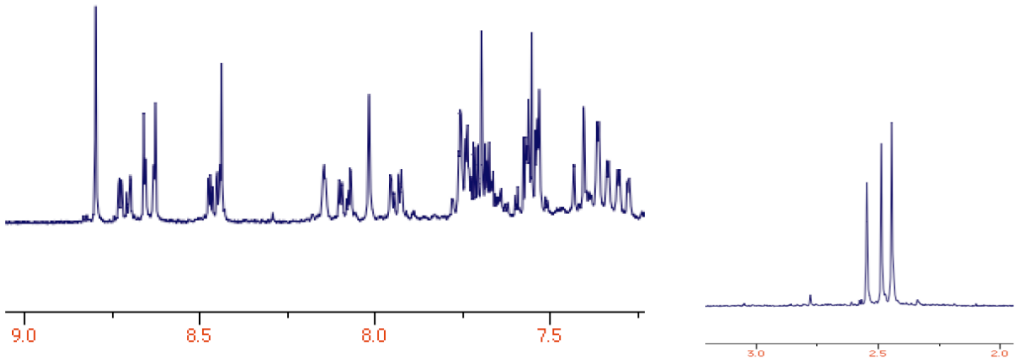
As referred to earlier, the methyl signal could be used to identify the number of products after purification of the FVP products. Ylide **145** was chosen to undergo pyrolysis. As mentioned above, there may potentially be five similar FVP products **201-205**.



After purification of the crude product by chromatography with ether-hexane (1:15) as eluent, the products were still not completely separated. The ^1H NMR showed that three compounds were present, most likely **201**, **202** and **205** above.



The peaks under the black arrow were due to the "bay region" proton of compound **205**.



On the above ^{1}H NMR spectrum, the peaks around 2.5 ppm were the peaks of the methyl linked to phenyl, which clearly indicated that there were three different compounds present. The peaks in the range from 8.75-8.4 ppm were the peaks of the two isomers **201** and **202**. As the spectrum was taken from a sample twice purified by chromatography, it was very difficult to achieve further separation.

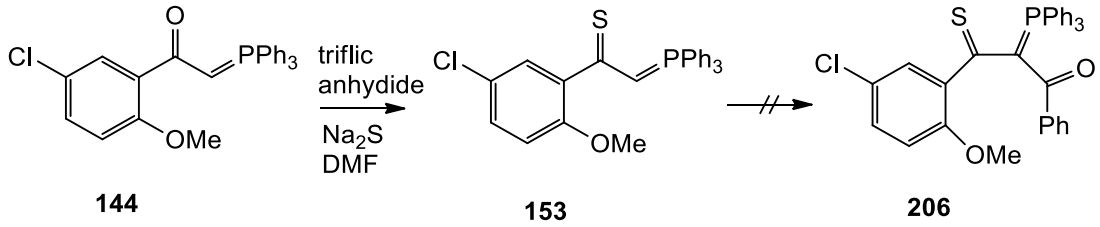
In conclusion, ylide **145** could undergo extrusion to form the cyclisation products **201**, **202** and **205**. Since the three compounds have similar structures, it was difficult to separate the products to obtain pure samples for identification. In addition, the ylide had shown quite poor selectivity under the FVP conditions and was also difficult to obtain in pure form, so it was concluded that this kind of β,β'-dioxo ylides were not good candidates for the cyclisation to the target product.

E Preparation and Pyrolysis of Thiocarbonyl Ylides

1. Preparation of Starting Materials

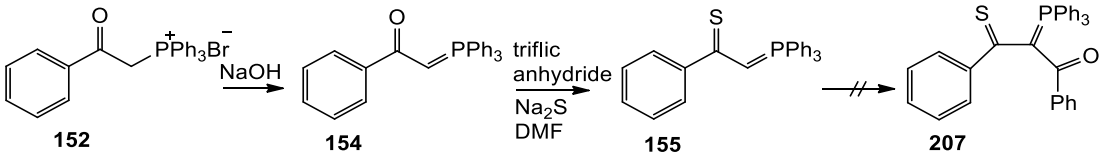
As seen in the last section, preparation and FVP the β,β'-dioxo stabilised ylides could lead to significant selectivity problems, so the dioxo stabilised ylide was not a good idea. Since thiocarbonyl ylides could also undergo the extrusion Ph_3PS, hopefully at a lower temperature, and so their pyrolysis could form cyclisation products, it was decided to investigate using ylides containing thiocarbonyl and carbonyl groups as a means of achieving the required regioselectivity.

At the beginning, the previously prepared ylide **144** was treated with triflic anhydride and then reacted with sodium sulfide in DMF to give the corresponding thiocarbonyl ylide **153** in a yield of 48%.[76] This was to be followed by addition of triethylamine and benzoyl chloride to get the target ylide **206**. However after the reaction, the ^{31}P NMR spectrum showed that the majority of the crude product was Ph_3PS with less than 20% of the desired product, and recrystallisation could not separate these products.



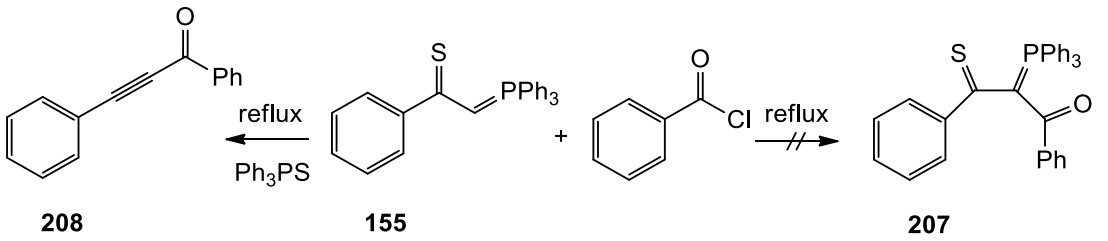
144 **153** **206**

To simplify the reaction, both the chloro and methoxy substitutents of the benzene ring were removed. Ylide **154** was chosen which was made from its corresponding salt and sodium hydroxide. Then ylide **154** was just treated like ylide **144** to get its thiocarbonyl derivative **155** in a yield of 58%. The recrystallisation could not remove all ylide **154**, there was a small amount of ylide **154** mixed in with ylide **155**. However, the result of the reaction ylide **155** and acid chloride with triethylamine was similar with the previous reaction. The majority of the product was Ph_3PS instead of the expected ylide **207**.



An alternative method to synthesise thiocarbonyl ylides was to react ylide **154** with Lawesson's reagent.[75] The results were no better than when ylide **154** was treated with triflic anhydride followed by Na_2S. Due to the instability of ylide **155** as a result of the compound possessing only one thiocarbonyl group, when purification was attempted by column chromatography with ether-hexane as eluent it would break down easily with less than 10% yield being recovered.

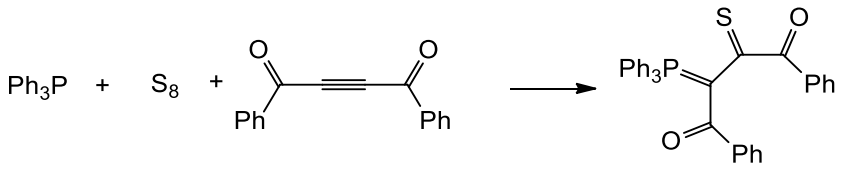
Despite problems in obtaining it in good yield and purity, a small quantity of thiocarbonyl ylide **155** was obtained allowing us to investigate the route to ylide **207** by reaction with benzoyl chloride. To a boiling solution of starting ylide in toluene containing triethylamine, a solution of benzoyl chloride in toluene was added dropwise over 1 h. After the addition, the mixture was heated under reflux for 3 h. During the reaction, there was no precipitate. The proton and phosphorus NMR spectra both showed that 1,3-diphenylprop-2-yn-1-one **208** had formed.



This result appeared to indicate that ylide **207** may have been formed but was not stable under reflux conditions. So the next two reactions were both performed under milder conditions; the first one was done at ambient temperature and the second was carried out in an ice bath. The major product of both reactions was again **208**.

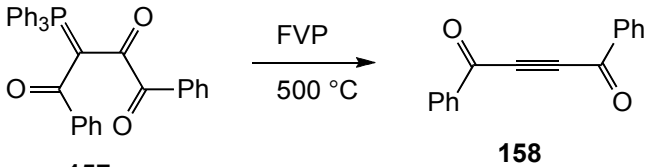
According to the literature, when triphenylphosphine in dry toluene was added to dibenzoylacetylene and sulfur in toluene, the ^{31}P NMR spectrum indicated that the

crude products contain Ph_3PS and **159** in a ratio of 4:1. The mixture could be purified by column chromatography using hexane/ether (1:1) as eluent to give the ylide **159** in low yield.[77]



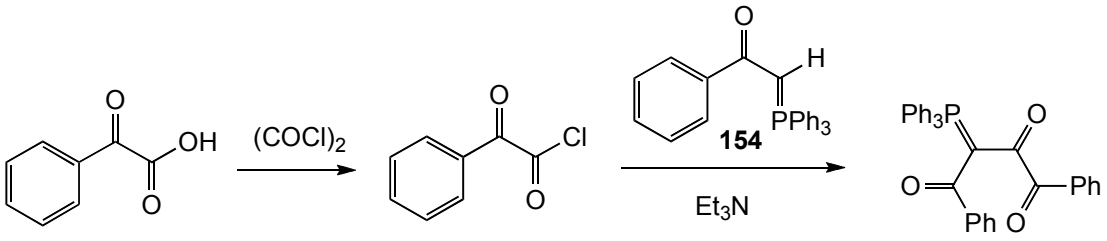
158 **159**

Previous work in this laboratory included the synthesis and FVP of trioxo stabilised ylide **157**, which underwent extrusion of Ph_3PO to give the acetylene **158** at 500 °C.[21]



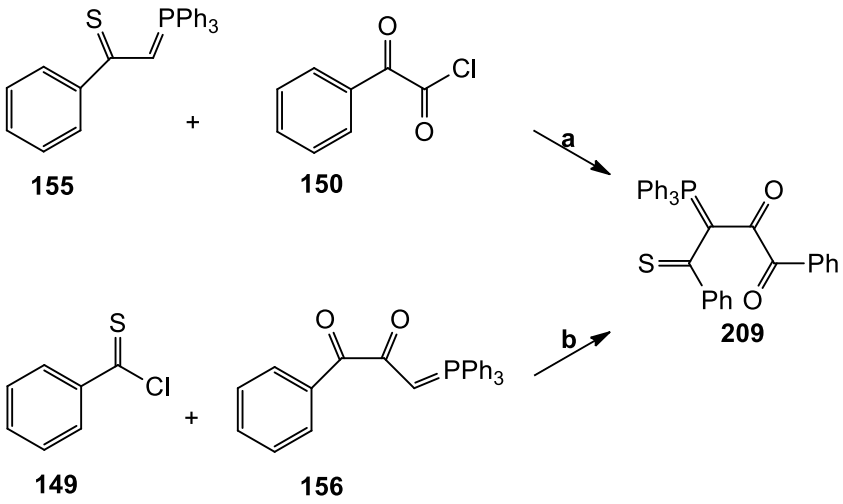
157 **158**

Using the previously developed methods,[21] ylide **157** was prepared from ylide **154** and phenylglyoxylyl chloride **150** in a yield of 68%, the acid chloride **150** being obtained from the corresponding acid by treatment with oxalyl chloride.



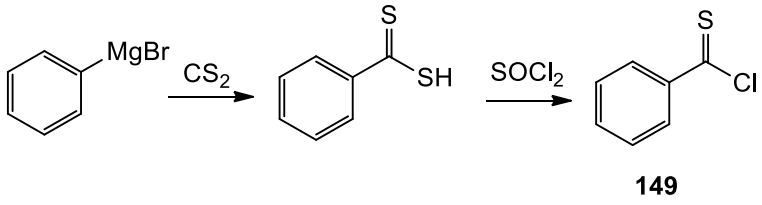
150 **157** 68%

To make a comparison with the ylide **159** under FVP conditions the isomeric ylide **209** would also be of interest. Two different ways were planned for the synthesis of this compound as shown below.

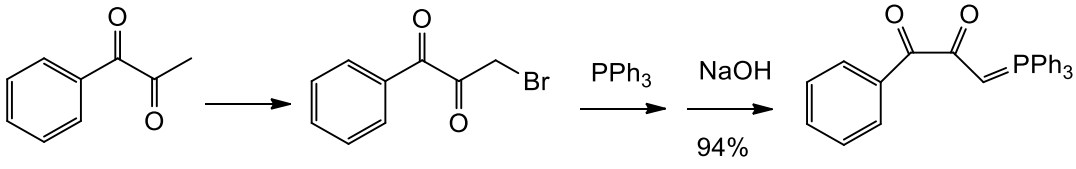


For path **a**, both starting materials had already been made. When the reaction was tried at room temperature under a N_2 atmosphere, the ^{31}P NMR spectrum showed that the majority of the starting ylide **155** was unreacted; when the mixture was heated under reflux, the majority of the crude product was Ph_3PS and a significant amount of Ph_3PO was also found, with ylide **209** was only obtained in a small quantity.

The thiobenzoyl chloride **149** required for path **b** was synthesised using an old method.[78] After the crude product was obtained, it was transferred to a flask for fractional distillation. The liquid was first distilled at 50 °C to remove $SOCl_2$ and a little S_2Cl_2, and then the temperature was raised to 200 °C to distil over the remaining products. During the process, a lot of the product had decomposed, so to keep the yield of the **149** high, the distillation was only performed once. In the end, the sample of **149** obtained was not entirely pure.



Ylide **156** had already been made by a former student in the group.[47] The starting material was 1-phenylpropane-1,2-dione, which was halogenated using bromine to get **151**. A previously prepared sample of this bromo ketone was reacted with PPh_3 to get the corresponding phosphonium salt, followed by addition of NaOH to the solution to give the ylide **156** in 95% yield.

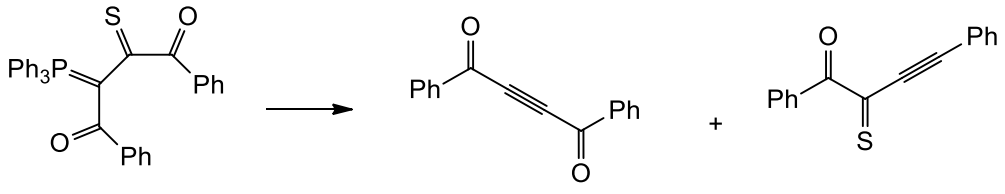


151 **156**

The result of reacting thiobenzoyl chloride **149** and ylide **156** was not a clean transformation. The ^{31}P NMR spectrum indicated that there were many different ylide peaks and some other phosphonium salt peaks. Neither recrystallisation nor column chromatography could purify the crude products to get ylide **209**. Therefore it was relucantly accepted that ylide **209** was not accessible by the above methods.

2. FVP of Ylide 159

FVP of ylide **159** was performed at two different temperatures. The first time the temperature 750 °C was tried. The ^{31}P NMR spectrum of the products indicated that the crude products were a mixture of Ph_3PO and Ph_3PS in a ratio of 1:1.2.



159 **158** **160**

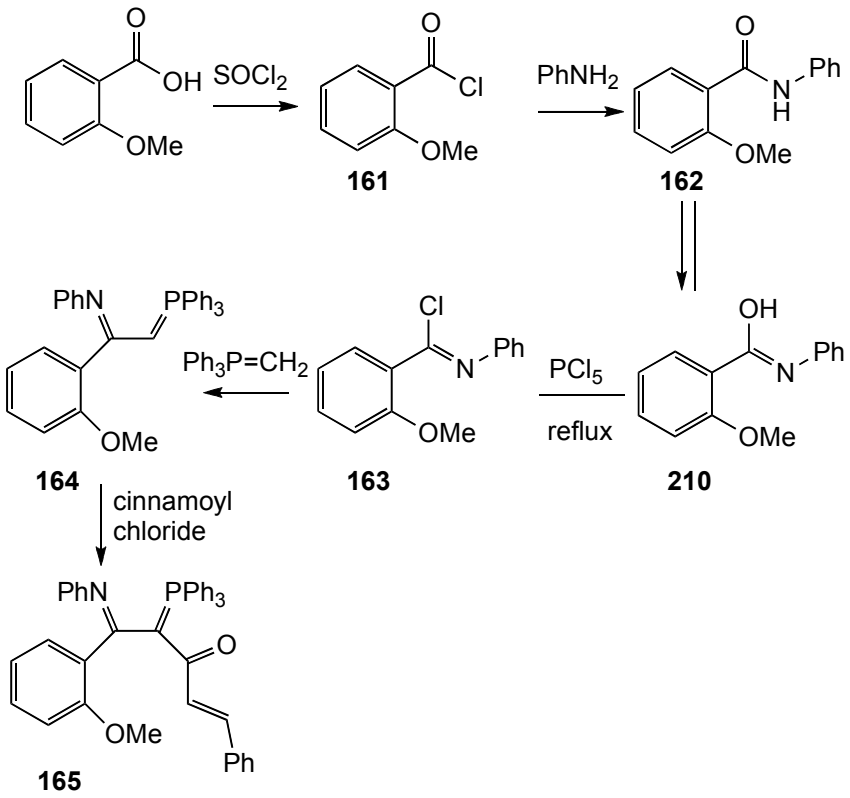
This result was quite unexpected, because Ph_3PS should be extruded more readily, and it was expected that the main pyrolysis product would be **158**. The pyrolysis was repeated at the lower temperature of 700 °C but the result was the same. Therefore it appeared as though any attempts to obtain regioselectivity in the extrusion reactions based on a difference of reactivity between C=O and C=S were unlikely to be successful.

In conclusion, the thiocarbonyl stabilised ylides such as **206**, **207** and **209** were not easy to synthesise. Even the available ylides such as the **153, 155** and **159** were not easy to purify by recrystallisation. Since the ylide **159** didn't show good selectivity between the thiocarbonyl and carbonyl group upon FVP, this kind of ylides did not seem likely to be of any value in preparation of a flavone.

F Preparation and Pyrolysis Imidoyl Ylides

1. Preparation of Starting Materials

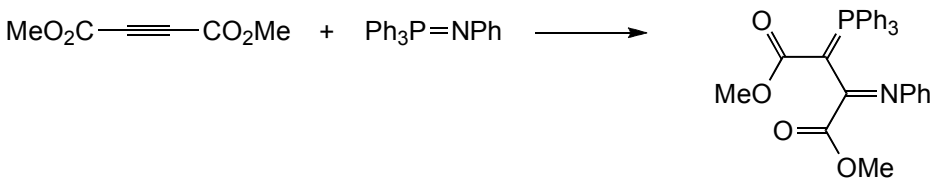
As the thiocarbonyl and carbonyl stabilised ylides did not show good selectivity and could extrude both Ph_3PO and Ph_3PS, a new kind of ylide had to be devised. The imdoyl ylides seemed likely to quite stable and might only undergo extrusion of Ph_3PO in preference to $Ph_3P{=}NR$. This might allow thermal cyclisation to give a 4-iminobenzopyran ring which could then simply be deprotected to afford the desired flavone or ring-fused benzopyranone. The following scheme shows the planned route for synthesis of a suitable imidoyl ylide.



2-Methoxybenzoic acid was heated under reflux with $SOCl_2$ for 1 h, and then the product was distilled at 100 °C to get the pure colourless liquid acid chloride **161** in a yield of 93%. This was reacted with aniline in the presence of aqueous NaOH to afford the anilide **162** as long brown needles, obtained after recrystallisation from ethyl acetate in a yield of 73%. When the benzamide **162** and PCl_5 were heated under reflux with a little $POCl_3$ as solvent to give a homogenous solution, the benzimidoyl chloride **163** could be obtained by vacuum distillation of the crude product at 170 °C in a yield of 32%.[79-82] To improve the yield of this step, the reaction time was extended from 5 h to 12 h, however the yield remained unchanged.

2. Preparation of Ylides

Very few β-imidoyl phosphonium ylides are known but quite recently the imidoyl dioxo ylide **211** was prepared following the analogous route to that used for **159**, from DMAD and the phosphinimine $Ph_3P{=}NPh$.[83]



211

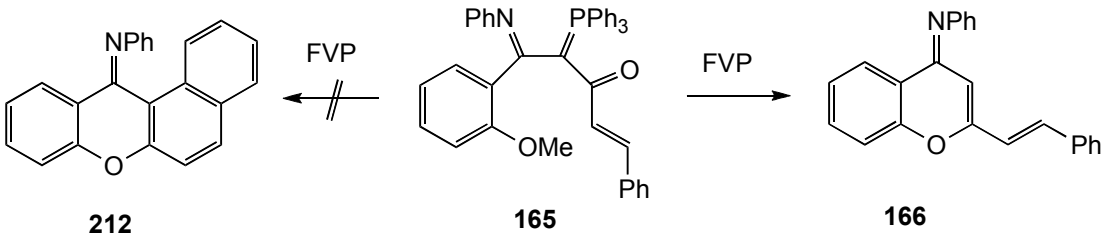
Ylide **164** was prepared from the imidoyl chloride **163** and methylenetriphenylphosphorane and was obtained as pure yellow crystals in a yield of 21% after slow recrystallisation from ethyl acetate with some drops of CH_2Cl_2. As the yield obtained in this way was low, column chromatography with diethyl ether as eluent was also tried, but the ylide could not be obtained pure by this method.

The ylide **164** was then treated with cinnamoyl chloride in dry toluene followed by the addition of triethylamine. After the mixture was stirred for 48 h it gave the crude product and, following recrystallisation from ethyl acetate, the product **165** was obtained as white crystals in a yield of 22%.

In an alternative procedure,[21] ylide **164** was treated with triethylamine in dry toluene then followed by the addition of cinnamoyl chloride and stirring for 48 h, but the ^{31}P NMR spectrum in this case showed only a trace of the product.

3. FVP of Ylide

When ylide **165** was subjected to FVP at 750 °C, the ^{1}H NMR spectrum of the crude product had a singlet peak at 6.12 ppm, which meant there may be a double bond in the mixture. In the ^{31}P NMR spectrum, the only peak was around 29.0 ppm confirming that the Ph_3PO had been eliminated.



212 **165** **166**

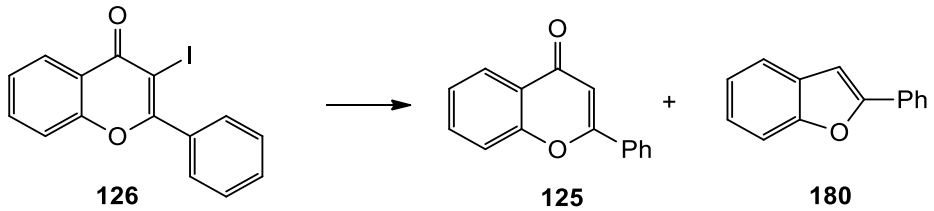
From the information of the mass spectrum, HRMS and ^{13}C NMR, the product of the FVP was confirmed to be the 4-iminobenzopyran **166** in a yield of 46%, with none of the cyclisation product **212** formed. Maybe for this a higher pyrolysis temperature was necessary and this will be the subject of future studies.

In conclusion, the imidoyl ylide was found to be quite stable and to show good selectivity during FVP. The overall yield was acceptable and, if the conversion of **162** into **163** had a higher yield, the whole route would have a better result. The other problem was the synthesis of ylide **165**, where the conditions could perhaps be optimised to give a higher yield in a shorter time.

G Conclusions, Summary and Future Work

In conclusion, the aim to synthesise flavones and flavonoids from stabilised ylides under FVP conditions has been successful, especially starting from ylides with two carbonyl groups on the same side. In addition, ylides with carbonyl and thiocarbonyl groups on either side were found not to give good selectivity, however the imidoyl ylides could solve the problem and could play a significant role in future work.

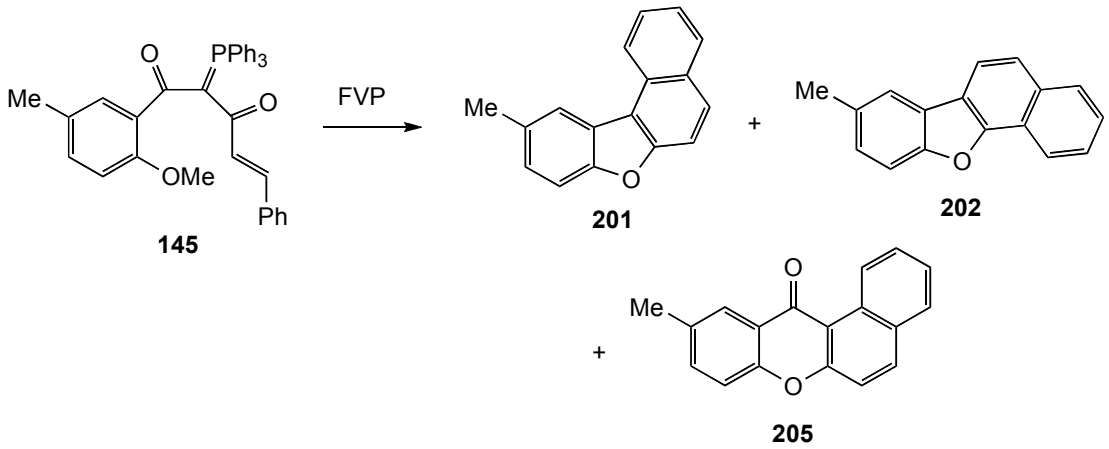
Initial studies suggested that β,γ-dioxo stabilised ylides would give flavones in a reasonable yield when they were exposed to FVP, however due to the instability of the intermediate radical, a benzofuran product **180** was always formed. To clarify the mechanism, flavone **125** and 3-iodoflavone **126** were made, and after comparing the results of the FVP of the two compounds, it was clear that the intermediate flavone-3-yl radical was undergoing an intramolecular cyclisation with loss of CO.



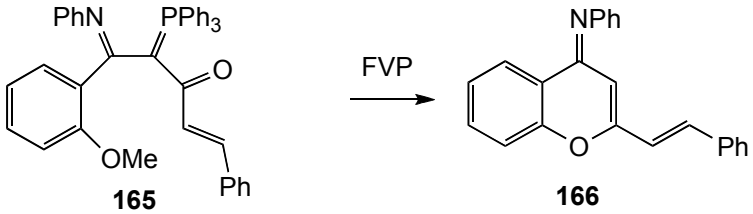
126 **125** **180**

In the following work, the aim was to make ylides with the carbonyl protected so that it wouldn't be lost during FVP. However, due to the neopentyl effect, ylides with CO protected as a 1,3-dioxolane could not be obtained.

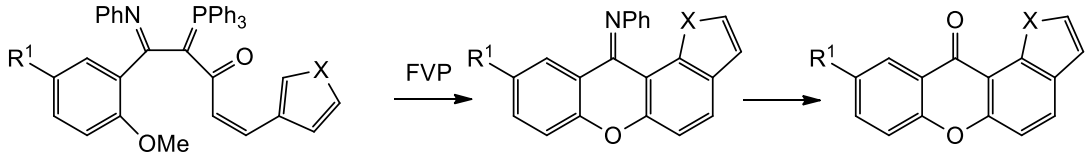
A series of β,β'-dioxo ylides were also synthesised. When there was a 5-methyl substituent, the ylide **145** was obtained in good yield, while with chorine or no substituent group on the same position, the ylides were not easily obtained. Since both carbonyl groups had the chance take part in extrusion of Ph_3PO, the FVP results were quite complex and only three closely related tetracyclic compounds **201, 202** and **205** being tentatively identified.



In an attempt to improve the selectivity, the thiocarbonyl was introduced into the ylides. From the results of FVP of the ylides, the Ph_3PO and Ph_3PS were both observed. In addition, the more complicated thiocarbonyl ylides were not easily synthesised. So the imidoyl ylides were introduced into the project. In terms of the whole range of ylides handled, the majority of the compounds involved here were formed quite easily and with good yields. The FVP result indicated that they did show the required selectivity.



Future work should focus on synthesis of a wider range of imidoyl ylides and their FVP at higher temperatures. It seems likely that a higher FVP temperature could lead to tandem cyclisation products with retention of the imidoyl group, thus opening up access, after hydrolytic cleavage, to a wide range of new carbonyl-containing fused polycyclic heteroaromatic ring systems such as those shown below.



R^1=Me, Cl
X=S, O

APPENDIX

Crystal Data for Ylide **121**

Identification code	DCAA 1	
Empirical formula	$C_{34}H_{27}O_3P$	
Formula weight	514.53	
Temperature	93(2) K	
Wavelength	0.71075 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.828 (2)	α = 74.94 (2)
	b = 10.622 (3)	β = 73.96 (2)
	c = 13.692 (2)	γ = 78.45 (2)
Volume	1313.76 $Å^3$	
Z	2	
Density (calculated)	1.301 Mg/m^3	
Absorption coefficient	0.139 mm^{-1}	
F(000)	540	
Crystal sise	0.12 x 0.12 x 0.03 mm	
Theta range for data collection	2.00 to 25.34°	
Index ranges	-7<=h<=11, -12<=k<=12, -13<= l <=16	
Reflections collected	8393	
Independent reflections	4628	
Data / restraints / parameters	2874/0/343	
Goodness-of-fit on F^2	0.706	
Final R indices [I>2 sigma (I)]	R_1=0.0579, wR_2=0.1550	
R indices (all data)	R_1=0.1007, wR_2=0.2029	

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2x10^3$) for **121**.

	X	Y	Z
P(1)	1284.8(9)	1835.9(8)	1508.6(5)
O(1)	2419(2)	1178(2)	4640.2(14)
O(2)	3780(2)	1648(2)	2279.2(15)
O(3)	3255(3)	4602(2)	2638.6(16)
C(1)	1435(3)	2774(3)	2344(2)
C(2)	2778(3)	2525(3)	2561(2)
C(3)	3229(3)	3441(3)	3082(2)
C(4)	3851(3)	2891(3)	4011(2)
C(5)	3458(3)	1762(3)	4767(2)
C(6)	4087(4)	1320(3)	5615(2)
C(7)	5102(4)	1976(3)	5711(2)
C(8)	5512(4)	3093(3)	4972(2)
C(9)	4877(3)	3537(3)	4134(2)
C(10)	1887(4)	132(3)	5468(2)
C(11)	2684(3)	2017(3)	323(2)
C(12)	3245(4)	999(3)	-214(2)
C(13)	4348(4)	1191(4)	1112(3)
C(14)	4877(4)	2365(4)	-1465(2)
C(15)	4314(4)	3384(4)	-950(2)
C(16)	3227(4)	3211(3)	-56(2)
C(17)	-413(3)	2322(3)	1164(2)
C(18)	-1661(4)	2075(3)	1948(2)
C(19)	-2970(4)	2357(3)	1723(3)
C(20)	-3101(4)	2922(4)	712(3)
C(21)	-1890(4)	3214(4)	-67(3)
C(22)	-550(4)	2904(3)	156(2)
C(23)	1236(3)	100(3)	2102(2)
C(24)	1764(3)	-482(3)	2992(2)
C(25)	1605(3)	-1769(3)	3487(2)
C(26)	945(4)	-2507(3)	3103(2)
C(27)	420(4)	-1936(3)	2224(2)
C(28)	576(4)	-649(3)	1719(2)
C(29)	250(4)	3729(3)	2782(2)
C(30)	-571(4)	4671(3)	2172(2)
C(31)	-1677(4)	5555(3)	2602(2)
C(32)	-1962(4)	5555(3)	3653(2)
C(33)	-1148(4)	4647(3)	4266(2)
C(34)	-74(3)	3738(3)	3845(2)

Bond lengths [Å] for **121**		C(10)-H(10A)	0.980(3)	C(23)-C(24)	1.402(4)
		C(10)-H(10B)	0.981(3)	C(23)-C(28)	1.393(5)
P(1)-C(1)	1.751(4)	C(10)-H(10C)	0.979(4)	C(24)-H(24)	0.949(4)
P(1)-C(11)	1.809(3)	C(11)-C(12)	1.402(4)	C(24)-C(25)	1.378(4)
P(1)-C(17)	1.799(3)	C(11)-C(16)	1.392(5)	C(25)-H(25)	0.949(3)
P(1)-C(23)	1.816(3)	C(12)-H(12)	0.950(3)	C(25)-C(26)	1.385(5)
O(1)-C(5)	1.366(4)	C(12)-C(13)	1.396(4)	C(26)-H(26)	0.950(3)
O(1)-C(10)	1.429(3)	C(13)-H(13)	0.949(4)	C(26)-C(27)	1.386(4)
O(2)-C(2)	1.263(3)	C(13)-C(14)	1.366(6)	C(27)-H(27)	0.949(4)
O(3)-C(3)	1.227(4)	C(14)-H(14)	0.951(3)	C(27)-C(28)	1.380(4)
C(1)-C(2)	1.392(4)	C(14)-C(15)	1.384(6)	C(28)-H(28)	0.951(3)
C(1)-C(29)	1.484(4)	C(15)-H(15)	0.950(4)	C(29)-C(30)	1.402(4)
C(2)-C(3)	1.536(5)	C(15)-C(16)	1.383(4)	C(29)-C(34)	1.403(4)
C(3)-C(4)	1.494(4)	C(16)-H(16)	0.950(3)	C(30)-H(30)	0.951(3)
C(4)-C(5)	1.407(4)	C(17)-C(18)	1.407(4)	C(30)-C(31)	1.391(4)
C(4)-C(9)	1.395(5)	C(18)-H(18)	0.949(3)	C(31)-H(31)	0.950(3)
C(5)-C(6)	1.396(4)	C(18)-C(19)	1.363(6)	C(31)-C(32)	1.388(4)
C(6)-H(6)	0.950(3)	C(19)-H(19)	0.951(3)	C(32)-H(32)	0.950(3)
C(6)-C(7)	1.377(6)	C(19)-C(20)	1.389(6)	C(32)-C(33)	1.384(5)
C(7)-H(7)	0.950(3)	C(20)-H(20)	0.950(4)	C(33)-H(33)	0.951(3)
C(7)-C(8)	1.391(4)	C(20)-(21)	1.387(5)	C(33)-C(34)	1.387(4)
C(8)-H(8)	0.950(4)	C(21)-H(21)	0.950(4)	C(34)-H(34)	0.950(3)
C(8)-C(9)	1.387(5)	C(21)-C(22)	1.390(6)		
C(9)-H(9)	0.950(3)	C(22)-H(22)	0.949(3)		

Bond angles [Å] for **121**	
C(1)-P(1)-C(11)	111.8(1)
C(1)-P(1)-C(17)	110.5(1)
C(1)-P(1)-C(23)	114.1(1)
C(11)-P(1)-C(17)	108.3(1)
C(11)-P(1)-C(17)	108.3(1)
C(11)-P(1)-C(23)	109.6(1)
C(17)-P(1)-C(23)	102.0(1)
C(5)-O(1)-C(10)	117.2(2)
P(1)-C(1)-C(2)	113.0(2)
P(1)-C(1)-C(29)	123.5(2)
C(2)-C(1)-C(29)	123.4(3)
O(2)-C(2)-C(1)	125.8(3)
O(2)-C(2)-C(3)	113.0(3)
C(1)-C(2)-C(3)	120.8(3)
O(3)-C(3)-C(2)	118.5(3)
O(3)-C(3)-C(4)	120.2(3)
C(2)-C(3)-C(4)	120.5(3)
C(3)-C(4)-C(5)	123.7(3)
C(3)-C(4)-C(9)	118.0(3)
C(5)-C(4)-C(9)	118.3(3)
O(1)-C(5)-C(4)	116.8(3)
O(1)-C(5)-C(6)	123.3(3)
C(4)-C(5)-C(6)	119.9(3)
C(5)-C(6)-H(6)	119.9(3)
C(5)-C(6)-C(7)	120.4(3)
H(6)-C(6)-C(7)	119.8(3)
C(6)-C(7)-H(7)	119.6(3)
C(6)-C(7)-C(8)	120.8(3)
H(7)-C(7)-C(8)	119.6(3)
C(7)-C(8)-H(8)	120.6(3)
C(7)-C(8)-C(9)	118.7(3)
H(8)-C(8)-C(9)	120.7(3)
C(4)-C(9)-C(8)	121.9(3)
C(4)-C(9)-H(9)	119.1(3)
C(8)-C(9)-H(9)	119.1(3)
O(1)-C(10)-H(10A)	109.5(3)
O(1)-C(10)-H(10B)	109.4(3)
O(1)-C(10)-H(10C)	109.5(3)
H(10A)-C(10)-H(10B)	109.5(3)
H(10A)-C(10)-H(10C)	109.5(3)
H(10B)-C(10)-H(10C)	109.4(3)
P(1)-C(11)-C(12)	122.4(2)
P(1)-C(11)-C(16)	118.3(2)
C(12)-C(11)-C(16)	119.3(3)
C(11)-C(12)-H(12)	120.1(3)
C(11)-C(12)-C(13)	119.6(3)
H(12)-C(12)-C(13)	120.2(3)
C(12)-C(13)-H(13)	119.9(4)
C(12)-C(13)-C(14)	120.2(4)
H(13)-C(13)-C(14)	119.9(4)
C(13)-C(14)-H(14)	119.7(4)
C(13)-C(14)-C(15)	120.6(3)
H(14)-C(14)-C(15)	119.7(4)
C(14)-C(15)-H(15)	120.0(4)
C(14)-C(15)-C(16)	120.1(3)
H(15)-C(15)-C(16)	119.9(3)
C(11)-C(16)-C(15)	120.2(3)

C(11)-C(16)-H(16)	120.0(3)	C(25)-C(26)-H(26)	120.3(3)
C(15)-C(16)-H(16)	119.9(3)	C(25)-C(26)-C(27)	119.6(3)
P(1)-C(17)-C(18)	118.5(2)	H(26)-C(26)-C(27)	120.1(3)
P(1)-C(17)-C(22)	123.2(2)	C(26)-C(27)-H(27)	119.8(3)
C(18)-C(17)-C(22)	118.4(3)	C(26)-C(27)-C(28)	120.5(3)
C(17)-C(18)-H(18)	119.5(3)	H(27)-C(27)-C(28)	119.7(3)
C(17)-C(18)-C(19)	121.1(3)	C(23)-C(28)-C(27)	120.2(3)
H(18)-C(18)-C(19)	119.4(3)	C(23)-C(28)-H(28)	119.9(3)
C(18)-C(19)-H(19)	119.8(4)	C(27)-C(28)-H(28)	119.9(3)
C(18)-C(19)-C(20)	120.4(3)	C(1)-C(29)-C(30)	122.8(3)
H(19)-C(19)-C(20)	119.8(4)	C(1)-C(29)-C(34)	120.3(3)
C(19)-C(20)-H(20)	120.2(4)	C(30)-C(29)-C(34)	116.9(3)
C(19)-C(20)-C(21)	119.5(4)	C(29)-C(30)-H(30)	119.2(3)
H(20)-C(20)-C(21)	120.2(4)	C(29)-C(30)-C(31)	121.7(3)
C(20)-C(21)-H(21)	119.9(4)	H(30)-C(30)-C(31)	119.1(3)
C(20)-C(21)-C(22)	120.2(4)	C(30)-C(31)-H(31)	119.9(3)
H(21)-C(21)-C(22)	119.9(4)	C(30)-C(31)-C(32)	120.2(3)
C(17)-C(22)-C(21)	120.4(3)	H(31)-C(31)-C(32)	119.8(3)
C(17)-C(22)-H(22)	119.9(3)	C(31)-C(32)-H(32)	120.5(3)
C(21)-C(22)-H(22)	119.8(3)	C(31)-C(32)-C(33)	119.0(3)
P(1)-C(23)-C(24)	120.8(2)	H(32)-C(32)-C(33)	120.5(3)
P(1)-C(23)-C(28)	120.0(2)	C(32)-C(33)-H(33)	119.6(3)
C(24)-C(23)-C(28)	119.0(3)	C(32)-C(33)-C(34)	120.9(3)
C(23)-C(24)-H(24)	119.9(3)	H(33)-C(33)-C(34)	119.5(3)
C(23)-C(24)-C(25)	120.1(3)	C(29)-C(34)-C(33)	121.3(3)
H(24)-C(24)-C(25)	120.0(3)	C(29)-C(34)-H(34)	119.3(3)
C(24)-C(25)-H(25)	119.8(3)	C(33)-C(34)-H(34)	119.3(3)
C(24)-C(25)-C(26)	120.5(3)		
H(25)-C(25)-C(26)	119.7(3)		

Torsion angles [°] for **121**	
C(11)-P(1)-C(1)-C(2)	-53.7(3)
C(11)-P(1)-C(1)-C(29)	126.7(3)
C(17)-P(1)-C(1)-C(2)	-174.5(2)
C(17)-P(1)-C(1)-C(29)	6.0(3)
C(23)-P(1)-C(1)-C(2)	71.3(3)
C(23)-P(1)-C(1)-C(29)	-108.2(3)
C(1)-P(1)-C(11)-C(12)	148.4(3)
C(1)-P(1)-C(11)-C(16)	-30.9(3)
C(17)-P(1)-C(11)-C(12)	-89.6(3)
C(17)-P(1)-C(11)-C(16)	91.1(3)
C(23)-P(1)-C(11)-C(12)	20.8(3)
C(23)-P(1)-C(11)-C(16)	-158.4(2)
C(1)-P(1)-C(17)-C(18)	-66.8(3)
C(1)-P(1)-C(17)-C(22)	114.7(3)
C(11)-P(1)-C(17)-C(18)	170.4(2)
C(11)-P(1)-C(17)-C(22)	-8.1(3)
C(23)-P(1)-C(17)-C(18)	54.9(3)
C(23)-P(1)-C(17)-C(22)	-123.6(3)
C(1)-P(1)-C(23)-C(24)	-20.8(3)
C(1)-P(1)-C(23)-C(28)	154.6(2)
C(11)-P(1)-C(23)-C(24)	105.43()
C(11)-P(1)-C(23)-C(28)	-79.2(3)
C(17)-P(1)-C(23)-C(24)	-139.9(3)
C(17)-P(1)-C(23)-C(28)	35.4(3)
C(10)-O(1)-C(5)-C(4)	-172.4(3)
C(10)-O(1)-C(5)-C(6)	5.2(4)
C(5)-O(1)-C(10)-H(10A)	58.1(4)
C(5)-O(1)-C(10)-H(10B)	-61.9(4)
C(5)-O(1)-C(10)-H(10C)	178.1(3)
P(1)-C(1)-C(2)-O(2)	-5.8(4)
P(1)-C(1)-C(2)-C(3)	167.0(2)
C(29)-C(1)-C(2)-O(2)	173.8(3)
C(29)-C(1)-C(2)-C(3)	-13.5(4)
P(1)-C(1)-C(29)-C(30)	-48.0(4)
P(1)-C(1)-C(29)-C(34)	133.5(3)
C(2)-C(1)-C(29)-C(30)	132.5(3)
C(2)-C(1)-C(29)-C(34)	-46.0(4)
O(2)-C(2)-C(3)-O(3)	113.8(3)
O(2)-C(2)-C(3)-C(4)	-56.2(4)
C(1)-C(2)-C(3)-O(3)	-59.8(4)
C(1)-C(2)-C(3)-C(4)	130.2(3)
O(3)-C(3)-C(4)-C(5)	157.2(3)
O(3)-C(3)-C(4)-C(9)	-22.7(4)
C(2)-C(3)-C(4)-C(5)	-32.9(4)
C(2)-C(3)-C(4)-C(9)	147.2(3)
C(3)-C(4)-C(5)-O(1)	-1.9(4)
C(3)-C(4)-C(5)-C(6)	-179.6(3)
C(9)-C(4)-C(5)-O(1)	178.0(3)
C(9)-C(4)-C(5)-C(6)	0.3(4)
C(3)-C(4)-C(9)-C(8)	-179.9(3)
C(3)-C(4)-C(9)-H(9)	0.2(4)
C(5)-C(4)-C(9)-C(8)	0.2(4)
C(5)-C(4)-C(9)-H(9)	-179.7(3)
O(1)-C(5)-C(6)-H(6)	1.8(5)
O(1)-C(5)-C(6)-(7)	-178.2(3)

C(4)-C(5)-C(6)-H(6)	179.4(3)	H(13)-C(13)-C(14)-C(15)	178.9(4)
C(4)-C(5)-C(6)-C(7)	-0.6(5)	C(13)-C(14)-C(15)-H(15)	-178.7(4)
C(5)-C(6)-C(7)-H(7)	-179.7(3)	C(13)-C(14)-C(15)-C(16)	1.4(6)
C(5)-C(6)-C(7)-C(8)	0.5(5)	H(14)-C(14)-C(15)-H(15)	1.3(6)
H(6)-C(6)-C(7)-H(7)	0.3(5)	H(14)-C(14)-C(15)-C(16)	-178.6(3)
H(6)-C(6)-C(7)-C(8)	-179.6(3)	C(14)-C(15)-C(16)-C(11)	-0.7(5)
C(6)-C(7)-C(8)-H(8)	-179.9(3)	C(14)-C(15)-C(16)-H(16)	179.3(3)
C(6)-C(7)-C(8)-C(9)	0.1(5)	H(15)-C(15)-C(16)-C(11)	179.4(3)
H(7)-C(7)-C(8)-H(8)	0.3(5)	H(15)-C(15)-C(16)-H(16)	-0.6(6)
H(7)-C(7)-C(8)-C(9)	-179.8(3)	P(1)-C(17)-C(18)-H(18)	3.5(4)
C(7)-C(8)-C(9)-C(4)	-0.4(5)	P(1)-C(17)-C(18)-C(19)	-176.5(3)
C(7)-C(8)-C(9)-H(9)	179.5(3)	C(22)-C(17)-C(18)-H(18)	-177.9(3)
H(8)-C(8)-C(9)-C(4)	179.5(3)	C(22)-C(17)-C(18)-C(19)	2.2(5)
H(8)-C(8)-C(9)-H(9)	-0.5(5)	P(1)-C(17)-C(22)-C(21)	177.7(3)
P(1)-C(11)-C(12)-H(12)	1.5(5)	P(1)-C(17)-C(22)-H(22)	-2.2(5)
P(1)-C(11)-C(12)-C(13)	-178.5(3)	C(18)-C(17)-C(22)-C(21)	-0.9(5)
C(16)-C(11)-C(12)-H(12)	-179.3(3)	C(18)-C(17)-C(22)-H(22)	179.2(3)
C(16)-C(11)-C(12)-C(13)	0.7(5)	C(17)-C(18)-C(19)-H(19)	178.6(3)
P(1)-C(11)-C(16)-C(15)	178.9(3)	C(17)-C(18)-C(19)-C(20)	-1.3(5)
P(1)-C(11)-C(16)-C(16)	-1.1(5)	H(18)-C(18)-C(19)-H(19)	-1.3(6)
C(12)-C(11)-C(16)-C(15)	-0.4(5)	H(18)-C(18)-C(19)-C(20)	178.8(3)
C(12)-C(11)-C(16)-C(16)	179.6(3)	C(18)-C(19)-C(20)-H(20)	179.2(4)
C(11)-C(12)-C(13)-H(13)	180.0(4)	C(18)-C(19)-C(20)-C(21)	-0.8(6)
C(11)-C(12)-C(13)-C(14)	-0.0(5)	H(19)-C(19)-C(20)-H(20)	-0.8(7)
H(12)-C(12)-C(13)-H(13)	0.0(6)	H(19)-C(19)-C(20)-C(21)	179.2(4)
H(12)-C(12)-C(13)-C(14)	-180.0(4)	C(19)-C(20)-C(21)-H(21)	-177.8(4)
C(12)-C(13)-C(14)-H(14)	178.9(4)	C(19)-C(20)-C(21)-C(22)	2.1(6)
C(12)-C(13)-C(14)-C(15)	-1.1(6)	H(20)-C(20)-C(21)-H(21)	2.2(7)
H(13)-C(13)-C(14)-H(14)	-1.1(6)	H(20)-C(20)-C(21)-C(22)	-177.9(4)

C(20)-C(21)-C(22)-C(17)	-1.2(6)	H(27)-C(27)-C(28)-H(28)	-1.3(5)
C(20)-C(21)-C(22)-H(22)	178.7(4)	C(1)-C(29)-C(30)-H(30)	0.1(5)
H(21)-C(21)-C(22)-C(17)	178.7(4)	C(1)-C(29)-C(30)-C(31)	180.0(3)
H(21)-C(21)-C(22)-H(22)	-1.4(6)	C(34)-C(29)-C(30)-H(30)	178.0(3)
P(1)-C(23)-C(24)-H(24)	-5.9(4)	C(34)-C(29)-C(30)-C(31)	-1.4(5)
P(1)-C(23)-C(24)-C(25)	174.2(2)	C(1)-C(29)-C(34)-C(33)	178.0(3)
C(28)-C(23)-C(24)-H(24)	178.7(3)	C(1)-C(29)-C(34)-H(34)	-2.1(5)
C(28)-C(23)-C(24)-C(25)	-1.2(4)	C(30)-C(29)-C(34)-C(33)	-0.6(5)
P(1)-C(23)-C(28)-C(27)	-174.1(3)	C(30)-C(29)-C(34)-H(34)	179.3(3)
P(1)-C(23)-C(28)-H(28)	5.9(5)	C(29)-C(30)-C(31)-H(31)	-177.7(3)
C(24)-C(23)-C(28)-C(27)	1.4(5)	C(29)-C(30)-C(31)-C(32)	2.4(5)
C(24)-C(23)-C(28)-H(28)	-178.7(3)	H(30)-C(30)-C(31)-H(31)	2.2(5)
C(23)-C(24)-C(25)-H(25)	-178.9(3)	H(30)-C(30)-C(31)-C(32)	-177.7(3)
C(23)-C(24)-C(25)-C(26)	1.1(5)	C(30)-C(31)-C(32)-H(32)	178.7(3)
H(24)-C(24)-C(25)-H(25)	1.1(5)	C(30)-C(31)-C(32)-C(33)	-1.2(5)
H(24)-C(24)-C(25)-C(26)	-178.9(3)	H(31)-C(31)-C(32)-H(32)	-1.2(5)
C(24)-C(25)-C(26)-H(26)	178.9(3)	H(31)-C(31)-C(32)-C(33)	178.8(3)
C(24)-C(25)-C(26)-C(27)	-1.1(5)	C(31)-C(32)-C(33)-H(33)	179.2(3)
H(25)-C(25)-C(26)-H(26)	-1.1(5)	C(31)-C(32)-C(33)-C(34)	-0.8(5)
H(25)-C(25)-C(26)-C(27)	178.9(3)	H(32)-C(32)-C(33)-H(33)	-0.7(5)
C(25)-C(26)-C(27)-H(27)	-178.9(3)	H(32)-C(32)-C(33)-C(34)	179.3(3)
C(25)-C(26)-C(27)-C(28)	1.3(5)	C(32)-C(33)-C(34)-C(29)	1.7(5)
H(26)-C(26)-C(27)-H(27)	1.3(5)	C(32)-C(33)-C(34)-H(34)	-178.3(3)
H(26)-C(26)-C(27)-C(28)	-178.7(3)	H(33)-C(33)-C(34)-C(29)	-178.3(3)
C(26)-C(27)-C(28)-C(23)	-1.4(5)	H(33)-C(33)-C(34)-H(34)	1.8(5)
C(26)-C(27)-C(28)-H(28)	178.6(3)		
H(27)-C(27)-C(28)-C(23)	178.6(3)		

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