Versatile Pyrolytic Synthesis of Fused Polycyclic Heteroaromatic Compounds

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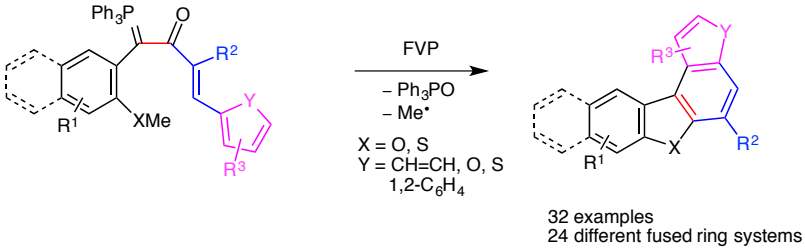

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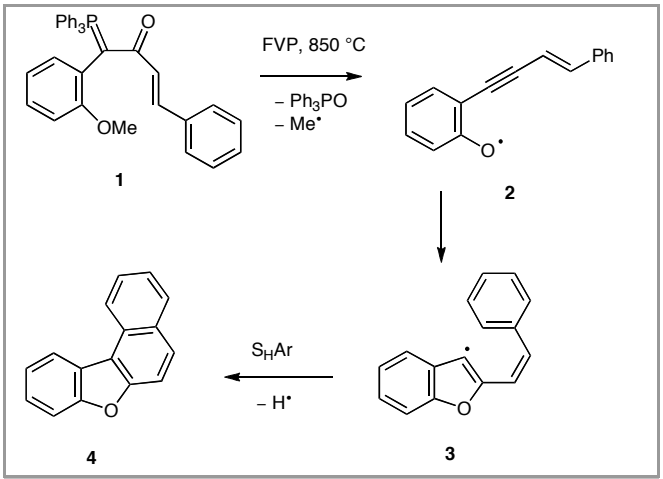
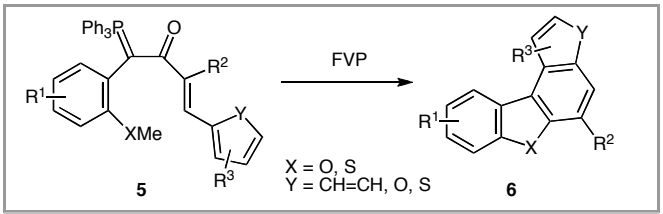
Abstract Thirty-six new stabilised phosphonium ylides designed to undergo thermal loss of Ph_3PO and radical domino cyclisation have been prepared and are generally found to undergo the desired reaction under flash vacuum pyrolysis conditions at 850 °C. A wide range ot tetra- and penta-cyclic fused ring heterocycles, many previously unknown, are thus formed in moderate to high yield in a single step. By using suitably substituted starting materials, substituents such as CH_3 and Cl can be installed at various positions in the products. The method has also been demonstrated in a combinatorial mode to generate a small library of twelve fused ring heterocycles in a single pyrolysis.

Key words cyclization; domino reaction; fused-ring systems; gas-phase reaction; heterocycles; radical reaction; ylides

There has been considerable recent interest in the use of gas-phase pyrolysis methods in synthesis of heterocyclic compounds.[1] The inherent thermodynamic stability of fused polycyclic heteroaromatic compounds makes them ideal targets for such methods. The efficiency of cascade or domino cyclisation processes for the construction of complex polycyclic systems also brings considerable advantages when compared to a step-wise coupling approach.[2] Some time ago we reported that the pyrolytic formation of alkynes by thermal extrusion of Ph_3PO from β-oxo phosphonium ylides could be adapted, in the presence of an *ortho*-methoxy- or methylthio-phenyl substituent, to give a convenient synthesis of 2-substituted benzofurans and benzothiophenes.[3] By having reactive groups at both ends of the alkyne-generating function, this approach was later extended to provide a few examples of domino cyclisation processes, illustrated by the formation of the tetracyclic naphthobenzofuran **4** by flash vacuum pyrolysis (FVP) of ylide **1** at 850 °C.[4] As shown in Scheme 1, this involves loss of both Ph_3PO and a methyl radical to give the alkynylaryloxy radical **2** which undergoes *5-endo-dig* cyclisation to give the 3-benzofuryl radical **3** which is set up for an intramolecular homolytic aromatic substitution. The success of this approach led us to explore its scope and limitations and we envisaged extending it to ylides with the general structure **5** which would lead directly to fused heterocyclic products **6** (Scheme 2) with various combinations of benzene, furan and thiophene rings and with substituents at essentially any chosen position. We now present the detailed results of these studies. It might also be noted that we have recently described related methods involving a nitrogen atom, either as the cyclising group



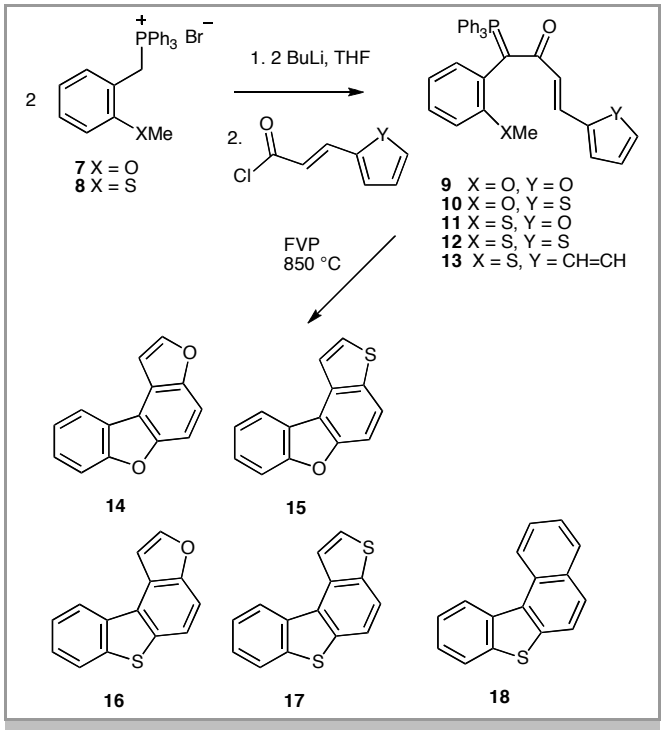
Scheme 1 Previously reported domino cyclisation process



Scheme 2 General synthetic approach to tetracyclic products

leading to ring-fused indoles (and quinolines),[5] or as a component of the base ring system by starting from 2-methylthio-3-pyridyl ylides leading to thieno[2,3-*b*]pyridines.[6]

Synthesis of the acyl ylides was easily accomplished (Scheme 3) by treatment of appropriate quaternary phosphonium salts **7** and **8** with *n*-butyllithium in THF to give the reactive benzylidene ylides, followed by acylation with 0.5 equiv of a cinnamoyl chloride or heterocyclic analogue. As first described by Bestmann,[7] this involves "transylidation" with one molecule of ylide reacting with the acid chloride to form an acylphosphonium salt which is then deprotonated by the second molecule of ylide to give the acyl ylide product and regenerate the chloride corresponding to the starting phosphonium salt. This gave the series of four ylides **9**–**12** and **13** the sulfur analogue of **1** was also prepared. The yields were variable but were sufficient to give reasonable quantities (1–5 g) of material for pyrolysis studies (Table 1). All ylides were highly crystalline, stable and high melting solids with ^{31}P NMR signals in the range δ +14–18 and highly informative and consistent ^{13}C NMR spectra with phosphorus coupling extending through three or four carbons in all directions.



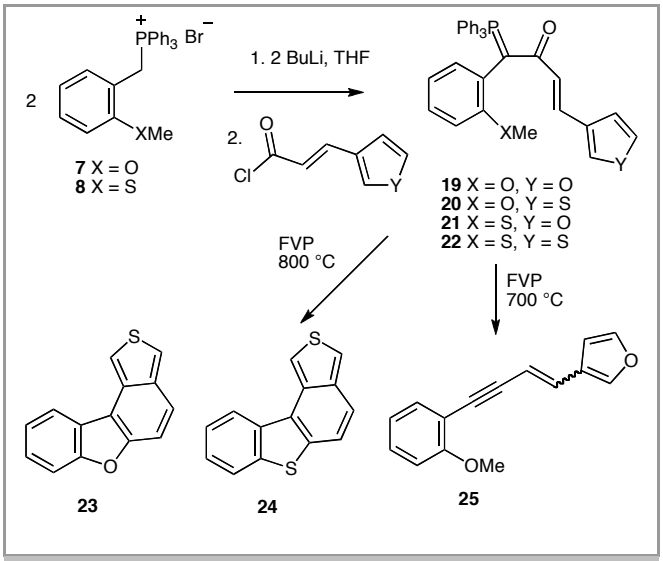
Scheme 3 Synthesis and pyrolysis of ylides **9**–**13**

When these ylides were subjected to FVP at 10^{-2} Torr and 850 °C, a single product band was obtained at the furnace exit in each case, which was shown to be a mixture of Ph_3PO and a heterocyclic product. Simple short-column chromatography using Et_2O/hexane separated the former and gave the heterocyclic products, which were then kugelrohr distilled to give the analytically pure tetracyclic products. As listed in Table 1, ylides **9**–**13** gave the respective products **14**–**18** in moderate to high yield. Among these simple fused heterocycles, **14**, **15** and **16** appear to be previously unknown, whereas both **17**[8] and **18**[9] gave good agreement with literature data.

Table 1 Synthesis of ylides and pyrolysis at 850 °C to give heterocyclic products.

Ylide	Yield (%)	^{31}P NMR δ	FVP Product(s)	Yield (%)
9	67	15.6	**14**	58
10	64	15.6	**15**	69
11	30	15.8	**16**	83
12	59	15.8	**17**	63
13	98	15.1	**18**	86
19	92	15.5	—	
			25[a]	*Z* 15, *E* 14
20	85	15.5	**23**[b]	60
21	67	15.8	—	
22	81	15.7	**24**[b]	36
26	67	15.5	**35, 36**	54, 10
27	70	15.7	**37**	57
28	81	15.7	**38**	46
29	81	16.0	**39**	50
30	78	15.6	—	
31	72	15.8	—	
32	76	15.8	**40**	38
33	87	16.0	**41**	28
34	86	15.4	—	
42	52	14.4	**44, 45**	23, 9
43	58	14.5	**46**	80
49	76	16.4	**51**	90
50	92	15.9	**52**	62
53	76	15.6	**55**	11
54	78	17.4	**56, 57, 58**	41, 5, 3
60	86	15.3	**61**	55
63	72	17.2	**64**	52
66	80	15.7	**69**[b]	45
67	83	16.0	**70**[b]	51
68	96	16.8	**71**[c]	90
			72, **73**[d]	22, 5
80	42	17.5	**82**[c]	54
81	71	17.9	**83**[b]	60
85	73	15.3	**86**	28
88	67	15.9	—	
89	73	15.1	**91**, **92**	33, 11
90	55	15.2	**93**	28
94	32	14.6	**95**	18

[a]at 700 °C. [b]at 800 °C. [c]at 750 °C. [d]from **71** at 800 °C.

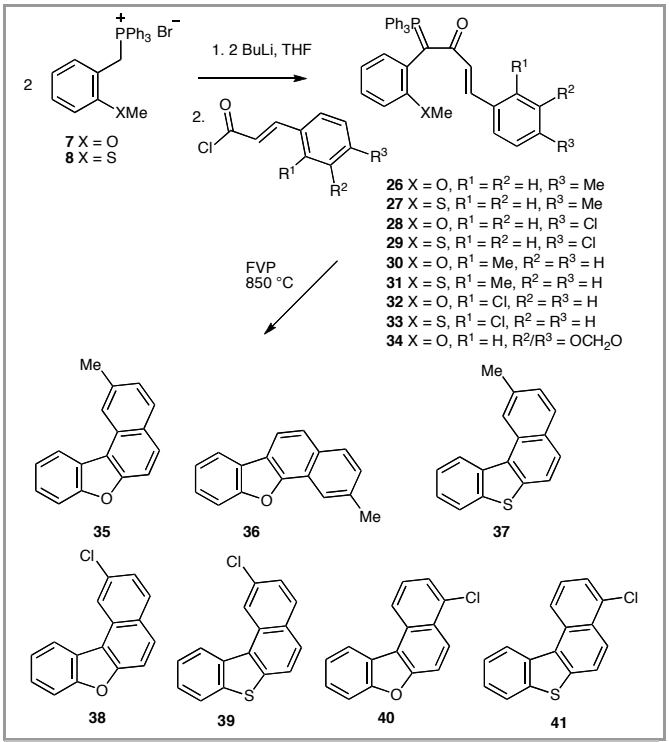


Scheme 4 Synthesis and pyrolysis of ylides **19**–**22**

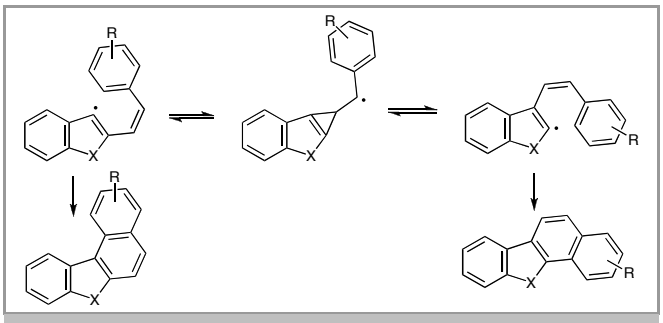
We next examined the series of four isomeric ylides **19**–**22** in which the furyl and thienyl groups are attached by position 3 rather than 2. While these were readily prepared in high yield (Scheme 4, Table 1) and characterised, their pyrolysis did not give such satisfactory results. In all cases there was extensive decomposition with complex mixtures of products being formed. From the two 3-thienyl ylides **20** and **22** impure samples of the expected [3,4-*a*]-fused heterocyclic products **23** and **24** were obtained but these contained various isomeric products including probably the [2,3-*a*] fused compounds resulting from cyclisation to the 2- rather than 4-position of the heterocyclic rings. From FVP of the 3-furyl compounds **19** and **21** at 850 °C no useful products could be obtained, but the expected enyne **25** was obtained in moderate yield as a mixture of *E* and *Z*-isomers from **19** at 700 °C suggesting that it is perhaps decomposition of the expected products rather than failure of the desired extrusion that is responsible for the poor results in these cases.

We then examined the ability to place substituents on the benzene ring which undergoes the final homolytic substitution by using substituted cinnamoyl chlorides and, by starting with either salt **7** or **8**, the nine ylides **26**–**34** were obtained (Scheme 5 , Table 1)**.**

The four *para*-substituted ylides **26**–**29** each gave the expected tetracyclic products **35** and **37**–**39** with the substituent at the 2-position, with only the methylnaphthobenzothiophene compound **37**[10] being previously known (Scheme 5, Table 1). However **35** was obtained as a mixture with a second isomer, presumed to be the 2-methylbenzo[*b*]naphtho[2,1-*d*]furan **36**. This is consistent with the behaviour of the closely related compound **1** which was found in our previous studies[4] to give the isomeric benzo[*b*]naphtho[2,1-*d*]furan (14%) in addition to the main product benzo[*b*]naphtho[1,2-*d*]furan **4** (44%). The



Scheme 5 Synthesis and pyrolysis of ylides **26**–**34**

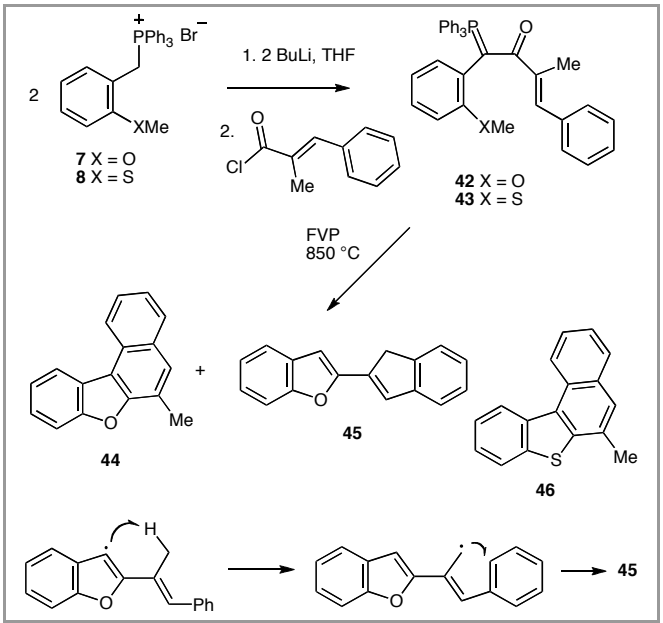


Scheme 6 Isomerisation process leading to **35** and **36**

proposed mechanism for formation of the isomeric byproduct involves a stable aryl(cyclopropyl)methyl radical (Scheme 6) and it is likely that small amounts of such isomeric products are formed in many of these pyrolyses but they are usually removed in purification of the main product.

The series of four *ortho*-substituted cinnamoyl ylides **30**–**33** were examined to determine whether, at the final cyclisation stage, the substituent would direct reaction to the other *ortho* position or itself be substituted to give the parent tetracycles. In the event, the chlorinated compounds **32** and **33** followed exclusively the former option to give, respectively, the previously unknown 4-substituted products **40** and **41** (Scheme 5, Table 1). The *ortho*-methylated compounds **30** and **31** however underwent extensive decomposition to give no useful products, showing another somewhat unexpected limitation of the present method. The methylenedioxy ylide **34** also gave a complex outcome upon pyrolysis with no products isolated in pure form consistent with the known[11] thermal lability of this function. The main recognisable products present were the expected 2,3-methylenedioxybenzo[*b*]naphtho[1,2-*d*]furan (<10%) as well as the products expected from breakdown of the methylebnedioxy function: 1-hydroxybenzo[*b*]naphtho[1,2-*d*]furan (5%) and 1-hydroxybenzo[*b*]naphtho[2,1-*d*]furan (5%).

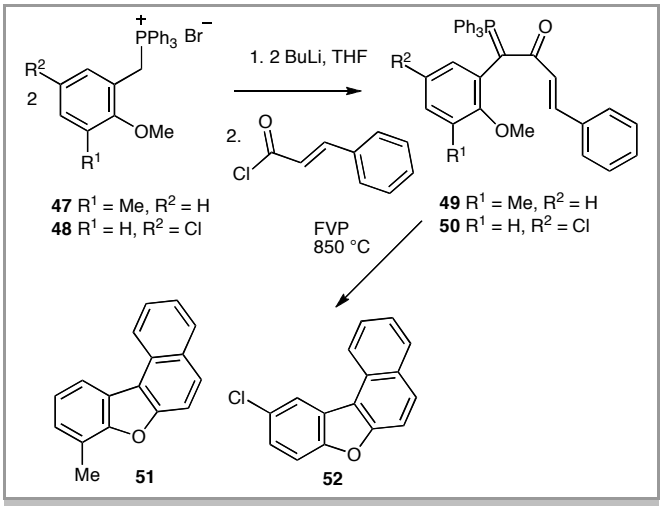
Methyl substitution on the alkene double bond of the cinnamoyl component led to the ylides **42** and **43** and when these were



Scheme 7 Synthesis and pyrolysis of ylides **42** and **43** and formation of **45**

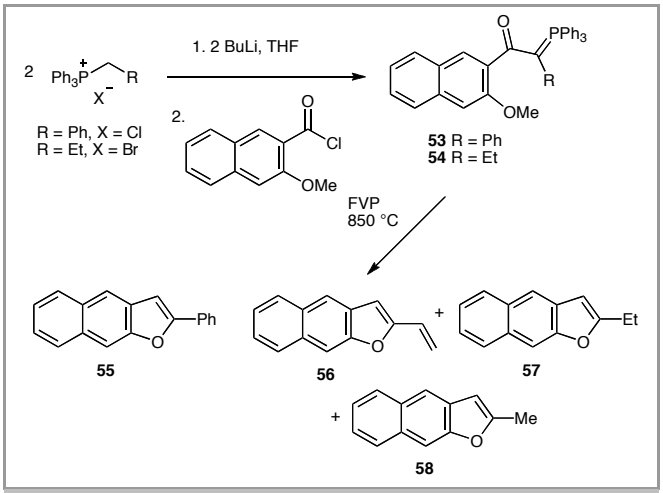
pyrolysed the expected 6-methyl tetracycles **44** and **46**[10] were formed, the latter in high yield (Scheme 7, Table 1). In the case of the furan compound **44**, the yield was low and it was accompanied by the 2-(inden-2-yl)benzofuran **45** formed, as shown, by intramolecular abstraction of a hydrogen atom.

To investigate the possibility of substitution on the methoxy-bearing ring, the new phosphonium salts **47** and **48** were prepared by treatment of the appropriate methoxybenzyl alcohols,[12,13] with PBr_3 followed by Ph_3P. These were then used to obtain the acyl ylides **49** and **50** (Scheme 8, Table 1), which in turn underwent clean pyrolytic conversion into the previously unknown 8- and 10-substituted tetracycles **51** and **52**.



Scheme 8 Synthesis and pyrolysis of ylides **49** and **50**

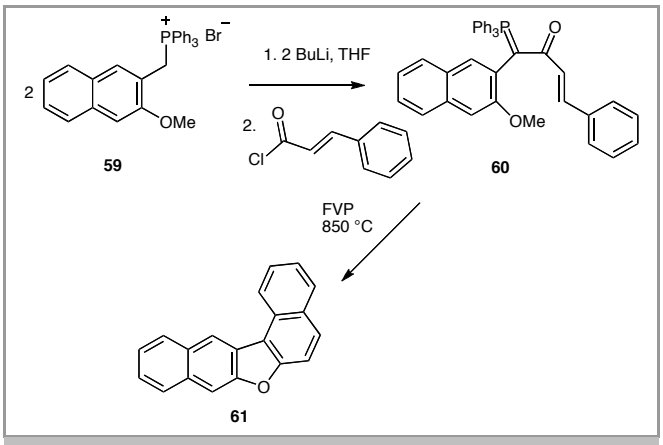
Having thus explored each of the main substitution possibilities for tetracyclic products as summarised in Scheme 2, we were interested to extend the method to pentacyclic products by incorporating a naphthyl fragment. Since the domino cyclisation process of stabilised ylides had not been demonstrated before with naphthalene containing systems, we first confirmed that the cyclisation would proceed as expected by preparing the simple model ylides **53** and **54** (Scheme 9, Table 1). As expected from our previous studies,[3] these did react cleanly at 850 °C to give naphthofurans with **53** giving the 2-phenyl product **55**[14] and **54** giving mainly the vinyl product **56** accompanied by



Scheme 9 Synthesis and pyrolysis of ylides **53** and **54**

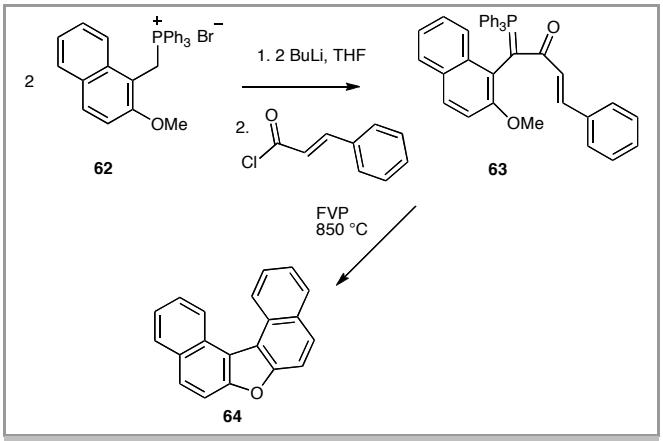
smaller amounts of **57** and **58**[14] (Scheme 9, Table 1).

For domino cyclisations, the two methoxynaphthyl phosphonium salts **59** and **62** were prepared starting from the appropriate methoxynaphthylmethanols,[15,16] by reaction with PBr_3 followed by Ph_3P. These were then converted respectively into ylides **60** and **63** (Schemes 10, 11, Table 1).



Scheme 10 Synthesis and pyrolysis of ylide **60**

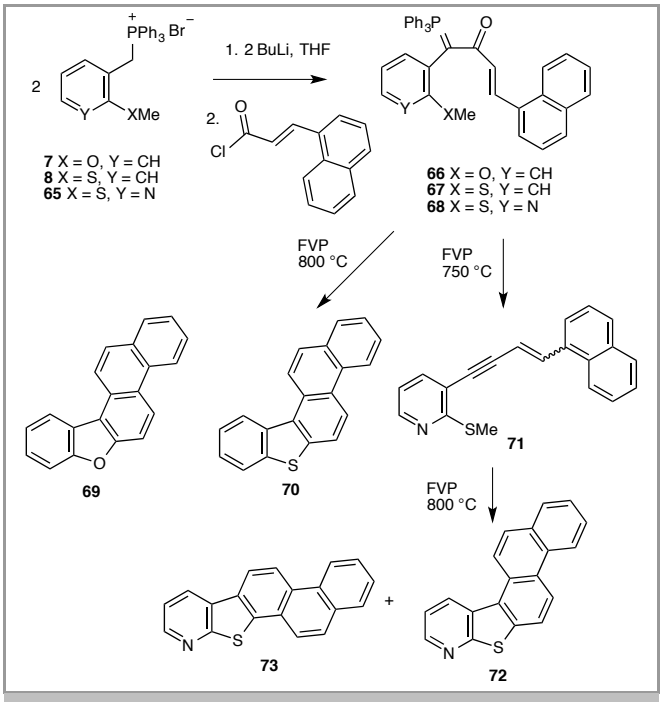
Upon pyrolysis these gave the isomeric dinaphthofurans **61**[17] and **64**[18], both known compounds, in moderate yield.



Scheme 11 Synthesis and pyrolysis of ylide **63**

Access to differently configured pentacyclic products could be gained by preparing acyl ylides with a naphthylpropenoyl rather than cinnamoyl group. In this way compounds **66** and **67** were prepared starting from the salts **7** and **8** and we also give here full details of the methylthiopyridine analogue **68** formed from the salt **65** and described briefly in our earlier communication[6] (Scheme 12, Table 1). The pyridyl salt **65** was formed in turn from 3-hydroxymethyl-2-methylthiopyridine[19] by the usual treatment with PBr_3 followed by Ph_3P.

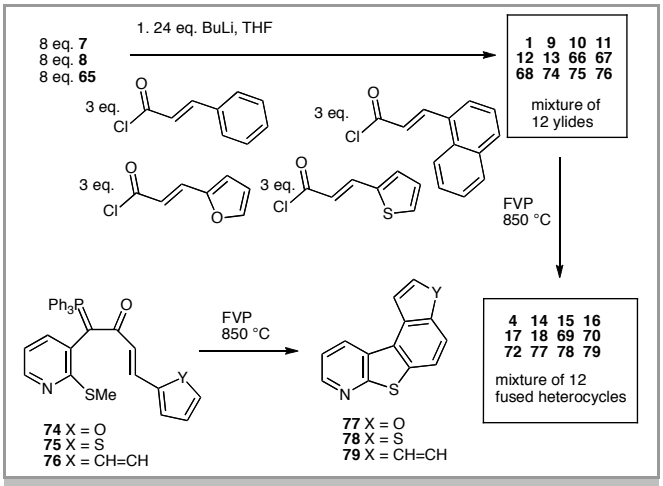
Upon pyrolysis, ylides **66** and **67** afforded the known pentacyclic products **69**[17] and **70**[20,21] with a lower temperature of 800 °C being optimal. In the case of the pyridyl ylide **68**, pyrolysis at 800 °C and above did not give clean products. The most effective procedure was found to be pyrolysis at 750 °C which led to extrusion of only Ph_3PO to give the enyne **71** (90%) as a 6:4 mixture of *E* and *Z* isomers, and then re-pyrolysis of this at 800 °C to give mainly the expected phenanthrothienopyridine



Scheme 12 Synthesis and pyrolysis of ylides **66**–**68**

72 (22%), accompanied by the isomer **73** (5%) formed by the process of Scheme 6 (Scheme 12, Table 1).

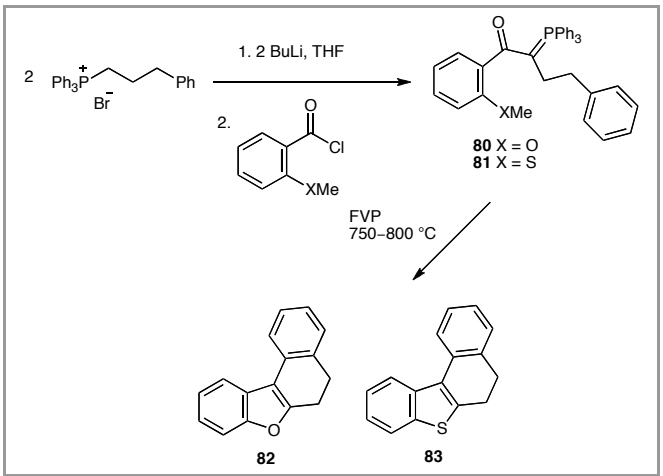
Although, as illustrated by the last examples, the conditions for optimum pyrolytic cyclisation vary slightly, both this stage and the preceeding ylide preparation uses much the same conditions regardless of the groups present and this led us to the idea of combinatorial synthesis[22] of a small library of ylides which could be pyrolysed together to directly afford a library of polycylic heteroaromatic products. This was realised by reacting appropriate proportions of the three phosphonium salts **7**, **8** and **65** with butyllithium and then treating this mixture with four different arylpropenoyl chlorides (Scheme 13) to give a mixture of twelve acyl ylides as an orange resin. Although this had very complex spectra as expected, the ^{1}H NMR data did clearly show 12 separate OMe and SMe signals in approximately equal size. Direct pyrolysis of this material at 850 °C followed by short-column chromatography to remove Ph_3PO then afforded



Scheme 13 Combinatorial synthesis of ylides and their conversion into fused ring heterocycles

an oil which was shown by GCMS and HPLC to contain all twelve expected heterocyclic products as confirmed by comparison with the individually prepared authentic samples. The three pyridine-based ylides **74**–**76** not so far mentioned in this paper and their pyrolysis products **77**–**79** were described previously.[6]

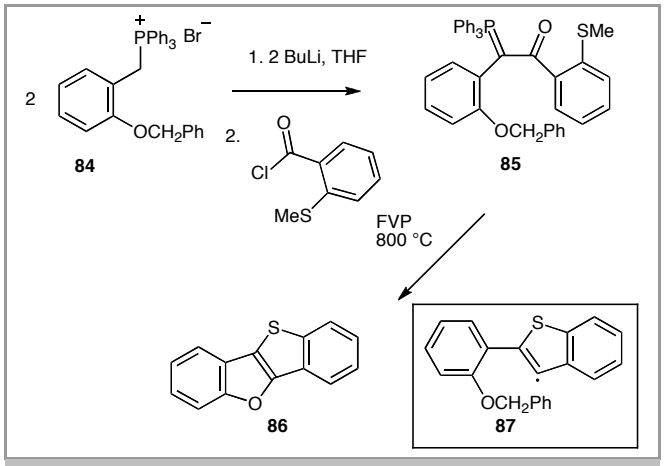
We were also interested to investigate formation of partly hydrogenated polycyclic heterocycles by this method and by starting from the 3-phenylpropylphosphonium salt the ylides **80** and **81** were prepared (Scheme 14, Table 1). Pyrolysis of these proceeded cleanly to give the 5,6-dihydro products **82**[23] and **83**[24] at optimal temperatures of 750 °C and 800 °C respectively.



Scheme 14 Synthesis and pyrolysis of ylides **80** and **81**

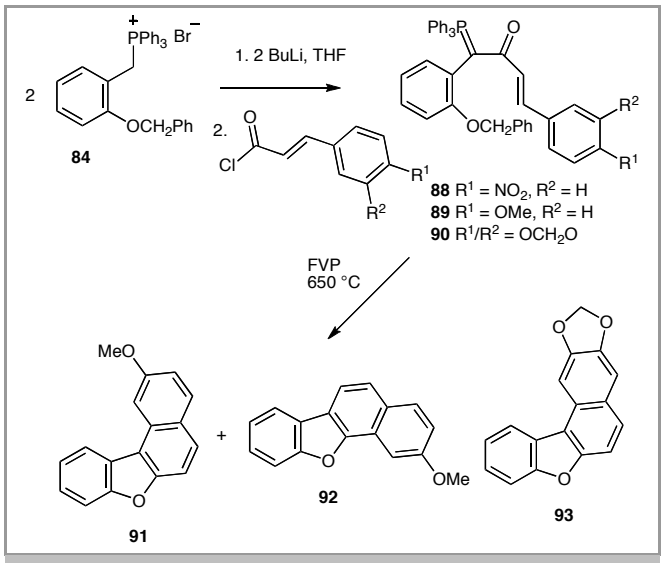
All the studies described so far have relied on loss of a methyl radical from OMe or SMe to initiate the cyclisation and this does require a relatively high temperature, which makes the method incompatible with certain thermally labile functional groups. We were interested to address this problem by using a more labile group and decided to test the effectiveness of *O*-benzyl as an initiating group. For this purpose we prepared the *O*-benzyl *S*-methyl ylide **85** starting from the benzyloxyphosphonium salt **84** and examined its pyrolysis (Scheme 15). In our previous work,[4] the *O,S*-dimethyl analogue of **85** was found to give a mixture of the tetracyclic product **86** and 2-phenylbenzothiophene, with these being the products resulting, respectively, from initial loss of *O*-methyl and *S*-methyl. This conclusion, supported by isotopic labelling, relies on the fact that the benzofuryl radical resulting from initial *O*-methyl loss cannot interact intramolecularly with the SMe group and instead undergoes cyclisation to **86** once the *S*-methyl is lost. In contrast the benzothienyl radical resulting from initial *S*-methyl loss abstracts a hydrogen atom intramolecularly from OMe setting in motion a rearrangement with loss of CO. Here the exclusive formation of **86** with no other products resulting from intramolecular interaction of the benzothienyl radical with *O*-benzyl in the intermediate **87** strongly suggests that, as hoped, the *O*-benzyl group is being lost more readily than *S*-methyl.

A range of acyl ylides **88**–**90** with both an *O*-benzyl group and a cinnamoyl function ready for domino cyclisation that contained a sensitive function were prepared starting from the phosphonium salt **84** (Scheme 16, Table 1). These underwent



Scheme 15 Synthesis and pyrolysis of ylide **85**

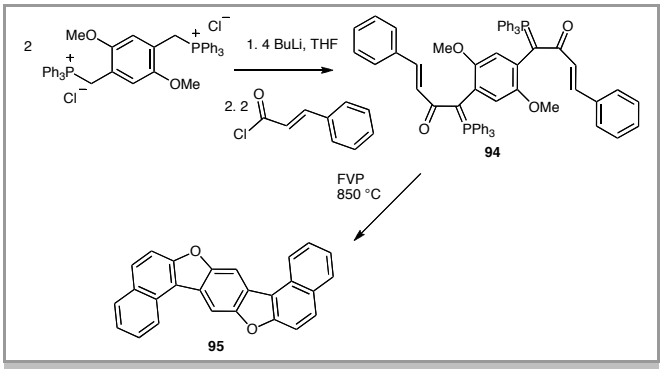
loss of Ph_3PO and cyclisation upon pyrolysis at a much lower temperature of 650 °C. Even under these conditions however the nitro group of **88** did not survive and a complex mixture of decomposition products resulted. In contrast the methoxycinnamoyl compound **89** behaved well and gave the previously unknown methoxynaphthobenzofuran **91** (Scheme 16, Table 1) accompanied by a smaller amount of the isomer **92** formed as in Scheme 6. The methylenedioxycinnamoyl ylide **90** also afforded a low yield of the pentacyclic product **93**.



Scheme 16 Synthesis and pyrolysis of ylides **88**–**90**

As a route to more extended polycyclic products, the application of this method to a bis(ylide) was explored in one case. Deprotonation and acylation of the known[25] bis(phosphonium salt) with cinnamoyl chloride gave the bis(ylide) **94** (Scheme 17, Table 1) and when this was pyrolysed at 850 °C the expected heptacyclic product **95** was formed in low yield accompanied by smaller amounts of at least two isomers. The identity of **95** was established by NMR comparison with an authentic sample prepared using the published route.[26]

In conclusion, we have developed a versatile route for the construction of fused-ring heterocyclic compounds by combined alkyne generation and domino cyclisation in a single gas-phase pyrolysis step from suitably designed carbonyl stabilised



Scheme 17 Synthesis and pyroysis of bis(ylide) **94**

phosphonium ylides. Although some limitations are apparent, the method allows construction of a wide range of fundamental but previously unknown heterocyclic products in moderate to high yield.

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^1H (300 MHz), ^{13}C (75 MHz) and ^{31}P NMR (121 MHz) spectra were recorded on a Varian Gemini 2000 instrument in $CDCl_3$ at 25 °C unless otherwise stated with internal TMS as reference for H and C and external H_3PO_4 as reference for P. IR spectra were recorded using a Perkin Elmer 1720 instrument. MS and HRMS measurements were made using EI ionization. Elemental analysis was carried out using a Carlo-Erba 1106 elemental analyser. Flash vacuum pyrolysis (FVP) was carried out in a conventional flow system by subliming the starting material through a horizontal quartz tube (30 × 2.5 cm) externally heated by a tube furnace at temperatures in the range 600–850 °C and maintained at a pressure of 2–9 × 10^{-2} Torr by a rotary vacuum pump. The apparatus used is illustrated and a step-by-step procedure given in a recent monograph.[27] Products were collected in a liquid N_2 cooled U-shaped trap and purified as noted.

The following compounds were prepared by literature methods as indicated: (2-methoxybenzyl)triphenylphosphonium bromide **7**,[28] 3-(2-thienyl)propenoyl chloride,[29] 3-(2-furyl)propenoyl chloride,[30] 3-(3-furyl)propenoyl chloride,[31] 3-(3,4-methylenedioxyphenyl)propenoyl chloride,[32] 3-(4-chlorophenyl)propenoyl chloride,[33] 2-methyl-3-phenylpropenoyl chloride,[34] 3-(2-methylphenyl)propenoyl chloride,[35] 3-(2-chlorophenyl)propenoyl chloride,[36] 3-methoxy-2-naphthoyl chloride,[37] 3-(1-naphthyl)propenoyl chloride,[38] (3-phenylpropyl)triphenylphosphonium bromide,[39] 2-methoxybenzoyl chloride,[40] 3-(4-methoxyphenyl)propenoyl chloride.[41]

3-(3-Thienyl)propenoyl chloride

A mixture of 3-(3-thienyl)propenoic acid[42] (4.63 g, 30 mmol) and oxalyl chloride (5.23 mL, 60 mmol) was heated under reflux for 30 min. The oxalyl chloride was removed under reduced pressure and the residue kugelrohr distilled to give the product (5.40g, 96%) as colourless prisms, mp 83–85 °C.

IR: 1608, 1507, 1245, 1206, 1169, 1099, 970, 879, 854, 790, 718, 665, 628 cm^{-1}.

^1H NMR (300 MHz): δ = 7.81 (d, *J* = 16 Hz, 1 H, vinyl-H), 7.68 (d, *J* = 2 Hz, 1 H, 2-H), 7.38 (dd, *J* = 5, 2 Hz, 1 H, 4-H), 7.30 (d, *J* = 5 Hz, 1 H, 5-H), 6.44 (d, *J* = 16 Hz, 1 H, vinyl-H).

^{13}C NMR (75 MHz): δ = 166.4 (C=O), 144.1 (vinyl), 136.6 (C-3), 132.0, 128.0, 125.4, 121.9 (vinyl).

MS (EI): *m/z* (%) = 174 (13) [^{37}Cl-M$^+$], 172 (31) [^{35}Cl-M$^+$], 137 (100), 109 (67), 81 (5), 65 (27).

Anal. Calcd for C_7H_5ClOS: C, 48.70; H, 2.92. Found: C, 48.85; H, 2.80.

(2-Methylthiobenzyl)triphenylphosphonium bromide 8

A solution of 2-methylthiobenzyl alcohol[43] (17.5 g, 113 mmol) and phosphorus tribromide (4.19 mL, 11.95 g, 44 mmol) in toluene (200 mL) was stirred at room temperature for 18 h. The reaction mixture was

added to water (500 mL), and the organic layer separated, washed with water and dried. The solution of the bromide was then heated under reflux with triphenylphosphine (29.57 g, 113 mmol) for 12 h. The resulting white precipitate was filtered off, washed with diethyl ether and dried at 100 ˚C to give the product (49.53 g, 91%) as colourless crystals, mp 232–234 ˚C.

IR: 1584, 1152, 1105, 994, 832, 779, 753, 690 cm^{-1}.

^1H NMR (300 MHz): δ = 7.80–7.65 (m, 3 H), 7.65–7.45 (m, 12 H), 7.35–7.15 (m, 2 H), 7.12–6.90 (m, 2 H), 5.32 (d, *J* = 13 Hz, 2 H, CH_2), 2.00 (s, 3 H, SMe).

^{13}C NMR (75 MHz): δ = 140.3 (d, *J* = 6 Hz, C-2), 135.4 (d, *J* = 3 Hz, C-4 of PPh), 134.6 (d, *J* = 10 Hz, C-2 of PPh), 131.9 (d, *J* = 5 Hz, C-6), 130.4 (d, *J* = 12 Hz, C-3 of PPh), 129.8 (d, *J* = 4 Hz), 129.0 (d, *J* = 3 Hz), 127.1 (d, *J* = 9 Hz, C-1), 126.9 (d, *J* = 4 Hz), 117.8 (d, *J* = 86 Hz, C-1 of PPh), 29.2 (d, *J* = 48 Hz, CH_2), 17.4 (SMe).

^{31}P NMR (121 MHz): δ = +22.7.

Anal. Calcd for $C_{26}H_{24}BrPS$: C, 65.14; H, 5.05. Found: C, 65.15; H, 4.98.

Preparation of Ylides

[(3-(2-Furyl)propenoyl)(2-methoxyphenyl)methylene]triphenylphosphorane 9

A suspension of (2-methoxybenzyl)triphenylphosphonium bromide **8** (10 g, 21.5 mmol) in dry THF (70 mL) was stirred under N_2 while a solution of butyllithium in hexanes (8.6 mL, 2.5 M, 21.5 mmol) was added. The resulting deep red solution was stirred for a further 2 h before adding a solution of 3-(2-furyl)propenoyl chloride (1.67 g, 10.7 mmol) in dry THF (5 mL). After stirring for a further 18 h the mixture was added to water (100 mL) and extracted with diethyl ether (2 × 100 mL) and ethyl acetate (2 × 100 mL). The combined extracts were washed with water (100 mL), dried and evaporated to give a yellow solid, which was recrystallised from ethyl acetate to give the product (3.55 g, 67%) as yellow crystals, mp 248–249 ˚C.

IR: 1635, 1558, 1240, 1158, 959, 748, 692 cm^{-1}.

^1H NMR (300 MHz): δ = 7.70–7.61 (m, 6 H, Ph), 7.46–7.24 (m, 10 H, Ph and Ar-H), 7.21 (m, 2 H, m), 7.40 (t, *J* = 9 Hz, 1 H, Ar-H), 6.83 (d, *J* = 9 Hz, 1 H, Ar-H), 6.68 (d, *J* = 14 Hz, 1 H, vinyl-H), 6.41 (d, *J* = 8 Hz, 1 H), 6.25 (m, 2 H), 3.23 (s, 3 H, OMe).

^{13}C NMR (75 MHz): δ = 179.3 (d, *J* = 6 Hz, CO), 158.9 (d, *J* = 3 Hz, C-2), 153.7 (C), 142.6 (CH), 137.4 (d, *J* = 5 Hz), 133.9 (d, *J* = 9 Hz, C-2 of PPh), 131.4 (d, *J* = 2 Hz, C-4 of PPh), 128.3 (d, *J* = 12 Hz, C-3 of PPh), 128.1 (d, *J* = 2 Hz, CH), 127.3 (d, *J* = 90 Hz, C-1 of PPh), 126.5 (d, *J* = 10 Hz, C-1), 124.8 (d, *J* = 12 Hz, CO-CH=), 121.9 (CH), 120.4 (CH), 111.7 (CH), 110.8 (CH), 110.1 (CH), 70.6 (d, *J* = 112 Hz, P=C), 54.3 (OMe).

^{31}P NMR (121 MHz): δ = +15.6.

MS (EI): *m/z* (%) = 502 (23) $[M^+]$, 471 (52), 367 (17), 277 (8), 262 (47), 49 (100).

Anal. Calcd for $C_{33}H_{27}O_3P$: C, 78.87; H, 5.42. Found: 78.89; H, 5.34.

[(2-Methoxyphenyl)(3-(2-thienyl)propenoyl)methylene]triphenylphosphorane 10

This was prepared as for **9** using (2-methoxybenzyl)triphenylphosphonium bromide **7** (10 g, 21.5 mmol), butyllithium in hexanes (8.6 mL, 2.5 M, 21.5 mmol) and 3-(2-thienyl)propenoyl chloride (1.86 g, 10.7 mmol) to give the product (3.54 g, 64%) as bright yellow crystals, mp 236–238 ˚C.

IR: 1622, 1505, 1377, 1340, 1198, 1123, 1103, 1048, 1025, 963, 836, 746, 658 cm^{-1}.

^1H NMR (300 MHz): δ = 7.74–7.54 (m, 6 H, Ph), 7.52–7.25 (m, 11 H, Ph and Ar-H), 7.16–6.76 (m, 5 H), 6.69 (d, *J* = 16 Hz, 1 H, vinyl-H), 6.42 (d, *J* = 8 Hz, 1 H, 3-H), 3.23 (s, 3 H, OMe).

^{13}C NMR (75 MHz): δ = 179.2 (d, *J* = 5 Hz, CO), 158.9 (C), 142.9 (CH), 137.3 (d, *J* = 5 Hz), 133.8 (d, *J* = 10 Hz, C-2 of PPh), 131.6 (d, *J* = 2 Hz, C-4 of PPh), 128.4 (d, *J* = 12 Hz, C-3 of PPh), 128.2 (CH), 127.7 (CH), 127.6 (CH), 127.2 (d, *J* = 90 Hz, C-1 of PPh), 127.2 (CH), 126.2 (br d, *J* = 11 Hz, C-1 and CO-CH=), 125.2 (CH), 120.3 (CH), 110.1 (CH), 70.4 (d, *J* = 113 Hz, P=C), 54.3 (OMe).

^{31}P NMR (121 MHz): δ = +15.6.

MS (EI): *m/z* (%) = 518 (20) $[M^+]$, 487 (46), 461 (24), 367 (15), 279 (22), 262 (75), 241 (10), 213 (11), 183 (57), 167 (30), 149 (80), 105 39), 83 (44) 71 (59), 57 (100).

Anal. Calcd for $C_{33}H_{27}O_2PS$: 76.43; H, 5.25. Found: C, 76.51; H, 5.21.

[(3-(2-Furyl)propenoyl)(2-methylthiophenyl)methylene]triphenylphosphorane 11

This was prepared as for **9** using (2-methylthiobenzyl)triphenylphosphonium bromide **8** (10 g, 20.8 mmol), butyllithium in hexanes (8.3 mL, 2.5 M, 20.8 mmol) and 3-(2-furyl)propenoyl chloride (1.62 g, 10.4 mmol) to give the product (1.61 g, 30%) as orange crystals, mp 263–264 ˚C.

IR: 1635, 1557, 1496, 1261, 1181, 1158, 1106, 1050, 1015, 960, 933, 815, 749, 724, 692, 595 cm^{-1}.

^1H NMR (300 MHz): δ = 7.84–7.54 (m, 6 H, Ph), 7.52–7.28 (m, 9 H, Ph), 7.28–7.20 (m, 2 H), 7.14–6.76 (m, 2 H), 6.92–6.74 (m, 2 H), 6.55 (d, *J* = 15 Hz, 1 H), 6.29 (s, 2 H), 2.20 (s, 3 H, SMe).

^{13}C NMR (75 MHz): δ = 180.1 (d, *J* = 5 Hz, CO), 153.6 (C), 145.3 (d, *J* = 5 Hz, C-2), 142.6 (CH), 136.3 (d, *J* = 4 Hz), 134.9 (d, *J* = 11 Hz, C-1), 134.0 (d, *J* = 10 Hz, C-2 of PPh), 131.6 (d, *J* = 2 Hz, C-4 of PPh), 128.4 (d, *J* = 12 Hz, C-3 of PPh), 127.5 (CH), 126.9 (d, *J* = 90 Hz, C-1 of PPh), 124.7 (d, *J* = 13 Hz, CO-CH=), 123.6 (CH), 123.0 (CH), 122.4 (CH), 111.7 (CH), 111.2 (CH), 71.9 (d, *J* = 110 Hz, P=C), 15.3 (SMe).

^{31}P NMR (121 MHz): δ = +15.8.

MS (EI): *m/z* (%) = 518 (58) $[M]^+$, 503 (18), 471 (100), 383 (5), 368 (27), 342 (5), 303 (4), 277 (6), 262 (37), 235 (12), 197 (11), 183 (35), 84 (31).

Anal. Calcd for $C_{33}H_{27}O_2PS$: C, 76.43; H, 5.25. Found: C, 76.13; H, 5.01.

[(2-Methylthiophenyl)(3-(2-thienyl)propenoyl)methylene]triphenylphosphorane 12

This was prepared as for **9** using (2-methylthiobenzyl)triphenylphosphonium bromide **8** (10 g, 20.8 mmol), butyllithium in hexanes (8.3 mL, 2.5 M, 20.8 mmol) and 3-(2-thienyl)propenoyl chloride (1.79 g, 10.4 mmol) to give the product (3.26 g, 59%) as yellow crystals, mp 243–244 ˚C.

IR: 1624, 1508, 1430, 1345, 1270, 1235, 1205, 1104, 1090, 1030, 963, 760, 693 cm^{-1}

^1H NMR (300 MHz): δ = 7.90–7.52 (m, 6 H, Ph), 7.58 (d, *J* = 15 Hz, 1 H, vinyl-H), 7.52–7.28 (m, 9 H, Ph), 7.18–6.96 (m, 4 H), 6.94–6.74 (m, 3 H), 6.48 (d, *J* = 15 Hz, 1 H, vinyl-H), 2.20 (s, 3 H, SMe).

^{13}C NMR (75 MHz): δ = 180.0 (d, *J* = 5 Hz, CO), 145.2 (d, *J* = 5 Hz, C-2), 142.8 (C), 136.3 (d, *J* = 3 Hz), 134.9 (d, *J* = 11 Hz, C-1), 134.0 (d, *J* = 10 Hz, C-2 of PPh), 131.6 (d, *J* = 2 Hz, C-4 of PPh), 128.4 (d, *J* = 13 Hz, C-3 of PPh), 127.6 (2CH), 127.5 (2CH), 126.9 (d, *J* = 90 Hz, C-1 of PPh), 126.3 (d, *J* = 12 Hz, CO-CH=), 125.3 (CH), 123.5 (CH), 123.0 (CH), 71.8 (d, *J* = 109 Hz, P=C), 15.3 (SMe).

^{31}P NMR (121 MHz): δ = +15.8.

MS (EI): *m/z* (%) = 534 (6) $[M]^+$, 508 (8), 487 (18), 461 (10), 368 (9), 277 (37), 262 (19), 236 (13), 201 (9), 183 (21), 167 (31), 149 (81), 111 (25), 97 (43), 83 (53), 71 (67), 57 (100).

Anal. Calcd for $C_{33}H_{27}OPS_2$: C, 74.13; H, 5.09. Found: C, 74.31; H, 5.11.

[(2-Methylthiophenyl)(3-phenylpropenoyl)methylene]triphenylphosphorane 13

This was prepared as for **9** using (2-methylthiobenzyl)triphenylphosphonium bromide **8** (8.3 g, 17.3 mmol), butyllithium in hexanes (6.9 mL, 2.5 M, 17.3 mmol) and 3-phenylpropenoyl chloride (1.44 g, 8.64 mmol) to give the product (4.50 g, 98%) as bright yellow crystals, mp 244–245 ˚C.

IR: 1630, 1575, 1500, 1367, 1275, 1212, 1102, 981, 956, 751, 727, 693, 559 cm^{-1}.

^{1}H NMR (300 MHz): δ = 7.82–7.52 (m, 6 H, Ph), 7.51–7.28 (m, 11 H, Ph), 7.44 (d, *J* = 15 Hz, 1 H, vinyl-H), 7.24–7.14 (m, 3 H, Ph), 7.09 (t, *J* = 8 Hz, 1 H), 7.00 (d, *J* = 8 Hz, 1 H), 6.89 (d, *J* = 8 Hz, 1 H), 6.80 (t, *J* = 8 Hz, 1 H), 6.64 (d, *J* = 15 Hz, 1 H, vinyl-H), 2.22 (s, 3 H, SMe).

^{13}C NMR (75 MHz, CD_2Cl_2): δ = 180.2 (d, *J* = 5 Hz, CO), 145.8 (d, *J* = 6 Hz, C-2), 137.5 (C), 136.5 (d, *J* = 4 Hz), 135.2 (d, *J* = 11 Hz, C-1), 134.4 (CH), 134.3 (d, *J* = 9 Hz, C-2 of PPh), 131.9 (d, *J* = 2 Hz, C-4 of PPh), 128.9 (2CH), 128.7 (d, *J* = 12 Hz, C-3 of PPh), 128.5 (2CH), 127.9 (CH), 127.8 (CH), 127.5 (d, *J* = 90 Hz, C-1 of PPh), 127.1 (d, *J* = 12 Hz, CO-CH=), 123.7 (CH), 123.2 (CH), 71.9 (d, *J* = 110 Hz, P=C), 15.3 (SMe).

^{31}P NMR (121 MHz): δ = +15.1.

MS (EI): *m/z* (%) = 528 (18) [M$^+$], 513 (14), 481 (90), 368 (15), 277 (44), 262 (35), 183 (35), 132 (32), 84 (73), 69 (91), 49 (100).

Anal. Calcd for $C_{35}H_{29}OPS$: 79.52; H, 5.53. Found: C, 79.70; H, 5.51.

FVP of [(3-(2-furyl)propenoyl)(2-methoxyphenyl)methylene]triphenylphosphorane 9

FVP of the title compound (0.5 g) at 850 ˚C and 2.0–5.0 × 10^{-2} Torr gave a brown oily solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:1) as eluant gave an oil which was kugelrohr distilled at 115 ˚C/0.4 Torr to give the product, **furo[3,2-*a*]dibenzofuran 14** (0.12 g, 58%) as a pale yellow solid, mp 69–73 ˚C.

IR: 1422, 1239, 1196, 1079, 1044, 885, 840, 794, 750, 654 cm^{-1}.

^{1}H NMR (300 MHz): δ = 8.07 (d, *J* = 7 Hz, 1 H), 7.85 (d, *J* = 2 Hz, 1 H), 7.70–7.22 (m, 6 H).

^{13}C NMR (75 MHz): δ = 156.7 (C), 153.0 (C), 152.0 (C), 146.6 (CH), 126.8 (CH), 124.5 (C), 122.9 (CH), 121.4 (CH), 120.9 (C), 116.4 (C), 111.9 (CH), 110.4 (CH), 108.1 (CH), 105.5 (CH).

MS (EI): *m/z* (%) = 208 (100) [M$^+$], 179 (9), 152 (13), 104 (7), 76 (7).

Anal. Calcd for $C_{14}H_8O_2$: C, 80.76; H, 3.87. Found: C, 81.02; H, 3.72.

FVP of [(2-methoxyphenyl)(3-(2-thienyl)propenoyl)methylene]triphenylphosphorane 10

FVP of the title compound (1.05 g) at 850 ˚C and 2.0-5.0 × 10^{-2} Torr gave a brown oily solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:1) as eluant gave an oil which was kugelrohr distilled at 250 ˚C/18 Torr to give the product, **thieno[3,2-*a*]dibenzofuran 15** (0.30 g, 69%) as a pale brown solid, mp 56–59 ˚C.

IR: 1602, 1580, 1401, 1230, 1195, 1124, 1023, 867, 747 cm^{-1}.

^{1}H NMR (300 MHz): δ = 8.19 (d, *J* = 8 Hz, 1 H), 7.85–7.74 (m, 2 H), 7.70–7.20 (m, 5 H).

^{13}C NMR (75 MHz): δ = 155.9 (C), 154.2 (C), 135.1 (C), 133.3 (C), 128.8 (CH), 126.4 (CH), 124.1 (C), 122.9 (CH), 121.3 (CH), 121.2 (CH), 121.0 (CH), 117.9 (C), 111.9 (CH), 109.4 (CH).

MS (EI): *m/z* (%) = 224 (100) [M$^+$], 210 (13), 200 (44), 184 (48), 168 (70), 152 (50), 139 (34), 115 (17).

Anal. Calcd for $C_{14}H_8OS$: C, 74.97; H, 3.60. Found: C, 75.03; H, 3.82.

FVP of [(3-(2-furyl)propenoyl)(2-methylthiophenyl)methylene]triphenylphosphorane 11

FVP of the title compound (0.50 g) at 850 ˚C and 2.0–5.0 × 10^{-2} Torr gave a brown oily solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:1) as eluant gave an oil which was kugelrohr distilled at 180 ˚C/0.2 Torr to give the product, **furo[3,2-*a*]dibenzothiophene 16** (0.18 g, 83%) as a pale brown solid, mp 159.5–160 ˚C.

IR: 1590, 1524, 1406, 1344, 1248, 1146, 909, 777, 634 cm^{-1}.

^{1}H NMR (300 MHz): δ = 8.37 (d, *J* = 8 Hz, 1 H), 7.95 (d, *J* = 8 Hz, 1 H), 7.86 (d, *J* = 3 Hz, 1 H), 7.81–7.40 (m, 5 H).

^{13}C NMR (75 MHz): δ = 153.6 (C), 145.7 (CH), 140.4 (C), 135.9 (C), 134.3 (C), 126.8 (C), 126.1 (CH), 124.5 (CH), 123.3 (CH), 123.1 (CH), 122.3 (C), 118.5 (CH), 111.1 (CH), 105.1 (CH).

MS (EI): *m/z* (%) = 224 (100) [M$^+$], 212 (15), 197 (23), 184 (28), 178 (13), 165 (10), 152 (17), 139 (6), 112 (6),98 (6).

Anal. Calcd for $C_{14}H_8OS$: C, 74.97; H, 3.60. Found: C, 74.98; H, 3.47.

FVP of [(2-methylthiophenyl)(3-(2-thienyl)propenoyl)methylene]triphenylphosphorane 12

FVP of the title compound (1.05 g) at 850 ˚C and 2.0–5.0 × 10^{-2} Torr gave a brown oily solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:1) as eluant gave an oil which was kugelohr distilled at 200 ˚C/0.1 Torr to give the product, **thieno[3,2-*a*]dibenzothiophene 17** (0.30 g, 63%) as a pale brown solid, mp 149–150 ˚C (lit.,[8] 148–149 ˚C).

IR: 1157, 1085, 856, 778, 742, 690 cm^{-1}.

^{1}H NMR (300 MHz): δ = 8.56 (d, *J* = 8 Hz, 1 H), 8.23 (d, *J* = 7 Hz, 1 H), 8.10–7.00 (m, 6 H, m) [Good agreement with lit.[8]].

^{13}C NMR (75 MHz): δ = 139.7 (C), 137.7 (C), 136.6 (C), 135.9 (C), 134.8 (C), 129.7 (C), 127.8 (CH), 125.9 (CH), 124.7 (CH), 123.8 (CH), 123.1 (CH), 121.4 (CH), 121.1 (CH), 119.1 (CH).

MS (EI): *m/z* (%) = 240 (100) [M$^+$], 222 (11), 208 (22), 195 (25), 163 (8), 120 (122), 69 (6).

Anal. Calcd for $C_{14}H_8S_2$: C, 69.96; H, 3.36. Found: C, 70.04; H, 3.22.

FVP of (2-methylthiophenyl)(3-phenylpropenoyl)methylene]triphenylphosphorane 13

FVP of the title compound (1.0 g) at 850 ˚C and 7.0–9.0 × 10^{-2} Torr gave an oily brown solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a pale brown oil which solidified with time. The solid was kugelrohr distilled at 140 ˚C/0.01 Torr to give a pale brown waxy solid which was recrystallised from ethanol to give the product, **benzo[*b*]naphtho[1,2-*d*]thiophene 18** (0.38 g, 86%) as off-white crystals, mp 101–102.5 ˚C (lit.,[9] 104–105 ˚C).

^{1}H NMR (300 MHz): δ = 9.07 (d, *J* = 8 Hz, 1 H), 8.91 (d, *J* = 8 Hz, 1 H), 8.12–7.92 (m, 4 H), 7.76 (t, *J* = 8 Hz, 1 H), 7.65–7.46 (m, 3 H).

^{13}C NMR (75 MHz): δ = 139.9 (C), 138.8 (C), 136.9 (C), 132.1 (C), 130.8 (C), 129.6 (CH), 129.2 (C), 128.0 (CH), 127.3 (CH), 125.4 (CH), 125.1 (CH), 125.0 (CH), 124.9 (CH), 123.4 (2CH), 121.2 (CH) [Good agreement with lit.[9]].

[(3-(3-Furyl)propenoyl)(2-methoxyphenyl)methylene]triphenylphosphorane 19

This was prepared as for **9** using (2-methoxybenzyl)triphenylphosphonium bromide **7** (10 g, 21.5 mmol) in dry THF (70 mL), butyllithium in hexanes (8.6 mL, 2.5 M, 21.5 mmol) and 3-(3-furyl)propenoyl chloride (1.67 g, 10.7 mmol) to give the product (4.93 g, 92%) as bright yellow prisms, mp 234–236 ˚C.

IR: 1639, 1575, 1504, 1363, 1249, 1194, 1101, 1071, 1026, 999, 972, 947, 870, 845, 753, 627, 598 cm^{-1}.

^{1}H NMR (300 MHz): δ = 7.75–7.53 (m, 6 H, Ph), 7.48–7.28 (m, 12 H), 7.26 (m, 1 H), 7.06 (t, *J* = 8 Hz, 1 H), 6.82 (t, *J* = 8 Hz, 1 H), 6.58 (d, *J* = 16 Hz, 1 H, vinyl-H), 6.42 (d, *J* = 8 Hz, 1 H), 6.35 (d, *J* = 2 Hz, 1 H), 3.22 (s, 3 H, OMe).

^{13}C NMR (75 MHz): δ = 179.7 (d, *J* = 5 Hz, CO), 158.9 (C-2), 143.4 (CH), 142.5 (CH), 137.4 (d, *J* = 6 Hz), 133.8 (d, *J* = 10 Hz, C-2 of PPh), 131.4 (d, *J* = 2 Hz, C-4 of PPh), 128.3 (d, *J* = 12 Hz, C-3 of PPh), 128.0 (d, *J* = 2 Hz, CH), 127.3 (d, *J* = 91 Hz, C-1 of PPh), 126.6 (d, *J* = 11 Hz, C-1), 126.5 (d, *J* = 12 Hz, CO-CH=), 124.4 (C), 124.0 (CH), 120.3 (CH), 108.2 (CH), 110.1 (CH), 69.7 (d, *J* = 111 Hz, P=C), 54.3 (OMe).

^{31}P NMR (121 MHz): δ = +15.5.

MS (EI): *m/z* (%) = 502 (39) [M$^+$], 471, (68), 410 (7), 386 (8), 368 (15), 277 (18), 262 (75), 236 (10), 183 (35), 81 (49), 69 (100).

Anal. Calcd for $C_{33}H_{27}O_3P$: C, 78.87; H, 5.42. Found: C, 78.45; H, 5.48.

[(2-Methoxyphenyl)(3-(3-thienyl)propenoyl)methylene]triphenylphosphorane 20

This was prepared as for **9** using (2-methoxybenzyl)triphenylphosphonium bromide **7** (10 g, 21.5 mmol), butyllithium in hexanes (8.6 mL, 2.5 M, 21.5 mmol) and 3-(3-thienyl)propenoyl chloride (1.86 g, 10.7 mmol) to give a bright yellow solid which was recrystallised from ethyl acetate to give the product (4.73 g, 85%) as bright orange prisms, mp 219–220 ˚C.

IR: 1628, 1495, 1436, 1208, 1196, 1110, 977, 865, 831, 777, 724, 694, 609 cm^{-1}.

^1H NMR (300 MHz): δ = 7.71–7.67 (m, 6 H), 7.48–7.30 (m, 12 H), 7.18–7.03 (m, 3 H), 6.81 (t, *J* = 7 Hz, 1 H), 6.69 (d, *J* = 16 Hz, 1 H, vinyl-H), 6.42 (d, *J* = 7 Hz, 1 H, 3'-H), 3.22 (s, 3 H, OMe).

^{13}C NMR (75 MHz): δ = 179.5 (d, *J* = 5 Hz, CO), 158.9 (d, *J* = 3 Hz, C-2), 140.2 (C), 137.4 (d, *J* = 6 Hz), 133.8 (d, *J* = 10 Hz, C-2 of PPh), 131.5 (d, *J* = 2 Hz, C-4 of PPh), 128.4 (CH), 128.3 (d, *J* = 12 Hz, C-3 of PPh), 128.2 (CH), 127.2 (d, *J* = 90 Hz, C-1 of PPh), 126.4 (d, *J* = 10 Hz, C-1), 126.4 (d, *J* = 12 Hz, CO-CH=), 125.9 (CH), 125.7 (CH), 124.3 (CH), 120.3 (CH), 110.1 (CH), 70.0 (d, *J* = 113 Hz, P=C), 54.3 (OMe).

^{31}P NMR (121 MHz): δ = +15.5.

MS (EI): *m/z* (%) = 518 (11) [M^+], 487 (24), 368 (7), 277 (62), 262 (42), 236 (8), 201 (14), 183 (32), 167 (8), 149 (15), 97 (30), 84 (100).

Anal. Calcd for $C_{33}H_{27}O_2PS$: C, 76.43; H, 5.25. Found: C, 76.15; H, 5.25.

[(3-(3-Furyl)propenoyl)(2-methylthiophenyl)methylene]triphenylphosphorane 21

This was prepared as for **9** using (2-methylthiobenzyl)triphenylphosphonium bromide **8** (10 g, 20.8 mmol), butyllithium in hexanes (8.3 mL, 2.5 M, 20.8 mmol) and 3-(3-furyl)propenoyl chloride (1.62 g, 10.4 mmol) to give an orange solid which was extracted into THF using a soxhlet apparatus. The yellow-orange material collected in the receiver flask was then recrystallised from ethyl acetate–dichloromethane (1:1) to give the product (3.67 g, 67%) as bright yellow-orange prisms, mp 275–276 ˚C.

IR: 1819, 1650, 1566, 1515, 1365, 1262, 1225, 1189, 1156, 1102, 1072, 973, 872, 789, 621, 594 cm^{-1}.

^1H NMR (300 MHz): δ = 7.80–7.50 (m, 6 H), 7.50–7.27 (m, 10 H), 7.31 (d, *J* = 16 Hz, 1 H, vinyl-H), 7.24 (m, 1 H), 7.07 (t, *J* = 8 Hz, 1 H), 6.98 (d, *J* = 8 Hz, 1 H), 6.87 (d, *J* = 8 Hz, 1 H), 6.78 (t, *J* = 8 Hz, 1 H), 6.36 (d, *J* = 16 Hz, 1 H, vinyl-H), 6.32 (d, *J* = 2 Hz, 1 H), 2.20 (s, 3 H, SMe).

^{13}C NMR (75 MHz): δ = 180.5 (d, *J* = 5 Hz, CO), 145.3 (d, *J* = 4 Hz, C-2), 143.4 (CH), 142.7 (CH), 136.4 (d, *J* = 3 Hz), 135.1 (d, *J* = 11 Hz, C-1), 134.0 (d, *J* = 10 Hz, C-2 of PPh), 131.6 (d, *J* = 2 Hz, C-4 of PPh), 128.4 (d, *J* = 12 Hz, C-3 of PPh), 127.5 (d, *J* = 2 Hz, CH), 127.0 (d, *J* = 91 Hz, C-1 of PPh), 126.5 (d, *J* = 13 Hz, CO-CH=), 124.5 (CH), 124.4 (C), 123.5 (CH), 122.9 (CH), 108.3 (CH), 71.1 (d, *J* = 110 Hz, P=C), 15.3 (SMe).

^{31}P NMR (121 MHz): δ = +15.8.

MS (EI): *m/z* (%) = 518 (5) [M^+], 503 (2), 471 (14), 368 (28), 256 (12), 236 (10), 142 (29), 114 (70), 81 (50), 72 (66), 69 (100).

Anal. Calcd for $C_{33}H_{27}O_2PS$: C, 76.43; H, 5.25. Found: C, 75.97; H, 5.08.

[(2-Methylthiophenyl)(3-(3-thienyl)propenoyl)methylene]triphenylphosphorane 22

This was prepared as for **9** using (2-methylthiobenzyl)triphenylphosphonium bromide **8** (10 g, 20.8 mmol), butyllithium in hexanes (8.3 mL, 2.5 M, 20.8 mmol) and 3-(3-thienyl)propenoyl chloride (1.79 g, 10.4 mmol) to give the product (4.50 g, 81%) as bright orange prisms, mp 256–258 ˚C.

IR: 1636, 1511, 1436, 1356, 1268, 1206, 1105, 1074, 972, 834, 782, 753, 699, 606 cm^{-1}.

^1H NMR (300 MHz): δ = 7.82–7.50 (m, 6 H), 7.50–7.28 (m, 11 H), 7.19–6.97 (m, 4 H), 6.87 (d, *J* = 7 Hz, 1 H), 6.78 (t, *J* = 7 Hz, 1 H), 6.45 (d, *J* = 16 Hz, 1 H, vinyl-H), 2.20 (s, 3 H, SMe).

^{13}C NMR (75 MHz): δ = 180.5 (d, *J* = 5 Hz, CO), 145.3 (d, *J* = 5 Hz, C-2), 140.1 (C), 136.4 (d, *J* = 2 Hz), 135.0 (d, *J* = 11 Hz, C-1), 134.0 (d, *J* = 10 Hz, C-2 of PPh), 131.7 (d, *J* = 2 Hz, C-4 of PPh), 128.6 (CH), 128.4 (d, *J* = 12 Hz, C-3 of PPh), 127.5 (CH), 127.0 (d, *J* = 90 Hz, C-1 of PPh), 126.5 (d, *J* = 12 Hz, CO-CH=), 126.0 (CH), 125,6 (CH), 124.5 (CH), 123.5 (CH), 122.9 (CH), 71.5 (d, *J* = 108 Hz, P=C), 15.3 (SMe).

^{31}P NMR (121 MHz): δ = +15.7.

MS (EI): *m/z* (%) = 534 (11) [M^+] 519 (6), 487 (41), 386 (13), 368 (15), 277 (8), 262 (28), 236 (34), 208 (10), 183 (19), 111 (30), 97 (56), 83 (63), 69 (100).

Anal. Calcd for $C_{33}H_{27}OPS_2$: C, 74.13; H, 5.09. Found: C, 74.02; H, 4.93.

FVP of [(3-(3-furyl)propenoyl)(2-methoxyphenyl)methylene]triphenylphosphorane 19

FVP of the title compound (0.5 g) at 700 ˚C and 3.0–7.0 × 10^{-2} Torr gave a product from which two pure compounds were separable by column chromatography;

***Z*-1-(2-methoxyphenyl)4-(3-furyl)but-3-en-1-yne 25** (33 mg, 15%) as a yellow oil.

^1H NMR (300 MHz): δ = 8.18 (s, 1 H), 7.47–7.41 (m, 2 H), 7.35–7.25 (m, 2 H), 7.17 (d, *J* = 4 Hz, 1 H), 6.94 (t, *J* = 7 Hz, 1 H), 6.81 (d, *J* = 7 Hz, 1 H), 6.56 (d, *J* = 11 Hz, 1 H, vinyl-H), 5.82 (d, *J* = 11 Hz, 1 H, vinyl-H), 3.96 (s, 3 H, OMe).

^{13}C NMR (75 MHz): δ = 160.3 (2'-C), 143.6 (CH), 142.8 (CH), 133.3 (CH), 130.0 (CH), 129.2 (CH), 123.6 (C), 120.8 (CH), 113.0 (C), 110.8 (CH), 110.4 (CH), 106.8 (CH), 93.4 (C≡C), 92.7 (C≡C), 55.6 (OMe).

MS (EI): *m/z* (%) = 224 (17) [M^+], 209 (7), 195 (8), 181 (100), 165 (13), 152 (41), 126 (15), 76 (96), 63 (90).

HRMS (EI): *m/z* calcd for $C_{15}H_{12}O_2$ [M^+]: 224.0837; found: 224.0842.

***E*-1-(2-methoxyphenyl)4-(3-furyl)but-3-en-1-yne 25** (29 mg, 14%) as a yellow oil.

^1H NMR (300 MHz): δ = 7.50 (d, *J* = 2 Hz, 1 H), 7.94–7.77 (m, 2 H), 7.28 (t, *J* = 7 Hz, 1 H), 7.95–6.85 (m, 3 H), 6.57 (d, *J* = 2 Hz, 1 H), 6.30 (d, *J* = 16 Hz, 1 H, vinyl-H), 3.89 (s, 3 H, OMe).

^{13}C NMR (75 MHz): δ = 160.1 (2'-C), 144.1 (CH), 141.6 (CH), 133.6 (CH), 131.1 (CH), 129.8 (CH), 124.4 (C), 120.7 (CH), 112.9 (C), 111.8 (CH), 108.2 (CH), 107.2 (CH), 92.9 (C≡C), 87.5 (C≡C), 55.6 (OMe).

MS (EI): *m/z* (%) = 224 (32) [M^+], 209 (8), 195 (13), 181 (79), 165 (25), 152 (69), 126 (14), 82 (43), 76 (100), 63 (88).

FVP of [(2-methoxyphenyl)(3-(3-thienyl)propenoyl)methylene]triphenylphosphorane 20

FVP of the title compound (1.0 g) at 800 ˚C and 2.0–5.0 × 10^{-2} Torr gave an orange-brown oily solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a waxy orange solid which was kugelrohr distilled at 120 ˚C and 0.2 Torr to give a yellow waxy solid. ^1H NMR, ^{13}C NMR and GCMS analysis indicated a mixture of four isomeric products, presumably the expected thienodibenzofurans, including **thieno[3,4-*a*]dibenzofuran 23** (0.25 g, 60%).

^1H NMR (300 MHz): δ = 7.98 (dd, *J* = 7, 2 Hz, 1 H), 7.79 (d, *J* = 8 Hz, 1 H), 7.58 (dd, *J* = 7, 2 Hz, 1 H), 7.55 (d, *J* = 8 Hz, 1 H), 7.43 (td, *J* = 7, 2 Hz, 1 H), 7.40 (s, 2 H), 7.37 (td, *J* = 7, 2 Hz, 1 H).

^{13}C NMR (75 MHz): δ = 156.1 (C), 154.1 (C), 136.1 (C), 136.0 (C), 126.7 (CH), 124.5 (CH), 124.2 (CH), 123.6 (C), 123.1 (CH), 122.5 (CH), 121.5 (CH), 118.0 (C), 111.7 (CH), 109.4 (CH).

MS (EI): *m/z* (%) = 224 (100) [M^+], 195 (18), 169 (8), 152 (18), 126 (7), 112 (31), 98 (38), 86 (16), 76 (26), 63 (33).

FVP of [(2-methylthiophenyl)(3-(3-thienyl)propenoyl)methylene]triphenylphosphorane 22

FVP of the title compound (0.5 g) at 800 ˚C and 3.0–7.0 × 10^{-2} Torr gave an yellow-brown oily solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a waxy yellow solid which was kugelrohr distilled at 170 ˚C and 1.0 Torr to give a yellow waxy solid. ^1H NMR, ^{13}C NMR and GCMS analysis indicated a mixture of three isomeric products, presumably the expected

thienodibenzothiophenes, including **thieno[3,4-*a*]dibenzothiophene 24** (0.16 g, 36%).

^{1}H NMR (300 MHz): δ = 8.46 (d, *J* = 7 Hz, 1 H), 7.98 (d, *J* = 7 Hz, 1 H), 7.94 (d, *J* = 7 Hz, 1 H), 7.86 (d, *J* = 7 Hz, 1 H), 7.64 (td, *J* = 7, 2 Hz, 1 H), 7.54 (s, 2 H), 7.53 (td, *J* = 7, 2 Hz, 1 H).

^{13}C NMR (75 MHz): δ = 139.9 (C), 137.7 (C), 136.5 (C), 135.0 (C), 134.1 (C), 129.4 (C), 126.2 (CH), 124.8 (CH), 124.4 (CH), 124.2 (CH), 123.9 (CH), 122.9 (CH), 122.4 (CH), 119.2 (CH).

MS (EI): *m/z* (%) = 240 (100) [M$^+$], 208 (17), 195 (22), 169(8), 153 (10), 150 (9), 120 (53), 107 (20), 98 (35), 69 (50).

[(2-Methoxyphenyl)(3-(4-methylphenyl)propenoyl)methylene]triphenylphosphorane 26

This was prepared as for **9** using (2-methoxybenzyl)triphenylphosphonium bromide **7** (8.00 g, 17 mmol), butyllithium in hexanes (6.9 mL, 2.5 M, 17 mmol) and 3-(4-methylphenyl)propenoyl chloride (1.56 g, 9 mmol) to give the product (3.05 g, 67%) as yellow crystals, mp 214–216.5 ˚C.

IR: 1628, 1494, 1241, 1106, 1049, 1025, 982, 948, 812, 750, 691 cm^{-1}.

^{1}H NMR (300 MHz): δ = 7.80–7.53 (m, 6 H, Ph), 7.55–7.29 (m, 11 H), 7.24 (d, *J* = 8 Hz, 2 H), 7.10 (t, *J* = 8 Hz, 1 H), 7.02 (d, *J* = 8 Hz, 2 H), 6.83 (t, *J* = 8 Hz, 1 H), 6.82 (d, *J* = 15 Hz, 1 H, vinyl-H), 6.43 (d, *J* = 8 Hz, 1 H, 3-H), 3.23 (s, 3 H, OMe), 2.28 (s, 3 H, ArMe).

^{13}C NMR (75 MHz): δ = 179.8 (CO), 158.9 (d, *J* = 3 Hz, C-2), 137.9 (C), 137.4 (d, *J* = 6 Hz, CH), 134.5 (C), 134.2 (CH), 133.8 (d, *J* = 9 Hz, C-2 of PPh), 131.4 (d, *J* = 2 Hz, C-4 of PPh), 129.2 (2CH), 128.3 (d, *J* = 12 Hz, C-3 of PPh), 128.1 (CH), 127.7 (2CH), 127.3 (d, *J* = 91 Hz, C-1 of PPh), 126.6 (d, *J* = 13 Hz, C-1), 125.6 (d, *J* = 12 Hz, =CH-), 120.3 (CH), 110.1 (C-3), 70.4 (d, *J* = 110 Hz, P=C), 54.3 (OMe), 21.3 (Me).

^{31}P NMR (121 MHz): δ = +15.5.

MS (EI): *m/z* (%) = 526 (36) [M$^+$], 495 (100), 367 (15), 303 (7), 277 (12), 262 (46), 248 (7), 201 (6), 183 (42), 165 (12), 145 (15), 115 13), 91 (28).

Anal. Calcd for $C_{36}H_{31}O_2P$: C, 82.11; H, 5.93. Found: C, 81.85; H, 6.18.

[(3-(4-Methylphenyl)propenoyl)(2-methylthiophenyl)methylene]triphenylphosphorane 27

This was prepared as for **9** using (2-methylthiobenzyl)triphenylphosphonium bromide **8** (8.30 g, 17 mmol), butyllithium in hexanes (6.9 mL, 2.5 M, 17 mmol) and 3-(4-methylphenyl)propenoyl chloride (1.56 g, 9 mmol) to give the product (3.27 g, 70%) as yellow crystals, mp 257.5–258 ˚C.

IR: 1633, 1500, 1479, 1434, 1206, 1098, 976, 951, 811, 755, 716, 694 cm^{-1}.

^{1}H NMR (300 MHz): δ = 7.85–7.54 (m, 6 H), 7.54–7.28 (m, 9 H), 7.42 (d, *J* = 16 Hz, 1 H, vinyl-H), 7.23 (d, *J* = 8 Hz, 2 H), 7.09 (t, *J* = 7 Hz, 1 H), 7.02 (d, *J* = 8 Hz, 3 H), 6.90 (d, *J* = 7 Hz, 1 H), 6.80 (t, *J* = 7 Hz, 1 H), 6.62 (d, *J* = 16 Hz, 1 H, vinyl-H), 2.28 (s, 3 H, ArMe), 2.21 (s, 3 H, SMe).

^{13}C NMR (75 MHz): δ = 180.6 (d, *J* = 5 Hz, CO), 145.3 (d, *J* = 5 Hz, C-2), 137.9 (C), 136.4 (d, *J* = 4 Hz, CH), 135.1 (d, *J* = 11 Hz, C-1), 134.6 (CH), 134.5 (C), 134.0 (d, *J* = 9 Hz, C-2 of PPh), 131.6 (d, *J* = 2 Hz, C-4 of PPh), 129.2 (2CH), 128.4 (d, *J* = 13 Hz, C-3 of PPh), 127.5 (CH), 127.7 (2CH), 127.0 (d, *J* = 91 Hz, C-1 of PPh), 125.7 (d, *J* = 12 Hz, =CH-), 123.5 (CH), 122.9 (CH), 71.4 (d, *J* = 108 Hz, P=C), 21.3 (Me), 15.2 (SMe).

^{31}P NMR (121 MHz): δ = +15.7.

MS (EI): *m/z* (%) = 542 (19) [M$^+$], 527 (17), 495 (100), 303 (6), 277 (7), 262 (25), 248 (9), 197 (9), 183 (34), 165 11), 145 (11), 135 (8), 115 (12), 84 (46).

Anal. Calcd for $C_{36}H_{31}OPS$: C, 79.68; H, 5.76. Found: C, 79.81; H, 5.56.

[(3-(4-Chlorophenyl)propenoyl)(2-methoxyphenyl)methylene]triphenylphosphorane 28

This was prepared as for **9** using (2-methoxybenzyl)triphenylphosphonium bromide **8** (10.00 g, 21.5 mmol), butyllithium in hexanes (8.6 mL, 2.5 M, 21.5 mmol) and 3-(4-chlorophenyl)propenoyl chloride (2.16 g, 10.7 mmol) to give the product (4.75 g, 81%) as bright yellow crystals, mp 236–238.5 ˚C.

IR: 1895, 1633, 1590, 1499, 1288, 1240, 1189, 1104, 1050, 983, 949, 851, 823, 751, 693 cm^{-1}.

^{1}H NMR (300 MHz): δ = 7.90–7.23 (m, 17 H), 7.23–7.05 (m, 5 H), 6.85 (t, *J* = 7 Hz, 1 H), 6.75 (d, *J* = 16 Hz, 1 H, vinyl-H), 6.43 (d, *J* = 7 Hz, 1 H, 3'-H), 3.23 (s, 3 H, OMe).

^{13}C NMR (75 MHz): δ = 179.2 (d, *J* = 5 Hz, CO), 158.9 (d, *J* = 3 Hz, C-2), 137.4 (d, *J* = 5 Hz, CH), 135.9 (C), 133.5 (2CH), 132.8 (CH), 133.8 (d, *J* = 10 Hz, C-2 of PPh), 131.5 (d, *J* = 2 Hz, C-4 of PPh), 128.9 (2CH), 128.7 (C), 128.4 (d, *J* = 12 Hz, C-3 of PPh), 128.2 (CH), 127.1 (d, *J* = 91 Hz, C-1 of PPh), 127.1 (d, *J* = 12 Hz, =CH-), 126.6 (d, *J* = 9 Hz, C-1), 120.3 (CH), 110.1 (C-3), 71.0 (d, *J* = 113 Hz, P=C), 54.3 (OMe).

^{31}P NMR (121 MHz): δ = +15.7.

MS (EI): *m/z* (%) = 548 (11) [^{37}Cl-M$^+$], 546 (32) [^{35}Cl-M$^+$], 517 (36), 515 (100), 367 (16), 303 (11), 277 (5), 262 (60), 201 (6), 183 (37), 165 (17), 152 (6).

Anal. Calcd for $C_{35}H_{28}ClO_2P$: C, 76.85; H, 5.16. Found: C, 77.15; H, 5.15.

[(3-(4-Chlorophenyl)propenoyl)(2-methythiophenyl)methylene]triphenylphosphorane 29

This was prepared as for **9** using (2-methylthiobenzyl)triphenylphosphonium bromide **8** (10.00 g, 20.8 mmol), butyllithium in hexanes (8.3 mL, 2.5 M, 20.8 mmol) and 3-(4-chlorophenyl)propenoyl chloride (2.09 g, 10.4 mmol) to give the product (4.76 g, 81%) as bright yellow crystals, mp 244.5–246 ˚C.

IR: 1634, 1505, 1435, 1270, 1209, 1097, 978, 849, 830, 817, 754, 729, 716, 694 cm^{-1}.

^{1}H NMR (300 MHz): δ = 7.95–7.52 (m, 6 H, Ph), 7.52–7.28 (m, 10 H), 7.28–7.10 (m, 5 H), 7.10–6.76 (m, 3 H), 6.58 (d, *J* = 16 Hz, 1 H, vinyl-H), 2.21 (s, 3 H, SMe).

^{13}C NMR (75 MHz): δ = 179.9 (d, *J* = 5 Hz, CO), 145.8 (d, *J* = 5 Hz, C-2), 136.6 (d, *J* = 4 Hz, CH), 136.2 (C), 135.1 (d, *J* = 11 Hz, C-1), 134.4 (d, *J* = 10 Hz, C-2 of PPh), 134.0 (2CH), 133.2 (CH), 132.1 (d, *J* = 3 Hz, C-4 of PPh), 129.2 (2CH), 129.1 (C), 128.8 (d, *J* = 12 Hz, C-3 of PPh), 128.0 (CH), 127.7 (d, *J* = 12 Hz, =CH-), 127.4 (d, *J* = 91 Hz, C-1 of PPh), 123.8 (CH), 123.2 (CH), 72.3 (d, *J* = 110 Hz, P=C), 15.3 (SMe).

^{31}P NMR (121 MHz): δ = +16.0.

MS (EI): *m/z* (%) = 564 (7) [^{37}Cl-M$^+$], 562 (18) [^{35}Cl-M$^+$], 549 (6), 547 (17), 517 (38), 515 (100), 368 (7), 334 (7), 318 (11), 303 (8), 277 (12), 262 (36), 183 (32), 105 (31), 91 (71).

Anal. Calcd for $C_{35}H_{28}ClOPS$: C, 74.66; H, 5.01. Found: C, 74.36; H, 4.94.

[(2-Methoxyphenyl)(3-(2-methylphenyl)propenoyl)methylene]triphenylphosphorane 30

This was prepared as for **9** using (2-methoxybenzyl)triphenylphosphonium bromide **7** (10.00 g, 21.5 mmol), butyllithium in hexanes (8.6 mL, 2.5 M, 21.5 mmol) and 3-(2-methylphenyl)propenoyl chloride (1.93 g, 10.7 mmol) to give the product (4.39 g, 78%) as bright yellow crystals, mp 199–202 ˚C.

IR: 1625, 1589, 1574, 1360, 1259, 1107, 1071, 1050, 1026, 999, 974, 953, 930, 854, 805, 785, 757, 721, 693 cm^{-1}.

^{1}H NMR (300 MHz): δ = 7.82–7.53 (m, 7 H), 7.53–7.28 (m, 11 H), 7.18–6.98 (m, 4 H), 6.83 (t, *J* = 7 Hz, 1 H), 6.82 (d, *J* = 16 Hz, 1 H, vinyl-H), 6.42 (d, *J* = 7 Hz, 1 H, 3-H), 3.25 (s, 3 H, OMe), 2.37 (s, 3 H, ArMe).

^{13}C NMR (75 MHz): δ = 179.8 (d, *J* = 5 Hz, CO), 158.8 (d, *J* = 3 Hz, C-2), 137.4 (d, *J* = 5 Hz, CH), 137.0 (C), 136.2 (C), 133.8 (d, *J* = 10 Hz, C-2 of PPh), 131.5 (CH), 131.4 (d, *J* = 2 Hz, C-4 of PPh), 130.4 (CH), 128.3 (d, *J* = 12 Hz, C-3 of PPh), 128.0 (CH), 127.9 (d, *J* = 11 Hz, =CH-), 127.7 (CH), 127.1 (d, *J* = 90 Hz, C-1 of PPh), 126.6 (d, *J* = 9 Hz, C-1), 126.2 (CH), 125.8 (CH), 120.3 (CH), 110.1 (C-3), 70.2 (d, *J* = 111 Hz, P=C), 54.3 (OMe), 20.1 (Me).

^{31}P NMR (121 MHz): δ = +15.6.

MS (EI): *m/z* (%) = 526 (18) [M+], 495 (55), 367 (8), 331 (12), 277 (6), 262 (28), 229 (7), 183 (20), 169 (58), 145 (13), 127 (16), 109 (42), 43 (100).

Anal. Calcd for $C_{36}H_{31}O_2P$: C, 82.11; H, 5.93. Found: C, 81.79; H, 6.09.

[(3-(2-Methylphenyl)propenoyl)(2-methythiophenyl)methylene]triphenylphosphorane 31

This was prepared as for **9** using (2-methylthiobenzyl)triphenylphosphonium bromide **8** (10.00 g, 20.8 mmol), butyllithium in hexanes (8.3 mL, 2.5 M, 20.8 mmol) and 3-(2-methylphenyl)propenoyl chloride (1.88 g, 10.4 mmol) to give the product (3.91 g, 72%) as bright yellow crystals, mp 248–249 ˚C.

IR: 1623, 1434, 1359, 1269, 1203, 1097, 1077, 1040, 999, 979, 951, 928, 851, 802, 754, 714, 694 cm^{-1}.

^1H NMR (300 MHz): δ = 7.83–7.54 (m, 6 H), 7.65 (d, *J* = 15 Hz, 1 H, vinyl-H), 7.54–7.24 (m, 11 H), 7.34–6.96 (m, 4 H), 6.89 (d, *J* = 7 Hz, 1 H), 6.80 (t, *J* = 7 Hz, 1 H), 6.58 (d, *J* = 15 Hz, 1 H, vinyl-H), 2.37 (s, 3 H, ArMe), 2.23 (s, 3 H, SMe).

^{13}C NMR (75 MHz): δ = 180.7 (d, *J* = 5 Hz, CO), 145.3 (d, *J* = 5 Hz, C-2), 137.2 (C), 136.4 (d, *J* = 3 Hz, CH), 136.2 (C), 135.1 (d, *J* = 12 Hz, C-1), 134.6 (d, *J* = 10 Hz, C-2 of PPh), 132.2 (CH), 131.7 (d, *J* = 2 Hz, C-4 of PPh), 130.4 (CH), 128.4 (d, *J* = 13 Hz, C-3 of PPh), 128.1 (d, *J* = 12 Hz, =CH-), 127.8 (CH), 127.5 (d, *J* = 3 Hz, CH), 127.0 (d, *J* = 91 Hz, C-1 of PPh), 126.4 (CH), 125.8 (CH), 123.5 (d, *J* = 2 Hz, CH), 122.9 (CH), 71.5 (d, *J* = 109 Hz, P=C), 20.1 (Me), 15.2 (SMe).

^{31}P NMR (121 MHz): δ = +15.8.

MS (EI): *m/z* (%) = 542 (5) [M+], 495 (16), 277 (100), 262 (16), 201 (19), 183 (22), 145 (16), 115 (10), 91 (9).

Anal. Calcd for $C_{36}H_{31}OPS$: C, 79.68; H, 5.76. Found: C, 79.40; H, 5.64.

[(3-(2-Chlorophenyl)propenoyl)(2-methoxyphenyl)methylene]triphenylphosphorane 32

This was prepared as for **9** using (2-methoxybenzyl)triphenylphosphonium bromide **7** (10.00 g, 21.5 mmol), butyllithium in hexanes (8.6 mL, 2.5 M, 21.5 mmol) and 3-(2-chlorophenyl)propenoyl chloride (2.16 g, 10.7 mmol) to give the product (4.45 g, 76%) as bright yellow crystals, mp 222–224.5 ˚C.

IR: 1632, 1589, 1573, 1268, 1209, 1106, 1050, 1027, 977, 953, 858, 846, 794, 748, 693 cm^{-1}.

^1H NMR (300 MHz): δ = 7.77 (d, *J* = 16 Hz, 1 H, vinyl-H), 7.72–7.53 (m, 6 H), 7.52–7.24 (m, 12 H), 7.15–7.03 (m, 3 H), 6.89 (d, *J* = 16 Hz, 1 H, vinyl-H), 6.83 (t, *J* = 7 Hz, 1 H), 6.43 (d, *J* = 7 Hz, 1 H), 3.25 (s, 3 H, OMe).

^{13}C NMR (75 MHz): δ = 179.1 (d, *J* = 5 Hz, CO), 158.9 (d, *J* = 3 Hz, C-2), 137.4 (d, *J* = 5 Hz, CH), 135.6 (C), 134.5 (CH), 133.8 (d, *J* = 10 Hz, C-2 of PPh), 131.5 (d, *J* = 2 Hz, C-4 of PPh), 129.4 (d, *J* = 13 Hz, =CH-), 130.0 (C), 129.9 (CH), 128.7 (CH), 128.4 (d, *J* = 12 Hz, C-3 of PPh), 128.2 (CH), 127.6 (CH), 127.1 (d, *J* = 91 Hz, C-1 of PPh), 126.6 (CH), 126.5 (d, *J* = 10 Hz, C-1), 120.3 (CH), 110.1 (C-3), 71.0 (d, *J* = 109 Hz, P=C), 54.3 (OMe).

^{31}P NMR (121 MHz): δ = +15.8.

MS (EI): *m/z* (%) = 548 (6) [^{37}Cl-M+], 546 (16) [^{35}Cl-M+], 517 (18), 515 (48), 367 (9), 303 (5), 277 (43), 262 (35), 218 (6), 201 (14), 183 (30), 147 (23), 122 (17), 84 (69), 49 (100).

Anal. Calcd for $C_{35}H_{28}ClO_2P$: C, 76.85; H, 5.16. Found: C, 76.74; H, 5.28.

[(3-(2-Chlorophenyl)propenoyl)(2-methylthiophenyl)methylene]triphenylphosphorane 33

This was prepared as for **9** using (2-methylthiobenzyl)triphenylphosphonium bromide **8** (10.00 g, 20.8 mmol), butyllithium in hexanes (8.3 mL, 2.5 M, 20.8 mmol) and of 3-(2-chlorophenyl)propenoyl chloride (2.09 g, 10.4 mmol) to give the product (5.11 g, 87%) as bright yellow crystals, mp 238–240 ˚C.

IR: 1625, 1266, 1207, 1108, 1078, 1032, 1001, 972, 933, 855, 775, 751, 718, 693 cm^{-1}.

^1H NMR (300 MHz): δ = 7.79 (d, *J* = 16 Hz, 1 H, vinyl-H), 7.78–7.55 (m, 6 H), 7.55–7.22 (m, 11 H), 7.15–6.96 (m, 4 H), 6.88 (d, *J* = 7 Hz, 1 H), 6.80 (t, *J* = 7 Hz, 1 H), 6.68 (d, *J* = 16 Hz, 1 H, vinyl-H), 2.22 (s, 3 H, SMe).

^{13}C NMR (75 MHz): δ = 179.9 (d, *J* = 6 Hz, CO), 145.8 (d, *J* = 5 Hz, C-2), 136.6 (d, *J* = 3 Hz, CH), 135.7 (C), 135.2 (d, *J* = 11 Hz, C-1), 134.7 (CH), 134.4 (d, *J* = 10 Hz, C-2 of PPh), 132.2 (d, *J* = 3 Hz, C-4 of PPh), 130.3 (C), 130.2 (CH), 130.1 (d, *J* = 12 Hz, =CH-), 129.5 (CH), 128.8 (d, *J* = 12 Hz, C-3 of PPh), 128.0 (CH), 127.9 (CH), 127.4 (d, *J* = 91 Hz, C-1 of PPh), 127.2 (CH), 123.8 (CH), 123.3 (CH), 72.5 (d, *J* = 110 Hz, P=C), 15.4 (SMe).

^{31}P NMR (121 MHz): δ = +16.0.

MS (EI): *m/z* (%) = 564 (9) [^{37}Cl-M+], 562 (19) [^{35}Cl-M+], 549 (8), 547 (18), 527 (17), 515 (100), 383 (5), 369 (14), 303 (9), 277 (37), 262 (50), 236 (16), 201 (14), 183 (55), 165 (25), 147 (17).

Anal. Calcd for $C_{35}H_{28}ClOPS$: C, 74.66; H, 5.01. Found: C, 74.39; H, 4.99.

[(3-(3,4-Methylenedioxyphenyl)propenoyl)(2-methoxyphenyl)methylene]triphenylphosphorane 34

This was prepared as for **9** using (2-methoxybenzyl)triphenylphosphonium bromide **7** (10 g, 21.5 mmol), butyllithium in hexanes (8.6 mL, 2.5 M, 21.5 mmol) and 3-(3,4-methylenedioxyphenyl)propenoyl chloride (2.32 g, 10.7 mmol) to give the product (5.29 g, 86%) as bright orange prisms, mp 227–229 ˚C.

IR: 1636, 1612, 1505, 1371, 1245, 1105, 1030, 978, 924, 851, 802, 747, 692 cm^{-1}.

^1H NMR (300 MHz): δ = 7.65–7.52 (m, 6 H, Ph), 7.48–7.28 (m, 11 H), 7.08 (t, *J* = 7 Hz, 1 H), 6.86–6.80 (m, 2 H), 6.82 (t, *J* = 7 Hz, 1 H), 6.70 (d, *J* = 16 Hz, 1 H, vinyl-H), 6.67 (d, *J* = 8 Hz, 1 H), 6.43 (d, *J* = 7 Hz, 1 H), 5.88 (s, 2 H, CH_2), 3.23 (s, 3 H, OMe).

^{13}C NMR (75 MHz): δ = 179.6 (d, *J* = 5 Hz, CO), 159.4 (d, *J* = 3 Hz, C-2), 148.5 (C), 148.2 (C), 137.7 (d, *J* = 6 Hz), 134.1 (d, *J* = 10 Hz, C-2 of PPh), 132.1 (C), 131.8 (d, *J* = 2 Hz, C-4 of PPh), 128.5 (d, *J* = 2 Hz, CH), 128.6 (d, *J* = 13 Hz, C-3 of PPh), 128.5 (CH), 127.9 (d, *J* = 90 Hz, C-1 of PPh), 126.8 (d, *J* = 11 Hz, C-1), 125.2 (d, *J* = 13 Hz, CO-CH=), 123.1 (CH), 120.6 (CH), 110.5 (CH), 108.6 (CH), 106.6 (CH), 101.7 (CH_2), 70.1 (d, *J* = 112 Hz, P=C), 54.3 (OMe).

^{31}P NMR (121 MHz): δ = +15.4.

MS (EI): *m/z* (%) = 556 (2) [M+], 525 (4), 270 (13), 248 (58), 218 (100), 91 (90).

Anal. Calcd for $C_{36}H_{29}O_4P$: C, 77.69; H, 5.25. Found: C, 77.22; H, 5.13. HRMS (EI): *m/z* calcd for $C_{36}H_{29}O_4P$ [M+]: 556.1803; found: 556.1816.

FVP of [(2-methoxyphenyl)-3-(4-methylphenyl)propenoyl)methylene]triphenylphosphorane 26

FVP of the title compound (1.0 g) at 850 ˚C and 3.0–5.0 × 10^{-2} Torr gave an oily red-brown solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a red oil which was kugelrohr distilled at 180 ˚C/0.04 Torr to give the product (0.3 g, 68%) as a deep red oil. ^1H NMR and ^{13}C NMR analysis indicated a mixture of two isomeric products;

2-methylbenzo[*b*]naphtho[1,2-*d*]furan 35 (~80%).

^1H NMR (300 MHz): δ = 8.50–8.39 (m, 2 H), 8.18–7.87 (m, 2 H), 7.85–7.68 (m, 2 H), 7.65–7.32 (m, 3 H), 2.71 (s, 3 H, Me).

^{13}C NMR (75 MHz): δ = 156.1 (C), 154.8 (C), 137.3 (C), 129.5 (C), 129.2 (CH), 128.8 (C), 128.5 (CH), 126.7 (CH), 125.8 (CH), 125.2 (C), 123.2 (CH), 122.9 (CH), 122.1 (CH), 116.9 (C), 111.9 (CH), 111.8 (CH), 22.2 (CH_3).

2-methylbenzo[*b*]naphtho[2,1-*d*] furan 36 (~20%).

^1H NMR (300 MHz): δ = 2.67 (s, 3 H, Me).

FVP of [(2-methylthiophenyl)(3-(4-methylphenyl)propenoyl)methylene]triphenylphosphorane 27

FVP of the title compound (1.0 g) at 850 ˚C and 7.0–9.0 × 10^{-2} Torr gave an oily brown solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a brown oil which

solidified with time. The solid was kugelrohr distilled at 170 °C/0.01 Torr to give a pale brown waxy solid which was recrystallised from ethanol to give the product, **2-methylbenzo[*b*]naphtho[1,2-*d*] thiophene 37** (0.26 g, 57%) as off-white crystals, mp 88–89.5 °C (lit.,[10] 92 °C).

^{1}H NMR (300 MHz): δ = 8.83 (d, *J* = 8 Hz, 1 H, 1-H), 8.73 (s, 1 H, 11-H), 8.00–7.78 (m, 4 H), 7.62–7.33 (m, 3 H), 2.64 (s, 3 H, Me) [Good agreement with Lit.[10]].

^{13}C NMR (75 MHz): δ = 139.8 (C), 138.8 (C), 137.03 (C), 136.96 (C), 1310 (C), 130.2 (C), 129.3 (CH), 128.6 (C), 127.7 (CH), 126.9 (CH), 125.1 (CH), 124.8 (2CH), 123.2 (CH), 122.7 (CH), 120.2 (CH), 223 (CH_3).

FVP of [(3-(4-chlorophenyl)propenoyl)(2-methoxyphenyl)methylene]triphenylphosphorane 28

FVP of the title compound (1.0 g) at 850 °C and 7.0–9.0 × 10^{-2} Torr gave an oily red-brown solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a red-orange crystalline material which was distilled at 178 °C and 0.01 Torr to give a red-orange oil. This crystallised with time to give a red-orange solid which was recrystallised from ethanol to give the product, **2-chlorobenzo[*b*]naphtho[1,2-*d*]furan 38** (0.21 g, 46%) as very pale pink crystals, mp 87–89 °C.

IR: 1624, 1580, 1516, 1363, 1254, 1214, 1105, 1079, 1032, 969, 857, 826, 782, 734, 672 cm^{-1}.

^{1}H NMR (300 MHz): δ = 8.55 (d, *J* = 2 Hz, 1 H, 11-H), 8.34 (dd, *J* = 7, 2 Hz, 1 H, 1-H), 7.95 (d, *J* = 7 Hz, 1 H), 7.88 (d, *J* = 7 Hz, 1 H), 7.75 (d, *J* = 7 Hz, 1 H), 7.59–7.40 (m, 4 H).

^{13}C NMR (75 MHz): δ = 155.9 (C), 154.7 (C), 133.1 (C), 130.5 (CH), 129.5 (C), 128.5 (C), 128.1 (CH), 126.1 (CH), 125.1 (CH), 124.3 (C), 123.3 (CH), 122.5 (CH), 121.7 (CH), 116.6 (C), 112.7 (CH), 111.9 (CH).

MS (EI): *m/z* (%) = 254 (32) [^{37}Cl-M$^+$], 252 (100) [^{35}Cl-M$^+$], 218 (7), 189 (23), 187 (10), 163 (3), 126 (8), 95 (7).

Anal. Calcd for $C_{16}H_9ClO$: C, 76.05; H, 3.59. Found: C, 75.78; H, 3.45.

FVP of [(3-(4-chlorophenyl)(2-methythiophenyl)propenoyl)methylene]triphenylphosphorane 29

FVP of the title compound (1.0 g) at 850 °C and 7.0–9.0 × 10^{-2} Torr gave an oily brown solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a pale brown crystalline material which was distilled at 225 °C and 0.05 Torr to give a yellow-brown oil. This crystallised with time to give a pale brown solid which was recrystallised from ethanol to give the product, **2-chlorobenzo[*b*]naphtho[1,2-*d*]thiophene 39** (0.24 g, 50%) as very pale brown crystals, mp 135–136 °C.

IR: 1610, 1501, 1461, 1354, 1310, 1155, 1139, 1087, 964, 922, 830, 772, 745, 717, 679, 658, 614 cm^{-1}.

^{1}H NMR (300 MHz): δ = 8.94 (d, *J* = 2 Hz, 1 H, 11-H), 8.72 (d, *J* = 7 Hz, 1 H), 8.06–7.92 (m, 2 H), 7.89 (d, *J* = 7 Hz, 1 H), 7.82 (d, *J* = 7 Hz, 1 H), 7.68–7.44 (m, 4 H).

^{13}C NMR (75 MHz): δ = 139.7 (C), 139.6 (C), 136.2 (C), 133.1 (C), 131.0 (C), 130.6 (CH), 130.0 (C), 127.2 (CH), 125.5 (2CH), 125.0 (CH), 124.6 (C), 124.4 (CH), 123.2 (CH), 122.5 (CH), 121.2 (CH).

MS (EI): *m/z* (%) = 270 (41) [^{37}Cl-M$^+$], 268 (100) [^{35}Cl-M$^+$], 232 (17), 189 (9), 187 (6), 134 (9), 116 (9).

Anal. Calcd for $C_{16}H_9ClS$: C, 71.50; H, 3.38. Found: C, 71.50; H, 3.40.

FVP of [(3-(2-chlorophenyl)propenoyl)(2-methoxyphenyl)methylene]triphenylphosphorane 32

FVP of the title compound (1.0 g) at 800 °C and 6.0–8.0 × 10^{-2} Torr gave an oily red-brown solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a red solid material which was distilled at 215 °C and 0.2 Torr to give a red oil. This crystallised with time to give a red solid which was recrystallised from ethanol to give the product, **4-chlorobenzo[*b*]naphtho[1,2-*d*] furan 40** (0.17 g, 38%) as very pale pink crystals, mp 112–113 °C.

IR: 1621, 1575, 1370, 1263, 1234, 1204, 1188, 1155, 1120, 1024, 1003, 987, 856, 795, 756, 736, 673 cm^{-1}.

^{1}H NMR (300 MHz): δ = 8.25 (d, *J* = 7 Hz, 1 H), 8.20 (d, *J* = 7 Hz, 1 H), 8.11 (d, *J* = 6 Hz, 1 H), 7.63 (d, *J* = 7 Hz, 1 H), 7.57 (d, *J* = 6 Hz, 1 H), 7.48 (d, *J* = 6 Hz, 1 H), 7.44–7.7.28 (m, 3 H, m).

^{13}C NMR (75 MHz): δ = 155.8 (C), 154.3 (C), 132.9 (C), 130.0 (C), 127.4 (C), 126.8 (CH), 126.1 (CH), 124.7 (2CH), 124.3 (C), 123.1 (CH), 122.3 (CH), 121.7 (CH), 117.4 (C), 113.3 (CH), 111.8 (CH).

MS (EI): *m/z* (%) = 254 (13) [^{37}Cl-M$^+$], 252 (45) [^{35}Cl-M$^+$], 190 (55), 188 (37), 164 (18), 151 (5), 137 (7), 126 (78), 111 (17), 94 (100), 82 (37), 74 (21).

Anal. Calcd for $C_{16}H_9ClO$: C, 76.05; H, 3.59. Found: C, 76.12; H, 3.55.

FVP of [(3-(2-chlorophenyl)propenoyl)(2-methylthiophenyl)methylene]triphenylphosphorane 33

FVP of the title compound (1.0 g) at 800 °C and 6.0–8.0 × 10^{-2} Torr gave an oily brown solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a pale brown solid material which was distilled at 237 °C and 0.3 Torr to give a pale yellow-brown oil. This crystallised with time to give a pale yellow-brown solid which was recrystallised from ethanol to give the product, **4-chlorobenzo[*b*]naphtho[1,2-*d*] thiophene 41** (0.13 g, 28%) as very pale brown crystals, mp 121–122 °C.

IR: 1578, 1502, 1205, 1169, 1122, 1071, 1030, 980, 904, 788, 758, 729, 657 cm^{-1}.

^{1}H NMR (300 MHz): δ = 8.73 (d, *J* = 7 Hz, 1 H), 8.62 (d, *J* = 7 Hz, 1 H), 8.24 (d, *J* = 7 Hz, 1 H), 7.89 (d, *J* = 7 Hz, 1 H), 7.84 (d, *J* = 7 Hz, 1 H), 7.64–7.35 (m, 4 H).

^{13}C NMR (75 MHz): δ = 139.8 (C), 139.2 (C), 136.1 (C), 133.1 (C), 131.6 (C), 129.2 (2C), 126.6 (CH), 125.4 (CH), 125.3 (CH), 124.8 (CH), 124.6 (CH), 123.6 (CH), 123.1 (CH), 122.1 (CH), 122.0 (CH).

MS (EI): *m/z* (%) = 270 (8) [^{37}Cl-M$^+$], 268 (22) [^{35}Cl-M$^+$], 233 (15), 200 (3), 190 (21), 188 (20), 164 (8), 135 (47), 117 (100), 94 (48), 69 (21).

Anal. Calcd for $C_{16}H_9ClS$: C, 71.50; H, 3.38. Found: C, 71.75; H, 3.42.

[(2-Methoxyphenyl)(2-methyl-3-phenylpropenoyl)methylene]triphenylphosphorane 42

This was prepared as for **9** using (2-methoxybenzyl)triphenylphosphonium bromide **7** (8.00 g, 17 mmol), butyllithium in hexanes (6.9 mL, 2.5 M, 17 mmol) and 2-methyl-3-phenylpropenoyl chloride (1.56 g, 9 mmol) to give the product (2.36 g, 52%) as yellow crystals, mp 159.5–161 °C.

IR: 1637, 1590, 1574, 1251, 1180, 1108, 1050, 1028, 971, 889, 843, 790, 754, 693 cm^{-1}.

^{1}H NMR (300 MHz): δ = 7.80–7.55 (m, 6 H), 7.55–7.30 (m, 9 H), 7.30–6.95 (m, 7 H), 6.75 (d, *J* = 8 Hz, 1 H), 6.71 (s, 1 H, vinyl-H), 6.43 (d, *J* = 8 Hz, 1 H, 3-H), 3.31 (s, 3 H, OMe), 1.91 (3 H, s, =CMe).

^{13}C NMR (75 MHz): δ = 189.1 (d, *J* = 5 Hz, CO), 158.7 (d, *J* = 3 Hz, C-2), 139.7 (d, *J* = 12 Hz, =C-), 138.5 (C), 136.9 (d, *J* = 5 Hz, CH), 133.7 (d, *J* = 9 Hz, C-2 of PPh), 131.3 (d, *J* = 2 Hz, C-4 of PPh), 129.6 (CH), 129.2 (2CH), 128.3 (d, *J* = 12 Hz, C-3 of PPh), 127.9 (2CH), 127.9 (d, *J* = 11 Hz, C-1), 127.7 (d, *J* = 91 Hz, C-1 of PPh), 127.6 (CH), 126.2 (CH), 120.3 (CH), 109.8 (d, *J* = 2 Hz, C-3), 66.2 (d, *J* = 110 Hz, P=C), 54.3 (OMe), 16.2 (Me).

^{31}P NMR (121 MHz): δ = +14.4.

MS (EI): *m/z* (%) = 526 (20) [M+], 495 (50), 303 (6), 277 (100), 262 (30), 240 (13), 201 (23), 183 (33), 157 (13), 115 (24).

Anal. Calcd for $C_{36}H_{31}O_2P$: C, 82.36; H, 6.07. Found: C, 82.41; H, 5.86.

[(2-Methyl-3-phenylpropenoyl)(2-methylthiophenyl)methylene]triphenylphosphorane 43

This was prepared as for **9** using (2-methylthiobenzyl)triphenylphosphonium bromide **8** (8.30 g, 17 mmol) butyllithium in hexanes (6.9 mL, 2.5 M, 17 mmol) and 2-methyl-3-

phenylpropenoyl chloride (1.56 g, 9 mmol) to give the product (2.69 g, 58%) as yellow crystals, mp 156–158 °.

IR: 1575, 1435, 1368, 1258, 1236, 1124, 1102, 978, 968, 764, 750, 691, 598 cm^{-1}.

^1H NMR (300 MHz): δ = 7.95–7.54 (m, 6 H), 7.54–7.28 (m, 9 H), 7.27–6.95 (m, 7 H), 6.87–6.75 (m, 2 H), 6.73 (s, 1 H, vinyl-H), 2.17 (s, 3 H, SMe), 1.99 (s, 3 H, =CMe).

^{13}C NMR (75 MHz): δ = 189.4 (d, *J* = 5 Hz, CO), 144.6 (d, *J* = 4 Hz, C-2), 139.2 (d, *J* = 12 Hz, =C-), 138.5 (C), 136.3 (d, *J* = 4 Hz, CH), 136.3 (d, *J* = 9 Hz, C-1), 134.0 (d, *J* = 9 Hz, C-2 of PPh), 131.5 (d, *J* = 2 Hz, C-4 of PPh), 129.8 (CH), 129.2 (2CH), 128.3 (d, *J* = 12 Hz, C-3 of PPh), 127.9 (2CH), 127.5 (d, *J* = 88 Hz, C-1 of PPh), 126.9 (CH), 126.2 (CH), 123.6 (d, *J* = 2 Hz, CH), 123.2 (CH), 68.8 (d, *J* = 108 Hz, P=C), 16.0 (Me), 15.2 (SMe).

^{31}P NMR (121 MHz): δ = +14.5.

MS (EI): *m/z* (%) = 542 (24) [M^+], 527 (15), 495 (100), 425 (8), 405 (9), 303 (25), 277 (28), 262 (32), 234 (10), 197 (10), 183 (36).

Anal. Calcd for $C_{36}H_{31}OPS$: C, 79.68; H, 5.76. Found: C, 79.86; H, 5.79.

FVP of [(2-methoxyphenyl)(2-methyl-3-phenylpropenoyl)methylene]triphenylphosphorane 42

FVP of the title compound (1.0 g) at 850 °C and 3.0–5.0 × 10^{-2} Torr gave an oily red-brown solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a red semi-solid mass which was distilled at 190 °C/0.02 Torr to give a red semi-solid mass. GCMS and 1H NMR analysis of this indicated the presence of two products. Further column chromatography using a longer column and n-hexane as eluant enabled partial separation of the two major products:

6-methylbenzo[*b*]naphtho[1,2-*d*]furan 44 (0.10 g 23%) as pale brown crystals, mp 79–81.5 °C.

IR: 1599, 1527, 1303, 1255, 1216, 1152, 1137, 1105, 965, 881, 740 cm^{-1}.

^1H NMR (300 MHz): δ = 8.50 (d, *J* = 8 Hz, 1 H), 8.30 (d, *J* = 9 Hz, 1 H), 7.87 (d, *J* = 8 Hz, 1 H), 7.72–7.53 (m, 3 H), 7.52–7.36 (m, 3 H), 2.68 (s, 3 H, Me).

^{13}C NMR (75 MHz): δ = 156.0 (C), 154.3 (C), 130.9 (C), 128.6 (CH), 128.0 (CH), 126.3 (CH), 125.8 (CH), 125.4 (C), 124.4 (CH), 123.4 (CH), 123.2 (CH), 123.0 (C), 122.1 (CH), 116.8 (C), 112.5 (C), 112.0 (CH), 15.8 (CH_3).

MS (EI): *m/z* (%) = 232 (100) [M^+], 202, (26), 176 (6), 116 (40), 101 (63), 88 (38), 75 (7), 63 (10).

HRMS (EI): *m/z* calcd for $C_{17}H_{12}O$ [M^+]: 232.0888; found: 232.0895.

2-(2-indenyl)benzofuran 45 (0.04 g 9%) as a pink solid, mp 198.5–200.5 °C.

IR: 1604, 1262, 1183, 1107, 1010, 933, 916, 875, 804, 751, 717 cm^{-1}.

^1H NMR (300 MHz): δ = 7.60–7.37 (m, 4 H), 7.36–7.15 (m, 5 H), 6.77 (s, 1 H, 3-H), 3.80 (s, 2 H, CH_2).

^{13}C NMR (75 MHz): δ = 154.9 (C), 153.7 (C), 144.7 (C), 142.8 (C), 135.8 (C), 129.1 (C), 128.6 (CH), 126.9 (CH), 125.4 (CH), 124.5 (CH), 123.8 (CH), 122.9 (CH), 121.6 (CH), 120.8 (CH), 111.0 (CH), 103.0 (CH), 38.3 (CH_2).

MS (EI): *m/z* (%) = 232 (100) [M^+], 216 (7), 202 (25), 116 (9), 101 (10);

HRMS (EI): *m/z* calcd for $C_{17}H_{12}O$ [M^+]: 232.0888; found: 232.0891.

FVP of [2-methyl-3-phenylpropenoyl)(2-methylthiophenyl)methylene]triphenylphosphorane 43

FVP of the title compound (1.1 g) at 850 °C and 5.0–8.0 × 10^{-2} Torr gave an oily brown solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a brown oil which solidified with time. The solid was kugelrohr distilled at 195 °C/0.1 Torr to give a pale brown waxy solid which was recrystallised from ethanol to give the product, **6-methylbenzo[*b*]naphtho[1,2-*d*]thiophene 46** (0.41 g, 80%) as pale brown crystals, mp 104–105 °C (lit.,[10] 105 °C).

^1H NMR (300 MHz): δ = 9.02 (d, *J* = 7 Hz, 1 H), 8.89 (d, *J* = 7 Hz, 1 H), 8.05 (d, *J* = 7 Hz, 1 H), 7.97 (d, *J* = 7 Hz, 1 H), 7.77–7.45 (m, 5 H), 2.69 (s, 3 H, Me).

(2-Methoxy-3-methylbenzyl)triphenylphosphonium bromide 47

This was prepared as for **8** using 2-methoxy-3-methylbenzyl alcohol[12] (17.50 g, 115 mmol), phosphorus tribromide (4.70 mL, 13.56 g, 50 mmol) and triphenylphosphine (30.16 g, 115 mmol) to give the product (51.82 g, 94%) as colourless crystals, mp 228–229 °C.

IR: 1584, 1436, 1251, 1217, 1151, 1114, 1000, 842, 798, 751, 721, 690 cm^{-1}.

^1H NMR (300 MHz): δ = 7.87–7.55 (m, 15 H, Ph), 7.18 (d, *J* = 7 Hz, 1 H, 6-H), 6.98 (d, *J* = 7 Hz, 1 H, 4-H), 6.80 (t, *J* = 7 Hz, 1 H, 5-H), 5.19 (d, *J* = 15 Hz, 2 H, CH_2), 3.58 (s, 3 H, OMe), 2.09 (s, 3 H, ArMe).

^{13}C NMR (75 MHz): δ = 157.7 (d, *J* = 6 Hz, C-2), 135.2 (d, *J* = 2 Hz, C-4 of PPh), 134.3 (d, *J* = 10 Hz, C-2 of PPh), 132.4 (d, *J* = 4 Hz, CH), 131.6 (d, *J* = 2 Hz, C-3), 130.3 (d, *J* = 13 Hz, C-3 of PPh), 129.0 (d, *J* = 5 Hz, CH), 124.5 (d, *J* = 3 Hz, CH), 120.6 (d, *J* = 9 Hz, C-1), 118.0 (d, *J* = 85 Hz, C-1 of PPh), 60.6 (OMe), 26.0 (d, *J* = 49 Hz, CH_2), 16.3 (ArMe).

^{31}P NMR (121 MHz): δ = +23.1.

Anal. Calcd for $C_{27}H_{26}BrOP$: C, 67.93; H, 5.49. Found: C, 67.66; H, 5.53.

(5-Chloro-2-methoxybenzyl)triphenylphosphonium bromide 48

This was prepared as for **8** using 5-chloro-2-methoxybenzyl alcohol[13] (21.6 g, 125 mmol), phosphorus tribromide (4.70 mL, 13.56 g, 50 mmol) and triphenylphosphine (32.79 g, 125 mmol) to give the product (55.55 g, 89%) as a colourless crystalline powder, mp 257–258 °C.

IR: 1586, 1495, 1436, 1252, 1125, 1110, 1030, 889, 858, 840, 759, 746, 688, 644 cm^{-1}.

^1H NMR (300 MHz): δ = 7.85–7.58 (m, 15 H, Ph), 7.29 (d, *J* = 2 Hz, 1 H, 6-H), 7.17 (dd, *J* = 9, 2 Hz, 1 H, 4-H), 6.57 (d, *J* = 9 Hz, 1 H, 3-H), 5.73 (d, *J* = 14 Hz, 2 H, CH_2), 3.20 (s, 3 H, OMe).

^{13}C NMR (75 MHz): δ = 156.1 (d, *J* = 5 Hz, C-2), 135.2 (d, *J* = 2 Hz, C-4 of PPh), 134.4 (d, *J* = 10 Hz, C-2 of PPh), 132.2 (d, *J* = 5 Hz, C-6), 130.3, (d, *J* = 13 Hz, C-3 of PPh), 130.1 (C-4), 126.1 (d, *J* = 4 Hz, C-5), 118.3 (d, *J* = 87 Hz, C-1 of PPh), 117.8 (d, *J* = 8 Hz, C-1), 111.8, (d, *J* = 3 Hz, C-3), 55.3 (OMe), 25.4 (d, *J* = 49 Hz, CH_2).

^{31}P NMR (121 MHz): δ = +22.6.

Anal. Calcd for $C_{26}H_{23}BrClOP$: C, 62.73; H, 4.66. Found: C, 62.78; H, 4.31.

[(2-Methoxy-3-methylphenyl)(3-phenylpropenoyl)methylene]triphenylphosphorane 49

This was prepared as for **9** using (2-methoxy-3-methylbenzyl)triphenylphosphonium bromide **47** (8.12 g, 17 mmol), butyllithium in hexanes (6.9 mL, 2.5 M, 17 mmol) and 3-phenylpropenoyl chloride (1.42 g, 8.5 mmol) in dry THF (20 mL) to give the product (3.40 g, 76%) as yellow crystals, mp 211–214 °C.

IR: 1632, 1573, 1503, 1442, 1368, 1228, 1210, 1106, 1054, 1014, 982, 872, 760, 706, 691 cm^{-1}.

^1H NMR (300 MHz): δ = 7.82–7.50 (m, 6 H), 7.49 (d, *J* = 16 Hz, 1 H, vinyl-H), 7.49–7.27 (m, 11 H), 7.27–7.10 (m, 4 H), 6.98 (d, *J* = 16 Hz, 1 H, vinyl-H), 6.94–6.77 (m, 2 H), 3.65 (s, 3 H, OMe), 2.03 (s, 3 H, ArMe).

^{13}C NMR (75 MHz): δ = 179.1 (d, *J* = 5 Hz, CO), 159.3 (d, *J* = 4 Hz, C-2), 137.2 (C), 135.6 (d, *J* = 5 Hz, CH), 134.6 (CH), 133.9 (d, *J* = 10 Hz, C-2 of PPh), 131.5 (d, *J* = 2 Hz, C-4 of PPh), 131.0 (d, *J* = 2 Hz, C-3), 130.0 (CH), 128.5 (2CH), 128.4 (d, *J* = 12 Hz, C-3 of PPh), 128.1 (2CH), 127.7 (CH), 126.8 (d, *J* = 91 Hz, C-1 of PPh), 126.5 (d, *J* = 13 Hz, =C-), 123.6 (CH), 70.8 (d, *J* = 110 Hz, P=C), 59.8 (OMe), 16.1 (Me) [one C signal not apparent].

^{31}P NMR (121 MHz): δ = +16.4.

MS (EI): *m/z* (%) = 526 (3) [M^+], 495 (15), 301 (8), 283 (10), 171 (23), 149 (23), 134 (46), 111 (44), 83 (84), 71 (96), 55 (100).

Anal. Calcd for $C_{36}H_{31}O_2P$: C, 82.11; H, 5.93. Found: C, 82.41; H, 5.86.

[(5-Chloro-2-methoxyphenyl)(3-phenylpropenoyl)methylene]triphenylphosphorane 50

This was prepared as for **9** using 5-chloro-(2-methoxybenzyl)triphenylphosphonium bromide **48** (10.00 g, 20.1 mmol), butyllithium in hexanes (8.0 mL, 2.5 M, 20.1 mmol) and 3-

phenylpropenoyl chloride (1.67 g, 10.0 mmol) to give the product (5.05 g, 92%) as bright yellow crystals, mp 246–248.5 ˚C

IR: 1634, 1579, 1500, 1369, 1242, 1208, 1106, 1024, 999, 890, 861, 802, 694, 576 cm^{-1}.

^1H NMR (300 MHz): δ = 7.78–7.55 (m, 6 H), 7.55–7.13 (m, 16 H), 7.04 (dd, *J* = 7, 1 Hz, 1 H), 6.84 (d, *J* = 16 Hz, 1 H, vinyl-H), 6.34 (d, *J* = 7 Hz, 1 H, 3-H), 3.22 (*s*, 3 H, OMe).

^{13}C NMR (75 MHz): δ =179.6 (d, *J* = 5 Hz, CO), 157.7 (d, *J* = 3 Hz, C-2), 137.1 (C), 136.5 (d, *J* = 6 Hz, CH), 134.7 (CH), 133.7 (d, *J* = 10 Hz, C-2 of PPh), 131.6 (d, *J* = 2 Hz, C-4 of PPh), 128.6 (CCl), 128.5 (2CH), 128.4 (d, *J* = 13 Hz, C-3 of PPh), 128.1 (CH), 127.7 (2CH), 127.5 (d, *J* = 11 Hz, =C-), 126.8 (d, *J* = 91 Hz, C-1 of PPh), 126.1 (d, *J* = 12 Hz, C-1), 124.6 (CH), 111.1 (C-3), 69.5 (d, *J* = 114 Hz, P=C), 54.6 (OMe).

^{31}P NMR (121 MHz): δ = +15.9.

MS (EI): *m/z* (%) = 548 (7) [^{37}Cl-M^+], 546 (17) [^{35}Cl-M^+], 517 (39), 515 (100), 401 (8), 352 (5), 331 (5), 303 (9), 277 (13), 262 (58), 183 (35), 169 (24), 84 (51).

Anal. Calcd for $C_{35}H_{28}ClO_2P$: C, 76.85; H, 5.16. Found: C, 76.77; H, 5.17.

FVP of [(2-methoxy-3-methylphenyl)(3-phenylpropenoyl)methylene]triphenylphosphorane 49

FVP of the title compound (1.0 g) at 850 ˚C and 7.0–9.0 × 10^{-2} Torr gave an oily red-brown solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a red oil which solidified with time. The solid was recrystallised from ethanol to give the product, **8-methylbenzo[*b*]naphtho[1,2-*d*]furan 51** (0.40 g, 90%) as off-white crystals, mp 96.5–98.5 ˚C.

IR: 1623, 1526, 1261, 1226, 1197, 1076, 999, 850, 810, 745 cm^{-1}.

^1H NMR (300 MHz): δ = 8.66 (d, *J* = 8 Hz, 1 H), 8.27 (d, *J* = 8 Hz, 1 H), 8.04 (d, *J* = 8 Hz, 1 H), 7.94 (d, *J* = 8 Hz, 1 H), 7.80 (d, *J* = 8 Hz, 1 H), 7.73 (t, *J* = 8 Hz, 1 H), 7.55 (t, *J* = 8 Hz, 1 H), 7.39 (t, *J* = 8 Hz, 1 H), 7.32 (d, *J* = 8 Hz, 1 H), 2.71 (s, 3 H, Me).

^{13}C NMR (75 MHz): δ = 154.9 (C), 154.2 (C), 130.5 (2C), 129.2 (CH), 128.4 (CH), 127.1 (CH), 127.0 (CH), 124.4 (C), 124.3 (CH), 123.5 (CH), 123.2 (CH), 122.1 (C), 119.5 (CH), 117.8 (C), 112.8 (CH), 15.3 (CH_3).

MS (EI): *m/z* (%) = 232 (100) [M^+], 202 (15), 189 (3), 176 (2), 116 (7), 101 (7).

Anal. Calcd for $C_{17}H_{12}O$: C, 87.90; H, 5.21. Found: C, 87.64; H, 5.03.

FVP of [(5-chloro-2-methoxyphenyl)(3-phenylpropenoyl)methylene]triphenylphosphorane 50

FVP of the title compound (1.0 g) at 850 ˚C and 7.0–9.0 × 10^{-2} Torr gave an oily red solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a red crystalline material which was recrystallised from ethanol to give the product, **10-chlorobenzo[*b*]naphtho[1,2-*d*]furan 52** (0.28 g, 62%) as very pale pink crystals, mp 112–115 ˚C.

IR: 1627, 1585, 1530, 1347, 1315, 1256, 1222, 1103, 1069, 1008, 862, 851, 799, 739, 728, 683 cm^{-1}.

^1H NMR (300 MHz): δ = 8.44 (d, *J* = 7 Hz, 1 H), 8.27 (d, *J* = 2 Hz, 1 H, 1-H), 7.99 (d, *J* = 7 Hz, 1 H), 7.90 (d, *J* = 7 Hz, 1 H), 7.71 (t, *J* = 7 Hz, 1 H), 7.69 (d, *J* = 7 Hz, 1 H), 7.56 (d, *J* = 7 Hz, 1 H), 7.54 (t, *J* = 7 Hz, 1 H), 7.41 (dd, *J* = 7, 2 Hz, 1 H, 3-H).

^{13}C NMR (75 MHz): δ = 155.0 (C), 154.1 (C), 130.4 (C), 129.3 (CH), 129.2 (CH), 128.7 (C), 127.4 (CH), 126.1 (C), 125.7 (CH), 124.6 (CH), 123.1 (CH), 121.5 (CH), 120.0 (C), 116.4 (C), 112.5 (CH), 112.4 (CH).

MS (EI): *m/z* (%) = 254 (35) [^{37}Cl-M^+], 252 (100) [^{35}Cl-M^+], 218 (7), 189 (20), 163 (3), 126 (9), 95 (7), 84 (6).

Anal. Calcd for $C_{16}H_9ClO$: C, 76.05; H, 3.59. Found: C, 76.37; H, 3.23.

[(3-Methoxy-2-naphthoyl)benzylidene]triphenylphosphorane 53

This was prepared as for **9** using benzyltriphenylphosphonium chloride (10.0 g, 26 mmol), butyllithium in hexanes (10.4 mL, 2.5 M, 26 mmol) and 3-methoxy-2-naphthoyl chloride (2.87 g, 13 mmol) to give the product (5.28 g, 76%) as pale yellow prisms, mp 230–231 ˚C.

IR: 1627, 1598, 1511, 1359, 1249, 1212, 1171, 1138, 1107, 1014, 965, 888, 851, 826, 692 cm^{-1}.

^1H NMR (300 MHz): δ = 7.80–7.64 (m, 7 H), 7.64 (d, *J* = 7 Hz, 1 H), 7.58 (d, *J* = 7 Hz, 1 H), 7.54–7.35 (m, 9 H), 7.29 (t, *J* = 7 Hz, 1 H), 7.20 (t, *J* = 7 Hz, 1 H), 6.89 (s, 1 H, 4-H), 6.87–6.77 (m, 2 H), 6.75–6.65 (m, 3 H), 3.82 (s, 3 H, OMe).

^{13}C NMR (75 MHz): δ = 185.2 (d, *J* = 6 Hz, CO), 155.4 (C-3), 137.8 (d, *J* = 12 Hz, C), 135.4 (d, *J* = 12 Hz, C-2), 134.3 (d, *J* = 4 Hz, 2CH), 134.2 (C), 134.0 (d, *J* = 9 Hz, C-2 of PPh), 131.6 (d, *J* = 3 Hz, C-4 of PPh), 128.7 (C), 128.6 (d, *J* = 12 Hz, C-3 of PPh), 128.2 (CH), 127.9 (CH), 127.1 (d, *J* = 91 Hz, C-1 of PPh), 126.9 (2CH), 126.4 (CH), 125.7 (CH), 124.4 (CH), 123.2 (CH), 105.0 (C-4), 74.0 (d, *J* = 107 Hz, P=C), 55.3 (OMe).

^{31}P NMR (121 MHz): δ = +15.6.

MS (EI): *m/z* (%) = 536 (50) [M^+], 505 (13), 379 (8), 368 (10), 352 (6), 328 (12), 277 (15), 274 (21), 262 (100), 236 (15), 215 (11), 183 (29).

Anal. Calcd for $C_{37}H_{29}O_2P$: C, 82.82; H, 5.45. Found: C, 82.62; H, 5.53.

[(3-Methoxy-2-naphthoyl)-1-propylidene]triphenylphosphorane 54

This was prepared as for **9** using propyltriphenylphosphonium bromide (10.0 g, 26 mmol), butyllithium in hexanes (10.4 mL, 2.5 M, 26 mmol) and 3-methoxy-2-naphthoyl chloride (2.87 g, 13 mmol) to give the product (4.94 g, 78%) as pale yellow prisms, mp 245–248 ˚C.

IR: 1632, 1602, 1255, 1175, 1101, 1033, 945, 891, 851, 796, 746, 620 cm^{-1}.

^1H NMR (300 MHz): δ = 7.90–7.65 (m, 9 H), 7.65–7.42 (m, 9 H), 7.40 (t, *J* = 7 Hz, 1 H), 7.32 (t, *J* = 7 Hz, 1 H), 7.17 (s, 1 H, 4-H), 4.04 (s, 3 H, OMe), 1.89 (dq, *J* = 22, 7 Hz, 2 H, CH_2), 0.60 (t, *J* = 7 Hz, 3 H, CH_3).

^{13}C NMR (75 MHz): δ = 185.7 (d, *J* = 6 Hz, CO), 155.6 (C-3), 135.5 (d, *J* = 13 Hz, C-2), 134.1 (C), 133.9 (d, *J* = 10 Hz, C-2 of PPh), 131.7 (d, *J* = 2 Hz, C-4 of PPh), 129.0 (C), 128.7 (d, *J* = 12 Hz, C-3 of PPh), 127.8 (CH), 127.4 (d, *J* = 90 Hz, C-1 of PPh), 127.0 (CH), 126.6 (CH), 125.8 (CH), 123.6 (CH), 105.5 (C-4), 68.7 (d, *J* = 98 Hz, P=C), 55.7 (OMe), 21.3 (d, *J* = 13 Hz, CH_2), 18.5 (Me).

^{31}P NMR (121 MHz): δ = +17.4.

MS (EI): *m/z* (%) = 488 (15) [M^+], 473 (36), 457 (5), 387 (57), 368 (27), 328 (91), 277 (9), 262 (90), 236 (30), 183 (33), 91 (100).

Anal. Calcd for $C_{33}H_{29}O_2P$: C, 81.13; H, 5.98. Found: C, 81.14; H, 6.18.

FVP of [(3-methoxy-2-naphthoyl)benzylidene]triphenylphosphorane 53

FVP of the title compound (1.10 g) at 800 ˚C and 3.0–5.0 × 10^{-2} Torr gave a brown oily solid at the furnace exit. This was purified by column chromatography using diethyl ether–hexane (1:9) as eluant to give a brown oil which was kugelrohr distilled at 217 ˚C/0.05 Torr to give a clear yellow oil which solidified on cooling. This was recrystallised from ethanol to give the product, **2-phenylnaphtho[2,3-*b*]furan 55** (0.05 g, 11%) as pale yellow plates, mp 220–223 ˚C (lit.,[14] 225–233 ˚C).

IR: 1588, 1565, 1265, 1152, 1098, 1020, 953, 904, 868, 805, 762, 744, 720, 690 cm^{-1}.

^1H NMR (300 MHz): δ = 8.06 (s, 1 H, 9-H), 8.02–7.92 (m, 5 H), 7.53–7.37 (m, 5 H), 7.17 (s, 1 H, 3-H).

^{13}C NMR (75 MHz): δ = 158.4 (C), 154.2 (C), 131.8 (C), 130.9 (C), 130.5 (C), 130.4 (C), 129.3 (CH), 129.1 (2CH), 128.2 (CH), 128.1 (CH), 125.6 (2CH), 125.0 (CH), 124.2 (CH), 118.7 (CH), 106.7 (CH), 100.9 (CH) [Good agreement with lit.[14]].

MS (EI): *m/z* (%) = 244 (100) [M^+], 216 (54), 190 (7), 164 (3), 140 (4), 122 (48), 108 (53), 95 (32).

Anal. Calcd for $C_{18}H_{12}O$: C, 88.50; H, 4.95. Found: C, 88.73; H, 5.13.

FVP of [(3-methoxy-2-naphthoyl)-1-propylidene]triphenylphosphorane 54

FVP of the title compound (1.0 g) at 850 °C and 6.0–8.0 × 10^{-2} Torr gave an oily brown solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a yellow-brown solid which was distilled at 110 °C and 0.02 Torr to give a pale yellow oil which crystallised with time to give a waxy pale yellow solid. This was found by ^{1}H NMR and GCMS to be mainly the expected[3] three products:

2-vinylnaphtho[2,3-*b*]furan 56 (41%)

^{1}H NMR (300 MHz): δ = 8.10–7.70 (m, 4 H), 7.55–7.35 (m, 2 H), 6.73 (dd, *J* = 17, 12 Hz, 1 H, vinyl-H), 6.72 (s, 1 H, 3-H), 6.09 (d, *J* = 17 Hz, 1 H, vinyl-H), 5.51 (d, *J* = 12 Hz, 1 H, vinyl-H).

MS (EI): *m/z* (%) = 194 (100) [M$^+$], 181 (3), 165 (70), 139 (14), 115 (7), 97 (15), 83 (28), 74 (12), 69 (17), 62 (18).

2-ethylnaphtho[2,3-*b*]furan 57 (5%).

^{1}H NMR (300 MHz): δ = 8.10–7.70 (m, 4 H), 7.55–7.35 (m, 2 H), 6.49 (s, 1 H, 3-H), 2.88 (q, *J* = 7 Hz, 2 H, CH_2), 1.39 (t, *J* = 7 Hz, 3 H, CH_3).

MS (EI): *m/z* (%) = 196 (58) [M$^+$], 182 (72), 178 (100), 165 (11), 152 (28), 139 (4), 127 (5), 89 (8), 77 (13), 63 (7);

2-methylnaphtho[2,3-*b*]furan 58 (3%).

^{1}H NMR (300 MHz): δ = 8.10–7.70 (m, 4 H), 7.55–7.35 (m, 2 H), 6.49 (s, 1 H, 3-H), 2.52 (s, 3 H, ArMe) [Good agreement with lit.[14]].

MS (EI): *m/z* (%) = 182 (100) [M$^+$], 165 (25), 152 (38), 139 (9), 126 (9), 115 (9), 90 (26), 76 (42), 63 (19).

(3-Methoxy-2-naphthylmethyl)triphenylphosphonium bromide 59

This was prepared as for **8** using 3-methoxy-2-naphthylmethanol[15] (16.25 g, 86 mmol), phosphorus tribromide (4.10 mL, 13.56 g, 43 mmol) and triphenylphosphine (23.61 g, 90 mmol) to give the product (37.89 g, 85%) as a colourless crystalline powder, mp 259–260 °C.

IR: 1632, 1505, 1465, 1439, 1378, 1341, 1261, 1118, 1022, 997, 884, 860, 754, 724, 692 cm^{-1}.

^{1}H NMR (300 MHz): δ = 7.88 (d, *J* = 3 Hz, 1 H), 7.82–7.48 (m, 17 H), 7.39 (t, *J* = 7 Hz, 1 H), 7.25 (t, *J* = 7 Hz, 1 H), 6.82 (s, 1 H, 4-H), 5.27 (d, *J* = 14 Hz, 2 H, CH_2), 3.22 (s, 3 H, OMe).

^{13}C NMR (75 MHz): δ = 154.9 (C-3), 135.2 (d, *J* = 2 Hz, C-4 of PPh), 134.6 (d, *J* = 2 Hz, C), 134.3, (d, *J* = 10 Hz, C-2 of PPh), 132.8 (d, *J* = 8 Hz, CH), 130.3 (d, *J* = 12 Hz, C-3 of PPh), 128.5 (d, *J* = 2 Hz, C), 128.1 (CH), 127.3 (CH), 126.7 (CH), 124.4 (CH), 118.3 (d, *J* = 85 Hz, C-1 of PPh), 117.3 (d, *J* = 10 Hz, C-2), 105.6 (C-4), 55.0 (OMe), 25.7 (d, *J* = 49 Hz, CH_2).

^{31}P NMR (121 MHz): δ = +22.1.

Anal. Calcd for $C_{30}H_{26}BrOP$: C, 70.18; H, 5.10. Found: C, 70.23; H, 4.94.

[(3-Methoxy-2-naphthyl)(3-phenylpropenoyl)methylene]triphenylphosphorane 60

This was prepared as for **9** using (3-methoxy-2-naphthylmethyl)triphenylphosphonium bromide **59** (10.0 g, 19.5 mmol), butyllithium in hexanes (7.80 mL, 2.5 M, 19.5 mmol) and 3-phenylpropenoyl chloride (1.62 g, 9.8 mmol) to give the product (4.72 g, 86%) as bright yellow needles, mp 236–239 °C

IR: 1626, 1574, 1503, 1366, 1251, 1217, 1173, 1104, 1033, 947, 905, 860, 823, 758, 745, 690 cm^{-1}.

^{1}H NMR (300 MHz): δ = 7.80 (d, *J* = 2 Hz, 1 H), 7.72–7.57 (m, 8 H), 7.50–7.24 (m, 13 H), 7.45 (d, *J* = 16 Hz, 1 H, vinyl-H), 7.20–7.08 (m, 3 H), 6.89 (d, *J* = 16 Hz, 1 H, vinyl-H), 6.69 (s, 1 H, 4'-H), 3.35 (s, 3 H, OMe)

^{13}C NMR (75 MHz): δ = 179.9 (d, *J* 4, C=O), 157.6, (C), 137.2 (C), 136.1 (d, *J* 8, CH), 134.5 (CH), 134.1 (C), 133.9 (d, *J* 10, C-3 of P-Ph), 131.5 (d, *J* 3, C-4 of P-Ph), 129.1 (C), 128.6 (d, *J* 12, CH), 128.5 (2CH), 128.4 (d, *J* 12, C-3 of P-Ph), 128.0 (CH), 127.7 (2CH), 127.5 (CH), 127.2 (d, *J* 91, C-1 of P-Ph), 126.4 (CH), 126.2 (d, *J* 11, CO-CH=), 125.8 (CH), 123.5 (CH), 104.8 (CH), 70.8 (d, *J* 113, C=P), 54.4 (OMe).

^{31}P NMR (121 MHz): δ = +15.3

MS (EI): *m/z* (%) = 562 (17) [M$^+$], 531 (21), 368 (5), 319 (11), 302 (6), 277 (5), 262 (37), 183 (18), 142 (43), 131 (18), 114 (100), 72 (88).

Anal. Calcd for $C_{39}H_{31}O_2P$: C, 83.25; H, 5.55. Found: C, 82.74; H, 5.49.

HRMS (EI): *m/z* calcd for $C_{39}H_{31}O_2P$ [M$^+$]: 562.2062; found: 562.2075.

(2-Methoxy-1-naphthylmethyl)triphenylphosphonium bromide 62

This was prepared as for **8** using 2-methoxy-1-naphthylmethanol[16] (8.00 g, 42 mmol), phosphorus tribromide (2.00 mL, 5.75 g, 21 mmol) and triphenylphosphine (11.0 g, 42 mmol) to give the product (20.30 g, 93%) as a colourless crystalline powder, mp 262–264 °C.

IR: 1624, 1595, 1514, 1440, 1397, 1256, 1159, 1109, 1082, 998, 913, 860, 820, 746, 692 cm^{-1}.

^{1}H NMR (300 MHz): δ = 7.85–7.40 (m, 18 H), 7.30–7.15 (m, 2 H), 6.93 (d, *J* = 8 Hz, 1 H), 5.24 (d, *J* = 13 Hz, 2 H, CH_2), 3.37 (s, 3 H, OMe).

^{13}C NMR (75 MHz): δ = 155.3 (d, *J* = 7 Hz, C-2), 135.2 (d, *J* = 3 Hz, C-4 of PPh), 134.3 (d, *J* = 10 Hz, C-2 of PPh), 132.8 (d, *J* = 4 Hz, C), 131.4 (d, *J* = 4 Hz, CH), 130.2 (d, *J* = 12 Hz, C-3 of PPh), 129.0 (d, *J* = 3 Hz, C), 128.9 (CH), 127.9 (CH), 124.0 (CH), 123.1 (CH), 118.3 (d, *J* = 85 Hz, C-1 of PPh), 112.0 (d, *J* = 3 Hz, C-3), 108.7 (d, *J* = 11 Hz, C-1), 55.6 (d, *J* = 4 Hz, OMe), 23.9 (d, *J* = 49 Hz, CH_2).

^{31}P NMR (121 MHz): δ = +21.1.

Anal. Calcd for $C_{30}H_{26}BrOP$: C, 70.18; H, 5.10. Found: C, 70.60; H, 4.88.

[(2-Methoxy-1-naphthyl)(3-phenylpropenoyl)methylene]triphenylphosphorane 63

This was prepared as for **9** using (2-methoxy-1-naphthylmethyl)triphenylphosphonium bromide **62** (8.0 g, 16.0 mmol), butyllithium in hexanes (6.20 mL, 2.5 M, 16.0 mmol) and 3-phenylpropenoyl chloride (1.33 g, 8.0 mmol) to give the product (3.14 g, 72%) as blood-red prisms, mp 260–262 °C.

IR: 1635, 1590, 1500, 1358, 1270, 1200, 1113, 1063, 974, 947, 892, 803, 748, 894 cm^{-1}.

^{1}H NMR (300 MHz): δ = (25 °C in $CDCl_3$) 8.40 (d, *J* = 8 Hz, 1 H, 8'-H), 8.38–7.65 (br m, 6 H, Ph), 7.65–6.20 (br m, 9 H, Ph), 7.70 (d, *J* = 8 Hz, 1 H), 7.62 (d, *J* = 8 Hz, 1 H), 7.46 (d, *J* = 16 Hz, 1 H, vinyl-H), 7.36 (t, *J* = 8 Hz, 1 H), 7.25 (t, *J* = 8 Hz, 1 H), 7.17–7.03 (m, 5 H, Ph), 6.78 (d, *J* = 8 Hz, 1 H, 3'-H), 6.50 (d, *J* = 16 Hz, 1 H, vinyl-H), 3.32 (s, 3 H, OMe).

^{1}H NMR (300 MHz): δ = (81 °C in $CDBr_3$) 8.21 (d, *J* = 8 Hz, 1 H, 8'-H), 7.70–7.40 (m, 6 H, Ph), 7.68 (d, *J* = 8 Hz, 1 H), 7.60 (d, *J* = 8 Hz, 1 H), 7.49–7.10 (m, 12 H), 7.10–7.00 (m, 5 H, Ph), 6.80 (d, *J* = 8 Hz, 1 H, 3'-H), 6.31 (d, *J* = 16 Hz, 1 H, vinyl-H), 3.42 (s, 3 H, OMe).

^{13}C NMR (75 MHz): δ = (25 °C in $CDCl_3$) 180.6 (CO), 156.3 (d, *J* = 4 Hz, C-2'), 138.3 (d, *J* = 5 Hz, C), 137.2 (C-1 of Ph), 135.9–132.7 (br s, C-2 of P-Ph), 134.3 (CH), 131.9–131.3 (br s, C-4 of P-Ph), 129.9–127.0 (br s, C-3 of P-Ph), 129.3 (CH), 128.9 (d, *J* = 2 Hz, CH), 128.4 (C), 128.3 (2CH), 128.0 (CH), 127.8 (CH), 127.6 (2CH), 127.5–126.2 (br s, C-1 of P-Ph), 126.8 (d, *J* = 12 Hz, -CH=), 126.7 (CH), 126.4 (CH), 123.3 (CH), 120.3 (d, *J* = 10 Hz, C-1'), 112.3 (d, *J* = 3 Hz, C-3'), 65.8 (d, *J* = 110 Hz, C=P), 55.0 (OMe).

^{13}C NMR (75 MHz): δ = (81 °C in $CDBr_3$) 131.1 (d, *J* = 10 Hz, C-2 of PPh), 128.7 (C-4 of PPh), 125.3 (d, *J* = 11 Hz, C-3 of PPh), 125.2 (d, *J* = 88 Hz, C-1 of PPh) [other signals similar to RT spectrum].

^{31}P NMR (121 MHz): δ = +17.2.

MS (EI): *m/z* (%) = 562 (6) [M$^+$], 531 (21), 396 (9), 368 (6), 277 (28), 262 (9), 220 (28), 107 (40), 91 (100).

Anal. Calcd for $C_{39}H_{31}O_2P$: C, 83.25; H, 5.55. Found: C, 82.91; H, 5.46.

FVP of [(3-methoxy-2-naphthyl)(3-phenylpropenoyl)methylene]triphenylphosphorane 60

FVP of the title compound (1.0 g) at 800 °C and 5.0–9.0 × 10^{-2} Torr gave a red-brown oily solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:19) as eluant gave an orange solid which was recrystallised from ethanol to give **dinaphtho[2,1-*b*;2',3'-*d*]furan 61** (0.26 g, 55%) as pale orange needles, mp 150–152 °C (lit.,[17] 156–157 °C).

^{1}H NMR (300 MHz): δ = 8.84 (s, 1 H, 1-H), 8.78 (d, *J* = 7 Hz, 1 H, 13-H), 8.18–7.99 (m, 4 H), 7.84–7.77 (m, 2 H), 7.62–7.42 (m, 4 H).

FVP of [(2-methoxy-1-naphthyl)(3-phenylpropenoyl)methylene]triphenylphosphorane 63

FVP of the title compound (1.0 g) at 800 ˚C and 5.0–7.0 × 10^{-2} Torr gave a red-brown oily solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave an orange solid which was recrystallised from ethanol to give **dinaphtho[2,1-*b*;1',2'-*d*]furan 64** (0.25 g, 52%), as pale orange needles, mp 140–144 ˚C (lit.,[18] 152–154 ˚C).

^{1}H NMR (300 MHz): δ = 9.14 (d, *J* = 7 Hz, 2 H, 1-H and 13-H), 8.05 (d, *J* = 7 Hz, 2 H, 4-H and 10-H), 7.94 (d, *J* = 7 Hz, 2 H, 5-H and 9-H), 7.82 (d, *J* = 7 Hz, 2 H, 6-H and 8-H), 7.74 (t, *J* = 7 Hz, 2 H, 3-H and 11-H), 7.57 (t, *J* = 7 Hz, 2 H, 2-H and 12-H).

^{13}C NMR (75 MHz): δ = 154.4 (C), 131.3 (C), 129.5 (CH), 128.7 (C), 128.4 (CH), 126.2 (CH), 125.7 (CH), 124.5 (CH), 119.5 (C), 112.8 (CH).

A small amount of the isomeric dinaphtho[1,2-*b*;1',2'-*d*]furan was observed by ^{1}H NMR.

(2-Methylthio-3-pyridylmethyl)triphenylphosphonium bromide 65

This was prepared as for **8**, with the important exception that the first bromination stage was left to react for one week, using 2-methylthiopyridine-3-methanol[19] (11.2 g, 61 mmol), phosphorus tribromide (4.7 mL, 13.56 g, 50 mmol) and triphenylphosphine (15.6 g, 60 mmol) to give the product (21.44 g, 74%) as a colourless powder, mp 242–243 ˚C.

IR: 1575, 1430, 1402, 1109, 993, 860, 816, 686 cm^{-1}.

^{1}H NMR (300 MHz): δ = 8.32 (m, 1 H, 6-H), 7.95–7.40 (m, 16 H), 6.88 (t, *J* = 7 Hz, 1 H, 5-H), 5.42 (d, *J* = 13 Hz, 2 H, CH_2), 2.14 (s, 3 H, SMe).

^{13}C NMR (75 MHz): δ = 160.6 (d, *J* = 5 Hz, C, C-2), 149.4 (d, *J* = 4 Hz, CH, C-6), 139.3 (d, *J* = 5 Hz, CH, C-4), 135.5 (d, *J* = 2 Hz, C-4 of PPh), 134.5 (d, *J* = 10 Hz, C-2 of PPh), 130.5 (d, *J* = 12 Hz, C-3 of PPh), 122.2 (d, *J* = 9 Hz, C, C-3), 119.9 (CH, C-5), 117.6 (d, *J* = 86 Hz, C-1 of PPh), 14.8 (d, *J* = 48 Hz, CH_2), 13.8 (CH_3).

^{31}P NMR (121 MHz): δ = +22.8.

Anal. Calcd for $C_{25}H_{23}BrNPS$: C, 62.50; H, 4.83; N, 2.92. Found: C, 62.78; H, 4.68; N, 2.89.

[(2-Methoxyphenyl)(3-(1-naphthyl)propenoyl)methylene]triphenylphosphorane 66

This was prepared as for **9** using (2-methoxybenzyl)triphenylphosphonium bromide **7** (7.0 g, 15 mmol), butyllithium in hexanes (6.0 mL, 2.5 M, 15 mmol) and 3-(1-naphthyl)propenoyl chloride (1.73 g, 8 mmol) to give the product (3.60 g, 80%) as bright orange prisms, mp 214–216 ˚C.

IR: 1627, 1510, 1497, 1370, 1251, 1214, 1115, 1073, 1026, 959, 783, 745, 716, 692 cm^{-1}.

^{1}H NMR (300 MHz): δ = 8.30 (d, *J* = 7 Hz, 1 H), 8.23 (d, *J* = 16 Hz, 1 H, vinyl-H), 7.78–7.56 (m, 8 H), 7.52 (d, *J* = 7 Hz, 1 H), 7.44–7.26 (m, 13 H), 7.04 (t, *J* = 7 Hz, 1 H), 6.97 (d, *J* = 16 Hz, 1 H, vinyl-H), 6.81 (t, *J* = 7 Hz, 1 H), 6.39 (d, *J* = 7 Hz, 1 H, 3-H), 3.20 (s, 3 H, OMe).

^{13}C NMR (75 MHz): δ = 179.6 (d, *J* = 6 Hz, CO), 158.9 (C-2), 137.4 (d, *J* = 5 Hz), 134.9 (CH), 133.8 (d, *J* = 10 Hz, C-2 of PPh), 133.7 (C), 131.9 (C), 131.4 (d, *J* = 2 Hz, C-4 of PPh), 130.7 (C), 129.8 (d, *J* = 12 Hz, CO-CH=), 128.4 (CH), 128.3 (d, *J* = 12 Hz, C-3 of PPh), 128.2 (CH), 128.1 (CH), 127.2 (d, *J* = 91 Hz, C-1 of PPh), 126.6 (d, *J* = 10 Hz, C-1), 125.9 (CH), 125.7 (CH), 125.6 (CH), 124.6 (CH), 124.1 (CH), 120.3 (CH), 110.1 (CH), 70.4 (d, *J* = 111 Hz, P=C), 54.3 (OMe).

^{31}P NMR (121 MHz): δ = +15.7.

MS (EI): *m/z* (%) = 562 (7) [M+], 531 (18), 262 (15), 248 (14), 218 (35), 156 (38), 128 (87), 86 (100).

Anal. Calcd for $C_{39}H_{31}O_2P$: C, 83.25; H, 5.55. Found: C, 83.56; H, 5.46.

[(2-Methylthiophenyl)(3-(1-naphthyl)propenoyl)methylene]triphenylphosphorane 67

This was prepared as for **9** using (2-methylthiobenzyl)triphenylphosphonium bromide **8** (7.0 g, 15 mmol), butyllithium in hexanes (6.0 mL, 2.5 M, 15 mmol) and 3-(1-naphthyl)propenoyl chloride (1.73 g, 8 mmol) to give the product (3.85 g, 83%) as bright orange prisms, mp 244–245 ˚C.

IR: 1625, 1510, 1437, 1368, 1214, 1103, 1076, 970, 802, 782, 750, 716, 692 cm^{-1}.

^{1}H NMR (300 MHz): δ = 8.30 (d, *J* = 7 Hz, 1 H), 8.23 (d, *J* = 16 Hz, 1 H, vinyl-H), 7.78–7.56 (m, 8 H), 7.49 (d, *J* = 7 Hz, 1 H), 7.47–7.23 (m, 12 H), 7.08–7.00 (m, 2 H), 6.87 (d, *J* = 7 Hz, 1 H), 6.78 (t, *J* = 7 Hz, 1 H), 6.75 (d, *J* = 16 Hz, 1 H, vinyl-H), 2.18 (s, 3 H, SMe).

^{13}C NMR (75 MHz): δ = 180.5 (d, *J* = 5 Hz, CO), 145.3 (d, *J* = 4 Hz, C-2), 134.8 (CH), 136.3 (d, *J* = 3 Hz), 135.1 (d, *J* = 11 Hz, C-1), 134.0 (d, *J* = 10 Hz, C-2 of PPh), 133.8 (C), 131.9 (C), 131.6 (d, *J* = 2 Hz, C-4 of PPh), 131.3 (C), 129.6 (d, *J* = 12 Hz, CO-CH=), 128.4 (d, *J* = 12 Hz, C-3 of PPh), 128.4 (CH), 128.3 (CH), 127.5 (CH), 126.9 (d, *J* = 90 Hz, C-1 of PPh), 125.9 (CH), 125.7 (CH), 125.5 (CH), 124.7 (CH), 124.3 (CH), 123.5 (CH), 122.9 (CH), 71.7 (d, *J* = 109 Hz, P=C), 15.2 (SMe).

^{31}P NMR (121 MHz): δ = +16.0.

MS (EI): *m/z* (%) = 578 (25) [M+], 563 (16), 531 (100), 303 (5), 277 (13), 262 (45), 218 (10), 183 (26), 152 (13), 128 (24).

Anal. Calcd for $C_{39}H_{31}OPS$: C, 80.94; H, 5.40. Found: C, 81.30; H, 5.31.

[(2-Methylthio-3-pyridyl)(3-(1-naphthyl)propenoyl)methylene]triphenylphosphorane 68

This was prepared as for **9** using (2-methylthio-3-pyridylmethyl)triphenylphosphonium bromide **65** (1.5 g, 3.1 mmol), butyllithium in hexanes (1.2 mL, 2.5 M, 3.1 mmol) and 3-(1-naphthyl)propenoyl chloride (0.34 g, 1.6 mmol) to give the product (0.86 g, 96%) as bright yellow needles, mp 248–249 ˚C.

IR: 1625, 1510, 1440, 1380, 1282, 1253, 1186, 1105, 968, 935, 800, 778, 758, 716, 692 cm^{-1}.

^{1}H NMR (300 MHz): δ = 8.30 (m, 1 H), 8.26 (d, *J* = 16 Hz, 1 H, vinyl-H), 8.18 (d, *J* = 5 Hz, 1 H, 6-H), 7.81–7.63 (m, 8 H), 7.55–7.30 (m, 13 H), 7.15 (d, *J* = 6 Hz, 1 H, 4-H), 6.68 (d, *J* = 16 Hz, 1 H, vinyl-H), 6.66 (dd, *J* = 6, 5 Hz, 1 H, 5-H), 2.38 (s, 3 H, SMe).

^{13}C NMR (75 MHz): δ = 180.7 (d, *J* = 5 Hz, CO), 165.7 (d, *J* = 5 Hz, C-2), 147.3 (d, *J* = 3 Hz, CH), 142.3 (d, *J* = 3 Hz, CH), 134.6 (CH), 133.9 (d, *J* = 10 Hz, C-2 of PPh), 133.8 (C), 132.1 (C), 132.0 (d, *J* = 3 Hz, C-4 of PPh), 131.9 (C), 131.6 (d, *J* = 12 Hz, C-3), 129.2 (d, *J* = 12 Hz, CO-CH=), 128.6 (CH), 128.6 (d, *J* = 12 Hz, C-3 of PPh), 128.4 (CH), 126.6 (d, *J* = 91 Hz, C-1 of PPh), 126.1 (CH), 125.8 (CH), 125.6 (CH), 124.6 (CH), 124.5 (CH), 118.1 (d, *J* = 3 Hz, CH), 69.7 (d, *J* = 113 Hz, P=C), 13.8 (SMe).

^{31}P NMR (121 MHz): δ = +16.8.

MS (EI): *m/z* (%) = 579 (8) [M+], 564 (6), 532 (50), 368 (10), 321 (11), 262 (12), 218 (9), 183 (10), 145 (46), 121 (73), 105 (94), 91 (100).

Anal. Calcd for $C_{38}H_{30}NOPS$: C, 78.73; H, 5.22; N, 2.42. Found: C, 78.61; H, 5.42; N, 2.44.

FVP of [(2-methoxyphenyl)(3-(1-naphthyl)propenoyl)methylene]triphenylphosphorane 66

FVP of the title compound (1.0 g) at 800 ˚C and 5.0–7.0 × 10^{-2} Torr gave a blood red oily solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a waxy red solid which was kugelrohr distilled at 140 ˚C and 0.1 Torr to give an orange-red solid. This was recrystallised from ethanol to give **benzo[*b*]phenanthro[1,2-*d*]furan 69** (0.20 g, 45%) as pale pink-brown needles, mp 193–197 ˚C (lit.,[17] 205 ˚C).

^{1}H NMR (300 MHz): δ = 8.75 (d, *J* = 8 Hz, 1 H), 8.68 (d, *J* = 8 Hz, 1 H), 8.53 (d, *J* = 8 Hz, 1 H), 8.39 (d, *J* = 8 Hz, 1 H), 7.97–7.90 (m, 2 H), 7.83 (d, *J* = 8 Hz, 1 H), 7.72–7.55 (m, 3 H), 7.53–7.42 (m, 2 H).

MS (EI): *m/z* (%) = 268 (100) [M+], 239, (32), 213 (3), 134 (30), 120 (30), 107 (20).

^{1}H NMR and GCMS analysis both indicated a small amount of an isomeric material, presumably phenanthro[1,2-*b*]benzofuran.

FVP of [(2-methylthiophenyl)(3-(1-naphthyl)propenoyl)methylene]triphenylphosphorane 67

FVP of the title compound (1.0 g) at 800 ˚C and 5.0–9.0 × 10^{-2} Torr gave a red-brown oily solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a waxy red solid which was kugelrohr distilled at 245 ˚C and 0.2 Torr to give an orange-red solid. This was recrystallised from ethanol to give **benzo[*b*]phenanthro[1,2-*d*]thiophene 70** (0.25 g, 51%) as pale brown needles, mp 167–169 ˚C (lit.,[20] 168.5–169 ˚C).

^{1}H NMR (300 MHz): δ = 8.93 (d, *J* = 9 Hz, 1 H), 8.82 (d, *J* = 9 Hz, 1 H), 8.71 (d, *J* = 8 Hz, 1 H), 8.70 (d, *J* = 8 Hz, 1 H), 8.01 (d, *J* = 9 Hz, 1 H), 7.98–7.90 (m, 3 H), 7.69–7.44 (m, 4 H) [Good agreement with lit.,[21]].

^{13}C NMR (75 MHz): δ = 140.3 (C), 139.1 (C), 136.8 (C), 131.2 (C), 131.1 (C), 130.5 (C), 129.4 (C), 128.7 (CH), 128.3 (C), 128.2 (CH), 127.1 (CH), 126.4 (CH), 125.7 (CH), 125.3 (CH), 125.0 (CH), 123.4 (CH), 123.2 (CH), 122.2 (CH), 122.1 (CH), 121.4 (CH).

FVP of [(2-methylthio-3-pyridyl)(3-(1-naphthyl)propenoyl)methylene]triphenylphosphorane 68

FVP of the title compound (0.4 g) at 750 ˚C and 2.0–5.0 × 10^{-2} Torr gave a brown oily solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:4) as eluant gave a yellow-brown oil. This was found to be a mixture of two products:

***E*-1-(2-methylthio-3-pyridyl)-4-(1-naphthyl)but-3-en-1-yne 71** (54%)

^{1}H NMR (300 MHz): δ = 8.36 (dd, *J* = 5, 2 Hz, 1 H, 6'-H), 8.14 (d, *J* = 7 Hz, 1 H), 7.90 (d, *J* = 16 Hz, 1 H, vinyl-H), 7.65 (d, *J* = 7 Hz, 1 H), 7.59 (dd, *J* = 6, 2 Hz, 1 H, 4'-H), 6.92 (dd, *J* = 6, 5 Hz, 1 H, 5'-H), 6.50 (d, *J* = 16 Hz, 1 H, vinyl-H), 2.60 (s, 3 H, SMe); the remaining 5 proton signals unidentified due to overlap with *Z*-isomer in region 7.86–7.38.

^{13}C NMR (75 MHz): δ = 161.9 (C), 148.1 (CH), 139.4 (CH), 138.5 (CH), 133.8 (C), 133.6 (C), 131.0 (C), 129.4 (CH), 128.8 (CH), 126.6 (CH), 126.2 (CH), 125.7 (CH), 123.7 (CH), 123.6 (CH), 118.4 (CH), 118.0 (C), 110.2 (CH), 98.1 (C≡C), 86.8 (C≡C), 13.2 (SMe).

MS (EI): *m/z* (%) = 301 (12) [M$^+$], 286 (31), 268 (32), 254 (71), 240 (11), 226 (30), 200 (20), 189 (13), 178 (85), 165 (100), 150 32), 136 (72), 127 (32), 113 (70), 100 (39).

HRMS (EI): *m/z* calcd for $C_{20}H_{15}NS$ [M$^+$] 301.0925; found: 301.0931.

***Z*-1-(2-methylthio-3-pyridyl)-4-(1-naphthyl)but-3-en-1-yne 71** (36%)

^{1}H NMR (300 MHz): δ = 8.42 (d, *J* = 7 Hz, 1 H), 8.31 (dd, *J* = 5, 2 Hz, 1 H, 6'-H), 8.04 (d, *J* = 7 Hz, 1 H), 7.42 (d, *J* = 11 Hz, 1 H, vinyl-H), 6.84 (dd, *J* = 6, 5 Hz, 1 H), 6.20 (d, *J* = 11 Hz, 1 H, vinyl-H), 2.55 (s, 3 H, SMe); the remaining 6 proton signals unidentified due to overlap with *E*-isomer in region 7.86–7.38.

^{13}C NMR (75 MHz): δ = 161.9 (C), 148.1 (CH), 138.9 (CH), 137.2 (CH), 133.7 (C), 132.7 (C), 131.5 (C), 129.1 (CH), 128.8 (CH), 127.1 (CH), 126.4 (CH), 125.9 (CH), 125.6 (CH), 123.7 (CH), 118.3 (CH), 117.9 (C), 109.2 (CH), 96.6 (C≡C), 90.1 (C≡C), 13.2 (SMe).

MS (EI): *m/z* (%) = 301 (40) [M$^+$], 286 (50), 268 (50), 254 (100), 226 (48), 178 (55), 165 (56), 136 (37), 113 (25).

FVP of *E*- and *Z*-1-(2-methylthio-3-pyridyl)-4-(1-naphthyl)but-3-en-1-yne 71

FVP of the title compounds (0.19 g) at 800 ˚C and 2.0–9.0 × 10^{-2} Torr gave a red-brown solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:4) as eluant gave three isolable products:

1. starting material, in an unchanged *E*:*Z* ratio;

2. a brown solid which was recrystallised from ethanol to give **phenanthro[1',2':4,5]thieno[2,3-*b*]pyridine 72** (40 mg, 22%) as brown prisms, mp 168–171 ˚C.

IR: 1562, 1544, 1358, 1272, 1226, 1207, 1134, 1109, 1082, 960, 907, 860, 837, 812, 759 cm^{-1}.

^{1}H NMR (300 MHz): δ = 8.94 (dd, *J* = 8, 2 Hz, 1 H), 8.76–8.64 (m, 3 H), 8.64 (dd, *J* = 4, 2 Hz, 1 H), 8.00 (d, *J* = 8 Hz, 1 H), 7.95–7.91 (m, 2 H), 7.70 (t, *J* = 7 Hz, 1 H), 7.62 (t, *J* = 7 Hz, 1 H), 7.44 (dd, *J* = 8, 4 Hz, 1 H).

^{13}C NMR (75 MHz): δ = 162.4 (C), 147.2 (CH), 137.8 (C), 132.2 (CH), 131.2 (C), 131.0 (C), 130.6 (C), 129.5 (C), 128.73 (CH), 128.67 (CH), 128.4 (C), 127.9 (C), 127.3 (CH), 126.7 (CH), 123.1 (CH), 122.8 (CH), 121.5 (CH), 121.4 (CH), 119.6 (CH).

MS (EI): *m/z* (%) = 285 (100) [M$^+$], 143 (50), 107 (30), 69 (25), 63 (20).

HRMS (EI): m/z calcd for $C_{19}H_{11}NS$ [M$^+$]: 285.0612; found: 285.0605.

3. **phenanthro[2',1':4,5]thieno[2,3-*b*]pyridine 73** (10 mg, 5%) in impure form as an oil.

^{1}H NMR (300 MHz): δ = 8.98 (dd, *J* = 7, 2 Hz, 1 H), 8.93 (d, *J* = 7 Hz, 1 H), 8.64 (dd, *J* = 5, 2 Hz, 1 H), 8.00 (d, *J* = 7 Hz, 1 H), 7.99 (d, *J* = 7 Hz, 1 H), 7.89 (d, *J* = 7 Hz, 1 H), 7.83 (s, 2 H), 7.64 (t, *J* = 7 Hz, 1 H), 7.52 (t, *J* = 7 Hz, 1 H), 7.30 (dd, *J* = 7, 5 Hz, 1 H).

^{13}C NMR (75 MHz): δ = 162.1 (C), 147.8 (CH), 139.1 (C), 134.0 (C), 133.4 (C), 132.2 (CH), 131.1 (C), 131.0 (C), 128.5 (C), 128.4 (C), 128.4 (CH), 128.2 (CH), 127.6 (CH), 127.5 (CH), 127.2 (CH), 126.8 (CH), 124.7 (CH), 121.9 (CH), 118.0 (CH).

MS (EI): *m/z* (%) = 285 (100) [M$^+$], 258 (18), 251 (13), 238 (12), 226 (12), 213 (16), 200 (8), 187 (14), 174 (6), 163 (6), 150 (9), 142 (51), 129 (20), 107 (16), 94 (21).

Preparation of Combinatorial Ylide Mixture

A suspension of (2-methylthiobenzyl)triphenylphosphonium bromide **8** (1.00 g, 2.1 mmol), (2-methoxybenzyl)triphenylphosphonium bromide **7** (0.96 g, 2.1 mmol) and (2-methylthio-3-pyridylmethyl)triphenylphosphonium bromide **65** (1.00 g, 2.1 mmol) in dry THF (50 mL) was stirred under N_2 while a solution of butyllithium in hexanes (2.5 mL, 2.5 M, 6.3 mmol) was added. The resulting deep red solution was stirred for a further 2 h before adding a solution of 3-(2-thienyl)propenoyl chloride (0.14 g, 0.8 mmol), 3-(2-furyl)propenoyl chloride (0.12 g, 0.8 mmol) 3-phenylpropenoyl chloride (0.13 g, 0.8 mmol) and 3-(1-naphthyl)propenoyl chloride (0.17 g, 0.8 mmol) in dry THF (10 mL). The reaction mixture was stirred for a further 4 h before adding to water (100 mL). The mixture was extracted with diethyl ether (2 × 100 mL) and ethyl acetate (2 × 100 mL), the combined organic extracts dried and evaporated to give an orange resin. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR of this indicated the expected mixture of products, with ^{1}H NMR giving good resolution of the XMe peaks for the twelve different ylides:

^{1}H NMR (300 MHz): δ = 3.20, 3.18, 3.17, 3.16 (OMe × 4); 2.36, 2.32, 2.31, 2.29 (PyrSMe × 4); 2.20, 2.14, 2.10, 2.09 (SMe × 4).

2. FVP of Ylide Mixture

FVP of the ylide mixture (0.5 g) at 800 ˚C and 5.0–9.0 × 10^{-2} Torr gave a yellow-brown solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:3) as eluant gave a yellow-brown oil. HPLC analysis using CH_2Cl_2 to dissolve the mixture and 0.5% ethyl acetate in hexane as the eluant gave a series of peaks with the following retention times (min.); 5.0–5.9 (strong), 5.9–6.6 (medium, broad), 6.9 (shoulder), 7.5–7.9 (strong), 8.0 (shoulder), 8.6 (medium), 9.3 (weak), 10.0 (weak), 11.6 (medium).

The individual pure products were then injected and the retention times noted; naphtho[1',2':4,5]thieno[2,3-*b*]pyridine **79** 5.5; phenanthro[1',2':4,5]thieno[2,3-*b*]pyridine **72** 5.5; benzothieno[4',5':4,5]thieno[2,3-*b*]pyridine **78** 5.7; benzofuro[4',5':4,5]thieno[2,3-b]pyridine **77** 5.7; benzo[*b*]naphtho[1,2-*d*]furan **4** 7.0; furo[3,2-*a*]dibenzofuran **14** 7.6; thieno[3,2-*a*]dibenzofuran **15** 7.7; benzo[*b*]naphtho[1,2-*d*]thiophene **18** 8.0; furo[3,2-*a*]dibenzothiophene **16** 8.3; thieno[3,2-*a*]dibenzothiophene **17** 9.1; benzo[*b*]phenanthro[1,2-*d*]furan **69** 10.3; benzo[*b*]phenanthro[1,2-*d*]thiophene **70** 11.9.

GCMS analysis gave a series of peaks with the following retention times (min.) and *m/z* values; 11.24 (weak, *m/z* = 208), 13.02 (medium, *m/z* = 218), 13.11 (strong, *m/z* = 224), 13.28 (weak, *m/z* = 225), 14.42 (strong, *m/z* = 234), 14.49 (strong, *m/z* = 240), 15.09 (weak, *m/z* = 235 and 241), 16.48 (weak, shoulder, *m/z* = 268), 19.06 (weak, *m/z* = 284), 19.18 (broad, weak, *m/z* = 285).

The individual pure products were then injected and the retention times and *m/z* values noted; furo[3,2-*a*]dibenzofuran **14** 11.20 (*m/z* = 208); benzo[*b*]naphtho[1,2-*d*]furan **4** 13.05 (*m/z* = 218); thieno[3,2-*a*]dibenzofuran **15** 13.06 (*m/z* = 224); furo[3,2-*a*]dibenzothiophene **16** 13.08 (*m/z* = 224); benzofuro[4',5':4,5]thieno[2,3-b]pyridine **77** 13.27 (*m/z* = 225); benzo[*b*]naphtho[1,2-*d*]thiophene **18** 14.41 (*m/z* = 234); thieno[3,2-*a*]dibenzothiophene **17** 14.48 (*m/z* = 240); naphtho[1',2':4,5]thieno[2,3-*b*]pyridine **79** 15.02 (*m/z* = 235); benzothieno[4',5':4,5]thieno[2,3-*b*]pyridine **78** 15.10 (*m/z* = 241); benzo[*b*]phenanthro[1,2-*d*]furan **69** 17.08 (*m/z* = 268); benzo[*b*]phenanthro[1,2-*d*]thiophene **70** 19.10 (*m/z* = 284); phenanthro[1',2':4,5]thieno[2,3-*b*]pyridine **72** 19.30 (*m/z* = 285).

[1-(2-Methoxybenzoyl)-3-phenylpropylidene]triphenylphosphorane 80

This was prepared as for **9** using (3-phenylpropyl)triphenylphosphonium bromide (10.0 g, 21.7 mmol), butyllithium in hexanes (8.67 mL, 2.5 M, 22 mmol) and 2-methoxybenzoyl chloride (1.84 g, 10.8 mmol) to give the product (2.40 g, 42%) as pale yellow crystals, mp 196–198 °C.

IR: 1595, 1579, 1477, 1392, 1242, 1185, 1159, 1099, 1064, 1043, 1027, 998, 983, 931, 829, 786, 755, 697 cm^{-1}.

^1H NMR (300 MHz): δ = 7.95–7.70 (m, 6 H, Ph), 7.65–7.43 (m, 9 H, Ph), 7.38 (d, *J* = 7 Hz, 1 H), 7.29 (t, *J* = 7 Hz, 1 H), 7.08–6.91 (m, 5 H), 6.96–6.36 (m, 2 H), 3.92 (s, 3 H, OMe), 2.28 (m, 2 H, CH_2), 2.09 (m, 2 H, CH_2).

^{13}C NMR (75 MHz): δ = 186.8 (d, *J* = 6 Hz, CO), 156.1 (C-2), 142.6 (C), 134.0 (d, *J* = 10 Hz, C-2 of PPh), 131.7 (d, *J* = 2 Hz, C-4 of PPh), 128.8 (d, *J* = 12 Hz, C-3 of PPh), 128.2 (2CH), 128.3 (2CH), 128.1 (2CH), 127.4 (d, *J* = 90 Hz, C-1 of PPh), 125.4 (CH), 120.5 (CH), 111.2 (C-3), 65.9 (d, *J* = 101 Hz, P=C), 55.8 (OMe), 40.7 (CH_2), 31.5 (d, *J* = 13 Hz, CH_2), [one C signal not apparent].

^{31}P NMR (121 MHz): δ = +17.5.

MS (EI): *m/z* (%) = 514 (3) [M^+], 423 (100), 287 (8), 277 (5), 262 (15), 183 (16), 108 (6), 91 (10).

Anal. Calcd for $C_{35}H_{31}O_2P$: C, 81.69; H, 6.07. Found: C, 81.51; H, 6.00.

[1-(2-Methylthiobenzoyl)-3-phenylpropylidene]triphenylphosphorane 81

This was prepared as for **9** using (3-phenylpropyl)triphenylphosphonium bromide (10.0 g, 21.7 mmol), butyllithium in hexanes (8.67 mL, 2.5 M, 22 mmol) and 2-methylthiobenzoyl chloride (2.02 g, 10.8 mmol) to give the product (3.96 g, 71%) as pale yellow crystals, mp 205–206 °C.

IR: 1583, 1436, 1384, 1312, 1278, 1258, 1187, 1160, 1108, 1066, 1030, 996, 931, 858, 837, 748, 714, 692 cm^{-1}.

^1H NMR (300 MHz): δ = 7.93–7.75 (m, 6 H, Ph), 7.65–7.45 (m, 9 H, Ph), 7.45–7.16 (m, 4 H), 7.08–6.97 (m, 3 H), 6.45–6.35 (m, 2 H), 2.51 (s, 3 H, SMe), 2.30 (m, 2 H, CH_2), 2.10 (m, 2 H,CH_2).

^{13}C NMR (75 MHz): δ = 187.4 (d, *J* = 8 Hz, CO), 144.3 (d, *J* = 13 Hz, C-1), 142.4 (C), 135.4 (C), 134.0 (d, *J* = 10 Hz, C-2 of PPh), 131.9 (d, *J* = 2 Hz, C-4 of PPh), 128.8 (d, *J* = 12 Hz, C-3 of PPh), 128.2 (2CH), 128.1 (2CH), 127.9 (2CH), 127.7 (CH), 127.5 (CH), 127.2 (d, *J* = 90 Hz, C-1 of PPh), 125.4 (CH), 125.2 (CH), 66.3 (d, *J* = 101 Hz, P=C), 40.8 (CH_2), 31.5 (d, *J* = 13 Hz, CH_2), 17.2 (SMe).

^{31}P NMR (121 MHz): δ = +17.9.

MS (EI): *m/z* (%) = 530 (2) [M^+], 515 (11), 439 (100), 287 (3), 277 (8), 262 (17), 183 (13), 151 (3), 108 (6).

Anal. Calcd for $C_{35}H_{31}OPS$: C, 79.22; H, 5.89. Found: C, 79.14; H, 5.92.

FVP of [1-(2-methoxybenzoyl)-3-phenylpropylidene]triphenylphosphorane 80

FVP of the title compound (1.1 g) at 750 °C and 2.0–5.0 × 10^{-2} Torr gave an oily yellow-brown solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a yellow oil. ^1H NMR, ^{13}C NMR and GCMS analysis indicated a mixture of two products: 1,2-diphenylethane (bibenzyl) and 5,6-dihydrobenzo[*b*]naphtho[1,2-*d*]furan. Preparative TLC of this oil using pentane as eluant gave the product, **5,6-dihydrobenzo[*b*]naphtho[1,2-*d*]furan 82** (0.23 g, 54%) as a yellow oil.

^1H NMR (300 MHz): δ = 7.89 (d, *J* = 7 Hz, 1 H), 7.71 (d, *J* = 7 Hz, 1 H), 7.44 (d, *J* = 7 Hz, 1 H), 7.37–7.08 (m, 5 H), 3.06 (m, 2 H, CH_2), 2.98 (m, 2 H, CH_2).

^{13}C NMR (75 MHz): δ = 156.9 (C), 155.5 (C), 133.7 (C), 131.9 (C), 128.3 (CH), 127.2 (CH), 126.2 (CH), 125.9 (C), 123.6 (CH), 123.3 (CH), 123.0 (CH), 120.1 (CH), 113.7 (C), 111.6 (CH), 29.4 (CH_2), 22.4 (CH_2) [Good agreement with lit.[23]].

MS (EI): *m/z* (%) = 220 (97) [M^+], 219 (100), 205 (6), 189 (51), 165 (30), 152 (11), 139 (11), 109 (50), 94 (89), 81 (29).

HRMS (EI): *m/z* calcd for $C_{16}H_{12}O$ [M^+]: 220.0888; found: 220.0880

FVP of [1-(2-methylthiobenzoyl)-3-phenylpropylidene]triphenylphosphorane 81

FVP of the title compound (1.1 g) at 800 °C and 2.0–3.0 × 10^{-2} Torr gave an oily yellow-brown solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:19) as eluant gave a yellow oil. Preparative TLC of this oil using pentane as eluant gave the product, **5,6-dihydrobenzo[*b*]naphtho[1,2-*d*]thiophene 83** (0.27 g, 60%) as a yellow oil.

^1H NMR (300 MHz): δ = 8.26 (d, *J* = 7 Hz, 1 H), 7.96 (d, *J* = 7 Hz, 1 H), 7.81 (d, *J* = 7 Hz, 1 H), 7.42–7.09 (m, 5 H), 2.95 (s, 4 H, CH_2CH_2) [Good agreement with lit.[24]].

^{13}C NMR (75 MHz): δ = 142.0 (C), 140.6 (C), 139.2 (C), 137.0 (C), 136.1 (C), 133.0 (C), 128.0 (CH), 127.0 (CH), 126.4 (CH), 124.8 (CH), 123.8 (CH), 123.6 (CH), 123.0 (CH), 122.6 (CH), 29.9 (CH_2), 24.7 (CH_2).

MS (EI): *m/z* (%) = 236 (100) [M^+], 221 (16), 202 (38), 189 (21), 163 (13), 150 (8), 139 (9), 117 (73), 104 (42).

HRMS (EI): *m/z* calcd for $C_{16}H_{12}S$ [M^+]: 236.0660; found: 236.0655

(2-(Phenylmethoxy)benzyl)triphenylphosphonium bromide 84

This was prepared as for **8** using 2-(phenylmethoxy)benzyl alcohol[44] (20.50 g, 96 mmol), phosphorus tribromide (4.70 mL, 50 mmol) and triphenylphosphine (27.60 g, 105 mmol) to give the product (44.62 g, 86%) as a colourless crystalline powder, mp 229–230 °C.

IR: 1591, 1438, 1247, 1157, 1114, 1008, 788, 748, 690 cm^{-1}.

^1H NMR (300 MHz): δ = 7.82–7.62 (m, 3 H), 7.60–7.43 (m, 11 H), 7.43–7.32 (m, 5 H), 7.23 (t, *J* = 7 Hz, 1 H), 7.16–7.06 (m, 2 H), 6.84 (t, *J* = 7 Hz, 1 H), 6.68 (d, *J* = 7 Hz, 1 H, 3-H), 5.38 (d, *J* = 15 Hz, 2 H, CH_2P^+), 4.45 (s, 2 H, OCH_2).

^{13}C NMR (75 MHz): δ = 156.7 (d, *J* = 5 Hz, C-2), 136.0 (C-1 of Bn), 136.0 (d, *J* = 2 Hz, C-4 of PPh), 134.2 (d, *J* = 10 Hz, C-2 of PPh), 132.3 (d, *J* = 5 Hz, CH), 130.5 (d, *J* = 2 Hz, CH), 130.2 (d, *J* = 12 Hz, C-3 of PPh), 128.8 (2CH), 128.6 (CH), 128.0 (2CH), 121.6 (d, *J* = 3 Hz, CH), 117.9 (d, *J* = 87 Hz, C-1 of PPh), 116.1 (d, *J* = 9 Hz, C-1), 111.8 (d, *J* = 1 Hz, CH), 70.0 (CH_2O), 25.9 (d, *J* = 49 Hz, CH_2P^+).

^{31}P NMR (121 MHz): δ = +22.0.

Anal. Calcd for $C_{32}H_{28}BrOP$: C, 71.25; H, 5.23. Found: C, 71.16; H, 5.47.

[(2-Methylthiobenzoyl)-2-(phenylmethoxy)benzylidene]triphenylphosphorane 85

This was prepared as for **9** using (2-(phenylmethoxy)benzyl)triphenylphosphonium bromide **84** (6.0 g, 11 mmol), butyllithium in hexanes (4.50 mL, 2.5 M, 11 mmol) and 2-methylthiobenzoyl chloride (1.05 g, 6 mmol) to give the product (2.50 g, 73%) as yellow prisms, mp 192–194 °C.

IR: 1894, 1822, 1596, 1510, 1249, 1160, 1106, 1050, 1011, 970, 927, 858, 749, 692 cm^{-1}.

^1H NMR (300 MHz): δ = 7.80–7.50 (m, 6 H), 7.46–7.32 (m, 9 H), 7.31–7.17 (m, 7 H), 7.12 (d, *J* = 7 Hz, 1 H), 6.99 (t, *J* = 7 Hz, 1 H), 6.88–6.78 (m, 2 H), 6.54 (t, *J* = 7 Hz, 1 H), 6.36 (d, *J* = 7 Hz, 1 H, 3-H), 4.76 and 4.21 (AB pattern, *J* = 10 Hz, 2 H, OCH_2Ph), 2.43 (s, 3 H, SMe).

^{13}C NMR (75 MHz): δ = 185.9 (d, *J* = 8 Hz, CO), 158.1 (d, *J* = 3 Hz, C-2), 143.5 (d, *J* = 12 Hz, C), 137.5 (d, *J* = 4 Hz, CH), 137.2 (C), 136.6 (C), 134.0 (d, *J* = 10 Hz, C-2 of PPh), 131.4 (d, *J* = 3 Hz, C-4 of PPh), 128.8 (2CH), 128.6 (2CH), 128.2 (d, *J* = 12 Hz, C-3 of PPh), 128.2 (CH), 127.8 (d, *J* = 6 Hz, CH), 127.8 (CH), 127.6 (CH), 127.1 (d, *J* = 11 Hz, C-1), 126.7 (d, *J* = 91 Hz, C-1 of PPh), 126.4 (CH), 124.0 (CH), 120.2 (CH), 110.3 (CH), 69.5 (CH_2), 67.6 (d, *J* = 109 Hz, P=C), 17.0 (SMe).

^{31}P NMR (121 MHz): δ = +15.3.

MS (EI): *m/z* (%) = 608 (10) [M^+], 501 (18), 487 (7), 346 (12), 277 (10), 262 (100), 241 (9), 225 (13), 183 (22), 151 (22), 91 (30).

Anal. Calcd for $C_{40}H_{33}O_2PS$: C, 78.92; H, 5.46; S, 5.26. Found: C, 78.67; H, 5.48; S, 4.98.

FVP of [(2-methylthiobenzoyl)-2-(phenylmethoxy)benzylidene]triphenylphosphorane 85

FVP of the title compound (1.0 g) at 800 °C and 2.0–5.0 × 10^{-2} Torr gave an oily brown solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a pale brown oil which was kugelrohr distilled at 140 °C and 0.6 Torr to give a pale yellow solid. This was found by ^1H NMR and GCMS analysis to be a mixture of bibenzyl and **benzothieno[3,2-*b*]benzofuran 86** (0.10 g, 28%), with only a tiny peak corresponding to 2-phenylbenzothiophene.

[(3-(4-Nitrophenyl)propenoyl)-2-(phenylmethoxy)benzylidene]triphenylphosphorane 88

This was prepared as for **9** using (2-(phenylmethoxy)benzyl)triphenylphosphonium bromide **84** (8.0 g, 15 mmol), butyllithium in hexanes (5.90 mL, 2.5 M, 15 mmol) and 3-(4-nitrophenyl)propenoyl chloride (1.69 g, 8 mmol) to give the product (3.40 g, 67%) as bright red prisms, mp 155–156 °C.

IR: 1740, 1632, 1599, 1511, 1338, 1230, 1105, 1050, 1025, 974, 842, 744, 694 cm^{-1}.

^1H NMR (300 MHz): δ = 8.09 (d, *J* = 9 Hz, 2 H), 7.62–7.38 (m, 12 H), 7.32–7.18 (m, 12 H), 7.12 (t, *J* = 8 Hz, 1 H), 6.98 (d, *J* = 16 Hz, 1 H, vinyl-H), 6.82 (t, *J* = 8 Hz, 1 H), 6.62 (d, *J* = 8 Hz, 1 H, 3-H), 4.83 and 4.38 (AB pattern, *J* = 11 Hz, 2 H, OCH_2Ph).

^{13}C NMR (75 MHz): δ = 178.3 (d, *J* = 5 Hz, CO), 158.7 (d, *J* = 3 Hz, C-2), 147.1 (C), 144.3 (C), 137.7 (d, *J* = 5 Hz, CH), 137.0 (C), 134.0 (CH), 133.9 (d, *J* = 10 Hz, C-2 of PPh), 131.7 (d, *J* = 3 Hz, C-4 of PPh), 131.4 (d, *J* = 12 Hz, CO-CH=), 128.8 (2CH), 128.5 (d, *J* = 12 Hz, C-3 of PPh), 128.2 (CH), 128.5 (d, *J* = 3 Hz, CH), 128.4 (2CH), 128.1 (2CH), 126.3 (d, *J* = 91 Hz, C-1 of PPh), 126.2 (d, *J* = 10 Hz, C-1), 124.0 (2CH), 120.5 (CH), 111.3 (CH), 72.1 (d, *J* = 110 Hz, P=C), 69.9 (CH_2).

^{31}P NMR (121 MHz): δ = +15.9.

MS (EI): *m/z* (%) = 633 (1) [M^+], 373 (8), 355 (22), 278 (100), 262 (65), 218 (9), 201 (50), 183 (61), 152 (28), 108 (14).

Anal. Calcd for $C_{41}H_{32}NO_4P$: C, 77.71; H, 5.09; N, 2.21. Found: C, 77.59; H, 5.07; N, 2.44.

[(3-(4-Methoxyphenyl)propenoyl)-2-(phenylmethoxy)benzylidene]triphenylphosphorane 89

This was prepared as for **9** using (2-(phenylmethoxy)benzyl)triphenylphosphonium bromide **84** (10.0 g, 18.5 mmol), butyllithium in hexanes (7.40 mL, 2.5 M, 18.5 mmol) and 3-(4-methoxyphenyl)propenoyl chloride (1.81 g, 9.3 mmol) to give an orange oil. This was triturated with diethyl ether to give an orange solid which was recrystallised from ethyl acetate to give the product (4.19 g, 73%) as bright yellow needles, mp 196–198 °C.

IR: 1633, 1605, 1575, 1515, 1224, 1105, 1027, 955, 831, 788, 754, 695, 621 cm^{-1}.

^1H NMR (300 MHz): δ = 7.62–7.44 (m, 6 H), 7.43–7.18 (m, 18 H), 7.06 (t, *J* = 8 Hz, 1 H), 6.78 (t, *J* = 8 Hz, 1 H), 6.76 (d, *J* = 8 Hz, 2 H), 6.74 (d, *J* = 16 Hz, 1 H, vinyl-H), 6.58 (d, *J* = 8 Hz, 1 H, 3-H), 4.82 and 4.41 (AB pattern, *J* = 12 Hz, 2 H, CH_2), 3.76 (s, 3 H, OMe).

^{13}C NMR (75 MHz): δ = 180.1 (d, *J* = 6 Hz, CO), 159,7 (C), 158.8 (d, *J* = 3 Hz, C-2), 138.0 (d, *J* = 5 Hz, CH), 137.2 (C), 133.7 (CH), 133.9 (d, *J* = 10 Hz, C-2 of PPh), 131.3 (d, *J* = 2 Hz, C-4 of PPh), 130.2 (C), 129.0 (2CH), 128.7 (2CH), 128.4 (2CH), 128.2 (d, *J* = 13 Hz, C-3 of PPh), 128.1 (d, *J* = 3 Hz, CH), 128.0 (CH), 127.1 (d, *J* = 91 Hz, C-1 of PPh), 126.8 (d, *J* = 11 Hz, C-1), 124.9 (d, *J* = 13 Hz, CO-CH=), 120.4 (CH), 114.0 (2CH), 111.3 (CH), 69.8 (CH_2), 69.4 (d, *J* = 113 Hz, P=C), 55.3 (OMe).

^{31}P NMR (121 MHz): δ = +15.1.

MS (EI): *m/z* (%) = 618 (7) [M^+], 512 (26), 410 (8), 396 (18), 382 (9), 368 (14), 356 (33), 319 (54), 277 (14), 262 (53), 183 (28), 161 (57), 104 (91), 91 (87), 69 (100).

Anal. Calcd for $C_{42}H_{35}O_3P$: C, 81.53; H, 5.70. Found: C, 81.36; H, 5.72.

[(3-(3,4-Methylenedioxyphenyl)propenoyl)-2-(phenylmethoxy)benzylidene]triphenylphosphorane 90

This was prepared as for **9** using (2-(phenylmethoxy)benzyl)triphenylphosphonium bromide **84** (7.0 g, 13.0 mmol) in dry THF (70 mL), butyllithium in hexanes (5.20 mL, 2.5 M, 13.0 mmol) and 3-(3,4-methylenedioxyphenyl)propenoyl chloride (1.37 g, 7.0 mmol) to give a red oil. This was triturated with diethyl ether to give an orange solid which was recrystallised from ethyl acetate to give the product (2.40 g, 55%) as yellow prisms, mp 206–209 °C.

IR: 1637, 1612, 1490, 1244, 1119, 1073, 984, 960, 924, 850, 800, 748, 693, 594 cm^{-1}.

^1H NMR (300 MHz): δ = 7.62–7.43 (m, 6 H), 7.42–7.16 (m, 16 H), 7.05 (t, *J* = 7 Hz, 1 H), 6.87–6.64 (m, 5 H), 6.58 (d, *J* = 7 Hz, 1 H), 5.83 (s, 2 H, OCH_2O), 4.81 and 4.39 (AB pattern, *J* = 12 Hz, 2 H, OCH_2).

^{13}C NMR (75 MHz): δ = 179.9 (d, *J* = 5 Hz, CO), 158.9 (d, *J* = 4 Hz, C-2), 137.9 (d, *J* = 5 Hz, CH), 147.9 (C), 147.7 (C), 137.1 (C), 133.7 (CH), 133.9 (d, *J* = 10 Hz, C-2 of PPh), 132.0 (C), 131.3 (d, *J* = 2 Hz, C-4 of PPh), 128.7 (2CH), 128.4 (2CH), 128.2 (d, *J* = 13 Hz, C-3 of PPh), 128.2 (CH), 128.0 (CH), 127.0 (d, *J* = 91 Hz, C-1 of PPh), 126.7 (d, *J* = 11 Hz, C-1), 125.3 (d, *J* = 12 Hz, CO-CH=), 122.9 (CH), 120.4 (CH), 111.3 (CH), 108.4 (CH), 106.6 (CH), 101.1 (CH_2), 69.9 (CH_2), 69.5 (d, *J* = 111 Hz, P=C).

^{31}P NMR (121 MHz): δ = +15.2.

MS (EI): *m/z* (%) = 632 (8) [M^+], 525 (23), 396 (12), 370 (42), 277 (48), 262 (82), 183 (68), 175 (87), 91 (100).

Anal. Calcd for $C_{41}H_{33}O_4P$: C, 79.34; H, 5.36. Found: C, 79.08; H, 5.24.

FVP of [(3-(4-methoxyphenyl)propenoyl)-2-(phenylmethoxy)benzylidene]triphenylphosphorane 89

FVP of the title compound (1.0 g) at 650 °C and 2.0–5.0 × 10^{-2} Torr gave a red-brown oily solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:19) as eluant gave a pale yellow solid which was found by ^1H NMR, ^{13}C NMR and GCMS analysis to be a mixture of two isomers. Column chromatography using hexane as eluant allowed partial separation of the two to give after recrystallisation from ethanol; **2-methoxybenzo[*b*]naphtho[1,2-*d*]furan 91** (0.12 g, 33%) as off-white needles, mp 99–100 °C.

IR: 1631, 1590, 1522, 1467, 1262, 1208, 1134, 1041, 1027, 867, 827, 789, 742, 611 cm^{-1}.

^1H NMR (300 MHz): δ = 8.24 (dd, *J* = 7, 2 Hz, 1 H, 11-H), 7.85 (d, *J* = 7 Hz, 1 H), 7.80 (d, *J* = 2 Hz, 1 H, 1-H), 7.78 (d, *J* = 7 Hz, 1 H), 7.64 (dd, *J* = 7, 2 Hz, 1 H), 7.56 (d, *J* = 7 Hz, 1 H), 7.48–7.39 (m, 2 H), 7.16 (dd, *J* = 7, 2 Hz, 1 H), 4.00 (s, 3 H, OMe).

^{13}C NMR (75 MHz): δ = 159.1 (C), 156.0 (C), 155.2 (C), 130.8 (CH), 130.5 (C), 128.5 (CH), 125.8 (CH), 125.7 (C), 125.2 (C), 123.2 (CH), 121.7 (CH), 116.7 (C), 116.2 (CH), 112.0 (CH), 110.2 (CH), 103.2 (CH), 55.4 (CH_3).

MS (EI): *m/z* (%) = 248 (100) [M^+], 205 (75), 176 (14), 151 (6), 124 (7), 88 (5).

Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.41; H, 4.69.

By comparison of the ^{13}C NMR spectrum of the mixture of isomers it was possible to identify the values for the minor isomer, presumed to be **2-methoxybenzo[*b*]naphtho[2,1-*d*]furan 92** (0.04 g, 11%).

^{13}C NMR (75 MHz): δ = 158.5 (C), 156.2 (C), 151.7 (C), 130.2 (CH), 128.6 (C), 126.3 (CH), 125.4 (C), 123.1 (CH), 123.0 (CH), 122.4 (C), 120.5 (CH), 119.8 (C), 118.8 (CH), 116.0 (CH), 111.8 (CH), 99.4 (CH), 55.4 (CH_3).

FVP of [(3-(3,4-methylenedioxyphenyl)propenoyl)-2-(phenylmethoxy)benzylidene]triphenylphosphorane 90

FVP of the title compound (1.0 g) at 650 ˚C and 5.0–9.0 × 10^{-2} Torr gave a brown oily solid at the furnace exit. Column chromatography of this using hexane as eluant gave a yellow-brown oil. ^1H NMR, ^{13}C NMR and GCMS analysis indicated a complex mixture of products, including partially cyclised material, although the major product was the expected **2,3-methylenedioxybenzo[*b*]naphtho[1,2-*d*]furan 93** (0.12 g, 28%).

^1H NMR (300 MHz): δ = 8.07 (d, *J* = 7 Hz, 1 H, 11-H), 7.65 (s, 1 H, 1-H), 7.60–7.30 (m, 4 H), 7.09 (s, 1 H, 4-H), 5.92 (s, 2 H, CH_2).

^{13}C NMR (75 MHz): δ = 155.9 (C), 153.8 (C), 148.7 (C), 146.2 (C), 127.4 (CH), 126.9 (C), 125.8 (CH), 125.6 (C), 124.9 (C), 122.9 (CH), 121.5 (CH), 117.4 (C), 111.7 (CH), 110.3 (CH), 105.5 (CH), 101.3 (CH_2), 100.5 (CH).

MS (EI): *m/z* (%) = 262 (100) [M^+], 233 (34), 205 (55), 176 (50), 149 (58), 131 (32), 88 (60).

2,5-Dimethoxy-1,4-phenylenebis(((3-phenylpropenoyl)methylene)triphenylphosphorane) 94

This was prepared as for **9** using 2,5-dimethoxy-*p*-xylylenebis(triphenylphosphonium chloride)[25] (5.0 g, 6.6 mmol), butyllithium in hexanes (5.26 mL, 2.5 M, 13.2 mmol) and 3-phenylpropenoyl chloride (1.10 g, 6.6 mmol) to give the product (1.00 g, 32%) as a bright yellow powder, mp 282–286 ˚C (dec.).

IR: 1474, 1265, 1208, 1108, 1044, 921, 763, 750, 721, 692 and 641 cm^{-1}.

^1H NMR (300 MHz): δ = 7.70–7.58 (m, 12 H), 7.52–7.20 (m, 30 H), 6.70 (d, *J* = 16 Hz, 2 H, vinyl-H), 6.53 (s, 2 H, 3'-H, 6'-H), 3.20 (s, 6 H, OMe).

^{13}C NMR (75 MHz): δ = 179.3 (2CO), 153.0 (2C, C-2', C-5'), 138.0 (2C, C-1 of Ph), 134.7 (2CH), 134.0 (d, *J* = 9 Hz, C-2 of P-Ph), 131.8 (C-4 of P-Ph), 128.9 (4CH), 128.6 (d, *J* =13 Hz, C-3 of P-Ph), 128.5 (2CH), 128.0 (d, *J* = 91 Hz, C-1 of P-Ph), 128.0 (4CH), 126.6 (d, *J* = 11 Hz, =CH–), 125.4 (d, *J* = 13 Hz, C-1', C-4'), 119.4 (2CH, C-3', C-6'), 71.4 (d, *J* = 111 Hz, C=P), 55.5 (OMe).

^{31}P NMR (121 MHz): δ = +14.6.

MS (FAB): *m/z* (%) = 947 (8) [M+H^+], 885 (4), 643 (5), 566 (5), 509 (10), 453 (4), 393 (6), 333 (5), 262 (11), 213 (7), 95 (100).

Anal. Calcd for. $C_{64}H_{52}O_4P_2$: C, 81.17; H, 5.53. Found: C, 80.98; H, 5.85.

FVP of 2,5-dimethoxy-1,4-phenylenebis(((3-phenylpropenoyl)methylene)triphenylphosphorane) 94

FVP of the title compound (0.30 g) at 850 ˚C and 2.0–5.0 × 10^{-2} Torr gave a brown oily solid at the furnace exit. Column chromatography of this using diethyl ether–hexane (1:9) as eluant gave a yellow-brown solid which was found by ^1H NMR and mass spectroscopy to be impure **dinaphtho[1,2-*d*;1',2'-*d*']benzo[1,2-*b*;4,5-*b*']difuran 95** (0.02 g, 18%) as a pale brown solid, mp 294–299 ˚C (lit.,[26] 300–302 ˚C (dec)).

^1H NMR (300 MHz): δ = 8.68 (d, *J* = 8 Hz, 2 H), 8.60 (s, 2 H), 8.06 (d, *J* = 8 Hz, 2 H), 7.98 (d, *J* = 9 Hz, 2 H), 7.82 (d, *J* = 9 Hz, 2 H), 7.79 (td, *J* = 8, 2 Hz, 2 H), 7.58 (td, *J* = 8, 2 Hz, 2 H).

MS (EI): *m/z* (%) = 358 (100) [M^+], 344 (8), 332 (15), 316 (10), 302 (21), 279 (6), 221 (8), 179 (18), 167 (7), 149 (32), 125 (8), 111 (15), 97 (25).

The identity of the product was confirmed by ^1H NMR comparison with a sample prepared by the literature method.[26]

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Supporting Information

No

Primary Data

No

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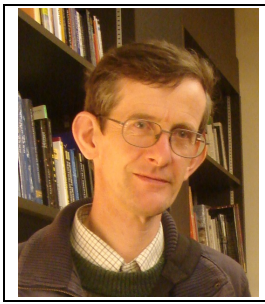
Biosketches



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