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Ionic Liquids: Synthesis and Characterisation of Triphenylphosphonium Tosylates

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Ionic liquids are currently attracting considerable interest from chemists, partly due to their potential as "green" alternatives to volatile molecular organic solvents. Phosphonium ionic liquids have received much less attention than ammonium salts in the past, but the situation is changing. The salts are applied in the liquid state but in this work, salts with higher melting points than is generally the case are investigated. They are solid at room temperature, thus enabling facile separation of liquid reaction products. Nine triphenylphosphonium tosylates have been prepared and characterised; their crystal structures have been determined and their melting points have been scrutinized, showing some sensitivity to the duration of drying. The structural information is expected to be invaluable in the understanding of the properties of the molten state.

Introduction

Although ionic liquids were first described as long ago as 1914,[1] it is only relatively recently that they have received much attention from chemists.[2–5] The last few decades have witnessed increased application, initially as media for organic synthesis and later on with multiple uses. A number of properties make ionic liquids particularly suited to application as solvents; they have high thermal stability, low vapour pressure and the ability to dissolve a large range of inorganic, organic and polymeric materials. In addition, they have a wide liquid range and are relatively cheap and easy to prepare.

The terms "ionic liquid" and "room temperature ionic liquid" often refer to ionic salts with melting points below ca. 100 °C. Many ionic liquids studied to date fall within this category and, in particular, salts containing quaternary nitrogen cations have been investigated extensively. A number of phosphonium salts also fall within this low melting point class. A factor in the growing interest in these materials is their potential as "green" alternatives to molecular organic solvents; replacement of volatile organic solvents by ionic liquids, which are involatile, would significantly reduce their detrimental impact on the environment. This aspect will undoubtedly become increasingly important as the level of awareness and concern for the habitat intensifies.

Although phosphonium salts have attracted much less interest in the literature than quaternary nitrogen salts to date, their potential as ionic solvents has been recognized for a long time. For example, the first palladium-catalysed reaction in an ionic liquid was carbon–carbon coupling in tributylhexadecylphosphonium bromide.[6] Tetrabutylphosphonium halides (TBPHs) featured prominently in the earlier application of phosphonium salts as ionic solvents. One of the first reported uses of a phosphonium salt as a solvent in an organic reaction was of TBPHs in regioselective *o*-alkylation leading to an efficient and recyclable catalytic system.[7] Several years earlier, in 1981, TBPHs had been used in the ruthenium-catalysed hydrogenation of carbon monoxide to ethyleneglycol.[8] Hydroformylation of olefins in TBPHs and other quaternary phosphonium salts has also been demonstrated.[9,10] Interest in application as alternative solvents and co-catalysts continues to grow.[11]

In this investigation, we consider triphenylphosphonium salts with higher melting points than conventional ionic liquids, focusing exclusively on the tosylates shown in Scheme 1. The efficacy of some of the tosylates has already been demonstrated. The first reported use of a phosphonium molten salt with a tosylate counterion was as the solvent for catalytic hydroformylation of hex-1-ene to heptanal and 2-methylhexanal using **1**, **3**, **5** and **9**.[12] This established that alteration of the substituents in the cation could affect product distribution. Diels–Alder reactions of isoprene with methyl acrylate, but-3-en-2-one and acrylonitrile have also been performed in phosphonium tosylates, including **1**, **3**, **5** and **9**.[13] The results indicate that product selectivity varies with cation substituent and also that the solvents are more suitable for the reactions of oxygen-containing dienophiles than for nitrogenous ones, showing high regioselectivity. Phosphonium salts including **1** and **9** have also been reported to be good co-catalysts for the Baylis–Hillman reac-

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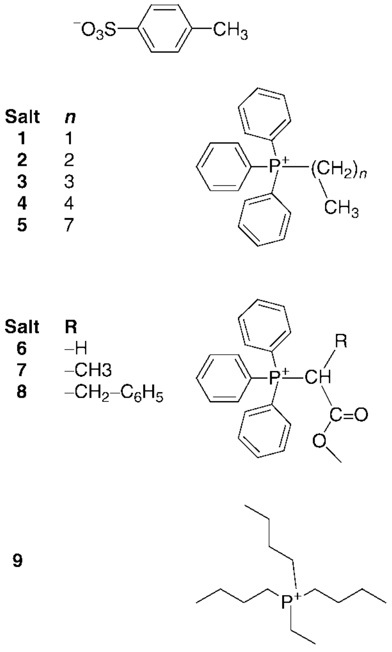
tion with the results showing that neither modification of the cation substituents nor a change in the anion has a major effect on the yield.[14] The tosylates have also been used in rhodium-catalysed transfer hydrogenation of acetophenone.[15]



Scheme 1. The phosphonium tosylates under investigation.

In addition to the general properties of ionic liquids mentioned above, phosphonium salts have a number of other advantages. They can be prepared without halide contamination and therefore be used with no adverse effect on metal catalysts. They are also more thermally stable than quaternary nitrogen salts and thus can be applied under more demanding reaction conditions. The tosylates are relatively inexpensive, easily available, noncorrosive and are stable in air as well as in moisture. A high melting point has been found to be beneficial for the following reason. At the reaction temperature (above the melting point of the salt), the phosphonium salts act as solvents (for catalysts and reagents), allowing homogeneous conditions. On cooling, the salts crystallise out and trap the catalyst thereby enabling easy separation of liquid products. For example, in the hydroformylation,[12] Diels–Alder[13] and hydrogenation[15] reactions mentioned above, product separation involved filtration or decantation of the liquid organic product. The catalyst system or ionic solvent was subsequently reusable.

The growing interest in these materials as well as their potential as alternatives to other ionic and volatile organic solvents makes more fundamental research into their properties imperative. The properties of triphenylphosphonium salts can be affected by a change in the nature of both cation and anion; as a consequence, solvents can be tailor-made for a specific reaction by tuning their properties. For this to be achievable, the correlation between the physicochemical properties of the solvents and the molecular structure needs to be established.[4] This is a sizeable challenge as the number of available cations and anions is immense. Any investigation, therefore, needs to be performed systematically.

Melting points, which are an indication of the lower temperature limit of application of ionic solvents, can be related to the crystal structures and are looked at in some detail in this study. However, ionic salts are applied in the liquid state, where the challenge is to understand properties such as viscosity and ion diffusion. The more ordered crystalline state can provide important information (such as molecular geometry, intra- and intermolecular contacts) to assist in the process of beginning to understand and possibly model the properties of the liquid state. This is a realistic approach as shown by studies of imidazolium ionic liquids in which a correlation has been found between the structural properties of the solid state and those of the liquid state.[16–20] To the best of our knowledge, no structural information has been published for any triphenylphosphonium tosylates. An aim of this study has been to obtain this information, and to this end, the salts shown in Scheme 1 have been synthesised and characterised.

Results and Discussion

Melting Points

Melting points are invaluable in the characterisation of materials. In the case of ionic liquids, accurate melting points (along with boiling points and decomposition temperatures) are essential as they give an indication of the range of application. Melting points are also sensitive to the purity of the material – an important consideration as impurities may change the nature of ionic solvents. The melting points determined during this study are shown in Table 1. The "initial" values in the Table were obtained after sample preparation and some showed significant deviations from previously reported values. There were also some

Table 1. Melting points (T_{mp}) for the triphenylphosphonium tosylates.

Salt	n	T_{mp} [°C]		
		initial	after additional drying	literature
–	0	–	–	137–139[21] 147–149[22]
1	1	118–120	139–141	94–95[12] 82–83[21]
2	2	142–143	143–145	141–143[21]
3	3	130–131	132–134	116–117[12] 139–140[21]
4	4	120–122	123–125	–
5	7	–	129–131[a]	70–71[12] 70–78[21]
–	9	–	–	94–96[23]
6		154–156	164–166	–
7		173–175	175–176	–
8		–	–	–
9		74–76	74–75	81–83[12]

[a] Solvate.

discrepancies between the various reports,[12,21–23] and hence further examination was undertaken.

The initial samples were rinsed using a volatile solvent and did not appear to be wet, but additional drying was found to raise the melting points significantly for some. The drying process was repeated until no further change was observed. Thus, for example, the melting point of **1** rose from 118–120 °C to 139–141 °C on storage under vacuum for several days and that of **6** increased from 154–156 °C to 164–166 °C under the same treatment. With the exception of **5**, which is a solvate, none of the analytical techniques indicated the presence of significant amounts of solvent in the initial samples and powder X-ray diffraction confirmed that no observable change in phase or crystallinity occurred during the drying process.

The final values of melting points obtained are also shown in Table 1. One literature value for **3** and that for **9** are significantly higher than the final values from this study, suggesting that even higher melting points might be obtained by further treatment. The final values from this study, along with the literature values for the *n*-alkyltriphenylphosphonium tosylates, are plotted in Figure 1. The need for reliable values is clearly illustrated by **1**. Going by the previously reported melting point, **1** falls within the conventional definition of ionic liquids (i.e. m.p. < 100 °C), whereas a considerably higher value has been obtained during this study. It is noted in passing, however, that **1**, **3** and **5** have been used at temperature as low as 80 °C, 40 °C and 60 °C[13] respectively although the melting points obtained for the pure phases are ca. 140 °C, 133 °C and 130 °C, respectively. This is attributable to the "impurity" effect of the reagents on the ionic solvents.

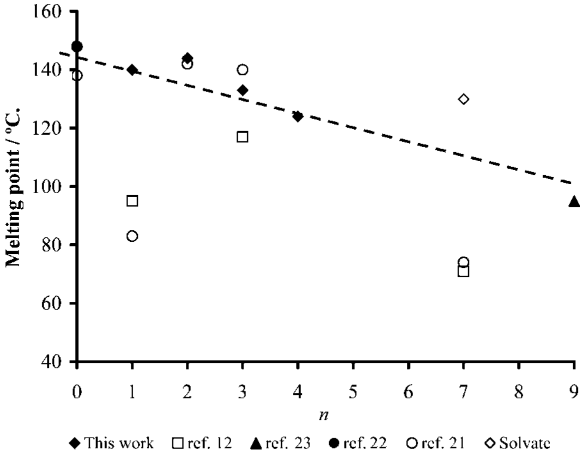


Figure 1. Melting points for the alkyltriphenylphosphonium tosylates.

Incorporation of solvent of crystallisation is clearly a consideration when selecting a salt for use as a solvent. Unlike the other samples investigated, the structure of **5** (n = 7) included the solvent (dichloromethane). Two values have been reported previously for the melting point of **5**, and it is noteworthy that although they are close to each other, the range is quite large for one (8 °C). If an assumption is made that melting points decrease gradually with increasing n for nonsolvated triphenylphosphonium tosylates (the dashed line in Figure 1), then a possible discrepancy is apparent for **5**, with the reported values falling well below that predicted.

The DSC results obtained indicate that endothermic processes occur at temperatures consistent with the melting

Table 2. Crystallographic data for the alkyltriphenylphosphonium tosylates.

Salt	1	2	3	4	5
Formula	$C_{20}H_{20}P^+$ $C_7H_7O_3S^-$	$C_{21}H_{22}P^+$ $C_7H_7O_3S^-$	$C_{22}H_{24}P^+$ $C_7H_7O_3S^-$	$C_{23}H_{26}P^+$ $C_7H_7O_3S^-$	$C_{26}H_{32}P^+$ $C_7H_7O_3S^-$ CH_2Cl_2
FW	462.52	476.54	490.57	504.59	631.60
T [K]	296	296	296	296	296
λ [Å]	0.71069	0.71069	0.71069	1.54178	1.54178
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/a$	$P2_1/a$	$P2_1/a$
a [Å]	13.663(2)	8.7830(8)	12.672(1)	12.6695(5)	12.782(3)
b [Å]	12.695(2)	16.244(2)	17.227(2)	17.2562(7)	17.906(4)
c [Å]	13.811(2)	17.643(2)	12.451(2)	12.6892(5)	15.554(4)
β [°]	90.967(5)	93.975(4)	97.426(9)	98.347(2)	104.553(7)
V [Å^3]	2395.2(7)	2511.0(4)	2695.1(5)	2744.82(19)	3446(1)
Z	4	4	4	4	4
$D_{\text{calcd.}}$ [Mg·m^{-3}]	1.283	1.261	1.209	1.221	1.218
μ [mm^{-1}]	0.228	0.220	0.207	1.819	2.940
$F(000)$	976	1008	1040	1072	1336
Crystal size [mm]	0.50 × 0.15 × 0.10	0.50 × 0.15 × 0.10	0.10 × 0.08 × 0.01	0.34 × 0.10 × 0.04	0.24 × 0.12 × 0.06
Total reflections	13305	12967	12939	27287	8675
Unique reflections	4380	4319	4377	4917	2313
R_{int}	0.042	0.034	0.065	0.096	0.094
S	1.048	1.047	1.047	1.007	1.037
R_1 [$I > 2\sigma(I)$]	0.052	0.054	0.063	0.045	0.096
wR_p	0.123	0.136	0.089	0.097	0.26

Table 3. Crystallographic data for the tosylates of triphenylphosphonium esters.

Salt	**6**	**7**	**8**	**9**
Formula	$C_{21}H_{20}O_2P^+$ $C_7H_7O_3S^-$	$C_{22}H_{22}O_2P^+$ $C_7H_7O_3S^-$	$C_{28}H_{26}O_2P^+$ $C_7H_7O_3S^-$	$C_{14}H_{32}P^+$ $C_7H_7O_3S^-$
FW	506.53	520.55	596.64	402.55
T [K]	296	293	296	296
λ [Å]	0.71069	0.71069	0.71069	0.71069
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	Cc	$P2_12_12_1$	Cc	$P2_1/n$
a [Å]	9.9121(9)	13.048(1)	17.752(2)	8.137(3)
b [Å]	16.843(1)	18.379(2)	9.6829(7)	13.249(6)
c [Å]	14.8464(9)	10.9741(8)	18.935(2)	22.652(9)
β / °	90.844(5)	–	109.629(2)	96.594(7)
V [Å^3]	2478.3(3)	2631.8(3)	3065.6(4)	2426(2)
Z	4	4	4	4
$D_{\text{calcd.}}$ [Mg·m^{-3}]	1.358	1.314	1.293	1.102
μ [mm^{-1}]	0.233	0.221	0.199	0.215
F(000)	1064	1096	1256	880
Crystal size [mm]	0.30 × 0.20 × 0.02	0.40 × 0.10 × 0.05	0.50 × 0.40 × 0.40	0.40 × 0.30 × 0.10
Total reflections	7224	15070	9088	6127
Unique reflections	4006	4636	4630	2702
R_{int}	0.072	0.047	0.030	0.103
S	1.078	1.192	1.041	1.045
R_1 [$I > 2\sigma(I)$]	0.056	0.064	0.039	0.118
wR_{p}	0.132	0.126	0.101	0.305
x (Flack)	0.01(13)	–0.04(12)	0.08(7)	–

points. The peaks are sharp for the alkyltriphenyl compounds (**1**–**4** and **9**), and there is no indication of thermal instability within the timescale and temperature range of the experiment. These salts have high thermal stability, are tolerant toward air and are reusable as solvents.[12,13] On the other hand, DSC shows broader features in the cases of **5**–**7**; loss of the solvent is clearly a factor in **5**, whereas the results may be an indication of thermal transformation close to the melting point for the esters **6** and **7**.

Structural Characterisation

Crystallographic data for **1**–**5** are shown in Table 2 and data for **6**–**9** are shown in Table 3. The asymmetric units are shown in Figure 2(a) to Figure 10(a).

Alkyltriphenylphosphonium Tosylates

In the structure of **1**, tosylate ions are linked by C(3)–H(3)···O(2) interactions (with a H···O distance of 2.4 Å, a C–H···O angle of 170°) to form zigzag chains along the *b*-axis. These chains are arranged side-by-side to form sheets parallel to the (1,0,–1) plane, leading to a layered structure (Figure 2, b). In the structure, a number of edge-to-face interactions with "nonideal" geometry are observed. For example, an aromatic ring of the cation is the donor to two anion rings with planes at ca. 60° and 70° to it and both with CH···π(ring-plane) distances of ca. 3 Å. In the anion, the oxygen closest to the plane of the aromatic ring forms a torsion angle [O(3)–S(1)–C(1)–C(6)] of 16.9(3)°.

For **2**, the propyl chains of the cations are in *trans* conformation relative to the phosphorus atoms to which they are attached. In the crystal, the cations form channels, which run parallel to the *a*-axis and are occupied by pairs of anion chains (Figure 3, c). The two closest C–H···O contacts involve aryl hydrogen atoms [with angles C(26)–H(26B)···O(3) = 160.9(4)° and C(13)–H(13)···O(1) = 164.0(3)° and distances O(3)···H(26B) = 2.39(1) Å and O(1)···H(13) = 2.33(1) Å]. In the crystal structure, pairs of cations are linked by edge-to-face interactions involving all six

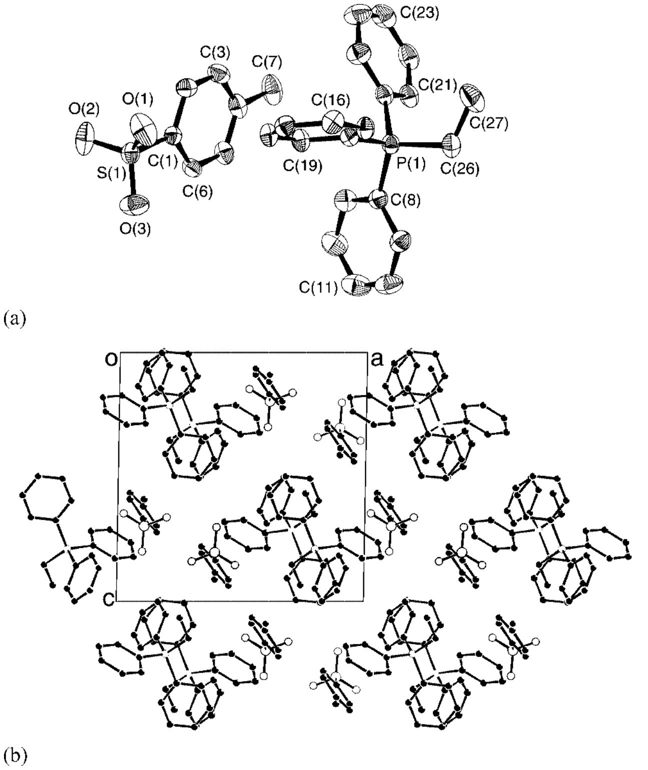


Figure 2. (a) The asymmetric unit and (b) the crystal structure of **1** viewed down the *b*-axis. Hydrogen atoms have been omitted for clarity.

phenyl rings as shown in Figure 3, (b) and, in addition, close CH···π contact occurs between a proton from a ring of the anion and one cation ring. For these interactions, the C–H···π(ring-plane) distances are in the 2.9–3.3 Å range. The oxygen closest to the plane of the aromatic ring of the anion forms a torsion angle O(2)–S(1)–C(1)–C(2) of –16.2(4)°.

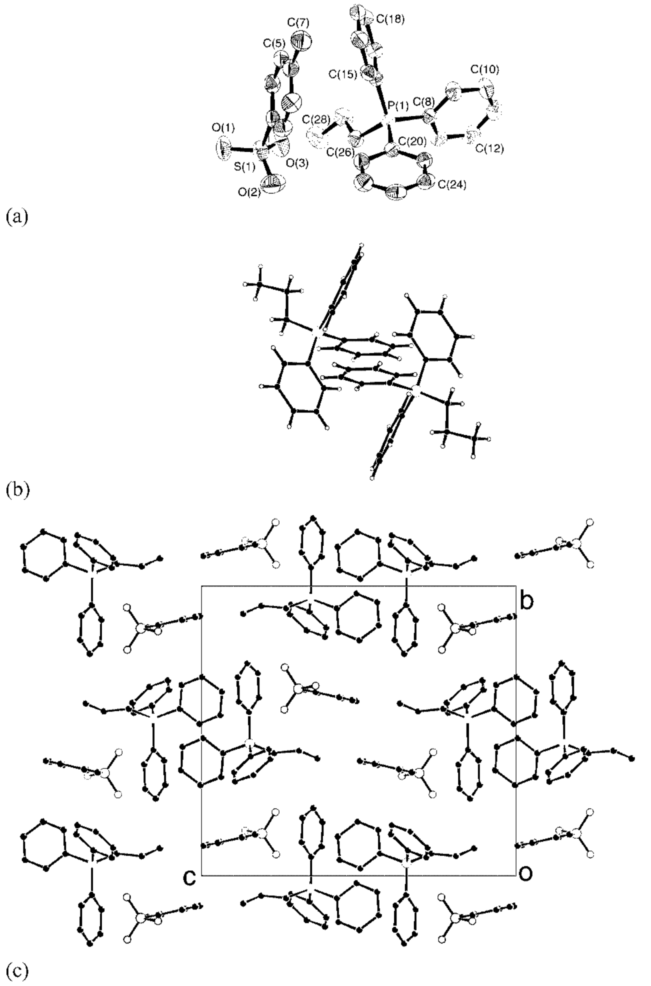


Figure 3. (a) The asymmetric unit, (b) a pair of cations and (c) the crystal structure of **2** viewed down the *a*-axis. Hydrogen atoms have been omitted from (a) and (c) for clarity.

The butyl chain in the crystal structure of **3** is also *all-trans* in conformation. In the structure (Figure 4, c), the tosylate anions are isolated from each other, with no direct contact between them. Pairs of symmetry related cations interact through edge-to-face contacts as shown in Figure 4, b. Each cation acts as both a donor and acceptor, with C–H···π(ring-centre) distance of ca. 2.64 Å. The two ions are also involved in π···π contact with a distance of ca. 3.5 Å between the planes of rings showing ca. 50% overlap. In the structure, a second type of π···π interaction occurs between phenyl rings of neighbouring cations with a separation distance of ca. 4.1 and an overlap of about 1/3 of a ring. The closest C–H···O contacts involve aryl–H and HC–H from the cation [with angles C(16)–H(16)···O(2) = 168.6(5)°, C(24)–H(24)···O(1) = 175.2(5)° and C(26)–H(26B)···O(1) = 173.4(4)° and contact distances O(2)···H(16) = 2.43(1) Å, O(1)···H(26B) = 2.29(1) Å, O(1)···H(24) = 2.37(1) Å]. The oxygen closest to the plane of the aromatic ring of the anion forms a torsion angle O(2)–S(1)–C(1)–C(2) of 12.8(4)°.

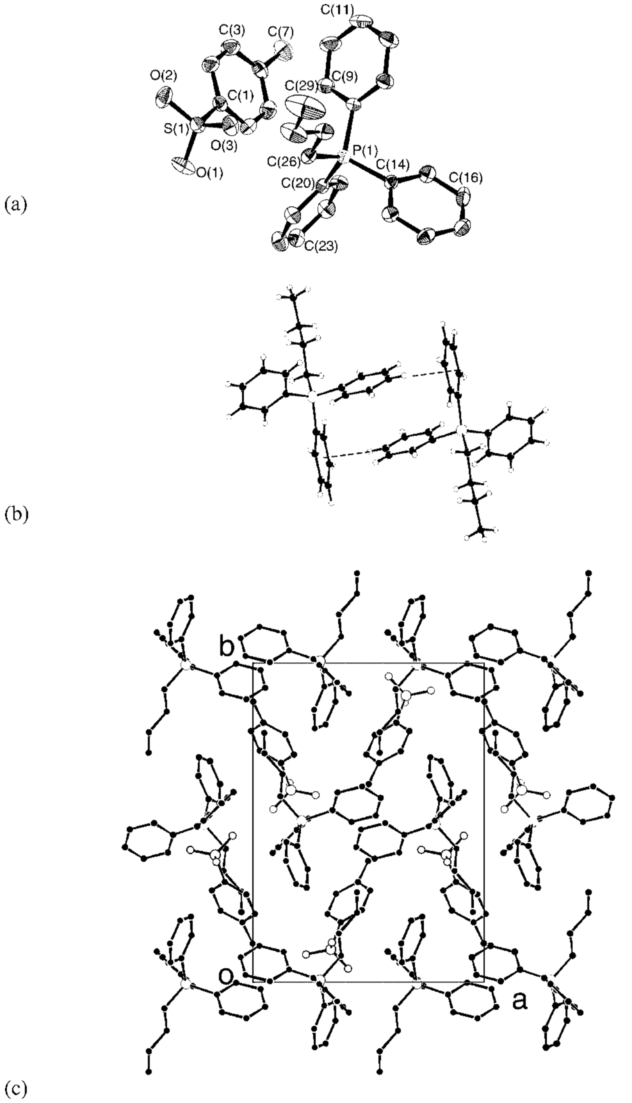


Figure 4. (a) The asymmetric unit of **3**, (b) a pair of cations with the dashed lines showing CH···π contacts and (c) the crystal structure viewed down the *c*-axis. Hydrogen atoms have been omitted from (a) and (c) for clarity.

In the structure of **4**, (Figure 5, c) the pentyl group of the cation is disordered with two components of 63% and 37% occupancy. For the major component, the chain adopts an all-*trans* conformation, except for the terminal methyl group which is *gauche*. As suggested by the similarity in the cell parameters and symmetry, the crystal structures of **3** and **4** are almost identical. Thus pairs of molecules interact in a manner similar to those discussed for **3**, with C–H···π(ring-centre) distance of ca. 2.67 Å and π···π contact interplanar distance of ca. 3.5 Å for rings showing 50% overlap (Figure 5, b). The separation between the planes of the pair of rings involved in the second type of π···π interaction (1/3 ring overlap) is also 4.1 Å. Aryl and CH$_2$

hydrogen atoms from the cation involved in the closest C–H···O contacts have CH···O distances: O(1)···H(19B) = 2.4(1) Å, O(1)···H(11) = 2.4(1) Å, O(2)···H(19A) = 2.4(1) Å and C–H···O angles: C(11)–H(11)···O(1) = 174.9(5)°, C(19)–H(19B)···O(1) = 170.6(5)°, C(19)–H(19A)···O(2) = 156.9(5)°. The oxygen closest to the plane of the aromatic ring of the anion forms a torsion angle O(3)–S(1)–C(24)–C(29) of 11.5(4)°.

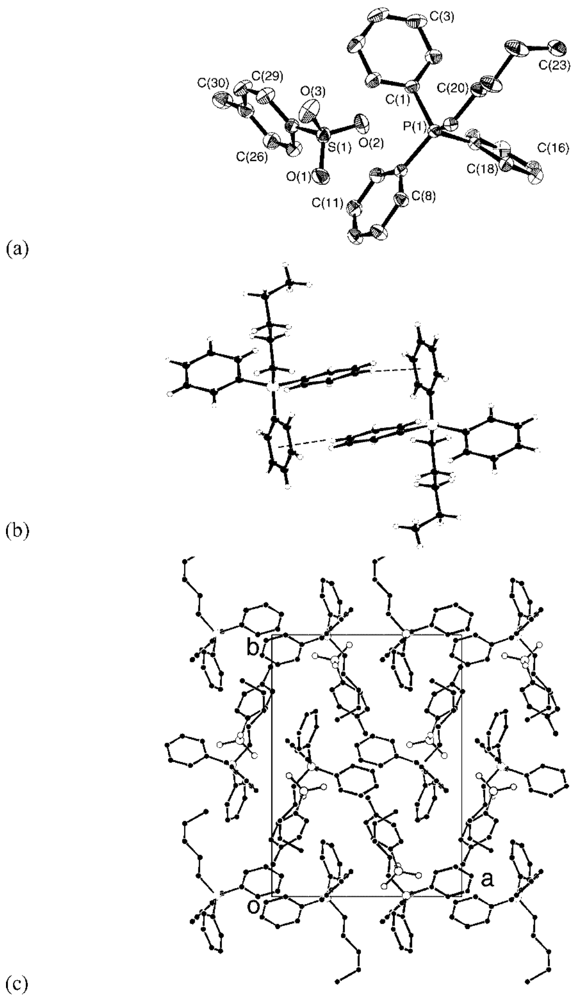


Figure 5. (a) The asymmetric unit of **4**, (b) a pair of cations with the dashed lines showing CH···π contacts and (c) the crystal structure viewed down the *c*-axis. Hydrogen atoms have been omitted from (a) and (c) for clarity.

Unlike the other salts, the crystals of **5** included the dichloromethane solvent (Figure 6, b). The structure consists of channels, parallel to the *a*-axis, which are occupied by the anions. The closest C–H···O contacts have distances: O(1)···H(26B) = 2.2(2) Å, O(1)···H(10) = 2.4(2) Å, O(2)···H(34A) = 2.4(2) Å and C–H···O angles: C(26)–H(26B)···O(1) = 178.7(9)°, C(10)–H(10)···O(1) = 176.0(9)°, C(34)–H(34A)···O(2) = 135.3(9)°. The oxygen closest to the plane of the aromatic ring of the anion forms a torsion angle O(2)–S(1)–C(1)–C(6) = 16.6(9)°. Interactions of π···π type also occur for a pair of cations (Figure 6, b), with an interplanar distance of ca. 3.5 Å for rings showing an overlap of ca. 1/3 of a ring. The rings involved are also donors in C–H···π interactions with –H···π distances of ca. 2.7 Å.

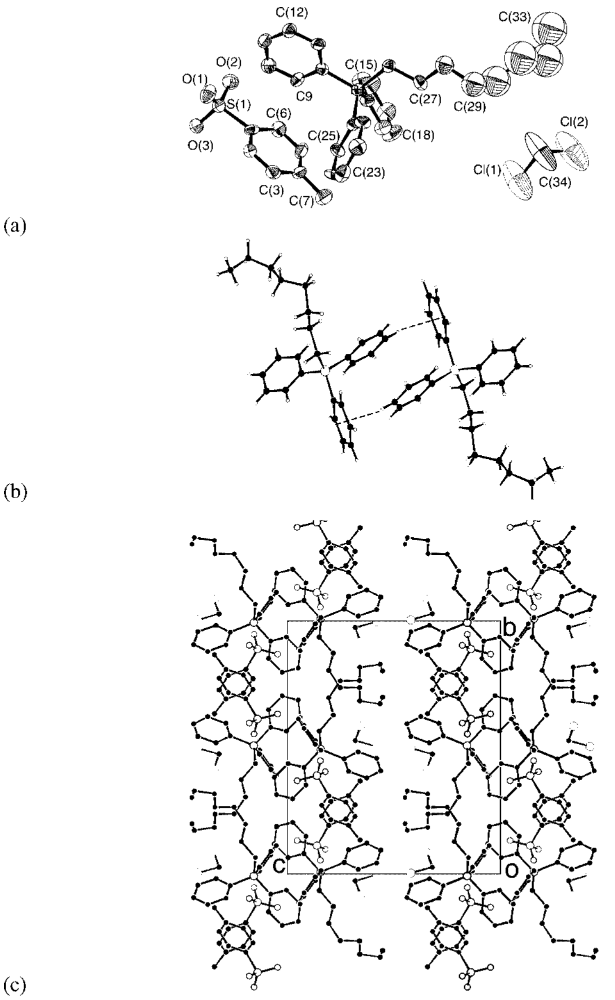


Figure 6. (a) The asymmetric unit, (b) a pair of cations with the dashed lines showing CH···π contacts and (c) the crystal structure of **5** viewed down the *a*-axis. Hydrogen atoms have been omitted from (a) and (c) for clarity.

Tosylates of Triphenylphosphonium Esters

In the crystal structure of **6**, the cations form channels, parallel to the *a*-axis, which are occupied by straight chains of tosylate anions (Figure 7, b). A number of edge-to-face interactions are observed with the tosylate anion as the donor and the cation as the acceptor. However, the planes of the rings involved are not perpendicular. For example, a C–H···π(ring-plane) distance of 2.9 Å is observed between rings with planes oriented ca. 60° relative to each other. The closest CH···O contacts involve cation methylene groups and tosylate oxygen atoms, with distances O(1)···H(26A) = 2.24(1) Å, O(2)···H(26B) = 2.26(1) Å, and angles C(26)–H(26A)···O(1) = 153.3(6)°, and C(26)–H(26B)···O(2) = 164.6(6)°. The oxygen closest to the plane of the aromatic ring of the anion forms a torsion angle O(1)–S(1)–C(1)–C(6) is –19.4(6)°.

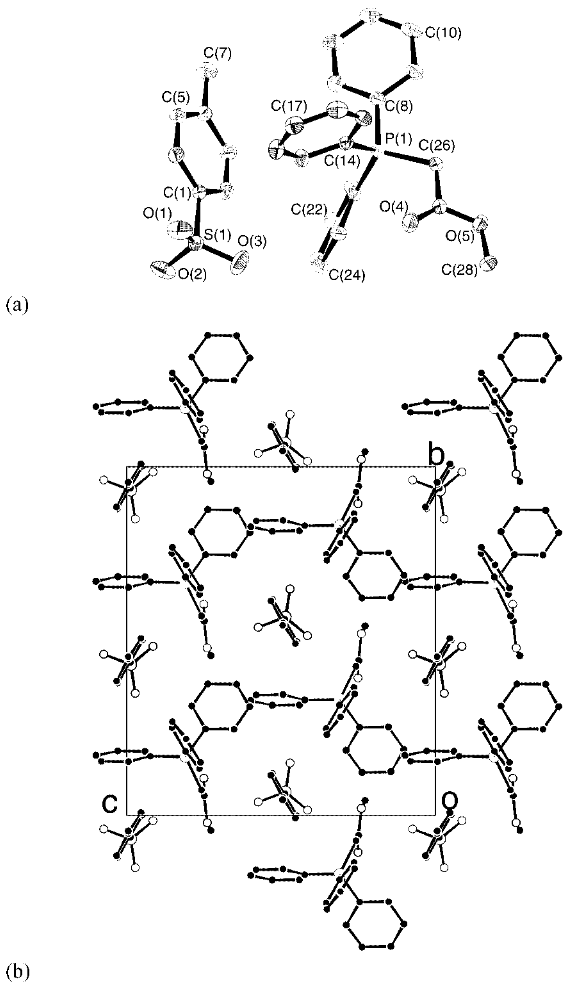


Figure 7. (a) The asymmetric unit and (b) the crystal structure of **6** viewed down the *a*-axis. Hydrogen atoms have been omitted for clarity.

In the crystal structure of **7**, the cations also form channels, running parallel to the *a*-axis (Figure 8, b), which are occupied by zigzag chains of tosylate anions. In the crystal structure, the closest C–H···π distance for an edge-to-face type of interaction involves a cation donor and anion acceptor with a distance of ca. 3.1 Å for rings oriented ca. 100° apart. The shortest C–H···O contact involves the tertiary proton of the cation and one tosylate oxygen with a distance O(2)···H(10) of 2.17(4) Å and angle C(10)–H(10)···O(2) of 175(3)°. The oxygen closest to the plane of the aromatic ring of the anion forms a torsion angle O(3)–S(1)–C(1)–C(2) of –11.7(4)°.

The crystal structure of **8** (Figure 9, b) does not contain channels. The cations pack in layers, parallel to the *ab* plane, between which isolated anions are located. Edge-to-face interactions are found and involve one cation ring acting as donor to two rings of two neighbouring cations. The two acceptor rings are almost perpendicular to the donor ring, with a C–H···π(ring-plane) distance of ca. 3 Å. The shortest CH···O contact involves an aryl proton and a tosylate oxygen with a distance O(3)···H(17) of 2.40(1) Å and angle C(17)–H(17)···O(3) of 141.5(4)°. The oxygen closest to the plane of the aromatic ring of the anion forms a torsion angle O(2)–S(1)–C(1)–C(2) of –29.2(8)°.

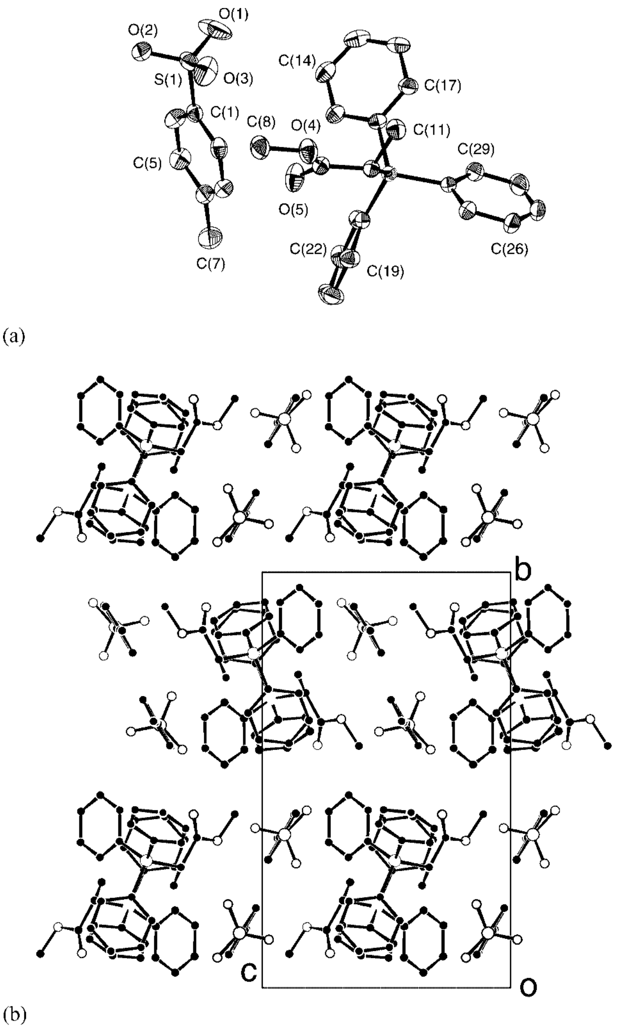
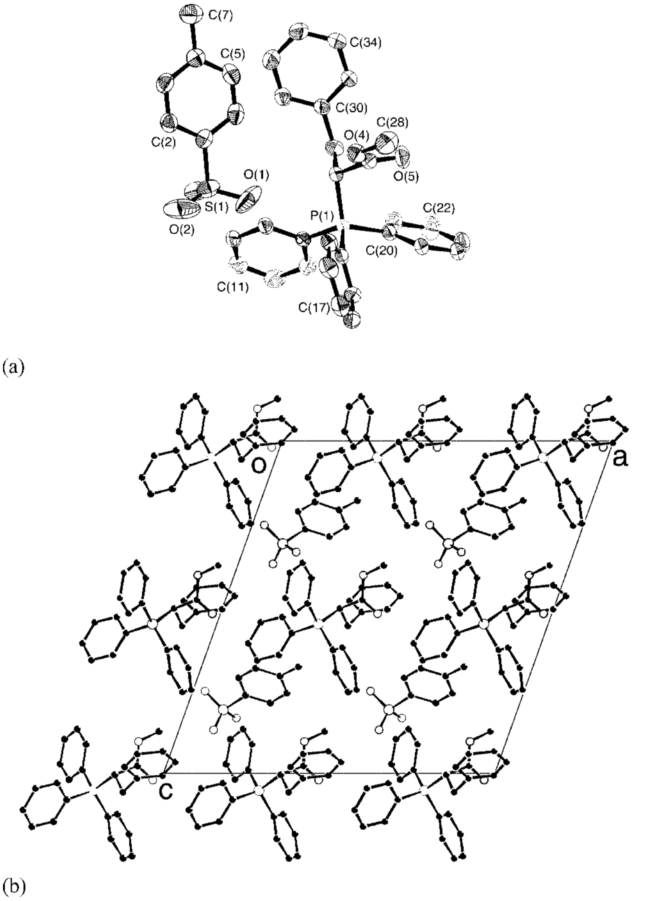


Figure 8. (a) The asymmetric unit and (b) the crystal structure of **7** viewed down the *a*-axis. Hydrogen atoms have been omitted for clarity.

Tributyl(ethyl)phosphonium Tosylate

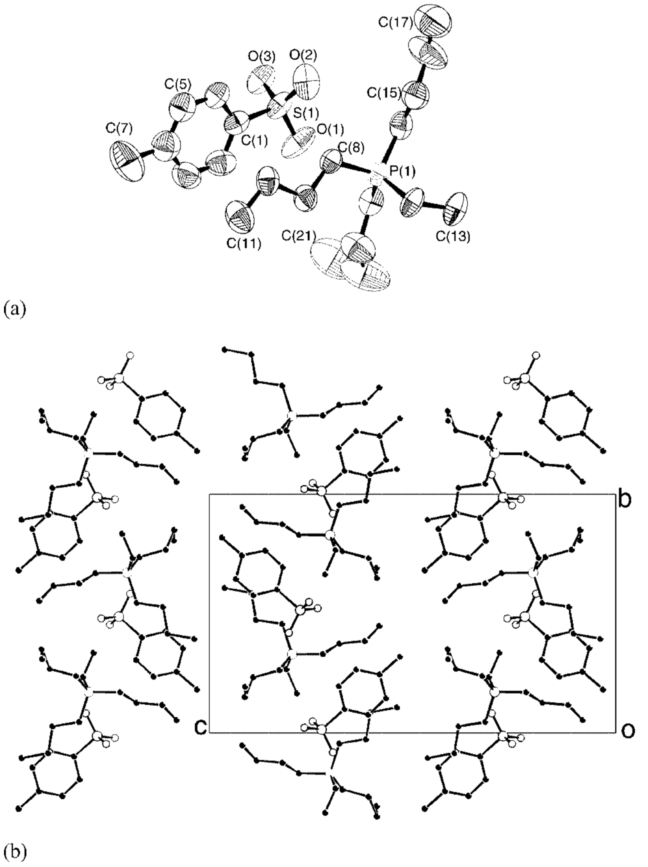
In the crystal structure of **9**, the methyl group of one butyl chain of the cation is disordered with two components of 60% and 40% occupancy. Considering just the major component, all the alkyl chains adopt *trans* conformation, apart from one, in which the methyl group is *gauche*. In the structure, the tosylate anions are isolated from each other, each being surrounded by cations. The structure can be visualised as being composed of sheets parallel to the *ab* (Figure 10, b), with intermolecular C–H···O contacts occurring within the sheets. The shortest CH···O contacts involve one tosylate oxygen with distances: O(1)···H(18A) = 2.4(3) Å, O(1)···H(12A) = 2.4(2) Å and angles: C(18)–H(18A)···O(1) = 173(1)°, C(12)–H(12A)···O(1) = 153(1)°. The oxygen closest to the plane of the aromatic ring of the anion forms a torsion angle O(1)–S(1)–C(1)–C(2) of –15.1(2)°.



(a)

(b)

Figure 9. (a) The asymmetric unit and (b) the crystal structure of **8** viewed down the *b*-axis. Hydrogen atoms have been omitted for clarity.



(a)

(b)

Figure 10. (a) The asymmetric unit and (b) the crystal structure of **9** viewed down the *a*-axis. Hydrogen atoms have been omitted for clarity.

Conclusions

The observations made during this study show that some care needs to be exercised when determining and using the melting points of these materials. The values obtained suggest that minute amounts of solvent can have a significant effect on the melting points, a possible explanation for the inconsistencies in the previously reported values.

Being ionic, coulombic interactions obviously exist in all these materials. Another feature common to all nine salts is the absence of strong hydrogen-bond donors. There is thus no single strong directional interaction to influence crystal packing. Despite this, a number of structural patterns, which may be valuable when modelling their liquid properties, are evident. In the tosylate anion the angles between the ring and the plane through the C–S–O group containing the oxygen atom closest to the ring fall within the range 11–20° (except for **8** in which the angle is ca. 30°). Apart from **5**, none of the salts contains solvent of crystallisation, a desirable characteristic in ionic solvents. All structures (**1**–**9**) show some degree of C–H···O contact with the tosylate ion acting as the acceptor. In addition, ring edge-to-face C–H···π interactions of variable geometry are also observed (the exception in the C–H···π case is **9**, in which the cation has no phenyl groups). C–H···X interactions (e.g. with X = halide or π) are a recurring theme in the field of ionic liquids and have been described extensively for, for example, imidazolium salts.[16–20]

The cations in the *n*-alkyltriphenylphosphonium salts **1**–**5** tend to pack in pairs (with the exception of **1**, in which the short alkyl chain may allow more favourable alternative packing in the crystal). This motif involving pairs of (phenyl)$_3$P groups is not unusual and has been observed in, for example, neutral triphenylphosphane oxides.[24] In the structures of **3**–**5**, the pairs of rings involved in C–H···π interactions are almost perpendicular, with interplanar angles of 86°, 85° and 81° respectively. The C–H···π distances (ca, 2.7 Å) in these three structures are also the shortest observed during this study and are similar to the average value obtained in a survey of organometallic materials (2.79 Å).[25] The donor rings in the ion pairs in **3**–**5** are also involved in π···π contacts, clearly leading to a stable motif. Although only a few structures have been determined, some clear differences are observed between the *n*-alkyl salts on the one hand and ester salts on the other. In the case of the esters, cation pairs are not observed and, in addition, the three structures are noncentrosymetric.

We believe that as in the case of imidazolium salts reported before, the structural information from this study will be important in future attempts to gain insight into the structural characteristics of ionic liquids of this type and will aid in the understanding of the nature of interactions with solutes.

Experimental Section

Techniques: NMR spectra were recorded with a Bruker AC-300 (^{1}H, 300 MHz; ^{13}C, 75.5 MHz) and a Bruker AV-300 (^{1}H, 300 MHz; ^{13}C, 75.5 MHz). Chemical shifts are described in parts per million (ppm) downfield shift from $\mathrm{SiMe_4}$ and are reported consecutively as position (δ_H or δ_C), multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, dd = doublet of doublet), coupling constant (J/Hz), relative integral and assignment. Proton NMR spectra were referenced to the chemical shift of residual proton signals ($\mathrm{CHCl_3}$ $\delta = 7.27$ ppm). Carbon spectra were referenced to a ^{13}C resonance of the solvent ($\mathrm{CDCl_3}$ $\delta = 77.16$ ppm). ^{31}P NMR spectra were referenced internally on $\mathrm{H_2PO_4}$ 5%/$\mathrm{D_2O}$ (δ, 0.00). Mass spectra were recorded with a VG Zabspec spectrometer. LSIMS (ceasium ionisation) was performed using 3-nitrobenzyl alcohol as the matrix. DSC results for **1**–**7**, **9** were obtained using a Perkin–Elmer Pyris 1 instrument between 25 and 200 °C at a heating rate of 20°/min with nitrogen purge gas and aluminium sample pans.

Single crystals were obtained by slow diffusion of diethyl ether into a dichloromethane solution of the salt. Single-crystal diffraction data for **1**–**3**, **6**–**9** were recorded at ca. 296 K with a Rigaku R-axis II diffractometer equipped with a molybdenum rotating anode source and an image plate detector system. Data for **4** and **5** were recorded with a Bruker Smart 6000 diffractometer equipped with a CCD detector and a copper-tube source. Structures were solved and refined using SHELXL.[26] During final refinement, aromatic C–H atoms were riding on the atoms they are bonded to with a bond length of 0.93 Å. Powder diffraction data confirm that the crystal structures obtained are representative of the bulk samples, except for **8**, where the amount of crystalline material obtained was too small for powder diffraction.

CCDC-277854 to -277862 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Syntheses: All manipulations were performed under argon using standard Schlenk techniques. All solvents were dried with the appropriate drying agent and distilled under dinitrogen: sodium benzophenone ketyl (diethyl ether, toluene) or calcium hydride (dichloromethane). Unless otherwise stated, all reagents were purchased from Aldrich, Acros or Lancaster and used as supplied. All the *p*-toluenesulfonates were obtained in good yield and high purity using known literature methods.[27]

The same method was used for all salts. Salts **1**–**5** were obtained by refluxing a 1:1 molar ratio solution of the alkyl *p*-toluenesulfonate (ca. 4 g) and triphenylphosphane (ca. 5 g) in toluene (ca. 50 mL) for 18 hours under argon. The solvent was then removed under reduced pressure and the residual was washed with diethyl ether. The resulting solid was recrystallised from dichloromethane/diethyl ether to a crystalline white solid.

The appropriate methoxycarbonylalkyl *p*-toluenesulfonate was used for **6** and **7**. The recrystallised product obtained for **6** had a pale brown colouration. For **8**, methyl 3-phenyl-2-(tolyl-4-sulfonyloxy)propionate was used and the solution was refluxed for 42 hours. The final recrystallised product was pale yellow in colour. A solution of ethyl *p*-toluenesulfonate and tributylphosphane was refluxed as described above to yield **9**.

Ethyltriphenylphosphonium Tosylate (1): Ethyl *p*-toluenesulfonate (3.8 g, 19.0 mmol) and triphenylphosphane (5.0 g, 19.1 mmol) afforded a crystalline white solid (8.1 g, 92%). M.p. 139–141 °C (ref.[21] 82–83 °C, ref.[12] 94–95 °C). FAB+: m/z (%) = 291 (100) $[\mathrm{M} - \mathrm{C_7H_7SO_3}]^+$, 753 (8) $[2\mathrm{M} - \mathrm{C_7H_7SO_3}]^+$. ^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz): $\delta = 1.34$ (dt, $^3J_{\mathrm{H,H}} = 7.4$, $^3J_{\mathrm{P-H}} = 20.1$ Hz, 3 H, $\mathrm{CH_2C}\mathit{H}_3$), 2.31 (s, 3 H, $\mathrm{C}C\mathit{H}_3$), 3.60 (m, 2 H, $\mathrm{C}\mathit{H}_2$), 7.08 (d, $^3J_{\mathrm{H,H}} = 8.0$ Hz, 2 H, $^{\text{tosylate}}$Ar-H), 7.63–7.79 (m, 17 H, Ar-H) ppm. ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 75.5 MHz): $\delta = 5.6$ (d, $^2J_{\mathrm{P,C}} = 5.2$ Hz, $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 14.8 (d, $^1J_{\mathrm{P,C}} = 52.3$ Hz, $\mathit{C}\mathrm{H_2}$), 20.3 ($\mathrm{C}\mathit{C}\mathrm{H_3}$), 116.8 (d, $^1J_{\mathrm{P,C}} =$ 86.2 Hz, $^{\text{phosphonium}}$Ar-C_{ipso}), 125.1, 127.3 ($^{\text{tosylate}}$Ar-CH), 129.4, 129.5, 132.4, 132.5, 134.0 ($^{\text{phosphonium}}$Ar-CH), 137.6, 143.5 ($^{\text{tosylate}}$Ar-C_{ipso}) ppm. ^{31}P NMR ($\mathrm{D_2O}$, 121 MHz): $\delta = 26.3$ ($^{\text{phosphonium}}P$) ppm.

Triphenyl(propyl)phosphonium Tosylate (2): Propyl *p*-toluenesulfonate (4.0 g, 18.7 mmol) and triphenylphosphane (4.9 g, 18.7 mmol) afford a crystalline white solid (8.4 g, 94%). M.p. 143–145 °C (ref.[21] 141–143 °C). FAB+: m/z (%) = 305 (100) $[\mathrm{M} - \mathrm{C_7H_7SO_3}]^+$, 781 (5) $[2\mathrm{M} - \mathrm{C_7H_7SO_3}]^+$. ^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz): $\delta = 1.18$ (m, 3 H, $\mathrm{CH_2C}\mathit{H}_3$), 1.61 (m, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.33 (s, 3 H, $\mathrm{CC}\mathit{H}_3$), 3.52 (m, 2 H, $\mathrm{PC}\mathit{H}_2$), 7.04 (d, $^3J_{\mathrm{H,H}} = 8.0$ Hz, 2 H, $^{\text{tosylate}}$Ar-H), 7.62–7.84 (m, 17 H, Ar-H) ppm. ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 75.5 MHz): $\delta = 14.7$ (d, $^3J_{\mathrm{P,C}} = 17.2$ Hz, $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 16.0 (d, $^2J_{\mathrm{P,C}} = 4.0$ Hz, $\mathit{C}\mathrm{H_2CH_3}$), 20.9 ($\mathrm{C}\mathit{C}\mathrm{H_3}$), 23.1 (d, $^1J_{\mathrm{P,C}} = 50.6$ Hz, $\mathrm{P}\mathit{C}\mathrm{H_2}$), 117.9 (d, $^1J_{\mathrm{P,C}} = 85.6$ Hz, $^{\text{phosphonium}}$Ar-C_{ipso}), 125.8, 127.8 ($^{\text{tosylate}}$Ar-CH), 130.0, 130.2, 133.0, 133.2, 134.5 ($^{\text{phosphonium}}$Ar-CH), 137.8, 144.5 ($^{\text{tosylate}}$Ar-C_{ipso}) ppm. ^{31}P NMR ($\mathrm{D_2O}$, 121 MHz): $\delta = 23.9$ ($^{\text{phosphonium}}P$) ppm.

***n*-Butyltriphenylphosphonium Tosylate (3):** *n*-Butyl *p*-toluenesulfonate (3.5 g, 15.3 mmol) and triphenylphosphane (4.0 g, 15.3 mmol) afforded a crystalline white solid (7.0 g, 93%). M.p. 132–134 °C (ref.[21] 139–140 °C, ref.[12] 116–117 °C). FAB+: m/z (%) = 319 (100) $[\mathrm{M} - \mathrm{C_7H_7SO_3}]^+$, 809 (11= $[2\mathrm{M} - \mathrm{C_7H_7SO_3}]^+$. ^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz): $\delta = 0.86$ (t, $^3J_{\mathrm{H,H}} = 7.1$ Hz, 3 H, $\mathrm{CH_2C}\mathit{H}_3$), 1.52 (m, 4 H, $\mathrm{C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 2.28 (s, 3 H, $\mathrm{CC}\mathit{H}_3$), 3.50 (m, 2 H, $\mathrm{PC}\mathit{H}_2$), 7.01 (d, $^3J_{\mathrm{H,H}} = 7.9$ Hz, 2 H, $^{\text{tosylate}}$Ar-H), 7.57–7.79 (m, 17 H, Ar-H) ppm. ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 75.5 MHz): $\delta = 13.3$ ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 20.9 ($\mathrm{C}\mathit{C}\mathrm{H_3}$), 21.3 (d, $^1J_{\mathrm{P,C}} = 50.6$ Hz, $\mathrm{P}\mathit{C}\mathrm{H_2}$), 23.2 (d, $^2J_{\mathrm{P,C}} = 16.7$ Hz, $\mathrm{PCH_2}\mathit{C}\mathrm{H_2}$), 24.5 (d, $^3J_{\mathrm{P,C}} = 4.0$ Hz, $\mathit{C}\mathrm{H_2CH_3}$), 118.0 (d, $^1J_{\mathrm{P,C}} =$ 85.6 Hz, $^{\text{phosphonium}}$Ar-C_{ipso}), 125.9, 127.8 ($^{\text{tosylate}}$Ar-CH), 130.1, 130.2, 133.1, 133.2, 134.6 ($^{\text{phosphonium}}$Ar-CH), 137.9, 144.5 ($^{\text{tosylate}}$Ar-C_{ipso}). ^{31}P NMR ($\mathrm{D_2O}$, 121 MHz): $\delta = 24.2$ ($^{\text{phosphonium}}P$) ppm.

***n*-Pentyltriphenylphosphonium Tosylate (4):** *n*-Pentyl *p*-toluenesulfonate (3.8 g, 15.6 mmol) and triphenylphosphane (4.1 g, 15.6 mmol) afforded a crystalline white solid (6.9 g, 87%). M.p. 123–125 °C. FAB+: m/z (%) = 333 (100) $[\mathrm{M} - \mathrm{C_7H_7SO_3}]^+$, 837 (9) $[2\mathrm{M} - \mathrm{C_7H_7SO_3}]^+$. ^{1}H NMR ($\mathrm{CDCl_3}$, 300 MHz): $\delta = 0.76$ (t, $^3J_{\mathrm{H,H}}$ = 7.1 Hz, 3 H, $\mathrm{CH_2C}\mathit{H}_3$), 1.24 (m, 2 H, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$), 1.53 (m, 4 H, $\mathrm{PCH_2C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CH_2}$), 2.31 (s, 3 H, $\mathrm{CC}\mathit{H}_3$), 3.61 (m, 2 H, $\mathrm{PC}\mathit{H}_2$), 7.08 (d, $^3J_{\mathrm{H,H}} = 8.0$ Hz, 2 H, $^{\text{tosylate}}$Ar-H), 7.62–7.84 (m, 17 H, Ar-H) ppm. ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 75.5 MHz): $\delta = 13.2$ ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 20.8 ($\mathrm{C}\mathit{C}\mathrm{H_3}$), 21.3 (d, $^1J_{\mathrm{P,C}} = 48.9$ Hz, $\mathrm{P}\mathit{C}\mathrm{H_2}$), 21.6 ($\mathit{C}\mathrm{H_2CH_3}$), 21.7 (d, $^3J_{\mathrm{P,C}} = 4.6$ Hz, $\mathit{C}\mathrm{H_2CH_2CH_3}$), 31.8 (d, $^2J_{\mathrm{P,C}} = 15.5$ Hz, $\mathrm{PCH_2}\mathit{C}\mathrm{H_2}$), 117.9 (d, $^1J_{\mathrm{P,C}} = 85.6$ Hz, $^{\text{phosphonium}}$Ar-C_{ipso}), 125.7, 127.7 ($^{\text{tosylate}}$Ar-CH), 130.0, 130.1, 133.0, 133.1, 134.5 ($^{\text{phosphonium}}$Ar-CH), 137.8, 144.4 ($^{\text{tosylate}}$Ar-C_{ipso}) ppm. ^{31}P NMR ($\mathrm{D_2O}$, 121 MHz): $\delta = 24.1$ ($^{\text{phosphonium}}P$) ppm.

***n*-Octyltriphenylphosphonium Tosylate (5):** *n*-Octyl *p*-toluenesulfonate (2.5 g, 8.8 mmol) and triphenylphosphane (2.3 g, 8.8 mmol) afforded a crystalline white solid (3.1 g, 65%). M.p. 129–131 °C, (ref.[12] 70–71 °C, ref.[21] 70–78 °C). FAB+: m/z (%) = 375 (100)

$[M - C_7H_7SO_3]^+$, 922 (6) $[2M - C_7H_7SO_3]^+$. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.79$ (t, $^{3}J_{H,H} = 6.6$ Hz, 3 H, CH_2CH_3), 1.11 (m, 8 H, CH_2CH_3), 1.48 (m, 4 H, $PCH_2CH_2CH_2CH_2$), 2.26 (s, 3 H, CCH_3), 3.46 (m, 2 H, PCH_2), 7.00 (d, $^{3}J_{H,H} = 8.1$ Hz, 2 H, $^{\text{tosylate}}$Ar-H), 7.62–7.76 (m, 17 H, Ar-H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75.5 MHz): $\delta = 13.6$ (CH_2CH_3), 20.8 (CCH_3), 21.4 (d, $^{1}J_{P,C} = 50.6$ Hz, PCH_2), 22.0, 28.4, 28.6 ($PCH_2CH_2CH_2CH_2CH_2$), 22.1 (CH_2CH_3), 29.8 (d, $^{2}J_{P,C} = 15.5$ Hz, PCH_2CH_2), 31.2 ($CH_2CH_2CH_3$), 117.8 (d, $^{1}J_{P,C} = 85.6$ Hz, $^{\text{phosphonium}}$Ar-C_{ipso}), 125.8, 127.7 ($^{\text{tosylate}}$Ar-CH), 129.9, 130.1, 133.0, 133.1, 134.5 ($^{\text{phosphonium}}$Ar-CH), 137.9, 144.1 ($^{\text{tosylate}}$Ar-C_{ipso}) ppm. ^{31}P NMR (D_2O, 121 MHz): $\delta = 24.3$ ($^{\text{phosphonium}}P$) ppm.

[(Methoxycarbonyl)methyl]triphenylphosphonium Tosylate (6): (Methoxycarbonyl)methyl *p*-toluenesulfonate (2.9 g, 11.9 mmol) and triphenylphosphane (3.1 g, 11.9 mmol) afforded a crystalline pale brown solid (4.7 g, 78%). M.p. 164–166 °C. FAB+: *m*/*z* (%) = 335 (100) $[M - C_7H_7SO_3]^+$, 841 (9) $[2M - C_7H_7SO_3]^+$. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 2.32$ (s, 3 H, CCH_3), 3.59 (s, 3 H, OCH_3), 5.30 (d, $^{2}J_{P-H} = 13.5$ Hz, 2 H, PCH_2), 7.08 (d, $^{3}J_{H,H} = 8.0$ Hz, 2 H, $^{\text{tosylate}}$Ar-H), 7.62–7.87 (m, 17 H, Ar-H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75.5 MHz): $\delta = 21.2$ (CCH_3), 31.3 (d, $^{1}J_{P,C} = 58.0$ Hz, PCH_2), 53.2 (OCH_3), 117.9 (d, $^{1}J_{P,C} = 89.1$ Hz, $^{\text{phosphonium}}$Ar-C_{ipso}), 126.1, 127.1 ($^{\text{tosylate}}$Ar-CH), 130.1, 130.3, 133.7, 133.8, 135.0 ($^{\text{phosphonium}}$Ar-CH), 138.3, 144.3 ($^{\text{tosylate}}$Ar-C_{ipso}), 165.3 (d, $^{2}J_{P,C} = 3.4$ Hz, CO) ppm. ^{31}P NMR (D_2O, 121 MHz): $\delta = 20.8$ ($^{\text{phosphonium}}P$) ppm.

[1-(Methoxycarbonyl)ethyl]triphenylphosphonium Tosylate (7): 1-(Methoxycarbonyl)ethyl *p*-toluenesulfonate (1.4 g, 5.4 mmol) and triphenylphosphane (1.42 g, 5.4 mmol) in toluene (50 mL) afforded crystalline white needles (1.8 g, 64%). M.p. 175–176 °C. FAB+: *m*/*z* (%) = 349 (100) $[M - C_7H_7SO_3]^+$, 869 (4) $[2M - C_7H_7SO_3]^+$. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.67$ (dd, $^{3}J_{H,H} = 7.0$, $^{2}J_{P-H} = 18.6$ Hz, 3 H, $CHCH_3$), 2.33 (s, 3 H, CCH_3), 3.54 (s, 3 H, OCH_3), 6.36 (m, 1 H, PCH), 7.11 (d, $^{3}J_{H,H} = 7.7$ Hz, 2 H, $^{\text{tosylate}}$Ar-H), 7.64–7.96 (m, 17 H, Ar-H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75.5 MHz): $\delta = 13.0$ (d, $^{2}J_{P,C} = 13.1$ Hz, $CHCH_3$), 21.2 (CCH_3), 36.2 (d, $^{1}J_{P,C} = 48.2$ Hz, PCH), 53.3 (OCH_3), 118.0 (d, $^{1}J_{P,C} = 79.7$ Hz, $^{\text{phosphonium}}$Ar-C_{ipso}), 126.1, 128.2 ($^{\text{tosylate}}$Ar-CH), 130.0, 130.2, 134.0, 134.1, 134.7 ($^{\text{phosphonium}}$Ar-CH), 138.7, 144.5 ($^{\text{tosylate}}$Ar-C_{ipso}), 166.1 (d, $^{2}J_{P,C} = 3.2$ Hz, CO). ^{31}P NMR (D_2O, 121 MHz): $\delta = 28.0$ ($^{\text{phosphonium}}P$) ppm.

[1-(Methoxycarbonyl)-2-phenylethyl]triphenylphosphonium Tosylate (8): Methyl 3-phenyl-2-(tolyl-4-sulfonyloxy)propionate (0.5 g, 1.5 mmol) and triphenylphosphane (0.4 g, 1.5 mmol) in toluene (20 mL) afforded a crystalline pale yellow solid (0.5 g, 56%). The material was the most difficult to obtain and it was not possible to carry out full characterisation.

Tributyl(ethyl)phosphonium Tosylate (9): Ethyl *p*-toluenesulfonate (2.0 g, 10.0 mmol) and tributylphosphane (2.0 g, 10.0 mmol) in toluene (50 mL) afforded a crystalline white solid (3.7 g, 93%). M.p. 74–76 °C (ref.[12] 81–83 °C). FAB+: *m*/*z* (%) = 231 (100) $[M - C_7H_7SO_3]^+$. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.97$ (m, 9 H, $CH_2CH_2CH_3$), 1.22 (m, 3 H, PCH_2CH_3), 1.46 (m, 12 H, $PCH_2CH_2CH_2$), 2.28 (m, 6 H, PCH_2CH_2), 2.31 (s, 3 H, CCH_3), 2.42 (m, 2 H, PCH_2), 7.10 (d, $^{3}J_{H,H} = 8.0$ Hz, 2 H, $^{\text{tosylate}}$Ar-H), 7.78 (d, $^{3}J_{H,H} = 8.0$ Hz, 2 H, $^{\text{tosylate}}$Ar-H) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75.5 MHz): $\delta = 5.1$ (d, $^{2}J_{P,C} = 5.7$ Hz, CH_2CH_3), 11.5 (d, $^{1}J_{P,C} = 48.9$ Hz, PCH_2CH_3), 12.6 ($CH_2CH_2CH_3$), 17.2 (d, $^{1}J_{P,C} = 47.7$ Hz, PCH_2CH_2), 20.4 (CCH_3), 22.7 (d, $^{3}J_{P,C} = 4.6$ Hz, $CH_2CH_2CH_3$), 23.0 (d, $^{2}J_{P,C} = 15.5$ Hz, PCH_2CH_2), 125.2, 127.5 ($^{\text{tosylate}}$Ar-CH), 137.8, 144.1 ($^{\text{tosylate}}$Ar-C_{ipso}) ppm. ^{31}P NMR (D_2O, 121 MHz): $\delta = 34.6$ ($^{\text{phosphonium}}P$) ppm.

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[1] P. Walden, *Bull. Acad. Imp. Sci. St. Petersbourg* **1914**, 1800.

[2] R. D. Rogers, K. R. Seddon, in: *Ionic Liquids: Industrial Applications to Green Chemistry*, ACS Symposium Series 818, American Chemical Society, Washington, DC, **2002**.

[3] P. Wasserscheid, T. Welton (Eds.), *Ionic Liquids in Synthesis*, Wiley-VCH: Weinheim, **2003**.

[4] C. Chiappe, D. Pieraccini, *J. Phys. Org. Chem.* **2005**, *18*, 275–297.

[5] a) C. M. Gordon, *Appl. Catal., A* **2001**, *222*, 101–117; b) J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, R. D. Rogers, *Green Chem.* **2001**, *3*, 156–164; c) R. Sheldon, *Chem. Commun. (Cambridge, U.K.)* **2001**, 2399–2407; d) T. Welton, *Chem. Rev. (Washington, DC, U.S.A.)* **1999**, *99*, 2071–2073; e) T. Welton, *Coord. Chem. Rev.* **2004**, *248*, 2459–2477; f) J. Dupont, R. F. de Souza, P. A. Z. Suarez, *Chem. Rev.* **2002**, *102*, 3667–3692.

[6] D. E. Kaufmann, M. Nouroozin, H. Henze, *Synlett* **1996**, 1091–1092.

[7] M. Badri, J. J. Brunet, R. Perron, *Tetrahedron Lett.* **1992**, *33*, 4435–4438.

[8] J. F. Knifton, *J. Am. Chem. Soc.* **1981**, *103*, 3959–3961.

[9] J. F. Knifton, *J. Mol. Catal.* **1987**, *43*, 65–77.

[10] J. F. Knifton, *J. Mol. Catal.* **1988**, *47*, 99–116.

[11] C. J. Bradaric, A. Downard, C. Kennedy, A. J. Robertson, Y. Zhou, *Green Chem.* **2003**, *5*, 143–152.

[12] N. Korodia, S. Guise, C. Newlands, J. Andersen, *Chem. Commun.* **1998**, 2341–2342.

[13] P. Ludley, N. Korodia, *Tetrahedron Lett.* **2001**, *42*, 2011–2014.

[14] C. L. Johnson, R. E. Donkor, W. Nawaz, N. Karodia, *Tetrahedron Lett.* **2004**, *45*, 7359–7361.

[15] C. Comyns, N. Karodia, S. Zeler, J. Andersen, *Catal. Lett.* **2000**, *67*, 113–115.

[16] J. Dupont, *J. Braz. Chem. Soc.* **2004**, *15*, 341–350.

[17] A. Elaiwi, P. B. Hitchcock, K. R. Seddon, N. Srinivasan, Y.-M. Tan, T. Welton, J. A. Zoraa, *J. Chem. Soc., Dalton Trans.* **1995**, 3467–3472.

[18] J. van den Broeke, M. Stam, M. Lutz, H. Kooijman, A. L. Spek, B.-J. Deelman, G. van Koten, *Eur. J. Inorg. Chem.* **2003**, 2798–2811.

[19] C. S. Consorti, P. A. Z. Suarez, R. F. de Souza, R. A. Burrow, D. H. Farrar, A. J. Lough, W. Loh, L. H. M. da Silva, J. Dupont, *J. Phys. Chem. B* **2005**, *109*, 4341–4349.

[20] , J. Dupont, P. A. Z. Suarez, R. F. de Souza, R. A. Burrow, J.-P. Kinkzinger, *Chem. Eur. J.* **2000**, *6*, 2377–2377.

[21] D. Klamann, P. Weyerstahl, *Ber.* **1964**, *97*, 2534–2538.

[22] D. E. Bugner, *J. Org. Chem* **1989**, *54*, 2580–2586.

[23] W. G. Dauben, J. M. Gerdes, R. A. Bunce, *J. Org. Chem.* **1984**, *49*, 4293–4295.

[24] P. Calcagno, B. M. Kariuki, S. Kitchin, J. M. A. Robinson, D. Philp, K. D. M. Harris, *Chem. Eur. J.* **2000**, *6*, 2338–2349.

[25] D. Braga, F. Grepioni, E. Tedesco, *Organometallics* **1998**, *17*, 2669–2672.

[26] G. M. Sheldrick, SHELXL. Program package for crystal structure determination. University of Göttingen, Germany.

[27] L. F Fieser, M. Fieser, in: *Reagents for Organic Synthesis*, Wiley, New York, **1967**.

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