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Tetraarylphosphonium Salts as Soluble Supports for Oxidative Catalysts and Reagents

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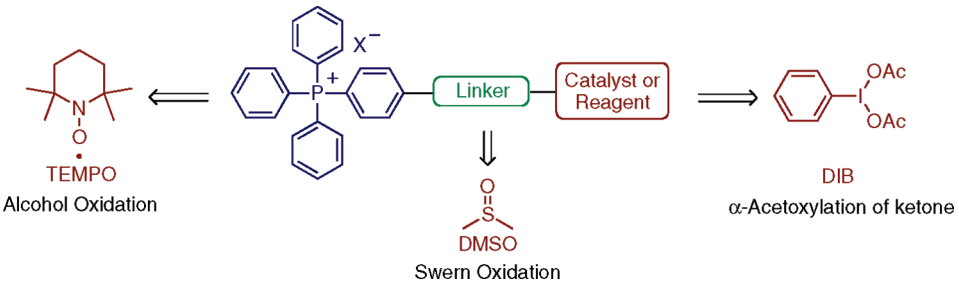

Tetraarylphosphonium (TAP)-supported DMSO, TEMPO, and DIB reagents were synthesized and used for the oxidation of alcohols, including Swern oxidation and for the α-acetoxylation of ketones. By taking advantage of the predictable solubility properties of the TAP unit, simple precipitation and filtration of the phosphonium moiety permit complete separation of the desired oxidation products. This paper describes the preparation of these three TAP-supported oxidative reagents and their activity in the aforementioned oxidative transformations. Furthermore, we have demonstrated that these reagents can be recycled directly when used in catalytic processes and following regeneration when used in stoichiometric processes.

Introduction

Oxidative processes are a class of chemical transformations of major importance and are continuously used in both laboratory and industrial scale.[1] In spite of their great utilities, these processes are not without drawbacks; they can implicate expensive reagents, large amount of waste, and tedious purifications. In light of these limitations, there has been much interest in the development of more simple and green strategies for these transformations, including facile separation techniques and recycle of used compounds.[2] Due to the importance of oxidative processes as well as the development of greener methodologies, devising supported oxidative reagents has become an active research area in recent years. Reagents of interest for alcohol oxidation into carbonyl compounds include dimethylsulfoxide (DMSO),[3] 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO),[4] 2-iodobenzoic acid (IBX),[5] Dess−Martin periodinane (DMP),[6] and (diacetoxy)iodobenzene (DIB).[7] Additionally, work in hypervalent iodine chemistry has extended the number of possible oxidative transformations, permitting the development of other applications for the supported derivatives, including functionalization of carbonyl derivatives, dearomatization of phenolic substrates, and metal-mediated functionalization of C−H bonds.[8]

Many strategies have been used to immobilize these reagents onto chemical scaffolds, not only to facilitate the

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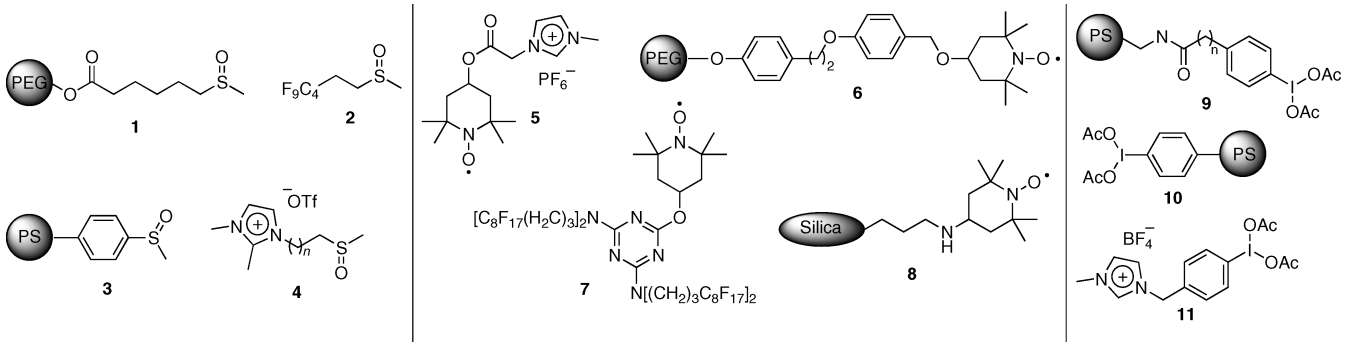

FIGURE 1. Examples of supported oxidative catalysts and reagents: DMSO, TEMPO, and DIB derivatives.

purification and the isolation of the desired compound but also to ease drawbacks of their use (e.g., volatility, solubility, and stability). Examples of such strategies include the attachment of the reagent onto soluble organic and inorganic polymers, ionic liquids, and perfluorous alkyl chains (Figure 1). More specifically, supported DMSO derivatives **1**−**4**[9−12] have been synthesized to eliminate the unpleasant smell of dimethylsulfide (DMS) byproduct by reducing its volatility. By extension, its disposal can be better mediated, thus reducing its environmental impact. Supported TEMPO derivatives **5**−**8**[13−16] have been synthesized to facilitate the separation of the catalyst from the desired product and permit the reuse of the rather expensive TEMPO. Both supported DMSO and TEMPO reagents have been applied in oxidation of alcohols. Simultaneously, supported DIB derivatives **9**−**11**[17−19] have been developed to facilitate the removal of the stoichiometric amount of iodobenzene generated during reactions. These hypervalent iodine derivatives have been applied in various types of transformations, notably the 1,2-aryl migration of alkyl ketones, the oxidation of hydroquinones, spirocyclizations, and the α-hydroxylation of ketones.[17−19]

Our research group has developed a new soluble scaffold utilizing tetraarylphosphonium (TAP) salts. These TAP units are used as a solubility control group to modify and predict the solubility properties of supported reagents and synthetic intermediates. We have demonstrated the efficiency of these salts in numerous transformations with TAP-bounded reagents derived from triphenylphosphine,[2,20] diethyl diazocarboxylate,[2] tributyltin chlorides,[21] and dialkylcarbodiimides.[22] Their utility in small-molecule synthesis utilizing derived chiral auxiliary for the synthesis of *N*-Boc-(−)-coniine was described as well as Wang and Sasrin analogues for peptide synthesis.[23] In each case, the process involves attaching a reagent or a synthetic intermediate to a TAP salt and then performing a chemical transformation in a solvent that will dissolve all the reaction components. Upon completion of the reaction, another solvent is added to induce the selective precipitation of the TAP-supported species, allowing its facile removal from the desired non-supported product, or non-supported reaction byproduct by a simple filtration. The solubility of these salts is predictable regardless of the type of reagents that is tethered to them. They are soluble in medium polarity solvent systems (DCM, MeCN, DMSO, DMF), and addition of a less polar solvent (hexane, Et_2O, toluene) induces their precipitation. Furthermore, these TAP salts are easy to handle due to their powder nature and are also robust scaffolds for harsh reaction conditions.

Following our previous work, we decided to extend the TAP salt technology to oxidative reagents and catalysts. Herein, we report the synthesis of the following TAP-supported derivatives, a DMSO reagent for Swern oxidation, a TEMPO for catalytic alcohol oxidation, and an in situ generated DIB for α-acetoxylation of ketone.[24] These supported reagents were successfully applied in their respective transformations, and their synthetic route is shown to be efficient and inexpensive.

Results and Discussion

We first explored the possibility of using a TAP-supported reagent in stoichiometric quantities and evaluating the efficiency of the separation. As a result, we reasoned that a TAP-supported DMSO for the Swern oxidation would be a suitable test substrate, in which the sulfoxide moiety would be attached to the TAP salt by an ester functionality

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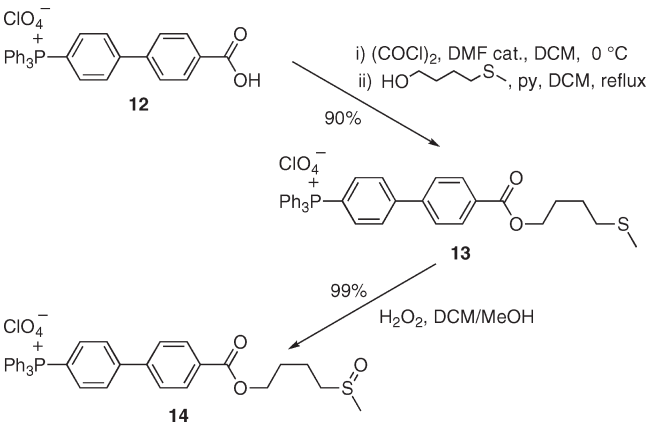
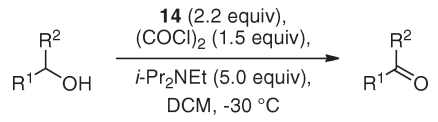
(Scheme 1). Previous work has shown that the biphenyl moiety was suitable for the functionalization of TAP salts, as the electron-withdrawing effects of the phosphonium salt,

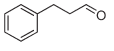
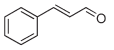
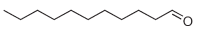
SCHEME 1



which can influence the reactivity of the supported reagent or synthetic intermediate, can be diminished.[21−23] Beginning with the previously reported acid **12**,[23] the supported sulfoxide **14** was prepared in a two-step esterification/oxidation sequence with an overall yield of 90%. In both steps, the TAP salts were purified and isolated via a precipitation/filtration sequence. We successfully applied TAP-supported DMSO **14** in the Swern oxidation of alkyl alcohols in the presence of oxalyl chloride at −30 °C in DCM and isolated the corresponding aldehydes in 61−86% yield (Table 1).

TABLE 1. TAP-Supported DMSO 14 Oxidation of Alcohol to Carbonyl Derivatives



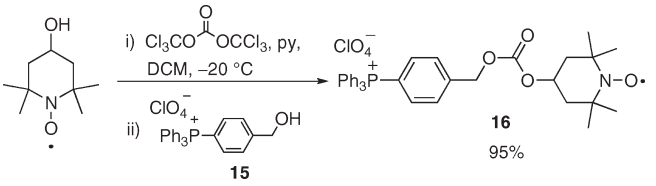
Entry	Product	Yield (%)
1		86[a]
2		61[b]
3		82[b]

[a]Reaction performed on a 1 mmol scale. [b]Reaction performed on a 0.25 mmol scale; 2.2 equiv of $(COCl)_2$.

Following completion of the reaction, the mixture of sulfide **13** and sulfoxide **14** could easily be separated from the desired product by a simple precipitation/filtration sequence. Concentration of the filtrate afforded carbonyl compounds, which, if needed, are subsequently purified. The TAP-supported DMSO **14** was recovered by treatment of the phosphonium mixture with a hydrogen peroxide solution in 96% yield. It should be noted that no degradation or leaching of the reagent was observed after the Swern oxidation or after its regeneration, demonstrating the efficiency of the ester functionality as a linker.

Encouraged by these results, we next investigated the possibility of using this technology in a catalytic system. As such, we envisioned using a TAP-supported TEMPO with the aim of recycling the catalyst. We also wanted to design a more efficient route toward the TAP-supported TEMPO. With this in mind, we attached the TEMPO via a carbonate functionality using the alcohol **15**[25] and 4-hydroxy-TEMPO due to its relative low cost (Scheme 2). Consequently, the

SCHEME 2



TAP-supported TEMPO **16** was synthesized in a two-step sequence, starting from the commercially available 4-bromobenzyl alcohol in a 92% overall yield. As a key step, 4-hydroxy-TEMPO was treated with triphosgene to generate a reactive chlorocarbonyl pyridinium intermediate. Subsequent addition of the alcohol **15** afforded the desired TAP-supported TEMPO **16** that was purified by a simple precipitation/filtration sequence.

The reactivity and the scope of TEMPO **16** were investigated under Annelli's conditions[4] using bleach as terminal oxidant in view of its versatility, simplicity, low cost, and common use in both academic and industrial processes. The typical procedure involved the use of catalytic amounts of TEMPO (1 mol %) and potassium bromide (10 mol %) in presence of an excess of bleach (1.25 equiv) buffered with sodium bicarbonate (pH 8.5−9.5) in DCM. Under these conditions, a variety of monoprotected diols, alkyl, and benzylic alcohols were oxidized into the corresponding carbonyl compounds in excellent yields (Table 2).

Primary alcohols were rapidly oxidized (5−10 min), while secondary alcohols required slightly longer reaction times (30 min). In all cases, complete conversion was observed, and no overoxidation byproducts could be detected in crude ^{1}H NMR. The carbonyl compounds were easily separated from the TAP-supported TEMPO by the formerly described precipitation/filtration sequence. Concentration of the filtration layer afforded pure carbonyl compounds in high yields.

We next investigated the possibility of recycling the TEMPO **16** using 3-phenylpropanol as test substrate under the same conditions and allowed the reaction to proceed for 15 min. After separation from the reaction products, the supported catalyst was reused up to three times without significant decrease in reactivity, as the starting alcohol was completely consumed and only the aldehyde was observed as a reaction product (Table 3). Following the fifth run, the activity of the catalyst remained high, although the starting alcohol was not completely consumed and overoxidation byproducts were also present in the crude mixture. Consequently, the aldehyde was isolated in good yield following purification by flash chromatography on silica gel. This outcome indicated degradation of the supported catalyst that can be explained either by decomposition of the TEMPO moiety or by a leaching from the TAP support in the reaction media. This observation suggested that a lower

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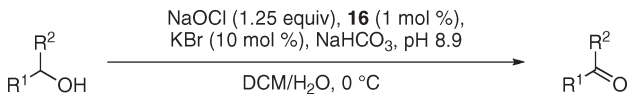
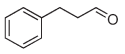
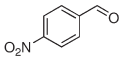
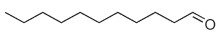
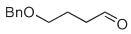
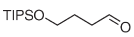
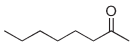
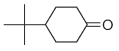
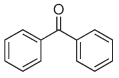
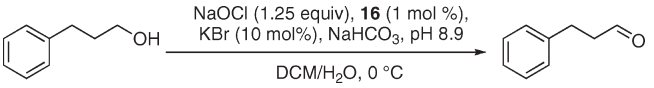
TABLE 2. TAP-Supported TEMPO 16 Oxidation of Alcohol to Carbonyl Derivatives



Entry[a]	Product	Time (min)	Yield (%)[b]
1		10	98
2		5	90
3		10	90
4		10	95
5		10	92
6		10	90
7		10	93
8		30	92
9		30	91
10		30	98

[a]Reaction performed on a 1 mmol scale. [b]Conversion (>99%) in all cases was determined by ^{1}H NMR of the crude mixture.

TABLE 3. Recycling of TAP-Supported TEMPO 16: Oxidation of 3-Phenylpropanol



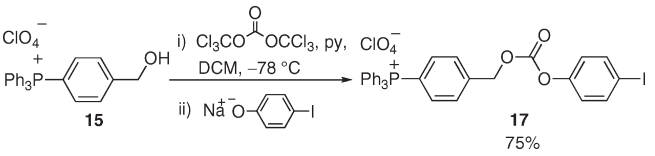
Run[a]	Time (min)	Yield (%)
1	15	98
2	15	95
3	15	97
4	15	93
5	15	77[b]

[a]Reaction performed on a 3 mmol scale. [b]Purified by flash chromatography on silica gel.

quantity (<1 mol %) of the TAP-supported TEMPO **16** is effective on the oxidation of alcohols.

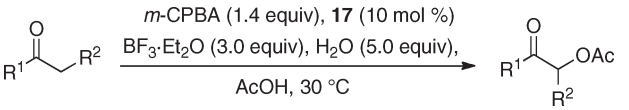
The last reported oxidizing reagent is a TAP-supported iodobenzene that is oxidized in situ in the applied reaction into the corresponding TAP-supported DIB for α-acetoxylation of ketone. In the light of the earlier results, we decided to link the iodobenzene moiety via the carbonate functionality to limit the number of synthetic steps (Scheme 3). The alcohol **15** was treated with triphosgene, and subsequent addition of sodium 4-iodophenolate afforded the desire TAP-supported iodobenzene **17** in 75% yield.

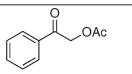
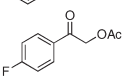
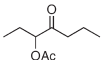
SCHEME 3



We applied the TAP-supported iodobenzene **17** for the preparation of several α-acetoxyketone using conditions developed by Ochiai and co-workers,[24] in which a catalytic amount of iodobenzene (10 mol %) is transformed in situ to its hypervalent derivative by treatment with *m*-CPBA in the presence of acetic acid (Table 4).

TABLE 4. TAP-Supported Iodobenzene 17 α-Acetoxylation of Ketones



Entry[a]	Product	Yield (%)[b]
1		52
2		48 (55)[c]
3		50 (46)[c]

[a]Reaction performed on a 1 mmol scale. [b]Parentheses are reported yields with iodobenzene.[24] [c]*m*-CPBA (2.0 equiv).

With these conditions, we isolated the desired product in 48−50% yields, which is consistent with Ochiai's results. The TAP-supported iodobenzene **17** could be selectively precipitated and recovered prior to the workup treatment by adding excess of Et_2O in the reaction media, and the α-acetoxyketones were easily isolated and further purified by flash chromatography to remove other reaction byproduct.

Conclusion

In summary, new soluble TAP-supported oxidative reagents have been efficiently prepared and have proven to be excellent reagents for oxidative processes. The TAP-supported DMSO **14** selectively oxidized primary alcohols into corresponding aldehydes with effective separation of the TAP salt species, without formation of unpleasant DMS. The TAP-supported TEMPO **16** was shown to be efficient not only in oxidizing a variety of primary and secondary alcohols but also in being reused several times. In another oxidative transformation, TAP-supported iodobenzene **17** has proven to be active in a catalytic version of α-acetoxylation of a ketone. In each case, TAP-supported byproducts were easily removed following simple workup procedures involving a precipitation/filtration sequence. Finally, the high reactivity, the simple separation procedure, and the possibility of recycling make these TAP salt derivatives attractive alternatives to non-supported reagents.

Experimental Section

(4′-{[4-(Methylthio)butoxy]carbonyl}-1,1′-biphenyl-4-yl)(triphenyl)phosphonium perchlorate (13). To a solution of acid **12** (9.0 g, 16.1 mmol, 1.0 equiv) in DCM (80 mL, 0.2 M) at 0 °C was added $(COCl)_2$ (1.69 mL, 19.32 mmol, 1.2 equiv) followed by DMF (5−6 drops). The solution was stirred for 2 h, and the excess of $(COCl)_2$ was evaporated under reduced pressure. The resultant foam was dissolved in DCM (80 mL, 0.2 M), and pyridine (3.26 mL, 40.25 mmol, 2.5 equiv) was added followed by a solution of 4-methyl(thio)butanol (2.35 mL, 19.32 mmol, 1.2 equiv) in THF (33 mL, 0.6 M). The mixture was heated to reflux for 16 h and cooled to rt. The solution was diluted with DCM (200 mL) and washed with aqueous 10% (w/w) HCl (3 × 20 mL), once with saturated aqueous $NaHCO_3$ (20 mL) and once with water (20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was dissolved with DCM (5 mL) and was precipitated upon Et_2O addition (50 mL, over 5 min). The ether layer was decanted, and the above isolation protocol was repeated twice to afford pure TAP-supported sulfide **13** as a yellowish solid (9.6 g, 90%): mp 72−75 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.0 Hz, 2H), 7.99 (dd, J = 2.1 Hz, 8.0 Hz, 2H), 7.86 (t, J = 7.2 Hz, 3H), 7.78−7.71 (m, 10H), 7.67−7.62 (m, 6H), 4.33 (t, J = 6.2 Hz, 2H), 2.55 (t, J = 7.0 Hz, 2H), 2.07 (s, 3H), 1.91−184 (m, 2H), 1.78−1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 147.0 (d, J = 3.0 Hz), 142.7, 135.8 (d, J = 2.9 Hz), 135.2 (d, J = 10.7 Hz), 134.5 (d, J = 10.4 Hz), 130.9 (d, J = 12.9 Hz), 130.8, 130.4, 129.4 (d, J = 13.3 Hz), 127.7, 117.5 (d, J = 89.7 Hz), 116.7 (d, J = 90.8 Hz), 64.8, 33.8, 27.8, 25.6, 15.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.3; IR (solid) 2915, 2160, 1709, 1437, 1273, 1080, 996, 724, 688 cm^{-1}; HRMS (API-ES, Pos) calcd for $C_{36}H_{34}O_2PS$ $[M]^+$ 561.2009, found 561.2012.

(4′-{[4-(Methylsulfinyl)butoxy]carbonyl}-1,1′-biphenyl-4-yl)-(triphenyl)phosphonium perchlorate (14). To a solution of sulfide **13** (5.0 g, 7.56 mmol, 1.0 equiv) in a mixture of DCM/MeOH (2:1, 27 mL, 0.3 M) at 0 °C was added H_2O_2 (35% (w/w) aq solution) (3.0 mL, 37.0 mmol, 5.0 equiv). The solution was vigorously stirred at rt for 3 h and diluted with DCM (100 mL). The organic layer was washed with brine (15 mL) and water (15 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was dissolved with DCM (3 mL) and was precipitated upon Et_2O addition (30 mL, over 3 min). The ether layer was decanted, and the above isolation protocol was repeated twice to afford pure TAP-supported sulfoxide **14** as a yellowish solid (5.15 g, 99%): mp 75−80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.4 Hz, 2H), 7.99 (dd, J = 3.1 Hz, 8.4 Hz, 2H), 7.86 (m, 3H), 7.79−7.70 (m, 10H), 7.67−7.62 (m, 6H), 4.35 (m, 2H), 2.79 (m, 2H), 2.58 (s, 3H), 1.91−184 (m, 2H), 1.97−1.95 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 147.0 (d, J = 3.1 Hz), 142.7, 135.9 (d, J = 3.0 Hz), 135.2 (d, J = 10.7 Hz), 134.5 (d, J = 10.4 Hz), 130.9 (d, J = 12.9 Hz), 130.7 130.6, 129.5 (d, J = 13.3 Hz), 127.7, 117.6 (d, J = 89.6 Hz), 116.7 (d, J = 90.9 Hz), 64.5, 54.0, 38.8, 27.9, 19.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.3; IR (solid) 2915, 2160, 1709, 1437, 1273, 1082, 996, 724, 688 cm^{-1}; HRMS (API-ES, Pos) calcd for $C_{36}H_{34}O_2PS$ $[M]^+$ 577.1961, found 577.1960.

General Procedure for the Swern Oxidation Using TAP-Supported DMSO 14. To a solution of oxalyl chloride (131 μL, 1.5 mmol, 1.5 equiv) in DCM (1.5 mL, 1 M) at −40 °C was slowly added a solution of TAP−DMSO **14** (1.49 g, 2.2 mmol, 2.2 equiv) in DCM (6.0 mL, 0.37 M). After 10 min, a solution of alcohol (1.0 mmol, 1.0 equiv) in DCM (2.5 mL, 0.4 M) was added and the solution was stirred at −30 °C for 1−2 h. After 1−2 h, DIPEA (871 μL, 5.0 mmol, 5.0 equiv) was added and the solution was stirred at −30 °C for 10 min and at rt for 30 min. The solution was diluted with DCM (40 mL), washed with aq 10% (w/w) HCl (2 × 5 mL) and water (5 mL), dried over Na_2SO_4, and concentrated under reduced pressure. Celite (3.0 g) was added to the residue followed by slow addition of Et_2O (10 mL, over 1 min) to induce the complete precipitation of the TAP-supported mixture of sulfide **13** and sulfoxide **14**. The mixture was filtered on Celite and concentrated under reduced pressure to afford pure aldehyde.

4-({[4-(Triphenylphosphonio)benzyl]oxy}carbonyl)oxy]-2,2,6,-6-tetramethylpiperidin-1-oxyl perchlorate (16). To a solution of triphosgene (356 mg, 1.2 mmol, 0.6 equiv) in DCM (4.0 mL) at −20 °C was added pyridine (970 μL, 12.0 mmol, 6.0 equiv) dropwise, followed by a solution of 4-hydroxy-TEMPO (690 mg, 4.0 mmol, 2.0 equiv) in DCM (4.0 mL). The mixture was stirred for 15 min and warmed to rt and stirred for 30 min. Alcohol **15** (936 mg, 2.0 mmol, 1.0 equiv) was added, and the solution was stirred for 2 h. The solution was diluted with DCM and washed with water (2 × 10 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was dissolved with DCM (2 mL) and was precipitated upon Et_2O addition (10 mL, over 1 min). The ether layer was decanted, and the above isolation protocol was repeated twice to afford pure TAP-supported TEMPO **16** as an orange solid (1.27 g, 95%): mp 80−85 °C; NMR characterization was achieved by in situ reduction of the radical TAP-supported TEMPO **16** to the hydroxylamine derivative with phenylhydrazine;[26] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.87 (m, 3H), 7.79−7.74 (m, 8H), 7.68−7.60 (m, 8H), 5.31 (s, 2H), 4.95 (m, 1H), 3.90 (br, 1H), 2.08 (dd, J = 4.1 Hz, 12.8 Hz, 2H), 1.84 (t, J = 12.0 Hz, 2H), 1.34 (s, 6H), 1.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 144.0 (d, J = 3.0 Hz), 136.0 (d, J = 2.8 Hz), 135.0 (d, J = 10.7 Hz), 134.6 (d, J = 10.4 Hz), 131.0 (d, J = 12.9 Hz), 129.6 (d, J = 13.3 Hz), 116.9 (d, J = 89.6 Hz), 117.0 (d, J = 90.4 Hz), 71.0, 68.0, 60.8, 42.9, 30.8, 21.0; ^{31}P NMR (162 MHz, CD_2Cl_2) δ 23.3; IR (solid) 2975, 2160, 1742, 1438, 1263, 1081, 689 cm^{-1}; HRMS (ES+) calcd for $C_{35}H_{38}N_1O_4P_1$ $[M]^+$ 567. 2529, found 567.2538.

General Procedure for Alcohol Oxidation Using TAP-Supported TEMPO 16. To a solution of alcohol (1.00 mmol, 1.00 equiv) in DCM (2.5 mL, 0.4 M) at 0 °C were added TAP-supported TEMPO **16** (6.7 mg, 0.01 mmol, 0.01 equiv), an aqueous solution of NaOCl (3.57 mL, 1.25 mmol, 1.25 equiv) buffered at pH 8.9 with $NaHCO_3$, and an aqueous solution of KBr (11.9 mg, 0.10 mmol, 0.10 equiv, 0.2 M). The reaction mixture was vigorously stirred until TLC analysis indicated complete consumption of the starting material. The solution was diluted with DCM (10 mL); the layers were separated, and the aqueous layer was extracted with DCM (3 mL). The combined organic layers were washed with water (2 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to a minimum volume. Celite (30 mg) was added to the residue followed by Et_2O (4 mL, over 1 min) to induce the complete precipitation of the TAP-supported TEMPO **16**. The mixture was filtered on Celite and concentrated under reduced pressure to afford pure aldehyde or ketone.

[4-({[(4-Iodophenoxy)carbonyl]oxy}methyl)phenyl](triphenyl)-phosphonium perchlorate (17). To a solution of triphosgene (1.27 g, 4.60 mmol, 0.43 equiv) in (75 mL) at −30 °C was added pyridine (2.25 mL, 27.8 mmol, 2.6 equiv) dropwise. The resulting mixture was warmed to rt and stirred for 30 min (it became a clear yellowish homogeneous solution) and then cooled to −78 °C (heterogeneous solution). A solution of alcohol **15** (5.0 g, 10.7 mmol, 1.0 equiv) in DCM (75 mL) at −78 °C was slowly added in a way to keep the internal reaction temperature below −70 °C. After 1 h, a solution of sodium 4-iodophenolate (5.18 g, 21.4 mmol, 2.0 equiv) in THF (30 mL) was added at −78 °C. The resulting yellow solution was left to warm to rt overnight. The solution was diluted with DCM (300 mL), washed with brine (2 × 40 mL), dried over Na_2SO_4, and

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concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (2% isopropanol/DCM). Organic solvents were concentrated under reduced pressure until the total volume was reduced to about 10 mL. Addition of Et_2O (50 mL) with vigorous stirring induces the complete precipitation of the phosphonium salt that was collected by filtration. TAP-supported iodobenzene **17** was obtained as a white solid (5.7 g, 75%): R_f 0.38 (2% isopropanol/DCM); mp 102−105 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.86 (m, 3H), 7.82−7.73 (m, 8H), 7.69−7.60 (m, 10H), 6.96 (d, J = 8.9 Hz, 2H), 5.40 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 151.0, 143.3 (d, J = 3.1 Hz), 138.7, 136.0 (d, J = 3.1 Hz), 135.0 (d, J = 10.5 Hz), 134.6 (d, J = 11.0 Hz), 131.0 (d, J = 13.0 Hz), 129.8 (d, J = 13.3 Hz), 123.3, 117.8 (d, J = 90.4 Hz), 117.5 (d, J = 89.9 Hz), 90.5, 68.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.3; IR (film) 3520, 3062, 2968, 1761, 1578, 1437, 1236,1208, 1080 cm^{-1}; HRMS (API-ES, Pos) calcd for $C_{32}H_{25}I_1O_3P_1$ $[M]^+$ 615.0583, found 615.0581.

General Procedure for the α-Acetoxylation of Ketone with TAP-Supported Iodobenzene 17. To a solution of *m*-CPBA (98% purity, 246 mg, 1.4 mmol, 1.0 equiv) in acetic acid (4 mL, 0.25 equiv) were added iodobenzene **17** (71 mg, 0.1 mmol, 0.1 equiv), ketone (1.0 mmol. 1.0 equiv), $BF_3 \cdot Et_2O$ (370 μL, 3.0 mmol, 3.0 equiv), and water (90 μL, 5.0 mmol, 5.0 equiv) at rt, and the mixture was stirred at 25−30 °C for 24−48 h. Celite (350 mg) was added followed by Et_2O (40 mL, over 2 min), under vigorous stirring, to induce the complete precipitation of the TAP salt. The precipitate was filtered on Celite, and the ether layer was neutralized with aq 10% (w/w) sodium carbonate solution, washed with pH 8.5 phosphate buffer, dried over Na_2SO_4, and concentrated under reduced pressure. The crude oil was purified by flash chromatography (10% EtOAc/hexane) to afford the pure 2-acetoxyketone as a white solid (93 mg, 52%).

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Supporting Information Available: General experimental procedures for the preparation of all reagents and compounds as well as characterization data for each reaction and detailed structural assignment. This material is available free of charge via the Internet at http://pubs.acs.org.