Electronic Supplementary Information (ESI)

Palladium-catalyzed phosphorylation of of arylsulfonium salts with P(O)H compounds via C-S bond cleavage

Huijin Liu, Kai Sun, Xiaolan Li, Jie Zhang, Wei Lu, Xuzhong Luo,* Haiqing Luo*

Department of Chemistry & Chemical Engineering, Gannan Normal University, Ganzhou341000, China

Email: luoxuzhong@hotmail.com; luohq@gnnu.cn

Table of Contents

1. General information..............................................................................................................................................2
2. General procedures for the synthesis of arylsulfonium triflates 1r-1w ..............................................................2
3. General procedure for palladium-catalyzed phosphonation of arylsulfonium salts with P(O)H compounds .........................................................................................................................3
4. One-pot phosphorylation of aryl sulfide ..................................................................................................................3
5. Characterization data for the products ...................................................................................................................4
6. 1H, 13C and 31P NMR spectra of the products ......................................................................................................12
7. References.............................................................................................................................................................49
1. **General information:**

All the palladium-catalyzed phosphonation reactions were carried out in oven-dried glassware sealed with rubber septa under N\textsubscript{2} atmosphere. Column chromatography was performed on silica gel 200 - 300 mesh. All the compounds were known and characterized by \textsuperscript{1}H NMR, \textsuperscript{13}C NMR and \textsuperscript{31}P NMR with 400 MHz Bruker AVANCE spectrometers (400 MHz, 100 MHz and 162 MHz, respectively). Chemical shifts are reported relative to tetramethylsilane (TMS, δ 0.0 ppm) for \textsuperscript{1}H NMR and CDCl\textsubscript{3} (δ 77.0 ppm) for \textsuperscript{13}C NMR.

**Materials:** Unless otherwise noted, all reagents were purchased energy chemistry, Ouhe and J&K and used without further purification. Solvents were purified according to standard operation procedure. The arylsulfonium salts 1r to 1q were prepared in accordance with references.\textsuperscript{[1]}

2. **General procedures for the synthesis of arylsulfonium triflates 1r-w\textsuperscript{[1-2].}

**GP A** (Arylsulfonium salts 1r and 1s)\textsuperscript{[1]}: To a stirred solution of methyl(phenyl)sulfane or ethyl(phenyl)sulfane (5.0 mmol) and EtOTf (6.5 mmol) in DCE (2.0 mL) was treated with EtOTf (6.5 mL) at 0 °C. The resulting solution was stirred at 60 °C for 12 h, poured into distilled water (20 mL), and extracted with dichloromethane (3 × 30 mL). The crude product was purified by column chromatography on silica gel using a mixture of dichloromethane/methanol = 10/1 (v/v) as eluents to give the desired arylsulfonium triflates 1r and 1s.

![Chemical Reaction](attachment:image.png)

**GP B** (Arylsulfonium salts 1t-w)\textsuperscript{[2]}: To a stirred mixture of diaryl sulfide (3.0 mmol) and alkyl formate (6.0 mmol) was added trifluoromethanesulfonic acid (1.5 mL) at
0 °C. The mixture was warmed to 20 °C for 10 h, poured into distilled water (20 mL), and extracted with dichloromethane (3 × 30 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and concentrated to dryness under reduced pressure. The crude product was purified by crystallization from dichloromethane/diethyl ether system to give the desired alkyl(diaryl)sulfonium triflates 1t-w.

3. General procedure for palladium-catalyzed phosphonation of arylsulfonium salts with P(O)H compounds.

```
SMe₂

1a
OTf

S

3.0 mmol

R' O CO

6.0 mmol

CF₃SO₂H (1.5 mL)

0 °C to 20 °C, 10 h

```

The phosphonation of 1a to synthesize 3a (Table 1, entry 22) is representative.

To a 10 mL of a flame-dried seal tube equipped with a magnetic bar were added Pd(PPh₃)₂Cl₂ (0.015 mmol, 3.4 mg), XPhos (0.015 mmol, 7.3 mg), [PhSMe₂][OTf] (1a, 0.36 mmol, 103.8 mg) and H₃PO₄ (0.3 mmol, 63.7 mg). The reaction flask was degassed three times with nitrogen and dry iPrOH (2.0 mL) was added using a syringe. Note that the H-phosphonate diester 2a in a liquid form was added to the reaction tube by syringe after being added in the solvent. The reaction was heated at 80 °C with stirring for 16 h, then cooled to room temperature. After completion of the reaction, the reaction was quenched with water and extracted with EA (25 ml × 3). The organic layers were combined and washed with brine twice. It was dried over anhydrous Na₂SO₄ and solvent was then removed in vacuo to leave a crude mixture, which is purified by silica gel column chromatography to afford the pure desired product 3a.

4. One-pot phosphonation of aryl sulfide.

A 10 mL of a flame-dried seal tube equipped with a magnetic bar was charged with methyl phenyl sulfide (44.7 mg, 0.40 mmol) and CH₂Cl₂ (2.0 mL). To this solution, methyl triflate (48 μL, 0.44 mmol) was added, and the resulting mixture was
stirred for 10 h at room temperature. All volatiles were removed under reduced pressure to afford the corresponding sulfonium salt 1a. To the tube, Pd(PPh$_3$)$_2$Cl$_2$ (0.015 mmol, 3.4 mg), XPhos (0.015 mmol, 7.3 mg), and H$_3$PO$_4$ (0.3 mmol, 63.7 mg). The reaction flask was degassed three times with nitrogen and dry iPrOH (2.0 mL) was added using a syringe. Note that the H-phosphonate diester 2a in a liquid form was added to the reaction tube by syringe after being added in the solvent. The reaction was heated at 80 ºC with stirring for 16 h, then cooled to room temperature. After completion of the reaction, the reaction was quenched with water and extracted with EA (25 ml × 3). The organic layers were combined and washed with brine twice. It was dried over anhydrous Na$_2$SO$_4$ and solvent was then removed in vacuo to leave a crude mixture, which is purified by silica gel column chromatography to afford the pure desired product 3a.

5. Characterization data for the products.

**Diethyl phenylphosphonate (3a).**

![Structure of Diethyl phenylphosphonate](image)

Colorless oil (phenyltriethyloxysilane, 38.5 mg, 72 % yield), $^1$H NMR (400 MHz, CDCl$_3$) δ 7.79 – 7.73 (m, 2H), 7.55 – 7.47 (m, 1H), 7.45 – 7.38 (m, 2H), 4.16 – 3.97 (m, 4H), 1.27 (t, $J$ = 7.1 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 132.3 (d, $J$ = 3.0 Hz), 131.6 (d, $J$ = 9.9 Hz), 128.4 (d, $J$ = 15.0 Hz), 128.2 (d, $J$ = 186.8 Hz), 62.0 (d, $J$ = 5.4 Hz), 16.2 (d, $J$ = 6.5 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 18.82. This compound is known.$^3$

**Diethyl p-tolylphosphonate (3b).**

![Structure of Diethyl p-tolylphosphonate](image)

Colorless oil (37.1 mg, 65 % yield): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.66 (dd, $J$ = 13.1, 8.0 Hz, 2H), 7.24 (dt, $J$ = 7.8, 4.0 Hz, 2H), 4.23 – 3.91 (m, 4H), 2.36 (s, 3H), 1.27 (t, $J$ = 7.1 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 142.8 (d, $J$ = 3.1 Hz), 131.7 (d, $J$ = 10.3 Hz), 129.1 (d, $J$ = 15.4 Hz), 124.8 (d, $J$ = 190.0 Hz), 61.8 (d, $J$ = 5.3 Hz), 21.5 (d,
J = 1.2 Hz), 16.2 (d, J = 6.6 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 19.57. This compound is known$^{[3]}$.

**Diethyl m-tolylphosphonate (3c).**

```
Me
O
P(OEt)$_2$
```

Colorless oil (38.8 mg, 68 % yield): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.70 – 7.49 (m, 2H), 7.31 (t, J = 4.1 Hz, 2H), 4.22 – 3.93 (m, 4H), 2.35 (s, 3H), 1.28 (t, J = 7.1 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 138.2 (d, J = 15.0 Hz), 133.1 (d, J = 3.2 Hz), 132.1 (d, J = 10.0 Hz), 128.6 (d, J = 9.7 Hz), 128.3 (d, J = 15.8 Hz), 127.9 (d, J = 185.7 Hz), 61.9 (d, J = 5.4 Hz), 21.2, 16.2 (d, J = 6.5 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 19.36. This compound is known$^{[3]}$.

**Diethyl o-tolylphosphonate (3d).**

```
Me
O
P(OEt)$_2$
```

Colorless oil (18.8 mg, 50 % yield): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.91 (ddd, J = 14.4, 7.9, 1.3 Hz, 1H), 7.42 (dd, J = 10.6, 4.5 Hz, 1H), 7.30 – 7.19 (m, 2H), 4.25 – 3.98 (m, 4H), 2.57 (d, J = 1.3 Hz, 3H), 1.32 (t, J = 7.1 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 141.8 (d, J = 10.2 Hz), 133.9 (d, J = 10.3 Hz), 132.4 (d, J = 3.0 Hz), 131.2 (d, J = 14.9 Hz), 126.7 (d, J = 183.8 Hz), 125.4 (d, J = 14.8 Hz), 61.9 (d, J = 5.5 Hz), 21.2 (d, J = 3.6 Hz), 16.3 (d, J = 6.6 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 19.50. This compound is known$^{[3]}$.

**Diethyl (4-(tert-butyl)phenyl)phosphonate (3e).**

```
rtBu
P(OEt)$_2$
```

Colorless oil (47.9 mg, 63 % yield): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.69 (ddd, J = 13.0, 8.4 Hz, 2H), 7.49 – 7.32 (m, 2H), 4.27 – 3.95 (m, 4H), 1.49 – 1.08 (m, 15H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.7 (d, J = 3.1 Hz), 131.5 (d, J = 10.3 Hz), 125.3 (d, J = 15.2 Hz), 124.7 (d, J = 189.0 Hz), 61.8 (d, J = 5.3 Hz), 34.9, 30.9, 16.2 (d, J = 6.6 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 19.51. This compound is known$^{[4]}$.
Diethyl (4-methoxyphenyl)phosphonate (3f)

Colorless oil (51.2 mg, 84 % yield): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 – 7.65 (m, 2H), 6.98 – 6.85 (m, 2H), 4.17 – 3.91 (m, 4H), 3.81 (s, 3H), 1.27 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.8 (d, $J = 3.4$ Hz), 133.7 (d, $J = 11.4$ Hz), 119.3 (d, $J = 194.9$ Hz), 113.9 (d, $J = 16.0$ Hz), 61.8 (d, $J = 5.3$ Hz), 55.2, 16.2 (d, $J = 6.6$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 19.77.

This compound is known.$^3$

diethyl (4-(3-chloropropoxy)phenyl)phosphonate (3g).

Colorless oil (66 % yield): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 – 7.63 (m, 2H), 7.02 – 6.90 (m, 2H), 4.13 (t, $J = 5.7$ Hz, 2H), 4.11 – 3.96 (m, 4H), 3.72 (t, $J = 6.3$ Hz, 2H), 2.22 (p, $J = 6.0$ Hz, 2H), 1.28 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.9 (d, $J = 3.4$ Hz), 133.7 (d, $J = 11.3$ Hz), 119.6 (d, $J = 194.7$ Hz), 114.4 (d, $J = 16.0$ Hz), 64.2, 61.8 (d, $J = 5.3$ Hz), 41.2, 31.9, 16.2 (d, $J = 6.6$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 19.62. HRMS (ESI) m/z: [M+K]$^+$ Calcd for C$_{13}$H$_{20}$ClO$_4$PK$^+$ 345.0419; found 345.0396.

diethyl (4-(4-bromobutoxy)phenyl)phosphonate (3h).

Colorless oil (68 % yield): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.78 – 7.63 (m, 2H), 6.97 – 6.87 (m, 2H), 4.08 (ddd, $J = 14.5, 7.2, 2.8$ Hz, 2H), 4.02 – 3.96 (m, 4H), 3.45 (t, $J = 6.5$ Hz, 2H), 2.08 – 1.98 (m, 2H), 1.97 – 1.88 (m, 2H), 1.27 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 162.0 (d, $J = 3.4$ Hz), 133.7 (d, $J = 11.3$ Hz), 119.4 (d, $J = 194.9$ Hz), 114.3 (d, $J = 16.0$ Hz), 66.8, 61.8 (d, $J = 5.3$ Hz), 33.2, 29.2, 27.6, 16.2 (d, $J = 6.6$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 19.69. HRMS (ESI) m/z: [M+H]$^+$ Calcd for C$_{14}$H$_{25}$BrO$_4$P$^+$ 365.0512; found 365.0492.

diethyl (4-hydroxyphenyl)phosphonate (3-3i).
Colorless oil (67 % yield): $^1$H NMR (400 MHz, CDCl$_3$) δ 9.95 (s, 1H), 7.65–7.60 (m, 2H), 7.08 – 6.92 (m, 2H), 4.23 – 3.91 (m, 4H), 1.30 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 161.8 (d, $J = 3.3$ Hz), 133.7 (d, $J = 11.7$ Hz), 116.1 (d, $J = 196.2$ Hz), 116.0 (d, $J = 16.4$ Hz), 62.3 (d, $J = 5.4$ Hz), 16.2 (d, $J = 6.6$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 21.10. This compound is known$^5$.

Diethyl (4-fluorophenyl)phosphonate (3j).

![diethyl (4-fluorophenyl)phosphonate](image)

Colorless oil (37.2 mg, 64 % yield): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.87 – 7.71 (m, 2H), 7.11 (td, $J = 8.7$, 3.1 Hz, 2H), 4.26 – 3.92 (m, 4H), 1.28 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.2 (dd, $J = 253.5$, 3.9 Hz), 134.3 (dd, $J = 11.3$, 8.9 Hz), 124.3 (dd, $J = 192.7$, 3.4 Hz), 115.7 (dd, $J = 21.4$, 16.3 Hz), 62.1 (d, $J = 5.4$ Hz), 16.2 (d, $J = 6.5$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 17.84. This compound is known$^3$.

Diethyl (4-(trifluoromethyl)phenyl)phosphonate (3k).

![diethyl (4-(trifluoromethyl)phenyl)phosphonate](image)

Colorless oil (49.5 mg, 70 % yield): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.91 (dd, $J = 13.0$, 8.0 Hz, 2H), 7.68 (dd, $J = 8.1$, 3.5 Hz, 2H), 4.23 – 3.96 (m, 4H), 1.29 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 133.9 (dd, $J = 32.7$, 3.3 Hz), 132.7 (d, $J = 185.7$ Hz), 132.1 (d, $J = 10.2$ Hz), 125.2 (dq, $J = 15.1$, 3.7 Hz), 123.4 (d, $J = 272.7$ Hz), 62.4 (d, $J = 5.5$ Hz), 16.2 (d, $J = 6.4$ Hz). $^{31}$P NMR (162 MHz, CDCl$_3$) δ 16.29. This compound is known$^3$.

diethyl (4-acetylphenyl)phosphonate (3l).

![diethyl (4-acetylphenyl)phosphonate](image)
Colorless oil (46 % yield): $^1\text{H NMR}$ (400 MHz, CDCl$_3$) δ 8.08 – 7.94 (m, 2H), 7.90-7.85 (m, 2H), 4.22 – 3.97 (m, 4H), 2.60 (s, 3H), 1.29 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl$_3$) δ 197.4, 139.7 (d, $J = 3.2$ Hz), 133.2 (d, $J = 186.5$ Hz), 132.0 (d, $J = 10.0$ Hz), 128.0 (d, $J = 15.1$ Hz), 62.3 (d, $J = 5.5$ Hz), 26.7, 16.2 (d, $J = 6.4$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl$_3$) δ 16.87. This compound is known.$^5$

methyl 4-(diethoxyphosphoryl)benzoate (3m).

Colorless oil (57 % yield): $^1\text{H NMR}$ (400 MHz, CDCl$_3$) δ 8.10-8.07 (m, 2H), 7.92 – 7.77 (m, 2H), 4.21 – 3.98 (m, 4H), 3.91 (s, 3H), 1.29 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl$_3$) δ 166.1, 133.4 (d, $J = 3.3$ Hz), 133.1 (d, $J = 185.3$ Hz), 131.7 (d, $J = 10.1$ Hz), 129.3 (d, $J = 15.0$ Hz), 62.3 (d, $J = 5.5$ Hz), 52.4, 16.2 (d, $J = 6.4$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl$_3$) δ 17.02. This compound is known.$^6$

4-(diethoxyphosphoryl)phenyl pivalate (3n).

Colorless oil (70 % yield): $^1\text{H NMR}$ (400 MHz, CDCl$_3$) δ 7.87 – 7.74 (m, 2H), 7.18 – 7.06 (m, 2H), 4.21 – 3.94 (m, 4H), 1.32 (s, 9H), 1.28 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl$_3$) δ 176.4, 154.3 (d, $J = 3.8$ Hz), 133.3 (d, $J = 11.0$ Hz), 125.5 (d, $J = 190.9$ Hz), 121.7 (d, $J = 15.9$ Hz), 62.1 (d, $J = 5.4$ Hz), 39.1, 26.9, 16.2 (d, $J = 6.5$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl$_3$) δ 18.06. HRMS (ESI) m/z: [M+K]$^+$ Calcd for C$_{15}$H$_{23}$O$_3$PK$^+$ 353.0915; found 353.0892.

4-(diethoxyphosphoryl)phenyl 4-methylbenzenesulfonate (3o).

Colorless oil (66 % yield): $^1\text{H NMR}$ (400 MHz, CDCl$_3$) δ 7.76 – 7.70 (m, 2H), 7.69-7.66 (m, 2H), 7.30-7.28 (m, 2H), 7.11 – 7.00 (m, 2H), 4.19 – 3.96 (m, 4H), 2.42 (s, 3H), 1.28 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl$_3$) δ 152.4 (d, $J = 4.0$ Hz),
145.7, 133.4 (d, J = 11.0 Hz), 131.9, 129.8, 128.4, 126.5, 122.4 (d, J = 15.9 Hz), 62.3 (d, J = 5.6 Hz), 21.6, 16.2 (d, J = 6.4 Hz). $^3$P NMR (162 MHz, CDCl$_3$) δ 17.12. This compound is known$^{[6]}$.

diethyl (4-acetamidophenyl)phosphonate (3p).

![diethyl (4-acetamidophenyl)phosphonate (3p).](image)

White solid (50 % yield): $^1$H NMR (400 MHz, CDCl$_3$) δ 9.26 (s, 1H), 7.71 (dd, J = 9.6, 5.2 Hz, 3H), 7.65 (d, J = 8.6 Hz, 1H), 4.12 – 3.97 (m, 4H), 2.17 (s, 3H), 1.28 (t, J = 7.1 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 169.5, 142.7 (d, J = 3.4 Hz), 132.6 (d, J = 10.8 Hz), 121.8 (d, J = 193.3 Hz), 119.2 (d, J = 15.3 Hz), 62.2 (d, J = 5.5 Hz), 24.4, 16.2 (d, J = 6.6 Hz). $^3$P NMR (162 MHz, CDCl$_3$) δ 18.91. This compound is known$^{[6]}$.

diethyl naphthalen-2-ylphosphonate (3q).

![diethyl naphthalen-2-ylphosphonate (3q).](image)

Colorless oil (70 % yield): $^1$H NMR (400 MHz, CDCl$_3$) δ 8.42 (d, J = 15.5 Hz, 1H), 7.90 (dd, J = 11.2, 6.6 Hz, 2H), 7.85 (d, J = 7.9 Hz, 1H), 7.78 – 7.71 (m, 1H), 7.61 – 7.50 (m, 2H), 4.35 – 3.88 (m, 4H), 1.32 (t, J = 7.1 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 134.9 (d, J = 2.7 Hz), 134.0 (d, J = 10.2 Hz), 132.2 (d, J = 16.7 Hz), 128.8, 128.3 (d, J = 14.3 Hz), 128.2, 127.7, 126.8 (d, J = 1.0 Hz), 126.3 (d, J = 9.8 Hz), 125.2 (d, J = 187.9 Hz), 62.1 (d, J = 5.3 Hz), 16.3 (d, J = 6.5 Hz). $^3$P NMR (162 MHz, CDCl$_3$) δ 19.17. This compound is known$^{[3]}$.

Dimethyl phenylphosphonate (4a).

![Dimethyl phenylphosphonate (4a).](image)

Colorless oil (53.1 mg, 95 % yield): $^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 – 7.71 (m, 2H), 7.56-7.52 (m, 1H), 7.47-7.42 (m, 2H), 3.72 (d, J = 11.1 Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 132.6 (d, J = 3.0 Hz), 131.8 (d, J = 9.9 Hz), 128.5 (d, J = 15.1 Hz),
126.7 (d, $J = 188.6$ Hz), 52.6 (d, $J = 5.5$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl$_3$) $\delta$ 21.66. This compound is known$^{[3]}$.

**Diisopropyl phenylphosphonate (4b).**

![Diisopropyl phenylphosphonate](image)

Colorless oil (34.2 mg, 47 % yield): $^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 7.81-7.76 (m, 2H), 7.51-7.47 (m, 1H), 7.44-7.39 (m, 2H), 4.65 (dq, $J = 18.8$, 6.2 Hz, 2H), 1.32 (dd, $J = 9.5$, 4.4 Hz, 6H), 1.19 (d, $J = 6.2$ Hz, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl$_3$) $\delta$ 132.0 (d, $J = 3.0$ Hz), 131.6 (d, $J = 9.8$ Hz), 129.8 (d, $J = 188.4$ Hz), 128.2 (d, $J = 15.0$ Hz), 70.6 (d, $J = 5.5$ Hz), 24.0 (d, $J = 4.0$ Hz), 23.7 (d, $J = 4.8$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl$_3$) $\delta$ 16.69. This compound is known$^{[3]}$.

**dibenzyl phenylphosphonate (4c).**

![Dibenzyl phenylphosphonate](image)

Colorless oil (65.1 mg, 64 % yield): $^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 7.82 (ddd, $J = 13.5$, 8.2, 1.4 Hz, 2H), 7.55 (td, $J = 7.4$, 1.5 Hz, 1H), 7.44 (ddd, $J = 8.5$, 6.9, 4.3 Hz, 2H), 7.35 – 7.29 (m, 10H), 5.20 – 4.93 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, CDCl$_3$) $\delta$ 136.1 (d, $J_{C-P} = 6.8$ Hz), 132.5 (d, $J_{C-P} = 3.1$ Hz), 131.8 (d, $J_{C-P} = 10.0$ Hz), 128.5, 128.5, 128.4, 128.3, 127.8, 67.6. $^{31}\text{P NMR}$ (162 MHz, CDCl$_3$) $\delta$ 19.7. This compound is known$^{[3]}$.

**ethyl diphenylphosphinate (4d).**

![Ethyl diphenylphosphinate](image)

Colorless oil (60.7 mg, 82 % yield): $^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 7.87 – 7.78 (m, 4H), 7.54 – 7.47 (m, 2H), 7.44 (td, $J = 8.2$, 3.4, 1.3 Hz, 4H), 4.10 (p, $J = 7.1$ Hz, 2H), 1.36 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl$_3$) $\delta$ 132.0 (d, $J = 2.7$ Hz), 131.5 (d, $J = 136.2$ Hz), 131.5 (d, $J = 10.1$ Hz), 128.4 (d, $J = 13.1$ Hz), 61.0 (d, $J = 5.9$ Hz), 16.4 (d, $J = 6.7$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl$_3$) $\delta$ 31.39. This compound is known$^{[7]}$. 

$^{[3]}$ A. F. Smith, J. Chem. Soc., Perkin Trans. 2, 1975, 653.

$^{[7]}$ G. A. Olah, J. Chem. Soc., Chem. Commun., 1971, 540.
triphenylphosphine oxide (4e).

White solid (19.2 mg, 23% yield): $^1\text{H NMR}$ (400 MHz, CDCl$_3$) δ 7.72 – 7.61 (m, 6H), 7.55-7.51 (m, 3H), 7.47-7.42 (m, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl$_3$) δ 132.95, 132.03 (d, $J_{C-P} = 9.9$ Hz), 131.89 (d, $J_{C-P} = 2.8$ Hz), 128.45 (d, $J_{C-P} = 12.1$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl$_3$) δ 29.25. This compound is known.$^7$

phenyldi-$p$-tolylphosphine oxide (4f).

Colorless oil (58.8 mg, 64% yield): $^1\text{H NMR}$ (400 MHz, CDCl$_3$) δ 7.69 – 7.61 (m, 2H), 7.58 – 7.48 (m, 5H), 7.43 (ddd, $J = 8.4$, 6.6, 2.9 Hz, 2H), 7.28 – 7.21 (m, 4H), 2.38 (s, 6H). $^{13}\text{C NMR}$ (101 MHz, CDCl$_3$) δ 142.3 (d, $J_{C-P} = 2.9$ Hz), 132.5, 132.0 (d, $J_{C-P} = 10.3$ Hz), 132.0 (d, $J_{C-P} = 9.9$ Hz), 131.7 (d, $J_{C-P} = 2.8$ Hz), 129.4 (d, $J_{C-P} = 106.4$ Hz), 129.2 (d, $J_{C-P} = 12.5$ Hz), 128.3 (d, $J_{C-P} = 12.1$ Hz), 21.6. $^{31}\text{P NMR}$ (162 MHz, CDCl$_3$) δ 29.4. This compound is known.$^7$

tetraethyl 1,4-phenylenebis(phosphonate) (5).

Colorless oil (23.1 mg, 22 % yield): $^1\text{H NMR}$ (400 MHz, CDCl$_3$) δ 8.10 – 7.76 (m, 4H), 4.36 – 3.88 (m, 8H), 1.33 (t, $J = 7.1$ Hz, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl$_3$) δ 132.9 (dd, $J = 186.9$, 3.1 Hz), 131.75 – 131.37 (m), 62.5 (d, $J = 5.6$ Hz), 16.3 (d, $J = 6.4$ Hz). $^{31}\text{P NMR}$ (162 MHz, CDCl$_3$) δ 16.84. This compound is known.$^8$

diethyl (4-(methylthio)phenyl)phosphonate (6).
Yellow oil (27.3 mg, 35 % yield): $^1$H NMR (400 MHz, CDCl$_3$) $\delta$7.76 – 7.55 (m, 2H), 7.38 – 7.11 (m, 2H), 4.21 – 3.96 (m, 4H), 2.48 (s, 3H), 1.29 (dd, $J = 8.9$, 5.3 Hz, 6H).
$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.8 (d, $J = 3.5$ Hz), 132.0 (d, $J = 10.6$ Hz), 125.0 (d, $J = 15.4$ Hz), 123.6 (d, $J = 192.1$ Hz), 62.0 (d, $J = 5.3$ Hz), 16.2 (d, $J = 6.6$ Hz), 14.6 (s).
$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 19.12. This compound is known $^{[5]}$. 

[Image of molecule]
5. \( ^1H, ^{13}C \) and \( ^{31}P \) NMR spectra of the products.

\( ^1H \) NMR of 3a

\( ^{13}C \) NMR of 3a
$^{31}$P NMR of 3a

$^{1}$H NMR of 3b
$^{31}$P NMR of 3b

$^{13}$C NMR of 3b
$^{13}$C NMR of 3c

$^{1}H$ NMR of 3c
$^{31}$P NMR of 3c

$^{1}$H NMR of 3d
$^1$H NMR of 3e

$^{13}$C NMR of 3e
$^1$H NMR of 3g

$^1$C NMR of 3g
$^{13}$C NMR of 3h

$^{31}$P NMR of 3h
H NMR of 3i

\[ \text{HO} \]
\[ \text{P} \]
\[ \text{OEt} \]
\[ \text{OEt} \]

| ppm | 9.949 | 7.651 | 7.629 | 7.624 | 7.619 | 7.597 | 7.017 | 7.008 | 7.001 | 6.999 | 6.997 | 4.093 | 4.084 | 4.088 | 4.048 | 4.043 | 4.031 | 4.013 | 4.005 | 3.988 |
|-----|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|

\[ 1^H \text{NMR of 3i} \]

\[ \text{HO} \]
\[ \text{P} \]
\[ \text{OEt} \]
\[ \text{OEt} \]

13C NMR of 3i

| ppm | 163.847 | 133.775 | 117.064 | 116.829 | 116.829 | 115.104 | 77.318 | 77.000 | 76.682 | 62.297 | 62.243 | 16.208 | 16.142 |
|-----|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|

\[ 13^C \text{NMR of 3i} \]
$^{31}$P NMR of $3i$

$^{1}$H NMR of $3j$
$^{13}$C NMR of $3j$

$^{31}$P NMR of $3j$
$^{1}H$ NMR of 3k

$^{13}C$ NMR of 3k
$^{31}$P NMR of 3k

$^1$H NMR of 3l
$^{13}$C NMR of 3l

$^{31}$P NMR of 3l
$\text{H NMR of } 3\text{m}$

$\text{C NMR of } 3\text{m}$
$^{13}$C NMR of 3n

$^{31}$P NMR of 3n
$^{1}H$ NMR of 3o

$^{13}C$ NMR of 3o
$^{31}$P NMR of 3o

$^{1}$H NMR of 3p
$^{13}$C NMR of 3p

$^{31}$P NMR of 3p
$^1$H NMR of 3q

$^{13}$C NMR of 3q
$^{31}$P NMR of 3q

$^1$H NMR of 4a
$^{31}$P NMR of 4a

$^{13}$C NMR of 4a
$^{13}$C NMR of 4c

$^{31}$P NMR of 4c
$^{1}H$ NMR of 4d

$^{13}C$ NMR of 4d
$^3\text{P NMR of 4d}$

$^1\text{H NMR of 4e}$
$^{13}$C NMR of 4e

$^{31}$P NMR of 4e
$^1$H NMR of 4f

$^{13}$C NMR of 4f
$^{31}$P NMR of 4f

$^{1}$H NMR of 5
$^{13}$C NMR of 5

$^{31}$P NMR of 5
$^{1}H$ NMR of 6

$^{13}C$ NMR of 6
6. References.

[1] (a) T. Yanagi, R. J. Somerville, K. Nogi, R. Martin, H. Yorimitsu, ACS Catal., 2020, 10, 2117; (b) Z.-Y. Tian, S.-M. Wang, S.-J. Jia, H.-X. Song, C.-P. Zhang, Org. Lett., 2017, 19, 5454.
[2] (a) K. Miyatake, K. Yamamoto, K. Endo, E. Tsuchida, J. Org. Chem. 1998, 63, 7522; (b) C. S. F. Tang, H. Rapoport, J. Org. Chem. 1973, 38, 2806.
[3] R. Zhuang, J. Xu, Z. Cai, G. Tang, M. Fang, Y. Zhao, Org. Lett., 2011, 13, 2110.
[4] T. Miao, L. Wang, Adv. Synth. Catal., 2014, 356, 967.
[5] L. J. Goossen, M. K. Dezfuli, Synlett., 2005, 445.
[6] C. Liu, C. L. Ji, T. Zhou, X. Hong, M. Szostak, Org. Lett., 2019, 21, 9256.
[7] G. Hu, W. Chen, T. Fu, Z. Peng, H. Qiao, Y. Gao and Y. Zhao, Org. Lett., 2013, 15, 5362.
[8] S. Sobhani, H. H. Moghadam, J. Skibsted, J. M. Sansano, Green Chem., 2020, 22, 1353.