Access to Stable Quaternary Phosphiranium Salts by P-Alkylation and P-Arylation of Phosphiranes

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## Contents

Table of contents

1. General Considerations

2. Synthesis of P-methyl phosphiranium cations 2a-f

3. Synthesis of P-alkyl phosphiranium cations 3a-b

4. Synthesis of P-methylene ester phosphiranium cations 5a-d

5. Synthesis of P-aryl phosphiranium cations 7a-c

6. $^1$H-, $^{13}$C and $^{31}$P-NMR spectra of new phosphiranium cations 2-7
1. General considerations

- **Solvents and reagents**

  Unless otherwise specified, reagents and deuterated solvents were purchased from commercial sources and used without further purification (Sigma-Aldrich®, Fisher scientific®, TCI®). All solvents were dried and freshly distilled prior to use, taking precaution to exclude moisture by refluxing over CaH₂ or Na/benzophenone. All reactions were performed under argon inert atmosphere. All glass apparatus was oven dried and cooled under vacuum before use. Thin layer chromatography (TLC) was performed on pre-coated sheets of silica gel 60 with fluorescent indicator UV254 (Merck). Detection was accomplished by irradiation with a UV lamp and by an ethanolic solution of p-anisaldehyde. Chromatographic separations were achieved on silica gel columns (Kieselgel 60, 40–63 μm, Merck) typically using a cyclohexane/ethyl acetate eluent system or dichloromethane/acetone eluent system.

  In most cases, yields are given for the crude products since most of the described products were found to be stable enough to be isolated but tend to decompose during purification process.

- **Characterization**

  **NMR spectra** were recorded on a Bruker Avance® 300 spectrometer. ¹H NMR spectra were recorded at 300 MHz and data are reported as followed: chemical shift (δ) in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, p = pentuplet, hept = heptuplet, b = broad, m = multiplet), coupling constants J in Hz and integration. ¹³C{¹H} NMR spectra were recorded at 75 MHz and data are reported as followed: chemical shift (δ) in ppm, multiplicity related to coupling with P or F, coupling constants J in Hz and multiplicity of carbon atom substitution with hydrogens determined from DEPT NMR experiments. ³¹P{¹H} and ¹⁹F{¹H} NMR spectra were recorded respectively at 121 and 282 MHz respectively. Chemical shifts are referenced relative to signals of the deuterated solvents.

  **High resolution mass spectra** (HRMS) were measured on an Agilent 6530 Q-ToF MS system. The Q-TOF MS instrument was operated under the following condition: Ion source ESI⁺ Agilent Jet Stream or APCI both in positive ionization mode. **FT-IR** spectra were recorded with a Perkin-Elmer Frontier and wave numbers (ν) are quoted in cm⁻¹. **Melting points** were determined in open capillaries on a Stuart Scientific SMP 10 analyzer and are uncorrected.
Synthesis of phosphiranium cations 2

The preparation of P-methyl phosphiraniums 2a-2f was performed using either MeOTf (1-2 equivalents, 20 °C, CH₂Cl₂, **Cond. A**) or the Meerwein reagent (Me₃O⁺BF₄⁻ (1 equivalent, 20 °C, CH₂Cl₂, **Cond. B**). P-alkylphosphiraniums 3a-3b, for their part, were formed by reacting the corresponding alkyl triflate reagents (1-1.2 equivalents, 20 °C, CH₂Cl₂, **Cond. C**) with 1-mesitylphosphirane. Diarylphosphiranium salts 7a-7c were prepared using a Cu/CuCl -catalyzed arylative quaternarization using diphenyl iodonium triflate (CuCl (10 mol%, Cu cat, 1,2-[CH₂Cl₂], 50°C, **Cond. D**). Last, the introduction of methylene ester groups on P was also realized to form methylene ester phosphiraniums 5a-5d (1-1.2 equivalents, 20 °C, CH₃CN, **Cond. E**). All the phosphiranium substrates synthesized and the conditions used are summarized in Scheme 1 below.

It should be noted that, due to instability issues, most of the phosphiranium salts could not be purified. As a consequence, the characterization data and the spectra given below stand for the crude products 2-7.

![Scheme 1. Synthesis of phosphiranium cations 2-7.](image-url)

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1. A sequential one-pot triflation/alkylation protocol was applied for the introduction of the benzyl and allyl group on P; see: Corey, E.J.; Helal, C. J. *Tetrahedron Lett.* 1996, 37, 5675.

2. Synthesis of P-methyl phosphiranium cations

- **1-mesityl-1-methylphosphiran-1-ium trifluoromethanesulfonate 2a**

![Chemical structure](image)

**Prepared using conditions A:** To a solution of 1-mesitylphosphirane 1a (150 mg, 0.84 mmol) in CH$_2$Cl$_2$ (1.8 mL), was added dropwise methyl trifluoromethanesulfonate (0.19 mL, 1.68 mmol, 2 equiv) at room temperature. The mixture was then stirred for 2h. Conversion of the starting material was monitored by $^{31}$P NMR. The reaction mixture was then concentrated under reduced pressure to give the title compound 2a as a beige solid (290 mg, 99% yield).

$R_f = 0.40$ (DCM/ EtOAc: 60/40); mp 83-85 °C (decomp.); IR (neat) ν 2988, 1604, 1455, 1386, 1250, 1148, 1089, 754 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$, 20°C) δ 6.99 (d, $^4$J$_{H-P} = 6.0$ Hz, 2H), 2.26 – 2.60 (m, 2H), 2.57 (d, $^2$J$_{H-P} = 1.6$ Hz, 6H), 2.26 (s, 3H), 2.20 (d, $^2$J$_{H-P} = 17.8$ Hz, 3H), 2.15 – 2.03 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$, 20°C) δ 146.9 (d, $^4$JC$_{P} = 3.0$ Hz, Cq), 144.5 (d, $^3$JC$_{P} = 11.0$ Hz, 2 CH), 130.0 (d, $^3$JC$_{P} = 13.2$ Hz, 2 Cq), 120.3 (q, $^1$JC$_{C,P} = 320.2$ Hz, CF$_3$), 110.7 (d, $^1$JC$_{C,P} = 93.8$ Hz, Cq), 22.0 (d, $^3$JC$_{C,P} = 9.1$ Hz, 2 CH$_3$), 21.3 (d, $^3$JC$_{C,P} = 1.7$ Hz, CH$_3$), 9.3 (d, $^1$JC$_{C,P} = 4.4$ Hz, 2 CH$_3$-P), 5.4 (d, $^1$JC$_{C,P} = 50.1$ Hz, CH$_3$-P); $^{31}$P NMR (121 MHz, CDCl$_3$, 20°C) δ -116.1; $^{19}$F NMR (282 MHz, CDCl$_3$, 20°C) δ -78.4; HRMS (ESI) m/z calculated for C$_{13}$H$_{18}$P $[M]$: 193.1146, found: 193.1144.

- **1-methyl-1-(2,4,6-tri-tert-butylphenyl)phosphiranium trifluoromethanesulfonate 2b**

![Chemical structure](image)

**Prepared using conditions A:** To a solution of 1-(2,4,6-tri-tert-butylphenyl)phosphirane 1b (150 mg, 0.49 mmol) in CH$_2$Cl$_2$ (1 mL) was added dropwise methyl trifluoromethanesulfonate (0.11 mL, 0.98 mmol, 2 equiv) at room temperature. The mixture was then stirred for 4h. Conversion of the starting material was monitored by $^{31}$P NMR. The reaction mixture was then concentrated under reduced pressure to give the title compound 2b as a beige solid (218 mg, 95% yield).

$R_f = 0.45$ (DCM/EtOAc: 60:40); mp 158-160 °C; IR (neat) ν 2986, 1595, 1465, 1395, 1360, 1250, 1150, 1029, 752 cm$^{-1}$; $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 20°C) δ 7.53 (d, $^4$J$_{H,P} = 6.5$ Hz, 2H), 2.72 – 2.51 (m, 2H), 2.66 (d, $^2$J$_{H,P} = 15.4$ Hz, 3H), 2.00 – 1.75 (m, 2H), 1.58 (s, 18H), 1.28 (s, 9H); $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$, 20°C) δ 160.4 (d, $^2$JC$_{P} = 15.4$ Hz, Cq), 157.4 (d, $^2$JC$_{C,P} = 1.7$ Hz, CH$_3$), 120.8 (q, $^1$JC$_{C,P} = 320.5$ Hz, CF$_3$), 108.0 (d, $^1$JC$_{C,P} = 85.6$ Hz, Cq), 39.6 (d, $^3$JC$_{C,P} = 3.3$ Hz, 2 Cq), 35.2 (Cq), 33.4 (6 CH$_3$), 30.4 (3 CH$_3$), 15.0 (d, $^1$JC$_{C,P} = 8.5$ Hz, 2 CH$_3$-P), 14.3 (d, $^1$JC$_{C,P} = 51.0$ Hz, CH$_3$-P); $^{31}$P NMR (121 MHz, CD$_2$Cl$_2$, 20°C) δ -115.3; $^{19}$F NMR (282 MHz, CD$_2$Cl$_2$, 20°C) δ -78.5; HRMS (ESI) m/z calculated for C$_{21}$H$_{36}$P $[M]$: 319.2555, found: 319.2552.
- 1-mesityl-1-methylphosphiran-1-ium trifluoromethanesulfonate 2c

Prepared using conditions A: To a solution of 1-phenylphosphirane 1c (40 mg, 0.29 mmol) in CH₂Cl₂ (2 mL) was added dropwise methyl trifluoromethanesulfonate (0.066 mL, 0.58 mmol, 2 equiv) at room temperature. The stirred was then stirred 2h. Conversion of the starting material was monitored by ³¹P NMR. The reaction mixture was then concentrated under reduced pressure to give the title compound 2c as a beige solid (70 mg, 80% yield).  

Rf = 0.40 (DCM/ EtOAc: 60/40); mp 72-74 °C (decomp.); ¹H NMR (300 MHz, CD₂Cl₂, 20°C) δ 5.90-7.61 (m, 5H), 2.57-2.36 (m, 4H), 2.45 (d, J_H-P = 18.3 Hz, 3H, CH₃-P); ³¹P NMR (121 MHz, CDCl₃, 20°C) δ -96.8; Data analyses were identical in all respects with previously reported data.³

- 1-mesityl-1,2-dimethylphosphiran-1-ium trifluoromethanesulfonate 2d

Prepared using conditions A: To a solution of a diastereoisomeric mixture of anti- and syn-1-mesityl-2-methylphosphirane 1d⁴ (d_{anti}/d_{syn} = 75:25, 280 mg, 1.56 mmol) in CH₂Cl₂ (1mL), was added dropwise methyl trifluoromethanesulfonate (0.30 mL, 3.12 mmol, 2 equiv.) at room temperature. The mixture was then stirred 2h. Conversion of the starting material was monitored by ³¹P NMR. The reaction mixture was then concentrated under reduced pressure to give the title compound 2d as a viscous colorless oil (545 mg, 98% yield, mixture of diastereoisomers d₁/d₂ = 77:23).  

Rf = 0.40 (DCM/ EtOAc: 60/40); IR (neat) ν 2978, 1602, 1456, 1392, 1250, 1148, 755 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 20°C) mixture of diastereoisomers (d₁/d₂ = 77:23) δ 7.10 (d, J_H-P = 5.6 Hz, 0.46H, 2H d₂), 7.07 (d, J_H-P = 5.7 Hz, 1.54H, 2H d₁), 3.04-2.69-2.04 (m, 3H, d₁+d₂), 2.62 (s, 6H, 2 CH₃ d₁+d₂), 2.36 (s, 0.69H, CH₃ d₂), 2.34 (s, 2.31H, CH₃ d₁), 2.25 (d, J_H-P = 17.6 Hz, 0.69H, CH₃-P d₂), 2.22 (d, J_H-P = 17.3 Hz, 2.31H, CH₃-P d₁), 1.70 (dd, J_H-P = 22.1 Hz, J_H-H = 6.1 Hz, 2.31H, CH₃ d₁), 1.34 (dd, J_H-P = 22.4 Hz, J_H-H = 6.4 Hz, 0.69H, CH₃ d₂); ¹³C NMR (75 MHz, CDCl₃, 20°C) mixture of diastereoisomers (d₁/d₂ = 77:23) δ 146.7 (d, J_C-P = 3 Hz, Cq d₂), 146.6 (d, J_C-P = 3 Hz, Cq d₁), 144.1 (d, J_C-P = 11.0 Hz, 2 CH d₁+d₂), 129.8 (d, J_C-P = 13.3 Hz, 2 Cq d₁+d₂), 120.7 (q, J_C-F = 320.1 Hz, CF₃ d₁+d₂), 111.5 (d, J_C-P = 90.2 Hz, Cq d₁), 108.7 (d, J_C-P = 90.2 Hz, Cq d₂), 21.2 (d, J_C-P = 8.9 Hz, 2 CH d₁+d₂), 21.2 (d, J_C-P = 1.7 Hz, CH₃ d₁+d₂), 19.5 (d, J_C-P = 3.3 Hz, CH₂ d₁), 19.4 (d, J_C-P = 3.3 Hz, CH₂ d₂), 16.5 (d, J_C-P = 2.3 Hz, CH d₁), 15.3 (d, J_C-P = 2.9 Hz, CH d₂), 12.2 (d, J_C-P = 6.6 Hz, CH₃ d₁), 12.1 (d, J_C-P = 6.2 Hz, CH₃ d₂), 6.0 (d, J_C-P = 47.7 Hz, d₂), 1.6 (d, J_C-P = 49.0 Hz, CH₃-P d₁); ³¹P NMR (121 MHz, CDCl₃, 20°C) mixture of diastereoisomers (d₁/d₂ = 77:23) δ -104.4 (d₂), -107.8 (d₁); ¹⁹F NMR (282 MHz, CDCl₃, 20°C) mixture of diastereoisomers (d₁/d₂ = 77:23) δ -78.4; HRMS (ESI) m/z calculated for C₁₃H₂₀P [M⁺]: 207.1303, found: 207.1299.


⁴ The stereochemistries anti and syn refer to the relative position of the substituent on the ring carbon to the mesityl substituent at phosphorus.
**1-mesityl-1-methylphosphiranium tetrafluoroborate 2f**

Prepared using conditions B: To a solution of 1-mesitylphosphirane 1a (25 mg, 0.14 mmol) in CH₂Cl₂ (1 mL) was added trimethyloxonium tetrafluoroborate (21 mg, 0.14 mmol, 1 equiv) at room temperature. The mixture was then stirred 2 h. Conversion of the starting material was monitored by ³¹P NMR. The reaction mixture was then concentrated under reduced pressure to give the title compound 2f as a beige pasty solid (38 mg, 96% yield).

\[ R_f = 0.40 \text{ (DCM/Acetone: 60/40)}; \quad \text{IR (neat) } \nu \text{ } 3001, 1604, 1392, 1031 \text{ cm}^{-1}; \quad \text{¹H NMR (300 MHz, CDCl₃, 20°C)} \delta \text{ } 7.05 (d, 4J_{H-P} = 5.7 \text{ Hz, } 2\text{H}), 2.78-2.67 (m, 2\text{H}), 2.64 (d, 4J_{H-P} = 1.7 \text{ Hz, } 6\text{H}), 2.33 (s, 3\text{H, H9}), 2.24 (d, 2J_{H-P} = 17.9 \text{ Hz, } 3\text{H}), 2.17-2.05 (m, 2\text{H}); \quad \text{¹³C NMR (75 MHz, CDCl₃, 20°C)} \delta \text{ } 147.0 (d, 4J_{C-P} = 3.1 \text{ Hz, } Cq), 144.9 (d, 2J_{C-P} = 11.0 \text{ Hz, } 2\text{CH}), 130.3 (d, 3J_{C-P} = 13.2 \text{ Hz, } 2\text{Cq}), 111.5 (d, 1J_{C-P} = 93.6 \text{ Hz, Cq}), 22.1 (d, 2J_{C-P} = 9.0 \text{ Hz, } 2\text{CH3}), 21.6 (d, 5J_{C-P} = 1.4 \text{ Hz, CH3}), 9.5 (d, 1J_{C-P} = 4.5 \text{ Hz, } 2\text{CH2-P}), 5.4 (d, 1J_{C-P} = 50.3 \text{ Hz, } CH2-P); \quad \text{¹³¹P NMR (121 MHz, CDCl₃, 20°C)} \delta \text{ } -115.9; \quad \text{¹⁹F NMR (282 MHz, CDCl₃, 20°C)} \delta \text{ } -150.8; \quad \text{HRMS (ESI) m/z calculated for } C_{12}H_{18}P [M]+: 193.1146, \text{ found: } 193.1137.\]
3. Synthesis of P-alkyl phosphiranium cations

- **1-allyl-1-mesitylphosphiranium trifluoromethanesulfonate 3a**

![Chemical Structure](image)

**Prepared using conditions C**: To a solution of diisopropylethylamine (0.207 mL, 1.2 mmol, 1.2 equiv) and allyl alcohol (0.082 mL, 1.2 mmol, 1.2 equiv) in dry CH2Cl2 (2 mL) at -30 °C was added dropwise trifluoromethanesulfonic anhydride (0.202 mL, 1.2 mmol, 1.2 equiv) under argon atmosphere. The reaction mixture was successively stirred 10 min at -30 °C, warmed to 0 °C and stirred for 10 min. The reaction mixture was again cooled to -30 °C. Then, dry Et2O (6 mL) was added to precipitate the ammonium salts. After decantation, the supernatant solution was added dropwise to a solution of phosphirane 1a (178 mg, 1 mmol, 1 equiv) in dry CH2Cl2 (0.8 mL) at -50 °C. The reaction mixture was then allowed to warm to room temperature over a period of 4 h. Evaporation of the solvent under reduced pressure then afforded the title product 3a as a thick colorless oil (350 mg, 95% crude yield).

**Rf** = 0.15 (AcOEt); **IR** (neat) ν 2944, 1605, 1250, 1153, 1025, 940 cm⁻¹; **1H NMR** (300 MHz, CDCl₃, 20°C) δ 7.03 (d, 4 J_H-P = 5.7 Hz, 2H), 5.70 (m, 1H), 5.55-5.39 (m, 2H), 3.41 (dd, 2 J_H-P = 18.7 Hz and 3 J_H-H = 7.6 Hz, 2H), 2.78-2.68 (m, 2H), 2.58 (bs, 6H), 2.31 (s, 3H), 2.20-2.10 (m, 2H) **13C NMR** (75 MHz, CDCl₃, 20°C) δ 147.3 (d, 4 J_C-P = 3.2 Hz, Cq), 145.2 (d, 3 J_C-P = 10.8 Hz, 2 CH), 130.2 (d, 2 J_C-P = 13.3 Hz, 2 Cq), 125.3 (d, 3 J_C-P = 16.2 Hz, CH₂), 123.5 (d, 2 J_C-P = 14.0 Hz, CH), 120.3 (q, 1 J_C-F = 319.6 Hz, CF₃), 109.3 (d, 1 J_C-P = 86.1 Hz, Cq), 25.8 (d, 1 J_C-P = 42.6 Hz, CH₂-P), 22.5 (d, 3 J_C-P = 7.9 Hz, 2 CH₃), 21.5 (d, 5 J_C-P = 1.2 Hz, CH₃), 9.0 (m, 2 CH₂-P); **31P NMR** (121 MHz, CDCl₃, 20°C) δ -114.1; **19F NMR** (282 MHz, CDCl₃, 20°C) δ -78.5; **HRMS** (ESI) m/z calculated for C₁₄H₂₀P [M]+: 219.1303, found: 219.1298.

- **1-benzyl-1-mesitylphosphiranium trifluoromethanesulfonate 3b**

![Chemical Structure](image)

**Prepared using conditions C**: To a solution of diisopropylethylamine (0.207 mL, 1.2 mmol, 1.2 equiv) and benzyl alcohol (0.125 mL, 0.168 mmol, 1.2 equiv) in dry CH₂Cl₂ (2 mL) at -30 °C was added dropwise trifluoromethanesulfonic anhydride (0.202 mL, 1.2 mmol, 1.2 equiv) under argon atmosphere. The reaction mixture was successively stirred 10 min at -30 °C, warmed to 0 °C and stirred for 10 min. The reaction mixture was again cooled to -30 °C. Then, dry Et₂O (6 mL) was added to precipitate the ammonium salts. After decantation, the supernatant solution was added dropwise to a solution of phosphirane 1a (178 mg, 1 mmol, 1 equiv) in dry CH₂Cl₂ (0.8 mL) at -50 °C. The reaction mixture was then allowed to warm to room temperature over a period of 4 h. Evaporation of the solvent under reduced pressure then afforded the title product 3b as a thick colorless oil (378 mg, 90% crude yield).

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be noted that 3b could only be obtained as a mixture with unreacted BnOH and BnOTf (as seen by \(^1\)H and \(^{13}\)C NMR analysis of the crude).

\( R_f = 0.25 \) (AcOEt); \( \text{IR (neat)} \) \( \nu \) 2994, 1605, 1223, 1160, 1026, 699 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\), 20 °C) \( \delta \) 7.29-7.13 (m, 3H), 7.06-7.02 (m, 2H), 6.87 (d, \(^4\)J\(_{H-P}\) = 5.8 Hz, 2H), 3.85 (d, \(^2\)J\(_{H-P}\) = 16.9 Hz, 2H), 2.78-2.68 (m, 2H), 2.21 (s, 3H), 2.15 (d, \(^4\)J\(_{H-P}\) = 1.9 Hz, 6H), 2.08-1.97 (m, 2H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\), 20°C) \( \delta \) 147.3 (d, \(^4\)J\(_{C-P}\) = 3.1 Hz, Cq), 145.4 (d, \(^2\)J\(_{C-P}\) = 10.7 Hz, 2 Cq), 138.6 (d, \(^2\)J\(_{C-P}\) = 60.3 Hz, Cq), 130.1 (d, \(^3\)J\(_{C-P}\) = 13.4 Hz, 2 CH), 129.7 (d, \(^4\)J\(_{C-P}\) = 2.8 Hz, 2 CH), 129.7 (CH), 129.0 (q, \(^3\)J\(_{C-P}\) = 5.2 Hz, 2 CH), 120.4 (q, \(^1\)J\(_{C-F}\) = 319.2 Hz, CF\(_3\)), 109.2 (d, \(^1\)J\(_{C-P}\) = 85.9 Hz, Cq), 28.6 (d, \(^1\)J\(_{C-P}\) = 40.3 Hz, CH\(_2\)-P), 22.0 (d, \(^3\)J\(_{C-P}\) = 7.6 Hz, 2 CH\(_2\)), 21.7 (CH\(_3\)), 10.1 (2 CH\(_2\)-P); \(^{31}\)P NMR (121 MHz, CDCl\(_3\), 20 °C) \( \delta \) -111.0; \(^{19}\)F NMR (282 MHz, CDCl\(_3\), 20 °C) \( \delta \) -78.4; HRMS (ESI) m/z calculated for C\(_{18}\)H\(_{22}\)P [M]\(^+\): 269.1459, found: 269.1458.
4. Synthesis of P-methylene ester phosphiranium cations

**General procedure for the synthesis of methylene ester phosphiraniums 5a-5d (Conditions E).**

**Step 1 : Triflate reagents 4a-4d formation**

To a solution of the corresponding glycolic ester (1 equiv.) and pyridine (1.3 equiv.) in dichloromethane (4 mL/mmol) at -10°C, was added triflic anhydride (1.15 equiv.) dropwise, under an inert atmosphere. Reaction was stirred 1h at -10°C and 3h30 at room temperature. Degazed water (5 mL/mmol) was next added to the reaction mixture. After decantation and phase separation, the aqueous layer was extracted with dichloromethane (3 x 5 mL/mmol). The combined organic layers were then combined, dried over MgSO₄, filtered and concentrated under vacuum to give the corresponding triflate reagent 4a-4d.

**Step 2 : Alkylation/Phosphiranium triflate 5 formation**

To a solution of phosphirane 1a in MeCN (7 mL/mmol) was added the triflate reagent 4a-4d (1 equiv.) neat. The reaction mixture was then stirred at room temperature under an inert atmosphere until conversion of phosphirane 1a was complete (31P NMR monitoring, ca. 24 hours). The solvent was then removed under vacuum to give the crude methylene ester phosphiranium salts 5a-5d.

- **1-mesityl-1-(2-methoxy-2-oxoethyl)phosphiran-1-ium trifluoromethanesulfonate 5a**

**Step 1 : Triflate 4a formation**

Prepared from methyl glycolate (0.30 mL, 3.9 mmol, 1 equiv) following the general procedure in dichloromethane (15 mL). Triflate reagent 4a was isolated as a clear oil. Yield: 70% (0.609 g, 2.7 mmol).

**Step 2 : Phosphiranium triflate 5a formation**

Prepared from mesitylphosphirane 1a (50 mg, 0.28 mmol, 1 equiv) and triflate reagent 4a (62 mg, 0.28 mmol, 1 equiv.) in MeCN (2 mL). Reaction time: 24 h. Product isolated as a thick yellow oil. Yield: 80% yield (90 mg, 0.224 mmol).

**Rf** = 0.33 (50/50 DCM/acetone); **IR** (neat) ν 2960, 1739, 1605, 1439, 1384, 1250, 1155, 1028, 757 cm⁻¹; **¹H NMR** (300 MHz, CDCl₃, 20°C) δ 7.09 (d, 4JP-H = 6.2 Hz, 2H), 4.02 (d, 2JP-H = 16.7 Hz, 2H), 3.75 (s, 3H), 3.13-3.03 (m, 2H), 2.70 (s, 6H), 2.37 (s, 3H), 2.30-2.19 (m, 2H); **¹³C NMR** (75 MHz, CDCl₃, 20°C) δ 165.2 (d, 2JC-P = 5.1 Hz, C=O), 147.7 (d, 2JC-P = 3.2 Hz, Cq), 145.8 (d, 2JC-P = 11.5 Hz, 2 CH), 130.6 (d, 2JC-P = 14.0 Hz, 2 Cq), 120.5 (q, 1JC-C = 319.7, CF₃), 109.1 (d, 1JC-P = 92.9 Hz, Cq), 53.9 (d, 1JC-P = 1.4 Hz, CH₂-P), 29.9 (d, 1JC-P = 56.9 Hz, CH₂-P), 22.4 (d, 1JC-P = 8.5 Hz, 2 CH₃), 21.7 (d, 1JC-P = 1.7 Hz, CH₃), 10.4 (d, 1JC-P = 2.8 Hz, 2 CH₂-P); **³¹P NMR** (121 MHz, CDCl₃, 20°C) δ -118.6; **¹⁹F NMR** (282 MHz, CDCl₃, 20°C) δ -78.5; **HRMS** (ESI) m/z calculated for C₁₄H₂₀O₂P [M]+: 251.1201; found: 251.1218.

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- 1-(2-ethoxy-2-oxoethyl)-1-mesitylphosphiran-1-ium trifluoromethanesulfonate 5b

Step 1: Triflate 4b formation
Prepared from ethyl glycolate (0.34 mL, 3.6 mmol, 1 equiv) following the general procedure in dichloromethane (14 mL). Triflate reagent 4b was isolated as a clear oil. Yield: 74% (0.629 g, 2.7 mmol).

Step 2: Phosphiranium triflate 5b formation
Prepared from mesitylphosphirane 1a (72 mg, 0.40 mmol, 1 equiv) and triflate reagent 4b (92 mg, 0.40 mmol, 1 equiv.) in MeCN (3 mL). Reaction time: 24 h. Product isolated as a clear yellow oil. Yield: 95% yield (158 mg, 0.381 mmol).

\[ \text{Rf} = 0.23 \text{ (50/50 DCM/Acetone); IR (neat) } \nu 2985, 1724, 1606, 1455, 1374, 1243, 1156, 1027, 757 \text{ cm}^{-1}; ^1H \text{ NMR (300 MHz, CDCl}_3, 20^\circ \text{C}) } \delta 7.09 \text{ (d, } ^4J_{\text{H-H}} = 6.2 \text{ Hz, 2H}, 4.19 \text{ (q, } ^3J_{\text{H-H}} = 7.2 \text{ Hz, 2H}), 4.03 \text{ (d, } ^2J_{\text{H-H}} = 16.8 \text{ Hz, 2H}), 3.17-3.07 \text{ (m, 2H), 2.71 (s, 6H), 2.37 (s, 3H), 2.82-2.18 (m, 2H), 1.24 (t, } ^5J_{\text{H-H}} = 7.2 \text{ Hz, 3H}); ^13\text{C NMR (75 MHz, CDCl}_3, 20^\circ \text{C}) } \delta 164.6 \text{ (d, } ^2J_{\text{C-P}} = 5.1 \text{ Hz, C=O}), 147.7 \text{ (d, } ^4J_{\text{C-P}} = 3.2 \text{ Hz, Cq}), 145.7 \text{ (d, } ^3J_{\text{C-P}} = 11.4 \text{ Hz, 2 CH}), 130.5 \text{ (d, } ^2J_{\text{C-P}} = 14.0 \text{ Hz, 2 Cq}), 120.4 \text{ (q, } ^1J_{\text{F-C}} = 319.4 \text{, CFs}), 109.1 \text{ (d, } ^1J_{\text{C-P}} = 93.0 \text{ Hz, Cq}), 63.5 \text{ (CH}_2), 30.0 \text{ (d, } ^1J_{\text{C-P}} = 56.2 \text{ Hz, CH}_2\text{-P), 22.4 \text{ (d, } ^1J_{\text{C-P}} = 8.5 \text{ Hz, 2CH}_2), 21.7 \text{ (d, } ^3J_{\text{C-P}} = 1.6 \text{ Hz, CH}_3), 13.8 \text{ (CH}_3), 10.3 \text{ (d, } ^1J_{\text{C-P}} = 2.7 \text{ Hz, 2CH}_2\text{-P); } ^3\text{P NMR (121 MHz, CDCl}_3, 20^\circ \text{C}) } \delta -118.6; ^19\text{F NMR (282 MHz, CDCl}_3, 20^\circ \text{C}) } \delta -78.5; \text{ HRMS (ESI) } m/z \text{ calculated for C}_{15}\text{H}_{22}\text{O}_2\text{P}[M]^+: 265.1357, \text{ found: 265.1360.}

- 1-(2-isopropoxy-2-oxoethyl)-1-mesitylphosphiran-1-ium trifluoromethanesulfonate 5c

Step 1: Triflate 4c formation
Prepared from isopropyl glycolate (0.30 mL, 2.5 mmol, 1 equiv) following the general procedure in dichloromethane (10 mL). Triflate reagent 4c was isolated as a clear oil. Yield: 30% (0.194 g, 0.74 mmol).

Step 2: Phosphiranium triflate 5c formation
Prepared from mesitylphosphirane 1a (88 mg, 0.50 mmol, 1 equiv) and triflate reagent 4c (124 mg, 0.50 mmol, 1 equiv.) in MeCN (4 mL). Reaction time: 24 h. Product isolated as a thick yellow oil. Yield: 90% yield (193 mg, 0.45 mmol).

\[ \text{Rf} = 0.20 \text{ (50/50 DCM/Acetone); IR (neat) } \nu 2922, 1722, 1606, 1457, 1377, 1248, 1156, 1029, 756 \text{ cm}^{-1}; ^1H \text{ NMR (300 MHz, CDCl}_3, 20^\circ \text{C}) } \delta 7.09 \text{ (d, } ^4J_{\text{H-H}} = 6.2 \text{ Hz, 2H}, 4.99 \text{ (hept, } ^3J_{\text{H-H}} = 6.2 \text{ Hz, 1H}), 3.99 \text{ (d, } ^2J_{\text{H-H}} = 16.9 \text{ Hz, 2H}), 3.19-3.08 \text{ (m, 2H), 2.70 (s, 6H), 2.37 (s, 3H), 2.22-2.18 (m, 2H), 1.21 (d, } ^5J_{\text{H-H}} = 6.2 \text{ Hz, 6H}); ^13\text{C NMR (75 MHz, CDCl}_3, 20^\circ \text{C}) } \delta 164.3 \text{ (d, } ^2J_{\text{C-P}} = 5.0 \text{ Hz, C=O}), 147.8 \text{ (d, } ^4J_{\text{C-P}} = 3.2 \text{ Hz, Cq}), 145.8 \text{ (d, } ^3J_{\text{C-P}} = 11.4 \text{ Hz, 2 CH}), 130.6 \text{ (d, } ^2J_{\text{C-P}} = 14.0 \text{ Hz, 2 Cq}), 120.5 \text{ (q, } ^1J_{\text{F-C}} = 319.9, \text{ CFs), 109.1 \text{ (d, } ^1J_{\text{C-P}} = 93.0 \text{ Hz, Cq}), 63.5 \text{ (CH}_2), 30.0 \text{ (d, } ^1J_{\text{C-P}} = 56.2 \text{ Hz, CH}_2\text{-P), 24.1 (d, } ^3J_{\text{C-P}} = 1.6 \text{ Hz, CH}_3, 13.8 \text{ (CH}_3), 10.3 \text{ (d, } ^1J_{\text{C-P}} = 2.7 \text{ Hz, 2CH}_2\text{-P); } ^3\text{P NMR (121 MHz, CDCl}_3, 20^\circ \text{C}) } \delta -118.6; ^19\text{F NMR (282 MHz, CDCl}_3, 20^\circ \text{C}) } \delta -78.5; \text{ HRMS (ESI) } m/z \text{ calculated for C}_{17}\text{H}_{24}\text{O}_2\text{P}[M]^+: 281.1357, \text{ found: 281.1360.} \]
109.4 (d, $^1J_{C,P} = 92.6$ Hz, Cq), 72.2 (CH), 30.4 (d, $^1J_{C,P} = 56.2$ Hz, CH$_2$-P), 22.6 (d, $^3J_{C,P} = 8.5$ Hz, 2 CH$_3$), 21.8 (d, $^5J_{C,P} = 1.3$ Hz, CH$_3$), 21.6 (2 CH$_3$), 10.5 (d, $^1J_{C,P} = 2.7$ Hz, 2 CH$_2$-P); $^{31}$P NMR (121 MHz, CDCl$_3$, 20°C) δ -118.6; $^{19}$F NMR (282 MHz, CDCl$_3$, 20°C) δ -78.5; HRMS (ESI) calculated for C$_{16}$H$_{24}$O$_2$P [M$^+$]: 279.1514, found: 279.1521.

- **1-(2-(benzyloxy)-2-oxoethyl)-1-mesitylphosphiran-1-ium trifluoromethanesulfonate 5d**

![Chemical structure](image)

**Step 1: Triflate reagent 4d formation**
Prepared from benzyl glycolate (0.35 mL, 1.8 mmol, 1 equiv) following the general procedure in dichloromethane (10 mL). Triflate reagent 4d was isolated as a clear oil. Yield: 73% (0.413 g, 1.32 mmol).

**Step 2: Phosphiranium triflate 5d formation**
Prepared from mesitylphosphirane 1a (88 mg, 0.50 mmol, 1 equiv) and triflate reagent 4d (156 mg, 0.50 mmol, 1 equiv.) in MeCN (4 mL). Reaction time: 24 h. Product isolated as a thick yellow oil. Yield: 86% yield (205 mg, 0.43 mmol).

$^{1}H$ NMR (300 MHz, CDCl$_3$, 20°C) δ 7.38-7.28 (m, 5H), 7.03 (d, $^4J_{P-H} = 6.2$ Hz, 2H), 5.14 (s, 2H), 4.04 (d, $^2J_{P-H} = 17.0$ Hz, 2H), 3.13-3.03 (m, 2H), 2.61 (s, 6H), 2.35 (s, 3H), 2.23-2.13 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$, 20°C) δ 164.5 (d, $^2J_{C,P} = 5.5$ Hz, C=O), 147.6 (d, $^4J_{C,P} = 3.3$ Hz, Cq), 145.8 (d, $^3J_{C,P} = 11.5$ Hz, 2 CH), 134.2 (CH), 130.5 (d, $^2J_{C,P} = 14.0$ Hz, 2 Cq), 128.9 (3CH), 128.7 (2CH) 120.4 (q, $^1J_{C,F} = 319.4$, CF$_3$), 109.0 (d, $^1J_{C,P} = 92.8$ Hz, Cq), 69.0 (CH$_2$), 29.8 (d, $^1J_{C,P} = 54.7$ Hz, CH$_2$-P), 22.3 (d, $^3J_{C,P} = 8.5$ Hz, 2CH$_3$), 21.7 (d, $^1J_{C,P} = 1.3$ Hz, CH$_3$), 10.4 (d, $^1J_{C,P} = 2.5$ Hz, 2CH$_2$-P); $^{31}$P NMR (121 MHz, CDCl$_3$, 20°C) δ -118.4; $^{19}$F NMR (282 MHz, CDCl$_3$, 20°C) δ -78.4; HRMS (ESI) calculated for C$_{20}$H$_{26}$O$_3$P [M$^+$]: 327.1514, found: 327.1517.
5. Synthesis of P-aryl phosphiranium cations

- **1-mesityl-1-phenylphosphiranium trifluoromethanesulfonate 7a**

![Chemical Structure of 1-mesityl-1-phenylphosphiranium trifluoromethanesulfonate 7a]

**Prepared using conditions D:** To a solution of 1-mesitylphosphirane 1a (25 mg, 0.14 mmol) in TCE (2 mL), diphenyliodonium trifluoromethanesulfonate (72 mg, 0.168 mmol, 1.2 equiv) were added copper chloride (1.4 mg, 10 %) and copper metal wire (Cat.) at room temperature. The reaction mixture was then heated 1h at 50°C. After cooling down to room temperature, the resulting crude mixture was directly purified by flash column chromatography on silica gel (eluent DCM then DCM/acetone 60 : 40) to yield the title product 7a as a colorless oil (42 mg, 81% yield).

\[R_f = 0.40 \text{ (DCM/Acetone: 60/40); IR (neat) } \nu \text{2970, 1603, 1257, 1169, 1034, 636 cm}^{-1}; \text{H NMR (300 MHz, Acetone-} d_6\text{, 20°C) } \delta \text{7.93 – 7.82 (m, 2H), 7.81–7.68 (m, 3H), 7.35 (d, } J_{H-P} = 5.9 \text{ Hz, 2H), 3.36 – 3.23 (m, 2H), 3.08 – 2.96 (m, 2H), 2.70 (d, } J_{H-P} = 1.7 \text{ Hz, 6H), 2.44 (s, 3H); C NMR (75 MHz, Acetone-} d_6\text{, 20°C) } \delta \text{148.5 (d, } J_{C-P} = 3.1 \text{ Hz, Cq), 147.1 (d, } J_{C-P} = 10.7 \text{ Hz, Cq), 144.7 (d, } J_{C-P} = 10.7 \text{ Hz, Cq), 135.8 (d, } J_{C-P} = 13.4 \text{ Hz, 2 CH), 133.4 (d, } J_{C-P} = 13.3 \text{ Hz, 2 CH), 131.6 (d, } J_{C-P} = 13.4 \text{ Hz, 2 CH), 122.3 (q, } J_{C-F} = 321.8 \text{ Hz, CF3), 115.2 (d, } J_{C-P} = 90.5 \text{ Hz, Cq), 109.2 (d, } J_{C-P} = 97.4 \text{ Hz, Cq), 22.6 (d, } J_{C-P} = 8.9 \text{ Hz, 2 CH3), 21.6 (d, } J_{C-P} = 1.4 \text{ Hz, CH3), 12.9 (d, } J_{C-P} = 3.2 \text{ Hz, 2 CH2-P); P NMR (121 MHz, Acetone-} d_6\text{, 20°C) } \delta \text{-113.8; F NMR (282 MHz, Acetone-} d_6\text{, 20°C) } \delta \text{-78.9; HRMS (ESI) m/z calculated for C17H20P [M]+: 255.1302; found: 255.1303.}

- **1-mesityl-1-phenylphosphiranium hexafluorophosphate 7b**

![Chemical Structure of 1-mesityl-1-phenylphosphiranium hexafluorophosphate 7b]

**Prepared using conditions D:** To a solution of 1-mesitylphosphirane 1a (25 mg, 0.14 mmol) in TCE (2 mL), diphenyliodonium hexafluorophosphate (72 mg, 0.168 mmol, 1.2 equiv) were added copper chloride (1.4 mg, 10 %) and copper metal wire (Cat.) at room temperature. The reaction was then heated 1h at 50°C. After cooling down to room temperature, the resulting crude was directly purified by flash column chromatography on silica gel (eluent DCM then DCM/acetone 6 : 4) to yield the title product 7b as a colorless oil (32 mg, 58% yield).

\[R_f = 0.36 \text{ (DCM/Acetone: 60/40); IR (neat) } \nu \text{2965, 1605, 1068, 652 cm}^{-1}; \text{H NMR (300 MHz, Acetone-} d_6\text{, 20°C) } \delta \text{7.99 – 7.61 (m, 5H), 7.35 (d, } J_{H-P} = 6.0 \text{ Hz, 2H), 3.41 – 3.16 (m, 2H), 3.10– 2.94 (m, 2H), 2.70 (d, } J_{H-P} = 1.9 \text{ Hz, 6H), 2.44 (s, 3H); C NMR (75 MHz, Acetone-} d_6\text{, 20°C) } \delta \text{148.5 (d, } J_{C-P} = 3.1 \text{ Hz, Cq), 147.1 (d, } J_{C-P} = 10.7 \text{ Hz, 2 Cq), 145.7 (d, } J_{C-P} = 10.7 \text{ Hz, 2 Cq), 135.9 (d, } J_{C-P} = 90.5 \text{ Hz, Cq), 109.2 (d, } J_{C-P} = 97.4 \text{ Hz, Cq), 22.6 (d, } J_{C-P} = 8.9 \text{ Hz, 2 CH3), 21.6 (d, } J_{C-P} = 1.4 \text{ Hz, CH3), 12.9 (d, } J_{C-P} = 3.2 \text{ Hz, 2 CH2-P); P NMR (121 MHz, Acetone-} d_6\text{, 20°C) } \delta \text{-114.8; F NMR (282 MHz, Acetone-} d_6\text{, 20°C) } \delta \text{-72.4 (d, } J_{P-F} = 707.5 \text{ Hz, PF6); HRMS (ESI) m/z calculated for C17H20P [M]+: 255.1302; found: 255.1303.}
1-(4-tert-butylphenyl)-1-mesitylphosphiranium hexafluorophosphate 7c

Prepared using conditions D: To a solution of 1-mesitylphosphirane 1a (25 mg, 0.14 mmol) in TCE (2 mL), bis(4-tert-butyphenyl)iodonium hexafluorophosphate (90 mg, 0.168 mmol, 1.2 equiv) were added copper chloride (1.4 mg, 10%) and copper metal wire (Cat.) at room temperature. The reaction was then heated 1h at 50°C. After cooling down to room temperature, the resulting crude was directly purified by flash column chromatography on silica gel (eluent DCM then DCM/acetone 6 : 4) to yield the title product 7c as a colorless oil (17 mg, 27% yield).

Rf: 0.36 (DCM/Acetone: 60/40); IR (neat) λ 2965, 1604, 1458, 1403, 1251, 1093, 824, 738 cm⁻¹; ¹H NMR (300 MHz, CHCl₃, 20 °C) δ 7.66–7.62 (m, 2H), 7.51–7.43 (m, 2H), 7.17 (d, 2J_H-P = 5.9 Hz, 2H,), 3.05–2.95 (m, 2H), 2.62–2.55 (m, 2H), 2.61 (d, 2J_H-P = 1.9 Hz, 6H), 2.42 (s, 3H), 1.31 (s, 9H); ¹³C NMR (75 MHz, Acetone-d₆, 20 °C) δ 159.1 (d, 2J_C-P = 4.5 Hz, Cq), 147.6 (d, 2J_C-P = 3.1 Hz, Cq), 146.2 (d, 2J_C-P = 10.7 Hz, 2 Cq), 132.5 (d, 2J_C-P = 13.7 Hz, 2 CH), 130.2 (d, 2J_C-P = 13.4 Hz, 2 CH), 127.9 (d, 2J_C-P = 16.7 Hz, 2 CH), 110.6 (d, 2J_C-P = 92.9 Hz, Cq), 108.6 (d, 2J_C-P = 97.7 Hz, Cq), 35.1 (Cq), 30.1 (3 CH₃), 21.7 (d, 2J_C-P = 8.9 Hz, 2 CH₃), 20.7 (d, 2J_C-P = 1.6 Hz, CH₃), 11.8 (d, 2J_C-P = 3.8 Hz, 2 CH₂-P); ³¹P NMR (121 MHz, Acetone-d₆, 20 °C) δ -114.0, -144.3 (hept, 1J_P-F = 707.6 Hz, PF₆); ¹⁹F NMR (282 MHz, Acetone-d₆, 20°C) δ -72.5 (d, 1J_F-P = 707.6 Hz); HRMS (ESI) m/z calculated for C₂₁H₂₈P [M⁺]: 311.1929; found: 311.1937.
6. NMR spectra of new phosphiranium cations

$^1$H NMR of compound 2a

$^{13}$C NMR of compound 2a
$^{31}$P NMR of compound 2a

$^{19}$F NMR of compound 2a
$^1$H NMR of compound 2b

$^{13}$C NMR of compound 2b
$^{31}$P NMR of compound 2b

$^{19}$F NMR of compound 2b
$^1$H NMR of compound 2d

![1H NMR spectrum](image)

$^{13}$C NMR of compound 2d

![13C NMR spectrum](image)
$^{31}$P NMR of compound 2d

$^{19}$F NMR of compound 2d
$^1$H NMR of compound 2f

$^{13}$C NMR of compound 2f
$^31$P NMR of compound 2f

$^{19}$F NMR of compound 2f
$^1$H NMR of compound 3a

$^{13}$C NMR of compound 3a
$^{31}$P NMR of compound 3a

$^{19}$F NMR of compound 3a
$^1$H NMR of compound 3b

$^{13}$C NMR of compound 3b
$^{31}$P NMR of compound 3b

$^{19}$F NMR of compound 3b
\[^1\text{H} \text{NMR of compound 5a}\]

\[\text{\includegraphics[width=\textwidth]{1H_NMR.png}}\]

\[^{13}\text{C} \text{NMR of compound 5a}\]

\[\text{\includegraphics[width=\textwidth]{13C_NMR.png}}\]
$^{31}$P NMR of compound 5a

$^{19}$F NMR of compound 5a
$^1$H NMR of compound 5b

$^{13}$C NMR of compound 5b
$^{31}$P NMR of compound 5b

$^{19}$F NMR of compound 5b
$^1$H NMR of compound 5c

$^{13}$C NMR of compound 5c
$^{31}$P NMR of compound 5c

$^{19}$F NMR of compound 5c
$^1$H NMR of compound 5d

![](image1)

$^{13}$C NMR of compound 5d

![](image2)
$^{31}$P NMR of compound 5d

$^{19}$F NMR of compound 5d
$^1$H NMR of compound 7a

$^{13}$C NMR of compound 7a
$^{31}$P NMR of compound 7a

$^{19}$F NMR of compound 7a
\(^1\)H NMR of compound 7b

\[^{13}\]C NMR of compound 7b
$^{31}$P NMR of compound 7b

$^{19}$F NMR of compound 7b
$^{31}$P NMR of compound 7c

$^{19}$F NMR of compound 7c