Supporting Information For:

Synthesis of Quaternary Aryl Phosphonim Salts: Photoredox Mediated Phosphine Arylation
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1. General Information

Glassware was dried in an oven overnight before use. All reactions were carried out under an argon balloon atmosphere unless stated otherwise. All reagents were used as supplied unless otherwise stated. Toluene and THF were obtained from stills and stored over sodium wire under argon until use. Liquid reagents were manipulated using a syringe/microsyringe of appropriate volume. Thin layer chromatography was carried out on Polgram SIL G/UV254 silica-aluminium plates and plates were visualized using ultra-violet light (254 nm) or KMnO₄ solution. For flash column chromatography, fluorochem silica gel 60, 35–70 mesh was used. NMR data was collected (unless stated otherwise) at 400 MHz for $^1$H; 101 MHz for $^{13}$C; 377 MHz for $^{19}$F. Data was manipulated directly from the spectrometer or via a networked PC with appropriate software. Reference values for residual solvent were taken as $\delta=7.26$ (CDCl₃) for $^1$H NMR; $\delta=77.00$ (CDCl₃) for $^{13}$C NMR; $\delta=3.31$ (MeOD) for $^1$H NMR; $\delta=49.00$ (MeOD) for $^{13}$C NMR. $^{19}$F-NMR shifts were referenced to CFCl₃ at 0.0 ppm. NMR-yields were calculated relative to one or a half equivalent of 1,1,2,2-tetrachloroethane as an internal standard that was added to the concentrated reaction before obtaining a solution in chloroform; $^1$H NMR (400 MHz, CDCl₃) $\delta$ 5.95 (s, 2H). Multiplicities for coupled signals are designated using the following abbreviations: s=singlet, d=doublet, t=triplet, q=quartet, quin=quintet, sex=sextet, br=broad signal. The coupling constants are reported in Hertz. Where appropriate, COSY, HMQC and HMBC experiments were performed to aid assignment. High-resolution mass spectrometry data were quoted to four decimal places (0.1 mDa) with error limits for acceptance of ±5.0 ppm (defined as calcd(found mass $10^{-6}$)). Mass spectra were acquired on a VG micromass 70E, VG autospec or micromass LCTOF. Infrared spectra were recorded on a Perkin–Elmer 1600 FTIR instrument as dilute chloroform solutions. Melting points were recorded on a Stuart manual melting point apparatus.
2.0 Synthesis of Phosphonium Salts

General method A: phosphine arylation using diphenyliodonium triflate

\[
\begin{align*}
R^\prime & \quad \begin{array}{c}
\text{Ph} \\
\text{Ph}
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\text{Ph} & \quad \begin{array}{c}
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\text{OTf} \\
R & \quad \begin{array}{c}
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\text{Ph} & \quad \begin{array}{c}
\text{Ph} \\
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\end{array} \\
\text{OTf}
\end{align*}
\]

To a solution of phosphine (0.23 mmol, 1.5 eq) in acetonitrile (1.60 mL) was added diphenyliodonium trifluoromethanesulfonate (68 mg, 0.16 mmol,) and tris(bipyridine)ruthenium(II) dichloride hexahydrate (2.0 mg, 3.0 μmol, 2 mol%). The reaction mixture was irradiated using a 10 W lamp for 1 h. The solvent was then removed in vacuo and the crude mixture was purified by flash column chromatography (10% methanol in dichloromethane) followed by recrystallisation from dichloromethane and diethyl ether to give the phosphonium trifluoromethanesulfonate product.

Tetraphenylphosphonium trifluoromethanesulfonate (2a)

Triphenylphosphine (63 mg, 0.24 mmol) was used to generate tetraphenylphosphonium trifluoromethanesulfonate as a white solid (65 mg, 85%).

Mp 315-317 °C (lit. >260,2 >2501); \(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta: 23.2\) (m); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta: 7.93 – 7.85\) (m, 4H, H\(_{Ar}\)), 7.80 – 7.72 (m, 8H, H\(_{Ar}\)), 7.68 – 7.56 (m, 8H, H\(_{Ar}\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta: 135.9\) (d, \(J = 3.0\) Hz, C\(_{Ar}\)), 134.5 (d, \(J = 10.3\) Hz, C\(_{Ar}\)), 130.9 (d, \(J = 13.0\) Hz, C\(_{Ar}\)), 117.6 (d, \(J = 89.9\) Hz, C\(_{Ar}\)); HRMS (ESI\(^+\))
m/z calculated for \([\text{C}_{24}\text{H}_{20}\text{P}(\text{M}^+)]\) calcd. 339.1297, found 339.1291; IR \(\nu_{\text{max}}\) (CHCl\(_3\))/cm\(^{-1}\): 3008, 1485, 1438, 1274, 1162, 1109, 1031, 998, 637.

Triphenyl(pyridin-2-yl)phosphonium trifluoromethanesulfonate (2c)

Diphenyl(pyridin-2-yl)phosphine (63 mg, 0.24 mmol) was used to generate triphenyl(pyridin-2-yl)phosphonium trifluoromethanesulfonate (64 mg, 82%). \(^{31}\)P NMR (162 MHz, CD\(_3\)CN) \(\delta\): 23.2 (m); \(^1\)H NMR (400 MHz, CD\(_3\)CN) \(\delta\): 9.04 – 8.96 (m, 1H, \(H_{\text{Ar}}\)), 8.07 (m, 1H, \(H_{\text{Ar}}\)), 7.95 – 7.88 (m, 3H, \(H_{\text{Ar}}\)), 7.83 – 7.70 (m, 14H, \(H_{\text{Ar}}\)); \(^{13}\)C NMR (100 MHz, CD\(_3\)CN) \(\delta\): 153.4 (d, \(J = 19.9\ Hz, C_{\text{Ar}}\)), 145.8 (d, \(J = 120.5\ Hz, C_q\)), 139.2 (d, \(J = 10.7\ Hz, C_{\text{Ar}}\)), 136.5 (d, \(J = 2.7\ Hz, C_{\text{Ar}}\)), 135.9 (d, \(J = 10.3\ Hz, C_{\text{Ar}}\)), 133.2 (d, \(J = 2.7\ Hz, C_{\text{Ar}}\)), 131.3 (d, \(J = 13.0\ Hz, C_{\text{Ar}}\)), 129.4 (d, \(J = 3.3\ Hz, C_{\text{Ar}}\)), 118.4 (d, \(J = 89.1\ Hz, C_q\)); HRMS (ESI\(^+\)) m/z calculated for \([\text{C}_{23}\text{H}_{19}\text{NP}(\text{M}^+)]\) calcd. 427.0625, found 427.0623.

Tris(4-fluorophenyl)(phenyl)phosphonium trifluoromethanesulfonate (2e)

Tris(4-fluorophenyl)phosphine (76 mg, 0.24 mmol) was used to generate tris(4-fluorophenyl)(phenyl)phosphonium trifluoromethanesulfonate as a white solid (59 mg, 69%). Mp 230-232 °C; \(^{31}\)P NMR (162 MHz, CD\(_3\)CN) \(\delta\): 22.0 (m); \(^{19}\)F NMR (376
MHz, CDCl$_3$) $\delta$: -78.3 (s), -98.4 (m); $^1$H NMR (400 MHz, CD$_3$CN) $\delta$: 7.99 – 7.88 (m, 1H, H$_{Ar}$), 7.83 – 7.62 (m, 9H, H$_{Ar}$), 7.59 – 7.44 (m, 5H, H$_{Ar}$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 167.2 (dd, $J$ = 261.6, 3.3 Hz, C$_q$), 137.5 (dd, $J$ = 12.3, 10.0 Hz, C$_{Ar}$), 136.0 (d, $J$ = 3.0 Hz, C$_{Ar}$), 134.4 (d, $J$ = 10.6 Hz, C$_{Ar}$), 131.0 (d, $J$ = 13.1 Hz, C$_{Ar}$), 118.8 (dd, $J$ = 22.5, 14.5 Hz, C$_{Ar}$), 117.4 (d, $J$ = 90.9 Hz, C$_q$), 113.2 (dd, $J$ = 94.6, 3.5 Hz, C$_q$); HRMS (ESI$^+$) $m/z$ calculated for [C$_{24}$H$_{17}$F$_3$P (M$^+$)] calcd. 393.1014, found 393.1013; IR $\nu_{\text{max}}$ (CHCl$_3$)/cm$^{-1}$: 3011, 1593, 1501, 1272, 1252, 1165, 1110, 1031, 834, 637.

Tris(4-methoxyphenyl)(phenyl)phosphonium trifluoromethanesulfonate (2d)

![Structural diagram]

Tris(4-methoxyphenyl)phosphine (84 mg, 0.24 mmol) was used to generate tris(4-methoxyphenyl)(phenyl)phosphonium trifluoromethanesulfonate as a brown oil (52 mg, 57%). $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$: 21.2 (m); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.86 – 7.79 (m, 1H, H$_{Ar}$), 7.74 – 7.66 (m, 2H, H$_{Ar}$), 7.61 – 7.53 (m, 2H, H$_{Ar}$), 7.52 – 7.44 (m, 6H, H$_{Ar}$), 7.24 – 7.15 (m, 6H, H$_{Ar}$), 3.93 (s, 9H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.06 (d, $J$ = 2.6 Hz, C$_q$), 136.19 (d, $J$ = 11.9 Hz, C$_{Ar}$), 135.08 (d, $J$ = 3.0 Hz, C$_{Ar}$), 133.99 (d, $J$ = 10.3 Hz, C$_{Ar}$), 130.38 (d, $J$ = 13.1 Hz, C$_{Ar}$), 119.85 (d, $J$ = 91.0 Hz, C$_q$), 116.36 (d, $J$ = 14.0 Hz, C$_{Ar}$), 108.26 (d, $J$ = 98.1 Hz, C$_q$), 56.07 (s, CH$_3$); HRMS (ESI$^+$) $m/z$ calculated for [C$_{27}$H$_{26}$O$_3$P$^+$ (M$^+$)] calcd. 429.1614, found 429.1614; IR $\nu_{\text{max}}$ (CHCl$_3$)/cm$^{-1}$: 3011, 1595, 1568, 1504, 1440, 1299, 1186, 1113, 1030, 834, 637.
Tris(4-chlorophenyl)(phenyl)phosphonium trifluoromethanesulfonate (2f)

![Chemical structure image]

Tris(4-chlorophenyl)phosphine (87 mg, 0.24 mmol) was used to generate tris(4-chlorophenyl)(phenyl)phosphonium trifluoromethanesulfonate as a solid (48 mg, 51%). Mp 244 – 246 °C; $^{31}$P NMR (162 MHz, CDCl$_3$) δ: 22.8 (m, 1 P); $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.99 – 7.90 (m, 1H, H$_{Ar}$), 7.84 – 7.58 (m, 16H, H$_{Ar}$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 143.5 (d, $J$ = 3.7 Hz, C$_q$), 136.3 (d, $J$ = 3.1 Hz, C$_{Ar}$), 135.9 (d, $J$ = 11.3 Hz, C$_{Ar}$), 134.5 (d, $J$ = 10.4 Hz, C$_{Ar}$), 131.5 (d, $J$ = 13.8 Hz, C$_{Ar}$), 131.2 (d, $J$ = 13.2 Hz, C$_{Ar}$), 116.7 (d, $J$ = 90.7 Hz, C$_{Ar}$), 115.5 (d, $J$ = 92.9 Hz, C$_{Ar}$); HRMS (ESI$^+$) m/z calculated for [C$_{24}$H$_{17}$Cl$_3$P (M$^+$)] calcd. 441.0128, found 441.0133; IR $\nu_{max}$ (CHCl$_3$)/cm$^{-1}$: 3069, 3048, 3009, 1579, 1483, 1439, 1394, 1271, 1163, 1088, 1030, 1013, 823, 637.

Tris(phenyl)methylphosphonium triflate (2b)$^2$

![Chemical structure image]

Diphenylmethylphosphine (44 µL, 0.24 mmol) was used to generate tri(phenyl)methylphosphonium triflate as a white solid (50 mg, 74%). $^{31}$P NMR (162 MHz, CDCl$_3$) δ: 22.5 (m, 1 P); $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.84 – 7.75 (m, 3H, H$_{Ar}$), 7.73 – 7.59 (m, 12H, H$_{Ar}$), 2.92 (d, $J$ = 13.4 Hz, 3H, H$_{Ar}$); $^{13}$C NMR (100 MHz,
CD$_3$CN $\delta$: 135.1 (d, $J = 3.0$ Hz, C$_{Ar}$), 133.3 (d, $J = 10.3$ Hz, C$_{Ar}$), 130.2 (d, $J = 12.7$ Hz, C$_{Ar}$), 119.4 (d, $J = 89.0$ Hz, C$_d$), 8.3 (d, $J = 58.4$ Hz, CH$_3$); HRMS (ESI$^+$) m/z calculated for [C$_{19}$H$_{18}$P$^+$ (M$^+$)] calcd. 277.1141, found 277.1125.

**General method B: phosphine arylation using (mesityl)chloroaryliodonium triflates**

![Diagram](image)

To a solution of phosphine (0.24 mmol, 1.5 eq) in acetonitrile (1.6 mL) was added (mesityl)aryliodonium trifluoromethanesulfonate (0.16 mmol) and tris(bipyridine)ruthenium(II) dichloride hexahydrate (2.0 mg, 3.0 $\mu$mol, 2 mol%). The reaction mixture was irradiated using a 10 W lamp for 1 h. The solvent was then removed in vacuo and the crude mixture was purified by flash column chromatography (10% methanol in dichloromethane) followed by recrystallisation from dichloromethane and diethyl ether to give a phosphonium trifluoromethanesulfonate.

**Tetraphenylphosphonium trifluoromethanesulfonate (2a)**

![Structure](image)

Triphenylphosphine (63 mg, 0.239 mmol) and phenyl(mesityl)iodonium trifluoromethanesulfonate (75 mg, 0.159 mmol) were used to generate tetraphenylphosphonium trifluoromethanesulfonate as a white solid (45 mg, 58%).

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$: 23.2 (m); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.95 – 7.88
(4-chlorophenyl)tris(4-fluorophenyl)phosphonium trifluoromethanesulfonate (2i)

![Chemical structure](image)

Tris(4-fluorophenyl) phosphine (76 mg, 0.24 mmol) and (4-chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate (81 mg, 0.16 mmol) were used to generate (4-chlorophenyl)tris(4-fluorophenyl)phosphonium trifluoromethanesulfonate as a solid (65 mg, 71%). Mp 229–230 °C;

$^{31}$P NMR (162 MHz, CD$_3$CN) δ: 22.0 (m);

$^{19}$F (376 MHz, CDCl$_3$) δ: -78.3 (s), -97.9 (m);

$^1$H NMR (400 MHz, CD$_3$CN) δ: 7.76 – 7.65 (m, 8H, H$_{Ar}$), 7.64 – 7.56 (m, 2H, H$_{Ar}$), 7.50 – 7.41 (m, 6H, H$_{Ar}$);

$^{13}$C NMR (100 MHz, CDCl$_3$) δ: 167.3 (dd, $J = 262.2, 3.4$ Hz, C$_q$), 143.4 (d, $J = 3.6$ Hz, C$_{Ar}$), 137.6 (dd, $J = 12.4, 9.9$ Hz, C$_{Ar}$), 135.8 (d, $J = 11.6$ Hz, C$_{Ar}$), 131.5 (d, $J = 13.8$ Hz, C$_{Ar}$), 119.0 (dd, $J = 22.4, 14.6$ Hz, C$_{Ar}$), 116.0 (d, $J = 93.4$ Hz, C$_q$), 112.9 (dd, $J = 95.2, 3.4$ Hz, C$_q$); HMRS (ESI$^+$) C$_{24}$H$_{18}$Cl$_3$F$_3$P [M$^+$] calcd. 427.0625, found 427.0647. IR $\nu_{max}$ (CHCl$_3$)/cm$^{-1}$: 3011, 1593, 1500, 1402, 1253, 1165, 1110, 1031, 834, 638.
Triphenylphosphine (63 mg, 0.24 mmol) and (4-chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate (81 mg, 0.16 mmol) were used to generate (4-chlorophenyl)triphenylphosphonium trifluoromethanesulfonate as a white solid (54 mg, 65%). $^{31}$P NMR (162 MHz, CDCl$_3$) δ: 23.0 (m); $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.91 - 7.88 (m, 3H, H$_{Ar}$), 7.80 - 7.72 (m, 8H, H$_{Ar}$), 7.65 - 7.59 (m, 8H, H$_{Ar}$). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 143.2 (d, $J = 3.0$ Hz, C$_q$), 136.2 (d, $J = 2.9$ Hz, C$_Ar$), 136.0 (d, $J = 11.7$ Hz, C$_Ar$), 134.7 (d, $J = 11.0$ Hz, C$_Ar$), 134.2 (d, $J = 9.5$ Hz, C$_Ar$), 133.7 (d, $J = 11.7$ Hz, C$_Ar$), 131.5 (d, $J = 13.2$ Hz, C$_Ar$), 131.1 (d, $J = 13.1$ Hz, C$_Ar$), 117.4 (d, $J = 90.6$ Hz, C$_q$), 116.3 (d, $J = 91.6$ Hz, C$_q$); HRMS (ESI$^+$) $m/z$ calculated for [C$_{24}$H$_{19}$ClP (M$^+$)] calcd. 339.1297, found 339.1293; IR $\nu_{\max}$ (CHCl$_3$)/cm$^{-1}$: 3053, 3008, 1581, 1484, 1440, 1393, 1273, 1162, 1110, 1090, 1030, 824, 637.

Tris(4-methoxyphenyl)phosphine (84 mg, 0.24 mmol) and (4-chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate (81 mg, 0.16 mmol) were
used to generate (4-chlorophenyl)tris(4-methoxyphenyl)phosphonium trifluoromethanesulfonate as an oil (53 mg, 55%). $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$: 21.0 (m); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.67 (dd, $J = 8.5, 2.7$ Hz, 2H, H$_{Ar}$), 7.58 – 7.44 (m, 6H, H$_{Ar}$), 7.21 (dd, $J = 8.8, 2.8$ Hz, 6H, H$_{Ar}$), 3.94 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 165.2 (d, $J = 3.1$ Hz, C$_q$), 142.3 (d, $J = 3.6$ Hz, C$_q$), 136.2 (d, $J = 12.1$ Hz, C$_{Ar}$), 135.4 (d, $J = 11.3$ Hz, C$_{Ar}$), 130.8 (d, $J = 13.6$ Hz, C$_{Ar}$), 118.5 (d, $J = 93.1$ Hz, C$_{Ar}$), 115.6 (d, $J = 14.1$ Hz, C$_{Ar}$), 107.8 (d, $J = 98.6$ Hz, C$_{Ar}$), 56.1 (s, CH$_3$); HRMS (ESI$^+$) m/z calculated for [C$_{27}$H$_{25}$ClO$_3$P$^+$ (M$^+$)] calcd. 463.1224, found 463.1253; IR $\nu_{max}$ (CHCl$_3$)/cm$^{-1}$: 3011, 1595, 1568, 1270, 1185, 1113, 1030, 9909, 834, 637.

(4-chlorophenyl)diphenyl(pyridin-2-yl)phosphonium trifluoromethanesulfonate (2g)

![Chemical structure](image)

Diphenyl(pyridine-2-yl)phosphine (63 mg, 0.24 mmol) and (4-chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate (81 mg, 0.16 mmol) were used to generate (4-chlorophenyl)diphenyl(pyridin-2-yl)phosphonium trifluoromethanesulfonate as a brown oil (52 mg, 63%). $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$: 14.8 (m); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 9.01 – 8.95 (m, 1H, H$_{Ar}$), 8.25 – 8.12 (m, 1H, H$_{Ar}$), 7.95 – 7.85 (m, 3H, H$_{Ar}$), 7.81 – 7.61 (m, 13H, H$_{Ar}$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 152.5 (d, $J = 19.8$ Hz, ), 144.3 (d, $J = 120.8$ Hz, C$_q$), 143.1 (d, $J = 3.7$ Hz, C$_q$), 139.2 (d, $J = 10.8$ Hz, C$_{Ar}$), 136.2 (d, $J = 11.0$ Hz, C$_{Ar}$), 136.0 (d, $J = 3.1$ Hz, C$_{Ar}$), 134.80 (d, $J = 10.2$ Hz, C$_{Ar}$), 132.67 (d, $J = 24.9$ Hz, C$_{Ar}$), 131.11 (d, $J = 13.9$ Hz, C$_{Ar}$), 130.8 (d, $J = 13.0$ Hz, C$_{Ar}$), 128.8 (d, $J = 3.6$ Hz, C$_{Ar}$), 116.9 (d, $J = 89.2$ Hz, C$_q$), 115.9 (d, $J = 91.8$ Hz, C$_q$); HRMS (ESI$^+$) m/z calculated for [C$_{23}$H$_{18}$ClNP$^+$ (M$^+$)] calcd.
374.0860, found 374.0856; IR 𝜈_{max} (CHCl₃)/cm⁻¹: 3011, 1580, 1483, 1440, 1394, 1273, 1161, 1112, 1031, 909.

(2-chlorophenyl)triphenylphosphonium trifluoromethanesulfonate (2k)

![Chemical Structure](image)

Triphenylphosphine (63 mg, 0.24 mmol) and (2-chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate (81 mg, 0.16 mmol) were used to generate (2-chlorophenyl)triphenylphosphonium trifluoromethanesulfonate as a white solid (38 mg, 46%). ³¹P NMR (162 MHz, CDCl₃) δ: 23.0 (m, 1P); ¹H NMR (400 MHz, CDCl₃) δ: 7.94 – 7.84 (m, 4H, Hₐ), 7.80 – 7.71 (m, 7H, Hₐ), 7.71 – 7.62 (m, 8H, Hₐ), 7.31 (ddd, J = 14.6, 7.9, 1.6 Hz, 1H, Hₐ); ¹³C NMR (100 MHz, CDCl₃) δ: 139.0 (d, J = 4.1 Hz, Cₐ), 138.4 (d, J = 10.3 Hz, Cₐ), 137.8 (d, J = 2.8 Hz, Cₐ), 135.7 (d, J = 3.0 Hz, Cₐ), 134.3 (d, J = 10.5 Hz, Cₐ), 133.1 (d, J = 6.7 Hz, Cₐ), 130.9 (d, J = 13.5 Hz, Cₐ), 129.5 (d, J = 12.4 Hz, Cₐ), 117.3 (d, J = 90.8 Hz, Cₐ); HMRS (ESI⁺) m/z calculated for [C₂₄H₁₉ClP⁺ (M⁺)] calcd. 373.0907, found 373.0908; IR 𝜈_{max} (CHCl₃)/cm⁻¹: 3070, 3008, 1578, 1485, 1456, 1439, 1273, 1162, 1124, 1108, 1044, 1030, 999, 909, 637.

**Diphenyliodonium trifluoromethanesulfonate**

![Chemical Structure](image)

Triflic acid (1.33 mL, 15.0 mmol) was added slowly drop wise to a solution of diacetoxyiodobenzene (2.42 g, 7.50 mmol) in dichloromethane (75.0 mL) at -40 °C.
(acetonitrile/CO$_2$ bath) and stirred for 30 minutes. The reaction mixture was then warmed to room temperature and stirred for a further 30 minutes. The reaction mixture was cooled to -40 °C and phenyl boronic acid (914 mg, 7.50 mmol) was added and the reaction mixture was stirred overnight. The solvent was removed in vacuo and diethyl ether was added. The resulting solid was filtered and washed with diethyl ether to give diphenyliodonium trifluoromethanesulfonate as a white solid (2.86 g, 89%). $^1$H NMR (400 MHz, CD$_3$CN) δ: 8.11 – 8.06 (m, 1H, H$_{Ar}$), 7.75 – 7.69 (m, 1H, H$_{Ar}$), 7.58 – 7.51 (m, 1H, H$_{Ar}$); $^{13}$C NMR (100 MHz, CD$_3$CN) δ: 136.3 (C$_{Ar}$), 133.9 (C$_{Ar}$), 133.4 (C$_{Ar}$), 114.4 (C$_q$); HRMS (ESI$^+$) m/z calculated for [C$_{12}$H$_{10}$I$^+$ (M$^+$)] calcd. 280.9822, found 280.9814; IR $\nu_{\text{max}}$ (CHCl$_3$)/cm$^{-1}$: 3011, 1472, 1444, 1289, 1243, 1170, 1026, 986, 637

**Formation of mesityl(aryl)iodonium trifluoromethanesulfonate**

![Diagram](image)

To a solution of iodoarene and mCPBA (dried under vacuum at room temperature for 1 hour, assume 65%) in dichloromethane, cooled in an ice bath was added trifluoromethanesulfonic acid slowly dropwise. The reaction was warmed to room temperature and stirred for 2 h. The reaction mixture was then cooled in an ice bath and mesitylene was added slowly dropwise. The reaction mixture was then stirred overnight at room temperature. The solvent was removed in vacuo and diethyl ether was added. The resulting solid was filtered and washed with diethyl ether to give mesityl(phenyl)iodonium trifluoromethanesulfonate (dried under vacuum at 100 °C for 1h) as a white solid.
Mesityl(phenyl)iodonium trifluoromethanesulfonate

Prepared according to the procedure above where iodobenzene (0.55 mL, 4.90 mmol), mCPBA (1.42 g, 8.23 mmol), triflic acid (0.72 mL, 8.04 mmol) and mesitylene (0.75 mL, 5.39 mmol) were used to generate mesityl(phenyl)iodonium trifluoromethanesulfonate (2.07 g, 90%). $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.71 – 7.66 (m, 2H), 7.58 – 7.51 (m, 1H), 7.45 – 7.38 (m, 2H), 7.11 (s, 2H), 2.63 (s, 6H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 144.6 (C$_1$), 142.6 (C$_2$), 133.1 (C$_3$), 132.3 (C$_4$), 131.9 (C$_5$), 130.5 (C$_6$), 120.5 (C$_7$), 111.9 (C$_8$), 27.2 (CH$_3$), 21.3 (CH$_3$); HRMS (ESI$^+$) m/z calculated for [C$_{15}$H$_{16}$I (M$^+$)] calcd. 323.0291, found 323.0290; IR $\nu_{max}$ (CHCl$_3$/cm$^{-1}$): 3011, 1472, 1444, 1284, 1242, 1172, 1027, 637.

(4-chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate

Prepared according to the procedure above where 4-chloro-1-iodobenzene (1.05 g, 4.42 mmol), mCPBA (1.28 g, 7.42 mmol), triflic acid (0.64 mL, 7.25 mmol) and mesitylene (0.63 mL, 4.86 mmol) were used to generate mesityl(4-chlorophenyl)iodonium trifluoromethanesulfonate (1.89 g, 84%). $^1$H NMR (400 MHz, CDCl$_3$) δ: 7.7 – 7.6 (m, 2H, H$_{Ar}$), 7.4 – 7.3 (m, 2H, H$_{Ar}$), 7.1 (s, 2H, H$_{Ar}$), 2.6 (s, 6H, H$_{Ar}$), 2.3 (s, 3H, H$_{Ar}$); $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 144.5 (C$_1$), 142.5 (C$_2$), 138.6 (C$_3$), 134.5 (C$_4$), 132.2 (C$_5$), 130.4 (C$_6$), 121.0 (C$_7$), 109.0 (C$_8$), 27.0 (CH$_3$), 21.2 (CH$_3$); HRMS (ESI$^+$) m/z calculated for [C$_{15}$H$_{15}$ClI (M$^+$)] calcd. 356.9901, found
356.9898; IR $\nu_{\text{max}}$ (CHCl$_3$)/cm$^{-1}$: 3011, 2927, 1471, 1388, 1286, 1243, 1170, 1093, 1026, 1000, 637.

(2-chlorophenyl)(mesityl)iodonium trifluoromethanesulfonate$^7$

![Structural formula](attachment:image)

Prepared according to the procedure above where 2-chloro-1-iodobenzene (0.42 mL, 3.45 mmol), mCPBA (1.00 g, 5.79 mmol), triflic acid (0.31 mL, 3.53 mmol) and mesitylene (0.53 mL, 3.80 mmol) were used to generate mesityl(4-chlorophenyl)iodonium trifluoromethanesulfonate (1.14 g, 65%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 7.61 (dd, $J = 8.0$, 1.5 Hz, 1H, $H_{\text{Ar}}$), 7.53 (td, $J = 7.7$, 1.4 Hz, 1H, $H_{\text{Ar}}$), 7.29 (ddd, $J = 8.6$, 7.4, 1.5 Hz, 1H, $H_{\text{Ar}}$), 7.17 (s, 2H, $H_{\text{Ar}}$), 7.10 (dd, $J = 8.2$, 1.4 Hz, 1H, $H_{\text{Ar}}$), 2.62 (s, 6H, CH$_3$), 2.39 (s, 3H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 145.4 (C$_q$), 143.0 (C$_q$), 135.5 (C$_q$), 133.5 (C$_{\text{Ar}}$), 132.6 (C$_{\text{Ar}}$), 131.4 (C$_{\text{Ar}}$), 130.9 (C$_{\text{Ar}}$), 130.6 (C$_{\text{Ar}}$), 120.8 (C$_q$), 112.5 (C$_q$), 27.2 (CH$_3$), 21.3 (CH$_3$); HRMS (ESI$^+$) $m/z$ calculated for [C$_{15}$H$_{15}$ClI (M$^+$)] calcd. 356.9901, found 356.9899; IR $\nu_{\text{max}}$ (CHCl$_3$)/cm$^{-1}$: 3011, 1448, 1292, 1242, 1170, 1025, 637.
3. NMR Spectra of phosphonium salt products

$^1$H NMR (400 MHz, CDCl$_3$): Tetraphenylphosphonium trifluoromethanesulfonate (2a)

![NMR Spectra Image](image)

$^{13}$C NMR (10 MHz, CDCl$_3$): Tetraphenylphosphonium trifluoromethanesulfonate (2a)
$^{31}$P NMR (162 MHz, CDCl$_3$): Tetraphenylphosphonium trifluoromethanesulfonate (2a)
$^1$H NMR (400 MHz, CDCl$_3$): Triphenyl(pyridin-2-yl)phosphonium trifluoromethanesulfonate (2c)
$^{13}$C NMR (100 MHz, CD$_3$CN): Triphenyl(pyridin-2-yl)phosphonium trifluoromethanesulfonate (2c)
$^{31}$P NMR (162 MHz, CDCl$_3$): Triphenyl(pyridin-2-yl)phosphonium trifluoromethanesulfonate (2c)
$^{13}$C NMR (100 MHz, CDCl$_3$):

Tris(4-fluorophenyl)(phenyl)phosphonium trifluoromethanesulfonate ($2e$)
$^{31}$P NMR (162 MHz, CDCl$_3$): Tris(4-fluorophenyl)(phenyl)phosphonium trifluoromethanesulfonate (2e)
$^{19}\text{F NMR (376 MHz, CDCl}_3\text{): Tris(4-fluorophenyl)(phenyl)phosphonium trifluoromethanesulfonate (2e)}$
$^1$H NMR (400 MHz, CDCl$_3$): Tris(4-methoxyphenyl)(phenyl)phosphonium trifluoromethanesulfonate (2d)
$^{13}$C NMR (100 MHz, CDCl$_3$): Tris(4-methoxyphenyl)(phenyl)phosphonium trifluoromethanesulfonate (2d)
$^{31}$P NMR (162 MHz, CDCl$_3$): Tris(4-methoxyphenyl)(phenyl)phosphonium trifluoromethanesulfonate (2d)
$^1$H NMR (400 MHz, CDCl$_3$): Tris(4-chlorophenyl)(phenyl)phosphonium trifluoromethanesulfonate (2f)
$^{13}\text{C} \text{ NMR} \ (100 \text{ MHz, } \text{CDCl}_3)$: Tris(4-chlorophenyl)(phenyl)phosphonium trifluoromethanesulfonate (2f)
$^{31}$P NMR (162 MHz, CDCl$_3$): Tris(4-chlorophenyl)(phenyl)phosphonium trifluoromethanesulfonate (2f)
NMR (400 MHz, CDCl$_3$): Tris(phenyl)methylphosphonium triflate (2b)
C NMR (100 MHz, CDCl$_3$):

Tris(phenyl)methylphosphonium triflate ($\text{2b}$)
$^{31}$P NMR (162 MHz, CDCl$_3$): Tris(phenyl)methylphosphonium triflate (2b)
$^1$H NMR (400 MHz, CDCl$_3$): (4-chlorophenyl)tris(4-fluorophenyl)phosphonium trifluoromethanesulfonate (2i)
$^{13}$C NMR (100 MHz, CDCl$_3$): (4-chlorophenyl)tris(4-fluorophenyl)phosphonium trifluoromethane sulfonate
$^{31}$P NMR (162 MHz, CDCl$_3$): (4-chlorophenyl)tris(4-fluorophenyl)phosphonium trifluoromethanesulfonate (2i)
$^{19}$F NMR (376 MHz, CDCl$_3$): (4-chlorophenyl)tris(4-fluorophenyl)phosphonium trifluoromethanesulfonate (2i)
$^{13}$C NMR (100 MHz, CDCl$_3$): (4-chlorophenyl)triphenylphosphonium trifluoromethanesulfonate (2h)
$^{31}$P NMR (162 MHz, CDCl$_3$): (4-chlorophenyl)triphenylphosphonium trifluoromethanesulfonate (2h)
$^1$H NMR (400 MHz, CDCl$_3$): (4-chlorophenyl)tris(4-methoxyphenyl)phosphonium trifluoromethanesulfonate (2j)
$^{13}$C NMR (400 MHz, CDCl$_3$): (4-chlorophenyl)tris(4-methoxyphenyl)phosphonium trifluoromethanesulfonate (2j)
$^{31}$P NMR (162 MHz, CDCl$_3$): (4-chlorophenyl)tris(4-methoxyphenyl)phosphonium trifluoromethanesulfonate (2j)
$^1$H NMR (400 MHz, CDCl$_3$): (4-chlorophenyl)diphenyl(pyridin-2-yl)phosphonium trifluoromethanesulfonate (2g)
$^{13}$C NMR (400 MHz, CDCl$_3$): (4-chlorophenyl)diphenyl(pyridin-2-yl)phosphonium trifluoromethanesulfonate (2g)
$^{31}$P NMR (162 MHz, CDCl$_3$): (4-chlorophenyl)diphenyl(pyridin-2-yl)phosphonium trifluoromethanesulfonate (2g)

4. References


