Supporting Information

Unique Triphenylphosphonium Derivatives for Enhanced Mitochondrial Uptake and Photodynamic Therapy

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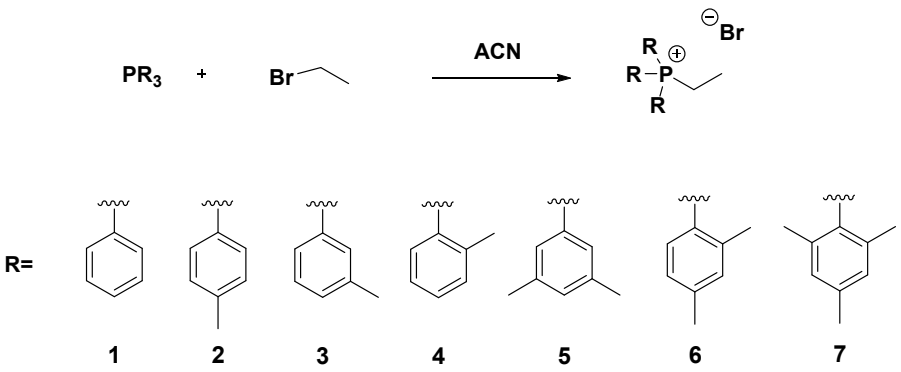
1. Experimental

1.1. Synthesis of lipophilic cations 1-7:



Scheme S1

Synthesis of triphenylethylphosphonium (1):

Triphenylphosphine (0.39 g, 5 mmol, 1 equiv.) was dissolved in dry ACN (20 mL), followed by drop-wise addition of ethyl bromide (2.2 g, 1.5 mL, 20 mmol, 4 equiv.). The reaction mixture was stirred for 30 min minutes and refluxed under argon for 72 hours. This mixture was cooled to room temperature and the solvent evaporated to dryness under vacuum. The residue was washed with toluene (3 x 10 mL) and dried under vacuum, affording **1** as a white solid. The product was recrystallized from ACN/diethyl ether. Isolated crystalline yield: 1.23 g, 66 %.

White solid, m.p.: 203-205 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 – 7.61 (m, 15H, Ar**H**), 3.86 (dq, *J* = 14.6, 7.3 Hz, 2H, C**H**$_2$-CH_3), 1.37 (dt, *J* = 20.1, 7.4 Hz, 3H, CH_2-C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.01 (d, *J* = 3.0 Hz), 133.70 (d, *J* = 9.9 Hz), 130.50 (d, *J* = 12.5 Hz), 77.71–76.86 (m), 76.63 (s), 6.86 (d, *J* = 5.3 Hz); ^{31}P-{^{1}H} NMR (121MHz, $CDCl_3$): δ 27.07; IR ($CHCl_3$): 1439 , 1145 (P-Ar), 690 (P-CH_2) cm^{-1}; HRMS (m/z): $[M]^+$ calcd. for $[C_{20}H_{20}P]^+Br^-$,291.13; found, 291.13.

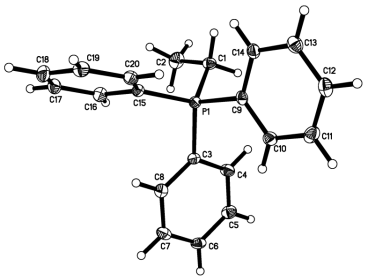


Figure S1. Molecular structure of $[Ph_3PEt]^+$ (**1**). Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles (°) for **1**: C1-C2 1.533(3), C1-P1 1.796(2), C3-C8 1.393(3), C3-C4 1.408(3), C3-P1 1.791(2), C4-C5 1.385(3), C5-C6 1.386(3), C6-C7 1.385(3), C7-C8 1.384(3), C9-C10 1.397(3), C9-C14 1.405(3), C9-P1 1.794(2), C10-C11 1.381(3), C11-C12 1.383(4), C12-C13 1.395(3), C13-C14 1.383(3), C15-C20 1.395(3), C15-C16 1.395(3), C15-P1 1.797(2), C16-C17 1.385(3), C17-C18 1.381(3), C18-C19 1.379(3), C19-C20 1.392(3); C2-C1-P1 115.73(18), C8-C3-C4 119.6(2), C8-C3-P1 121.22(17), C4-C3-P1 119.00(18), C5-C4-C3 119.2(2), C4-C5-C6 120.7(2), C7-C6-C5 120.0(2), C8-C7-C6 120.1(2), C7-C8-C3 120.2(2), C10-C9-C14 119.7(2), C10-C9-P1 121.54(18), C14-C9-P1 118.72(17), C11-C10-C9 119.9(2), C10-C11-C12 120.7(2), C11-C12-C13 119.7(2), C14-C13-C12 120.4(2), C13-C14-C9 119.6(2), C20-C15-C16 119.5(2), C20-C15-P1 121.39(18), C16-C15-P1 119.07(16), C17-C16-C15 120.2(2), C18-C17-C16 119.7(2), C19-C18-C17 120.8(2), C18-C19-C20 119.9(2), C19-C20-C15 119.8(2), C3-P1-C9 108.92(11), C3-P1-C1 110.53(11), C9-P1-C1 105.97(11), C3-P1-C15 107.88(11), C9-P1-C15 110.19(10), C1-P1-C15 113.30(11).

Table S1. Sample and crystal data for **1**

Identification code	fg237	
Chemical formula	$C_{20}H_{20}BrP$	
Formula weight	371.24 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.020 x 0.280 x 0.320 mm	
Crystal habit	colorless plate	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 14.1409(6) Å	α = 90°
	b = 12.5104(5) Å	β = 93.126(3)°
	c = 19.6334(8) Å	γ = 90°
Volume	3468.1(2) $Å^3$	

Z	8
Density (calculated)	1.422 g/cm^3
Absorption coefficient	2.457 mm^{-1}
F(000)	1520

Table S2. Data collection and structure refinement for **1**

Theta range for data collection	2.17 to 31.09°	
Index ranges	-20<=h<=20, -18<=k<=18, -28<=l<=20	
Reflections collected	21497	
Independent reflections	5541 [R(int) = 0.0766]	
Coverage of independent reflections	99.4%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9520 and 0.5070	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5541 / 0 / 200	
Goodness-of-fit on F^2	1.007	
Δ/σ_{max}	0.001	
Final R indices	3941 data; $I>2\sigma(I)$	R1 = 0.0409, wR2 = 0.0804
	all data	R1 = 0.0745, wR2 = 0.0914
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0334P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.521 and -0.431 eÅ^{-3}	
R.M.S. deviation from mean	0.111 eÅ^{-3}	

Synthesis of tri-*p*-tolyethylphosphonium (2):

Synthesized from tri-*p*-tolylphosphine (0.61 g, 2 mmol, 1 equiv.) according to the same synthetic procedure used for **1**. The residue obtained was washed with toluene (3 x 10 mL) and dried under vacuum, affording crystalline solid **2**. The product was recrystallized from ACN/diethyl ether. Isolated crystalline yield: 0.48 g, 58 %.

White solid, m.p. 207-209 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68–7.34 (m, 12H, Ar**H**), 3.71 – 3.65 (m, 2H, C**H**$_2$-CH$_3$), 2.45 (s, 9H, Ar-C**H**$_3$), 1.36 (dt, $^{3}J_{P\text{-}H}$ = 19.9 Hz, $^{3}J_{H\text{-}H}$ = 7.4 Hz, 3H, CH$_2$-C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.13 (d, J = 3.0 Hz), 133.55 (d, J = 10.2 Hz), 131.11 (d, J = 12.9 Hz), 77.69–76.84 (m), 76.61 (s), 21.82 (d, J = 1.3 Hz), 6.84 (d, J = 5.2 Hz); ^{31}P{^{1}H} NMR (121MHz, $CDCl_3$): δ 25.93; IR ($CHCl_3$): 1400, 1111 (P-Ar), 732 (P-CH$_2$) cm^{-1}; HRMS (m/z): $[M]^+$ calcd. for $[C_{23}H_{26}P]^+Br^-$,333.18; found, 333.17.

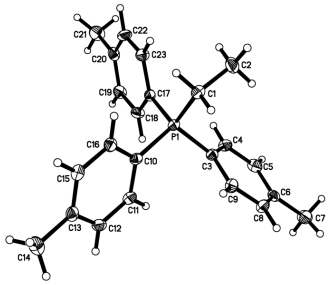


Figure S2. Molecular structure of **2**. Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles (°) for **2:** C1-C2 1.529(4), C1-P1 1.793(3), C3-C9 1.400(4) C3-C4 1.401(4), C3-P1 1.791(3) C4-C5 1.385(4), C5-C6 1.395(4) C6-C8 1.388(4), C6-C7 1.506(4) C8-C9 1.382(4), C10-C16 1.392(4) C10-C11 1.393(4), C10-P1 1.801(3) C11-C12 1.383(4), C12-C13 1.393(4) C13-C15 1.384(4), C13-C14 1.506(4) C15-C16 1.389(4), C17-C18 1.387(4) C17-C23 1.395(4), C17-P1 1.790(3) C18-C19 1.389(4), C19-C20 1.391(4) C20-C22 1.385(4), C20-C21 1.496(4) C22-C23 1.383(4); C2-C1-P1 112.1(2) C9-C3-C4 118.8(3), C9-C3-P1 118.4(2) C4-C3-P1 122.4(2), C5-C4-C3 120.1(3) C4-C5-C6 121.2(3), C8-C6-C5 118.2(3) C8-C6-C7 121.7(3), C5-C6-C7 120.2(3) C9-C8-C6 121.5(3), C8-C9-C3 120.1(3) C16-C10-C11 119.4(2), C16-C10-P1 119.5(2) C11-C10-P1 121.0(2), C12-C11-C10 120.8(3) C11-C12-C13 120.2(3), C15-C13-C12 118.6(3) C15-C13-C14 121.2(3), C12-C13-C14 120.2(3) C13-C15-C16 121.9(3), C15-C16-C10 119.1(3) C18-C17-C23 119.2(2), C18-C17-P1 119.9(2) C23-C17-P1 120.8(2), C17-C18-C19 120.6(3) C18-C19-C20 120.4(3), C22-C20-C19 118.4(3) C22-C20-C21 120.9(3), C19-C20-C21 120.7(3) C23-C22-C20 121.8(3), C22-C23-C17 119.5(3)

C17-P1-C3 110.30(13), C17-P1-C1 110.46(13) C3-P1-C1 107.97(13), C17-P1-C10 109.41(12) C3-P1-C10 109.44(13), C1-P1-C10 109.24(13).

Table S3. Sample and crystal data for **2**

Identification code	fg236	
Chemical formula	$C_{23}H_{26}BrP$	
Formula weight	413.32 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.220 x 0.240 x 0.300 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 11.1176(5) Å	α = 90°
	b = 12.9191(5) Å	β = 94.886(3)°
	c = 14.4760(7) Å	γ = 90°
Volume	2071.62(16) $Å^3$	
Z	4	
Density (calculated)	1.325 g/cm^3	
Absorption coefficient	2.064 mm^{-1}	
F(000)	856	

Table S4. Data collection and structure refinement for **2**

Theta range for data collection	2.22 to 29.70°	
Index ranges	-15<=h<=15, -17<=k<=18, -13<=l<=20	
Reflections collected	19817	
Independent reflections	5838 [R(int) = 0.0644]	
Coverage of independent reflections	99.3%	
Absorption correction	multi-scan	
Max. and min. transmission	0.6590 and 0.5760	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5838 / 0 / 230	
Goodness-of-fit on F^2	1.001	
Δ/σ_{max}	0.002	
Final R indices	3893 data; I>2σ(I)	R1 = 0.0401, wR2 = 0.0919
	all data	R1 = 0.0802, wR2 = 0.1133
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0541P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.435 and -0.375 eÅ^{-3}	
R.M.S. deviation from mean	0.101 eÅ^{-3}	

Synthesis of tri-*m*-tolyethylphosphonium (3):

Synthesized from tri-*m*-tolylphosphine (0.61 g, 2 mmol, 1 equiv.) according to the procedure used to obatin **1**. The residue was washed with toluene (3 x 10 mL) and dried under vacuum, followed by recrystallization from ACN/diethyl ether to afford **3** as a white solid. Isolated crystalline yield: 0.45 g, 54 %.

White solid, m.p. 207-209 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 – 7.50 (m, 12H, Ar**H**), 3.84 – 3.77 (m, 2H, C**H**$_2$-CH$_3$), 2.46 (s, 9H, Ar-C**H**$_3$), 1.39 (dt, $^{3}J_{P\text{-}H}$ = 19.9 Hz, $^{3}J_{H\text{-}H}$ = 7.4 Hz, 3H, CH$_2$-C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.86 (d, J = 12.4 Hz), 135.76 (d, J = 3.1 Hz), 133.68 (d, J = 9.9 Hz), 130.78 (d, J = 9.7 Hz), 130.19 (d, J = 13.2 Hz), 77.65 – 76.84 (m), 76.61 (s), 21.58 (s). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 26.68; IR ($CHCl_3$): 1408, 1119 (P-Ar), 752 (P-CH$_2$) cm^{-1}; HRMS (m/z): [M]+ calcd. for $[C_{23}H_{26}P]^{+}Br^{-}$, 333.18; found, 333.18.

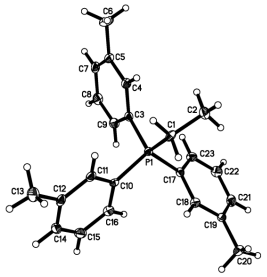


Figure S3. Molecular structure of **3**. Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles (°) for **3:** C1-C2 1.537(3) C1-P1 1.796(2), C3-C4 1.394(3) C3-C9 1.395(3), C3-P1 1.793(2) C4-C5 1.397(3), C5-C7 1.383(4) C5-C6 1.509(4), C7-C8 1.386(4) C8-C9 1.378(3), C10-C11 1.392(3) C10-C16 1.396(3), C10-P1 1.795(2) C11-C12 1.395(3), C12-C14 1.396(4) C12-C13 1.491(4), C14-C15 1.381(4) C15-C16 1.386(4), C17-C18 1.391(3) C17-C23 1.396(3), C17-P1 1.786(2) C18-C19 1.392(3), C19-C21 1.397(4) C19-C20 1.500(3), C21-C22 1.385(4) C22-C23 1.383(3);C2-C1-P1 112.42(17) C4-C3-C9 120.1(2), C4-C3-P1 120.17(18) C9-C3-P1 119.47(19), C3-C4-C5 120.2(2) C7-C5-C4 118.5(2), C7-C5-C6 121.8(2) C4-C5-C6 119.6(2), C5-C7-C8 121.7(2) C9-C8-C7 119.7(2), C8-C9-C3 119.8(2) C11-C10-C16 120.8(2), C11-C10-P1 118.23(18) C16-C10-P1 120.83(19), C10-C11-C12 119.8(2) C11-C12-C14 118.7(2), C11-C12-C13 120.2(2) C14-C12-C13 121.1(2), C15-C14-C12 121.5(2) C14-C15-C16 119.8(2), C15-C16-C10 119.3(2) C18-C17-C23 120.6(2), C18-C17-P1 117.29(18) C23-C17-P1 121.59(19), C17-C18-C19 120.8(2)

C18-C19-C21 117.8(2), C18-C19-C20 119.8(2) C21-C19-C20 122.4(2), C22-C21-C19 121.6(2) C23-C22-C21 120.2(2), C22-C23-C17 119.0(2) C17-P1-C3 111.81(11), C17-P1-C10 109.00(11) C3-P1-C10 107.88(11), C17-P1-C1 107.71(11) C3-P1-C1 110.62(11), C10-P1-C1 109.79(12).

Table S5. Sample and crystal data for **3**

Identification code	fg231	
Chemical formula	$C_{23}H_{26}BrP$	
Formula weight	413.32 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.390 x 0.400 x 0.420 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 9.3519(5) Å	α = 90°
	b = 13.2528(5) Å	β = 101.335(3)°
	c = 16.5587(8) Å	γ = 90°
Volume	2012.24(17) $Å^3$	
Z	4	
Density (calculated)	1.364 g/cm^3	
Absorption coefficient	2.125 mm^{-1}	
F(000)	856	

Table S6. Data collection and structure refinement for **3.**

Theta range for data collection	2.79 to 31.14°	
Index ranges	-13<=h<=13, -19<=k<=19, -23<=l<=24	
Reflections collected	40688	
Independent reflections	6480 [R(int) = 0.1043]	
Coverage of independent reflections	99.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.4910 and 0.4690	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	6480 / 0 / 230	
Goodness-of-fit on F^2	1.020	
Δ/σ_{max}	0.001	
Final R indices	4431 data; $I>2\sigma(I)$	R1 = 0.0449, wR2 = 0.0847
	all data	R1 = 0.0853, wR2 = 0.0965
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0350P)^2+0.9076P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.719 and -0.443 eÅ^{-3}	
R.M.S. deviation from mean	0.111 eÅ^{-3}	

Synthesis of tri-*o*-tolyethylphosphonium (4):

Tri-*o*-tolylphosphine (0.61 g, 2 mmol, 1 equiv.) was dissolved in dry ACN (10mL) and ethyl bromide (3.27 g, 2.25 cm^3, 30 mmol, 15 equiv.) was added to the reaction mixture before heating to reflux under argon for 5 days. The reaction was cooled to room temperature, and the excess of ethyl bromide and THF were evaporated under vacuum. The residue was washed with toluene (3 x 10 mL), then dried under vacuum, affording **4** as an off white solid. The product was recrystallized from ACN/diethyl ether. Isolated crystalline yield: 0.02 g, 2.4 %.

White solid, m.p. 207-209 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75–7.48 (m, 12H, Ar**H**), 3.88 – 3.76 (m, 2H, C**H**$_2$-CH_3), 2.31 (s, 9H, Ar-C**H**$_3$), 1.37 (dt, $^{3}J_{P\text{-}H}$ = 20.8 Hz, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 3H, CH_2-C**H**$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.49 (d, J = 8.6 Hz), 136.32 – 130.32 (m), 127.84 (d, J = 12.6 Hz), 116.45 (d, J = 81.5 Hz), 22.94 (d, J = 4.2 Hz), 18.66 (d, J = 50.2 Hz), 9.51 (d, J = 5.5 Hz); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 29.83; IR ($CHCl_3$): 1454, 1138 (P-Ar), 752 (P-CH_2) cm^{-1}; HRMS (m/z): $[M]^+$ calcd. for $[C_{23}H_{26}P]^+Br^-$, 333.18; found, 333.18.

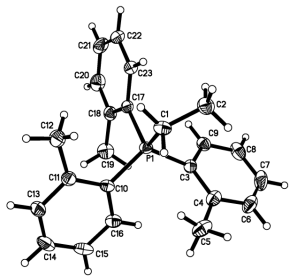


Figure S4. Molecular structure of $[C_{23}H_{26}P]^+$. Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles (°) for **4**: C1-C2 1.526(3), C1-P1 1.815(2), C3-C9 1.402(3), C3-C4 1.409(3), C3-P1 1.8116(19), C4-C6 1.392(3), C4-C5 1.507(3), C6-C7 1.377(3), C7-C8 1.382(3), C8-C9 1.381(3), C10-C16 1.401(3), C10-C11 1.408(3), C10-P1 1.8004(19), C11-C13 1.394(3), C11-C12 1.506(3), C13-C14 1.384(3), C14-C15 1.382(3), C15-C16 1.384(3), C17-C23 1.398(3), C17-C18 1.415(3), C17-P1 1.8125(19), C18-C20 1.392(3), C18-C19 1.506(3), C20-C21 1.384(3), C21-C22 1.374(3), C22-C23 1.389(3); C2-C1-P1 113.46(14), C9-C3-C4 119.97(18), C9-C3-P1 116.66(15), C4-C3-P1 122.40(15), C6-C4-C3 117.5(2), C6-C4-C5 117.36(19), C3-C4-C5 125.10(19), C7-C6-C4 121.9(2), C6-C7-C8 120.6(2), C9-C8-C7 119.0(2), C8-C9-C3 120.9(2), C16-C10-C11 120.55(18), C16-C10-P1 118.13(15), C11-C10-P1 121.06(15), C13-C11-C10 117.45(19), C13-C11-C12 118.26(18), C10-C11-C12 124.27(18), C14-C13-C11 121.8(2), C15-C14-C13 120.3(2), C14-C15-C16 119.6(2), C15-C16-C10 120.3(2), C23-C17-C18 119.98(18), C23-C17-P1 117.92(16), C18-C17-P1 122.10(14), C20-C18-C17 117.29(19), C20-C18-C19 118.67(19), C17-C18-C19 124.05(18), C21-C20-C18 122.5(2), C22-C21-C20 119.6(2),C21-C22-C23 120.0(2), C22-C23-C17 120.6(2), C10-P1-C3 112.32(9), C10-P1-C17 108.68(9), C3-P1-C17 109.41(9), C10-P1-C1 111.91(9), C3-P1-C1 105.82(9), C17-P1-C1 108.60(9).

Table S7. Sample and crystal data for **4.**

Identification code	fg234	
Chemical formula	$C_{23}H_{26}BrP$	
Formula weight	413.32 g/mol	
Temperature	158(2) K	
Wavelength	0.71073 Å	
Crystal size	0.280 x 0.380 x 0.420 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 12.4164(4) Å	α = 90°
	b = 13.5781(4) Å	β = 107.9694(13)°
	c = 12.3395(4) Å	γ = 90°
Volume	1978.85(11) $Å^3$	
Z	4	
Density (calculated)	1.387 g/cm^3	
Absorption coefficient	2.161 mm^{-1}	
F(000)	856	

Table S8. Data collection and structure refinement for **4**.

Theta range for data collection	2.29 to 28.32°	
Index ranges	-16<=h<=14, -18<=k<=18, -16<=l<=16	
Reflections collected	31775	
Independent reflections	4936 [R(int) = 0.0543]	
Coverage of independent reflections	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.5830 and 0.4640	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4936 / 0 / 230	
Goodness-of-fit on F^2	1.009	
Δ/σ_{max}	0.001	
Final R indices	3728 data; I>2σ(I)	R1 = 0.0340, wR2 = 0.0681
	all data	R1 = 0.0564, wR2 = 0.0766
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0289P)^2+1.0077P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.448 and -0.485 eÅ^{-3}	
R.M.S. deviation from mean	0.063 eÅ^{-3}	

Synthesis of tris-(3,5-dimethylphenyl)ethylphosphonium (5):

Synthesized from tris-(3,5-dimethylphenyl)phosphine (0.69 g, 2 mmol, 1 equiv.) following the an analogous synthetic procedure as that used for **4**. The residue was then washed with toluene (3 x 10 mL) and dried under vacuum affording solid **5**. The product was recrystallized from ACN/diethyl ether. Isolated crystalline yield: 0.48 g, 53 %.

White solid, m.p. 215-217°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 – 7.29 (m, 9H, Ar**H**), 3.74 – 3.62 (m, 2H, C**H$_2$**-CH$_3$), 2.41 (s, 18H, Ar-C**H$_3$**), 1.38 (dt, $^3J_{P\text{-}H}$ = 19.8 Hz, $^3J_{H\text{-}H}$ = 7.4 Hz, 3H, CH$_2$-C**H$_3$**); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.43 (d, J = 13.1 Hz), 136.59 (d, J = 3.1 Hz), 130.88 (d, J = 9.8 Hz), 118.41 (d, J = 84.4 Hz), 21.44 (s), 17.36 (d, J = 52.1 Hz), 7.11 (d, J = 5.2 Hz); ^{31}P{^{1}H} NMR (121

MHz, $CDCl_3$): δ 26.31; IR ($CHCl_3$): 1454, 1134 (P-Ar), 748 (P-CH_2) cm^{-1}; HRMS (m/z): $[M]^+$ calcd. For $[C_{26}H_{32}P]^+Br^-$, 375.22; found, 375.22.

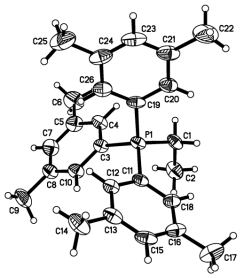


Figure S5. Molecular structure of **5**. Thermal ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles (°) for **5**: C1-C2 1.534(5), C1-P1 1.789(4), C3-C10 1.387(5), C3-C4 1.399(5), C3-P1 1.798(4), C4-C5 1.388(5), C5-C7 1.385(6), C5-C6 1.510(5), C7-C8 1.375(5), C8-C10 1.394(5), C8-C9 1.515(6), C11-C18 1.385(5), C11-C12 1.395(5), C11-P1 1.807(3), C12-C13 1.385(5), C13-C15 1.387(5), C13-C14 1.495(5), C15-C16 1.379(6), C16-C18 1.396(5), C16-C17 1.505(6), C19-C20 1.385(5), C19-C26 1.390(5), C19-P1 1.794(4), C20-C21 1.391(5), C21-C23 1.377(6), C21-C22 1.511(6), C23-C24 1.370(6), C24-C26 1.395(6), C24-C25 1.505(6), C27-C28 1.524(5), C27-P2 1.789(4), C29-C30 1.386(5), C29-C36 1.389(5), C29-P2 1.789(4), C30-C31 1.399(5), C31-C33 1.384(6), C31-C32 1.520(6), C33-C34 1.385(6), C34-C36 1.381(5), C34-C35 1.514(6), C37-C44 1.378(5), C37-C38 1.394(5), C37-P2 1.797(4), C38-C39 1.393(6), C39-C41 1.380(6), C39-C40 1.508(6), C41-C42 1.376(6), C42-C44 1.399(5), C42-C4 1.504(6), C45-C52 1.393(5), C45-C46 1.395(5), C45-P2 1.795(3), C46-C47 1.390(5), C47-C49 1.376(5), C47-C48 1.498(5), C49-C50 1.385(5), C50-C52 1.398(5), C50-C51 1.503(5), C53-N1 1.112(8), C53-C54 1.390(9), C2-C1-P1 112.8(3), C10-C3-C4 120.6(3), C10-C3-P1 123.3(3), C4-C3-P1 116.1(3), C5-C4-C3 119.9(4), C7-C5-C4 118.0(4), C7-C5-C6 122.0(4), C4-C5-C6 120.0(4), C8-C7-C5 123.4(4), C7-C8-C10 118.2(4), C7-C8-C9 121.8(4) , C10-C8-C9 120.0(4), C3-C10-C8 119.9(3), C18-C11-C12 120.5(3), C18-C11-P1 120.0(3), C12-C11-P1 119.2(3), C13-C12-C11 120.2(4), C12-C13-C15 118.4(4), C12-C13-C14 120.7(4), C15-C13-C14 120.9(3), C16-C15-C13 122.5(3), C15-C16-C18 118.6(4), C15-C16-C17 121.8(4), C18-C16-C17 119.5(4), C11-C18-C16 119.8(4), C20-C19-C26 120.6(4), C20-C19-P1 119.0(3), C26-C19-P1 120.1(3), C19-C20-C21 120.0(4), C23-C21-C20 118.5(4), C23-C21-C22 122.3(4), C20-C21-C22 119.2(5), C24-C23-C21 122.5(4), C23-C24-C26 119.1(4), C23-C24-C25 121.4(4), C26-C24-C25 119.5(4), C19-C26-C24 119.2(4), C28-C27-P2 113.6(3), C30-C29-C36 120.7(3), C30-C29-P2 121.9(3), C36-C29-P2 117.2(3), C29-C30-C31 119.9(3), C33-C31-C30 117.9(4), C33-C31-C32 122.2(4), C30-C31-C32 119.8(4), C31-C33-C34 122.9(4), C36-C34-C33 118.4(4), C36-C34-C35 120.8(4), C33-C34-C35 120.8(4), C34-C36-C29 120.2(4), C44-C37-C38 120.8(4), C44-C37-P2 119.4(3), C38-C37-P2 119.0(3), C39-C38-C37 119.5(4), C41-C39-C38 118.5(4), C41-C39-C40 121.4(4), C38-C39-C40 120.1(5), C42-C41-C39 123.0(4),

C41-C42-C44 118.0(4), C41-C42-C43 121.6(4), C44-C42-C43 120.3(4), C37-C44-C42 120.2(4), C52-C45-C46 120.5(3), C52-C45-P2 120.1(3), C46-C45-P2 119.1(3), C47-C46-C45 120.4(3), C49-C47-C46 117.9(3), C49-C47-C48 121.5(3), C46-C47-C48 120.6(4) , C47-C49-C50 123.2(3), C49-C50-C52 118.5(3), C49-C50-C51 122.4(3), C52-C50-C51 119.1(4), C45-C52-C50 119.4(3), N1-C53-C54 176.7(11), C1-P1-C19 109.67(18), C1-P1-C3 107.78(17), C19-P1-C3 109.74(17), C1-P1-C11 111.24(18), C19-P1-C11 106.95(16), C3-P1-C11 111.45(17), C27-P2-C29 108.05(17), C27-P2-C45 111.96(17), C29-P2-C45 110.57(16), C27-P2-C37 108.85(18), C29-P2-C37 111.90(17), C45-P2-C37 105.52(15).

Table S9. Sample and crystal data for **5**.

Identification code	fg232	
Chemical formula	$C_{54}H_{67}Br_2NP_2$	
Formula weight	951.84 g/mol	
Temperature	158(2) K	
Wavelength	0.71073 Å	
Crystal size	0.240 x 0.380 x 0.420 mm	
Crystal habit	colorless block	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.8772(8) Å	α = 92.863(3)°
	b = 12.9643(5) Å	β = 100.771(4)°
	c = 15.6479(9) Å	γ = 97.931(3)°
Volume	2534.0(2) $Å^3$	
Z	2	
Density (calculated)	1.247 g/cm^3	
Absorption coefficient	1.697 mm^{-1}	
F(000)	996	

Table S10. Data collection and structure refinement for **5**

Theta range for data collection	1.89 to 26.00°	
Index ranges	-15<=h<=15, -15<=k<=15, -19<=l<=19	
Reflections collected	38546	
Independent reflections	9940 [R(int) = 0.0847]	
Coverage of independent reflections	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.6860 and 0.5360	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	9940 / 0 / 547	
Goodness-of-fit on F^2	1.016	
Final R indices	6093 data; $I>2\sigma(I)$	R1 = 0.0488, wR2 = 0.1005
	all data	R1 = 0.1027, wR2 = 0.1259
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0463P)^2+1.4819P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.351 and -0.423 eÅ^{-3}	
R.M.S. deviation from mean	0.072 eÅ^{-3}	

Synthesis of tris-(2,4- dimethylphenyl)ethylphosphonium (6):

Tris-(2,4-dimethylphenyl)phosphine (0.35 g, 1 mmol, 1 equiv.) was dissolved in 10mL dry ACN and ethyl bromide (3.27 g, 2.25 cm^3, 30 mmol, 30 equiv.) was added and the reaction mixture was heated to reflux under argon for 6 days. The reaction mixture was cooled to room temperature and excess ethyl bromide and THF were evaporated under vacuum. The residue washed with toluene, then dried under vacuum, affording solid **6a**. The product was recrystallized from ACN/diethyl ether. Isolated crystalline yield: 0.03 g, 3.3 %.

White solid, m.p. 214-216°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 – 7.25 (m, 9H, Ar-**H**), 3.63 – 3.48 (m, 2H, P-C**H$_2$**), 2.43 (s, 9H, *m*-C**H$_3$**), 2.21 (s, 9H, *p*-C**H$_3$**), 1.30 (dt, $^3J_{P\text{-}H}$ = 20.4 Hz, $^3J_{H\text{-}H}$ = 7.4 Hz, 3H, P-C-C**H$_3$**); ^{13}C NMR (75 MHz, DMSO): δ 146.11 (d, *J* = 2.9 Hz), 143.34 (d, *J* = 8.9 Hz), 134.87 (dd, *J* = 26.9, 11.5 Hz), 128.70 (d, *J* = 12.9 Hz), 113.57 (d, *J* = 84.0 Hz), 31.15 (s), 22.25 (d, *J* = 4.0 Hz), 21.43 (d, *J* = 1.3 Hz), 9.18 (d, *J* = 5.4 Hz); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 28.34; IR ($CHCl_3$): 1450, 1230, 1069 (P-Ar), 748 cm^{-1} (P-CH_2); HRMS (m/z): $[M]^+$ calcd. for $[C_{26}H_{32}P]^+Br^-$, 375.22; found, 375.22.

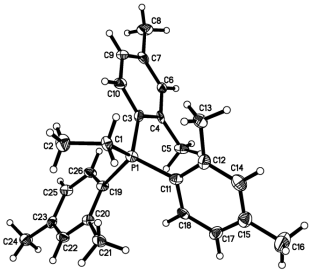


Figure S6. Molecular structure of $[C_{26}H_{32}P]^+$. Thermal ellipsoids are drawn at the 50 % probability level. Bond lengths (Å) and angles (°) for **6**: C1-C2 1.511(10), C1-P1 1.813(7), C3-C10 1.400(10), C3-C4 1.435(9), C3-P1 1.795(7), C4-C6 1.386(9), C4-C5 1.525(10) C6-C7 1.390(10), C7-C9, 1.396(10), C7-C8 1.507(10), C9-C10 1.370(10), C11-C18 1.405(10), C11-C12 1.407(10), C11-P1 1.804(8), C12-C14 1.395(11), C12-C13 1.520(10), C14-C15 1.400(11), C15-C17 1.389(11), C15-C16 1.495(11), C17-C18 1.371(10), C19-C20 1.408(9), C19-C26 1.409(9), C19-P1 1.794(7), C20-C22 1.389(10), C20-C21 1.498(9), C22-C23 1.415(10), C23-C25 1.396(9), C23-C24 1.498(10), C25-C26 1.381(10), C27-C28 1.545(10), C27-P2 1.825(7), C29-C36 1.388(10), C29-C30 1.411(9), C29-P2 1.807(7), C30-C32 1.412(10), C30-C31 1.511(10), C32-C33 1.382(11), C33-C35 1.381(10), C33-C34 1.516(10), C35-C36 1.393(10),

C37-C38 1.403(10), C37-C44 1.409(10), C37-P2 1.815(8), C38-C40 1.378(10), C38-C39 1.510(10), C40-C41 1.391(11), C41-C43 1.423(10), C41-C42 1.503(11), C43-C44 1.372(11), C45-C52 1.386(10), C45-C46 1.420(9), C45-P2 1.803(7), C46-C48 1.392(10), C46-C47 1.510(11), C48-C49 1.381(11), C49-C51 1.407(10), C49-C50 1.513(10), C51-C52 1.388(10), C2-C1-P1 115.1(5), C10-C3-C4 118.8(6), C10-C3-P1 119.7(5), C4-C3-P1 121.4(5), C6-C4-C3 117.6(6), C6-C4-C5 118.7(6), C3-C4-C5 123.6(6), C4-C6-C7 122.9(7), C6-C7-C9 118.8(6), C6-C7-C8 120.1(6), C9-C7-C8 121.1(7), C10-C9-C7 120.0(7), C9-C10-C3 121.9(7), C18-C11-C12 119.9(7), C18-C11-P1 118.9(6), C12-C11-P1 121.2(5), C14-C12-C11 117.4(7), C14-C12-C13 118.7(7), C11-C12-C13 123.8(7), C12-C14-C15 123.2(8), C17-C15-C14 117.1(7), C17-C15-C16 122.3(7), C14-C15-C16 120.6(8), C18-C17-C15 121.8(7), C17-C18-C11 120.3(7), C20-C19-C26 118.0(6), C20-C19-P1 123.1(5), C26-C19-P1 118.3(5), C22-C20-C19 118.8(6), C22-C20-C21 116.9(6), C19-C20-C21 124.2(7), C20-C22-C23 123.4(6), C25-C23-C22 116.7(7), C25-C23-C24 120.9(6), C22-C23-C24 122.4(6), C26-C25-C23 120.8(6), C25-C26-C19 122.3(6), C28-C27-P2 114.6(5), C36-C29-C30 119.8(7), C36-C29-P2 118.2(5), C30-C29-P2 122.0(6), C29-C30-C32 117.3(7), C29-C30-C31 125.0(7), C32-C30-C31 117.7(6), C33-C32-C30 122.3(7), C35-C33-C32 119.6(7), C35-C33-C34 119.7(7), C32-C33-C34 120.8(7), C33-C35-C36 119.5(7) , C29-C36-C35 121.5(7), C38-C37-C44 120.1(7), C38-C37-P2 120.5(6), C44-C37-P2 119.1(5), C40-C38-C37 117.1(7), C40-C38-C39 119.1(7), C37-C38-C39 123.8(7), C38-C40-C41 124.0(7), C40-C41-C43 118.3(7), C40-C41-C42 121.6(7), C43-C41-C42 120.2(7), C44-C43-C41 118.5(7), C43-C44-C37 121.9(7), C52-C45-C46 119.6(6), C52-C45-P2 118.4(5), C46-C45-P2 121.8(6), C48-C46-C45 117.3(7), C48-C46-C47 118.0(6), C45-C46-C47 124.7(7), C49-C48-C46 123.3(7), C48-C49-C51 118.8(7), C48-C49-C50 121.3(7) , C51-C49-C50 119.8(7), C52-C51-C49 118.8(7), C45-C52-C51 122.1(7), C19-P1-C3 108.2(3), C19-P1-C11 111.6(3), C3-P1-C11 111.0(3), C19-P1-C1 108.3(3), C3-P1-C1 108.8(3), C11-P1-C1 108.9(3), C45-P2-C29 108.2(3), C45-P2-C37 112.0(3), C29-P2-C37 108.5(3), C45-P2-C27 108.6(3), C29-P2-C27 110.4(3), C37-P2-C27 109.2(3).

Table S11. Sample and crystal data for **6**.

Identification code	fg238	
Chemical formula	$C_{26}H_{34}BrOP$	
Formula weight	473.41 g/mol	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.140 x 0.180 x 0.200 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 13.1049(9) Å	α = 90°
	b = 21.7175(13) Å	β = 91.322(4)°
	c = 17.0605(9) Å	γ = 90°
Volume	4854.2(5) $Å^3$	
Z	8	
Density (calculated)	1.296 g/cm^3	
Absorption coefficient	1.774 mm^{-1}	
F(000)	1984	

Table S12. Data collection and structure refinement for **6**.

Theta range for data collection	1.52 to 25.26°	
Index ranges	-15<=h<=15, -26<=k<=26, -20<=l<=19	
Reflections collected	47469	
Independent reflections	8753 [R(int) = 0.1760]	
Coverage of independent reflections	99.5%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7890 and 0.7180	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	8753 / 7 / 549	
Goodness-of-fit on F^2	1.011	
Final R indices	4776 data; $I>2\sigma(I)$	R1 = 0.0657, wR2 = 0.1602
	all data	R1 = 0.1497, wR2 = 0.2289
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1178P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.984 and -0.778 eÅ^{-3}	
R.M.S. deviation from mean	0.152 eÅ^{-3}	

Synthesis of tris-(2,4,6-trimethylphenyl)ethylphosphonium (7):

Tris-(2,4,6-trimethylphenyl)phosphine (0.39 g, 1 mmol, 1 equiv.) and ethyl bromide (5.45 g, 3.75 cm^3, 50 mmol, 50 equiv.) were mixed under microwave at 100 °C for 10 h. Excess ethyl bromide was evaporated. Precipitate obtained was washed with hexane, then further purified by HPLC. The product was recrystallized from ACN/diethyl ether. Isolated crystalline yield: 0.05 g, 10 %.

White solid, m.p. 223-225 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.06 (d, *J* = 80.3 Hz, 6H, Ar-**H**), 3.31 (s, 2H, P-C**H$_2$**), 2.42 – 2.21 (m, 18H, *p*-C**H$_3$** and *o*-C**H$_3$**), 1.94 (s, 9H, 9H, *o*-C**H$_3$**), 1.36 (dt, *J* = 20.1, 7.0 Hz, 3H, CH_2-C**H$_3$**); ^{13}C NMR (75 MHz, $CDCl_3$, 27°C): δ 144.33 (dd, *J* = 70.4, 6.5 Hz), 132.96 (d, *J* = 11.4 Hz), 119.83 (d, *J* = 76.6 Hz), 113.99 – 113.43 (m), 29.49 (d, *J* = 54.6 Hz), 25.64 – 22.97 (m), 21.09 (d, *J* = 1.4 Hz), 11.68 (d, *J* = 6.0 Hz); ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 27°C): δ 17.51; IR ($CHCl_3$): 1211 (P-Ar), 756 cm^{-1} (P-CH_2); HRMS (m/z): [M]+ calcd. for $C_{29}H_{38}BrP$ $[C_{29}H_{38}P]^+$ 417.23, found, 417.23.

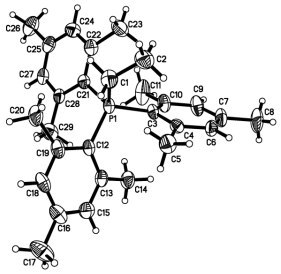


Figure S7. Molecular structure of $[C_{29}H_{38}P]^+$. Thermal ellipsoids are drawn at the 50 % probability level. Bond lengths (Å) and angles (°) for **7**: C1-C2 1.540(6), C1-P1 1.866(4), C3-C10 1.409(5), C3-C4 1.419(5), C3-P1 1.821(4), C4-C6 1.392(5), C4-C5 1.498(5), C6-C7 1.370(6), C7-C9 1.383(6), C7-C8 1.521(6), C9-C10 1.387(6), C10-C11 1.517(6), C12-C13 1.411(5), C12-C19 1.419(5), C12-P1 1.825(4), C13-C15 1.398(6), C13-C14 1.523(6), C15-C16 1.386(6), C16-C18 1.391(6), C16-C17 1.510(6), C18-C19 1.393(6), C19-C20 1.523(6), C21-C28 1.413(5), C21-C22 1.416(6), C21-P1 1.827(4), C22-C24 1.379(6), C22-C23 1.516(6), C24-C25 1.377(6), C25-C27 1.361(6), C25-C26 1.511(6), C27-C28 1.392(5), C28-C29 1.501(6), C2-C1-P1 122.1(3), C10-C3-C4 119.6(3), C10-C3-P1 124.6(3), C4-C3-P1 115.9(3), C6-C4-C3 118.7(3), C6-C4-C5 115.8(4), C3-C4-C5 125.2(3), C7-C6-C4 122.1(4), C6-C7-C9 118.6(4), C6-C7-C8 120.9(4), C9-C7-C8 120.5(4), C7-C9-C10 122.5(4), C9-C10-C3 118.5(4), C9-C10-C11 116.1(4), C3-C10-C11 125.4(4), C13-C12-C19

119.0(4), C13-C12-P1 123.0(3), C19-C12-P1 118.0(3), C15-C13-C12 118.9(4), C15-C13-C14 115.4(4), C12-C13-C14 125.7(4), C16-C15-C13 122.7(4), C15-C16-C18 117.4(4), C15-C16-C17 121.2(4), C18-C16-C17 121.3(4), C16-C18-C19 122.5(4), C18-C19-C12 119.0(4), C18-C19-C20 116.3(4), C12-C19-C20 124.3(4), C28-C21-C22 118.8(4), C28-C21-P1 123.4(3), C22-C21-P1 117.8(3), C24-C22-C21 119.3(4), C24-C22-C23 116.5(4), C21-C22-C23 124.2(4), C25-C24-C22 122.5(4), C27-C25-C24 117.7(4), C27-C25-C26 120.5(4), C24-C25-C26 121.7(4), C25-C27-C28 123.6(4), C27-C28-C21 118.1(4), C27-C28-C29 115.9(4), C21-C28-C29 126.0(4), C3-P1-C12, 110.20(18), C3-P1-C21 113.78(17), C12-P1-C21 111.38(18), C3-P1-C1 107.66(18), C12-P1-C1 106.67(19), C21-P1-C1 106.76(19).

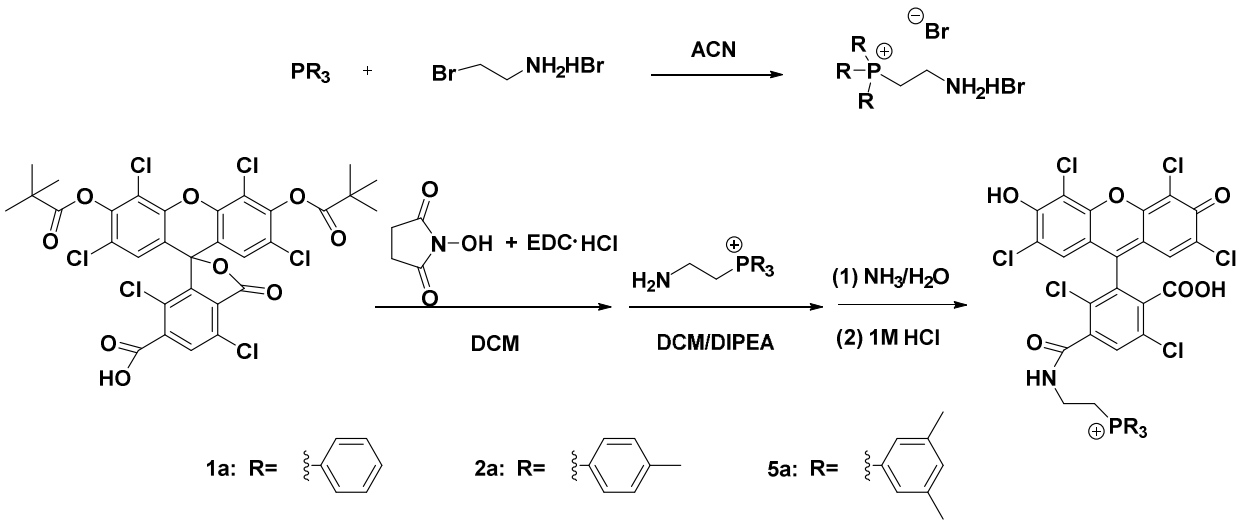
Table S13. Sample and crystal data for **7**.

Identification code	fg233	
Chemical formula	$C_{29}H_{38}BrP$	
Formula weight	497.47 g/mol	
Temperature	158(2) K	
Wavelength	0.71073 Å	
Crystal size	0.140 x 0.220 x 0.280 mm	
Crystal habit	colorless block	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 20.1236(8) Å	α = 90°
	b = 11.6665(4) Å	β = 112.6201(18)°
	c = 23.6222(9) Å	γ = 90°
Volume	5119.2(3) $Å^3$	
Z	8	
Density (calculated)	1.291 g/cm^3	
Absorption coefficient	1.683 mm^{-1}	
F(000)	2096	

Table S14. Data collection and structure refinement for **7**.

Theta range for data collection	1.87 to 26.40°	
Index ranges	-24<=h<=25, -14<=k<=14, -29<=l<=23	
Reflections collected	28297	
Independent reflections	5260 [R(int) = 0.0804]	
Coverage of independent reflections	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7990 and 0.6500	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/6 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5260 / 0 / 292	
Goodness-of-fit on F^2	1.034	
Δ/σ_{max}	0.001	
Final R indices	3224 data; I>2σ(I)	R1 = 0.0514, wR2 = 0.1334
	all data	R1 = 0.1050, wR2 = 0.1794
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0986P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.608 and -0.403 eÅ^{-3}	
R.M.S. deviation from mean	0.117 eÅ^{-3}	

1.2. Synthesis of (hexachloro-fluorescein)-DLC conjugates 1a, 2a and 5a:



Scheme S2

Synthesis of (2-aminoethyl)triphenylphosphonium bromide hydrobromide:

To a 50 mL round-bottom flask equipped with a magnetic stir bar triphenylphosphine (1.07 g, 4.88 mmol, 1 equiv.), 2-bromopropylamine hydrobromide (1.0 g, 4.88 mmol, 1 equiv.), and acetonitrile (5 mL) were added. The resulting solution was heated to reflux for one day. The reaction was cooled to room temperature and the resulting solid was separated and washed with hexane. The product was recrystallized from isopropanol and a minimal amount of diethyl ether. Yield: 0.98 g, 43 %.

White solid, ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19(s, 3H, -N**H$_3$**), 7.98 – 7.77(m, 15H, Ar-**H**), 4.10 – 3.72 (m, 2H, CH_2-C**H$_2$**-N), 3.34 – 2.92 (m, 2H, C**H$_2$**-CH_2-N); ^{31}P{^{1}H} NMR (121MHz, DMSO): δ 22.02; HRMS (m/z): $[M]^+$ calcd. for $[C_{20}H_{21}PN]^+$, 306.14; found, 306.14.

Synthesis of (2-aminoethyl)tri-*p*-tolylphosphonium bromide hydrobromide:

Synthesized from tri-p-tolylphosphine (0.37g, 1.22 mmol, 1 equiv.) according to similar procedure as (2-aminoethyl)triphenylphosphonium bromide hydrobromide. The product was recrystallized from isopropanol and a minimal amount of diethyl ether. Yield: 0.24 g, 39 %.

White solid, ^{1}H NMR (400MHz, DMSO): δ 8.90(s, 3H, -N**H$_3$**), 7.67 – 7.28(m, 12H, Ar-**H**), 4.45 – 3.35 (m, 2H, CH_2-C**H$_2$**-N), 3.37 – 2.33 (m, 2H, C**H$_2$**-CH_2-N), 2.52 (s, 9H, Ar-C**H$_3$**); ^{31}P{^{1}H} NMR (121MHz, DMSO): δ 21.27; HRMS (m/z): $[M]^+$ calcd. for $[C_{23}H_{27}PN]^+$, 348.19; found, 348.19.

Synthesis of (2-aminoethyl)tris(3,5-dimethylphenyl)phosphonium bromide hydrobromide:

Synthesized from tris-(3, 5-dimethylphenyl)phosphine (0.42g, 1.22mmol, 1 equiv.) according to similar procedure as (2-aminoethyl)triphenylphosphonium bromide hydrobromide. The product was recrystallized from isopropanol and a minimal amount of diethyl ether. Yield: 0.23 g, 34 %.

White solid, ^{1}H NMR (400MHz, DMSO): δ 8.10(s, 3H, -N**H$_3$**), 7.55 – 7.42(m, 9H, Ar-**H**), 3.78 – 3.70 (m, 2H, CH_2-C**H$_2$**-N), 3.04 – 3.00 (m, 2H, C**H$_2$**-CH_2-N), 2.37 (s, 18H, Ar-C**H$_3$**); ^{31}P{^{1}H} NMR (121MHz, DMSO): δ 20.19; HRMS (m/z): $[M]^+$ calcd. for $[C_{26}H_{33}PN]^+$, 390.23; found, 390.23.

Synthesis of (hexachloro-fluorescein)-triphenylethylphosphonium (1a):

NHS (61.3 mg, 0.532 mmol) and EDC·HCl (56.3 mg, 0.294mmol) were added to the solution of 6-HEX dipivaloate (200 mg, 0.267 mmol) in DCM (10 mL) and the reaction mixture was stirred at room temperature for 30 min. (2-aminoethyl)triphenylphosphonium bromide hydrobromide (124.7 mg, 0.267mmol) and 10 times of DIPEA (46.5 μL, 2.67 mmol) in DCM (5 mL) was then quickly added into the solution and the mixture stirred at room temperature for further 3 h. After treated with ammonia, the reaction mixture was acidified with 1M HCl to give a red solution. The final compound was extracted from water by DCM and purified by HPLC.

Compound **1a**: ^{31}P{^{1}H} NMR (121MHz, DMSO): δ 22.21; HRMS (m/z): $[M]^+$ calcd. for $[C_{41}H_{25}Cl_6NO_6P]^+$, 871.33; found, 871.33. Yield: 18 mg, 7 %.

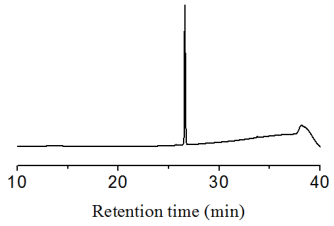


Figure S8. HPLC chromatogram of **1a** monitored at absorbance of 220 nm.

Synthesis of (hexachloro-fluorescein)-tri-*p*-tolyethylphosphonium (2a):

Synthesized from (2-aminoethyl)tri-p-tolylphosphonium bromide hydrobromide (136.0 mg, 0.267 mmol) according to similar procedure as **1a**.

Compound **2a**: $^{31}P\{^{1}H\}$ NMR (121MHz, DMSO): δ 21.14; HRMS (m/z): $[M]^+$ calcd. for $[C_{44}H_{31}Cl_6NO_6P]^+$, 913.41; found, 913.41. Yield: 12 mg, 5 %.

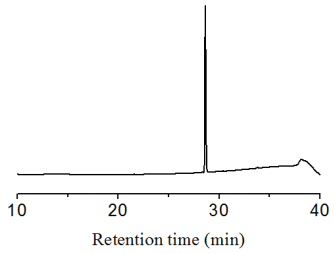


Figure S9. HPLC chromatogram of **2a** monitored at absorbance of 220 nm.

Synthesis of hexachloro-fluorescein)-tris-(3,5-dimethylphenyl) ethylphosphonium (5a):

Synthesized from (2-aminoethyl)tris(3,5-dimethylphenyl)phosphonium bromide hydrobromide (147.2 mg, 0.267 mmol) according to similar procedure as **1a**.

Compound **5a**: $^{31}P\{^{1}H\}$ NMR (121MHz, DMSO): δ 20.39; HRMS (m/z): $[M]^+$ calcd. for $[C_{47}H_{37}Cl_6NO_6P]^+$, 955.49; found, 955.48. Yield: 14 mg, 5 %.

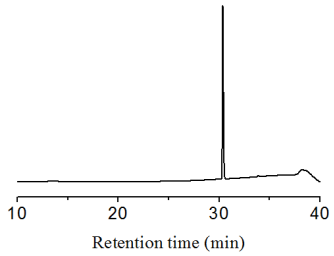


Figure S10. HPLC chromatogram of **5a** monitored at absorbance of 220 nm.

2. Figure S11

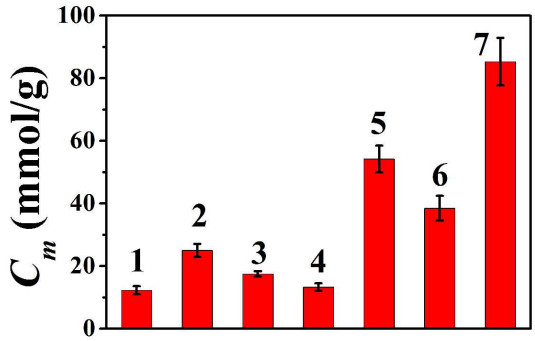


Figure S11. Amount of DLC **1-7** accumulated in isolated FU97 mitochondria.

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3. Figure S12

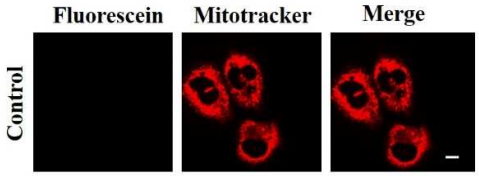

Figure S12. Confocal fluorescence microscopy image of FU97 cells treated with hexachloro-fluorescein. Scale bar = 20 μm.

4. Figure S13

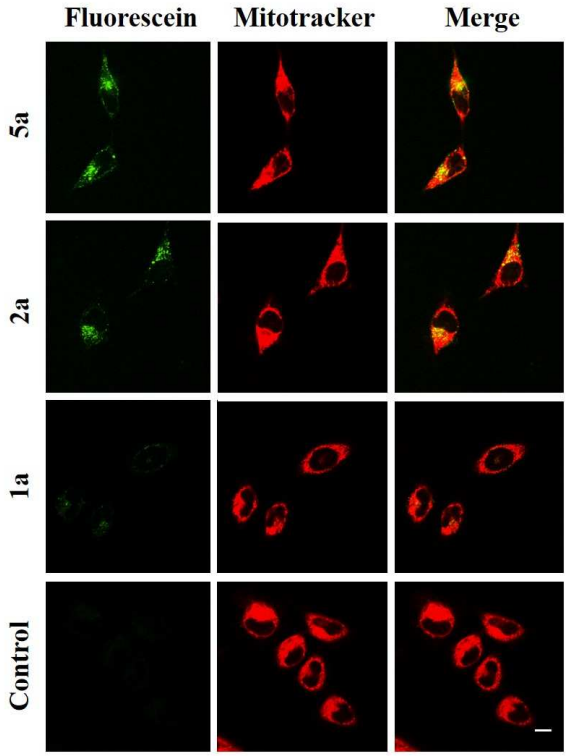

Figure S13. Subcellular localization of hexachloro-fluorescein, **1a**, **2a** and **5a** in HeLa cells. The cells were treated with 20 μM compounds at 37 °C for 3 h. Scale bar = 20 μm.

5. Figure S14

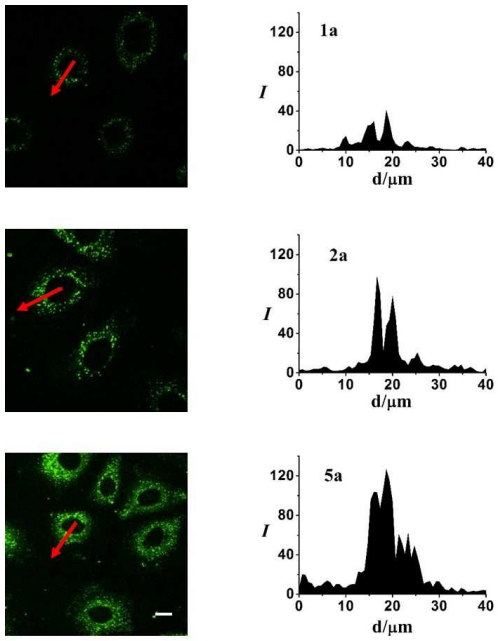

Figure S14. (left column) Confocal fluorescence images of FU97 cells treated with **1a** (top)**, 2a** (middle) and **5a** (bottom). (right column) Fluorescence intensity profile of a section of the cell (red arrow in corresponding image) plotted as a function of distance (d) along the arrow. Clearly, the overall intensity from **5a** is the largest followed by **2a** and **1a**. Scale bar = 20 μm.

6. Figure S15

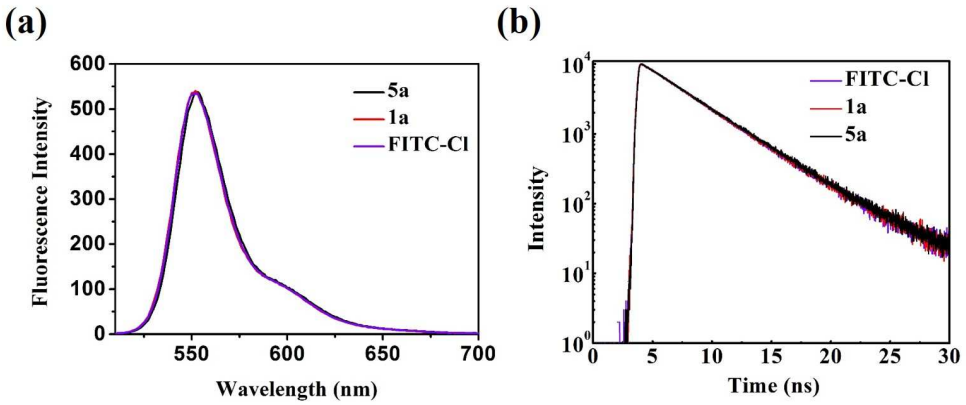

Figure S15. (a) Fluorescence spectra of hexachloro-fluorescein (FITC-Cl), **1a** and **5a** in PBS. The OD at the excitation wavelength (500 nm) is the same for all samples. The emission spectra are not significantly different for FITC-Cl, **1a** and **5a**. (b) The time-resolved fluorescence lifetime decays of **1a**, **5a** and hexachloro-fluorescein in water. The profiles were described using a mono-exponential decay function with a lifetime of 3.9 ns.

7. Figure S16

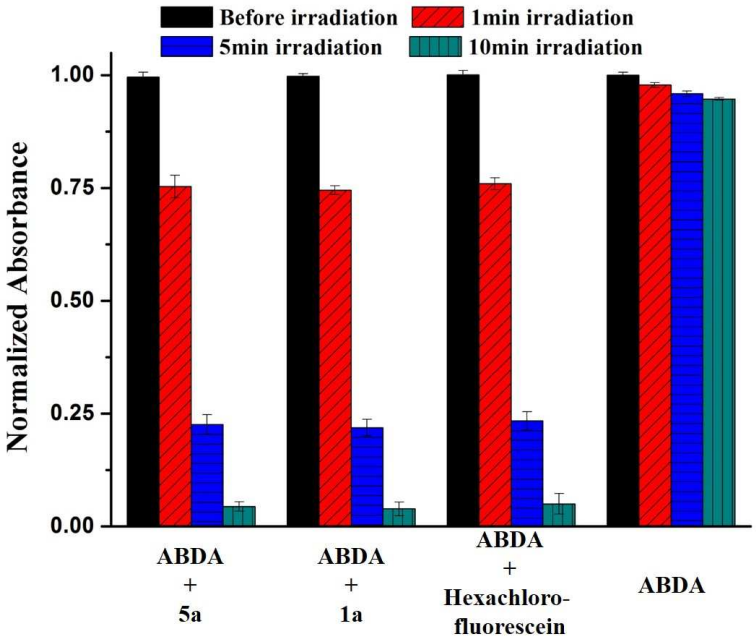

Figure S16. Normalized absorbance at 378 nm of ABDA (200 μM) for sample solutions containing ABDA and hexachloro-fluorescein, **1a** and **5a** conjugates (10 μM) in PBS buffer before and after light irradiation for 1, 5 and 10 min. In the absence of hexachloro-fluorescein, **1a** and **5a**, the absorbance of ABDA displays only small reduction with irradiation time due to photo-bleaching of ABDA. In the presence of hexachloro-fluorescein, **1a** and **5a,** the absorbance of ABDA decreases with increasing irradiation time. This is because more $^1O_2$ are produced which then degrades the ABDA.