Supplementary Material for

Solvent-free photochemical decomposition of sulfur hexafluoride by phosphines: Formation of difluorophosphoranes as versatile fluorination reagents

Philipp Rotering,[a,b] Christian Mück-Lichtenfeld,[c] and Fabian Dielmann*[a]

[a] Institute of General, Inorganic and Theoretical Chemistry, Leopold-Franzens-Universität Innsbruck, Innrain 80-82, 6020 Innsbruck (Austria), E-mail: fabian.dielmann@uibk.ac.at
[b] Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstrasse 30, 48149 Münster (Germany)
[c] Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstrasse 40, 48149 Münster (Germany)

CONTENTS:

Synthetic Details

General remarks: All manipulations were performed under an inert atmosphere of dry argon, using standard Schlenk and drybox techniques. Dry and oxygen-free solvents were employed. All glassware was oven-dried at 160 °C prior to use. NMR spectra were recorded at 300 K on Bruker AVANCE I 400 or Bruker AVANCE III 400 spectrometers. Chemical shifts (δ) are given in parts per million (ppm) relative to $SiMe_4$ (^1H, ^{13}C), $CFCl_3$ (^{19}F) or 85% H_3PO_4 (^{31}P) and they were referenced to the residual solvent signals (C_6D_6: ^1H δ_H = 7.16, ^{13}C δ_C = 128.06; CD_3CN: δ_H = 1.94, ^{13}C δ_C = 118.26; THF-d_8: ^1H δ_H = 1.73, ^{13}C δ_C = 67.57, CD_2Cl_2: ^1H δ_H = 5.32, ^{13}C δ_C = 53.84) or internally by the instrument after locking and shimming to the deuterated solvent (^{19}F, ^{31}P). NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, p = pentet, sept = septet, m = multiplet, br = broad signal.

Reagents and Handling: Ph_2(pyrrolidine)P[1], $Ph(N(iPr)_2)_2P$[2] and Ph_2(2-NMe_2-C_6H_4)P[3] were synthesized according to the literature. Sulfur hexafluoride 3.0 (99.9%) was generously donated by the company DILO GmbH. All other compounds were purchased from commercial sources (Sigma Aldrich, Alfa Aesar, abcr GmbH) and used as received.

Irradiation: Irradiations were performed with a Seoulviosys LED Type CUD1KFMA (310 nm), EvoluChem™ LED Type P205-18-1 (365 nm), EvoluChem™ LED Type P206-18-1 (405 nm), EvoluChem™ LED Type P201-18-2 (450 nm), or VCClilte LED Type VAOL-SA1xAx-SA (585 nm).

EvoluChem™ LEDs were used in combination with the EvoluChem™ PhotoRedOx Box and show a relative irradiance of 8 mW/cm^2 (365 nm) or 28 mW/cm^2 (405 nm) in the set-up.

For large-scale synthesis of *TPP-Fluor* we used an array of 72 x Luminus SST-10-UV with λ = 365 nm and a total radiometric flux of Φ = 63 Watt.

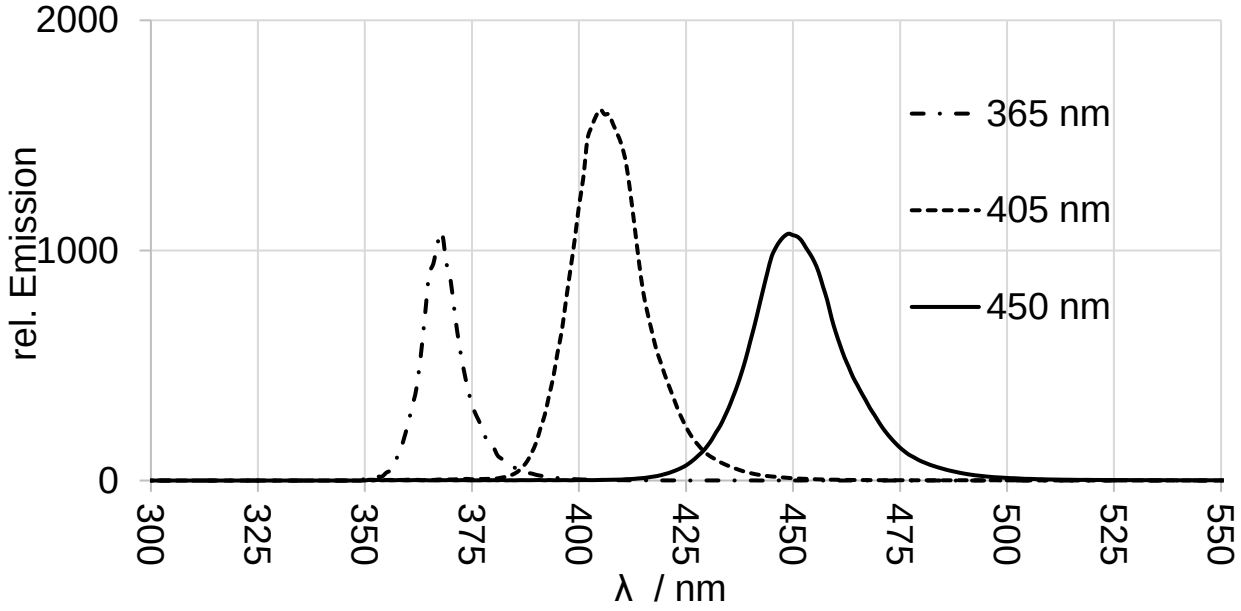
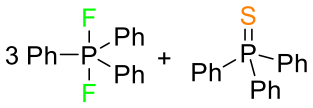


Figure S1: Emission spectra of the EvoluChem™ LEDs used in the present study (provided by HepatoChem Inc.).

Phosphine Screening

General procedure for the reaction of phosphines with SF_6: The indicated amount of phosphine was dissolved in the indicated solvent in a teflon-sealed glass vessel. The solution was frozen in liquid nitrogen and the argon atmosphere was removed *in vacuo*. After warming the solution to room temperature, the vessel was pressurized with SF_6 (2 bar) and was subsequently irradiated with UV light (λ = 365 nm) for 12 h. The reaction mixture was analysed using NMR spectroscopy. The conversion was determined by ^{31}P NMR spectroscopy.

Triphenylphosphine Ph_3P:



A solution of Ph_3P (1.00 g, 3.81 mmol) in MeCN (5 mL) was irradiated according to the general procedure, giving a 3:1 mixture of triphenyldifluorophosphorane and triphenylphosphine sulfide (*TPP-Fluor*) in quantitative yield. *TPP-Fluor* was isolated as a white solid after removal of the volatiles *in vacuo*. The reaction gave similar results using THF, toluene, benzene, butanone, propylene carbonate, sulfolane or dimethylformamide as the solvent.

^{1}H NMR (CD_2Cl_2, 400 MHz) δ (ppm) = 8.07 – 7.98 (m, Ar-H), 7.77 – 7.70 (m, Ar-H), 7.58 – 7.44 (m, Ar-H).

^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz) δ (ppm) = 137.7 (m), 136.2 (m), 134.1 (m), 133.8, 133.2, 132.6 (m), 132.0 (m), 131.9 (m), 129.10 – 128.53 (m).

^{19}F NMR (CD_2Cl_2, 376 MHz) δ (ppm) = -39.5 (d, $^{1}J_{PF}$ = 659.5 Hz, Ph_3PF_2).

^{31}P NMR (CD_2Cl_2, 160 MHz) δ (ppm) = 43.0 (m, Ph_3PS), -54.9 (t, $^{1}J_{PF}$ = 659.5 Hz, Ph_3PF_2).

^{19}F NMR ($CDCl_3$, 376 MHz) δ (ppm) = -39.8 (d, $^{1}J_{PF}$ = 659.8 Hz, Ph_3PF_2).

^{31}P NMR ($CDCl_3$, 160 MHz) δ (ppm) = 43.3 (m, Ph_3PS), -54.6 (t, $^{1}J_{PF}$ = 659.8 Hz, Ph_3PF_2).

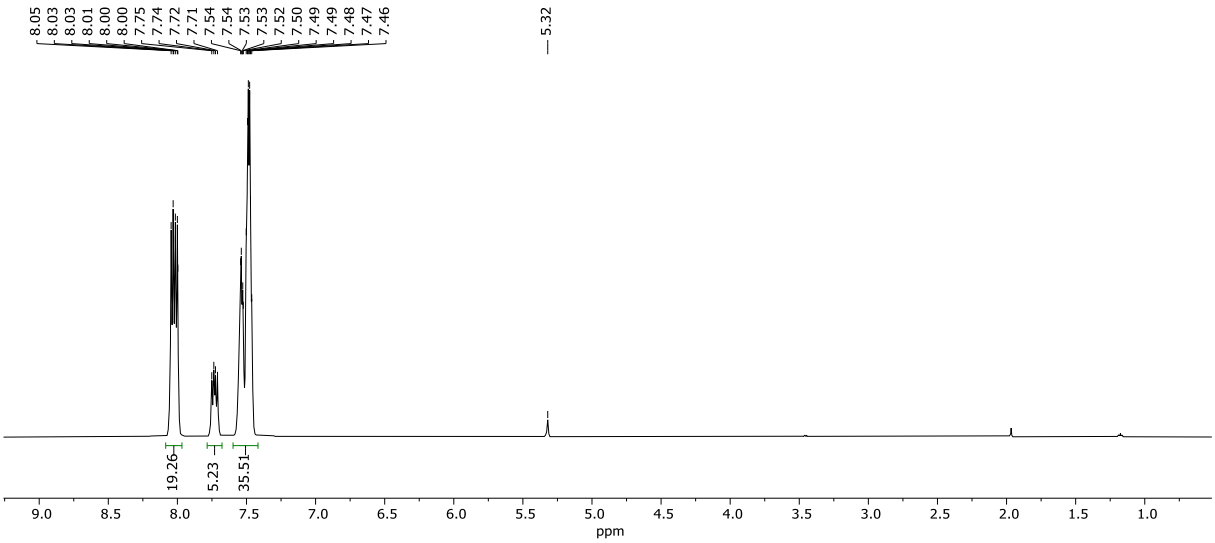


Figure S2: ^{1}H NMR spectrum (CD_2Cl_2, 300 K, 400 MHz) of the isolated solid containing Ph_3PF_2 and Ph_3PS in a ratio of 3:1.

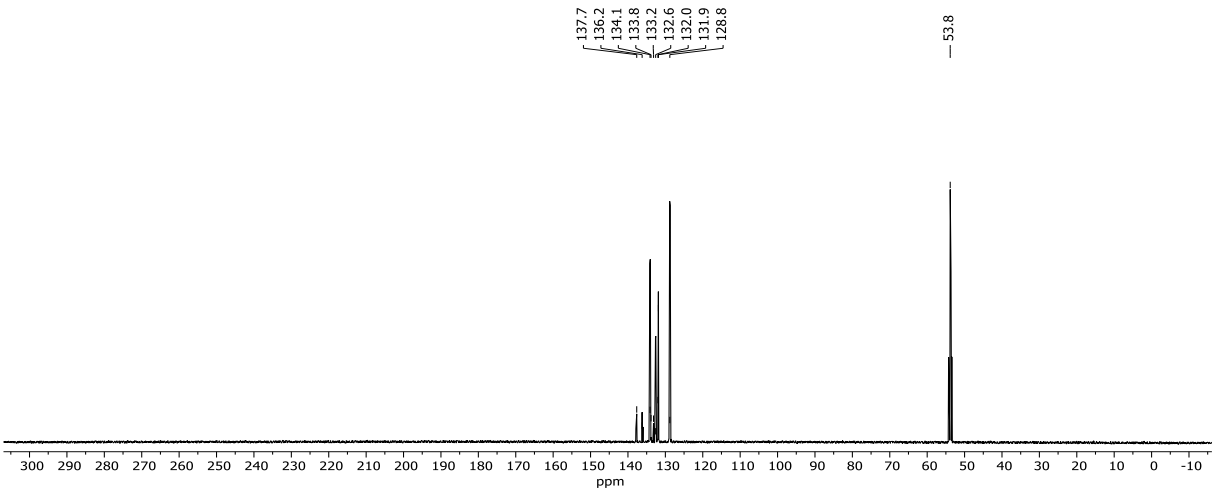


Figure S3: $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 300 K, 100 MHz) of the isolated solid containing Ph_3PF_2 and Ph_3PS in a ratio of 3:1.

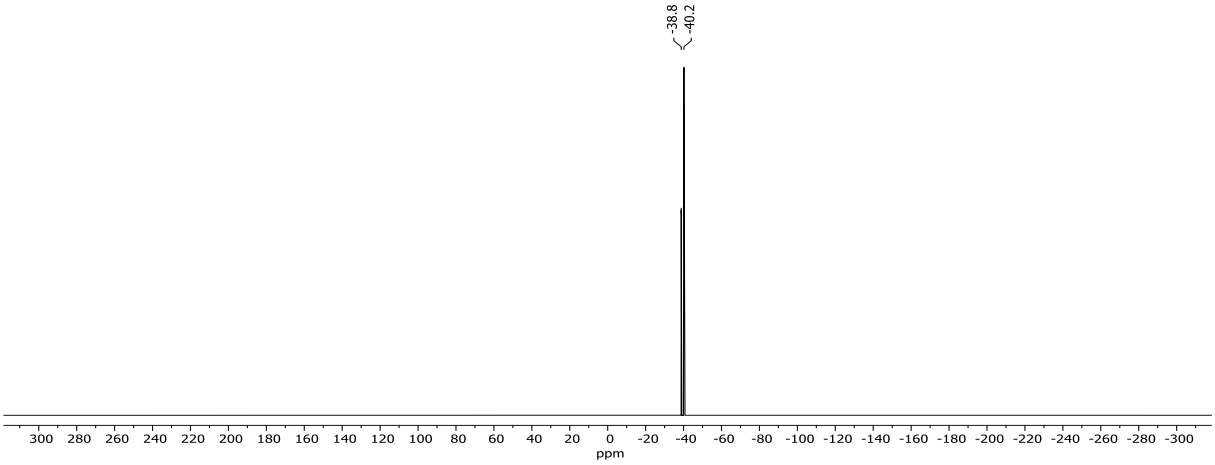


Figure S4: ^{19}F NMR spectrum (CD_2Cl_2, 300 K, 376 MHz) of the isolated solid containing Ph_3PF_2 and Ph_3PS in a ratio of 3:1.

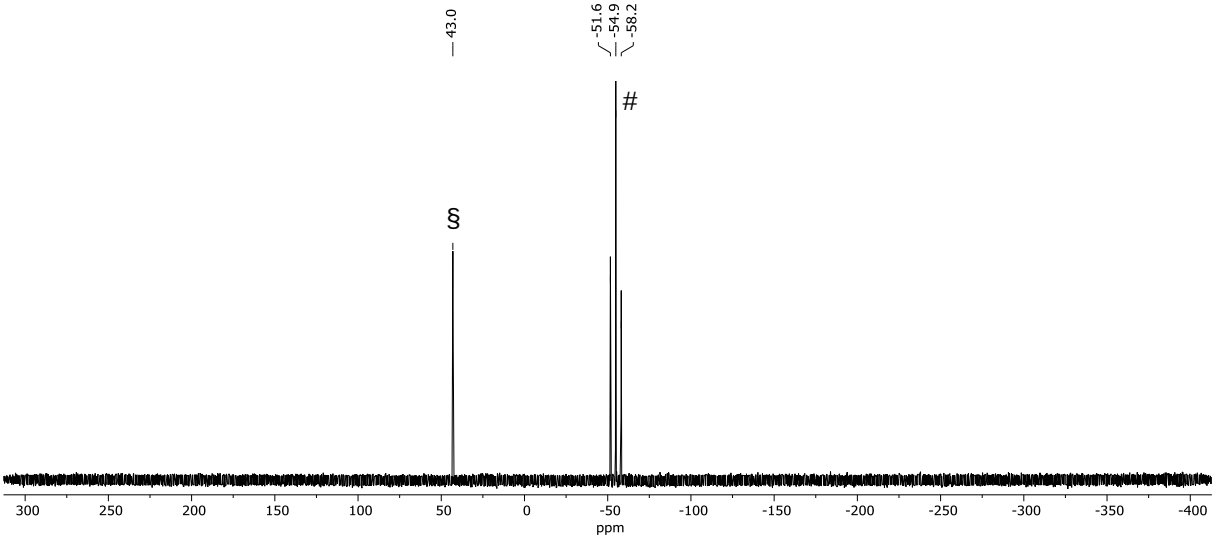
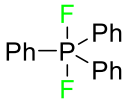


Figure S5: ^{31}P NMR spectrum (CD_2Cl_2, 300 K, 160 MHz) of the isolated solid containing Ph_3PF_2 (#) and Ph_3PS (§) in a ratio of 3:1.

Isolation of Ph_3PF_2:



The isolated solid containing Ph_3PF_2 and Ph_3PS in a ratio of 3:1 (150 mg, 0.126 mmol) was suspended in α,α,α-trifluorotoluene. Gentle heating gave a clear solution that was then allowed to cool to room temperature. The formed crystalline material was isolated by filtration and it was washed with α,α,α-trifluorotoluene (1 mL) to afford Ph_3PF_2 as colourless crystals in 81% yield.

^{1}H NMR (CD_2Cl_2, 400 MHz) δ (ppm) = 8.01 (m, 2H, Ar-H), 7.53 (m, 1H, Ar-H), 7.48 (m, 2H, Ar-H).

^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz) δ (ppm) = 134.1(dt, J = 12.8 Hz, J = 9.0 Hz, Ar-H), 131.8 (m, Ar-H), 128.8 (dd, J = 16.6 Hz, J = 1.6 Hz, Ar-H).

^{19}F NMR (CD_2Cl_2, 376 MHz) δ (ppm) = -39.5 (d, $^{1}J_{PF}$ = 659.5 Hz, Ph_3PF_2).

^{31}P NMR (CD_2Cl_2, 160 MHz) δ (ppm) = -54.9 (t, $^{1}J_{PF}$ = 659.5 Hz, Ph_3PF_2).

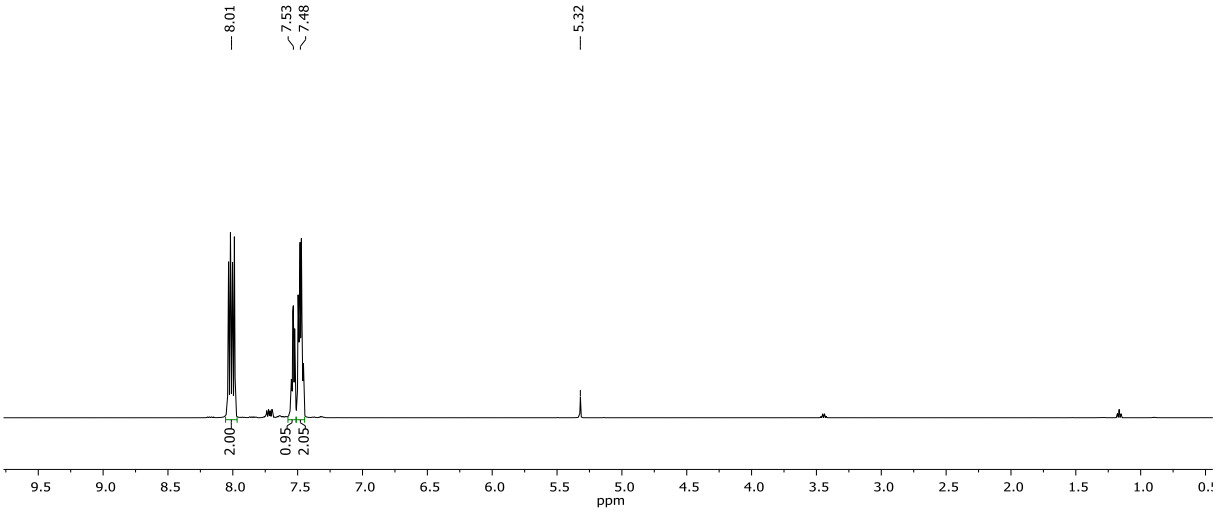


Figure S6: ^{1}H NMR spectrum (CD_2Cl_2, 300 K, 400 MHz) of Ph_3PF_2.

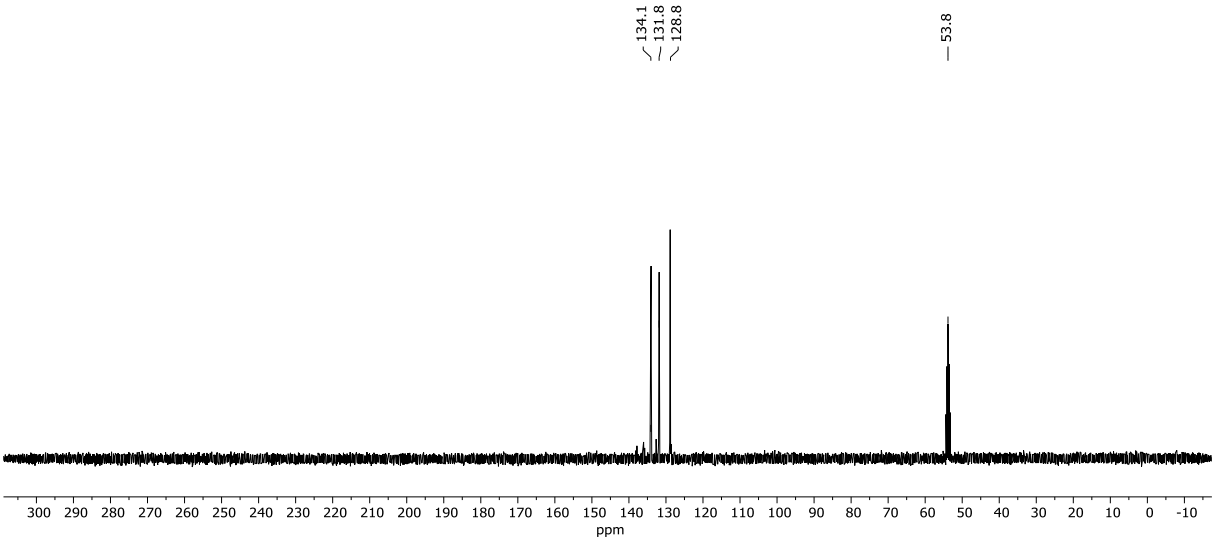


Figure S7: ^{13}C{^{1}H} NMR spectrum (CD_2Cl_2, 300 K, 100 MHz) of Ph_3PF_2.

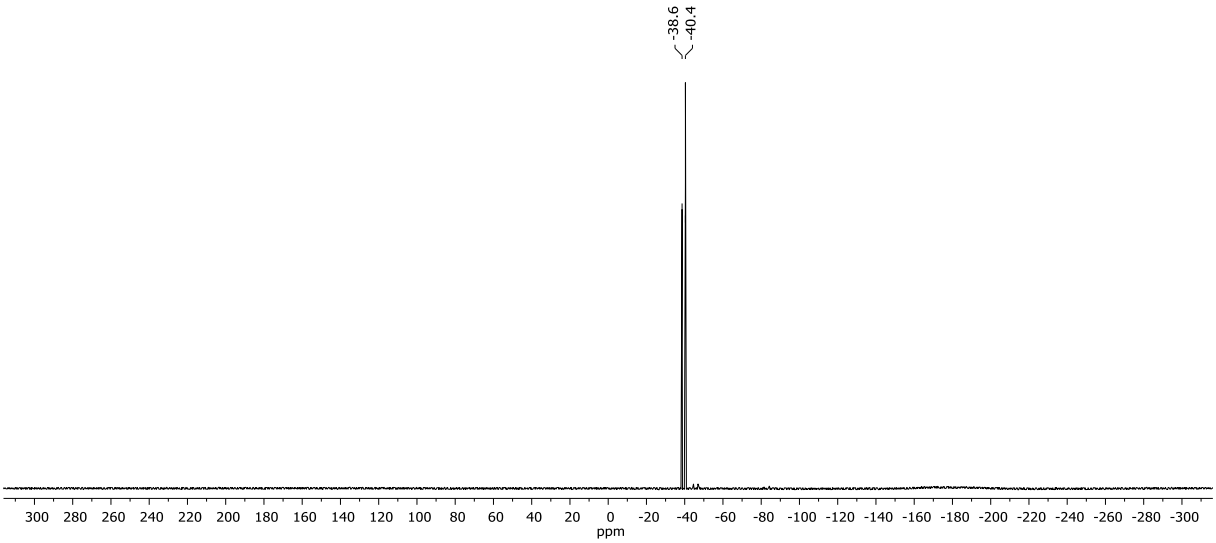


Figure S8: ^{19}F NMR spectrum (CD_2Cl_2, 300 K, 376 MHz) of Ph_3PF_2.

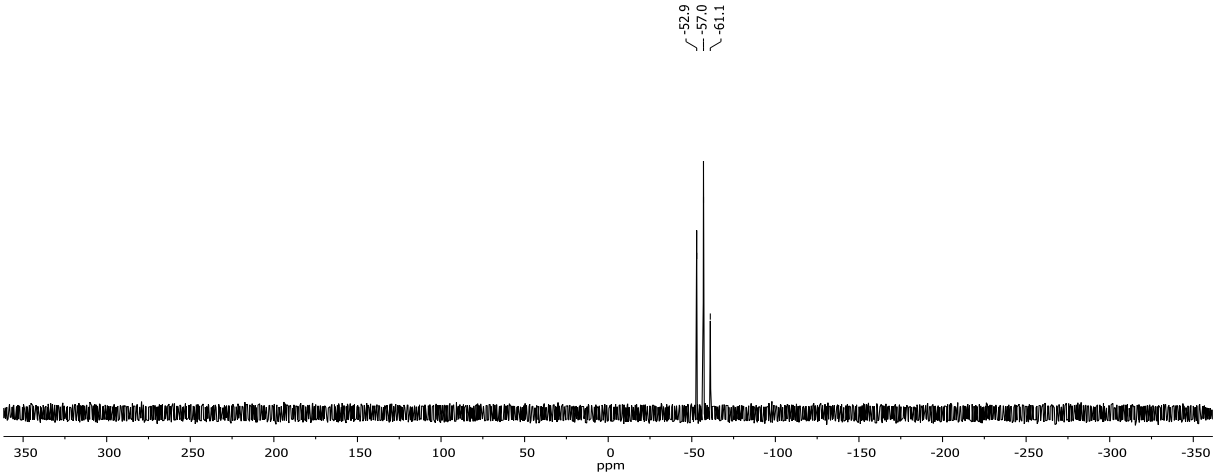
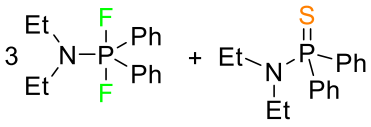


Figure S9: ^{31}P NMR spectrum (CD_2Cl_2, 300 K, 160 MHz) of Ph_3PF_2.

<u>(Diethylamino)diphenylphosphine ($Et_2N)Ph_2P$</u>



According to the general procedure, a solution of (diethylamino)diphenylphosphine (39 mg, 0.15 mmol) in MeCN-d_3 (0.7 mL) was irradiated, resulting in 89% conversion to a 3:1 mixture of ($Et_2N)Ph_2PF_2$ and ($Et_2N)Ph_2PS$.

^{1}H NMR (MeCN-d_3, 500 MHz) δ (ppm) = 7.99 (m, Ar-H), 7.82 – 7.69 (m, Ar-H), 7.93 – 7.80 (m, Ar-H) 7.59 – 7.30 (m, Ar-H), 3.21 (m, 12H, CH_2), 3.09 – 2.94 (m, 4H, CH_2), 1.16 (t, J = 6.9 Hz, 18H, CH_3), 1.06 (t, J = 7.1 Hz, 6H, CH_3).

^{19}F NMR (MeCN-d_3, 376 MHz) δ (ppm) = -37.3 (d, $^1J_{PF}$ = 694.5 Hz, R_3PF_2).

^{31}P NMR (MeCN-d_3, 160 MHz) δ (ppm) = 67.6 (m, R_3PS), -49.9 (t, $^1J_{PF}$ = 694.5 Hz, R_3PF_2).

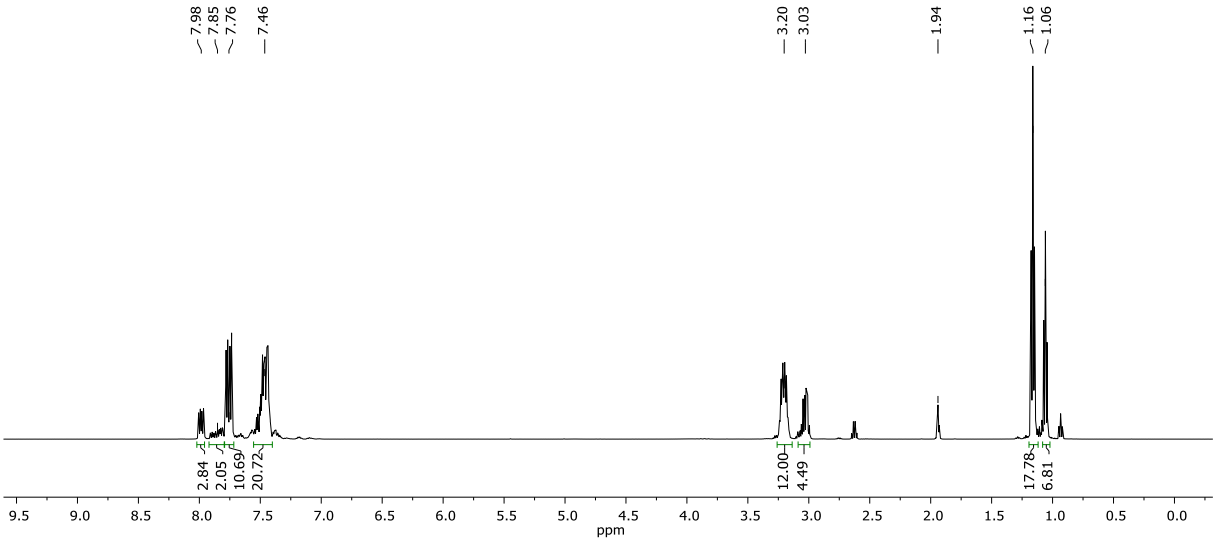


Figure S10: ^{1}H NMR spectrum (MeCN-d_3, 300 K, 400 MHz) of the reaction solution containing $(Et_2N)Ph_2P$, $(Et_2N)Ph_2PF_2$ and $(Et_2N)Ph_2PS$.

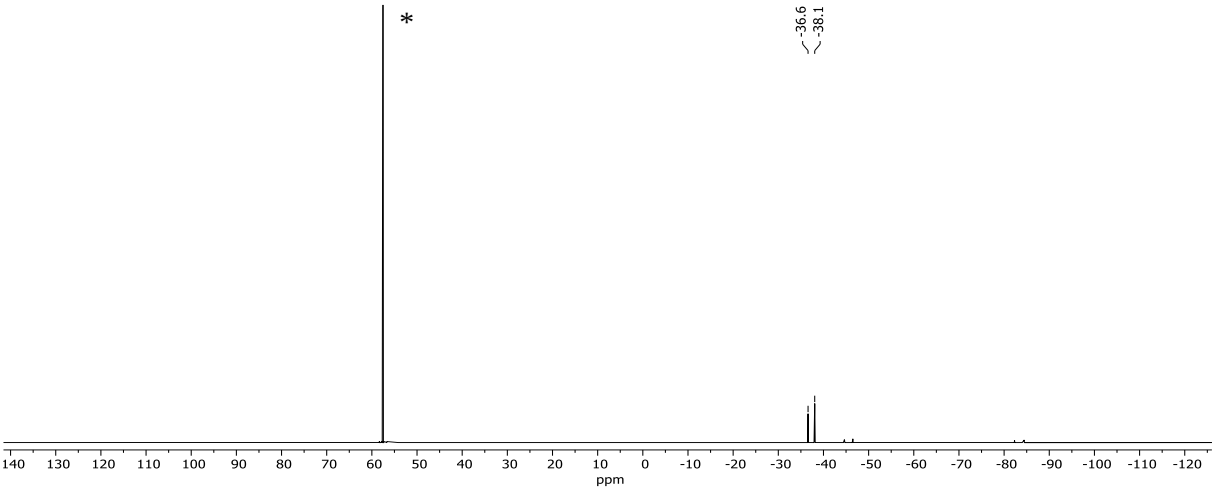


Figure S11: ^{19}F NMR spectrum (MeCN-d_3, 300 K, 376 MHz) of the reaction solution containing $(Et_2N)Ph_2P$, $(Et_2N)Ph_2PF_2$ and $(Et_2N)Ph_2PS$. * SF_6

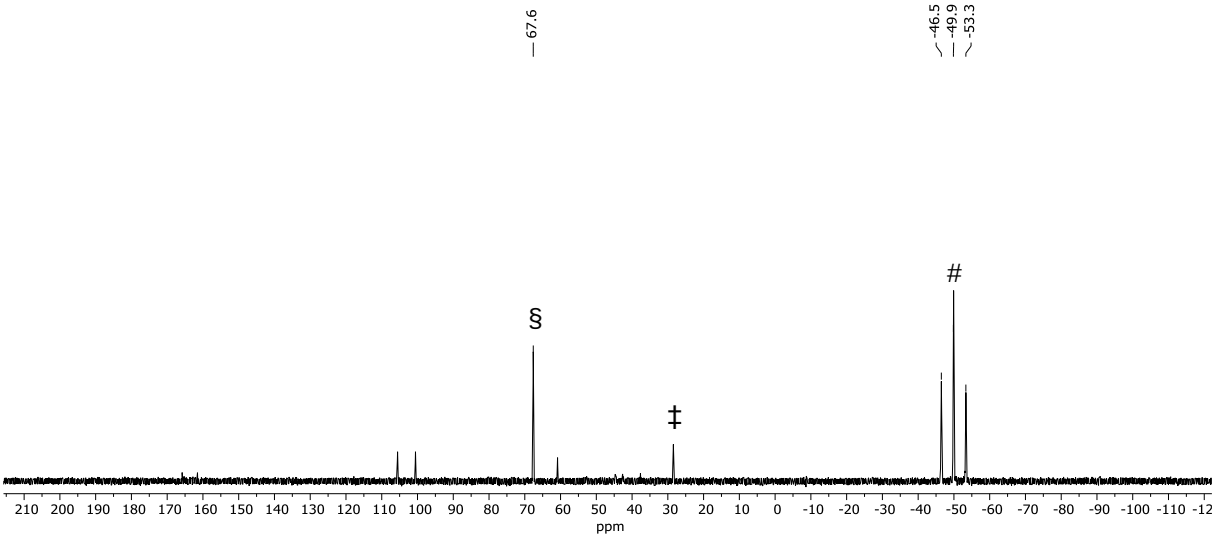
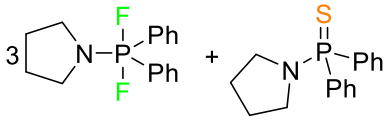


Figure S12: ^{31}P NMR spectrum (MeCN-d_3, 300 K, 160 MHz) of the reaction solution containing $(Et_2N)Ph_2P$ (‡), $(Et_2N)Ph_2PF_2$ (#) and $(Et_2N)Ph_2PS$ (§).

<u>Diphenyl(pyrrolidine)phosphine (pyr)Ph_2P</u>



According to the general procedure, a solution of diphenyl(pyrrolidine)phosphine (38 mg, 0.15 mmol) in MeCN-d_3 (0.7 mL) was irradiated, resulting in 92% conversion to a 3:1 mixture of $(pyr)Ph_2PF_2$ and $(pyr)Ph_2PS$.

^{1}H NMR (MeCN-d_3, 500 MHz) δ (ppm) = 8.10 – 7.99 (m, Ar-H), 7.94 – 7.82 (m, Ar-H), 7.81 – 7.74 (m, Ar-H), 7.61 – 7.54 (m, Ar-H), 7.54 – 7.38 (m, Ar-H), 3.42 (m, CH_2), 2.99 – 2.88 (m, CH_2), 1.94 (m, CH_2), 1.89 – 1.76 (m, CH_2).

^{13}C{^{1}H} NMR (MeCN-d_3, 126 MHz) δ (ppm) = 141.4 (m), 139.8 (m), 135.3 (m), 132.9 – 132.5 (m), 132.3 (m), 131.7 – 131.3 (m), 129.6 (m), 129.1 (m), 49.5 (m), 48.0 (m), 27.1 (m), 26.7 (m).

^{19}F NMR (MeCN-d_3, 376 MHz) δ (ppm) = -32.1 (d, $^1J_{PF}$ = 681.7 Hz, R_3PF_2).

^{31}P NMR (MeCN-d_3, 160 MHz) δ (ppm) = 64.4 (m, R_3PS), -53.4 (t, $^1J_{PF}$ = 681.7 Hz, R_3PF_2).

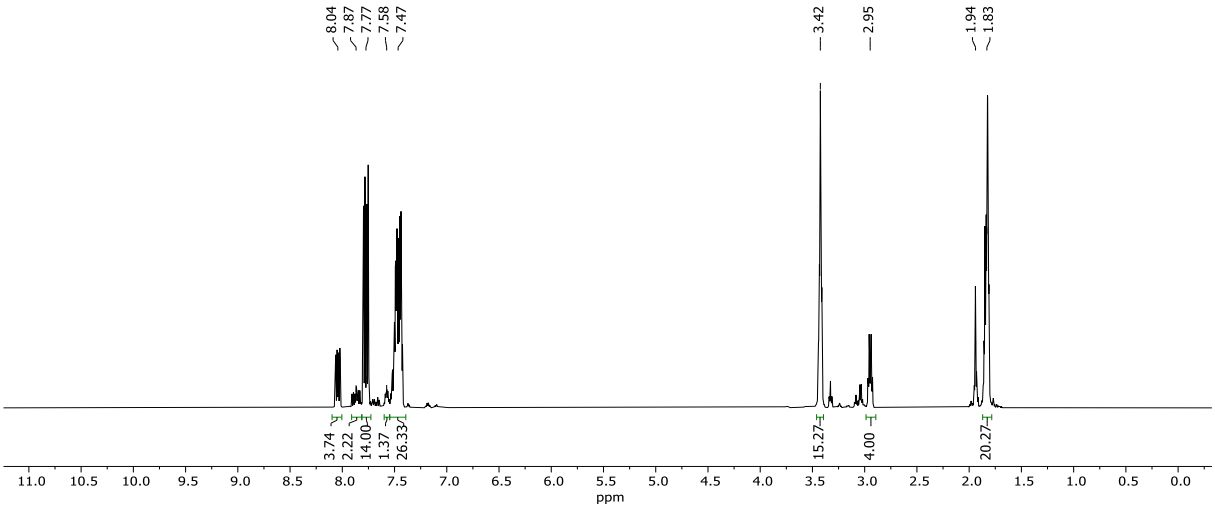


Figure S13: ^{1}H NMR spectrum (MeCN-d_3, 300 K, 400 MHz) of the reaction solution containing (pyr)Ph_2P, (pyr)Ph_2PF_2 and (pyr)Ph_2PS.

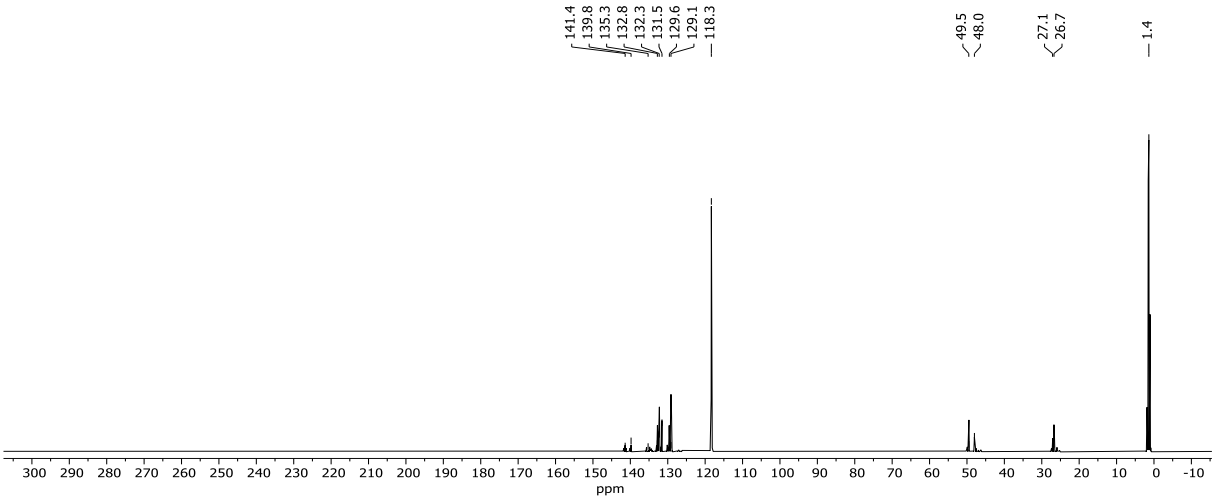


Figure S14: $^{13}C\{^{1}H\}$ NMR spectrum (MeCN-d_3, 300 K, 100 MHz) of the reaction solution containing (pyr)Ph_2P, (pyr)Ph_2PF_2 and (pyr)Ph_2PS.

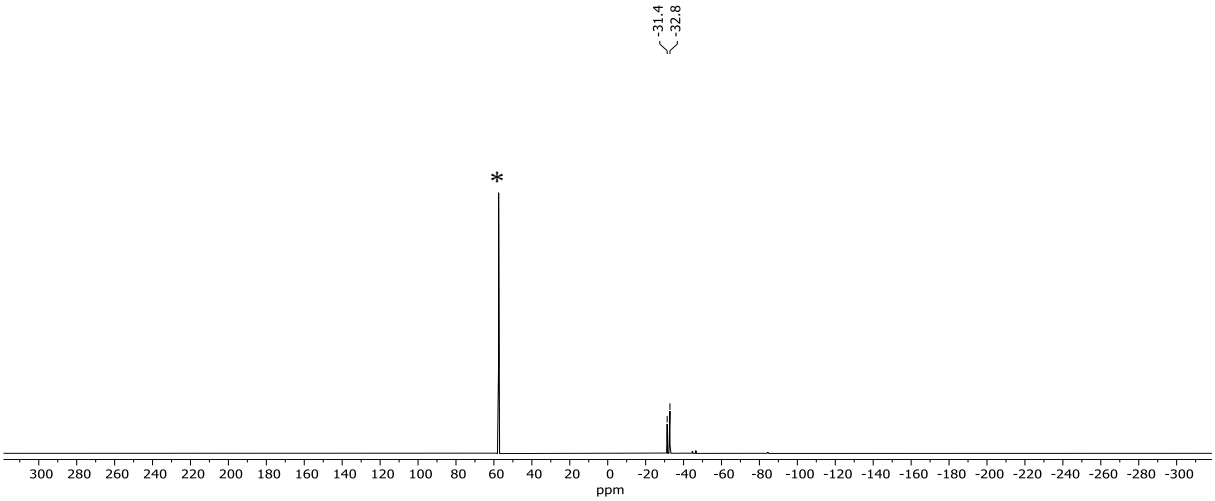


Figure S15: ^{19}F NMR spectrum (MeCN-d_3, 300 K, 376 MHz) of the reaction solution containing (pyr)Ph_2P, (pyr)Ph_2PF_2 and (pyr)Ph_2PS. * SF_6

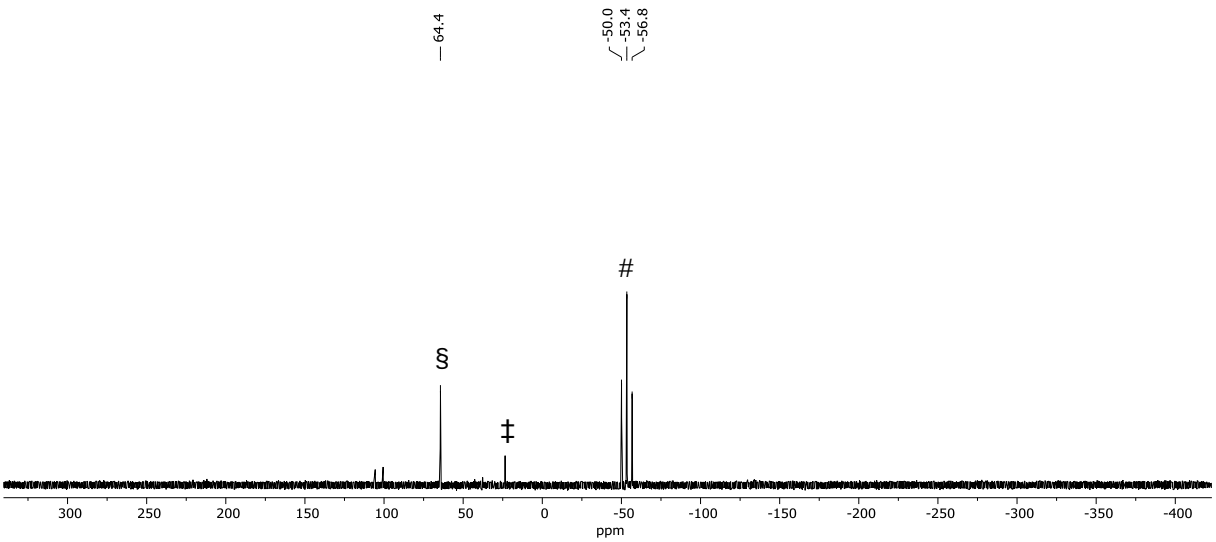
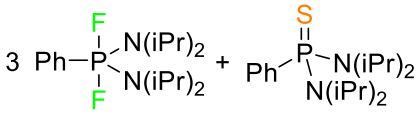


Figure S16: ^{31}P NMR spectrum (MeCN-d_3, 300 K, 160 MHz) of the reaction solution containing (pyr)Ph_2P (‡), (pyr)Ph_2PF_2 (#) and (pyr)Ph_2PS (§).

(Diisopropylamino)phenylphosphine $(iPr_2N)_2PhP$



According to the general procedure, a solution of (diisopropylamino)phenylphosphine (46 mg, 0.15 mmol) in THF (0.7 mL) was irradiated, resulting in 60% conversion to a 3:1 mixture of $(iPr_2N)_2PhPF_2$ and $(iPr_2N)_2PhPS$.

^{19}F NMR (THF, 376 MHz) δ (ppm) = -36.7 (d, $^1J_{PF}$ = 732.5 Hz, R_3PF_2).

^{31}P NMR (THF, 160 MHz) δ (ppm) = 58.4 (m, R_3PS), -48.8 (t, $^1J_{PF}$ = 732.5 Hz, R_3PF_2).

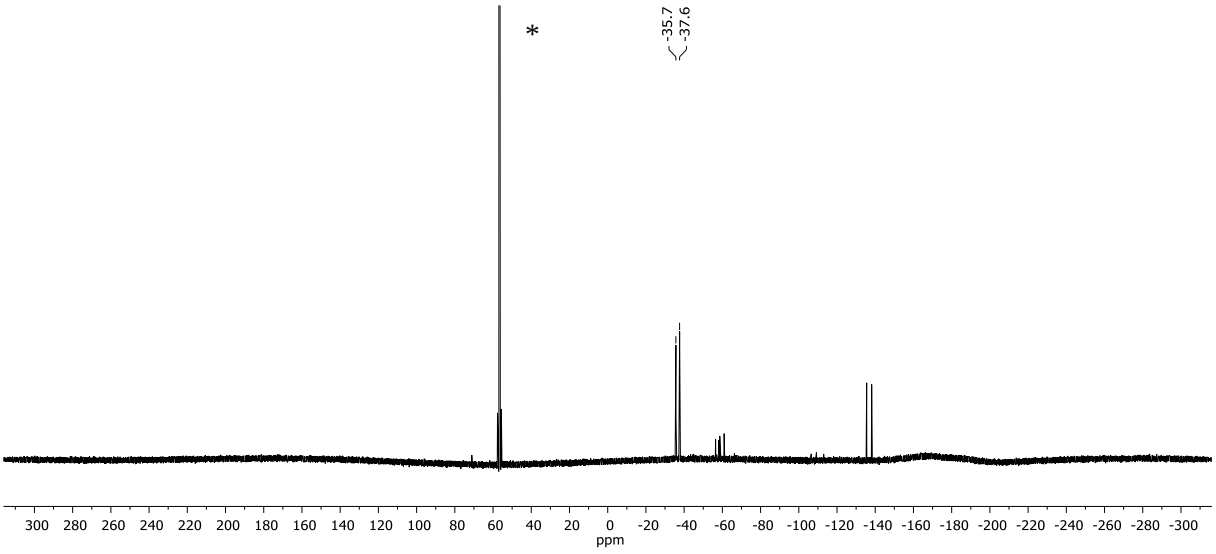


Figure S17: ^{19}F NMR spectrum (THF, 300 K, 376 MHz) of the reaction solution containing $(iPr_2N)_2PhP$, $(iPr_2N)_2PhPF_2$ and $(iPr_2N)_2PhPS$. * SF_6

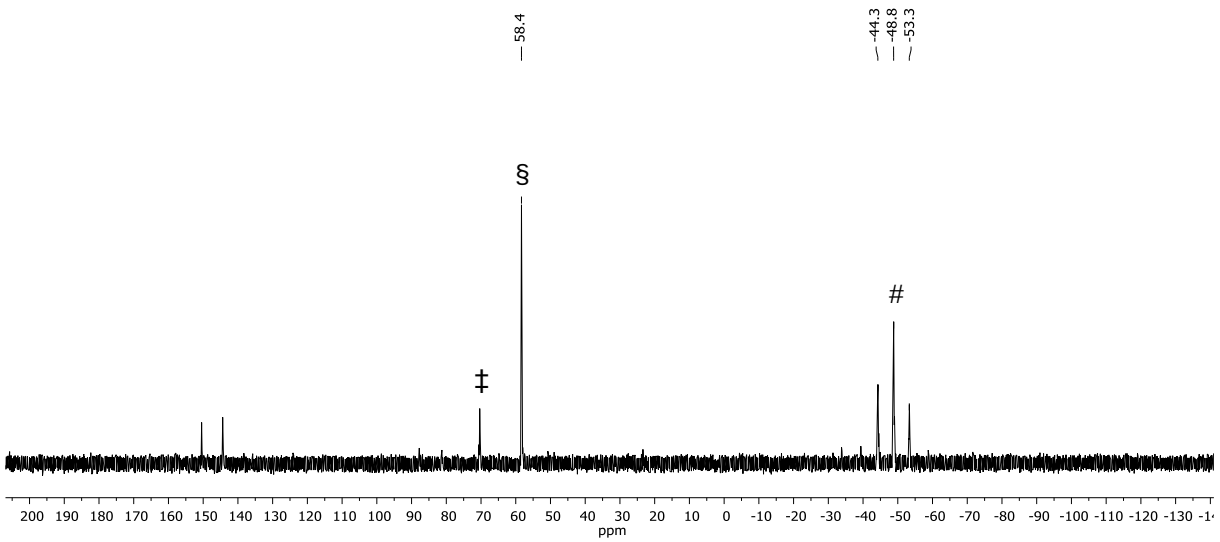


Figure S18: ^{31}P NMR spectrum (THF, 300 K, 160 MHz) of the reaction solution containing $(iPr_2N)_2PhP$ (‡), $(iPr_2N)_2PhPF_2$ (#) and $(iPr_2N)_2PhPS$ (§).

Tris(dimethylamino)phosphine $(Me_2N)_3P$

According to the general procedure, a solution of tris(dimethylamino)phosphine (24 mg, 0.15 mmol) in THF (0.7 mL) was irradiated. The ^{31}P NMR spectrum of the reaction mixture was identical to that of the starting material indicating no reaction of tris(dimethylamino)phosphine with SF_6.

Tri-*tert*-butylphosphine tBu_3P

According to the general procedure, a solution of tri-*tert*-butylphosphine (30 mg, 0.15 mmol) in THF (0.7 mL) was irradiated. The ^{31}P NMR spectrum of the reaction mixture was identical to that of the starting material indicating no reaction of the alkylphosphines with SF_6.

Tri-*n*-butylphosphine nBu_3P

According to the general procedure, a solution of tri-*n*-butylphosphine (30 mg, 0.15 mmol) in THF (0.7 mL) was irradiated. The ^{31}P NMR spectrum of the reaction mixture was identical to that of the starting material indicating no reaction of the alkylphosphines with SF_6.

Triphenyl phosphite $(PhO)_3P$

Following the general procedure, a solution of triphenyl phosphite (47 mg, 0.15 mmol) in THF (0.7 mL) was irradiated. The ^{31}P NMR spectrum of the reaction mixture was identical to that of the starting material indicating no reaction of triphenyl phosphite with SF_6.

Triethyl phosphite $(EtO)_3P$

Following the general procedure, a solution of triethyl phosphite (25 mg, 0.15 mmol) in THF (0.7 mL) was irradiated. The ^{31}P NMR spectrum of the reaction mixture was identical to that of the starting material indicating no reaction of triethyl phosphite with SF_6.

Tri(*o*-tolyl)phosphine (*o*-tol)$_3$P

According to the general procedure, a solution of (*o*-tol)$_3$P (46 mg, 0.15 mmol) in THF (0.7 mL) was irradiated. The ^{31}P NMR spectrum of the reaction mixture showed the resonances of two new phosphorus species. An identical ^{31}P NMR spectrum was obtained, when the irradiation was performed in the absence of SF_6 under an argon atmosphere, consistent with a photochemical decomposition of the phosphine.

When using a LED with a longer wavelength (405 nm) according the general procedure no reaction was observed.

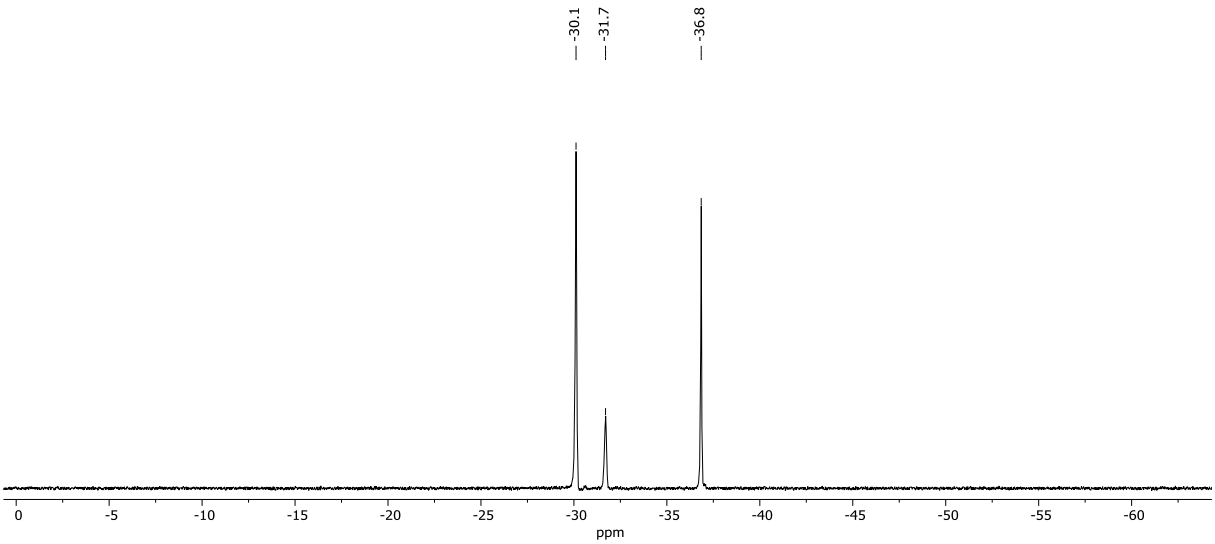


Figure S19: ^{31}P NMR spectrum (THF, 300 K, 160 MHz) of the reaction mixture with SF_6 after irradiation.

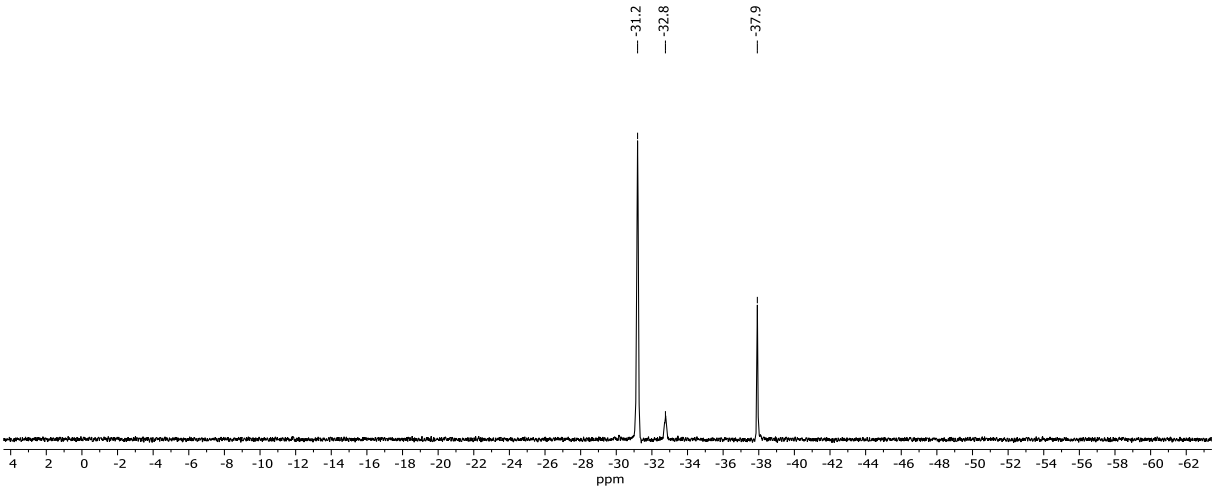


Figure S20: ^{31}P NMR spectrum (THF, 300 K, 160 MHz) of the reaction mixture without SF_6 after irradiation.

Tris(2,4,6-trimethylphenyl)phosphine (Mes)$_3$P

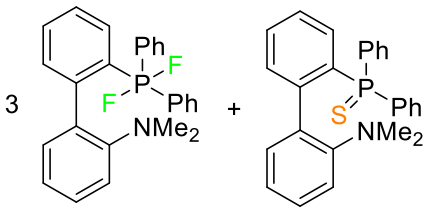
According to the general procedure, a solution of tris(2,4,6-trimethylphenyl)phosphine (58 mg, 0.09 mmol) in THF (0.7 mL) was irradiated. The ^{31}P NMR spectrum of the reaction mixture was identical to that obtained when irradiated in the absence of SF_6 under an argon atmosphere, consistent with a photochemical

decomposition of the phosphine. The same reactivity was observed when using a LED with a longer wavelength (405 nm).

Tris(pentafluorophenyl)phosphine ($C_6F_5)_3P$

According to the general procedure, a solution of tris(pentafluorophenyl)phosphine (80 mg, 0.15 mmol) in THF (0.7 mL) was irradiated. The ^{31}P NMR spectrum of the reaction mixture was identical to that of the starting materials indicating no reaction of tris(pentafluorophenyl)phosphine with SF_6.

2-Diphenylphosphino-2'-(N,N-dimethylamino)-biphenyl



According to the general procedure, a suspension of 2-Diphenylphosphino-2'-(N,N-dimethylamino)-biphenyl (57 mg, 0.15 mmol) in MeCN (0.7 mL) was irradiated. The volatiles were evaporated to afford a brown oil. The ^{31}P NMR spectrum indicated complete consumption of the phosphine and formation of a 3:1 mixture of the corresponding difluorophosphorane and phosphine sulfide in 97% yield.

^{1}H NMR (CD_2Cl_2, 400 MHz) δ (ppm) = 7.83 (m, Ar-H), 7.60 (m, Ar-H), 7.58 – 7.52 (m, Ar-H), 7.48 – 7.22 (m, Ar-H), 7.13 – 6.98 (m, Ar-H), 6.68 (m, Ar-H), 6.58 (m, Ar-H), 2.35 (s, NMe_2).

^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz) δ (ppm) = 151.4, 136.0 (m), 133.1, 132.2, 132.0, 131.7 (m), 130.2 (m), 129.5 – 129.1 (m), 129.0 – 128.1 (m), 126.5 (m), 120.6, 118.1, 43.5.

^{19}F NMR (CD_2Cl_2, 376 MHz) δ (ppm) = -39.0 (d, $^{1}J_{PF}$ = 677.0 Hz, R_3PF_2).

^{31}P NMR (CD_2Cl_2, 160 MHz) δ (ppm) = 43.3 (m, R_3PS), -51.9 (t, $^{1}J_{PF}$ = 677.0 Hz, R_3PF_2).

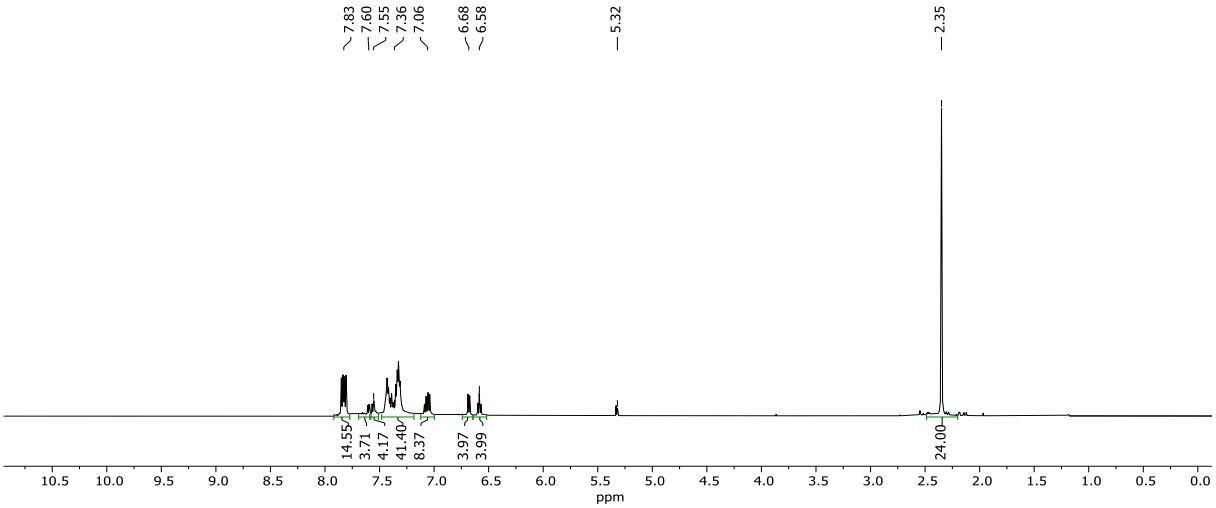


Figure S21: ^{1}H NMR spectrum (CD_2Cl_2, 300 K, 400 MHz) of the isolated oil containing RPh_2P, RPh_2PF_2 and RPh_2PS (R = dimethylamino-biphenyl).

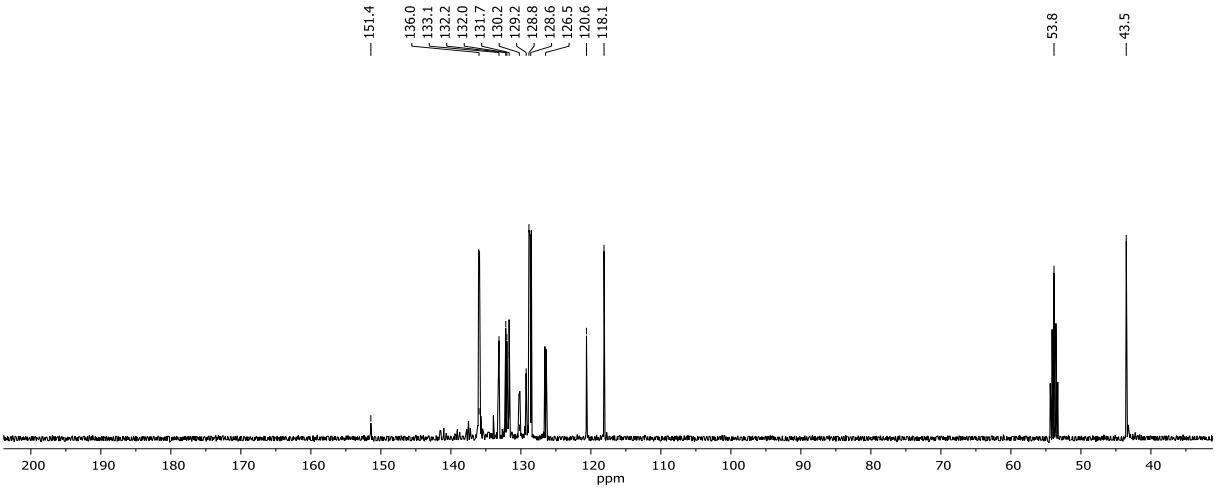


Figure S22: $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 300 K, 100 MHz) of the isolated oil containing RPh_2P, RPh_2PF_2 and RPh_2PS (R = dimethylamino-biphenyl).

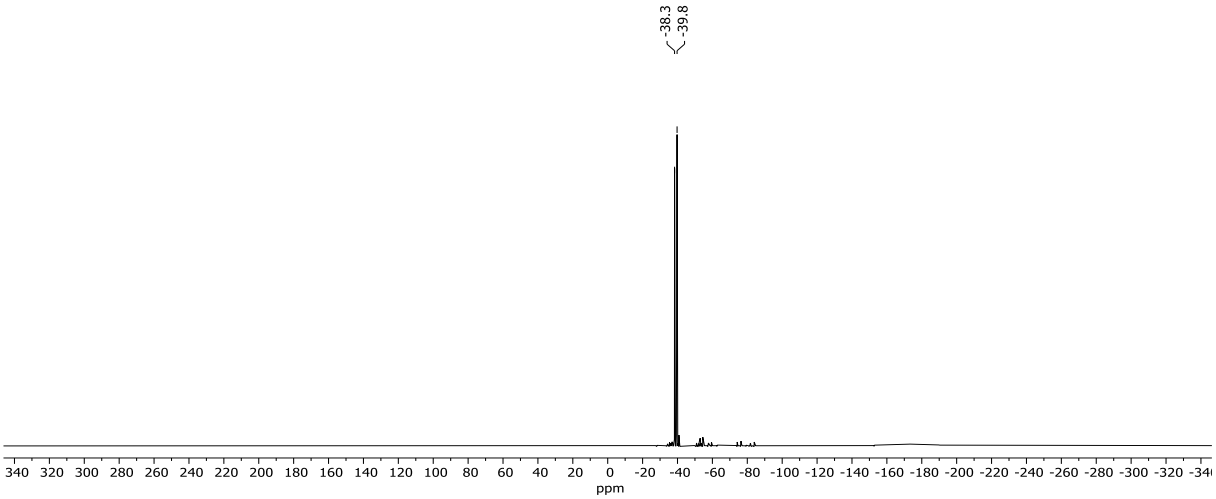


Figure S23: ^{19}F NMR spectrum (CD_2Cl_2, 300 K, 376 MHz) of the isolated oil containing RPh_2P, RPh_2PF_2 and RPh_2PS (R = dimethylamino-biphenyl).

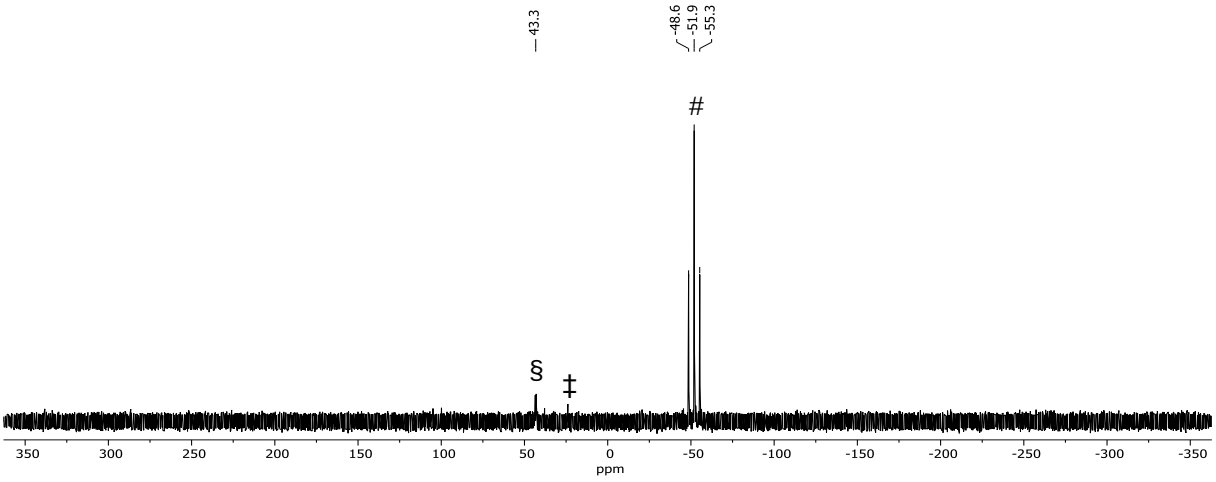
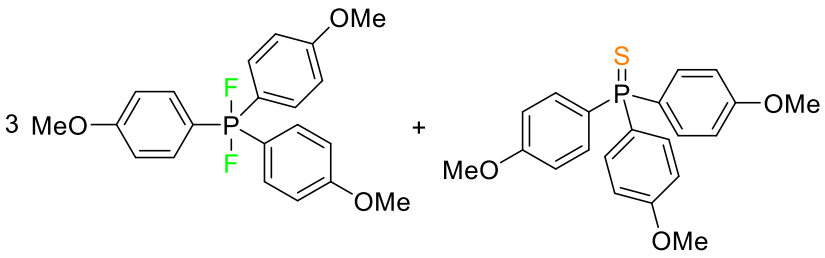


Figure S24: ^{31}P NMR spectrum (CD_2Cl_2, 300 K, 160 MHz) of the isolated oil containing RPh_2P (‡), RPh_2PF_2 (#) and RPh_2PS (§) (R = dimethylamino-biphenyl).

Tris(2-methoxyphenyl)phosphine (2-MeO-C_6H_4)$_3$P

Following the general procedure, a solution of tris(2-methoxyphenyl)phosphine (53 mg, 0.15 mmol) in THF (0.7 mL) was irradiated. The ^{31}P NMR spectrum of the reaction mixture was identical to that of the starting materials indicating no reaction of tris(2-methoxyphenyl)phosphine with SF_6.

Tris(4-methoxyphenyl)phosphine (4-MeO-C_6H_4)$_3$P



According to the general procedure, a suspension of tris(4methoxy-phenyl)phosphine (53 mg, 0.15 mmol) in MeCN (0.7 mL) was irradiated. The volatiles were evaporated to afford a brown oil. The ^{31}P NMR spectrum indicated complete consumption of the phosphine and formation of a 3:1 mixture of the corresponding difluorophosphorane and phosphine sulfide in 98% yield.

^{1}H NMR (MeCN-d_3, 400 MHz) δ (ppm) = 8.15 – 7.85 (m, Ar-H), 7.61 (m, Ar-H), 6.98 (m, Ar-H), 3.79 (s, OMe).

^{13}C{^{1}H} NMR (MeCN-d_3, 100 MHz) δ (ppm) = 164.0 – 161.3 (m), 136.9 (m), 136.0 – 133.5 (m), 130.0 (m), 128.1 (m), 126.2, 125.3, 115.7 – 113.8 (m), 56.2 (m).

^{19}F NMR (MeCN-d_3, 376 MHz) δ (ppm) = -42.6 (d, $^{1}J_{PF}$ = 652.2 Hz, R_3PF_2).

^{31}P NMR (MeCN-d_3, 160 MHz) δ (ppm) = 40.2 (s, R_3PS), -59.5 (t, $^{1}J_{PF}$ = 652.2 Hz, R_3PF_2).

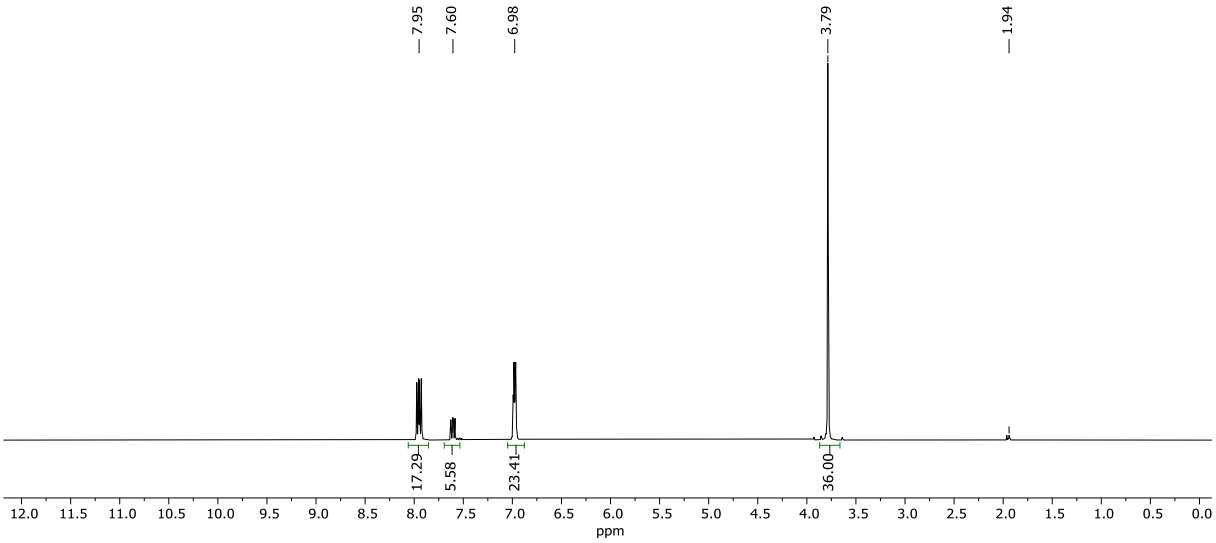


Figure S25: ^{1}H NMR spectrum (MeCN-d_3, 300 K, 400 MHz) of the isolated oil containing (4-MeO-C_6H_4)$_3$P, (4-MeO-C_6H_4)$_3$$PF_2$ and (4-MeO-C_6H_4)$_3$PS.

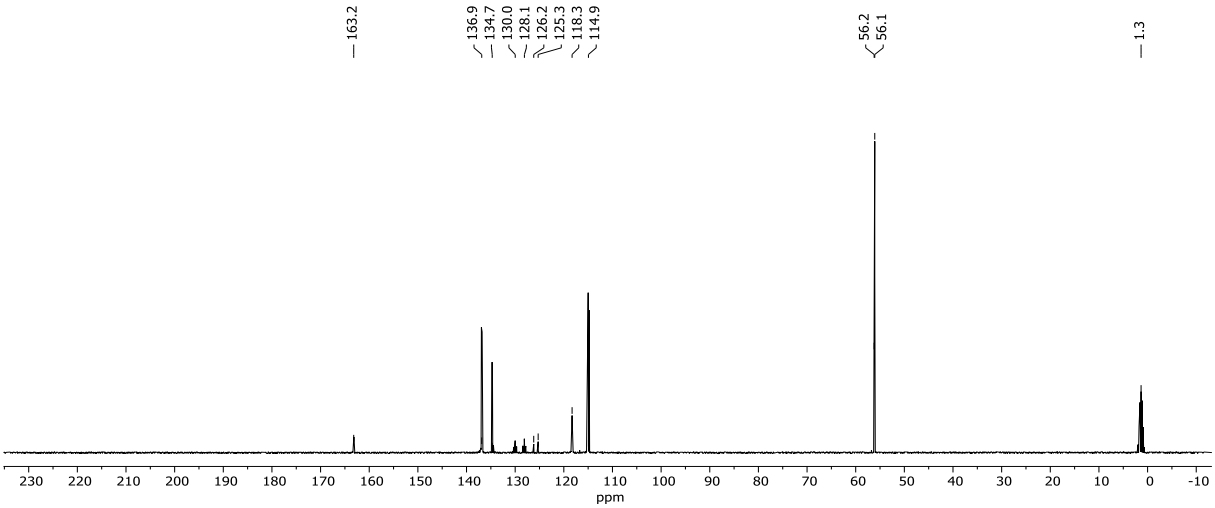


Figure S26: $^{13}C\{^{1}H\}$ NMR spectrum (MeCN-d_3, 300 K, 100 MHz) of the isolated oil containing (4-MeO-$C_6H_4)_3P$, (4-MeO-$C_6H_4)_3PF_2$ and (4-MeO-$C_6H_4)_3PS$.

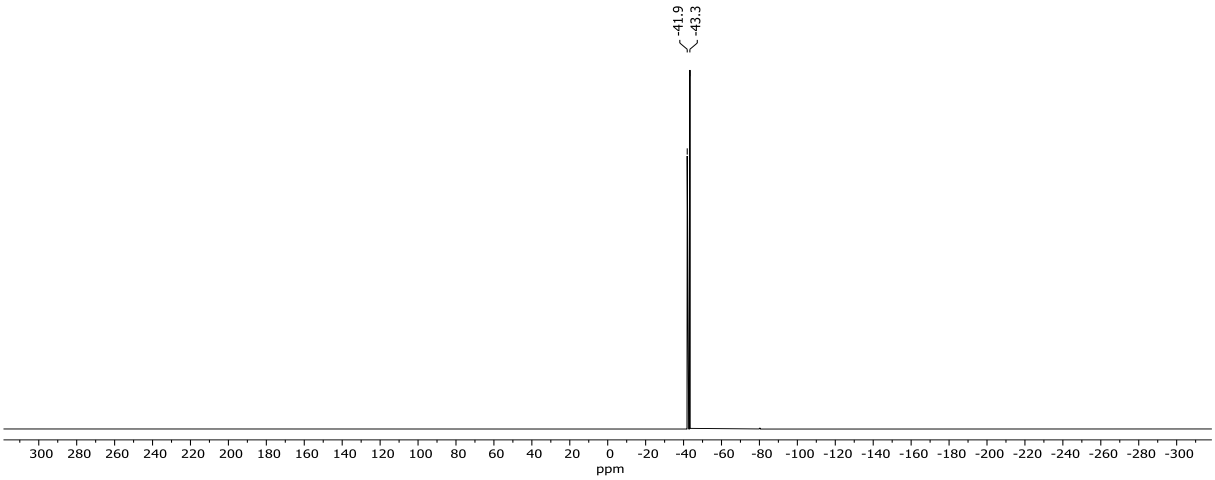


Figure S27: ^{19}F NMR spectrum (MeCN-d_3, 300 K, 376 MHz) of the isolated oil containing (4-MeO-$C_6H_4)_3P$, (4-MeO-$C_6H_4)_3PF_2$ and (4-MeO-$C_6H_4)_3PS$.

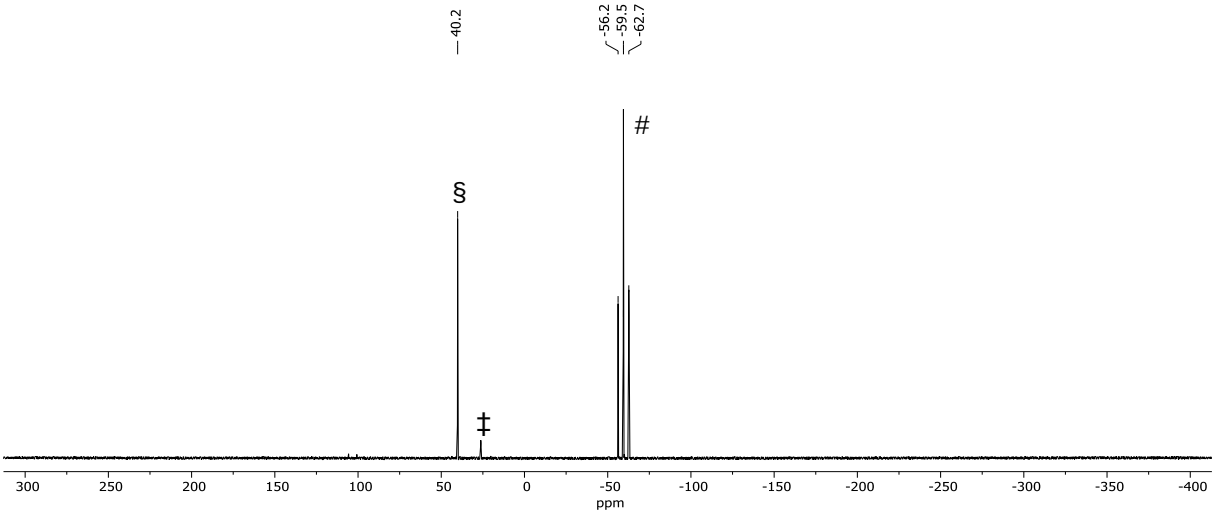
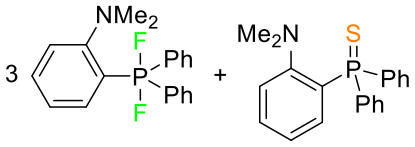


Figure S28: ^{31}P NMR spectrum (MeCN-d_3, 300 K, 160 MHz) of the isolated oil containing (4-MeO-$C_6H_4)_3P$ (‡), (4-MeO-$C_6H_4)_3PF_2$ (#) and (4-MeO-$C_6H_4)_3PS$ (§).

2-(Diphenylphosphino)-N,N-dimethylaniline ($Me_2NC_6H_4$)Ph_2P



According to the general procedure, a solution of 2-(Diphenylphosphino)-N,N-dimethylaniline (46 mg, 0.15 mmol) in benzene-d_6 (0.7 mL) was irradiated. The ^{31}P NMR spectrum of the reaction mixture indicated 96% conversion to a 3:1 mixture of ($Me_2NC_6H_4$)Ph_2PF_2 and ($Me_2NC_6H_4$)Ph_2PS.

^{1}H NMR (MeCN-d_3, 500 MHz) δ (ppm) = 8.38 (m, Ar-H), 8.09 – 7.89 (m, Ar-H), 7.47 (m, Ar-H), 7.42 – 7.30 (m, Ar-H), 7.28 – 6.60 (m, Ar-H), 2.29 (s, Me), 2.26 (s, Me).

^{19}F NMR (MeCN-d_3, 376 MHz) δ (ppm) = -36.0 (d, $^1J_{PF}$ = 666.5 Hz, R_3PF_2).

^{31}P NMR (MeCN-d_3, 160 MHz) δ (ppm) = 39.2 (m, R_3PS), -49.7 (t, $^1J_{PF}$ = 666.5 Hz, R_3PF_2).

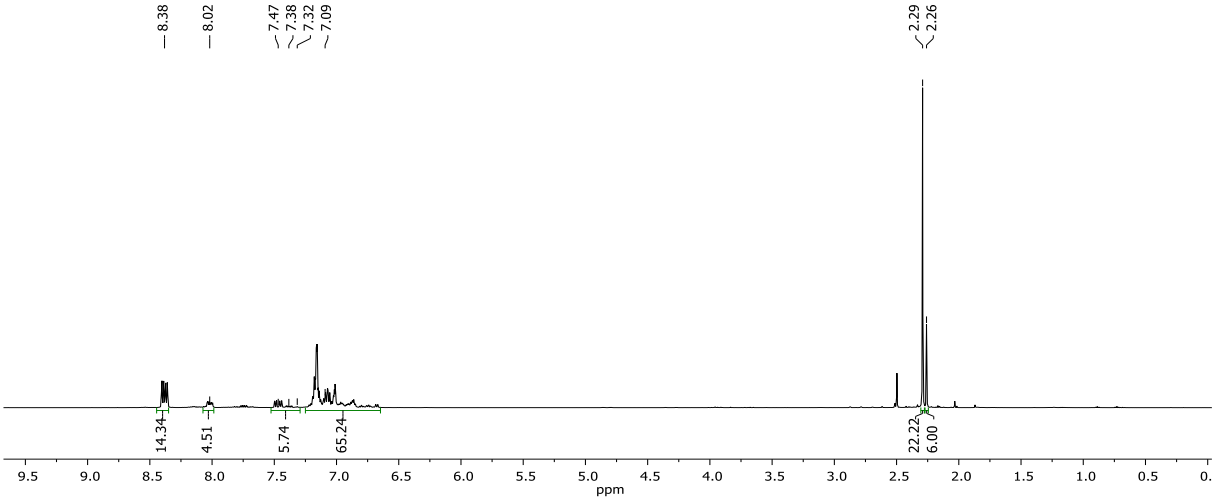


Figure S29: ^{1}H NMR spectrum (benzene-d_6, 300 K, 400 MHz) of the reaction mixture containing ($Me_2NC_6H_4$)Ph_2PF_2 and ($Me_2NC_6H_4$)Ph_2PS.

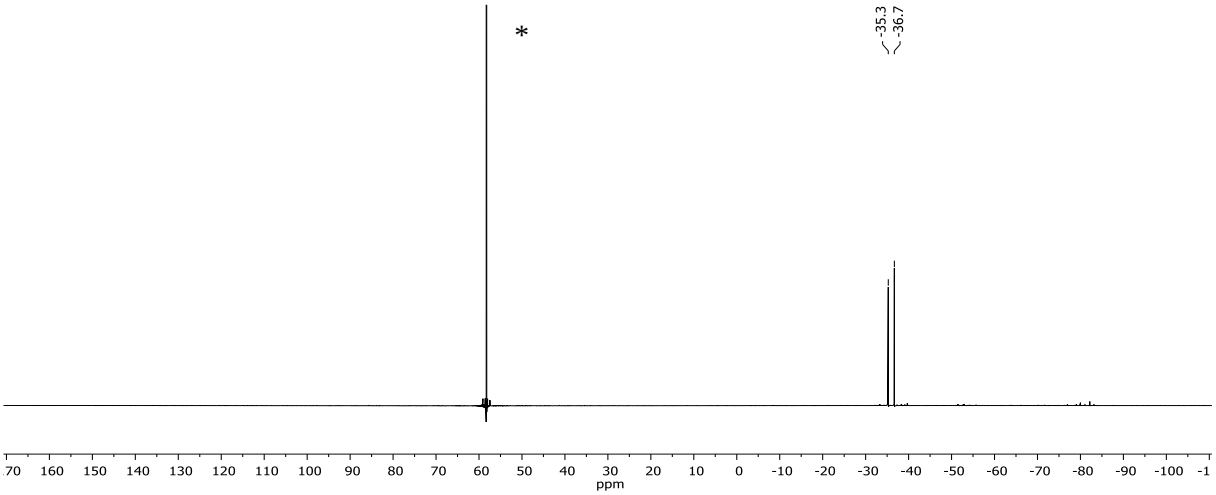


Figure S30: ^{19}F NMR spectrum (benzene-d_6, 300 K, 376 MHz) of the reaction mixture containing ($Me_2NC_6H_4$)Ph_2PF_2 and ($Me_2NC_6H_4$)Ph_2PS. * SF_6

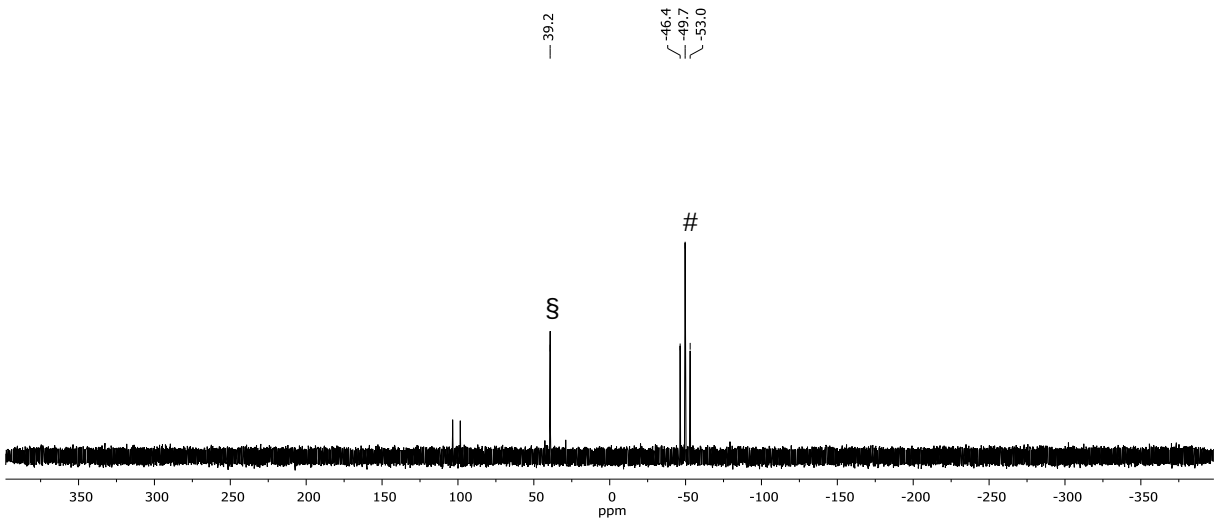


Figure S31: ^{31}P NMR spectrum (benzene-d_6, 300 K, 160 MHz) of the reaction mixture containing $(Me_2NC_6H_4)Ph_2PF_2$ (#) and $(Me_2NC_6H_4)Ph_2PS$ (§).

Control Experiments Without Irradiation

Ph_3P (30 mg, 0.115 mmol) was heated at 300 °C for 4 h under SF_6 atmosphere (2 bar). After cooling to room temperature, the resulting solid was analysed by ^{19}F and ^{31}P NMR spectroscopy. The spectra indicate no reaction of Ph_3P with SF_6.

$(OEt)_3P$ (50 mg, 0.30 mmol) was refluxed under an SF_6 atmosphere (2 bar) for 24 h. After cooling to room temperature, the reaction mixture was analyses by ^{19}F and ^{31}P NMR spectroscopy. The spectra indicate no reaction of Ph_3P with SF_6.

A thermal reaction of $(n\text{Bu})_3P$ with SF_6 was observed at high temperature in refluxing $(n\text{Bu})_3P$ (b.p. 240 °C). Multiple decomposition products were observed in the ^{19}F and ^{31}P NMR spectra of the product mixture. At lower temperatures (120 °C) no reaction of $(n\text{Bu})_3P$ with SF_6 was observed.

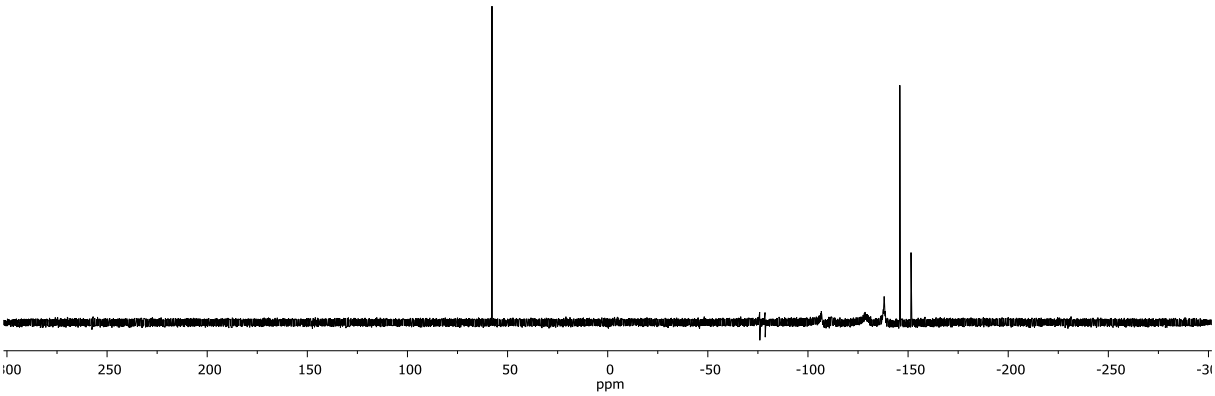


Figure S32: ^{19}F NMR spectrum (THF-d_8, 300 K, 376 MHz) of the product mixture after refluxing $(n\text{Bu})_3P$ under SF_6 atmosphere.

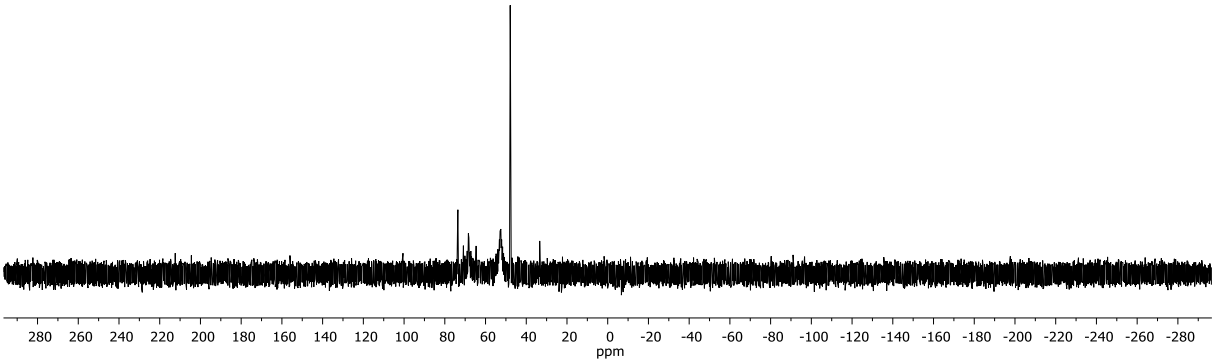


Figure S33: ^{31}P NMR spectrum (THF-d_8, 300 K, 160 MHz) of the product mixture after refluxing $(n\text{Bu})_3P$ under SF_6 atmosphere.

Wavelength Screening

a) Irradiation of Ph_3P/SF_6 with λ = 310 nm

In an NMR tube, Ph_3P (30 mg) was dissolved in THF (0.7 mL). The solution was pressurized with SF_6 (2 bar) and irradiated with UV light (λ = 310 nm) for 15 minutes.

^{19}F NMR (THF, 376 MHz) δ (ppm) = -40.8 (d, $^1J_{PF}$ = 669.3 Hz, PF_2Ph_3), -46.1 (d, $^1J_{PF}$ = 872.8 Hz, PF_3Ph_2), -82.5 (d, $^1J_{PF}$ = 1017.3 Hz, $PFPh_3^+$).

^{31}P NMR (THF, 160 MHz) δ (ppm) = 101.4 (d, $^1J_{PF}$ = 1017.3 Hz, $PFPh_3^+$), 42.3 (s, $PSPh_3$), 22.9 (s, Ph_4P^+), -57.0 (t, $^1J_{PF}$ = 669.3 Hz, PF_2Ph_3), -132.6 (q, $^1J_{PF}$ = 872.8 Hz, PF_3Ph_2).

HRMS (ESI): m/z calculated for Ph_4P^+ $[C_{24}H_{20}P]^+$ $(M)^+$ 339.12971, found: 339.12970.

HRMS (ESI): m/z calculated for $PFPh_3^+$ $[C_{18}H_{15}FP]^+$ $(M)^+$ 281.08899, found: 281.08883.

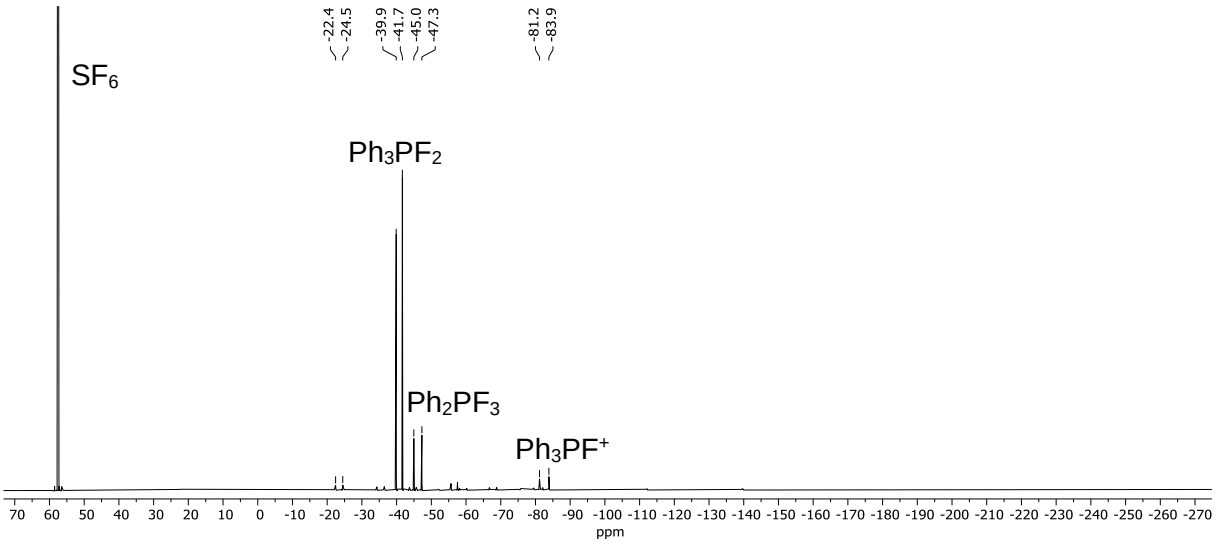


Figure S34: ^{19}F NMR spectrum (THF, 300 K, 376 MHz) of the reaction mixture after irradiating with λ = 310 nm.

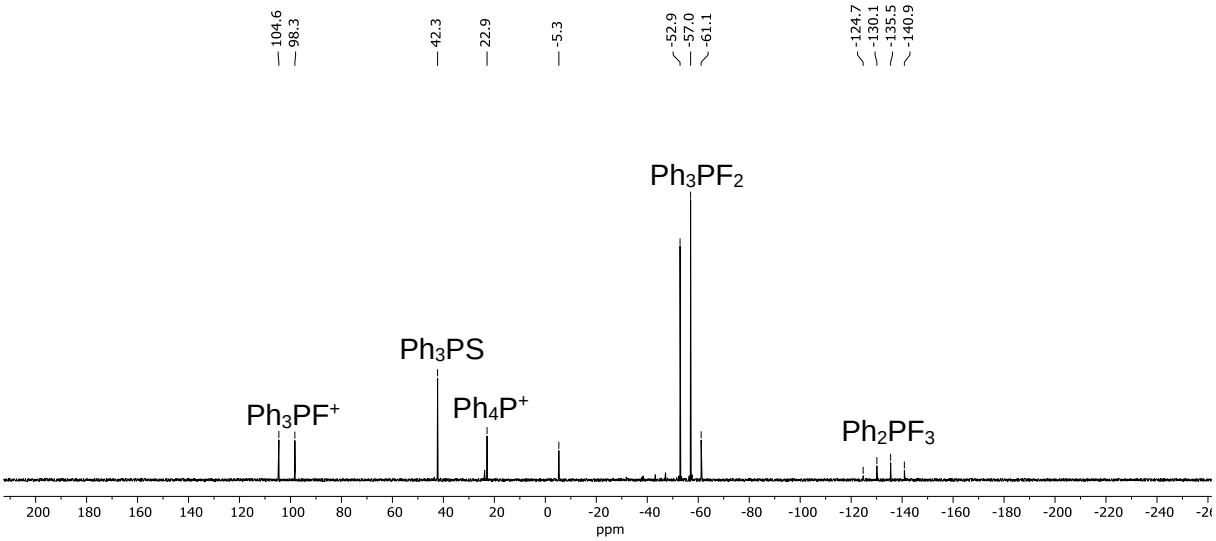


Figure S35: ^{31}P NMR spectrum (THF, 300 K, 160 MHz) of the reaction mixture after irradiating with λ = 310 nm.

b) Irradiation of Ph_3P/SF_6 with λ = 365 nm

In an NMR tube, Ph_3P (30 mg) was dissolved in THF (0.7 mL). The solution was pressurized with SF_6 (2 bar) and irradiated with UV light (λ = 365 nm). The reaction progress was monitored by ^{31}P NMR spectroscopy. After 6 h, the reaction reached full conversion to a 3:1 mixture of triphenyldifluorophosphorane and triphenylphosphine sulfide.

c) Irradiation of Ph_3P/SF_6 with λ = 405 nm

In an NMR tube, Ph_3P (30 mg) was dissolved in THF (0.7 mL). The solution was pressurized with SF_6 (2 bar) and irradiated with UV light (λ = 405 nm). The reaction progress was monitored by ^{31}P NMR spectroscopy. After 12 h, the reaction reached full conversion to a 3:1 mixture of triphenyldifluorophosphorane and triphenylphosphine sulfide.

d) Irradiation of Ph_3P/SF_6 with λ = 450 nm

In an NMR tube, Ph_3P (30 mg) was dissolved in THF (0.7 mL). The solution was pressurized with SF_6 (2 bar) and irradiated with blue light (λ = 450 nm) for 24 h. The ^{31}P NMR spectrum of the reaction mixture was identical to that of the starting material indicating no reaction between Ph_3P and SF_6.

Synthesis of *TPP-Fluor*

A flat-bottomed glass vessel with a three-way valve was charged with solid Ph_3P (1.5 g, 5.7 mmol). The vessel was connected to a U-tube filled with silicone oil, which was connected to a gas-tight syringe (Fig. S36). The atmosphere in the system was changed to SF_6 using the three-way valve. The reaction chamber was heated to 80 °C and it was subsequently irradiated with light at 365 nm. After irradiation for 7.7 h, the consumption of SF_6 during the experiment (≈33 mL) matches the theoretical calculated volume for full conversion (33.06 mL). In a second experiment, the yield was determined gravimetrically using 10.00 g of Ph_3P. The ^{31}P NMR spectrum of the dissolved solid indicates quantitative consumption of Ph_3P. The weight increase (1.296 g) corresponds to 93% yield. A time-lapse of the reaction can be found as supplementary material.

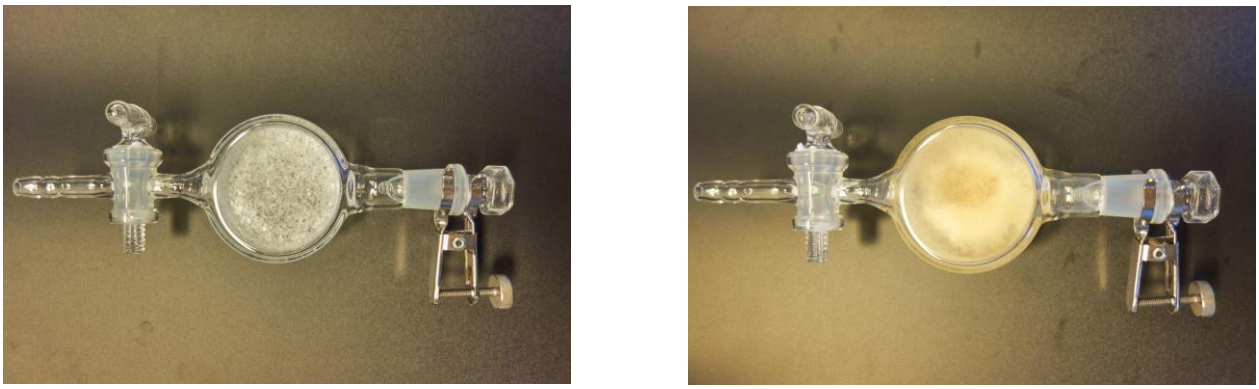


Figure S36: Gas vessel charged with Ph_3P before (left) and after irradiation (right).

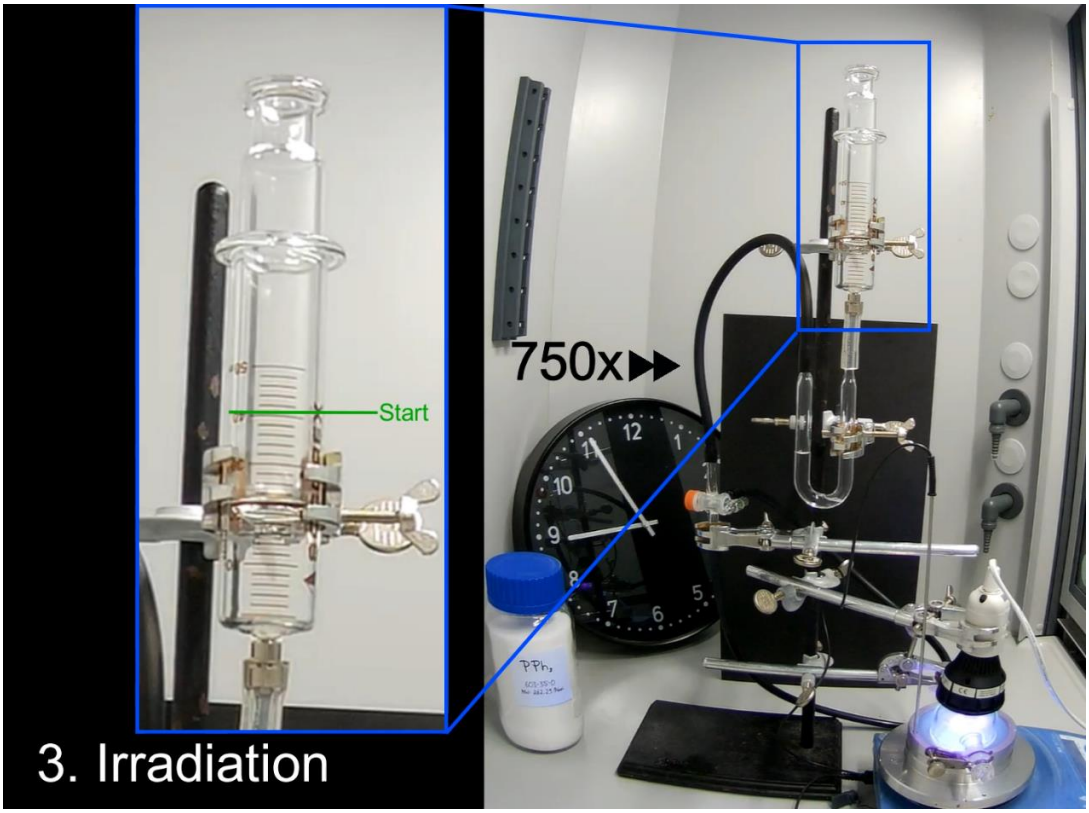


Figure S37: Setup for the solvent-free reaction of Ph_3P with SF_6. Paraffin oil was used to lubricate the plunger of the syringe to make it gas tight and smooth running.

Large-Scale Synthesis of *TPP-Fluor*

Large-scale synthesis of *TPP-Fluor* was performed in a flat-bottomed glass vessel containing 100 g Ph_3P. The vessel was irradiated from below with an LED array and heated exclusively by the heat of the LEDs. The pressure in the vessel was kept constant at 1 bar.

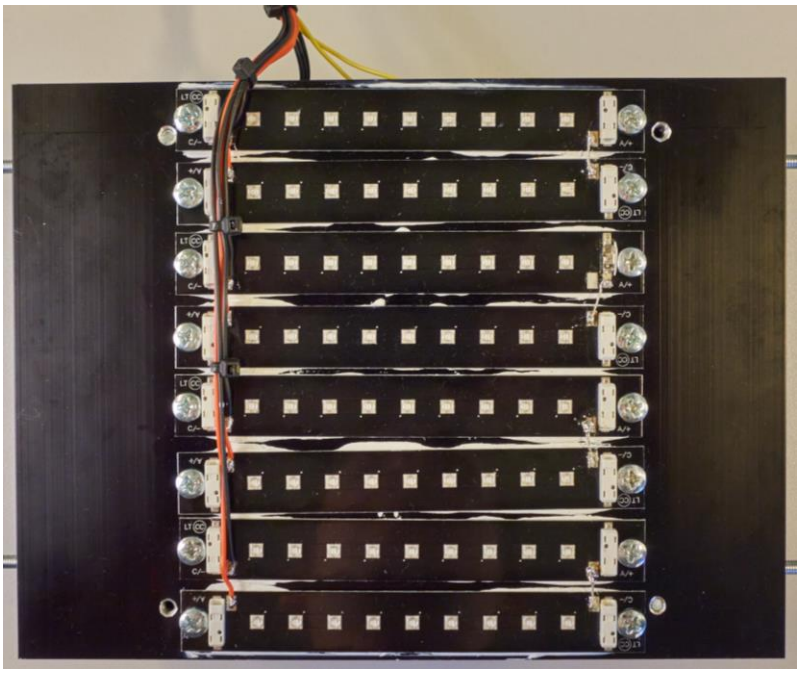


Figure S38: LED array for large-scale synthesis of *TPP-Fluor*.

Figure S39: Flat-bottomed glass vessel charged with 100 g Ph_3P.

Photochemical Reaction of SF_6 with Alkyl Phosphines

(nBu)$_3$P (30 mg, 0.15 mmol, 1 eq.) and a photosensitizer (**I**: acetophenone, **II**: benzophenone) were dissolved in THF-d_8 (0.7 mL). The solution was pressurized with SF_6 (2 bar) and it was irradiated with light at 365 nm for the indicated time. The reaction progress was monitored by ^{31}P NMR spectroscopy.

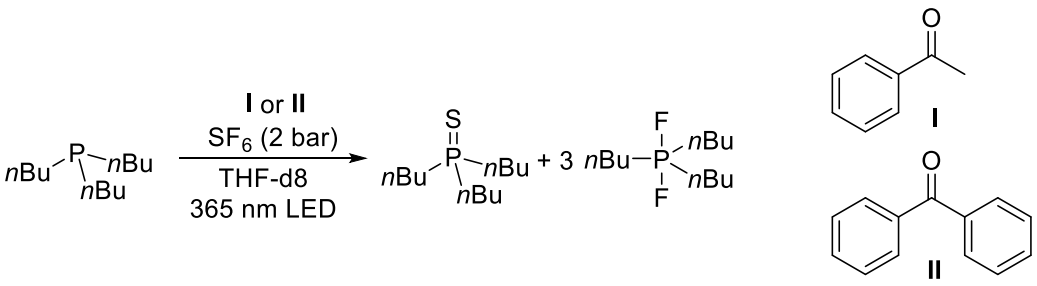


Table S1: Photochemical Reaction of (nBu)$_3$P with SF_6 using photosensitizers.

Photosensitizer	Irradiation Time	Conversion (%)*
none	24 h	0
0.2 eq. **I**	24 h	33
0.2 eq. **I**	72 h	91
1 eq. **I**	24 h	99
1 eq. **II**	24 h	80

*^{31}P NMR yield by quantitative NMR spectroscopy

^{19}F NMR (THF-d_8, 376 MHz) δ (ppm) = -35.2 (dt, $^1J_{PF}$ = 583.9 Hz, $^3J_{FH}$ = 11.2 Hz, (nBu)$_3$PF$_2$).

^{31}P NMR (THF-d_8, 162 MHz) δ (ppm) = 47.3 (s, (nBu)$_3$PS), -14.9 (t, $^1J_{PF}$ = 583.9 Hz, (nBu)$_3$PPF$_2$).

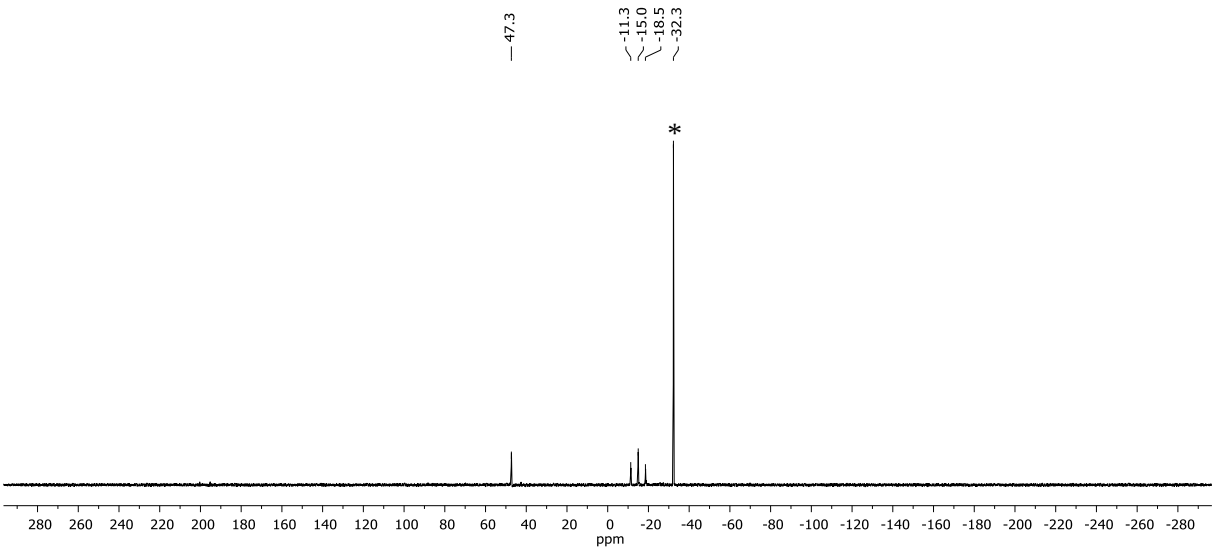


Figure S40: ^{31}P NMR spectrum (THF-d_8, 300 K, 160 MHz) using 0.2 eq. acetophenone and irradiating for 24 h. * (nBu)$_3$P

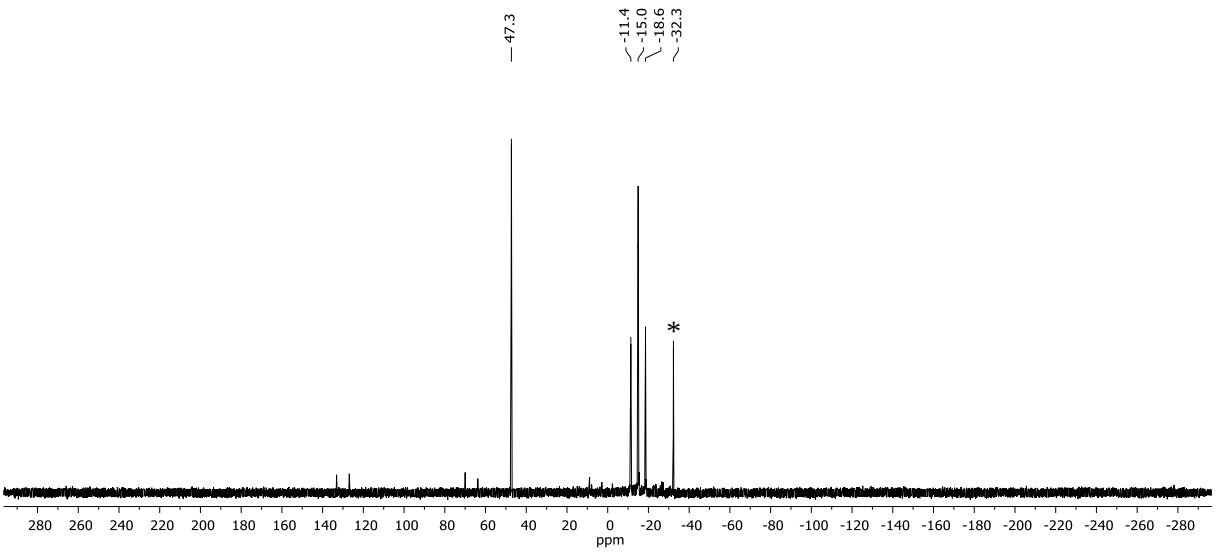


Figure S41: ^{31}P NMR spectrum (THF-d_8, 300 K, 160 MHz) using 0.2 eq. acetophenone and irradiating for 72 h. * (nBu)$_3$P

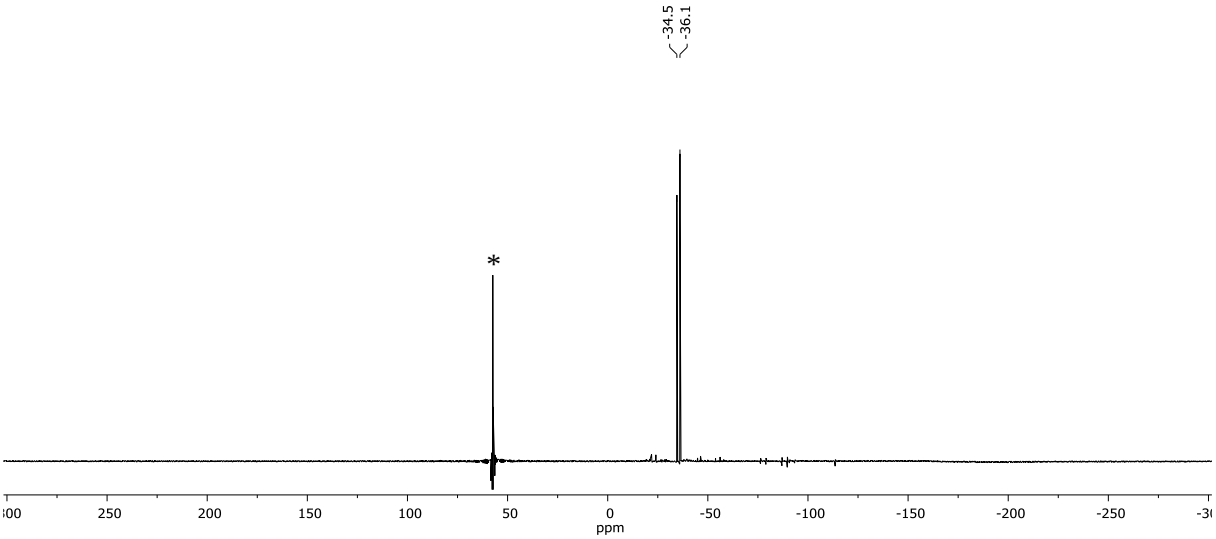


Figure S42: ^{19}F NMR spectrum (THF-d_8, 300 K, 376 MHz) using 1 eq. acetophenone and irradiating for 24 h. * SF_6

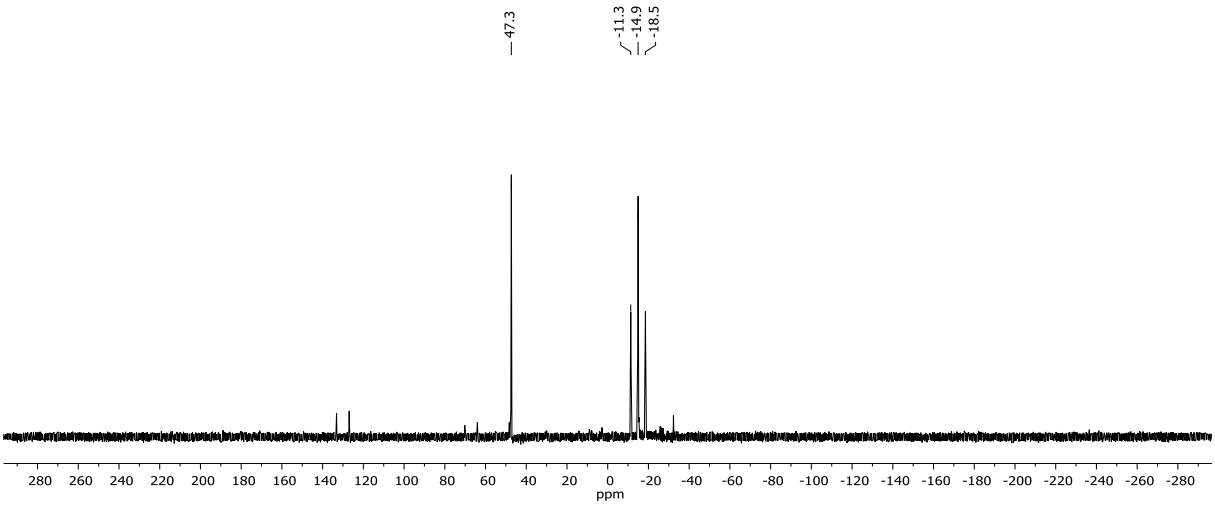


Figure S43: ^{31}P NMR spectrum (THF-d_8, 300 K, 160 MHz) using 1 eq. acetophenone and irradiating for 24 h.

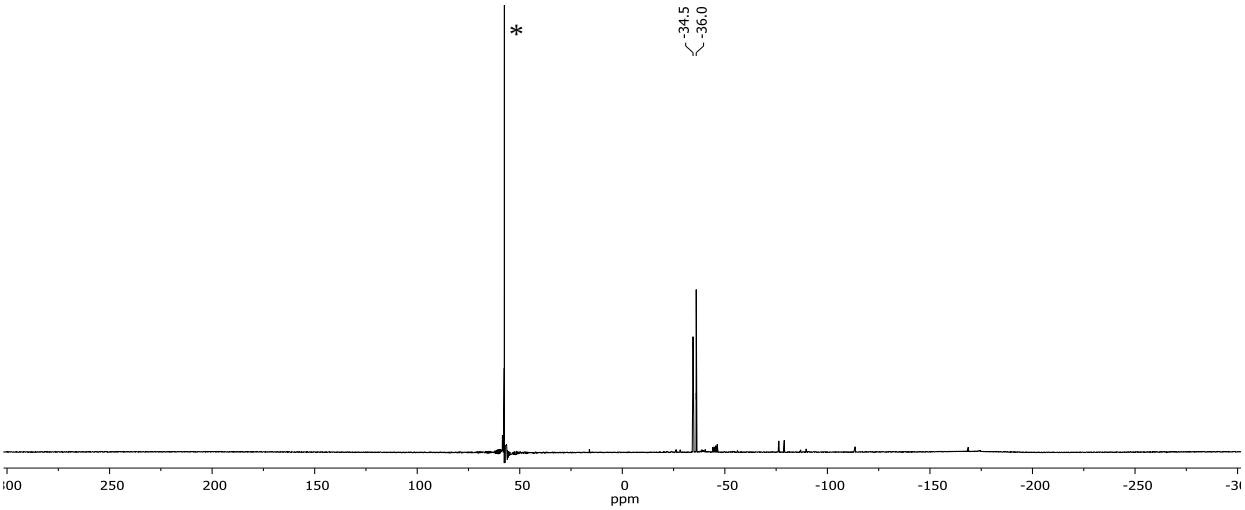


Figure S44: ^{19}F NMR spectrum (THF-d_8, 300 K, 376 MHz) using 1 eq. benzophenone and irradiating for 24 h. * SF_6

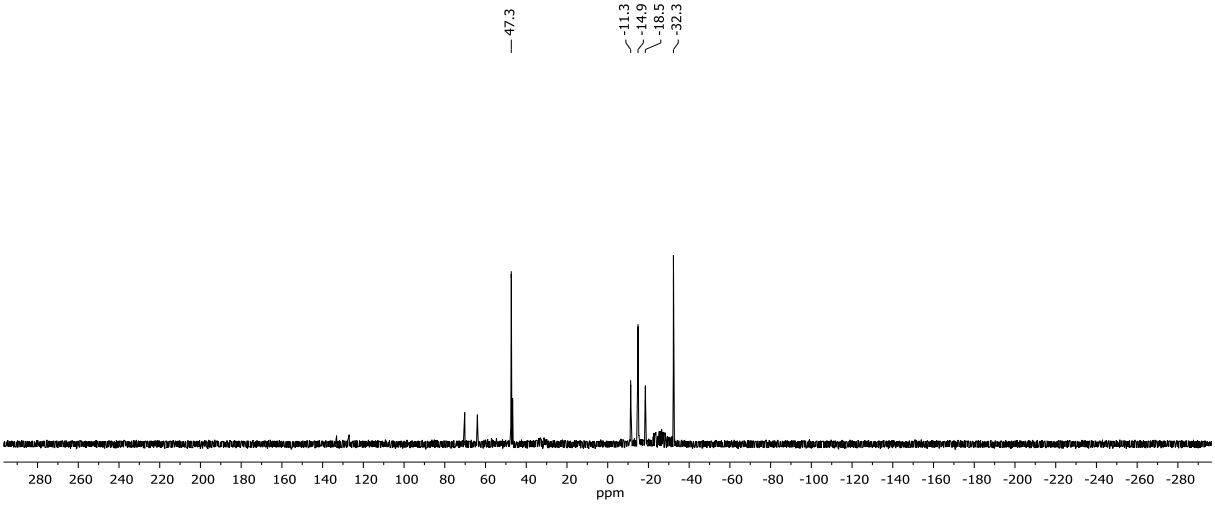


Figure S45: ^{31}P NMR spectrum (THF-d_8, 300 K, 160 MHz) using 1 eq. benzophenone and irradiating for 24 h.

TPP-Fluor as Fluorinating Agent

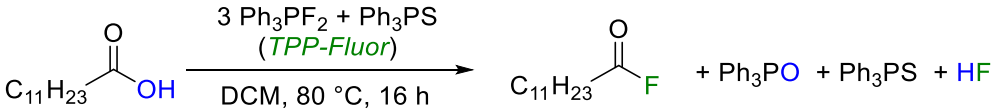
Deoxyfluorination of 1-hexanol: *TPP-Fluor* (100 mg, 0.08 mmol, 1 eq.) and 1-hexanol (10 µL, 0.08 mmol, 1 eq.) were dissolved in MeCN (0.5 mL) in a Teflon sealed NMR tube containing a Teflon inlay to avoid glass contact of the solution. The tube was heated at 170 °C for 8 h. α,α,α-trifluorotoluene (10 µL) was added afterwards as ^{19}F NMR standard. The quantitative ^{19}F NMR spectrum shows the resonance of 1-fluorohexane at δ = -217.5 ppm with a yield of 22%.

General procedure for the deoxyfluorination of carboxylic acids: *TPP-Fluor* (100 mg, 0.08 mmol, 1 eq.), the carboxylic acid (0.08 mmol, 1 eq.) and α,α,α-trifluorotoluene (0.066 mmol) as internal ^{19}F NMR standard were dissolved in DCM (0.7 mL) in a Teflon sealed NMR tube. The reaction mixture was heated at 80 °C for 16 h and was then analysed by quantitative ^{19}F NMR spectroscopy. In addition to the sharp resonance of the acyl fluoride, the ^{19}F NMR spectrum shows a broad signal at δ = -142.6 ppm which is in the typical range of HF/FHF.

Table S2: Deoxyfluorination of carboxylic acids using *TPP-Fluor*.

Acyl fluoride	^{19}F NMR Shift of Acyl Fluoride [ppm]	Yield (%)
17	43.7	88
18	17.5	6
19	24.4	85
20	54.8	88
21	16.8	20
22	13.3	62
23	10.4	85
24	-	-
25	17.4	4
26	17.8	1

Example: Deoxyfluorination of lauric acid using *TPP-Fluor*



The deoxyfluorination was carried out according to the general procedure. In the ^{19}F NMR spectrum of the reaction mixture (*vide infra*), the ratio of the internal standard to acyl fluoride equals 10.00 / 3.63. Considering that the standard contains 3 fluoride atoms the yield equals to 88%.

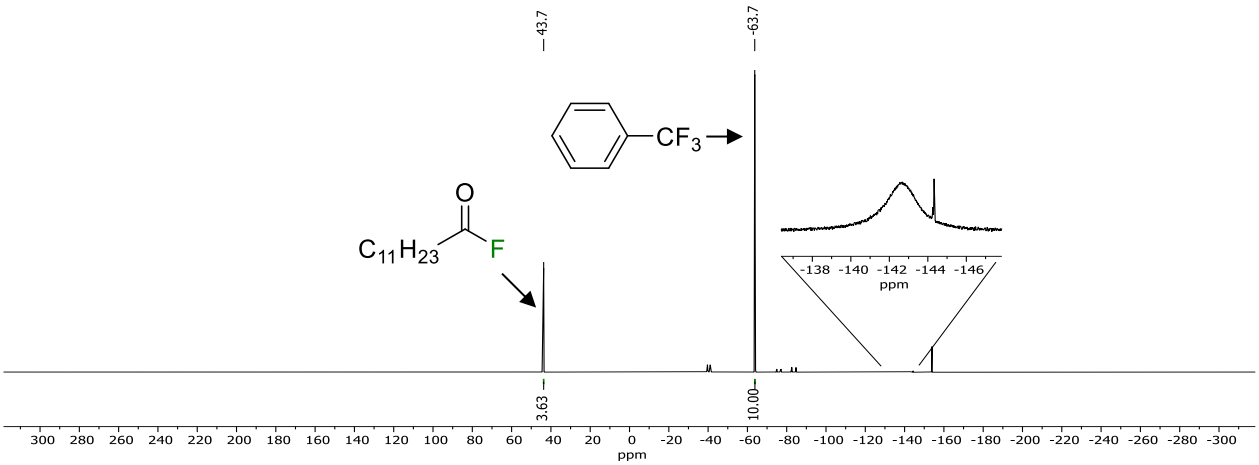
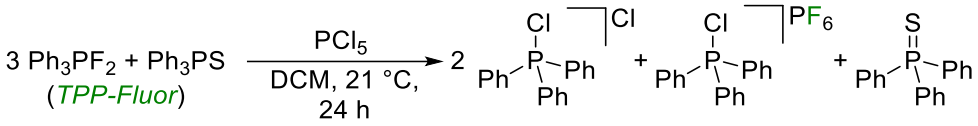


Figure S46: ^{19}F qNMR spectrum (DCM, D_1 = 35 sec, aq. Time = 0.44 sec, zg90) of the deoxyfluorination of lauric acid.

Synthesis of PF_6 salts using *TPP-Fluor*:



TPP-Fluor (87 mg) and PCl_5 (15 mg, 0.072 mmol) were dissolved in DCM (0.7 mL) and stirred for 24 h at ambient temperature to give two equivalents chlorophosphonium chloride and one equivalent chlorophosphonium hexafluorophosphate in 99% yield.

^{19}F NMR (CD_2Cl_2, 376 MHz) δ (ppm) = -73.1 (d, $^1J_{PF}$ = 711.0 Hz, PF_6).

^{31}P NMR (CD_2Cl_2, 160 MHz) δ (ppm) = 60.2 (s, Ph_3PCl_2), 43.0 (s, Ph_3PS), -144.5 (sept, $^1J_{PF}$ = 711.0 Hz, PF_6).

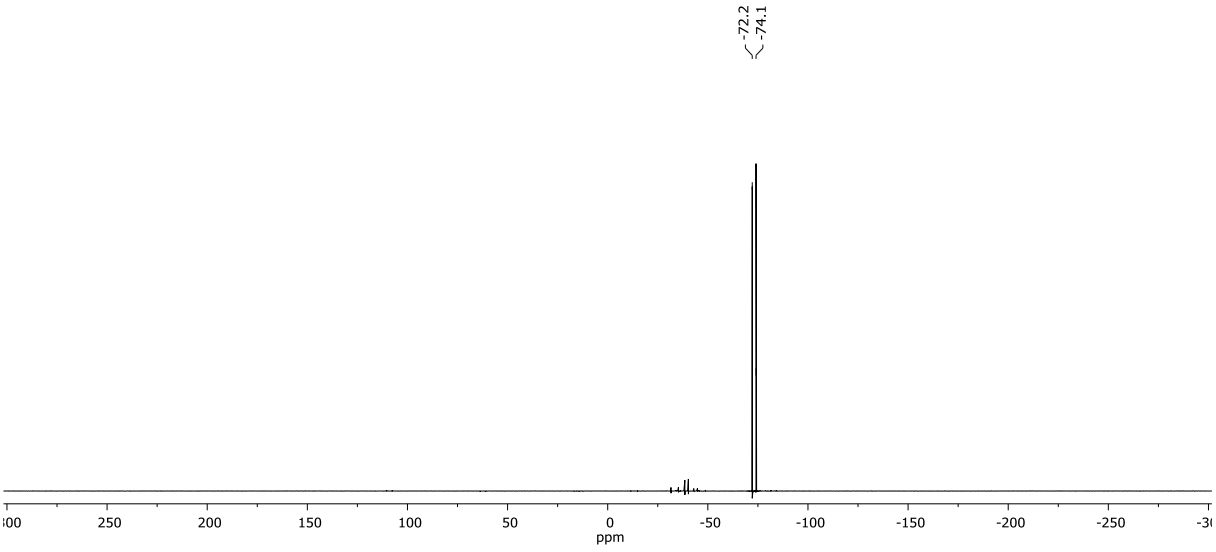


Figure S47: ^{19}F NMR spectrum (CD_2Cl_2, 300 K, 376 MHz) of the reaction mixture.

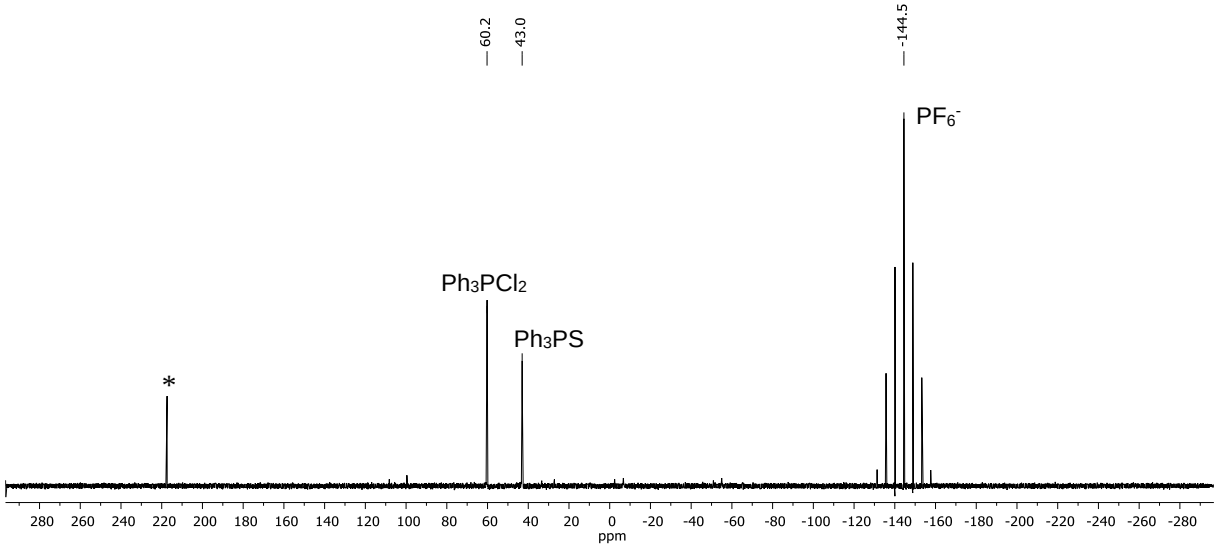
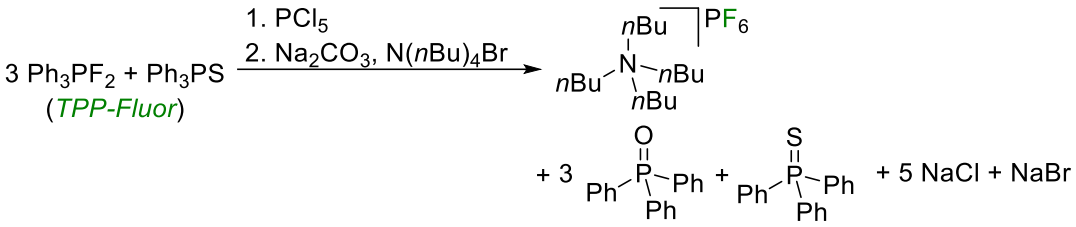


Figure S48: ^{31}P NMR spectrum (CD_2Cl_2, 300 K, 160 MHz) of the reaction mixture. * PCl_3 (<1%)



TPP-Fluor (500 mg) and PCl_5 (87 mg, 0.42 mmol) were dissolved in DCM (20 mL) and stirred for 16 h at ambient temperature. The reaction mixture was quenched with water (5 mL) and the aqueous layer was made basic using sat. Na_2CO_3. N(*n*Bu)$_4$Br (135 mg, 0.42 mmol) was added and the emulsion was vigorously stirred. The organic layer was separated, washed with water (3 x 5 mL) and dried over Na_2SO_4. After partial removal of the solvent under reduced pressure, the product was crystallized by slow diffusion of Et_2O into a saturated DCM solution of the crude product. Yield: 128 mg (0.33 mmol, 79%).

^{1}H NMR (MeCN-d_3, 400 MHz) δ (ppm) = 3.08 (m, 8H, NCH_2), 1.60 (m, 8H, NCH_2CH_2), 1.35 (m, 8H, CH_2CH_3), 0.97 (t, $^3J_{HH}$ = 7.3 Hz, 12H, CH_3).

^{13}C{^{1}H} NMR (MeCN-d_3, 100 MHz) δ (ppm) = 59.4 (NCH_2), 24.3 (NCH_2CH_2), 20.3 (CH_2CH_3), 13.7 (CH_3).

^{19}F NMR (MeCN-d_3, 376 MHz) δ (ppm) = -72.9 (d, $^1J_{PF}$ = 706.2 Hz, PF_6).

^{31}P NMR (MeCN-d_3, 160 MHz) δ (ppm) = -144.6 (sept, $^1J_{PF}$ = 706.2 Hz, PF_6).

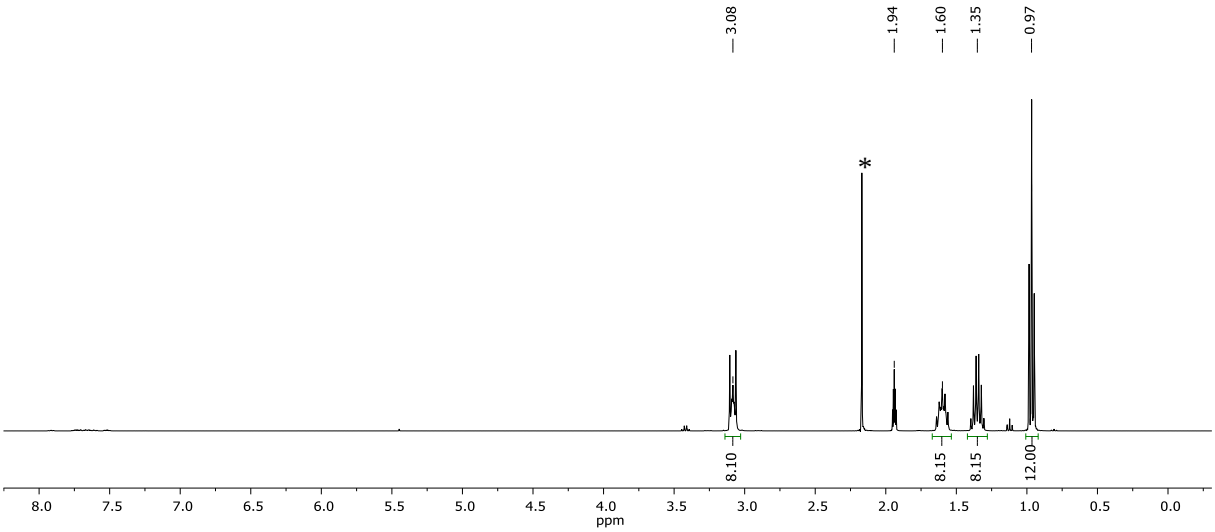


Figure S49: ^{1}H NMR spectrum (MeCN-d_3, 300 K, 400 MHz) of the isolated N(nBu)$_4$PF$_6$. * water

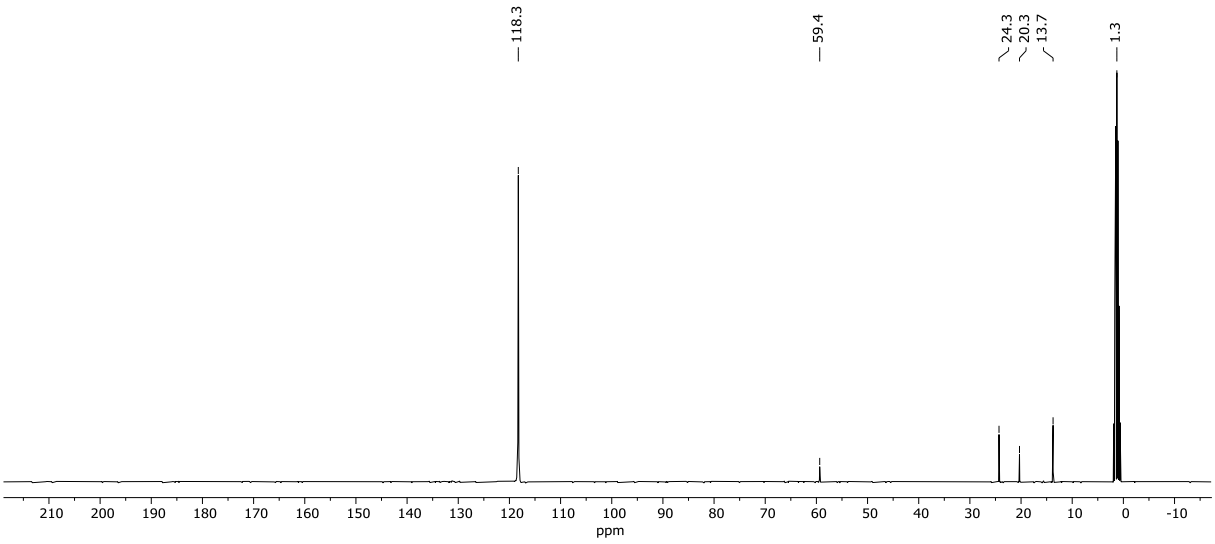


Figure S50: ^{13}C{^{1}H} NMR spectrum (MeCN-d_3, 300 K, 100 MHz) of the isolated N(nBu)$_4$PF$_6$.

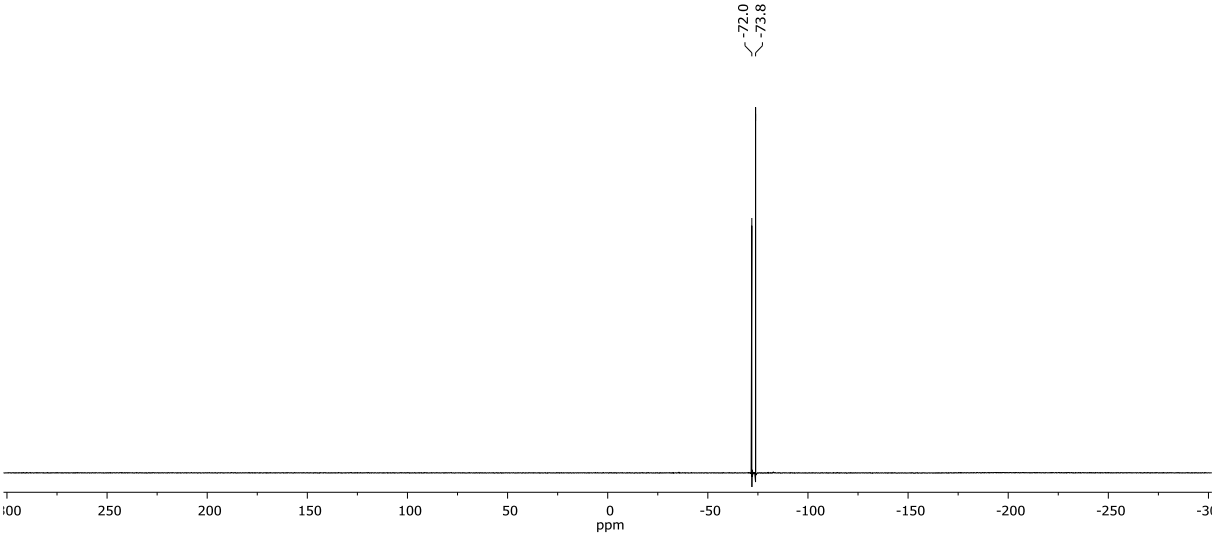


Figure S51: ^{19}F NMR spectrum (MeCN-d_3, 300 K, 376 MHz) of the isolated N(nBu)$_4$PF$_6$.

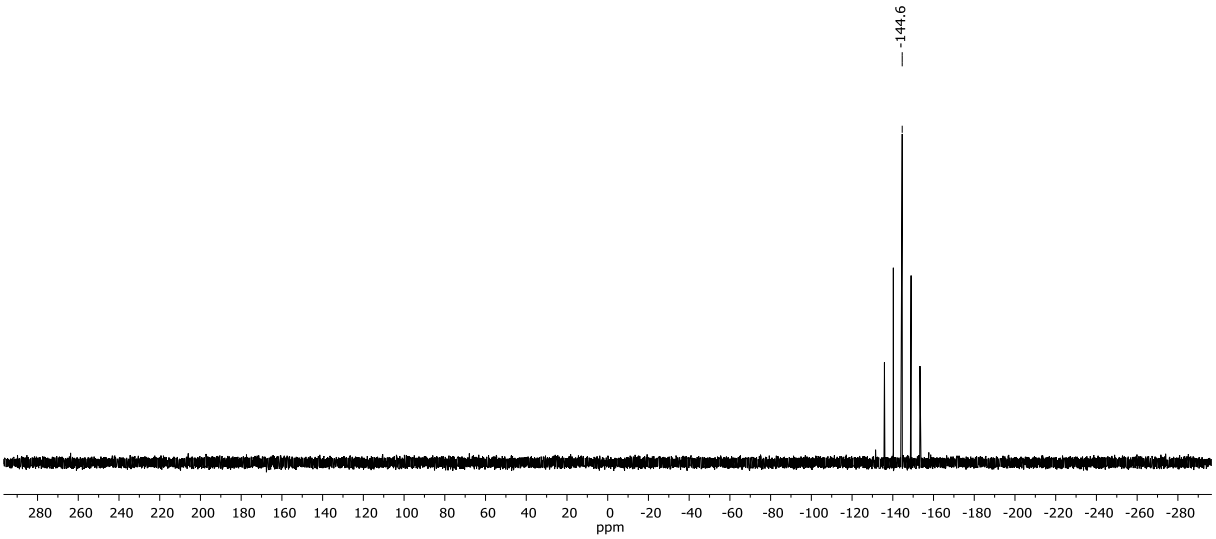
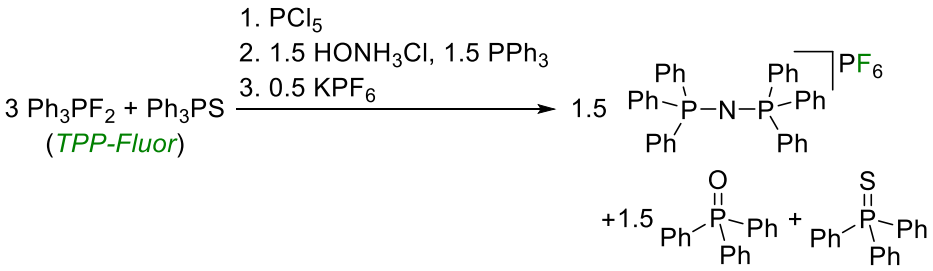


Figure S52: ^{31}P NMR spectrum (MeCN-d_3, 300 K, 160 MHz) of the isolated N(nBu)$_4$PF$_6$.



TPP-Fluor (500 mg) and PCl_5 (87 mg, 0.42 mmol, 1 eq.) were dissolved in DCM (20 mL) and stirred for 16 h at ambient temperature. Hydroxylammonium chloride (44 mg, 0.63 mmol, 1.5 eq.) and triphenyl phosphine (165 mg, 0.63 mmol. 1.5 eq.) were added and the reaction mixture was heated in a sealed Teflon flask at 120 °C for 24 h. Water (5 mL) and KPF_6 (39 mg, 0.21 mmol, 0.5 eq.) were added and the emulsion was vigorously stirred. The organic layer was separated, washed with water (3 x 5 mL) and dried over Na_2SO_4. After partial removal of the solvent under reduced pressure, the product was crystallized by slow diffusion of Et_2O into a saturated DCM solution of the crude product. Yield: 203 mg (0.35 mmol, 84%).

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) = 7.65 (m, 6H, 4-H), 7.47 (m, 24H, 2-H, 3-H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) = 134.0 (s, Ar-C), 132.2 (m, Ar-C), 129.7 (m, Ar-C), 127.1 (dd, $^1J_{PC}$ = 108.0, $^3J_{PC}$ = 1.9 Hz, 1-C).

^{19}F NMR ($CDCl_3$, 376 MHz) δ (ppm) = -73.9 (d, $^1J_{PF}$ = 711.3 Hz, PF_6).

^{31}P NMR ($CDCl_3$, 160 MHz) δ (ppm) = 21.2 (s, [PPN]$^+$) -144.8 (sept, $^1J_{PF}$ = 711.3 Hz, PF_6).

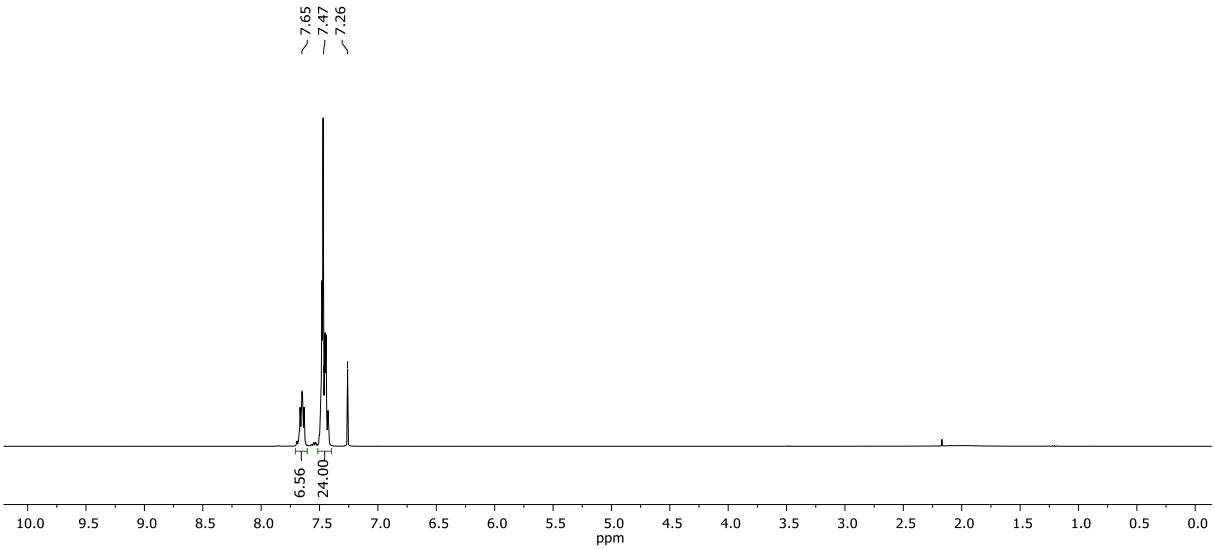


Figure S53: ^{1}H NMR spectrum ($CDCl_3$, 300 K, 400 MHz) of the isolated $(PPN)PF_6$.

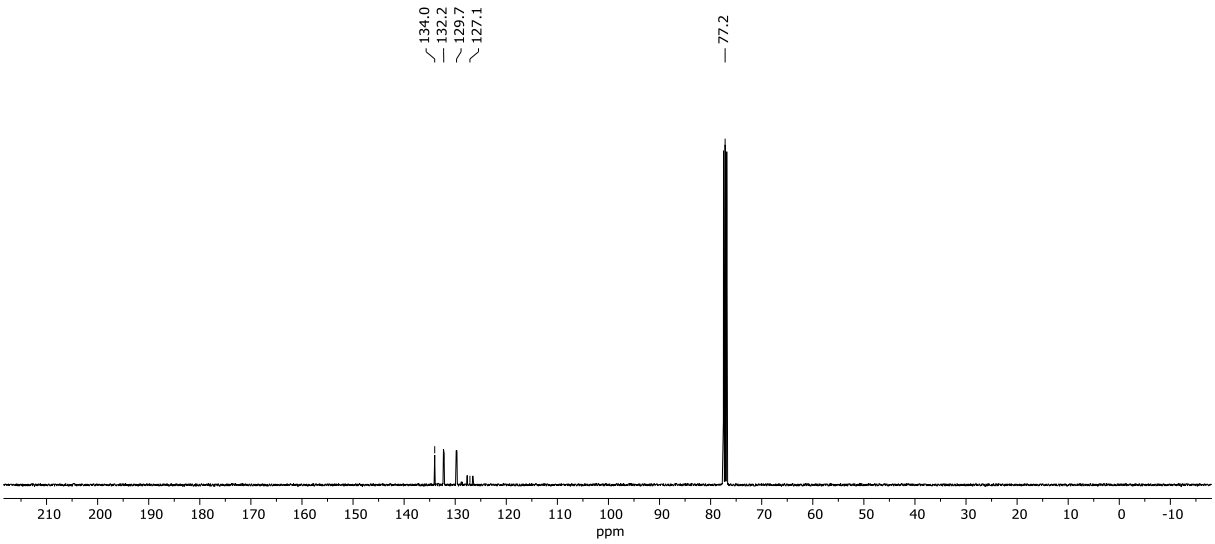


Figure S54: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 300 K, 100 MHz) of the isolated $(PPN)PF_6$.

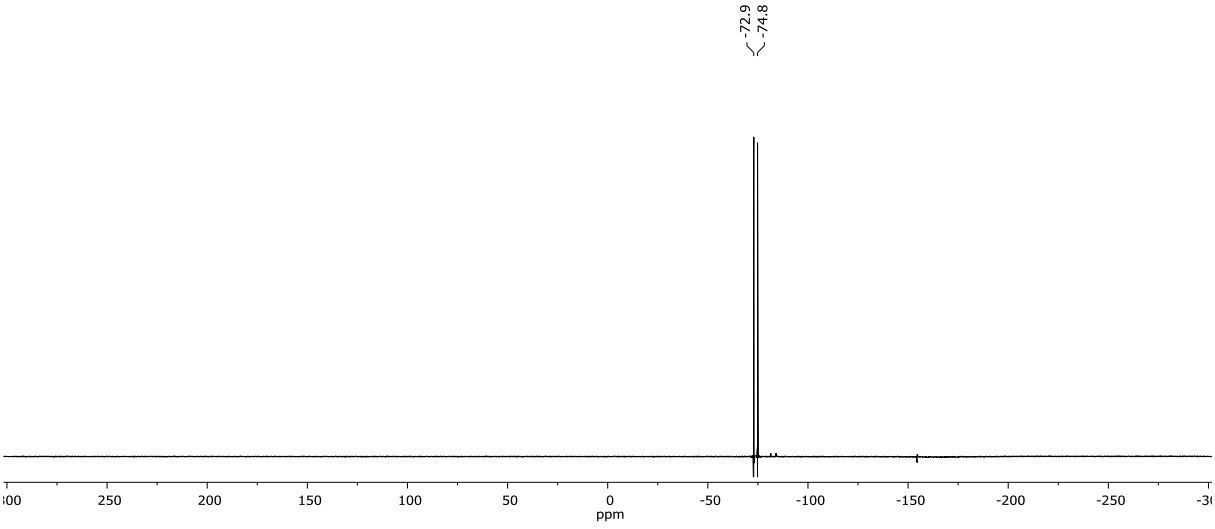


Figure S55: ^{19}F NMR spectrum ($CDCl_3$, 300 K, 376 MHz) of the isolated $(PPN)PF_6$.

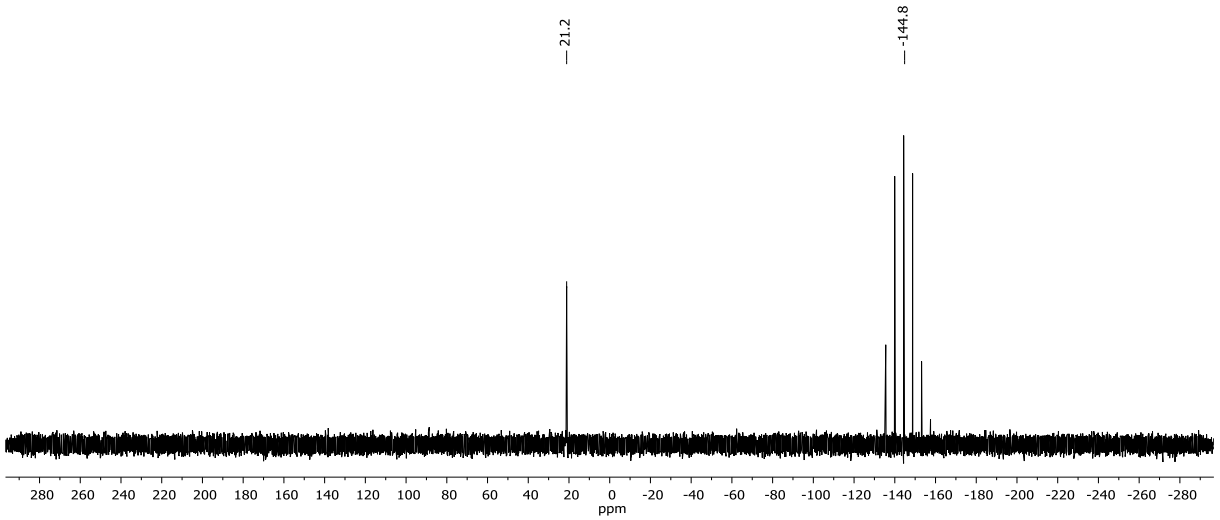


Figure S56: ^{31}P NMR spectrum ($CDCl_3$, 300 K, 160 MHz) of the isolated $(PPN)PF_6$.

UV-vis spectroscopy

All spectra were recorded in a gas-tight quartz cuvette with a concentration of c = 3.8×10^{-5} M in THF.

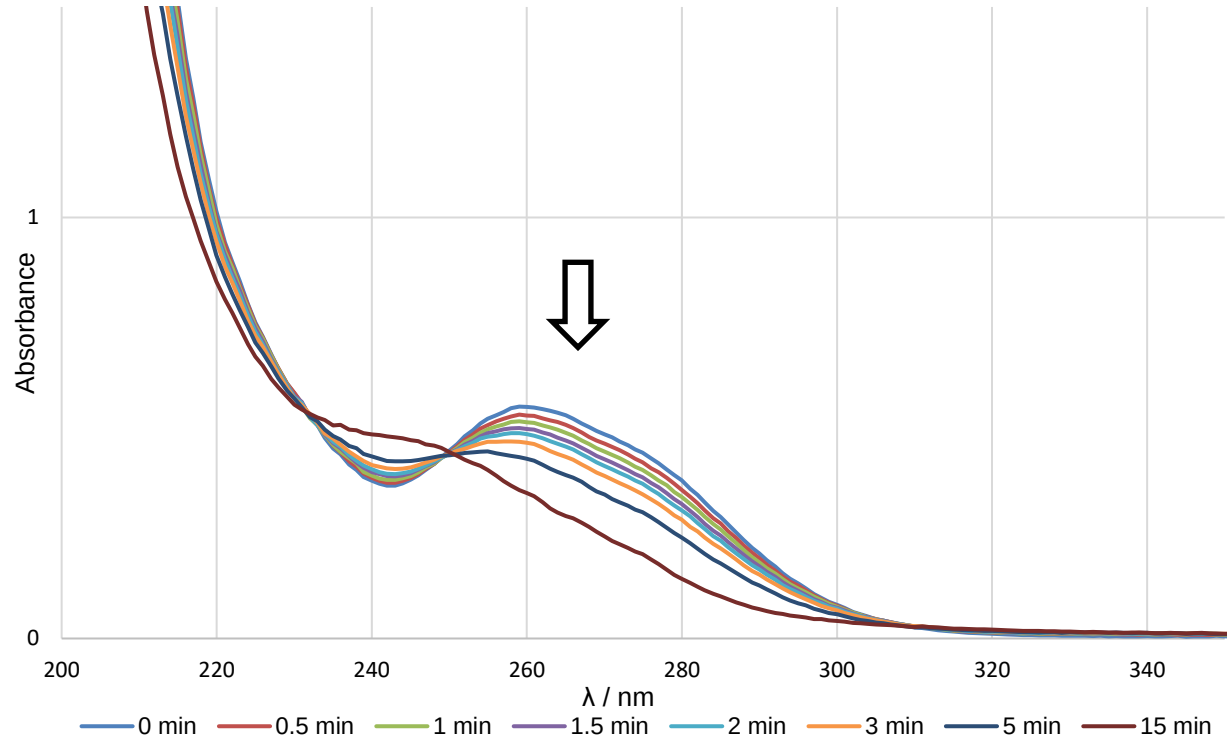


Figure S57: UV-vis spectra of Ph_3P after irradiation with λ = 310 nm as long as indicated.

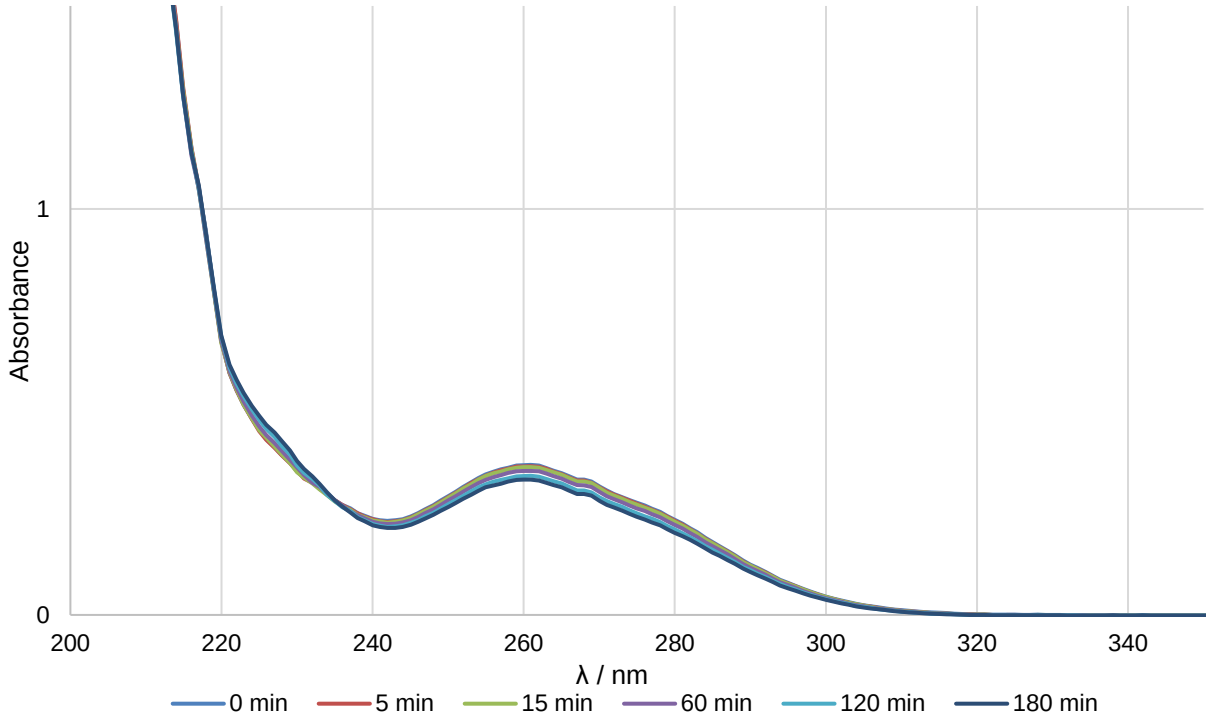


Figure S58: UV-vis spectra of Ph_3P after irradiation with λ = 365 nm as long as indicated.

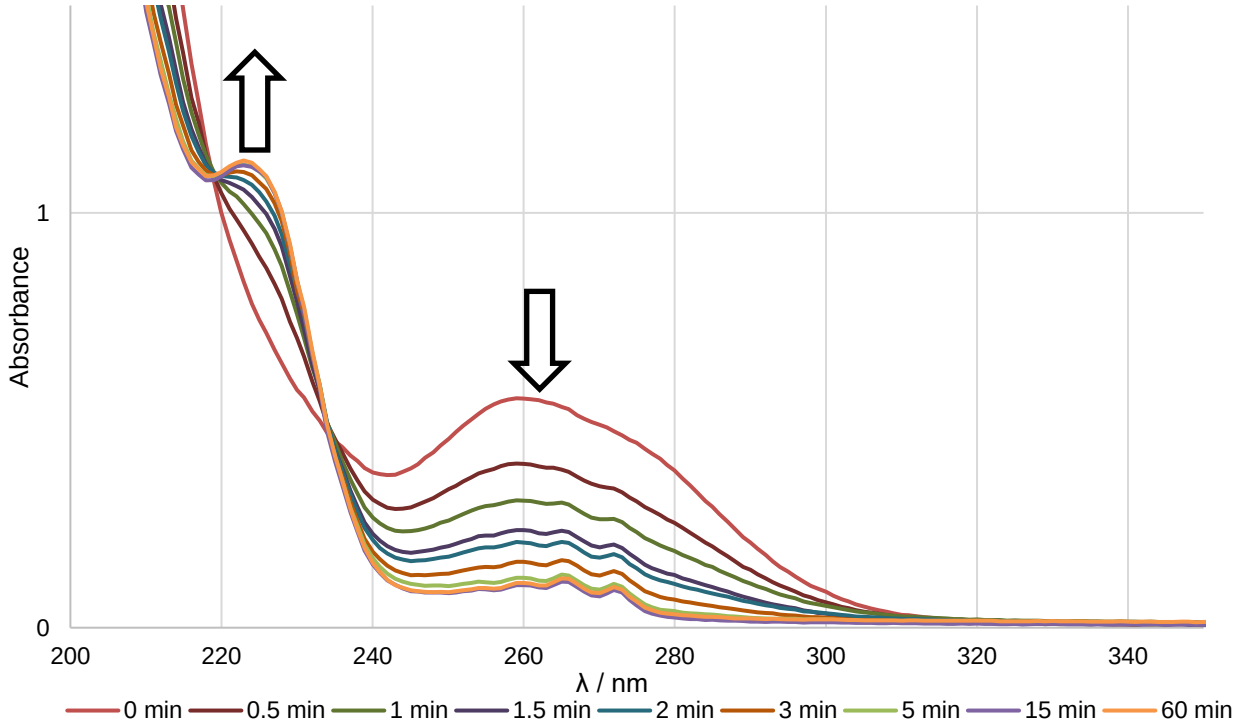


Figure S59: UV-vis spectra of Ph_3P under SF_6 atmosphere after irradiation with λ = 310 nm as long as indicated.

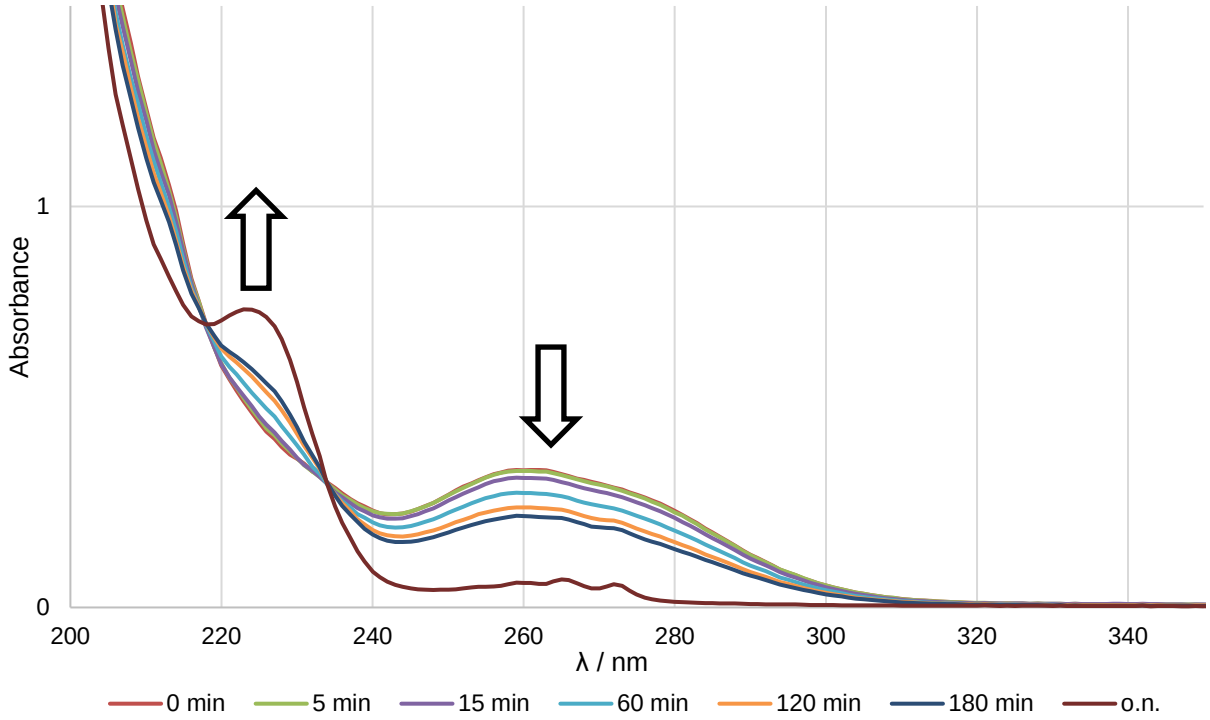


Figure S60: UV-vis spectra of Ph_3P under SF_6 atmosphere after irradiation with $\lambda = 365$ nm as long as indicated.

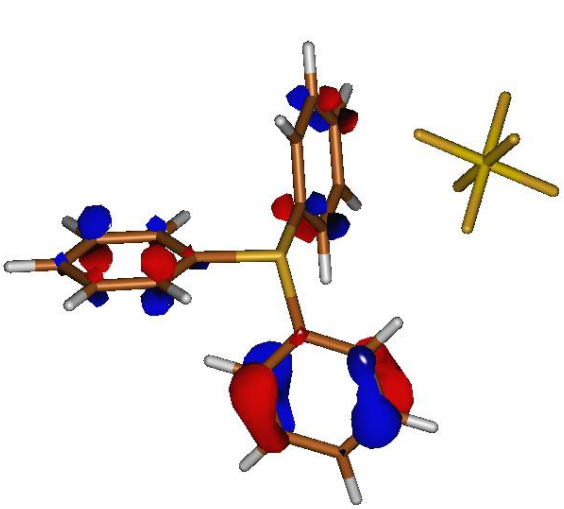
DFT Calculations

Methods

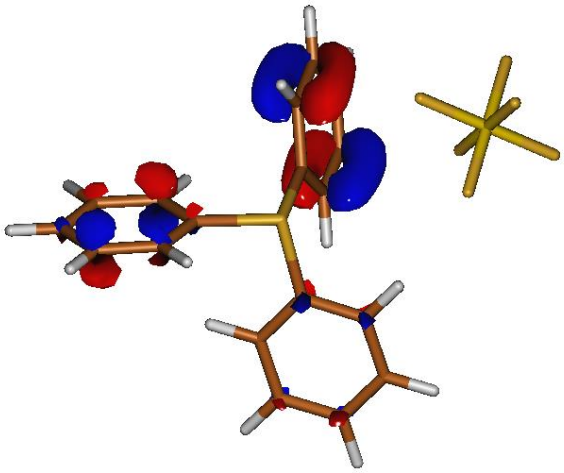
All geometry optimizations and energy evaluations were performed with the TURBOMOLE 7.4[4] program. The structures were optimized without any geometry constraints using the TPSS meta-GGA functional[5] and an atom-pairwise dispersion correction (D3)[6]. A flexible triple zeta basis set (def2-TZVP)[7] was used in all calculations. For the calculation of free energy contributions of translation, rotations and harmonic vibrations (G^{RRHO}_{298}), a rotor approximation was applied for vibrational modes with wave numbers below 100 cm^{-1}[8]. Single point calculations were performed with the hybrid functional PW6B95(-D3).[9] Free energies of solvation (G^{solv}_{298}) were obtained with the COSMO-RS[10] model for 298 K using THF as solvent.

Theoretical electronic excitation spectra (UV/VIS) were obtained using the TD-DFT formalism implemented in ORCA.[11] The hybrid functional B3LYP[12] was chosen as it qualitatively reproduced the UV spectra of phosphines well. TD-DFT calculations employed the def2-TZVP basis set and an implicit solvent model (CPCM).[13] The conical intersection S0/S1 of the SF_6 complexes of Ph_3P was optimized with the range-separated hybrid functional CAM-B3LYP[14] and the def2-SVP basis set.

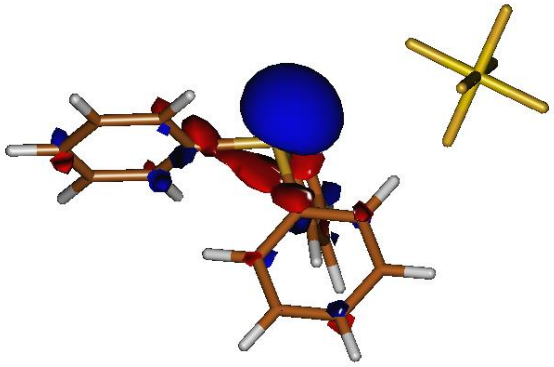
Figure S61: Frontier orbitals of the encounter complex [Ph_3P...SF_6]. Orbital energies calculated with B3LYP/def2-TZVP+CPCM(THF). Isosurface value 0.05 a.u.



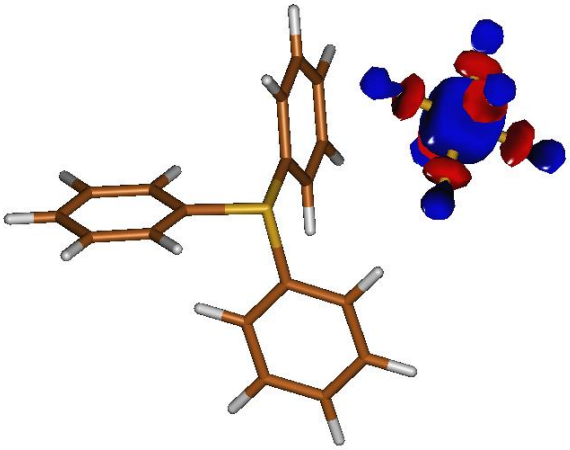
101a (HOMO-2) ε = -6.9721 eV



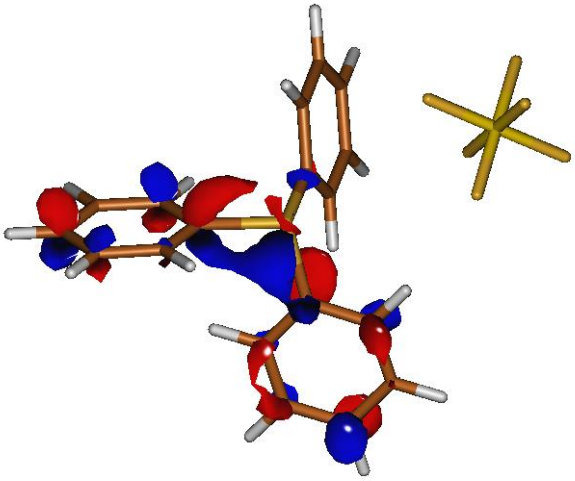
102a (HOMO-1) ε = -6.9614 eV



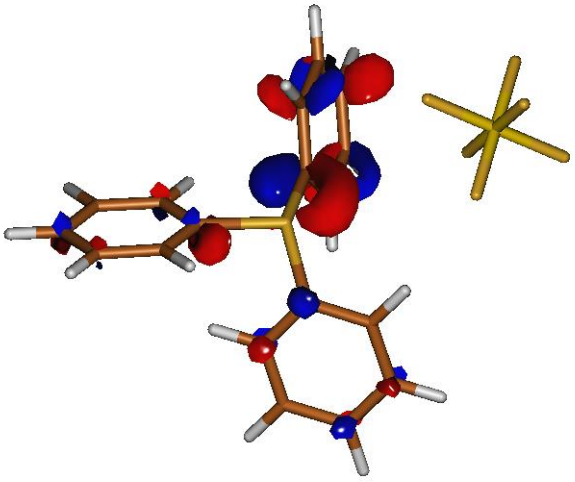
103a (HOMO) ε = -6.0029 eV



104a (LUMO) ε = -2.1771 eV



105a (LUMO+1) ε = -0.8901 eV



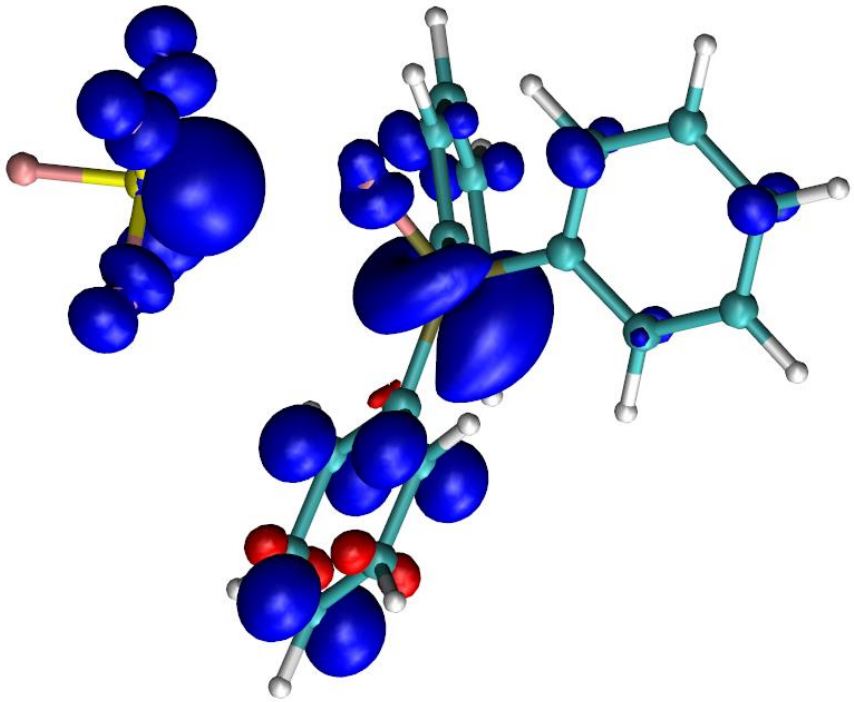
106a (LUMO+2) ε = -0.8608 eV

Table S3: Relative energies of molecular species in the reaction of Ph_3P with SF_6, calculated with DFT[a]. The relative free energy *with respect to isolated Ph_3P and SF_6* is $\Delta G(298)_{solv} = \Delta E$(PW6B95-D3//TPSS-D3/def2-TZVP) + $\Delta G^{RRHO}{}_{298} + \Delta G^{solv}{}_{298}$

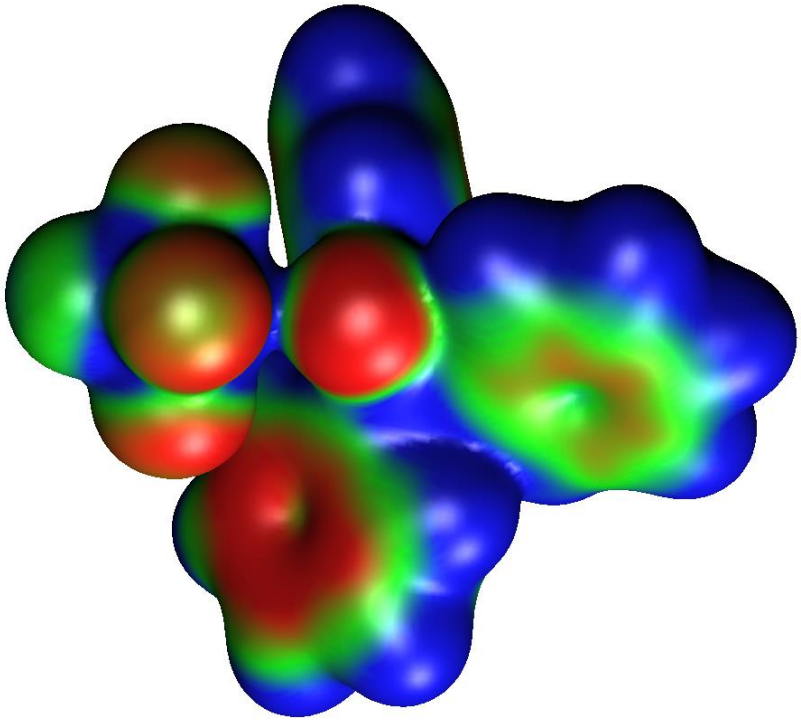
	E(TPSS-D3) [E_h]	E(PW6B95-D3) [E_h]	$G^{RRHO}{}_{298}$ [kcal/mol]	$G^{solv}{}_{298}$ (THF) [kcal/mol]	**$\Delta G(298)_{solv}$ (THF) [kcal/mol]**
Ph_3P	-1036.77148025	-1037.79879736	141.946289	-11.529	
SF_6	-997.54592519	-998.41670244	-6.29516	3.392	
$Ph_3P + SF_6$	-2034.317405	-2036.215500	135.651	-8.137	**0.0**
$[Ph_3P\cdots SF_6]$	-2034.3223637	-2036.2206741	148.208	-11.803	**+5.6**
$^3[Ph_3P\cdots SF_6]_{S0}$[b]		-2036.0742436[b]			**ΔE = +91.9**[c]
$[Ph_3P\cdots SF_6]_{CI}$[d]		-2036.1770221			**ΔE = +27.4**[c]
$^3[Ph_3P\cdots SF_6]_{CI}$[d]		-2036.1071200			**ΔE = +71.3**[c]
$[Ph_3P]^+$	-1036.524386	-1037.5448667	142.803	-42.178	
$[SF_6]^-$	-997.606067	-998.4556861	-13.395	-45.112	
$[Ph_3P]^+ + [SF_6]^-$	*-2034.13045281*	*-2036.00055277*	*129.409*	*-87.291*	**+49.5**
$^3[Ph_3PF\cdots SF_5]$	-2034.2810208	-2036.1633405	145.407	-12.090	**+38.5**
Ph_3PF	-1136.655301	-1137.77212248	141.465	-11.469	
SF_5	-897.617778	-898.38138868	-9.644	2.385	
$Ph_3PF + SF_5$	*-2034.2730781*	*-2036.1535112*	*131.821*	*-9.086*	**+34.1**
Ph_3PF^+	-1136.493153	-1137.61522193	144.493	-42.039	
SF_5^-	-897.755632	-898.51933205	-11.837	-46.550	
$Ph_3PF^+ + SF_5^-$	*-2034.13045281*	*-2036.00055277*	*129.408667*	*-87.291*	**-32.7**
Ph_3PF_2	-1236.631048	-1237.8541761	145.485	-12.043	
SF_4	-797.771418	-798.4434374	-11.070	1.307	
$Ph_3PF_2 + SF_4$	*-2034.4024665*	*-2036.29761357*	*134.414375*	*-10.73601*	**-55.4**

[a] all calculations were performed with the def2-TZVP basis set
[b] Energy of Triplet state (T_1) at the optimized ground state structure of the complex
[c] Gas phase electronic energy (PW6B95-D3/def2-TZVP) of the ground state (S_0 or T_1, resp.)
[d] Optimized structure of the conical intersection S_0/S_1 (CAM-B3LYP/def2-SVP)

***Figure S62*:** (a) Spin density ρ_α-ρ_β (isosurface value = 0.005 a.u.,) and (b) electrostatic potential (isodensity value 0.02 a.u.) of the optimized triplet state $^3[Ph_3PF...SF_5]$ (PW6B95//TPSS-D3/def2-TZVP).



(a)



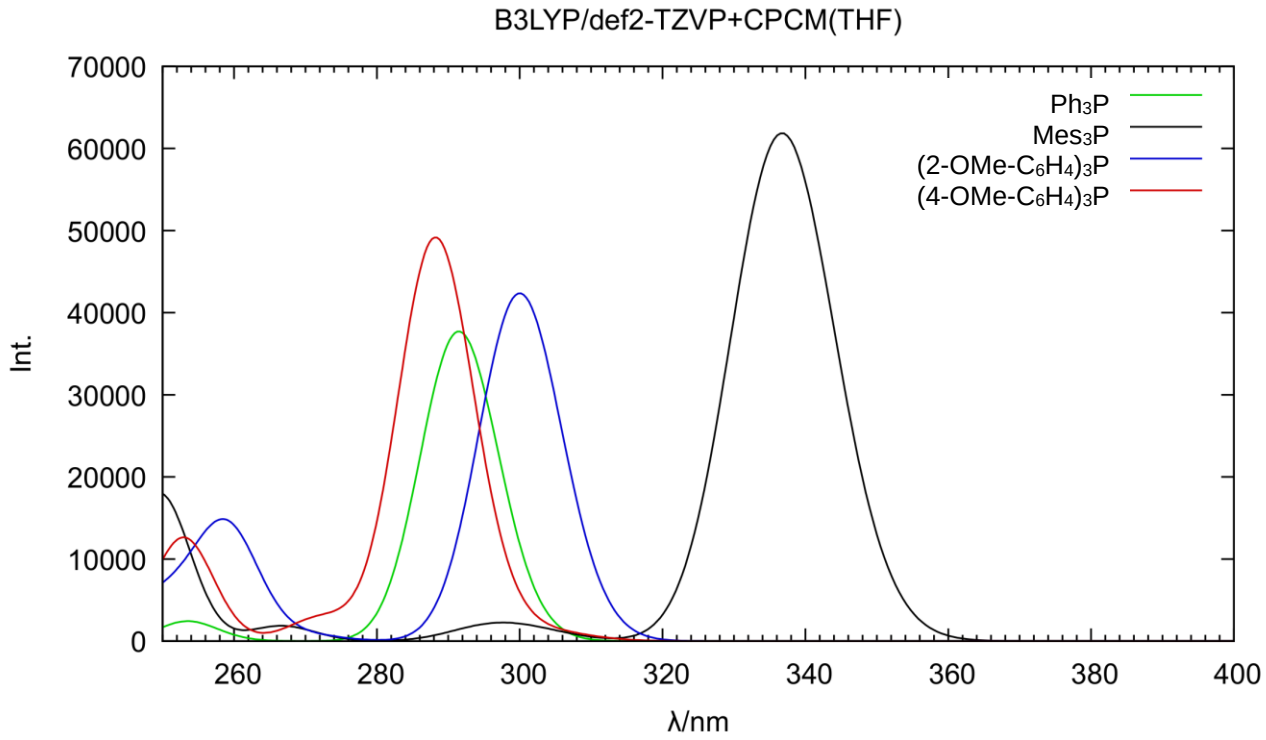
(b)

Table S4: Relative energies of phosphines and noncovalent complexes with SF_6 as calculated with DFT[a]. The relative free energy *with respect to isolated R_3P and SF_6* is $\Delta G(298)_{solv} = \Delta E$(PW6B95-D3//TPSS-D3/def2-TZVP) + $\Delta G^{RRHO}{}_{298} + \Delta G^{solv}{}_{298}$

	E(TPSS-D3) [E_h]	E(PW6B95-D3) [E_h]	$G^{RRHO}{}_{298}$ [kcal/mol]	$G^{solv}{}_{298}$ (THF) [kcal/mol]	**$\Delta G(298)_{solv}$ (THF) [kcal/mol]**
SF_6	-997.54592519	-998.41670244	-6.29516	3.392	
Mes_3P	-1390.828460	-1392.226365	286.051	-14.400	
[$Mes_3P\cdots SF_6$]	-2388.381017	-2390.650483	293.720	-14.583	**+5.7**
Et_3P	-579.219311	-579.730250	100.572	-2.295	
[$Et_3P\cdots SF_6$]	-1576.769062	-1578.150790	106.484	-3.012	**+5.7**
(2-MeOPh)$_3$P	-1380.548874	-1381.915049	196.980	-17.008	
[(2-MeOPh)$_3$P$\cdots SF_6$]	-2378.101864	-2380.339657	204.192	-16.317	**+5.8**
(4-MeOPh)$_3$P	-1380.548337	-1381.913911	196.644	-17.335	
[(4-MeOPh)$_3$P$\cdots SF_6$]	-2378.100768	-2380.337909	203.314	-17.358	**+5.0**

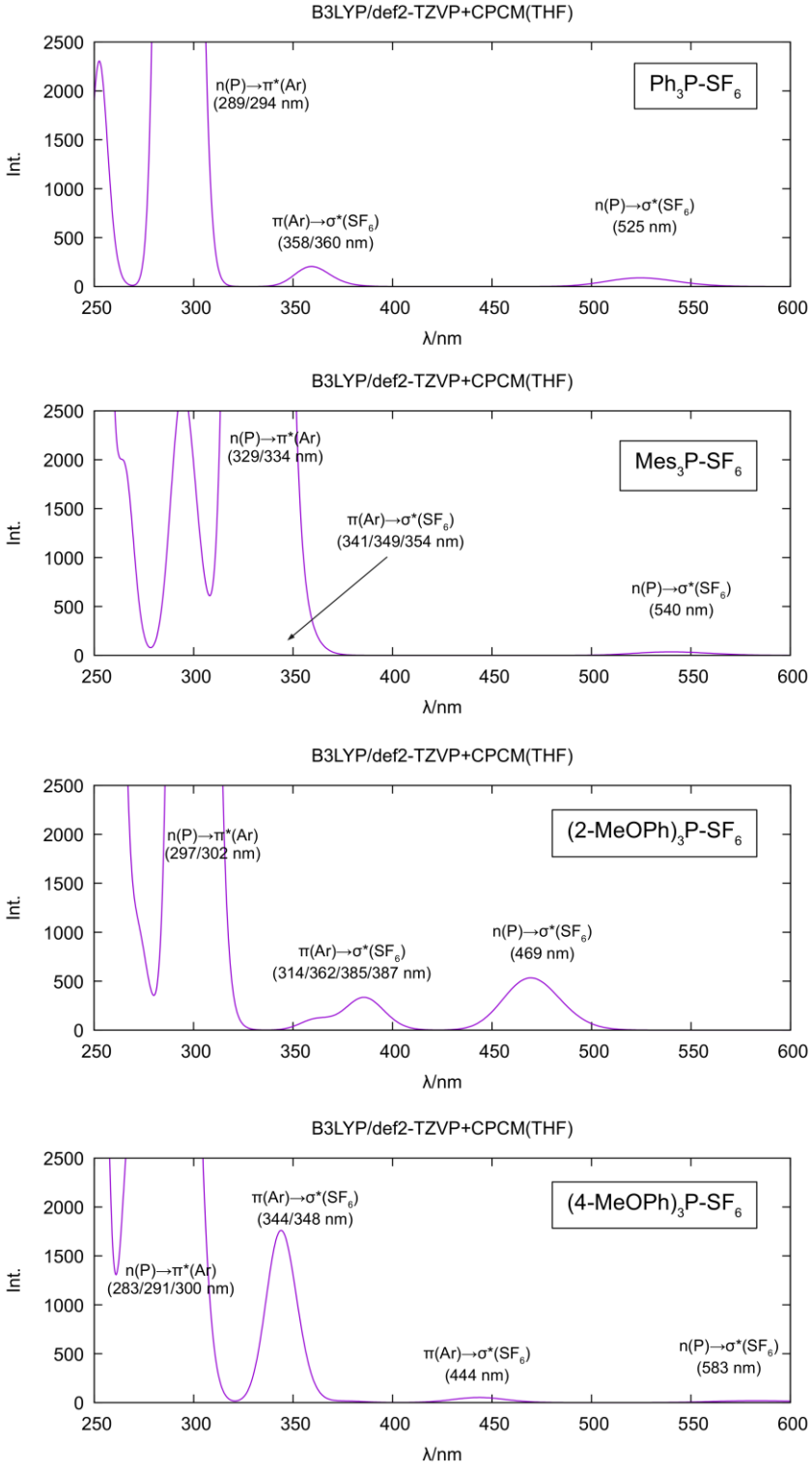
[a] all calculations were performed with the def2-TZVP basis set

Figure S63: TD-DFT calculated electronic excitation spectra of selected phosphines.



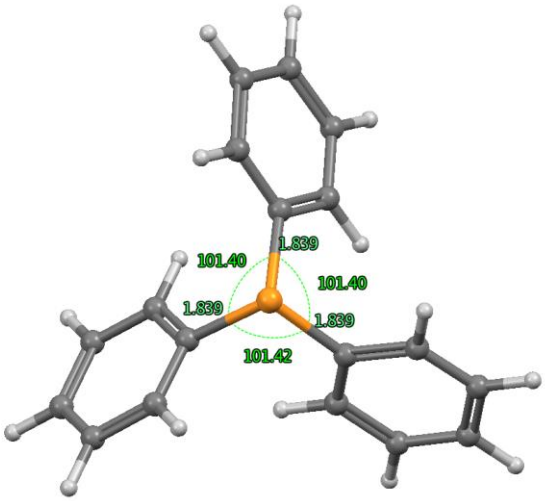
Phosphine	calculated wavelength of n(P)→π*(Ar) absorptions
Ph_3P	291.1 / 291.9 nm
Mes_3P	336.4 / 337.1 nm
$(2\text{-MeOPh})_3P$	299.4 / 300.7 nm
$(4\text{-MeOPh})_3P$	288.0 / 288.4 nm

***Figure S64*:** TD-DFT calculated spectra of [$R_3P\cdots SF_6$] (R= Ph, Mes, 2-MeOPh, 4-MeOPh).



DFT optimized (TPSS-D3/def2-TZVP) cartesian coordinates

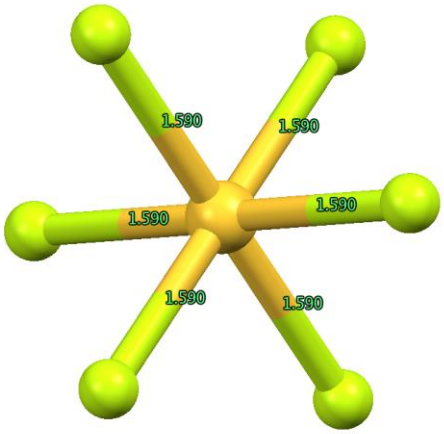
Ph_3P



E(TPSS-D3/def2-TZVP) = -1036.771480251 (conv)
Lowest Freq. = 22.79 cm^-1
34
Ph3P (001/c1/tpss-d3.def2-TZVP)

P	0.3210152	-0.3989570	-1.3525594
C	1.3163172	-1.1641810	-0.0083857
C	1.5845595	-2.5385634	-0.1128352
C	1.8229995	-0.4592194	1.0915067
C	2.5733494	-1.1160092	2.0678480
C	2.3206542	-3.1965064	0.8700328
C	2.8197323	-2.4850030	1.9631824
H	1.6288512	0.6050928	1.1838363
H	1.2095135	-3.0921188	-0.9707582
H	2.9617102	-0.5561347	2.9145090
H	2.5141025	-4.2617962	0.7782772
H	3.4025923	-2.9946675	2.7252670
C	0.4891067	1.3896031	-0.9573795
C	1.6124540	2.0568371	-1.4714660
C	-0.4338737	2.1135518	-0.1907005
C	-0.2327236	3.4710625	0.0623566
C	1.8202981	3.4086667	-1.2059703
C	0.8953320	4.1205608	-0.4393975
H	-1.3106263	1.6129538	0.2090439
H	2.3266713	1.5079200	-2.0810821
H	-0.9576602	4.0205194	0.6570591
H	2.6978273	3.9094534	-1.6057717
H	1.0505301	5.1772086	-0.2402071
C	-1.3920409	-0.7392579	-0.7754011
C	-1.7067198	-1.2471325	0.4921688
C	-2.4357229	-0.4770437	-1.6773597
C	-3.7626071	-0.6947894	-1.3128237
C	-3.0351519	-1.4791304	0.8512454
C	-4.0656341	-1.1996146	-0.0465248
H	-2.2012593	-0.0975748	-2.6693750
H	-0.9103018	-1.4601805	1.1988328
H	-4.5595808	-0.4809713	-2.0197922
H	-3.2645106	-1.8748848	1.8370764
H	-5.0992035	-1.3796936	0.2355475

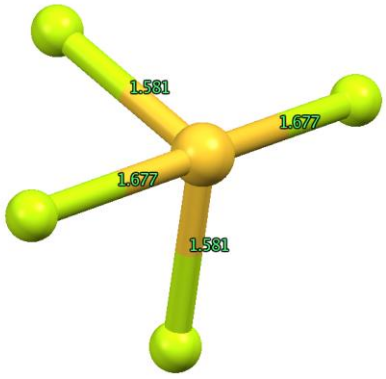
SF_6



E(TPSS-D3/def2-TZVP) = -997.5459251875 (conv)
Lowest Freq. = 320.64 cm^-1
7
SF6 (002/c1/tpss-d3.def2-TZVP)

F	-0.6491881	1.1241472	-0.9170930
S	-0.0000006	-0.0000000	0.0008627
F	0.6491858	-1.1241385	0.9188558
F	-1.2984093	0.0000000	0.9188833
F	1.2984146	0.0000000	-0.9171194
F	-0.6491881	-1.1241472	-0.9170930
F	0.6491858	1.1241385	0.9188558

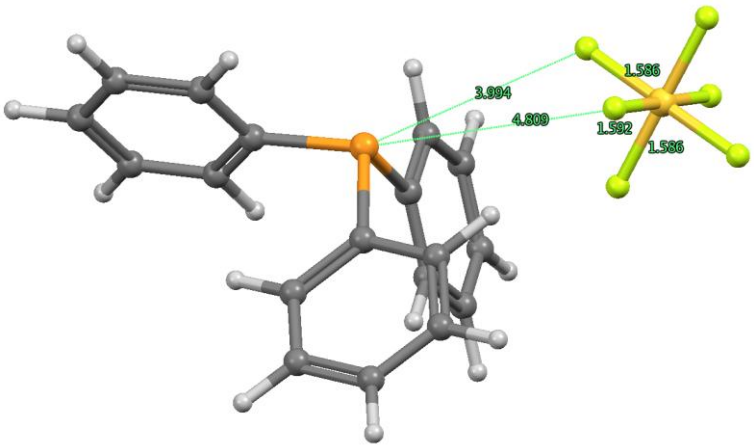
SF_4



E(TPSS-D3/def2-TZVP) = -797.7714180734 (conv)
Lowest Freq. = 205.57 cm^-1
5
SF4 (009/c1/tpss-d3.def2-TZVP)

F	-0.6828666	1.0976807	-1.0704321
S	-0.0327748	-0.0356434	-0.0195444
F	0.6837916	-1.2692112	0.8619079
F	1.3334949	0.1147520	-0.8012164
F	-0.7547791	-1.1514562	-0.8759863

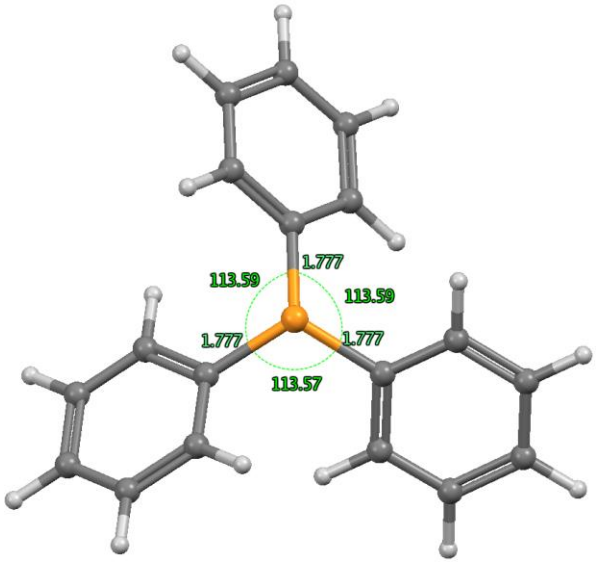
[Ph_3P-SF_6]



E(TPSS-D3/def2-TZVP) = -2034.322363702 (conv)
Lowest Freq. = 5.75 cm^-1
41
[Ph3P-SF6] (003/c1/tpss-d3.def2-TZVP)

P	-0.6089820	-0.1350764	-0.8219114
C	0.5019324	-0.9446933	0.3993581
C	0.6513355	-2.3378388	0.3047065
C	1.2280979	-0.2537767	1.3779897
C	2.0826097	-0.9406489	2.2418012
C	1.4925643	-3.0243640	1.1765381
C	2.2153634	-2.3256493	2.1462414
H	1.1271925	0.8239555	1.4621522
H	0.1052238	-2.8830129	-0.4617163
H	2.6425460	-0.3905151	2.9933837
H	1.5940659	-4.1029674	1.0924518
H	2.8813450	-2.8584326	2.8191440
C	-0.3395526	1.6438794	-0.4397467
C	0.7341329	2.2834929	-1.0798488
C	-1.1426251	2.3863316	0.4363950
C	-0.8722430	3.7347020	0.6729469
C	1.0127838	3.6258429	-0.8309559
C	0.2075132	4.3563113	0.0452509
H	-1.9804911	1.9074555	0.9340459
H	1.3536670	1.7219390	-1.7742110
H	-1.5050257	4.2989338	1.3528992
H	1.8514890	4.1047347	-1.3288969
H	0.4171309	5.4058117	0.2320899
C	-2.2587448	-0.4270001	-0.0635332
C	-2.4489011	-0.8947648	1.2438434
C	-3.3853094	-0.1652525	-0.8592609
C	-4.6710239	-0.3455315	-0.3533469
C	-3.7365689	-1.0887691	1.7450899
C	-4.8496024	-0.8109268	0.9509946
H	-3.2481209	0.1829875	-1.8804901
H	-1.5867045	-1.1066199	1.8690460
H	-5.5331418	-0.1334704	-0.9798047
H	-3.8697766	-1.4538024	2.7600224
H	-5.8512561	-0.9620511	1.3435846
F	3.5051417	-0.7443613	-1.1869683
S	3.6818636	-1.2713750	-2.6720341
F	3.8648674	-1.7941993	-4.1641681
F	4.5751140	-2.4758143	-2.1417164
F	2.7927629	-0.0646741	-3.2081707
F	2.3810765	-2.1657247	-2.5201886
F	4.9882508	-0.3750650	-2.8330068

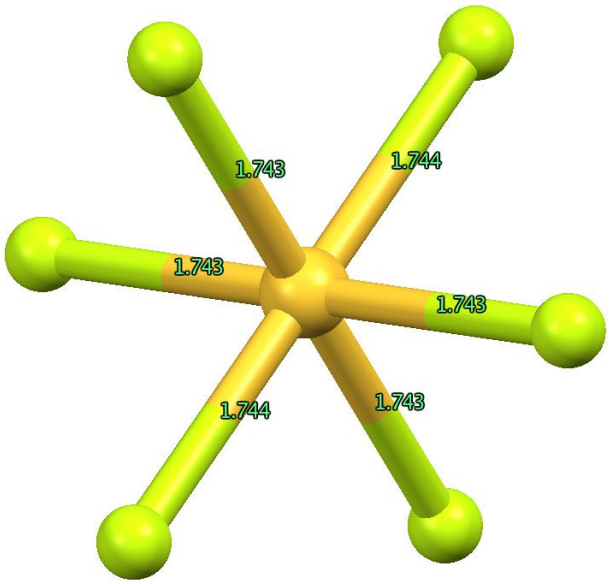
$[Ph_3P]^+$



E(TPSS-D3/def2-TZVP) = -1036.524385914 (conv)
Lowest Freq. = 35.23 cm^-1
34
[Ph3P]cat (004/c1/tpss-d3.def2-TZVP)

P	0.1779459	-0.2223137	-0.7528739
C	1.3186627	-1.1210012	0.2713110
C	1.3581531	-2.5274146	0.1558845
C	2.1973701	-0.4560847	1.1496564
C	3.0829573	-1.1993017	1.9210311
C	2.2465014	-3.2551354	0.9365912
C	3.1094124	-2.5932863	1.8163480
H	2.1642145	0.6245057	1.2397673
H	0.7010592	-3.0365822	-0.5433690
H	3.7492326	-0.6925832	2.6118888
H	2.2770776	-4.3366610	0.8530029
H	3.8070975	-3.1657357	2.4196081
C	0.4281751	1.5368249	-0.7222077
C	1.6865680	2.0418424	-1.1148953
C	-0.6084482	2.4191859	-0.3580995
C	-0.3716885	3.7887166	-0.3621226
C	1.9074568	3.4127739	-1.1099563
C	0.8803265	4.2857729	-0.7365511
H	-1.5742793	2.0299948	-0.0538218
H	2.4754544	1.3621139	-1.4240271
H	-1.1616991	4.4711481	-0.0652533
H	2.8747002	3.8042874	-1.4078497
H	1.0553035	5.3571152	-0.7409460
C	-1.5169966	-0.7030857	-0.5205581
C	-1.8962642	-1.5790447	0.5160241
C	-2.4814446	-0.2184462	-1.4303887
C	-3.8123140	-0.5846952	-1.2791766
C	-3.2320154	-1.9386185	0.6509461
C	-4.1878548	-1.4448546	-0.2420167
H	-2.1830487	0.4329216	-2.2469091
H	-1.1548656	-1.9485560	1.2164937
H	-4.5569017	-0.2111217	-1.9746043
H	-3.5314702	-2.5988113	1.4586820
H	-5.2283781	-1.7338697	-0.1316085

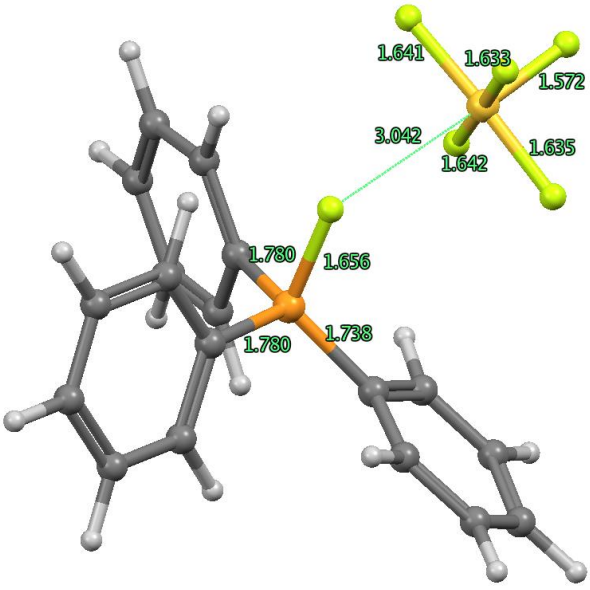
$[SF_6]^-$



E(TPSS-D3/def2-TZVP) = -997.6060668984 (conv)
Lowest Freq. = 127.42 cm^-1
7
[SF6]anion (005/c1/tpss-d3.def2-TZVP)

F	-0.7118737	1.2325965	-1.0056387
S	0.0000003	0.0000000	0.0008824
F	0.7118764	-1.2325989	1.0073941
F	-1.4238051	-0.0000000	1.0074328
F	1.4237993	-0.0000000	-1.0056739
F	-0.7118737	-1.2325965	-1.0056387
F	0.7118764	1.2325989	1.0073941

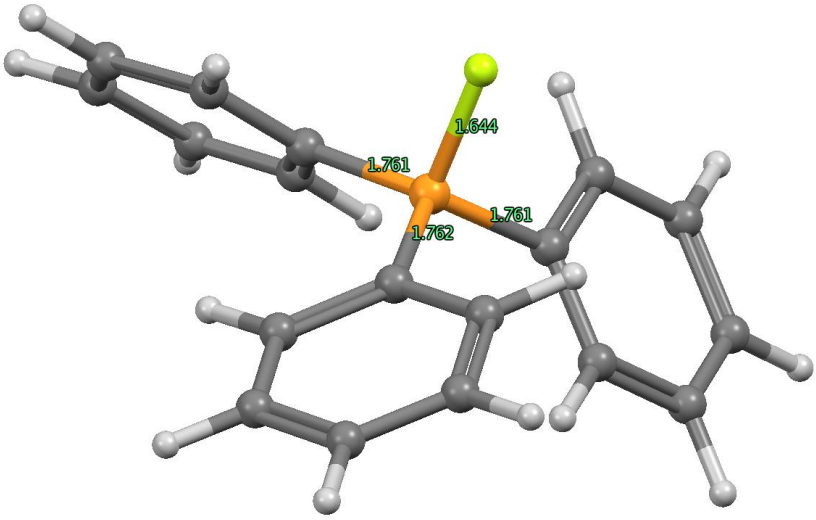
$^3[Ph_3PF\text{-}SF_5]$



E(TPSS-D3/def2-TZVP) = -2034.281020752 (conv)
Lowest Freq. = 6.04 cm^-1
41
3[Ph3PF-SF5] (003-T/c1/tpss-d3.def2-TZVP)

P	-0.3526039	-0.0756808	-0.2032386
C	0.8294031	-1.0932679	0.6546661
C	1.1048564	-2.4049141	0.2139278
C	1.3732001	-0.6568476	1.8810967
C	2.2021177	-1.4917165	2.6175186
C	1.9171532	-3.2419876	0.9748504
C	2.4757105	-2.7914005	2.1708321
H	1.1334810	0.3356634	2.2502736
H	0.6972554	-2.7551681	-0.7276524
H	2.6259132	-1.1365802	3.5524685
H	2.1241890	-4.2485573	0.6225541
H	3.1154073	-3.4454407	2.7557253
C	0.0169373	1.6200039	-0.1031460
C	1.3504114	2.0709124	0.1242322
C	-0.9748709	2.5966793	-0.4139964
C	-0.6587811	3.9447988	-0.4060490
C	1.6422856	3.4240417	0.1251974
C	0.6451034	4.3780682	-0.1250707
H	-1.9817323	2.2790004	-0.6649355
H	2.1423357	1.3478592	0.2858146
H	-1.4338982	4.6711513	-0.6351651
H	2.6641761	3.7437727	0.3102631
H	0.8853496	5.4364002	-0.1287977
C	-2.0735469	-0.4257695	0.0875853
C	-2.7887781	0.3230390	1.0457159
C	-2.6856266	-1.5582230	-0.4901766
C	-3.9805222	-1.9165728	-0.1225770
C	-4.0888918	-0.0278694	1.3825322
C	-4.6908759	-1.1536318	0.8045267
H	-2.1495091	-2.1415345	-1.2306607
H	-2.3123291	1.1730339	1.5247178
H	-4.4408357	-2.7912807	-0.5735430
H	-4.6326866	0.5670244	2.1107734
H	-5.7031987	-1.4327592	1.0809331
F	3.4280188	-0.2434585	-1.6858240
S	2.5101436	-0.4140834	-3.0366237
F	1.5385435	-0.5942750	-4.3370651
F	2.6840695	-2.0428256	-2.9433016
F	2.2723196	1.2024566	-3.0790886
F	-0.2112233	-0.7367233	-1.7155296
F	3.7815295	-0.2933373	-3.9537635

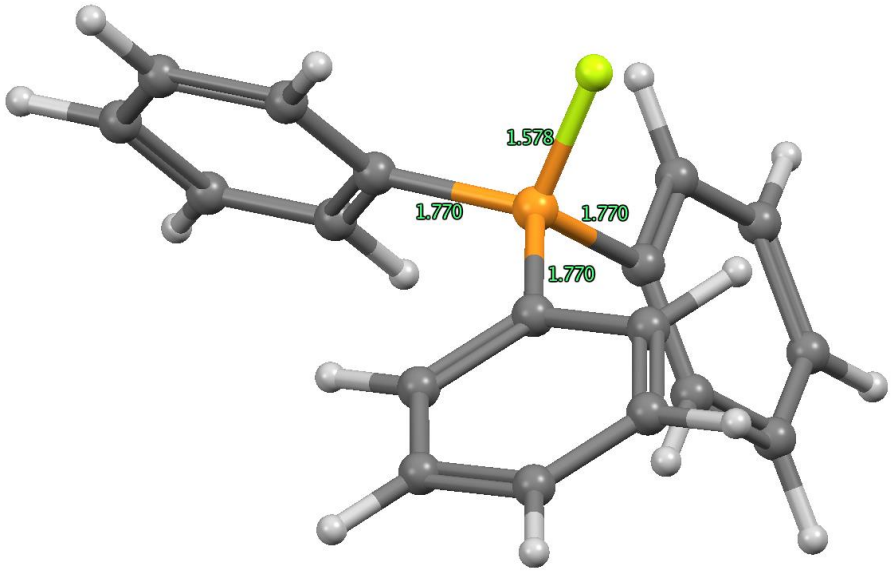
Ph_3PF



E(TPSS-D3/def2-TZVP) = -1136.655300530 (conv)
Lowest Freq. = 21.12 cm^-1
35
Ph3PF (012/c1/tpss-d3.def2-TZVP)

P	0.1958228	-0.2439101	-0.8219902
C	1.3565917	-1.1236192	0.1683797
C	1.3743376	-2.5403324	0.1321103
C	2.2238850	-0.4532919	1.0608373
C	3.0720416	-1.1757827	1.8862623
C	2.2120571	-3.2504777	0.9852415
C	3.0678094	-2.5790850	1.8620470
H	2.2114756	0.6312832	1.1049683
H	0.7357816	-3.0700934	-0.5686568
H	3.7345981	-0.6464584	2.5652382
H	2.2106536	-4.3366364	0.9521058
H	3.7283948	-3.1386215	2.5171912
C	0.4206622	1.5035265	-0.8276155
C	1.6889778	2.0445058	-1.1543603
C	-0.6151861	2.3815301	-0.4356553
C	-0.3865748	3.7476725	-0.3713911
C	1.9094311	3.4144036	-1.0591816
C	0.8785218	4.2748068	-0.6738757
H	-1.5877170	1.9771995	-0.1727434
H	2.4869030	1.3865610	-1.4857228
H	-1.1933505	4.4103689	-0.0712085
H	2.8886528	3.8156553	-1.3059828
H	1.0531451	5.3446176	-0.6127816
C	-1.4753188	-0.7584157	-0.6105644
C	-1.8558394	-1.6179438	0.4451746
C	-2.4797674	-0.2383640	-1.4646251
C	-3.8166508	-0.5496407	-1.2411468
C	-3.1907171	-1.9394319	0.6382990
C	-4.1827631	-1.4020272	-0.1966136
H	-2.2016955	0.4000338	-2.2980543
H	-1.0965621	-2.0135554	1.1125405
H	-4.5773807	-0.1383968	-1.8991526
H	-3.4674201	-2.6029693	1.4527607
H	-5.2270225	-1.6505139	-0.0338636
F	0.5630723	-0.6939624	-2.3600295

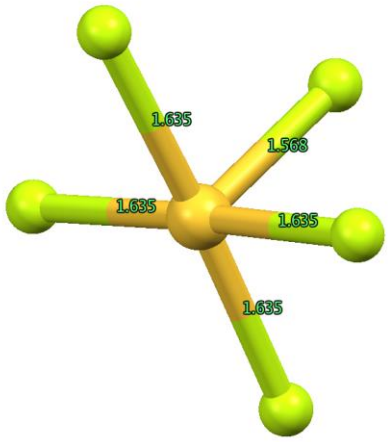
[Ph_3PF]$^+$



E(TPSS-D3/def2-TZVP) = -1136.493153045 (conv)
Lowest Freq. = 20.43 cm^-1
35
[Ph3PF]cat (006/c1/tpss-d3.def2-TZVP)

P	0.2100567	-0.2593326	-0.8771841
C	1.3227562	-1.1482828	0.1738909
C	1.4409030	-2.5438178	0.0254998
C	2.0529142	-0.4686870	1.1632244
C	2.9004395	-1.1885007	2.0011833
C	2.2964747	-3.2468843	0.8651627
C	3.0220032	-2.5707851	1.8511280
H	1.9567771	0.6069734	1.2716186
H	0.8781629	-3.0662111	-0.7426467
H	3.4677171	-0.6702596	2.7673577
H	2.4007003	-4.3209896	0.7511699
H	3.6873947	-3.1267470	2.5043928
C	0.4588722	1.4919971	-0.8111655
C	1.6653834	2.0339732	-1.2944848
C	-0.5264453	2.3226812	-0.2516513
C	-0.3012465	3.6947190	-0.1784881
C	1.8717574	3.4063987	-1.2210325
C	0.8918734	4.2332383	-0.6627515
H	-1.4541798	1.8978848	0.1183337
H	2.4235553	1.3899508	-1.7303086
H	-1.0579285	4.3424674	0.2519527
H	2.7943079	3.8334144	-1.6005916
H	1.0604557	5.3043010	-0.6078073
C	-1.4806341	-0.7167825	-0.6207557
C	-1.8496616	-1.4395957	0.5261360
C	-2.4503943	-0.3183358	-1.5610562
C	-3.7818923	-0.6552560	-1.3491699
C	-3.1888386	-1.7630683	0.7275185
C	-4.1494430	-1.3737002	-0.2071062
H	-2.1622129	0.2378442	-2.4483193
H	-1.0971472	-1.7425104	1.2471723
H	-4.5339497	-0.3607425	-2.0738879
H	-3.4809640	-2.3214870	1.6108497
H	-5.1917259	-1.6320740	-0.0474527
F	0.5630077	-0.6931585	-2.3527902

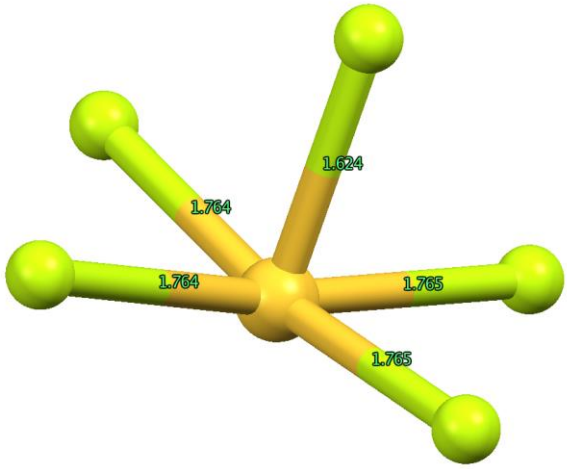
SF_5



E(TPSS-D3/def2-TZVP) = -897.6177775607 (conv)
Lowest Freq. = 215.80 cm^-1
6
SF5 (013/c1/tpss-d3.def2-TZVP)

F	-0.6773203	1.1557333	-0.9355896
S	0.0292537	-0.0000000	-0.0198138
F	0.6571274	-1.1553066	0.9517782
F	1.3095408	-0.0000000	-0.9252953
F	-0.6773203	-1.1557333	-0.9355896
F	0.6571274	1.1553066	0.9517782

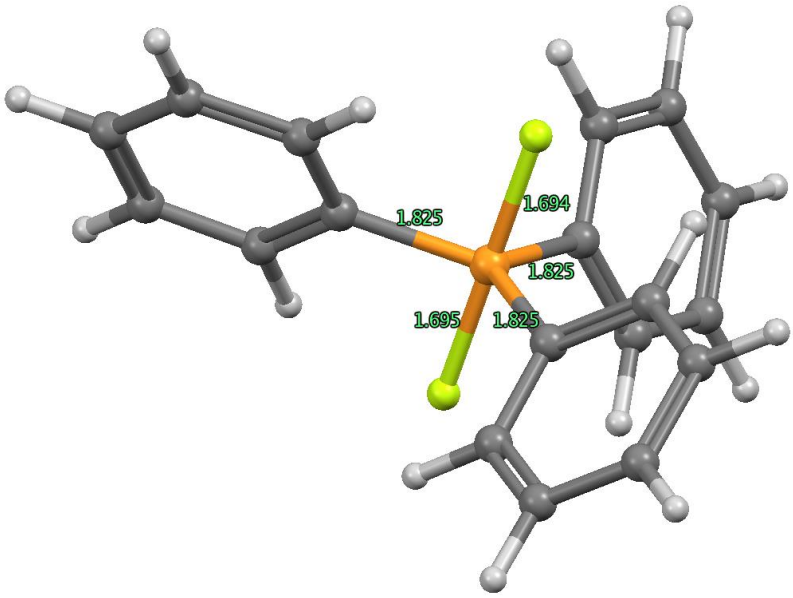
$[SF_5]^-$



E(TPSS-D3/def2-TZVP) = -897.7556316581 (conv)
Lowest Freq. = 223.87 cm^-1
6
[SF5]- (007/c1/tpss-d3.def2-TZVP)

F	-0.6849557	1.2440791	-1.0381749
S	-0.0806432	0.0000000	0.0579212
F	0.7515426	-1.2438782	0.9925397
F	1.2458783	-0.0000000	-0.8793825
F	-0.6849557	-1.2440791	-1.0381749
F	0.7515426	1.2438782	0.9925397

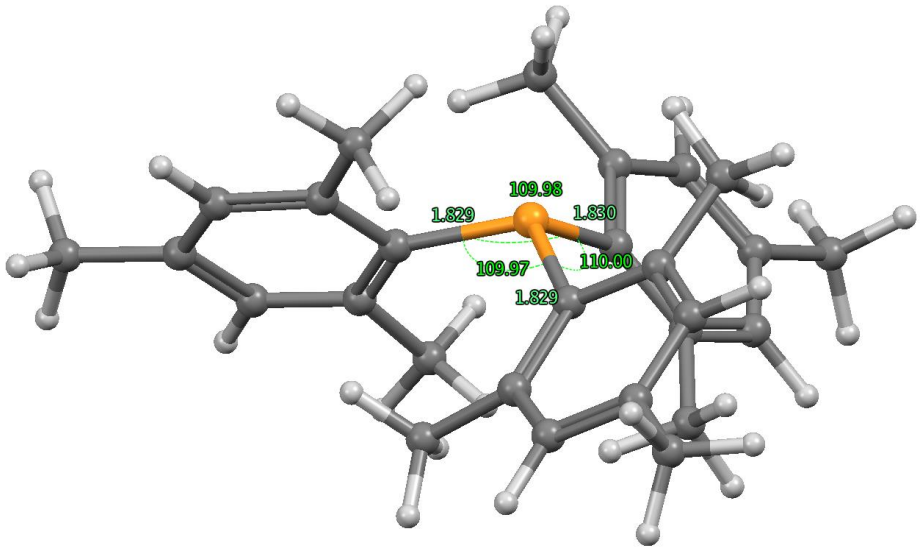
Ph_3PF_2



E(TPSS-D3/def2-TZVP) = -1236.631048428 (conv)
Lowest Freq. = 29.90 cm^-1
36
Ph3PF2 (008/c1/tpss-d3.def2-TZVP)

P	0.4216789	-0.1372490	-0.4685022
C	1.5427356	-1.2402727	0.4569772
C	1.6188820	-2.6032088	0.1371741
C	2.3371744	-0.7336774	1.4952754
C	3.2054421	-1.5748055	2.1886179
C	2.4628961	-3.4465997	0.8572205
C	3.2639579	-2.9336133	1.8777775
H	2.2745789	0.3166276	1.7550803
H	1.0161105	-2.9987788	-0.6719554
H	3.8302655	-1.1685084	2.9790056
H	2.5007662	-4.5045729	0.6134966
H	3.9313871	-3.5903561	2.4289084
C	1.0818678	1.3466165	-1.3000857
C	2.1166708	1.2314380	-2.2389608
C	0.5593882	2.6141045	-1.0065900
C	1.0533347	3.7439735	-1.6558782
C	2.6307478	2.3686189	-2.8592412
C	2.0951702	3.6253939	-2.5761678
H	-0.2328319	2.7110883	-0.2734362
H	2.5171206	0.2533123	-2.4786282
H	0.6289959	4.7192789	-1.4348025
H	3.4449714	2.2704903	-3.5716975
H	2.4883453	4.5092106	-3.0709346
C	-1.3605636	-0.5171300	-0.5632231
C	-2.1150050	-0.6738184	0.6080942
C	-1.9900267	-0.6550620	-1.8084358
C	-3.3550701	-0.9269957	-1.8781719
C	-3.4724143	-0.9803173	0.5324641
C	-4.0971979	-1.0987850	-0.7093436
H	-1.4100863	-0.5466258	-2.7174807
H	-1.6368953	-0.5575470	1.5736939
H	-3.8367931	-1.0136233	-2.8480049
H	-4.0439968	-1.1176410	1.4460442
H	-5.1585951	-1.3240446	-0.7659700
F	0.6898671	-1.0445830	-1.8742618
F	0.1539168	0.7700782	0.9372017

Mes_3P

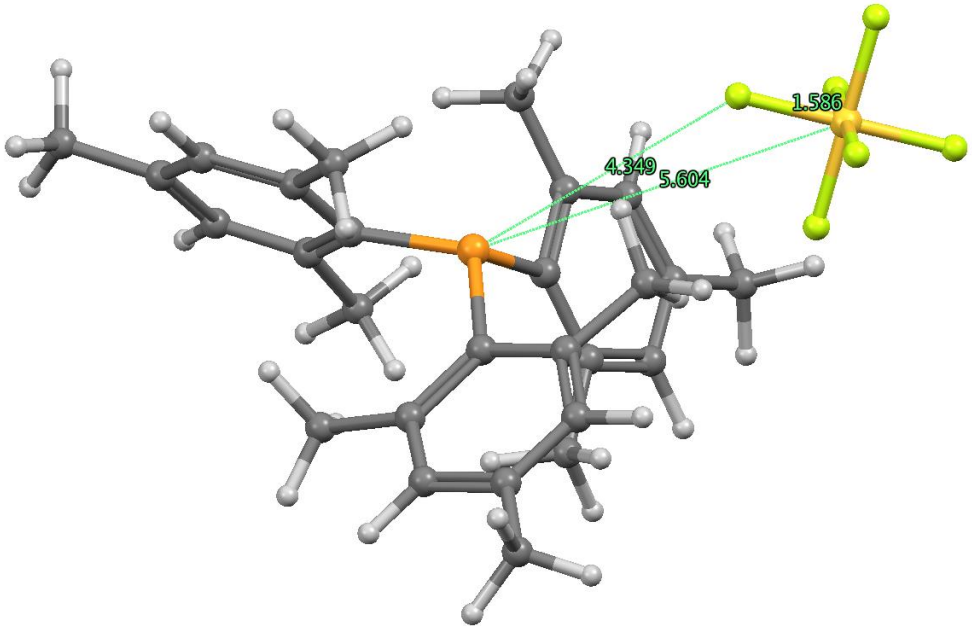


E(TPSS-D3/def2-TZVP) = -1390.828460454 (conv)
Lowest Freq. = 26.25 cm^-1
61
PMes3 (014/c1/tpss-d3.def2-TZVP)

P	0.1942997	-0.2428554	-0.8239117
C	1.3242559	-1.1021056	0.3302302
C	1.5546064	-2.4656200	0.0061228
C	2.0515379	-0.5201018	1.3968534
C	2.9955803	-1.2954575	2.0780187
C	2.4933131	-3.2018409	0.7307592
C	3.2403573	-2.6327176	1.7631804
H	3.5414699	-0.8374183	2.9015349
H	2.6446374	-4.2493689	0.4752298
C	0.4044335	1.5682274	-0.6731520
C	1.5564902	2.0734183	-1.3329207
C	-0.5049810	2.4821749	-0.0880439
C	-0.2580409	3.8542205	-0.2040910
C	1.7674588	3.4512057	-1.4029637
C	0.8631709	4.3649137	-0.8589860
H	-0.9611675	4.5456424	0.2579644
H	2.6639698	3.8170315	-1.9008908
C	-1.5385830	-0.7032473	-0.4607738
C	-2.0142127	-1.3749107	0.6903875
C	-2.4406242	-0.4485831	-1.5290417
C	-3.7670794	-0.8690761	-1.4319208
C	-3.3489154	-1.7944364	0.7292426
C	-4.2425547	-1.5603515	-0.3153830
H	-4.4444190	-0.6521432	-2.2563903
H	-3.7037160	-2.3038475	1.6239211
C	-2.0086025	0.3033791	-2.7638351
H	-2.8067645	0.3018473	-3.5115762
H	-1.1063486	-0.1433032	-3.1988508
H	-1.7580322	1.3459513	-2.5322870
C	-1.1767997	-1.6202466	1.9212036
H	-0.5989876	-0.7334082	2.1960691
H	-0.4550387	-2.4314519	1.7807362
H	-1.8258537	-1.8845159	2.7612823
C	-5.6693047	-2.0442895	-0.2473061
H	-5.7917107	-2.9791278	-0.8093271
H	-6.3588112	-1.3116870	-0.6797686
H	-5.9727185	-2.2370546	0.7861188
C	2.5891836	1.1519602	-1.9339877

H	3.1079239	0.5713653	-1.1611536
H	3.3366372	1.7252175	-2.4897422
H	2.1201518	0.4236893	-2.6066562
C	-1.7116478	2.0621633	0.7142643
H	-2.5262016	1.6942031	0.0820805
H	-2.0860000	2.9140412	1.2896079
H	-1.4682937	1.2547743	1.4105977
C	1.0828708	5.8515453	-0.9852721
H	0.6114163	6.2392404	-1.8976879
H	2.1492233	6.0921578	-1.0390193
H	0.6479885	6.3902464	-0.1374185
C	0.7796249	-3.1590143	-1.0871469
H	1.1775651	-4.1628142	-1.2609484
H	0.8237148	-2.5868720	-2.0217832
H	-0.2827834	-3.2516163	-0.8297130
C	1.8278112	0.8880995	1.8901996
H	2.2557996	1.6392115	1.2184430
H	2.2883095	1.0107556	2.8749626
H	0.7619460	1.1179759	1.9759579
C	4.2842550	-3.4296048	2.5045893
H	5.2727907	-3.3001306	2.0451594
H	4.0519327	-4.4989428	2.4896718
H	4.3634671	-3.1064972	3.5475607

$Mes_3P\text{-}SF_6$

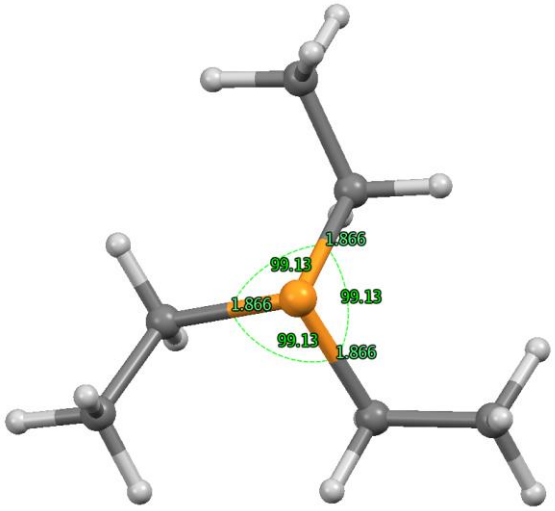


E(TPSS-D3/def2-TZVP) = -2388.381017313 (conv)
Lowest Freq. = 12.24 cm^-1
68
PMes3-SF6 (015/c1/tpss-d3.def2-TZVP)

P	-0.4161413	0.0108795	-0.5361269
C	0.8376572	-0.9090268	0.4262597
C	0.9648698	-2.2746640	0.0558033
C	1.7389913	-0.3717383	1.3766938
C	2.7506810	-1.1896397	1.8913591
C	1.9763795	-3.0541594	0.6172585
C	2.8975832	-2.5271944	1.5235303
H	3.4356639	-0.7640702	2.6232277
H	2.0514491	-4.1000485	0.3245297

C	-0.1622480	1.8151109	-0.3634446
C	0.8861630	2.3336863	-1.1701308
C	-0.9697465	2.7168254	0.3702242
C	-0.7329637	4.0910739	0.2521431
C	1.0932599	3.7114812	-1.2385820
C	0.2831174	4.6145236	-0.5471160
H	-1.3563032	4.7730553	0.8284952
H	1.9097359	4.0860632	-1.8538542
C	-2.0919497	-0.4353947	0.0452276
C	-2.4190242	-1.1268150	1.2362359
C	-3.1250732	-0.1424977	-0.8848840
C	-4.4330274	-0.5490489	-0.6190305
C	-3.7421997	-1.5309490	1.4453480
C	-4.7641863	-1.2622737	0.5347841
H	-5.2122124	-0.3027101	-1.3385668
H	-3.9816819	-2.0553218	2.3692264
F	4.3449661	-1.2401538	-1.2598674
S	4.3731264	-1.9706404	-2.6671763
F	4.4096540	-2.7030521	-4.0800469
F	4.3509982	-3.3838403	-1.9381765
F	4.4016890	-0.5594272	-3.4013727
F	2.7877063	-1.9647636	-2.7139099
F	5.9654374	-1.9793534	-2.6283308
C	1.6409623	1.0326086	1.9195146
H	1.9805559	1.7846936	1.2000907
H	2.2550818	1.1226795	2.8203818
H	0.6097378	1.2910589	2.1764204
C	0.0104932	-2.9216102	-0.9166004
H	0.3583822	-3.9229333	-1.1855097
H	-0.0889883	-2.3181950	-1.8271270
H	-0.9969141	-3.0106912	-0.4919608
C	4.0274128	-3.3665002	2.0636821
H	4.8955024	-3.3242702	1.3927427
H	3.7348314	-4.4173301	2.1544222
H	4.3530545	-3.0103966	3.0459822
C	1.8167867	1.4224512	-1.9301755
H	1.2543148	0.7115361	-2.5471955
H	2.4309719	0.8230553	-1.2481709
H	2.4863873	2.0032540	-2.5707019
C	-2.0480876	2.2822544	1.3318521
H	-1.7120871	1.4544058	1.9622652
H	-2.9516849	1.9380229	0.8184533
H	-2.3232700	3.1201893	1.9791918
C	0.4930966	6.1029127	-0.6688968
H	-0.0082115	6.4957019	-1.5629538
H	1.5564489	6.3485583	-0.7564659
H	0.0853446	6.6325473	0.1975440
C	-1.4274849	-1.4096191	2.3376004
H	-0.7541014	-2.2370288	2.0907055
H	-1.9617519	-1.6692042	3.2563531
H	-0.7930620	-0.5419746	2.5392635
C	-2.8518114	0.6364538	-2.1480488
H	-2.5593389	1.6702370	-1.9264707
H	-3.7422931	0.6617746	-2.7824823
H	-2.0212293	0.1927274	-2.7102579
C	-6.1745681	-1.7358351	0.7815855
H	-6.3529766	-2.7015279	0.2909743
H	-6.9074283	-1.0266587	0.3835420
H	-6.3664466	-1.8692635	1.8507201

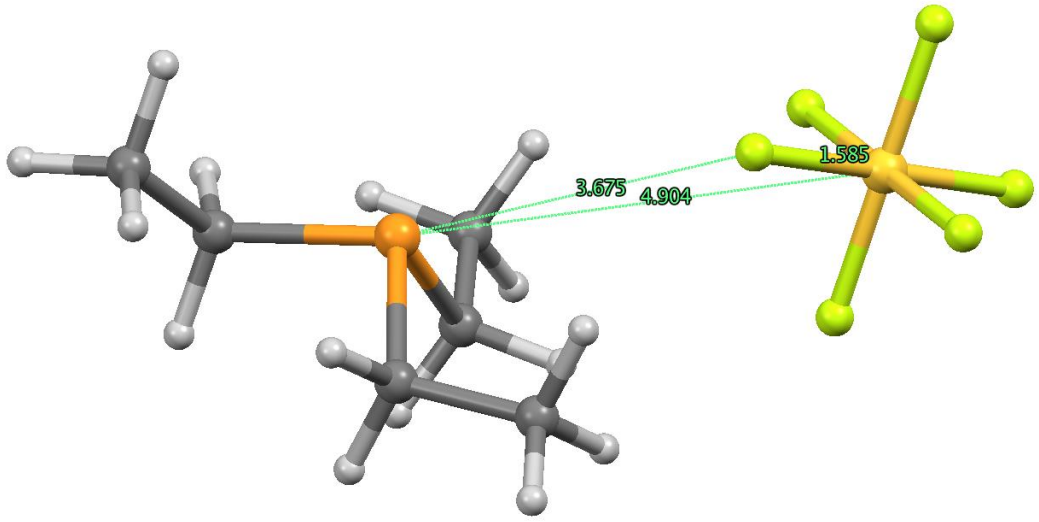
Et_3P



E(TPSS-D3/def2-TZVP) = -579.2193107818 (conv)
Lowest Freq. = 55.62 cm^-1
22
PEt3 (016/c1/tpss-d3.def2-TZVP)

P	0.1482642	0.0047831	-0.0016999
C	1.0532754	1.3391071	-0.9401702
H	2.1373839	1.1898308	-0.8377676
H	0.8109901	2.2903261	-0.4512561
C	0.9756194	0.1979054	1.6591818
H	2.0655716	0.2412961	1.5242505
H	0.7570193	-0.7128337	2.2295448
C	1.0836854	-1.4831801	-0.6270837
H	2.1615558	-1.3297926	-0.4763523
H	0.9130344	-1.5327864	-1.7091947
C	0.6523477	1.4065968	-2.4195346
H	-0.4275249	1.5544909	-2.5252482
H	0.9161712	0.4846207	-2.9483548
H	1.1609226	2.2348584	-2.9253043
C	0.6261093	-2.7945240	0.0245840
H	0.8187613	-2.7944570	1.1025926
H	1.1563586	-3.6511930	-0.4060194
H	-0.4478736	-2.9498297	-0.1224165
C	0.4763161	1.4222150	2.4373203
H	-0.6097249	1.3831462	2.5721230
H	0.7141373	2.3539491	1.9133512
H	0.9411389	1.4721525	3.4282246

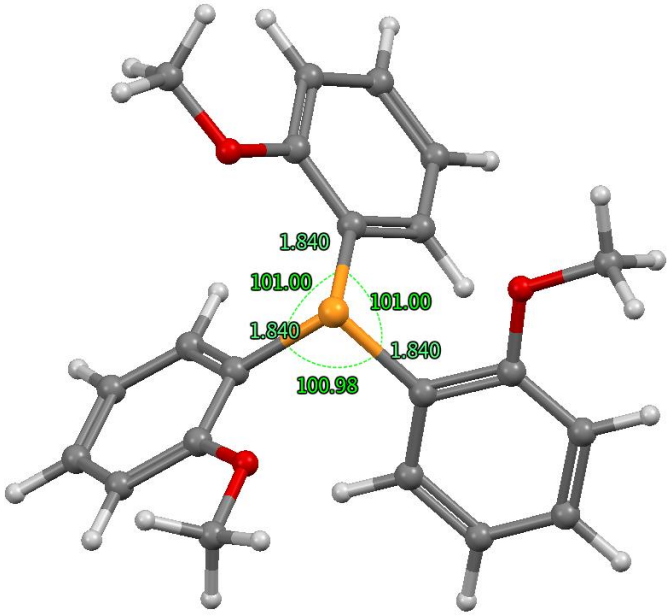
$Et_3P\text{-}SF_6$



E(TPSS-D3/def2-TZVP) = -1576.769061660 (conv)
Lowest Freq. = 12.77 cm^-1
29
PEt3-SF6 (017/c2/tpss-d3.def2-TZVP)

P	-0.6619011	-0.0082367	-0.7711103
F	3.7176156	-0.9648726	-1.1942201
S	3.5948221	-1.5111117	-2.6858896
F	3.4781442	-2.0592352	-4.1733852
F	4.9250355	-2.3592947	-2.4786199
F	2.2694314	-0.6649784	-2.8884620
F	2.7330986	-2.7409319	-2.1631721
F	4.4624097	-0.2827636	-3.2039197
C	0.3624902	-0.8628195	0.5323950
H	0.1152192	-0.4509159	1.5208702
H	1.4090779	-0.6083520	0.3305881
C	-0.2174963	1.7611582	-0.3803467
H	-0.9812022	2.3918478	-0.8510755
H	-0.2867810	1.9249691	0.7042523
C	-2.3276397	-0.0875964	0.0646869
H	-2.5689688	-1.1502228	0.1881940
H	-2.2546899	0.3466871	1.0716386
C	0.1921937	-2.3874221	0.5229368
H	0.8523070	-2.8592224	1.2592449
H	0.4303977	-2.8012144	-0.4619921
H	-0.8355149	-2.6766195	0.7668419
C	-3.4358593	0.5994052	-0.7436400
H	-4.4070363	0.4893568	-0.2484514
H	-3.5135441	0.1659690	-1.7462520
H	-3.2428033	1.6713932	-0.8578639
C	1.1693607	2.1602233	-0.9013936
H	1.3790596	3.2137203	-0.6854025
H	1.2369592	2.0145574	-1.9843513
H	1.9601244	1.5630941	-0.4355276

(2-OMe-C_6H_4)$_3$P

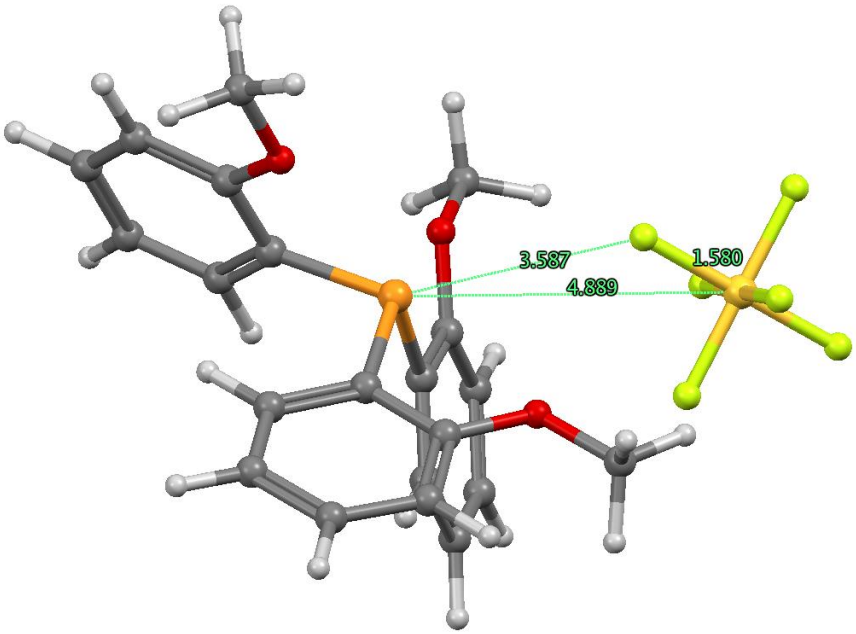


E(TPSS-D3/def2-TZVP) = -1380.548874095 (conv)
Lowest Freq. = 23.61 cm^-1
46
P(oOMePh)3 (020/c1/tpss-d3.def2-TZVP)

P	0.2835248	-0.4243899	-1.4294559
C	1.3525911	-1.1165525	-0.1019487
C	1.5611392	-2.5129705	-0.0926535
C	2.0393923	-0.3445793	0.8375795
C	2.9156699	-0.9249158	1.7577308
C	2.4294061	-3.1058950	0.8276881
C	3.1075909	-2.3034800	1.7488411
H	3.4370960	-0.3015997	2.4781749
H	2.5811827	-4.1795805	0.8334426
C	0.3896427	1.3750945	-1.0623985
C	1.5510855	2.0598019	-1.4817232
C	-0.6369217	2.1211443	-0.4793720
C	-0.5321657	3.5048379	-0.3188585
C	1.6704370	3.4426211	-1.3201956
C	0.6211098	4.1603215	-0.7404116
H	-1.3450509	4.0612432	0.1383979
H	2.5669796	3.9620171	-1.6402151
C	-1.3895812	-0.8184211	-0.7740122
C	-1.6253446	-1.5130331	0.4143507
C	-2.5018827	-0.4737823	-1.5725897
C	-3.8001342	-0.8175416	-1.1868335
C	-2.9179468	-1.8684530	0.8070581
C	-4.0004164	-1.5193395	0.0047070
H	-4.6507930	-0.5459059	-1.8020426
H	-3.0736775	-2.4080255	1.7365935
O	-2.2048697	0.2234165	-2.7125036
O	2.5271953	1.2689643	-2.0249054
O	0.8428445	-3.2136794	-1.0236362
H	-5.0115725	-1.7857107	0.3000554
H	-0.7799188	-1.7754771	1.0432000
H	1.8800144	0.7294388	0.8489110
H	3.7836717	-2.7685516	2.4610512
H	-1.5313124	1.6058940	-0.1422192
H	0.7173362	5.2357167	-0.6184989

C	-3.2859156	0.6224024	-3.5550028
H	-3.9718312	1.2923119	-3.0212815
H	-3.8373820	-0.2497366	-3.9282587
H	-2.8241322	1.1529827	-4.3879535
C	3.7363081	1.8953533	-2.4528518
H	3.5403768	2.6332816	-3.2409861
H	4.3571422	1.0898402	-2.8456236
H	4.2453396	2.3807815	-1.6106285
C	0.9925748	-4.6328805	-1.0566083
H	0.3408826	-4.9748555	-1.8609392
H	0.6779854	-5.0822123	-0.1062081
H	2.0308157	-4.9146790	-1.2725888

$(2\text{-OMe-}C_6H_4)_3P\text{-}SF_6$

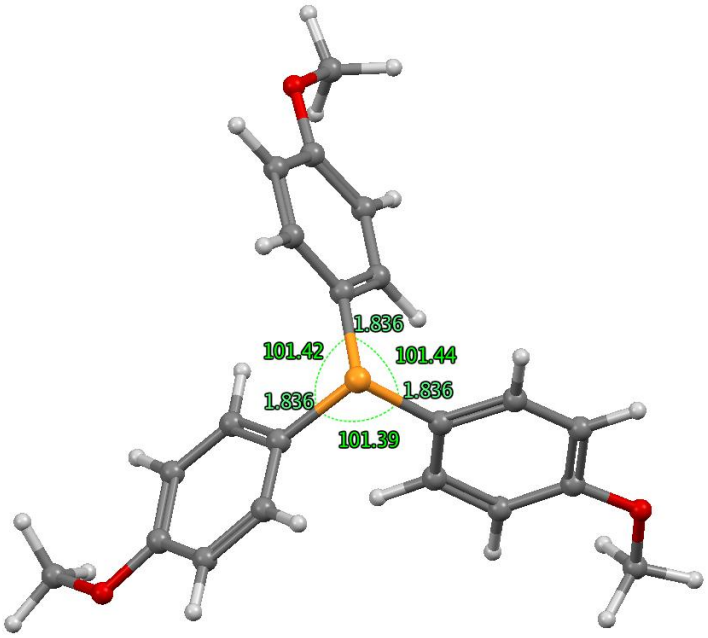


E(TPSS-D3/def2-TZVP) = -2378.101863743 (conv)
Lowest Freq. = 11.51 cm^-1
53
P(oOMePh)3-SF6 (021/c1/tpss-d3.def2-TZVP)

P	-0.2564029	-0.1235448	-1.0863655
C	0.9247500	-0.8641761	0.1121672
C	1.1056273	-2.2641637	0.0730401
C	1.7279235	-0.1235757	0.9823382
C	2.6900132	-0.7382164	1.7870505
C	2.0555407	-2.8913213	0.8825576
C	2.8499874	-2.1199226	1.7343246
H	3.3025973	-0.1387986	2.4539997
H	2.1860791	-3.9672591	0.8500608
C	-0.1538663	1.6577156	-0.6363082
C	0.9416667	2.4028798	-1.1244244
C	-1.1410602	2.3374188	0.0814026
C	-1.0623869	3.7129915	0.3092110
C	1.0343567	3.7788393	-0.8966982
C	0.0255888	4.4288420	-0.1816507
H	-1.8435256	4.2154652	0.8720077
H	1.8797963	4.3457262	-1.2700955
C	-1.8689518	-0.5795551	-0.3279959
C	-2.0058270	-1.3174940	0.8495217
C	-3.0416224	-0.2302106	-1.0323089

C	-4.3022474	-0.6156705	-0.5686372
C	-3.2599352	-1.7136492	1.3200018
C	-4.4033117	-1.3622412	0.6080536
H	-5.1997216	-0.3410953	-1.1117814
H	-3.3387455	-2.2869394	2.2390111
F	3.9339878	-1.0930043	-1.8414059
S	3.7674410	-2.0082239	-3.1246885
F	3.6165891	-2.9290524	-4.4164276
F	3.5995962	-3.2904794	-2.1963618
F	3.9521237	-0.7322878	-4.0634096
F	2.2052902	-1.7751950	-3.1050867
F	5.3440208	-2.2459052	-3.1537945
O	0.2824928	-2.9313103	-0.7935183
O	1.8872384	1.6806143	-1.8021051
O	-2.8405447	0.5153798	-2.1622742
H	-5.3854026	-1.6614640	0.9638249
H	-1.1126915	-1.5824988	1.4073401
H	-1.9843219	1.7750159	0.4707317
H	0.1024716	5.4989134	-0.0095696
H	1.5927333	0.9526181	1.0310870
H	3.5914335	-2.6113075	2.3582599
C	3.0285647	2.3810550	-2.2992367
H	3.5907426	2.8442679	-1.4786729
H	2.7328508	3.1495521	-3.0243421
H	3.6435502	1.6271199	-2.7886072
C	0.3873012	-4.3537874	-0.8598500
H	1.3888966	-4.6606882	-1.1842121
H	-0.3528082	-4.6644650	-1.5975982
H	0.1574473	-4.8080074	0.1121192
C	-3.9861483	0.9173659	-2.9130791
H	-4.6480001	1.5506289	-2.3090172
H	-4.5426244	0.0456952	-3.2799885
H	-3.5951878	1.4884492	-3.7554804

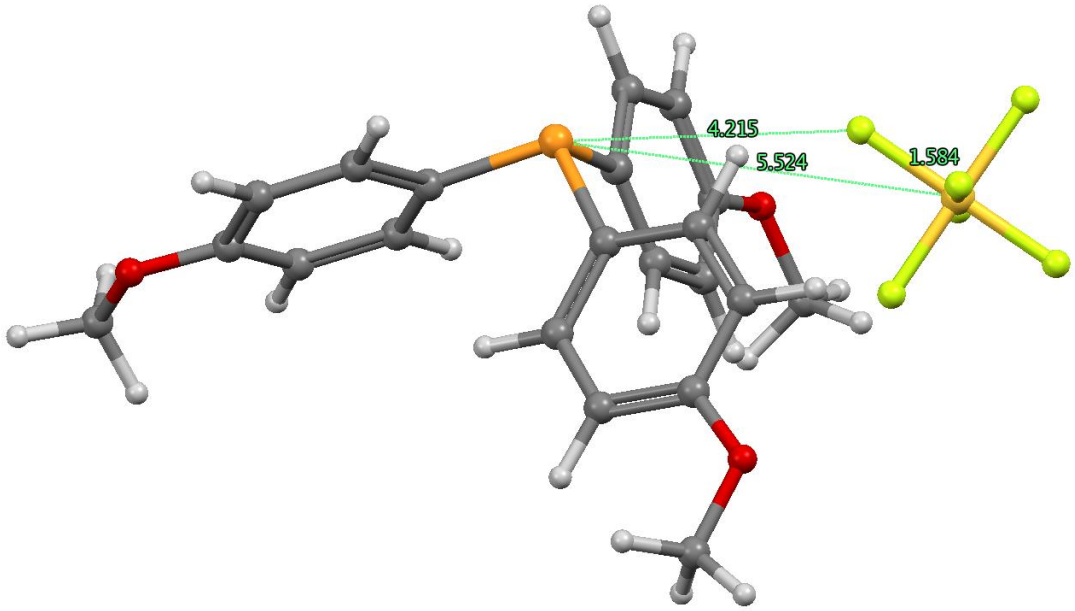
$(4\text{-OMe-}C_6H_4)_3P$



E(TPSS-D3/def2-TZVP) = -1380.548337127 (conv)
Lowest Freq. = 20.64 cm^-1
46
P(pOMePh)3 (022/c1/tpss-d3.def2-TZVP)

P	0.3380420	-0.4093530	-1.4912579
C	1.4106055	-1.1335571	-0.1885601
C	1.7846167	-2.4838661	-0.3212402
C	1.8891980	-0.4263540	0.9181002
C	2.7082091	-1.0341282	1.8733042
C	2.5833982	-3.1072564	0.6252687
C	3.0531059	-2.3820579	1.7303545
H	1.6235357	0.6194743	1.0417018
H	1.4378266	-3.0514436	-1.1818191
H	3.0656241	-0.4521119	2.7156057
H	2.8685839	-4.1501074	0.5249096
C	0.4231069	1.3780213	-1.0790828
C	1.4848688	2.1269246	-1.6200066
C	-0.5047729	2.0436004	-0.2729241
C	-0.3866792	3.4089295	0.0000420
C	1.6263854	3.4788907	-1.3466834
C	0.6863189	4.1297864	-0.5340697
H	-1.3388133	1.4924558	0.1516921
H	2.2116446	1.6350750	-2.2625740
H	-1.1288086	3.8927365	0.6254899
H	2.4480169	4.0556758	-1.7604682
C	-1.3339331	-0.8463089	-0.8708163
C	-1.5902328	-1.3549048	0.4057564
C	-2.4251347	-0.6663596	-1.7412050
C	-3.7208537	-0.9586324	-1.3432093
C	-2.8876134	-1.6699637	0.8180750
C	-3.9593372	-1.4656141	-0.0571955
H	-2.2495921	-0.2875441	-2.7455264
H	-0.7659934	-1.5122884	1.0953057
H	-4.5632110	-0.8158000	-2.0132694
H	-3.0476286	-2.0681138	1.8139922
O	3.8457618	-3.0753944	2.6057069
O	0.8991592	5.4668753	-0.3291197
O	-5.2675001	-1.7353708	0.2445167
C	4.3508678	-2.3606939	3.7360575
H	4.9504559	-3.0813003	4.2930138
H	3.5321933	-1.9919026	4.3669355
H	4.9794876	-1.5185858	3.4204784
C	-5.5426506	-2.2633040	1.5442087
H	-5.0346789	-3.2242305	1.6943627
H	-6.6230283	-2.4068987	1.5783274
H	-5.2363980	-1.5592929	2.3283245
C	-0.0484307	6.1617250	0.4851205
H	0.2973413	7.1953368	0.5180966
H	-0.0750661	5.7460397	1.5003510
H	-1.0522943	6.1192317	0.0442089

(4-OMe-C_6H_4)$_3$P-SF_6

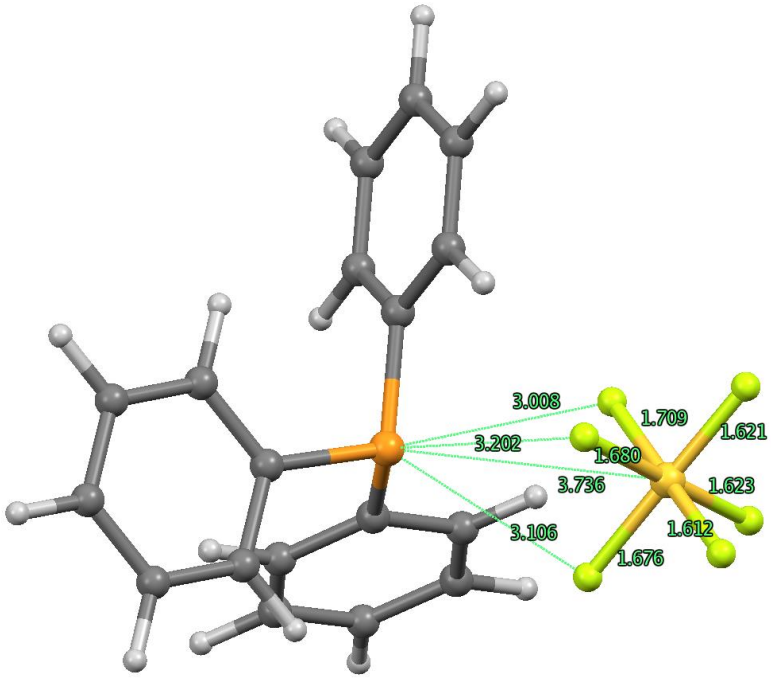


E(TPSS-D3/def2-TZVP) = -2378.100767722 (conv)
Lowest Freq. = 3.35 cm^-1
53
P(pOMePh)3-SF6 (023/c1/tpss-d3.def2-TZVP)

P	-1.0833341	-0.5334827	-1.1023451
C	0.1888764	-1.3218436	-0.0387769
C	0.5454724	-2.6553566	-0.3071359
C	0.8516840	-0.6616431	1.0007482
C	1.8406414	-1.2959507	1.7538617
C	1.5202483	-3.3049206	0.4365755
C	2.1805986	-2.6231132	1.4684822
H	0.6070853	0.3739264	1.2192895
H	0.0538537	-3.1843589	-1.1201873
H	2.3438541	-0.7475929	2.5424236
H	1.8008405	-4.3323374	0.2254258
C	-0.6774290	1.2425627	-0.8654086
C	0.3236883	1.7967749	-1.6845175
C	-1.2920722	2.0754901	0.0737588
C	-0.9222876	3.4162787	0.2110347
C	0.7145594	3.1199053	-1.5506907
C	0.0903246	3.9400138	-0.5992084
H	-2.0748024	1.6770979	0.7129467
H	0.8051703	1.1733390	-2.4341203
H	-1.4243555	4.0339416	0.9475302
H	1.4934481	3.5438693	-2.1771359
C	-2.5972528	-0.6989660	-0.0779551
C	-2.6163597	-1.2076308	1.2233518
C	-3.8227397	-0.3120435	-0.6532161
C	-5.0119787	-0.4041669	0.0530071
C	-3.8086558	-1.3239388	1.9436594
C	-5.0113788	-0.9147816	1.3597693
H	-3.8375128	0.0719872	-1.6707781
H	-1.6875947	-1.5223032	1.6899579
H	-5.9558726	-0.0996811	-0.3889558
H	-3.7849190	-1.7284436	2.9495361
F	3.5580691	1.0806503	-0.1183869
S	4.3751413	0.3018587	-1.2333100
F	5.2043646	-0.4721707	-2.3496395

F	4.8491027	-0.7615667	-0.1473785
F	3.9119762	1.3684189	-2.3206907
F	3.1060897	-0.5878336	-1.5586865
F	5.6558474	1.1938119	-0.9111646
O	3.1481384	-3.3307079	2.1289972
O	0.5340152	5.2344917	-0.5443741
O	-6.2331349	-0.9793724	1.9752439
C	-6.2677604	-1.5061980	3.3036628
H	-5.9068868	-2.5421970	3.3258524
H	-7.3155602	-1.4732541	3.6036903
H	-5.6661206	-0.8928620	3.9864227
C	-0.0897189	6.0987517	0.4081516
H	0.3992982	7.0660416	0.2889709
H	0.0593024	5.7304808	1.4311087
H	-1.1637206	6.1974616	0.2061886
C	3.8677057	-2.6489778	3.1598033
H	4.5890868	-3.3730652	3.5395177
H	3.1955779	-2.3353615	3.9684535
H	4.3940310	-1.7742076	2.7581324

Optimized (CAM-B3LYP/def2-SVP) structure of the conical intersection of Ph_3P-SF_6 (S_0/S_1)



41
Coordinates from ORCA-job orca

P	-0.14881013889931	-0.16775076417422	-0.41853810734622
C	0.84389284587418	-0.92526324297377	0.89171446554333
C	1.28552443394731	-2.24029642281345	0.70355552843586
C	1.17565458970153	-0.23934520669622	2.06525260927899
C	1.91401453141374	-0.87793852278580	3.05605582519293
C	2.02011658732727	-2.87325409545541	1.69986263600420
C	2.33195076991780	-2.19481644364137	2.87599484988765
H	0.85045823813418	0.79313299394786	2.20548328852378
H	1.07674258549537	-2.75009256296263	-0.23842156581894
H	2.16617868209493	-0.34324944904547	3.97399859629075
H	2.36553052206163	-3.89764583120175	1.54957369569373
H	2.91434384761901	-2.69222031632708	3.65448524869842
C	0.05400883937385	1.62564081007536	-0.27970258820056
C	1.26659149304723	2.17473363568836	-0.72527966659934
C	-0.94660562724615	2.47007399820207	0.21900048489840
C	-0.72843339974732	3.84184436587059	0.28954108930501
C	1.47587608214569	3.54607624945904	-0.64772598747325
C	0.48162286625805	4.38107546067155	-0.14170831498187
H	-1.89448200718096	2.05347812237826	0.56233360249541
H	2.03541273582586	1.52205345040355	-1.13734836490757
H	-1.50879220539389	4.49356176911442	0.68767575884867
H	2.42153639964177	3.96638795886248	-0.99484451860307
H	0.64916295904549	5.45881899998847	-0.08648476615340
C	-1.88205045356027	-0.53857713761062	-0.05290951094576
C	-2.27735779043888	-1.29210965979171	1.05883897633857
C	-2.85223079777112	-0.10401087115650	-0.96919249597676
C	-4.19458273351710	-0.39011931031362	-0.75738634985494
C	-3.62298653156399	-1.58362317263658	1.26059492737640
C	-4.58222496772458	-1.13212310989243	0.35784963616418
H	-2.54914082723654	0.46083851478028	-1.85410680861243
H	-1.53045081086901	-1.64323820466400	1.77199115752245
H	-4.94258362753520	-0.04228159656691	-1.47236520015825
H	-3.92433101887241	-2.16579733711203	2.13370082461401

H	-5.63673246646003	-1.36435035639162	0.51968517209344
F	2.61954155620592	-0.60892130290471	-1.50893698329789
S	2.27349215197627	-1.05097577134996	-3.12275004815758
F	1.96073604053325	-1.46962409610426	-4.64811156328985
F	3.39688639389094	-2.21496158096030	-3.02274228370818
F	1.12485884427576	0.16431644475200	-3.23179295518624
F	1.11516024004759	-2.14767618788507	-2.59424035874317
F	3.40250116816204	-0.00177022077678	-3.63259993519088

TD-DT calculated electronic excitations of phosphines and R_3P-SF_6 complexes

Only excitations with λ > 260 nm are reported here.

TD-DFT calculated electronic excitations of Ph_3P

Excited States:

Assignment

STATE 1: E= 0.156076 au 4.247 eV 34254.7 cm**-1
62a -> 69a : 0.010475 (c= 0.10234560)
68a -> 69a : 0.945081 (c= 0.97215269) n(P)→π*(Ar)
68a -> 70a : 0.013722 (c= 0.11714164)

STATE 2: E= 0.156522 au 4.259 eV 34352.7 cm**-1
62a -> 70a : 0.010573 (c= -0.10282343)
68a -> 69a : 0.013210 (c= 0.11493275)
68a -> 70a : 0.942501 (c= -0.97082506) n(P)→π*(Ar)

STATE 3: E= 0.158540 au 4.314 eV 34795.5 cm**-1
66a -> 69a : 0.018442 (c= 0.13580163)
67a -> 70a : 0.016904 (c= -0.13001483)
68a -> 71a : 0.929061 (c= -0.96387797) n(P)→π*(Ar)

UV/VIS Absorptions:

State	Energy (cm-1)	Wavelength (nm)	fosc (au**2)	T2 (au)	TX (au)	TY (au)	TZ
1	34254.7	291.9	0.129522972	1.24481	0.20559	-1.03897	0.35084
2	34352.7	291.1	0.130001320	1.24584	1.07059	0.26772	0.16735
3	34795.5	287.4	0.002728884	0.02582	-0.09845	0.00608	-0.12685

TD-DFT calculated electronic excitations of Ph_3P-SF_6

Excited States:

	Assignment
STATE 1: E= 0.086861 au 2.364 eV 19063.8 cm**-1	
103a -> 104a : 0.996184 (c= 0.99809010)	n(P)→σ*(SF_6)
STATE 2: E= 0.122171 au 3.324 eV 26813.4 cm**-1	
98a -> 104a : 0.023659 (c= 0.15381435)	
99a -> 104a : 0.052547 (c= 0.22923049)	
101a -> 104a : 0.153617 (c= 0.39194007)	π(Ar)→σ*(SF_6)
102a -> 104a : 0.768874 (c= 0.87685461)	π(Ar)→σ*(SF_6)
STATE 3: E= 0.126557 au 3.444 eV 27776.1 cm**-1	
99a -> 104a : 0.017426 (c= 0.13200796)	
100a -> 104a : 0.111794 (c= -0.33435600)	π(Ar)→σ*(SF_6)
101a -> 104a : 0.737662 (c= -0.85887254)	π(Ar)→σ*(SF_6)
102a -> 104a : 0.118302 (c= 0.34394993)	π(Ar)→σ*(SF_6)
STATE 4: E= 0.155252 au 4.225 eV 34073.9 cm**-1	
103a -> 105a : 0.947834 (c= -0.97356770)	n(P)→π*(Ar)
103a -> 107a : 0.011641 (c= -0.10789461)	
STATE 5: E= 0.157553 au 4.287 eV 34578.9 cm**-1	
103a -> 106a : 0.808694 (c= 0.89927413)	n(P)→π*(Ar)
103a -> 107a : 0.126354 (c= -0.35546344)	
STATE 6: E= 0.153412 au 4.175 eV 33670.1 cm**-1	
98a -> 104a : 0.100783 (c= -0.31746364)	
100a -> 104a : 0.393900 (c= -0.62761428)	π(Ar)→σ*(SF_6)
101a -> 104a : 0.047213 (c= 0.21728543)	
103a -> 106a : 0.035771 (c= -0.18913248)	
103a -> 107a : 0.385718 (c= -0.62106179)	n(P)→π*(Ar)
STATE 7: E= 0.156473 au 4.258 eV 34341.9 cm**-1	
98a -> 104a : 0.072487 (c= -0.26923498)	
100a -> 104a : 0.334782 (c= -0.57860327)	π(Ar)→σ*(SF_6)
101a -> 104a : 0.031304 (c= 0.17692997)	
103a -> 106a : 0.108502 (c= 0.32939610)	n(P)→π*(Ar)
103a -> 107a : 0.412003 (c= 0.64187448)	n(P)→π*(Ar)
STATE 8: E= 0.127289 au 3.464 eV 27936.6 cm**-1	
97a -> 104a : 0.011998 (c= 0.10953427)	
98a -> 104a : 0.011513 (c= -0.10729887)	
99a -> 104a : 0.868155 (c= -0.93174832)	π(Ar)→σ*(SF_6)
100a -> 104a : 0.010575 (c= 0.10283325)	
102a -> 104a : 0.087949 (c= 0.29656224)	
STATE 9: E= 0.124444 au 3.386 eV 27312.2 cm**-1	
98a -> 104a : 0.783139 (c= -0.88495144)	π(Ar)→σ*(SF_6)
99a -> 104a : 0.039307 (c= 0.19826032)	π(Ar)→σ*(SF_6)
100a -> 104a : 0.136511 (c= 0.36947363)	π(Ar)→σ*(SF_6)
101a -> 104a : 0.015597 (c= -0.12488830)	
102a -> 104a : 0.023556 (c= 0.15347911)	

UV/VIS Absorptions:

State	Energy (cm-1)	Wavelength (nm)	fosc (au**2)	T2 (au)	TX (au)	TY (au)	TZ	π(Ar)→π*(Ar)
1	19063.8	524.6	0.000606085	0.01047	0.08003	-0.01820	-0.06108	
2	26813.4	372.9	0.000098217	0.00121	0.02044	0.02206	0.01736	
3	27776.1	360.0	0.000450328	0.00534	-0.02377	0.03026	0.06211	
4	34073.9	293.5	0.105510946	1.01941	-0.48601	-0.85580	0.22543	
5	34578.9	289.2	0.095445249	0.90870	-0.71639	0.60464	-0.17289	
6	33670.1	297.0	0.017871055	0.17474	0.40242	0.02293	0.11075	
7	34341.9	291.2	0.042748337	0.40980	-0.62638	0.08112	-0.10422	
8	27936.6	358.0	0.000883155	0.01041	0.08892	-0.00938	-0.04912	
9	27312.2	366.1	0.000092286	0.00111	-0.03062	-0.01256	-0.00413	

TD-DFT calculated electronic excitations of Mes_3P

Excited States:

	Assignment
STATE 1: E= 0.135169 au 3.678 eV 29666.2 cm**-1	
104a -> 105a : 0.962056 (c= -0.98084464)	n(P)→π*(Ar)
STATE 2: E= 0.135454 au 3.686 eV 29728.6 cm**-1	
104a -> 106a : 0.962327 (c= 0.98098290)	n(P)→π*(Ar)
STATE 3: E= 0.153152 au 4.167 eV 33613.1 cm**-1	
100a -> 106a : 0.031675 (c= 0.17797333)	
101a -> 106a : 0.011474 (c= 0.10711807)	
104a -> 107a : 0.876175 (c= 0.93604195)	n(P)→π*(Ar)
104a -> 109a : 0.015748 (c= 0.12549223)	
104a -> 110a : 0.022069 (c= 0.14855766)	
STATE 4: E= 0.150769 au 4.103 eV 33090.0 cm**-1	
99a -> 105a : 0.019434 (c= -0.13940583)	
102a -> 105a : 0.011216 (c= 0.10590399)	
103a -> 105a : 0.030142 (c= -0.17361545)	
104a -> 108a : 0.891971 (c= -0.94444212)	n(P)→π*(Ar)
104a -> 109a : 0.010361 (c= 0.10178863)	
STATE 5: E= 0.154576 au 4.206 eV 33925.4 cm**-1	
103a -> 106a : 0.034383 (c= -0.18542778)	
104a -> 107a : 0.016351 (c= 0.12786909)	
104a -> 109a : 0.886769 (c= -0.94168393)	n(P)→π*(Ar)
STATE 6: E= 0.170840 au 4.649 eV 37495.0 cm**-1	
101a -> 105a : 0.054621 (c= -0.23371156)	
102a -> 106a : 0.047213 (c= 0.21728629)	
104a -> 107a : 0.024764 (c= -0.15736728)	
104a -> 110a : 0.830516 (c= 0.91132643)	n(P)→π*(Ar)

UV/VIS Absorptions:

State	Energy (cm-1)	Wavelength (nm)	fosc (au**2)	T2 (au)	TX (au)	TY (au)	TZ
1	29666.2	337.1	0.213041391	2.36416	0.33146	1.45880	-0.35524
2	29728.6	336.4	0.215237636	2.38352	-1.46998	0.23401	-0.40978
3	33613.1	297.5	0.003164218	0.03099	0.13081	0.03074	-0.11374
4	33090.0	302.2	0.006847765	0.06813	-0.23000	0.02762	-0.12028
5	33925.4	294.8	0.008486695	0.08235	0.02353	0.28533	-0.01974
6	37495.0	266.7	0.012839860	0.11274	0.06762	-0.08312	-0.31820

TD-DFT calculated electronic excitations of Mes_3P-SF_6

Excited States:

		Assignment
STATE 1: E= 0.084370 au 2.296 eV 18517.0 cm**-1		
139a -> 140a : 0.997153 (c= 0.99857554)		n(P)→σ*(SF_6)
STATE 2: E= 0.124188 au 3.379 eV 27256.1 cm**-1		
134a -> 140a : 0.017994 (c= -0.13414326)		
135a -> 140a : 0.078256 (c= -0.27974351)		
136a -> 140a : 0.054391 (c= -0.23321937)		
138a -> 140a : 0.847227 (c= 0.92044944)		π(Ar)→σ*(SF_6)
STATE 3: E= 0.130439 au 3.549 eV 28628.0 cm**-1		
133a -> 140a : 0.015422 (c= 0.12418533)		
134a -> 140a : 0.030723 (c= -0.17527887)		
137a -> 140a : 0.922657 (c= 0.96055019)		π(Ar)→σ*(SF_6)
STATE 4: E= 0.136525 au 3.715 eV 29963.8 cm**-1		
139a -> 141a : 0.958127 (c= 0.97883986)		n(P)→π*(Ar)
STATE 5: E= 0.138623 au 3.772 eV 30424.2 cm**-1		
139a -> 142a : 0.953192 (c= -0.97631555)		n(P)→π*(Ar)
STATE 6: E= 0.127361 au 3.466 eV 27952.4 cm**-1		
134a -> 140a : 0.012136 (c= -0.11016499)		
135a -> 140a : 0.037636 (c= 0.19400038)		
136a -> 140a : 0.869511 (c= 0.93247555)		π(Ar)→σ*(SF_6)
138a -> 140a : 0.076811 (c= 0.27714755)		
STATE 7: E= 0.133536 au 3.634 eV 29307.8 cm**-1		
135a -> 140a : 0.865677 (c= 0.93041780)		π(Ar)→σ*(SF_6)
136a -> 140a : 0.066490 (c= -0.25785662)		
138a -> 140a : 0.044764 (c= 0.21157576)		
STATE 8: E= 0.128771 au 3.504 eV 28262.0 cm**-1		
134a -> 140a : 0.930379 (c= 0.96456142)		π(Ar)→σ*(SF_6)
137a -> 140a : 0.035748 (c= 0.18907064)		
138a -> 140a : 0.026629 (c= 0.16318444)		
STATE 9: E= 0.152115 au 4.139 eV 33385.5 cm**-1		
134a -> 141a : 0.028163 (c= 0.16781758)		
139a -> 143a : 0.922756 (c= 0.96060195)		n(P)→π*(Ar)
STATE 10: E= 0.155244 au 4.224 eV 34072.0 cm**-1		
135a -> 141a : 0.015172 (c= -0.12317525)		
138a -> 141a : 0.019574 (c= -0.13990675)		
138a -> 142a : 0.011962 (c= 0.10937207)		
139a -> 144a : 0.907236 (c= -0.95248918)		n(P)→π*(Ar)
STATE 11: E= 0.155718 au 4.237 eV 34176.2 cm**-1		
135a -> 142a : 0.018709 (c= -0.13678120)		
138a -> 142a : 0.041266 (c= 0.20314050)		
139a -> 145a : 0.858179 (c= -0.92637948)		n(P)→π*(Ar)
139a -> 146a : 0.040410 (c= -0.20102170)		
STATE 12: E= 0.151820 au 4.131 eV 33320.5 cm**-1		
133a -> 140a : 0.972155 (c= -0.98597942)		π(Ar)→σ*(SF_6)

137a -> 140a : 0.011200 (c= 0.10583167)

STATE 13: E= 0.171765 au 4.674 eV 37698.1 cm**-1
136a -> 141a : 0.047571 (c= -0.21810753)
137a -> 142a : 0.053056 (c= 0.23033789)
139a -> 145a : 0.041210 (c= -0.20300149)
139a -> 146a : 0.817590 (c= 0.90420685) n(P)→π*(Ar)

UV/VIS Absorptions:

State	Energy (cm-1)	Wavelength (nm)	fosc (au**2)	T2 (au)	TX (au)	TY (au)	TZ
1	18517.0	540.0	0.000244680	0.00435	0.03824	-0.01144	-0.05251
2	27256.1	366.9	0.000024941	0.00030	-0.01184	-0.00808	-0.00979
3	28628.0	349.3	0.003453138	0.03971	-0.10498	0.16881	-0.01387
4	29963.8	333.7	0.210879193	2.31692	0.78343	1.27725	-0.26795
5	30424.2	328.7	0.225572584	2.44086	-1.34365	0.74648	-0.27971
6	27952.4	357.8	0.000135862	0.00160	0.02465	-0.03106	0.00523
7	29307.8	341.2	0.000121647	0.00137	0.03175	-0.00241	0.01877
8	28262.0	353.8	0.000050521	0.00059	-0.00916	0.02081	-0.00846
9	33385.5	299.5	0.006318732	0.06231	-0.08236	0.22557	0.06815
10	34072.0	293.5	0.009836875	0.09505	0.29797	-0.04303	0.06642
11	34176.2	292.6	0.005217208	0.05026	0.04856	0.17544	-0.13084
12	33320.5	300.1	0.000012048	0.00012	0.00286	0.00164	-0.01040
13	37698.1	265.3	0.013059688	0.11405	0.03696	0.04434	0.33274

TD-DFT calculated electronic excitations of Et_3P-SF_6

Excited States:

Assignment

STATE 1: E= 0.078413 au 2.134 eV 17209.7 cm**-1
67a -> 68a : 0.999297 (c= -0.99964835) n(P)→σ*(SF_6)

STATE 2: E= 0.156305 au 4.253 eV 34304.9 cm**-1
65a -> 68a : 0.077675 (c= 0.27870261)
66a -> 68a : 0.921376 (c= 0.95988355) σ(P-C)→σ*(SF_6)

STATE 3: E= 0.153296 au 4.171 eV 33644.6 cm**-1
65a -> 68a : 0.920979 (c= 0.95967658) σ(P-C)→σ*(SF_6)
66a -> 68a : 0.077568 (c= -0.27851043)

UV/VIS Absorptions:

State	Energy (cm-1)	Wavelength (nm)	fosc (au**2)	T2 (au)	TX (au)	TY (au)	TZ
1	17209.7	581.1	0.007307751	0.13979	-0.31322	0.10266	0.17648
2	34304.9	291.5	0.000068063	0.00065	0.00109	0.02532	0.00330
3	33644.6	297.2	0.000074602	0.00073	-0.00833	0.02554	0.00285

TD-DFT calculated electronic excitations of (2-OMe-C_6H_4)$_3$P

Excited States:

		Assignment
STATE 1: E= 0.151538 au 4.124 eV 33258.8 cm**-1		
92a -> 93a :	0.964646 (c= 0.98216397)	n(P)→π*(Ar)
STATE 2: E= 0.152207 au 4.142 eV 33405.5 cm**-1		
92a -> 94a :	0.964248 (c= -0.98196127)	n(P)→π*(Ar)
STATE 3: E= 0.168461 au 4.584 eV 36973.0 cm**-1		
87a -> 93a :	0.017246 (c= -0.13132237)	
88a -> 94a :	0.016704 (c= 0.12924312)	
89a -> 96a :	0.041280 (c= -0.20317523)	
90a -> 93a :	0.068998 (c= -0.26267481)	
91a -> 93a :	0.011089 (c= -0.10530224)	
91a -> 94a :	0.059999 (c= -0.24494665)	
92a -> 95a :	0.481551 (c= 0.69393892)	n(P)→π*(Ar)
92a -> 96a :	0.268018 (c= -0.51770483)	n(P)→π*(Ar)
STATE 4: E= 0.174815 au 4.757 eV 38367.6 cm**-1		
89a -> 94a :	0.019497 (c= 0.13963109)	
90a -> 93a :	0.318440 (c= 0.56430467)	π(Ar)→π*(Ar)
91a -> 93a :	0.267880 (c= -0.51757145)	π(Ar)→π*(Ar)
91a -> 94a :	0.031460 (c= 0.17736899)	
92a -> 95a :	0.181256 (c= 0.42574148)	π(Ar)→π*(Ar)
92a -> 96a :	0.081841 (c= 0.28607881)	
92a -> 98a :	0.048211 (c= -0.21957068)	

UV/VIS Absorptions:

State	Energy (cm-1)	Wavelength (nm)	fosc (au**2)	T2 (au)	TX (au)	TY (au)	TZ
1	33258.8	300.7	0.147138393	1.45645	0.86741	-0.72982	0.41400
2	33405.5	299.4	0.147697463	1.45556	-0.80271	-0.89513	0.09983
3	36973.0	270.5	0.004817094	0.04289	-0.04623	0.05534	0.19414
4	38367.6	260.6	0.021223631	0.18211	-0.39472	-0.02293	0.16055

TD-DFT calculated electronic excitations of (2-OMe-C_6H_4)$_3$P-SF_6

Excited States:

Assignment

STATE 1: E= 0.097063 au 2.641 eV 21302.8 cm**-1
127a -> 128a : 0.987234 (c= 0.99359670) n(P)→σ*(SF_6)

STATE 2: E= 0.117861 au 3.207 eV 25867.6 cm**-1
124a -> 128a : 0.038421 (c= 0.19601384)
125a -> 128a : 0.019985 (c= 0.14136917)
126a -> 128a : 0.931705 (c= 0.96524870) π(Ar)→σ*(SF_6)

STATE 3: E= 0.118451 au 3.223 eV 25996.9 cm**-1
124a -> 128a : 0.070038 (c= -0.26464622)
125a -> 128a : 0.888672 (c= -0.94269418) π(Ar)→σ*(SF_6)
126a -> 128a : 0.037915 (c= 0.19471843)

STATE 4: E= 0.125884 au 3.425 eV 27628.3 cm**-1
124a -> 128a : 0.876555 (c= 0.93624495) π(Ar)→σ*(SF_6)
125a -> 128a : 0.087584 (c= -0.29594516)
126a -> 128a : 0.020823 (c= -0.14430318)

STATE 5: E= 0.146069 au 3.975 eV 32058.4 cm**-1
121a -> 128a : 0.014962 (c= -0.12231951)
122a -> 128a : 0.051301 (c= 0.22649625)
123a -> 128a : 0.909395 (c= 0.95362199) π(Ar)→σ*(SF_6)
124a -> 128a : 0.012235 (c= -0.11061007)

STATE 6: E= 0.151005 au 4.109 eV 33141.7 cm**-1
127a -> 129a : 0.960689 (c= 0.98014729) n(P)→π*(Ar)

STATE 7: E= 0.153228 au 4.170 eV 33629.6 cm**-1
127a -> 130a : 0.951650 (c= -0.97552544) n(P)→π*(Ar)

STATE 8: E= 0.145037 au 3.947 eV 31832.0 cm**-1
122a -> 128a : 0.938215 (c= -0.96861481) π(Ar)→σ*(SF_6)
123a -> 128a : 0.057034 (c= 0.23881781)

STATE 9: E= 0.167548 au 4.559 eV 36772.6 cm**-1
122a -> 129a : 0.015324 (c= 0.12379019)
123a -> 130a : 0.015838 (c= -0.12585060)
124a -> 132a : 0.035329 (c= 0.18796072)
125a -> 129a : 0.054488 (c= 0.23342625)
126a -> 130a : 0.042623 (c= -0.20645355)
127a -> 131a : 0.519663 (c= 0.72087686) n(P)→π*(Ar)
127a -> 132a : 0.279739 (c= -0.52890376) n(P)→π*(Ar)

UV/VIS Absorptions:

State	Energy (cm-1)	Wavelength (nm)	fosc (au**2)	T2 (au)	TX (au)	TY (au)	TZ
1	21302.8	469.4	0.003692845	0.05707	0.17021	-0.09403	-0.13876
2	25867.6	386.6	0.001418317	0.01805	-0.08748	0.08085	0.06214
3	25996.9	384.7	0.000888841	0.01126	0.08834	-0.02834	-0.05146
4	27628.3	361.9	0.000784866	0.00935	-0.04783	0.04748	0.06935
5	32058.4	311.9	0.000917902	0.00943	-0.08856	0.02152	-0.03348
6	33141.7	301.7	0.137981294	1.37063	0.75084	0.88991	-0.12221

7	33629.6	297.4	0.159683340	1.56320	0.95160	-0.76634	0.26531
8	31832.0	314.1	0.000514410	0.00532	-0.03391	-0.06115	0.02075
9	36772.6	271.9	0.006429305	0.05756	0.02206	0.03612	0.23615

TD-DFT calculated electronic excitations of (4-OMe-C_6H_4)$_3$P

Excited States:

Assignment

STATE 1: E= 0.150089 au 4.084 eV 32940.7 cm**-1
89a -> 95a : 0.010189 (c= 0.10094044)
92a -> 93a : 0.953264 (c= 0.97635238) n(P)→π*(Ar)

STATE 2: E= 0.158000 au 4.299 eV 34677.0 cm**-1
92a -> 94a : 0.919020 (c= -0.95865505) n(P)→π*(Ar)
92a -> 95a : 0.022762 (c= 0.15086965)

STATE 3: E= 0.158179 au 4.304 eV 34716.3 cm**-1
92a -> 94a : 0.022711 (c= 0.15070153)
92a -> 95a : 0.918320 (c= 0.95828997) n(P)→π*(Ar)

STATE 4: E= 0.167204 au 4.550 eV 36697.1 cm**-1
86a -> 94a : 0.016497 (c= 0.12844138)
89a -> 95a : 0.010268 (c= 0.10133015)
92a -> 96a : 0.928593 (c= -0.96363543) n(P)→π*(Ar)

STATE 5: E= 0.167373 au 4.554 eV 36734.1 cm**-1
86a -> 95a : 0.015709 (c= 0.12533664)
89a -> 94a : 0.010418 (c= 0.10206632)
89a -> 98a : 0.012391 (c= 0.11131318)
92a -> 97a : 0.927619 (c= 0.96312961) n(P)→π*(Ar)

UV/VIS Absorptions:

State	Energy (cm-1)	Wavelength (nm)	fosc (au**2)	T2 (au)	TX (au)	TY (au)	TZ
1	32940.7	303.6	0.008221656	0.08217	0.06698	-0.06345	-0.27140
2	34677.0	288.4	0.170457324	1.61826	-0.18095	-1.22595	0.28736
3	34716.3	288.0	0.169374486	1.60616	-1.22406	0.11922	-0.30597
4	36697.1	272.5	0.009779757	0.08773	-0.05734	-0.28510	0.05626
5	36734.1	272.2	0.010475038	0.09388	0.29299	-0.04056	0.07994

TD-DFT calculated electronic excitations of (4-OMe-C_6H_4)$_3$P-SF_6

Excited States:

		Assignment
STATE 1: E= 0.078198 au 2.128 eV 17162.6 cm**-1		
126a -> 128a :	0.013222 (c= 0.11498503)	
127a -> 128a :	0.985982 (c= 0.99296643)	n(P)→σ*(SF_6)
STATE 2: E= 0.106356 au 2.894 eV 23342.5 cm**-1		
125a -> 128a :	0.494748 (c= 0.70338296)	π(Ar)→σ*(SF_6)
126a -> 128a :	0.492470 (c= 0.70176189)	π(Ar)→σ*(SF_6)
STATE 3: E= 0.102539 au 2.790 eV 22504.7 cm**-1		
125a -> 128a :	0.502631 (c= -0.70896460)	π(Ar)→σ*(SF_6)
126a -> 128a :	0.480913 (c= 0.69347900)	π(Ar)→σ*(SF_6)
STATE 4: E= 0.151682 au 4.127 eV 33290.3 cm**-1		
127a -> 129a :	0.947260 (c= 0.97327280)	n(P)→π*(Ar)
STATE 5: E= 0.128936 au 3.509 eV 28298.3 cm**-1		
121a -> 128a :	0.041415 (c= 0.20350788)	
122a -> 128a :	0.058024 (c= 0.24088241)	
123a -> 128a :	0.454038 (c= 0.67382313)	π(Ar)→σ*(SF_6)
124a -> 128a :	0.438359 (c= -0.66208678)	π(Ar)→σ*(SF_6)
STATE 6: E= 0.131050 au 3.566 eV 28762.1 cm**-1		
121a -> 128a :	0.076833 (c= 0.27718821)	
122a -> 128a :	0.013162 (c= -0.11472657)	
123a -> 128a :	0.456471 (c= -0.67562606)	π(Ar)→σ*(SF_6)
124a -> 128a :	0.419348 (c= -0.64757105)	π(Ar)→σ*(SF_6)
127a -> 130a :	0.024444 (c= -0.15634707)	
STATE 7: E= 0.156733 au 4.265 eV 34399.0 cm**-1		
123a -> 128a :	0.017487 (c= -0.13223900)	
127a -> 130a :	0.895912 (c= 0.94652643)	n(P)→π*(Ar)
127a -> 131a :	0.020919 (c= 0.14463372)	
STATE 8: E= 0.161126 au 4.384 eV 35363.0 cm**-1		
121a -> 128a :	0.010846 (c= 0.10414296)	
122a -> 128a :	0.049273 (c= 0.22197509)	
122a -> 131a :	0.013516 (c= 0.11625856)	
127a -> 130a :	0.017434 (c= 0.13203940)	
127a -> 131a :	0.852380 (c= -0.92324426)	n(P)→π*(Ar)
STATE 9: E= 0.132614 au 3.609 eV 29105.4 cm**-1		
121a -> 128a :	0.138436 (c= 0.37207033)	
122a -> 128a :	0.702650 (c= 0.83824241)	π(Ar)→σ*(SF_6)
123a -> 128a :	0.035837 (c= -0.18930790)	
124a -> 128a :	0.047561 (c= 0.21808486)	π(Ar)→σ*(SF_6)
127a -> 131a :	0.062376 (c= 0.24975177)	π(Ar)→π*(Ar)
STATE 10: E= 0.121049 au 3.294 eV 26567.2 cm**-1		
121a -> 128a :	0.727886 (c= -0.85316225)	π(Ar)→σ*(SF_6)
122a -> 128a :	0.170640 (c= 0.41308628)	π(Ar)→σ*(SF_6)
123a -> 128a :	0.024721 (c= -0.15723014)	
STATE 11: E= 0.168161 au 4.576 eV 36907.0 cm**-1		
121a -> 130a :	0.011115 (c= 0.10543003)	

123a -> 134a : 0.011417 (c= 0.10685175)
127a -> 132a : 0.908349 (c= -0.95307369) n(P)→π*(Ar)
127a -> 134a : 0.011897 (c= -0.10907211)

STATE 12: E= 0.170555 au 4.641 eV 37432.6 cm**-1
121a -> 131a : 0.016035 (c= -0.12662879)
123a -> 130a : 0.012318 (c= -0.11098629)
127a -> 133a : 0.913503 (c= 0.95577367) n(P)→π*(Ar)

UV/VIS Absorptions:

State	Energy (cm-1)	Wavelength (nm)	fosc (au**2)	T2 (au)	TX (au)	TY (au)	TZ
1	17162.6	582.7	0.000130797	0.00251	-0.04189	-0.02711	0.00442
2	23342.5	428.4	0.000043429	0.00061	0.00412	0.01399	-0.02000
3	22504.7	444.4	0.000341615	0.00500	0.06876	-0.00769	-0.01452
4	33290.3	300.4	0.014025226	0.13870	0.25491	0.14012	0.23256
5	28298.3	353.4	0.000015664	0.00018	0.00407	0.00605	-0.01136
6	28762.1	347.7	0.001266909	0.01450	0.00390	-0.10674	0.05562
7	34399.0	290.7	0.137763314	1.31845	-0.98398	0.58621	-0.08111
8	35363.0	282.8	0.174122789	1.62100	0.63638	1.02123	-0.41607
9	29105.4	343.6	0.011059738	0.12510	-0.19373	-0.27219	0.11608
10	26567.2	376.4	0.000108911	0.00135	0.02615	-0.02530	0.00508
11	36907.0	271.0	0.009627953	0.08588	0.17814	-0.23270	-0.00006
12	37432.6	267.1	0.012177731	0.10710	-0.27129	-0.16572	0.07770

Literature

[1] M. N. Chevykalova, L. F. Manzhukova, N. V. Artemova, Y. N. Luzikov, I. E. Nifant´ev, E. E. Nifant´ev, *Russ.Chem.Bull., Int. Ed.* **2003**, *52*, 78.

[2] P. W. Dyer, J. Fawcett, M. J. Hanton, R. D. W. Kemmitt, R. Padda, N. Singh, *Dalton Trans.* **2003**, 104.

[3] D. M. Roundhill, S. G. N. Roundhill, W. B. Beaulieu, U. Bagchi, *Inorg. Chem.* **1980**, *19*, 3365.

[4] TURBOMOLE V7.4 2019, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, TURBOMOLE GmbH, since 2007, available from http://www.turbomole.com.

[5] J. Tao, J. P. Perdew, V. N. Staroverov, G. E. Scuseria, *Phys. Rev. Lett.* **2003**, *91*, 146401.

[6] a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456.

[7] F. Weigend, R. Ahlrichs., *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

[8] S. Grimme, *Chem. Eur. J.* **2012**, *18*, 9955.

[9] Y. Zhao, D. G. Truhlar, *J. Phys. Chem. A* **2005**, *109*, 5656.

[10] a) A. Klamt, *J. Phys. Chem.* **1995**, *99*, 2224; b) F. Eckert, A. Klamt, COSMOtherm, Version C3.0, COSMOlogic GmbH & Co. KG, Leverkusen, Germany **2013**.

[11] F. Neese, The ORCA program system, *Wiley Interdiscip. Rev.-Comput. Mol. Sci.* **2012**, *2*, 73.

[12] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.

[13] M. C. V. Barone, *J. Phys. Chem. A* **1998**, *102*, 1995.

[14] T. Yanai, D. P. Tew, N. C. Handy, *Chem. Phys. Lett.* **2004**, *393*, 51.