

Facile Modification of Phosphole-Based Aggregation-Induced Emission Luminogens with Sulfonyl Isocyanates

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1 Experimental

1.1 Methods

General

All reactions were carried out under dry high purity nitrogen using standard SCHLENK techniques. Experiments including elemental lithium were carried out under dry high purity argon. THF was degassed and distilled from potassium. Chloroform, *N,N*-dimethylformamide, diethyl ether, toluene, hexane (mixture of isomers) and dichloromethane were dried and degassed with a solvent purification system SPS-800 SERIES from MBRAUN. Triphenylphosphane oxide, diphenylphosphane oxide, diphenylacetylene, dichlorophenylphosphane, 1,4-diphenylbutadiene, chlorosulfonyl isocyanate (CSI) and *p*-toluenesulfonyl isocyanate (TSI) are commercially available and were used without further purifications. Stock solutions were prepared from CSI and TSI and stored at 4 °C. Lithium was cut into pieces about 2 cm long, peeled, and washed with Et₂O before use.

Analytical Methods

The NMR spectra were recorded with a BRUKER AVANCE DRX 400 spectrometer (¹H NMR 400.13 MHz, ¹³C NMR 100.63 MHz, ³¹P NMR 161.98 MHz) or a BRUKER ASCEND 400 spectrometer (¹H NMR 400.16 MHz, ¹³C NMR 100.63 MHz, ³¹P NMR 161.99 MHz). For ¹H NMR and ¹³C NMR spectra, TMS was used as the internal standard. The ³¹P NMR spectra were referenced to TMS using the Ξ -scale.^[1] Assignment of the configurations and chemical shifts was done using HSQC, HMQC, HMBC, COSY, and NOESY techniques.

Mass spectra (ESI) were measured using a Bruker Daltonics Esquire 3000 Plus spectrometer. High-resolution mass spectra (HRMS; ESI) were measured using a Bruker Daltonics Impact II ESI-TOF spectrometer. IR spectra were recorded on a Thermo Scientific Nicolet iS5 with a diamond ATR (400–4000 cm⁻¹). Elemental analyses were obtained with a Heraeus Vario EL oven. The melting points were determined in glass capillaries sealed under vacuum using a Gallenkamp apparatus and are uncorrected.

Steady-state excitation and emission spectra were recorded on a FluoTime300 spectrometer from PicoQuant equipped with a 300 W ozone-free Xe lamp (250-900 nm), a 10 W Xe flash-lamp (250-900 nm, pulse width < 10 μ s) with repetition rates of 0.1 – 300 Hz, double excitation monochromators (Czerny-Turner type, grating with 1200 g/mm, blazed wavelength: 300 nm), diode lasers (pulse width < 80 ps) operated by a computer-controlled laser driver PDL-828 “Sepia II” (repetition rate up to 80 MHz, burst mode for slow and weak decays), two double-grating emission monochromators (Czerny-Turner, selectable gratings blazed at 500 nm with 2.7 nm/mm dispersion and 1200 grooves/mm, or blazed at 1200 nm with 5.4 nm/mm dispersion and 600 grooves/mm) with adjustable slit width between 25 μ m and 7 mm, Glan-Thompson polarizers for excitation (Xe-lamps) and emission. Different sample holders (Peltier cooled sample mounting unit ranging from – 15 °C to 110 °C and adjustable front face sample holder). Two detectors, namely a PMA Hybrid-07 (transit time spread FWHM < 50 ps, 200 – 850 nm) and an H10330C-45-C3 NIR detector (transit time spread FWHM 0.4 ns, 950-1700 nm) from Hamamatsu. Steady-state and fluorescence lifetimes were recorded in TCSPC mode by a PicoHarp 300 (minimum base resolution 4 ps) or MSC mode by a TimeHarp 260, where up to several ms can be detected. Emission and excitation spectra were corrected for source intensity (lamp and grating) by standard correction curves. For samples with lifetime in ns order instrument response function calibration (IRF) was performed

using a diluted Ludox[®] solution. Lifetime analysis was performed using the commercially available EasyTau 2 software (PicoQuant). The quality of the fit was assessed by minimizing the reduced chi squared function (χ^2) and visual inspection of the weighted residuals and their autocorrelation. The uncertainties for τ_{av_amp} were obtained directly from Easy Tau 2 software at a 95 % of confidence

The rate constants were calculated by applying the following equations:

$$k_r = \frac{\Phi_L}{\tau_L}$$

$$k_{nr} = \frac{1 - \Phi_L}{\tau_L}$$

In case of multiexponential decays, the amplitude-weighted average lifetimes were used for estimation of the rate constants. The uncertainties of the rate constants were calculated by the total differential method using the following equations:

$$\Delta k_r = \frac{\Delta \Phi_L}{\tau_L} + \frac{\Delta \tau}{\tau_L^2} \cdot \Phi_L$$

$$\Delta k_{nr} = \frac{\Delta \tau_L}{\tau_L^2} + \frac{\Delta \Phi_L}{\tau_L} + \frac{\Delta \tau_L}{\tau_L^2} \Phi_L$$

Luminescence quantum yields were measured with a Hamamatsu Photonics absolute PL quantum yield measurement system (C9920-02) equipped with a L9799-01 CW Xenon light source (150 W), monochromator, C7473 photonic multi-channel analyzer, integrating sphere and employing U6039-05 PLQY measurement software (Hamamatsu Photonics, Ltd., Shizuoka, Japan). All solvents used were of spectrometric grade (Uvasol[®]). For all measurements, round quartz cuvettes were used.

The UV/Vis spectra in reflection mode were recorded with a CARY 5000 (AGILENT) with a 150 mm diameter DRA-2500 unit (DRA: diffuse reflection accessory) and a polytetrafluoroethylene coating. The samples were embedded between a metal support and a quartz glass plate. The use of an integrating sphere in combination with a UV/Vis spectrometer in reflection position can completely reflect the light lost by diffuse reflection, by spectralon in integrating sphere and direct it to a detector. This allows absorption in reflection mode. The light absorbed by the sample cannot be detected by the detector. Luminescence spectra were recorded with an inverted confocal microscope (IX71, Olympus) fiber-coupled to a spectrometer (iHR320, synapse CCD, HORIBA JobinYvon) at 355 nm photoexcitation (xenon lamp as source). The light was focused and captured in the backscatter geometry with a 10x objective (Olympus LUCPlan FLN 10x NA = 0.3).

The fully corrected fluorescence spectra, quantum yield and fluorescence lifetimes in solution were measured using a Fluoromax 4 (Horiba) equipped with a 366 nm or 254 nm laser diode and a TCSPC unit (Fluorohub, Horiba):

For all fluorescence spectra the measurements were performed under identical parameter settings except the excitation wavelength, which was chosen according to the absorption behavior of the solution. To avoid aggregation, inner-filter effects and quenching events, the absorption of each solution was adjusted to 0.1 at the excitation wavelength and the linear fluorescence to absorption ratio was controlled. Fluorescence quantum yields were determined for diluted solutions by the comparative approach using 1,6-diphenyl-1,3,5-hexatriene (DPHT) in cyclohexane as standard reference ($\Phi F(R) = 0.78$).

Under the condition of an identical excitation light intensity the fluorescence quantum yields of the samples $\Phi_F(P)$ were determined using:

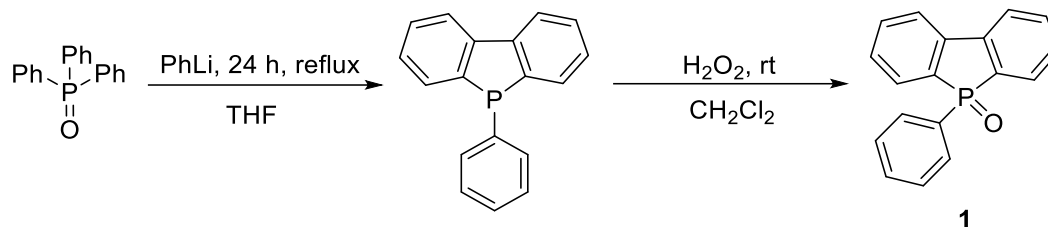
$$\Phi_F(P) = \frac{\varphi_F(R) \cdot A_R \cdot F_P}{A_P \cdot F_R} \cdot \left(\frac{\eta_P}{\eta_R} \right)^2,$$

where A_R and A_P denote the absorption values of the reference and sample solution at the excitation wavelength. As the fluorescence intensity of the reference (F_R) and sample (F_P) solution were determined in different solvents. Therefore, a correction using the refractive indexes of the used solvents ($\eta_R(\text{cyclohexane}) = 1.426$ and $\eta_P(\text{acetonitrile}) = 1.342$) needed to be applied.^[2]

1.2 Synthesis

1.2.1 5-Phenyldibenzophosphole oxide (DBPO) (1)

The synthesis was performed as a modified version of the original report from Ogawa *et al.*^[3]



In a 500 mL two-neck flask with reflux condenser and dropping funnel 9.0 g (32 mmol, 1.0 eq.) triphenylphosphane oxide was dissolved in 200 mL THF and cooled to 0 °C. Then 36 mL (68 mmol, 2.1 eq.) of a 1.9 M phenyllithium solution in dibutyl ether were slowly added. The brown solution was stirred for 24 h under reflux. The reaction mixture was then cooled to 0 °C, hydrolyzed with 20 mL degassed H₂O and the solvents were removed. 150 mL H₂O, 40 mL of a 3 N HCl solution and 200 mL CH₂Cl₂ were added to the brown residue. The organic phase was separated and the aqueous phase extracted twice with 200 mL CH₂Cl₂. The combined organic phases were mixed with 7 mL of a 30 % H₂O₂ solution and stirred at rt for one hour. The organic phase was washed three times with 200 mL H₂O, dried with Na₂SO₄ and the solvent was completely removed. The resulting orange oil was purified in EtOAc by column chromatography. After recrystallization in EtOAc (reflux), 3.9 g of DBPO (1) could be obtained as colorless crystals.

Yield: 3.9 g (44 %).

R_f = 0.43 (EtOAc).

¹H NMR (400 MHz, CDCl₃) δ = 7.83 (dd, *J* = 7.8 Hz, 3.0 Hz, 2H), 7.72 (dd, *J* = 9.8 Hz, 7.4 Hz, 2H), 7.68–7.62 (m, 2H), 7.61–7.55 (m, 2H), 7.52–7.45 (m, 1H), 7.42–7.34 (m, 4H) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 33.6 ppm.

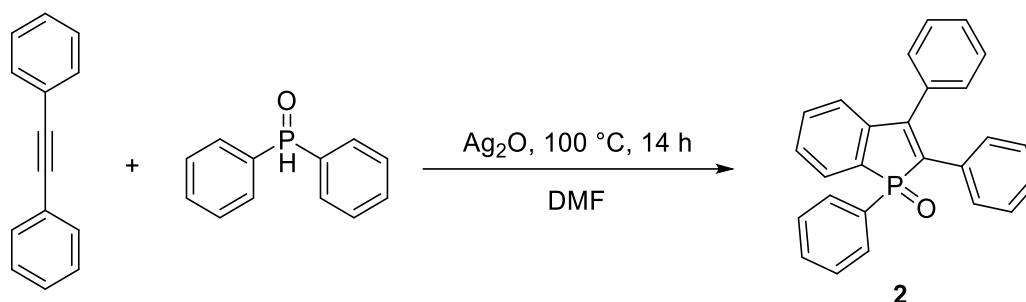
UV/Vis (MeCN): λ_{max} (ε) = 328 nm (1640 mol⁻¹ dm³ cm⁻¹).

Fluorescence (MeCN): λ_{em} = 364 nm.

PLQY (solid): 33 ± 2 %.

1.2.2 1,2,3-Triphenylphosphindole oxide (TPPIO) (**2**)

The synthesis was performed as a modified version of the original report from Chen *et al.*^[4]



0.9 g (5 mmol, 1 eq.) diphenylacetylene, 2.0 g (10 mmol, 2 eq.) diphenylphosphane oxide and 2.3 g (10 mmol, 2 eq.) silver oxide were added to a 250 mL Schlenk flask with reflux condenser. Then, 80 mL DMF were added to the mixture and stirred at $100\text{ }^\circ\text{C}$ for 14 hours. The gray suspension was cooled to rt, mixed with 120 mL EtOAc and filtered through Celite[®] celite. The yellowish filtrate was washed three times with 80 mL brine, and the aqueous phase was extracted once with 100 mL EtOAc. The combined organic phases were dried over MgSO_4 and the solvent was removed under reduced pressure. The residue was purified by column chromatography (hexane/EtOAc 1:2) to obtain 1.2 g of TPPIO (**2**) as a slightly yellowish solid.

Yield: 1.2 g (63 %).

R_f = 0.47 (EtOAc/hexane 3:1).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ = 7.75–7.67 (m, 2H), 7.67–7.61 (m, 1H), 7.45–7.29 (m, 8H), 7.29–7.24 (m, 2H), 7.18–7.12 (m, 3H), 7.02 (dd, J = 5.1, 1.9 Hz, 3H) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 38.7 ppm.

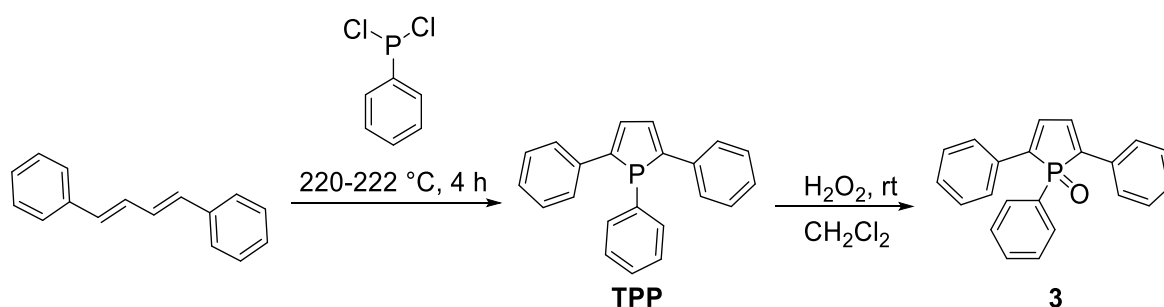
UV/Vis (MeCN): λ_{max} (ϵ) = 346 nm (7000 $\text{mol}^{-1}\text{ dm}^3\text{ cm}^{-1}$).

Fluorescence (MeCN): λ_{em} = 460 nm.

PLQY (solid): $72 \pm 2\%$ (lit. 68 %).^[5]

1.2.4 1,2,5-Triphenylphosphole oxide (TPPO) (3)

The synthesis was performed as a modified version of the original report from Lukas *et al.*^[6]



4.05 g (19.6 mmol, 1 eq.) 1,4-diphenylbutadiene was placed in a 50 mL Schlenk flask with reflux condenser and 14 mL dichlorophenylphosphane were added. The suspension was heated to 220–222 °C, resulting in a yellowish solution. The reaction mixture was stirred at this temperature for 4 hours and then slowly cooled to rt. The resulting yellowish crystalline mass was washed with 20 mL pentane, 20 mL Et₂O and 30 mL H₂O. The yellow residue was recrystallized from toluene to obtain **TPP** as yellow-greenish crystals. The crystals were suspended with 150 mL CH₂Cl₂, cooled to 0 °C and carefully mixed with 3 mL of a 30 % H₂O₂ solution. After stirring for 30 minutes, an orange solution was formed, which was washed three times with 100 mL H₂O and then dried over Na₂SO₄. After removing the solvents the yellow residue was purified by column chromatography (EtOAc/hexane 1:1) to obtain 4.85 g of TPPO (**3**) as yellow crystals.

Yield: 4.85 g (76 %).

R_f = 0.39 (EtOAc/hexane 1:1).

¹H NMR (400 MHz, CDCl₃) δ = 7.82–7.74 (m, 2H), 7.58–7.52 (m, 4H), 7.33–7.14 (m, 11H) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 41.4 ppm.

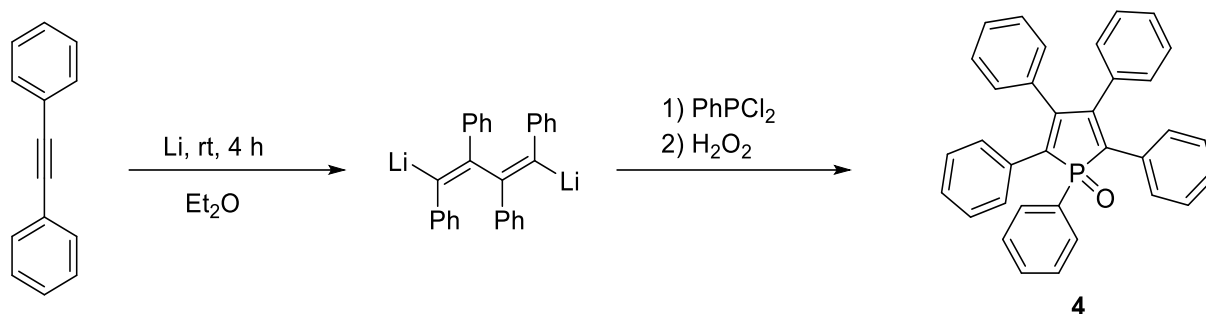
UV/Vis (MeCN): λ_{max} (ε) = 392 nm (13900 mol⁻¹ dm³ cm⁻¹).

Fluorescence (MeCN): λ_{em} = 508 nm.

PLQY (solid): 45 ± 2 %.

1.2.3 1,2,3,4,5-Pentaphenylphosphole oxide (PPPO) (4)

The synthesis was performed as a modified version of the original report from Braye *et al.*^[7]



Under an argon atmosphere, 5.1 g (28 mmol, 1.0 eq.) diphenylacetylene were dissolved in 25 mL Et₂O and transferred to a 100 mL Schlenk flask containing 1.3 g lithium (pieces). The mixture was stirred for 4 hours at rt. After 30 minutes, an intense red color was observed and after 2 hours, a yellow precipitate was formed. This precipitate was isolated by filtration with an inert frit and washed twice with Et₂O. 3.6 g (49 %) of the diphenylacetylene dimer was obtained as a yellow solid.

3.6 g (6.8 mmol, 1.0 eq.) of the diphenylacetylene dimer were suspended in 30 mL THF and cooled to 0 °C. Then 2 mL (15.1 mmol, 2.2 eq.) dichlorophenylphosphane was slowly added. This formed a dark green solution and then a green-yellowish precipitate. The precipitate was filtered off and washed twice with Et₂O. The solid was then suspended in 30 mL CH₂Cl₂ and cooled to 0 °C. 3 mL of a 30 % H₂O₂ solution were added to the suspension and stirred for 1 hour. This procedure dissolved the precipitate and a yellow-brownish solution was formed. The organic phase was washed twice with 100 mL H₂O and dried over Na₂SO₄. After removing the solvent, PPPO (4) was purified by column chromatography (EtOAc/hexane 1:1) and dried under reduced pressure. 3.1 g of PPPO (4) were obtained as a bright yellow solid.

Yield: 3.1 g (48 %).

R_f = 0.48 (EtOAc/hexane 1:1).

¹H NMR (400 MHz, CDCl₃) δ = 7.91–7.84 (m, 2H), 7.47–7.35 (m, 3H), 7.13–7.03 (m, 10H), 7.03–6.98 (m, 6H), 6.88–6.83 (m, 4H) ppm.

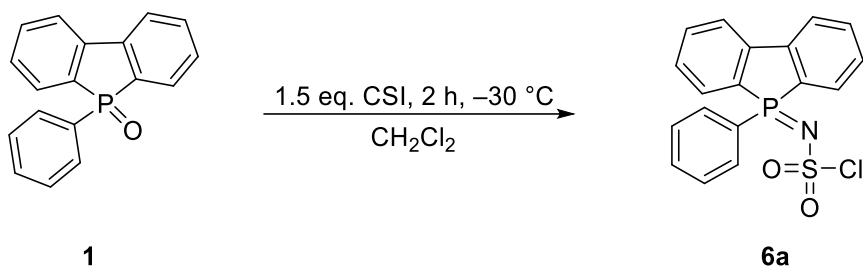
³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 44.1 ppm.

UV/Vis (MeCN): λ_{max} (ε) = 387 nm (6800 mol⁻¹ dm³ cm⁻¹).

Fluorescence (MeCN): λ_{em} = 521 nm.

PLQY (solid): 36 ± 2 % (lit. 33 %).^[5]

1.2.5 Chlorosulfonylimino-5-phenyldibenzophosphole (6a)



In a SCHLENK flask, 640 mg (2.32 mmol, 1 eq.) DBPO (**1**) were dissolved in 6 mL CH_2Cl_2 and cooled to $-30 \text{ }^\circ\text{C}$. Then 5.2 mL (3.54 mmol, 1.5 eq.) of a 0.68 molar CSI stock solution in CH_2Cl_2 were added. The mixture was stirred at this temperature for two hours; after one hour, a white precipitate was formed. At rt, the precipitate dissolved. The solvent was completely removed. The remaining white solid was recrystallized in MeCN to obtain 794 mg of **6a** as colorless crystals.

Yield: 794 mg (92 %).

M.p.: 209–211 $^\circ\text{C}$.

$^1\text{H NMR}$ (400 MHz, CD_3CN): δ = 8.10 (dd, J = 7.8 Hz, 3.5 Hz, 2H, H_{ar}), 7.93–7.87 (m, 2H, H_{ar}), 7.85–7.75 (m, 4H, H_{ar}), 7.75–7.70 (m, 1H, H_{ar}), 7.60–7.54 (m, 4H, H_{ar}) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_3CN): δ = 143.1 (d, J = 22.3 Hz), 135.6 (d, J = 2.3 Hz), 134.5 (d, J = 3.3 Hz), 131.7 (d, J = 12.2 Hz), 131.53 (d, J = 9.9 Hz), 130.3 (d, J = 11.8 Hz), 129.8 (d, J = 14.2 Hz), 125.2 (d, $^1J_{\text{C-P}}$ = 102.5 Hz), 122.7 (d, J = 10.5 Hz), 122.4 (d, $^1J_{\text{C-P}}$ = 117.5 Hz) ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_3CN): δ = 21.2 ppm.

IR (ATR): $\tilde{\nu}$ = 3060 (m), 1990 (w), 1944(w), 1834 (w), 1593 (m), 1571 (w), 1480(w), 1473 (m), 1440 (s), 1337 (s, SO_2), 1323 (s), 1286 (m), 1272 (m), 1203 (s, SO_2), 1143 (s, P=N), 1126 (m), 1078 (m), 1068 (m), 1025 (w), 996 (w), 955 (w), 877 (w), 795 (s), 764 (s), 753 (s), 731 (s), 718 (s), 694 (m), 682 (m), 616 (w), 573 (s, S-Cl), 554 (s), 529 (s), 515 (s) cm^{-1} .

UV/Vis (MeCN): λ_{max} (ϵ) = 335 nm ($1590 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$).

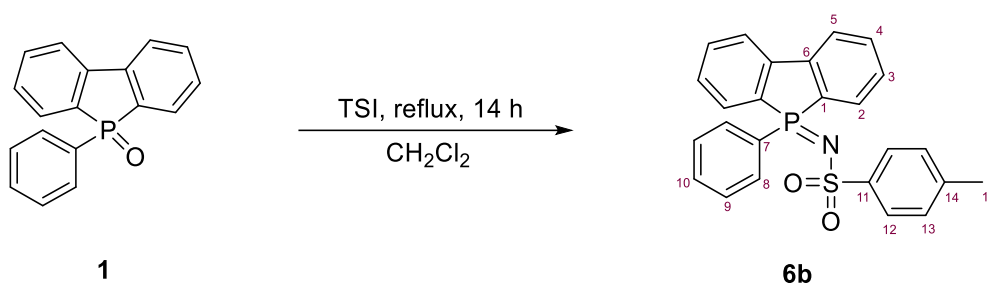
Fluorescence (MeCN): λ_{em} = 385 nm.

PLQY (solid): $34 \pm 2 \%$.

HRMS (ESI(+), MeCN): m/z = found: 338.0411, calculated: for $[\text{C}_{18}\text{H}_{13}\text{NO}_2\text{PS}]^+$: 338.0400.

Elemental analysis: found: N 3.77 %, C 57.76 %, H 3.41 %

calc.: N 3.75 %, C 57.84 %, H 3.51 %.

1.2.6 *p*-Tolylsulfonylimino-5-phenyldibenzophosphole (**6b**)

In a SCHLENK flask, 550 mg (2.0 mmol, 1.0 eq.) DBPO (**1**) were dissolved in 5 mL CH₂Cl₂ and 3 mL (3.0 mmol, 1.5 eq.) of a 1.0 molar TSI stock solution were added. The reaction mixture was stirred for 14 hours under reflux. The solvent was then removed, producing a colorless oil. By boiling in 7 mL *n*-hexane, a white solid could be obtained. This was filtered off and recrystallized in toluene to give 685 mg **6b** as colorless crystals.

Yield: 685 mg (80 %).

M.p.: 174–176 °C.

¹H NMR (400 MHz, CDCl₃) δ = 7.80 (dd, *J* = 7.8 Hz, 3.5 Hz, 2H, H-**2**), 7.74–7.64 (m, 4H, H-**5**, H-**8**), 7.63–7.57 (m, 2H, H-**4**), 7.56–7.48 (m, 3H, H-**10**, H-**12**), 7.43–7.36 (m, 2H, H-**9**), 7.36–7.30 (m, 2H, H-**3**), 6.97 (d, ³*J*_{H-H} = 7.9 Hz, 2H, H-**13**), 2.27 (s, 3H, H-**15**) ppm.

¹³C{¹H} NMR (101 MHz, CDCl₃): δ = 142.5 (s, **C11**), 142.3 (d, ²*J*_{C-P} = 22.3 Hz, **C6**), 140.8 (s, **C14**), 133.9 (d, ⁴*J*_{C-P} = 2.0 Hz, **C4**), 133.1 (d, ⁴*J*_{C-P} = 3.0 Hz, **C10**), 131.6 (d, *J*_{C-P} = 11.8 Hz, **C5** or **C8**), 131.0 (d, *J*_{C-P} = 9.6 Hz, **C5** or **C8**), 129.6 (d, ³*J*_{C-P} = 11.5 Hz, **C3**), 129.0 (d, ³*J*_{C-P} = 13.9 Hz, **C9**), 128.5 (s, **C13**), 128.4 (d, ¹*J*_{C-P} = 102.3 Hz, **C1**), 125.9 (s, **C12**), 125.6 (d, ¹*J*_{C-P} = 114.7 Hz, **C7**), 121.5 (d, ²*J*_{C-P} = 10.3 Hz, **C2**), 21.2 (s, **C15**) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 17.1 ppm.

IR (ATR): $\tilde{\nu}$ = 3053 (w), 1944 (w), 1742 (w), 1596 (w), 1473 (w), 1262 (m), 1128 (s, SO₂), 1103 (s, P=N), 1078 (s), 1064 (s), 1012 (m), 997 (m), 950 (w), 880 (w), 811 (m), 787 (m), 767 (m), 748 (s), 720 (s), 682 (m), 663 (s), 617 (w), 582 (w), 558 (s), 525 (s), 481 (s) cm⁻¹.

UV/Vis (MeCN): λ_{max} (ε) = 330 nm (1690 mol⁻¹ dm³ cm⁻¹).

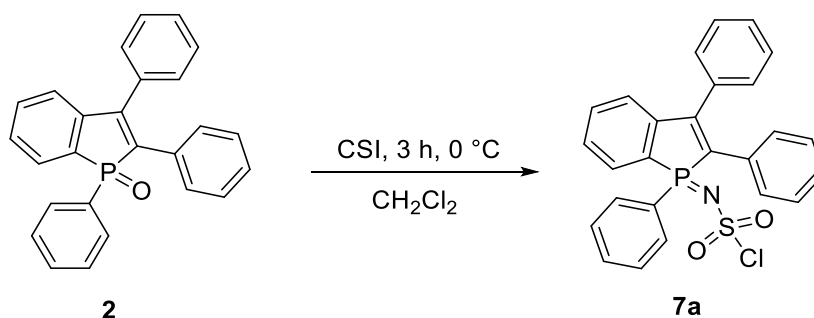
Fluorescence (MeCN): λ_{em} = 378 nm.

PLQY (solid): 54 ± 2 %.

HRMS (ESI(+), MeCN): *m/z* = found: 430.1021, calculated: for [M+H]⁺: 430.1026.

Elemental analysis: found: N 3.16 %, C 69.65 %, H 3.31 %

calc.: N 3.26 %, C 69.92 %, H 3.26 %.

1.2.7 Chlorosulfonylimino-1,2,3-triphenylphosphindole (**7a**)

In a SCHLENK flask, 510 mg (1.35 mmol, 1.0 eq.) TPPIO (**2**) were dissolved in 6 mL CH_2Cl_2 and cooled to 0°C . Then 3.0 mL (2.02 mmol, 1.5 eq.) of a 0.68 molar CSI stock solution in CH_2Cl_2 were added and the mixture was stirred for 3 hours at this temperature. After slowly warming up to room temperature, the solution was reduced to one-third and 12 mL *n*-hexane were added. The solution was again reduced to one-third resulting in a slightly yellowish solid. The precipitate was filtered off and washed with 10 mL Et_2O . After drying under reduced pressure, 578 mg **7a** could be obtained as a slightly yellowish solid. Suitable single crystals for X-ray structure analysis were obtained by layering a solution of **7a** in CHCl_3 with *n*-hexane.

Yield: 578 mg (90 %).

M.p.: 171–173 $^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3): δ = 7.93–7.79 (m, 3H, H_{ar}), 7.66–7.59 (m, 2H, H_{ar}), 7.53–7.46 (m, 3H, H_{ar}), 7.46–7.41 (m, 3H, H_{ar}), 7.40–7.33 (m, 3H, H_{ar}), 7.19–7.07 (s, 5H, H_{ar}) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ = 154.6, 145.0, 134.8, 134.2, 133.1, 131.8, 131.7, 130.8, 129.8, 129.6, 129.4, 129.1, 129.0, 128.6, 128.5, 125.5, 124.6, 121.3 ppm

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 25.8 ppm

IR (ATR): $\tilde{\nu}$ = 3059 (w), 1587 (w), 1567 (w), 1483 (w), 1440 (m), 1333 (s, SO_2), 1175 (s, SO_2), 1136 (s, P=N), 1120 (s), 1066 (m), 1027 (w), 1000 (w), 922 (w), 878(w), 840(w), 822 (m), 787 (w), 761 (m), 750 (m), 729 (s), 698 (s), 688 (m), 673 (w), 597 (m), 584 (s, S–Cl), 566 (s) cm^{-1} .

UV/Vis (MeCN): λ_{max} (ϵ) = 357 nm (5800 $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$).

Fluorescence (MeCN): λ_{em} = 451 nm.

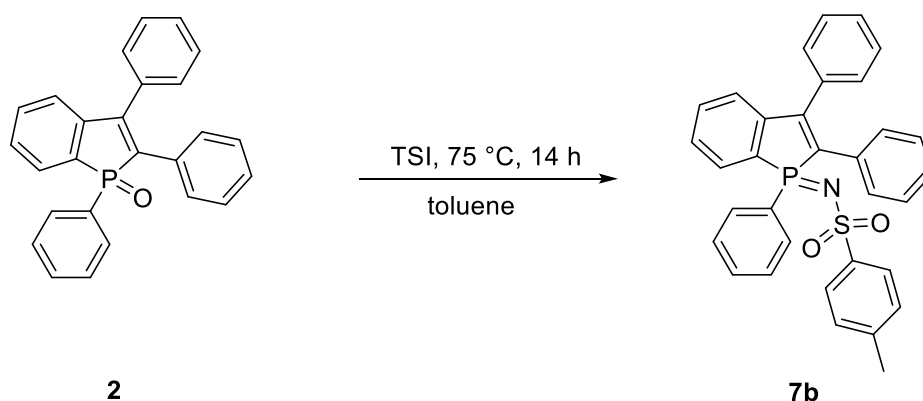
PLQY (solid): 46 ± 2 %.

HRMS (ESI(+), MeCN): m/z = found: 440.0881, calculated: for $[\text{C}_{26}\text{H}_{19}\text{NO}_2\text{PS}]^+$: 440.0869.

Elemental analysis: found: N 2.89 %, C 65.27 %, H 3.93 %

calc.: N 2.94 %, C 65.62 %, H 4.02 %

1.2.8 *p*-Tolylsulfonylimino-1,2,3-triphenylphosphindole (**7b**)



378 mg (1.0 mmol, 1.0 eq.) TPPIO (**2**) were suspended in 2.5 mL toluene and 1.5 mL (1.5 mmol, 1.5 eq.) of a 1 molar TSI stock solution in toluene were added. The mixture was stirred at 75 °C for 14 hours. After removing the solvent and washing with 10 mL dry Et₂O, the residue was purified by column chromatography (hexane/EtOAc 1:1) to obtain 507 mg **7b** as a slightly yellowish solid. Suitable single crystals for X-ray structure analysis were obtained by diffusion of hexane vapor into a solution of **7b** in CH₂Cl₂ at room temperature.

Yield: 507 mg (97 %).

R_f = 0.57 (hexane/EtOAc 1:2).

M.p.: 124–126 °C.

¹H NMR (400 MHz, CDCl₃): δ = 7.84–7.76 (m, 2H, H_{ar}), 7.62–7.47 (m, 5H, H_{ar}), 7.44–7.37 (m, 5H, H_{ar}), 7.34–7.24 (m, 4H, H_{ar}), 7.12–6.95 (m, 7H, H_{ar}), 2.30 (s, 3H, CH₃) ppm.

¹³C{³¹P, ¹H} NMR (101 MHz, CDCl₃): δ = 152.3, 144.3, 142.6, 140.8, 133.5, 133.4, 133.1, 131.6, 131.5, 131.2, 130.6, 129.4, 129.2, 129.1, 129.0, 128.9, 128.8, 128.6, 128.1, 128.0, 127.6, 126.0, 124.6, 124.0, 21.2 (CH₃) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 21.0 ppm

IR (ATR): $\tilde{\nu}$ = 3065 (w), 2620 (w), 1740 (w), 1586 (w), 1483 (w), 1438 (m), 1276 (s, SO₂), 1185(m), 1168 (s, SO₂), 1157 (s, P=N), 1042 (s), 1087 (s), 1025 (m), 990 (m), 923 (w), 877 (w), 853 (w), 823 (m), 807 (m), 770 (m), 767 (m), 741 (s), 725 (s), 705 (s), 689 (s), 669 (s), 647 (w), 625 (w), 614 (w), 596 (w), 552 (s), 542 (s), 520 (s), 501 (s) cm⁻¹.

UV/Vis (MeCN): λ_{max} (ε) = 353 nm (4300 mol⁻¹ dm³ cm⁻¹).

Fluorescence (MeCN): λ_{em} = 445 nm.

PLQY (solid): 82 ± 2 %.

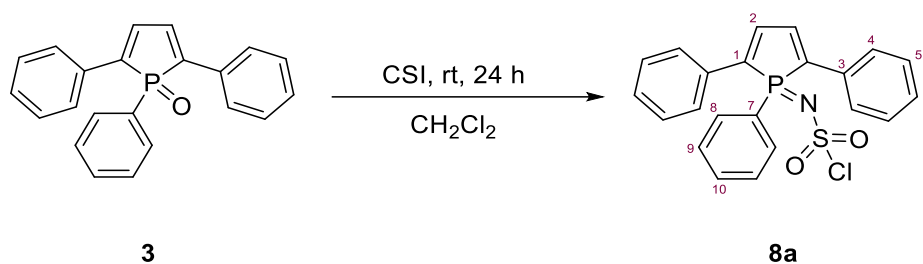
HRMS (ESI(+), MeCN): *m/z* = found: 532.1497, calculated: for [M+H]⁺: 532.1495

m/z = found: 570.1056, calculated: for [M+K]⁺: 570.1054

Elemental analysis: found: N 2.45 %, C 73.95 %, H 4.81 %

calc.: N 2.63 %, C 74.56 %, H 4.93 %

1.2.9 Chlorosulfonylimino-1,2,5-triphenylphosphole (8a)



375 mg (1.15 mmol, 1 eq.) TPPO (**3**) were dissolved in 3 mL CH₂Cl₂ and then 2.5 mL (1.73 mmol, 1.5 eq.) of a 0.68 molar CSI stock solution in CH₂Cl₂ were added. After standing for 24 h at room temperature, orange crystals were formed. The solvent was completely removed under reduced pressure and the resulting solid was washed with 6 mL Et₂O. After recrystallization in MeCN 445 mg **7a** could be obtained as orange crystals.

Yield: 445 mg (91 %).

M.p.: 250 °C decomposition.

¹H NMR (400 MHz, CD₃CN): δ = 8.02–7.94 (m, 2H, H-**8**), 7.80 (d, ³J_{H-P} = 40.8 Hz, 2H, H-**2**), 7.74–7.68 (m, 1H, H-**10**), 7.62–7.55 (m, 6H, H-**5**, H-**9**), 7.39–7.32 (m, 6H, H-**4**, H-**6**) ppm.

¹³C {¹H} NMR (101 MHz, CD₃CN): δ = 138.35 (d, *J* = 27.3 Hz), 134.71 (d, *J* = 3.0 Hz), 133.71 (d, ¹J_{C-P} = 86.0 Hz), 130.91 (d, *J* = 12.0 Hz), 130.61 (d, *J* = 12.2 Hz), 130.37 (d, *J* = 13.9 Hz), 129.76, 129.12, 126.42 (d, *J* = 6.6 Hz) ppm.

³¹P {¹H} NMR (162 MHz, CD₃CN): δ = 28.0 ppm.

IR (ATR): $\tilde{\nu}$ = 3058 (w), 1575 (w), 1492 (w), 1439 (w), 1332 (s, SO₂), 1263 (w), 1174 (s, SO₂), 1160 (m), 1115 (s, P=N), 1032 (w), 997 (w), 930 (w), 862 (w), 793 (w), 761 (s), 742 (m), 727 (w), 686 (m), 645 (w), 604 (m), 579 (s, S-Cl), 562 (m), 536 (m), 502 (m), 482 (s) cm⁻¹.

UV/Vis (MeCN): λ_{max} (ε) = 410 nm (12600 mol⁻¹ dm³ cm⁻¹).

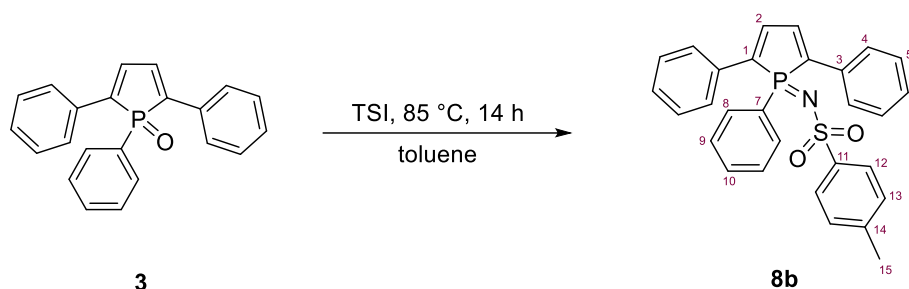
Fluorescence (MeCN): λ_{em} = 554 nm.

PLQY (solid): 18 ± 2 %.

HRMS (ESI(+), MeCN): *m/z* = found: 426.0481, calculated: for [M+H]⁺: 426.0479.

Elemental analysis: found: N 3.16 %, C 61.91 %, H 4.13 %

calc.: N 3.29 %, C 62.05 %, H 4.02 %

1.2.10 *p*-Tolylsulfonylimino-1,2,5-triphenylphosphole (8b)

370 mg (1.1 mmol, 1 eq.) TPPO (**4**) were suspended in 3 mL toluene and then mixed with 1.7 mL (1.7 mmol, 1.5 eq.) of a 1 molar TSI stock solution in toluene. After heating to 85 °C and stirring overnight a yellow-orange crystalline mass was formed. This was washed with 6 mL Et₂O and then heated in toluene. After filtration and washing with *n*-pentane 445 mg **7b** were obtained as yellow-orange crystals. Suitable single crystals for X-ray structure analysis were obtained by recrystallization in MeCN.

Yield: 445 mg (85 %).

M.p.: 242–244 °C.

¹H NMR (400 MHz, DMSO-*d*₆): δ = 7.90–7.82 ppm (m, 2H, H-**8**), 7.85 (d, ³J_{H-P} = 39.3 Hz, 2H, H-**2**), 7.65–7.59 (m, 1H, H-**10**), 7.58–7.50 (m, 2H, H-**9**), 7.48–7.44 (m, 4H, H-**5**), 7.40 (d, ³J_{H-H} = 8.2 Hz, 2H, H-**12**), 7.27–7.19 (m, 6H, H-**4**, H-**6**), 6.92 (d, ³J_{H-H} = 8.2 Hz, 2H, H-**13**), 2.18 (s, 3H, H-**15**) ppm.

¹³C{¹H} NMR (101 MHz, DMSO-*d*₆): δ = 142.1 (s, **C11**), 141.3 (s, **C14**), 137.4 (d, ²J_{C-P} = 26.1 Hz, **C2**), 135.4 (d, ¹J_{C-P} = 85.3 Hz, **C1**), 134.2 (d, ⁴J_{C-P} = 2.7 Hz, **C10**), 131.5 (d, ²J_{C-P} = 12.5 Hz, **C3**), 130.9 (d, ²J_{C-P} = 11.4 Hz, **C8**), 130.5 (d, ³J_{C-P} = 13.1 Hz, **C9**), 129.4–128.8 (overlap, **C5**, **C6**, **C13**), 130.5 (d, ³J_{C-P} = 13.1 Hz, **C9**), 126.5 (d, ³J_{C-P} = 6.5 Hz, **C4**), 125.9 (s, **C12**), 122.2 (d, ¹J_{C-P} = 111.1 Hz, **C7**), 21.3 (s, **C15**) ppm.

³¹P{¹H} NMR (162 MHz, DMSO-*d*₆): δ = 22.5 ppm.

IR (ATR): $\tilde{\nu}$ = 3022 (w), 1914 (w), 1600 (w), 1576 (w), 1548 (w), 1517 (w), 1492 (m), 1481 (m), 1439 (m, SO₂), 1394 (w), 1349 (w), 1291 (w), 1272 (s, SO₂), 1257 (m), 1127 (s, P=N), 1084 (s), 1034 (m), 1027 (m), 1016 (m), 997 (w), 983 (w), 929 (w), 862 (m), 819 (w), 807 (w), 786 (m), 758 (s), 749 (s), 726 (m), 704 (m), 690 (m), 678 (s), 665 (s), 653 (m), 602 (w), 554 (s), 555 (s), 504 (w), 484 (s), 436 (m) cm⁻¹.

UV/Vis (MeCN): λ_{max} (ε) = 405 nm (16300 mol⁻¹ dm³ cm⁻¹).

Fluorescence (MeCN): λ_{em} = 537 nm.

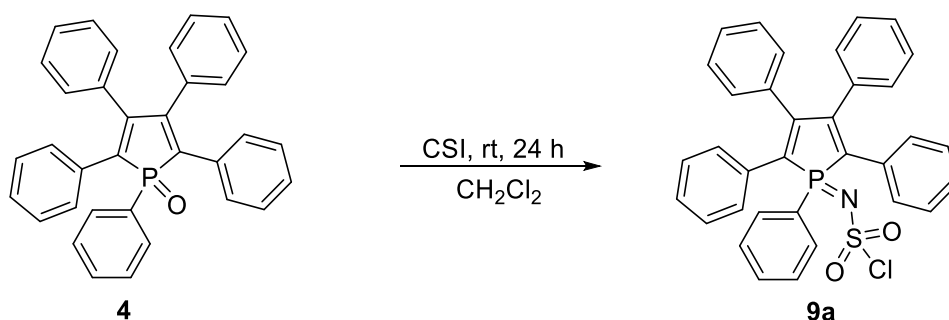
PLQY (solid): 55 ± 2 %.

HRMS (ESI(+), MeCN): *m/z* = found: 482.1339, calculated: for [M+H]⁺: 482.1339.

Elemental analysis: found: N 2.81 %, C 72.17 %, H 5.07 %

calc.: N 2.91 %, C 72.33 %, H 5.02 %

1.2.11 Chlorosulfonylimino-1,2,3,4,5-pentaphenylphosphole (9a)



500 mg (1.05 mmol, 1 eq.) PPPO (**3**) were dissolved in 8 mL CH_2Cl_2 and then 2.3 mL (1.58 mmol, 1.5 eq.) of a 0.68 molar CSI stock solution in CH_2Cl_2 were slowly added. The mixture was then stirred for 24 h at room temperature. A slight gas evolution was observed and the mixture turned orange. The solvent was completely removed and the resulting orange foam was washed with 10 mL Et_2O . The residue was recrystallized in toluene to obtain 628 mg **8a** as orange crystals.

Yield: 628 mg (98 %).

M.p.: 218–220 °C.

^1H NMR (400 MHz, CDCl_3): δ = 7.93–7.86 (m, 2H, H_{ar}), 7.57–7.51 (m, 1H, H_{ar}), 7.47–7.41 (m, 2H, H_{ar}), 7.15–7.09 (m, 2H, H_{ar}), 7.08–6.93 (m, 14H, H_{ar}), 6.91–6.86 (m, 4H, H_{ar}) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ = 155.1, 134.1, 131.5, 130.7, 129.8, 129.6, 129.4, 128.8, 128.7, 128.5, 128.3, 128.2, 119.9 ppm.

$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ = 31.0 ppm.

IR (ATR): $\tilde{\nu}$ = 3058 (w), 1575 (w), 1492 (w), 1439 (w), 1332 (s, SO_2), 1263 (w), 1174 (s, SO_2), 1160 (m), 1115 (s, P=N), 1032 (w), 997 (w), 930 (w), 862 (w), 793 (w), 761 (s), 742 (m), 727 (w), 686 (m), 645 (w), 604 (m), 579 (s, S-Cl), 562 (m), 536 (m), 502 (m), 482 (s) cm^{-1} .

UV/Vis (MeCN): λ_{max} (ϵ) = 405 nm (5200 $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$).

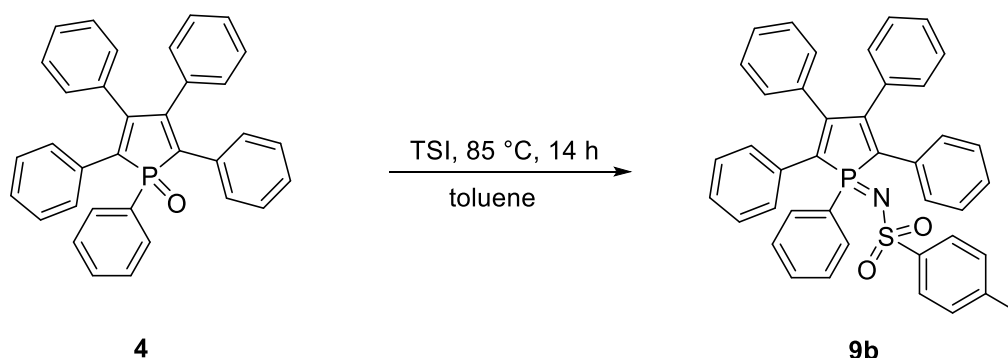
Fluorescence (MeCN): λ_{ex} = 405 nm; λ_{em} = 558 nm.

PLQY (solid): 10 ± 2 %.

HRMS (ESI(+), MeCN): m/z = found: 542.1339, calculated: for $[\text{C}_{34}\text{H}_{25}\text{NO}_2\text{PS}]^+$: 542.1339.

Elemental analysis: found: N 2.28 %, C 69.54 %, H 4.33 %

calc.: N 2.42 %, C 69.65 %, H 4.36 %

1.2.13 *p*-Tolylsulfonylimino-1,2,3,4,5-pentaphenylphosphole (9b)

620 mg (1.3 mmol, 1 eq.) PPPO (**4**) were suspended in 12 mL toluene and 2 mL (2.0 mmol, 1.5 eq.) of a 1 molar TSI solution in toluene were added. The mixture was stirred for 14 h at 85 °C, producing a clear yellow solution. The solvent was completely removed and the yellow residue was washed with 15 mL hexane and 15 mL Et₂O. After drying under reduced pressure 703 mg **9b** could be obtained as a yellow solid. Suitable single crystals for X-ray structure analysis were obtained by recrystallization in MeCN.

Yield: 703 mg (85 %).

M.p.: 223–225 °C.

¹H NMR (400 MHz, CDCl₃): δ = 8.02–7.95 (m, 2H, H_{ar}), 7.58–7.50 (m, 1H, H_{ar}), 7.50–7.42 (m, 2H, H_{ar}), 7.22–7.10 (m, 6H, H_{ar}), 7.09–6.93 (m, 14H, H_{ar}), 6.91–6.86 (m, 2H, H_{ar}), 2.24 (s, 3H, CH₃) ppm.

¹³C{³¹P, ¹H} NMR (101 MHz, CDCl₃): δ = 152.8, 142.4, 140.5, 134.6, 133.1, 131.5, 131.3, 131.3, 129.7, 129.5, 129.4, 128.5, 128.2, 128.0, 127.8, 125.8, 122.6, 21.2 ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 26.1 ppm.

IR (ATR): $\tilde{\nu}$ = 3055 (w), 1597 (w), 1575 (w), 1479 (w), 1437 (m, SO₂), 1303 (w), 1295 (w), 1281 (m), 1268 (m), 1179 (w), 1162 (w), 1125 (s, P=N), 1087 (s), 1020 (m), 996 (w), 938 (w), 915 (w), 812 (m), 789 (w), 758 (s), 745 (m), 713 (s), 694 (s), 665 (s), 649 (w), 612 (w), 587 (w), 573 (s), 555 (s), 520 (s), 502 (m), 478 (m) cm⁻¹.

UV/Vis (MeCN): λ_{max} (ε) = 398 nm (5000 mol⁻¹ dm³ cm⁻¹).

Fluorescence (MeCN): λ_{ex} = 398 nm; λ_{em} = 547 nm.

PLQY (solid): 75 ± 2 %.

HRMS (ESI(+), MeCN): *m/z* = found: 634.1966, calculated: for [M+H]⁺: 634.1965.

Elemental analysis: found: N 2.12 %, C 77.12 %, H 5.17 %

calc.: N 2.21 %, C 77.70 %, H 5.09 %

1.2.14 Investigation of the reaction between CSI (5a) and triphenylphosphane oxide

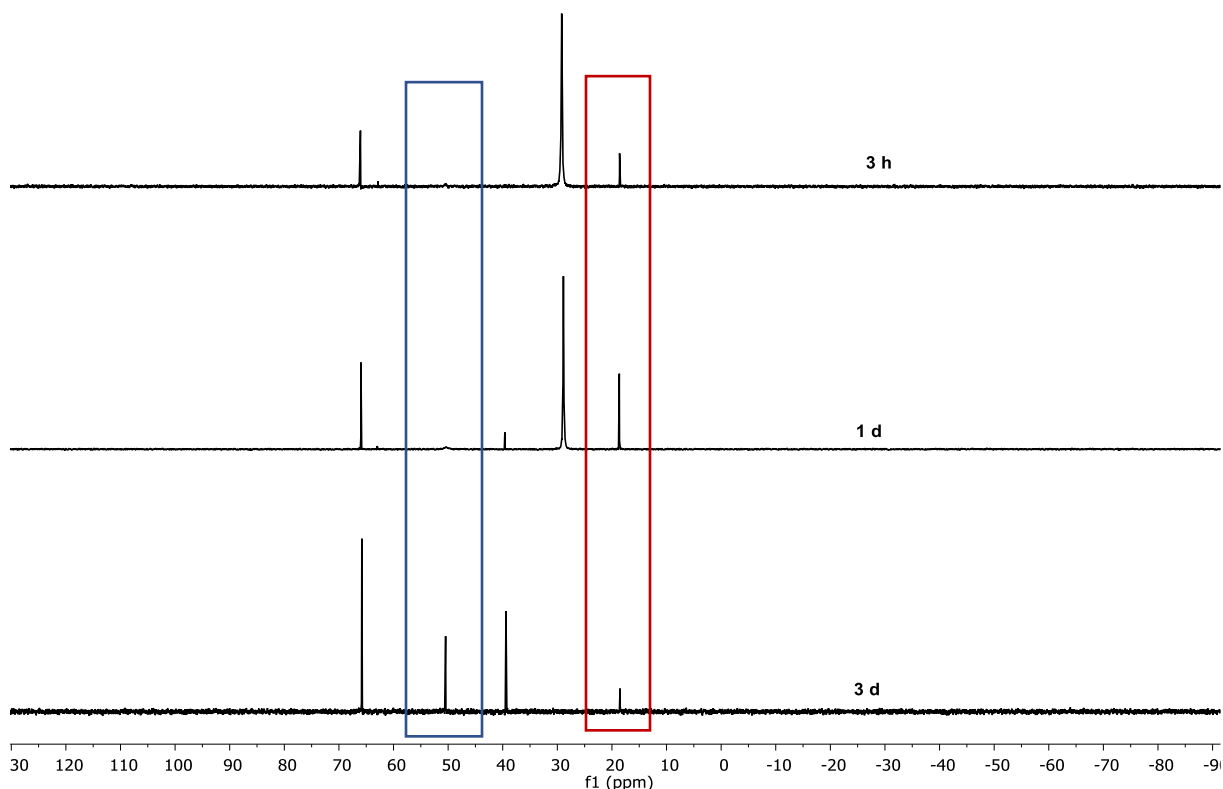
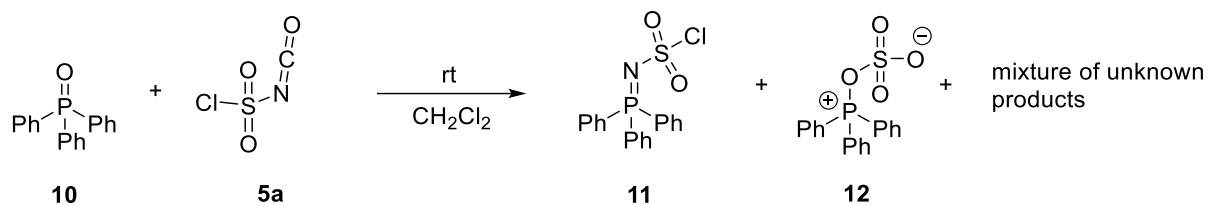


Figure S1.1: Comparison of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the reaction mixture after 3 h, 1 d and 3 d. Signal of the isolated product **12** (blue) and proposed target compound **11** (red).

For the investigation of the reaction with acyclic phosphane oxides, 200 mg (0.71 mmol, 1.0 eq) triphenylphosphane oxide were dissolved in 3 mL CH_2Cl_2 and 1.6 mL (1.07 mmol, 1.5 eq) of a 0.68 molar CSI stock solution in CH_2Cl_2 were added at 0 °C. The mixture was allowed to warm to rt. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows that the reaction takes significantly longer and is less selective compared to the cyclic phospholes. The desired cycloaddition product **11** could not be isolated. However, the signal at ppm indicates the formation of the chlorosulfonylimino phosphane **11**. The shift of the signals to higher wavelengths suggests various addition products of **10** and **5a**. After 3 days of reaction at rt, **12** could be isolated by removing the solvent and subsequent recrystallization in MeCN. The product **12** is unstable and rapidly decomposes in solution.

1.2.15 Investigation of the reaction between TSI (5b) and triphenylphosphane oxide

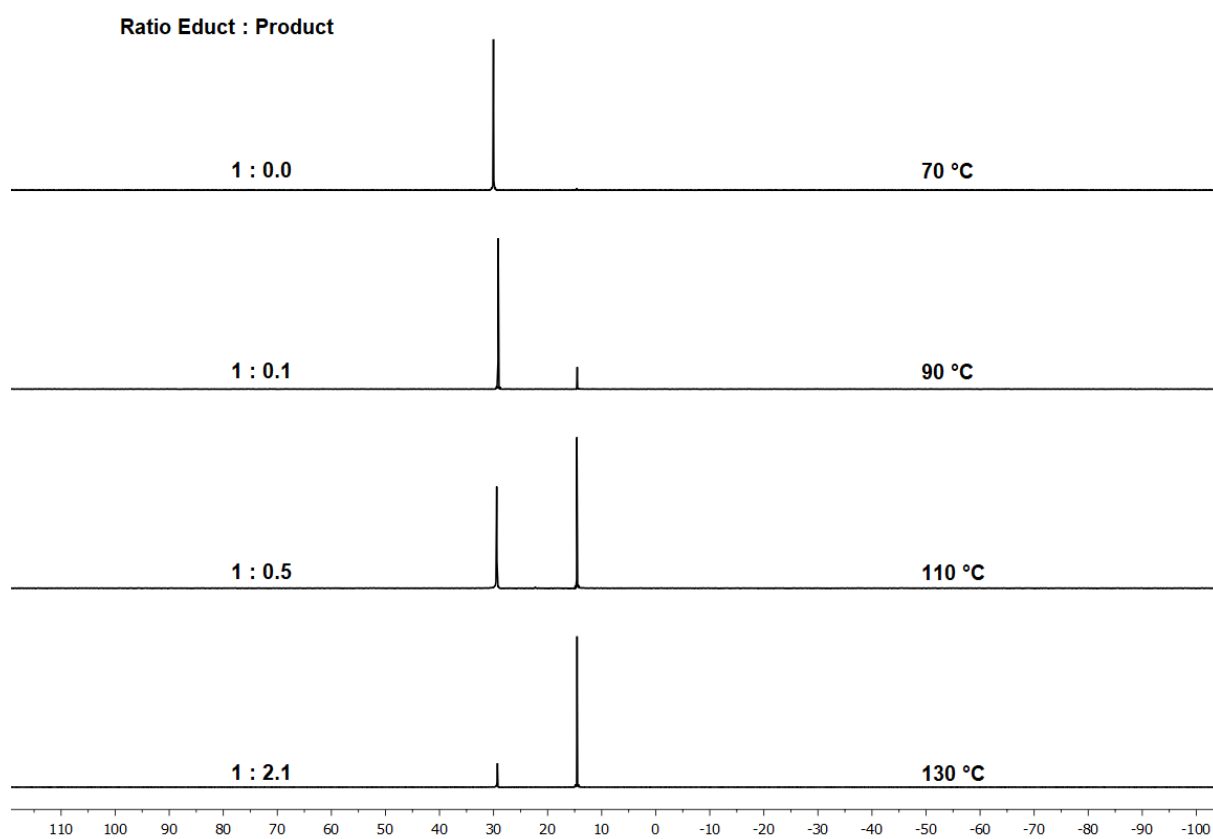
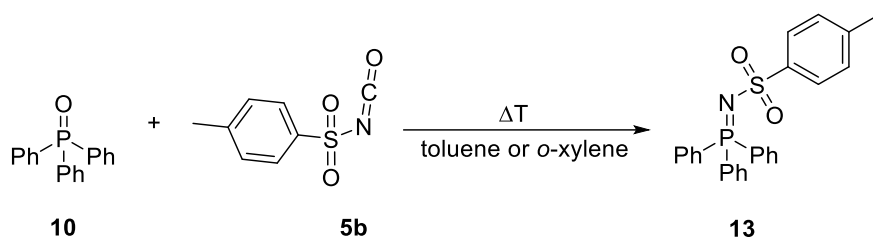
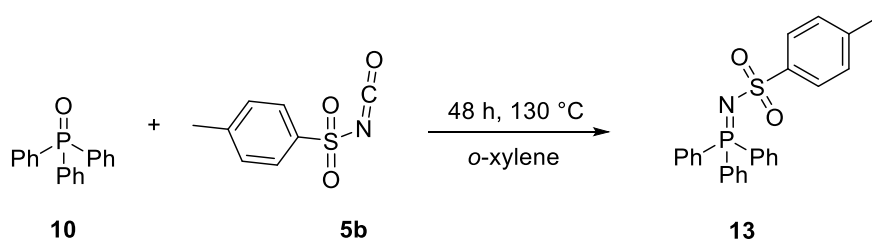


Figure S1.2: Comparison of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra in CDCl_3 of the reaction mixture after 16 h at 70 °C (in toluene), 90 °C (in toluene), 110 °C (in toluene) and 130 °C (in *o*-xylene).

1.2.16 Synthesis of *P,P,P*-triphenyl-*N*-(toluene-4-sulfonyl)phosphane imide (**13**)

In a Schlenk tube, 350 mg (1.3 mmol, 1 eq.) **10** was suspended in 1.5 mL *o*-xylene and 0.3 mL (2.6 mmol, 2 eq.) TSI (**5b**) was added. The mixture was stirred for 48 h at 130 °C. After cooling to rt, the solvent was completely removed and the oily residue was washed two times with 4 mL Et₂O. The gray-white solid was recrystallized in MeOH to obtain 409 mg **13** as colorless crystals.

Yield: 409 mg (73 %).

¹H NMR (400 MHz, CDCl₃): δ = 7.73 (ddt, *J* = 13.0, 7.0, 1.3 Hz, 6H), 7.56 (td, *J* = 7.3, 1.6 Hz, 3H), 7.52–7.48 (m, 2H), 7.44 (td, *J* = 7.7, 3.2 Hz, 6H), 7.00 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H, CH₃) ppm.

¹³C{¹H} NMR (101 MHz, CDCl₃): δ = 143.5 (d, *J* = 2.6 Hz), 140.5 (s), 133.1 (d, *J* = 10.8 Hz), 132.8 (d, *J* = 3.0 Hz), 128.7 (d, *J* = 13.0 Hz), 128.6 (s), 127.3 (d, ¹*J*_{C-P} = 104.2 Hz), 125.7 (s), 21.3 (s, CH₃) ppm.

³¹P{¹H} NMR (162 MHz, CDCl₃): δ = 14.3 ppm.

2 Molecular Structures and Crystallographic Data

The data were collected on a Gemini diffractometer (Rigaku Oxford Diffraction) using Mo-K α radiation ($\lambda = 71.073$ pm) and ω -scan rotation. Data reduction was performed with CrysAlis Pro^[8] including the program SCALE3 ABSPACK for empirical absorption correction. The structures were solved by dual-space methods with SHELXT-2018^[9] and the refinement was performed with SHELXL-2018^[10]. All non-hydrogen atoms were refined with anisotropic displacement parameters. CCDC 2219165 (**6a**), 2219166 (**6b**), 2219167 (**7a**), 2219168 (**7b**), 2219169 (**8a**), 2219170 (**8b**), 2219171 (**9a**), 2219172 (**9b**) and 2219173 (**13**) contains the supplementary crystallographic data for this paper. The data is accessible free of charge from the Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures/>.

2.1 Molecular structure, selected bond lengths and bond angles of **6a**

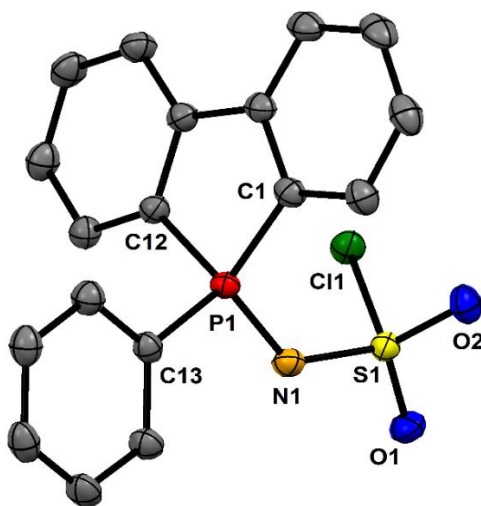


Table S2.1. Selected bond lengths and bond angles in **6a** (values of the second molecule in []):

Bond lengths in Å		Bond angles in °	
P(1)-N(1) [P(2)-N(2)]	1.603(1) [1.607(1)]	C(1)-P(1)-C(12)	93.61(7)
S(1)-N(1) [S(2)-N(2)]	1.550(1) [1.548(1)]	[C(19)-P(2)-C(30)]	[93.37(7)]
S(1)-O(1) [S(2)-O(3)]	1.426(1) [1.427(1)]	N(1)-S(1)-Cl(1)	104.14(5)
Cl(1)-S(1) [Cl(2)-S(2)]	2.0778(5) [2.0854(5)]	[N(2)-S(2)-Cl(2)]	[105.09(5)]
P(1)-C(12) [P(2)-C(30)]	1.790(2) [1.787(1)]	S(1)-N(1)-P(1)	127.13(8)
P(1)-C(13) [P(2)-C(31)]	1.787(1) [1.78.(2)]	[S(2)-N(2)-P(2)]	[126.42(8)]

Structure parameters for **6a**:

C₁₈H₁₃ClNO₂PS, $M = 373.77$, $T = 130(2)$ K, monoclinic space group $P2_1/n$, $a = 921.83(1)$ pm, $b = 3479.39(4)$ pm, $c = 1025.64(1)$ pm, $\alpha = 90^\circ$, $\beta = 91.784(1)^\circ$, $\gamma = 90^\circ$, $V = 3.28805(6)$ nm³, $\rho_{calc} = 1.510$ Mg·m⁻³, $Z = 8$, $\mu = 0.467$ mm⁻¹, crystal size 0.40 x 0.35 x 0.30 mm³, reflections collected 47252, independent reflections 10511 [R(int) = 0.0362], completeness to $\theta = 30.510^\circ$: 100.0 %, 537 parameters,

0 restraints. All H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. R indices (all data): R1 = 0.0489, wR2 = 0.1092, R indices [$I > 2\sigma(I)$]: R1 = 0.0408, wR2 = 0.1036.

2.2 Molecular structure, selected bond lengths and bond angles of 6b

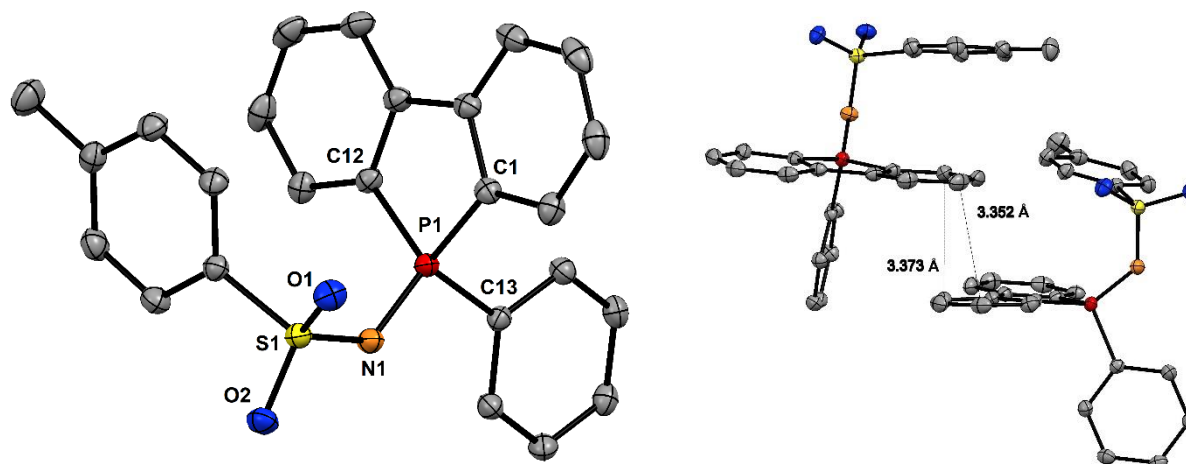


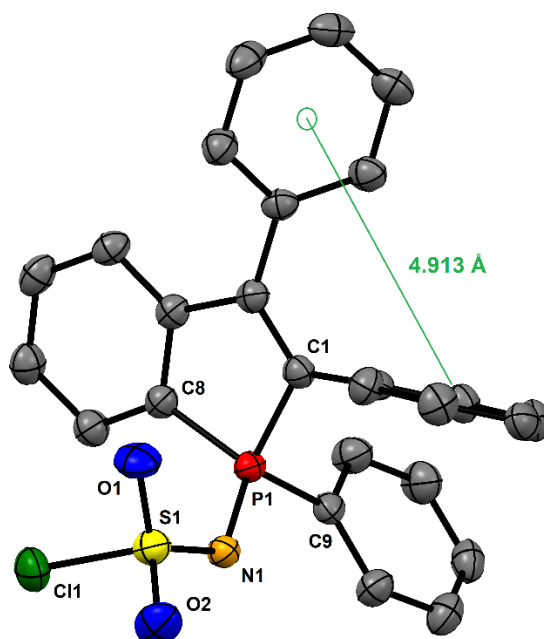
Table S2.2. Selected bond lengths and bond angles in **6b**

Bond lengths in Å		Bond angles in °	
P(1)-N(1)	1.591(1)	P(1)-N(1)-S(1)	128.99(8)
P(1)-C(1)	1.792(1)	C(1)-P(1)-C(12)	93.03(7)
P(1)-C(12)	1.792(1)	N(1)-P(1)-C(13)	104.82(6)
P(1)-C(13)	1.795(1)	O(2)-S(1)-O(1)	116.96(6)
S(1)-N(1)	1.582(1)	N(1)-S(1)-C(19)	106.89(6)
S(1)-O(1)	1.446(1)	N(1)-P(1)-C(1)	122.58(6)

Structure parameters for **6b**:

$C_{25}H_{20}NO_2PS$, $M = 429.45$, $T = 130(2)$ K, orthorhombic space group $Pbca$ $a = 1791.94(3)$ pm, $b = 1220.42(1)$ pm, $c = 1865.76(2)$ pm, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 4.08027(9)$ nm³, $\rho_{calc} = 1.398$ Mg·m⁻³, $Z = 8$, $\mu = 0.260$ mm⁻¹, crystal size 0.30 x 0.20 x 0.10 mm³, reflections collected 46581, independent reflections 5831 [$R(int) = 0.0390$], completeness to $\theta = 28.285^\circ$: 100.0 %, 351 parameters, 0 restraints. All H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. R indices (all data): R1 = 0.0481, wR2 = 0.0932, R indices [$I > 2\sigma(I)$]: R1 = 0.0383, wR2 = 0.0883.

2.3 Molecular structure, selected bond lengths and bond angles of 7a



Distance between centers of exocyclic phenyl rings (green).

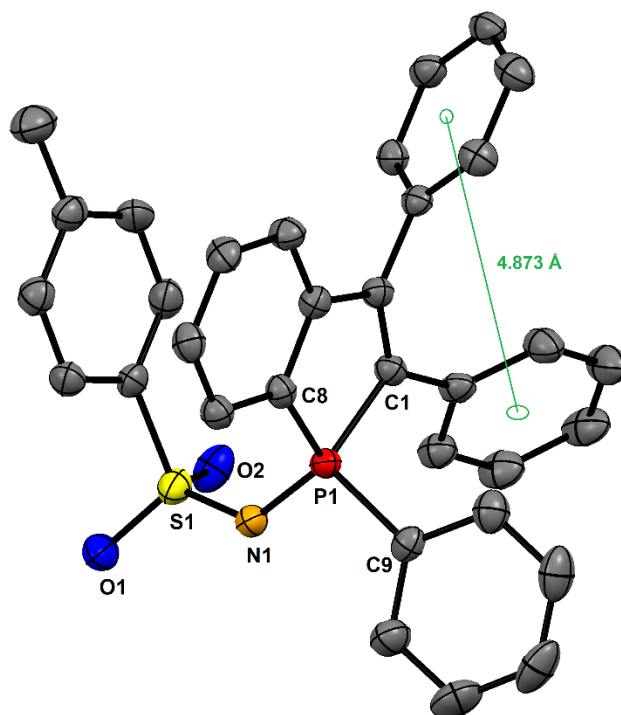
Table S2.3. Selected bond lengths and bond angles in **7a**

Bond lengths in Å		Bond angles in °	
P(1)-N(1)	1.610(2)	C(8)-P(1)-C(1)	94.0(1)
P(1)-C(1)	1.791(2)	N(1)-P(1)-C(9)	105.54(9)
P(1)-C(8)	1.785(2)	N(1)-S(1)-Cl(1)	102.49(8)
P(1)-C(9)	1.772(2)	S(1)-N(1)-P(1)	123.2(1)
S(1)-N(1)	1.548(2)	O(2)-S(1)-N(1)	110.6(1)
Cl(1)-S(1)	2.080(1)		

Structure parameters for **7a**:

$C_{26}H_{19}ClNO_2PS$, $M = 475.90$, $T = 130(2)$ K, orthorhombic space group $Pbca$, $a = 1569.06(3)$ pm, $b = 1494.91(3)$ pm, $c = 1892.71(4)$ pm, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 4.4396(2)$ nm³, $\rho_{calc} = 1.424$ Mg·m⁻³, $Z = 8$, $\mu = 0.363$ mm⁻¹, crystal size 0.30 x 0.20 x 0.15 mm³, reflections collected 45014, independent reflections 6442 [$R(int) = 0.0564$], completeness to $\theta = 28.285^\circ$: 100.0 %, 365 parameters, 0 restraints. All H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. R indices (all data): $R1 = 0.0812$, $wR2 = 0.1413$, R indices [$I > 2\sigma(I)$]: $R1 = 0.0476$, $wR2 = 0.1221$.

2.4 Molecular structure, selected bond lengths and bond angles of **7b**



Distance between centers of exocyclic phenyl rings (green).

Table S2.4. Selected bond lengths and bond angles in **7b**

Bond lengths in Å		Bond angles in °	
N(1)-P(1)	1.587(2)	C(8)-P(1)-C(1)	93.0(1)
P(1)-C(1)	1.807(2)	N(1)-P(1)-C(1)	122.6(1)
P(1)-C(8)	1.794(2)	S(1)-N(1)-P(1)	129.5(1)
P(1)-C(9)	1.789(2)	O(1)-S(1)-N(1)	107.15(9)
S(1)-N(1)	1.586(2)	N(1)-S(1)-C(27)	107.88(9)
S(1)-C(27)	1.761(2)		

Structure parameters for **7b**:

$C_{33}H_{26}NO_2PS$, $M = 531.58$, $T = 130(2)$ K, monoclinic space group $P2_1/c$, $a = 1565.78(4)$ pm, $b = 1150.15(2)$ pm, $c = 1510.26(4)$ pm, $\alpha = 90^\circ$, $\beta = 101.945(3)^\circ$, $\gamma = 90^\circ$, $V = 2.6609(1)$ nm³, $\rho_{calc} = 1.327$ Mg·m⁻³, $Z = 4$, $\mu = 0.214$ mm⁻¹, crystal size 0.30 x 0.20 x 0.10 mm³, reflections collected 28514, independent reflections 7452 [$R(int) = 0.0641$], completeness to $\theta = 28.285^\circ$, 100.0 %, 530 parameters, 96 restraints. Marginally disordered molecule (P1, C1 to C26) with a ratio of 0.948(1) : 0.052(1). All H atoms of the main 95% disordered part were located on difference Fourier maps, whereas hydrogen atoms of the 5 % disordered fraction are calculated. R indices (all data): $R1 = 0.0991$, $wR2 = 0.1205$, R indices [$I > 2\sigma(I)$]: $R1 = 0.0564$, $wR2 = 0.1058$.

2.5 Molecular structure, selected bond lengths and bond angles of 8a

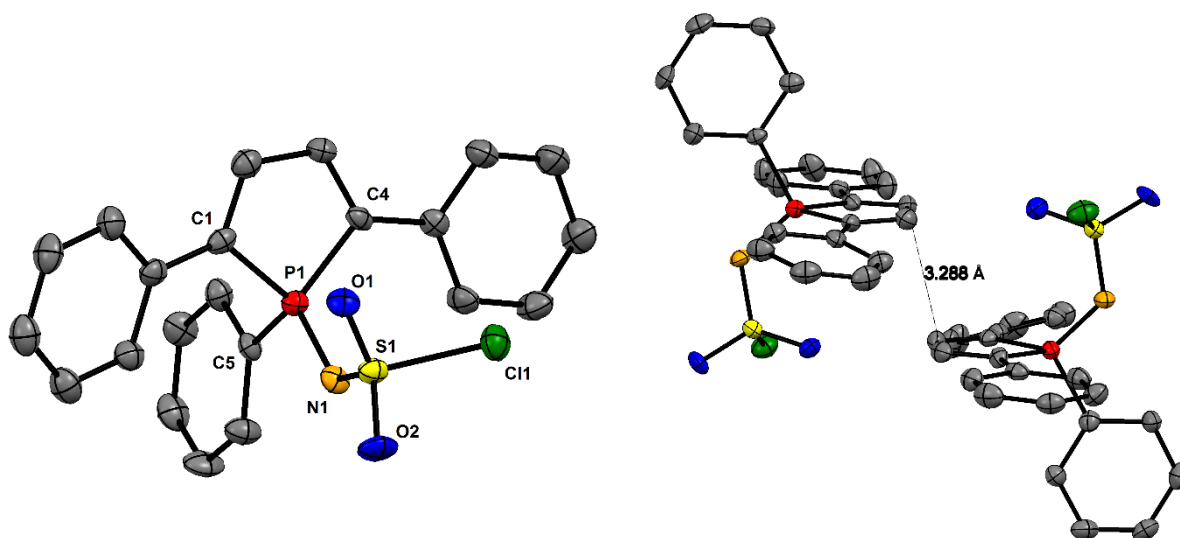


Table S2.5. Selected bond lengths and bond angles in **8a** (values of the second molecule in [])

Bond lengths in Å		Bond angles in °	
P(1)-N(1) [P(2)-N(2)]	1.609(4) [1.603(4)]	C(1)-P(1)-C(4)	94.8(2)
S(1)-N(1) [S(2)-N(2)]	1.557(4) [1.546(4)]	[C(23)-P(2)-C(26)]	[94.4(3)]
S(1)-O(1) [S(2)-O(3)]	1.432(4) [1.424(4)]	N(1)-S(1)-Cl(1)	103.9(2)
Cl(1)-S(1) [Cl(2)-S(2)]	2.079(2) [2.081(2)]	[N(2)-S(2)-Cl(2)]	[103.8(2)]
P(1)-C(4) [P(2)-C(26)]	1.816(5) [1.817(5)]	S(1)-N(1)-P(1)	122.3(3)
P(1)-C(5) [P(2)-C(27)]	1.788(5) [1.790(6)]	[S(2)-N(2)-P(2)]	[124.8(3)]

Structure parameters for **8a**:

$C_{23}H_{18.50}ClN_{1.50}O_2PS$, $M = 446.37$, $T = 130(2)$ K, monoclinic space group Cc , $a = 805.45(2)$ pm, $b = 2725.03(6)$ pm, $c = 1891.44(5)$ pm, $\alpha = 90^\circ$, $\beta = 91.813(2)^\circ$, $\gamma = 90^\circ$, $V = 4.1494(2)$ nm³, $\rho_{calc} = 1.429$ Mg·m⁻³, $Z = 8$, $\mu = 0.384$ mm⁻¹, crystal size 0.25 x 0.10 x 0.10 mm³, reflections collected 13347, independent reflections 13347 [R(int) = 0.0468], completeness to $\theta = 28.285^\circ$: 100.0 %, 534 parameters, 2 restraints. Absolute structure parameter: 0.06(7). All hydrogen atoms were calculated on idealized positions. All tested crystals were twinned. R indices (all data): $R_1 = 0.0737$, $wR_2 = 0.1029$, R indices [$I > 2\sigma(I)$]: $R_1 = 0.0467$, $wR_2 = 0.0979$.

2.6 Molecular structure, selected bond lengths and bond angles of **8b**

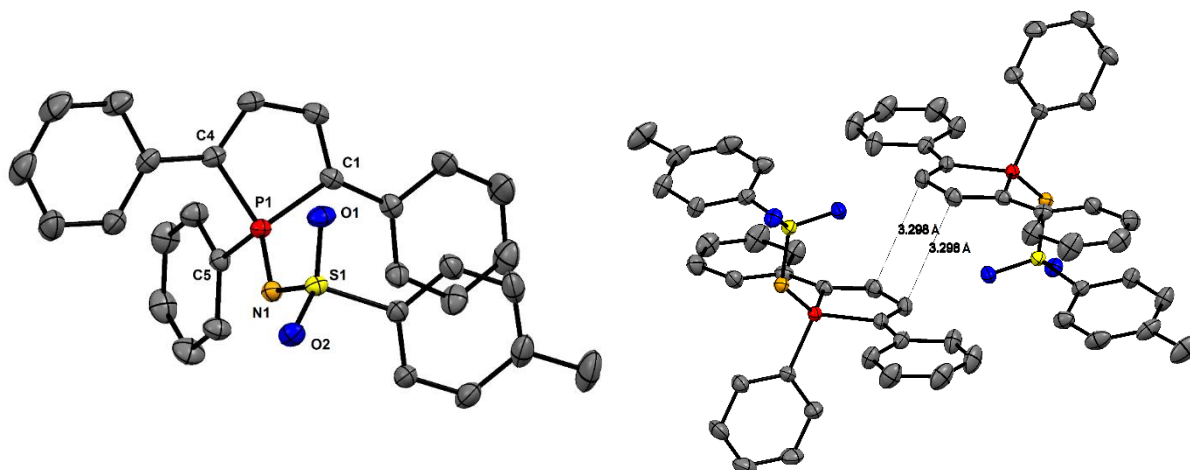


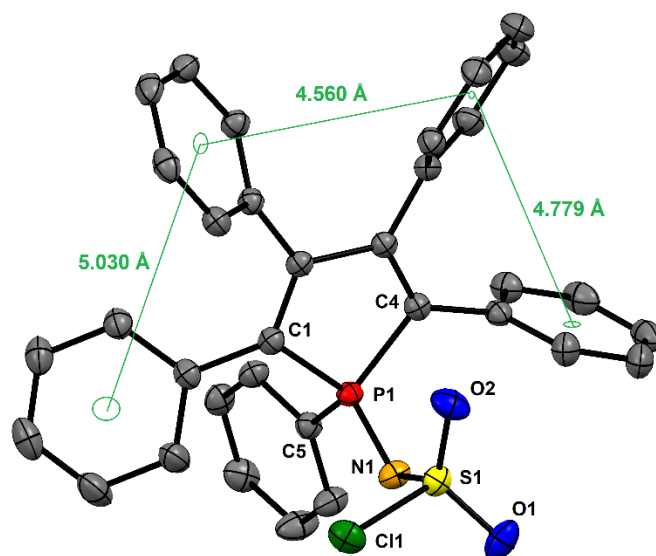
Table S2.6. Selected bond lengths and bond angles in **8b**

Bond lengths in Å		Bond angles in °	
P(1)-N(1)	1.595(1)	C(4)-P(1)-C(1)	94.18(6)
P(1)-C(1)	1.814(1)	N(1)-P(1)-C(1)	120.18(5)
P(1)-C(4)	1.812(1)	S(1)-N(1)-P(1)	121.73(6)
P(1)-C(5)	1.789(1)	O(2)-S(1)-C(23)	107.24(6)
S(1)-N(1)	1.591(1)	O(2)-S(1)-N(1)	107.98(5)
S(1)-C(23)	1.767(1)		

Structure parameters for **8b**:

$C_{29}H_{24}NO_2PS$, $M = 481.52$, $T = 130(2)$ K, monoclinic space group $P2_1/n$, $a = 1116.66(2)$ pm, $b = 1715.21(3)$ pm, $c = 1284.70(2)$ pm, $\alpha = 90^\circ$, $\beta = 103.054(2)^\circ$, $\gamma = 90^\circ$, $V = 2.39701(7)$ nm³, $\rho_{calc} = 1.334$ Mg·m⁻³, $Z = 4$, $\mu = 0.229$ mm⁻¹, crystal size 0.40 x 0.30 x 0.20 mm³, reflections collected 40268, independent reflections 8154 [R(int) = 0.0417], completeness to $\theta = 30.510^\circ$, 100.0 %, 403 parameters, 0 restraints. All H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. R indices (all data): R1 = 0.0569, wR2 = 0.1065, R indices [$I > 2\sigma(I)$]: R1 = 0.0410, wR2 = 0.0990.

2.7 Molecular structure, selected bond lengths and bond angles of **9a**



Distances between centers of exocyclic phenyl rings (green).

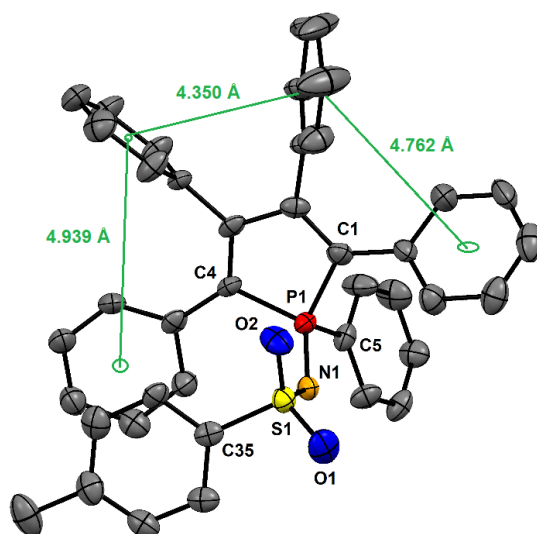
Table S2.7. Selected bond lengths and bond angles in **9a** (values of the second molecule in [])

Bond lengths in Å		Bond angles in °	
P(1)-N(1) [P(2)-N(2)]	1.613(1) [1.617(1)]	C(1)-P(1)-C(4)	94.69(7)
Cl(1)-S(1) [Cl(2)-S(2)]	2.077(1) [2.0852(6)]	[C(35)-P(2)-C(38)]	[95.12(7)]
P(1)-C(1) [P(2)-C(35)]	1.798(2) [1.784(1)]	N(1)-S(1)-Cl(1)	102.85(6)
P(1)-C(4) [P(2)-C(38)]	1.794(1) [1.799(1)]	[N(2)-S(2)-Cl(2)]	[103.55(5)]
P(1)-C(5) [P(2)-C(39)]	1.786(2) [1.785(2)]	S(1)-N(1)-P(1)	125.61(8)
S(1)-N(1) [S(2)-N(2)]	1.561(1) [1.558(1)]	[S(2)-N(2)-P(2)]	[123.55(8)]

Structure parameters for **9a**:

$C_{34}H_{25}ClNO_2PS$, $M = 578.03$, $T = 130(2)$ K, monoclinic space group $P2_1/c$, $a = 1643.40(2)$ pm, $b = 1568.04(2)$ pm, $c = 2217.48(3)$ pm, $\alpha = 90^\circ$, $\beta = 92.558(1)^\circ$, $\gamma = 90^\circ$, $V = 5.7086(1)$ nm³, $\rho_{calc} = 1.345$ Mg·m⁻³, $Z = 8$, $\mu = 0.296$ mm⁻¹, crystal size 0.40 x 0.30 x 0.10 mm³, reflections collected 73955, independent reflections 18861 [R(int) = 0.0465], completeness to $\theta = 30.510^\circ$, 100.0%, 934 parameters, 15 restraints. One SO₂Cl substituent (Cl1, S1, O1 and O2) is disordered with a ratio of 0.872(2) : 0.128(2). All H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. R indices (all data): R1 = 0.0715, wR2 = 0.1139, R indices [$I > 2\sigma(I)$]: R1 = 0.0437, wR2 = 0.0998.

2.8 Molecular structure, selected bond lengths and bond angles of **9b**



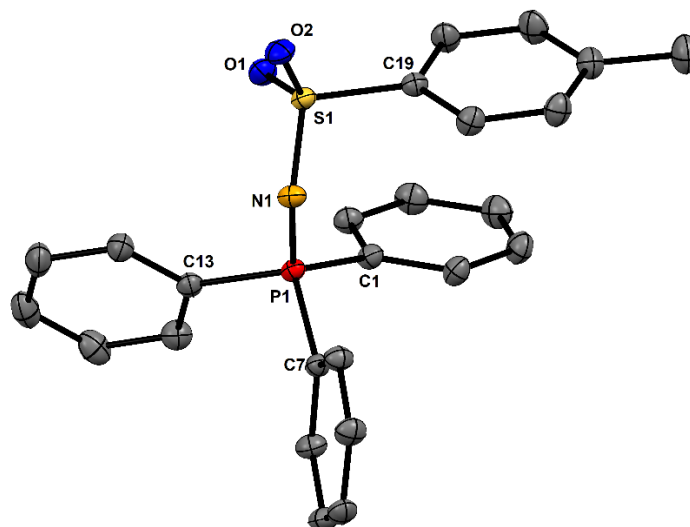
Distances between centers of exocyclic phenyl rings (green).

Table S2.8. Selected bond lengths and bond angles in **9b**

Bond lengths in Å		Bond angles in °	
P(1)-N(1)	1.569(6)	S(1)-N(1)-P(1)	125.1(4)
P(1)-C(1)	1.798(9)	C(4)-P(1)-C(1)	94.7(4)
P(1)-C(4)	1.807(8)	C(5)-P(1)-C(1)	108.0(4)
P(1)-C(5)	1.778(7)	N(1)-P(1)-C(5)	104.7(3)
S(1)-N(1)	1.601(6)	O(2)-S(1)-C(35)	108.0(4)
S(1)-C(35)	1.748(9)	N(1)-S(1)-C(35)	105.1(4)

Structure parameters for **9b**:

$C_{41}H_{32}NO_2PS$, $M = 633.70$, $T = 130(2)$ K, Orthorhombic space group $Pna2_1$, $a = 5012.88(8)$ pm, $b = 1019.11(2)$ pm, $c = 1874.59(4)$ pm, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 9.5767(3)$ nm³, $\rho_{calc} = 1.319$ Mg·m⁻³, $Z = 12$, $\mu = 0.190$ mm⁻¹, crystal size 0.40 x 0.25 x 0.10 mm³, reflections collected 63968, independent reflections 17297 [$R(int) = 0.0564$], completeness to $\theta = 25.350^\circ$, 99.9 %, 1430 parameters, 463 restraints. Refined as racemic twin: Twin domain ratio 0.6(2) : 0.4(2). One molecule (P3 to C123) was slightly disordered with a ratio of 0.783(7) : 0.217(7). All hydrogen atoms were calculated on idealized positions. R indices (all data): $R1 = 0.0967$, $wR2 = 0.2178$, R indices [$I > 2\sigma(I)$]: $R1 = 0.0845$, $wR2 = 0.2096$.

2.9 Molecular structure, selected bond lengths and bond angles of **13****Table S2.9.** Selected bond lengths and bond angles in **13**

Bond lengths in pm		Bond angles in °	
P(1)-N(1)	1.599(1)	S(1)-N(1)-P(1)	124.37(6)
P(1)-C(1)	1.798(1)	C(1)-P(1)-C(13)	108.91(5)
P(1)-C(13)	1.798(1)	N(1)-S(1)-C(19)	105.11(5)
S(1)-N(1)	1.578(1)	O(2)-S(1)-C(19)	107.05(6)
S(1)-C(19)	1.769(1)	O(1)-S(1)-C(19)	107.11(5)

Structure parameters for **13**:

$C_{25}H_{22}NO_2PS$, $M = 431.46$, $T = 130(2)$ K, triclinic space group $P\bar{1}$, $a = 887.31(3)$ pm, $b = 1056.34(3)$ pm, $c = 1294.78(4)$ pm, $\alpha = 106.562(2)^\circ$, $\beta = 99.860(2)^\circ$, $\gamma = 107.702(3)^\circ$, $V = 1.06305(6)$ nm³, $\rho_{calc} = 1.348$ Mg·m⁻³, $Z = 2$, $\mu = 0.250$ mm⁻¹, crystal size 0.31 x 0.18 x 0.11 mm³, reflections collected 25163, independent reflections 7081 [R(int) = 0.0295], completeness to $\theta = 30.510^\circ$, 100.0 %, 359 parameters, 0 restraints. All H atoms were located on difference Fourier maps calculated at the final stage of the structure refinement. R indices (all data): R1 = 0.0466, wR2 = 0.0991, R indices [$I > 2\sigma(I)$]: R1 = 0.0376, wR2 = 0.0935.

3 Spectra

3.1 NMR Spectra

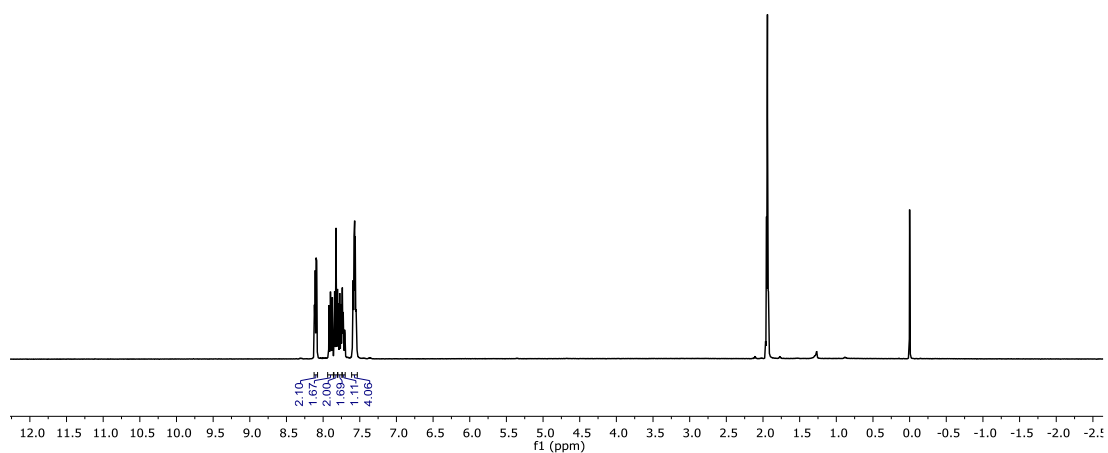
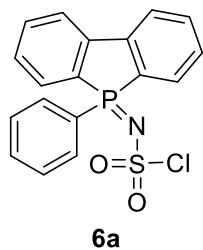


Fig. S3.1: ^1H NMR spectrum of 6a in CD_3CN .

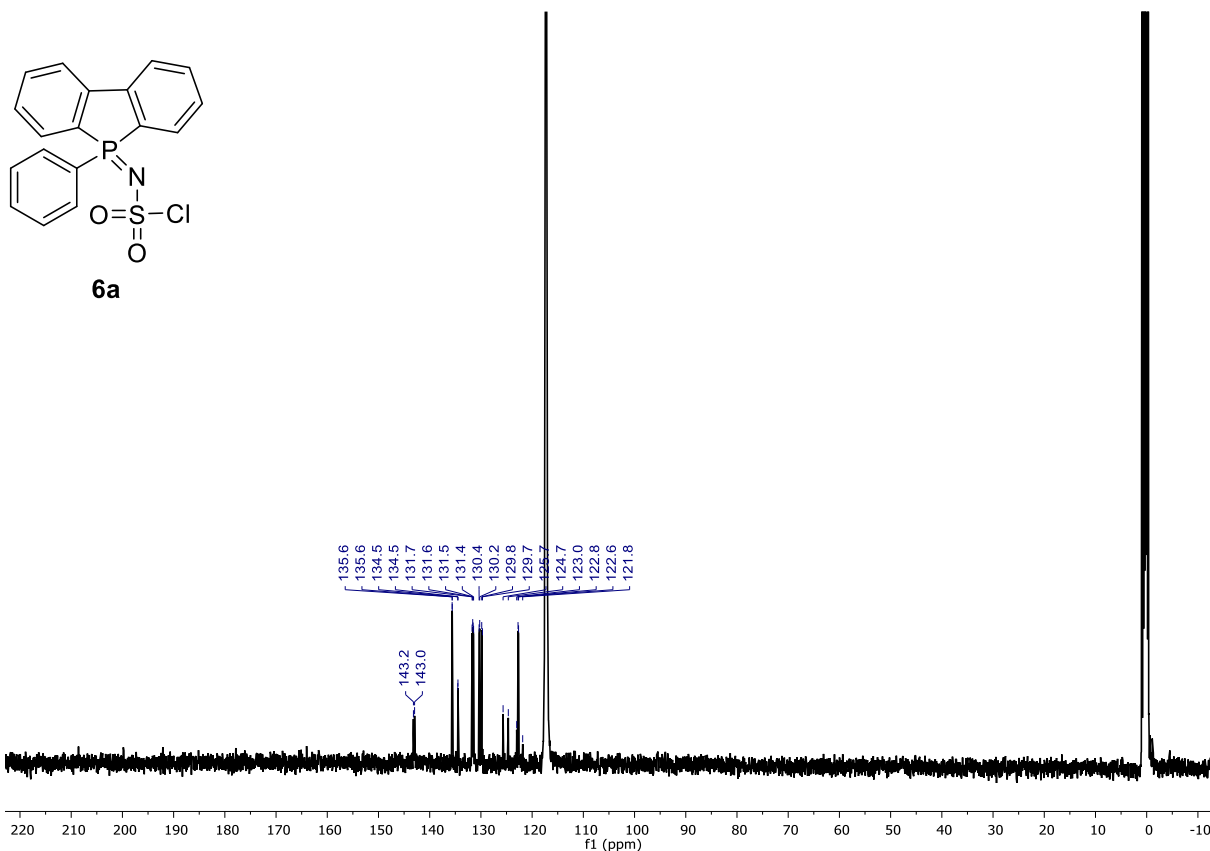


Fig S3.2: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of 6a in CD_3CN .

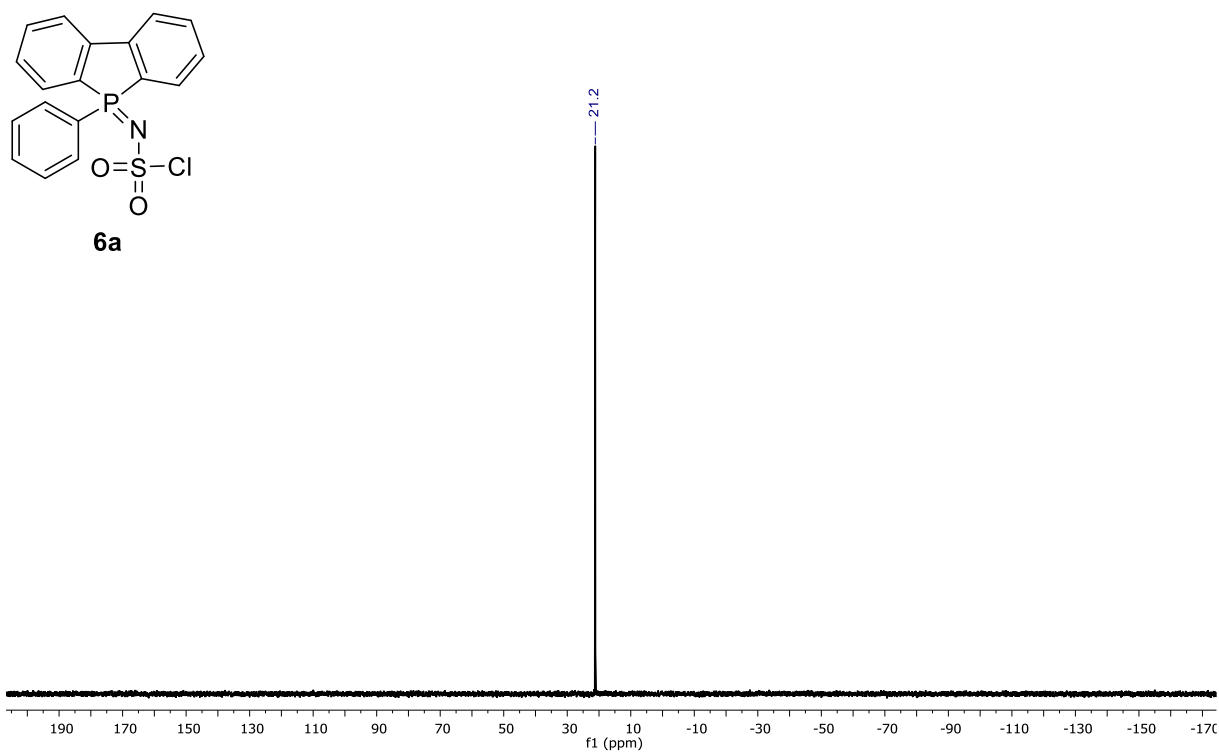


Fig. S3.3: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6a** in CD_3CN .

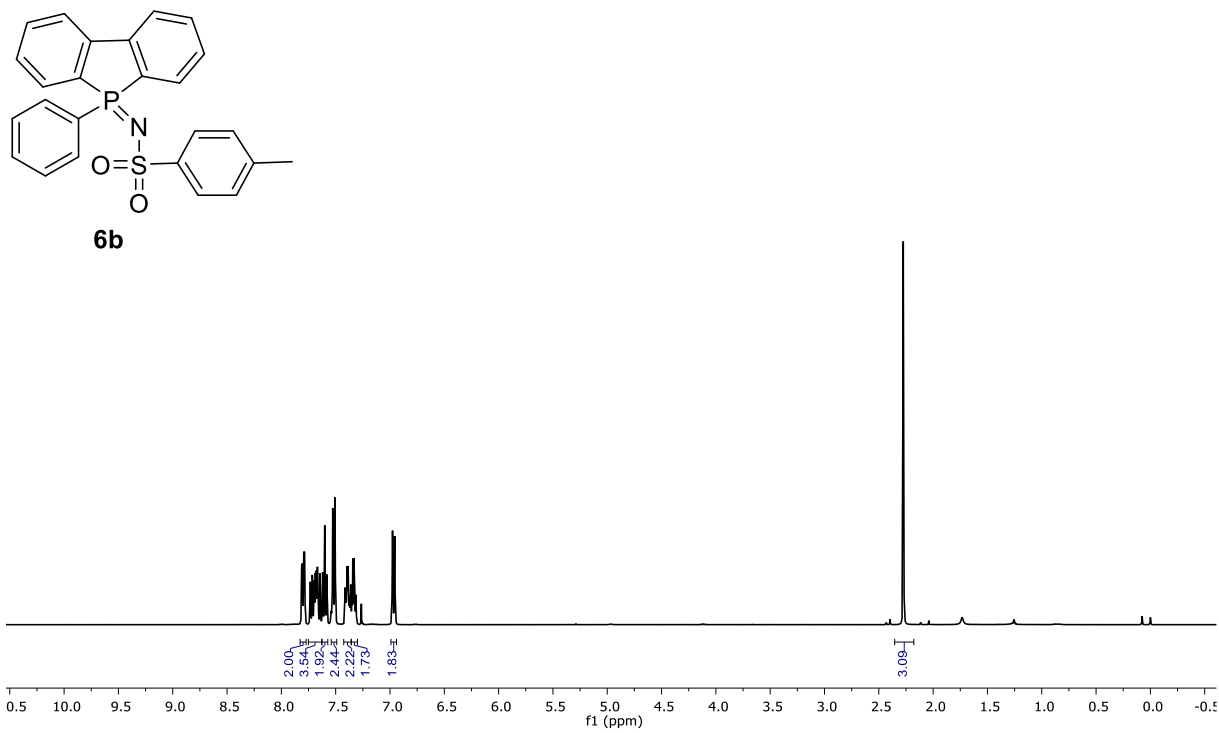


Fig S3.4: ^1H NMR spectrum of **6b** in CDCl_3 .

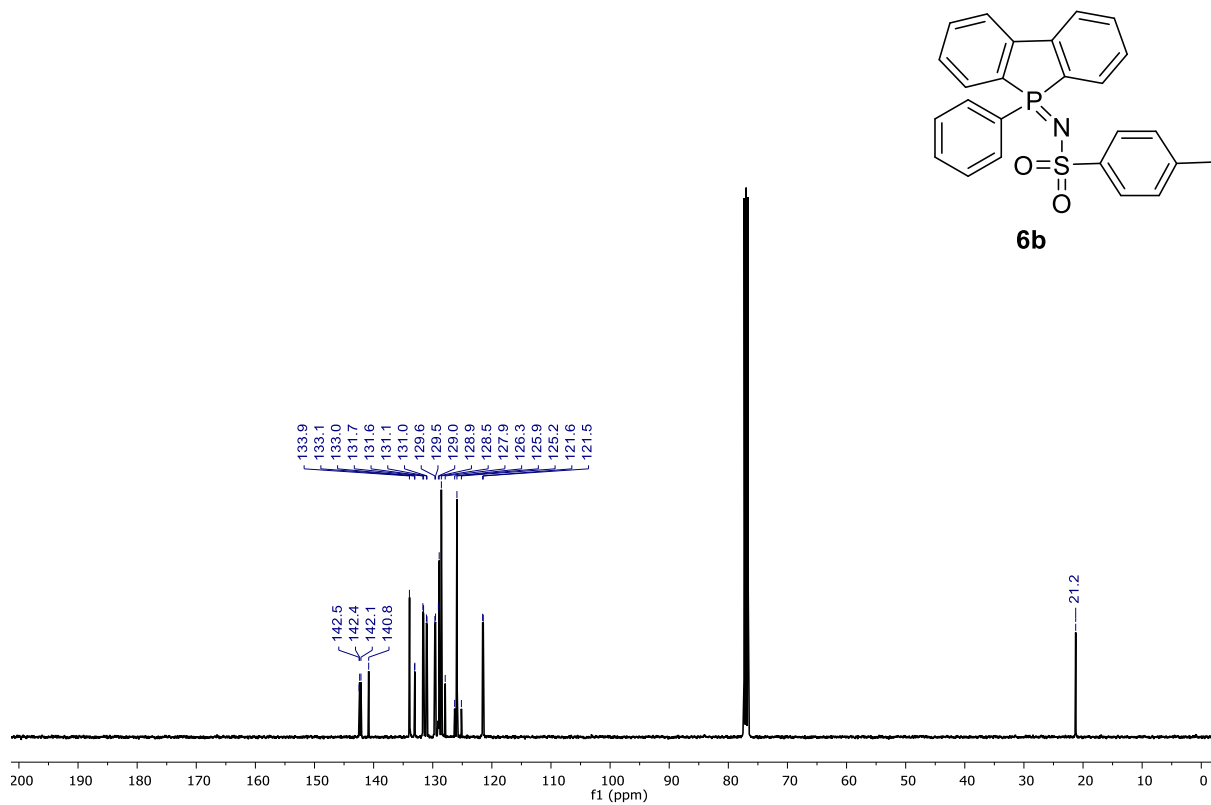


Fig S3.5: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6b** in CDCl_3 .

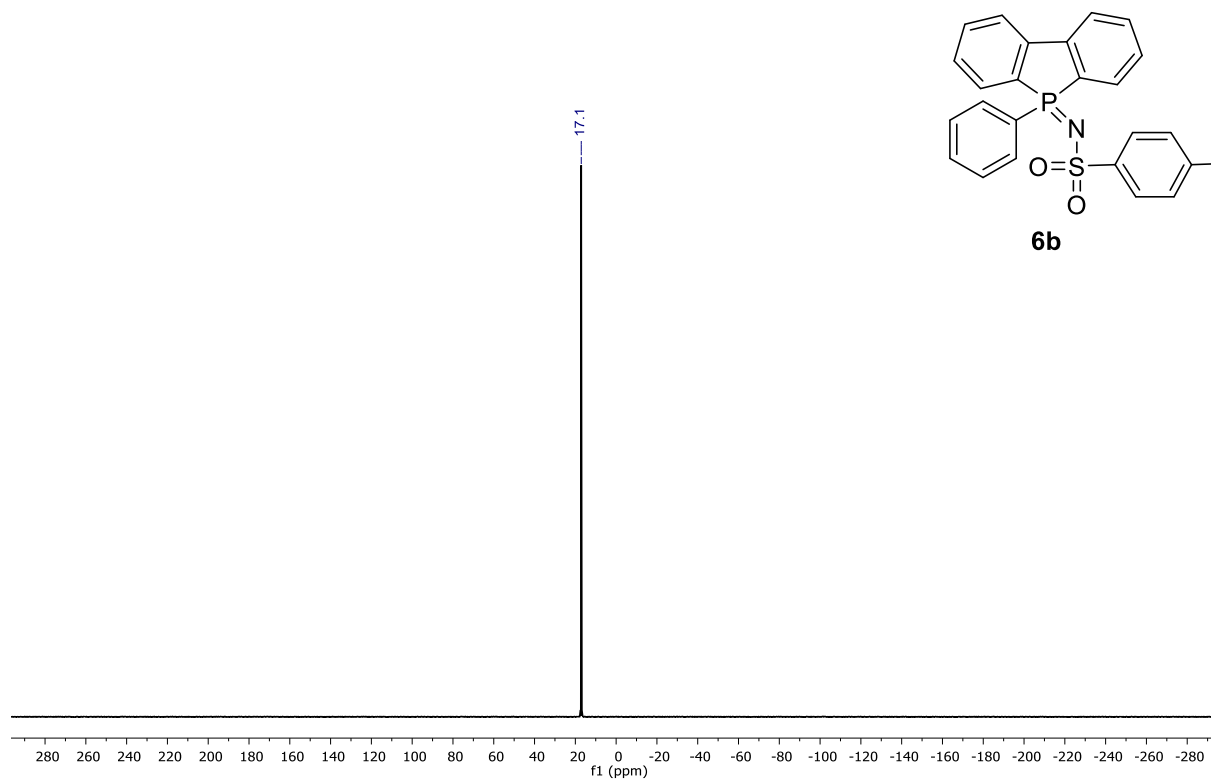
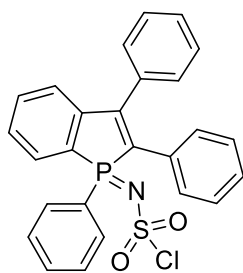
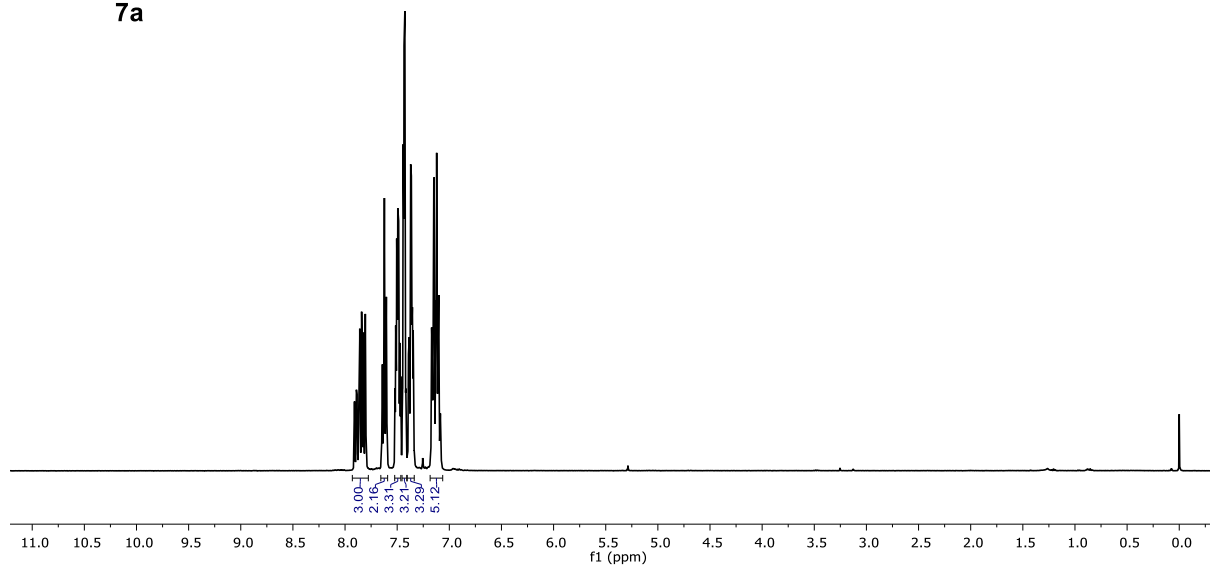
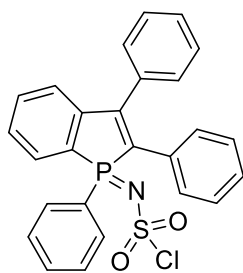
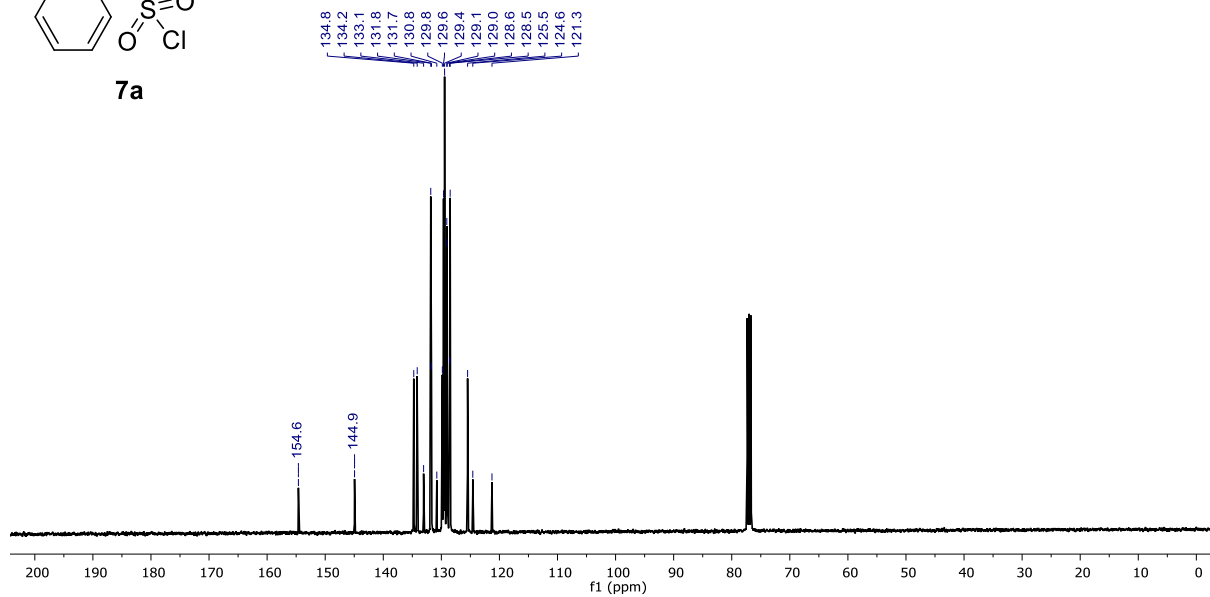


Fig S3.6: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6b** in CDCl_3 .

**7a****Fig S3.7:** ^1H NMR spectrum of **7a** in CDCl_3 .**7a****Fig S3.8:** $^{13}\text{C}\{^1\text{H},^{31}\text{P}\}$ NMR spectrum of **7a** in CDCl_3 .

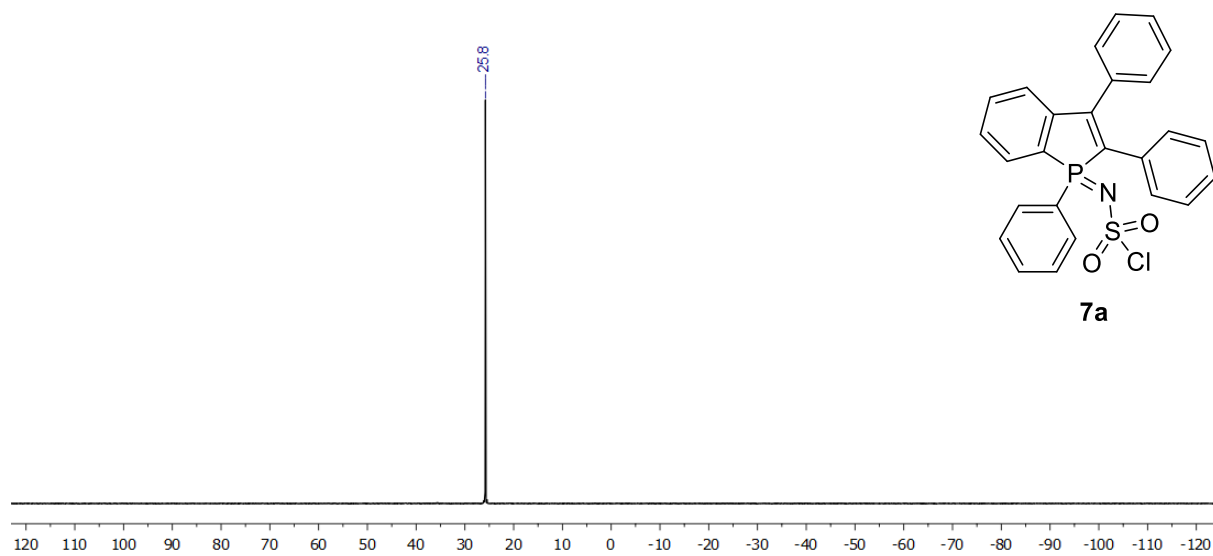


Fig S3.9: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **7a** in CDCl_3 .

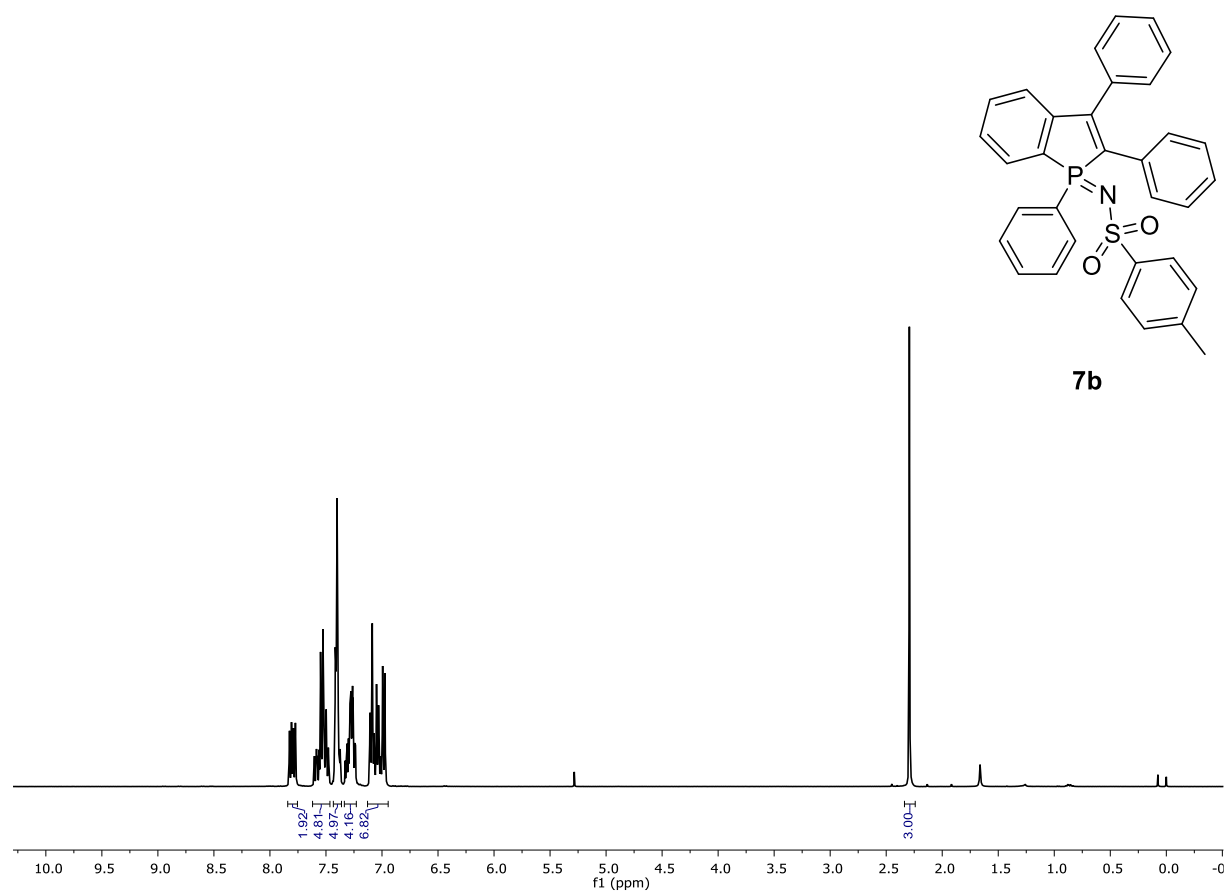


Fig S3.10: ^1H NMR spectrum of **7b** in CDCl_3 .

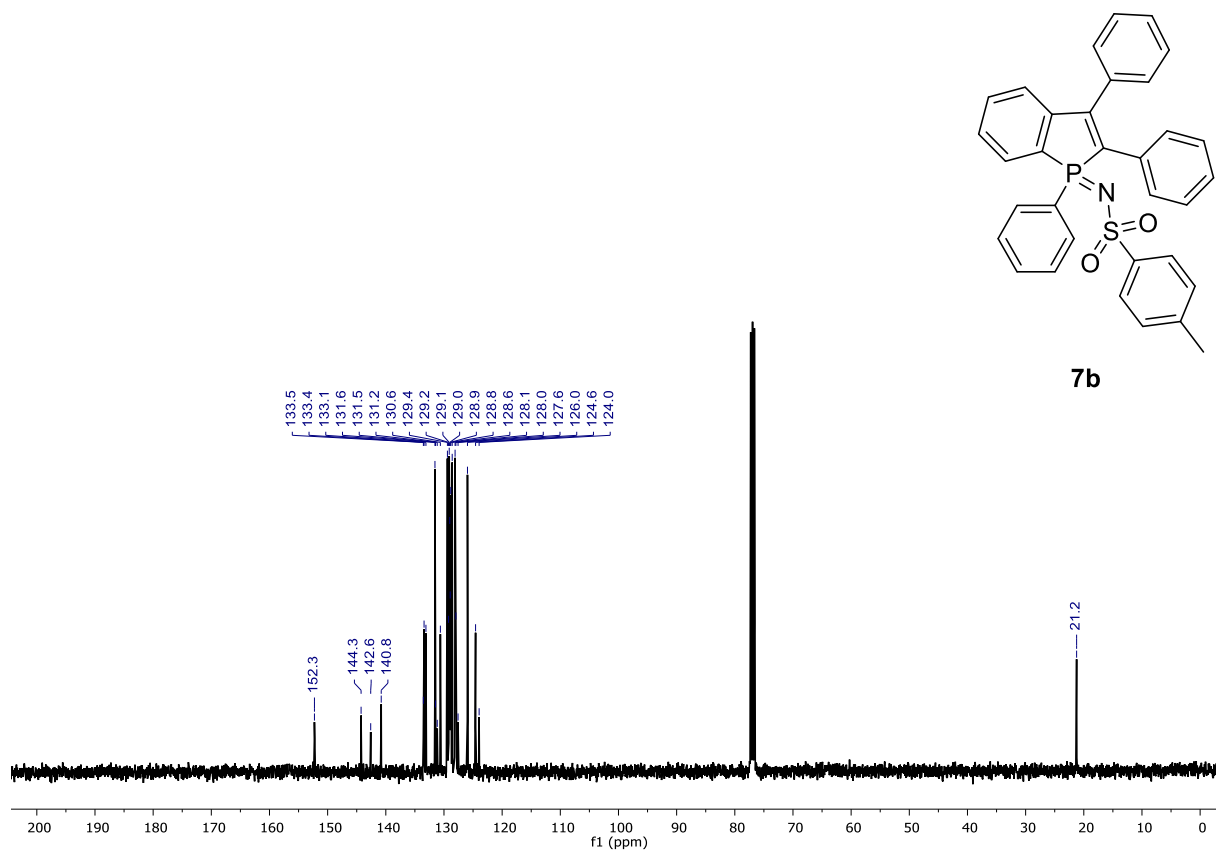


Fig S3.11: ¹³C{¹H,³¹P} NMR spectrum of **7b** in CDCl₃.

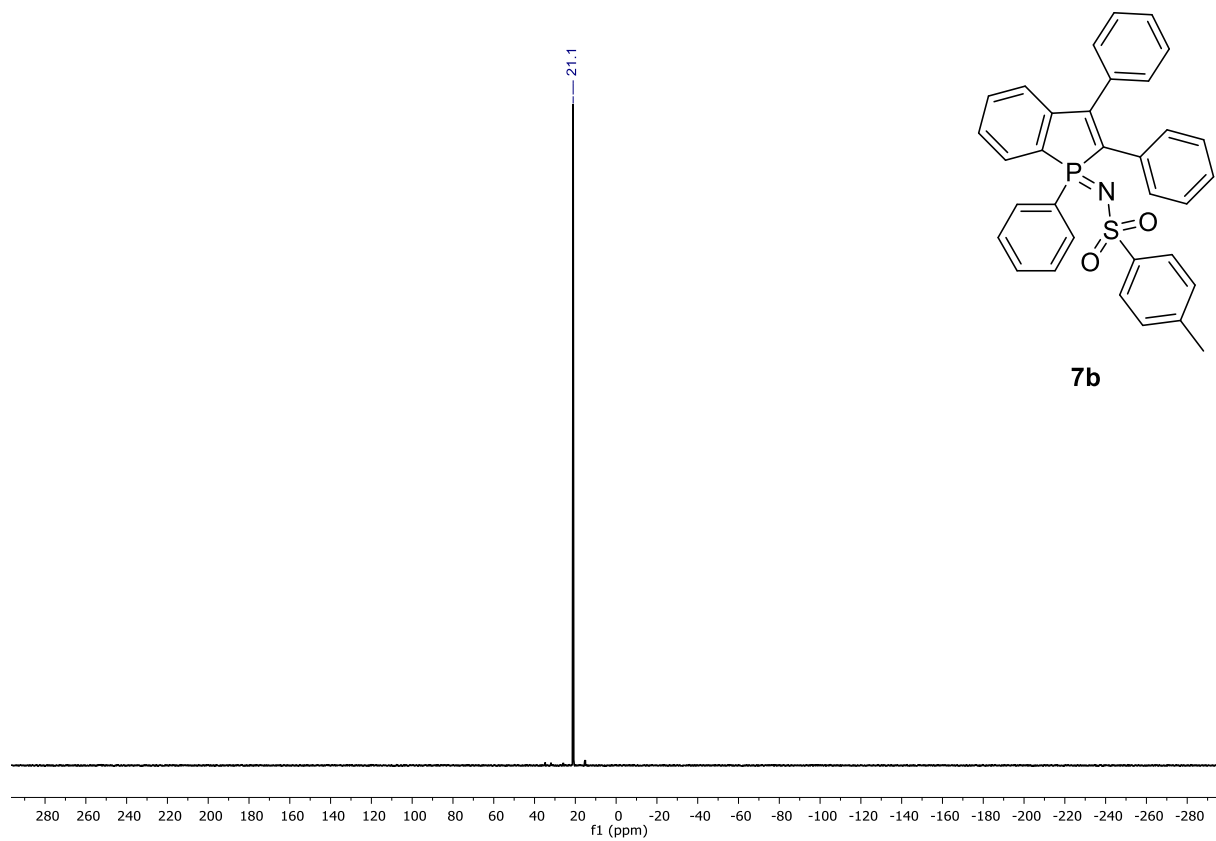
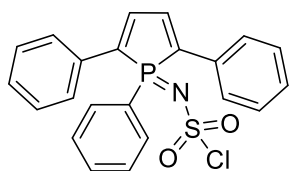
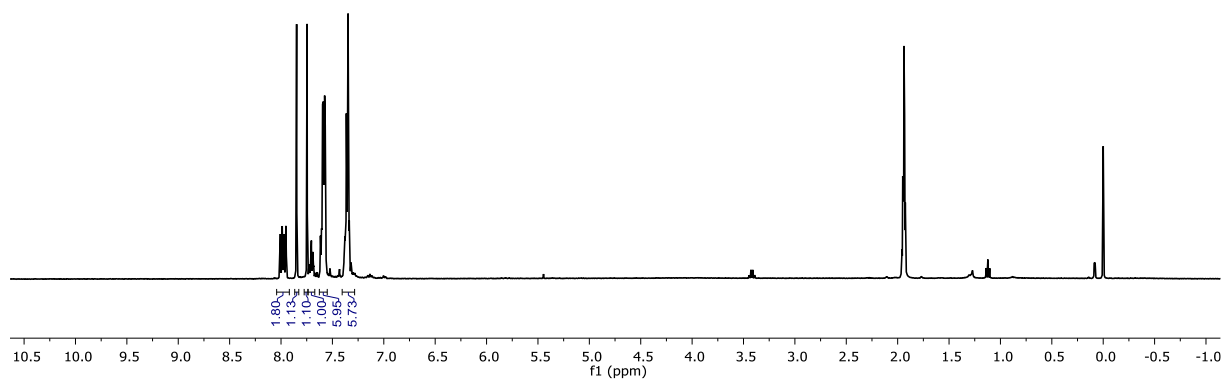
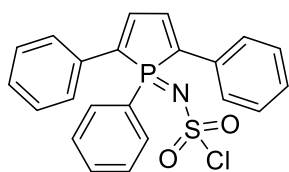
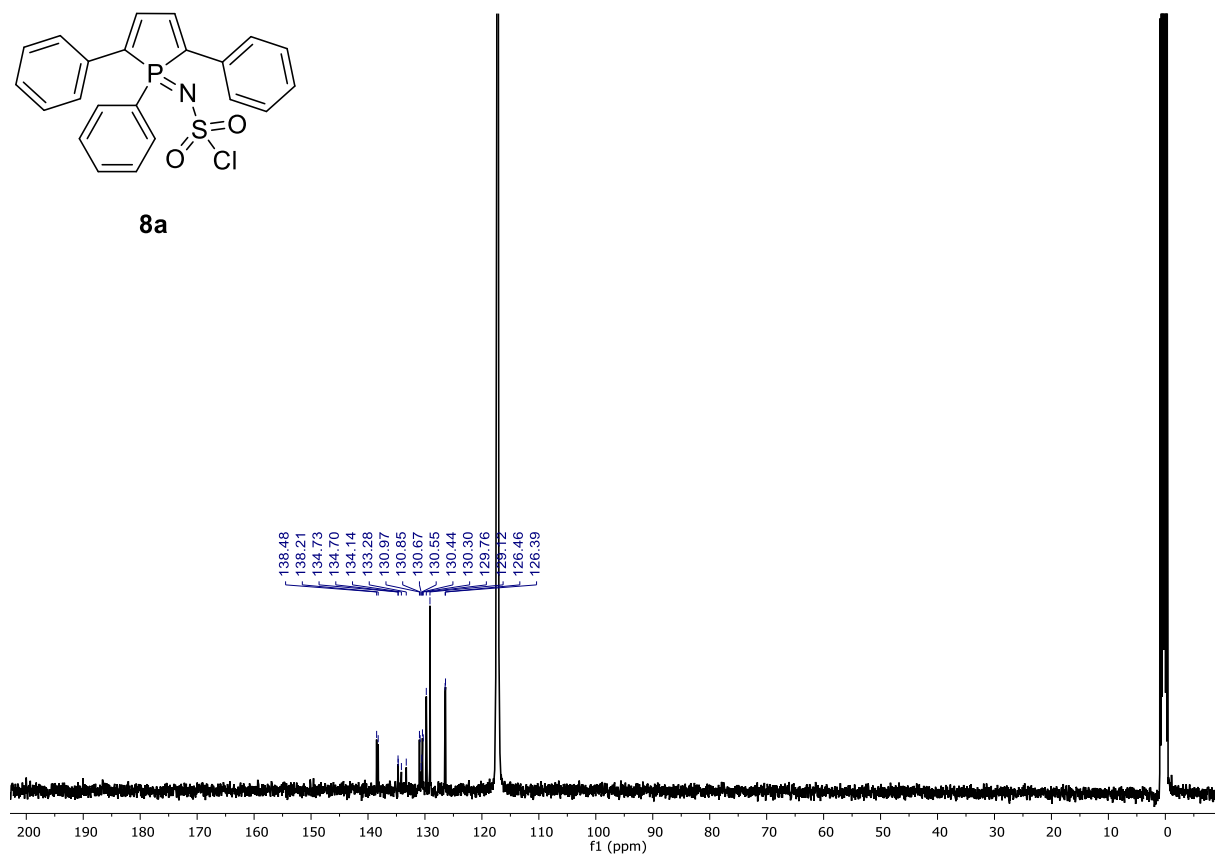


Fig S3.12: ³¹P{¹H} NMR spectrum of **7b** in CDCl₃.

**8a****Fig S3.13:** ^1H NMR spectrum of **8a** in CD_3CN .**8a****Fig S3.14:** $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **8a** in CD_3CN .

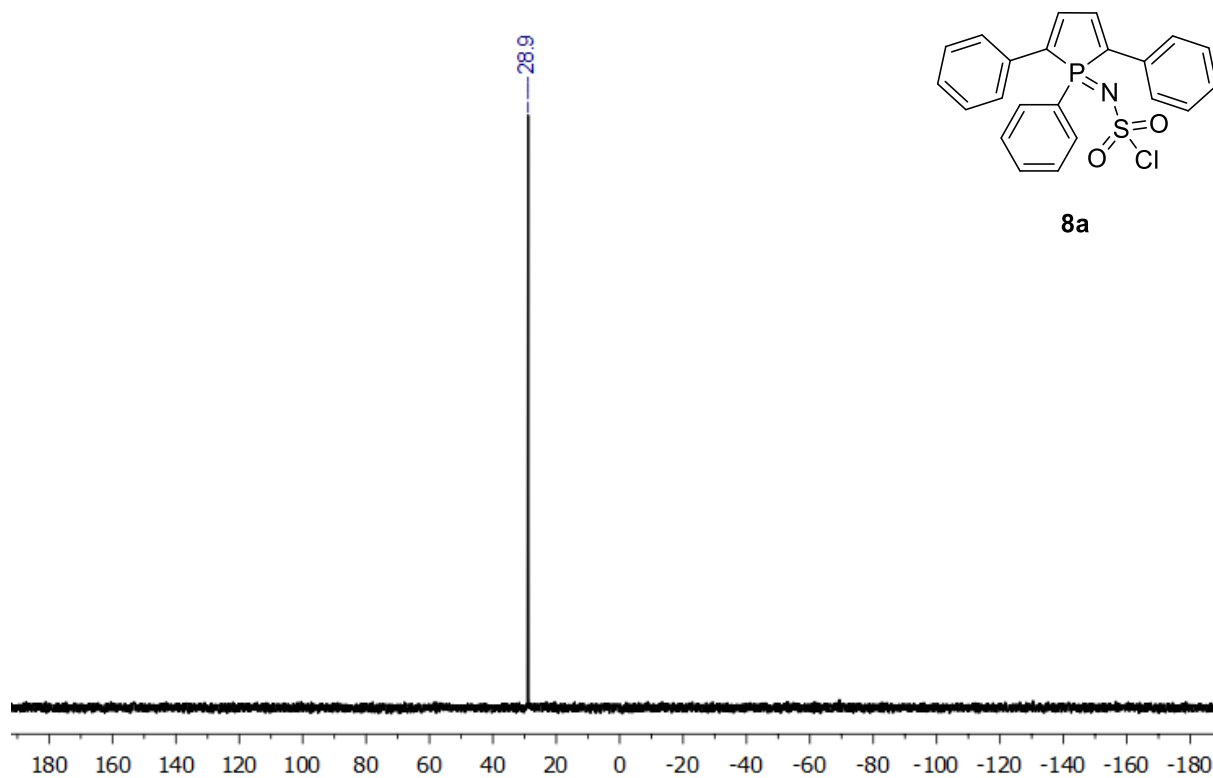


Fig S3.15: ³¹P{¹H} NMR spectrum of **8a** in CD₃CN.

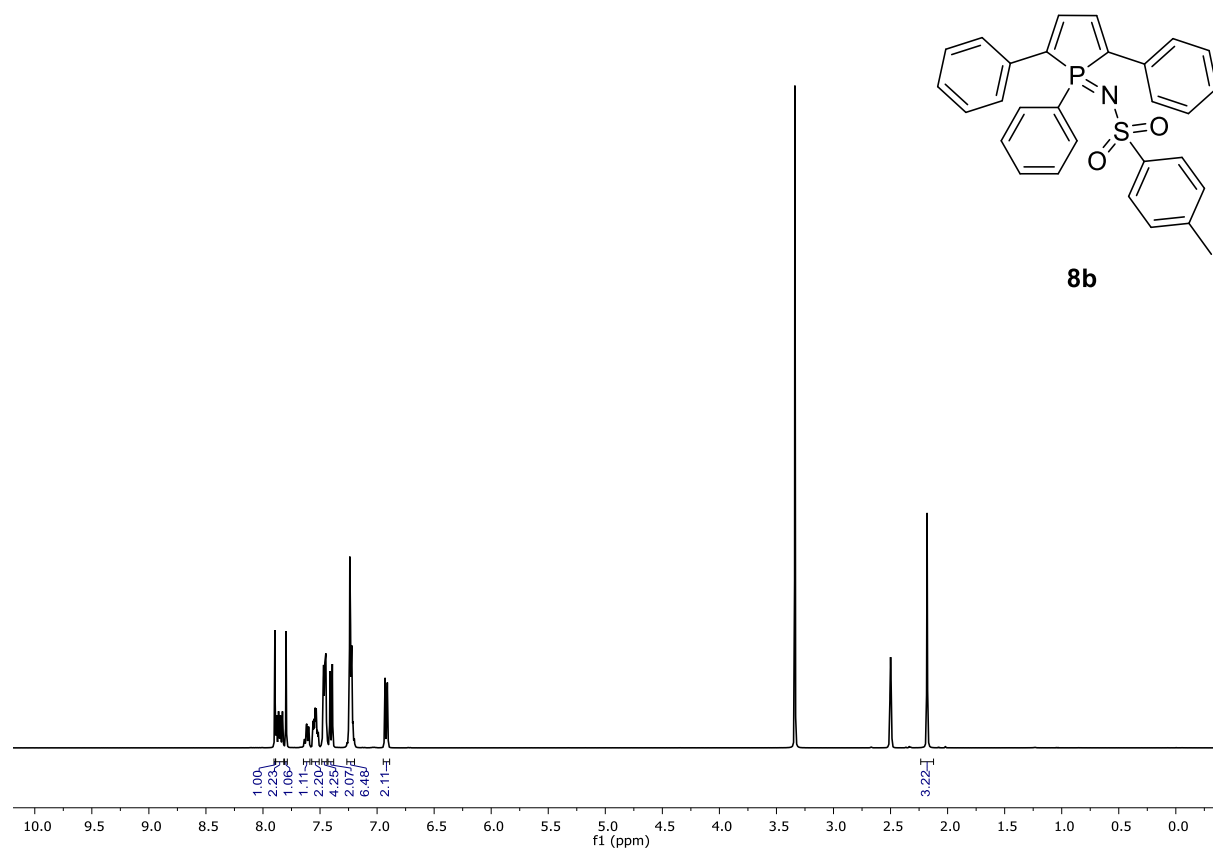


Fig S3.16: ¹H NMR spectrum of **8b** in DMSO-d₆.

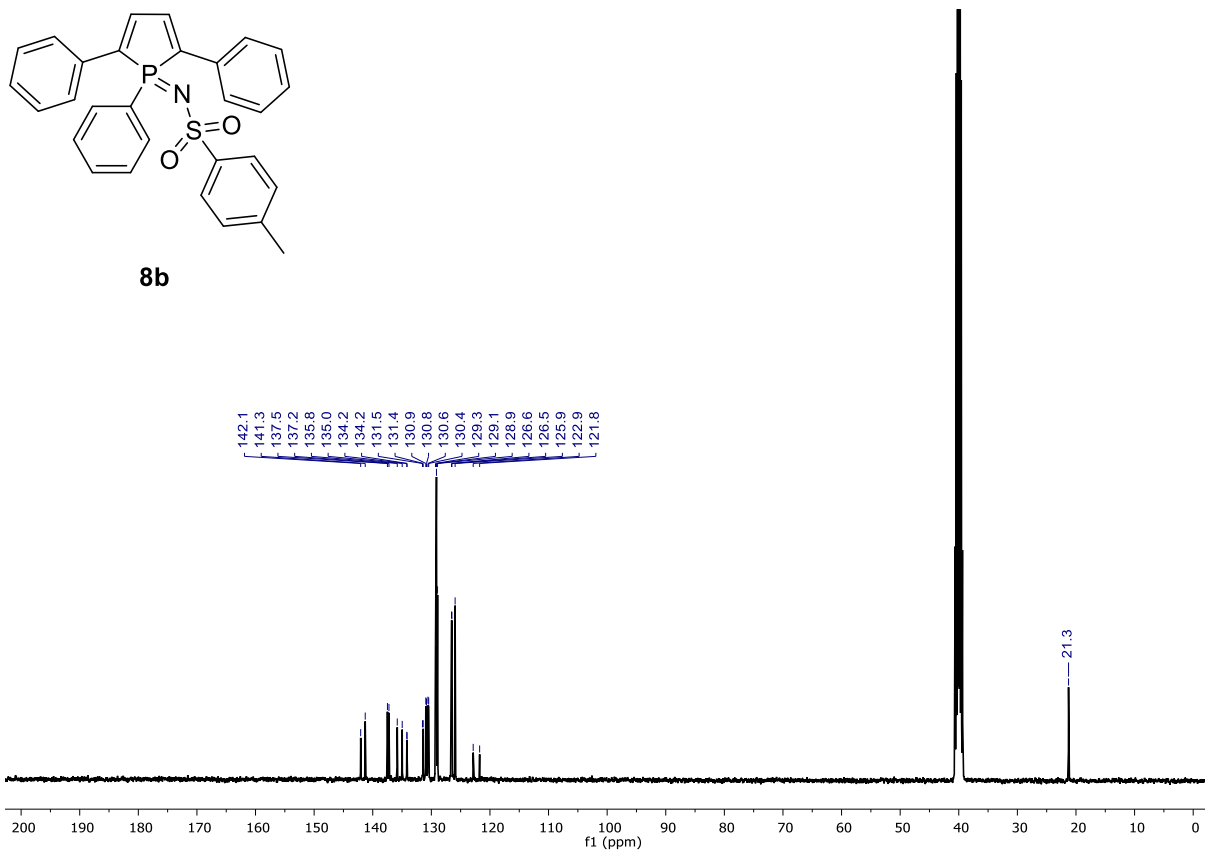


Fig S3.17: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **8a** in DMSO-d_6 .

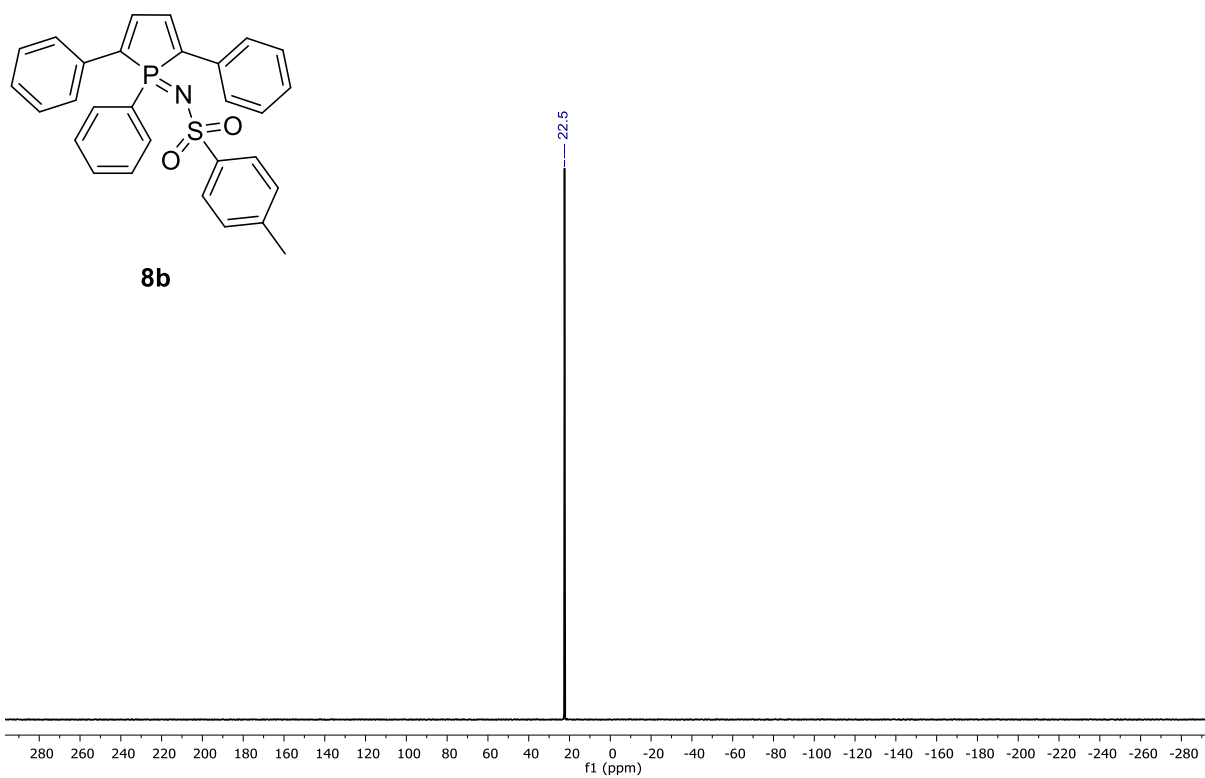


Fig S3.18: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **8b** in DMSO-d_6 .

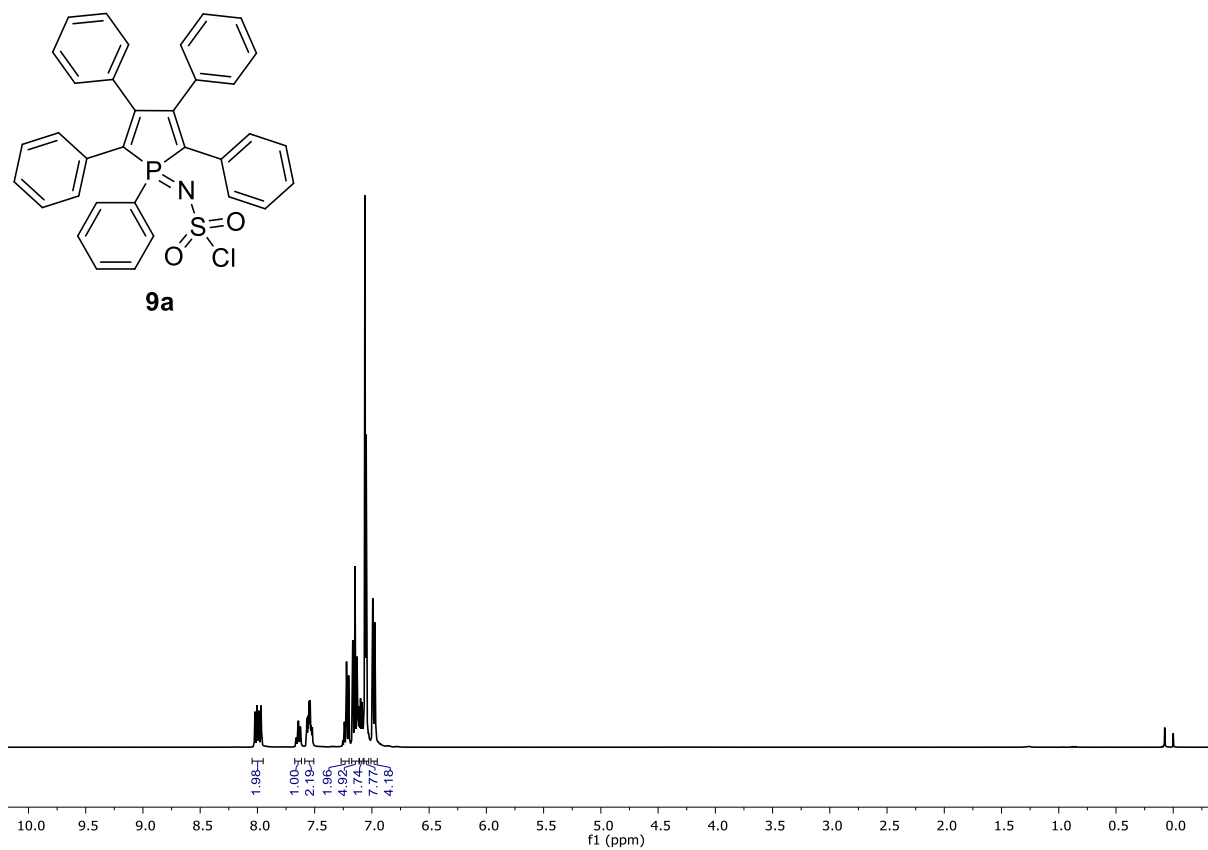


Fig S3.19: ¹H NMR spectrum of **9a** in CDCl₃.

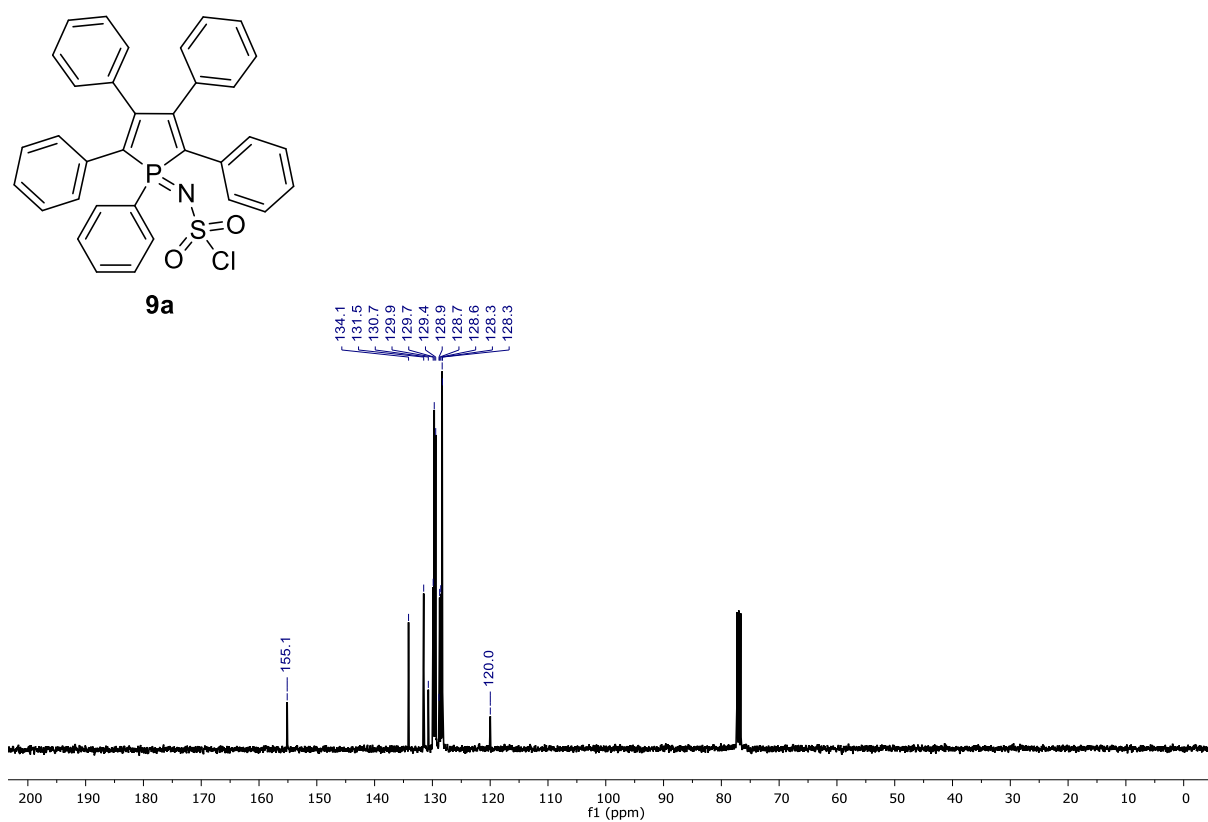


Fig S3.20: ¹³C{¹H,³¹P} NMR spectrum of **9a** in CDCl₃.



Fig S3.21: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **9a** in CDCl_3 .

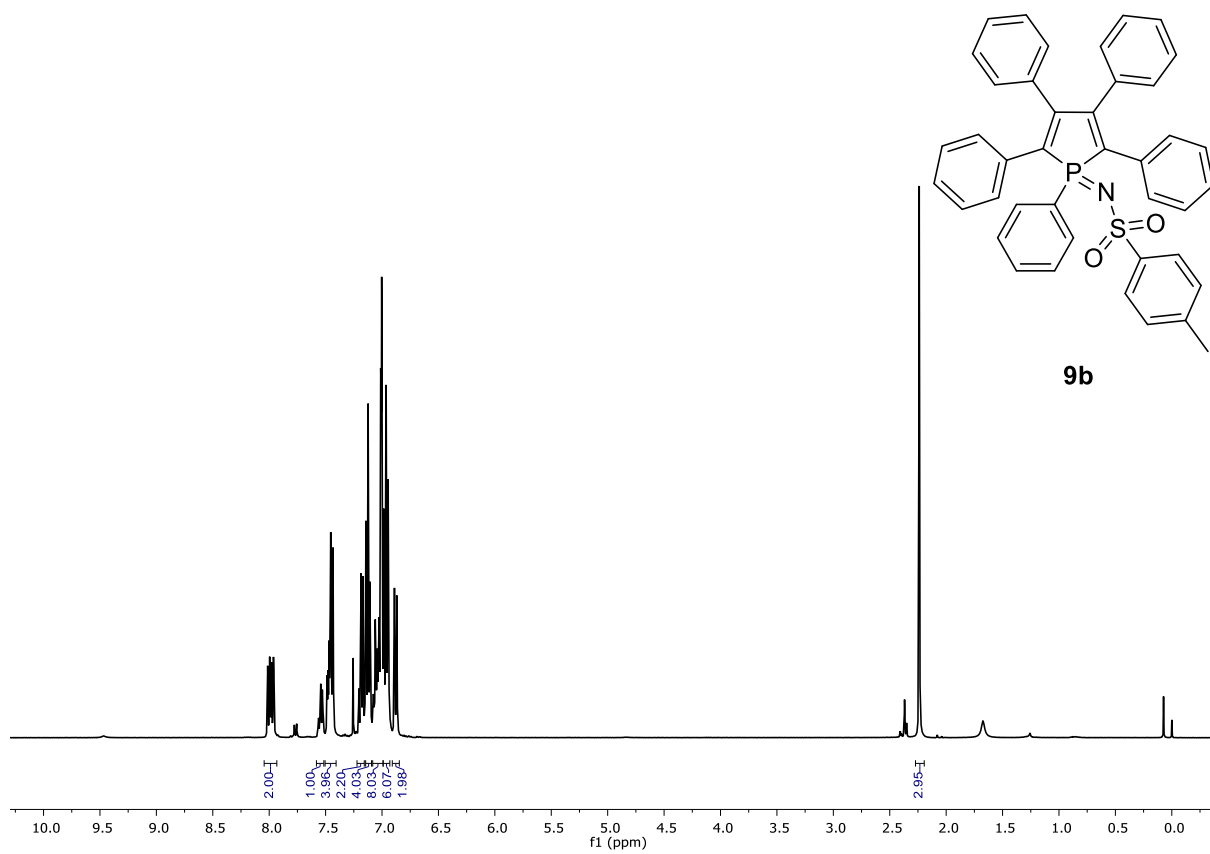


Fig S3.22: ^1H NMR spectrum of **9b** in CDCl_3 .

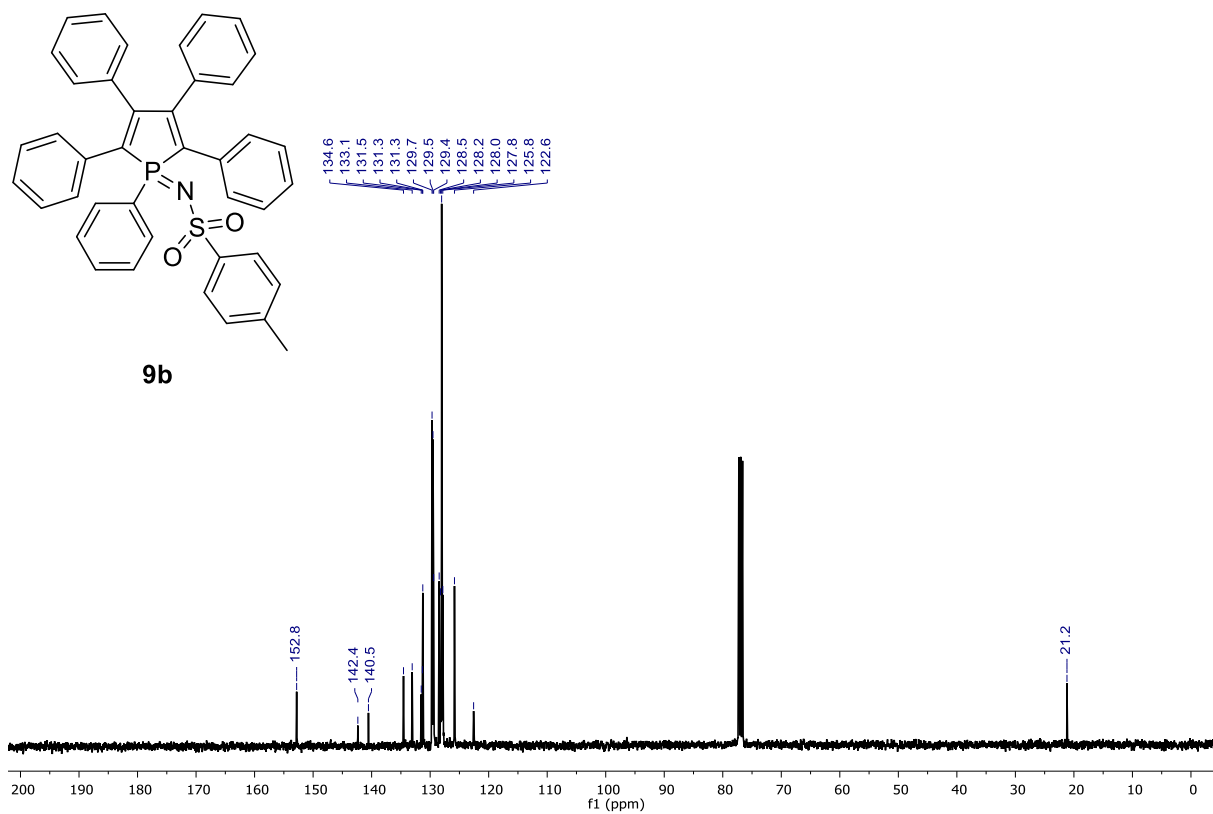


Fig S3.23: $^{13}\text{C}\{^1\text{H},^{31}\text{P}\}$ NMR spectrum of **9b** in CDCl_3 .

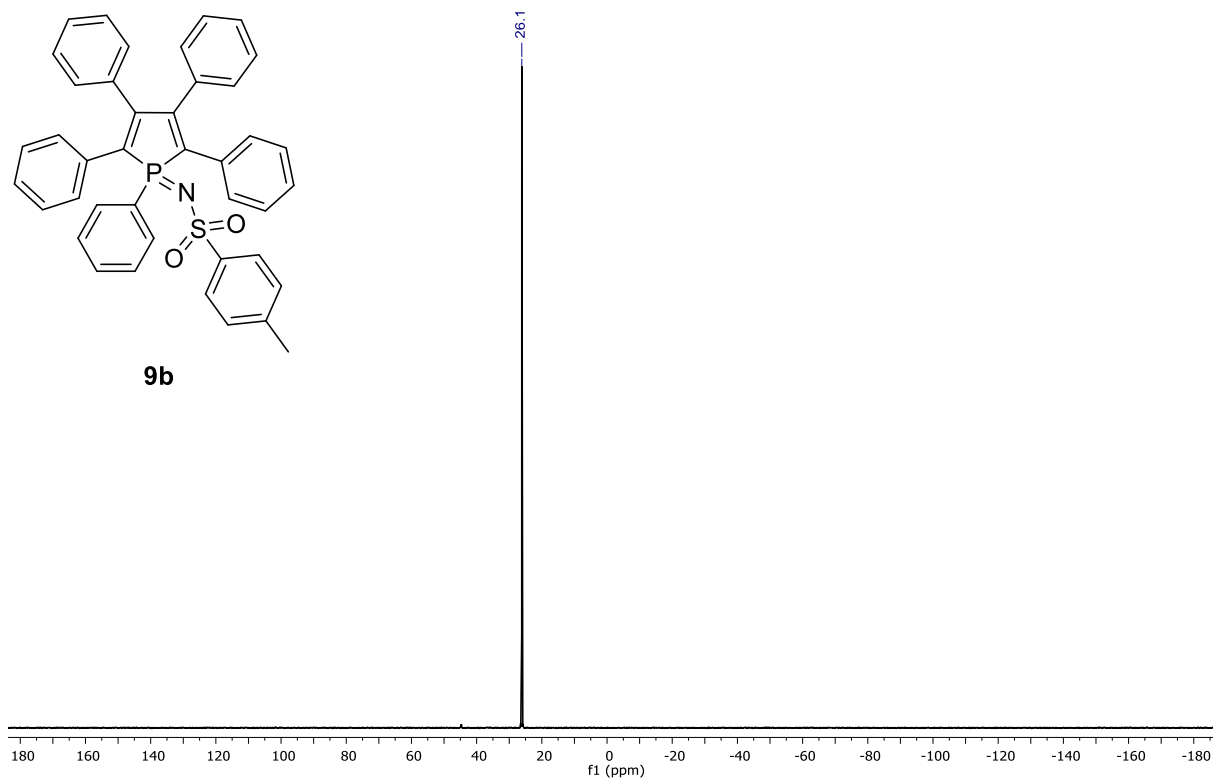
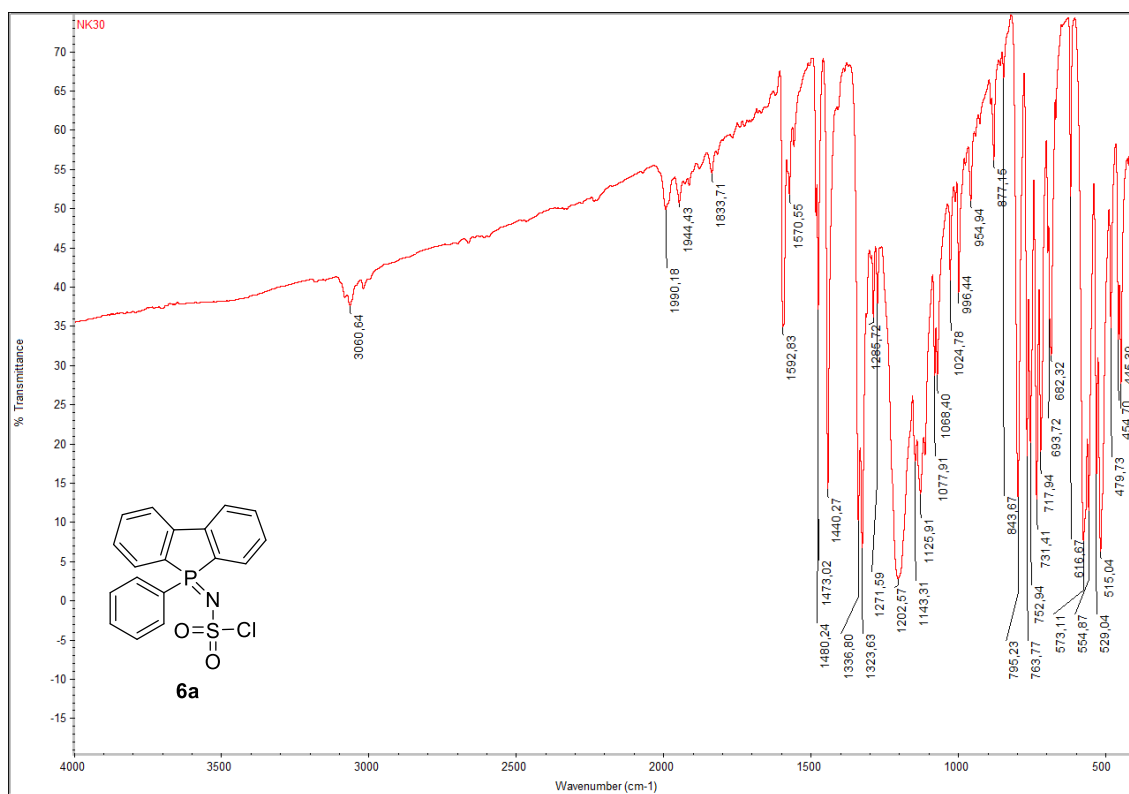
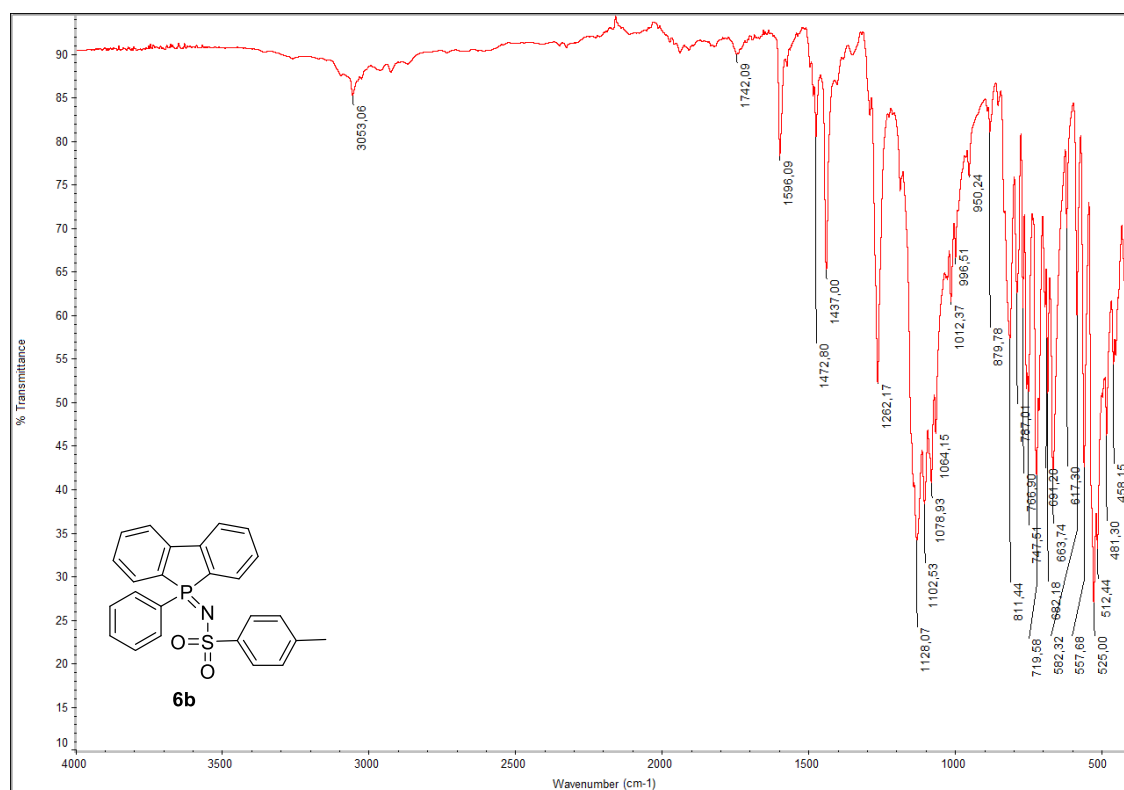


Fig S3.24: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **9b** in CDCl_3 .

3.2 IR Spectra

Fig S3.25: IR spectrum of **6a**.Fig S3.26: IR spectrum of **6b**.

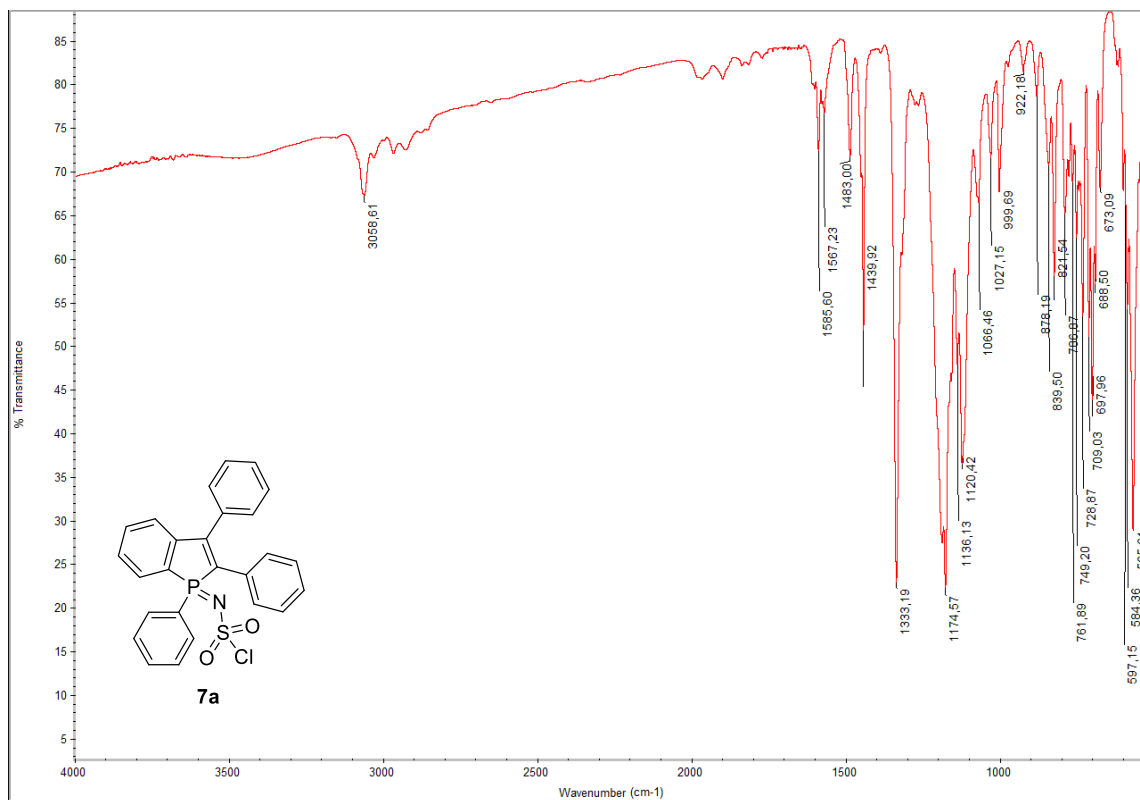


Fig S3.27: IR spectrum of 7a.

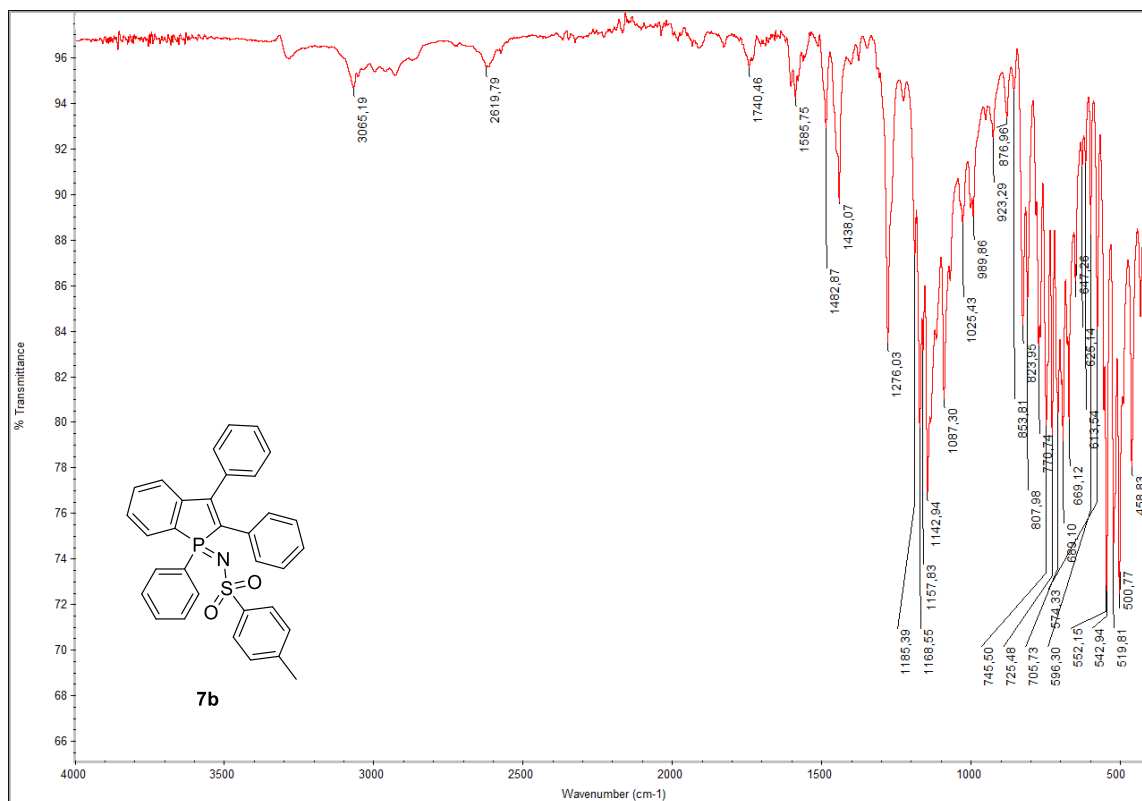
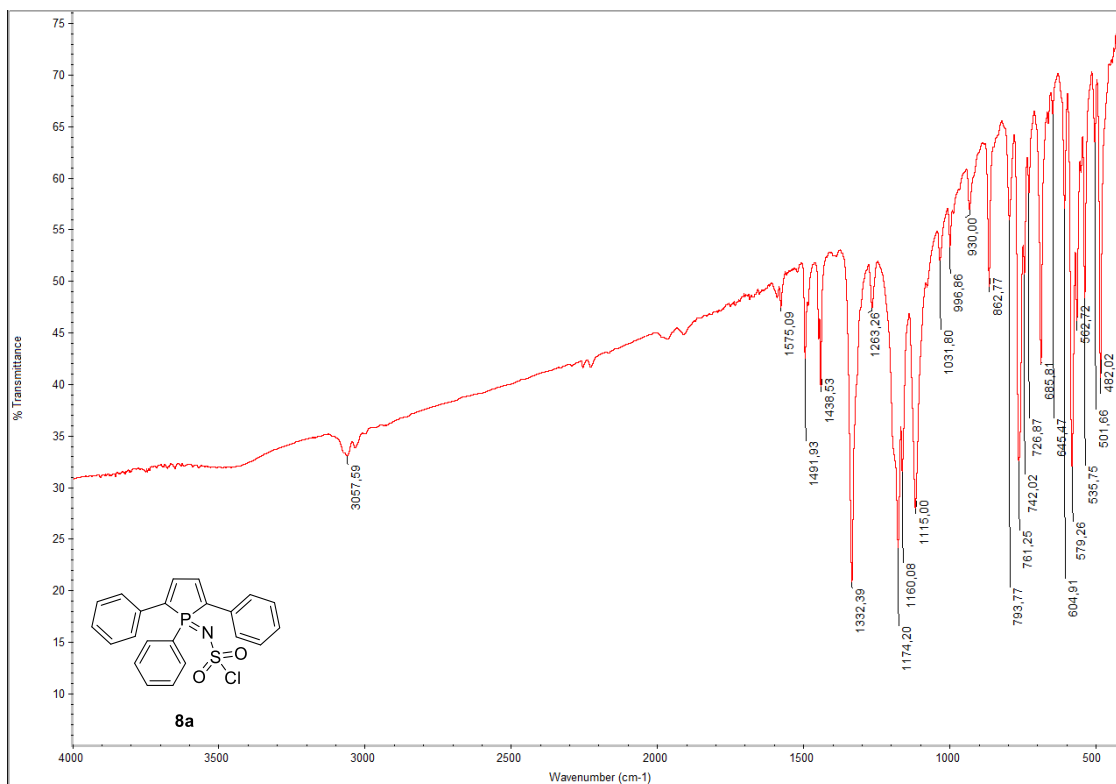
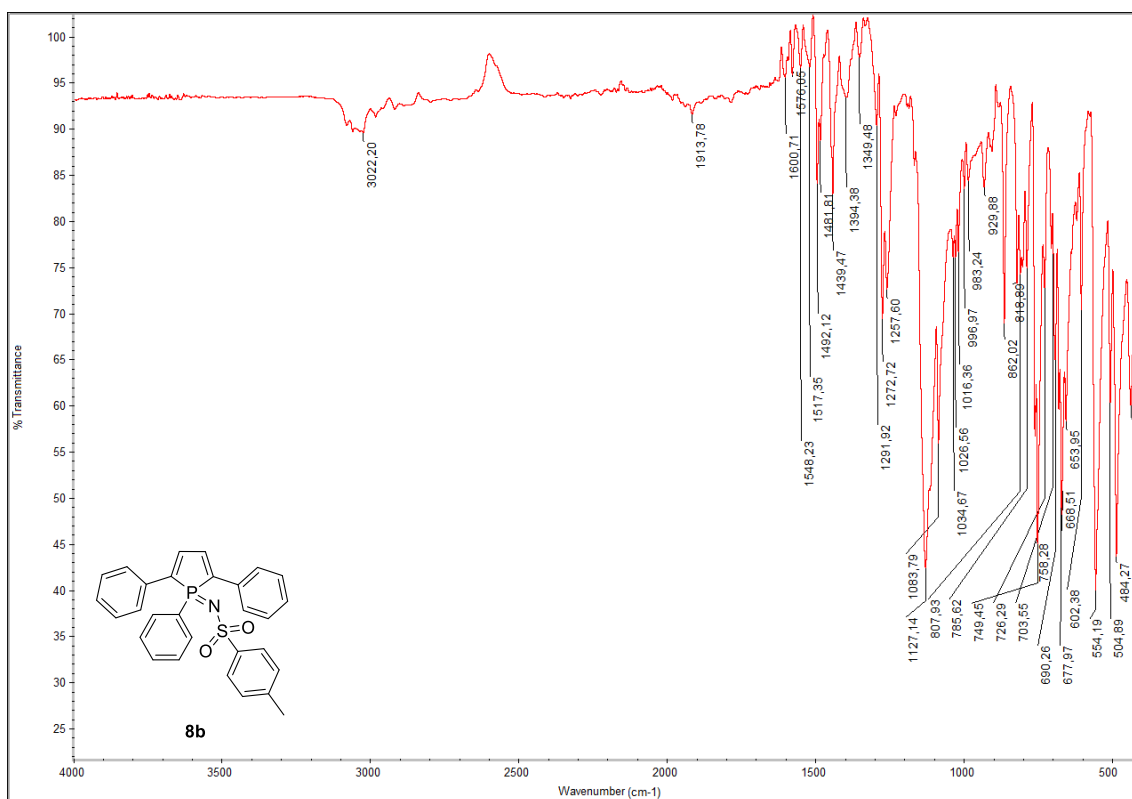
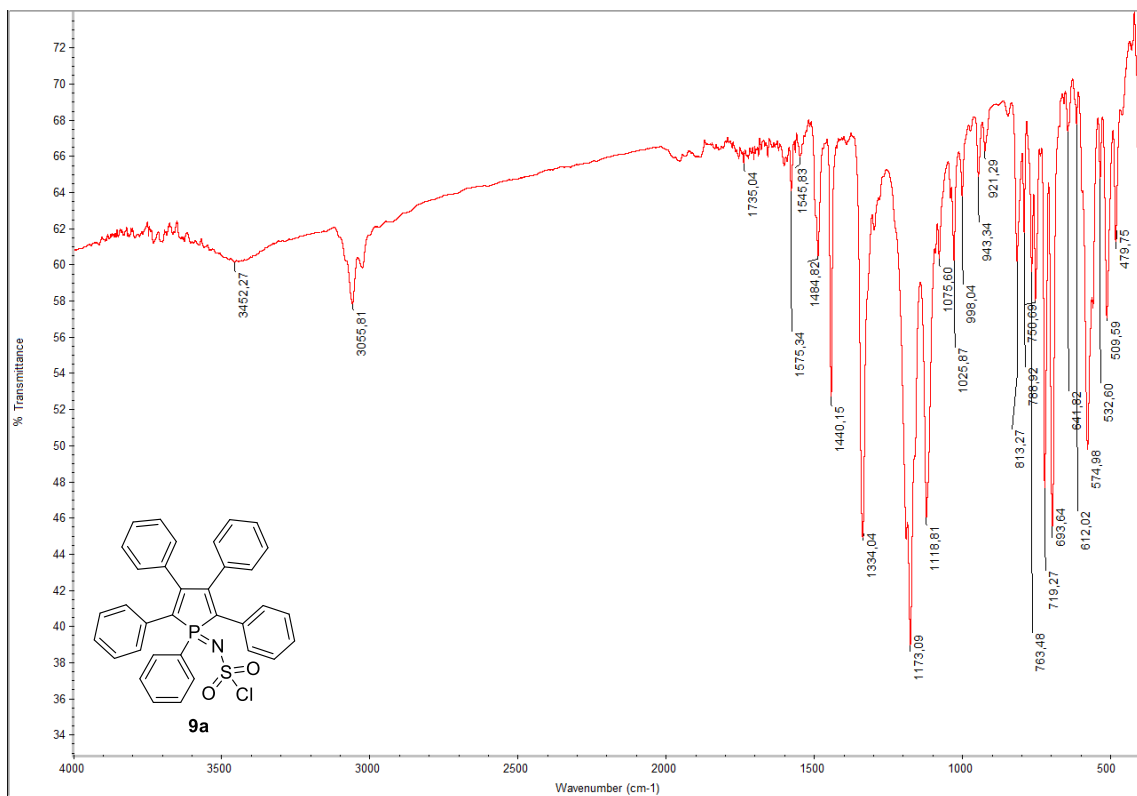
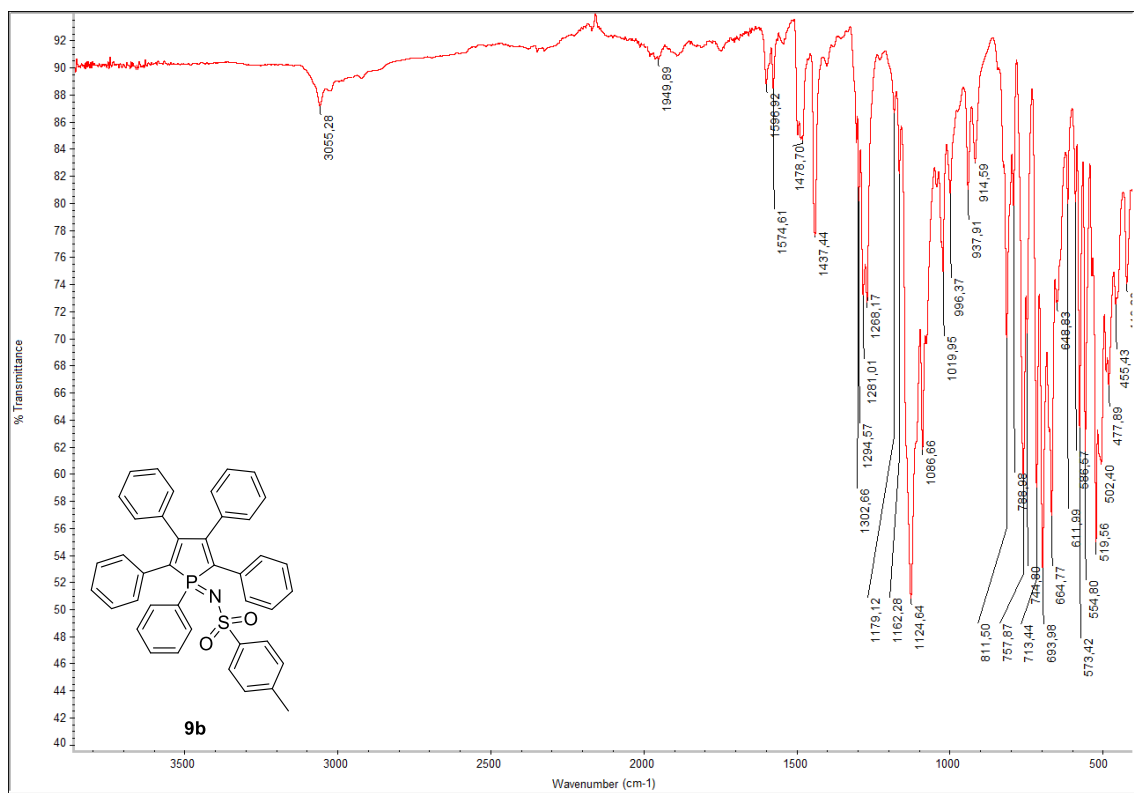


Fig S3.28: IR spectrum of 7b.

Fig S3.29: IR spectrum of **8a**.Fig S3.30: IR spectrum of **8b**.

Fig S3.31: IR spectrum of **9a**.Fig S3.32: IR spectrum of **9b**.

3.3 High-resolution Mass Spectra (HRMS)

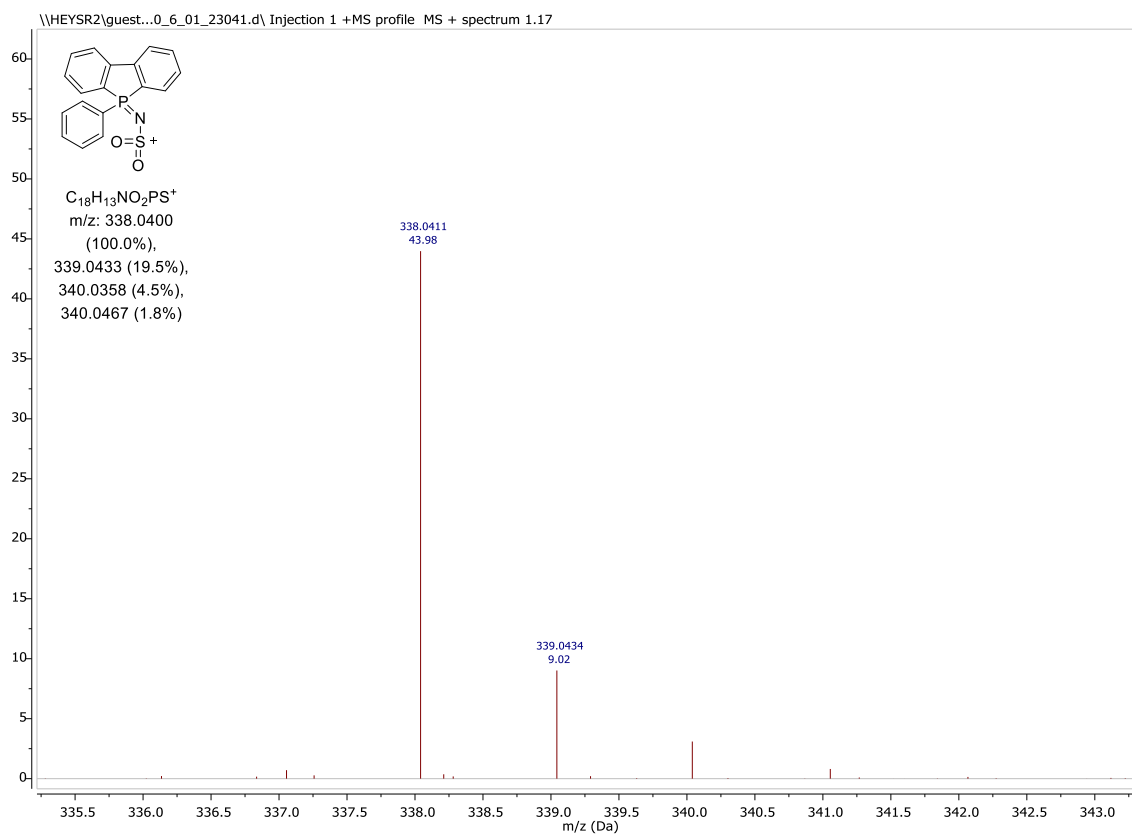


Fig S3.33: HRMS of **6a** in MeCN.

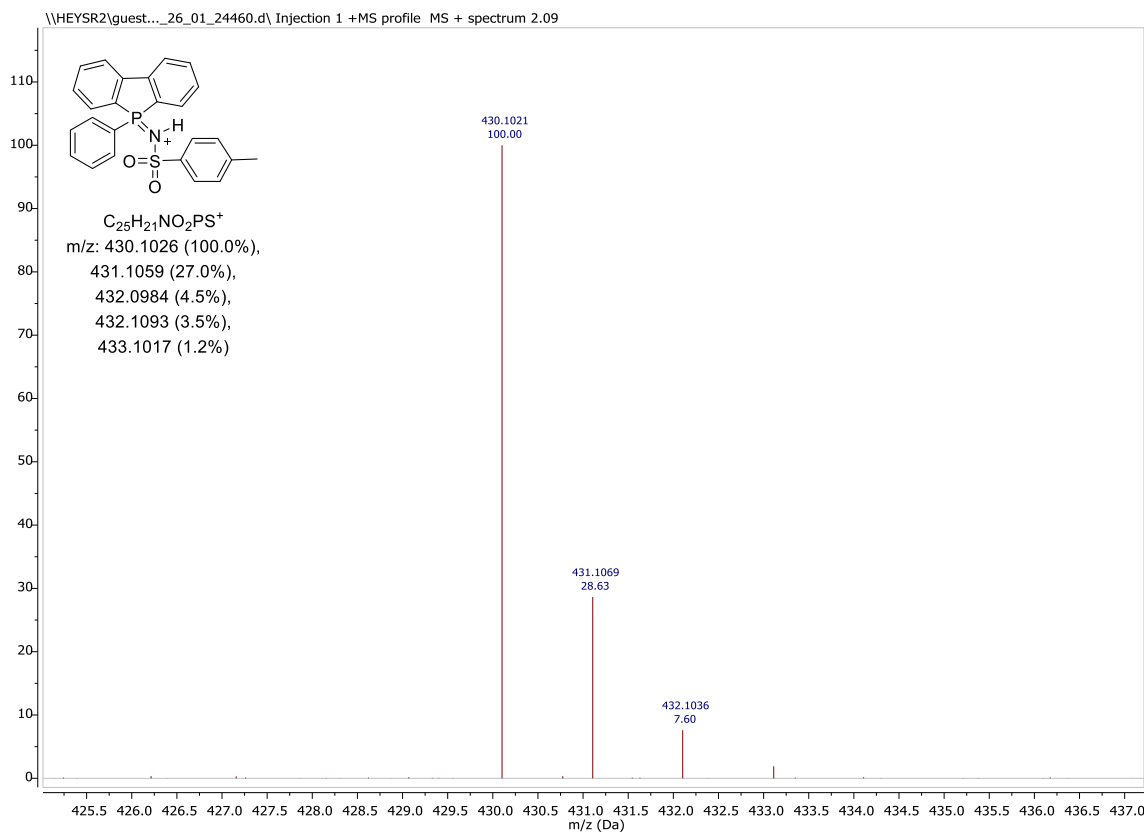


Fig S3.34: HRMS of **6b** in MeCN.

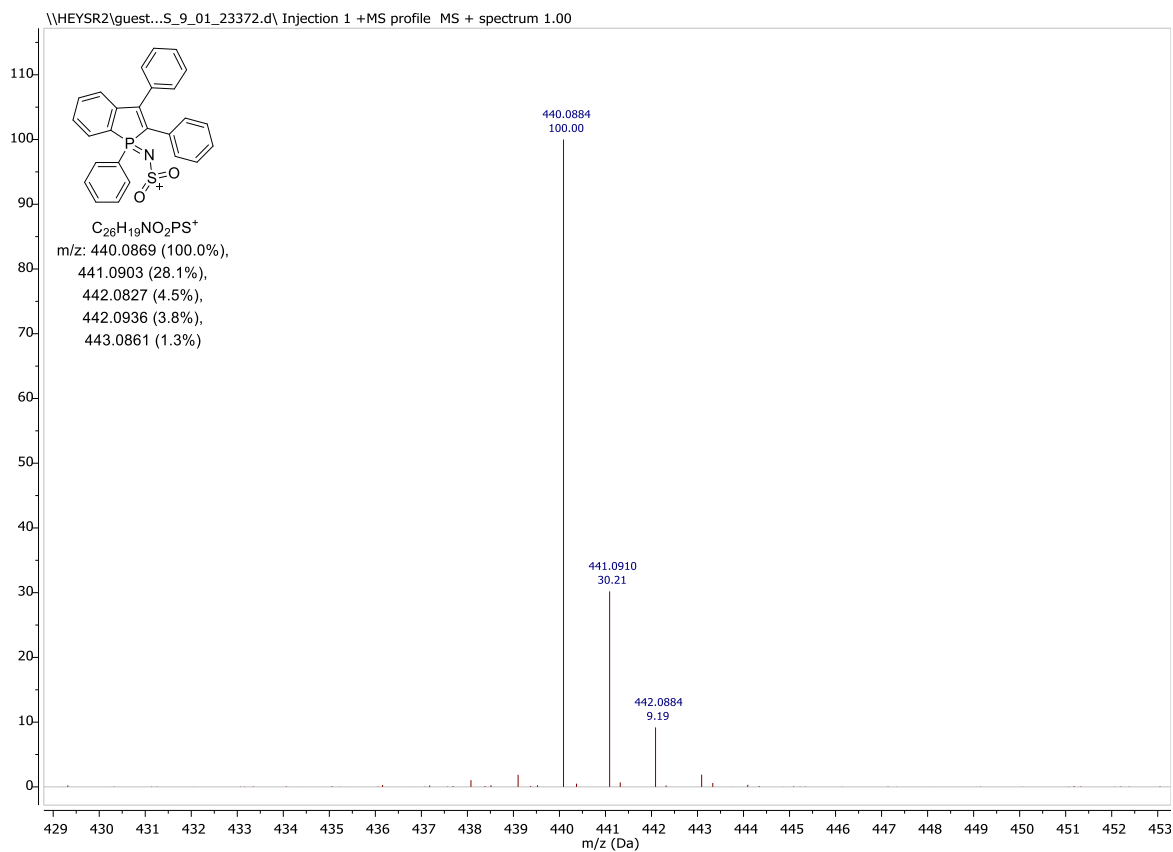


Fig S3.35: HRMS of 7a in MeCN.

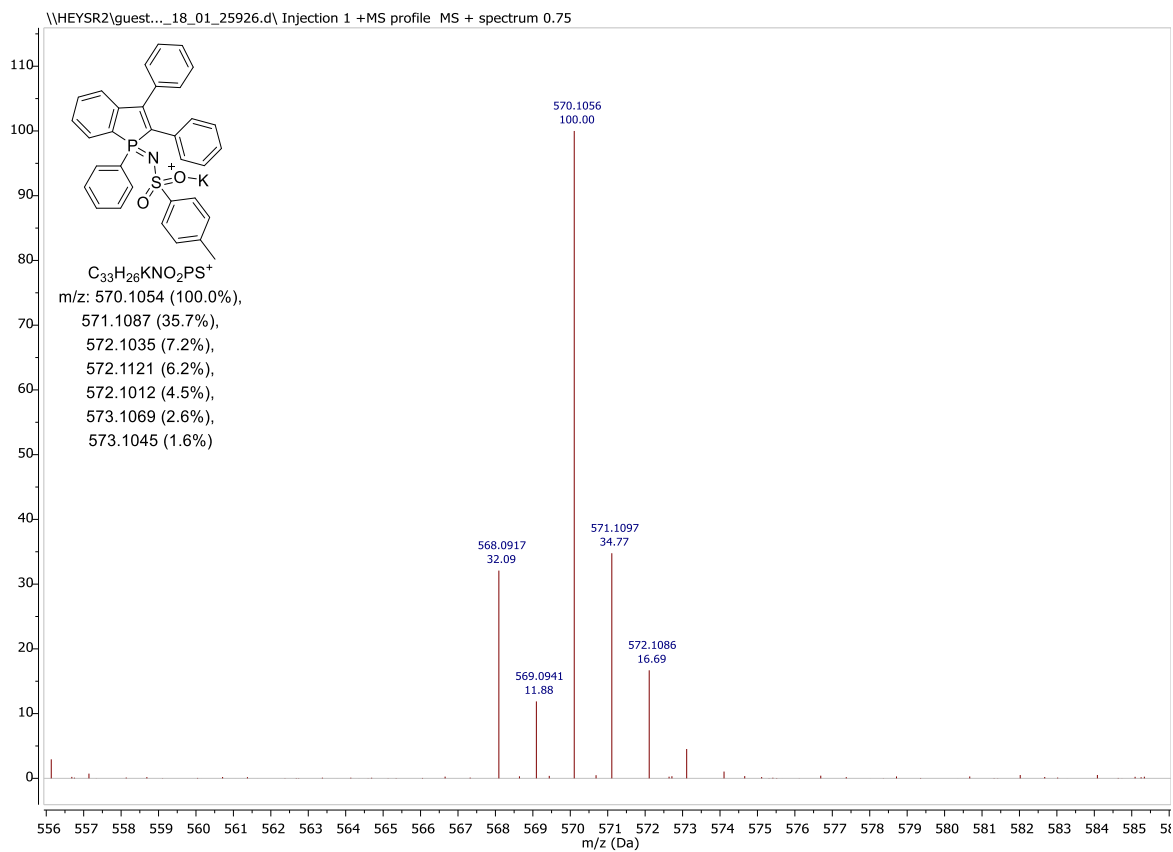
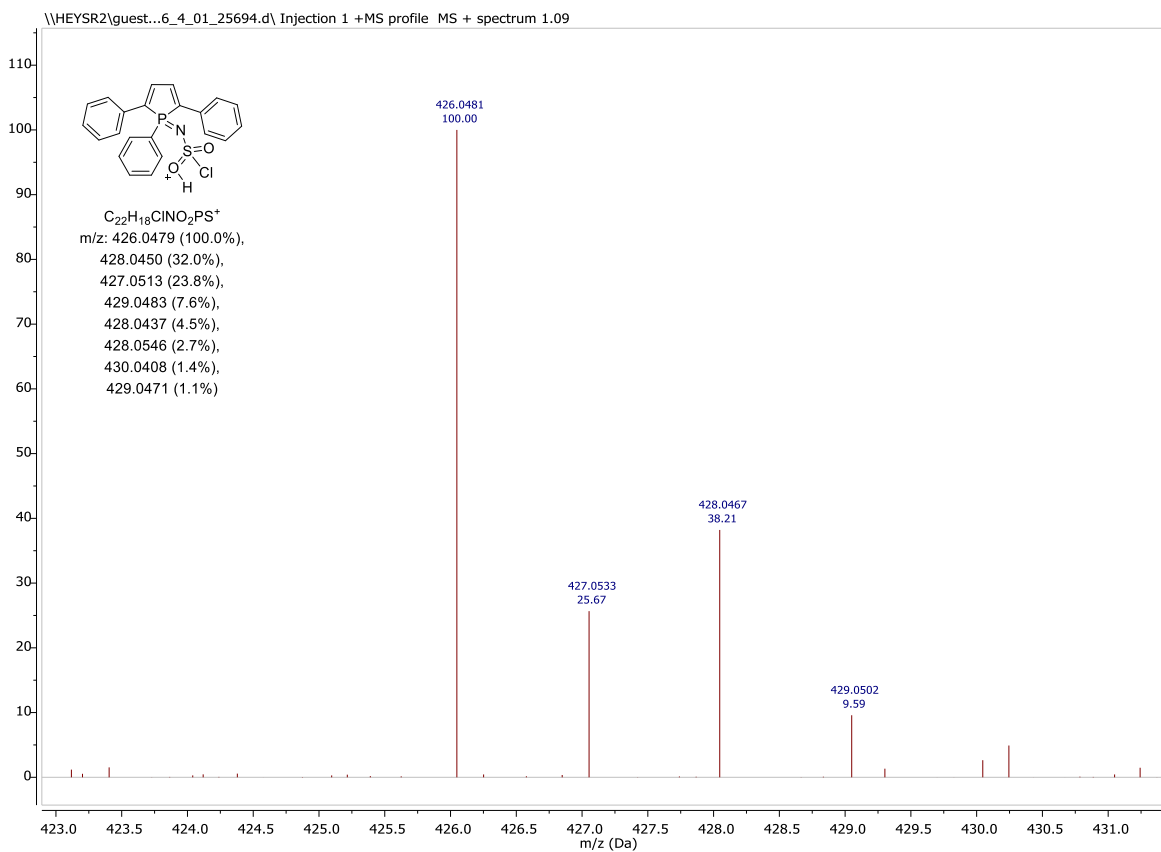
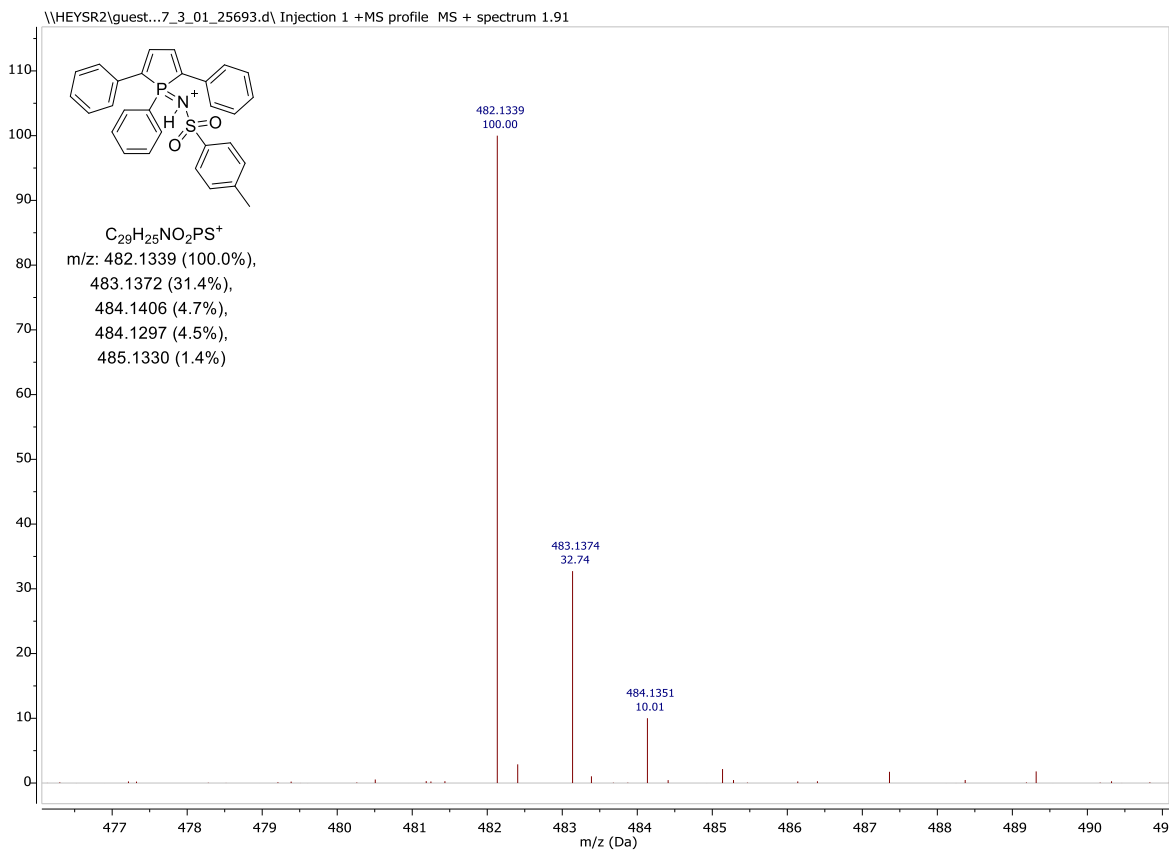
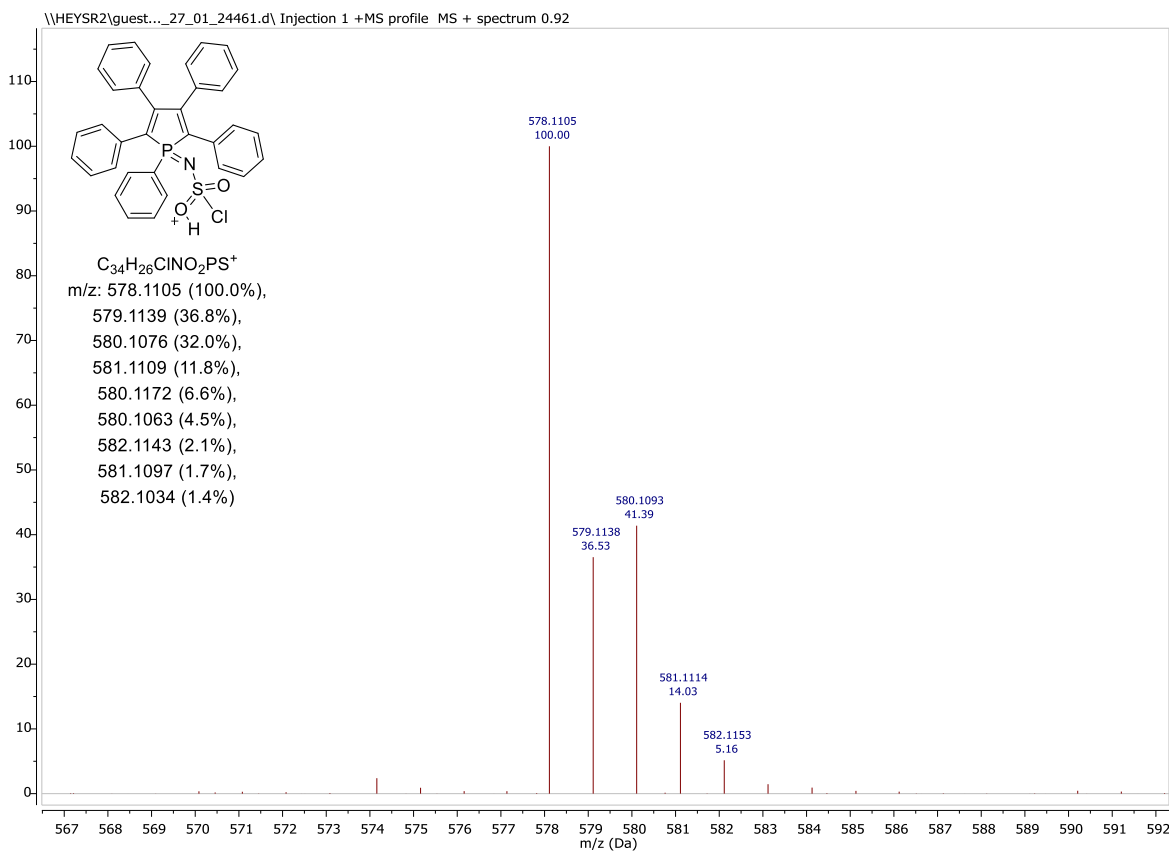
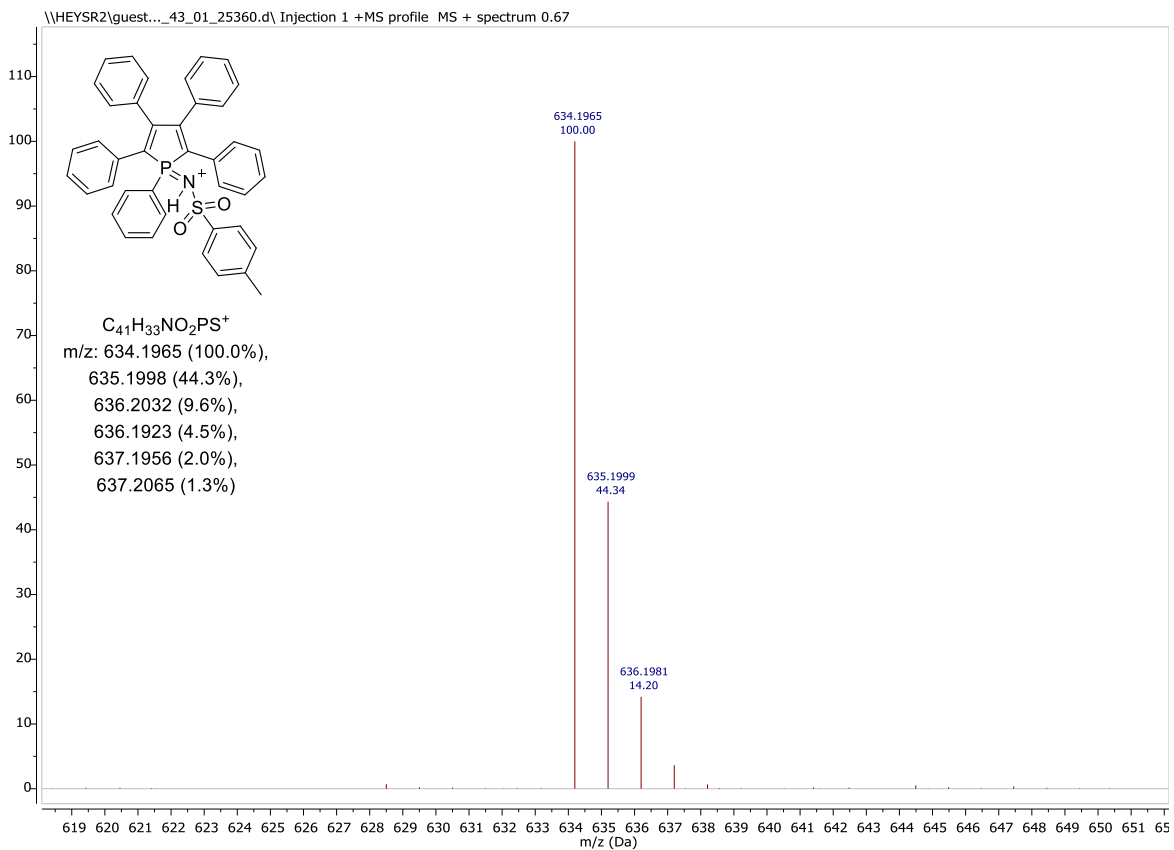


Fig S3.36: HRMS of 7b in MeCN.

Fig S3.37: HRMS of **8a** in MeCN.Fig S3.38: HRMS of **8b** in MeCN.

**Fig S3.39:** HRMS of **9a** in MeCN.**Fig S3.40:** HRMS of **9b** in MeCN.

4 Optical Properties

4.1 Photophysical Data

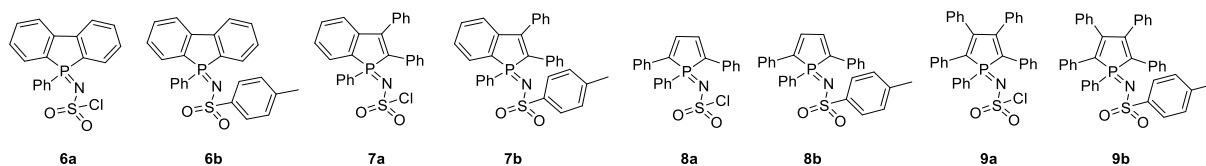


Figure S4.1: Structures of iminophospholes **6-9 a,b**.

Table S4.1: Summary of photoluminescence properties in MeCN solutions at RT.

Compound	λ_{ex} [nm]	ϵ [mol ⁻¹ dm ³ cm ⁻¹]	λ_{em} [nm]	τ [ns] ^[a]	$\Phi_{F(IS)}$ [%] ^[b]	$\Phi_{F(SR)}$ [± 2 %] ^[c]	$k_{r(RT)}$ [10 ⁷ s ⁻¹] ^[d]	$k_{nr(RT)}$ [10 ⁷ s ⁻¹] ^[d]
6a	335	1590	385	2.33 \pm 0.01	16	15	7.0 \pm 0.9	36 \pm 1
6b	330	1690	378	12.57 \pm 0.04	10	12	8 \pm 2	7.2 \pm 2
7a	357	5800	480	12.4 \pm 0.1 (4.4 %) 0.31 \pm 0.01 (95.6 %) $\tau_{av_amp} = 0.84 \pm 0.01$	5	4	6 \pm 3	119 \pm 5
7b	353	4300	472	9.84 \pm 0.09 (5 %) 0.43 \pm 0.01 (31 %) 0.19 \pm 0.01 (64 %) $\tau_{av_amp} = 0.74 \pm 0.01$	5	10	7 \pm 3	128 \pm 5
8a	410	12600	555	0.104 \pm 0.002	< 2	< 1	< 20	920 < k_{nr} < 940
8b	405	16300	537	0.407 \pm 0.001	3	4	6 \pm 5	239 \pm 5
9a	405	5200	558	n. d.	< 2	< 1	n. d.	n. d.
9b	398	5000	547	3.54 \pm 0.08	< 2	< 1	< 0.6	277 < k_{nr} < 283

[a] For multiexponential decays, the amplitude-weighted average lifetimes (τ_{av_amp}) are shown along with the different decay components and the relative amplitude in brackets.^[11] [b] $\Phi_{F(IS)}$ was obtained using a calibrated integrating sphere system [c] $\Phi_{F(SR)}$ was determined for diluted solutions in MeCN by the comparative approach using 1,6-diphenyl-1,3,5-hexatriene (DPHT) in cyclohexane as standard reference ($\Phi_{F(RT)} = 0.78$). [d] The decay rate constants are determined according to $k_r = 1/\tau = \Phi_F/\tau_{obs}$ and $k_{nr} = 1 - \Phi_F/\tau$.^[11]

Table S4.2: Summary of photoluminescence properties of frozen glassy matrix in butyronitrile at 77 K.

Compound	λ_{ex} [nm]	λ_{em} [nm]	τ (77 K) [ns] ^[a]	$\Phi_{F(77 K)}$ [%] ^[b]	$k_{r(77 K)}$ [10 ⁷ s ⁻¹] ^[c]	$k_{nr(77 K)}$ [10 ⁷ s ⁻¹] ^[c]
6a	352	384	8.5 \pm 0.1 (18 %) 2.77 \pm 0.04 (82 %) $\tau_{av_amp} = 3.82 \pm 0.06$	98	32 \pm 1	< 1.3
6b	335	497	12.26 \pm 0.07 (84 %) 21.5 \pm 0.3 (16 %) $\tau_{av_amp} = 13.7 \pm 0.1$	77	5.6 \pm 0.2	1.7 \pm 0.2
7a	394	469	12.90 \pm 0.04 (88 %) 6.9 \pm 0.4 (12 %) $\tau_{av_amp} = 12.21 \pm 0.08$	85	6.9 \pm 0.2	1.3 \pm 0.2
7b	386	470	12.16 \pm 0.04	98	8.4 \pm 0.2	< 0.2
8a	430	538	7.65 \pm 0.03 (56 %) 4.91 \pm 0.05 (44 %) $\tau_{av_amp} = 6.46 \pm 0.04$	78	12.0 \pm 0.4	3.5 \pm 0.5
8b	430	523	7.63 \pm 0.02	62	8.1 \pm 0.3	5.0 \pm 0.3
9a	430	539	14.74 \pm 0.08 (58 %) 6.2 \pm 0.1 (42 %) $\tau_{av_amp} = 11.1 \pm 0.1$	83	7.5 \pm 0.3	1.5 \pm 0.2
9b	400	512	16.05 \pm 0.06 (84 %) 8.7 \pm 0.4 (16 %) $\tau_{av_amp} = 14.9 \pm 0.1$	89	6.0 \pm 0.2	0.8 \pm 0.1

[a] For multiexponential decays, the amplitude-weighted average lifetimes (τ_{av_amp}) are shown along with the different decay components and the relative amplitude in brackets.^[11] [b] $\Phi_{F(77 K)}$ was obtained using a calibrated integrating sphere system. [c] The decay rate constants are determined according to $k_r = 1/\tau = \Phi_F/\tau_{obs}$ and $k_{nr} = 1 - \Phi_F/\tau$.^[11]

Table S4.3: Summary of photoluminescence properties in solid state at RT.

Compound	λ_{em} [nm]	τ [ns] ^[a]	$\Phi_F(\text{solid})$ [± 2 %] ^[b]	$k_r(\text{solid})$ [10^7 s^{-1}] ^[c]	$k_{nr}(\text{solid})$ [10^7 s^{-1}] ^[c]
6a	417	12 \pm 1 (20 %)	34	4.0 \pm 0.4	8 \pm 1
		7.5 \pm 0.3 (80 %)			
		$\tau_{av_amp} = 8.4 \pm 0.4$			
6b	407	14.8 \pm 0.2 (91 %)	54	3.8 \pm 0.2	3.2 \pm 0.4
		9 \pm 2 (9 %)			
		$\tau_{av_amp} = 14.2 \pm 0.3$			
7a	491	9.8 \pm 0.2 (25 %)	46	10.4 \pm 0.8	12 \pm 1
		4.2 \pm 0.2 (38 %)			
		1.08 \pm 0.05 (37 %)			
		$\tau_{av_amp} = 4.4 \pm 0.1$			
7b	479	9.8 \pm 0.5 (56 %)	82	9.6 \pm 0.8	2.2 \pm 0.2
		6.9 \pm 0.6 (44 %)			
		$\tau_{av_amp} = 8.5 \pm 0.5$			
8a	557	2.8 \pm 0.1 (52 %)	18	8 \pm 1	36 \pm 4
		1.8 \pm 0.2 (48 %)			
		$\tau_{av_amp} = 2.3 \pm 0.1$			
8b	548	10.2 \pm 0.3 (74 %)	55	5.9 \pm 0.5	5 \pm 1
		7 \pm 1 (26 %)			
		$\tau_{av_amp} = 9.2 \pm 0.5$			
9a	555	1.97 \pm 0.06 (86 %)	10	3.8 \pm 0.9	36 \pm 2
		5.9 \pm 0.1 (14 %)			
		$\tau_{av_amp} = 2.5 \pm 0.1$			
9b	528	8.24 \pm 0.02 (83 %)	75	9.7 \pm 0.3	3.2 \pm 0.4
		5.5 \pm 0.1 (17 %)			
		$\tau_{av_amp} = 8.1 \pm 0.1$			

[a] For multiexponential decays, the amplitude-weighted average lifetimes (τ_{av_amp}) are shown along with the different decay components and the relative amplitude in brackets.^[11] [b] Φ_F of solids at rt were obtained using a calibrated integrating sphere with a suitable sample holder. [c] The decay rate constants are determined according to $k_r = 1/\tau = \Phi_F/\tau_{obs}$ and $k_{nr} = 1 - \Phi_F/\tau$.^[11]

4.2 Photophysical properties

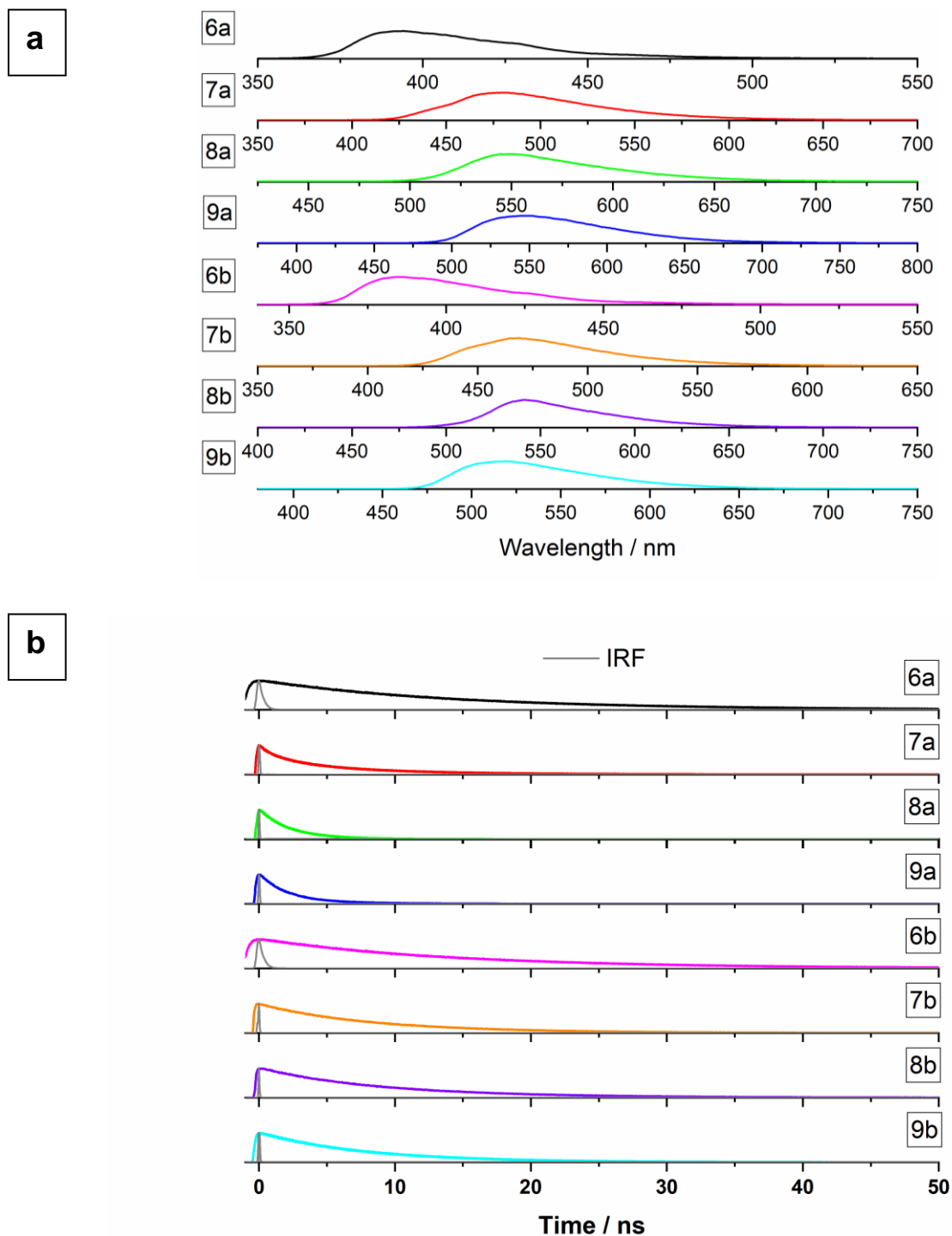


Figure S4.2: Photoluminescence properties of compounds **6-9 a,b** in solid at rt: **a)** normalized emission spectra of **6a** (black, $\lambda_{\text{ex}} = 325$ nm), **7a** (red, $\lambda_{\text{ex}} = 325$ nm), **8a** (green, $\lambda_{\text{ex}} = 350$ nm), **9a** (blue, $\lambda_{\text{ex}} = 375$ nm), **6b** (purple, $\lambda_{\text{ex}} = 325$ nm), **7b** (orange, $\lambda_{\text{ex}} = 325$ nm), **8b** (violet, $\lambda_{\text{ex}} = 350$ nm), **9b** (cyan, $\lambda_{\text{ex}} = 375$ nm); **b)** time-resolved photoluminescence decay of **6a** (black) and **6b** (purple) after excitation with $\lambda_{\text{ex}} = 317$ nm and **7a** (red), **8a** (green), **9a** (blue), **6b** (purple), **7b** (orange), **8b** (violet), and **9b** (cyan) after excitation with $\lambda_{\text{ex}} = 373$ nm (IRF shown in gray).

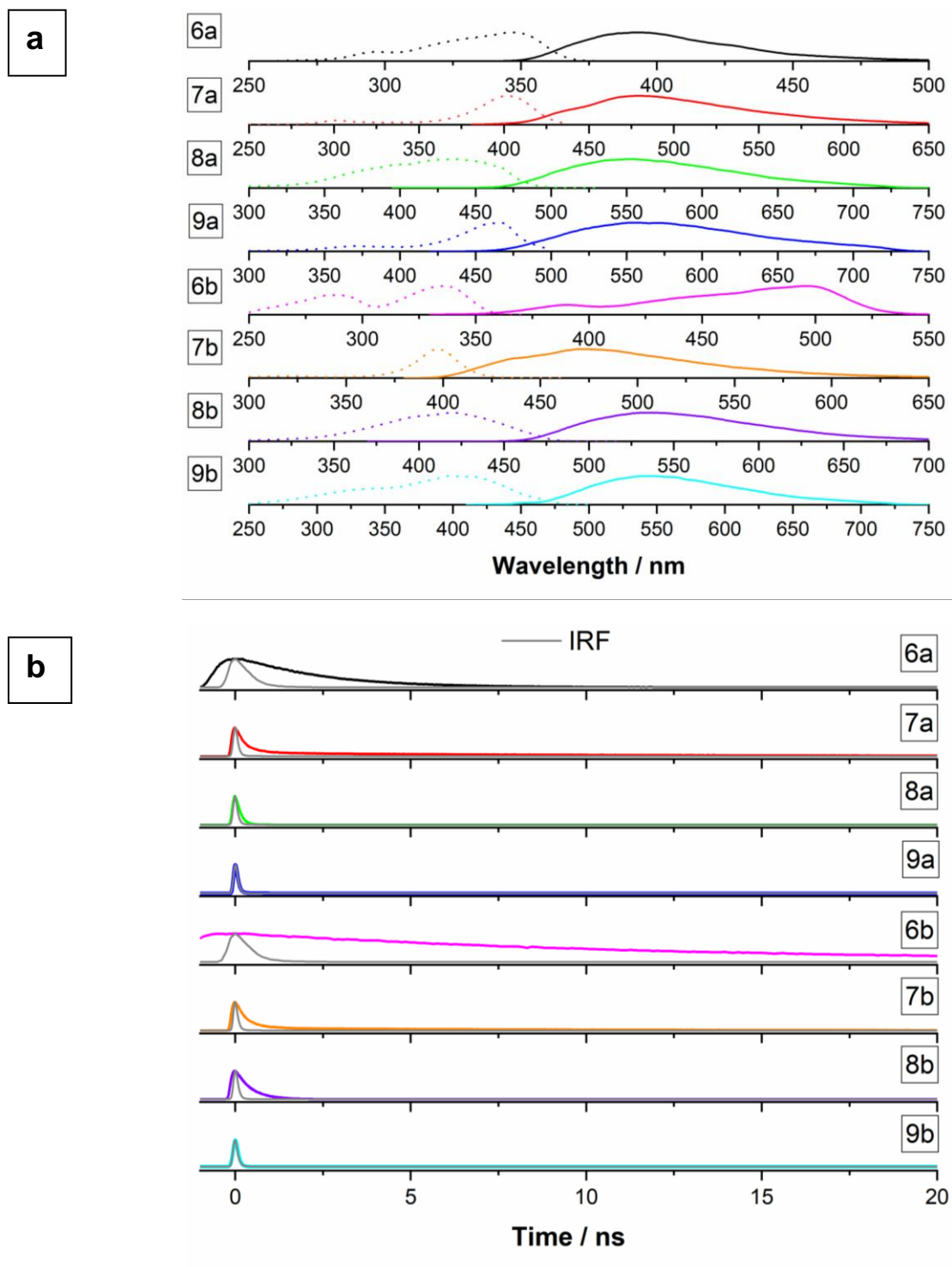


Figure S4.3: Photoluminescence properties of compounds **6-9 a,b** in MeCN solutions at RT: **a**) normalized emission and excitation spectra of **6a** (black, $\lambda_{\text{ex}} = 310$ nm), **7a** (red, $\lambda_{\text{ex}} = 350$ nm), **8a** (green, $\lambda_{\text{ex}} = 350$ nm), **9a** (blue, $\lambda_{\text{ex}} = 375$ nm), **6b** (purple, $\lambda_{\text{ex}} = 320$ nm), **7b** (orange, $\lambda_{\text{ex}} = 350$ nm), **8b** (violet, $\lambda_{\text{ex}} = 350$ nm), **9b** (cyan, $\lambda_{\text{ex}} = 350$ nm); **b**) time-resolved photoluminescence decay of **6a** (black) and **6b** (purple) after excitation with $\lambda_{\text{ex}} = 310$ nm and **7a** (red), **8a** (green), **9a** (blue), **7b** (orange), **8b** (violet), **9b** (cyan) after excitation with $\lambda_{\text{ex}} = 375$ nm (IRF shown in gray).

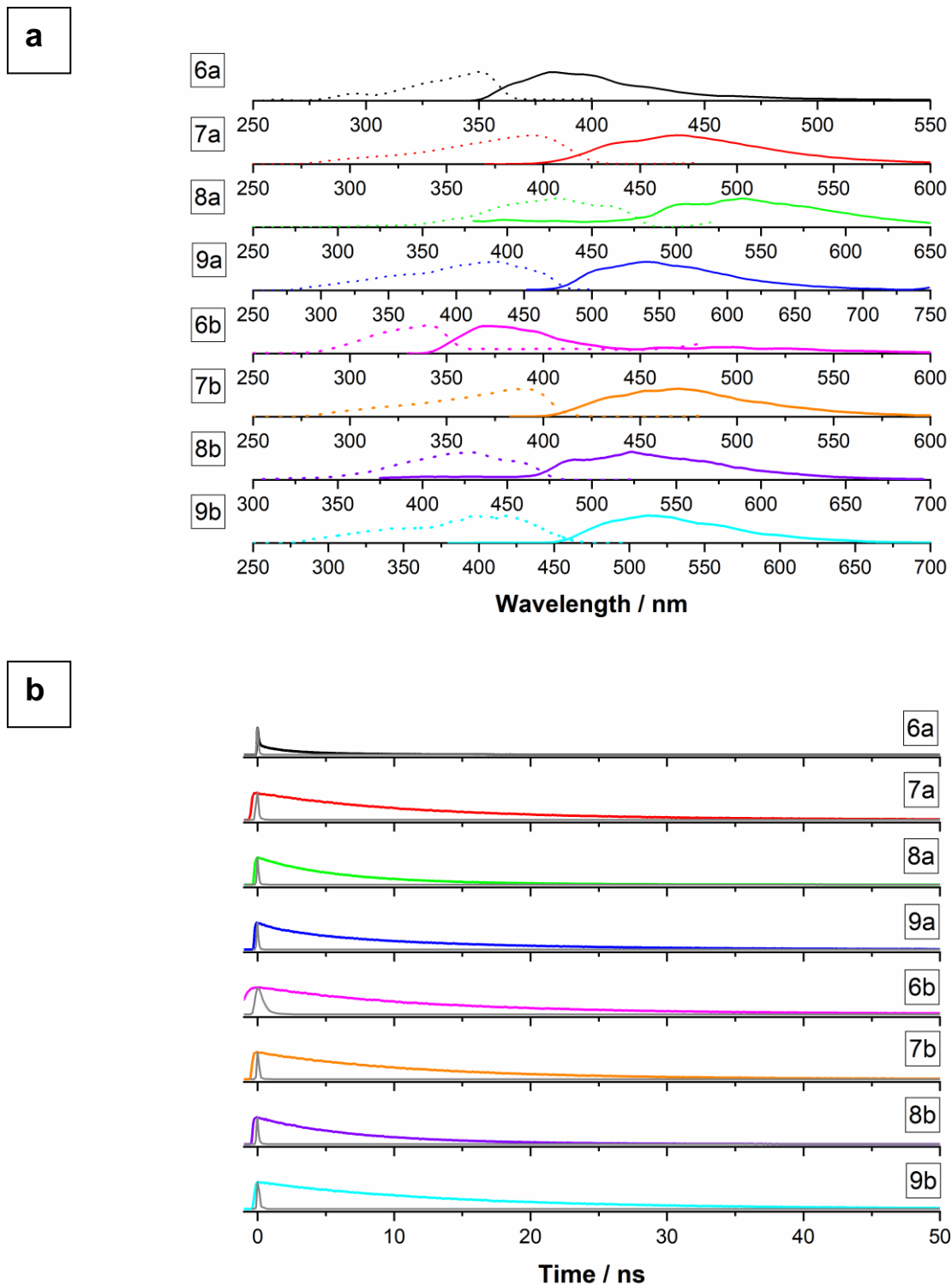


Figure S4.4: Photoluminescence properties of compounds **6-9 a,b** in butyronitrile glass matrix at 77 K: **a)** normalized emission and excitation spectra of **6a** (black, $\lambda_{\text{ex}} = 310$ nm), **7a** (red, $\lambda_{\text{ex}} = 350$ nm), **8a** (green, $\lambda_{\text{ex}} = 350$ nm), **9a** (blue, $\lambda_{\text{ex}} = 350$ nm), **6b** (purple, $\lambda_{\text{ex}} = 310$ nm), **7b** (orange, $\lambda_{\text{ex}} = 350$ nm), **8b** (violet, $\lambda_{\text{ex}} = 350$ nm), **9b** (cyan, $\lambda_{\text{ex}} = 350$ nm); **b)** time-resolved photoluminescence decay of **6b** (purple) after excitation with $\lambda_{\text{ex}} = 310$ nm and **6a** (black), **7a** (red), **8a** (green), **9a** (blue), **7b** (orange), **8b** (violet), **9b** (cyan) after excitation with 375 nm (IRF shown in gray).

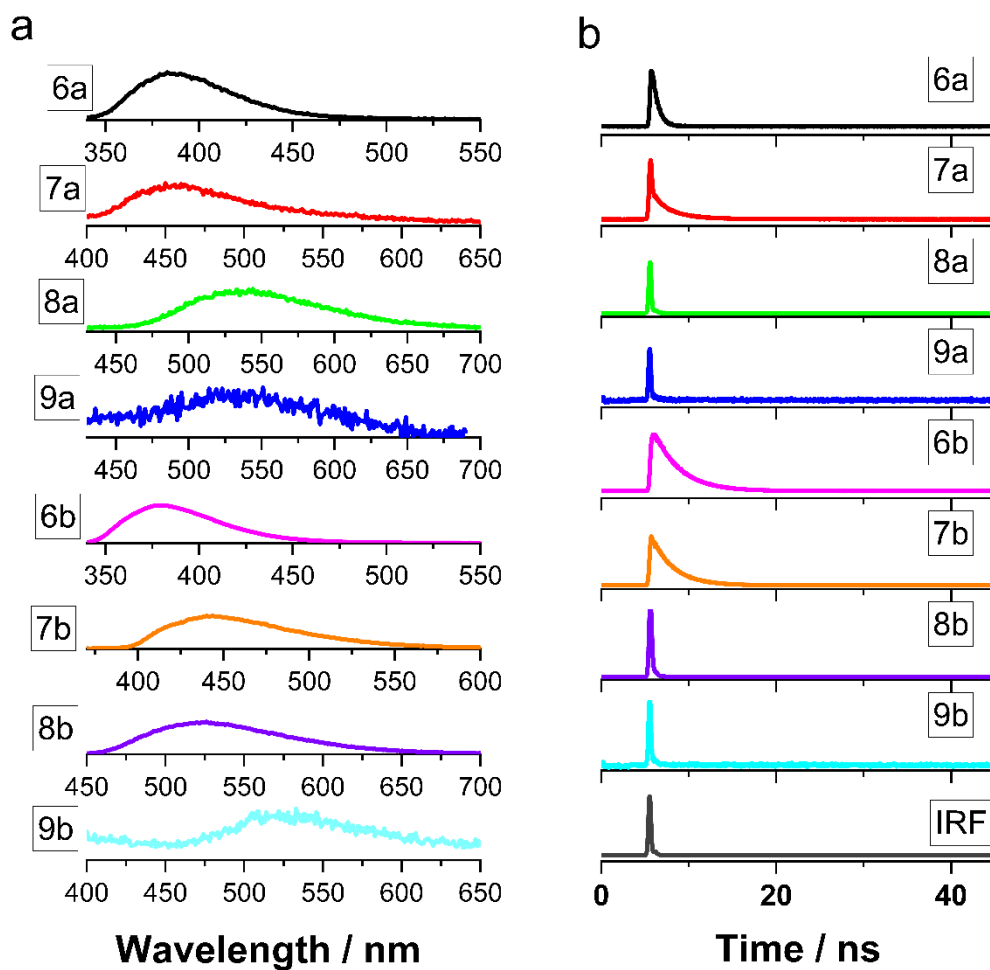


Figure S4.5: Photoluminescence properties of compounds **6-9 a,b** in MeCN: **a)** normalized emission spectra of **6a** (black, $\lambda_{\text{ex}} = 300$ nm), **7a** (red, $\lambda_{\text{ex}} = 350$ nm), **8a** (green, $\lambda_{\text{ex}} = 370$ nm), **9a** (blue, $\lambda_{\text{ex}} = 370$ nm), **6b** (purple, $\lambda_{\text{ex}} = 300$ nm), **7b** (orange, $\lambda_{\text{ex}} = 330$ nm), **8b** (violet, $\lambda_{\text{ex}} = 370$ nm), **9b** (cyan, $\lambda_{\text{ex}} = 330$ nm); **b)** time profiles of the luminescence decay of **6a** (black) and **6b** (purple) after excitation with $\lambda_{\text{ex}} = 254$ nm and **7a** (red), **8a** (green), **9a** (blue), **7b** (orange), **8b** (violet), **9b** (cyan) after excitation with 365 nm (IRF shown in gray).

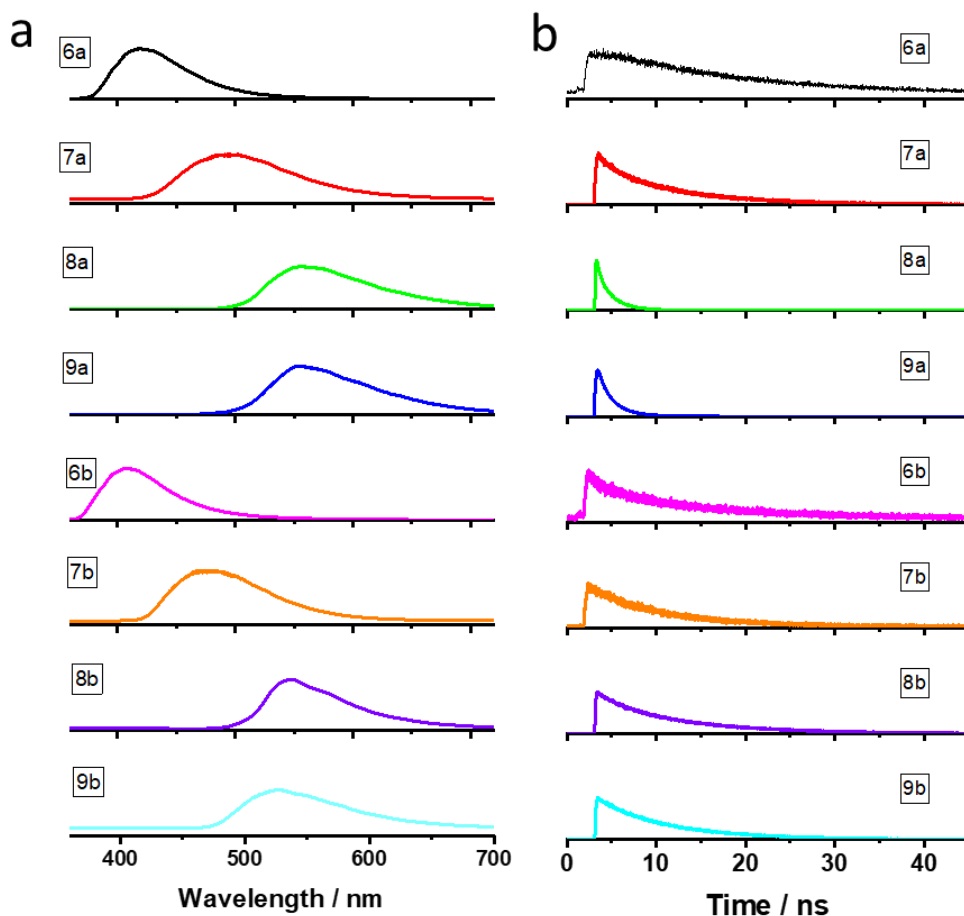


Figure S4.6: Photoluminescence properties of compounds **6-9 a,b** as solid sample: **a)** Photoluminescence spectra of **6a** (black), **7a** (red, $\lambda_{\text{ex}} = 350$ nm), **8a** (red, $\lambda_{\text{ex}} = 370$ nm), **9a** (blue), **6b** (purple), **7b** (orange), **8b** (violet), **9b** (cyan) after excitation with 350 nm; **b)** time profiles of the luminescence decay of **6a** (black), **7a** (red), **8a** (green), **9a** (blue), **6b** (purple), **7b** (orange), **8b** (violet) and **9b** (cyan) after excitation with 375 nm, 60 ps pulse duration.

4.3 Correlation between structure and photophysical properties

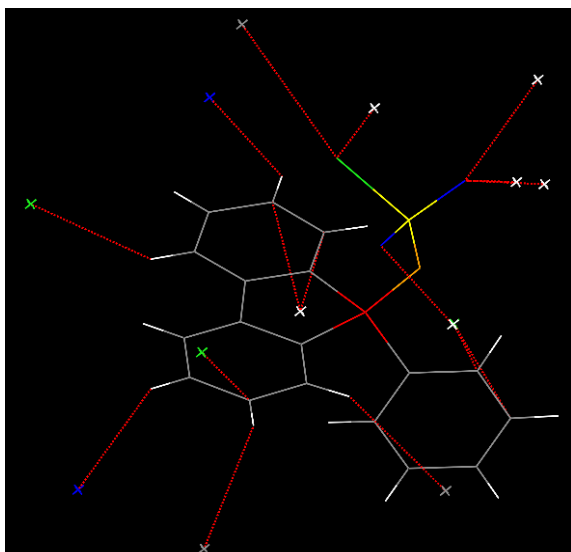


Figure S4.7: Molecular structure of **6a** in the crystal. Multiple C_{aryl}-H...π and C_{aryl}-H...Cl interactions were observed (red).

$$\Phi_{F(\text{solid})} = 34 \pm 2 \%$$

$$k_r = 4.0 \pm 0.4 \cdot 10^7 \text{ s}^{-1}$$

$$k_{nr} = 8 \pm 1 \cdot 10^7 \text{ s}^{-1}$$

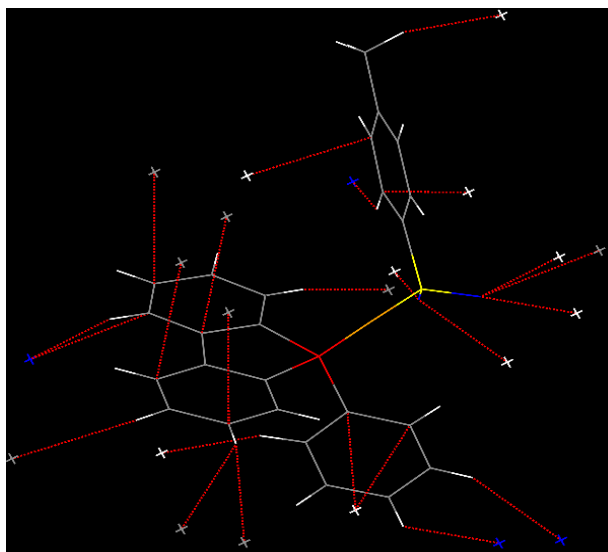


Figure S4.8: Molecular structure of **6b** in the crystal. Multiple C_{aryl}-H...π interactions and intermolecular π stacking were observed (red).

$$\Phi_{F(\text{solid})} = 54 \pm 2 \%$$

$$k_r = 3.8 \pm 0.2 \cdot 10^7 \text{ s}^{-1}$$

$$k_{nr} = 3.2 \pm 0.4 \cdot 10^7 \text{ s}^{-1}$$

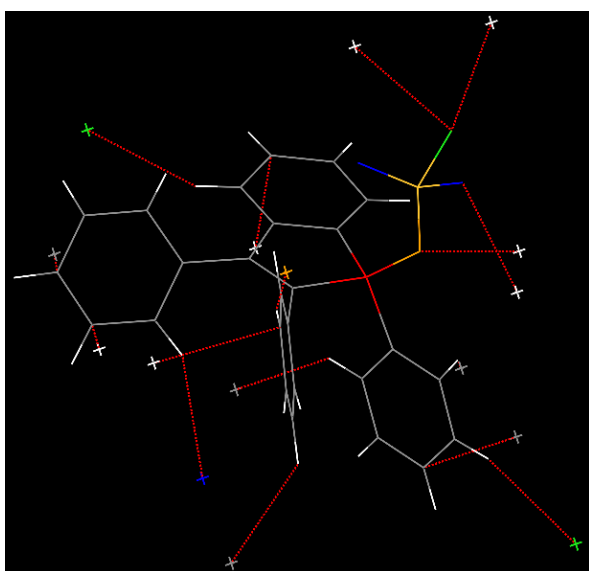


Figure S4.9: Molecular structure of **7a** in the crystal. Multiple C_{aryl}-H...π and C_{aryl}-H...Cl interactions were observed (red).

$$\Phi_{F(\text{solid})} = 46 \pm 2 \%$$

$$k_r = 10.4 \pm 0.8 \cdot 10^7 \text{ s}^{-1}$$

$$k_{nr} = 12 \pm 1 \cdot 10^7 \text{ s}^{-1}$$

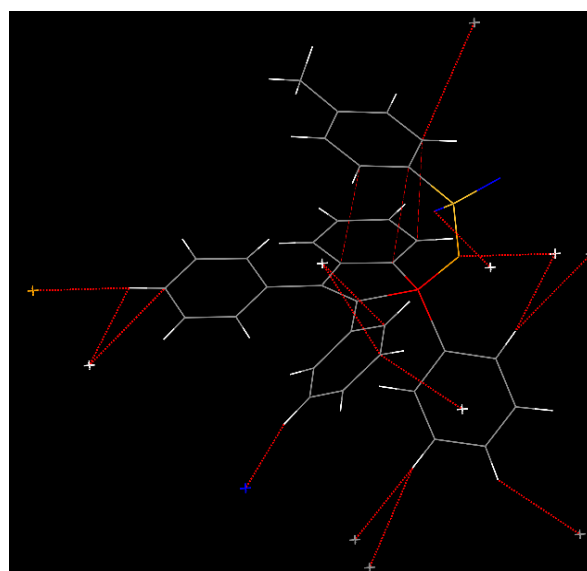


Figure S4.10: Molecular structure of **7b** in the crystal. Multiple C_{aryl}-H...π interactions and intramolecular π stacking were observed (red).

$$\Phi_{F(\text{solid})} = 82 \pm 2 \%$$

$$k_r = 9.6 \pm 0.8 \cdot 10^7 \text{ s}^{-1}$$

$$k_{nr} = 2.2 \pm 0.2 \cdot 10^7 \text{ s}^{-1}$$

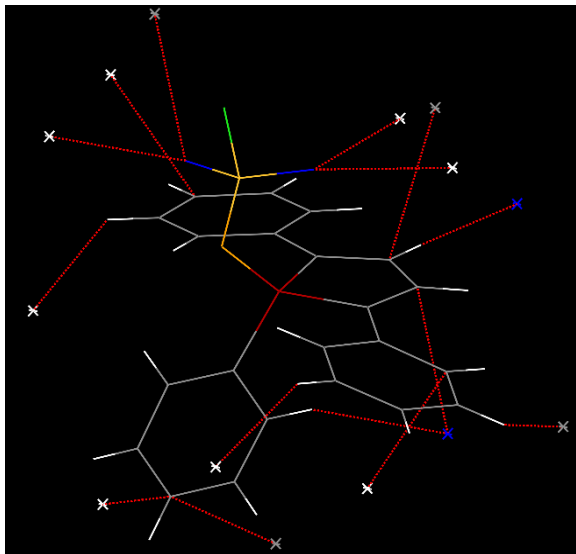


Figure S4.11: Molecular structure of **8a** in the crystal. Multiple C_{aryl}-H... π intermolecular π stacking, but no C_{aryl}-H...Cl interactions were observed (red).

$$\Phi_{F(\text{solid})} = 18 \pm 2 \%$$

$$k_r = 8 \pm 1 \cdot 10^7 \text{ s}^{-1}$$

$$k_{nr} = 36 \pm 4 \cdot 10^7 \text{ s}^{-1}$$

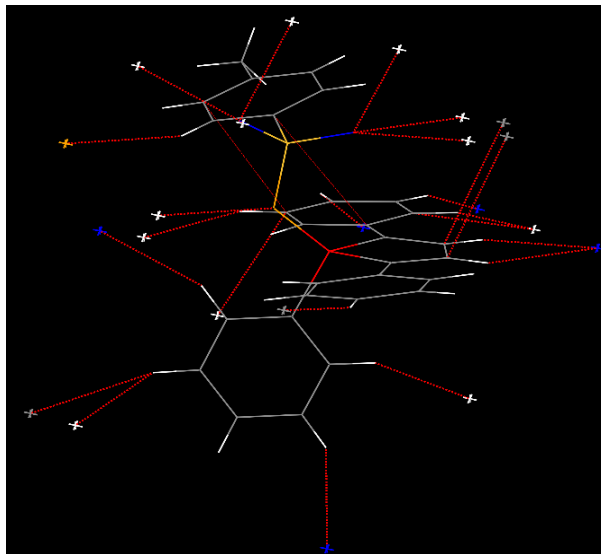


Figure S4.12: Molecular structure of **8b** in the crystal. Multiple C_{aryl}-H... π interactions, intramolecular and intermolecular π stacking were observed (red).

$$\Phi_{F(\text{solid})} = 55 \pm 2 \%$$

$$k_r = 5.9 \pm 0.5 \cdot 10^7 \text{ s}^{-1}$$

$$k_{nr} = 5 \pm 1 \cdot 10^7 \text{ s}^{-1}$$

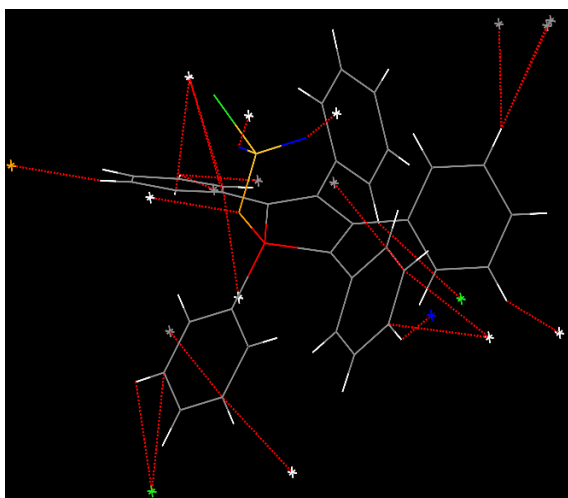


Figure S4.13: Molecular structure of **9a** in the crystal. Multiple C_{aryl}-H... π and less C_{aryl}-H...Cl interactions were observed (red).

$$\Phi_{F(\text{solid})} = 10 \pm 2 \%,$$

$$k_r = 3.8 \pm 0.9 \cdot 10^7 \text{ s}^{-1}$$

$$k_{nr} = 36 \pm 2 \cdot 10^7 \text{ s}^{-1}$$

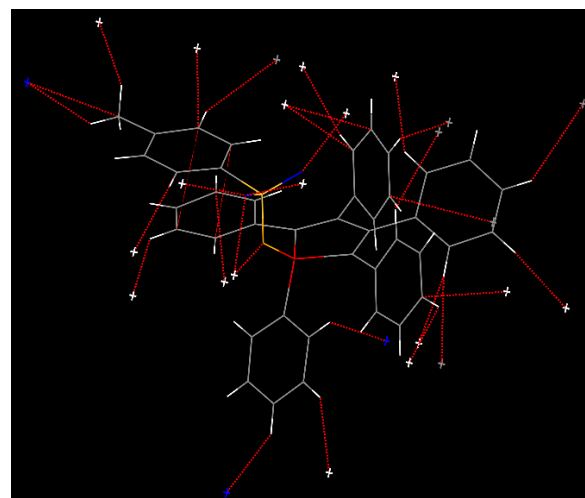


Figure S4.14: Molecular structure of **9b** in the crystal. Significantly more C_{aryl}-H... π interactions than in **9a** were observed. Additional intramolecular π stacking leads to strong restriction of motions (red).

$$\Phi_{F(\text{solid})} = 75 \pm 2 \%$$

$$k_r = 9.7 \pm 0.3 \cdot 10^7 \text{ s}^{-1}$$

$$k_{nr} = 3.2 \pm 0.4 \cdot 10^7 \text{ s}^{-1}$$

5 DFT Calculations

5.1 HOMO-LUMO Energy Gaps

All calculations presented in this paper were carried out with the molecular ADF program, version 2018.107.^[12] Molecular geometries were optimized using the B3LYP functional in conjunction with the D3 version of Grimme's dispersion correction with Becke-Johnson damping^[13,14] and if applicable the COSMO solvation model.^[15] The TZP basis set was used for all atoms during geometry optimization, frequency analysis and for single point calculations. Frequency calculations were performed to verify the nature of all stationary points and to calculate Gibbs free energies at 298.15 K. The numerical quality was set to "very good". For transition state search the Nudged Elastic Band method^[16] was used starting from relaxed geometries at the B3LYP-D3(BJ)/TZP level of theory.

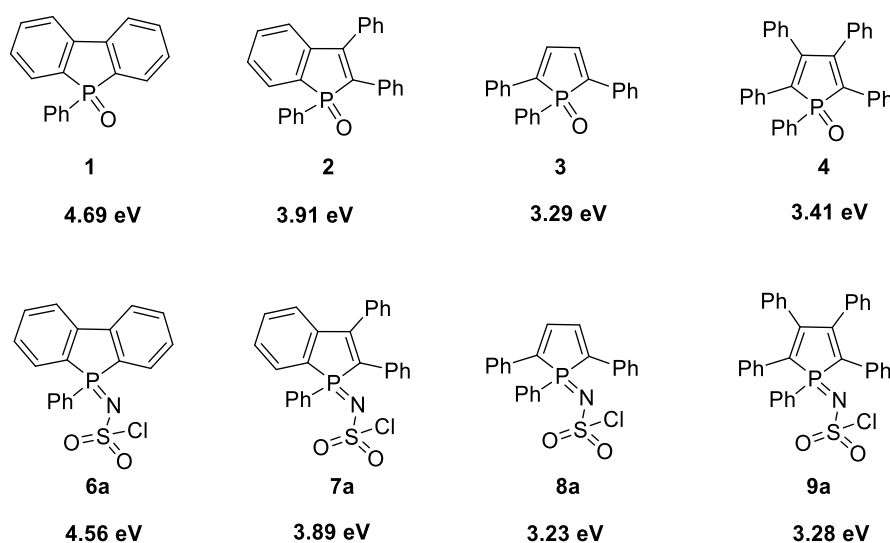


Figure S5.1: DFT calculations at the B3LYP-D3(BJ)/TZP level were used to calculate HOMO-LUMO gaps of compounds 1-4 and 6a-9a.

Table S5.1: Total bonding energies and Gibbs free energies for compounds 1-4 and 6a-9a.

compound	TBE (hartree)	G (kcal/mol)	No. imag. freq.
1	-9.220501	-5651.44	0
2	-13.093724	-8017.69	0
3	-11.284348	-6910.22	0
4	-16.963104	-10379.16	0
6a	-10.129305	-6219.01	0
7a	-14.000925	-8581.57	0
8a	-12.190589	-7473.81	0
9a	-17.876949	-10948.39	0

Coordinates:**1**

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C	1.01760161	3.08076473	0.00000000
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C	0.03580547	-1.81575363	0.74018412
C	-0.56375865	-2.74779528	1.58184536
C	-0.44920282	-2.59758297	2.96175623
C	0.25725018	-1.52819949	3.50784639
C	0.85516239	-0.58714387	2.67162743
C	0.03580547	-1.81575363	-0.74018412
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H	1.40666235	0.24663143	3.08796574

2

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C	3.44250567	1.64276796	-0.78419118
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3

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4

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6a

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9a

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C	3.68312704	6.90578974	-1.92602649
C	3.78569719	8.01612548	-1.09331802
C	3.60583328	7.87038284	0.27903949
C	3.32898010	6.62012416	0.81565683

C	3.69204342	3.59971796	1.52619065
C	4.94863933	4.06031952	2.12805080
C	5.97312962	4.59279572	1.33625426
C	7.16075965	5.01152967	1.91577893
C	7.34998430	4.90236982	3.29155868
C	6.34455028	4.36142317	4.08496514
C	5.15390894	3.93752691	3.50722889
Cl	3.53975909	-0.11881616	-1.29277597
O	5.93669314	-0.39587659	0.26101920
H	0.95449145	3.15000056	3.30476909
H	0.17327264	2.83973623	5.62907583
H	1.26529824	1.16354190	7.08743432
H	3.13325547	-0.20859206	6.22026300
H	3.91975847	0.10665319	3.88135452
H	1.84036523	-0.52599164	1.06895221
H	0.01975268	-2.16935269	1.12173803
H	-2.32334189	-1.45192481	0.73265823
H	-2.81702210	0.94305120	0.31658941
H	-1.00025323	2.59096396	0.27281414
H	1.19947759	2.08936555	-2.19379099
H	-0.29160209	2.85598157	-4.01534045
H	-1.46972998	5.02817164	-3.81901531
H	-1.13009649	6.43640238	-1.80930658
H	0.38507033	5.68537066	-0.01520136
H	3.31418476	4.79577725	-2.04242262
H	3.82798086	7.01200665	-2.99362201
H	4.00614444	8.99019672	-1.51177345
H	3.68601962	8.73013648	0.93229086
H	3.20202034	6.50142637	1.88373816
H	5.83932096	4.65016297	0.26636713
H	7.94846605	5.41230055	1.29036336
H	8.28064909	5.22743586	3.73968367
H	6.48634798	4.26592796	5.15417982
H	4.37408875	3.52190436	4.13122970

5.2 Frontier Molecular Orbitals

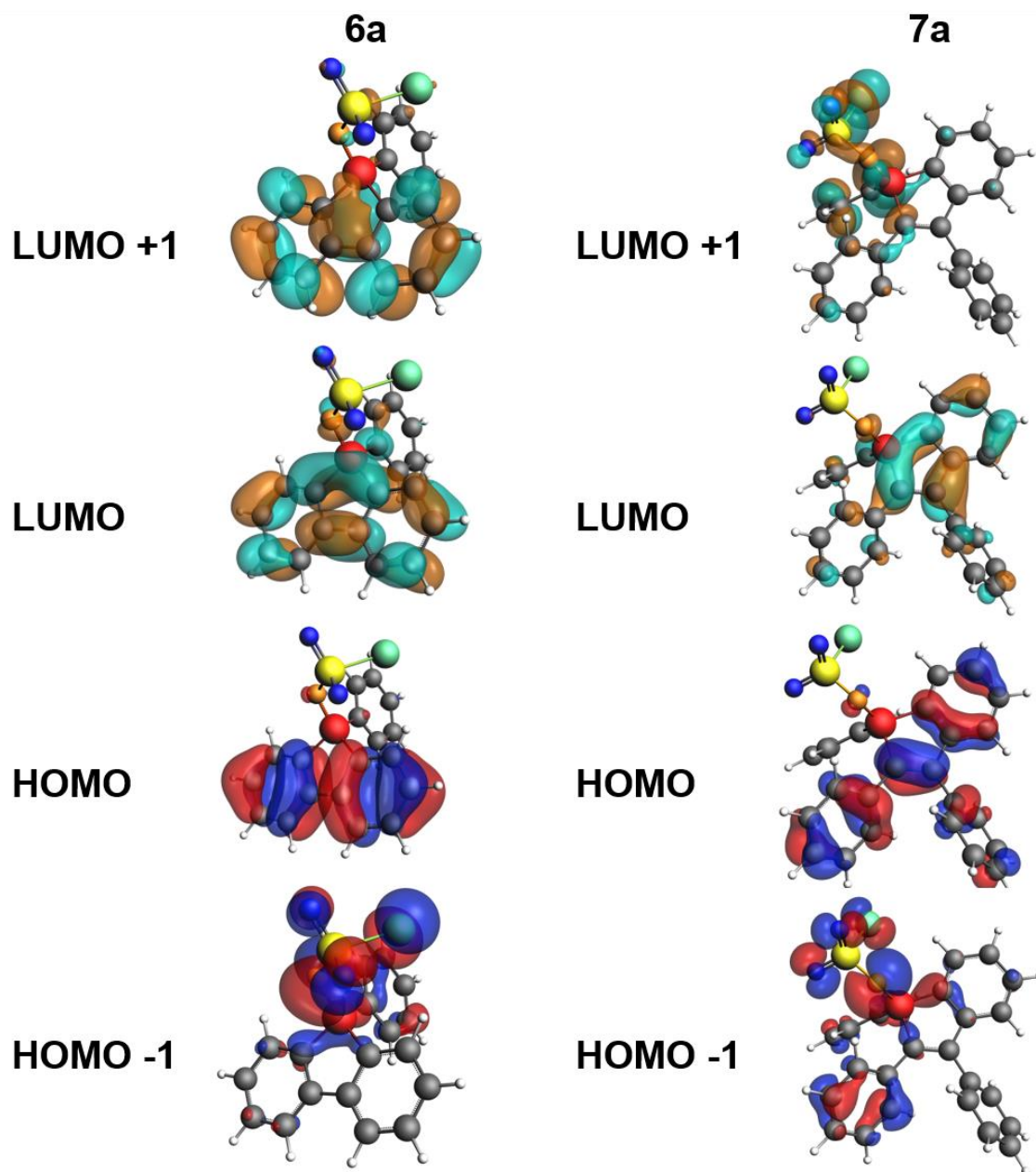


Figure S5.2: Frontier Molecular Orbitals of **6a** and **7a**. HOMO/HOMO-1: blue/red. LUMO/LUMO+1: cyan/orange. All isosurface values were set to 0.035.

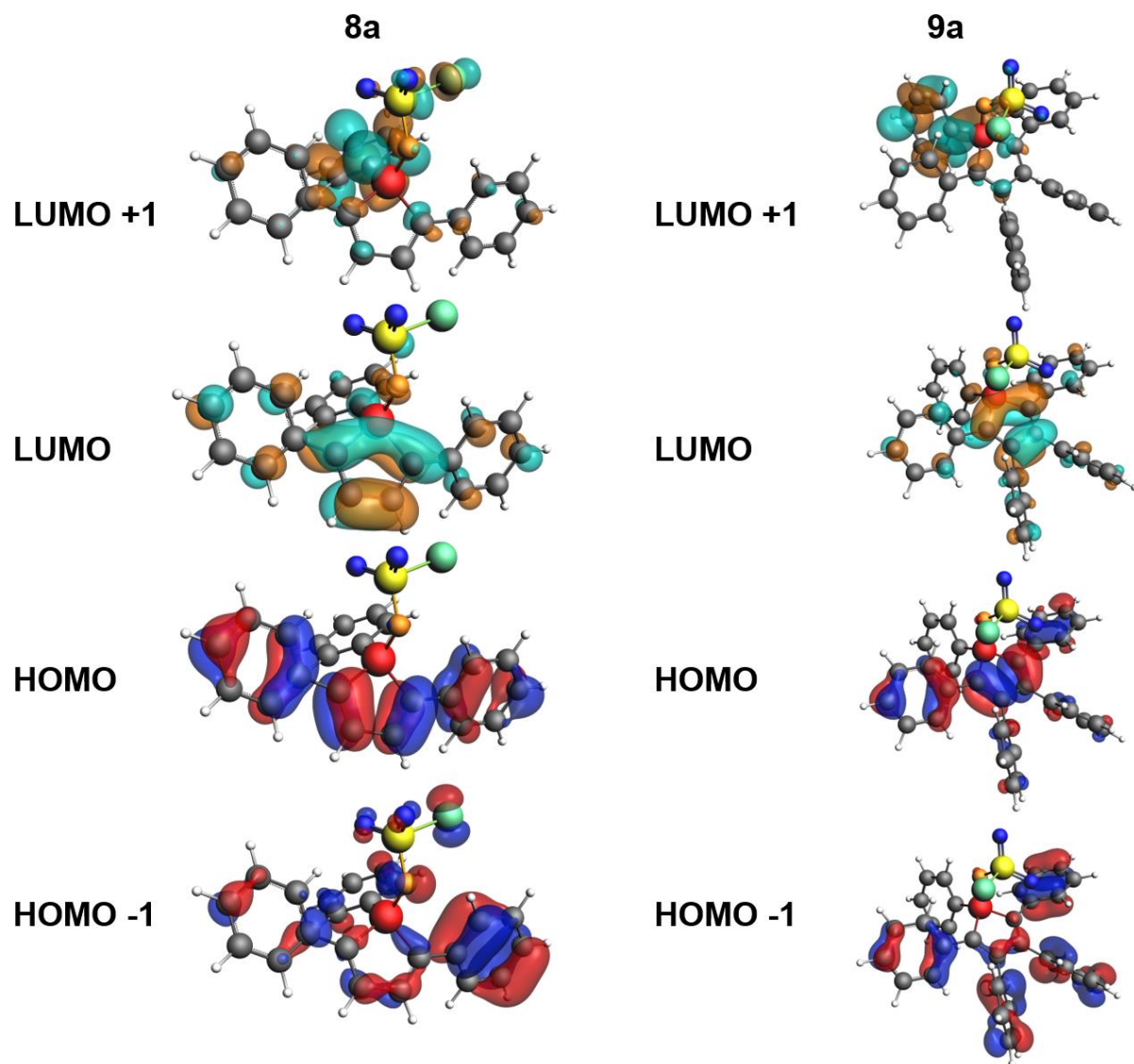


Figure S5.3: Frontier Molecular Orbitals of **8a** and **9a**. HOMO/HOMO-1: blue/red. LUMO/LUMO+1: cyan/orange. All isosurface values were set to 0.035.

5.3 Mechanism

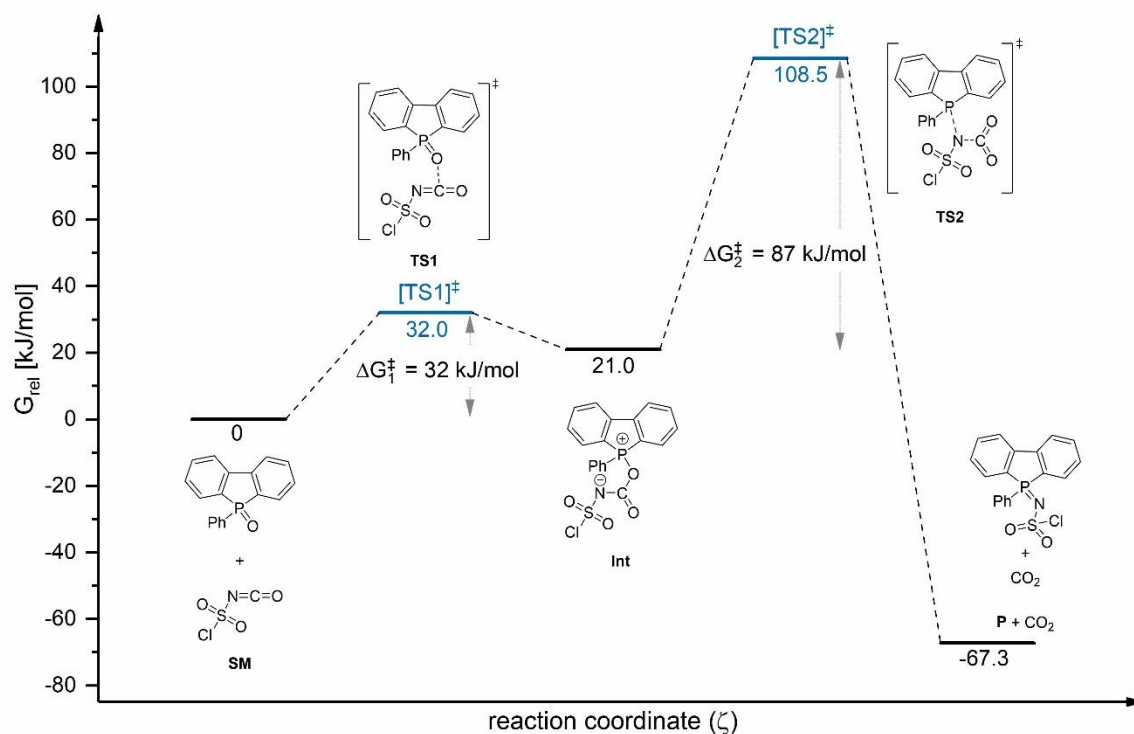


Figure S5.4: Relative Gibbs free energy profile of the reaction with respect to the starting materials.

Table S5.2: Total bonding energies and Gibbs free energies for all investigated compounds in Figure S5.2.

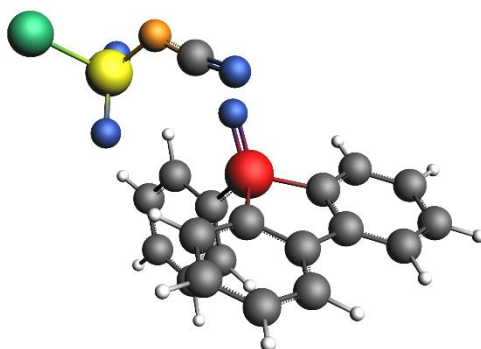
entry	compound	TBE (hartree)	G (kcal/mol)	No. imag. freq. ($\tilde{\nu}$)
1	SM	-11.133184	-6844.23	0
2	TS1	-11.125089	-6836.60	1 (-126 cm ⁻¹)*
3	Int	-11.128651	-6839.22	0
4	TS2	-11.097660	-6818.30	1 (-159 cm ⁻¹)
5	P	-11.158380	-6860.32	0

*) a low negative eigenvalue with close to zero intensity was found.

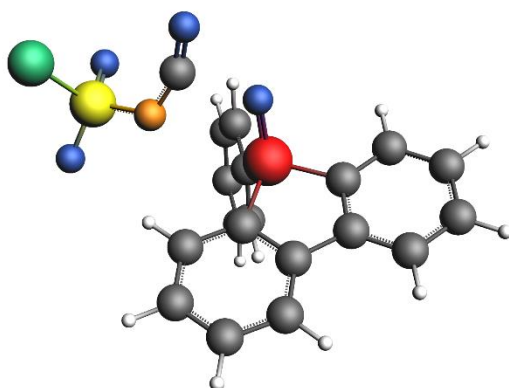
Structures:

Color code: C black, H white, P red, O blue, S yellow, N orange, Cl green.

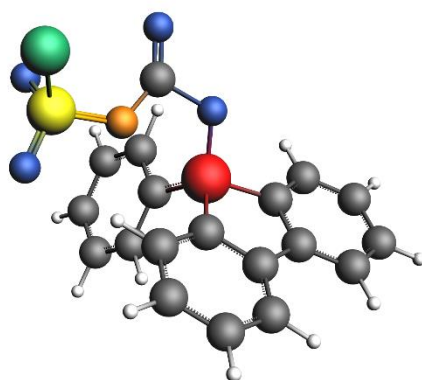
SM:



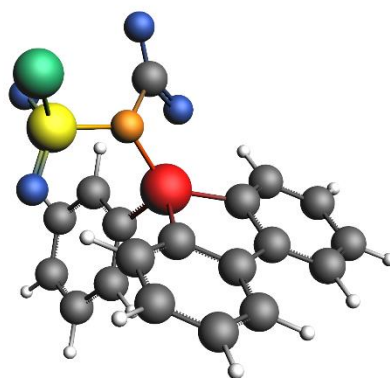
TS1:



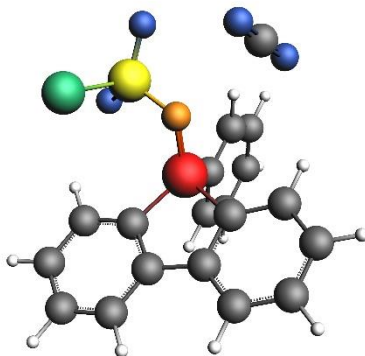
Int:



TS2:



P:

**Coordinates:**

TS2:

O	-1.92950000	0.24510000	-2.14700000
P	-0.72840000	0.11950000	-0.31550000
C	-0.08510000	-1.54060000	-0.60110000
C	1.03100000	-1.97360000	0.11910000
C	1.50650000	-3.26620000	-0.06110000
C	0.86540000	-4.12980000	-0.94480000
C	-0.24370000	-3.69510000	-1.66300000
C	-0.71730000	-2.40030000	-1.50240000
C	-0.07710000	0.75140000	1.29730000
C	-0.43120000	0.42790000	2.60410000
C	0.20500000	1.05950000	3.67180000
C	1.19700000	2.00720000	3.44480000
C	1.54860000	2.34910000	2.14370000
C	0.90780000	1.73310000	1.07360000
C	1.16270000	2.00980000	-0.34770000
C	0.31390000	1.31660000	-1.22090000
C	0.47730000	1.40150000	-2.59850000
C	1.49430000	2.20300000	-3.10780000

C	2.32710000	2.91490000	-2.24770000
C	2.16660000	2.82170000	-0.86900000
H	1.51280000	-1.31480000	0.82890000
H	2.36750000	-3.60380000	0.50160000
H	1.22590000	-5.14320000	-1.06890000
H	-0.75010000	-4.36350000	-2.34750000
H	-1.57370000	-2.06200000	-2.06490000
H	-1.18630000	-0.31220000	2.80360000
H	-0.07930000	0.80540000	4.68500000
H	1.69240000	2.48650000	4.28020000
H	2.31120000	3.09680000	1.96780000
H	-0.17830000	0.85570000	-3.25680000
H	1.63380000	2.27100000	-4.17900000
H	3.11260000	3.53980000	-2.65420000
H	2.83140000	3.36450000	-0.20990000
O	-3.82660000	-2.13540000	-0.10790000
S	-3.13930000	-1.26460000	0.79580000
Cl	-4.59700000	-0.30800000	1.91010000
N	-2.45830000	0.00700000	-0.04070000
C	-2.99840000	0.24400000	-1.45000000
O	-4.16400000	0.40120000	-1.67000000
O	-2.17080000	-1.78690000	1.72120000
P:			
O	-2.44191004	-0.80245392	-3.48867017
P	-0.54530086	-0.11405151	-0.16704393
C	0.12800887	-1.76412409	-0.40779210
C	1.35012332	-2.11785877	0.16933180
C	1.88517144	-3.37573336	-0.07097435
C	1.20444245	-4.27797619	-0.88504794
C	-0.01252253	-3.92382746	-1.45817086
C	-0.55608323	-2.66708323	-1.22258830
C	0.02216217	0.57634614	1.39942581
C	-0.29698776	0.17289423	2.68741636
C	0.24363055	0.87826411	3.75995511
C	1.08609833	1.96354324	3.53326305
C	1.40361854	2.36714941	2.23834424

C	0.87005019	1.67522160	1.15729239
C	1.08715450	1.95404965	-0.27814670
C	0.39254064	1.07959805	-1.13372972
C	0.48692485	1.18153088	-2.51202724
C	1.28142789	2.18803166	-3.05610595
C	1.96847223	3.06490418	-2.21971376
C	1.87859693	2.95319484	-0.83449681
H	1.87258490	-1.41854125	0.80946102
H	2.82844377	-3.65520370	0.38076328
H	1.62184056	-5.26026344	-1.06781855
H	-0.54429005	-4.62754405	-2.08551539
H	-1.50296519	-2.38828450	-1.66289349
H	-0.96450906	-0.66234419	2.84578797
H	0.00134878	0.58409388	4.77272060
H	1.49878052	2.50543688	4.37497426
H	2.05828377	3.21472173	2.08189439
H	-0.04641064	0.49203420	-3.15326866
H	1.36526594	2.28800919	-4.13038034
H	2.58339974	3.84413831	-2.65210997
H	2.42170197	3.64229383	-0.20078322
O	-4.35860160	-1.02861726	-0.38917293
S	-3.19944624	-0.66522986	0.38032383
Cl	-3.83306090	0.97298523	1.58236266
N	-2.10425757	-0.00565781	-0.55298516
C	-3.23146702	0.00776419	-3.20065872
O	-4.01996888	0.82471998	-2.96731834
O	-2.64517562	-1.60429730	1.33876018

SM:

O	-1.91913751	0.14772262	-0.88966505
P	-0.47792277	0.08298042	-0.50269063
C	0.18984149	-1.59125874	-0.62758454
C	1.52222290	-1.86680060	-0.30879874
C	2.00489433	-3.16344466	-0.41430705
C	1.15956436	-4.18840196	-0.83685777
C	-0.16625339	-3.91483178	-1.15371482
C	-0.65589696	-2.61616348	-1.05058103

C	0.01210357	0.75670314	1.11122251
C	-0.45140959	0.39182219	2.36605695
C	0.05150921	1.04629020	3.48899471
C	1.01077024	2.04581929	3.34519843
C	1.48081097	2.40830039	2.08505908
C	0.98096785	1.76489806	0.95744911
C	1.35389706	2.01520160	-0.45304954
C	0.66598744	1.19673443	-1.36579562
C	0.88477042	1.30115999	-2.73020302
C	1.80616623	2.23558137	-3.19909971
C	2.49539229	3.04706539	-2.30060671
C	2.27521187	2.94279517	-0.92917809
H	2.17843370	-1.07072333	0.02142618
H	3.03705066	-3.37767312	-0.16695484
H	1.53764630	-5.20014008	-0.91699345
H	-0.82354336	-4.71124479	-1.47911121
H	-1.68614659	-2.39095748	-1.28966979
H	-1.19571574	-0.38610947	2.46764177
H	-0.30403568	0.77648640	4.47516213
H	1.39675296	2.54847240	4.22323773
H	2.22760393	3.18642693	1.99140875
H	0.34365698	0.66788118	-3.42208702
H	1.98609479	2.33236479	-4.26209463
H	3.21033664	3.77035077	-2.67244610
H	2.81839579	3.58299840	-0.24579286
O	-4.16869630	-2.13977614	-0.67113684
S	-4.12805042	-1.43527058	0.57009328
Cl	-5.81237386	-2.03460655	1.63234306
N	-4.57166359	0.13305474	0.32574342
C	-3.87163992	1.11360423	0.55921489
O	-3.37341443	2.12998779	0.78749609
O	-3.02418188	-1.53729918	1.48067096
Int:			
O	-1.84929433	0.59317844	-1.20954679
P	-0.45217924	0.26248979	-0.53682728
C	-0.03544874	-1.46445068	-0.73926612

C	0.91142404	-2.05605435	0.09801353
C	1.24969330	-3.39004862	-0.08721923
C	0.64419543	-4.12930163	-1.09837389
C	-0.30178843	-3.53701261	-1.92993688
C	-0.64421631	-2.20341967	-1.75671903
C	-0.01006030	0.91553721	1.07792900
C	-0.47188401	0.53921220	2.33232658
C	0.06639504	1.16496125	3.45475390
C	1.04753983	2.14174553	3.31473961
C	1.52071496	2.50650209	2.05584406
C	0.99842408	1.89281018	0.92484983
C	1.40303913	2.13011014	-0.47722698
C	0.71677837	1.32225085	-1.39944275
C	0.95971270	1.40359123	-2.76136194
C	1.91031993	2.31338497	-3.21806991
C	2.59840352	3.11787478	-2.31259670
C	2.35171244	3.03259381	-0.94419112
H	1.36553226	-1.48653566	0.89769469
H	1.97459302	-3.85552916	0.56774913
H	0.90029815	-5.17269844	-1.23083256
H	-0.78573904	-4.11715948	-2.70450558
H	-1.39748095	-1.75049302	-2.38752843
H	-1.23125017	-0.22146651	2.43353680
H	-0.28710289	0.88736760	4.43887334
H	1.45434718	2.62302367	4.19524325
H	2.29306936	3.25901556	1.96568709
H	0.41728211	0.77795103	-3.45822980
H	2.11270240	2.39655374	-4.27773000
H	3.33493546	3.82254257	-2.67721058
H	2.89411109	3.66896551	-0.25733074
O	-3.95701198	-2.83562560	0.46942649
S	-3.47453505	-1.76823464	1.30416204
Cl	-5.19703067	-0.72929233	1.95722139
N	-2.62849798	-0.65090325	0.51022209
C	-3.05511083	-0.14065783	-0.64062111
O	-4.04532820	-0.09289170	-1.29585972
O	-2.73116469	-2.05838698	2.50585433

TS1:

O	-1.89971649	0.71192108	-1.10677117
P	-0.49773017	0.41223254	-0.56863504
C	-0.08788713	-1.33232402	-0.72068429
C	0.87430258	-1.92019681	0.10205658
C	1.17609853	-3.26770783	-0.04498139
C	0.51895050	-4.02880777	-1.00694495
C	-0.43991664	-3.44314800	-1.82748603
C	-0.74403550	-2.09563882	-1.68927373
C	0.00211965	1.01394448	1.06058651
C	-0.49148818	0.66605424	2.31074083
C	0.07803534	1.24615778	3.44253304
C	1.12759162	2.15161586	3.31622485
C	1.63126520	2.49094699	2.06265488
C	1.07192503	1.92309546	0.92416190
C	1.48968020	2.15267207	-0.47614946
C	0.74235373	1.41532008	-1.40997739
C	0.98634821	1.50789687	-2.77077227
C	2.00152271	2.35199624	-3.21504621
C	2.75215911	3.08356492	-2.29743544
C	2.50287506	2.99011572	-0.93018016
H	1.36996869	-1.33409425	0.86446663
H	1.91300177	-3.72698264	0.60131819
H	0.74597743	-5.08243458	-1.10920500
H	-0.96271039	-4.03814227	-2.56488797
H	-1.50350287	-1.64277905	-2.31309985
H	-1.29980947	-0.04365759	2.40381437
H	-0.29972278	0.98737931	4.42301577
H	1.56254933	2.59570466	4.20289776
H	2.45431063	3.18921320	1.98198227
H	0.39544238	0.93835959	-3.47667623
H	2.20625906	2.44069666	-4.27403838
H	3.53971639	3.73681549	-2.65149151
H	3.09486446	3.56926890	-0.23332107
O	-3.69376033	-3.14493365	0.50132292

S	-3.49057978	-2.03603827	1.39192155
Cl	-5.40926308	-1.36508140	1.93378953
N	-2.83708365	-0.74394027	0.63524042
C	-3.32525391	-0.35794055	-0.48151700
O	-4.16141665	-0.29958076	-1.29072156
O	-2.76294061	-2.18694360	2.62076809

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