

Chemistry–A European Journal

Supporting Information

Phosphorus-Containing Dibenzonaphthanthrenes: Electronic Fine Tuning of Polycyclic Aromatic Hydrocarbons through Organophosphorus Chemistry

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1. Experimental Details

General. All reactions involving oxygen- or moisture-sensitive compounds were carried out in a dry reaction vessel under an inert atmosphere of nitrogen or argon using anhydrous solvents and standard Schlenk techniques unless otherwise noted. Dry solvents were obtained from a M. Braun MB SPS-800 solvent purification system or purchased from Fisher Scientific. All oxygen- and moisture sensitive liquids and anhydrous solvents were transferred via a syringe or a stainless-steel cannula. Reaction mixtures were degassed by bubbling argon through the solution for 10 min. Photoreactions were carried out in a custom-built photoreactor system (Peschel Ultraviolett) using a water-cooled medium-pressure Hg lamp (TQ150, 150 W) in a quartz glass tube. Analytical thin-layer chromatography (TLC) analysis was performed on aluminum plates coated with 0.20 mm silica gel containing a fluorescent indicator (Macherey-Nagel, ALUGRAM[®], SIL G/UV₂₅₄) or on aluminum plates coated with 0.20 mm Al₂O₃ containing a fluorescent indicator (Macherey-Nagel, ALUGRAM[®], Alox N/UV₂₅₄). TLC plates were visualized by exposure to ultraviolet light ($\lambda = 254$ nm and 366 nm). Column chromatography was performed on silica gel (Macherey-Nagel, M-N Silica Gel 60A, 230–400 mesh) or Al₂O₃ (Macherey-Nagel, aluminum oxide 90 neutral or basic, 50–200 μ m). Reagents were purchased at reagent grade from commercial suppliers and used without further purification. MgSO₄ was used as the drying agent after aqueous work-up.

Instrumentation. ¹H, ¹³C, ¹⁹F, and ³¹P NMR spectra were recorded on a Bruker Avance 400 (400 MHz for ¹H, 366 MHz for ¹⁹F, 162 MHz for ³¹P, and 101 MHz for ¹³C) and a Bruker Avance 300 (300 MHz for ¹H, 121 MHz for ³¹P, and 75 MHz for ¹³C) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to the residual solvent signal as an internal reference (C₂D₂Cl₄: 6.00 ppm for H, 73.8 ppm for ¹³C, CD₂Cl₂: 5.32 ppm for ¹H, 53.8 ppm for ¹³C; CDCl₃: 7.24 ppm for ¹H, 77.2 ppm for ¹³C). Coupling constants (*J*) are given in Hz and the apparent resonance multiplicity is reported as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet) or m (multiplet). C₂D₂Cl₄ (Armar, 99.8%) CD₂Cl₂ (Sigma-Aldrich, 99.9%) and CDCl₃ (Armar, 99.8%) were dried over molecular sieves (4 Å) prior to use. All spectra were recorded at ambient probe temperature, if not otherwise stated.

Mass spectra were obtained from a MicroTOF II (Bruker, HR ESI and APPI), a UltraflexTOF/TOF (Bruker, HR MALDI) mass spectrometer (Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg), a ApexQe hybrid 9.4 T FT-ICR (Bruker, ESI, MALDI, DART) or a AutoFlex Speed TOF (Bruker, LDI, MALDI) (Institute of Organic Chemistry, Heidelberg University).

UV/Vis spectra were recorded on a Varian Cary 5000, a Jasco V-770 UV/Vis/NIR or an Agilent Technologies Cary 60 spectrophotometer. The fluorescence spectra were recorded on a Jasco

spectrofluorometer FP-8500. All measurements were carried out under ambient conditions in QS Quartz Suprasil cells (Hellma Analytics, 10 mm light path) or J/3 Quartz cells (Jasco 10 mm light path). The absorption maxima (λ_{\max}) are reported in nm and the extinction coefficient (ϵ) in $\text{L M}^{-1} \text{cm}^{-1}$.

Infrared absorption (IR) spectra were recorded on a Varian 660-IR (ATR mode) or a Jasco FT/IR-4600 (ATR mode) spectrometer and characteristic IR absorptions are reported in cm^{-1} and labelled as broad (br), strong (s), medium (m), and weak (w).

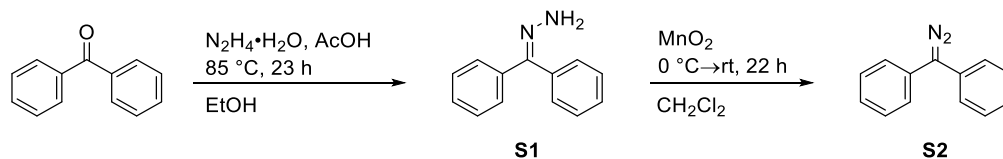
Melting points were determined on a Büchi M-560 melting point apparatus in open capillaries.

Elemental analyses were carried out by the Microanalytic Laboratory (Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg).

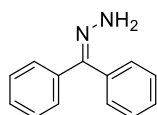
Cyclic voltammetry (CV) was performed on a computer-controlled BASi Cell Stand instrument under nitrogen atmosphere using a standard three-electrode assembly connected to a potentiostat and at a scan rate of 100 mV sec^{-1} . The working electrode was a glassy carbon disk electrode (3.0 mm diameter), a platinum wire was used as auxiliary electrode and the quasi-reference electrode was an Ag/AgCl (3 M NaCl) electrode. The samples were measured in 0.1 M electrolyte solutions of *n*-Bu₄NPF₆ (used without further purification) in anhydrous CH₂Cl₂ and were purged with nitrogen for 20 min prior to analysis. Each measurement was calibrated with an internal standard (Fc/Fc⁺).

X-Ray crystallographic data of **3**, **4** and **5** were measured on a Supernova CCD diffractometer (Agilent) at 153 K (Department of Chemistry and Pharmacy, University of Erlangen-Nürnberg). The structures were solved and refined with SHELXS-2014. After full-matrix least-square refinement of the non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in calculated positions using a riding model. X-Ray crystallographic data of **7** were measured on a Stoe Stadivari diffractometer at 200 K (Institute of Organic Chemistry, University of Heidelberg). The structures were solved with SHELXT-2014 and refined against F^2 with a full-matrix least-squares algorithm using the SHELXL-2018/3 software.^[1] Atoms were treated using appropriate riding models. X-Ray crystallographic data of **3**, **4**, **5** and **7** can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Synthesis of Diphenyldiazomethane



Scheme S1 Synthetic route towards the diphenyldiazomethane **S2**.



(Diphenylmethylidene)hydrazine (S1).^[2] To a solution of benzophenone (5.00 g, 27.4 mmol) in ethanol (60 mL) hydrazine monohydrate (13.4 mL, 274 mmol) was added slowly. The mixture was treated with glacial acetic acid (0.5 mL) and afterwards heated to 85°C for 23 h. After cooling to rt, the volume was reduced by ca. 50 % under reduced pressure whereupon the product **S1** precipitated as white, needle shaped crystals (4.79 g, 89%).

$R_f = 0.76$ (SiO₂, CH₂Cl₂/EtOAc 10:1).

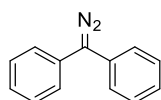
Mp: 96–98 °C, (lit. 97–100 °C).^[3]

¹H NMR (300 MHz, CD₂Cl₂) $\delta = 7.73$ – 7.45 (m, 5H), 7.34 (ddd, $J = 7.6, 3.5, 1.2$ Hz, 5H), 5.56 (s, 2H) ppm.

¹³C NMR (75 MHz, CD₂Cl₂) $\delta = 148.5, 139.0, 133.5, 129.7, 129.2, 129.1, 128.4, 128.2, 126.7$ ppm.

HRMS (APPI, MeOH, positive mode): Calcd for C₁₃H₁₃N₂: 197.1073 [M + H]⁺, found 197.1078.

Analytical data are consistent with those reported in literature.^[2]



1,1'-(Diazomethylene)dibenzene (S2).^[2] To anhydrous MgSO₄ (750 mg) was added dry CH₂Cl₂ (10 mL) in a round bottom flask. Subsequently **S1** (1.50 g, 7.64 mmol) was added to this suspension. The mixture was cooled to 0 °C and activated MnO₂ was added in one portion. After warming to rt, the reaction mixture was stirred for 22 h. After filtration and evaporation of the solvent under reduced pressure the crude product was purified by column chromatography

(basic Al₂O₃, petroleum ether/ Et₃N 20:1). The product **58** (480 mg, 32%) was obtained as a purple oil which transforms into purple-black crystals upon cooling to -18 °C.

*R*_f = 0.79 (basic Al₂O₃, petroleum ether/Et₃N 20:1).

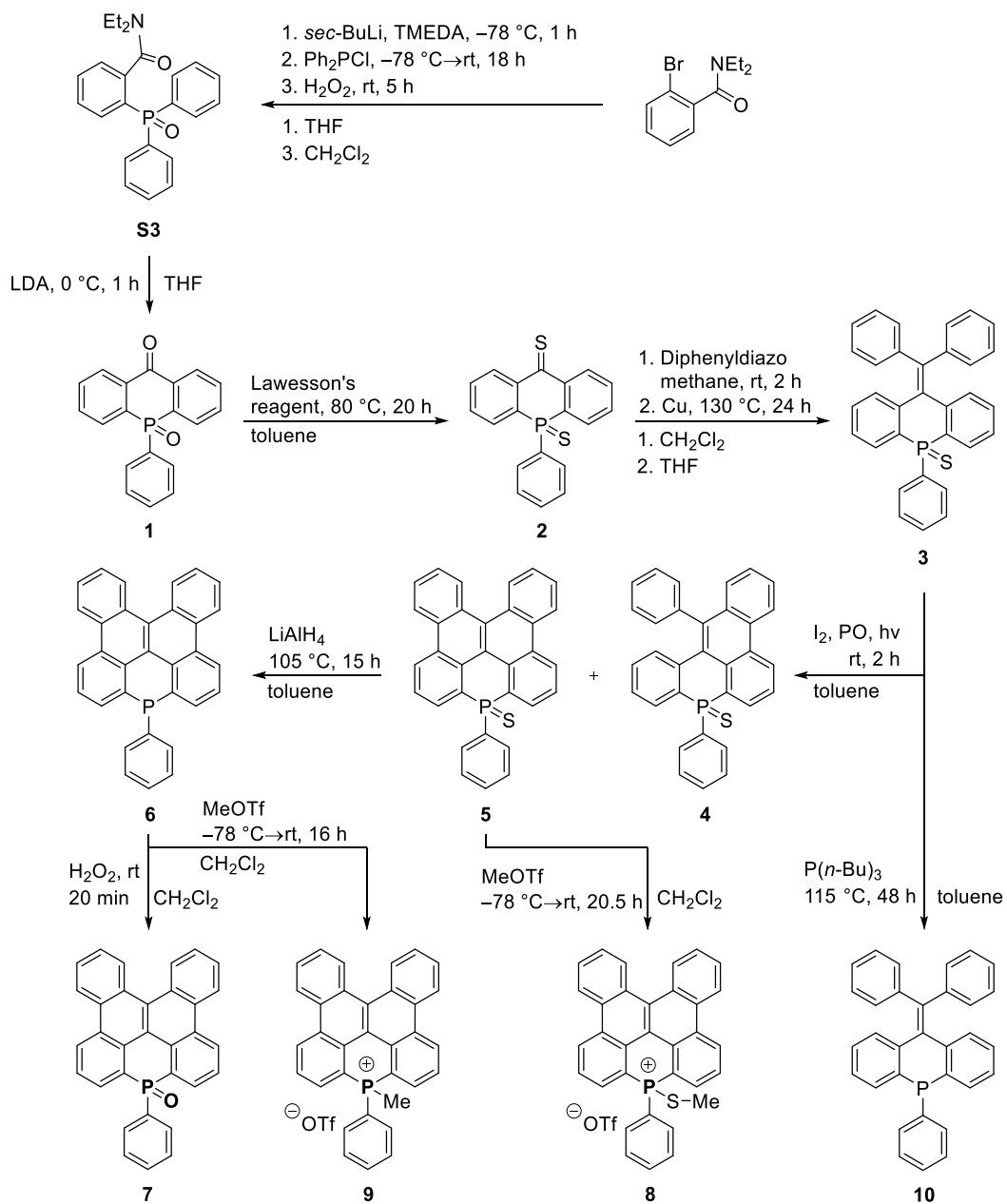
Mp.: 29–31 °C (lit. 29–31 °C).^[4]

¹H NMR (300 MHz, CD₂Cl₂) δ = 7.42 (t, *J* = 6.8 Hz, 4H), 7.33 (t, *J* = 6.3 Hz, 4H), 7.26–7.17 (m, 2H) ppm.

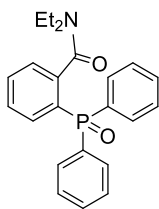
¹³C NMR (75 MHz, CD₂Cl₂) δ = 130.0, 129.5, 126.8, 125.5, 62.7 ppm.

Analytical data are consistent with those reported in literature.^[2,5]

Synthesis of the Organophosphorus Compounds



Scheme S2 Synthetic routes towards phosphorus-containing dibenzonaphthanthrenes. PO: propylene oxide.



2-(Diphenylphosphoryl)-*N,N*-diethylbenzamide (S3).^[6,7] To a solution of TMEDA (3.58 g, 30.8 mmol) in THF (120 mL) *sec*-BuLi (1.30 M in hexanes, 21.5 mL, 28.0 mmol) was added via cannula at -78 °C. The resulting yellow solution was stirred for 30 min at -78 °C before *N,N*-diethylbenzamide (5.00 g, 28.0 mmol), dissolved in THF (30 mL) was added dropwise via syringe. After the mixture was stirred for 1 h at -78 °C, Ph_2PCI (5.93 g, 26.9 mmol) was added and the cooling bath was removed. The reaction mixture was allowed to warm to rt overnight (18 h), upon which its color turned from yellow to dark green. Water (30 mL) and aqueous HCl (1 M, 8 mL) was added and the volatiles were removed under reduced pressure. The aqueous phase was extracted with CH_2Cl_2 (3 \times 60 mL), washed with water (40 mL) and the combined organic phases were dried (MgSO_4). After filtration, the solvent was removed under reduced pressure and the resulting crude product was dissolved in CH_2Cl_2 (100 mL). H_2O_2 (30wt.-%, 10 mL) was added at rt and the mixture vigorously stirred for 5 h. The organic phase was separated, washed with water (30 mL) and the combined organic phases were dried (MgSO_4). Column chromatography (SiO_2 , THF/hexanes 1:1) afforded the product **S3** (6.49 g, 64%) as a white solid.

Mp.: 119–123 °C (lit. 121.4–122.4 °C).^[7]

^1H NMR (CD_2Cl_2 , 400 MHz): δ 7.67–7.62 (m, 4H), 7.57–7.51 (m, 4H), 7.49–7.42 (m, 5H), 7.32 (dd, J = 4.0, 2.7 Hz, 1H), 3.21 (q, 2H), 2.99 (br s 2H), 1.10 (t, J = 7.2, 3H), 1.02 (t, J = 7.2, 3H) ppm.

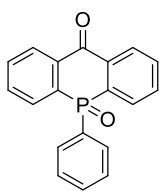
^{13}C $\{^{31}\text{P}\}$ NMR (101 MHz, CD_2Cl_2) δ = 169.5, 142.3, 134.1, 133.5, 132.6, 132.13, 132.11, 130.0, 128.6, 128.3, 127.5, 44.1, 39.5, 13.9, 12.8; Four signals coincident or not observed.

^{31}P NMR (CDCl_3 , 162 MHz): δ = 28.6 ppm.

IR (ATR): $\tilde{\nu}$ 3055 (br), 2971 (w), 2933 (w), 2872 (w), 1627 (s), 1433 (m), 1185 (m), 720 (s), 693 (s) cm^{-1} .

HRMS (MALDI, dnb): Calcd. for $\text{C}_{23}\text{H}_{25}\text{NO}_2\text{P}^+[\text{M} + \text{H}]^+$: 378.4318, found 378.2791; Calcd. for $\text{C}_{23}\text{H}_{24}\text{NO}_2\text{PNa}^+[\text{M} + \text{Na}]^+$: 400.1442, found 400.2608.

Analytical data are consistent with those reported in literature.^[7]



5-Phenyl-5λ⁵-acridophosphine-5,10(5H)-dione (1).^[6,7] To a solution of phosphine oxide **S3** (15.0 g, 39.8 mmol) in THF (250 mL), lithium diisopropylamide (2 M in THF/*n*-heptane/ethylbenzene, 43.7 mL, 87.4 mmol) was added dropwise at 0 °C within 10 min. The mixture was stirred for 1 h at 0°C before the reaction was stopped by slowly adding sat. aq. NH₄Cl (75 mL) and water (50 mL). The volatiles were removed under reduced pressure. The aqueous phase was extracted with EtOAc (3 × 30 mL), washed with water (50 mL) and the combined organic phases were dried (MgSO₄). After filtration, the solvent was removed under reduced pressure. Recrystallization from boiling EtOAc afforded the product (5.24 g, 43%) as a pale yellow solid.

$R_f = 0.64$ (SiO₂, CH₂Cl₂/MeOH 15:1).

Mp: 218–221 °C (lit. 222–223 °C).^[6]

¹H NMR (300 MHz, CD₂Cl₂) δ = 8.45–8.40 (m, 2H), 8.02–7.95 (m, 2H), 7.78–7.75 (m, 4H), 7.57 (td, $J = 1.5, 12.7$ Hz, 1H), 7.54 (dd, $J = 1.6, 12.7$ Hz, 1H), 7.48–7.43 (m, 1H), 7.41–7.34 (m, 2H) ppm.

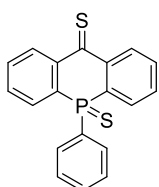
¹³C {³¹P} NMR (CD₂Cl₂, 101 MHz): δ = 183.0, 136.3, 134.1, 134.0, 133.9, 133.0, 132.3, 131.4, 131.1, 129.4, 129.2 ppm.

³¹P NMR (121 MHz, CD₂Cl₂) δ = 2.6 (s) ppm.

IR (ATR): $\tilde{\nu}$ 2966 (w), 2024 (m), 1974 (w), 1662 (s), 1296 (s), 1195 (s), 1138 (s), 920 (m) cm⁻¹.

HRMS (APPI, toluene, positive mode): Calcd for C₁₉H₁₄O₂P: 305.0726 [M + H]⁺, found 305.0728.

Analytical data are consistent with those reported in literature.^[7]



5-Phenyl-5λ⁵-acridophosphine-5,10(5H)-dithione (2). To a solution of **1** (500 mg, 1.64 mmol) in anhydrous toluene (3.00 mL) was added Lawesson's reagent (997 mg,

2.47 mmol) in one portion under an argon atmosphere and light exclusion. The solution was stirred for 10 min. at rt and heated for 20 h to 80 °C using microwave irradiation. After cooling to rt, the solvent was removed under reduced pressure and the residue was directly purified by column chromatography (deact. (Et₃N) SiO₂, CH₂Cl₂/ hexanes 1:1). After removal of the solvent under reduced pressure, the product **2** (126 mg, 23%) was obtained as green-blue crystals.

$R_f = 0.74$ (SiO₂, CH₂Cl₂/hexanes 1:1).

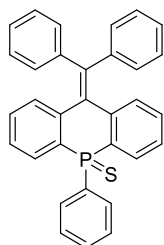
Mp: 161–163 °C

¹H NMR (300 MHz, CD₂Cl₂) $\delta = 8.41$ – 8.23 (m, 4H), 7.79 (tdd, $J = 7.5, 1.9, 1.2$ Hz, 2H), 7.68– 7.58 (m, 2H), 7.52– 7.41 (m, 2H), 7.35 (dd, $J = 7.3, 2.2$ Hz, 1H), 7.32– 7.23 (m, 2H) ppm.

¹³C {³¹P} NMR (CD₂Cl₂, 101 MHz): $\delta = 225.6, 145.0, 135.0, 132.9, 132.4, 131.8, 131.3, 130.6, 130.1, 129.0, 126.6$ ppm.

³¹P NMR (121 MHz, CD₂Cl₂) $\delta = 21.0$ (s) ppm.

HRMS (APPI, MeOH, positive mode): Calcd for C₁₉H₁₄PS₂: 337.0269 [M + H]⁺, found 337.0271.



10-(Diphenylmethylidene)-5-phenyl-5,10-dihydro-5λ⁵-acridophosphine-5-thione (3**).** To a solution of thiocarbonyl compound **2** (100 mg, 0.303 mmol) in dry THF (10.0 mL) was added a solution of diphenyldiazomethane (70.5 mg, 0.363 mmol) in dry THF (10.0 mL) under exclusion of light. The resulting solution was stirred at rt for 2 h before the solvent was removed under reduced pressure. The obtained residue was dissolved in dry xylenes (20.0 mL) and copper powder (192 mg, 3.03 mmol) was added in one portion. The resulting suspension was stirred at 130 °C for 24 h, subsequently cooled to rt and the solvent removed under reduced pressure. After a short plug (SiO₂, CH₂Cl₂) and purification via column chromatography (SiO₂, CH₂Cl₂/ hexanes 1:1) the diphenylvinylidene-bridged triphenylphosphine **3** (128 mg, 90%) was obtained as a white solid.

$R_f = 0.44$ (SiO₂, CH₂Cl₂/hexanes 1:1).

Mp.: 256–260 °C.

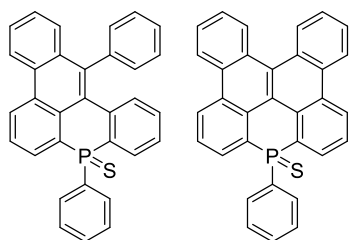
¹H NMR (300 MHz, CD₂Cl₂) $\delta = 8.48$ (q, $J = 7.1$ Hz, 2H), 7.50–7.42 (m, 7H), 7.26–7.18 (m, 4H), 7.13–7.11 (m, 6H), 6.79 (s, 4H) ppm.

¹³C {³¹P} NMR (101 MHz, CD₂Cl₂) $\delta = 144.5, 142.0, 141.8, 138.0, 136.3, 134.3, 132.7, 132.2, 131.8, 131.1, 130.7, 130.3, 130.2, 129.3, 129.11, 129.06, 128.6, 128.3, 127.3, 127.2$ ppm.

³¹P NMR (121 MHz, CD₂Cl₂) $\delta = 25.7$ (s) ppm.

IR (ATR): $\tilde{\nu}$ 3052 (w), 2921 (w), 2853 (w), 2361 (w), 1587 (w), 1486 (m), 1436 (s), 1102 (m), 839 (m), 755 (s), 684 (s), 640 (s), 579 (m), 534 (m), 476 (s) cm⁻¹.

HRMS (ESI, MeOH, positive mode): Calcd for C₃₂H₂₄PS: 471.1330 [M + H]⁺, found: 471.1336.



8,13-Diphenyl-8H-8 λ^5 -naphtho[1,2,3-*k*]acridophosphine-8-thione (4) and 8-phenyl-8H-8 λ^5 -benzo[3,4]phenanthro[2,1,10,9-*klmn*]acridophosphine-8-thione (5). The

photocyclization apparatus was dried and flushed with argon. Compound **3** (50.0 mg, 0.106 mmol), I₂ (59.3 mg, 0.234 mmol), and propylene oxide (PO; 10 mL) were dissolved in dry toluene (150 mL) and the reaction solution was degassed with argon for 20 min. The apparatus was irradiated (Hg medium-pressure lamp, 150 W) at rt for 12 h under a steady bubbling of argon and addition of another 2 equiv. of I₂ and PPO (10 mL) after 3.5 h and 8 h. The solvent was subsequently removed under reduced pressure. Purification via column chromatography (SiO₂, hexanes/EtOAc 5:1) provided **4** as a pale yellow solid (25.8 mg, 52%) and **5** as a pale yellow solid (14.3 mg, 29%).

Compound **4**:

$R_f = 0.58$ (SiO₂, hexanes/EtOAc 5:1).

Mp.: 285 °C (decomp.).

¹H NMR (400 MHz, CD₂Cl₂) $\delta = 8.99$ (d, $J = 8.5$ Hz, 1H), 8.80–8.71 (m, 2 H), 8.47 (ddd, $J = 1.2, 15.6, 7.6$ Hz, 1H), 7.96 (ddd, $J = 2.2, 8.3, 7.2$ Hz, 1H), 7.84–7.80 (m, 2H), 7.75–7.71 (m,

1H), 7.61–7.54 (m, 2H), 7.45–7.37 (m, 2H), 7.30–7.17 (m, 7H), 7.12–7.07 (m, 1H), 6.69 (d, $J = 7.4$ Hz, 1H) ppm.

^{13}C $\{^{31}\text{P}\}$ NMR (101 MHz, CD_2Cl_2) $\delta = 140.5, 140.4, 139.6, 137.1, 133.6, 133.3, 132.6, 132.3, 132.1, 131.9, 131.3, 131.3, 130.7, 130.4, 130.3, 130.0, 129.5, 129.1, 128.8, 128.7, 128.5, 128.3, 128.2, 128.1, 127.7, 127.5, 127.0, 126.9, 126.3, 123.0$ ppm.

^{31}P NMR (162 MHz, CD_2Cl_2) $\delta = 22.8$ (s) ppm.

IR (ATR): $\tilde{\nu}$ 3055 (w), 2919 (m), 2850 (m), 1565 (w), 1463 (m), 1432 (m), 1100 (w), 849 (m), 806 (m), 763 (s) cm^{-1} .

UV/Vis (CH_2Cl_2) λ_{max} (ϵ) 374 (4700), 345 (14000), 267 (28400) nm ($\text{L mol}^{-1} \text{cm}^{-1}$).

HRMS (ESI, toluene, positive mode): Calcd for $\text{C}_{32}\text{H}_{22}\text{PS}$: 469.1177 $[\text{M} + \text{H}]^+$, found: 469.1174.

Elemental analysis: Calcd for $\text{C}_{32}\text{H}_{21}\text{PS}$: C, 82.0; H, 4.52; S, 6.84; found: C, 81.8; H, 4.60; S, 6.70%.

Compound **5**:

$R_f = 0.48$ (SiO_2 , hexanes/EtOAc 5:1).

Mp.: 307 °C (decomp.).

^1H NMR (300 MHz, CD_2Cl_2) $\delta = 9.00$ (d, $J = 8.3$ Hz, 2H), 8.76 (dt, $J = 1.2, 8.3$ Hz, 4H), 8.53 (ddd, $J = 1.3, 16.5, 7.3$ Hz, 2H), 7.90 (ddd, $J = 1.9, 8.2, 7.3$ Hz, 2H), 7.79 (ddd, $J = 1.4, 8.2, 6.9$ Hz, 2H), 7.71 (ddd, $J = 1.3, 8.2, 7.1$ Hz, 2H), 7.60–7.52 (m, 2H), 7.30–7.19 (m, 3H) ppm.

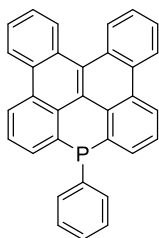
^{13}C $\{^{31}\text{P}\}$ NMR (101 MHz, CD_2Cl_2) $\delta = 137.9, 133.8, 131.5, 131.2, 131.1, 130.8, 130.7, 130.4, 129.4, 128.7, 128.7, 128.2, 127.8, 127.4, 127.4, 127.0, 123.9, 121.3$ ppm.

^{31}P NMR (121 MHz, CD_2Cl_2) $\delta = 21.1$ (s) ppm.

IR (ATR): $\tilde{\nu}$ 3024 (w), 2920 (w), 2850 (w), 1571 (w), 1473 (w), 1432 (w), 1096 (m), 862 (w), 810 (m), 762 (s) cm^{-1} .

UV/Vis (CH_2Cl_2) λ_{max} (ϵ) 382 (12600), 366 (14800), 346 (14900) 329 (12300) 312 (28000) 276 (49400) nm ($\text{L mol}^{-1} \text{cm}^{-1}$).

HRMS (APPI, acetonitrile, toluene, CH_2Cl_2 , positive mode): Calcd for $\text{C}_{32}\text{H}_{20}\text{PS}$: 467.1018 $[\text{M} + \text{H}]^+$, found: 467.1018.



8-Phenyl-8H-benzo[3,4]phenanthro[2,1,10,9-*klmn*]acridophosphine (6). Dry dioxane (10 mL) was degassed with a steady stream of argon for 10 min. Phosphine sulfide **5** (10.0 mg, 0.021 mmol) was subsequently dissolved and LiAlH₄ (1 M in THF, 0.322 mL, 0.322 mmol) was added dropwise via syringe. The solution was degassed with a steady stream of argon for another 5 min and afterwards heated to 105°C for 15 h via μ W irradiation. Wet CH₂Cl₂ (20 mL) was added to quench the reaction. The reaction mixture was filtered through a short pad of basic Al₂O₃ (CH₂Cl₂) and the solvent was removed under reduced pressure at rt. The pure phosphine **6** was obtained as a slightly yellow powder (8.2 mg, 88%).

$R_f = 0.91$ (Al₂O₃, CH₂Cl₂/hexanes 1:1).

¹H NMR (400 MHz, CD₂Cl₂) $\delta = 8.76$ (dd, $J = 1.2, 8.3$ Hz, 2H), 8.71–8.67 (m, 4H), 7.92 (ddd, $J = 1.4, 12.5, 7.1$ Hz, 2H), 7.73–7.68 (m, 4H), 7.63 (ddd, $J = 1.3, 8.3, 7.0$ Hz, 2H), 7.26–7.21 (m, 2H), 7.13–7.07 (m, 3H) ppm.

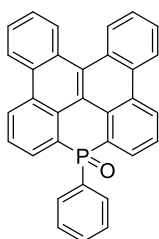
¹³C {³¹P} NMR (101 MHz, CD₂Cl₂) $\delta = 142.9, 134.5, 132.3, 131.9, 131.4, 130.6, 130.0, 129.3, 129.1, 128.6, 128.5, 128.0, 127.1, 126.8, 126.1, 124.4, 124.2, 123.4$ ppm.

³¹P NMR (162 MHz, CD₂Cl₂) $\delta = -37.0$ (s) ppm.

IR (ATR): $\tilde{\nu}$ 3053 (w), 2918 (m), 2849 (m), 2689 (w), 1949 (w), 1579 (w), 1448 (m), 1395 (m), 1250 (m), 1116 (s), 870 (s) cm⁻¹.

UV/Vis (CH₂Cl₂) λ_{max} (ϵ) 371 (3100), 363 (3300), 310 (6500), 297 (6200), 272 (9300) nm (L mol⁻¹ cm⁻¹).

HRMS (MALDI TOF, dctb, positive mode): Calcd for C₃₂H₁₉P: 434.1219 [M]⁺, found: 434.1212.



8-Phenyl-8H-8 λ^5 -benzo[3,4]phenanthro[2,1,10,9-*klmn*]acridophosphin-8-one (7). Phosphine **6** (10.0 mg, 0.023 mmol) was dissolved in CH₂Cl₂ (10 mL) and H₂O₂ (30wt.% in H₂O) (5 mL) was added. The solution was vigorously stirred for 20 min. The two phases were

separated and the aqueous phase was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic phases were dried (MgSO₄) and the solvent was removed under reduced pressure. The resulting white residue was purified via column chromatography (SiO₂, CH₂Cl₂/MeOH 25:1) and recrystallization from EtOAc. Phosphine oxide **7** (9.2 mg, 89%) was obtained as a white solid.

R_f = 0.50 (SiO₂, CH₂Cl₂/MeOH 25:1).

Mp.: 319 °C (decomp.).

¹H NMR (400 MHz, CD₂Cl₂) δ = 9.04 (d, *J* = 8.2 Hz, 2H), 8.80–8.76 (m, 4H), 8.35 (ddd, *J* = 1.3, 13.7, 7.2 Hz, 2H), 7.92–7.88 (m, 2H), 7.83–7.78 (m, 2H), 7.73–7.69 (m, 2H), 7.52–7.47 (m, 2H), 7.36–7.34 (m, 1H), 7.30–7.25 (m, 2H) ppm.

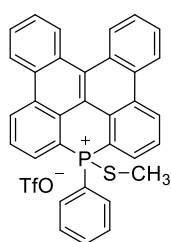
¹³C {³¹P} NMR (101 MHz, CD₂Cl₂) δ = 137.2, 132.9, 131.7, 131.6, 131.3, 130.9, 130.7, 130.5, 129.6, 129.5, 128.8, 128.2, 127.7, 127.6, 127.4, 127.0, 123.9, 121.5 ppm.

³¹P NMR (162 MHz, CD₂Cl₂) δ = 7.3 (s) ppm.

IR (ATR): $\tilde{\nu}$ 3065 (w), 2357 (w), 1573 (w), 1438 (w), 1397 (m), 1186 (m), 1106 (m), 861 (m), 817 (m) cm⁻¹.

UV/Vis (CH₂Cl₂) λ_{max} (ε) 381 (5000), 364 (5800), 341 (5800), 325 (5100), 312 (14900), 274 (23400) nm (L mol⁻¹ cm⁻¹).

HRMS (APPI, toluene, positive mode): Calcd for C₃₂H₁₉PO: 450.1168 [M]⁺, found: 450.1170.



8-Methylthio-8-phenyl-8H-benzo[3,4]phenanthro[2,1,10,9-*klmn*]acridophosphin-8-ium trifluoromethanesulfonate (8). Phosphine sulfide **5** (20.0 mg, 0.043 mmol) was dissolved in dry CH₂Cl₂ (20 mL) at -78 °C. Methyl triflate (0.005 mL, 0.047 mmol) was added dropwise to the solution. The reaction mixture was stirred for 20 min at -78 °C and subsequently warmed to rt. After 20.5 h at rt more methyl triflate (0.010 mL, 0.094 mmol) was added to the mixture. After another 6.5 h the total conversion of the starting material was confirmed by TLC analysis (SiO₂, hexanes/ EtOAc 5:1). The solvent was removed under reduced pressure and the crude

product was recrystallized from CH₂Cl₂ and *n*-pentane to yield the pure phosphonium salt **8** (24.3 mg, 95%) as a yellow solid.

$R_f = 0.29$ (SiO₂, CH₂Cl₂/MeOH 15:1).

Mp.: 253 °C (decomp.).

¹H NMR (400 MHz, CD₂Cl₂) $\delta = 9.36$ (d, $J = 8.3$ Hz, 2H), 8.88–8.79 (m, 4H), 8.49 (ddd, $J = 1.2, 17.0, 7.4$ Hz, 2H), 8.19–8.15 (m, 2H), 7.96–7.92 (m, 2H), 7.86–7.74 (m, 5H), 7.68–7.63 (m, 2H), 2.15 (d, $J = 16.1$ Hz, 3H) ppm.

¹³C {³¹P} NMR (101 MHz, CD₂Cl₂) $\delta = 136.0, 135.1, 134.9, 132.6, 132.1, 131.7, 131.4, 131.2, 131.0, 131.0, 129.7, 129.4, 128.9, 128.5, 124.2, 124.0, 118.2, 110.0, 12.8$ ppm. The signal of the C atom of OTf is coincident or not observed.

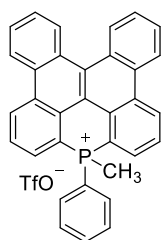
¹⁹F NMR (377 MHz, CD₂Cl₂) $\delta = -78.9$ (s, 3F) ppm.

³¹P NMR (162 MHz, CD₂Cl₂) $\delta = 29.2$ (s) ppm.

IR (ATR): $\tilde{\nu}$ 3053 (w), 1570 (w), 1475 (w), 1402 (m), 1259 (s), 1151 (s), 1027 (s), 822 (w), 761 (s) cm⁻¹.

UV/Vis (CH₂Cl₂) λ_{\max} (ϵ) 416 (16800), 347 (10400), 330 (22600), 317 (18600), 282 (61200) nm (L mol⁻¹ cm⁻¹)

MALDI-TOF MS (dctb, positive mode) m/z 481 ([M-OTf]⁺, 100).



8-Methyl-8-phenyl-8H-benzo[3,4]phenanthro[2,1,10,9-*klmn*]acridophosphin-8-ium trifluoromethanesulfonate (9). Dry CH₂Cl₂ (1.0 mL) was degassed with a steady stream of argon for 15 min. Phosphine **6** (7.7 mg, 0.018 mmol) was added and the solution was cooled to -78 °C. Methyl triflate (0.010 mL, 0.091 mmol) was added dropwise to the solution. The reaction mixture was stirred for 25 min at -78 °C, warmed to rt, and subsequently stirred for 16 h at rt. The solvent was removed under a faint stream of nitrogen and the residue was subjected to column chromatography (SiO₂, CH₂Cl₂/MeOH 25:1). Further purification of the crude product via preparative TLC (SiO₂, CH₂Cl₂/MeOH 25:1) afforded the pure phosphonium salt **9** (2.9 mg, 27%) as a yellow solid.

$R_f = 0.33$ (SiO₂, CH₂Cl₂/MeOH 25:1).

Mp.: 223 °C (decomp.).

¹H NMR (600 MHz, CD₂Cl₂) $\delta = 9.27$ (d, $J = 8.4$ Hz, 2H), 8.84–8.78 (m, 4H), 8.26 (dd, $J = 15.8, 7.1$ Hz, 2H), 8.07 (td, $J = 7.7, 2.4$ Hz, 2H), 7.91 (ddd, $J = 8.3, 7.0, 1.2$ Hz, 2H), 7.85–7.77 (m, 5H), 7.66 (td, $J = 7.7, 3.5$ Hz, 2H), 2.91 (d, $J = 13.5$ Hz, 3H) ppm.

¹³C {³¹P} NMR (151 MHz, CD₂Cl₂) $\delta = 135.5, 134.6, 133.8, 133.1, 131.6, 131.3, 131.1, 131.0, 130.8, 129.6, 129.5, 129.4, 128.6, 128.2, 124.1, 123.7, 119.1, 111.4, 29.8$ ppm. The signal of the C atom of OTf is coincident or not observed.

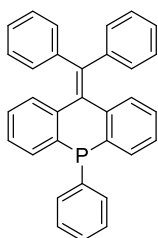
¹⁹F NMR (283 MHz, CDCl₃) $\delta = -78.1$ (s, 3F) ppm.

³¹P NMR (243 MHz, CD₂Cl₂) $\delta = 0.0$ (s) ppm.

IR (ATR): $\tilde{\nu}$ 1574 (w), 1440 (m), 1256 (s), 1156 (s), 1029 (s), 805 (m), 746 (m) cm⁻¹.

UV/Vis (CH₂Cl₂) λ_{\max} (ϵ) 248 (16000), 279 (25700), 309 (9200), 320 (11300), 342 (5200), 380 (5400), 399 (6600) nm (L mol⁻¹ cm⁻¹).

HRMS (ESI, CH₂Cl₂, positive mode): Calcd for C₃₃H₂₂P: 449.1454 [M]⁺, found: 449.1447.



10-(Diphenylmethylidene)-5-phenyl-5,10-dihydroacridophosphine (10). In a sealed tube, phosphine sulfide **3** (50.0 mg, 0.106 mmol) and (*n*-Bu)₃P (0.540 mL, 430 mg, 2.13 mmol) was dissolved in dry, degassed toluene. The reaction mixture was heated for 48 h to 105 °C via microwave irradiation. The solvent was removed under reduced pressure and the resulting white residue was washed with hexanes (3 × 2 mL). After filtration, phosphine **9** (36.0 mg, 77%) was obtained as a white solid.

$R_f = 0.84$ (SiO₂, CH₂Cl₂/hexanes 1:1).

Mp.: 186–190 °C.

¹H NMR (300 MHz, C₂D₂Cl₄) $\delta = 7.93$ (br s, 1H), 7.69–7.50 (br m, 2H), 7.35–7.11 (br m, 15H), 6.94–6.84 (br m, 5H) ppm.

^{13}C $\{^{31}\text{P}\}$ NMR (75 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 100 °C) δ = 142.2, 141.9, 137.3, 130.1, 130.0, 129.8, 129.7, 129.2, 128.7, 128.3, 128.2, 127.7, 127.5, 127.2, 126.6, 126.5, 126.1, 125.6 ppm.

^{31}P NMR (121 MHz, CD_2Cl_2) δ = -17.7 (s), -25.2 (s) ppm.

IR (ATR): $\tilde{\nu}$ 3050 (w), 2921 (w), 1588 (w), 1488 (w), 1436 (m), 1077 (w), 1029 (w), 750 (s) cm^{-1} .

UV/Vis (CH_2Cl_2) λ_{max} (ϵ) 332 (4800) nm ($\text{L mol}^{-1} \text{cm}^{-1}$).

HRMS (APPI, toluene, positive mode): Calcd for $\text{C}_{32}\text{H}_{24}\text{P}$: 439.1615 $[\text{M} + \text{H}]^+$, found: 439.1610.

2. Nuclear Magnetic Resonance Spectra

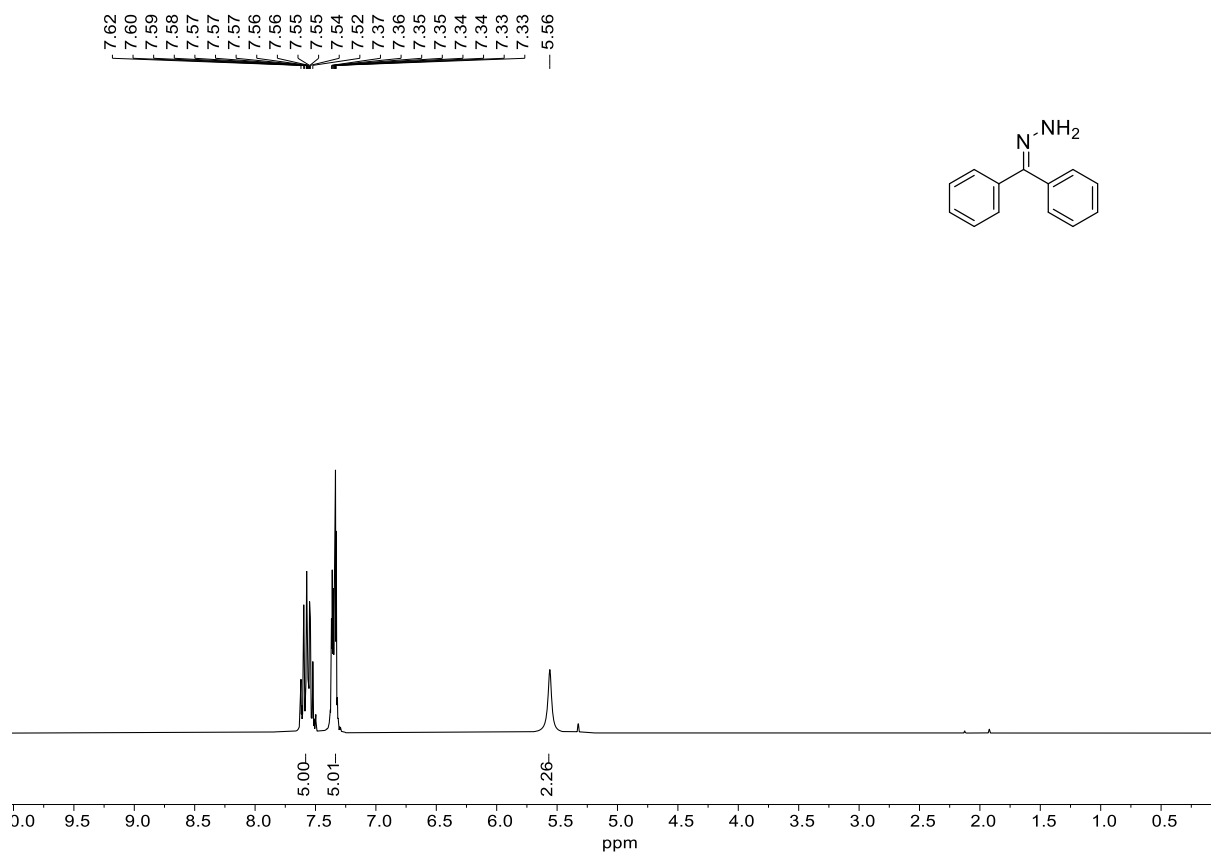


Figure S1 ^1H NMR (300 MHz, CD_2Cl_2 , rt) spectrum of **S1**.

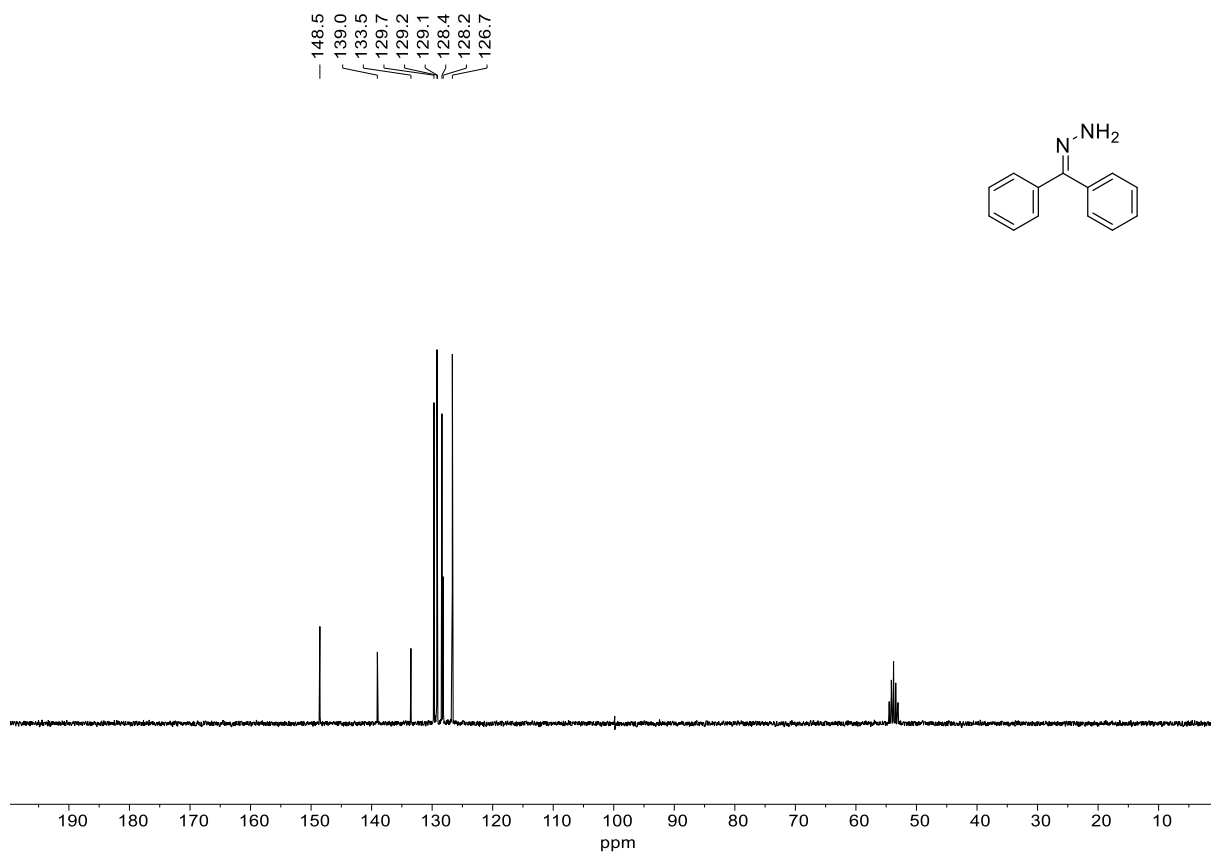


Figure S2 ¹³C NMR (75 MHz, CD₂Cl₂, rt) spectrum of S1.

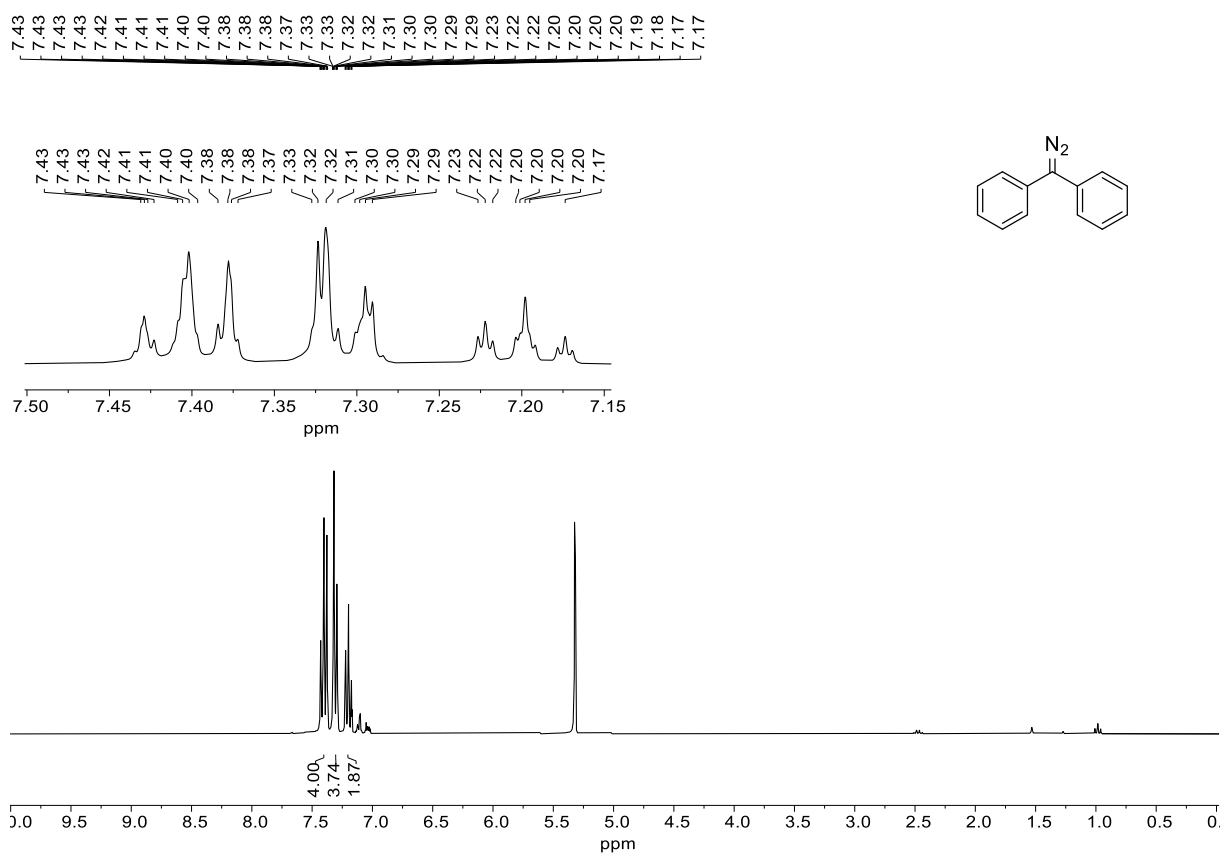


Figure S3 ¹H NMR (300 MHz, CD₂Cl₂, rt) spectrum of S2.

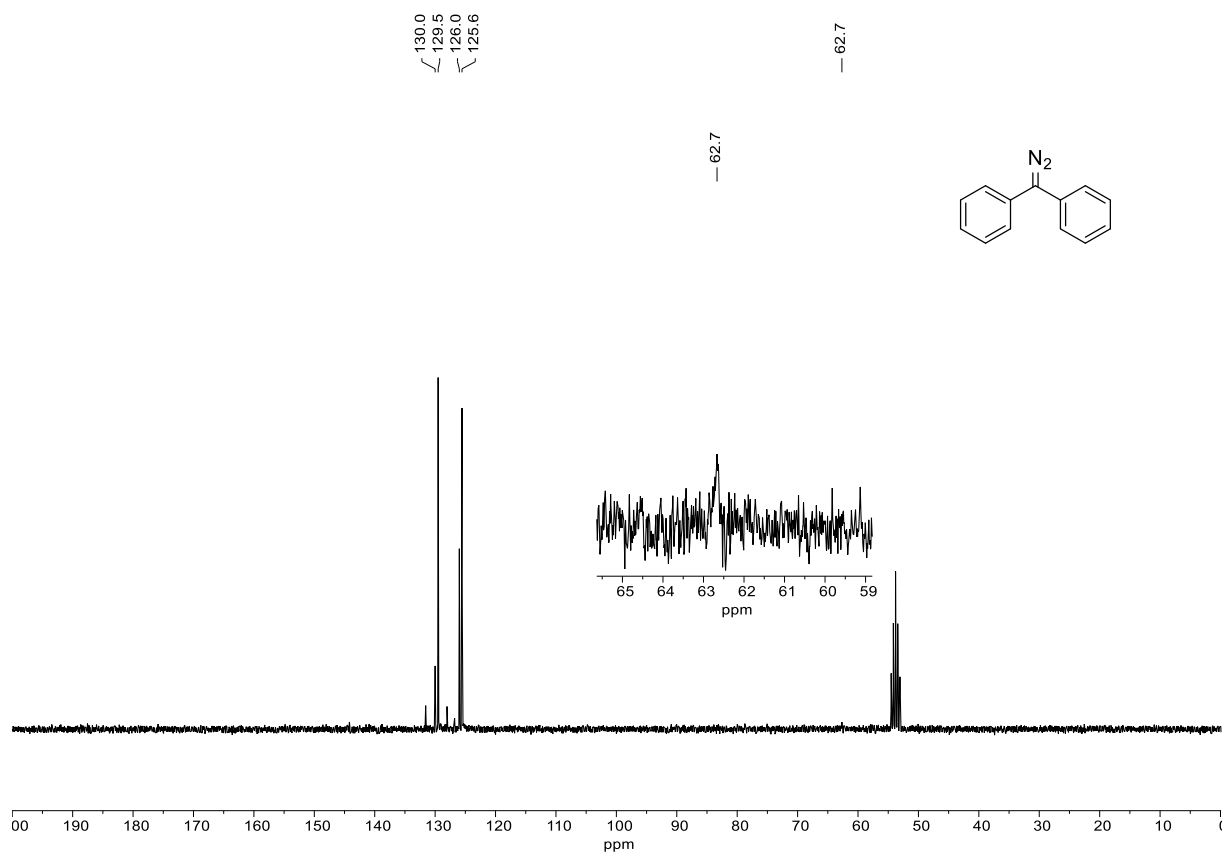


Figure S4 ^{13}C NMR (75 MHz, CD_2Cl_2 , rt) spectrum of S2.

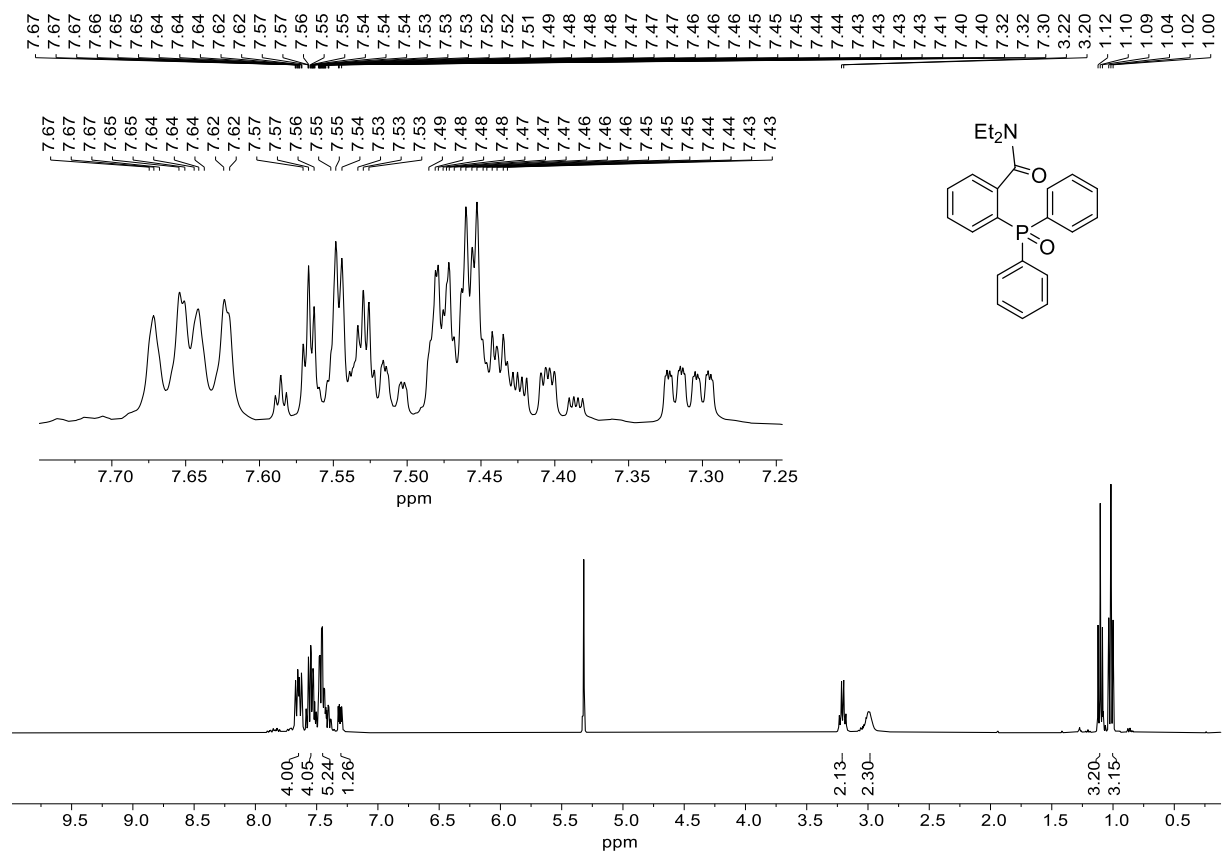


Figure S5 ^1H NMR (400 MHz, CD_2Cl_2 , rt) spectrum of S3.

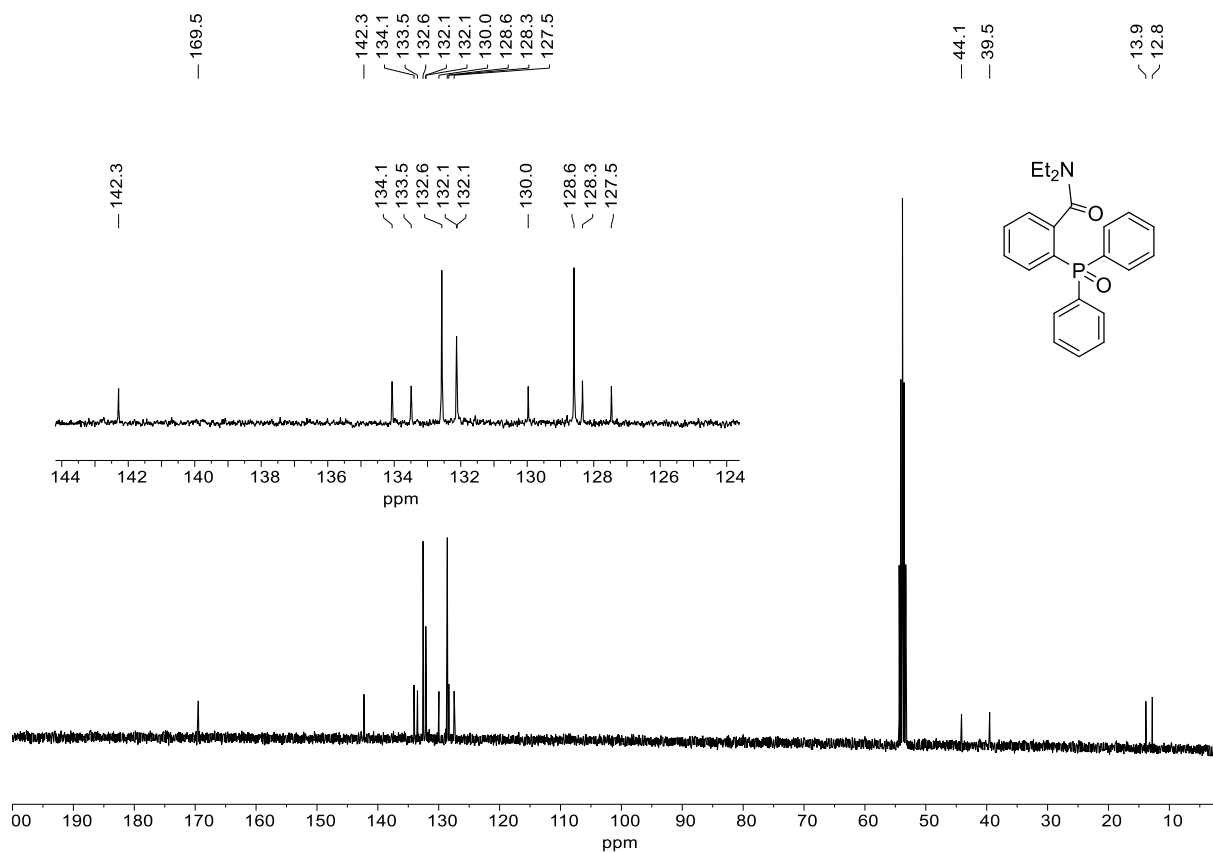


Figure S6 ^{13}C $\{^{31}\text{P}\}$ NMR (101 MHz, CD_2Cl_2 , rt) spectrum of **S3**.

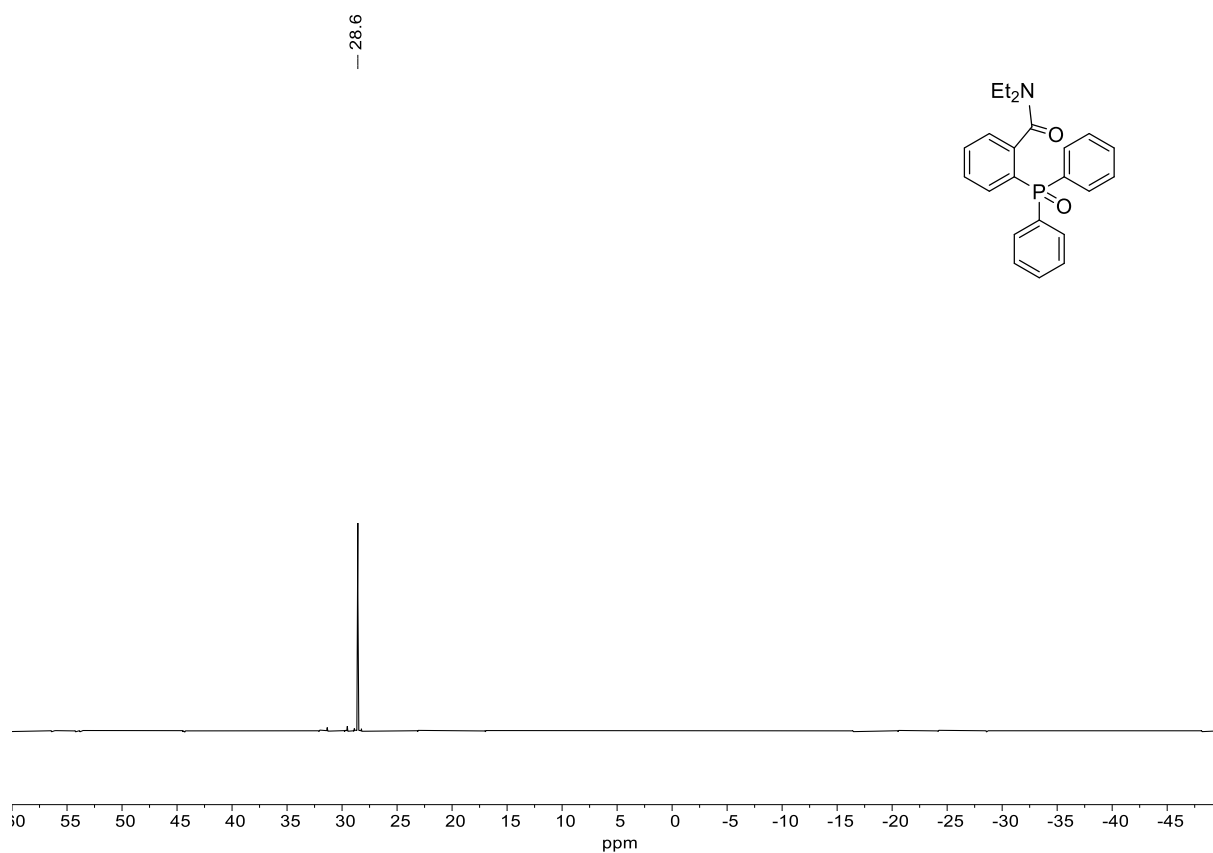


Figure S7 ^{31}P NMR (162 MHz, CD_2Cl_2 , rt) spectrum of **S3**.

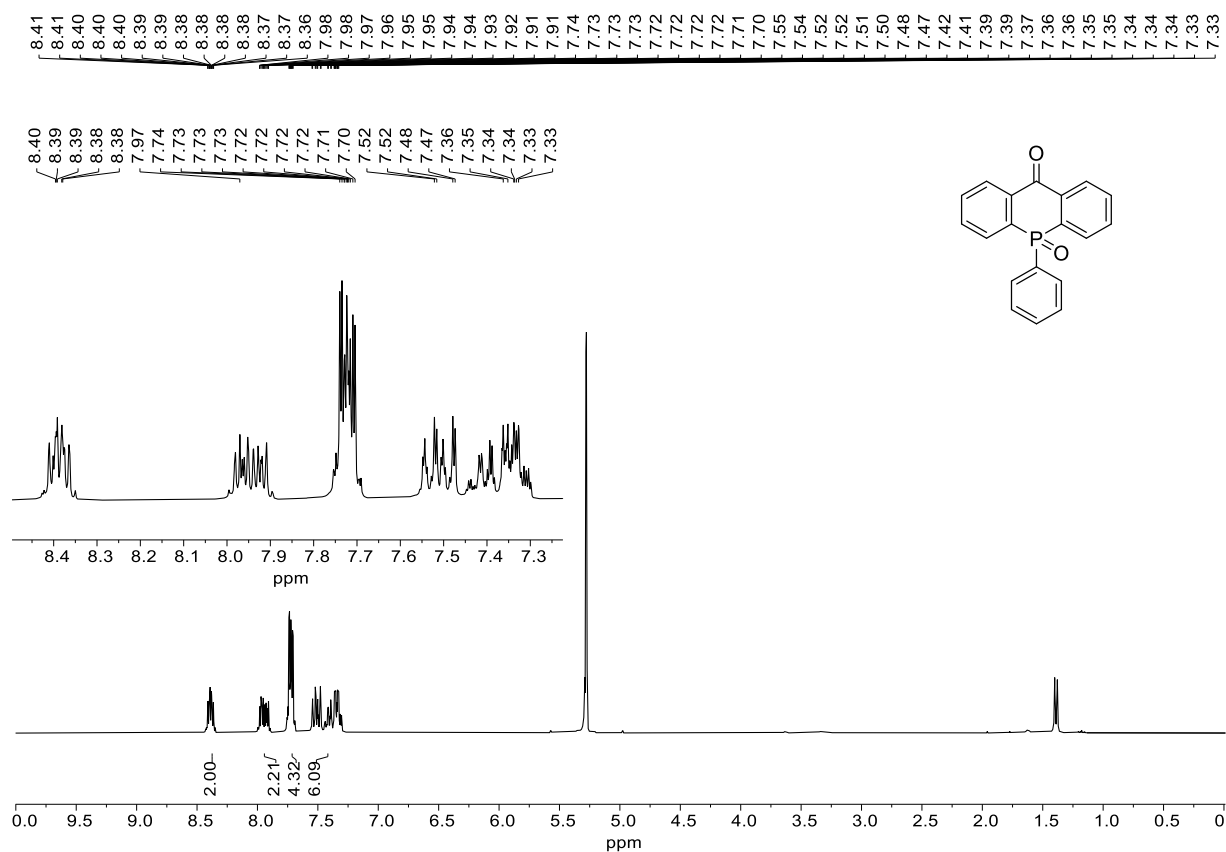


Figure S8 ¹H NMR (300 MHz, CD₂Cl₂, rt) spectrum of 1.

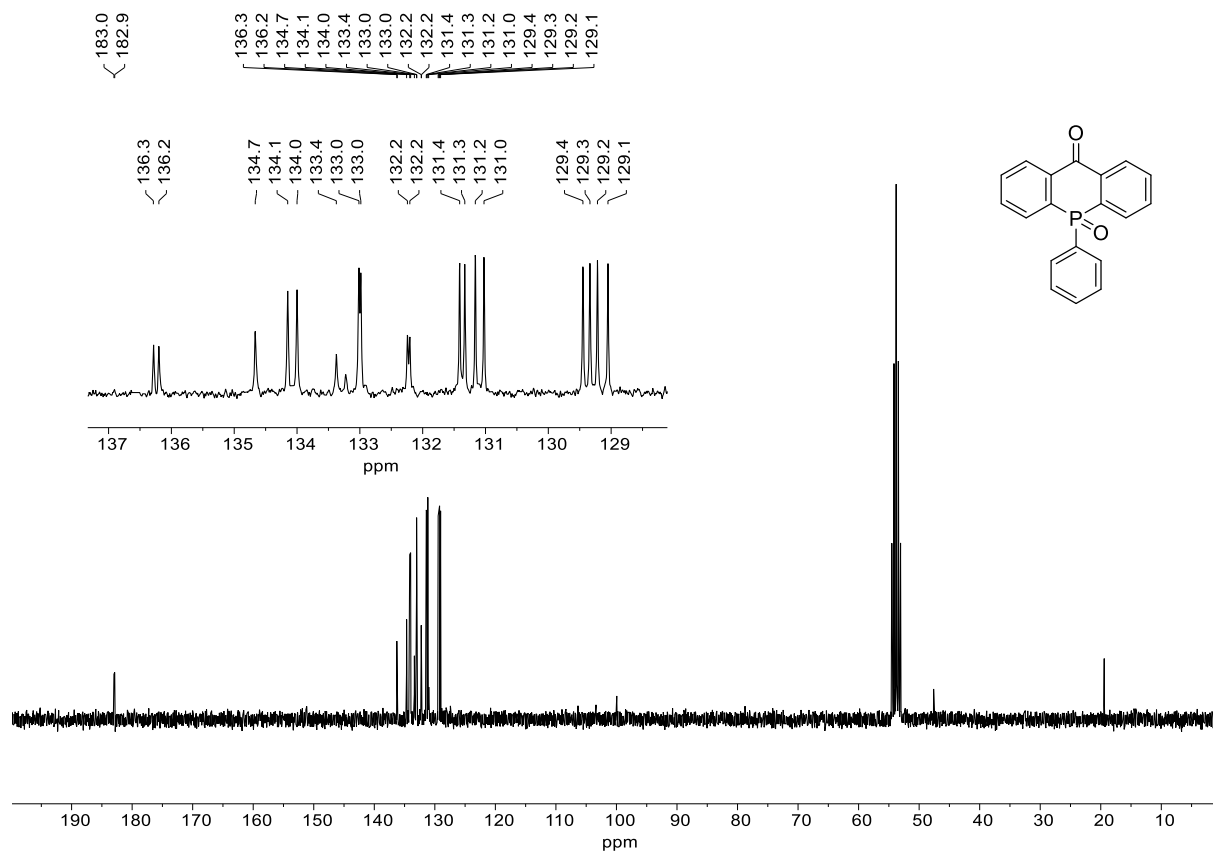


Figure S9 ¹³C NMR (75 MHz, CD₂Cl₂, rt) spectrum of 1.

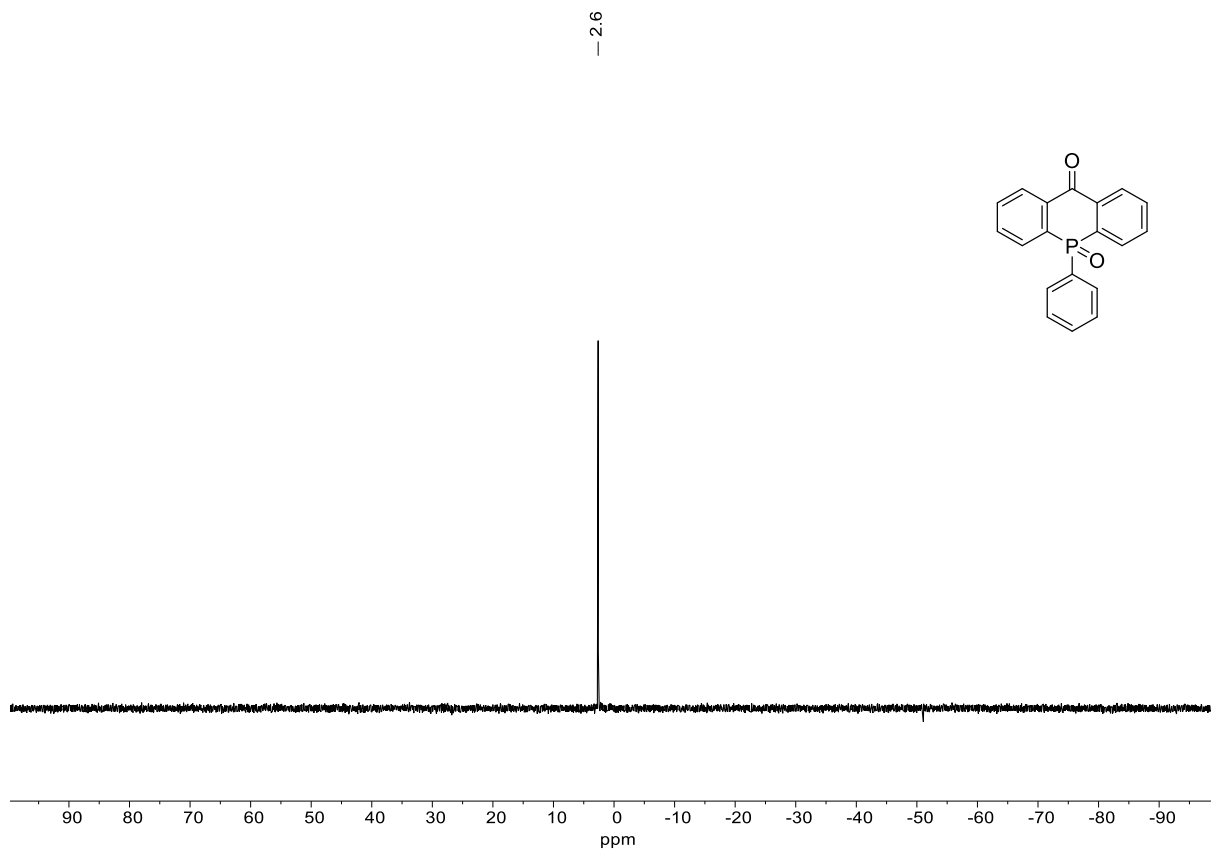


Figure S10 ^{31}P NMR (121 MHz, CD_2Cl_2 , rt) spectrum of 1.

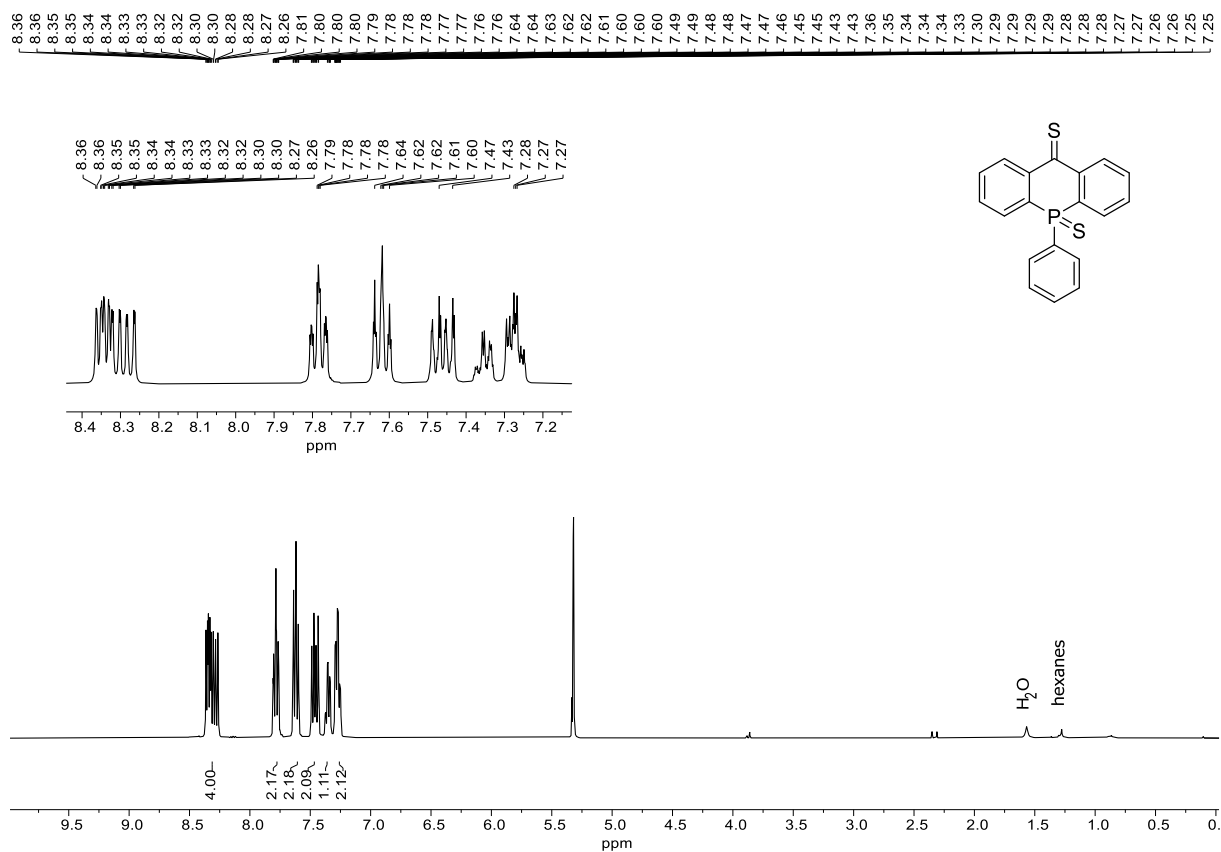


Figure S11 ^1H NMR (400 MHz, CD_2Cl_2 , rt) spectrum of 2.

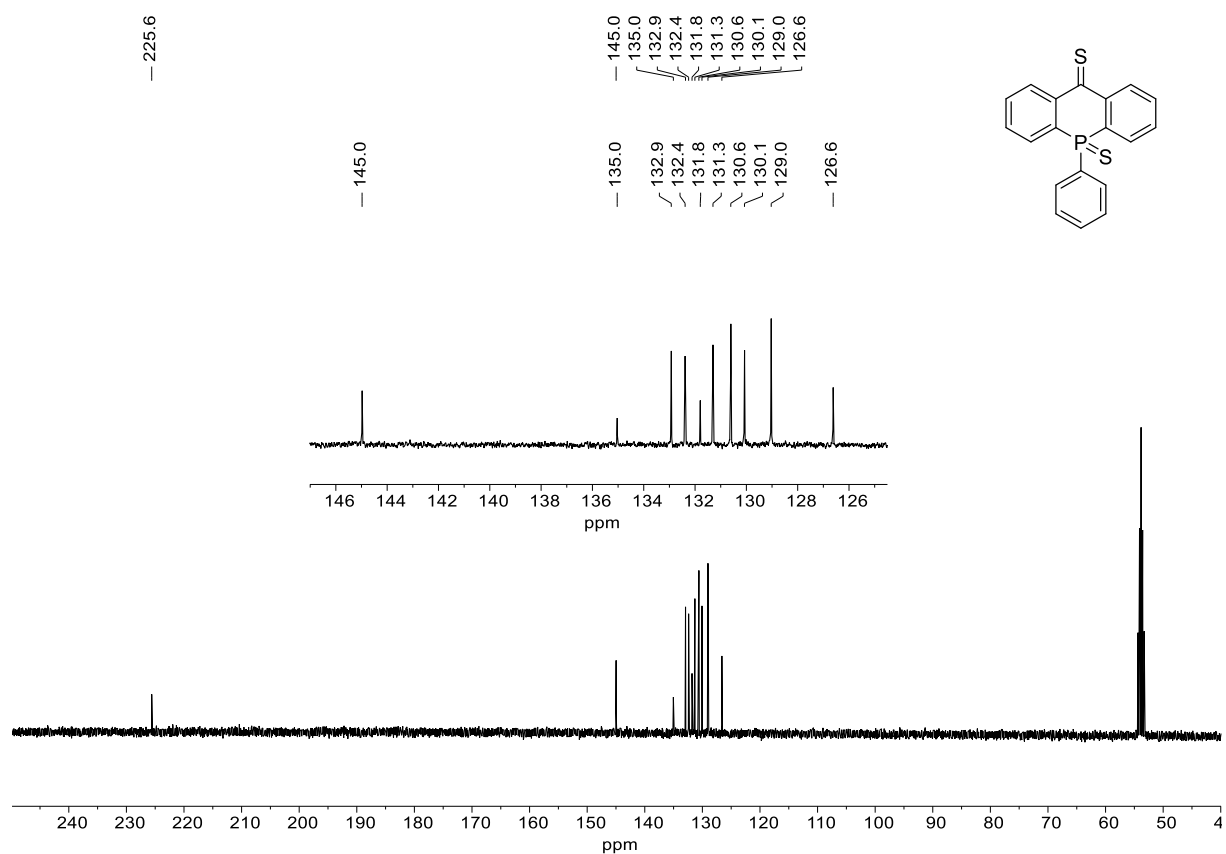


Figure S12 ^{13}C $\{^{31}\text{P}\}$ NMR (101 MHz, CD_2Cl_2 , rt) spectrum of **2**.

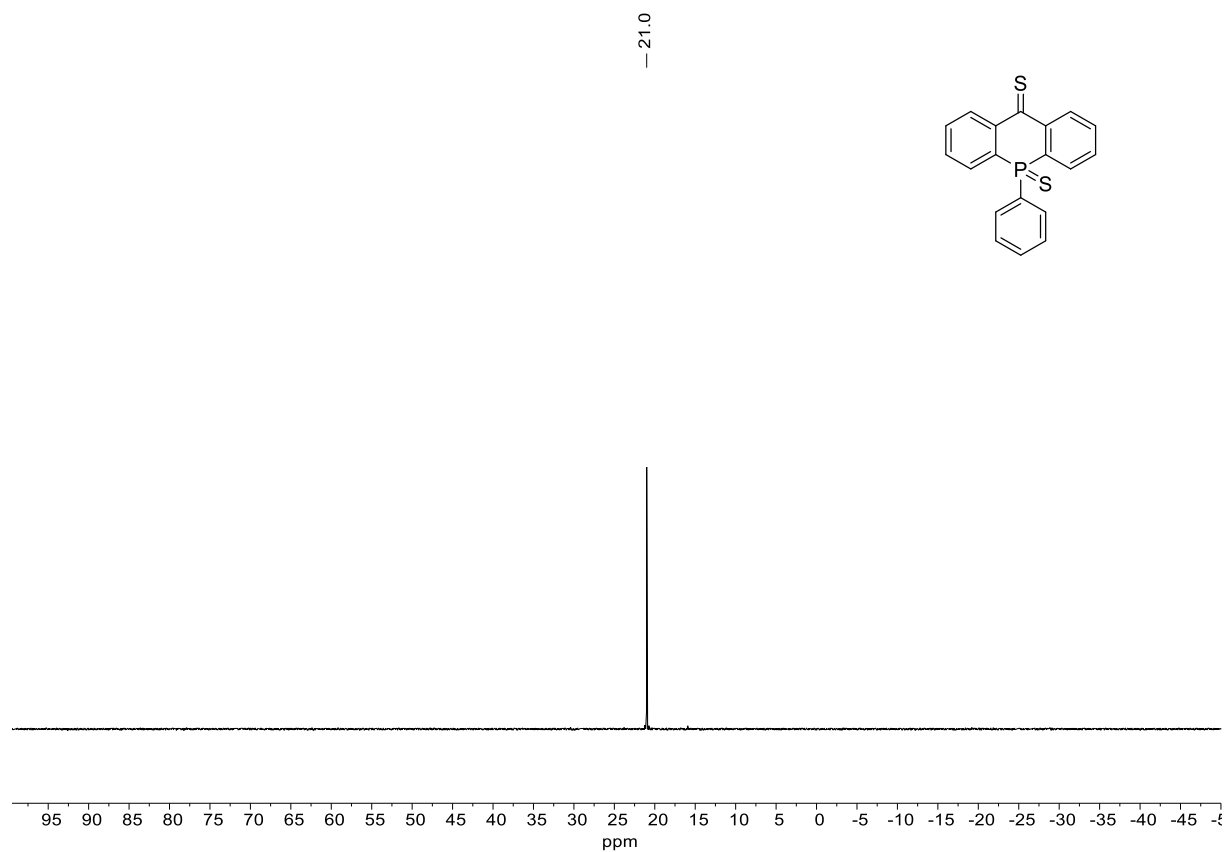


Figure S13 ^{31}P NMR (162 MHz, CD_2Cl_2 , rt) spectrum of **2**.

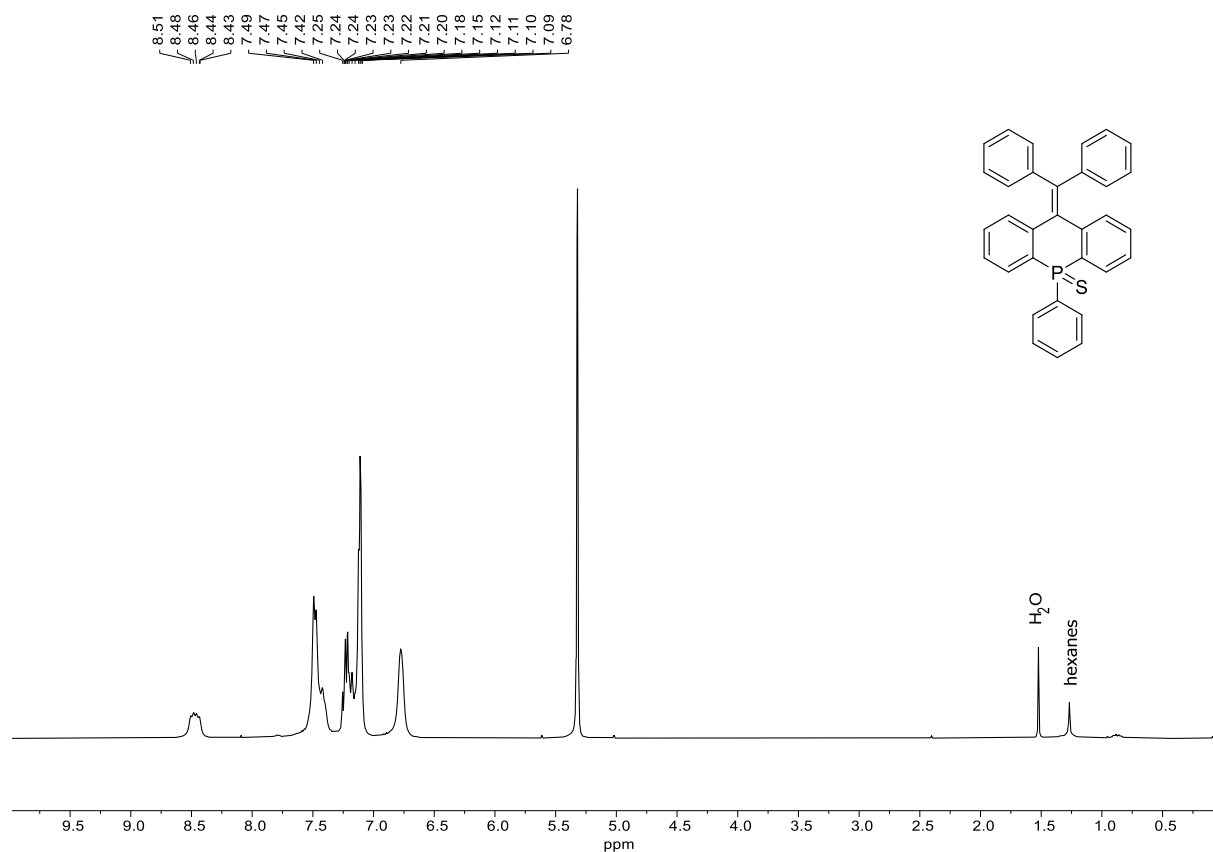


Figure S14 ¹H NMR (300 MHz, CD₂Cl₂, rt) spectrum of 3.

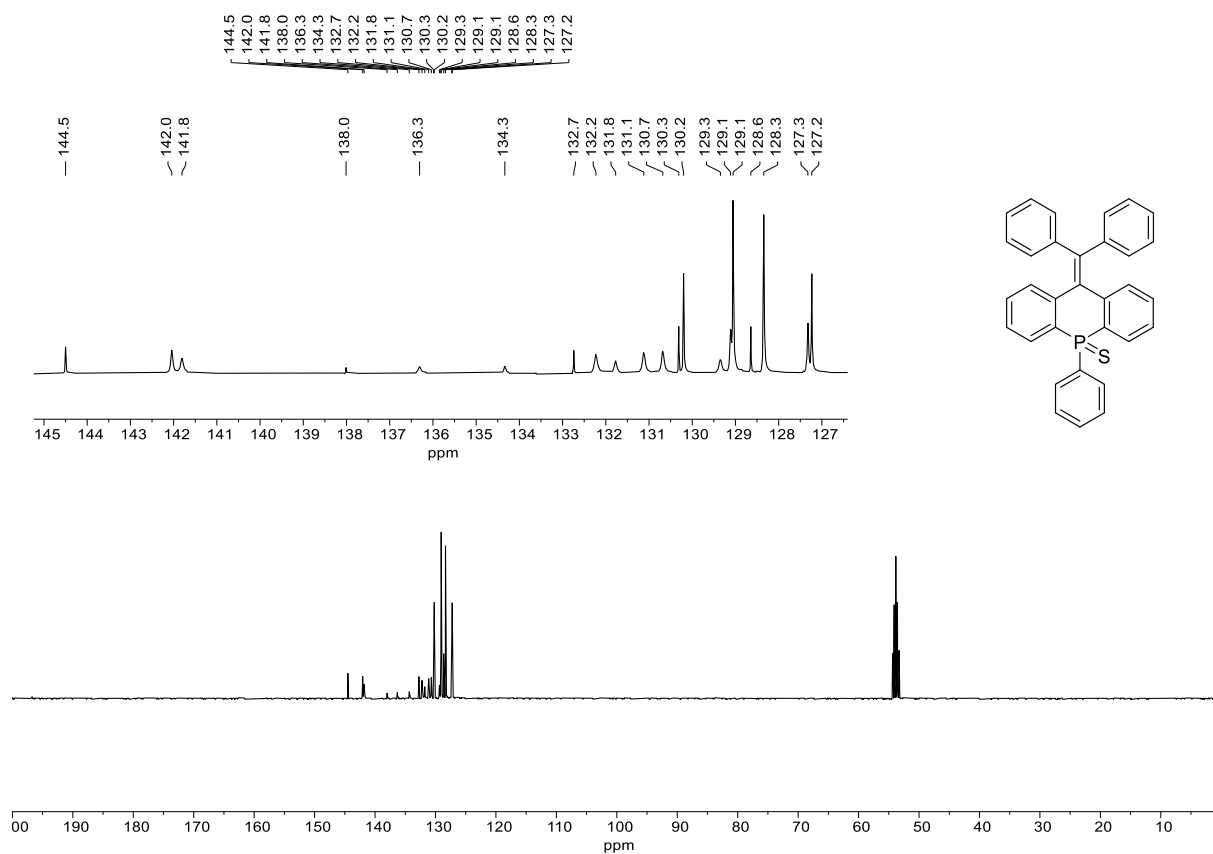


Figure S15 ¹³C {³¹P} NMR (101 MHz, CD₂Cl₂, rt) spectrum of 3.

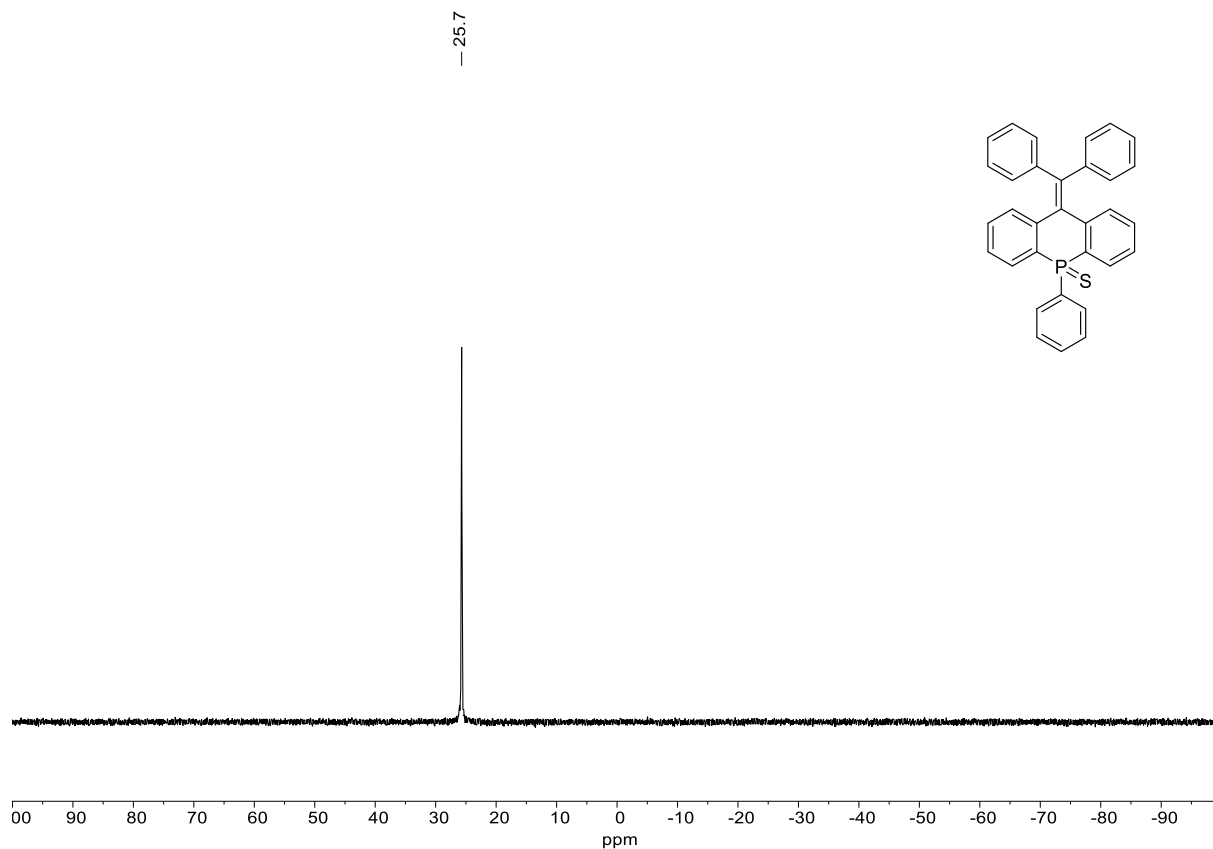


Figure S16 ^{31}P NMR (121 MHz, CD_2Cl_2 , rt) spectrum of **3**.

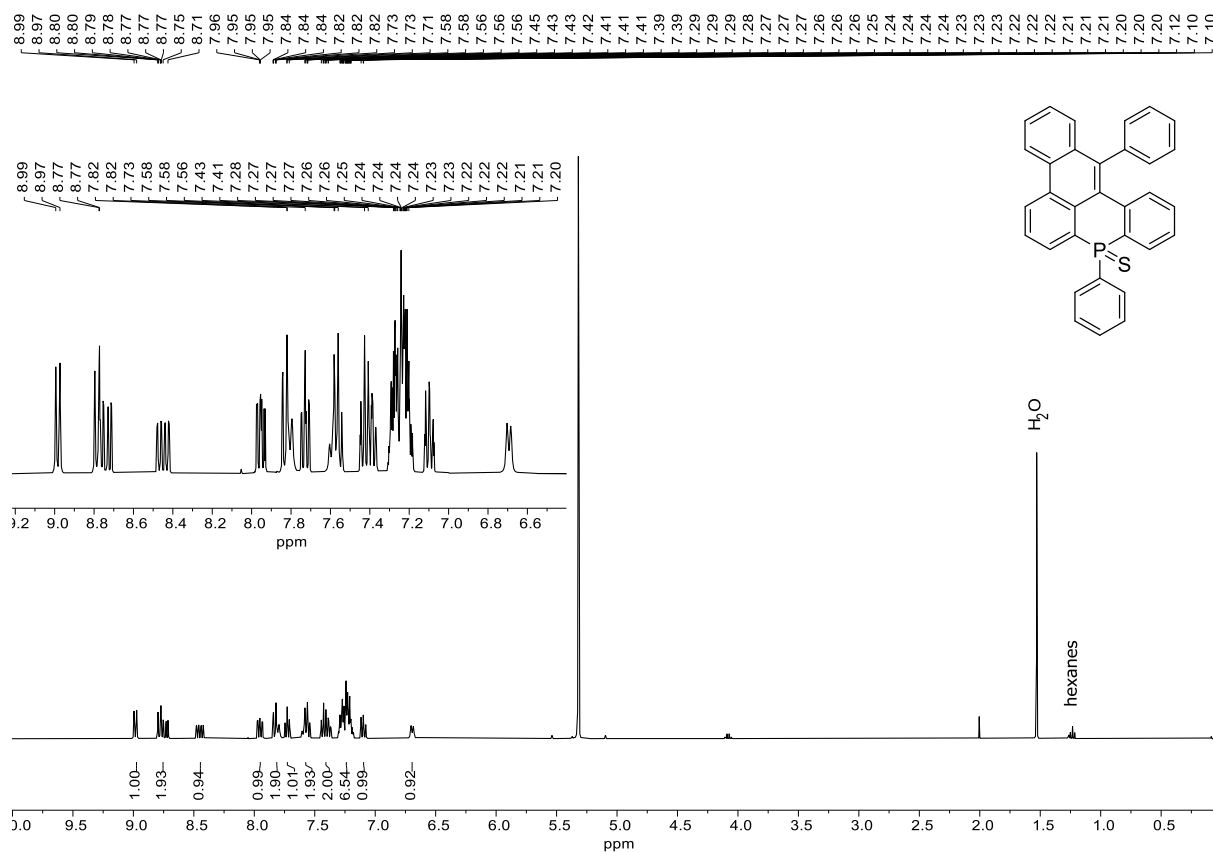


Figure S17 ^1H NMR (400 MHz, CD_2Cl_2 , rt) spectrum of **4**.

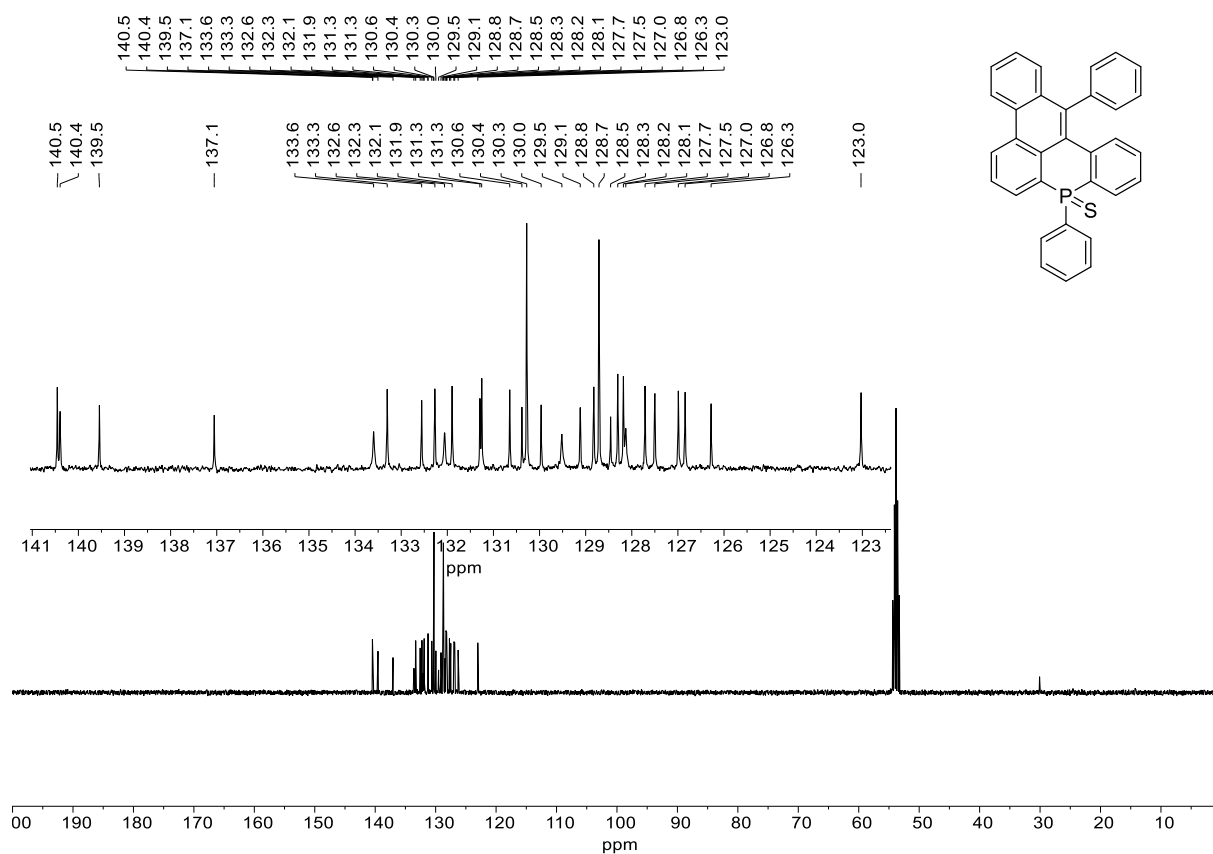


Figure S18 ^{13}C { $^{31}\text{P}}$ NMR (101 MHz, CD_2Cl_2 , rt) spectrum of 4.

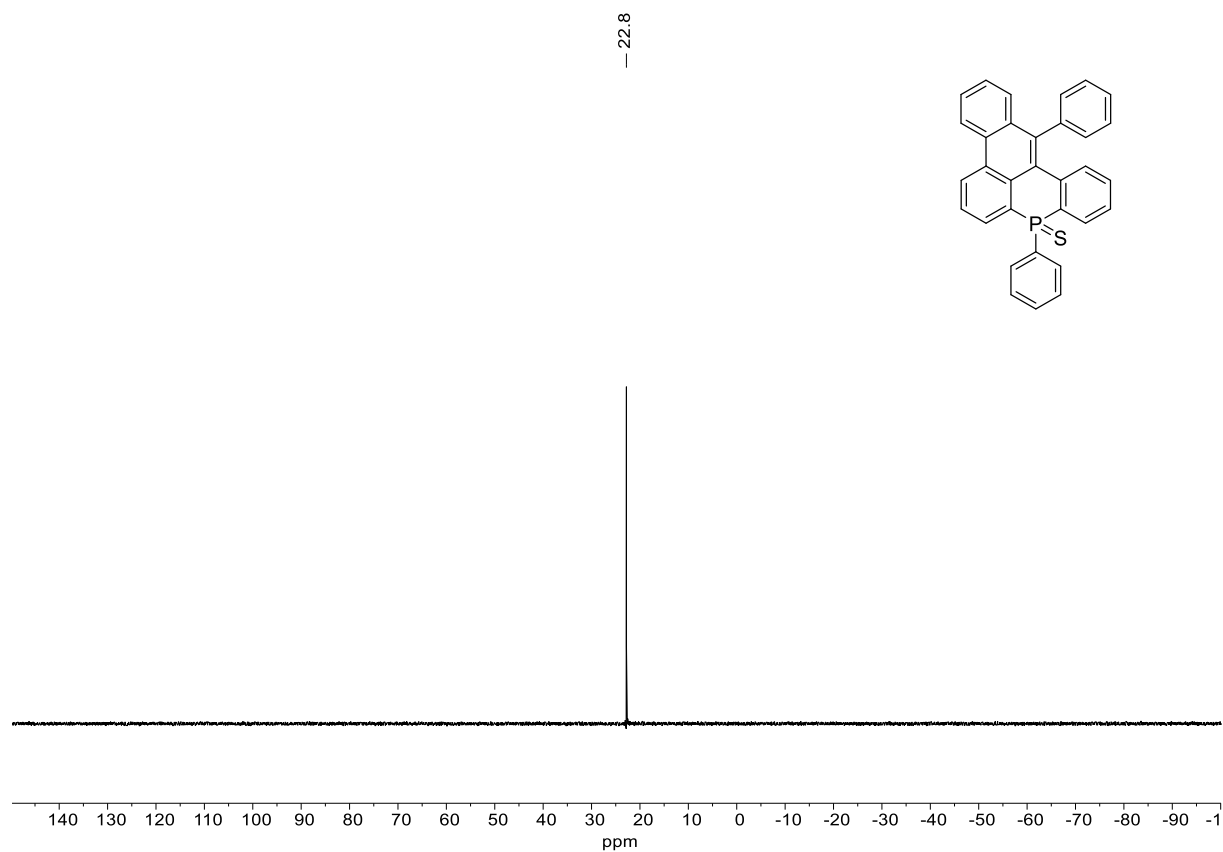


Figure S19 ^{31}P NMR (162 MHz, CD_2Cl_2 , rt) spectrum of 4.

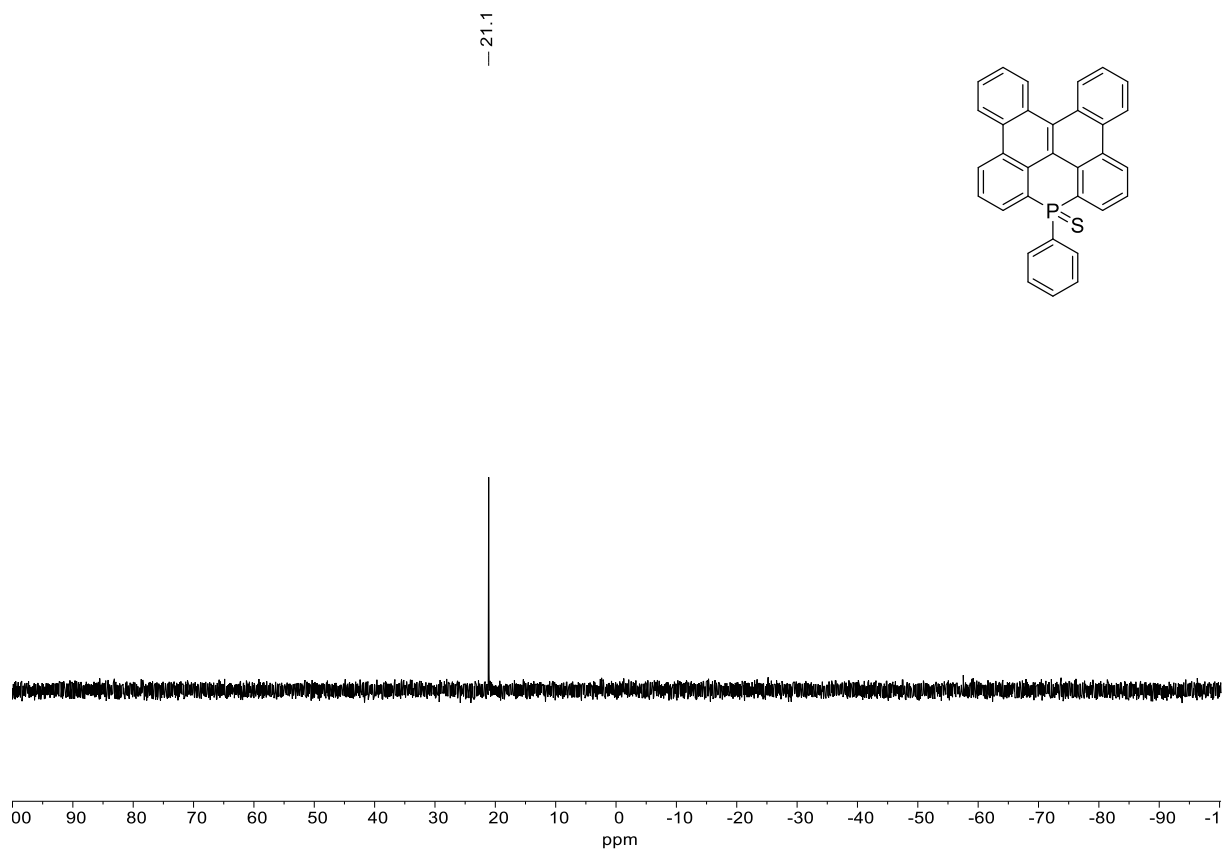


Figure S22 ^{31}P NMR (121 MHz, CD_2Cl_2 , rt) spectrum of **5**.

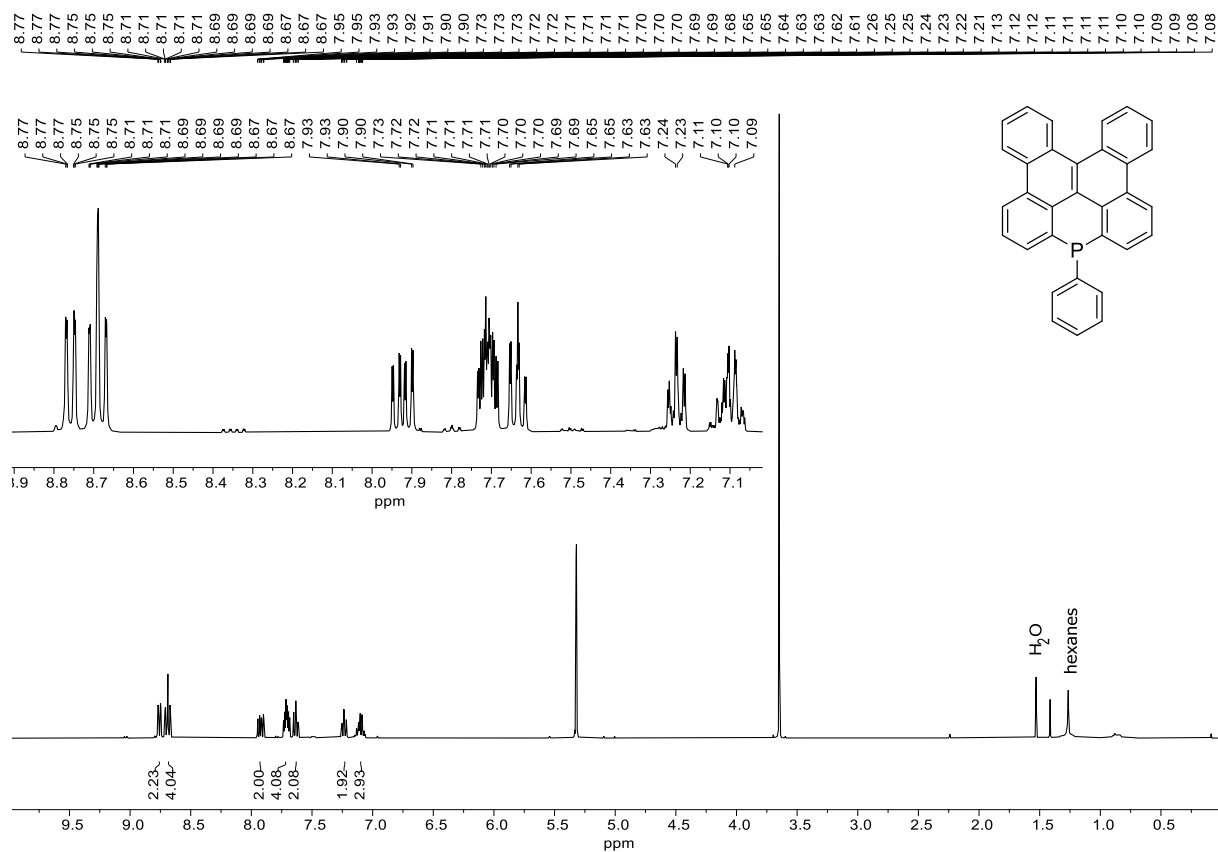


Figure S23 ^1H NMR (400 MHz, CD_2Cl_2 , rt) spectrum of **6**.

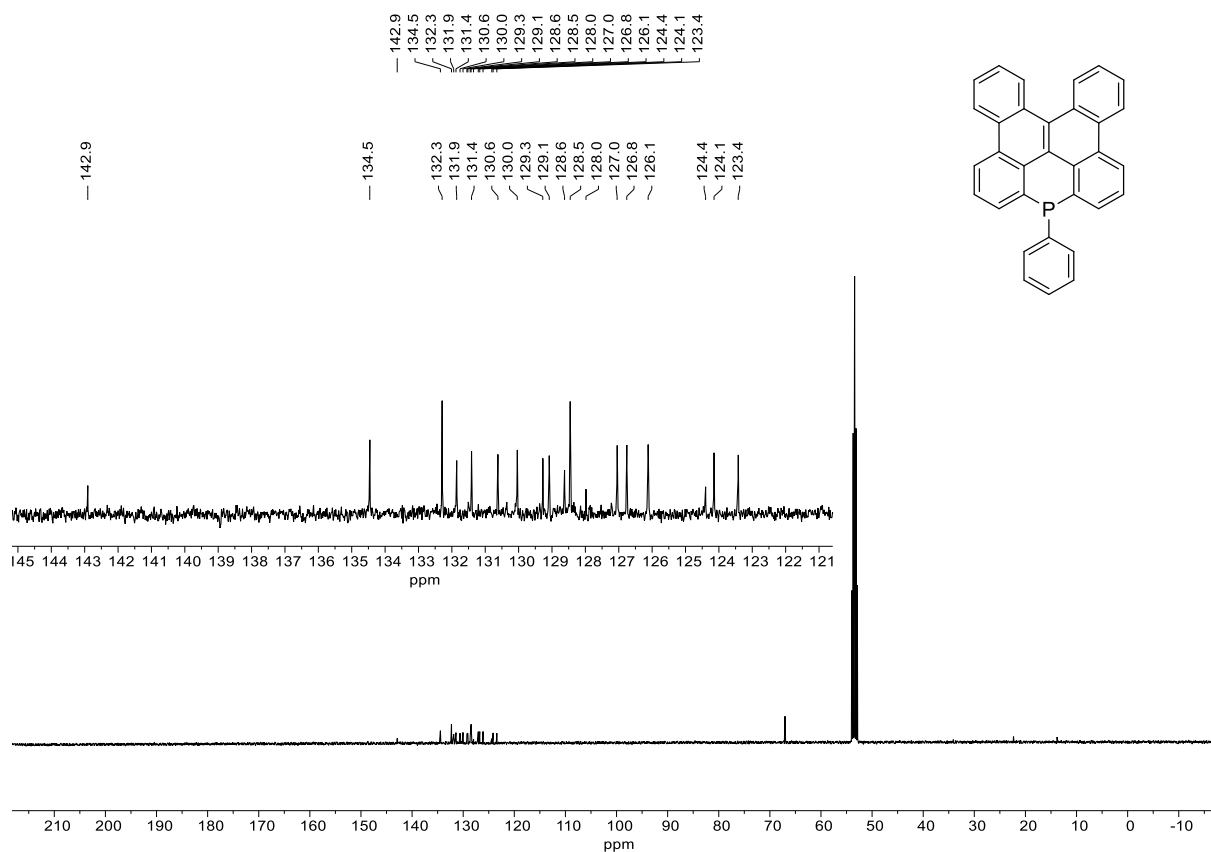


Figure S24 ^{13}C { $^{31}\text{P}}$ NMR (101 MHz, CD_2Cl_2 , rt) spectrum of 6.

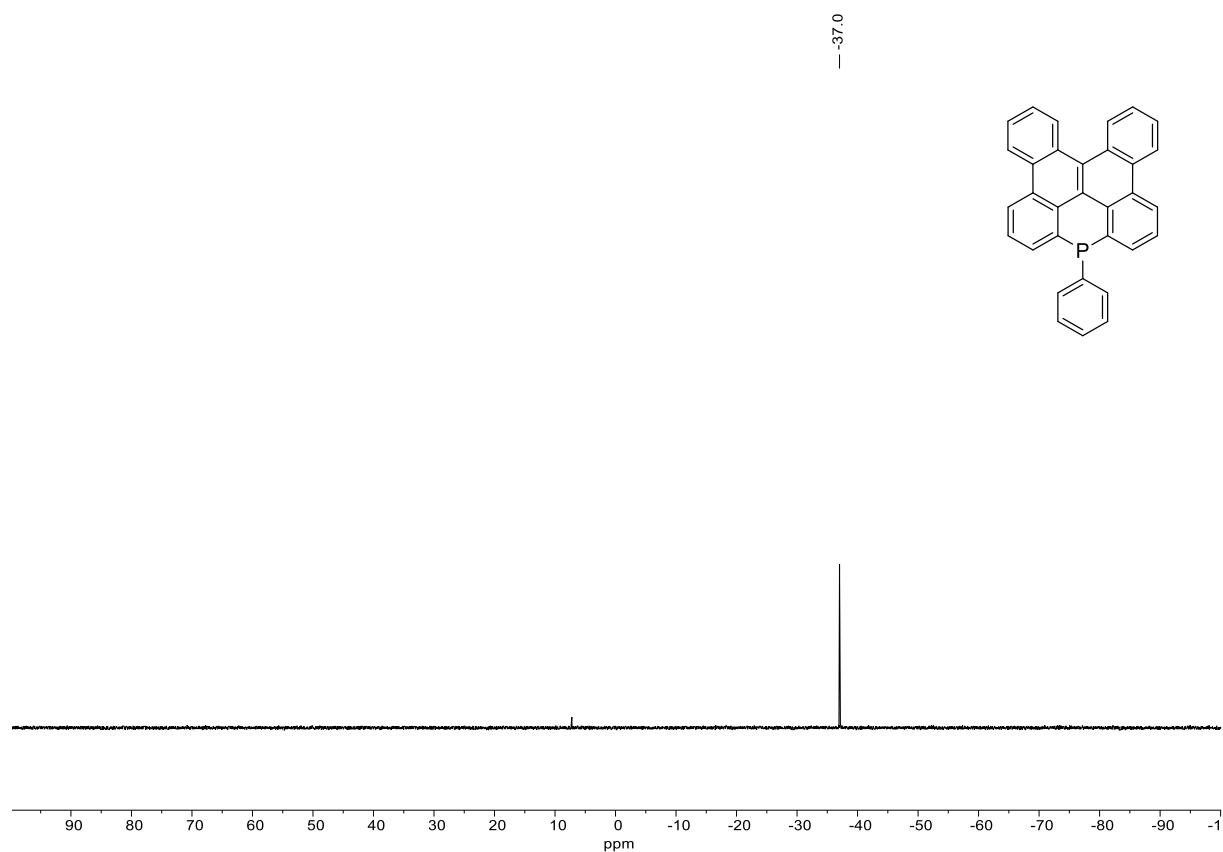


Figure S25 ^{31}P NMR (162 MHz, CD_2Cl_2 , rt) spectrum of 6.

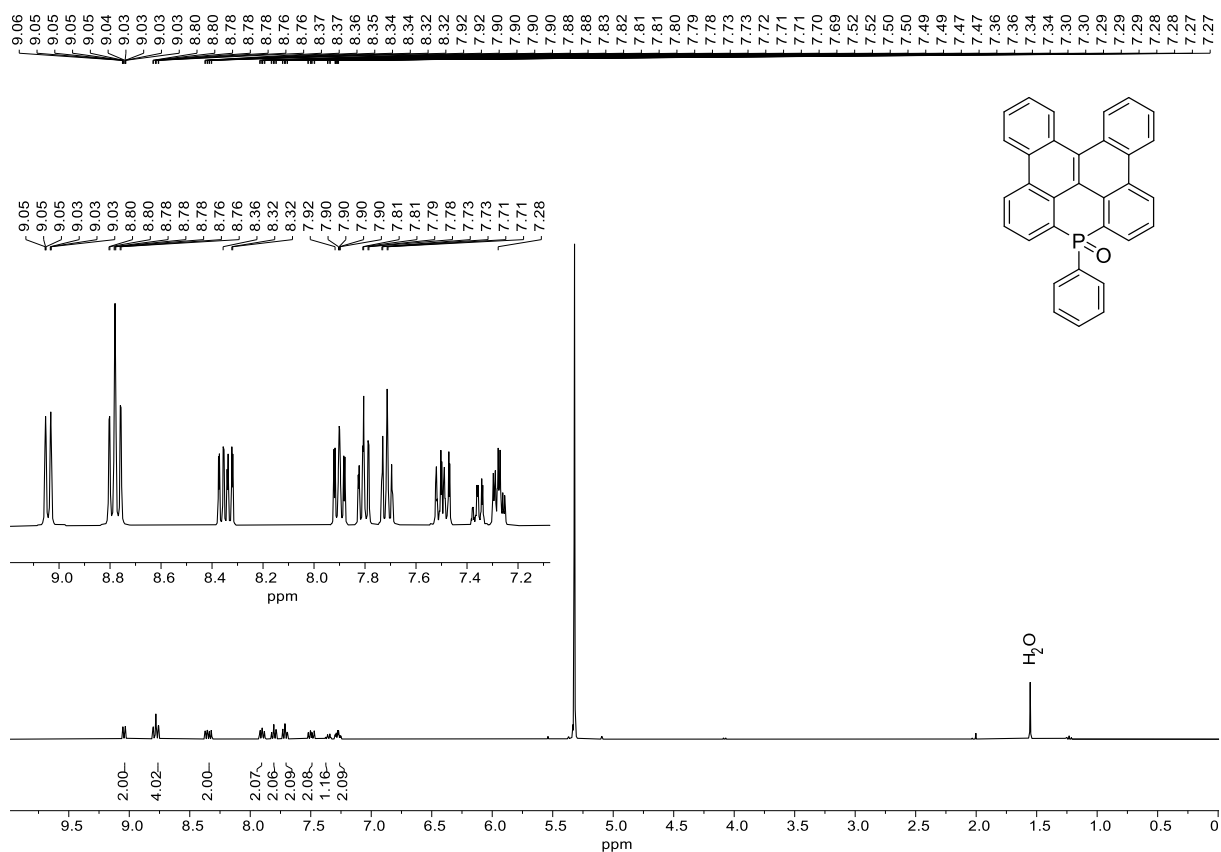


Figure S26 ¹H NMR (400 MHz, CD₂Cl₂, rt) spectrum of 7.

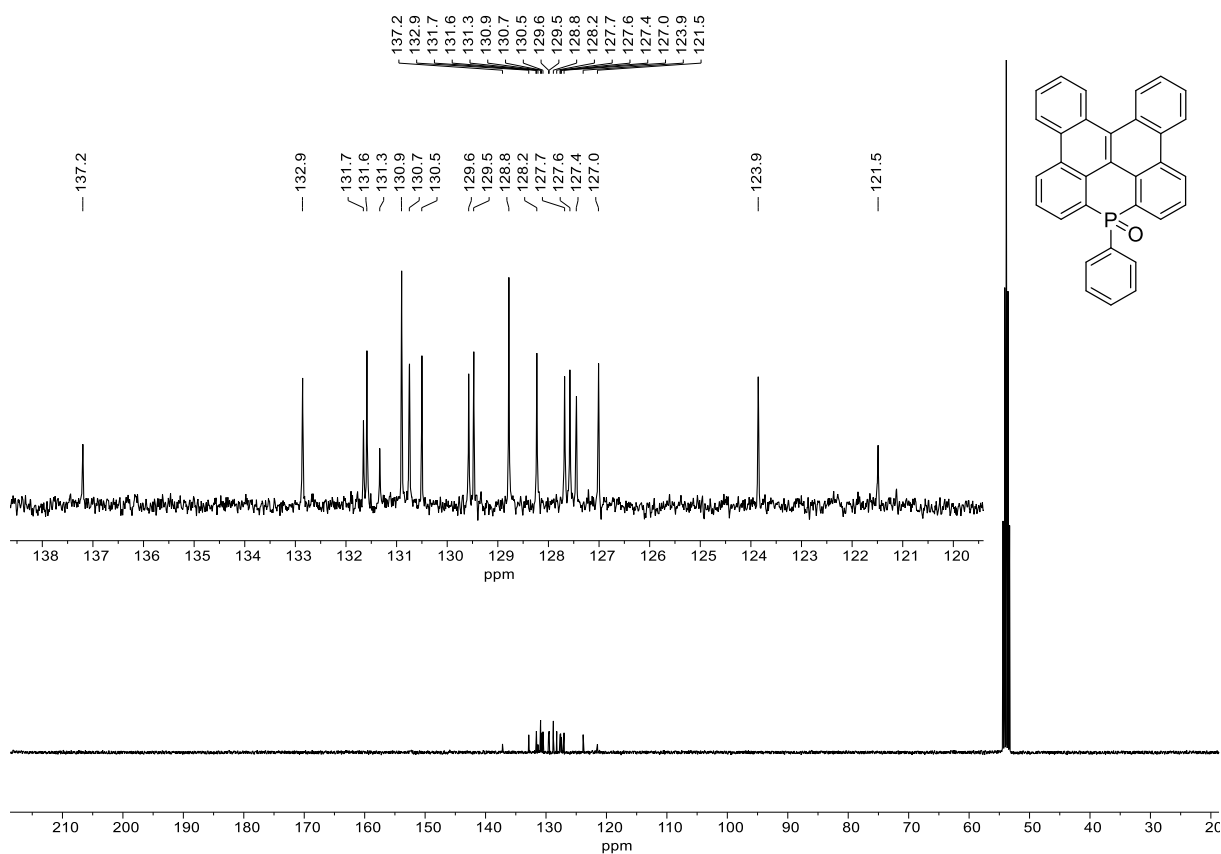


Figure S27 ¹³C {³¹P} NMR (101 MHz, CD₂Cl₂, rt) spectrum of 7.

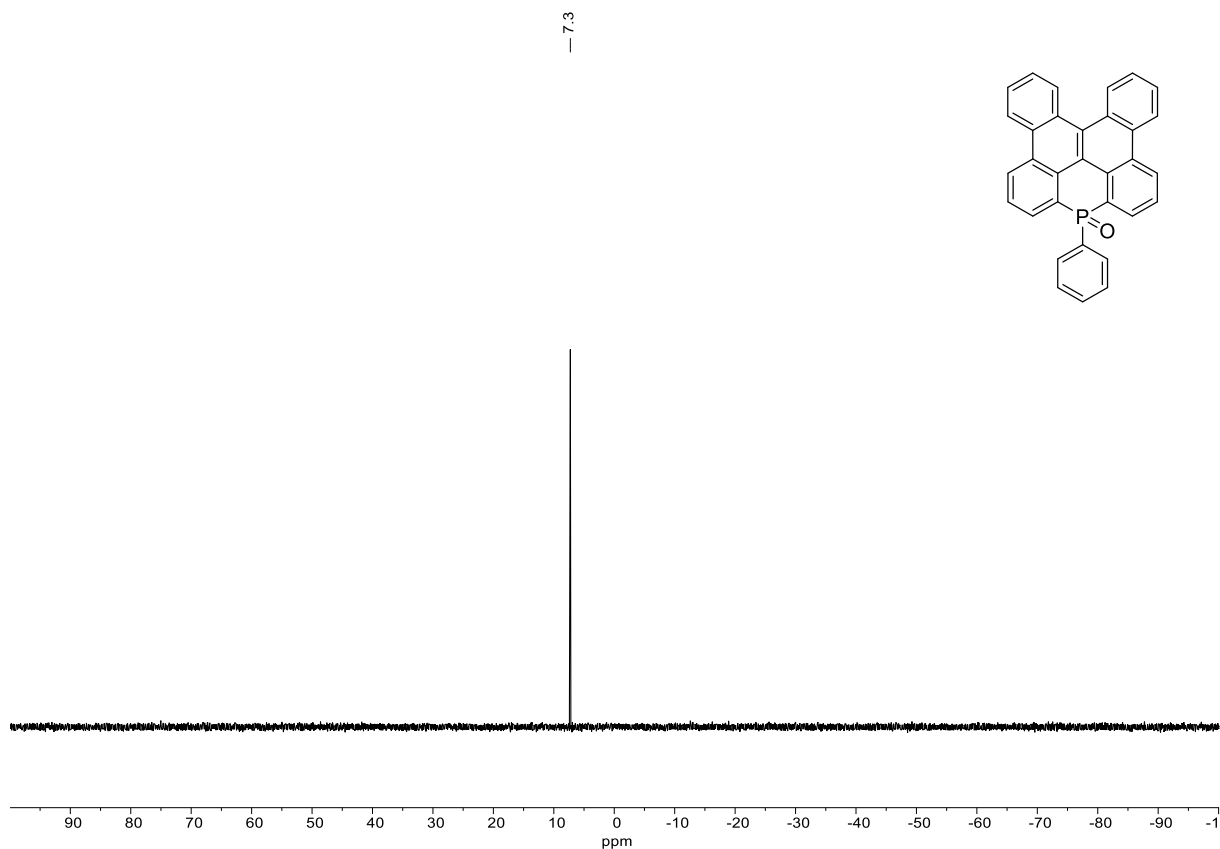


Figure S28 ^{31}P NMR (162 MHz, CD_2Cl_2 , rt) spectrum of 7.

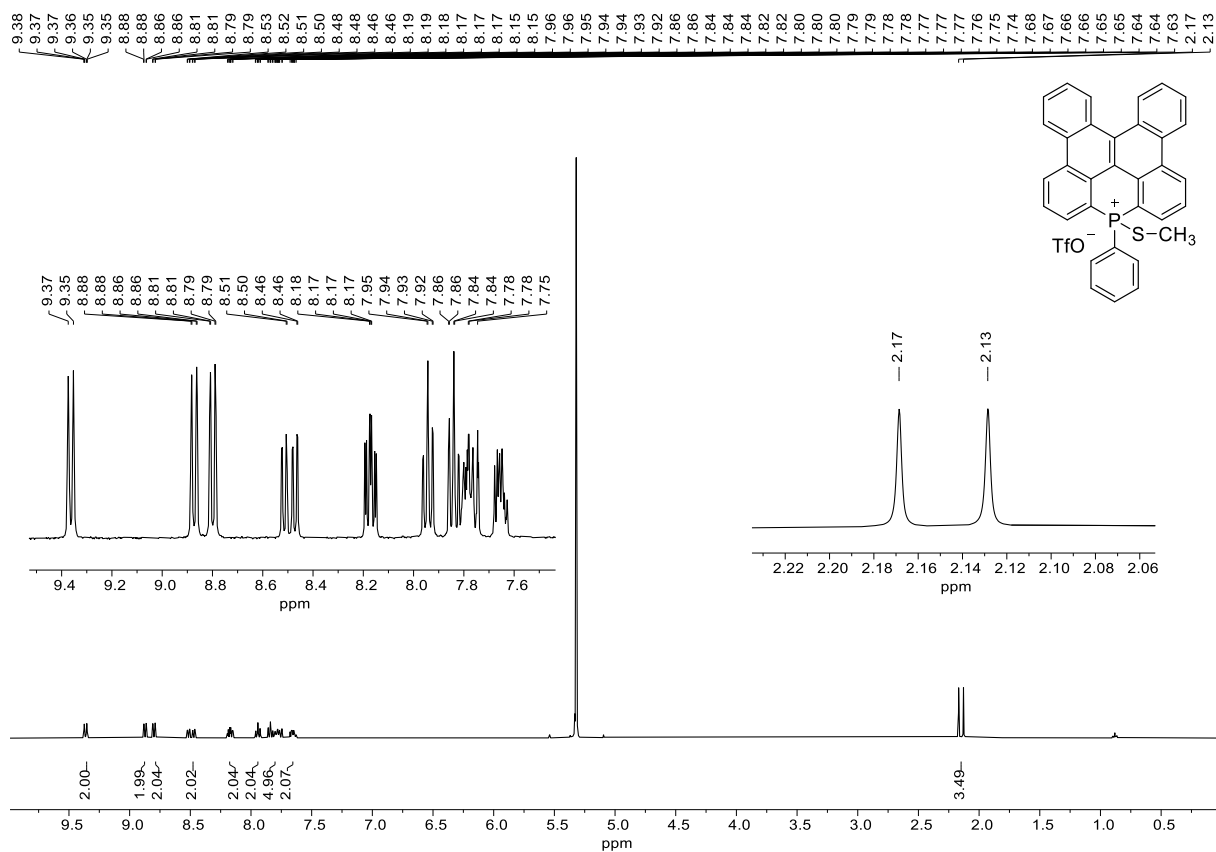


Figure S29 ^1H NMR (400 MHz, CD_2Cl_2 , rt) spectrum of 8.

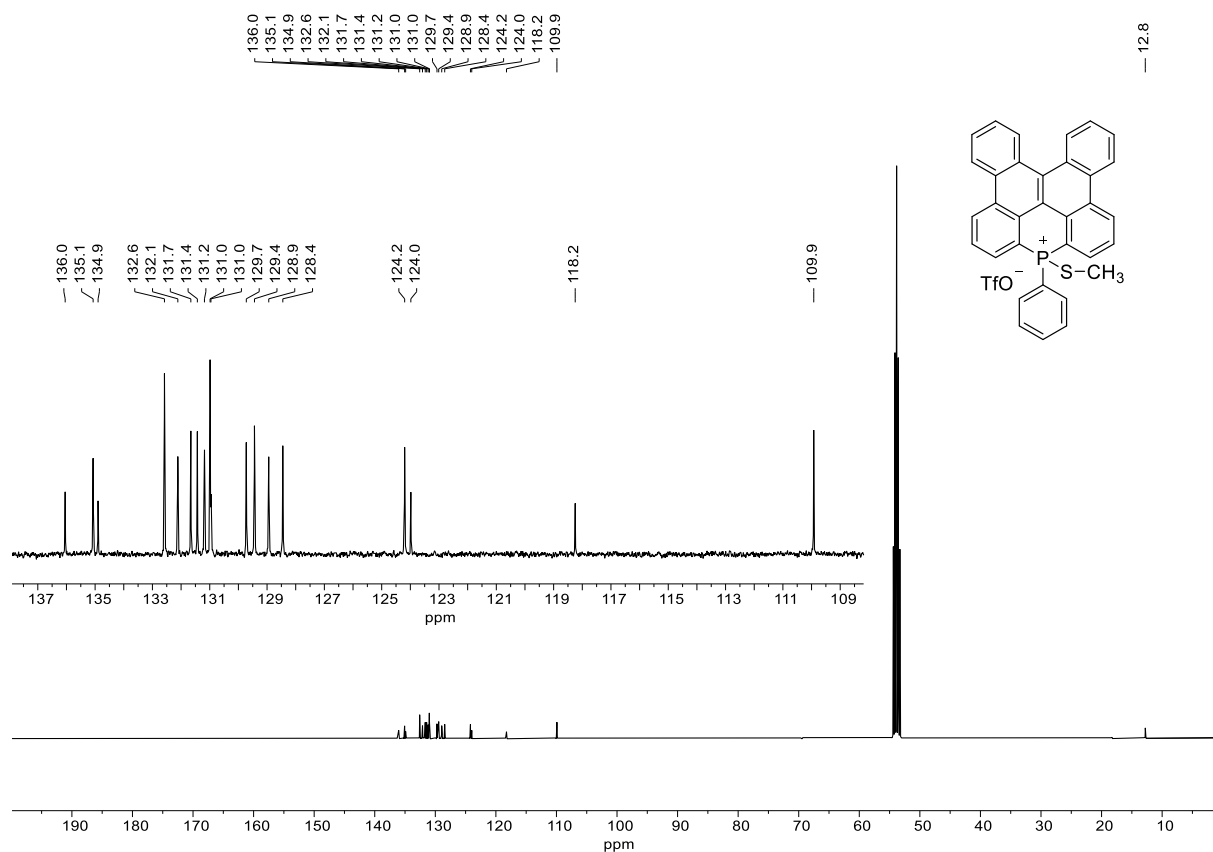


Figure S30 ^{13}C $\{^{31}\text{P}\}$ NMR (101 MHz, CD_2Cl_2 , rt) spectrum of **8**.

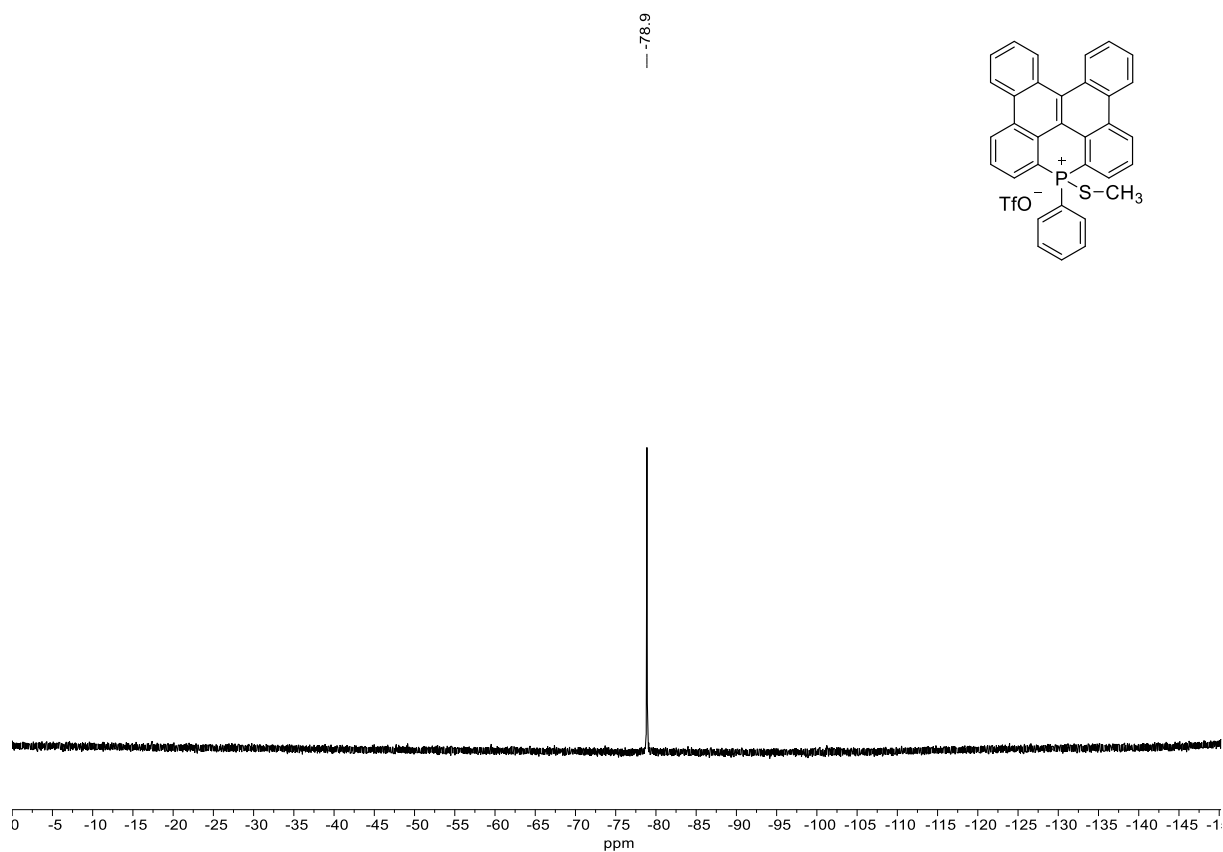


Figure S31 ^{19}F NMR (377 MHz, CD_2Cl_2 , rt) spectrum of **8**.

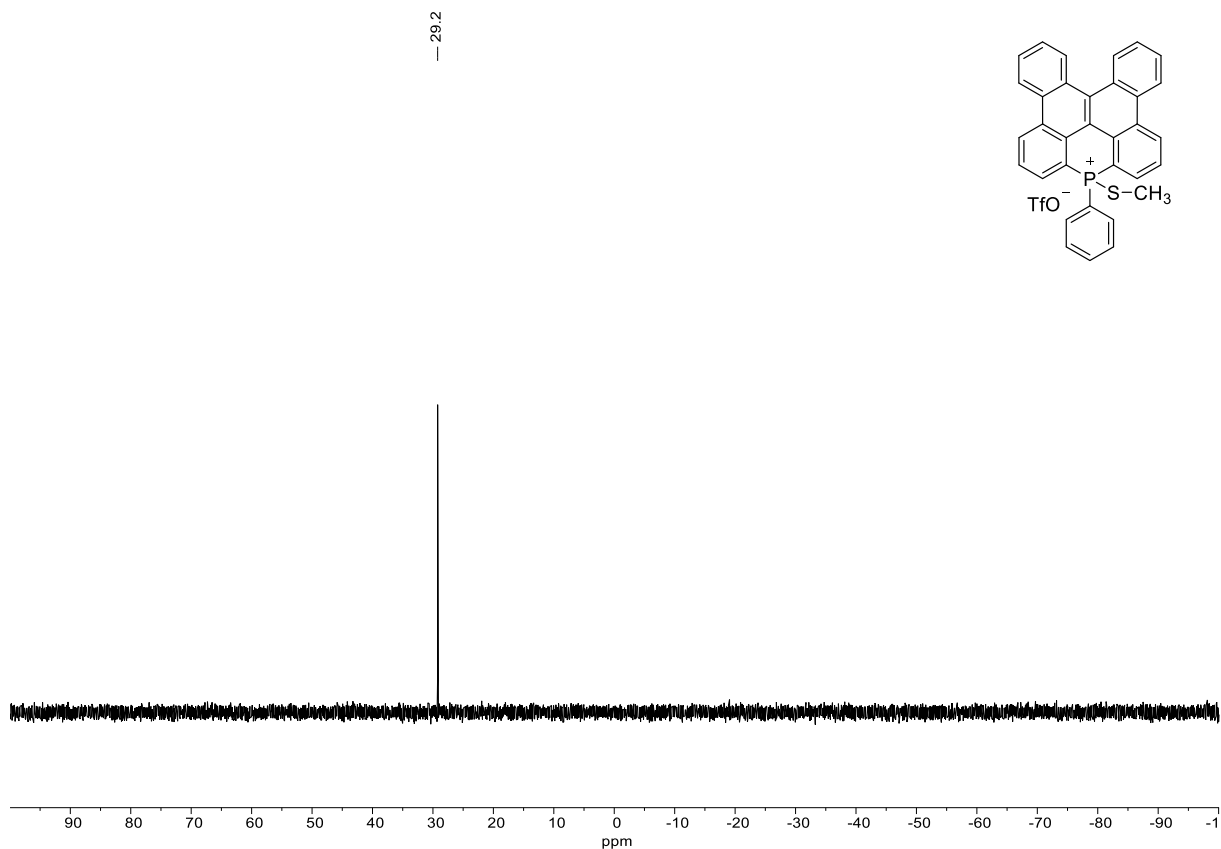


Figure S32 ^{31}P NMR (162 MHz, CD_2Cl_2 , rt) spectrum of **8**.

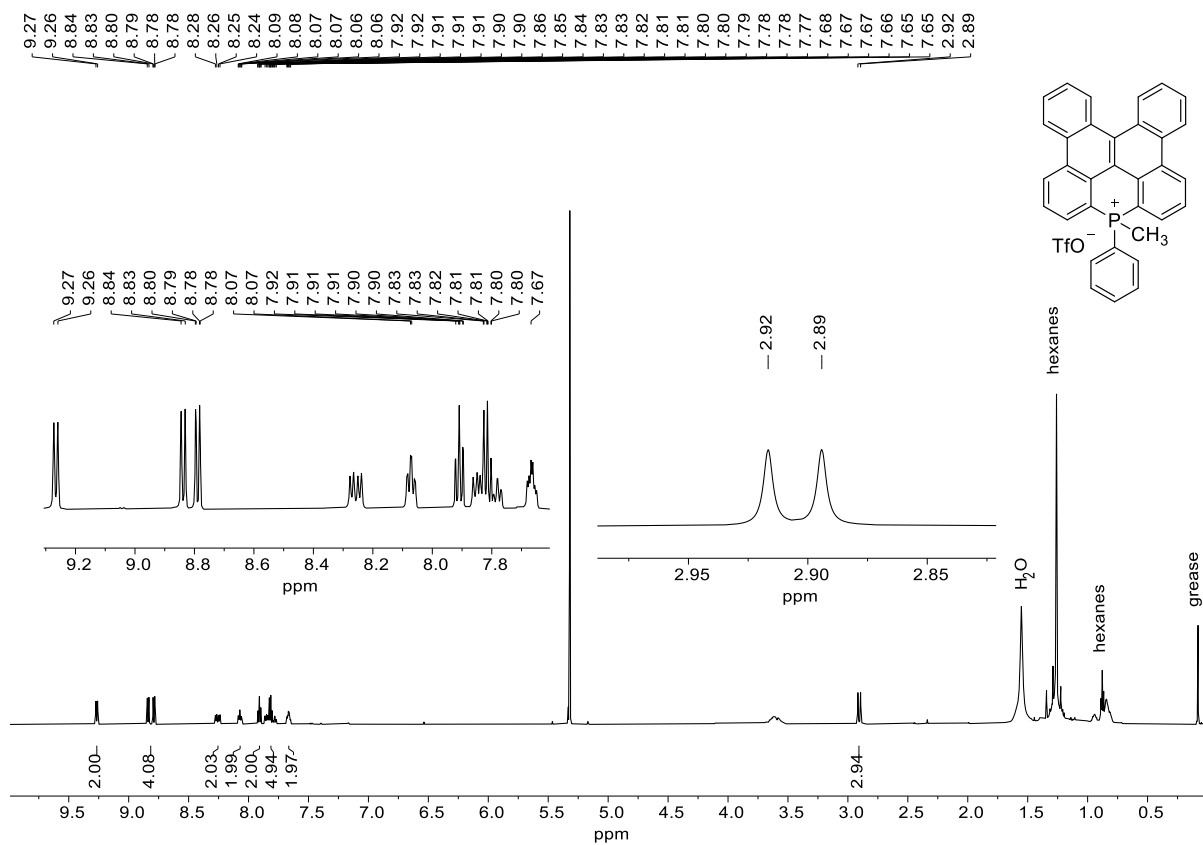


Figure S33 ^1H NMR (600 MHz, CD_2Cl_2 , rt) spectrum of **9**.

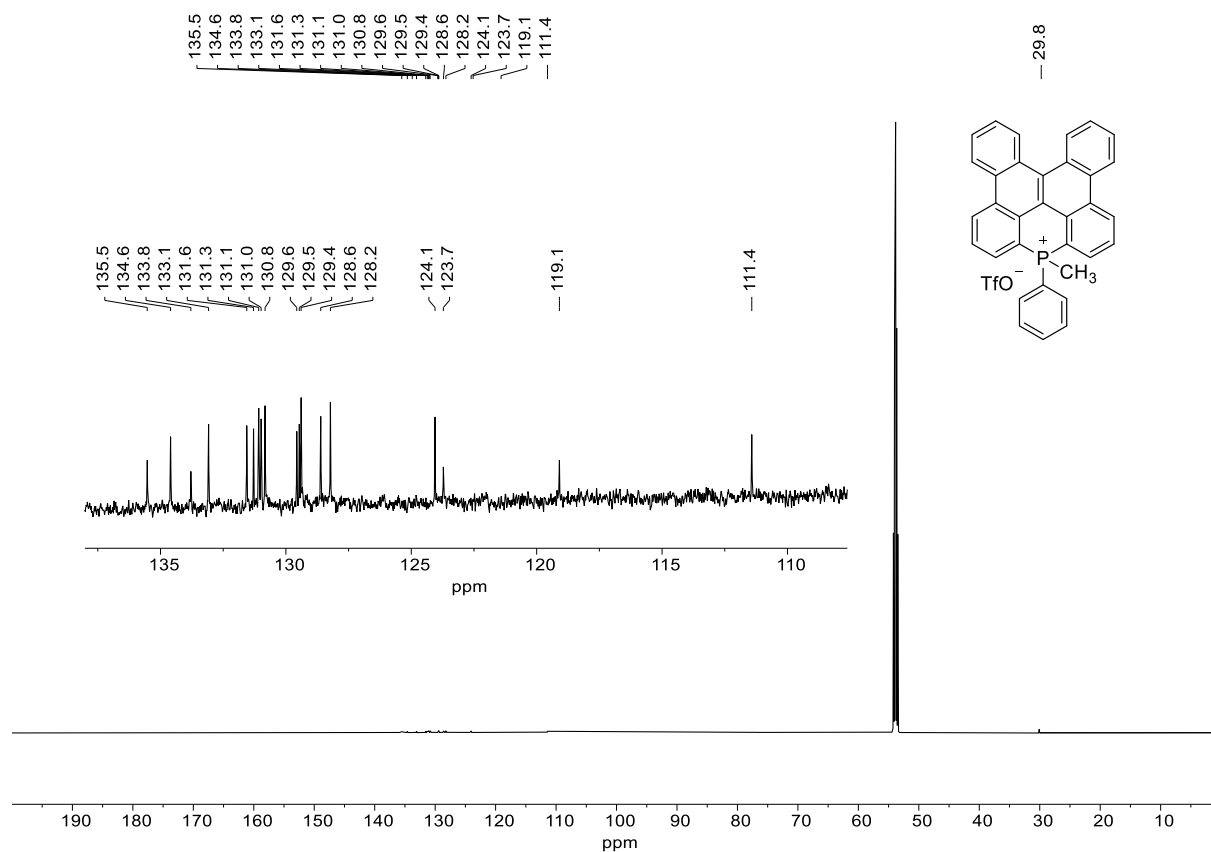


Figure S34 ¹³C {³¹P} NMR (151 MHz, CD₂Cl₂, rt) spectrum of **9**.

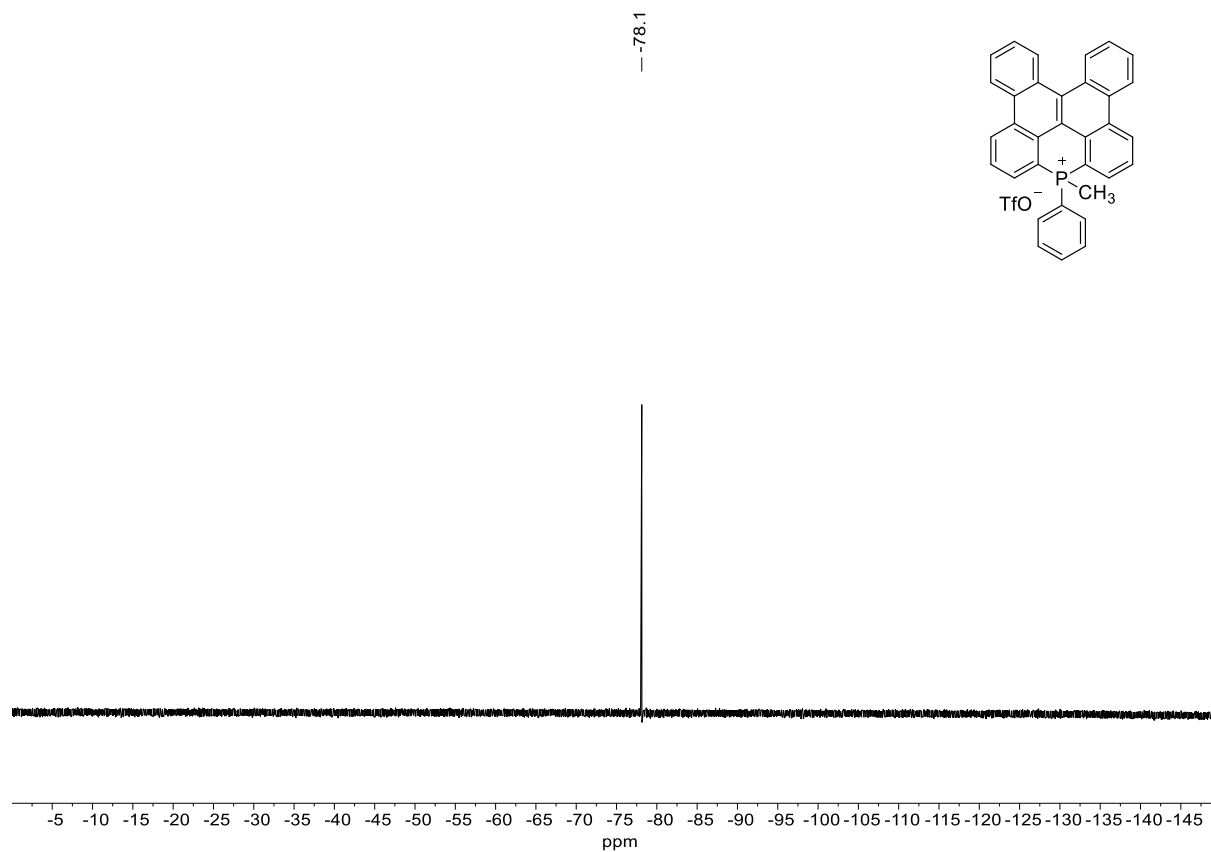
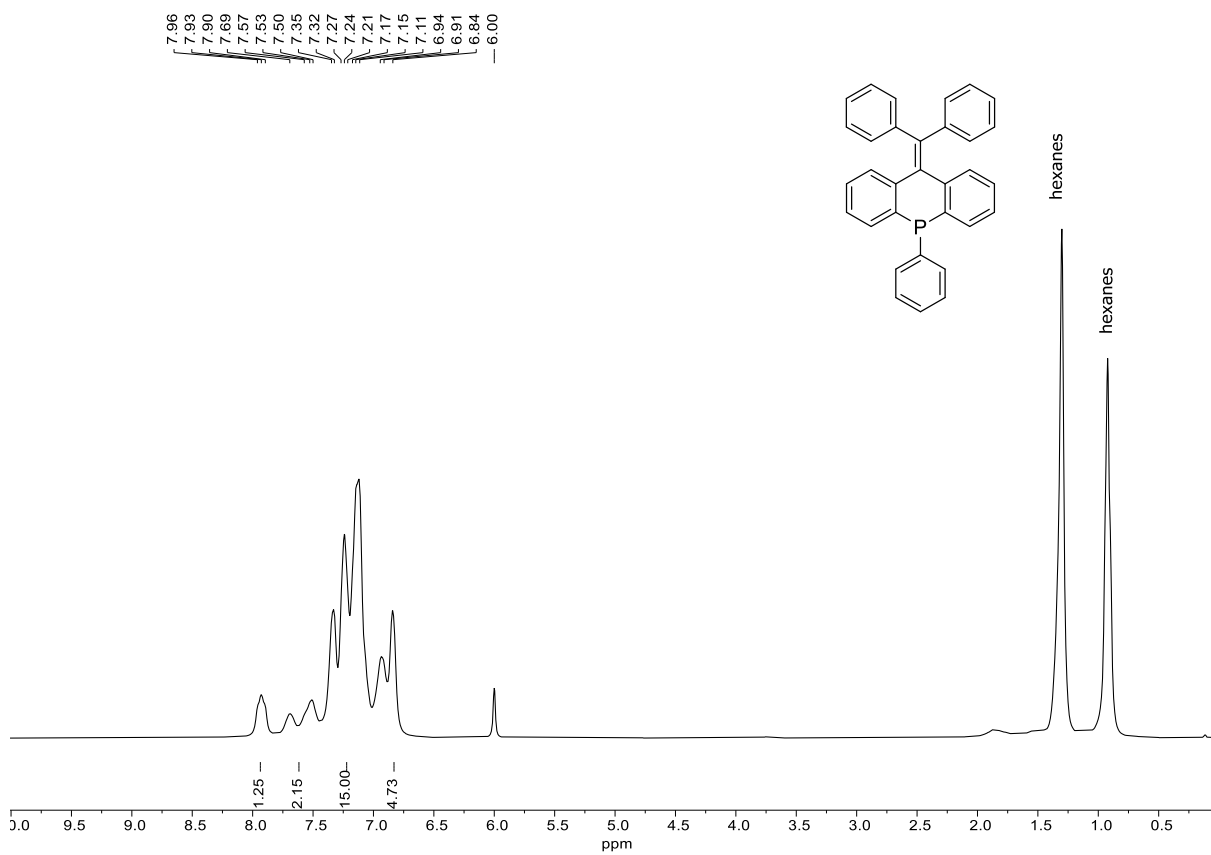
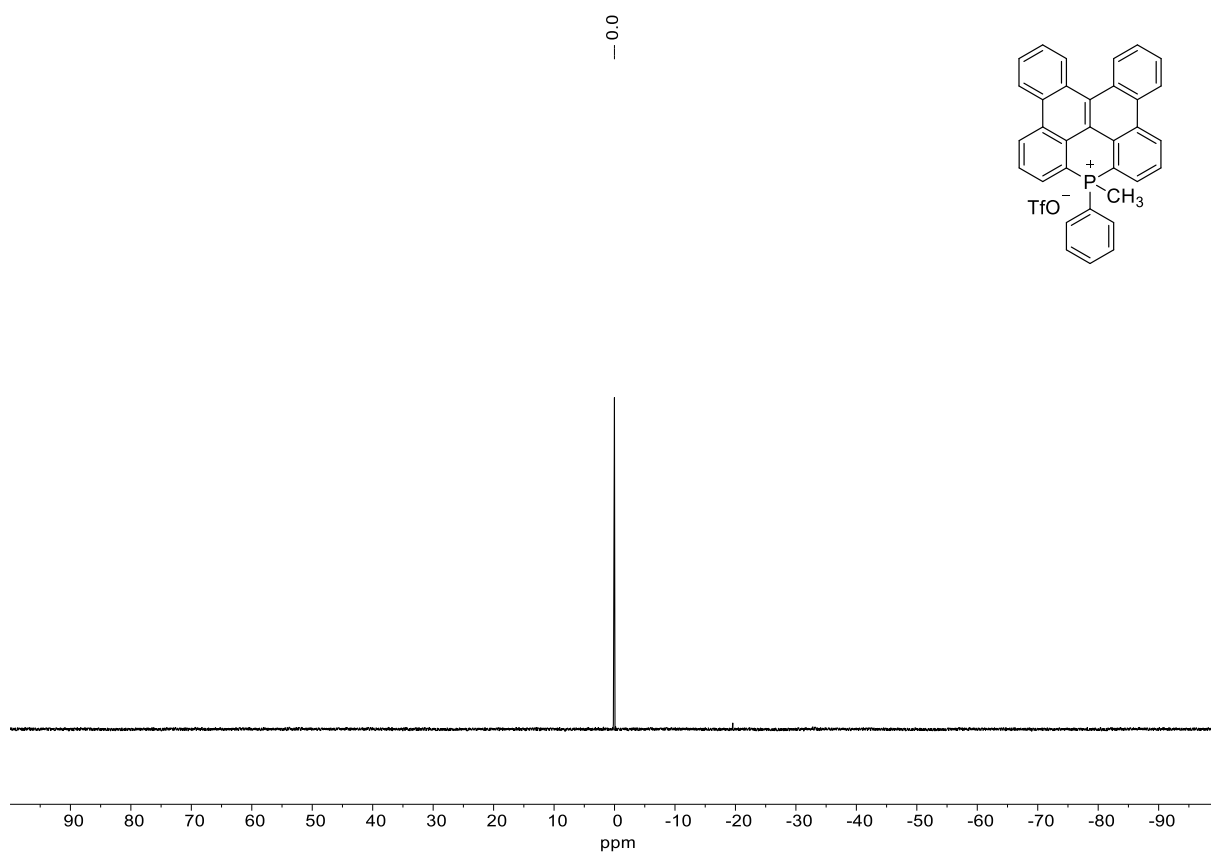


Figure S35 ¹⁹F NMR (283 MHz, CDCl₃, rt) spectrum of **9**.



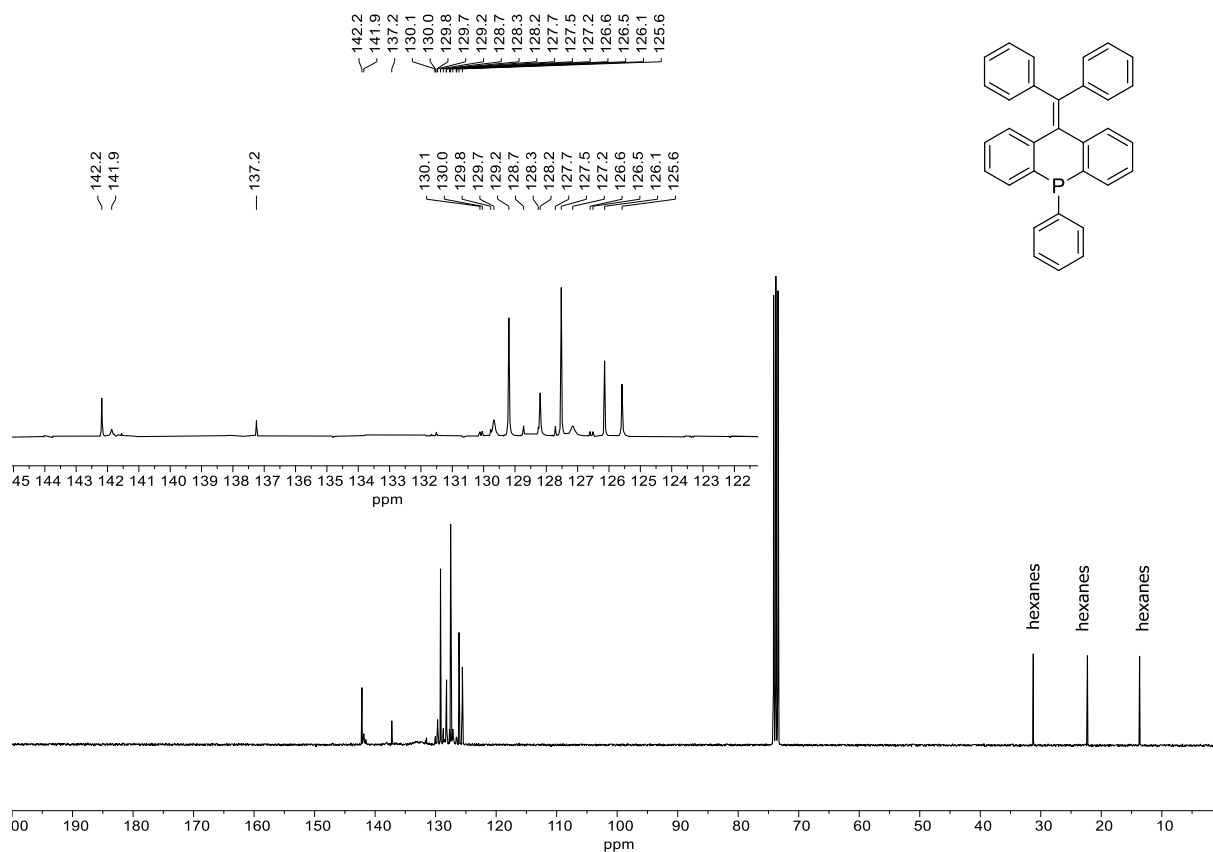


Figure S38 ^{13}C $\{^{31}\text{P}\}$ NMR (75 MHz, CD_2Cl_2 , 100 °C) spectrum of **10**.

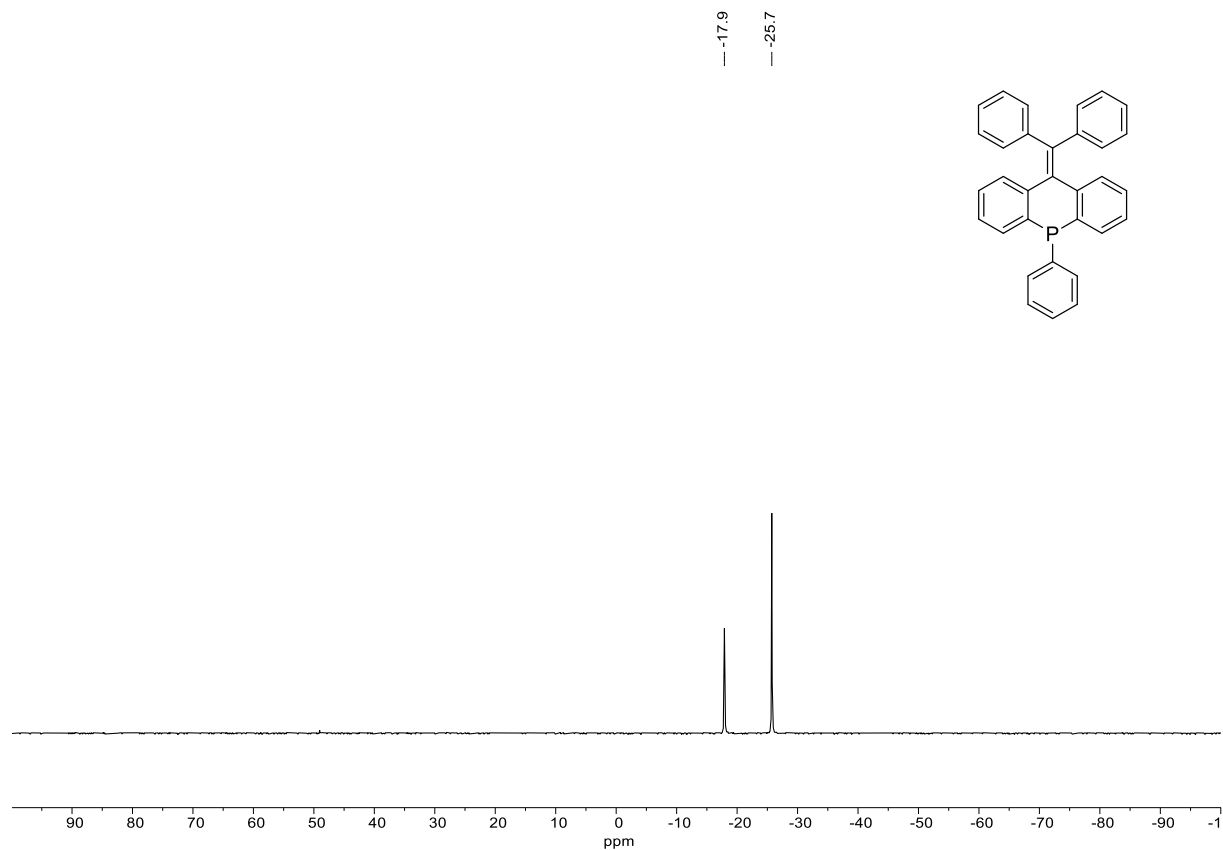


Figure S39 ^{31}P NMR (121 MHz, CD_2Cl_2 , rt) spectrum of **10**.

3. Variable Temperature NMR

Rate constants k at the corresponding temperatures T were determined by iterative line shape fitting performed with the software GNMR as a part of TopSpin 4.0.7 and using the Eyring equation:

$$(1) \quad k = \frac{k_B T}{h} e^{\frac{-\Delta G^\ddagger}{RT}}$$

Since $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$, equation (1) can be written as:

$$(2) \quad \ln \frac{k}{T} = -\frac{\Delta H^\ddagger}{R} + \frac{\Delta S^\ddagger}{R} + \ln \left(\frac{k_B}{h} \right)$$

Plotting $\ln(k/T)$ vs T^{-1} and fitting the data to a linear function, gave the slope (b) and y-axis intercept (a, Figure S41).

$$(3) \quad b = -\frac{\Delta H^\ddagger}{R}$$

$$(4) \quad a = \frac{\Delta S^\ddagger}{R} + \ln \left(\frac{k_B}{h} \right)$$

ΔH^\ddagger and ΔS^\ddagger were determined (k_B Boltzmann constant, h Planck constant, R gas constant) and ΔG^\ddagger was obtained using:

$$(5) \quad \Delta G^\ddagger = RT \left[\ln \left(\frac{k_B}{h} \right) + \ln \left(\frac{T}{k} \right) \right]$$

The activation energy E_a was determined using the Arrhenius equation:

$$(6) \quad k = A e^{\frac{-E_a}{RT}}$$

which can be rewritten as:

$$(7) \quad \ln(k) = \ln(A) - \frac{E_a}{R} \left(\frac{1}{T} \right)$$

Plotting $\ln(k)$ vs T^{-1} and fitting the data to a linear function, gave the slope (b, Figure S42).

$$(8) \quad b = -\frac{E_a}{R} \left(\frac{1}{T} \right)$$

E_a was determined (R gas constant, $T = 293$ K).

The obtained values are:

$$\begin{aligned} \Delta H^\ddagger &= 16.14 \pm 0.05 \frac{\text{kcal}}{\text{mol}} \\ \Delta S^\ddagger &= 1.79 \pm 0.30 \frac{\text{cal}}{\text{mol} \cdot \text{K}} \\ \Delta G^\ddagger &= 15.55 \pm 0.11 \frac{\text{kcal}}{\text{mol}} \end{aligned}$$

$$E_a = 16.80 \frac{\text{kcal}}{\text{mol}}$$

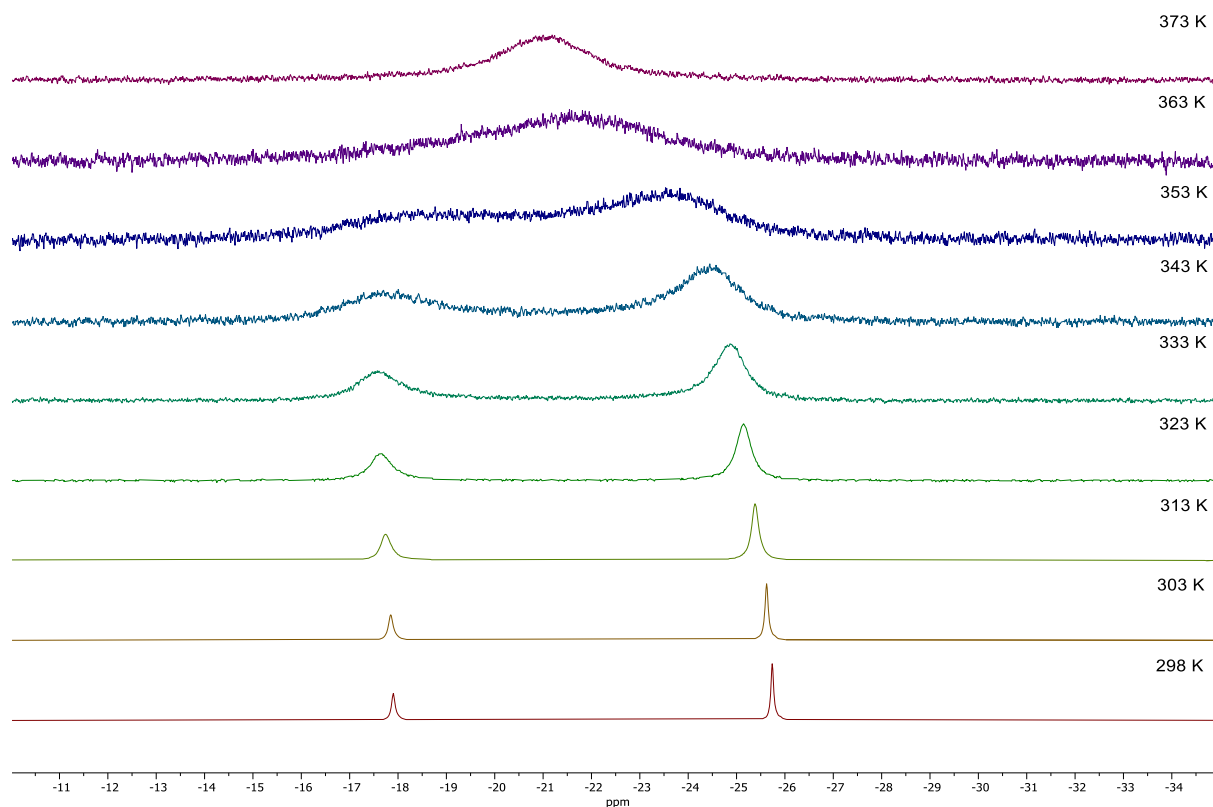


Figure S40 Variable temperature ^{31}P NMR (121 MHz) spectra of **10** in 1,1,2,2-tetrachloroethane- d_2 over a temperature range from 298 K to 373 K; Peak intensities are scaled for clarity.

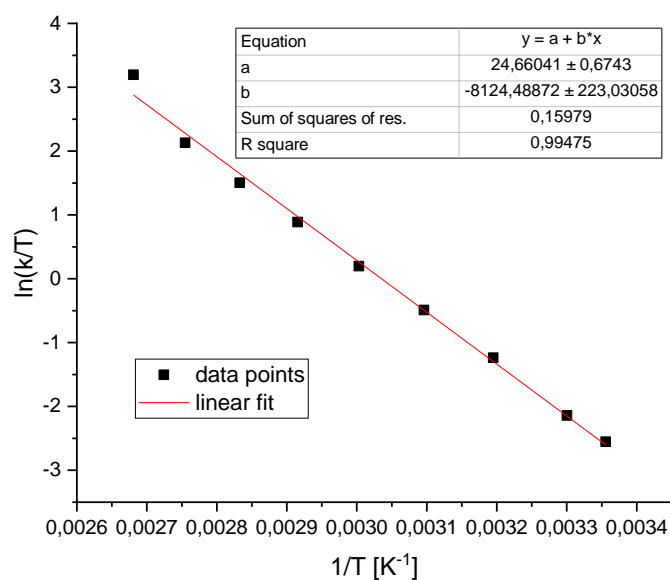


Figure S41 Eyring plot used to determine ΔH^\ddagger and ΔS^\ddagger for the conformational dynamics of **10** in 1,1,2,2-tetrachloroethane- d_2 .

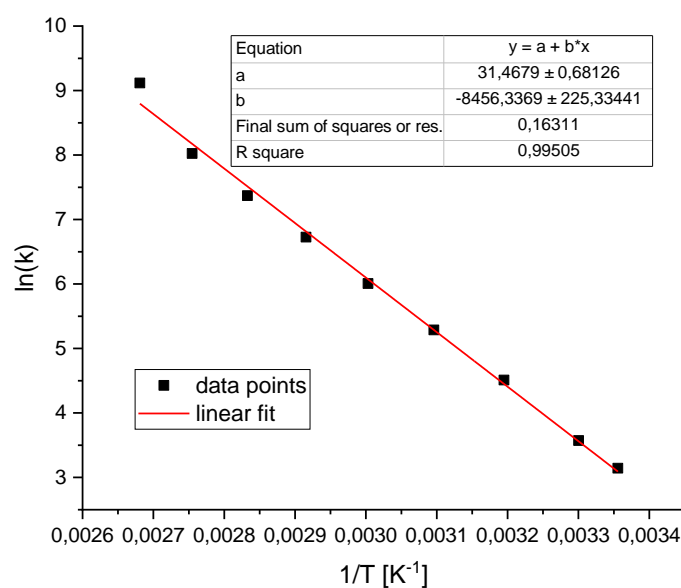


Figure S42 Arrhenius plot used to determine E_a for the conformational dynamics of **10** in 1,1,2,2-tetrachloroethane- d_2 .

Table S1 Rate constants k for the dynamic interconversion of the two conformers of **10** at given temperatures T in 1,1,2,2-tetrachloroethane- d_2 .

T [K]	1/T [K ⁻¹]	ln(k/T)	ln(k)	k [s ⁻¹]
298	0.00336	-2.55294	3.14415	23.2
303	0.0033	-2.14139	3.57235	35.6
313	0.00319	-1.23644	4.50976	90.9
323	0.0031	-0.48939	5.28827	198
333	0.003	0.19821	6.00635	406
343	0.00292	0.8885	6.72623	834
353	0.00283	1.50376	7.37023	1588
363	0.00275	2.12882	8.02322	3051
373	0.00268	3.19467	9.11625	9102

Compound 3. Single crystals of compound **3** suitable for X-ray crystallographic analysis were obtained by slow evaporation of a solution of the compound in CH₂Cl₂ and *n*-hexane. A summary of the X-ray crystallographic data and structure refinement of compound **3** can be found in Table S2.

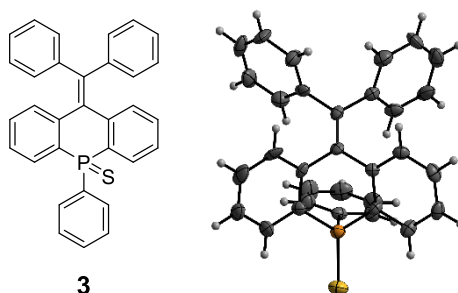


Table S2 X-ray crystallographic data and structure refinement of compound **3**.

Empirical Formula	C ₃₂ H ₂₃ PS
Formula Weight	470.52
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal System	monoclinic
Space Group	<i>P</i> 2 ₁ / <i>n</i>
Z	8
<i>a</i> / Å	13.8121(10)
<i>b</i> / Å	20.0512(13)
<i>c</i> / Å	18.6752(12)
α / deg	90
β / deg	111.516(1)
γ / deg	90
Volume / Å ³	4811.7(6)
Density (calculated) / g/cm ³	1.299
Absorption coefficient / mm ⁻¹	0.220
Crystal size / mm ³	0.212 × 0.072 × 0.034
Theta range for data collection / deg	1.551 to 1.658
Index ranges	-14 ≤ <i>h</i> ≤ 14, -20 ≤ <i>k</i> ≤ 20, -19 ≤ <i>l</i> ≤ 19
Reflections collected	31572
Reflections (independent)	5628 (R(int) = 0.0787)
Goodness-of-fit on F ²	1.15
Final R indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> ₁ = 0.094, <i>wR</i> ₂ = 0.228

Compound 4. Single crystals of compound **4** suitable for X-ray crystallographic analysis were obtained by slow evaporation of a solution of the compound in CH₂Cl₂ and *n*-hexane. A summary of the X-ray crystallographic data and structure refinement of compound **4** can be found in Table S3.

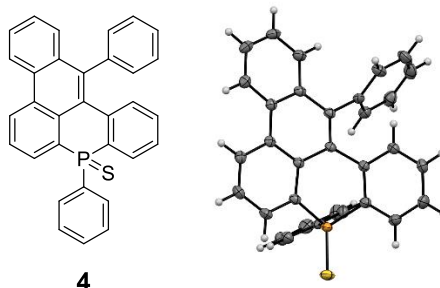


Table S3 X-ray crystallographic data and structure refinement of compound **4**.

Empirical Formula	C ₃₂ H ₂₁ PS
Formula Weight	468.52
Temperature	153.00(10) K
Wavelength	CuKα 1.54184 Å
Crystal System	monoclinic
Space Group	<i>P</i> 2 ₁ / <i>n</i>
Z	4
<i>a</i> / Å	14.1386(2)
<i>b</i> / Å	8.04580(12)
<i>c</i> / Å	20.2463(3)
<i>α</i> / deg	90
<i>β</i> / deg	99.7339(15)
<i>γ</i> / deg	90
Volume / Å ³	2269.98(6)
Density (calculated) / g/cm ³	1.371
Absorption coefficient / mm ⁻¹	2.069
Crystal size / mm ³	0.349 × 0.264 × 0.205
Theta range for data collection / deg	8.33 to 129.068
Index ranges	-16 ≤ <i>h</i> ≤ 16, -9 ≤ <i>k</i> ≤ 9, -22 ≤ <i>l</i> ≤ 23
Reflections collected	12638
Reflections (independent)	3745 (R(int) = 0.0232)
Goodness-of-fit on F ²	1.051
Final R indices (I > 2σ(I))	R ₁ = 0.0289, wR ₂ = 0.0756

Compound 5. Single crystals of compound **5** suitable for X-ray crystallographic analysis were obtained by slow evaporation of a solution of the compound in CH₂Cl₂ and *n*-hexane. A summary of the X-ray crystallographic data and structure refinement of compound **5** can be found in Table S4.

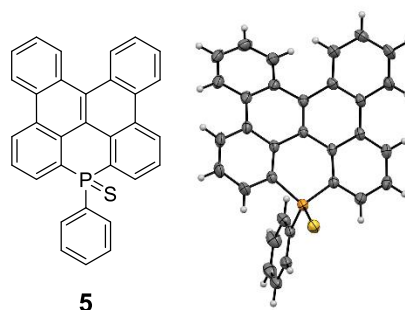


Table S4 X-ray crystallographic data and structure refinement of compound **5**.

Empirical Formula	C ₃₂ H ₁₉ PS
Formula Weight	466.50
Temperature	153.00(10) K
Wavelength	CuKα 1.54184 Å
Crystal System	monoclinic
Space Group	<i>P2₁/c</i>
Z	4
<i>a</i> / Å	11.4701(2)
<i>b</i> / Å	8.27675(16)
<i>c</i> / Å	24.0338(6)
α / deg	90
β / deg	101.500(2)
γ / deg	90
Volume / Å ³	2235.84(8)
Density (calculated) / g/cm ³	1.386
Absorption coefficient / mm ⁻¹	2.100
Crystal size / mm ³	0.352 × 0.257 × 0.185
Theta range for data collection / deg	7.508 to 129.316
Index ranges	-13 ≤ <i>h</i> ≤ 8, -9 ≤ <i>k</i> ≤ 9, -28 ≤ <i>l</i> ≤ 27
Reflections collected	6889
Reflections (independent)	3635 (R(int) = 0.0223)
Goodness-of-fit on F ²	1.043
Final R indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> ₁ = 0.0380, <i>wR</i> ₂ = 0.0968

Compound 7. Single crystals of compound **7** suitable for X-ray crystallographic analysis were obtained by slow evaporation of a solution of the compound in CH₂Cl₂ and *n*-hexane. A summary of the X-ray crystallographic data and structure refinement of compound **7** can be found in Table S5.

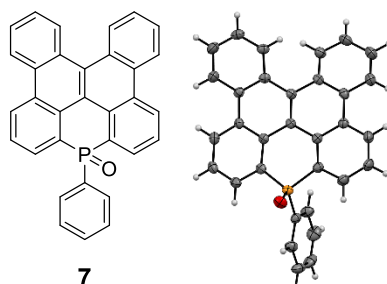


Table S5 X-ray crystallographic data and structure refinement of compound **7**.

Empirical Formula	C ₃₂ H ₁₉ OP
Formula Weight	450.44
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal System	monoclinic
Space Group	<i>P</i> 2 ₁ / <i>n</i>
Z	4
<i>a</i> / Å	12.3028(5)
<i>b</i> / Å	8.4571(3)
<i>c</i> / Å	20.4867(7)
α / deg	90
β / deg	92.0325(16)
γ / deg	90
Volume / Å ³	2130.22(14)
Density (calculated) / g/cm ³	1.40
Absorption coefficient / mm ⁻¹	0.15
Crystal size / mm ³	0.239 × 0.069 × 0.030
Theta range for data collection / deg	1.9 to 27.1
Index ranges	-15 ≤ <i>h</i> ≤ 15, -10 ≤ <i>k</i> ≤ 10, -26 ≤ <i>l</i> ≤ 26
Reflections collected	28378
Reflections (independent)	4673 (R(int) = 0.0933)
Observed reflections	3220 (<i>I</i> > 2σ(<i>I</i>))
Goodness-of-fit on F ²	1.03
Final R indices (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> ₁ = 0.047, <i>wR</i> ₂ = 0.101

5. Cyclic Voltammetry

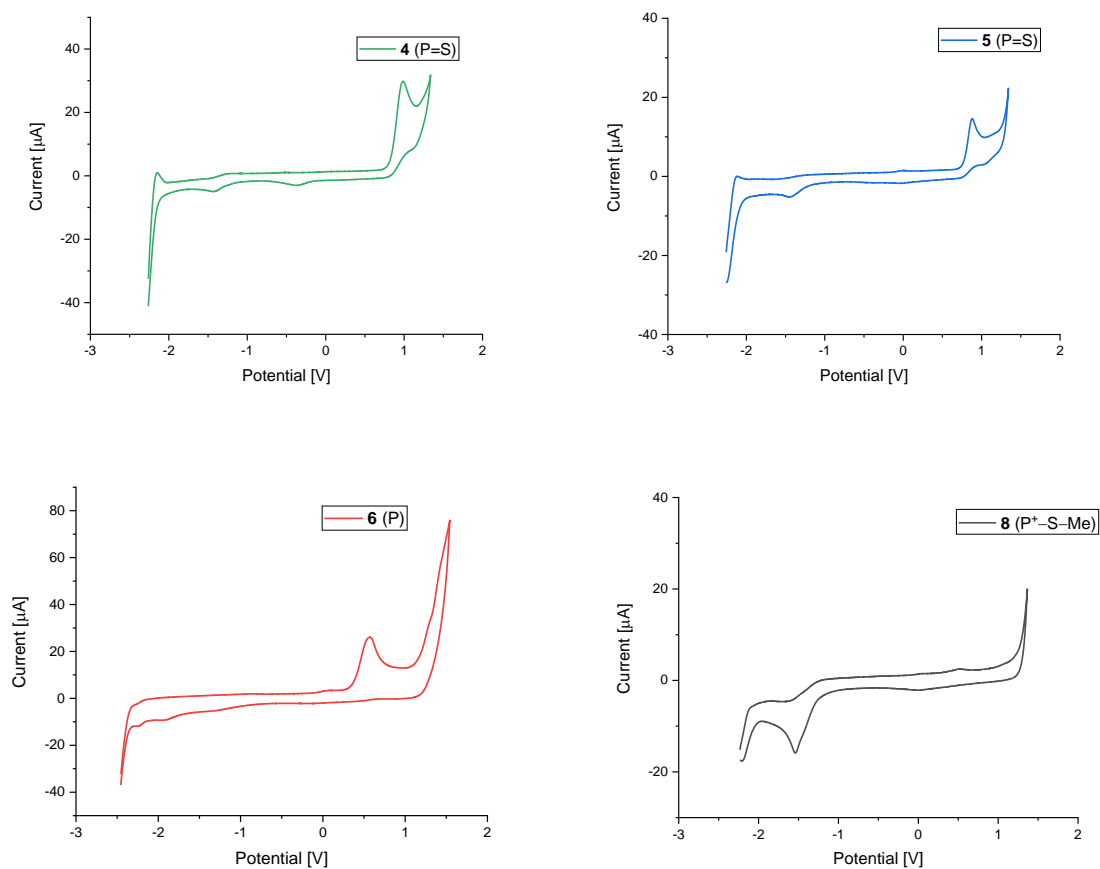


Figure S44 Cyclic voltammograms of **4–6** and **8** (CH_2Cl_2 with 0.1 M $n\text{Bu}_4\text{NPF}_6$, glassy carbon working electrode, scan rate 100 mV s^{-1} , referenced vs. Fc/Fc^+).

The cyclic voltammograms of compounds **4–6** exhibit one irreversible oxidation event at +0.98 V, +0.88 V, and +0.57 V, respectively (all potentials are referenced against Fc/Fc^+). The cyclic voltammogram of phosphine oxide **7** shows neither reduction nor oxidation event. The phosphonium salt **8** features one irreversible reduction event at -1.55 V.

6. DFT Calculations

Computational details

All calculations were performed using the program package Turbomole (version 7.3).^[8] Geometry optimizations were carried out by calculations based on density-functional theory with the Kohn-Sham formalism applying the B3LYP exchange-correlation functional^[9] and the def2-TZVP basis set family^[10] (in the following, the prefix def2- will be omitted). Throughout, the multipole accelerated RI method^[11,12,13] was used to calculate the Coulomb part of the electronic energy. To account for dispersion interactions, Grimme's D3 correction^[14] was adopted. Solvent effects are captured within the conductor-like screening model (COSMO)^[15] with the dielectric constant $\epsilon_r = 8.93$ mimicking methylene chloride. Compound **8** was calculated without the counter ion.

Electronic excitation energies, i.e. UV/Vis spectra, and frontier molecular orbitals (FMOs) were calculated at the ground state equilibrium geometries within the time-dependent DFT (TD-DFT) method using the BHLYP exchange-correlation functional;^[16] solvent effects have been included in the TD-DFT computations within the COSMO model as described above. Broadened spectra were obtained by convolution with a Gaussian curve (full width at half maximum (FWHM) = 0.4 eV) and were converted to extinction coefficients. For comparison with experimental data, the excitation energies were red-shifted by 0.3 eV to account for the systematic overestimation of BHLYP-based excitation energies.

Frontier Molecular Orbitals

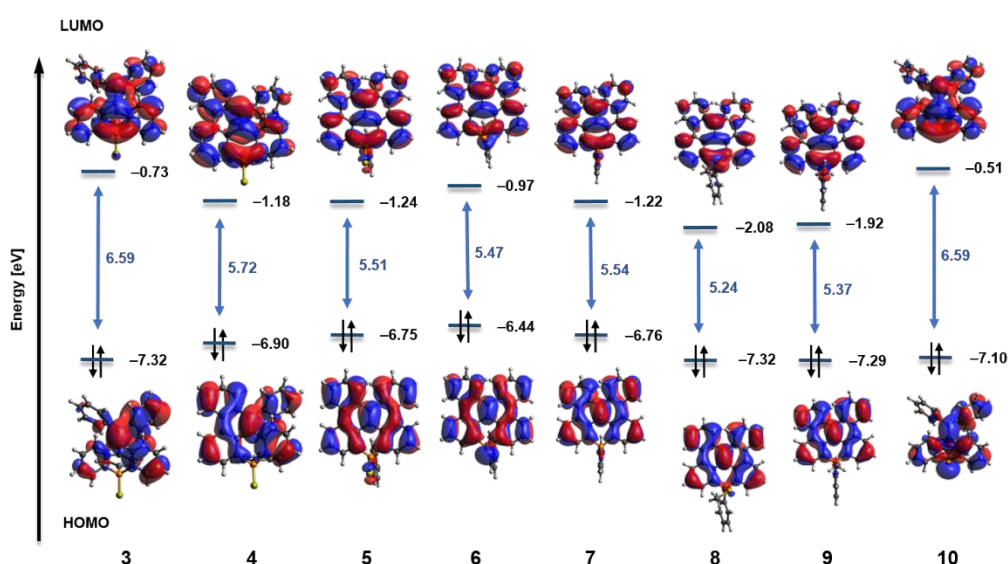


Figure S45 Frontier molecular orbitals of **3–10**. Orbital energies are given in eV at the COSMO-BHLYP/TZVP level of theory.

Table S6 Calculated energies of the frontier molecular orbitals of compounds **3–10**. Orbital energies are given in eV at the COSMO-BHLYP/TZVP level of theory.

Compound	E_{HOMO}	E_{LUMO}	$\Delta E_{\text{HOMO-LUMO}}$
3	-7.32	-0.73	6.59
4	-6.90	-1.18	5.72
5	-6.75	-1.24	5.51
6	-6.44	-0.97	5.47
7	-6.76	-1.22	5.54
8	-7.32	-2.08	5.24
9	-7.29	-1.92	5.37
10	-7.10	-0.51	6.59

Cartesian Coordinates

Compound 3:

C	1.9883069	4.0134273	-1.5101761
C	0.6992271	3.8167514	-1.9938794
C	2.6712285	2.9499862	-0.9331099
C	2.0589834	1.7044838	-0.8185367
C	0.7399475	1.5030604	-1.2690991
H	3.6873404	3.0767066	-0.5812857
H	2.4663563	4.9807251	-1.5982320
P	2.9616131	0.2900078	-0.1270210
C	0.1070010	0.1609247	-1.1178775
C	0.9613593	-0.9818274	-1.5496056
C	2.3114431	-1.0494132	-1.1636563
C	2.2515637	-0.0028590	1.5257961
C	2.3337161	-1.2817667	2.0838108
C	1.6839188	1.0366431	2.2629863
C	1.1935000	0.7963706	3.5426771
C	1.2685818	-0.4797556	4.0913263
C	1.8415944	-1.5183657	3.3607619
H	1.6121123	2.0302622	1.8393074
H	0.7476216	1.6056819	4.1071785
H	0.8811770	-0.6660953	5.0851789
H	1.8998216	-2.5135170	3.7835413
H	2.7710093	-2.0960254	1.5186905
C	0.4629954	-1.9821583	-2.3877786
C	1.2701204	-3.0347372	-2.7988049
C	2.5981903	-3.1061821	-2.3870128
C	3.1198050	-2.1062111	-1.5757247
C	-1.1207817	-0.0167727	-0.5841149
C	-1.6710281	-1.3639020	-0.2515251
C	-1.9875232	1.1184835	-0.1397413
C	-0.9757704	-2.2026484	0.6245289
C	-2.9040705	-1.7924238	-0.7518882
C	-1.4867370	-3.4465499	0.9741644
C	-2.7028062	-3.8755269	0.4500104
C	-3.4094897	-3.0429501	-0.4140134
H	-3.4668348	-1.1533304	-1.4197156
H	-4.3583688	-3.3662086	-0.8243942

C	-3.0280471	1.6002531	-0.9363779
C	-3.8413502	2.6353494	-0.4872477
C	-3.6278372	3.1998330	0.7670434
C	-2.5986003	2.7185586	1.5708545
C	-1.7889312	1.6810668	1.1219841
H	-0.9913410	1.3047345	1.7488862
H	-4.2588998	4.0083400	1.1149069
H	-2.4250204	3.1512524	2.5487281
H	-4.6382239	3.0048710	-1.1211390
S	4.9207381	0.4587126	-0.0944018
H	0.8621289	-3.7981362	-3.4496134
H	3.2275480	-3.9265302	-2.7077677
H	4.1575857	-2.1334122	-1.2682279
H	-3.1001083	-4.8468687	0.7173334
H	-0.9343679	-4.0806622	1.6570588
H	-3.1896241	1.1805536	-1.9216659
C	0.0855349	2.5752114	-1.8791322
H	-0.9079439	2.4347430	-2.2771641
H	-0.0320399	-1.8720551	1.0352507
H	-0.5651412	-1.9306790	-2.7193934
H	0.1688172	4.6305765	-2.4726806

Compound 4:

C	1.8347664	-2.8920441	-2.7860673
C	0.4440301	-2.8884484	-2.8416549
C	2.4848434	-1.8994961	-2.0663568
C	1.7498690	-0.9368511	-1.3783598
C	0.3422022	-0.9457043	-1.3791650
H	3.5663769	-1.8541935	-2.0439631
H	2.4054336	-3.6433531	-3.3167829
P	2.5668567	0.4089324	-0.5022739
C	-0.4632513	0.1080210	-0.6986918
C	0.0268369	1.4727699	-0.7203723
C	1.4128937	1.7613845	-0.8372572
C	2.2869588	0.0310969	1.2636308
C	2.0110416	1.0487853	2.1785935
C	2.3718582	-1.2909239	1.7068030
C	2.1777873	-1.5909458	3.0501761
C	1.8978807	-0.5739923	3.9588655
C	1.8171826	0.7452823	3.5215425
H	2.5741821	-2.0898125	1.0043695
H	2.2373305	-2.6190714	3.3847106
H	1.7393695	-0.8094618	5.0039151
H	1.5960771	1.5388242	4.2244903
H	1.9341894	2.0763506	1.8462668
C	-0.8741647	2.5534751	-0.5659447
C	-0.3844126	3.8663538	-0.7368398
C	0.9493753	4.1163058	-0.9712862
C	1.8652151	3.0576787	-0.9698664
C	-1.6980610	-0.1484295	-0.1420194
C	-2.5917994	0.9419880	0.1850378
C	-2.1074880	-1.5455488	0.1759714
C	-2.2355480	2.2780018	-0.1491094
C	-3.8466486	0.7132674	0.7952901

C	-3.1901150	3.2987209	0.0323186
C	-4.4265759	3.0368554	0.5812508
C	-4.7475597	1.7357820	0.9904847
H	-4.1084992	-0.2852214	1.1113037
H	-5.7038142	1.5320571	1.4558042
C	-1.3232674	-2.2931320	1.0591630
C	-1.6577983	-3.6062967	1.3690096
C	-2.7818855	-4.1942163	0.7966130
C	-3.5737032	-3.4563315	-0.0802717
C	-3.2428486	-2.1409551	-0.3822181
H	-3.8562297	-1.5764125	-1.0734834
H	-3.0407687	-5.2190666	1.0321975
H	-4.4482668	-3.9071999	-0.5328880
H	-1.0383868	-4.1711064	2.0550241
S	4.4526267	0.7329978	-0.9517586
H	-1.0594735	4.7062178	-0.6575233
H	1.2974263	5.1330863	-1.0992470
H	2.9284146	3.2499746	-1.0411945
H	-5.1400597	3.8406852	0.7129761
H	-2.9539932	4.3152722	-0.2480219
H	-0.4418875	-1.8409812	1.4962795
C	-0.2862754	-1.9259207	-2.1596596
H	-0.0783113	-3.6314736	-3.4314096
H	-1.3613845	-1.9271265	-2.2493769

Compound 5:

C	-1.3122575	3.2317050	-2.1073756
C	-0.0489485	3.3873121	-1.5789724
C	-1.9894021	2.0336236	-1.9010484
C	-1.3728488	0.9826480	-1.2408648
C	-0.0345576	1.0758175	-0.7807475
C	0.5939327	2.3485241	-0.8853461
H	-3.0030791	1.9130733	-2.2619893
H	-1.7830164	4.0393549	-2.6525447
H	0.4579239	4.3323176	-1.7116340
P	-2.4047332	-0.4378757	-0.8460377
C	0.7378831	-0.0751277	-0.3189158
C	0.1786387	-1.4209819	-0.2341683
C	-1.2028147	-1.6999498	-0.3912481
C	-3.2067914	0.0316859	0.7312822
C	-2.4081173	0.3445578	1.8368247
C	-4.5941822	0.0946909	0.8424815
C	-5.1803701	0.4682439	2.0491031
C	-4.3840169	0.7795797	3.1459388
C	-2.9955802	0.7168722	3.0384126
H	-5.2114371	-0.1510139	-0.0121136
H	-6.2592931	0.5142358	2.1294866
H	-4.8413197	1.0695381	4.0838267
H	-2.3717513	0.9571347	3.8902206
H	-1.3282744	0.2982083	1.7654123
C	1.0255793	-2.5176652	0.0978264
C	0.4609667	-3.7781888	0.3560167
C	-0.8922928	-4.0074172	0.2349832
C	-1.7209602	-2.9662290	-0.1675008
C	2.0804071	0.1140107	0.0081001

C	2.9881801	-1.0221893	0.0261552
C	2.5603184	1.4562451	0.3027279
C	2.4661966	-2.3331747	0.1063492
C	4.3813241	-0.8675685	-0.1589200
C	3.3583553	-3.4245185	0.1105768
C	4.7189018	-3.2415393	-0.0076569
C	5.2323538	-1.9505010	-0.1731840
H	4.7904712	0.1149626	-0.3358320
H	6.2927398	-1.8003307	-0.3323686
C	1.8544848	2.5712140	-0.1999243
C	2.3395651	3.8661695	0.0704218
C	3.4526120	4.0636936	0.8595553
C	4.0986087	2.9643032	1.4360876
C	3.6581645	1.6878373	1.1602374
H	4.1416225	0.8524608	1.6438539
H	3.7977493	5.0691390	1.0651116
H	4.9326073	3.1131266	2.1102122
H	1.8093472	4.7306624	-0.3020869
S	-3.6820608	-0.9769908	-2.2445816
H	1.0973327	-4.5953034	0.6620174
H	-1.3037844	-4.9871123	0.4397105
H	-2.7808798	-3.1402369	-0.3044778
H	5.3809838	-4.0981516	-0.0137787
H	2.9780083	-4.4337150	0.1643164

Compound 6:

C	0.4242148	-3.8126971	0.1110267
C	0.9332501	-2.5173227	-0.0810271
C	-0.9006021	-4.1082970	-0.1265666
C	-1.7443963	-3.1056661	-0.5935861
C	-1.2928751	-1.8014241	-0.7472787
C	0.0530477	-1.4597491	-0.4555503
C	0.5361329	-0.0800106	-0.4338945
C	-0.2747647	1.0492581	-0.8860689
C	-1.5589552	0.8901257	-1.4663795
P	-2.5450188	-0.6337060	-1.3567166
C	-2.1887064	1.9508883	-2.1009271
C	0.2656481	2.3656934	-0.8417334
C	-0.3991019	3.4148772	-1.5010606
C	-1.6003008	3.2130871	-2.1441056
C	1.8349988	0.1685900	0.0095629
H	1.0795406	-4.6002640	0.4531604
H	-1.2746127	-5.1124792	0.0276704
H	-2.7767508	-3.3412696	-0.8272014
C	-3.4976177	-0.2883429	0.1935841
C	-4.8917591	-0.3107315	0.1312502
C	-2.8774764	-0.0000766	1.4144712
C	-3.6376686	0.2612679	2.5468590
C	-5.0308411	0.2385249	2.4746634
C	-5.6565866	-0.0473240	1.2667875
H	0.0424733	4.4008918	-1.5173269
H	-2.0888968	4.0282976	-2.6625498
H	-1.7961226	0.0203514	1.4816583
H	-3.1466570	0.4831290	3.4867415
H	-5.6226194	0.4424319	3.3586351

H	-6.7378525	-0.0678069	1.2049637
H	-5.3845155	-0.5354271	-0.8076302
C	2.2051565	1.5142553	0.4210426
C	2.8058421	-0.9140367	0.0411832
C	1.4558291	2.6162208	-0.0480321
C	1.8309908	3.9160384	0.3475905
C	2.3572871	-2.2540254	0.0363104
C	3.3096538	-3.2933154	0.0594437
C	2.8759679	4.1272838	1.2215591
C	3.5628057	3.0320377	1.7579007
C	3.2300760	1.7541358	1.3636320
C	4.1965172	-0.6743580	-0.0432765
C	4.6625369	-3.0303912	0.0405489
C	5.1091898	-1.7065236	-0.0404985
H	4.5571064	0.3368368	-0.1537641
H	6.1672569	-1.4907573	-0.1215150
H	2.9846881	-4.3233535	0.0485755
H	5.3727879	-3.8477381	0.0464006
H	1.2652924	4.7694510	0.0024782
H	3.1343231	5.1348570	1.5225347
H	4.3415870	3.1835479	2.4948035
H	3.7409942	0.9189042	1.8183421
H	-3.1559914	1.7940907	-2.5650940

Compound 7:

C	-0.0272169	3.4659023	-1.4290353
C	1.1869481	3.3821684	-2.0781457
C	1.9073818	2.1924572	-2.0149372
C	1.3728014	1.0820428	-1.3787653
C	0.0797588	1.1078773	-0.7976936
C	-0.5833578	2.3656887	-0.7544412
C	-0.6203015	-0.0958368	-0.3541723
C	-0.0272293	-1.4279288	-0.4314175
P	2.4595507	-0.3284814	-1.2056356
C	1.3381436	-1.6475137	-0.7446586
C	-0.8131037	-2.5720479	-0.1154096
C	1.9032748	-2.9129526	-0.6951915
C	1.1395198	-4.0122091	-0.3162370
C	-0.1976522	-3.8336416	-0.0349932
C	-1.9294961	0.0298022	0.1085421
C	-2.8046037	-1.1321203	0.1273314
C	-2.4091678	1.3347724	0.5423487
C	-2.2485616	-2.4302959	0.0545726
C	-3.1123359	-3.5443047	0.0659091
C	-4.2124353	-1.0059262	0.0900723
C	-5.0369697	-2.1091080	0.0769993
C	-4.4815672	-3.3932637	0.0952930
H	-0.7813268	-4.6944247	0.2564634
H	2.9497938	-3.0407394	-0.9452469
H	1.5876296	-4.9950731	-0.2487932
H	2.8893993	2.1253074	-2.4671848
H	-2.7065585	-4.5432978	0.0083925
H	-4.6587168	-0.0255186	0.0273838
H	-5.1220330	-4.2661999	0.0903036
H	-6.1109049	-1.9785310	0.0326283

C	-1.7796461	2.5030241	0.0576531
C	-2.2664291	3.7609983	0.4641924
C	-3.4244300	1.4743270	1.5136302
C	-3.8660485	2.7151194	1.9199917
C	-3.3035927	3.8704602	1.3660065
H	-3.8401605	0.5937213	1.9797522
H	-4.6345517	2.7921215	2.6787598
H	-3.6502510	4.8485361	1.6751638
H	-1.7941271	4.6643207	0.1056672
C	3.4525761	0.0229916	0.2750762
C	4.8438987	0.0346216	0.1743409
C	2.8442943	0.2856319	1.5064709
C	3.6216912	0.5574284	2.6245079
C	5.0121265	0.5692995	2.5198365
C	5.6214178	0.3080262	1.2967750
H	6.7012669	0.3164649	1.2146418
H	5.3093724	-0.1711054	-0.7810732
H	1.7639467	0.2781940	1.5960196
H	3.1463599	0.7595804	3.5762835
H	5.6176134	0.7820607	3.3922474
O	3.3299075	-0.6219451	-2.3832121
H	-0.5627705	4.4043609	-1.4483934
H	1.5873528	4.2389785	-2.6043194

Compound 8:

C	0.0452234	3.5827211	-0.6260352
C	1.4083498	3.5493368	-0.8237782
C	2.0722143	2.3317781	-0.7432448
C	1.3560707	1.1665044	-0.5002159
C	-0.0508926	1.1649581	-0.2856041
C	-0.7011938	2.4292241	-0.3223419
C	-0.8254243	-0.0494654	-0.0701617
C	-0.2090023	-1.3481991	0.1745732
P	2.2289187	-0.3694971	-0.6023097
C	1.1954524	-1.5580278	0.1937146
C	-1.0158166	-2.4655920	0.5178808
C	1.7730759	-2.7263755	0.6723004
C	0.9600066	-3.7507839	1.1442332
C	-0.4100391	-3.6235599	1.0347549
C	-2.2174596	0.0438507	0.0000574
C	-3.0149917	-1.1694216	-0.1107898
C	-2.8482131	1.3334061	0.2229078
C	-2.4388412	-2.4121795	0.2358771
C	-3.2325151	-3.5739308	0.1809764
C	-4.3265275	-1.1596686	-0.6319227
C	-5.0745108	-2.3145801	-0.7122297
C	-4.5354368	-3.5268125	-0.2677818
H	-1.0316548	-4.4451217	1.3602786
H	2.8498965	-2.8383418	0.6804919
H	1.3968845	-4.6494967	1.5579756
H	3.1462112	2.2976630	-0.8703383
H	-2.8095303	-4.5326087	0.4438090
H	-4.7425029	-0.2389331	-1.0124329
H	-5.1223032	-4.4350876	-0.3173703
H	-6.0716049	-2.2826478	-1.1323296

C	-2.1086828	2.5234677	0.0220748
C	-2.7411830	3.7642320	0.2401980
C	-4.1528981	1.4409917	0.7586505
C	-4.7401579	2.6645074	0.9884326
C	-4.0392702	3.8392910	0.6947599
H	-4.6916611	0.5492102	1.0365269
H	-5.7351463	2.7133076	1.4119008
H	-4.4976677	4.8055557	0.8622983
H	-2.2000395	4.6857845	0.0871964
C	3.8578479	-0.2328339	0.1422489
C	4.9843028	-0.8022624	-0.4546684
C	3.9634882	0.4167212	1.3795226
C	5.1961651	0.4899513	2.0108291
C	6.3213655	-0.0756326	1.4135970
C	6.2157597	-0.7188856	0.1848840
H	7.0899911	-1.1571054	-0.2784652
H	4.9048535	-1.3135293	-1.4045977
H	3.0926572	0.8596902	1.8456013
H	5.2793434	0.9892928	2.9672251
H	7.2820433	-0.0132295	1.9087577
C	3.2568074	0.2317294	-3.4522284
H	2.6048678	0.6247667	-4.2280664
H	4.1438536	-0.2218426	-3.8871351
H	3.5521201	1.0360200	-2.7843771
H	-0.4556579	4.5361007	-0.6996799
H	1.9555799	4.4575323	-1.0368006
S	2.3339649	-1.0832923	-2.5571696

Compound 9:

C	-0.0403039	3.6193214	-0.8565819
C	1.2855325	3.5930381	-1.2346847
C	1.9742504	2.3878421	-1.1897876
C	1.3142972	1.2233035	-0.8199010
C	-0.0582802	1.2077007	-0.4590492
C	-0.7232760	2.4661753	-0.4339696
C	-0.8033103	-0.0162129	-0.1909904
C	-0.1675593	-1.3243335	-0.0809940
P	2.2777018	-0.2654771	-0.8484382
C	1.2354179	-1.5231446	-0.1638390
C	-0.9516332	-2.4698367	0.2298414
C	1.8369349	-2.7290649	0.1728087
C	1.0577857	-3.8000762	0.5932046
C	-0.3155580	-3.6677980	0.5951287
C	-2.1803313	0.0715991	0.0175821
C	-2.9956388	-1.1294322	-0.0882642
C	-2.7793837	1.3523227	0.3574658
C	-2.3946258	-2.3958226	0.0869129
C	-3.1970811	-3.5508367	0.0125938
C	-4.3576927	-1.0782326	-0.4565084
C	-5.1181661	-2.2233045	-0.5543515
C	-4.5407506	-3.4689407	-0.2850251
H	-0.9143436	-4.5157154	0.8941759
H	2.9137741	-2.8341987	0.1190296
H	1.5210103	-4.7307070	0.8919086
H	3.0259166	2.3603282	-1.4487028

H	-2.7548652	-4.5278920	0.1419222
H	-4.8079004	-0.1294761	-0.7059762
H	-5.1348889	-4.3713744	-0.3519249
H	-6.1559901	-2.1567594	-0.8547306
C	-2.0747837	2.5489239	0.0911311
C	-2.6713657	3.7812259	0.4237407
C	-4.0035716	1.4386790	1.0585995
C	-4.5557148	2.6542104	1.3968373
C	-3.8984450	3.8388763	1.0480203
H	-4.5023442	0.5363471	1.3760146
H	-5.4874163	2.6882320	1.9469808
H	-4.3296813	4.7983554	1.3036278
H	-2.1509316	4.7071569	0.2290549
C	3.7786067	-0.0694650	0.1165556
C	5.0451089	-0.1939193	-0.4586066
C	3.6497094	0.2230023	1.4801447
C	4.7844877	0.3881210	2.2591775
C	6.0486582	0.2636382	1.6844032
C	6.1782609	-0.0260724	0.3307722
H	7.1597270	-0.1231364	-0.1147440
H	5.1620458	-0.4197192	-1.5095947
H	2.6691819	0.3198151	1.9305121
H	4.6850189	0.6129565	3.3130664
H	6.9330350	0.3928007	2.2952507
C	2.7056125	-0.6915793	-2.5455135
H	1.7744015	-0.8161364	-3.0972948
H	3.2690732	-1.6243551	-2.5655913
H	3.2899319	0.1101198	-2.9970142
H	-0.5622425	4.5641837	-0.8884980
H	1.7855637	4.4988356	-1.5499421

Compound 10:

C	-0.0755533	-4.3928151	-1.4717337
C	1.0299621	-3.6906780	-1.9384609
C	-1.1394773	-3.6942927	-0.9109622
C	-1.0971464	-2.3050080	-0.7859766
C	0.0403542	-1.5952788	-1.2188822
H	-2.0181010	-4.2322138	-0.5739797
H	-0.1199691	-5.4709481	-1.5623650
P	-2.5689362	-1.4365067	-0.1221804
C	0.0815819	-0.1144018	-1.0583808
C	-1.1568110	0.5929683	-1.4892639
C	-2.4191636	0.0999940	-1.1126999
C	-1.9751924	-0.8562560	1.5296532
C	-2.5274531	0.3006301	2.0916234
C	-1.0706003	-1.6028091	2.2890566
C	-0.7105880	-1.1914739	3.5693804
C	-1.2521448	-0.0307132	4.1127797
C	-2.1647773	0.7130513	3.3688385
H	-0.6268737	-2.5000941	1.8757568
H	0.0021495	-1.7762307	4.1385664
H	-0.9664367	0.2917638	5.1062523
H	-2.5905259	1.6202282	3.7802834
H	-3.2303138	0.8972914	1.5218526
C	-1.0939888	1.7241716	-2.3070966

C	-2.2503286	2.3819044	-2.7075668
C	-3.4966106	1.9118135	-2.3059765
C	-3.5753836	0.7660577	-1.5213579
C	1.1334823	0.5360155	-0.5170349
C	1.1025550	1.9912086	-0.1807401
C	2.3744335	-0.1594185	-0.0536340
C	0.1487519	2.4738362	0.7197367
C	2.0445293	2.8839731	-0.6996695
C	0.1230233	3.8162975	1.0777044
C	1.0511388	4.7022902	0.5381405
C	2.0120693	4.2300797	-0.3522794
H	2.7989870	2.5307186	-1.3904325
H	2.7400843	4.9108348	-0.7766917
C	3.5452720	-0.1571997	-0.8151794
C	4.6981050	-0.7764760	-0.3434337
C	4.6980140	-1.4030001	0.8998492
C	3.5372464	-1.4036191	1.6681462
C	2.3861608	-0.7820127	1.1959438
H	1.4843044	-0.7816036	1.7935299
H	5.5952253	-1.8865409	1.2662072
H	3.5273391	-1.8885751	2.6369340
H	5.5951613	-0.7742107	-0.9506182
H	-2.1766127	3.2584923	-3.3395083
H	-4.4005387	2.4212010	-2.6160932
H	-4.5449762	0.3802447	-1.2284522
H	1.0306804	5.7497165	0.8128961
H	-0.6228866	4.1699517	1.7794110
H	3.5501445	0.3108622	-1.7916988
C	1.0826748	-2.3067397	-1.8178102
H	1.9417089	-1.7740246	-2.1978999
H	-0.5737292	1.7880858	1.1400764
H	-0.1290506	2.0928033	-2.6281937
H	1.8525762	-4.2179883	-2.4059578

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