Supplementary Material for

Photoswitchable Electron-rich Phosphines: Using Light to Modulate the Electron-donating ability of Phosphines

Florenz Buß,[a] Mowpriya Das,[b] Daniel Janssen-Müller,[b,c] Alexander Sietmann,[d] Ankita Das,[b] Lukas F. B. Wilm,[a] Matthias Freitag,[b] Michael Seidl,[d] Frank Glorius*[b] and Fabian Dielmann*[a,d]

a) Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster Corrensstrasse 30, 48149 Münster (Germany)

b) Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster Corrensstrasse 40, 48149 Münster (Germany)
E-mail: Glorius@uni-muenster.de

c) Institut für Organische und Biomolekulare Chemie, Georg-August-Universität Göttingen, Tammannstr. 2, 37077 Göttingen (Germany).

d) Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Center for Chemistry and Biomedicine, Innrain 80-82, A-6020 Innsbruck (Austria)
E-mail: Fabian.Dielmann@uibk.ac.at

CONTENTS:

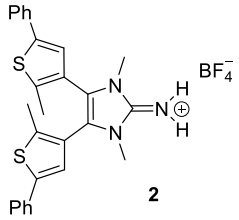
Synthetic Details

General remarks: Unless otherwise noted, all manipulations were performed under an inert atmosphere of dry argon, using standard Schlenk and drybox techniques. Dry and oxygen-free solvents were employed. All glassware was oven-dried at 160 °C prior to use. ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded at 300 K on Agilent DD2 600, Bruker AVANCE I 400, Bruker AVANCE III 400 or Bruker AVANCE II 200 spectrometers. Chemical shifts are given in parts per million (ppm) relative to $SiMe_4$ (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P), and they were referenced to the residual solvent signals ($CDCl_3$: ^{1}H δ_H = 7.26, ^{13}C δ_C = 77.16; CD_2Cl_2: ^{1}H δ_H = 5.32, ^{13}C δ_C = 54.00; C_6D_6: ^{1}H δ_H = 7.16, ^{13}C δ_C = 128.06; CD_3CN: δ_H = 1.94, ^{13}C δ_C = 118.26; toluene-d_8: ^{1}H δ_H = 2.09, ^{13}C δ_C = 20.40; THF-d_8: ^{1}H δ_H = 1.73, ^{13}C δ_C = 67.57) or internally by the instrument after locking and shimming to the deuterated solvent (^{31}P). Chemical shifts (δ) are reported in ppm. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, p = pentet, sept = septet, m = multiplet, br = broad signal. Mass spectrometry was recorded using an Orbitrap LTQ XL (Thermo Scientific) spectrometer. IR spectra were obtained on a Bruker Alpha Spectrometer. UV/vis spectra were acquired using a Perkin-Elmer Lambda 35 UV/vis Spectrometer in 6Q Spectrosil quartz cuvettes (Starna) with 1.0 cm path lengths and 3.0 mL sample solution volumes. Photochemical reactions were monitored by UV/vis and/or NMR spectroscopy were performed in the aforementioned quartz cuvettes using 4.0 mL sample solution volumes at substrate concentrations of 0.1 mM. The irradiation source for photochemical reactions was a self-designed photoreactor (*vide infra*).

Reagents and Handling: DTE-annulated imidazolium salt **1** was prepared according to the reported procedure.[1] $P(tmg)_3$•HCl was prepared as published.[2] All other compounds were purchased from commercial sources (Sigma Aldrich, Alfa Aesar, abcr GmbH, Strem Chemicals) and used as received.

Preparation of iminium salt **2** and imine **9**

DTE-annulated N-heterocyclic iminium salt 2: DTE-annulated imidazolium salt **1**[1] (160 mg, 284 µmol, 1.00 eq.) was dissolved in DCM (10 mL) and NH_3 (g) was bubbled through the solution for 30 min. The reaction mixture was stirred for 16 h and the solvent was removed *in vacuo*. The residue was dissolved in H_2O and $NaBF_4$ (100 mg, 911 µmol, 3.20 eq) was added. The precipitated solid was filtered, washed with Et_2O (3 x 5 mL) and dried for 16 h at 80 °C. **2** was obtained as a white solid in 93% yield (143 mg, 263 µmol).



2

Note: Although the DTE-annulated N-heterocyclic iminium salt can be obtained in a straightforward fashion, the synthesis of **1** involves several steps making **2** quite valuable.[1] We therefore developed a recycling protocol to recover iminium salt **2** from subsequent uses with respect to the preparation of PS-IAPs (*vide infra*), because the polar P–N bond of the free PS-IAPs is sensitive towards hydrolysis: A collected mixture of species containing PS-IAPs and the corresponding hydrolysis products was treated with an excess of HCl in diethyl ether and was then purified via flash column chromatography using silica with DCM/methanol (19:1 to 9:1, v/v) as the eluent. The recovered compound **2'** (chloride counteranion instead of BF_4^-) was obtained analytically pure and was reused for the synthesis of PS-IAPs such as **3-o**, **4-o** or **5-o** or the photoswitchable imine **9**.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.90 (s, 2H, NH), 7.50 (d, $^3J_{HH}$ = 7.3 Hz, 4H, Ph), 7.37 (dd, $^3J_{HH}$ = 7.3 Hz, 4H, Ph), 7.28 (t, $^3J_{HH}$ = 7.3 Hz, 2H, Ph), 7.04 (br, 2H, *thiophene*-H), 3.72 (s, 6H, NCH_3), 2.05 (br, 6H, *thiophene*-CH_3) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 148.0 (NCN_2), 142.5 (SCC_{aryl}), 140.5 ($SCCH_3$), 133.5, 129.2, 128.1, 125.7, 123.9, 123.4 (br.), 121.3, 32.6 (2xNCH_3), 14.2 (2xCH_3) ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ = -151.0 ppm.

HRMS (ESI): m/z calc. for $[C_{27}H_{26}N_3S_2]^+$ $(M)^+$ 456.15627, found 456.15607.

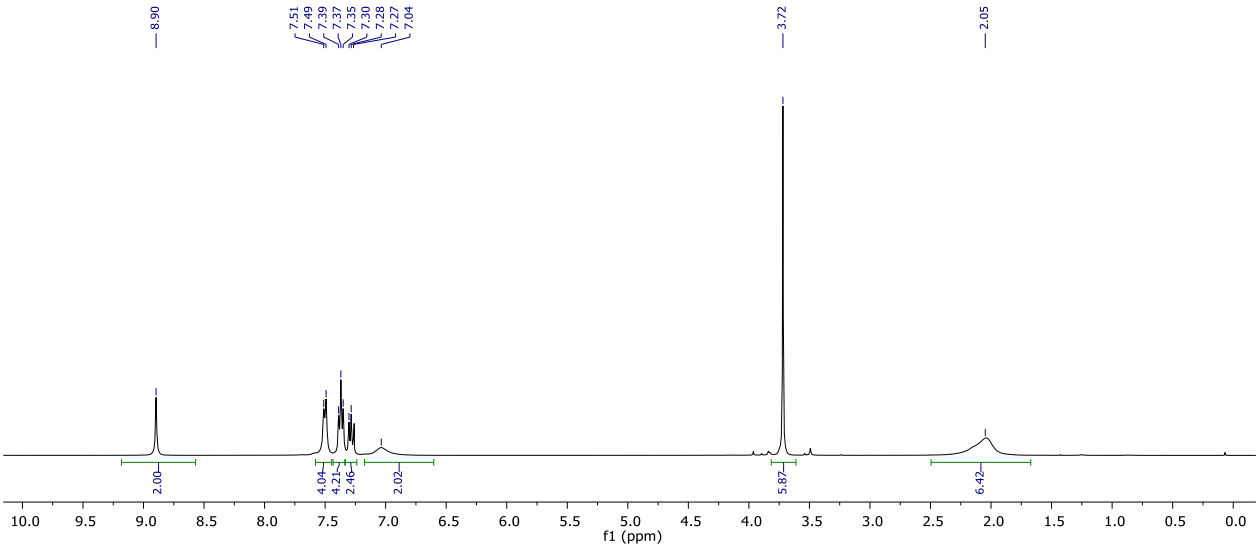


Figure S1: ^{1}H NMR spectrum ($CDCl_3$, 300 K, 400 MHz) of **2**.

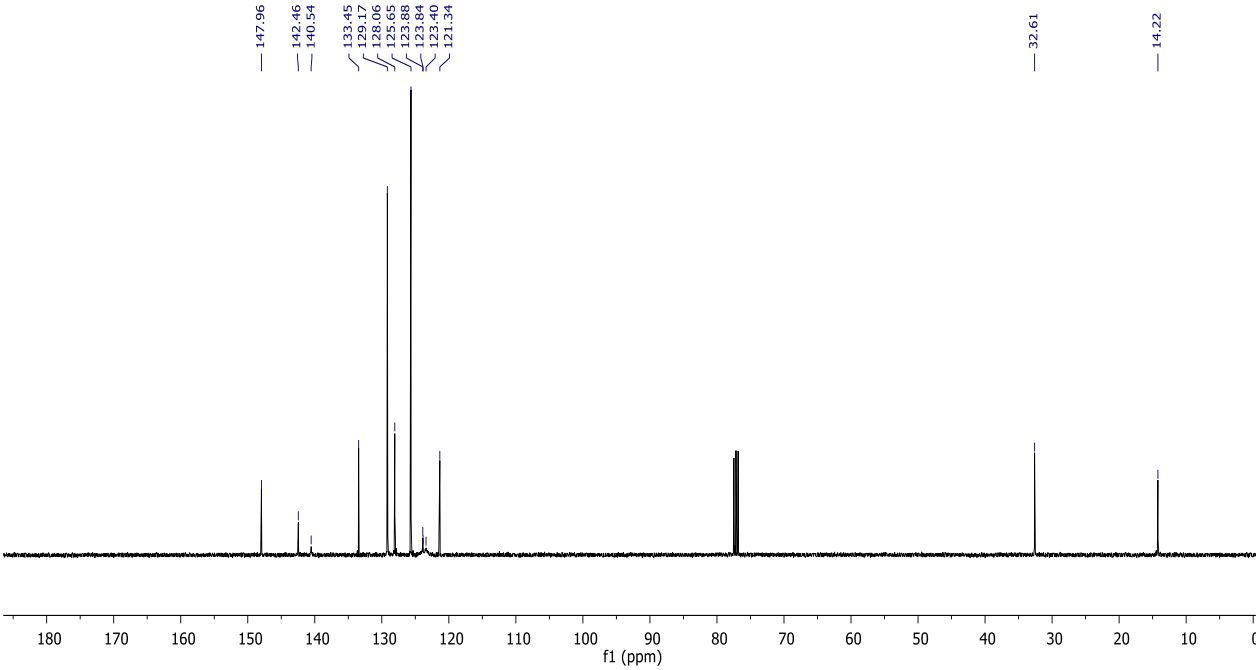


Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 300 K, 101 MHz) of **2**.

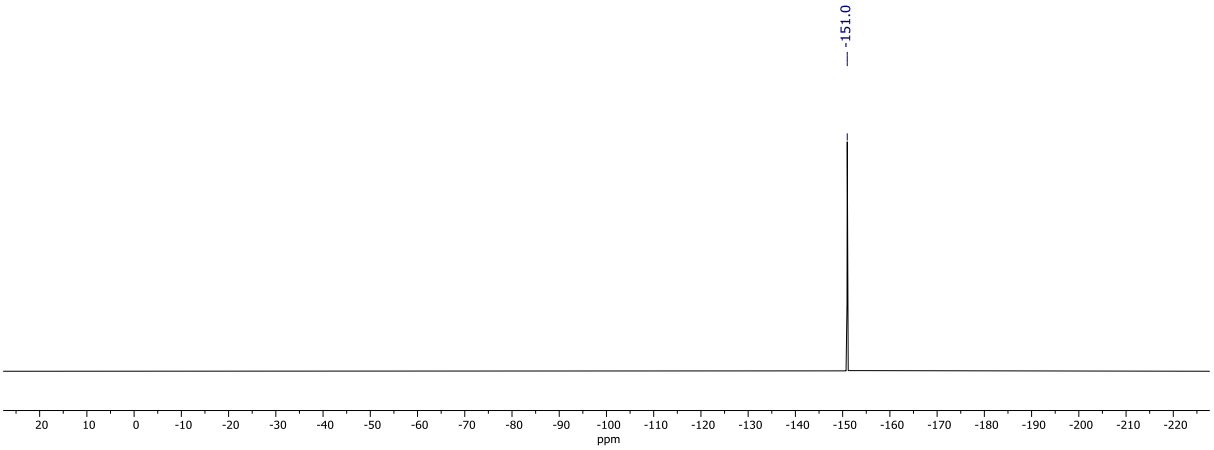
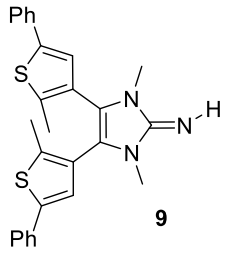


Figure S3: ^{19}F NMR spectrum ($CDCl_3$, 300 K, 376 MHz) of **2**.

DTE-annulated N-heterocyclic imine 9: Iminium salt **2** (127 mg, 233 µmol) was dissolved in THF (3 mL) and a solution of KO*t*Bu (26 mg, 233 µmol) in THF (2 mL) was added dropwise. The resulting suspension was stirred for 2 h at room temperature and the solvent was removed *in vacuo*. The residue was extracted with diethyl ether (2 x 3 mL). The solvent was removed *in vacuo* and **9** was obtained as a white solid in 95% yield (101 mg, 222 µmol).



9

^{1}H-NMR (400 MHz, THF-d_8): δ = 8.03 (d, $^{3}J_{HH}$ = 7.3 Hz, 4H, Ph), 7.81 (dd, $^{3}J_{HH}$ = 7.3 Hz, 4H, Ph), 7.77-7.67 (br, 2H, *thiophene*-H), 7.70 (t, $^{3}J_{HH}$ = 7.3 Hz, 2H, Ph), 4.71 (s, br, 1H, NH), 4.07 (s, 3H, NCH_3), 2.51 (s, br, 6H, CH_3), 2.21 (s, 3H, NCH_3) ppm.

^{13}C{^{1}H}-NMR (101 MHz, THF-d_8): δ = 156.1 (NCN_2), 141.9 (SCC_{Aryl}), 138.6 ($SCCH_3$), 135.3 (C_q), 129.8 (Aryl-CH), 129.1 (Aryl-CH), 128.3 (*thiophene*-CH), 126.2 (aryl-CH), 125.7 (*imidazol*-C_q), 118.4 (*thiophene*-C_q), 33.6 (NCH_3), 29.8 (NCH_3), 14.3 (2xCH_3) ppm.

HRMS (ESI): m/z calc. for $[C_{27}H_{26}N_3S_2]^+$ $(M+H)^+$ 456.15627, found 456.15950.

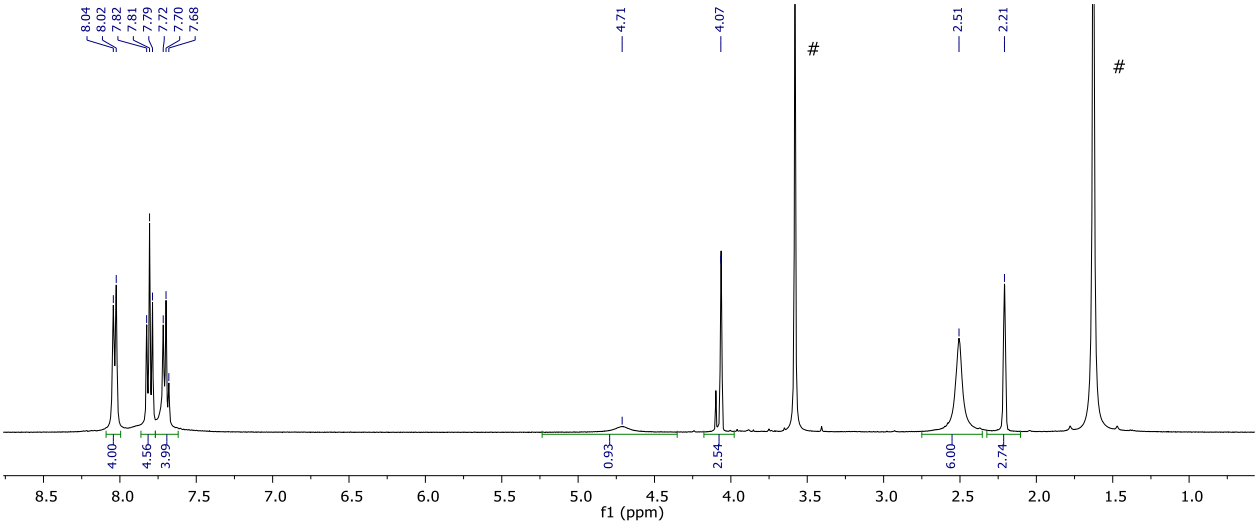


Figure S4: ^{1}H NMR spectrum (THF-d_8, 300 K, 400 MHz) of **9**.

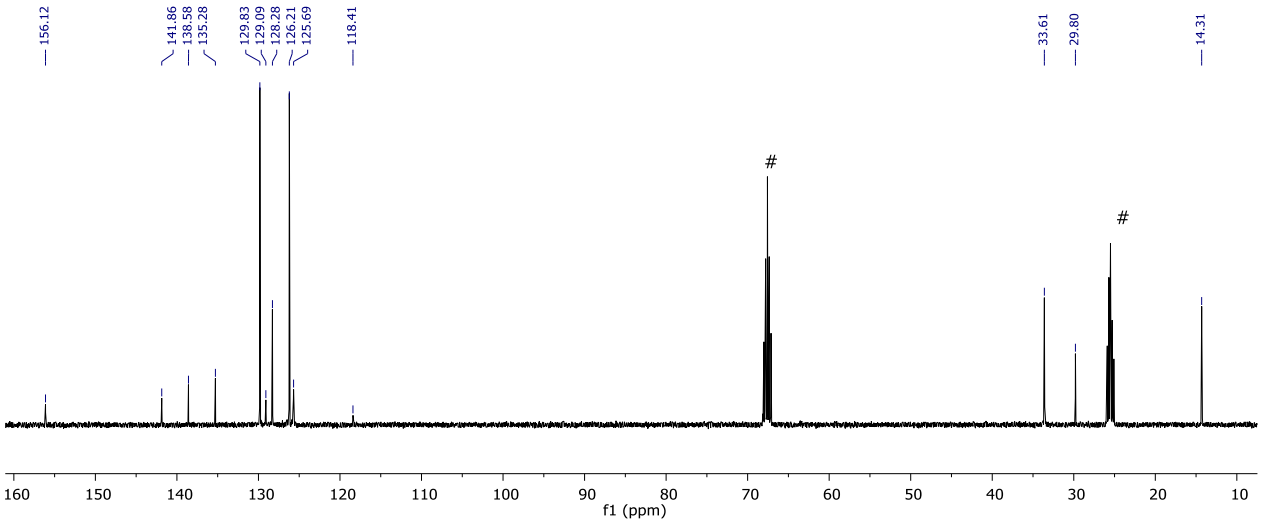
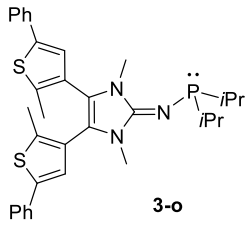


Figure S5: $^{13}C\{^{1}H\}$ NMR spectrum (THF-d_8, 300 K, 101 MHz) of **9**.

Preparation of phosphines **3-o**, **4-o**, and **5-o**

DTE-annulated (imidazolin-2-ylidenamino)diisopropylphosphine 3-o: A solution of *n*BuLi (1.18 mL, 1.355 mmol, 1.6 M in n-hexane, 2 eq.) was added dropwise to a stirred solution of **2** (368 mg, 0.677 mmol, 1 eq.) in THF (5 mL) at –78 °C. After complete addition, the cold bath was removed, and the solution was stirred at room temperature for 1 h. At –78 °C chlorodiisopropylphosphine (0.37 mL, 0.677 mmol, 0.25 M in THF, 1 eq.) was added and the stirred reaction was allowed to warm to room temperature overnight. The volatiles were removed *in vacuo* and the residue was extracted with hexane (2 x 5 mL). The solid components were filtered off and the filtrate was evaporated to dryness. Phosphine **3-o** was obtained as a purple solid in 93% yield (360 mg, 0.630 mmol). Phosphine **3-o** is soluble in toluene, benzene, THF, fluorobenzene, *n*-hexane and *n*-pentane. An NMR analysis revealed that **3-o** is stable up to 140 °C in THF. **3-o** slowly decomposes in dichloromethane (90% within 45 minutes). The ^{7}Li{^{1}H}NMR spectrum of **3-o** showed no signals, indicating no residual LiCl impurities from its preparation. **3-o** is an air- and light-sensitive (*vide infra*) compound but can be stored under an atmosphere of dry argon in the dark for more than one year without decomposition.



3-o

^{1}H NMR (400 MHz, C_6D_6): δ = 7.43 (m, 4H, aryl-H), 7.10-7.06 (m, 4H, aryl-H), 7.02-6.98 (m, 2H, aryl-H), 6.87 (m, 2H, thiophen/vinyl-H), 3.39 (s, br, 6H, N-CH_3), 1.97 (sept, $^{3}J_{HH}$ = 6.9 Hz, 2H, CH(CH_3)$_2$), 1.81 (s, 6H, *thiophen*-CH_3), 1.45 (m, 6H, CH(CH_3)$_2$, 1.34 (m, 6H, CH(CH_3)$_2$.

^{1}H NMR (400 MHz, THF-d_8): δ = 7.58-7.53 (m, 4H, aryl-H), 7.35-7.18 (m, 8H, *aryl*-H and *thiophen/vinyl*-H), 3.36 (s, 6H, N-CH_3), 2.03 (s, br, 6H, *thiophene*-CH_3), 2.19 (sept, $^{3}J_{HH}$ = 6.9 Hz, 2H, CH(CH_3)$_2$), 1.14-0.99 (m, 12H, CH(CH_3)$_2$.

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ = 151.5 (d, $^{2}J_{CP}$ = 17.6 Hz, N_2CN), 141.5 (S-C=C-aryl), 138.1 (S-C=C-CH_3), 134.4 (C=C), 129.2 (aryl-CH), 125.7 (aryl-CH), 124.7 (aryl-CH), 118.8 (C=C), 32.4 (d, $^{4}J_{CP}$ = 13.1 Hz, NCH_3), 28.7 (d, PCH(CH_3)$_2$)), 19.4 (d, J_{CP} = 20.6 Hz, PCH(CH$_3$)$_2$), 17.9, 13.9 (CH_3).

^{31}P NMR (C_6D_6, 162.0 MHz): δ = 60.7 (m).

^{31}P{^{1}H} NMR (C_6D_6, 162.0 MHz): δ = 60.7 (s).

^{31}P NMR (THF-d_8, 162.0 MHz): δ = 59.6 (m).

^{31}P{^{1}H} NMR (THF-d_8, 162.0 MHz): δ = 59.6 (s).

HRMS (ESI): m/z calc. for $[C_{33}H_{39}N_3PS_2]^+$ $(M+H)^+$ 572.23175, found 572.23316.

CHN analysis: found (calculated) C 68.81 (69.32) H 6.52 (6.70) N 7.18 (7.35).

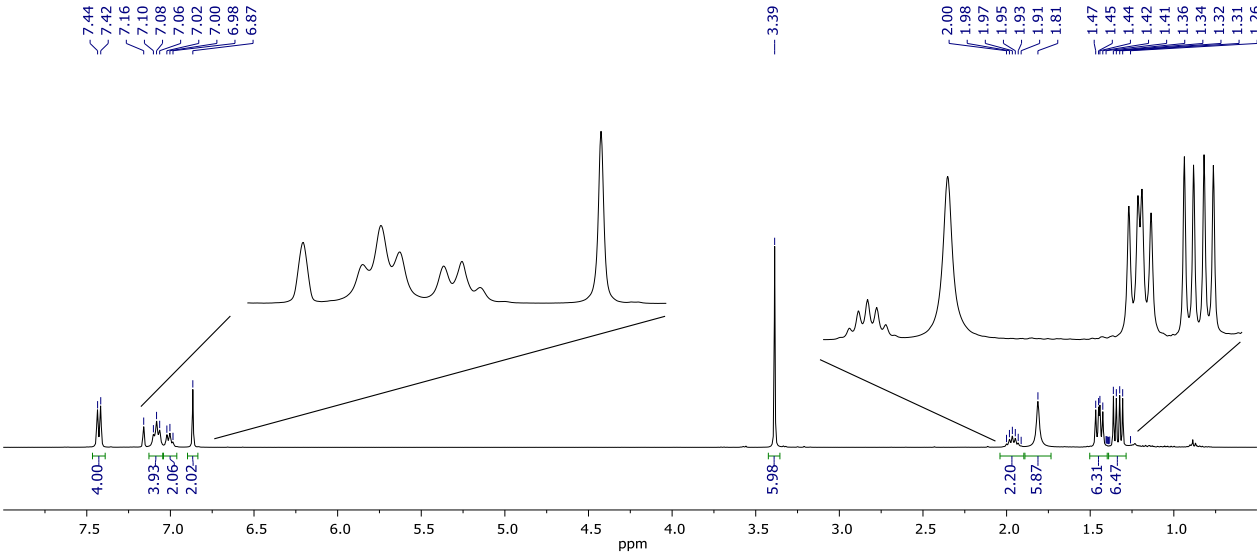


Figure S6: ^{1}H NMR spectrum (C_6D_6, 300 K, 400 MHz) of **3-o**.

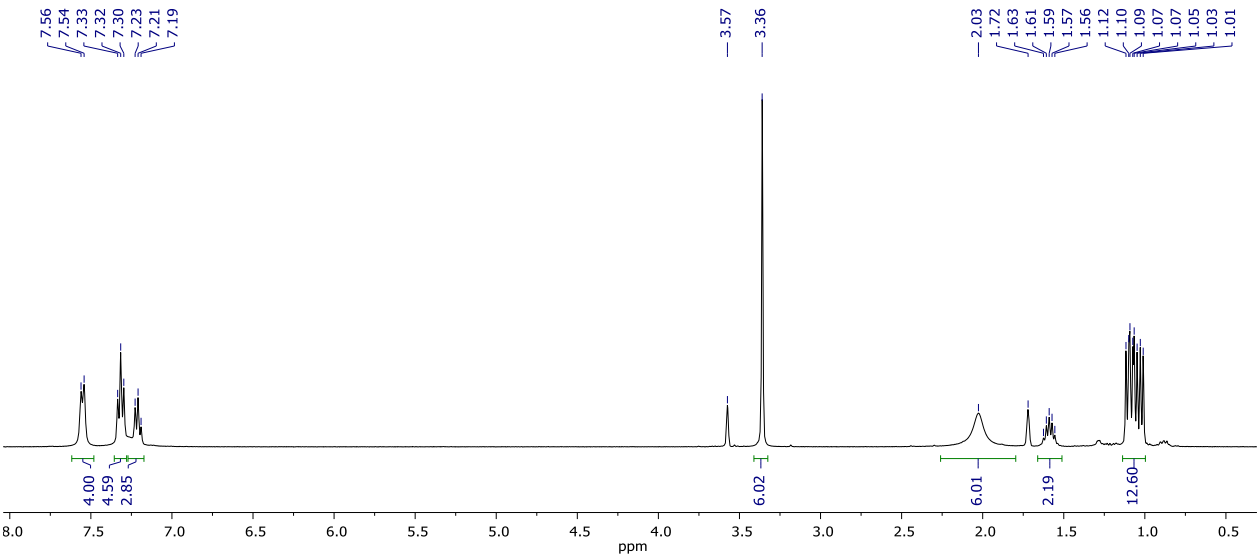


Figure S7: ^{1}H NMR spectrum (THF-d_8, 300 K, 400 MHz) of **3-o**.

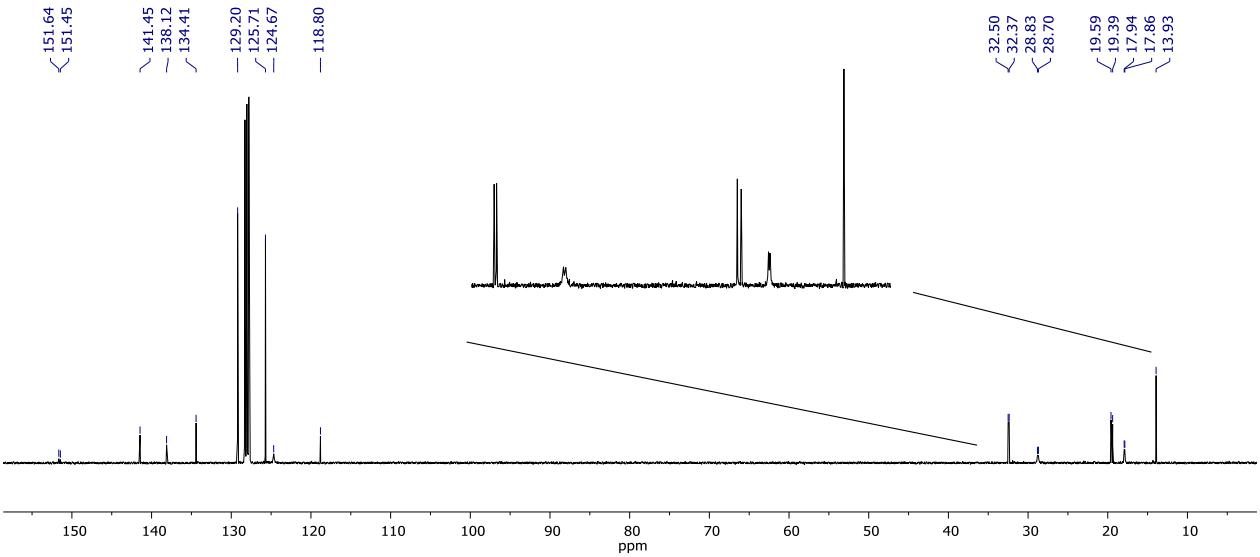


Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 300 K, 101 MHz) of **3-o**.

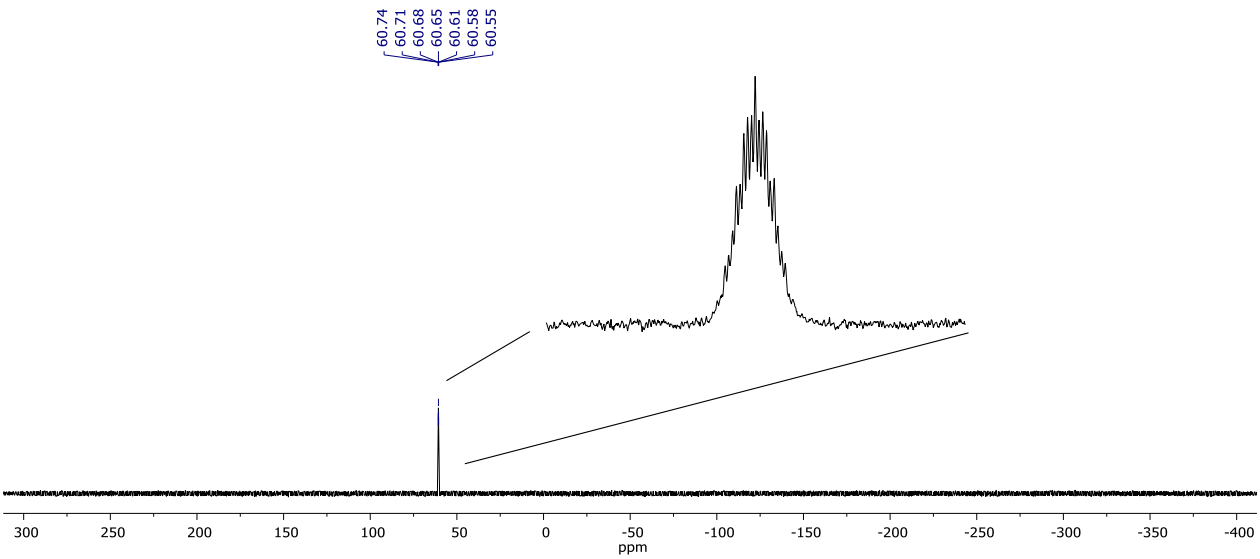


Figure S9: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **3-o**.

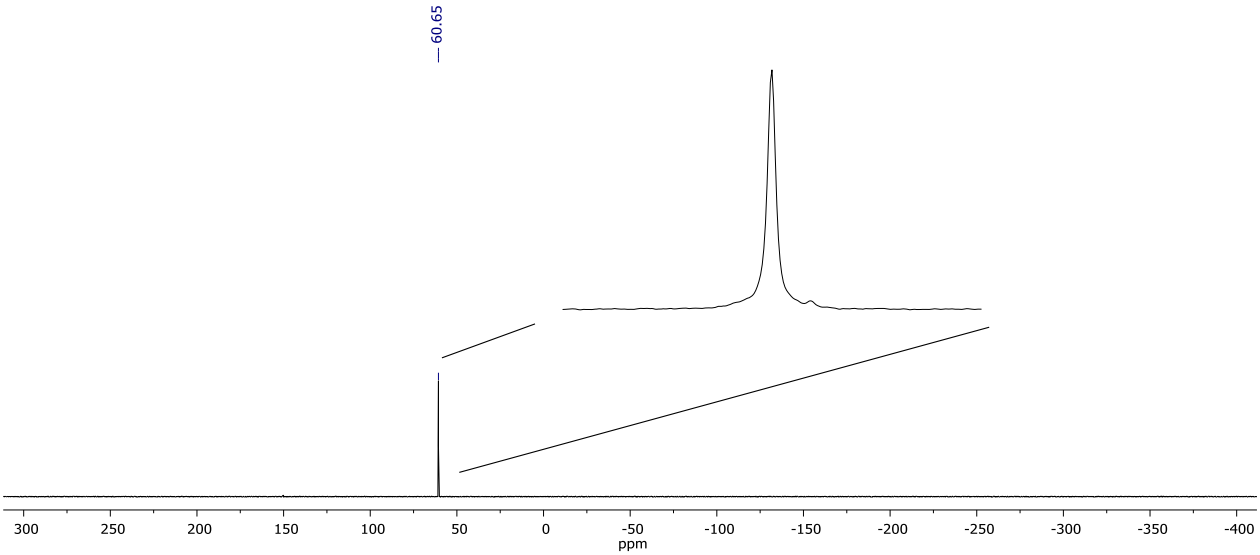


Figure S10: $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6, 300 K, 162 MHz) of **3-o**.

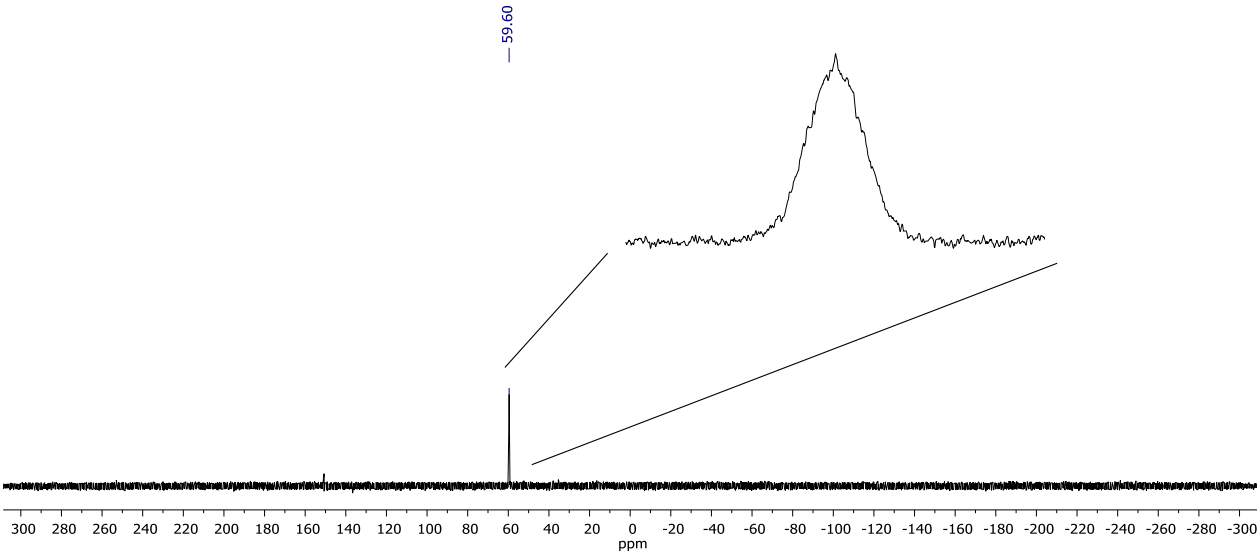


Figure S11: ^{31}P NMR spectrum (THF-d_8, 300 K, 162 MHz) of **3-o**.

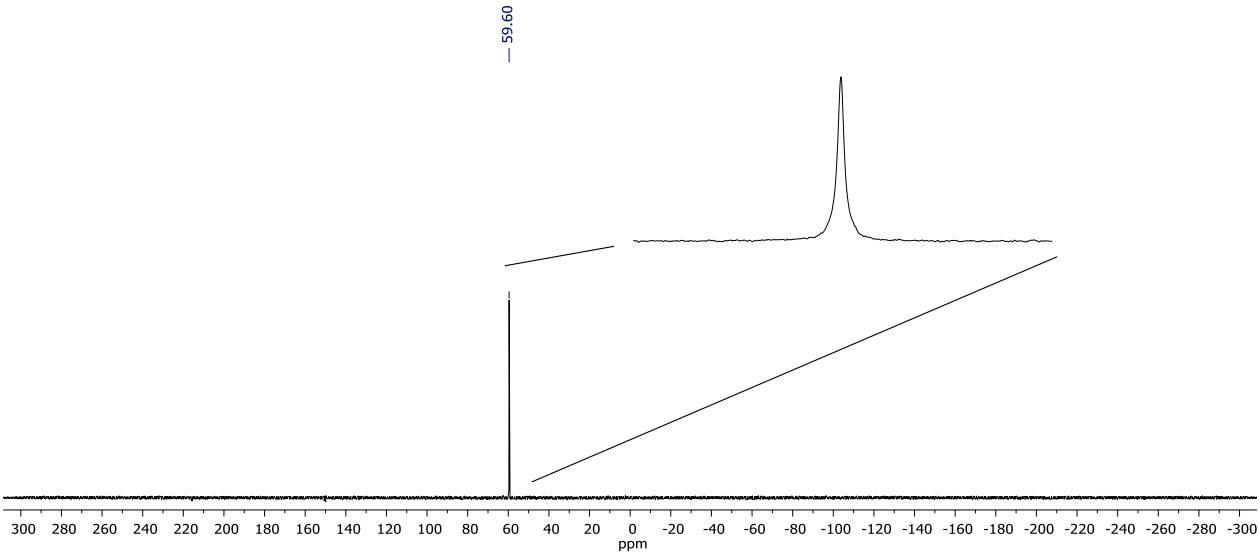


Figure S12: $^{31}P\{^{1}H\}$ NMR spectrum (THF-d_8, 300 K, 162 MHz) of **3-o**.

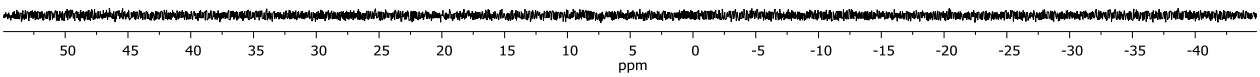
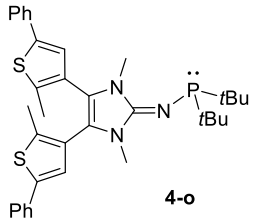


Figure S13: $^{7}Li\{^{1}H\}$ NMR spectrum (C_6D_6, 300 K, 155.8 MHz) of **3-o**.

DTE-annulated (imidazolin-2-ylidenamino)di-*tert*-butylphosphine 4-o: A solution of *n*BuLi (1.77 mL, 2.033 mmol, 1.6 M in n-hexane, 2 eq.) was added dropwise to a stirred solution of **2** (552 mg, 1.015 mmol, 1 eq.) in THF (5 mL) at –78 °C. After complete addition, the cold bath was removed and the solution was stirred at room temperature for 1 h. At –78 °C chlorodi-*tert*-butylphosphine (1.85 mL, 1.015 mmol, 0.55 M in THF, 1 eq.) was added and the stirred reaction was allowed to warm to room temperature overnight. The volatiles were removed *in vacuo* and the residue was extracted with toluene (2 x 6 mL). The solid components were filtered off and the filtrate was evaporated to dryness. Phosphine **4-o** was isolated as a purple solid in 97% yield (590 mg, 0.985 mmol). Phosphine **4-o** is soluble in toluene, benzene, THF, fluorobenzene, *n*-hexane and *n*-pentane. An NMR analysis revealed that **4-o** is stable up to 140 °C in THF. **4-o** is air- and light-sensitive (*vide infra*) but can be stored under an atmosphere of dry argon in the dark.



4-o

^{1}H NMR (400 MHz, C_6D_6): δ = 7.49 (m, 4H, *aryl*-H), 7.14 (m, 4H, *aryl*-H), 7.07 (m, 2H, *aryl*-H), 6.99 (s, br, 2H, *thiophen/vinyl*-H), 3.51 (s, br, 6H, NC*H*$_3$), 1.90 (s, 6H, *thiophen/vinyl*-CH_3), 1.49 (d, 18H, $^{3}J_{PH}$ = 10.9 Hz, P-C-C*H*$_3$.

^{1}H NMR (400 MHz, THF-d_8): δ = δ = 7.55 (m, 4H, *aryl*-H), 7.37-7.16 (m, 4H, *aryl*-H, 4H, *aryl*-H, 2H, *thiophen/vinyl*-H), 3.42 (s, 6H, NC*H*$_3$), 2.04 (s, br, 6H, *thiophen*-CH_3), 1.11 (d, 18H, $^{3}J_{PH}$ = 10.9 Hz, P-C-CH_3).

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ = 150.7 (d, $^{2}J_{PC}$ = 17.4 Hz, N_2CN), 141.5 (S-C=C-*aryl*), 138.1 (S-C-CH_3), 134.4 (C=C), 129.2 (*aryl*-CH), 125.3 (*aryl*-CH), 118.7 (*C*=*C*), 34.3 (d, J_{CP} = 22.5 Hz), 32.4 (br, NCH_3), 28.6 (d, J_{CP} = 16.1 Hz), 13.9 (CH_3).

^{31}P NMR (C_6D_6, 162.0 MHz): δ = 72.8 (m).

^{31}P{^{1}H} NMR (C_6D_6, 162.0 MHz): δ = 72.8 (s).

^{31}P NMR (THF-d_8, 162.0 MHz): δ = 72.1 (m).

HRMS (ESI): m/z calc. for $[C_{35}H_{43}N_3PS_2]^+$ $(M+H)^+$ 600.26305, found 600.26288.

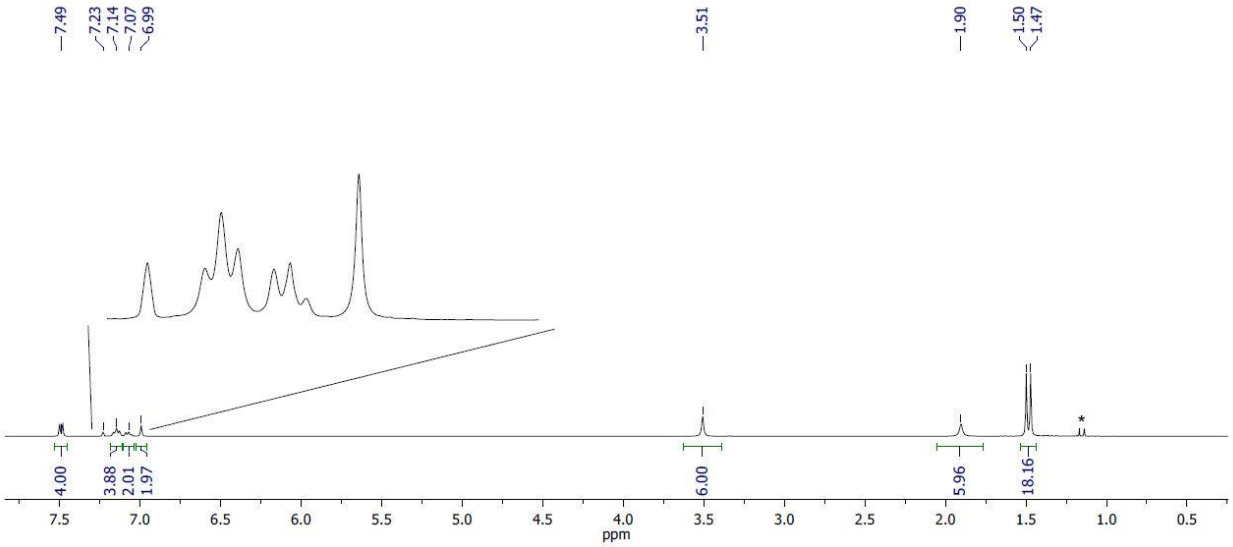


Figure S14: ^{1}H NMR spectrum (C_6D_6, 300 K, 400 MHz) of **4-o**. *impurity

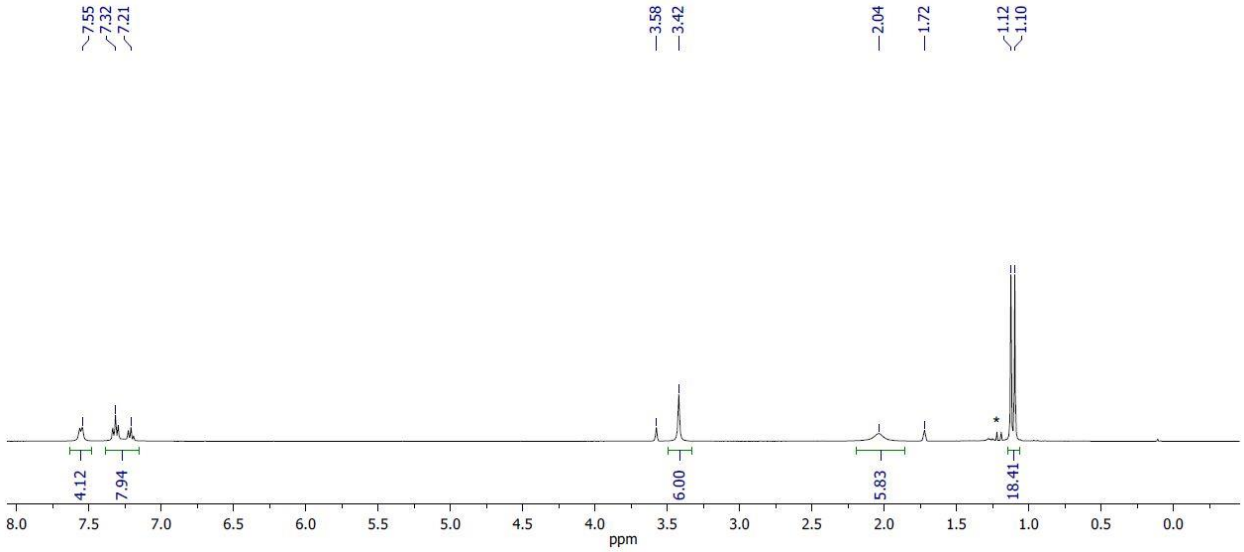


Figure S15: ^{1}H NMR spectrum (THF-d_8, 300 K, 400 MHz) of **4-o**. *impurity

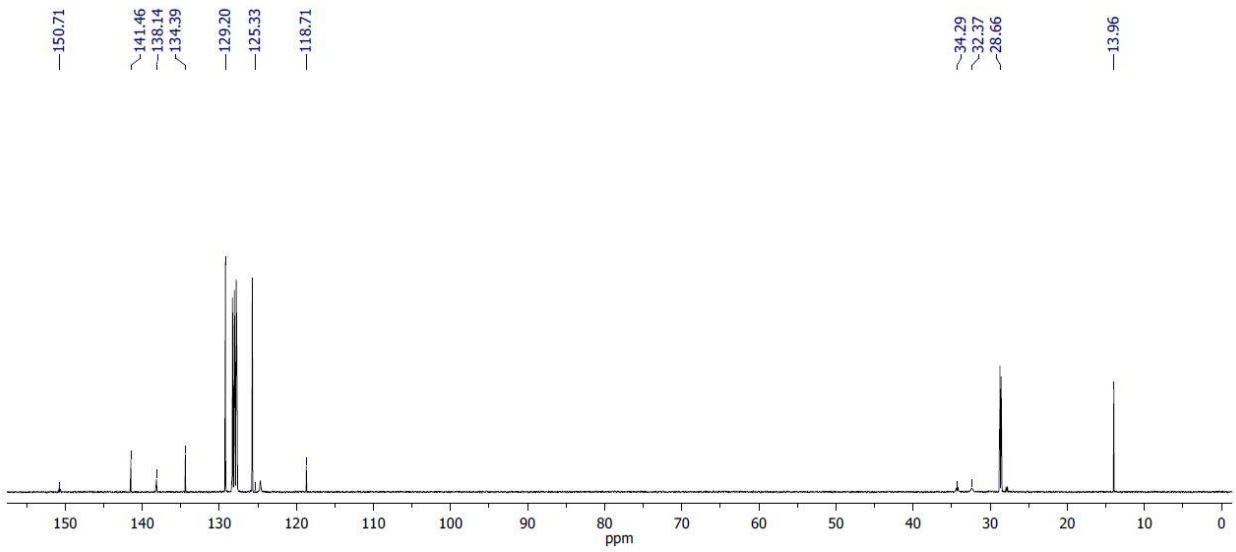


Figure S16: $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 300 K, 101 MHz) of **4-o**.

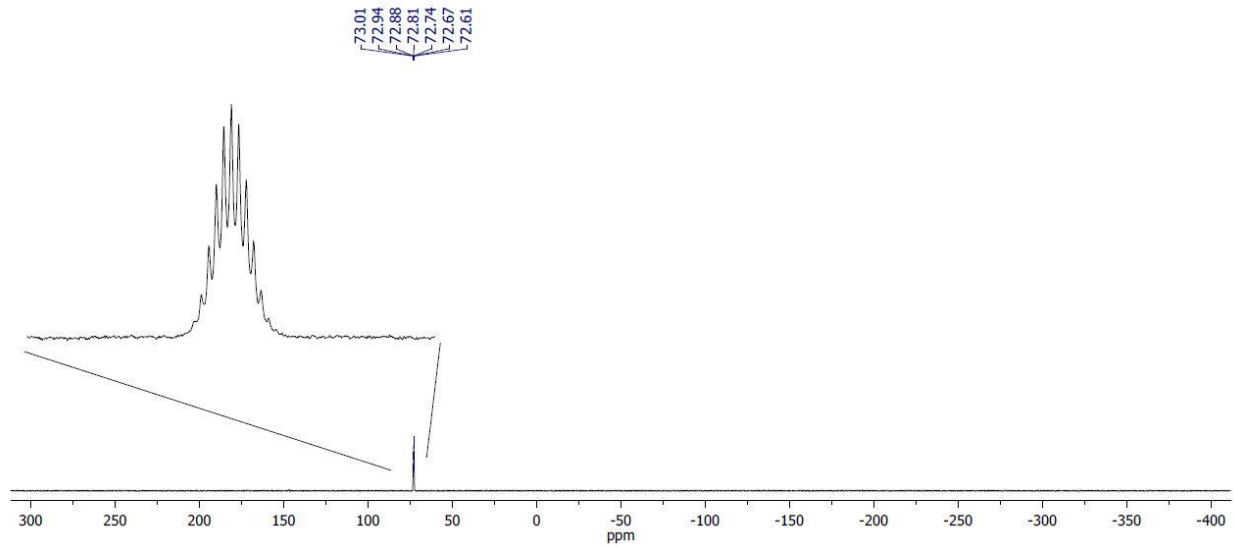


Figure S17: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **4-o**.

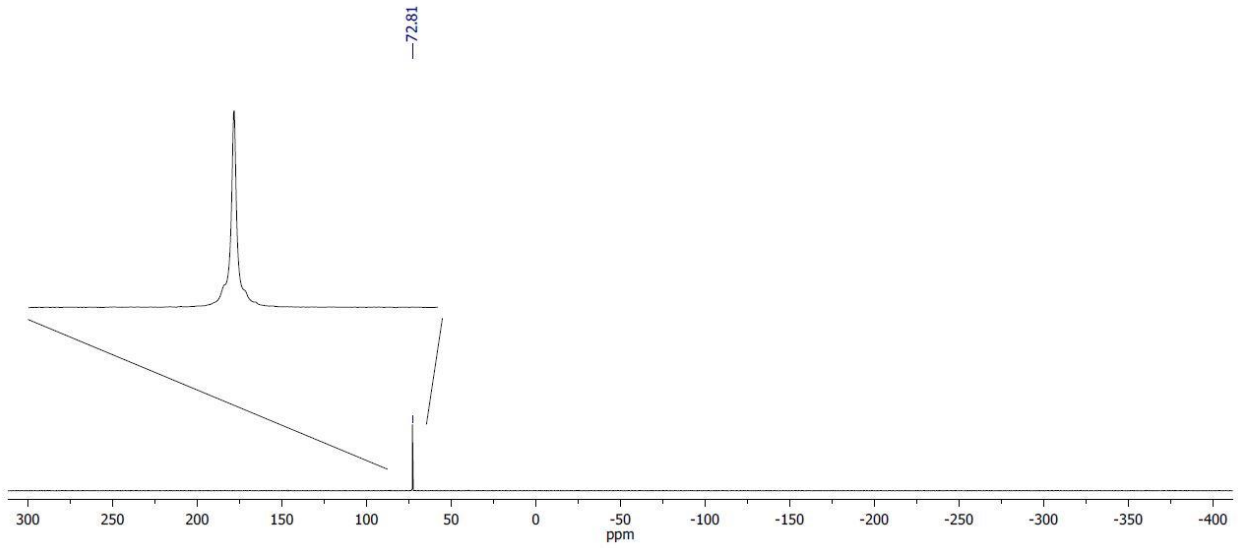


Figure S18: $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6, 300 K, 162 MHz) of **4-o**.

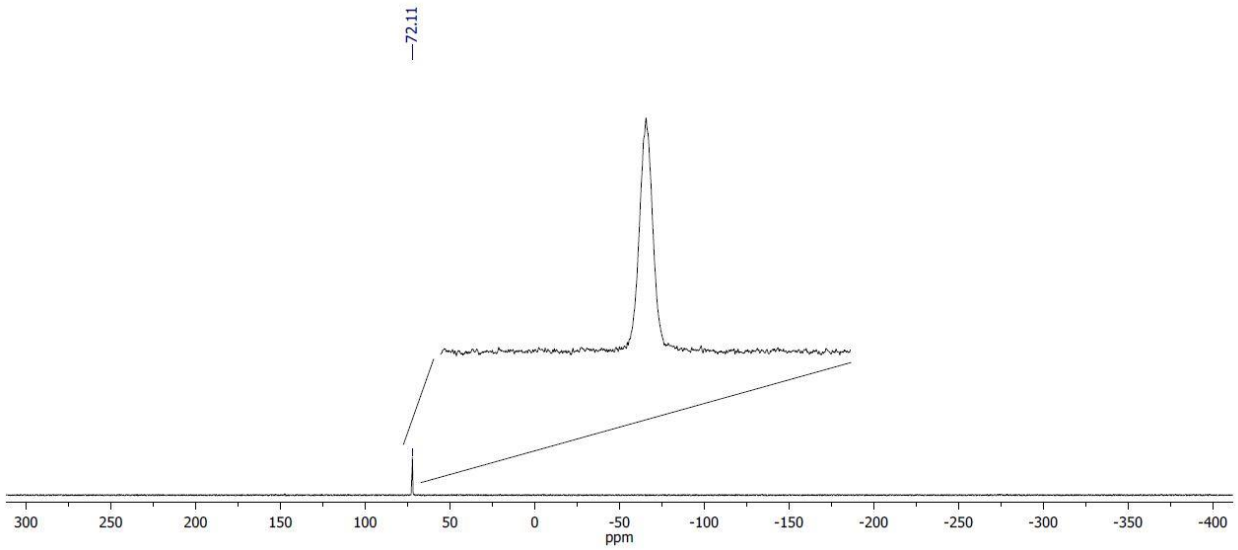
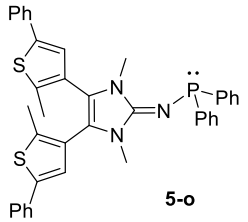


Figure S19: ^{31}P NMR spectrum (THF-d_8, 300 K, 162 MHz) of **4-o**.

DTE-annulated (imidazolin-2-ylidenamino)diphenylphosphine 5-o: A solution of *n*BuLi (0.37 mL, 5.888 mmol, 1.6 M in n-hexane, 2 eq.) was added dropwise to a stirred solution of **2** (160 mg, 0.294 mmol, 1 eq.) in THF (5 mL) at –78 °C. After complete addition, the cold bath was removed, and the solution was stirred at room temperature for 1 h. At –78 °C chlorodiphenylphosphine (0.6 mL, 0.294 mmol, 0.499 M in THF, 1 eq.) was added and the stirred reaction was allowed to warm to room temperature overnight. The volatiles were removed *in vacuo* and the residue was extracted with hexane (2 x 5 mL). the solid components were filtered off and the filtrate was evaporated to dryness. Phosphine **5-o** was isolated as a pale purple solid in 95% yield (179 mg, 0.280 mmol). Phosphine **5-o** is soluble in toluene, benzene, THF, fluorobenzene, *n*-hexane and *n*-pentane. An NMR analysis revealed that **5-o** is stable up to 145 °C in THF. The ^{7}Li{H}NMR spectrum of **5-o** showed no signals, indicating no residual LiCl impurities from its preparation. **5-o** is air- and light-sensitive (*vide infra*) but can be stored under an atmosphere of dry argon in the dark.



5-o

^{1}H NMR (400 MHz, C_6D_6): δ = 8.14 (m, 4H, P-Ph$_2$), 7.43 (m, 4H, *aryl*-H), 7.29 (m, 4H, P-Ph$_2$), 7.12 (m, 4H, *aryl*-H), 7.10 (m, 2H, P-Ph$_2$), 7.02-6.98 (m, 2H, *thiophen/vinyl*-H), 3.30 (s, br, 6H, N-C*H*$_3$), 1.78 (s, 6H, *thiophen*-C*H*$_3$).

^{1}H NMR (400 MHz, THF-d_8): δ = δ = 7.69 (m, 4H, P-Ph$_2$), 7.55 (m, 4H, *aryl*-H), 7.32 (m, 4H, P-Ph$_2$), 7.12 (m, 6H, *aryl*-H and P-Ph$_2$), 7.12 (m, 2H *thiophen/vinyl*-H), 6.83 (*thiophen/vinyl*-H), 3.43 (s, 6H, N-C*H*$_3$), 2.04 (s, br, 6H, *thiophen*-C*H*$_3$).

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ = 141.4 (d, $^{2}J_{PC}$ = 17.6 Hz, N_2CN), 138.2 (S-C=C-*aryl*), 134.1 (S-C-CH$_3$), 130.7 (P-Ph$_2$), 130.5 (P-Ph$_2$), 129.0 (C=C), 125.5 (*aryl*-CH), 124.4 (*aryl*-CH), 118.9 (P-Ph$_2$), 31.6 (d, $^{4}J_{CP}$ = 10.9 Hz, NCH$_3$), 13.7 (CH$_3$).

^{31}P NMR (C_6D_6, 162.0 MHz): δ = 33.8 (m).

^{31}P{^{1}H} NMR (C_6D_6, 162.0 MHz): δ = 33.8 (s).

^{31}P NMR (THF-d_8, 162.0 MHz): δ = 32.7 (m).

^{31}P{^{1}H} NMR (THF-d_8, 162.0 MHz): δ = 32.7 (s).

HRMS (ESI): m/z calc. for $[C_{39}H_{35}N_3PS_2]^+$ $(M+H)^+$ 640.20184, found 640.20045.

CHN analysis: found (calculated) C 72.19 (73.21) H 5.62 (5.36) N 6.53 (6.57).

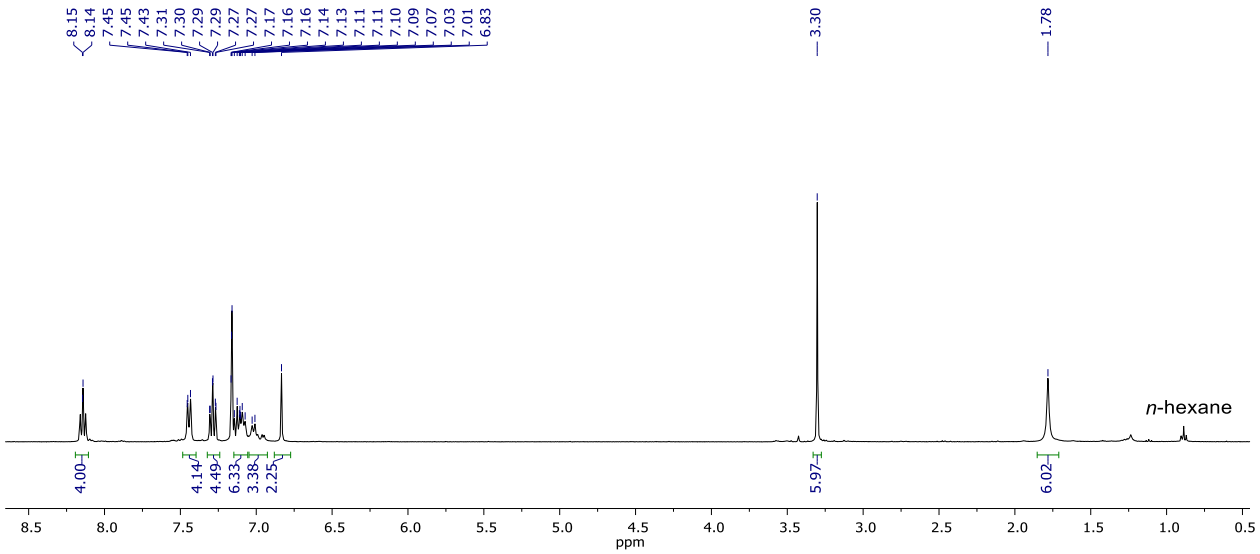


Figure S20: ^{1}H NMR spectrum (C_6D_6, 300 K, 400 MHz) of **5-o**.

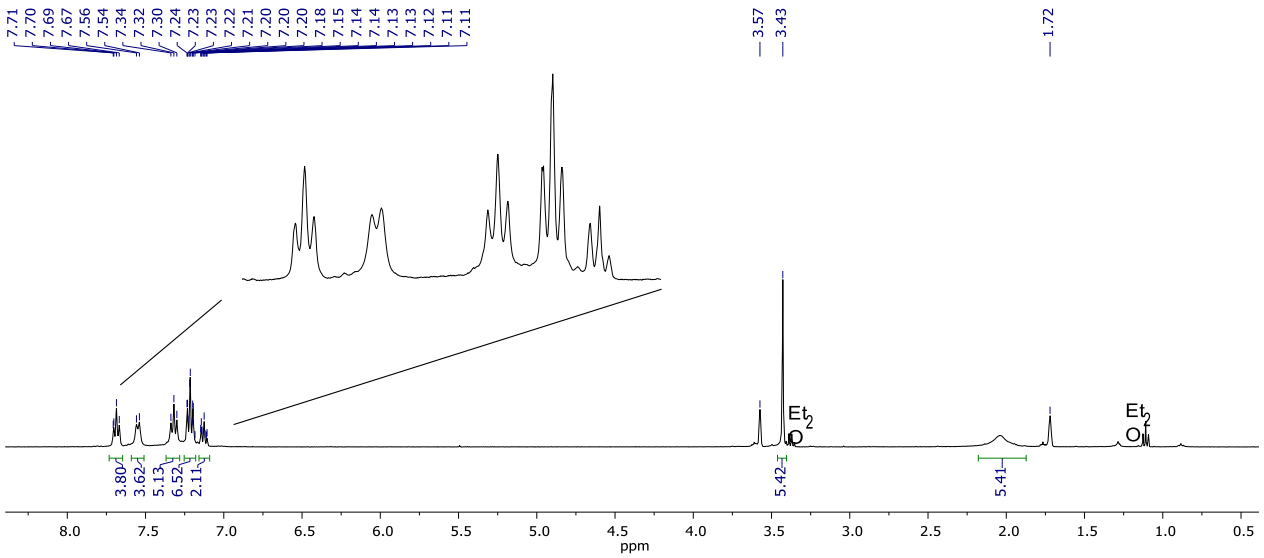


Figure S21: ^{1}H NMR spectrum (THF-d_8, 300 K, 400 MHz) of **5-o**.

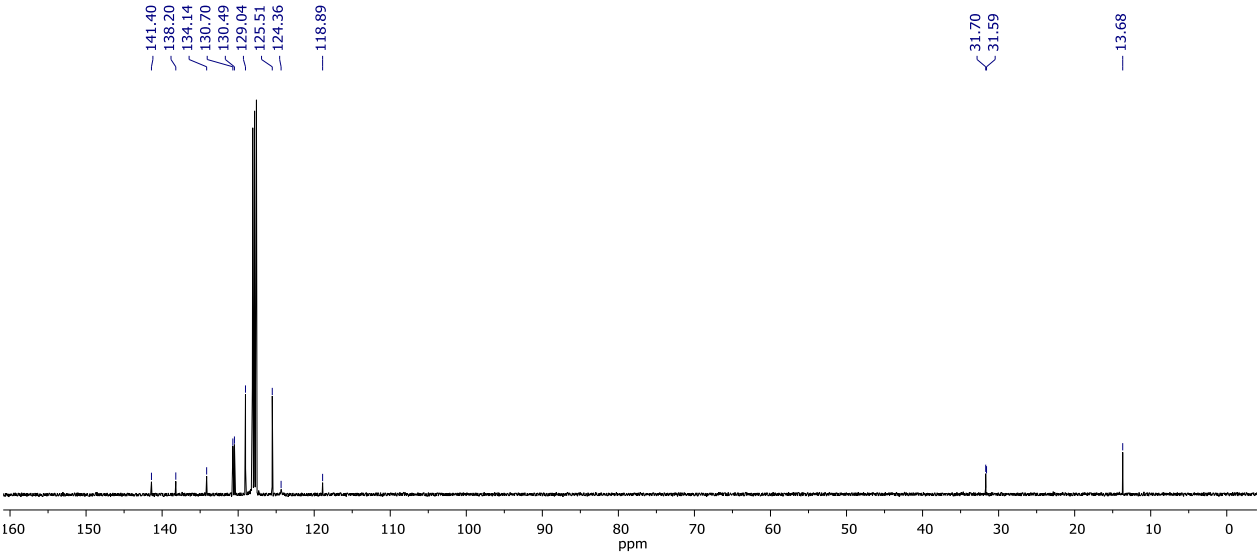


Figure S22: $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 300 K, 101 MHz) of **5-o**.

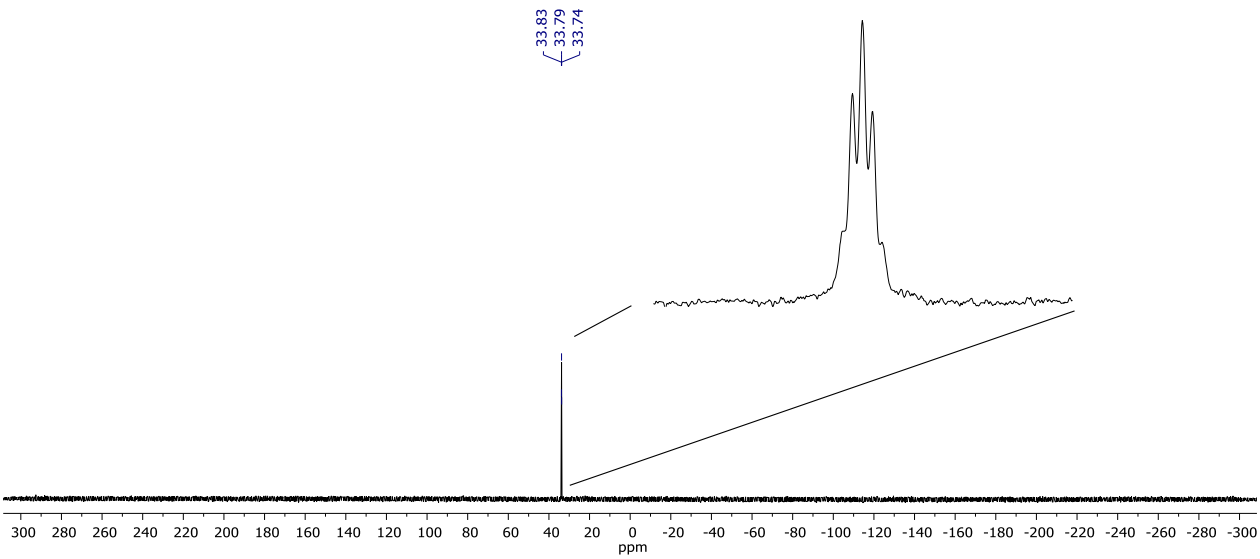


Figure S23: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **5-o**.

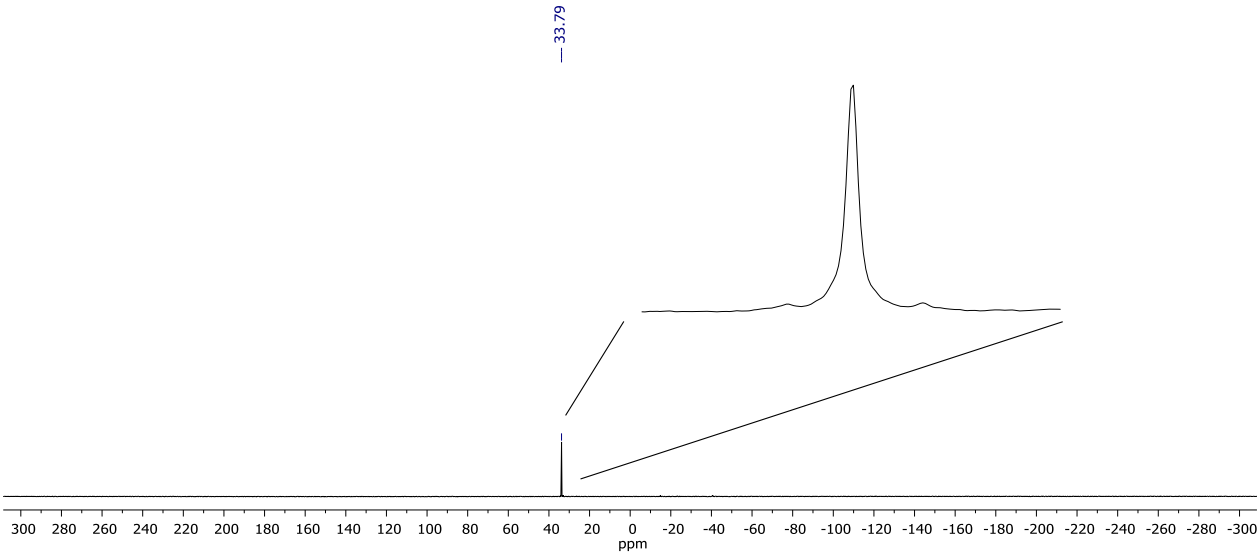


Figure S24: $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6, 300 K, 162 MHz) of **5-o**.

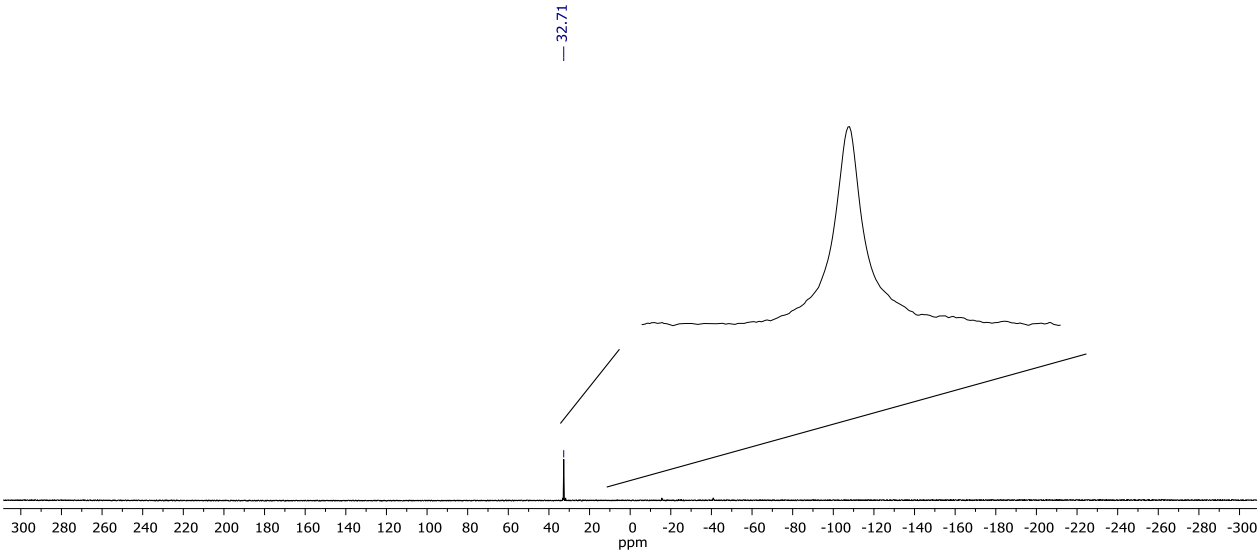


Figure S25: ^{31}P NMR spectrum (THF-d_8, 300 K, 162 MHz) of **5-o**.

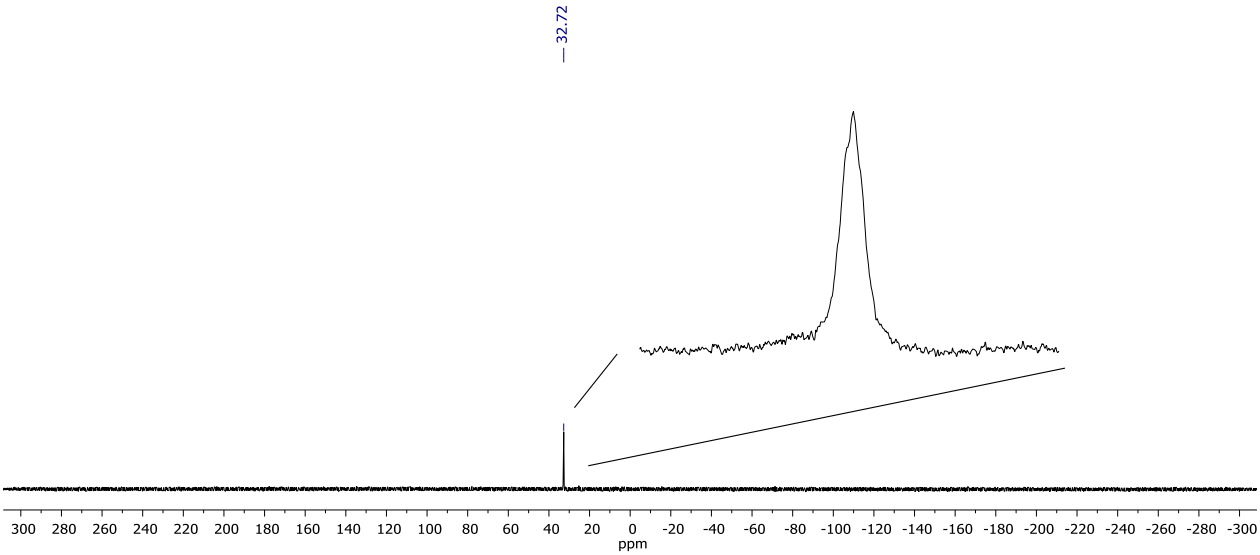


Figure S26: $^{31}P\{^{1}H\}$ NMR spectrum (THF-d_8, 300 K, 162 MHz) of **5-o**.

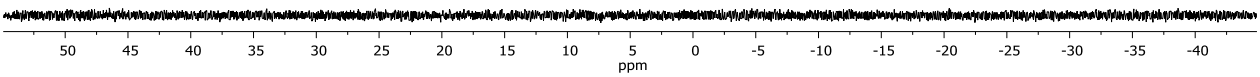


Figure S27: $^{7}Li\{^{1}H\}$ NMR spectrum (C_6D_6, 300 K, 155.8 MHz) of **5-o**.

Photochromism of phosphines **3-o**, **4-o** and **5-o** monitored by ^{1}H and ^{31}P NMR spectroscopy

General procedure: In a quartz NMR tube equipped with a gas-tight cap, a THF-d_8 solution of the photoswitchable phosphine (0.1 mmol) was irradiated with UV light (310 nm, 140 mW) for the time indicated. ^{1}H and ^{31}P NMR spectra were recorded before and after irradiation. Subsequent irradiation of the same NMR tube with 585 nm (145 mW, 1 hour) restored the initial spectra.

Photochromism of phosphine 3-o:

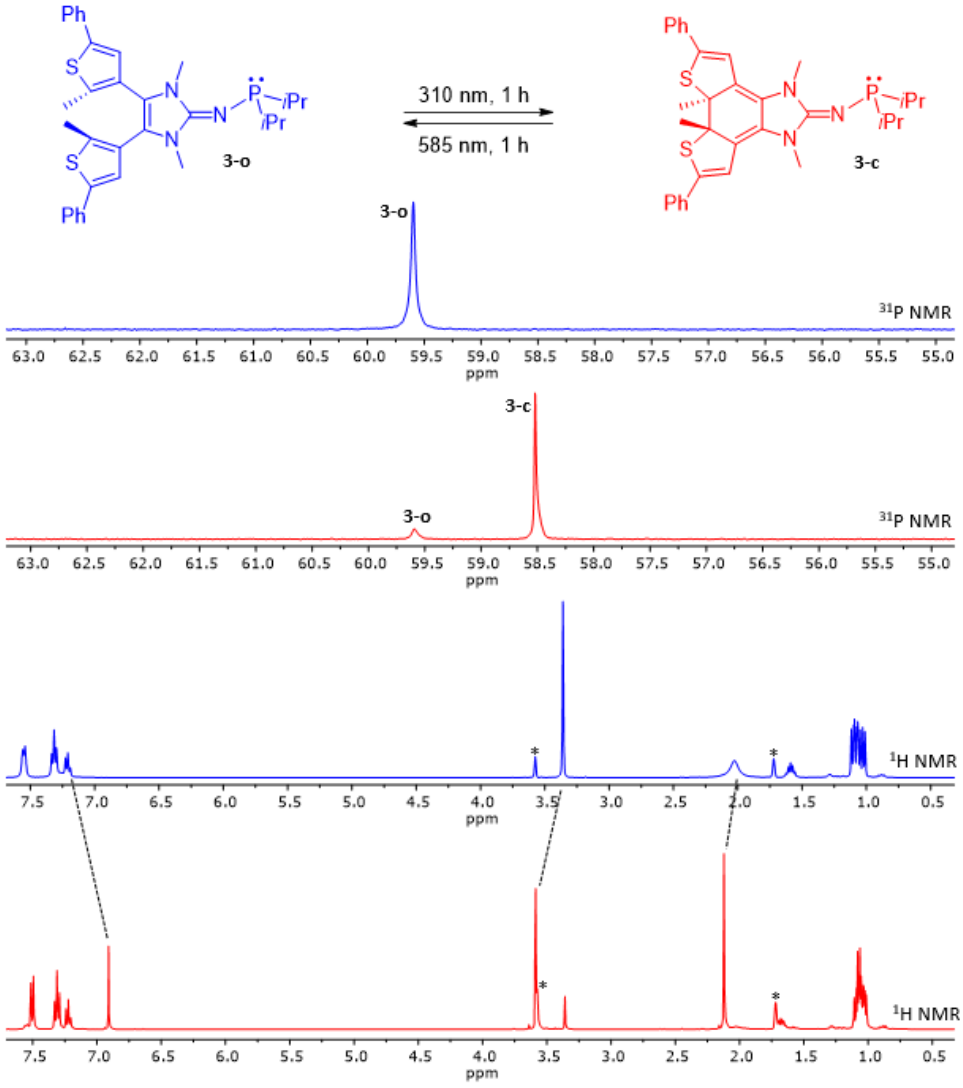


Figure S28: Quantitative ^{31}P NMR spectra (top) and ^{1}H NMR spectra (bottom) of the THF-d_8 solution of **3-o** before (blue spectrum) and after exposure to UV irradiation (λ = 310 nm) for 1 h (red spectrum) showing a photoconversion of 86%. Subsequent irradiation with visible light (λ = 585 nm) for 1 hour restores the initial spectra.

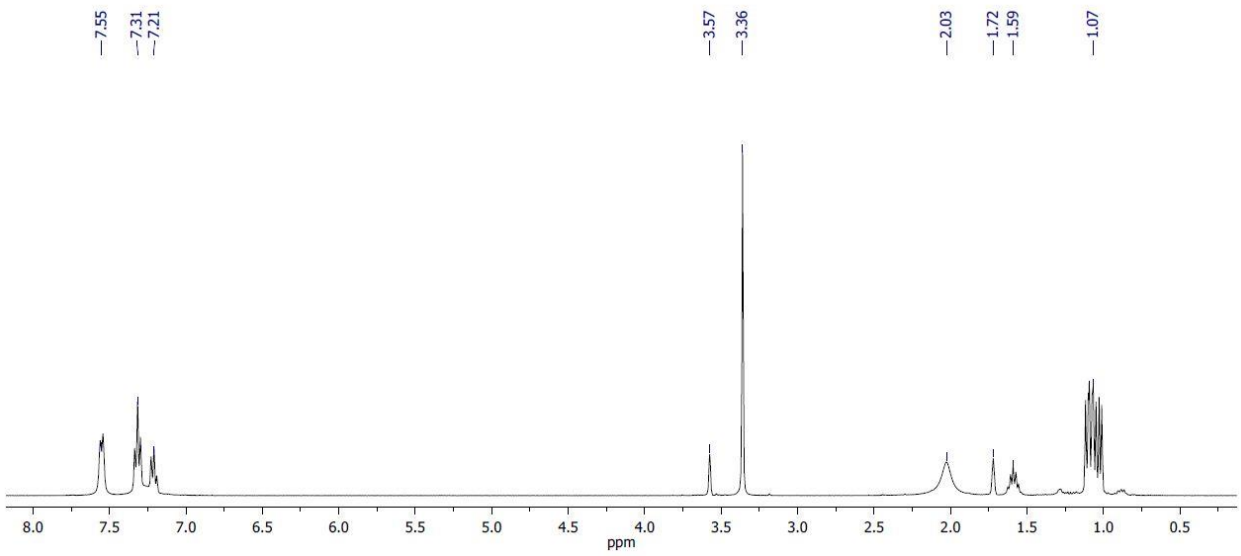


Figure S29: ^{1}H NMR spectrum (THF-d_8, 300 K, 400 MHz) after irradiation of **3-o** with UV light (310 nm, 140 mW) for 30 minutes in a quartz glass NMR tube.

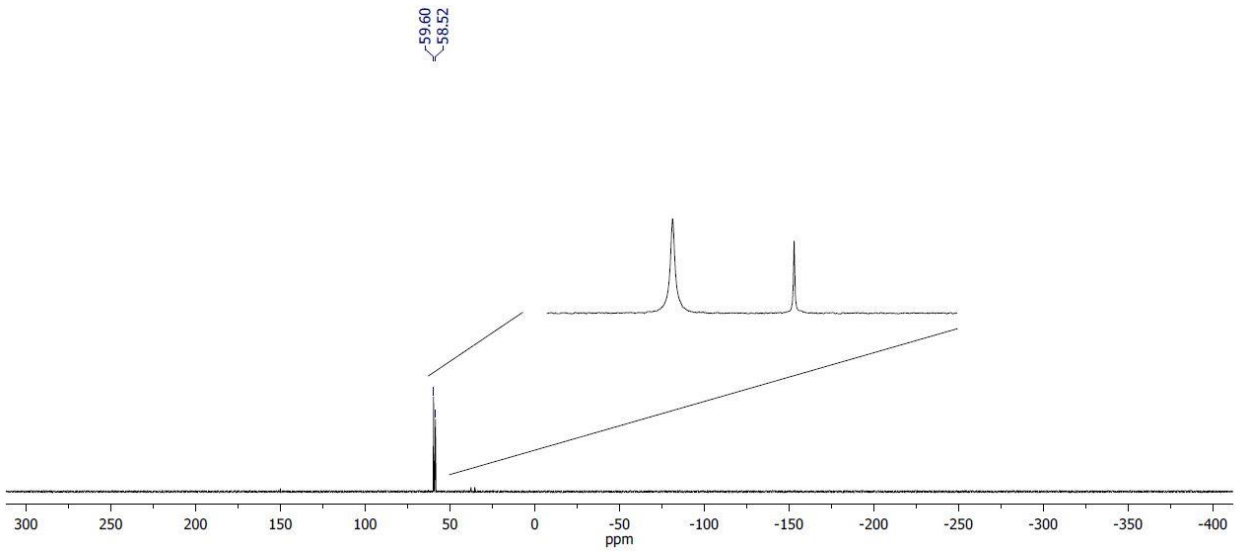


Figure S30: ^{31}P{^{1}H} NMR spectrum (THF-d_8, 300 K, 162 MHz) after irradiation of **3-o** with UV light (310 nm, 140 mW) for 30 minutes in a quartz glass NMR tube.

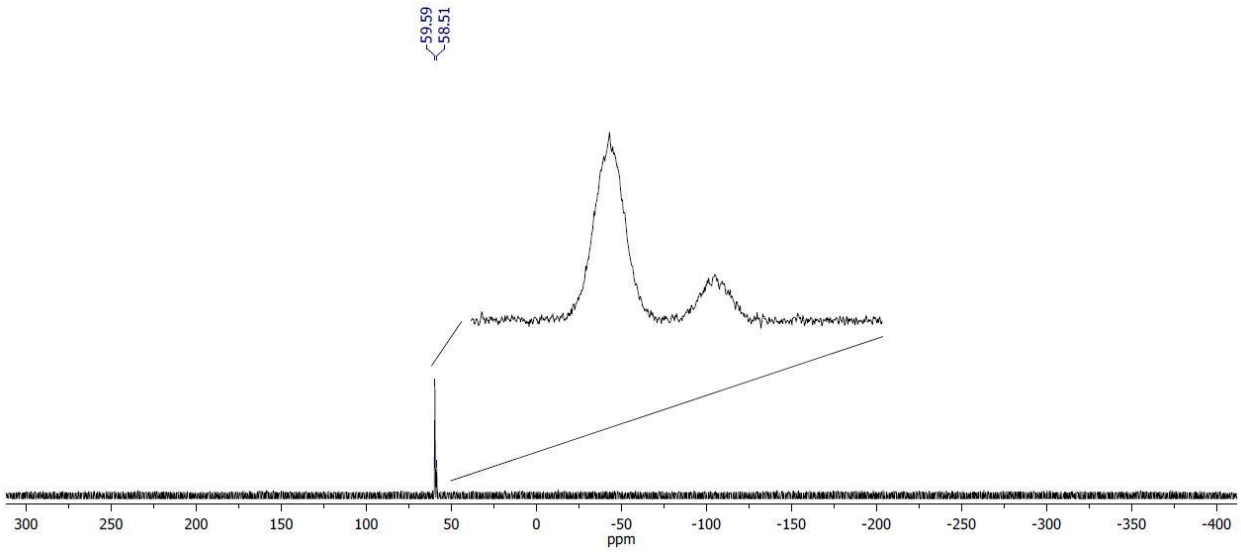


Figure S31: ^{31}P NMR spectrum (THF-d_8, 300 K, 162 MHz) after irradiation of **3-o** with UV light (310 nm, 140 mW) for 30 minutes in a quartz glass NMR tube.

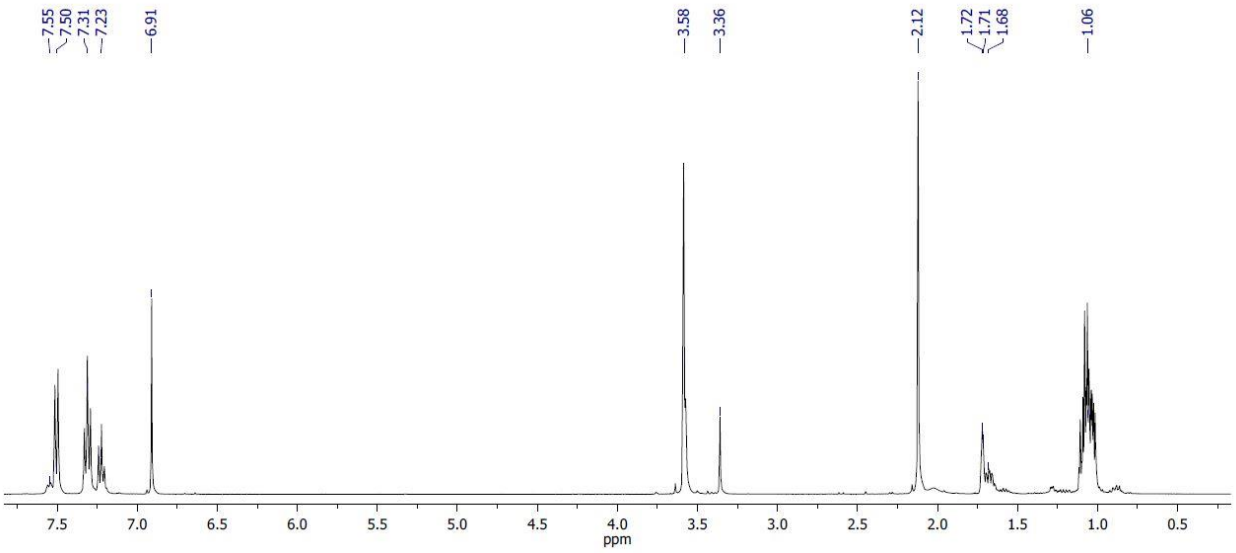


Figure S32: ^{1}H NMR spectrum (THF-d_8, 300 K, 400 MHz) after irradiation of **3-o** with UV light (310 nm, 140 mW) for 1 hour in a quartz glass NMR tube.

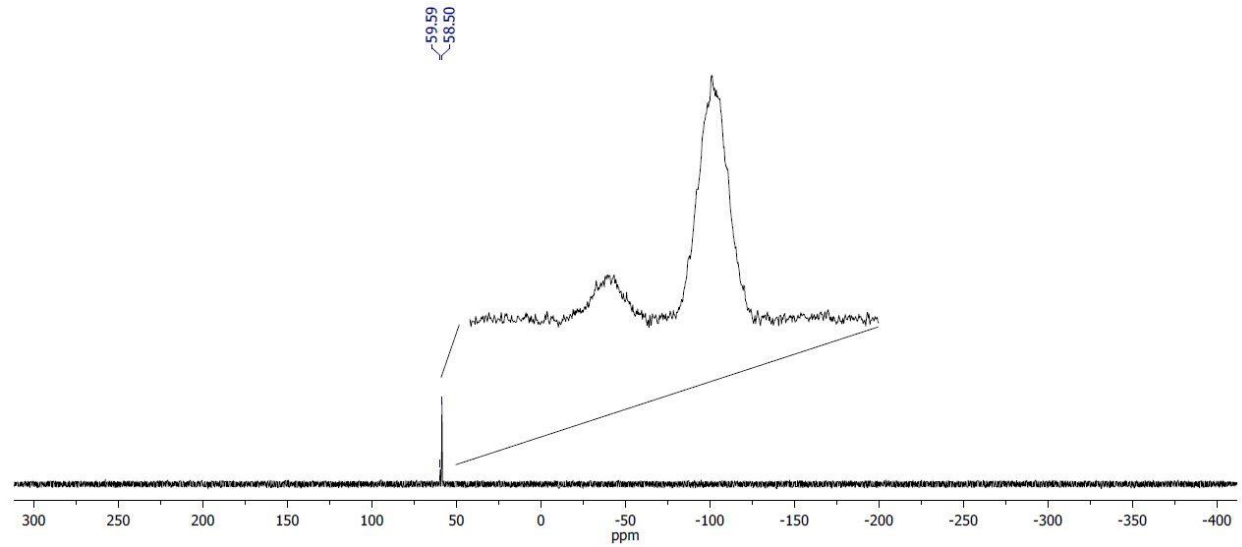


Figure S33: ^{31}P NMR spectrum (THF-d_8, 300 K, 162 MHz) after irradiation of **3-o** with UV light (310 nm, 140 mW) for 1 hour in a quartz glass NMR tube.

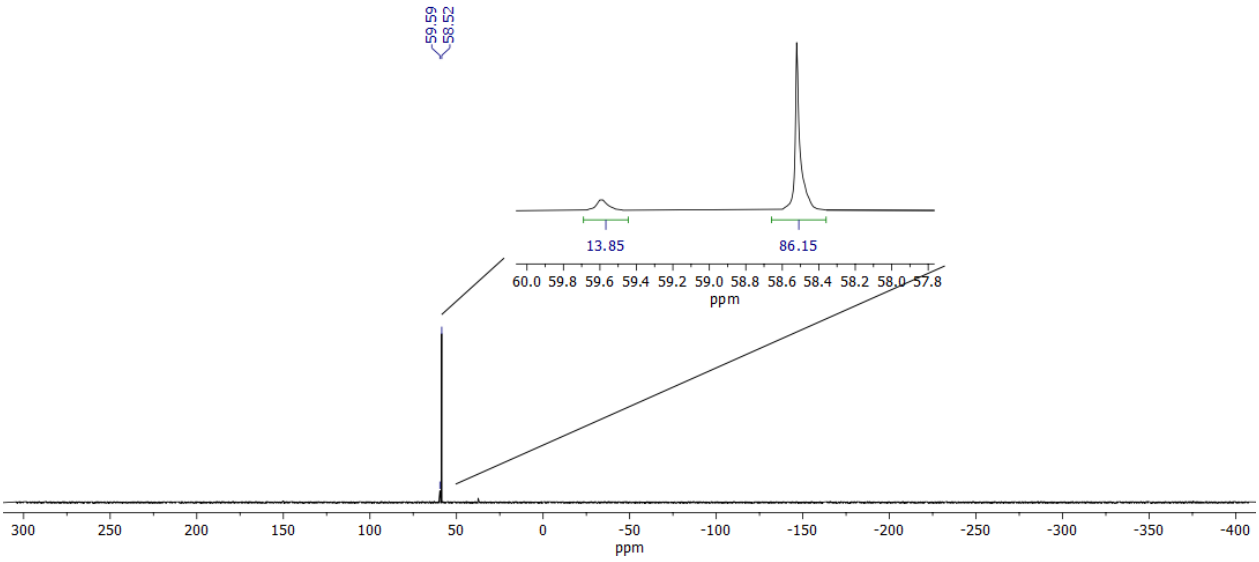


Figure S34: ^{31}P{^{1}H} NMR spectrum (THF-d_8, 300 K, 162 MHz) after irradiation of **3-o** with UV light (310 nm, 140 mW) for 1 hour in a quartz glass NMR tube.

Photochromism of phosphine 4-o:

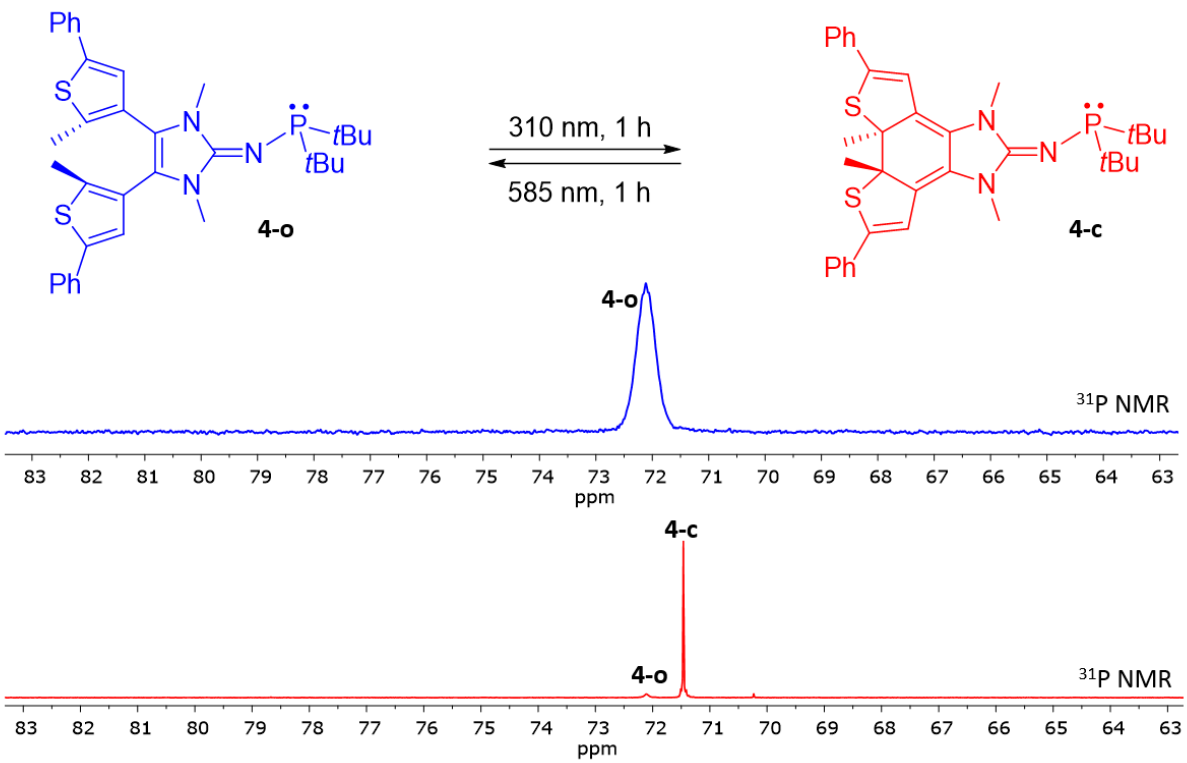


Figure S35: Quantitative ^{31}P NMR spectra of the THF-d_8 solution of **4-o** before (blue spectrum) and after exposure to UV irradiation (λ = 310 nm) for 1 h (red spectrum) showing a photoconversion of 88%. Subsequent irradiation with visible light (λ = 585 nm) for 1 hour restores the initial spectra.

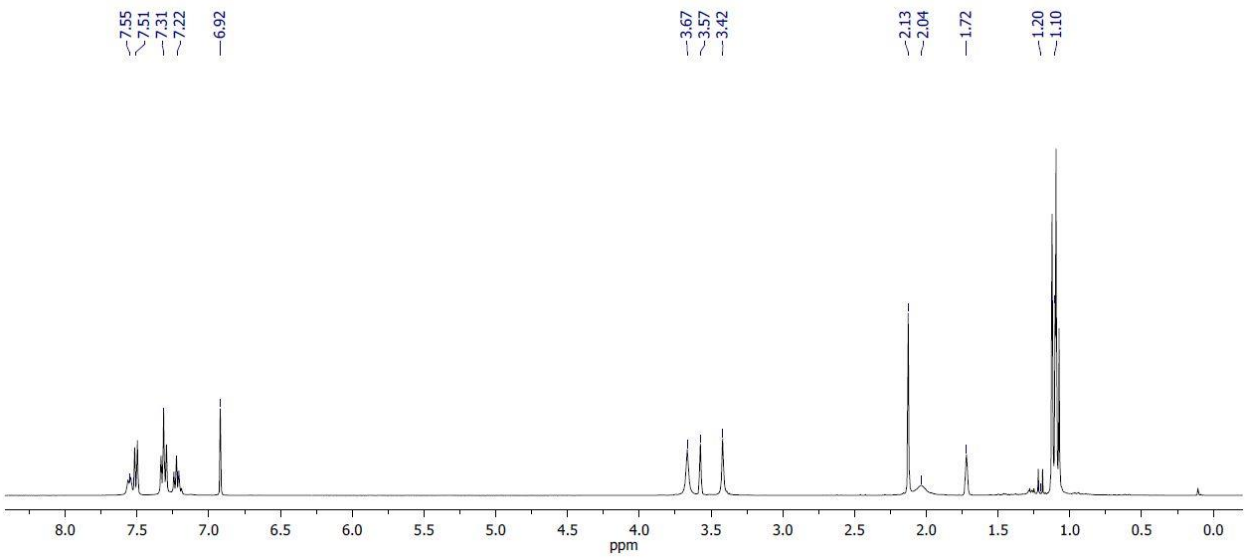


Figure S36: ^{1}H NMR spectrum (THF-d_8, 300 K, 400 MHz) after irradiation of **4-o** with UV light (310 nm, 140 mW) for 30 minutes in a quartz glass NMR tube.

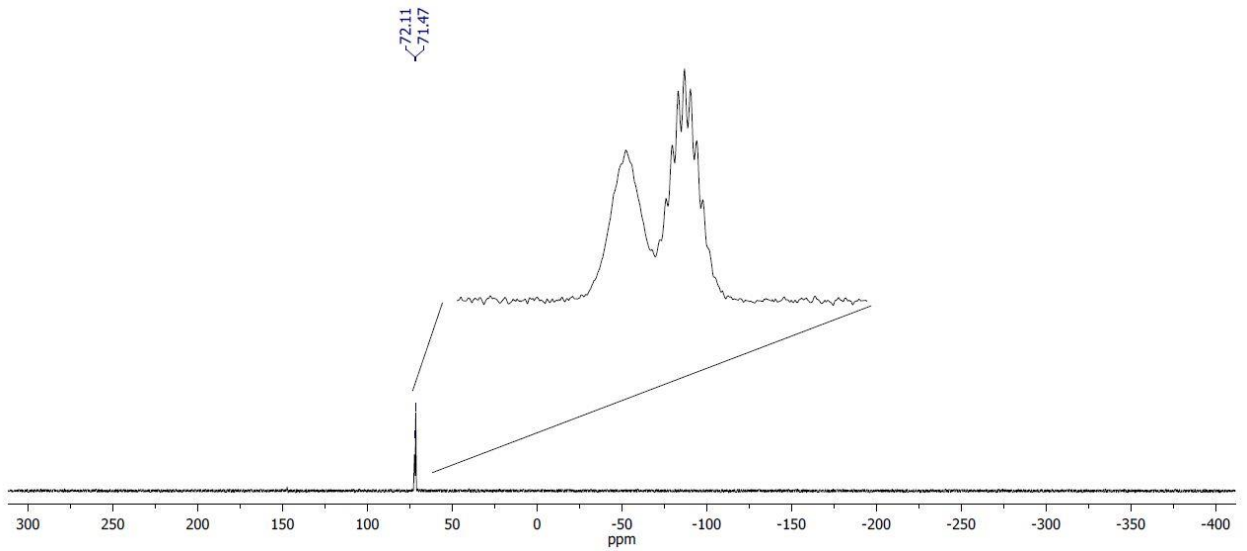


Figure S37: ^{31}P NMR spectrum (THF-d_8, 300 K, 162 MHz) after irradiation of **4-o** with UV light (310 nm, 140 mW) for 30 minutes in a quartz glass NMR tube.

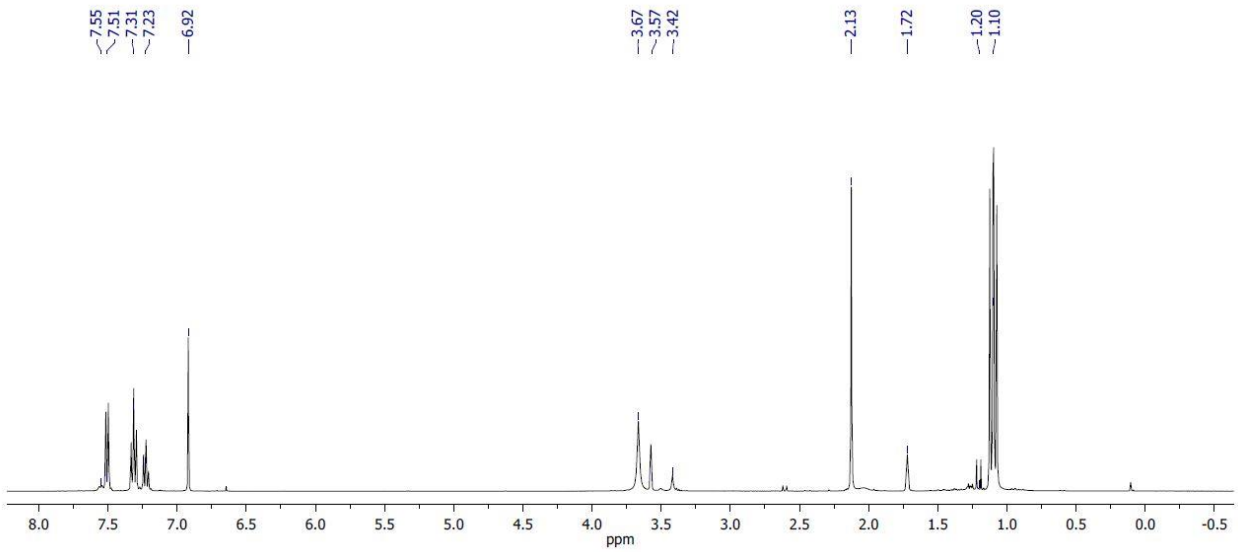


Figure S38: ^{1}H NMR spectrum (THF-d_8, 300 K, 400 MHz) after irradiation of **4-o** with UV light (310 nm, 140 mW) for 1 hour in a quartz glass NMR tube.

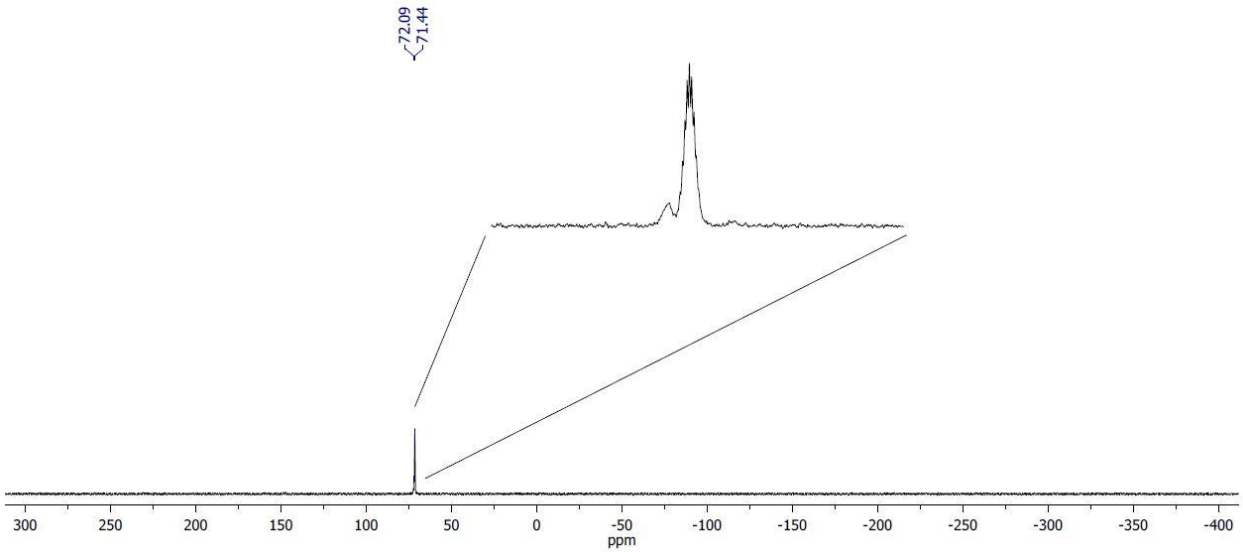


Figure S39: ^{31}P NMR spectrum (THF-d_8, 300 K, 162 MHz) after irradiation of **4-o** with UV light (310 nm, 140 mW) for 1 hour in a quartz glass NMR tube.

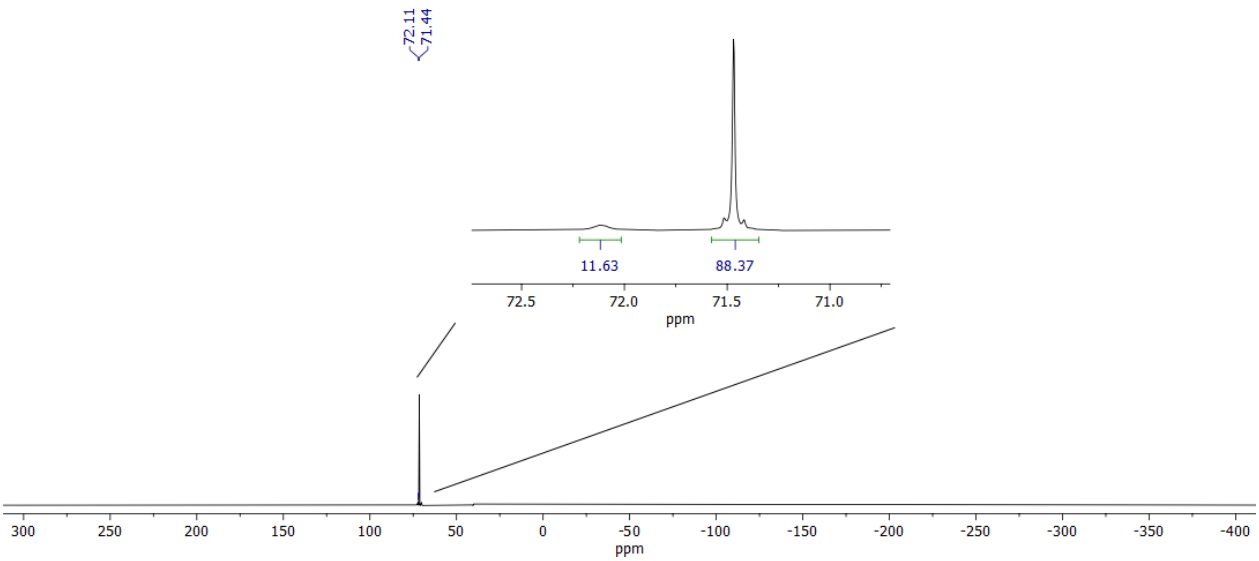


Figure S40: $^{31}P\{^{1}H\}$ NMR spectrum (THF-d_8, 300 K, 162 MHz) after irradiation of **4-o** with UV light (310 nm, 140 mW) for 1 hour in a quartz glass NMR tube.

Photochromism of phosphine 5-o:

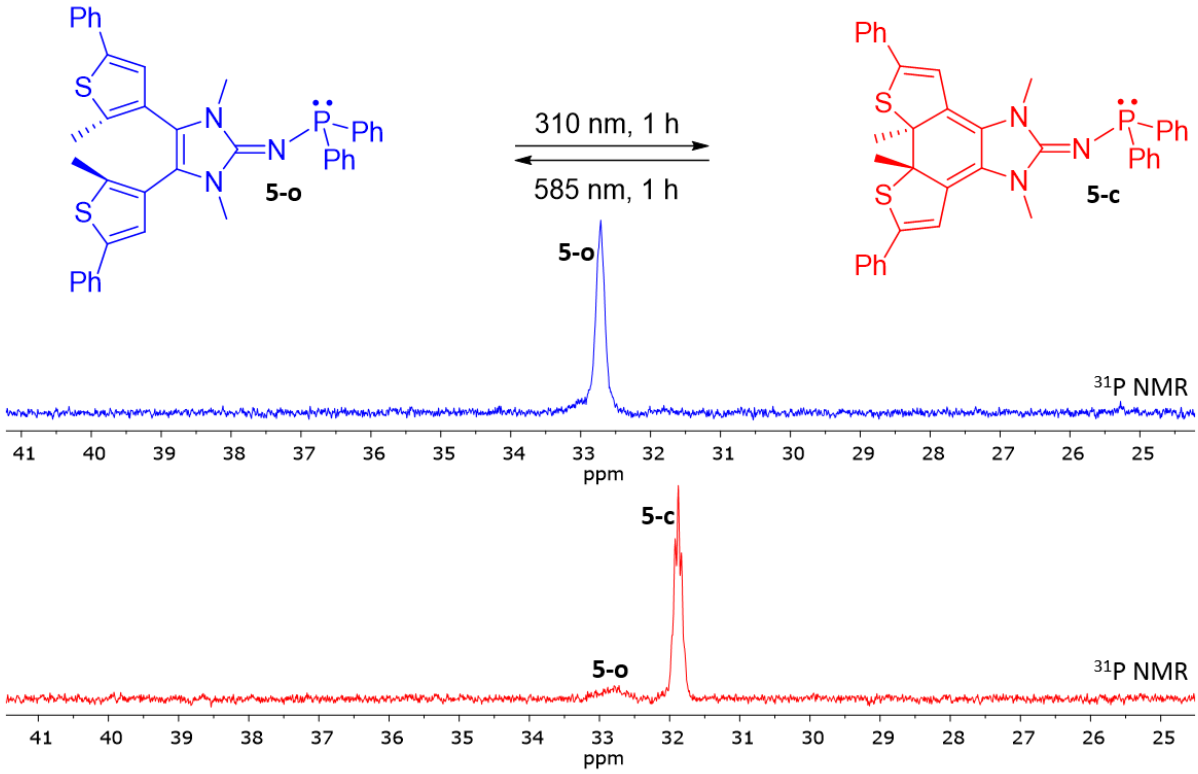


Figure S41: Quantitative ^{31}P NMR spectra of the THF-d_8 solution of **5-o** before (blue spectrum) and after exposure to UV irradiation (λ = 310 nm) for 1 h (red spectrum) showing a photoconversion of 90%. Subsequent irradiation with visible light (λ = 585 nm) for 1 hour restores the initial spectra.

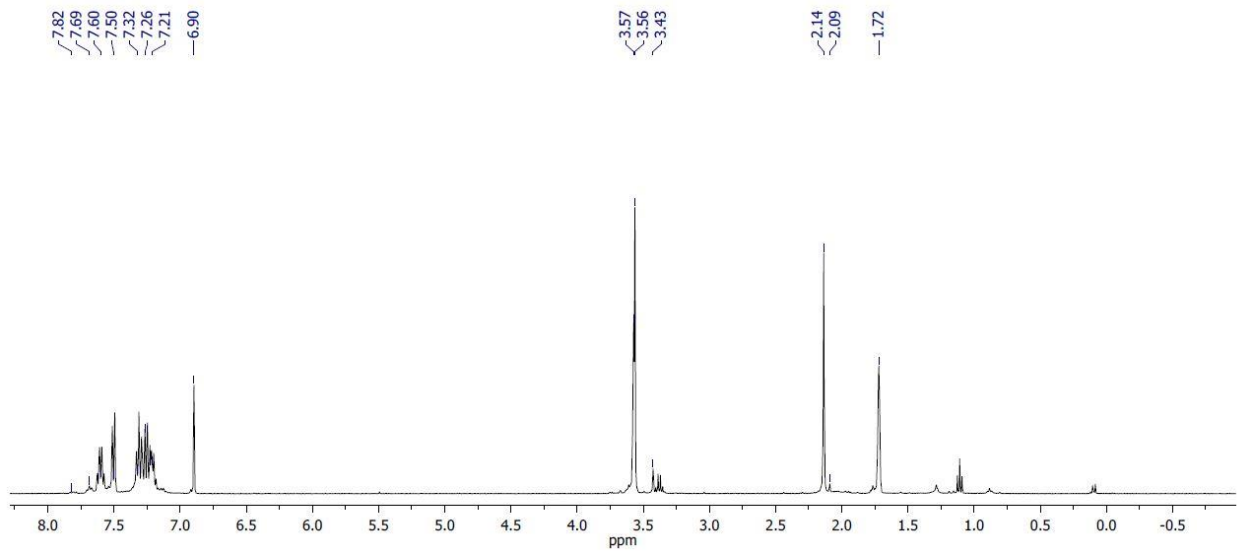


Figure S42: ^{1}H NMR spectrum (THF-d_8, 300 K, 400 MHz) after irradiation of **5-o** with UV light (310 nm, 140 mW) for 1 hour in a quartz glass NMR tube.

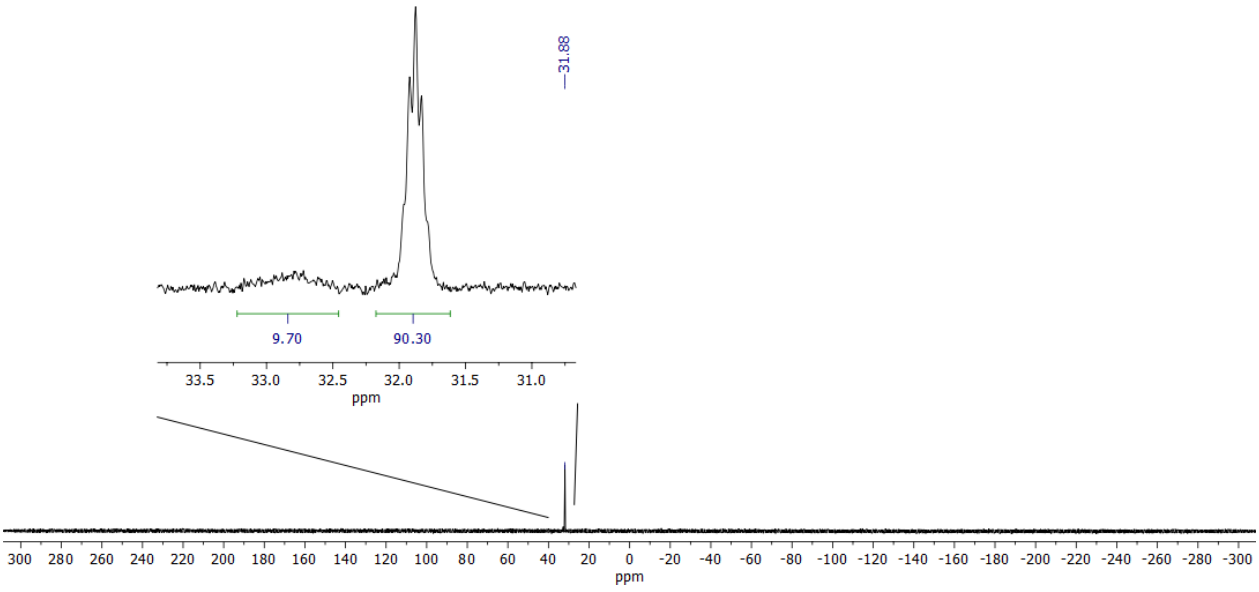


Figure S43: ^{31}P NMR spectrum (THF-d_8, 300 K, 162 MHz) after irradiation of **5-o** with UV light (310 nm, 140 mW) for 1 hour in a quartz glass NMR tube.

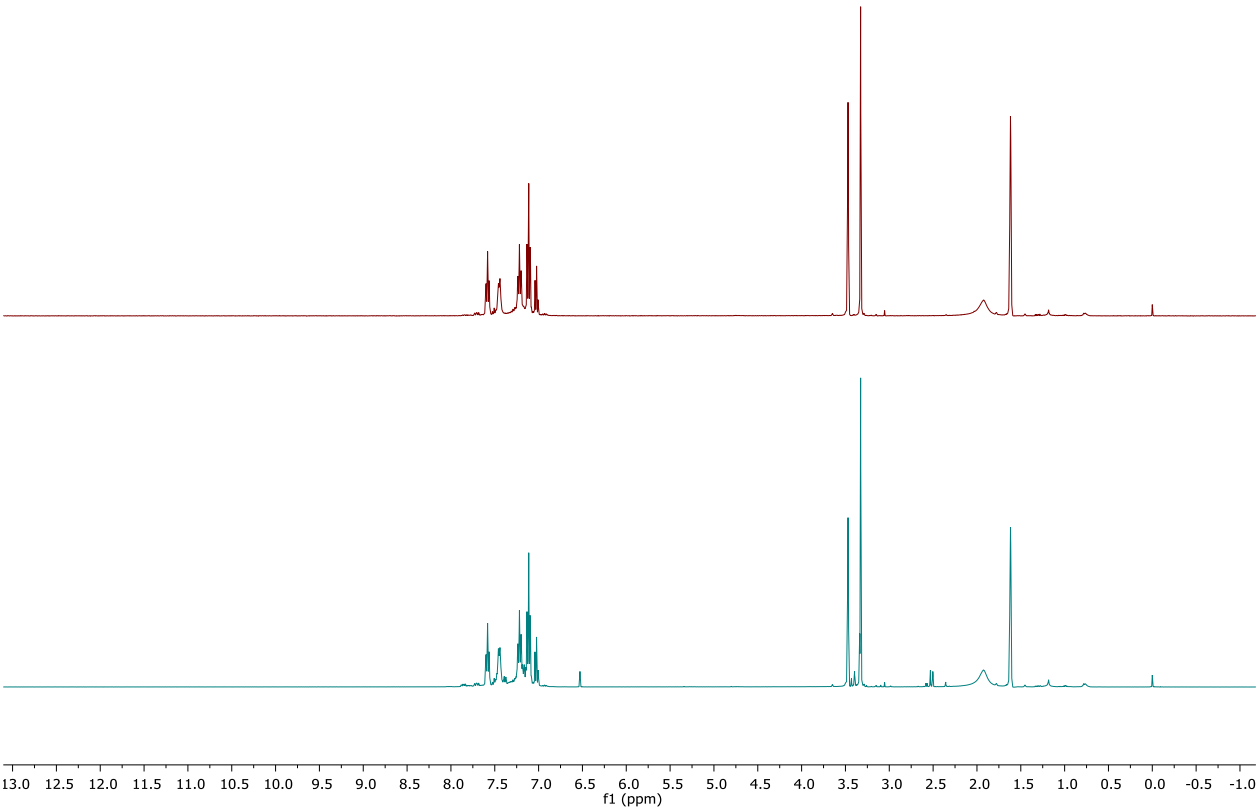


Figure S44: Fatigue resistance testing. ^{1}H NMR spectra (THF-d_8) of **5-o** before (top) and after (bottom) performing the ring-closing/ring-opening cycle 10 times: irradiating the solution with UV light (λ = 310 nm) for 1 hour followed by irradiation with visible light (λ = 585 nm) for 3 hours for 10 times.

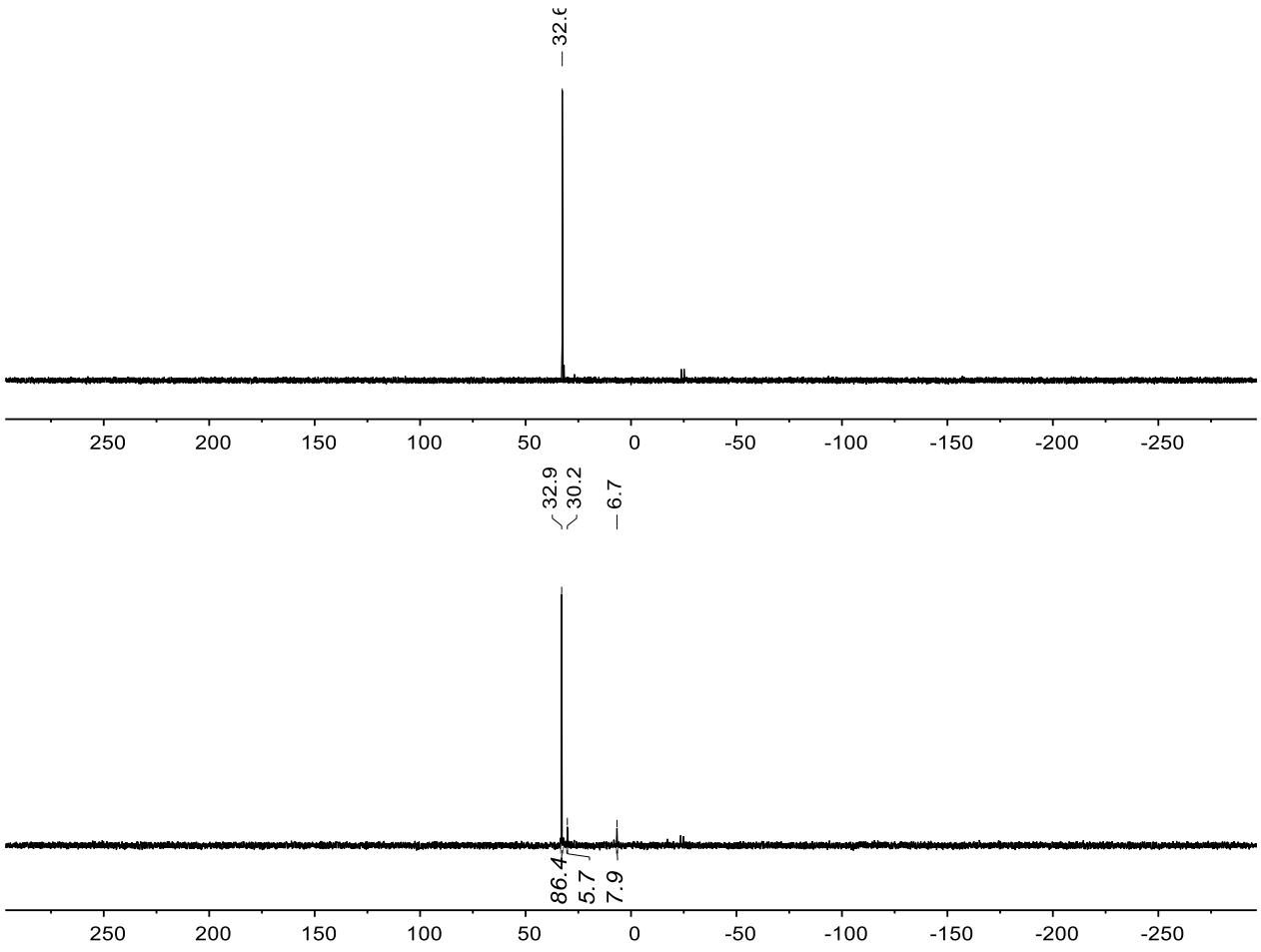


Figure S45: Fatigue resistance testing. ^{31}P NMR spectra (THF-d_8) of **5-o** before (top) and quantitative ^{31}P NMR spectra after (bottom) performing the ring-closing/ring-opening cycle 10 times: irradiating the solution with UV light (λ = 310 nm) for 1 hour followed by irradiation with visible light (λ = 585 nm) for 3 hours for 10 times.

Photochromism of **3-o**, **4-o** and **5-o** monitored by UV/vis spectroscopy

General procedure: UV/vis spectra of solutions of **3-o**, **4-o**, and **5-o** in THF ($[PS\text{-}IAP]_0 = 10^{-4}$ M) were recorded before and after UV irradiation (λ = 310 nm) for the time indicated.

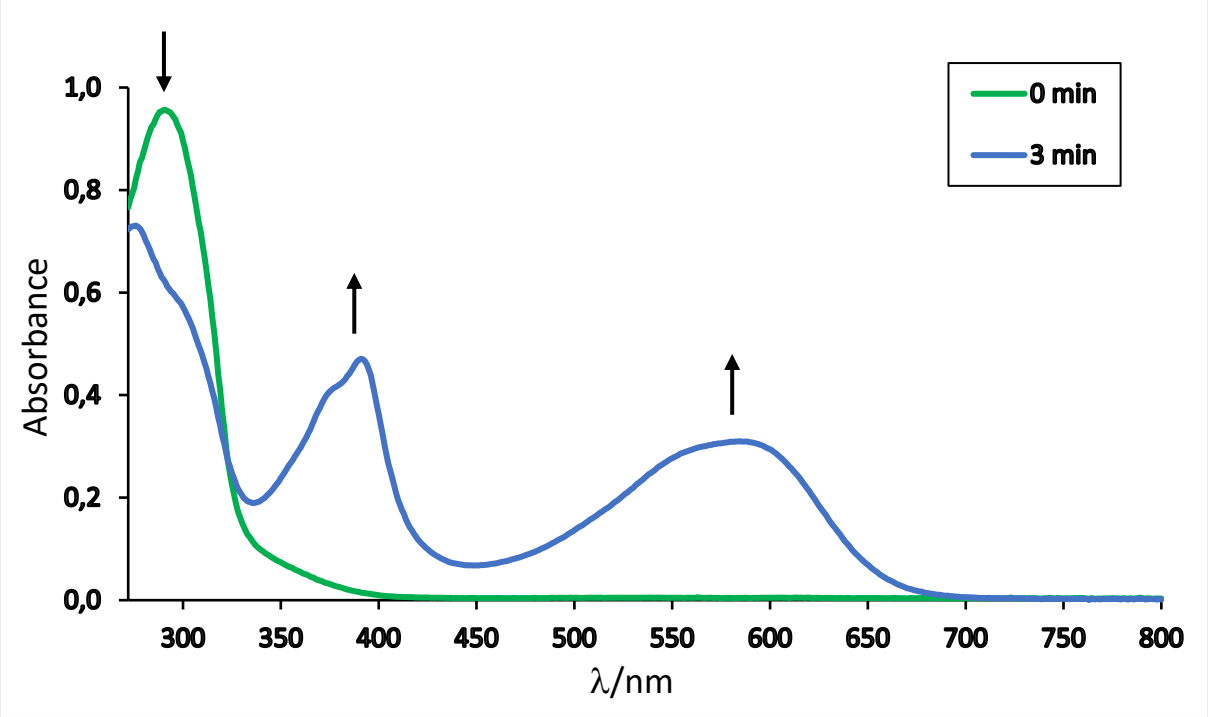


Figure S46: UV/vis spectral changes of **3-o** in THF ($[\mathbf{3\text{-}o}]_0 = 10^{-4}$ M) upon UV irradiation (λ_{irr} = 310 nm, 140 mW). The spectra were recorded after irradiation for 0 min (green line) and 3 min (blue line).

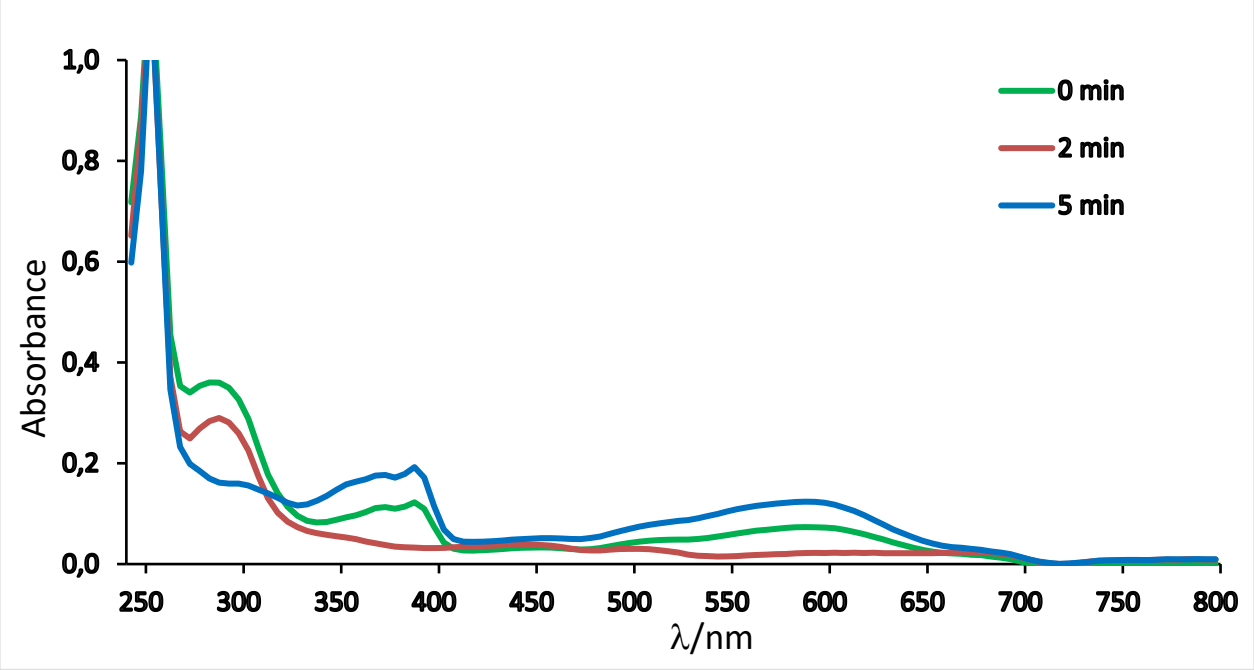


Figure S47: UV/vis spectral changes of **4-o** in THF ([**4-o**]$_0$ = 10^{-4} M) upon UV irradiation (λ_{irr} = 310 nm, 140 mW). The spectra were recorded after irradiation for 0 min (green line), 2 min (red line) and 5 min (blue line).

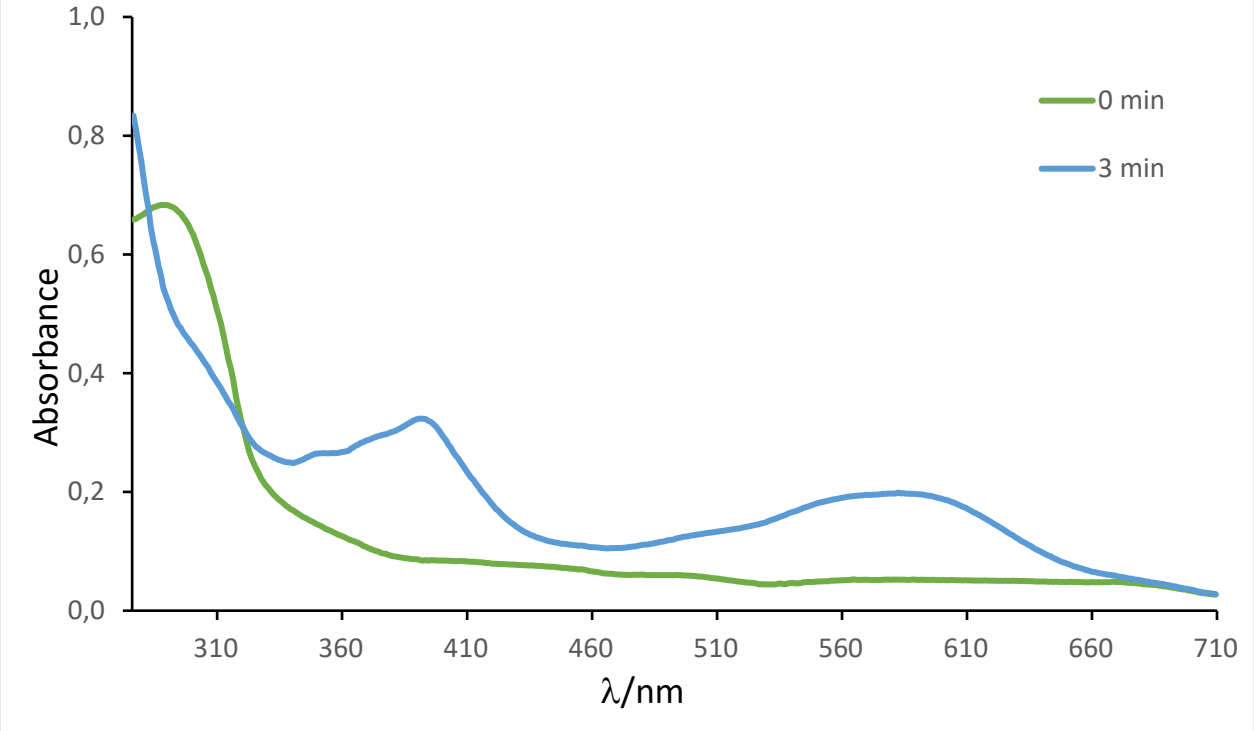


Figure S48: UV/vis spectral changes of **5-o** in THF ([**5-o**]$_0$ = 10^{-4} M) upon UV irradiation (λ_{irr} = 310 nm, 140 mW). The spectra were recorded after irradiation for 0 min (green line) and 3 min (blue line).

Electron donor properties of phosphines **3-o/3-c**, **4-o/4-c**, and **5-o/5-c**

General procedure for the preparation of the nickel complexes 6-o, 7-o, and 8-o

The nickel complexes **6-o**, **7-o**, **8-o**, and **8-c** were prepared via the following procedure: A standard solution of $Ni(CO)_4$ in toluene (0.2 M, 1.1 eq.) was added to the phosphine (1 eq.) and the resulting solution was stirred for 30 min at room temperature. The volatiles were removed *in vacuo* to afford the nickel complex as off-white solid for **6-o**, **7-o**, **8-o**, and purple solid for **8-c**.

Determination of the Tolman electronic parameter (TEP) of 3-o/3-c, 4-o/4-c, and 5-o/5-c

TEP values of 3-o and 3-c: An IR spectrum of a freshly prepared solution of **6-o** in dichloromethane was recorded. After irradiation of the solution with light at 310 nm (140 mW) for 1 hour, the deep purple solution of **6-c** was analyzed by IR spectroscopy.

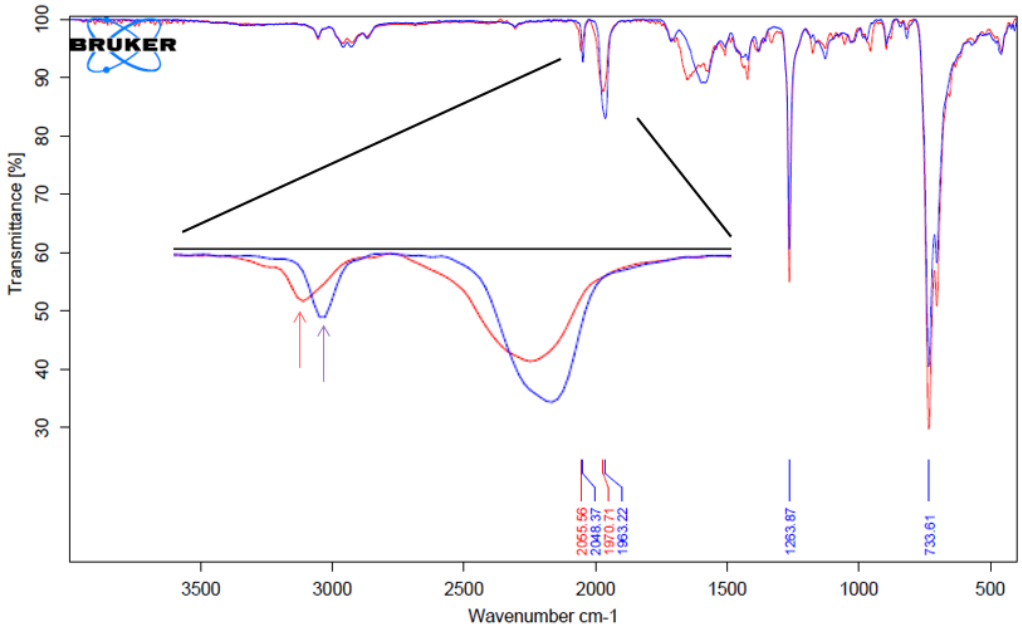


Figure S49: IR spectrum of **6-o** (blue line) and **6-c** (red line) in dichloromethane.

TEP values of 4-o and 4-c: An IR spectrum of a freshly prepared solution of **7-o** in dichloromethane was recorded. After irradiation of the solution with light at 310 nm (140 mW) for 1 hour, the deep purple solution of **7-c** was analyzed by IR spectroscopy.

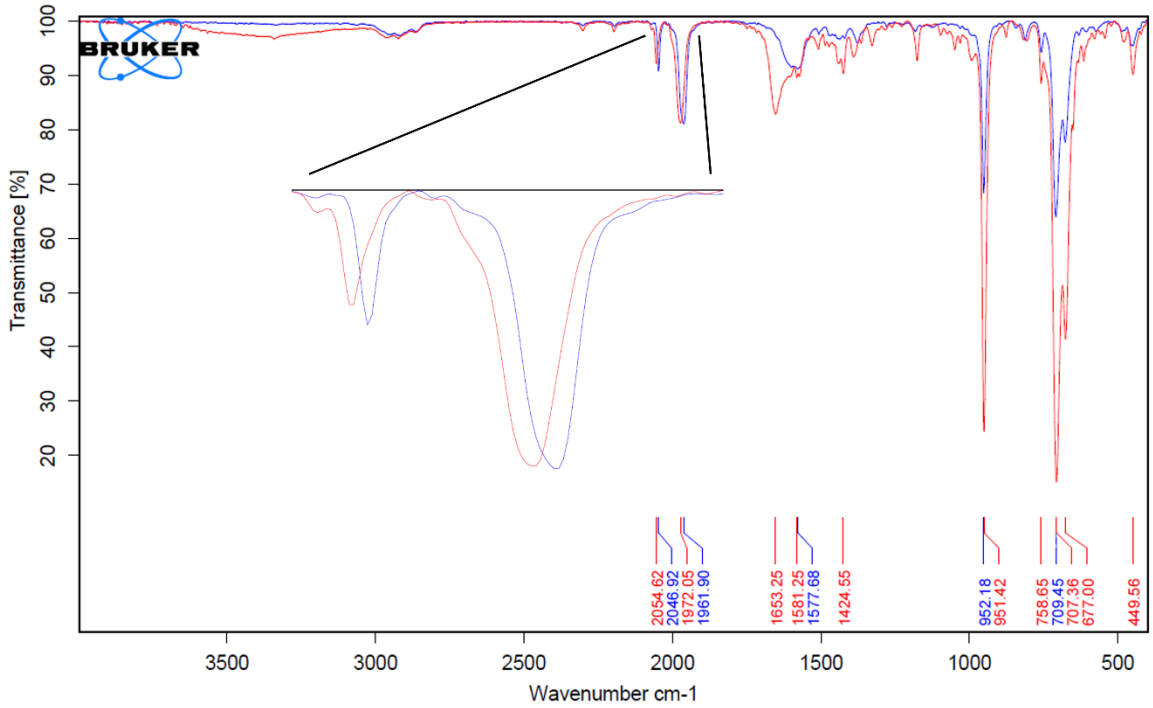


Figure S50: IR spectrum of **7-o** (blue line) and **7-c** (red line) in dichloromethane.

TEP values of 5-o and 5-c: An IR spectrum of a freshly prepared solution of **8-o** in dichloromethane was recorded. After irradiation of the solution with light at 310 nm (140 mW) for 1 hour, the IR spectrum of the solution was identical to that of **8-o**, indicating that no photoisomerization had occurred (***Figure S51***). Therefore, photoisomerization of the free phosphine to the closed form was performed first and the resulting 90:10 mixture of **5-c** and **5-o** was used to prepare the nickel complexes according to the general procedure. The resulting IR spectrum reveals the TEP value of the closed form of phosphine **5-c** (***Figure S52***). Subsequently, the solution of **8-c** was irradiated with light at 585 nm for 1 hour. The IR spectrum showed the successful photoisomerization to the open form **8-o** (***Figure S53***).

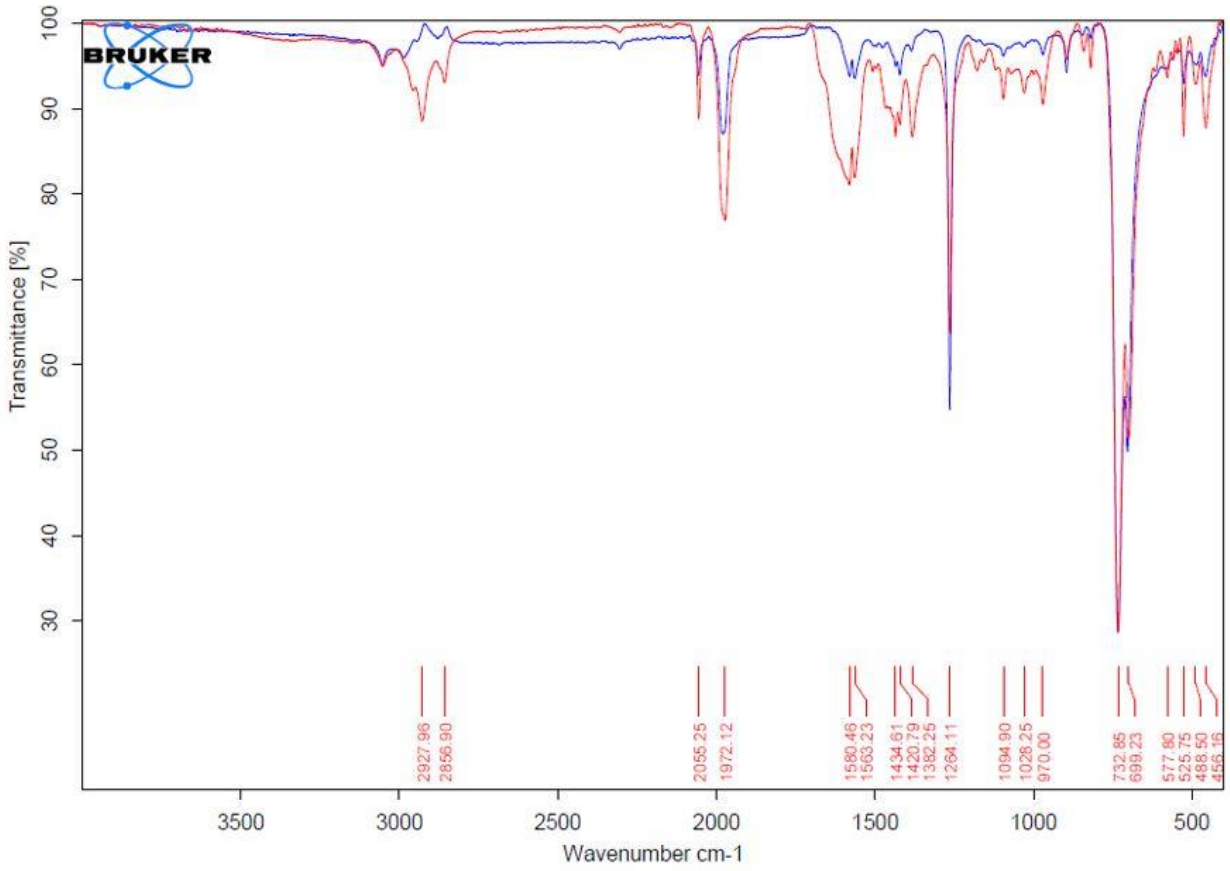


Figure S51: IR spectrum of **8-o** in dichloromethane (blue line) and of the same solution after irradiation with light at 310 nm for 1 hour (red line).

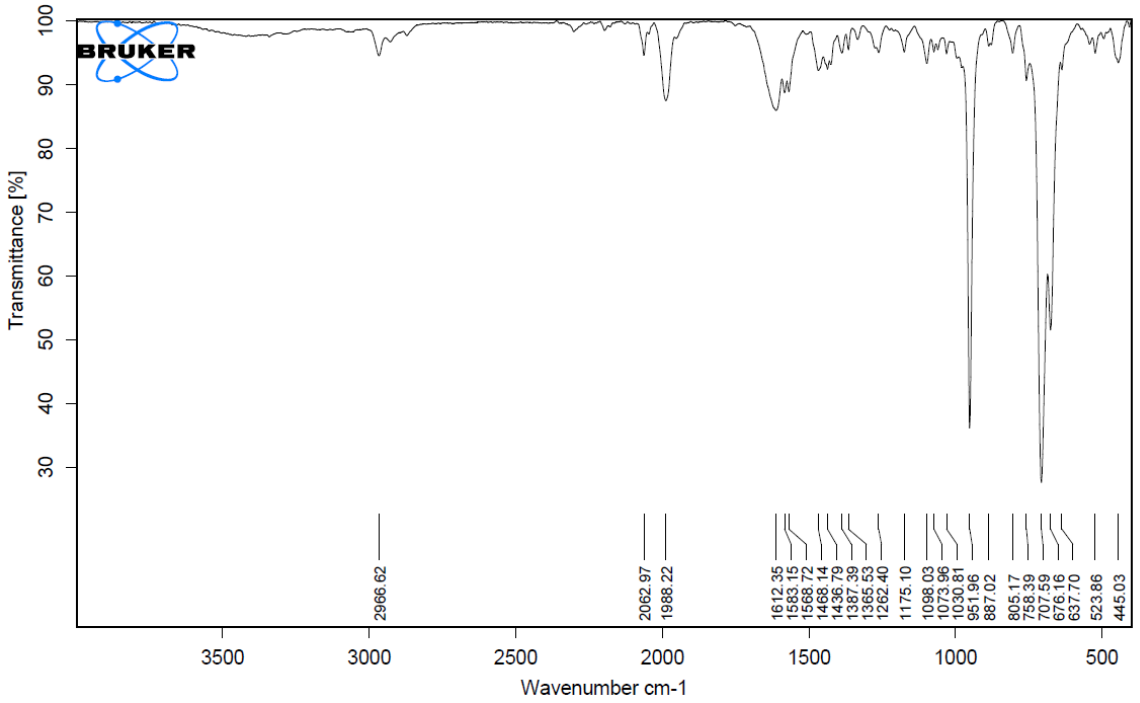


Figure S52: IR spectrum of **8-c** in dichloromethane. Note that **8-c** contains about 10% of **8-o** visible as small shoulder of the carbonyl resonances. This is due to the preparation by reacting the 90:10 mixture of **5-c** and **5-o** with $Ni(CO)_4$.

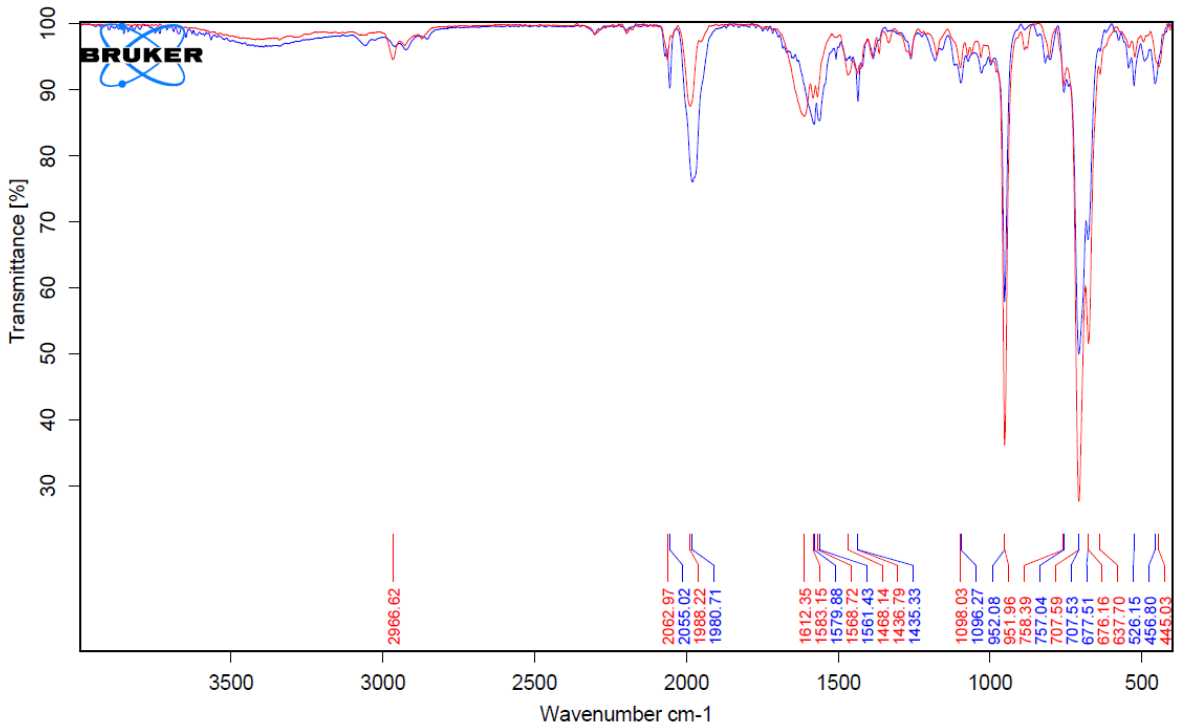
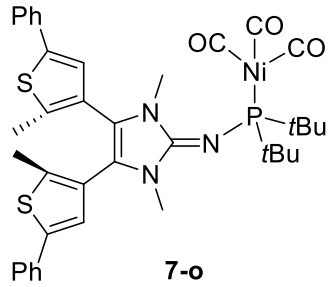


Figure S53: IR spectrum of **8-c** (red line) and **8-o** after irradiation with light at 585 nm for 1 hour (blue line).

Characterization data of nickel complexes 7-o and 7-c



7-o

HRMS (ESI): m/z calc. for $[C_{35}H_{43}N_3OPS_2]^+$ $(M+OH)^+$ 616.2580, found 616.2556.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.54 (m, 4H, aryl-H), 7.36 (m, 4H, *aryl*-H), 7.27 (m, 2H, *aryl* -H), 7.09 (s, br, 2H, *thiophen/vinyl*-H), 3.40 (s, 6H, NCH_3), 2.08 (s, br, 6H, *thiophen/vinyl* -CH_3), 1.31 (d, 18H, $^3J_{PH}$ = 10.9 Hz, P-C-CH_3.

^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2): δ =199.8 (d, $^2J_{PC}$ = 1.94 Hz, CO), 141.5 (d, $^2J_{PC}$ = 17.4 Hz, N_2CN), 139.8 (S-C=C-*aryl*), 134.5 (S-C-CH_3), 129.5 (C=C), 128.1 (*aryl*-CH), 127.4 (*aryl*-CH), 125.9 () 124.9 () 120.2 (C=C), 33.2 (d, J_{CP} = 22.5 Hz), 29.2 (br, NCH_3), 29.2 (d, J_{CP} = 16.1 Hz), 14.4 (CH_3).

^{31}P NMR (CD_2Cl_2, 162.0 MHz): δ = 107.4 (br, m).

^{31}P{^{1}H} NMR (CD_2Cl_2, 162.0 MHz): δ = 107.3 (br, s).

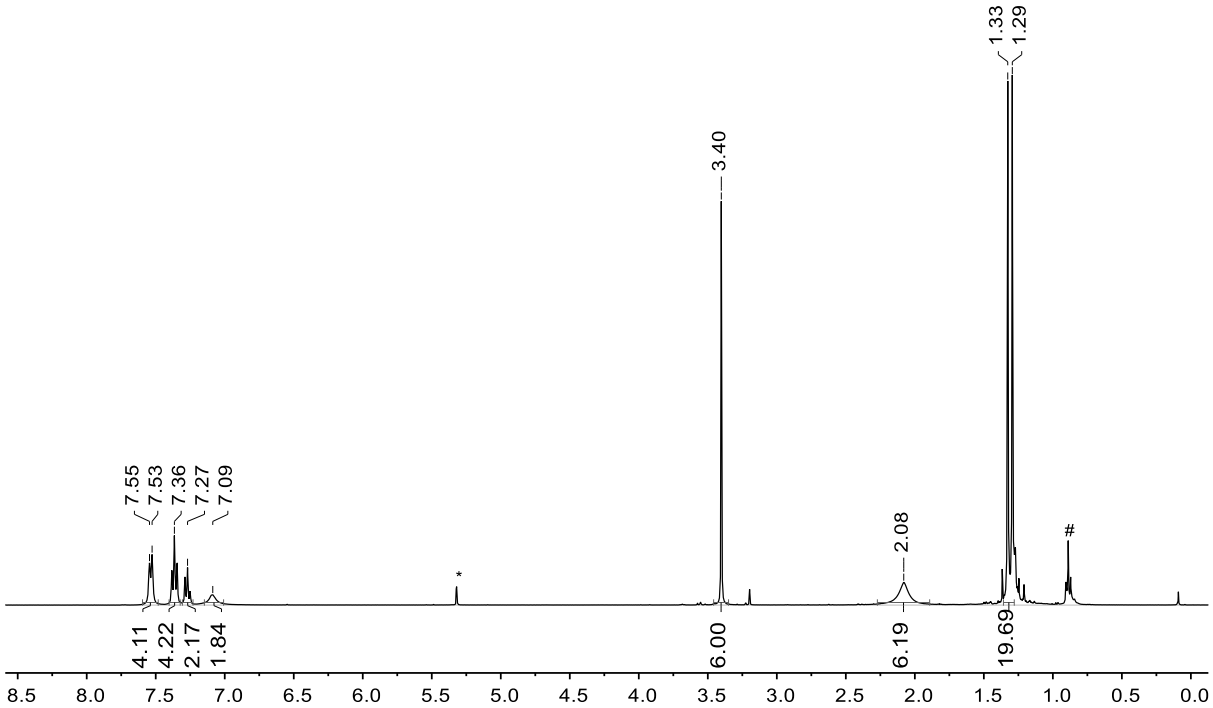


Figure S54: ^{1}H NMR spectrum (CD_2Cl_2, 300 K, 400 MHz) of **7-o**. *CH_2Cl_2; $^{\#}$*n*-hexane.

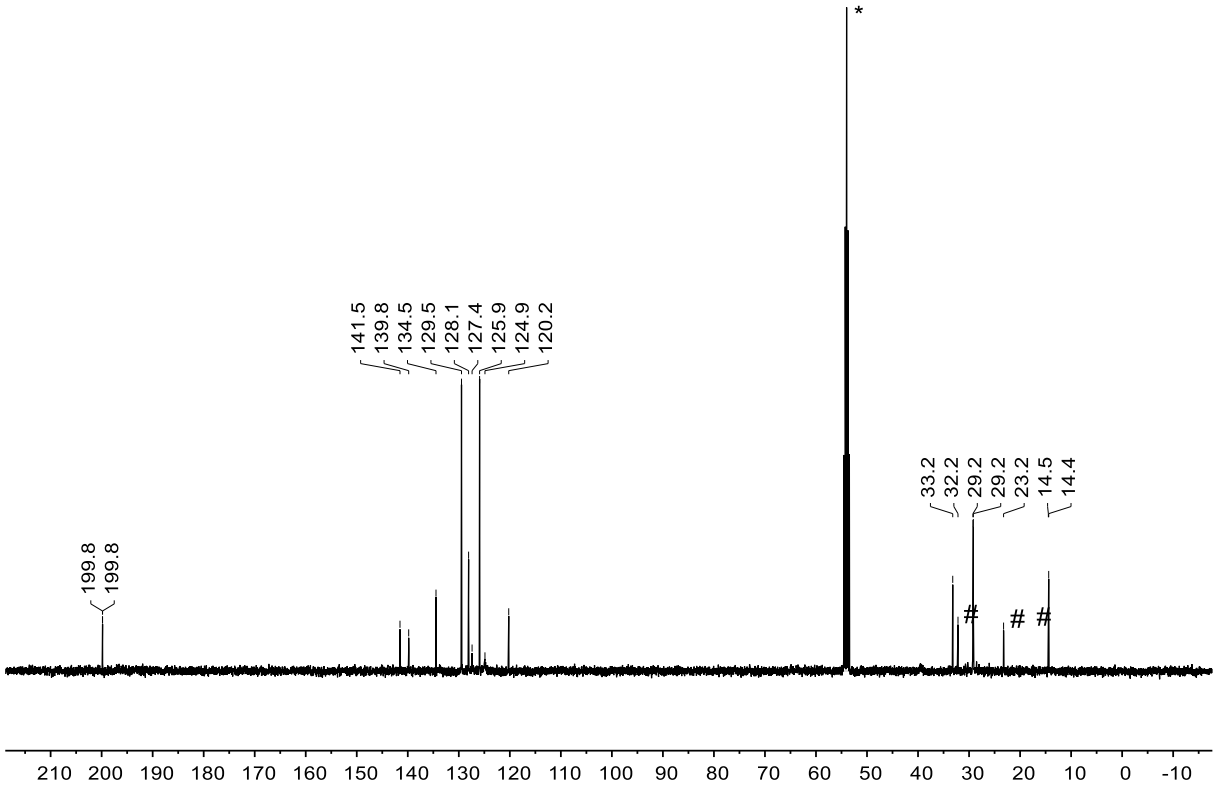


Figure S55: ^{13}C NMR spectrum (CD_2Cl_2, 300 K, 101 MHz) of **7-o**. *CD_2Cl_2; $^{\#}$*n*-hexane.

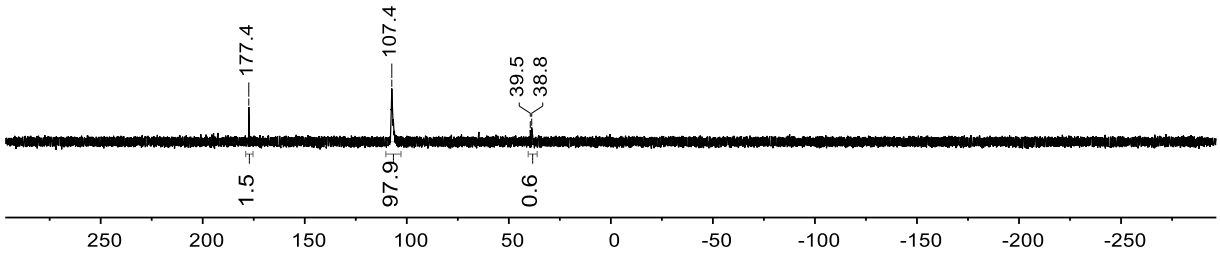


Figure S56: $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 300 K, 162 MHz) of **7-o**.

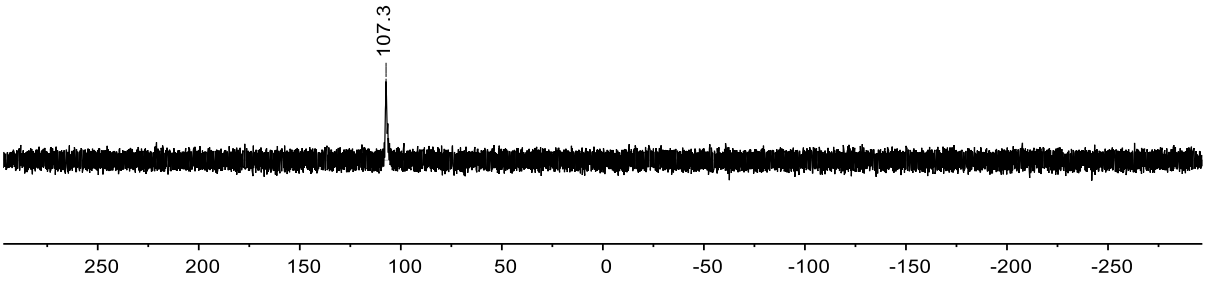
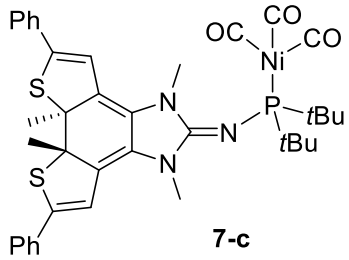


Figure S57: ^{31}P NMR spectrum (CD_2Cl_2, 300 K, 162 MHz) of **7-o**.

After irradiation of the NMR tube containing **7-o** in CD_2Cl_2 with light at 310 nm for one hour:



7-c

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.50 (m, 4H, aryl-H), 7.39 (m, 4H, *aryl*-H), 7.29 (m, 2H, *aryl* -H), 6.76 (s, br, 2H, *thiophen/vinyl*-H), 3.58 (s, 6H, NCH_3), 2.16 (s, br, 6H, *thiophen/vinyl* -CH_3), 1.27 (dd, 18H, $^3J_{PH}$ = 10.9 Hz, P-C-CH_3).

^{13}C NMR (100.6 MHz, CD_2Cl_2): δ =198.5 (s, CO), 143.9 (d, $^2J_{PC}$ = 17.4 Hz, N_2CN), 135.0 (S-C=C-*aryl*), 129.4 (S-C-CH_3), 129.1 (C=C), 128.8 (*aryl*-CH), 127.9 (*aryl*-CH), 126.3 () 125.9 () 122.4 (C=C), 113.7 (), 66.8 (), 33.7 (d, J_{CP} = 22.5 Hz), 29.0 (br, NCH_3), 28.9 (d, J_{CP} = 16.1 Hz), 28.6 (CH_3).

^{31}P NMR (CD_2Cl_2, 162.0 MHz): δ = 106.6 (m).

^{31}P{^{1}H} NMR (CD_2Cl_2, 162.0 MHz): δ = 106.6 (s).

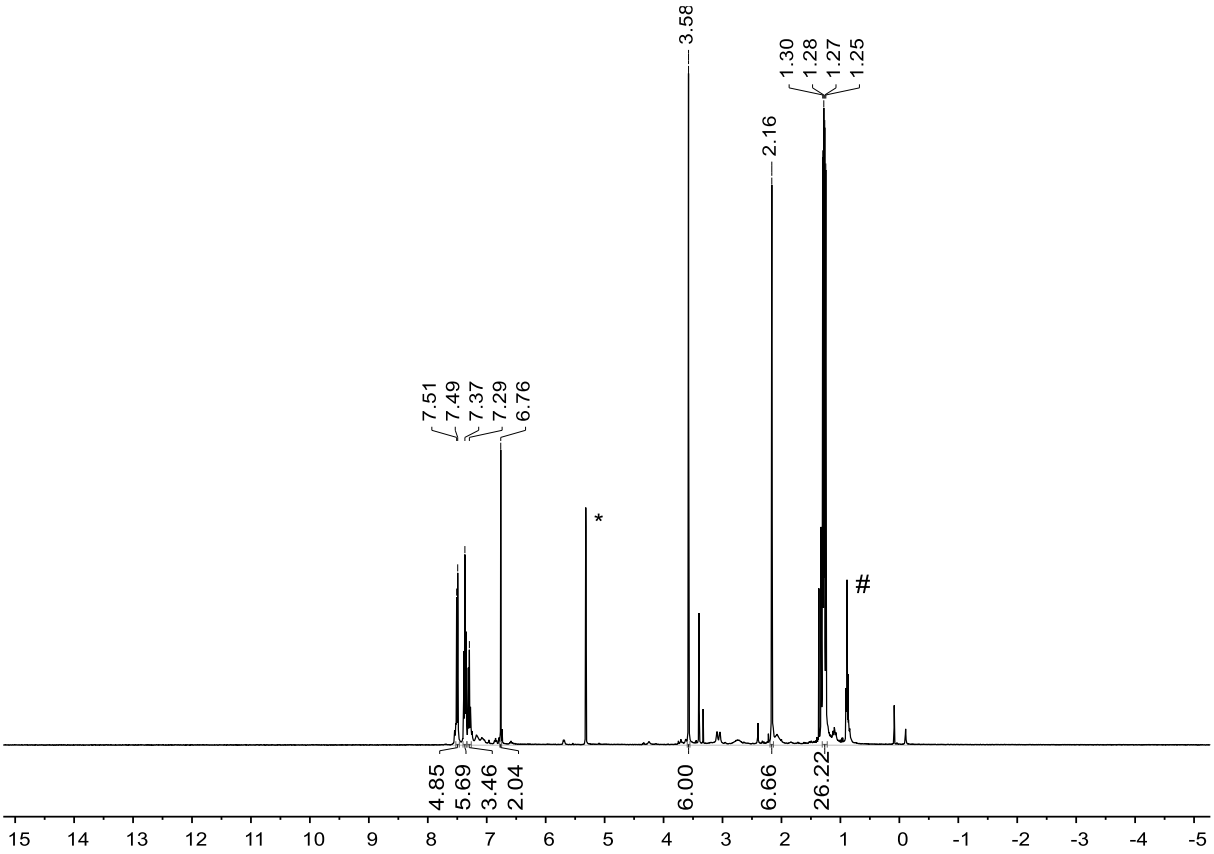


Figure S58: ^{1}H NMR spectrum (CD_2Cl_2, 300 K, 400 MHz) of **7-c**. *CD_2Cl_2; #*n*-hexane.

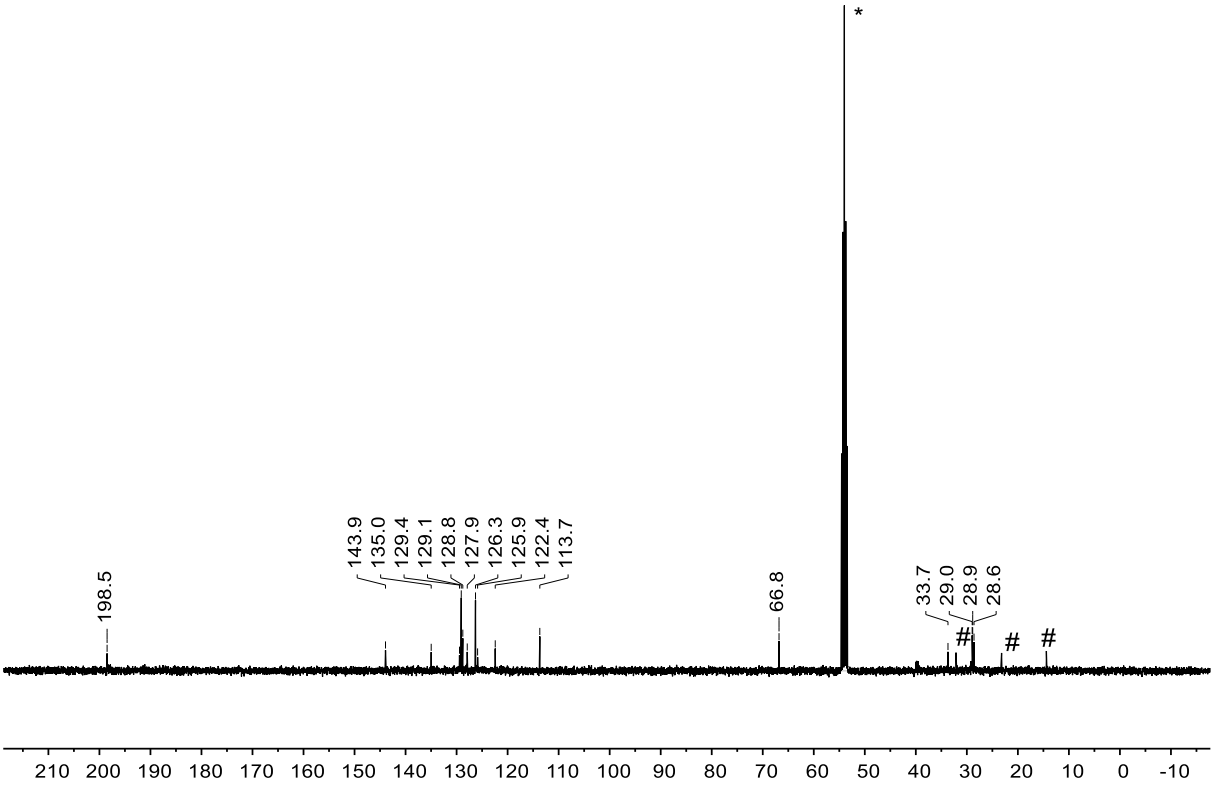


Figure S59: ^{13}C NMR spectrum (CD_2Cl_2, 300 K, 100.6 MHz) of **7-c**. *CD_2Cl_2; #*n*-hexane.

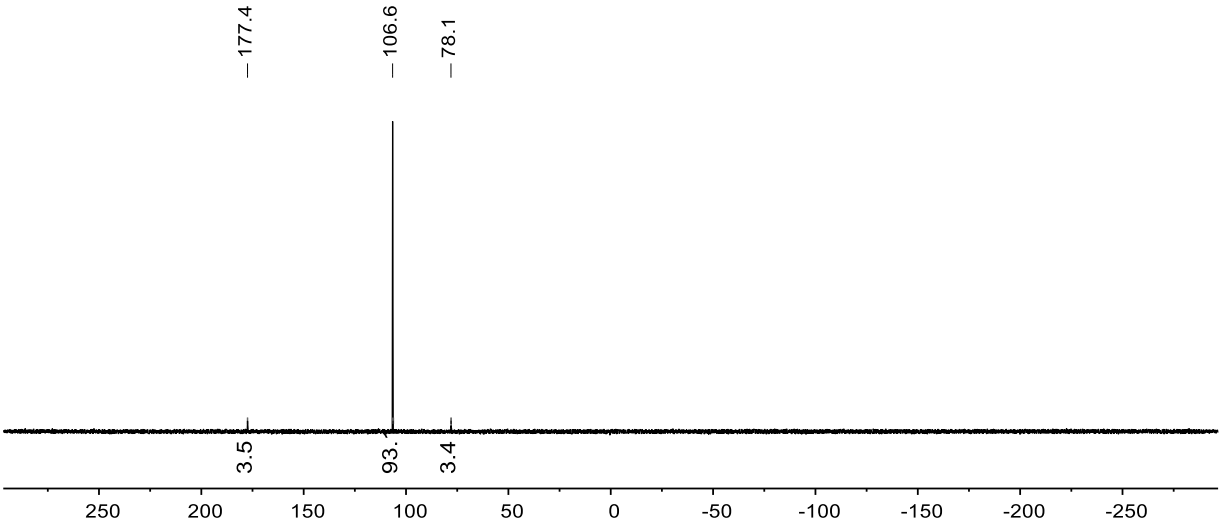


Figure S60: $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 300 K, 162 MHz) of **7-c**.

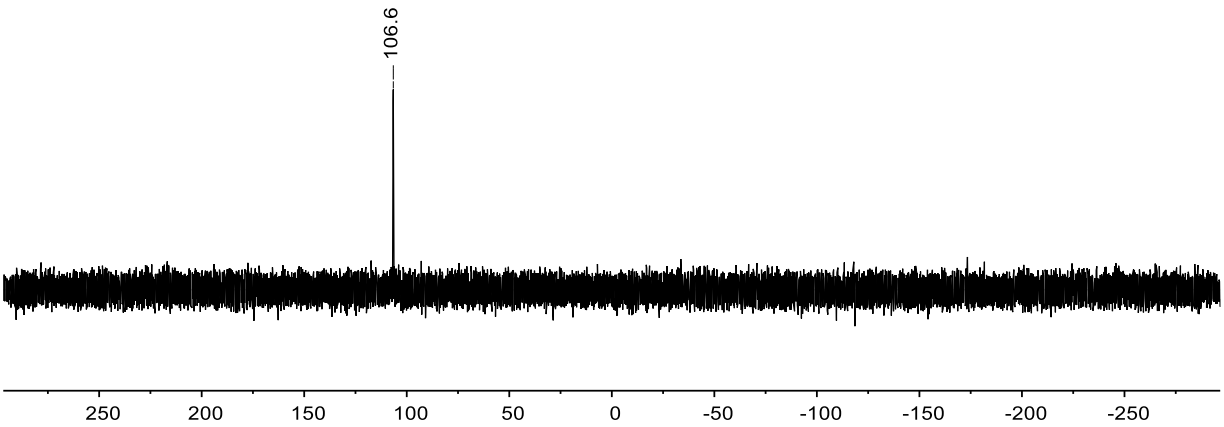


Figure S61: ^{31}P NMR spectrum (CD_2Cl_2, 300 K, 162 MHz) of **7-c**.

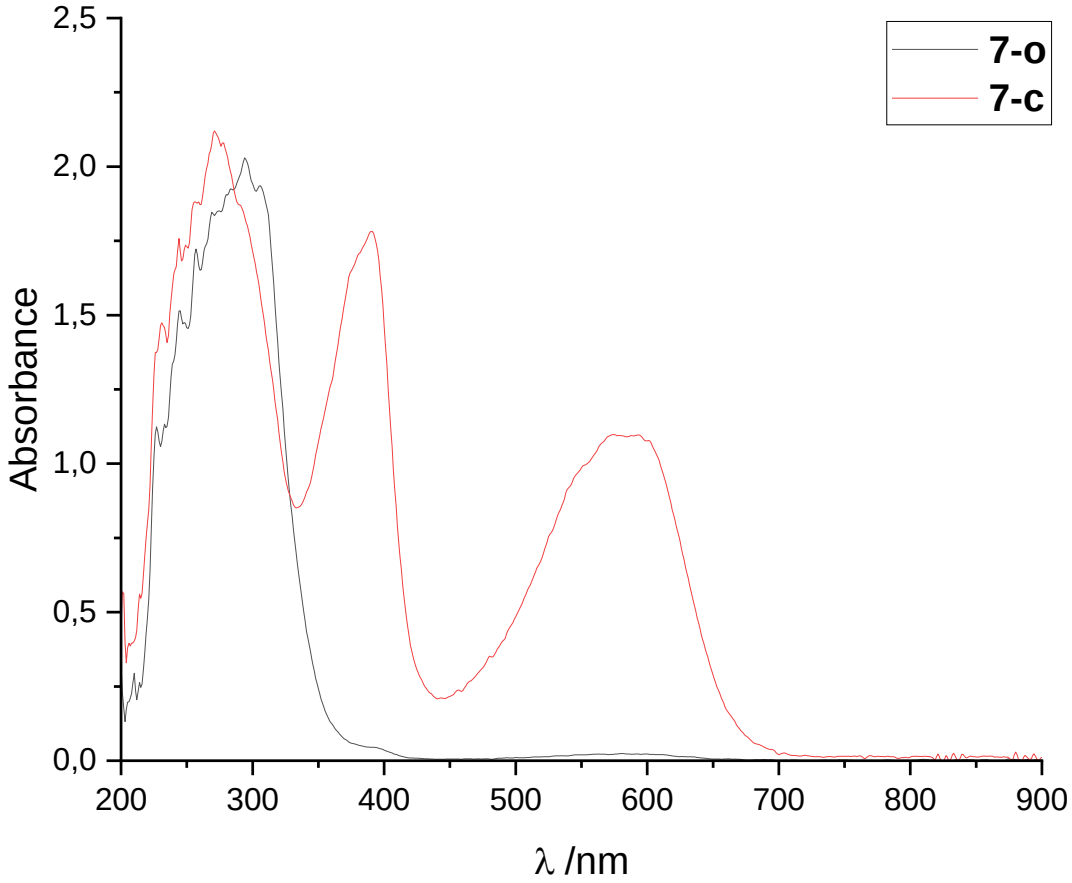


Figure S62: UV/vis absorption spectra of **7-o** (black line) and of **7-c** (red line, after irradiation λ = 310 nm for 10 min) in THF.

Preparation of compounds **10-o•**[HCl], and **10-o**

DTE-annulated tris(imidazolin-2-ylidenamino)phosphonium chloride 10-o•HCl: Imine **9** (240 mg, 0.527 mmol) was added to a stirred solution of bis(dimethylamino)chlorophosphine (27.2 mg, 0.176 mmol) in acetonitrile (3 mL) at room temperature after stirring the mixture for 30 minutes at 60 °C. The volatiles were removed *in vacuo* and the residue dissolved in chloroform (2 mL). A white precipitate was formed via diffusion of diethyl ether (3 mL) in the mixture. The solid components were filtered off, washed with diethyl ether (4 x 2 mL) and the residue was evaporated to dryness. Compound **10-o•**HCl was isolated as a white solid in 59% yield (148 mg, 0.104 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.26 (d, $^{1}J_{PH}$ = 566.8 Hz, 1H, P-*H*), 7.51 (m, 13H, *aryl*-H), 7.35 (m, 13H, *aryl*-H), 7.31-7.22 (m, 4H, *aryl*-H), 7.11 (m, br, 6H, *thiophen/vinyl*-H), 3.63 (s, 6H, N-CH_3), 2.04 (s, br, 6H, *thiophen*-CH_3).

^{31}P NMR ($CDCl_3$, 162.0 MHz): δ = –22.3 (d, $^{1}J_{PH}$ = 566.8 Hz).

^{31}P{^{1}H} NMR ($CDCl_3$, 162.0 MHz): δ = –22.3 (s).

HRMS (ESI): m/z calc. for $[C_{81}H_{73}N_9PS_6]^+$ $(M+H)^+$ 1429.3739, found: 1429.3684.

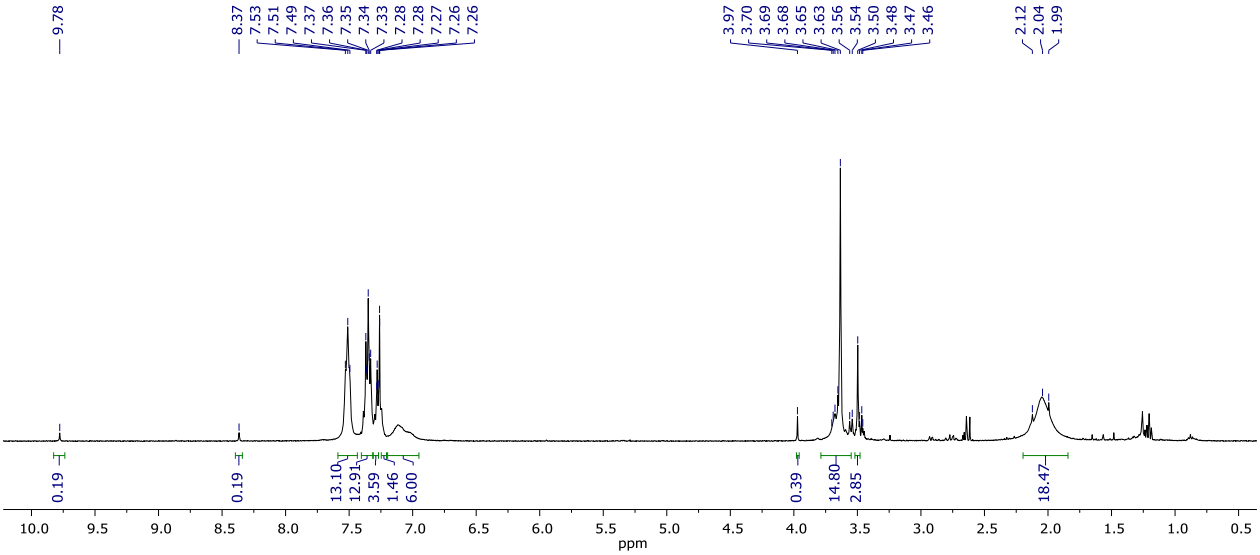


Figure S63: ^{1}H NMR spectrum ($CDCl_3$, 300 K, 400 MHz) of **10-o•**HCl.

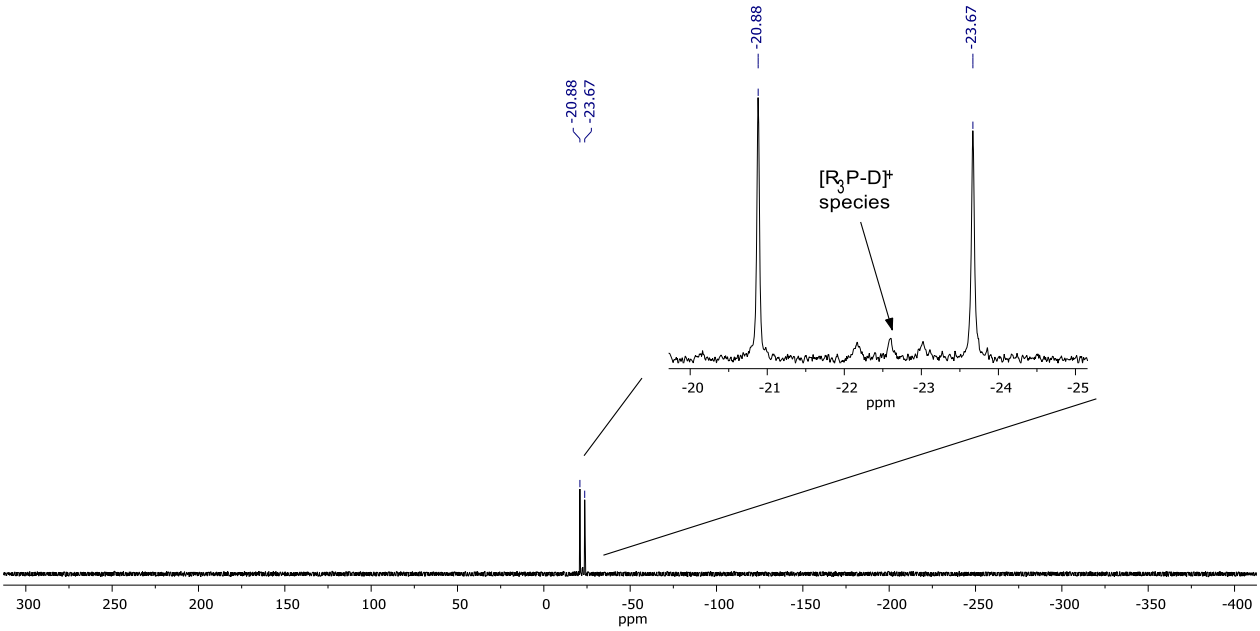


Figure S64: ^{31}P NMR spectrum ($CDCl_3$, 300 K, 162 MHz) of **10-o**•HCl.

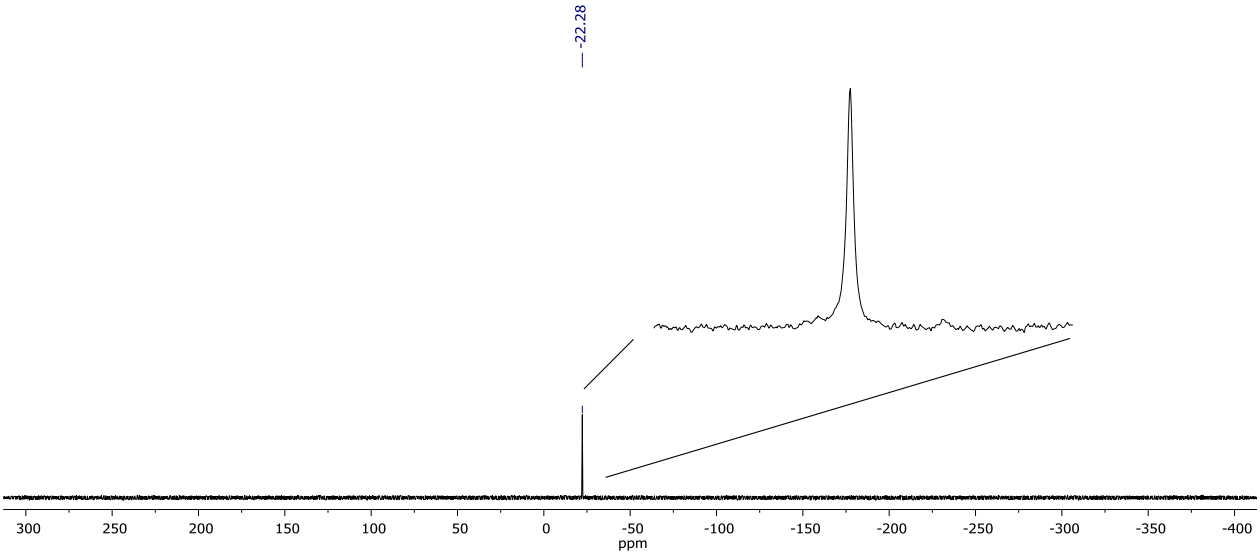


Figure S65: $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$, 300 K, 162 MHz) of **10-o**•HCl.

Test reaction to assess the use of *t*-Bu-P$_4$ for the deprotonation of superbasic phosphines using the example of P(tmg)$_3$ (tmg = 1,1,3,3-tetramethylguanidinyl)

To a stirred solution of P(tmg)$_3$•HCl[2] (96 mg, 0.234 mmol, 1 eq.) in THF (2 mL) was added phosphazene superbase *t*-Bu-P$_4$ (0.3 mL, 0.234 mmol, 0.8M in *n*-hexane, 1 eq.). The mixture was stirred for 30 minutes, and the volatiles were removed *in vacuo*. The residue was extracted with 5 mL *n*-hexane. Removal of the solvent *in vacuo* and subsequent sublimation gave phosphine P(tmg)$_3$ in quantitative yield.[2] The same reaction was performed in THF-d_8 by use of an excess of *t*-Bu-P$_4$ (2 eq.) to assign the resonances of the relevant compounds in the ^{31}P NMR spectrum (Figure 57).

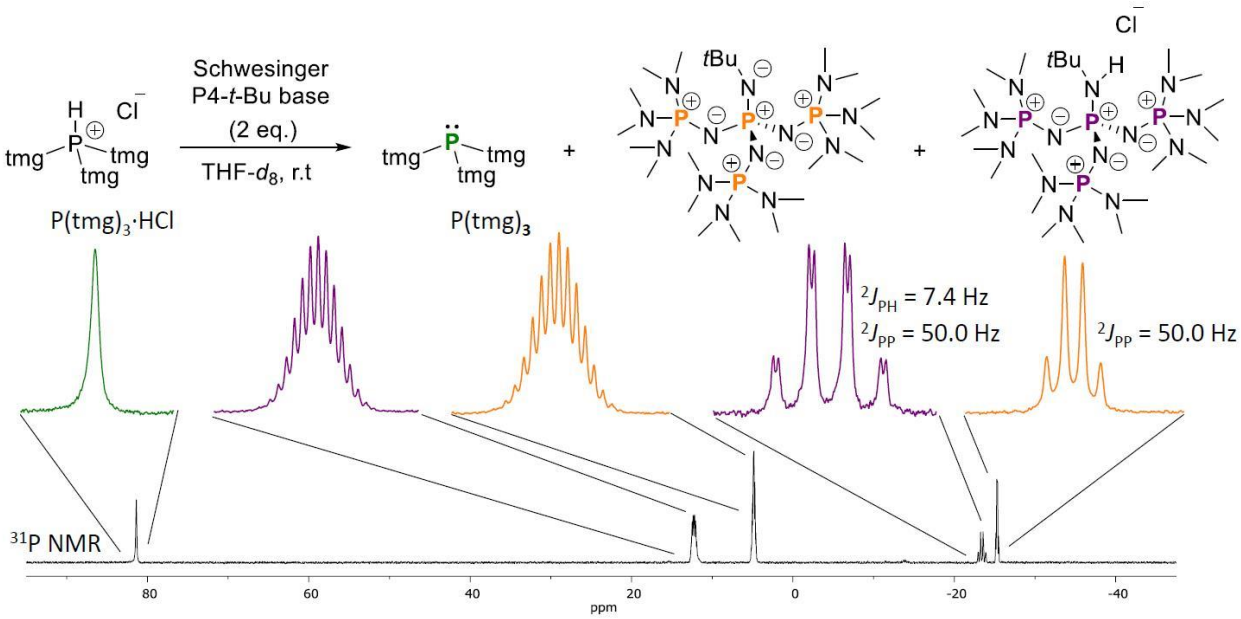


Figure S66: ^{31}P NMR spectrum in THF-d_8 of the reaction mixture for the deprotonation of P(tmg)$_3$•HCl using phosphazene superbase *t*-Bu-P$_4$ (2 eq.).

In situ formation of 10-o via deprotonation of 10-o•HCl with *t*-Bu-P$_4$

To a stirring solution of **10-o**•HCl (112 mg, 0.078 mmol, 1 eq.) in THF-d_8 (1 mL) was added phosphazene superbase *t*-Bu-P$_4$ (0.1 mL, 0.078 mmol, 0.8 M in *n*-hexane, 1 eq.). The mixture was stirred for 30 minutes, and 0.5 mL of the mixture was transferred into a Teflon-sealed NMR tube. The ^{31}P NMR spectrum of the reaction mixture (Overview: S67, as well as Figure S68 and Figure S69) revealed the formation of phosphine **10-o** by its characteristic signal at 75.9 ppm, which was observed concomitant with the resonances of *t*-Bu-P$_4$•HCl at 12.3 ppm and –23.4 ppm (dq, $^2J_{PP}$ = 50 Hz, $^2J_{PH}$ = 7.5 Hz). After removing the volatiles, the following ion was identified in the high-resolution mass spectrum (HRMS/ESI) of the solid: m/z calculated for $[C_{81}H_{73}N_9PS_6]^+$ $(M+H)^+$ 1429.3739, found 1429.3696. PS-IAP **10-o** could not be isolated due to the low solubility of **10-o** in toluene, *n*-hexane, and diethyl ether.

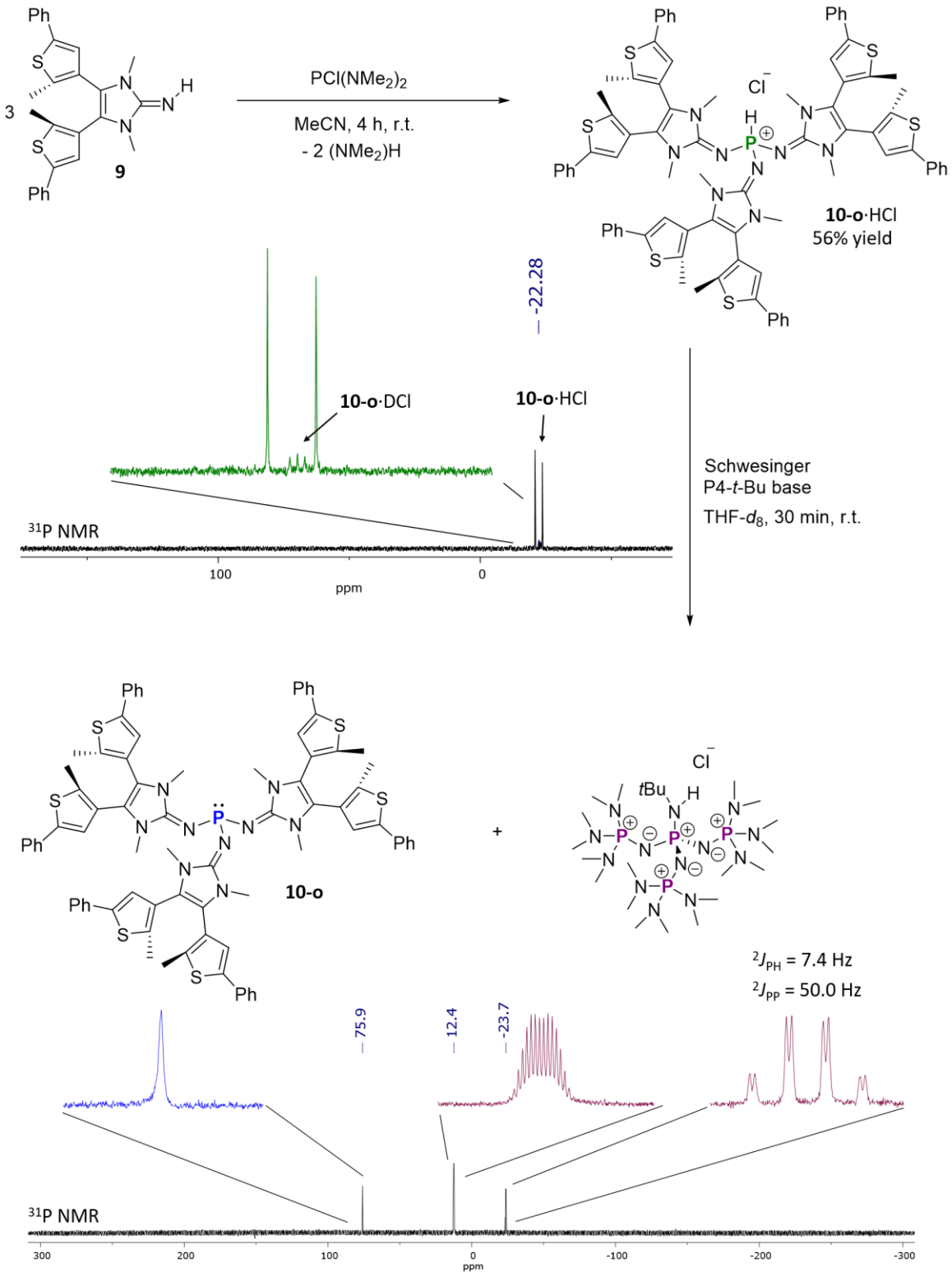


Figure S67: Overview: Preparation of **10-o**•HCl and subsequent in situ formation of **10-o** with *t*-Bu-P_4. ^{31}P NMR spectrum of **10-o**•HCl in dichloromethane-d_2 and ^{31}P NMR spectrum of the mixture containing **10-o** measured in THF-d_8.

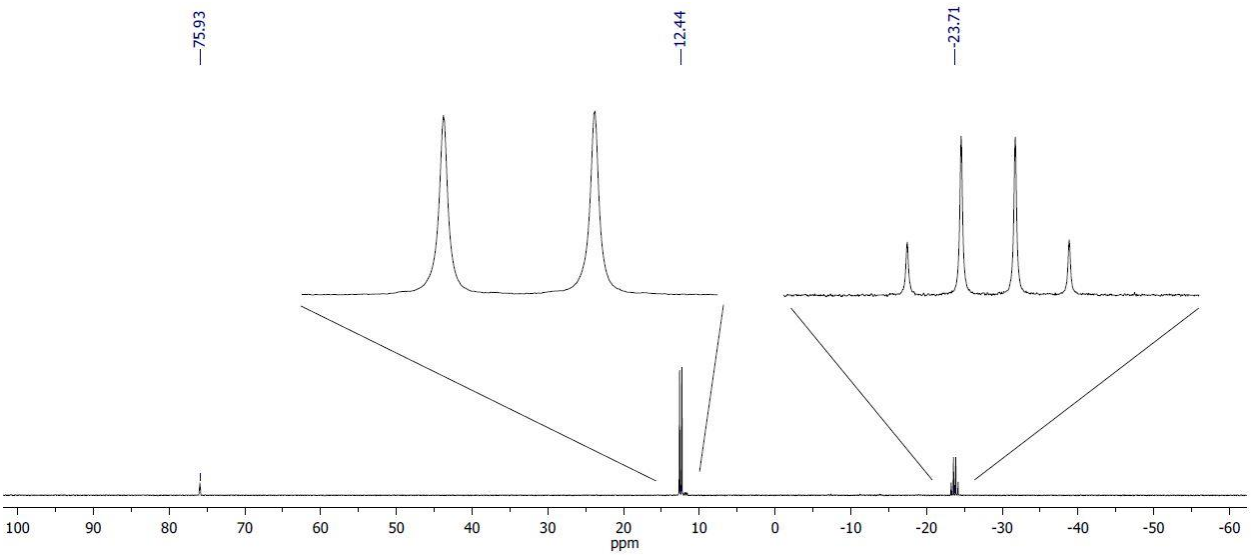


Figure S68: $^{31}P\{^{1}H\}$ NMR spectrum (THF-d_8, 300 K, 162 MHz) of the reaction mixture containing **10-o**.

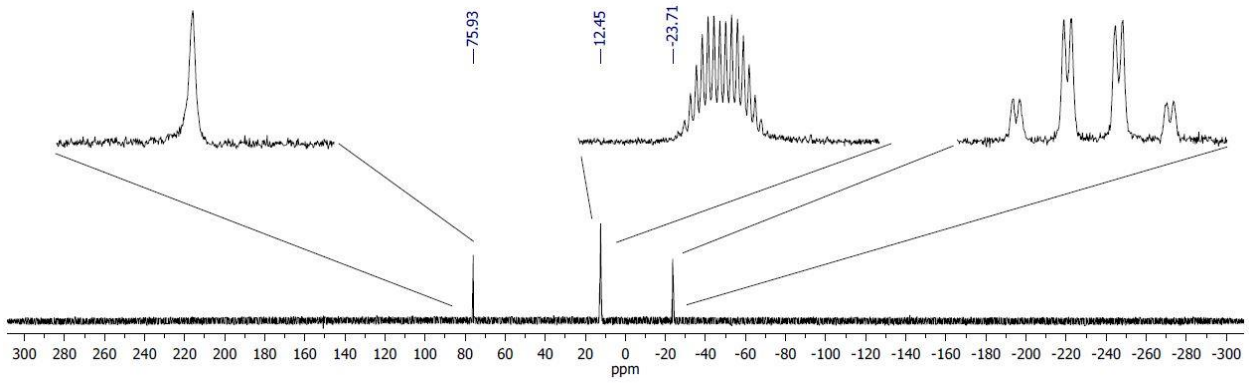


Figure S69: ^{31}P NMR spectrum (THF-d_8, 300 K, 162 MHz) of the reaction mixture containing **10-o**.

Photochromism of 10-o monitored by UV/vis-spectroscopy

UV/vis spectra of the mixture containing **10-o** and *t*-Bu-P_4•HCl in THF ([**10-o**/ t-Bu-P_4•HCl]$_0$ = 10^{-4} M) were recorded upon UV irradiation with λ = 315 nm. The spectra were recorded after 0 minutes, and the time indicated.

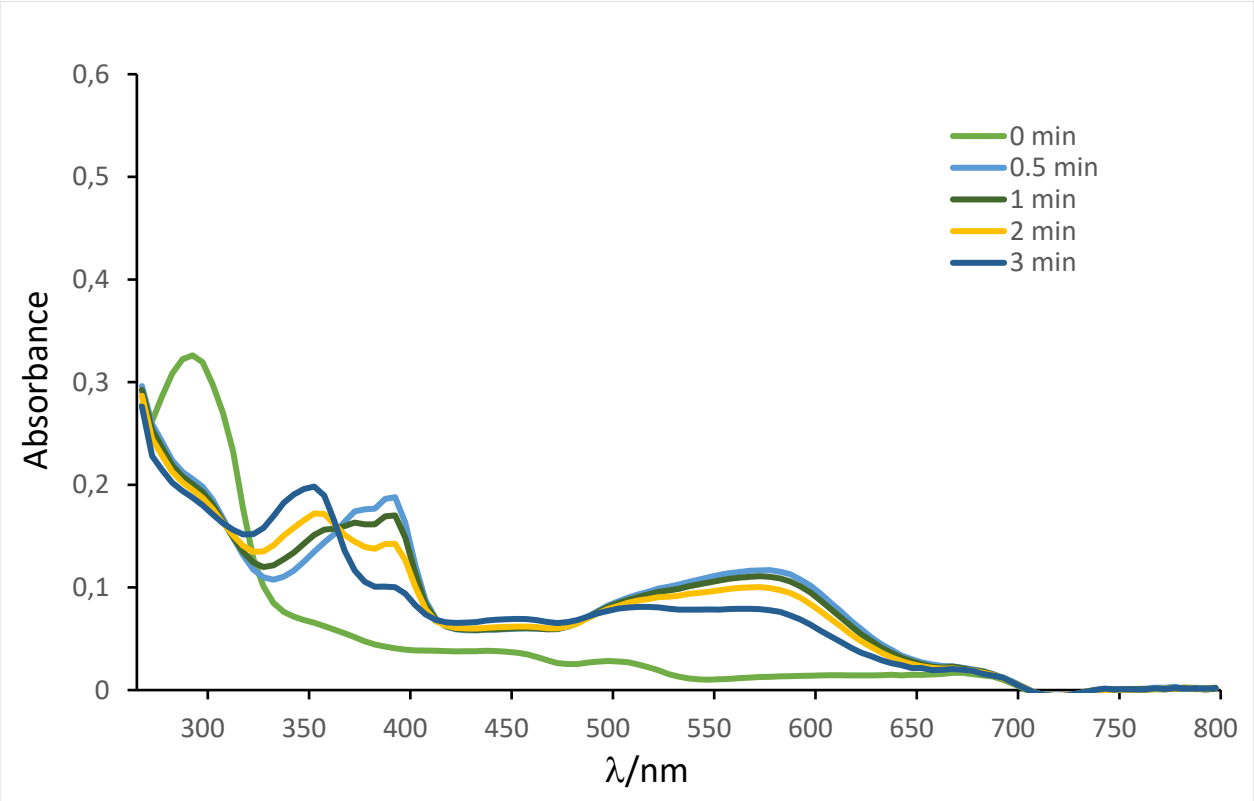


Figure S70: UV/ Vis spectral changes of the mixture containing **10-o** in THF ([**10-o**/ *t*-Bu-P_4•HCl]$_0$ = 10^{-4} M) upon UV irradiation (λ_{irr} = 315 nm, 140 mW). The spectra were recorded after irradiation for 0 min (green line), 1 min (dark-green line), 2 min (yellow line) and 3 min (dark-blue line).

Single-crystal X-ray diffraction study of **7-o**

A single crystal was selected under oil, mounted on a MiTeGen MicroLoop and immediately placed in a cold stream of N_2 on a diffractometer. Data were collected on a Bruker D8 QUEST PHOTON III (**7-o**) diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Using Olex2,[3] the structures were solved with the ShelXT[4] structure solution program using intrinsic phasing and refined with the ShelXL[5] refinement package using Least Squares minimization.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 2289253 (**7-o**). The data can be obtained free of charge via www.ccdc.cam.uk/data_request/cif (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Crystal structure data of compound 7-o

CCDC deposition number	2289253
Empirical formula	$C_{81}H_{96}N_6Ni_2O_6P_2S_4$
Formula weight	1557.23
Temperature/K	150
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.6213(5)
b/Å	17.5686(6)
c/Å	17.6681(5)
α/°	90
β/°	111.5820(10)
γ/°	90
Volume/Å^3	3931.7(2)
Z	2

ρ_{calc}g/cm^3	1.315
μ/mm^{-1}	0.681
F(000)	1644
Crystal size/mm^3	0.25 × 0.10 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	1.982 to 27.158
Index ranges	$-14 \le h \le 14$, $-14 \le k \le 14$, $-20 \le l \le 20$
Reflections collected	88253
Independent reflections	8721 [R_{int} = 0.0525, R_{sigma} = 0.0231]
Data/restraints/parameters	8721/24/490
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0335, wR_2 = 0.0862
Final R indexes [all data]	R_1 = 0.0424, wR_2 = 0.0927
Largest diff. peak/hole / e Å^{-3}	0.303/-0.468

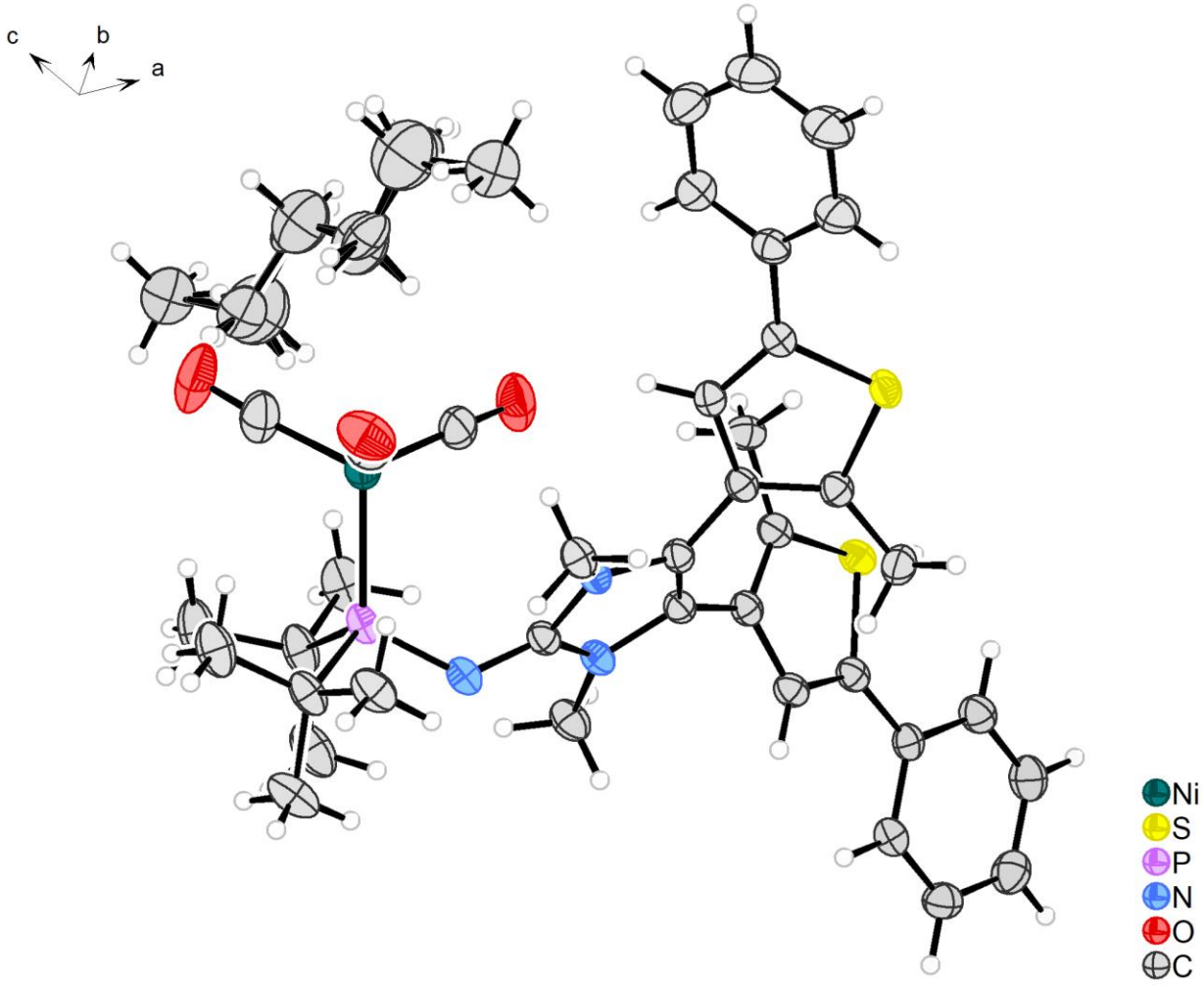


Figure S71: Molecular structure of **7-o** in the solid state (ellipsoids at 50% probability). The asymmetric unit contains one molecule of **7-o** and a pentane solvent molecule which is disordered over two positions (50:50).

UV/vis light source

The following custom-build technical equipment was used as UV/vis light source (310 nm/ 585 nm) for the irradiation experiments:

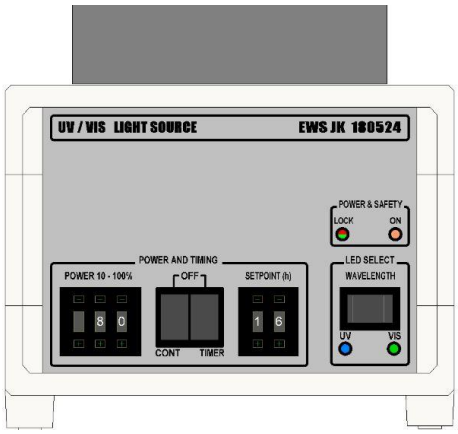


Figure S72: Frontal view (drawing) of the UV/vis light source.

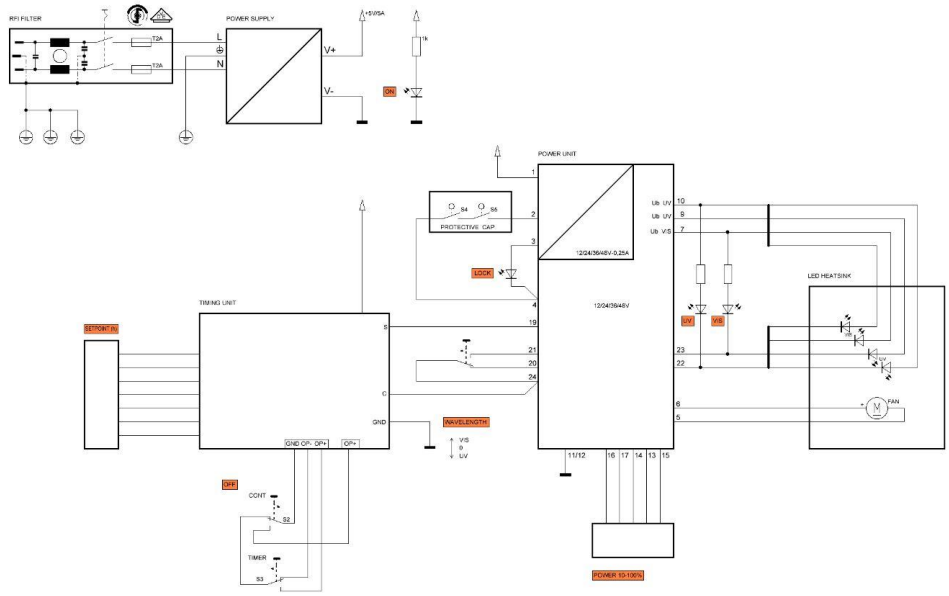


Figure S73: Schematic circuit diagram and setup by Jürgen Kröninger (electrical engineer, WWU Münster).

Figure S74: Frontal view (picture) of the UV/vis light source. Closed irradiation chamber (left), open chamber (right).

References

1 L. F. B. Wilm, M. Das, D. Janssen-Müller, C. Mück-Lichtenfeld, F. Glorius and F. Dielmann, Photoswitchable Nitrogen Superbases: Using Light for Reversible Carbon Dioxide Capture, *Angew. Chem. Int. Ed.*, 2022, **61**, e202112344.

2 F. Buß, M. B. Röthel, J. A. Werra, P. Rotering, L. F. B. Wilm, C. G. Daniliuc, P. Löwe and F. Dielmann, Tris(tetramethylguanidinyl)phosphine: The Simplest Non-ionic Phosphorus Superbase and Strongly Donating Phosphine Ligand, *Chem. Eur. J.*, 2022, **28**, e202104021.

3 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, 2009, **42**, 339-341.

4 G. M. Sheldrick, ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, 2015, **A71**, 3-8.

5 G. M. Sheldrick, Crystal structure refinement with ShelXL, *Acta Cryst.*, 2015, **C71**, 3-8.