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Supplementary Material for

Crystalline, Room-Temperature Stable Phophine–SO_2 Adducts: Generation of Sulfur Monoxide from Sulfur Dioxide

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CONTENTS:

Synthetic Details

General remarks: All manipulations were performed under an inert atmosphere of dry argon, using standard Schlenk and drybox techniques. Dry and oxygen-free solvents were employed. All glassware was oven-dried at 160 °C prior to use. ^{1}H, ^{13}C 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), 85% H_3PO_4 (^{31}P) and they were referenced to the residual solvent signals (C_6D_6: ^{1}H $\delta_H = 7.16$, ^{13}C $\delta_C = 128.06$; CD_3CN: $\delta_H = 1.94$, ^{13}C $\delta_C = 118.26$; toluene-d_8: ^{1}H $\delta_H = 2.09$, ^{13}C $\delta_C = 20.40$; THF-d_8: ^{1}H $\delta_H = 1.73$, ^{13}C $\delta_C = 67.57$) 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.

Reagents and Handling: Phosphines **1a**, **1b** and **1c** as well as phosphine sulfides **3a** and **3b** were prepared as published. [1,2] Sulfur dioxide was purchased from Messer Griesheim GmbH (47805 Krefeld, Germany) as SO_2 3.8 (99.98%). All other compounds were purchased from commercial sources (Sigma Aldrich, Alfa Aesar, abcr GmbH, Strem Chemicals) and used as received.

Reaction of selected phosphines with excess sulfur dioxide

General procedure: The reaction of SO_2 with phosphines was studied by NMR experiments, which were performed with samples of the respective phosphine under SO_2 pressure in Wilmad® low pressure/vacuum NMR tubes purchased from Sigma Aldrich in the solvent indicated. The NMR tube containing the solution of the phosphine was frozen in liquid nitrogen and the argon atmosphere was removed *in vacuo*. After warming the NMR tube to room temperature, it was pressurized with 2 bar SO_2.

P(*i*Pr)$_3$, P(*o*-tol)$_3$, PPh$_3$: After pressurizing solutions of P(*i*Pr)$_3$, P(*o*-tol)$_3$ and PPh$_3$ in C_6D_6 with 2 bar SO_2 at room-temperature for 5 hours the solutions turned yellow, which has been observed previously.[3] However, the ^{1}H and ^{31}P NMR spectra of the reaction mixtures were identical to those without SO_2, indicating no reaction of alkyl or aryl phosphines with SO_2 at ambient conditions.

P(NI*i*Pr)*i*Pr$_2$ (1a): Pressurizing a solution of phosphine **1a** in C_6D_6 with 2 bar SO_2 at room-temperature resulted in the formation of multiple species. The phosphorus containing species show singlets at 104.5, 67.6, 42.8, 38.3, 36.7 ppm in the ^{31}P NMR spectrum (Figure S1), with different chemical shift to the corresponding phosphine oxide **4a** (33.4 ppm) and phosphine sulfide **3a** (66.1 ppm).

P(NI*i*Pr)$_2$*i*Pr (1b): Pressurizing a solution of phosphine **1b** in C_6D_6 with 2 bar SO_2 at room-temperature resulted in the formation of four new compounds after 10 minutes, which show singlets in the ^{31}P NMR spectrum at 50.2, 15.4, 12.9 and 9.4 ppm (Figure S2) in a ratio of 2:12:16:1, respectively. After 3 hours at room temperature the signal at 15.4 ppm had disappeared (Figure S3) concomitant with increasing the relative intensity of the signals of the remaining species. The ^{31}P resonances matched to those of phosphine sulfide **3b** (50.2 ppm), phosphine oxide **4b** (12.9 ppm) and phosphine–SO_3 **5b** (9.4 ppm) with excess of SO_2 (*vide infra*, independent preparation of the latter).

P(NI*i*Pr)$_3$ (1c): After pressurizing a solution of phosphine **1c** in C_6D_6 with 2 bar SO_2 at room-temperature, a new species was formed, which show a signal at –14.4 ppm in the ^{31}P NMR spectrum (Figure S4). A preliminary XRD study of crystals grown from the reaction mixture indicate the formation of the phosphine oxide, which is coordinated to three SO_2 molecules (see Figure S54). The volatiles were removed *in vacuo* at room temperature to afford a colorless solid.

The phosphine oxide OP(NI*i*Pr)$_3$ (**4c**) was detected in the high resolution mass spectrum (HRMS/ESI) as the major species: m/z calculated for $[C_{33}H_{61}N_9PO]^+$ $(M+H)^+$ 630.47312, found 630.47672.

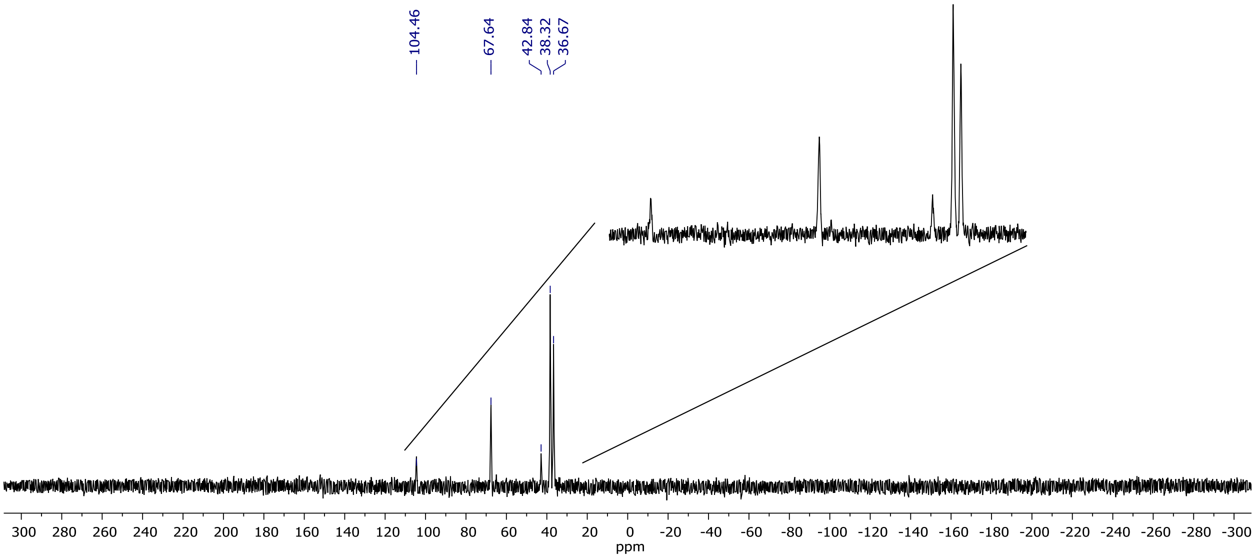


Figure S1: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **1a** after pressurizing the NMR tube with 2 bar SO_2 for 1 hour.

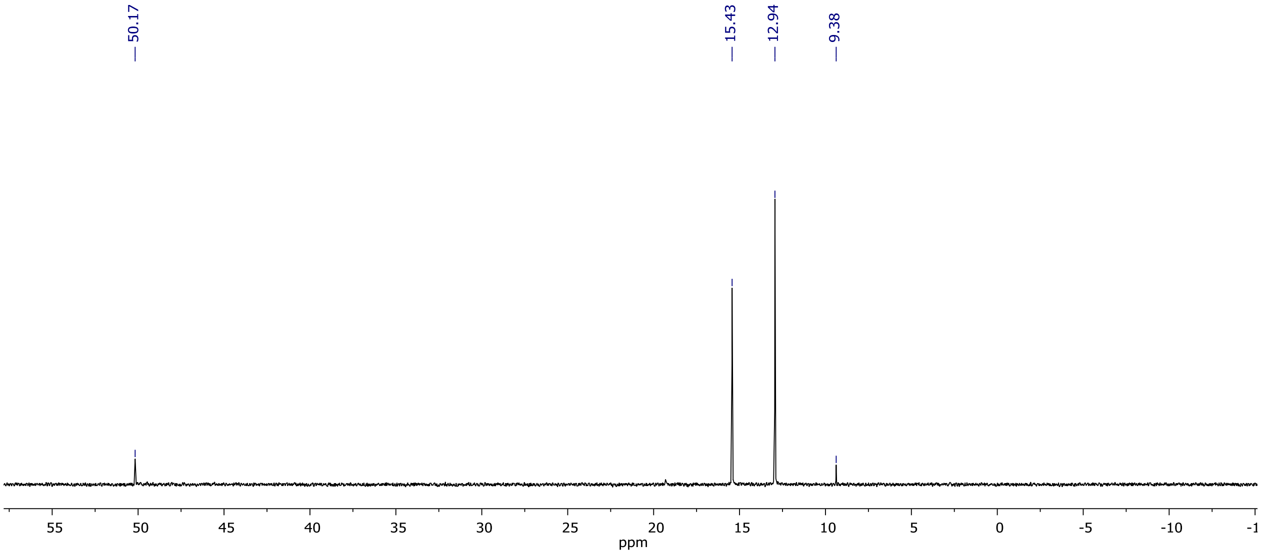


Figure S2: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **1b** after pressurizing the NMR tube with 2 bar SO_2 for 10 minutes.

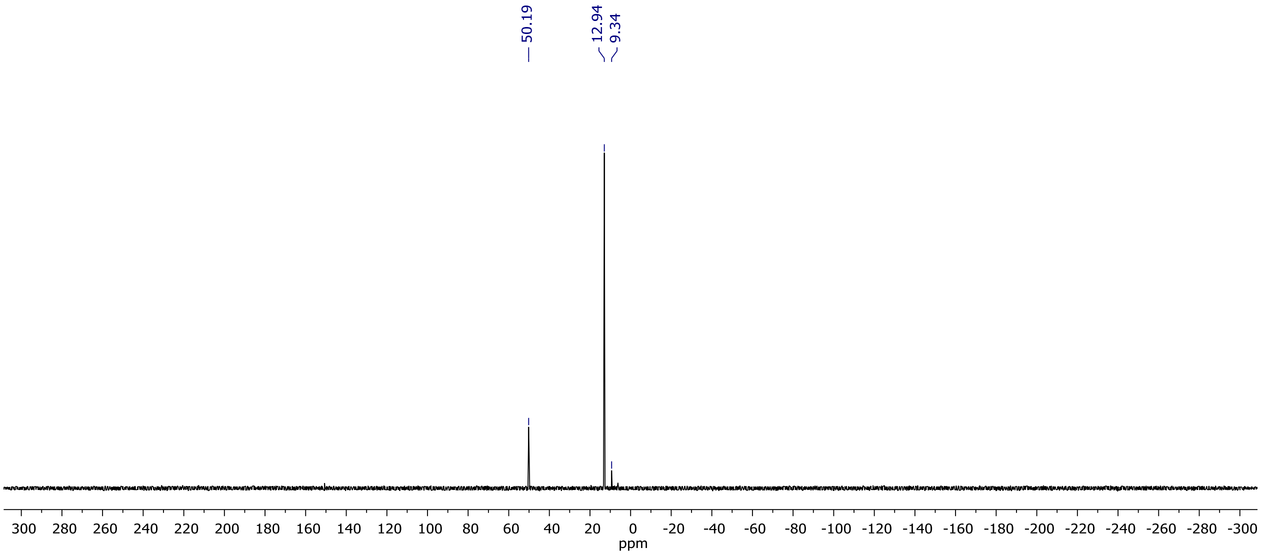


Figure S3: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **1b** after pressurizing the NMR tube with 2 bar SO_2 for 3 hours.

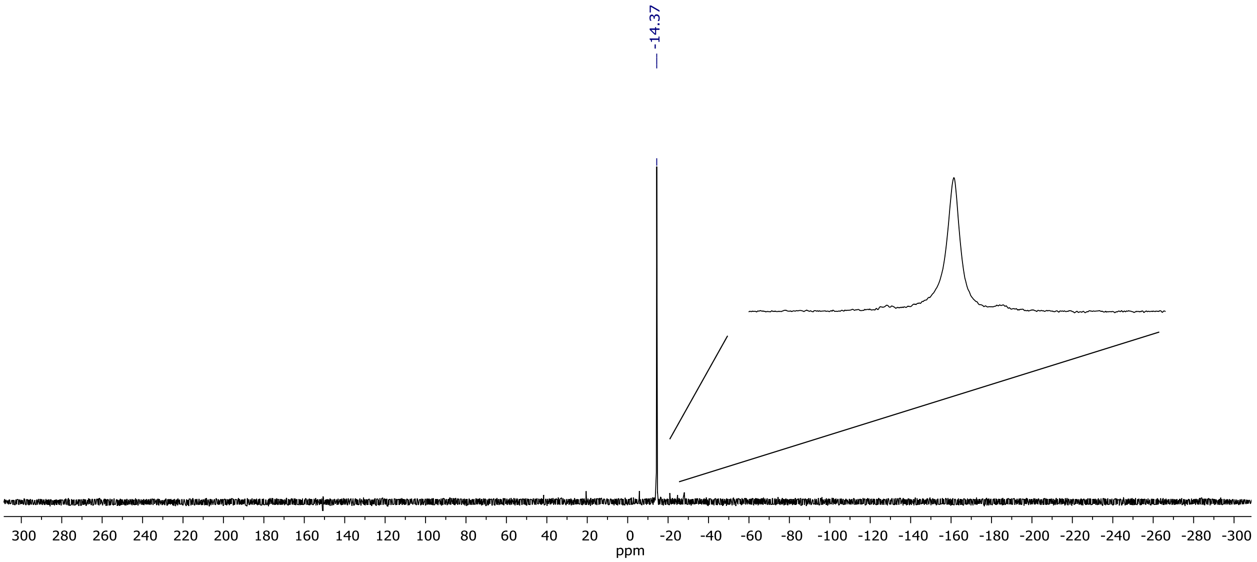
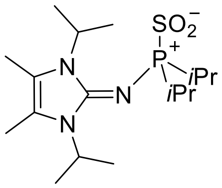


Figure S4: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **1c** after pressurizing the NMR tube with 2 bar SO_2.

Preparation of phosphine–SO$_2$ adducts **2a-c**

Phosphine–SO$_2$ adducts **2a**, **2b** and **2c** were prepared from the reaction of phosphines **1a**, **1b** and **1c** with 1,4-Diazabicyclo[2.2.2]octane bis(sulfur dioxide), which is abbreviated by DABSO hereafter. DABSO was used as a convenient source of stoichiometric amounts of SO$_2$.

Compound 2a: Phosphine **1a** (60 mg, 0.1926 mmol, 2 eq.) and DABSO (24 mg, 0.0962 mmol, 1 eq.) were dissolved in 1,2-difluorobenzene (3 mL) at –78 °C. The reaction mixture was immediately analyzed by NMR spectroscopy. DABCO could not be separated from **2a**, owing to the rapid decomposition of **2a** at room temperature.



^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 4.93 (s, br, 2H, NC*H*Me$_2$), 2.53 (s, 6H, CH$_3$), 2.41 (h, $^3J_{HH}$ = 7.0 Hz, 2H, PC*H*Me$_2$), 1.39 (dd, $^3J_{PH}$ = 15.2 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, PCHC*H*$_3$), 1.26 (dd, $^3J_{PH}$ = 14.9 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, PCHC*H*$_3$), 1.23 ppm (d, $^3J_{HH}$ = 7.1 Hz, 12H, NCHC*H*$_3$).

^{31}P NMR (161.9 MHz, C$_6$D$_6$): δ = 39.8 ppm (m).

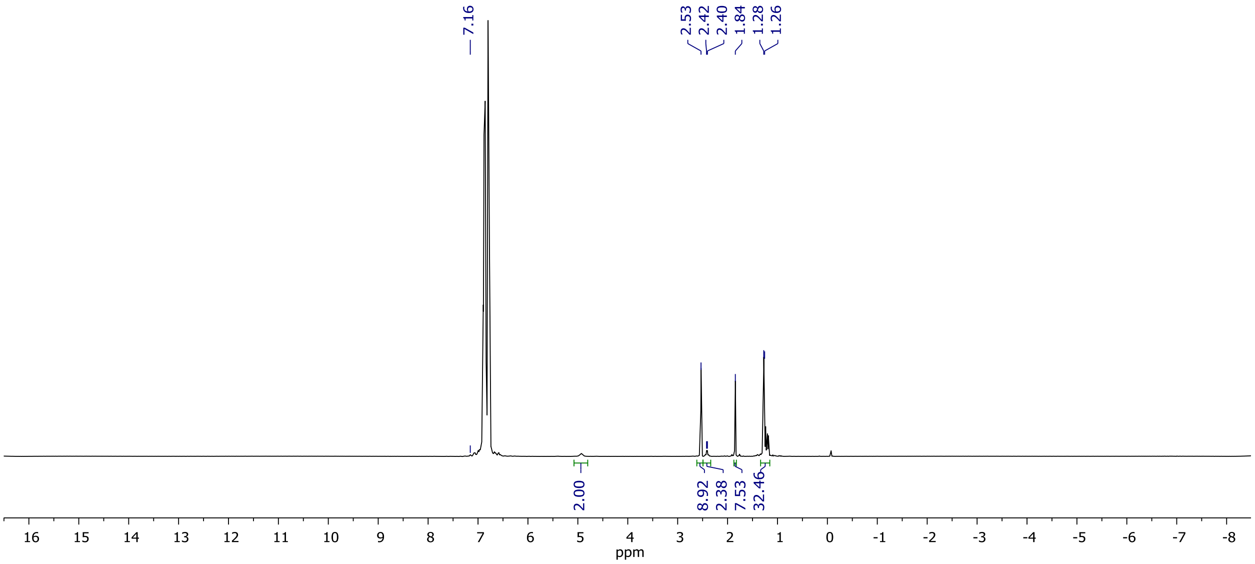


Figure S5: ^{1}H NMR spectrum (C$_6$D$_6$, 300 K, 400 MHz) of **2a**. * Difluorobenzene

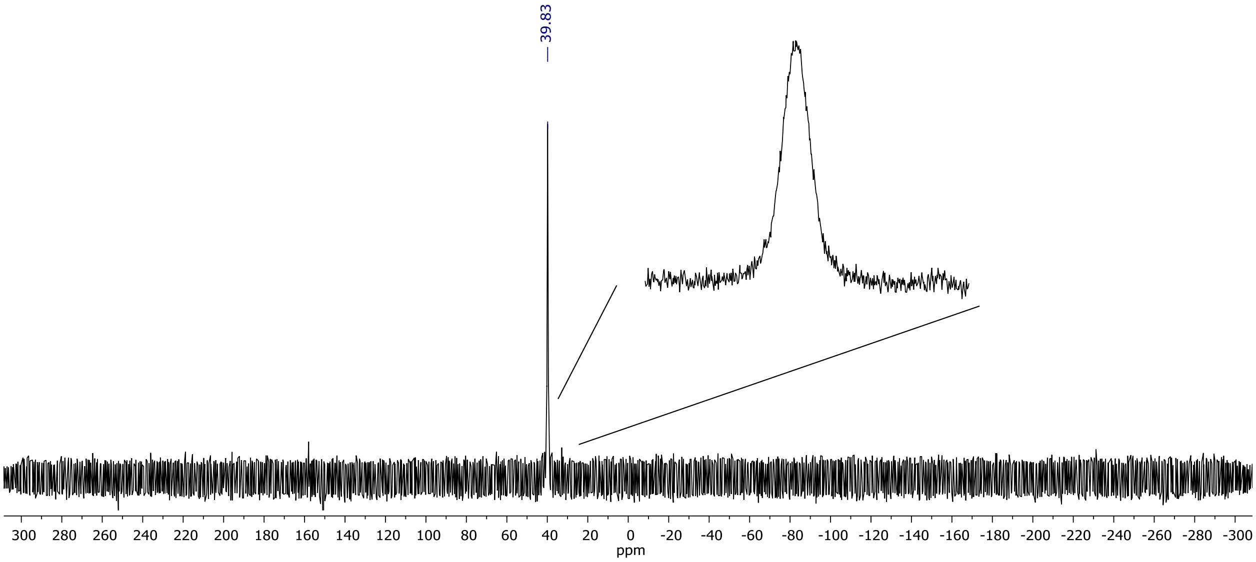
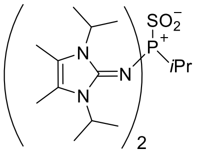


Figure S6: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **2a**.

Compound 2b: Phosphine **1b** (120 mg, 0.256 mmol, 2 eq.) and DABSO (32 mg, 0.128 mmol, 1 eq.) were suspended in THF (3 mL) at −78 °C. After stirring for 20 minutes at −78 °C, the NMR spectra of the solution showed quantitative formation of **2b**. To remove DABCO from the mixture, *n*-hexane (10 mL) was added. The resulting precipitate was filtered off and washed with *n*-hexane (3 x 5 mL). After evaporation to dryness, **2b** was isolated as a white solid in 70% yield (94 mg, 0.179 mmol). Single crystals of **2b** were grown by slow diffusion of *n*-hexane into a solution of **2b** in benzene. The phosphine–SO_2 adduct **2b** is soluble in benzene and THF, and insoluble in *n*-hexane and diethyl ether. Slow decomposition (40%) of **2b** was observed by ^{31}P NMR analysis, when the solid **2b** was stored under an atmosphere of dry argon for 2.5 weeks.



^{1}H NMR (400 MHz, C_6D_6): δ = 5.28 (sept, $^3J_{HH}$ = 7.0 Hz, 4H, NC*H*Me$_2$), 2.85 (m, 1H, PC*H*Me$_2$), 1.67 (s, 12H, CH$_3$), 1.64 (dd, $^3J_{PH}$ = 15.1 Hz, $^3J_{HH}$ = 7.3 Hz, 6H, 6H, PCHC*H*$_3$), 1.29 ppm (d, $^3J_{HH}$ = 7.1 Hz, 24H, NCHC*H*$_3$).

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ = 146.5 (N_2CN), 117.2 (C=C), 47.0 (N*C*HMe$_2$), 29.4 (d, $^1J_{PC}$ = 52.8 Hz, P*C*HMe$_2$), 21.6 (m, NCH(*C*H$_3$)$_2$), 17.6 (s, PCH(*C*H$_3$)$_2$), 17.6 (s, PCH(*C*H$_3$)$_2$), 9.95 ppm (CH$_3$).

^{31}P NMR (161.9 MHz, C_6D_6): δ = 20.4 ppm (m).
HRMS (ESI): m/z calculated for $[N_6H_{48}C_{25}P]^+$ $(M+H\text{-}SO_2)^+$ 463.36726, found 463.36765.
IR ν/cm^{-1} = 2972.70, 2933.71, 1559.42, 1517.95, 1466.77, 1398.43, 1367.17, 1209.64, 1139.05, 1078.34, 974.85, 959.99.
CHN analysis: found (calculated): C 56.54 (57.01) H 9.07 (8.99) N 15.75 (15.96).

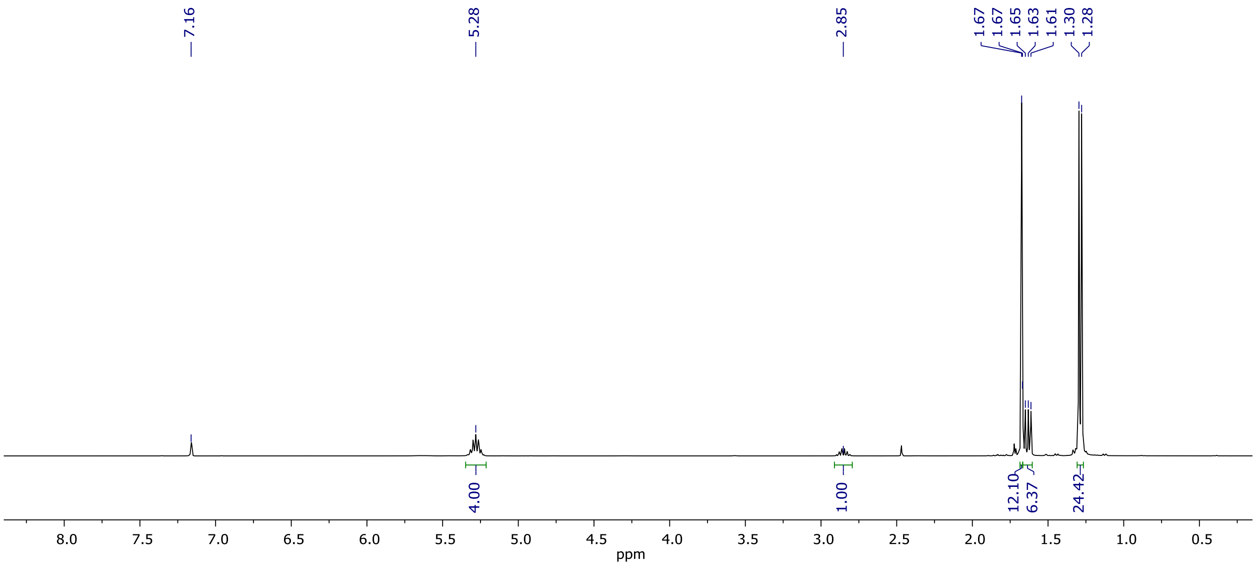


Figure S7: ^{1}H NMR spectrum (C_6D_6, 300 K, 400 MHz) of **2b**.

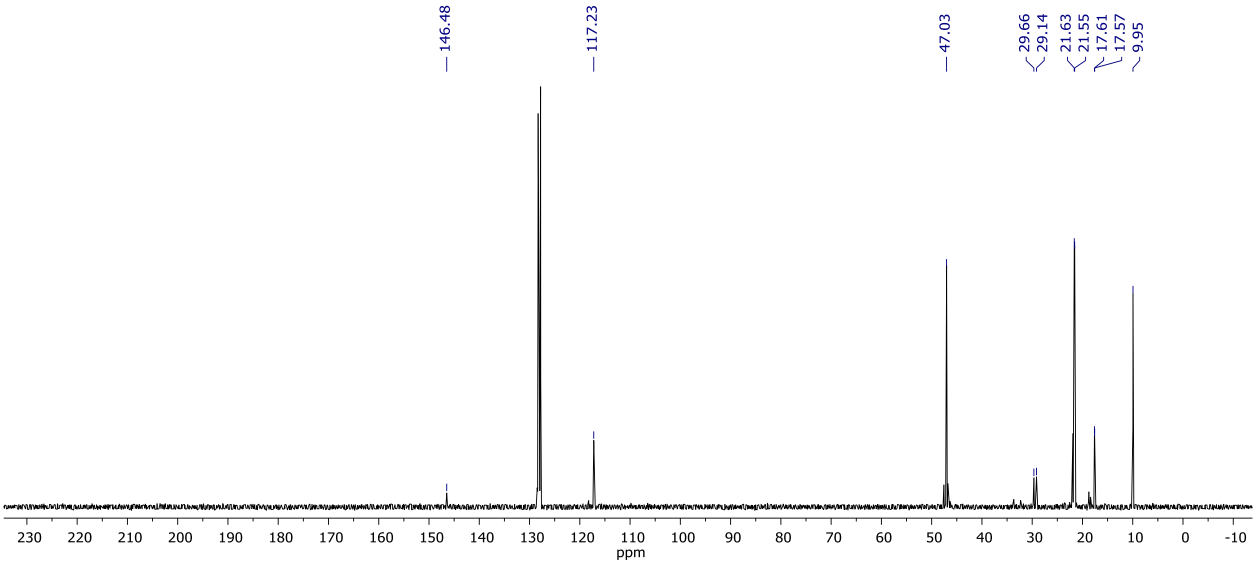


Figure S8: ^{13}C{^{1}H} NMR spectrum (CD_3CN, 300 K, 101 MHz) of **2b**.

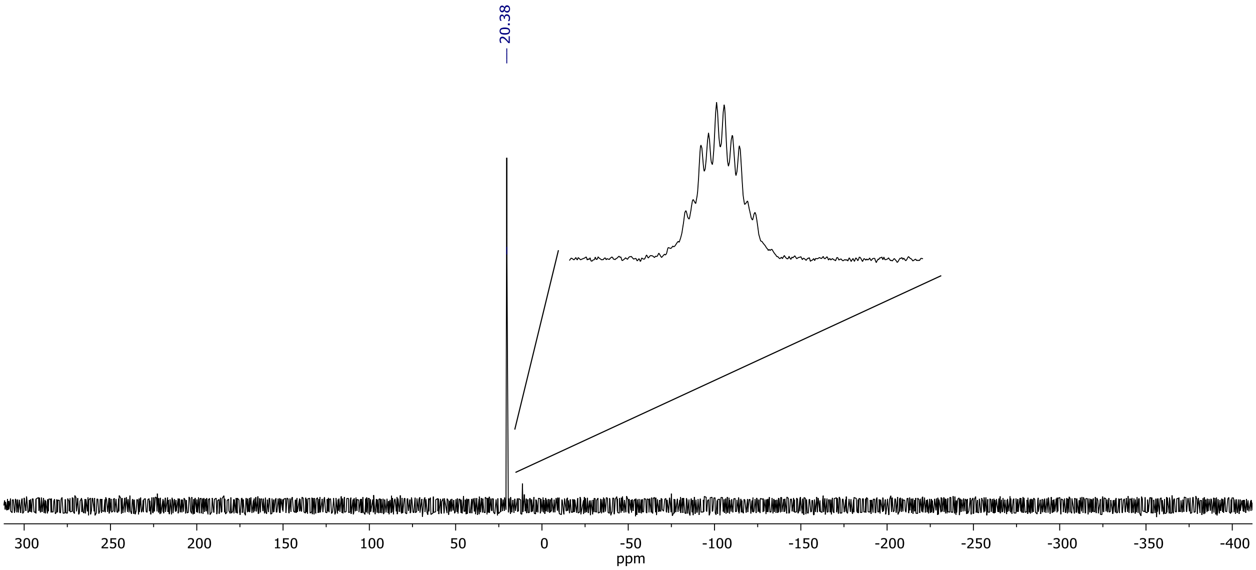


Figure S9: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **2b**.

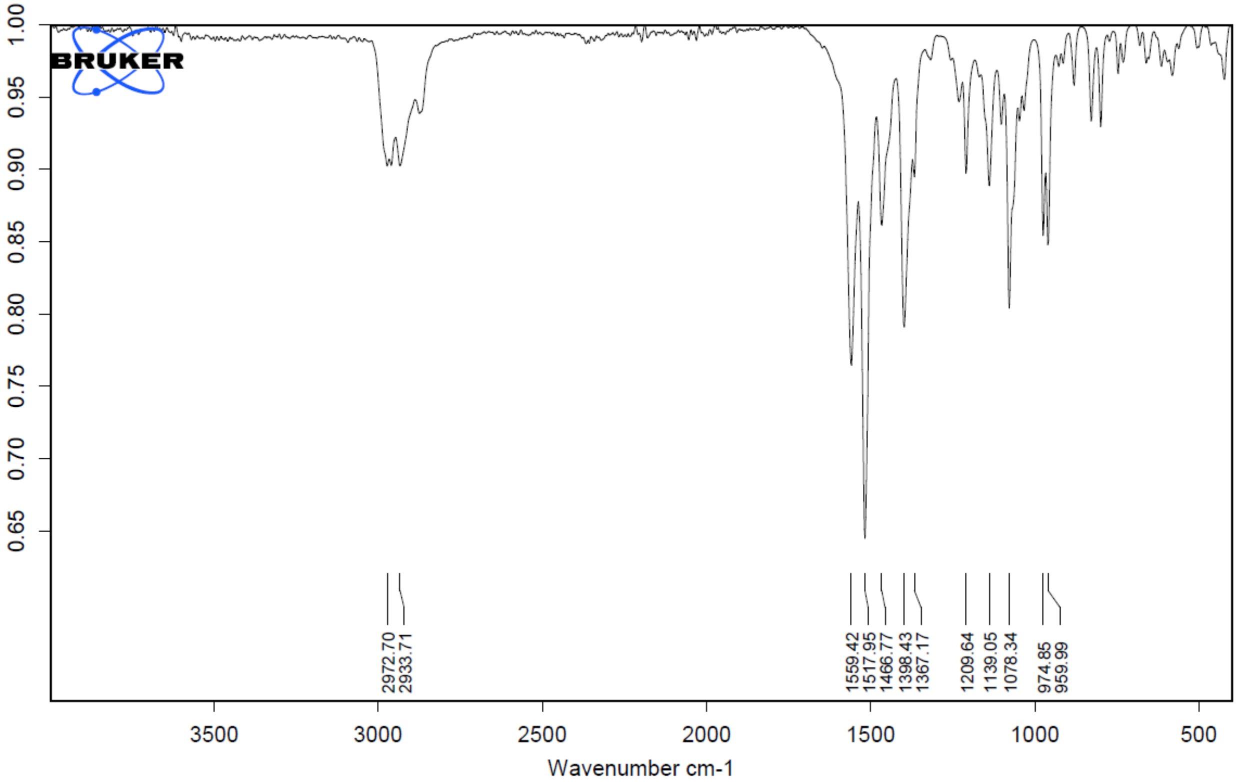
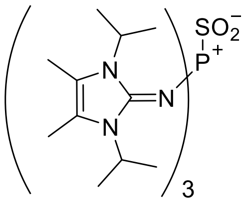


Figure S10: IR spectra of **2b**.

Compound 2c: Phosphine **1c** (100 mg, 0.1628 mmol, 2 eq.) and DABSO (20 mg, 0.0814 mmol, 1 eq.) were dissolved in THF (3 mL). Stirring the reaction mixture for 5 minutes at room temperature resulted in precipitation of a white solid, which was filtered off and washed with *n*-hexane (3 x 5 mL). After evaporation to dryness, **2c** was isolated as a white solid in 97% yield (106 mg, 0.1578 mmol). Single crystals of **2c** were formed by slow cooling of a saturated solution of **2c** in THF. Phosphine–SO_2 adduct **2c** is good soluble in acetonitrile, 1,2-difluorobenzene and fluorobenzene, and insoluble in THF, diethyl ether, *n*-hexane and benzene.



^{1}H NMR (400 MHz, CD_3CN): δ = 5.25 (sept, $^3J_{HH}$ = 7.1 Hz, 6H, NCHMe$_2$), 2.14 (s, 18H, CH_3), 1.32 ppm (d, $^3J_{HH}$ = 7.1 Hz, 36H, NCHCH_3).

^{13}C{^{1}H} NMR (100.6 MHz, CD_3CN): δ = 147.0 (N_2CN), 118.3 (C=C), 47.5 (NCHMe$_2$), 21.8 (NCH(CH$_3$)$_2$), 10.4 ppm (CH_3).

^{31}P NMR (161.9 MHz, CD_3CN): δ = –7.2 ppm (m).

^{1}H NMR (400 MHz, fluorobenzene + C_6D_6): δ = 5.67 (sept, $^3J_{HH}$ = 7.1 Hz, 6H, NCHMe$_2$), 1.82 (s, 18H, CH_3), 1.34 ppm (d, $^3J_{HH}$ = 7.1 Hz, 36H, NCHCH_3).

^{13}C{^{1}H} NMR (100.6 MHz, fluorobenzene + C_6D_6): δ = 146.6 (N_2CN), 116.6 (C=C), 46.6 (NCHMe$_2$), 21.3 (NCH(CH$_3$)$_2$), 9.4 ppm (CH_3).

^{31}P NMR (161.9 MHz, fluorobenzene + C_6D_6): δ = –4.91 ppm (m).

HRMS (ESI): m/z calculated for $[C_{66}H_{121}N_{18}O_4P_2S_2]^+$ $(2M+H)^+$ 1355.87294, found 1355.87574.
IR ν/cm^{-1} = 2970.28, 2936.22, 1537.11, 1461.26, 1386.46, 1364.40, 1243.55, 1204.60, 1137.44, 1096.81, 1064.46, 966.93, 950.62, 814.25, 728.00.
CHN analysis: found (calculated): C 58.03 (58.38) H 9.00 (9.06) N 17.86 (18.57).

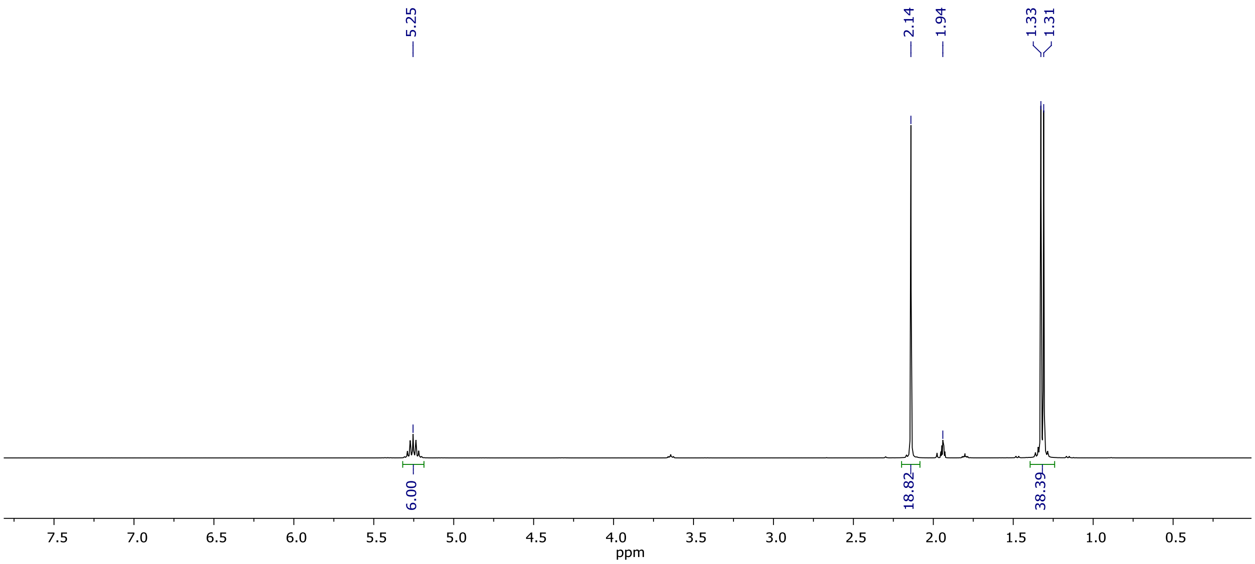


Figure S11: ^{1}H NMR spectrum (CD_3CN, 300 K, 400 MHz) of **2c**.

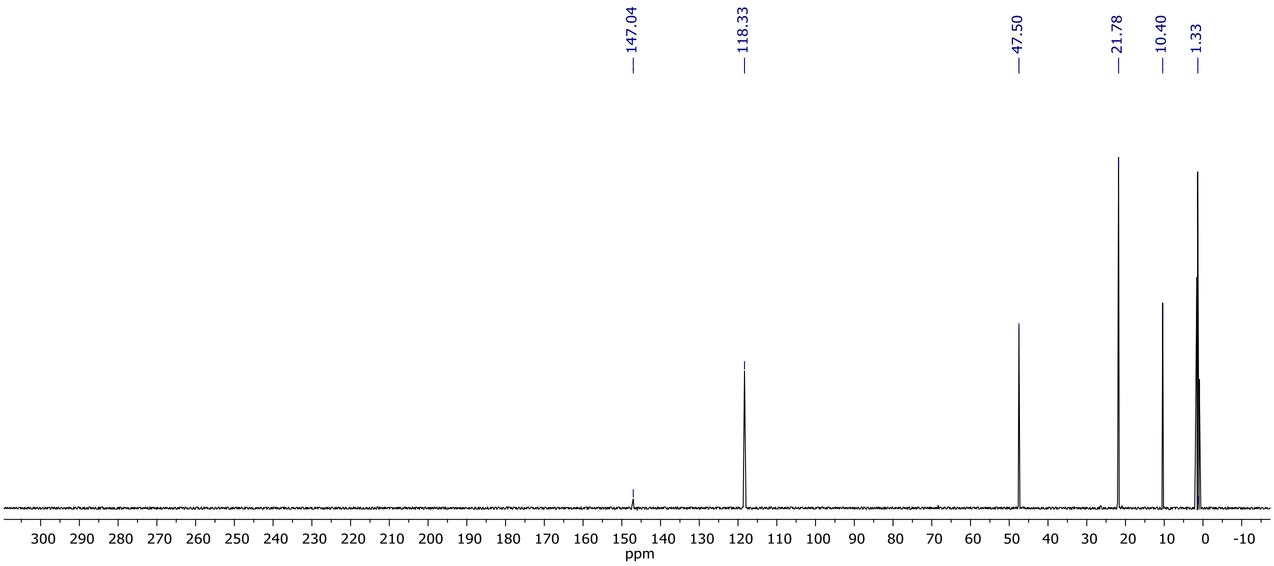


Figure S12: $^{13}C\{^{1}H\}$ NMR spectrum (CD_3CN, 300 K, 101 MHz) of **2c**.

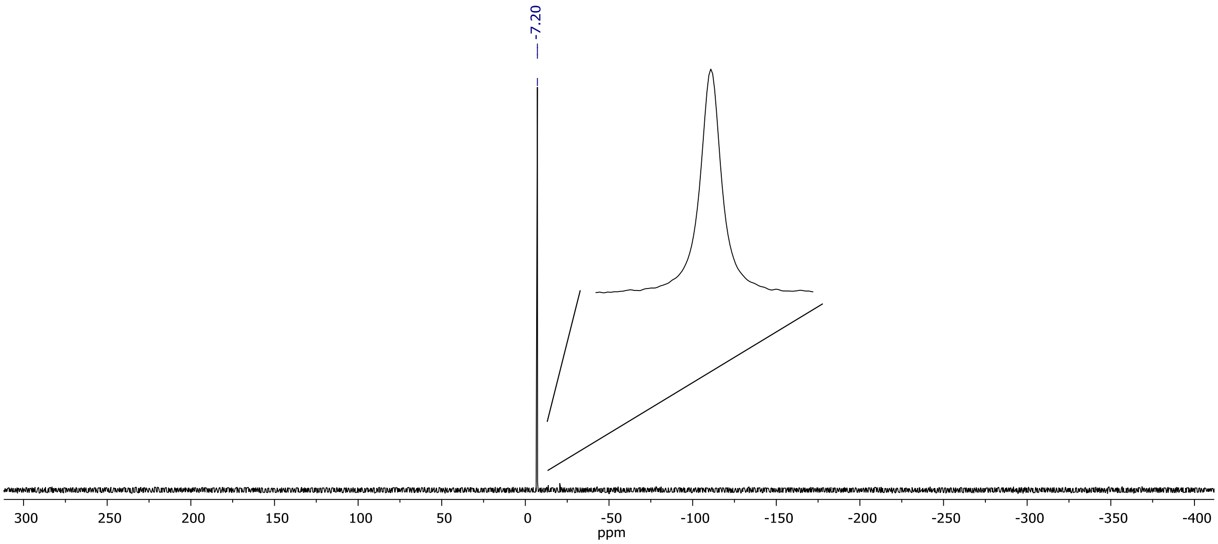


Figure S13: ^{31}P NMR spectrum (CD_3CN, 300 K, 162 MHz) of **2c**.

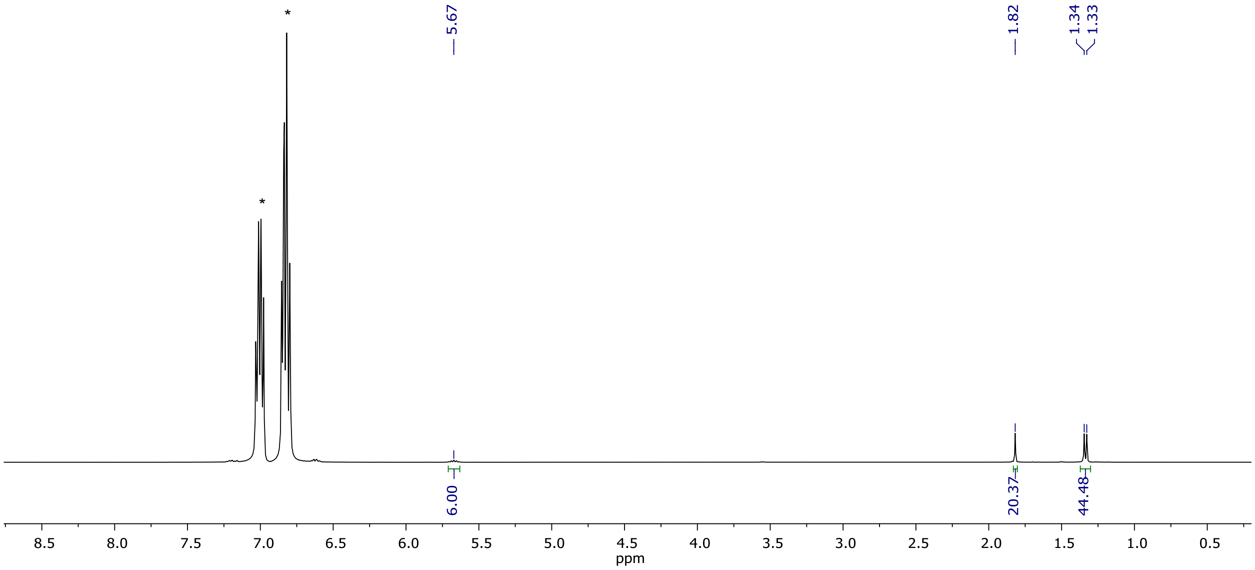


Figure S14: ^{1}H NMR spectrum (fluorobenzene + C_6D_6, 300 K, 400 MHz) of **2c**. * fluorobenzene

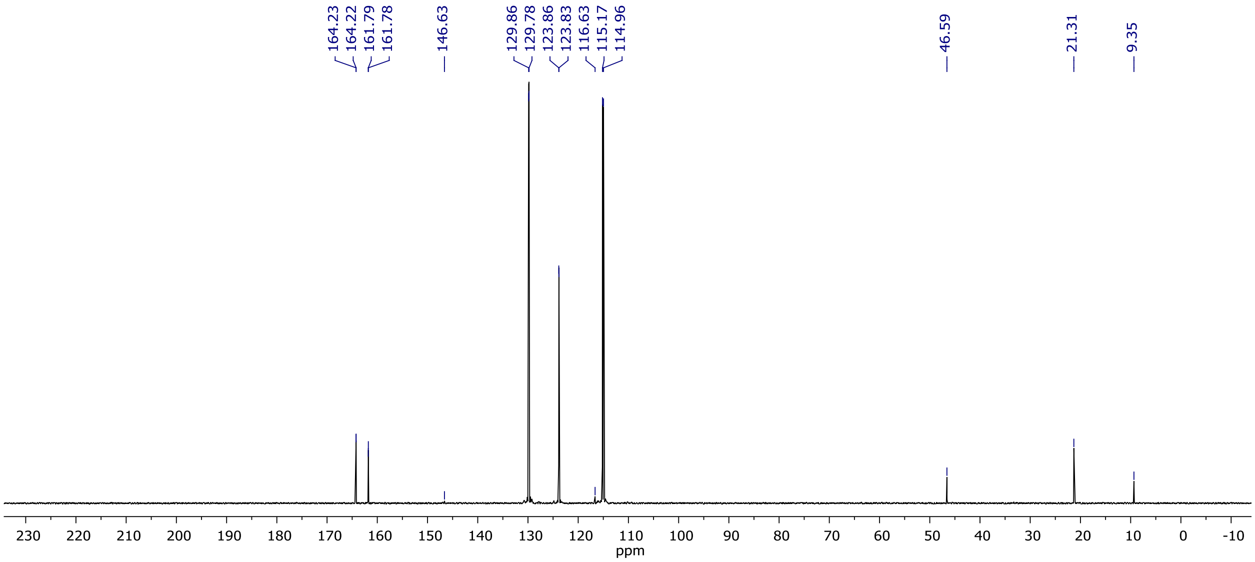


Figure S15: ^{13}C{^{1}H} NMR spectrum (fluorobenzene + C_6D_6, 300 K, 101 MHz) of **2c**. * fluorobenzene

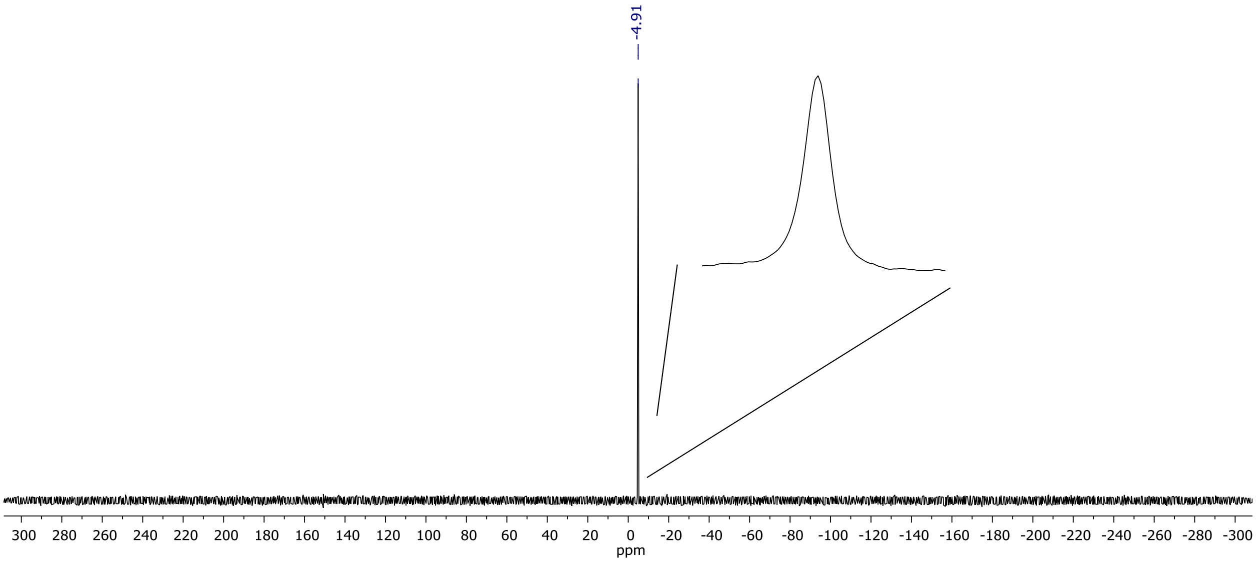


Figure S16: ^{31}P NMR spectrum (fluorobenzene + C_6D_6, 300 K, 162 MHz) of **2c**.

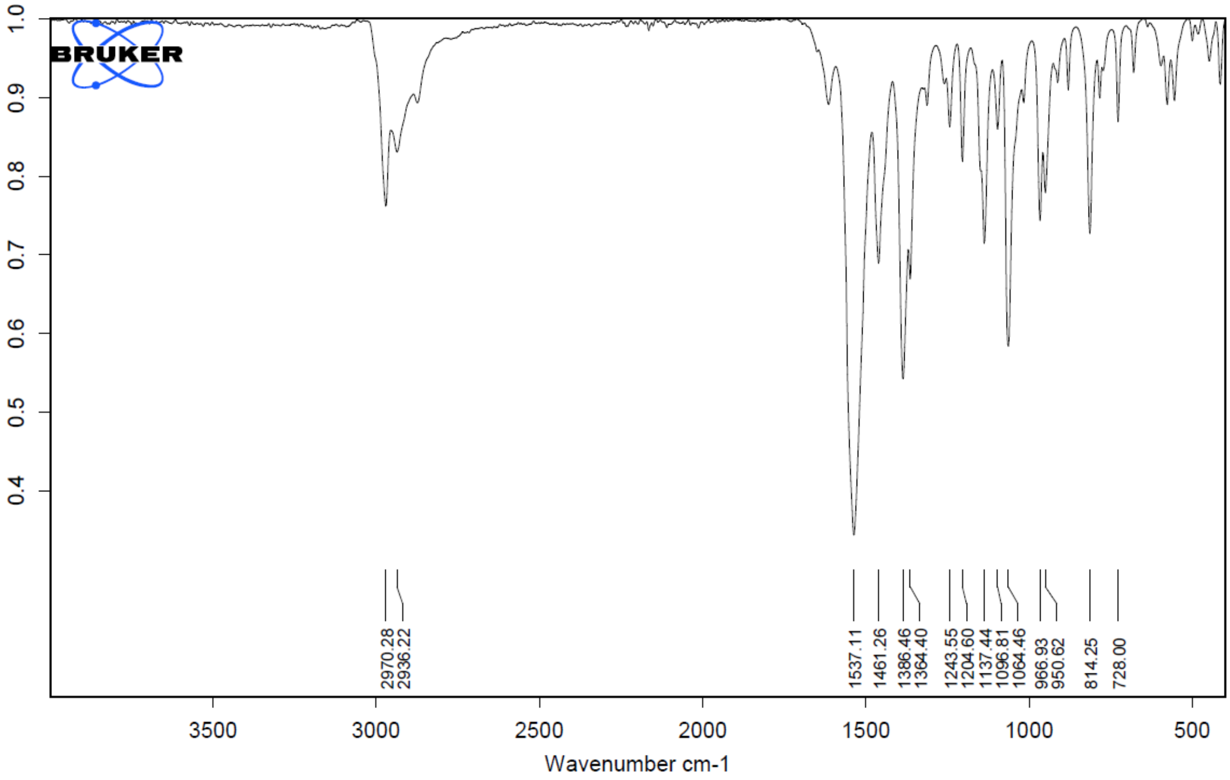
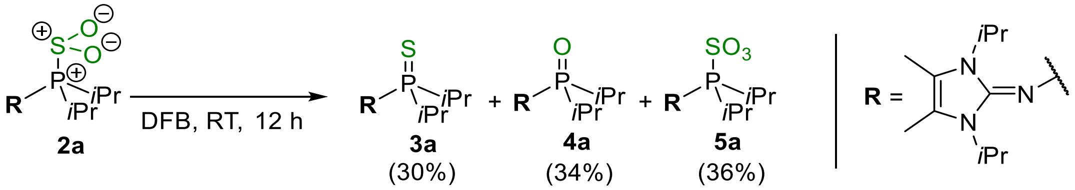


Figure S17: IR spectrum of **2c**.

Thermal decomposition of phosphine–SO_2 adducts **2a-c**

<u>Decomposition of **2a** at room temperature:</u>

Phosphine–SO_2 adduct **2a** was prepared by the reaction of **1a** and DABSO in diflourobenzene at –78 °C. The ^{31}P NMR spectrum of the mixture was recorded immediately (Figure S18), which showed the resonance of **2a** at –39.8 ppm (m). The decomposition reaction was monitored by recording ^{31}P and ^{1}H NMR spectra after 2, 10, 20, 80, 130 and 260 minutes, respectively (Figure S19). After 5 h at room temperature full consumption of **2a** was observed in the ^{31}P NMR spectrum, indicating the selective formation of phosphine sulfide **3a** (65.8 ppm), phosphine oxide **4a** (33.2 ppm) and phosphine–SO_3 adduct **5a** (37.6 ppm) in 1:1:1 ratio, respectively (Figure S20). The reaction products **3a**, **4a** and **5a** were identified by their independent preparation from the reaction of phosphine **1a** with elemental sulfur, N_2O or pyridine–SO_3, respectively (*vide infra*).



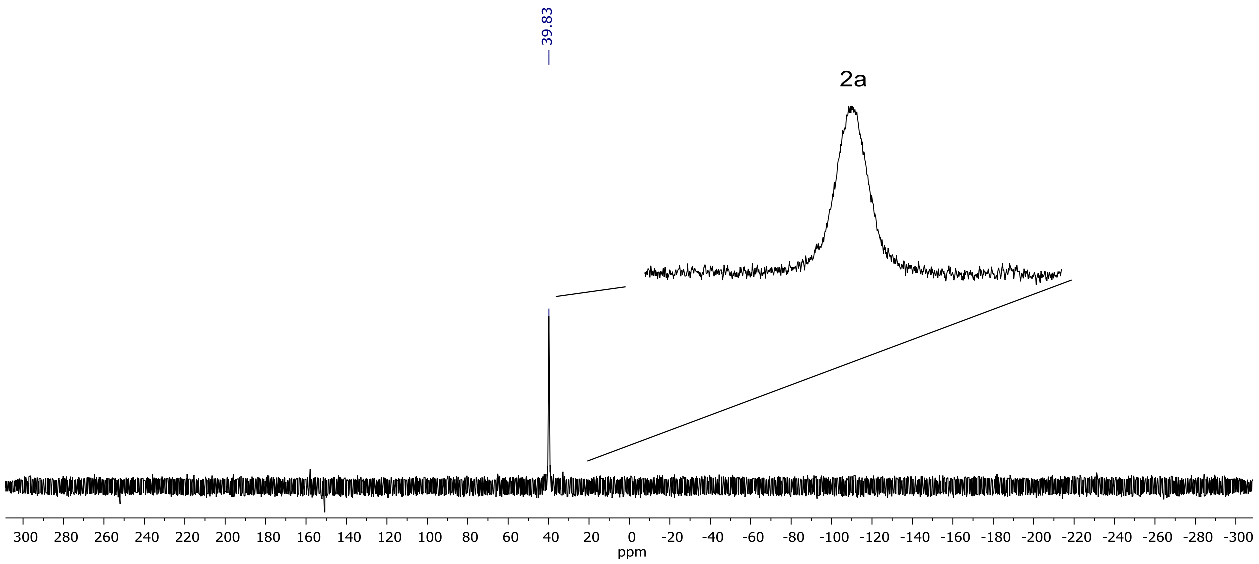


Figure S18: ^{31}P NMR spectrum (fluorobenzene + C_6D_6, 300 K, 162 MHz) of **2a** instantaneously after allowing the sample to warm up to room-temperature.

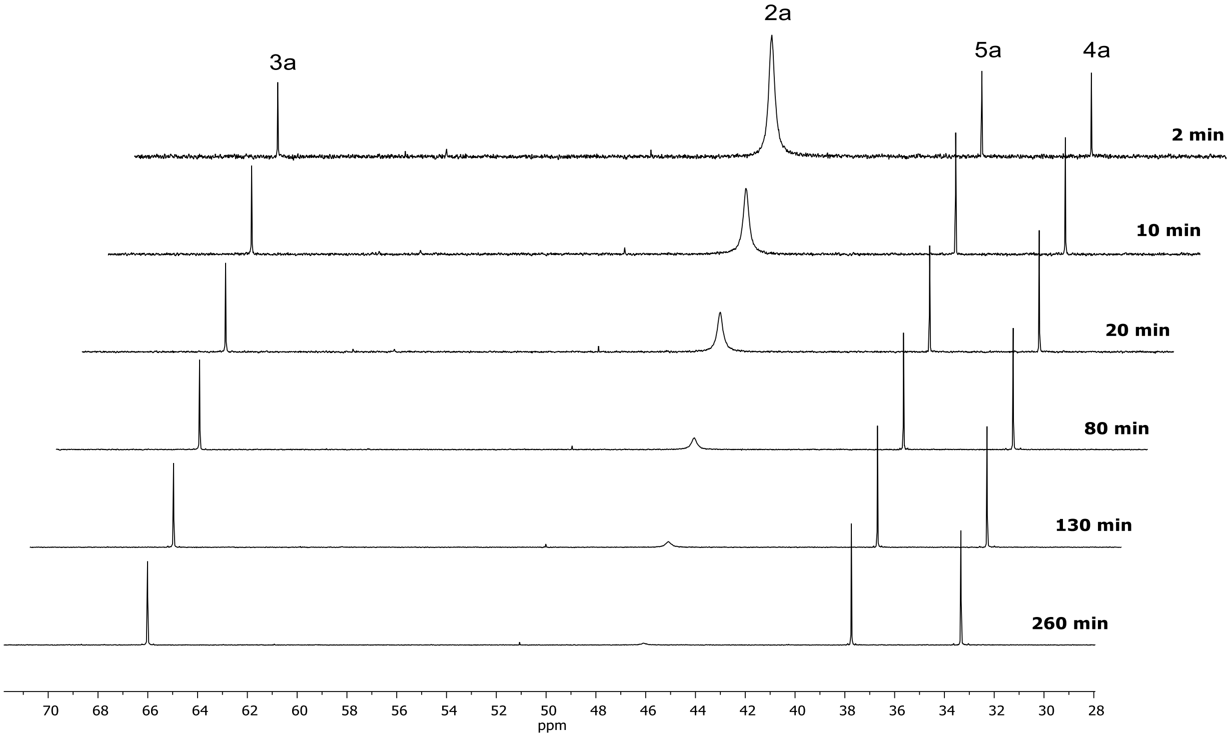


Figure S19: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **2a** after keeping the sample at room-temperature for the times indicated.

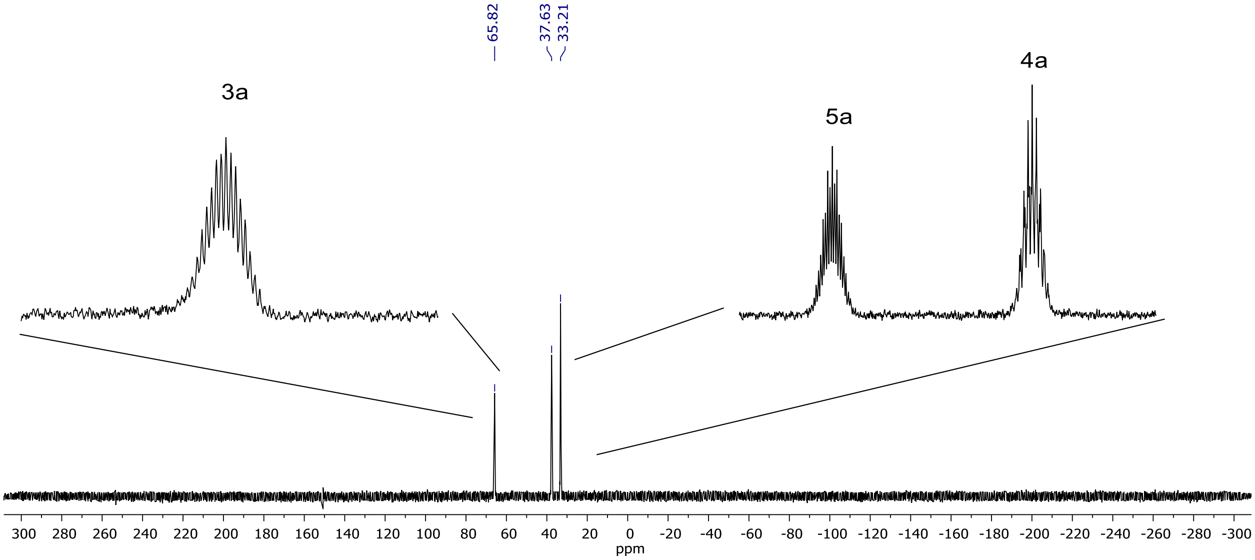


Figure S20: ^{31}P NMR spectrum (fluorobenzene + C_6D_6, 300 K, 162 MHz) of **2a** after keeping the sample at room-temperature for 5 hours.

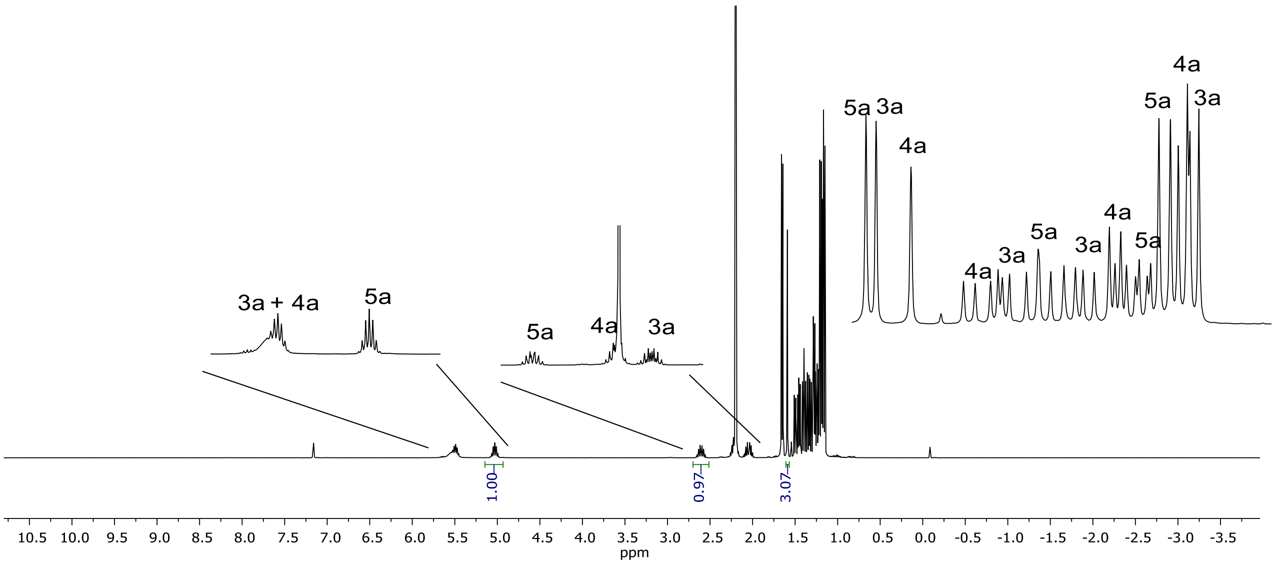


Figure S21: ^{1}H NMR spectrum (fluorobenzene + C_6D_6, 300 K, 400 MHz) of **2a** after keeping the sample at room-temperature for 5 hours.

The following ions were identified in the high-resolution mass spectrum (HRMS/ESI) of the reaction mixture:

[**4a**+H]$^+$: m/z calc. for $[C_{17}H_{35}N_3PO]^+$ $(M+H)^+$ 328.25123, found: 328.25114.

[**4a**+Na]$^+$: m/z calc. for $[C_{17}H_{34}N_3PONa]^+$ $(M+Na)^+$ 350.23317, found: 350.23307.

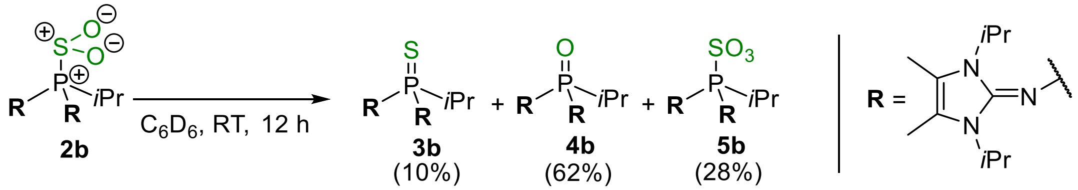
[**3a**+H]$^+$: m/z calc. for $[C_{17}H_{35}N_3PS]^+$ $(M+H)^+$ 344.22838, found: 344.22805.

[**3a**+Na]$^+$: m/z calc. for $[C_{17}H_{34}N_3PSNa]^+$ $(M+Na)^+$ 366.21033, found: 366.20999.

[**5a**+Na]$^+$: m/z calc. for $[C_{17}H_{34}N_3PSO_3Na]^+$ $(M+Na)^+$ 414.19507, found: 414.19461.

Decomposition of **2b** at room-temperature:

Phosphine–SO_2 adduct **2b** was prepared by the reaction of **1b** and DABSO in THF at –78 °C. **2b** is stable when stored as solid at –40 °C. The ^{31}P NMR spectrum in C_6D_6 at room temperature showed the resonance of **2b** at 20.4 ppm (m) (Figure S22). The decomposition reaction was monitored by recording ^{31}P and ^{1}H NMR spectra after 10, 20, 85, 130, 265 and 385 minutes, respectively. After 23 h at room temperature full consumption of **2b** was observed and the ^{31}P NMR indicated the selective formation of phosphine sulfide **3b** (46.2 ppm), phosphine oxide **4b** (11.6 ppm) and phosphine–SO_3 **5b** (9.6 ppm) in 1:6:2 ratio, respectively (Figure S23). The reaction products **3b**, **4b** and **5b** were identified by their independent preparation from the reaction of phosphine **1b** with elemental sulfur, N_2O or pyridine–SO_3, respectively (*vide infra*).



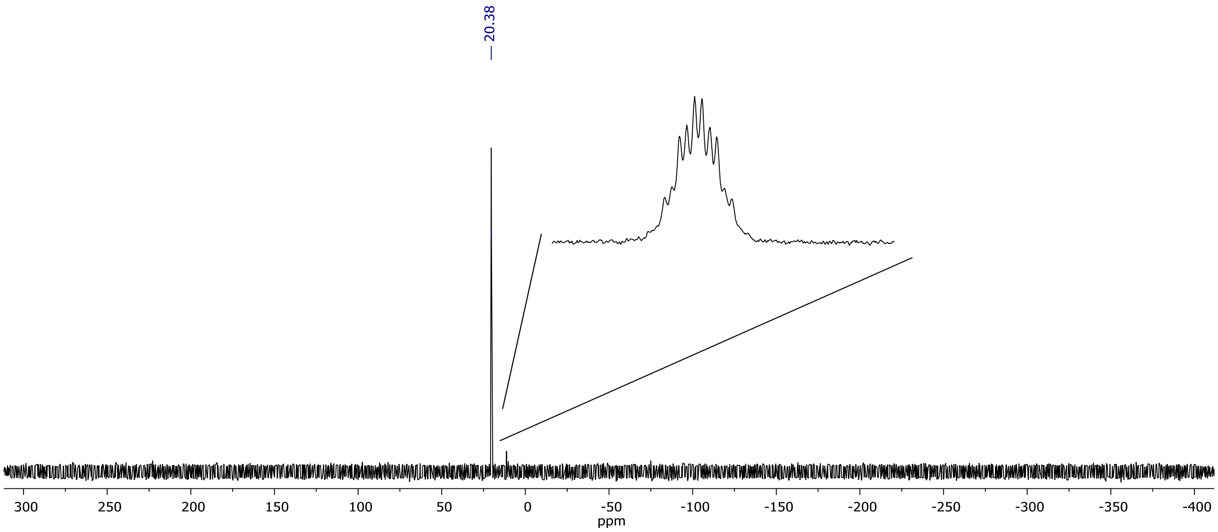


Figure S22: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **2b** at room-temperature.

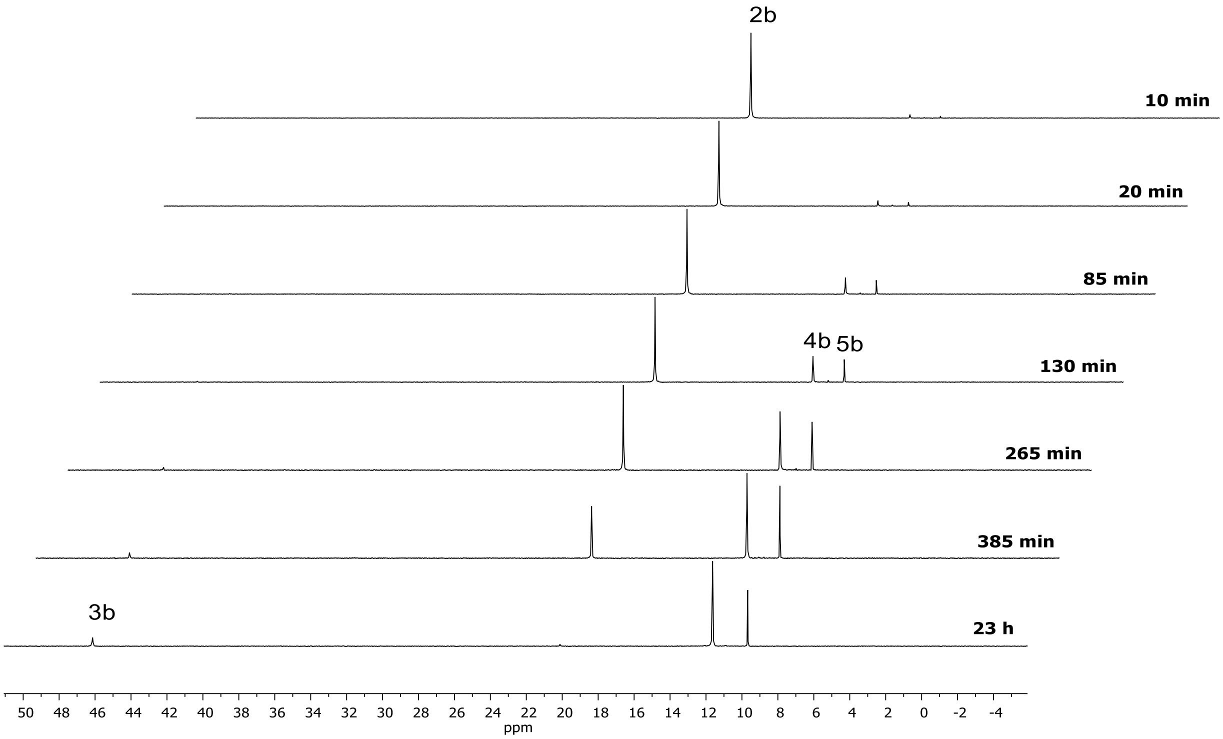


Figure S23: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **2b** after keeping the sample at room-temperature for the time indicated.

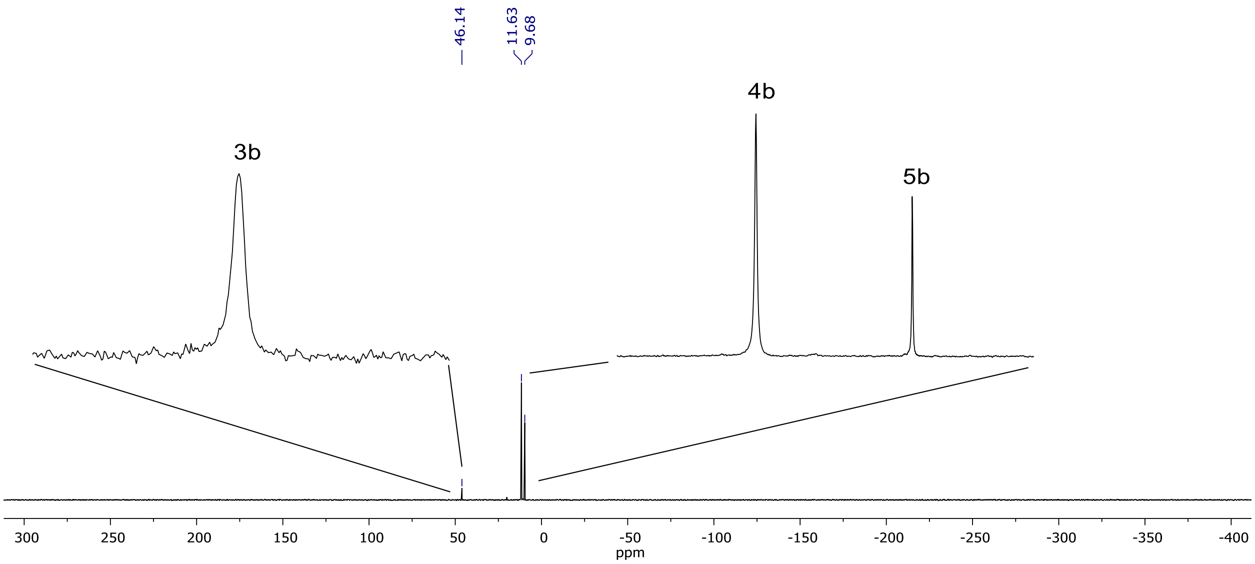


Figure S24: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **2b** after keeping the sample at room-temperature for 23 h.

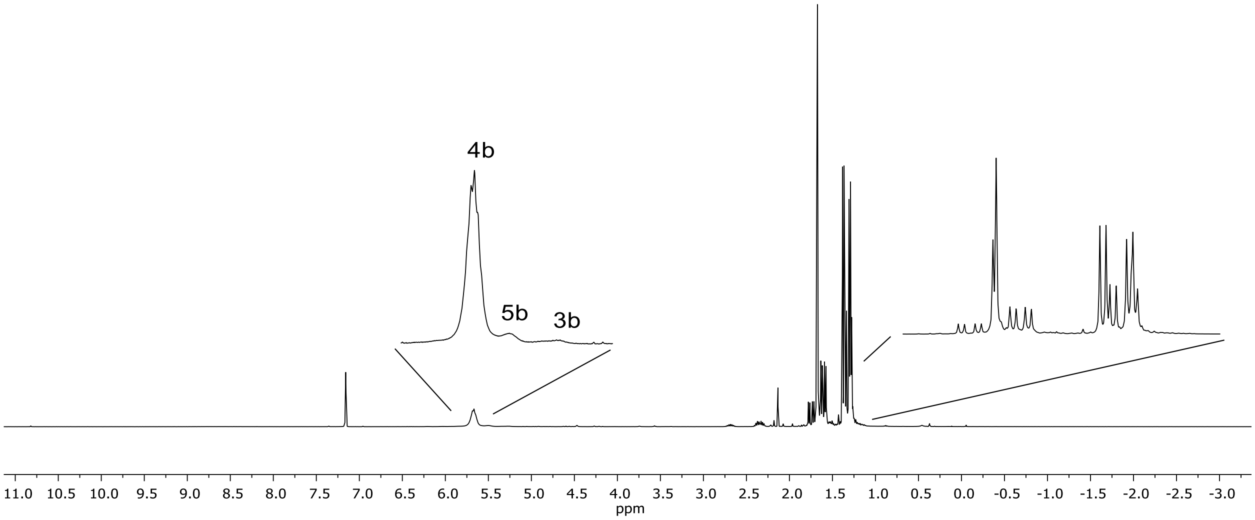


Figure S25: ^{1}H NMR spectrum (C_6D_6, 300 K, 400 MHz) of **2b** after keeping the sample at room-temperature for 23 hours.

The following ions were identified in the high-resolution mass spectrum (HRMS/ESI) of the reaction mixture:

(**3b**+H)$^+$: m/z calc. for $[C_{25}H_{48}N_6PS]^+$ (M+H)$^+$ 495.33933, found: 495.33933.

(**4b**+H)$^+$: m/z calc. for $[C_{25}H_{48}N_6PO]^+$ (M+H)$^+$ 479.36170, found: 479.36211.

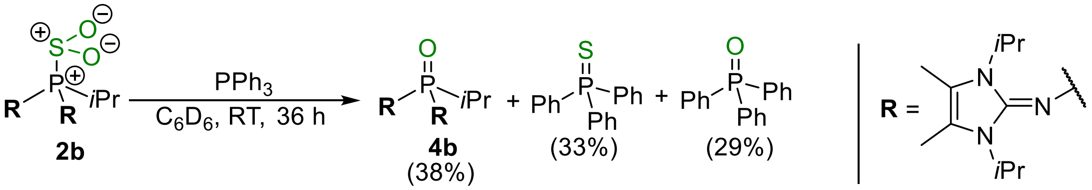
(**5b**+K)$^+$: m/z calc. for $[C_{25}H_{47}N_6PSO_3K]^+$ (M+K)$^+$ 581.27995, found: 581.30106.

Thermal decomposition of **2b** in presence of PPh_3.

In an NMR tube **2b** (25 mg, 0.047 mmol, 1 eq.) and PPh_3 (50 mg, 0.190 mmol, 4 eq.) were dissolved in C_6D_6. The NMR spectrum of the mixture showed no immediate reaction (Figure S26). After storing the sample at room temperature for 36 h, the formation of **4b**, $SPPh_3$ and $OPPh_3$ was observed in the ^{31}P NMR spectrum of the reaction mixture (Figure S27). **4b** and $OPPh_3$ were identified by high-resolution mass spectrometry (HRMS/ESI) of the reaction mixture:

$(OPPh_3+Na)^+$: m/z calc. for $[C_{18}H_{15}NaPO]^+$ $(M+Na)^+$ 301.07527, found: 301.07510.

(**4b**$+H)^+$: m/z calc. for $[C_{25}H_{48}N_6PO]^+$ $(M+H)^+$ 479.36170, found: 479.36188.



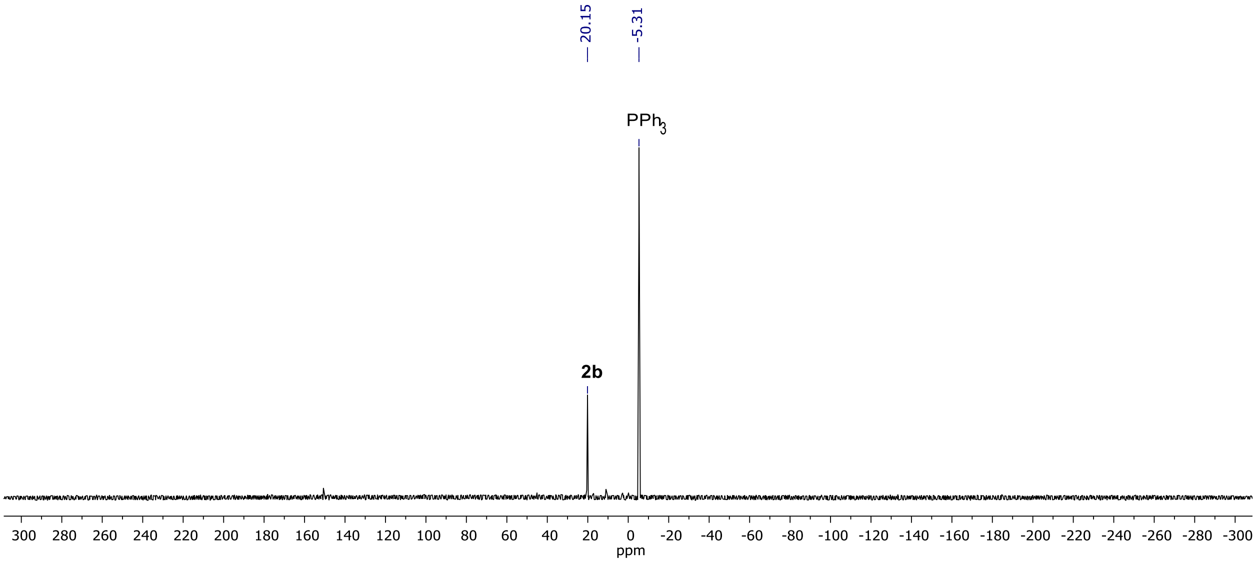


Figure S26: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **2b** and PPh_3.

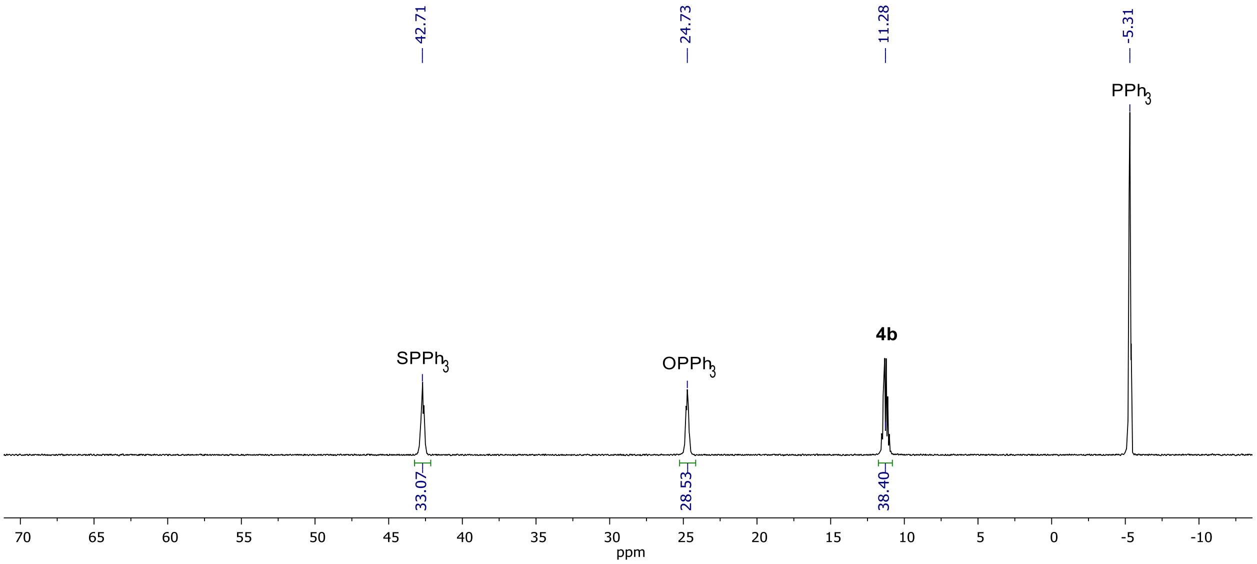


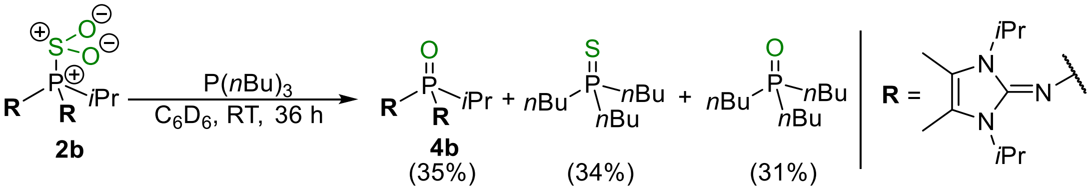
Figure S27: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz, D_1 = 25 sec., aq. Time = 0.66 sec., zg 90) of **2b** and PPh_3 after keeping the sample at room temperature for 36 h.

<u>Thermal decomposition of **2b** in presence of P(*n*Bu)$_3$.</u>

In an NMR tube **2b** (25 mg, 0.047 mmol, 1 eq.) and P(*n*Bu)$_3$ (38 mg, 0.190 mmol, 4 eq.) were dissolved in C_6D_6 (Figure S28). After storing the sample at room temperature for 36 h, the formation of **4b**, SP(*n*Bu)$_3$ and OP(*n*Bu)$_3$ was observed in the ^{31}P NMR spectrum of reaction mixture (Figure S29). **4b** and OP(*n*Bu)$_3$ were identified by high-resolution mass spectrometry (HRMS/ESI) of the reaction mixture:

(2 x OP(*n*Bu)$_3$+Na)$^+$: m/z calc. for $[C_{18}H_{15}NaPO]^+$ (M+Na)$^+$ 301.07527, found: 301.07510.

(**4b**+H)$^+$: m/z calc. for $[C_{25}H_{48}N_6PO]^+$ (M+H)$^+$ 459.34913, found: 459.35078.



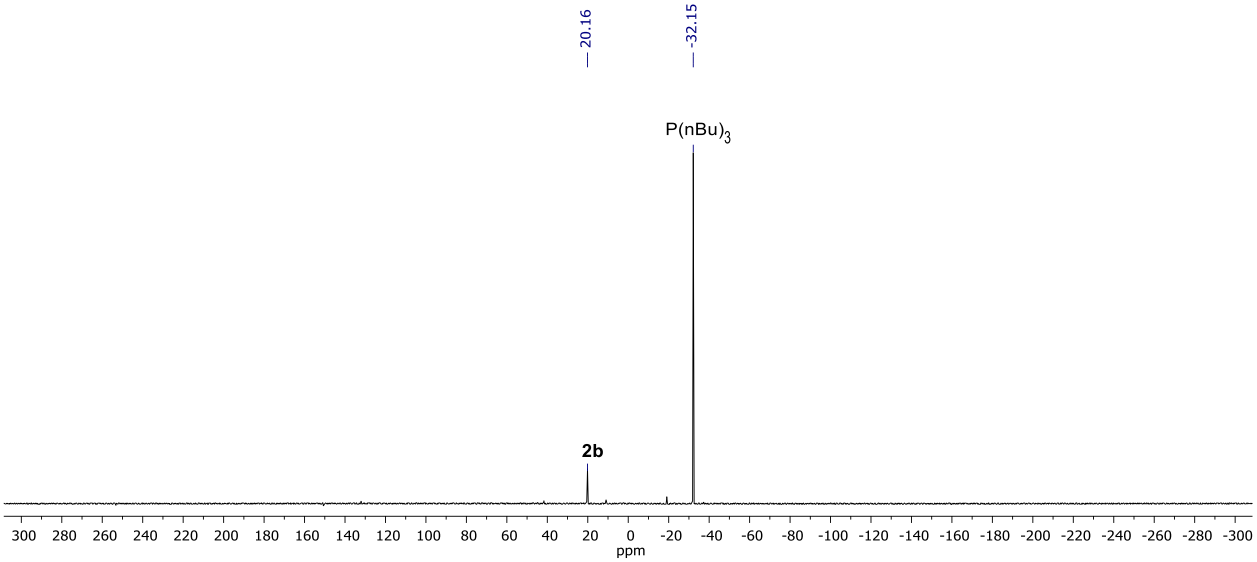


Figure S28: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **2b** and P(*n*Bu)$_3$.

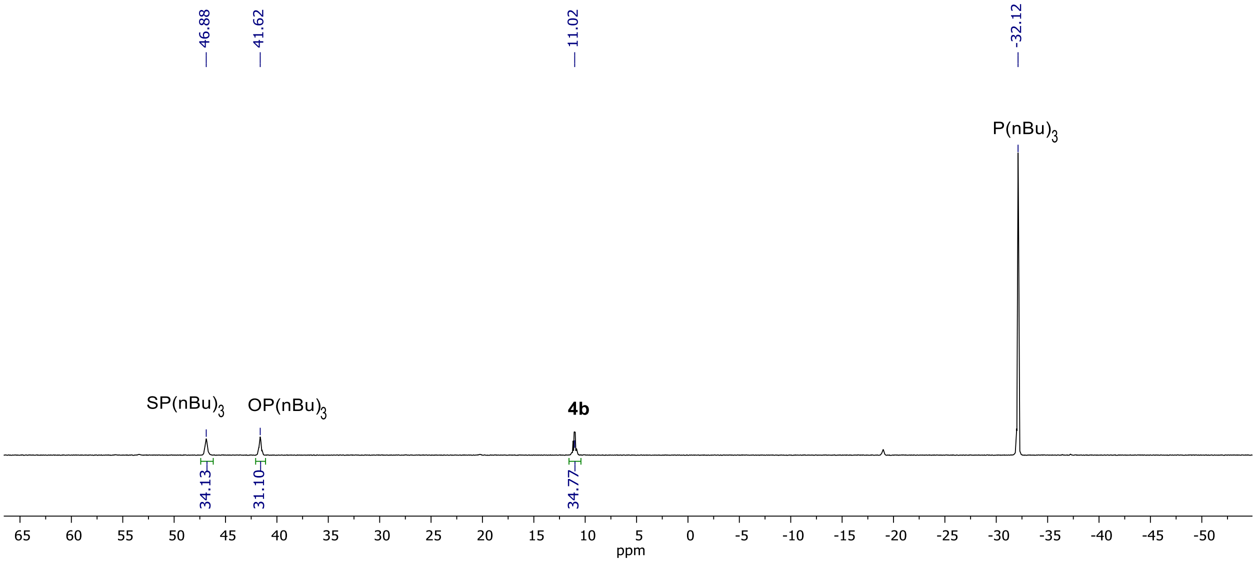
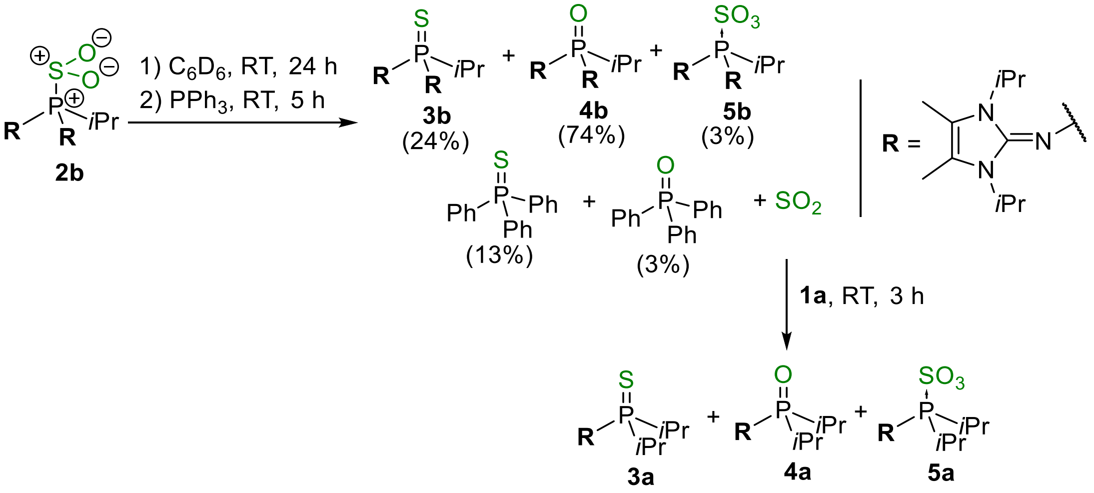


Figure S29: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz, D_1 = 25 sec., aq. Time = 0.66 sec., zg 90) of **2b** and P(*n*Bu)$_3$ after keeping the sample at room temperature for 36 h.

Trapping of the sulfur-containing products from the decomposition of **2b** using PPh_3 and **1a**:

In an NMR tube **1b** (30 mg, 0.064 mmol, 1 eq.) and DABSO (8 mg, 0.032 mmol, 0.5 eq.) were dissolved in C_6D_6 and the sample was kept at room temperature for 24 h. The ^{31}P NMR spectrum showed the formation of **3b-5b** (*cf.* Figure S24). PPh_3 (50 mg, 0.190 mmol, 3 eq.) was added to the NMR tube and the sample was kept for 5 h at room temperature. The NMR spectrum of the mixture showed new singlets for $SPPh_3$ in addition to small amounts of $OPPh_3$ (Figure S30), which might result from the presence of elemental sulfur or polysulfuroxides in the mixture. To identify SO_2 in the mixture, **1a** (30 mg, 0.095 mmol, 1.5 eq.) was added to the NMR tube. In addition to the previously observed species, the ^{31}P NMR spectrum show the characteristic signals from the decomposition of the phosphine-SO_2 adduct **3a-5a** in about equimolar amounts (Figure S31).



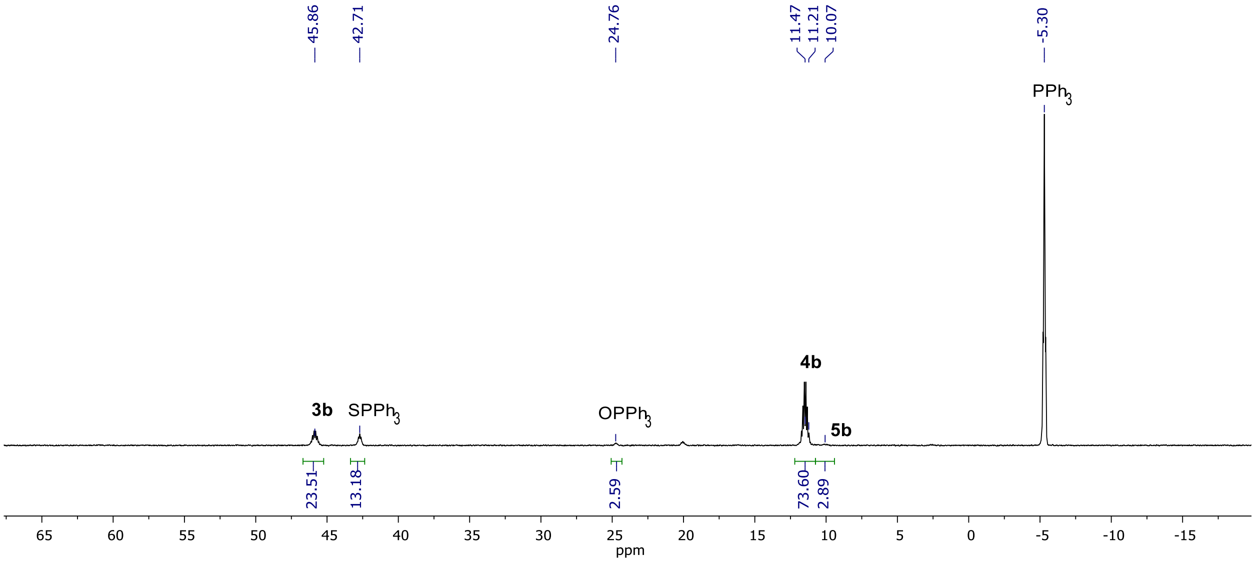


Figure S30: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz, D_1 = 25 sec., aq. Time = 0.66 sec., zg 90) after adding of PPh_3 and storing the NMR tube for 5 h at room temperature.

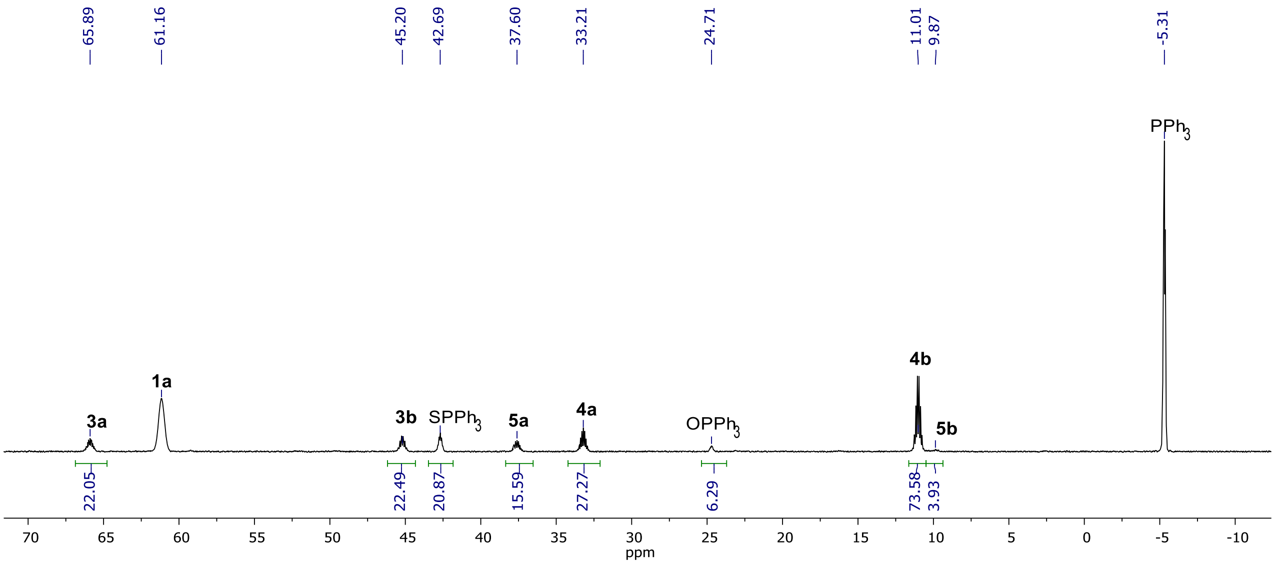
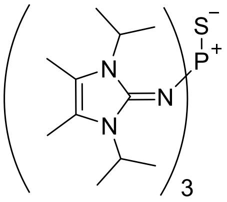


Figure S31: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz, D_1 = 25 sec., aq. Time = 0.66 sec., zg 90) after adding of **1a** and storing the NMR tube for 3 h at room temperature.

Preparation of phosphine sulfide **3c**

Phosphine sulfide **3c** was prepared from the reaction of the phosphine **1c** with elemental sulfur according to a previously published procedure for **3a** and **3b**:[4] A solution of **1c** (30 mg, 0.049 mmol, 1 eq.) in C_6D_6 was added to S_8 (2 mg, 0.072 mmol, 1.6 eq.). The solution was filtered from the excess of S_8 and analyzed by NMR spectroscopy, which showed quantitative conversion of **1c**.



^{1}H NMR (400 MHz, C_6D_6): δ = 5.88 (s, br, 6H, NC*H*Me$_2$), 1.81 (s, 18H, CH_3), 1.44 ppm (d, $^3J_{HH}$ = 7.1 Hz, 36H, NCHCH_3).

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ = 146.9 (d, $^2J_{PC}$ = 4.1 Hz, N_2CN), 116.1 (C=C), 46.4 (s, N*C*HMe$_2$), 22.3 (NCH(CH_3)$_2$), 10.1 ppm (CH_3).

^{31}P NMR (161.9 MHz, C_6D_6): δ = 20.6 ppm (s).

HRMS (ESI): m/z calculated for $[C_{33}H_{61}N_9PS]^+$ $(M+H)^+$ 646.45028, found 646.45063.

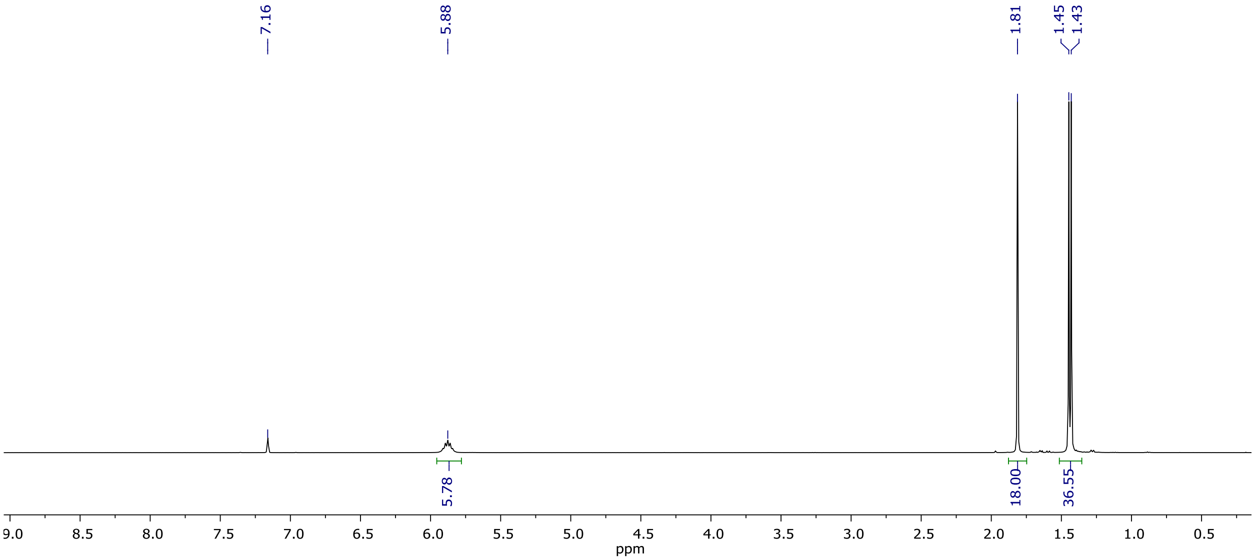


Figure S32: ^{1}H NMR spectrum (C_6D_6, 300 K, 400 MHz) of **3c**.

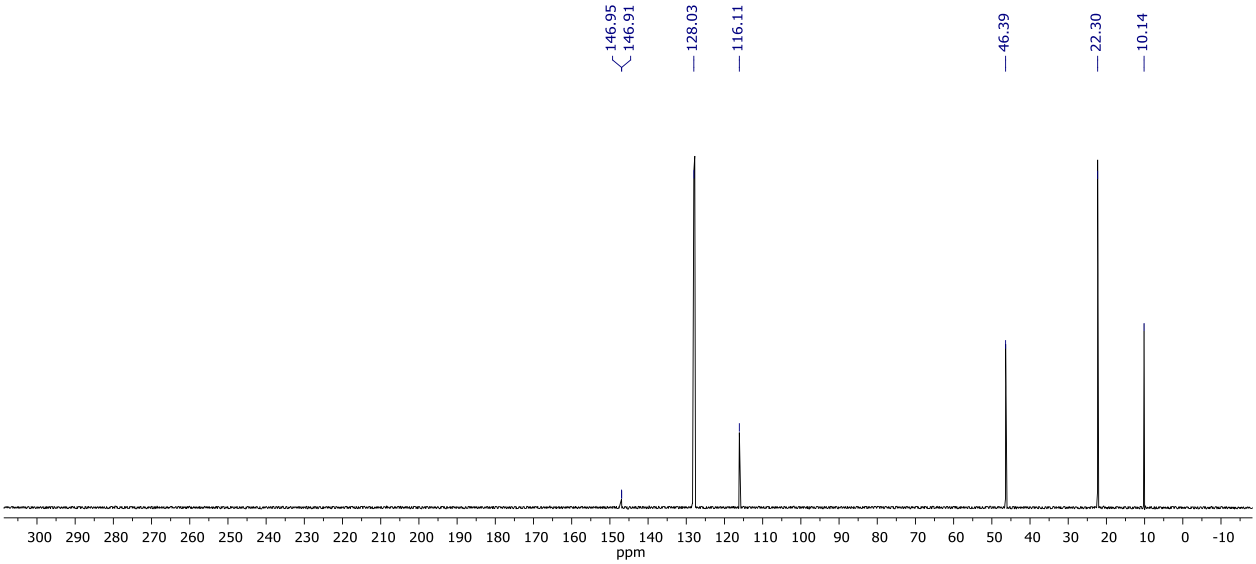


Figure S33: $^{13}C\{^1H\}$ NMR spectrum (C_6D_6, 300 K, 101 MHz) of **3c**.

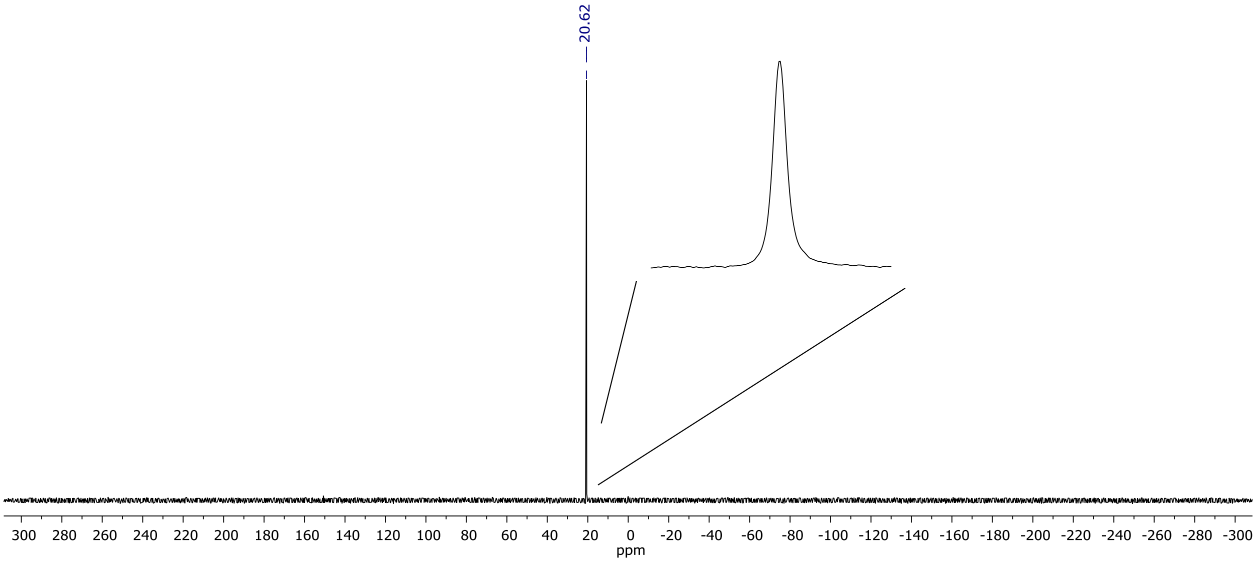


Figure S34: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **3c**.

Herein, the ^{31}P NMR spectra of the previously published phosphine sulfides **3a** and **3b** are displayed for comparison.[4]

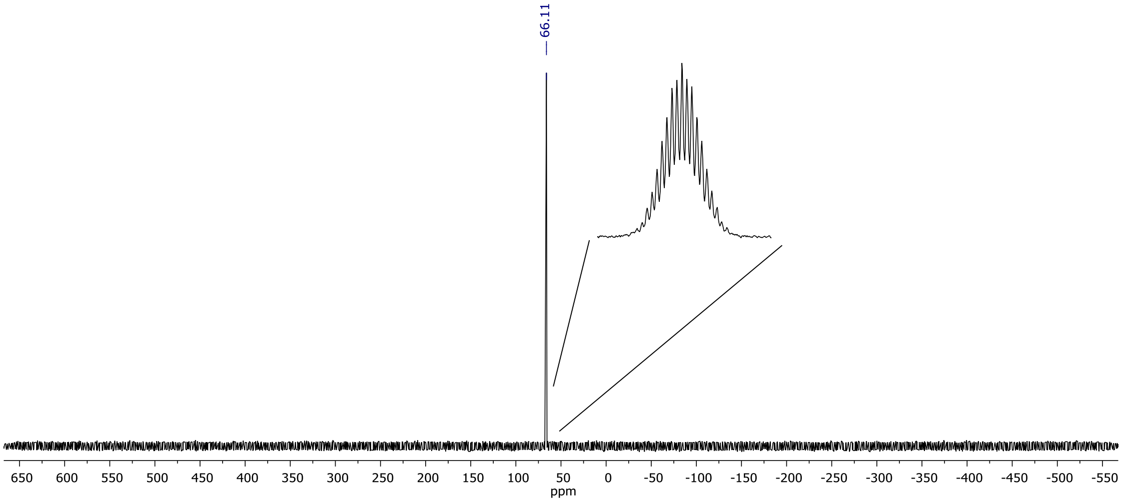


Figure S35: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **3a**.

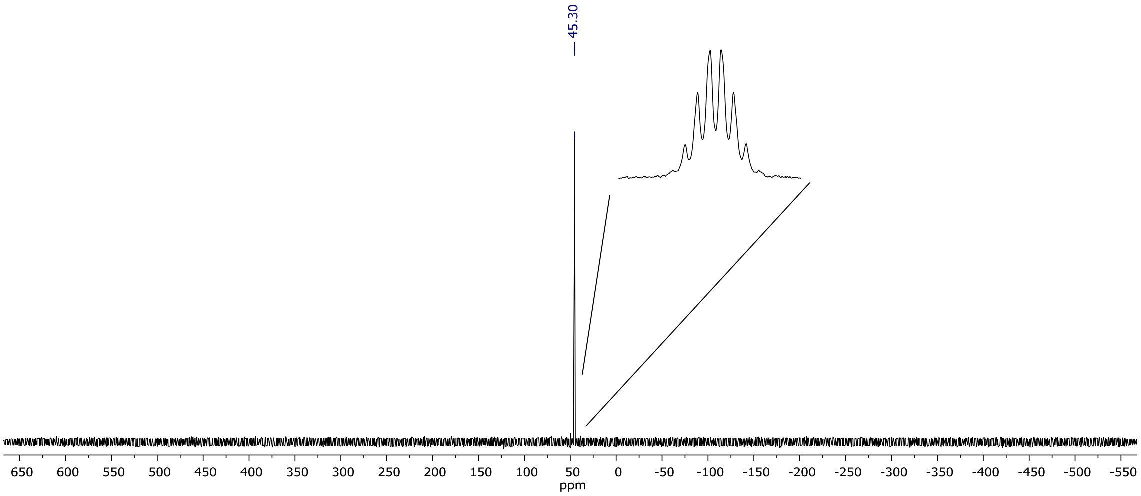


Figure S36: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **3b**.

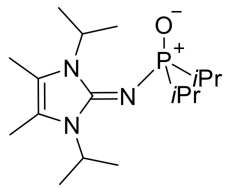
After pressurizing a solution of phosphine sulfide **3b** in C_6D_6 with 2 bar SO_2 at room-temperature the signal for **3b** showed up at 50.2 ppm in the ^{31}P NMR spectrum. The downfield-shift in the ^{31}P NMR spectrum is explained by the SO_2–complexation *via* the imine-N atoms of **3b** due to the excess of SO_2.

Preparation of phosphine oxides **4a-c**

General procedure: The reactions were performed in Wilmad® low pressure/vacuum NMR tubes purchased from Sigma Aldrich. Phosphine oxides **4a**, **4b** and **4c** were prepared by pressurizing phosphines **1a**, **1b** and **1c** with 2 bar nitrous oxide (N_2O) in the solvent indicated. The NMR tube containing a solution of the phosphine was frozen in liquid nitrogen and the argon atmosphere in the tube was removed *in vacuo*. After warming the solution up to room temperature, the NMR tube was pressurized with 2 bar N_2O. In all cases NMR analysis showed quantitative formation of the respective phosphine oxide **4a-c**.

It is worth mentioning that the reaction of the less basic alkyl- or aryl phosphines with N_2O required much harsher conditions (100-140 bar N_2O, supercritical N_2O).[5]

Compound 4a: A solution of **1a** (30 mg, 0.096 mmol) in C_6D_6 was pressurized with 2 bar N_2O. Full conversion was observed at 80 °C for 12 hours.



^{1}H NMR (400 MHz, C_6D_6): δ = 5.55 (s, br, 2H, NCHMe$_2$), 2.07 (dsept, $^2J_{PH}$ = 10.7 Hz $^3J_{HH}$ = 7.1 Hz, 2H, PCHMe$_2$), 1.65 (s, 6H, CH$_3$), 1.39 (dd, $^3J_{PH}$ = 15.2 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, PCHCH_3), 1.26 (dd, $^3J_{PH}$ = 14.9 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, PCHCH_3), 1.23 ppm (d, $^3J_{HH}$ = 7.1 Hz, 12H, NCHCH_3).

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ = 147.5 (N_2CN), 116.4 (C=C), 46.3 (NCHMe$_2$), 28.2 (d, $^1J_{PC}$ = 95.8 Hz, PCHMe$_2$), 21.5 (s, NCH(CH$_3$)$_2$), 17.2 (m, PCH(CH$_3$)$_2$), 9.9 ppm (CH$_3$).

^{31}P NMR (161.9 MHz, C_6D_6): δ = 33.4 ppm (m).

HRMS (ESI): m/z calculated for $[C_{17}H_{34}N_3PONa]^+$ $(M+Na)^+$ 350.23317, found 350.23298.

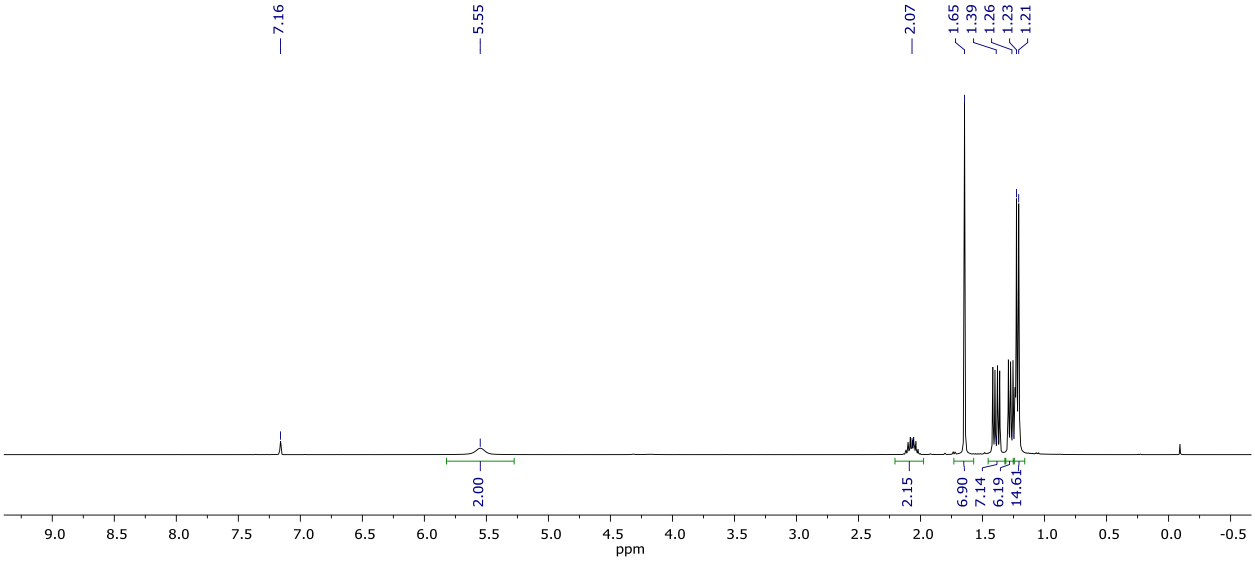


Figure S37: ^{1}H NMR spectrum (C_6D_6, 300 K, 400 MHz) of **4a**.

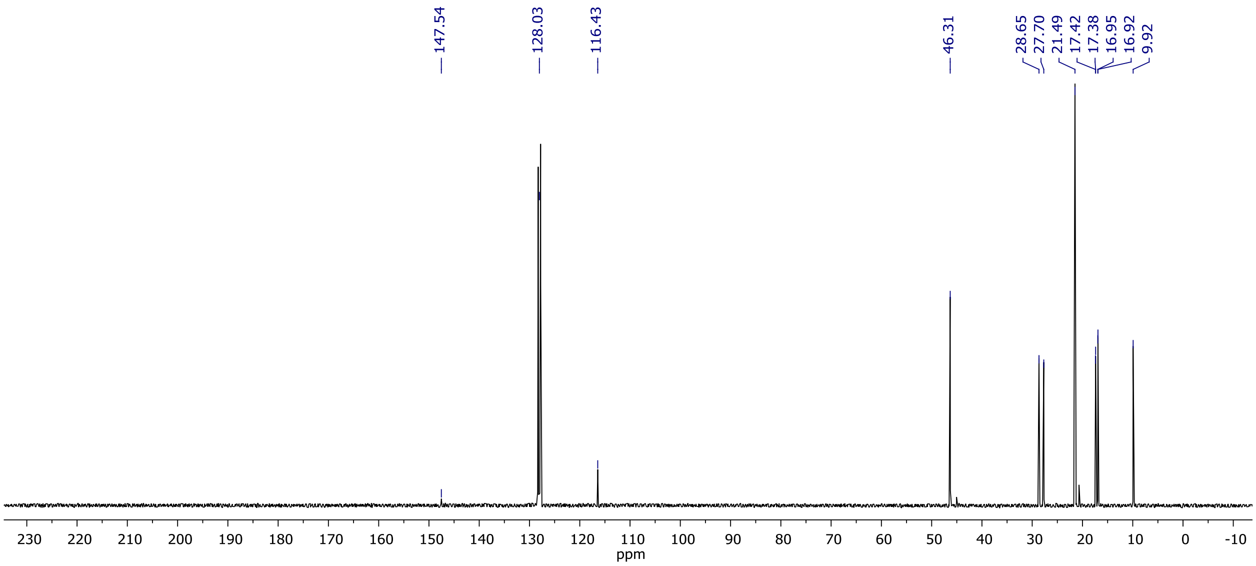


Figure S38: $^{13}C\{^1H\}$ NMR spectrum (C_6D_6, 300 K, 101 MHz) of **4a**.

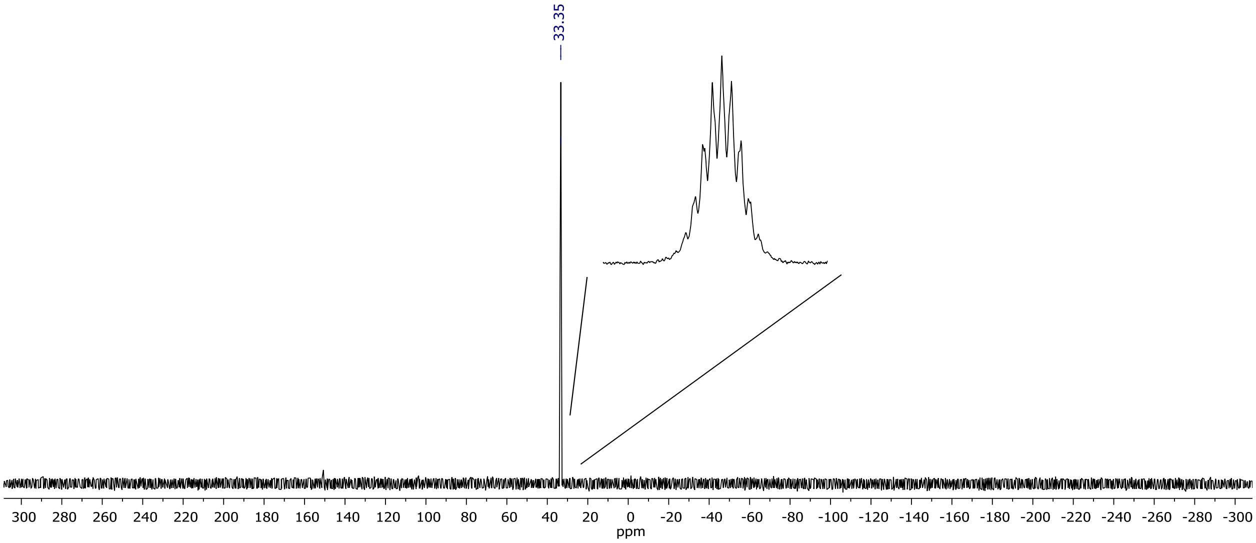
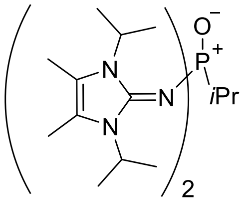


Figure S39: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **4a**.

Compound 4b: A solution of **1b** (30 mg, 0.064 mmol) in C_6D_6 was pressurized with 2 bar N_2O. Full conversion was observed after 5 hours at room temperature or 1 hour at 60 °C.



^{1}H NMR (400 MHz, C_6D_6): δ = 5.66 (s, br, 4H, NC*H*Me$_2$), 2.53 (dsept, $^2J_{PH}$ = 17.1 Hz, $^3J_{HH}$ = 7.1 Hz, 1H, PC*H*Me$_2$), 1.72 (s, 12H, CH_3), 1.68 (dd, $^3J_{PH}$ = 16.6 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, PCHC*H*$_3$), 1.33 ppm (d, $^3J_{HH}$ = 7.0 Hz, 12H, NCHC*H*$_3$), 1.28 ppm (d, $^3J_{HH}$ = 7.1 Hz, 12H, NCHC*H*$_3$).

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ = 146.5 (N_2CN), 115.7 (C=C), 46.1 (N*C*HMe$_2$), 33.3 (d, $^1J_{PC}$ = 143.0 Hz, P*C*HMe$_2$), 21.8 (m, NCH(*C*H$_3$)$_2$), 19.1 (s, PCH(*C*H$_3$)$_2$), 19.0 (s, PCH(*C*H$_3$)$_2$), 10.0 ppm (CH_3).

^{31}P NMR (161.9 MHz, C_6D_6): δ = 11.2 ppm (m).
HRMS (ESI): m/z calculated for $[C_{25}H_{48}N_6PO]^+$ $(M+H)^+$ 479.36217, found 479.36191.

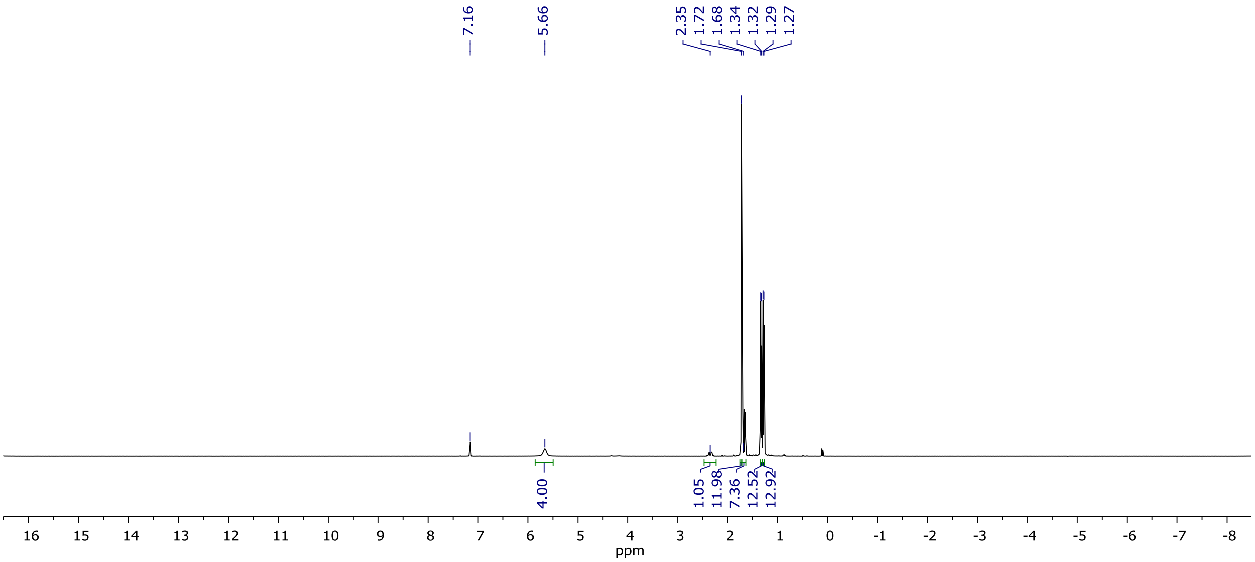


Figure S40: ^{1}H NMR spectrum (C_6D_6, 300 K, 400 MHz) of **4b**.

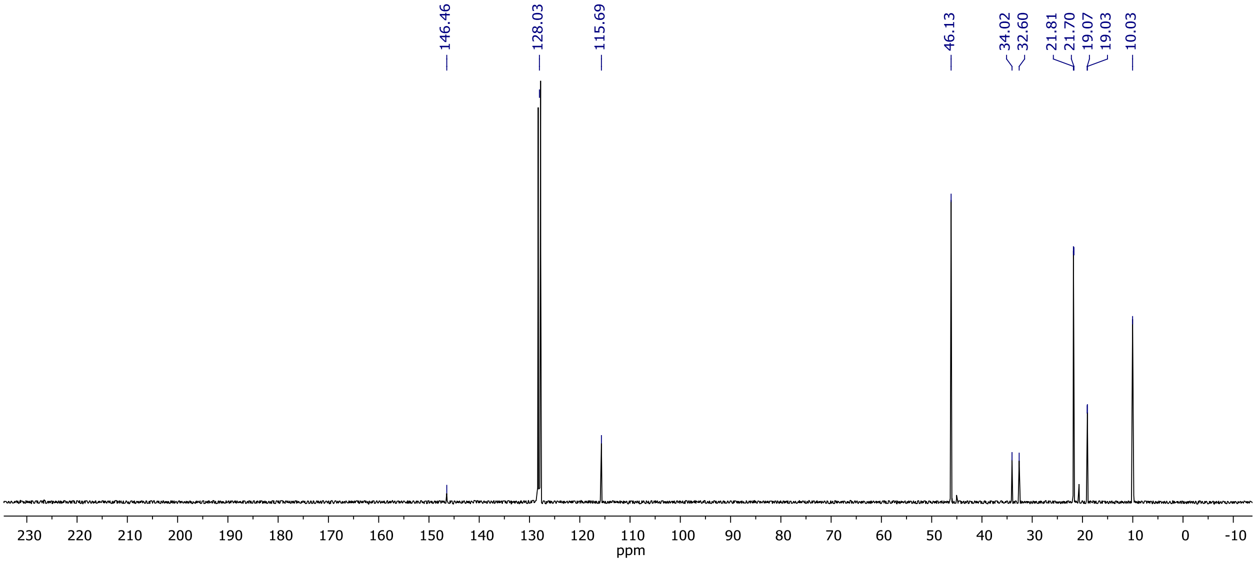


Figure S41: ^{13}C{^{1}H} NMR spectrum (C_6D_6, 300 K, 101 MHz) of **4b**.

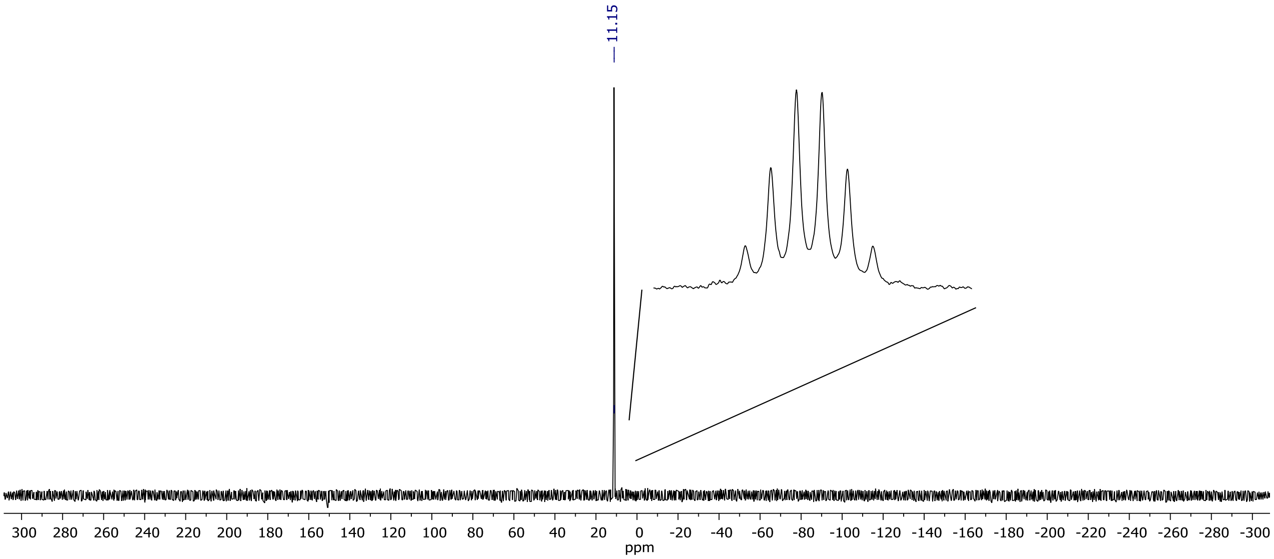
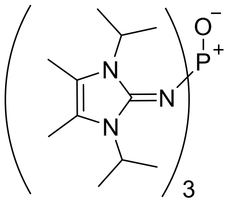


Figure S42: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **4b**.

After pressurizing a solution of phosphine oxide **4b** in C_6D_6 with 2 bar SO_2 at room-temperature the signal for **4b** showed up at 12.9 ppm in the ^{31}P NMR spectrum. The downfield-shift in the ^{31}P NMR spectrum is explained by the SO_2–complexation *via* the imine-N atoms of **4b** due to the excess of SO_2.

Compound 4c: A solution of **1c** (30 mg, 0.049 mmol) in C_6D_6 was pressurized with 2 bar N_2O. Full conversion was observed after 5 minutes at room temperature.



^{1}H NMR (400 MHz, C_6D_6): $\delta = 5.75$ (s, br, 6H, NC*H*Me$_2$), 1.80 (s, 18 H, CH_3), 1.40 ppm (d, $^3J_{HH} = 7.0$ Hz, 36 H, NCHC*H*$_3$).

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): $\delta = 146.2$ (d, $^2J_{PC} = 5.9$ Hz, N_2CN), 115.2 (C=C), 45.9 (N*C*HMe$_2$), 22.1 (NCH(*C*H$_3$)$_2$), 10.2 ppm (CH_3).

^{31}P NMR (161.9 MHz, C_6D_6): $\delta = –11.9$ ppm (s).

HRMS (ESI): m/z calculated for $[C_{33}H_{61}N_9OP]^+$ $(M+H)^+$ 630.47312, found 630.47335.

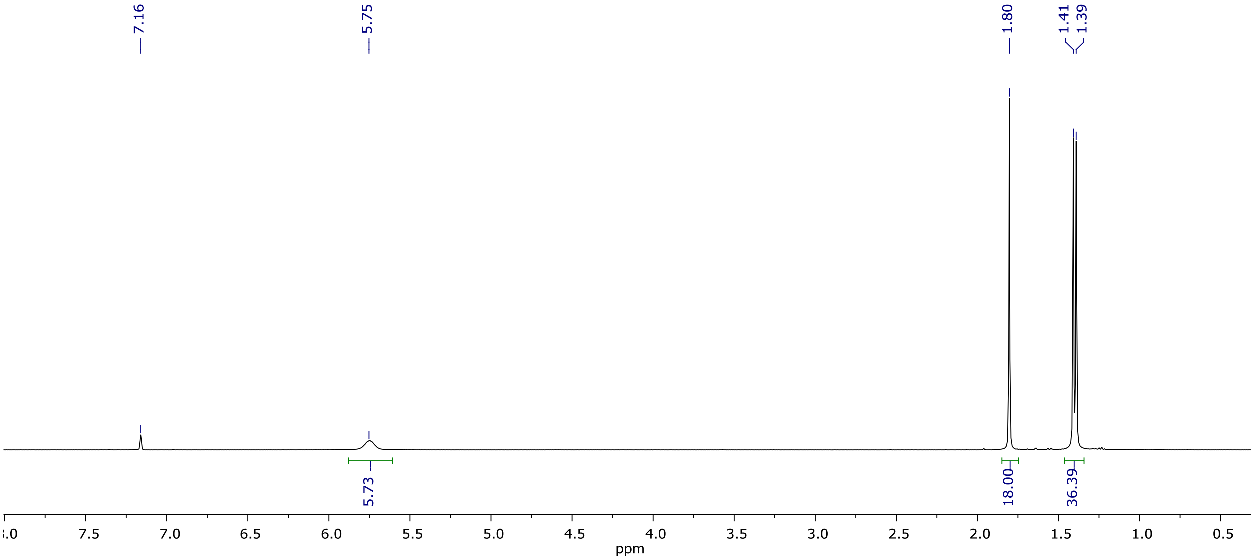


Figure S43: ^{1}H NMR spectrum (C_6D_6, 300 K, 400 MHz) of **4c**.

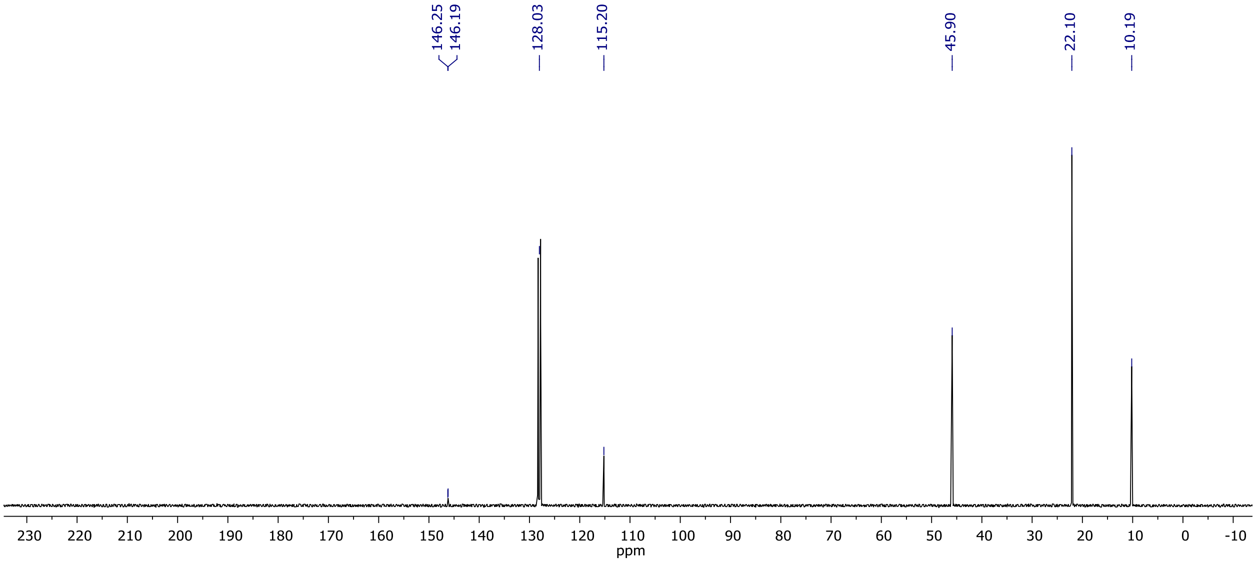


Figure S44: $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 300 K, 101 MHz) of **4c**.

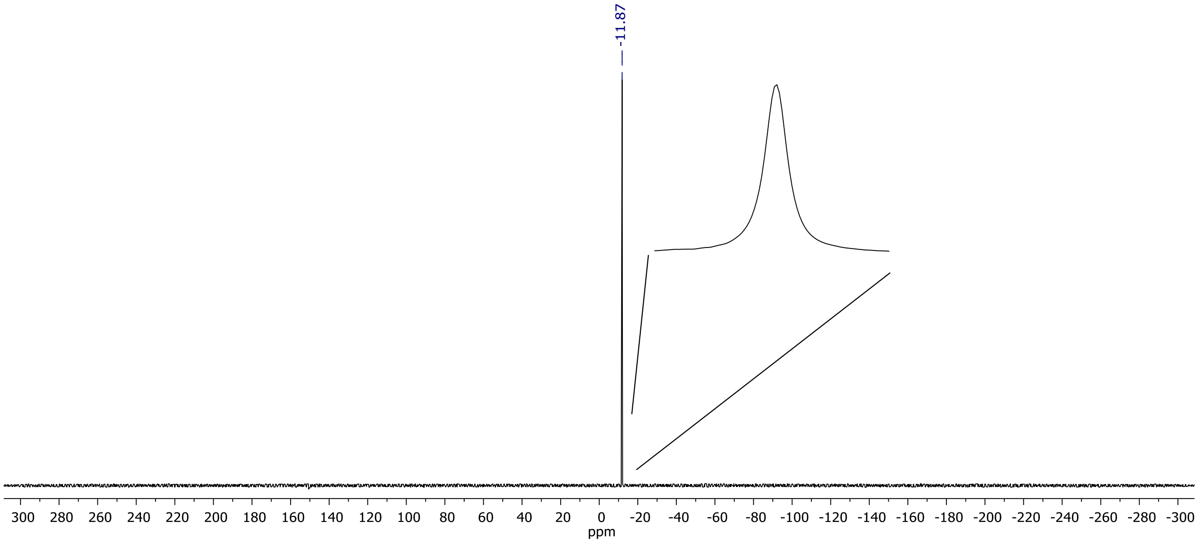


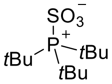
Figure S45: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **4c**.

Preparation of phosphine-SO_3 adducts **5a-b** and P*t*Bu_3–SO_3

Phosphine–SO_3 adducts **5a**, **5b** and P*t*Bu_3–SO_3 were prepared from the reaction of phosphines **1a** and **1b** with pyridine–SO_3 according to the following procedure: A solution of the phosphine in the solvent indicated was added to pyridine–SO_3 and the reaction mixture was stirred for 30 minutes at room temperature (**5a** and **5b**) or at 60 °C (P*t*Bu_3–SO_3). All volatiles were removed *in vacuo* and the residue was analyzed by NMR spectroscopy, which showed quantitative formation of phosphine–SO_3 adducts **5a**, **5b** and P*t*Bu_3–SO_3.

The reaction of phosphine **1c** with pyridine–SO_3 under the same conditions is unselective, and multiple phosphorus-containing species were detected in the ^{31}P NMR spectrum (Figure S49).

Compound P*t*Bu_3–SO_3: A solution of P*t*Bu_3 (30 mg, 0.148 mmol, 1 eq.) in benzene (3 mL) was added to pyridine–SO_3 (24 mg, 0.148 mmol, 1 eq.)



^{1}H NMR (400 MHz, C_6D_6): δ = 1.31 (d, $^3J_{PH}$ = 13.5 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ = 40.6 (d, $^1J_{PC}$ = 11.8 Hz, *C*(CH_3)$_3$), 30.0 (s, CH_3).

^{31}P NMR (161.9 MHz, C_6D_6): δ = 59.7 ppm (s).

HRMS (ESI): m/z calculated for $[S_2P_2O_6H_{54}C_{24}Na]^+$ $(2M+Na)^+$ 587.27292, found 587.27297.

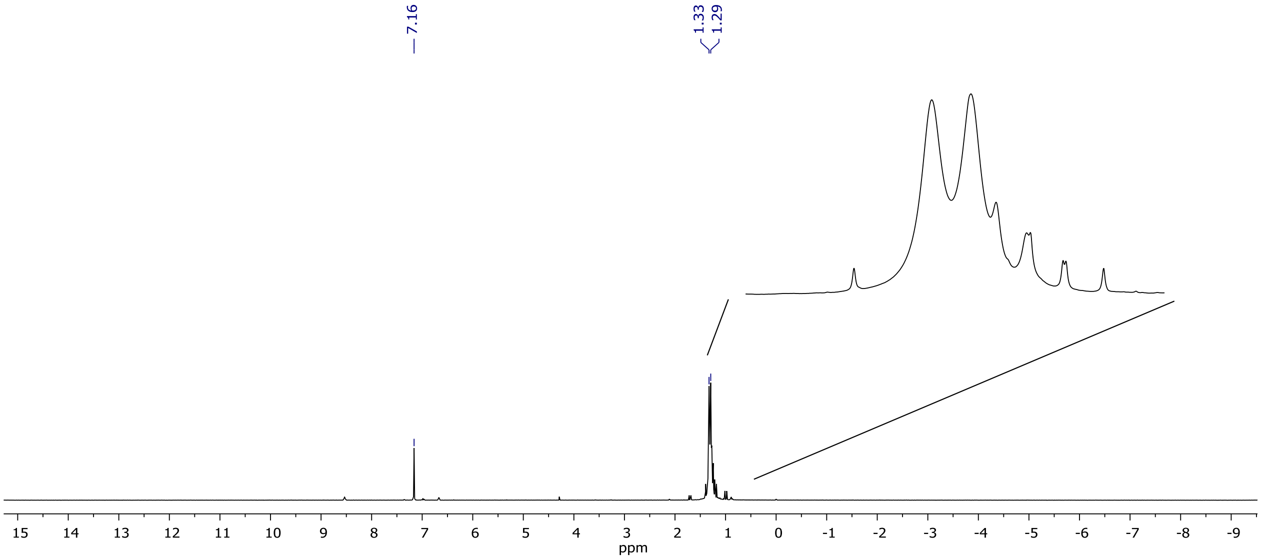


Figure S46: ^{1}H NMR spectrum (C_6D_6, 300 K, 400 MHz) of P*t*Bu_3–SO_3.

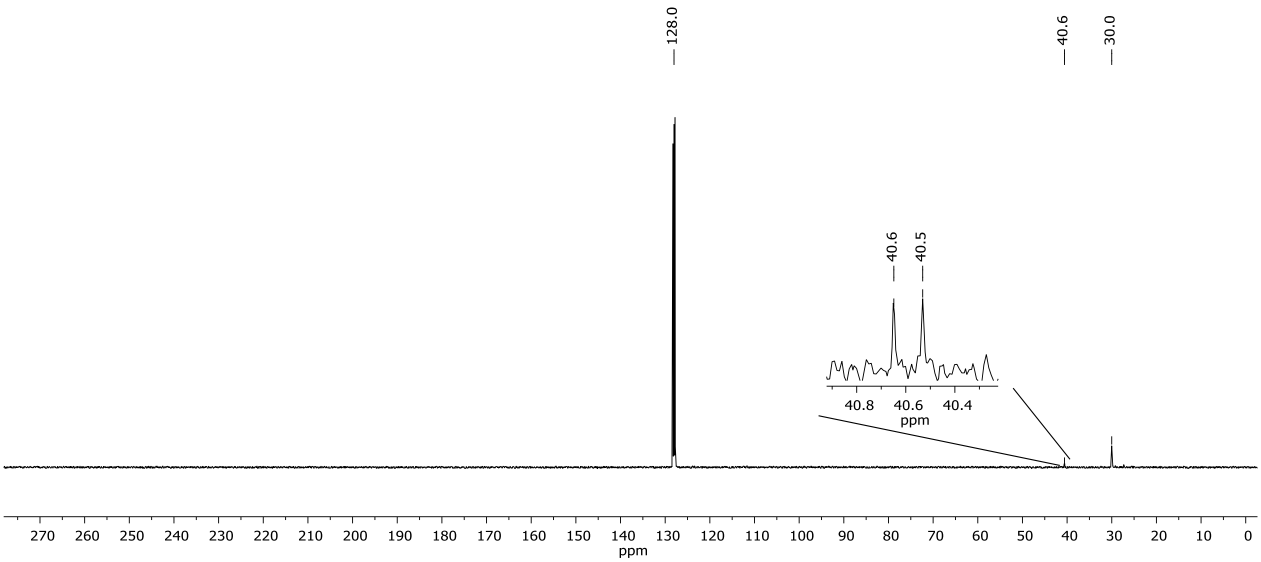


Figure S47: $^{13}C\{^1H\}$ NMR spectrum (C_6D_6, 300 K, 101 MHz) of P*t*Bu_3–SO_3.

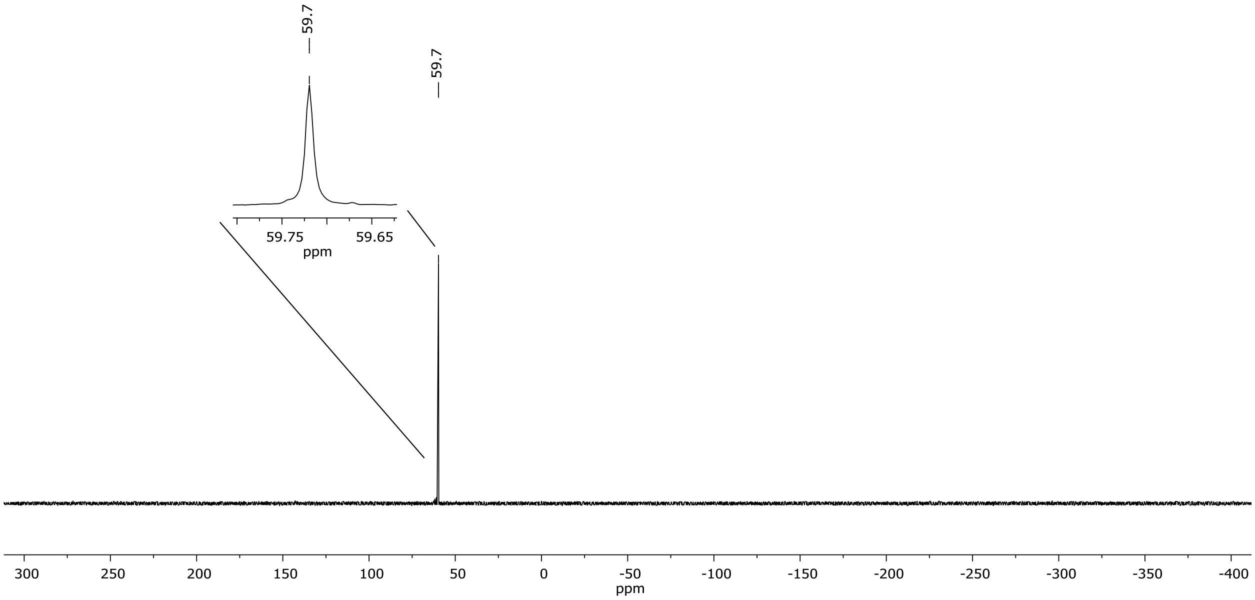
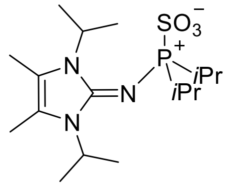


Figure S48: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of P*t*Bu_3–SO_3.

Compound 5a: A solution of **1a** (25 mg, 0.080 mmol, 1 eq.) in THF (3 mL) was added to pyridine–SO_3 (13 mg, 0.080 mmol, 1 eq.)



^{1}H NMR (400 MHz, C_6D_6): δ = 5.06 (sept, $^3J_{HH}$ = 7.1 Hz, 2H, NC*H*Me$_2$), 2.62 (dsept, $^2J_{PH}$ = 9.1 Hz $^3J_{HH}$ = 7.1 Hz, 2H, PC*H*Me$_2$), 1.61(s, 6H, CH_3), 1.50 (dd, $^3J_{PH}$ = 16.6 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, PCHC*H*$_3$), 1.27 (dd, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, PCHC*H*$_3$), 1.19 ppm (d, $^3J_{HH}$ = 7.0 Hz, 12H, NCHC*H*$_3$).

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): δ = 144.5 (N_2CN), 118.8 (C=C), 47.5 (N*C*HMe$_2$), 27.6 (d, $^1J_{PC}$ = 51.2 Hz, P*C*HMe$_2$), 21.3 (NCH(*C*H$_3$)$_2$), 16.8 (m, PCH(*C*H$_3$)$_2$, 9.8 ppm (CH_3).

^{31}P NMR (161.9 MHz, C_6D_6): δ = 37.6 ppm (m).

HRMS (ESI): m/z calculated for $[S_2P_2O_6N_6H_{68}C_{34}Na]^+$ $(2M+Na)^+$ 805.40092, found 805.40178.

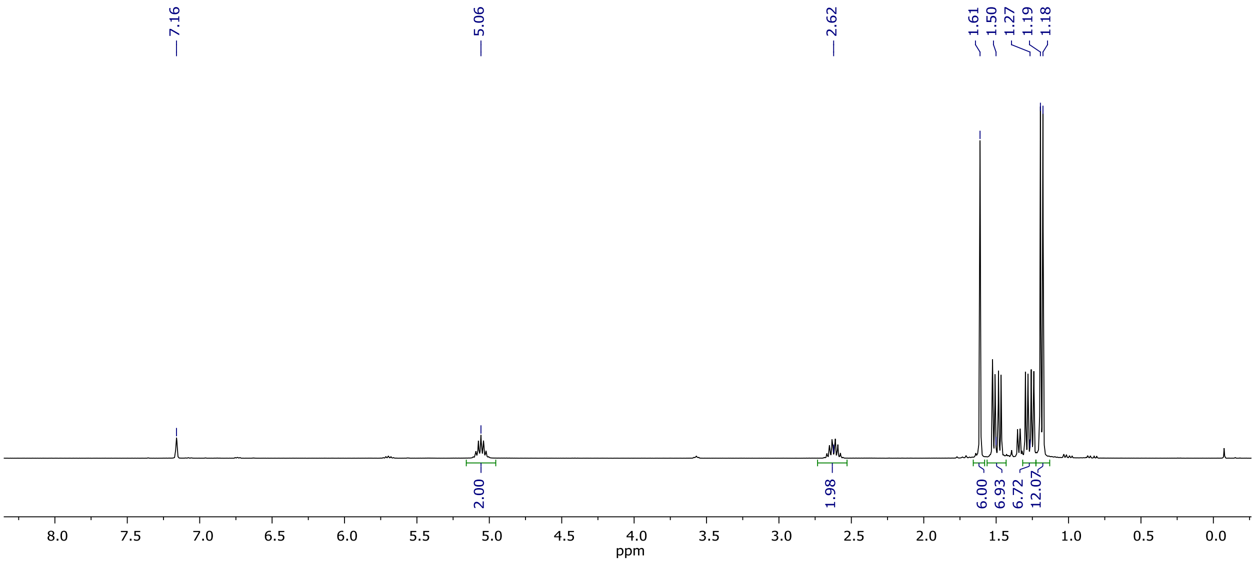


Figure S49: ^{1}H NMR spectrum (C_6D_6, 300 K, 400 MHz) of **5a**.

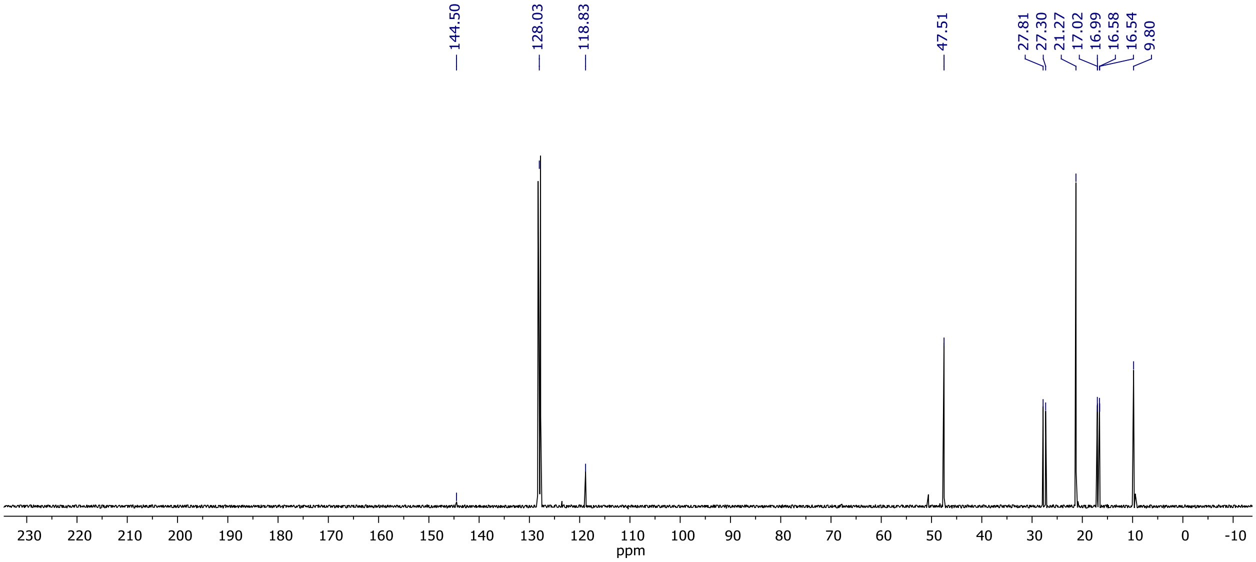


Figure S50: ^{13}C{^{1}H} NMR spectrum (C_6D_6, 300 K, 101 MHz) of **5a**.

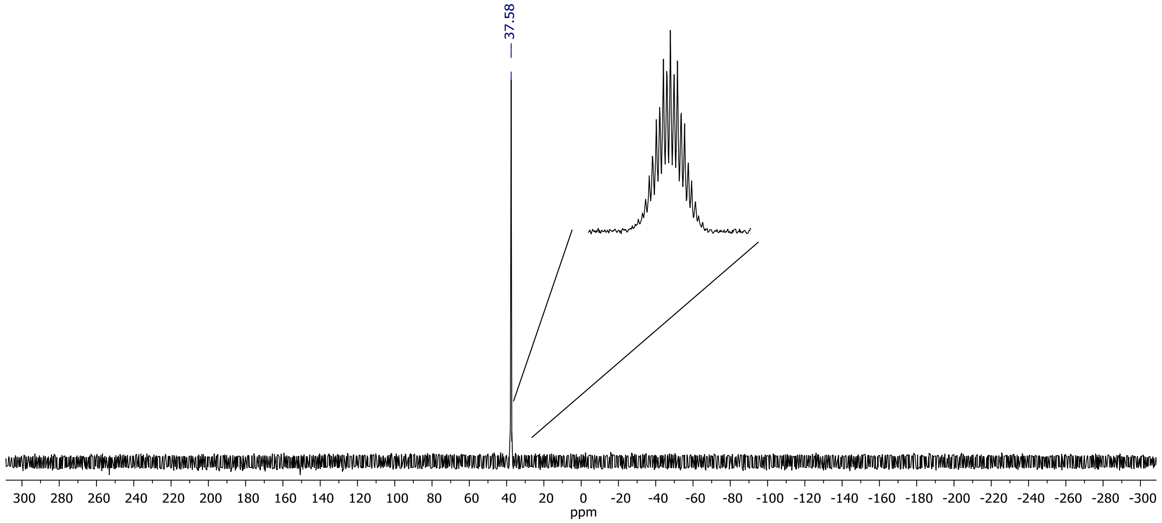
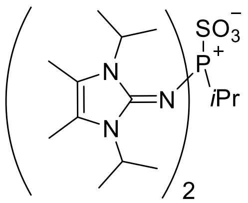


Figure S51: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **5a**.

Compound 5b: A solution of **1b** (30 mg, 0.065 mmol, 1 eq.) in THF (3 mL) was added to pyridine–SO_3 (10 mg, 0.065 mmol, 1 eq.).



^{1}H NMR (400 MHz, C_6D_6): $\delta = 5.19$ (sept, $^3J_{HH} = 7.1$ Hz, 4H, NC*H*Me$_2$), 2.77 (dsept, $^2J_{PH} = 11.9$ Hz, $^3J_{HH} = 7.0$ Hz, 1H, PC*H*Me$_2$), 1.76 (s, 12H, CH_3), 1.62 (dd, $^3J_{PH} = 17.6$ Hz, $^3J_{HH} = 7.0$ Hz, 6H, PCHC*H*$_3$), 1.26 ppm (m, 24H, NCHC*H*$_3$),

^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): $\delta = 150.1$ (N_2CN), 118.3 (C=C), 47.6 (N*C*HMe$_2$), 31.3 (d, $^1J_{PC} = 93.9$ Hz, P*C*HMe$_2$), 21.5 (s, NCH(*C*H$_3$)$_2$), 17.5 (m, PCH(*C*H$_3$)$_2$), 9.6 ppm (CH_3).

^{31}P NMR (161.9 MHz, C_6D_6): $\delta = 10.4$ ppm (m).
HRMS (ESI): m/z calculated for $[C_{25}H_{48}N_6O_3PS]^+$ $(M+H)^+$ 543.32407, found 543.32522.

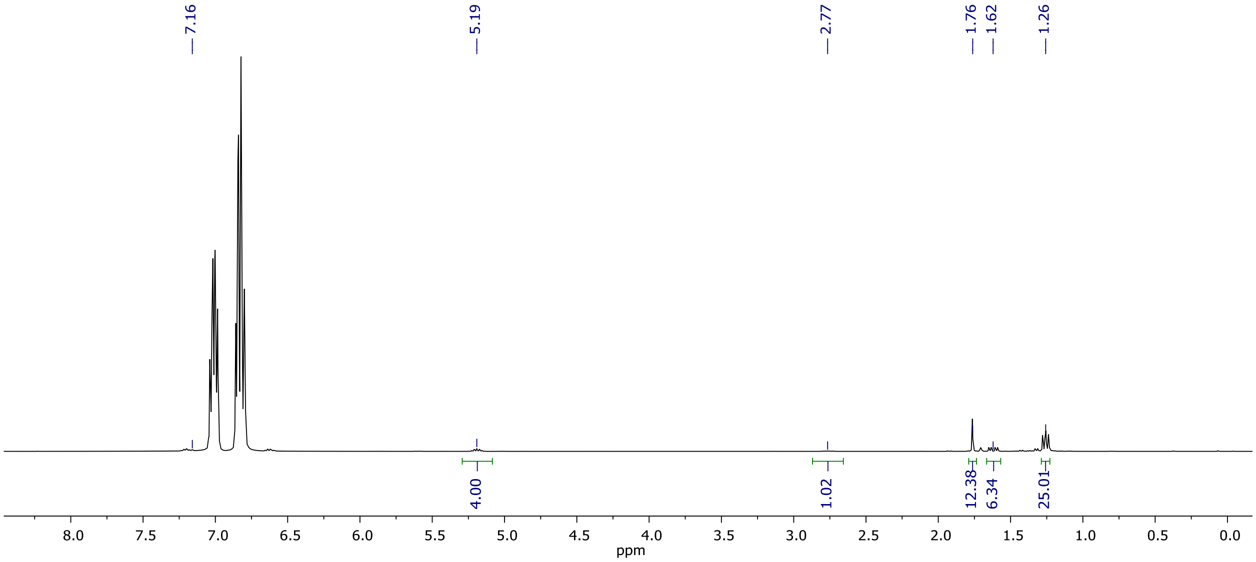


Figure S52: ^{1}H NMR spectrum (C_6D_6, 300 K, 400 MHz) of **5b**.

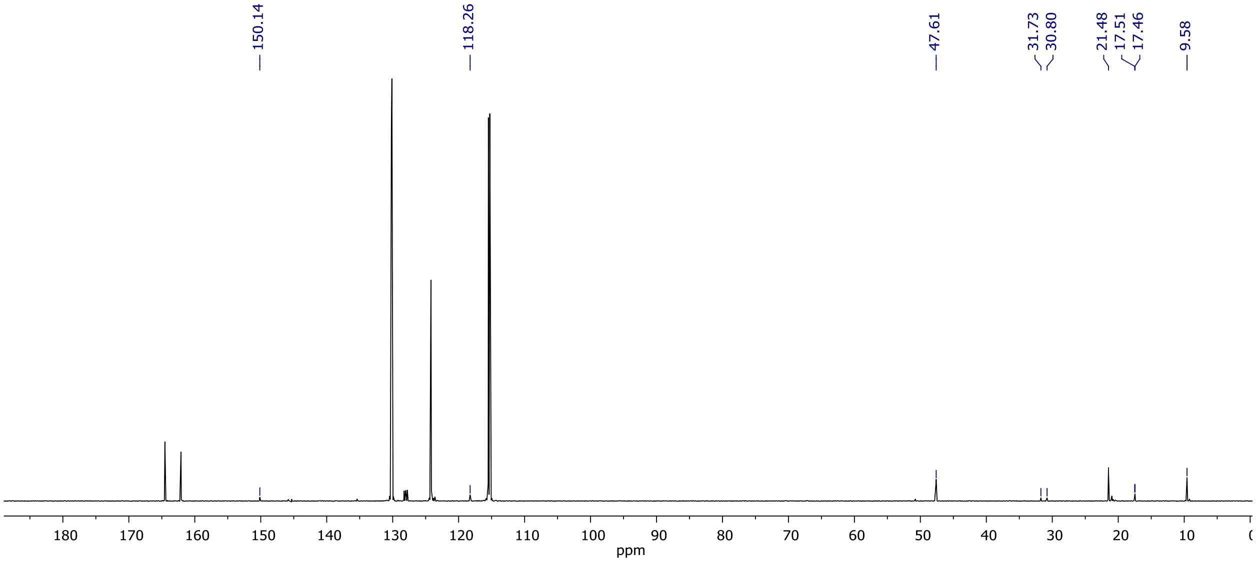


Figure S53: ^{13}C{^{1}H} NMR spectrum (C_6D_6, 300 K, 101 MHz) of **5b**.

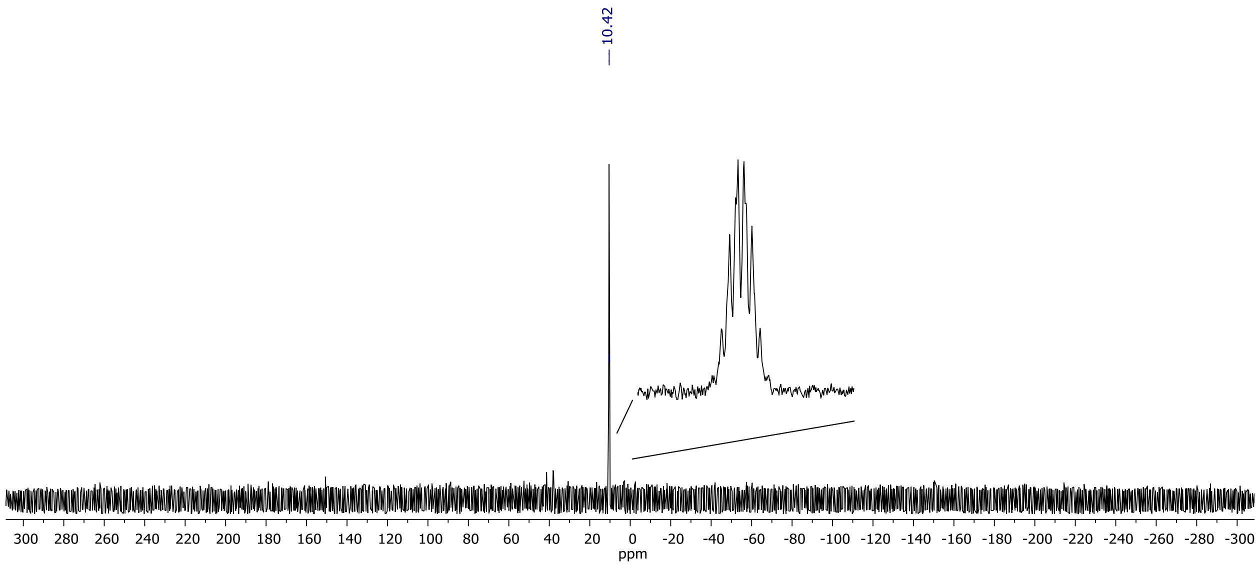


Figure S54: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of **5b**.

After pressurizing a solution of phosphine **5b** in C_6D_6 with 2 bar SO_2 at room-temperature the signal of **5b** showed up at 9.4 ppm in the ^{31}P NMR spectrum. The upfield-shift in the ^{31}P NMR spectrum is explained by the SO_2–complexation *via* the imine-N atoms of **5b** due to the excess of SO_2.

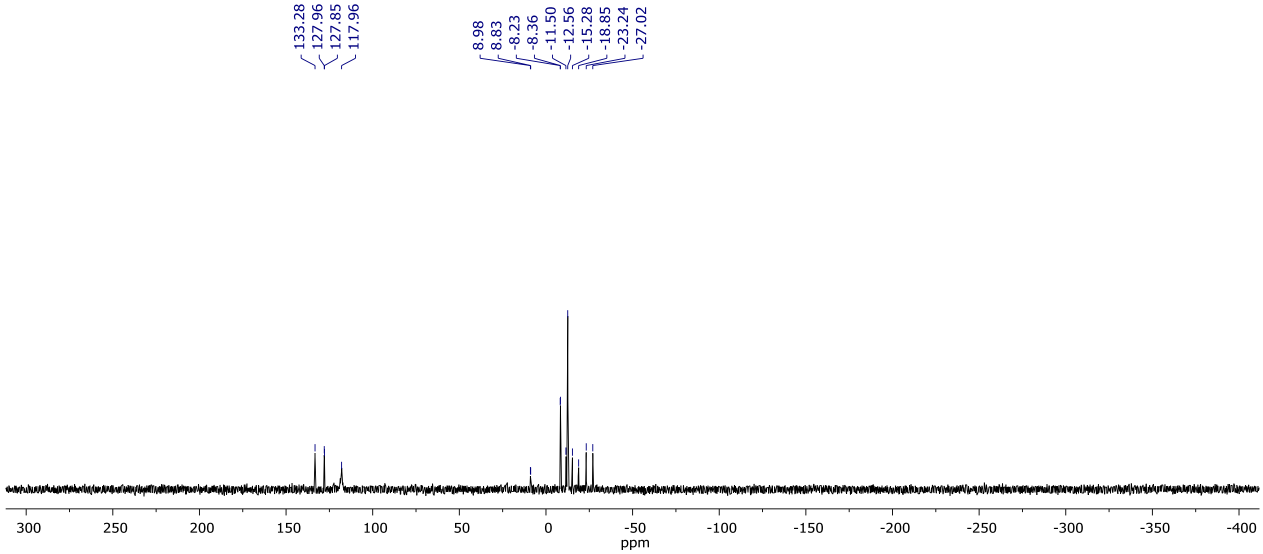


Figure S55: ^{31}P NMR spectrum (C_6D_6, 300 K, 162 MHz) of the reaction mixture of **1c** with pyridine–SO_3.

X-ray Diffraction Studies

General: Single-crystal X-ray diffraction data were collected on a Bruker AXS detector using Mo-K_α radiation (λ = 0.71073 Å). Crystals were selected under oil, mounted on nylon loops and then immediately placed in a cold stream of N_2 on a diffractometer. Using Olex2,[9] the structures were solved with the Superflip[10] structure solution program using Charge Flipping and refined with the ShelXL[11] refinement package using Least Squares minimisation.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1837294 (**2b**), CCDC-1837295 (**2c**), CCDC-1837296 (**5a**), CCDC-1837297 (tBu$_3$P-SO$_3$). These 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).

Single-crystal X-ray structure analysis of 2c:

Single crystals were obtained by cooling down a hot solution of **2c** in THF. A Single-crystal X-ray structure analysis revealed that **2c** crystallizes in the cubic space group *I*-43*d*. The asymmetric unit contains one molecule of **2c**.

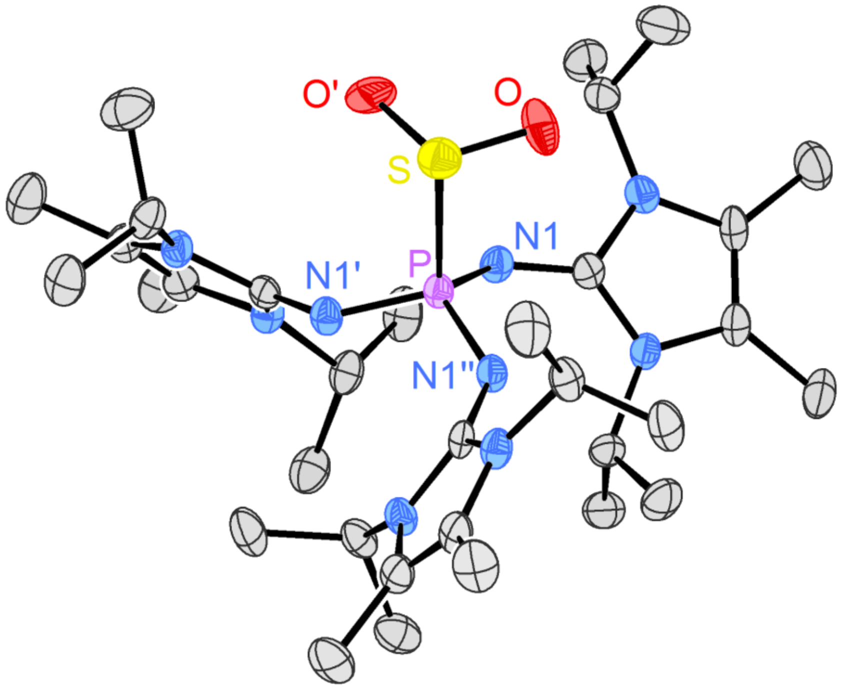


Figure S56: Molecular view of **2c** in the solid state with thermal ellipsoid plot at the 50% levels of probability. Hydrogen atoms are omitted for clarity.

Table S1. Crystal data and structure refinement for **2c**.

CCDC number	1837295	m/mm^{-1}	0.173
Empirical formula	$C_{33}H_{60}N_9O_2PS$	F(000)	5888.0
Formula weight	677.93	Crystal size/mm^3	0.08 × 0.06 × 0.06
Temperature/K	100(2)	Radiation	MoKα (λ = 0.71073)
Crystal system	cubic	2Θ range for data collection	7.426 to 52.718
Space group	*I*-43*d*	Index ranges	$-20 \leq h \leq 27$, $-28 \leq k \leq 25$, $-29 \leq l \leq 30$
a/Å	24.5396(3)	Reflections collected	41644
b/Å	24.5396(3)	Independent reflections	2505 [R_{int} = 0.0526, R_{sigma} = 0.0282]
c/Å	24.5396(3)	Data/restraints/parameters	2505/0/148
α/°	90	Goodness-of-fit on F^2	1.084
β/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.0441, wR_2 = 0.0926
γ/°	90	Final R indexes [all data]	R_1 = 0.0543, wR_2 = 0.0968
Volume/Å^3	14777.6(5)	Largest diff. peak/hole / e Å^{-3}	0.23/-0.21
Z	16	Flack parameter	-0.01(3)
ρ_{calc}mg/mm^3	1.219		

Single-crystal X-ray structure analysis of 2b:

Single crystals were obtained by slow diffusion of *n*-hexane in a solution of **2b** in benzene. A Single-crystal X-ray structure analysis revealed that **2b** crystallizes in the monoclinic space group *P*2$_1$/*c*. The asymmetric unit contains one molecule of **2b**. The SO_2 unit is disordered over two positions (occupancies: 91:9).

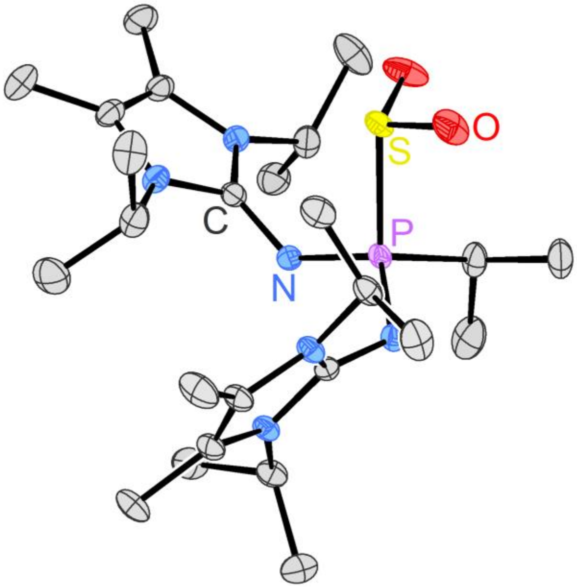


Figure S57: Molecular view of **2b** in the solid state with thermal ellipsoid plot at the 50% levels of probability. Hydrogen atoms are omitted for clarity.

Table S2. Crystal data and structure refinement for **2b**.

CCDC number	1837294	m/mm^{-1}	0.195
Empirical formula	$C_{25}H_{47}N_6O_2PS$	F(000)	1144.0
Formula weight	526.71	Crystal size/mm^3	0.47 × 0.16 × 0.05
Temperature/K	100(2)	Radiation	MoKα ($\lambda = 0.71073$)
Crystal system	monoclinic	2Θ range for data collection	4.022 to 56.594°
Space group	*P*2$_1$/*c*	Index ranges	$-19 \leq h \leq 19$, $-12 \leq k \leq 12$, $-27 \leq l \leq 27$
a/Å	14.9831(2)	Reflections collected	38731
b/Å	9.7363(2)	Independent reflections	7311 [$R_{int} = 0.0278$, $R_{sigma} = 0.0201$]
c/Å	20.8595(3)	Data/restraints/parameters	7311/0/349
α/°	90	Goodness-of-fit on F^2	1.026
β/°	103.8892(8)	Final R indexes [I>=2σ (I)]	$R_1 = 0.0353$, $wR_2 = 0.0870$
γ/°	90	Final R indexes [all data]	$R_1 = 0.0430$, $wR_2 = 0.0912$
Volume/Å^3	2954.01(8)	Largest diff. peak/hole / e Å^{-3}	0.37/-0.31
Z	4		
ρ_{calc}mg/mm^3	1.184		

Single-crystal X-ray structure analysis of 5a:

Single crystals were obtained by slow diffusion of *n*-Hexane in a solution of **5a** in THF. A Single-crystal X-ray structure analysis revealed that **5a** crystallizes in the orthorhombic space group $P2_12_12_1$. The asymmetric unit contains one molecule of **5a**.

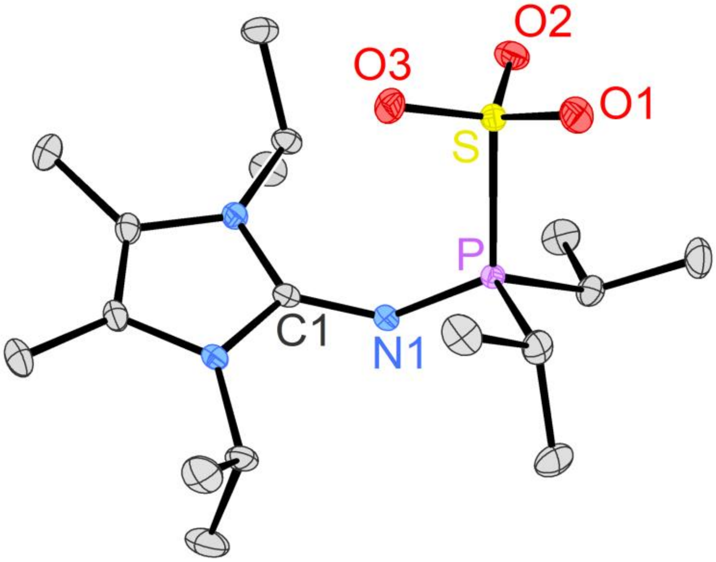


Figure S58: Molecular view of **5a** in the solid state with thermal ellipsoid plot at the 50% levels of probability. Hydrogen atoms are omitted for clarity; thermal ellipsoids are set at 50% probability. Selected bond length [Å] and angles [°]: P–S 2.1809(4), S–O1 1.4524(10), S–O2 1.4518(11), S–O3 1.4540(10), P–N1 1.5799(11), O1–S–O2 114.59(6), O1–S–O3 114.31(7), O2–S–O3 114.08(6), P–S–O1 103.18(4), P–S–O2 106.45(4), P–S–O3 102.42(5).

Table S3. Crystal data and structure refinement for **5a**.

CCDC number	1837296	μ/mm^{-1}	0.253
Empirical formula	$C_{17}H_{34}N_3O_3PS$	F(000)	848.0
Formula weight	391.50	Crystal size/mm^3	0.57 × 0.27 × 0.21
Temperature/K	100	Radiation	MoKα (λ = 0.71073)
Crystal system	orthorhombic	2Θ range for data collection	3.61 to 60.972
Space group	$P2_12_12_1$	Index ranges	$-13 \leq h \leq 13$, $-14 \leq k \leq 14$, $-32 \leq l \leq 32$
a/Å	9.35040(10)	Reflections collected	37810
b/Å	9.84690(10)	Independent reflections	6329 [R_{int} = 0.0241, R_{sigma} = 0.0157]
c/Å	22.5631(3)	Data/restraints/parameters	6329/0/236
α/°	90	Goodness-of-fit on F^2	1.097
β/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.0219, wR_2 = 0.0607
γ/°	90	Final R indexes [all data]	R_1 = 0.0223, wR_2 = 0.0610
Volume/Å^3	2077.44(4)	Largest diff. peak/hole / e Å^{-3}	0.33/-0.22
Z	4	Flack parameter	-0.002(10)
ρ_{calc}mg/mm^3	1.252		

Single-crystal X-ray structure analysis of *t*Bu$_3$P-SO$_3$:

Single crystals were obtained by slow diffusion of *n*-Hexane in a solution of *t*Bu$_3$P-SO$_3$ in benzene. A Single-crystal X-ray structure analysis revealed that *t*Bu$_3$P-SO$_3$ crystallizes in the monoclinic space group *P*2$_1$/*n*. The asymmetric unit contains one molecule of *t*Bu$_3$P-SO$_3$.

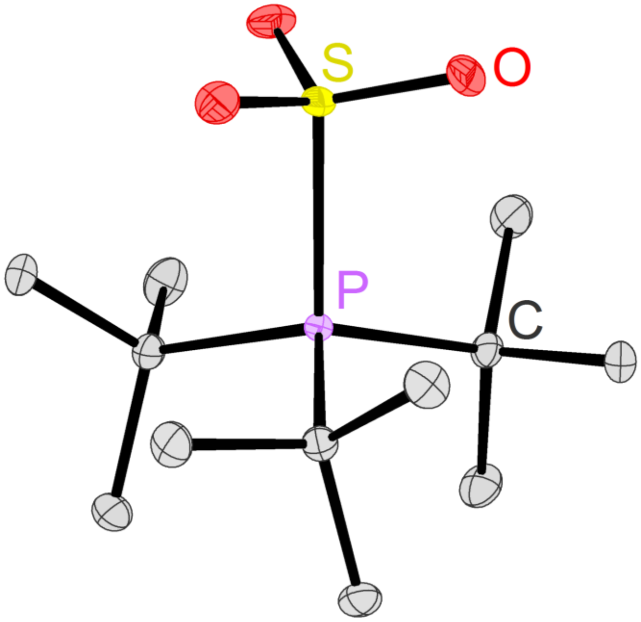


Figure S59: Molecular view of *t*Bu$_3$P-SO$_3$ in the solid state with thermal ellipsoid plot at the 50% levels of probability. Hydrogen atoms are omitted for clarity; thermal ellipsoids are set at 50% probability. Selected bond length [Å] and angles [°]: P–S 2.2098(3), S–O1 1.4477(7), S–O2 1.4479(7), S–O3 1.4465(7), O1–S–O2 114.43(4), O1–S–O3 114.62(4), O2–S–O3 114.79(4), P–S–O1 103.89(3), P–S–O2 103.35(3), P–S–O3 103.69(3).

Table S4. Crystal data and structure refinement for *t*Bu$_3$P-SO$_3$.

CCDC number	1837297	μ/mm^{-1}	0.321
Empirical formula	$C_{12}H_{27}O_3PS$	F(000)	616.0
Formula weight	282.36	Crystal size/mm^3	0.27 × 0.17 × 0.1
Temperature/K	100	Radiation	MoKα (λ = 0.71073)
Crystal system	monoclinic	2Θ range for data collection	7.814 to 61.018
Space group	*P*2$_1$/*n*	Index ranges	$-11 \le h \le 9$, $-16 \le k \le 19$, $-19 \le l \le 19$
a/Å	8.04457(8)	Reflections collected	16409
b/Å	13.7032(1)	Independent reflections	4532 [R_{int} = 0.0165, R_{sigma} = 0.0153]
c/Å	13.5041(1)	Data/restraints/parameters	4532/0/163
α/°	90	Goodness-of-fit on F^2	1.057
β/°	91.7658(4)	Final R indexes [I>=2σ (I)]	R_1 = 0.0244, wR_2 = 0.0693
γ/°	90	Final R indexes [all data]	R_1 = 0.0262, wR_2 = 0.0708
Volume/Å^3	1487.96(2)	Largest diff. peak/hole / e Å^{-3}	0.42/-0.27
Z	4		
ρ_{calc}mg/mm^3	1.260		

Preliminary Single-crystal X-ray structure analysis of 4c·3SO$_2$:

Single crystals were obtained by pressurizing a THF solution of **2c** with 1 bar SO$_2$ at 0 °C and diffusion of *n*-hexane in the reaction mixture at –40 °C over 2 days. Attempts to obtain better crystal by recrystallization were not successful. Single-crystal X-ray structure analysis revealed that **4c·3SO$_2$** crystallizes in the monoclinic space group *C*2/*c*. The asymmetric unit contains a molecule of **4c·3SO$_2$** coordinated to three SO$_2$ molecules via rather short N–S bond distances [N1–S2 1.962(13) Å, N7–S3 1.962(14) Å] and a long O–S bond distances [O1–S1 2.547(13) Å].

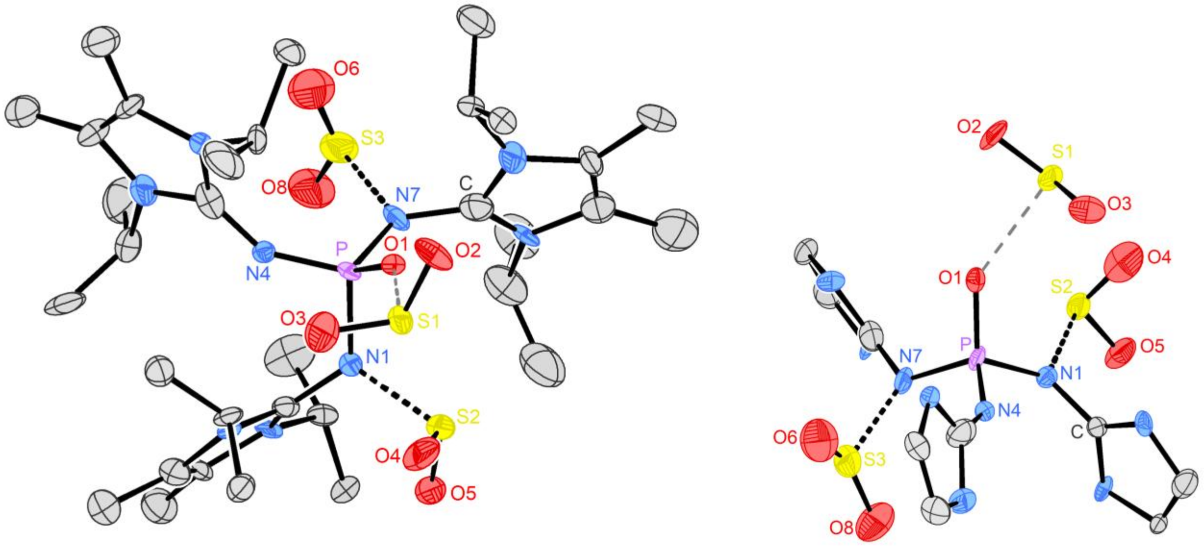
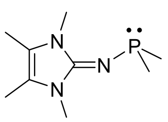


Figure S60: Two molecular views of the preliminary solid-state structure of **4c·3SO$_2$** showing the interaction of three donor atoms of the phosphine oxide with SO$_2$ molecules. (Isopropyl and methyl groups are omitted in the right picture for clarity).

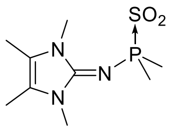
DFT Calculations

All structures were optimized without geometry constraints using the meta-GGA TPSS or (only for $^1\Delta$ SO) the TPSSh hybrid functional[12] and an atom-pairwise dispersion correction (D3)[13,14]. A flexible triple zeta basis set (def2-TZVP)[15] was used in all calculations. In all calculations, the COSMO model[16] for implicit solvation was applied with a dielectric constant of 7.58 (THF). For the calculation of the free energy contributions (G^{RRHO}(298K)), a rotor approximation was applied for vibrational modes with wave numbers below 100 cm^{-1}.[17] The nature of all optimized stationary points was proven by the presence of either 0 (minimum) or 1 (transition structure) imaginary vibrational frequency. The character of TS_{B-C} was further proven by a calculation of the intrinsic reaction coordinate (IRC). Electronic energies were recalculated with the hybrid functional PW6B95(-D3)[18] using the structures optimized with TPSS-D3. The final value for the free enthalpy $\Delta G(298)$ was obtained using the PW6B95-D3 electronic energies and G^{RRHO}(298K), obtained with TPSS-D3 and COSMO solvation (THF). All calculations were performed with the TURBOMOLE 7.2 program.[19]

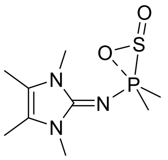
Table S5 reports the calculated electronic energies and free energy corrections at 298 K. **Figure S55** depicts the conformations and most important interatomic distance of the intermediates of the reaction of phosphine **A** with SO_2, followed by a listing of cartesian coordinates for all calculated stationary points.



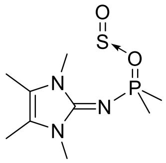
A



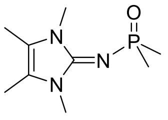
B



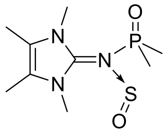
TS_{B-C}



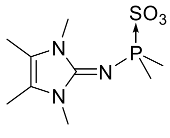
C



D



E



F

Table S5. Electronic energies (E) and thermodynamic correction to the Gibbs Free Energy at T = 298.15 K (G298) for the structures involved in the reactions.

Structure	E(TPSS-D3)[a] [E_h]	G^{RRHO}(298)[a] [kcal/mol]	E(PW6B95-D3)[a][b] [E_h]	ΔG(298)[c] [kcal/mol]
SO_2	-548.759549	-11.46	-549.197418	-
$^1\Delta$ SO[d]	(-473.384964)	(-11.44)	-473.773039	-
$^3\Sigma^-$ SO	-473.449114	-11.49	-473.816133	-
S_8	-3185.946387	-16.62	-3188.316614	-
A	-859.784677	136.69	-860.589611	0.0
B	-1408.582417	140.04	-1409.823680	-8.2
TS_{B-C}	-1408.551107	139.78	-1409.789643	+12.9
C	-1408.578119	139.46	-1409.824373	-9.2
D	-935.125254	138.64	-936.006253	+6.8/-20.3[e]
E	-1408.596684	141.23	-1409.843143	-19.2
F	-1483.878513	141.93	-1485.199139	-58.9[f]

[a] All energies and the free enthalpy corrections have been calculated with the def2-TZVP basis set with an implicit solvent model (COSMO, ε = 7.58)

[b] Energy calculation using the structure optimized with TPSS-D3/def2-TZVP

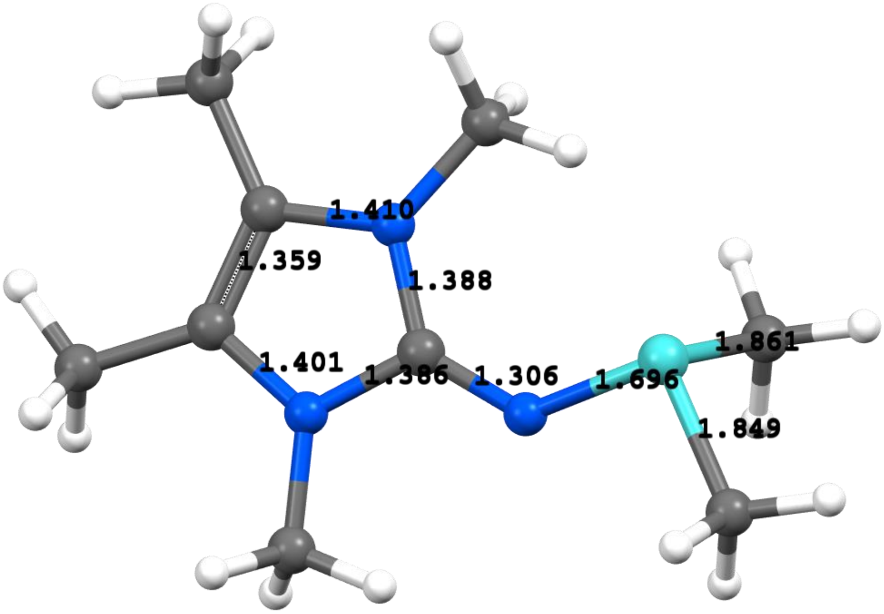
[c] ΔG(298) = ΔE(PW6B95-B3) + ΔG^{RRHO}(298K, TPSS-D3). The value corresponds to the relative ΔG for the formation of the intermediate from **A** and SO_2.

[d] The $^1\Delta$ SO molecule was optimized with the (hybrid) functional TPSSh-D3, the electronic structure could not be converged with TPSS-D3.

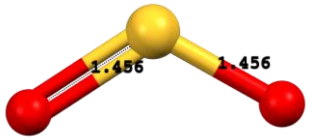
[e] with $^1\Delta$ SO and $^3\Sigma^-$ SO, respectively

[f] ΔG(298) for the reaction **A** + SO_2 + $^3\Sigma^-$ SO -> **F** + 1/8 S_8.

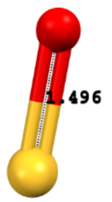
Figure S55. Optimized structures (TPSS-D3/def2-TZVP+COSMO(ε=7.58)) of the intermediates during the reaction of phosphine **A** with SO_2. ($^1\Delta$ SO has been optimized with TPSSh-D3/def2-TZVP)



A

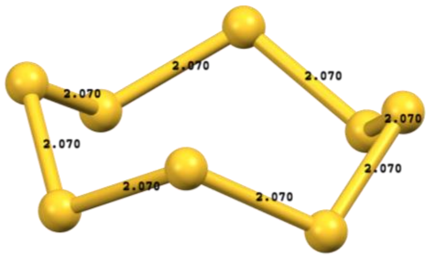


SO_2

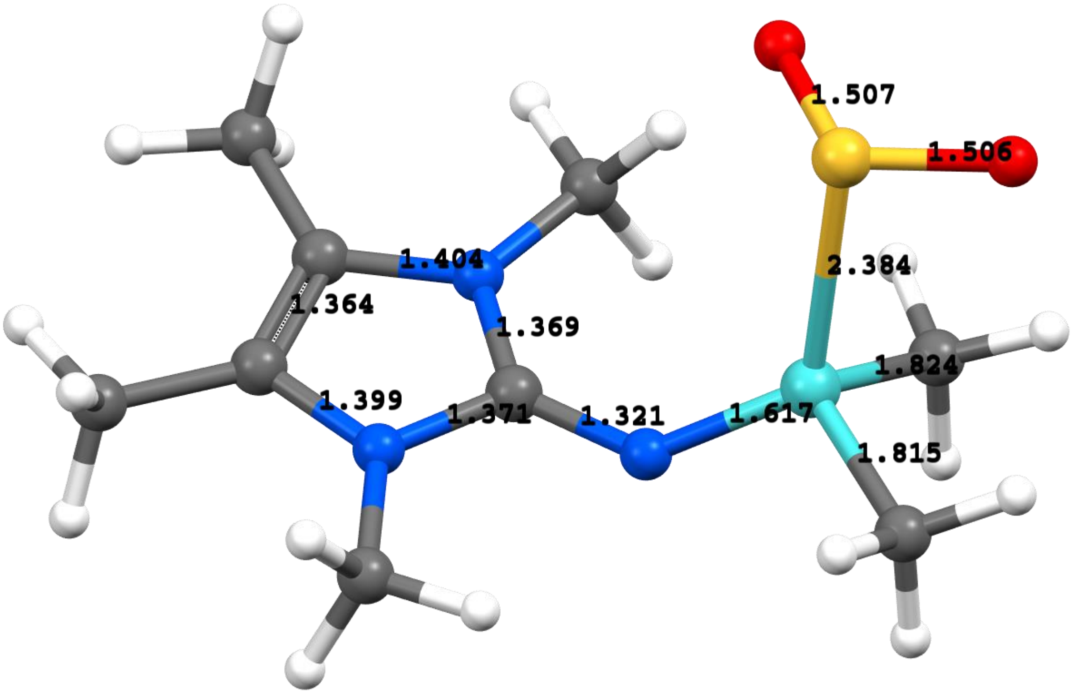


$^1\Delta$ SO

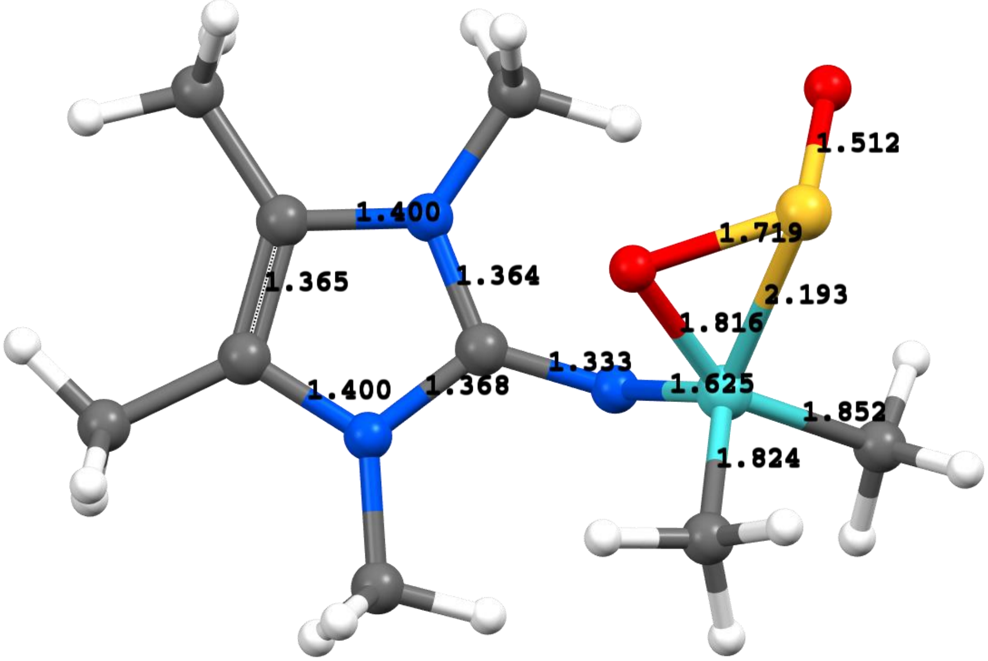
$^3\Sigma^-$ SO



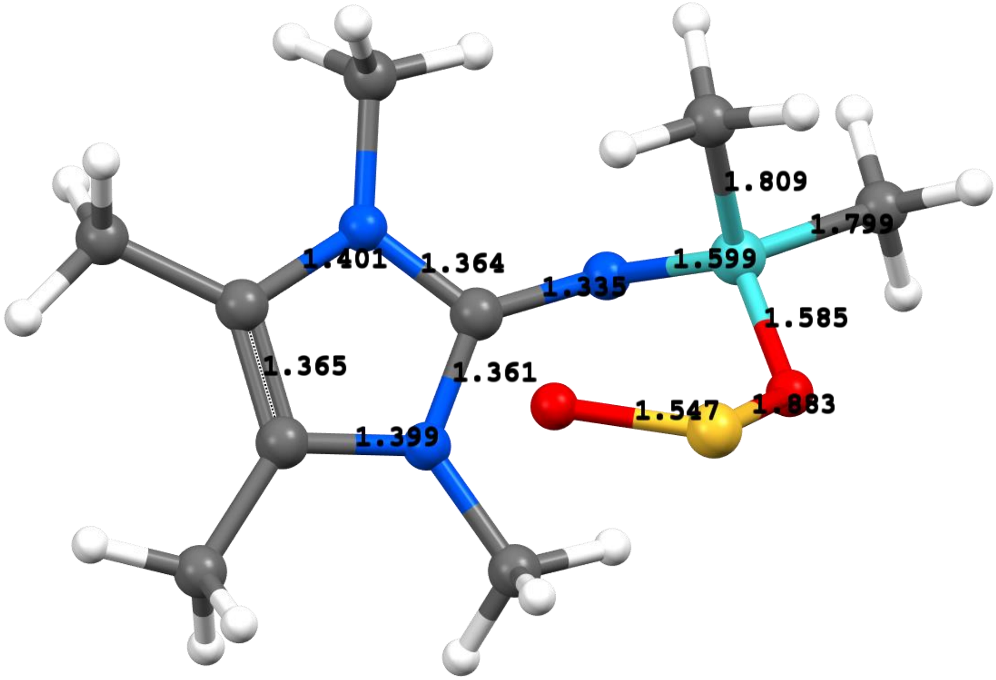
S_8


1.507
1.506
1.404
2.384
1.364
1.369
1.824
1.399
1.371
1.321
1.617
1.815

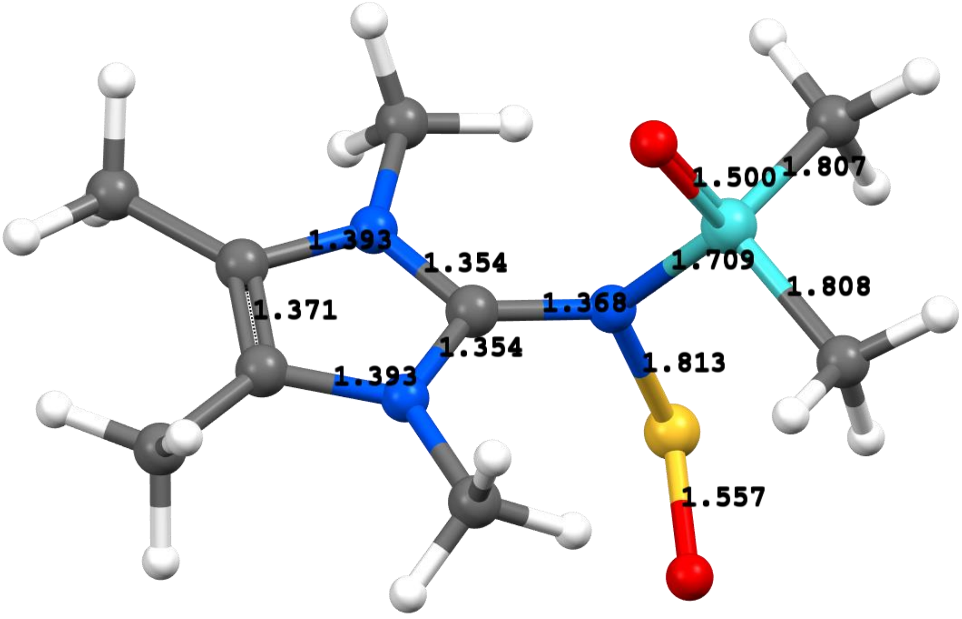
B


1.512
1.400
1.719
1.365
1.364
2.193
1.816
1.333
1.400
1.368
1.625
1.852
1.824

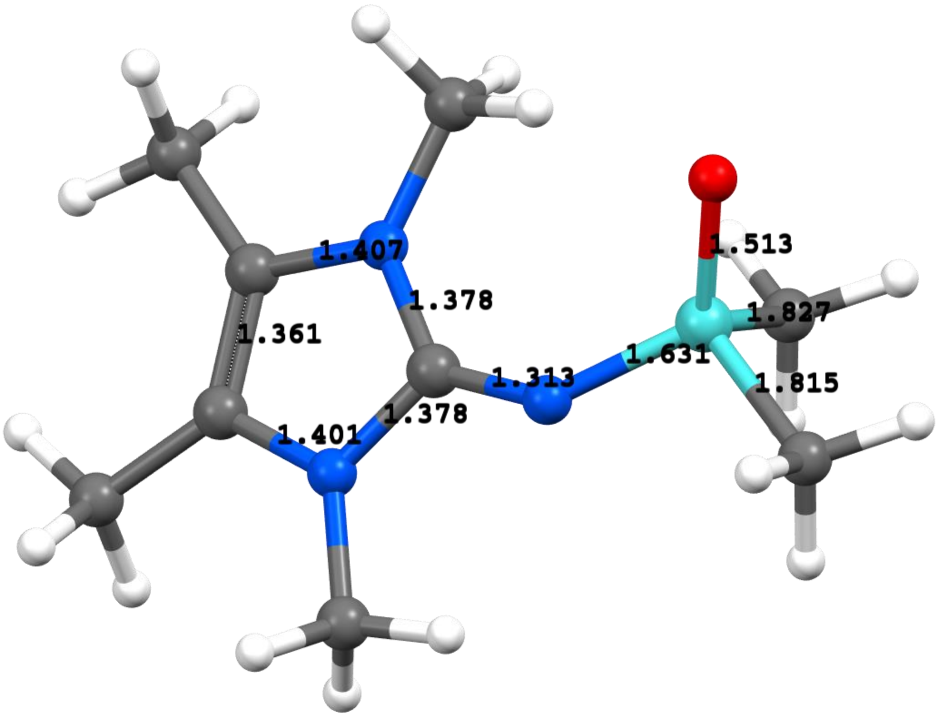
TS$_{B\text{-}C}$


1.809
1.799
1.401
1.364
1.335
1.599
1.585
1.365
1.361
1.547
1.883
1.399

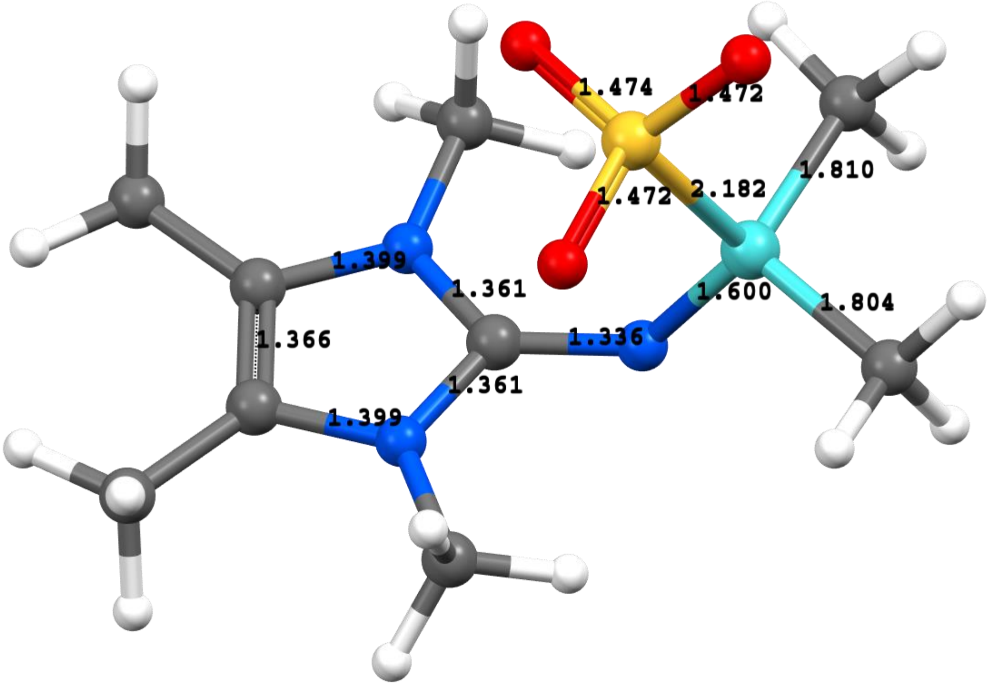
C


1.500
1.807
1.393
1.354
1.709
1.808
1.371
1.368
1.354
1.813
1.393
1.557

E


1.407
1.378
1.361
1.313
1.631
1.513
1.827
1.815
1.378
1.401

D


1.474
1.472
1.472
2.182
1.810
1.399
1.361
1.600
1.804
1.366
1.336
1.361
1.399

F

CARTESIAN COORDINATES OF ALL DFT-OPTIMIZED STRUCTURES

SO$_2$

```
E(TPSS-D3/def2-TZVP) = -548.7595489211 (conv)
Lowest Freq. =   494.17 cm^-1
3
SO2 (SO2/c1/tpss-d3.def2-TZVP_COSMO_7.58)
S     0.0000000   -0.3170546   -0.0817435
O     0.0000000    0.2193040    1.2714446
O     0.0000000    0.6269278   -1.1897012
```

$^1\Delta$ SO

```
E(TPSSh-D3/def2-TZVP) = -473.3849637510 (conv)
Lowest Freq. =  1140.74 cm^-1
2
1SO (SO/c1/tpssh-d3.def2-TZVP_COSMO_7.58)
S     0.0000000   -0.2603669   -0.3314153
O     0.0000000    0.1655555    1.1029119
```

$^3\Sigma^-$ SO

```
E(TPSS-D3/def2-TZVP) = -473.4491138585 (conv)
Lowest Freq. =  1111.31 cm^-1
2
SO (SO/c1/tpss-d3.def2-TZVP_COSMO_7.58)
S     0.0000000   -0.3186193   -0.1040781
O     0.0000000    0.2238079    1.2994509
```

S$_8$

```
E(TPSS-D3/def2-TZVP) = -3185.946386685 (conv)
Lowest Freq. =    67.98 cm^-1
8
S8 (S8/c1/tpss-d3.def2-TZVP_COSMO_7.58)
S     0.0383450    2.9550746   -1.1886141
S     1.3119537   -0.1401807   -0.8708668
S    -1.8251270    3.0360209   -0.2915661
S    -3.1221569   -0.0595806   -0.0955541
S    -1.7951834   -1.4232600   -0.9102006
S    -3.0685743    1.6719383   -1.2280317
S    -0.0242637   -1.3402897    0.1577530
S     1.2730400    1.7550226   -0.0398907
```

A

```
E(TPSS-D3/def2-TZVP) = -859.7846766353 (conv)
Lowest Freq. =    14.39 cm^-1
31
A (001/c1b/tpss-d3.def2-TZVP_COSMO_7.58)
P    -0.7944955   -2.2197281    1.5114545
N    -0.9972437   -0.6588470    0.8798866
C    -2.2114663   -2.2139218    2.6988789
C    -0.1341593    0.0895298    0.2467574
```

```
N    -0.3109062    1.4562946    0.0959313
N     1.0448187   -0.1788188   -0.4342476
C     0.7036601    2.0093036   -0.6968328
C    -1.4343092    2.1745382    0.6727067
C     1.5464728    0.9966143   -1.0302987
C     1.5842258   -1.5047542   -0.7030918
C     0.7452292    3.4639020   -1.0158239
H    -1.0805167    3.0418100    1.2371020
C     2.8006955    0.9960375   -1.8342218
H     1.2075621   -2.1994702    0.0480824
H    -0.1613693    3.7871590   -1.5422341
H     1.6037462    3.6813463   -1.6551959
H     0.8348230    4.0753797   -0.1089206
H     3.6659767    0.6788645   -1.2380413
H     3.0003539    2.0035649   -2.2060182
H     2.7323353    0.3243017   -2.6989525
C    -1.5769053   -3.2911857    0.2071672
H    -0.9183696   -3.3622434   -0.6644622
H    -1.9817601   -1.5461476    3.5349274
H    -3.1264713   -1.8668969    2.2037149
H    -2.3673474   -3.2250025    3.0918740
H    -1.7339027   -4.3010272    0.6041102
H    -2.5397341   -2.8697729   -0.1070368
H     1.2998895   -1.8494278   -1.7045796
H     2.6734647   -1.4778639   -0.6273121
H    -1.9445110    1.4783218    1.3399876
H    -2.1297858    2.5081403   -0.1053109
```

B

```
E(TPSS-D3/def2-TZVP) = -1408.582417370 (conv)
Lowest Freq. =    23.37 cm^-1
34
B (002/c3/tpss-d3.def2-TZVP_COSMO_7.58)
S     0.5405765    1.9700679   -3.2462088
P     1.1928709    0.8271309   -1.2586957
O     1.7271064    2.8964240   -3.2893394
O     0.6378791    0.8523859   -4.2525112
N     0.3048230   -0.3606310   -0.6145225
C    -0.4766663   -1.3058603   -1.1061559
N    -1.6638948   -1.6793484   -0.5309432
N    -0.3006287   -2.1501134   -2.1694283
C    -2.2268752   -2.7511256   -1.2325108
C    -1.3791175   -3.0446296   -2.2597340
C    -3.5256225   -3.3577434   -0.8286531
C    -1.4710003   -4.0789829   -3.3271740
H    -3.4813995   -3.7602494    0.1904794
H    -3.7806155   -4.1755610   -1.5055178
H    -4.3395731   -2.6234474   -0.8609222
H    -1.4850646   -3.6279946   -4.3265391
H    -2.3926721   -4.6513863   -3.2025798
H    -0.6294266   -4.7809796   -3.2870759
C     1.3347136    2.0931602    0.0342673
H     1.8046227    1.6652467    0.9254288
H     0.3357499    2.4563649    0.2891311
H     1.9405635    2.9213700   -0.3426011
```

C	2.9187250	0.3772351	-1.6426173
H	3.3794433	-0.0867020	-0.7653728
H	3.4567796	1.2914571	-1.9074486
H	2.9534565	-0.3108942	-2.4887651
C	-2.2435114	-1.0171623	0.6295158
H	-3.2306293	-0.6184106	0.3812894
H	-1.5735948	-0.2019193	0.9032619
H	-2.3311913	-1.7187176	1.4636106
C	0.8724141	-2.1288512	-3.0352487
H	0.9522957	-1.1568703	-3.5359774
H	0.7608086	-2.9092210	-3.7865961
H	1.7697278	-2.3293215	-2.4433804

TSB-C

E(TPSS-D3/def2-TZVP) = -1408.551106993 (conv)

Lowest Freq. = -118.15 cm^-1

34

TSB-C (TS002-004/c1/tpss-d3.def2-TZVP_COSMO_7.58)

P	-0.1653635	-1.3612839	1.6405532
N	-0.6536144	-0.7429526	0.2192421
C	0.1786240	-0.1725783	2.9805536
C	0.1221902	-0.1612184	-0.6948178
N	0.2703043	1.1842548	-0.8897025
N	0.8195286	-0.7585204	-1.7034008
C	1.0669194	1.4280172	-2.0149105
C	-0.3304403	2.1964164	-0.0311326
C	1.4154663	0.2093088	-2.5211016
C	0.9362877	-2.2013875	-1.8753772
C	1.3933811	2.8092195	-2.4661597
H	-0.9987847	1.6811139	0.6591006
C	2.2498939	-0.1595388	-3.6981857
H	0.2234515	-2.6778817	-1.2041702
H	0.4897105	3.3699865	-2.7340799
H	2.0392529	2.7692550	-3.3457148
H	1.9161764	3.3740599	-1.6850901
H	3.1021798	-0.7834627	-3.4044031
H	2.6371671	0.7426916	-4.1762251
H	1.6707896	-0.7173251	-4.4439056
C	-1.8098289	-2.0342767	2.1617684
H	-2.0646103	-2.8818271	1.5178262
H	0.9620485	0.5184842	2.6610830
H	-0.7349035	0.3757767	3.2293876
H	0.5261112	-0.7086087	3.8703298
H	-1.7356405	-2.3860696	3.1962706
H	-2.5923115	-1.2729106	2.0789558
H	0.7157958	-2.4622715	-2.9130353
H	1.9418468	-2.5350941	-1.6097431
H	-0.9005615	2.9068803	-0.6341158
H	0.4415996	2.7300697	0.5303005
S	1.1521210	-3.0893966	1.9384092
O	1.5813138	-1.5963555	1.2019283
O	0.8802303	-4.1615018	0.9070634

C

```
E(TPSS-D3/def2-TZVP) = -1408.578119270 (conv)
Lowest Freq. =    18.88 cm^-1
34
C (004/c1/tpss-d3.def2-TZVP_COSMO_7.58)
P    -0.0266197   -1.1668600    1.9103011
N     0.8463721   -0.0451291    1.1772476
C     0.2404376   -0.9141923    3.6712022
C     0.9892405    0.1617420   -0.1340671
N     0.4084449    1.1642320   -0.8546408
N     1.8240724   -0.4830325   -0.9937950
C     0.8614260    1.1301852   -2.1795690
C    -0.5552539    2.1069817   -0.3024387
C     1.7428464    0.0918301   -2.2663987
C     2.6093086   -1.6602443   -0.6407221
C     0.3843962    2.1029562   -3.2011282
H    -0.5473558    1.9845820    0.7808845
C     2.5151229   -0.4405697   -3.4225279
H     2.7242434   -1.6714135    0.4433008
H    -0.7036304    2.0508434   -3.3275372
H     0.8484207    1.8848223   -4.1651721
H     0.6394947    3.1340073   -2.9277602
H     3.5961105   -0.3897109   -3.2461131
H     2.2908004    0.1424543   -4.3181390
H     2.2575842   -1.4874557   -3.6217714
C    -1.7932482   -1.0052673    1.5539476
H    -1.9321920   -1.0985003    0.4727094
H     1.2966603   -1.0845850    3.8960830
H    -0.0260914    0.1109590    3.9414506
H    -0.3717694   -1.6193914    4.2390527
H    -2.3535876   -1.7986138    2.0557545
H    -2.1396316   -0.0249561    1.8934776
H     2.0800593   -2.5617670   -0.9569525
H     3.5877039   -1.5960514   -1.1200941
H    -1.5573785    1.9021080   -0.6896370
H    -0.2649582    3.1276269   -0.5606449
O     0.3913095   -2.6722998    1.6429089
S    -0.4405078   -3.5758325    0.2149870
O    -0.4316316   -2.6061221   -0.9900512
```

D

```
E(TPSS-D3/def2-TZVP) = -935.1252536583 (conv)
Lowest Freq. =    21.94 cm^-1
32
E (005/c1/tpss-d3.def2-TZVP_COSMO_7.58)
P    -0.0151281   -1.3055112    1.8220926
N     0.4413625    0.0205760    0.9895215
C    -0.4846324   -0.6105486    3.4313073
C     0.6898147    0.2483134   -0.2799467
N     0.6359469    1.5100380   -0.8300955
N     1.0776178   -0.5726772   -1.3158682
C     0.9821886    1.4755574   -2.1867298
C     0.2544477    2.6934269   -0.0745854
C     1.2534571    0.1776655   -2.4932109
```

C	1.3184777	-2.0077178	-1.2193446
C	1.0038953	2.7072896	-3.0237543
H	-0.0008255	2.3584455	0.9313174
C	1.6702742	-0.4578065	-3.7741305
H	1.3772580	-2.2874449	-0.1647040
H	0.0199168	3.1912007	-3.0552966
H	1.2907037	2.4568385	-4.0472878
H	1.7216836	3.4425328	-2.6398709
H	2.6608061	-0.9225889	-3.6944986
H	1.7152214	0.2964027	-4.5628422
H	0.9639979	-1.2362244	-4.0875120
C	-1.5728736	-1.9159675	1.0882236
H	-1.3684604	-2.3139678	0.0893600
H	0.4019855	-0.1569065	3.8848706
H	-1.2585044	0.1539493	3.3174008
H	-0.8494365	-1.4094639	4.0840076
H	-1.9806738	-2.7219299	1.7067431
H	-2.3082697	-1.1099442	1.0069408
H	0.5122664	-2.5686993	-1.7032873
H	2.2649870	-2.2483188	-1.7093743
H	-0.6112452	3.1765680	-0.5364759
H	1.0851614	3.4038552	-0.0274342
O	0.9745970	-2.4369427	1.9920249

E

E(TPSS-D3/def2-TZVP) = -1408.596683700 (conv)

Lowest Freq. =   27.50 cm^-1

34

D (006/c1/tpss-d3.def2-TZVP_COSMO_7.58)

P	-0.5529978	-1.0511454	1.6780216
N	0.3419896	0.2943090	1.1211051
C	0.5025126	-1.8737256	2.8936056
C	0.7373782	0.4053765	-0.1832711
N	0.1462351	1.1726977	-1.1296007
N	1.8115353	-0.1802291	-0.7623808
C	0.8549157	1.0740630	-2.3243308
C	-1.0369630	1.9983633	-0.9051685
C	1.8998927	0.2161469	-2.0951500
C	2.7132097	-1.1123483	-0.0812402
C	0.4489061	1.8185577	-3.5476844
H	-1.8453421	1.6697510	-1.5614339
C	2.9790335	-0.2674749	-2.9994878
H	2.6742192	-0.8952595	0.9865607
H	-0.5651085	1.5457351	-3.8612732
H	1.1328277	1.5879565	-4.3664191
H	0.4694774	2.9014798	-3.3798032
H	2.9659292	-1.3595756	-3.0863342
H	3.9686701	0.0306133	-2.6348902
H	2.8427883	0.1561185	-3.9962773
C	-1.9177733	-0.3151198	2.6060535
H	-2.5895025	0.1903755	1.9063906
H	1.0293433	-1.1278615	3.4968455
H	-0.1113075	-2.5158511	3.5325672
H	1.2348163	-2.4894105	2.3644554

```
H    -2.4655239   -1.1050154    3.1286387
H    -1.5265981    0.4054421    3.3298363
H     2.4100167   -2.1417297   -0.2892605
H     3.7274384   -0.9439868   -0.4437754
H    -0.7962063    3.0447867   -1.1036365
H    -1.3306014    1.8813310    0.1367079
O    -0.9774354   -1.9147448    0.5268142
S     1.1475201    1.4151225    2.2961072
O     2.5308777    0.8048207    2.6667881
```

F

```
E(TPSS-D3/def2-TZVP) = -1483.878512576 (conv)
Lowest Freq. =    10.14 cm^-1
35
F (011/c1a/tpss-d3.def2-TZVP_COSMO_7.58)
P    -0.3799245   -1.0967515    1.6700156
N    -0.8498329   -0.5195510    0.2541105
C    -1.1239916   -0.1462227    3.0107614
C    -0.0991564   -0.2533766   -0.8190320
N     0.3412484    0.9759993   -1.2032111
N     0.2912184   -1.1166815   -1.7963507
C     1.0371403    0.8811428   -2.4126548
C     0.1564122    2.1876900   -0.4127678
C     1.0087712   -0.4331937   -2.7839851
C     0.0537087   -2.5538173   -1.7424922
C     1.6521745    2.0704243   -3.0641156
H    -0.6195626    1.9829150    0.3246614
C     1.5874670   -1.1268657   -3.9676535
H    -0.8683537   -2.7236871   -1.1851177
H     0.8972883    2.8195338   -3.3309847
H     2.1665487    1.7675800   -3.9783529
H     2.3835233    2.5522851   -2.4047806
H     2.2944519   -1.9086167   -3.6664033
H     2.1222364   -0.4076874   -4.5913320
H     0.8098414   -1.5958333   -4.5822620
C    -0.8163377   -2.8314362    1.9489297
H    -0.2712596   -3.4576982    1.2393939
H    -0.7703151    0.8854930    2.9487578
H    -2.2125284   -0.1697919    2.9012849
H    -0.8382352   -0.5793944    3.9725379
H    -0.5466572   -3.1164845    2.9691107
H    -1.8934661   -2.9550026    1.8001979
H    -0.0581276   -2.9367863   -2.7571746
H     0.8862587   -3.0547353   -1.2415675
H    -0.1575601    3.0039948   -1.0657518
H     1.0850135    2.4475658    0.1000591
S     1.7860972   -0.9964422    1.9179828
O     2.2672258   -1.8325045    0.8037977
O     2.0384835   -1.5521740    3.2580146
O     2.0865987    0.4374765    1.7778424
```

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