SUPPORTING INFORMATION

Deoxygenation chalcogen oxides EO_2 (E = S, Se) with phospha-Wittig reagents

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1 Experimental

General Information. If not stated otherwise, all manipulations were carried out under oxygen- and moisture-free conditions under an inert atmosphere of argon using standard Schlenk techniques. All reactants were stored and handled in a mBraun glovebox. Solvents and reactants were either obtained from commercial sources, local trade or synthesized as depicted in Table S1. Activation of molecular sieves was achieved through heating with a heatgun at >600°C and applying vacuum for several hours.

Table S1: Origin and purification of solvents and reactants.

Substance	Origin	Purification
Mes*$PPMe_3$	Synthesized according to literature procedures.[1]	-
^{Mes}TerPPMe_3	Synthesized according to literature procedures.[1]	-
^{Dip}TerPPMe_3	Synthesized according to literature procedures.[1]	-
DABSO (=1,4-Diazabicyclo[2.2.2]octan·2SO_2)	TCI >98%	used as received, transferred to glovebox
SeO_2	≥99.9%, trace metals basis	Dried *in vacuo* for several hours, transferred to glovebox
Benzene	local trade	dried over Na/benzophenone, stored over activated, 3Å molecular sieves and transferred to glovebox
Toluene	local trade	Purified with a solvent Purification system, transferred to glovebox

Table S1 continued.

Substance	Origin	Purification
MeCN	SIGMA ALDRICH, HPLC grade ≥99.9%	Purified with a solvent Purification system, distilled from P_2O_5 and stored over 3Å molecular sieves
C_6D_6	euro-isotope	dried over Na/benzophenone, freshly distilled prior to use
n-hexane	local trade	Purified with a solvent Purification system, stored over activated, 3Å molecular sieves

NMR spectra were recorded on Bruker spectrometers (AVANCE 400 or Fourier 300) and were referenced internally to the deuterated solvent (^{13}C: C_6D_6 δ_{ref} = 128.06 ppm) or to protic impurities in the deuterated solvent (^{1}H: C_6D_5H δ_{ref} = 7.16 ppm). All measurements were carried out at ambient temperature unless denoted otherwise. NMR signals were assigned using experimental data (e.g. chemical shifts, coupling constants (=*J*), integrals) where applicable.

IR spectra of crystalline samples or purified powders were recorded on a Bruker Alpha II FT-IR spectrometer equipped with an ATR unit at ambient temperature under argon atmosphere. Relative intensities are reported according to the abbreviations: very weak (=vw), weak (=w), medium (=m), strong (=s), very strong (=vs), broad (=br).

Elemental analyses were obtained using a Leco Tru Spec elemental analyzer device.

Mass spectra were obtained using a Thermo Electron MAT 95-XP (EI) and an Agilent 1200/6210 Time-of-Flight LC-MS (ESI) device.

2 Structure elucidation and refinement

X-ray Structure Determination: X-ray quality crystals were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature. In special cases, low-temperature resistant oils were employed for a low-temperature set-up. The samples were cooled to 150(2) K during measurement if not stated otherwise. The data were collected on a STOE IPDS II diffractometer or a Bruker Apex II Duo diffractometer using MoK_α (λ = 0.71073 Å) or CuK_α radiation (λ = 1.54178 Å), respectively. The structures were solved by intrinsic phasing (SHELXT)[2] and refined by full matrix least squares procedures (SHELXL)[3] within the Olex2 platform.[4] Semi-empirical absorption corrections (multiscan and additional spherical absorption correction) were applied to the diffraction data recorded with the STOE device using the LANA application within the STOE X-AREA platform.[5] Semi-empirical absorption corrections (multiscan and additional spherical absorption correction) were applied to the diffraction data collected with the Bruker device using the SADABS application within the APEX II platform.[6] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model. All special refinement details for disordered structures, molecular structure representations as well as a compilation of standard crystallographic details are summarized down below.

Special Refinement Details:

1:Mes*: Two *t*Bu groups are rotationally disordered. Both have been refined independently with a single split position according to FVAR2 and FVAR3. The split positions of the *p*-*t*Bu group converged to occupancies of 0.79 and 0.21. The *o*-*t*Bu groups converged to occupancies of 0.60 and 0.40.

1:^{Mes}Ter: The whole P-S-P moiety appears disordered. To fix the disorderer, a split position for both P atoms and the S atom were occupied by reasonable occupancies of 0.5. SADI and SIMU restraints as well as EADP constraints were employed for both split positions. For both split positions, reasonable P-P, P-S and P-C atom distances were then successfully obtained upon refinement.

2:^{Dip}Ter: The whole P-Se-P moiety appears disordered around the center of inversion. To fix the disorderer, a split position for both P atoms and the S atom were occupied by reasonable occupancies of 0.5. To fix the disorder, soft SADI restraints were employed for the C-P bonds. For both split positions, reasonable P-P, P-S and P-C atom distances were then successfully obtained upon refinement.

(DipTerP)$_2$S$_{3-x}$O$_x$: After integrating and generating an electron density map within Olex2, it could be revealed that several atom positions are between and on-top of both P atoms (which are disordered by themselves) giving asymmetric, mixed S/O species. Crystallographically, it is in general possible to assign several compounds to be present. However, it is difficult to judge which compounds are indeed incorporated into the crystal lattice and thus we here solely rely on MS spectrometric investigations of the *bulk* crystalline sample. A refinement giving a general formula sum of $C_{74}H_{90}O_{0.64}P_2S_{2.2}$ let us obtain a reliability factor (R_1) of 4.65% and weighted reliability factor (wR_2) of 13.63% (all data) which indicates that the refined model might indeed suit the experimental data reasonably well. However, we want to emphasize that it is

questionable to solely rely on MS data (see Chapter 3.7) and a disordered structure model and thus it is in general questionable how far the determined atom distances are in fact reasonable. As there are too many variables which decline a clear assignment on which compounds are present in *this particular* crystal, we decided to not deposit the structure data to the CCDC. The removal of the center of inversion and employing *P*1 as a space group (with concomitant inversion twinning) did not solve the problem.

$(DipTerP)_2S_{3-x}O_x$ crystallizes as its toluene solvate. One out of of two toluene molecules was treated with the SQUEEZE implementation due to disorder.

Molecular Structure Representations: All molecular structure representations in the ESI as well as the main article have been prepared with the Diamond software package.[7] A mixed representation of ellipsoid plots as well as wires/sticks was chosen for clarity. All ellipsoids are represented at the 50% probability level.

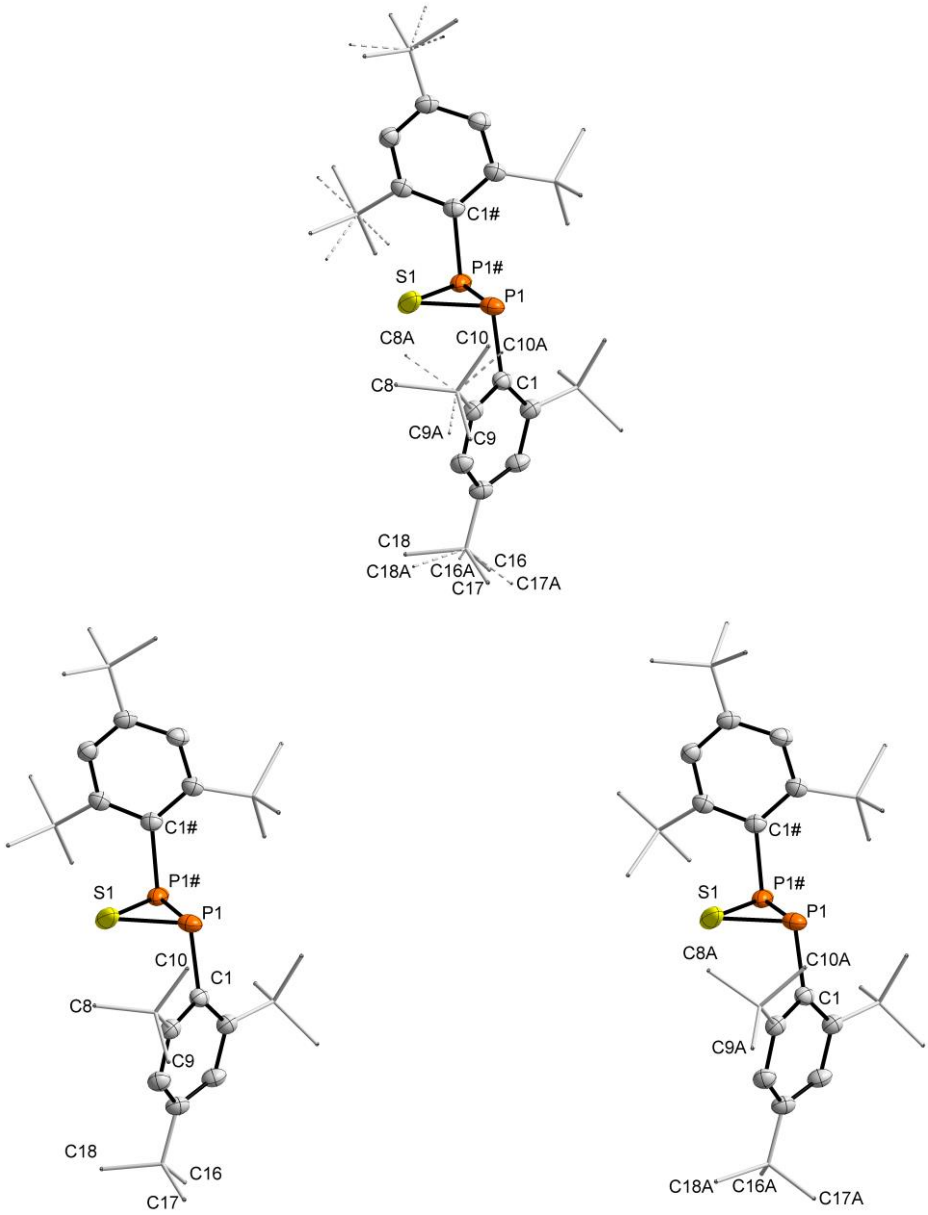


Figure S1: *Molecular structure of* ***1:Mes**** *in the crystal including disordered parts.* Selected bond lengths [pm] and angles [°] (main part): P1-P1# 223.42(8), C1-P1 188.33(18), P1-S1 211.45(10), P1-S1-P1# 63.783(22), S1-P1-P1# 58.108(20), C1-P1-S1 99.748(62), C1-P1-P1# 106.622(66). Atoms depicted with # are symmetry generated over 1-x, y, 3/2-z.

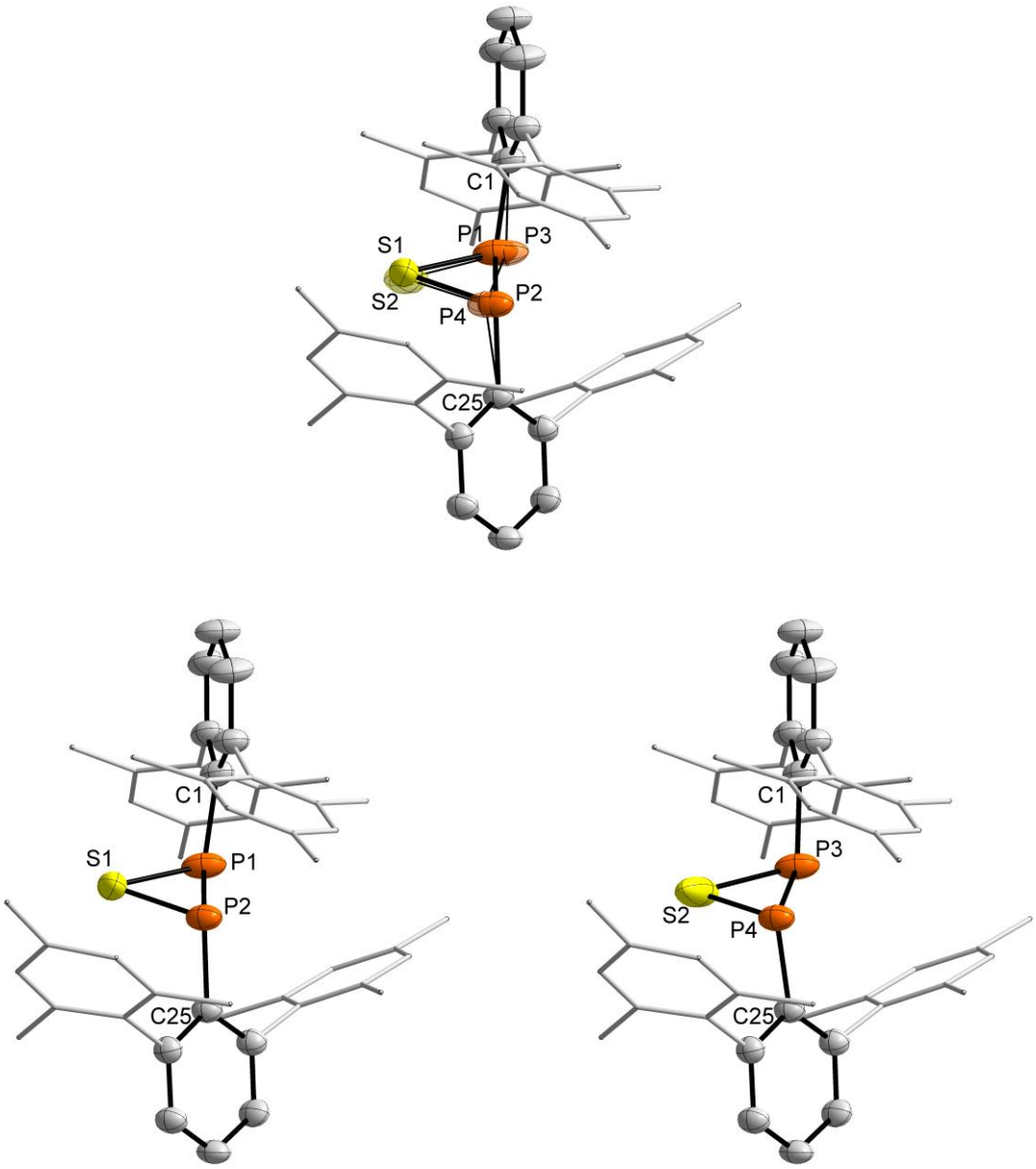


Figure S2: *Molecular structure of* ***1:^{Mes}Ter*** *in the crystal including disordered parts.* Selected bond lengths [pm] and angles [°] (main part): P1-P2 218.7(26), P1-S1 211.1(15), C1-P1 187.5(13), P2-S1 212.4(13), C25-P2 186.6(15), P1-S1-P2 62.17(52), S1-P1-P2 59.18(53), C1-P1-S1 101.72(57), C25-P2-P1 105.57(65), C25-P2-S1 102.80(63).

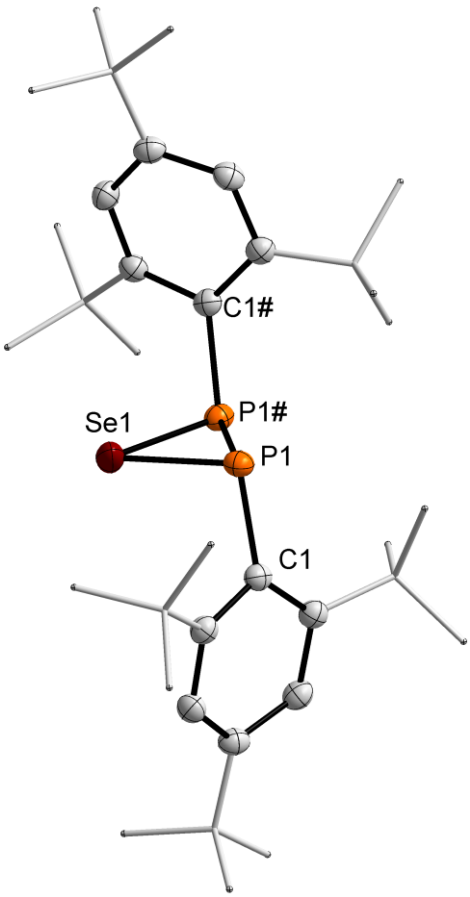


Figure S3: *Molecular structure of* ***2:Mes**** *in the crystal.* Selected bond lengths [pm] and angles [°] (main part): P1-P1# 225.02(8), C1-P1 188.12(18), P1-Se1 226.14(6), P1-Se1-P1# 59.673(17), Se1-P1-P1# 60.163(18), C1-P1-Se1 99.599(58), C1-P1-P1# 105.988(64). Atoms depicted with # are symmetry generated over 1-x, y, 3/2-z.

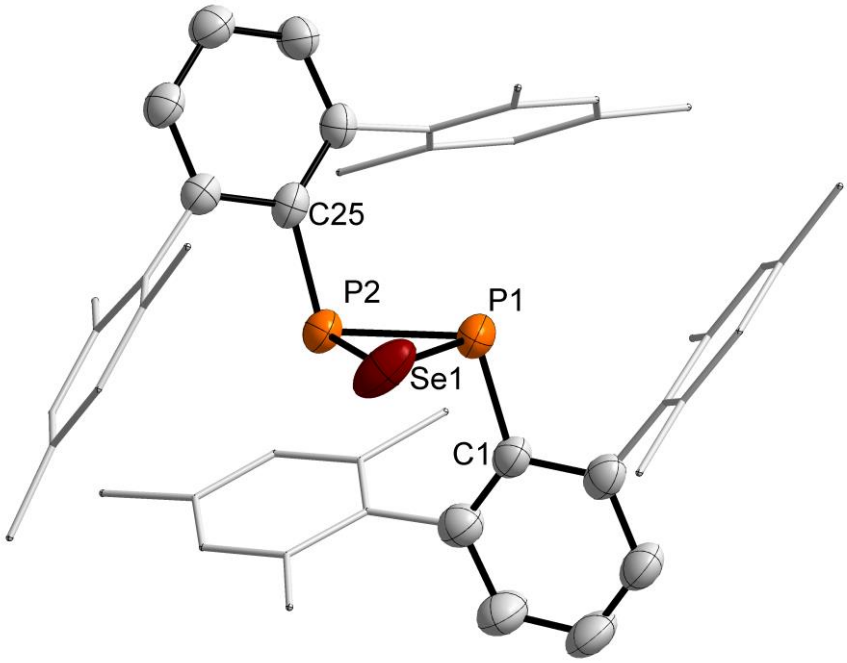


Figure S4: *Molecular structure of* ***2:^{Mes}Ter*** *in the crystal.* Selected bond lengths [pm] and angles [°]: P1-P2 219.85(17), P1-Se1 227.01(13), C1-P1 186.95(38), P2-Se1 227.05(10), C25-P2 186.33(37), P1-Se1-P2 57.919(41), Se1-P1-P2 61.050(42), C1-P1-Se1 100.79(11), C25-P2-P1 105.18(10), C25-P2-S1 102.47(10).

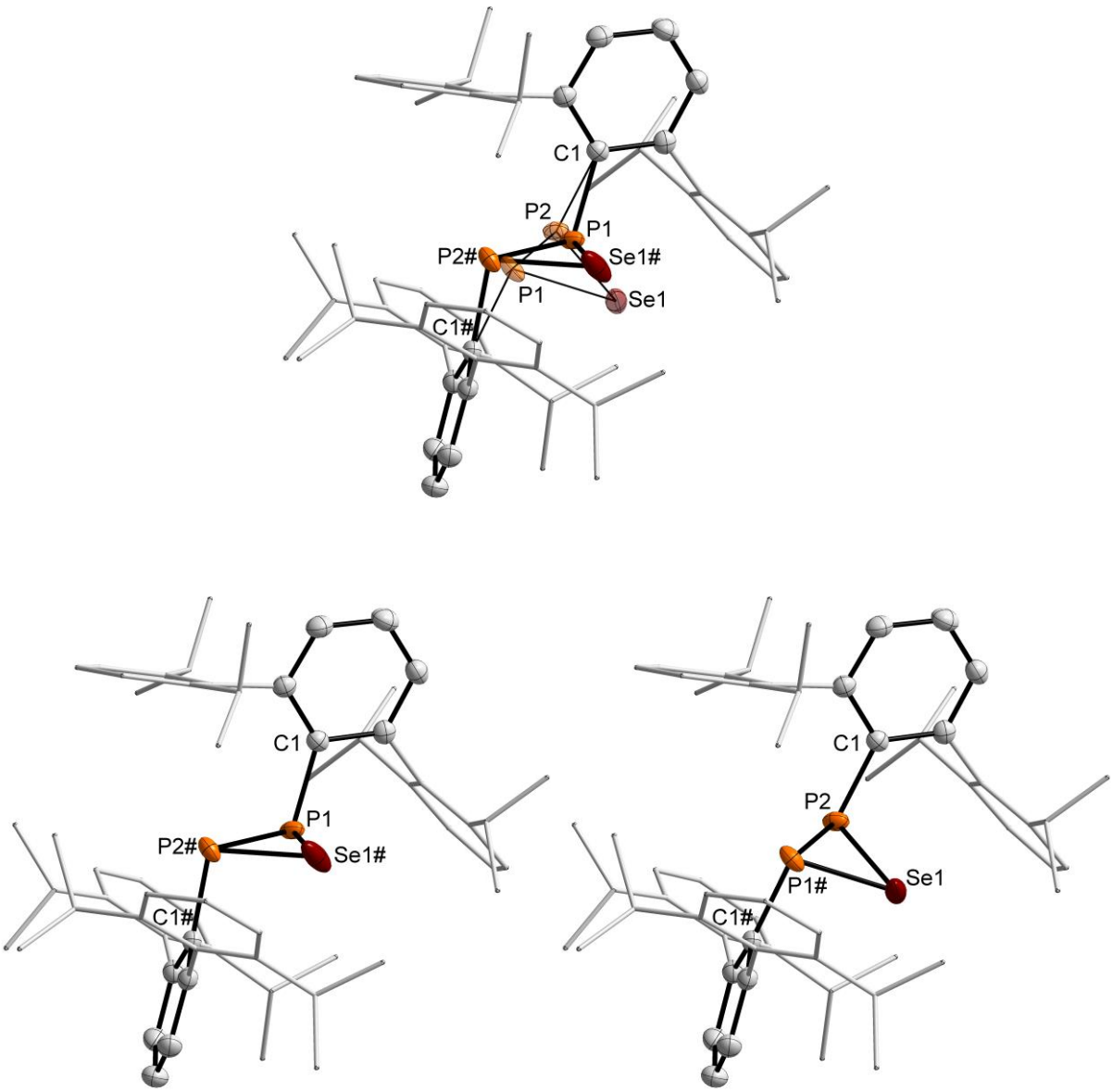


Figure S5: *Molecular structure of* ***2:^{Dip}Ter*** *in the crystal including disordered parts.* Selected bond lengths [pm] and angles [°] (main part): C1-P1 186.29(24), P1-P2# 223.30(25), P1-Se1# 226.26(19), P2#-Se1# 225.61(16), C1-P1-Se1# 95.867(82), C1-P1-P2# 109.226(93). Atoms depicted with # are symmetry generated over 1-x, y, 1/2-z.

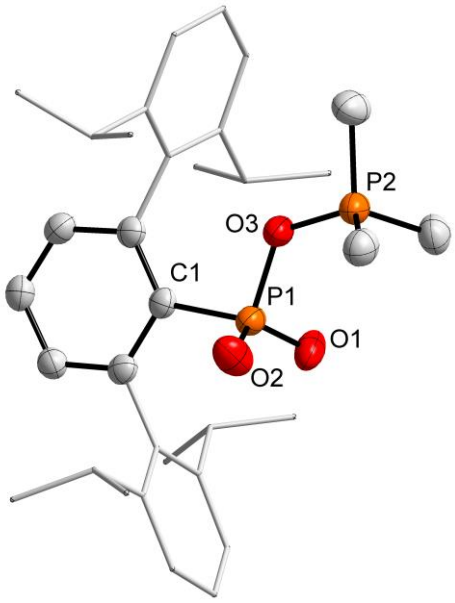


Figure S6: *Molecular structure of* ***4:^{Dip}Ter*** *in the crystal including disordered parts.* Selected bond lengths [pm] and angles [°] (main part): C1-P1 182.42(17), O1-P1 146.41(19), O2-P1 147.21(17), O3-P1 169.03(13), O2-P2 152.00(14), C1-P1-O3 101.33(8), P1-O3-P2 125.84(9).

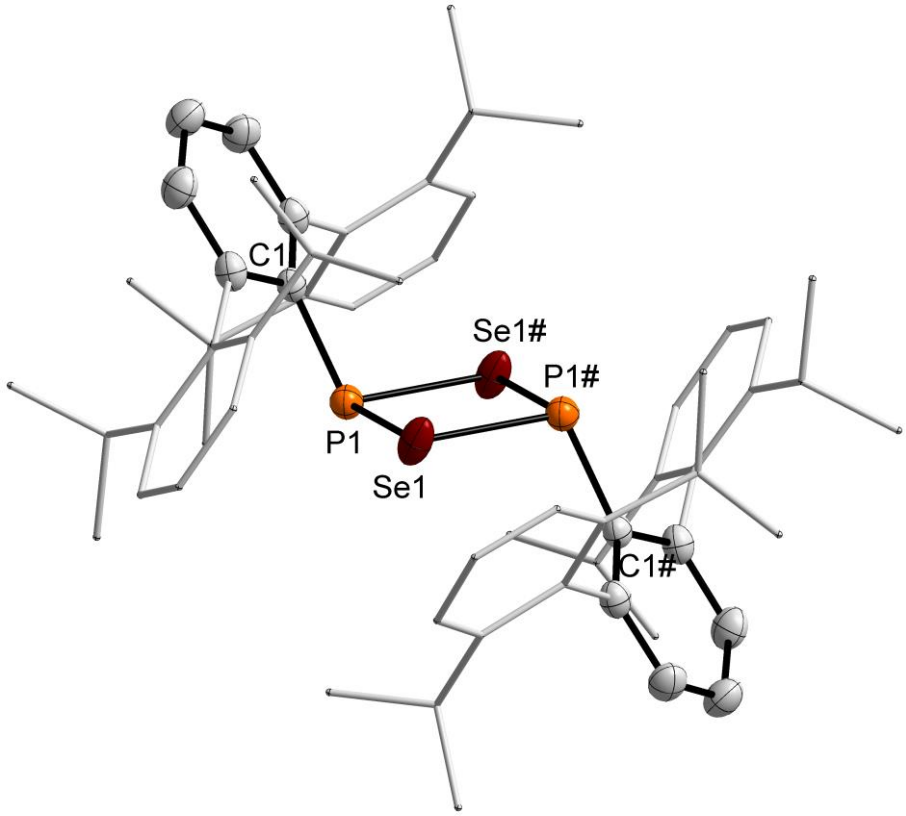


Figure S7: *Molecular structure of* ***3:^{Dip}Ter*** *in the crystal including disordered parts.* Selected bond lengths [pm] and angles [°] (main part): C1-P1 184.69(24), P1···P2 323.78(7), Se1···Se1# 321.42(4), P1-Se1 228.01(6), C1-P1-Se1 105.942(62).

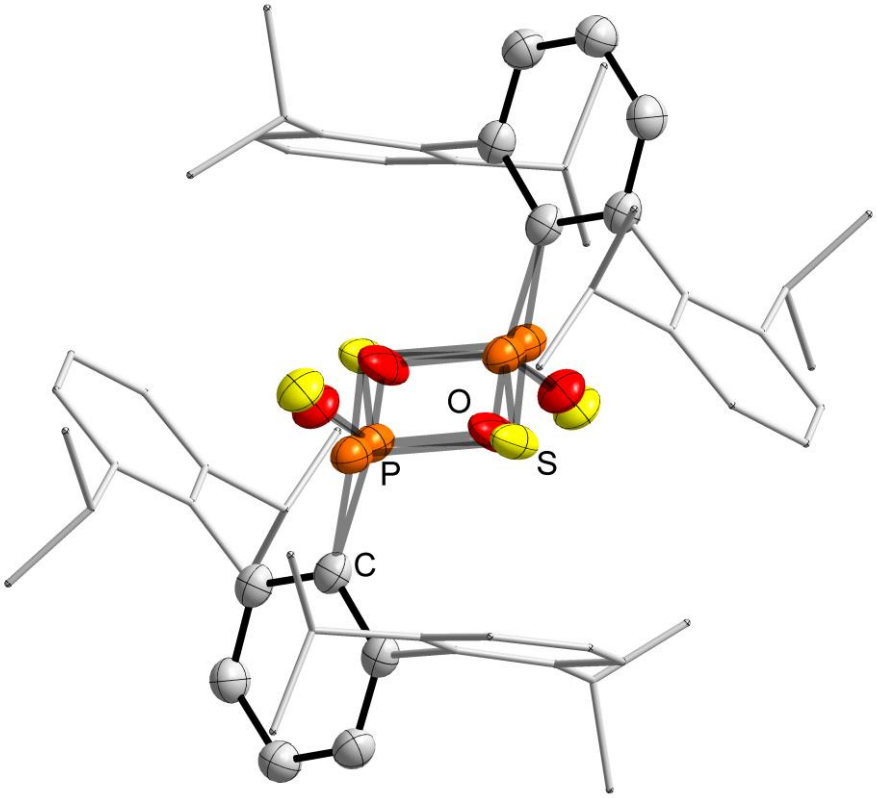


Figure S8: *Preliminary structure model of a compound following the general formula (^{Dip}TerP)$_2$S$_{3-x}$O$_x$ when considering disorder around the center of inversion.*

Summary of X-ray Crystallographic Refinement:

Table S2: Crystallographic details #1.

Compound	**1:Mes***	**1:^{Mes}Ter**
Empirical formula	$C_{36}H_{58}P_2S$	$C_{48}H_{50}P_2S$
Formula weight	584.82	720.88
Temperature/K	150(2)	150(2)
Crystal system	monoclinic	monoclinic
Space group	*C2/c*	$P2_1/n$
a/Å	18.4987(11)	12.9047(5)
b/Å	9.3637(6)	20.0414(8)
c/Å	20.6165(10)	16.3540(7)
α/°	90	90
β/°	102.173(4)	108.973(3)
γ/°	90	90
Volume/Å^3	3490.8(4)	3999.8(3)
Z	4	4
ρ_{calc}g/cm^3	1.113	1.197
μ/mm^{-1}	1.834	1.708
F(000)	1280	1536
Crystal size/mm^3	0.24 × 0.17 × 0.11	0.34 × 0.05 × 0.02
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.776 to 127.326	7.22 to 124.994
Index ranges	-21 ≤ h ≤ 19, -10 ≤ k ≤ 10, -23 ≤ l ≤ 23	-14 ≤ h ≤ 14, -23 ≤ k ≤ 22, -18 ≤ l ≤ 18
Reflections collected	7795	23543
Independent reflections	2763 [R_{int} = 0.0427, R_{sigma} = 0.0420]	6312 [R_{int} = 0.0726, R_{sigma} = 0.0619]
Data/restraints/parameters	2763/0/248	6312/39/487
Goodness-of-fit on F^2	1.027	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0428, wR_2 = 0.1033	R_1 = 0.0662, wR_2 = 0.1731
Final R indexes [all data]	R_1 = 0.0572, wR_2 = 0.1132	R_1 = 0.0968, wR_2 = 0.1940
Largest diff. peak/hole / e Å^{-3}	0.32/-0.54	0.78/-0.41
Absolute structure parameter	-	-
CCDC #	2174939	2174940

Table S3: Crystallographic details #2.

Compound	**2:Mes***	**2:^{Mes}Ter**	**2:^{Dip}Ter**·$3C_6H_6$
Empirical formula	$C_{36}H_{58}P_2Se$	$C_{48}H_{50}P_2Se$	$C_{78}H_{92}P_2Se$
Formula weight	631.72	767.78	1170.41
Temperature/K	150(2)	150(2)	150(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C2/c*	$P2_1/n$	*C2/c*
a/Å	18.976(2)	12.8943(14)	21.8358(15)
b/Å	9.1370(6)	20.007(3)	12.9906(9)
c/Å	20.677(2)	16.3852(19)	23.4455(16)
α/°	90	90	90
β/°	104.096(8)	108.913(8)	95.1150(10)
γ/°	90	90	90
Volume/Å^3	3477.1(6)	3998.9(8)	6624.1(8)
Z	4	4	4
ρ_{calc}g/cm^3	1.207	1.275	1.174
μ/mm^{-1}	1.194	1.052	0.657
F(000)	1352.0	1608.0	2496.0
Crystal size/mm^3	0.34 × 0.11 × 0.04	0.2 × 0.12 × 0.05	0.31 × 0.23 × 0.13
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2*Θ* range for data collection/°	4.062 to 58.408	3.324 to 50.996	3.488 to 57.412
Index ranges	-26 ≤ h ≤ 26, -11 ≤ k ≤ 12, -28 ≤ l ≤ 28	-15 ≤ h ≤ 15, -24 ≤ k ≤ 24, -19 ≤ l ≤ 19	-29 ≤ h ≤ 29, -17 ≤ k ≤ 17, -31 ≤ l ≤ 31
Reflections collected	29825	35099	48049
Independent reflections	4704 [R_{int} = 0.0793, R_{sigma} = 0.0590]	7449 [R_{int} = 0.1357, R_{sigma} = 0.1197]	8547 [R_{int} = 0.0434, R_{sigma} = 0.0381]
Data/restraints/parameters	4704/0/186	7449/0/472	8547/1/387
Goodness-of-fit on F^2	0.891	0.793	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0379, wR_2 = 0.0838	R_1 = 0.0484, wR_2 = 0.1014	R_1 = 0.0538, wR_2 = 0.1162
Final R indexes [all data]	R_1 = 0.0729, wR_2 = 0.0921	R_1 = 0.1220, wR_2 = 0.1136	R_1 = 0.0850, wR_2 = 0.1319
Largest diff. peak/hole / e Å^{-3}	0.55/-0.28	0.52/-0.52	0.97/-1.00
Absolute structure parameter	-	-	-
CCDC #	2174941	2174942	2174943

Table S4: Crystallographic details #3.

Compound	**3:^{Dip}Ter**·$3C_6H_6$	**4:^{Dip}Ter**·$3C_7H_8$	**(DipTerP)$_2$S$_{3-x}$O$_x$**·C_7H_8
Empirical formula	$C_{78}H_{92}P_2Se_2$	$C_{54}H_{70}O_3P_2$	$C_{74}H_{90}O_{0.64}P_2S_{2.2}$
Formula weight	1249.37	829.04	1122.17
Temperature/K	150(2)	150(2)	150(2)
Crystal system	triclinic	triclinic	triclinic
Space group	*P*-1	*P*-1	*P*-1
a/Å	10.6443(5)	13.3067(17)	12.0676(2)
b/Å	13.4424(5)	14.058(2)	13.0445(2)
c/Å	13.6754(6)	15.661(2)	13.1449(2)
α/°	75.973(2)	114.769(10)	98.1820(10)
β/°	71.929(2)	95.470(11)	106.0080(10)
γ/°	67.041(2)	108.119(11)	101.2670(10)
Volume/Å^3	1696.32(13)	2440.2(6)	1907.93(5)
Z	1	2	1
ρ_{calc}g/cm^3	1.223	1.128	0.977
μ/mm^{-1}	2.112	0.130	1,342
F(000)	658.0	896.0	604.0
Crystal size/mm^3	0.15 × 0.06 × 0.03	0.27 × 0.19 × 0.17	0.2 × 0.11 × 0.1
Radiation	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)
2*Θ* range for data collection/°	6.866 to 133.34	3.324 to 52.998	7.064 to 133.176
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -16 ≤ l ≤ 15	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19	-14 ≤ h ≤ 14, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections collected	20466	24209	27310
Independent reflections	5891 [R_{int} = 0.0349, R_{sigma} = 0.0329]	10109 [R_{int} = 0.0359, R_{sigma} = 0.0601]	6739 [R_{int} = 0.0282, R_{sigma} = 0.0227]
Data/restraints/parameters	5891/0/378	10109/0/546	6739/6/3911.042
Goodness-of-fit on F^2	1.052	0.890	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0343, wR_2 = 0.0868	R_1 = 0.0436, wR_2 = 0.0972	R_1 = 0.0465, wR_2 = 0.1316
Final R indexes [all data]	R_1 = 0.0393, wR_2 = 0.0905	R_1 = 0.0866, wR_2 = 0.1062	R_1 = 0.0505, wR_2 = 0.1363
Largest diff. peak/hole / e Å^{-3}	0.62/-0.50	0.31/-0.22	0.53/-0.25
Absolute structure parameter	-	-	-
CCDC #	2174945	2174944	*not deposited*

3 Syntheses of compounds

Additional Information. All starting materials synthesized by literature procedures (see table S1) were synthesized with slight modifications. All analytical data was in good agreement with those published in earlier works. In this work, the following abbreviations are used for the organic framework around P.

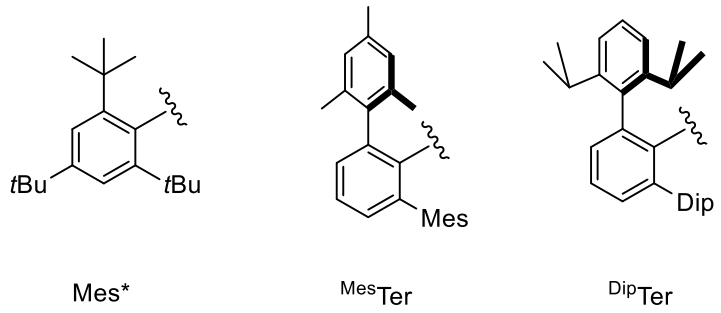


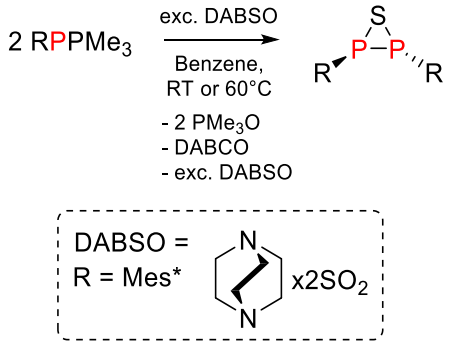
Figure S9: *Structural motifs and their abbreviations relevant for this ESI.*

As the phospha-Wittig reagents are sensitive towards light, we recommend wrapping all flasks with tinfoil and switching off the lights in the laboratory and fume hoods. Especially the ^{Mes}Ter derivative is experienced to decompose quickly due to light sensitivity. The provided NMR spectra were processed and analyzed with the MestReNova[8] software package. Resonances are depicted with the following abbreviations: s, singlet; d, doublet; t, triplet; hept, septet; m, multiplet; ps, pseudo; br, broad. IR spectra were processed and analysed using either the OPUS[9] and/or the OMNIC[10] software package. Isotope patterns of MS spectra were partially compared with calculated ones from enviPat[11].

Important Note: Currently we are unable to obtain suitable CHN values. The deviations are currently in between 3 to 5% for both C and H values. Even though in very rare cases suitable values could be observed, we refuse to provide these because in our eyes there is no evidence beyond a reasonable doubt that the material is pure at the point of measurement. However, the state-of-the-art characterization such as

with NMR spectroscopy (see displayed spectra) demonstrates the existence and analytical pureness of the herein published compounds if not stated otherwise. We are aware that elemental analysis is an important purity control, but reliable results were not obtained. As CHN analysis is unfortunately already prone to manipulations (see ref.[12]) we decided to not provide any values and provide high-resolution mass spectrometry data for all compounds.

3.1 $(Mes^*P)_2S$ (1:Mes*)



A 0.200 g portion of Mes^*PPMe_3 (0.57 mmol, 1.0 eq) together with 0.068 g DABSO (0.28 mmol, 0.5 eq [= 1.0 eq of SO_2]) are dissolved in 4 mL of benzene. The brown solution is stirred for 2 hours at ambient temperature under exclusion of light. Then, the solution is stirred at 60°C overnight. The solvent is removed under reduced pressure and 5 mL of MeCN are added which is subsequently layered with 15 mL of *n*-hexane. The obtained solution is then vigorously stirred stirred for another 10 min. followed by separating the hexane-phase from the MeCN phase. Removing *n*-hexane under reduced pressure gives **1:Mes*** as a slight beige powder (63%, 0.18 mmol, 0.105 g). Platelet-shaped single crystals suitable for X-ray diffraction are obtained from a saturated MeCN/benzene solution at 6°C.

^{1}H NMR (C_6D_6, 300 MHz, 298K): δ = 7.31 (s, 2H, Ar*H*), 1.71 (s, 36H, o-CH_3), 1.19 (s, 18H, p-CH_3). **^{13}C{^{1}H} NMR** (C_6D_6, 75.5 MHz, 298K): δ = 156.6 (^{ps}t, ArC_q), 149.2 (s, ArC_q), 136.6 (^{ps}t, ArC_{ipso}), 123.3 (s, Ar*C*H), 39.2 (s, *p*-*C*$(CH_3)_3$), [34.8, 34.7, 34.6, 34.4] (s, *o*-*C*$(CH_3)_3$ + *o*-C(*C*$H_3)_3$), 31.3 (s, *p*-C(*C*$H_3)_3$) ppm. **^{31}P{^{1}H} NMR** (C_6D_6, 122 MHz, 298K): δ = -66.01 (s, *P*(S)*P*) ppm. **IR** (ATR, cm^{-1}): 2960 (vs), 2903 (s), 2864 (s), 1589 (s), 1519 (w), 1468 (s), 1391 (s), 1361 (vs), 1292 (w), 1238 (s), 1211 (m), 1193 (m), 1122 (s), 1058 (w), 1025 (w), 922 (w), 897 (w), 874 (vs), 849 (w), 804 (m), 772 (w), 743 (vs), 675 (w), 646 (m), 624 (w), 580 (m), 556 (m), 532 (w), 487 (m), 453 (w), 433 (w), 412 (m). **MS** (HR, ESI$^+$) calc. for $C_{36}H_{59}P_2S$ $[M+H]^+$ (found): 585.3818 (585.3817).

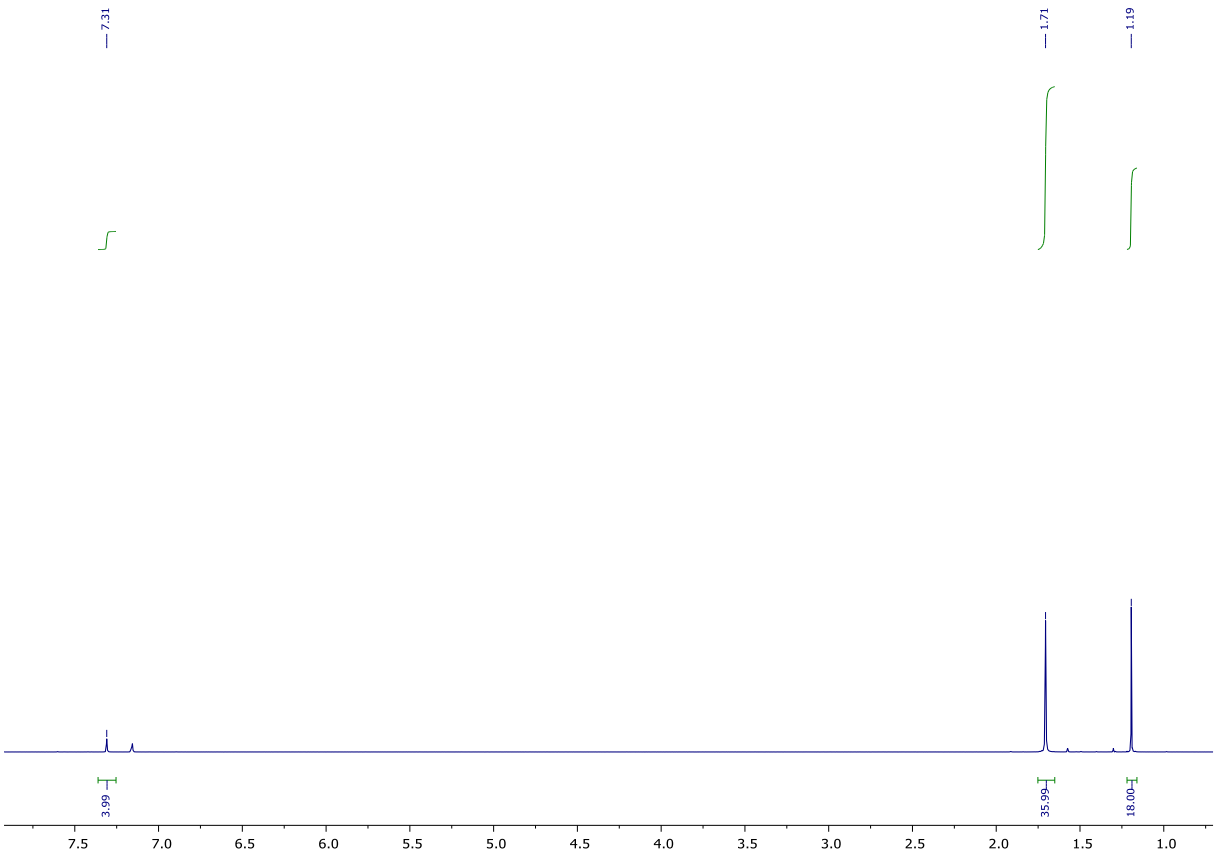


Figure S10: *^{1}H NMR of* ***1:Mes**** (given in ppm, C_6D_6, 300 MHz, 298K).

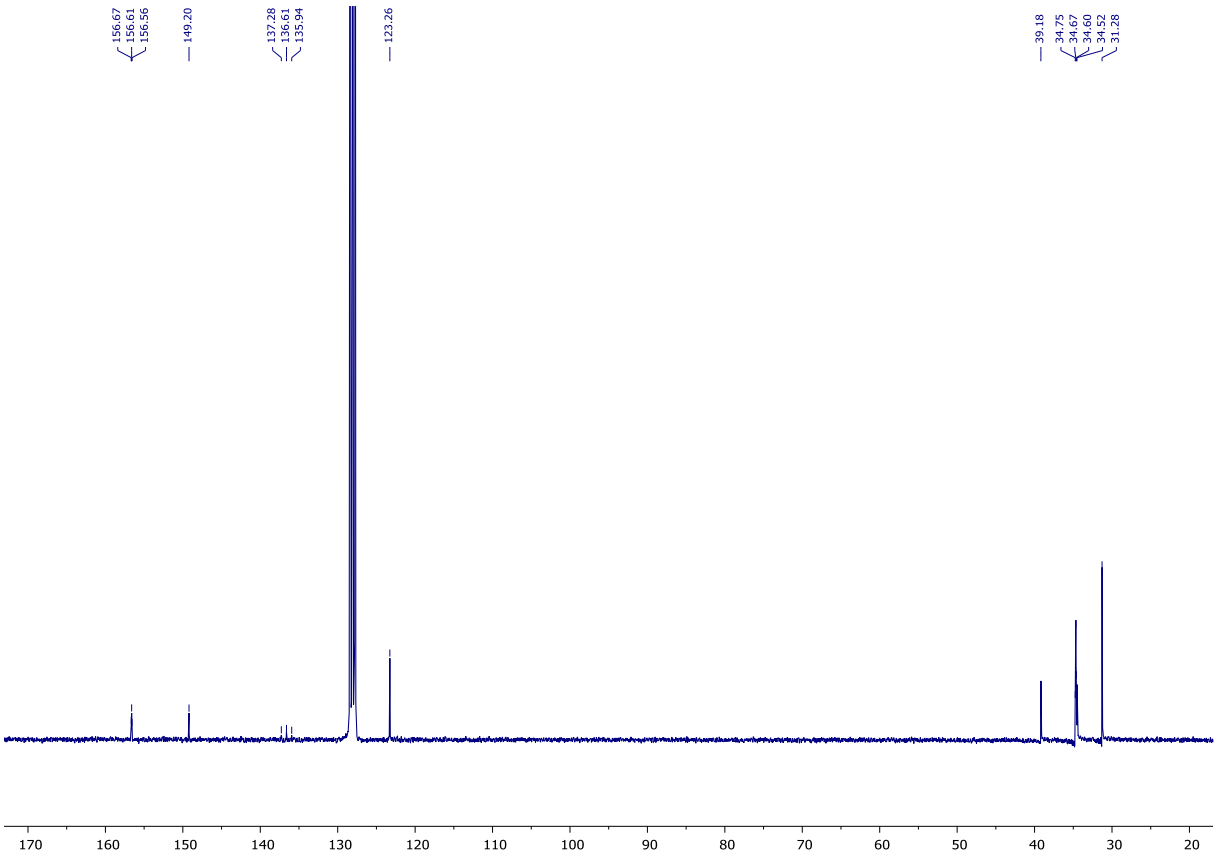


Figure S11: *$^{13}C\{^{1}H\}$ NMR of* ***1:Mes**** (given in ppm, C_6D_6, 75.5 MHz, 298K).

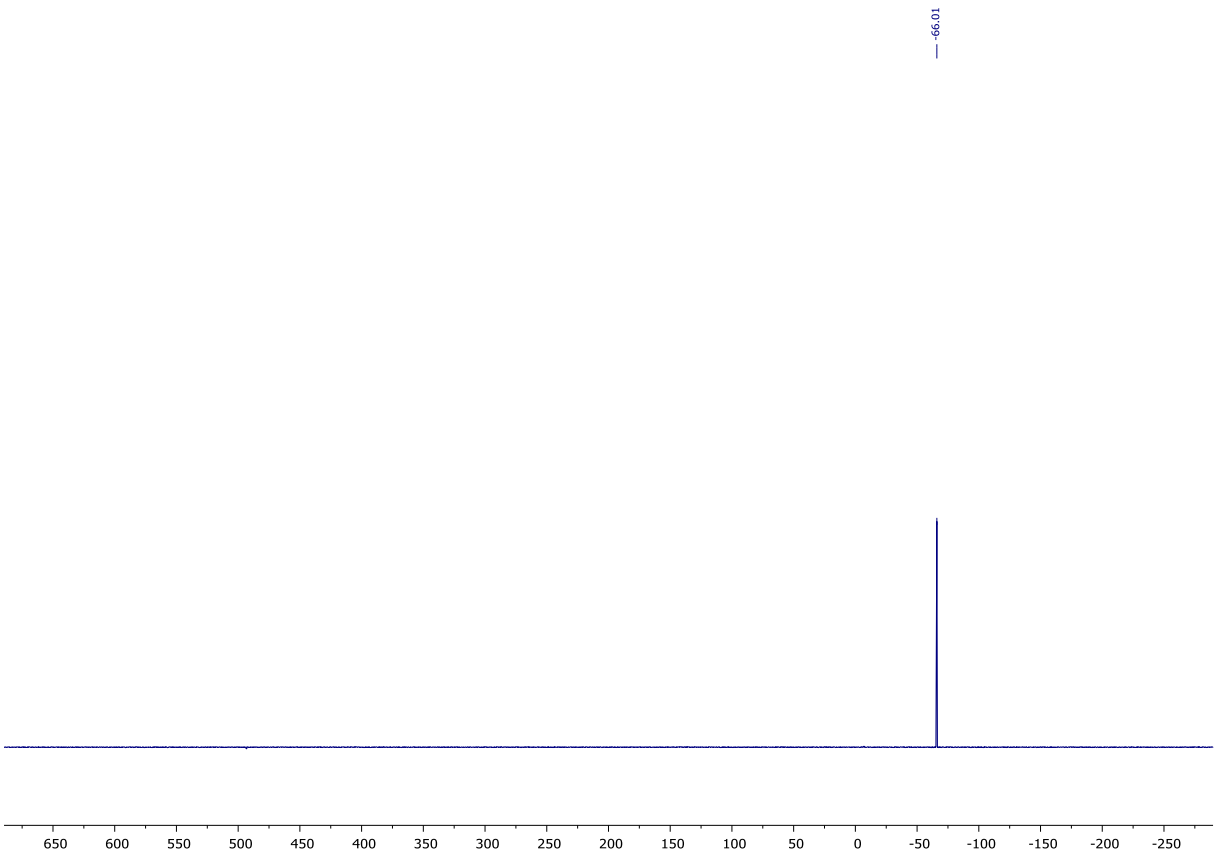


Figure S12: *$^{31}P\{^{1}H\}$ NMR of* ***1:Mes**** (given in ppm, C_6D_6, 122 MHz, 298K).

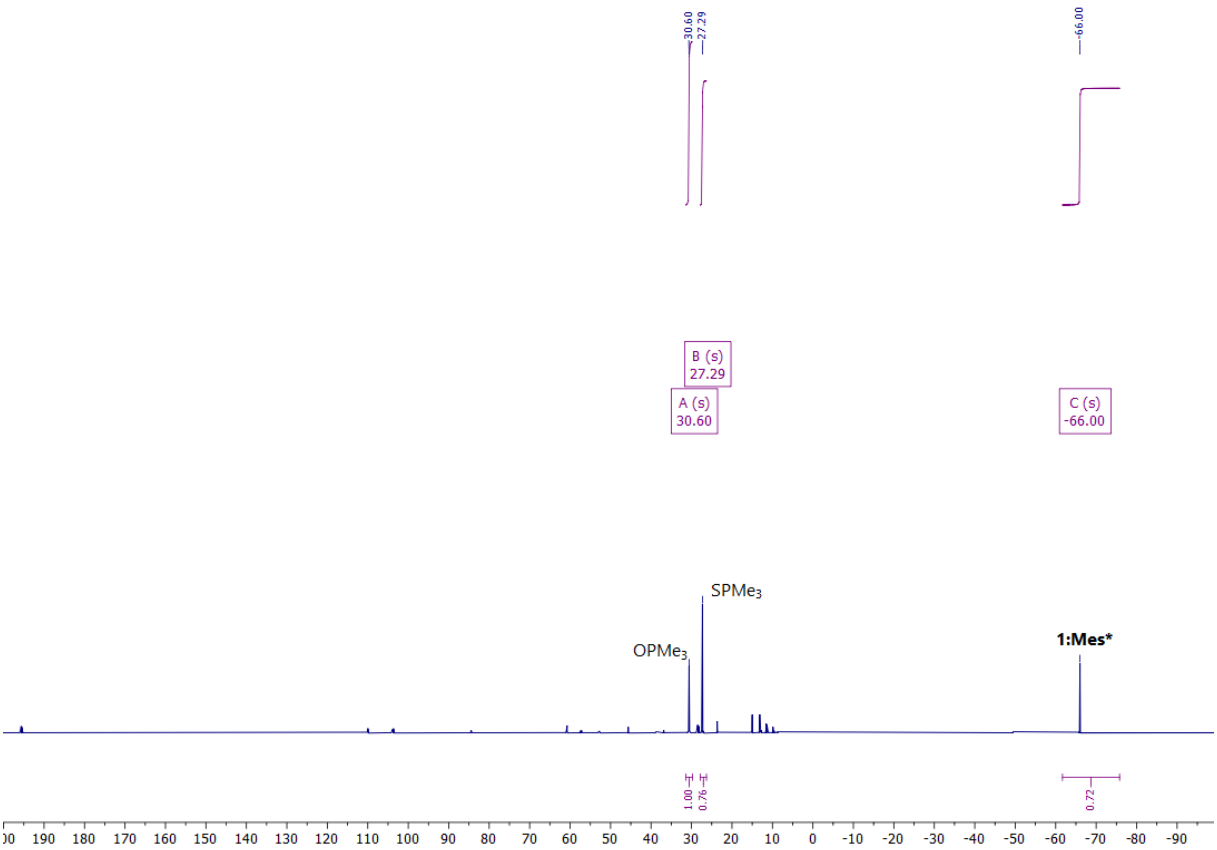


Figure S13: *$^{31}P\{^{1}H\}$ NMR of the crude reaction mixture of* ***1:Mes**** (given in ppm, C_6D_6, 122 MHz, 298K).

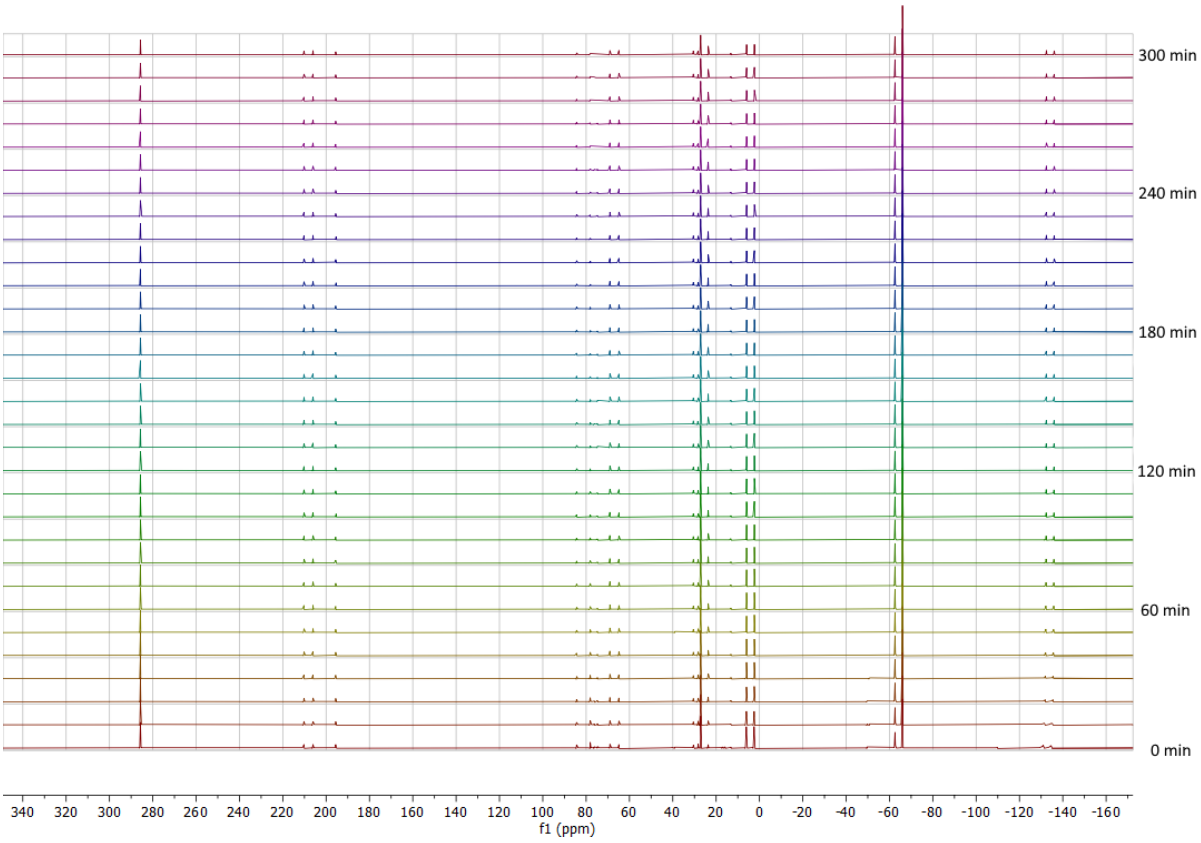


Figure S14: *$^{31}P\{^{1}H\}$ NMR spectra of the reaction mixture of Mes*P(PMe$_3$) with 0.5 eq DABSO over a period of 5 h in increments of 10 minutes at room temperature* (given in ppm, C_6D_6, 162 MHz, 298K).

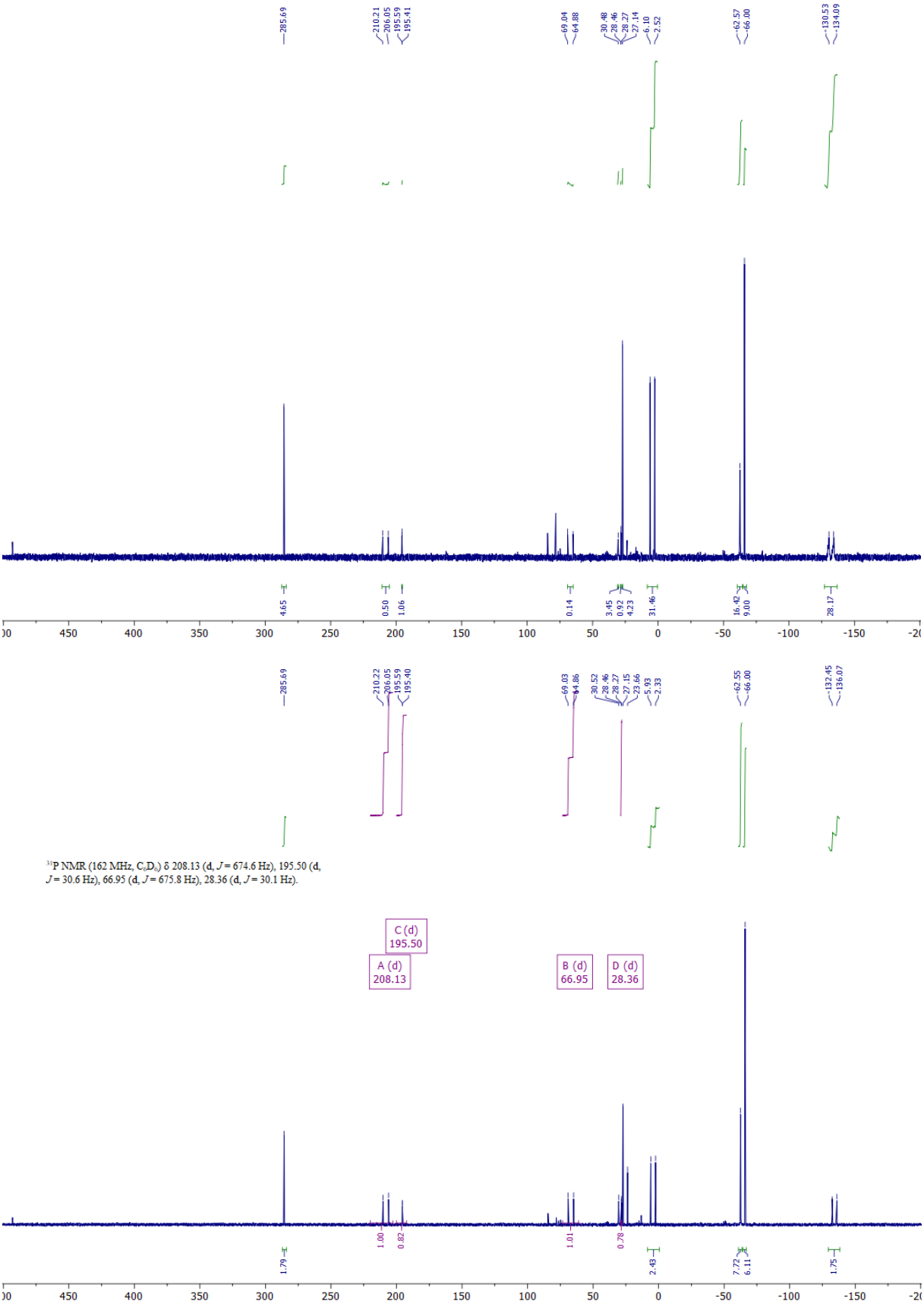
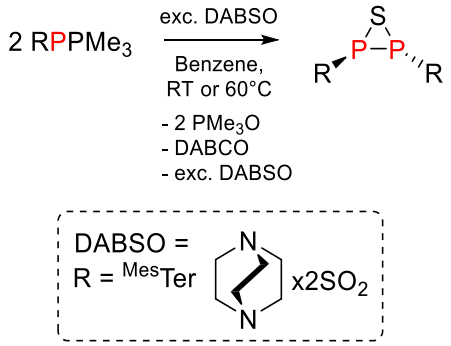


Figure S15: : *$^{31}P\{^1H\}$ NMR spectra of the reaction mixture of Mes*P(PMe$_3$) with 0.5 eq DABSO at room temperature at 0 min (top) and 300 min (bottom)* (given in ppm, C_6D_6, 162 MHz, 298K).

3.2 (^{Mes}TerP)$_2$S (1:^{Mes}Ter)



A 0.200 g portion of ^{Mes}TerPPMe$_3$ (0.57 mmol, 1.0 eq) together with 0.057 g DABSO (0.24 mmol, 0.5 eq [= 1.0 eq of SO_2]) are dissolved in 4 mL of benzene. The brown solution is stirred for 3 hours at ambient temperature under exclusion of light. Then, the solution is stirred at 60°C overnight. The solvent is removed under reduced pressure and 5 mL of MeCN are added which is subsequently layered with 10 mL of *n*-hexane. The obtained solution is then vigorously stirred for another 10 min. followed by separating the *n*-hexane-phase from the MeCN phase. The procedure is repeated with 4 portions of 10 mL of *n*-hexane. Combined *n*-hexane phases are then freed of the solvent to yield **1:^{Mes}Ter** as a slight colorless powder (35%, 0.08 mmol, 0.060 g). Single crystals suitable for X-ray diffraction are obtained from a hot MeCN solution which is slowly cooled to ambient temperature.

^{1}H NMR (C_6D_6, 300 MHz, 298K): δ = 6.95 – 6.91 (m, 3H, Ar*H*), 6.94 (^{br}s, 2H, Ar*H*), [6.67, 6.64] (^{br}s, 2H, *m*-Ar*H*), 2.28 (s, 6H, C*H*$_3$ of Mes), 1.98 (s, 6H, C*H*$_3$ of Mes), 1.93 (s, 6H, C*H*$_3$ of Mes) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 75.5 MHz, 298K): δ =146.6 (^{ps}t, ArC_q)**, 139.0 (^{ps}t, ArC_q)**, 137.9 (ArC_{ipso})***, 136.9 (s, Ar*C*), 136.7 (^{ps}t, ArC_q)**, 136.6 (^{ps}t, ArC_q)**, 129.4 (s, Ar*C*), 129.2 (s, Ar*C*), 128.9 (s, Ar*C*), 128.8 (s, Ar*C*), [21.8, 21.7, 21.6, 21.4] (s, *C*H$_3$ of Mes)* ppm. * Chemically inequivalent CH_3 groups of Mes: two CH_3 groups each have an equal chemical shift which makes a total of six C atoms. ** These pseudo triplets indicate chemically, but not magnetically equivalent C atoms. Assignment should be interpreted for two C atoms. ***Assignment with ^{1}H/^{13}C HMBC spectrum. ***Note:*** Due to the inequivalence of the C atoms as well as partial assignment to multiple C atoms, an

ambiguous number of resonances is observed. **$^{31}P\{^{1}H\}$ NMR** (C_6D_6, 162 MHz, 298K): δ = -112.53 (s, *P*(S)*P*) ppm. **IR** (ATR, cm^{-1}): 2912 (m), 2852 (s), 2729 (m), 1611 (m), 1557 (w), 1481 (w), 1442 (s), 1373 (m), 1260 (m), 1179 (w), 1107 (m), 1053 (w), 1029 (m), 877 (w), 845 (vs), 804 (vs), 778 (m), 747 (m), 718 (m), 591 (m), 576 (w), 561 (m), 548 (m), 513 (w), 495 (w), 438 (m), 411 (s). **MS** (HR, ESI^+) calc. for $C_{48}H_{51}P_2S$ $[M+H]^+$ (found): 721.3187 (721.3188).

Figure S16: *^{1}H NMR of* ***1:^{Mes}Ter*** (given in ppm, C_6D_6, 300 MHz, 298K).

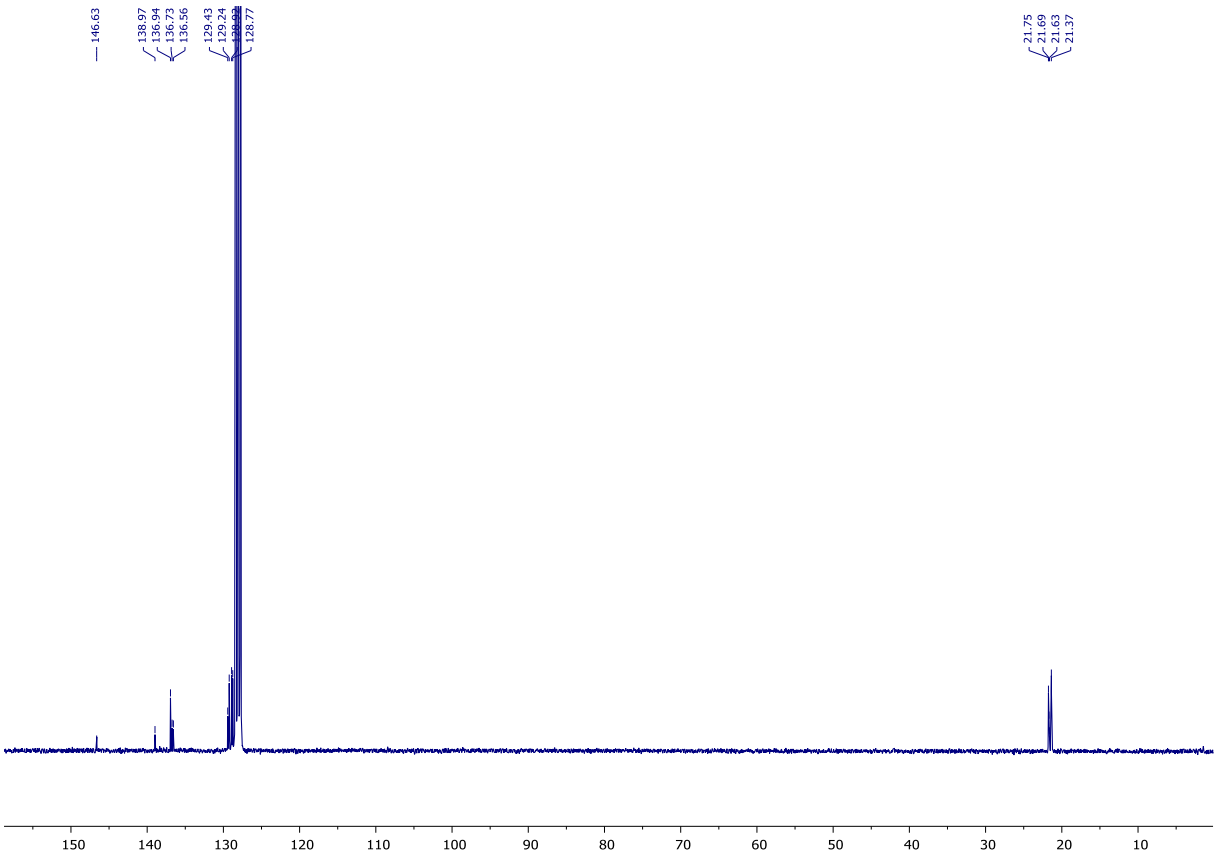


Figure S17: *$^{13}C\{^{1}H\}$ NMR of* ***1:^{Mes}Ter*** (given in ppm, C_6D_6, 75.5 MHz, 298K).

Figure S18: *$^{31}P\{^{1}H\}$ NMR of* ***1:^{Mes}Ter*** (given in ppm, C_6D_6, 122 MHz, 298K).

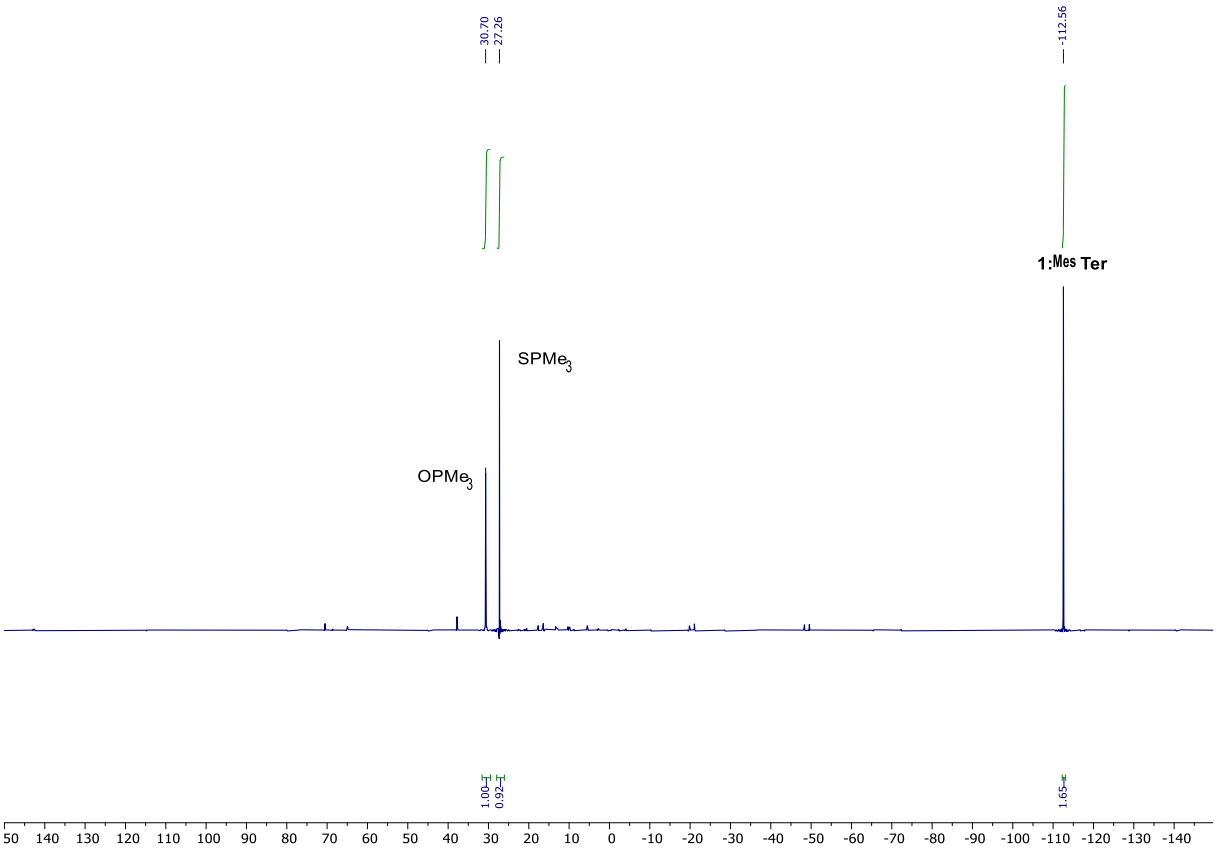
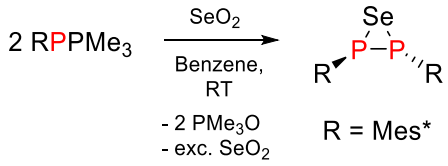


Figure S19: *$^{31}P\{^{1}H\}$ NMR of the reaction mixture containing* ***1:^{Mes}Ter*** (given in ppm, C_6D_6, 122 MHz, 298K).

3.3 $(Mes^*P)_2Se$ (2:Mes*)



A 0.200 g portion of Mes^*PPMe_3 (0.57 mmol, 1.0 eq) together with 0.063 g SeO_2 (0.57 mmol) are dissolved in 4 mL of benzene. The yellow solution is stirred at ambient temperature overnight under strict exclusion of light. The solvent is removed under reduced pressure and 5 mL of MeCN are added which is subsequently layered with 15 mL of *n*-hexane. The obtained solution is then vigorously stirred for another 10 min. followed by separating the *n*-hexane phase from the MeCN phase. Removing *n*-hexane under reduced pressure gives **2:Mes*** as a colorless powder (58%, 0.17 mmol, 0.104 g). Single crystals suitable for X-ray diffraction are obtained from a saturated benzene solution at 6°C as colorless needles.

Note: At elevated temperatures, concomitant formation of Mes*P(Se)Se can occur. Strict exclusion of light and an ambient reaction temperature are recommended.

^{1}H NMR (C_6D_6, 400 MHz, 298K): δ = 7.29 (s, 2H, Ar*H*), 1.68 (s, 36H, o-CH_3), 1.21 (s, 18H, p-CH_3).**^{13}C{^{1}H} NMR** (C_6D_6, 100 MHz, 298K): δ =157.5 (^{ps}t, ArC_q)*, 149.6 (s, ArC_q), 134.1 (^{ps}t, ArC_{ipso}), 123.2 (s, ArCH), 39.3 (s, *p*-*C*$(CH_3)_3$), [34.7, 34.7, 34.6, 34.5] (s, *o*-*C*$(CH_3)_3$ + *o*-C(*C*$H_3)_3$), 31.3 (s, *p*-C(*C*$H_3)_3$) ppm. **^{31}P{^{1}H} NMR** (C_6D_6, 162 MHz, 298K): δ = -49.12 (s, *P*(Se)*P*) ppm. **^{77}Se{^{1}H} NMR** (C_6D_6, 57 MHz, 298K): 43.1 (t, $^1J_{PSe}$ = 138.6 Hz, P(*Se*)P) ppm. **IR** (ATR, cm^{-1}): 2961 (s), 2902 (m), 2864 (m), 1587 (m), 1518 (w), 1466 (m), 1391 (s), 1361 (s), 1240 (m), 1210 (m), 1192 (w), 1122 (m), 1026 (w), 927 (w), 896 (w), 874 (s), 804 (w), 742 (s), 714 (vw), 645 (w), 580 (m), 497 (m), 487 (m), 411 (w). **MS** (HR, ESI^+) calc. for $C_{36}H_{59}P_2Se$ $[M+H]^+$ (found): 629.3285 (629.3283).

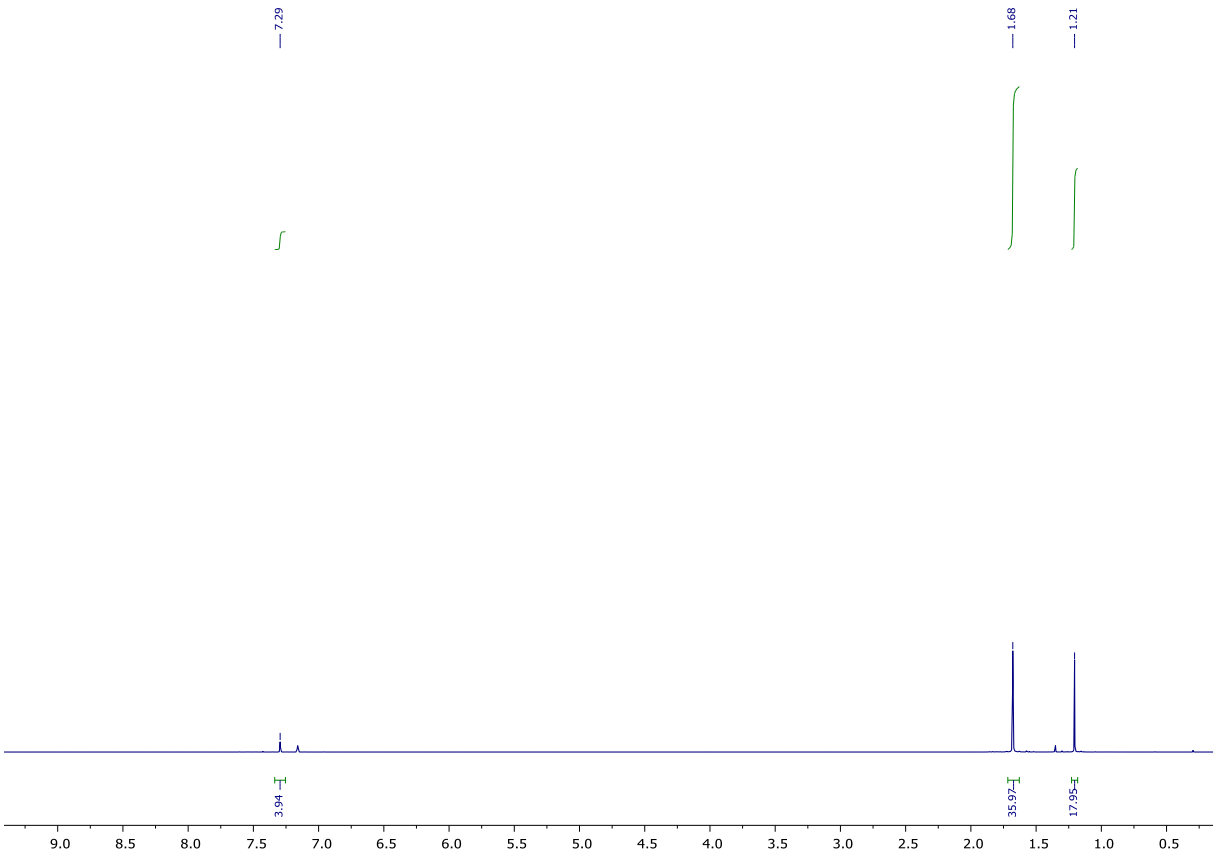


Figure S20: *^{1}H NMR of* ***2:Mes**** (given in ppm, C_6D_6, 300 MHz, 298K).

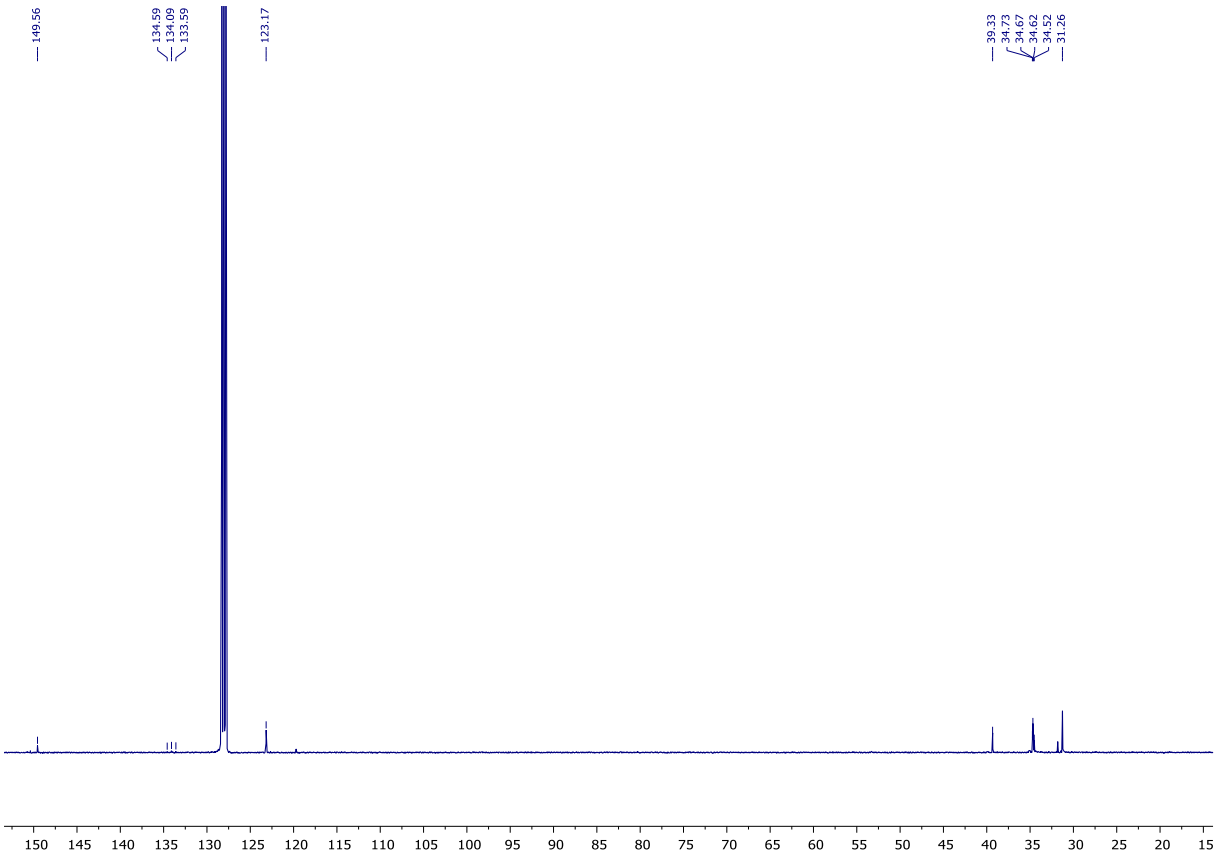


Figure S21: *$^{13}C\{^{1}H\}$ NMR of* ***2:Mes**** (given in ppm, C_6D_6, 75.5 MHz, 298K).

Figure S22: *$^{31}P\{^{1}H\}$ NMR of* ***2:Mes**** (given in ppm, C_6D_6, 162 MHz, 298K).

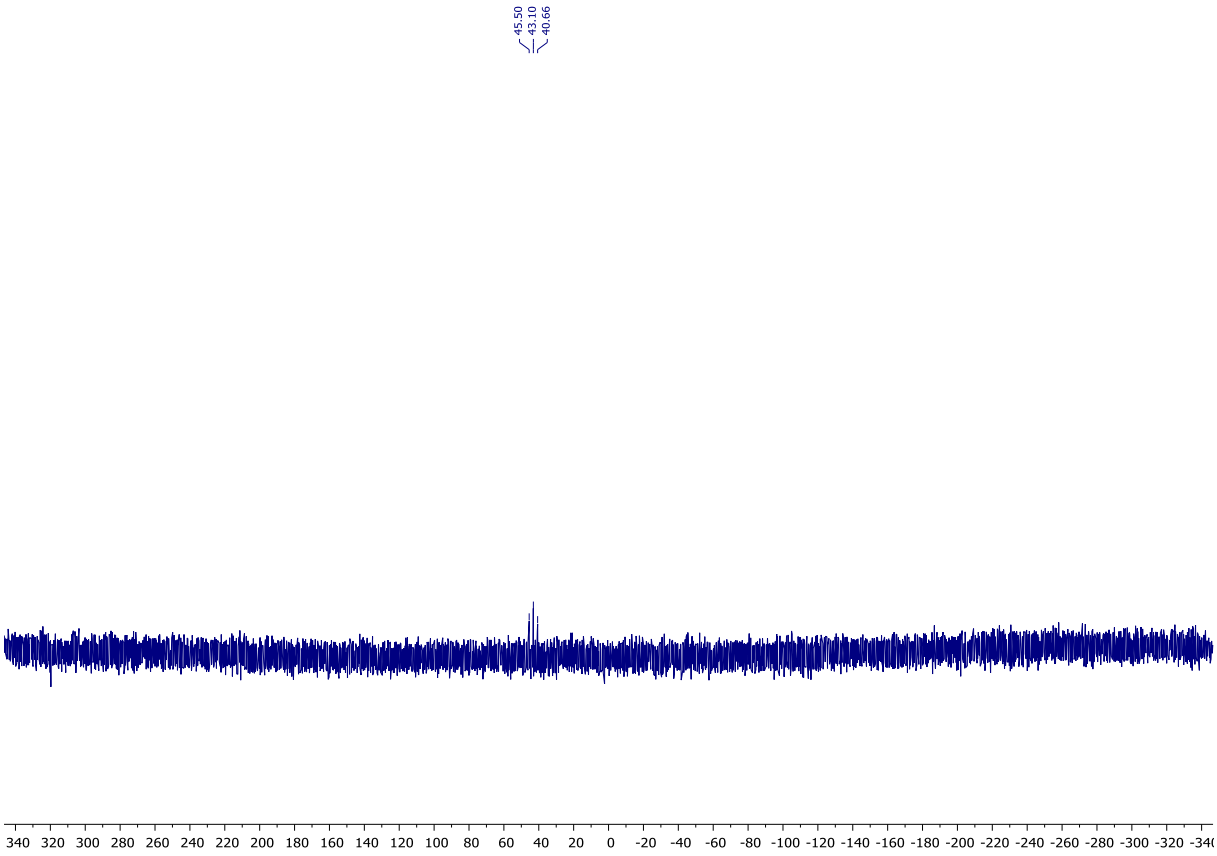


Figure S23: *$^{77}Se\{^{1}H\}$ NMR of* ***2:Mes**** (given in ppm, C_6D_6, 57 MHz, 298K).

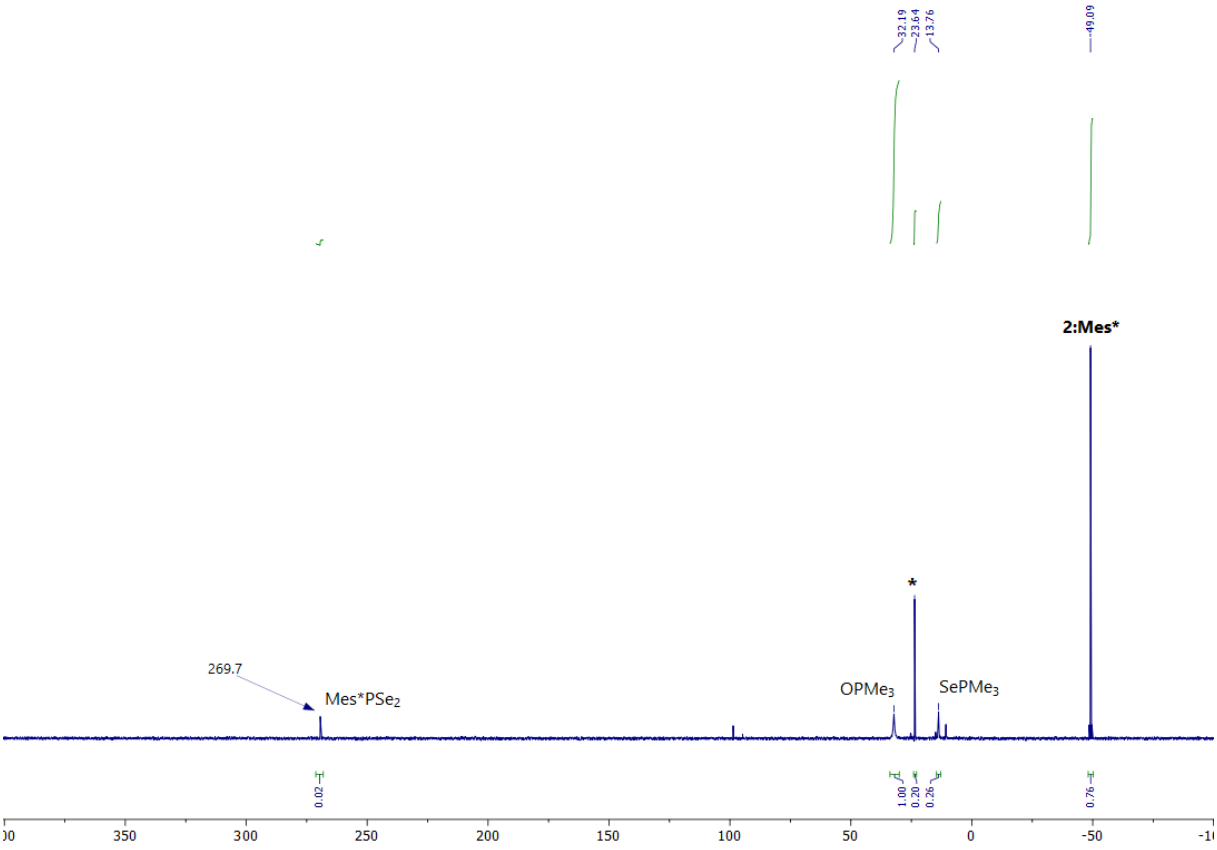
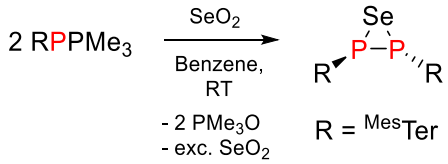


Figure S24: *$^{31}P\{^{1}H\}$ NMR of the crude reaction mixture of* ***2:Mes**** (given in ppm, C_6D_6, 122 MHz, 298K). * unidentified side-product.

3.4 (^{Mes}TerP)$_2$Se (2:^{Mes}Ter)



A 0.200 g portion of ^{Mes}TerPPMe$_3$ (0.57 mmol, 1.0 eq) together with 0.052 g SeO_2 (0.24 mmol) are dissolved in 4 mL of benzene. The yellow solution is stirred at ambient temperature overnight under strict exclusion of light. The solvent is removed under reduced pressure and 5 mL of MeCN are added which is subsequently layered with 10 mL of *n*-hexane. The obtained solution is then vigorously stirred for another 10 min. followed by separating the hexane-phase from the MeCN phase. The procedure is repeated with 4 portions of 10 mL of *n*-hexane. Combined *n*-hexane phases are then freed of the solvent to yield **2:^{Mes}Ter** as a slight yellow powder (44%, 0.13 mmol, 0.080 g). Single crystals suitable for X-ray diffraction are obtained from a saturated benzene solution at 6°C.

^{1}H NMR (C_6D_6, 300 MHz, 298K): δ = [6.96 – 6.94, 6.92 – 6.98, 6.87 – 6.86] (m, 5H, Ar*H*), [6.67, 6.86] (^{br}s, 2H, *m*-Ar*H*), 2.28 (s, 6H, C*H*$_3$ of Mes), 2.00 (s, 6H, C*H*$_3$ of Mes), 1.91 (s, 6H, C*H*$_3$ of Mes) ppm. **^{13}C{^{1}H} NMR** (C_6D_6, 75.5 MHz, 298K): δ =146.4 (^{ps}*t*, Ar*C*$_q$)**, 139.2 (^{ps}*t*, Ar*C*$_q$)**, 138.4 (^{ps}t, Ar*C*$_{ipso}$)**, 136.9 (^{ps}t, Ar*C*$_q$)**, 136.4 (^{ps}t, Ar*C*$_q$)**, 129.3 (s, Ar*C*), 129.2 (s, Ar*C*), 129.0 (s, Ar*C*), 128.8 (s, Ar*C*), [21.9, 21.8, 21.7, 21.6, 21.4] (s, *C*H$_3$ of Mes)* ppm. * Chemically inequivalent CH_3 groups of Mes: two CH_3 groups have an equal chemical shift which makes a total of six C atoms. ** These pseudo triplets indicate chemically, but not magnetically equivalent C atoms. Assignment is thus to be interpreted for two C atoms. ***Note:*** Due to the inequivalence of the C atoms as well as partial assignment to multiple C atoms, an ambiguous number of resonances is observed. **^{31}P{^{1}H} NMR** (C_6D_6, 162 MHz, 298K): δ = -100.39 (s, *P*(Se)*P*) ppm. **^{77}Se{^{1}H} NMR** (C_6D_6, 57 MHz, 298K): -90.4 (t, $^1J_{PSe}$ = 114.8 Hz, P(*Se*)P) ppm. **IR** (ATR, cm^{-1}): 2959 (m), 2913 (s), 2852 (m), 2730 (w), 1611 (m), 1557 (w), 1441 (m), 1373 (s), 1296 (m), 1217 (w), 1179 (w), 1106 (m), 1029 (m), 931 (m), 877 (w), 844 (w), 803 (s), 746 (s), 717 (s), 660

(w), 590 (w), 576 (w), 560 (w), 549 (w), 525 (w), 494 (w), 469 (m), 436 (w), 419 (w). **MS** (HR, ESI$^+$) calc. for $C_{48}H_{51}P_2Se$ $[M+H]^+$ (found): 765.2659 (765.2679).

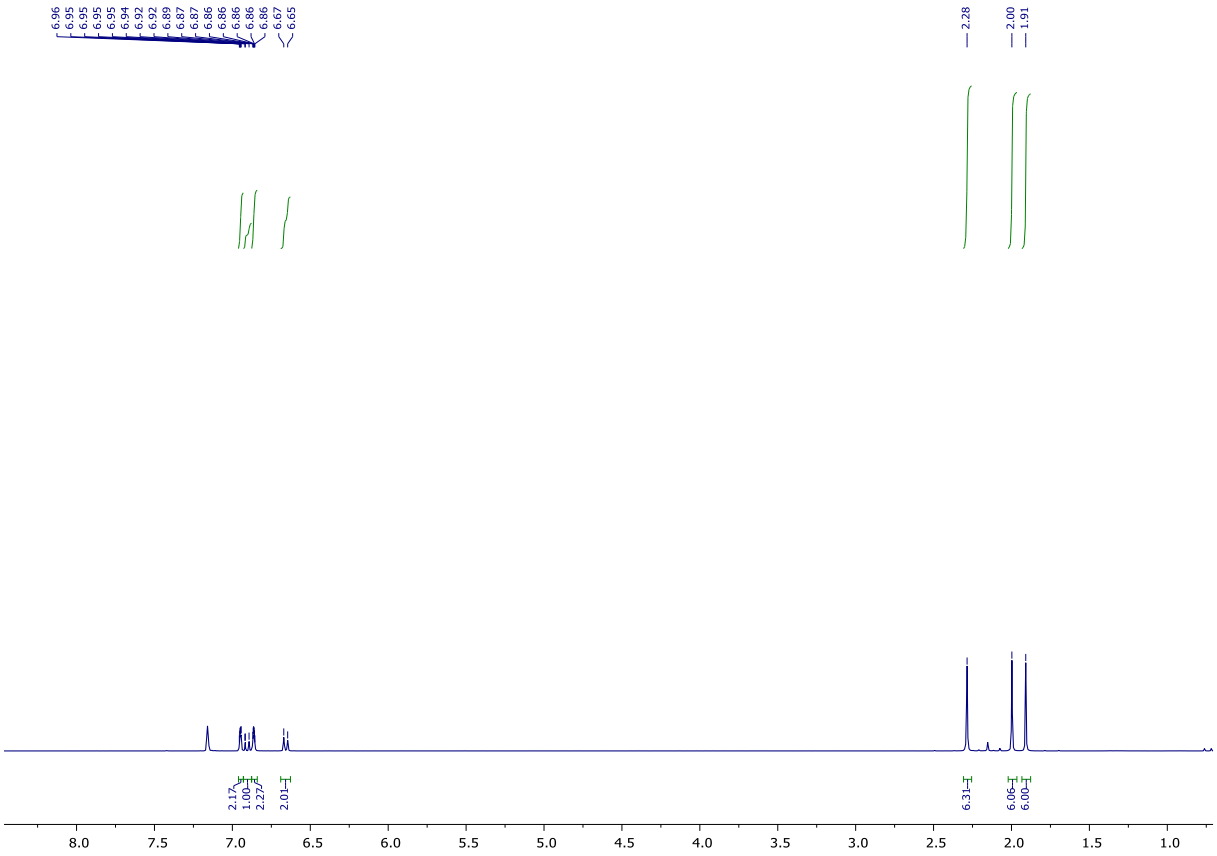


Figure S25: *^{1}H NMR of* ***2:^{Mes}Ter*** (given in ppm, C_6D_6, 300 MHz, 298K).

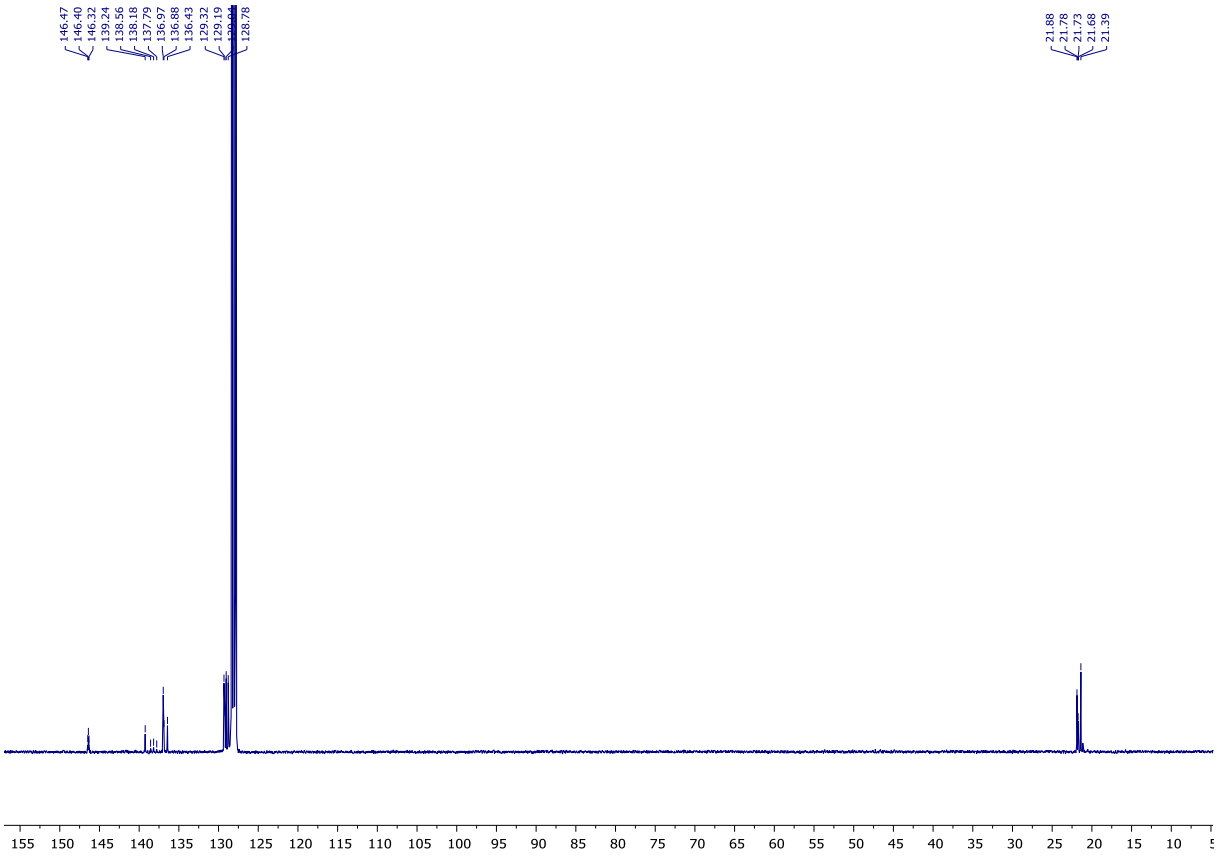


Figure S26: *$^{13}C\{^{1}H\}$ NMR of* ***2:^{Mes}Ter*** (given in ppm, C_6D_6, 75.5 MHz, 298K).

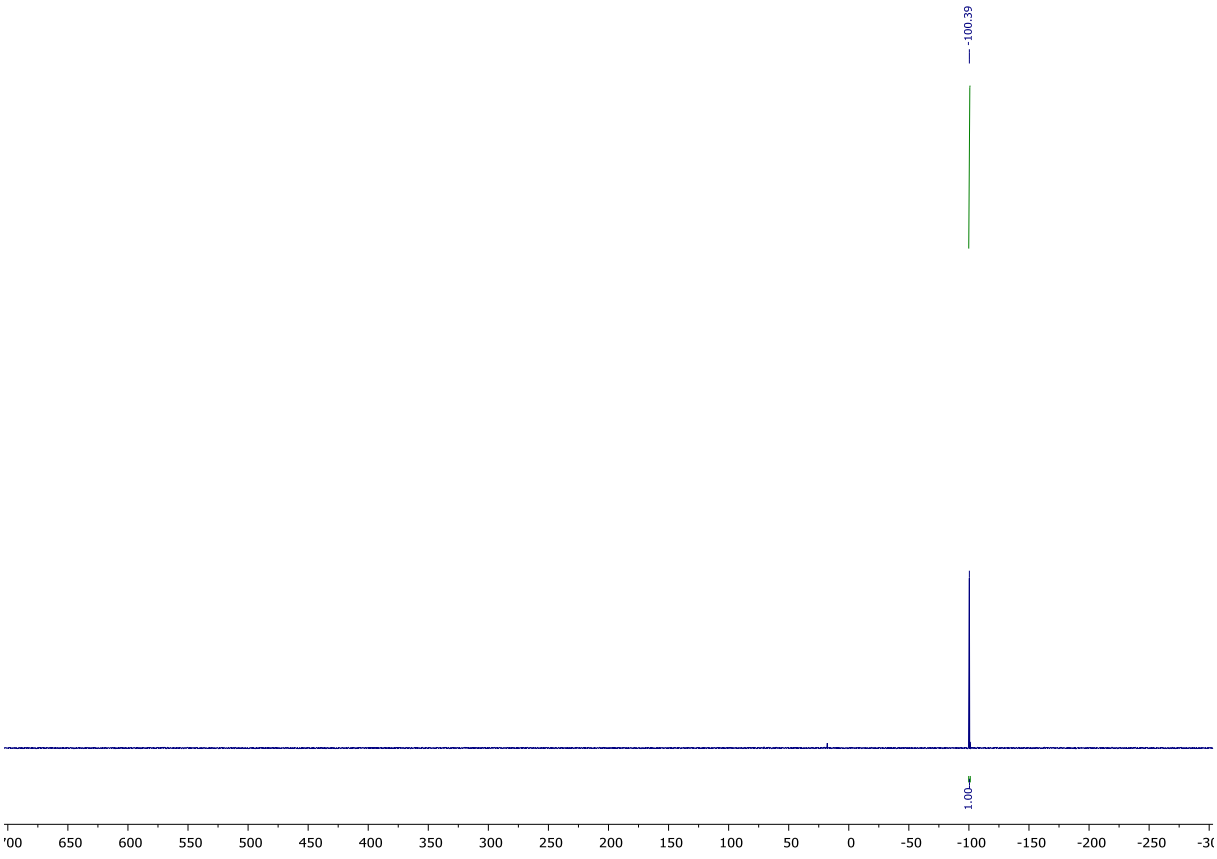


Figure S27: *$^{31}P\{^{1}H\}$ NMR of* ***2:^{Mes}Ter*** (given in ppm, C_6D_6, 122 MHz, 298K).

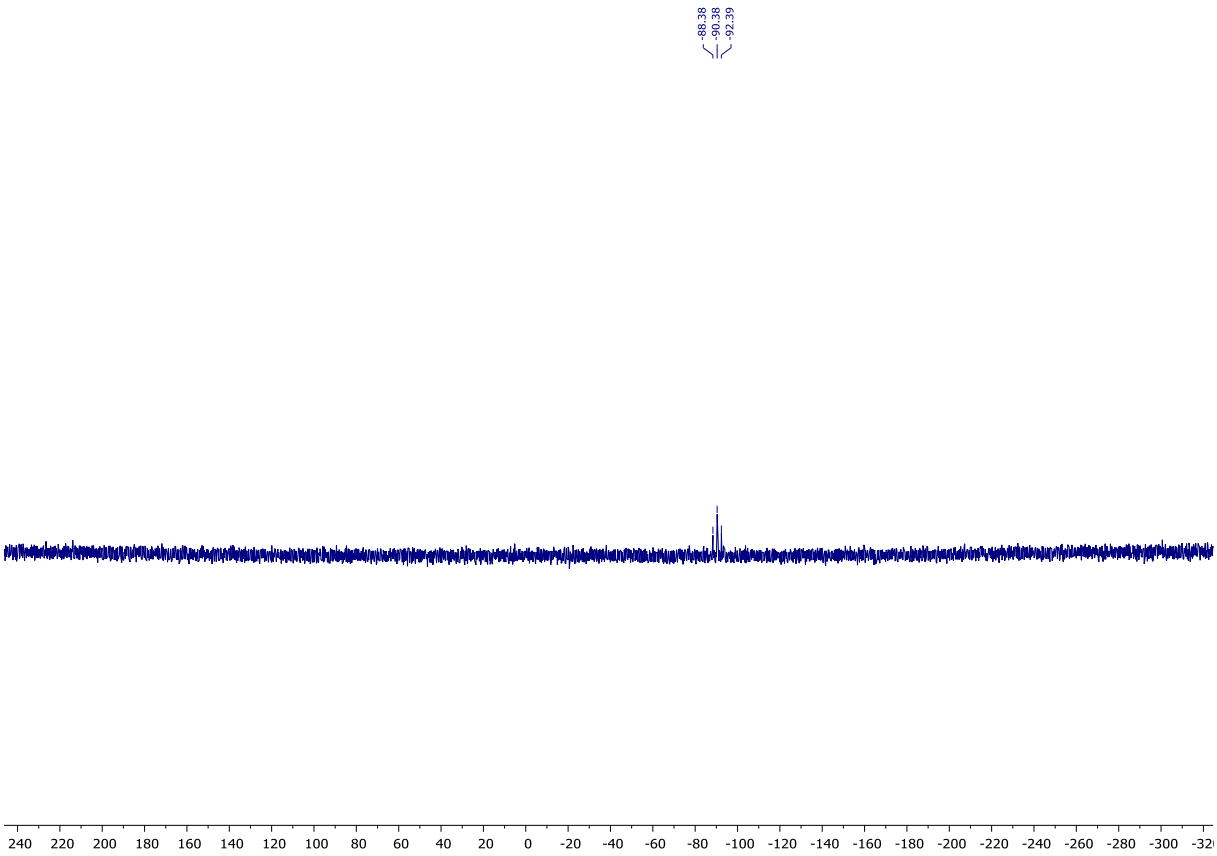


Figure S28: *$^{77}Se\{^{1}H\}$ NMR of* ***2:^{Mes}Ter*** (given in ppm, C_6D_6, 57 MHz, 298K).

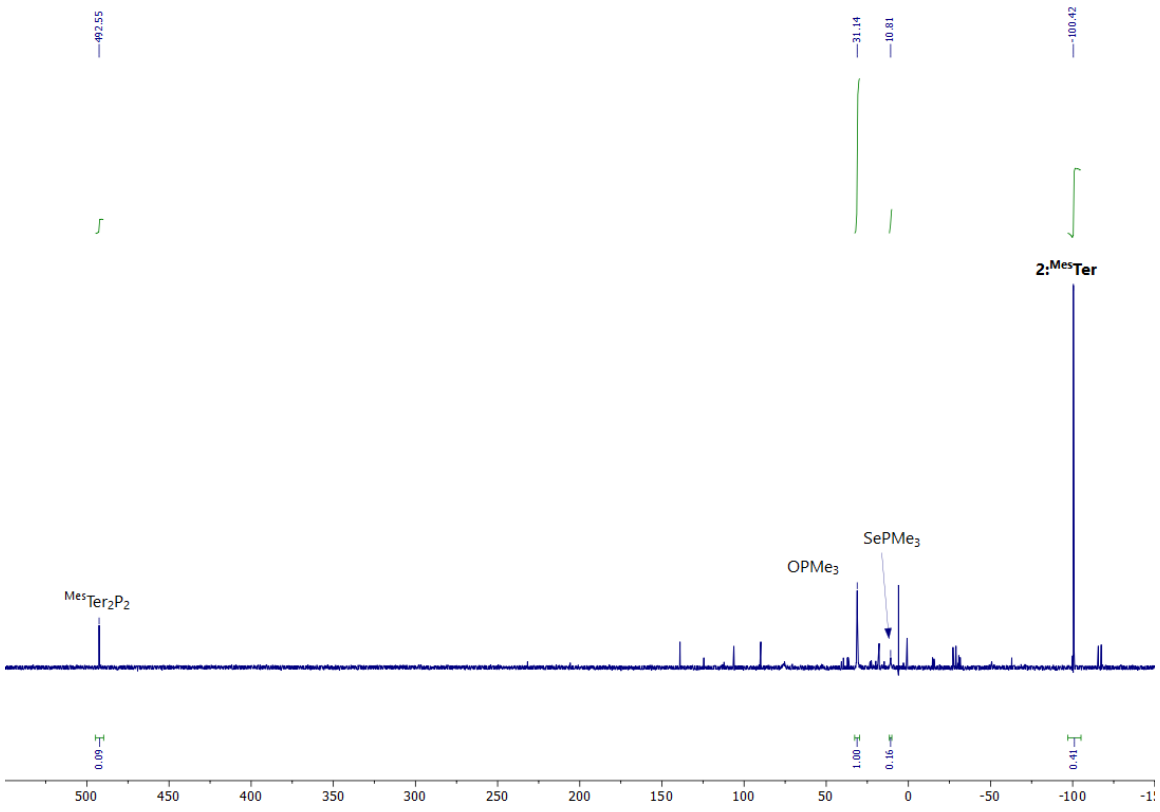
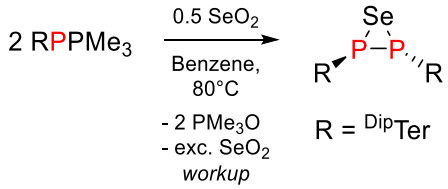


Figure S29: *$^{31}P\{^{1}H\}$ NMR of the crude reaction mixture of* ***2:^{Mes}Ter*** *before work-up* (given in ppm, C_6D_6, 122 MHz, 298K).

3.5 (^{Dip}TerP)$_2$Se (2:^{Dip}Ter)



A 0.100 g portion of ^{Dip}TerPPMe$_3$ (0.198 mmol, 1.0 eq) together with 0.011 g of SeO_2 (0.1 mmol, 0.5 eq) are dissolved in 2 mL of benzene. Subsequently, the solution is stirred at 80°C overnight. The solvent is then removed under reduced pressure and 8 mL of n-hexane are added. After filtration, the residue is dissolved in 2 mL of benzene followed by slowly saturating the solution. Placing the saturated solution at 6°C gives yellow crystals of **3:^{Dip}Ter** among powdery **2:^{Dip}Ter** first. Then, the supernatant is filtered off from the mixture and is freed of the solvent. Final washing of the obtained residue with 1.5 mL of MeCN followed by drying *in vacuo* yields **2:^{Dip}Ter** as a slight beige powder (13%, 0.013 mmol, 0.012 g).

^{1}H NMR (C_6D_6, 400 MHz, 298K): δ = 7.29 – 7.25 (m, 4H, Ar*H*), 7.18 – 7.14 (m, 10H, Ar*H*)*, 6.86 (s, 4H, Ar*H*), 2.60 (hept, $^3J_{HH}$ = 7.0 Hz, 4H, C*H*(CH$_3$)$_2$), 2.48 (hept, $^3J_{HH}$ = 6.18Hz, 4H, C*H*(CH$_3$)$_2$), 1.38 (d, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$, 12H), 1.01 (d, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$, 12H), [0.93, 0.93] (d, $^3J_{HH}$ = 6.7 Hz, CH(C*H*$_3$)$_2$, 24H)** ppm. *overlap with C_6D_5H signal, **resonances overlap each other. **^{13}C{^{1}H} NMR** (C_6D_6, 101 MHz, 298K): δ = 147.0 (s, *o*–C of Dip), 146.4 (s, *o*–C of Dip), 144.5 (^{ps}t, *o*–C$_{Aryl}$), 140.0 (^{ps}t, *ipso*–C$_{Aryl}$), 139.1 (^{br}s, *ipso*–C of Dip), [131.4, 128.8] (s, *p*–C of Dip and *m*–C$_{Aryl}$), 126.7 (s, *p*–C$_{Aryl}$), [123.9, 123.5] (s, *m*–C of Dip), [31.3, 30.1] (s, *C*H(CH$_3$)$_2$), [26.0, 25.8, 24.6, 23.42] (s, CH(*C*H$_3$)$_2$) ppm. **^{31}P{^{1}H} NMR** (C_6D_6, 162 MHz, 298K): δ = -86.77 (s, *P*(Se)*P*) ppm. **^{77}Se{^{1}H} NMR** (C_6D_6, 57 MHz, 298K): -13.1 (t, $^1J_{PSe}$ = 117.5 Hz, P(*Se*)P) ppm. **IR** (ATR, cm^{-1}): 2957 (s), 2924 (m), 2864 (m), 1589 (w) 1576 (w), 1559 (w), 1459 (m), 1381 (m), 1360 (s), 1324 (w), 1249 (w), 1178 (w), 1121 (w), 1056 (m), 933 (w), 897 (w), 874 (w), 818 (w), 804 (s), 791 (s), 746 (vs), 689 (w), 646 (w), 584 (m), 556 (w), 532 (w), 486 (w), 462 (w), 409 (m). **MS** (HR, ESI$^+$) calc. for

$C_{60}H_{75}P_2Se_1$ $[M+H]^+$ (found): 937.4509 (937.4525); $C_{60}H_{74}P_2Se_1Na_1$ $[M+Na]^+$ (found): 959.4328 (959.4326).

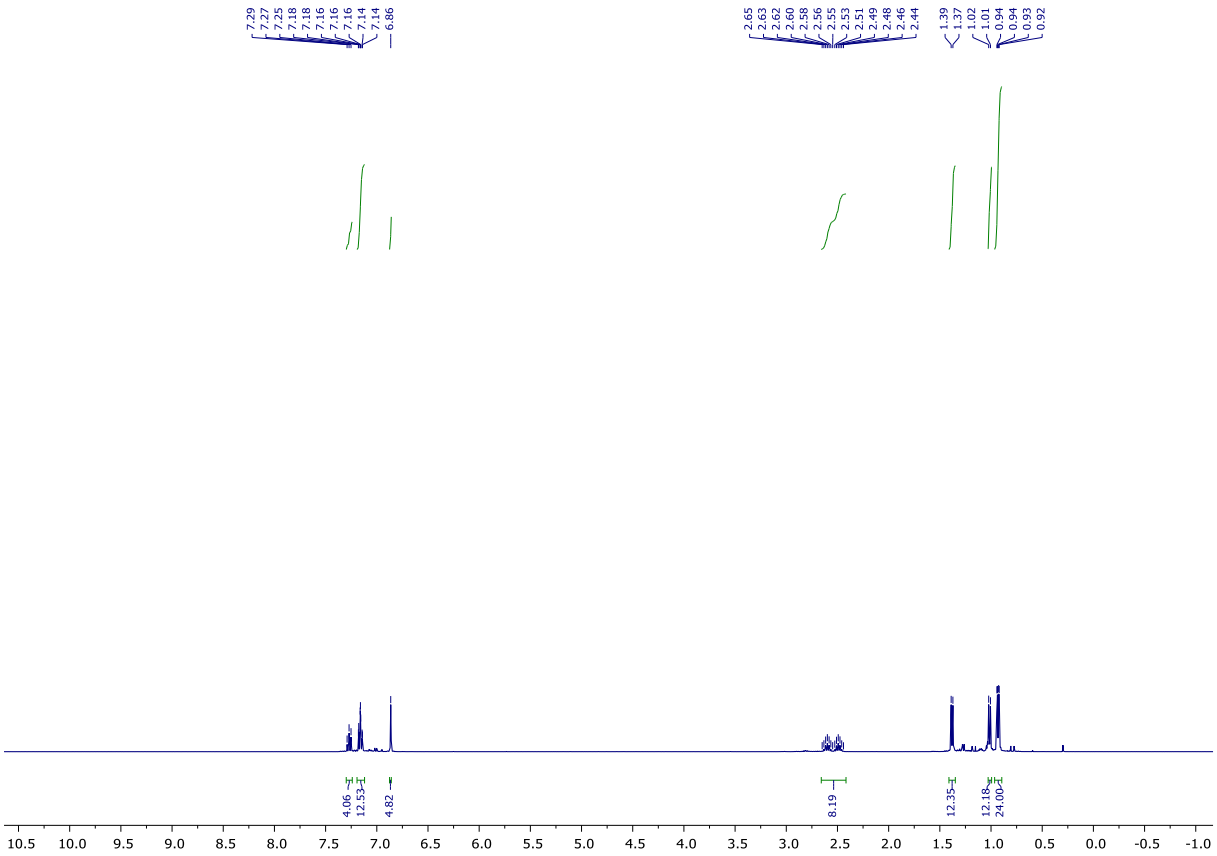


Figure S30: *^{1}H NMR of* ***2:^{Dip}Ter*** (given in ppm, C_6D_6, 400 MHz, 298K).

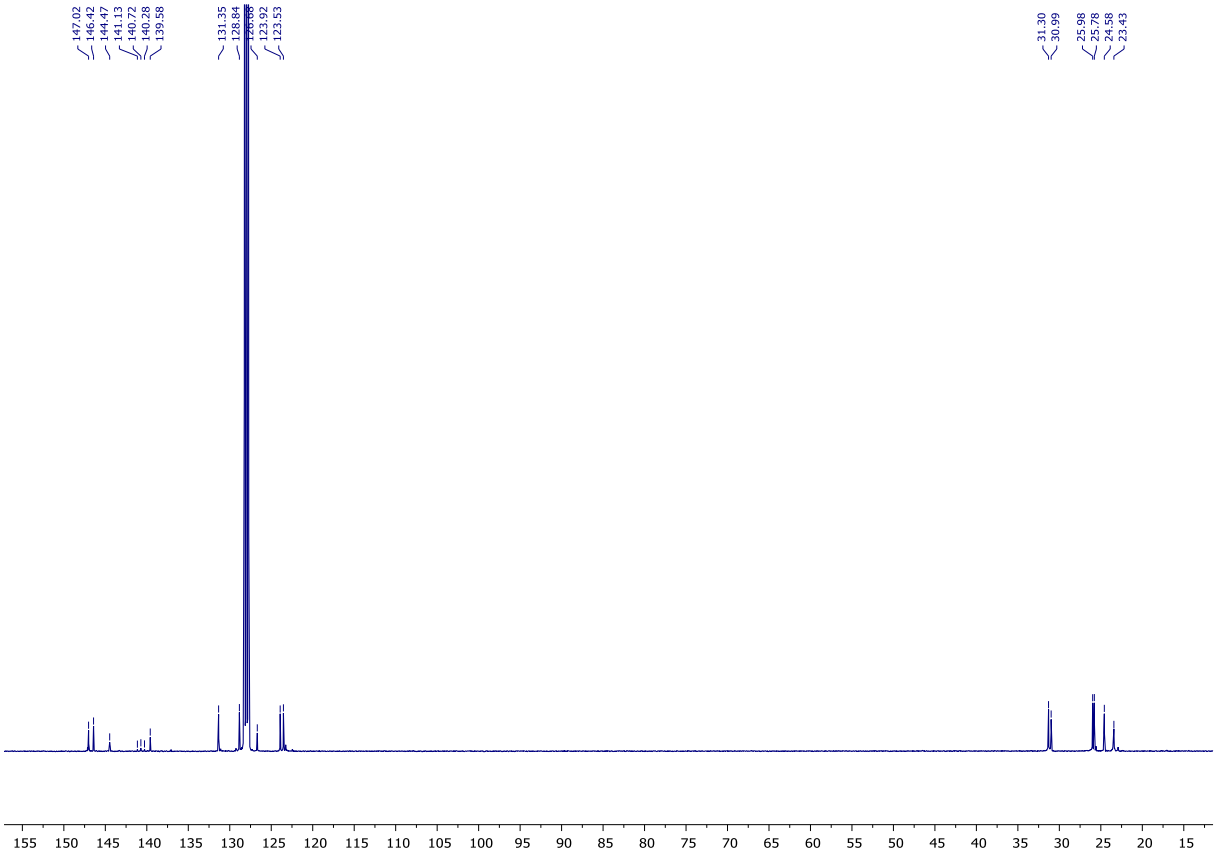


Figure S31: *$^{13}C\{^{1}H\}$ NMR of* ***2:^{Dip}Ter*** (given in ppm, C_6D_6, 101 MHz, 298K).

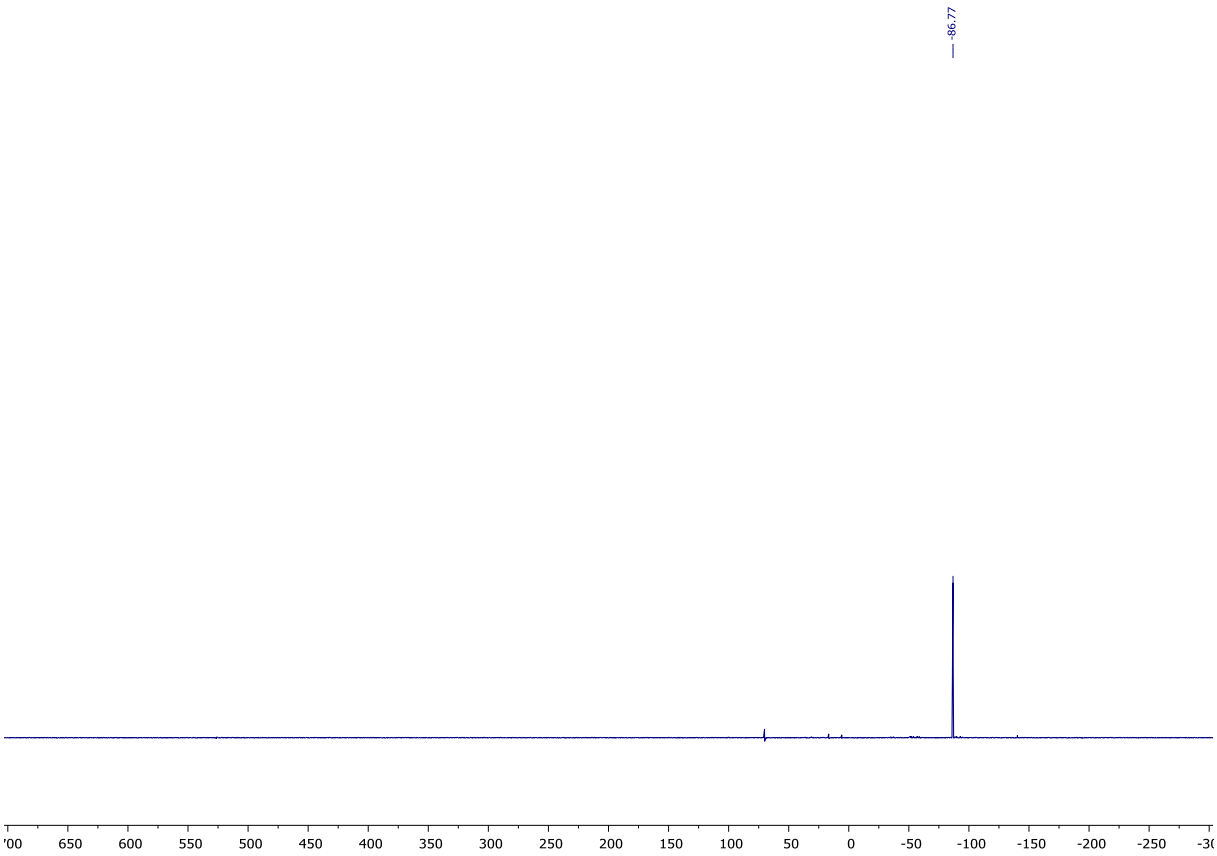


Figure S32: *$^{31}P\{^{1}H\}$ NMR of* ***2:^{Dip}Ter*** (given in ppm, C_6D_6, 162 MHz, 298K).

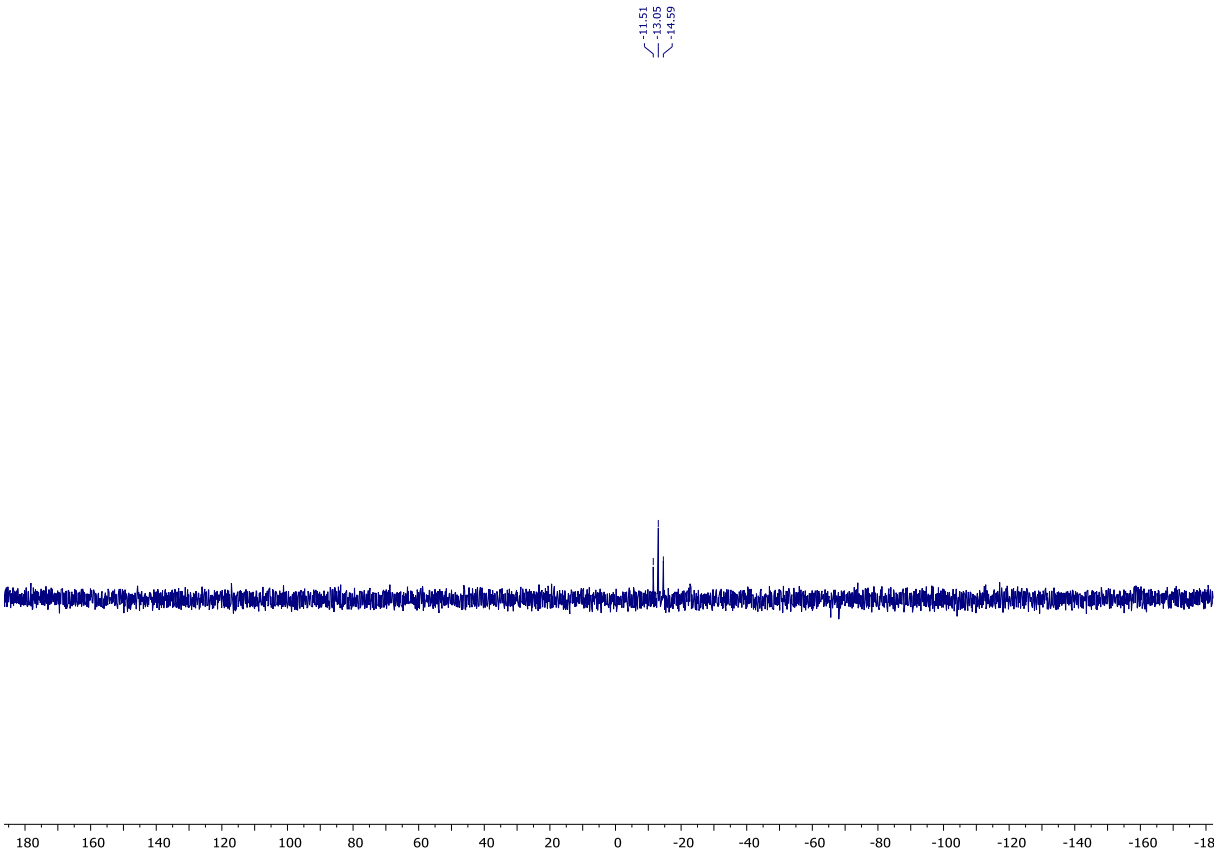
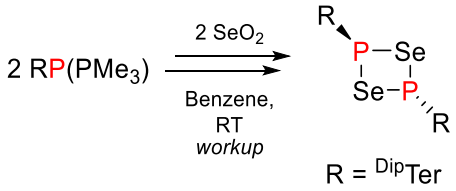


Figure S33: *$^{77}Se\{^{1}H\}$ NMR of* ***2:^{Dip}Ter*** (given in ppm, C_6D_6, 122 MHz, 298K).

3.6 [Se(μ-P^{Dip}Ter)]$_2$ (3:^{Dip}Ter)



A 0.100 g portion of ^{Dip}TerP(PMe$_3$) (0.198 mmol, 1.0 eq) together with 0.022 g of SeO$_2$ (0.198 mmol, 1.0 eq) are dissolved in 2 mL of benzene. The solution is then stirred at ambient temperature overnight to give an orange- to red-colored solution. Then, the solvent is removed under reduced pressure and 5 mL of MeCN as well as 20 mL of *n*-hexane are added. The mixture is vigorously stirred for 10 min. and the two phases are separated from each other. Removing the solvent under reduced pressure gives a yellowish powder which is washed with 2 mL of MeCN. Recrystallization from benzene solution at 6°C finally yields [Se(μ-P^{Dip}Ter)]$_2$ (**3:^{Dip}Ter**) as yellow rods/platelets (0.032 g, 0.032 mmol; 32% based on ^{Dip}TerPPMe$_3$). The respective crystals turned out to be suitable for SC-XRD.

^{1}H NMR (C$_6$D$_6$, 300 MHz, 298K): δ =7.24 – 7.19 (m, 4H, Ar*H*), 7.12 – 7.00 (m, 14H, Ar*H*), 2.81 (hept, $^3J_{HH}$ = 6.8 Hz, 4H, C*H*(CH$_3$)$_2$),1.27 (d, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$, 24H), 1.02 (d, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$, 24H). **^{13}C{^{1}H} NMR** (C$_6$D$_6$, 101 MHz, 298K): δ =147.2 (s, *o*–C of Dip), 143.4 (^{ps}t, *o*–C$_{Aryl}$), 138.3 (^{ps}t, *ipso*–C$_{Aryl}$), 137.2 (s, *ipso*–C of Dip), 131.2 (s, *p*–C of Dip), 129.3 (s, *m*–C$_{Aryl}$), 127.4 (s, *p*–C$_{Aryl}$)*, 123.3 (s, *m*–C of Dip), 31.4 (s, *C*H(CH$_3$)$_2$), [26.1, 23.0] (s, CH(*C*H$_3$)$_2$) ppm. * Overlap with the C$_6$D$_5$H signal; assignment with a 1H/13C HSQC spectrum. **^{31}P{^{1}H} NMR** (C$_6$D$_6$, 122 MHz, 298K): δ = 70.12 (s, *P*(Se)) ppm. **^{77}Se{^{1}H} NMR** (C$_6$D$_6$, 57 MHz, 298K): -22.7 (t, $^1J_{PSe}$ = 14.1 Hz, P(*Se*)) ppm. **IR** (ATR, cm^{-1}): 3056 (w), 2957 (s), 2924 (m), 2865 (m), 1574 (w), 1559 (w), 1458 (m), 1443 (m), 1381 (s), 1360 (m), 1324 (w), 1249 (w), 1178 (w), 1100 (w), 1056 (m), 933 (vw), 819 (m), 801 (s), 792 (s), 750 (vs), 688 (w), 586 (w), 554 (s), 505 (w), 485 (w), 439 (m), 427 (m). **MS** (HR, ESI$^+$) calc. for C$_{60}$H$_{75}$P$_2$Se$_2$ [M+H]$^+$ (found): 1017.3674 (1017.3692); C$_{60}$H$_{74}$P$_2$Se$_2$Na [M+Na]$^+$ (found): 1039.3493 (1039.3528).

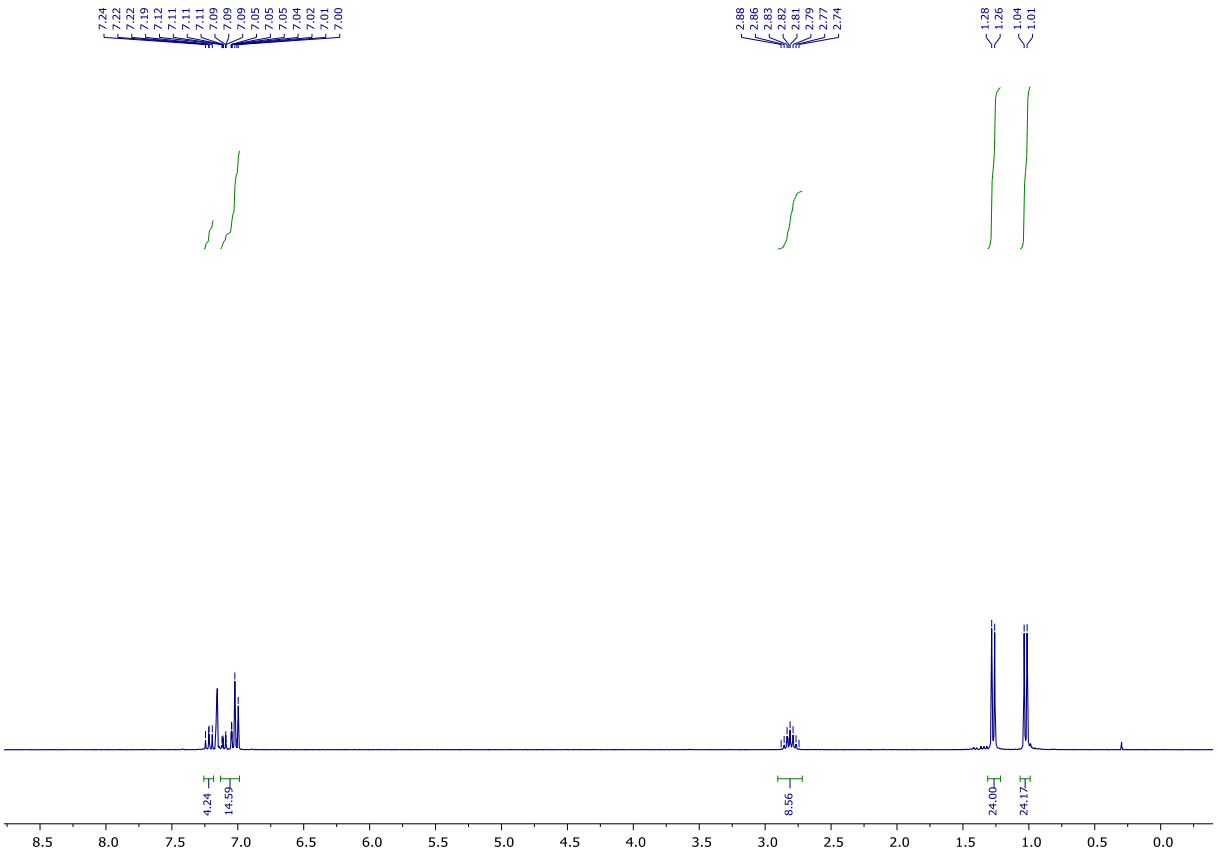


Figure S34: *^{1}H NMR of* ***3:^{Dip}Ter*** (given in ppm, C_6D_6, 300 MHz, 298K).

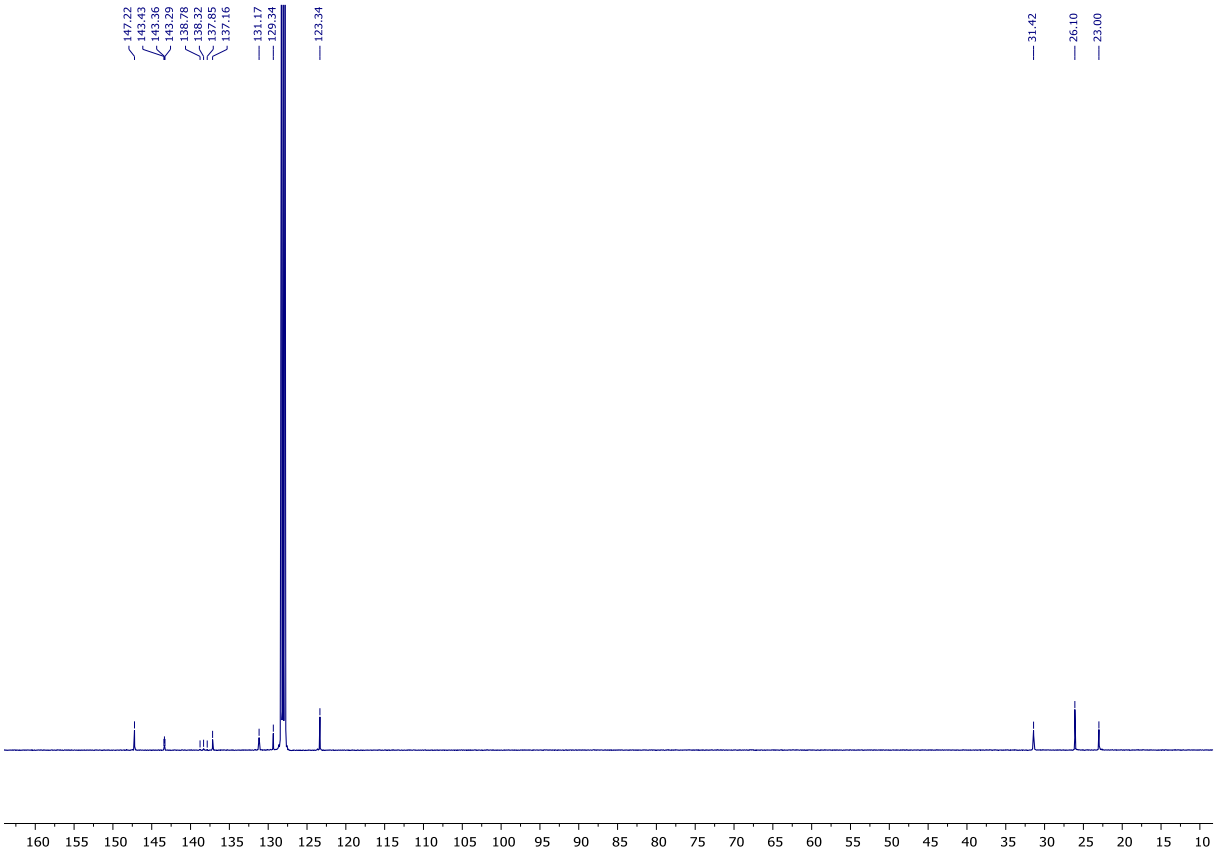


Figure S35: *$^{13}C\{^{1}H\}$ NMR of* ***3:^{Dip}Ter*** (given in ppm, C_6D_6, 101 MHz, 298K).

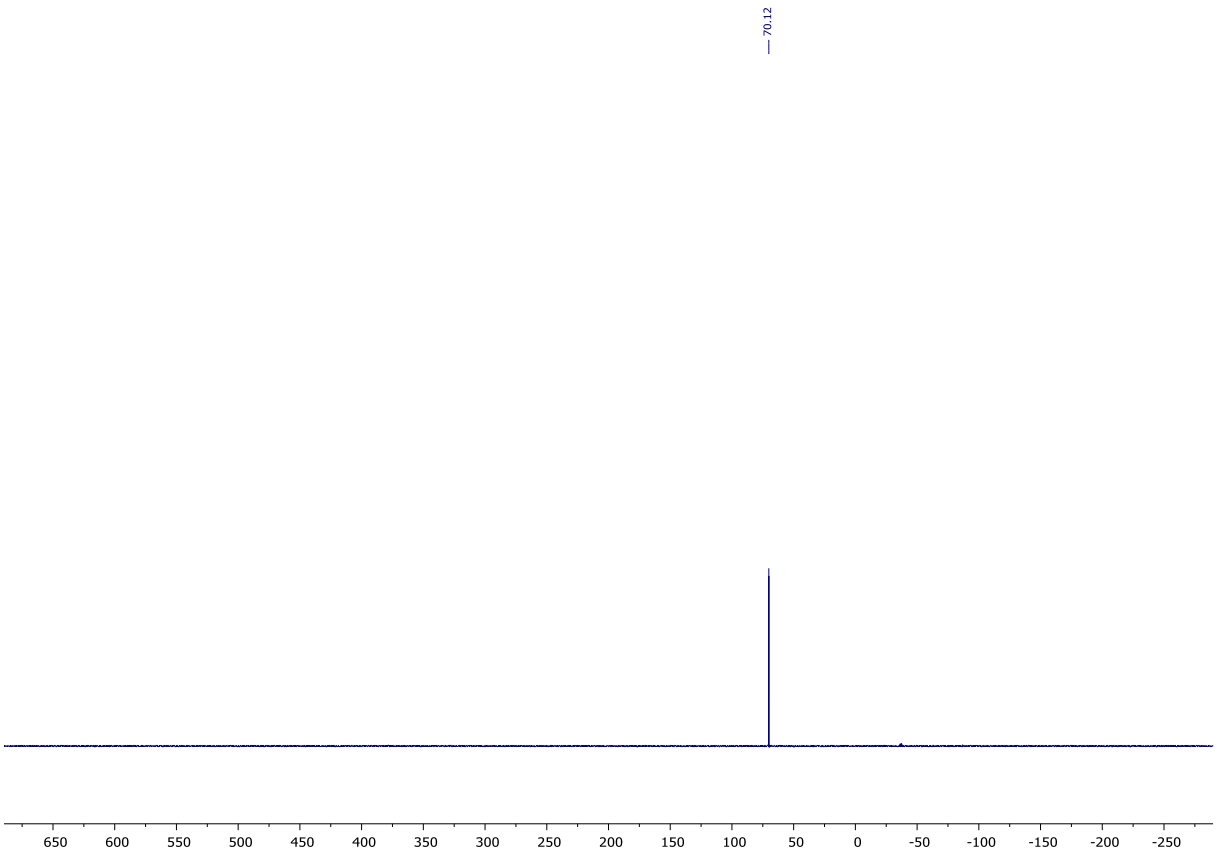


Figure S36: *$^{31}P\{^{1}H\}$ NMR of* ***3:^{Dip}Ter*** (given in ppm, C_6D_6, 122 MHz, 298K).

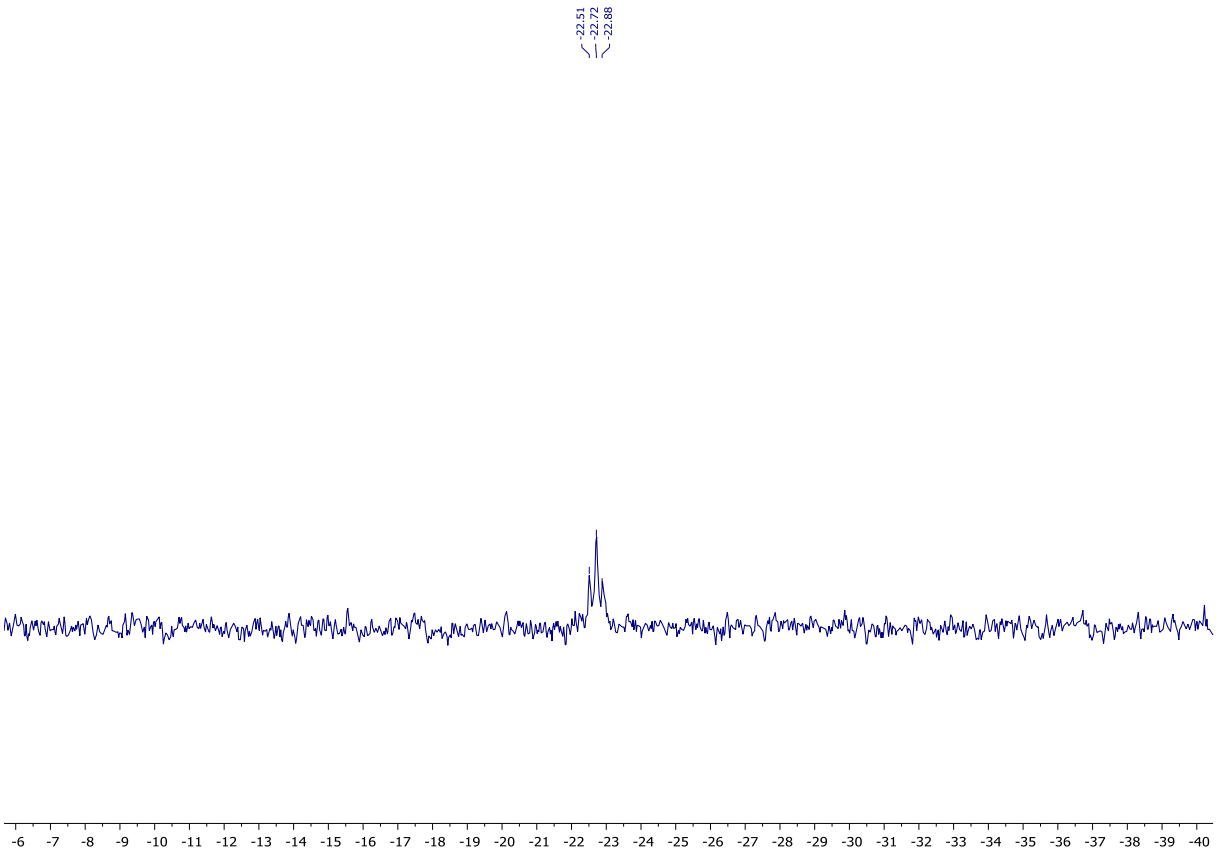


Figure S37: *$^{77}Se\{^{1}H\}$ NMR of* ***3:^{Dip}Ter*** (given in ppm, C_6D_6, 57 MHz, 298K).

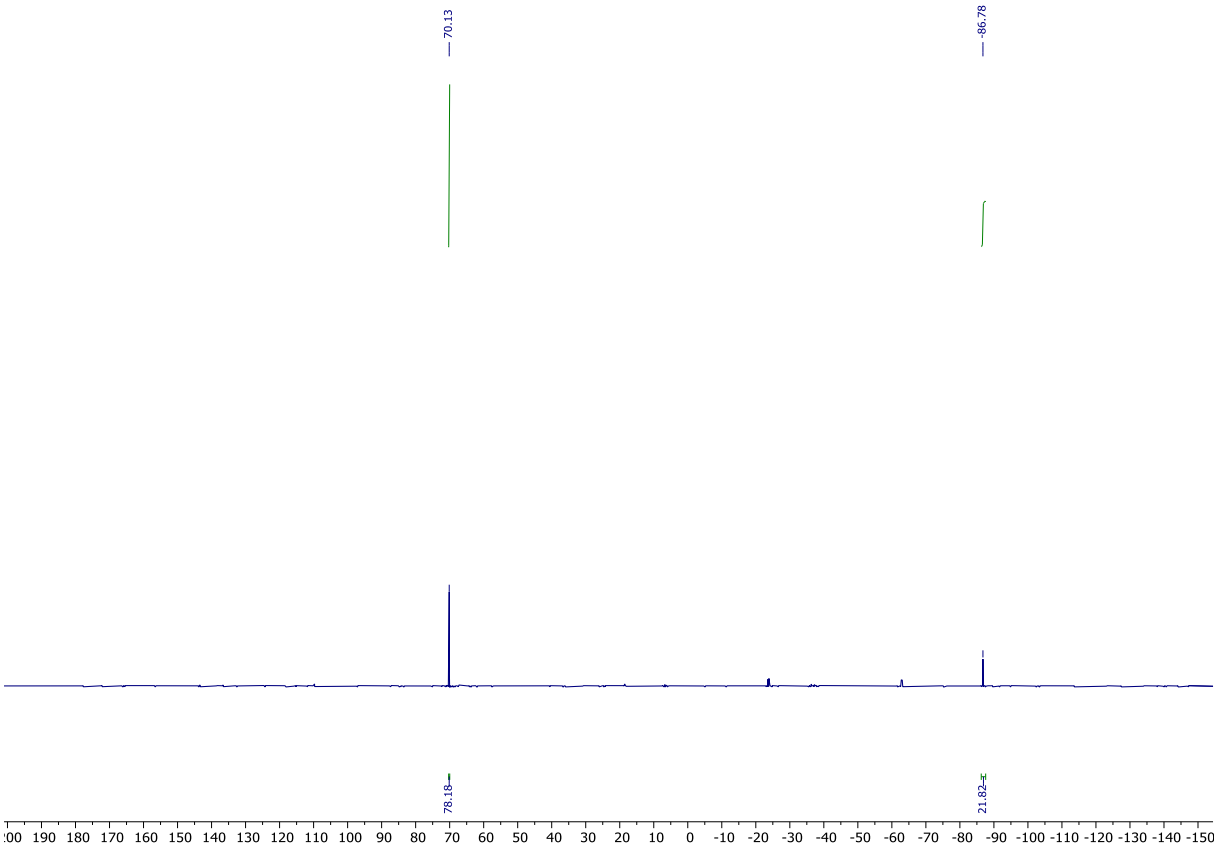
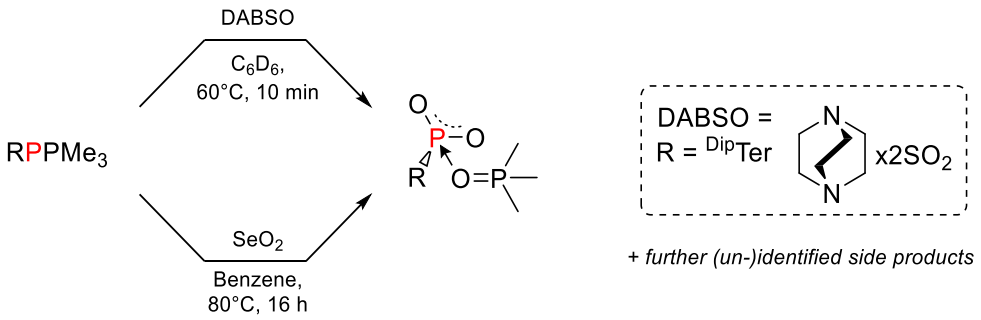


Figure S38: *$^{31}P\{^{1}H\}$ NMR of the reaction mixture containing* ***3:^{Dip}Ter*** *after workup with MeCN/n-hexane* (given in ppm, C_6D_6, 122 MHz, 298K).

3.7 ^{Dip}TerP(O)$_2$OPMe$_3$ (4:^{Dip}Ter)



Using DABSO:

A 0.050 g portion of ^{Dip}TerPPMe$_3$ (0.1 mmol, 1.0 eq) together with 0.012 g of DABSO (0.05 mmol, 0.5 eq [1.0 eq of SO_2]) are dissolved in 0.8 mL of C_6D_6. The initially brown solution is then sonicated at 60°C for 10 minutes, giving a colorless solution. **4:^{Dip}Ter** among SPMe$_3$ as well as other side products are detected *via* ^{31}P NMR spectroscopy. The composition of the side products was determined by combined analytical methods (^{31}P NMR, SC-XRD, MS) and theoretical studies.

Using SeO_2:

A 0.050 g portion of of ^{Dip}TerPPMe$_3$ (0.1 mmol, 1.0 eq) together with 0.011 g of SeO_2 (0.1 mmol, 1.0 eq) are dissolved in 1.5 mL of benzene. The obtained suspension is stirred vigorously at 80°C overnight (16 h). Then, the solvent is carefully removed under reduced pressure and 12 mL of *n*-hexane are added. After filtration which leaves a reddish residue (presumably a mixture of $Se_{(red)}$, $Se_{(grey)}$, and unidentified SeO-species, see Figure SXX) the solvent is carefully(!) removed under reduced pressure again. NMR of the yet crude product indicates formation of **4:^{Dip}Ter** as the main product among **2:^{Dip}Ter** and further unidentified side products.

Crystallization:

The yet crude product from the SeO_2 route is dissolved in 2 mL of toluene. Concentration of the solvent volume to ca. 0.3 mL and placing the solution at −32°C yielded a few of block-shaped crystals of **4:^{Dip}Ter** (among $OPMe_3$) which were just enough for SC-XRD and MS spectrometry.

Note: **4:^{Dip}Ter** is stable within the reaction mixture, but our attempts to isolate the compound in pure form failed due to considerable decomposition into various unknown products and similar solubilities of the accompanying side products. **4:^{Dip}Ter** is sensitive towards coordinating solvents such as MeCN. Recrystallization also causes problems due to concomitant formation and precipitating of free $OPMe_3$.

^{1}H NMR (C_6D_6, 300 MHz, 298K): δ = 7.23 – 7.18 (m, 3H, Ar*H*), 7.12 – 7.01 (m, 6H, Ar*H*), 3.08 (hept, $^3J_{HH}$ = 6.9 Hz, 4H, C*H*(CH_3)$_2$), 1.40 (d, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3$)$_2$, 12H), 1.12 (d, $^3J_{HH}$ = 6.9 Hz, CH(C*H*$_3$)$_2$, 12H), 1.08 (d, $^3J_{HH}$ = 6.9 Hz, O–P(C*H*$_3$)$_3$, 9H)* ppm. *overlap with PMe_3O signal. **^{31}P{^{1}H} NMR** (C_6D_6, 162 MHz, 298K): δ = 74.79 (d, $^2J_{PP}$ = 19.8 Hz, *P*(O)$_2$OPMe$_3$), 11.35 (d, $^2J_{PP}$ = 19.8 Hz, P(O)$_2$O*P*Me$_3$) ppm. **^{31}P NMR** (C_6D_6, 122 MHz, 298K): δ = 74.71 (m, P(O)$_2$O*P*Me$_3$)*, 11.73 (d, $^2J_{PP}$ = 18.6 Hz, P(O)$_2$O*P*Me$_3$) ppm. *an expected decett of doublets could not be resolved. **MS** (HR, ESI$^+$) calc. for $C_{33}H_{47}O_3P_2$ $[M+H]^+$ (found): 553.3000 (553.3014); $C_{33}H_{46}O_3P_2Na_1$ $[M+Na]^+$ (found): 575.2820 (575.2834).

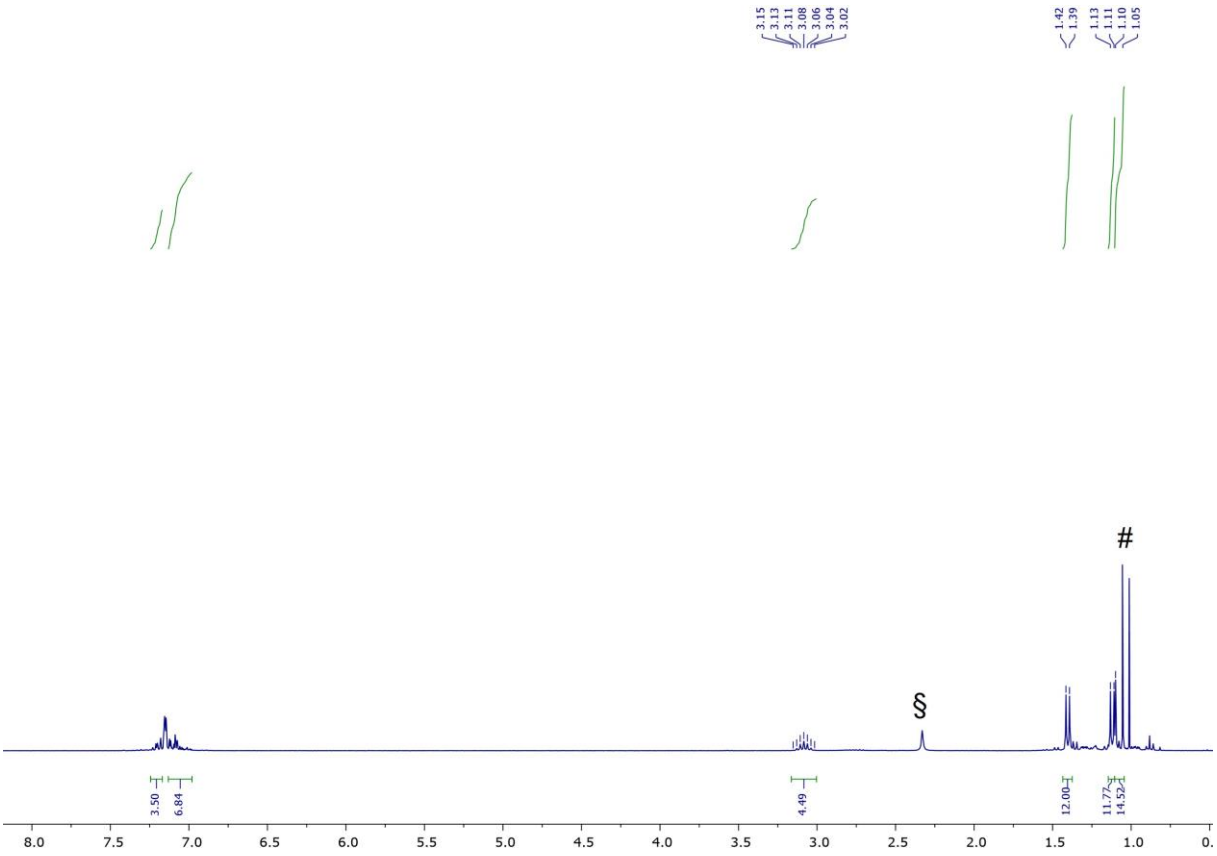


Figure S39: *^{1}H NMR of* ***3:^{Dip}Ter*** (given in ppm, C_6D_6, 300 MHz, 298K). # = $SPMe_3$, § = DABCO

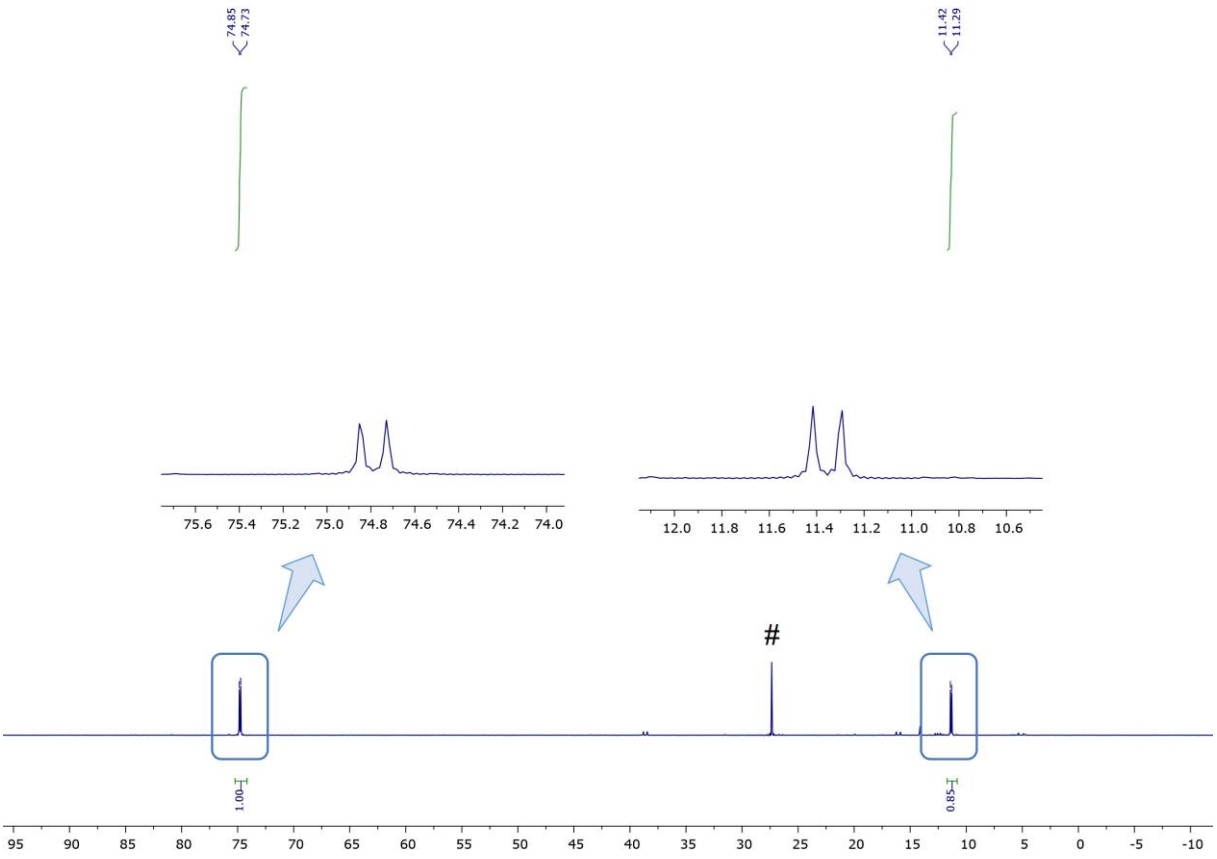


Figure S40: *$^{31}P\{^{1}H\}$ NMR of* ***3:^{Dip}Ter*** (given in ppm, C_6D_6, 162 MHz, 298K). # = $SPMe_3$

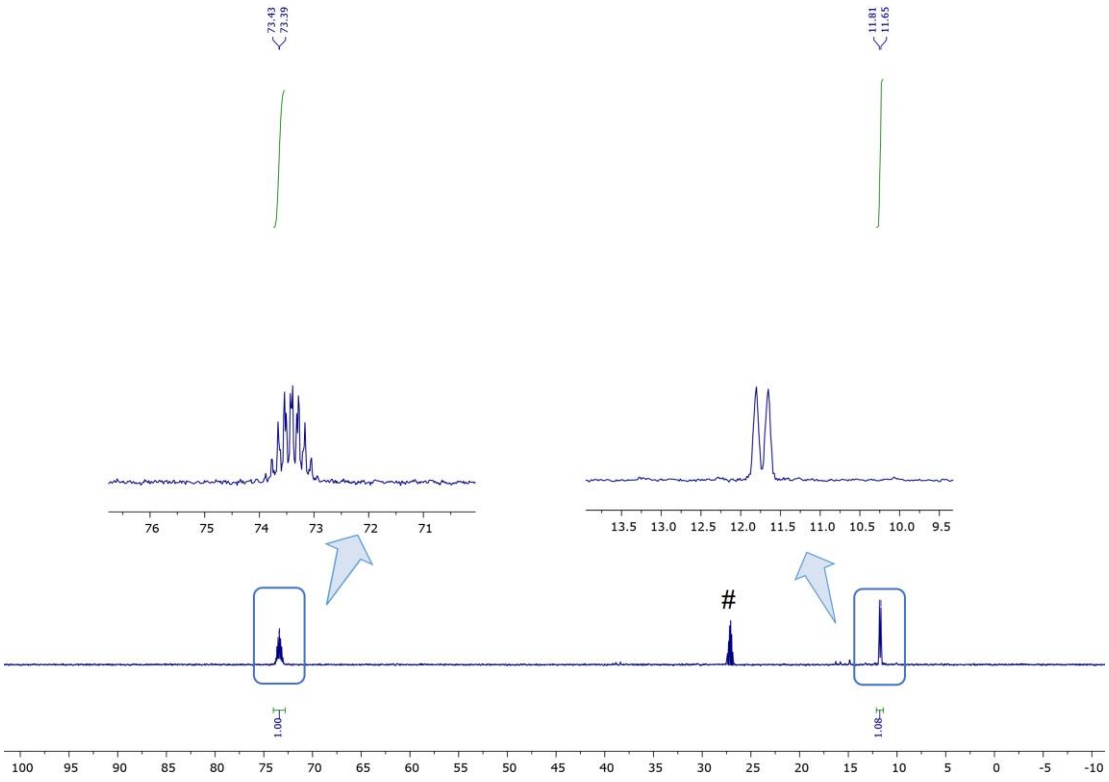


Figure S41: *^{31}P NMR of* ***3:^{Dip}Ter*** (given in ppm, C_6D_6, 162 MHz, 298K). # = DABCO·PMe_3O

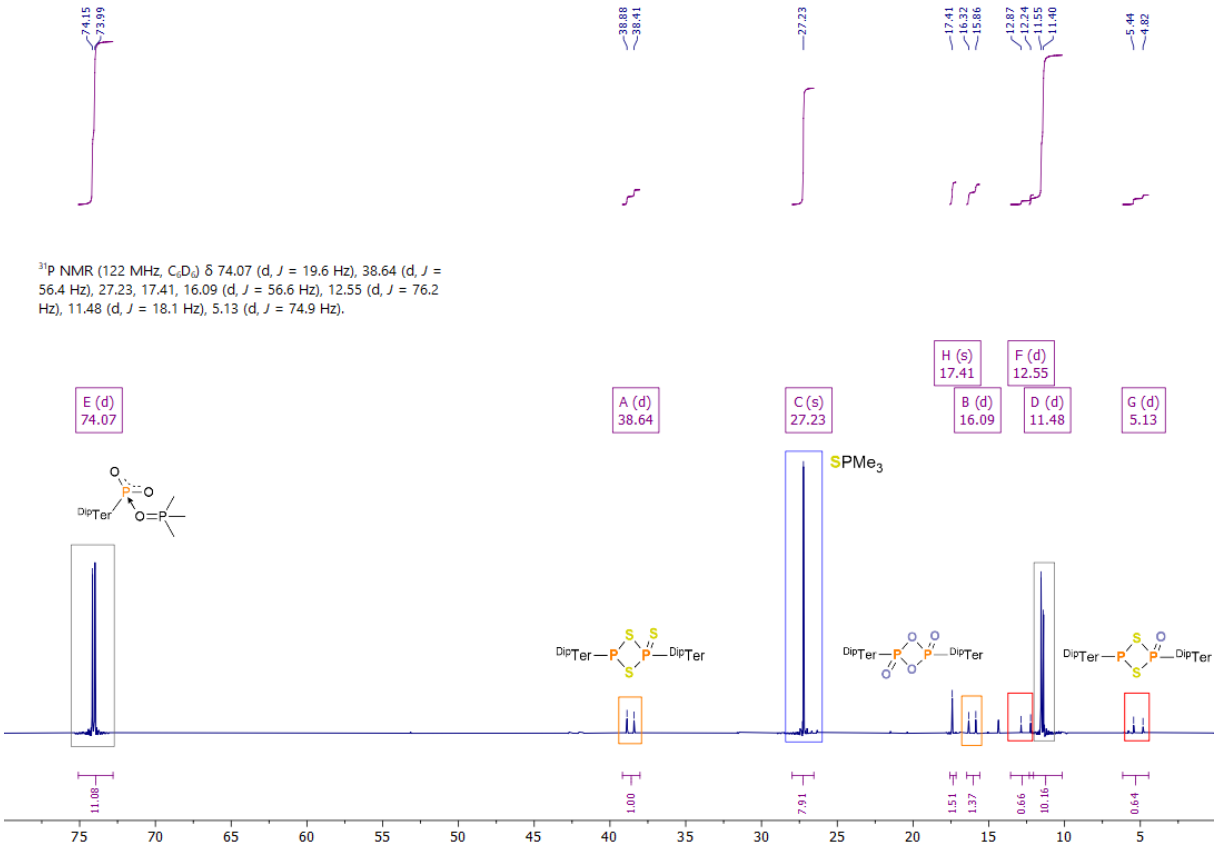


Figure S42: *^{31}P{^{1}H} NMR of the reaction between ^{Dip}TerP(PMe_3) and 0.5 eq DABSO at 60 °C after 10 minutes* (given in ppm, C_6D_6, 162 MHz, 298K). Identified species are indicated in the spectrum.

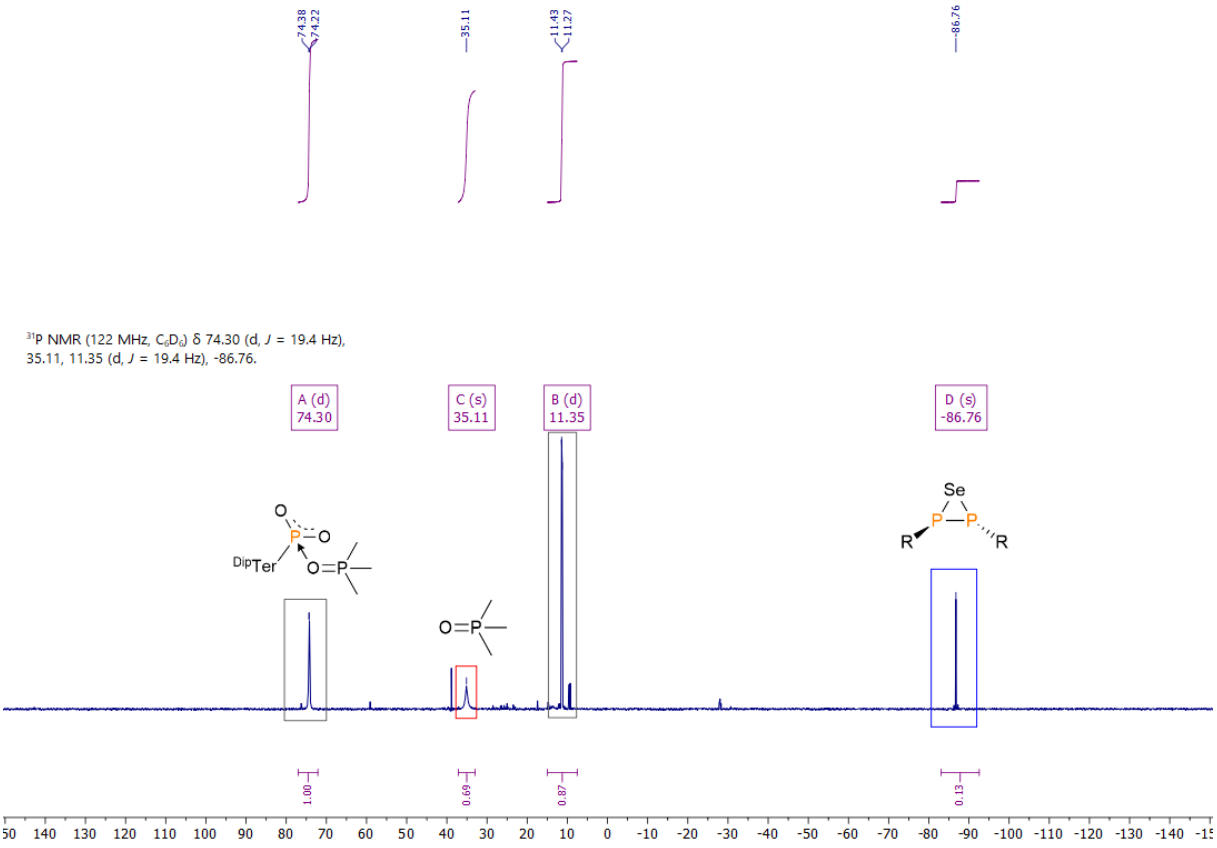


Figure S43: *$^{31}P\{^1H\}$ NMR of the reaction mixture of the reaction of ^{Dip}TerP(PMe$_3$) and 1 eq SeO_2 at 80 °C after 16 h* (given in ppm, C_6D_6, 162 MHz, 298K). Identified species are indicated in the spectrum.

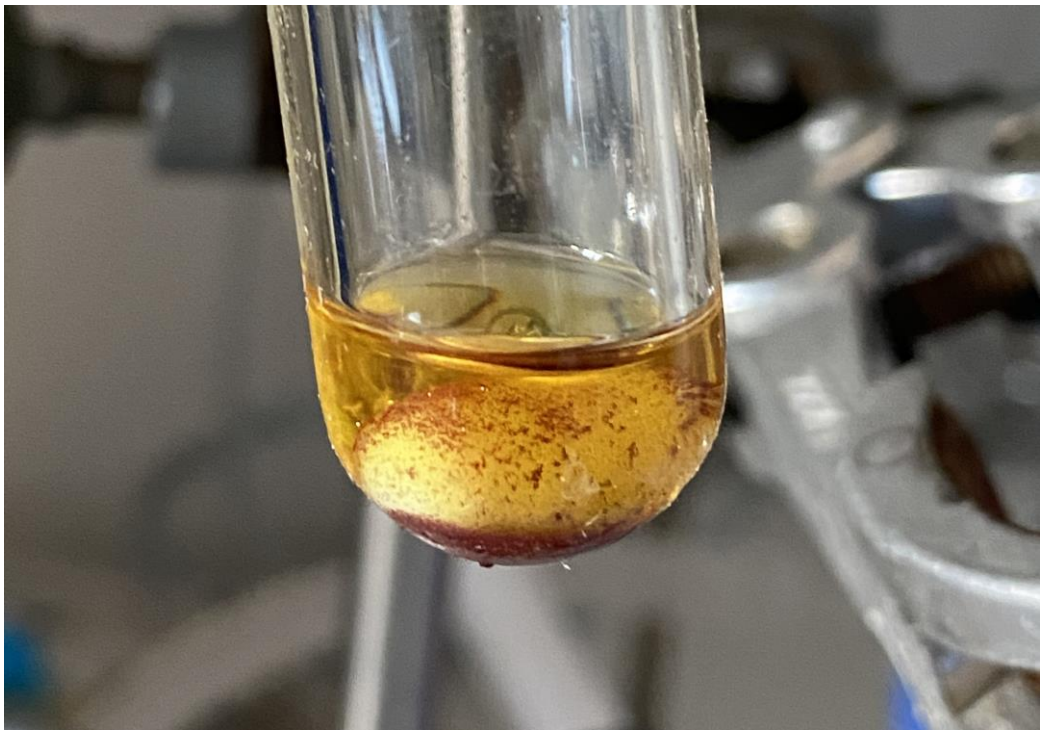
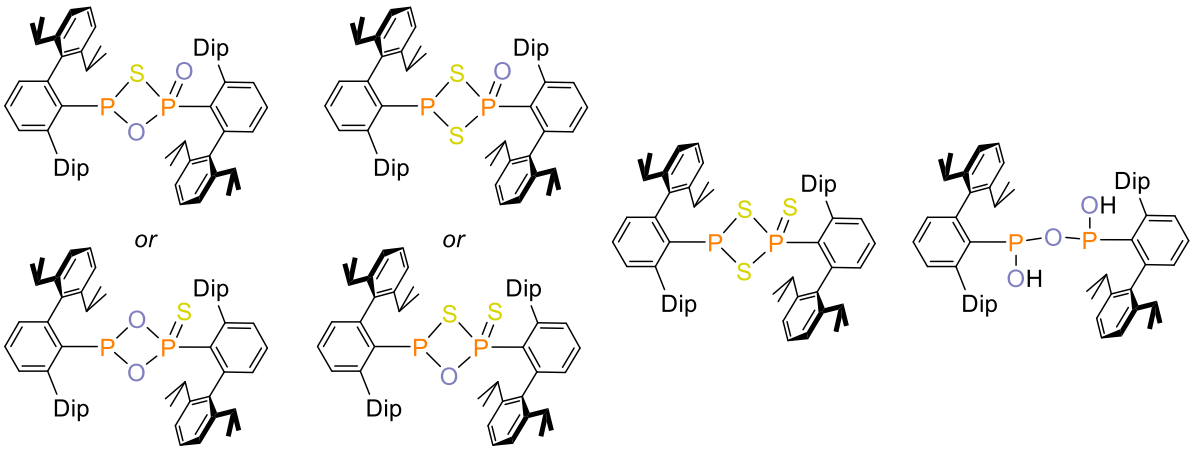


Figure S44: Image of the reddish residue obtained after reacting ^{Dip}TerP(PMe$_3$) with 1 eq SeO_2 in C_6H_6 at 80 °C over a period of 16 h.

3.8 Determination of sulphur-containing side-products in the reaction between ^{Dip}TerP(PMe$_3$) and DABSO

A 0.100 g portion of ^{Dip}TerPPMe$_3$ (0.2 mmol, 1.0 eq) together with 0.024 g of DABSO (0.1 mmol, 0.5 eq [1.0 eq of SO_2]) are dissolved in 1.6 mL of benzene. The brown solution is then sonicated at 60°C until a colourless solution is obtained. Then, the solvent is carefully(!) removed under reduced pressure. The residue is extracted with 8 mL of *n*-hexane followed by filtration. The solvent is again carefully removed under reduced pressure and subsequently 2 mL of toluene are added. The colourless solution is then concentrated and placed immediately at −78°C. A few small colourless crystals can be obtained after a few days. The one single crystal used for SC-XRD was refined to follow a formula sum of $C_{74}H_{90}O_{0.64}P_2S_{2.2}$ (see Figure S8 and Table S4). According to mass spectrometry, the bulk crystals revealed the three reasonable molecular structures shown below, as well as a hydrolysis product, due to sample preparation.



Expected mass (found) [g/mol]				
$[M+H]^+$	921.4963 (921.4953)	937.4734 (937.4717)	953.4506 (953.4498)	907.5348 (907.5341)
$[M+Na]^+$	943.4777 (943.4766)	959.4548 (959.4538)	975.4320 (975.4314)	929.5162 (929.5161)

Figure S45: *Mass spectrometry report for possible (side) products of the reaction of ^{Dip}TerPPMe$_3$ with DABSO. From left to right:* ***4:^{Dip}Ter***, ***5:^{Dip}Ter***, ***6:^{Dip}Ter*** *and* ***7:^{Dip}Ter***.

ESI-TOF Accurate Mass Report Page 1

Results file: E:\Projects\2202.PRO\SampleDB\2202.rpt
Last modified: Tuesday, March 01, 2022 12:32:32

Sample Summary:

Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa
93	22021023	FDP76R1	Dankert	952.4428	C60H74P2S3	953.4506 975.4320	953.4498 975.4314	-0.8 -0.6	-0.8 -0.6

ESI-TOF Accurate Mass Report Page 2

File:22021023
Vial:1:F,2
Description:MeOH/0,1%HCOOH in H2O 98:2

Sample Name:FDP76R1
Date:10-Feb-2022

UserName:Dankert
Time:16:14:15

Sample Report:

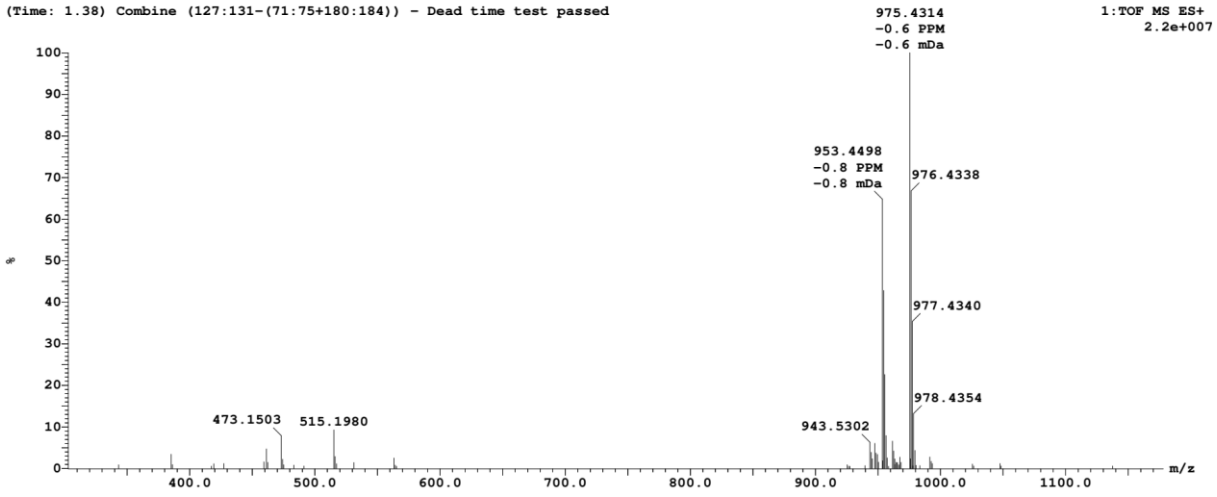


Figure S46: *ESI-TOF accurate mass for ^{Dip}TerP(S)(μ_2-S)(μ_2-S)P^{Dip}Ter (**5:^{Dip}Ter**) a side product of the reaction of ^{Dip}TerPPMe$_3$ with DABSO.*

ESI-TOF Accurate Mass Report Page 1

Results file: E:\Projects\2202.PRO\SampleDB\2202.rpt
Last modified: Tuesday, March 01, 2022 12:31:17

Sample Summary:

Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa
93	22021023	FDP76R1	Dankert	936.4656	C60H74OP2S2	937.4734 959.4548	937.4717 959.4538	-1.8 -1.0	-1.7 -1.0

ESI-TOF Accurate Mass Report Page 2

File:22021023
Vial:1:F,2
Description:MeOH/0,1%HCOOH in H2O 98:2

Sample Name:FDP76R1
Date:10-Feb-2022

UserName:Dankert
Time:16:14:15

Sample Report:

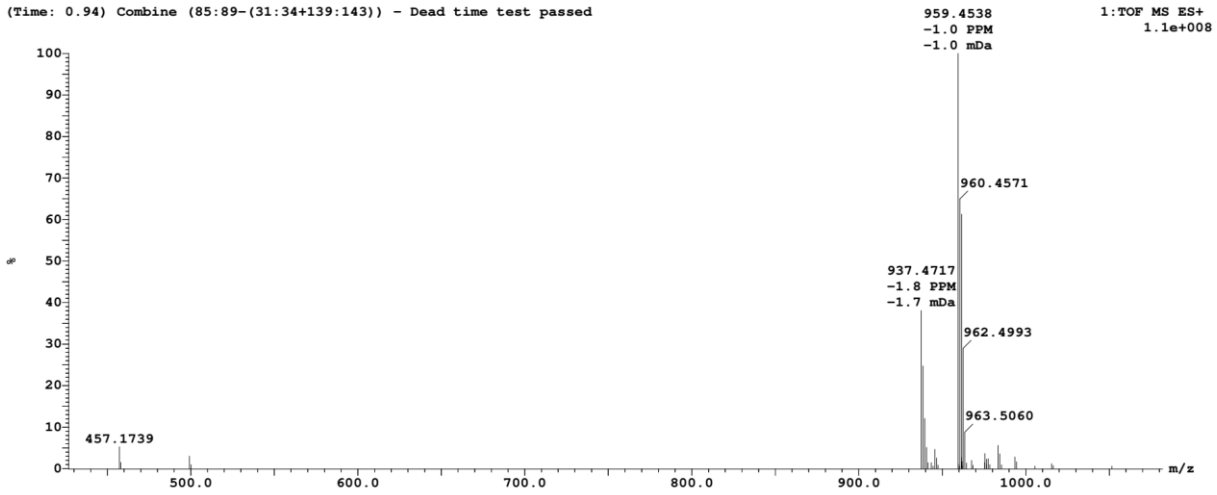


Figure S47: *ESI-TOF accurate mass for ^{Dip}TerP(O)(μ_2-S)(μ_2-S)P^{Dip}Ter (**6:^{Dip}Ter**) a side product of the reaction of ^{Dip}TerPPMe$_3$ with DABSO.*

ESI-TOF Accurate Mass Report Page 1

Results file: E:\Projects\2202.PRO\SampleDB\2202.rpt
Last modified: Tuesday, March 01, 2022 12:39:33

Sample Summary:

Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa
93	22021023	FDP76R1	Dankert	920.4885	C60H74O2P2S	921.4963 943.4777	921.4953 943.4766	-1.1 -1.2	-1.0 -1.1

ESI-TOF Accurate Mass Report Page 3

File:22021023
Vial:1:F,2
Description:MeOH/0,1%HCOOH in H2O 98:2

Sample Name:FDP76R1
Date:10-Feb-2022

UserName:Dankert
Time:16:14:15

Sample Report (continued):

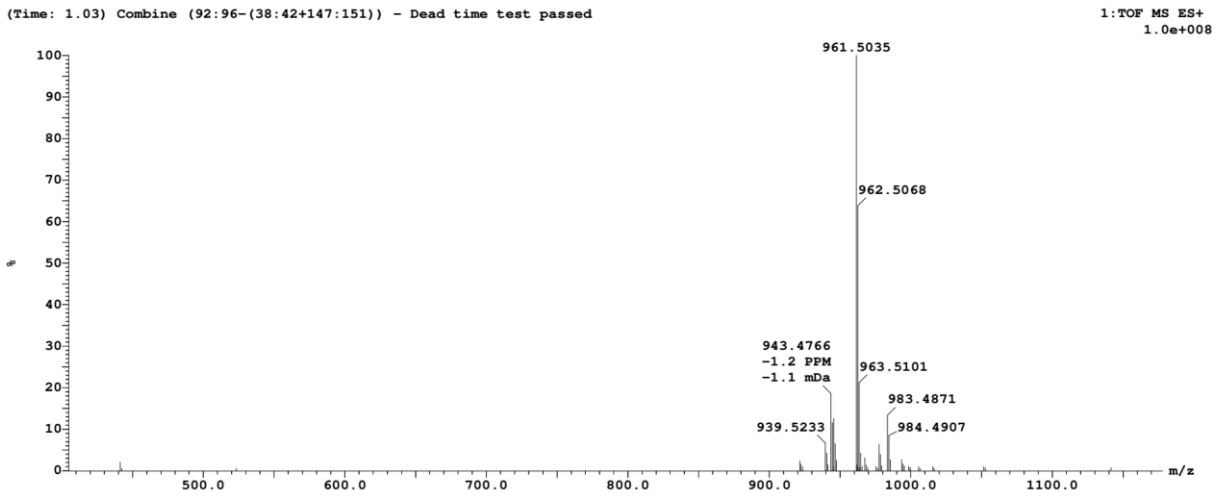


Figure S48: *ESI-TOF accurate mass for ^{Dip}TerP(S)(μ_2-O)(μ_2-O)P^{Dip}Ter or ^{Dip}TerP(O)(μ_2-S)(μ_2-O)P^{Dip}Ter a side product of the reaction of ^{Dip}TerPPMe$_3$ with DABSO.*

ESI-TOF Accurate Mass Report Page 1

Results file: E:\Projects\2202.PRO\SampleDB\2202.rpt
Last modified: Tuesday, March 01, 2022 12:34:49

Sample Summary:

Sample	File	Sample Name	User	Target	Formula	Expected Mass	Observed Mass	Error PPM	Error mDa
93	22021023	FDP76R1	Dankert	906.5270	C60H76P2O3	907.5348 929.5162	907.5341 929.5161	-0.8 -0.1	-0.7 -0.1

ESI-TOF Accurate Mass Report Page 2

File:22021023
Vial:1:F,2
Description:MeOH/0,1%HCOOH in H2O 98:2

Sample Name:FDP76R1
Date:10-Feb-2022

UserName:Dankert
Time:16:14:15

Sample Report:

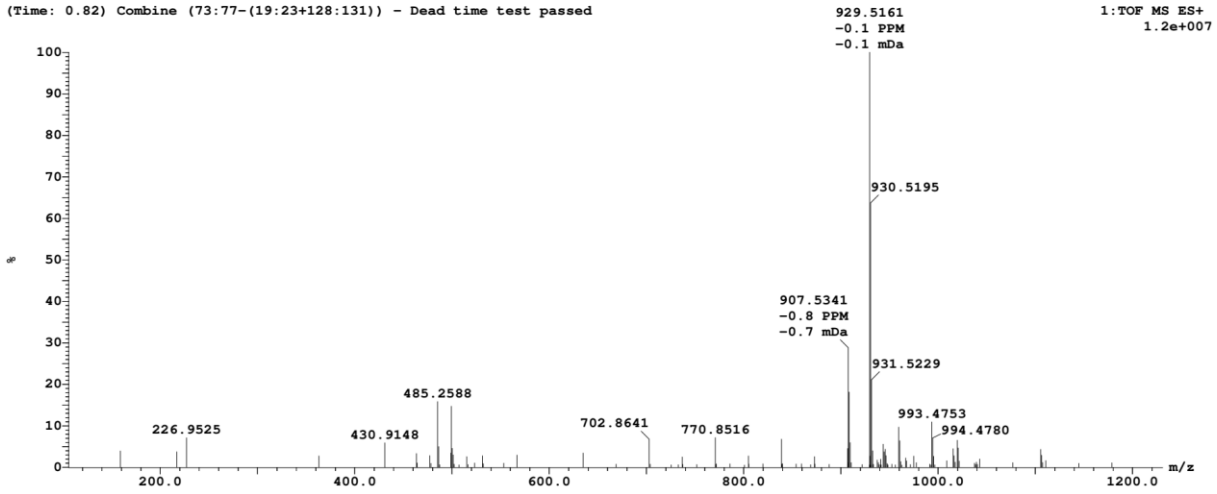
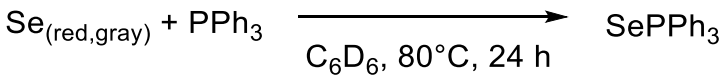


Figure S49: *ESI-TOF accurate mass for ^{Dip}TerP(OH)(μ_2-O)(OH)P^{Dip}Ter a hydrolysis product (under MS conditions) of ^{Dip}TerP(O)(μ_2-O)(μ_2-O)P^{Dip}Ter a side product of the reaction of ^{Dip}TerPPMe$_3$ with DABSO.*

3.9 Control experiments

3.9.1 Identification of elemental Se



A 0.050 g portion of of ^{Dip}TerPPMe$_3$ (0.1 mmol, 1.0 eq) together with 0.011 g of SeO_2 (0.1 mmol, 1.0 eq) are dissolved in 1.5 mL of benzene. The obtained suspension is stirred vigorously at 80°C overnight (16 h). After cooling to room temperature a reddish precipitate (Figure S44) formed. The supernatant solution was removed by canula filtration and the reddish solid was washed with three portions of n-hexane (3x 2 mL). After drying 0.0078 g (0.098 mmol, assuming full conversion to elemental selenium) of this solid were obtained. Considering that this solid mainly contained $Se_{(red)}$ and $Se_{(grey)}$ equimolar amounts of PPh_3 (0.026 g, 0.098 mmol) were added to the red solid in a J-Young NMR-tube and C_6D_6 (0.5 mL) were added. The mixture was then heated to 80 °C for 24 h, showing the formation of $SePPh_3$, $OPPh_3$ (2.3:1) and unreacted PPh_3.

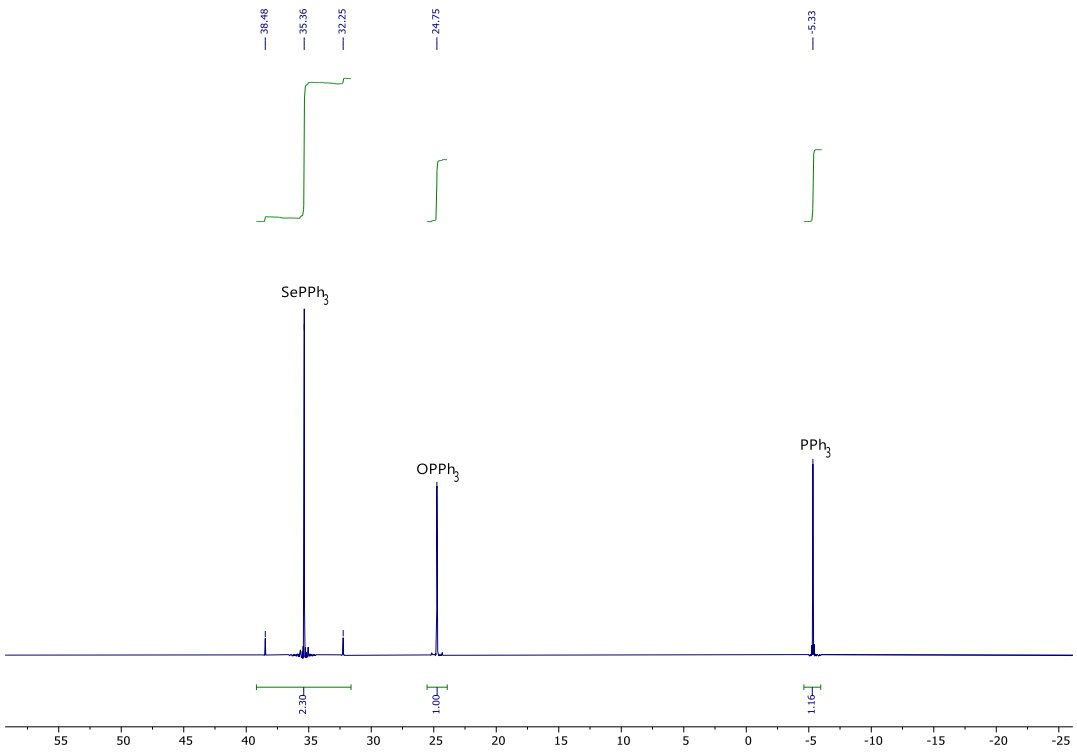
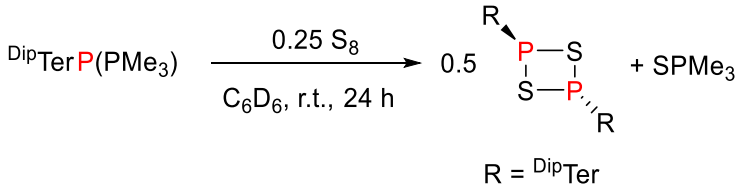


Figure S50: *$^{31}P\{^1H\}$ NMR of the reaction mixture of PPh_3 with the red residue obtained when ^{Dip}TerP(PMe$_3$) was reacted with 1 eq SeO_2 at 80 °C for 16 h* (given in ppm, C_6D_6, 122 MHz, 298K).

3.9.2 Reaction of ^{Dip}TerP(PMe$_3$) with S$_8$.



^{Dip}TerP(PMe$_3$) (0.1 mmol, 0.051 g) and S$_8$ (0.025 mmol, 0.0064 g) were combined in a J-Young NMR tube and C6D6 (0.5 mL) were added, giving a pale yellow solution, which was allowed to stand at room temperature for 24 h. ^{31}P{^{1}H} NMR spectroscopic investigations of the reaction mixture revealed the formation of [S(μ-P^{Dip}Ter)]$_2$ (δ(^{31}P) = 140.9 ppm) by comparison with the ^{31}P NMR shift reported for [S(μ-P^{Mes}Ter)]$_2$:[13] 124 ppm. Furthermore, the formation of SPMe$_3$ (δ(^{31}P) = 140.9 ppm) was noted.

When adding additional S$_8$ to the reaction mixture and heating the mixture to 80 °C for 16 h, the formation of an additional species was observed. This was assigned to ^{Dip}Ter$_2$P$_2$S$_3$: δ(^{31}P) = 38.6 ($^2J_{PP}$ = 56.6 Hz), 16.1 ($^2J_{PP}$ = 58.1 Hz) ppm.

Attempts to isolate [S(μ-P^{Dip}Ter)]$_2$ and ^{Dip}Ter$_2$P$_2$S$_3$ will the objective of an individual study.

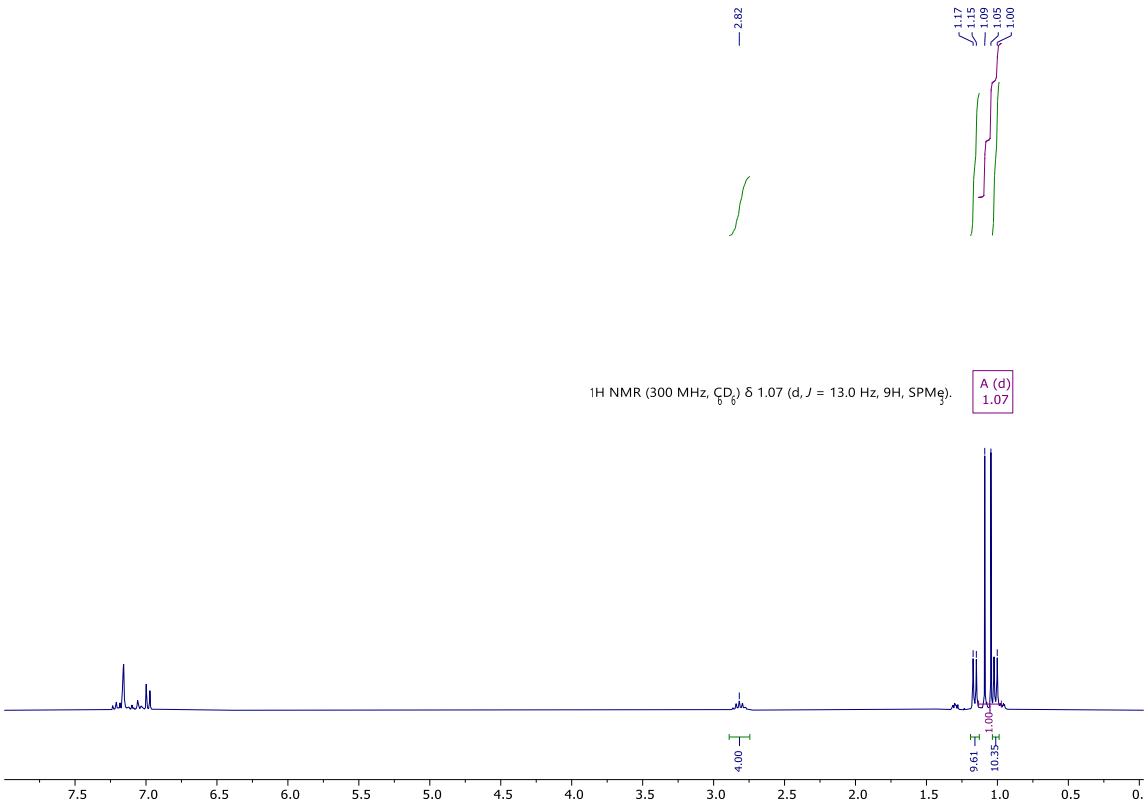


Figure S51: *^{1}H NMR of the reaction mixture of ^{Dip}TerP(PMe$_3$) with 0.25 eq S_8* (given in ppm, C_6D_6, 300 MHz, 298K).

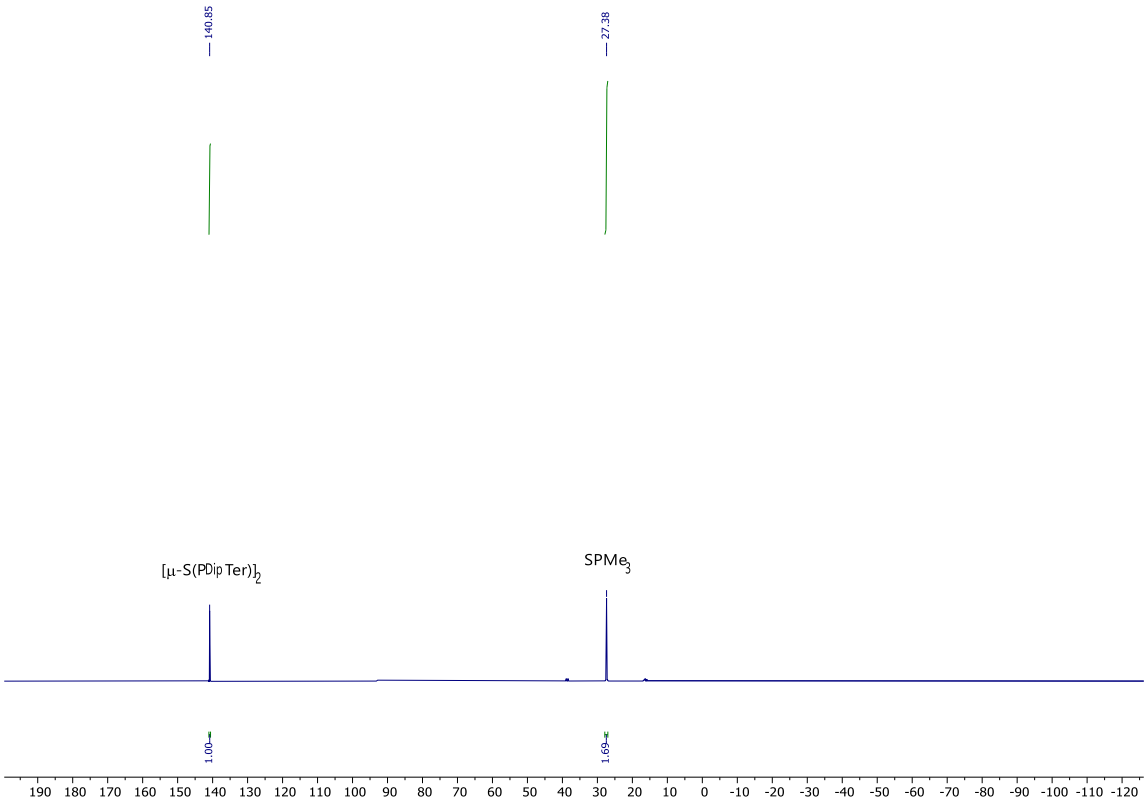


Figure S52: *$^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture of ^{Dip}TerP(PMe$_3$) with 0.25 eq S_8* (given in ppm, C_6D_6, 300 MHz, 298K).

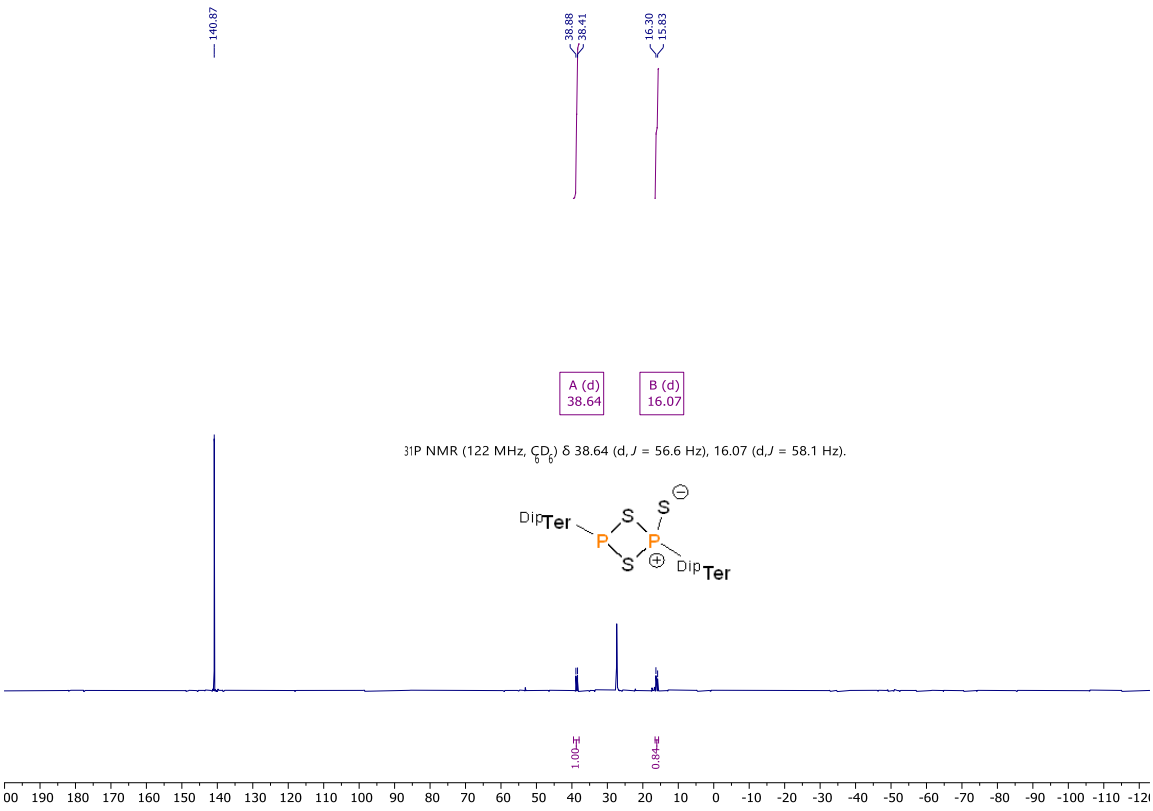
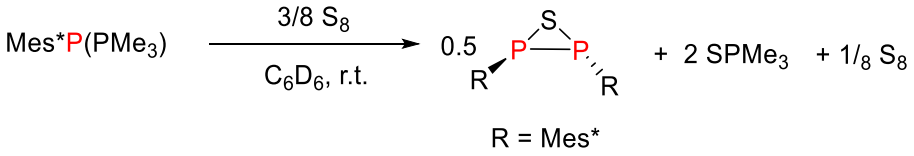


Figure S53: *$^{31}P\{^1H\}$ NMR spectrum of the reaction mixture of ^{Dip}TerP(PMe$_3$) with 0.25 eq S_8 after addition of an excess S_8* (given in ppm, C_6D_6, 300 MHz, 298K).

3.9.3 Reaction of Mes*P(PMe$_3$) with S_8.



Mes*P(PMe$_3$) (0.05 mmol, 0.018 g) and S_8 (0.019 mmol, 0.004.8 g) were combined in a J-Young NMR tube and C_6D_6 (0.5 mL) was added, giving a pale yellow solution immediately. $^{31}P\{^1H\}$ NMR spectroscopic investigations of the reaction mixture revealed the formation of **1:Mes*** as the major product and Mes*PS$_2$ ($\delta(^{31}P)$ = 296.3 ppm)[14] was identified as minor component. Furthermore, the formation of SPMe$_3$ ($\delta(^{31}P)$ = 27.2 ppm) was noted.

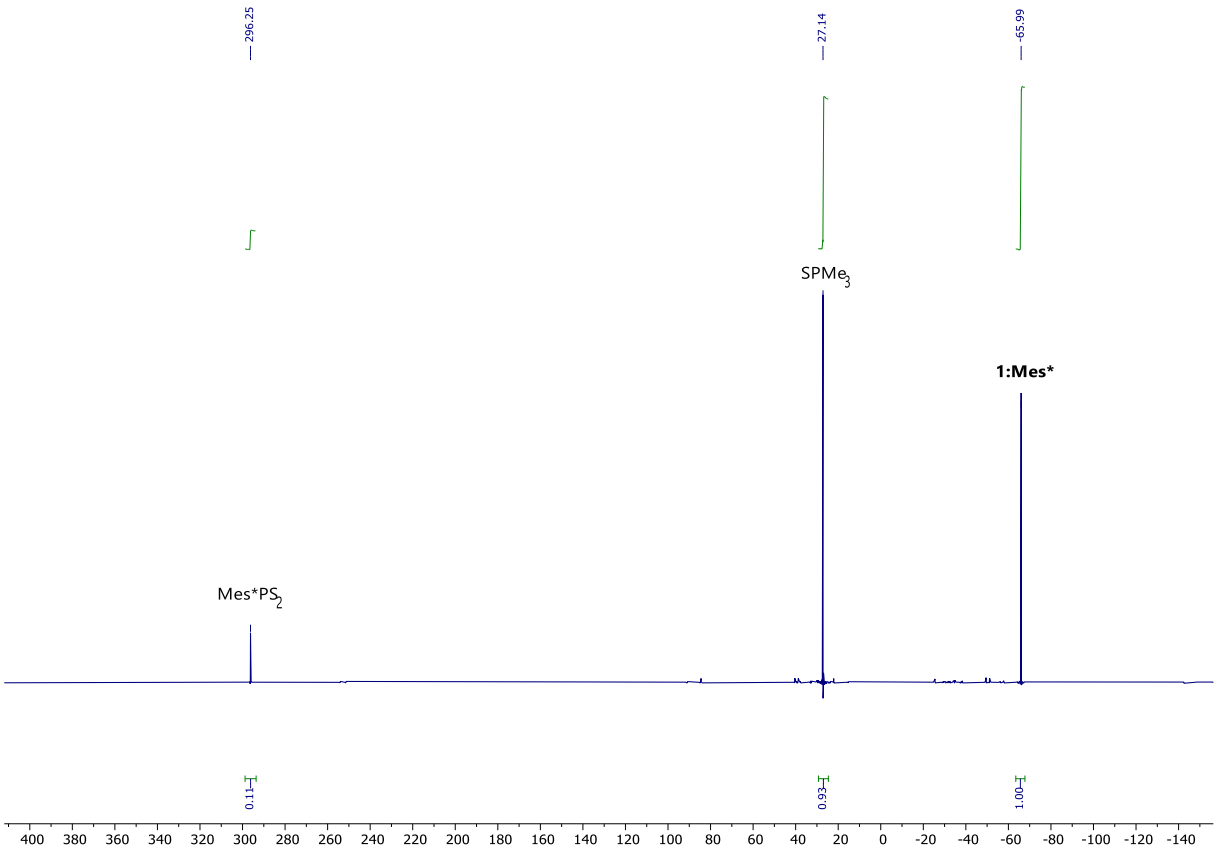


Figure S54: *$^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture of Mes*P(PMe$_3$) with 0.375 eq S_8* (given in ppm, C_6D_6, 300 MHz, 298K).

4 Computational Details

Computations were carried out using Gaussian16[15] and the standalone version of NBO 6.0.[16–19]

Structure optimizations employed the hybrid DFT functional PBE0[20–22] in conjunction with Grimme's dispersion correction D3(BJ)[23,24] and the def2-SVP basis set[25] (notation PBE0-D3/def2-SVP). All structures were fully optimized and confirmed as minima by frequency analyses. Partial charges were determined by Natural Population analysis using the NBO program.

Chemical shifts and coupling constants were derived by the GIAO method[26-29] using Gaussian16. The calculated absolute ^{77}Se shifts ($\sigma_{calc,X}$) were referenced to the calculated isotropic shieldings of Me_2Se at the PBE0-D3/def2-TZVP//PBE0-D3/def2-SVP level of theory.

$$\delta_{calc,Se} = \sigma_{Me_2Se} - \sigma_{calc,Se}$$

At the PBE0-D3/def2-TZVP//PBE0-D3/def2-SVP level of theory, σ_{Me_2Se} amounts to +1827.9 ppm.

The calculated absolute ^{31}P shifts ($\sigma_{calc,X}$) were referenced to the experimental absolute shift of 85% H_3PO_4 in the gas phase ($\sigma_{ref,1}$ = 328.35 ppm),[30] using PH_3 ($\sigma_{ref,2}$ = 594.45 ppm) as a secondary standard:[31]

$$\begin{aligned}\delta_{calc,X} &= (\sigma_{ref,1} - \sigma_{ref,2}) - (\sigma_{calc,X} - \sigma_{calc,PH_3}) \\ &= \sigma_{calc,PH_3} - \sigma_{calc,X} - 266.1 \text{ ppm}\end{aligned}$$

At the PBE0-D3/def2-TZVP//PBE0-D3/def2-SVP level of theory, σ_{calc,PH_3} amounts to +567.77 ppm.

Please note that all computations were carried out for single, isolated molecules in the gas phase (ideal gas approximation). There may well be significant differences between gas phase and condensed phase/solution.

4.1 Summary of calculated data

Table S5. Summary of calculated data at the PBE0-D3/def2-SVP level of theory, including electronic energies.

Compd.	NIMAG	ZPE [kcal·mol^{-1}]	E_{tot}[a]	H_{tot}[a]	G_{tot}[a]
2:Mes*	0	539.42766	-4487.4285	-4486.5210	-4486.6463
2:^{Mes}Ter	0	528.30582	-4939.2018	-4938.3057	-4938.4491
3:^{Dip}Ter	0	745.91134	-7811.0745	-7809.8157	-7809.9925
4:^{Dip}Ter	0	452.82501	-2190.5271	-2189.7625	-2189.8783
[Se(μ-P^{Mes}Ter)]$_2$	0	529.00229	-7340.19903	-7339.2999	-7339.4467
Mes*PSO (linear)	0	272.21838	-1516.17836	-1515.7187	-1515.7988
Mes*P(S)O	0	273.22895	-1516.2605	-1515.7998	-1515.8768
^{Dip}Ter$_2$P$_2$S$_3$	0	749.38692	-4202.9394	-4201.6753	-4201.8478
^{Dip}Ter$_2$P$_2$S$_2$O (μ-S$_2$)	0	750.37338	-3880.0941	-3878.8284	-3879.0021
Me$_2$Se	0	46.70634	-2480.6389	-2480.5583	-2480.5923

[a] Total SCF energy in a.u

4.2 Summary of calculated NMR shifts

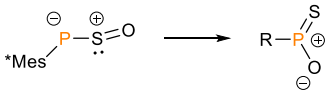
Table S6. Summary of calculated NMR data.

Compd.	$\sigma_{calc,P}$	$\delta_{calc,P}$[a]	$\sigma_{calc,Se}$	$\delta_{calc,Se}$[a]
2:Mes*	326.9	-25.2	1792.3	35.5
2:^{Mes}Ter	389.3	-87.6	1926.0	-98.1
3:^{Dip}Ter	234.4	67.3	1926.1	-98.3
4:^{Dip}Ter	264.4, 222.1	79.6, 37.2	-	-
Mes*PSO (linear)	-281.7	583.4	-	-
Mes*P(S)O	51.4	250.3	-	-
Mes*PS_2	-47.7	349.4	-	-
$^{Dip}Ter_2P_2S_3$	272.3, 242.4	59.3, 29.4	-	-
$^{Dip}Ter_2P_2S_2O$ (μ-S_2)	271.6, 279.6	30.0, 22.1	-	-
[Se(μ-P^{Mes}Ter)]$_2$	**248.3**	53.3	1426.8	401.0
Me_2Se	-	-	1827.9	0

[a] values in ppm

4.3 Thermodynamic Considerations

Isomerisation of Mes*PSO to Mes*P(S)O:



$\Delta_R G°_{298}$ = −204.6 kJ/mol ($\Delta_R H°_{298}$ = −212.8 kJ/mol)

4.4 Bonding and NBO Analysis

The electronic structure of **4:^{Dip}Ter** was investigated using the full model.

NBO analyses were carried out on the PBE0-D3/def2-TZVP//PBE0-D3/def2-SVP level of theory and additionally Wiberg-Bond-Indices (WBI) were determined and NLMOs

(Natural localized molecular orbitals) were calculated. The results of this natural bond orbital analysis is summarized below.

Summary of NBO results for **4:^{Dip}Ter**:

NPA Charges

P1 2.347

P2 1.977

O3 -1.050

C41 -1.038

H42 0.292

H43 0.248

H44 0.301

C57 -1.021

H58 0.281

H59 0.252

H60 0.269

C61 -1.036

H62 0.302

H 63 0.251

H 64 0.271

$\Sigma(OPMe_3)$ = 0.3 e

WBIs

P1-O3 0.454

Bonding

150. (0.54969) LV (1) P 1 s(4.42%)p21.57(95.32%)d 0.06(0.25%)

47. (1.93557) LP (1) O 3 s(43.04%)p 1.32(56.79%)d 0.00(0.17%)

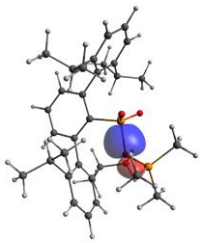
48. (1.88909) LP (2) O 3 s(0.24%)p99.99(99.53%)d 0.93(0.22%)

49. (1.68655) LP (3) O 3 s(26.34%)p 2.79(73.46%)d 0.01(0.20%)

2nd order perturbation [kcal/mol]

49. LP (3) O 3 150. LV (1) P 1 239.03

Figure S55. Selected NLMOs of **4:^{Dip}Ter** (PBE0/def2-TZVP).



LP3 (O3)
−20.3 eV
P1: 15.8%
O3: 82.2%

s: 26.8%
p: 73.0%

4.5 Optimized structures (.xyz-files)

4.5.1 Mes*P(Se)PMes* (2:Mes*)

```
97
2:Mes* @ PBE0-D3/def2-SVP
Se         -0.00006        1.58231       -0.00104
P          -0.39431       -0.39508        1.05988
C          -2.26341       -0.40632        0.80914
C          -2.94526       -1.34573       -0.00564
C          -2.99289        0.72470        1.28574
C          -4.75306        0.26812       -0.36712
C          -4.14531       -0.95576       -0.61480
H          -4.61653       -1.65124       -1.30731
C          -4.19376        1.04017        0.65178
H          -4.72454        1.93805        0.97260
C          -2.53311       -2.81571       -0.20928
C          -2.01610       -3.05097       -1.63431
H          -2.81168       -2.85293       -2.36867
H          -1.68721       -4.09442       -1.76400
H          -1.17857       -2.38474       -1.87973
C          -2.67008        1.59308        2.52985
C          -6.00895        0.74559       -1.09375
C          -1.52517       -3.27051        0.84409
H          -0.57422       -2.72848        0.80077
H          -1.28261       -4.33545        0.70633
H          -1.93479       -3.13942        1.85727
C          -3.76986       -3.71077        0.00530
H          -4.23247       -3.51962        0.98547
H          -3.46455       -4.76843       -0.02954
H          -4.53885       -3.57021       -0.76641
C          -7.15478        0.91250       -0.08537
```

```
H          -7.38034       -0.04258        0.41343
H          -8.06848        1.25834       -0.59479
H          -6.90936        1.64842        0.69464
C          -5.70728        2.09598       -1.75993
H          -5.41108        2.85576       -1.02153
H          -6.59623        2.47103       -2.29204
H          -4.88563        1.99928       -2.48586
C          -1.45593        1.16246        3.35871
H          -1.47695        0.08661        3.59006
H          -1.47521        1.70460        4.31728
H          -0.49517        1.39705        2.88223
C          -6.45441       -0.23937       -2.17502
H          -5.66714       -0.39954       -2.92739
H          -7.34017        0.15435       -2.69645
H          -6.72888       -1.21729       -1.75063
C          -3.87941        1.45240        3.47933
H          -4.81621        1.80529        3.02737
H          -3.70595        2.04125        4.39388
H          -4.02406        0.40066        3.77048
C          -2.50470        3.07166        2.15321
H          -1.64804        3.21950        1.48007
H          -2.33578        3.67592        3.05861
H          -3.39629        3.46903        1.64681
P           0.39453       -0.39578       -1.06050
C           2.26357       -0.40676       -0.80929
C           2.94511       -1.34587        0.00606
C           2.99322        0.72411       -1.28599
C           4.75269        0.26813        0.36778
C           4.14489       -0.95568        0.61562
H           4.61583       -1.65092        1.30857
C           4.19382        1.03982       -0.65164
H           4.72472        1.93759       -0.97255
C           2.53295       -2.81581        0.20987
C           2.01572       -3.05086        1.63487
H           2.81118       -2.85278        2.36934
H           1.68675       -4.09427        1.76463
H           1.17817       -2.38455        1.88005
C           2.67093        1.59206       -2.53054
C           6.00825        0.74591        1.09480
C           1.52512       -3.27074       -0.84354
H           0.57418       -2.72869       -0.80040
H           1.28253       -4.33566       -0.70561
H           1.93487       -3.13985       -1.85669
C           3.76978       -3.71083       -0.00446
H           4.23229       -3.51999       -0.98474
H           3.46461       -4.76852        0.03080
H           4.53883       -3.56987        0.76712
C           7.15449        0.91261        0.08687
H           7.38033       -0.04259       -0.41157
H           8.06795        1.25866        0.59658
H           6.90936        1.64830       -0.69345
C           5.70619        2.09647        1.76047
H           5.41025        2.85601        1.02173
H           6.59489        2.47173        2.29286
H           4.88423        1.99991        2.48608
C           1.45694        1.16139       -3.35960
H           1.47775        0.08544       -3.59047
H           1.47668        1.70310       -4.31841
H           0.49608        1.39645       -2.88356
C           6.45332       -0.23871        2.17655
```

```
H           5.66574       -0.39874        2.92862
H           7.33883        0.15523        2.69825
H           6.72805       -1.21673        1.75255
C           3.88049        1.45078       -3.47962
H           4.81724        1.80363       -3.02751
H           3.70742        2.03934       -4.39444
H           4.02499        0.39890       -3.77035
C           2.50575        3.07083       -2.15450
H           1.64916        3.21903       -1.48136
H           2.33688        3.67475       -3.06013
H           3.39743        3.46829       -1.64832
```

4.5.2 ^{Mes}TerP(Se)P^{Mes}Ter (2:^{Mes}Ter)

```
101
2:MesTer @ PBE0-D3/def2-SVP
Se          0.52084       -0.24768       -1.96254
P           1.11943        0.17292        0.20265
P          -1.02134       -0.19755       -0.27475
C           2.35603        2.56809       -0.40385
C           3.39752        1.65587       -0.95704
C           4.25828        0.97010       -0.07801
C           0.24079        2.90373        0.76466
C           3.51268        1.47300       -2.34921
C           1.60861        4.81111        0.11286
H           1.76902        5.89162        0.09047
C          -3.44982       -1.38529       -1.25488
C           1.17828        2.03374        0.17333
C          -0.96881        2.45493        1.51011
C          -2.57931       -2.40111       -0.59353
C           2.55268        3.94918       -0.43757
H           3.46731        4.34189       -0.88892
C           0.47153        4.28646        0.71417
H          -0.26083        4.95173        1.17887
C           5.26193       -0.19093       -1.97615
C           5.17274        0.05548       -0.60551
H           5.83679       -0.47984        0.08010
C           4.43656        0.54369       -2.83125
H           4.51178        0.38794       -3.91172
C          -3.34597       -1.15401       -2.63809
C          -0.55291       -2.97856        0.63344
C          -2.25017        2.63463        0.95446
C           1.91822       -1.81184        3.23527
H           1.89885       -1.36516        4.23412
C          -0.82694        1.94045        2.81272
C           0.73265       -2.66421        1.31346
C          -3.25612        1.79758        3.01657
C           1.95719       -2.96731        0.69114
C          -4.12610       -0.14691       -3.21137
H          -4.03408        0.04486       -4.28462
C          -1.34341       -2.01235       -0.02293
C           2.66971        2.26952       -3.30380
H           1.61553        2.28708       -2.99006
H           2.72137        1.85117       -4.31879
H           3.01007        3.31658       -3.35449
C          -1.97420        1.61839        3.54134
H          -1.86057        1.22509        4.55626
C          -4.36437       -0.65158       -0.47526
```

```
C          0.53241        1.73501        3.41718
H          0.45716        1.51029        4.49032
H          1.17158        2.62137        3.28901
H          1.06110        0.89180        2.94093
C         -3.36950        2.30408        1.72086
H         -4.36253        2.43738        1.28267
C          3.14889       -2.09074        2.63375
C          0.70822       -2.09115        2.59831
C          6.20174       -1.22987       -2.51503
H          7.07463       -1.36514       -1.85985
H          6.56348       -0.96765       -3.52002
H          5.69735       -2.20785       -2.59533
C         -2.41786        3.12124       -0.45476
H         -3.47870        3.14218       -0.73931
H         -1.89566        2.44976       -1.15567
H         -1.99602        4.12721       -0.59901
C         -2.99493       -3.73294       -0.52934
H         -3.95065       -4.01005       -0.98145
C          4.19268        1.19812        1.40354
H          4.03130        2.25813        1.64625
H          5.11654        0.86205        1.89374
H          3.35759        0.62858        1.84631
C         -2.42103       -1.98054       -3.48338
H         -2.78715       -3.01610       -3.57368
H         -1.41488       -2.04372       -3.04053
H         -2.32807       -1.56402       -4.49583
C         -5.01352        0.62002       -2.45387
C          3.14462       -2.66384        1.36196
H          4.09653       -2.87787        0.86774
C         -5.13036        0.33902       -1.08992
H         -5.83783        0.91213       -0.48274
C         -4.46936        1.43707        3.82371
H         -4.53678        0.34709        3.97435
H         -5.39476        1.76257        3.32794
H         -4.43849        1.89936        4.82254
C         -4.48292       -0.91291        0.99630
H         -3.56090       -0.61340        1.52140
H         -4.63824       -1.98185        1.20583
H         -5.31422       -0.34484        1.43507
C          4.43642       -1.81978        3.35614
H          4.68065       -2.64485        4.04611
H          4.37812       -0.90000        3.95667
H          5.27729       -1.71860        2.65516
C         -0.59606       -1.75245        3.25834
H         -0.44455       -1.44666        4.30291
H         -1.29245       -2.60424        3.24027
H         -1.10115       -0.91982        2.74157
C         -1.00250       -4.30375        0.68650
H         -0.38324       -5.04054        1.20472
C         -5.79971        1.73596       -3.07822
H         -6.78654        1.84953       -2.60569
H         -5.95092        1.57254       -4.15493
H         -5.27089        2.69764       -2.96450
C         -2.20733       -4.68635        0.10675
H         -2.53566       -5.72714        0.15925
C          1.99783       -3.57130       -0.68199
H          1.51963       -4.56276       -0.70409
H          3.03364       -3.68033       -1.03210
H          1.45847       -2.93499       -1.40096
```

4.5.3 [Se(μ-P^{Dip}Ter)]$_2$ (3:^{Dip}Ter)

```
138
[Se(μ-P^DipTer)]2 @ PBE0-D3/def2-SVP
C     11.0294352512     7.3332389383     9.1765217462
 C     11.3750554821     6.1965542901     9.9481356067
 C     12.2550209437     6.3339449233     11.0235807005
 H     12.4895853078     5.4553511297     11.6280622687
 C     12.8000998324     7.5728606251     11.3473266097
 H     13.4839630496     7.6690153458     12.1936289535
 C     12.4433417249     8.6909979578     10.6047646142
 H     12.84081564     9.6755182852     10.8635091859
 C     11.5497065635     8.5954969285     9.5298538787
 C     10.743791394     4.865873502     9.6793532587
 C     11.4640512548     3.8473957816     9.0074328862
 C     10.8303815348     2.6232765748     8.7760496241
 H     11.3670880267     1.8331156901     8.2485088731
 C     9.5210379138     2.4027235126     9.1864076458
 H     9.039762604     1.4429151628     8.9825836574
 C     8.8256295584     3.4001055447     9.8579035745
 H     7.8029943331     3.2124718661     10.191151457
 C     9.4204774948     4.6369729826     10.1255631834
 C     12.9053040098     4.0473499884     8.5687244366
 H     13.0535541937     5.1323543764     8.4420640046
 C     13.2366607688     3.3781231483     7.2365222329
 H     13.2530996526     2.2799820176     7.3231504849
 H     14.2372839084     3.6890085556     6.8992760161
 H     12.5143240286     3.6487729329     6.4542039368
 C     13.8746500464     3.5536482668     9.6463396386
 H     13.7237374691     4.0647267397     10.6061643017
 H     14.9176839739     3.721476819     9.3347872295
 H     13.7421954821     2.4733567805     9.8182604547
 C     8.6821928129     5.658115333     10.9738947403
 H     9.1525626047     6.6374098131     10.8001737947
 C     8.8696322829     5.3290097674     12.4564012276
 H     8.4322356045     4.3474324245     12.6999466864
 H     8.3809961209     6.086587094     13.0895072244
 H     9.9362245068     5.2970608015     12.7246820629
 C     7.2075712369     5.7995877555     10.612753636
 H     7.0862137093     6.0278113416     9.5438970059
 H     6.7540244907     6.619658679     11.1906579115
 H     6.6335463462     4.8879248402     10.8416830665
 C     11.1599956015     9.8620365379     8.8434655972
 C     9.9073808938     10.449837956     9.1207482843
 C     9.5702815739     11.6451886993     8.4745785443
 H     8.6025485522     12.1109714706     8.6750930013
 C     10.4500743753     12.2497532969     7.5854685675
 H     10.16942448     13.1805727029     7.0865761679
 C     11.6848375148     11.664976703     7.3257975548
 H     12.360966094     12.1342743355     6.607286484
 C     12.0559153243     10.4663933127     7.9366887708
 C     8.9434030437     9.8469120842     10.1274070017
 H     9.3048474523     8.8362321221     10.370447901
 C     8.9621374415     10.648414528     11.4293047264
 H     9.9784428174     10.6963355688     11.8485766801
 H     8.3021191941     10.1888349904     12.1820572232
 H     8.6189888636     11.6822917967     11.2631483111
 C     7.5278795545     9.6975351147     9.5745452207
 H     7.066334067     10.6725942641     9.3526570138
```

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H     6.882922915     9.1862007993     10.3056193288
H     7.5219588038     9.1013856095     8.6488200511
C     13.3734682562     9.8123757467     7.5641961491
H     13.3952334245     8.8230645333     8.0458469856
C     13.4834519953     9.5778036096     6.0578695015
H     12.6240781155     9.0030427303     5.6839200744
H     14.4026489936     9.0189603869     5.821683298
H     13.5170246238     10.5246081995     5.4961090528
C     14.5622076013     10.6116239606     8.0961102284
H     14.5910348382     11.6216144731     7.6562080744
H     15.511848342     10.1113225583     7.8489656659
H     14.5126222849     10.7273038275     9.1894420196
P     9.617713402     7.0808410786     8.0005775143
Se     10.405046436     5.502194365     6.5315218295
C     9.1004177488     6.847042761     3.6987173027
C     8.7547975179     7.9837274091     2.9271034422
C     7.8748320563     7.846336776     1.8516583484
H     7.6402676922     8.7249305695     1.2471767802
C     7.3297531676     6.6074210741     1.5279124391
H     6.6458899504     6.5112663534     0.6816100954
C     7.6865112751     5.4892837415     2.2704744346
H     7.28903736     4.504763414     2.011729863
C     8.5801464365     5.5847847707     3.3453851701
C     9.386061606     9.3144081972     3.1958857902
C     8.6658017452     10.3328859176     3.8678061627
C     9.2994714652     11.5570051245     4.0991894248
H     8.7627649733     12.3471660092     4.6267301758
C     10.6088150862     11.7775581867     3.6888314031
H     11.090090396     12.7373665364     3.8926553915
C     11.3042234416     10.7801761546     3.0173354744
H     12.3268586669     10.9678098332     2.6840875918
C     10.7093755052     9.5433087166     2.7496758654
C     7.2245489902     10.1329317108     4.3065146123
H     7.0762988063     9.0479273228     4.4331750443
C     6.8931922312     10.8021585509     5.638716816
H     6.8767533474     11.9002996816     5.552088564
H     5.8925690916     10.4912731437     5.9759630327
H     7.6155289714     10.5315087663     6.4210351121
C     6.2552029536     10.6266334325     3.2288994102
H     6.4061155309     10.1155549595     2.2690747472
H     5.2121690261     10.4588048802     3.5404518193
H     6.3876575179     11.7069249187     3.0569785941
C     11.4476601871     8.5221663662     1.9013443086
H     10.9772903953     7.5428718862     2.0750652542
C     11.2602207171     8.8512719319     0.4188378213
H     11.6976173955     9.8328492748     0.1752923624
H     11.7488568791     8.0936946052     -0.2142681755
H     10.1936284932     8.8832208977     0.1505569859
C     12.9222817631     8.3806939438     2.2624854129
H     13.0436392907     8.1524703576     3.331342043
H     13.3758285093     7.5606230203     1.6845811374
H     13.4963066538     9.2923568591     2.0335559824
C     8.9698573985     4.3182451613     4.0317734516
C     10.2224721062     3.7304437433     3.7544907646
C     10.5595714261     2.5350929999     4.4006605046
H     11.5273044478     2.0693102287     4.2001460476
C     9.6797786247     1.9305284024     5.2897704813
H     9.96042852     0.9997089964     5.788662881
C     8.4450154852     2.5153049963     5.549441494
H     7.768886906     2.0460073637     6.2679525648
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C      8.0739376757     3.7138883865     4.938550278
C     11.1864499563     4.3333696151     2.7478320472
H     10.8250055477     5.3440495772     2.5047911479
C     11.1677155585     3.5318671713     1.4459343225
H     10.1514101826     3.4839461305     1.0266623688
H     11.8277338059     3.9914467089     0.6931818257
H     11.5108641364     2.4979899025     1.6120907377
C     12.6019734455     4.4827465845     3.3006938281
H     13.063518933      3.5076874351     3.522582035
H     13.246930085      4.9940808999     2.5696197201
H     12.6078941962     5.0788960897     4.2264189977
C     6.7563847438      4.3679059525     5.3110428997
H     6.7346195755      5.3572171659     4.8293920633
C     6.6464010047      4.6024780896     6.8173695474
H     7.5057748845      5.177238969      7.1913189745
H     5.7272040064      5.1613213124     7.0535557509
H     6.6128283762      3.6556734998     7.3791299961
C     5.5676453987      3.5686577386     4.7791288205
H     5.5388181618      2.5586672262     5.2190309745
H     4.618004658       4.068959141      5.0262733829
H     5.6172307151      3.4529778718     3.6857970292
P     10.512139598      7.0994406207     4.8746615346
Se     9.724806564      8.6780873342     6.3437172194
```

4.5.4 ^{Dip}TerPO$_2$(OPMe$_3$) (3:^{Dip}Ter)

```
84
DipTerPO2(OPMe3) @ PBE0-D3/def2-SVP
P           0.24844       -0.18552        1.06303
P          -2.09585       -0.07909        2.70676
O          -1.50326       -0.37504        1.28263
O           0.47285        1.12817        1.76484
O           0.76810       -1.49642        1.55826
C           2.89828        0.03151       -0.26545
C          -0.64469       -0.07165       -1.70154
C           3.56449       -1.15132        0.11243
C           1.74180       -0.03854       -1.21068
C          -2.08812        0.00472       -1.33227
C           0.40130       -0.07731       -0.75717
C          -2.84527       -1.17297       -1.18358
C           3.32598        1.29115        0.20171
C           4.68458       -1.04899        0.94067
H           5.21433       -1.95501        1.24336
C           0.97755       -0.06641       -3.51229
H           1.19874       -0.06952       -4.58219
C           4.45005        1.34689        1.03029
H           4.79863        2.31352        1.40023
C          -0.33786       -0.07969       -3.06949
H          -1.16273       -0.08148       -3.78633
C           2.01045       -0.02993       -2.58141
H           3.05167        0.00717       -2.90937
C          -2.67309        1.27542       -1.15862
C           5.12771        0.18878        1.39331
H           6.00494        0.25059        2.04265
C           3.10132       -2.50776       -0.38357
H           2.07181       -2.38024       -0.75102
C           2.62272        2.56879       -0.21803
H           1.61637        2.28691       -0.56210
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C          -2.23212       -2.54220       -1.41700
H          -1.24363       -2.38083       -1.87334
C          -1.88921        2.55065       -1.42298
H          -0.95272        2.25528       -1.91879
C          -4.18386       -1.06040       -0.79679
H          -4.78790       -1.96375       -0.67664
C          -4.75935        0.18578       -0.56261
H          -5.80841        0.25677       -0.26163
C          -4.00958        1.34398       -0.75120
H          -4.48031        2.32017       -0.60613
C          -0.98057       -0.58589        4.01768
H          -0.61600       -1.59748        3.79038
H          -1.49450       -0.54830        4.98910
H          -0.11574        0.09248        3.99464
C           3.04084       -3.55010        0.72895
H           2.60982       -4.48826        0.34422
H           2.40388       -3.18072        1.54358
H           4.04024       -3.79111        1.12581
C          -3.05642       -3.36823       -2.40335
H          -2.54050       -4.31203       -2.63851
H          -3.21903       -2.82351       -3.34583
H          -4.04529       -3.63015       -1.99381
C          -1.99831       -3.30091       -0.10908
H          -2.94338       -3.43283        0.44487
H          -1.27833       -2.77847        0.53606
H          -1.59479       -4.30410       -0.31851
C          -3.60403       -1.03984        2.80045
H          -4.23678       -0.76316        1.94457
H          -4.12970       -0.84741        3.74641
H          -3.34719       -2.10533        2.72050
C          -2.47996        1.65796        2.89268
H          -1.52970        2.19967        2.78036
H          -2.93187        1.85166        3.87602
H          -3.16787        1.95173        2.08777
C           3.96754       -2.98020       -1.55193
H           5.01626       -3.10727       -1.23750
H           3.95530       -2.25926       -2.38312
H           3.61086       -3.94891       -1.93735
C           2.43017        3.54660        0.93641
H           3.38727        3.95325        1.30058
H           1.91050        3.04376        1.76324
H           1.81918        4.40265        0.60800
C          -2.63023        3.48026       -2.38233
H          -3.55677        3.87734       -1.93745
H          -2.90226        2.96175       -3.31427
H          -1.99807        4.34325       -2.64308
C           3.35124        3.21904       -1.39504
H           2.82405        4.12726       -1.72925
H           3.42262        2.53292       -2.25240
H           4.37654        3.50718       -1.11150
C          -1.49488        3.27009       -0.13464
H          -0.90549        4.17160       -0.36557
H          -0.87939        2.62642        0.51153
H          -2.38598        3.59580        0.42798
```

4.5.5 [Se(μ-P^{Mes}Ter)]$_2$

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[Se(μ-P^{Mes}Ter)]$_2$ @ PBE0-D3/def2-SVP

Se	3.9780682278	9.8616932129	6.1182561905
P	5.8672151478	10.7863549392	5.1397966233
P	5.5107363122	9.0292175262	7.6390884928
Se	6.8792692442	10.854719334	7.2197119737
C	5.3989558441	12.5350082131	4.7460117423
C	4.7855502463	9.3453002549	9.3142831471
C	4.2853216474	12.7316252202	3.8962656865
C	6.2209313338	13.6345869921	5.0724041576
C	3.4074562408	9.2082472607	9.5850162878
C	5.6888741919	9.5122880487	10.3899486846
C	3.9786398299	14.0146517832	3.4368010442
C	3.4313080333	11.5918557828	3.4585313627
C	5.8827029286	14.9066480872	4.5911225218
C	7.4757028691	13.5361174483	5.87152532
C	2.9598477937	9.2958698106	10.910214622
C	2.3728864177	8.9260504394	8.5492719749
C	5.2055065487	9.5962204211	11.6978523944
C	7.1600073239	9.5842424565	10.1649838238
H	3.1132542177	14.1437256046	2.7816250337
C	4.7694454579	15.1045521666	3.7843526024
C	2.1518377253	11.4201061294	4.0280647746
C	3.8806835889	10.7174934006	2.4483698392
H	6.531365669	15.747589834	4.8500481101
C	7.5080805866	14.0611383411	7.1802101839
C	8.6499498664	13.0160956249	5.2892497031
H	1.8897639116	9.1843345889	11.1037816095
C	3.8441494521	9.4937770373	11.9629343623
C	1.4542973447	9.9353008162	8.1929196351
C	2.2470468673	7.6314263869	8.0048454153
H	5.9212591462	9.7258580743	12.5137580591
C	7.8200954421	10.8276204406	10.2605754854
C	7.8946677827	8.4099454693	9.9038013558
H	4.529506958	16.1029486809	3.4114799077
C	1.3719691258	10.3361800173	3.6222124221
C	1.6381131655	12.3773337424	5.0642085173
C	3.06708258	9.6439994487	2.0787653387
C	5.1934009744	10.9394827227	1.7515062966
C	8.7162855736	14.060873025	7.878333144
C	6.2521741498	14.55375284	7.8361593958
C	9.8341389895	13.0289102831	6.0300721481
C	8.6452293025	12.4580401594	3.8948735742
H	3.4751774071	9.5489117218	12.9896862693
C	0.4241915596	9.627539199	7.3033945606
C	1.6178714268	11.3335842504	8.7108976951
C	1.205032593	7.3727816243	7.1111808258
C	3.2067137819	6.5363203193	8.3729581374
C	9.1951124988	10.8818786781	10.0276454204
C	7.0582244713	12.0774539658	10.5941490359
C	9.2681083506	8.514759051	9.6723910162
C	7.2334749365	7.0605260064	9.9011377236
H	0.3899632344	10.1942435242	4.0808698883
C	1.8196134511	9.4245359722	2.6640242317
H	2.347468527	12.4694027714	5.9007683089
H	1.4983212639	13.3875020144	4.6498310513
H	0.675199694	12.0368514469	5.4664437821
H	3.4204677091	8.9608985153	1.300708521
H	5.3188305552	11.9928887214	1.45961639
H	6.0415702641	10.6826160934	2.4069978025
H	5.2671012998	10.3168968761	0.8492984544

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H     8.7385972372     14.4695729497     8.8926477241
C     9.8918526255     13.552115505     7.3223818834
H     5.495163587     13.7522878491     7.8473591192
H     6.4422884428     14.8648703171     8.8722931264
H     5.8072577687     15.4032944926     7.2972377524
H     10.7428923147     12.6246741492     5.5740912141
H     8.0806674024     13.1000935353     3.2026211583
H     9.669057983     12.345390011     3.5126495007
H     8.1704166927     11.4616650861     3.8662624898
H     -0.2872679041     10.4119211654     7.0296559822
C     0.2789500975     8.3528422527     6.7520682205
H     1.5435124149     11.3822138601     9.8073631522
H     2.6150912531     11.7193395435     8.4421123674
H     0.8604161445     12.0050712616     8.2844152915
H     1.1111035482     6.366687411     6.6915257352
H     3.4094991754     6.5207382134     9.4540732812
H     2.8155013078     5.5537709559     8.0753731206
H     4.1787197362     6.671880719     7.8671292703
H     9.6995778569     11.8500852852     10.0818799077
C     9.9342053725     9.7402074109     9.71161692
H     6.2129858353     12.2190621516     9.9034859372
H     6.6382034372     12.037637943     11.6108596829
H     7.7078041071     12.9597743773     10.5272208455
H     9.835996188     7.6038301261     9.4612205223
H     6.5725374207     6.9367244355     10.7720347954
H     6.6117641557     6.9225039269     9.0014531444
H     7.983429388     6.2578068297     9.9161508237
C     0.9954344973     8.2270342435     2.2929702414
C     11.1853529722     13.5703654872     8.0831415364
C     -0.8420907933     8.0359915255     5.8059654096
C     11.3981584516     9.8307359291     9.3959982827
H     -0.0816242001     8.4374399041     2.3650591881
H     1.2121985692     7.8863712655     1.2702418419
H     1.2135360397     7.3849298318     2.9714710636
H     11.0568115517     13.9956099606     9.0886509053
H     11.5952606234     12.55492296     8.194813106
H     11.9466636499     14.1706314692     7.559846961
H     -1.4676771318     8.9185481959     5.6106779792
H     -0.4571859439     7.6734298297     4.8405625587
H     -1.4940115763     7.245827005     6.2114448966
H     11.8846132972     10.6427914375     9.9558418483
H     11.9217468771     8.891699405     9.6264197387
H     11.5481584446     10.0339569696     8.3220893961
```

4.5.6 Mes*PSO (linear)

```
50
Mes*PSO (linear) @ PBE0-D3/def2-SVP
C         -0.00125       -1.24285        0.35194
C          0.67297        0.00746        0.40838
C         -1.36720       -1.23321        0.04265
C         -0.06494        1.22695        0.34787
C         -2.08938       -0.06364       -0.16337
C         -1.42340        1.14476        0.04228
H         -1.88614       -2.18268       -0.04244
H         -1.99702        2.06485       -0.04329
P          2.52082        0.06181        0.42238
C          0.52479        2.62220        0.67372
```

```
C          -3.56816       -0.05926       -0.55182
C           0.65327       -2.61020        0.67422
S           2.61151        0.02888       -1.59482
O           4.00327        0.07230       -2.14193
C          -0.41605       -3.68282        0.93592
H          -1.13298       -3.37214        1.71069
H          -0.97719       -3.94900        0.02800
H           0.07997       -4.60015        1.28580
C           1.48072       -2.51285        1.96365
H           1.89405       -3.50070        2.22013
H           2.33923       -1.82839        1.87100
H           0.86208       -2.16606        2.80535
C           1.52771       -3.13699       -0.47693
H           2.47141       -2.58907       -0.58143
H           1.78193       -4.19282       -0.29236
H           0.99259       -3.08018       -1.43714
C           1.29072        2.56640        2.00367
H           2.16621        1.89917        1.96318
H           1.66806        3.56786        2.26315
H           0.63881        2.21915        2.81966
C           1.43713        3.16488       -0.44058
H           1.63072        4.23527       -0.26727
H           2.41064        2.66220       -0.48066
H           0.96083        3.06190       -1.42771
C          -0.59066        3.66115        0.86484
H          -1.12523        3.87988       -0.07157
H          -1.32512        3.34686        1.62146
H          -0.14145        4.60523        1.20662
C          -3.73251        0.70345       -1.87463
H          -4.79181        0.72489       -2.17606
H          -3.38712        1.74454       -1.79163
H          -3.15637        0.22231       -2.67971
C          -4.38006        0.63799        0.54969
H          -4.06053        1.68025        0.69689
H          -5.44995        0.65060        0.28762
H          -4.26883        0.11346        1.51108
C          -4.11970       -1.47328       -0.73749
H          -3.58002       -2.02208       -1.52434
H          -4.06516       -2.06067        0.19181
H          -5.17824       -1.42292       -1.03411
```

4.5.7 Mes*P(S)O

```
50
Mes*P(S)O @ PBE0-D3/def2-SVP
C           0.02844        1.27625        0.10036
C          -0.66382        0.03538        0.15929
C           1.42003        1.22998       -0.02180
C           0.04095       -1.19553        0.20536
C           2.14220        0.04096       -0.07018
C           1.42904       -1.14606        0.07222
H           1.96335        2.16694       -0.08380
H           1.98189       -2.08383        0.07779
P          -2.46865        0.02745        0.00588
C          -0.59007       -2.59357        0.38090
C          -1.94505       -2.56526        1.09646
C          -0.75088       -3.24118       -1.00277
C           0.32214       -3.48205        1.24504
```

```
H          -1.92665       -1.96013        2.01419
H          -2.76710       -2.21715        0.45159
H          -2.23268       -3.59100        1.37269
H           0.22347       -3.33451       -1.50590
H          -1.18466       -4.24929       -0.90583
H          -1.40925       -2.64009       -1.64625
H          -0.18465       -4.43899        1.43957
H           1.27524       -3.72549        0.75636
H           0.54270       -3.00909        2.21422
C           3.66054        0.00017       -0.24403
C           4.29035       -0.67951        0.98071
C           3.99509       -0.80290       -1.50966
C           4.26250        1.39868       -0.38496
H           4.05550       -0.12496        1.90211
H           3.92899       -1.71060        1.10860
H           5.38597       -0.71998        0.87459
H           3.54837       -0.33631       -2.40086
H           5.08575       -0.84931       -1.65645
H           3.62184       -1.83595       -1.44952
H           5.35193        1.32151       -0.51928
H           3.85768        1.93241       -1.25829
H           4.08328        2.01466        0.50947
C          -0.64294        2.65805        0.25434
C          -1.83906        2.85240       -0.68936
C          -1.09586        2.80756        1.71751
C           0.33404        3.80141       -0.04976
H          -1.60179        2.56646       -1.72409
H          -2.74034        2.30891       -0.36978
H          -2.13771        3.91179       -0.68372
H          -0.23362        2.72140        2.39622
H          -1.55296        3.79843        1.86988
H          -1.83452        2.04366        1.99460
H          -0.19807        4.75838        0.05224
H           1.17972        3.83041        0.65226
H           0.73101        3.74658       -1.07518
S          -3.14405       -0.39587       -1.73167
O          -3.23302        0.40734        1.22161
```

4.5.8 $^{Dip}Ter_2P_2S_3$

```
139
DipTer2P2S3 @ PBE0-D3/def2-SVP
P          -1.21716        0.00002       -0.50542
C          -2.70090        0.00006        0.57380
C          -3.30459       -1.22571        0.93828
C          -4.49322       -1.19829        1.67632
H          -4.95480       -2.14963        1.94840
C          -5.08849        0.00010        2.04620
H          -6.02060        0.00011        2.61560
C          -4.49315        1.19847        1.67637
H          -4.95466        2.14983        1.94852
C          -3.30453        1.22585        0.93832
C          -2.76784       -2.57613        0.57944
C          -3.13117       -3.16560       -0.65092
C          -2.66664       -4.45510       -0.93385
H          -2.92717       -4.92248       -1.88495
C          -1.88478       -5.15058       -0.02122
H          -1.53004       -6.15616       -0.26118
```

```
C          -1.55076       -4.56962        1.19729
H          -0.92678       -5.12119        1.90240
C          -1.97991       -3.28157        1.51993
C          -2.76768        2.57627        0.57959
C          -1.97971        3.28155        1.52016
C          -1.55044        4.56959        1.19765
H          -0.92642        5.12104        1.90284
C          -1.88438        5.15068       -0.02082
H          -1.52954        6.15626       -0.26067
C          -2.66626        4.45536       -0.93354
H          -2.92672        4.92284       -1.88460
C          -3.13092        3.16587       -0.65073
C          -4.07982       -2.47098       -1.61126
H          -3.96713       -1.38639       -1.45748
C          -3.77128       -2.74659       -3.07888
H          -2.71888       -2.53365       -3.31169
H          -4.39441       -2.10387       -3.71911
H          -3.98919       -3.79003       -3.35738
C          -5.52843       -2.84610       -1.28844
H          -5.68678       -3.92980       -1.40977
H          -6.22289       -2.32309       -1.96481
H          -5.79887       -2.58043       -0.25685
C          -1.60269       -2.66587        2.85681
H          -1.64574       -1.57166        2.72797
C          -0.18527       -3.01492        3.30457
H          -0.09700       -4.07232        3.60046
H           0.09333       -2.41085        4.18177
H           0.54807       -2.82492        2.50883
C          -2.60776       -3.05264        3.94424
H          -3.62834       -2.73309        3.69385
H          -2.33543       -2.58962        4.90588
H          -2.62244       -4.14515        4.08617
C          -1.60255        2.66566        2.85697
H          -1.64578        1.57148        2.72802
C          -0.18505        3.01445        3.30471
H           0.54824        2.82434        2.50895
H           0.09345        2.41029        4.18188
H          -0.09659        4.07182        3.60063
C          -2.60753        3.05249        3.94445
H          -2.62203        4.14499        4.08649
H          -2.33527        2.58932        4.90603
H          -3.62817        2.73314        3.69404
C          -4.07956        2.47141       -1.61119
H          -3.96700        1.38679       -1.45746
C          -5.52816        2.84666       -1.28848
H          -5.79873        2.58096       -0.25693
H          -6.22262        2.32377       -1.96494
H          -5.68639        3.93039       -1.40975
C          -3.77086        2.74706       -3.07877
H          -3.98865        3.79053       -3.35723
H          -4.39398        2.10442       -3.71909
H          -2.71845        2.53404       -3.31148
P           1.52687        0.00005        0.71001
C           2.79279       -0.00005       -0.63723
C           3.37738        1.22204       -1.03392
C           4.49340        1.20136       -1.87654
H           4.94815        2.15138       -2.16539
C           5.04410       -0.00015       -2.30786
H           5.92368       -0.00018       -2.95554
C           4.49333       -1.20160       -1.87651
```

```
H          4.94802       -2.15166       -2.16532
C          3.37730       -1.22219       -1.03388
C          2.90469        2.53990       -0.51042
C          3.28851        2.94000        0.78810
C          2.86206        4.18830        1.25774
H          3.14899        4.51287        2.26026
C          2.08957        5.02356        0.46225
H          1.76507        5.99485        0.84397
C          1.71985        4.62155       -0.81741
H          1.09090        5.27499       -1.42429
C          2.10693        3.37974       -1.32164
C          2.90456       -2.54004       -0.51039
C          2.10674       -3.37982       -1.32163
C          1.71964       -4.62164       -0.81744
H          1.09065       -5.27503       -1.42432
C          2.08939       -5.02370        0.46220
H          1.76488       -5.99501        0.84388
C          2.86192       -4.18850        1.25770
H          3.14890       -4.51314        2.26018
C          3.28840       -2.94020        0.78810
C          4.21755        2.09513        1.64284
H          4.22139        1.07691        1.22559
C          3.76461        1.98274        3.09538
H          2.73992        1.58792        3.16128
H          4.42674        1.29886        3.64825
H          3.79274        2.95325        3.61499
C          5.64959        2.62192        1.53723
H          5.72124        3.64947        1.92851
H          6.34331        1.98887        2.11303
H          5.98964        2.63727        0.49089
C          1.64740        2.93626       -2.69865
H          1.69759        1.83507       -2.71296
C          0.20023        3.31947       -2.99387
H          0.07745        4.40740       -3.11665
H         -0.13060        2.84384       -3.92930
H         -0.47353        2.98688       -2.19312
C          2.57476        3.47056       -3.79175
H          3.61338        3.14117       -3.65012
H          2.24288        3.12444       -4.78317
H          2.57088        4.57255       -3.79905
C          1.64720       -2.93626       -2.69862
H          1.69745       -1.83507       -2.71290
C          0.20000       -3.31939       -2.99383
H         -0.47371       -2.98683       -2.19303
H         -0.13084       -2.84368       -3.92921
H          0.07719       -4.40730       -3.11667
C          2.57453       -3.47056       -3.79176
H          2.57063       -4.57254       -3.79910
H          2.24262       -3.12439       -4.78316
H          3.61316       -3.14118       -3.65015
C          4.21748       -2.09538        1.64286
H          4.22150       -1.07720        1.22554
C          5.64946       -2.62235        1.53746
H          5.98962       -2.63782        0.49115
H          6.34319       -1.98933        2.11328
H          5.72097       -3.64988        1.92884
C          3.76437       -1.98282        3.09534
H          3.79228       -2.95330        3.61501
H          4.42652       -1.29901        3.64825
H          2.73974       -1.58785        3.16108
```

```
S          0.10101       -1.52436        0.14510
S          0.10105        1.52442        0.14494
S         -1.63421        0.00001       -2.39927
```

4.5.9 $^{Dip}Ter_2P_2S_2O$ (μ-S_2)

```
139
DipTer2P2S2O (μ-S2) @PBE0-D3/def2-SVP
P         -1.20361       -0.00013       -0.44433
C         -2.72157       -0.00045        0.56996
C         -3.34765       -1.22529        0.88556
C         -4.56588       -1.20236        1.57240
H         -5.05312       -2.15201        1.80250
C         -5.16806       -0.00084        1.92613
H         -6.12432       -0.00101        2.45423
C         -4.56623        1.20085        1.57253
H         -5.05370        2.15036        1.80275
C         -3.34799        1.22416        0.88564
C         -2.80606       -2.54837        0.45117
C         -3.04111       -2.97991       -0.87344
C         -2.56044       -4.23669       -1.25660
H         -2.72802       -4.58578       -2.27713
C         -1.88615       -5.05024       -0.35537
H         -1.51978       -6.02972       -0.67332
C         -1.67408       -4.62147        0.95054
H         -1.13221       -5.26414        1.64671
C         -2.11997       -3.36936        1.37528
C         -2.80676        2.54751        0.45154
C         -2.12105        3.36848        1.37596
C         -1.67545        4.62083        0.95157
H         -1.13389        5.26349        1.64799
C         -1.88740        5.04981       -0.35428
H         -1.52125        6.02946       -0.67199
C         -2.56126        4.23626       -1.25582
H         -2.72878        4.58555       -2.27630
C         -3.04172        2.97929       -0.87301
C         -3.89147       -2.16523       -1.83223
H         -3.84174       -1.11561       -1.50993
C         -3.39940       -2.19889       -3.27418
H         -2.35919       -1.85379       -3.33650
H         -4.01293       -1.52423       -3.89101
H         -3.47674       -3.20385       -3.71880
C         -5.35167       -2.61249       -1.73043
H         -5.46204       -3.66498       -2.03775
H         -5.99197       -1.99830       -2.38329
H         -5.73072       -2.52248       -0.70155
C         -1.86425       -2.91146        2.80038
H         -1.95121       -1.81255        2.80444
C         -0.46260       -3.25695        3.29801
H         -0.33644       -4.34073        3.44963
H         -0.27363       -2.77096        4.26770
H          0.30630       -2.92353        2.58805
C         -2.92100       -3.47112        3.75498
H         -3.93728       -3.17028        3.46517
H         -2.74340       -3.11735        4.78289
H         -2.88890       -4.57245        3.76559
C         -1.86534        2.91033        2.80100
H         -1.95222        1.81141        2.80482
```

```
C         -0.46371        3.25580        3.29879
H          0.30523        2.92263        2.58878
H         -0.27474        2.76955        4.26834
H         -0.33765        4.33955        3.45074
C         -2.92218        3.46970        3.75565
H         -2.89025        4.57103        3.76644
H         -2.74456        3.11579        4.78350
H         -3.93842        3.16874        3.46577
C         -3.89172        2.16459       -1.83212
H         -3.84166        1.11489       -1.51014
C         -5.35207        2.61135       -1.73039
H         -5.73120        2.52096       -0.70157
H         -5.99208        1.99708       -2.38346
H         -5.46279        3.66386       -2.03749
C         -3.39947        2.19881       -3.27398
H         -3.47707        3.20387       -3.71834
H         -4.01268        1.52412       -3.89110
H         -2.35913        1.85406       -3.33622
P          1.50448        0.00009        0.78581
C          2.82172        0.00041       -0.51825
C          3.42259        1.22033       -0.89790
C          4.57174        1.20139       -1.69512
H          5.02096        2.15431       -1.98474
C          5.14275        0.00078       -2.10112
H          6.04340        0.00091       -2.71915
C          4.57214       -1.20003       -1.69507
H          5.02176       -2.15280       -1.98455
C          3.42303       -1.21934       -0.89784
C          2.89050        2.53845       -0.44571
C          3.11738        2.96212        0.88263
C          2.60045        4.19817        1.28642
H          2.76449        4.54238        2.30971
C          1.89257        4.99998        0.39960
H          1.49333        5.96111        0.73269
C          1.69289        4.58125       -0.91102
H          1.12626        5.21384       -1.59780
C          2.17841        3.35045       -1.35531
C          2.89143       -2.53767       -0.44563
C          2.17915       -3.34968       -1.35513
C          1.69437       -4.58079       -0.91100
H          1.12775       -5.21347       -1.59771
C          1.89485       -4.99979        0.39944
H          1.49623       -5.96123        0.73242
C          2.60261       -4.19786        1.28621
H          2.76711       -4.54223        2.30937
C          3.11884       -2.96145        0.88255
C          3.99144        2.16199        1.83405
H          4.05253        1.13293        1.44797
C          3.43145        2.07660        3.25027
H          2.41016        1.66792        3.24899
H          4.05870        1.41465        3.86705
H          3.40810        3.05891        3.74759
C          5.41506        2.72209        1.82295
H          5.43091        3.76254        2.18522
H          6.07642        2.12495        2.47067
H          5.83495        2.71482        0.80588
C          1.92046        2.91389       -2.78621
H          2.26730        1.87403       -2.88143
C          0.43567        2.91923       -3.14311
H         -0.00444        3.92540       -3.06316
```

```
H           0.29352         2.57575        -4.17960
H          -0.13165         2.24641        -2.48686
C           2.73373         3.76285        -3.76398
H           3.81025         3.72298        -3.53807
H           2.58840         3.41205        -4.79776
H           2.42600         4.82018        -3.72260
C           1.92050        -2.91258        -2.78575
H           2.26506        -1.87184        -2.88001
C           0.43587        -2.92088        -3.14315
H          -0.13324        -2.25060        -2.48586
H           0.29323        -2.57581        -4.17904
H          -0.00185        -3.92826        -3.06529
C           2.73584        -3.75901        -3.76403
H           2.43053        -4.81708        -3.72318
H           2.58972        -3.40796        -4.79761
H           3.81224        -3.71678        -3.53808
C           3.99263        -2.16101         1.83394
H           4.05330        -1.13194         1.44783
C           5.41646        -2.72055         1.82288
H           5.83632        -2.71323         0.80580
H           6.07759        -2.12305         2.47051
H           5.43275        -3.76095         2.18528
C           3.43260        -2.07576         3.25016
H           3.40949        -3.05806         3.74751
H           4.05968        -1.41364         3.86695
H           2.41121        -1.66734         3.24886
S           0.08478         1.52997         0.21792
S           0.08530        -1.53017         0.21738
O          -1.50761         0.00001        -1.90889
```

4.5.10 Me_2Se

```
9
Me2Se @ PBE0-D3/def2-SVP
Se         -0.00000        -0.00000         0.47163
C           0.00000         1.45256        -0.81453
H          -0.90066         1.41719        -1.44346
H           0.00025         2.39107        -0.24357
H           0.90053         1.41689        -1.44359
C          -0.00000        -1.45256        -0.81453
H          -0.00025        -2.39107        -0.24357
H          -0.90053        -1.41689        -1.44359
H           0.90066        -1.41719        -1.44346
```

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