Supporting Information

Water-Soluble Triarylphosphines as Biomarkers for Protein S-Nitrosation

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Supporting Information

1. ^{31}P NMR of the (^{13}C)-Cys-SNO and TXPTS reaction

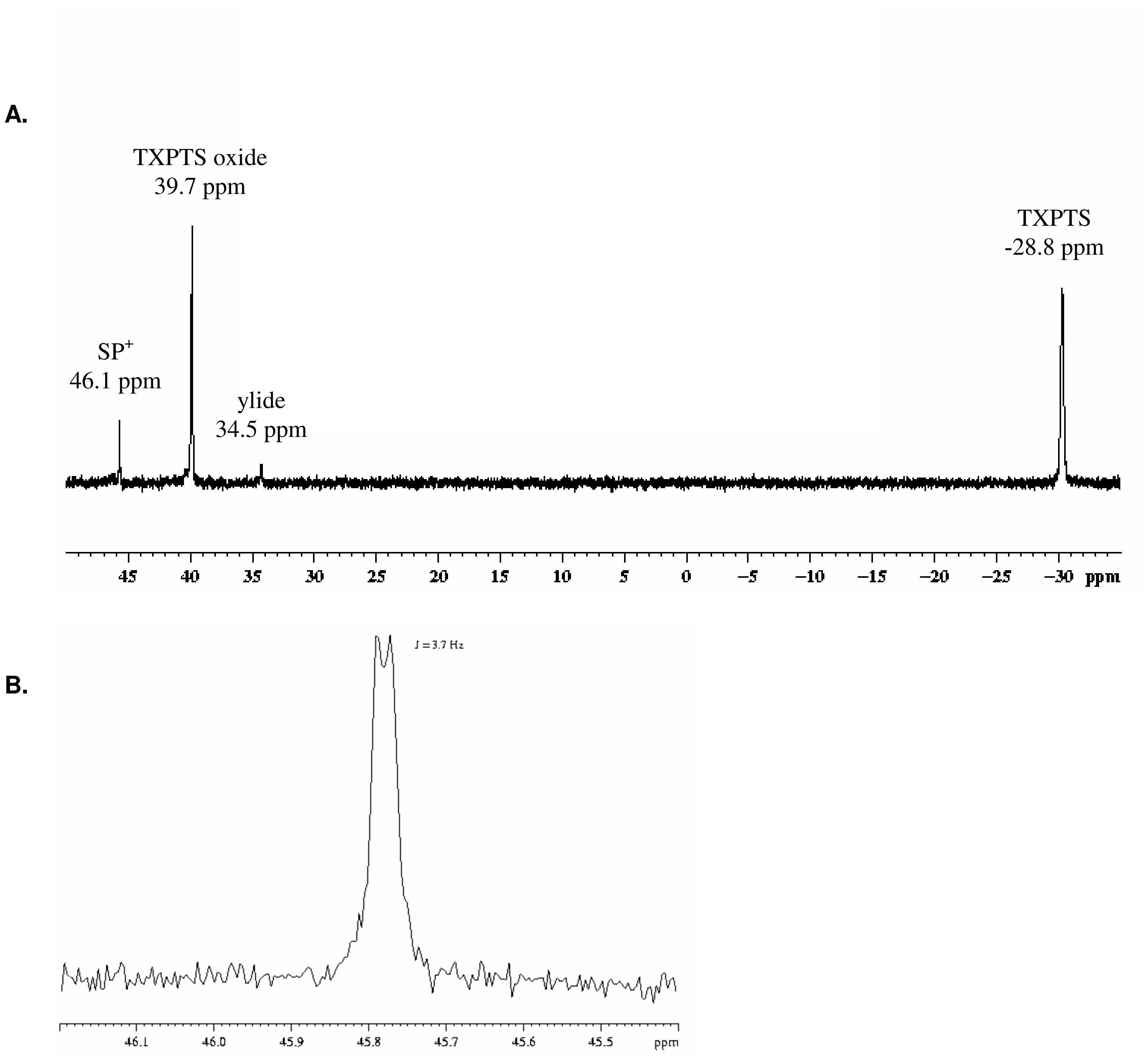

Figure S1 ^{31}P NMR for the (^{13}C)-Cys-SNO/TXPTS reaction mixture. a) ^{31}P NMR in HEPES buffer with 10% D_2O. b) 203 MHz field ^{31}P NMR zoomed in showing **6** from the reaction mixture ($^2J_{P\text{-}C}$ = 3.7 Hz).

2. ^{13}C NMR of the (^{13}C)-Cys-SNO and TXPTS reaction

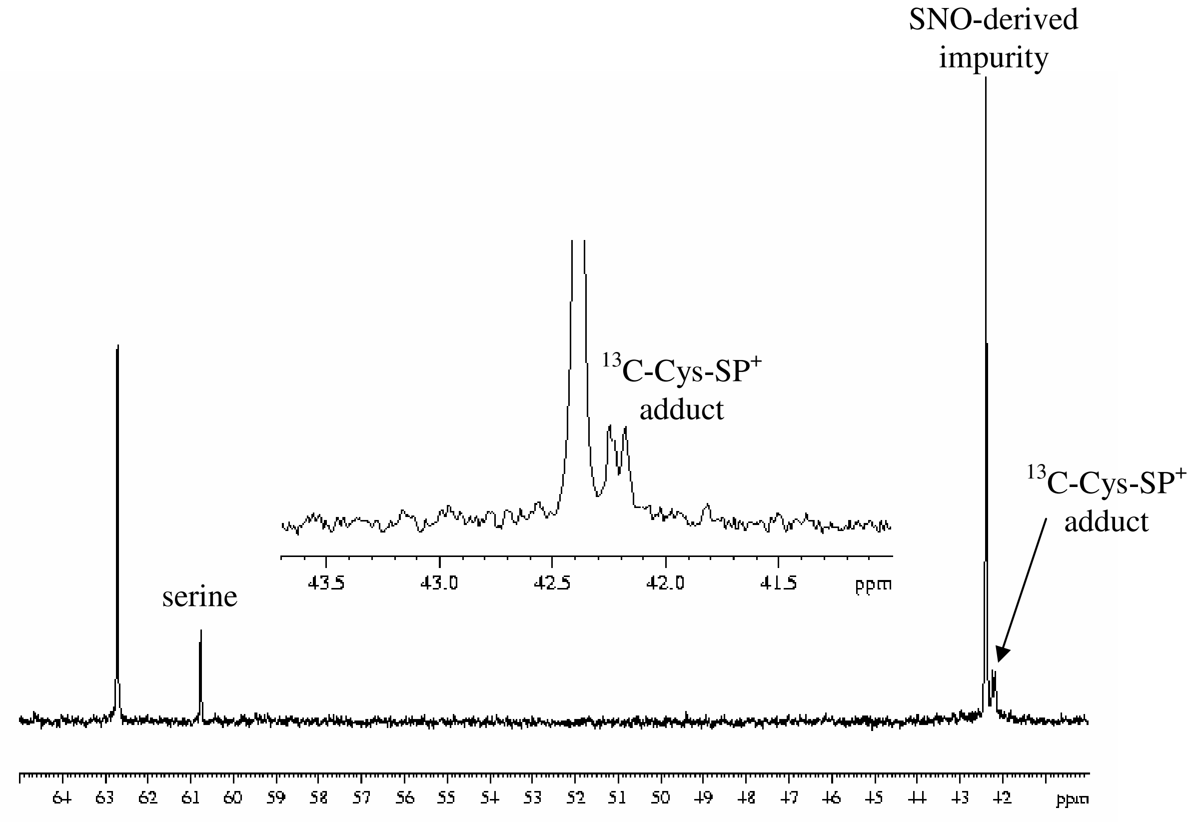

Figure S2. ^{13}C NMR for the (^{13}C)-Cys-SNO/TXPTS reaction mixture. The peak at 42.2 ppm corresponds to **6** with a weak ^{2}J coupling of 8.6 Hz. The peak at 42.4 ppm emerges during the Cys-SNO preparation, 60.8 ppm corresponds to the serine CH_2, and the 62.7 ppm peak is currently unknown.

3. LC-MS of the Cys-SNO and TXPTS reaction

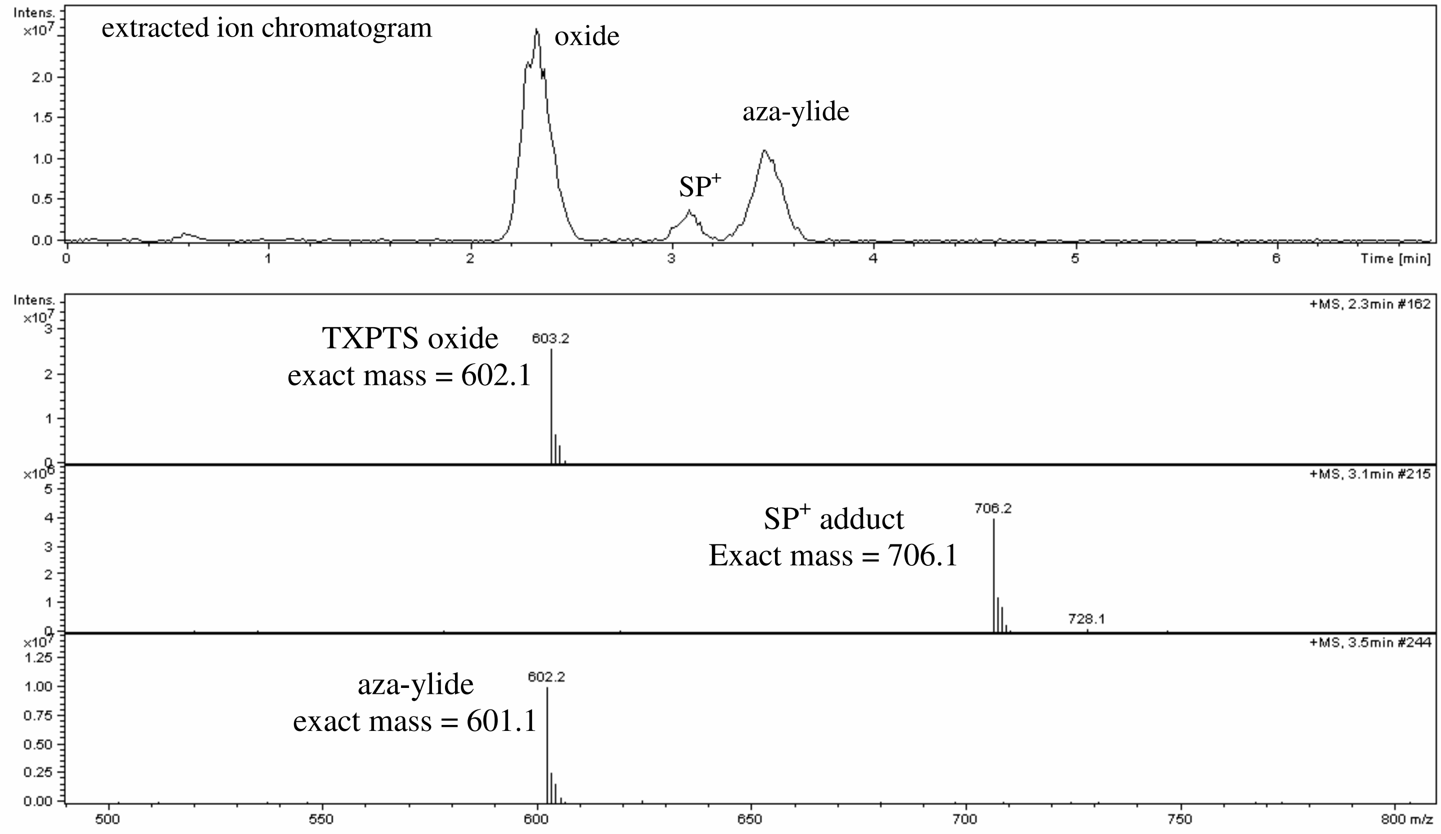

Figure S3. LC-MS for the (^{12}C)-Cys-SNO + TXPTS reaction

4. LC-MS of the (^{13}C)-Cys-SNO and TXPTS reaction

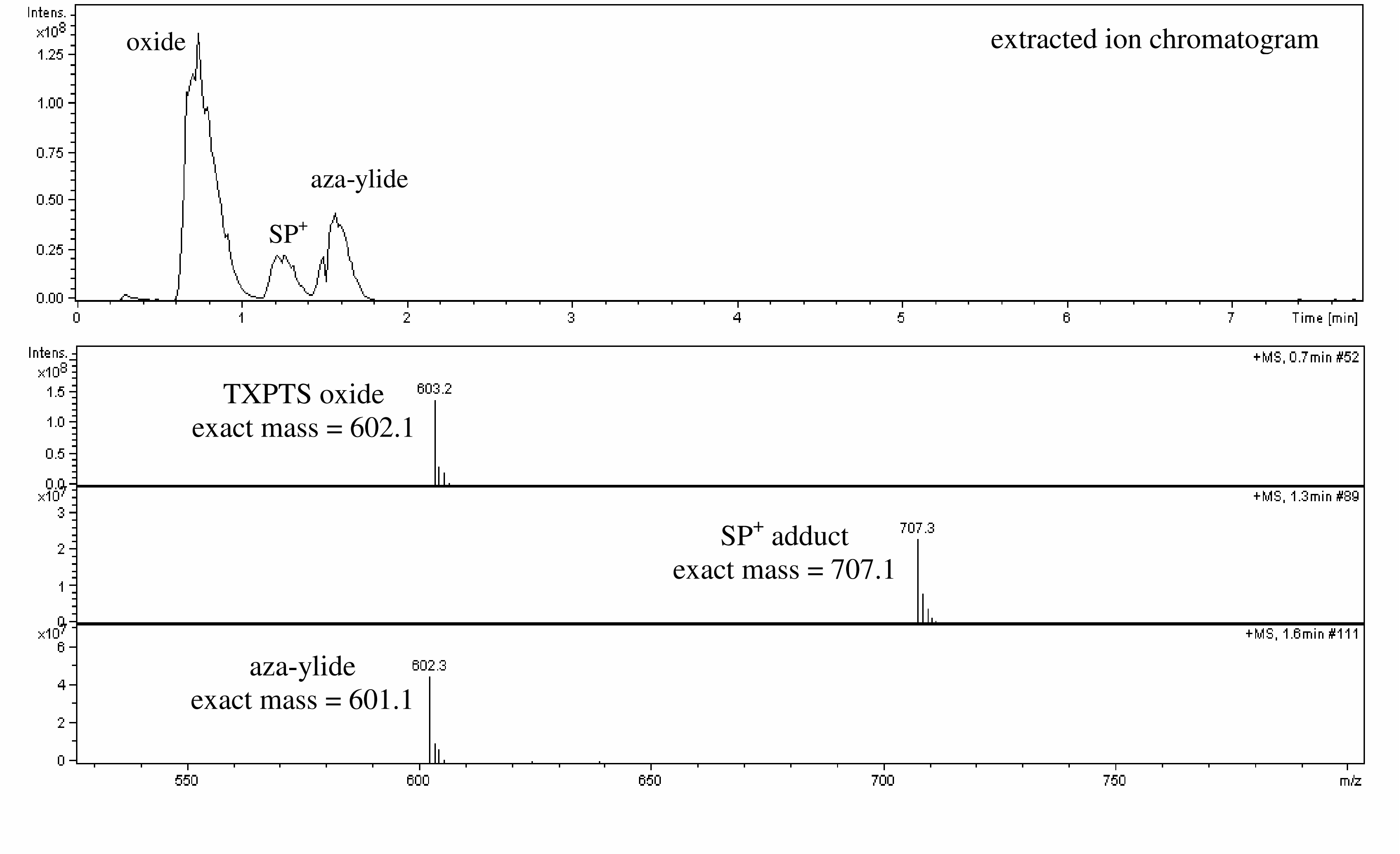

Figure S4. LC-MS for the (^{13}C)-Cys-SNO + TXPTS

5. LC-MS of the GSNO and TXPTS reaction

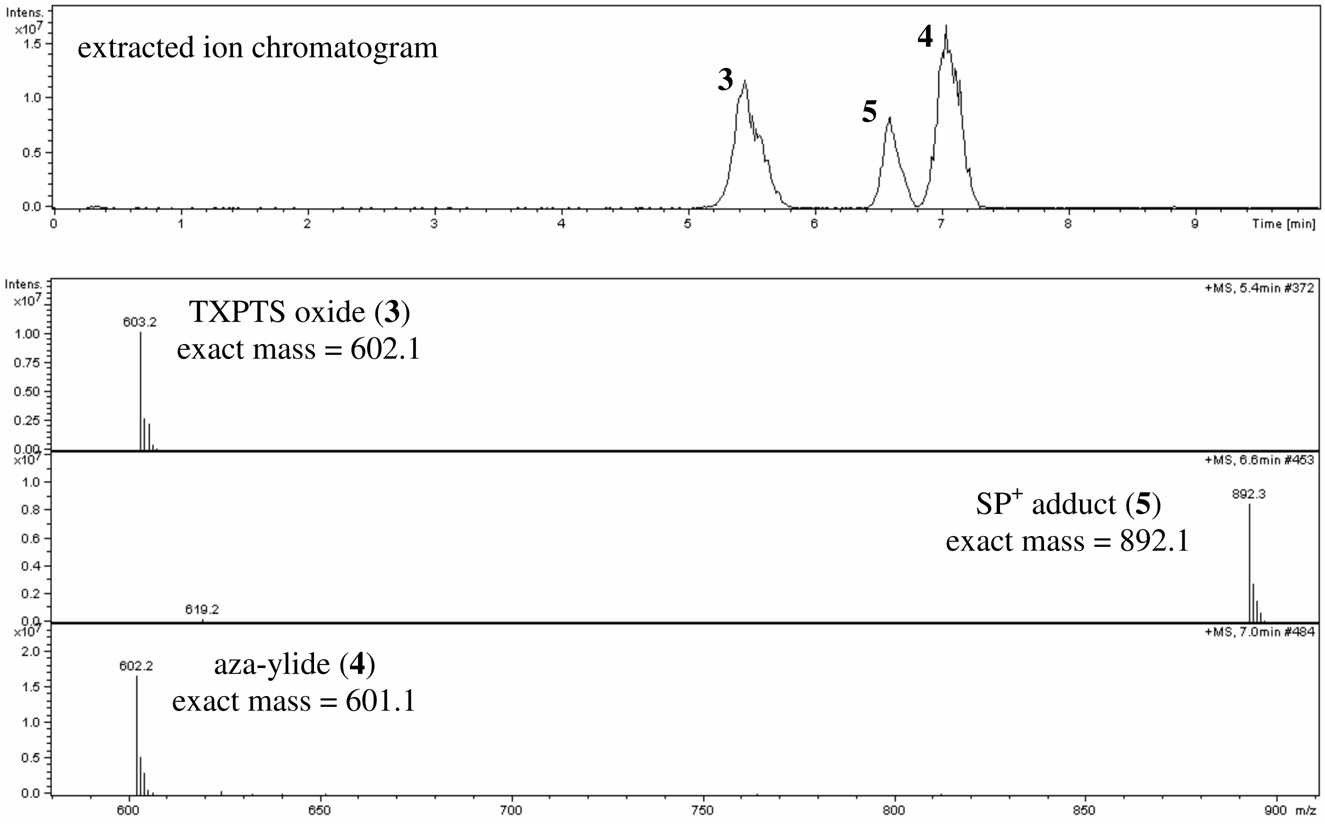

Figure S5. LC-MS analysis of the reaction between GSNO and TXPTS. LC retention times and observed masses are as follows: TXPTS oxide (**3**) = 5.4 min (M + 1) m/z = 603.2; SP^+ adduct (**5**) = 6.5 min (M^+) m/z = 892.3; aza-ylide (**4**) = 7.1 min (M + 1) m/z = 602.2. All observed m/z are in agreement with the reported exact masses for each compound.

6. LC-MS of the ^{15}N-GSNO/TXPTS reaction

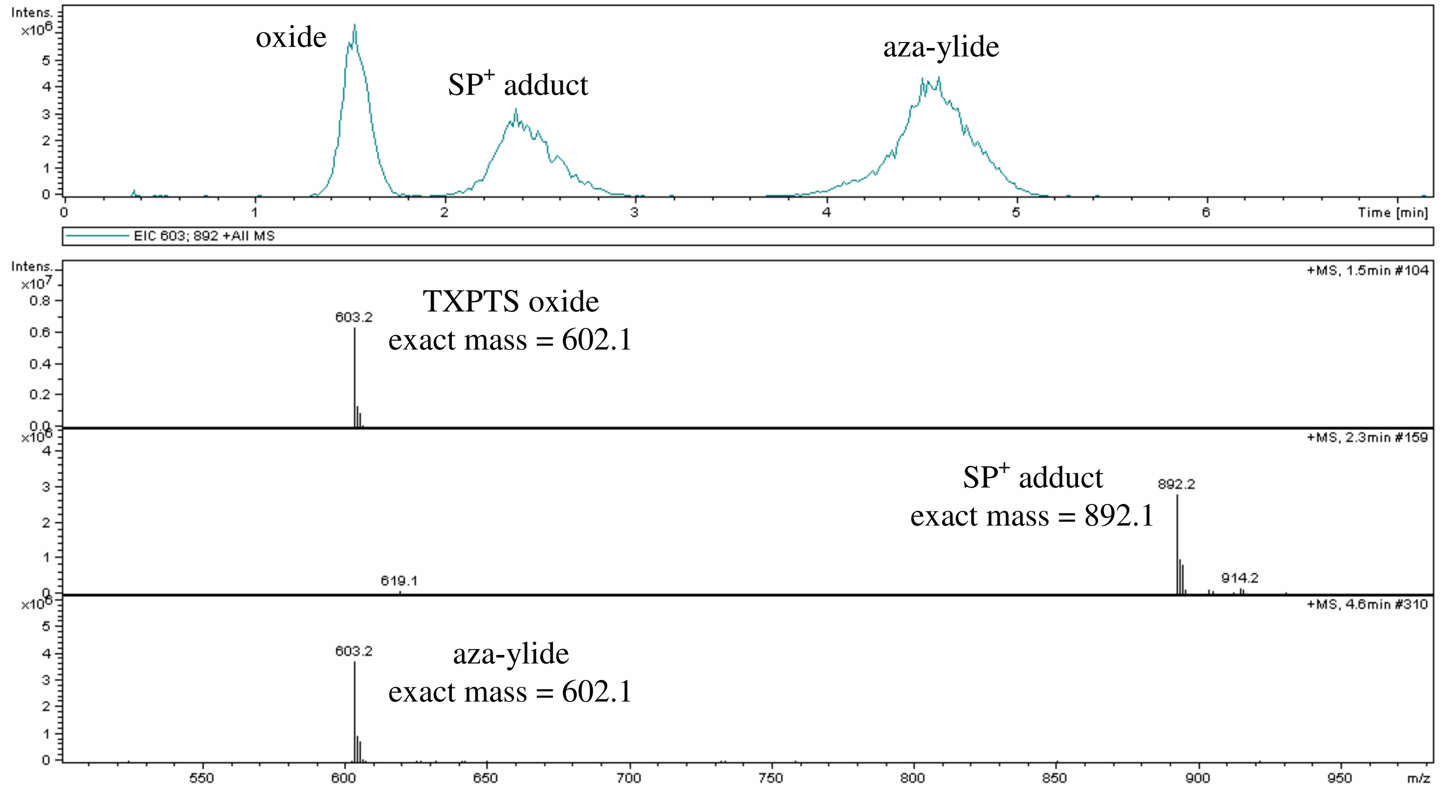

Figure S6. LC-MS for the ^{15}N-GSNO/TXPTS reaction.

7. ^{31}P NMR of the GSH and TXPTS reaction

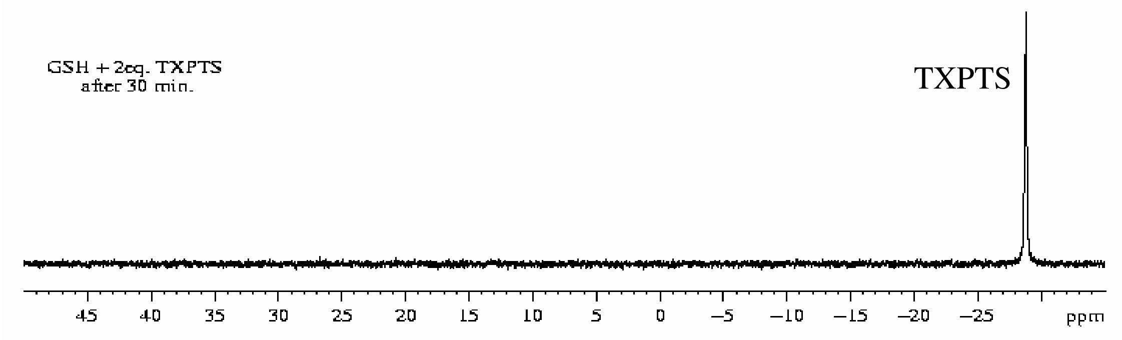

Figure S7. ^{31}P NMR of the reaction between GSH (20 mM) and TXPTS (40 mM) in Tris buffer (200 mM, pH 7). After 30 min. there is no sign of reaction.

8. ^{31}P NMR of the GSSG and TXPTS reaction

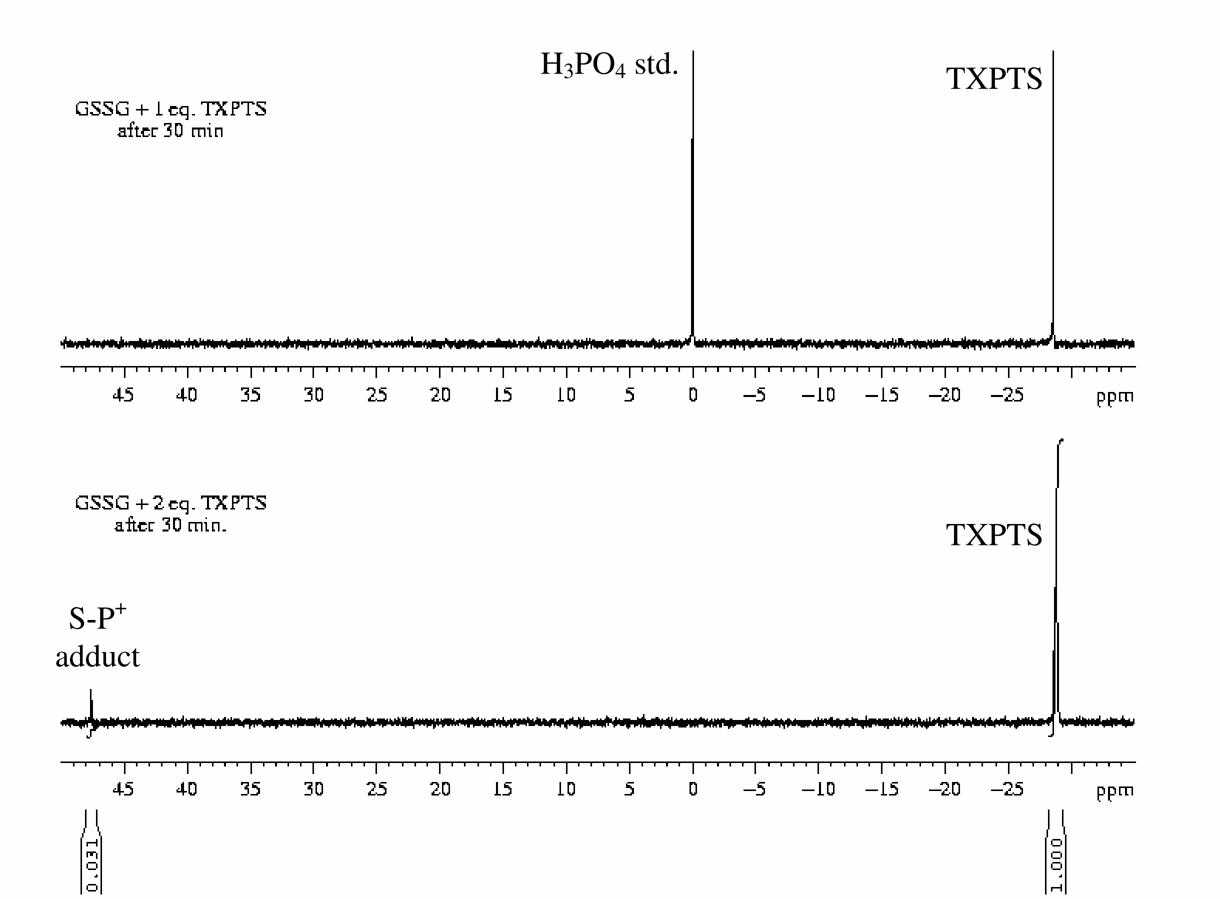

Figure S8. ^{31}P NMR of the reaction between GSSG (20 mM) and TXPTS. (top) with 20 mM TXPTS (bottom) with 40 mM TXPTS (2 eq.) roughly 3% reacts to form **5**. Both spectra were taken after 30 min.

9. ^{31}P NMR showing the treatment of the GSNO/TXPTS mixture with DTT

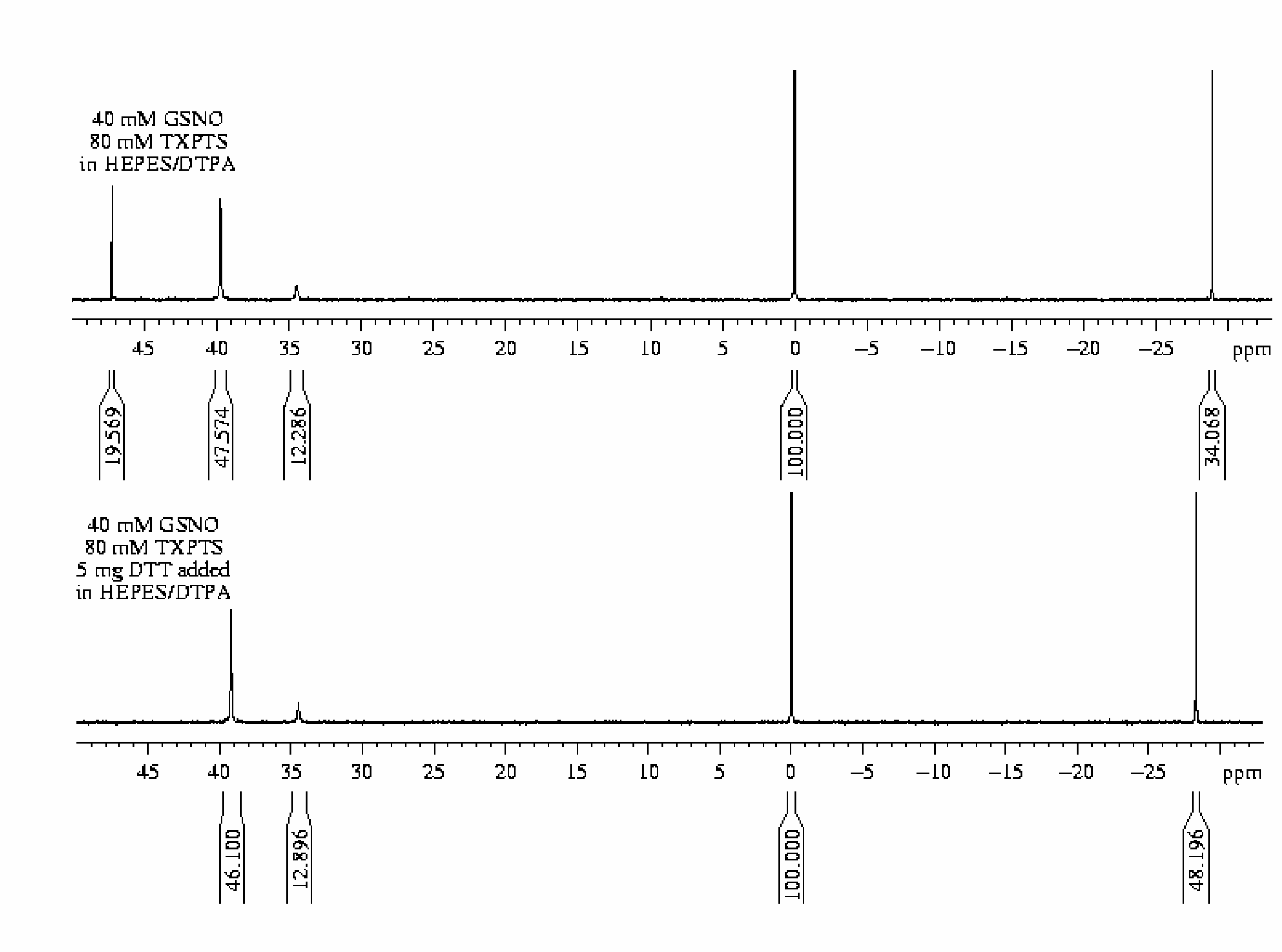

Figure S9. **(Top)** ^{31}P NMR of the GSNO/TXPTS reaction mixture showing TXPTS (-28.8 ppm), ylide (34.5 ppm), oxide (39.7 ppm), S-P$^+$ adduct (47.2 ppm), and the external H_3PO_4 standard (0 ppm). **(Bottom)** The addition of DTT to this mixture completely reduces the S-P$^+$ adduct, regenerating TXPTS starting material as seen by the changes in integration.

10. UV/vis of GSNO (16 mM) with TXPTS (32 mM)

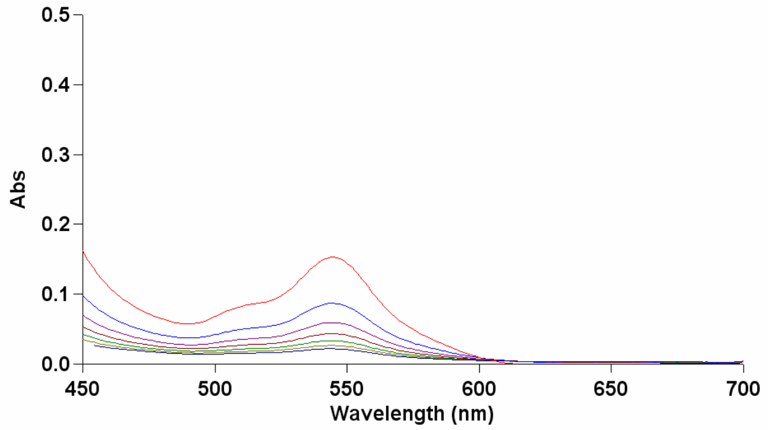

Figure S10. UV/Vis of GSNO (16 mM) with TXPTS (32 mM) at 545 nm with 1 scan taken every 30 sec.

11. ^{31}P NMR of the reaction between cysteine and cystine with TXPTS

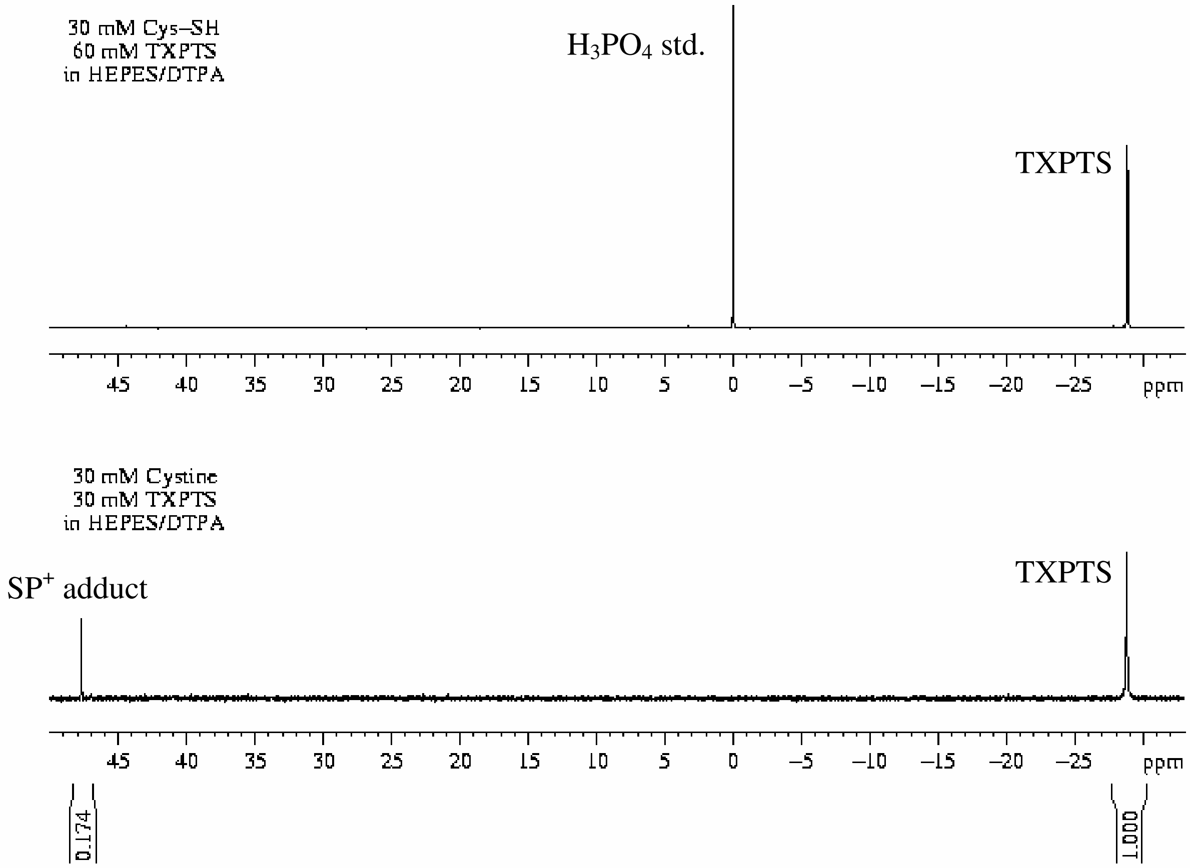

Figure S11. (Top) ^{31}P NMR of a reaction mixture containing Cys-SH (30 mM) and TXPTS (60 mM) in HEPES buffer (100 mM). Only TXPTS (-28.8 ppm) and the external H_3PO_4 standard (0 ppm) are observed. **(Bottom)** ^{31}P NMR of a reaction mixture containing Cys-S-S-Cys (30 mM) and TXPTS (30 mM) in HEPES buffer (100 mM). Based on integration, roughly 15% of the TXPTS reacts to form the SP$^+$ adduct (46 ppm).

12. ^{31}P NMR showing the treatment of the Cys-SNO/TXPTS reaction with DTT

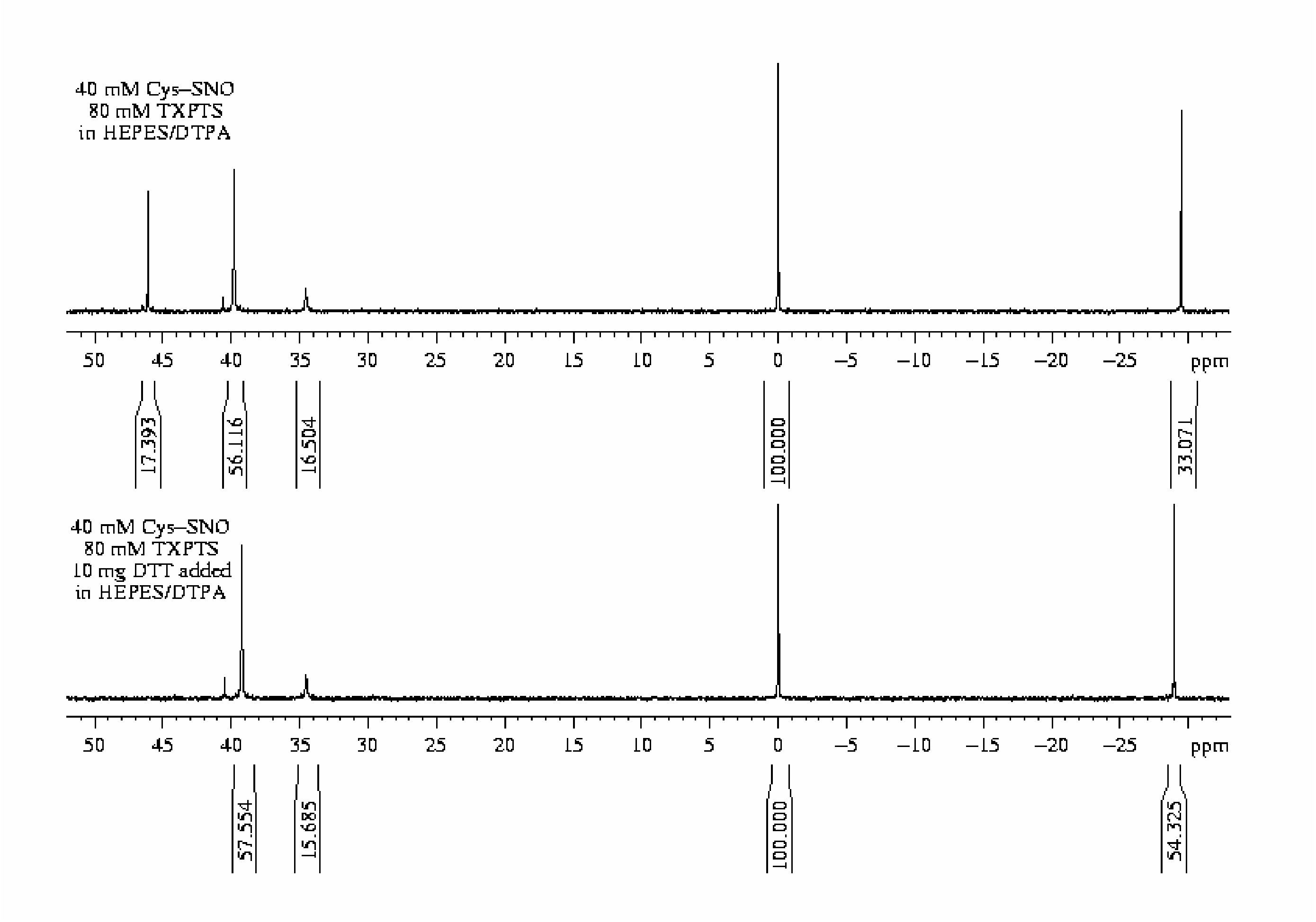

Figure S12. (Top) ^{31}P NMR of Cys-SNO/TXPTS reaction mixture showing TXPTS (-28.8 ppm), ylide (34.5 ppm), oxide (39.7 ppm), S-P$^+$ adduct (46.1 ppm), and the external H_3PO_4 standard (0 ppm). **(Bottom)** The addition of DTT to this mixture completely reduces the S-P$^+$ adduct and regenerates TXPTS starting material as seen by the changes in integration.

13. ESI-TOF MS of the reaction between AhpC-SH with TXPTS

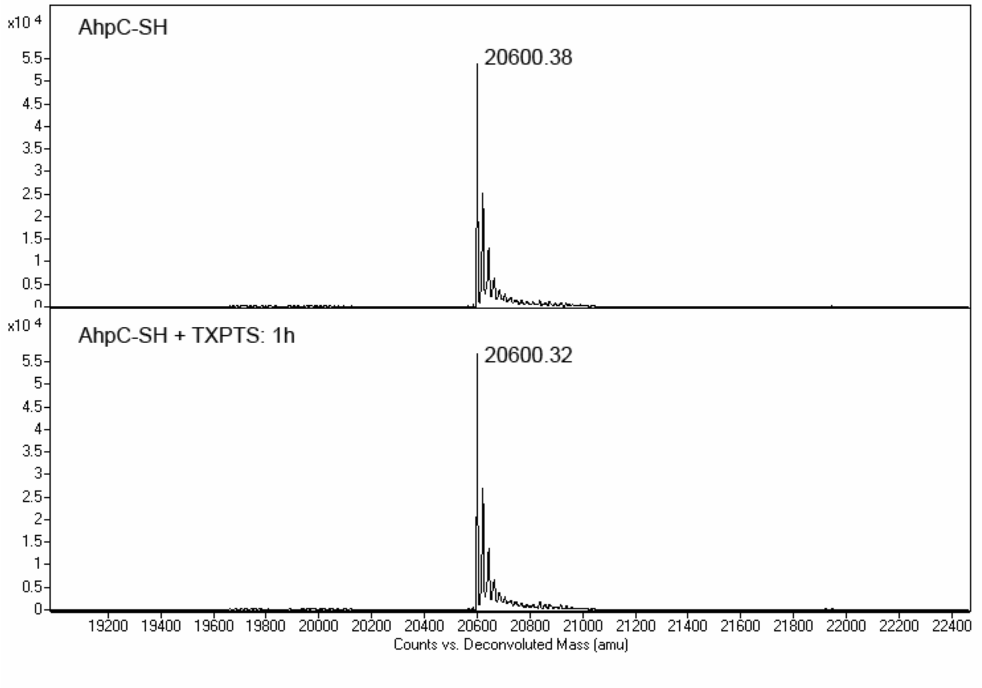

Figure S13. ESI-TOF MS data for AhpC-SH + TXPTS over 1h. TXPTS shows no affinity for the free thiol (Cys 46) of C165S AhpC.

14. ESI-TOF MS of labeled AhpC-S-P$^+$ in normal and denaturing conditions

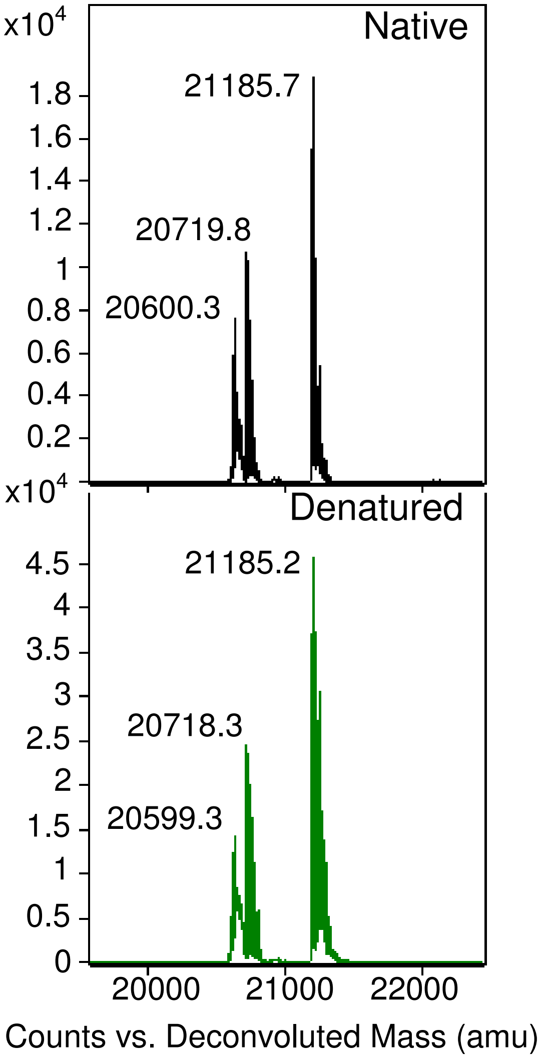

Figure S14. Comparison of SNO-labeled AhpC under normal and denaturing (40% acetonitrile) conditions

15. ^{31}P NMR of **1**

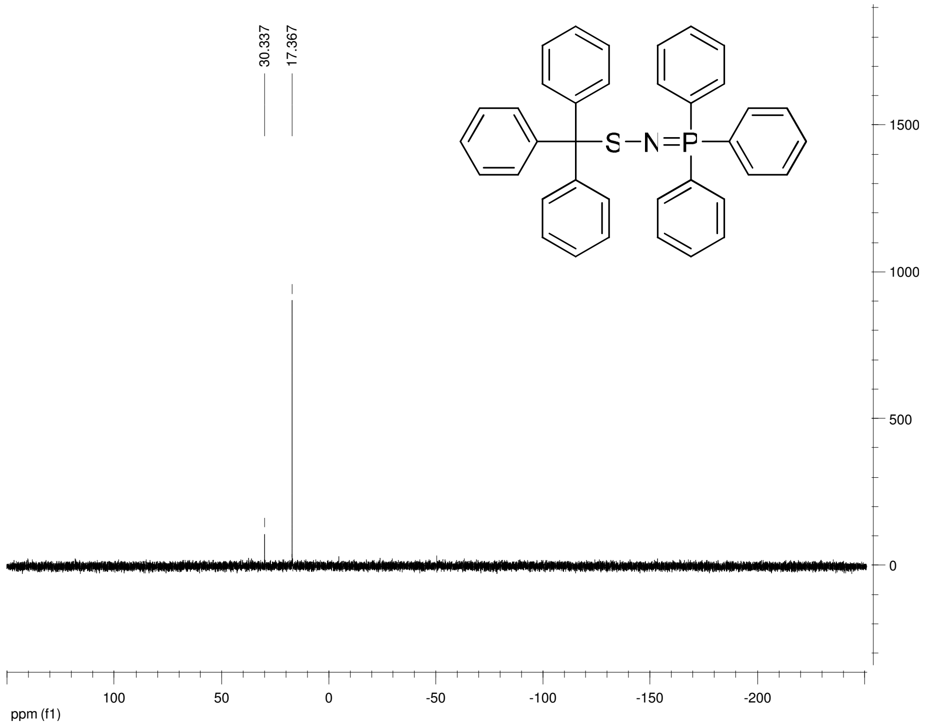

Figure S15. ^{31}P NMR of **1** in $CDCl_3$. The product appears at 17.3 ppm and trace triphenylphosphine oxide (by-product of the reaction) at 30.3 ppm.

CRYSTAL STRUCTURE ANALYSIS REPORT and TABLES for **1**

Brief Experimental Description to be Included as Text or as a Footnote at Time of Publication

Colorless crystals of $C_{37}H_{30}NPS$ – 0.5 C_7H_8 are, at 193(2) K, monoclinic, space group $P2_1/c$ – C_{2h}^5 (No. 14) with $\underline{a}$ = 17.631(2) Å, $\underline{b}$ = 10.525(1) Å, $\underline{c}$ = 17.177(2) Å, β = 101.859(2)° , V = 3119.5(7) $Å^3$, and Z = 4 {d_{calcd} = 1.273gcm^{-3}; $\mu_a(MoK\overline{\alpha})$ = 0.186 mm^{-1}}. A full hemisphere of diffracted intensities (1868 30-second frames with an ω scan width of 0.30°) was measured for a single-domain specimen using graphite-monochromated $MoK\overline{\alpha}$ radiation (λ= 0.71073 Å) on a Bruker SMART APEX CCD Single Crystal Diffraction System. X-rays were provided by a fine-focus sealed x-ray tube operated at 50kV and 30mA.

Lattice constants were determined with the Bruker SAINT software package using peak centers for 3979 reflections having 7.72° ≤ 2θ ≤ 52.08°. A total of 25048 integrated reflection intensities having $2\theta((MoK\overline{\alpha}) \leq 53.00°$ were produced using the Bruker program SAINT; 6427 of these were unique and gave R_{int} = 0.054 with a coverage which was 99.4% complete. The data were corrected for scaling and variable absorption effects using SADABS; the ratio of minimum and maximum transmission values was 0.81618.

The Bruker software package SHELXTL was used to solve the structure using "direct methods" techniques. All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data with the SHELXTL Version 6.14 software package. The resulting structural parameters have been refined to convergence {$\underline{R}_1$ (unweighted, based on F) = 0.0591 for 5070 independent reflections having $2\Theta(MoK\overline{\alpha}) < 53.00^o$ and $F^2>2\sigma(F^2)$} {$\underline{R}_1$ (unweighted, based on F) = 0.0761 and $w\underline{R}_2$ (weighted, based on F^2) = 0.1476 for all 6427 reflections} using counter-weighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all nonhydrogen atoms. The toluene solvent molecule of crystallization lies on a crystallographic inversion center at ½,½,0 in the unit cell and is therefore disordered with two orientations in the crystal. Restraints were imposed on the positional and displacement parameters of the seven (half-occupancy) carbon atoms. The hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp^2- hybridization of the carbon atoms and C-H bond lengths of 0.95Å) "riding" on their respective carbon atoms. The isotropic thermal parameters of the hydrogen atoms were fixed at values 1.2(non-methyl) times the equivalent isotropic thermal parameters of the carbon atoms to which they are covalently bonded. Hydrogen atoms on the methyl group of the disordered toluene molecule were not included in the structural model. A total of 409 parameters were refined using 61 restraints and 6427 data. The largest shift/s.u. was 0.000 in the final refinement cycle. The final difference map had maxima and minima of 0.482 and -0.585 $e^-/\text{Å}^3$, respectively.

Acknowledgment

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References

(1) International Tables for Crystallography, Vol A, 4th ed., Kluwer Academic Publishers: Boston (1996).

(2) Data Collection: SMART (Version 5.628) (2002). Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.

(3) Data Reduction: SAINT (Version 6.36) (2003). Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373, USA.

(4) G. M. Sheldrick, (2006). SADABS, Version 2006/3. Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.

(5) G. M. Sheldrick (2001). SHELXTL (Version 6.14). Bruker-AXS, 5465 E. Cheryl Parkway, Madison, WI 53711-5373 USA.

Table 1. Crystal data and structure refinement for $C_{37}H_{30}NPS - 0.5\ C_7H_8$

Identification code	a13m
Empirical formula	C40.50 H34 N P S
Formula weight	597.72
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c – C_{2h}^{5} (No. 14)
Unit cell dimensions	a = 17.631(2) Å b = 10.5248(13) Å, β = 101.859(2)° c = 17.177(2) Å
Volume	3119.5(7) Å^3
Z	4
Density (calculated)	1.273 g/cm^3
Absorption coefficient	0.186 mm^{-1}
F(000)	1260
Crystal size	0.32 x 0.08 x 0.04 mm^3
Theta range for data collection	3.86 to 26.50°
Index ranges	$-22 \leq h \leq 22$, $-13 \leq k \leq 13$, $-21 \leq l \leq 21$
Reflections collected	25048
Independent reflections	6427 [R(int) = 0.0539]
Completeness to theta = 26.50°	99.4 %
Absorption correction	Multi-scan (SADABS)
Ratio of Min./Max. transmission	0.8162
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6427 / 61 / 409
Goodness-of-fit on F^2	1.114
Final R indices [5070 I>2σ(I) data]	$R_1 = 0.0591$, $wR_2 = 0.1386$
R indices (all data)	$R_1 = 0.0761$, $wR_2 = 0.1476$
Largest diff. peak and hole	0.482 and -0.585 $^{-}$/Å^3

$R_1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$

$wR_2 = \{ \Sigma \, [w(F_o^2 - F_c^2)^2] \, / \, \Sigma \, [w(F_o^2)^2] \}^{1/2}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $C_{37}H_{30}NPS – 0.5\ C_7H_8$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	2531(1)	3970(1)	1802(1)	25(1)
P(1)	3438(1)	1916(1)	1357(1)	25(1)
N(1)	3092(1)	3312(2)	1231(1)	30(1)
C(1)	1619(1)	4444(2)	1099(1)	22(1)
C(1A)	1084(1)	4768(2)	1671(1)	25(1)
C(2A)	1320(2)	5700(2)	2254(2)	32(1)
C(3A)	841(2)	6079(3)	2752(2)	41(1)
C(4A)	114(2)	5541(3)	2680(2)	44(1)
C(5A)	-121(2)	4619(3)	2120(2)	45(1)
C(6A)	359(1)	4231(2)	1618(2)	35(1)
C(1B)	1319(1)	3336(2)	545(1)	24(1)
C(2B)	1082(1)	3477(2)	-270(1)	31(1)
C(3B)	799(2)	2453(3)	-756(2)	38(1)
C(4B)	748(2)	1272(3)	-428(2)	40(1)
C(5B)	980(2)	1108(2)	383(2)	36(1)
C(6B)	1265(1)	2126(2)	865(2)	29(1)
C(1C)	1736(1)	5646(2)	627(1)	24(1)
C(2C)	1123(2)	6478(2)	378(2)	33(1)
C(3C)	1216(2)	7560(2)	-56(2)	39(1)
C(4C)	1915(2)	7828(3)	-248(2)	43(1)
C(5C)	2525(2)	7003(3)	-13(2)	45(1)
C(6C)	2442(2)	5917(2)	422(2)	36(1)
C(1D)	2979(1)	815(2)	1923(2)	28(1)
C(2D)	2601(2)	-260(2)	1580(2)	39(1)
C(3D)	2221(2)	-1057(3)	2014(2)	52(1)
C(4D)	2221(2)	-784(3)	2794(2)	54(1)
C(5D)	2586(2)	297(3)	3142(2)	50(1)
C(6D)	2968(2)	1101(3)	2710(2)	37(1)
C(1E)	4457(1)	1907(2)	1832(1)	29(1)
C(2E)	4793(2)	921(3)	2311(2)	48(1)

C(3E)	5583(2)	927(3)	2637(2)	54(1)
C(4E)	6036(2)	1922(3)	2487(2)	48(1)
C(5E)	5718(2)	2861(3)	1970(2)	51(1)
C(6E)	4928(2)	2861(3)	1643(2)	41(1)
C(1F)	3403(1)	1208(2)	392(1)	29(1)
C(2F)	2825(2)	1601(3)	-239(2)	34(1)
C(3F)	2763(2)	1055(3)	-984(2)	41(1)
C(4F)	3274(2)	127(3)	-1100(2)	44(1)
C(5F)	3846(2)	-276(3)	-477(2)	48(1)
C(6F)	3914(2)	250(3)	268(2)	41(1)
		Disordered Toluene of Crystallization[d]		
C(1G)	4903(4)	4180(8)	-257(4)	114(3)
C(2G)	4366(4)	4975(8)	-36(4)	121(4)
C(3G)	4563(5)	6110(9)	358(5)	142(4)
C(4G)	5315(6)	6465(9)	556(5)	138(4)
C(5G)	5884(5)	5682(11)	335(6)	144(4)
C(6G)	5688(4)	4568(10)	-58(6)	155(5)
C(7G)	4677(5)	2973(8)	-681(5)	137(5)

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[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

[b] Atoms are labeled in agreement with Figures 1 - 4.

[c] U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

[d] The toluene solvent molecule of crystallization lies on a crystallographic inversion center at ½,½,0 in the unit cell and is therefore disordered with two orientations in the crystal. Restraints were imposed on the positional and displacement parameters of the seven (half-occupancy) carbon atoms.

Table 3. Bond lengths [Å] and angles [°] for $C_{37}H_{30}NPS - 0.5\ C_7H_8$

S(1)-N(1)	1.679(2)	S(1)-C(1)	1.870(2)
P(1)-N(1)	1.589(2)		
P(1)-C(1D)	1.807(2)	C(1)-C(1B)	1.530(3)
P(1)-C(1F)	1.806(2)	C(1)-C(1A)	1.533(3)
P(1)-C(1E)	1.813(2)	C(1)-C(1C)	1.539(3)
C(1A)-C(6A)	1.384(3)	C(4D)-C(5D)	1.382(5)
C(1A)-C(2A)	1.402(3)	C(5D)-C(6D)	1.388(4)
C(2A)-C(3A)	1.379(4)	C(1E)-C(2E)	1.380(4)
C(3A)-C(4A)	1.384(4)	C(1E)-C(6E)	1.384(4)
C(4A)-C(5A)	1.370(4)	C(2E)-C(3E)	1.390(4)
C(5A)-C(6A)	1.387(4)	C(3E)-C(4E)	1.373(4)
C(1B)-C(2B)	1.384(3)	C(4E)-C(5E)	1.370(4)
C(1B)-C(6B)	1.398(3)	C(5E)-C(6E)	1.391(4)
C(2B)-C(3B)	1.392(3)	C(1F)-C(2F)	1.390(3)
C(3B)-C(4B)	1.376(4)	C(1F)-C(6F)	1.397(3)
C(4B)-C(5B)	1.379(4)	C(2F)-C(3F)	1.386(4)
C(5B)-C(6B)	1.384(3)	C(3F)-C(4F)	1.371(4)
C(1C)-C(2C)	1.389(3)	C(4F)-C(5F)	1.379(4)
C(1C)-C(6C)	1.391(3)	C(5F)-C(6F)	1.378(4)
C(2C)-C(3C)	1.390(4)	C(1G)-C(2G)	1.3739
C(3C)-C(4C)	1.368(4)	C(1G)-C(6G)	1.4165
C(4C)-C(5C)	1.378(4)	C(1G)-C(7G)	1.4769
C(5C)-C(6C)	1.390(4)	C(2G)-C(3G)	1.3812
C(1D)-C(2D)	1.382(4)	C(3G)-C(4G)	1.3519
C(1D)-C(6D)	1.389(4)	C(4G)-C(5G)	1.4084
C(2D)-C(3D)	1.384(4)	C(5G)-C(6G)	1.3625
C(3D)-C(4D)	1.370(5)		
N(1)-S(1)-C(1)	105.34(10)	P(1)-N(1)-S(1)	123.91(12)
N(1)-P(1)-C(1D)	117.62(11)	N(1)-P(1)-C(1F)	108.43(11)

C(1D)-P(1)-C(1F)	107.14(11)	C(1D)-P(1)-C(1E)	105.45(11)
N(1)-P(1)-C(1E)	112.56(11)	C(1F)-P(1)-C(1E)	104.78(11)
		C(1B)-C(1)-S(1)	109.86(14)
C(1B)-C(1)-C(1A)	112.85(18)	C(1A)-C(1)-S(1)	101.91(14)
C(1B)-C(1)-C(1C)	111.44(18)	C(1C)-C(1)-S(1)	111.64(15)
C(1A)-C(1)-C(1C)	108.79(17)		
C(6A)-C(1A)-C(2A)	117.9(2)	C(2D)-C(1D)-C(6D)	119.4(2)
C(6A)-C(1A)-C(1)	123.3(2)	C(2D)-C(1D)-P(1)	121.7(2)
C(2A)-C(1A)-C(1)	118.8(2)	C(6D)-C(1D)-P(1)	118.83(19)
C(3A)-C(2A)-C(1A)	121.0(2)	C(1D)-C(2D)-C(3D)	120.7(3)
C(2A)-C(3A)-C(4A)	120.1(3)	C(4D)-C(3D)-C(2D)	119.9(3)
C(5A)-C(4A)-C(3A)	119.5(2)	C(3D)-C(4D)-C(5D)	120.1(3)
C(4A)-C(5A)-C(6A)	120.7(3)	C(4D)-C(5D)-C(6D)	120.4(3)
C(1A)-C(6A)-C(5A)	120.8(3)	C(1D)-C(6D)-C(5D)	119.6(3)
C(2B)-C(1B)-C(6B)	117.7(2)	C(2E)-C(1E)-C(6E)	118.7(2)
C(2B)-C(1B)-C(1)	122.8(2)	C(2E)-C(1E)-P(1)	122.5(2)
C(6B)-C(1B)-C(1)	119.5(2)	C(6E)-C(1E)-P(1)	118.48(19)
C(1B)-C(2B)-C(3B)	121.3(2)	C(1E)-C(2E)-C(3E)	120.6(3)
C(4B)-C(3B)-C(2B)	119.9(2)	C(4E)-C(3E)-C(2E)	120.1(3)
C(3B)-C(4B)-C(5B)	119.8(2)	C(5E)-C(4E)-C(3E)	119.7(3)
C(4B)-C(5B)-C(6B)	120.2(2)	C(4E)-C(5E)-C(6E)	120.3(3)
C(5B)-C(6B)-C(1B)	121.0(2)	C(1E)-C(6E)-C(5E)	120.3(3)
C(2C)-C(1C)-C(6C)	118.2(2)	C(2F)-C(1F)-C(6F)	119.2(2)
C(2C)-C(1C)-C(1)	120.0(2)	C(2F)-C(1F)-P(1)	118.34(18)
C(6C)-C(1C)-C(1)	121.7(2)	C(6F)-C(1F)-P(1)	122.4(2)
C(1C)-C(2C)-C(3C)	120.8(2)	C(3F)-C(2F)-C(1F)	120.2(2)
C(4C)-C(3C)-C(2C)	120.6(2)	C(4F)-C(3F)-C(2F)	120.0(3)
C(3C)-C(4C)-C(5C)	119.2(2)	C(3F)-C(4F)-C(5F)	120.3(3)
C(4C)-C(5C)-C(6C)	120.9(3)	C(6F)-C(5F)-C(4F)	120.5(3)
C(5C)-C(6C)-C(1C)	120.2(2)	C(5F)-C(6F)-C(1F)	119.8(3)

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[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

[b] Atoms are labeled in agreement with Figures 1 -4.

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for $C_{37}H_{30}NPS – 0.5\ C_7H_8$. The anisotropic displacement factor exponent takes the form: $-2\Pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	23(1)	24(1)	25(1)	-1(1)	1(1)	2(1)
P(1)	22(1)	23(1)	29(1)	3(1)	5(1)	3(1)
N(1)	28(1)	25(1)	39(1)	6(1)	11(1)	6(1)
C(1)	18(1)	21(1)	26(1)	-1(1)	2(1)	0(1)
C(1A)	25(1)	22(1)	27(1)	3(1)	4(1)	4(1)
C(2A)	34(1)	29(1)	33(1)	-3(1)	5(1)	2(1)
C(3A)	54(2)	37(2)	32(1)	-5(1)	11(1)	11(1)
C(4A)	50(2)	49(2)	41(2)	9(1)	25(1)	18(1)
C(5A)	33(1)	50(2)	60(2)	2(2)	22(1)	1(1)
C(6A)	29(1)	33(1)	45(2)	-4(1)	9(1)	1(1)
C(1B)	17(1)	24(1)	31(1)	-4(1)	3(1)	1(1)
C(2B)	28(1)	30(1)	33(1)	-2(1)	1(1)	3(1)
C(3B)	35(1)	44(2)	31(1)	-8(1)	-3(1)	3(1)
C(4B)	36(1)	35(2)	47(2)	-18(1)	1(1)	-4(1)
C(5B)	32(1)	25(1)	50(2)	-5(1)	7(1)	-3(1)
C(6B)	25(1)	27(1)	34(1)	-2(1)	4(1)	-2(1)
C(1C)	29(1)	22(1)	21(1)	-1(1)	1(1)	0(1)
C(2C)	32(1)	29(1)	36(1)	3(1)	4(1)	3(1)
C(3C)	50(2)	25(1)	36(1)	4(1)	-1(1)	7(1)
C(4C)	63(2)	26(1)	38(2)	7(1)	6(1)	-5(1)
C(5C)	46(2)	42(2)	50(2)	13(1)	15(1)	-6(1)
C(6C)	33(1)	33(1)	43(2)	7(1)	9(1)	0(1)
C(1D)	23(1)	26(1)	36(1)	7(1)	5(1)	5(1)
C(2D)	36(1)	30(1)	49(2)	7(1)	2(1)	-1(1)
C(3D)	39(2)	37(2)	74(2)	16(2)	0(2)	-8(1)
C(4D)	31(2)	53(2)	80(2)	31(2)	15(2)	-2(1)
C(5D)	43(2)	63(2)	49(2)	19(2)	20(1)	10(2)
C(6D)	33(1)	39(2)	41(2)	6(1)	10(1)	4(1)
C(1E)	27(1)	27(1)	33(1)	-1(1)	6(1)	4(1)
C(2E)	30(1)	55(2)	59(2)	23(2)	8(1)	7(1)

C(3E)	33(2)	68(2)	58(2)	21(2)	2(1)	14(2)
C(4E)	26(1)	52(2)	60(2)	-9(2)	-2(1)	6(1)
C(5E)	33(2)	34(2)	83(2)	-6(2)	4(2)	-7(1)
C(6E)	33(1)	29(1)	58(2)	5(1)	1(1)	-1(1)
C(1F)	28(1)	27(1)	33(1)	0(1)	9(1)	1(1)
C(2F)	33(1)	36(1)	34(1)	3(1)	10(1)	6(1)
C(3F)	40(2)	51(2)	31(1)	1(1)	6(1)	2(1)
C(4F)	46(2)	53(2)	34(1)	-9(1)	13(1)	-1(1)
C(5F)	47(2)	48(2)	52(2)	-10(1)	17(1)	13(1)
C(6F)	36(2)	45(2)	40(2)	-2(1)	4(1)	13(1)
			Disordered Toluene of Crystallization[d]			
C(1G)	50(5)	202(10)	87(8)	60(7)	11(5)	-25(4)
C(2G)	52(5)	207(10)	101(8)	99(7)	10(5)	3(5)
C(3G)	63(6)	263(13)	98(8)	41(8)	6(6)	17(7)
C(4G)	82(7)	268(13)	55(6)	37(8)	-3(6)	-21(7)
C(5G)	46(5)	255(13)	119(9)	18(8)	-10(5)	-40(6)
C(6G)	52(5)	222(12)	185(13)	31(9)	11(8)	-28(6)
C(7G)	106(9)	175(10)	122(11)	82(7)	7(7)	-57(7)

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[a] The numbers in parentheses are the estimated standard deviations in the last significant digit.

[b] The form of the anisotropic thermal parameter is: $\exp[-2\pi^2 (U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

[c] Atoms are labeled in agreement with Figures 1 - 4.

[d] The toluene solvent molecule of crystallization lies on a crystallographic inversion center at ½,½,0 in the unit cell and is therefore disordered with two orientations in the crystal. Restraints were imposed on the positional and displacement parameters of the seven (half-occupancy) carbon atoms.

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for $C_{37}H_{30}NPS$ – 0.5 C_7H_8

	x	y	z	U(eq)
H(2A)	1818	6076	2306	39
H(3A)	1011	6710	3145	49
H(4A)	-221	5810	3018	53
H(5A)	-617	4241	2074	55
H(6A)	188	3590	1233	42
H(2B)	1113	4290	-502	37
H(3B)	641	2570	-1315	46
H(4B)	554	571	-758	48
H(5B)	944	294	611	43
H(6B)	1426	2001	1422	35
H(2C)	634	6305	507	39
H(3C)	790	8119	-222	46
H(4C)	1978	8574	-539	52
H(5C)	3010	7178	-151	54
H(6C)	2869	5357	579	43
H(2D)	2603	-455	1040	47
H(3D)	1961	-1791	1772	62
H(4D)	1969	-1340	3096	65
H(5D)	2576	491	3679	60
H(6D)	3220	1843	2951	44
H(2E)	4482	233	2419	57
H(3E)	5809	243	2965	65
H(4E)	6568	1958	2740	57
H(5E)	6038	3516	1835	61
H(6E)	4711	3519	1287	49
H(2F)	2471	2245	-160	41
H(3F)	2366	1324	-1414	49
H(4F)	3233	-240	-1612	53
H(5F)	4197	-922	-563	57
H(6F)	4306	-38	697	49

		Disordered Toluene of Crystallization		
H(2G)	3836	4734	-159	145
H(3G)	4172	6639	489	171
H(4G)	5458	7232	841	165
H(5G)	6412	5936	462	173
H(6G)	6079	4049	-200	186

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[a] Hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp^2- hybridization of the carbon atoms and C-H bond lengths of 0.95Å) "riding" on their respective carbon atoms. The isotropic thermal parameters of the hydrogen atoms were fixed at values 1.2(non-methyl) times the equivalent isotropic thermal parameters of the carbon atoms to which they are covalently bonded. Hydrogen atoms on the methyl group of the disordered toluene molecule were not included in the structural model.

[b] Hydrogen atoms bonded to carbon are labeled with the same numerical and literal subscripts as their respective carbon atoms.

Table 6. Torsion angles [°] for $C_{37}H_{30}NPS – 0.5\ C_7H_8$

C(1D)-P(1)-N(1)-S(1)	19.9(2)
C(1F)-P(1)-N(1)-S(1)	141.56(15)
C(1E)-P(1)-N(1)-S(1)	-102.99(16)
C(1)-S(1)-N(1)-P(1)	-123.64(15)
N(1)-S(1)-C(1)-C(1B)	48.73(17)
N(1)-S(1)-C(1)-C(1A)	168.60(14)
N(1)-S(1)-C(1)-C(1C)	-75.43(17)
C(1B)-C(1)-C(1A)-C(6A)	-8.3(3)
C(1C)-C(1)-C(1A)-C(6A)	115.9(2)
S(1)-C(1)-C(1A)-C(6A)	-126.0(2)
C(1B)-C(1)-C(1A)-C(2A)	175.1(2)
C(1C)-C(1)-C(1A)-C(2A)	-60.7(3)
S(1)-C(1)-C(1A)-C(2A)	57.3(2)
C(6A)-C(1A)-C(2A)-C(3A)	-0.7(4)
C(1)-C(1A)-C(2A)-C(3A)	176.1(2)
C(1A)-C(2A)-C(3A)-C(4A)	-0.2(4)
C(2A)-C(3A)-C(4A)-C(5A)	0.9(4)
C(3A)-C(4A)-C(5A)-C(6A)	-0.8(4)
C(2A)-C(1A)-C(6A)-C(5A)	0.8(4)
C(1)-C(1A)-C(6A)-C(5A)	-175.9(2)
C(4A)-C(5A)-C(6A)-C(1A)	-0.1(4)
C(1A)-C(1)-C(1B)-C(2B)	114.1(2)
C(1C)-C(1)-C(1B)-C(2B)	-8.6(3)
S(1)-C(1)-C(1B)-C(2B)	-132.9(2)
C(1A)-C(1)-C(1B)-C(6B)	-64.8(3)
C(1C)-C(1)-C(1B)-C(6B)	172.46(19)
S(1)-C(1)-C(1B)-C(6B)	48.2(2)
C(6B)-C(1B)-C(2B)-C(3B)	0.0(3)
C(1)-C(1B)-C(2B)-C(3B)	-178.9(2)
C(1B)-C(2B)-C(3B)-C(4B)	0.2(4)
C(2B)-C(3B)-C(4B)-C(5B)	-0.2(4)
C(3B)-C(4B)-C(5B)-C(6B)	-0.2(4)
C(4B)-C(5B)-C(6B)-C(1B)	0.4(4)
C(2B)-C(1B)-C(6B)-C(5B)	-0.4(3)

C(1)-C(1B)-C(6B)-C(5B)	178.6(2)
C(1B)-C(1)-C(1C)-C(2C)	87.1(2)
C(1A)-C(1)-C(1C)-C(2C)	-38.0(3)
S(1)-C(1)-C(1C)-C(2C)	-149.67(19)
C(1B)-C(1)-C(1C)-C(6C)	-91.4(3)
C(1A)-C(1)-C(1C)-C(6C)	143.5(2)
S(1)-C(1)-C(1C)-C(6C)	31.8(3)
C(6C)-C(1C)-C(2C)-C(3C)	-0.7(4)
C(1)-C(1C)-C(2C)-C(3C)	-179.3(2)
C(1C)-C(2C)-C(3C)-C(4C)	0.0(4)
C(2C)-C(3C)-C(4C)-C(5C)	0.8(4)
C(3C)-C(4C)-C(5C)-C(6C)	-0.8(4)
C(4C)-C(5C)-C(6C)-C(1C)	0.0(4)
C(2C)-C(1C)-C(6C)-C(5C)	0.7(4)
C(1)-C(1C)-C(6C)-C(5C)	179.2(2)
N(1)-P(1)-C(1D)-C(2D)	114.9(2)
C(1F)-P(1)-C(1D)-C(2D)	-7.4(2)
C(1E)-P(1)-C(1D)-C(2D)	-118.7(2)
N(1)-P(1)-C(1D)-C(6D)	-61.3(2)
C(1F)-P(1)-C(1D)-C(6D)	176.39(19)
C(1E)-P(1)-C(1D)-C(6D)	65.2(2)
C(6D)-C(1D)-C(2D)-C(3D)	-0.6(4)
P(1)-C(1D)-C(2D)-C(3D)	-176.8(2)
C(1D)-C(2D)-C(3D)-C(4D)	-0.4(4)
C(2D)-C(3D)-C(4D)-C(5D)	1.3(4)
C(3D)-C(4D)-C(5D)-C(6D)	-1.2(4)
C(2D)-C(1D)-C(6D)-C(5D)	0.7(4)
P(1)-C(1D)-C(6D)-C(5D)	177.0(2)
C(4D)-C(5D)-C(6D)-C(1D)	0.2(4)
N(1)-P(1)-C(1E)-C(2E)	150.3(2)
C(1D)-P(1)-C(1E)-C(2E)	20.8(3)
C(1F)-P(1)-C(1E)-C(2E)	-92.1(2)
N(1)-P(1)-C(1E)-C(6E)	-36.4(2)
C(1D)-P(1)-C(1E)-C(6E)	-165.8(2)
C(1F)-P(1)-C(1E)-C(6E)	81.3(2)
C(6E)-C(1E)-C(2E)-C(3E)	4.0(4)

P(1)-C(1E)-C(2E)-C(3E)	177.3(2)
C(1E)-C(2E)-C(3E)-C(4E)	0.3(5)
C(2E)-C(3E)-C(4E)-C(5E)	-4.6(5)
C(3E)-C(4E)-C(5E)-C(6E)	4.7(5)
C(2E)-C(1E)-C(6E)-C(5E)	-3.9(4)
P(1)-C(1E)-C(6E)-C(5E)	-177.5(2)
C(4E)-C(5E)-C(6E)-C(1E)	-0.4(5)
N(1)-P(1)-C(1F)-C(2F)	-28.8(2)
C(1D)-P(1)-C(1F)-C(2F)	99.1(2)
C(1E)-P(1)-C(1F)-C(2F)	-149.2(2)
N(1)-P(1)-C(1F)-C(6F)	153.8(2)
C(1D)-P(1)-C(1F)-C(6F)	-78.3(2)
C(1E)-P(1)-C(1F)-C(6F)	33.4(2)
C(6F)-C(1F)-C(2F)-C(3F)	-0.7(4)
P(1)-C(1F)-C(2F)-C(3F)	-178.1(2)
C(1F)-C(2F)-C(3F)-C(4F)	-0.1(4)
C(2F)-C(3F)-C(4F)-C(5F)	0.5(4)
C(3F)-C(4F)-C(5F)-C(6F)	-0.2(5)
C(4F)-C(5F)-C(6F)-C(1F)	-0.7(5)
C(2F)-C(1F)-C(6F)-C(5F)	1.1(4)
P(1)-C(1F)-C(6F)-C(5F)	178.4(2)
C(6G)-C(1G)-C(2G)-C(3G)	0.4
C(7G)-C(1G)-C(2G)-C(3G)	-179.7
C(1G)-C(2G)-C(3G)-C(4G)	-1.4
C(2G)-C(3G)-C(4G)-C(5G)	1.8
C(3G)-C(4G)-C(5G)-C(6G)	-1.4
C(4G)-C(5G)-C(6G)-C(1G)	0.4
C(2G)-C(1G)-C(6G)-C(5G)	0.1
C(7G)-C(1G)-C(6G)-C(5G)	-179.8

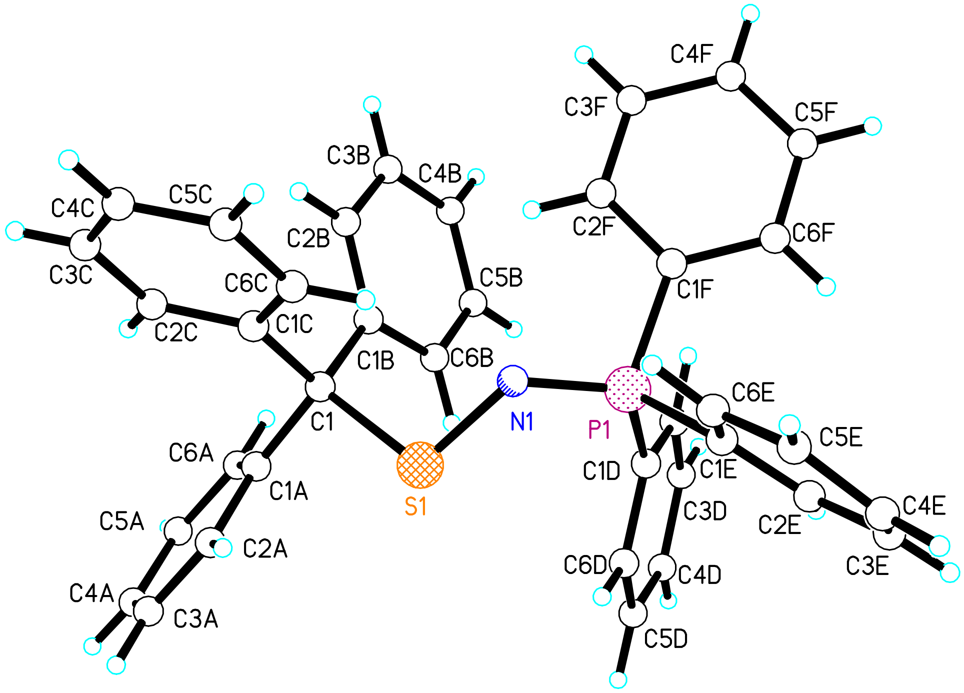
FIGURE CAPTIONS

Figure 1.

shows a perspective drawing of the $C_{37}H_{30}NPS$ molecule present in the solid state structure of $C_{37}H_{30}NPS$ – 0.5 C_7H_8. The sulfur and phosphorous atoms are represented by a large cross-hatched and dotted sphere, respectively. The nitrogen atom is represented by a medium-sized shaded sphere and carbon and hydrogen atoms are represented by medium and small open spheres, respectively.

Figure 2.

shows a perspective drawing of the $C_{37}H_{30}NPS$ molecule present in the solid state structure of $C_{37}H_{30}NPS$ – 0.5 C_7H_8. Nonhydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density. Hydrogen atoms are represented by arbitrarily-small spheres, which are in no way representative of their true thermal motion.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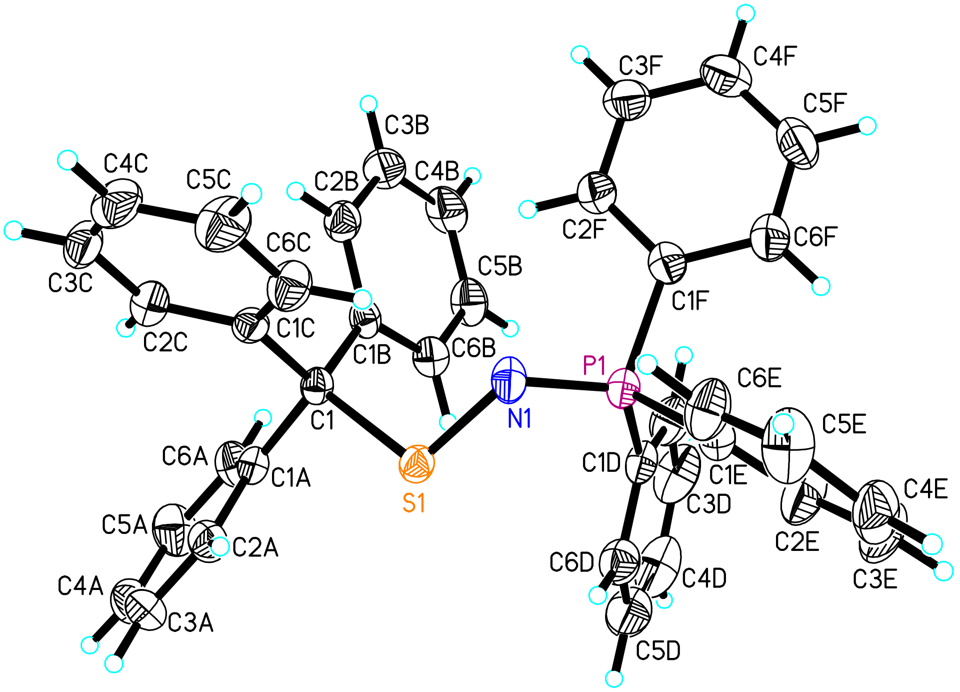
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