Direct observation of key intermediates by negative-ion electrospray ionization mass spectrometry in palladium-catalyzed cross-coupling

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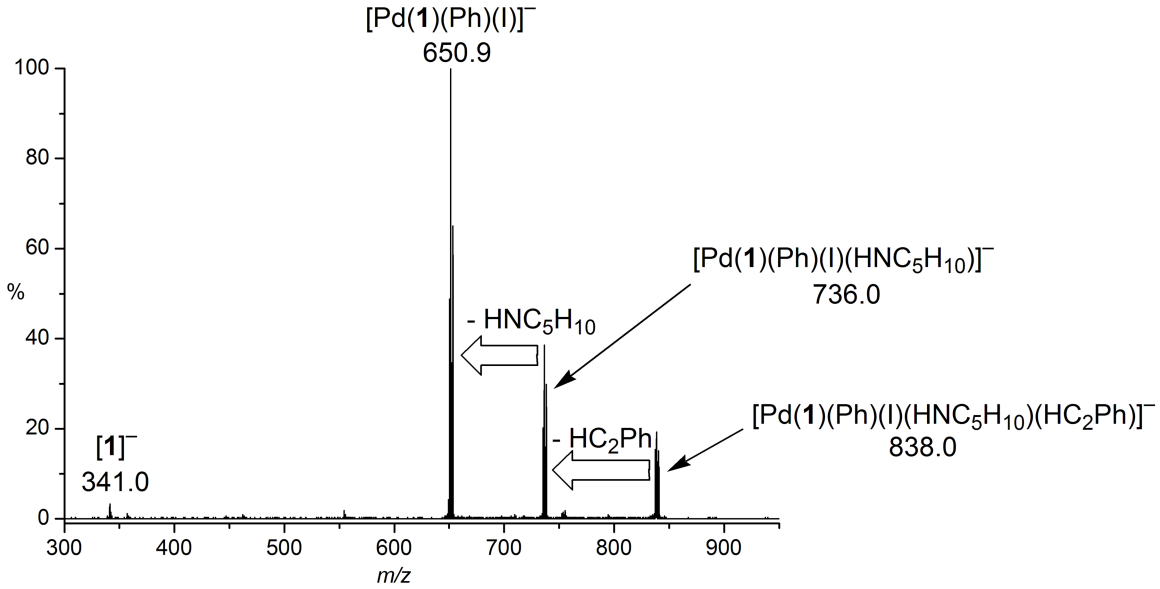

Figure SI1. Negative-ion ESI-MS/MS of [Pd(**1**)(Ph)(I)(HNC_5H_{10})(HC_2Ph)]$^-$. Analogous data was obtained for the complex with morpholine in place of piperidine.

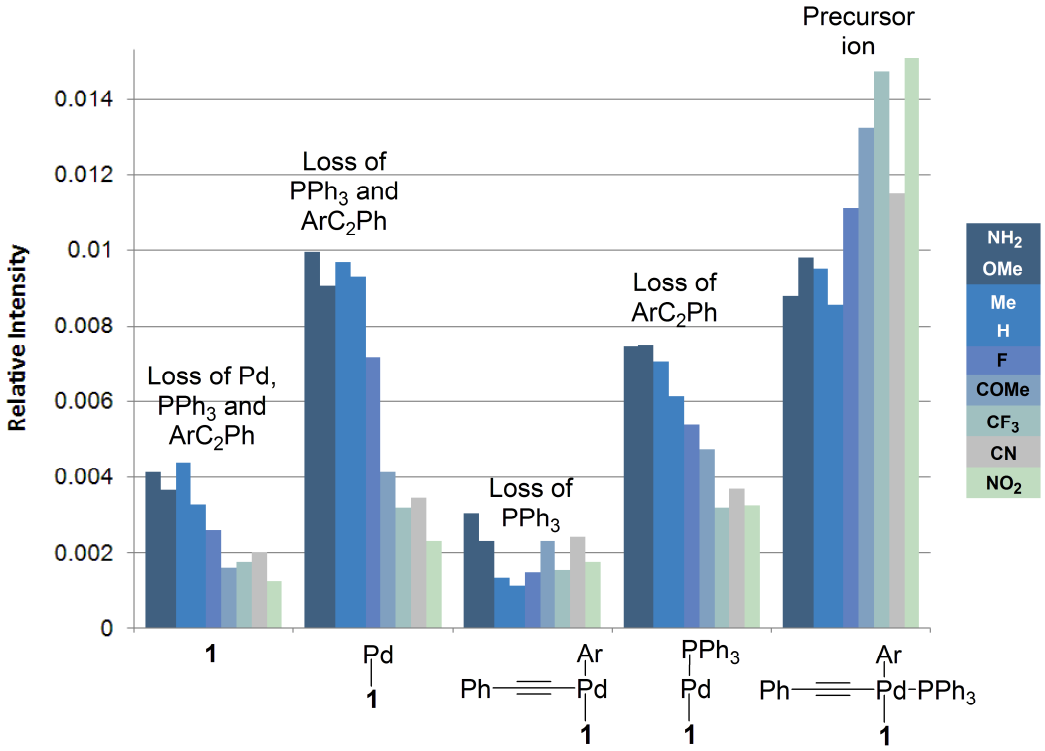

Figure SI2. Summary of all negative-ion ESI-MS/MS of $[Pd(\mathbf{1})(PPh_3)(Ar)(C_2Ph)]^-$, showing the precursor ion and the four product ions, at a collision voltage of 15 V. This plot uses peak height instead of the integral. The leftmost bar in each set is the most electron-releasing substituent (NH_2), the rightmost is the most electron-withdrawing (NO_2), and the remainder are plotted in order of their Hammett σ_p parameter.

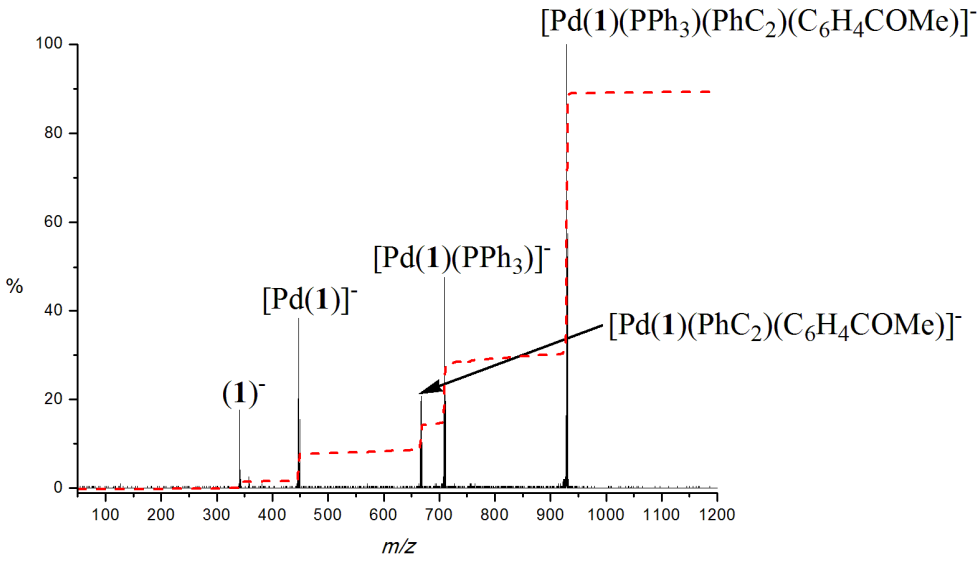

Figure SI3. Negative-ion ESI-MS/MS of $[Pd(\mathbf{1})(PPh_3)(C_6H_4COMe)(C_2Ph)]^-$, showing reductive elimination to $[Pd(\mathbf{1})(PPh_3)]^-$, at a collision voltage of 15 V.

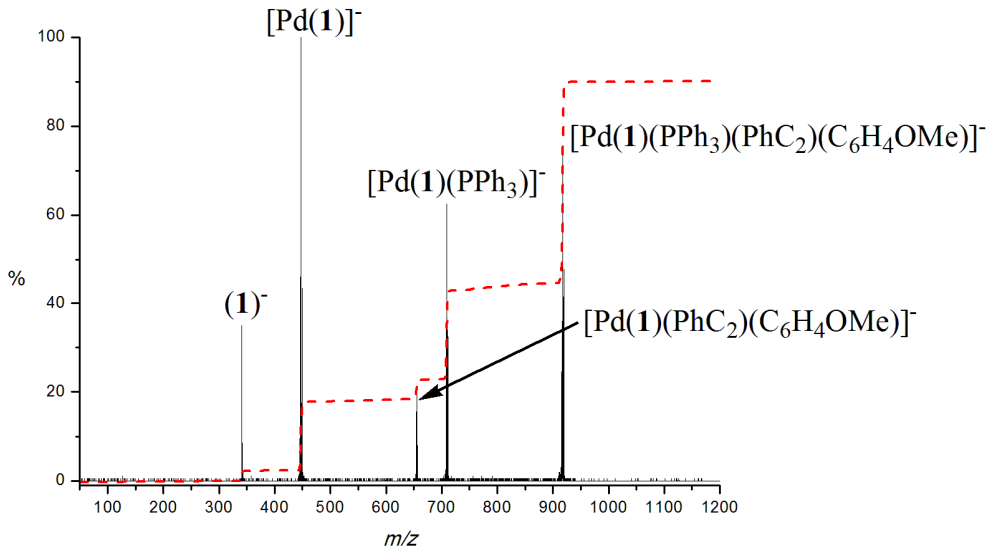

Figure SI4. Negative-ion ESI-MS/MS of $[Pd(\mathbf{1})(PPh_3)(C_6H_4OMe)(C_2Ph)]^-$, showing reductive elimination to $[Pd(\mathbf{1})(PPh_3)]^-$, at a collision voltage of 15 V.

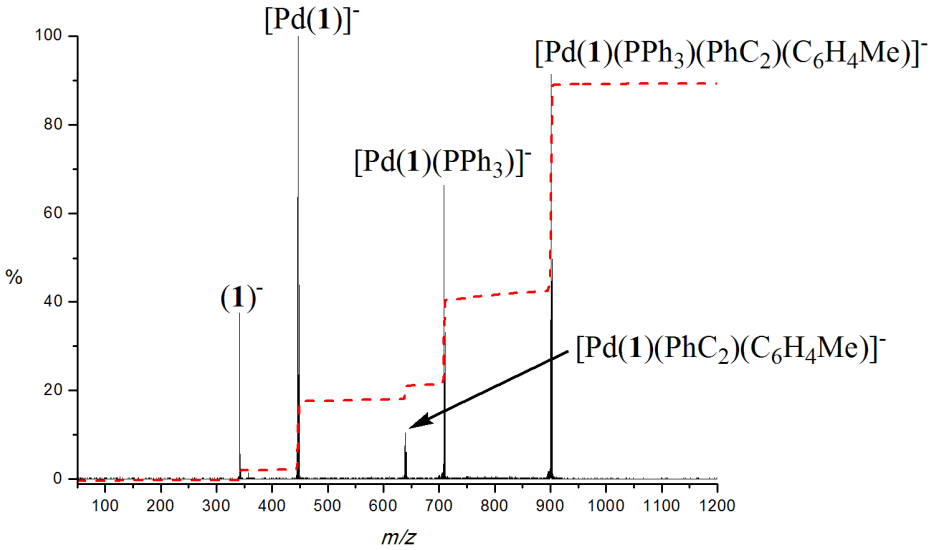

Figure SI5. Negative-ion ESI-MS/MS of $[Pd(\mathbf{1})(PPh_3)(C_6H_4Me)(C_2Ph)]^-$, showing reductive elimination to $[Pd(\mathbf{1})(PPh_3)]^-$, at a collision voltage of 15 V.

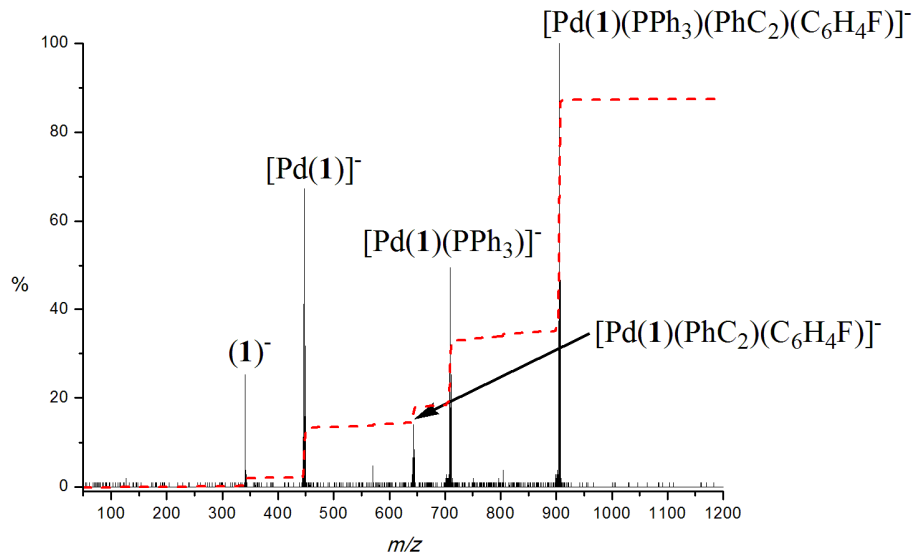

Figure SI6. Negative-ion ESI-MS/MS of [Pd(**1**)(PPh_3)(C_6H_4F)(C_2Ph)]$^-$, showing reductive elimination to [Pd(**1**)(PPh_3)]$^-$, at a collision voltage of 15 V.

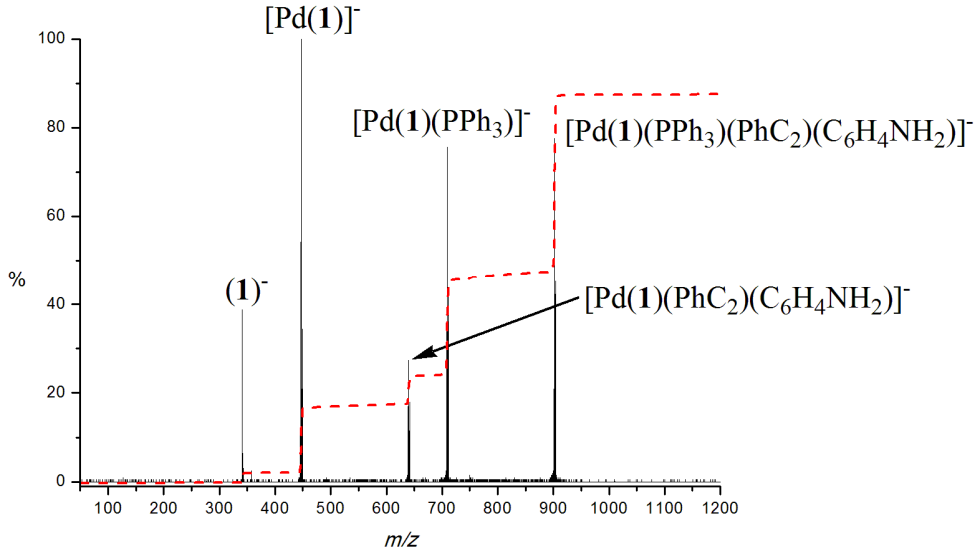

Figure SI7. Negative-ion ESI-MS/MS of [Pd(**1**)(PPh_3)($C_6H_4NH_2$)(C_2Ph)]$^-$, showing reductive elimination to [Pd(**1**)(PPh_3)]$^-$, at a collision voltage of 15 V.

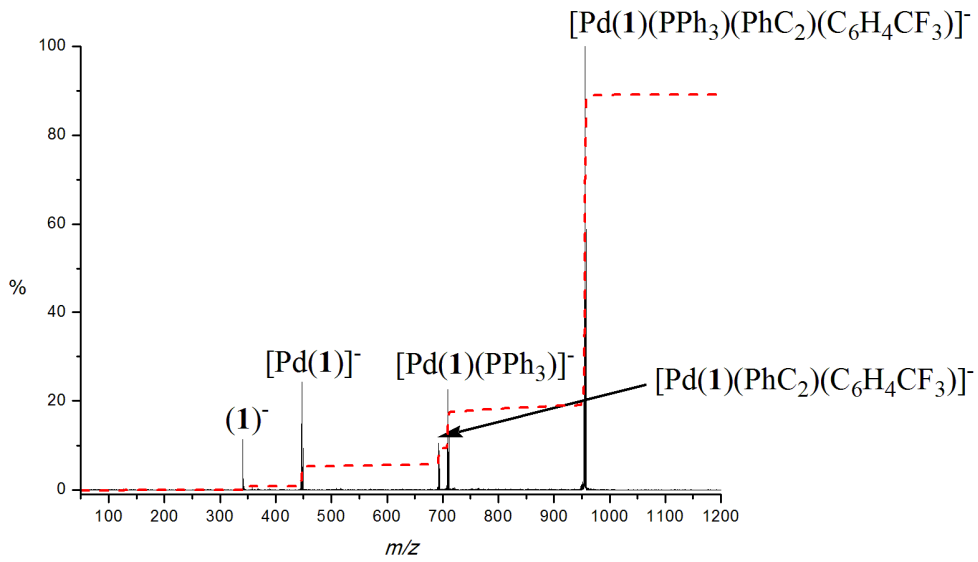

Figure SI8. Negative-ion ESI-MS/MS of [Pd(**1**)(PPh_3)($C_6H_4CF_3$)(C_2Ph)]$^-$, showing reductive elimination to [Pd(**1**)(PPh_3)]$^-$, at a collision voltage of 15 V.

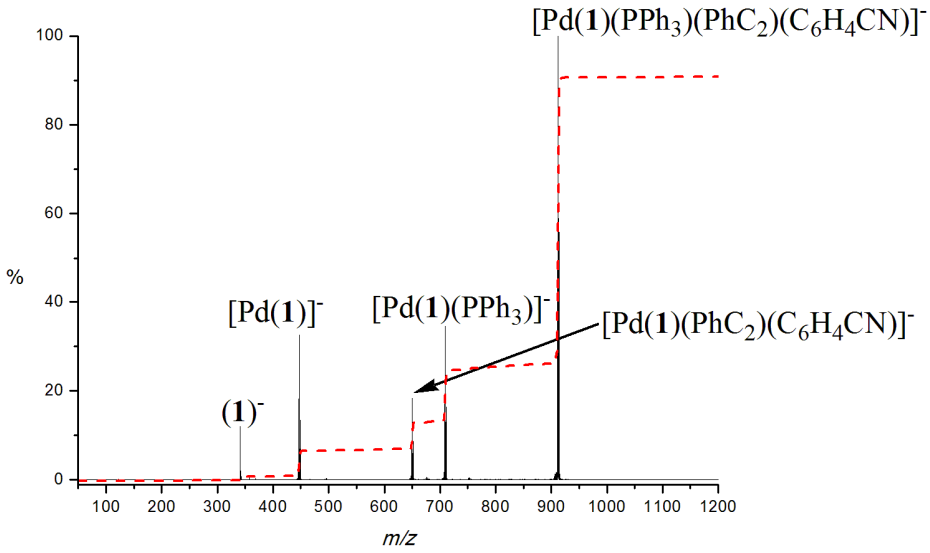

Figure SI9. Negative-ion ESI-MS/MS of [Pd(**1**)(PPh_3)(C_6H_4CN)(C_2Ph)]$^-$, showing reductive elimination to [Pd(**1**)(PPh_3)]$^-$, at a collision voltage of 15 V.

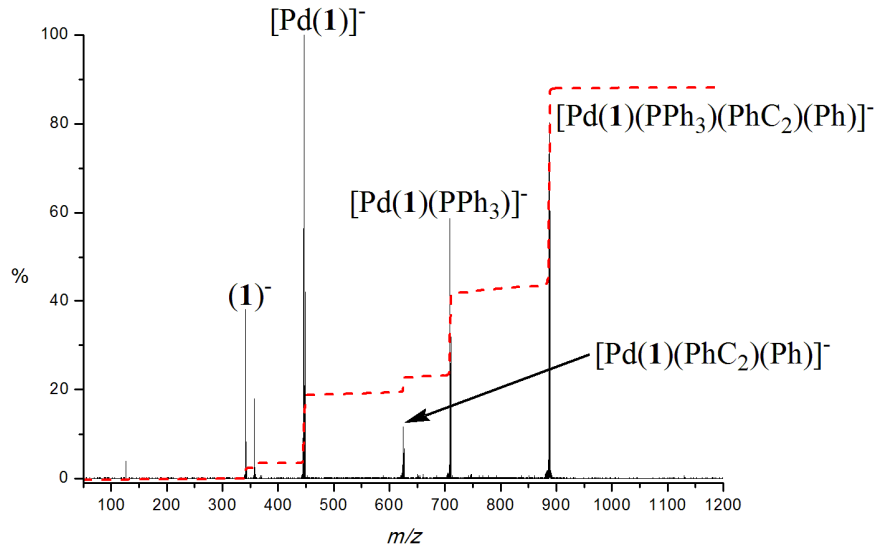

Figure SI10. Negative-ion ESI-MS/MS of $[Pd(\mathbf{1})(PPh_3)(C_6H_5)(C_2Ph)]^-$, showing reductive elimination to $[Pd(\mathbf{1})(PPh_3)]^-$, at a collision voltage of 15 V.

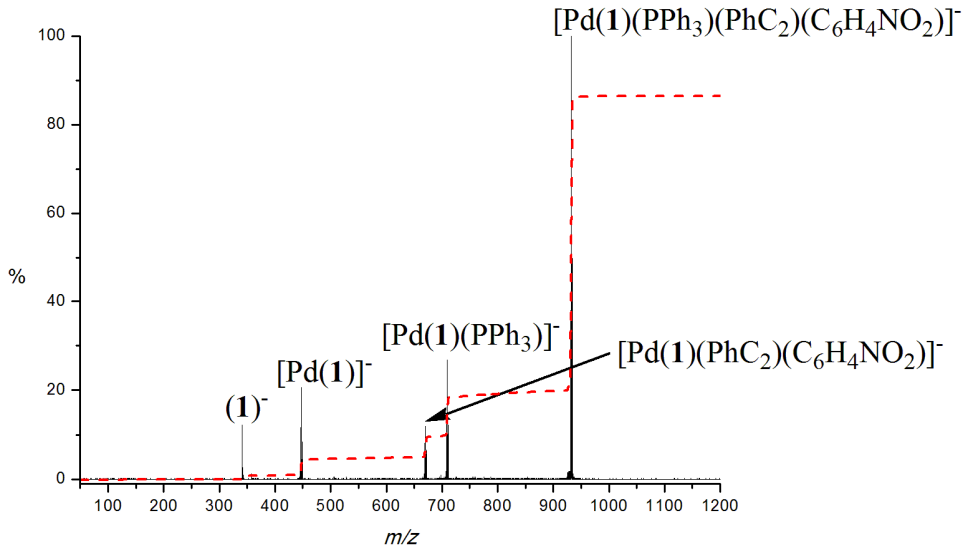

Figure SI11. Negative-ion ESI-MS/MS of $[Pd(\mathbf{1})(PPh_3)(C_6H_4NO_2)(C_2Ph)]^-$, showing reductive elimination to $[Pd(\mathbf{1})(PPh_3)]^-$, at a collision voltage of 15 V.

X-ray Structure Report for $[Ph_3NPh_3]^+$ $[PPh_2(m\text{-}C_6H_4SO_3)]^-$ = [PPN][1]

Crystal data for $C_{54}H_{44}NO_3P_3S$; M_r = 879.87; triclinic; space group P-1; a = 10.2219(12) Å; b = 15.1177(17) Å; c = 15.1616(17) Å; α = 104.5580(10)°; β = 96.5030(10)°; γ = 99.5370(10)°; V = 2206.7(4) $Å^3$; Z = 2; T = 150(2) K; λ(Mo-Kα) = 0.71073 Å; μ(Mo-Kα) = 0.229 mm^{-1}; d_{calc} = 1.324g.cm^{-3}; 25164 reflections collected; 10846 unique (R_{int} = 0.0224); giving R_1 = 0.0360, wR_2 = 0.0928 for 9273 data with [I>2σ(I)] and R_1 = 0.0432, wR_2 = 0.0978 for all 10846 data. Residual electron density ($e^-.Å^{-3}$) max/min: 0.502/-0.364.

An arbitrary sphere of data were collected on a colourless block-like crystal, having approximate dimensions of 0.27 × 0.24 × 0.18 mm, on a Bruker APEX-II diffractometer using a combination of ω- and φ-scans of 0.3°. Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by direct methods and expanded routinely. The model was refined by full-matrix least-squares analysis of F^2 against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.2 × for all H).

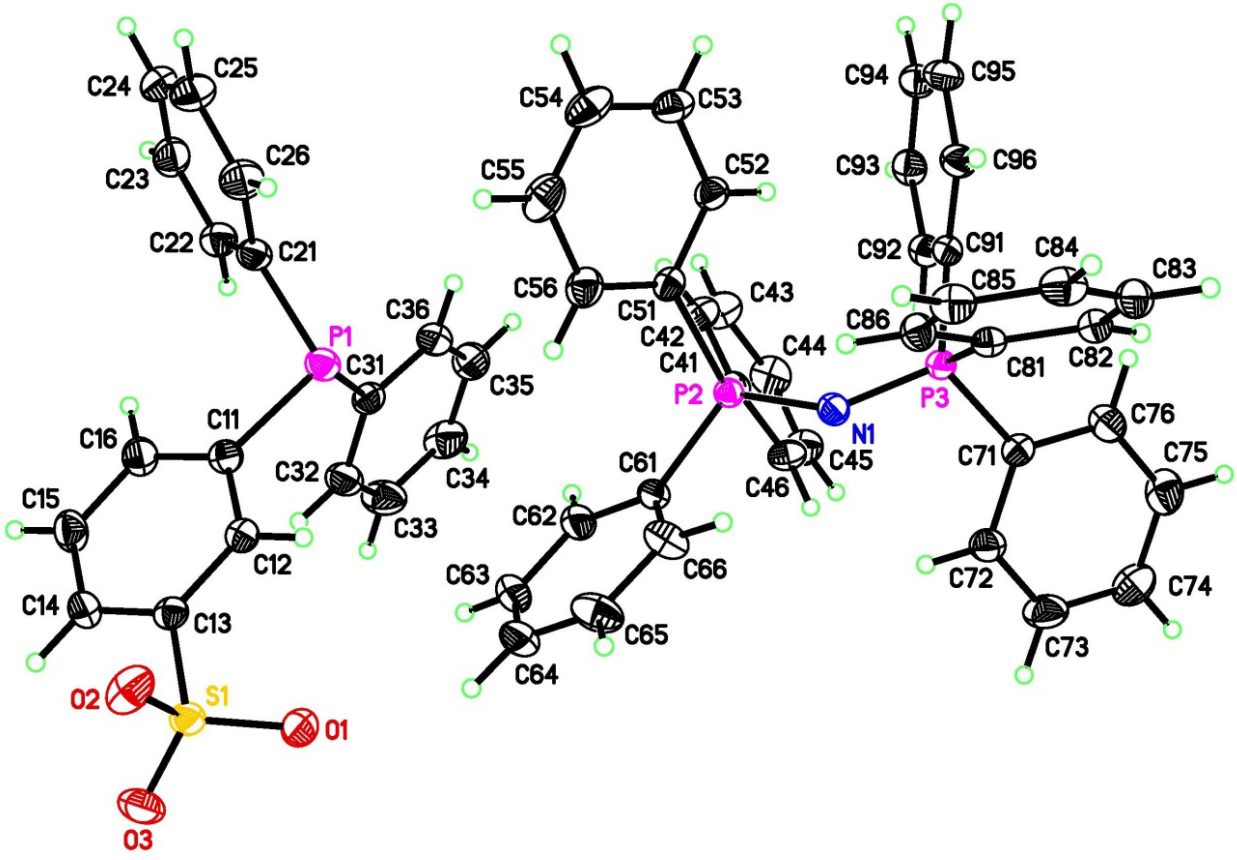

Figure SI12. Labeled ORTEP plot of $[Ph_3NPh_3]^+$ $[PPh_2(m\text{-}C_6H_4SO_3)]^-$ = [PPN][**1**].

Table 1. Crystal data and structure refinement for jsm009.

Identification code	jsm009
Empirical formula	$C_{54}H_{44}NO_3P_3S$
Formula weight	879.87
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 10.2219(12) Å α = 104.5580(10)°
	b = 15.1177(17) Å β = 96.5030(10)°
	c = 15.1616(17) Å γ = 99.5370(10)°
Volume	2206.7(4) $Å^3$
Z	2
Density (calculated)	1.324 $g.cm^{-3}$
Absorption coefficient (μ)	0.229 mm^{-1}
F(000)	920
Crystal size	0.27 × 0.24 × 0.18 mm^3
θ range for data collection	2.24 to 28.47°
Index ranges	$-13 \leq h \leq 13$, $-19 \leq k \leq 20$, $-20 \leq l \leq 19$
Reflections collected	25164
Independent reflections	10846 [R_{int} = 0.0224]
Completeness to θ = 28.47°	97.0 %
Absorption correction	empirical
Max. and min. transmission	0.9599 and 0.9407
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10846 / 0 / 559
Goodness-of-fit on F^2	1.040
Final R indices [I>2σ(I)]	R_1 = 0.0360, wR_2 = 0.0928
R indices (all data)	R_1 = 0.0432, wR_2 = 0.0978
Largest diff. peak and hole	0.502 and -0.364 $e^-.Å^{-3}$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for jsm009. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	0.48660(4)	0.15874(2)	0.25203(2)	0.021(1)
P(1)	0.36721(4)	0.51063(3)	0.33772(3)	0.022(1)
P(2)	0.76521(3)	0.72585(2)	0.20995(2)	0.016(1)
P(3)	1.02367(3)	0.85279(2)	0.21452(2)	0.016(1)
O(1)	0.59691(11)	0.21226(7)	0.22293(8)	0.027(1)
O(2)	0.52234(12)	0.14233(9)	0.34100(8)	0.034(1)
O(3)	0.41699(12)	0.07503(8)	0.18105(9)	0.034(1)
N(1)	0.91940(11)	0.76029(8)	0.20698(8)	0.020(1)
C(11)	0.30792(14)	0.38418(10)	0.31120(10)	0.021(1)
C(12)	0.40296(14)	0.32793(10)	0.29331(9)	0.020(1)
C(13)	0.36453(14)	0.23104(10)	0.26957(9)	0.020(1)
C(14)	0.23054(15)	0.18990(10)	0.26303(11)	0.025(1)
C(15)	0.13546(16)	0.24499(11)	0.28028(12)	0.030(1)
C(16)	0.17412(15)	0.34143(11)	0.30460(11)	0.027(1)
C(21)	0.25405(15)	0.55777(10)	0.41499(10)	0.023(1)
C(22)	0.12290(15)	0.56455(10)	0.38492(11)	0.026(1)
C(23)	0.04434(17)	0.60285(11)	0.44742(12)	0.032(1)
C(24)	0.09721(19)	0.63629(12)	0.54021(13)	0.037(1)
C(25)	0.2268(2)	0.63091(13)	0.57151(12)	0.039(1)
C(26)	0.30525(18)	0.59161(12)	0.50907(11)	0.033(1)
C(31)	0.29691(14)	0.53303(10)	0.23049(10)	0.023(1)
C(32)	0.23697(17)	0.46385(11)	0.14963(11)	0.030(1)
C(33)	0.1929(2)	0.48727(12)	0.07014(12)	0.037(1)
C(34)	0.20663(19)	0.57966(13)	0.07014(12)	0.037(1)
C(35)	0.26602(18)	0.64945(12)	0.15030(12)	0.033(1)
C(36)	0.31153(16)	0.62642(10)	0.22930(11)	0.028(1)
C(41)	0.65745(13)	0.76525(9)	0.13238(9)	0.019(1)
C(42)	0.55941(15)	0.81513(11)	0.15992(10)	0.025(1)
C(43)	0.49343(16)	0.85497(12)	0.09892(11)	0.031(1)
C(44)	0.52356(17)	0.84375(12)	0.01074(11)	0.032(1)
C(45)	0.61917(17)	0.79216(11)	-0.01782(11)	0.029(1)
C(46)	0.68601(15)	0.75331(10)	0.04242(10)	0.024(1)
C(51)	0.72547(13)	0.76187(10)	0.32464(9)	0.020(1)
C(52)	0.73897(14)	0.85735(10)	0.36680(10)	0.022(1)
C(53)	0.72210(15)	0.88831(11)	0.45798(10)	0.027(1)
C(54)	0.69053(17)	0.82458(13)	0.50766(11)	0.033(1)
C(55)	0.67574(18)	0.73029(13)	0.46651(12)	0.036(1)
C(56)	0.69280(16)	0.69811(11)	0.37493(11)	0.028(1)
C(61)	0.73288(14)	0.60079(9)	0.17734(10)	0.020(1)
C(62)	0.60505(15)	0.54848(11)	0.13726(11)	0.028(1)
C(63)	0.58002(17)	0.45238(11)	0.12389(13)	0.036(1)

C(64)	0.67931(19)	0.40896(11)	0.15168(12)	0.035(1)
C(65)	0.80674(19)	0.46098(11)	0.19041(12)	0.036(1)
C(66)	0.83459(17)	0.55657(10)	0.20240(11)	0.029(1)
C(71)	1.07308(13)	0.84874(10)	0.10366(9)	0.019(1)
C(72)	1.04848(15)	0.76270(10)	0.03775(10)	0.025(1)
C(73)	1.09109(18)	0.75536(12)	-0.04706(11)	0.034(1)
C(74)	1.16068(18)	0.83329(13)	-0.06577(11)	0.035(1)
C(75)	1.18528(18)	0.91901(13)	-0.00074(12)	0.034(1)
C(76)	1.14052(16)	0.92739(11)	0.08381(10)	0.027(1)
C(81)	1.16817(13)	0.85970(9)	0.29689(9)	0.018(1)
C(82)	1.29057(14)	0.91971(10)	0.30159(10)	0.021(1)
C(83)	1.39694(15)	0.92809(11)	0.37108(11)	0.025(1)
C(84)	1.38139(15)	0.87801(11)	0.43561(10)	0.027(1)
C(85)	1.26096(16)	0.81829(11)	0.43094(10)	0.026(1)
C(86)	1.15411(14)	0.80877(10)	0.36151(10)	0.022(1)
C(91)	0.96328(13)	0.95887(9)	0.25440(10)	0.019(1)
C(92)	0.85737(14)	0.97666(10)	0.19868(10)	0.022(1)
C(93)	0.78913(15)	1.04594(10)	0.23554(11)	0.025(1)
C(94)	0.82826(16)	1.09951(10)	0.32678(11)	0.028(1)
C(95)	0.93696(16)	1.08476(10)	0.38099(11)	0.028(1)
C(96)	1.00385(15)	1.01418(10)	0.34546(10)	0.024(1)
H(12A)	0.4945	0.3561	0.2974	0.024
H(14A)	0.2040	0.1239	0.2467	0.030
H(15A)	0.0438	0.2167	0.2754	0.036
H(16A)	0.1086	0.3788	0.3169	0.032
H(22A)	0.0869	0.5427	0.3210	0.031
H(23A)	-0.0455	0.6060	0.4264	0.039
H(24A)	0.0438	0.6632	0.5828	0.044
H(25A)	0.2625	0.6539	0.6355	0.047
H(26A)	0.3945	0.5878	0.5307	0.039
H(32A)	0.2262	0.4000	0.1490	0.035
H(33A)	0.1531	0.4394	0.0154	0.044
H(34A)	0.1757	0.5955	0.0157	0.044
H(35A)	0.2753	0.7131	0.1507	0.040
H(36A)	0.3532	0.6745	0.2834	0.033
H(42A)	0.5374	0.8221	0.2202	0.030
H(43A)	0.4275	0.8899	0.1181	0.038
H(44A)	0.4788	0.8713	-0.0304	0.038
H(45A)	0.6386	0.7836	-0.0789	0.035
H(46A)	0.7517	0.7183	0.0228	0.029
H(52A)	0.7598	0.9011	0.3326	0.026
H(53A)	0.7322	0.9532	0.4864	0.032
H(54A)	0.6790	0.8458	0.5703	0.040
H(55A)	0.6537	0.6870	0.5010	0.043
H(56A)	0.6822	0.6331	0.3469	0.034
H(62A)	0.5356	0.5781	0.1192	0.034

H(63A)	0.4935	0.4162	0.0953	0.043
H(64A)	0.6603	0.3436	0.1443	0.042
H(65A)	0.8755	0.4310	0.2089	0.043
H(66A)	0.9227	0.5918	0.2276	0.035
H(72A)	1.0023	0.7087	0.0508	0.030
H(73A)	1.0724	0.6967	-0.0923	0.041
H(74A)	1.1916	0.8279	-0.1233	0.042
H(75A)	1.2330	0.9725	-0.0138	0.041
H(76A)	1.1560	0.9867	0.1278	0.032
H(82A)	1.3008	0.9544	0.2577	0.025
H(83A)	1.4804	0.9682	0.3743	0.031
H(84A)	1.4540	0.8848	0.4834	0.032
H(85A)	1.2513	0.7838	0.4751	0.031
H(86A)	1.0715	0.7676	0.3581	0.027
H(92A)	0.8322	0.9414	0.1358	0.026
H(93A)	0.7155	1.0567	0.1983	0.030
H(94A)	0.7806	1.1462	0.3520	0.033
H(95A)	0.9657	1.1230	0.4426	0.034
H(96A)	1.0772	1.0035	0.3831	0.028

Table 3. Anisotropic displacement parameters ($Å^2$) for jsm009.
The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2 a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	0.0263(2)	0.0193(2)	0.0212(2)	0.0072(1)	0.0070(1)	0.0082(1)
P(1)	0.0220(2)	0.0192(2)	0.0246(2)	0.0047(1)	0.0035(1)	0.0054(1)
P(2)	0.0174(2)	0.0160(2)	0.0150(2)	0.0039(1)	0.0022(1)	0.0025(1)
P(3)	0.0169(2)	0.0161(2)	0.0159(2)	0.0039(1)	0.0025(1)	0.0033(1)
O(1)	0.0290(5)	0.0251(5)	0.0303(6)	0.0101(4)	0.0118(4)	0.0083(4)
O(2)	0.0395(6)	0.0468(7)	0.0307(6)	0.0232(5)	0.0133(5)	0.0236(5)
O(3)	0.0379(6)	0.0211(5)	0.0398(7)	-0.0011(5)	0.0075(5)	0.0066(5)
N(1)	0.0191(5)	0.0178(5)	0.0224(6)	0.0047(4)	0.0035(4)	0.0033(4)
C(11)	0.0238(7)	0.0211(7)	0.0205(7)	0.0071(5)	0.0037(5)	0.0064(5)
C(12)	0.0201(6)	0.0217(7)	0.0172(7)	0.0063(5)	0.0019(5)	0.0043(5)
C(13)	0.0245(7)	0.0217(7)	0.0147(6)	0.0063(5)	0.0037(5)	0.0068(5)
C(14)	0.0277(7)	0.0205(7)	0.0270(8)	0.0076(6)	0.0056(6)	0.0020(6)
C(15)	0.0227(7)	0.0269(8)	0.0403(9)	0.0116(7)	0.0076(6)	0.0018(6)
C(16)	0.0232(7)	0.0259(7)	0.0348(9)	0.0110(6)	0.0075(6)	0.0080(6)
C(21)	0.0268(7)	0.0191(6)	0.0226(7)	0.0045(5)	0.0049(6)	0.0058(5)
C(22)	0.0285(8)	0.0255(7)	0.0253(8)	0.0063(6)	0.0050(6)	0.0079(6)
C(23)	0.0311(8)	0.0286(8)	0.0423(10)	0.0115(7)	0.0145(7)	0.0100(6)
C(24)	0.0488(10)	0.0277(8)	0.0373(10)	0.0063(7)	0.0254(8)	0.0077(7)
C(25)	0.0531(11)	0.0385(9)	0.0215(8)	0.0022(7)	0.0086(7)	0.0044(8)
C(26)	0.0346(9)	0.0357(9)	0.0253(8)	0.0058(7)	0.0017(6)	0.0070(7)
C(31)	0.0246(7)	0.0225(7)	0.0237(7)	0.0074(6)	0.0086(6)	0.0076(5)
C(32)	0.0403(9)	0.0220(7)	0.0266(8)	0.0061(6)	0.0075(7)	0.0071(6)
C(33)	0.0543(11)	0.0320(9)	0.0229(8)	0.0043(7)	0.0042(7)	0.0110(8)
C(34)	0.0526(11)	0.0391(9)	0.0272(9)	0.0153(7)	0.0111(7)	0.0180(8)
C(35)	0.0433(9)	0.0259(8)	0.0382(9)	0.0152(7)	0.0147(7)	0.0130(7)
C(36)	0.0329(8)	0.0211(7)	0.0305(8)	0.0061(6)	0.0098(6)	0.0071(6)
C(41)	0.0188(6)	0.0177(6)	0.0173(7)	0.0037(5)	-0.0003(5)	0.0006(5)
C(42)	0.0238(7)	0.0316(8)	0.0205(7)	0.0074(6)	0.0035(5)	0.0086(6)
C(43)	0.0299(8)	0.0385(9)	0.0294(8)	0.0107(7)	0.0032(6)	0.0169(7)
C(44)	0.0344(8)	0.0350(8)	0.0272(8)	0.0127(7)	-0.0019(6)	0.0104(7)
C(45)	0.0360(8)	0.0353(8)	0.0169(7)	0.0080(6)	0.0013(6)	0.0081(7)
C(46)	0.0278(7)	0.0267(7)	0.0181(7)	0.0034(6)	0.0029(5)	0.0090(6)
C(51)	0.0172(6)	0.0252(7)	0.0164(7)	0.0059(5)	0.0023(5)	0.0032(5)
C(52)	0.0214(7)	0.0251(7)	0.0187(7)	0.0045(5)	0.0040(5)	0.0039(5)
C(53)	0.0245(7)	0.0337(8)	0.0199(7)	0.0008(6)	0.0028(6)	0.0078(6)
C(54)	0.0330(8)	0.0508(10)	0.0177(7)	0.0090(7)	0.0063(6)	0.0141(7)
C(55)	0.0434(10)	0.0464(10)	0.0263(9)	0.0203(7)	0.0124(7)	0.0112(8)
C(56)	0.0333(8)	0.0292(8)	0.0254(8)	0.0123(6)	0.0084(6)	0.0067(6)
C(61)	0.0246(7)	0.0166(6)	0.0190(7)	0.0035(5)	0.0050(5)	0.0028(5)
C(62)	0.0229(7)	0.0230(7)	0.0361(9)	0.0030(6)	0.0072(6)	0.0025(6)

C(63)	0.0308(8)	0.0220(7)	0.0488(11)	0.0010(7)	0.0128(7)	-0.0035(6)
C(64)	0.0502(10)	0.0176(7)	0.0376(10)	0.0060(6)	0.0162(8)	0.0049(7)
C(65)	0.0483(10)	0.0233(8)	0.0341(9)	0.0064(7)	-0.0012(7)	0.0131(7)
C(66)	0.0327(8)	0.0211(7)	0.0289(8)	0.0040(6)	-0.0039(6)	0.0053(6)
C(71)	0.0188(6)	0.0226(7)	0.0168(6)	0.0056(5)	0.0021(5)	0.0052(5)
C(72)	0.0301(8)	0.0228(7)	0.0225(7)	0.0048(6)	0.0067(6)	0.0052(6)
C(73)	0.0462(10)	0.0328(8)	0.0220(8)	0.0022(6)	0.0095(7)	0.0098(7)
C(74)	0.0435(10)	0.0466(10)	0.0203(8)	0.0131(7)	0.0115(7)	0.0107(8)
C(75)	0.0392(9)	0.0387(9)	0.0261(8)	0.0165(7)	0.0060(7)	0.0004(7)
C(76)	0.0338(8)	0.0239(7)	0.0212(7)	0.0074(6)	0.0019(6)	0.0007(6)
C(81)	0.0194(6)	0.0187(6)	0.0157(6)	0.0028(5)	0.0022(5)	0.0055(5)
C(82)	0.0210(7)	0.0206(6)	0.0211(7)	0.0043(5)	0.0044(5)	0.0044(5)
C(83)	0.0191(7)	0.0266(7)	0.0274(8)	0.0031(6)	0.0015(5)	0.0038(5)
C(84)	0.0249(7)	0.0299(8)	0.0226(8)	0.0022(6)	-0.0028(6)	0.0099(6)
C(85)	0.0317(8)	0.0270(7)	0.0206(7)	0.0083(6)	0.0022(6)	0.0101(6)
C(86)	0.0229(7)	0.0218(7)	0.0223(7)	0.0077(5)	0.0035(5)	0.0038(5)
C(91)	0.0190(6)	0.0166(6)	0.0208(7)	0.0042(5)	0.0049(5)	0.0033(5)
C(92)	0.0265(7)	0.0191(6)	0.0202(7)	0.0071(5)	0.0032(5)	0.0042(5)
C(93)	0.0254(7)	0.0215(7)	0.0312(8)	0.0105(6)	0.0052(6)	0.0073(6)
C(94)	0.0284(8)	0.0195(7)	0.0357(9)	0.0045(6)	0.0099(6)	0.0073(6)
C(95)	0.0293(8)	0.0232(7)	0.0263(8)	-0.0025(6)	0.0041(6)	0.0049(6)
C(96)	0.0219(7)	0.0227(7)	0.0231(7)	0.0021(6)	0.0014(5)	0.0033(5)

Table 4. Bond lengths [Å] for jsm009.

atom-atom	distance	atom-atom	distance
S(1)-O(2)	1.4496(12)	S(1)-O(3)	1.4524(12)
S(1)-O(1)	1.4527(11)	S(1)-C(13)	1.7897(14)
P(1)-C(11)	1.8324(15)	P(1)-C(31)	1.8349(16)
P(1)-C(21)	1.8382(15)	P(2)-N(1)	1.5853(12)
P(2)-C(61)	1.7928(14)	P(2)-C(41)	1.7965(14)
P(2)-C(51)	1.8006(14)	P(3)-N(1)	1.5820(12)
P(3)-C(81)	1.7939(14)	P(3)-C(71)	1.7985(14)
P(3)-C(91)	1.8010(14)	C(11)-C(16)	1.393(2)
C(11)-C(12)	1.3993(19)	C(12)-C(13)	1.3934(19)
C(13)-C(14)	1.389(2)	C(14)-C(15)	1.387(2)
C(15)-C(16)	1.387(2)	C(21)-C(26)	1.395(2)
C(21)-C(22)	1.395(2)	C(22)-C(23)	1.389(2)
C(23)-C(24)	1.381(3)	C(24)-C(25)	1.378(3)
C(25)-C(26)	1.392(2)	C(31)-C(32)	1.395(2)
C(31)-C(36)	1.400(2)	C(32)-C(33)	1.387(2)
C(33)-C(34)	1.380(2)	C(34)-C(35)	1.391(3)
C(35)-C(36)	1.382(2)	C(41)-C(42)	1.391(2)
C(41)-C(46)	1.401(2)	C(42)-C(43)	1.395(2)
C(43)-C(44)	1.381(2)	C(44)-C(45)	1.389(2)
C(45)-C(46)	1.381(2)	C(51)-C(56)	1.394(2)
C(51)-C(52)	1.400(2)	C(52)-C(53)	1.384(2)
C(53)-C(54)	1.384(2)	C(54)-C(55)	1.380(3)
C(55)-C(56)	1.392(2)	C(61)-C(62)	1.392(2)
C(61)-C(66)	1.393(2)	C(62)-C(63)	1.391(2)
C(63)-C(64)	1.379(3)	C(64)-C(65)	1.384(3)
C(65)-C(66)	1.386(2)	C(71)-C(76)	1.391(2)
C(71)-C(72)	1.391(2)	C(72)-C(73)	1.388(2)
C(73)-C(74)	1.382(2)	C(74)-C(75)	1.381(2)
C(75)-C(76)	1.393(2)	C(81)-C(86)	1.3956(19)
C(81)-C(82)	1.4016(19)	C(82)-C(83)	1.391(2)
C(83)-C(84)	1.387(2)	C(84)-C(85)	1.384(2)
C(85)-C(86)	1.390(2)	C(91)-C(96)	1.397(2)
C(91)-C(92)	1.4006(19)	C(92)-C(93)	1.390(2)
C(93)-C(94)	1.391(2)	C(94)-C(95)	1.388(2)
C(95)-C(96)	1.390(2)	C(12)-H(12A)	0.9500
C(14)-H(14A)	0.9500	C(15)-H(15A)	0.9500
C(16)-H(16A)	0.9500	C(22)-H(22A)	0.9500
C(23)-H(23A)	0.9500	C(24)-H(24A)	0.9500
C(25)-H(25A)	0.9500	C(26)-H(26A)	0.9500
C(32)-H(32A)	0.9500	C(33)-H(33A)	0.9500
C(34)-H(34A)	0.9500	C(35)-H(35A)	0.9500
C(36)-H(36A)	0.9500	C(42)-H(42A)	0.9500

C(43)-H(43A)	0.9500	C(44)-H(44A)	0.9500
C(45)-H(45A)	0.9500	C(46)-H(46A)	0.9500
C(52)-H(52A)	0.9500	C(53)-H(53A)	0.9500
C(54)-H(54A)	0.9500	C(55)-H(55A)	0.9500
C(56)-H(56A)	0.9500	C(62)-H(62A)	0.9500
C(63)-H(63A)	0.9500	C(64)-H(64A)	0.9500
C(65)-H(65A)	0.9500	C(66)-H(66A)	0.9500
C(72)-H(72A)	0.9500	C(73)-H(73A)	0.9500
C(74)-H(74A)	0.9500	C(75)-H(75A)	0.9500
C(76)-H(76A)	0.9500	C(82)-H(82A)	0.9500
C(83)-H(83A)	0.9500	C(84)-H(84A)	0.9500
C(85)-H(85A)	0.9500	C(86)-H(86A)	0.9500
C(92)-H(92A)	0.9500	C(93)-H(93A)	0.9500
C(94)-H(94A)	0.9500	C(95)-H(95A)	0.9500
C(96)-H(96A)	0.9500		

Symmetry transformations used to generate equivalent atoms:

Table 5. Bond angles [°] for jsm009.

atom-atom-atom	angle	atom-atom-atom	angle
O(2)-S(1)-O(3)	113.37(8)	O(2)-S(1)-O(1)	113.57(7)
O(3)-S(1)-O(1)	113.44(7)	O(2)-S(1)-C(13)	104.74(6)
O(3)-S(1)-C(13)	104.82(7)	O(1)-S(1)-C(13)	105.76(6)
C(11)-P(1)-C(31)	101.03(7)	C(11)-P(1)-C(21)	103.12(7)
C(31)-P(1)-C(21)	100.40(7)	N(1)-P(2)-C(61)	106.99(6)
N(1)-P(2)-C(41)	112.04(6)	C(61)-P(2)-C(41)	109.66(6)
N(1)-P(2)-C(51)	112.14(6)	C(61)-P(2)-C(51)	106.48(7)
C(41)-P(2)-C(51)	109.33(6)	N(1)-P(3)-C(81)	108.29(6)
N(1)-P(3)-C(71)	109.36(6)	C(81)-P(3)-C(71)	109.56(6)
N(1)-P(3)-C(91)	114.69(6)	C(81)-P(3)-C(91)	106.25(6)
C(71)-P(3)-C(91)	108.58(6)	P(3)-N(1)-P(2)	140.37(8)
C(16)-C(11)-C(12)	118.72(13)	C(16)-C(11)-P(1)	123.89(11)
C(12)-C(11)-P(1)	117.34(11)	C(13)-C(12)-C(11)	120.61(13)
C(14)-C(13)-C(12)	119.70(13)	C(14)-C(13)-S(1)	119.36(11)
C(12)-C(13)-S(1)	120.89(11)	C(15)-C(14)-C(13)	120.16(14)
C(14)-C(15)-C(16)	120.03(14)	C(15)-C(16)-C(11)	120.77(14)
C(26)-C(21)-C(22)	118.53(14)	C(26)-C(21)-P(1)	117.35(12)
C(22)-C(21)-P(1)	124.08(12)	C(23)-C(22)-C(21)	120.74(15)
C(24)-C(23)-C(22)	119.77(16)	C(25)-C(24)-C(23)	120.54(15)
C(24)-C(25)-C(26)	119.77(16)	C(25)-C(26)-C(21)	120.64(16)
C(32)-C(31)-C(36)	118.35(14)	C(32)-C(31)-P(1)	124.61(11)
C(36)-C(31)-P(1)	116.95(12)	C(33)-C(32)-C(31)	120.67(15)
C(34)-C(33)-C(32)	120.42(16)	C(33)-C(34)-C(35)	119.57(16)
C(36)-C(35)-C(34)	120.21(15)	C(35)-C(36)-C(31)	120.77(15)
C(42)-C(41)-C(46)	119.38(13)	C(42)-C(41)-P(2)	123.46(11)
C(46)-C(41)-P(2)	116.75(11)	C(41)-C(42)-C(43)	119.90(14)
C(44)-C(43)-C(42)	120.22(14)	C(43)-C(44)-C(45)	120.09(15)
C(46)-C(45)-C(44)	120.07(14)	C(45)-C(46)-C(41)	120.30(14)
C(56)-C(51)-C(52)	119.38(13)	C(56)-C(51)-P(2)	121.73(11)
C(52)-C(51)-P(2)	118.67(11)	C(53)-C(52)-C(51)	120.38(14)
C(52)-C(53)-C(54)	119.90(15)	C(55)-C(54)-C(53)	120.19(15)
C(54)-C(55)-C(56)	120.58(15)	C(55)-C(56)-C(51)	119.58(15)
C(62)-C(61)-C(66)	119.94(13)	C(62)-C(61)-P(2)	121.17(11)
C(66)-C(61)-P(2)	118.50(11)	C(63)-C(62)-C(61)	119.34(15)
C(64)-C(63)-C(62)	120.76(16)	C(63)-C(64)-C(65)	119.74(15)
C(64)-C(65)-C(66)	120.37(16)	C(65)-C(66)-C(61)	119.79(15)
C(76)-C(71)-C(72)	119.45(13)	C(76)-C(71)-P(3)	122.25(11)
C(72)-C(71)-P(3)	118.22(11)	C(73)-C(72)-C(71)	120.28(14)
C(74)-C(73)-C(72)	120.11(15)	C(75)-C(74)-C(73)	119.95(15)
C(74)-C(75)-C(76)	120.34(15)	C(71)-C(76)-C(75)	119.85(14)
C(86)-C(81)-C(82)	119.89(13)	C(86)-C(81)-P(3)	118.49(11)
C(82)-C(81)-P(3)	121.46(11)	C(83)-C(82)-C(81)	119.49(13)

C(84)-C(83)-C(82)	120.16(14)	C(85)-C(84)-C(83)	120.54(14)
C(84)-C(85)-C(86)	119.90(14)	C(85)-C(86)-C(81)	120.01(14)
C(96)-C(91)-C(92)	119.57(13)	C(96)-C(91)-P(3)	120.56(11)
C(92)-C(91)-P(3)	118.89(10)	C(93)-C(92)-C(91)	119.89(14)
C(92)-C(93)-C(94)	120.21(14)	C(95)-C(94)-C(93)	120.00(14)
C(94)-C(95)-C(96)	120.21(14)	C(95)-C(96)-C(91)	120.02(14)
C(13)-C(12)-H(12A)	119.7	C(11)-C(12)-H(12A)	119.7
C(15)-C(14)-H(14A)	119.9	C(13)-C(14)-H(14A)	119.9
C(14)-C(15)-H(15A)	120.0	C(16)-C(15)-H(15A)	120.0
C(15)-C(16)-H(16A)	119.6	C(11)-C(16)-H(16A)	119.6
C(23)-C(22)-H(22A)	119.6	C(21)-C(22)-H(22A)	119.6
C(24)-C(23)-H(23A)	120.1	C(22)-C(23)-H(23A)	120.1
C(25)-C(24)-H(24A)	119.7	C(23)-C(24)-H(24A)	119.7
C(24)-C(25)-H(25A)	120.1	C(26)-C(25)-H(25A)	120.1
C(25)-C(26)-H(26A)	119.7	C(21)-C(26)-H(26A)	119.7
C(33)-C(32)-H(32A)	119.7	C(31)-C(32)-H(32A)	119.7
C(34)-C(33)-H(33A)	119.8	C(32)-C(33)-H(33A)	119.8
C(33)-C(34)-H(34A)	120.2	C(35)-C(34)-H(34A)	120.2
C(36)-C(35)-H(35A)	119.9	C(34)-C(35)-H(35A)	119.9
C(35)-C(36)-H(36A)	119.6	C(31)-C(36)-H(36A)	119.6
C(41)-C(42)-H(42A)	120.0	C(43)-C(42)-H(42A)	120.0
C(44)-C(43)-H(43A)	119.9	C(42)-C(43)-H(43A)	119.9
C(43)-C(44)-H(44A)	120.0	C(45)-C(44)-H(44A)	120.0
C(46)-C(45)-H(45A)	120.0	C(44)-C(45)-H(45A)	120.0
C(45)-C(46)-H(46A)	119.9	C(41)-C(46)-H(46A)	119.9
C(53)-C(52)-H(52A)	119.8	C(51)-C(52)-H(52A)	119.8
C(52)-C(53)-H(53A)	120.1	C(54)-C(53)-H(53A)	120.1
C(55)-C(54)-H(54A)	119.9	C(53)-C(54)-H(54A)	119.9
C(54)-C(55)-H(55A)	119.7	C(56)-C(55)-H(55A)	119.7
C(55)-C(56)-H(56A)	120.2	C(51)-C(56)-H(56A)	120.2
C(63)-C(62)-H(62A)	120.3	C(61)-C(62)-H(62A)	120.3
C(64)-C(63)-H(63A)	119.6	C(62)-C(63)-H(63A)	119.6
C(63)-C(64)-H(64A)	120.1	C(65)-C(64)-H(64A)	120.1
C(64)-C(65)-H(65A)	119.8	C(66)-C(65)-H(65A)	119.8
C(65)-C(66)-H(66A)	120.1	C(61)-C(66)-H(66A)	120.1
C(73)-C(72)-H(72A)	119.9	C(71)-C(72)-H(72A)	119.9
C(74)-C(73)-H(73A)	119.9	C(72)-C(73)-H(73A)	119.9
C(75)-C(74)-H(74A)	120.0	C(73)-C(74)-H(74A)	120.0
C(74)-C(75)-H(75A)	119.8	C(76)-C(75)-H(75A)	119.8
C(71)-C(76)-H(76A)	120.1	C(75)-C(76)-H(76A)	120.1
C(83)-C(82)-H(82A)	120.3	C(81)-C(82)-H(82A)	120.3
C(84)-C(83)-H(83A)	119.9	C(82)-C(83)-H(83A)	119.9
C(85)-C(84)-H(84A)	119.7	C(83)-C(84)-H(84A)	119.7
C(84)-C(85)-H(85A)	120.0	C(86)-C(85)-H(85A)	120.0
C(85)-C(86)-H(86A)	120.0	C(81)-C(86)-H(86A)	120.0
C(93)-C(92)-H(92A)	120.1	C(91)-C(92)-H(92A)	120.1

C(92)-C(93)-H(93A)	119.9	C(94)-C(93)-H(93A)	119.9
C(95)-C(94)-H(94A)	120.0	C(93)-C(94)-H(94A)	120.0
C(94)-C(95)-H(95A)	119.9	C(96)-C(95)-H(95A)	119.9
C(95)-C(96)-H(96A)	120.0	C(91)-C(96)-H(96A)	120.0

Symmetry transformations used to generate equivalent atoms:

Table 6. Torsion angles [°] for jsm009.

atom-atom-atom-atom	angle	atom-atom-atom-atom	angle
C(81)-P(3)-N(1)-P(2)	129.98(12)	C(71)-P(3)-N(1)-P(2)	-110.68(13)
C(91)-P(3)-N(1)-P(2)	11.54(15)	C(61)-P(2)-N(1)-P(3)	171.61(12)
C(41)-P(2)-N(1)-P(3)	51.39(14)	C(51)-P(2)-N(1)-P(3)	-71.99(14)
C(31)-P(1)-C(11)-C(16)	-70.85(14)	C(21)-P(1)-C(11)-C(16)	32.70(14)
C(31)-P(1)-C(11)-C(12)	106.69(12)	C(21)-P(1)-C(11)-C(12)	-149.77(11)
C(16)-C(11)-C(12)-C(13)	-0.2(2)	P(1)-C(11)-C(12)-C(13)	-177.82(10)
C(11)-C(12)-C(13)-C(14)	0.4(2)	C(11)-C(12)-C(13)-S(1)	-176.96(11)
O(2)-S(1)-C(13)-C(14)	-84.23(13)	O(3)-S(1)-C(13)-C(14)	35.36(13)
O(1)-S(1)-C(13)-C(14)	155.51(12)	O(2)-S(1)-C(13)-C(12)	93.15(12)
O(3)-S(1)-C(13)-C(12)	-147.25(12)	O(1)-S(1)-C(13)-C(12)	-27.11(13)
C(12)-C(13)-C(14)-C(15)	-0.2(2)	S(1)-C(13)-C(14)-C(15)	177.25(12)
C(13)-C(14)-C(15)-C(16)	-0.3(2)	C(14)-C(15)-C(16)-C(11)	0.6(2)
C(12)-C(11)-C(16)-C(15)	-0.4(2)	P(1)-C(11)-C(16)-C(15)	177.15(12)
C(11)-P(1)-C(21)-C(26)	103.77(13)	C(31)-P(1)-C(21)-C(26)	-152.20(12)
C(11)-P(1)-C(21)-C(22)	-78.54(14)	C(31)-P(1)-C(21)-C(22)	25.49(14)
C(26)-C(21)-C(22)-C(23)	-1.0(2)	P(1)-C(21)-C(22)-C(23)	-178.63(12)
C(21)-C(22)-C(23)-C(24)	1.3(2)	C(22)-C(23)-C(24)-C(25)	-0.8(3)
C(23)-C(24)-C(25)-C(26)	0.1(3)	C(24)-C(25)-C(26)-C(21)	0.2(3)
C(22)-C(21)-C(26)-C(25)	0.3(2)	P(1)-C(21)-C(26)-C(25)	178.09(14)
C(11)-P(1)-C(31)-C(32)	-9.68(14)	C(21)-P(1)-C(31)-C(32)	-115.39(13)
C(11)-P(1)-C(31)-C(36)	173.83(11)	C(21)-P(1)-C(31)-C(36)	68.11(12)
C(36)-C(31)-C(32)-C(33)	-0.1(2)	P(1)-C(31)-C(32)-C(33)	-176.50(13)
C(31)-C(32)-C(33)-C(34)	-0.6(3)	C(32)-C(33)-C(34)-C(35)	0.5(3)
C(33)-C(34)-C(35)-C(36)	0.3(3)	C(34)-C(35)-C(36)-C(31)	-1.0(2)
C(32)-C(31)-C(36)-C(35)	0.9(2)	P(1)-C(31)-C(36)-C(35)	177.58(12)
N(1)-P(2)-C(41)-C(42)	-125.32(12)	C(61)-P(2)-C(41)-C(42)	116.03(12)
C(51)-P(2)-C(41)-C(42)	-0.37(14)	N(1)-P(2)-C(41)-C(46)	47.32(13)
C(61)-P(2)-C(41)-C(46)	-71.34(12)	C(51)-P(2)-C(41)-C(46)	172.27(11)
C(46)-C(41)-C(42)-C(43)	-1.9(2)	P(2)-C(41)-C(42)-C(43)	170.60(12)
C(41)-C(42)-C(43)-C(44)	1.1(2)	C(42)-C(43)-C(44)-C(45)	0.4(3)
C(43)-C(44)-C(45)-C(46)	-1.1(3)	C(44)-C(45)-C(46)-C(41)	0.3(2)
C(42)-C(41)-C(46)-C(45)	1.2(2)	P(2)-C(41)-C(46)-C(45)	-171.78(12)
N(1)-P(2)-C(51)-C(56)	-109.90(13)	C(61)-P(2)-C(51)-C(56)	6.81(14)
C(41)-P(2)-C(51)-C(56)	125.21(12)	N(1)-P(2)-C(51)-C(52)	64.66(13)
C(61)-P(2)-C(51)-C(52)	-178.63(11)	C(41)-P(2)-C(51)-C(52)	-60.23(12)
C(56)-C(51)-C(52)-C(53)	1.0(2)	P(2)-C(51)-C(52)-C(53)	-173.70(11)
C(51)-C(52)-C(53)-C(54)	-0.6(2)	C(52)-C(53)-C(54)-C(55)	-0.1(2)
C(53)-C(54)-C(55)-C(56)	0.2(3)	C(54)-C(55)-C(56)-C(51)	0.2(3)
C(52)-C(51)-C(56)-C(55)	-0.8(2)	P(2)-C(51)-C(56)-C(55)	173.73(12)
N(1)-P(2)-C(61)-C(62)	-153.65(12)	C(41)-P(2)-C(61)-C(62)	-31.92(14)
C(51)-P(2)-C(61)-C(62)	86.26(13)	N(1)-P(2)-C(61)-C(66)	33.57(14)
C(41)-P(2)-C(61)-C(66)	155.30(12)	C(51)-P(2)-C(61)-C(66)	-86.52(13)

C(66)-C(61)-C(62)-C(63)	0.9(2)	P(2)-C(61)-C(62)-C(63)	-171.78(12)
C(61)-C(62)-C(63)-C(64)	1.4(3)	C(62)-C(63)-C(64)-C(65)	-2.3(3)
C(63)-C(64)-C(65)-C(66)	0.8(3)	C(64)-C(65)-C(66)-C(61)	1.5(3)
C(62)-C(61)-C(66)-C(65)	-2.4(2)	P(2)-C(61)-C(66)-C(65)	170.51(13)
N(1)-P(3)-C(71)-C(76)	165.92(12)	C(81)-P(3)-C(71)-C(76)	-75.53(13)
C(91)-P(3)-C(71)-C(76)	40.11(14)	N(1)-P(3)-C(71)-C(72)	-17.41(13)
C(81)-P(3)-C(71)-C(72)	101.14(12)	C(91)-P(3)-C(71)-C(72)	-143.22(11)
C(76)-C(71)-C(72)-C(73)	0.1(2)	P(3)-C(71)-C(72)-C(73)	-176.65(13)
C(71)-C(72)-C(73)-C(74)	1.3(3)	C(72)-C(73)-C(74)-C(75)	-1.4(3)
C(73)-C(74)-C(75)-C(76)	0.1(3)	C(72)-C(71)-C(76)-C(75)	-1.4(2)
P(3)-C(71)-C(76)-C(75)	175.21(12)	C(74)-C(75)-C(76)-C(71)	1.3(3)
N(1)-P(3)-C(81)-C(86)	-21.20(13)	C(71)-P(3)-C(81)-C(86)	-140.41(11)
C(91)-P(3)-C(81)-C(86)	102.48(12)	N(1)-P(3)-C(81)-C(82)	163.41(11)
C(71)-P(3)-C(81)-C(82)	44.20(13)	C(91)-P(3)-C(81)-C(82)	-72.91(12)
C(86)-C(81)-C(82)-C(83)	-0.2(2)	P(3)-C(81)-C(82)-C(83)	175.11(11)
C(81)-C(82)-C(83)-C(84)	-0.6(2)	C(82)-C(83)-C(84)-C(85)	0.9(2)
C(83)-C(84)-C(85)-C(86)	-0.5(2)	C(84)-C(85)-C(86)-C(81)	-0.3(2)
C(82)-C(81)-C(86)-C(85)	0.6(2)	P(3)-C(81)-C(86)-C(85)	-174.83(11)
N(1)-P(3)-C(91)-C(96)	102.50(12)	C(81)-P(3)-C(91)-C(96)	-17.08(13)
C(71)-P(3)-C(91)-C(96)	-134.85(12)	N(1)-P(3)-C(91)-C(92)	-66.15(13)
C(81)-P(3)-C(91)-C(92)	174.27(11)	C(71)-P(3)-C(91)-C(92)	56.50(13)
C(96)-C(91)-C(92)-C(93)	-3.2(2)	P(3)-C(91)-C(92)-C(93)	165.57(11)
C(91)-C(92)-C(93)-C(94)	1.9(2)	C(92)-C(93)-C(94)-C(95)	0.9(2)
C(93)-C(94)-C(95)-C(96)	-2.4(2)	C(94)-C(95)-C(96)-C(91)	1.1(2)
C(92)-C(91)-C(96)-C(95)	1.7(2)	P(3)-C(91)-C(96)-C(95)	-166.90(12)

Symmetry transformations used to generate equivalent atoms: