Supporting Information

Sterically Encumbered Tin and Phosphorus *Peri*-Substituted Acenaphthenes

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1. Experimental Details

[Acenap(PPh$_2$)(P^{i}Pr$_2$)] (4): Raman data (glass capillary, cm^{-1}) υ = 3048m (ν_{Ar-H}), 2929m (ν_{C-H}), 1609w, 1447w, 1416w, 1320vs, 1000m (ν_{Ar-P}), 714w (ν_{P-C}).

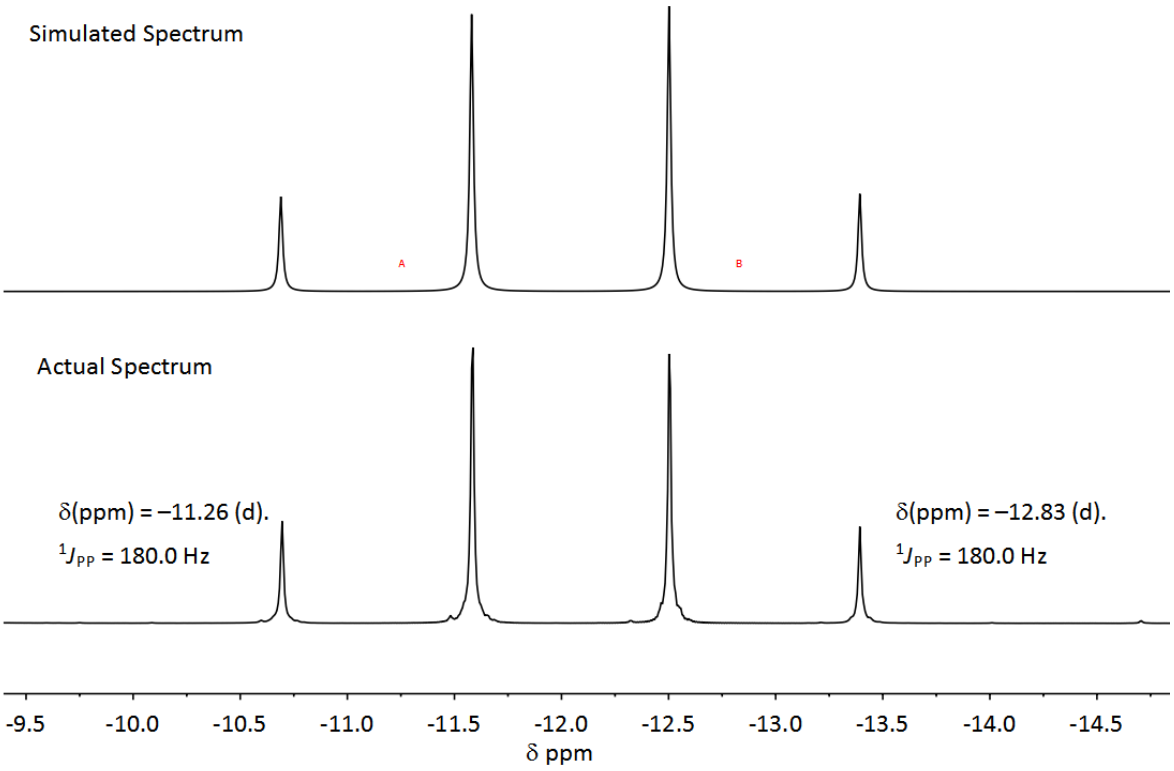

Figure S1 Simulated and experimental coupling pattern for the AB system of **4**.

Calculation of true centre of AB system:

$|J_{AB}| = (\nu_1 - \nu_2) = (\nu_3 - \nu_4) = 179.97$

$\nu_{centre} = ½ (\nu_2 + \nu_3) = 2438.405$

$\nu_{AB} = \sqrt{(\nu1 - \nu4)(\nu2 - \nu3)}$

$= \sqrt{(546.14)(186.17)}$

$= \sqrt{101674.8838}$

$= 318.865$

$½ \nu_{AB} = 159.4325$

$\nu_A = \nu_{centre} + ½ \nu_{AB} = 2597.8375$ Hz = -12.83 ppm (@ 202.4563 MHz)

$\nu_B = \nu_{centre} - ½ \nu_{AB} = 2278.9725$ Hz = -11.26 ppm (@ 202.4563 MHz)

[Acenap(S=PPh$_2$)(S=P^{i}Pr$_2$)] (4-S): Infra-Red data (KBr disc, cm^{-1}) υ = 3052w (ν_{Ar-H}), 2964m (ν_{C-H}), 1599w, 1582w, 1435w, 1259m, 1092s, 1026m, 927w (ν_{Ar-P}), 810m, 755w (ν_{P-C}), 695s, 640m, 570w ($\nu_{P=S}$); Raman data (glass capillary, cm^{-1}) υ = 3054m (ν_{Ar-H}), 2933m (ν_{C-H}), 1586m, 1409m, 1307vs, 1000s (ν_{Ar-P}), 735w (ν_{P-C}), 528w ($\nu_{P=S}$).

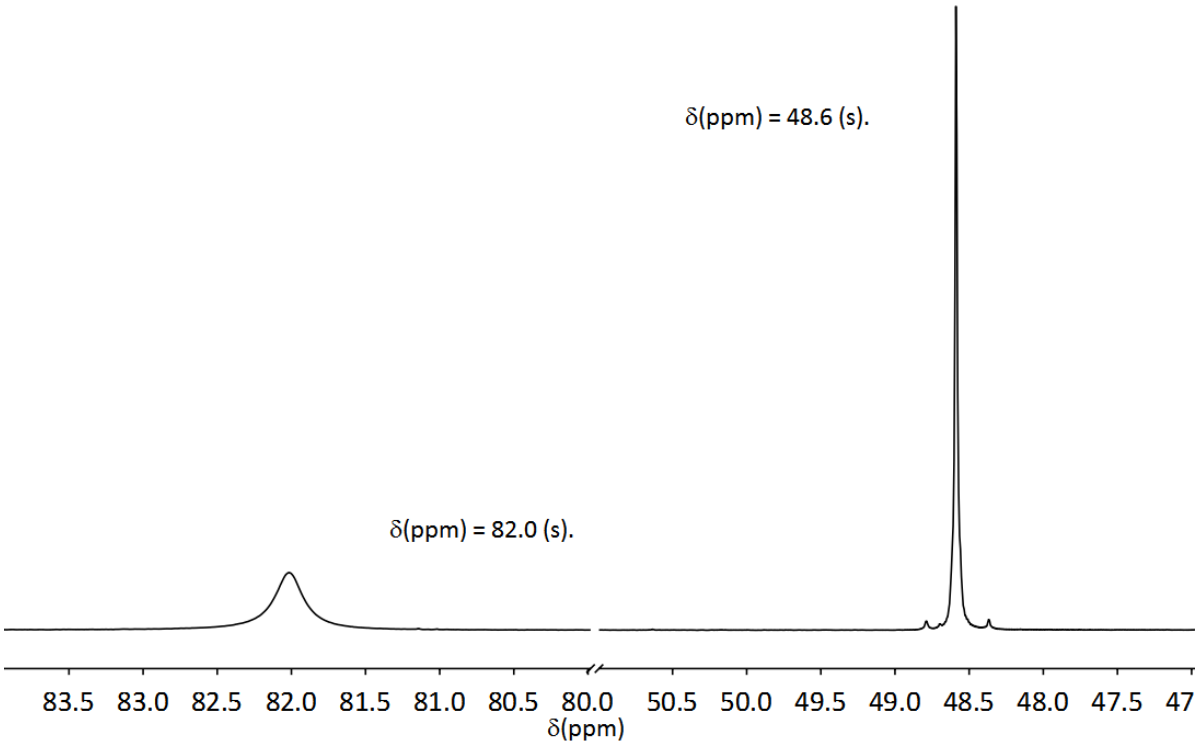

Figure S2 The $^{31}P[^1H]$ NMR spectrum of **4-S**.

[Acenap(PPh$_2$)(P^{i}Pr$_2$)]PtCl$_2$ (4-Pt): Infra-Red data (KBr disc, cm^{-1}) υ = 3050s (ν_{Ar-H}), 2925s (ν_{C-H}), 1601s, 1571w, 1482m, 1458m, 1436m, 1336m, 1098vs, 1041vs, 928w (ν_{Ar-P}), 852m, 749s, 730w (ν_{P-C}), 695vs, 565s,

519s, 435w (ν_{P-Pt}), 312m (ν_{Pt-Cl}); Raman data (glass capillary, cm^{-1}) υ = 3054s (ν_{Ar-H}), 2927s (ν_{C-H}), 1588w, 1570m, 1435m, 1339vs, 1000m (ν_{Ar-P}), 732w (ν_{P-C}), 420w (ν_{P-Pt}), 313m (ν_{Pt-Cl}).

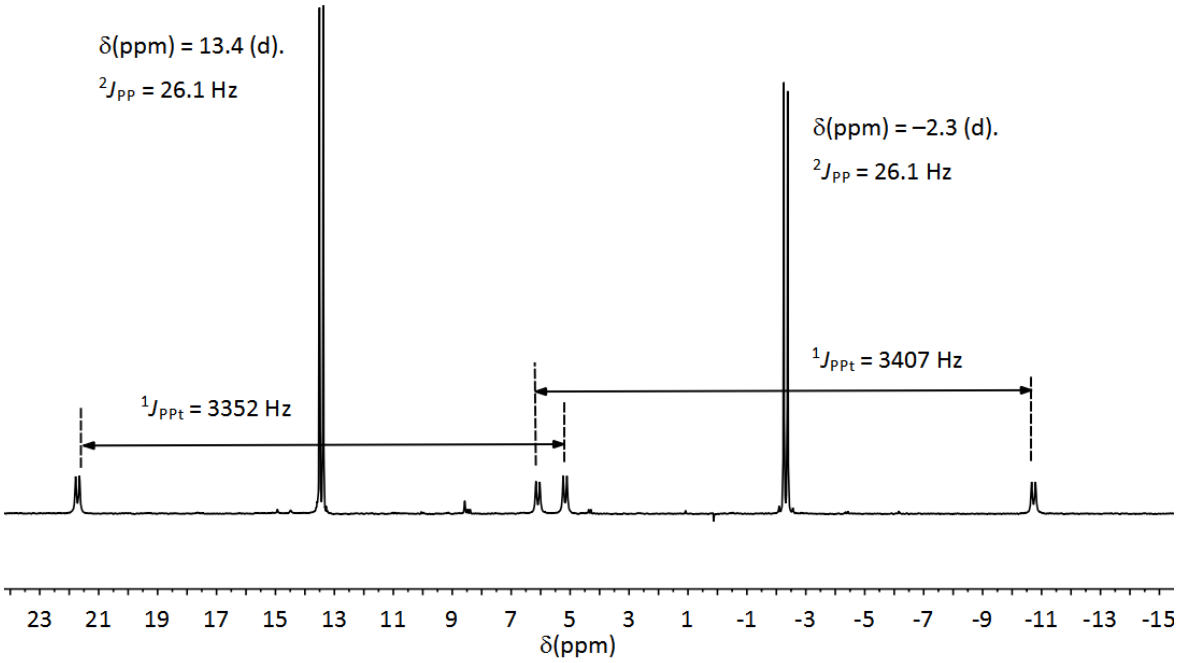

Figure S3 The $^{31}P[^1H]$ NMR spectrum of **4-Pt**.

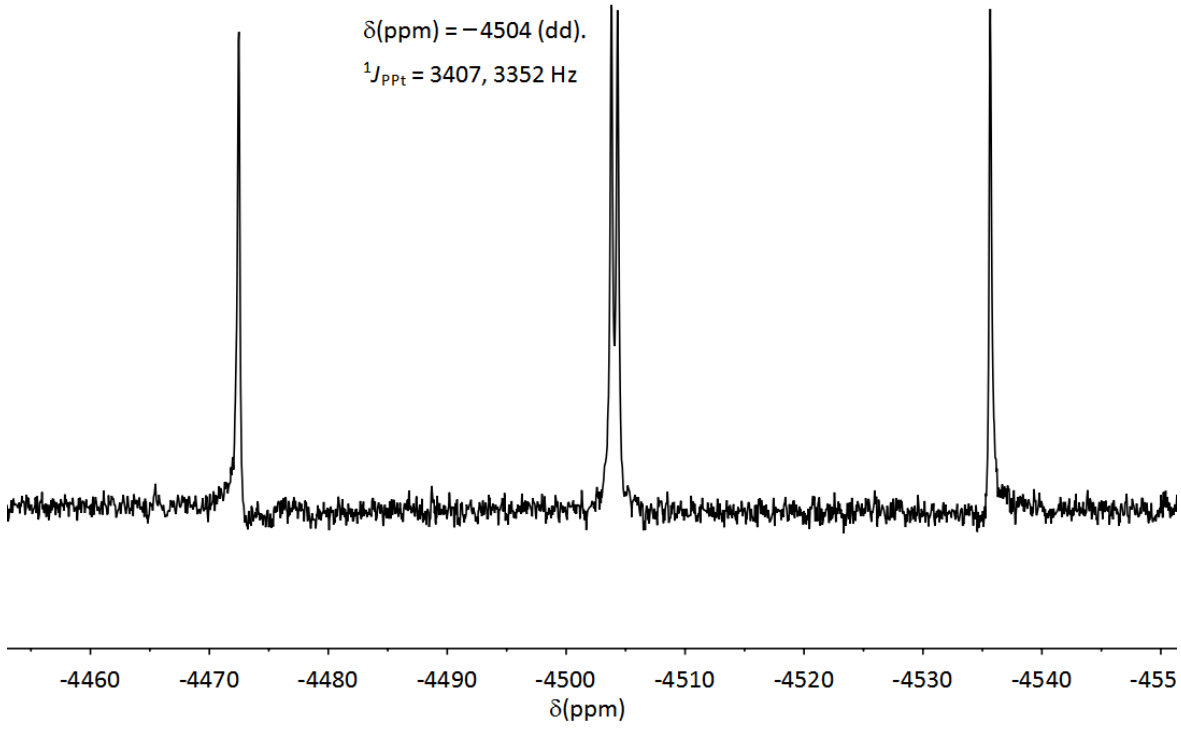

Figure S4 The $^{195}Pt[^1H]$ NMR spectrum of **4-Pt**.

[Acenap(PPh$_2$)(P^{i}Pr$_2$)]Mo(CO)$_4$ (4-Mo): Infra-Red data (KBr disc, cm^{-1}) υ = 3048m (ν_{Ar-H}), 2900s (ν_{C-H}), 2174vs ($\nu_{C=O}$), 2000vs ($\nu_{C=O}$), 1941vs ($\nu_{C=O}$), 1841vs ($\nu_{C=O}$), 1438m, 1000m (ν_{Ar-P}), 720s (ν_{P-C}), 510w (ν_{Mo-C});

Raman data (glass capillary, cm^{-1}) υ = 3068m, 2927w, 2014s ($\nu_{C=O}$), 1909vs ($\nu_{C=O}$), 1879vs ($\nu_{C=O}$), 1588w, 1444w, 1321m, 1002m (ν_{Ar-P}), 720m (ν_{P-C}), 500w (ν_{Mo-C}).

[Acenap(PPh^{i}Pr)(P^{i}Pr$_2$)] (5):

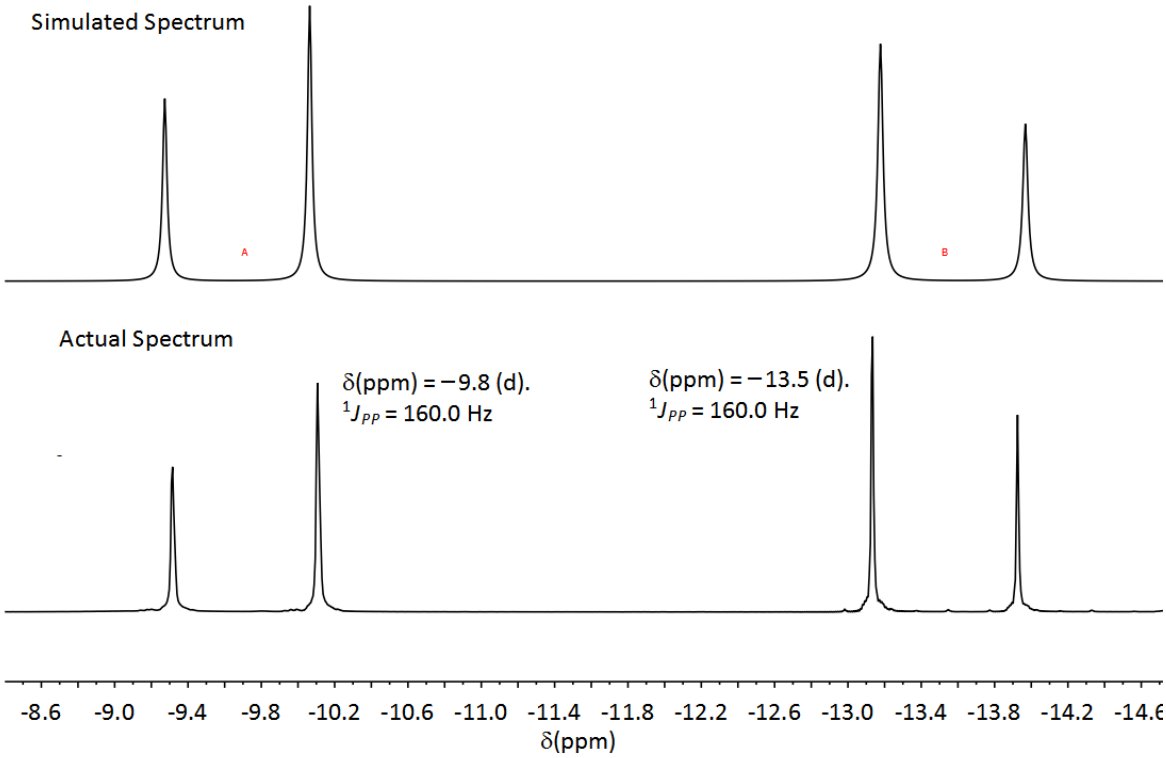

Figure S5 Simulated and experimental coupling pattern for the AB system of **5**.

Calculation of true centre of AB system:

$|J_{AB}| = (\nu_1 - \nu_2) = (\nu_3 - \nu_4) = 160.09$

$\nu_{centre} = ½ (\nu_2 + \nu_3) = 2351.62$

$\nu_{AB} = \sqrt{(\nu 1 - \nu 4)(\nu 2 - \nu 3)}$

$= \sqrt{(932.7)(612.54)}$

$= \sqrt{571316.06}$

$= 755.85$

$½ \nu_{AB} = 377.93$

$\nu_A = \nu_{centre} + ½ \nu_{AB} = 2729.55$ Hz = -13.49 ppm (@ 202.3632 MHz)

$\nu_B = \nu_{centre} - ½ \nu_{AB} = 1973.69$ Hz = -9.75 ppm (@ 202.3632 MHz)

[Acenap(S=PPh^{i}Pr)(S=P^{i}Pr$_2$)] (5-S): Infra-Red data (KBr disc, cm^{-1}) υ = 3033m (υ_{Ar-H}), 2990s (υ_{C-H}), 1601s, 1556m, 1433s, 1247s, 1013m (υ_{Ar-P}), 762s (υ_{P-C}), 700vs, 679vs, 582m ($\upsilon_{P=S}$); Raman data (glass capillary, cm^{-1}) υ = 3060m (υ_{Ar-H}), 2933s (υ_{C-H}), 1599s, 1409s, 1308s, 997w (υ_{Ar-P}), 728w (υ_{P-C}), 517w ($\upsilon_{P=S}$).

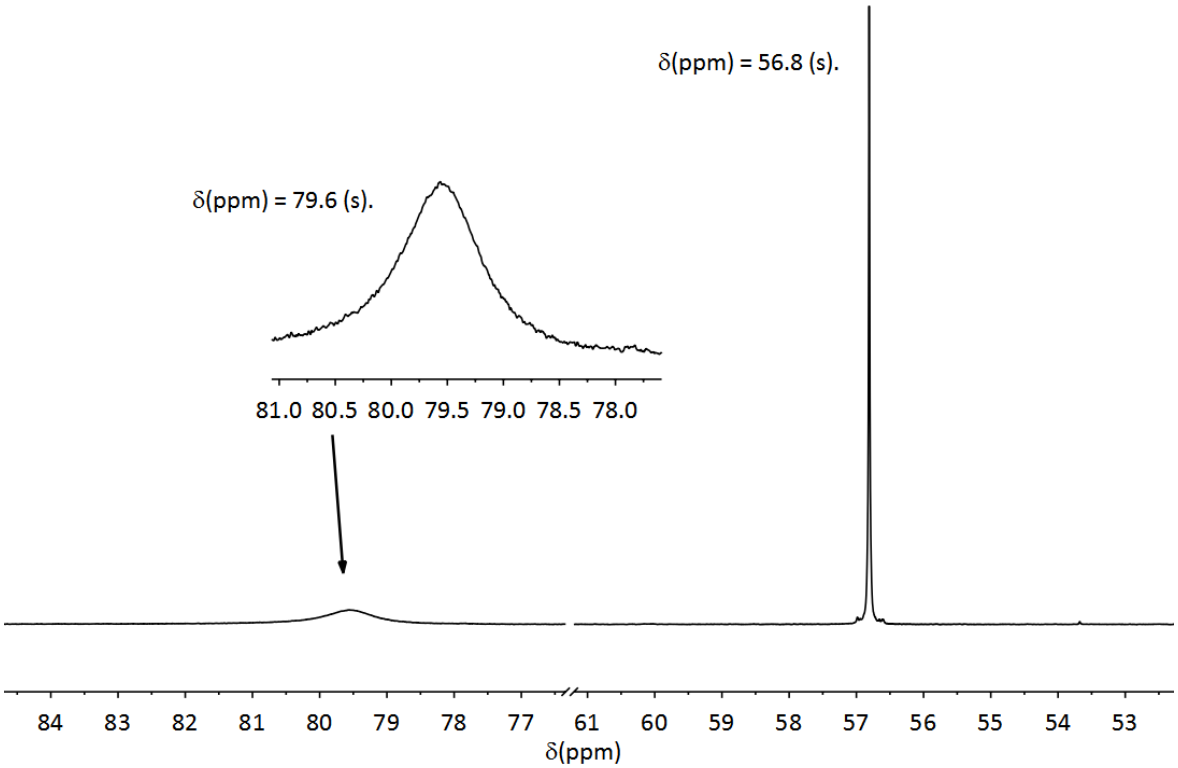

Figure S6 The $^{31}P[^{1}H]$ NMR spectrum of **5-S**.

[Acenap(Br)(P^{i}PrPh)] (7): Infra-Red data (KBr disc, cm^{-1}) υ = 3046m (υ_{Ar-H}), 2918s (υ_{C-H}), 2862s, 2365m, 1599s, 1481m, 1433s, 1318vs, 1253m, 1200m, 1052s, 840vs, 812s, 741s, 697vs, 638s, 554m, 483s, 425m, 332m; Raman data (glass capillary, cm^{-1}) υ = 3049s (υ_{Ar-H}), 2939s (υ_{C-H}), 2866m, 1603s, 1564s, 1439s, 1320vs, 1001vs, 817m, 714m, 641m, 557s, 491m, , 307vs (υ_{C-Br}), 281s, 247m.

^{i}Pr(Ph)PCl: Magnesium turnings (7.04 g, 290 mmol) were added to tetrahydrofuran (30 mL) with a crystal of iodine. The mixture was cooled to 0 °C and equipped with a reflux condenser. To this 2-chloropropane (22.0 mL, 240 mmol) in THF (40 mL) was added dropwise (little reaction occurs at 0 °C). Upon warming to room temperature, the Grignard reaction begins. The mixture was heated under reflux (~80 °C) for two hours. The solution was cooled to room temperature and used immediately. To a cooled (-78 °C) rapidly stirring solution of dichlorophenylphosphine (20.6 mL, 0.11 mol) in tetrahydrofuran (150 mL), isopropylmagnesium chloride (20 mL) was added over 2 hours. Extra THF (40 mL) was added to allow stirring to continue. The reaction was warmed to room temperature and stirred for 2 hours. The reaction was followed by ^{31}P NMR (unlocked) using the $PhPCl_2$:^{i}Pr(Ph)PCl ratio to calculate how much ^{i}PrMgCl is required. This was repeated until all the $PhPCl_2$ was consumed. The suspension was filtered through a sinter. Approx. 80% of the THF was removed *in vacuo* without additional heating. The mixture was distilled under reduced pressure (0.1 torr, t_{oil} = 127 °C, t_{vapour} = 78 °C) to give ^{i}Pr(Ph)PCl as a colourless liquid (20.4 g,

58%). ^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz) δ_H 7.59–7.53 (5H, m, P*Ph-o,m,p* 4,5,6-H), 2.07–1.99 (1H, m, PC*H* 1-H), 1.21 (6H, dd, $^{3}J_{HP}$ = 20.6 Hz, $^{3}J_{HH}$ = 7.1 Hz, CH_3 2-H); ^{13}C{^{1}H} NMR ($CDCl_3$, Me_4Si, 126 MHz) δ_C 137.4 (d, $^{1}J_{CP}$ = 36.2 Hz, qC-3), 131.5 (s, P*Ph-o* 4-C), 131.2 (s, P*Ph-p* 6-C), 130.5 (s, P*Ph-m* 5-C), 34.2 (d, $^{1}J_{CP}$ = 26.2 Hz, P*C*H 1-C), 17.6 (d, $^{2}J_{CP}$ = 17.7 Hz, *C*H_3 2-C); ^{31}P{^{1}H} NMR ($CDCl_3$, H_3PO_4, 162 MHz) δ_P 102.0 (s).

2. Crystal Structure Analyses

Table S1. Crystallographic data for compounds **1-3**.

	1	**2**	**3**
Empirical Formula	$C_{48}H_{38}Sn_2$	$C_{18}H_{26}Sn_2$	$C_{28}H_{28}Sn_2$
Formula Weight	852.21	479.78	601.91
Temperature (°C)	-100(1)	-148(1)	-148(1)
Crystal Colour, Habit	colorless, prism	colorless, prism	colorless, prism
Crystal Dimensions (mm^3)	0.200 X 0.200 X 0.200	0.150 X 0.030 X 0.020	0.200 X 0.050 X 0.040
Crystal System	triclinic	Monoclinic	triclinic
Lattice Parameters	a = 9.7934(17) Å	a = 17.147(3) Å	a = 7.419(1) Å
	b = 10.2626(15) Å	b = 8.0259(13) Å	b = 8.172(1) Å
	c = 19.442(3) Å	c = 14.092(3) Å	c = 10.625(2) Å
	α = 75.210(14)°	-	α = 108.784(8)°
	β = 78.183(16)°	β = 107.314(8)°	β = 108.004(8)°
	γ = 85.544(15)°	-	γ = 90.700(6)°
Volume ($Å^3$)	V = 1848.6(6)	V = 1851.5(6)	V = 575.6(2)
Space Group	P-1	$P2_1/c$	P-1
Z value	2	4	1
Dcalc (g/cm^3)	1.531	1.721	1.736
F000	852	936	296
μ(MoKα) (cm^{-1})	13.842	26.879	21.818
No. of Reflections Measured	19769	13315	4963
Rint	0.0675	0.0293	0.0415
Min and Max Transmissions	0.414 - 0.758	0.674 - 0.948	0.713 - 0.916
Independ. Reflection (No. Variables)	6469(451)	3393(187)	2021(136)
Reflection/Parameter Ratio	14.34	18.14	14.86
Residuals: R_1 (I>2.00σ(I))	0.0324	0.0277	0.0310
Residuals: R (All reflections)	0.0346	0.0310	0.0363
Residuals: *w*R_2 (All reflections)	0.0920	0.0647	0.0737
Goodness of Fit Indicator	0.998	1.185	1.190
Maximum peak in Final Diff. Map	1.13 $e^-/Å^3$	1.55 $e^-/Å^3$	0.56 $e^-/Å^3$
Minimum peak in Final Diff. Map	-1.05 $e^-/Å^3$	-0.55 $e^-/Å^3$	-0.69 $e^-/Å^3$

Table S2. Crystallographic data for compounds **4**, **4-S** and **4-Pt**.

	4	**4-S**	**4-Pt**
Empirical Formula	$C_{30}H_{32}P_2$	$C_{30}H_{32}P_2S_2$	$C_{31}H_{34}Cl_4P_2Pt$
Formula Weight	454.53	518.65	805.46
Temperature (°C)	-180(1)	-180(1)	-180(1)
Crystal Colour, Habit	yellow, chunk	colourless, block	colourless, block
Crystal Dimensions (mm^3)	0.120 X 0.060 X 0.030	0.150 X 0.090 X 0.040	0.240 X 0.140 X 0.060
Crystal System	triclinic	monoclinic	orthorhombic
Lattice Parameters	a = 9.837(5) Å	a = 8.950(2) Å	a = 14.753(2) Å
	b = 11.404(5) Å	b = 11.086(3) Å	b = 17.857(3) Å
	c = 11.644(5) Å	c = 14.038(4) Å	c = 11.238(2) Å
	α = 91.096(16) °	-	-
	β = 107.303(17)°	β = 97.158(7)°	-
	γ = 92.747(17) °	-	-
Volume ($Å^3$)	V = 1245.0(10)	V = 1382.1(6)	V = 2960.5(7)
Space Group	P-1	P_n	$Pna2_1$
Z value	2	2	4
Dcalc (g/cm^3)	1.212	1.246	1.807
F000	484.00	548.00	1584.00
μ(MoKα) (cm^{-1})	1.903	3.253	52.107
No. of Reflections Measured	7674	7554	23836
Rint	0.1024	0.0612	0.1104
Min and Max Transmissions	0.155 - 0.994	0.583 - 0.987	0.462 - 0.732
Independ. Reflection (No. Variables)	4245(289)	3626(307)	5193(343)
Reflection/Parameter Ratio	14.69	11.81	15.14
Residuals: R_1 ($I>2.00\sigma(I)$)	0.0754	0.0517	0.0578
Residuals: R (All reflections)	0.1262	0.0844	0.0772
Residuals: wR_2 (All reflections)	0.1757	0.1201	0.1253
Goodness of Fit Indicator	0.996	1.032	1.097
Maximum peak in Final Diff. Map	0.40 $e^-/Å^3$	0.21 $e^-/Å^3$	1.41 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.34 $e^-/Å^3$	-0.20 $e^-/Å^3$	-1.66 $e^-/Å^3$

Table S3. Crystallographic data for compounds **4-Mo**, **5-S**, **6** and **7**.

	4-Mo	**5-S**	**6**	**7**
Empirical Formula	$C_{34}H_{32}MoO_4P_2$	$C_{27}H_{34}P_2S_2$	$C_{18}H_{22}BrP$	$C_{21}H_{20}PBr$
Formula Weight	662.51	484.63	349.25	383.27
Temperature (°C)	-180(1)	-180(1)	-180(1)	-180(1)
Crystal Colour, Habit	yellow, platelet	colourless, block	colourless, block	colourless, block
Crystal Dimensions (mm^3)	0.120 X 0.090 X 0.030	0.180 X 0.150 X 0.060	0.120 X 0.090 X 0.050	0.120 X 0.090 X 0.030
Crystal System	orthorhombic	triclinic	Monoclinic	monoclinic
Lattice Parameters	a = 13.850(1) Å	a = 8.522(2) Å	a = 8.3177(7) Å	a = 11.194(3) Å
	b = 14.508(1) Å	b = 9.832(2) Å	b = 8.6114(7) Å	b = 14.043(3) Å
	c = 30.183(3) Å	c = 16.798(4) Å	c = 22.579(2) Å	c = 12.014(3) Å
	-	α = 96.603(7)°	-	-
	-	β = 93.163(7)°	β = 99.088(7) °	β = 111.185(8)°
	-	γ = 113.597(8)°	-	-
Volume ($Å^3$)	V = 6064.7(8)	V = 1273.2(5)	1597.0(2)	V = 1760.9(7)
Space Group	Pbca	P-1	$P2_1/c$	$P2_1/n$
Z value	8	2	4	4
Dcalc (g/cm^3)	1.451	1264	1.452	1.446
F000	2720.00	516.00	720.00	784.00
μ(MoKα) (cm^{-1})	5.744	3.479	26.702	24.292
No. of Reflections Measured	42358	7352	11759	10018
Rint	0.0873	0.0335	0.0555	0.0436
Min and Max Transmissions	0.767 - 0.983	0.446 - 0.979	0.718 – 0.875	0.518 - 0.930
Independ. Reflection (No. Variables)	5339(370)	4262(280)	2805(181)	3076(208)
Reflection/Parameter Ratio	14.43	15.22	15.50	14.79
Residuals: R_1 (I>2.00σ(I))	0.0438	0.0419	0.0397	0.0543
Residuals: R (All reflections)	0.0728	0.0604	0.0618	0.0698
Residuals: wR_2 (All reflections)	0.0959	0.1013	0.0947	0.1349
Goodness of Fit Indicator	1.042	1.028	1.047	1.152
Maximum peak in Final Diff. Map	0.50 $e^-/Å^3$	0.35 $e^-/Å^3$	0.45 $e^-/Å^3$	1.35 $e^-/Å^3$
Minimum peak in Final Diff. Map	-0.41 $e^-/Å^3$	-0.34 $e^-/Å^3$	-0.34 $e^-/Å^3$	-0.48 $e^-/Å^3$

Table S4. Selected interatomic distances [Å] and angles [°] for **6** and **7**.

Compound	**6**	**7**
Peri-region-distances		
P(1)···Br(1)	3.2186(12)	3.203(3)
Σr_{vdW} - P···Br[a]	0.4314	0.447
% Σr_{vdW}[a]	88	88
P(1)-C(1)	1.846(4)	1.854(6)
Br(1)-C(9)	1.906(4)	1.892(5)
Peri-region bond angles		
P(1)-C(1)-C(10)	122.8(3)	122.5(5)
C(1)-C(10)-C(9)	131.2(4)	130.7(5)
Br(1)-C(9)-C(10)	123.7(3)	122.0(4)
Σ of bay angles	**377.7(10)**	**375.2(8)**
Splay angle[b]	17.7	15.2
C(4)-C(5)-C(6)	111.1(4)	111.3(5)
Out-of-plane displacement		
P(1)	-0.275(1)	-0.560(1)
Br(1)	0.084(1)	0.183(1)
Central naphthalene ring torsion angles		
C:(6)-(5)-(10)-(1)	177.6(3)	-177.6(5)
C:(4)-(5)-(10)-(9)	-177.3(3)	-176.3(5)

[a] van der Waals radii used for calculations: r_{vdW}(Br) 1.85 Å, r_{vdW}(P) 1.80 Å; **[b]** Splay angle: Σ of the three bay region angles – 360.

Table S5. Non-bonded (hydrogen bond) intramolecular interactions [Å] and angles [°] for **4**, **4-S** and **5-S**.

	D-H···A	**H···A**	**D···A**	**D-H···A**
4	C(15)-H(15B)···Cg(25-30)	3.137(1)	3.945(1)	141(1)
4-S	C(14)-H(14C)···Cg(25-30)	3.008(1)	3.606(1)	121(1)
	C(13)-H(13)···S(2)	2.691(1)	3.564(1)	146(1)
	C(16)-H(16)···S(2)	2.678(1)	3.466(1)	136(1)
	C(20)-H(20)···S(2)	2.720(1)	3.242(1)	115(1)
5-S	C(15)-H(15C)···Cg(22-27)	2.688(1)	3.320(1)	123(1)
	C(13)-H(13)···S(2)	2.864(1)	3.761(1)	150(1)
	C(16)-H(16)···S(2)	2.676(1)	3.520(1)	142(1)
	C(21)-H(21C)···S(2)	2.868(1)	3.404(1)	115(1)