# ELECTRONIC SUPPLEMENTARY INFORMATION

Ms. ID: DT-ART-12-2017-004561.R1

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# Synthesis and some coordination chemistry of the PSnP pincer-type stannylene $Sn(NCH_2P^tBu_2)_2C_6H_4$, attempts to prepare the PSiP analogue, and effect of the E atom on the molecular structures of $E(NCH_2P^tBu_2)_2C_6H_4$ (E = C, Si, Ge, Sn)

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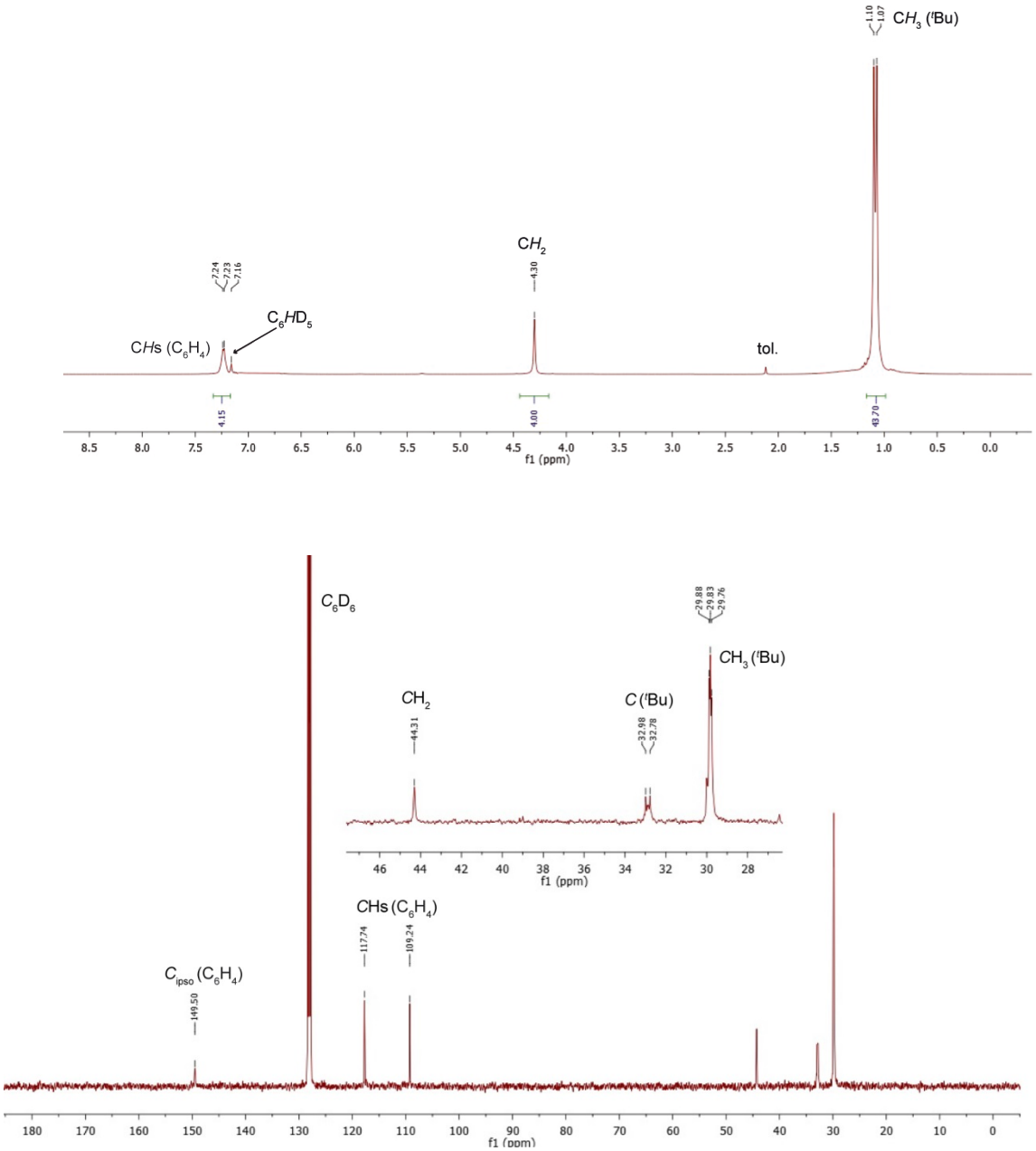


**Fig. S1** $^{1}$H (top, 400.1 MHz) and $^{13}$C{$^{1}$H} (bottom, 100.6 MHz) NMR spectra ($C_6D_6$, 293 K) of $Sn(NCH_2P^tBu_2)_2C_6H_4$ (**1**).

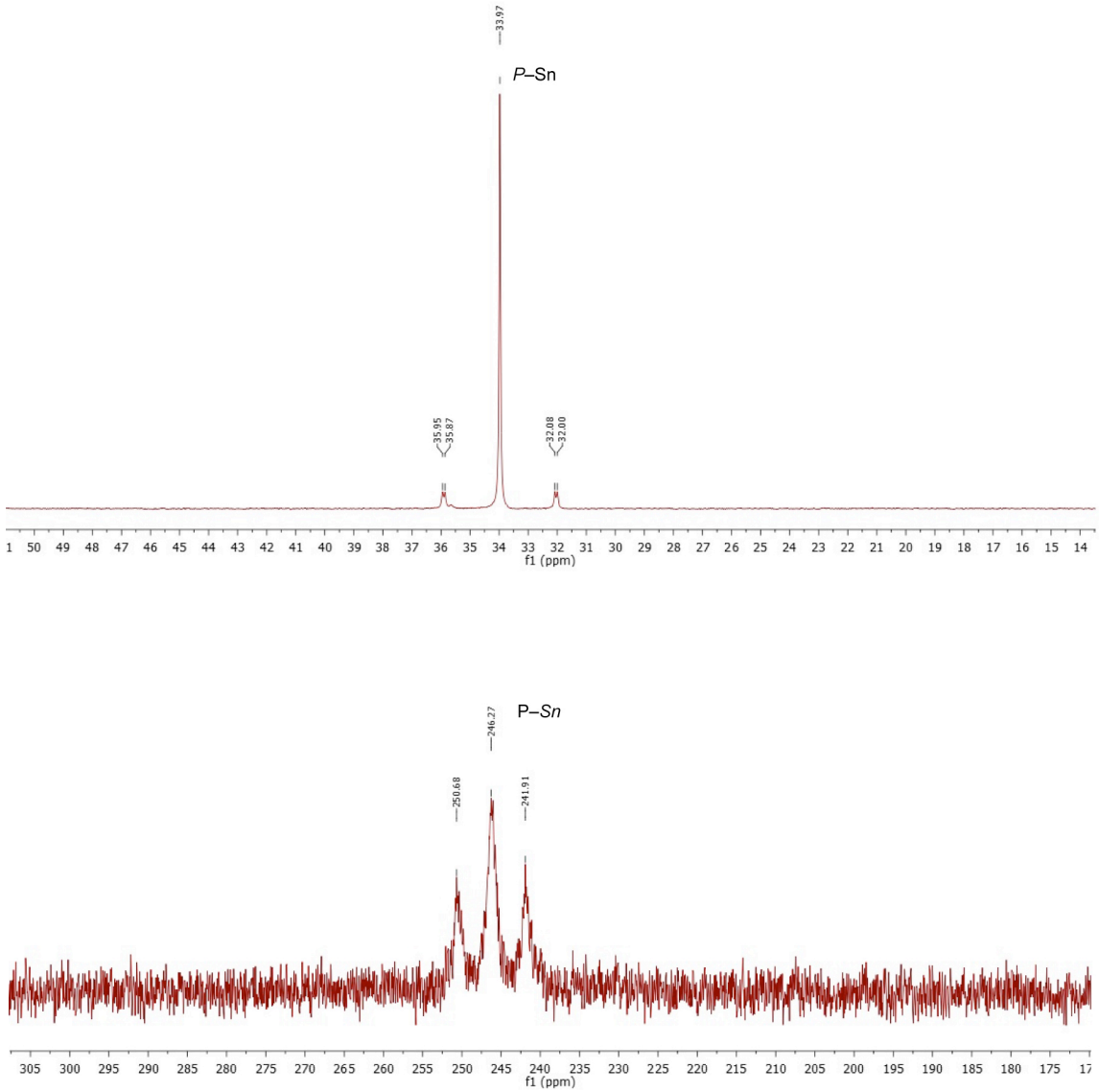


**Fig. S2** $^{31}P\{^{1}H\}$ (top, 162.0 MHz) and $^{119}Sn\{^{1}H\}$ (bottom, 149.2 MHz) NMR spectra ($C_6D_6$, 293 K) of $Sn(NCH_2P^tBu_2)_2C_6H_4$ (**1**).

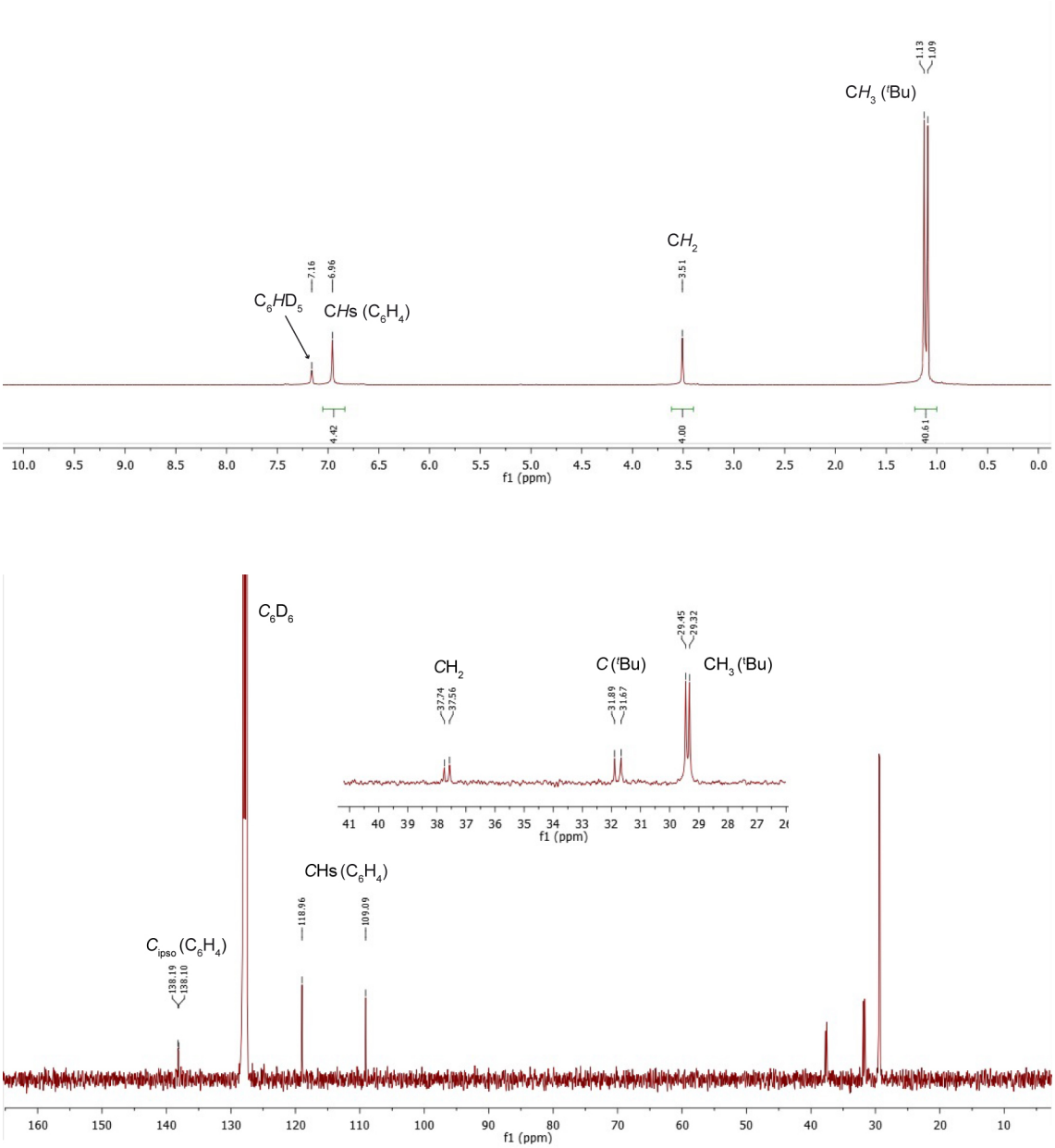


**Fig. S3** $^{1}$H (top, 300.1 MHz) and $^{13}$C{$^{1}$H} (bottom, 100.6 MHz) NMR spectra ($C_6D_6$, 293 K) of $SiCl_2(NCH_2P^tBu_2)_2C_6H_4$ (**2**).

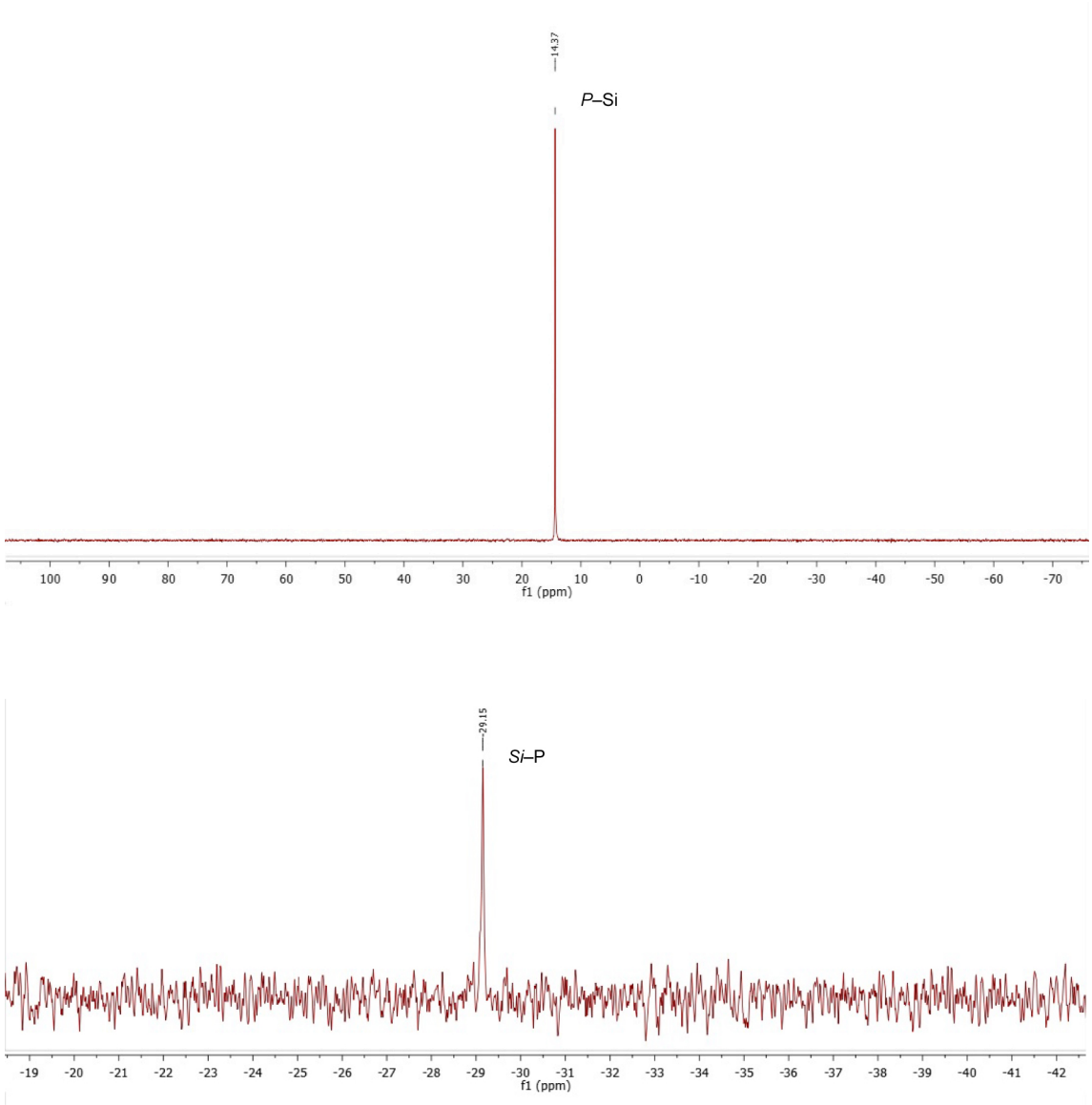


**Fig. S4** $^{31}P\{^{1}H\}$ (top, 121.5 MHz) and $^{29}Si\{^{1}H\}$ (bottom, 79.6 MHz) NMR spectra ($C_6D_6$, 293 K) of $SiCl_2(NCH_2P^tBu_2)_2C_6H_4$ (**2**).

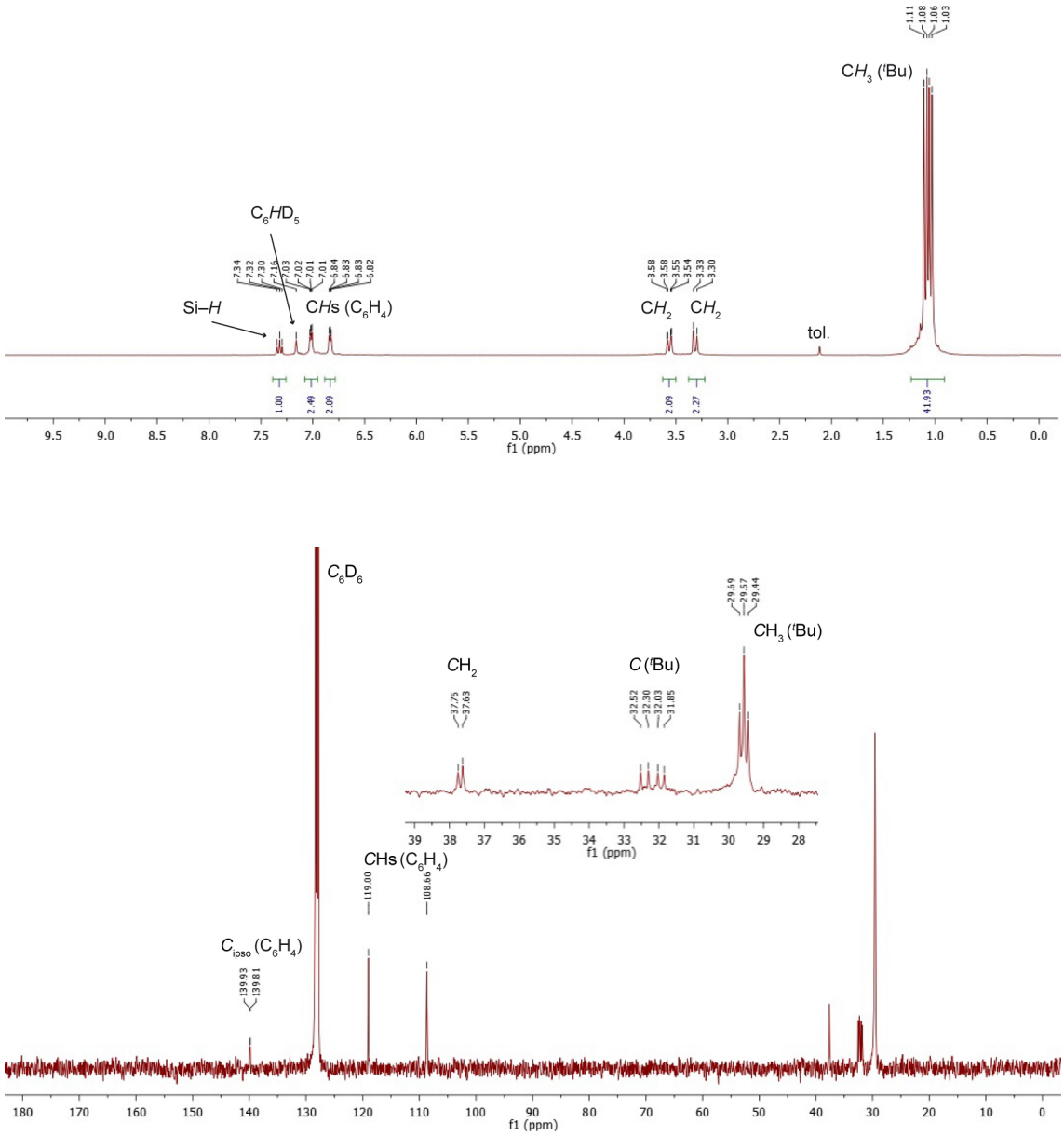


**Fig. S5** $^{1}$H (top, 400.1 MHz) and $^{13}$C{$^{1}$H} (bottom, 100.6 MHz) NMR spectra ($C_6D_6$, 293 K) of $SiHCl(NCH_2P^tBu_2)_2C_6H_4$ (**3**).

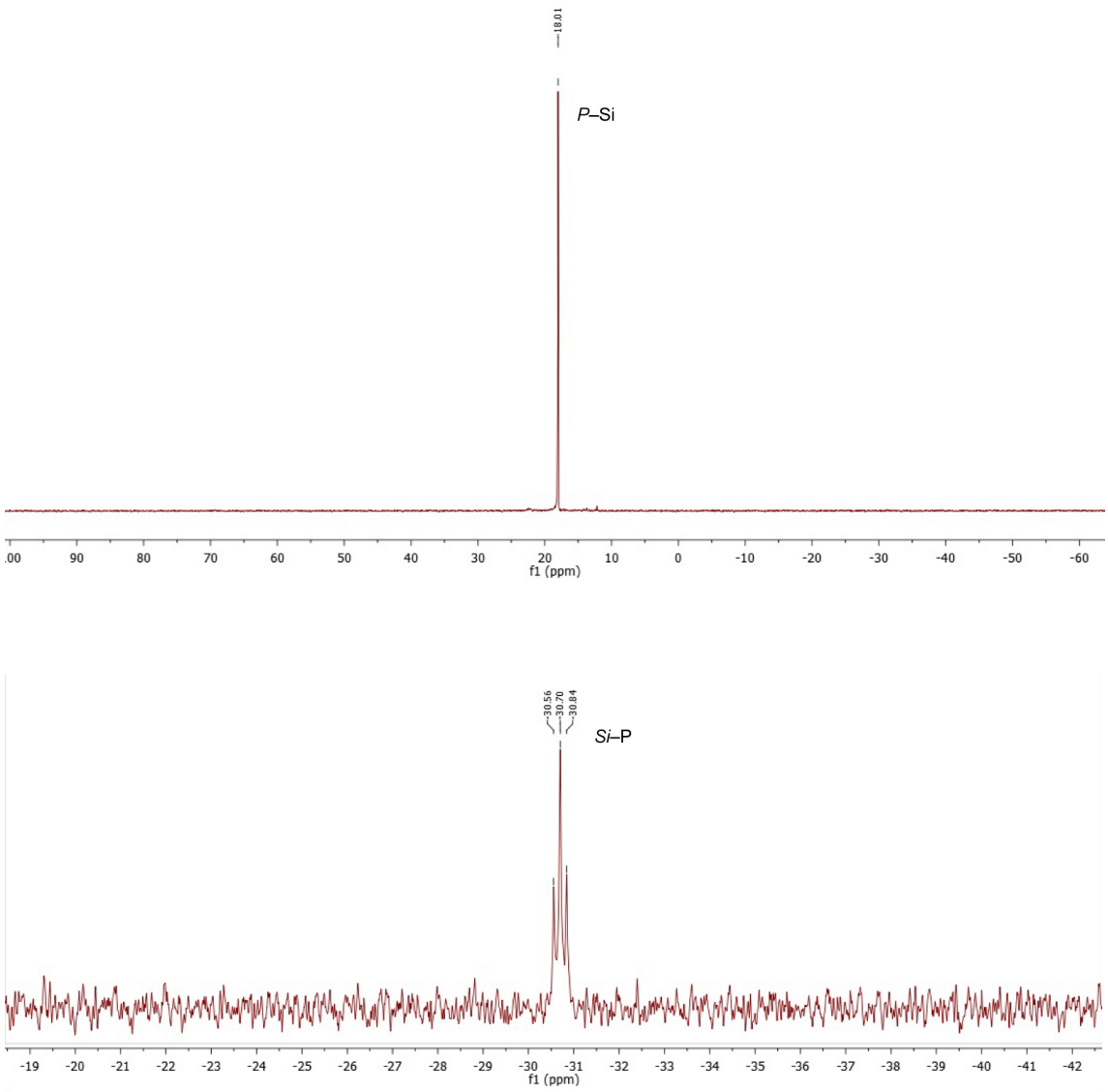


**Fig. S6** $^{31}P\{^{1}H\}$ (top, 162.0 MHz) and $^{29}Si\{^{1}H\}$ (bottom, 79.6 MHz) NMR spectra ($C_6D_6$, 293 K) of $SiHCl(NCH_2P^tBu_2)_2C_6H_4$ (**3**).

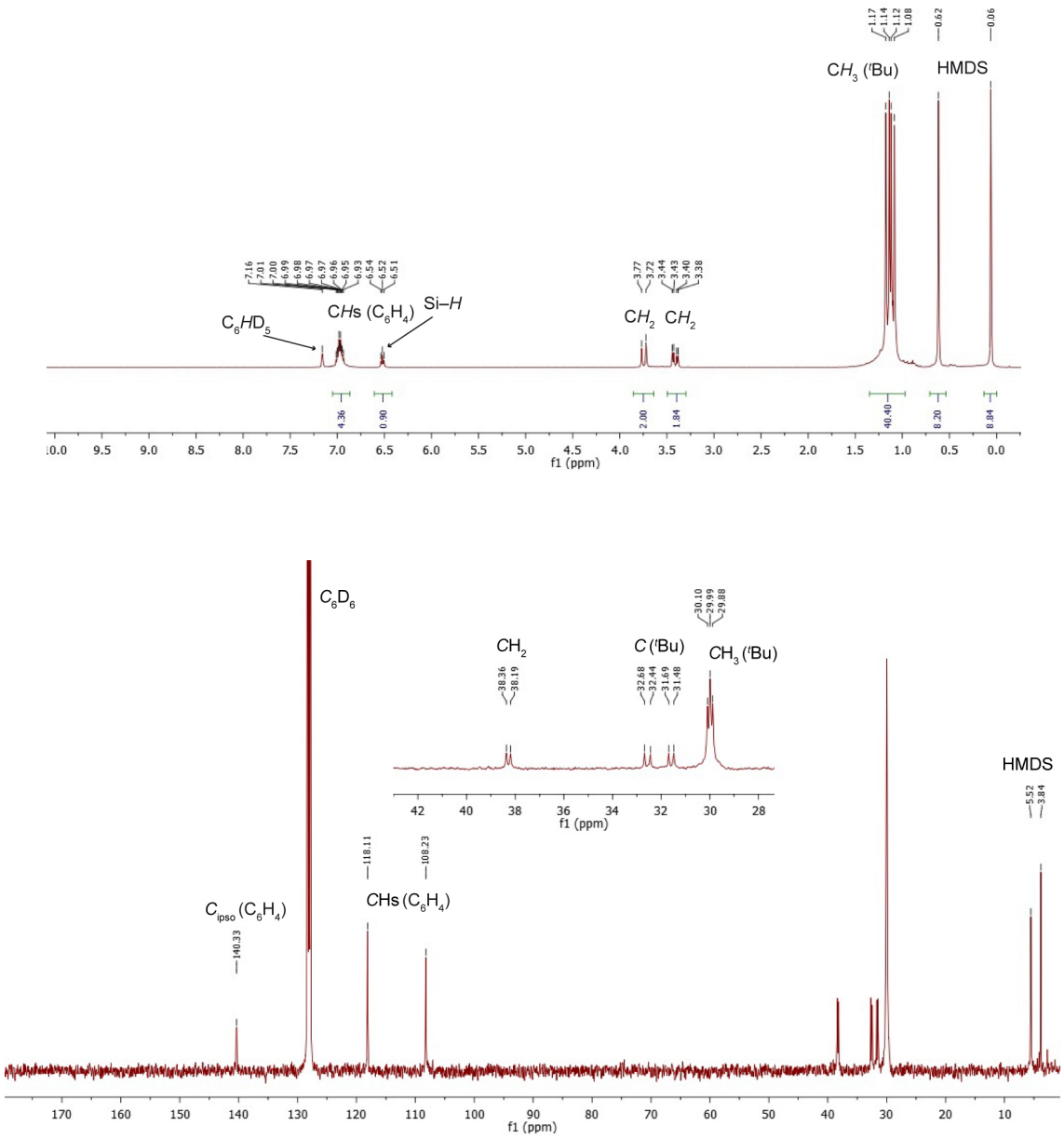


**Fig. S7** $^{1}$H (top, 300.1 MHz) and $^{13}$C{$^{1}$H} (bottom, 100.6 MHz) NMR spectra ($C_6D_6$, 293 K) of SiH(HMDS)(NCH$_2$P$^t$Bu$_2$)$_2$C$_6$H$_4$ (**4**).

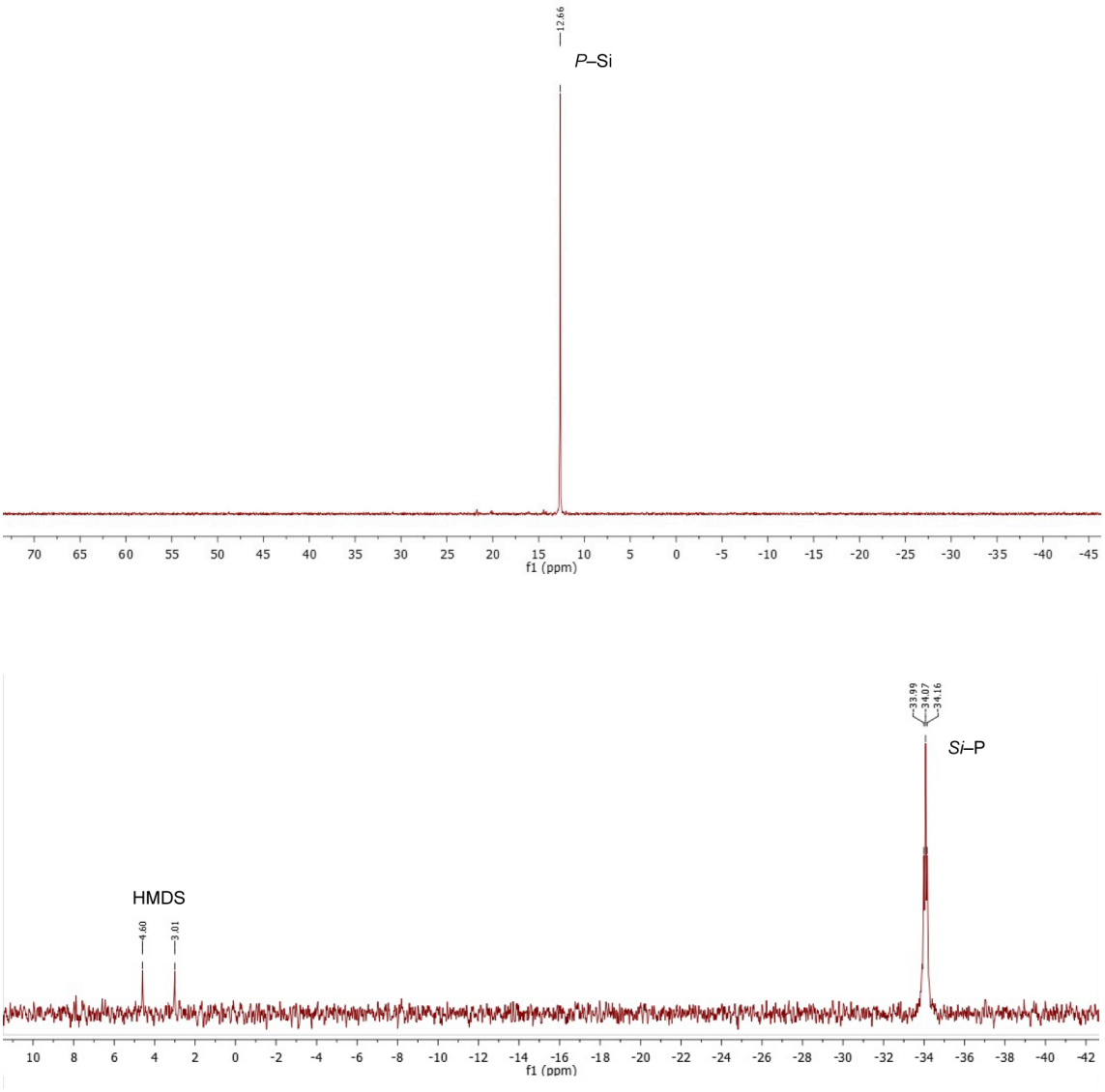


**Fig. S8** $^{31}P\{^{1}H\}$ (top, 121.5 MHz) and $^{29}Si\{^{1}H\}$ (bottom, 79.6 MHz) NMR spectra ($C_6D_6$, 293 K) of $SiH(HMDS)(NCH_2P^tBu_2)_2C_6H_4$ (**4**).

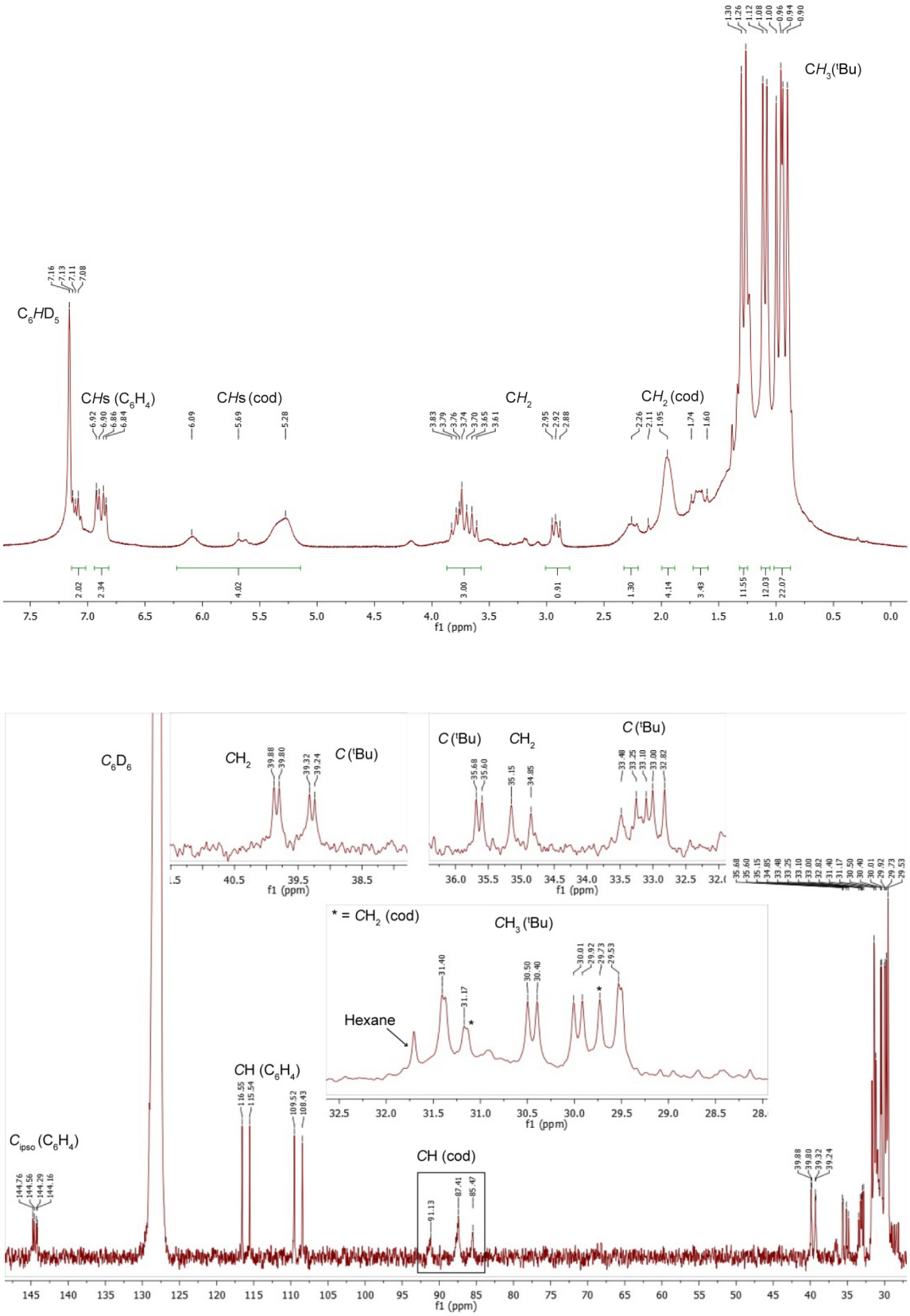


**Fig. S9** $^{1}$H (top, 300.1 MHz) and $^{13}$C{$^{1}$H} (bottom, 100.6 MHz) NMR spectra ($C_6D_6$, 293 K) of [Rh{κ$^2$*Sn*,*P*-SnCl(NCH$_2$P$^t$Bu$_2$)$_2$C$_6$H$_4$}(η$^4$-cod)] (**5**).

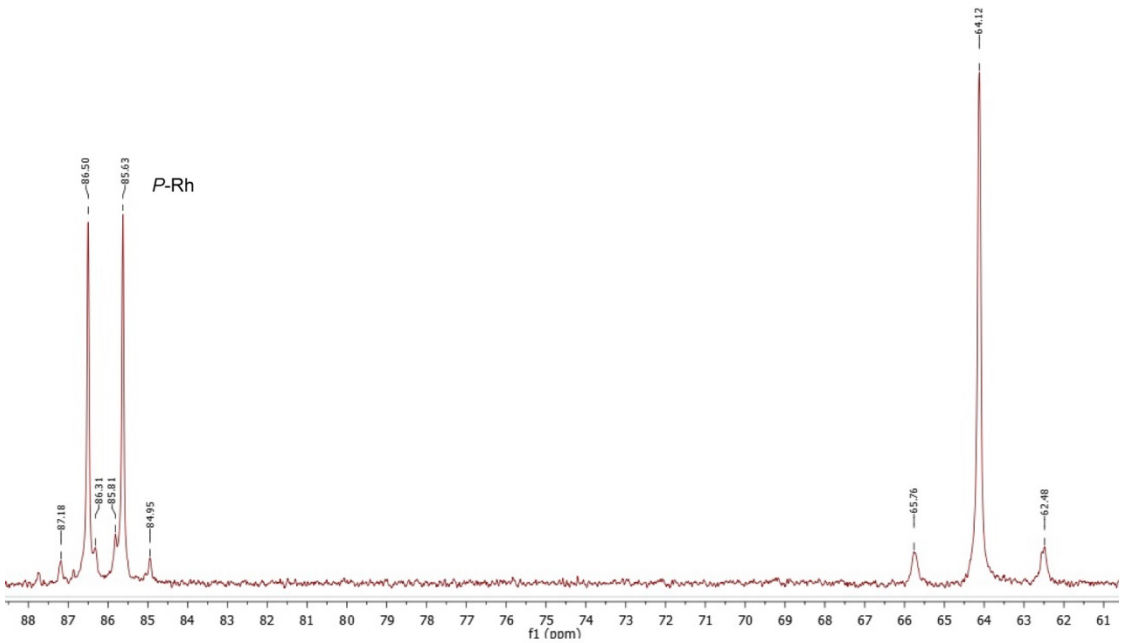


**Fig. S10** $^{31}P\{^{1}H\}$ (121.5 MHz) NMR spectrum ($C_6D_6$, 293 K) of [Rh{$\kappa^2$*Sn*,*P*-SnCl($NCH_2P^tBu_2$)$_2C_6H_4$}($\eta^4$-cod)] (**5**).

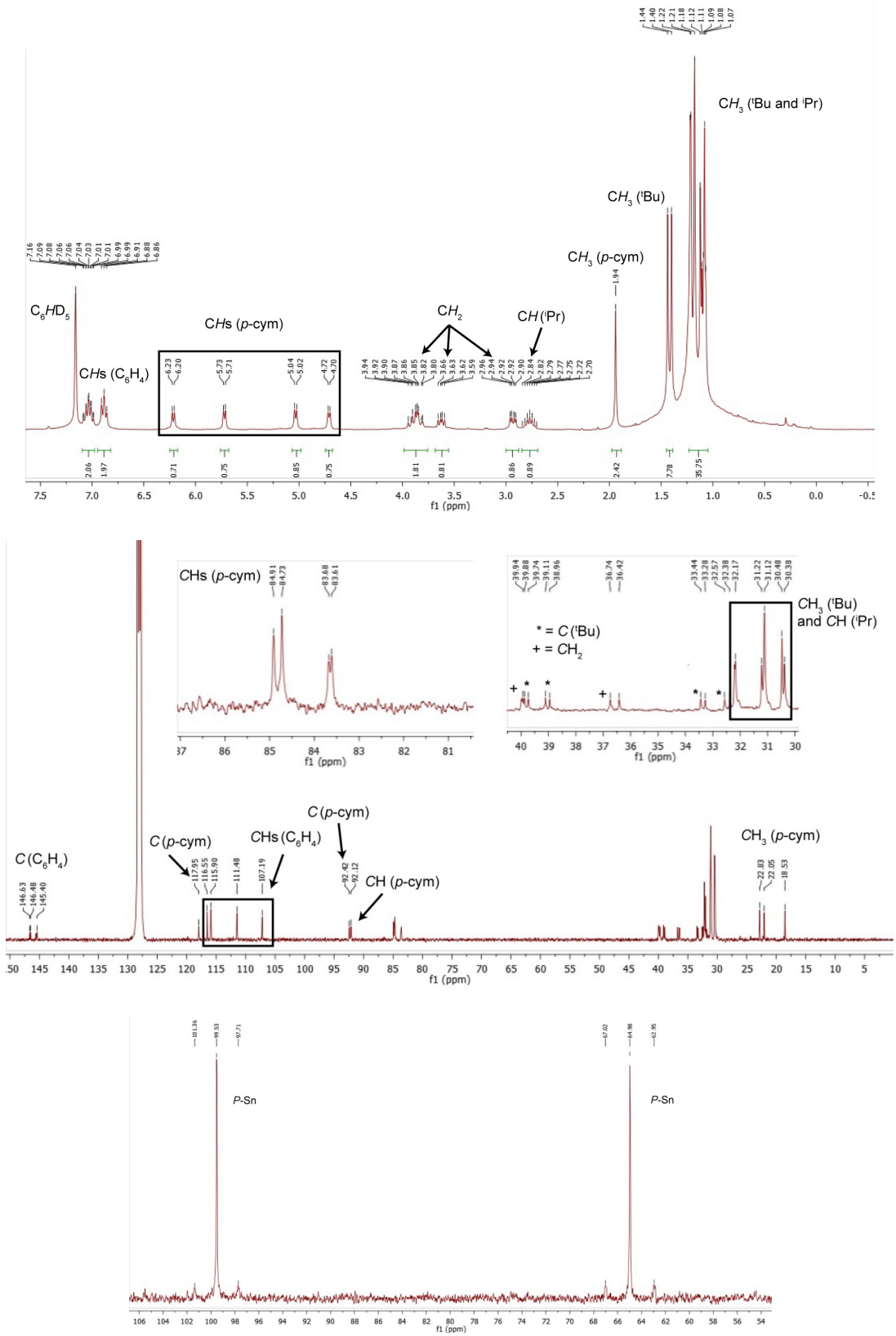


**Fig. S11** $^{1}$H (top, 300.1 MHz), $^{13}$C{$^{1}$H} (center, 100.6 MHz) and $^{31}$P{$^{1}$H} (bottom, 121.5 MHz) NMR spectra ($C_6D_6$, 293 K) of [RuCl{$\kappa^2$*Sn*,*P*- SnCl(NCH$_2$P$^t$Bu$_2$)$_2$C$_6$H$_4$}($\eta^6$-cym)] (**6**).

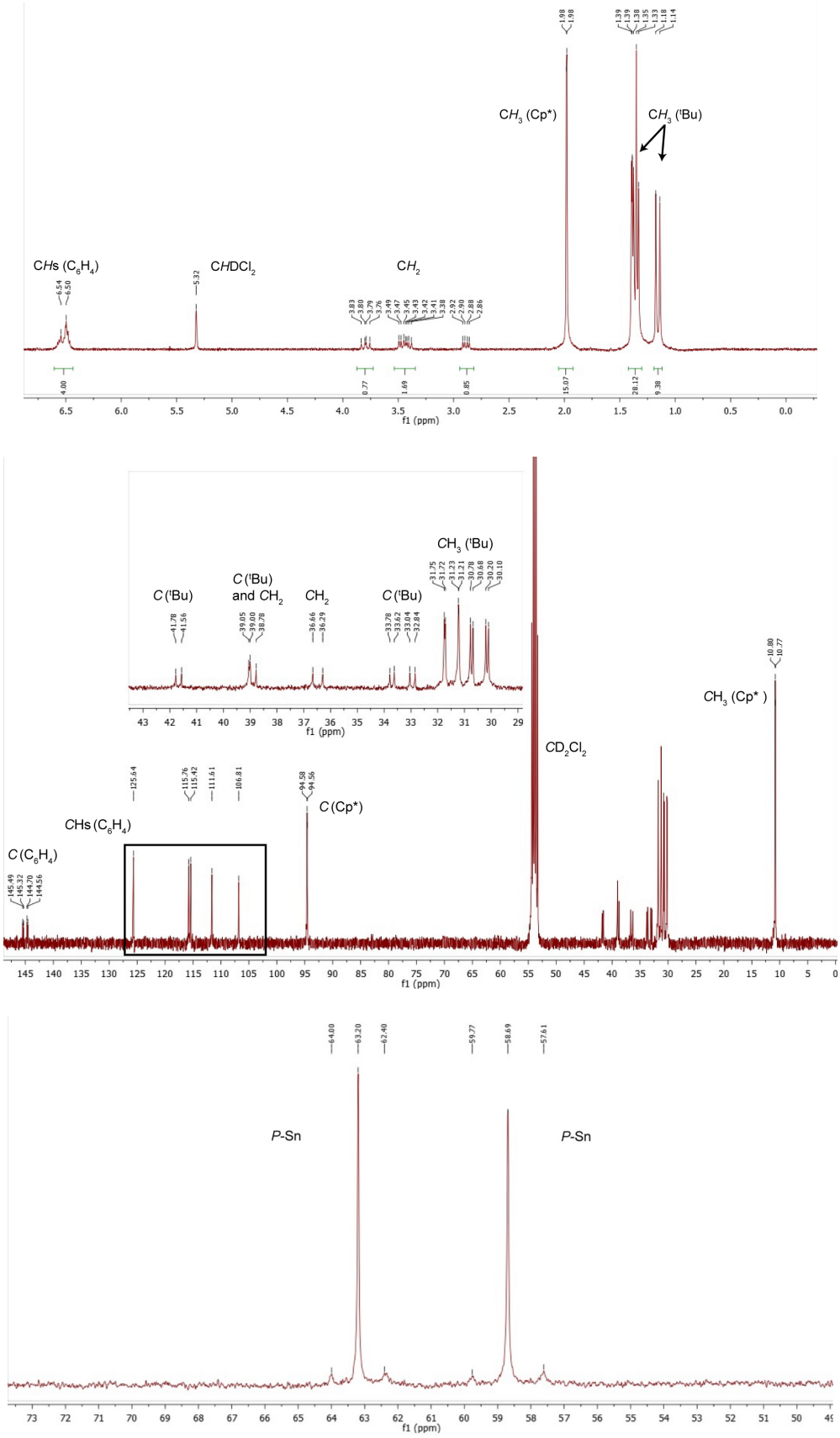


**Fig. S12** $^{1}$H (top, 300.1 MHz), $^{13}$C{$^{1}$H} (center, 100.6 MHz) and $^{31}$P{$^{1}$H} (bottom, 162.0 MHz) NMR spectra ($CD_2Cl_2$, 293 K) of [IrCl{$\kappa^2$*Sn*,*P*- $SnCl(NCH_2P^tBu_2)_2C_6H_4$}($\eta^5$-Cp*)] (**7**).

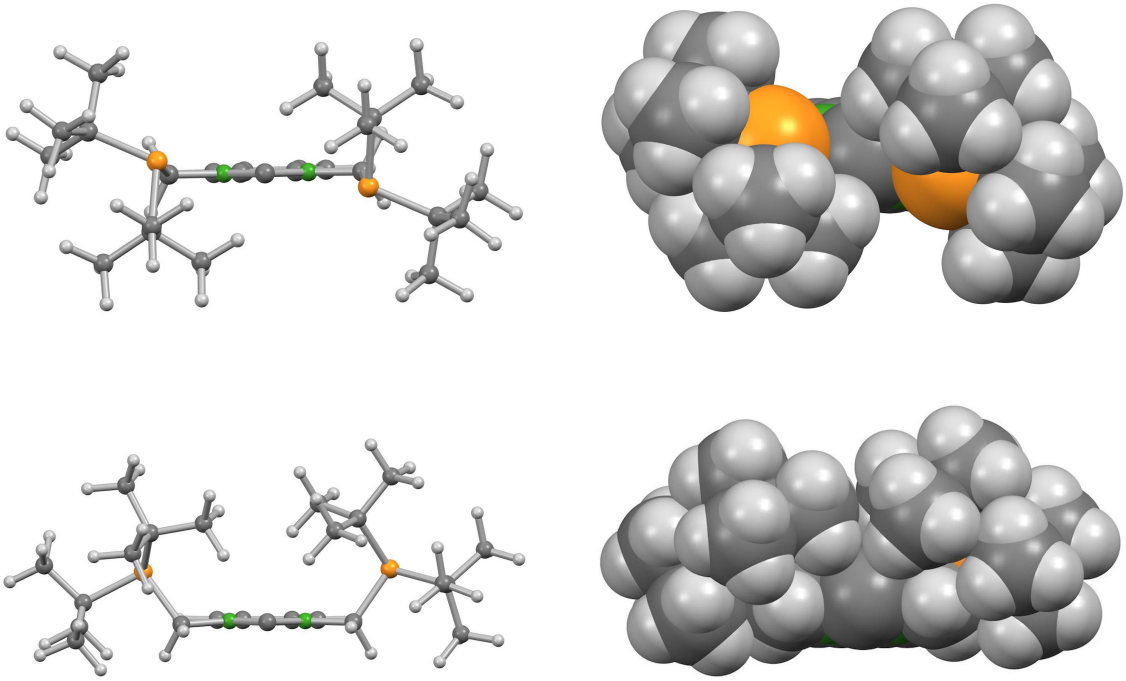

**Fig. S13** DFT-optimized ball and sticks (left) and space-filling (right) structures of the "planar" (top, $\mathbf{C_{tBu\text{-}pl}}$) and "non-planar" (bottom, $\mathbf{C_{tBu\text{-}npl}}$) conformers of $C(NCH_2P^tBu_2)_2C_6H_4$.

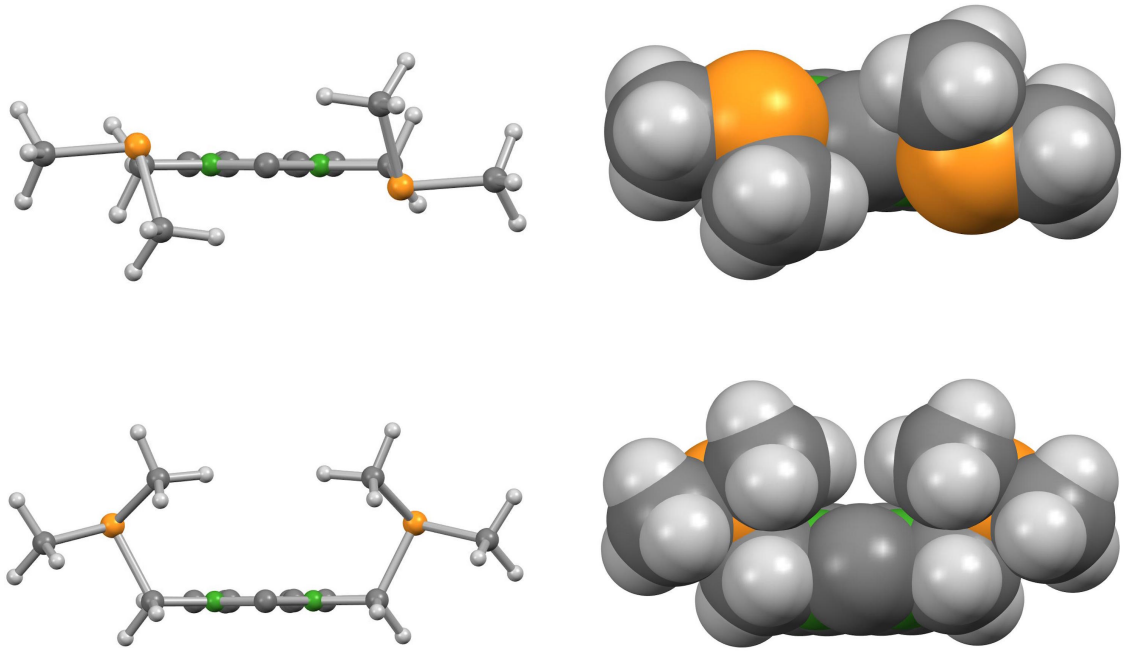

**Fig. S14** DFT-optimized ball and sticks (left) and space-filling (right) structures of the "planar" (top, $\mathbf{C_{Me\text{-}pl}}$) and the "non-planar" (bottom, $\mathbf{C_{Me\text{-}npl}}$) conformers of $C(NCH_2PMe_2)_2C_6H_4$.

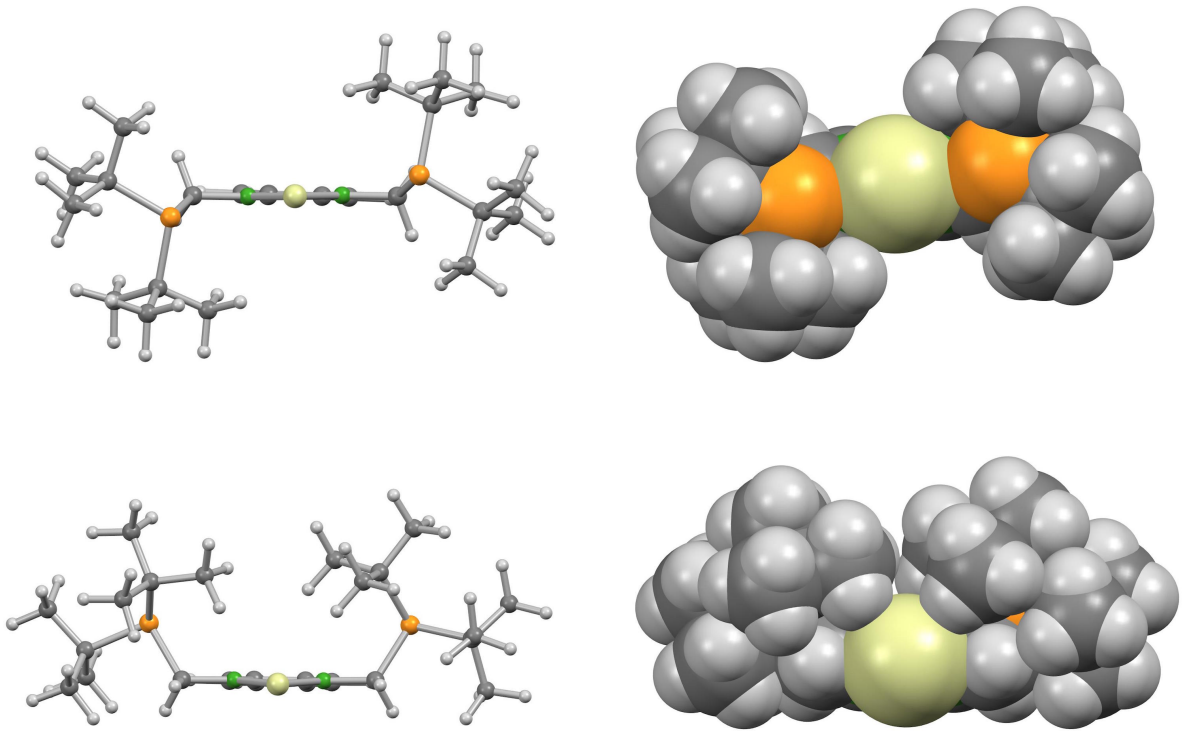

**Fig. S15** DFT-optimized ball and sticks (left) and space-filling (right) structures of the "planar" (top, **$Si_{tBu-pl}$**) and "non-planar" (bottom, **$Si_{tBu-npl}$**) conformers of $Si(NCH_2P^tBu_2)_2C_6H_4$.

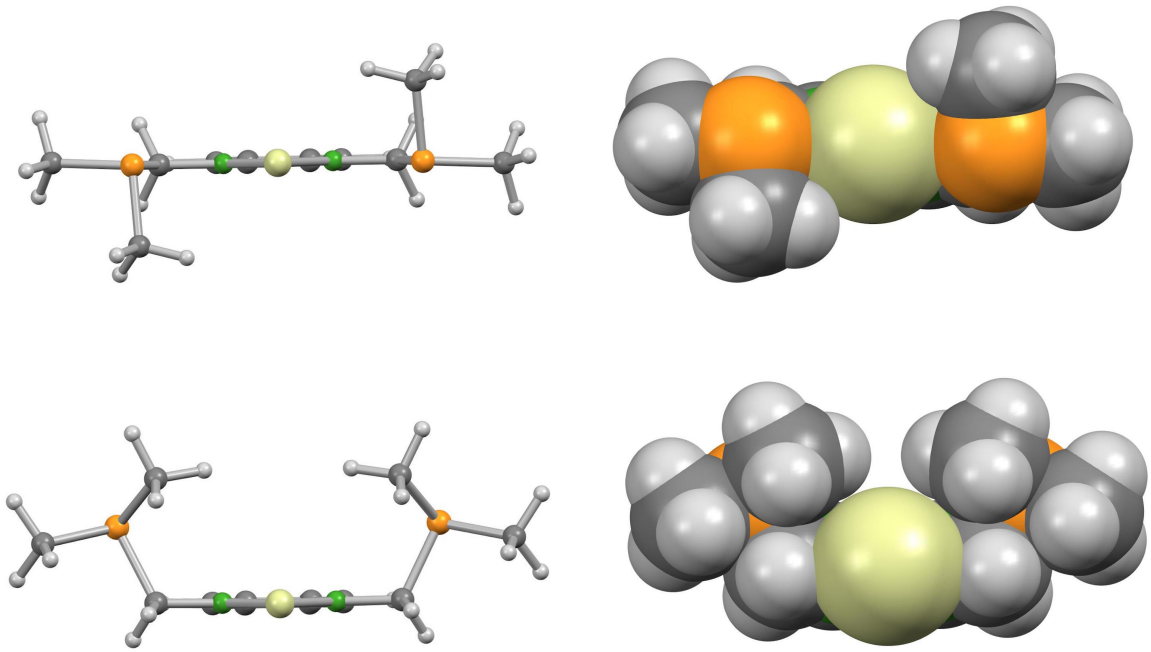

**Fig. S16** DFT-optimized ball and sticks (left) and space-filling (right) structures of the "planar" (top, **$Si_{Me-pl}$**) and the "non-planar" (bottom, **$Si_{Me-npl}$**) conformers of $Si(NCH_2PMe_2)_2C_6H_4$.

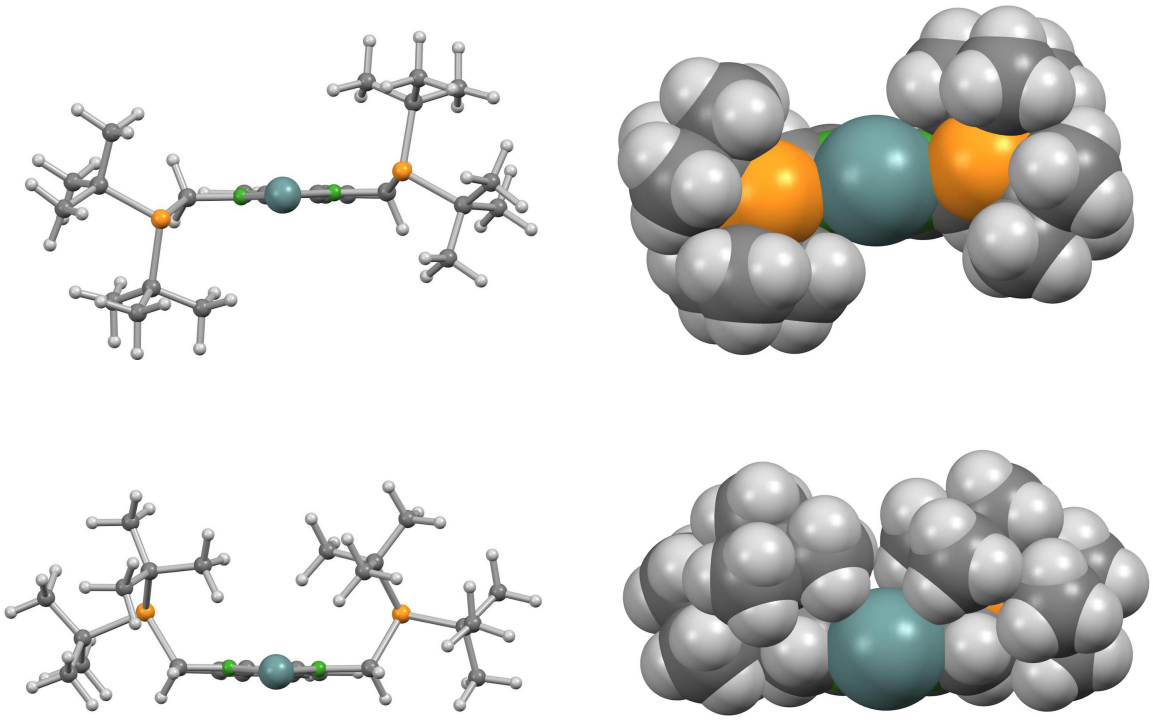

**Fig. S17** DFT-optimized ball and sticks (left) and space-filling (right) structures of the "planar" (top, **$Ge_{tBu-pl}$**) and "non-planar" (bottom, **$Ge_{tBu-npl}$**) conformers of $Ge(NCH_2P^tBu_2)_2C_6H_4$.

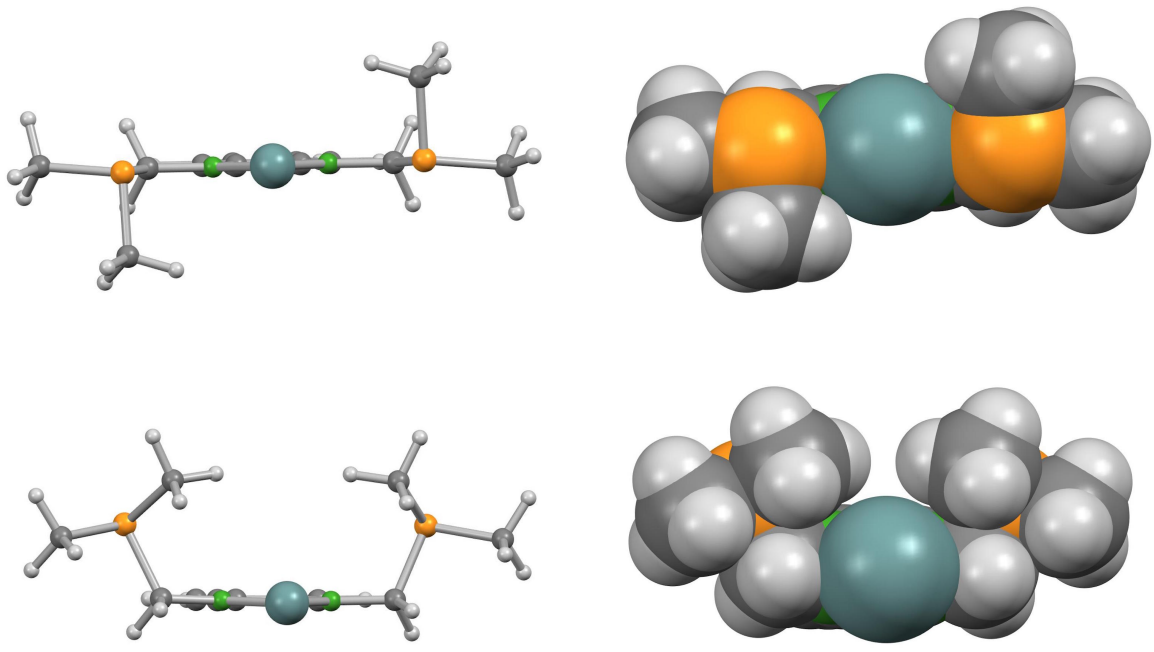

**Fig. S18** DFT-optimized ball and sticks (left) and space-filling (right) structures of the "planar" (top, **$Ge_{Me-pl}$**) and the "non-planar" (bottom, **$Ge_{Me-npl}$**) conformers of $Ge(NCH_2PMe_2)_2C_6H_4$.

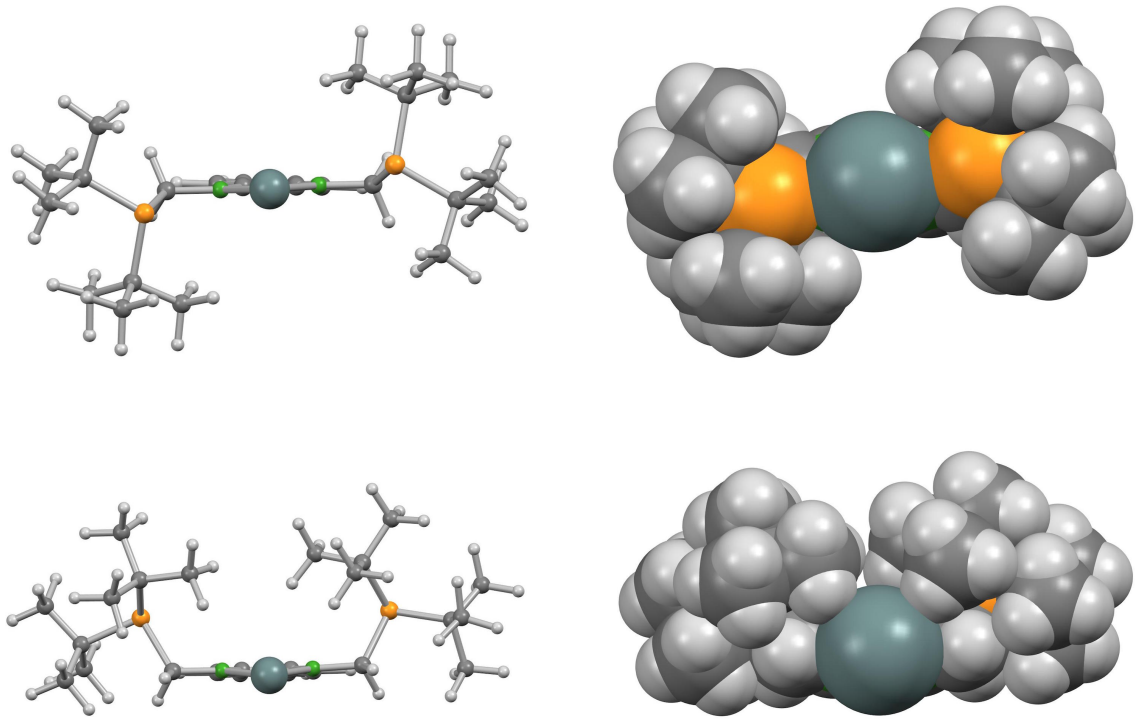

**Fig. S19** DFT-optimized ball and sticks (left) and space-filling (right) structures of the "planar" (top, **$Sn_{tBu-pl}$**) and the "non-planar" (bottom, **$Sn_{tBu-npl}$**) conformers of $Sn(NCH_2P^tBu_2)_2C_6H_4$.

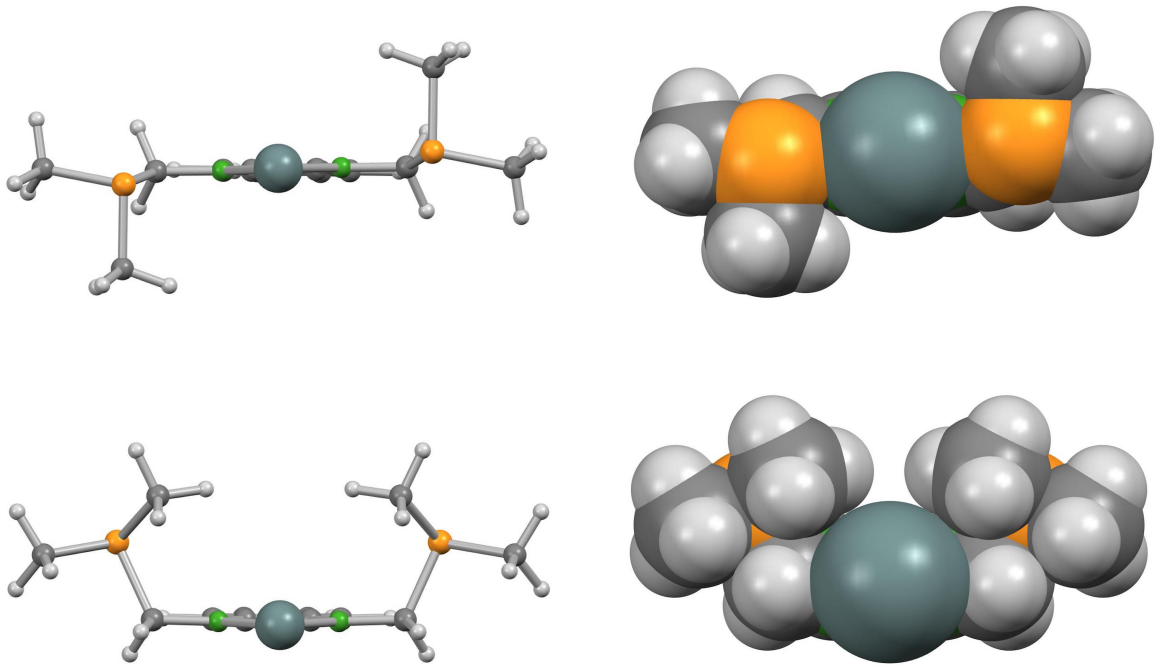

**Fig. S20** DFT-optimized ball and sticks (left) and space-filling (right) structures of the "planar" (top, **$Sn_{Me-pl}$**) and the "non-planar" (bottom, **$Sn_{Me-npl}$**) conformers of $Sn(NCH_2PMe_2)_2C_6H_4$.

**Table S1** DFT-optimized atomic coordinates for **$C_{tBu\text{-}pl}$**.

| | | | |
|---|---|---|---|
| C | 0.000056 | 0.772939 | -0.000273 |
| P | -2.698649 | -0.646547 | 0.223667 |
| N | -1.072519 | 1.611437 | -0.059355 |
| C | -0.698851 | 2.952159 | -0.042815 |
| C | -2.459775 | 1.183241 | -0.128368 |
| H | -2.887579 | 1.472437 | -1.103861 |
| H | -3.017038 | 1.736947 | 0.642613 |
| C | -0.699646 | 5.331007 | -0.046622 |
| H | -1.232487 | 6.282385 | -0.083497 |
| C | -4.484543 | -0.548631 | 0.915525 |
| C | -2.750957 | -1.389370 | -1.539871 |
| C | -1.423639 | 4.139793 | -0.093282 |
| H | -2.511709 | 4.141035 | -0.169176 |
| C | -5.096110 | -1.957203 | 0.915263 |
| H | -6.013202 | -1.964088 | 1.528817 |
| H | -4.402982 | -2.700401 | 1.340676 |
| H | -5.376383 | -2.288767 | -0.094963 |
| C | -2.688513 | -2.918221 | -1.379378 |
| H | -2.608715 | -3.393121 | -2.372184 |
| H | -3.581642 | -3.328812 | -0.887928 |
| H | -1.808006 | -3.216659 | -0.790051 |
| C | -1.470856 | -0.945464 | -2.269543 |
| H | -0.563798 | -1.156898 | -1.686271 |
| H | -1.475449 | 0.133518 | -2.490144 |
| H | -1.408754 | -1.478045 | -3.234107 |
| C | -4.296181 | -0.121527 | 2.384434 |
| H | -5.277269 | -0.067518 | 2.886497 |
| H | -3.827495 | 0.871503 | 2.477020 |
| H | -3.667208 | -0.838156 | 2.933413 |
| C | -3.957237 | -1.010684 | -2.405454 |
| H | -3.825015 | -1.426962 | -3.419230 |
| H | -4.064746 | 0.080053 | -2.514338 |
| H | -4.901038 | -1.412640 | -2.010358 |
| C | -5.461599 | 0.429947 | 0.246941 |
| H | -5.651344 | 0.188597 | -0.806031 |
| H | -5.109894 | 1.471484 | 0.298047 |
| H | -6.431263 | 0.396021 | 0.773537 |
| P | 2.698683 | -0.646573 | -0.223664 |
| N | 1.072607 | 1.611470 | 0.058875 |
| C | 0.698893 | 2.952180 | 0.042445 |
| C | 2.459876 | 1.183307 | 0.127878 |
| H | 2.887743 | 1.472744 | 1.103262 |
| H | 3.017094 | 1.736801 | -0.643280 |
| C | 0.699608 | 5.331028 | 0.046439 |
| H | 1.232416 | 6.282422 | 0.083386 |
| C | 4.484576 | -0.548938 | -0.915528 |
| C | 2.750929 | -1.388891 | 1.540091 |
| C | 1.423641 | 4.139835 | 0.093004 |
| H | 2.511712 | 4.141109 | 0.168892 |
| C | 5.096013 | -1.957569 | -0.914952 |
| H | 6.013114 | -1.964680 | -1.528486 |
| H | 4.402817 | -2.700775 | -1.340227 |
| H | 5.376232 | -2.288953 | 0.095343 |
| C | 2.688286 | -2.917772 | 1.380007 |
| H | 2.608500 | -3.392412 | 2.372935 |
| H | 3.581329 | -3.328597 | 0.888595 |
| H | 1.807701 | -3.216246 | 0.790819 |
| C | 1.470898 | -0.944618 | 2.269663 |
| H | 0.563811 | -1.156039 | 1.686431 |
| H | 1.475671 | 0.134409 | 2.490051 |
| H | 1.408701 | -1.476982 | 3.234341 |
| C | 4.296265 | -0.122136 | -2.384529 |
| H | 5.277361 | -0.068339 | -2.886595 |
| H | 3.827682 | 0.870926 | -2.477316 |
| H | 3.667220 | -0.838806 | -2.933366 |
| C | 3.957264 | -1.010132 | 2.405561 |
| H | 3.825027 | -1.426199 | 3.419424 |
| H | 4.064863 | 0.080618 | 2.514234 |
| H | 4.901026 | -1.412251 | 2.010530 |
| C | 5.461689 | 0.429731 | -0.247164 |
| H | 5.651133 | 0.188868 | 0.805990 |
| H | 5.110199 | 1.471336 | -0.298893 |
| H | 6.431470 | 0.395322 | -0.773530 |

Energy= -1771.0754311 hartree

**Table S2** DFT-optimized atomic coordinates for **$C_{tBu\text{-}npl}$**.

| | | | |
|---|---|---|---|
| C | 0.145422 | 0.459034 | -1.347906 |
| P | -3.337071 | 0.105094 | 0.328798 |
| N | -0.950774 | 1.073593 | -0.814198 |
| C | -0.614623 | 2.170604 | -0.025472 |
| C | -2.307806 | 0.678968 | -1.142850 |
| H | -2.228612 | -0.089755 | -1.923272 |
| H | -2.821440 | 1.547658 | -1.583456 |
| C | -0.688188 | 4.103734 | 1.357467 |
| H | -1.250974 | 4.846036 | 1.925497 |
| C | -5.073224 | 0.499279 | -0.368397 |
| C | -3.040462 | -1.777060 | 0.327272 |
| C | -1.376430 | 3.100122 | 0.681144 |
| H | -2.463312 | 3.033683 | 0.718216 |
| C | -6.131357 | -0.246664 | 0.456210 |
| H | -7.132624 | 0.151865 | 0.220523 |
| H | -5.968022 | -0.122779 | 1.538468 |
| H | -6.145581 | -1.322773 | 0.230151 |
| C | -3.680772 | -2.351284 | 1.602034 |
| H | -3.410597 | -3.416224 | 1.702671 |
| H | -4.777447 | -2.289760 | 1.591384 |
| H | -3.319648 | -1.825238 | 2.499095 |
| C | -1.516648 | -1.952138 | 0.448025 |
| H | -1.105377 | -1.360390 | 1.280764 |
| H | -0.984913 | -1.658943 | -0.468783 |
| H | -1.287554 | -3.013214 | 0.646048 |
| C | -5.255731 | 2.009162 | -0.122593 |
| H | -6.256980 | 2.325814 | -0.460718 |
| H | -4.521328 | 2.615062 | -0.677648 |
| H | -5.160817 | 2.255662 | 0.945949 |
| C | -3.532625 | -2.552722 | -0.897443 |
| H | -3.193112 | -3.600712 | -0.830015 |
| H | -3.131344 | -2.142611 | -1.837231 |
| H | -4.630134 | -2.569997 | -0.965329 |
| C | -5.301161 | 0.211934 | -1.859740 |
| H | -5.170986 | -0.848677 | -2.107985 |
| H | -4.631594 | 0.796898 | -2.507275 |
| H | -6.334057 | 0.490789 | -2.131566 |
| P | 3.661963 | 0.444717 | 0.295324 |
| N | 1.195771 | 1.179620 | -0.854424 |
| C | 0.782811 | 2.242547 | -0.053627 |
| C | 2.573222 | 0.872681 | -1.187614 |
| H | 3.023105 | 1.756648 | -1.664824 |
| H | 2.536754 | 0.066245 | -1.932508 |
| C | 0.713294 | 4.174954 | 1.330101 |
| H | 1.219190 | 4.972822 | 1.876110 |
| C | 2.834713 | -1.141767 | 0.966384 |
| C | 5.273104 | -0.000294 | -0.632777 |
| C | 1.473680 | 3.245214 | 0.625583 |
| H | 2.562539 | 3.286820 | 0.619856 |
| C | 3.847228 | -1.915345 | 1.823159 |
| H | 3.320042 | -2.705644 | 2.384022 |
| H | 4.347368 | -1.263760 | 2.557501 |
| H | 4.618687 | -2.407451 | 1.213192 |

| | | | |
|---|---|---|---|
| C | 6.390464 | -0.121639 | 0.417934 |
| H | 7.358218 | -0.282322 | -0.087300 |
| H | 6.233971 | -0.962229 | 1.106444 |
| H | 6.469493 | 0.797184 | 1.019090 |
| C | 5.617290 | 1.205427 | -1.528463 |
| H | 5.525886 | 2.160778 | -0.986147 |
| H | 4.984048 | 1.253380 | -2.426815 |
| H | 6.661088 | 1.117241 | -1.872912 |
| C | 1.720129 | -0.636633 | 1.904417 |
| H | 1.237841 | -1.498955 | 2.395994 |
| H | 0.938608 | -0.085383 | 1.363758 |
| H | 2.120593 | 0.025031 | 2.687471 |
| C | 5.237524 | -1.262729 | -1.500367 |
| H | 6.185052 | -1.354690 | -2.059198 |
| H | 4.421627 | -1.237423 | -2.238646 |
| H | 5.124683 | -2.175161 | -0.898145 |
| C | 2.220561 | -2.079515 | -0.080287 |
| H | 2.972328 | -2.492411 | -0.766369 |
| H | 1.443452 | -1.580782 | -0.677819 |
| H | 1.741601 | -2.931215 | 0.434048 |

Energy= -1771.08759791 hartree

**Table S3** DFT-optimized atomic coordinates for **$C_{Me\text{-}pl}$**.

| | | | |
|---|---|---|---|
| C | 0.000648 | -0.263959 | -0.007579 |
| P | -2.602051 | -1.707554 | 0.403677 |
| N | -1.071776 | 0.575570 | 0.003282 |
| C | -0.694716 | 1.915129 | -0.001192 |
| C | -2.447334 | 0.118032 | -0.000573 |
| H | -2.916105 | 0.344622 | -0.974870 |
| H | -3.008790 | 0.666287 | 0.774739 |
| C | -0.690494 | 4.293155 | 0.001381 |
| H | -1.222187 | 5.245829 | 0.001867 |
| C | -2.176255 | -2.457087 | -1.236659 |
| C | -1.418886 | 3.104489 | -0.001658 |
| H | -2.509538 | 3.108002 | -0.005780 |
| H | -4.783793 | -2.811468 | 0.307420 |
| H | -2.456895 | -3.521663 | -1.221779 |
| H | -1.090510 | -2.376646 | -1.384360 |
| H | -4.914512 | -1.240891 | 1.125815 |
| H | -2.700418 | -1.963098 | -2.071310 |
| H | -4.838213 | -1.312891 | -0.665576 |
| P | 2.597577 | -1.720913 | -0.404425 |
| N | 1.076810 | 0.570783 | -0.015192 |
| C | 0.705722 | 1.911960 | -0.005122 |
| C | 2.450478 | 0.107581 | -0.010349 |
| H | 2.920414 | 0.337112 | 0.962702 |
| H | 3.013921 | 0.649709 | -0.788571 |
| C | 0.712478 | 4.289934 | 0.003636 |
| H | 1.248486 | 5.240186 | 0.007786 |
| C | 4.453827 | -1.782766 | -0.258846 |
| C | 2.157792 | -2.458330 | 1.237704 |
| C | 1.435381 | 3.097940 | 0.000923 |
| H | 2.526036 | 3.096300 | 0.004977 |
| H | 4.773039 | -2.835624 | -0.291831 |
| H | 2.430334 | -3.525071 | 1.230561 |
| H | 1.071791 | -2.368428 | 1.378447 |
| H | 4.916216 | -1.268965 | -1.115716 |
| H | 2.680964 | -1.963440 | 2.072444 |
| H | 4.829922 | -1.333419 | 0.675495 |
| C | -4.459377 | -1.760411 | 0.268535 |

Energy= -1299.44703901 hartree

**Table S4** DFT-optimized atomic coordinates for **$C_{Me\text{-}npl}$**.

| | | | |
|---|---|---|---|
| C | -0.000089 | -0.407996 | 1.187696 |
| P | 3.293749 | -0.517575 | -0.585349 |
| N | 1.073536 | 0.363783 | 0.836897 |
| C | 0.699996 | 1.582542 | 0.275982 |
| C | 2.440276 | -0.071160 | 1.029726 |
| H | 2.402198 | -0.939446 | 1.703238 |
| H | 3.018563 | 0.727710 | 1.523762 |
| C | 0.702474 | 3.753426 | -0.692975 |
| H | 1.236379 | 4.619422 | -1.086945 |
| C | 2.334920 | -2.052388 | -0.982677 |
| C | 1.427985 | 2.666886 | -0.210473 |
| H | 2.517981 | 2.658238 | -0.229852 |
| H | 5.406871 | -1.751985 | -0.636336 |
| H | 2.765230 | -2.529680 | -1.875829 |
| H | 1.295072 | -1.774082 | -1.208832 |
| H | 5.444574 | -0.477637 | 0.601384 |
| H | 2.328849 | -2.771773 | -0.148456 |
| H | 4.584400 | -2.017323 | 0.932172 |
| P | -3.293197 | -0.517809 | -0.585679 |
| N | -1.073449 | 0.364103 | 0.836813 |
| C | -0.699510 | 1.582752 | 0.275941 |
| C | -2.440372 | -0.070386 | 1.029431 |
| H | -3.018601 | 0.729036 | 1.522616 |
| H | -2.402811 | -0.938164 | 1.703625 |
| C | -0.701296 | 3.753636 | -0.693001 |
| H | -1.234927 | 4.619799 | -1.086981 |
| C | -2.335323 | -2.053797 | -0.980855 |
| C | -4.820072 | -1.266564 | 0.157953 |
| C | -1.427153 | 2.667308 | -0.210559 |
| H | -2.517151 | 2.658995 | -0.229957 |
| H | -2.765982 | -2.532083 | -1.873337 |
| H | -5.407286 | -1.750528 | -0.636823 |
| H | -5.444607 | -0.475211 | 0.599910 |
| H | -1.295263 | -1.776538 | -1.207406 |
| H | -4.585824 | -2.015339 | 0.932283 |
| H | -2.329763 | -2.772001 | -0.145601 |
| C | 4.819634 | -1.268153 | 0.158508 |

Energy= -1299.44922095 hartree

**Table S5** DFT-optimized atomic coordinates for **$Si_{tBu\text{-}pl}$**.

| | | | |
|---|---|---|---|
| Si | 0.000010 | -0.397441 | -0.000074 |
| P | -3.308339 | -0.944295 | 0.061190 |
| N | -1.214369 | 0.902301 | 0.212692 |
| C | -0.693833 | 2.190594 | 0.137643 |
| C | -2.632652 | 0.748870 | 0.504687 |
| H | -3.207194 | 1.519144 | -0.036582 |
| H | -2.812723 | 0.922851 | 1.578688 |
| C | -0.680214 | 4.601969 | 0.152812 |
| H | -1.210923 | 5.547188 | 0.277409 |
| C | -4.750310 | -1.039601 | 1.309128 |
| C | -3.980511 | -0.628268 | -1.698283 |
| C | -1.373700 | 3.400595 | 0.300807 |
| H | -2.435928 | 3.414190 | 0.545375 |
| C | -5.718195 | -2.148617 | 0.874829 |
| H | -6.420159 | -2.370734 | 1.696347 |
| H | -5.186446 | -3.080959 | 0.627418 |
| H | -6.319685 | -1.853024 | 0.002698 |
| C | -4.364862 | -1.989678 | -2.300976 |
| H | -4.623578 | -1.863544 | -3.366124 |
| H | -5.233511 | -2.440871 | -1.801818 |
| H | -3.529192 | -2.703306 | -2.237358 |
| C | -2.799664 | -0.071789 | -2.515152 |
| H | -1.923159 | -0.737218 | -2.468750 |
| H | -2.486016 | 0.927524 | -2.177980 |
| H | -3.099813 | 0.012632 | -3.573294 |

| | | | |
|---|---|---|---|
| C | -4.080384 | -1.475153 | 2.626179 |
| H | -4.843611 | -1.580315 | 3.415883 |
| H | -3.340756 | -0.739201 | 2.980106 |
| H | -3.565289 | -2.440750 | 2.513414 |
| C | -5.161095 | 0.340148 | -1.819244 |
| H | -5.377512 | 0.526368 | -2.885363 |
| H | -4.951111 | 1.316727 | -1.355669 |
| H | -6.077344 | -0.066712 | -1.367912 |
| C | -5.539412 | 0.253469 | 1.561083 |
| H | -6.052154 | 0.617720 | 0.662171 |
| H | -4.901687 | 1.064915 | 1.941529 |
| H | -6.310868 | 0.065998 | 2.328025 |
| P | 3.308406 | -0.944331 | -0.061226 |
| N | 1.214427 | 0.902262 | -0.212971 |
| C | 0.693952 | 2.190566 | -0.137807 |
| C | 2.632747 | 0.748822 | -0.504803 |
| H | 3.207218 | 1.519093 | 0.036535 |
| H | 2.812926 | 0.922808 | -1.578782 |
| C | 0.680432 | 4.601943 | -0.152855 |
| H | 1.211176 | 5.547152 | -0.277381 |
| C | 4.750408 | -1.039687 | -1.309116 |
| C | 3.980376 | -0.628240 | 1.698348 |
| C | 1.373864 | 3.400550 | -0.300936 |
| H | 2.436091 | 3.414108 | -0.545509 |
| C | 5.718351 | -2.148644 | -0.874769 |
| H | 6.420282 | -2.370787 | -1.696313 |
| H | 5.186646 | -3.081006 | -0.627319 |
| H | 6.319844 | -1.852981 | -0.002671 |
| C | 4.364660 | -1.989626 | 2.301140 |
| H | 4.623206 | -1.863443 | 3.366322 |
| H | 5.233391 | -2.440820 | 1.802116 |
| H | 3.529000 | -2.703259 | 2.237417 |
| C | 2.799436 | -0.071746 | 2.515036 |
| H | 1.922860 | -0.737051 | 2.468318 |
| H | 2.485991 | 0.927668 | 2.177999 |
| H | 3.099361 | 0.012513 | 3.573250 |
| C | 4.080518 | -1.475351 | -2.626136 |
| H | 4.843740 | -1.580375 | -3.415880 |
| H | 3.340741 | -0.739531 | -2.980010 |
| H | 3.565613 | -2.441044 | -2.513358 |
| C | 5.160929 | 0.340203 | 1.819484 |
| H | 5.377165 | 0.526432 | 2.885644 |
| H | 4.950989 | 1.316803 | 1.355919 |
| H | 6.077256 | -0.066618 | 1.368249 |
| C | 5.539459 | 0.253416 | -1.561217 |
| H | 6.052026 | 0.617889 | -0.662250 |
| H | 4.901716 | 1.064706 | -1.941950 |
| H | 6.311017 | 0.065844 | -2.328033 |

Energy= -2022.53348763 hartree

**Table S6** DFT-optimized atomic coordinates for **$Si_{tBu\text{-}npl}$**.

| | | | |
|---|---|---|---|
| Si | -0.162834 | 0.124038 | 1.975436 |
| P | 3.427988 | 0.103004 | -0.322290 |
| N | 1.099530 | 0.963296 | 1.058141 |
| C | 0.610398 | 1.955850 | 0.209720 |
| C | 2.526021 | 0.733134 | 1.217691 |
| H | 2.665437 | 0.037887 | 2.061271 |
| H | 3.018442 | 1.676868 | 1.505980 |
| C | 0.667760 | 3.809080 | -1.325617 |
| H | 1.239913 | 4.510662 | -1.934607 |
| C | 5.201336 | 0.647194 | 0.151669 |
| C | 3.285272 | -1.795483 | -0.173583 |
| C | 1.343795 | 2.858116 | -0.565299 |
| H | 2.431336 | 2.815010 | -0.587553 |
| C | 6.216177 | -0.084790 | -0.737513 |
| H | 7.208981 | 0.383068 | -0.624897 |
| H | 5.940085 | -0.031544 | -1.802441 |
| H | 6.321644 | -1.143462 | -0.460264 |
| C | 3.811031 | -2.393683 | -1.490017 |
| H | 3.638944 | -3.483613 | -1.494542 |
| H | 4.887668 | -2.229605 | -1.631190 |
| H | 3.286829 | -1.963968 | -2.357344 |
| C | 1.781208 | -2.108872 | -0.094562 |
| H | 1.199104 | -1.540655 | -0.836964 |
| H | 1.367037 | -1.894045 | 0.901577 |
| H | 1.619341 | -3.182996 | -0.286831 |
| C | 5.262274 | 2.145836 | -0.202962 |
| H | 6.278980 | 2.531415 | -0.016572 |
| H | 4.573282 | 2.750449 | 0.408118 |
| H | 5.020169 | 2.319779 | -1.262478 |
| C | 3.989694 | -2.454593 | 1.015483 |
| H | 3.725398 | -3.525430 | 1.058155 |
| H | 3.689658 | -2.006212 | 1.975532 |
| H | 5.084365 | -2.392454 | 0.933108 |
| C | 5.607066 | 0.477543 | 1.623681 |
| H | 5.595916 | -0.571066 | 1.946544 |
| H | 4.961492 | 1.050898 | 2.305125 |
| H | 6.634548 | 0.855638 | 1.764411 |
| P | -3.760135 | 0.425132 | -0.345679 |
| N | -1.362244 | 1.062757 | 1.069791 |
| C | -0.802802 | 2.016840 | 0.219472 |
| C | -2.799871 | 0.916197 | 1.217042 |
| H | -3.234408 | 1.875301 | 1.542886 |
| H | -2.981365 | 0.190172 | 2.026339 |
| C | -0.727246 | 3.868233 | -1.316082 |
| H | -1.245917 | 4.616918 | -1.916788 |
| C | -2.988080 | -1.253626 | -0.831716 |
| C | -5.484460 | 0.147070 | 0.438814 |
| C | -1.470269 | 2.976930 | -0.545598 |
| H | -2.558743 | 3.018806 | -0.552723 |
| C | -3.951075 | -1.980585 | -1.782220 |
| H | -3.426404 | -2.825745 | -2.259277 |
| H | -4.312620 | -1.317319 | -2.584036 |
| H | -4.822618 | -2.394321 | -1.254384 |
| C | -6.500854 | 0.027737 | -0.710309 |
| H | -7.521856 | -0.031420 | -0.295585 |
| H | -6.341371 | -0.869799 | -1.322046 |
| H | -6.453736 | 0.903205 | -1.375972 |
| C | -5.826346 | 1.430837 | 1.219770 |
| H | -5.606110 | 2.339208 | 0.635160 |
| H | -5.287750 | 1.494389 | 2.176673 |
| H | -6.904264 | 1.439668 | 1.452339 |
| C | -1.724577 | -0.889296 | -1.637488 |
| H | -1.260716 | -1.811065 | -2.029040 |
| H | -0.974192 | -0.369215 | -1.026371 |
| H | -1.967508 | -0.238789 | -2.491222 |
| C | -5.630975 | -1.053019 | 1.380639 |
| H | -6.624883 | -1.028622 | 1.860218 |
| H | -4.879402 | -1.047654 | 2.185128 |
| H | -5.552429 | -2.009593 | 0.844655 |
| C | -2.602097 | -2.198465 | 0.310833 |
| H | -3.466727 | -2.516727 | 0.907143 |
| H | -1.864474 | -1.752796 | 0.993773 |
| H | -2.136761 | -3.107650 | -0.108250 |

Energy= -2022.53624806 hartree

**Table S7** DFT-optimized atomic coordinates for **$Si_{Me\text{-}pl}$**.

| | | | |
|---|---|---|---|
| Si | -0.000041 | -1.119297 | 0.000164 |
| P | 3.256475 | -1.767853 | -0.294955 |
| N | 1.229925 | 0.165353 | -0.097434 |

| | | | |
|---|---|---|---|
| C | 0.704289 | 1.454221 | -0.055728 |
| C | 2.669201 | 0.010700 | -0.225739 |
| H | 3.182638 | 0.531037 | 0.604618 |
| H | 3.013815 | 0.483348 | -1.164064 |
| C | 0.695192 | 3.862246 | -0.057738 |
| H | 1.237417 | 4.807970 | -0.104073 |
| C | 3.283682 | -2.171257 | 1.516462 |
| C | 1.403186 | 2.661708 | -0.114676 |
| H | 2.489658 | 2.670923 | -0.205950 |
| H | 5.636028 | -2.309302 | -0.431059 |
| H | 3.802253 | -3.131536 | 1.659463 |
| H | 2.254654 | -2.289637 | 1.887246 |
| H | 5.218521 | -0.999456 | -1.558615 |
| H | 3.794663 | -1.395485 | 2.109348 |
| H | 5.431929 | -0.641361 | 0.187010 |
| P | -3.256623 | -1.767860 | 0.295266 |
| N | -1.230036 | 0.165334 | 0.097651 |
| C | -0.704425 | 1.454209 | 0.055866 |
| C | -2.669322 | 0.010672 | 0.225794 |
| H | -3.182647 | 0.530865 | -0.604723 |
| H | -3.014077 | 0.483471 | 1.163991 |
| C | -0.695381 | 3.862234 | 0.057731 |
| H | -1.237626 | 4.807950 | 0.104014 |
| C | -5.056219 | -1.380689 | 0.538845 |
| C | -3.283142 | -2.171829 | -1.516036 |
| C | -1.403349 | 2.661685 | 0.114735 |
| H | -2.489822 | 2.670881 | 0.206000 |
| H | -5.636241 | -2.309226 | 0.430713 |
| H | -3.801887 | -3.132029 | -1.658930 |
| H | -2.253985 | -2.290593 | -1.886341 |
| H | -5.219136 | -0.998918 | 1.557877 |
| H | -3.793685 | -1.396139 | -2.109406 |
| H | -5.431876 | -0.641551 | -0.187972 |
| C | 5.055984 | -1.380795 | -0.539360 |

Energy= -1550.89847066 hartree

**Table S8** DFT-optimized atomic coordinates for **$Si_{Me\text{-}npl}$**.

| | | | |
|---|---|---|---|
| Si | -0.000039 | -1.139951 | 1.422985 |
| P | 3.480393 | -0.513683 | -0.715899 |
| N | 1.230224 | 0.016544 | 0.877098 |
| C | 0.706610 | 1.195545 | 0.348703 |
| C | 2.661117 | -0.203822 | 0.956622 |
| H | 2.837371 | -1.078072 | 1.606120 |
| H | 3.161903 | 0.658665 | 1.430966 |
| C | 0.698245 | 3.408601 | -0.593761 |
| H | 1.241986 | 4.276459 | -0.969759 |
| C | 2.637128 | -2.107676 | -1.143860 |
| C | 1.409276 | 2.306367 | -0.125726 |
| H | 2.499073 | 2.306145 | -0.146495 |
| H | 5.694830 | -1.548181 | -0.898417 |
| H | 3.130526 | -2.552044 | -2.021481 |
| H | 1.590784 | -1.902659 | -1.415608 |
| H | 5.652653 | -0.351518 | 0.413898 |
| H | 2.655908 | -2.834534 | -0.314464 |
| H | 4.949436 | -1.980713 | 0.672073 |
| P | -3.480838 | -0.513330 | -0.715684 |
| N | -1.230457 | 0.016462 | 0.877275 |
| C | -0.707006 | 1.195512 | 0.348835 |
| C | -2.661306 | -0.204128 | 0.956875 |
| H | -3.162160 | 0.658049 | 1.431714 |
| H | -2.837314 | -1.078736 | 1.605957 |
| C | -0.698919 | 3.408585 | -0.593592 |
| H | -1.242774 | 4.276435 | -0.969443 |
| C | -2.635640 | -2.105744 | -1.145661 |
| C | -5.088842 | -1.171840 | -0.061238 |
| C | -1.409813 | 2.306327 | -0.125406 |
| H | -2.499615 | 2.306092 | -0.145898 |
| H | -3.128971 | -2.549937 | -2.023406 |
| H | -5.694033 | -1.550447 | -0.898409 |
| H | -5.652836 | -0.355158 | 0.415187 |
| H | -1.589750 | -1.899002 | -1.417864 |
| H | -4.947427 | -1.983729 | 0.671309 |
| H | -2.652903 | -2.833422 | -0.316954 |
| C | 5.089507 | -1.169432 | -0.061407 |

Energy= -1550.90412242 hartree

**Table S9** DFT-optimized atomic coordinates for **$Ge_{tBu\text{-}pl}$**.

| | | | |
|---|---|---|---|
| Ge | -0.000143 | -0.524611 | -0.001028 |
| P | -3.345004 | -0.928332 | 0.063421 |
| N | -1.244741 | 0.888665 | 0.212918 |
| C | -0.696076 | 2.159710 | 0.136152 |
| C | -2.664285 | 0.763755 | 0.498982 |
| H | -3.230803 | 1.533185 | -0.052271 |
| H | -2.852654 | 0.947955 | 1.570468 |
| C | -0.679107 | 4.578739 | 0.152243 |
| H | -1.210883 | 5.523164 | 0.279030 |
| C | -4.783939 | -1.030379 | 1.312468 |
| C | -4.016856 | -0.624697 | -1.697335 |
| C | -1.368970 | 3.376691 | 0.300602 |
| H | -2.430317 | 3.391951 | 0.549109 |
| C | -5.749776 | -2.142676 | 0.882388 |
| H | -6.449015 | -2.365204 | 1.706052 |
| H | -5.216512 | -3.073755 | 0.635177 |
| H | -6.354271 | -1.849511 | 0.011469 |
| C | -4.404425 | -1.988556 | -2.292747 |
| H | -4.660296 | -1.867764 | -3.359170 |
| H | -5.275981 | -2.433382 | -1.793157 |
| H | -3.571531 | -2.704717 | -2.223239 |
| C | -2.835819 | -0.075511 | -2.518322 |
| H | -1.965046 | -0.749061 | -2.478945 |
| H | -2.510317 | 0.919807 | -2.180669 |
| H | -3.140401 | 0.013247 | -3.574960 |
| C | -4.109479 | -1.460383 | 2.629232 |
| H | -4.870285 | -1.563339 | 3.421453 |
| H | -3.369704 | -0.721676 | 2.977578 |
| H | -3.593974 | -2.426050 | 2.518437 |
| C | -5.195887 | 0.345125 | -1.821046 |
| H | -5.414191 | 0.526758 | -2.887723 |
| H | -4.983234 | 1.323540 | -1.362311 |
| H | -6.111838 | -0.058481 | -1.366082 |
| C | -5.575302 | 0.261588 | 1.562422 |
| H | -6.090027 | 0.621954 | 0.663159 |
| H | -4.938144 | 1.075486 | 1.939273 |
| H | -6.345181 | 0.074333 | 2.330818 |
| P | 3.344613 | -0.928646 | -0.062217 |
| N | 1.244855 | 0.888034 | -0.216248 |
| C | 0.696708 | 2.159389 | -0.140202 |
| C | 2.664461 | 0.762044 | -0.502082 |
| H | 3.230883 | 1.533013 | 0.047951 |
| H | 2.852998 | 0.944398 | -1.573985 |
| C | 0.680579 | 4.578361 | -0.157962 |
| H | 1.212418 | 5.522658 | -0.285464 |
| C | 4.784064 | -1.033981 | -1.310460 |
| C | 4.016254 | -0.620760 | 1.698151 |
| C | 1.369947 | 3.376273 | -0.305962 |
| H | 2.431276 | 3.390978 | -0.554117 |
| C | 5.749676 | -2.145275 | -0.877393 |
| H | 6.449102 | -2.370115 | -1.700343 |
| H | 5.216295 | -3.076041 | -0.627576 |
| H | 6.354127 | -1.849968 | -0.007134 |

| | | | |
|---|---|---|---|
| C | 4.403560 | -1.982992 | 2.296963 |
| H | 4.659076 | -1.859524 | 3.363175 |
| H | 5.274967 | -2.429728 | 1.798640 |
| H | 3.570477 | -2.699327 | 2.229165 |
| C | 2.835019 | -0.068960 | 2.517470 |
| H | 1.964107 | -0.742421 | 2.479146 |
| H | 2.510051 | 0.925448 | 2.177198 |
| H | 3.139116 | 0.021824 | 3.573904 |
| C | 4.110118 | -1.467123 | -2.626187 |
| H | 4.870959 | -1.572134 | -3.418219 |
| H | 3.370519 | -0.729540 | -2.976675 |
| H | 3.594558 | -2.432524 | -2.513321 |
| C | 5.195412 | 0.349341 | 1.819934 |
| H | 5.413563 | 0.533148 | 2.886071 |
| H | 4.982972 | 1.326376 | 1.358703 |
| H | 6.111256 | -0.055534 | 1.365813 |
| C | 5.575655 | 0.257353 | -1.563141 |
| H | 6.089931 | 0.620115 | -0.664434 |
| H | 4.938819 | 1.070018 | -1.942194 |
| H | 6.345995 | 0.068219 | -2.330830 |

Energy= -3810.09296914 hartree

**Table S10** DFT-optimized atomic coordinates for **$Ge_{tBu\text{-}npl}$**.

| | | | |
|---|---|---|---|
| Ge | -0.124069 | -0.228068 | 1.871278 |
| P | 3.489477 | -0.113338 | -0.539013 |
| N | 1.171562 | 0.696018 | 0.891249 |
| C | 0.655402 | 1.694909 | 0.074106 |
| C | 2.602406 | 0.486736 | 1.023471 |
| H | 2.771071 | -0.218073 | 1.854080 |
| H | 3.089145 | 1.432621 | 1.316144 |
| C | 0.711537 | 3.584078 | -1.428849 |
| H | 1.285867 | 4.296651 | -2.022742 |
| C | 5.262335 | 0.458769 | -0.095650 |
| C | 3.386662 | -2.015502 | -0.402256 |
| C | 1.383366 | 2.617210 | -0.687225 |
| H | 2.470565 | 2.576608 | -0.711410 |
| C | 6.271149 | -0.244181 | -1.014738 |
| H | 7.258594 | 0.238117 | -0.914965 |
| H | 5.972816 | -0.180562 | -2.072967 |
| H | 6.399253 | -1.304921 | -0.754816 |
| C | 3.889486 | -2.593440 | -1.736688 |
| H | 3.738199 | -3.686345 | -1.746149 |
| H | 4.958789 | -2.407454 | -1.903225 |
| H | 3.335380 | -2.166603 | -2.586612 |
| C | 1.891681 | -2.358966 | -0.285679 |
| H | 1.275764 | -1.787467 | -0.997795 |
| H | 1.507284 | -2.170555 | 0.727260 |
| H | 1.743143 | -3.432342 | -0.492032 |
| C | 5.288408 | 1.961897 | -0.434582 |
| H | 6.302980 | 2.362948 | -0.270939 |
| H | 4.605941 | 2.548009 | 0.201762 |
| H | 5.015110 | 2.143405 | -1.485103 |
| C | 4.133368 | -2.671677 | 0.762331 |
| H | 3.890771 | -3.747788 | 0.802258 |
| H | 3.849833 | -2.236847 | 1.733632 |
| H | 5.224289 | -2.587184 | 0.652907 |
| C | 5.702522 | 0.280815 | 1.365345 |
| H | 5.730894 | -0.772223 | 1.672673 |
| H | 5.053267 | 0.823979 | 2.068090 |
| H | 6.720731 | 0.688600 | 1.491991 |
| P | -3.719174 | 0.202853 | -0.573996 |
| N | -1.349719 | 0.799392 | 0.904019 |
| C | -0.761806 | 1.756430 | 0.084305 |
| C | -2.790685 | 0.673967 | 1.015315 |
| H | -3.222771 | 1.636968 | 1.334374 |
| H | -3.008539 | -0.052959 | 1.815034 |
| C | -0.683597 | 3.643855 | -1.418087 |
| H | -1.203489 | 4.404608 | -2.002499 |
| C | -2.965931 | -1.489596 | -1.041081 |
| C | -5.470059 | -0.045945 | 0.160237 |
| C | -1.422910 | 2.736788 | -0.665583 |
| H | -2.511263 | 2.780350 | -0.672003 |
| C | -3.913357 | -2.194915 | -2.022889 |
| H | -3.392276 | -3.050441 | -2.485224 |
| H | -4.234843 | -1.522466 | -2.834174 |
| H | -4.809982 | -2.590095 | -1.523871 |
| C | -6.454676 | -0.140718 | -1.018507 |
| H | -7.488603 | -0.181522 | -0.634720 |
| H | -6.294445 | -1.038454 | -1.629908 |
| H | -6.370639 | 0.736551 | -1.678161 |
| C | -5.809921 | 1.241112 | 0.936503 |
| H | -5.557608 | 2.147035 | 0.361122 |
| H | -5.295851 | 1.292129 | 1.907454 |
| H | -6.893365 | 1.269025 | 1.140102 |
| C | -1.670846 | -1.148920 | -1.806060 |
| H | -1.213849 | -2.078379 | -2.187634 |
| H | -0.930250 | -0.645253 | -1.169851 |
| H | -1.874340 | -0.490236 | -2.663838 |
| C | -5.667877 | -1.246328 | 1.092211 |
| H | -6.674050 | -1.203309 | 1.544096 |
| H | -4.939139 | -1.259324 | 1.917268 |
| H | -5.593870 | -2.202524 | 0.554508 |
| C | -2.635904 | -2.445157 | 0.109851 |
| H | -3.526084 | -2.751523 | 0.673774 |
| H | -1.916889 | -2.012573 | 0.820142 |
| H | -2.169302 | -3.359924 | -0.295511 |

Energy= -3810.09220612 hartree

**Table S11** DFT-optimized atomic coordinates for **$Ge_{Me\text{-}pl}$**.

| | | | |
|---|---|---|---|
| Ge | -0.000100 | -1.282428 | -0.000089 |
| P | -3.312345 | -1.769684 | 0.259492 |
| N | -1.260255 | 0.120098 | 0.113949 |
| C | -0.706078 | 1.390772 | 0.065779 |
| C | -2.698350 | -0.001001 | 0.263028 |
| H | -3.218454 | 0.560102 | -0.536794 |
| H | -3.022031 | 0.439428 | 1.225251 |
| C | -0.694118 | 3.807232 | 0.070441 |
| H | -1.237179 | 4.751975 | 0.127883 |
| C | -3.420681 | -2.068111 | -1.569372 |
| C | -1.396966 | 2.605879 | 0.138458 |
| H | -2.481473 | 2.617454 | 0.250413 |
| H | -5.689138 | -2.303529 | 0.454899 |
| H | -3.933370 | -3.025626 | -1.747274 |
| H | -2.409418 | -2.147950 | -1.995630 |
| H | -5.211238 | -1.084825 | 1.658281 |
| H | -3.966241 | -1.265018 | -2.090948 |
| H | -5.489895 | -0.596236 | -0.046150 |
| P | 3.312097 | -1.769823 | -0.258832 |
| N | 1.260133 | 0.120044 | -0.113886 |
| C | 0.706013 | 1.390745 | -0.065616 |
| C | 2.698193 | -0.001119 | -0.263236 |
| H | 3.218468 | 0.560388 | 0.536183 |
| H | 3.021684 | 0.438806 | -1.225756 |
| C | 0.694115 | 3.807206 | -0.070497 |
| H | 1.237198 | 4.751929 | -0.128076 |
| C | 5.094219 | -1.391165 | -0.608429 |
| C | 3.421261 | -2.067042 | 1.570168 |
| C | 1.396929 | 2.605828 | -0.138430 |
| H | 2.481422 | 2.617373 | -0.250515 |
| H | 5.688776 | -2.303881 | -0.454609 |

| | | | |
|---|---|---|---|
| H | 3.933936 | -3.024493 | 1.748455 |
| H | 2.410177 | -2.146497 | 1.996919 |
| H | 5.210437 | -1.086457 | -1.659102 |
| H | 3.967129 | -1.263662 | 2.090979 |
| H | 5.489770 | -0.596055 | 0.044701 |
| C | -5.094620 | -1.390666 | 0.607976 |

Energy= -3338.45587385 hartree

**Table S12** DFT-optimized atomic coordinates for **$Ge_{Me\text{-}npl}$**.

| | | | |
|---|---|---|---|
| Ge | 0.000073 | -1.239807 | -1.466351 |
| P | -3.473461 | -0.295268 | 0.691125 |
| N | -1.259700 | 0.062344 | -0.997188 |
| C | -0.708832 | 1.271387 | -0.590412 |
| C | -2.692874 | -0.141731 | -1.023233 |
| H | -2.900113 | -1.068638 | -1.585265 |
| H | -3.200032 | 0.680470 | -1.559458 |
| C | -0.698530 | 3.571278 | 0.137901 |
| H | -1.244170 | 4.470637 | 0.427541 |
| C | -2.600127 | -1.832147 | 1.249076 |
| C | -1.405801 | 2.428851 | -0.222271 |
| H | -2.495496 | 2.433708 | -0.201560 |
| H | -5.673144 | -1.324050 | 1.027547 |
| H | -3.077039 | -2.206156 | 2.167633 |
| H | -1.554528 | -1.587408 | 1.489281 |
| H | -5.670096 | -0.271091 | -0.403213 |
| H | -2.616951 | -2.629381 | 0.486573 |
| H | -4.955698 | -1.912502 | -0.504632 |
| P | 3.473688 | -0.295174 | 0.691061 |
| N | 1.259897 | 0.062324 | -0.997265 |
| C | 0.709075 | 1.271374 | -0.590453 |
| C | 2.693061 | -0.141804 | -1.023312 |
| H | 3.200231 | 0.680328 | -1.559632 |
| H | 2.900260 | -1.068774 | -1.585254 |
| C | 0.698868 | 3.571261 | 0.137873 |
| H | 1.244539 | 4.470608 | 0.427491 |
| C | 2.599741 | -1.831515 | 1.249519 |
| C | 5.088484 | -1.030594 | 0.142933 |
| C | 1.406092 | 2.428818 | -0.222335 |
| H | 2.495789 | 2.433640 | -0.201677 |
| H | 3.076631 | -2.205532 | 2.168083 |
| H | 5.672999 | -1.324706 | 1.027673 |
| H | 5.670234 | -0.272304 | -0.403489 |
| H | 1.554296 | -1.586240 | 1.489830 |
| H | 4.955157 | -1.913454 | -0.504201 |
| H | 2.616083 | -2.628929 | 0.487197 |
| C | -5.088600 | -1.029835 | 0.142860 |

Energy= -3338.46040961 hartree

**Table S13** DFT-optimized atomic coordinates for **$Sn_{tBu\text{-}pl}$**.

| | | | |
|---|---|---|---|
| Sn | -0.000018 | -0.805658 | -0.001150 |
| P | -3.417981 | -0.893264 | 0.059447 |
| N | -1.296684 | 0.849006 | 0.216657 |
| C | -0.700658 | 2.094723 | 0.139514 |
| C | -2.721001 | 0.789461 | 0.488304 |
| H | -3.264841 | 1.562478 | -0.083635 |
| H | -2.925561 | 0.995869 | 1.554064 |
| C | -0.677584 | 4.526991 | 0.161492 |
| H | -1.211025 | 5.469608 | 0.295942 |
| C | -4.835152 | -1.027047 | 1.326851 |
| C | -4.110944 | -0.598245 | -1.693186 |
| C | -1.360270 | 3.322732 | 0.312141 |
| H | -2.418977 | 3.341342 | 0.570485 |
| C | -5.798571 | -2.144355 | 0.905247 |
| H | -6.480200 | -2.380372 | 1.739902 |
| H | -5.262165 | -3.068889 | 0.639280 |
| H | -6.422056 | -1.848410 | 0.048642 |
| C | -4.507010 | -1.961598 | -2.283462 |
| H | -4.771008 | -1.841025 | -3.347896 |
| H | -5.375457 | -2.404145 | -1.776680 |
| H | -3.675395 | -2.680270 | -2.220630 |
| C | -2.942819 | -0.048241 | -2.532348 |
| H | -2.083961 | -0.738046 | -2.531686 |
| H | -2.588895 | 0.932809 | -2.183052 |
| H | -3.273449 | 0.065886 | -3.578412 |
| C | -4.133956 | -1.457488 | 2.629061 |
| H | -4.878861 | -1.564869 | 3.435673 |
| H | -3.390299 | -0.716733 | 2.964077 |
| H | -3.618119 | -2.421687 | 2.506526 |
| C | -5.292940 | 0.370833 | -1.796362 |
| H | -5.530404 | 0.552228 | -2.858727 |
| H | -5.072804 | 1.348151 | -1.339794 |
| H | -6.199668 | -0.035082 | -1.325289 |
| C | -5.631898 | 0.257871 | 1.595924 |
| H | -6.160253 | 0.620480 | 0.705372 |
| H | -4.994420 | 1.072870 | 1.968515 |
| H | -6.390492 | 0.060104 | 2.372992 |
| P | 3.418009 | -0.893460 | -0.060039 |
| N | 1.296908 | 0.848912 | -0.218152 |
| C | 0.701034 | 2.094690 | -0.140620 |
| C | 2.721286 | 0.789240 | -0.489421 |
| H | 3.265024 | 1.562285 | 0.082580 |
| H | 2.926185 | 0.995461 | -1.555150 |
| C | 0.678229 | 4.526966 | -0.161787 |
| H | 1.211768 | 5.469565 | -0.295942 |
| C | 4.836121 | -1.027173 | -1.326373 |
| C | 4.109739 | -0.598279 | 1.693032 |
| C | 1.360782 | 3.322679 | -0.312834 |
| H | 2.419487 | 3.341260 | -0.571198 |
| C | 5.799429 | -2.144268 | -0.903958 |
| H | 6.481866 | -2.380085 | -1.738008 |
| H | 5.262998 | -3.068938 | -0.638515 |
| H | 6.422067 | -1.848217 | -0.046773 |
| C | 4.505033 | -1.961645 | 2.283794 |
| H | 4.768447 | -1.840980 | 3.348360 |
| H | 5.373629 | -2.404567 | 1.777585 |
| H | 3.673226 | -2.680070 | 2.220592 |
| C | 2.941147 | -0.047819 | 2.531241 |
| H | 2.081965 | -0.737226 | 2.529809 |
| H | 2.587950 | 0.933386 | 2.181651 |
| H | 3.270933 | 0.066147 | 3.577579 |
| C | 4.135982 | -1.457839 | -2.629069 |
| H | 4.881510 | -1.565276 | -3.435094 |
| H | 3.392525 | -0.717182 | -2.964752 |
| H | 3.620115 | -2.422059 | -2.506796 |
| C | 5.291859 | 0.370578 | 1.796904 |
| H | 5.528697 | 0.551974 | 2.859401 |
| H | 5.072163 | 1.347930 | 1.340174 |
| H | 6.198811 | -0.035486 | 1.326395 |
| C | 5.632844 | 0.257878 | -1.594929 |
| H | 6.160524 | 0.620595 | -0.704029 |
| H | 4.995475 | 1.072752 | -1.967969 |
| H | 6.391997 | 0.060222 | -2.371477 |

Energy= -1947.41891481 hartree

**Table S14** DFT-optimized atomic coordinates for **$Sn_{tBu\text{-}npl}$**.

| | | | |
|---|---|---|---|
| Sn | 0.189231 | -0.384240 | -2.353554 |
| P | -3.458910 | 0.115718 | 0.304683 |
| N | -1.170351 | 0.751771 | -1.269015 |

| | | | |
|---|---|---|---|
| C | -0.601138 | 1.791641 | -0.546526 |
| C | -2.612606 | 0.592733 | -1.325014 |
| H | -2.851266 | -0.154213 | -2.100310 |
| H | -3.084931 | 1.534985 | -1.654285 |
| C | -0.655801 | 3.803595 | 0.812997 |
| H | -1.234916 | 4.557830 | 1.348303 |
| C | -5.229159 | 0.731122 | -0.094448 |
| C | -3.439254 | -1.795019 | 0.273946 |
| C | -1.318075 | 2.778822 | 0.148416 |
| H | -2.404613 | 2.742478 | 0.179461 |
| C | -6.218137 | 0.127928 | 0.913072 |
| H | -7.191533 | 0.640074 | 0.826760 |
| H | -5.866850 | 0.247190 | 1.950130 |
| H | -6.395872 | -0.941514 | 0.729156 |
| C | -3.892577 | -2.274587 | 1.663725 |
| H | -3.784111 | -3.370768 | 1.731703 |
| H | -4.943701 | -2.033572 | 1.871617 |
| H | -3.278208 | -1.822695 | 2.457296 |
| C | -1.967859 | -2.207912 | 0.101976 |
| H | -1.290273 | -1.621381 | 0.742082 |
| H | -1.639356 | -2.094503 | -0.941913 |
| H | -1.848175 | -3.273429 | 0.361222 |
| C | -5.183733 | 2.252381 | 0.147320 |
| H | -6.193554 | 2.679576 | 0.024946 |
| H | -4.527482 | 2.769982 | -0.569928 |
| H | -4.832086 | 2.489322 | 1.162976 |
| C | -4.268952 | -2.488317 | -0.810278 |
| H | -4.070452 | -3.574177 | -0.793764 |
| H | -4.019027 | -2.125849 | -1.819945 |
| H | -5.348550 | -2.352756 | -0.654054 |
| C | -5.745284 | 0.481326 | -1.519458 |
| H | -5.845671 | -0.586494 | -1.750647 |
| H | -5.099898 | 0.936894 | -2.284834 |
| H | -6.744588 | 0.937124 | -1.631362 |
| P | 3.780516 | 0.436094 | 0.340258 |
| N | 1.465824 | 0.859613 | -1.288710 |
| C | 0.824685 | 1.854718 | -0.561649 |
| C | 2.913868 | 0.778377 | -1.318231 |
| H | 3.340405 | 1.730949 | -1.676670 |
| H | 3.201956 | 0.010279 | -2.055687 |
| C | 0.738034 | 3.866379 | 0.794990 |
| H | 1.260513 | 4.671651 | 1.314025 |
| C | 3.060287 | -1.249609 | 0.879855 |
| C | 5.573511 | 0.199202 | -0.290169 |
| C | 1.471194 | 2.901811 | 0.114397 |
| H | 2.558508 | 2.956553 | 0.117878 |
| C | 3.969035 | -1.849890 | 1.962766 |
| H | 3.453549 | -2.696403 | 2.447788 |
| H | 4.210298 | -1.113183 | 2.745215 |
| H | 4.911374 | -2.236515 | 1.547611 |
| C | 6.498346 | 0.228206 | 0.939300 |
| H | 7.551915 | 0.183876 | 0.613153 |
| H | 6.326538 | -0.618360 | 1.617076 |
| H | 6.358756 | 1.155232 | 1.515861 |
| C | 5.909987 | 1.437840 | -1.142805 |
| H | 5.604012 | 2.373388 | -0.646547 |
| H | 5.438637 | 1.401681 | -2.135884 |
| H | 7.000283 | 1.487630 | -1.300909 |
| C | 1.707847 | -0.910375 | 1.539142 |
| H | 1.265630 | -1.827804 | 1.965212 |
| H | 0.990270 | -0.488284 | 0.822060 |
| H | 1.830837 | -0.179444 | 2.352328 |
| C | 5.860084 | -1.057172 | -1.119328 |
| H | 6.883638 | -1.006286 | -1.529812 |
| H | 5.170878 | -1.160559 | -1.971775 |
| H | 5.798119 | -1.973390 | -0.514758 |
| C | 2.838032 | -2.294010 | -0.218616 |
| H | 3.775552 | -2.633154 | -0.676825 |
| H | 2.186932 | -1.919808 | -1.021964 |
| H | 2.337903 | -3.180309 | 0.208946 |

Energy= -1947.41005864 hartree

**Table S15** DFT-optimized atomic coordinates for **$Sn_{Me\text{-}pl}$**.

| | | | |
|---|---|---|---|
| Sn | -0.000109 | -1.636128 | -0.002435 |
| P | -3.423122 | -1.775334 | 0.154026 |
| N | -1.309293 | 0.003540 | 0.161939 |
| C | -0.706635 | 1.248405 | 0.096512 |
| C | -2.744248 | -0.047114 | 0.367419 |
| H | -3.270528 | 0.623848 | -0.338232 |
| H | -3.013596 | 0.290080 | 1.387368 |
| C | -0.687237 | 3.679192 | 0.111499 |
| H | -1.228731 | 4.622014 | 0.205800 |
| C | -3.729545 | -1.761724 | -1.675592 |
| C | -1.378558 | 2.475994 | 0.215239 |
| H | -2.453626 | 2.493340 | 0.393870 |
| H | -5.774758 | -2.334070 | 0.526365 |
| H | -4.183694 | -2.715107 | -1.984389 |
| H | -2.767439 | -1.658825 | -2.200150 |
| H | -5.128615 | -1.356613 | 1.866305 |
| H | -4.388393 | -0.932027 | -1.978696 |
| H | -5.587896 | -0.564873 | 0.323086 |
| P | 3.422800 | -1.776278 | -0.152577 |
| N | 1.309862 | 0.003121 | -0.164986 |
| C | 0.707696 | 1.248186 | -0.099001 |
| C | 2.744912 | -0.048149 | -0.369679 |
| H | 3.270905 | 0.623685 | 0.335280 |
| H | 3.015065 | 0.287315 | -1.389970 |
| C | 0.689190 | 3.678978 | -0.113010 |
| H | 1.231025 | 4.621640 | -0.206959 |
| C | 5.143246 | -1.470878 | -0.768831 |
| C | 3.726504 | -1.759427 | 1.677502 |
| C | 1.380059 | 2.475573 | -0.217307 |
| H | 2.455107 | 2.492581 | -0.396106 |
| H | 5.774496 | -2.337149 | -0.521139 |
| H | 4.178589 | -2.712903 | 1.988950 |
| H | 2.763731 | -1.653895 | 2.200259 |
| H | 5.130684 | -1.361492 | -1.863424 |
| H | 4.386117 | -0.930204 | 1.980066 |
| H | 5.588627 | -0.567492 | -0.320925 |
| C | -5.142608 | -1.467827 | 0.771929 |

Energy= -1475.77874298 hartree

**Table S16** DFT-optimized atomic coordinates for **$Sn_{Me\text{-}npl}$**.

| | | | |
|---|---|---|---|
| Sn | 0.000324 | -1.721863 | -1.335157 |
| P | -3.528209 | -0.137540 | 0.723011 |
| N | -1.316396 | -0.144002 | -1.020402 |
| C | -0.712853 | 1.086001 | -0.803591 |
| C | -2.757620 | -0.272031 | -1.000792 |
| H | -3.025547 | -1.259822 | -1.415443 |
| H | -3.239522 | 0.484437 | -1.647219 |
| C | -0.697495 | 3.480988 | -0.417023 |
| H | -1.245978 | 4.411203 | -0.261049 |
| C | -2.651350 | -1.560340 | 1.525248 |
| C | -1.397717 | 2.296353 | -0.606587 |
| H | -2.487121 | 2.307221 | -0.584745 |
| H | -5.717180 | -1.109141 | 1.247013 |
| H | -3.128533 | -1.779343 | 2.492466 |
| H | -1.606738 | -1.276760 | 1.722305 |
| H | -5.738921 | -0.299680 | -0.334169 |

| | | | |
|---|---|---|---|
| H | -2.668070 | -2.474305 | 0.905543 |
| H | -5.013489 | -1.932268 | -0.180213 |
| P | 3.529111 | -0.137304 | 0.722732 |
| N | 1.317378 | -0.144222 | -1.020794 |
| C | 0.714114 | 1.085888 | -0.803862 |
| C | 2.758560 | -0.272600 | -1.001092 |
| H | 3.240687 | 0.483352 | -1.647953 |
| H | 3.026203 | -1.260717 | -1.415140 |
| C | 0.699332 | 3.480880 | -0.417342 |
| H | 1.248038 | 4.411010 | -0.261648 |
| C | 2.649258 | -1.557269 | 1.526675 |
| C | 5.144800 | -0.960924 | 0.320413 |
| C | 1.399272 | 2.296125 | -0.607188 |
| H | 2.488690 | 2.306809 | -0.585897 |
| H | 3.125615 | -1.775719 | 2.494422 |
| H | 5.716036 | -1.112490 | 1.248578 |
| H | 5.739822 | -0.304888 | -0.333525 |
| H | 1.605113 | -1.271339 | 1.722803 |
| H | 5.011241 | -1.935932 | -0.177936 |
| H | 2.664491 | -2.472190 | 0.908347 |
| C | -5.145357 | -0.957580 | 0.319211 |

Energy= -1475.77919585 hartree

**Table S17** DFT-optimized atomic coordinates for compound **6**.

| | | | |
|---|---|---|---|
| C | -5.304646 | -0.203290 | -0.725951 |
| H | -5.877619 | 0.375337 | 0.010536 |
| H | -4.953217 | -1.131225 | -0.247248 |
| H | -6.003476 | -0.491197 | -1.528123 |
| C | -3.614229 | -0.218714 | -2.528493 |
| H | -4.428268 | -0.335572 | -3.263008 |
| H | -3.284091 | -1.215862 | -2.213412 |
| H | -2.764745 | 0.265023 | -3.025442 |
| C | -4.659669 | 1.929148 | -1.895496 |
| H | -5.467547 | 1.716004 | -2.614897 |
| H | -3.875818 | 2.469634 | -2.444334 |
| H | -5.068664 | 2.598043 | -1.131639 |
| C | -4.142958 | 0.591179 | -1.339073 |
| C | -4.210880 | 0.404228 | 2.380316 |
| H | -3.495466 | -0.359435 | 2.695322 |
| H | -5.039949 | -0.082137 | 1.852292 |
| H | -4.623948 | 0.858191 | 3.296113 |
| C | -4.508692 | 2.638867 | 1.328251 |
| H | -4.774838 | 3.070372 | 2.306796 |
| H | -5.442298 | 2.296191 | 0.862756 |
| H | -4.090227 | 3.454901 | 0.722653 |
| C | -2.362022 | 2.040836 | 2.428774 |
| H | -1.803972 | 2.848989 | 1.936824 |
| H | -1.646337 | 1.254749 | 2.704037 |
| H | -2.783420 | 2.436978 | 3.367264 |
| C | -3.509049 | 1.496549 | 1.564794 |
| C | -1.807431 | 2.282307 | -0.728335 |
| H | -1.776044 | 2.146026 | -1.826860 |
| H | -2.445180 | 3.163308 | -0.527939 |
| C | 0.387953 | 3.347235 | -0.741735 |
| C | -0.007008 | 4.492515 | -1.431117 |
| H | -1.070867 | 4.695166 | -1.568419 |
| C | 0.939034 | 5.393594 | -1.937183 |
| H | 0.603980 | 6.286208 | -2.468389 |
| C | 2.291324 | 5.152475 | -1.747717 |
| H | 3.036257 | 5.858938 | -2.118750 |
| C | 2.713571 | 3.997658 | -1.076465 |
| H | 3.780768 | 3.820355 | -0.934332 |
| C | 1.787178 | 3.071641 | -0.594412 |
| C | 3.453284 | 1.399900 | 0.237298 |
| H | 3.831473 | 1.688047 | 1.236037 |
| H | 4.162696 | 1.795524 | -0.508689 |
| C | 3.098270 | 0.240754 | -2.591660 |
| H | 3.227240 | -0.048483 | -3.648237 |
| H | 3.517976 | 1.250527 | -2.475125 |
| H | 2.021212 | 0.291302 | -2.388284 |
| C | 3.255464 | -2.187915 | -2.061565 |
| H | 2.158473 | -2.190925 | -1.966378 |
| H | 3.670412 | -2.983451 | -1.423716 |
| H | 3.499900 | -2.436668 | -3.108272 |
| C | 5.313873 | -0.736528 | -2.029931 |
| H | 5.457708 | -0.868269 | -3.115838 |
| H | 5.890120 | -1.526025 | -1.527246 |
| H | 5.747599 | 0.238255 | -1.758925 |
| C | 3.815877 | -0.798438 | -1.712586 |
| C | 4.930932 | -2.594861 | 1.044148 |
| H | 5.412422 | -2.797935 | 0.077022 |
| H | 3.983915 | -3.157724 | 1.080308 |
| H | 5.588487 | -2.998946 | 1.832140 |
| C | 4.111023 | -0.921006 | 2.694958 |
| H | 3.172733 | -1.482916 | 2.815554 |
| H | 3.887937 | 0.130071 | 2.929068 |
| H | 4.831867 | -1.290513 | 3.443852 |
| C | 6.035797 | -0.338099 | 1.218918 |
| H | 6.709995 | -0.714622 | 2.007513 |
| H | 5.899349 | 0.739245 | 1.394671 |
| H | 6.549582 | -0.465843 | 0.258654 |
| C | 4.702419 | -1.096372 | 1.285110 |
| C | -1.458030 | -1.732897 | 3.563414 |
| H | -1.086363 | -2.545073 | 4.207258 |
| H | -2.485250 | -1.512317 | 3.876336 |
| H | -0.825821 | -0.850008 | 3.736279 |
| C | -1.382352 | -2.178676 | 2.129411 |
| C | -2.522592 | -2.448181 | 1.325831 |
| H | -3.512217 | -2.236383 | 1.730082 |
| C | -2.427504 | -3.047618 | 0.033022 |
| H | -3.335808 | -3.267597 | -0.524843 |
| C | -1.158780 | -3.309596 | -0.521025 |
| C | -0.000324 | -2.950183 | 0.234267 |
| H | 0.987139 | -3.049700 | -0.216561 |
| C | -0.109520 | -2.403082 | 1.530338 |
| H | 0.795063 | -2.131273 | 2.078079 |
| C | -0.946710 | -3.942332 | -1.881548 |
| H | -0.162461 | -3.345079 | -2.373631 |
| C | -0.421434 | -5.371624 | -1.680477 |
| H | 0.504531 | -5.388296 | -1.086342 |
| H | -0.206231 | -5.836298 | -2.654030 |
| H | -1.167758 | -5.995566 | -1.162693 |
| C | -2.174745 | -3.929487 | -2.784704 |
| H | -2.997680 | -4.534523 | -2.370126 |
| H | -1.917848 | -4.358576 | -3.763923 |
| H | -2.533750 | -2.906004 | -2.954582 |
| Cl | 1.018223 | 0.953094 | 3.058455 |
| Cl | -0.408938 | -0.556892 | -2.077979 |
| N | -0.486728 | 2.417355 | -0.180621 |
| N | 2.107652 | 1.859933 | 0.001294 |
| P | -2.733227 | 0.796291 | -0.049907 |
| P | 3.354784 | -0.459965 | 0.107213 |
| Ru | -1.225545 | -1.128674 | 0.149661 |
| Sn | 0.485402 | 0.766149 | 0.633781 |

Energy= -3352.04208234 hartree

**Table S18** Crystal, measurement and refinement data for the compounds studied by X-ray diffraction.

| | **1**·$C_7H_8$ | **6**·$(C_7H_8)_{0.5}$ |
|---|---|---|
| formula | $C_{24}H_{44}N_2P_2Sn·C_7H_8$ | $2(C_{34}H_{58}Cl_2N_2P_2RuSn)·C_7H_8$ |
| fw | 633.37 | 1786.97 |
| cryst syst | orthorhombic | monoclinic |
| space group | *P*bca | *C*2/c |
| *a*, Å | 23.5126(3) | 27.890(1) |
| *b*, Å | 11.8347(1) | 19.6719(7) |
| *c*, Å | 23.8529(3) | 16.2784(5) |
| $\alpha$, deg | 90 | 90 |
| $\beta$, deg | 90 | 98.159(4) |
| $\gamma$, deg | 90 | 90 |
| *V*, Å$^3$ | 6637.4(1) | 8840.7(5) |
| *Z* | 8 | 4 |
| *F*(000) | 2656 | 3672 |
| $D_{calcd}$, g cm$^{-3}$ | 1.268 | 1.343 |
| $\mu$, mm$^{-1}$ (Cu K$\alpha$) | 7.175 | 9.239 |
| cryst size, mm | 0.39 x 0.29 x 0.20 | 0.17 x 0.08 x 0.03 |
| *T*, K | 150(2) | 150(2) |
| $\theta$ range, deg | 3.71 to 69.82 | 3.73 to 66.69 |
| min./max. *h*, *k*, *l* | –28/25, –13/14, –17/28 | –30/33, –23/16, –18/19 |
| no. collected reflns | 20205 | 22033 |
| no. unique reflns | 6173 | 8179 |
| no. reflns with $I > 2\sigma(I)$ | 5683 | 6150 |
| no. params/restraints | 338/0 | 339/0 |
| GOF (on $F^2$) | 1.023 | 1.061 |
| $R_1$ (on *F*, $I > 2\sigma(I)$) | 0.032 | 0.050 |
| $wR_2$ (on $F^2$, all data) | 0.084 | 0.174 |
| min./max. $\Delta\rho$, e Å$^{-3}$ | –1.589/0.547 | –1.800/1.323 |
| CCDC dep. no. | 1588313 | 1588314 |