Electronic Supplementary Material (ESI) for Dalton Transactions.

Symmetrical and unsymmetrical diphosphanes with diversified alkyl, aryl and amino substituents

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Supplementary Information

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Preparation of $(Et_2N)(^iPr_2N)PCl$

To a solution of $(i Pr_2N)PCl_2$ (4.23 g, 20.94 mmol) in Et_2O cooled to 0°C Et_2NH (2 eq, 4.33 cm^3, 3.06 g, 41.89 mmol) was added dropwise and stirred for 1 hour at this temperature. The reaction mixture was allowed to warm to room temperature and subsequently stirred overnight. After filtration and evaporation of the solvent residue was extracted with 15 cm^3 of petroleum ether and filtrated again. Removal of solvent under vacuum afforded yellowish crude oil. By vaccum distillation 4.71 g (19.69 mmol) of purified product was obtained (product was collected at 95-100°C under 2 mmHg). Yield 94% . $^{31}P\{^1H\}$ NMR (C_6D_6): δ 148.3. ^1H NMR (C_6D_6): δ 3.52 (b m, 2H, $CH$$CH_3$), 3.06 (b, 2H, $CH_2$$CH_3$), 2.93 (b, 2H, $CH_2$$CH_3$), 1.22 (b, 6H, CH$CH_3$), 1.03 (b, 6H, CH$CH_3$), 0.96 (b, 6H, $CH_2$$CH_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 46.9 (d, $^2J_{PC}$ = 12.5 Hz, $CH$$CH_3$), 41.1 (d, $^2J_{PC}$ = 17.6 Hz, $CH_2$$CH_3$), 41.1 (d, $^2J_{PC}$ = 17.6 Hz, $CH_2$$CH_3$), 23.8 (d, $^3J_{PC}$ = 5.1 Hz, CHCH_3), 22.6 (d, $^3J_{PC}$ = 12.5 Hz, CHCH_3), 13.8 (d, $^3J_{PC}$ = 5.1 Hz, $CH_2$$CH_3$).

Preparation of $tBu_2PPtBuPh$ 2

To a solution of $t Bu_2PLi$ (0.453 g, 2.98 mmol) in 40 cm^3 of THF cooled to -50°C, *t*BuPhPCl (0.598 g, 2.98 mmol) was added dropwise. The reaction mixture was successively stirred at -50°C for 30 minutes and then allowed to warm to room temperature for further 30 minutes. The solvent was evaporated and the residue was dried under vacuum (0.01 mmHg) for 30 minutes at 50°C to remove all volatiles. The crude product was dissolved in 15 cm^3 of petroleum ether and filtered. Removal of the solvent under vacuum afforded 0.81 g (2.60 mmol) of **2** as a colourless oil with 87% yield.

$^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 30.8 (d, $^{1}J_{PP}$ = 370.3 Hz, P*t*Bu$_2$) , 1.4 (d, $^{1}J_{PP}$ = 370.3 Hz, P*t*BuPh). ^{1}H NMR (C_6D_6): δ 7.81 (m, 2H, *o*-C*H*), 7.09 – 6.98 (m, 3H, *m,p*-C*H*), 1.48 (d, $^{3}J_{PH}$ = 12.1 Hz, 9H, C(C*H*$_3$)$_3$, P*t*Bu$_2$), 1.44 (d, $^{3}J_{PH}$ = 13.7 Hz, 9H, C(C*H*$_3$)$_3$, P*t*BuPh), 1.04 (d, $^{3}J_{PH}$ = 11.8 Hz, 9H, C(C*H*$_3$)$_3$, P*t*Bu$_2$) . $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 136.1 (dd, $^{1}J_{PC}$ = 38.1 Hz, $^{2}J_{PC}$ = 4.4 Hz, *ipso*-CH), 135.5 (d, $^{2}J_{PC}$ = 21.3 Hz, *ortho*-CH), 127.8 (s, *para*-CH), 127.8 (d, $^{3}J_{PC}$ = 7.4 Hz, *meta*-CH), 35.7 (d, $^{1}J_{PC}$ = 35.2 Hz, *C*(CH$_3$)$_3$, P*t*Bu$_2$), 33.4 (dd, $^{1}J_{PC}$ = 21.3, $^{2}J_{PC}$ = 18.3 Hz, *C*(CH$_3$)$_3$, P*t*BuPh), 31.9 (dd, $^{2}J_{PC}$ = 11.7 Hz, $^{3}J_{PC}$ = 11.0 Hz, C(*CH*$_3$)$_3$, P*t*Bu$_2$), 31.6 (d, $^{2}J_{PC}$ = 14.7 Hz, C(*CH*$_3$)$_3$, P*t*Bu$_2$), 30.5 (dd, $^{2}J_{PC}$ = 14.7 Hz, $^{3}J_{PC}$ = 5.9 Hz, C(*CH*$_3$)$_3$, P*t*BuPh).

Preparation of tBu$_2$PPPh$_2$ 3

Diphosphane **3** was prepared via an analogous procedure as described for **2**, using *t*Bu$_2$PLi (0.770 g, 5.06 mmol) and Ph$_2$PCl (1.117 g, 5.06 mmol) in 85% yield (1.42 g, 4.30 mmol) as a white solid. Crystals of **3** suitable for X-ray analysis were obtained from concentrated toluene solution at 4°C. Elemental analysis calcd for $C_{20}H_{28}P_2$: C, 72.71; H, 8.54. Found: C, 72.23; H, 8.34. $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 33.0 (d, $^{1}J_{PP}$ = 254.3 Hz, P*t*Bu$_2$) , -25.9 (d, $^{1}J_{PP}$ = 254.3 Hz, PPh$_2$). ^{1}H NMR (C_6D_6): δ 7.96 (m, 4H, *o*-C*H*), 7.04 (m, 4H, *m*-C*H*), 6.91-7.0 (m, 2H, *p*-C*H*), 1.20 (d, $^{3}J_{PH}$ = 11.2 Hz, 18H, C(C*H*$_3$)$_3$). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 138.5 (dd, $^{1}J_{PC}$ = 19.8 Hz, $^{2}J_{PC}$ = 8.1 Hz, *ipso*-CH), 135.5 (dd, $^{2}J_{PC}$ = 20.5 Hz, $^{3}J_{PC}$ = 7.3 Hz, *ortho*-CH), 128.2 (s, *para*-CH), 128.1 (d, $^{3}J_{PC}$ = 7.3 Hz, *meta*-CH), 34.3 (dd, $^{1}J_{PC}$ = 30.1 Hz, $^{2}J_{PC}$ = 8.1 Hz *C*(CH$_3$)$_3$), 31.6 (dd, $^{2}J_{PC}$ = 12.5 Hz, $^{3}J_{PC}$ = 5.1 Hz, C(*CH*$_3$)$_3$).

Preparation of tBuPhPPPh$_2$ 6

Diphosphane **6** was prepared via an analogous procedure as described for **2**, using Ph$_2$PLi (1.225 g, 6.38 mmol) and *t*BuPhPCl (1.28 g, 6.38 mmol, 0.92 cm^3) in 80% yield (1.78 g, 5.08 mmol) as a white solid. In the case of **6** toluene was used as an extracting

agent instead of petroleum ether as described for **2**. Crystals of **6** suitable for X-ray analysis were obtained from concentrated toluene solution at -20°C. Elemental analysis calcd for $C_{22}H_{24}P_2$: C, 75.42; H, 6.90. Found: C, 74.96; H, 6.95. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 9.7 (d, $^1J_{PP}$ = 158.5 Hz, P*t*BuPh), -30.8 (d, $^1J_{PP}$ = 158.5 Hz, PPh_2). ^1H NMR (C_6D_6): δ 8.09 (m, 2H, *o*-C*H*, PPh_2), 7.83 (m, 2H, *o*-C*H*, P*t*BuPh), 7.57 (m, 2H, *o*-C*H*, PPh_2), 7.13 – 7.01 (m, 3H, *m,p*-C*H*, PPh_2), 7.00 – 6.90 (m, 3H, *m,p*-C*H*, P*t*BuPh), 6.87 – 6.73 (m, 2H, m,*p*-C*H*, PPh_2), 1.08 (d, $^3J_{PH}$ = 11.9 Hz, 9H, C(C*H*$_3$)$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 137.6 (dd, $^1J_{PC}$ = 19.1 Hz, $^2J_{PC}$ = 13.2 Hz, *ipso*-CH, PPh_2), 137.3 (dd, $^1J_{PC}$ = 20.5 Hz, $^2J_{PC}$ = 8.1 Hz, *ipso*-CH, PPh_2), 136.5 (dd, $^2J_{PC}$ = 20.7 Hz, $^3J_{PC}$ = 9.4 Hz, *ortho*-CH, P*t*BuPh), 135.9 (dd, $^2J_{PC}$ = 21.2 Hz, $^3J_{PC}$ = 8.9 Hz, *ortho*-CH, PPh_2), 135.1 (dd, $^1J_{PC}$ = 25.7 Hz, $^2J_{PC}$ = 7.3 Hz, *ipso*-CH, P*t*BuPh), 134.2 (dd, $^2J_{PC}$ = 19.2 Hz, $^3J_{PC}$ = 5.9 Hz, *ortho*-CH, PPh_2), 129.2 (s, *para*-CH, PPh_2), 129.1 (s, *para*-CH, P*t*BuPh), 128.4 (d, $^3J_{PC}$ = 7.9 Hz, *meta*-CH, PPh_2), 128.0 (s, *para*-CH, PPh_2), 127.9 (d, $^3J_{PC}$ = 6.7 Hz, *meta*-CH, P*t*BuPh), 127.8 (d, $^3J_{PC}$ = 7.9 Hz, *meta*-CH, PPh_2), 31.5 (dd, $^1J_{PC}$ = 21.3 Hz, $^2J_{PC}$ = 11.0 Hz *C*$(CH_3)_3$), 29.3 (dd, $^2J_{PC}$ = 13.3 Hz, $^3J_{PC}$ = 4.9 Hz, C(*CH*$_3$)$_3$).

Preparation of $(iPr_2N)_2PPPh_2$ 8

Diphosphane **8** was prepared via an analogous procedure as described for **2**, using Ph_2PLi (0.935 g, 4.87 mmol) and $(iPr_2N)_2PCl$ (1.30 g, 4.87 mmol) in 91% yield (1.85 g, 4.43 mmol) as a yellowish solid. In the case of **8** toluene was used as an extracting agent instead of petroleum ether as described for **2.** Crystals of **6** suitable for X-ray analysis where obtained from concentrated toluene solution at -20°C. Elemental analysis calcd for $C_{24}H_{38}N_2P_2$: C, 69.21; H, 9.20; N, 6.73. Found: C, 69.06; H, 9.19; N, 6.84. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 71.8 (d, $^1J_{PP}$ = 119.3 Hz, P(iPr_2N_2)$_2$) , -38.0 (d, $^1J_{PP}$ = 119.3 Hz, PPh_2). ^1H NMR (C_6D_6): δ 8.06 (m, 4H, *o*-C*H*), 7.08 (m, 4H, *m*-C*H*), 7.01 (m, 2H, *p*-C*H*), 3.65 (bs, 4H, C*H* CH-

$_3$), 1.20 (d, $^3J_{HH}$ = 6.84 Hz, 12H, CHC*H$_3$*), 0.84 (d, $^3J_{HH}$ = 6.72 Hz, 12H, CHC*H$_3$*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 138.1 (dd, $^1J_{PC}$ = 18.3 Hz, $^2J_{PC}$ = 16.9 Hz, *ipso*-CH), 136.4 (dd, $^2J_{PC}$ = 20.5 Hz, $^3J_{PC}$ = 8.1 Hz, *ortho*-CH), 128.7 (bs, *para*-CH), 127.9 (d, $^3J_{PC}$ = 7.9 Hz, *meta*-CH), 48.6 (bs, *CH*(CH_3)$_2$), 24.3 (bd, $^3J_{PC}$ = 4.9 Hz CH(*CH$_3$*)$_2$), 24.1 (bd, $^3J_{PC}$ = 4.9 Hz CH(*CH$_3$*)$_2$).

Preparation of (iPr$_2$N)$_2$PPtBu$_2$ 9

Diphosphane **9** was prepared via an analogous procedure as described for **2**, using *t*Bu$_2$PLi (0.87 g, 5.72 mmol) and (*i*Pr$_2$N)$_2$PCl (1.525 g, 5.72 mmol) in 80% yield (1.72 g, 4.57 mmol) as a yellowish solid. Crystals of **9** suitable for X-ray analysis were obtained from concentrated petroleum ether solution at -20°C. Elemental analysis calcd for $C_{20}H_{46}N_2P_2$: C,63.80; H, 12.31; N, 7.44. Found: C,63.64; H, 12.33; N, 7.60. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 88.2 (d, $^1J_{PP}$ = 358.2 Hz, P(*i*Pr$_2$N$_2$)$_2$) , 62.6 (d, $^1J_{PP}$ = 358.2 Hz, P*t*Bu$_2$). ^1H NMR (C_6D_6): δ 3.60 (d sept, $^3J_{HH}$ = 6.72 Hz CH_3, $^3J_{JH}$ = 11.25 Hz, 2H, *CH*CH_3), 1.48 (d, $^3J_{PH}$ = 10.62 Hz, 18H, *CH$_3$*C), 1.29 (d, $^3J_{HH}$ = 6.72 Hz, 12H, *CH$_3$*CH), 1.28 (d, $^3J_{HH}$ = 6.72 Hz, 12H, *CH$_3$*CH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 51.5 (dd, $^2J_{PC}$ = 12.5 Hz, $^3J_{PC}$ = 5.1 Hz, CH), 35.4 (dd, $^1J_{PC}$ = 35.9 Hz, $^2J_{PC}$ = 10.3 Hz, *C*(CH_3)$_3$), 32.4 (dd, $^2J_{PC}$ = 13.2 Hz, $^3J_{PC}$ = 6.6 Hz, C*(CH$_3$)$_3$*), 24.4 (dd, $^3J_{PC}$ = 5.9 Hz, $^4J_{PC}$ = 2.9 Hz, CH*(CH$_3$)$_2$*), 24.3 (d, $^3J_{PC}$ = 6.6 Hz, CH*(CH$_3$)$_2$*).

Preparation of (iPr$_2$N)$_2$PPtBuPh 10

Diphosphane **10** was prepared via an analogous procedure as described for **2**, using *t*BuPhPLi (0.80 g, 4.65 mmol) and (*i*Pr$_2$N)$_2$PCl (1.24 g, 4.65 mmol) in 98% yield (1.80 g, 4.54 mmol) as a yellowish solid. Crystals of **10** suitable for X-ray analysis were obtained from concentrated petroleum ether solution at -20°C. Elemental analysis calcd for $C_{22}H_{42}N_2P_2$: C, 66.64; H, 10.68; N, 7.06. Found: C, 66.50; H, 10.63; N, 7.27. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 72.2 (d, $^1J_{PP}$ = 155.3 Hz, P(*i*Pr$_2$N$_2$)$_2$) , -9.5 (d, $^1J_{PP}$ = 155.3 Hz, P*t*BuPh). ^1H NMR

(C_6D_6): δ 7.84 (m, 2H, *o*-C*H*), 7.09-7.12 (m, 3H, *m,p*-C*H*), 3.81 (m, 2H, C*H* CH_3), 3.57 (m, 2H, C*H* CH_3), 1.36 (d, $^3J_{HH}$ = 6.72 Hz, 12H, CHC*H*$_3$), 1.33 (d, $^3J_{HH}$ = 6.6 Hz, 12H, CHC*H*$_3$), 1.32 (d, $^3J_{PH}$ = 11.5 Hz, 9H, CC*H*$_3$), 1.13 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CHC*H*$_3$), 0.67 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 137.6 (dd, $^1J_{PC}$ = 19.8 Hz, $^2J_{PC}$ = 8.1 Hz, *ipso*-CH), 137.4 (dd, $^2J_{PC}$ = 22.0 Hz, $^3J_{PC}$ = 8.1 Hz, *ortho*-CH), 128.7 (s, broad, *para*-CH), 127.3 (d, $^3J_{PC}$ = 8.1 Hz, *meta*-CH), 49.7 (m, broad, *CH*$(CH_3)_2$), 31.4 (dd, $^1J_{PC}$ = 20.5 Hz, $^2J_{PC}$ = 18.3 Hz, *C*$(CH_3)_3$), 30.6 (dd, $^2J_{PC}$ = 20.5 Hz, $^3J_{PC}$ = 18.3 Hz, C(*CH*$_3$)$_3$), 25.6 (broad, d, $^3J_{PC}$ = 5.9 Hz, CH(*CH*$_3$)$_2$), 25.0 (d, $^3J_{PC}$ = 5.9 Hz, CH(*CH*$_3$)$_2$), 23.3 (d, $^3J_{PC}$ = 6.6 Hz, CH(*CH*$_3$)$_2$).

Preparation of $(Et_2N)_2PPPh_2$ 11

Diphosphane **11** was prepared via an analogous procedure as described for **2**, using Ph_2PLi (0.78 g, 4.08 mmol) and $(Et_2N)_2PCl$ (0.86 g, 4.08 mmol, 0.86 cm^3) in 89% yield (1.30 g, 3.61 mmol) as a white solid. In the case of **11** toluene was used as an extracting agent instead of petroleum ether as described for **2.** Due to melting point of crystals close to room temperature elemental analysis was not performed. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 108.4 (d, $^1J_{PP}$ = 135.0 Hz, $P(Et_2N_2)_2$), -38.3 (d, $^1J_{PP}$ = 135.0 Hz, PPh_2). ^1H NMR (C_6D_6): δ 7.81 – 7.75 (m, 4H, o-C*H*), 7.14 – 7.08 (m, 4H, m-C*H*), 7.07 – 7.02 (m, 2H, p-C*H*), 3.28 – 3.04 (m, 8H, *CH*$_2$$CH_3$), 0.84 (t, $^3J_{HH}$ = 7.1 Hz, 12H, CH_2*CH*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 138.0 (dd, $^1J_{PC}$ = 16.9 Hz, $^2J_{PC}$ = 15.4 Hz, *ipso*-CH), 134.9 (dd, $^2J_{PC}$ = 17.6 Hz, $^3J_{PC}$ = 7.3 Hz, *ortho*-CH), 128.1 (d, $^3J_{PC}$ = 6.9 Hz, *meta*-CH), 128.0 (s, *para*-CH), 44.6 (dd, $^2J_{PC}$ = 15.4 Hz, $^3J_{PC}$ = 9.5 Hz, *CH*$_2$$CH_3$), 14.4 (d, $^3J_{PC}$ = 3.7 Hz, CH_2*CH*$_3$).

Preparation of (Et2N)2PPtBu2 12

Diphosphane **12** was prepared via an analogous procedure as described for **2**, using *t*Bu_2PLi (0.86 g, 5.65 mmol) and $(Et_2N)_2PCl$ (1.19 g, 5.65 mmol, 1.19 cm^3) in 97%

yield (1.75 g, 5.46 mmol) as a colourless oil. Crystals of **12** were obtained from concentrated petroleum ether solution at -20°C. Due to melting point of crystals close to room temperature elemental analysis was not performed. $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 111.1 (d, $^{1}J_{PP}$ = 193.7 Hz, $P(Et_2N_2)_2$) , 11.8 (d, $^{1}J_{PP}$ = 193.7 Hz, P*t*Bu$_2$). ^{1}H NMR (C_6D_6): δ 3.26 (m, 4H, C*H*$_2$), 3.13 (m, 4H, C*H*$_2$), 1.38 (d, $^{3}J_{PH}$ = 10.3 Hz, 18H, C(C*H*$_3$)$_3$), 1.02 (t, $^{3}J_{HH}$ = 7.2 Hz, 12H, C*H*$_3$CH$_2$). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 45.6 (dd, $^{2}J_{PC}$ = 16.9 Hz, $^{3}J_{PC}$ = 6.6 Hz, *C*H$_2$CH$_3$), 33.2 (dd, $^{1}J_{PC}$ = 33.2 Hz, $^{2}J_{PC}$ = 11.7 Hz, *C*(CH$_3$)$_3$), 31.9 (dd, $^{2}J_{PC}$ = 12.5 Hz, $^{3}J_{PC}$ = 5.1 Hz, C*(CH$_3$)$_3$*), 14.1 (d, $^{3}J_{PC}$ = 3.7 Hz, CH$_2$*CH*$_3$).

Preparation of $(Et_2N)_2$PPtBuPh 13

Diphosphane **13** was prepared via an analogous procedure as described for **2**, using *t*BuPhPLi (0.80 g, 4.65 mmol) and $(Et_2N)_2PCl$ (0.98 g, 4.65 mmol, 0.98 cm^3) in 86% yield (1.37 g, 4.02 mmol) as a yellow oil. $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 99.5 (d, $^{1}J_{PP}$ = 145.3 Hz, $P(Et_2N_2)_2$), -15.7 (d, $^{1}J_{PP}$ = 145.3 Hz, P*t*BuPh). ^{1}H NMR (C_6D_6): δ 7.84 – 7.79 (m, 2H, o-C*H*), 7.14 – 7.10 (m, 3H, m,p-C*H*), 3.40 – 3.17 (m, 4H,C*H*$_2$), 3.40 – 3.17 (m, 4H,C*H*$_2$), 3.15 – 2.85 (m, 6H, C*H*$_2$), 1.27 (d, $^{3}J_{PH}$ = 11.7 Hz, 9H, C(C*H*$_3$)$_3$), 1.07 (t, $^{3}J_{HH}$ = 7.1 Hz,6H, C*H*$_3$CH$_2$), 0.67 (t, $^{3}J_{HH}$ = 7.1 Hz, 6H, C*H*$_3$CH$_2$). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 137.3 (dd, $^{2}J_{PC}$ = 19.1 Hz, $^{3}J_{PC}$ = 10.3 Hz, *ortho*-CH), 136.4 (dd, $^{1}J_{PC}$ = 21.3.1 Hz, $^{2}J_{PC}$ = 9.5 Hz, *ipso*-CH), 128.5 (bs, *para*-CH), 127.4 (d, $^{3}J_{PC}$ = 7.4 Hz, *meta*-CH), 45.0 (dd, $^{2}J_{PC}$ = 15.4 Hz, $^{3}J_{PC}$ = 8.8 Hz, *C*H$_2$CH$_3$), 44.6 (dd, $^{2}J_{PC}$ = 15.4 Hz, $^{3}J_{PC}$ = 9.5 Hz, *C*H$_2$CH$_3$), 40.9 (d, $^{1}J_{PC}$ = 18.3 Hz, 30.5 (dd, $^{1}J_{PC}$ = 17.6 Hz, $^{2}J_{PC}$ = 15.4 Hz, *C*(CH$_3$)$_3$), 29.5 (dd, $^{2}J_{PC}$ = 12.5 Hz, $^{3}J_{PC}$ = 5.9 Hz, C(*CH*$_3$)$_3$) 14.3 (d, $^{3}J_{PC}$ = 4.4 Hz, CH$_2$*CH*$_3$), 14.0 (d, $^{3}J_{PC}$ = 2.9 Hz, CH$_2$*CH*$_3$).

Preparation of (iPr_2N)PhPPPh$_2$ 14

Diphosphane **14** was prepared via an analogous procedure as described for **2**, using Ph_2PLi (0.68 g, 3.54 mmol) and (*i*Pr_2N)PhPCl (0.86 g, 3.54 mmol) in 78% yield (1.08 g, 2.75 mmol) as a white solid. In the case of **14** toluene was used as an extracting agent instead of petroleum ether as described for **2**. Crystals of **14** suitable for X-ray analysis were obtained from concentrated toluene solution at -20°C. Elemental analysis calcd for $C_{24}H_{29}NP_2$: C, 73.27; H, 7.43; N, 3.57. Found: C, 73.16; H, 7.46; N, 3.64. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 45.5 (d, $^1J_{PP}$ = 144.8 Hz, P(*i*Pr_2N_2)Ph) , -36.0 (d, $^1J_{PP}$ = 144.8 Hz, PPh_2). ^1H NMR (C_6D_6): δ 7.98 – 7.88 (m, 4H, *o*-C*H*), 7.58 (m, 2H, *o*-C*H,* PPh_2), 7.13 – 6.95 (m, 6H, *m*,*p*-C*H*), 6.92 – 6.85 (m, 3H, *m*,*p*-C*H,* PPh_2), 3.55 (bm, 2H, C*H* CH_3), 0.91 (d, $^3J_{HH}$ = 6.48 Hz, 6H, CHC*H*$_3$), 0.83 (d, $^3J_{HH}$ = 6.60 Hz, 6H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 140.3 (dd, $^1J_{PC}$ = 29.3 Hz, $^2J_{PC}$ = 18.3 Hz, *ipso*-CH, P(*i*Pr_2N_2)Ph), 137.3 (dd, $^1J_{PC}$ = 19.8 Hz, $^2J_{PC}$ = 14.7 Hz, *ipso*-CH, PPh_2), 137.1 (dd, $^1J_{PC}$ = 18.3 Hz, $^2J_{PC}$ = 13.2 Hz, *ipso*-CH, PPh_2), 136.6 (dd, $^2J_{PC}$ = 19.8 Hz, $^3J_{PC}$ = 6.6 Hz, *ortho*-CH, PPh_2), 134.2 (dd, $^2J_{PC}$ = 16.9 Hz, $^3J_{PC}$ = 8.1 Hz, *ortho*-CH, PPh_2), 133.4 (dd, $^2J_{PC}$ = 20.5 Hz, $^3J_{PC}$ = 10.3 Hz, *ortho*-CH, P(*i*Pr_2N_2)Ph), 128.9 (bs, *para*-CH, P(*i*Pr_2N_2)Ph), 128.7 (bd, $^4J_{PC}$ = 1.5 Hz *para*-CH, PPh_2), 128.1 (d, $^3J_{PC}$ = 6.4 Hz, *meta*-CH, PPh_2), 128.0 (d, $^3J_{PC}$ = 7.9 Hz, *meta*-CH, PPh_2), 127.96 (d, $^3J_{PC}$ = 8.4 Hz, $^4J_{PC}$ = 1.5 Hz *meta*-CH, P(*i*Pr_2N_2)Ph), 48.5 (bm, *CH*CH_3), 23.6 (bd, $^3J_{PC}$ = 5.1 Hz, CH*CH*$_3$), 23.3 (bd, $^3J_{PC}$ = 6.6 Hz, CH*CH*$_3$).

Preparation of pseudo-meso-(iPr_2N)PhPPtBuPh 15 and pseudo-rac-(iPr_2N)PhPPtBuPh 16

Mixture of diphosphanes **15** and **16** were prepared via an analogous procedure as described for **2**, using *t*BuPhPLi (0.50 g, 2.91 mmol) and (*i*Pr_2N)PhPCl (0.71 g, 2.91 mmol) in 92% yield (1.0 g, 2.68 mmol) as a white solid. In the case of **15/16** toluene was used as an extracting agent instead of petroleum ether as described for **2.** Diastereomeric ratio 1.36:1 for **15**:**16** was determined by integration of corresponding signals from ^1H NMR

spectra. Elemental analysis calcd for $C_{22}H_{33}NP_2$: C, 70.75; H, 8.91; N, 3.75. Found: C, 70.68; H, 9.01; N, 3.70. **15:** $^{31}P\{^1H\}$ NMR (C_6D_6): δ 28.3 (d, $^1J_{PP}$ = 138.0 Hz, P(*i*Pr$_2$N)Ph), -7.5 (d, $^1J_{PP}$ = 138.0 Hz, P*t*BuPh). ^1H NMR (C_6D_6): δ 8.16 (m, 2H, *o*-C*H*, P(*i*Pr$_2$N)Ph), 8.03 (m, 2H, *o*-C*H*, P*t*BuPh), 7.21 – 7.09 (m, 6H, *m,p-CH*), 3.62 (b, 2H, *CH*CH$_3$), 1.00 (d, $^3J_{PH}$ = 11.4 Hz, 9H, C(C*H$_3$*)$_3$), 0.89 (bd, $^3J_{HH}$ = 6.4 Hz, 6H, CHC*H$_3$*), 0.78 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CHC*H$_3$*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 142.2 (dd, $^1J_{PC}$ = 33.0 Hz, $^2J_{PC}$ = 22.7 Hz, *ipso*-CH, P(*i*Pr$_2$N$_2$)Ph), 137.7 (dd, $^2J_{PC}$ = 20.5 Hz, $^3J_{PC}$ = 8.8 Hz, *ortho*-CH, P*t*BuPh), 135.8 (dd, $^1J_{PC}$ = 23.5 Hz, $^2J_{PC}$ = 9.5 Hz, *ipso*-CH, P*t*BuPh), 134.7 (dd, $^2J_{PC}$ = 24.9 Hz, $^3J_{PC}$ = 9.5 Hz, *ortho*-CH, P(*i*Pr$_2$N$_2$)Ph), 129.4 (b, *para*-CH, P(*i*Pr$_2$N$_2$)Ph), 129.1 (b, *para*-CH, P*t*BuPh), 128.1 (d, $^3J_{PC}$ = 8.9 Hz, *meta*-CH, P(*i*Pr$_2$N$_2$)Ph), 127.6 (d, $^3J_{PC}$ = 7.9 Hz, *meta*-CH, P*t*BuPh), 48.6 (b, *CH*CH$_3$), 30.5 (dd, $^1J_{PC}$ = 21.3 Hz, $^2J_{PC}$ = 14.7 Hz, *C*(CH$_3$)$_3$), 30.0 (dd, $^2J_{PC}$ = 13.2 Hz, $^3J_{PC}$ =5.1 Hz, C*(CH$_3$)$_3$*), 23.3 (bd, $^3J_{PC}$ = 2.9 Hz, CH*CH$_3$*). **16**: $^{31}P\{^1H\}$ NMR (C_6D_6): δ 27.61 (d, $^1J_{PP}$ = 145.3 Hz, P(*i*Pr$_2$N)Ph) , -11.1 (d, $^1J_{PP}$ = 145.3 Hz, P*t*BuPh). ^1H NMR (C_6D_6): δ 7.81 (m, 2H, *o*-C*H*, P(*i*Pr$_2$N)Ph), 7.63 (m, 2H, *o*-C*H*, P*t*BuPh), 6.92 – 6.86 (m, 3H, *m,p-CH,* P(*i*Pr$_2$N$_2$)Ph), 6.86 – 6.79 (m, 3H, *m,p-CH,* P*t*BuPh), 3.83 (b, 2H, *CH*CH$_3$), 1.37 (d, $^3J_{PH}$ = 12.0 Hz, 9H, C(C*H$_3$*)$_3$), 1.26 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CHC*H$_3$*), 0.92 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHC*H$_3$*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 139.5 (dd, $^1J_{PC}$ = 32.3 Hz, $^2J_{PC}$ = 13.2 Hz, *ipso*-CH, P(*i*Pr$_2$N$_2$)Ph), 136.7 (dd, $^2J_{PC}$ = 19.1 Hz, $^3J_{PC}$ = 10.3 Hz, *ortho*-CH, P*t*BuPh), 135.4 (dd, $^1J_{PC}$ = 21.3 Hz, $^2J_{PC}$ = 8.8 Hz, *ipso*-CH, P*t*BuPh), 134.5 (dd, $^2J_{PC}$ = 23.1 Hz, $^3J_{PC}$ = 8.4 Hz, *ortho*-CH, P(*i*Pr$_2$N$_2$)Ph), 128.5 (b, *para*-CH, P(*i*Pr$_2$N$_2$)Ph), 128.4 (b, *para*-CH, P*t*BuPh), 128.1 (d, $^3J_{PC}$ = 6.4 Hz, *meta*-CH, P(*i*Pr$_2$N$_2$)Ph), 127.4 (d, $^3J_{PC}$ = 7.9 Hz, *meta*-CH, P*t*BuPh), 48.6 (b, *CH*CH$_3$), 30.5 (dd, $^1J_{PC}$ = 19.1 Hz, $^2J_{PC}$ = 14.7 Hz, *C*(CH$_3$)$_3$), 29.6 (dd, $^2J_{PC}$ = 13.2 Hz, $^3J_{PC}$ =5.1 Hz, C*(CH$_3$)$_3$*), 23.1 (b, CH*CH$_3$*).

Preparation of (iPr_2N)PhPPtBu_2 17

Diphosphane **17** was prepared via an analogous procedure as described for **2**, using tBu$_2$PLi (0.70 g, 4.60 mmol) and (iPr$_2$N)PhPCl (1.12 g, 4.60 mmol) in 74% yield (1.20 g, 3.39 mmol) as a white solid. Crystals of **17** suitable for X-ray analysis were obtained from concentrated petroleum ether solution at -30°C. Elemental analysis calcd for $C_{20}H_{37}NP_2$: C, 67.96; H, 10.55; N, 3.96. Found: C, 67.53; H, 10.45; N, 4.13. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 38.7 (d, $^1J_{PP}$ = 303.2 Hz, PtBu$_2$) , 36.8 (d, $^1J_{PP}$ = 303.2 Hz, P(iPr$_2$N)Ph). ^1H NMR (C_6D_6): δ 7.88 – 7.82 (m, 2H, *o*-C*H*), 7.17 – 7.13 (m, 2H, *m*-C*H*), 7.17 – 7.13 (m, 2H, *m*-C*H*), 7.06 – 7.00 (m, 1H, *p*-C*H*), 3.62 (bm, 2H, *CH*CH$_3$), 1.53 (bs, 9H, C(C*H$_3$)$_3$*), 1.31 (d, $^3J_{HH}$ = 6.72 Hz, 6H, CHC*H$_3$*), 1.08 (ov bs, 9H, C(C*H$_3$)$_3$*), 1.07 (d, $^3J_{HH}$ = 6.72 Hz, 6H, CHC*H$_3$*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 143.8 (dd, $^1J_{PC}$ = 18.3 Hz, $^2J_{PC}$ = 12.5 Hz, *ipso*-CH), 132.0 (dd, $^2J_{PC}$ = 14.7 Hz, $^3J_{PC}$ = 12.5 Hz, *ortho*-CH), 127.8 (dd, $^3J_{PC}$ = 3.9 Hz, $^4J_{PC}$ = 3.4 Hz, *meta*-CH), 127.5 (s, *para*-CH), 50.3 (bs, *CH*CH$_3$), 35.1 (b, *C*(CH$_3$)), 34.1 (b, *C*(CH$_3$)$_3$), 32.1 (b, C*(CH$_3$)$_3$*), 23.9 (b, CH*CH$_3$*), 23.4 (dd, $^3J_{PC}$ = 4.9 Hz, $^3J_{PC}$ = 4.4 Hz, CH*CH$_3$*).

Preparation of meso-(iPr_2N)PhPP(iPr_2N)Ph 18 and rac-(iPr_2N)PhPP(iPr_2N)Ph 19

To a magnesium turnings (0.24 g, 9.85 mmol) in 40 cm^3 of Et$_2$O previously activated by iodine a solution of (iPr$_2$N)PhPCl (1.2 g, 4.92 mmol) in 5 cm^3 of Et$_2$O was added at room temperature and vigorously stirred overnight. Solvent was evaporated/removed in a vacuum and the residue was extracted by 15 cm^3 of toluene and filtered. The filtrate was evaporated to dryness giving the product as a white solid (0.8 g, 2.03 mmol) in 82% yield. Diastereomeric ratio 2.84:1 for **18**:**19** was determined by integration of corresponding signals from ^1H NMR spectra Elemental analysis calcd for $C_{24}H_{38}N_2P_2$: C, 69.21; H, 9.20; N, 6.73. Found: C, 69.15; H, 9.03; N, 6.80. **18:** $^{31}P\{^1H\}$ NMR (C_6D_6): δ 23.6 (s). ^1H NMR (C_6D_6): δ 8.53 (m, 2H, *o*-CH), 7.66 (m, 2H, *o*-CH), 7.21 – 7.15 (m,

3H, *m,p*-CH), 6.88 (m, 3H, *m,p*-CH), 3.89 (bm, 2H, *CH*CH_3), 3.79 (b, 2H, *CH*CH_3), 1.34 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CHC*H₃*), 1.04 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CHC*H₃*), 1.02 (dd, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 3.6 Hz, 3H, CHC*H₃*), 0.99 (dd, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 2.0 Hz, 9H, CHC*H₃*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 140.0 (dd, $^1J_{PC}$ = 5.1 Hz, $^2J_{PC}$ = 5.1 Hz, *ipso*-CH), 134.2 (dd, $^2J_{PC}$ = 16.1 Hz, $^3J_{PC}$ = 15.4 Hz, *ortho*-CH), 128.0 (s, *para*-CH), 127.5 (dd, $^3J_{PC}$ = 4.4 Hz, $^4J_{PC}$ = 4.4 Hz, *meta*-CH), 48.7 (b, *CH*CH_3), 46.5 (b, *CH*CH_3), 24.5 (bm, CH*CH₃*), 23.0 (s, CH*CH₃*), 22.1 (s, CH*CH₃*), 21.8 (b, CH*CH₃*). **19:** $^{31}P\{^1H\}$ NMR (C_6D_6): δ 21.5 (s). ^1H NMR (C_6D_6): δ 8.14 (m, 4H, *o*-CH) , 7.21 (m, 3H, *m,p*-CH), 7.18 (m, 3H, *m,p*-CH), 3.61 (b, 4H, *CH*CH_3), 0.94 (d, $^3J_{HH}$ = 6.5 Hz, 12H, CHC*H₃*), 0.80 (d, $^3J_{HH}$ = 6.6 Hz, 12H, CHC*H₃*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 140.7 (dd, $^1J_{PC}$ = 4.4 Hz, $^2J_{PC}$ = 4.4 Hz, *ipso*-CH), 135.1 (dd, $^2J_{PC}$ = 16.1 Hz, $^3J_{PC}$ = 16.1 Hz, *ortho*-CH), 129.0 (s, *para*-CH), 127.7 (dd, $^3J_{PC}$ = 4.4 Hz, $^4J_{PC}$ = 4.4 Hz, *meta*-CH), 48.7 (b, *CH*CH_3), 23.3 (b, CH*CH₃*), 23.1 (b, CH*CH₃*).

Preparation of (iPr₂N) PhPP(iPr₂N)₂ 20

To magnesium turnings (0.19 g, 8.0 mmol) in 30 cm^3 of Et_2O previously activated by iodine solutions of (*i*Pr_2N)PhPCl (0.49 g, 2.0 mmol) in 5 cm^3 of Et_2O and (*i*$Pr_2N)_2$PCl (0.53 g, 2.0 mmol) in 5 cm^3 of Et_2O were added simultaneously at room temperature and vigorously stirred overnight. $^{31}P\{^1H\}$ NMR spectra revealed that diphosphane **20** was formed as one of three products with corresponding symmetrical diphosphanes **18/19** and **30**. Diphosphane **20** was obtained only in the reaction mixture and pure compound was not isolated. Approximate composition of the final reaction mixture was estimated on the basis of ^{31}P NMR spectra: **20** (69.7mol%), **30** (15.9mol%), **19** (13.0mol%), **18** (1.4mol%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 83.5 (s, P(*i*$Pr_2N)_2$, **30**), 63.3 (d, $^1J_{PP}$ = 101.7 Hz, P(*i*$Pr_2N)_2$, **20**), 23.6 (s, P(*i*Pr_2N)Ph, **18**), 21.5 (s, P(*i*Pr_2N)Ph, **19**), 16.1 (d, $^1J_{PP}$ = 101.7 Hz, P(*i*Pr_2N)Ph, **20**).

Preparation of (iPr_2N)tBuPPPh_2 21

Diphosphane **21** was prepared via an analogous procedure as described for **2**, using Ph_2PLi (0.65 g, 3.38 mmol) and (*i*Pr_2N)*t*BuPCl (0.76 g, 3.38 mmol, 0.70 cm^3) in 76% yield (0.96 g, 2.57 mmol) as a white solid. In the case of **21** toluene was used as an extracting agent instead of petroleum ether as described for **2.** Crystals of **21** suitable for X-ray analysis were obtained from concentrated toluene solution at -30°C. Elemental analysis calcd for $C_{22}H_{33}NP_2$: C, 70.75; H, 8.91; N, 3.75. Found: C, 70.62; H, 8.88; N, 3.92. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 68.5 (d, $^1J_{PP}$ = 185.8 Hz, P(*i*Pr_2N)*t*Bu) , -30.7 (d, $^1J_{PP}$ = 185.8 Hz, PPh_2).). ^1H NMR (C_6D_6): δ 8.16 (m, 2H, *o*-C*H*), 8.03 (m, 2H, *o*-C*H*), 7.13 – 6.94 (m, 6H, *m,p*-C*H*), 4.22 (bs, 1H, *CH*CH_3), 2.85 (bm, 1H, *CH*CH_3), 1.18 (d, $^3J_{HH}$ = 5.99 Hz, 3H, CHC*H*$_3$), 1.12 (d, $^3J_{PH}$ = 12.7 Hz, 9H, C(C*H*$_3$)$_3$) 1.05 (bd, $^3J_{HH}$ = 6.11 Hz, 3H, CHC*H*$_3$), 0.84 (bdd, $^3J_{HH}$ = 11.00, $^5J_{HH}$ = 6.60, Hz, 6H, CHC*H*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 138.4 (dd, $^1J_{PC}$ = 24.2 Hz, $^2J_{PC}$ = 12.5 Hz, *ipso*-CH), 137.5 (dd, $^1J_{PC}$ = 19.1 Hz, $^2J_{PC}$ = 11.8 Hz, *ipso*-CH), 136.8 (dd, $^2J_{PC}$ = 21.3 Hz, $^3J_{PC}$ = 8.1 Hz, *ortho*-CH), 135.7 (dd, $^2J_{PC}$ = 21.3 Hz, $^3J_{PC}$ = 5.1 Hz, *ortho*-CH), 128.9 (s, *para*-CH), 128.6 (s, *para*-CH), 128.1 (d, $^3J_{PC}$ = 8.1 Hz, *meta*-CH), 127.9 (d, $^3J_{PC}$ = 7.9 Hz, *meta*-CH), 53.5 (bdd, $^2J_{PC}$ =13.9 Hz, $^4J_{PC}$ =13.2 Hz, *CH*CH_3), 44.6 (bd, $^2J_{PC}$ =27.9 Hz, *CH*CH_3), 35.6 (dd, $^1J_{PC}$ = 27.9 Hz, $^2J_{PC}$ = 16.9 Hz, *C*$(CH_3)_3$), 29.6 (dd, $^2J_{PC}$ = 16.1 Hz, $^3J_{PC}$ = 4.4 Hz, C(*CH*$_3$)$_3$), 25.7 (dd, $^3J_{PC}$ = 36.7 Hz, $^3J_{PC}$ = 10.3 Hz, CH*CH*$_3$), 23.2 (s, CH*CH*$_3$), 22.3 (s, CH*CH*$_3$).

Preparation of pseudo-meso-(iPr_2N)tBuPPtBuPh 22 and pseudo-rac-(iPr_2N)tBuPPtBuPh 23

Mixture of diphosphanes **22** and **23** were prepared via an analogous procedure as described for **2**, using *t*BuPhPLi (0.515 g, 2.99 mmol) and (*i*Pr_2N)*t*BuPCl (0.67 g, 2.99 mmol, 0.62 cm^3) in 89% yield (0.94 g, 2.66 mmol) as a white solid. In the case of **22/23** toluene was used as an extracting agent instead of petroleum ether as described for **2**. Crystals of **23** suitable for X-ray analysis were obtained from concentrated toluene

solution at -30°C. Diastereomeric ratio 1.14:1 for **22**:**23** was determined by integration of corresponding signals from ^{1}H NMR spectra. Elemental analysis calcd for $C_{20}H_{37}NP_2$: C, 69.96; H, 10.55; N, 3.96; found: C, 67.40; H, 10.46; N, 4.19. **23:** $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 70.3 (d, $^{1}J_{PP}$ = 283.4 Hz, P(*i*Pr$_2$N)*t*Bu), 7.7 (d, $^{1}J_{PP}$ = 283.4 Hz, P*t*BuPh). ^{1}H NMR (C_6D_6): δ 7.93 (m, 2H, *o*-C*H*), 7.13 – 7.00 (m, 3H, *m,p*-C*H*), 3.53 (b, 1H, *CH*CH$_3$), 2.86 (b, 1H, *CH*CH$_3$), 1.41 (d, $^{3}J_{PH}$ = 13.8 Hz, 9H, C(*CH$_3$*)$_3$, P(*i*Pr$_2$N)*t*Bu), 1.37 (d, $^{3}J_{HH}$ = 7.0 Hz, 3H, CHC*H$_3$*), 1.33 (d, $^{3}J_{PH}$ = 12.0 Hz, 9H, C(*CH$_3$*)$_3$, P*t*BuPh), 0.94 (b, 6H, CHC*H$_3$*), 0.42 (b, 3H, CHC*H$_3$*). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 137.6 (dd, $^{1}J_{PC}$ = 32.3 Hz, $^{2}J_{PC}$ = 4.4 Hz, *ipso*-CH), 137.4 (dd, $^{2}J_{PC}$ = 22.0 Hz, $^{3}J_{PC}$ = 4.4 Hz, *ortho*-CH), 128.4 (bs, *para*-CH), 127.9 (d, $^{3}J_{PC}$ = 7.9 Hz, *meta*-CH), 54.6 (bm, *CH*CH$_3$), 45.2 (bd, $^{2}J_{PC}$ = 27.9 Hz, *CH*CH$_3$), 34.9 (dd, $^{1}J_{PC}$ = 22.7 Hz, $^{2}J_{PC}$ = 21.3 Hz, *C*(CH$_3$)$_3$, P(*i*Pr$_2$N)*t*Bu), 31.7 (dd, $^{1}J_{PC}$ = 21.3 Hz, $^{2}J_{PC}$ = 13.2 Hz, *C*(CH$_3$)$_3$, P*t*BuPh), 30.7 (dd, $^{2}J_{PC}$ = 14.3 Hz, $^{3}J_{PC}$ = 4.4 Hz, C*(CH$_3$)*$_3$, P*t*BuPh), 29.8 (dd, $^{2}J_{PC}$ = 16.7 Hz, $^{3}J_{PC}$ = 6.9 Hz, C*(CH$_3$)*$_3$, P(*i*Pr$_2$N)*t*Bu), 25.6 (bm, CH*CH$_3$*), 24.9 (d, $^{3}J_{PC}$ = 14.8 Hz, CH*CH$_3$*), 22.7 (bm, CH*CH$_3$*). **22:** $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 57.7 (d, $^{1}J_{PP}$ = 348.8 Hz, P(*i*Pr$_2$N)*t*Bu), 14.9 (d, $^{1}J_{PP}$ = 348.8 Hz, P*t*BuPh). ^{1}H NMR (C_6D_6): δ 7.87 (m, 2H, *o*-C*H*), 7.13 – 7.00 (m, 3H, *m,p*-C*H*), 3.88 (bm, 1H, *CH*CH$_3$), 3.11 (bm, 1H, *CH*CH$_3$), 1.49 (d, $^{3}J_{HH}$ = 6.8 Hz, 3H, CHC*H$_3$*), 1.45 (d, $^{3}J_{PH}$ = 13.0 Hz, 9H, C(*CH$_3$*)$_3$, P*t*BuPh), 1.19 (d, $^{3}J_{HH}$ = 6.4 Hz, 6H, CHC*H$_3$*), 1.05 (d, $^{3}J_{HH}$ = 6.4 Hz, 3H, CHC*H$_3$*), 0.99 (d, $^{3}J_{PH}$ = 13.8 Hz, 9H, C(*CH$_3$*)$_3$, P(*i*Pr$_2$N)*t*Bu). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 137.6 (dd, $^{1}J_{PC}$ = 32.3 Hz, $^{2}J_{PC}$ = 4.4 Hz, *ipso*-CH), 137.4 (d, $^{2}J_{PC}$ = 22.7 Hz, *ortho*-CH), 128.2 (bs, *para*-CH), 127.6 (d, $^{3}J_{PC}$ = 7.9 Hz, *meta*-CH), 55.8 (dd, $^{2}J_{PC}$ = 10.3 Hz, $^{3}J_{PC}$ =9.5 Hz, *CH*CH$_3$), 45.3 (d, $^{2}J_{PC}$ = 27.1 Hz, *CH*CH$_3$), 37.1 (d, $^{1}J_{PC}$ = 27.1 Hz, *C*(CH$_3$)$_3$, P(*i*Pr$_2$N)*t*Bu), 31.8 (dd, $^{1}J_{PC}$ = 33.7 Hz, $^{2}J_{PC}$ = 15.4 Hz, *C*(CH$_3$)$_3$, P*t*BuPh), 31.1 (dd, $^{2}J_{PC}$ = 14.3 Hz, $^{3}J_{PC}$ = 5.4 Hz, C*(CH$_3$)*$_3$, P*t*BuPh), 29.5 (d, $^{2}J_{PC}$ = 17.2 Hz, C*(CH$_3$)*$_3$, P(*i*Pr$_2$N)*t*Bu), 25.9 (d, $^{3}J_{PC}$ = 7.4 Hz, CH*CH$_3$*), 22.9 (s, CH*CH$_3$*), 22.1 (bd, $^{3}J_{PC}$ = 4.9 Hz, CH*CH$_3$*).

Preparation of (iPr_2N)tBuPPtBu_2 24

Diphosphane **24** was prepared via an analogous procedure as described for **2**, using tBu$_2$PLi (0.48 g, 3.13 mmol) and (iPr$_2$N)tBuPCl (0.70 g, 3.13 mmol, 0.65 cm^3) in 65% yield (0.68 g, 2.03 mmol) as a white solid. Time of stirring at ambient temperature was prolonged to 3 hours. Crystals of **24** suitable for X-ray analysis were obtained from concentrated petroleum ether solution at 4°C. Elemental analysis calcd for $C_{18}H_{41}NP_2$: C, 64.83; H, 12.39; N, 4.20. Found: C, 64.42; H, 12.27; N, 4.18. $^{31}P\{^1H\}$ NMR (toluene-d_8, 248K): δ 69.5 (d, $^1J_{PP}$ = 489.5 Hz, P(iPr$_2$N)tBu), 65.6 (d, $^1J_{PP}$ = 489.5 Hz, PtBu$_2$). ^1H NMR (C_6D_6): δ 3.39 (b, 2H, *CH*CH$_3$), 1.47 (dd, $^3J_{PH}$ = 5.7 Hz, $^4J_{PH}$ = 5.7 Hz, 18H, C(*CH$_3$*)$_3$, PtBu$_2$), 1.36 (dd, $^3J_{PH}$ = 7.3 Hz, $^4J_{PH}$ = 7.3 Hz, 9H, C(*CH$_3$*)$_3$, P(iPr$_2$N)tBu), 1.30 (b, 6H, CH*CH$_3$*), 1.16 (b, 6H, CH*CH$_3$*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 37.4 (bm, *C*CH$_3$), 35.6 (bm, *C*CH$_3$), 33.4 (bdd, $^2J_{PC}$ = 9.5 Hz, $^3J_{PC}$ = 8.8 Hz, C*(CH$_3$)$_3$*, PtBu$_2$), 31.4 (bdd, $^2J_{PC}$ = 10.3 Hz, $^3J_{PC}$ = 10.3 Hz, C*(CH$_3$)$_3$*, P(iPr$_2$N)tBu), 23.7 (b, CH*CH$_3$*).

Preparation of meso-(iPr_2N)tBuPP(iPr_2N)tBu 25 and rac-(iPr_2N)tBuPP(iPr_2N)tBu 26

Mixture of diphosphanes **25** and **26** was prepared via an analogous procedure as described for **18/19**, using Mg (0.20 g, 8.2 mmol) and (iPr$_2$N)tBuPCl (0.92 g, 4.10 mmol, 0.85 cm^3) in 84% yield (0.65 g, 1.72 mmol) as a colorless crystals. Diastereomeric ratio 1**:**1.1 for **25**:**26** was determined by integration of corresponding signals from ^1H NMR spectra. Crystals of **25/26** suitable for X-ray analysis were obtained from highly concentrated toluene solution at room temperature. Due to melting point of crystals close to room temperature elemental analysis was not performed. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 88.8 (bs), 82.0 (s). ^1H NMR (C_6D_6): δ 3.64 (b, 4H, *CH*CH$_3$), 3.12 (b, 4H, *CH*CH$_3$), 1.42 (bdd, $^3J_{PH}$ = 6.8 Hz, $^4J_{PH}$ = 6.8 Hz, 36H, C(*CH$_3$*)$_3$), 1.34 (b, 6H, CH*CH$_3$*), 1.30 – 1.07 (bm, 42H, CH*CH$_3$*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 57.5 (bm, *CH*CH$_3$), 55.7 (b, *CH*CH$_3$), 46.0 (b, *CH*CH$_3$), 45.1 (bm,

CHCH_3), 37.6 (bdd, $^1J_{PC}$ = 17.6 Hz, $^2J_{PC}$ = 17.6 Hz, *C*$(CH_3)_3$), 36.6 (bdd, $^1J_{PC}$ = 7.3 Hz, $^2J_{PC}$ = 7.3 Hz, *C*$(CH_3)_3$), 31.1 (bdd, $^2J_{PC}$ = 10.3 Hz, $^3J_{PC}$ = 10.3 Hz, C*(CH₃)₃*), 30.7 (bdd, $^2J_{PC}$ = 9.8 Hz, $^3J_{PC}$ = 9.8 Hz, C*(CH₃)₃*), 26.5 (bs, CH*CH₃*), 26.1 (bs, CH*CH₃*), 25.1 (b, CH*CH₃*), 22.9 (bs, CH*CH₃*), 22.1 (bs, CH*CH₃*). ^{1}H and ^{13}C NMR data of selected diastereoisomers were presented together due to insignificant chemical-shift difference and partially overlapped signals of corresponding groups.

Preparation of (iPr$_2$N)tBuPP(iPr$_2$N)$_2$ 27

To magnesium turnings (0.19 g, 8.0 mmol) in 30 cm^3 of Et_2O, previously activated by iodine, solutions of (*i*Pr$_2$N)*t*BuPCl (0.45 g, 2.0 mmol) in 5 cm^3 of Et_2O and (*i*Pr$_2$N)$_2$PCl (0.53 g, 2.0 mmol) in 5 cm^3 of Et_2O were added simultaneously at room temperature and vigorously stirred overnight. ^{31}P{^{1}H} NMR spectra revealed that diphosphane **27** was formed as one of three products with corresponding symmetrical diphosphanes **26** and **30**. Diphosphosphane **27** was obtained only in the reaction mixture and pure compound was not isolated. Approximate composition of the final reaction mixture was estimated on the basis of ^{31}P NMR spectra: **27** (45.7mol%), **30** (40.9 mol%), **26** (13.3mol%) (also (*i*Pr$_2$N)*t*BuPH and (*i*Pr$_2$N)*t*BuPCl). ^{31}P{^{1}H} NMR (C_6D_6): δ 92.1 (d, $^1J_{PP}$ = 327.0 Hz, P(*i*Pr$_2$N)*t*Bu, **27**), 88.7 (d, $^1J_{PP}$ = 327.0 Hz, P(*i*Pr$_2$N)$_2$, **27**), 83.5 (s, P(*i*Pr$_2$N)$_2$, **30**), 82.0 (s, P(*i*Pr$_2$N)*t*Bu, **26**).

Preparation of pseudo-meso-(Et$_2$N)(iPr$_2$N)PPtBuPh 28 and pseudo-rac-(Et$_2$N)(iPr$_2$N)PPtBuPh 29

Mixture of diphosphanes **28** and **29** was prepared via an analogous procedure as described for **2**, using *t*BuPhPLi (0.47 g, 2.71 mmol) and (Et$_2$N)(*i*Pr$_2$N)PCl (0.65 g, 2.71 mmol) in 91% yield (0.91 g, 2.47 mmol) as a yellowish oil. Diastereomeric ratio 1.1:1 for **28**:**29** was determined by integration of corresponding ^{1}H NMR signals. The small

amount of crystals of **28** suitable for X-ray analysis were obtained from concentrated petroleum ether solution at -20°C. Due to melting point of crystals close to room temperature elemental analysis was not performed. $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 79.5 (d, $^{1}J_{PP}$ = 143.1 Hz, P(Et_2N)(*i*Pr_2N)), 79.3 (d, $^{1}J_{PP}$ = 140.4 Hz, P(Et_2N)(*i*Pr_2N)), -13.8 (d, $^{1}J_{PP}$ = 140.4 Hz, P*t*BuPh), -14.9 (d, $^{1}J_{PP}$ = 140.4 Hz, P*t*BuPh). ^{1}H NMR (C_6D_6): δ 7.86 (m, 2H, *o*-C*H*), 7.80 (m, 2H, *o*-C*H*), 7.15 – 7.08 (m, 6H, *m,p*-C*H*), 3.37 (bm, 2H, *CH*CH_3), 3.15 (bm, 1H, *CH*CH_3), 3.15 (m, 4H, *CH_2*CH_3), 2.95 (bm, 1H, *CH*CH_3), 2.95 (m, 4H, *CH_2*CH_3), 1.30 (d, $^{3}J_{PH}$ = 11.6 Hz, 9H, C(*CH_3*)$_3$), 1.30 (d, $^{3}J_{PH}$ = 12.0 Hz, 9H, C(*CH_3*)$_3$), 1.23 (b, 9H, CH*CH_3*), 1.17 (d, $^{3}J_{HH}$ = 6.7 Hz, 3H, CHC*H_3*), 1.12 (t, $^{3}J_{HH}$ = 7.1 Hz, 6H, CH_2*CH_3*), 1.05 (bm, 9H, CH*CH_3*), 0.92 (b, 3H, CH*CH_3*), 0.55 (bm, 6H, CH_2*CH_3*). $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 137.7 (dd, $^{2}J_{PC}$ = 22.7 Hz, $^{3}J_{PC}$ = 10.3 Hz, *ortho*-CH), 137.5 (dd, $^{2}J_{PC}$ = 22.0 Hz, $^{3}J_{PC}$ = 10.3 Hz, *ortho*-CH), 137.0 (dd, $^{1}J_{PC}$ = 21.3 Hz, $^{2}J_{PC}$ = 8.1 Hz, *ipso*-CH), 136.4 (dd, $^{1}J_{PC}$ = 21.3 Hz, $^{2}J_{PC}$ = 9.5 Hz, *ipso*-CH), 128.8 (bm, *para*-CH), 128.4 (bm, *para*-CH), 127.3 (d, $^{3}J_{PC}$ = 7.4 Hz, *meta*-CH), 127.2 (d, $^{3}J_{PC}$ = 7.4 Hz, *meta*-CH), 44.75 (b, *CH_2*CH_3), 43.6 (d, $^{2}J_{PC}$ = 11.7 Hz, *CH*CH_3), 39.3 (d, $^{2}J_{PC}$ = 19.8 Hz, *CH_2*CH_3), 30.7 (dd, $^{1}J_{PC}$ = 22.4 Hz, $^{2}J_{PC}$ = 16.5 Hz, *C*(CH_3)$_3$), 30.5 (dd, $^{1}J_{PC}$ = 22.0 Hz, $^{2}J_{PC}$ = 16.9 Hz, *C*(CH_3)$_3$), 29.9 (dd, $^{2}J_{PC}$ = 12.8 Hz, $^{3}J_{PC}$ = 6.4 Hz, C(*CH_3*)$_3$), 29.8 (dd, $^{2}J_{PC}$ = 12.8 Hz, $^{3}J_{PC}$ = 6.4 Hz, C(*CH_3*)$_3$), 24.0 (d, $^{3}J_{PC}$ = 8.4 Hz, CH*CH_3*), 14.6 (d, $^{3}J_{PC}$ = 4.4 Hz, CH_2*CH_3*), 13.7 (d, $^{3}J_{PC}$ = 2.5 Hz, CH*CH_3*), 13.3 (d, $^{3}J_{PC}$ = 2.0 Hz, CH_2*CH_3*). ^{1}H and ^{13}C NMR data of selected diastereoisomers were presented together due to insignificant chemical-shift difference and partially overlapped signals of corresponding groups.

Reactivity of diphosphanes towards excess of substrates

Reactivity of diphosphanes towards RR'PLi phosphides

A: Mixture of **2** (0.053 g, 0.170 mmol) and *t*Bu_2PLi (0.0026 g, 0.017 mmol)

Result: pale yellow solution transformed into deep green. No P-P bond cleavage products were obtained. Formation of *t*Bu$_2$PH and *t*Bu$_2$P*P*tBu$_2$ from *t*Bu$_2$PLi. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 39.1 (s, **1**, P*t*Bu$_2$), 30.8 (d, $^1J_{PP}$ = 370.3 Hz, **2**, P*t*Bu$_2$), 19.1 (s, *t*Bu$_2$PH) 1.4 (d, $^1J_{PP}$ = 370.3 Hz, **2**, P*t*BuPh).

B: Mixture of **3** (0.056 g, 0.170 mmol) and *t*Bu$_2$PLi (0.0026 g, 0.017 mmol)

Result: pale yellow solution transformed into deep green. No P-P bond cleavage products were obtained. Formation of *t*Bu$_2$PH and *t*Bu$_2$P*P*tBu$_2$ from *t*Bu$_2$PLi. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 39.1 (s, **1**, P*t*Bu$_2$), 33.0 (d, $^1J_{PP}$ = 254.3 Hz, **3**, P*t*Bu$_2$), 19.1 (s, *t*Bu$_2$PH), -25.9 (d, $^1J_{PP}$ = 254.3 Hz, **3**, PPh$_2$).

C: Mixture of **6** (0.060 g, 0.170 mmol) and *t*BuPhPLi (0.0029 g, 0.017 mmol)

Result: orange solution transformed into yellow. About 6mol% of **6** undergoes the P-P bond cleavage that leads to the formation of respective symmetrical diphosphanes (**4/5** and **7**). Composition of the final reaction mixture: **6** (85.2 mol%), **5** (7.0 mol%), *t*BuPhPH (4.2 mol%), **7** (2.5 mol%) **4** (1.1 mol%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 9.7 (d, $^1J_{PP}$ = 158.5 Hz, **6**, P*t*BuPh), 1.9 (s, **4**, P*t*BuPh), -4.4 (s, **5**, P*t*BuPh), -6.1 (s, *t*BuPhPH), -15.3 (s, **7**, PPh$_2$), -30.8 (d, $^1J_{PP}$ = 158.5 Hz, **6**, PPh$_2$).

D: Mixture of **8** (0.071 g, 0.170 mmol) and Ph$_2$PLi (0.0033 g, 0.017 mmol)

Result: red solution transformed into yellow. About 31mol% of **8** undergoes the P-P bond cleavage that leads to the formation of respective symmetrical diphosphanes (**7** and **30**). Composition of the final reaction mixture: **8** (71.2 mol%), **7** (17.8 mol%), **30** (11.0 mol%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 83.5 (s, **30**, P(*i*Pr$_2$N)$_2$), 71.8 (d, $^1J_{PP}$ = 119.3 Hz, **8,** P(iPr$_2$N)$_2$), -15.3 (s, **7**, PPh$_2$), -38.0 (d, $^1J_{PP}$ = 119.3 Hz, **8,** PPh$_2$).

E: Mixture of **9** (0.064 g, 0.170 mmol) and *t*Bu_2PLi (0.0026 g, 0.017 mmol)

Result: pale yellow solution transformed into deep green. No P-P bond cleavage products were obtained. Formation of *t*Bu_2PH and *t*Bu_2P*P*tBu_2 from *t*Bu_2PLi. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 88.2 (d, $^1J_{PP}$ = 358.2 Hz, **9**, P(*i*$Pr_2N_2)_2$), 62.6 (d, $^1J_{PP}$ = 358.2 Hz, **9**, P*t*Bu_2), 39.1 (s, **1**, P*t*Bu_2), 19.1 (s, *t*Bu_2PH).

F: Mixture of **14** (0.067 g, 0.170 mmol) and Ph_2PLi (0.0033 g, 0.017 mmol)

Result: red solution transformed into yellow. About 4.4mol% of **14** undergoes the P-P bond cleavage that leads to the formation of respective symmetrical diphosphanes (**7** and **20**). Composition of the final reaction mixture: **14** (87.5 mol%), **7** (10.4 mol%), **19** (2.0 mol%) and traces of **18**. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 45.5 (d, $^1J_{PP}$ = 144.8 Hz, **14**, P(*i*Pr_2N)Ph), 21.5 (s, **19**, P(*i*Pr_2N)Ph), -15.3 (s, **7**, PPh_2), -36.0 (d, $^1J_{PP}$ = 144.8 Hz, **14**, PPh_2).

G: Mixture of **15/16** (0.063 g, 0.170 mmol) and *t*BuPhPLi (0.0029 g, 0.017 mmol)

Result: orange solution transformed into yellow. About 4.0mol% of **15/16** undergoes the P-P bond cleavage that leads to the formation of respective symmetrical diphosphanes (**5** and **20**). Composition of the final reaction mixture: **15/16** (85.0 mol%), *t*BuPhPH (8.0 mol%), **5** (5.3 mol%), **20** (1.7 mol%) and traces of **4** and **19**. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 28.3 (d, $^1J_{PP}$ = 138.0 Hz, **15**, P(*i*Pr_2N)Ph), 27.6 (d, $^1J_{PP}$ = 145.3 Hz, **16**, P(*i*Pr_2N)Ph), 21.5 (s, **20**, P(*i*Pr_2N)Ph), -4.4 (s, **5**, P*t*BuPh), -6.1 (s, *t*BuPhPH), -7.5 (d, $^1J_{PP}$ = 138.0 Hz, **15**, P*t*BuPh), -11.1 (d, $^1J_{PP}$ = 145.3 Hz, **16**, P*t*BuPh).

H: Mixture of **17** (0.060 g, 0.170 mmol) and *t*Bu_2PLi (0.0026 g, 0.017 mmol)

Result: pale yellow solution transformed into deep green. No P-P bond cleavage products were obtained. Formation of *t*Bu_2PH and *t*Bu_2P*P*tBu_2 from *t*Bu_2PLi. $^{31}P\{^1H\}$ NMR (C_6D_6):

δ 39.1 (s, **1**, P*t*Bu$_2$), 38.7 (d, $^1J_{PP}$ = 303.2 Hz, **17**, P*t*Bu$_2$) , 36.8 (d, $^1J_{PP}$ = 303.2 Hz, **17**, P(*i*Pr$_2$N)Ph), 19.1 (s, *t*Bu$_2$PH).

I: Mixture of **24** (0.057 g, 0.170 mmol) and *t*Bu$_2$PLi (0.0026 g, 0.017 mmol)

Result: pale yellow solution transformed into deep green. No P-P bond cleavage products were obtained. Formation of *t*Bu$_2$PH and *t*Bu$_2$PP*t*Bu$_2$ from *t*Bu$_2$PLi. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 68.8 (b, **24**, P(*i*Pr$_2$N)*t*Bu) 66.0 (b, **24**, P*t*Bu$_2$), 39.1 (s, **1**, P*t*Bu$_2$), 19.1 (s, *t*Bu$_2$PH).

Reactivity of diphosphanes towards R"R"'PCl chlorophosphanes

A: Mixture of **2** (0.053 g, 0.170 mmol) and *t*BuPhPCl (0.010 g, 0.051 mmol)

Result: no evidence of reaction according to ^{31}P NMR spectra after 4 days of mixing. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 107.8 (s, *t*BuPhPCl) 30.8 (d, $^1J_{PP}$ = 370.3 Hz, **2**, P*t*Bu$_2$), 1.4 (d, $^1J_{PP}$ = 370.3 Hz, **2**, P*t*BuPh).

B: Mixture of **3** (0.056 g, 0.170 mmol) and Ph$_2$PCl (0.011 g, 0.051 mmol)

Result: no evidence of reaction according to ^{31}P NMR spectra after 4 days of mixing. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 82.1 (s, Ph$_2$PCl), 33.0 (d, $^1J_{PP}$ = 254.3 Hz, **3**, P*t*Bu$_2$), -25.9 (d, $^1J_{PP}$ = 254.3 Hz, **3**, PPh$_2$).

C: Mixture of **6** (0.060 g, 0.170 mmol) and Ph$_2$PCl (0.011 g, 0.051 mmol)

Result: in the presence of 30 mol% Ph$_2$PCl **6** undergoes the P-P bond cleavage that leads to the formation of *t*BuPhPCl and *t*BuPhPH as well as symmetrical system **7**. Composition of the final reaction mixture: **6** (56.5 mol%), Ph$_2$PCl (21.2 mol%), *t*BuPhPCl (8.3 mol%), *t*BuPhPH (8.0 mol%), **7** (6.0 mol%). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 107.8 (s, *t*BuPhPCl), 82.1 (s,

Ph_2PCl), 9.7 (d, $^1J_{PP}$ = 158.5 Hz, **6**, P*t*BuPh), -6.1 (s, *t*BuPhPH), -15.3 (s, **7**, PPh_2), -30.8 (d, $^1J_{PP}$ = 158.5 Hz, **6**, PPh_2).

D: Mixture of **8** (0.071 g, 0.170 mmol) and $(iPr_2N)_2PCl$ (0.014 g, 0.051 mmol)

Result: no evidence of reaction according to ^{31}P NMR spectra after 4 days of mixing. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 134.8 (s, $(iPr_2N)_2PCl$), 71.8 (d, $^1J_{PP}$ = 119.3 Hz, **8,** $P(iPr_2N)_2$), -38.0 (d, $^1J_{PP}$ = 119.3 Hz, **8,** PPh_2).

E: Mixture of **9** (0.064 g, 0.170 mmol) and $(iPr_2N)_2PCl$ (0.014 g, 0.051 mmol)

Result: no evidence of reaction according to ^{31}P NMR spectra after 4 days of mixing. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 134.8 (s, $(iPr_2N)_2PCl$), 88.2 (d, $^1J_{PP}$ = 358.2 Hz, **9**, $P(iPr_2N_2)_2$), 62.6 (d, $^1J_{PP}$ = 358.2 Hz, **9**, $PtBu_2$).

F: Mixture of **14** (0.067 g, 0.170 mmol) and $(iPr_2N)PhPCl$ (0.012 g, 0.051 mmol)

Result: no evidence of reaction according to ^{31}P NMR spectra after 4 days of mixing. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 130.9 (s, $(iPr_2N)PhPCl$), 45.5 (d, $^1J_{PP}$ = 144.8 Hz, **14**, $P(iPr_2N)Ph$), -36.0 (d, $^1J_{PP}$ = 144.8 Hz, **14**, PPh_2).

G: Mixture of **15/16** (0.063 g, 0.170 mmol) and $(iPr_2N)PhPCl$ (0.012 g, 0.051 mmol)

Result: no evidence of reaction according to ^{31}P NMR spectra after 4 days of mixing. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 130.9 (s, $(iPr_2N)PhPCl$), 28.3 (d, $^1J_{PP}$ = 138.0 Hz, **15**, $P(iPr_2N)Ph$), 27.6 (d, $^1J_{PP}$ = 145.3 Hz, **16**, $P(iPr_2N)Ph$), -7.5 (d, $^1J_{PP}$ = 138.0 Hz, **15**, P*t*BuPh), -11.1 (d, $^1J_{PP}$ = 145.3 Hz, **16**, P*t*BuPh).

H: Mixture of **17** (0.060 g, 0.170 mmol) and $(iPr_2N)PhPCl$ (0.012 g, 0.051 mmol)

Result: no evidence of reaction according to ^{31}P NMR spectra after 4 days of mixing. $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 130.9 (s, (*i*Pr$_2$N)PhPCl), 38.7 (d, $^{1}J_{PP}$ = 303.2 Hz, **17**, P*t*Bu$_2$) , 36.8 (d, $^{1}J_{PP}$ = 303.2 Hz, **17**, P(*i*Pr$_2$N)Ph).

I: Mixture of **24** (0.057 g, 0.170 mmol) and (*i*Pr$_2$N)*t*BuPCl (0.011 g, 0.051 mmol)

Result: no evidence of reaction according to ^{31}P NMR spectra after 4 days of mixing. $^{31}P\{^{1}H\}$ NMR (C_6D_6): δ 130.9 (s, (*i*Pr$_2$N)*t*BuPCl), 68.8 (b, **24**, P(*i*Pr$_2$N)*t*Bu) 66.0 (b, **24**, P*t*Bu$_2$).

Crystallographic structures

X-ray structure of 3

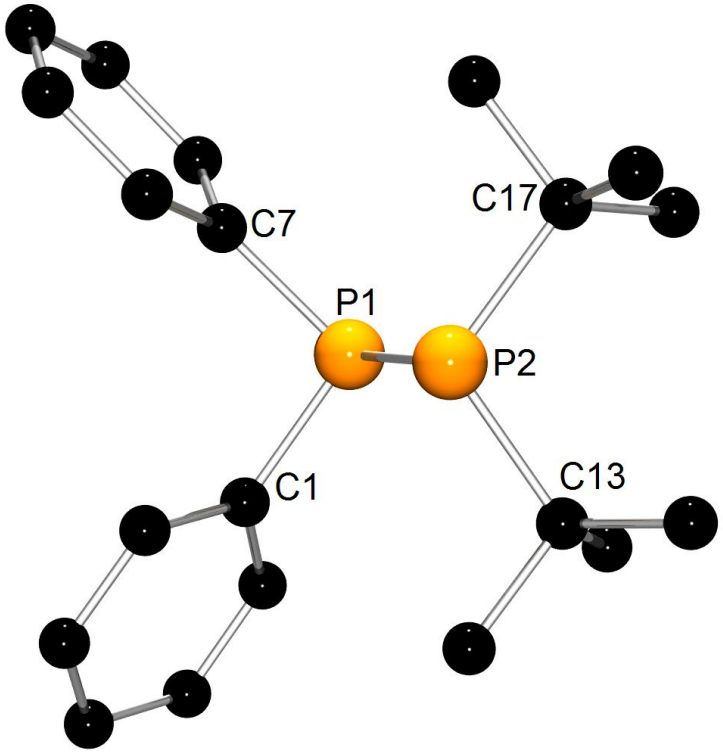

Fig. S1. Structure of *t*Bu_2PPPh_2 (**3**). Hydrogen atoms were omitted for clarity.

X-ray structure of 6

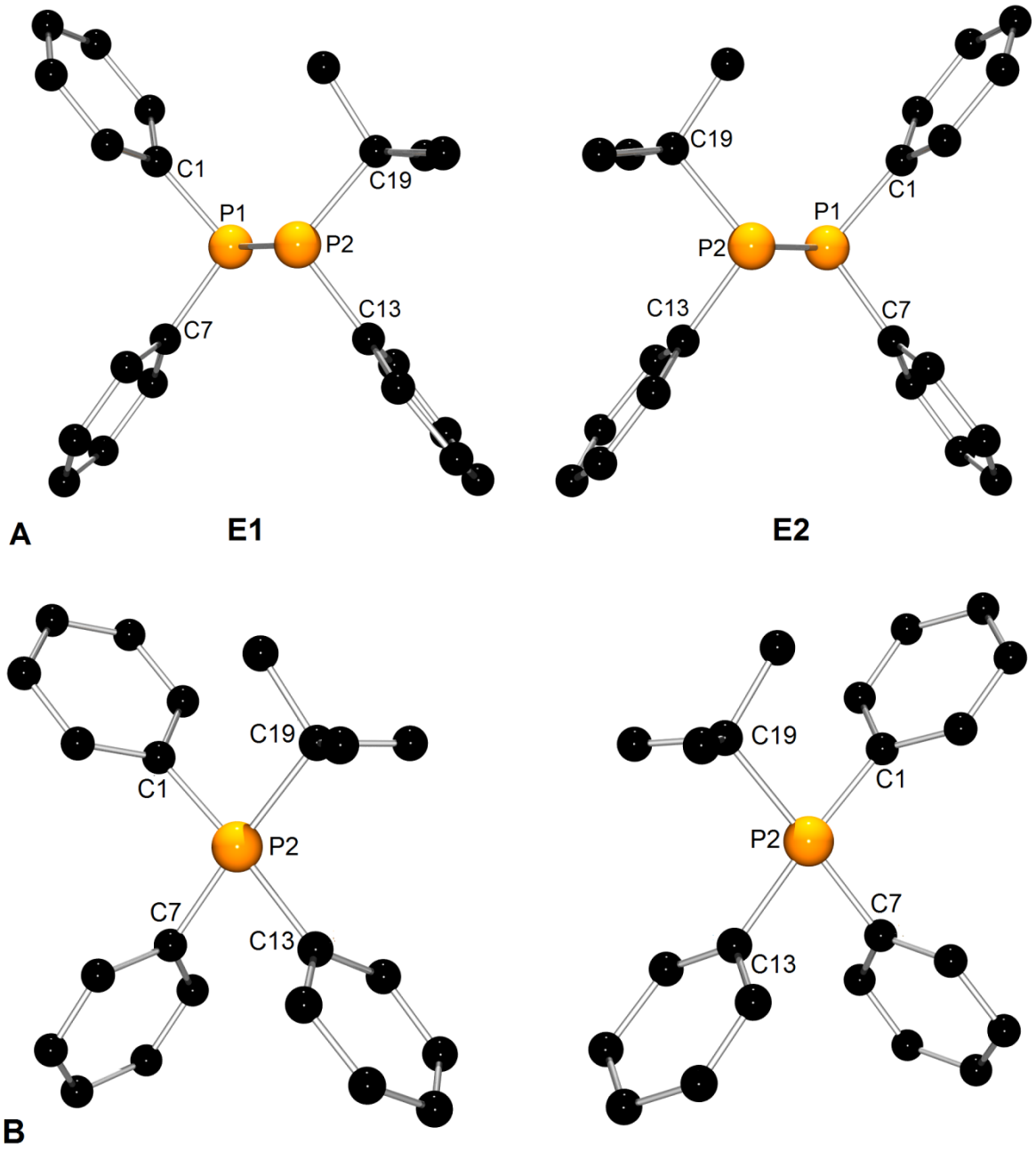

Fig. S2. (A) Structure of two enantiomers (**E1**, **E2**) of *t*BuPhPPPh$_2$ (**6**). (B) View along P2-P1 bond. Hydrogen atoms were omitted for clarity.

X-ray structure of 8

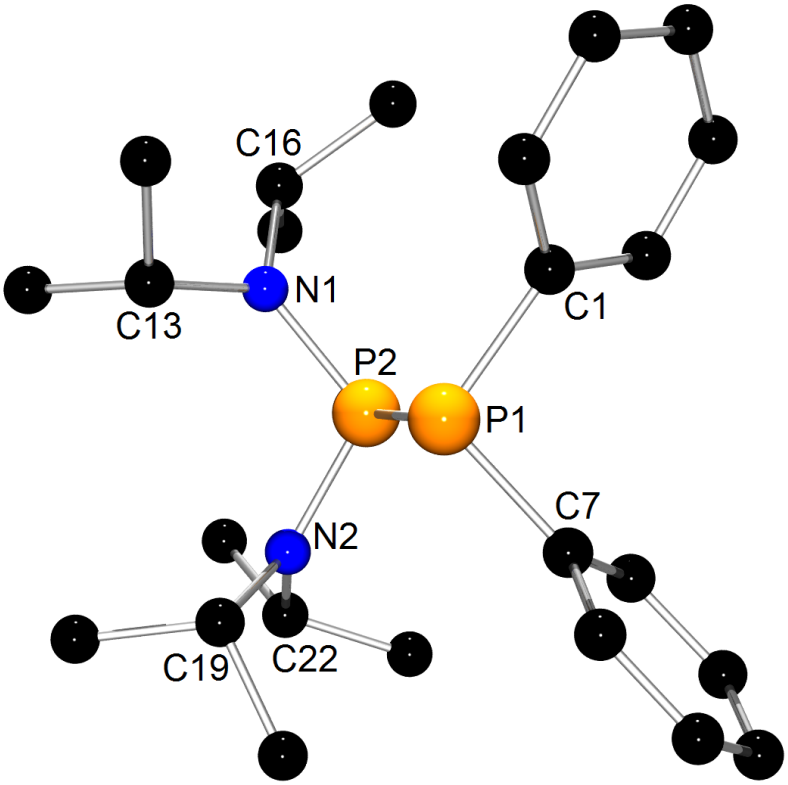

Fig. S3. Structure of (iPr$_2$N)$_2$PhPPPh$_2$ (**8**)

X-ray structure of 9

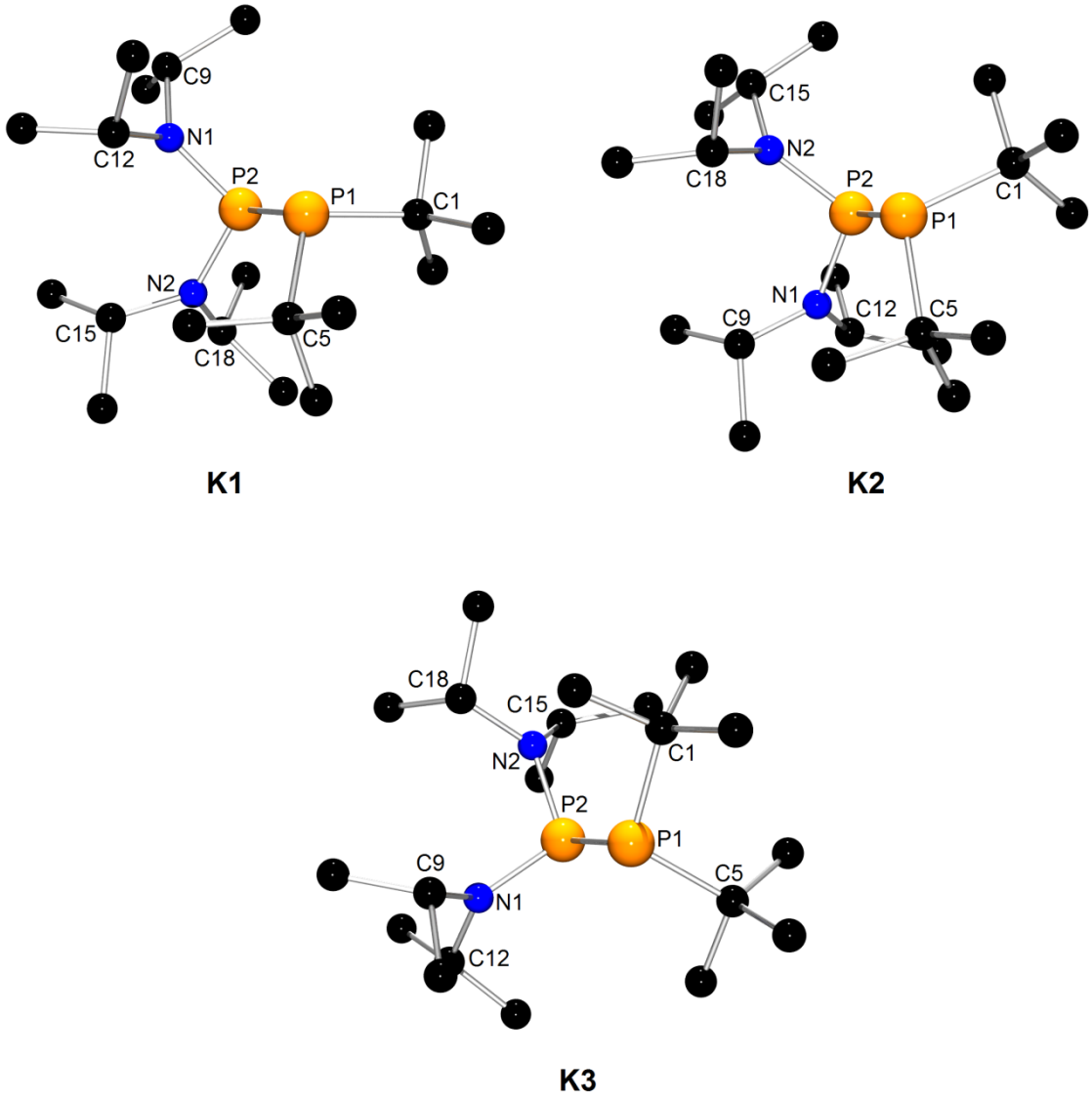

Fig. S4. Structure of conformers **K1**, **K2** and **K3** of (iPr$_2$N)$_2$PPtBu$_2$ (**9**)

X-ray structure of 10

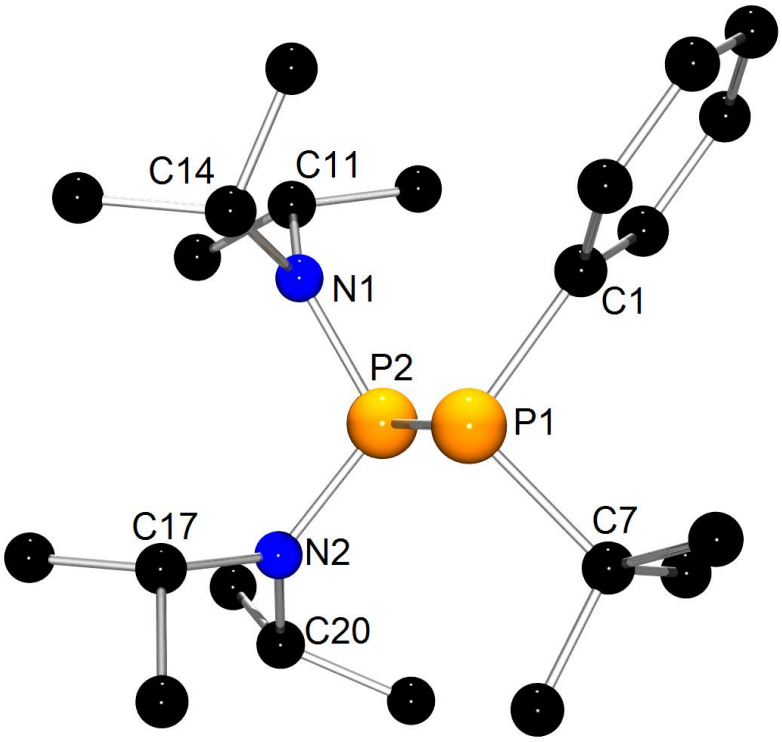

Fig. S5. Structure of (iPr$_2$N)$_2$PtBuPh (**10**)

X-ray structure of 12

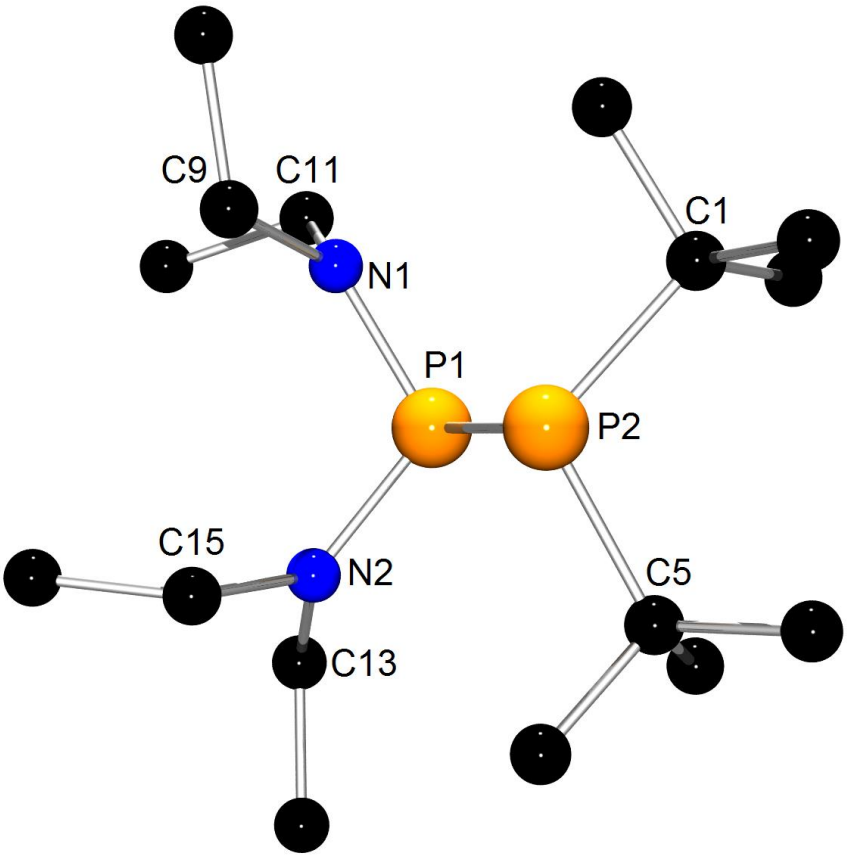

Fig. S6. Structure of $(Et_2N)_2PPtBu_2$ (**12**)

X-ray structure of 14

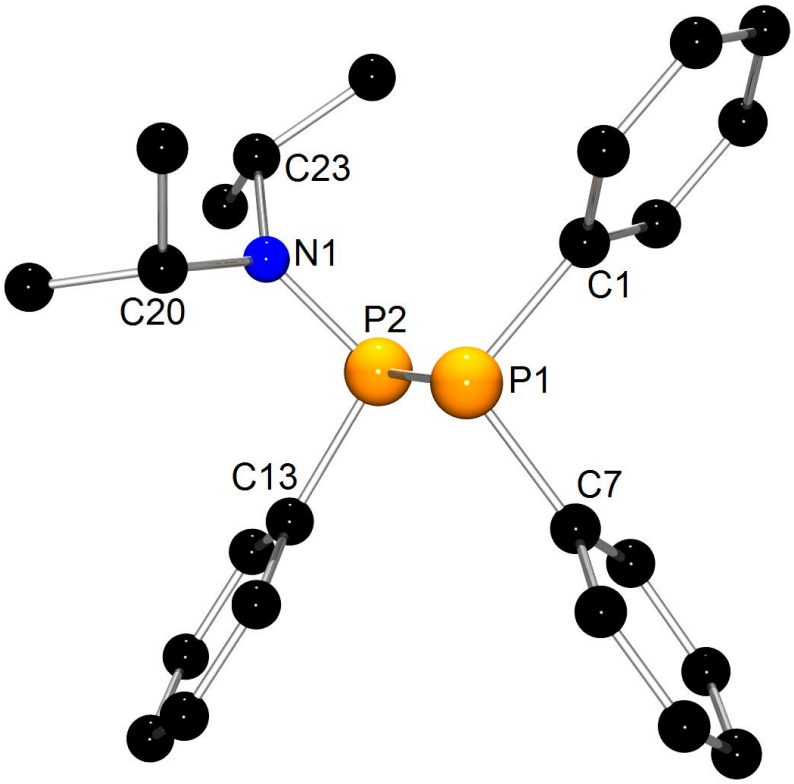

Fig. S7. Structure of (iPr$_2$N)PhPPPh$_2$ (**14**)

X-ray structure of 17

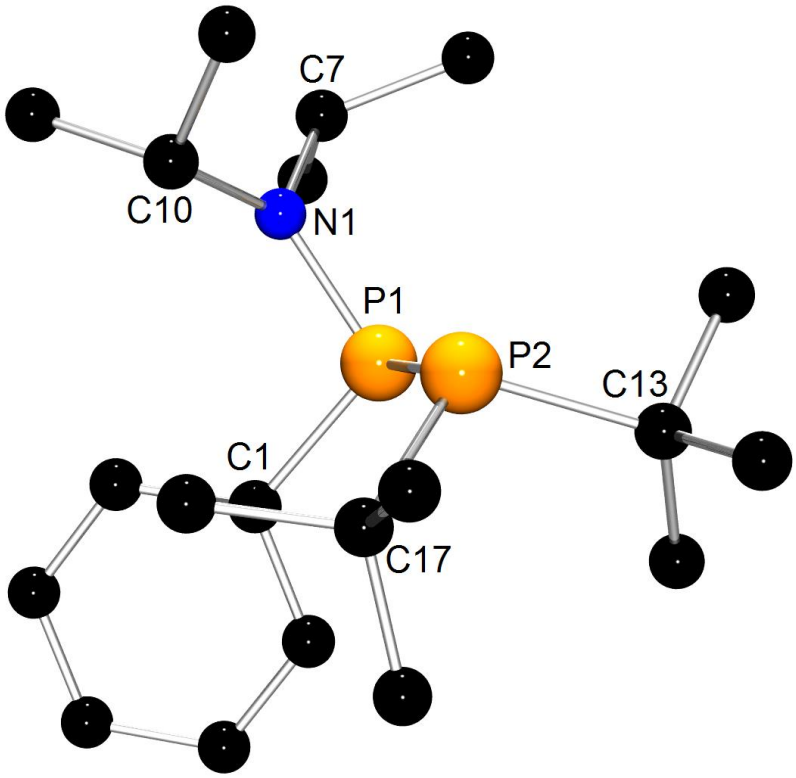

Fig. S8. Structure of (*i*Pr$_2$N)PhPP*t*Bu$_2$ (**17**)

X-ray structure of 21

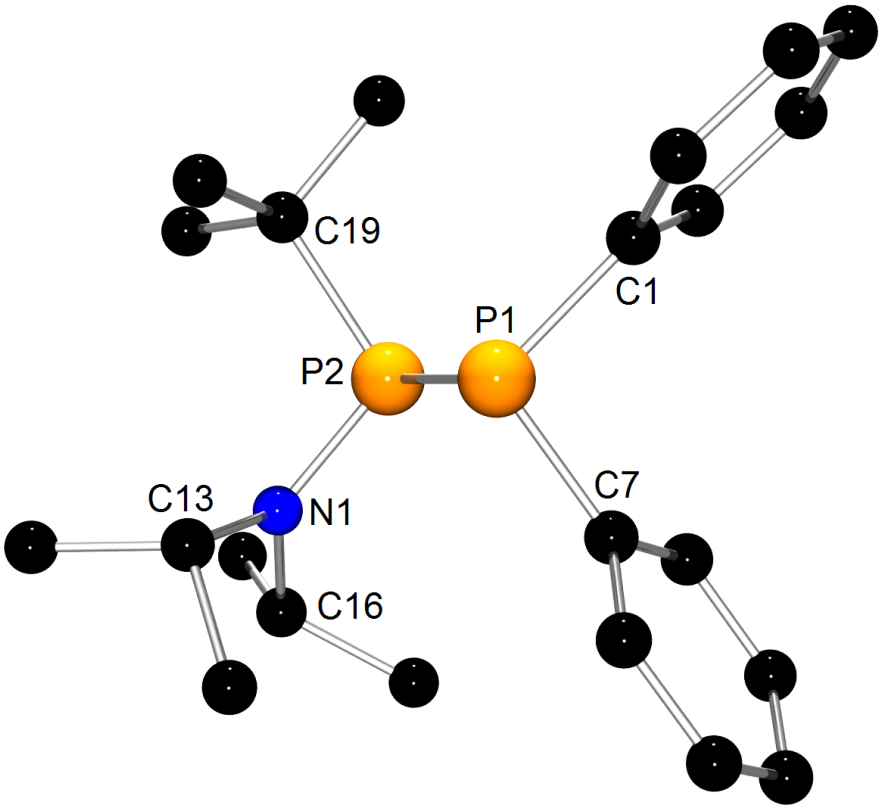

Fig. S9. Structure of (iPr$_2$N)tBuPPPh$_2$ (**21**)

X-ray structure of 23

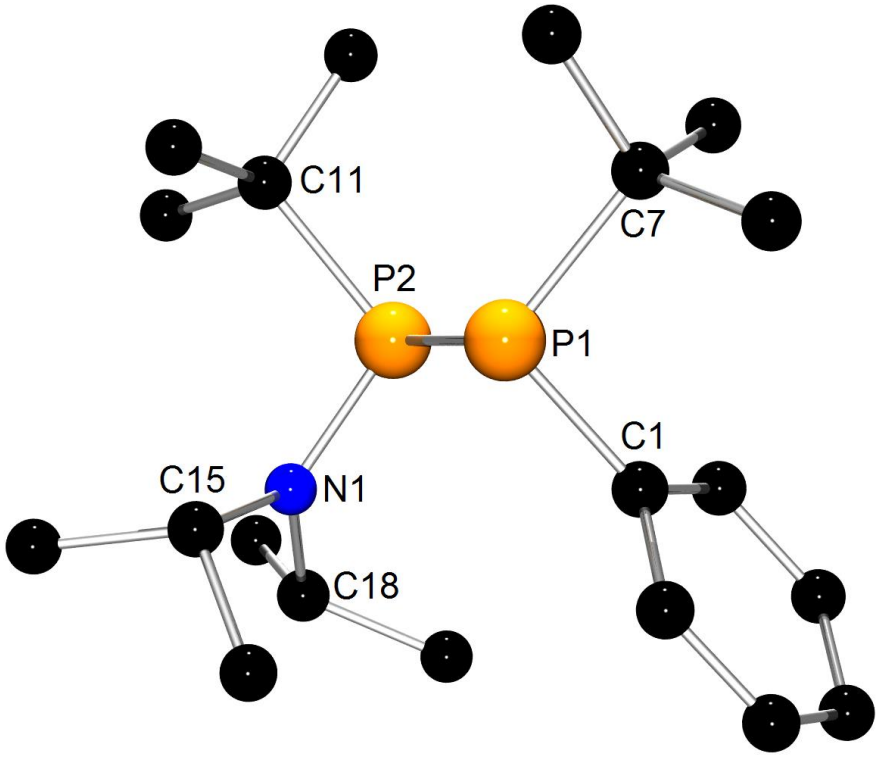

Fig. S10. Structure of *rac*-(*i*Pr$_2$N)*t*BuPP*t*BuPh (**23**)

X-ray structure of 24

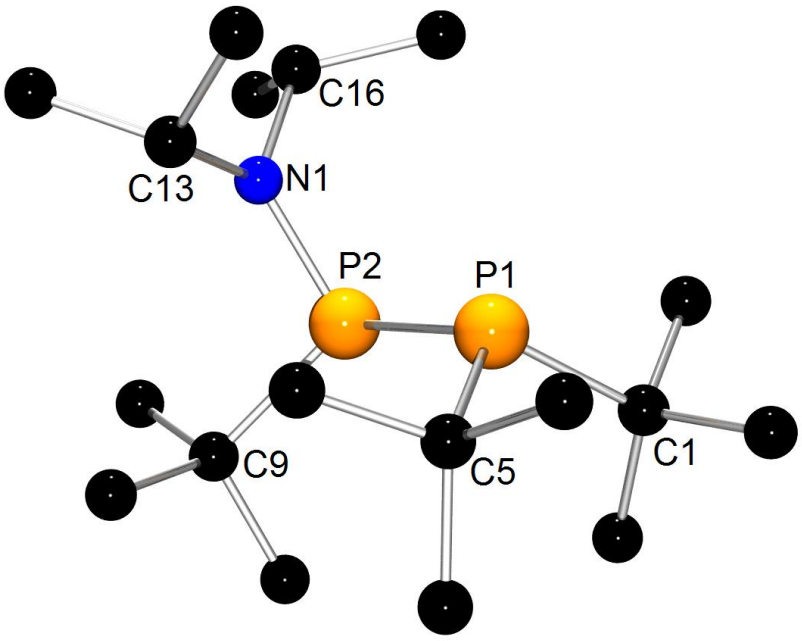

Fig. S11. Structure of (iPr$_2$N)tBuP$P$$tBu_2$ (**24**)

X-ray structure of 25

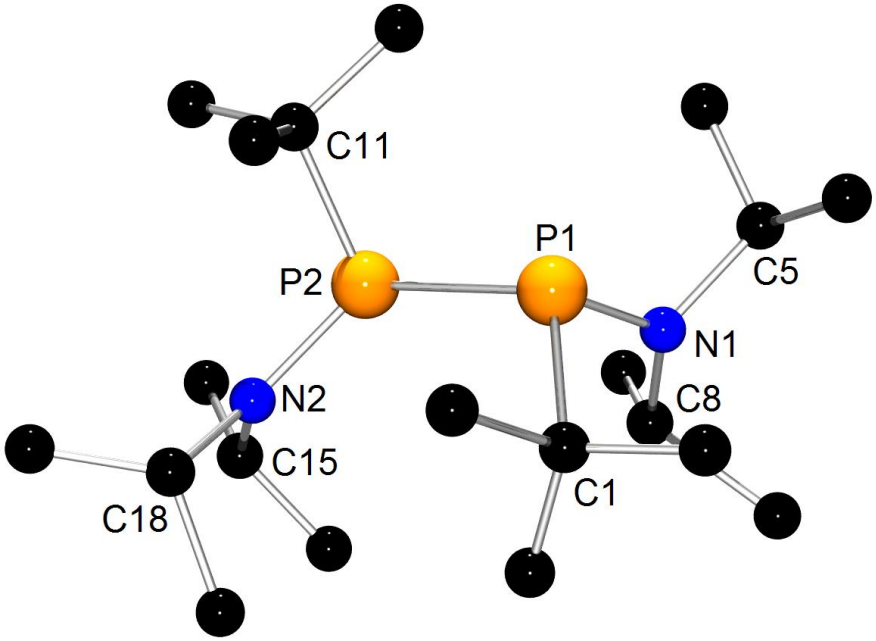

Fig. S12. Structure of *meso*-(*i*Pr$_2$N)*t*BuPP(*i*Pr$_2$N)*t*Bu (**25**)

X-ray structure of 28

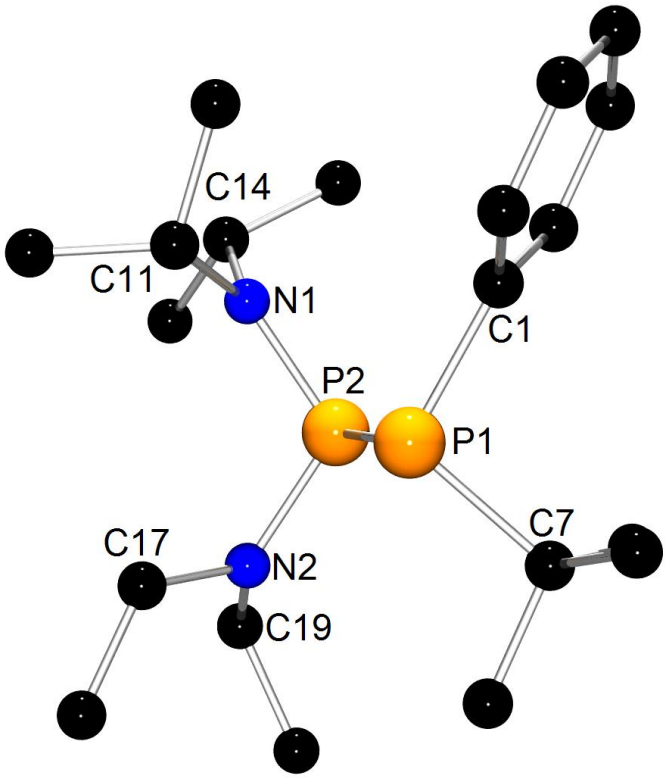

Fig. S13. Structure of *meso*-(Et_2N)(iPr_2N)PP*t*BuPh (**28**)

Table. S1. Selected bond lengths and geometries around phosphorus and nitrogen atoms for compounds 3, 6, 8, 9, 10, 12, 14, 17, 21, 23, 24, 25 and 28

C.	P1-P2 (Å)	P1-C (Å)	P2-C (Å)	P1-N (Å)	P2-N (Å)	ΣP1(°) ΣP2(°)	ΣN1(°) ΣN2(°)
3	2.237(1)	1.850(3) 1.840(3)	1.912(3) 1.902(3)			302.53 310.07	
6	2.225(1)[b]	1.844(3)[b] 1.843(3)[b]	1.837(3)[b] 1.889(3)[b]			300.90[b] 304.49[b]	
8	2.2444(6)	1.841(1) 1.838(1)			1.696(1) 1.696(1)	300.38 310.49	359.67 359.98
9	2.295(2)[a]	1.908(6)[a] 1.894(7)[a]			1.702(5)[a] 1.709(6)[a]	320.10[a] 320.65[a]	357.60[a] 359.10[a]
10	2.252(1)	1.837(2) 1.903(3)			1.700(3) 1.707(2)	305.69 310.04	359.99 358.29
12	2.2603(6)	1.908(1) 1.912(2)			1.695(2) 1.705(1)	309.14 312.91	354.61 357.60
14	2.229(1)	1.843(5) 1.834(5)	1.844(5)		1.684(4)	302.30 305.01	359.56
17	2.2445(5)	1.835(1)	1.907(2) 1.902(1)	1.692(1)		319.79 323.37	358.88
21	2.2432(9)	1.843(2) 1.846(2)	1.895(2)		1.693(2)	302.53 309.19	359.29
23	2.265(2)	1.849(6) 1.906(6)	1.907(6)		1.704(5)	308.21 310.20	359.72
24	2.2508(6)	1.900(3) 1.904(2)	1.913(2)		1.692(2)	330.04 330.23	357.77
25	2.314(3)	1.85(1)	1.94(2)	1.68(1)	1.65(3)	329.07 318.41	359.74 357.67
28	2.228(1)	1.834(3) 1.894(4)			1.694(2) 1.705(3)	305.92 309.03	359.73 345.97

(a) average value for three conformers (b) average value for two enantiomers

X-ray structure of oxidized 18/19

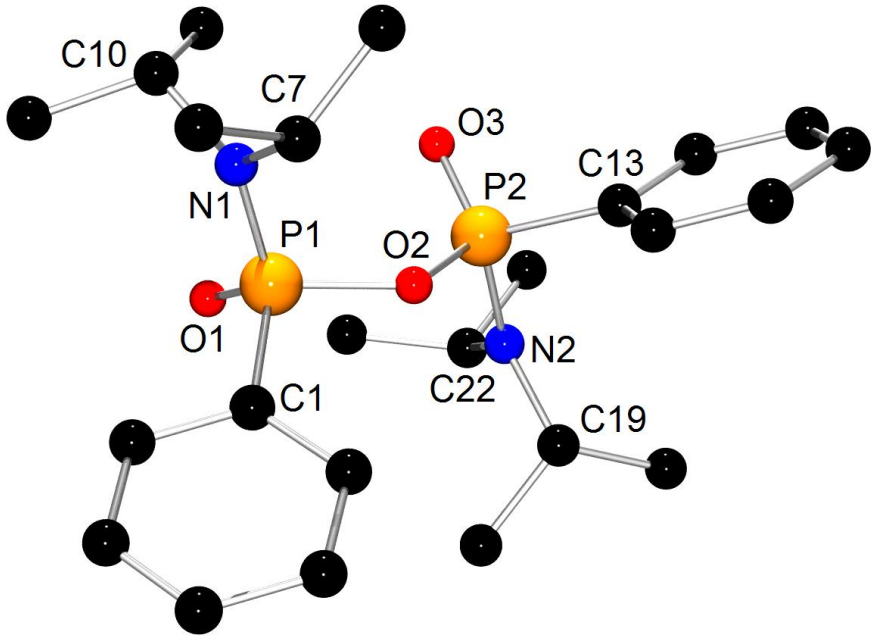

Fig. S14. Structure of (iPr$_2$N)PhP(O)-O-P(O)(iPr$_2$N)Ph (oxidized 18/19)

Table. S2. Selected structural parameters of (iPr$_2$N)PhP(O)-O-P(O)(iPr$_2$N)Ph (oxidized 18/19)

Bond lengths [Å]		**Bond angles [°]**	
P1-O1	1.400(1)	P1-O2-P2	124.2
P1-O2	1.635	C7-N1-P1	119.1(5)
P1-N1	1.641(6)	C10-N1-P1	122.9(6)
P1-C1	1.817(5)	C7-N1-C10	117.9(6)
N1-C7	1.480(1)		
N1-C10	1.480(1)		

Table. S3. Crystallographic parameters of presented structures

	3	**6**	**8**
Empirical formula	$C_{20}H_{28}P_2$	$C_{22}H_{24}P_2$	$C_{24}H_{38}N_2P_2$
M_r [g mol^{-1}]	330.36	350.35	416.5
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1
a [Å]	17.4482(13)	12.3090(3)	9.3641(18)
b [Å]	6.2244(3)	20.0750(4)	10.299(2)
c [Å]	17.8241(11)	16.5350(4)	12.778(3)
α [°]	90	90	91.018(17)
β [°]	98.474(6)	109.950(2)	95.368(16)
γ [°]	90	90	105.102(16)
V [Å^3]	1914.6(2)	3840.66(16)	1183.4(4)
Z	4	8	2
Calculated density [g cm^{-3}]	1.146	1.212	1.169
T [K]	120	130	120
μ [mm^{-1}]	0.223	0.226	0.196
λ [Å] (Mo/CuKα)	0.71073	0.71073	0.71073
Final R indices	R_1 = 0.0812	R_1 = 0.0583	R_1 = 0.0371
[*I>2σ(I)*]	*w*R_2 = 0.225	*w*R_2 = 0.1441	*w*R_2 = 0.0977
R indices (all data)	R_1 = 0.1179	R_1 = 0.0748	R_1 = 0.0442
	wR_2 = 0.2643	*w*R_2 = 0.1551	*w*R_2 = 0.1026
CCDC	1560642	1560638	1560637

	9	**10**	**12**
Empirical formula	$C_{20}H_{46}N_2P_2$	$C_{22}H_{42}N_2P_2$	$C_{16}H_{38}N_2P_2$
M_r [g mol^{-1}]	376.55	396.51	320.42
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	$Pna2_1$	$P2_1/n$	P-1
a [Å]	15.252(3)	12.3408(8)	8.5142(8)
b [Å]	10.681(2)	14.1744(8)	9.8037(10)
c [Å]	43.197(9)	14.1341(10)	12.7706(12)
α [°]	90	90	100.535(8)

β [°]	90	107.363(5)	96.438(8)
γ [°]	90	90	109.184(7)
V [Å^3]	7037.0(2)	2359.7(3)	972.63(17)
Z	4	4	2
Calculated density [g cm^{-3}]	1.066	1.116	1.094
T [K]	123	120	120
μ [mm^{-1}]	0.191	0.193	0.219
λ [Å] (Mo/CuKα)	0.71073	0.71073	0.71073
Final R indices	R_1 = 0.0615	R_1 = 0.0682	R_1 = 0.0449
[$I>2\sigma(I)$]	wR_2 = 0.1071	wR_2 = 0.1381	wR_2 = 0.1241
R indices (all data)	R_1 = 0.1417	R_1 = 0.1369	R_1 = 0.0512
	wR_2 = 0.1349	wR_2 = 0.1576	wR_2 = 0.1293
CCDC	1560636	1560635	1576835

	14	**17**	**21**
Empirical formula	$C_{24}H_{29}NP_2$	$C_{20}H_{37}NP_2$	$C_{22}H_{33}NP_2$
M_r [g mol^{-1}]	393.42	353.44	373.43
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	C2/c	P-1	P-1
a [Å]	37.194(2)	9.1194(5)	9.3935(5)
b [Å]	8.2421(4)	10.2329(6)	11.1597(6)
c [Å]	15.7504(9)	13.1351(7)	11.2752(6)
α [°]	90	78.296(4)	110.014(4)
β [°]	113.193(4)	89.626(4)	100.623(4)
γ [°]	90	63.969(4)	95.397(4)
V [Å^3]	4438.1(5)	1073.75(11)	1075.63(10)
Z	8	2	2
Calculated density [g cm^{-3}]	1.178	1.097	1.153
T [K]	120	120	120
μ [mm^{-1}]	0.204	0.204	0.207
λ [Å] (Mo/CuKα)	0.71073	0.71073	0.71073
Final R indices	R_1 = 0.077	R_1 = 0.0384	R_1 = 0.0637
[$I>2\sigma(I)$]	wR_2 = 0.2279	wR_2 = 0.1104	wR_2 = 0.1673
R indices (all data)	R_1 = 0.1032	R_1 = 0.0513	R_1 = 0.0801

	wR_2 = 0.2517	wR_2 = 0.1205	wR_2 = 0.1792
CCDC	1560634	1560639	1576836

	23	**24**	**25**
Empirical formula	$C_{20}H_{37}NP_2$	$C_{18}H_{41}NP_2$	$C_{20}H_{46}N_2P_2$
M_r [g mol^{-1}]	353.45	333.46	376.53
Crystal system	Orthorhombic	Triclinic	Orthorhombic
Space group	$Pca2_1$	P-1	$P2_12_12_1$
a [Å]	14.3144(10)	8.5271(5)	10.3368(3)
b [Å]	12.1120(9)	9.5290(5)	13.5116(7)
c [Å]	12.1179(10)	13.9449(9)	17.2599(7)
α [°]	90	93.186(5)	90
β [°]	90	90.722(5)	90
γ [°]	90	110.634(4)	90
V [Å^3]	2101.0(3)	1058.13(11)	2410.63(17)
Z	4	2	4
Calculated density [g cm^{-3}]	1.117	1.047	1.037
T [K]	120	130	120
μ [mm^{-1}]	1.857	0.203	0.185
λ [Å] (Mo/CuKα)	1.54186	0.71073	0.71073
Final R indices	R_1 = 0.0602	R_1 = 0.0498	R_1 = 0.0965
[*I>2σ(I)*]	wR_2 = 0. 0.1620	wR_2 = 0.1255	wR_2 = 0.2623
R indices (all data)	R_1 = 0.0668	R_1 = 0.0776	R_1 = 0.1232
	wR_2 = 0.1785	wR_2 = 0.1396	wR_2 = 0.2943
CCDC	1585541	1560641	1576833

	28	**ox_18/19**
Empirical formula	$C_{20}H_{38}N_2P_2$	$C_{24}H_{38}N_2O_3P_2$
M_r [g mol^{-1}]	368.46	464.50
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	Fdd2
a [Å]	9.9020(5)	23.2044(13)
b [Å]	18.9837(7)	28.9097(17)
c [Å]	11.9159(6)	7.4145(4)
α [°]	90	90
β [°]	95.506(4)	90
γ [°]	90	90
V [Å^3]	2229.58(18)	4973.9(5)
Z	4	8
Calculated density [g cm^{-3}]	1.099	1.241
T [K]	120	120
μ [mm^{-1}]	0.200	0.202
λ [Å] (Mo/CuKα)	0.71073	0.71073
Final R indices	R_1 = 0.0656	R_1 = 0.077
[*I>2σ(I)*]	*w*R_2 = 0.149	*w*R_2 = 0.2154
R indices (all data)	R_1 = 0.1617	R_1 = 0.1357
	wR_2 = 0.1872	*w*R_2 = 0.2993
CCDC	1560640	1576834

NMR spectra of synthesized compounds

$^{31}P\{^{1}H\}$ NMR spectra of diphosphanes in reaction mixtures

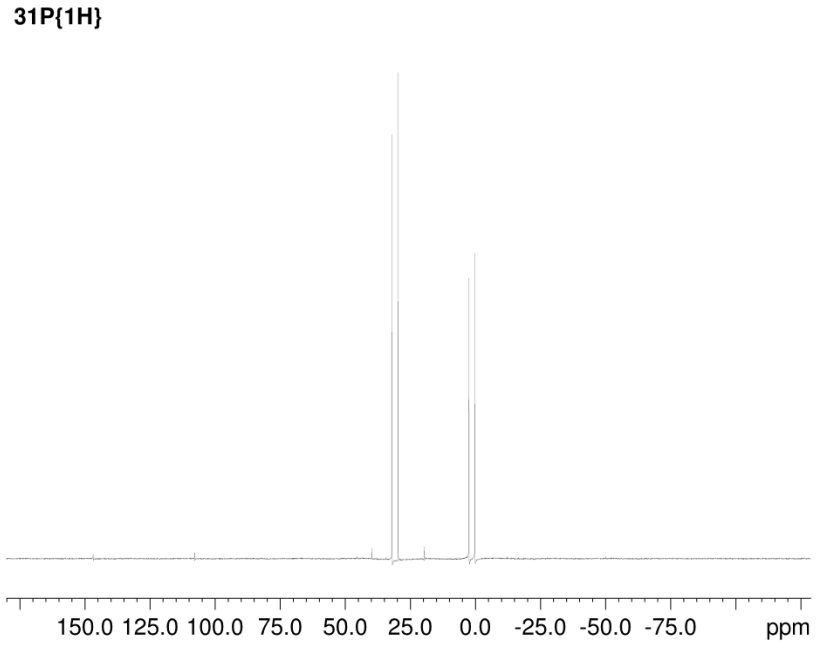

Fig. S15. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of reaction mixture of *t*Bu$_2$PP*t*BuPh **2** in THF

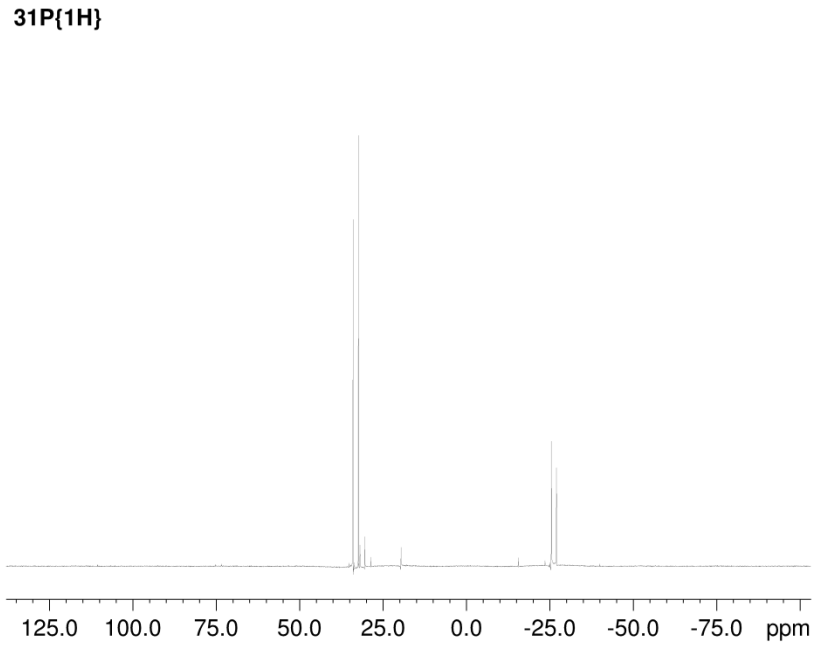

Fig. S16. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of reaction mixture of *t*Bu_2PPPh_2 **3** in THF

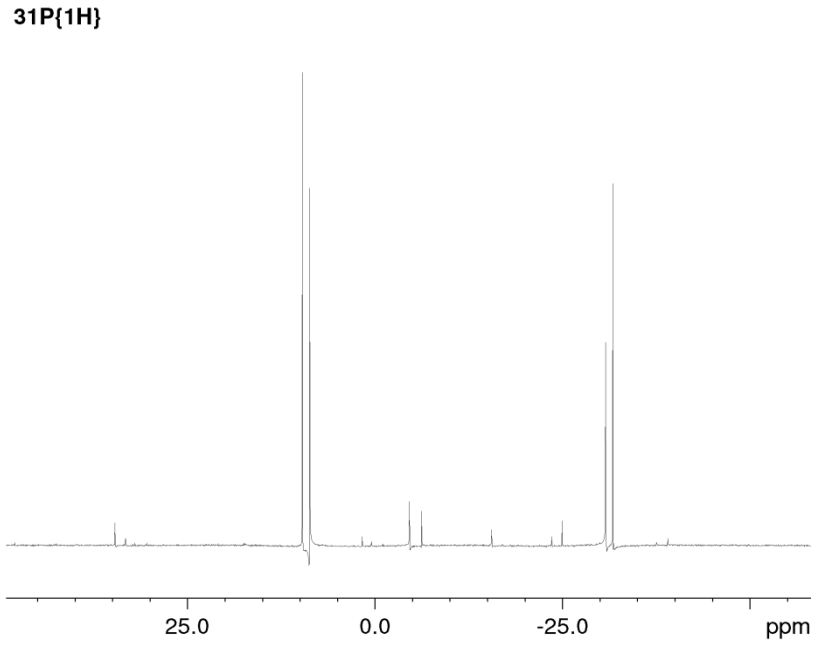

Fig. S17. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of reaction mixture of *t*BuPhPPPh$_2$ **6** in THF

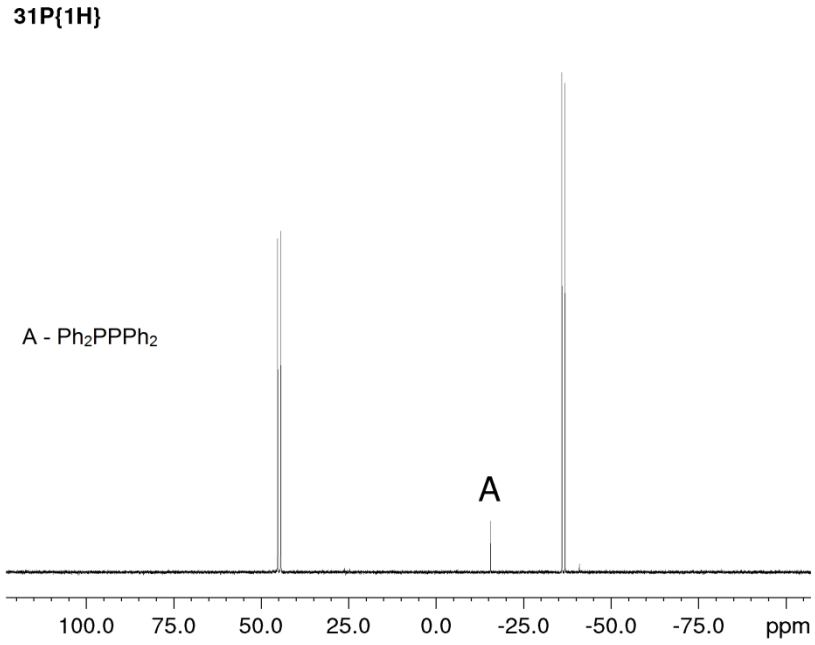

Fig. S18. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of reaction mixture of (iPr$_2$N)$_2$PPPh$_2$ **8** in THF

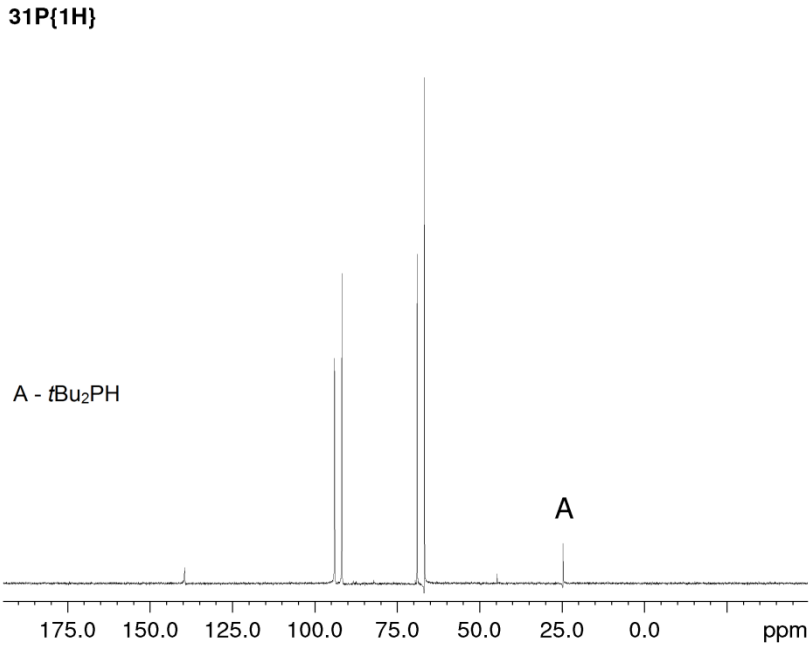

Fig. S19. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of reaction mixture of $(i\mathrm{Pr}_2\mathrm{N})_2\mathrm{PP}t\mathrm{Bu}_2$ **9** in THF

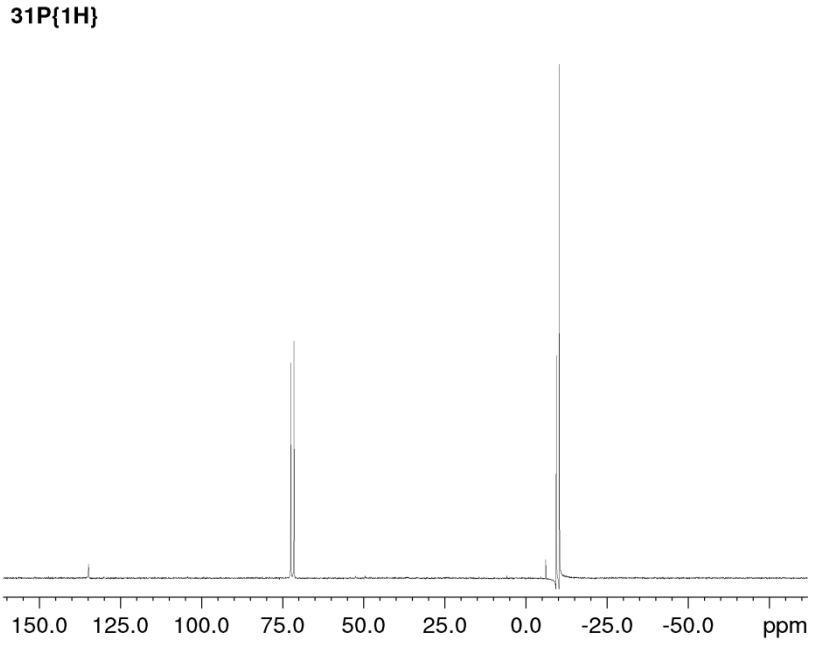

Fig. S20. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of reaction mixture of $(i\mathrm{Pr}_2\mathrm{N})_2\mathrm{PP}t\mathrm{BuPh}$ **10** in THF

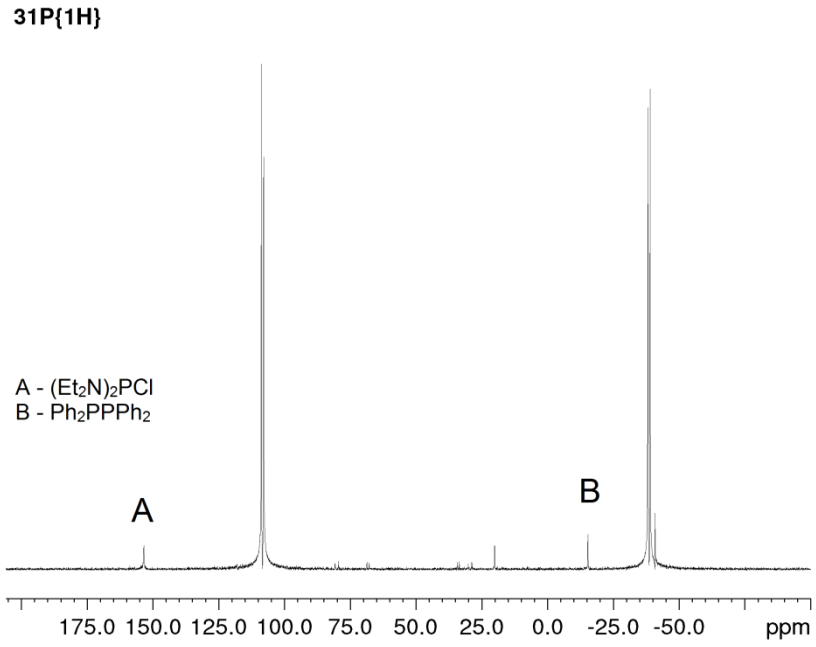

Fig. S21. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of reaction mixture of $(Et_2N)_2PPPh_2$ **11** in THF

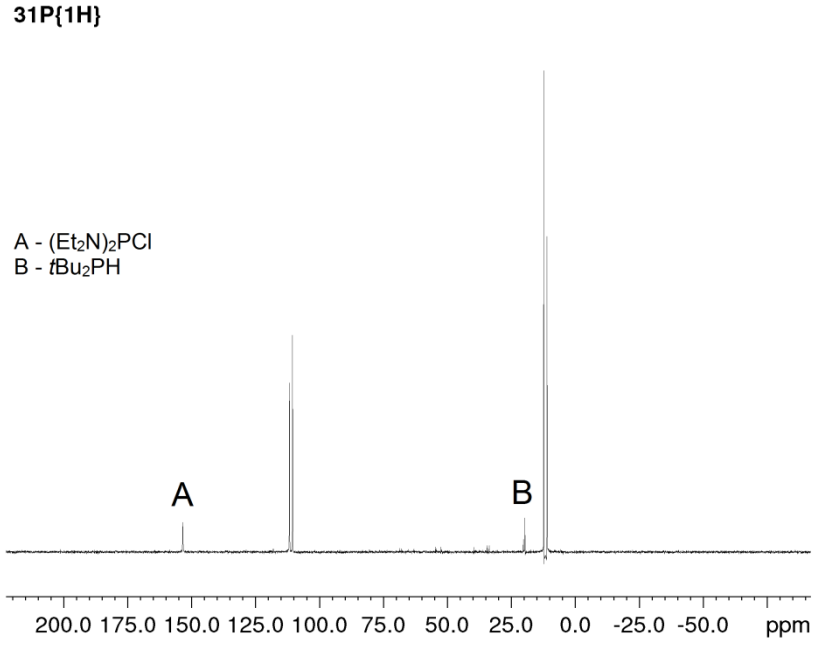

Fig. S22. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of reaction mixture of $(Et_2N)_2PP$*t*Bu_2 **12** in THF

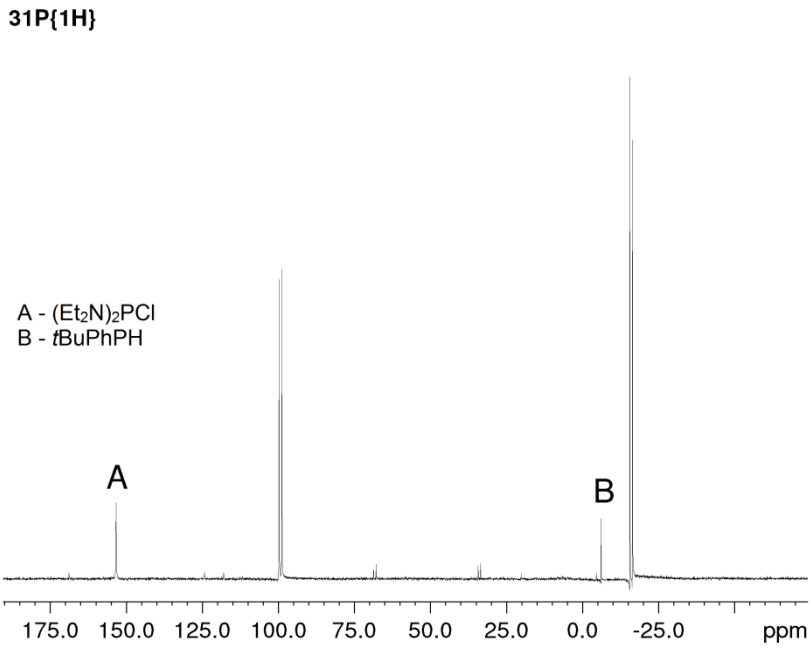

Fig. S23. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of reaction mixture of $(Et_2N)_2PPtBuPh$ **13** in THF

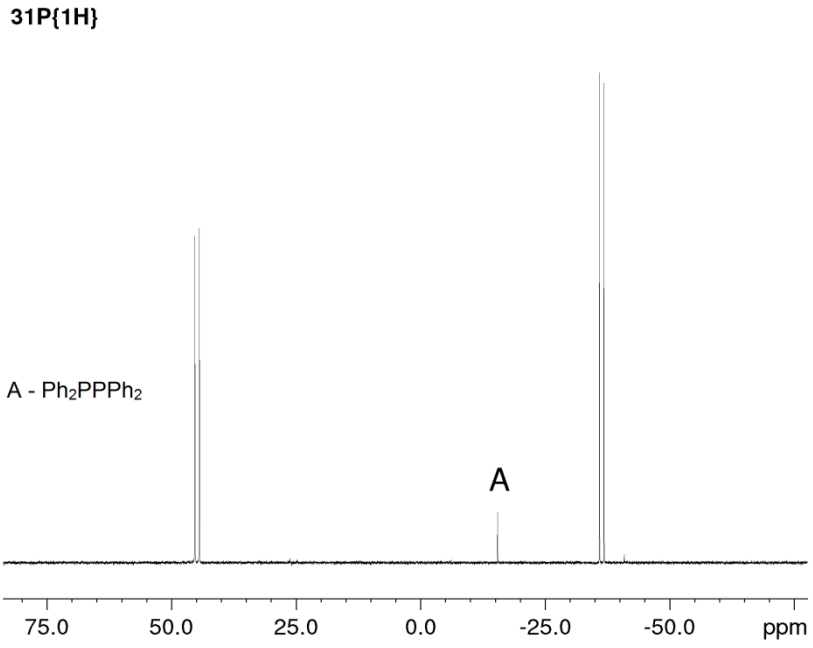

Fig. S24. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of reaction mixture of $(iPr_2N)PhPPPh_2$ **14** in THF

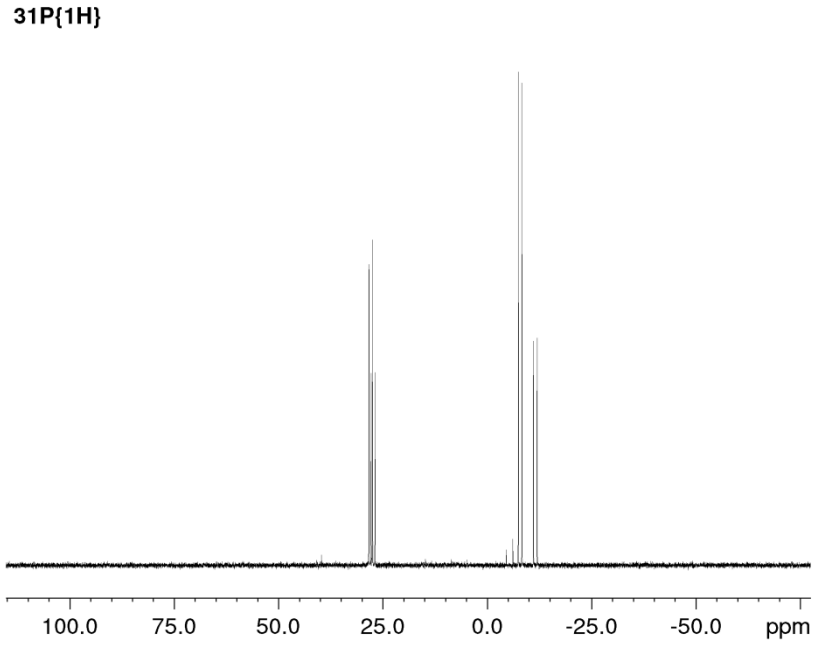

Fig. S25. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of reaction mixture of pseudo-*meso*-(*i*Pr_2N)PhPP*t*BuPh **15** and pseudo-*rac*-(*i*Pr_2N)PhPP*t*BuPh **16** in THF

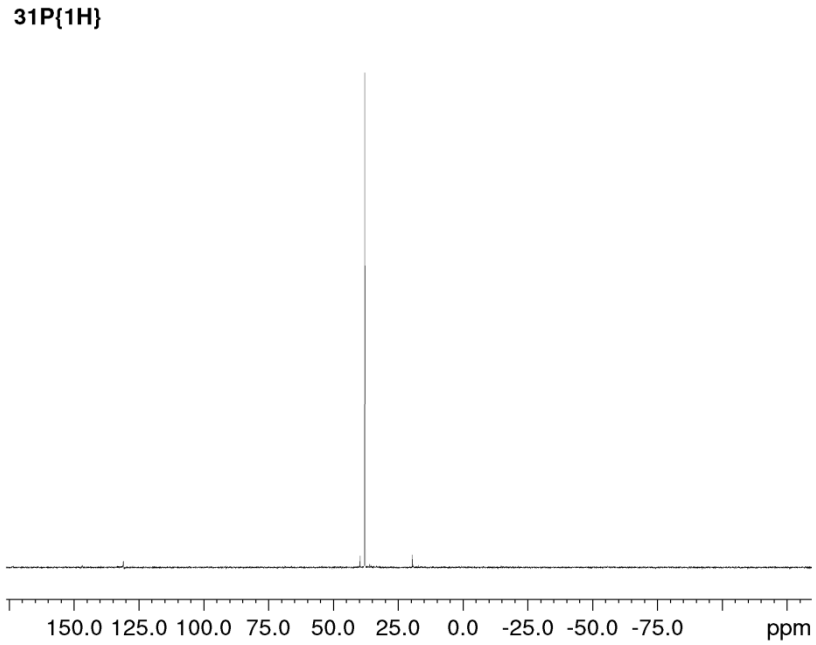

Fig. S26. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of reaction mixture of (*i*Pr_2N)PhPP*t*Bu_2 **17** in THF

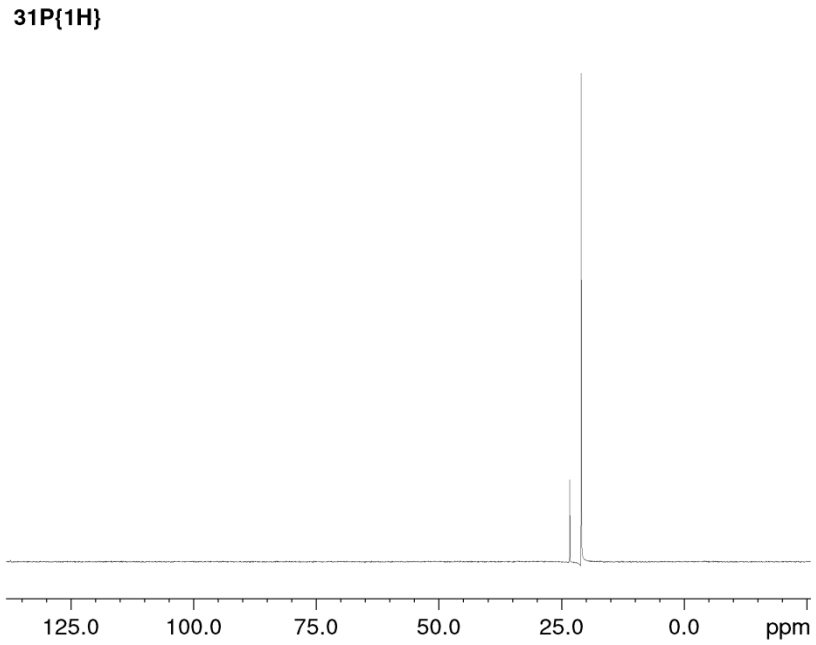

Fig. S27. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of reaction mixture of *meso*-(*i*Pr_2N)PhPP(*i*Pr_2N)Ph **18** and *rac*-(*i*Pr_2N)PhPP(*i*Pr_2N)Ph **19** in THF

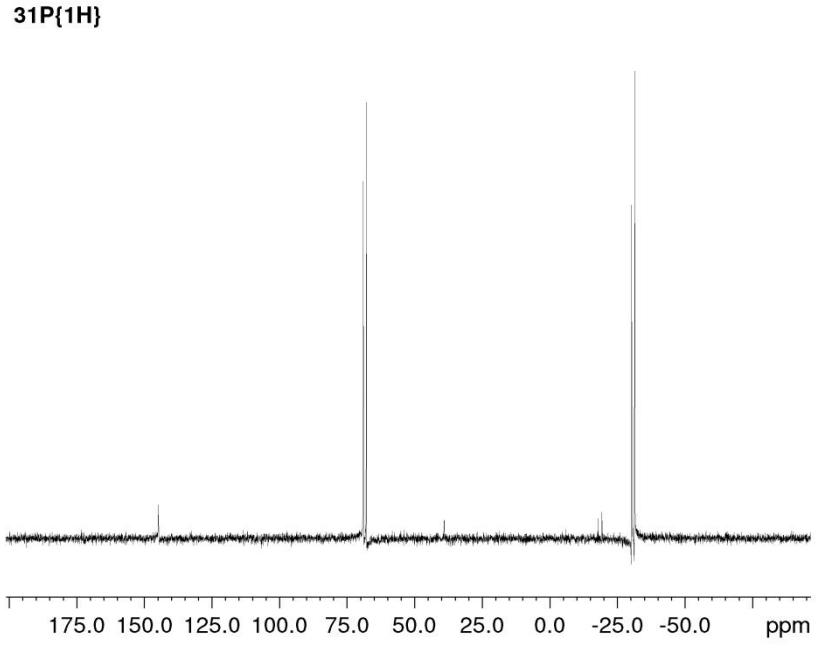

Fig. S28. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of reaction mixture of (*i*Pr_2N)tBuPPPh_2 **21** in THF

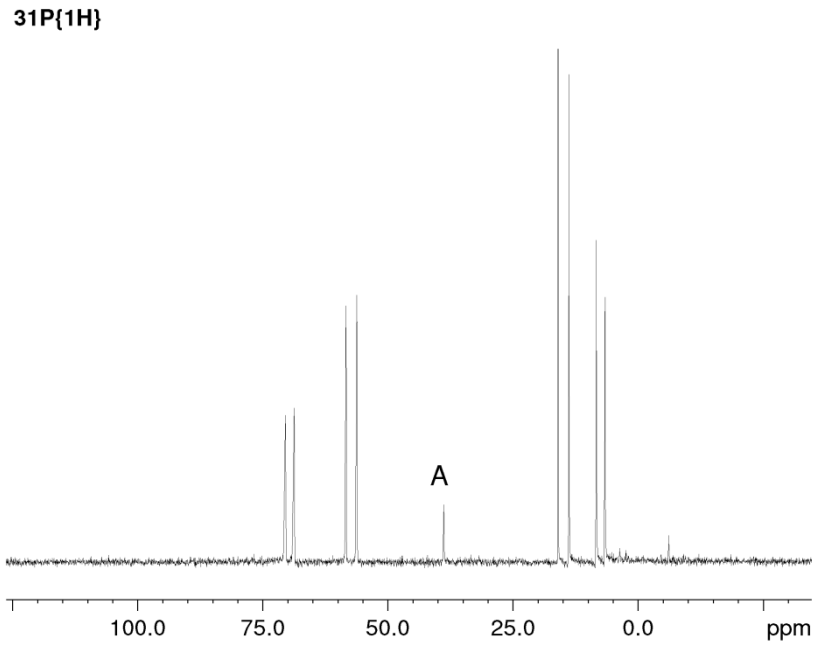

Fig. S29. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of reaction mixture of pseudo-*meso*-(*i*Pr$_2$N)*t*BuPP*t*BuPh **22** and pseudo-*rac*-(*i*Pr$_2$N)*t*BuPP*t*BuPh **23**

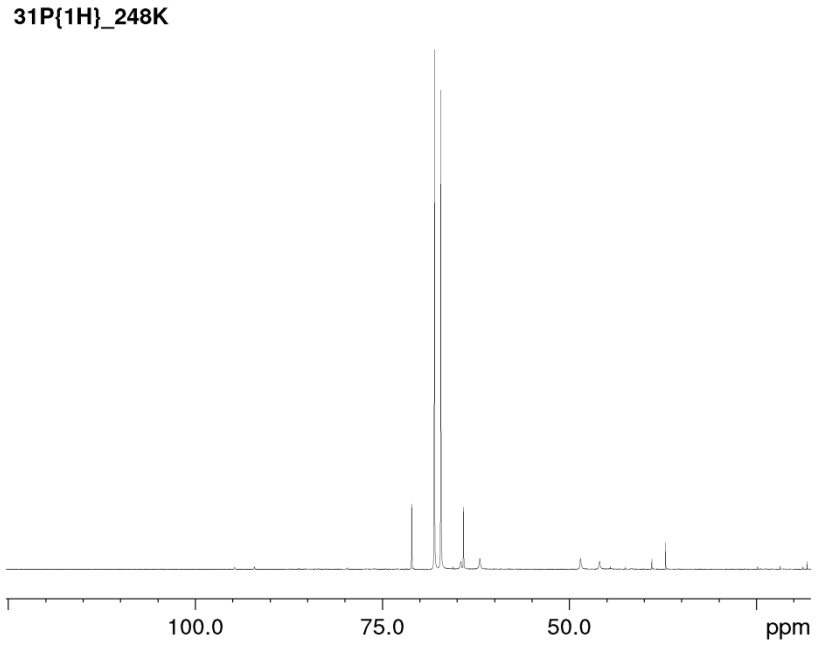

Fig. S30. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of reaction mixture of (*i*Pr$_2$N)*t*BuPP*t*Bu$_2$ **24** in THF

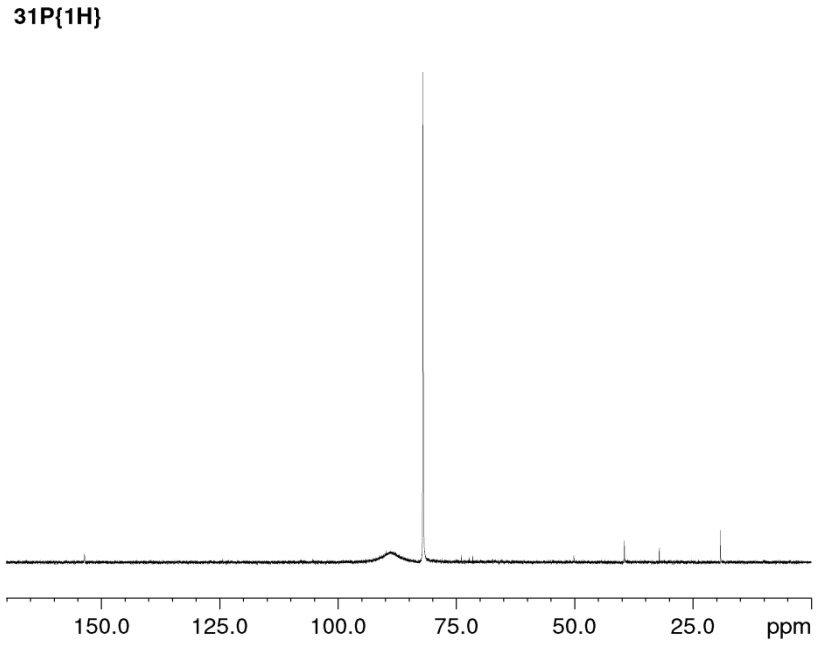

Fig. S31. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of reaction mixture of *meso*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **25** and *rac*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **26** in THF

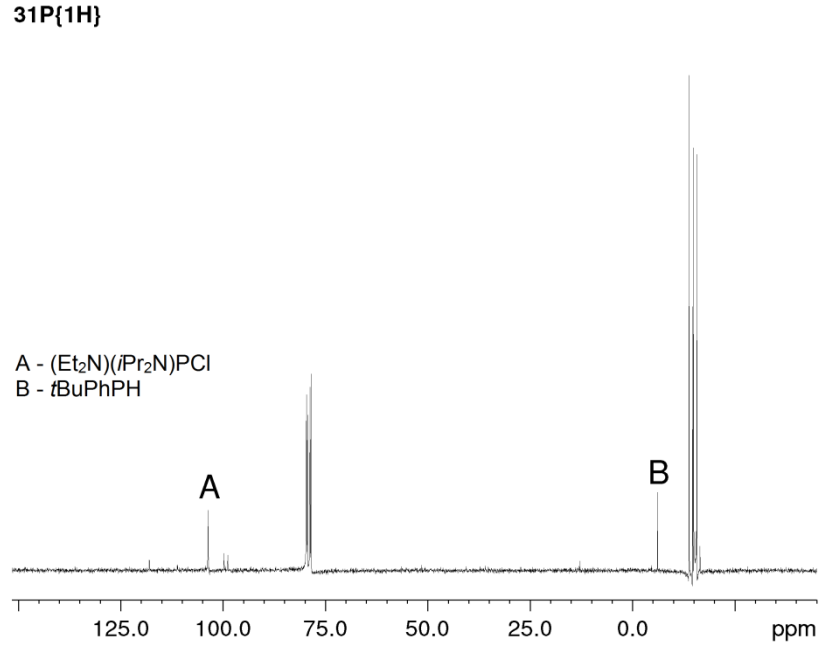

Fig. S32. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of reaction mixture of pseudo-*meso*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **28** and pseudo-*rac*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **29** in THF

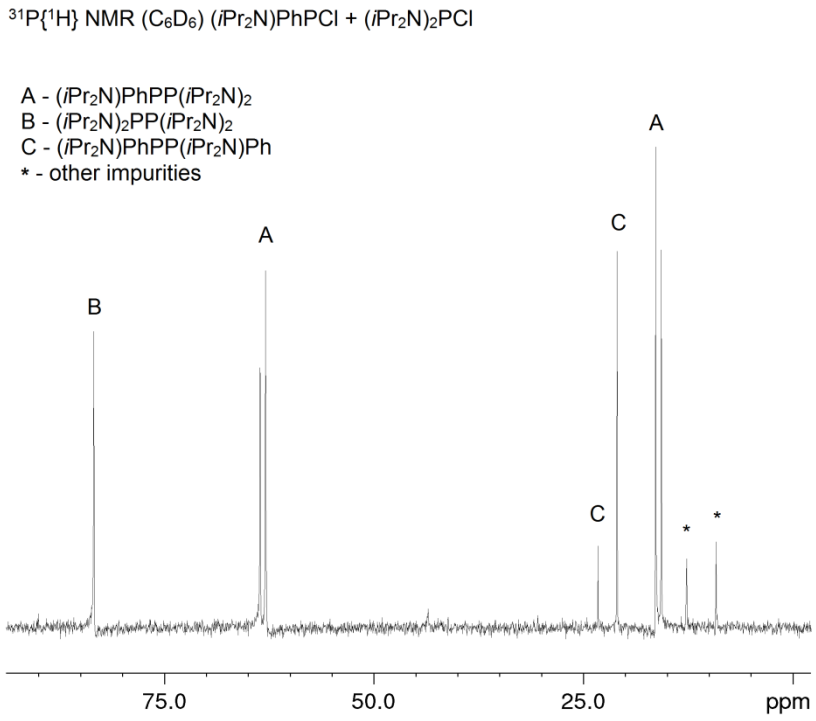

Fig. S33. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of $(i\mathrm{Pr_2N})\mathrm{PhPCl}$ + $(i\mathrm{Pr_2N})_2\mathrm{PCl}$ + Mg reaction mixture

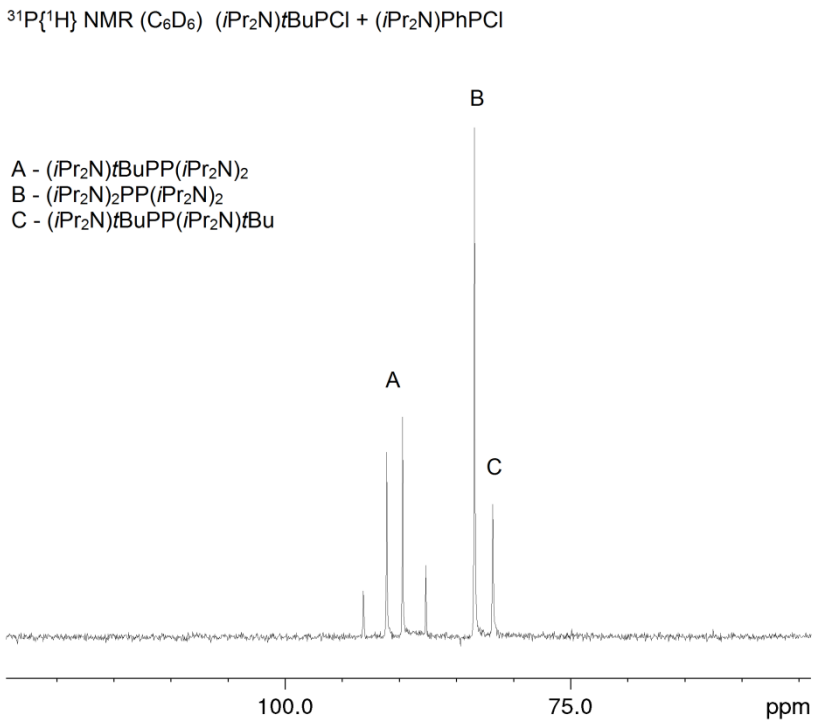

Fig. S34. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of $(i\mathrm{Pr_2N})t\mathrm{BuPCl}$ + $(i\mathrm{Pr_2N})_2\mathrm{PCl}$ + Mg reaction mixture

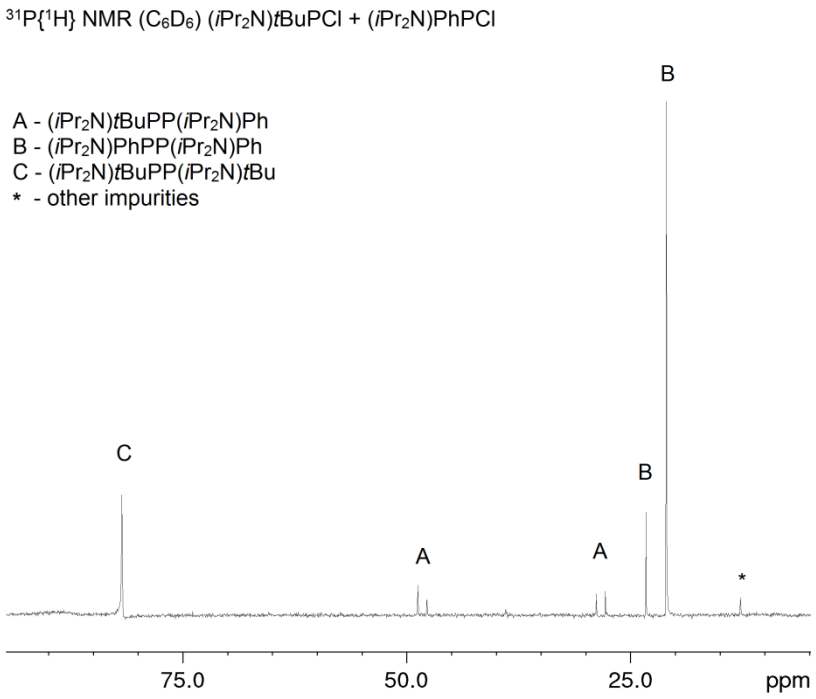

Fig. S35. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of (iPr$_2$N)tBuPCl + (iPr$_2$N)PhPCl + Mg reaction mixture

1D and 2D NMR spectra of isolated diphosphanes

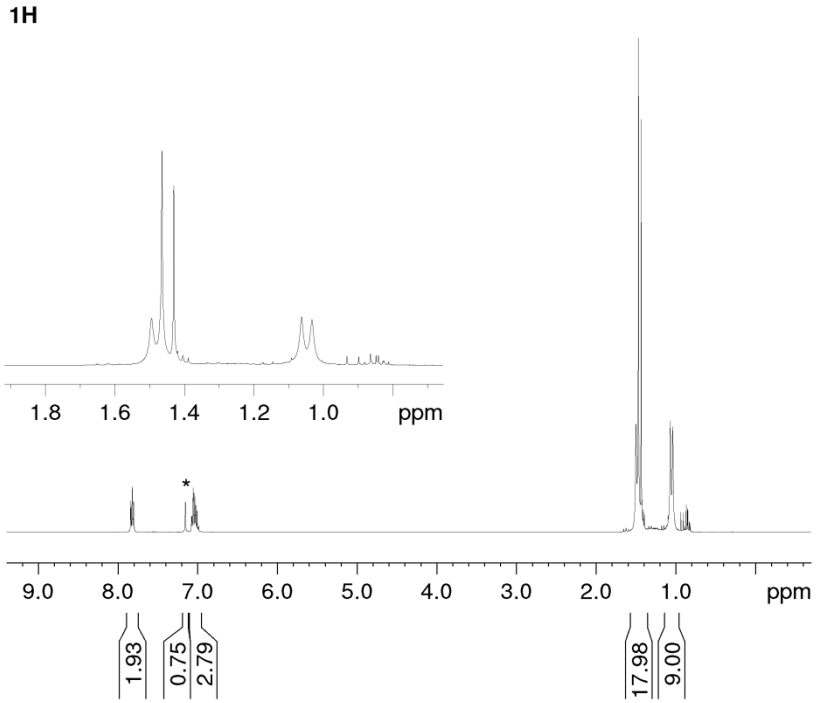

Fig. S36. ^{1}H NMR (C_6D_6) spectra of isolated tBu$_2$PPtBuPh **2**

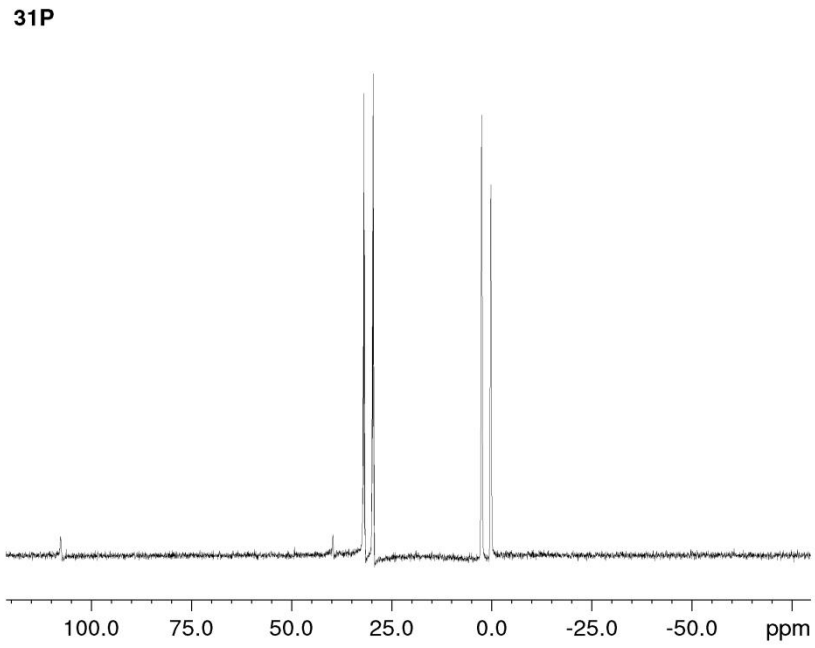

Fig. S37. ^{31}P NMR (C_6D_6) spectra of isolated *t*Bu_2PP*t*BuPh **2**

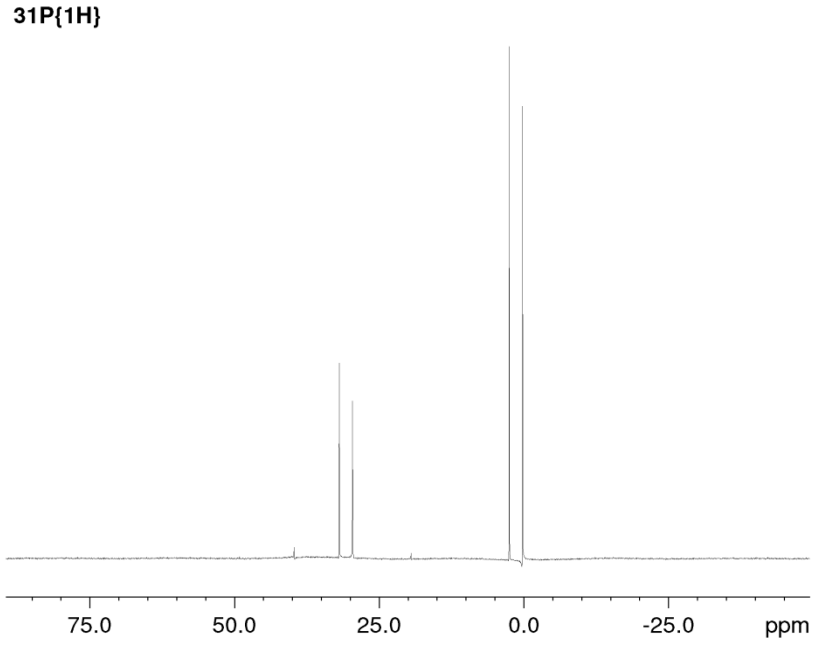

Fig. S38. $^{31}P\{^1H\}$ NMR (C_6D_6) spectra of isolated *t*Bu_2PP*t*BuPh **2**

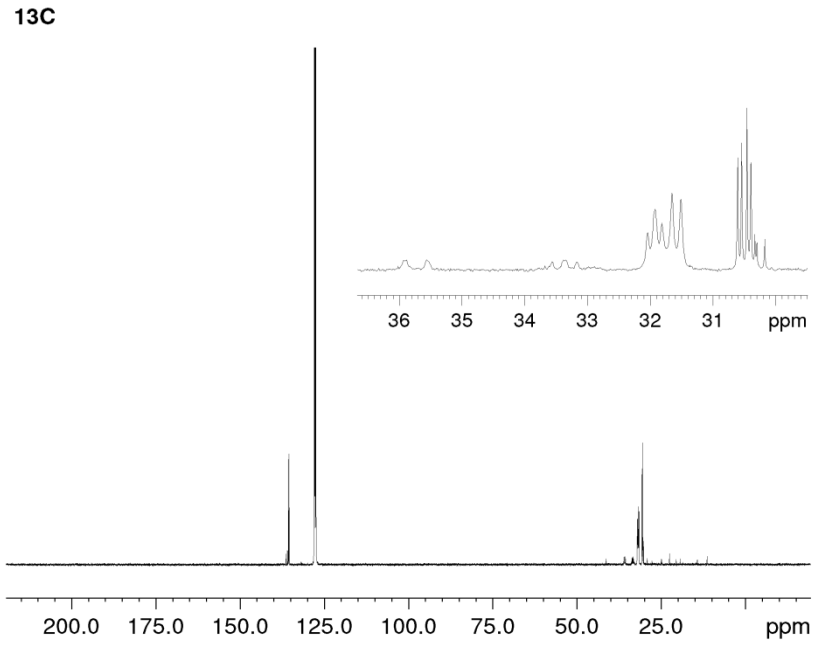

Fig. S39. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectra of isolated *t*Bu$_2$PP*t*BuPh **2**

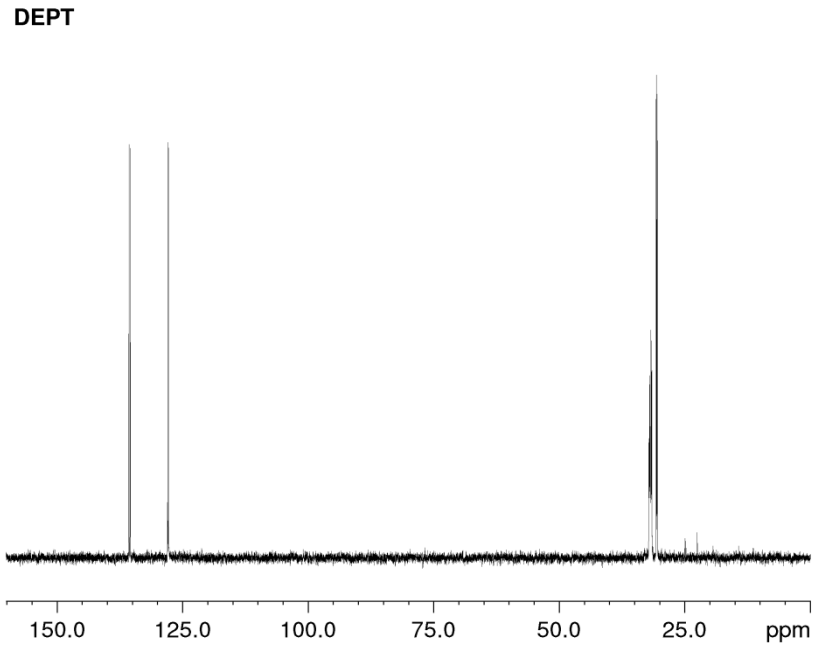

Fig. S40. ^{13}C with DEPT NMR (C_6D_6) spectra of isolated *t*Bu$_2$PP*t*BuPh **2**

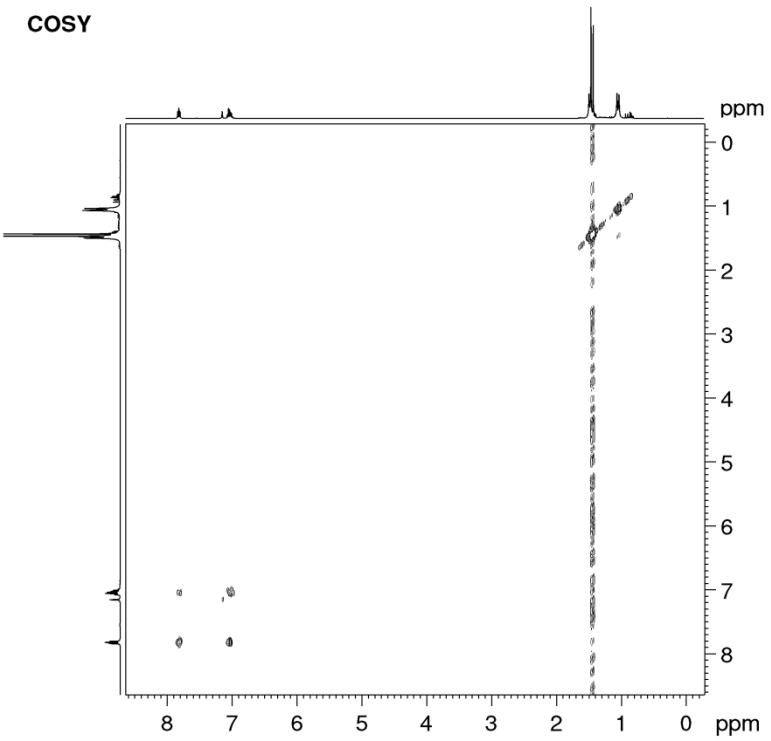

Fig. S41. COSY NMR (C_6D_6) spectra of isolated *t*Bu_2PP*t*BuPh **2**

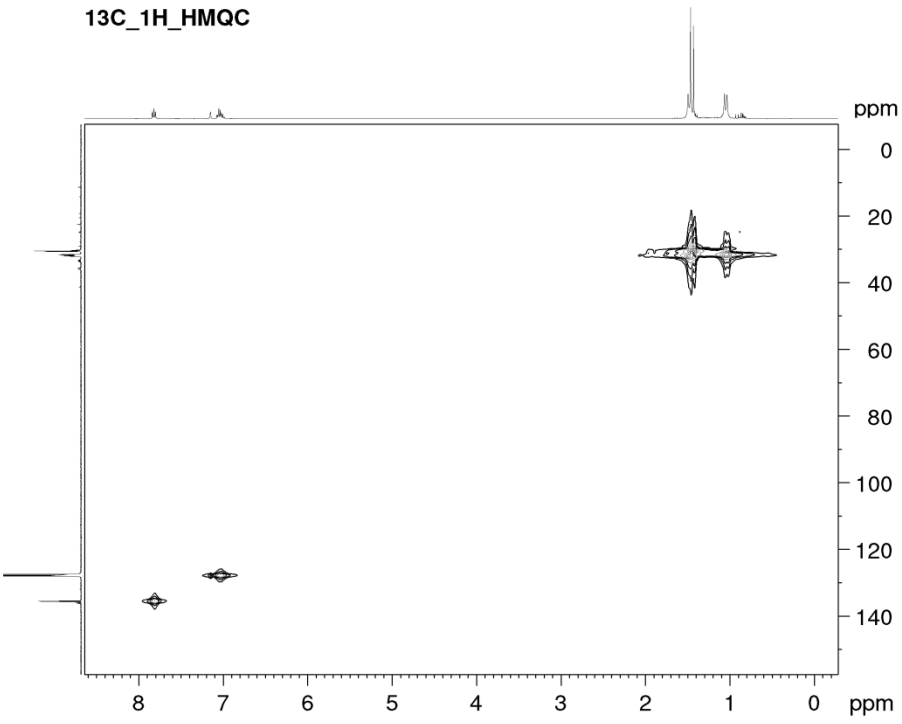

Fig. S42. ^{13}C ^{1}H HMQC NMR (C_6D_6) spectra of isolated *t*Bu_2PP*t*BuPh **2**

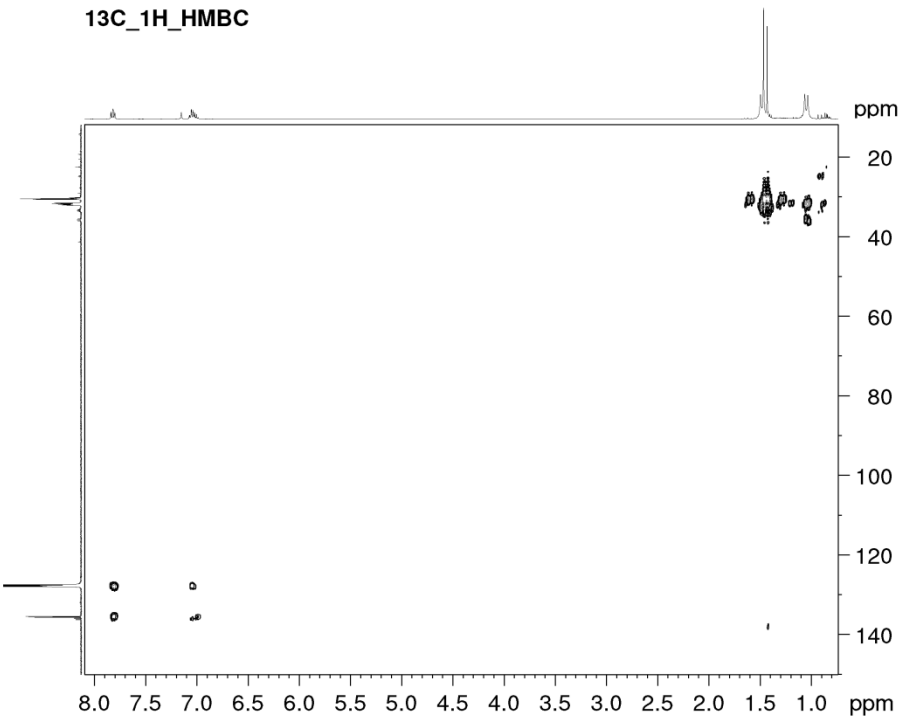

Fig. S43. ^{13}C ^{1}H HMBC NMR (C_6D_6) spectra of isolated *t*Bu_2PP*t*BuPh **2**

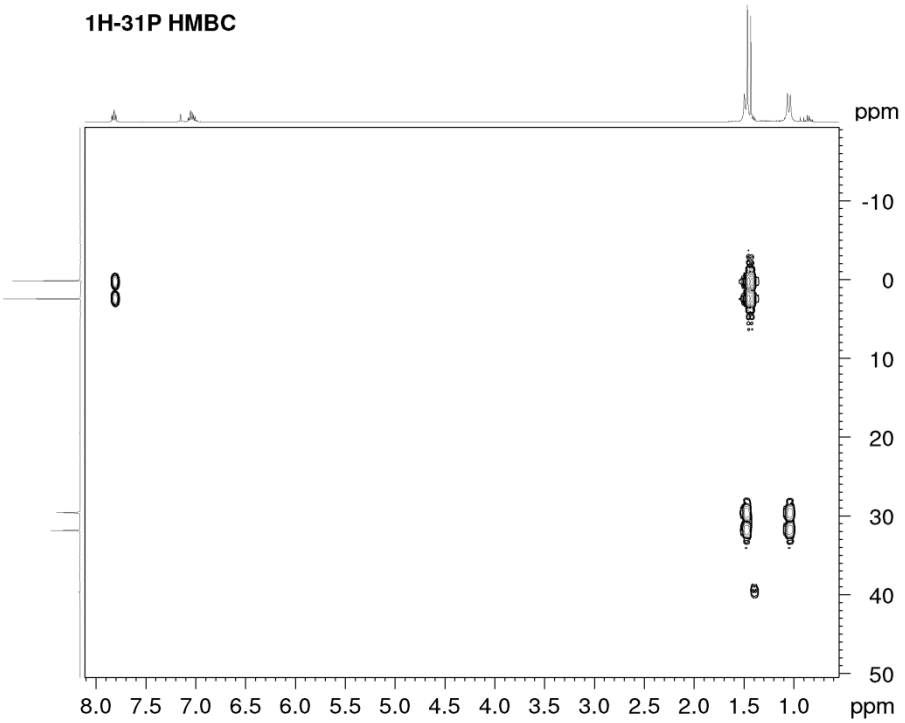

Fig. S44. ^{31}P ^{1}H HMBC NMR (C_6D_6) spectra of isolated *t*Bu_2PP*t*BuPh **2**

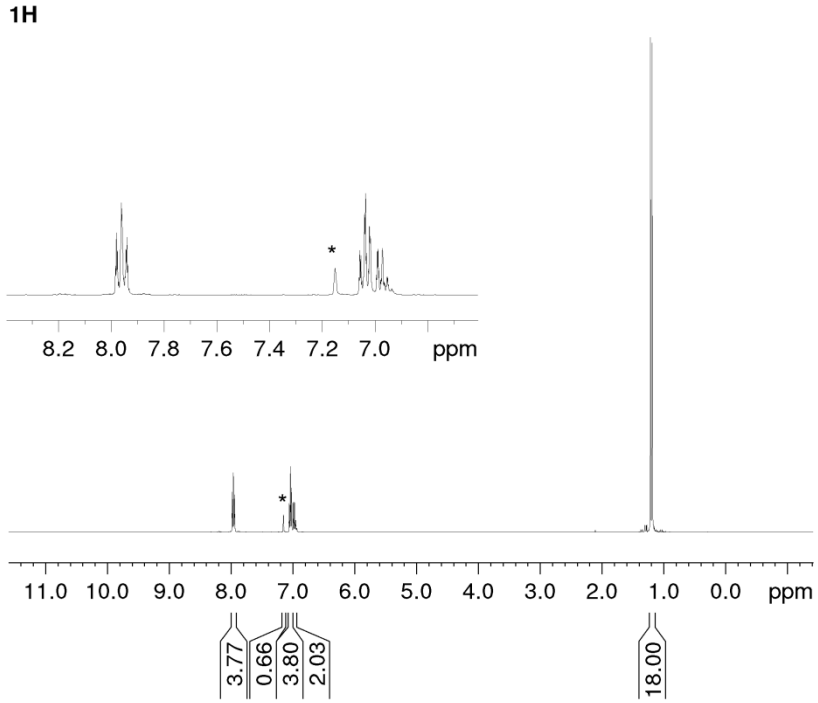

Fig. S45. ^{1}H NMR (C_6D_6) spectra of isolated *t*Bu_2PPPh_2 **3**

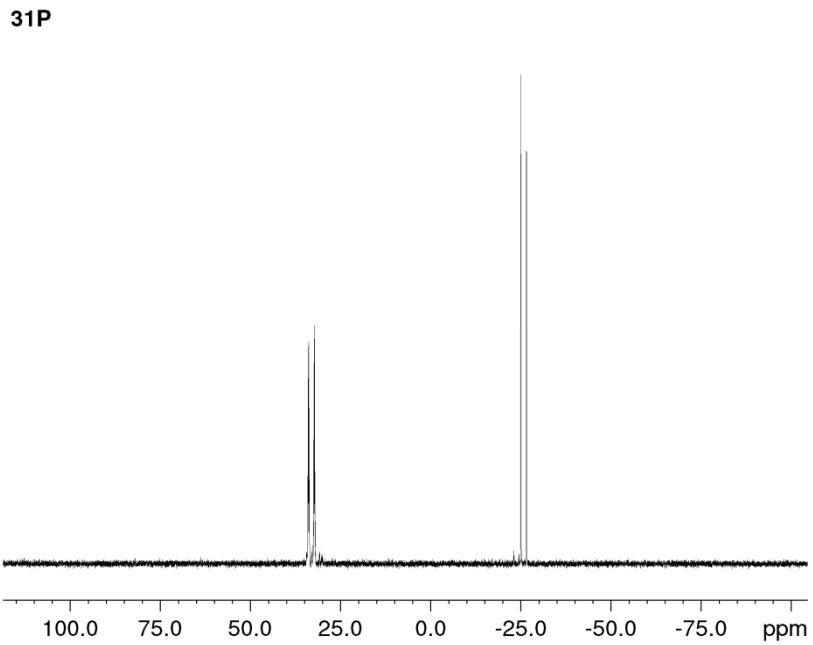

Fig. S46. ^{31}P NMR (C_6D_6) spectra of isolated *t*Bu_2PPPh_2 **3**

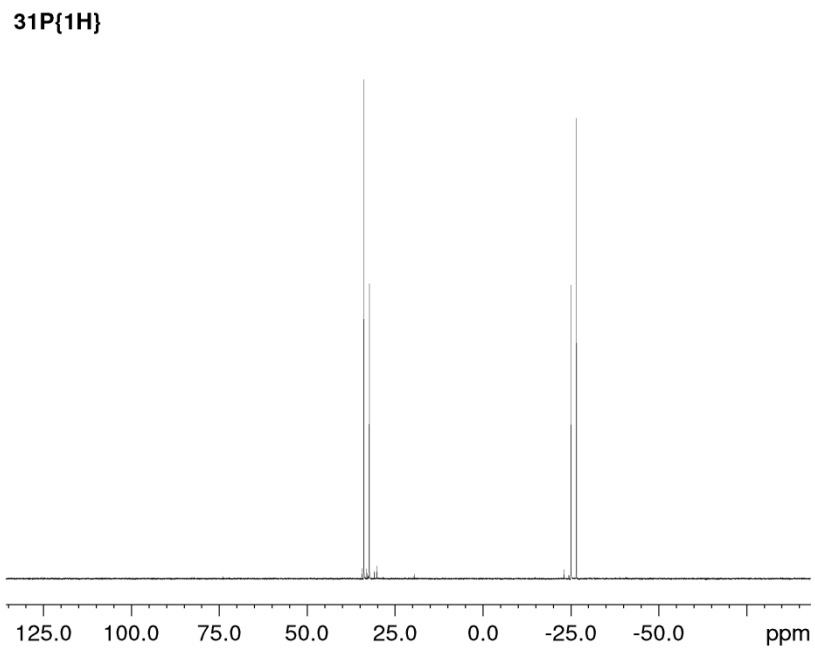

Fig. S47. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of isolated *t*Bu_2PPPh_2 **3**

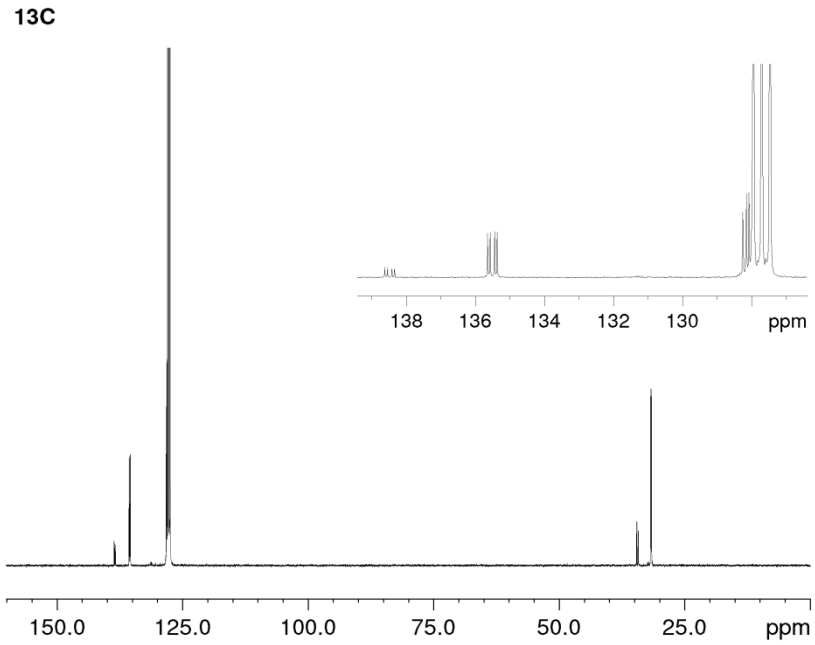

Fig. S48. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectra of isolated *t*Bu_2PPPh_2 **3**

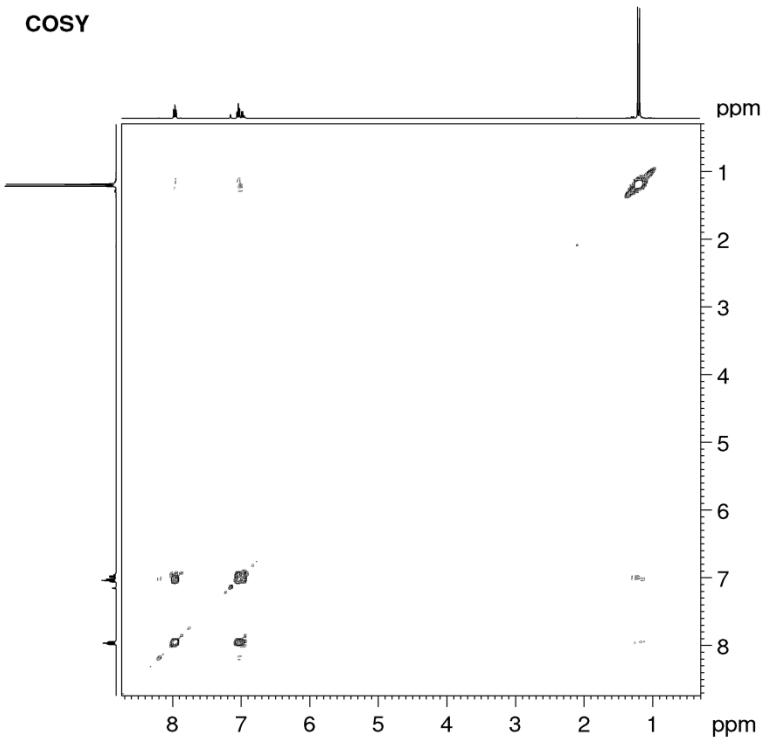

Fig. S49. COSY NMR (C_6D_6) spectra of isolated *t*Bu_2PPPh_2 **3**

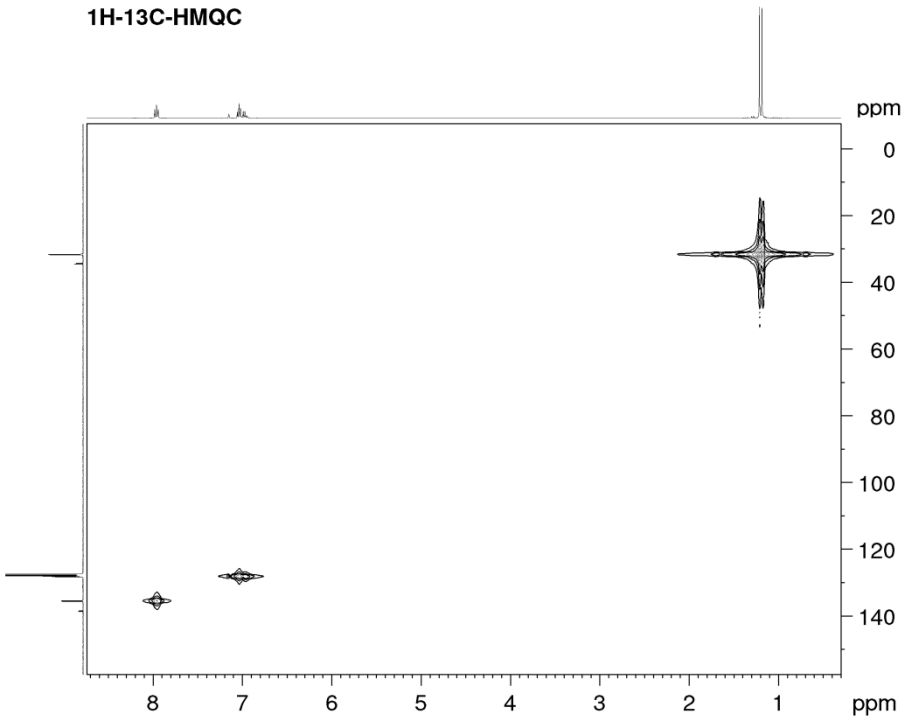

Fig. S50. ^{13}C ^{1}H HMQC NMR (C_6D_6) spectra of isolated *t*Bu_2PPPh_2 **3**

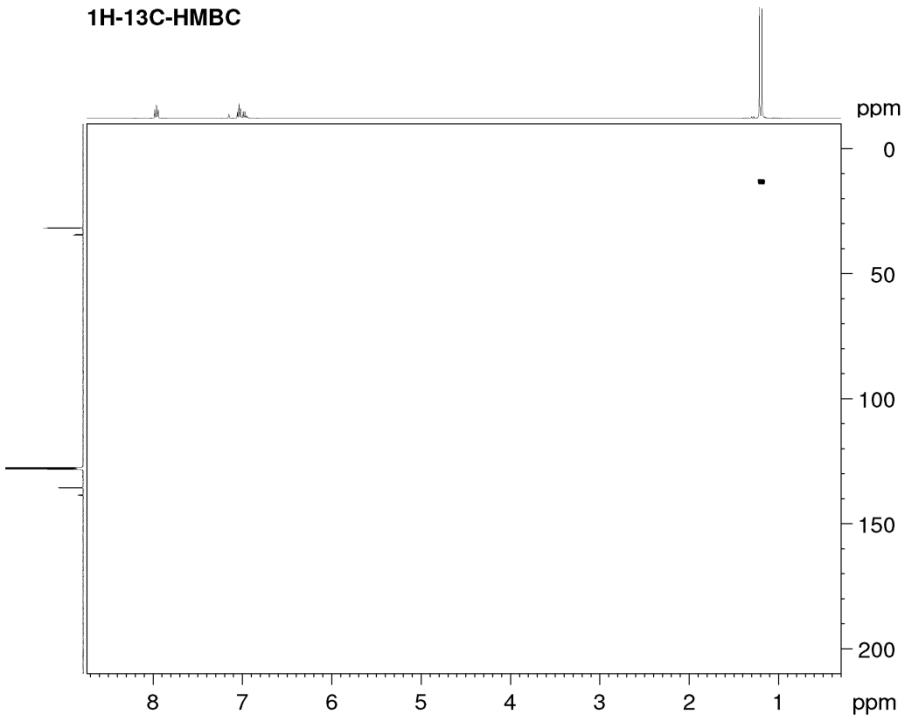

Fig. S51. ^{13}C ^{1}H HMBC NMR (C_6D_6) spectra of isolated tBu$_2$PPPh$_2$ **3**

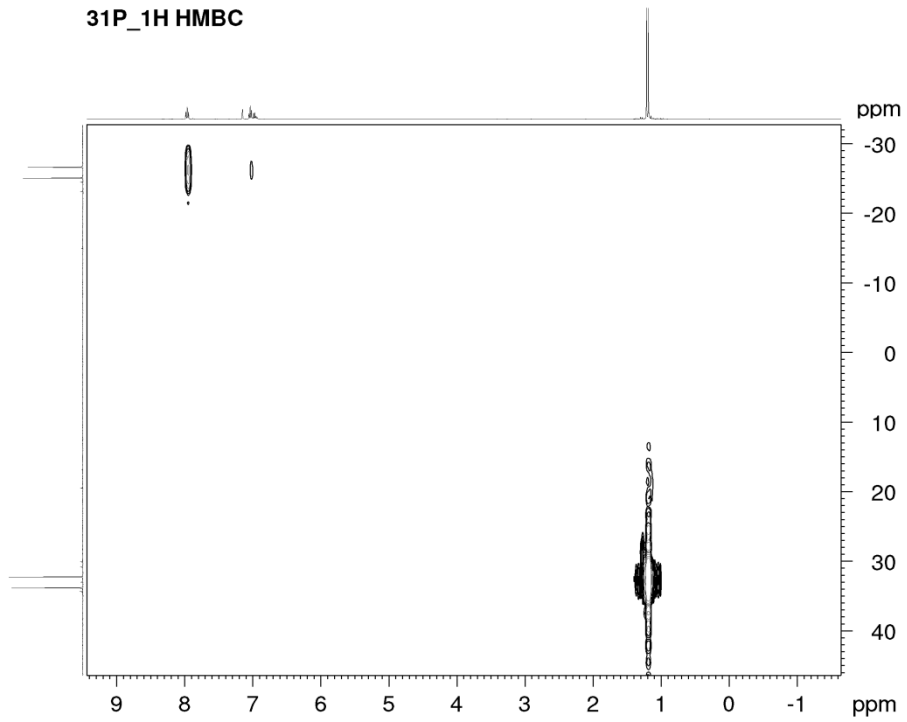

Fig. S52. ^{31}P ^{1}H HMBC NMR (C_6D_6) spectra of isolated tBu$_2$PPPh$_2$ **3**

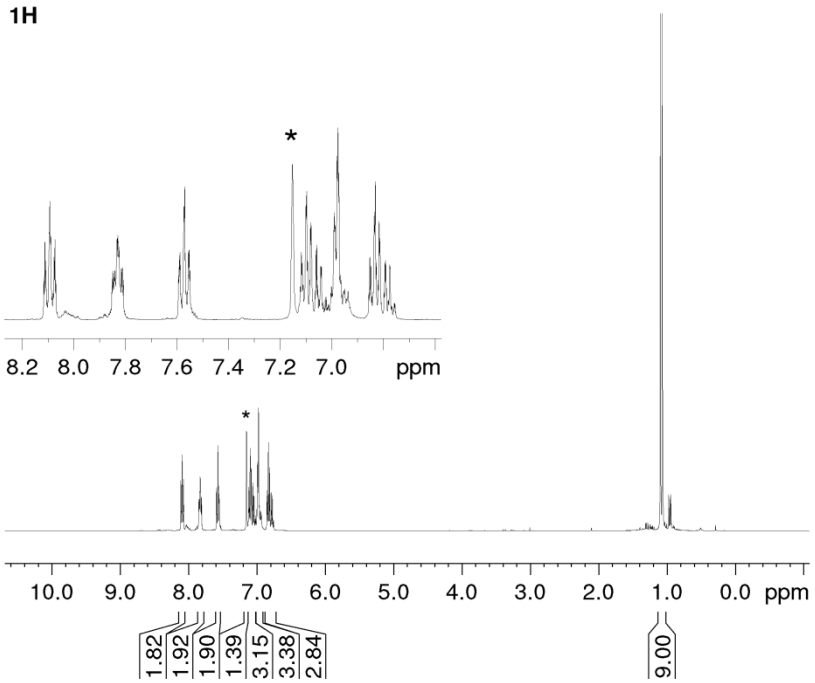

Fig. S53. ^{1}H NMR (C_6D_6) spectra of isolated *t*BuPhPPPh$_2$ **6**

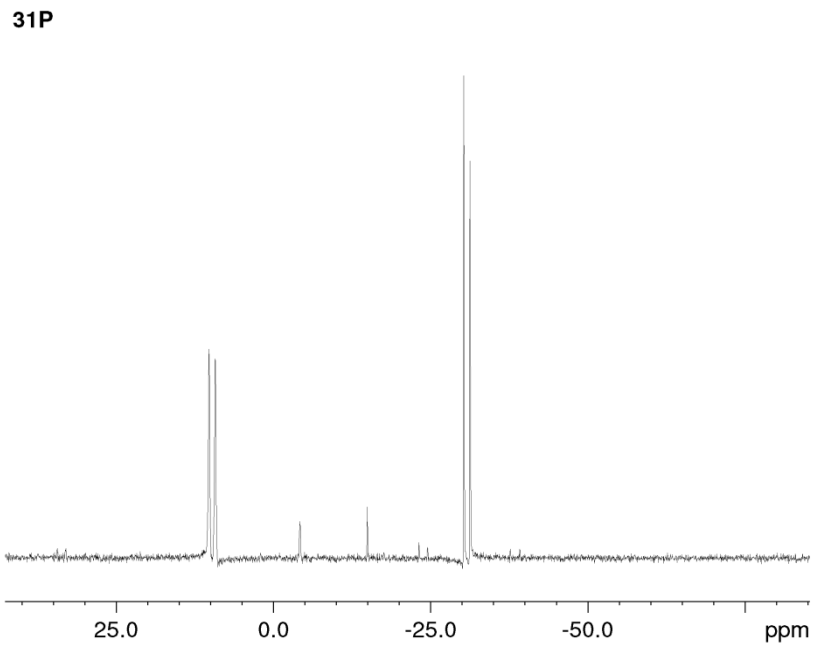

Fig. S54. ^{31}P NMR (C_6D_6) spectra of isolated *t*BuPhPPPh$_2$ **6**

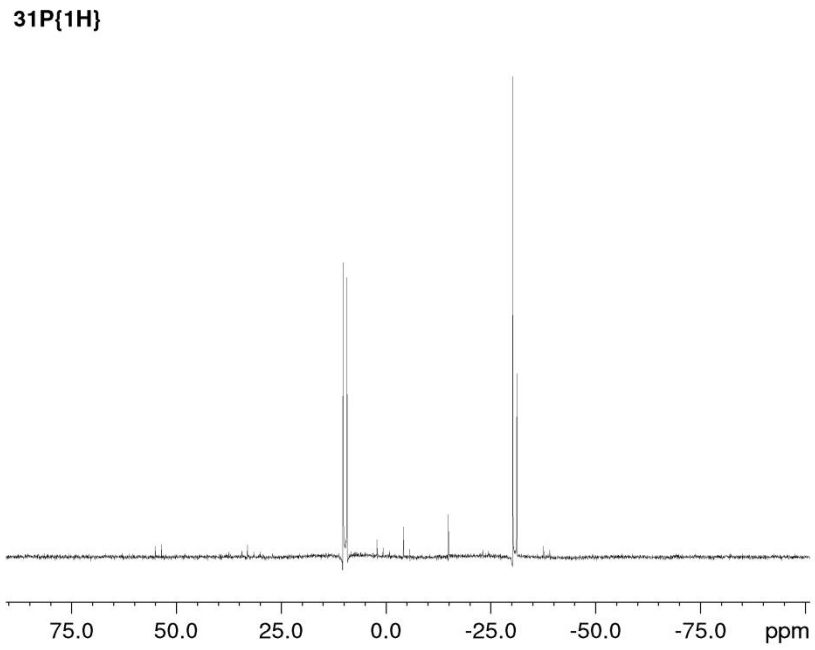

Fig. S55. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of isolated *t*BuPhPPPh$_2$ **6**

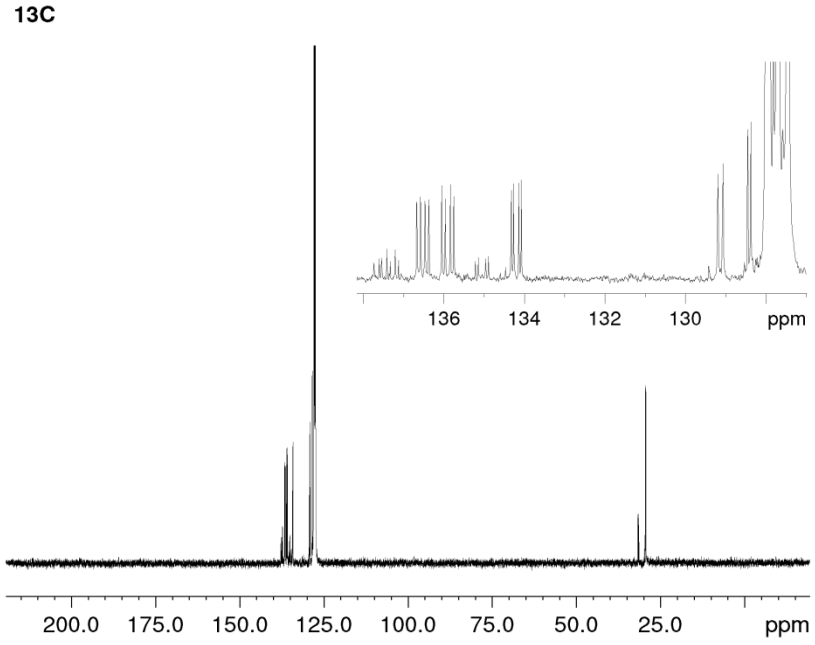

Fig. S56. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectra of isolated *t*BuPhPPPh$_2$ **6**

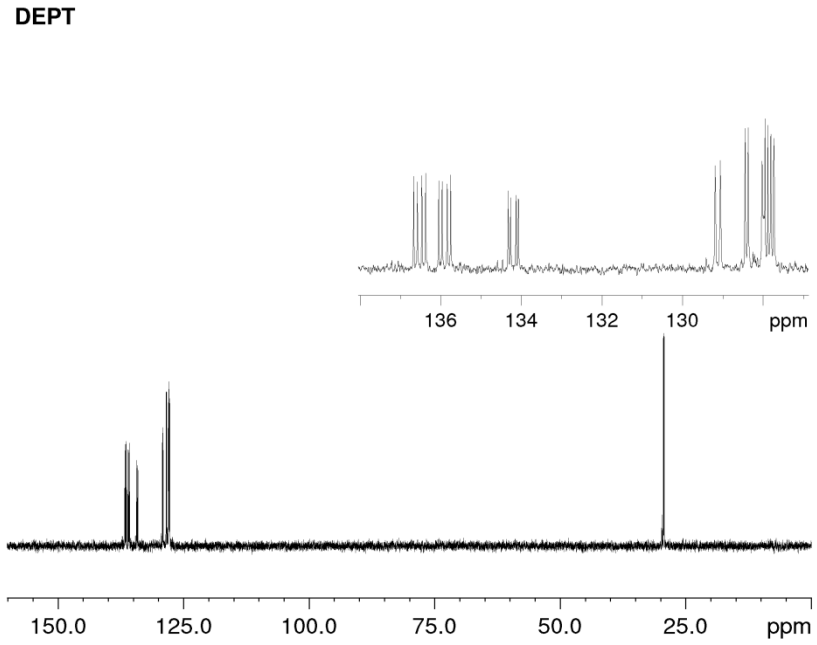

Fig. S57. ^{13}C with DEPT NMR (C_6D_6) spectra of isolated *t*BuPhPPPh$_2$ **6**

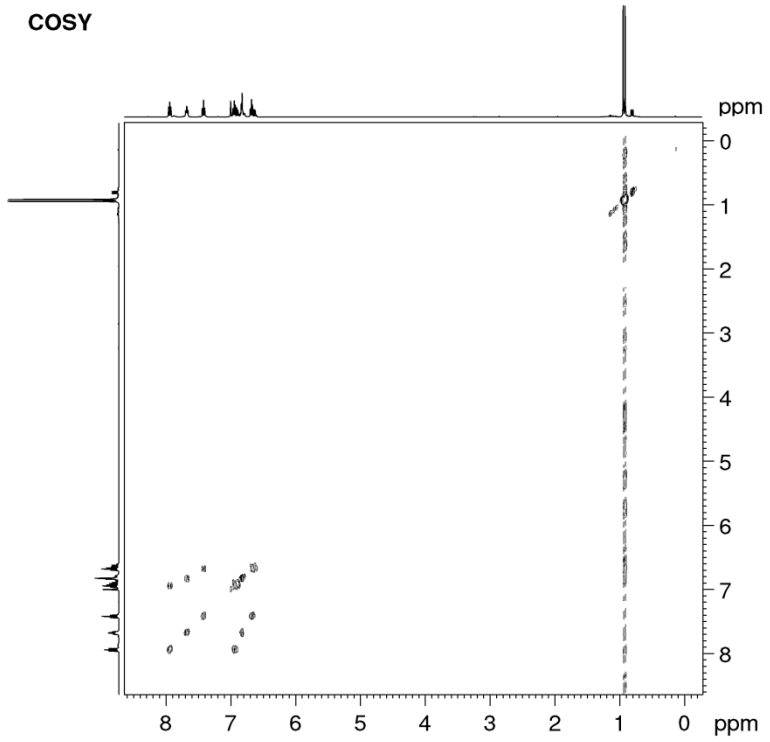

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Fig. S58. COSY NMR (C_6D_6) spectra of isolated *t*BuPhPPPh$_2$ **6**

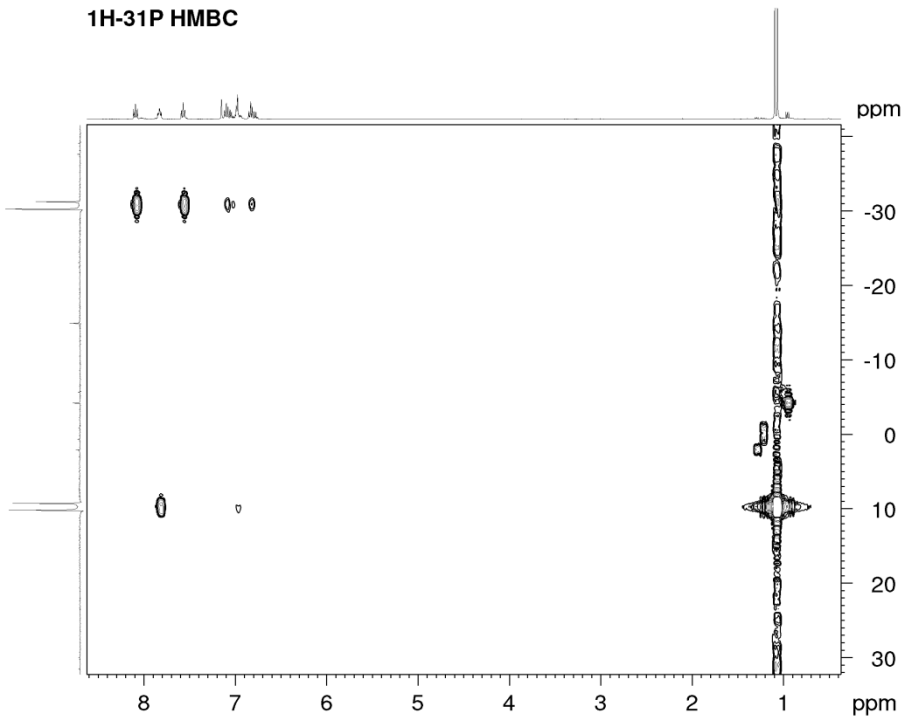


Fig. S59. $^{31}P\{^{1}H\}$ ^{1}H HMBC NMR (C_6D_6) spectra of isolated *t*BuPhPPPh$_2$ **6**

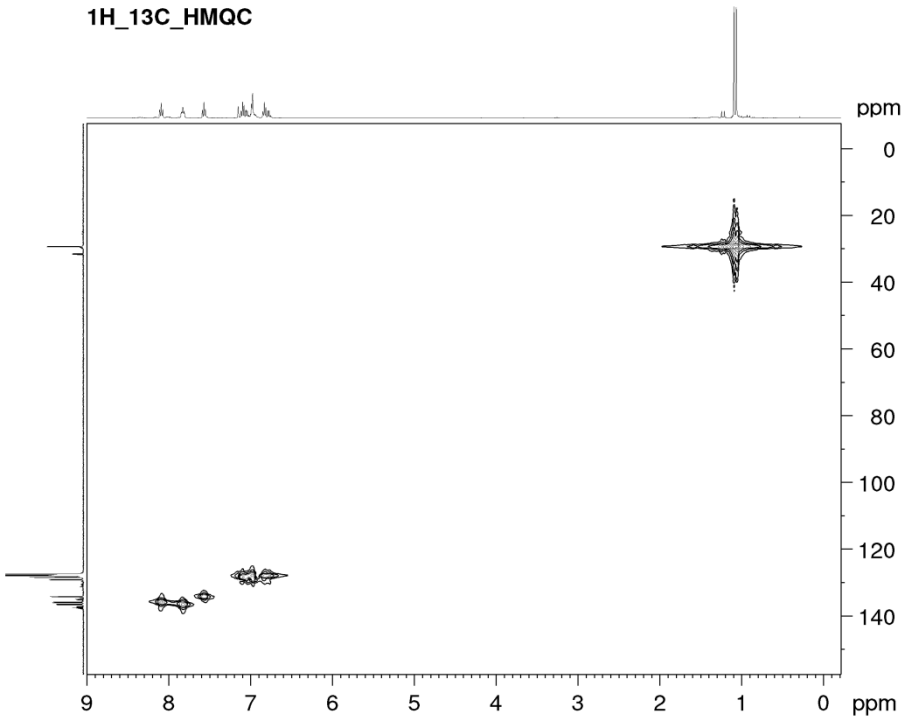


Fig. S60. ^{13}C ^{1}H HMQC NMR (C_6D_6) spectra of isolated *t*BuPhPPPh$_2$ **6**

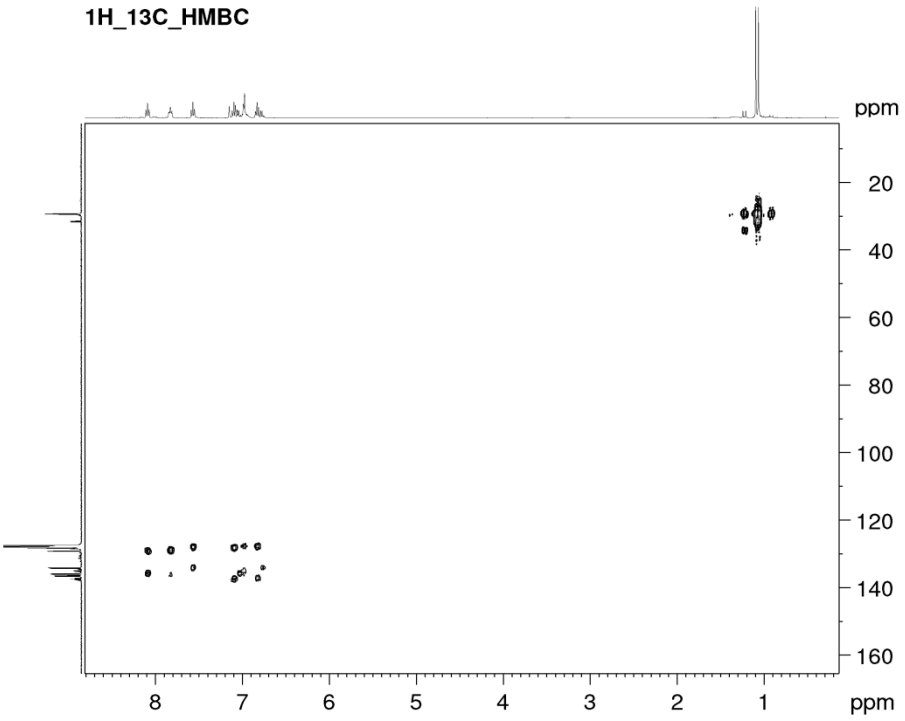


Fig. S61. ^{13}C ^{1}H HMBC NMR (C_6D_6) spectra of isolated *t*BuPhPPPh$_2$ **6**

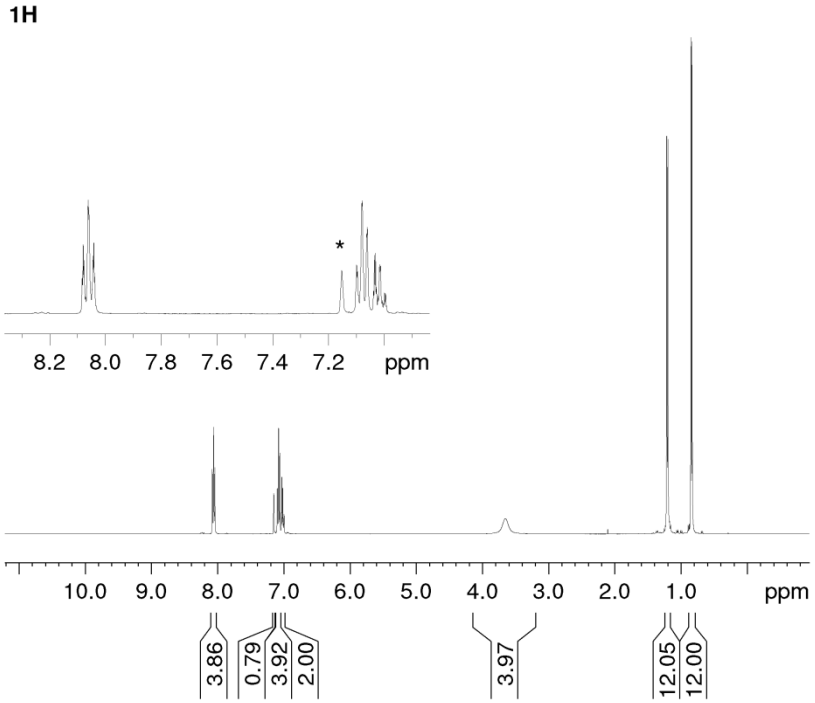


Fig. S62. ^{1}H NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPPh$_2$ **8**

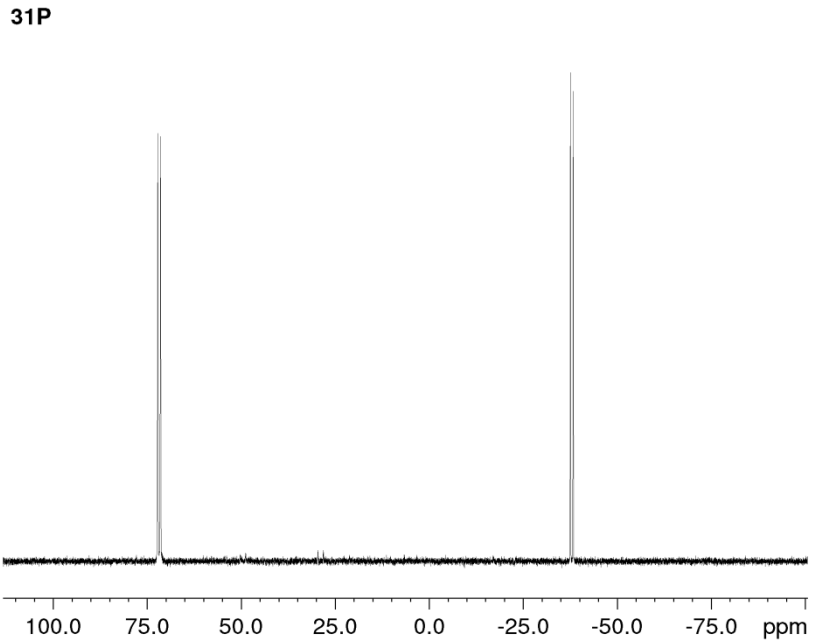


Fig. S63. ^{31}P NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPPh$_2$ **8**

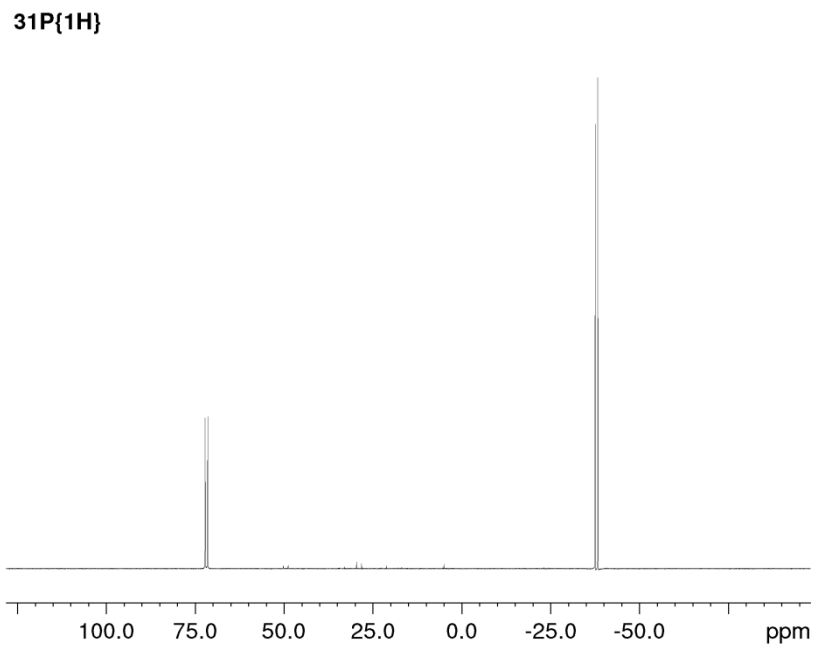


Fig. S64. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPPh$_2$ **8**

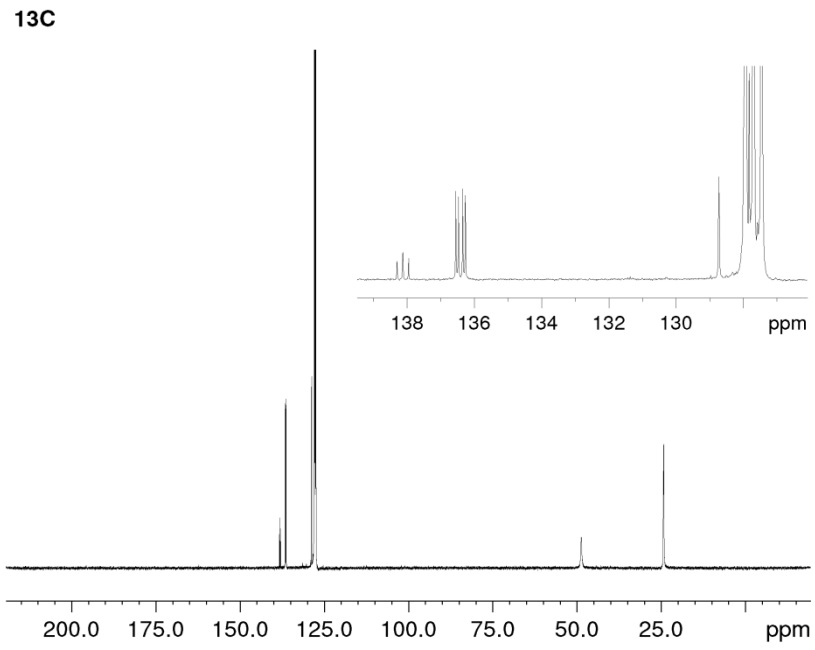


Fig. S65. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPPh$_2$ **8**

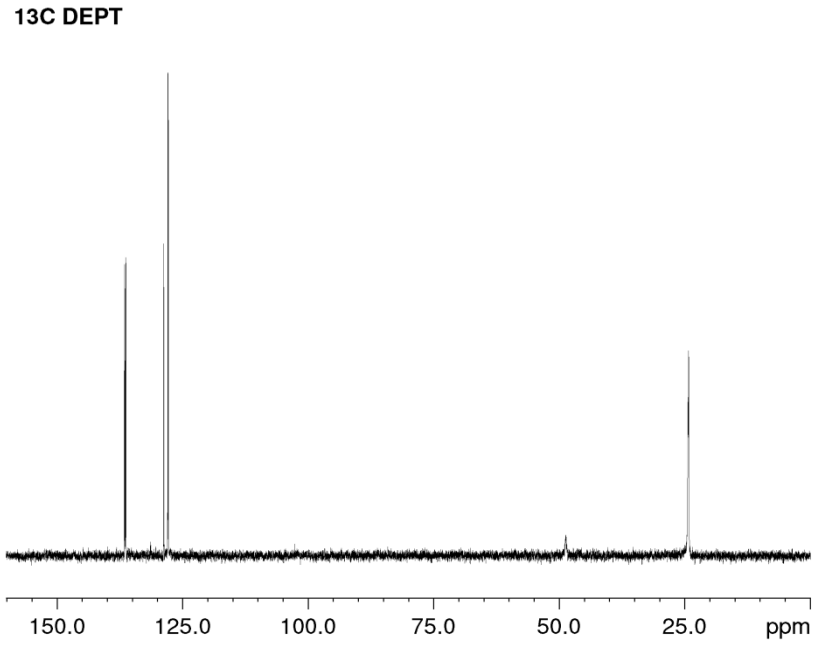


Fig. S66. ^{13}C with DEPT NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPPh$_2$ **8**

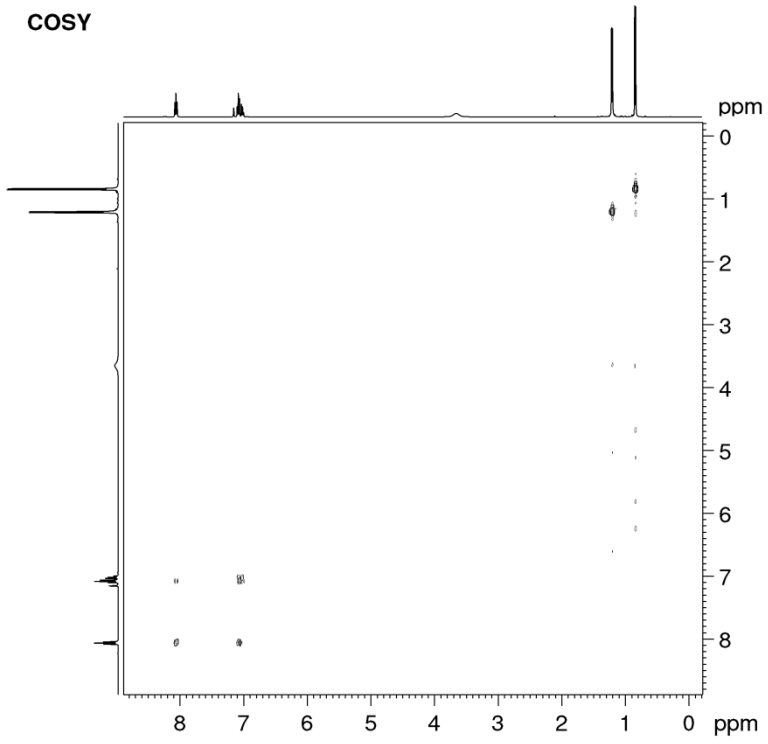


Fig. S67. COSY NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPPh$_2$ **8**

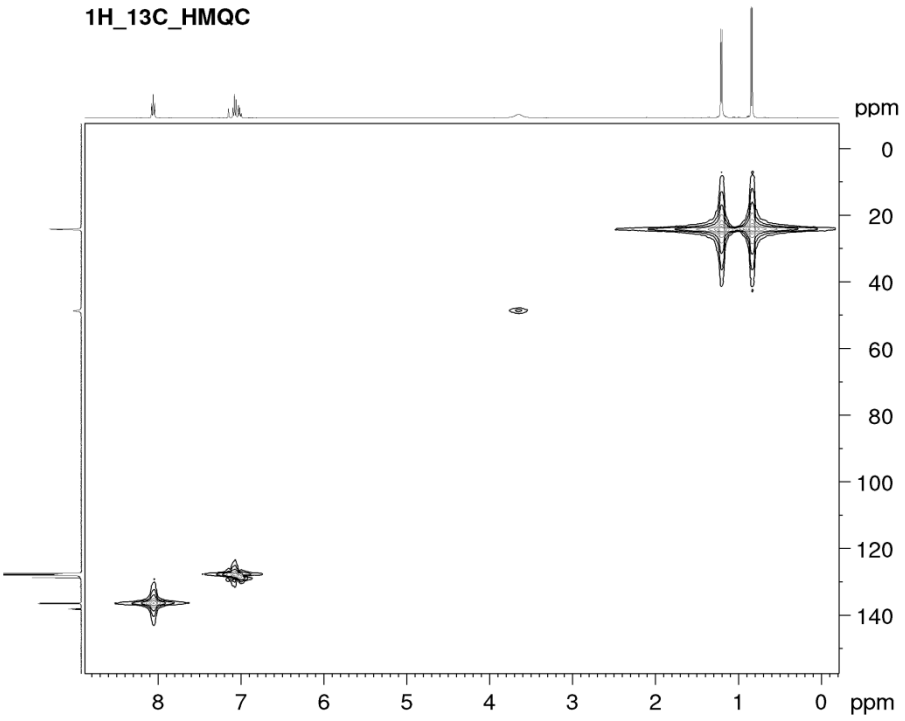


Fig. S68. ^{13}C ^{1}H HMQC NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPPh$_2$ **8**

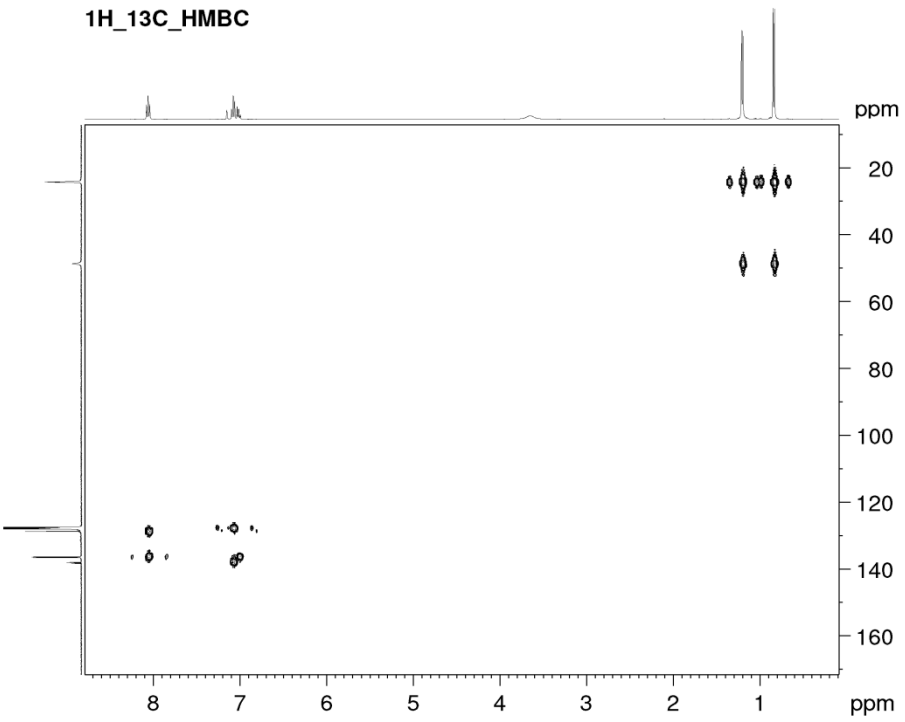


Fig. S69. ^{13}C ^{1}H HMBC NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPPh$_2$ **8**

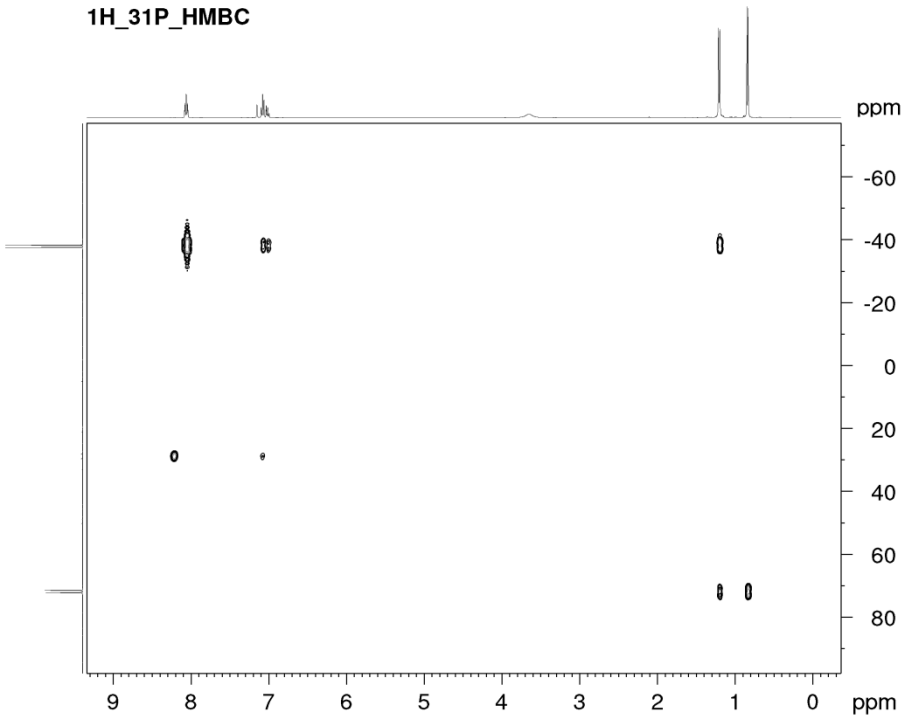


Fig. S70. ^{31}P ^{1}H HMBC NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPPh$_2$ **8**

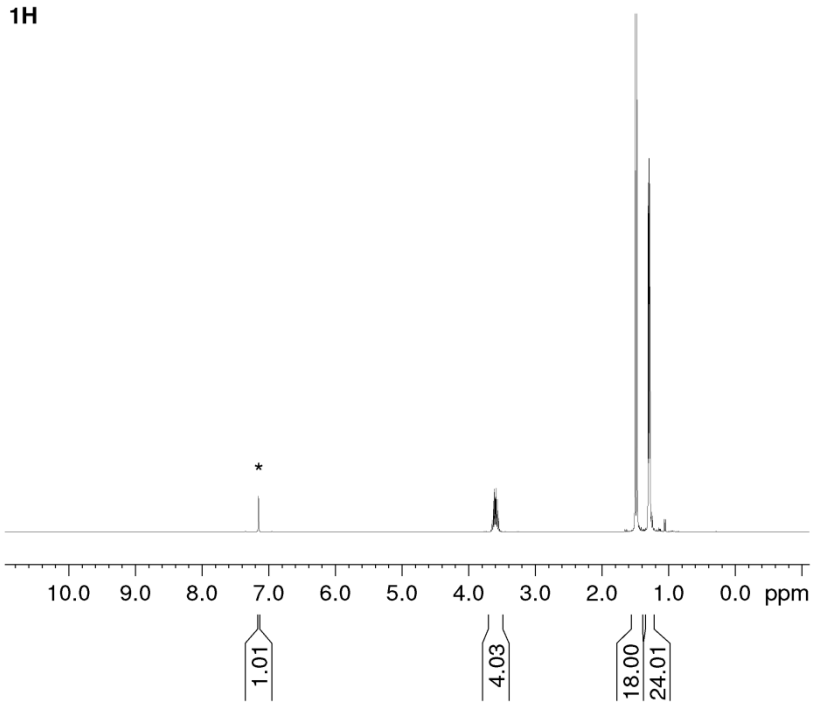


Fig. S71. ^{1}H NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPtBu$_2$ **9**

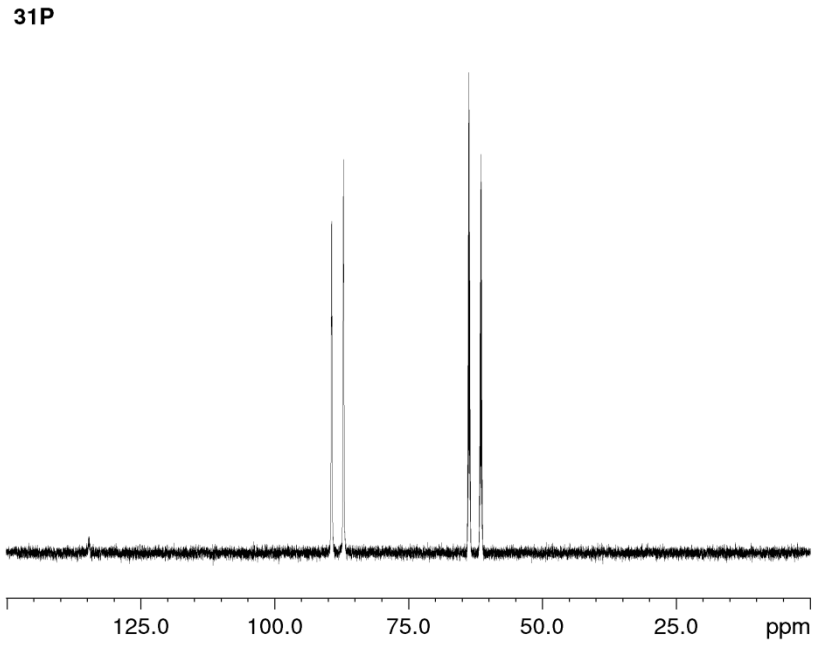


Fig. S72. ^{31}P NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPtBu$_2$ **9**

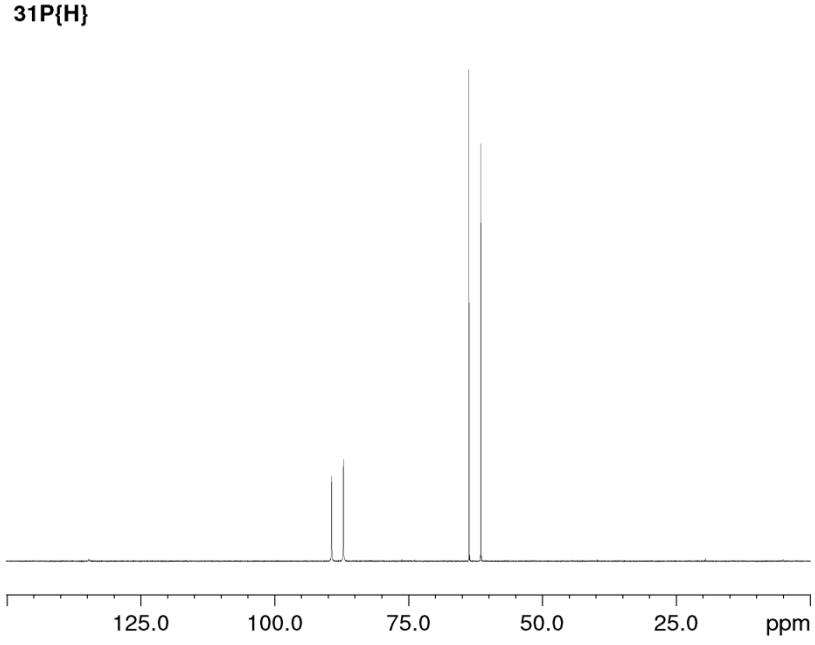


Fig. S73. $^{31}P\{^1H\}$ NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPtBu$_2$ **9**

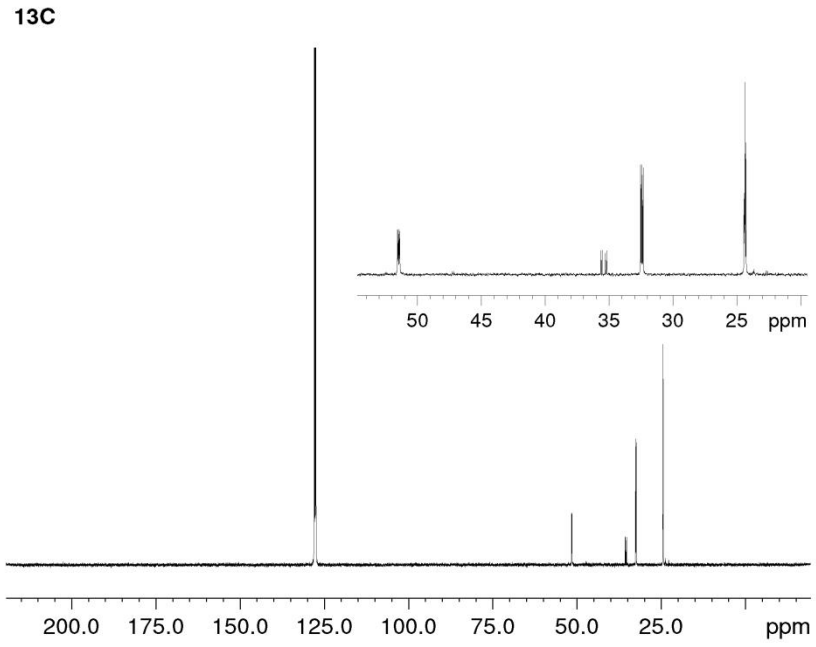


Fig. S74. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPtBu$_2$ **9**

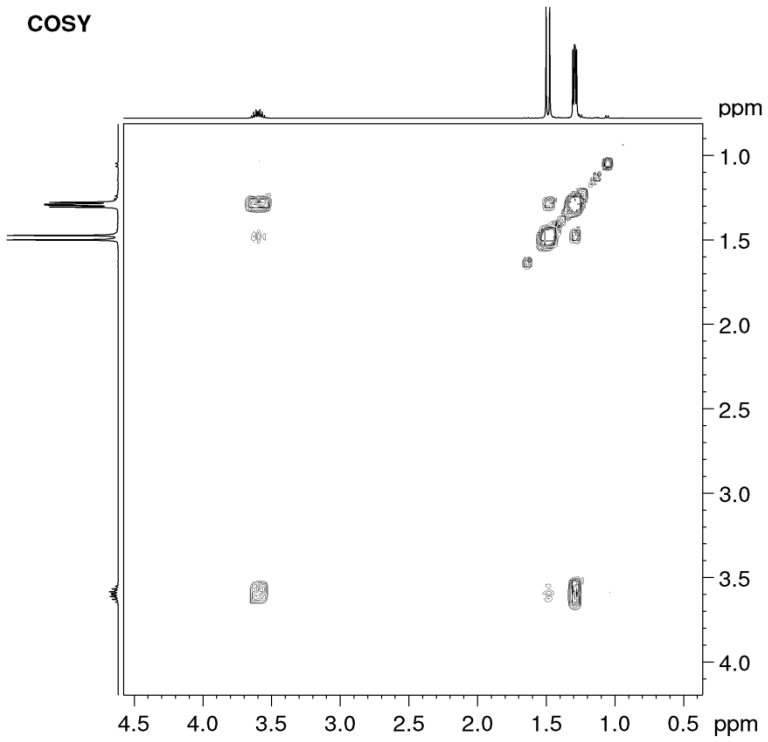


Fig. S75. COSY NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPtBu$_2$ **9**

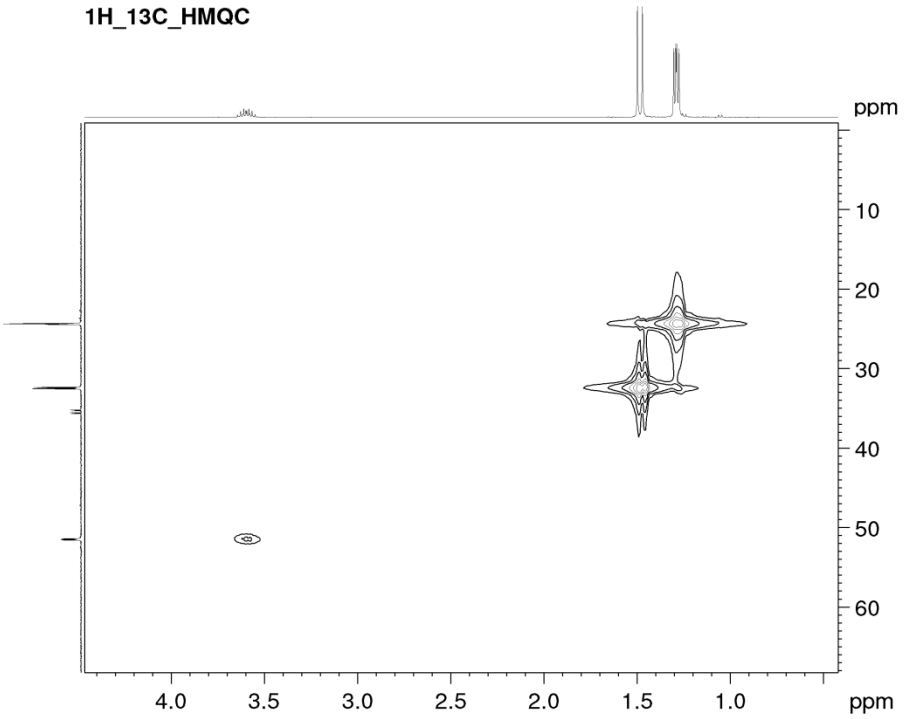


Fig. S76. ^{1}H ^{13}C HMQC NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPtBu$_2$ **9**

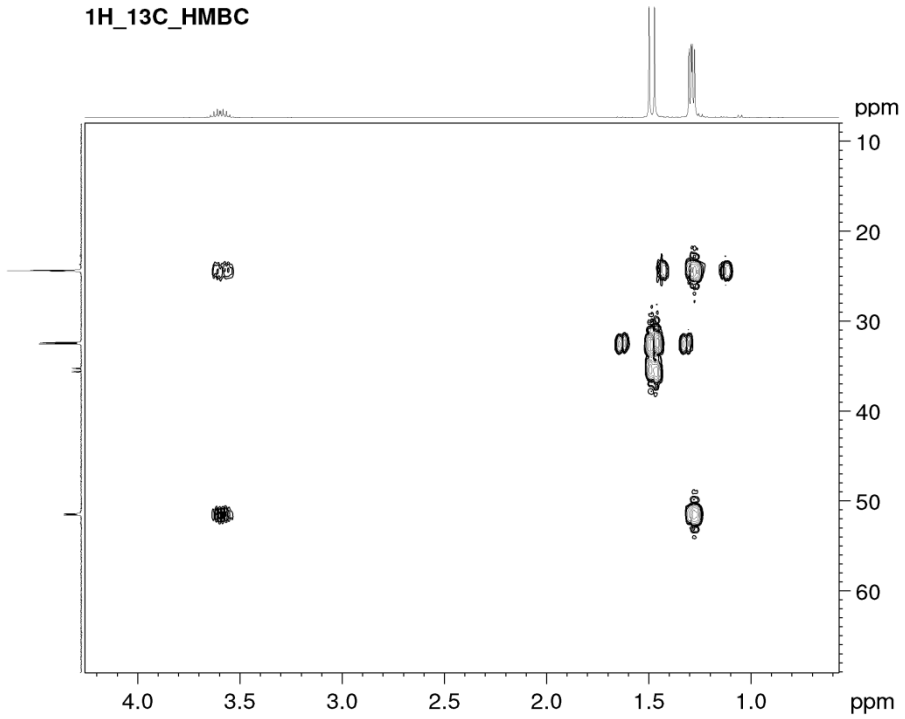


Fig. S77. ^{1}H ^{13}C HMBC NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPtBu$_2$ **9**

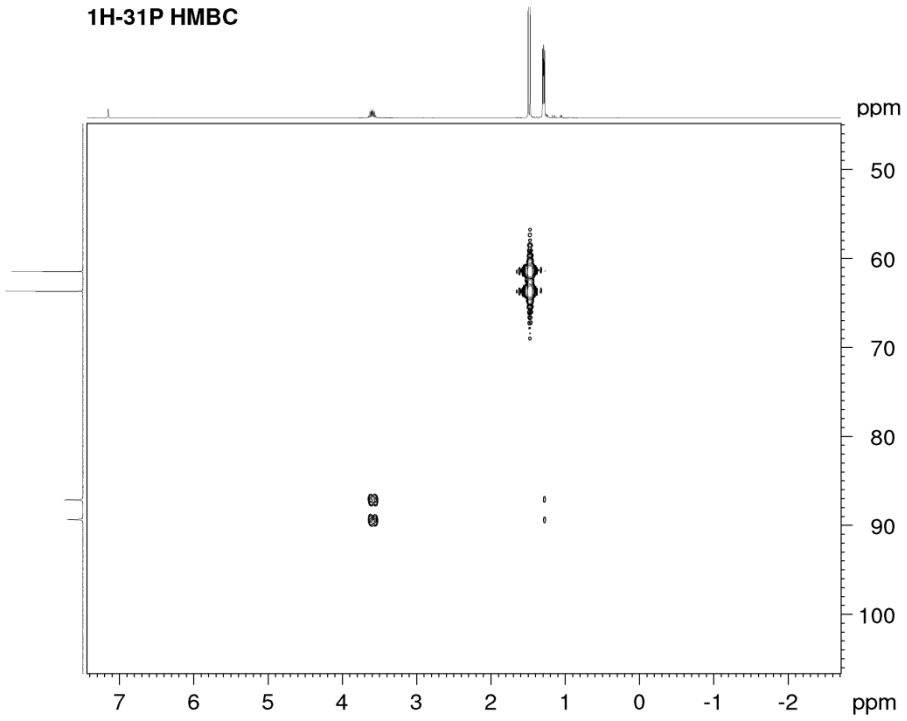


Fig. S78. ^{1}H ^{31}P HMBC NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPtBu$_2$ **9**

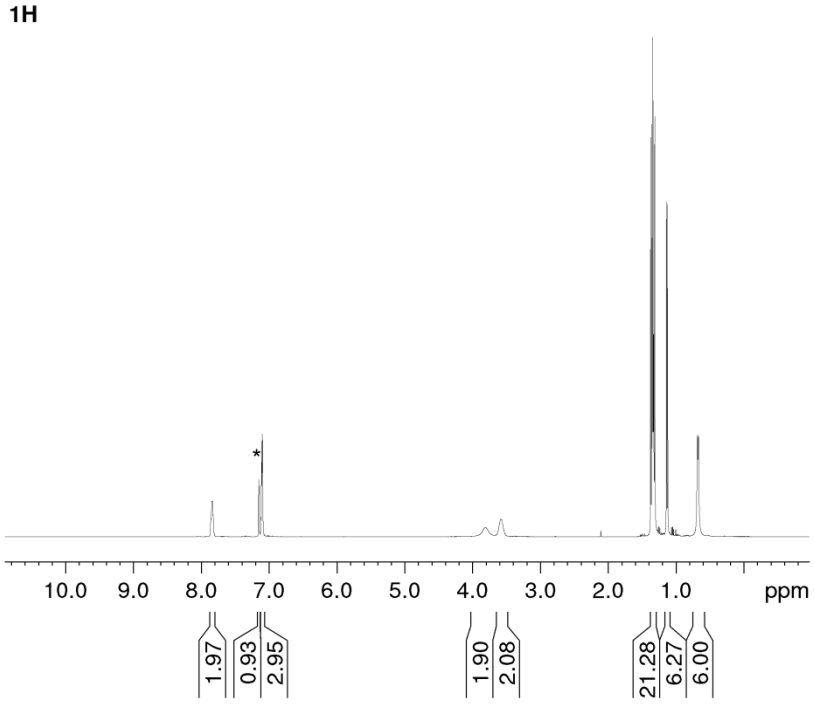


Fig. S79. ^{1}H NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPtBuPh **10**

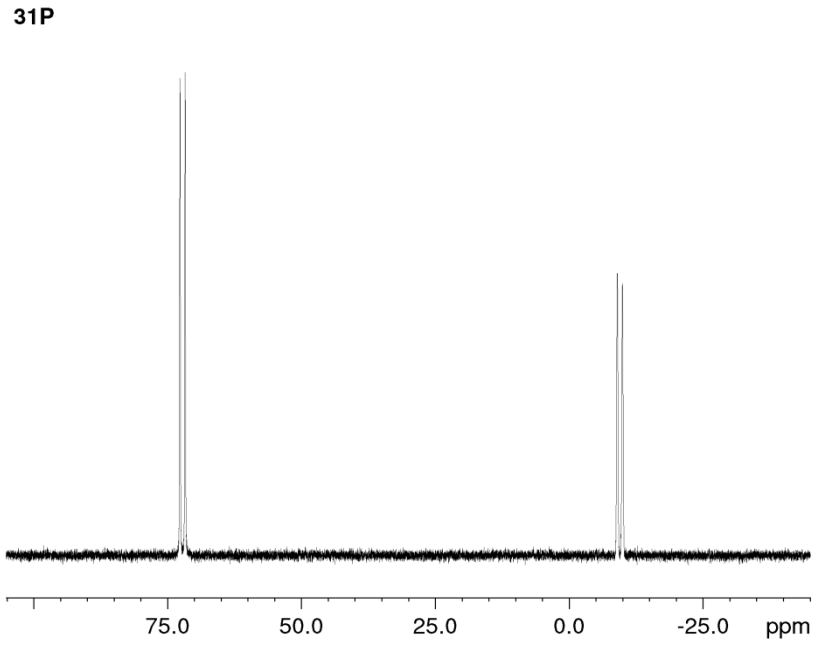


Fig. S80. ^{31}P NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPtBuPh **10**

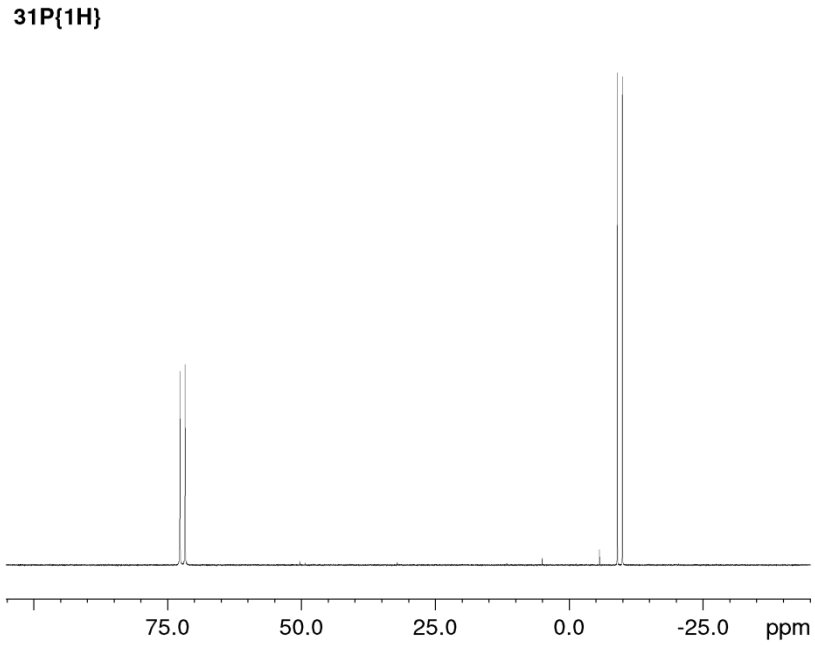


Fig. S81. $^{31}P\{^1H\}$ NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPtBuPh **10**

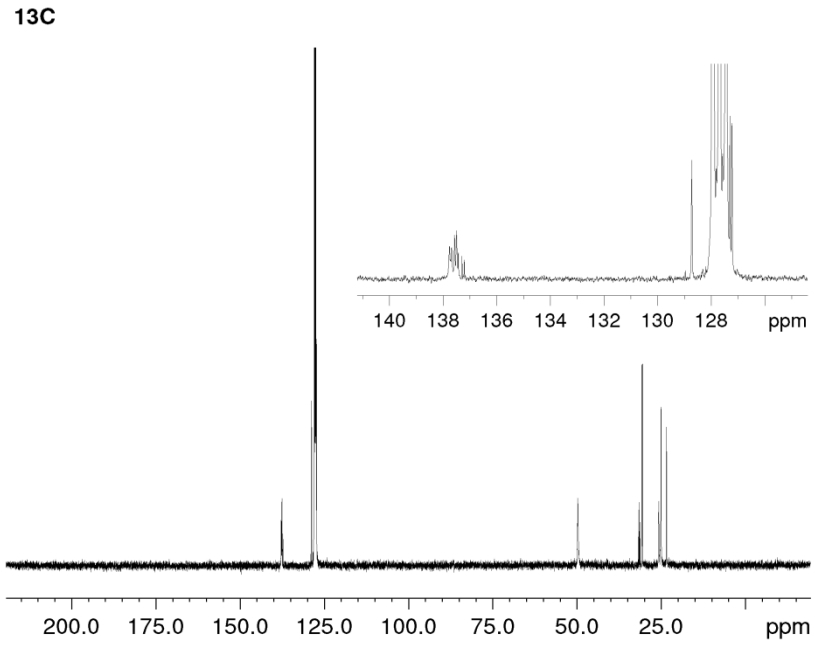


Fig. S82. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPtBuPh **10**

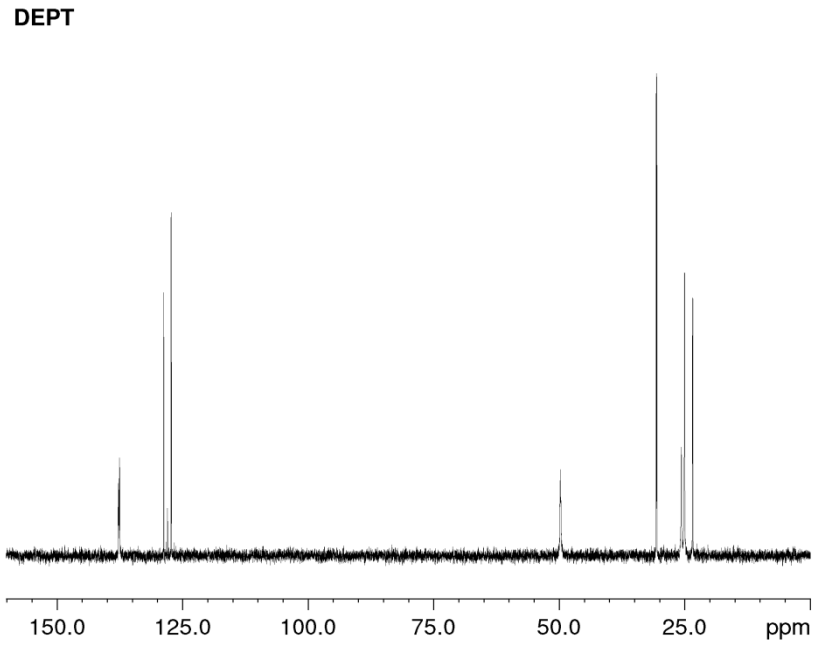


Fig. S83. ^{13}C with DEPT NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPtBuPh **10**

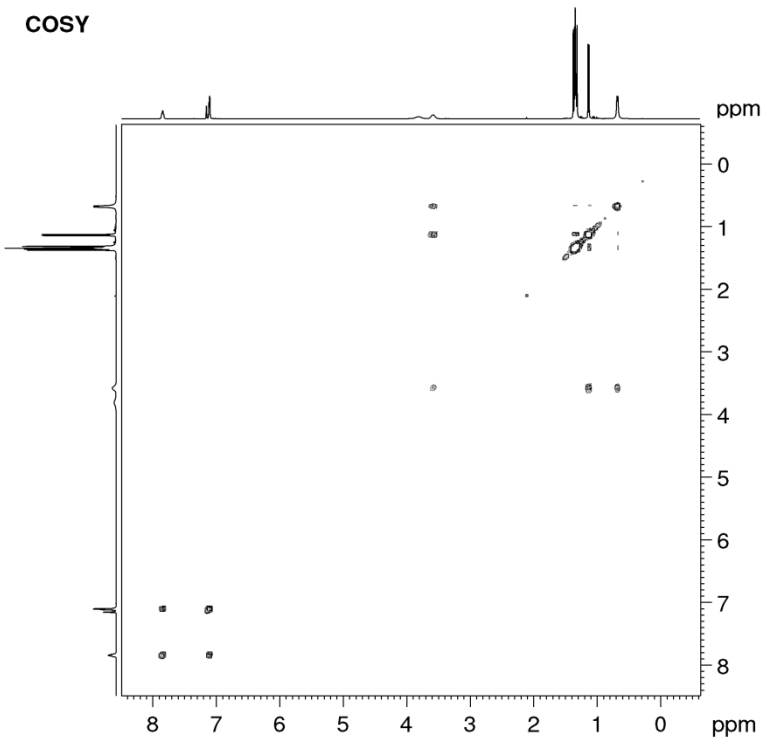


Fig. S84. COSY NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPtBuPh **10**

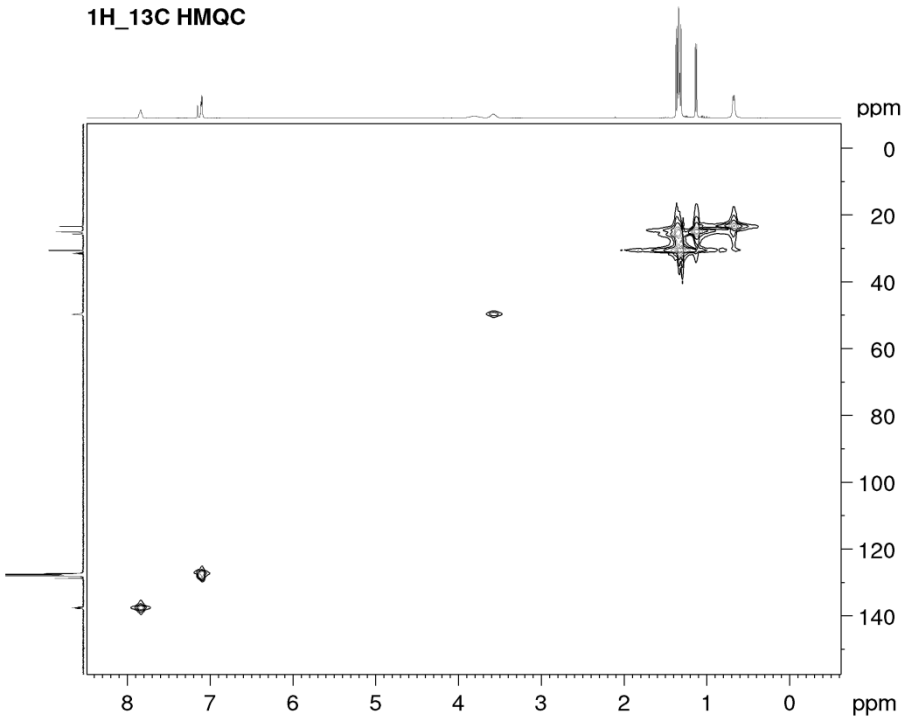


Fig. S85. ^{1}H ^{13}C HMQC NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPtBuPh **10**

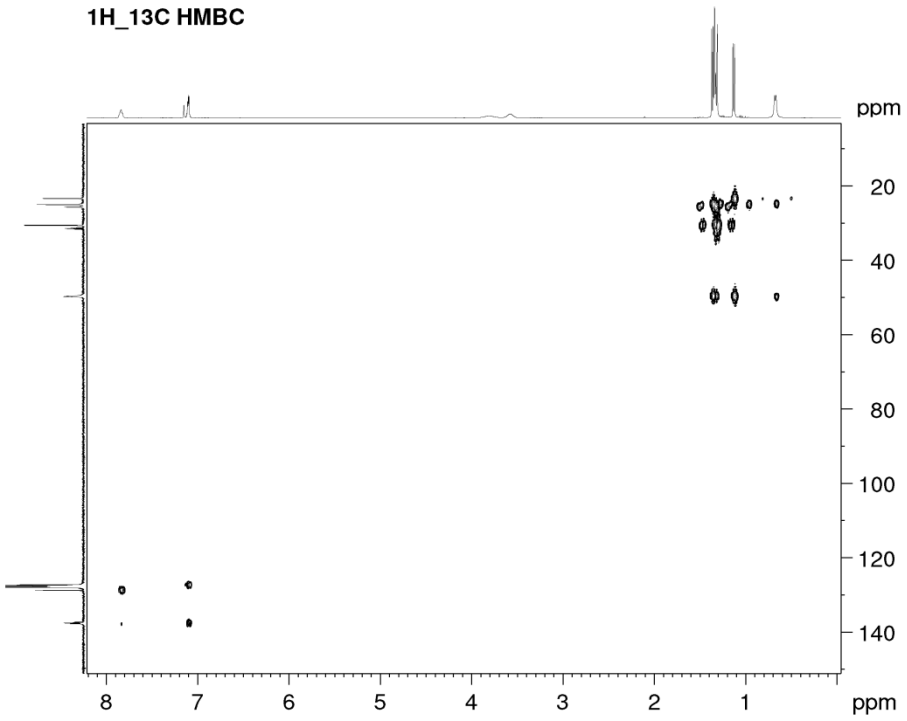


Fig. S86. ^{1}H ^{13}C HMBC NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPtBuPh **10**

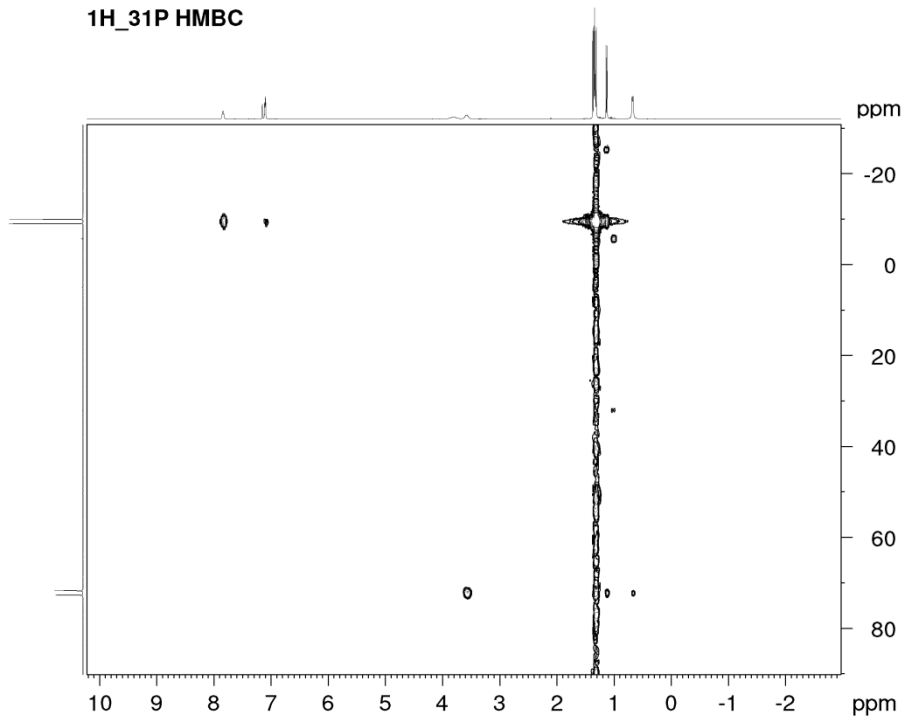


Fig. S87. ^{1}H ^{31}P HMBC NMR (C_6D_6) spectra of isolated (iPr$_2$N)$_2$PPtBuPh **10**

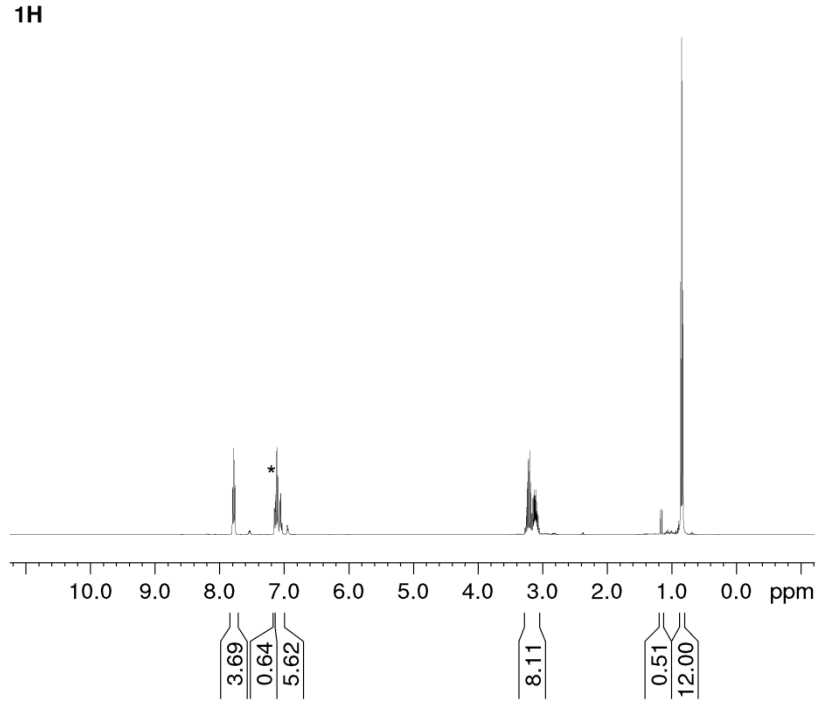


Fig. S88. ^{1}H NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPPh_2$ **11**

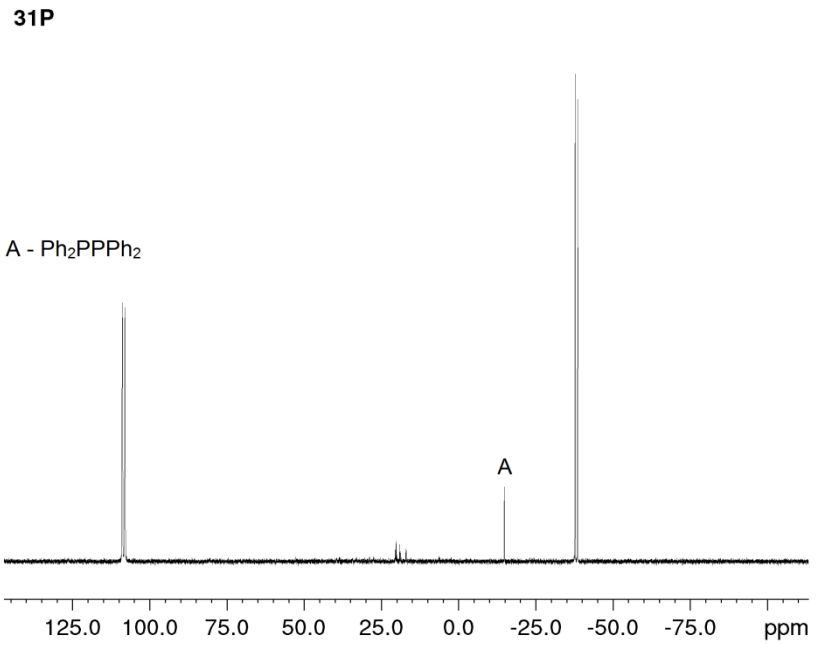


Fig. S89. ^{31}P NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPPh_2$ **11**

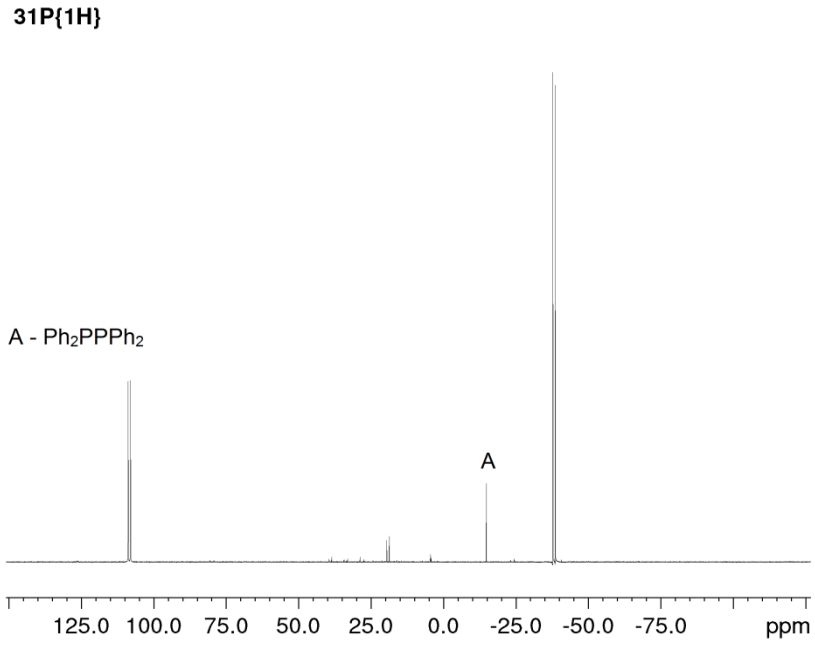


Fig. S90. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPPh_2$ **11**

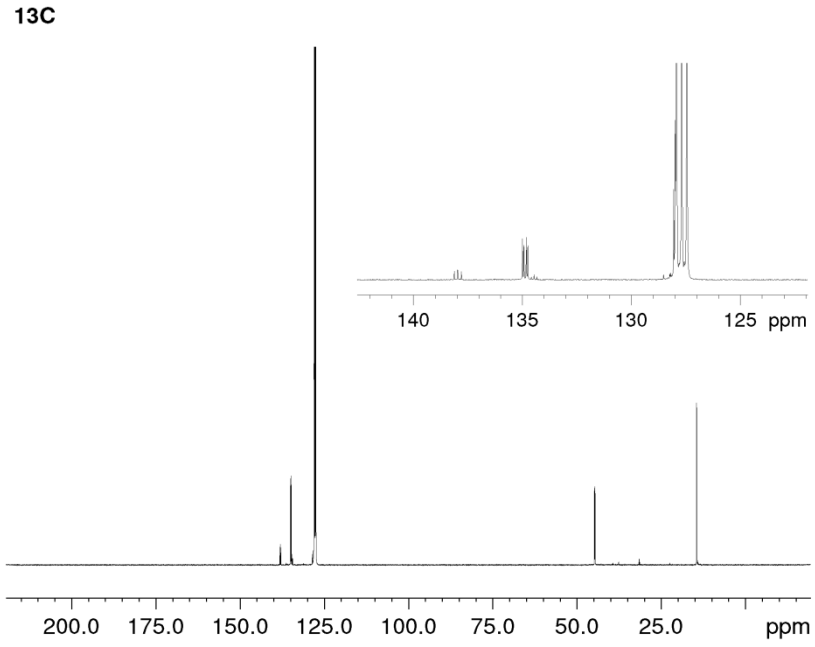


Fig. S91. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPPh_2$ **11**

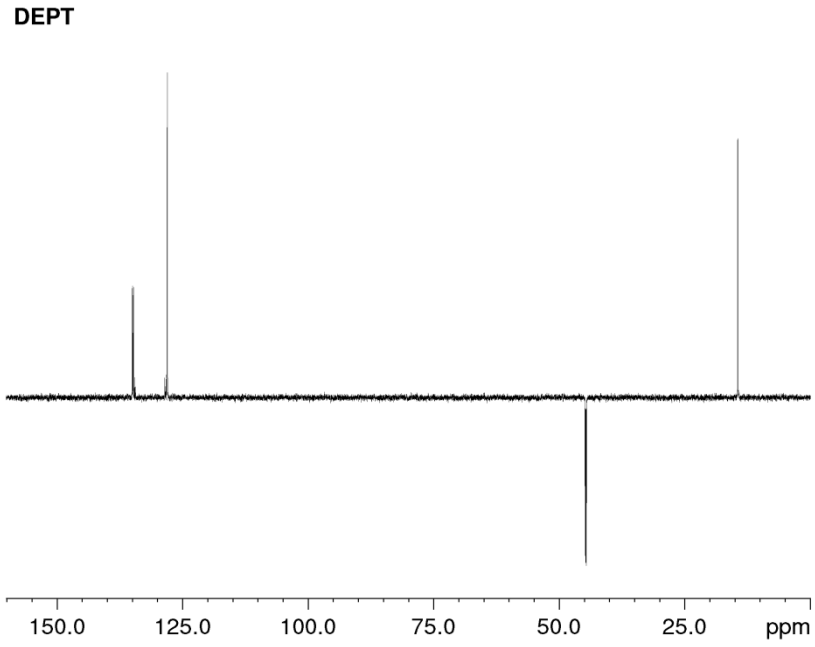


Fig. S92. ^{13}C with DEPT NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPPh_2$ **11**

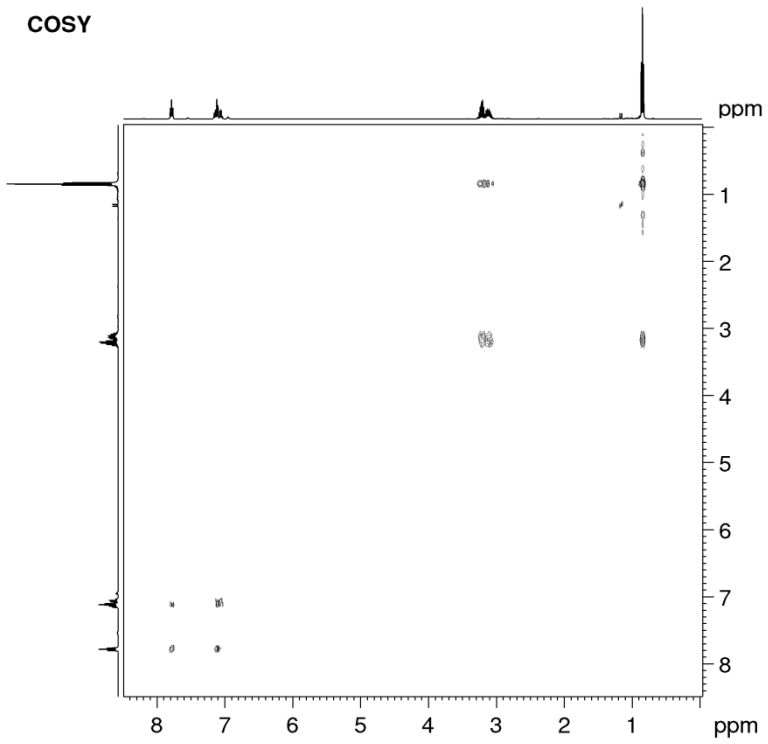


Fig. S93. COSY NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPPh_2$ **11**

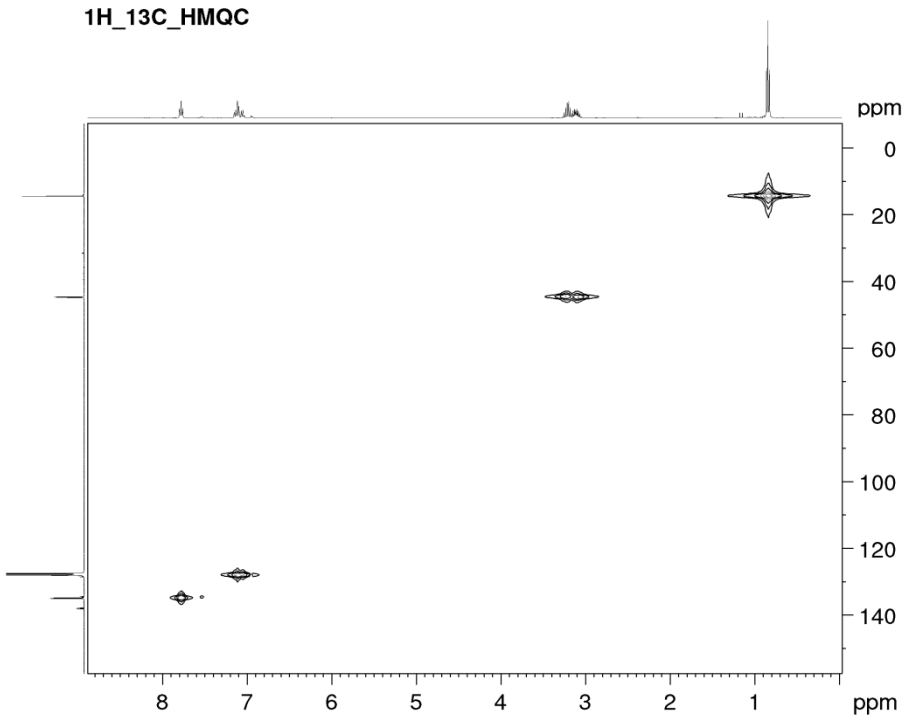


Fig. S94. ^{13}C ^{1}H HMQC NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPPh_2$ **11**

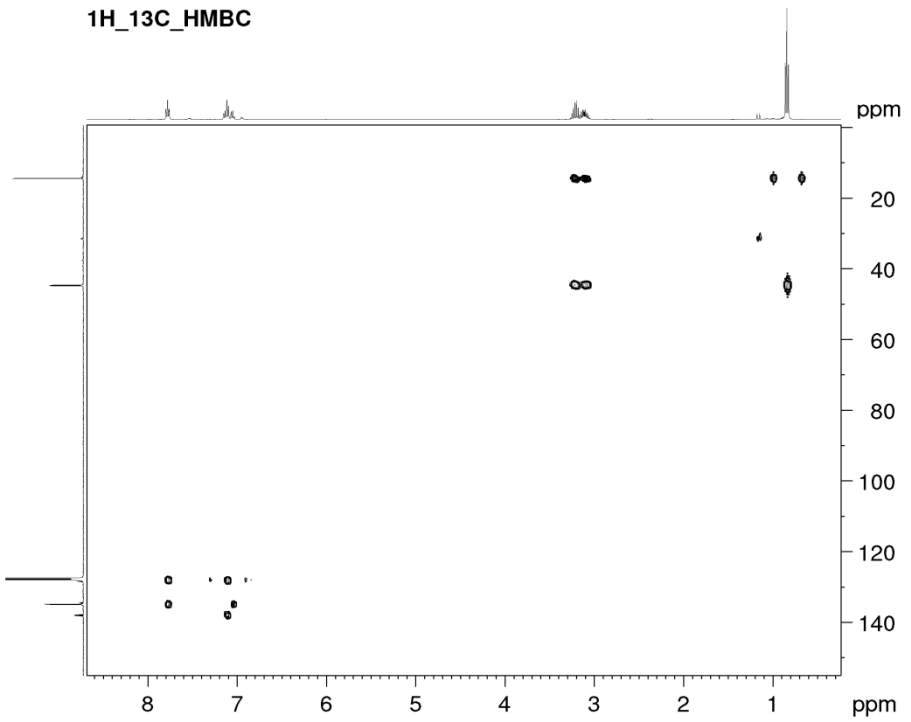


Fig. S95. ^{13}C ^{1}H HMBC NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPPh_2$ **11**

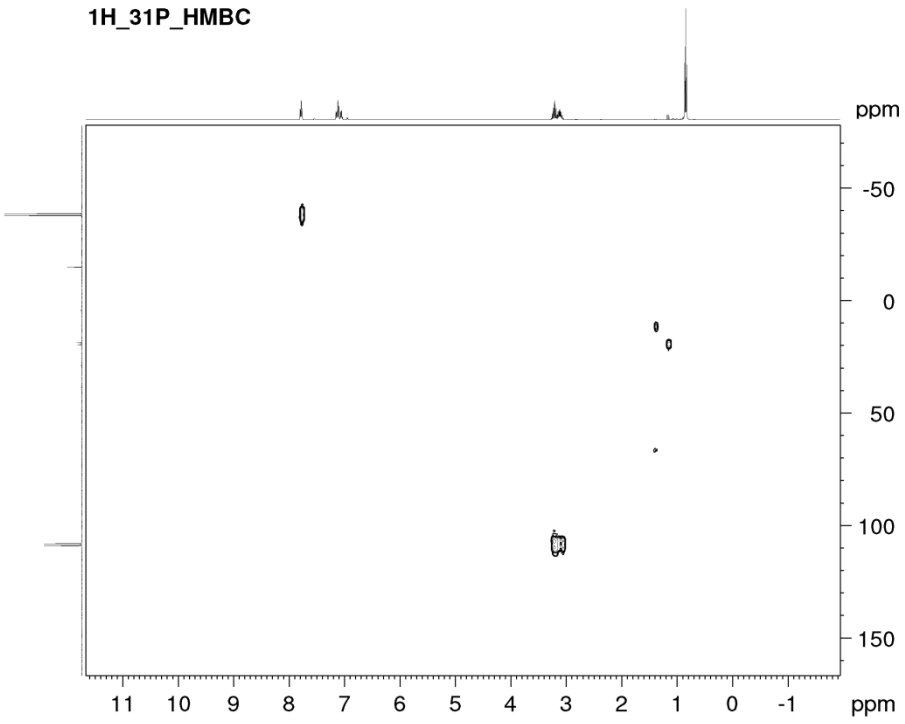


Fig. S96. ^{31}P ^{1}H HMBC NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPPh_2$ **11**

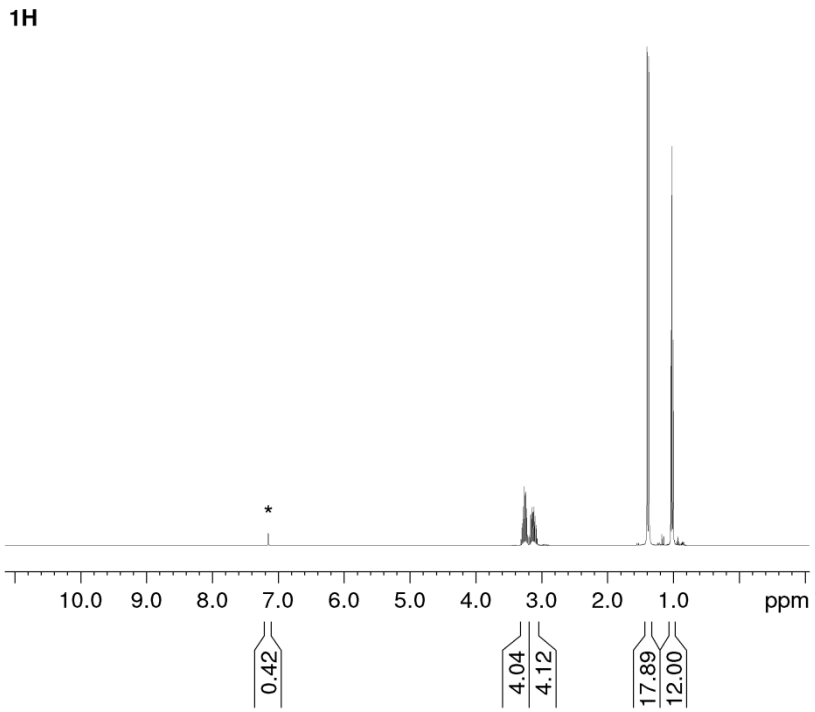


Fig. S97. ^{1}H NMR (C_6D_6) spectra of isolated $(Et_2N)_2PP\textit{t}Bu_2$ **12**

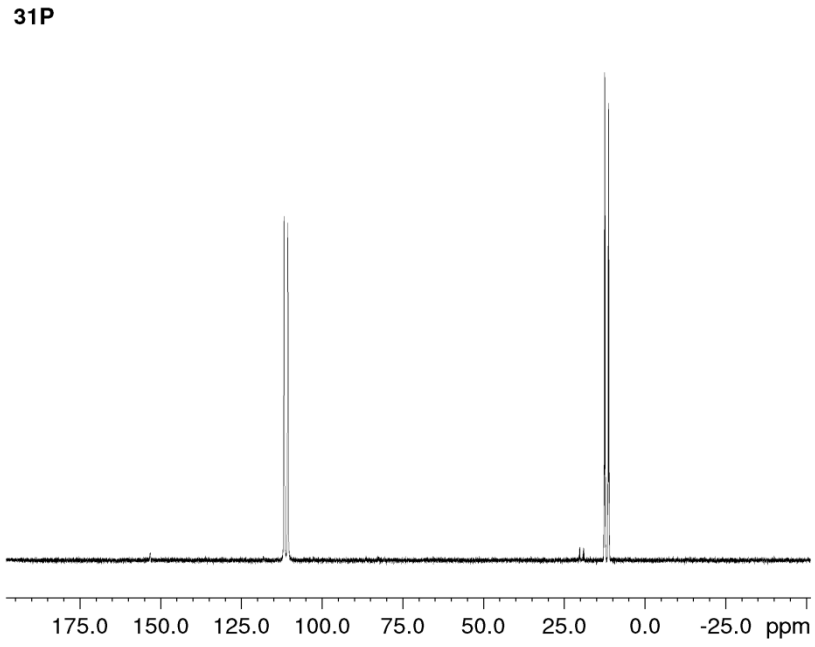


Fig. S98. ^{31}P NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPtBu_2$ **12**

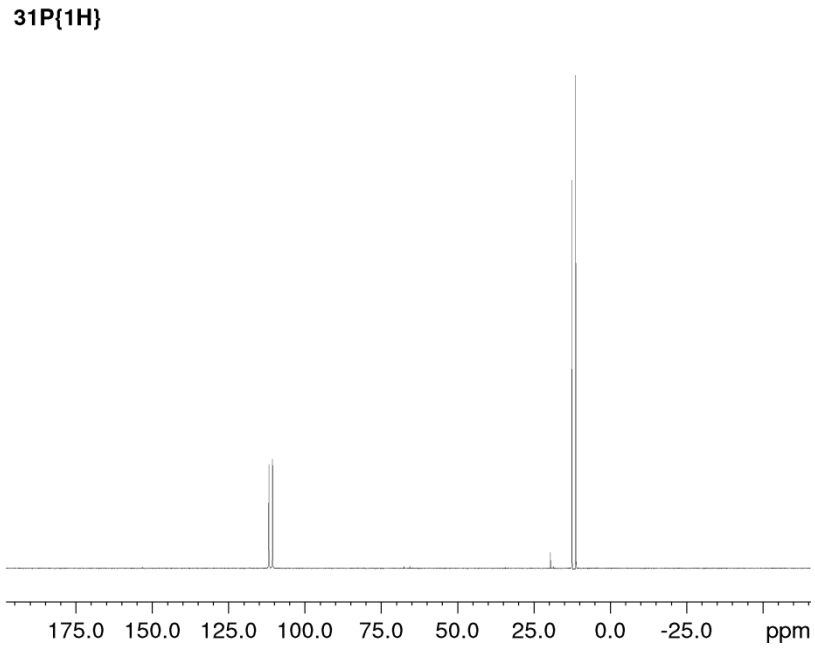


Fig. S99. $^{31}P\{^1H\}$ NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPtBu_2$ **12**

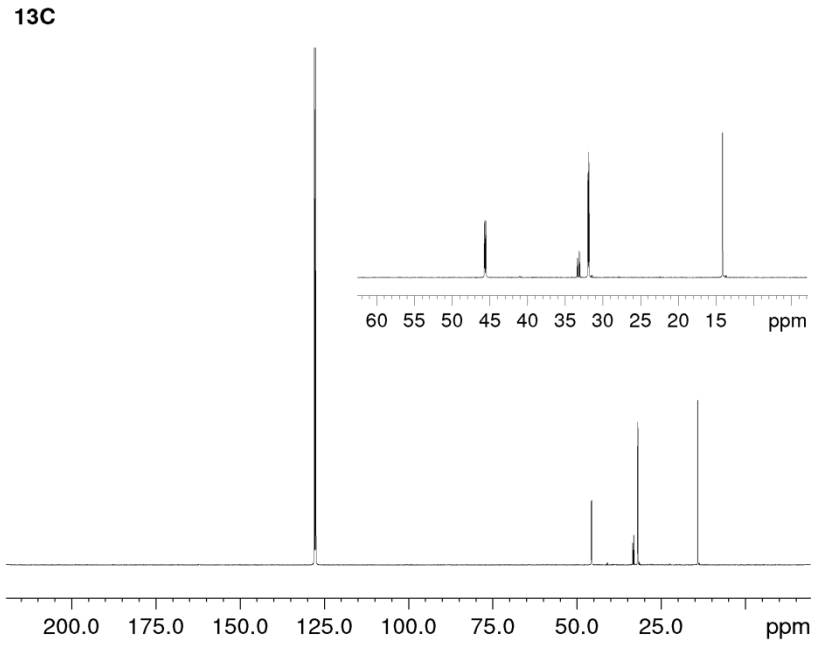


Fig. S100. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectra of isolated $(Et_2N)_2PP\textit{t}Bu_2$ **12**

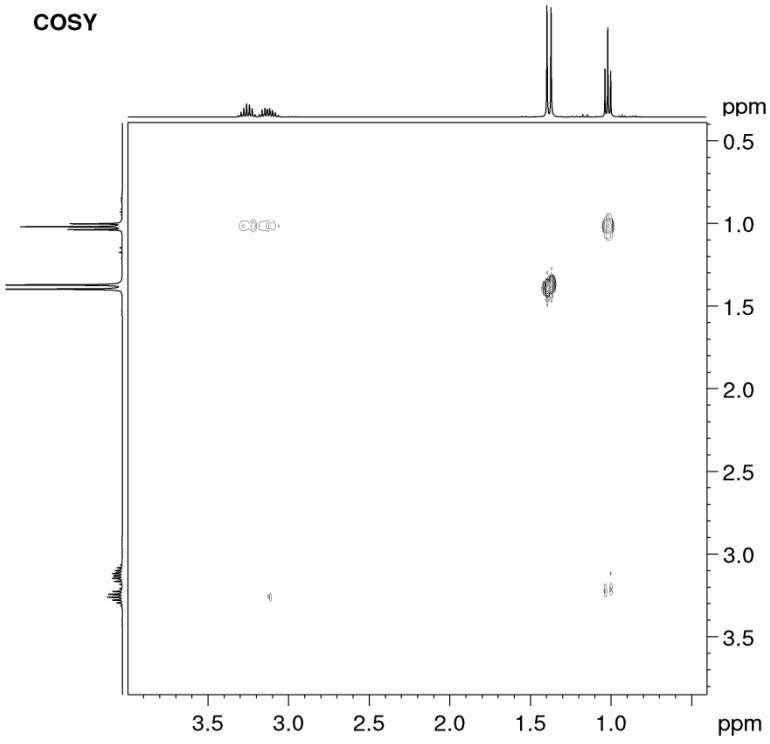


Fig. S101. COSY NMR (C_6D_6) spectra of isolated $(Et_2N)_2PP\textit{t}Bu_2$ **12**

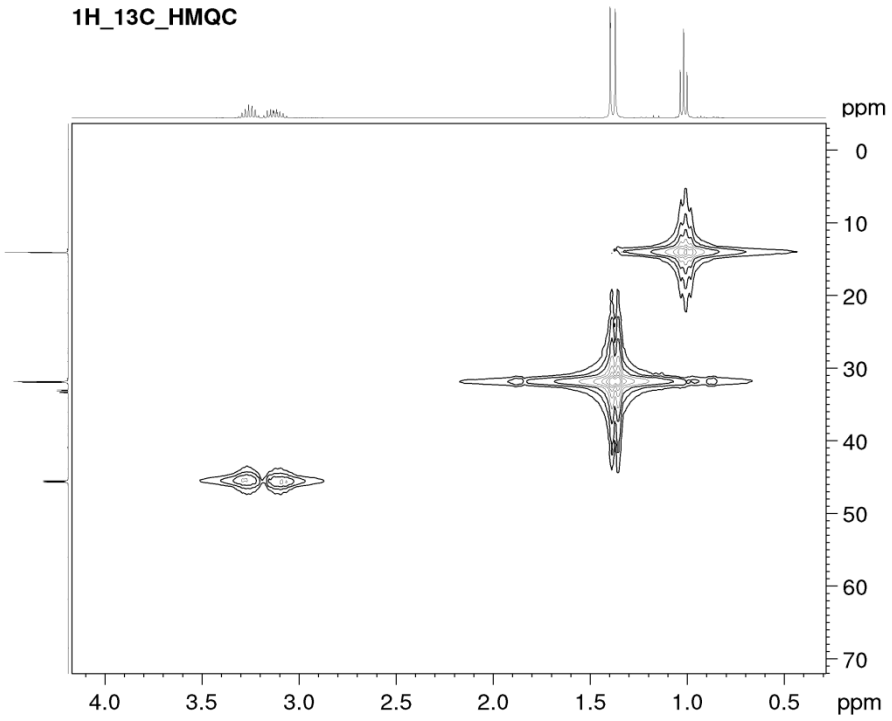


Fig. S102. ^{13}C ^{1}H HMQC NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPtBu_2$ **12**

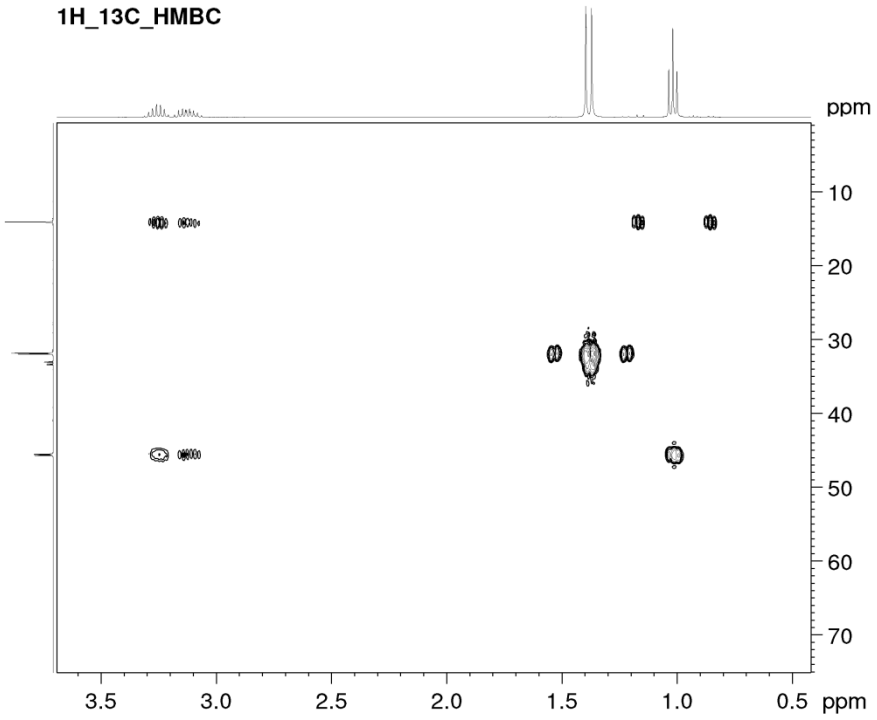


Fig. S103. ^{13}C ^{1}H HMBC NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPtBu_2$ **12**

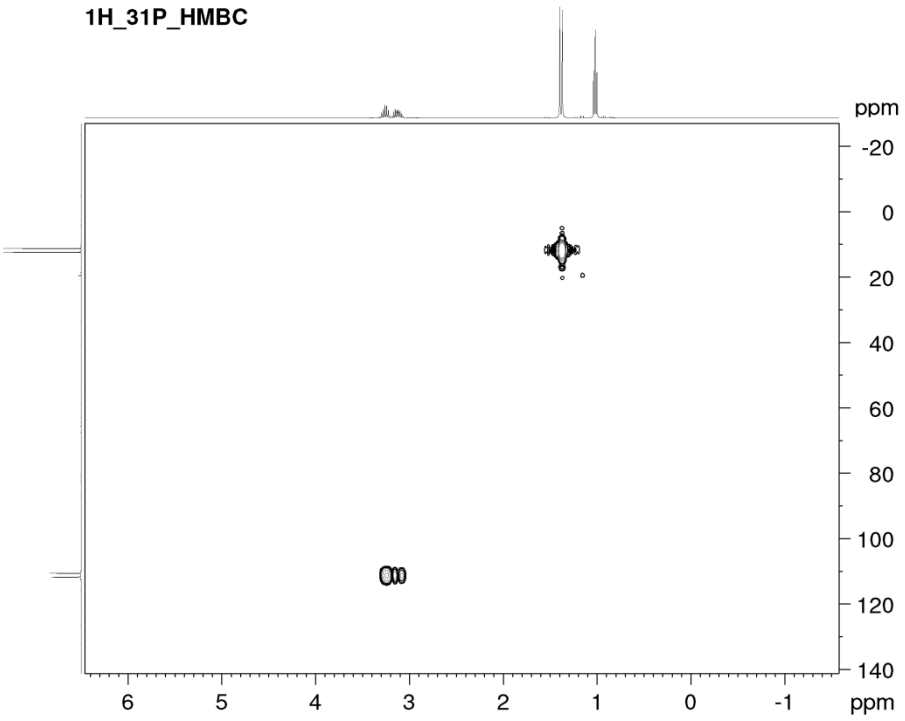


Fig. S104. ^{31}P ^{1}H HMBC NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPtBu_2$ **12**

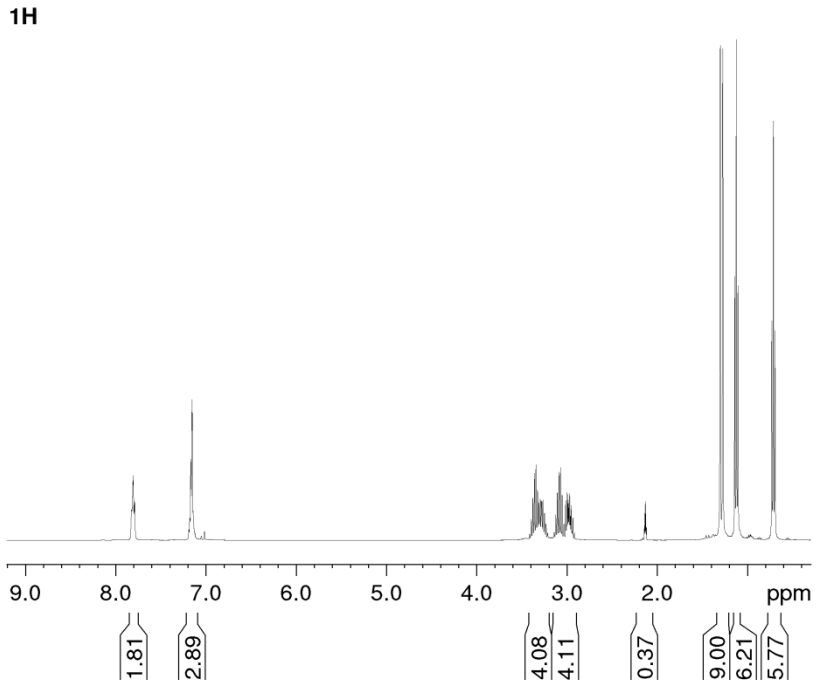


Fig. S105. ^{1}H NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPtBuPh$ **13**

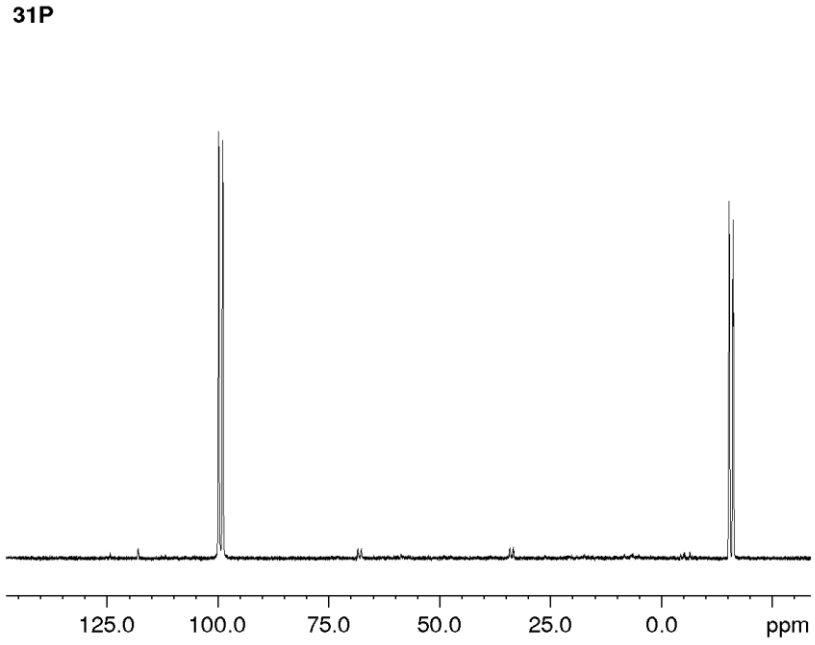


Fig. S106. ^{31}P NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPtBuPh$ **13**

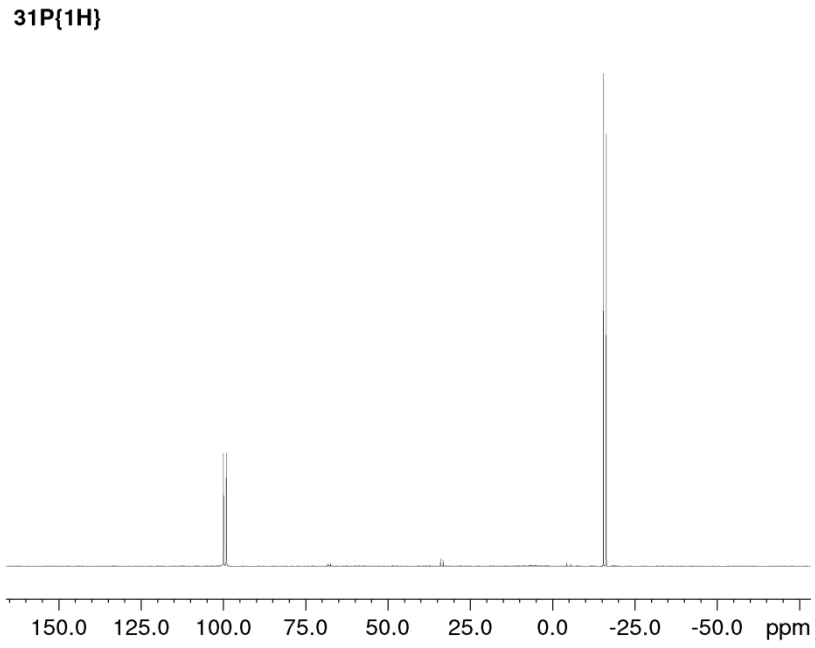


Fig. S107. $^{31}P\{^1H\}$ NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPtBuPh$ **13**

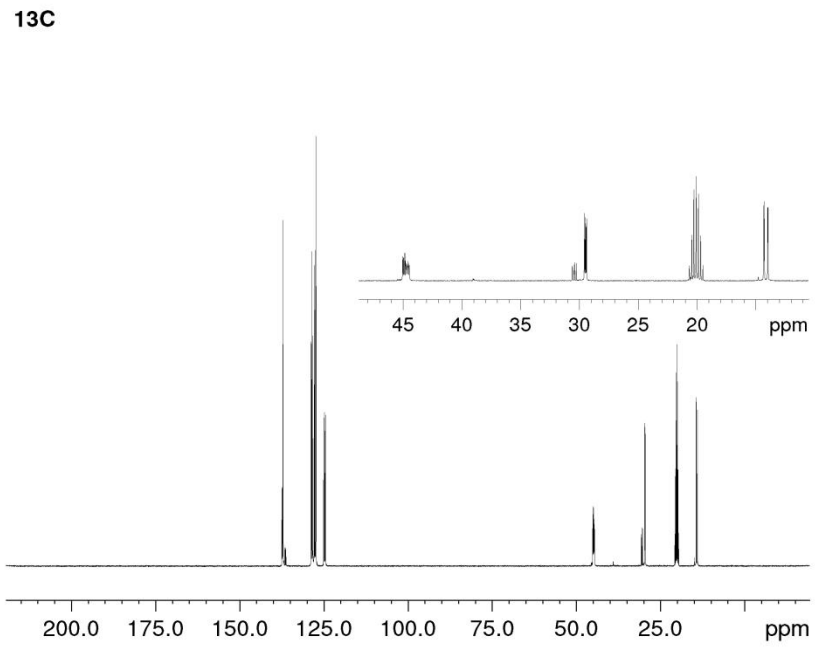


Fig. S108. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPtBuPh$ **13**

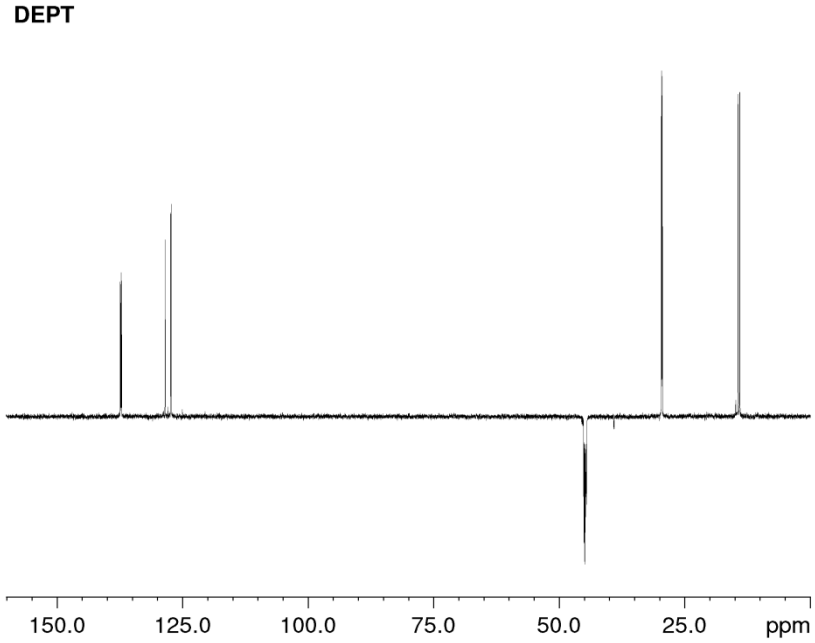


Fig. S109. ^{13}C with DEPT NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPtBuPh$ **13**

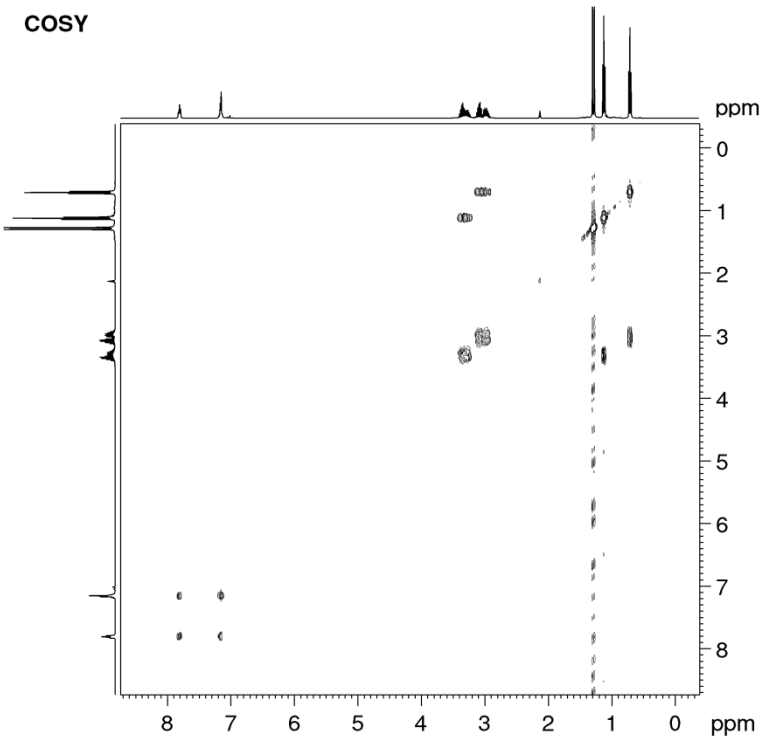


Fig. S110. COSY NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPtBuPh$ **13**

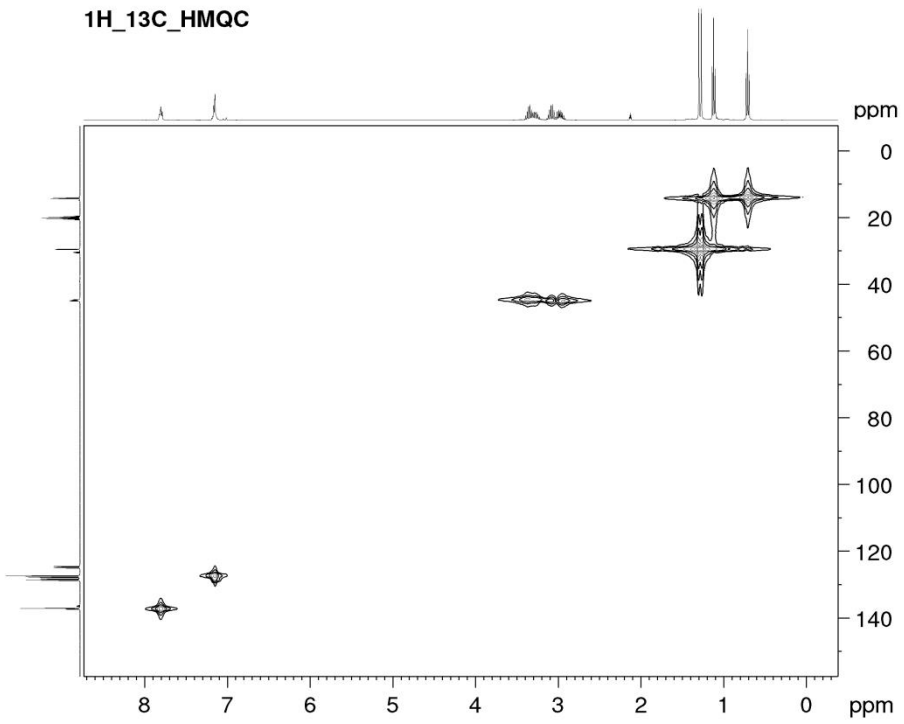


Fig. S111. ^{13}C ^{1}H HMQC NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPtBuPh$ **13**

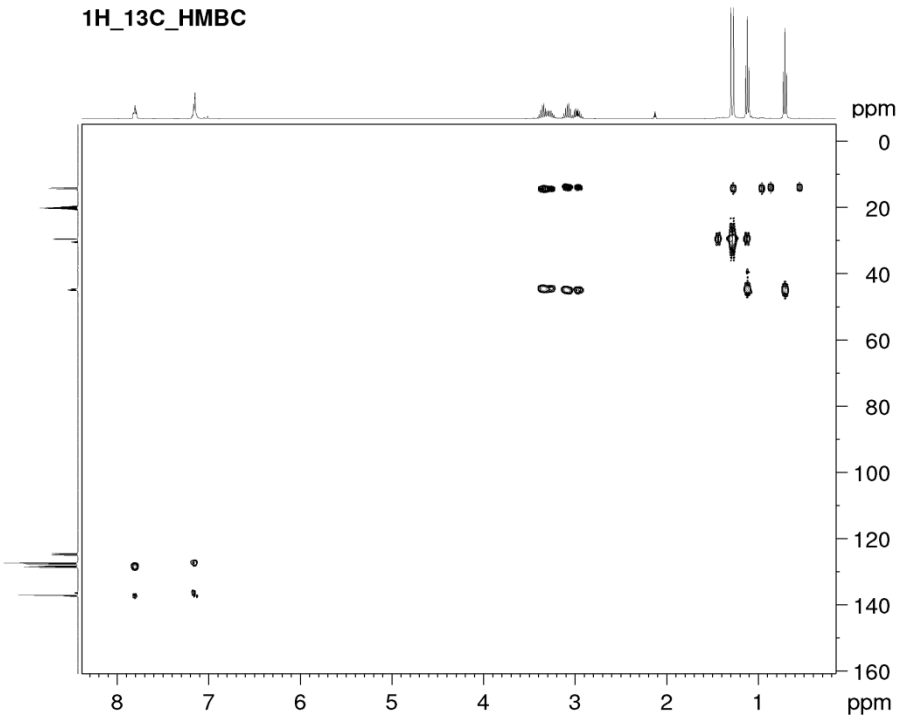


Fig. S112. ^{13}C ^{1}H HMBC NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPtBuPh$ **13**

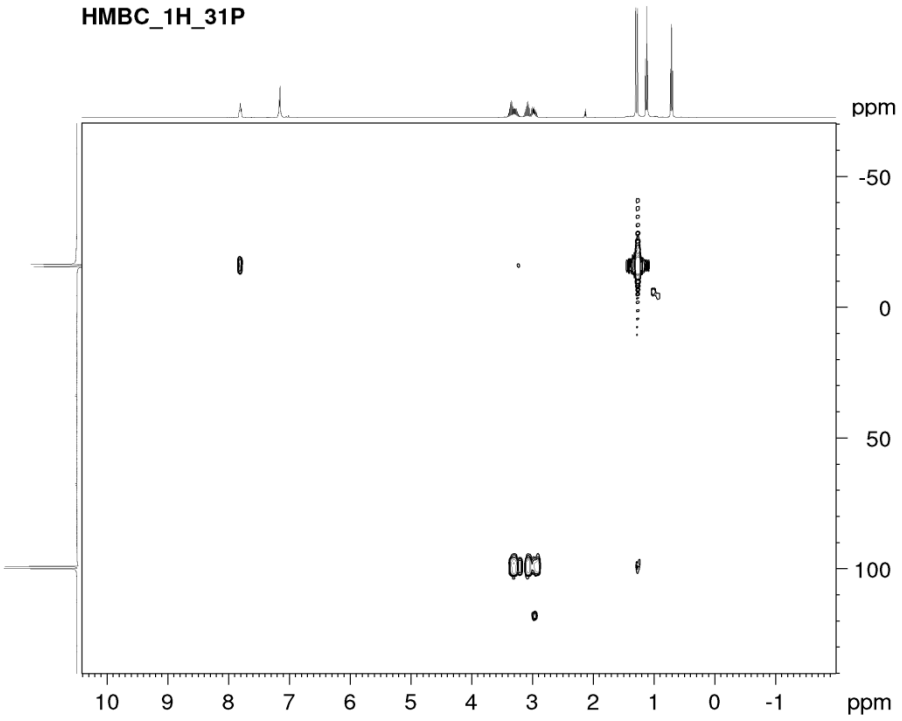


Fig. S113. ^{31}P ^{1}H HMBC NMR (C_6D_6) spectra of isolated $(Et_2N)_2PPtBuPh$ **13**

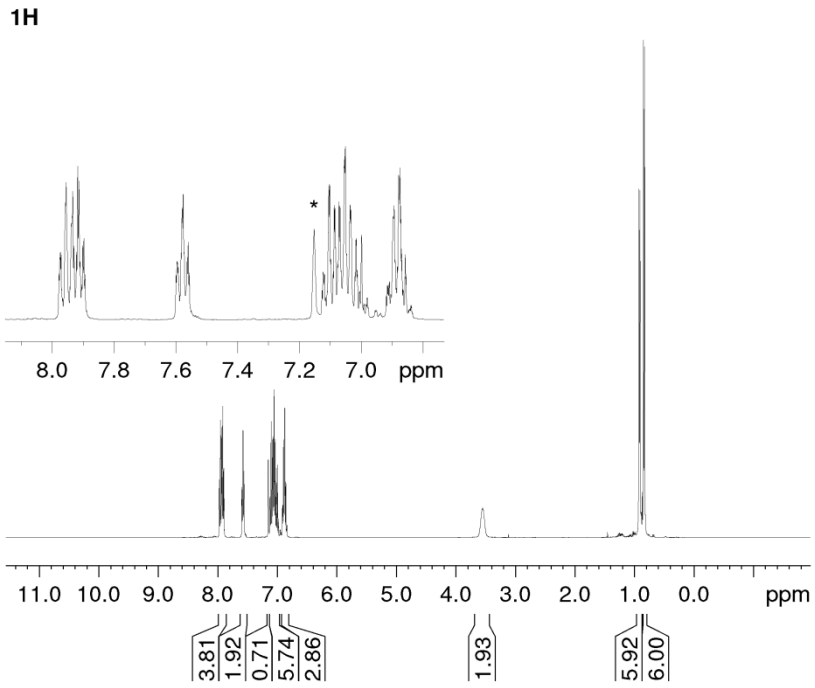


Fig. S114. ^{1}H NMR (C_6D_6) spectra of isolated (iPr$_2$N)PhPPPh$_2$ **14**

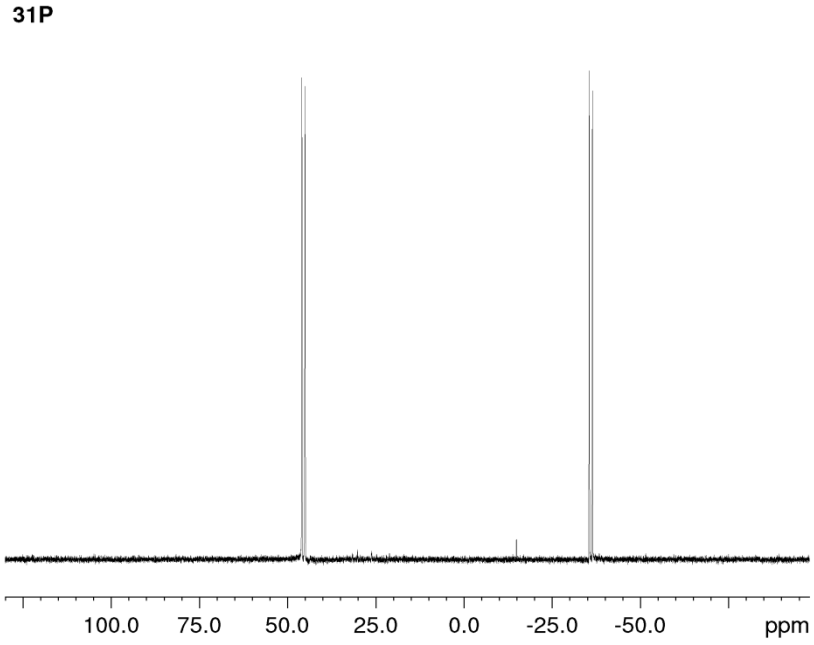


Fig. S115. ^{31}P NMR (C_6D_6) spectra of isolated (iPr$_2$N)PhPPPh$_2$ **14**

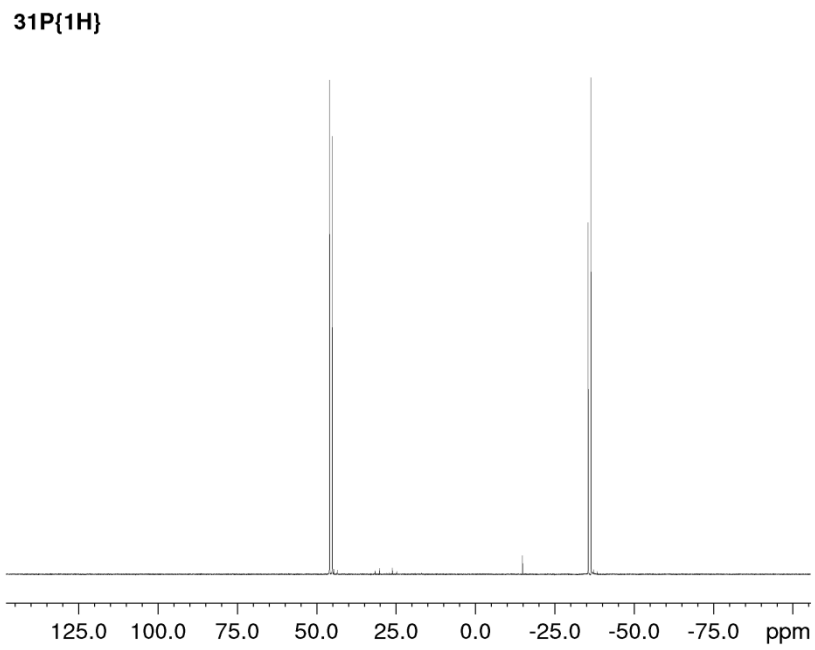


Fig. S116. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of isolated (iPr$_2$N)PhPPPh$_2$ **14**

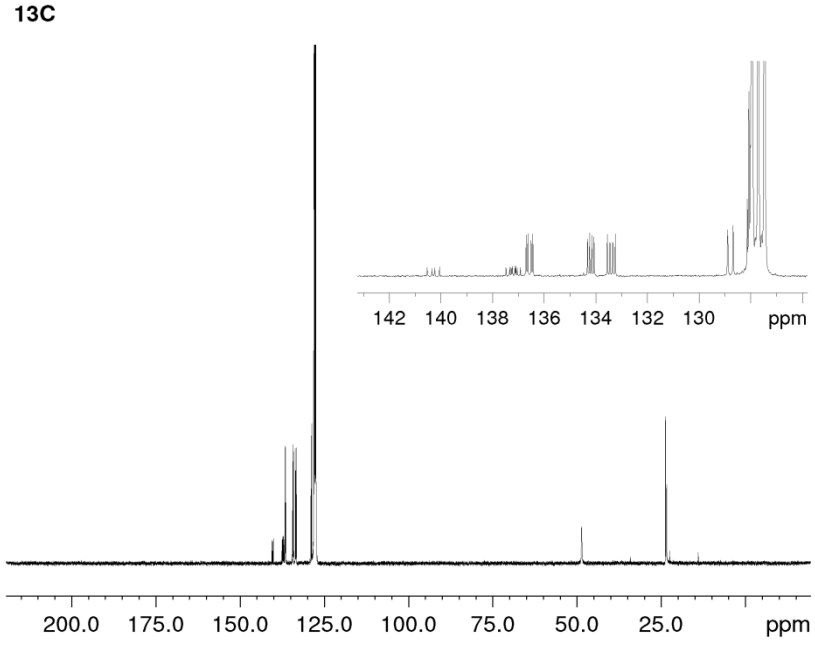


Fig. S117. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectra of isolated (iPr$_2$N)PhPPPh$_2$ **14**

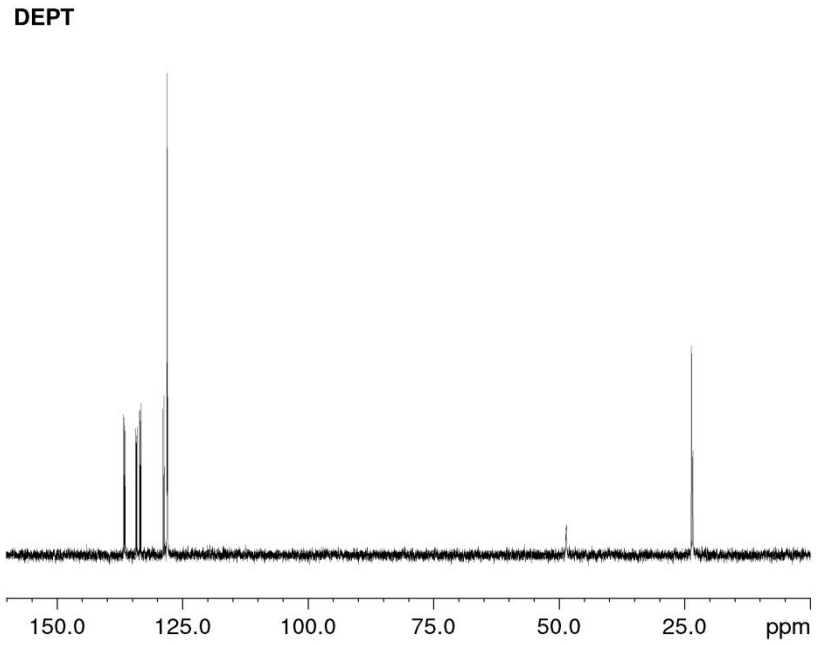


Fig. S118. ^{13}C with DEPT NMR (C_6D_6) spectra of isolated (iPr$_2$N)PhPPPh$_2$ **14**

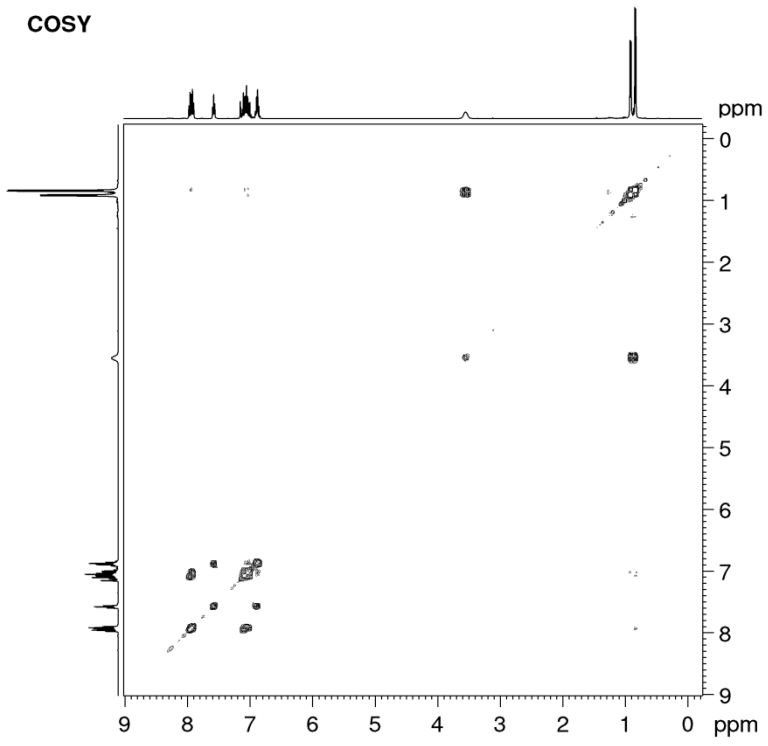


Fig. S119. COSY NMR (C_6D_6) spectra of isolated (iPr$_2$N)PhPPPh$_2$ **14**

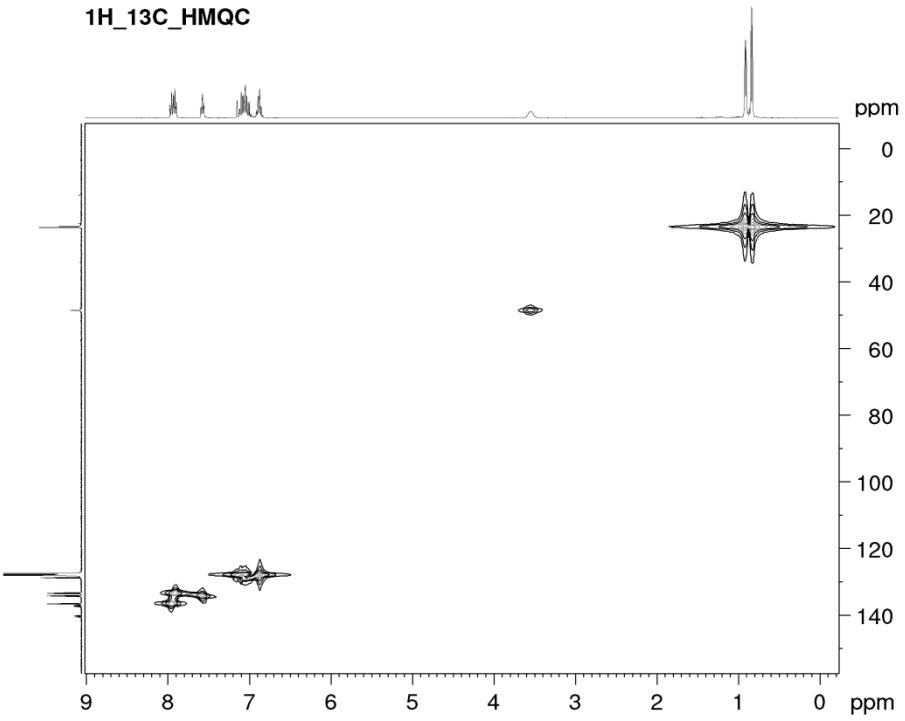


Fig. S120. ^{13}C ^{1}H HMQC NMR (C_6D_6) spectra of isolated (iPr$_2$N)PhPPPh$_2$ **14**

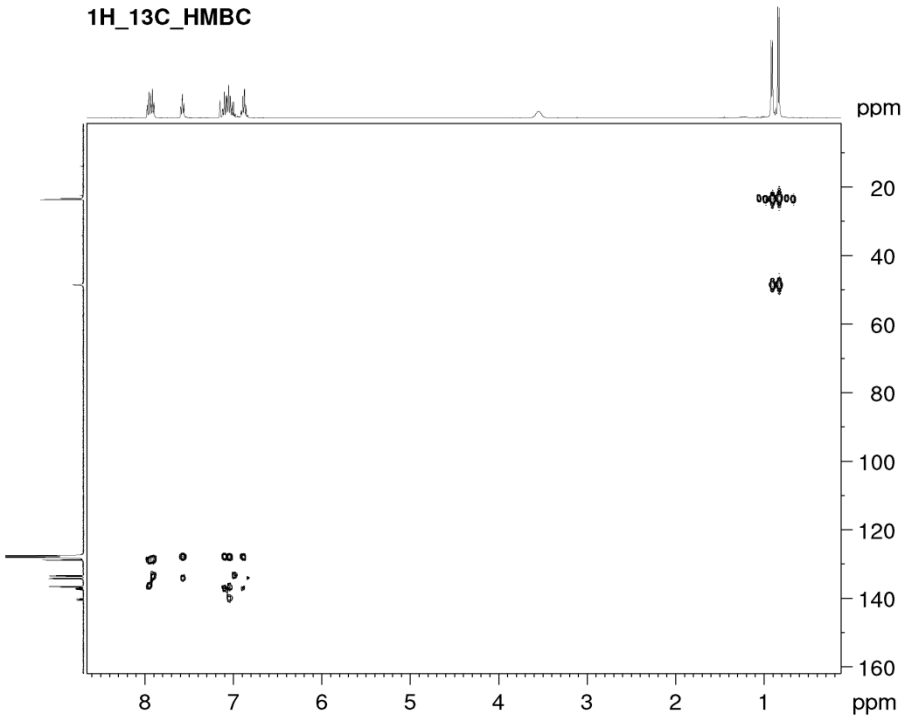


Fig. S121. ^{13}C ^{1}H HMBC NMR (C_6D_6) spectra of isolated (iPr$_2$N)PhPPPh$_2$ **14**

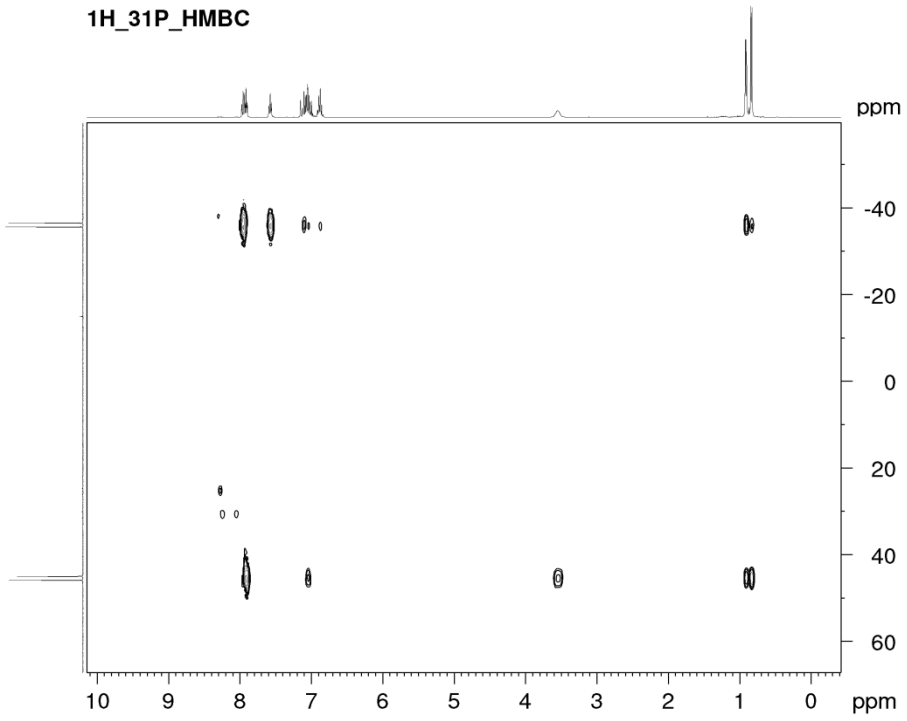


Fig. S122. ^{31}P ^{1}H HMBC NMR (C_6D_6) spectra of isolated (iPr$_2$N)PhPPPh$_2$ **14**

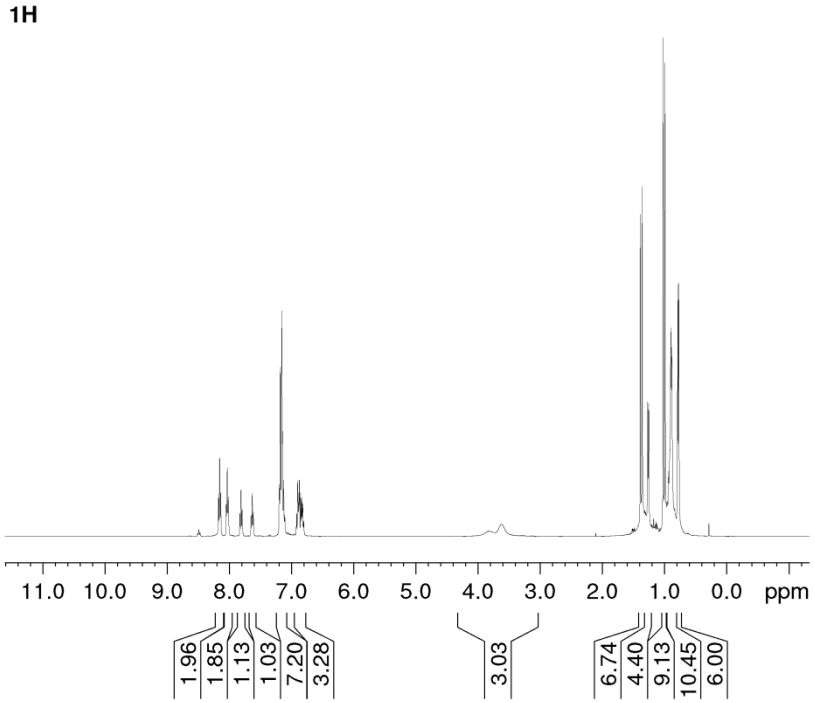


Fig. S123. ^{1}H NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr$_2$N)PhPP*t*BuPh **15** and *rac*-(*i*Pr$_2$N)PhPP*t*BuPh **16**

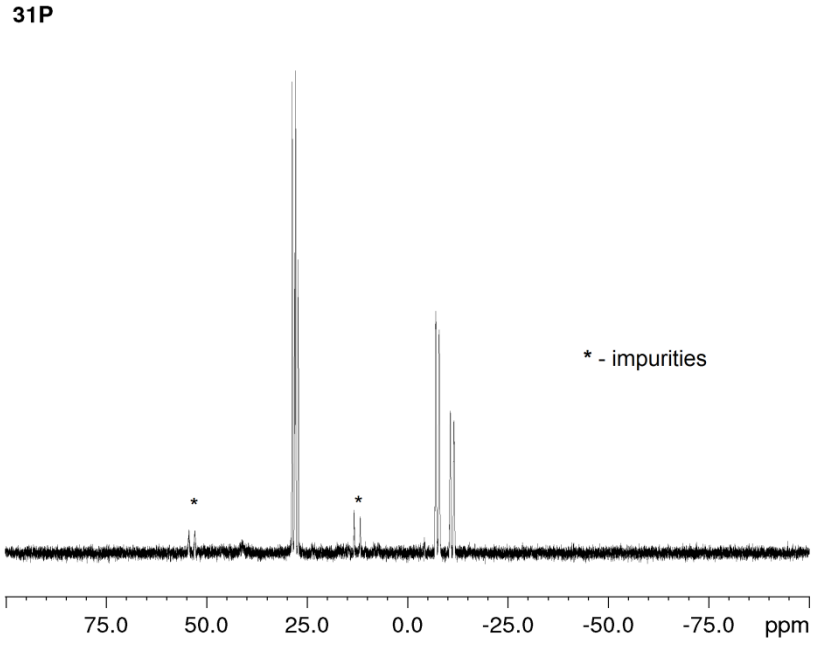


Fig. S124. ^{31}P NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr$_2$N)PhPP*t*BuPh **15** and *rac*-(*i*Pr$_2$N)PhPP*t*BuPh **16**

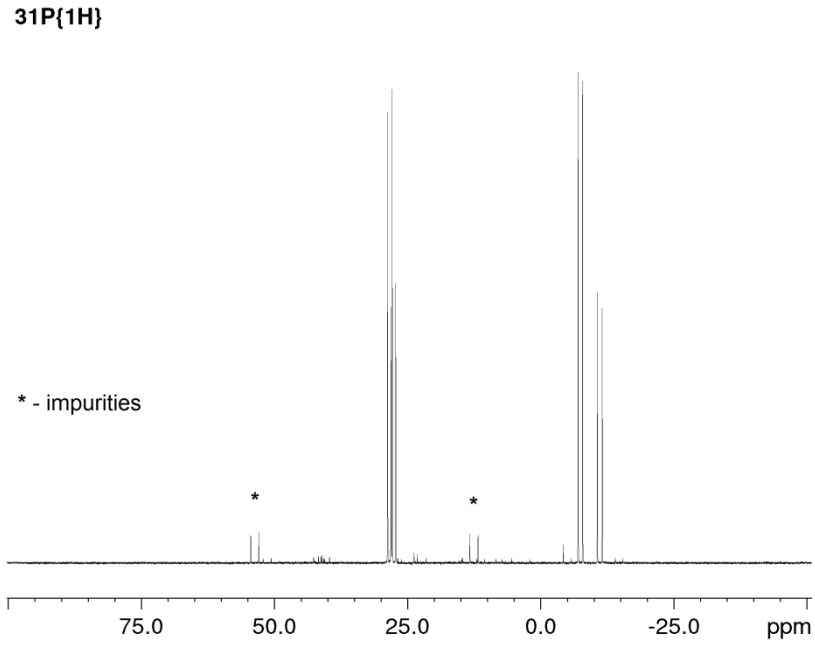


Fig. S125. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)PhPP*t*BuPh **15** and *rac*-(*i*Pr_2N)PhPP*t*BuPh **16**

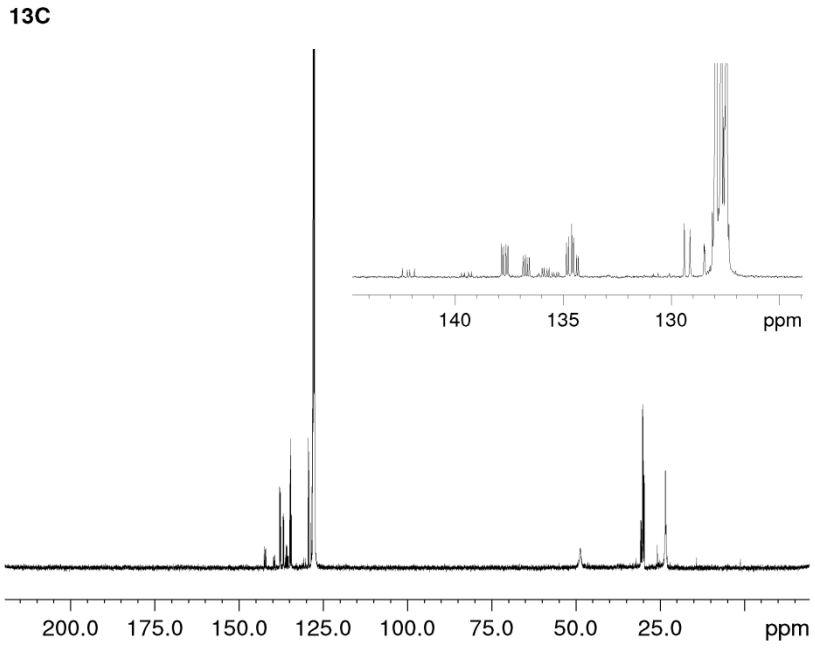


Fig. S126. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)PhPP*t*BuPh **15** and *rac*-(*i*Pr_2N)PhPP*t*BuPh **16**

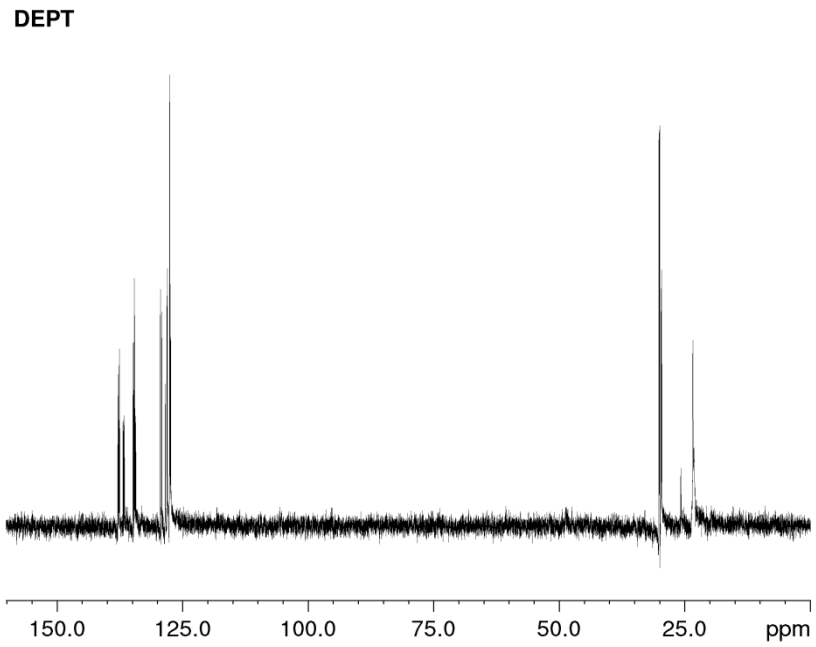


Fig. S127. ^{13}C with DEPT NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)PhPP*t*BuPh **15** and *rac*-(*i*Pr_2N)PhPP*t*BuPh **16**

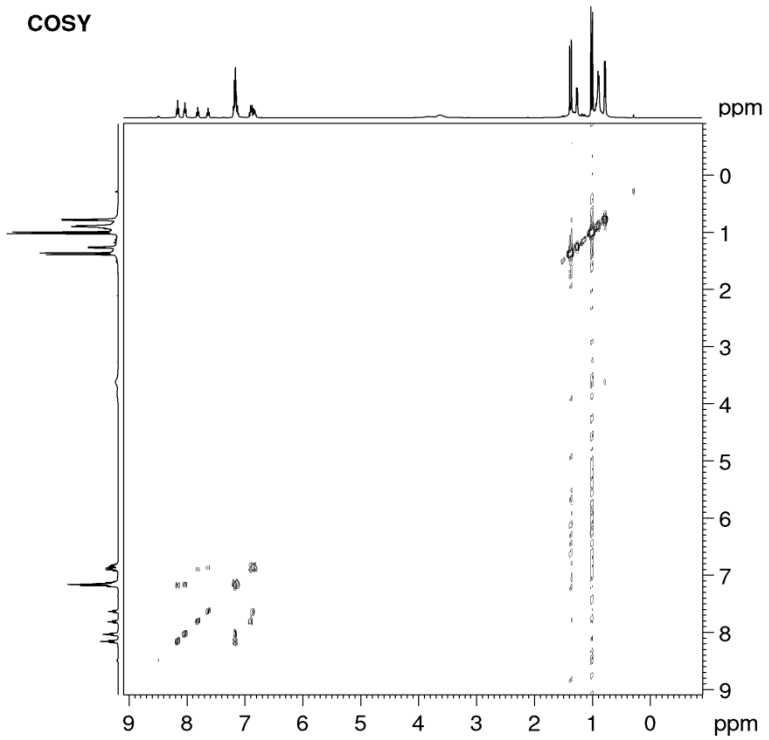


Fig. S128. COSY NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)PhPP*t*BuPh **15** and *rac*-(*i*Pr_2N)PhPP*t*BuPh **16**

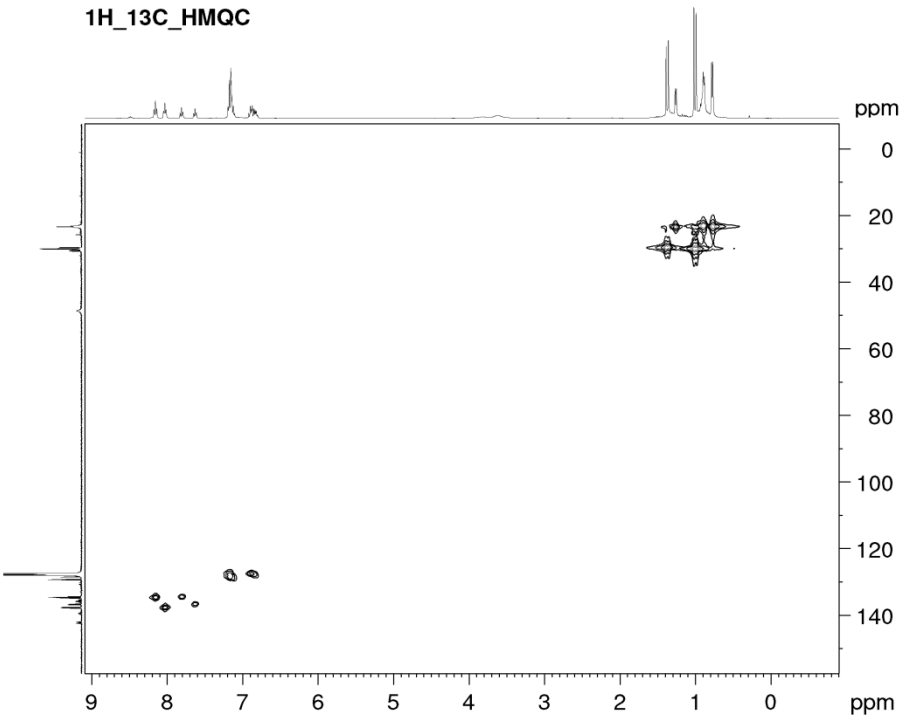


Fig. S129. ^{13}C ^{1}H HMQC NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)PhPP*t*BuPh **15** and *rac*-(*i*Pr_2N)PhPP*t*BuPh **16**

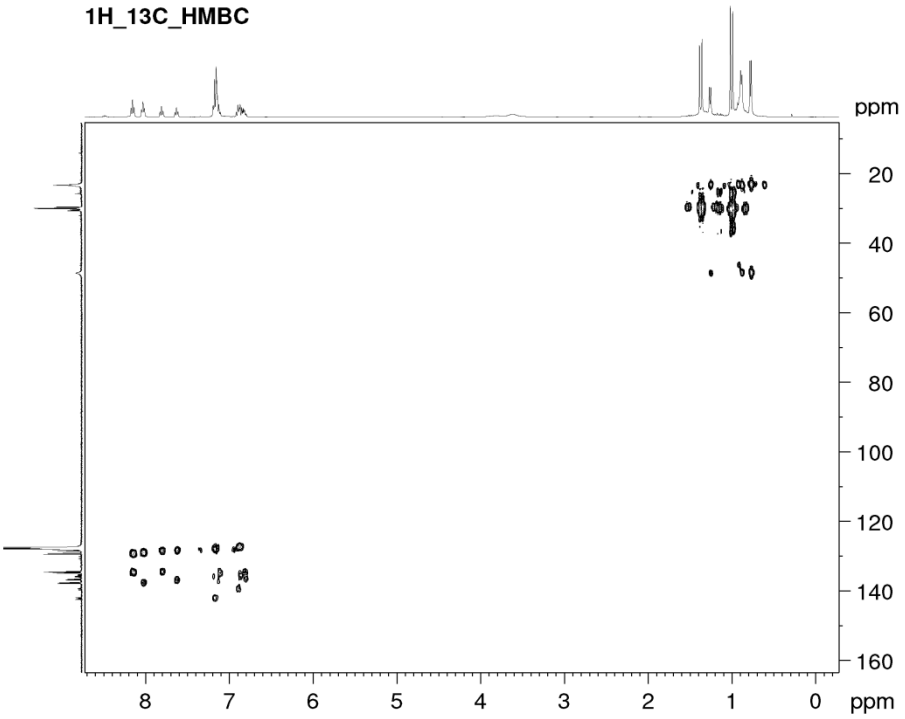


Fig. S130. ^{13}C ^{1}H HMBC NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)PhPP*t*BuPh **15** and *rac*-(*i*Pr_2N)PhPP*t*BuPh **16**

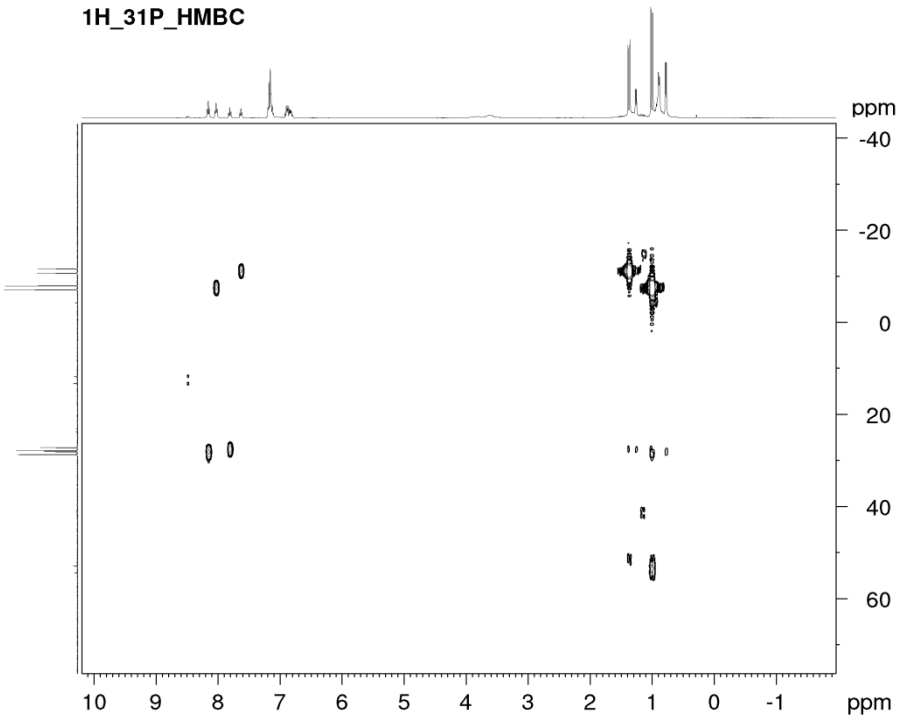


Fig. S131. ^{31}P ^{1}H HMBC NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)PhPP*t*BuPh **15** and *rac*-(*i*Pr_2N)PhPP*t*BuPh **16**

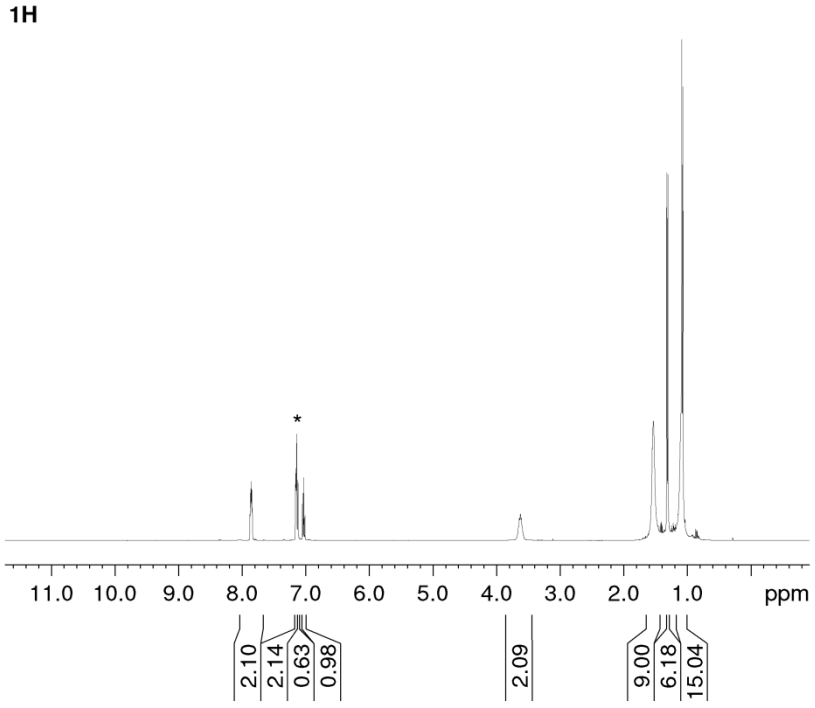


Fig. S132. ^{1}H NMR (C_6D_6) spectra of isolated (*i*Pr_2N)PhPP*t*Bu_2 **17**

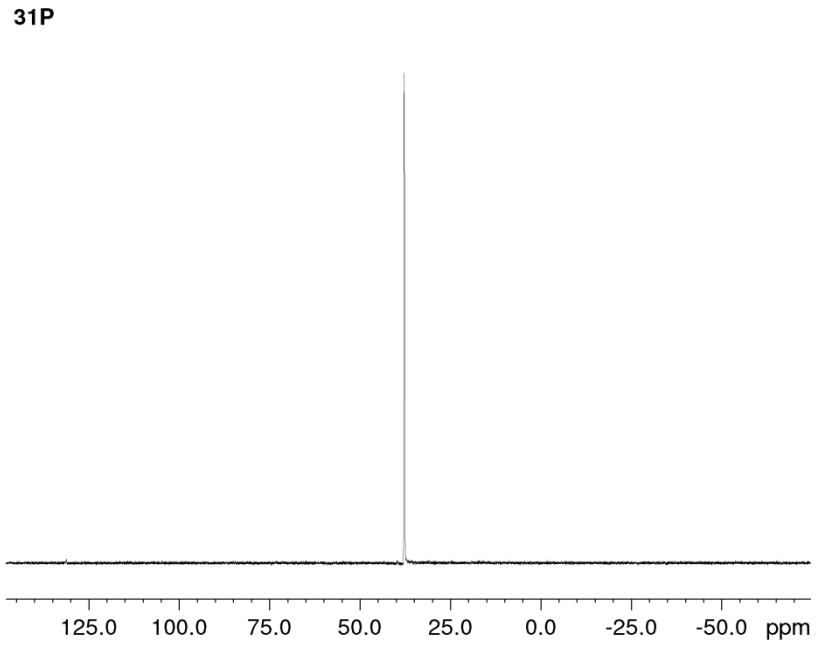


Fig. S133. ^{31}P NMR (C_6D_6) spectra of isolated (*i*Pr_2N)PhPP*t*Bu_2 **17**

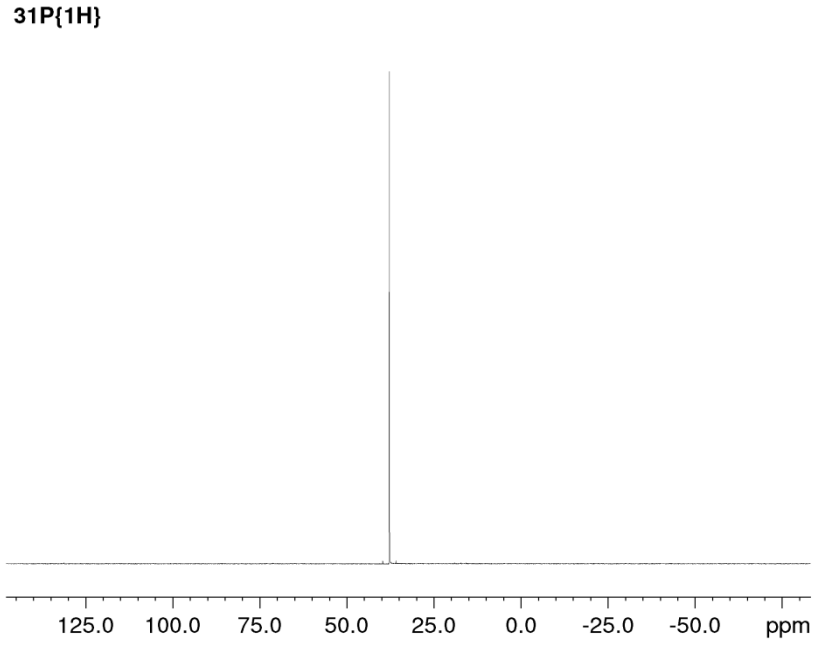


Fig. S134. $^{31}P\{^1H\}$ NMR (C_6D_6) spectra of isolated (*i*Pr_2N)PhPP*t*Bu_2 **17**

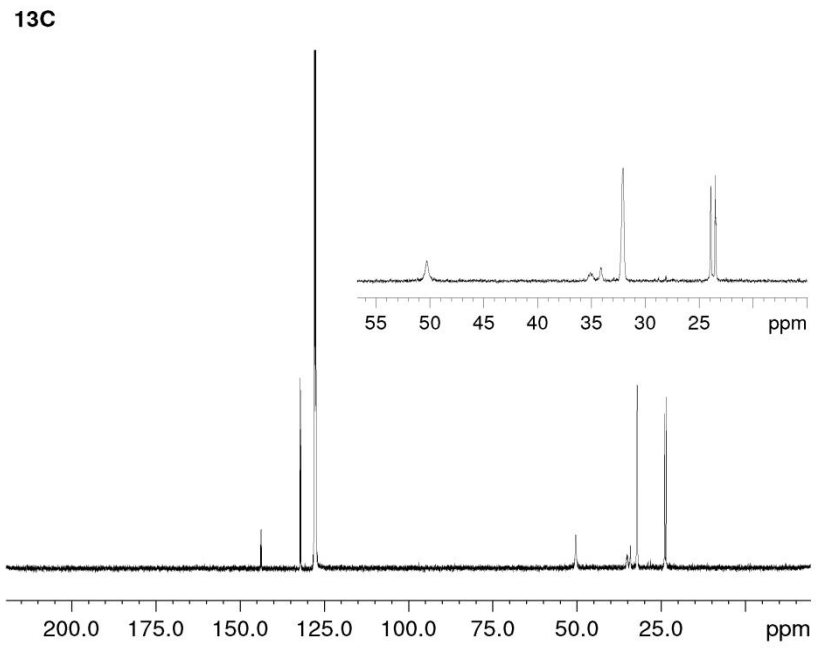


Fig. S135. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectra of isolated (iPr$_2$N)PhPPtBu$_2$ **17**

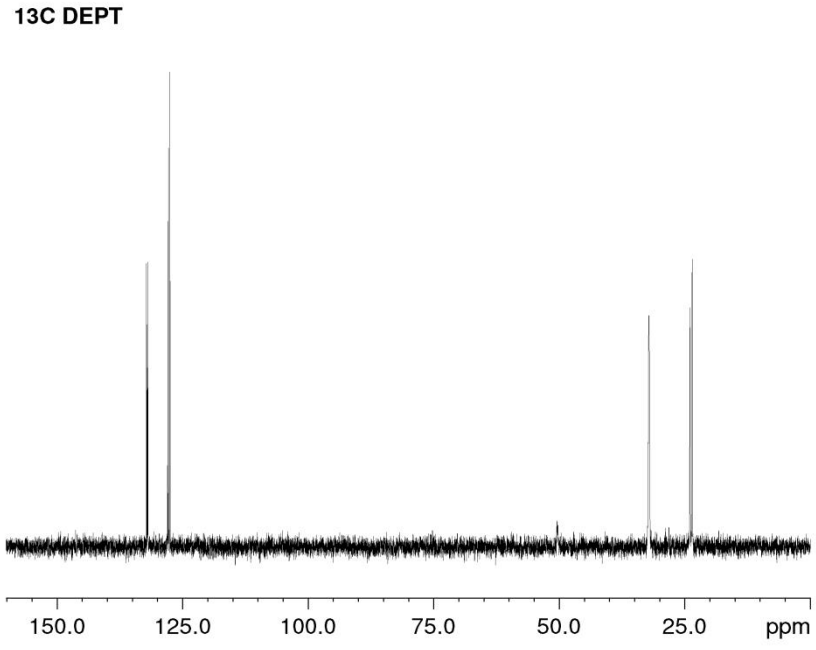


Fig. S136. ^{13}C with DEPT NMR (C_6D_6) spectra of isolated (iPr$_2$N)PhPPtBu$_2$ **17**

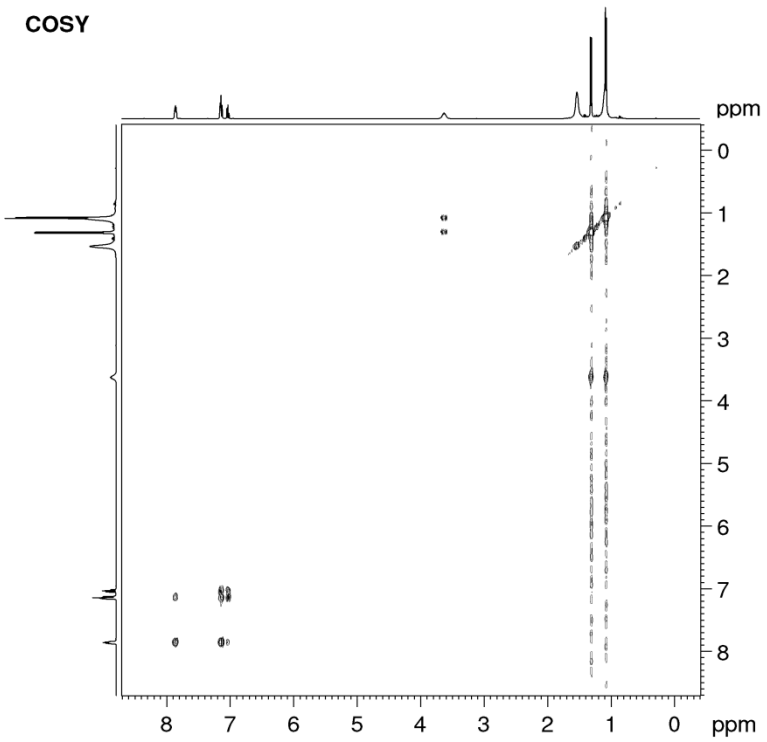


Fig. S137. COSY NMR (C_6D_6) spectra of isolated (iPr$_2$N)PhPPtBu$_2$ **17**

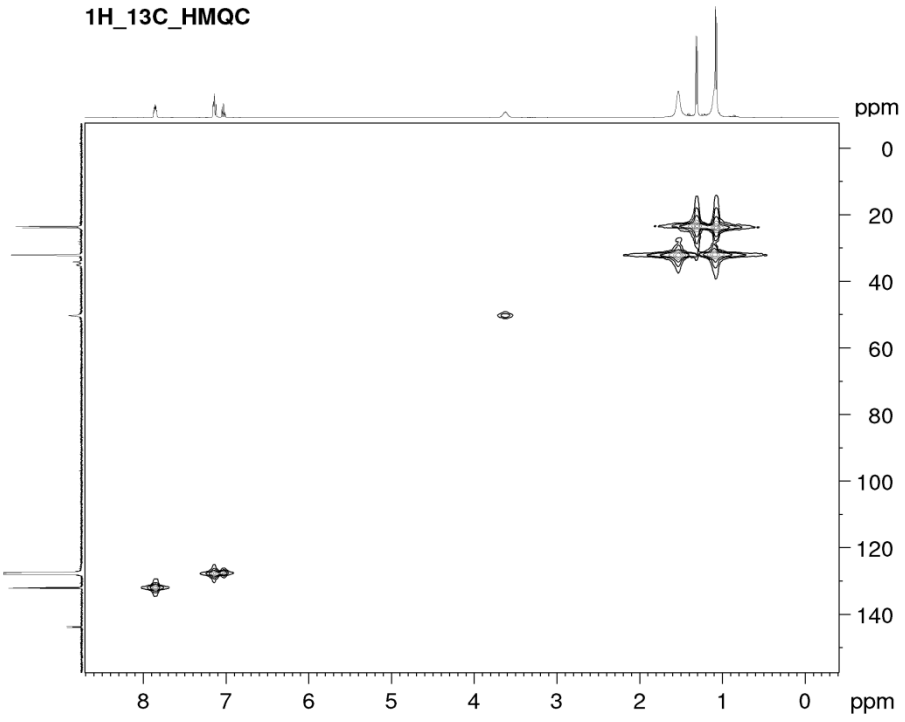


Fig. S138. ^{13}C ^{1}H HMQC NMR (C_6D_6) spectra of isolated (iPr$_2$N)PhPPtBu$_2$ **17**

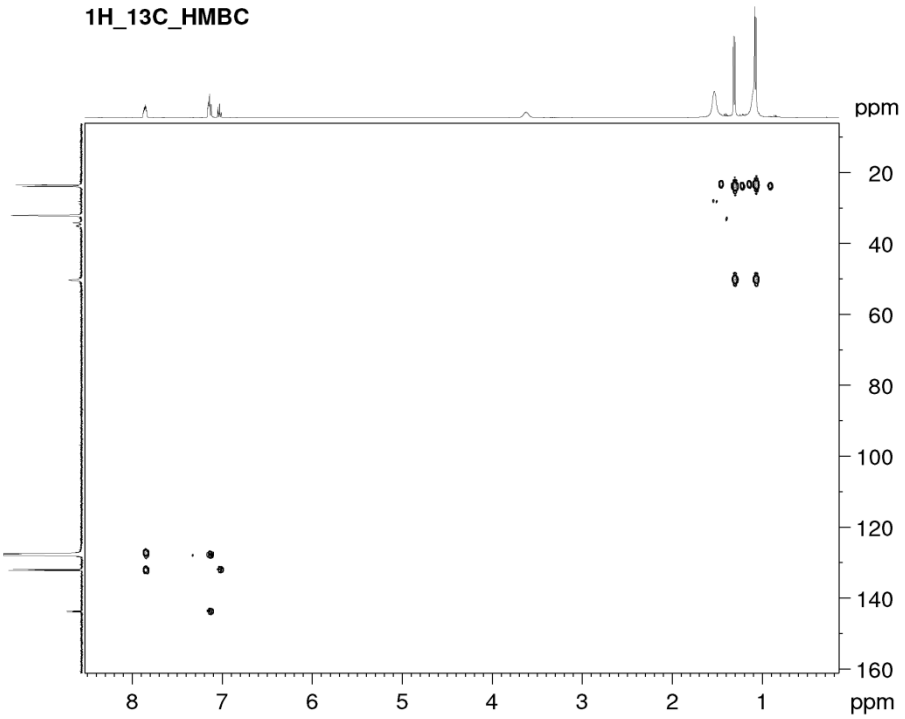


Fig. S139. ^{13}C ^{1}H HMBC NMR (C_6D_6) spectra of isolated (*i*Pr_2N)PhPP*t*Bu_2 **17**

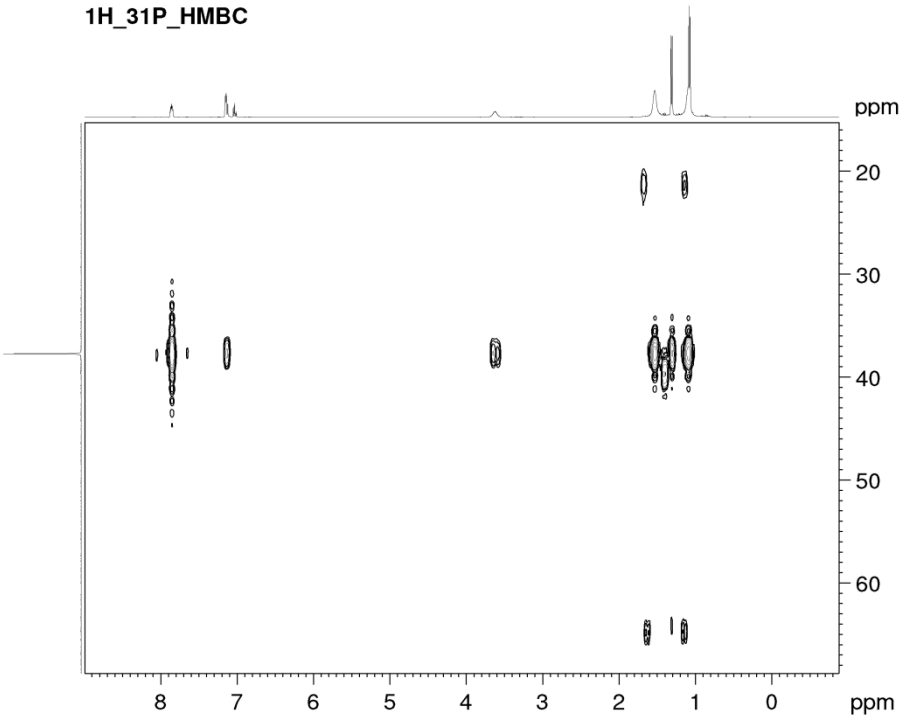


Fig. S140. ^{31}P ^{1}H HMBC NMR (C_6D_6) spectra of isolated (*i*Pr_2N)PhPP*t*Bu_2 **17**

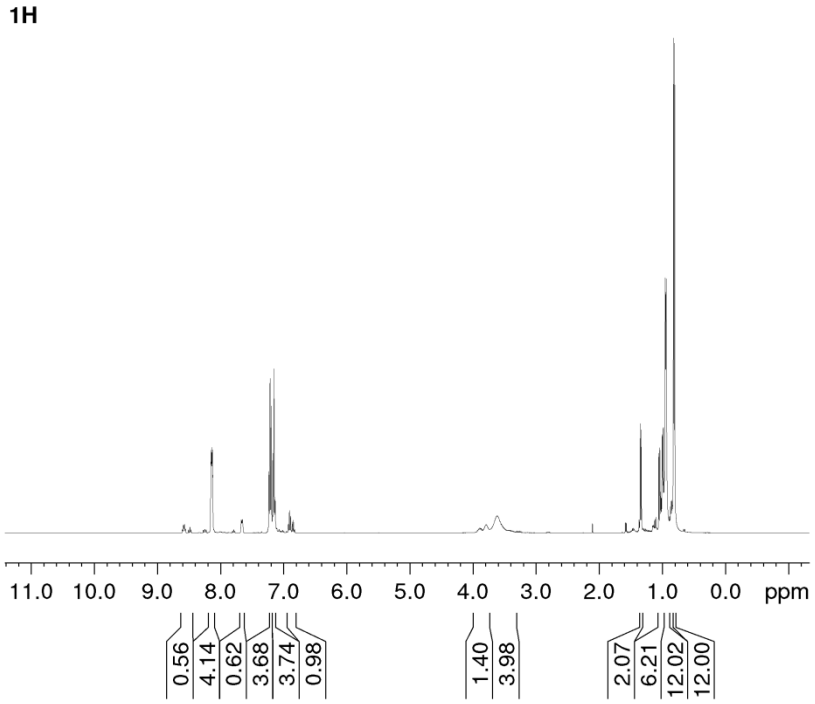


Fig. S141. ^{1}H NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr$_2$N)PhPP(*i*Pr$_2$N)Ph **18** and *rac*-(*i*Pr$_2$N)PhPP(*i*Pr$_2$N)Ph **19**

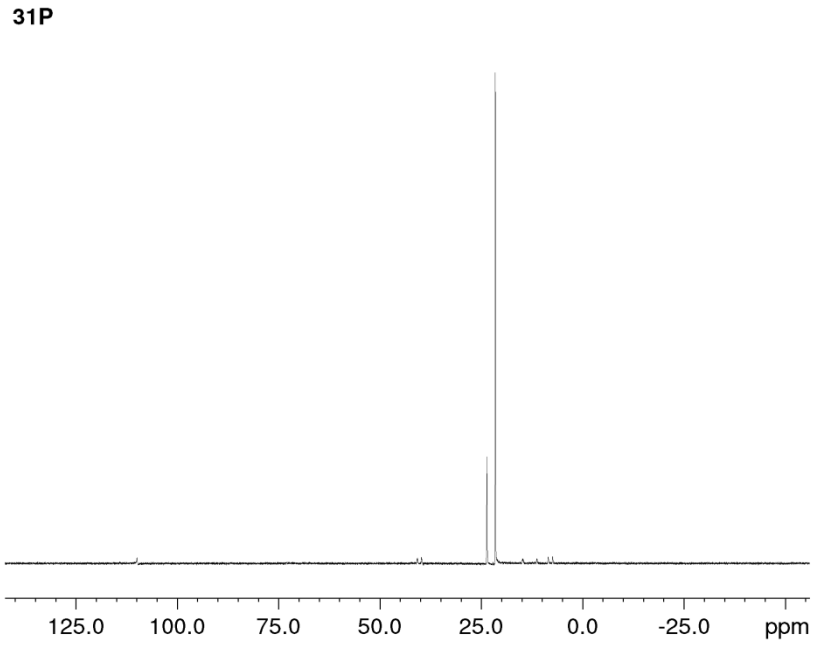


Fig. S142. ^{31}P NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr$_2$N)PhPP(*i*Pr$_2$N)Ph **18** and *rac*-(*i*Pr$_2$N)PhPP(*i*Pr$_2$N)Ph **19**

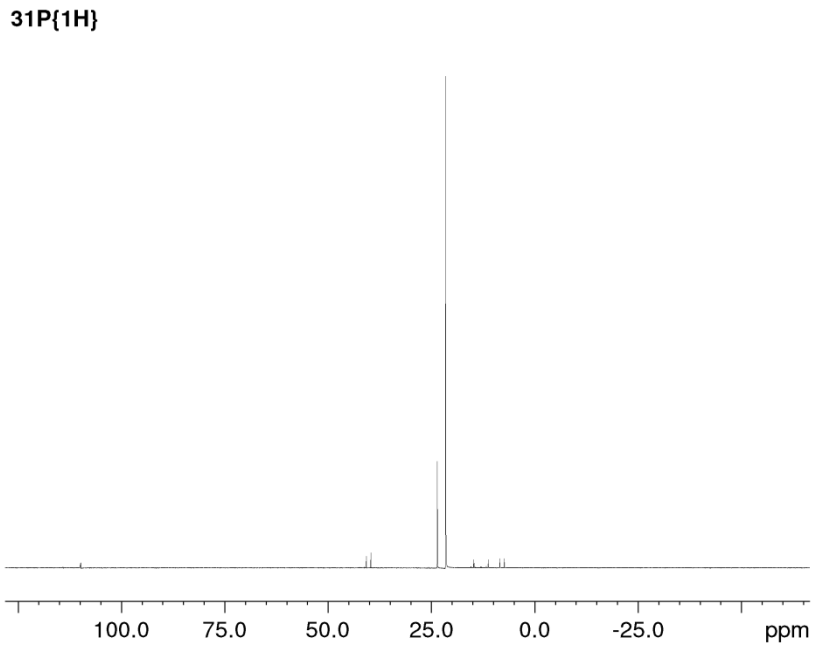


Fig. S143. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)PhPP(*i*Pr_2N)Ph **18** and *rac*-(*i*Pr_2N)PhPP(*i*Pr_2N)Ph **19**

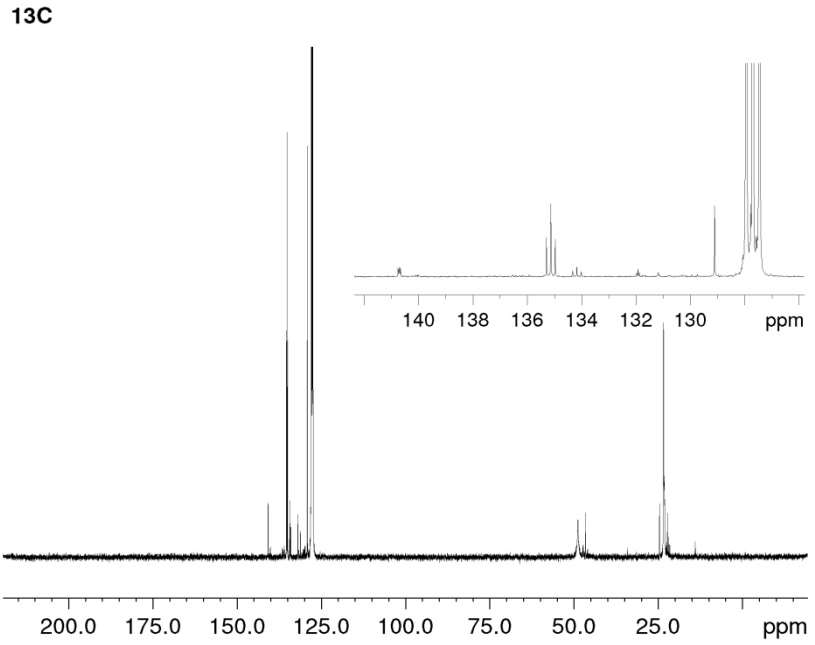


Fig. S144. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)PhPP(*i*Pr_2N)Ph **18** and *rac*-(*i*Pr_2N)PhPP(*i*Pr_2N)Ph **19**

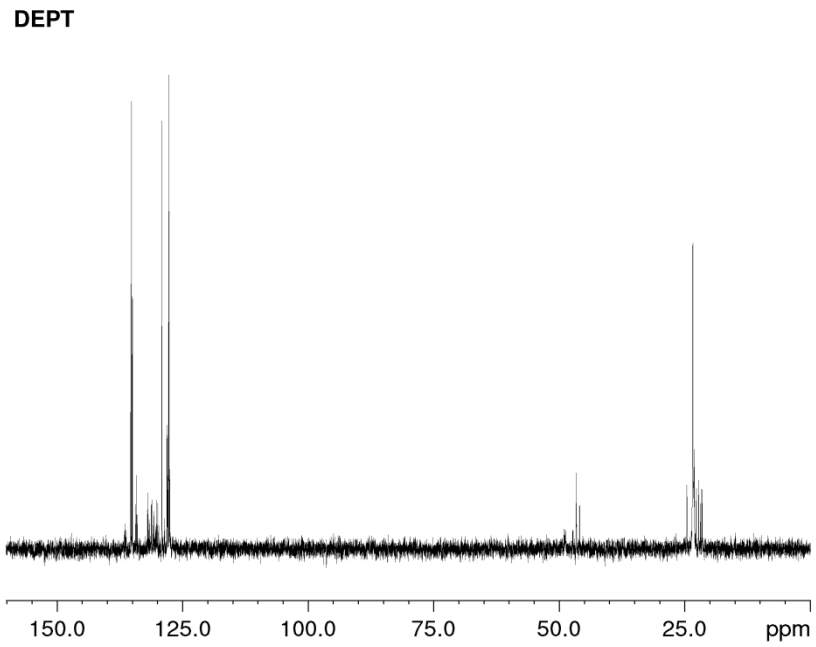


Fig. S145. ^{13}C with DEPT NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)PhPP(*i*Pr_2N)Ph **18** and *rac*-(*i*Pr_2N)PhPP(*i*Pr_2N)Ph **19**

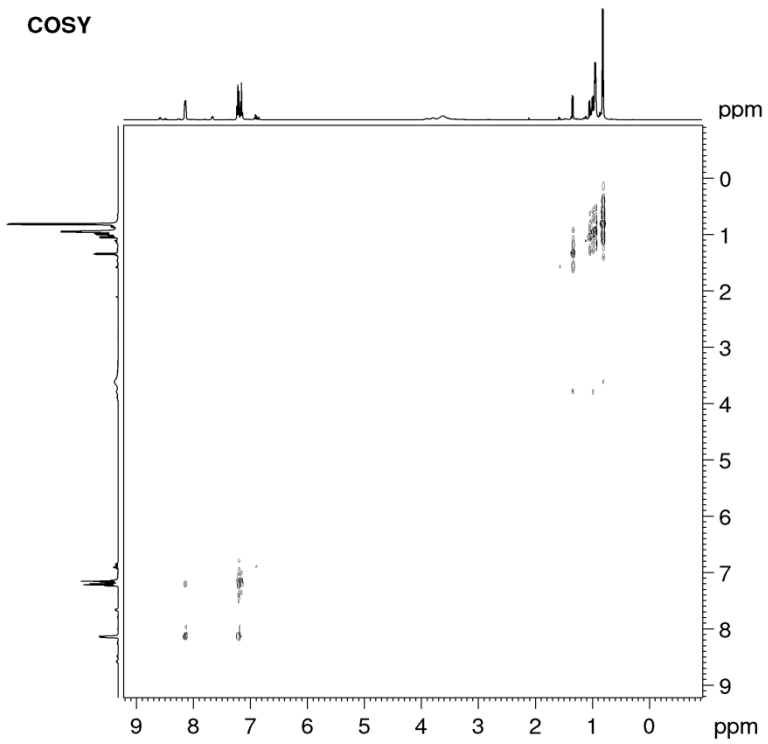


Fig. S146. COSY NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)PhPP(*i*Pr_2N)Ph **18** and *rac*-(*i*Pr_2N)PhPP(*i*Pr_2N)Ph **19**

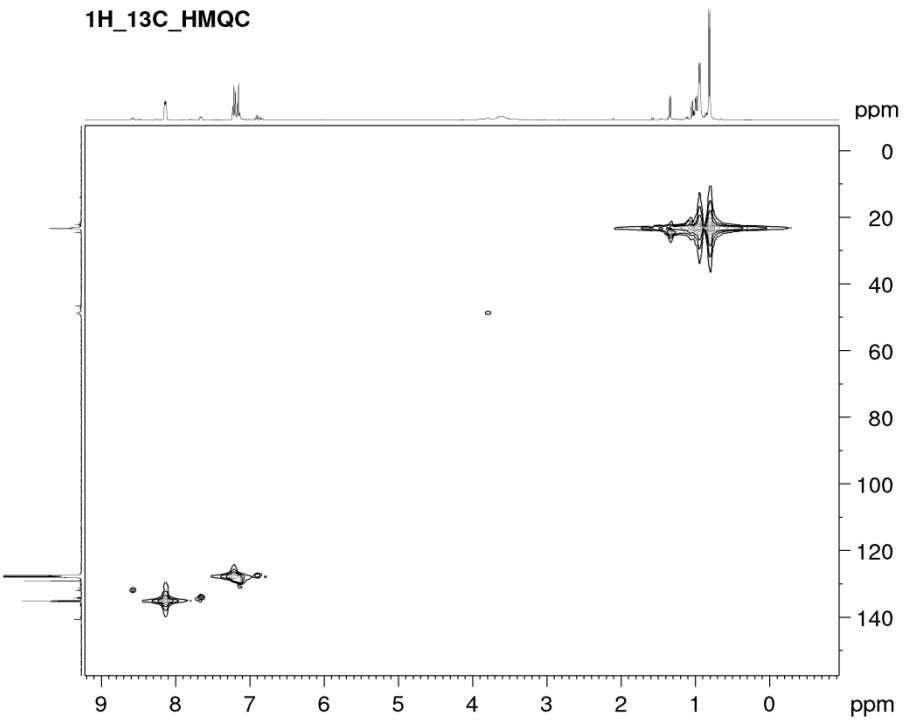


Fig. S147. ^{13}C ^{1}H HMQC NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)PhPP(*i*Pr_2N)Ph **18** and *rac*-(*i*Pr_2N)PhPP(*i*Pr_2N)Ph **19**

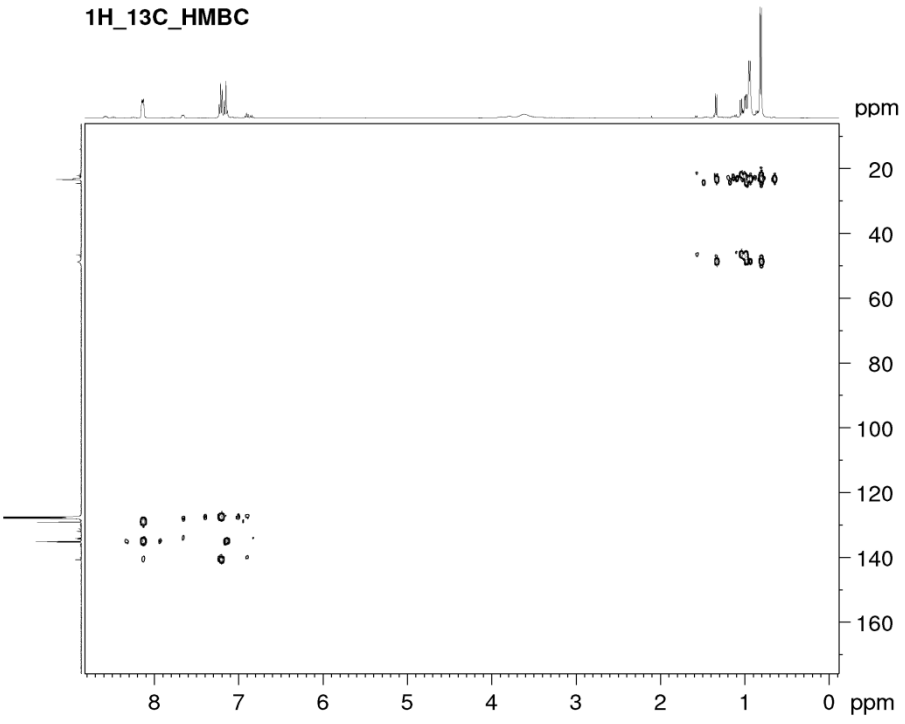


Fig. S148. ^{13}C ^{1}H HMQC NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)PhPP(*i*Pr_2N)Ph **18** and *rac*-(*i*Pr_2N)PhPP(*i*Pr_2N)Ph **19**

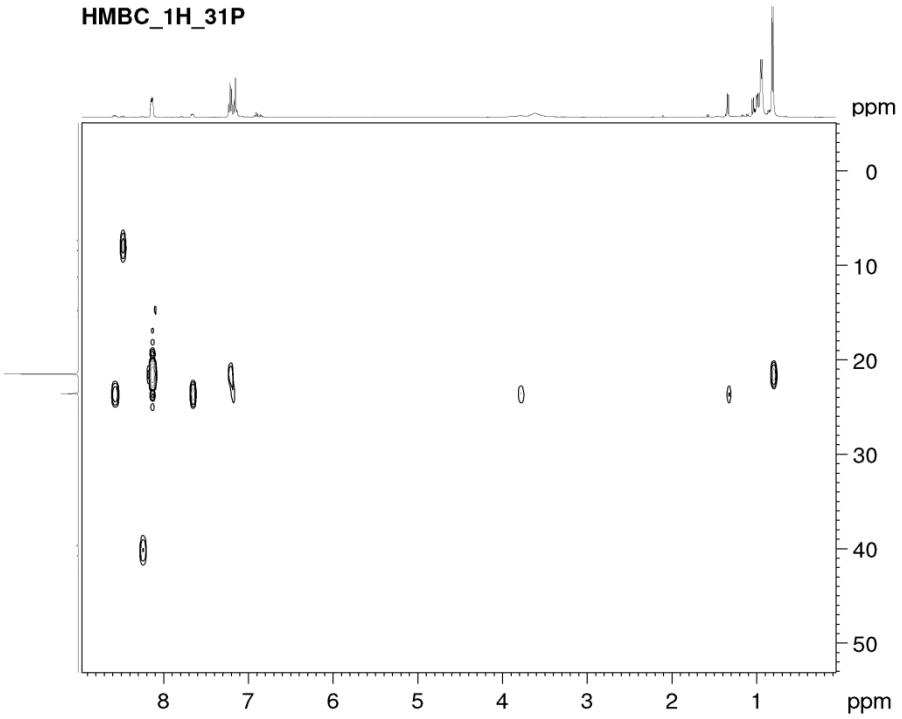


Fig. S149. ^{31}P ^{1}H HMQC NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)PhPP(*i*Pr_2N)Ph **18** and *rac*-(*i*Pr_2N)PhPP(*i*Pr_2N)Ph **19**

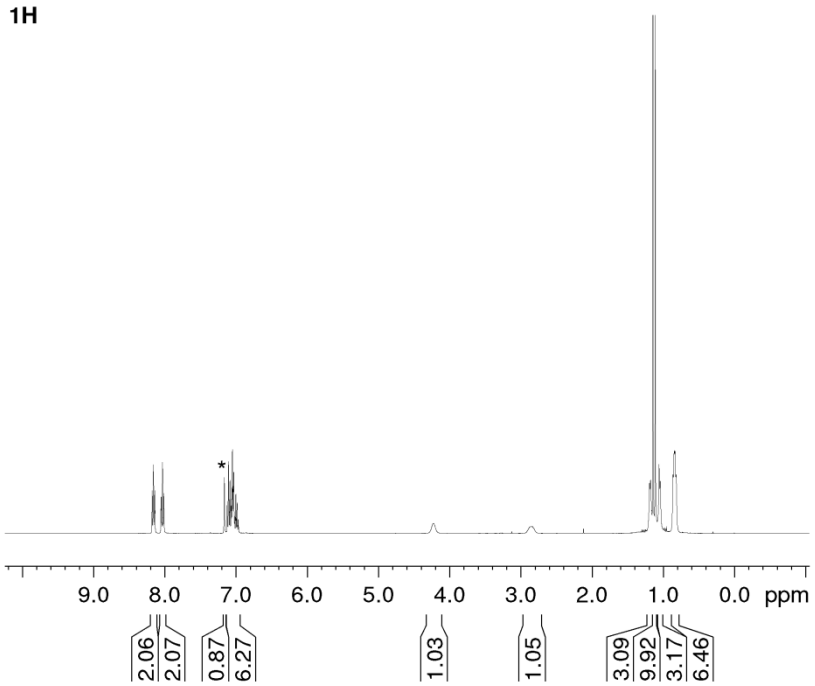


Fig. S150. ^{1}H NMR (C_6D_6) spectra of isolated (*i*Pr_2N)*t*BuPPPh_2 **21**

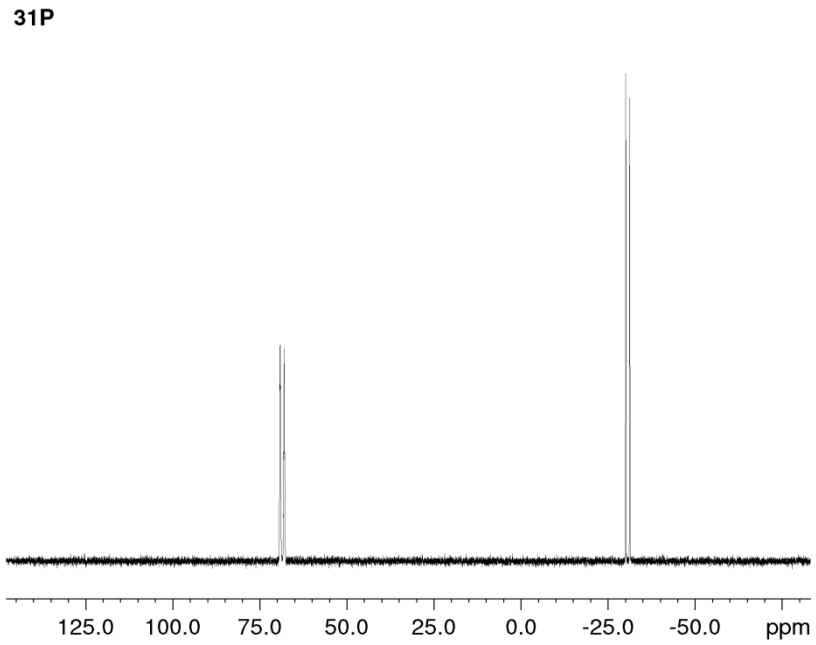


Fig. S151. ^{31}P NMR (C_6D_6) spectra of isolated (iPr$_2$N)tBuPPPh$_2$ **21**

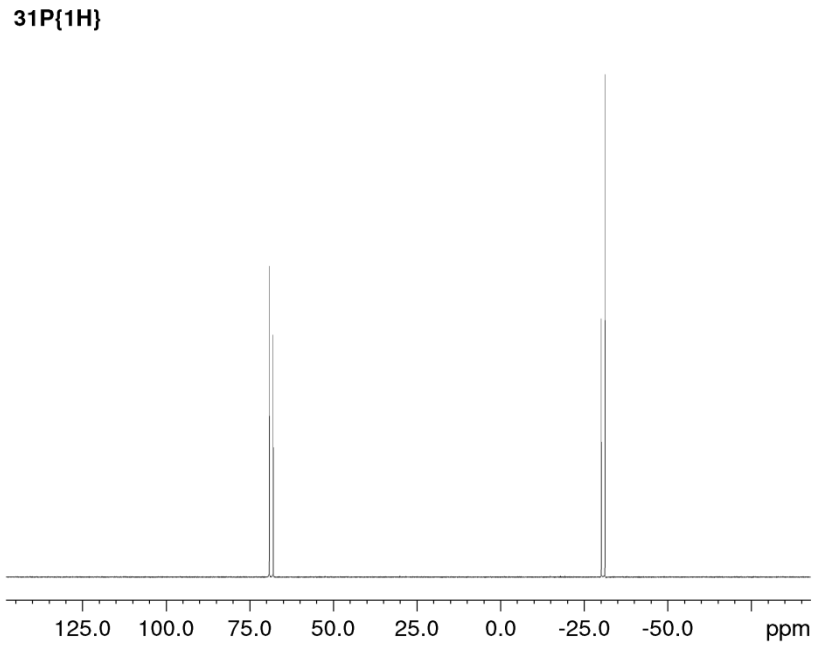


Fig. S152. $^{31}P\{^1H\}$ NMR (C_6D_6) spectra of isolated (iPr$_2$N)tBuPPPh$_2$ **21**

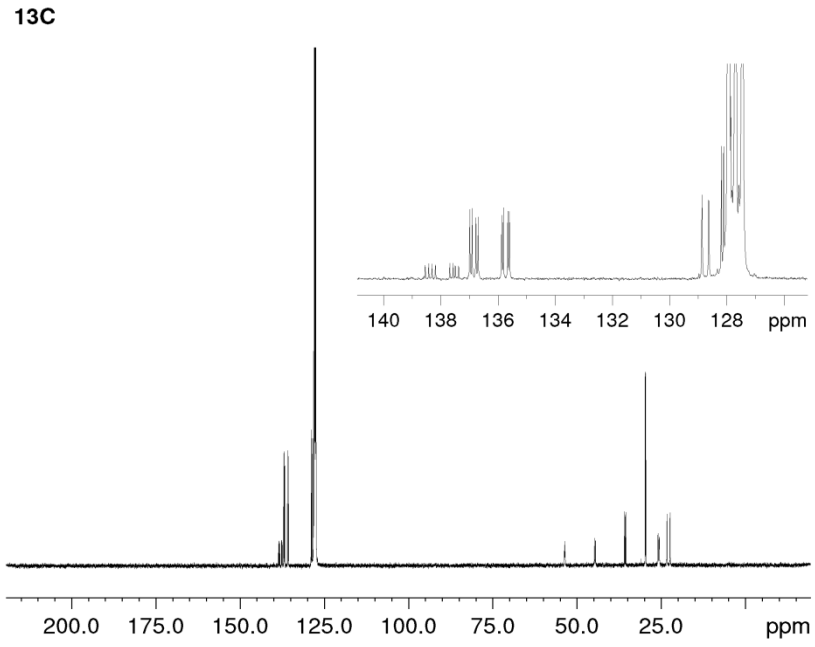


Fig. S153. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectra of isolated (iPr$_2$N)tBuPPPh$_2$ **21**

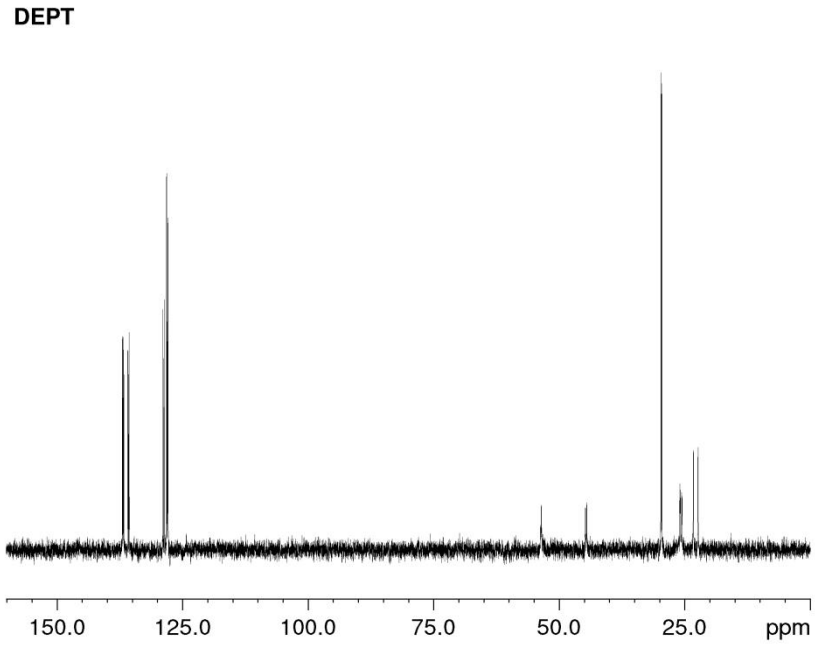


Fig. S154. $^{13}C\{^{1}H\}$ with DEPT NMR (C_6D_6) spectra of isolated (iPr$_2$N)tBuPPPh$_2$ **21**

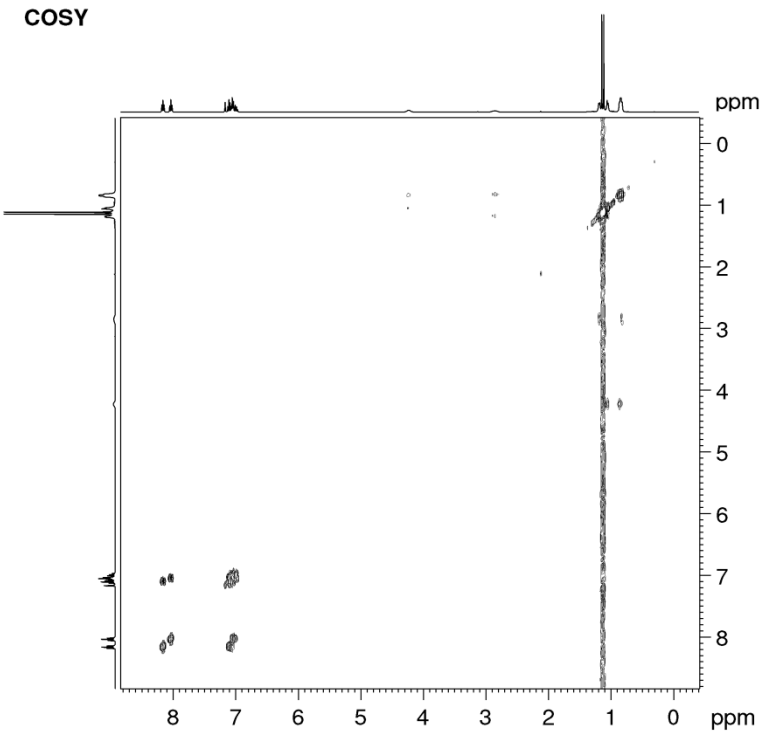


Fig. S155. COSY NMR (C_6D_6) spectra of isolated (iPr$_2$N)tBuPPPh$_2$ **21**

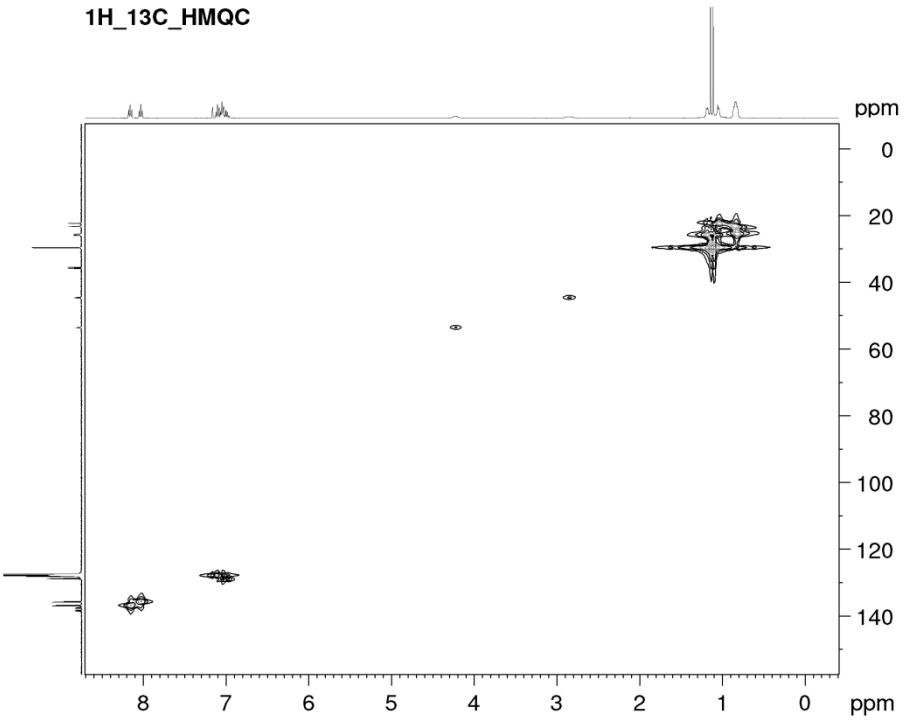


Fig. S156. ^{13}C ^{1}H HMQC NMR (C_6D_6) spectra of isolated (iPr$_2$N)tBuPPPh$_2$ **21**

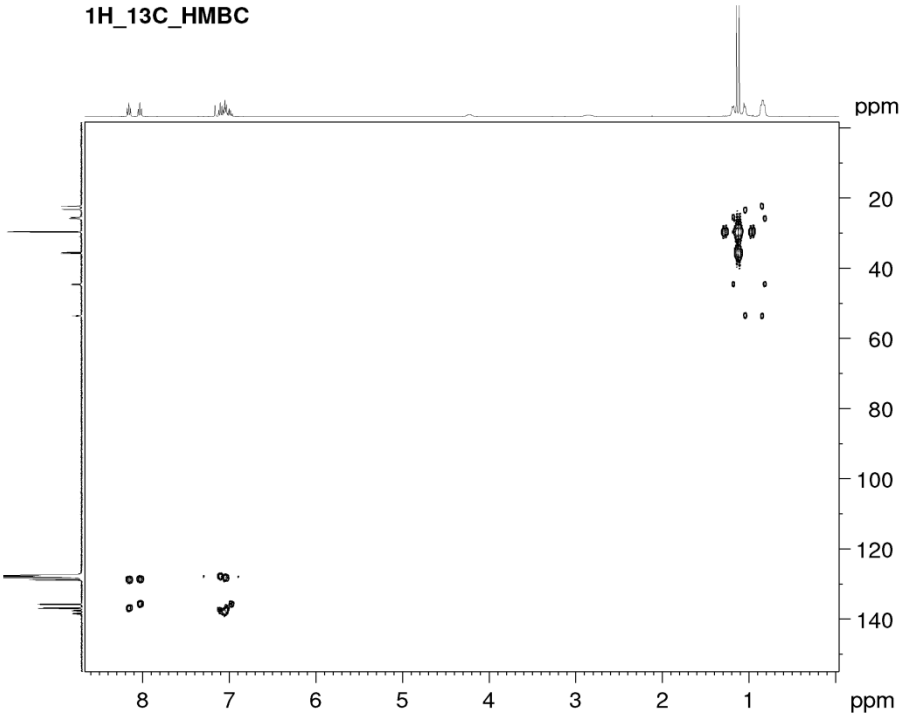


Fig. S157. ^{13}C ^{1}H HMBC NMR (C_6D_6) spectra of isolated (iPr$_2$N)tBuPPPh$_2$ **21**

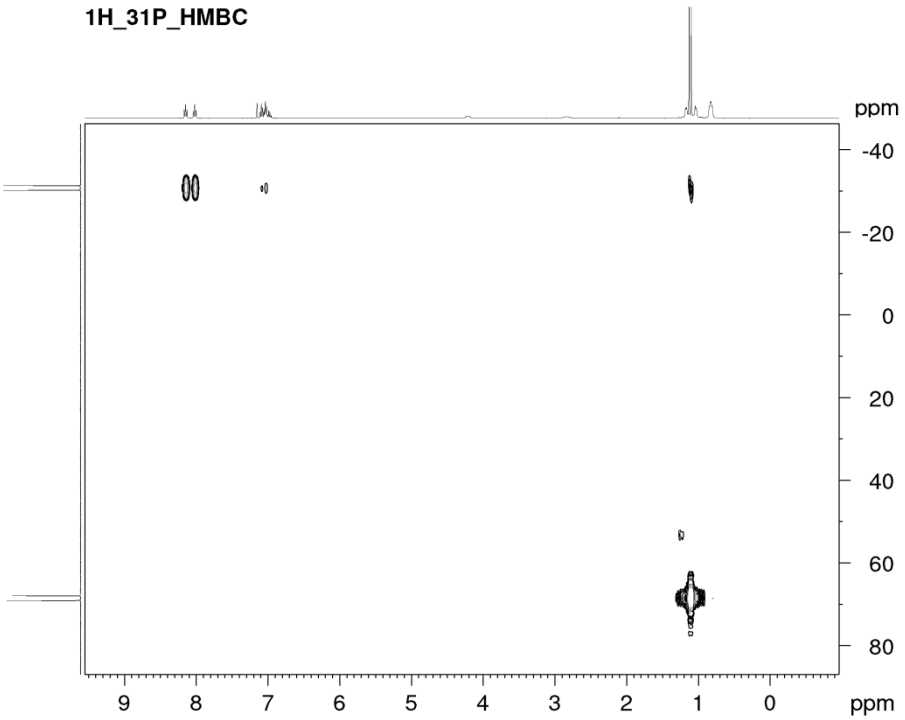


Fig. S158. ^{31}P ^{1}H HMBC NMR (C_6D_6) spectra of isolated (iPr$_2$N)tBuPPPh$_2$ **21**

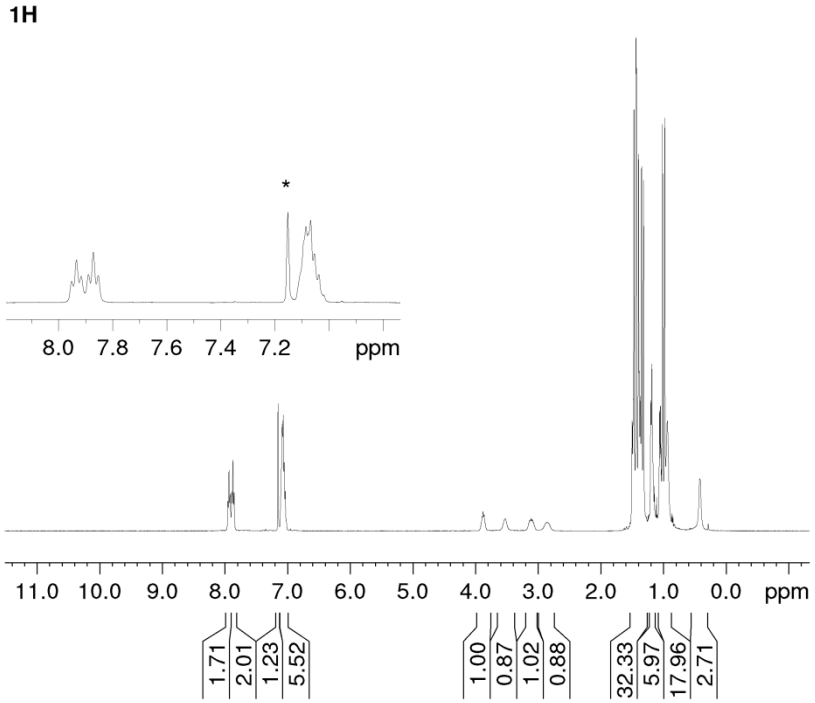


Fig. S159. ^{1}H NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr$_2$N)*t*BuPP*t*BuPh **22** and *rac*-(*i*Pr$_2$N)*t*BuPP*t*BuPh **23**

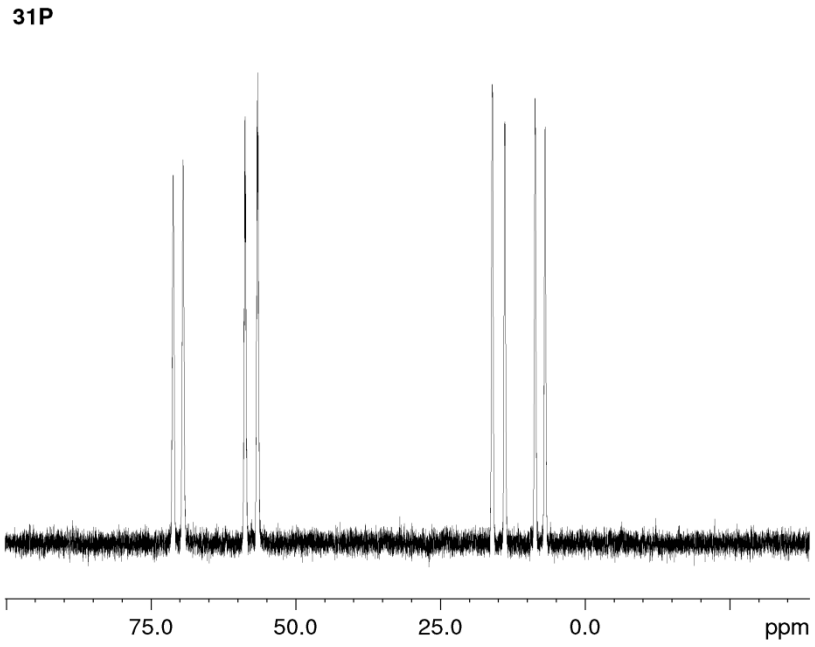


Fig. S160. ^{31}P NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr$_2$N)*t*BuPP*t*BuPh **22** and *rac*-(*i*Pr$_2$N)*t*BuPP*t*BuPh **23**

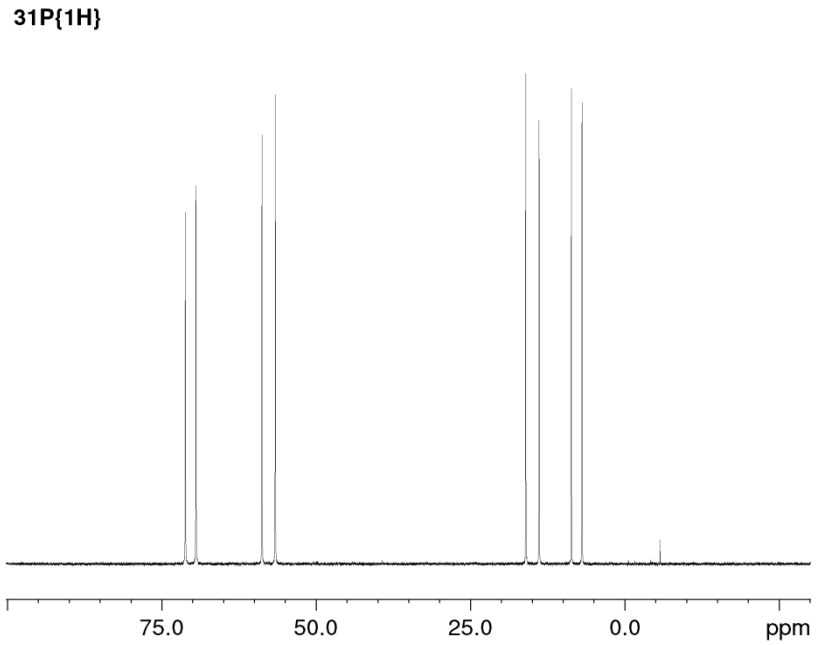


Fig. S161. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)*t*BuPP*t*BuPh **22** and *rac*-(*i*Pr_2N)*t*BuPP*t*BuPh **23**

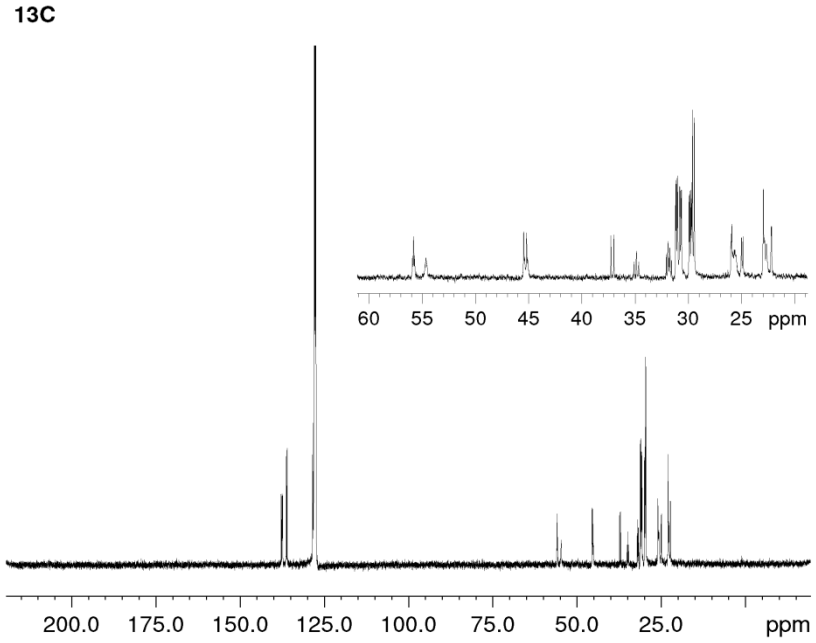


Fig. S162. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)*t*BuPP*t*BuPh **22** and *rac*-(*i*Pr_2N)*t*BuPP*t*BuPh **23**

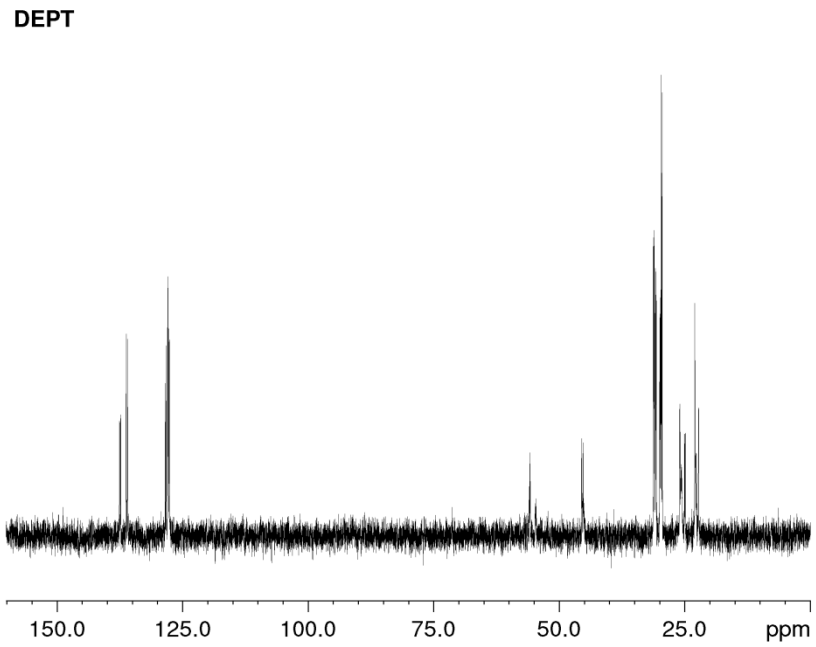


Fig. S163. ^{13}C with DEPT NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)*t*BuPP*t*BuPh **22** and *rac*-(*i*Pr_2N)*t*BuPP*t*BuPh **23**

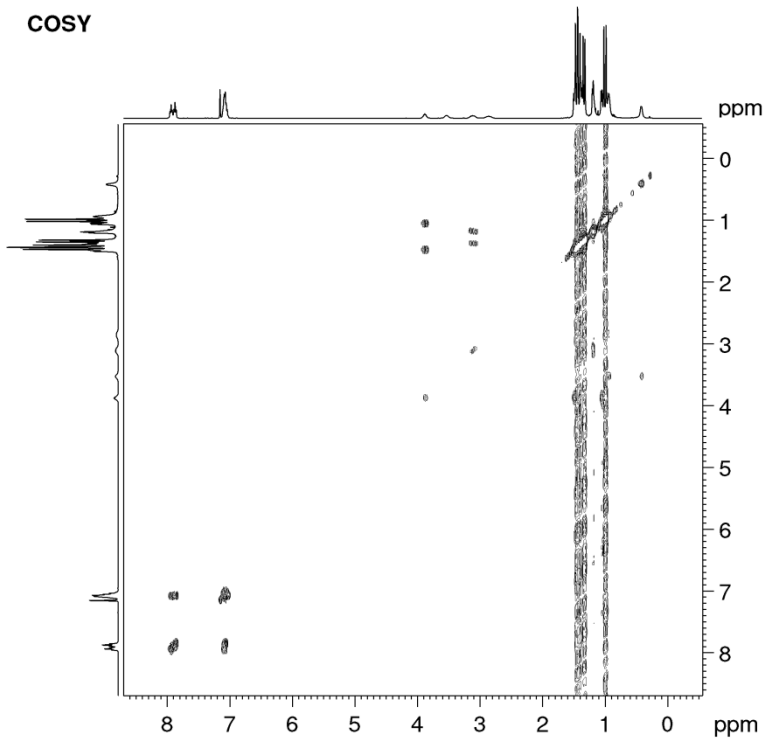


Fig. S164. COSY NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)*t*BuPP*t*BuPh **22** and *rac*-(*i*Pr_2N)*t*BuPP*t*BuPh **23**

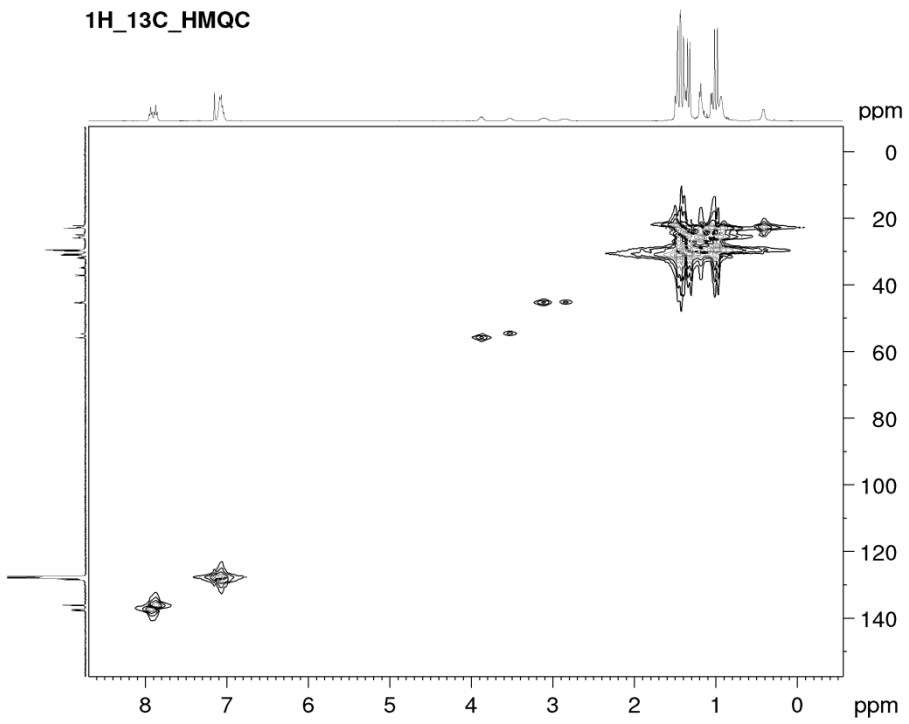


Fig. S165. ^{13}C ^{1}H HMQC NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)*t*BuPP*t*BuPh **22** and *rac*-(*i*Pr_2N)*t*BuPP*t*BuPh **23**

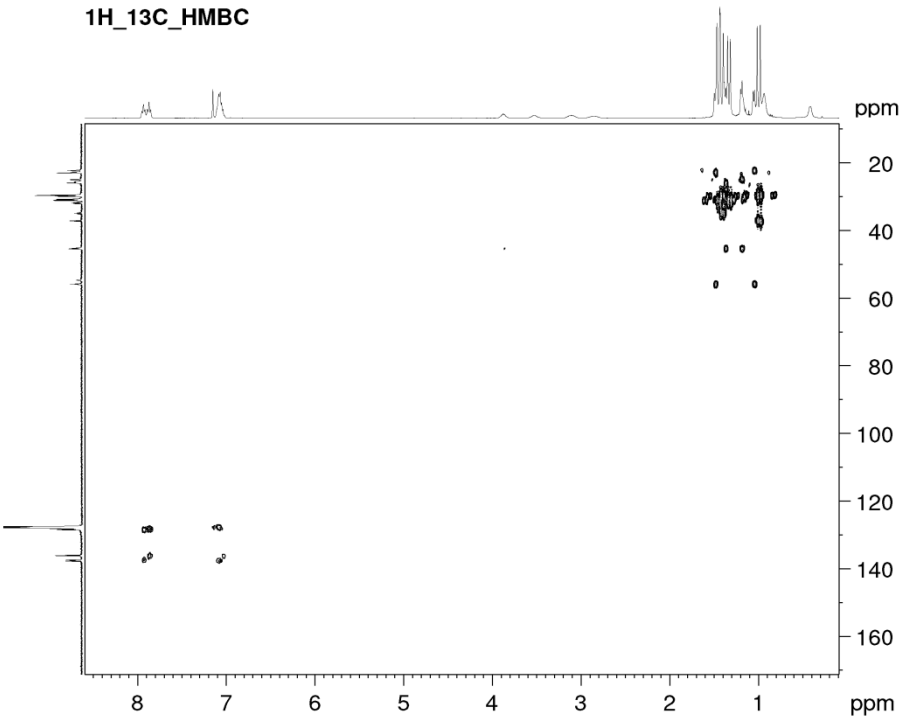


Fig. S166. ^{13}C ^{1}H HMBC NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)*t*BuPP*t*BuPh **22** and *rac*-(*i*Pr_2N)*t*BuPP*t*BuPh **23**

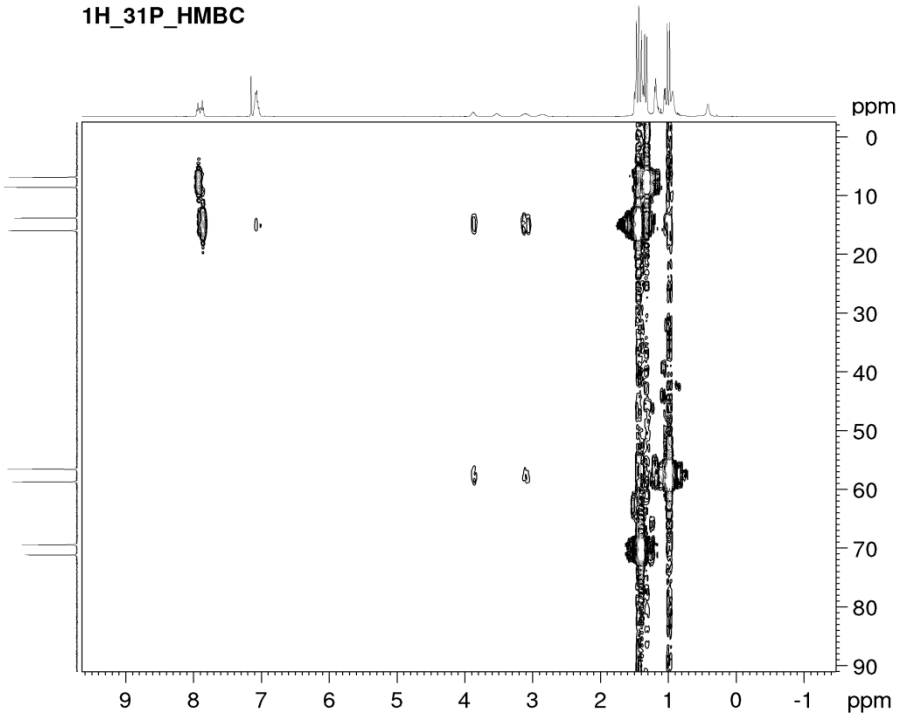


Fig. S167. ^{31}P ^{1}H HMBC NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)*t*BuPP*t*BuPh **22** and *rac*-(*i*Pr_2N)*t*BuPP*t*BuPh **23**

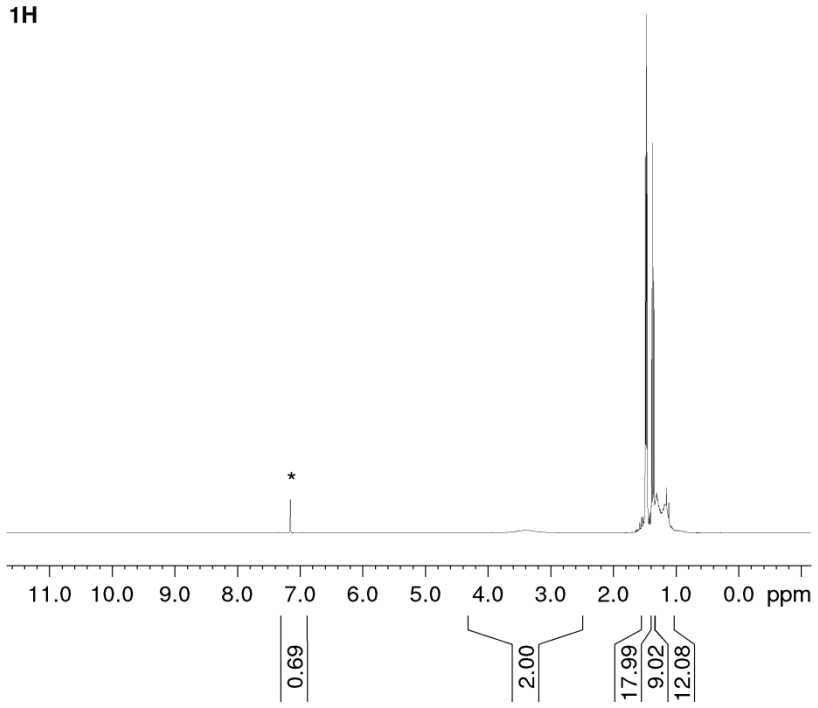


Fig. S168. ^{1}H NMR (C_6D_6) spectra of isolated (*i*Pr_2N)*t*BuPP*t*Bu_2 **24**

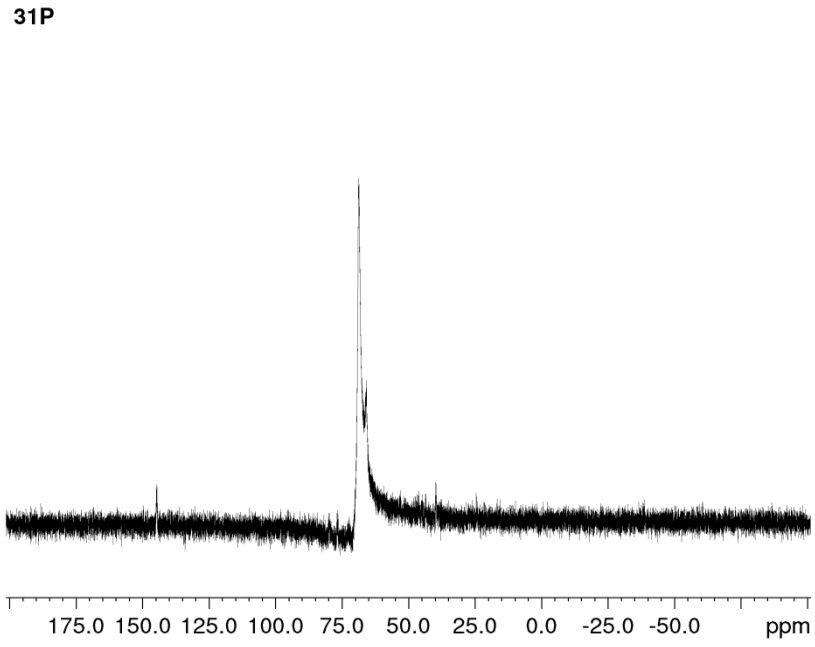


Fig. S169. ^{31}P NMR (C_6D_6) spectra of isolated (iPr$_2$N)tBuP$P$$tBu_2$ **24**

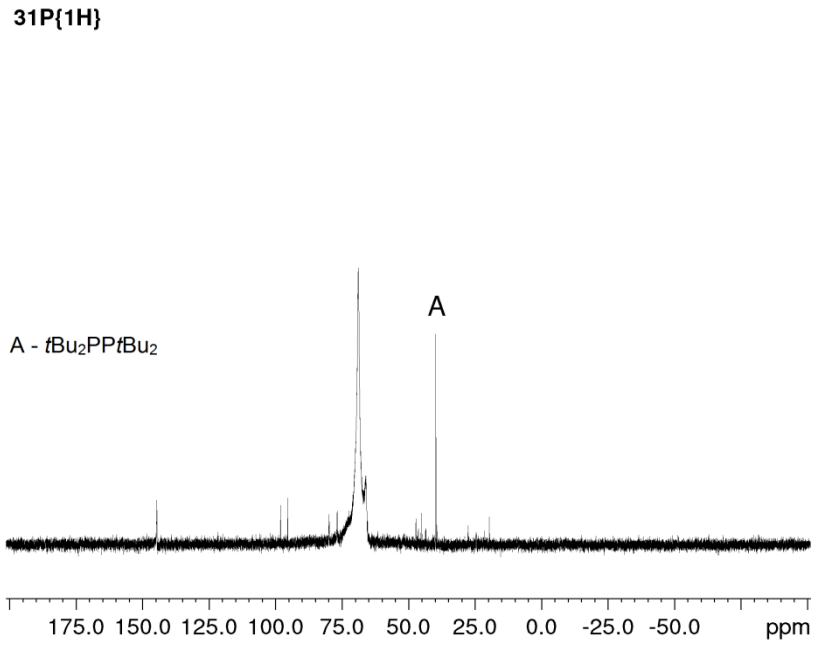


Fig. S170. $^{31}P\{^1H\}$ NMR (C_6D_6) spectra of isolated (iPr$_2$N)tBuP$P$$tBu_2$ **24**

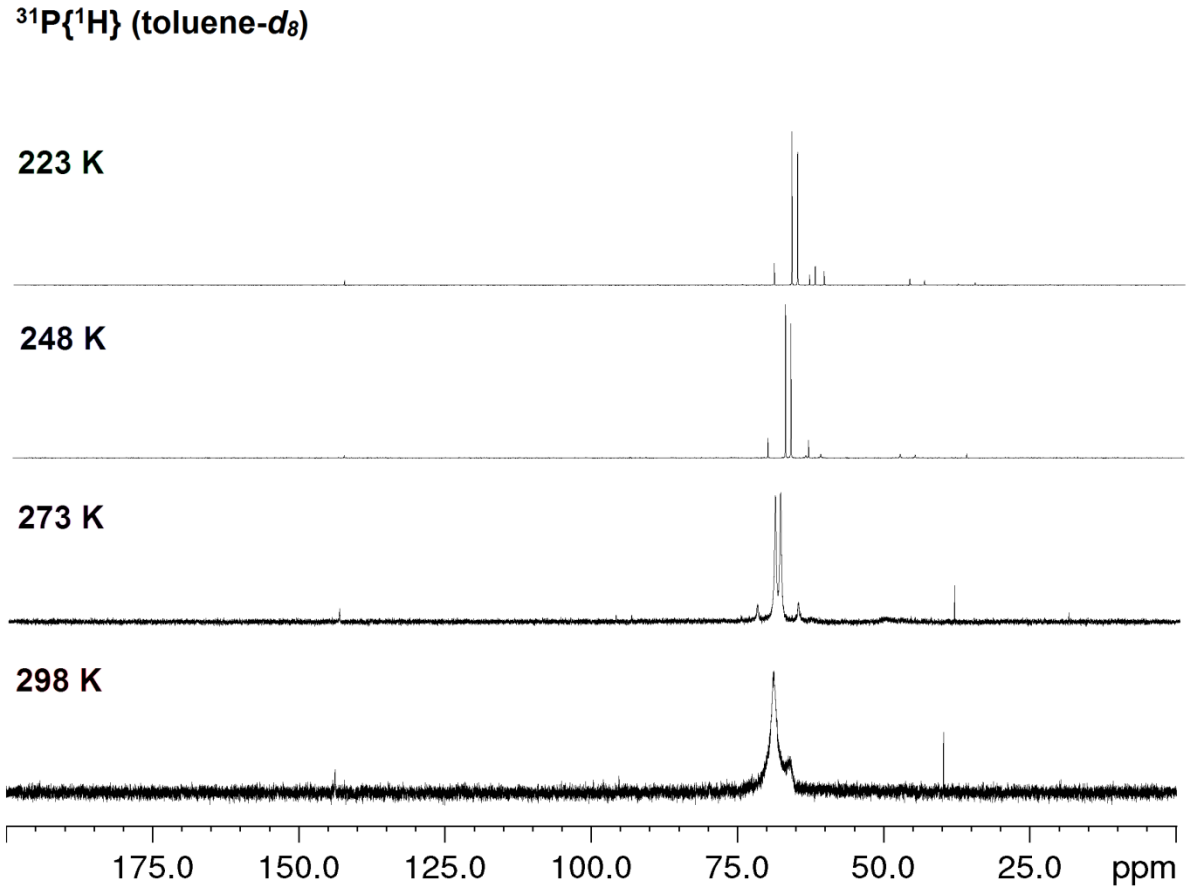


Fig. S171. Low-temperature $^{31}P\{^{1}H\}$ NMR experiment of isolated (iPr$_2$N)tBuP$P$$tBu_2$ **24**

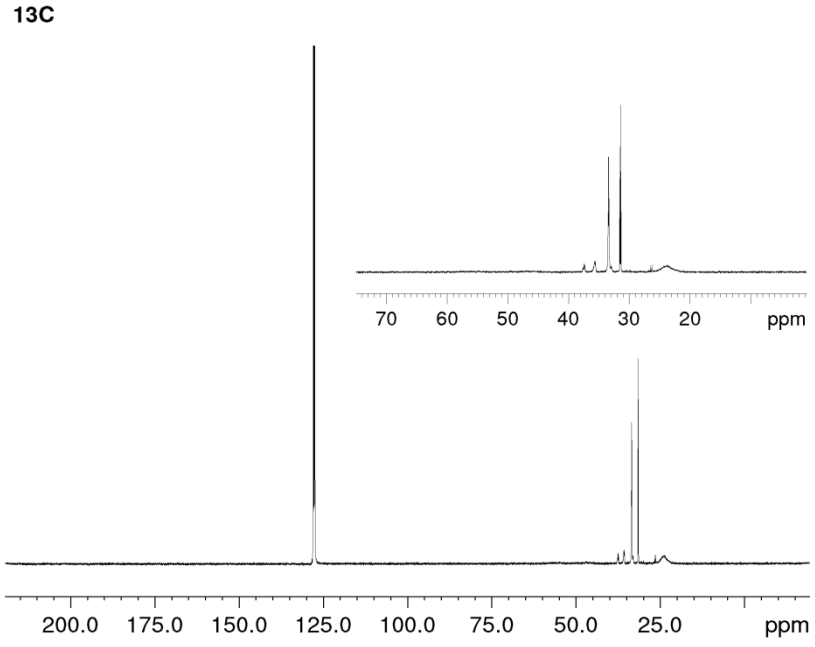


Fig. S172. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectra of isolated (iPr$_2$N)tBuP$P$$tBu_2$ **24**

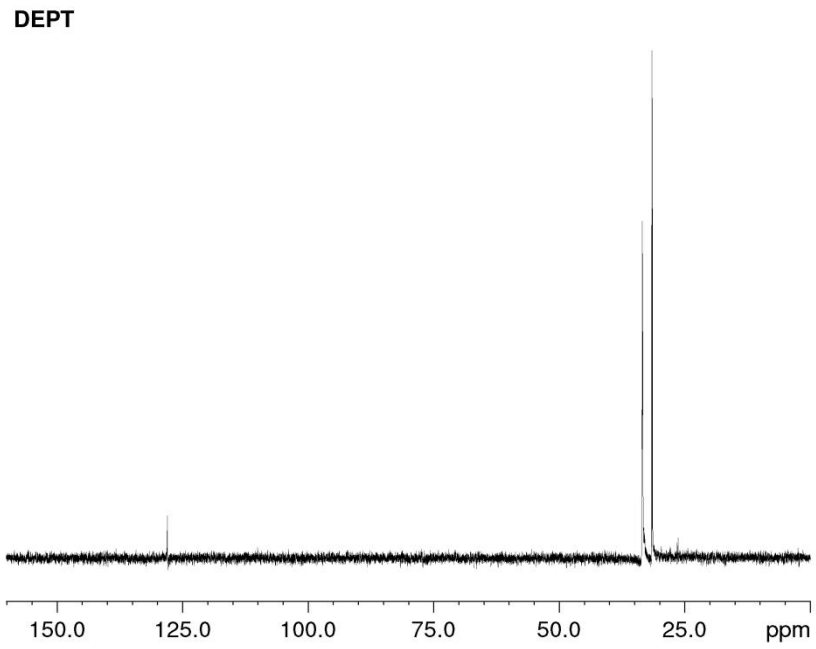


Fig. S173. ^{13}C with DEPT NMR (C_6D_6) spectra of isolated (iPr$_2$N)tBuPPtBu$_2$ **24**

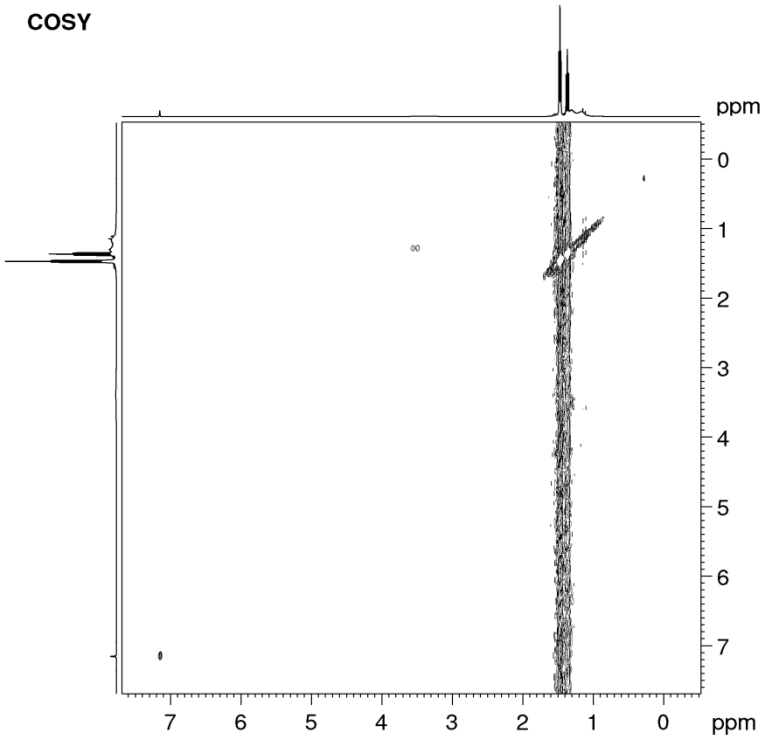


Fig. S174. COSY NMR (C_6D_6) spectra of isolated (iPr$_2$N)tBuPPtBu$_2$ **24**

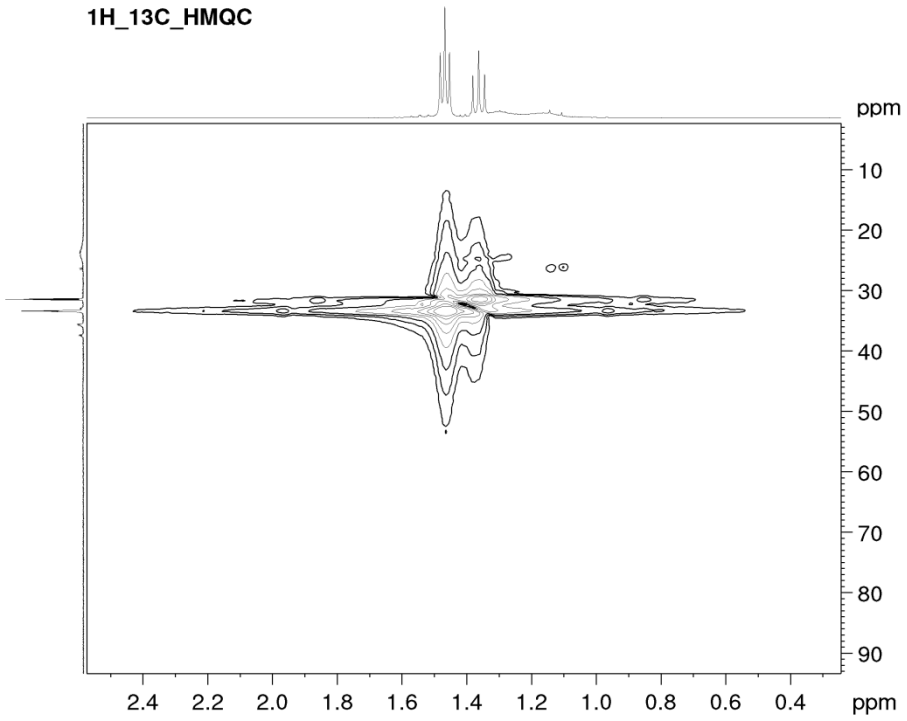


Fig. S175. ^{13}C ^{1}H HMQC NMR (C_6D_6) spectra of isolated (iPr$_2$N)tBuPPtBu$_2$ **24**

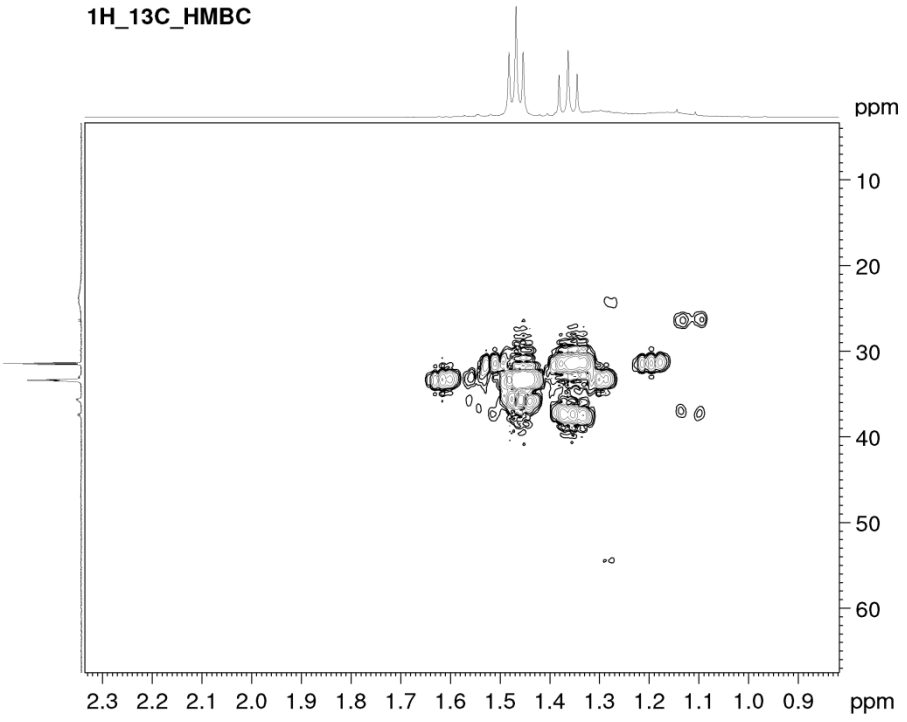


Fig. S176. ^{13}C ^{1}H HMBC NMR (C_6D_6) spectra of isolated (iPr$_2$N)tBuPPtBu$_2$ **24**

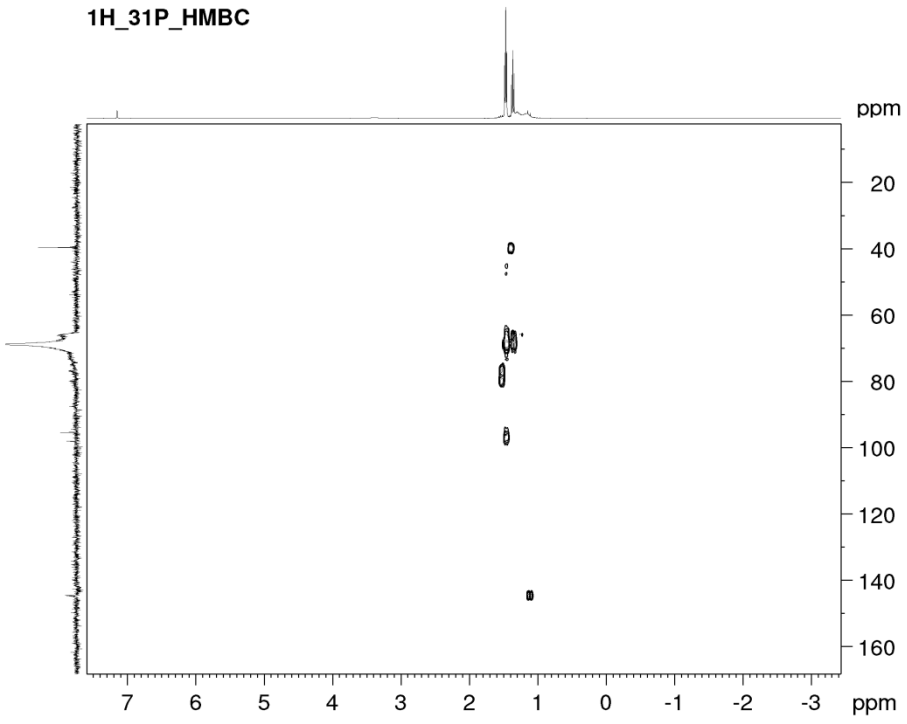


Fig. S177. ^{31}P ^{1}H HMBC NMR (C_6D_6) spectra of isolated (*i*Pr_2N)*t*BuPP*t*Bu_2 **24**

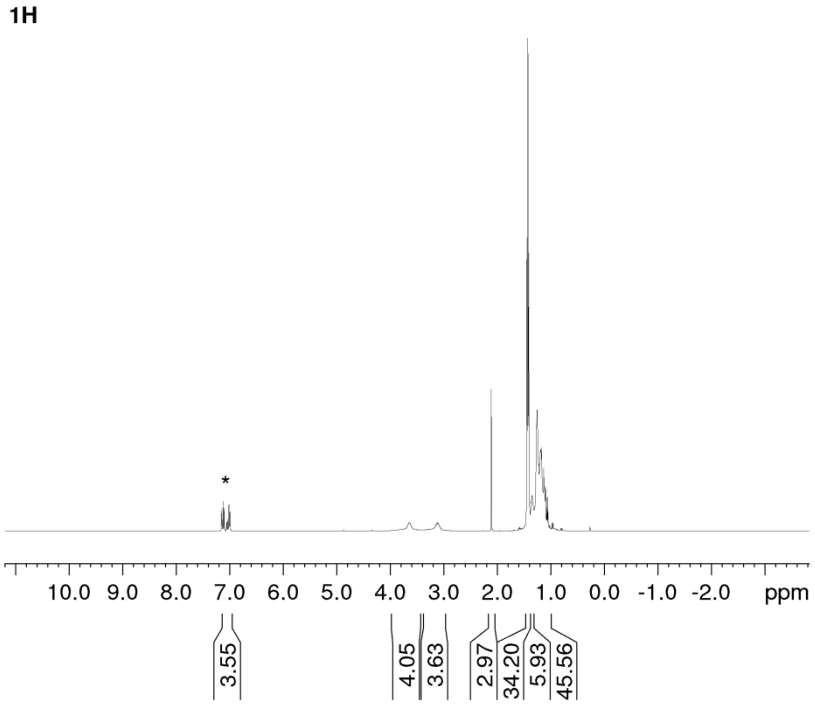


Fig. S178. ^{1}H NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **25** and *rac*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **26**

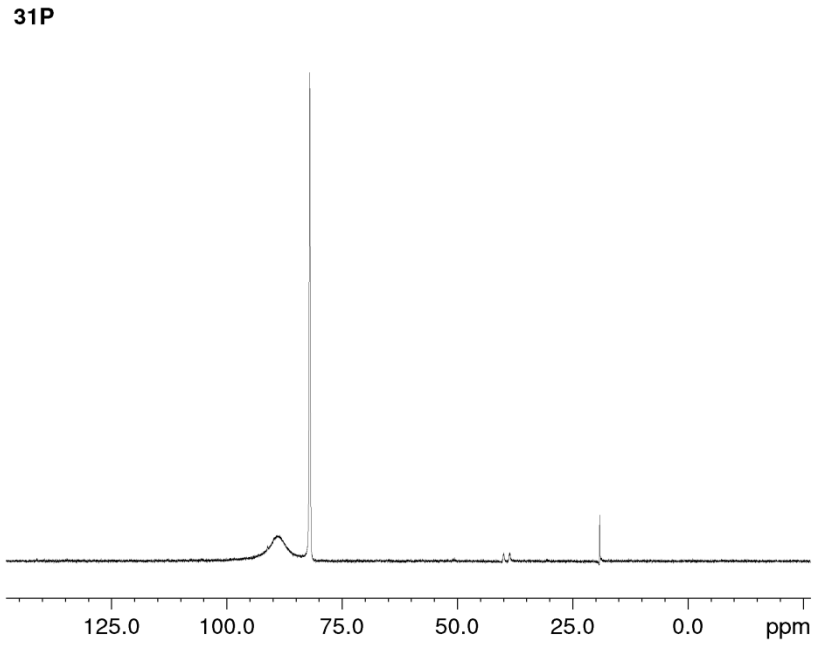


Fig. S179. ^{31}P NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **25** and *rac*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **26**

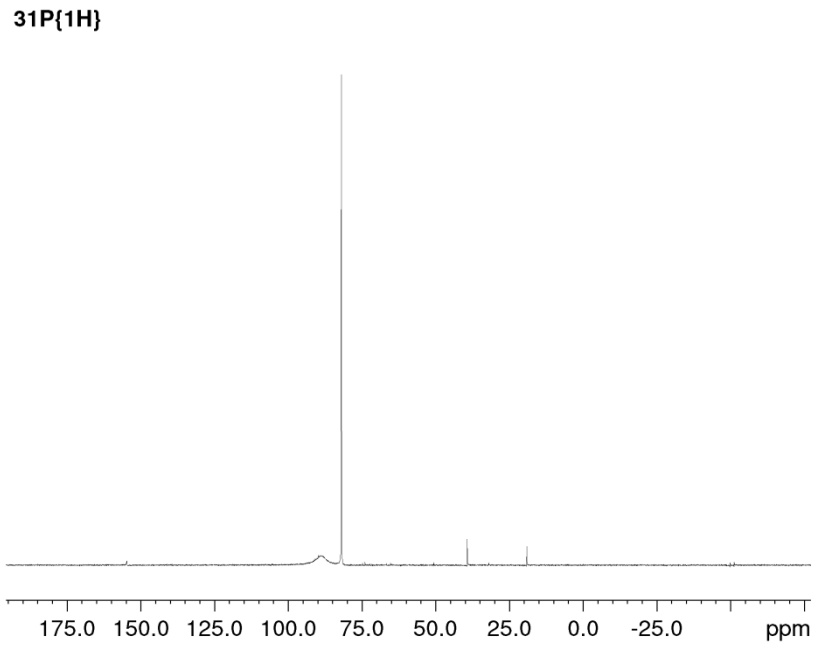


Fig. S180. $^{31}P\{^1H\}$ NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **25** and *rac*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **26**

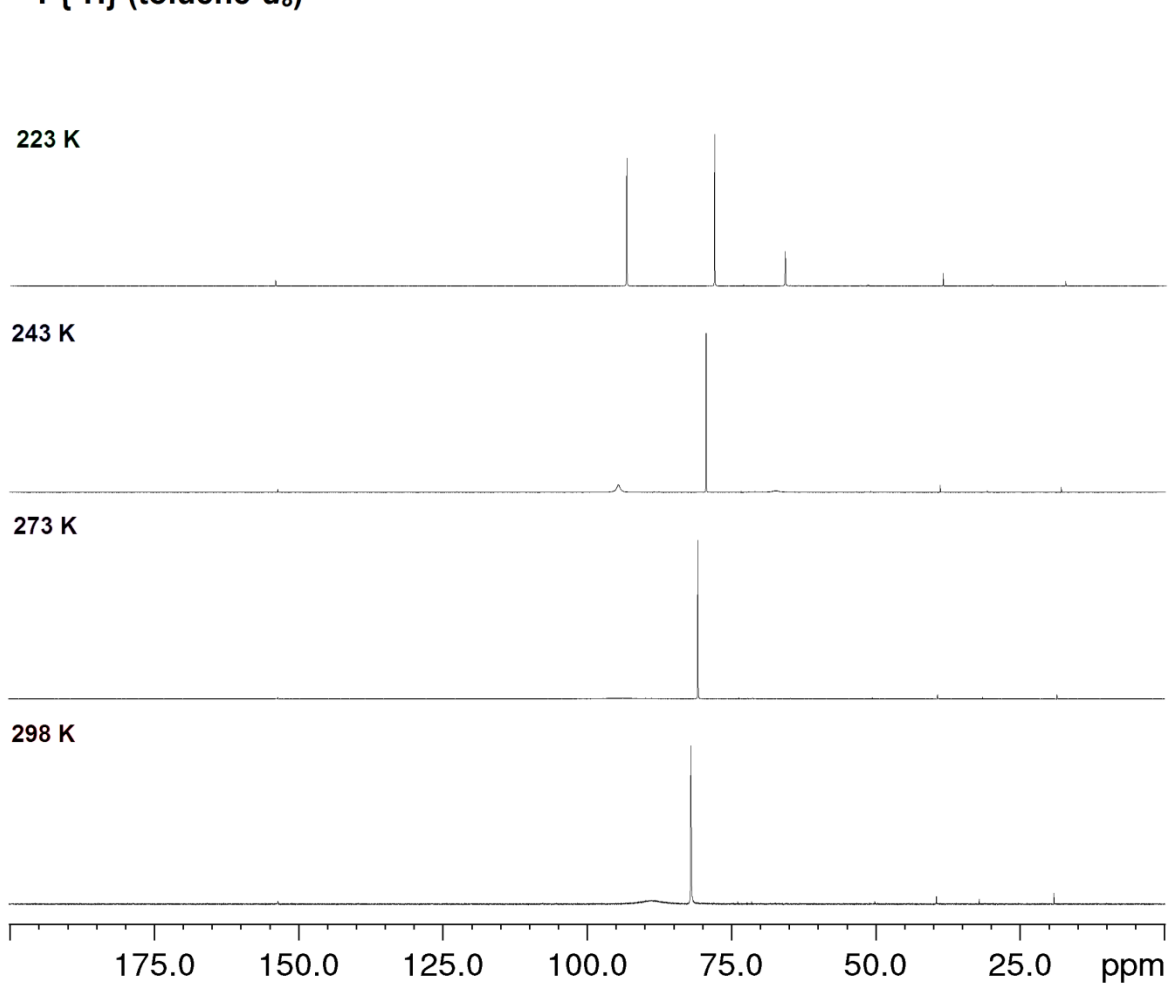


Fig. S181. Low-temperature $^{31}P\{^{1}H\}$ NMR experiment of isolated *meso*-(*i*Pr$_2$N)*t*BuPP(*i*Pr$_2$N)*t*Bu **25** and *rac*-(*i*Pr$_2$N)*t*BuPP(*i*Pr$_2$N)*t*Bu **26**

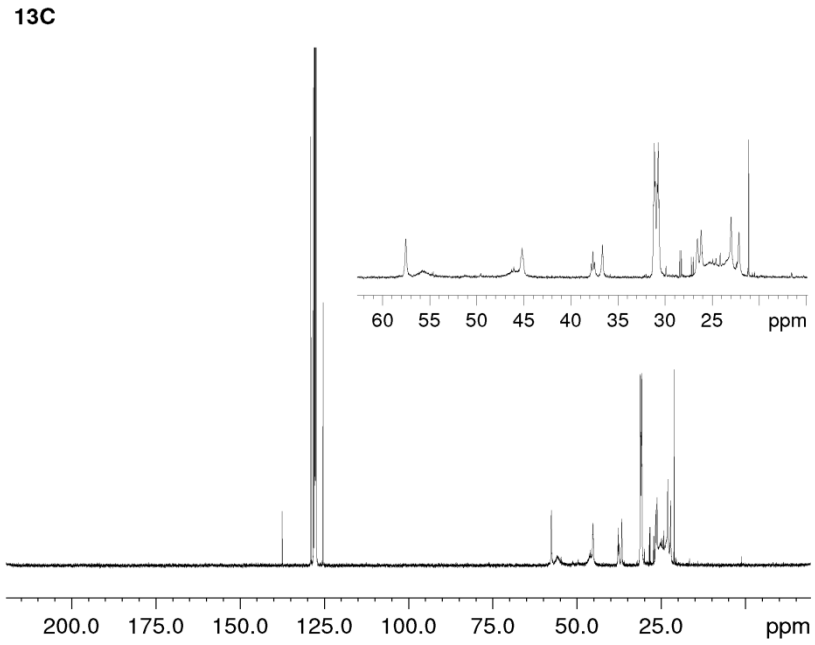


Fig. S182. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **25** and *rac*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **26**

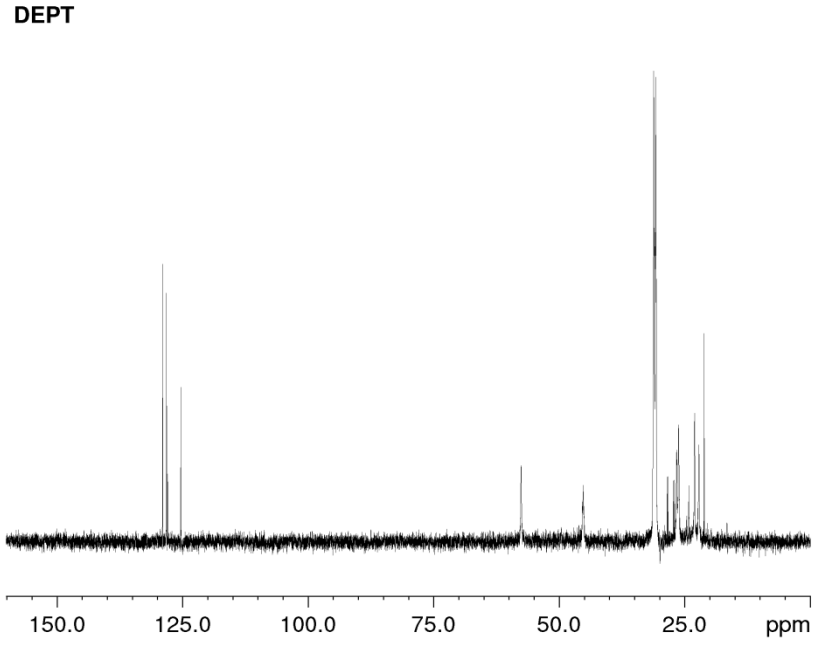


Fig. S183. ^{13}C with DEPT NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **25** and *rac*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **26**

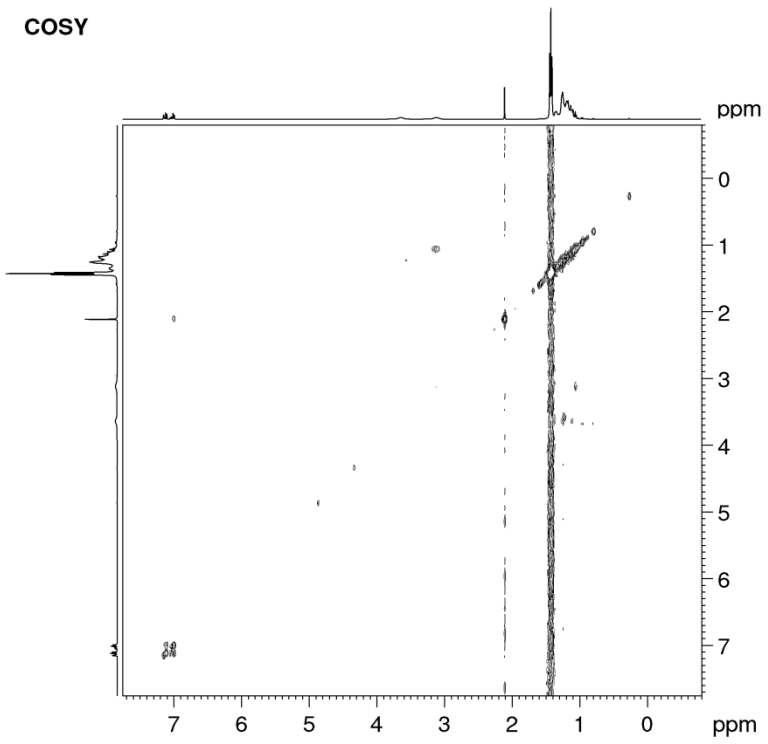


Fig. S184. COSY NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **25** and *rac*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **26**

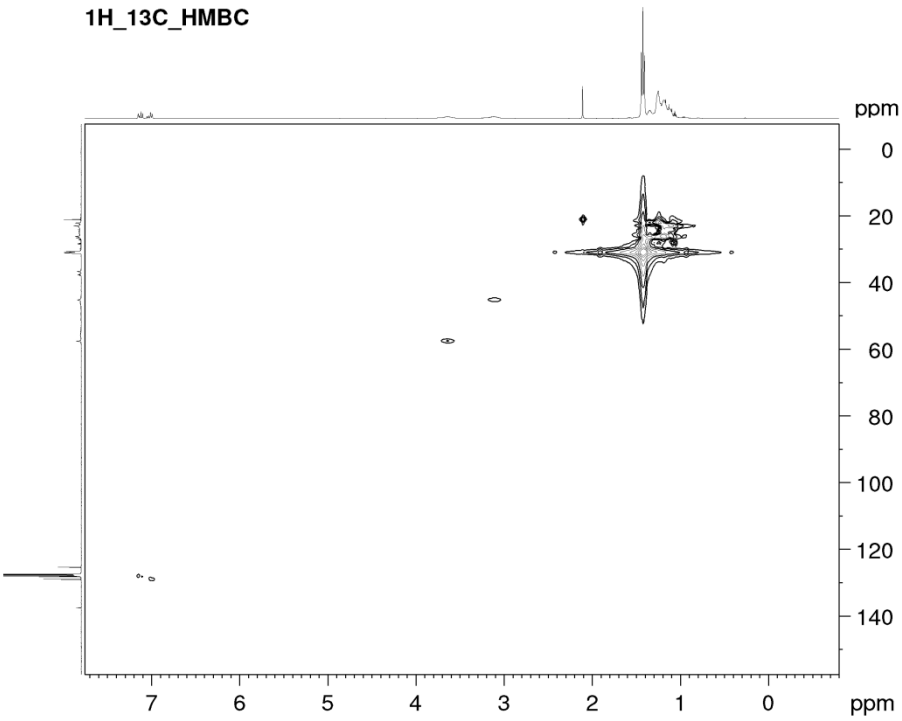


Fig. S185. ^{13}C ^{1}H HMQC NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **25** and *rac*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **26**

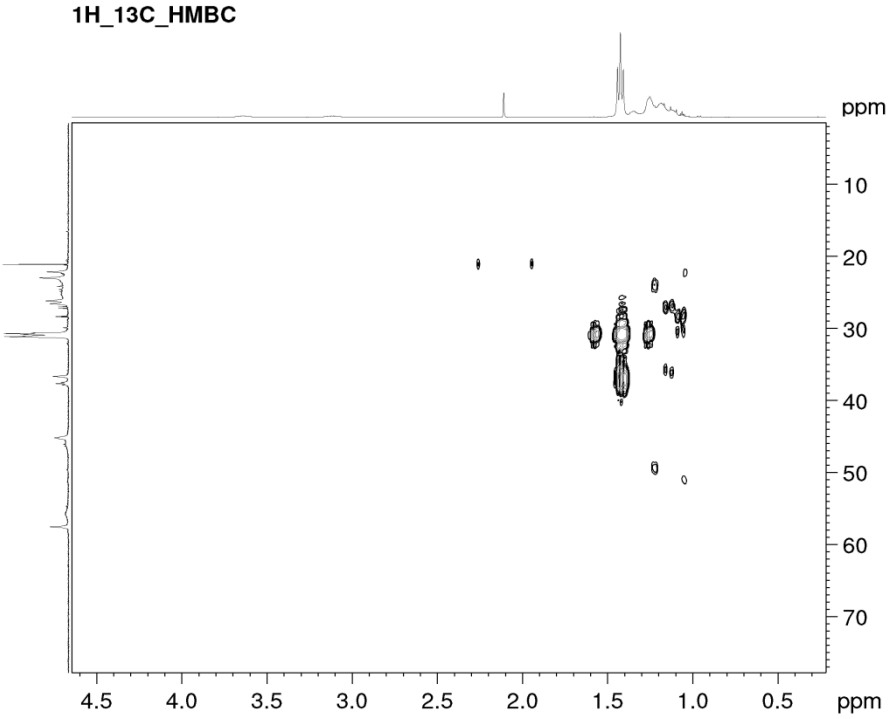


Fig. S186. ^{13}C ^{1}H HMBC NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **25** and *rac*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **26**

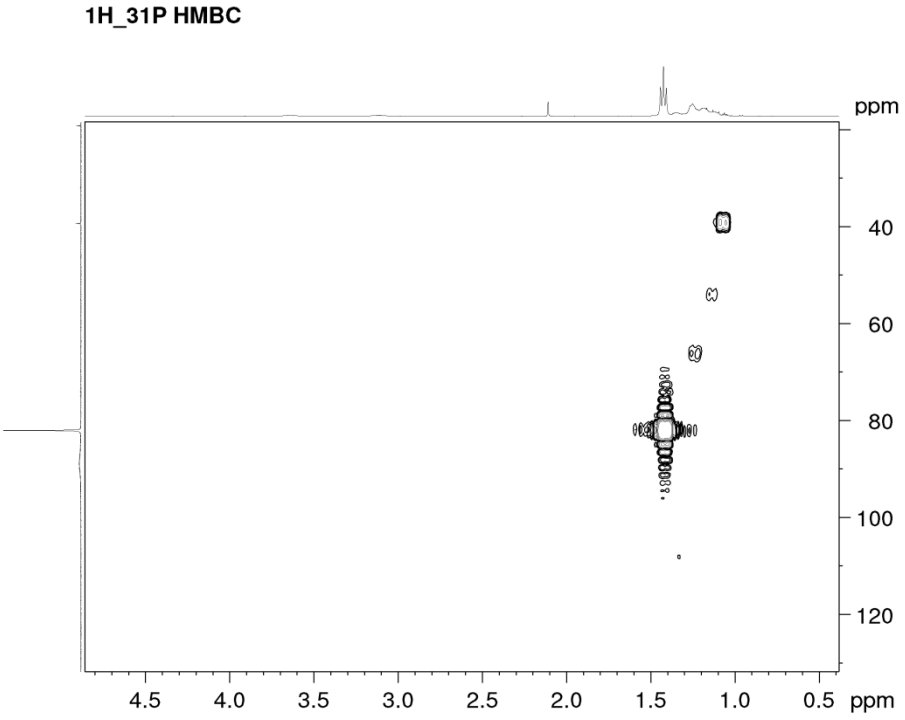


Fig. S187. ^{31}P ^{1}H HMBC NMR (C_6D_6) spectra of isolated *meso*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **25** and *rac*-(*i*Pr_2N)*t*BuPP(*i*Pr_2N)*t*Bu **26**

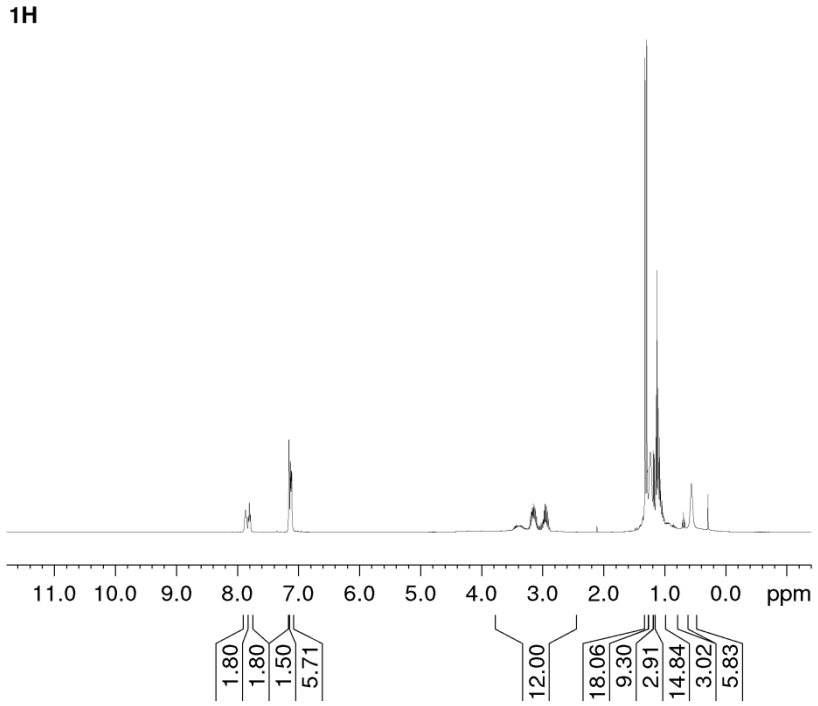


Fig. S188. ^{1}H NMR (C_6D_6) spectra of isolated *meso*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **28** and *rac*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **29**

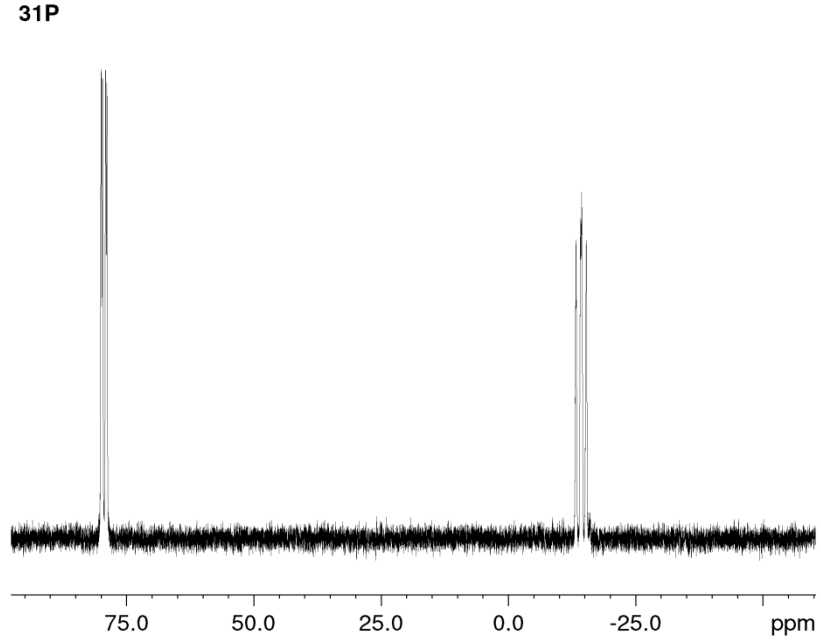


Fig. S189. ^{31}P NMR (C_6D_6) spectra of isolated *meso*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **28** and *rac*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **29**

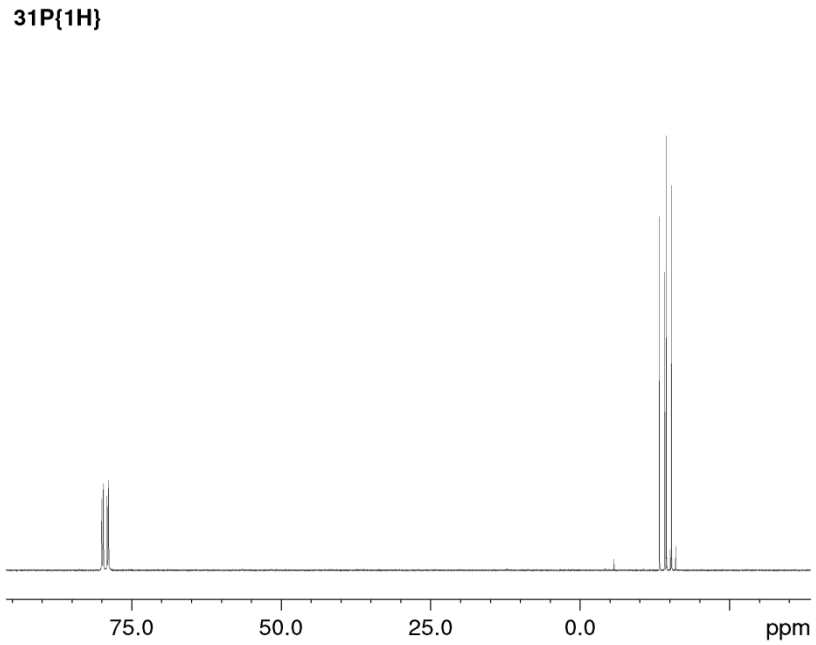


Fig. S190. $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectra of isolated *meso*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **28** and *rac*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **29**

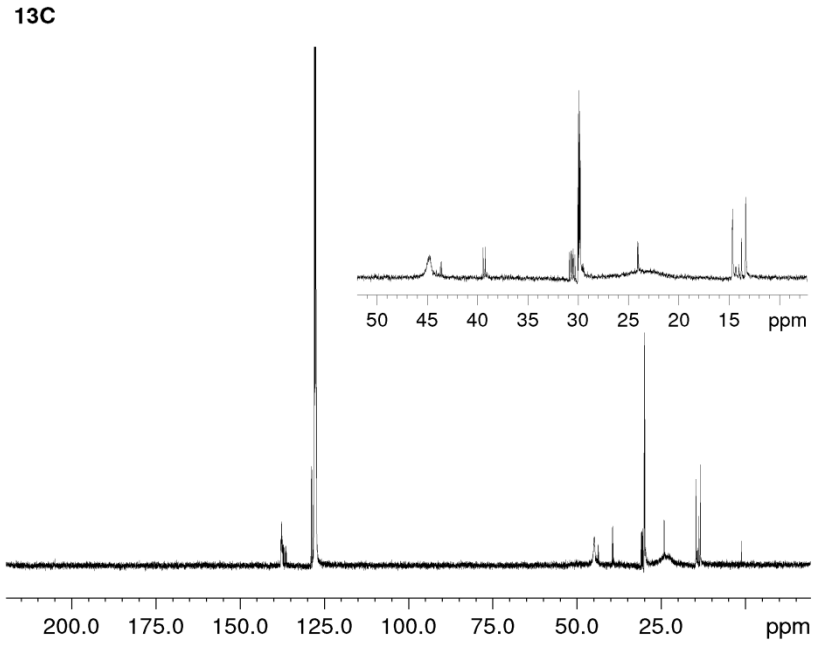


Fig. S191. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectra of isolated *meso*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **28** and *rac*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **29**

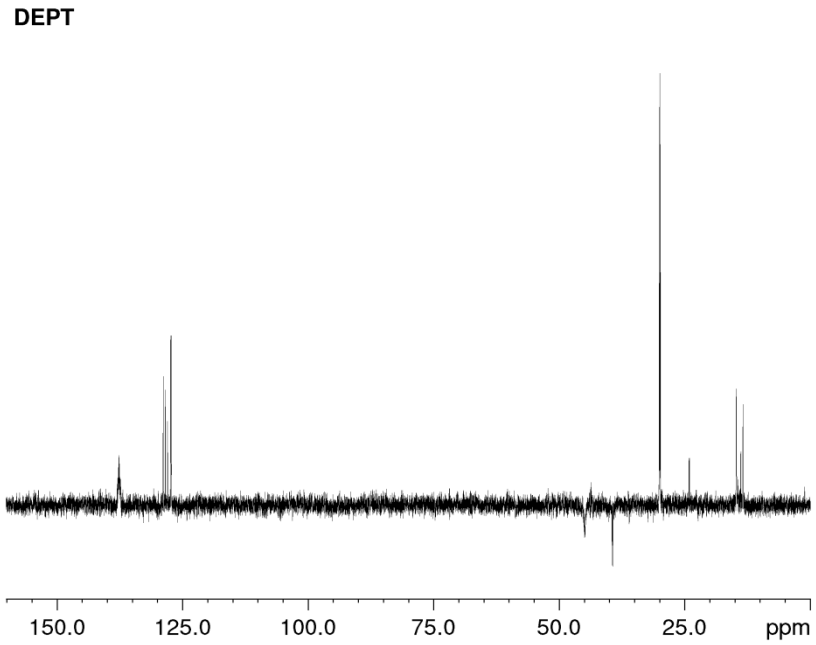


Fig. S192. ^{13}C with DEPT NMR (C_6D_6) spectra of isolated *meso*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **28** and *rac*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **29**

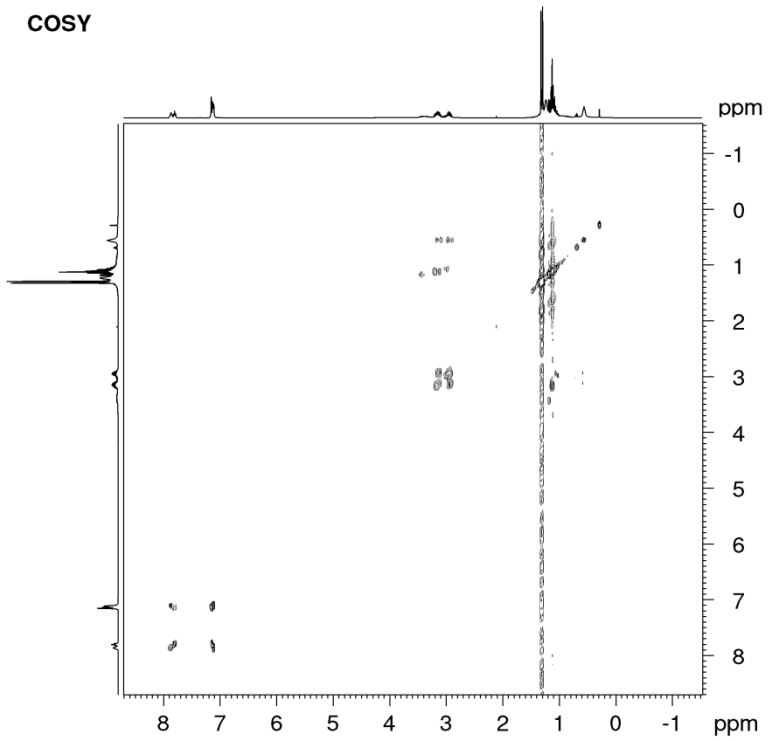


Fig. S193. COSY NMR (C_6D_6) spectra of isolated *meso*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **28** and *rac*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **29**

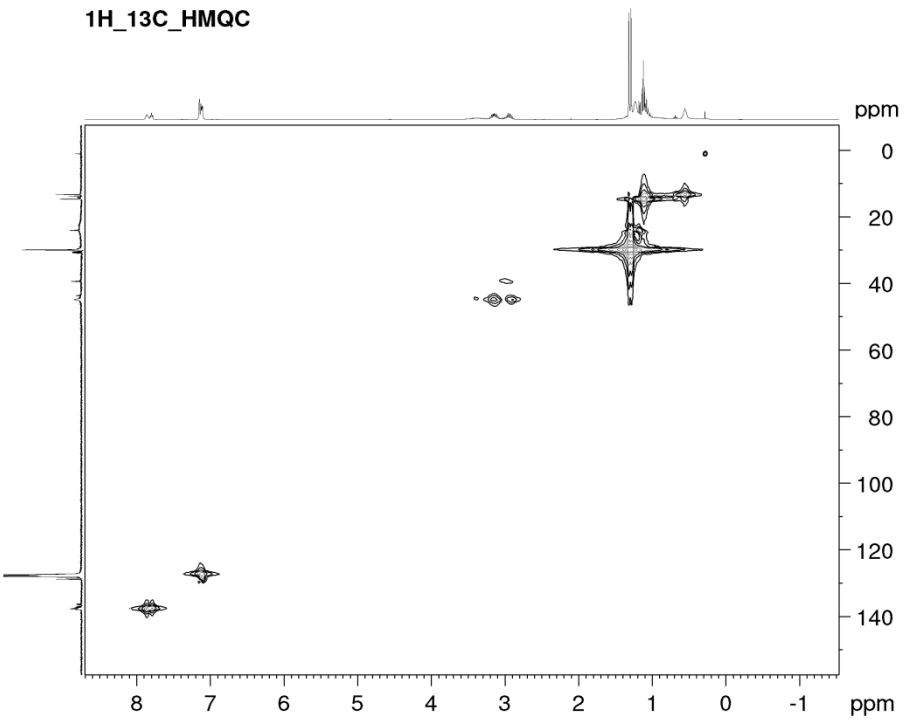


Fig. S194. ^{13}C ^{1}H HMQC NMR (C_6D_6) spectra of isolated *meso*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **28** and *rac*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **29**

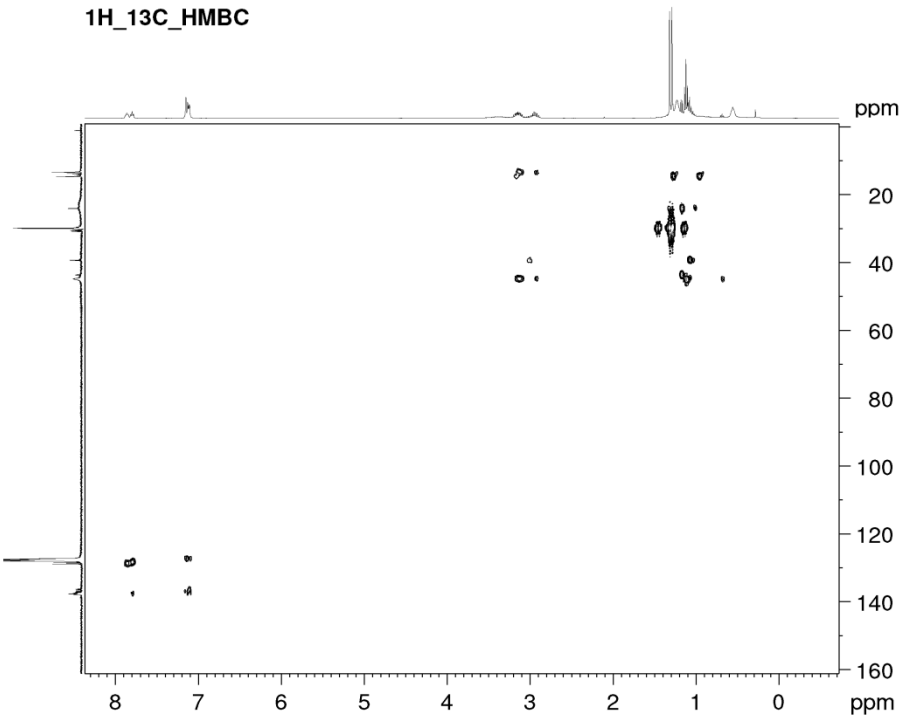


Fig. S195. ^{13}C ^{1}H HMBC NMR (C_6D_6) spectra of isolated *meso*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **28** and *rac*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **29**

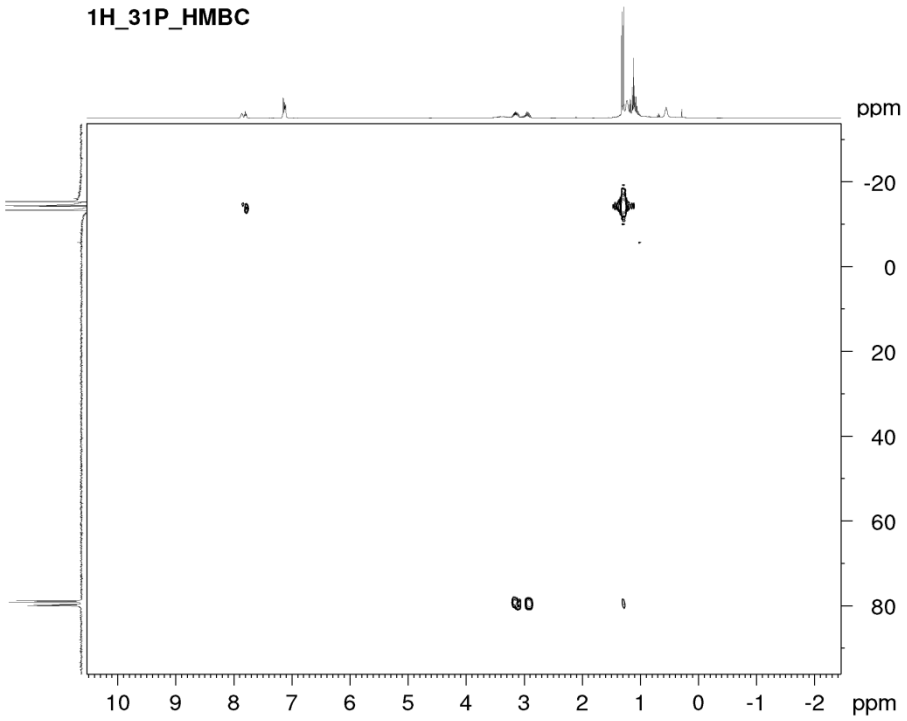


Fig. S196. ^{31}P ^{1}H HMBC NMR (C_6D_6) spectra of isolated *meso*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **28** and *rac*-(Et_2N)(*i*Pr_2N)PP*t*BuPh **29**

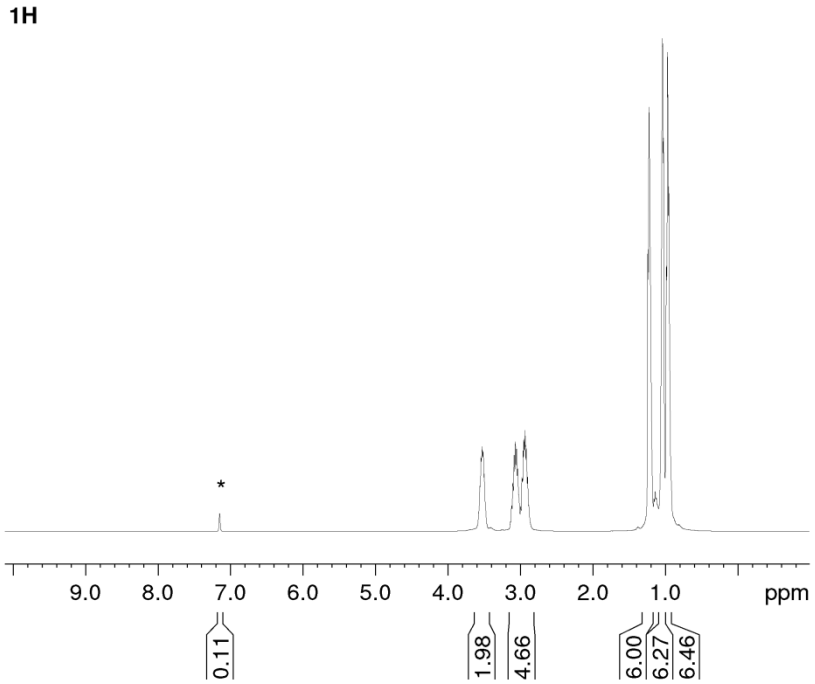


Fig. S197. ^{1}H NMR (C_6D_6) spectra of isolated (Et_2N)(*i*Pr_2N)PCl

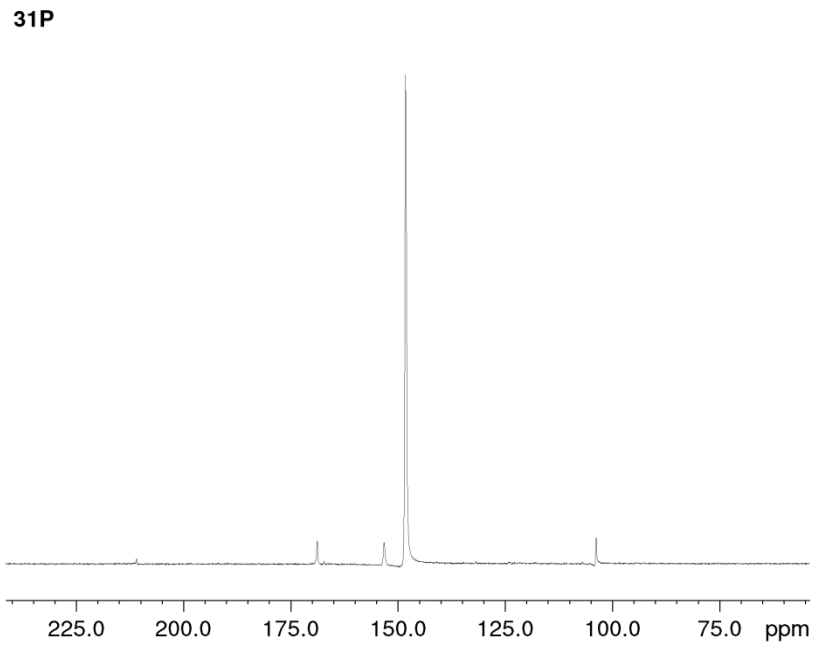


Fig. S198. ^{31}P NMR (C_6D_6) spectra of isolated (Et_2N)(*i*Pr_2N)PCl

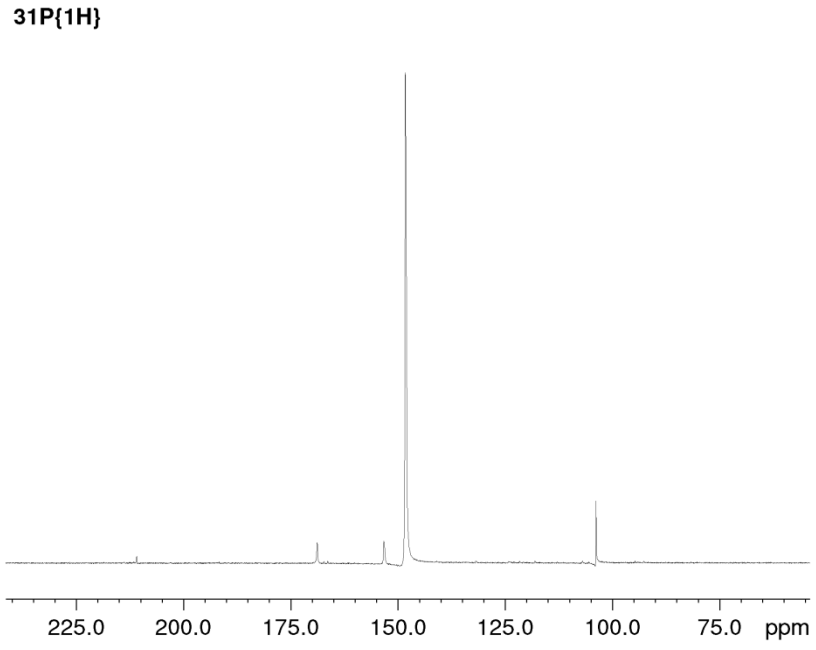


Fig. S199. $^{31}P\{^1H\}$ NMR (C_6D_6) spectra of isolated (Et_2N)(*i*Pr_2N)PCl

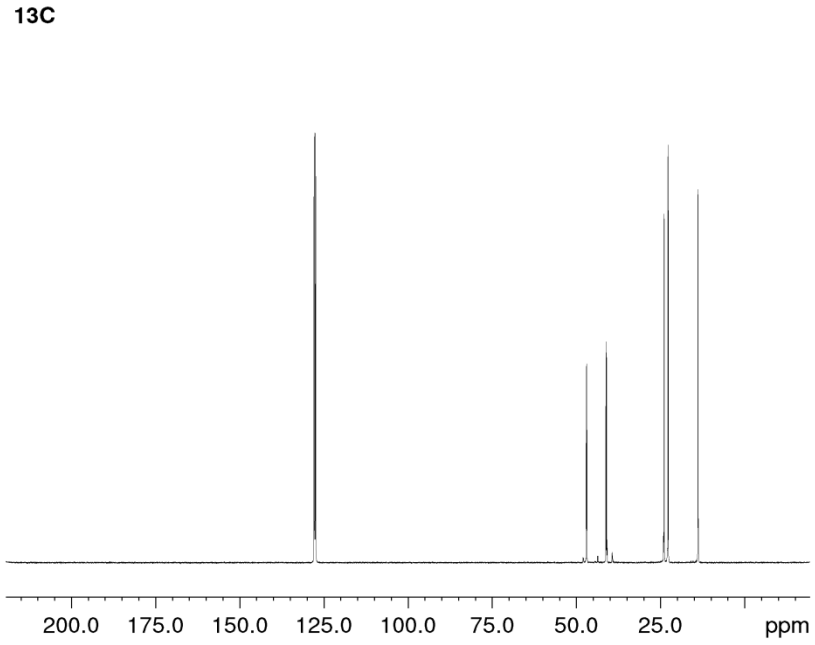


Fig. S200. $^{13}C\{^{1}H\}$ NMR (C_6D_6) spectra of isolated $(Et_2N)(iPr_2N)PCl$

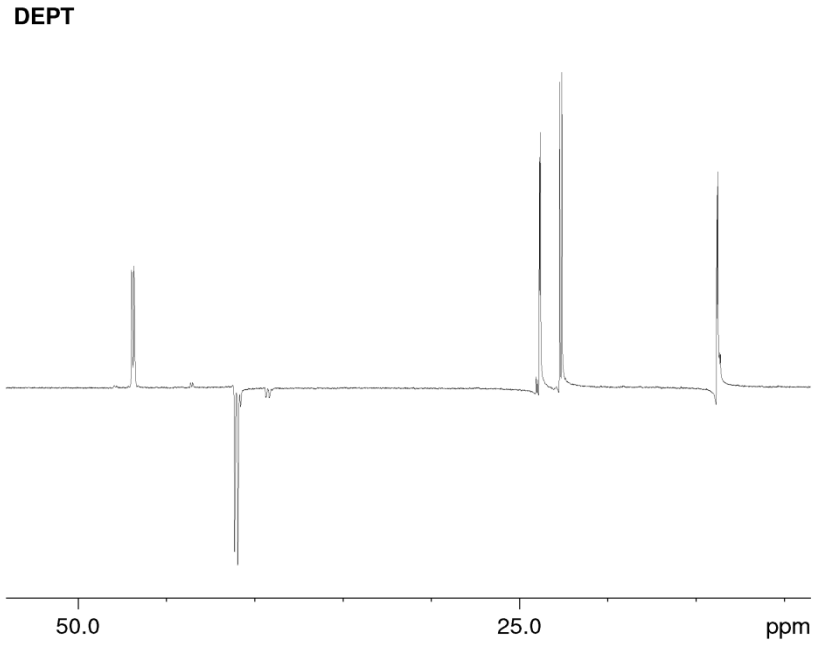


Fig. S201. ^{13}C with DEPT NMR (C_6D_6) spectra of isolated $(Et_2N)(iPr_2N)PCl$

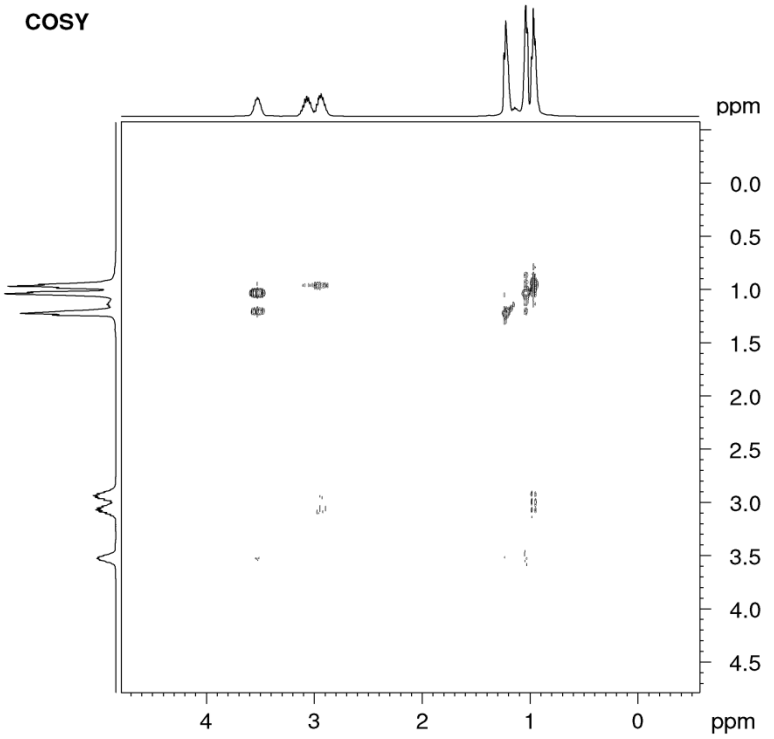


Fig. S202. COSY NMR (C_6D_6) spectra of isolated $(Et_2N)(iPr_2N)PCl$

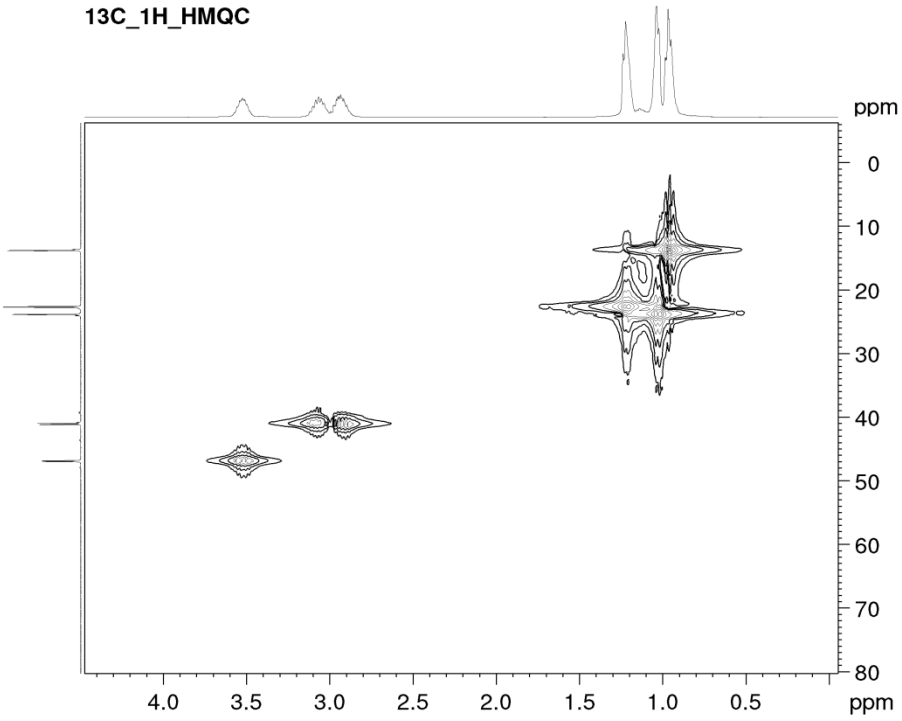


Fig. S203. ^{13}C ^{1}H HMQC NMR (C_6D_6) spectra of isolated $(Et_2N)(iPr_2N)PCl$

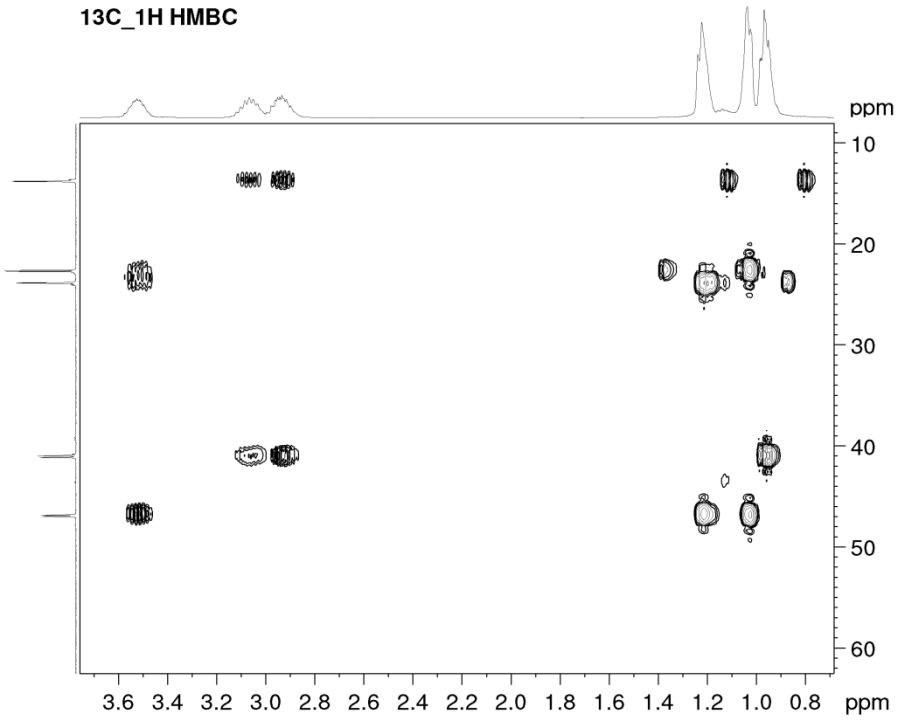


Fig. S204. ^{13}C ^{1}H HMBC NMR (C_6D_6) spectra of isolated (Et_2N)(iPr$_2$N)PCl

DFT calculations and data analysis

General methods

Molecular geometries of all diphosphanes (1-30) and radicals discussed in this paper were optimized using density functional theory at the ωB97XD functional by Head-Gordon[1,2] with cc-pVDZ basis set. The ωB97XD exchange-correlation functional has been chosen, as it has good overall performance for the description of main-group element compounds, and it also accounts well for long-range and dispersion interactions as methods taking account of the latter are reported as giving results coherent with experimental data for diphosphanes[3,4]. Molecular geometries were energy optimized and the most stable (the lowest energy) conformer was identified during the potential energy surface scanning. Nature of the final gas phase geometries as a local minima on the potential energy surface was then validated by harmonic frequency calculations at the same level of theory. Values of calculated energies, enthalpies and free energies derived from thermochemical calculations were corrected for the zero-point energy (ZPE). Enthalpies (ΔH_{diss}) and free energies (ΔG_{diss}) of the heterolytic P-P bond dissociation as well as energies of fragmentation ($\Delta E_{frag} = E_{F1} + E_{F2} - E_{DIPH}$) were corrected for basis set superposition error (BSSE)[5,6] obtained by counterpoise calculations. Difference between energy of total dispersion interactions in separated F_1 and F_2 fragments (with geometry as in RR'P-PR"R"') and respective diphosphane, corrected for BSSE as well, estimates dispersion interaction between PR_2 units in molecule (E_{F1-F2}). Due to similar values of chemical shifts and couple constants of diastereoisomers, for diastereomeric pairs of diphosphanes 4/5, 15/16, 18/19, 22/23, 25/26 and 28/29 theoretical ^{31}P NMR shift were determined using obtained from ωB97xd/cc-pVDZ (IGAIM method) calculations NMR shielding tensors. Values of σ_{P1} and σ_{P2} calculated for compound **13** were averaged, validated by comparison of the computed chemical shifts with experimental ones and used to determination of ^{31}P [ppm] for analyzed compounds. All calculations presented in the paper were performed using the Gaussian 09[7] program package.

Tabel. S4. Selected computational parameters obtained for diphosphanes 1-30 : μ – dipol moment, E_0 – total electronic energy, H – enthalpy, G – free energy, E_{HOMO} – energy of HOMO orbital, E_{LUMO} – energy of LUMO orbital, E_{H-L} – energy of HOMO-LUMO gap, $E_{F1/F2}$ – energy of fragment (~PR_2) F_1/F_2, energy of BSSE (calculated for decomposition along P-P bond into two F_1, F_2 fragments), $E_{D/D[F1]/D[F2]}$ – energy of total dispersion interaction in fragment F_1/F_2 or diphosphane, E_{F1-F2} – energy of dispersion interaction between two PR_2 units

No.	Diphosphane	μ [D]	E_0 [a. u.]	H [a. u.]	G [a. u.]	E_{HOMO} [eV]	E_{LUMO} [eV]	$E_{\Delta H-L}$ [eV]	E_{F1} [a. u.]	E_{F2} [a. u.]	E_{BSSE} [a. u.]	$E_{D[F1]}$ [a. u.]	$E_{D[F2]}$ [a. u.]	E_D [a. u.]	E_{F1-F2} [a. u.]
1	*t*Bu_2P-P*t*Bu_2	1.434	-1313.94	-1313.42	-1313.49	-7.280	2.532	9.811	-656.93	656.93	0.0047	-0.0214	-0.0212	-0.0604	-0.0178
2	*t*Bu_2P-P*t*BuPh	1.319	-1387.73	-1387.24	-1387.32	-7.299	1.082	8.381	-730.71	-656.93	0.0047	-0.0167	-0.0213	-0.0554	-0.0175
3	*t*Bu_2P-PPh_2	0.482	-1461.50	-1461.05	-1461.12	-7.391	0.954	8.344	-656.93	-804.48	0.0045	-0.0214	-0.0129	-0.0492	-0.0149
4	*rac*-*t*BuPhP-P*t*BuPh	1.292	-1461.51	-1461.06	-1461.13	-7.522	1.019	8.541	-730.71	-730.71	0.0043	-0.0171	-0.0171	-0.0490	-0.0148
5	*meso*-*t*BuPhP-P*t*BuPh	0.000	-1461.51	-1461.06	-1461.13	-7.464	1.063	8.526	-730.71	-730.71	0.0042	-0.0172	-0.0172	-0.0487	-0.0143
6	*t*BuPhP-PPh_2	0.361	-1535.28	-1534.86	-1534.94	-7.547	0.993	8.540	-804.48	-730.71	0.0040	-0.0127	-0.0169	-0.0427	-0.0130
7	Ph_2P-PPh_2	2.272	-1609.06	-1608.66	-1608.74	-7.502	0.736	8.239	-804.49	-804.49	0.0046	-0.0128	-0.0129	-0.0417	-0.0160
8	(*i*Pr_2N)$_2$P-PPh_2	0.377	-1729.41	-1728.80	-1728.89	-7.224	1.011	8.235	-924.83	-804.48	0.0058	-0.0422	-0.0126	-0.0751	-0.0203
9	(*i*Pr_2N)$_2$P-P*t*Bu_2	1.129	-1581.84	-1581.16	-1581.26	-6.802	2.513	9.315	-924.83	-656.93	0.0064	-0.0429	-0.0214	-0.0867	-0.0224
10	(*i*Pr_2N)$_2$P-P*t*BuPh	0.570	-1655.63	-1654.99	-1655.08	-7.207	1.296	8.503	-924.82	-730.71	0.0063	-0.0424	-0.0173	-0.0815	-0.0218
11	(Et_2N)$_2$P-PPh_2	1.030	-1572.18	-1571.69	-1571.77	-7.113	1.112	8.225	-767.61	-804.49	0.0061	-0.0261	-0.0128	-0.0530	-0.0142
12	(Et_2N)$_2$P-P*t*Bu_2	0.863	-1424.62	-1424.07	-1424.15	-7.101	2.534	9.635	-767.60	-656.93	0.0068	-0.0265	-0.0212	-0.0647	-0.0170
13	(Et_2N)$_2$P-P*t*BuPh	0.489	-1498.41	-1497.88	-1497.97	-7.240	1.247	8.486	-767.60	-730.71	0.0063	-0.0256	-0.0169	-0.0585	-0.0160
14	(*i*Pr_2N)PhP-PPh_2	0.927	-1669.23	-1668.73	-1668.82	-7.284	0.995	8.279	-864.66	-804.48	0.0049	-0.0276	-0.0129	-0.0559	-0.0154
15	p-*meso*-(*i*Pr_2N)PhP-P*t*BuPh	0.620	-1595.46	-1594.93	-1595.01	-7.463	1.061	8.524	-864.65	-730.71	0.0052	-0.0275	-0.0170	-0.0611	-0.0166
16	p-*rac*-(*i*Pr_2N)PhP-P*t*BuPh	0.667	-1595.46	-1594.93	-1595.01	-7.456	1.159	8.615	-864.65	-730.71	0.0052	-0.0279	-0.0171	-0.0601	-0.0151
17	(*i*Pr_2N)PhP-P*t*Bu_2	0.986	-1521.67	-1521.11	-1521.19	-7.197	1.305	8.502	-864.66	-656.93	0.0052	-0.0262	-0.0213	-0.0669	-0.0194
18	*meso*-(*i*Pr_2N)PhP-P(*i*Pr_2N)Ph	0.238	-1729.41	-1728.79	-1728.89	-7.299	1.051	8.351	-864.65	-864.65	0.0058	-0.0271	-0.0267	-0.0723	-0.0186
19	*rac*-(*i*Pr_2N)PhP-P(*i*Pr_2N)Ph	0.177	-1729.40	-1728.79	-1728.88	-7.538	1.148	8.686	-864.65	-864.65	0.0054	-0.0272	-0.0272	-0.0709	-0.0164
20	(*i*Pr_2N)PhP-P(*i*Pr_2N)$_2$	0.092	-1789.58	-1788.86	-1788.96	-7.181	1.253	8.434	-864.65	-924.83	0.0070	-0.0279	-0.0423	-0.0937	-0.0235
21	(*i*Pr_2N)*t*BuP-PPh_2	0.158	-1595.46	-1594.92	-1595.01	-7.424	0.937	8.362	-790.88	-804.48	0.0049	-0.0319	-0.0126	-0.0619	-0.0174
22	p-*meso*-(*i*Pr_2N)*t*BuP-P*t*BuPh	1.201	-1521.68	-1521.11	-1521.20	-7.330	1.089	8.419	-790.88	-730.71	0.0051	-0.0317	-0.0166	-0.0677	-0.0194
23	p-*rac*-(*i*Pr_2N)*t*BuP-P*t*BuPh	0.366	-1521.68	-1521.11	-1521.19	-7.053	1.266	8.319	-790.88	-730.71	0.0053	-0.0320	-0.0172	-0.0688	-0.0197
24	(*i*Pr_2N)*t*BuP-P*t*Bu_2	1.282	-1447.89	-1447.29	-1447.38	-7.285	2.609	9.894	-790.88	-656.93	0.0050	-0.0315	-0.0214	-0.0728	-0.0198
25	*meso*-(*i*Pr_2N)*t*BuP-P(*i*Pr_2N)*t*Bu	1.316	-1581.84	-1581.16	-1581.26	-7.037	2.546	9.583	-790.88	-790.87	0.0062	-0.0321	-0.0325	-0.0866	-0.0220
26	*rac*-(*i*Pr_2N)*t*BuP-P(*i*Pr_2N)*t*Bu	2.067	-1581.84	-1581.16	-1581.26	-7.073	2.591	9.664	-790.88	790.87	0.0062	-0.0321	-0.0329	-0.0890	-0.0240
27	(*i*Pr_2N)*t*BuP-P(*i*Pr_2N)$_2$	0.946	-1715.80	-1715.04	-1715.14	-6.863	2.598	9.461	-924.83	-790.88	0.0069	-0.0320	-0.0429	-0.1004	-0.0255
28	p-*meso*-(Et_2N)(*i*Pr_2N)P-P*t*BuPh	0.374	-1577.02	-1576.44	-1576.53	-7.287	1.283	8.571	-846.22	-730.71	0.0061	-0.0335	-0.0171	-0.0691	-0.0185
29	p-*rac*-(Et_2N)(*i*Pr_2N)P-P*t*BuPh	0.666	-1577.02	-1576.44	-1576.53	-7.370	1.278	8.648	-846.21	-730.71	0.0062	-0.0337	-0.0171	-0.0683	-0.0175
30	(*i*Pr_2N)$_2$P-P(*i*Pr_2N)$_2$	0.702	-1849.74	-1848.91	-1849.02	-6.613	2.776	9.390	-924.83	-924.83	0.0076	-0.0427	-0.0427	-0.1138	-0.0283

Tab. S5. Selected experimental and calculated parameters used for assignment ^{31}P NMR chemical shifts to appropriate diastereoisomers: $^{1}J_{P\text{-}Pexp}$ - P-P constant coupling, $\delta P_{1/2\ (calc/exp)}$ – calculated/experimental chemical shift of phosphorus 1/2 , $\sigma P_{1\ calc}$ - calculated shielding tensors, ΔE – relative energy of diastereoisomers, n_{rac}: n_{meso} – molar ratio of two isomers obtained from experimental NMR data

	Diphosphane	$^{1}J_{P\text{-}Pexp}$ [Hz]	$\delta P_{1\ exp}$ [ppm]	$\delta P_{2\ exp}$ [ppm]	$\sigma P_{1\ calc}$	$\sigma P_{2\ calc}$	$\delta P_{1\ calc}$ [ppm]	$\delta P_{2\ calc}$ [ppm]	ΔE [kJ/mol]	n_{rac}:n_{meso} (exp)
4	*rac*-*t*BuPhP-P*t*BuPh	-	2.1	2.1	375.9	375.9	2.3	2.3	3.19	4.816 : 1
5	*meso*-*t*BuPhP-P*t*BuPh	-	-4.2	-4.2	384.8	384.8	-6.5	-6.5	0.00	
15	p-*meso*-(*i*Pr$_2$N)PhP-P*t*BuPh	138.0	28.3	-7.5	383.2	356.3	21.9	-4.9	0.00	1 : 1.36
16	p-*rac*-(*i*Pr$_2$N)PhP-P*t*BuPh	145.3	27.6	-11.1	390.5	354.3	23.9	-12.3	1.56	
18	*meso*-(*i*Pr$_2$N)PhP-P(*i*Pr$_2$N)Ph	-	23.6	23.6	350.4	367.2	19.4	19.4	0.00	1 : 2.84
19	*rac*-(*i*Pr$_2$N)PhP-P(*i*Pr$_2$N)Ph		21.5	21.5	362.3	362.3	15.9	15.9	10.47	
22	p-*meso*-(*i*Pr$_2$N)*t*BuP-P*t*BuPh	348.8	57.7	14.9	330.9	363.4	47.4	14.8	0.00	1 : 1.14
23	p-*rac*-(*i*Pr$_2$N)*t*BuP-P*t*BuPh	283.4	70.3	7.7	298.8	367.7	79.4	10.5	11.74	
25	*meso*-(*i*Pr$_2$N)*t*BuP-P(*i*Pr$_2$N)*t*Bu	-	88.8	88.8	303.2	270.0	91.6	91.6	4.31	1 : 1.11
26	*rac*-(*i*Pr$_2$N)*t*BuP-P(*i*Pr$_2$N)*t*Bu	-	82.0	82.0	322.5	280.2	76.9	76.9	0.00	
28	p-*meso*-(Et$_2$N)(*i*Pr$_2$N)P-P*t*BuPh	143.1	79.5	-13.7	298.1	391.1	80.2	-12.9	0.00	1 : 1.03
29	p-*rac*-(Et$_2$N)(*i*Pr$_2$N)P-P*t*BuPh	140.4	79.3	-14.9	290.0	392.2	88.2	-13.9	0.18	

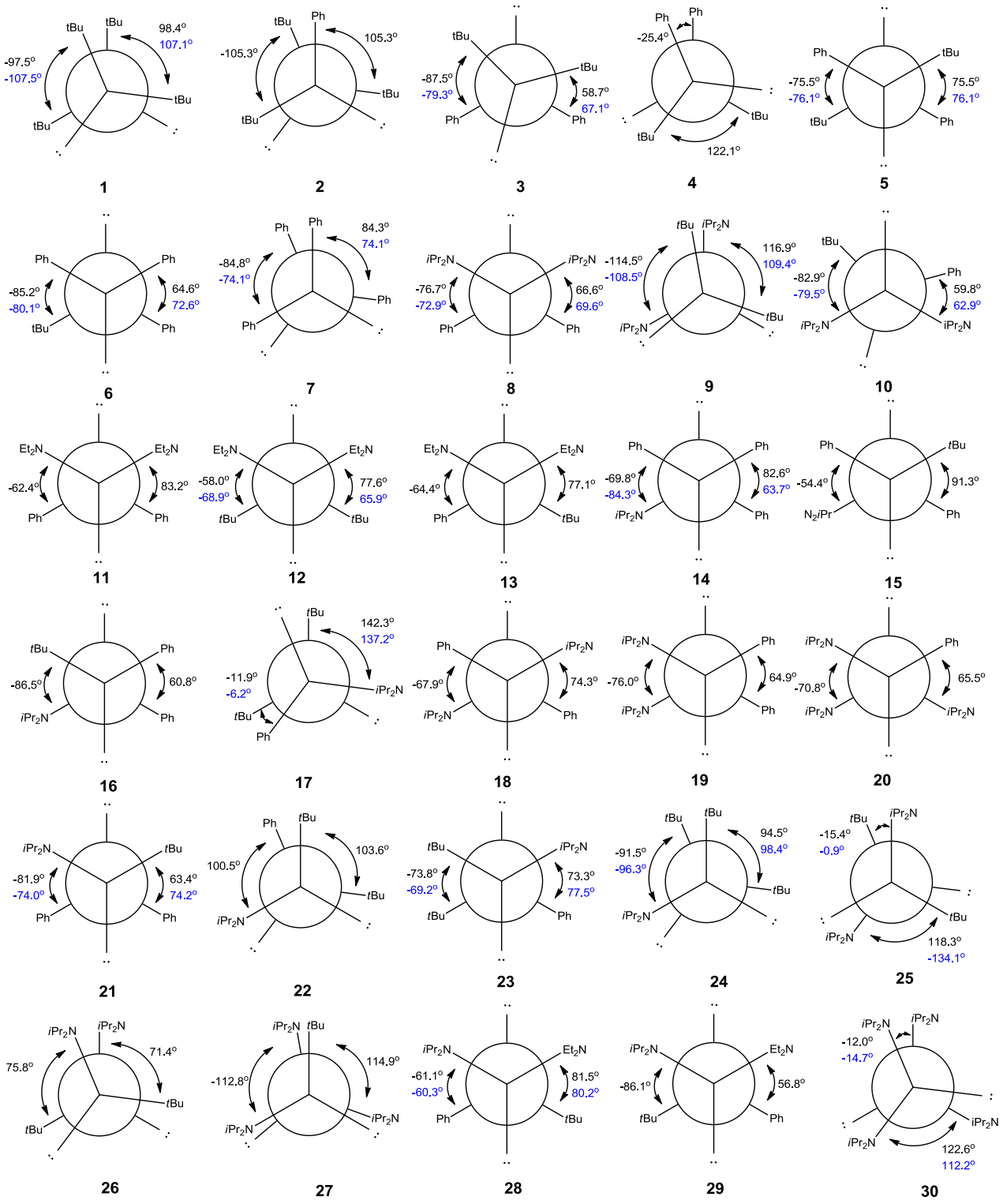
Conformational analysis

Table. S6. Selected conformers of diphosphanes 1-30. Respective dihedrals **D_n [°]** are presented at **Fig.207-236.** **$R_{P1\text{-}P2}$** – length of the P-P bond, **ΔE –** energy of conformer related to the lowest-energetic structure

1			**2**			**3**		
$D_{3C\text{-}1P\text{-}2P\text{-}5C}$ [°]	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{3C\text{-}1P\text{-}2P\text{-}6C}$ [°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{11C\text{-}1P\text{-}2P\text{-}4C}$ [°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**
23.404	2.235	0.00	105.283	2.244	0.00	58.725	2.264	0.00
83.404	2.226	5.86	165.283	2.292	23.56	118.725	2.262	13.52
143.403	2.307	42.51	-134.717	2.284	30.29	178.725	2.241	9.88
-156.596	2.322	69.52	-74.717	2.229	31.52	-121.275	2.328	69.99
-96.596	2.234	0.04	-14.717	2.318	80.15	-61.275	2.233	23.17
-36.596	2.290	60.20	45.283	2.251	32.33	-1.275	2.245	7.00
4			**5**			**6**		
$D_{25C\text{-}1P\text{-}2P\text{-}38C}$ [°]	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{25C\text{-}1P\text{-}2P\text{-}3C}$ [°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{25C\text{-}1P\text{-}2P\text{-}3C}$ [°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**
-122.143	2.257	0.00	75.475	2.252	0.00	-85.161	2.252	0.00
-62.143	2.267	21.67	125.926	2.260	25.38	-25.161	2.260	20.42
-2.143	2.248	38.51	174.343	2.230	37.47	34.839	2.230	12.35
57.857	2.234	42.52	-129.321	2.299	72.50	94.839	2.299	41.80
117.857	2.303	65.42	-62.554	2.258	41.30	154.839	2.258	18.33
177.857	2.228	16.50	1.324	2.251	23.16	-145.161	2.251	3.05
7			**8**			**9**		
$D_{4C\text{-}1P\text{-}2P\text{-}6CC}$ [°]	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{3C\text{-}1P\text{-}2P\text{-}7C}$ [°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{14C\text{-}69P\text{-}70P\text{-}68N}$ [°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**
98.676	2.258	0.69	-76.659	2.262	0.00	58.879	2.274	45.22
158.676	2.250	2.21	-16.659	2.279	20.00	118.879	2.353	79.85
-141.324	2.281	19.50	43.341	2.260	19.81	178.879	2.288	32.61
-81.324	2.297	31.35	103.341	2.290	43.27	-121.121	2.305	1.59
-21.324	2.252	0.00	163.341	2.276	27.17	-61.121	2.312	34.20
38.676	2.269	5.52	-136.659	2.271	16.23	-1.121	2.296	0.00
10			**11**			**12**		
$D_{3N\text{-}1P\text{-}2P\text{-}4C}$ [°]	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{21N\text{-}1P\text{-}2P\text{-}4C}$ [°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{29N\text{-}1P\text{-}2P\text{-}46C}$ [°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**
82.917	2.271	0.00	-62.405	2.265	0.00	-57.990	2.275	0.00
142.917	2.264	20.25	-2.405	2.292	14.27	2.010	2.279	20.07
-157.083	2.271	41.26	57.595	2.270	28.07	62.010	2.261	43.31

-97.083	2.308	85.72	117.595	2.321	43.63	122.010	2.335	68.50
-37.083	2.258	42.52	177.595	2.260	23.24	-177.990	2.267	23.94
22.917	2.285	27.85	-122.405	2.296	14.68	-117.990	2.290	14.53
	13			**14**			**15**	
$D_{3N\text{-}1P\text{-}2P\text{-}4C}$ [°]	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{4C\text{-}1P\text{-}2P\text{-}3N}$ [°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{4C\text{-}1P\text{-}2P\text{-}3N}$[°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**
77.068	2.250	0.00	-69.836	2.261	0.00	-54.440	2.257	0.00
137.068	2.263	18.89	-9.836	2.267	13.55	5.560	2.246	23.24
-162.932	2.254	35.70	50.164	2.244	21.67	65.560	2.227	29.76
-102.932	2.314	56.04	110.164	2.334	43.05	125.560	2.324	68.09
-42.932	2.253	48.44	170.164	2.250	25.30	-174.440	2.246	42.34
17.068	2.280	34.86	-129.836	2.259	20.53	-114.440	2.266	25.15
	16			**17**			**18**	
$D_{4C\text{-}1P\text{-}2P\text{-}3N}$ [°]	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{3C\text{-}1P\text{-}2P\text{-}29C}$ [°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{11C\text{-}1P\text{-}34P\text{-}35N}$ [°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**
-86.482	2.250	0.00	-99.998	2.256	0.00	-7.876	2.265	17.65
-26.482	2.279	31.76	-39.998	2.231	12.65	52.124	2.249	21.63
33.518	2.222	39.63	20.002	2.287	11.34	112.124	2.322	74.05
93.518	2.281	50.51	80.002	2.276	5.91	172.124	2.273	19.40
153.518	2.273	35.13	140.002	2.255	0.07	-127.876	2.265	16.80
-146.482	2.246	12.46	-159.998	2.284	46.41	-67.876	2.246	0.00
	19			**20**			**21**	
$D_{11C\text{-}1P\text{-}34P\text{-}44C}$ [°]	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{66C\text{-}4P\text{-}5P\text{-}3N}$ [°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{3N\text{-}1P\text{-}2P\text{-}11C}$ [°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**
124.946	2.293	39.64	65.472	2.261	0.00	-81.934	2.265	0.00
-175.053	2.238	40.66	125.472	2.282	24.55	-21.934	2.276	5.33
-115.053	2.326	70.41	-174.528	2.254	28.81	38.066	2.249	17.23
-55.053	2.246	15.89	-114.528	2.321	73.84	98.066	2.308	40.87
4.946	2.264	7.80	-54.528	2.244	33.86	158.066	2.270	27.51
64.947	2.241	0.00	5.472	2.278	8.24	-141.934	2.249	10.19
	22			**23**			**24**	
$D_{3N\text{-}1P\text{-}2P\text{-}48C}$ [°]	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{3N\text{-}1P\text{-}2P\text{-}4C}$ [°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{3N\text{-}1P\text{-}2P\text{-}37C}$ [°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**
-84.292	2.270	3.91	73.305	2.276	0.00	-88.737	2.338	25.63
-24.292	2.294	19.21	133.306	2.255	23.53	-28.737	2.319	33.70
35.708	2.234	29.25	-166.695	2.273	46.32	31.263	2.236	12.88
95.708	2.287	60.28	-106.694	2.302	59.73	91.263	2.277	70.45
155.708	2.286	35.28	-46.694	2.226	9.80	151.263	2.374	70.54
-144.292	2.253	0.00	13.305	2.276	1.82	-148.737	2.253	0.00
	25			**26**			**27**	
$D_{3N\text{-}1P\text{-}2P\text{-}37C}$ [°]	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{14C\text{-}1P\text{-}2P\text{-}37C}$ [°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{3N\text{-}1P\text{-}2P\text{-}37C}$ [°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**
-75.446	2.310	13.95	106.274	2.322	32.61	61.166	2.293	33.41
-15.446	2.298	0.00	166.274	2.243	0.00	121.166	2.294	46.67
44.554	2.240	26.57	-133.726	2.377	61.20	-178.834	2.269	35.81
104.554	2.318	83.98	-73.726	2.284	77.23	-118.834	2.380	105.28
164.554	2.296	46.77	-13.726	2.263	4.19	-58.834	2.273	43.81
-135.446	2.288	2.77	46.274	2.300	14.04	1.166	2.299	0.00
	28			**29**			**30**	
$D_{3N\text{-}1P\text{-}2P\text{-}4C}$ [°]	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{34N\text{-}1P\text{-}2P\text{-}4C}$ [°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**	**$D_{3N\text{-}1P\text{-}2P\text{-}37C}$ [°]**	**$R_{P1\text{-}P2}$ [Å]**	**ΔE [kJ/mol]**
141.536	2.254	27.78	-26.138	2.281	38.33	-122.643	2.300	0.00
-158.464	2.276	46.57	33.862	2.246	42.82	-62.643	2.275	24.24
-98.464	2.309	54.38	93.862	2.303	56.73	-2.643	2.303	25.77
-38.464	2.259	44.11	153.862	2.285	39.44	57.357	2.270	40.48
21.536	2.285	30.32	-146.138	2.268	15.47	117.357	2.330	89.31
81.536	2.264	0.00	-86.138	2.258	0.00	177.357	2.294	23.96

Chart S1. Calculated, optimal conformations for **1**-**30**. The calculated (black) and experimental (blue) values of dihedral angles are provided



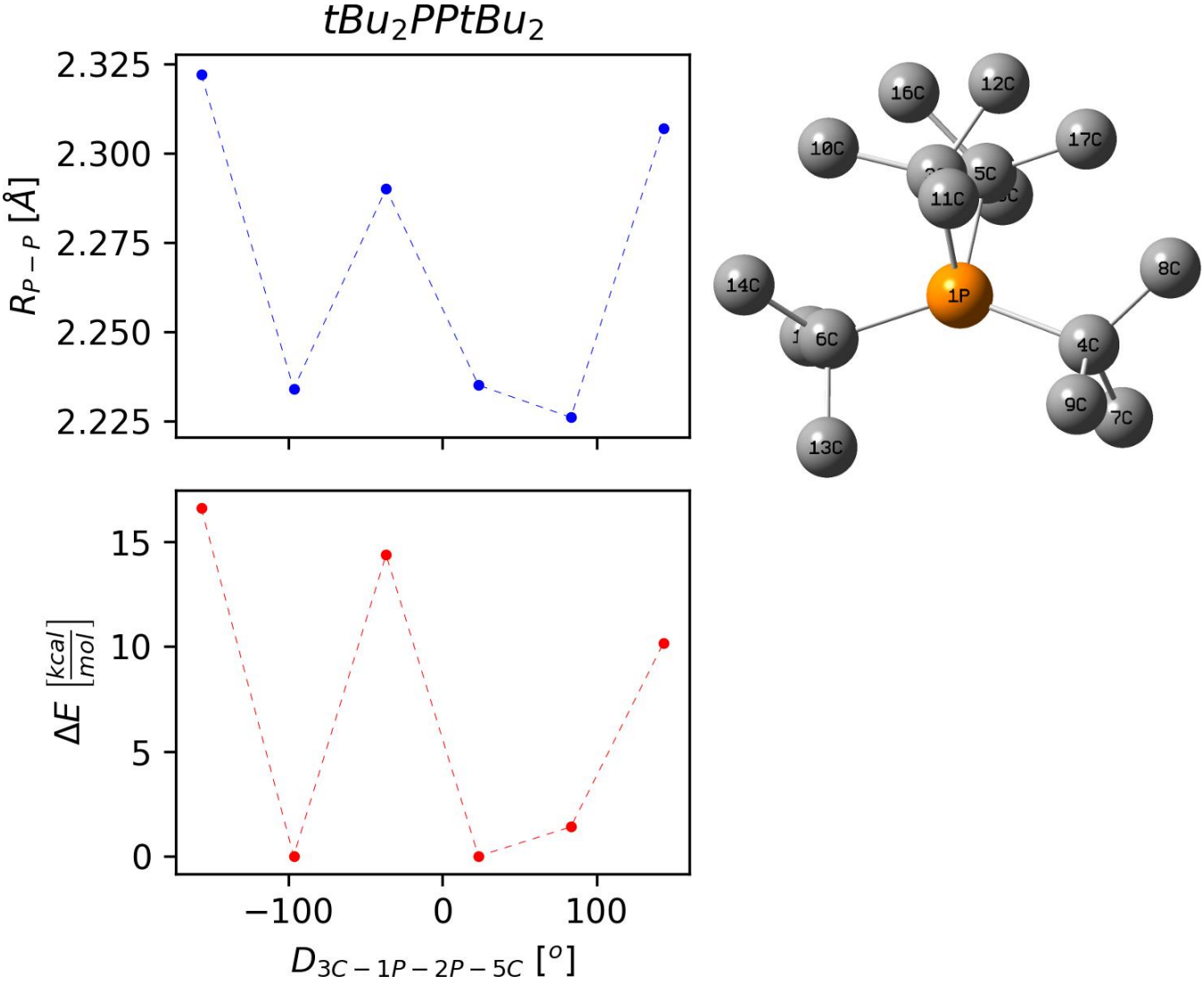


Fig. S205. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **1** (view along P-P bond)

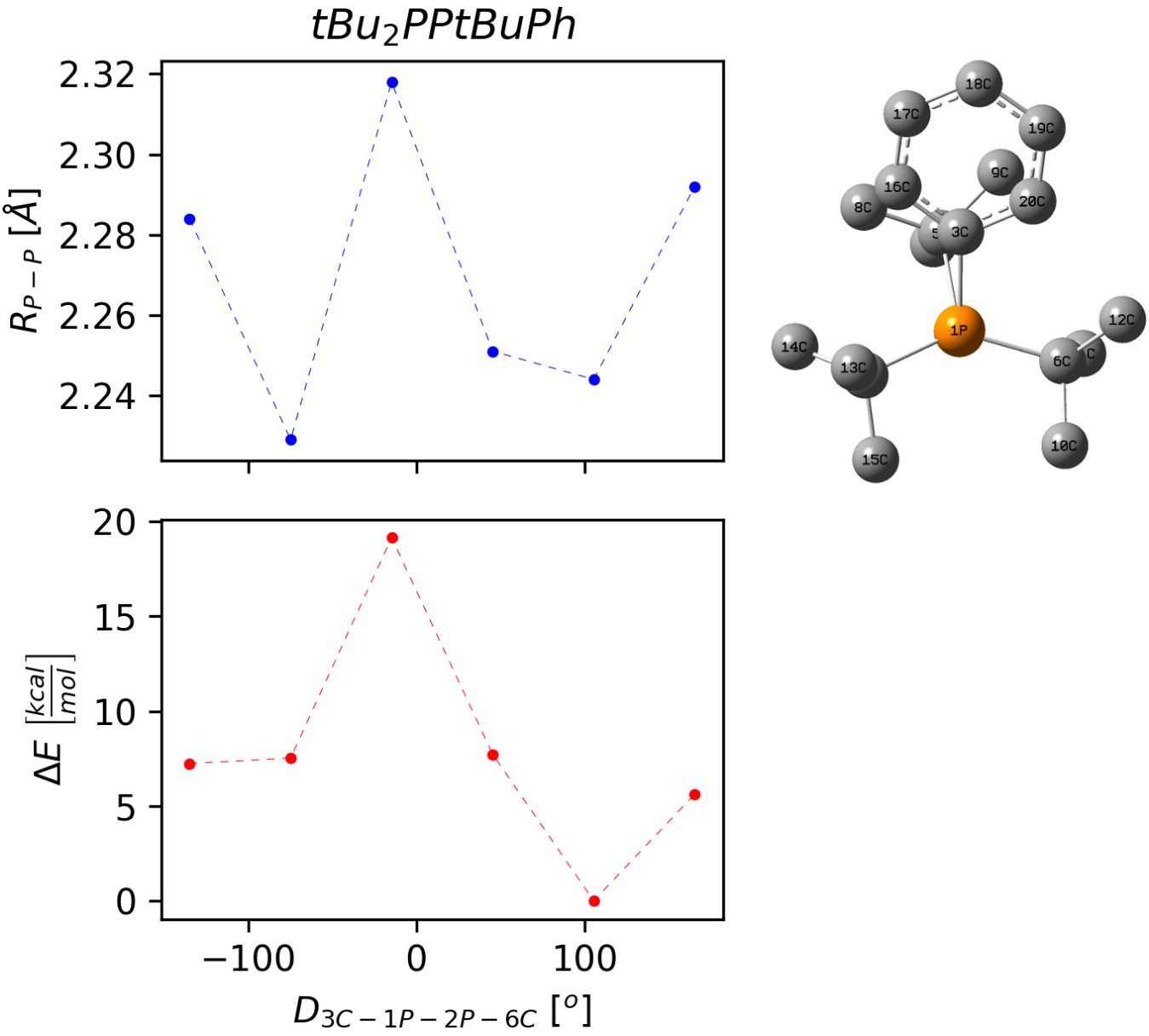


Fig. S206. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **2** (view along P-P bond)

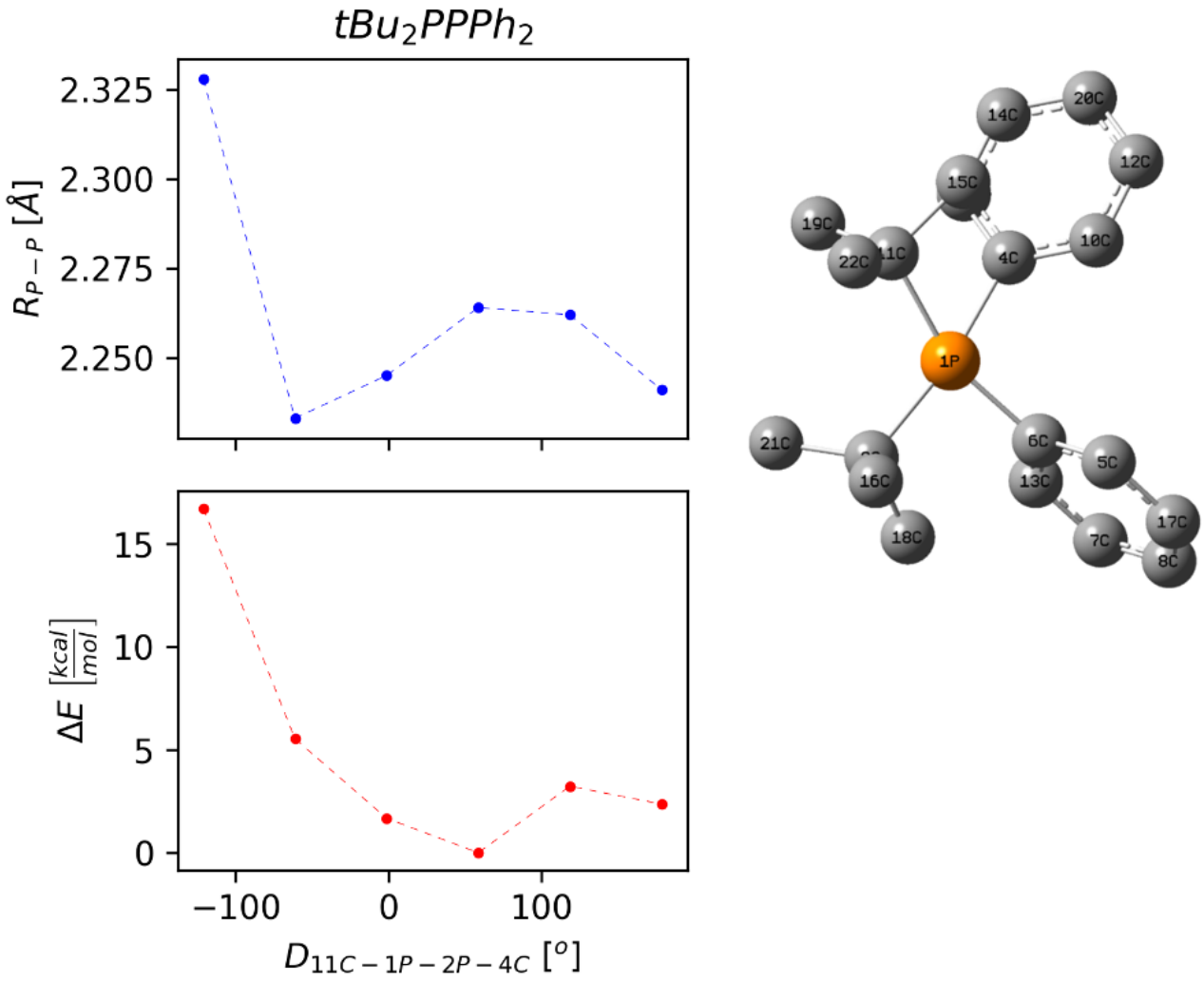


Fig. S207. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **3** (view along P-P bond)

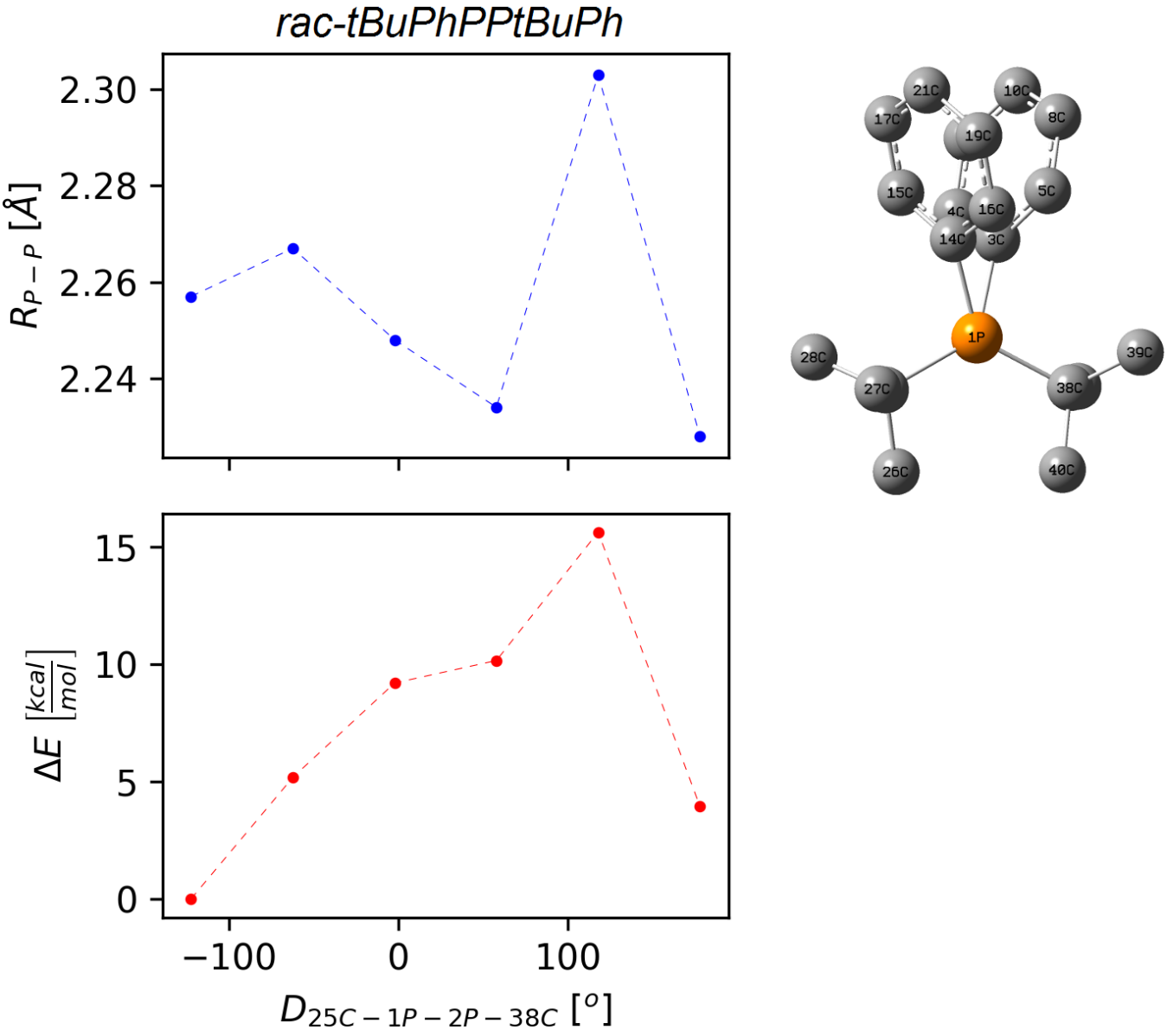


Fig. S208. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **4** (view along P-P bond)

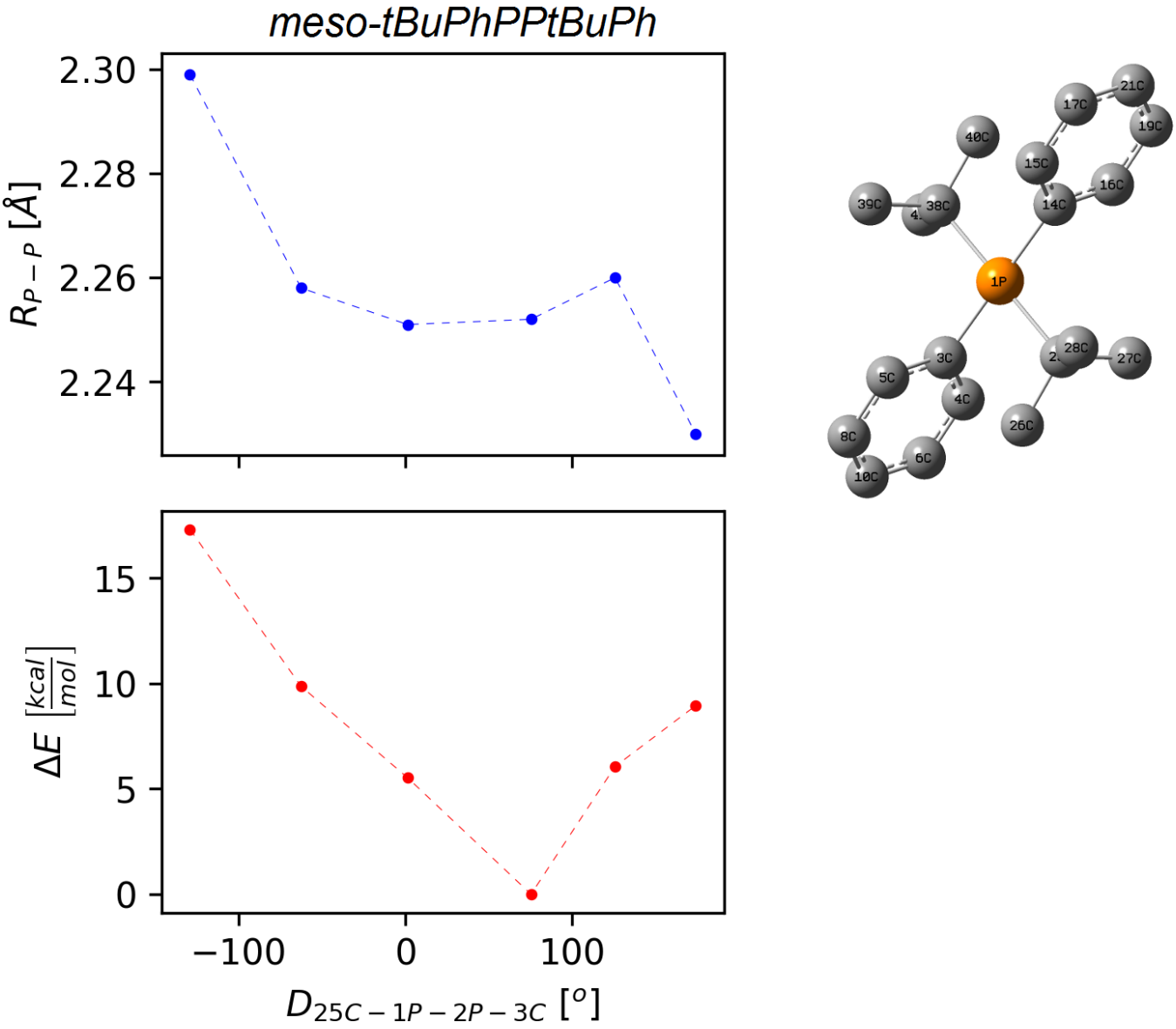


Fig. S209. Dependence of conformer relative energy (**ΔE**) and P-P bond length (**R_{P-P}**) on selected dihedral **D_n** (graph) with structure of diphosphane **5** (view along P-P bond)

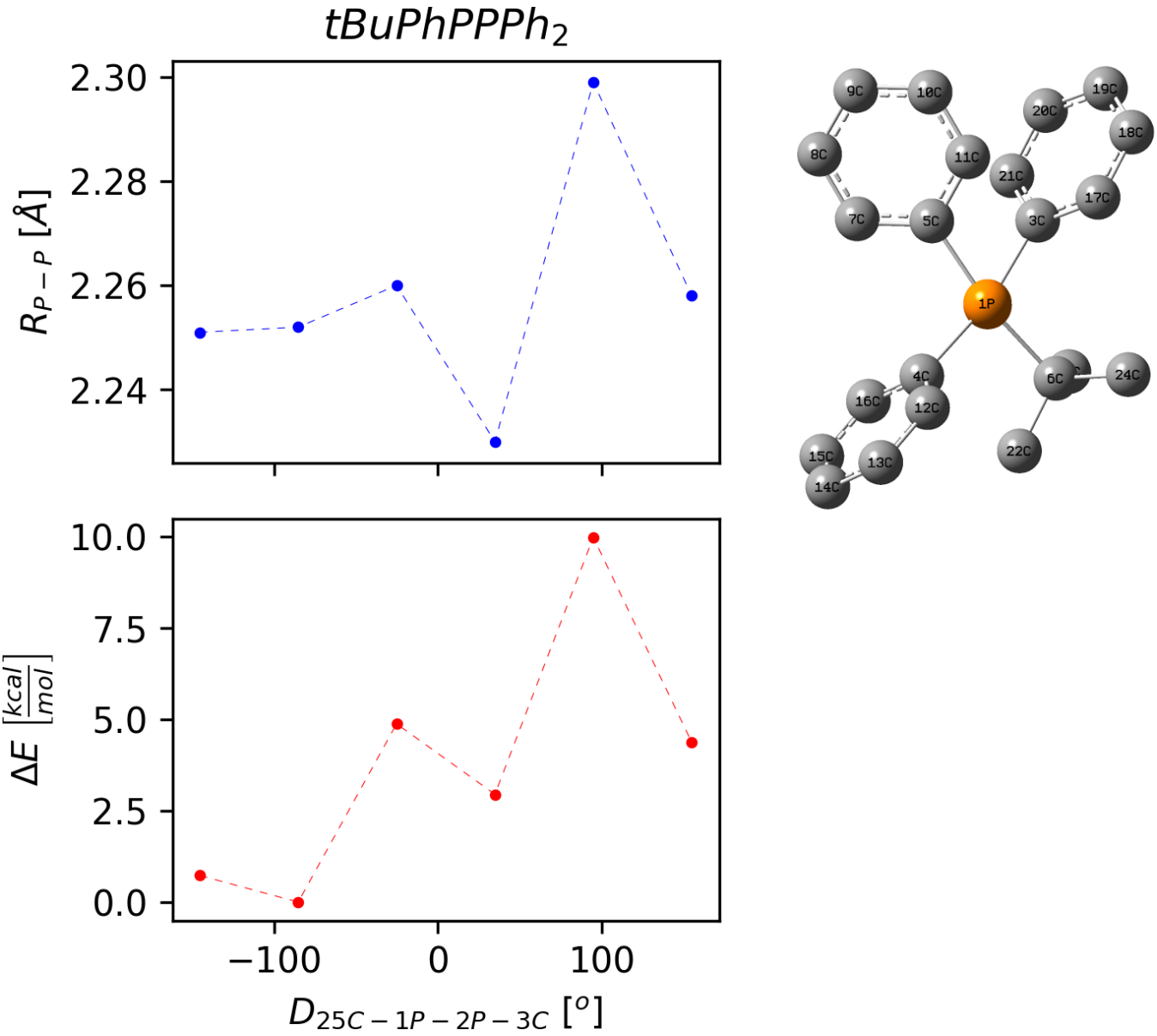


Fig. S210. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **6** (view along P-P bond)

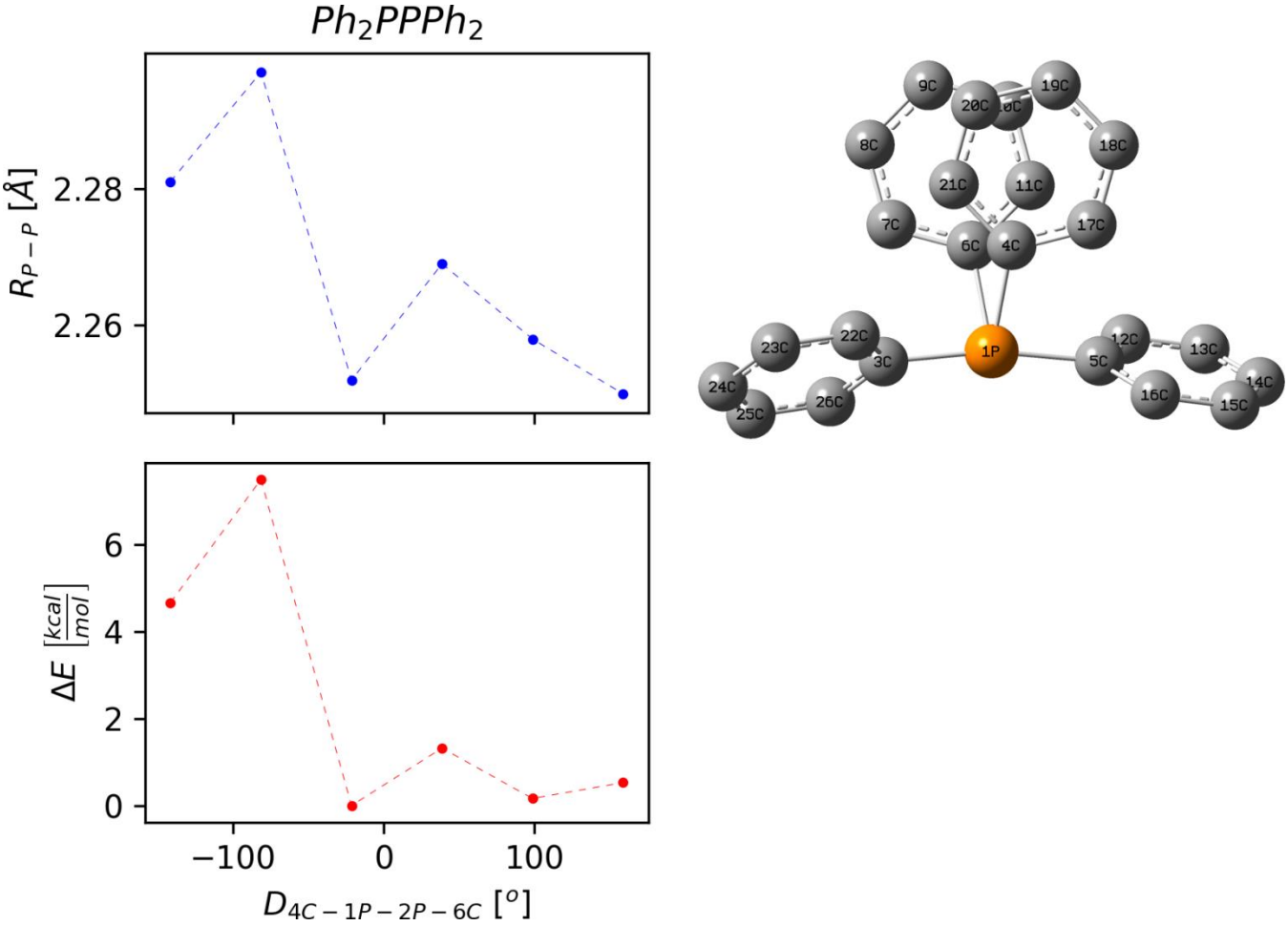


Fig. S211. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **7** (view along P-P bond)

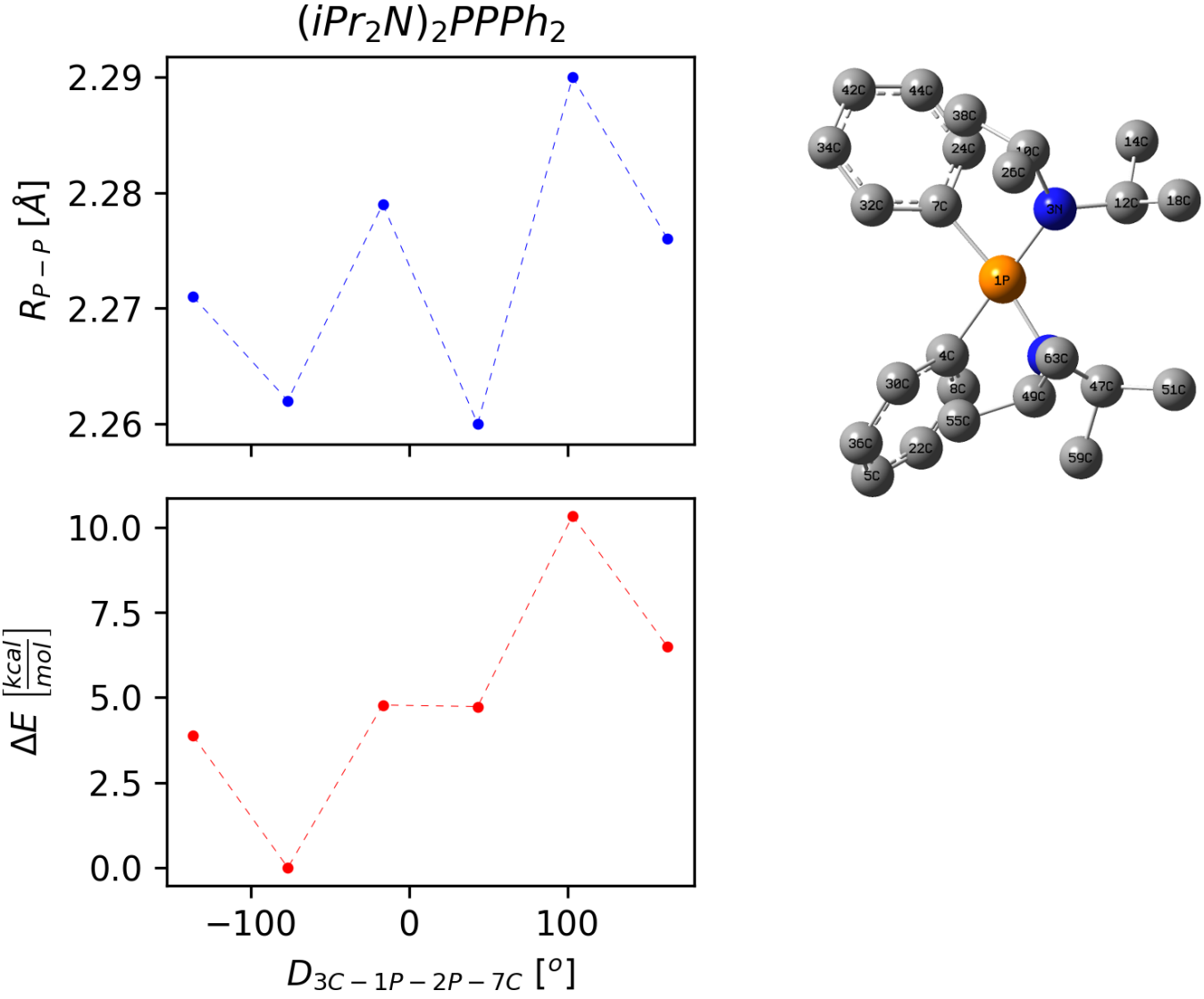


Fig. S212. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **8** (view along P-P bond)

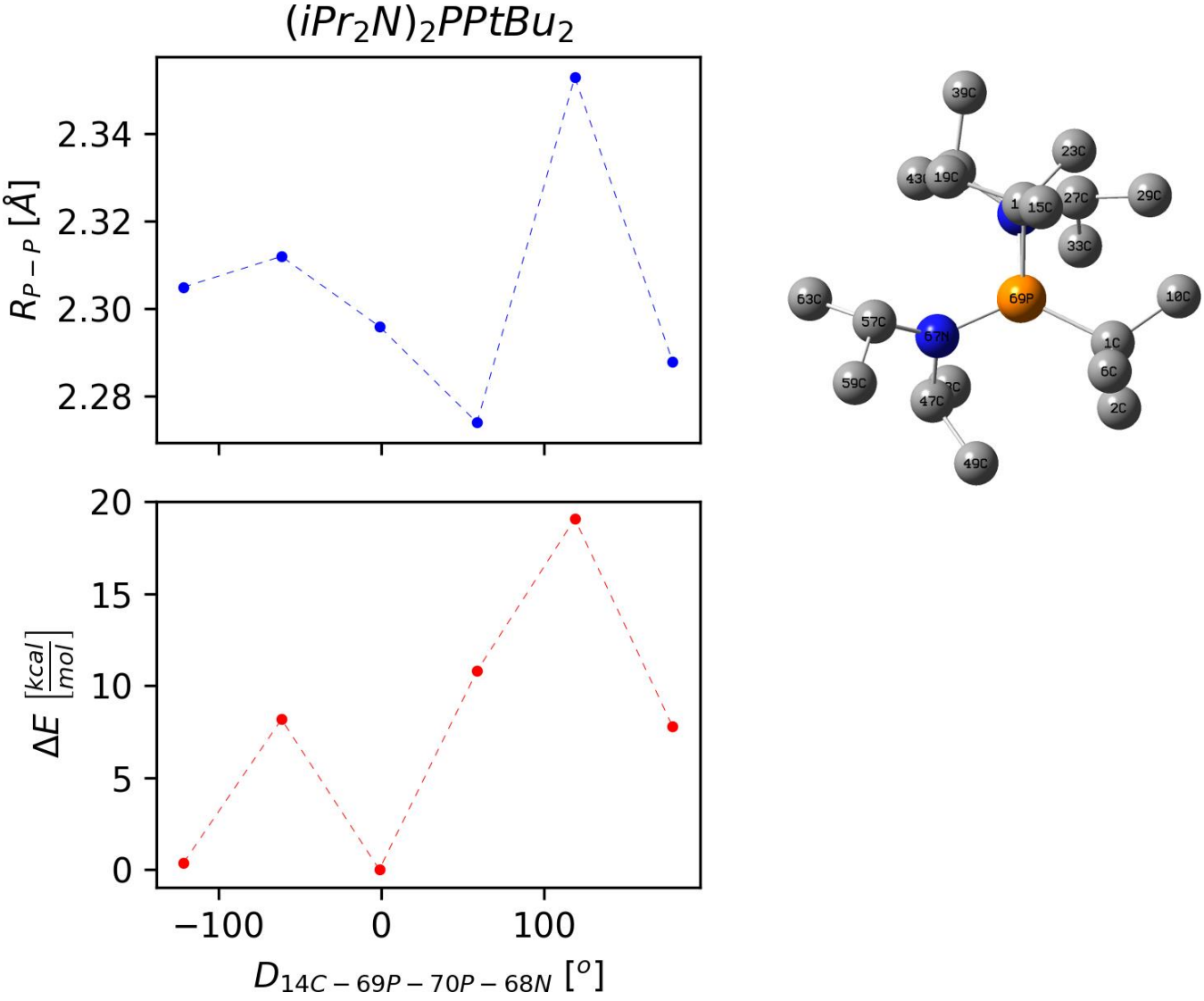


Fig. S213. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **9** (view along P-P bond)

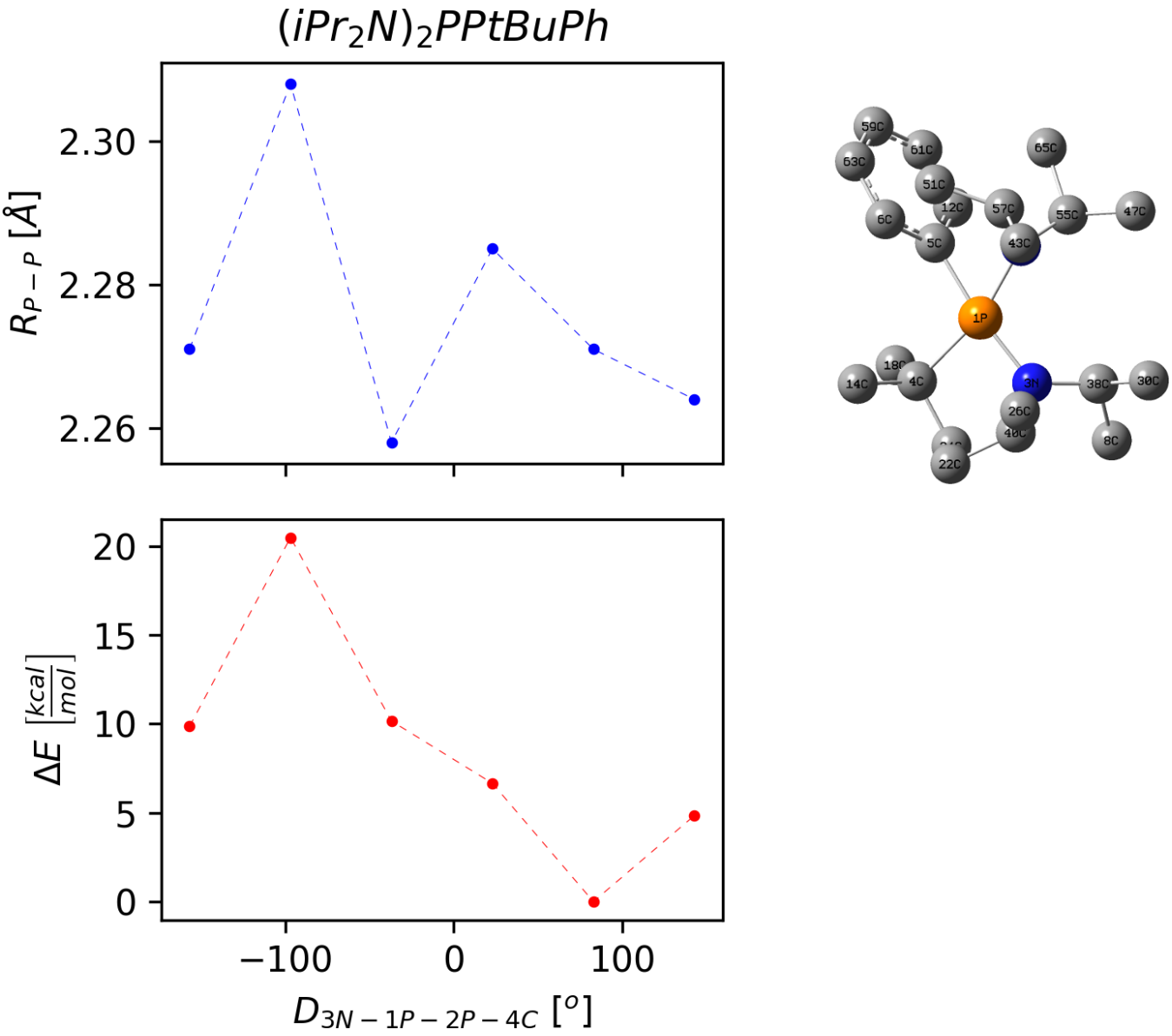


Fig. S214. Dependence of conformer relative energy (**ΔE**) and P-P bond length (**R_{P-P}**) on selected dihedral **D_n** (graph) with structure of diphosphane **10** (view along P-P bond)

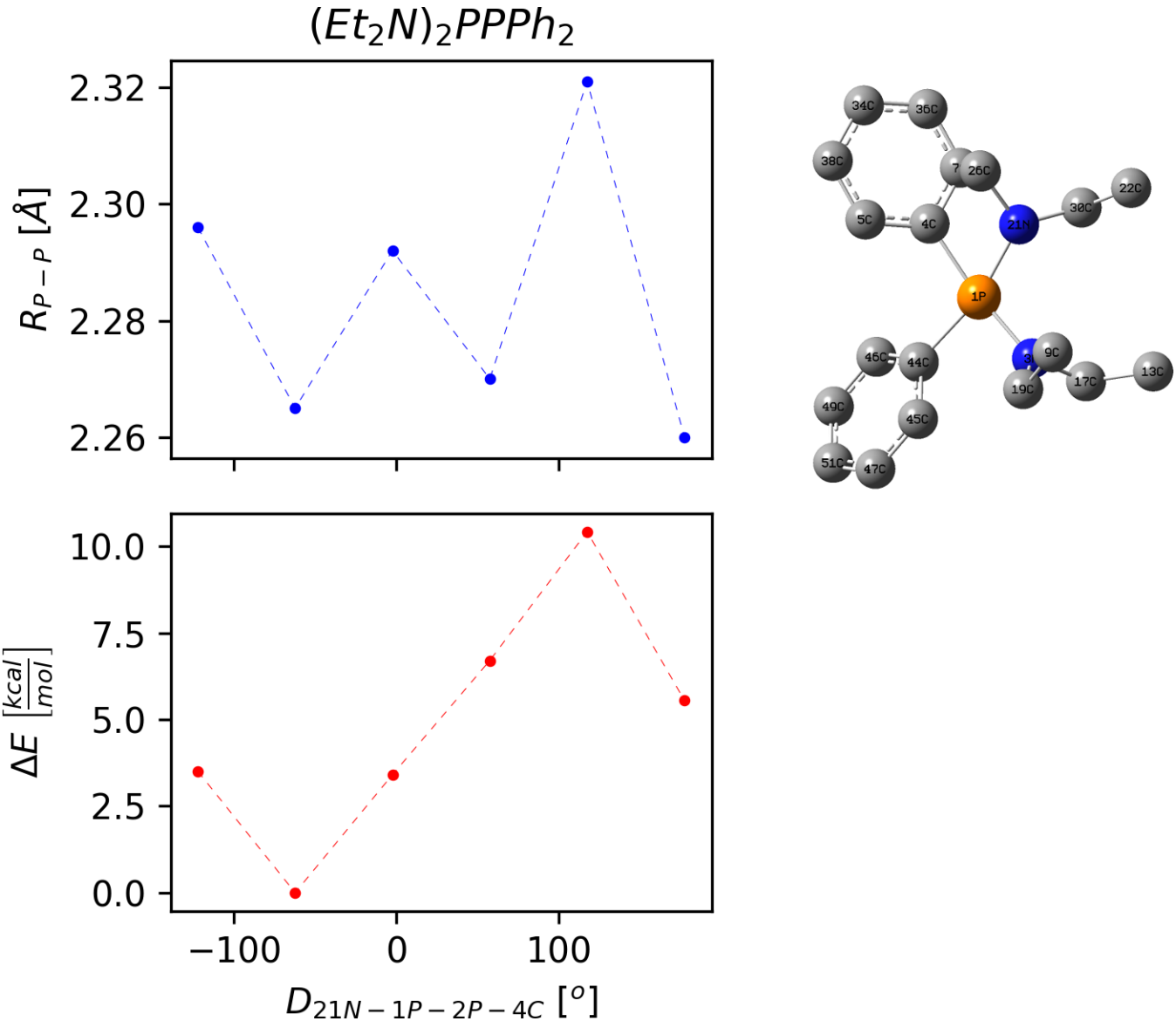


Fig. S215. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **11** (view along P-P bond)

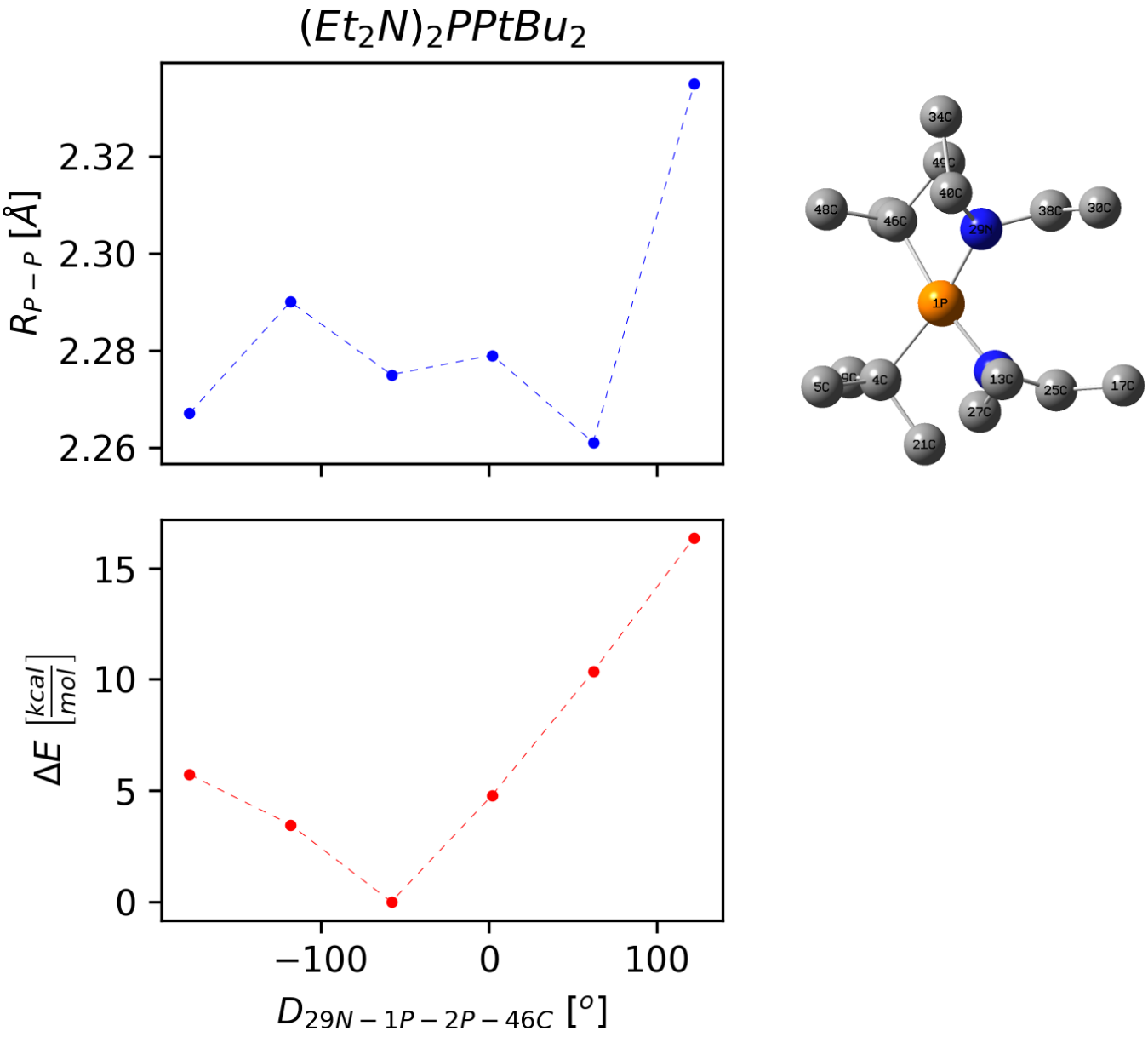


Fig. S216. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **12** (view along P-P bond)

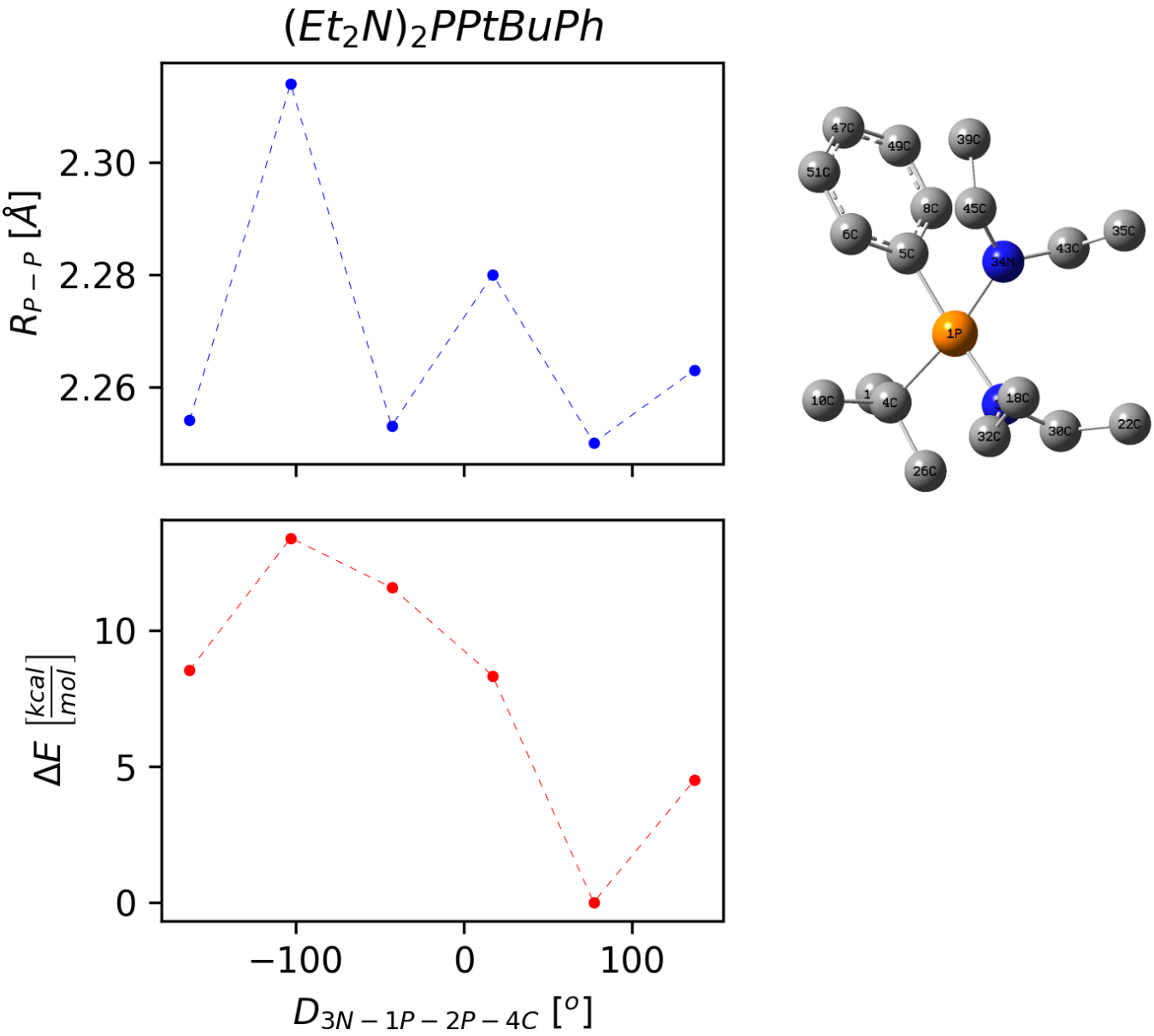


Fig. S217. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **13** (view along P-P bond)

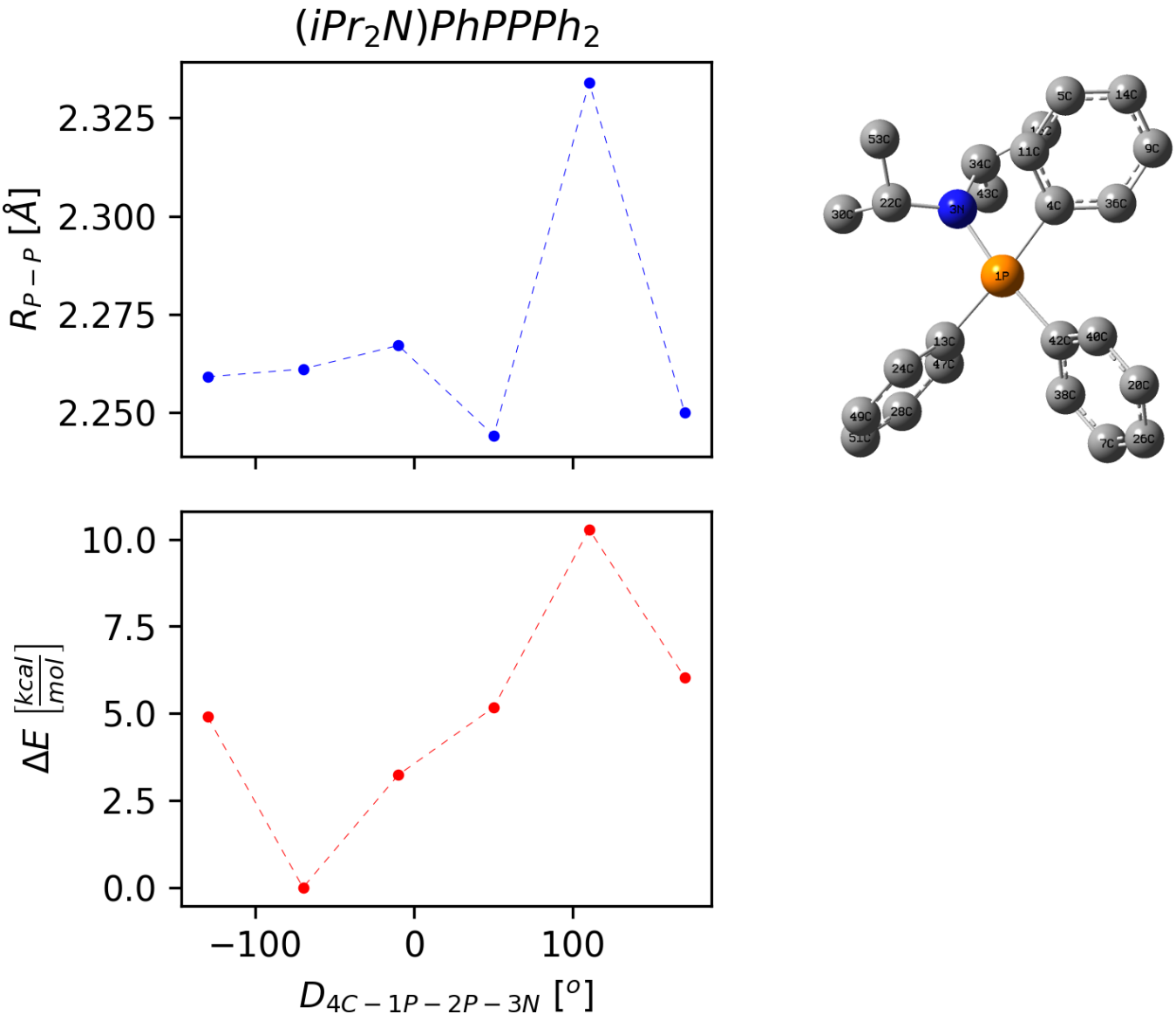


Fig. S218. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **14** (view along P-P bond)

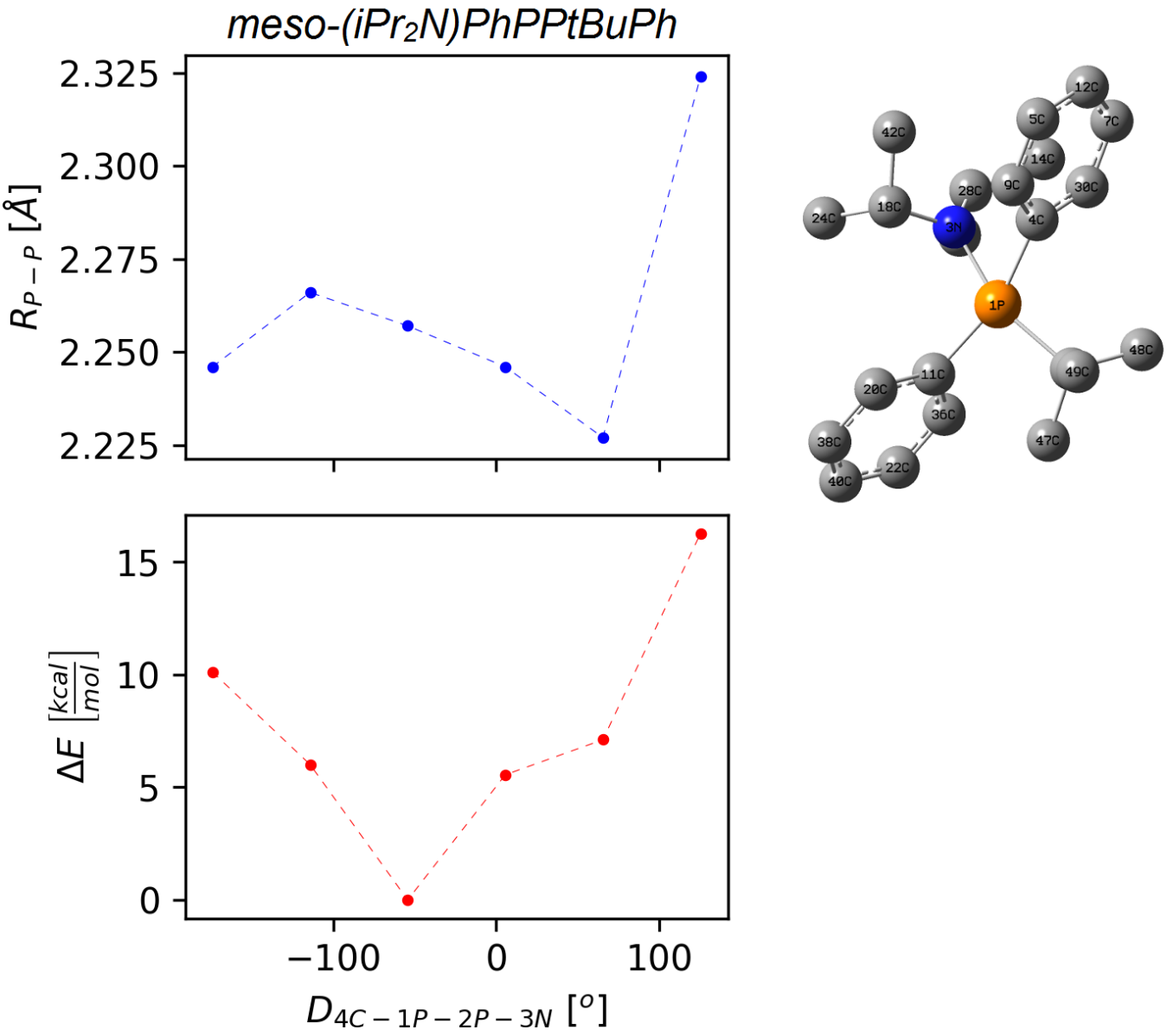


Fig. S219. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **15** (view along P-P bond)

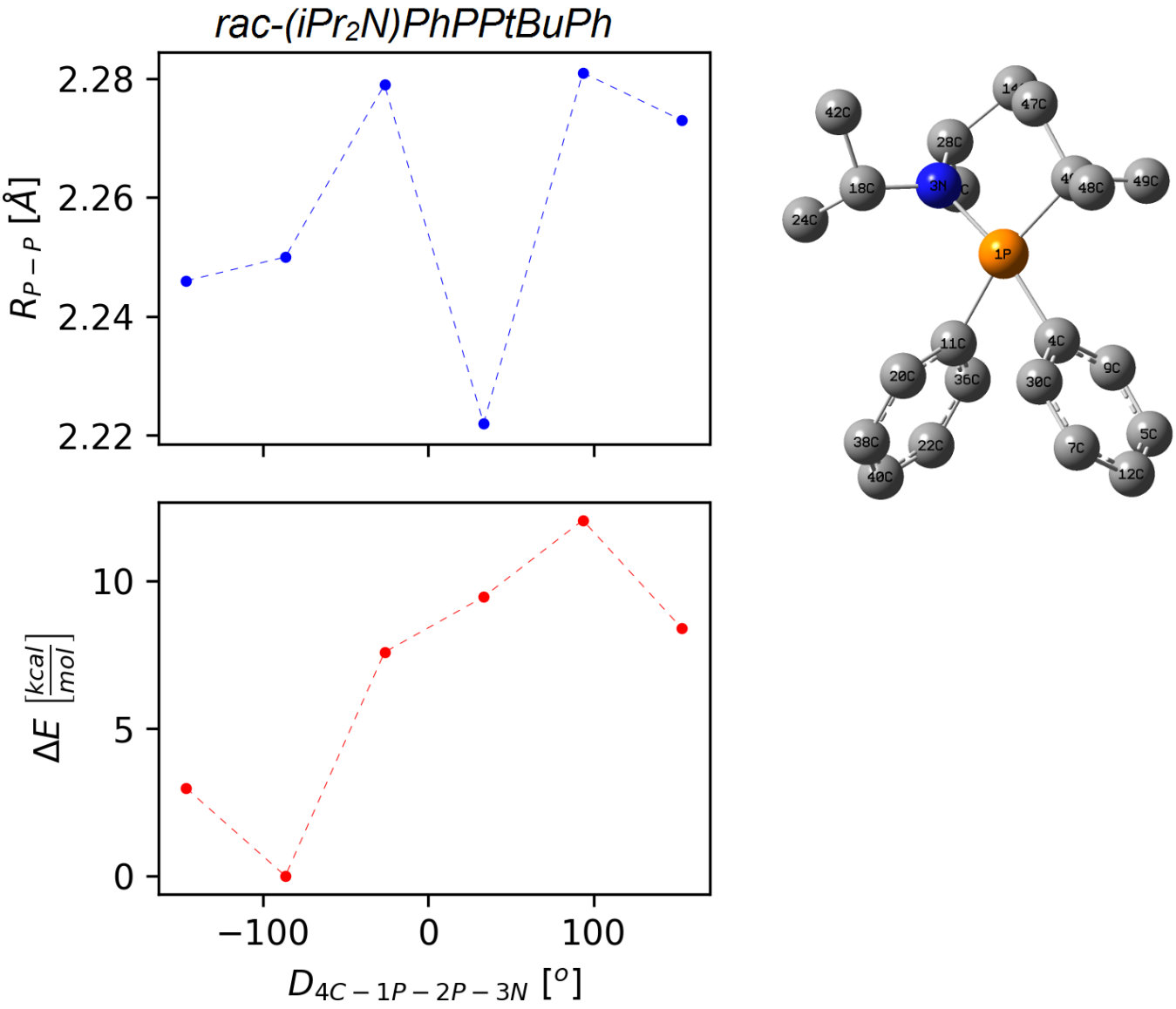


Fig. S220. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **16** (view along P-P bond)

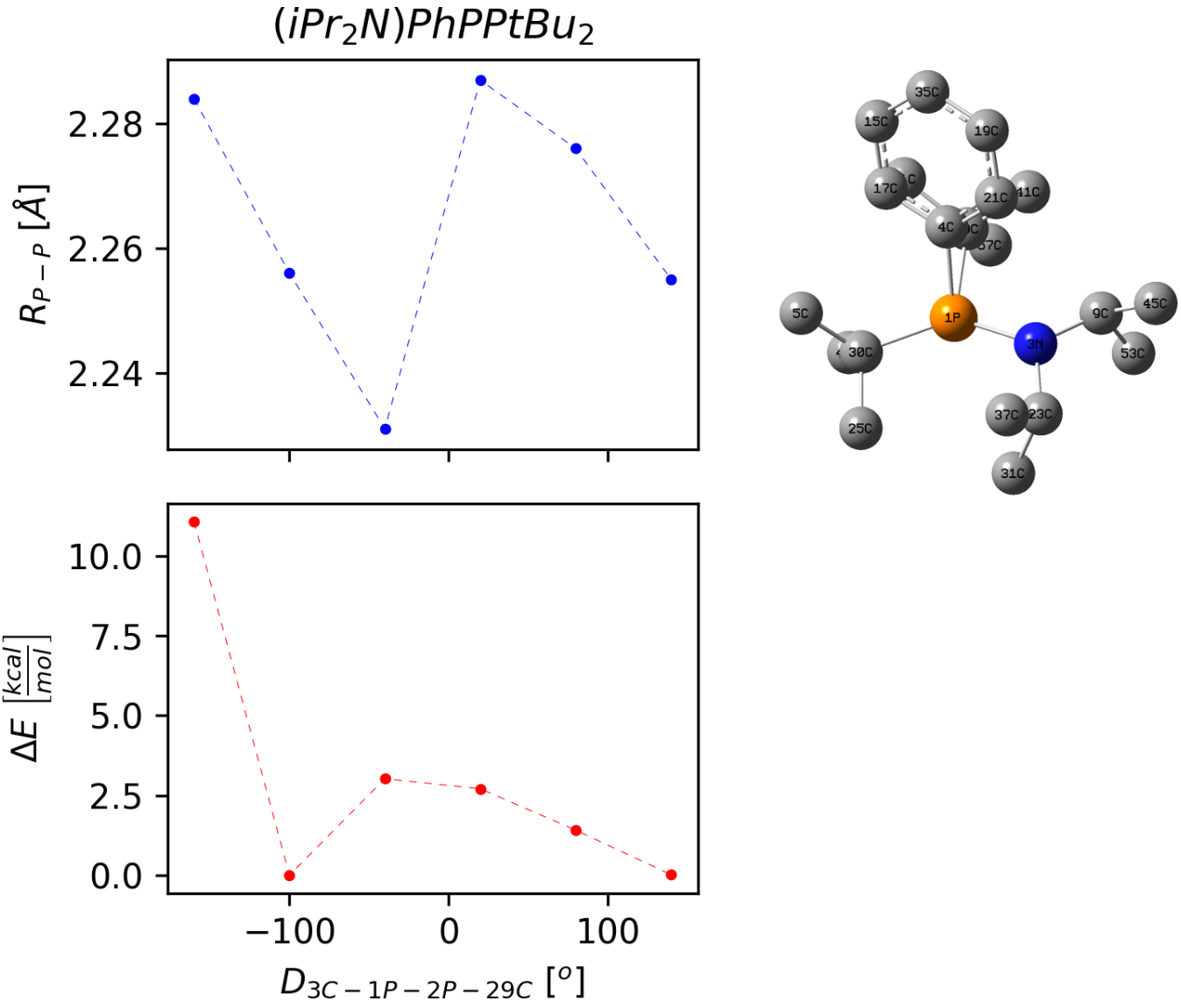


Fig. S221. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **17** (view along P-P bond)

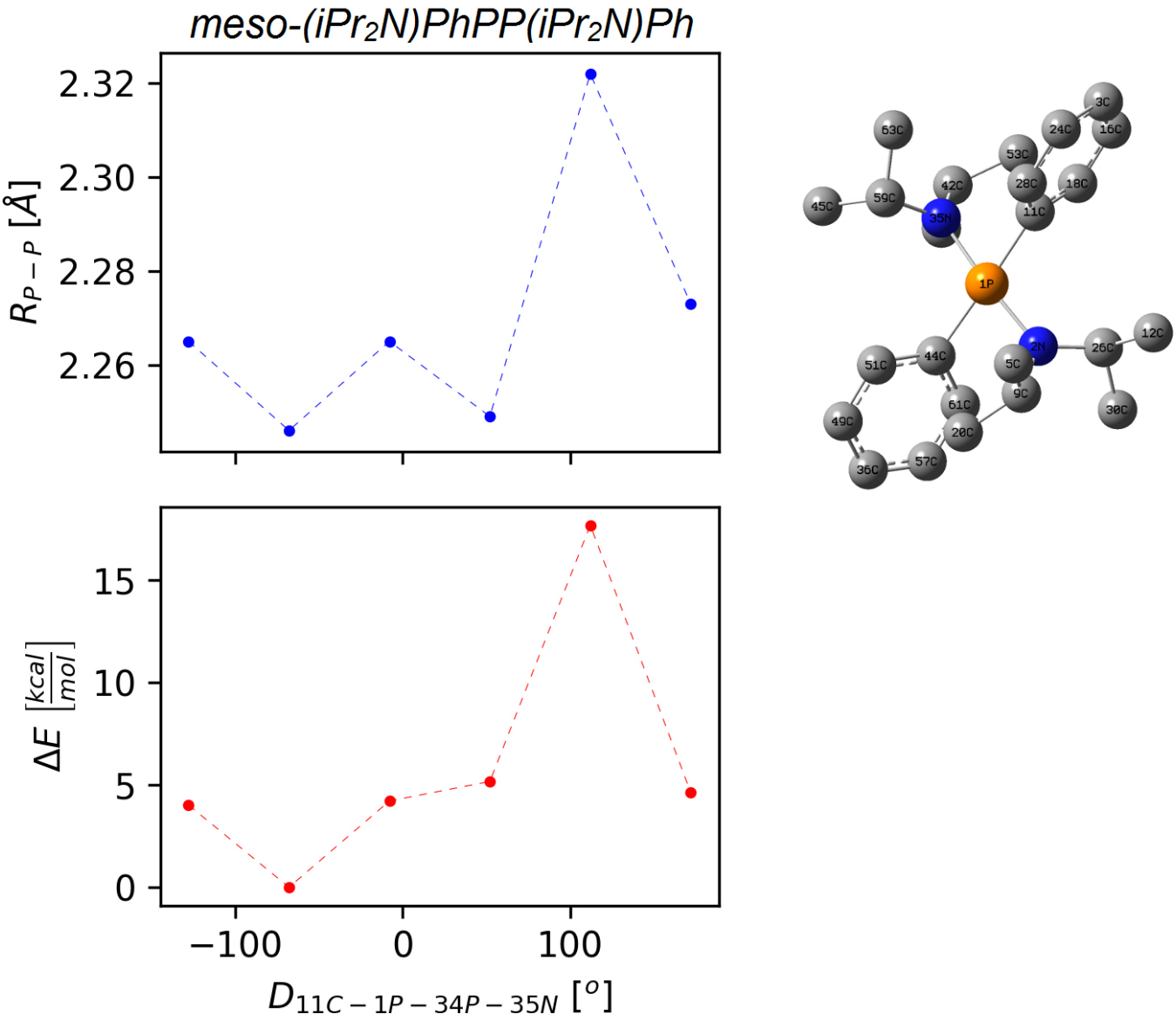


Fig. S222. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **18** (view along P-P bond)

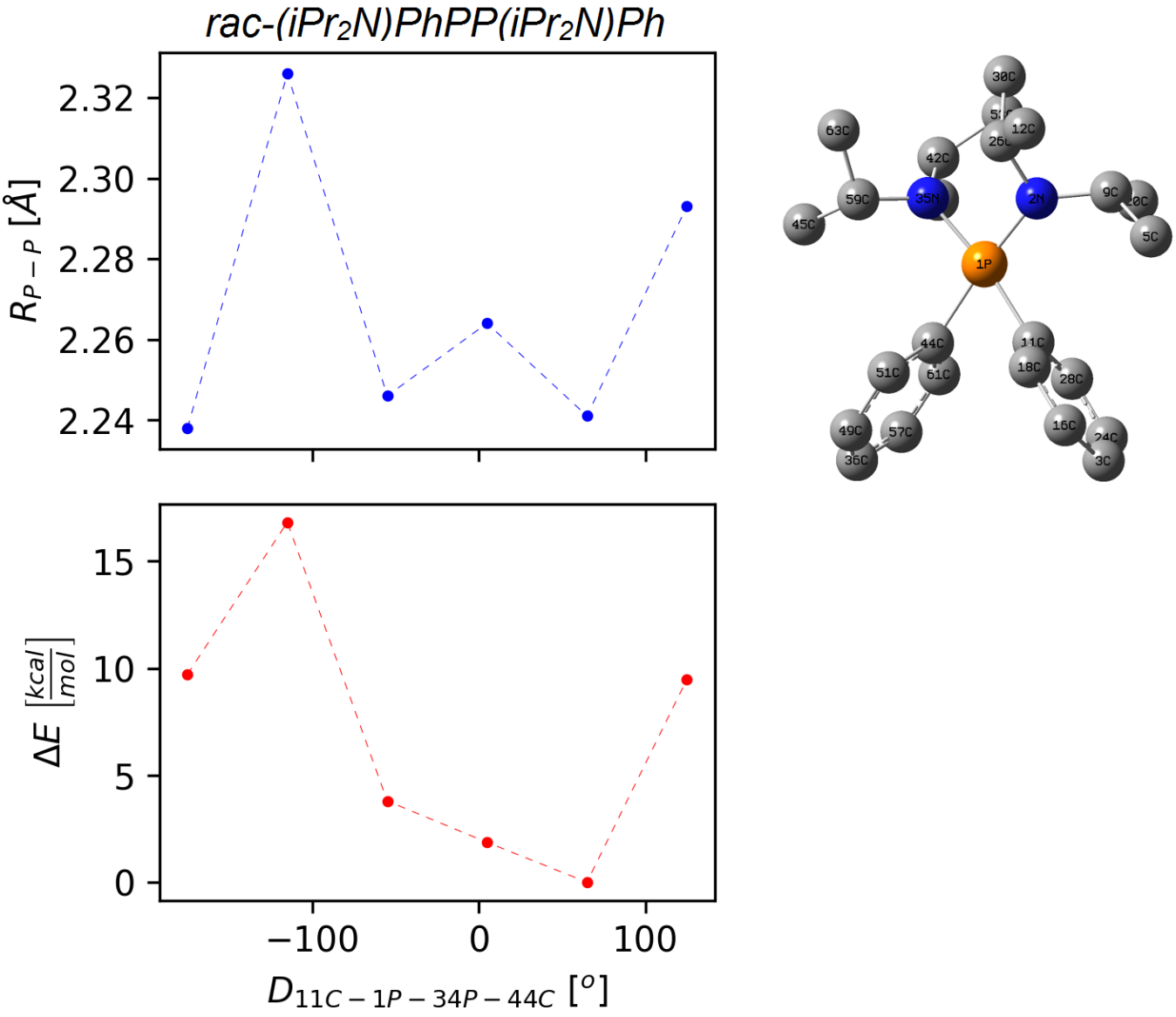


Fig. S223. Dependence of conformer relative energy (**ΔE**) and P-P bond length (**R_{P-P}**) on selected dihedral **D_n** (graph) with structure of diphosphane **20** (view along P-P bond)

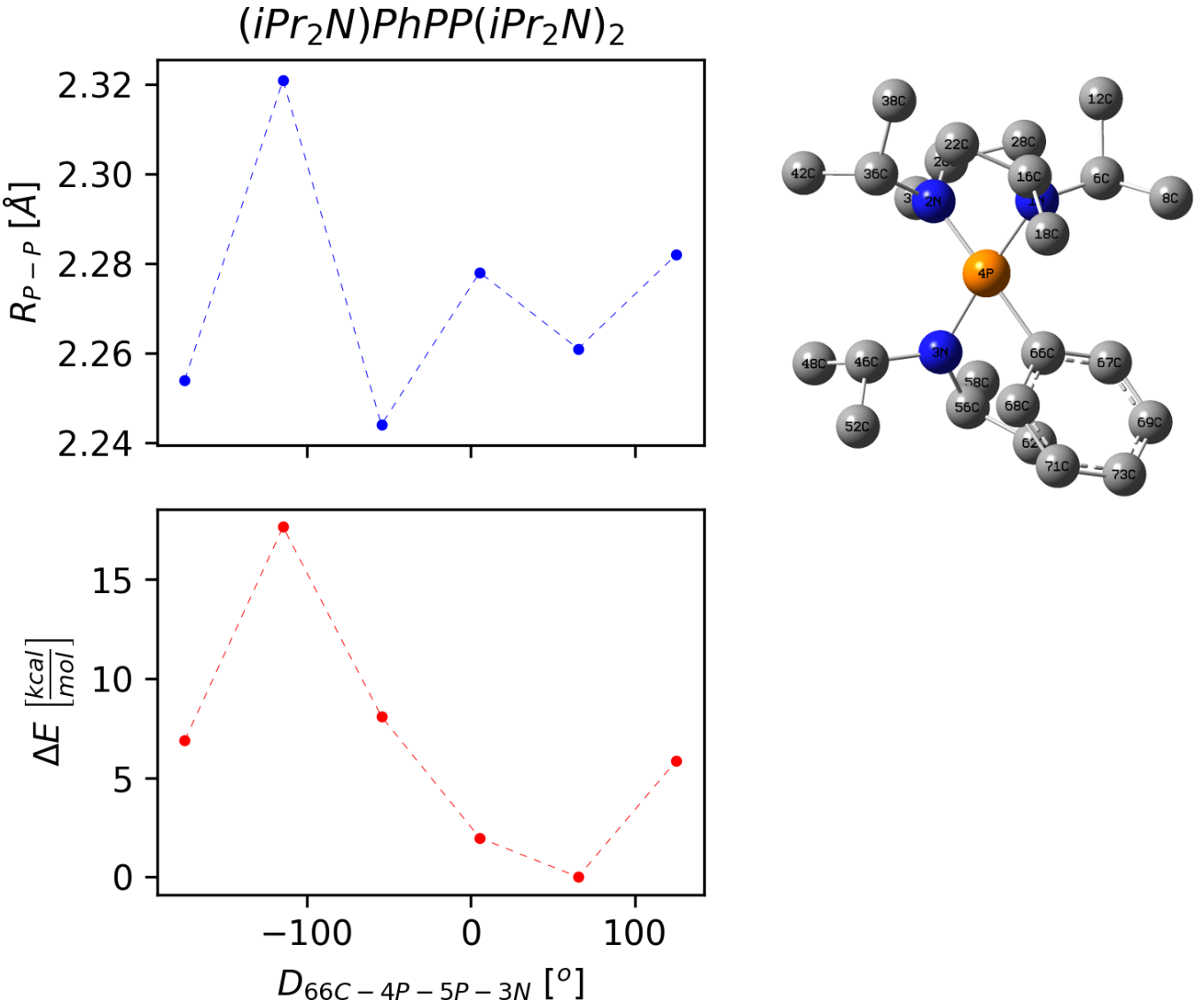


Fig. S224. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **20** (view along P-P bond)

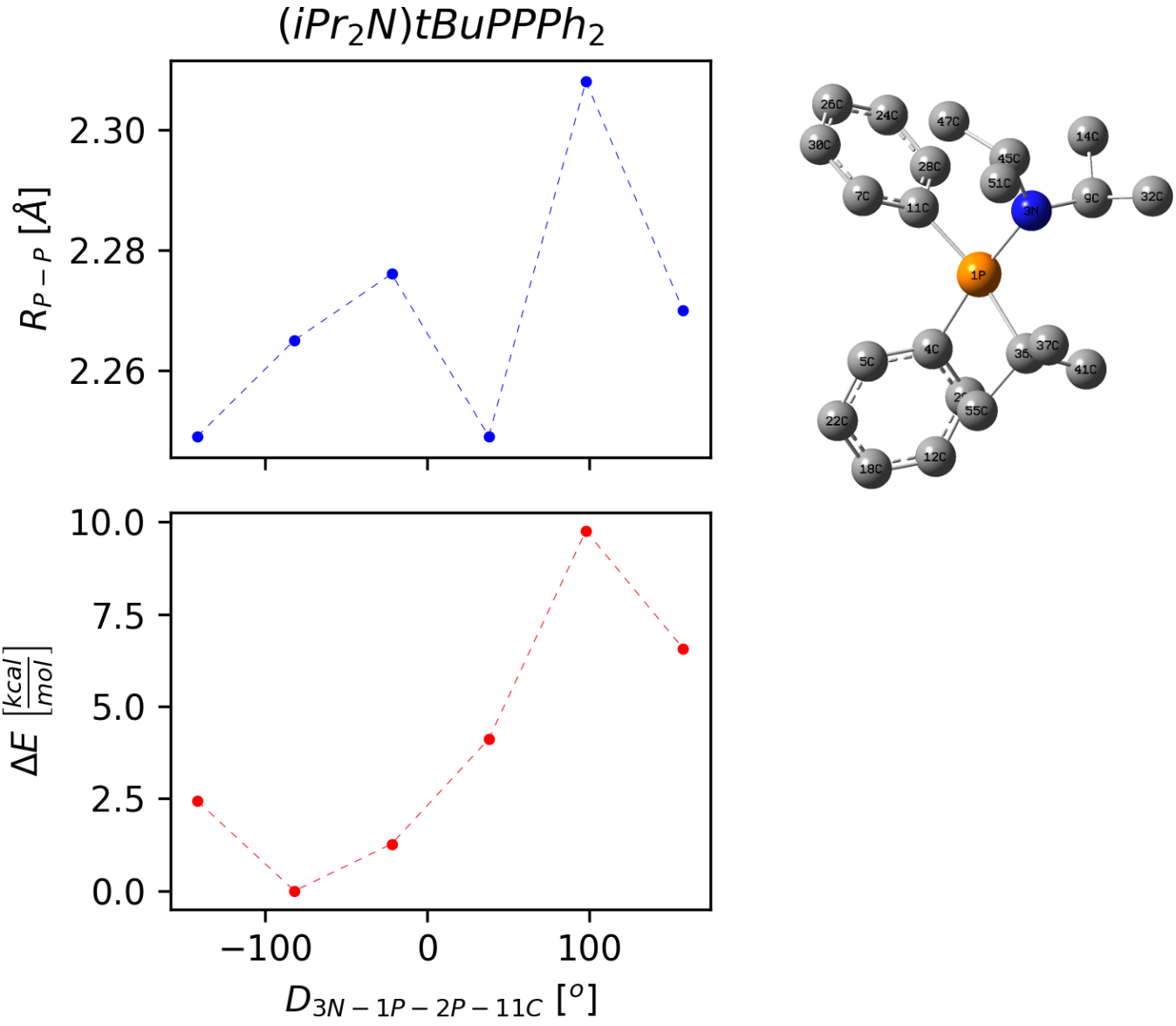


Fig. S225. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **21** (view along P-P bond)

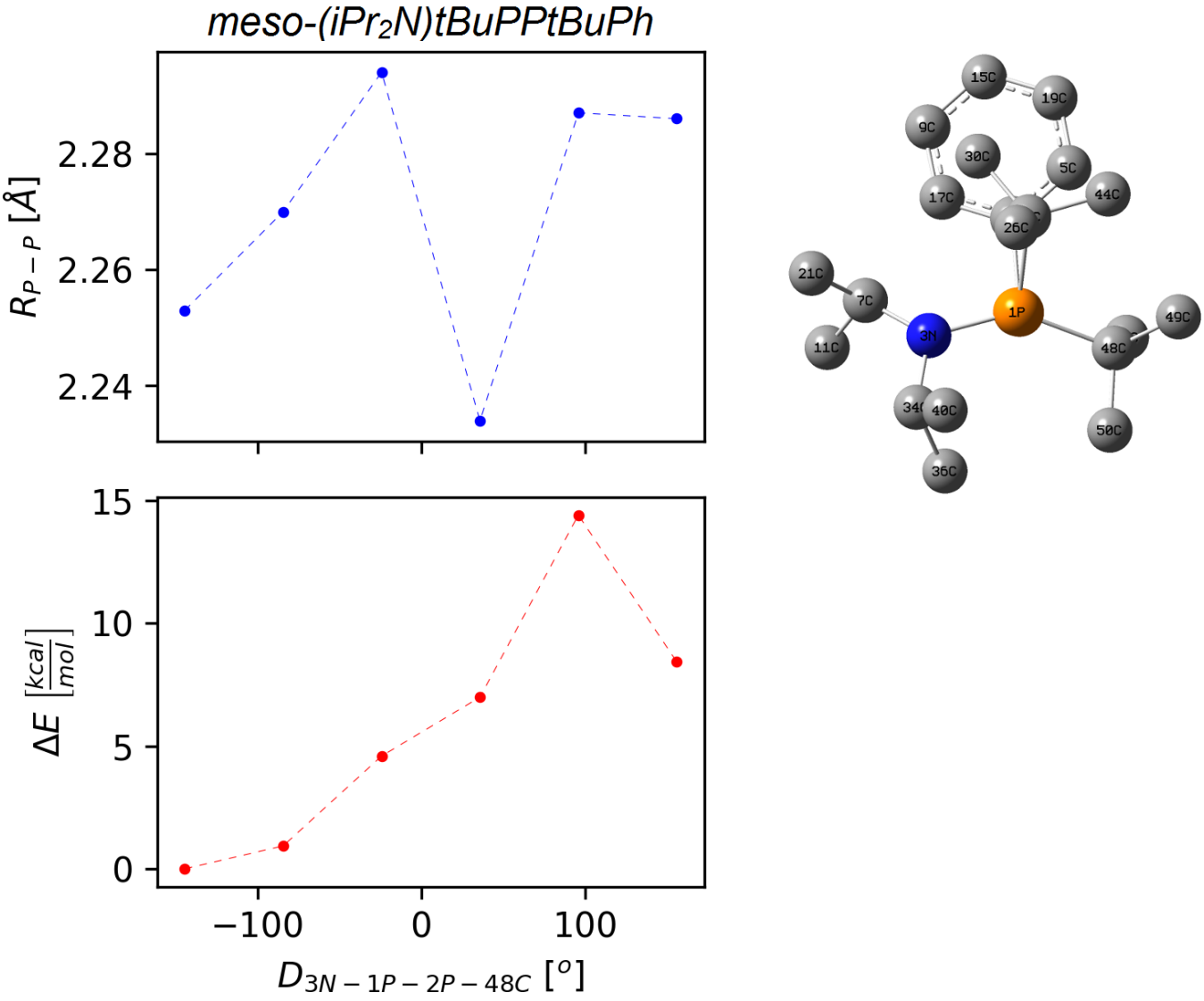


Fig. S226. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **22** (view along P-P bond)

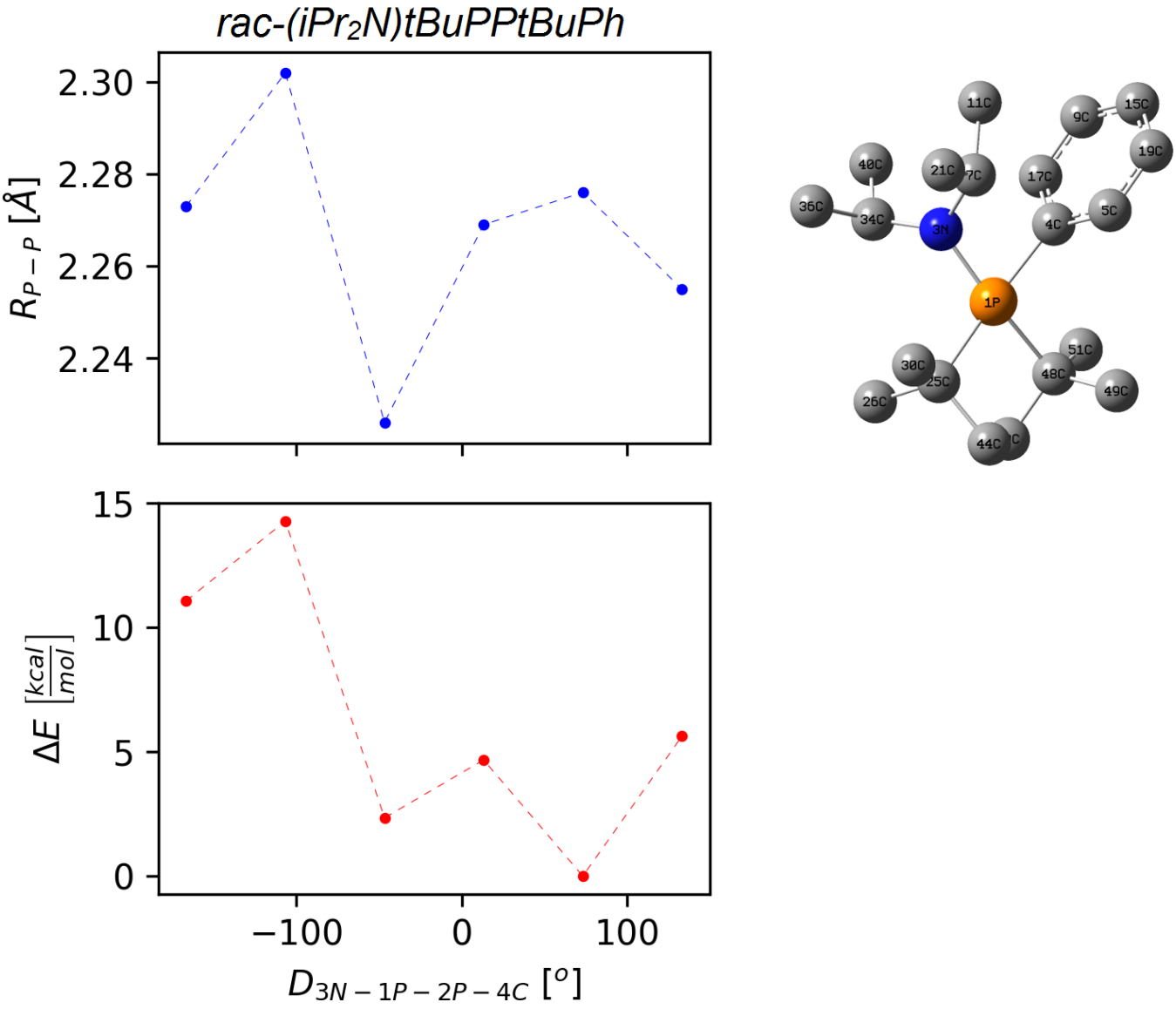


Fig. S227. Dependence of conformer relative energy (**ΔE**) and P-P bond length (**$R_{P\text{-}P}$**) on selected dihedral **D_n** (graph) with structure of diphosphane **23** (view along P-P bond)

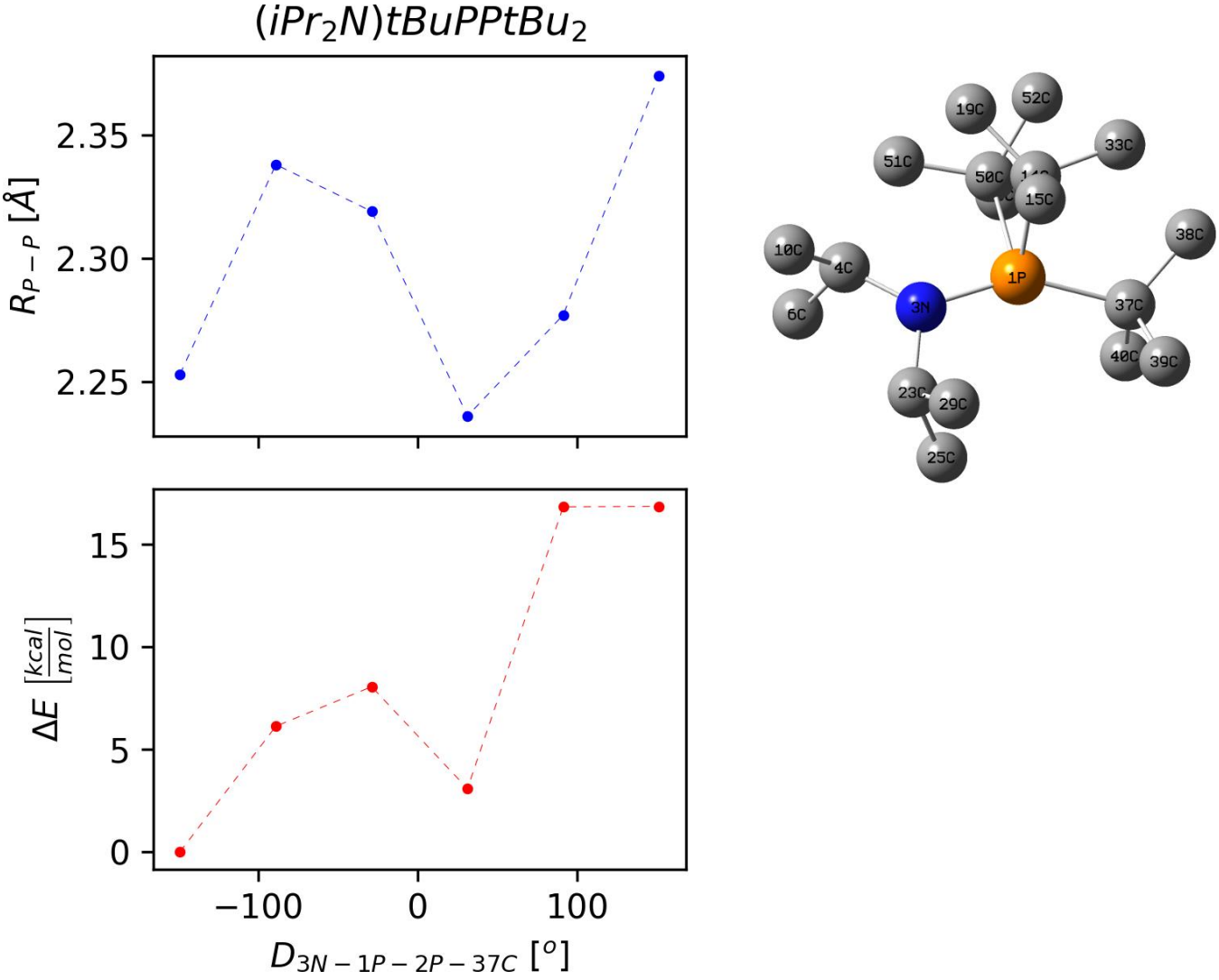


Fig. S228. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **24** (view along P-P bond)

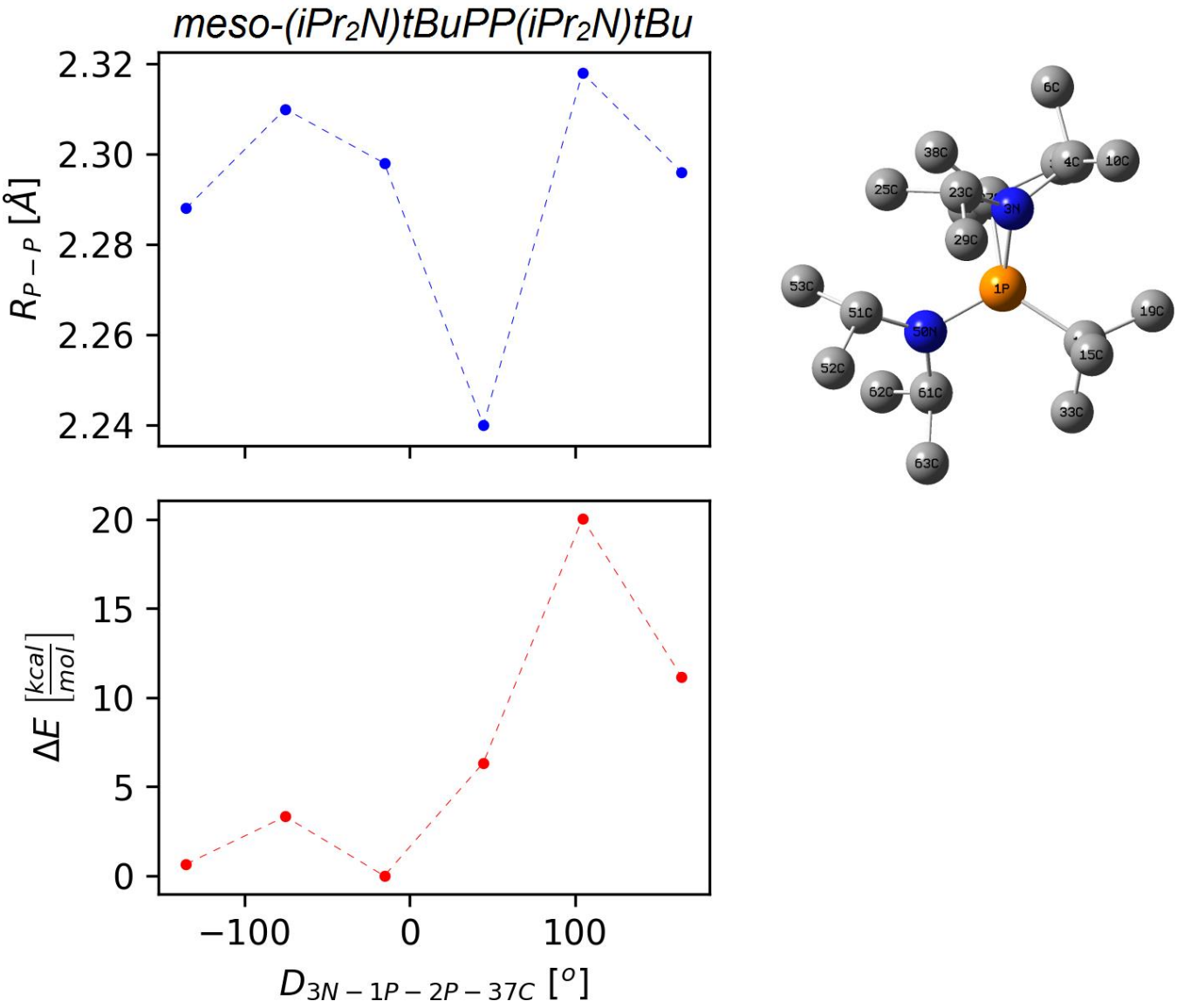


Fig. S229. Dependence of conformer relative energy (**ΔE**) and P-P bond length (**$R_{P\text{-}P}$**) on selected dihedral **D_n** (graph) with structure of diphosphane **25** (view along P-P bond)

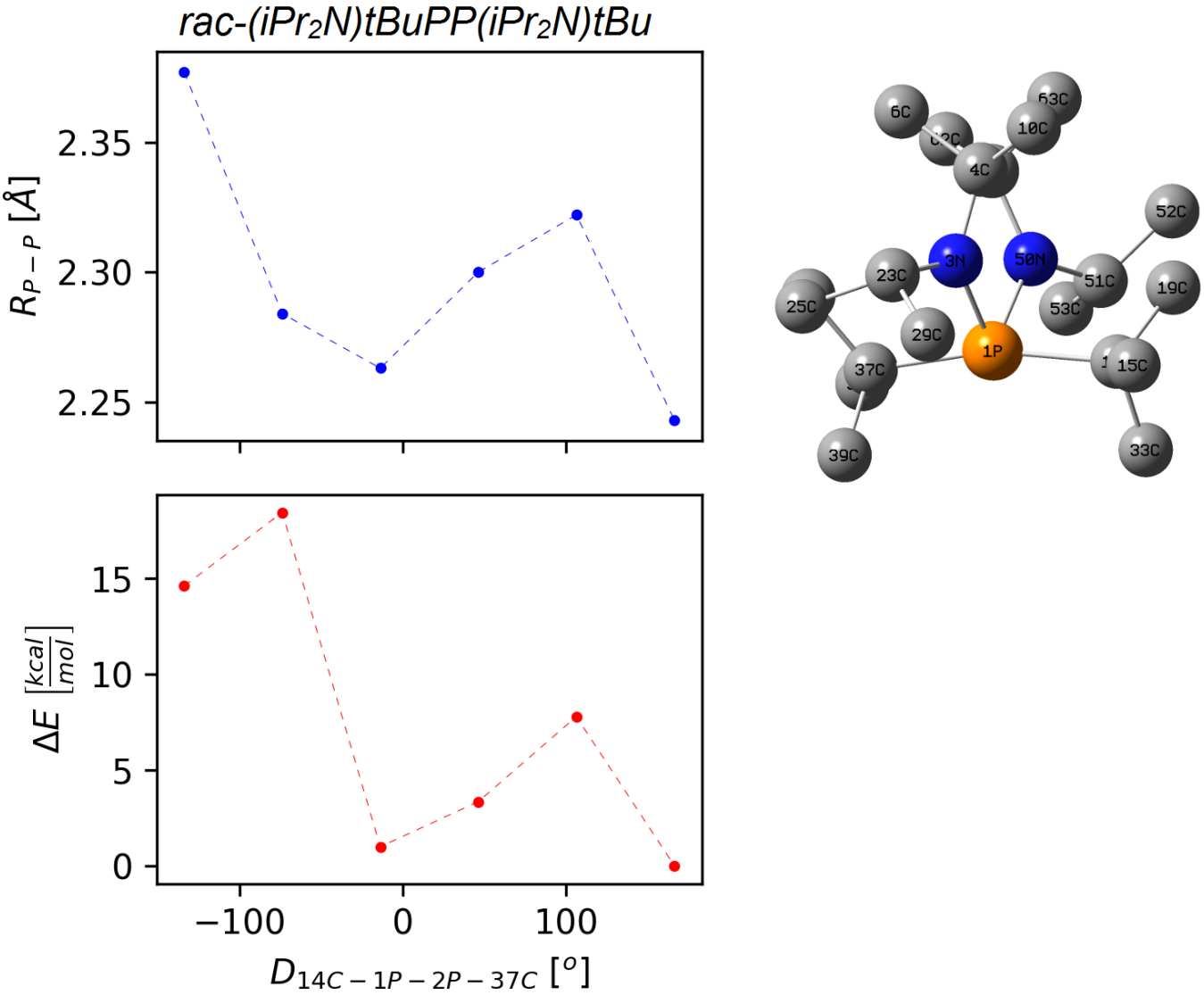


Fig. S230. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **26** (view along P-P bond)

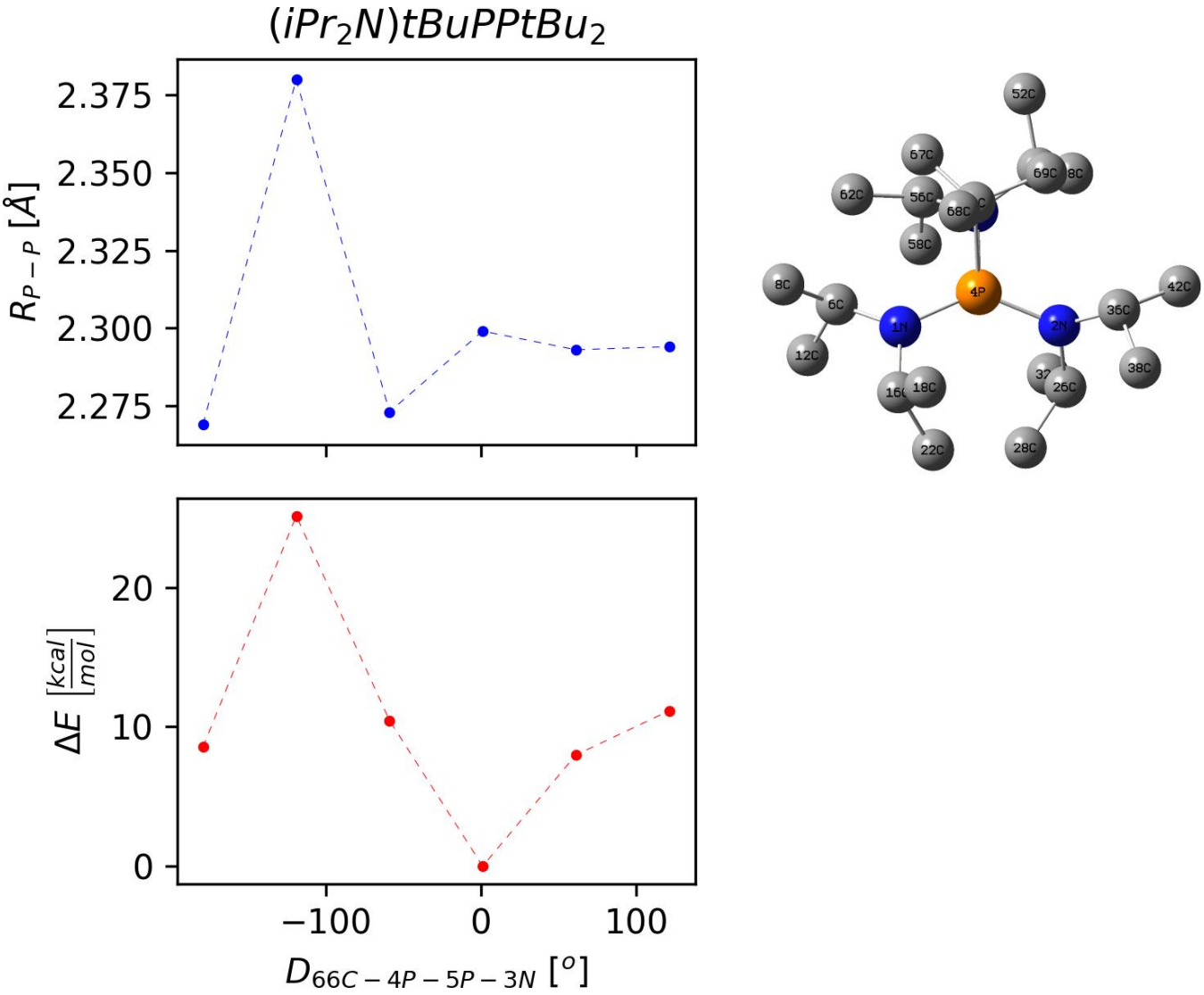


Fig. S231. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **27** (view along P-P bond)

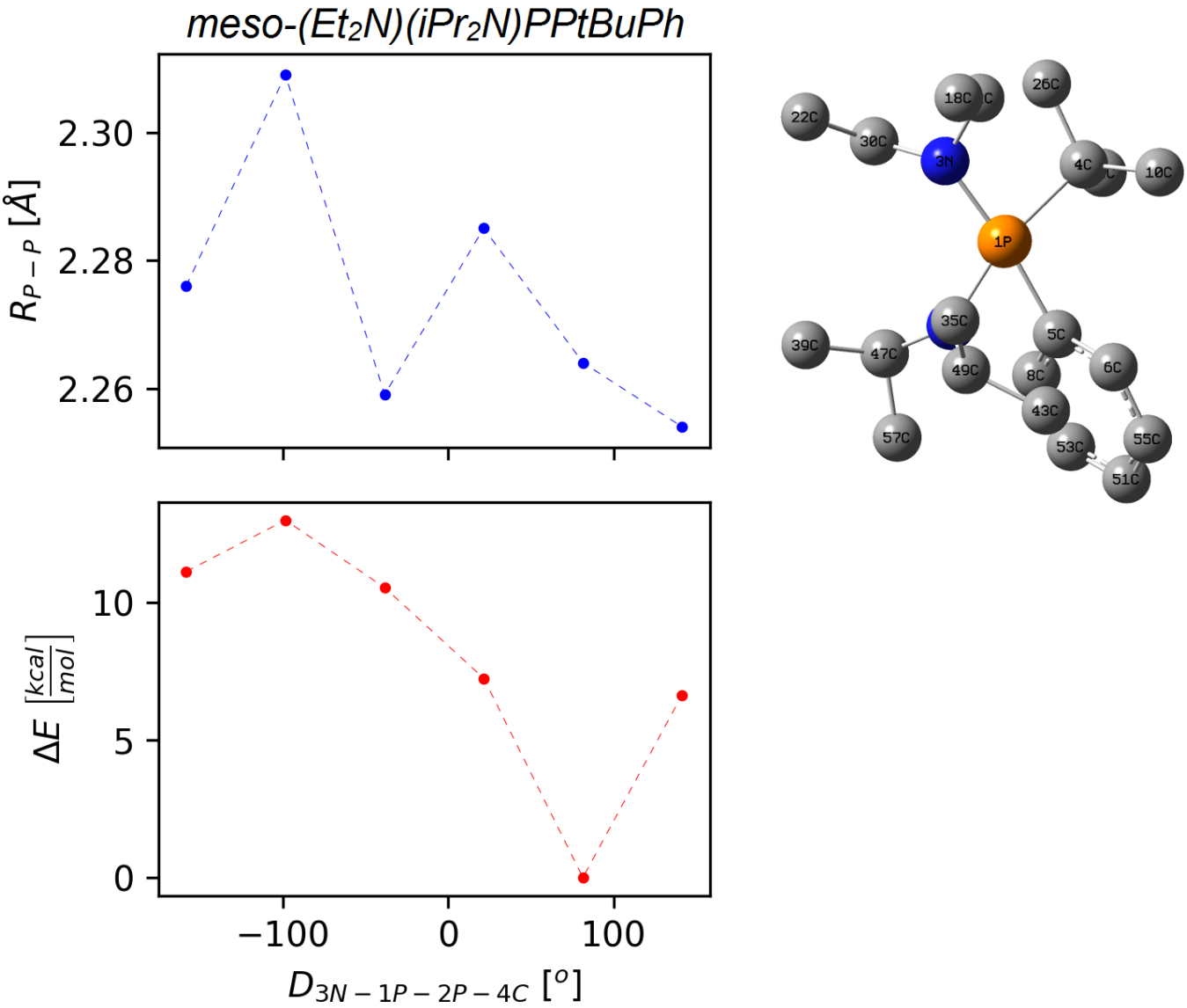


Fig. S232. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **28** (view along P-P bond)

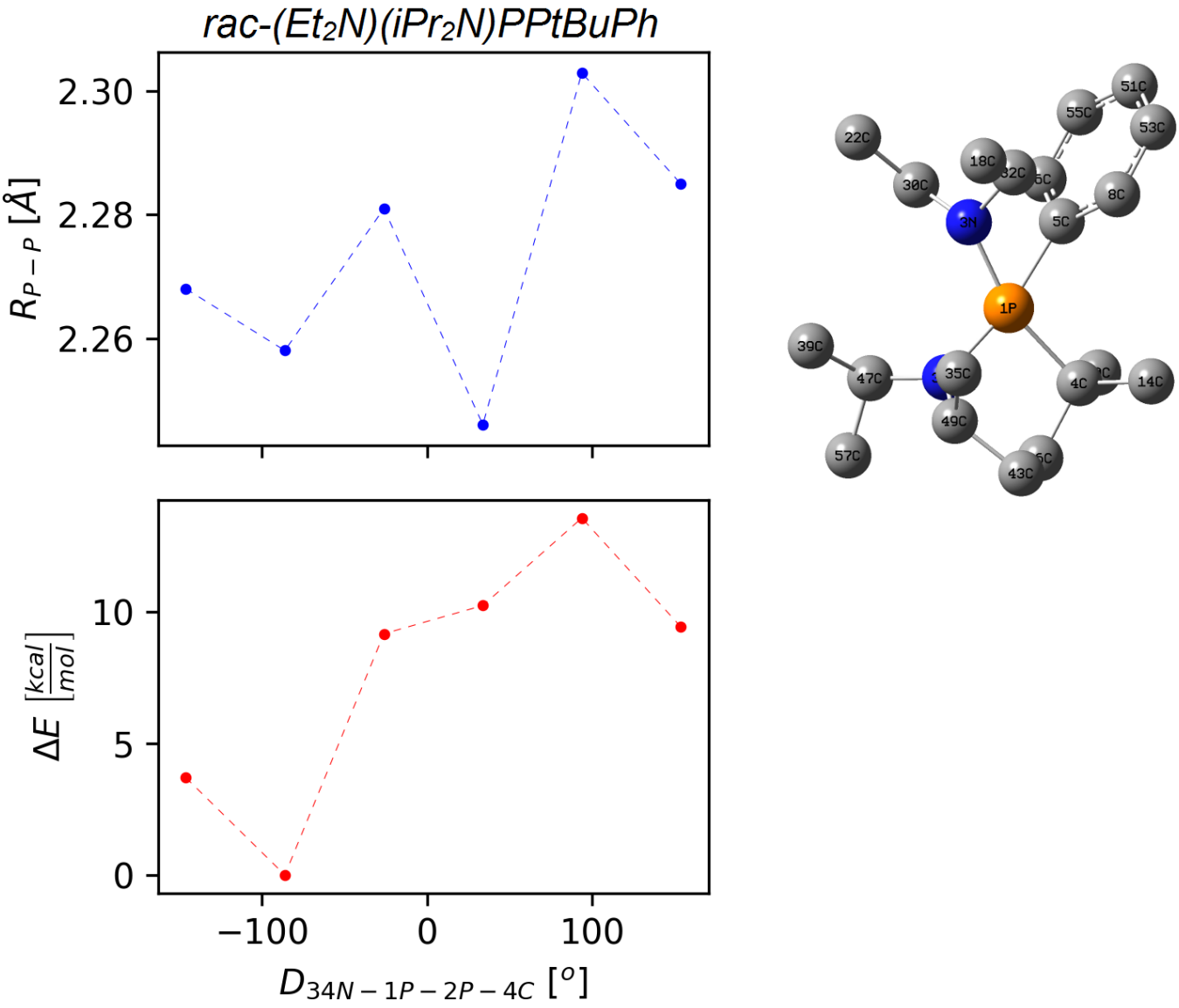


Fig. S233. Dependence of conformer relative energy (**ΔE**) and P-P bond length (**R_{P-P}**) on selected dihedral **D_n** (graph) with structure of diphosphane **29** (view along P-P bond)

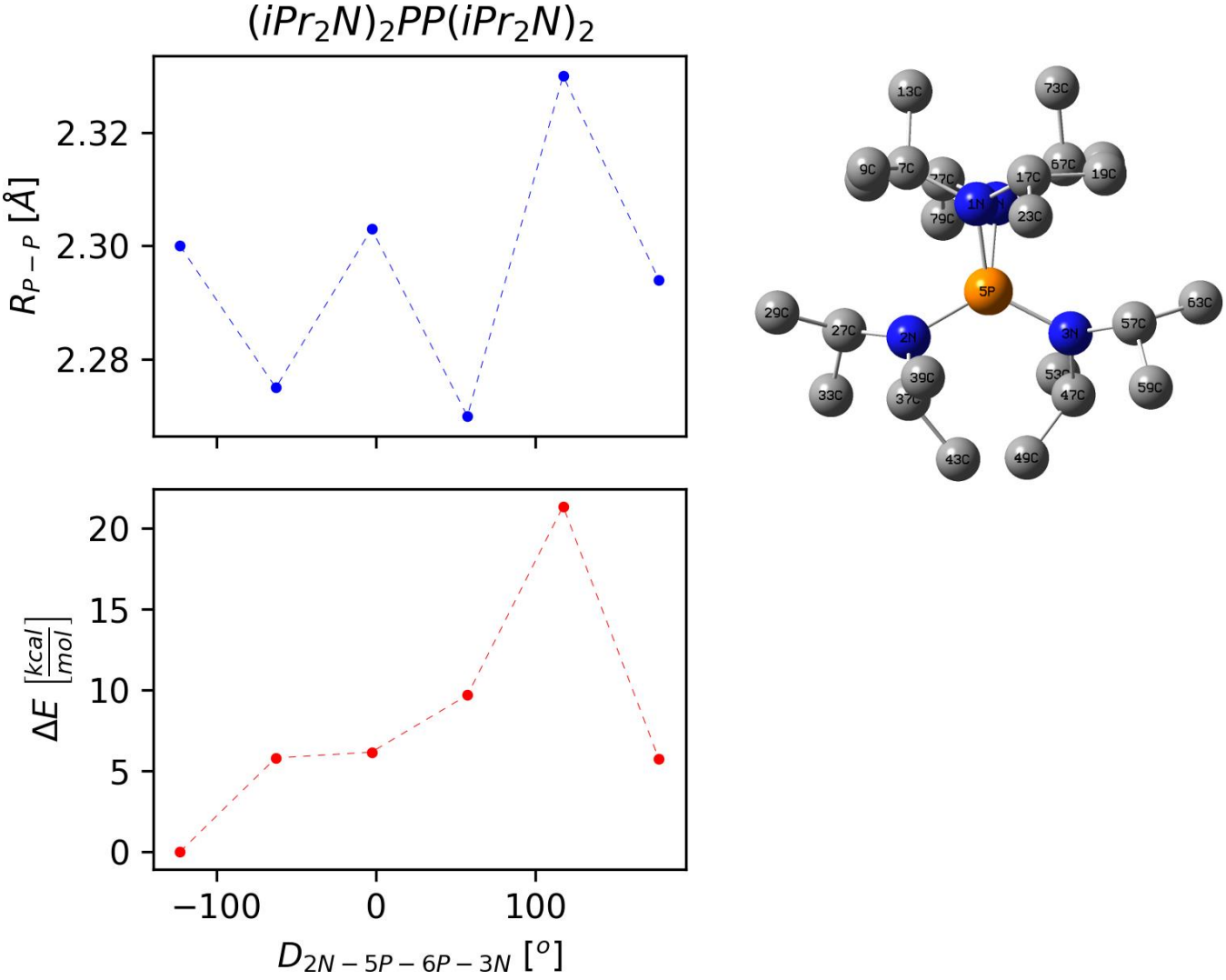


Fig. S234. Dependence of conformer relative energy (**ΔE**) and P-P bond length ($\mathbf{R_{P\text{-}P}}$) on selected dihedral $\mathbf{D_n}$ (graph) with structure of diphosphane **30** (view along P-P bond)

Hirshfeld atomic charges and output coordinates of diphoshanes 1-30

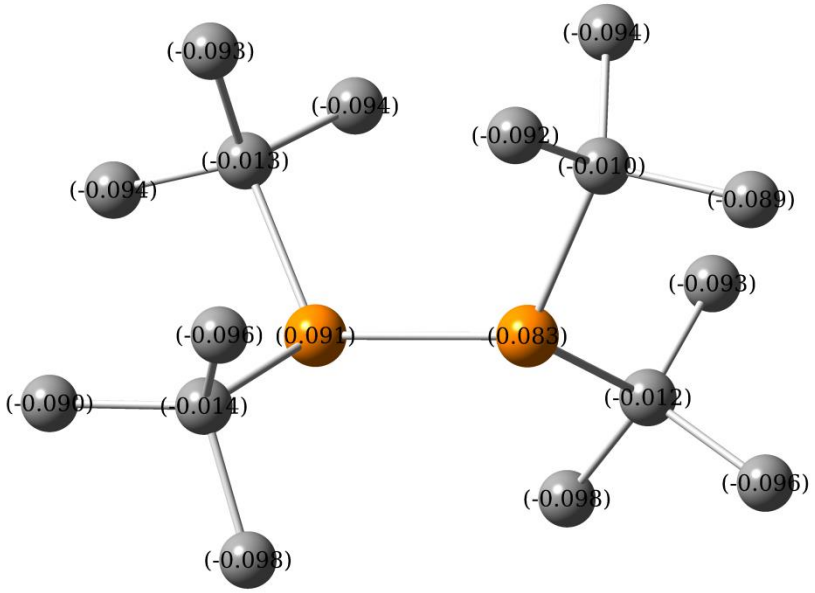


Fig. S235. Hirshfeld atomic charges of diphosphane **1**

P	0.973580	-0.463531	0.468347
P	-1.047167	-0.501300	-0.486485
C	1.681034	1.200125	1.147470
C	2.143901	-1.130108	-0.917377
C	-1.706209	1.140735	-1.210539
C	-2.137043	-1.096423	0.978372
C	1.376723	-2.142755	-1.782396
C	2.777327	-0.087725	-1.844965
C	3.258432	-1.917440	-0.198906
C	0.839040	1.561551	2.380467
C	3.106054	0.900445	1.649017
C	1.744266	2.432303	0.236043
C	-1.722707	-2.563017	1.199166
C	-2.004662	-0.345962	2.306119
C	-3.611457	-1.087288	0.548152
C	-2.047707	2.245806	-0.208591
C	-0.636515	1.611620	-2.208027
C	-2.959761	0.820553	-2.050086
H	2.102988	-2.699466	-2.398928
H	0.820164	-2.870780	-1.172437
H	0.654842	-1.656253	-2.450867
H	3.376125	-0.601671	-2.617019
H	3.458091	0.589967	-1.310848

H	2.018828	0.516073	-2.362896
H	2.834662	-2.713488	0.431441
H	3.915081	-2.389244	-0.950034
H	3.891079	-1.285115	0.436558
H	1.245095	2.478732	2.839979
H	-0.211975	1.753367	2.127082
H	0.867159	0.764113	3.137738
H	3.450546	1.744446	2.270548
H	3.824726	0.791344	0.824986
H	3.140948	-0.009334	2.267586
H	0.747221	2.825472	0.004387
H	2.291267	3.235850	0.759751
H	2.267842	2.241637	-0.708462
H	-2.320116	-2.993792	2.020947
H	-1.895983	-3.166462	0.294869
H	-0.660066	-2.646510	1.471064
H	-2.712989	-0.768093	3.040733
H	-2.231444	0.725109	2.206948
H	-0.994301	-0.453150	2.722462
H	-3.758545	-1.551778	-0.439031
H	-4.201731	-1.664609	1.279706
H	-4.031196	-0.071143	0.524325
H	-2.371181	3.156197	-0.743568
H	-2.872292	1.946151	0.454929
H	-1.191243	2.515540	0.422588
H	-0.981938	2.527982	-2.715671
H	-0.458836	0.846943	-2.981035
H	0.320647	1.833673	-1.726490
H	-2.778294	-0.017892	-2.739656
H	-3.836218	0.577644	-1.438028
H	-3.219464	1.706472	-2.655083

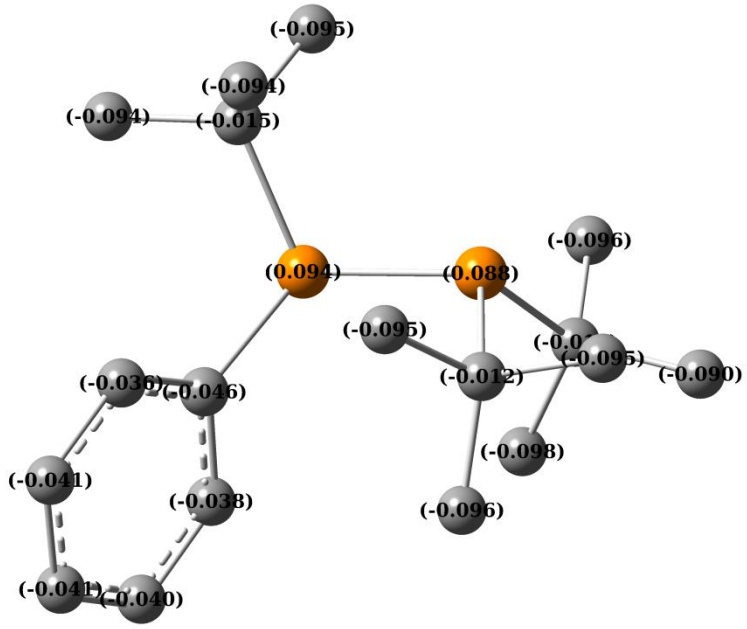


Fig. S236. Hirshfeld atomic charges of diphosphane **2**

P	-0.371476	0.954388	-0.692450
P	1.463215	0.309328	0.427123
C	-1.713685	-0.314292	-0.550057
C	-0.911956	2.520926	0.247950
C	1.146960	-1.221188	1.540593
C	2.554267	-0.182692	-1.076562
C	2.426380	-1.456869	2.366854
C	0.048243	-0.824270	2.536959
C	0.752306	-2.519002	0.830268
C	2.978155	1.159809	-1.698683
C	3.819795	-0.902327	-0.589506
C	1.880847	-1.031551	-2.162207
C	-2.275871	2.949661	-0.315736
C	-0.959136	2.446678	1.777638
C	0.134492	3.578942	-0.146536
C	-2.726404	-0.372345	0.418393
C	-3.698104	-1.371498	0.386989
C	-3.678471	-2.343161	-0.610885
C	-2.689988	-2.292645	-1.591994
C	-1.732155	-1.282261	-1.567830
H	2.209246	-2.192371	3.160342
H	3.253711	-1.858176	1.769656
H	2.770194	-0.529660	2.850634
H	-0.083495	-1.637109	3.271199
H	-0.918730	-0.663646	2.047449
H	0.317390	0.086199	3.093152

H	-0.175272	-2.409205	0.252536
H	1.545115	-2.873126	0.155645
H	0.586157	-3.311232	1.581404
H	3.610902	0.972518	-2.583165
H	2.107092	1.745882	-2.030272
H	3.554954	1.770225	-0.986917
H	4.551627	-0.944363	-1.413883
H	3.613850	-1.938911	-0.286015
H	4.297010	-0.378494	0.253228
H	1.084619	-0.464863	-2.665971
H	2.625652	-1.307093	-2.928988
H	1.449725	-1.960489	-1.764687
H	-2.530346	3.953525	0.063839
H	-2.256766	3.000330	-1.415870
H	-3.086041	2.266192	-0.024804
H	-1.266658	3.425815	2.184164
H	0.032938	2.211680	2.189913
H	-1.669932	1.698702	2.154078
H	1.141786	3.294927	0.196113
H	0.169275	3.726319	-1.236942
H	-0.120701	4.543987	0.322810
H	-2.767267	0.367478	1.216527
H	-4.473203	-1.390490	1.155401
H	-4.435792	-3.128678	-0.629723
H	-2.669411	-3.037533	-2.389652
H	-0.977758	-1.245593	-2.355186

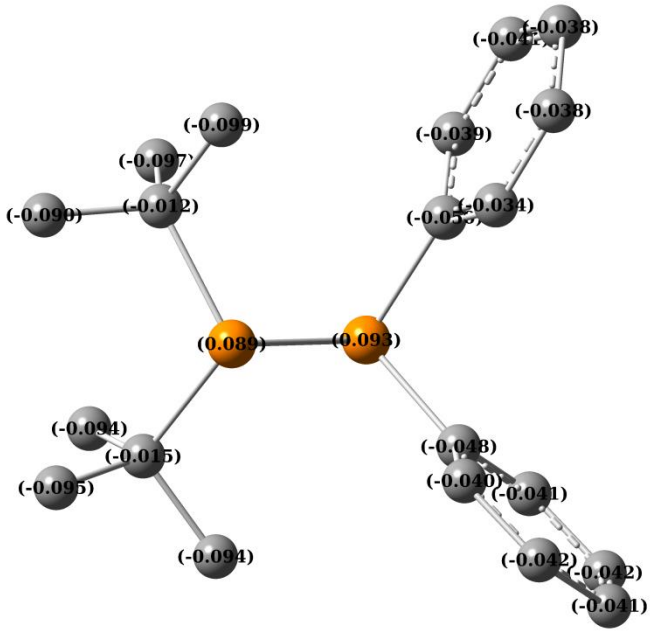


Fig. S237. Hirshfeld atomic charges of diphosphane **3**

P	1.289469	-0.417757	-0.600648
P	-0.355128	-0.067252	0.915623
C	2.114883	-1.957814	0.209817
C	-1.037535	1.577299	0.389036
C	-1.818694	-1.588126	-1.087420
C	-1.695332	-1.168475	0.243714
C	-3.736296	-2.379452	0.773103
C	-3.849885	-2.787581	-0.554263
C	-0.985395	2.621382	1.320265
C	-1.616746	1.823525	-0.863125
C	2.441509	1.104361	-0.358445
C	-2.106506	3.087034	-1.181207
C	-2.664163	-1.580468	1.167770
C	-1.470346	3.889932	1.001449
C	1.887416	2.207682	-1.279867
C	3.115810	-2.537174	-0.806489
C	-2.887160	-2.391284	-1.481853
C	1.016741	-3.017882	0.409688
C	2.565004	1.659513	1.066007
C	-2.028641	4.125718	-0.252334
C	2.805775	-1.723392	1.557227
C	3.840568	0.740383	-0.881149
H	-1.680892	1.023179	-1.601421
H	-2.551552	3.262883	-2.162448
H	-2.412125	5.116195	-0.504411
H	-1.417339	4.692413	1.739552
H	-0.560161	2.437750	2.310009

H	-2.574531	-1.271438	2.212238
H	-4.481823	-2.688715	1.508067
H	-4.684925	-3.418111	-0.865582
H	-2.967441	-2.710046	-2.523119
H	-1.062859	-1.295626	-1.819574
H	1.776221	1.848376	-2.314500
H	0.914656	2.587592	-0.943130
H	2.591499	3.057278	-1.287559
H	2.629527	-2.735967	-1.774017
H	3.973301	-1.877208	-0.987662
H	3.511325	-3.493597	-0.423306
H	0.308282	-2.745313	1.205654
H	0.442200	-3.201087	-0.510786
H	1.490820	-3.968841	0.705634
H	1.605268	2.036749	1.443653
H	2.943305	0.916158	1.778649
H	3.268913	2.510070	1.063842
H	3.689469	-1.076155	1.468093
H	2.118459	-1.275836	2.291185
H	3.150747	-2.689184	1.965922
H	4.375866	0.054583	-0.210400
H	3.798727	0.287208	-1.884043
H	4.443913	1.660731	-0.956710

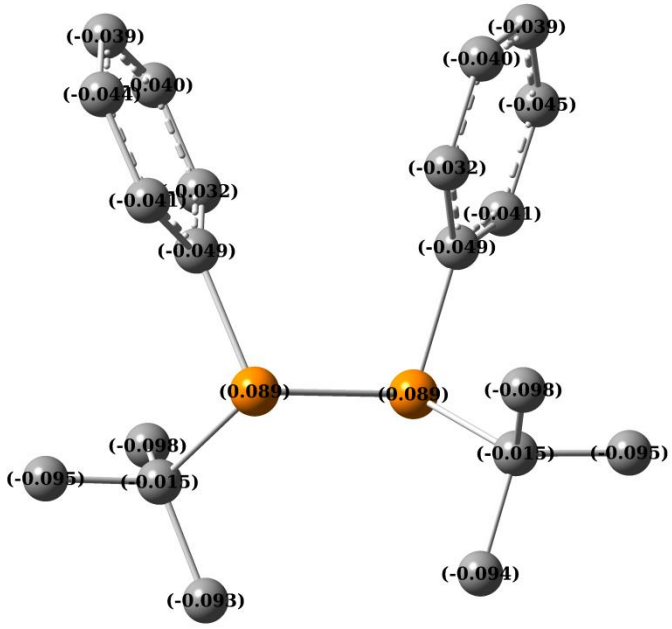


Fig. S238. Hirshfeld atomic charges of diphosphane **4**

P	0.808898	-1.159140	0.551294
P	1.181573	0.776372	-0.547827
C	-0.417626	1.702273	-0.438746

C	-0.799424	2.411005	-1.585654
C	-1.268612	1.735434	0.676889
C	-1.991233	3.136180	-1.620381
H	-0.152880	2.388792	-2.466293
C	-2.459585	2.453843	0.643406
H	-1.014969	1.173414	1.575976
C	-2.824891	3.156551	-0.505487
H	-2.269000	3.680319	-2.525231
H	-3.112897	2.456435	1.517915
H	-3.762677	3.714997	-0.530872
C	-1.019260	-1.428831	0.440290
C	-1.822483	-1.141861	-0.674418
C	-1.635536	-1.951052	1.585208
C	-3.194480	-1.370465	-0.642181
H	-1.379248	-0.709730	-1.571617
C	-3.010665	-2.186297	1.618419
H	-1.027138	-2.171562	2.465688
C	-3.792924	-1.893868	0.504436
H	-3.801889	-1.129042	-1.516492
H	-3.469704	-2.594751	2.520758
H	-4.870178	-2.069342	0.529073
C	1.488401	-2.437723	-0.699883
C	3.003840	-2.216877	-0.792519
C	1.210516	-3.815171	-0.079454
C	0.879422	-2.375493	-2.102929
H	3.242482	-1.251254	-1.264636
H	3.483484	-2.247952	0.198413
H	3.456226	-3.010015	-1.411280
H	0.130383	-4.002092	0.025232
H	1.627038	-4.605683	-0.726493
H	1.673309	-3.912118	0.915313
H	1.393678	-3.098921	-2.759008
H	-0.187351	-2.640721	-2.095124
H	0.992911	-1.376654	-2.552463
C	2.285083	1.718098	0.699678
C	1.704338	1.874713	2.107321
C	3.619725	0.965360	0.779680
C	2.517514	3.105170	0.081688
H	0.809861	2.513807	2.109939
H	1.445983	0.900655	2.550938
H	2.452157	2.354006	2.762601
H	4.070203	0.824004	-0.215432
H	4.332234	1.541235	1.393953
H	3.500008	-0.022713	1.250821
H	3.196586	3.690881	0.724230
H	2.975512	3.031138	-0.917273
H	1.576094	3.668439	-0.012822

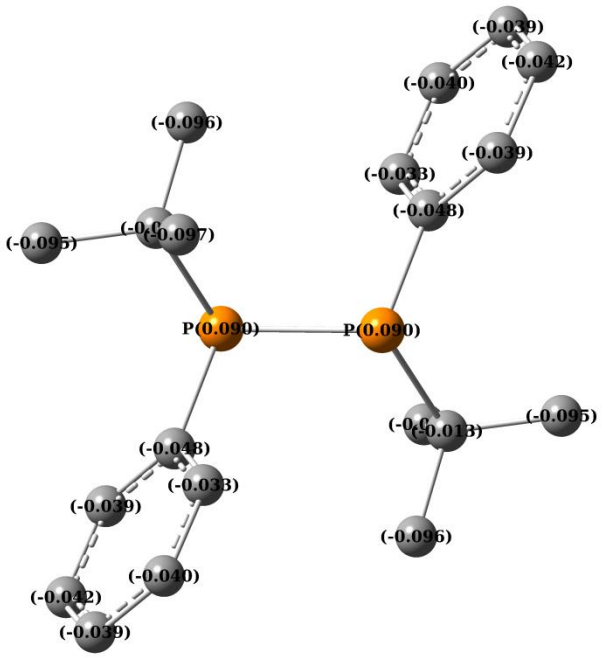


Fig. S239. Hirshfeld atomic charges of diphosphane **5**

P	-0.583245	-0.662652	-0.698777
P	0.583242	0.662680	0.698765
C	2.303819	0.149463	0.234298
C	3.246435	0.097851	1.269974
C	2.719592	-0.188702	-1.062591
C	4.569046	-0.268224	1.019836
H	2.935754	0.346215	2.287774
C	4.038383	-0.558488	-1.313592
H	1.997628	-0.184410	-1.881079
C	4.967658	-0.596598	-0.273893
H	5.288655	-0.300199	1.840143
H	4.341827	-0.821573	-2.328887
H	6.001393	-0.885897	-0.472438
C	-2.303824	-0.149456	-0.234292
C	-3.246457	-0.097881	-1.269954
C	-2.719585	0.188713	1.062599
C	-4.569074	0.268159	-1.019799
H	-2.935785	-0.346250	-2.287756
C	-4.038383	0.558467	1.313617
H	-1.997609	0.184448	1.881077
C	-4.967675	0.596537	0.273932
H	-5.288696	0.300104	-1.840096
H	-4.341818	0.821555	2.328914
H	-6.001415	0.885808	0.472489
C	-0.456497	-2.392462	0.123004
C	0.933814	-2.967414	-0.186954

C	-0.699267	-2.426609	1.633915
C	-1.517304	-3.251098	-0.584346
H	1.175766	-2.894501	-1.258840
H	1.728604	-2.456989	0.375140
H	0.957164	-4.034355	0.093271
H	-1.726201	-2.126413	1.887056
H	-0.555628	-3.456313	2.004314
H	-0.001872	-1.772932	2.179579
H	-1.457718	-4.287791	-0.211989
H	-2.536476	-2.882319	-0.392734
H	-1.358469	-3.274386	-1.674279
C	0.456509	2.392485	-0.123026
C	0.699316	2.426629	-1.633931
C	-0.933811	2.967431	0.186897
C	1.517298	3.251126	0.584348
H	1.726260	2.126446	-1.887046
H	0.001943	1.772942	-2.179609
H	0.555673	3.456331	-2.004336
H	-1.175787	2.894525	1.258778
H	-0.957162	4.034370	-0.093336
H	-1.728585	2.456997	-0.375211
H	1.457724	4.287816	0.211981
H	1.358433	3.274422	1.674275
H	2.536474	2.882344	0.392766

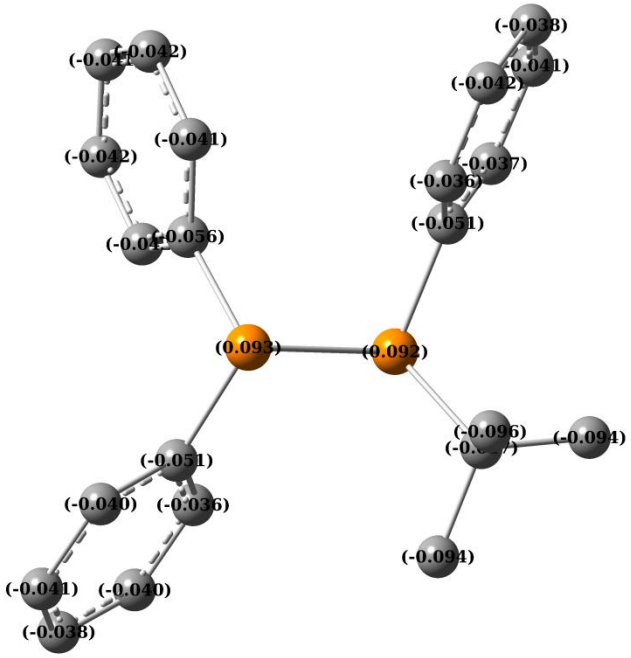


Fig. S240. Hirshfeld atomic charges of diphosphane **6**

P	-0.674819	0.175408	0.935273
P	0.337161	-1.029042	-0.676393

C	2.092909	-0.635312	-0.242893
C	-2.438523	0.133033	0.364166
C	-0.100228	1.833612	0.329765
C	0.123362	-2.835249	-0.094026
C	-0.641498	2.494286	-0.779722
C	-0.131357	3.723576	-1.190867
C	0.932607	4.307886	-0.505126
C	1.476513	3.661661	0.603086
C	0.957490	2.438111	1.021988
C	-3.409336	0.353405	1.350322
C	-4.766661	0.350422	1.031969
C	-5.174249	0.114612	-0.279447
C	-4.218933	-0.115197	-1.268919
C	-2.862449	-0.105096	-0.951184
C	2.612061	-0.566284	1.059306
C	3.951351	-0.252315	1.276221
C	4.796995	0.000774	0.195998
C	4.294380	-0.056195	-1.101478
C	2.952096	-0.367399	-1.316270
C	-1.345867	-3.208854	-0.344664
C	1.025111	-3.674630	-1.012118
C	0.479099	-3.118160	1.367705
H	-1.474348	2.051609	-1.327307
H	-0.567098	4.225704	-2.056813
H	1.335447	5.268227	-0.832640
H	2.307316	4.112662	1.148881
H	1.384055	1.943165	1.896626
H	-3.095773	0.527642	2.382509
H	-5.508147	0.526583	1.813575
H	-6.236816	0.105170	-0.529816
H	-4.530760	-0.304463	-2.297935
H	-2.123552	-0.292963	-1.733362
H	1.960175	-0.745118	1.916221
H	4.337306	-0.201273	2.296330
H	5.846850	0.245668	0.367938
H	4.947066	0.148890	-1.952143
H	2.557985	-0.399084	-2.334523
H	-1.489552	-4.287307	-0.162980
H	-2.029233	-2.663888	0.324192
H	-1.649151	-2.998215	-1.382338
H	0.879726	-4.746952	-0.797330
H	2.089754	-3.440598	-0.856469
H	0.789616	-3.508212	-2.075285
H	1.550878	-2.968952	1.560703
H	-0.092577	-2.483009	2.061744
H	0.246454	-4.170882	1.604157

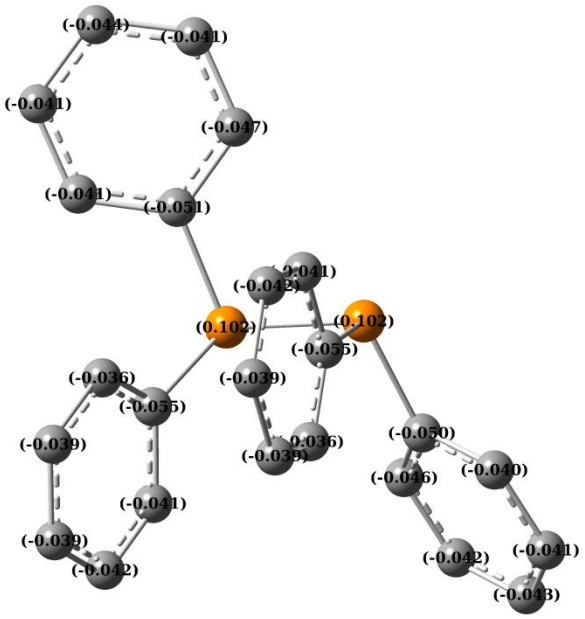


Fig. S241. Hirshfeld atomic charges of diphosphane **7**

P	0.517113	-0.709321	-1.534504
P	-0.781069	1.090924	-1.154467
C	-0.765250	-2.027311	-1.734720
C	1.221741	-1.044703	0.136412
C	0.466625	2.455287	-1.203127
C	-1.151003	0.935566	0.645292
C	-2.333783	0.266671	0.987755
C	-2.650717	0.022951	2.323497
C	-1.797195	0.461346	3.333991
C	-0.624253	1.139438	3.002771
C	-0.298826	1.369602	1.669525
C	0.124574	3.670963	-0.588950
C	0.972530	4.772076	-0.661904
C	2.174399	4.687175	-1.364559
C	2.513712	3.494339	-1.997496
C	1.667765	2.387606	-1.920422
C	2.473729	-0.477274	0.409061
C	3.047535	-0.595271	1.674113
C	2.384894	-1.298876	2.677672
C	1.144279	-1.878489	2.412160
C	0.562432	-1.746549	1.154843
C	-0.396028	-3.359522	-1.488561
C	-1.284570	-4.403436	-1.731497
C	-2.555644	-4.140988	-2.241343
C	-2.925495	-2.825522	-2.510056
C	-2.039484	-1.777567	-2.261503
H	-3.009808	-0.075559	0.200646

H	-3.573313	-0.504415	2.573341
H	-2.045522	0.276033	4.380790
H	0.054302	1.477531	3.788008
H	0.636653	1.874317	1.424220
H	-0.815222	3.755385	-0.038100
H	0.689920	5.704020	-0.168623
H	2.841029	5.549556	-1.421160
H	3.448474	3.417076	-2.556216
H	1.949234	1.463154	-2.427865
H	3.002285	0.070140	-0.374809
H	4.020396	-0.141060	1.871311
H	2.836224	-1.398195	3.666767
H	0.614502	-2.422795	3.196135
H	-0.422131	-2.179008	0.971311
H	0.597601	-3.584585	-1.094427
H	-0.978229	-5.430681	-1.524653
H	-3.252394	-4.958955	-2.432783
H	-3.914162	-2.607044	-2.918271
H	-2.347854	-0.754030	-2.482291

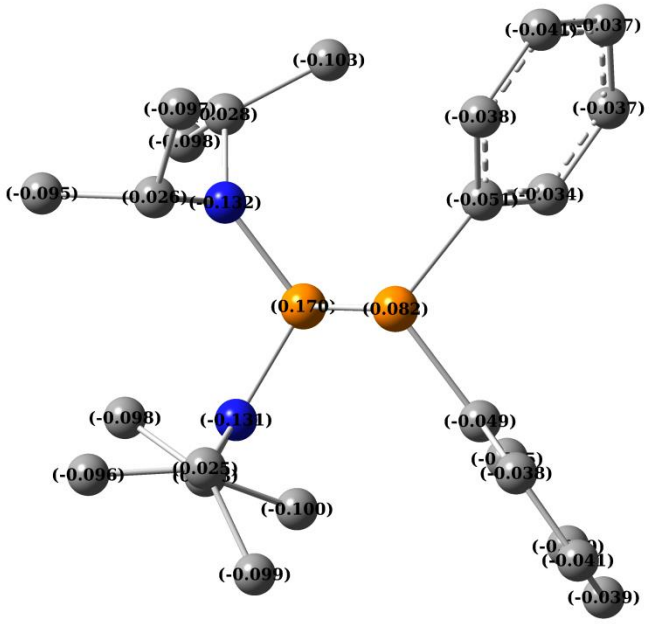


Fig. S242. Hirshfeld atomic charges of diphosphane **8**

P	0.358656	-0.584697	0.544130
P	-0.429555	0.897399	-0.972128
N	1.957766	-0.778710	-0.068466
C	-2.167510	1.125149	-0.376372
C	-4.872008	1.427700	0.326480
H	-5.922937	1.541080	0.599126
C	0.409313	2.413913	-0.319527

C	-3.119565	1.502272	-1.332248
H	-2.804645	1.665566	-2.365662
C	3.105465	-0.497238	0.817062
H	4.000530	-0.680833	0.202758
C	2.266426	-1.263638	-1.417567
H	1.297616	-1.423323	-1.911778
C	3.028760	-0.236092	-2.259344
H	2.470628	0.708662	-2.309694
H	4.025179	-0.022621	-1.840862
H	3.173165	-0.611169	-3.284702
C	2.991824	-2.613196	-1.387671
H	4.005319	-2.519613	-0.965977
H	2.435664	-3.333965	-0.770967
H	3.093853	-3.025061	-2.404005
C	-4.460785	1.658108	-0.984963
H	-5.187937	1.952910	-1.743848
C	1.268764	3.091777	-1.192076
H	1.385316	2.731251	-2.216713
C	3.193400	-1.444224	2.015184
H	2.348505	-1.284587	2.703607
H	3.183962	-2.494423	1.689299
H	4.122645	-1.263884	2.578306
C	-2.594258	0.901855	0.939724
H	-1.875679	0.588043	1.698749
C	0.247519	2.910416	0.980522
H	-0.423111	2.405739	1.677533
C	0.943214	4.040646	1.400005
H	0.808318	4.412792	2.417492
C	-3.935172	1.049390	1.287743
H	-4.249816	0.863492	2.316658
C	3.170914	0.963375	1.265562
H	3.138879	1.646056	0.404421
H	2.322491	1.211915	1.921499
H	4.100119	1.150247	1.827269
C	1.814395	4.694168	0.527408
H	2.362533	5.577452	0.860731
C	1.973005	4.220561	-0.772517
H	2.642900	4.732639	-1.465824
N	-0.615179	-1.950413	0.129024
C	-1.169809	-2.270357	-1.197737
H	-0.858736	-1.454891	-1.867960
C	-0.937444	-2.915504	1.199850
H	-1.604476	-3.658138	0.737239
C	-0.618286	-3.574874	-1.783959
H	0.478063	-3.556459	-1.843658
H	-0.910852	-4.448020	-1.178861
H	-1.016320	-3.732496	-2.798595

C	-1.724218	-2.287088	2.351323
H	-1.122693	-1.526973	2.874091
H	-2.638833	-1.806970	1.974219
H	-2.010038	-3.056420	3.085662
C	-2.704233	-2.282095	-1.199904
H	-3.108659	-3.134413	-0.630544
H	-3.107107	-1.356878	-0.767155
H	-3.078952	-2.374302	-2.231276
C	0.288413	-3.679072	1.701559
H	0.837866	-4.128534	0.861110
H	0.975184	-3.012524	2.241476
H	-0.011301	-4.483718	2.391679

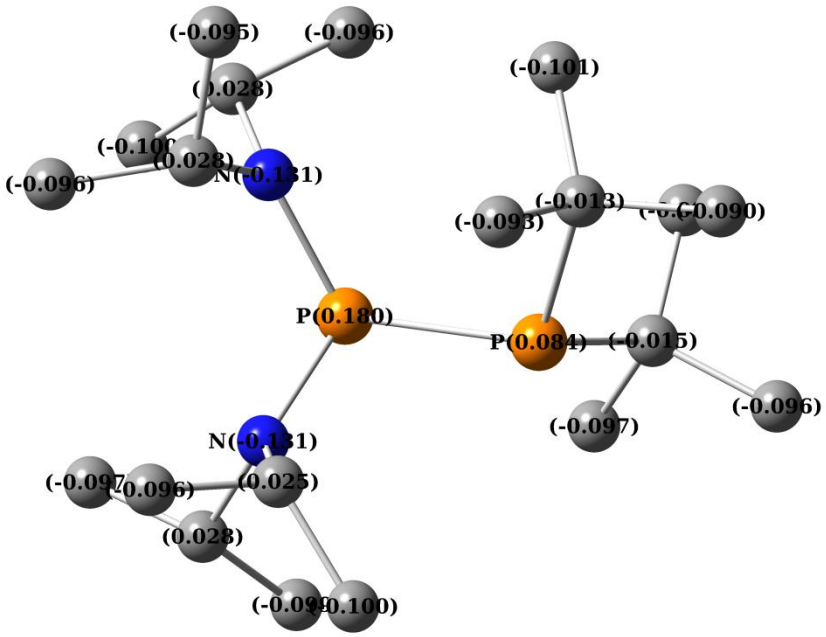


Fig. S243. Hirshfeld atomic charges of diphosphane **9**

C	2.736761	-0.933954	-1.091481
C	1.982744	-1.879205	-2.040419
H	1.560383	-2.741671	-1.501831
H	2.688310	-2.269050	-2.793689
H	1.163638	-1.371675	-2.567485
C	3.950641	-1.720122	-0.560207
H	3.632041	-2.625972	-0.022347
H	4.581775	-1.129978	0.116018
H	4.581798	-2.033506	-1.410073
C	3.219957	0.282799	-1.885446

H	3.911827	0.906772	-1.301931
H	2.383530	0.914336	-2.215703
H	3.764902	-0.053141	-2.785043
C	2.249128	0.962503	1.344235
C	3.709285	0.720764	1.757907
H	3.843252	-0.254616	2.251447
H	4.015094	1.505030	2.471565
H	4.397057	0.775753	0.902748
C	1.419226	1.036391	2.637079
H	1.491120	0.101201	3.213721
H	0.358448	1.235671	2.437727
H	1.791680	1.858506	3.271598
C	2.151882	2.298547	0.601995
H	2.845703	2.351776	-0.246512
H	2.408437	3.124657	1.289205
H	1.136974	2.460721	0.224712
C	-1.284515	2.217686	-1.590403
H	-1.686508	3.178099	-1.231570
C	-0.018582	2.538999	-2.385853
H	0.731413	3.052277	-1.769688
H	-0.263108	3.185360	-3.243278
H	0.430011	1.615453	-2.784852
C	-2.335350	1.609020	-2.527644
H	-3.256704	1.340498	-1.994807
H	-1.941965	0.703609	-3.014430
H	-2.594295	2.329775	-3.319301
C	-1.724427	1.853436	0.844372
H	-1.448980	1.130062	1.622432
C	-1.311514	3.240649	1.350681
H	-0.231868	3.306351	1.532952
H	-1.831245	3.459481	2.296573
H	-1.585703	4.035205	0.639356
C	-3.249307	1.785244	0.696803
H	-3.558147	0.793143	0.343323
H	-3.620954	2.541851	-0.012124
H	-3.735835	1.977718	1.666201
C	-2.193399	-2.273876	-0.429879
H	-2.685967	-2.877936	0.347332
C	-1.338933	-3.232733	-1.263419
H	-0.539770	-3.678162	-0.653626
H	-0.873067	-2.708916	-2.111595
H	-1.960013	-4.047535	-1.668178
C	-3.310635	-1.666418	-1.275181
H	-3.969957	-1.033454	-0.663467
H	-3.922720	-2.461932	-1.728638
H	-2.900380	-1.053846	-2.089990
C	-1.270818	-1.503085	1.751969

H	-0.565253	-0.745554	2.119311
C	-0.657065	-2.867300	2.090579
H	0.312168	-2.987445	1.588643
H	-1.318023	-3.699763	1.801360
H	-0.493258	-2.943539	3.177049
C	-2.592445	-1.307239	2.502938
H	-3.009848	-0.306143	2.333990
H	-2.437522	-1.439784	3.585137
H	-3.349108	-2.044063	2.189294
N	-1.408777	-1.258387	0.304072
N	-0.997892	1.434378	-0.365578
P	1.596736	-0.585386	0.420340
P	-0.409968	-0.186627	-0.622525

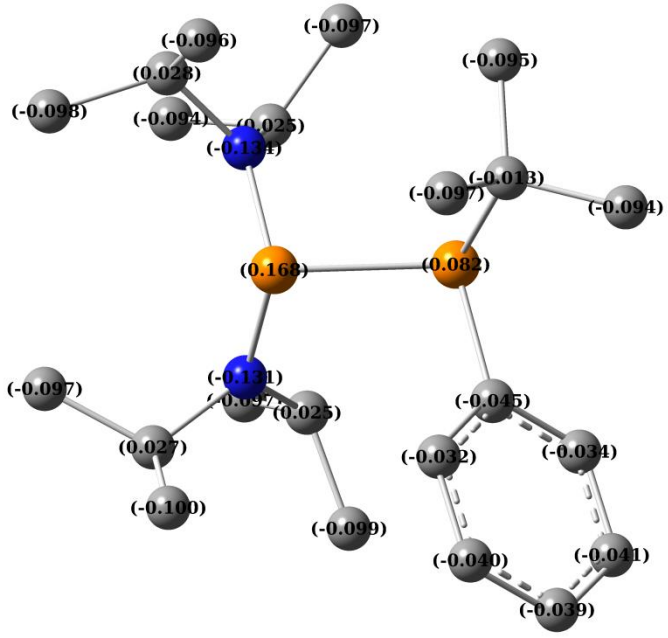


Fig. S244. Hirshfeld atomic charges of diphosphane **10**

P	0.657085	-0.102296	-0.596121
P	-0.740003	1.124371	0.707769
N	2.160742	0.451932	0.075294
C	-0.816926	2.845080	-0.132148
C	-2.374456	0.417618	0.209628
C	-2.681591	-0.040146	-1.078775
H	-1.927302	0.007316	-1.865418
C	2.826519	1.576436	2.209570
H	3.671222	2.109649	1.744283
H	1.952249	2.239763	2.199837
H	3.096890	1.382469	3.259505

C	-3.359544	0.321307	1.201708
H	-3.131685	0.662416	2.214470
C	-0.808829	2.829255	-1.662442
H	0.103519	2.372577	-2.067812
H	-1.675083	2.283627	-2.064227
H	-0.867646	3.864003	-2.042976
C	-2.114319	3.508784	0.355646
H	-3.006732	3.027281	-0.070227
H	-2.200434	3.478608	1.453971
H	-2.119179	4.568210	0.047250
C	2.899026	1.927014	-1.822393
H	2.124425	1.574541	-2.520952
H	2.529702	2.830850	-1.321407
H	3.782526	2.204634	-2.418439
C	3.921443	-0.332909	-1.586654
H	4.136126	-1.189994	-0.936377
H	3.265953	-0.673942	-2.401738
H	4.867505	-0.000501	-2.043149
C	3.650361	-0.751018	1.697808
H	3.436940	-1.694919	1.176522
H	4.613179	-0.364955	1.327313
H	3.775060	-0.967969	2.770175
C	0.372769	3.652931	0.402506
H	0.291477	3.799728	1.491018
H	1.327016	3.149561	0.202915
H	0.398599	4.647789	-0.073617
C	2.516171	0.259818	1.491670
H	1.619370	-0.155113	1.972494
C	3.271334	0.828624	-0.825501
H	4.042024	1.253976	-0.162803
N	0.265597	-1.687759	-0.012737
C	1.750803	-3.077088	-1.489057
H	2.059648	-2.295745	-2.196435
H	2.478115	-3.102134	-0.664240
H	1.791226	-4.041505	-2.019745
C	0.752589	-2.915990	2.120433
H	0.931569	-3.879003	1.615107
H	1.720784	-2.418208	2.251804
H	0.342966	-3.140206	3.117886
C	-0.665119	-2.703742	-2.112431
H	-1.688666	-2.603562	-1.725051
H	-0.443421	-1.825679	-2.739809
H	-0.620070	-3.598294	-2.753962
C	-0.231116	-2.046974	1.329170
H	-0.352525	-1.099601	1.875964
C	0.340474	-2.816433	-0.965141
H	0.058835	-3.706345	-0.383287

C	-4.901316	-0.676832	-0.364176
H	-5.878626	-1.109576	-0.586153
C	-4.614287	-0.216691	0.919636
H	-5.366495	-0.285791	1.707804
C	-3.931924	-0.585788	-1.362744
H	-4.147049	-0.948634	-2.369912
C	-1.609381	-2.724944	1.294985
H	-2.312161	-2.179773	0.653504
H	-1.545354	-3.764059	0.934176
H	-2.031191	-2.761691	2.311337

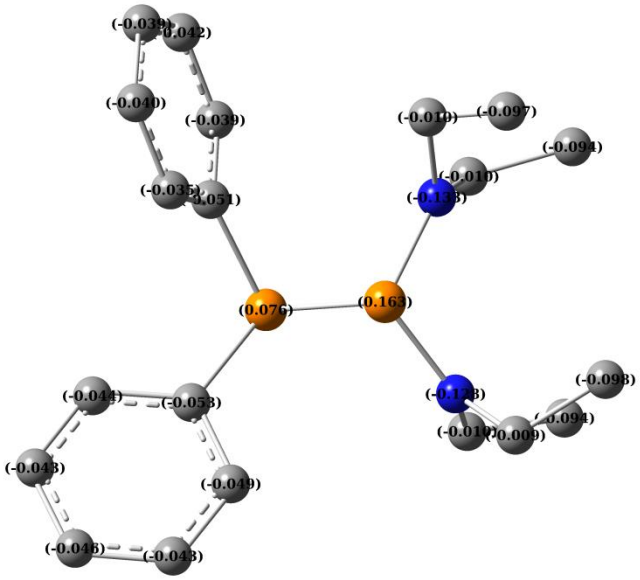


Fig. S245. Hirshfeld atomic charges of diphosphane **11**

P	0.692702	-0.357641	0.560456
P	-0.879340	-0.076933	-1.045776
N	1.363793	-1.873829	0.101965
C	-1.285385	1.638390	-0.484249
C	-1.873967	1.931569	0.754481
H	-2.179282	1.117119	1.414679
C	-0.898548	2.697236	-1.313651
H	-0.447927	2.480826	-2.285305
C	3.391354	-2.177803	1.569958
H	4.093060	-2.278273	0.729118
H	3.383905	-1.119923	1.872112
H	3.775392	-2.774760	2.412311
C	2.882638	-2.619709	-1.784825
H	3.419776	-1.660448	-1.814140
H	3.474392	-3.323306	-1.179991

H	2.836626	-3.022524	-2.808711
C	1.467623	-2.452736	-1.232904
H	0.879018	-1.829842	-1.922190
C	1.981721	-2.631962	1.189492
H	1.991438	-3.697028	0.896968
N	1.795382	0.883188	0.104570
C	3.908710	1.078191	-1.199636
H	4.280652	1.960124	-0.655699
H	4.312193	0.181028	-0.705247
H	4.307519	1.126974	-2.225150
C	2.940446	1.851580	2.112230
H	2.667126	1.004156	2.760367
H	3.938633	1.652286	1.694350
H	2.999494	2.753625	2.742142
C	2.382620	1.037406	-1.216294
H	2.048201	0.199789	-1.845490
C	1.900657	2.029584	1.009059
H	0.918370	2.238742	1.464609
C	-1.662231	4.300726	0.321272
H	-1.808933	5.335674	0.636032
C	-1.078698	4.021080	-0.912244
H	-0.767920	4.835049	-1.570066
C	-2.064739	3.252843	1.150795
H	-2.524891	3.466041	2.117615
H	1.332769	-2.560214	2.079251
H	0.973737	-3.444315	-1.223259
H	1.995314	1.956128	-1.699963
H	2.137196	2.919281	0.400443
C	-2.268190	-1.071826	-0.341081
C	-2.044813	-2.315275	0.265447
C	-3.591154	-0.636925	-0.511301
C	-3.116221	-3.094243	0.701935
H	-1.023699	-2.676763	0.404504
C	-4.658660	-1.414522	-0.070642
H	-3.788240	0.326817	-0.986819
C	-4.425383	-2.647537	0.538336
H	-2.922572	-4.057496	1.178173
H	-5.680417	-1.054309	-0.206498
H	-5.262277	-3.257764	0.882860

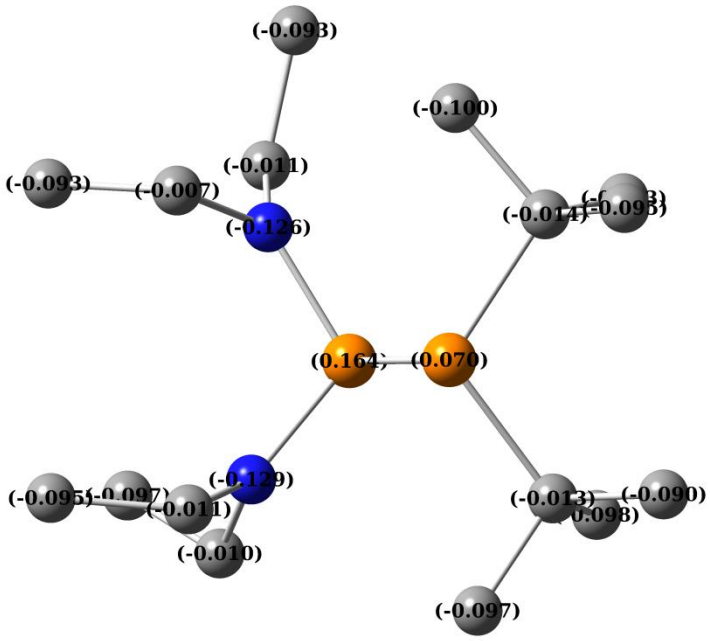


Fig. S246. Hirshfeld atomic charges of diphosphane **12**

P	-0.458435	-0.128244	-0.675140
P	1.370411	-0.144690	0.677464
N	-1.214567	-1.565034	-0.081664
C	2.360778	-1.509946	-0.275516
C	2.210220	-1.531583	-1.803226
H	1.177782	-1.746079	-2.112766
H	2.505034	-0.583088	-2.271246
H	2.854870	-2.326775	-2.216995
C	3.853374	-1.402215	0.067900
H	4.337664	-0.568519	-0.459389
H	4.025095	-1.281313	1.148598
H	4.362680	-2.327377	-0.251305
C	-3.320307	-1.731779	-1.454428
H	-3.979965	-1.651309	-0.577640
H	-3.194619	-0.722262	-1.876915
H	-3.824746	-2.355297	-2.209663
C	-2.692684	-2.094648	1.913805
H	-3.151455	-1.098007	1.957589
H	-3.369864	-2.758846	1.355160
H	-2.623735	-2.486064	2.941000
C	1.854522	-2.855156	0.274920
H	1.936185	-2.903127	1.371809
H	0.807953	-3.031505	-0.004976
H	2.460003	-3.674372	-0.149310
C	-1.298664	-2.055861	1.291059
H	-0.630233	-1.442615	1.912278

C	-1.960988	-2.325163	-1.082807
H	-2.088759	-3.353341	-0.701198
N	-1.393379	1.239717	-0.195955
C	-3.449707	1.426234	1.231464
H	-3.909003	2.306661	0.757107
H	-3.854315	0.529068	0.739576
H	-3.765849	1.418850	2.285818
C	-1.782506	3.513632	-1.178979
H	-2.177271	3.925271	-0.236652
H	-0.712375	3.763535	-1.236530
H	-2.298474	4.025974	-2.005670
C	-1.924378	1.462070	1.143642
H	-1.495442	0.696566	1.806126
C	-2.002955	2.006556	-1.280008
H	-3.089632	1.802577	-1.343748
H	-1.350237	-2.409662	-1.998286
H	-0.881594	-3.081305	1.327112
H	-1.568010	2.431219	1.542859
H	-1.569003	1.637353	-2.221507
C	2.190390	1.564959	0.362176
C	3.507981	1.635504	1.156604
C	2.442859	1.926817	-1.104279
C	1.256913	2.612599	0.991713
H	3.366330	1.305199	2.197537
H	4.314279	1.039961	0.715028
H	3.853048	2.683376	1.182349
H	1.522210	1.863047	-1.704977
H	2.822881	2.961213	-1.175456
H	3.196754	1.270654	-1.562923
H	1.759581	3.594621	0.986259
H	0.318675	2.702389	0.436713
H	1.020450	2.362441	2.038473

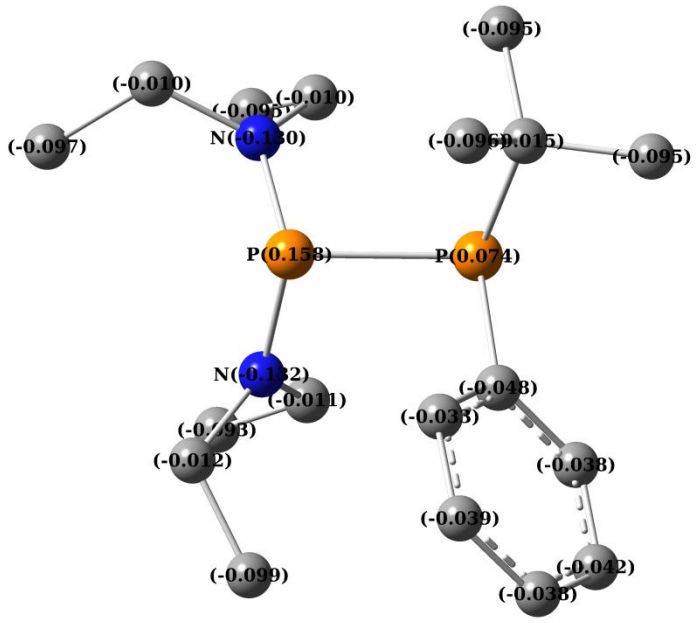


Fig. S247. Hirshfeld atomic charges of diphosphane **13**

P	-0.800304	-0.018183	0.728675
P	0.550211	1.012574	-0.746337
N	-2.319430	0.683006	0.320027
C	0.796298	2.758000	-0.012962
C	2.090942	0.100716	-0.268492
C	2.477055	-0.191869	1.049436
H	1.844487	0.118403	1.882119
C	2.905201	-0.356060	-1.313282
H	2.613119	-0.149133	-2.345577
C	1.109950	2.816158	1.484753
H	0.341853	2.307511	2.087639
H	2.085749	2.363764	1.711880
H	1.152510	3.869822	1.811171
C	1.953267	3.389673	-0.801108
H	2.897603	2.847354	-0.636865
H	1.747889	3.398937	-1.883158
H	2.102630	4.433183	-0.474682
C	-3.926930	-0.662910	1.722753
H	-4.427801	-1.095313	0.844427
H	-3.152504	-1.374351	2.049614
H	-4.667700	-0.568969	2.532875
C	-3.913333	0.202157	-1.593406
H	-3.598247	-0.847168	-1.681780
H	-4.829510	0.233200	-0.983993
H	-4.173782	0.569173	-2.598628
C	-0.498341	3.535766	-0.292492
H	-0.771583	3.496954	-1.358921

H	-1.338364	3.133168	0.292596
H	-0.362670	4.595186	-0.016945
C	-2.808664	1.073535	-0.997383
H	-1.951568	1.098908	-1.686538
C	-3.302283	0.695994	1.403494
H	-4.089437	1.421186	1.133450
N	-0.703910	-1.614944	0.097147
C	-1.946299	-3.080703	-1.491694
H	-1.600096	-4.044983	-1.089143
H	-2.887663	-2.823781	-0.981573
H	-2.155152	-3.225199	-2.562684
C	0.925060	-3.461873	0.566452
H	0.741489	-4.038171	-0.353840
H	1.768595	-2.781368	0.379416
H	1.219434	-4.178221	1.348664
C	-0.907875	-1.977411	-1.297842
H	-1.227244	-1.077163	-1.840693
C	-0.315069	-2.686618	1.007866
H	-1.153598	-3.395739	1.155039
C	4.451050	-1.340868	0.259039
H	5.366750	-1.898605	0.464574
C	4.075230	-1.070870	-1.054766
H	4.694125	-1.418026	-1.884487
C	3.647737	-0.899745	1.310749
H	3.928443	-1.116843	2.343286
H	-2.820154	1.088941	2.314822
H	-3.178765	2.115622	-0.937590
H	0.047499	-2.284508	-1.765996
H	-0.129556	-2.224506	1.989540

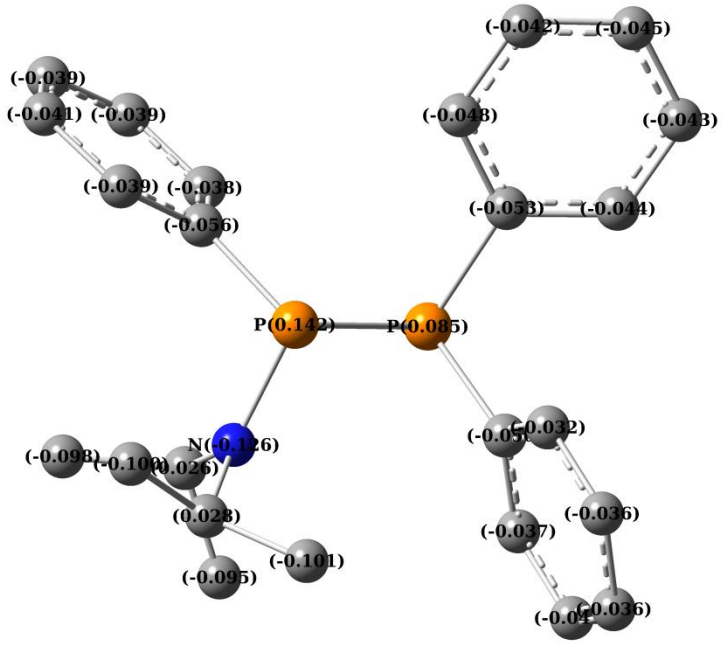


Fig. S248. Hirshfeld atomic charges of diphosphane **14**

P	0.826668	0.501445	-0.993070
P	-0.618815	-0.106801	0.636316
N	-1.026023	-1.690245	0.107173
C	2.168607	-0.661839	-0.475097
C	3.517945	-2.608412	-1.013585
H	3.800961	-3.390310	-1.720755
C	1.201319	4.211665	0.858612
H	0.571616	4.885894	1.442300
C	3.769024	-1.527244	1.128566
H	4.247466	-1.466468	2.107909
C	2.548498	-1.668993	-1.368239
H	2.082414	-1.715258	-2.355186
C	-2.123947	0.884305	0.173970
C	4.127456	-2.539711	0.236785
H	4.887032	-3.271872	0.516944
C	0.393138	-3.080828	1.601282
H	1.069104	-3.281108	0.756912
H	0.388722	-3.956411	2.269761
H	0.802978	-2.227613	2.164007
C	3.302969	3.693717	-0.194450
H	4.332098	3.961107	-0.442558
C	-1.681520	-1.951840	-1.182406
H	-1.553747	-1.033179	-1.774634
C	-2.337949	1.512992	-1.058741
H	-1.572964	1.463728	-1.837666
C	2.511469	4.567804	0.551165
H	2.916942	5.522658	0.890815

C	-4.311847	1.657856	0.902865
H	-5.079952	1.714845	1.676506
C	-3.186403	-2.204755	-1.048046
H	-3.681246	-1.361323	-0.544826
H	-3.388785	-3.122453	-0.472195
H	-3.644865	-2.330605	-2.041442
C	-1.019519	-2.774954	1.105514
H	-1.378465	-3.668420	0.571767
C	2.796537	-0.596565	0.776735
H	2.514883	0.187717	1.482461
C	0.682847	2.988640	0.431284
H	-0.348460	2.739786	0.686252
C	2.786498	2.475106	-0.624477
H	3.419497	1.799105	-1.204296
C	1.470883	2.099287	-0.310342
C	-1.985370	-2.528621	2.268808
H	-3.000628	-2.320703	1.899645
H	-1.654358	-1.669250	2.874232
H	-2.029095	-3.407659	2.931227
C	-3.122826	0.977498	1.154478
H	-2.966957	0.503401	2.127055
C	-3.523817	2.202826	-1.309711
H	-3.673443	2.686251	-2.277063
C	-4.515075	2.272065	-0.333012
H	-5.444906	2.808252	-0.531882
C	-0.987612	-3.075137	-1.957367
H	0.090641	-2.880704	-2.035077
H	-1.407180	-3.150704	-2.972505
H	-1.122752	-4.055830	-1.474143

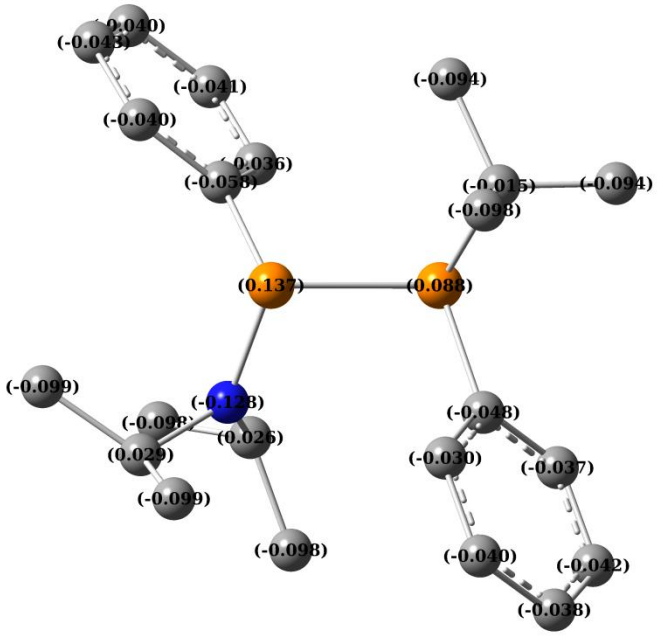


Fig. S249. Hirshfeld atomic charges of diphosphane **15**

P	0.605172	1.250403	-0.581928
P	-0.640177	-0.074344	0.754509
N	-0.266943	-1.634779	0.127570
C	2.270616	0.485886	-0.352453
C	4.385634	-0.101314	-1.402358
H	5.034252	-0.091863	-2.280532
C	3.974556	-0.717288	0.892585
H	4.301201	-1.193938	1.819004
C	3.121387	0.485234	-1.465947
H	2.779742	0.941108	-2.398353
C	-2.324375	0.353522	0.075874
C	4.812297	-0.708242	-0.223392
H	5.796711	-1.177319	-0.172435
C	0.760483	-2.752654	2.103415
H	1.745176	-2.718444	1.616017
H	0.712652	-3.650211	2.740186
H	0.665210	-1.871038	2.757603
C	-0.239732	-1.950360	-1.308551
H	-0.214385	-0.980856	-1.829961
C	-2.612637	0.658725	-1.261969
H	-1.806497	0.704872	-1.996495
C	-4.691311	0.593492	0.593625
H	-5.499664	0.572918	1.327064
C	-1.488322	-2.696192	-1.791773
H	-2.402118	-2.138205	-1.541501
H	-1.560642	-3.697904	-1.338069
H	-1.453539	-2.831821	-2.884127

C	-0.353386	-2.776749	1.057451
H	-0.188781	-3.672314	0.438929
C	2.717379	-0.122768	0.828588
H	2.069645	-0.143278	1.705812
C	-1.731673	-2.930202	1.708713
H	-2.529563	-2.921648	0.952135
H	-1.924123	-2.108885	2.417660
H	-1.792312	-3.876553	2.269300
C	-3.381703	0.333185	0.995355
H	-3.173357	0.111696	2.045415
C	-3.920625	0.917165	-1.667578
H	-4.126144	1.148357	-2.714773
C	-4.963372	0.883057	-0.741811
H	-5.987173	1.087297	-1.061189
C	1.045873	-2.690262	-1.692451
H	1.929962	-2.134085	-1.349938
H	1.106773	-2.806368	-2.785894
H	1.082931	-3.700563	-1.254549
C	0.700516	2.848779	0.458923
C	-0.722605	3.419111	0.547773
C	1.277696	2.676107	1.866170
C	1.589859	3.808805	-0.345573
H	-1.195132	3.502739	-0.443668
H	-1.375385	2.797500	1.180186
H	-0.688595	4.426750	0.995390
H	2.325818	2.344057	1.836834
H	1.250296	3.644415	2.395082
H	0.698601	1.951815	2.459057
H	1.668241	4.776140	0.179326
H	2.609287	3.408489	-0.464877
H	1.175265	3.997487	-1.348051

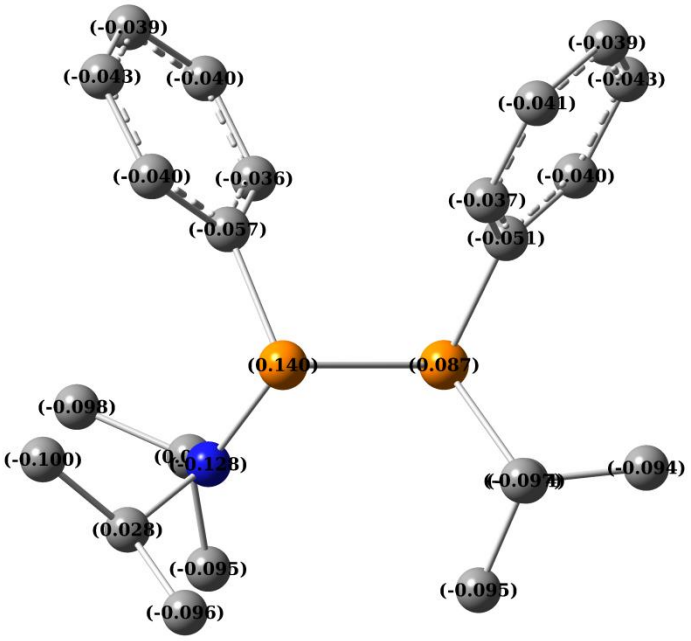


Fig. S250. Hirshfeld atomic charges of diphosphane **16**

P	0.779727	-1.037522	-0.748531
P	-0.638296	-0.038503	0.684125
N	-2.168912	-0.438056	-0.014612
C	2.358225	-0.266352	-0.162117
C	3.833526	0.709569	1.504393
H	4.013250	1.014121	2.537202
C	4.576698	0.519220	-0.780582
H	5.340233	0.671895	-1.545957
C	2.615928	0.127413	1.159546
H	1.854961	-0.013310	1.930290
C	-0.326330	1.731917	0.192809
C	4.818568	0.903253	0.536613
H	5.772268	1.359462	0.808581
C	-3.181394	-1.893482	1.728460
H	-3.158563	-2.771324	1.066462
H	-4.034411	-2.001519	2.416545
H	-2.259475	-1.891005	2.331824
C	-2.502397	-0.112908	-1.411689
H	-1.538045	0.036059	-1.919955
C	0.111803	2.160721	-1.067775
H	0.337039	1.428581	-1.846641
C	-0.433004	4.058999	0.896073
H	-0.642705	4.798039	1.671830
C	-3.312646	1.178686	-1.568266
H	-2.798272	2.028687	-1.097357
H	-4.314421	1.084575	-1.118309
H	-3.452341	1.410845	-2.635517

C	-3.301584	-0.602890	0.918319
H	-4.194352	-0.702881	0.281775
C	3.353405	-0.053751	-1.125676
H	3.162132	-0.339736	-2.162866
C	-3.538178	0.603202	1.835079
H	-3.583671	1.539543	1.260541
H	-2.729127	0.694512	2.577477
H	-4.485624	0.487768	2.384840
C	-0.585221	2.700734	1.170901
H	-0.912345	2.384912	2.164643
C	0.271866	3.516362	-1.344020
H	0.616716	3.830190	-2.331265
C	-0.004820	4.469773	-0.364706
H	0.121321	5.532128	-0.582100
C	-3.185266	-1.292930	-2.107532
H	-2.564798	-2.196749	-2.032417
H	-3.344901	-1.067869	-3.173429
H	-4.171132	-1.515446	-1.668484
C	0.900327	-2.814789	-0.063190
C	-0.389441	-3.529434	-0.489280
C	2.099372	-3.465666	-0.768185
C	1.081830	-2.919666	1.452830
H	-1.276161	-3.054272	-0.047229
H	-0.509127	-3.517248	-1.584384
H	-0.361248	-4.582672	-0.162250
H	3.049146	-2.994995	-0.471387
H	2.152615	-4.534351	-0.499234
H	2.009808	-3.397781	-1.864208
H	1.130968	-3.982713	1.745787
H	2.016532	-2.441994	1.781902
H	0.247045	-2.456577	1.999625

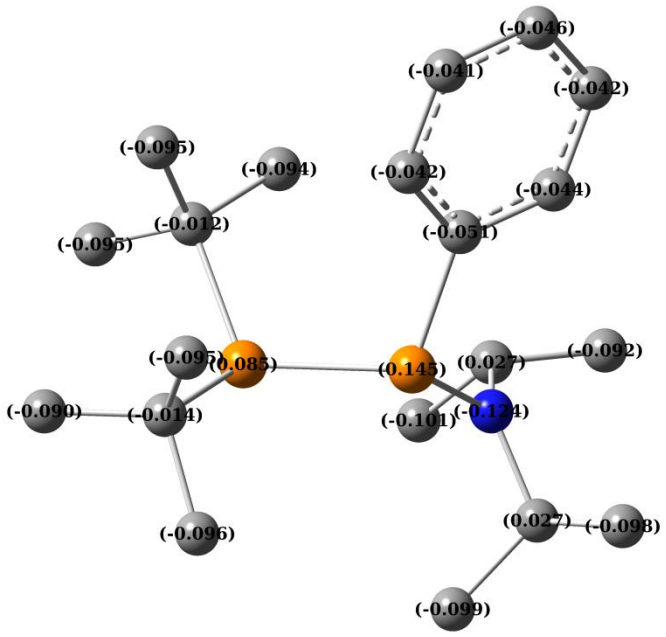


Fig. S251. Hirshfeld atomic charges of diphosphane **17**

P	-0.500015	-0.270552	-0.798193
P	1.351429	-0.779109	0.386405
N	-1.807906	-0.999607	0.051206
C	-0.848566	1.539307	-0.695260
C	2.712791	0.043825	-2.095977
H	1.753045	0.201931	-2.611285
H	3.450610	-0.248500	-2.863299
H	3.045339	0.998804	-1.667125
C	-2.068950	-0.826769	1.489990
H	-1.568988	0.111340	1.766442
C	2.760414	1.780658	0.901407
H	3.660924	1.449420	0.366345
H	3.091598	2.475289	1.693191
H	2.129053	2.352552	0.210336
C	-0.185863	3.808063	-1.270643
H	0.552310	4.489614	-1.698239
C	0.073176	2.441055	-1.246645
H	1.007310	2.069240	-1.668411
C	-2.324172	3.416155	-0.242808
H	-3.275313	3.788510	0.143628
C	-2.062590	2.046490	-0.218999
H	-2.815594	1.359099	0.160277
C	-2.448655	-2.160354	-0.599694
H	-3.180067	-2.539020	0.129854
C	2.120732	-2.348086	-1.749491
H	2.020434	-3.186670	-1.043655
H	2.852126	-2.634741	-2.524274
H	1.151603	-2.195183	-2.246000

C	2.002311	0.614986	1.544620
C	2.598962	-1.066636	-1.044262
C	-1.487823	-3.312982	-0.904908
H	-0.797980	-3.045081	-1.718875
H	-2.047928	-4.207386	-1.220892
H	-0.885809	-3.570533	-0.021074
C	-1.384201	4.305159	-0.757771
H	-1.587703	5.377283	-0.773448
C	-3.230145	-1.733805	-1.842123
H	-3.967777	-0.958637	-1.587612
H	-3.758864	-2.592041	-2.285885
H	-2.550027	-1.322501	-2.605083
C	0.809651	1.174778	2.333184
H	0.109051	1.730008	1.694123
H	1.183295	1.872564	3.101712
H	0.262247	0.375787	2.856559
C	-3.561202	-0.642267	1.798415
H	-4.028820	0.104342	1.140830
H	-3.686426	-0.309209	2.840108
H	-4.124473	-1.582040	1.690913
C	3.984347	-1.351615	-0.444014
H	4.446146	-0.455438	-0.006583
H	4.659174	-1.710447	-1.239624
H	3.938132	-2.131461	0.331924
C	-1.488640	-1.947535	2.360533
H	-1.990646	-2.907321	2.156514
H	-1.638889	-1.718482	3.427766
H	-0.413459	-2.075027	2.174194
C	2.928076	-0.088735	2.557048
H	2.408448	-0.913664	3.067919
H	3.251030	0.638330	3.322206
H	3.833113	-0.498720	2.089267

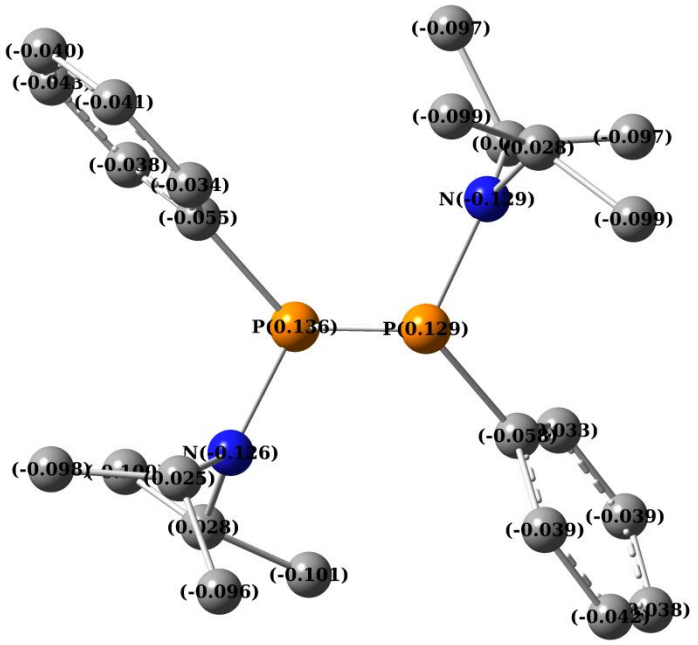


Fig. S252. Hirshfeld atomic charges of diphosphane **18**

P	-0.564264	-0.610723	-0.702594
N	-0.466414	-2.116580	0.118160
C	-4.917059	0.912931	-0.002595
H	-5.943798	1.258393	0.132642
C	-1.249104	-3.570006	-1.767060
H	-2.262239	-3.573749	-1.338489
H	-1.077543	-4.536804	-2.266338
H	-1.203216	-2.781297	-2.535144
C	-0.198178	-3.325185	-0.680003
H	-0.260393	-4.166097	0.028099
C	-2.270831	0.027923	-0.349072
C	-2.285504	-3.009091	1.581300
H	-3.041431	-2.462401	0.998170
H	-2.629003	-3.066651	2.626043
H	-2.226539	-4.039537	1.194526
C	-3.970639	1.120671	1.000123
H	-4.253175	1.629653	1.923850
C	-2.660161	0.679661	0.828027
H	-1.929762	0.852273	1.620535
C	1.218525	-3.320738	-1.254212
H	1.962076	-3.152931	-0.460765
H	1.334939	-2.516697	-1.997783
H	1.438760	-4.277992	-1.752964
C	-4.544772	0.266592	-1.180443
H	-5.279075	0.105067	-1.972175
C	-0.930012	-2.301332	1.499205
H	-1.063054	-1.289509	1.909793
C	-3.230423	-0.164861	-1.352553

H	-2.940970	-0.659809	-2.283182
C	0.131869	-2.983153	2.366162
H	1.090478	-2.451646	2.280373
H	0.296317	-4.032479	2.073554
H	-0.178778	-2.981934	3.422672
P	0.651452	0.642096	0.709947
N	0.487074	2.207023	0.018335
C	4.809101	-1.206597	-0.335576
H	5.780336	-1.657152	-0.548847
C	1.957843	3.428915	1.630419
H	2.778120	3.396691	0.898527
H	2.049265	4.355937	2.218358
H	2.083654	2.578068	2.319690
C	0.599210	3.361768	0.927525
H	0.522054	4.254074	0.287039
C	2.302117	-0.053935	0.207620
C	1.708242	3.222842	-1.918297
H	2.617378	2.667563	-1.644507
H	1.681776	3.330208	-3.014037
H	1.786660	4.235381	-1.491005
C	4.031819	-0.693016	-1.374542
H	4.393173	-0.745011	-2.403567
C	2.787322	-0.129120	-1.105761
H	2.178806	0.235428	-1.934980
C	-0.558270	3.432426	1.924813
H	-1.523348	3.408601	1.397854
H	-0.525265	2.583626	2.626530
H	-0.502802	4.359715	2.516642
C	4.339776	-1.143589	0.974352
H	4.942065	-1.541750	1.793287
C	0.454313	2.495116	-1.422244
H	0.420240	1.517953	-1.927480
C	3.098472	-0.564711	1.239864
H	2.736031	-0.506812	2.269797
C	-0.829148	3.233547	-1.815769
H	-1.713077	2.665723	-1.490004
H	-0.878623	4.236374	-1.361959
H	-0.879532	3.363479	-2.908214

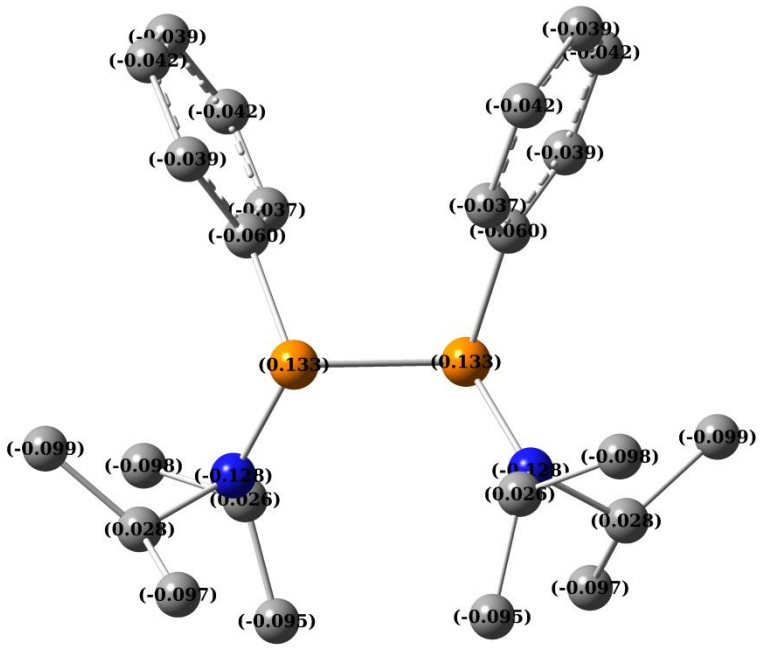


Fig. S253. Hirshfeld atomic charges of diphosphane **19**

P	-0.865110	-0.085210	0.711741
N	-1.824675	-1.405019	0.166235
C	-2.838531	3.894851	-0.740562
H	-3.307943	4.830734	-1.049783
C	-1.916537	-2.829925	2.204846
H	-1.329383	-3.620084	1.715199
H	-2.594415	-3.302145	2.933340
H	-1.223293	-2.177491	2.758624
C	-2.708256	-2.032702	1.168901
H	-3.324365	-2.754517	0.611108
C	-1.633042	1.481087	0.052441
C	-1.845366	-3.162829	-1.569131
H	-0.829057	-3.430714	-1.249911
H	-1.934634	-3.343404	-2.651698
H	-2.556284	-3.835590	-1.062837
C	-2.668189	3.610569	0.612501
H	-3.000636	4.324513	1.368555
C	-2.069928	2.412759	1.002090
H	-1.933395	2.196371	2.064652
C	-3.671186	-1.042109	1.831848
H	-4.224734	-0.464714	1.077126
H	-3.123102	-0.330513	2.469951
H	-4.397259	-1.573269	2.467362
C	-2.401173	2.981082	-1.699332
H	-2.525604	3.200590	-2.761619
C	-2.118215	-1.691957	-1.244345
H	-1.393975	-1.103378	-1.827540

C	-1.800048	1.787625	-1.306145
H	-1.448103	1.092285	-2.070836
C	-3.523284	-1.263289	-1.680387
H	-3.697182	-0.200321	-1.459764
H	-4.303360	-1.852847	-1.172327
H	-3.650304	-1.417052	-2.763545
P	0.865126	-0.085253	-0.711734
N	1.824737	-1.404973	-0.166090
C	2.838392	3.895034	0.740162
H	3.307768	4.830967	1.049286
C	3.671254	-1.042169	-1.831711
H	4.224781	-0.464700	-1.077031
H	4.397342	-1.573364	-2.467176
H	3.123157	-0.330637	-2.469876
C	2.708339	-2.032726	-1.168691
H	3.324458	-2.754481	-0.610828
C	1.632999	1.481142	-0.052596
C	3.523301	-1.263054	1.680559
H	3.697172	-0.200096	1.459868
H	3.650303	-1.416742	2.763729
H	4.303404	-1.852621	1.172554
C	2.401103	2.981328	1.699024
H	2.525551	3.200936	2.761289
C	1.800026	1.787807	1.305958
H	1.448131	1.092521	2.070719
C	1.916646	-2.830056	-2.204574
H	1.329498	-3.620179	-1.714862
H	1.223396	-2.177680	-2.758417
H	2.594538	-3.302329	-2.933018
C	2.668029	3.610624	-0.612872
H	3.000422	4.324517	-1.368997
C	2.118253	-1.691793	1.244519
H	1.393985	-1.103187	1.827651
C	2.069817	2.412749	-1.002339
H	1.933268	2.196260	-2.064879
C	1.845431	-3.162646	1.569412
H	0.829140	-3.430582	1.250177
H	2.556383	-3.835429	1.063197
H	1.934665	-3.343135	2.651996

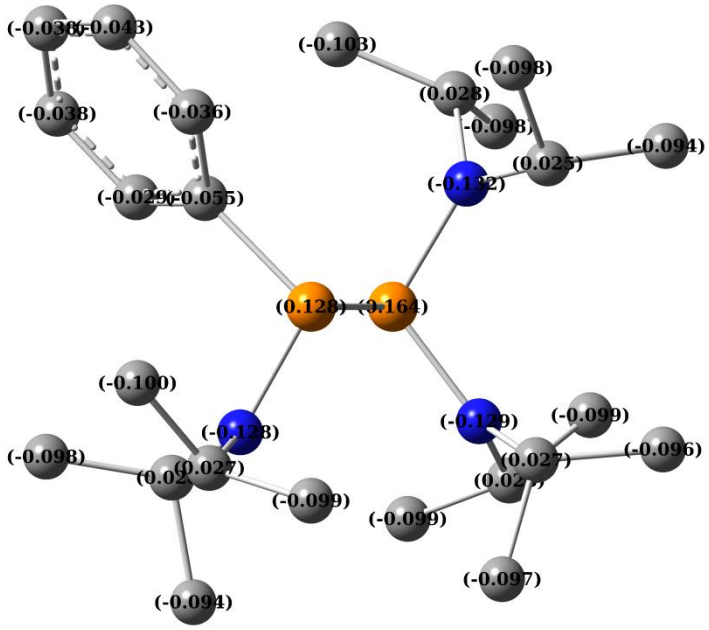


Fig. S254. Hirshfeld atomic charges of diphosphane **20**

N	-1.486588	-1.765195	0.141250
N	1.915623	-1.074632	-0.283561
N	1.375701	1.672173	0.271031
P	-0.883470	-0.252887	0.736564
P	0.868041	0.261334	-0.593887
C	-1.676718	-2.055898	-1.291346
H	-1.046925	-1.329970	-1.829245
C	-3.118746	-1.891594	-1.790708
H	-3.533362	-0.910056	-1.526671
H	-3.778890	-2.667678	-1.371312
H	-3.150687	-1.994096	-2.886872
C	-1.153261	-3.447611	-1.658698
H	-0.091249	-3.550200	-1.402712
H	-1.265994	-3.621024	-2.740379
H	-1.708903	-4.244745	-1.139076
C	-2.350613	-2.517398	1.078887
H	-2.716431	-3.386892	0.510389
C	-3.581409	-1.734804	1.555652
H	-4.134082	-1.293493	0.715055
H	-3.284708	-0.916738	2.231384
H	-4.264307	-2.395860	2.112522
C	-1.565000	-3.060674	2.272448
H	-2.236790	-3.601293	2.957247
H	-1.094602	-2.239925	2.836385
H	-0.777217	-3.751906	1.946393
C	2.869566	-1.457453	-1.344590
H	3.319410	-2.404522	-1.009429
C	2.185266	-1.749055	-2.681228

H	2.923055	-2.113161	-3.413286
H	1.714915	-0.843918	-3.094019
H	1.406179	-2.515200	-2.563284
C	4.013543	-0.455904	-1.522355
H	4.494565	-0.226901	-0.560670
H	3.643275	0.484736	-1.951559
H	4.779088	-0.858603	-2.204942
C	2.060461	-1.797002	0.993059
H	1.303129	-1.376445	1.671697
C	1.730253	-3.284429	0.846139
H	0.724076	-3.397349	0.427428
H	1.758854	-3.778894	1.829708
H	2.447883	-3.809137	0.195592
C	3.428952	-1.616153	1.658318
H	3.668356	-0.556421	1.811374
H	4.234344	-2.065581	1.055630
H	3.438085	-2.114947	2.639911
C	1.753776	1.681861	1.689816
H	1.626136	0.650812	2.047082
C	3.226406	2.058116	1.896015
H	3.874249	1.468308	1.231668
H	3.529531	1.872358	2.938303
H	3.410153	3.123752	1.686430
C	0.834294	2.562279	2.541665
H	-0.212865	2.254377	2.418823
H	0.913416	3.625199	2.262478
H	1.100065	2.478302	3.607313
C	1.535476	2.954397	-0.446149
H	1.870140	3.673178	0.317174
C	2.621210	2.920508	-1.522232
H	3.582992	2.592489	-1.102590
H	2.758078	3.921201	-1.961801
H	2.341899	2.232845	-2.336177
C	0.225530	3.501968	-1.010668
H	-0.555926	3.540591	-0.238316
H	-0.141945	2.869909	-1.832485
H	0.377852	4.517746	-1.409498
C	-2.027580	1.067363	0.083405
C	-2.275198	1.322954	-1.272404
C	-2.702741	1.843182	1.034050
C	-3.173775	2.312047	-1.663393
H	-1.742055	0.757475	-2.038729
C	-3.592786	2.845854	0.649243
H	-2.528524	1.655847	2.096945
C	-3.832071	3.080121	-0.702960
H	-3.350967	2.494066	-2.725267
H	-4.103328	3.441791	1.408322

H -4.530707 3.860805 -1.009903

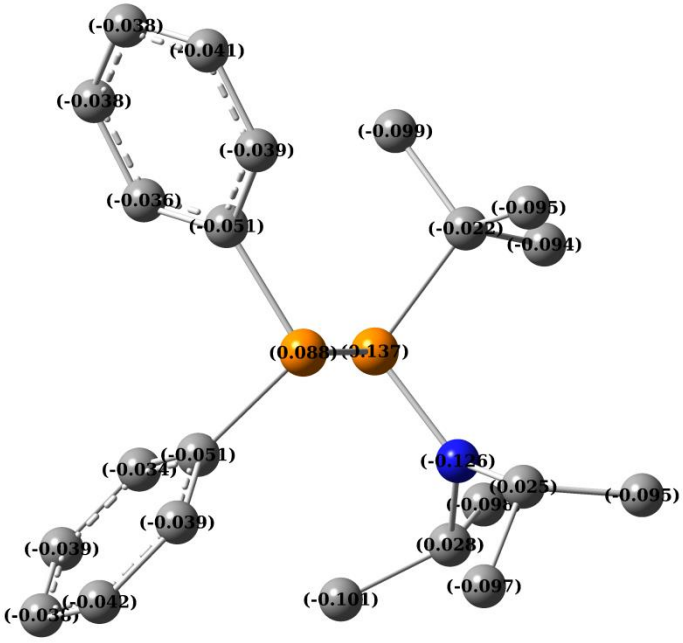


Fig. S255. Hirshfeld atomic charges of diphosphane **21**

P -0.557000 -0.768754 -0.645756
P 0.700630 0.294028 0.909391
N -2.125812 -0.499285 0.020040
C 2.418784 -0.147892 0.375303
C 2.977606 0.150547 -0.874460
H 2.403874 0.714670 -1.609865
C 0.428269 2.419088 -1.049570
H 0.435447 1.658214 -1.832037
C -2.450994 -0.589360 1.452704
H -1.539211 -0.949306 1.948167
C 0.513567 2.033981 0.295416
C 4.476579 -1.297935 0.975513
H 5.060241 -1.861094 1.706190
C -2.774353 0.771922 2.079037
H -1.960166 1.488573 1.898358
H -3.703910 1.203379 1.674683
H -2.905632 0.665693 3.167152
C 5.014723 -1.005611 -0.275512
H 6.021199 -1.341490 -0.532103
C 3.190514 -0.866032 1.298375
H 2.774807 -1.089233 2.283933
C 4.264031 -0.273554 -1.196108
H 4.682805 -0.036262 -2.175939
C 0.312873 4.374346 0.931702
H 0.264244 5.135121 1.712947
C 0.235100 4.741711 -0.410043

H	0.122745	5.792113	-0.685208
C	0.449575	3.030708	1.278753
H	0.506612	2.746399	2.332449
C	0.293104	3.760481	-1.399166
H	0.221669	4.039435	-2.452291
C	-3.559869	-1.608837	1.729781
H	-4.512960	-1.313216	1.262904
H	-3.288592	-2.601684	1.342439
H	-3.737676	-1.699853	2.812711
C	-0.159967	-2.618600	-0.350960
C	-1.308292	-3.397652	-1.007827
H	-2.269572	-3.191542	-0.517308
H	-1.413180	-3.145863	-2.074869
H	-1.108607	-4.480025	-0.934318
C	-0.013640	-3.069789	1.106350
H	0.760735	-2.502322	1.643413
H	-0.957034	-2.975106	1.662801
H	0.277469	-4.134302	1.135990
C	-3.166277	0.079497	-0.852855
H	-4.060207	0.174205	-0.217131
C	-2.830839	1.482497	-1.363374
H	-2.518480	2.142794	-0.541721
H	-2.011908	1.445625	-2.097577
H	-3.706731	1.930242	-1.859471
C	-3.544728	-0.850926	-2.005760
H	-2.683067	-1.019778	-2.671009
H	-3.884735	-1.826421	-1.628817
H	-4.354725	-0.409067	-2.607144
C	1.136510	-2.930093	-1.118696
H	1.092604	-2.553809	-2.153037
H	2.023828	-2.498068	-0.637370
H	1.280689	-4.023127	-1.163348

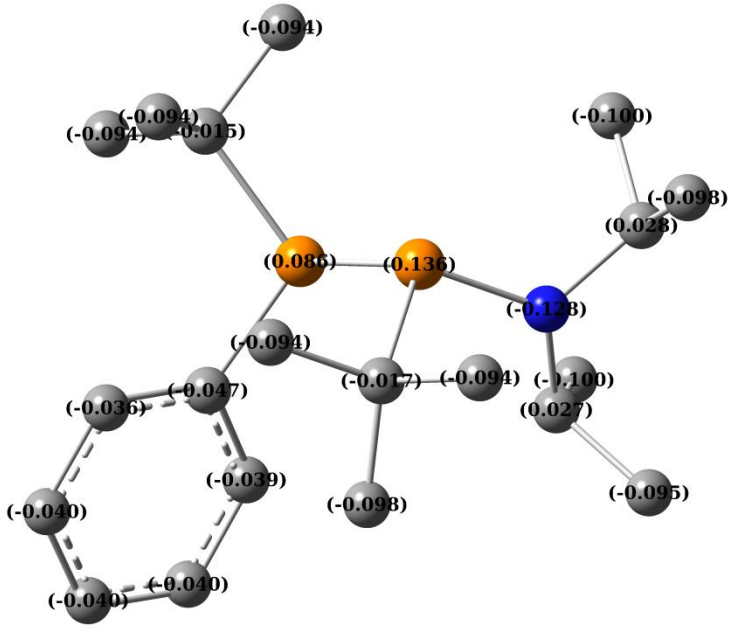


Fig. S256. Hirshfeld atomic charges of diphosphane **22**

P	0.955007	0.433749	0.705218
P	-0.697181	0.899472	-0.753238
N	2.113001	-0.356178	-0.297096
C	-2.076589	-0.320005	-0.580812
C	-3.118766	-0.301647	0.356789
H	-3.192000	0.509367	1.080045
C	1.783783	-1.461518	-1.210016
H	0.754327	-1.758082	-0.963149
C	-2.987411	-2.402189	-1.464026
H	-2.932788	-3.217190	-2.188300
C	1.782992	-1.066559	-2.692362
H	1.109967	-0.214942	-2.865623
H	2.789848	-0.795863	-3.047625
H	1.438096	-1.914344	-3.305748
C	-4.003766	-2.378294	-0.510912
H	-4.746969	-3.176808	-0.477348
C	-2.045783	-1.376424	-1.505617
H	-1.264258	-1.393155	-2.269129
C	-4.072343	-1.317100	0.390453
H	-4.870762	-1.281322	1.134092
C	2.682722	-2.677128	-0.962810
H	3.735755	-2.455736	-1.200027
H	2.635945	-2.992430	0.089830
H	2.373295	-3.524779	-1.594307
C	0.455638	-0.873305	2.006627
C	1.752395	-1.166062	2.777830
H	2.504604	-1.632734	2.125953
H	2.191556	-0.249701	3.202115

H	1.538539	-1.858932	3.609281
C	-0.132757	-2.202312	1.518561
H	-1.059882	-2.070476	0.947916
H	0.580136	-2.769048	0.904810
H	-0.371148	-2.830267	2.394957
C	3.386650	0.346081	-0.545733
H	3.941772	-0.288115	-1.254585
C	3.212127	1.717468	-1.205790
H	2.572063	1.649806	-2.097329
H	2.747372	2.429019	-0.505730
H	4.188063	2.130881	-1.506191
C	4.238593	0.444767	0.719582
H	3.726057	1.045984	1.487231
H	4.433130	-0.553137	1.139099
H	5.204731	0.926288	0.501094
C	-0.541289	-0.195819	2.955221
H	-0.144122	0.748724	3.358380
H	-1.499077	0.013166	2.460130
H	-0.750549	-0.864222	3.807355
C	-1.332864	2.597237	-0.158848
C	-1.545860	2.785275	1.346800
C	-0.250719	3.591604	-0.615910
C	-2.631262	2.893349	-0.924417
H	-2.331414	2.134949	1.754560
H	-0.617530	2.594851	1.904494
H	-1.849146	3.827496	1.547725
H	-0.069357	3.522885	-1.699244
H	-0.569928	4.621663	-0.383432
H	0.702734	3.411317	-0.096196
H	-2.932329	3.939812	-0.747846
H	-2.496794	2.759260	-2.009431
H	-3.461284	2.246234	-0.605510

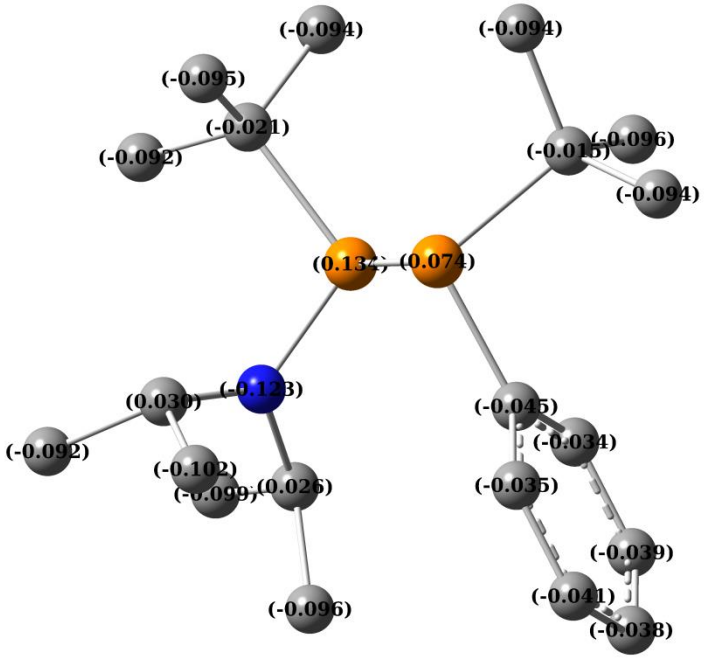


Fig. S257. Hirshfeld atomic charges of diphosphane **23**

P	-0.827820	0.608122	-0.668635
P	0.933539	0.891082	0.754994
N	-1.475867	-0.875860	-0.068140
C	1.825117	-0.641558	0.191355
C	1.950546	-1.054989	-1.143860
H	1.484340	-0.470724	-1.938560
C	-1.407426	-1.985978	-1.043494
H	-0.710690	-1.624525	-1.814531
C	3.104979	-2.604278	0.859768
H	3.552523	-3.207260	1.652230
C	-0.795636	-3.278512	-0.499706
H	0.174319	-3.087254	-0.019525
H	-1.455235	-3.783997	0.221819
H	-0.630539	-3.978753	-1.333421
C	3.218804	-3.000210	-0.471099
H	3.754013	-3.916214	-0.728523
C	2.414784	-1.436273	1.183490
H	2.328897	-1.133848	2.229914
C	2.640204	-2.220392	-1.471849
H	2.721368	-2.523523	-2.517693
C	-2.731232	-2.252275	-1.773093
H	-3.480206	-2.738163	-1.132598
H	-3.157819	-1.310748	-2.150062
H	-2.554282	-2.914885	-2.635541
C	-2.062232	2.001464	-0.221126
C	-1.986646	2.588694	1.194494
H	-2.207393	1.847640	1.975181

H	-0.996880	3.010163	1.417254
H	-2.724962	3.403357	1.294542
C	-3.477621	1.473770	-0.492002
H	-3.551467	0.995136	-1.481206
H	-3.800022	0.744332	0.262076
H	-4.192079	2.314079	-0.472610
C	-2.008456	-1.055701	1.293916
H	-2.204039	-0.037485	1.654516
C	-3.353311	-1.789543	1.344306
H	-4.080748	-1.359730	0.641737
H	-3.247217	-2.860500	1.116590
H	-3.770678	-1.712586	2.360232
C	-1.035177	-1.674122	2.308402
H	-0.804216	-2.724354	2.085773
H	-0.095200	-1.110499	2.345521
H	-1.487647	-1.636101	3.312631
C	-1.773694	3.118380	-1.241276
H	-0.752278	3.515873	-1.149764
H	-1.900687	2.758984	-2.273774
H	-2.469002	3.959816	-1.081697
C	2.062566	2.267373	0.035788
C	2.101962	2.371647	-1.491532
C	1.602632	3.603228	0.638893
C	3.478125	1.971922	0.558908
H	2.534739	1.469806	-1.947075
H	1.104611	2.526655	-1.928825
H	2.736427	3.225186	-1.788273
H	1.542325	3.549623	1.737242
H	2.322068	4.396873	0.375767
H	0.619908	3.917733	0.260292
H	4.149452	2.806105	0.292653
H	3.491511	1.865283	1.655626
H	3.892339	1.051584	0.122001

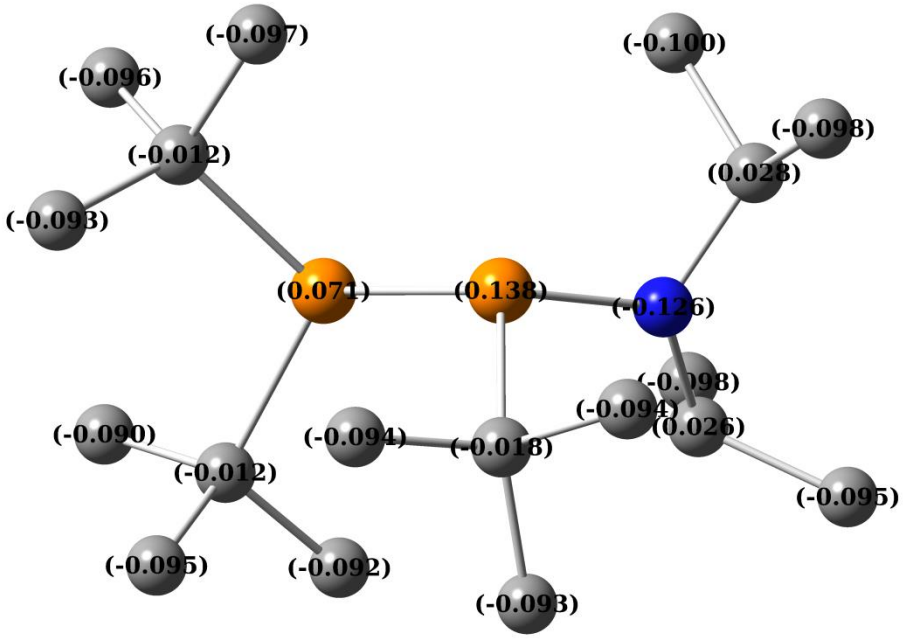


Fig. S258. Hirshfeld atomic charges of diphosphane **24**

P	0.620751	0.363388	0.708609
P	-1.216543	0.319169	-0.593150
N	1.948046	0.252919	-0.381754
C	2.145088	-0.826428	-1.358016
H	1.436856	-1.612916	-1.073226
C	1.812261	-0.422286	-2.799329
H	0.811191	0.029040	-2.851213
H	2.539258	0.303545	-3.197551
H	1.834748	-1.305351	-3.457529
C	3.550613	-1.427704	-1.258899
H	4.324981	-0.705104	-1.561823
H	3.770009	-1.741783	-0.227675
H	3.643149	-2.304340	-1.919170
C	0.862399	-1.057714	1.951078
C	2.134103	-0.681703	2.730553
H	3.009981	-0.653896	2.066097
H	2.038526	0.303105	3.212778
H	2.322388	-1.432372	3.517103
C	1.048357	-2.475076	1.400738
H	0.230305	-2.788072	0.740665
H	1.990348	-2.567562	0.842618
H	1.094607	-3.194988	2.236539
C	2.712971	1.493104	-0.630220
H	3.434353	1.239770	-1.422257
C	1.863708	2.654237	-1.155447
H	1.242115	2.339291	-2.005842

H	1.194451	3.033522	-0.368368
H	2.509482	3.485953	-1.479359
C	3.529144	1.911709	0.592329
H	2.867344	2.144955	1.441232
H	4.213846	1.107363	0.899387
H	4.126110	2.810527	0.370099
C	-0.334106	-1.000437	2.909433
H	-0.447062	0.003784	3.348763
H	-1.277407	-1.261242	2.412077
H	-0.184919	-1.713580	3.737343
C	-2.432919	1.520394	0.313706
C	-3.376890	0.895659	1.346517
C	-1.634510	2.633338	1.011535
C	-3.262776	2.206460	-0.790620
H	-4.089411	0.192518	0.893376
H	-2.825177	0.371519	2.140364
H	-3.971651	1.692622	1.826093
H	-0.888530	3.085551	0.341444
H	-2.336939	3.426700	1.319021
H	-1.106525	2.275919	1.904908
H	-3.934160	2.953720	-0.333047
H	-2.608732	2.728425	-1.505084
H	-3.889972	1.507357	-1.357914
C	-2.125229	-1.354514	-0.906793
C	-1.194765	-2.190577	-1.799804
C	-2.546637	-2.213760	0.291635
C	-3.379841	-1.035667	-1.740434
H	-0.894924	-1.642455	-2.704924
H	-0.283864	-2.503742	-1.272003
H	-1.718726	-3.108745	-2.115293
H	-3.201102	-1.679202	0.989911
H	-3.102702	-3.095035	-0.073809
H	-1.683867	-2.588955	0.853917
H	-3.796152	-1.976511	-2.139317
H	-4.169366	-0.561324	-1.141173
H	-3.148141	-0.381008	-2.594524

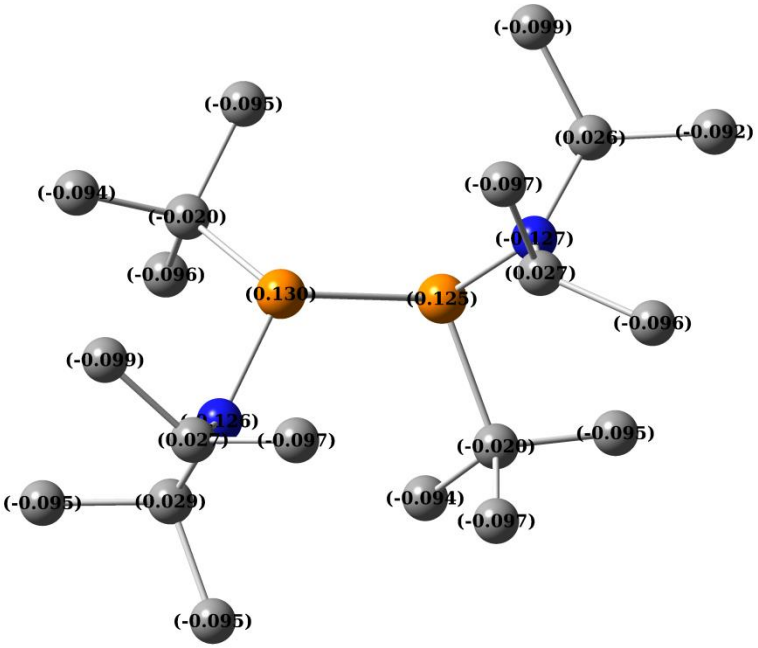


Fig. S259. Hirshfeld atomic charges of diphosphane **25**

P	-0.750818	0.761230	0.173014
P	0.993355	-0.078064	-1.057386
N	-2.043880	-0.333099	0.551689
C	-2.975738	-0.974128	-0.393912
H	-2.547303	-0.803296	-1.389170
C	-3.092813	-2.492914	-0.203749
H	-2.118826	-2.991456	-0.255674
H	-3.558704	-2.751418	0.759780
H	-3.731836	-2.914967	-0.994946
C	-4.385270	-0.366578	-0.391313
H	-4.888094	-0.522630	0.576332
H	-4.371730	0.710959	-0.597506
H	-5.003773	-0.849965	-1.163483
C	-1.401206	2.064098	-1.071111
C	-2.497582	2.867569	-0.356923
H	-3.344360	2.242392	-0.048491
H	-2.103732	3.361365	0.544757
H	-2.883046	3.651107	-1.031412
C	-1.917978	1.535151	-2.415301
H	-1.187599	0.863332	-2.892716
H	-2.873136	1.002173	-2.314916
H	-2.093218	2.378947	-3.105177
C	-2.426141	-0.410812	1.980834
H	-3.227403	-1.164063	2.028189
C	-1.294645	-0.919560	2.875653
H	-0.887244	-1.870149	2.501917
H	-0.476873	-0.184865	2.928243
H	-1.665798	-1.082608	3.899479

C	-3.001388	0.896002	2.535273
H	-2.241549	1.692523	2.512949
H	-3.868975	1.232468	1.950182
H	-3.324279	0.761626	3.579772
C	-0.232685	3.026863	-1.340251
H	0.185618	3.421643	-0.400747
H	0.575735	2.547259	-1.910319
H	-0.599258	3.884401	-1.929533
C	0.864887	-1.959723	-1.304955
C	0.504773	-2.780525	-0.063275
C	-0.163325	-2.183020	-2.421974
C	2.242461	-2.399063	-1.825066
H	1.332155	-2.808074	0.657438
H	-0.374414	-2.368043	0.445188
H	0.286141	-3.825486	-0.346788
H	0.100293	-1.613021	-3.327040
H	-0.196498	-3.251938	-2.693079
H	-1.177722	-1.891507	-2.122589
H	2.236185	-3.484730	-2.022488
H	2.503870	-1.884265	-2.763246
H	3.032387	-2.186481	-1.090619
N	2.301689	0.128523	0.061563
C	2.198956	-0.277283	1.471744
C	2.227705	0.876976	2.478750
C	3.186254	-1.374380	1.905513
H	1.197550	-0.721054	1.552449
H	1.512725	1.660648	2.193060
H	1.949509	0.498469	3.475829
H	3.231117	1.319822	2.569903
H	3.295808	-2.149920	1.134892
H	4.186068	-0.975673	2.125510
H	2.816598	-1.856291	2.824875
C	3.407089	0.963562	-0.447379
C	4.798887	0.419965	-0.116692
C	3.319121	2.455405	-0.093711
H	3.301119	0.901323	-1.542112
H	4.882200	-0.650158	-0.354306
H	5.552341	0.964187	-0.707012
H	5.053645	0.563041	0.944301
H	2.307543	2.839258	-0.276857
H	3.575742	2.654748	0.955996
H	4.020130	3.029280	-0.720945

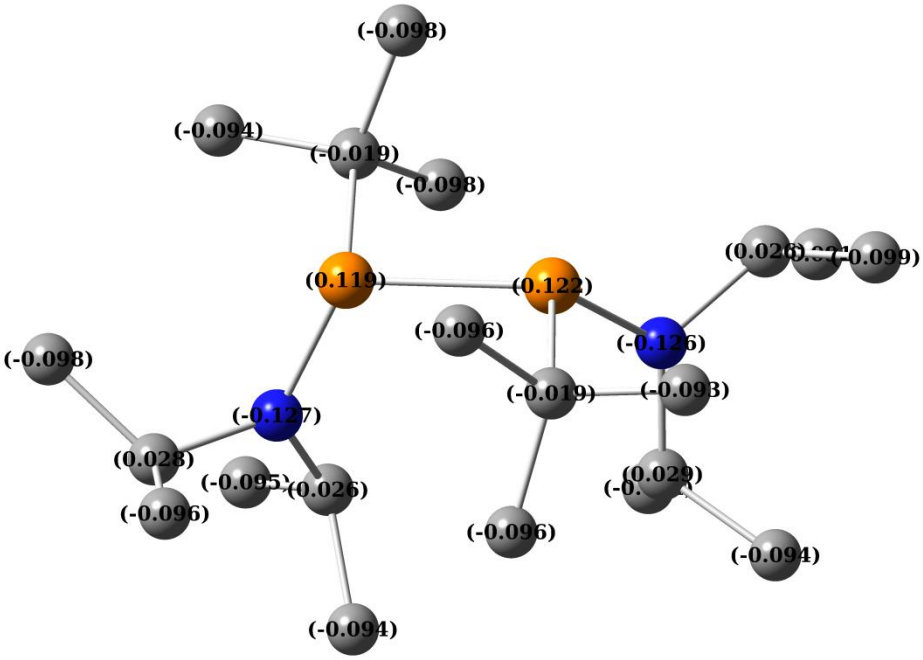


Fig. S260. Hirshfeld atomic charges of diphosphane **26**

P	-1.222479	0.004157	-0.998952
P	0.989506	0.425596	-1.048143
N	-2.074182	0.147732	0.500686
C	-1.683959	-0.484499	1.765043
H	-0.724349	-0.970208	1.560282
C	-1.454404	0.529551	2.892670
H	-0.744633	1.311669	2.590500
H	-2.391325	1.023187	3.195058
H	-1.051645	0.024046	3.784172
C	-2.658958	-1.573863	2.228224
H	-3.650888	-1.157879	2.466543
H	-2.793451	-2.346294	1.458459
H	-2.279059	-2.062574	3.139248
C	-1.199852	-1.849313	-1.491628
C	-2.657213	-2.317225	-1.587916
H	-3.165162	-2.270829	-0.615210
H	-3.233704	-1.707898	-2.300431
H	-2.686532	-3.364362	-1.934382
C	-0.429890	-2.788326	-0.555839
H	0.605963	-2.454709	-0.412473
H	-0.904750	-2.864414	0.433118
H	-0.407694	-3.805859	-0.984117
C	-3.326362	0.936182	0.523636
H	-3.743495	0.790799	1.532456
C	-3.104598	2.440034	0.353506
H	-2.446027	2.836464	1.139109
H	-2.649495	2.660963	-0.623916

H	-4.063554	2.978526	0.410032
C	-4.387092	0.429939	-0.455506
H	-4.045523	0.536158	-1.496694
H	-4.618850	-0.628489	-0.273975
H	-5.316826	1.009128	-0.341905
C	-0.581037	-1.923054	-2.898260
H	-1.068728	-1.219645	-3.591366
H	0.493418	-1.692644	-2.889050
H	-0.711043	-2.942129	-3.301107
C	1.070069	2.316747	-0.800997
C	2.528451	2.748310	-1.004767
C	0.234570	2.927295	-1.939922
C	0.565140	2.852851	0.542270
H	3.201770	2.294241	-0.264954
H	2.892169	2.477734	-2.008304
H	2.605951	3.844164	-0.902077
H	-0.839012	2.733237	-1.816189
H	0.387711	4.019749	-1.958146
H	0.535514	2.524308	-2.919654
H	0.499393	3.954430	0.506579
H	-0.432585	2.461905	0.773570
H	1.242027	2.596384	1.369780
N	1.989254	-0.365218	0.131501
C	3.095418	-1.139026	-0.482909
C	3.497390	-2.405738	0.275174
C	4.338525	-0.302112	-0.809323
H	2.689951	-1.479221	-1.450092
H	2.632857	-3.042379	0.506118
H	4.185613	-2.988618	-0.355495
H	4.028537	-2.182189	1.212196
H	4.084536	0.522716	-1.488084
H	4.797464	0.123649	0.095170
H	5.095061	-0.927216	-1.309972
C	1.889634	-0.145845	1.582004
C	3.075348	0.602793	2.201569
C	1.590568	-1.400875	2.425602
H	1.012323	0.503360	1.688282
H	3.283625	1.545302	1.676917
H	2.856816	0.838851	3.255436
H	3.991708	-0.007146	2.186400
H	0.921285	-2.094779	1.900858
H	2.500997	-1.950930	2.697733
H	1.102245	-1.097392	3.364911

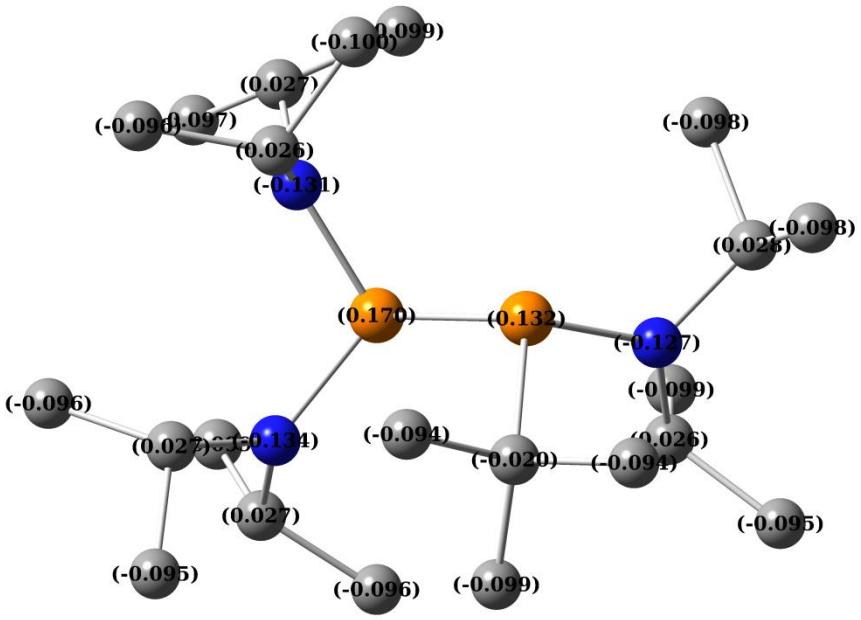


Fig. S261. Hirshfeld atomic charges of diphosphane **27**

N	2.481451	0.156483	-0.359517
N	-1.555666	1.450811	0.106323
N	-1.566109	-1.328066	-0.313054
P	1.212427	0.274288	0.802703
P	-0.639643	0.132710	-0.552665
C	2.558856	-0.877789	-1.398494
H	1.751114	-1.585491	-1.171660
C	3.877018	-1.657040	-1.337911
H	4.033379	-2.091885	-0.339817
H	4.741215	-1.011777	-1.563866
H	3.875777	-2.475068	-2.075246
C	2.298513	-0.344898	-2.812756
H	1.327332	0.168602	-2.855247
H	2.284910	-1.176930	-3.534822
H	3.081715	0.357762	-3.138529
C	3.383788	1.312994	-0.513284
H	4.089602	1.032721	-1.310857
C	4.219991	1.574921	0.739925
H	4.795188	0.681139	1.022081
H	3.575706	1.852556	1.588913
H	4.926752	2.401498	0.565387
C	2.666649	2.584428	-0.971224
H	3.390034	3.391612	-1.168174
H	1.969944	2.934557	-0.193782
H	2.089718	2.402537	-1.888722
C	-2.006263	2.510470	-0.820749

H	-2.499625	3.263361	-0.186842
C	-0.858559	3.217219	-1.545868
H	-1.240792	4.045716	-2.162965
H	-0.326968	2.515513	-2.207582
H	-0.132652	3.625564	-0.829792
C	-3.058916	2.024489	-1.814146
H	-3.908573	1.555941	-1.296295
H	-2.632780	1.291849	-2.513457
H	-3.442286	2.869529	-2.407365
C	-1.606813	1.803913	1.536843
H	-1.128245	0.970363	2.070530
C	-0.806408	3.064233	1.889216
H	0.234191	2.964345	1.553274
H	-0.802445	3.212341	2.980520
H	-1.243713	3.968811	1.437659
C	-3.043099	1.916982	2.060150
H	-3.608920	0.992831	1.885703
H	-3.587380	2.742736	1.574594
H	-3.038489	2.120578	3.142398
C	-2.521717	-1.503165	0.792373
H	-2.229475	-0.773110	1.558428
C	-3.969726	-1.180871	0.403424
H	-4.033359	-0.183011	-0.049886
H	-4.620180	-1.203262	1.292317
H	-4.369049	-1.916096	-0.313094
C	-2.447254	-2.891020	1.440138
H	-1.431306	-3.128028	1.780236
H	-2.768437	-3.684909	0.748051
H	-3.118247	-2.931271	2.312625
C	-1.829743	-2.157847	-1.512092
H	-2.486607	-2.968465	-1.161204
C	-2.567583	-1.445274	-2.651097
H	-3.477126	-0.943478	-2.296385
H	-2.855642	-2.173117	-3.426074
H	-1.917531	-0.692974	-3.123484
C	-0.567604	-2.825759	-2.058446
H	-0.037860	-3.389434	-1.278234
H	0.119538	-2.075096	-2.476841
H	-0.829387	-3.522885	-2.869729
C	1.421032	-1.254091	1.923651
C	1.259577	-2.621066	1.253992
C	2.826855	-1.150192	2.530252
C	0.395384	-1.096947	3.054708
H	0.317285	-2.676086	0.696366
H	2.086696	-2.834326	0.562026
H	1.262349	-3.418213	2.018518
H	2.973009	-0.195690	3.059368

H	2.978208	-1.968804	3.254675
H	3.602008	-1.229195	1.755364
H	0.541496	-1.889353	3.808203
H	0.504138	-0.125124	3.562022
H	-0.637580	-1.181090	2.692238

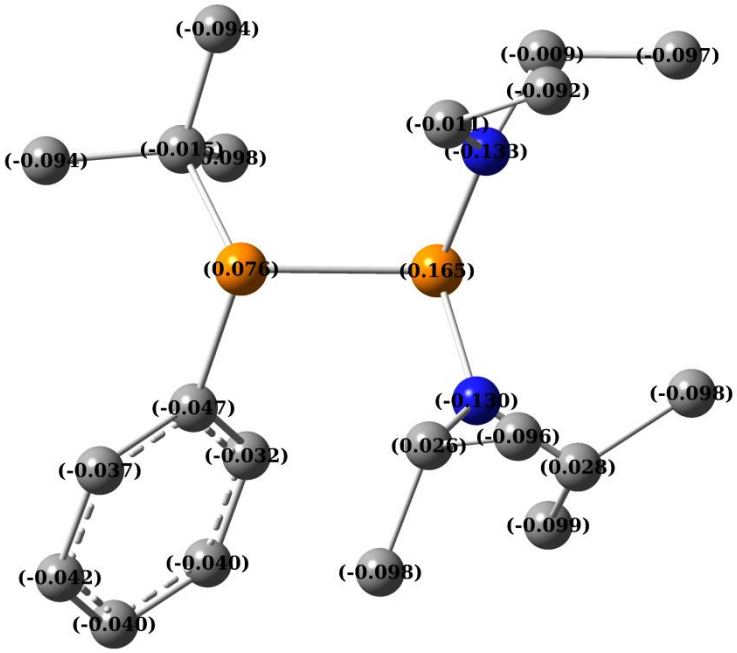


Fig. S262. Hirshfeld atomic charges of diphosphane **28**

P	0.794332	0.060199	-0.590871
P	-0.715877	1.121418	0.719462
N	2.271538	0.726309	0.019609
C	-0.890456	2.814370	-0.151478
C	-2.263615	0.245790	0.213394
C	-2.491053	-0.299731	-1.057637
H	-1.730112	-0.201247	-1.833076
C	-3.254830	0.087638	1.191823
H	-3.086614	0.495178	2.191645
C	-1.064689	2.751968	-1.671046
H	-0.212642	2.258123	-2.162116
H	-1.981536	2.211886	-1.950272
H	-1.146642	3.774633	-2.078591
C	-2.119405	3.488789	0.476250
H	-3.045301	2.938022	0.250220
H	-2.023418	3.565758	1.570949
H	-2.228150	4.509981	0.072614
C	4.272169	0.651958	-1.515926
H	4.940789	0.277098	-0.728356
H	3.902851	-0.214191	-2.082299
H	4.865142	1.280278	-2.199766

C	3.966426	0.507890	1.856370
H	4.143202	-0.546638	1.594336
H	4.751904	1.112239	1.378009
H	4.080564	0.621810	2.945551
C	0.361418	3.630833	0.199522
H	0.512680	3.687805	1.289076
H	1.267464	3.200935	-0.249427
H	0.253988	4.660397	-0.181822
C	2.570353	0.953265	1.428067
H	1.822540	0.417856	2.028432
C	3.105544	1.451622	-0.937713
H	3.486353	2.365969	-0.445504
N	0.599813	-1.539004	0.005113
C	2.278468	-2.596492	-1.533527
H	2.365983	-1.761703	-2.246133
H	3.038026	-2.459399	-0.750014
H	2.497860	-3.527248	-2.080169
C	1.563648	-2.569088	2.071784
H	1.816072	-3.536061	1.607854
H	2.445357	-1.917807	1.996024
H	1.362602	-2.758075	3.137936
C	-0.196113	-2.774684	-2.016217
H	-1.196139	-2.862114	-1.567542
H	-0.188953	-1.891134	-2.674723
H	-0.010074	-3.662784	-2.640946
C	0.345878	-1.923180	1.402098
H	0.128959	-0.988789	1.942007
C	0.873496	-2.648331	-0.930618
H	0.823322	-3.566269	-0.325657
C	-4.648653	-1.132507	-0.355856
H	-5.572221	-1.670909	-0.577181
C	-4.440818	-0.589826	0.910701
H	-5.200440	-0.701389	1.686942
C	-3.670372	-0.985408	-1.339188
H	-3.823605	-1.412242	-2.332516
C	-0.898827	-2.807781	1.537332
H	-1.768020	-2.334981	1.059571
H	-0.749207	-3.799093	1.079962
H	-1.132124	-2.971309	2.601020
H	2.474587	1.800016	-1.772925
H	2.447254	2.027443	1.676188

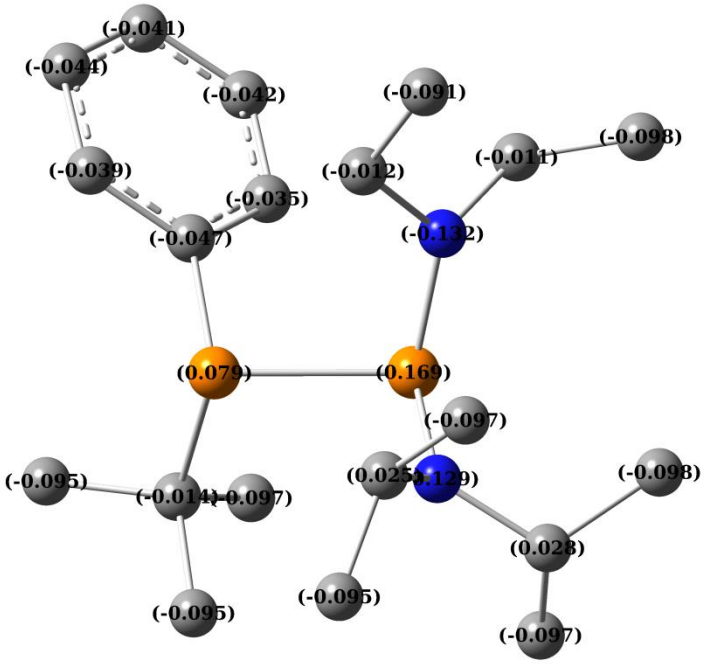


Fig. S263. Hirshfeld atomic charges of diphosphane **29**

P	0.619551	0.131712	-0.604564
P	-0.799736	-1.023466	0.717477
N	0.316643	1.761316	-0.079155
C	-0.955925	-2.702845	-0.182079
C	-2.371054	-0.165274	0.239143
C	-3.354738	-0.037175	1.229938
H	-3.166861	-0.451284	2.223597
C	-2.627989	0.387298	-1.024202
H	-1.879398	0.306536	-1.814400
C	-2.178267	-3.404641	0.427102
H	-2.092604	-3.489198	1.522178
H	-3.112057	-2.869738	0.195395
H	-2.263097	-4.424488	0.014458
C	-1.122686	-2.615579	-1.701237
H	-2.042751	-2.079343	-1.977040
H	-0.271209	-2.108530	-2.178830
H	-1.193965	-3.632277	-2.125192
C	0.961435	3.733977	-1.501397
H	1.243543	4.354826	-0.639768
H	1.872757	3.245787	-1.875089
H	0.581230	4.400838	-2.292025
C	0.353323	3.469305	1.772618
H	1.450497	3.542876	1.730954
H	-0.068209	4.304909	1.194336
H	0.038004	3.604477	2.818747
C	0.309456	-3.500638	0.159609
H	1.211697	-3.000193	-0.218590

H	0.420818	-3.625943	1.248463
H	0.253566	-4.504596	-0.294103
C	-0.141412	2.118290	1.263305
H	0.193945	1.338242	1.961055
C	-0.092361	2.689361	-1.136624
H	-1.036570	3.181800	-0.836180
N	2.115190	-0.417052	0.054023
C	3.532542	0.865862	-1.598550
H	2.732338	1.088263	-2.322122
H	3.589411	1.699254	-0.884470
H	4.483008	0.814976	-2.152838
C	3.255091	0.899431	1.857567
H	4.274488	0.860654	1.440435
H	2.763206	1.802061	1.469966
H	3.349023	0.990684	2.950975
C	3.127561	-1.609150	-1.879433
H	3.064298	-2.576110	-1.359373
H	2.220374	-1.486934	-2.492005
H	3.994196	-1.637607	-2.558552
C	2.449105	-0.349583	1.486565
H	1.484879	-0.299046	2.013055
C	3.262187	-0.460135	-0.880075
H	4.145528	-0.674507	-0.259413
C	-4.797299	1.160600	-0.290959
H	-5.737039	1.676528	-0.496982
C	-3.826307	1.048258	-1.285520
H	-4.002327	1.477653	-2.273865
C	-4.560774	0.611829	0.967853
H	-5.314715	0.695447	1.753056
C	3.135183	-1.626834	1.976951
H	2.519107	-2.508291	1.752696
H	4.125217	-1.772383	1.515779
H	3.287357	-1.577525	3.066380
H	-0.330447	2.111179	-2.043877
H	-1.249714	2.113323	1.301967

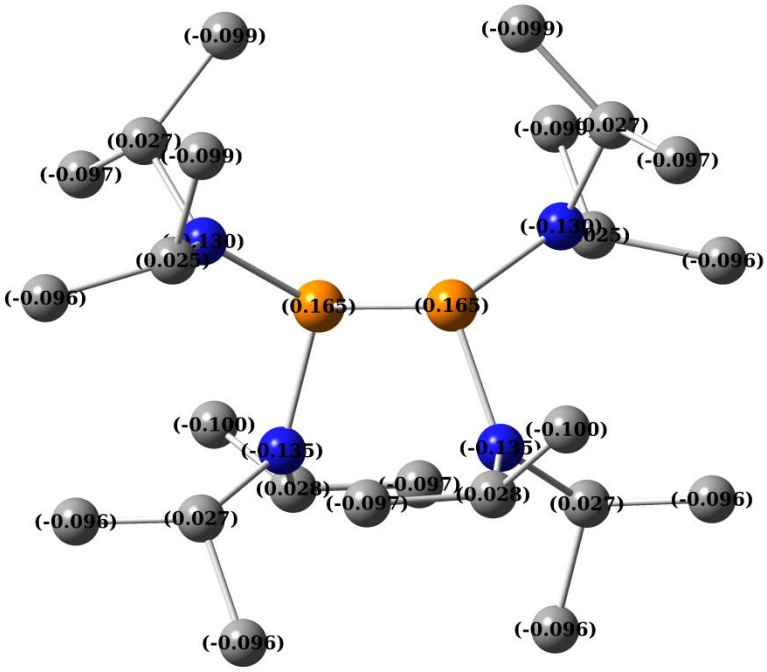


Fig. S264. Hirshfeld atomic charges of diphosphane **30**

N	-1.545470	-1.303030	-0.715525
N	-1.964075	1.164186	0.589142
N	1.964095	1.164166	-0.589145
N	1.545471	-1.303034	0.715535
P	-0.989381	0.339273	-0.586234
P	0.989397	0.339267	0.586237
C	-2.193573	-2.011153	0.398421
H	-1.911683	-1.459762	1.304334
C	-3.725752	-2.003184	0.318833
H	-4.105464	-0.982084	0.178483
H	-4.158703	-2.411791	1.245768
H	-4.090040	-2.627039	-0.512814
C	-1.688269	-3.442862	0.589453
H	-0.610065	-3.449566	0.781891
H	-1.887360	-4.075529	-0.290192
H	-2.196752	-3.908340	1.448680
C	-1.872168	-1.787465	-2.074056
H	-2.188058	-2.834470	-1.939499
C	-0.651753	-1.813050	-2.996979
H	0.192686	-2.340756	-2.536222
H	-0.332431	-0.788934	-3.245969
H	-0.900996	-2.317638	-3.943514
C	-3.017477	-1.048895	-2.779512
H	-3.294313	-1.577841	-3.705517
H	-2.704019	-0.031245	-3.058524
H	-3.911668	-0.970644	-2.148580
C	-1.866198	1.004174	2.050894

H	-1.183671	0.160639	2.215396
C	-3.205301	0.642912	2.703189
H	-3.640552	-0.261134	2.260032
H	-3.942272	1.455568	2.603276
H	-3.062657	0.464266	3.780466
C	-1.238962	2.212358	2.754614
H	-0.255699	2.436644	2.322529
H	-1.102877	1.997104	3.826232
H	-1.872683	3.110263	2.677505
C	-2.766989	2.317815	0.137113
H	-3.274704	2.694334	1.038399
C	-3.864903	1.925294	-0.848757
H	-4.502856	1.132313	-0.431310
H	-3.432853	1.559306	-1.790856
H	-4.500916	2.793235	-1.084282
C	-1.921822	3.473135	-0.405103
H	-2.552157	4.352907	-0.611116
H	-1.426611	3.187823	-1.345516
H	-1.146792	3.763527	0.317807
C	2.767055	2.317761	-0.137118
H	3.274784	2.694259	-1.038405
C	1.921934	3.473116	0.405096
H	2.552306	4.352860	0.611116
H	1.426703	3.187823	1.345505
H	1.146923	3.763544	-0.317820
C	3.864954	1.925195	0.848751
H	4.502860	1.132175	0.431309
H	3.432889	1.559241	1.790857
H	4.501014	2.793105	1.084263
C	1.866230	1.004138	-2.050895
H	1.183682	0.160619	-2.215394
C	1.239030	2.212331	-2.754632
H	0.255769	2.436644	-2.322558
H	1.102952	1.997072	-3.826249
H	1.872773	3.110221	-2.677522
C	3.205330	0.642834	-2.703172
H	3.640557	-0.261214	-2.259995
H	3.942319	1.455476	-2.603267
H	3.062693	0.464173	-3.780447
C	2.193506	-2.011203	-0.398419
H	1.911654	-1.459787	-1.304327
C	3.725686	-2.003354	-0.318843
H	4.105479	-0.982281	-0.178504
H	4.158598	-2.412000	-1.245778
H	4.089934	-2.627228	0.512806
C	1.688072	-3.442866	-0.589445
H	0.609860	-3.449454	-0.781842

H	1.887133	-4.075556	0.290192
H	2.196482	-3.908387	-1.448692
C	1.872144	-1.787491	2.074062
H	2.188011	-2.834502	1.939498
C	3.017468	-1.048951	2.779523
H	3.911663	-0.970732	2.148594
H	3.294283	-1.577899	3.705533
H	2.704038	-0.031290	3.058526
C	0.651720	-1.813058	2.996972
H	-0.192725	-2.340740	2.536196
H	0.332418	-0.788938	3.245970
H	0.900940	-2.317664	3.943504

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