Electronic Supplementary Information for Dalton Transactions


# *Supporting Information*

# [1,2,3]Triazolo[1,5-*a*]pyridyl Phosphines Reflecting the Influence of Phosphorus Lone Pair Orientation on Spectroscopic Properties

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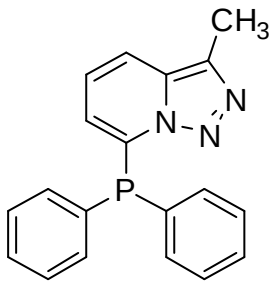
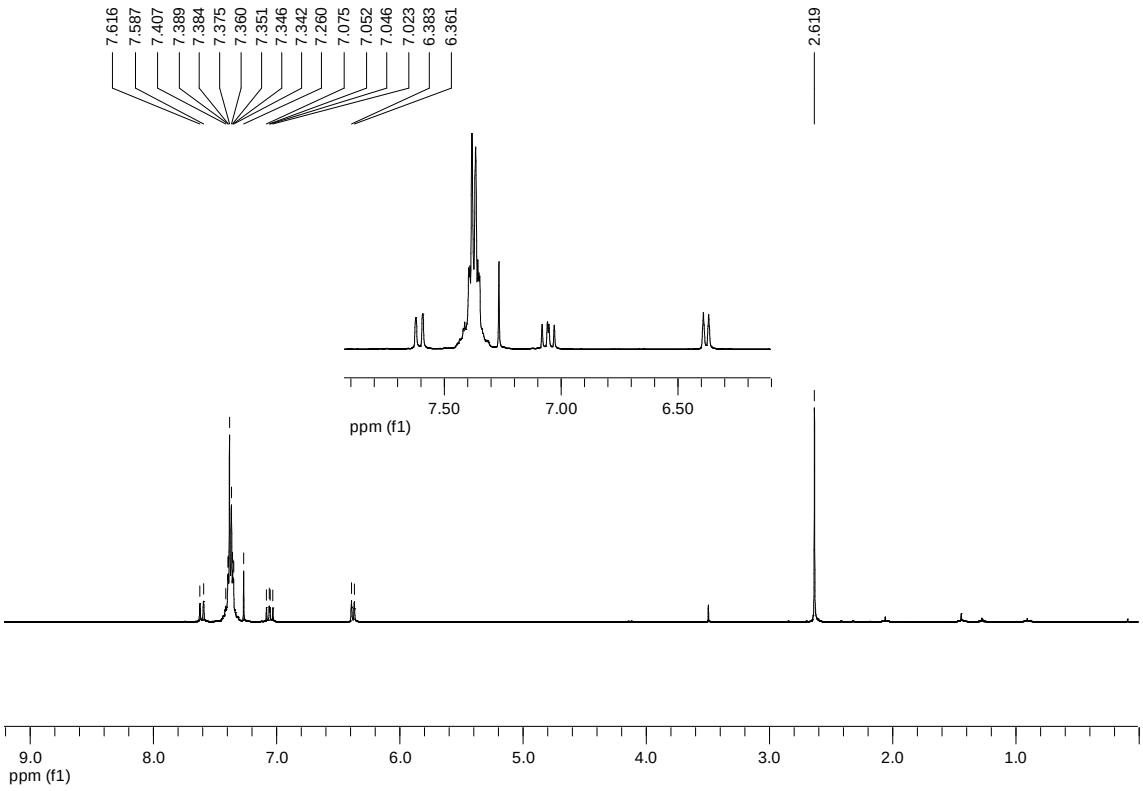
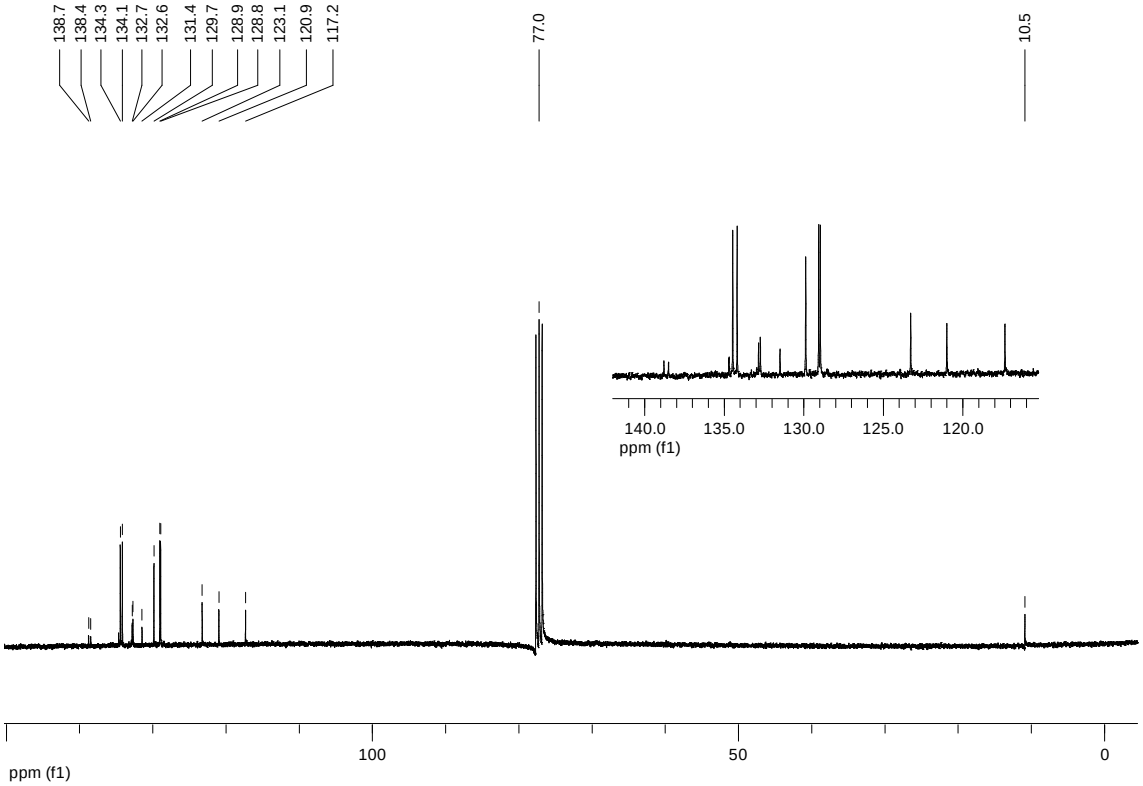
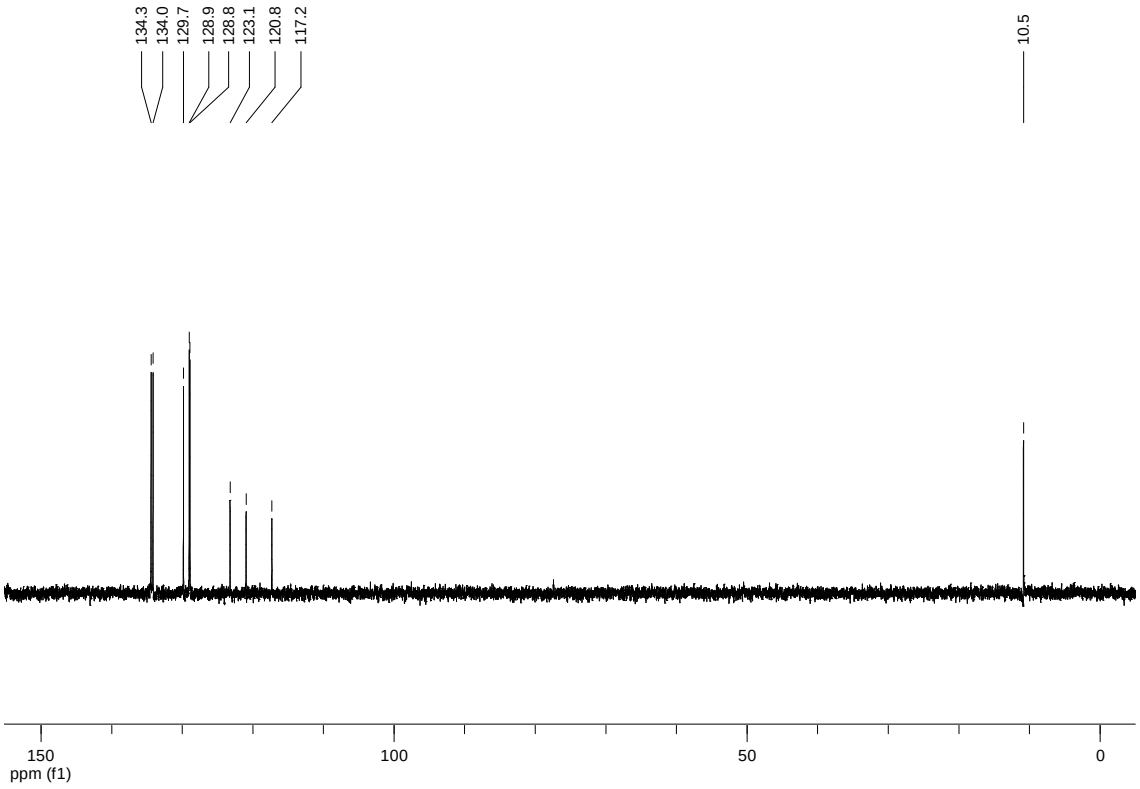
# Experimental Section

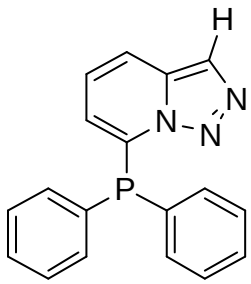


**7-(Diphenylphosphino)-3-methyl-[1,2,3]triazolo[1,5-*a*]pyridine (4a):** Starting from 3-methyl-[1,2,3]triazolo[1,5-*a*] pyridine (**3a,** 1.0 g, 7.5 mmol) in toluene (50 mL). The crude product was purified by filtration on silicagel to afford 7-(diphenylphosphino)-3-methyl-[1,2,3]triazolo[1,5-*a*]pyridine (**4a**; 1.0 g, 42%) as a colorless solid. mp 142 – 144 °C. – $^{1}$H NMR (300 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.8 Hz, 1 H, H4), 7.45-7.30 (m, 10 H, $PPh_2$), 7.05 (dd, *J* = 8.8, 6.9 Hz, 1 H, H5), 6.37 (d, *J* = 6.8 Hz, 1 H, H6), 2.62 (s, 3 H, $CH_3$). – $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 138.4 (d, *J* = 22 Hz, C7) 134.5(d, *J* = 1.2 Hz, 1 C, C3), 134.2 (d, *J* = 21 Hz, 4 CH, *o*-Ph), 132.6 (d, *J* = 8,3 Hz, 2 C, *ipso*-Ph), 131.3 (s, 1 C, C3a), 129.7 (s, 2 CH, *p*-Ph), 128.84 (d, *J* = 7.7 Hz, 4 CH, *m*-Ph), 123.1(s, CH, C5), 120.8 (s, CH, C6), 117.2 (s, CH, C4), 10.5 (s, $CH_3$). – $^{31}$P NMR (161 MHz, $CDCl_3$): δ= -15.4. – MS (EI): m/z(%) = 317.1 (63) [$M^+$], 288 (100) [$M^+ - N_2$], 212.1 (39) [$M^+ - N_2$ - Ph], 183.1 (93). – HRMS for $C_{19}H_{17}N_3P$: calcd. 318.1155; found 318.1145.

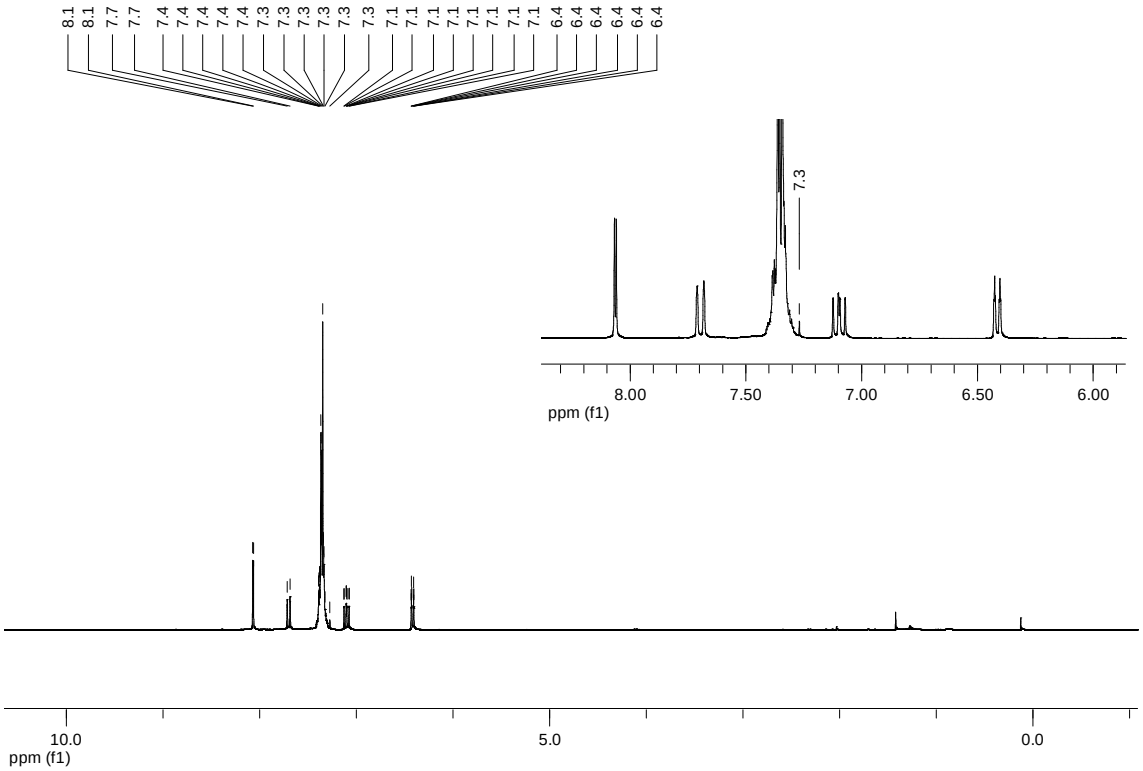


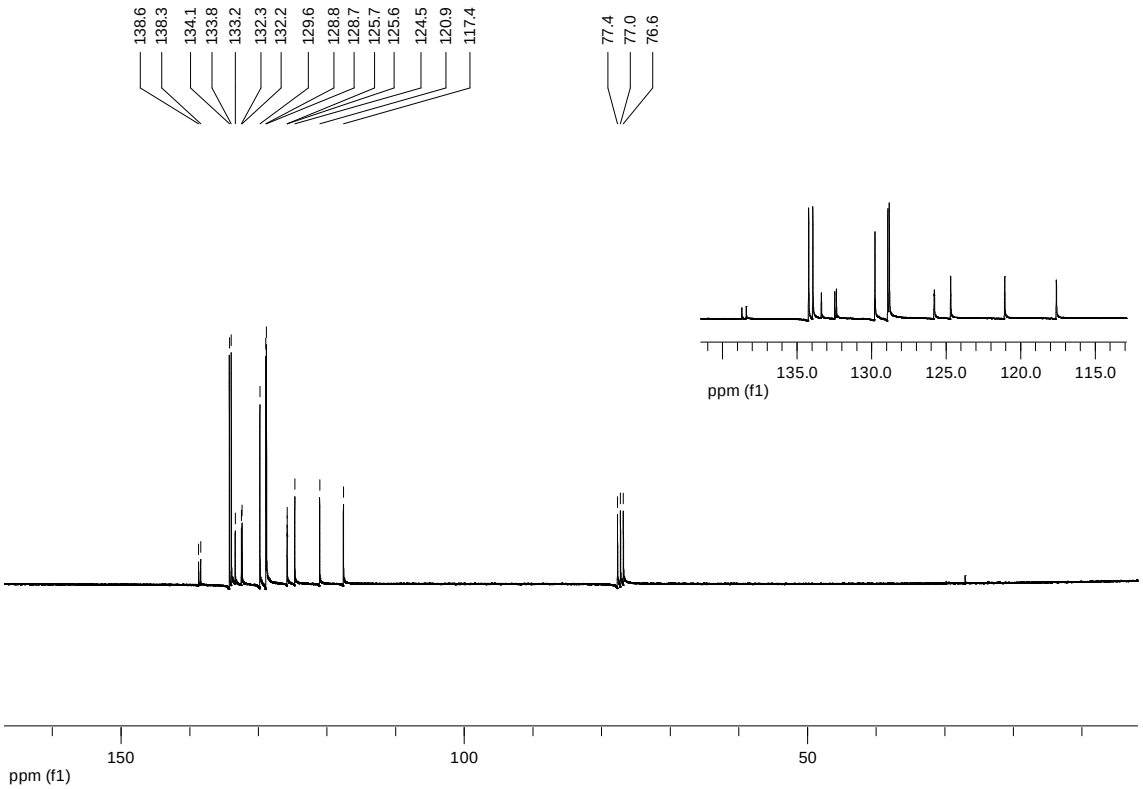


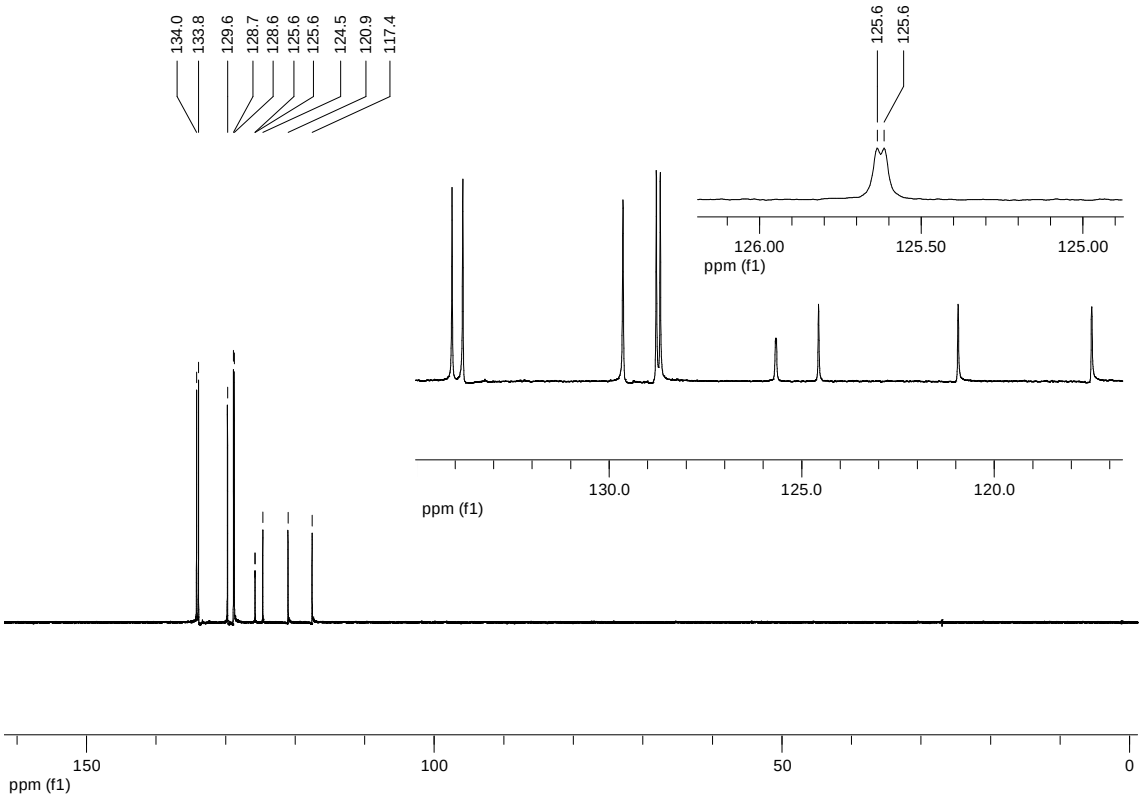



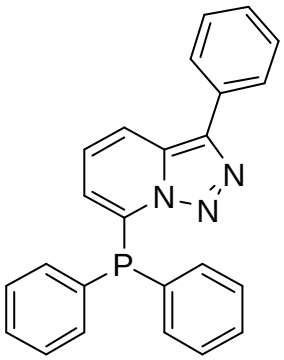


**7-(Diphenylphosphine)-[1,2,3]triazolo[1,5-*a*]pyridine (4b)**: Starting from [1,2,3]triazolo[1,5-*a*]pyridine (**3b**, 0.4 g, 3.4 mmol) in toluene (17 mL). The crude product was purified by filtration on silicagel to afford 7-(diphenylphosphine)-[1,2,3]triazolo[1,5-*a*]pyridine (**4b**, 0.5 g, 44%) as a colorless solid. mp 160 – 162 °C**.** – $^{1}$H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 2.4 Hz, 1 H, H3), 7.61 (d, *J* = 8.8 Hz, 1 H, H4), 7.30-7.21 (m, 10 H, $PPh_2$), 7.01 (dd, *J* = 8.8, 6.9 Hz, 1 H, H5), 6.32 (d, *J* = 6.8 Hz, 1 H, H6). – $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 138.5 (d, *J* = 22.4 Hz, 1 C, C7) 133.9(d, *J* = 21.1 Hz, 4 CH, *o*-Ph), 133.2 (s, 1 C, C3a), 132.3 (d, *J* = 8.2 Hz, 2 CH, *ipso*-Ph), 129.6 (s, 2 CH, *p*-Ph) 128.7 (d, *J* = 7.8 Hz, 4 CH, *m*-Ph) , 125.6 (d, *J* = 1.6 Hz, 1 C, C3), 124.5 (s, 1 CH, C5), 120.8 (s, 1 CH, C6), 117.2 (s, 1 CH, C4). – $^{31}$P NMR (161 MHz, $CDCl_3$): δ= -15.0. – MS (EI): m/z(%) = 303.1 (78) [$M^+$], 275.1 (10) [$M^+$ - $N_2$], 274.1 (55) [$M^+$ - $N_2$ - H], 198.1 (23) [$M^+$ - $N_2$ - Ph], 183.1 (93). – HRMS for $C_{18}H_{14}N_3P$: [M+$H^+$] calcd. 304.0998; found 304.0969.

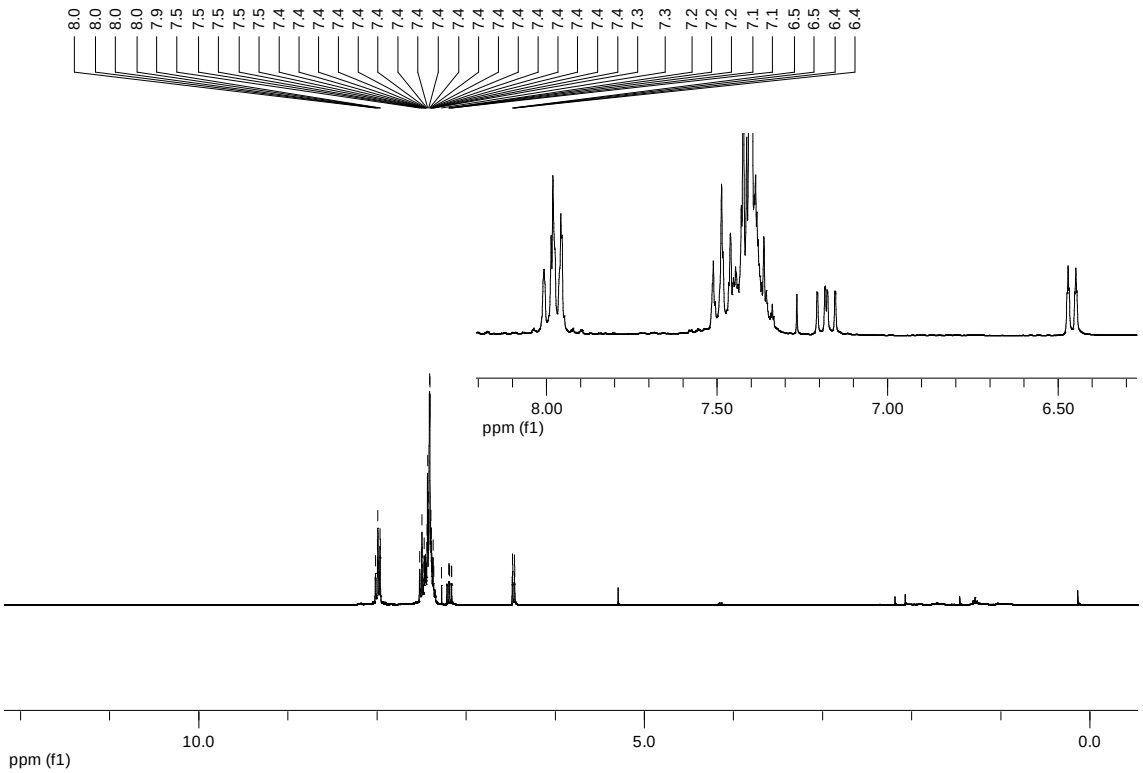


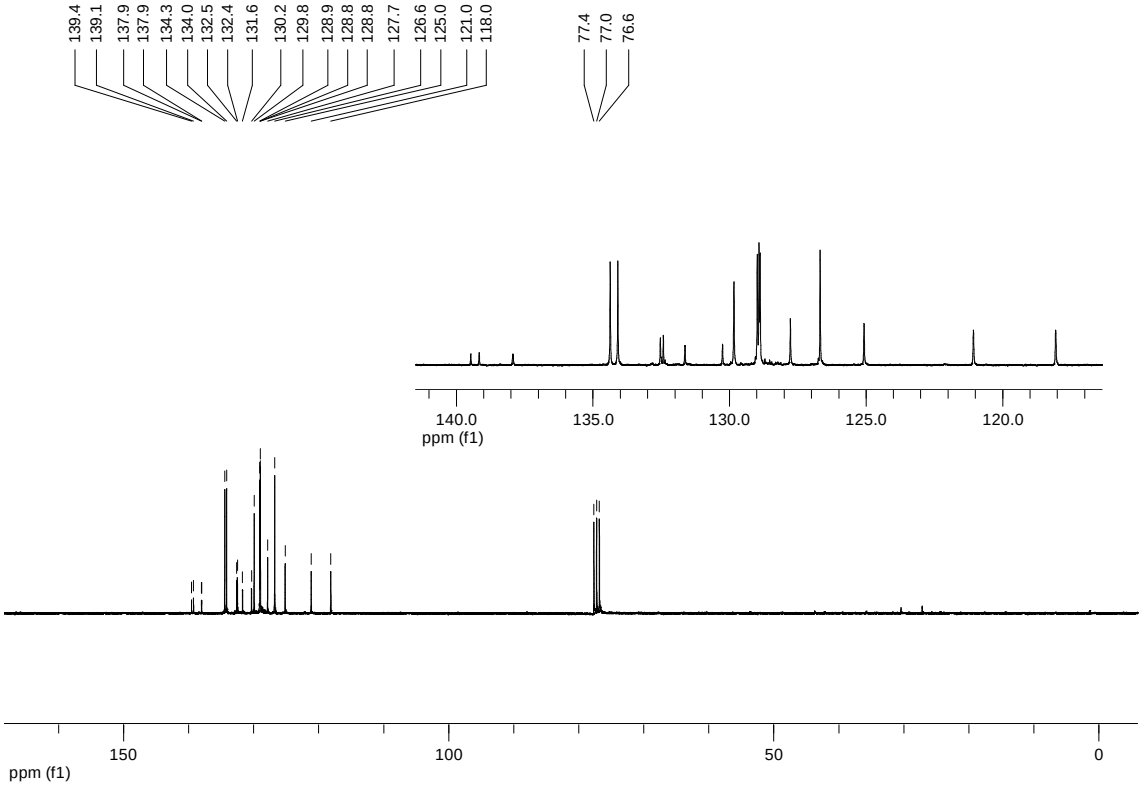


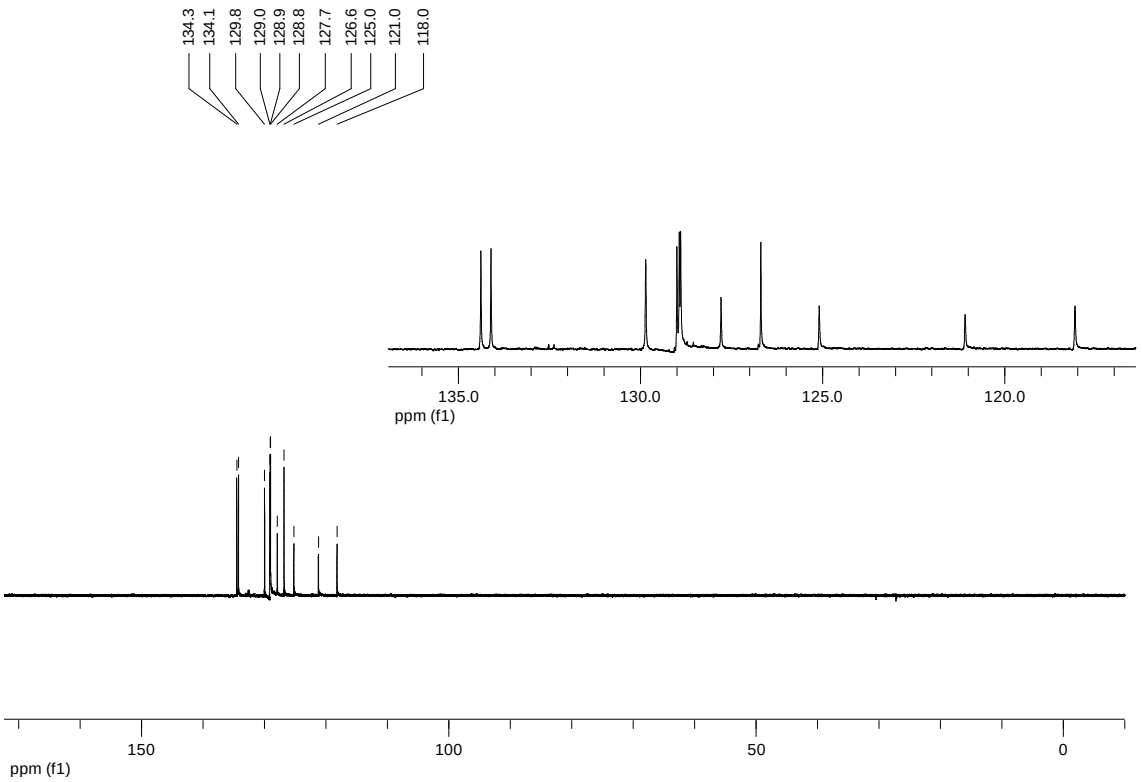



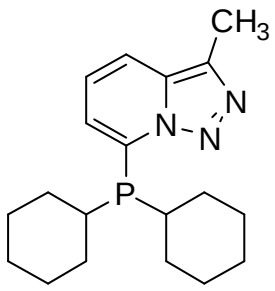


**7-(Diphenylphosphino)-3-phenyl-[1,2,3]triazolo[1,5-*a*] pyridine (4c)**: Starting from 3-phenyl-[1,2,3]triazolo[1,5-*a*] pyridine (**3c**, 0.4 g, 2.1 mmol) in toluene (14 mL). The crude product was purified by filtration on silicagel to afford 7-(diphenylphosphine)-[1,2,3]triazolo[1,5-*a*]pyridine (**4c**; 1.1 g, 52%) as a yellow oil. – $^{1}$H NMR (300 MHz, $CDCl_3$): 7.98 (m, 3 H, H4 + 3-*o*-Ph), 7.52-7.33 (m, 13 H, $PPh_2$ + 3-*m*-Ph+ 3-*p*-Ph), 7.17 (dd, *J* = 8.8, 6.9 Hz, 1 H, H5), 6.45 (d, *J* = 6.9 Hz, 1 H, H6). – $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 139.3 (d, *J* = 23.3 Hz, 1 C, C7), 137.8 (d, *J* = 1.9 Hz, 1 C, C3), 134.2 (d, *J* = 21.2 Hz, 4 CH, P(*o*-Ph)$_2$), 132.4 (d, *J* = 8.3 Hz, 2 C, *ipso*-$PPh_2$), 131.6 (s, 1 C, C3a), 130.2 (s, C, 3-*ipso*-Ph), 129.8 (s, 2 C, P(*p*-Ph)$_2$), 128.9 (d, *J* = 7.8 Hz, 4 CH, P(*m*-Ph)$_2$), 128.8 (s, 2 CH. 3-*o*-Ph), 127.7 (s, 1 CH, 3-*p*-Ph), 126.6 (s, 2 CH, 3-*m*-Ph ), 124.9 (s, 1 CH, C5), 120.9 (s, 1 CH, C6), 117.9 (s, 1 CH, C4). – $^{31}$P NMR (161 MHz, $CDCl_3$): δ= -14.6**.** – MS (EI): mz/z(%) = 379.1 (8) [$M^+$], 351.1.1 (37) [$M^+$ - $N_2$], 350.1 (20) [$M^+$ - $N_2$ - H], 185.1 (72) [$P(Ph)_2$], 183.1 (100). – HRMS for $C_{24}H_{18}N_3P$: [M+O+$Li^+$] calcd. 402.1343; found 402.1316.

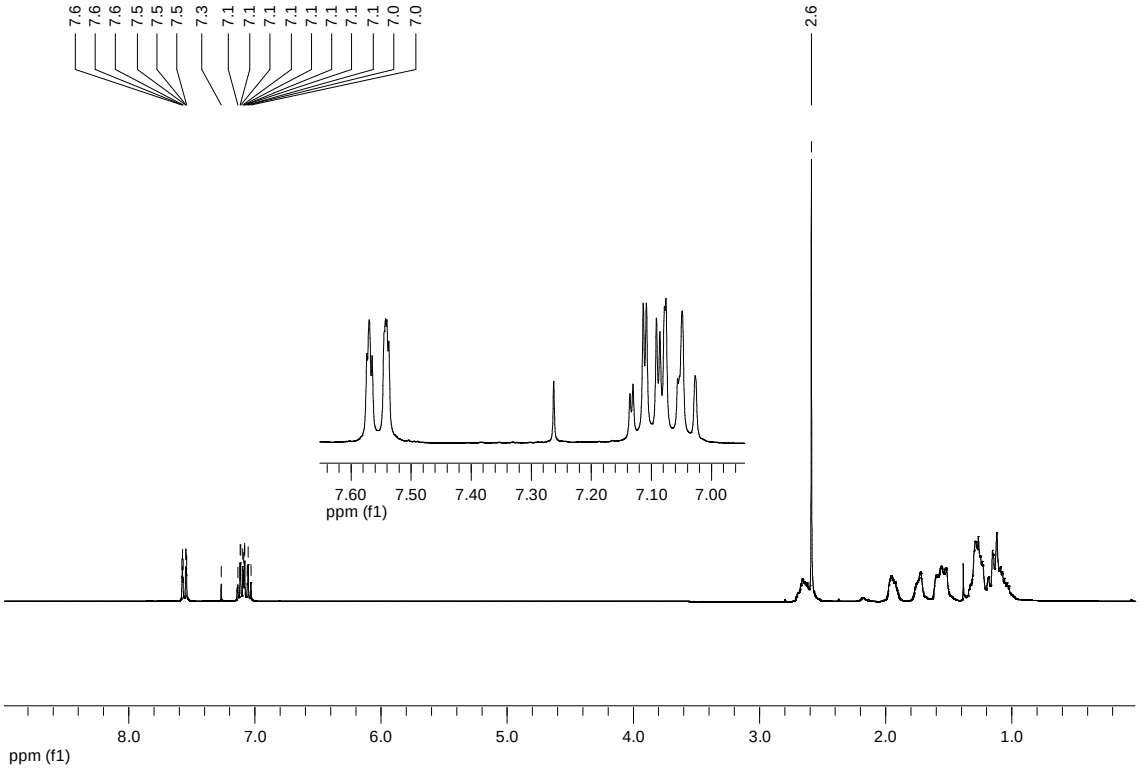


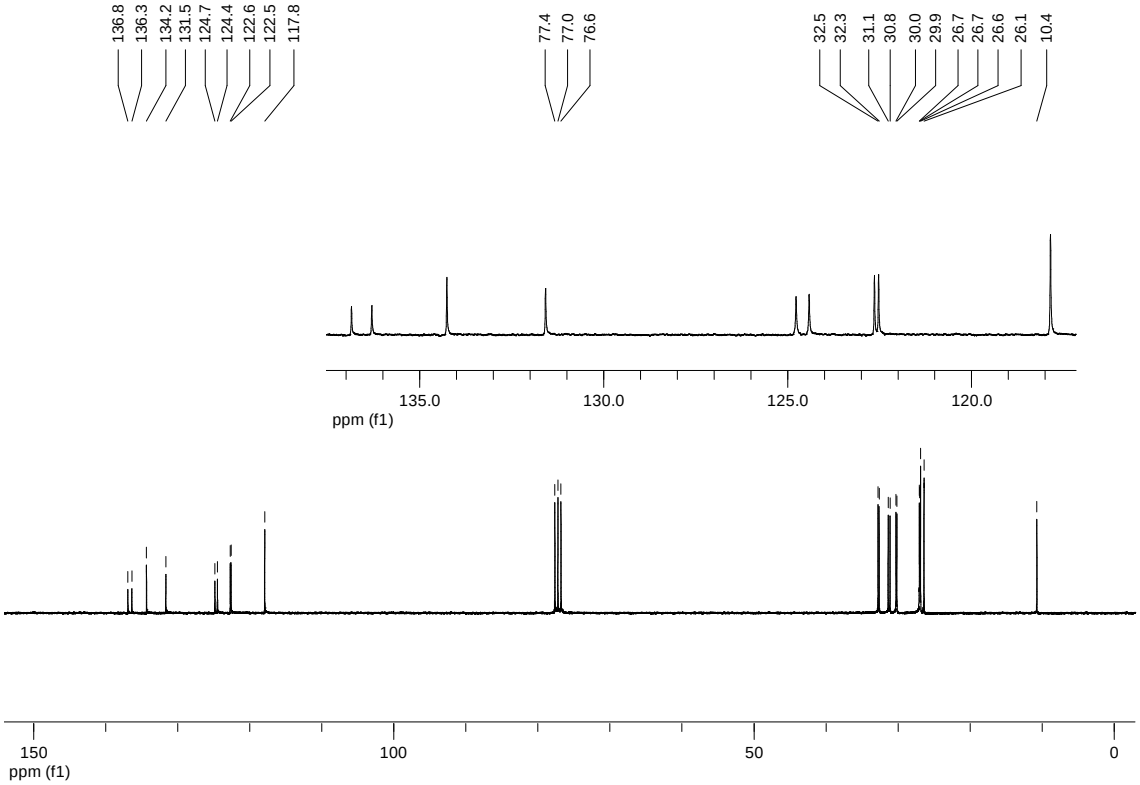


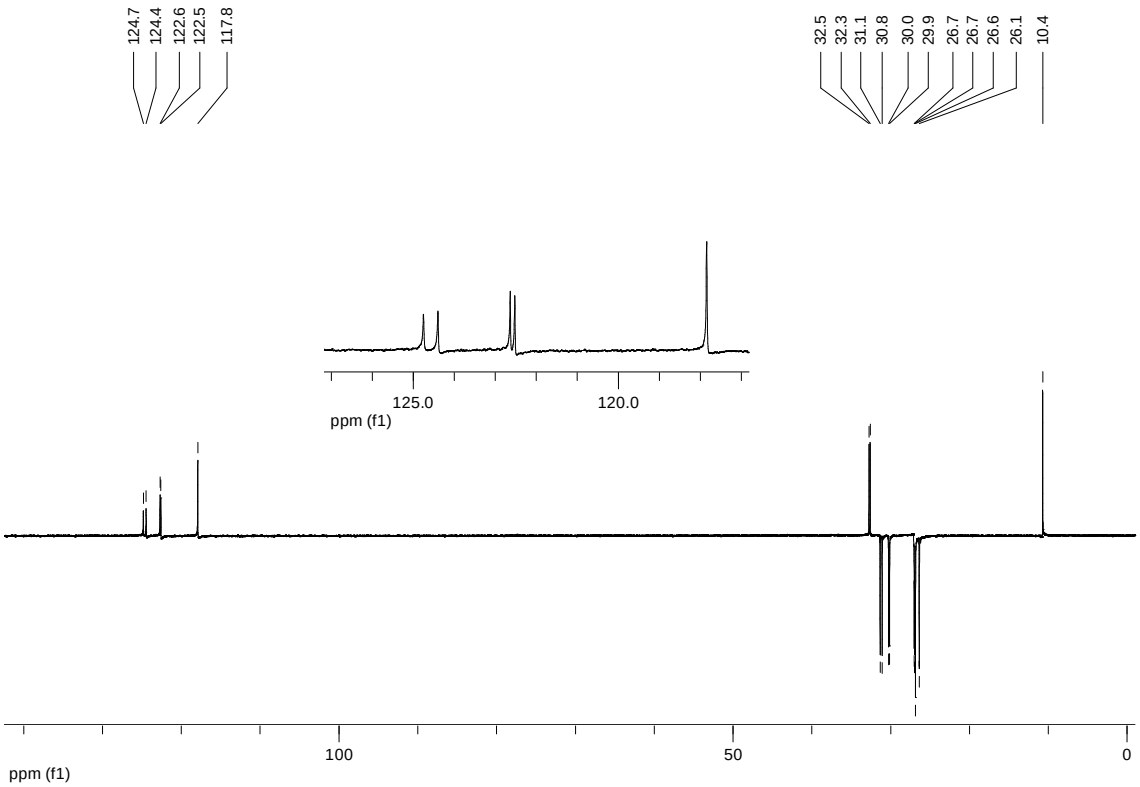



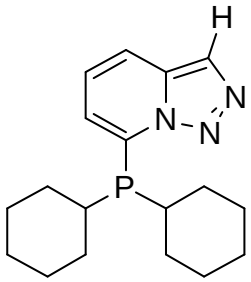


**7-(Dicyclohexylphosphino)-3-methyl-[1,2,3]triazolo[1,5-*a*] pyridine (5a)**: Starting from 3-methyl-[1,2,3]triazolo[1,5-*a*] pyridine (**3a,** 1.0 g, 7.5 mmol) in toluene (50 mL). The crude product was purified by filtration on silicagel to afford 7-(dicyclohexylphosphino)-3-methyl-[1,2,3]triazolo[1,5-*a*] pyridine (**5a**; 1.0 g 45%) as a colorless solid. mp 93 – 95 °C. – $^{1}$H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 8.2 Hz, 1 H, H4), 7.15-7.00 (m, 2 H, H6 + H5), 2.73-2.57 (m, 2 H, $PCy_2$), 1.94 (dd, *J* = 16.5, 8.6 Hz, 2 H, $PCy_2$), 1.72 (d, *J* = 7.5 Hz, 2 H, $PCy_2$), 1.53 (m, 4H, $PCy_2$), 1.14 (m, 12 H, $PCy_2$). – $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 137.1 (d, *J* = 41.2 Hz, 1C, C7) 134.2 (s, 1 C, C3), 131.5 (s, 1 C, C3a), 124.1 (d, *J* = 25.9 Hz, 1 CH, C6), 122.5 (d, *J* = 9 Hz, 1 CH. C5), 117.8 (s, 1 CH, C4), 32.4 (d, *J* = 11 Hz, 2 CH, (CH)-$PCy_2$), 30.9 (d, *J* = 19 Hz, 2 $CH_2$, $CH_2$), 29.9 (d, *J* = 9 Hz, 2 $CH_2$, $CH_2$), 26.7 (d, *J* = 3.2, Hz, 2 $CH_2$, $CH_2$), 26.6 (bs, 2 $CH_2$, $CH_2$), 26.2-25.9 (bs, 2 $CH_2$, $CH_2$), 10.4 (s, $CH_3$). – $^{31}$P (161 MHz, $CDCl_3$): δ= 6.5. – MS (EI): m/z(%) = 329.2 (35) [$M^+$], 301.2 (33) [$M^+$ - $N_2$], 246. (81) [$M^+$ - Cy], 218.2 (100) [$M^+$ - $N_2$ - Cy], 137 (66) [$M^+$ - $N_2$ - 2Cy]. – HRMS for $C_{19}H_{28}N_3P$ [M+Li]: calcd. 336.2176; found 336.2215.

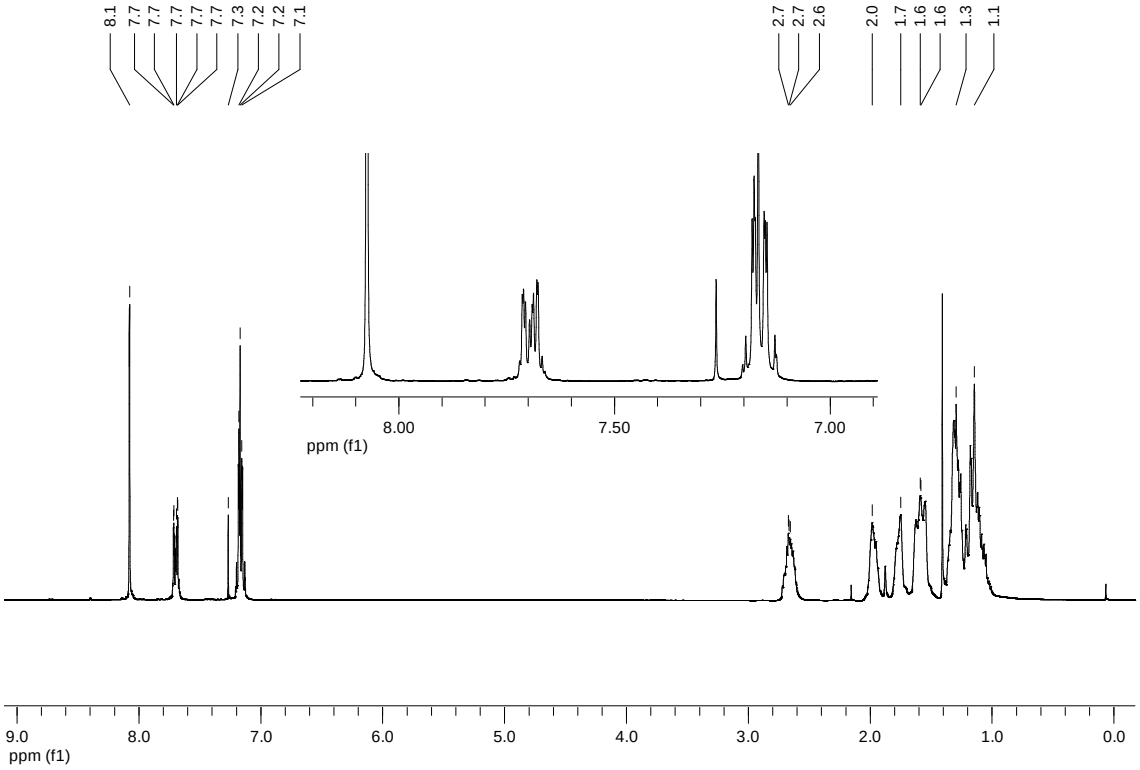


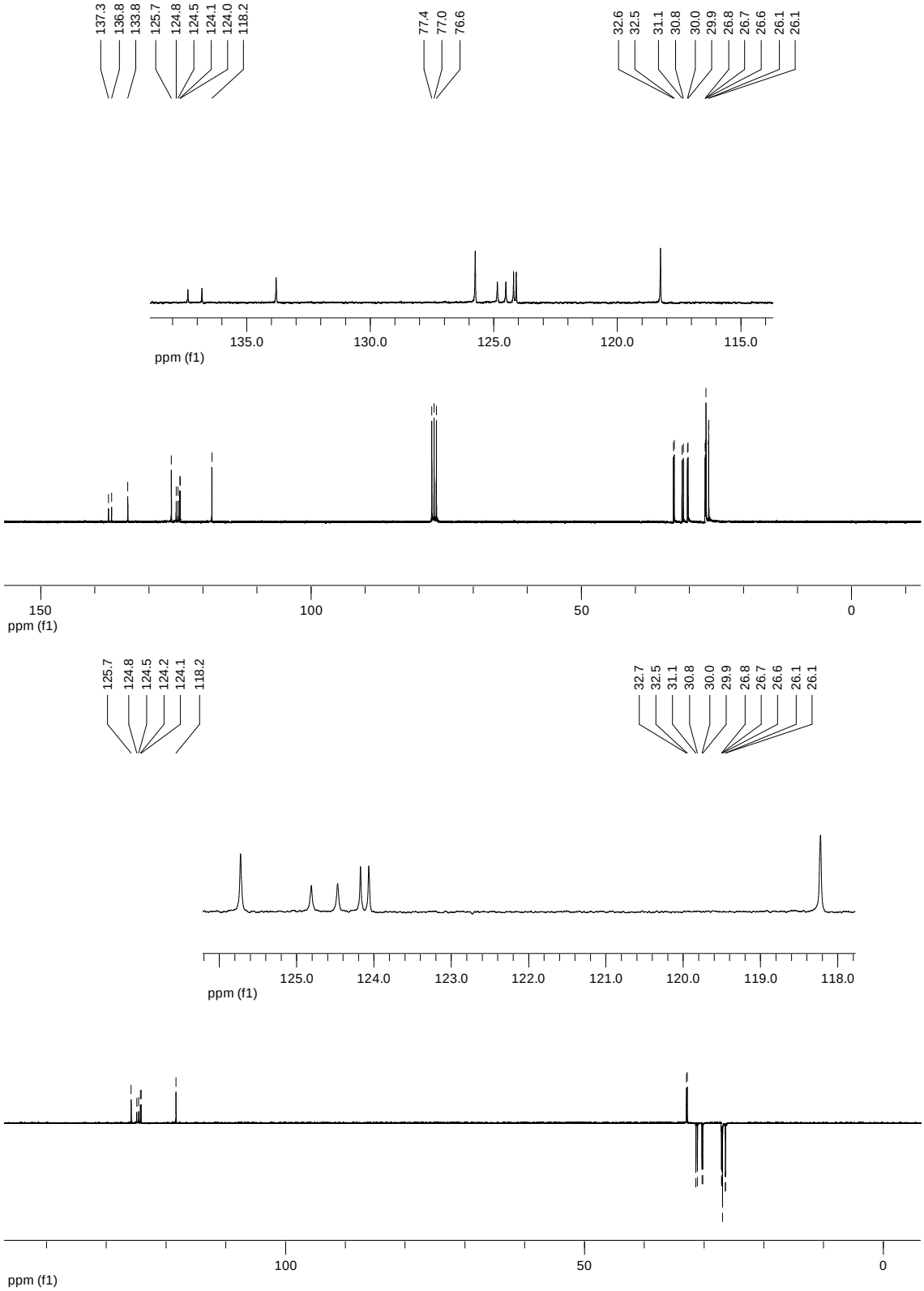




**7-(Dicyclohexylphosphino)-[1,2,3]triazolo[1,5-*a*]pyridine (5b):** Starting from [1,2,3]triazolo[1,5-*a*]pyridine (**3b**, 0.4 g, 3.4 mmol) in toluene (17 mL). The crude product was purified by filtration on silicagel to afford 7-(dicyclohexylphosphino)-[1,2,3]triazolo[1,5-*a*]pyridine (**5b**; 0.6 g, 58%) as a colorless solid. mp 124 – 126 °C. – $^{1}$H NMR (300 MHz, $CDCl_3$): δ = 8.07 (s, 1 H, H3), 7.73-7.65 (m, 1 H, H4), 7.21-7.10 (m, 2 H, H5 + H6), 2.72-2.55 (m, 2 H, CH-$PCy_2$), 2.02-1.90 (m, 2 H, $CH_2$), 1.79-1.70 (m, 2 H, $CH_2$), 1.63-1.51 (m, 4 H, $CH_2$), 1.35.1.16 (m 10 H, $CH_2$). – $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 137.1 (d, *J* = 41.8 Hz, 1 C, C7), 133.7 (s, 1 C, C3a), 125.6 (s, 1 C, C3), 124.6 (d, *J* = 25.9 Hz, 1 CH, C6) , 124.1(d, *J* = 8.2 Hz, 1 CH, C5), 118.2 (s, 1 CH, C4), 32.6 (d, *J* = 11.3 Hz, 2 CH, (CH)-$PCy_2$), 30.9 (d, *J* = 19.1 Hz, 2 $CH_2$, $CH_2$), 30.0 (d, *J* = 9.0 Hz, 2 $CH_2$, $CH_2$), 26.7 (d, *J* = 3.6 Hz, 2 $CH_2$, $CH_2$), 26.6 (s, 2 $CH_2$, $CH_2$), 26.8 (d, *J* = 1.1 Hz, 2 $CH_2$, $CH_2$). – $^{31}$P NMR (161 MHz, $CDCl_3$): δ= 7.0. – MS (EI): m/z(%) = 315.2 (42) [$M^+$], 287.2 (33) [$M^+$ - $N_2$], 232.1 (57) [$M^+$ - Cy], 204.2 (100) [$M^+$ - $N_2$ - Cy], 151,1 (45) [$M^+$ - 2Cy + 2H], 123 (25) [$M^+$ - $N_2$ - 2Cy + 2H]. – HRMS for $C_{18}H_{26}N_3P$ [M+Li]: calcd. 322.2019; found 322.1975.

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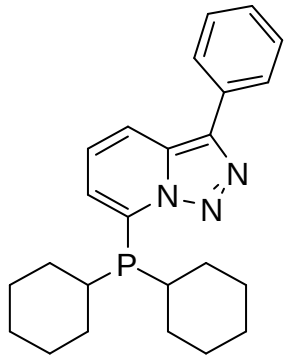
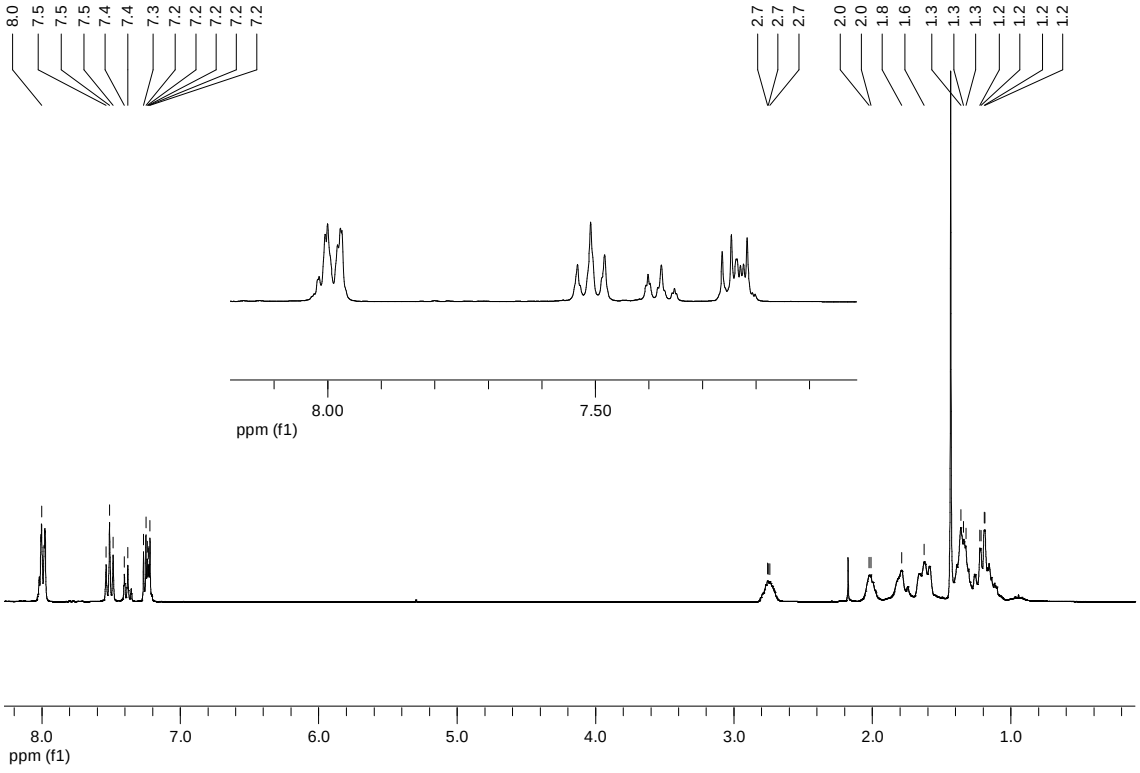
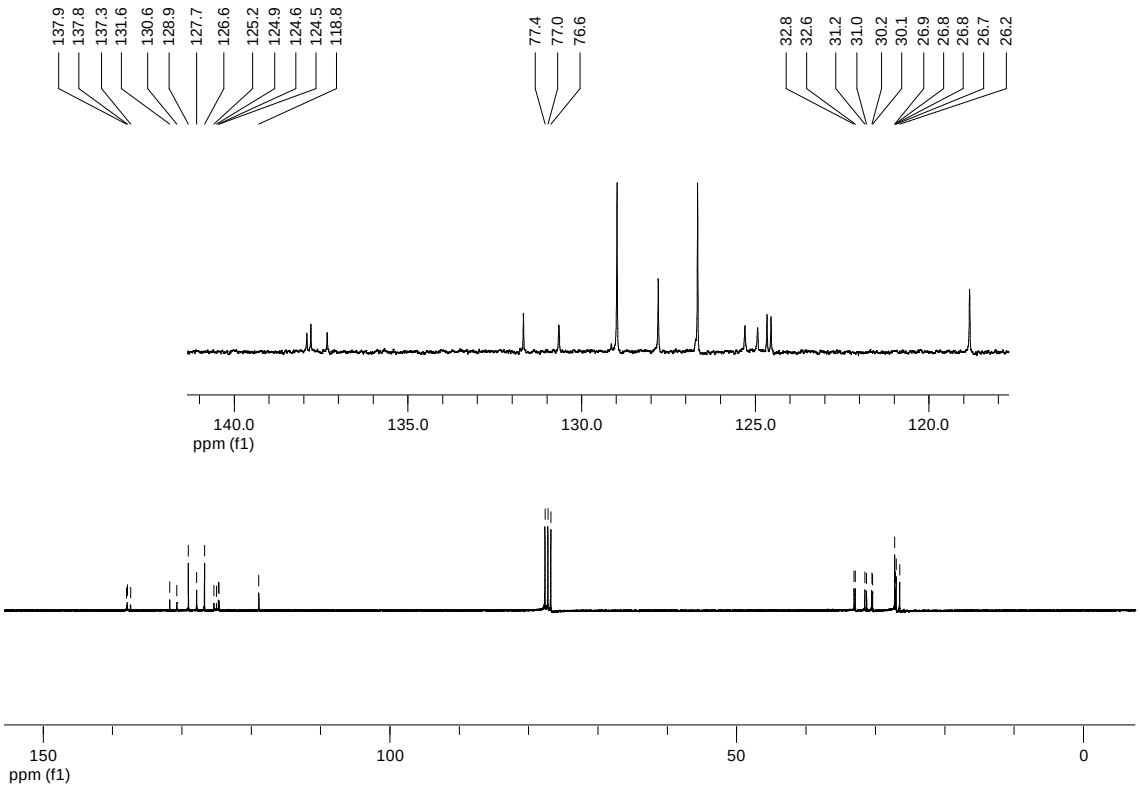
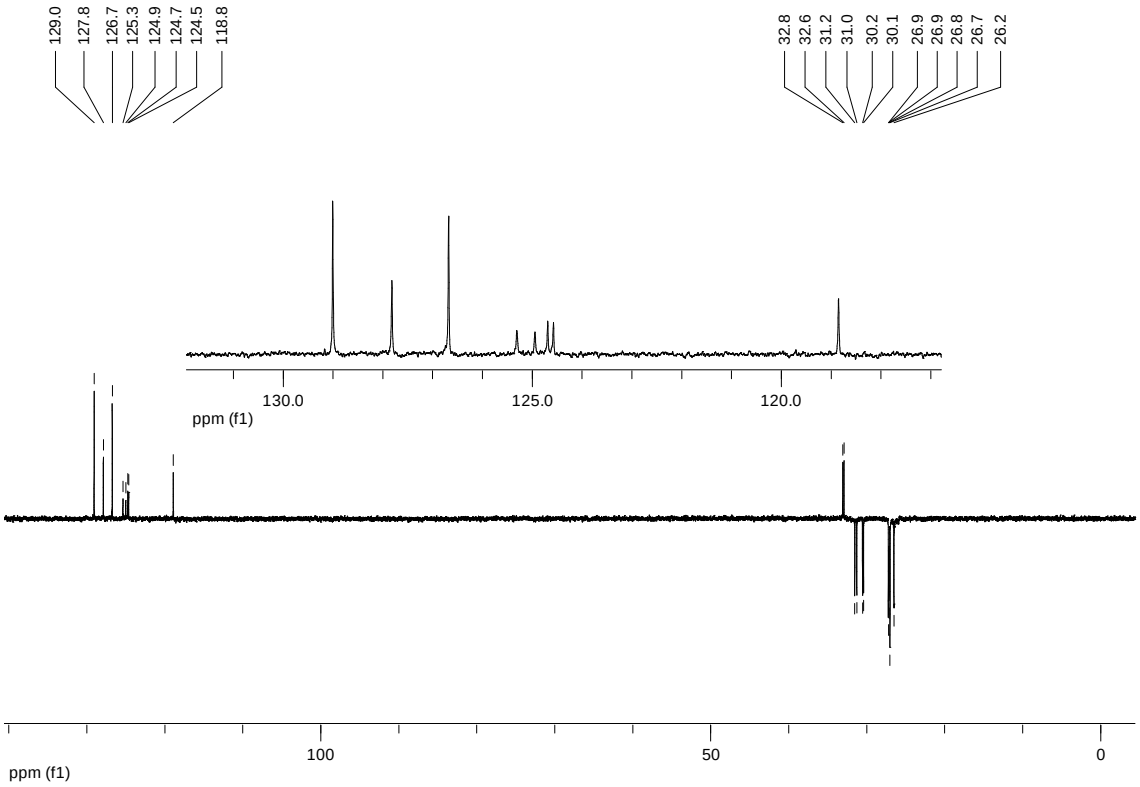
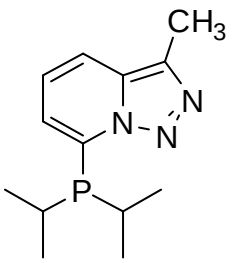


**7-(Dicyclohexylphosphino)-3-phenyl-[1,2,3]triazolo[1,5-*a*] pyridine (5c):** Starting from 3-phenyl-[1,2,3]triazolo[1,5-*a*] pyridine (**3c,** 0.3 g, 1.3 mmol) in toluene (25 mL). The crude product was purified by filtration on silicagel to afford 7-(dicyclohexylphosphino)-3-methyl-[1,2,3]triazolo[1,5-*a*] pyridine (**5c**; 0.3 g, 52%) as a colorless solid. mp 93 – 95 °C. – $^{1}$H NMR (300 MHz, $CDCl_3$): δ 8.00 (m, 3 H, H4 + 3-*o*-Ph), 7.51 (, *J* = 7.6, 7.6 Hz, 2 H, 3-*m*-Ph), 7.37 (m, 1 H, 3-*p*-Ph), 7.25-7.20 (m, 2 H, H5 + H6), 2.82-2.60 (m, 2 H, CH-$PCy_2$), 2.02-1.91 (m, 2 H, $CH_2$), 1.81-1.70 (m, 3 H, $CH_2$), 1.63-1.51 (m, 5 H, $CH_2$), 1.39-1.04 (m 10 H, $CH_2$). – $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 137.8 (s, 1 C, C3), 137.6 (d, *J* = 44.5 Hz, 1 C, C7), 131.7 (s, 1 C, C3a), 130.7 (s, 1 C, 3-*ipso*-Ph), 128.9 (s, 2 CH, 3-*o*-Ph) 127.7 (s, CH, 3-*p*-Ph), 126.6 (s, 2 CH, 3-*m*-Ph), 125.1 (d, *J* = 27.6 Hz, 1 CH, C6), 24.6 (d, *J* = 8.7 Hz, 1 CH, C5), 118.8 (s, 1 CH, C4), 32.7 (d, *J* = 27.6 Hz, 2 CH, (CH)-$PCy_2$ ), 31.1 (d, *J* = 19.3 Hz, 2 $CH_2$, $CH_2$), 30.2 (d, *J* = 9.0 Hz, 2 $CH_2$, $CH_2$), 26.9 (s, 2 $CH_2$, $CH_2$), 26.8 (d, *J* = 3.5 Hz, 2 $CH_2$, $CH_2$), 26.7 (s, 2 $CH_2$, $CH_2$), 26.2 (s, 2 $CH_2$, $CH_2$). – $^{31}$P NMR (161 MHz, $CDCl_3$): δ= 6.5. – MS (EI): m/z(%) = 391.2 (25) [$M^+$], 363.2 (80) [$M^+$ - $N_2$], 280. (100) [$M^+$ - $N_2$ -Cy], 199.1 (90), 146.1 (90). – HRMS for $C_{24}H_{30}N_3P$ [M+O+Li]: calcd. 414.2280; found. 414.2270.

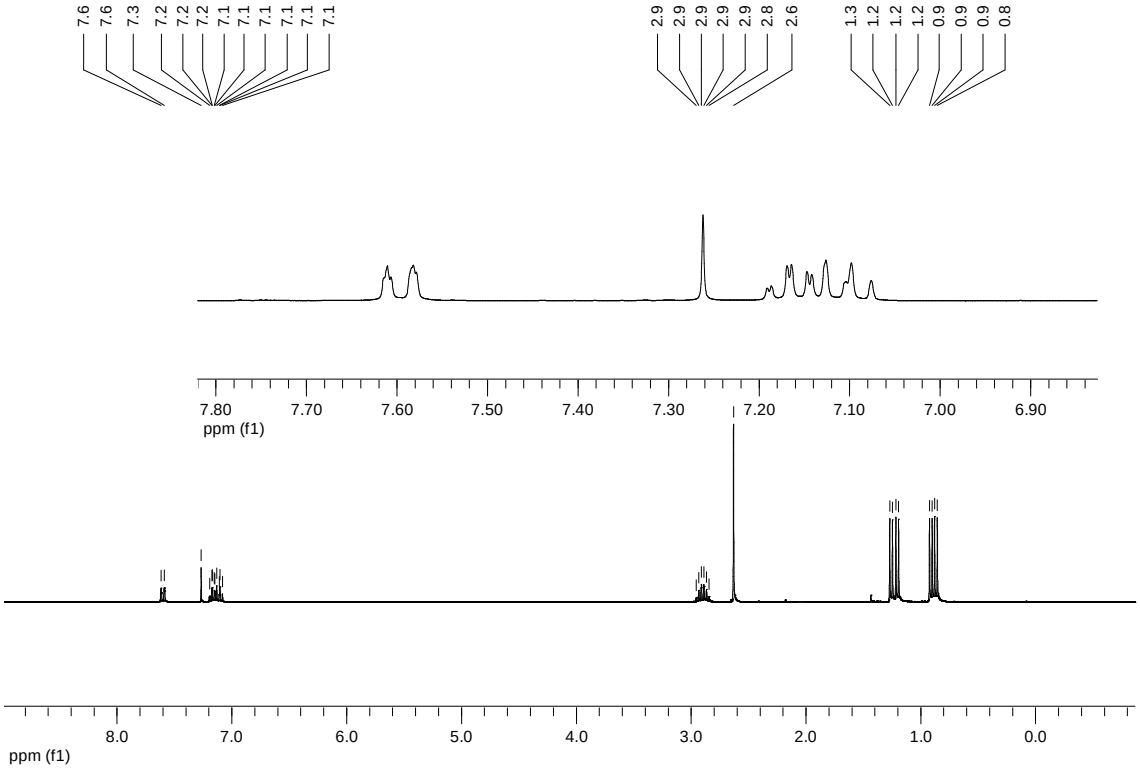


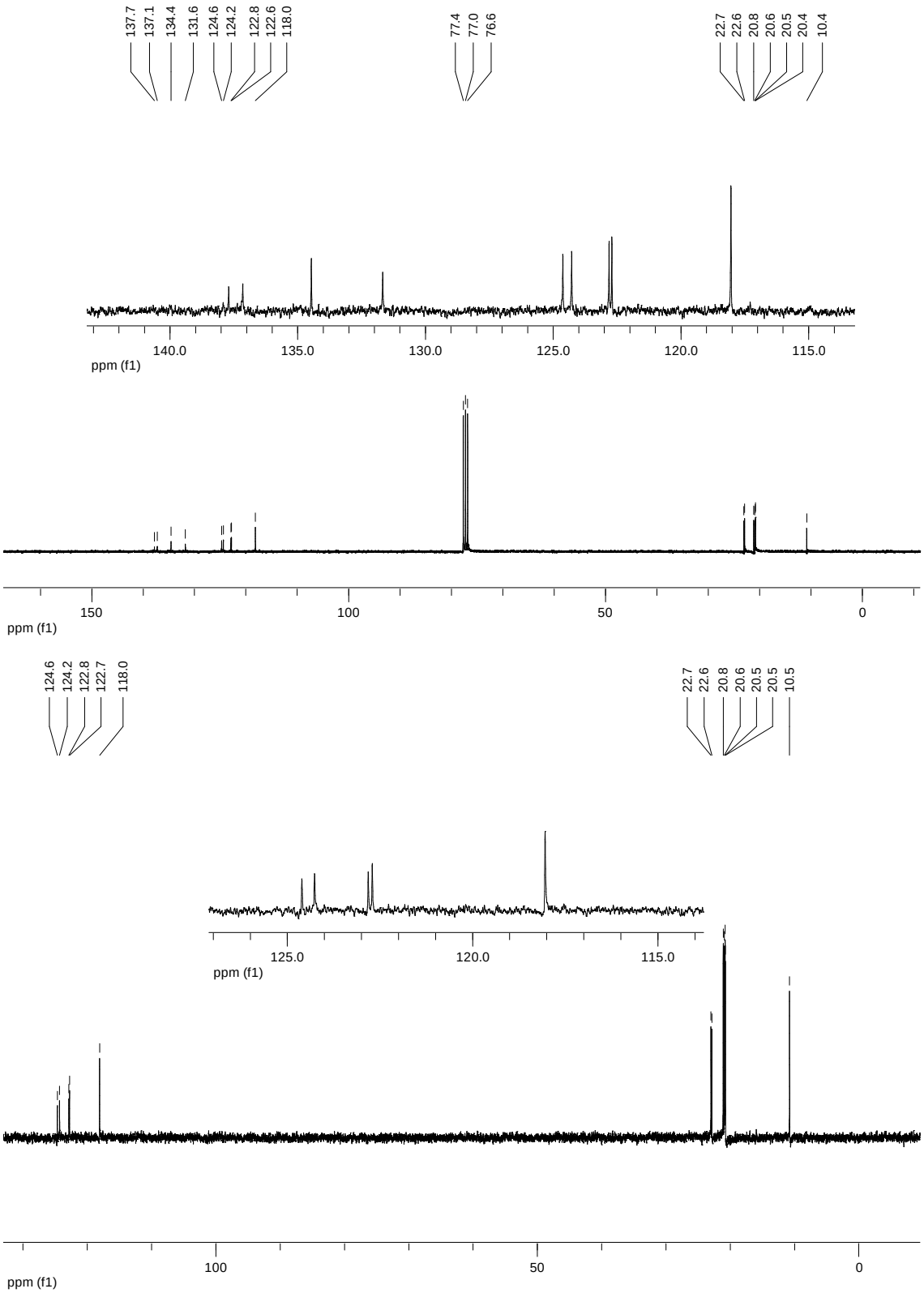


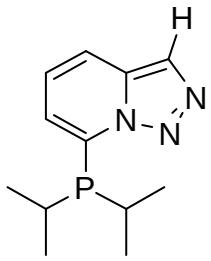





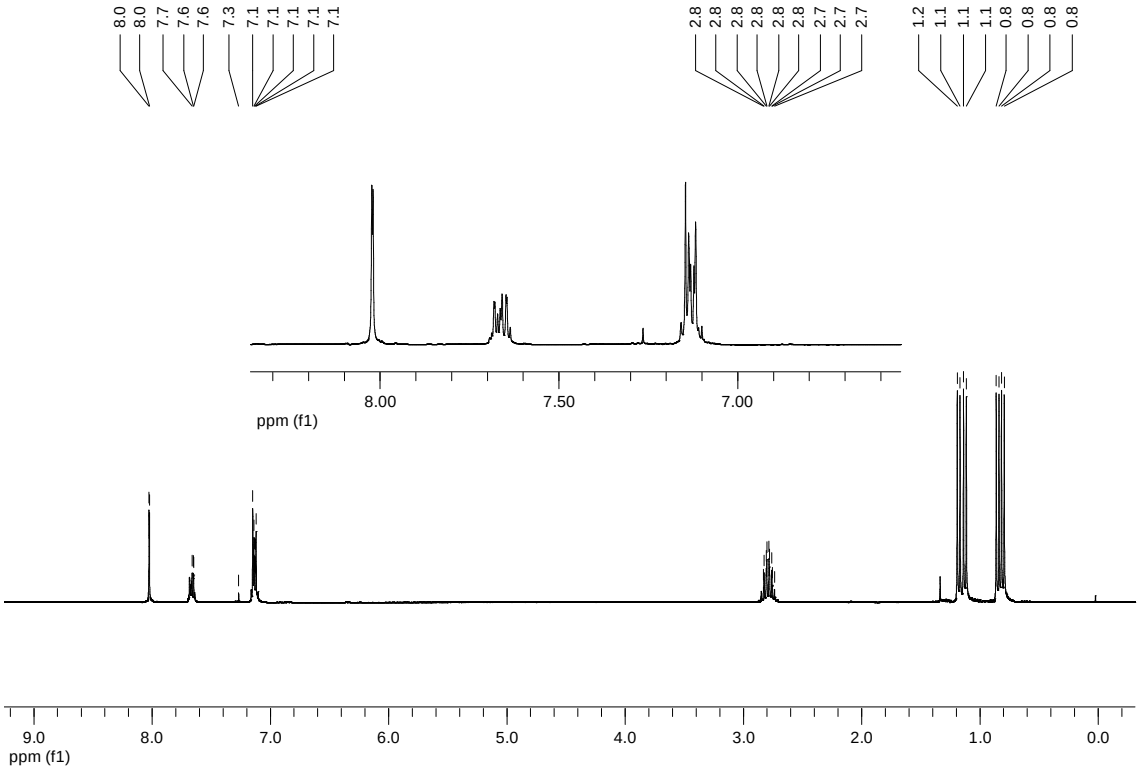
**7-(*Di-iso*-propylphosphino)-3-methyl-[1,2,3]triazolo[1,5-*a*] pyridine (6a):** Starting from 3-methyl-[1,2,3]triazolo[1,5-*a*] pyridine (**3a,** 1 g, 7.5 mmol) in toluene (17 mL). The crude product was purified by filtration on silicagel to afford 7-(di-*iso*-propylphosphino)-3-methyl-[1,2,3]triazolo[1,5-*a*]pyridine (**6a**, 0.9 g, 48%) as a brown oil. – $^{1}$H NMR (300 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.6 Hz, 1 H, H4), 7.21-7.06 (m, 2 H, H5 + H6), 2.97-2.78 (m, 2 H, P(C*H*$(CH_3)_2)_2$), 2.61 (s, 3 H, 3-$CH_3$), 1.21 (dd, *J* = 16.1, 7.0 Hz, 6 H, P(CH(C*H*$_3)_2)_2$), 0.88 (dd, *J* = 13.2, 7.0 Hz, 6 H, P(CH(C*H*$_3)_2)_2$). – $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 137.4 (d, *J* = 41.8 Hz, C7), 134.4 (s, 1 C, C3a), 131.6 (s, 1 C, C3), 124.4 (d, *J* = 26.1 Hz, 1 CH, C6), 122.7 (d, *J* = 8.3 Hz, 1 CH, C6), 117.9 (s, 1 CH, C4), 22.6 (d, *J* = 10.4 Hz, 2 CH, P(*C*H$(CH_3)_2)_2$), 20.7 5 (d, *J* = 14.5 Hz, 2 $CH_3$, P(CH(*C*H$_3)_2)_2$), 20,5 (d, *J* = 4.6 Hz, 2 $CH_3$, P(CH(*C*H$_3)_2)_2$), 10.4 (s, 3-$CH_3$). – $^{31}$P NMR (161 MHz, $CDCl_3$): δ= 16.1. – MS (EI): m/z(%) = 249.2 (56) [$M^+$], 221.2 (11) [$M^+$ - $N_2$], 206.1 (26) [$M^+$ - $^{i}$Prop], 178.1 (100) [$M^+$ - $N_2$ - $^{i}$Prop], 136.1 (64) [$M^+$ - $N_2$ - 2Cy]. – HRMS for $C_{13}H_{20}N_3P$ [M+Li]: calcd. 256.1550; found 256.1519.

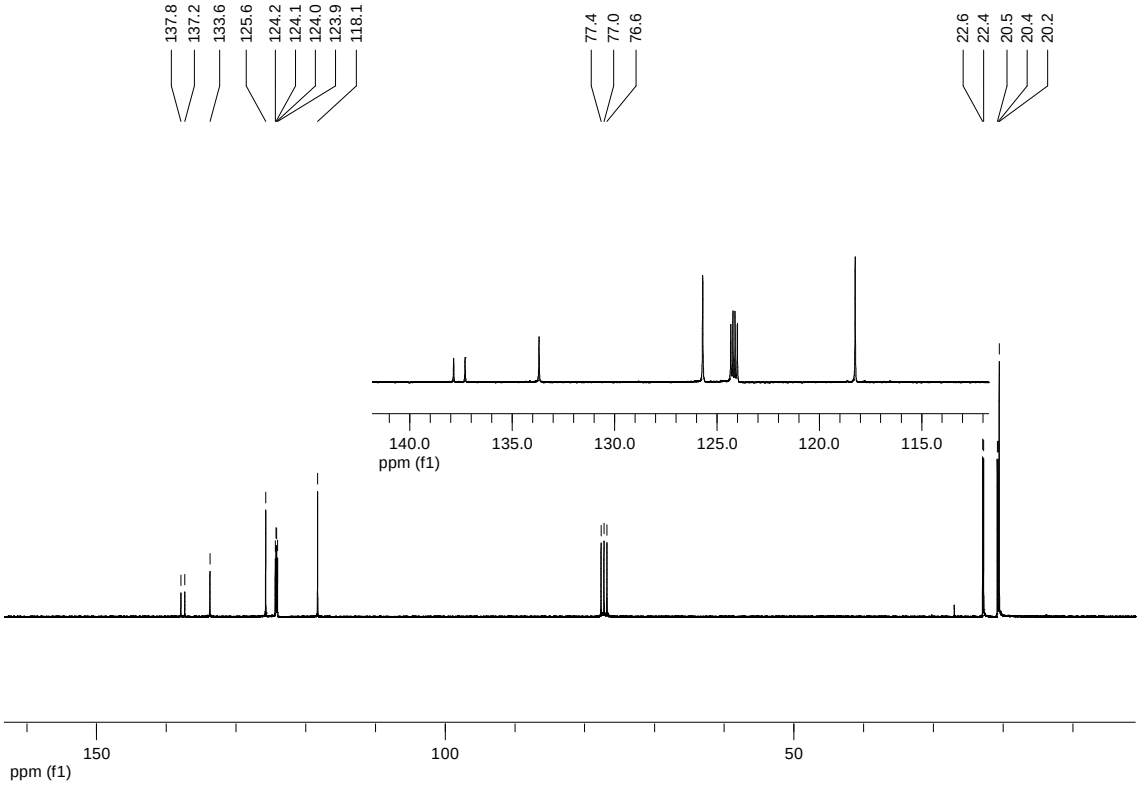






**7-(Di-*iso*-propylphosphino)-[1,2,3]triazolo[1,5-*a*]pyridine (6b)**: Starting from [1,2,3]triazolo[1,5-*a*]pyridine (**3b,** 0.4 g, 3.4 mmol) in toluene (17 mL). The crude product was purified by filtration on silicagel to afford 7-(di-*iso*-propylphosphino)-[1,2,3]triazolo[1,5-*a*]pyridine (**6b**; 0.4 g, 50%) as a brown oil. – $^{1}$H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.9 Hz, 1 H, H3), 7.71-7.62 (m, 1 H, H4), 7.17-7.09 (m, 2 H, H5 + H6), 2.77 (m, 2 H, P(C*H*$(CH_3)_2)_2$), 1.13 (dd, *J* = 15.9, 7.0 Hz, 6 H, P(CH(C*H*$_3)_2)_2$), 0.81 (dd, *J* = 13.4, 7.0 Hz, 6 H, P(CH(C*H*$_3)_2)_2$). – $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 137.5 (d, *J* = 42.2 Hz, 1 C, C7) 133.6 (s, 1 C, C3a), 125.6 (s, 1 C, C3), 124.3 (d, *J* = 24.2 Hz, 1 CH, C6), 124.2 (d, *J* = 7,6.7 Hz, 1 CH, C5), 118.1 (s, 1 CH, C4), 22.5 (d, *J* = 10.9 Hz, 2 CH, P(*C*H$(CH_3)_2)_2$), 20.4 (d, *J* = 10.0 Hz, 2 $CH_3$, P(CH(*C*H$_3)_2)_2$), 20.2 (s, 2 $CH_3$, P(CH(*C*H$_3)_2)_2$). – $^{31}$P NMR (161 MHz, $CDCl_3$): δ= 15.4. – MS (EI): m/z(%) = 235.2 (49) [$M^+$], 207.2 (21) [$M^+$ - $N_2$], 192.1 (100) [$M^+$ - $^{i}$Prop], 164.1 (39) [$M^+$ - $N_2$ - $^{i}$Prop], 149.1 (85) [ $M^+$- 2$^{i}$Prop], 122.1 (42) [$M^+$ - $N_2$ – 2$^{i}$Prop + H]. – HRMS for $C_{12}H_{18}N_3P$ [M+Li]: calcd. 242.1393; found 242.1371.




137.8
137.2
133.6
125.6
124.2
124.1
124.0
123.9
118.1
77.4
77.0
76.6
22.6
22.4
20.5
20.4
20.2
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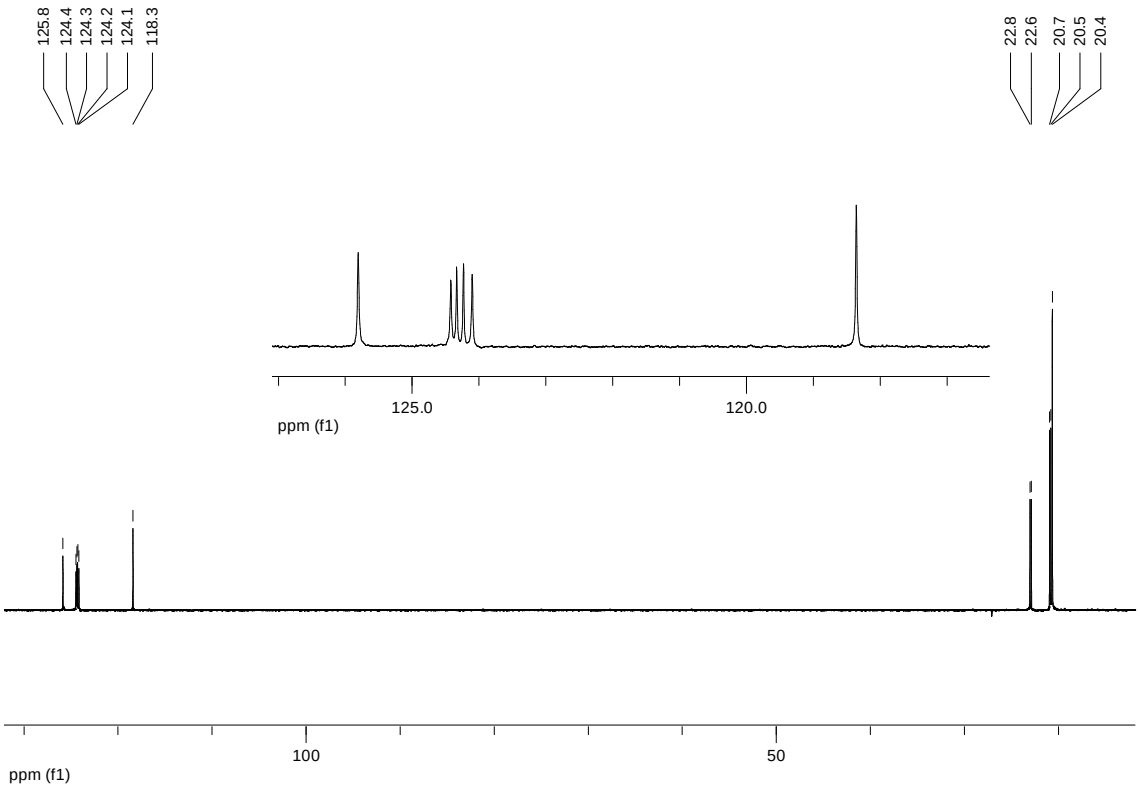
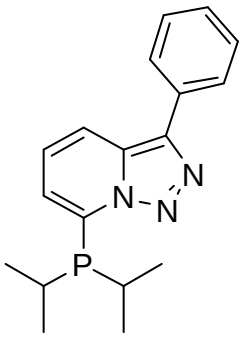
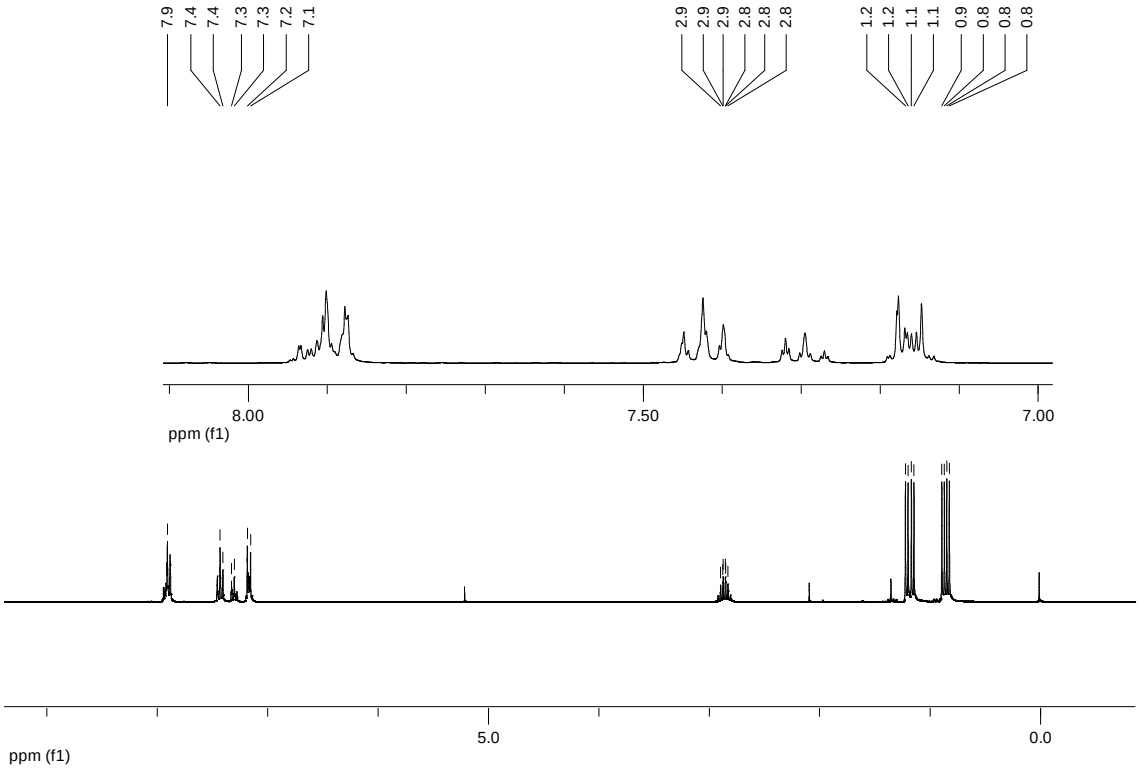
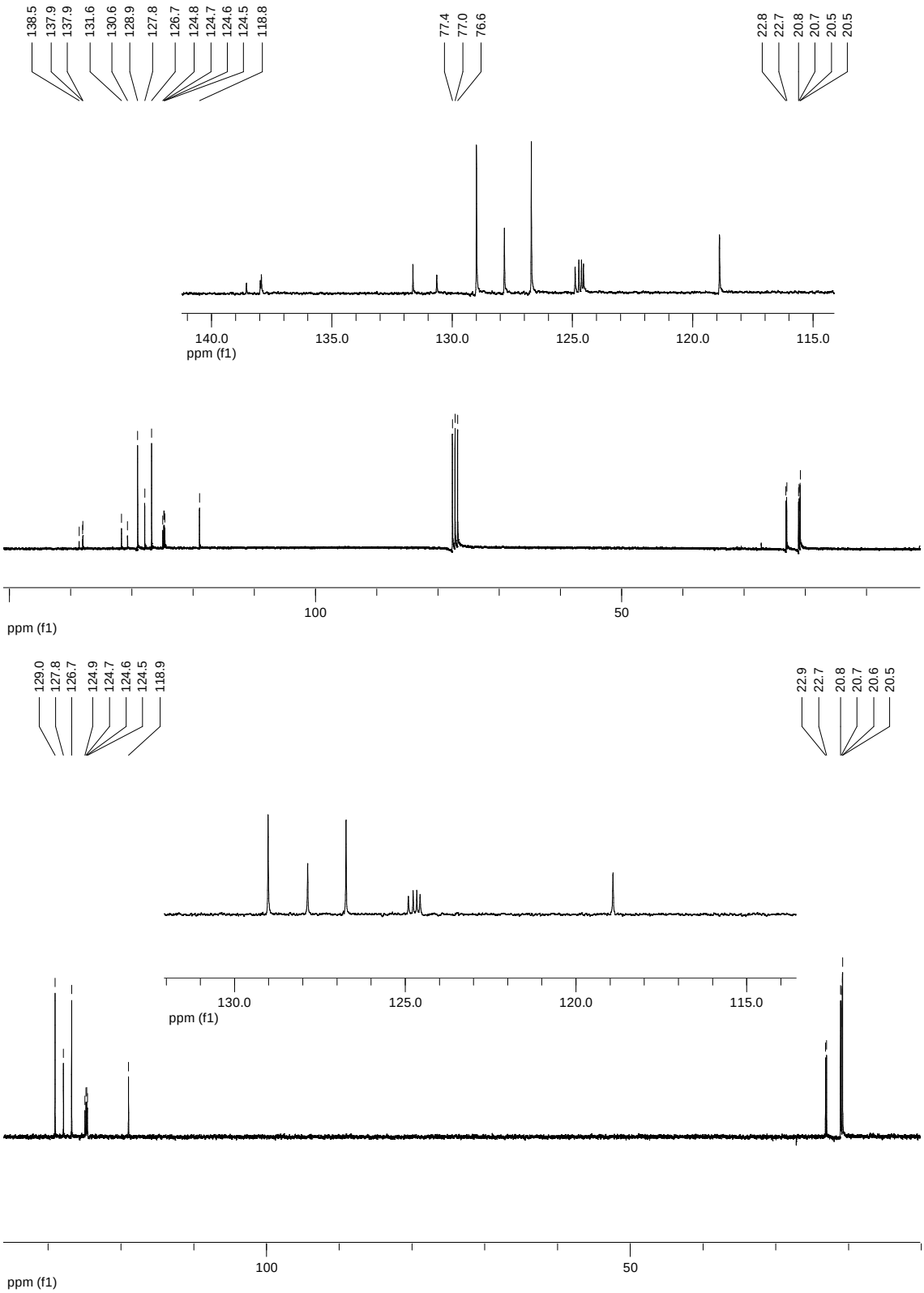
135.0
130.0
125.0
120.0
115.0
ppm (f1)
150
100
50
ppm (f1)

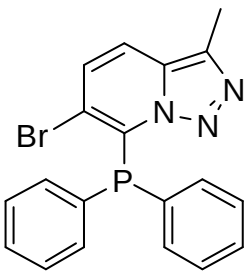

125.8
124.4
124.3
124.2
124.1
118.3
22.8
22.6
20.7
20.5
20.4
125.0
120.0
ppm (f1)
100
50
ppm (f1)



**7-(Di-*iso*-propylphosphino)-3-phenyl-[1,2,3]triazolo[1,5-*a*] pyridine (6c)**: Starting from 3-phenyl-[1,2,3]triazolo[1,5-*a*] pyridine (**3c,** 0.4 g, 2.1 mmol) in toluene (14 mL). The crude product was purified by filtration on silicagel to afford 7-(di-*iso*-propylphosphino)-3-phenyl-[1,2,3]triazolo[1,5-*a*]pyridine (**6c**; 0.3 g, 23%) as a brown oil. – $^{1}$H NMR (300 MHz, $CDCl_3$): δ = 7.95-7.85 (m, 3 H, H4 + 3-*o*-Ph), 7.46-7.39 (m, 2 H, 3-*m*-Ph), 7.34-7.26 (m, 1 H, 3-*p*-Ph), 7.19-7.13 (m, 2 H, H5 + H6), 2.85 (m, 2 H, $P(CH(CH_3)_2)_2$ ), 1.17 (dd, *J* = 16.1, 7.0 Hz, 6 H, $P(CH(CH_3)_2)_2$), 0.84 (dd, *J* = 13.5, 7.0 Hz, 6 H, $P(CH(CH_3)_2)_2$). – $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 138.2 (d, *J* = 43.6 Hz, 1 C, C7), 137.9 (s, 1 C, 3-*ipso*-Ph), 131.6 (s, 1 C, C3a), 130.6 (s, 1 C, C3), 128.9 (s, 2 CH, 3-*o*-Ph), 127.8 (s, 1 CH, 3-*p*-Ph), 126.7 (s, 2 CH, 3-*m*-Ph), 124.7 (d, *J* = 26.2 Hz, 1 CH, C6), 124.6 (d, *J* = 8.3 Hz, 1 CH, C5), 118.8 (s, 1 CH, C4), 22.8 (d, *J* = 10.7 Hz, 2 CH, $P(CH(CH_3)_2)_2$), 20.7 (d, *J* = 7. 9 Hz, 2 $CH_3$, $P(CH(CH_3)_2)_2$), 20.5 (d, *J* = 1.7 Hz, 2 $CH_3$, $P(CH(CH_3)_2)_2$). – $^{31}$P NMR (161 MHz, $CDCl_3$): δ= 17.3. – MS (EI): m/z(%) = 311.2 (28) [$M^+$], 283.2 (58) [$M^+ - N_2$], 240.1 (55) [$M^+ - N_2 - {}^{i}$Prop], 198.1 (100) [ $HM^+-N_2 - 2{}^{i}$Prop], 167.1 (51) [$M^+ - N_2 - 2{}^{i}$Prop + H]. – HRMS for $C_{18}H_{22}N_3P$ [M+Li]: calcd. 318.1716; found 318.1721.

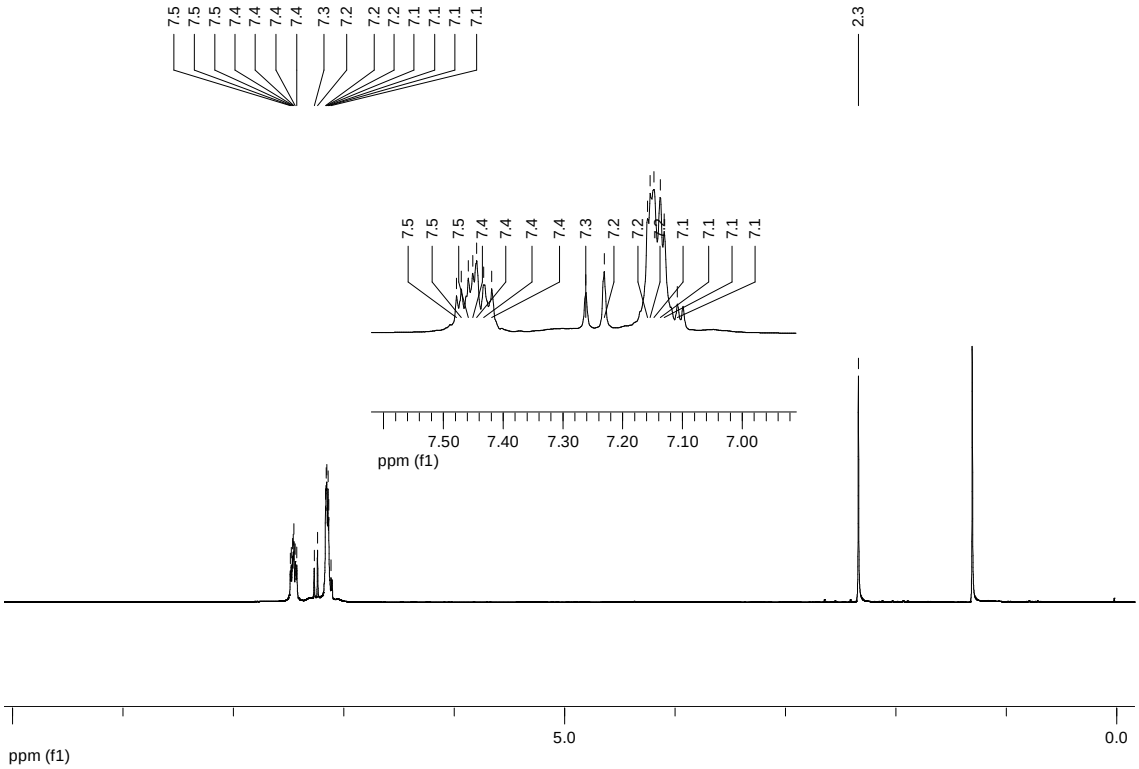


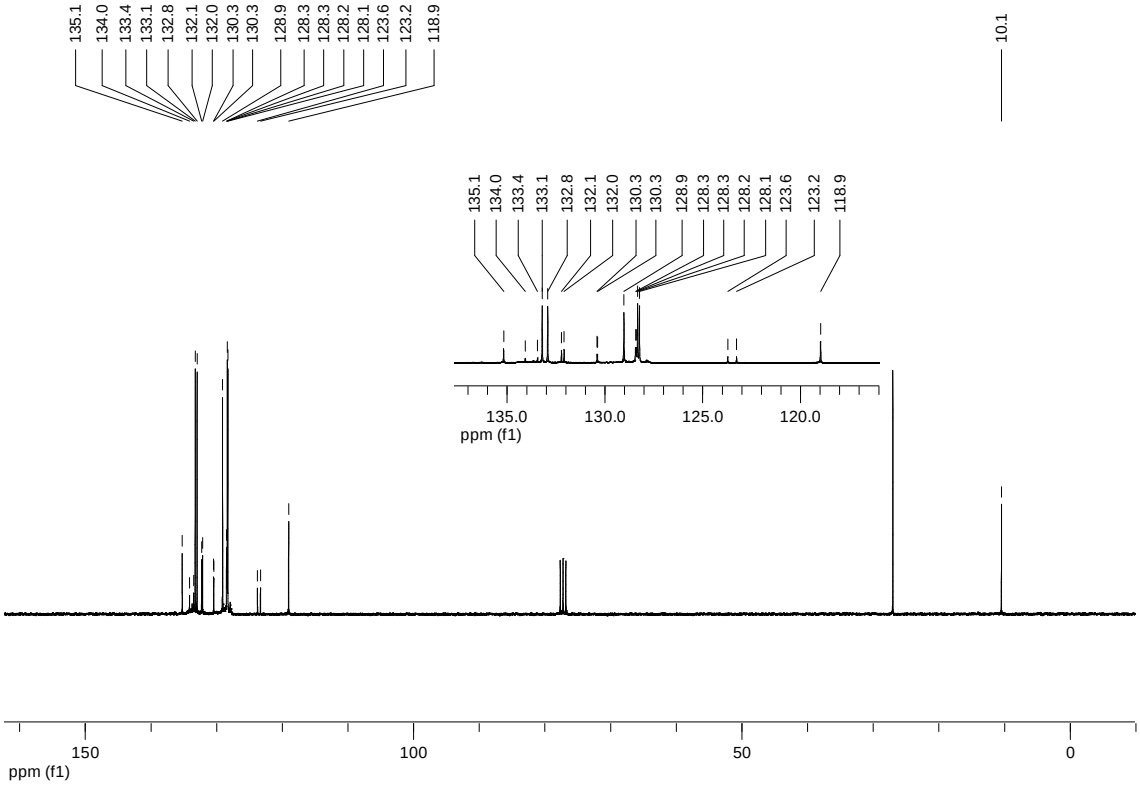





**7-(Diphenylphosphino)-6-bromo-3-methyl-[1,2,3]triazolo [1,5-*a*]pyridine (8):**

At 0 ºC butillihium (18.2 mmol, 11.6 mL, 1.3 eq) in hexanes (1.56 M) was added to a solution of di-*iso*-propylamine (18.2 mmol, 2.6 mL, 1.3 eq) in terahydrofurane (150 mL). Then it was colled to -40 ºC and added to a stirred solution of 6-bromo-3-methyl-[1,2,3]triazolo[1,5-*a*]pyridine (**7**; 3.0 g, 14.1 mmol, 1.0 eq) in tetrahydrofurane (150 mL) at -40 ºC. The mixtures was kept at -40 ºC for one hour before diphenylphosphine chloride (0.9 g, 42 mmol, 1.3 eq) in tetrahydrofurane (5 mL) was added. After 1 h, the solution was allowed to reach room temperature. Water (20.0 mL) was added, followed by extraction with dichloromethane (3 x 20.0 mL). The combined organic layers were dried over sodium sulfate, filtered, and evaporated. The crude product was purified by chromatography on silicagel (ethyal acetate/cyclohexane 1:4) to afford 7-(diphenylphosphino)-6-bromo-3-methyl-[1,2,3]triazolo[1,5-*a*]pyridine (**8**; 3.2 g. 57%) as a yellow oil. – $^{1}$H NMR (300 MHz, $CDCl_3$): 7.49-7.40 (m, 4H), 7.24 (d, $J$ = 9.22 Hz, 1H, H4), 7.18-7.08 (m, 7H), 2.32 (s, 3H, $CH_3$). – $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 135.4 (s, C, C3), 133.9 (d, $J$ = 47.30 Hz, 1 C, C7), 133.3 (d, $J$ = 21.17 Hz, 4 CH, *o*-Ph ), 132.3 (d, $J$ = 10.17 Hz, 2 C, *ipso*-Ph), 130.62 (d, $J$ = 1.5 Hz, C, C3a), 129.25 (s, 2 CH, *p*-Ph), 128.64 (d, $J$ = 3.00 Hz, CH, C5), 128.50 (d, $J$ = 6.96 Hz, 4 CH, *m*-Ph), 123.71 (d, $J$ = 34.04 Hz, C, C6), 119.18 (s, CH, C4), 26.99 (s, $CH_3$). $^{31}$P NMR (161 MHz, $CDCl_3$): δ= -2.0. – MS (EI): m/z(%) = 397.1 (25) [$M^+$], 368.0 (60) [$M^+$ - $N_2$], 288.1 (80) [$M^+$ - $N_2$ - Br], 183.1 (100). – HRMS for $C_{19}H_{15}{}^{79}BrN_3P$: [M+H] calcd. 396.0265 found 396.0261. $C_{19}H_{15}{}^{81}BrN_3P$: [M+H] calcd. 398.0245 found 398.0241.

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130.3
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128.3
128.3
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128.1
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120.0
ppm (f1)
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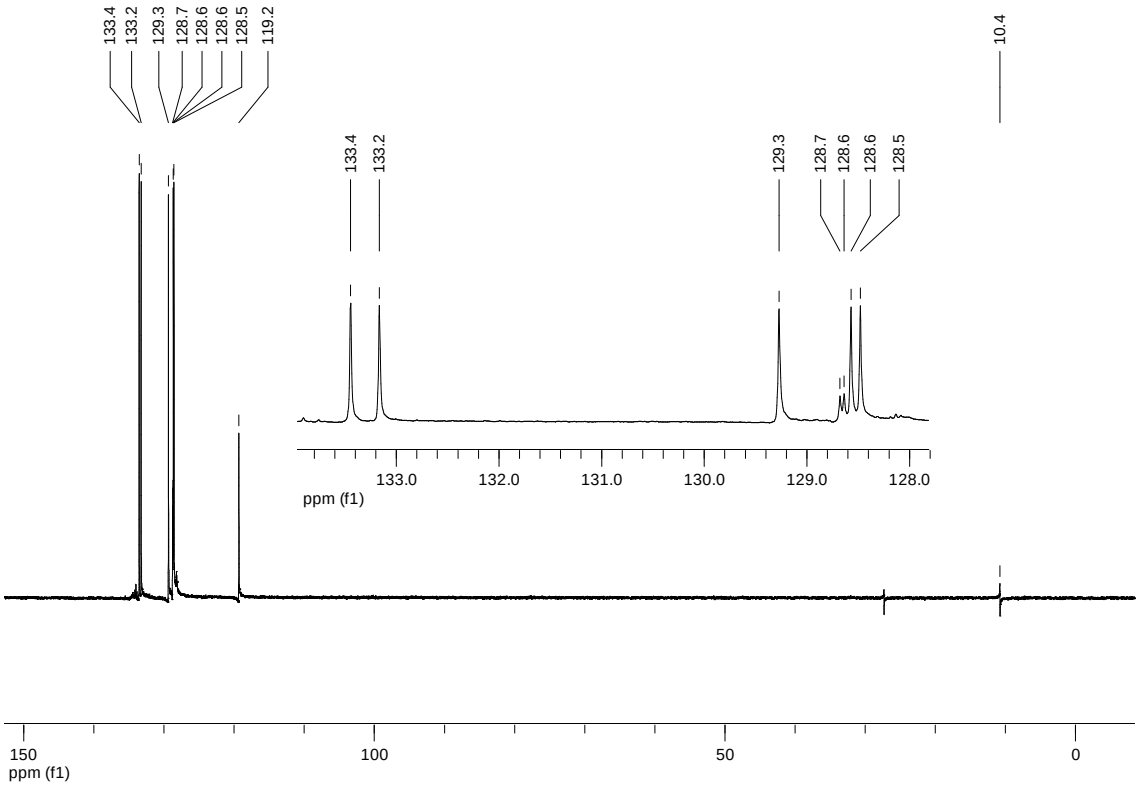
50
0
ppm (f1)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128.6
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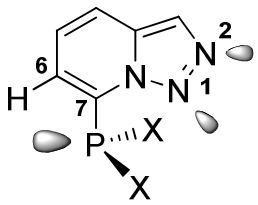
10.4
133.0
132.0
131.0
130.0
129.0
128.0
ppm (f1)
150
100
50
0
ppm (f1)

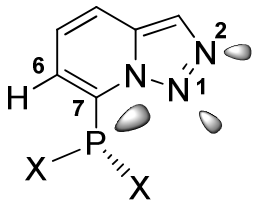
# Theoretical Section

**Absolute energies (Hartrees) of the optimized isomers (TZP-$PX_2$) at the B3LYP/6-31g(d,p) computational level.**

CONFORMER A




CONFORMER B




| X | Conf. | Point Group | Im. Freq. | ENERGY (h) | Dipole Moment | E rel ($kJmol^{-1}$) |
|---|---|---|---|---|---|---|
| **H** | **A** | CS | 0 | -737.808401912 | 4.17 | 0.91 |
| **H** | **B** | C1 | 0 | -737.808748475 | 4.87 | |
| **F** | **A** | CS | 0 | -936.336694348 | 6.05 | 9.90 |
| **F** | **B** | C1 | 0 | -936.340463819 | 5.03 | |
| **Br** | **A** | CS | 0 | -5880.069393820 | 5.85 | 11.16 |
| **Br** | **B** | C1 | 0 | -5880.073644260 | 5.18 | |
| **Me** | **A** | CS | 0 | -816.456196943 | 3.27 | -0.81 |
| **Me** | **B** | C1 | 0 | -816.455888502 | 4.98 | |
| **iPr** | **A** | C1 | 0 | -973.713080150 | 3.07 | -7.38 |
| **iPr** | **B** | C1 | 0 | -973.710267504 | 4.99 | |
| **Cy** | **A** | C1 | 0 | -1207.197779300 | 2.93 | -7.54 |
| **Cy** | **B** | C1 | 0 | -1207.194909110 | 5.00 | |
| **Ph** | **A** | C1 | 0 | -1199.924468080 | 3.03 | 8.13 |
| **Ph** | **B** | C1 | 0 | -1199.927565000 | 5.16 | |

## Cartesian coordinates of the optimized isomers (TZP-$PX_2$) at B3LYP/6-31g(d,p) Level.

**X = H – CONFORMER A**

0 1

| | X | Y | Z |
|---|---|---|---|
| **P** | 2.47357629 | 0.48971363 | 0 |
| **N** | -1.10470363 | -2.19390533 | 0 |
| **N** | 0.03852759 | -1.54425426 | 0 |
| **N** | -0.26361944 | -0.21804293 | 0 |
| **C** | -2.1386379 | -1.32900536 | 0 |
| **H** | -3.16508985 | -1.66408334 | 0 |
| **C** | -1.64161059 | -0.02657592 | 0 |
| **C** | -2.14249081 | 1.29656742 | 0 |
| **H** | -3.21476584 | 1.45777539 | 0 |
| **C** | -1.25318385 | 2.34076993 | 0 |
| **H** | -1.61007728 | 3.36516126 | 0 |
| **C** | 0.14992357 | 2.09062364 | 0 |
| **H** | 0.84850242 | 2.91967933 | 0 |
| **C** | 0.65651112 | 0.81445395 | 0 |
| **H** | 2.47034526 | -0.49104174 | 1.02929153 |
| **H** | 2.47034526 | -0.49104174 | -1.02929153 |

**X = H – CONFORMER B**

0 1

| | X | Y | Z |
|---|---|---|---|
| **P** | -2.00610585 | -0.46805794 | -0.45088405 |
| **N** | 2.00414806 | -2.0078043 | -0.09244262 |
| **N** | 0.74035831 | -1.65513247 | -0.15917537 |
| **N** | 0.7092918 | -0.29800267 | -0.07771344 |
| **C** | 2.78979278 | -0.91835158 | 0.03339731 |
| **H** | 3.86376132 | -0.99541531 | 0.10960963 |
| **C** | 1.98922113 | 0.22475733 | 0.04726034 |
| **C** | 2.13037593 | 1.62913365 | 0.14583226 |
| **H** | 3.11976467 | 2.06143119 | 0.24198739 |
| **C** | 0.99899243 | 2.40650054 | 0.11633909 |
| **H** | 1.07751353 | 3.48591603 | 0.19365363 |
| **C** | -0.29135146 | 1.81543733 | -0.01142884 |

| | | | |
|---|---|---|---|
| **H** | -1.17265682 | 2.44627122 | -0.030136 |
| **C** | -0.44392802 | 0.45405456 | -0.11063003 |
| **H** | -2.01503813 | -1.26254556 | 0.72654035 |
| **H** | -2.84756267 | 0.54991697 | 0.07867233 |

**X = F – CONFORMER A**

0 1

| | **X** | **Y** | **Z** |
|---|---|---|---|
| **P** | 2.45771948 | 0.55273653 | 0 |
| **N** | -1.13968167 | -2.20015489 | 0 |
| **N** | 0.00745039 | -1.56031599 | 0 |
| **N** | -0.28492878 | -0.23588289 | 0 |
| **C** | -2.16891164 | -1.32690602 | 0 |
| **H** | -3.19748718 | -1.6552751 | 0 |
| **C** | -1.66258438 | -0.0303849 | 0 |
| **C** | -2.14945441 | 1.29940396 | 0 |
| **H** | -3.22063499 | 1.46856871 | 0 |
| **C** | -1.2564316 | 2.34071452 | 0 |
| **H** | -1.60746003 | 3.36671964 | 0 |
| **C** | 0.14412758 | 2.07675044 | 0 |
| **H** | 0.85130407 | 2.90033367 | 0 |
| **C** | 0.63415893 | 0.79467077 | 0 |
| **F** | 2.58318328 | -0.48709226 | 1.21782151 |
| **F** | 2.58318328 | -0.48709226 | -1.21782151 |

**X = F – CONFORMER B**

0 1

| | **X** | **Y** | **Z** |
|---|---|---|---|
| **P** | -1.97543259 | -0.53053286 | -0.42583806 |
| **N** | 2.06225606 | -2.01091742 | -0.13696828 |
| **N** | 0.79285232 | -1.67370226 | -0.17943948 |
| **N** | 0.74577905 | -0.32204578 | -0.0813992 |
| **C** | 2.83431751 | -0.91210983 | -0.00404818 |
| **H** | 3.909821 | -0.97652794 | 0.05892109 |
| **C** | 2.01732388 | 0.21873532 | 0.03671315 |
| **C** | 2.1283335 | 1.62575731 | 0.15744327 |
| **H** | 3.11026949 | 2.07509778 | 0.25445997 |
| **C** | 0.98572207 | 2.38765231 | 0.14590652 |
| **H** | 1.04992397 | 3.46660976 | 0.23763617 |
| **C** | -0.29590594 | 1.77650959 | 0.00865946 |
| **H** | -1.19598296 | 2.3787242 | -0.01139904 |

| | | | |
|---|---|---|---|
| **C** | -0.41526538 | 0.41551155 | -0.09764496 |
| **F** | -2.15702785 | -1.1980826 | 1.02574419 |
| **F** | -2.95040713 | 0.74742985 | -0.22786462 |

**X = Br – CONFORMER A**

0 1

| | **X** | **Y** | **Z** |
|---|---|---|---|
| **P** | 2.44059049 | 0.67951836 | 0 |
| **N** | -1.12942036 | -2.18034084 | 0 |
| **N** | 0.00997031 | -1.52882659 | 0 |
| **N** | -0.29485091 | -0.20617202 | 0 |
| **C** | -2.16748523 | -1.31780728 | 0 |
| **H** | -3.19223087 | -1.65728425 | 0 |
| **C** | -1.67523108 | -0.0160842 | 0 |
| **C** | -2.1831281 | 1.30430636 | 0 |
| **H** | -3.25663032 | 1.4573971 | 0 |
| **C** | -1.30421577 | 2.35735138 | 0 |
| **H** | -1.66731114 | 3.37911762 | 0 |
| **C** | 0.09875234 | 2.11387302 | 0 |
| **H** | 0.79076707 | 2.94942774 | 0 |
| **C** | 0.61068265 | 0.83720252 | 0 |
| **Br** | 2.74664663 | -0.67744249 | 1.77166048 |
| **Br** | 2.74664663 | -0.67744249 | -1.77166048 |

**X = Br – CONFORMER B**

0 1

| | **X** | **Y** | **Z** |
|---|---|---|---|
| **P** | -1.888118 | -0.61044857 | -0.50567459 |
| **N** | 2.09962536 | -2.00009631 | -0.1979877 |
| **N** | 0.83236259 | -1.65910202 | -0.27018395 |
| **N** | 0.78042279 | -0.31211402 | -0.13407861 |
| **C** | 2.86592588 | -0.90629096 | -0.0111907 |
| **H** | 3.93940822 | -0.97163343 | 0.07961071 |
| **C** | 2.04813152 | 0.22411106 | 0.03632654 |
| **C** | 2.15972003 | 1.62585266 | 0.19168233 |
| **H** | 3.13885448 | 2.07131492 | 0.32638973 |
| **C** | 1.01728491 | 2.38735424 | 0.16356829 |
| **H** | 1.07679136 | 3.46421105 | 0.27908111 |
| **C** | -0.261416 | 1.78397699 | -0.01507369 |
| **H** | -1.15447146 | 2.39534732 | -0.03569293 |
| **C** | -0.38602892 | 0.42584396 | -0.15968319 |
| **Br** | -2.1792095 | -1.48276147 | 1.56150146 |

| | | | |
|---|---|---|---|
| **Br** | -3.44270627 | 1.03254358 | -0.54771281 |

**X = Me – CONFORMER A**

0 1

| | X | Y | Z |
|---|---|---|---|
| **P** | -2.28352518 | 0.69956927 | 0 |
| **N** | 1.17309119 | -2.28275173 | 0 |
| **N** | 0.06776135 | -1.57302906 | 0 |
| **N** | 0.43503239 | -0.2612605 | 0 |
| **C** | 2.25016175 | -1.47314951 | 0 |
| **H** | 3.25751809 | -1.86121158 | 0 |
| **C** | 1.82196813 | -0.14688055 | 0 |
| **C** | 2.40253635 | 1.14317084 | 0 |
| **H** | 3.48263405 | 1.23875528 | 0 |
| **C** | 1.57571933 | 2.23638935 | 0 |
| **H** | 1.99065888 | 3.238831 | 0 |
| **C** | 0.16117303 | 2.06550732 | 0 |
| **H** | -0.48799825 | 2.93374201 | 0 |
| **C** | -0.43045547 | 0.82440244 | 0 |
| **C** | -2.592528 | -0.45153464 | -1.43409525 |
| **C** | -2.592528 | -0.45153464 | 1.43409525 |
| **H** | -2.04007682 | -1.38860527 | -1.3485242 |
| **H** | -2.32511043 | 0.05201878 | -2.36722405 |
| **H** | -3.66695163 | -0.65920544 | -1.46350422 |
| **H** | -2.32511043 | 0.05201878 | 2.36722405 |
| **H** | -3.66695163 | -0.65920544 | 1.46350422 |
| **H** | -2.04007682 | -1.38860527 | 1.3485242 |

**X = Me – CONFORMER B**

0 1

| | X | Y | Z |
|---|---|---|---|
| **P** | -1.93138856 | -0.46600015 | -0.48860756 |
| **N** | 2.09727492 | -1.99107766 | 0.03799244 |
| **N** | 0.83426144 | -1.64783182 | -0.07027934 |
| **N** | 0.7925357 | -0.28687336 | -0.05786972 |
| **C** | 2.87579038 | -0.89320994 | 0.122646 |
| **H** | 3.94862359 | -0.95997859 | 0.22172233 |
| **C** | 2.06999328 | 0.24381806 | 0.06395543 |
| **C** | 2.21647887 | 1.65051144 | 0.09209348 |
| **H** | 3.20597599 | 2.08316752 | 0.18602073 |
| **C** | 1.08903984 | 2.42618151 | -0.00392963 |
| **H** | 1.16806034 | 3.50833219 | 0.01576237 |
| **C** | -0.19874161 | 1.82971979 | -0.1305922 |
| **H** | -1.06927254 | 2.46842628 | -0.20914807 |

| | | | |
|---|---|---|---|
| **C** | -0.36520703 | 0.46445138 | -0.15865782 |
| **C** | -2.151265 | -1.38572309 | 1.11937984 |
| **C** | -3.17243909 | 0.90262577 | -0.24359725 |
| **H** | -1.37279612 | -2.14623761 | 1.19360975 |
| **H** | -3.12606818 | -1.88191814 | 1.09186256 |
| **H** | -2.1093263 | -0.72881552 | 1.99315764 |
| **H** | -3.04889576 | 1.44572927 | 0.69871566 |
| **H** | -4.1649521 | 0.44234766 | -0.252123 |
| **H** | -3.13300907 | 1.60763154 | -1.0783399 |

**X = iPr – CONFORMER A**

0 1

| | **X** | **Y** | **Z** |
|---|---|---|---|
| **P** | -0.03515391 | -0.51161012 | -1.11606106 |
| **N** | 0.14651796 | 2.25032292 | 2.50327772 |
| **N** | 0.05761858 | 1.32166291 | 1.5782489 |
| **N** | 0.1976736 | 1.94330628 | 0.37375498 |
| **C** | 0.33777874 | 3.45851495 | 1.93799945 |
| **H** | 0.43440718 | 4.35743841 | 2.52798307 |
| **C** | 0.37562421 | 3.31148277 | 0.55227456 |
| **C** | 0.52523078 | 4.13530548 | -0.58816791 |
| **H** | 0.66538588 | 5.20255292 | -0.45759764 |
| **C** | 0.48352924 | 3.55327875 | -1.82858954 |
| **H** | 0.59201123 | 4.15836242 | -2.72262805 |
| **C** | 0.29797069 | 2.14625027 | -1.95627166 |
| **H** | 0.26921615 | 1.69253745 | -2.94024816 |
| **C** | 0.15481577 | 1.32036494 | -0.86605818 |
| **C** | 1.41049635 | -1.13718389 | -0.05737555 |
| **H** | 1.31691701 | -0.68713635 | 0.93543815 |
| **C** | 2.73545314 | -0.68952845 | -0.69417709 |
| **H** | 2.85678793 | -1.10987587 | -1.69916044 |
| **H** | 2.80998124 | 0.39894661 | -0.77549819 |
| **C** | 1.36981292 | -2.66598354 | 0.08465515 |
| **H** | 1.34221417 | -3.16539543 | -0.89109656 |
| **H** | 0.5089958 | -3.00444859 | 0.66698926 |
| **C** | -1.57273525 | -0.93285189 | -0.08453537 |
| **H** | -1.27871411 | -0.97318987 | 0.96927809 |
| **C** | -2.67005133 | 0.12987774 | -0.24747331 |
| **H** | -2.38430686 | 1.08751599 | 0.19252476 |
| **H** | -2.91830936 | 0.29400185 | -1.30275836 |
| **C** | -2.10826457 | -2.3041991 | -0.53550778 |
| **H** | -2.43979247 | -2.26971293 | -1.57918057 |
| **H** | -1.36609893 | -3.10204811 | -0.45261295 |

| | | | |
|---|---|---|---|
| **H** | -3.58520514 | -0.20358391 | 0.25531378 |
| **H** | -2.96967256 | -2.58908249 | 0.07988702 |
| **H** | 2.26978607 | -3.01223523 | 0.60608539 |
| **H** | 3.57915341 | -1.033861 | -0.08504561 |

**X = iPr – CONFORMER B**

0 1

| | **X** | **Y** | **Z** |
|---|---|---|---|
| **P** | 0.23474269 | -0.12196598 | -0.89560264 |
| **N** | -4.03800581 | 0.17186823 | -1.46402253 |
| **N** | -2.73047561 | 0.19240586 | -1.34297818 |
| **N** | -2.40883985 | -0.70023955 | -0.36570436 |
| **C** | -4.57550019 | -0.70501577 | -0.59209984 |
| **H** | -5.64071014 | -0.86836871 | -0.52893634 |
| **C** | -3.55288612 | -1.29657916 | 0.14899688 |
| **C** | -3.41241414 | -2.24475587 | 1.18877326 |
| **H** | -4.29435909 | -2.72203849 | 1.60050958 |
| **C** | -2.15063597 | -2.52565107 | 1.64667497 |
| **H** | -2.00753412 | -3.2424158 | 2.44887483 |
| **C** | -1.00984479 | -1.88540991 | 1.08177756 |
| **H** | -0.02990634 | -2.13105507 | 1.46909939 |
| **C** | -1.11649136 | -0.96902762 | 0.06009994 |
| **C** | 0.01933932 | 1.63064695 | -0.1844801 |
| **H** | -1.05415944 | 1.78909864 | -0.33729095 |
| **C** | 0.74866904 | 2.66859257 | -1.05352056 |
| **H** | 1.8373002 | 2.58437879 | -0.98093961 |
| **H** | 0.47241007 | 2.56844947 | -2.10697011 |
| **C** | 0.32769469 | 1.7933896 | 1.30885685 |
| **H** | 1.39411396 | 1.67086728 | 1.52570055 |
| **H** | -0.22553049 | 1.07341771 | 1.91951159 |
| **C** | 1.76833231 | -0.85238545 | -0.06481836 |
| **H** | 1.64925466 | -0.85339387 | 1.02592841 |
| **C** | 1.96945201 | -2.29611465 | -0.5628882 |
| **H** | 1.10962813 | -2.94013928 | -0.36189605 |
| **H** | 2.14307238 | -2.30862599 | -1.64403595 |
| **C** | 3.01213851 | -0.0153043 | -0.41055389 |
| **H** | 3.12368387 | 0.10441695 | -1.49409211 |
| **H** | 2.98654531 | 0.9798937 | 0.03850866 |
| **H** | 0.47772587 | 3.68025262 | -0.72985524 |
| **H** | 2.84527916 | -2.74422671 | -0.07900791 |
| **H** | 0.04404078 | 2.79845721 | 1.6436738 |
| **H** | 3.91262626 | -0.51971819 | -0.04171317 |

**X = Cy – CONFORMER A**

0 1

| | X | Y | Z |
|---|---|---|---|
| **P** | -0.2978925 | -0.04376948 | -0.87395586 |
| **N** | 3.98641065 | -1.25325842 | -1.85780325 |
| **N** | 2.74861869 | -0.82890237 | -1.73967589 |
| **N** | 2.27746802 | -1.29826414 | -0.55024682 |
| **C** | 4.33512676 | -1.98726295 | -0.78288608 |
| **H** | 5.31434526 | -2.43150796 | -0.68651704 |
| **C** | 3.25476536 | -2.04840989 | 0.09597002 |
| **C** | 2.94877431 | -2.63814301 | 1.34501283 |
| **H** | 3.7054842 | -3.22328379 | 1.85562105 |
| **C** | 1.69569091 | -2.45275218 | 1.86901624 |
| **H** | 1.42899436 | -2.89486345 | 2.82329242 |
| **C** | 0.7304235 | -1.67574934 | 1.16561274 |
| **H** | -0.25703953 | -1.52987203 | 1.58809235 |
| **C** | 1.00094906 | -1.08616609 | -0.04704012 |
| **C** | 0.67159734 | 1.57220801 | -1.0855398 |
| **H** | 1.61291886 | 1.33629847 | -1.59433494 |
| **C** | 0.9856313 | 2.16898101 | 0.30317195 |
| **H** | 0.04491777 | 2.32301322 | 0.85138758 |
| **H** | 1.57852909 | 1.46402194 | 0.89681321 |
| **C** | 1.7313049 | 3.50903659 | 0.19489733 |
| **H** | 1.9112057 | 3.91503698 | 1.19780235 |
| **H** | 2.71899844 | 3.33730166 | -0.25498391 |
| **C** | 0.95319514 | 4.51784577 | -0.65998035 |
| **H** | 1.5201506 | 5.45095271 | -0.76156832 |
| **H** | 0.01390398 | 4.77619301 | -0.15028925 |
| **C** | 0.63551574 | 3.93460078 | -2.04276938 |
| **H** | 1.57325543 | 3.78444916 | -2.59551887 |
| **H** | 0.03778423 | 4.64276751 | -2.62942664 |
| **C** | -0.10724346 | 2.59035384 | -1.94326604 |
| **H** | -1.10281493 | 2.75713685 | -1.50654609 |
| **H** | -0.2659198 | 2.19624058 | -2.95217631 |
| **C** | -0.38186511 | -0.76032823 | -2.62849167 |
| **H** | 0.45901439 | -0.35759953 | -3.20609291 |
| **C** | -0.28138873 | -2.30021642 | -2.63886314 |
| **H** | 0.67781316 | -2.6230293 | -2.22556235 |
| **H** | -1.06640294 | -2.721716 | -1.99397423 |
| **C** | -0.43342808 | -2.86831696 | -4.06028492 |
| **H** | 0.42043265 | -2.53702827 | -4.66714776 |
| **H** | -0.38418858 | -3.96354669 | -4.0262826 |

| | | | |
|---|---|---|---|
| **C** | -1.73782034 | -2.41267985 | -4.72727715 |
| **H** | -2.59196191 | -2.85073835 | -4.19122403 |
| **H** | -1.79064106 | -2.78675023 | -5.75675887 |
| **C** | -1.86178246 | -0.88369315 | -4.70575947 |
| **H** | -2.82431045 | -0.57152412 | -5.12899631 |
| **H** | -1.08251065 | -0.44606592 | -5.34546914 |
| **C** | -1.71720693 | -0.32848003 | -3.27944671 |
| **H** | -2.5473452 | -0.69802446 | -2.66124498 |
| **H** | -1.81293629 | 0.76190168 | -3.29661571 |

**X = Cy – CONFORMER B**

0 1

| | **X** | **Y** | **Z** |
|---|---|---|---|
| **P** | 0.24684146 | -0.11556536 | -0.8914266 |
| **N** | -4.02242443 | 0.1493277 | -1.49561693 |
| **N** | -2.71584254 | 0.17642149 | -1.36563615 |
| **N** | -2.39726287 | -0.70744852 | -0.37922012 |
| **C** | -4.5622934 | -0.72371311 | -0.62128757 |
| **H** | -5.62720766 | -0.89135325 | -0.56444114 |
| **C** | -3.54244827 | -1.30510023 | 0.13157952 |
| **C** | -3.40577095 | -2.24433109 | 1.17987504 |
| **H** | -4.28869225 | -2.72240386 | 1.58860117 |
| **C** | -2.14629983 | -2.51466822 | 1.65041606 |
| **H** | -2.00604984 | -3.22370963 | 2.45998083 |
| **C** | -1.00439493 | -1.87320719 | 1.08946105 |
| **H** | -0.02631157 | -2.10933797 | 1.48727151 |
| **C** | -1.10690217 | -0.96633809 | 0.05887717 |
| **C** | 0.02260126 | 1.62976151 | -0.17505612 |
| **H** | -1.05660542 | 1.77965769 | -0.3117289 |
| **C** | 0.72212883 | 2.69547057 | -1.04569384 |
| **H** | 1.81131092 | 2.56354671 | -1.00990616 |
| **H** | 0.42595096 | 2.56997474 | -2.09286704 |
| **C** | 0.37551786 | 4.11428315 | -0.56260165 |
| **H** | 0.9130197 | 4.85487401 | -1.16702957 |
| **H** | -0.69581269 | 4.29589238 | -0.7260726 |
| **C** | 0.69917844 | 4.30321997 | 0.92649421 |
| **H** | 0.40753298 | 5.30808935 | 1.25442239 |
| **H** | 1.78669975 | 4.23126619 | 1.07310657 |
| **C** | 0.00221135 | 3.24031033 | 1.7879926 |
| **H** | -1.08568604 | 3.38452758 | 1.73022133 |
| **H** | 0.27764373 | 3.36179529 | 2.84283226 |
| **C** | 0.34586226 | 1.81512586 | 1.31832116 |
| **H** | 1.41400899 | 1.63292584 | 1.49737923 |

| | | | |
|---|---|---|---|
| **H** | -0.20273686 | 1.08080685 | 1.9193465 |
| **C** | 1.77794527 | -0.85469036 | -0.06593079 |
| **H** | 1.66382805 | -0.85895369 | 1.02721452 |
| **C** | 1.97328837 | -2.30681725 | -0.56456701 |
| **H** | 1.09955633 | -2.92304595 | -0.3303247 |
| **H** | 2.04931988 | -2.29086224 | -1.66036177 |
| **C** | 3.24036699 | -2.95143607 | 0.02004205 |
| **H** | 3.13104373 | -3.04831963 | 1.10993113 |
| **H** | 3.35192412 | -3.96934657 | -0.37222732 |
| **C** | 4.48957224 | -2.11747644 | -0.29275242 |
| **H** | 4.66913344 | -2.13095464 | -1.37698239 |
| **H** | 5.37526917 | -2.56256417 | 0.17592652 |
| **C** | 4.31310204 | -0.66619844 | 0.17191618 |
| **H** | 5.18570216 | -0.06540384 | -0.11121738 |
| **H** | 4.26160478 | -0.64089117 | 1.26976416 |
| **C** | 3.03802486 | -0.02650351 | -0.40446925 |
| **H** | 3.13414517 | 0.05552001 | -1.49636276 |
| **H** | 2.94419262 | 0.99383726 | -0.02207201 |

**X = Ph – CONFORMER A**

0 1

| | **X** | **Y** | **Z** |
|---|---|---|---|
| **C** | -0.05331964 | -0.77534862 | 9.79719433 |
| **H** | -0.59151655 | -1.49880989 | 10.3908511 |
| **C** | 1.18026017 | -0.90595354 | 9.16374026 |
| **C** | 2.17852221 | -1.89589699 | 9.00871842 |
| **H** | 2.03973246 | -2.86561284 | 9.47375397 |
| **C** | 3.29532763 | -1.5953334 | 8.27350601 |
| **H** | 4.08021901 | -2.33185443 | 8.13802979 |
| **C** | 3.43693972 | -0.30647687 | 7.68363081 |
| **H** | 4.32694077 | -0.06931538 | 7.11207137 |
| **C** | 2.47824605 | 0.6719156 | 7.80976924 |
| **C** | 1.40563601 | 2.44878675 | 5.74067577 |
| **C** | 1.79071078 | 2.3606945 | 4.39273267 |
| **H** | 2.83924221 | 2.21933626 | 4.14489085 |
| **C** | 0.84458056 | 2.45877228 | 3.37122536 |
| **H** | 1.15869964 | 2.38801804 | 2.33388253 |
| **C** | -0.49940967 | 2.65599061 | 3.68698971 |
| **H** | -1.23867902 | 2.73616487 | 2.89498154 |
| **C** | -0.89280747 | 2.75416921 | 5.02394595 |
| **H** | -1.93911841 | 2.90709644 | 5.27270298 |
| **C** | 0.04885448 | 2.65160905 | 6.04755844 |
| **H** | -0.26200084 | 2.71148139 | 7.08351568 |

| | | | |
|---|---|---|---|
| **C** | 2.39026972 | 3.53636714 | 8.28533733 |
| **C** | 2.83788098 | 3.32556315 | 9.59906217 |
| **H** | 3.30193854 | 2.38119511 | 9.87075667 |
| **C** | 2.68630405 | 4.3133152 | 10.5701314 |
| **H** | 3.02585831 | 4.12539354 | 11.5847392 |
| **C** | 2.09884322 | 5.53679459 | 10.2431065 |
| **H** | 1.98041355 | 6.30627088 | 11.0001917 |
| **C** | 1.66746958 | 5.76356394 | 8.93655439 |
| **H** | 1.21079031 | 6.71258329 | 8.67016002 |
| **C** | 1.81358899 | 4.77370681 | 7.96346579 |
| **H** | 1.46696885 | 4.96544262 | 6.95304299 |
| **N** | -0.53748064 | 0.46075341 | 9.56428972 |
| **N** | 0.30017646 | 1.14662909 | 8.82090601 |
| **N** | 1.35948 | 0.33618328 | 8.55922262 |
| **P** | 2.78113163 | 2.30153009 | 6.97043361 |

**X = Ph – CONFORMER B**

0 1

| | **X** | **Y** | **Z** |
|---|---|---|---|
| **C** | -0.01776794 | -0.51941012 | 9.21555969 |
| **H** | -0.64956824 | -1.19245064 | 9.7751775 |
| **C** | 1.32225969 | -0.66748095 | 8.85916391 |
| **C** | 2.36832215 | -1.60637086 | 9.02023546 |
| **H** | 2.18322981 | -2.52288741 | 9.56900569 |
| **C** | 3.59390177 | -1.32198697 | 8.47265665 |
| **H** | 4.4148145 | -2.02385395 | 8.57804953 |
| **C** | 3.81085495 | -0.10776133 | 7.75849582 |
| **H** | 4.78602155 | 0.10119538 | 7.33713581 |
| **C** | 2.80822618 | 0.81768254 | 7.59074654 |
| **C** | 4.70180462 | 2.46766396 | 6.26491394 |
| **C** | 5.66484489 | 3.01594152 | 7.12869742 |
| **H** | 5.35382581 | 3.42553657 | 8.08636881 |
| **C** | 7.01235442 | 3.04783704 | 6.76912182 |
| **H** | 7.74373133 | 3.47231284 | 7.45075881 |
| **C** | 7.41507821 | 2.54896188 | 5.52931399 |
| **H** | 8.46209256 | 2.58229221 | 5.24230319 |
| **C** | 6.46582447 | 2.01653208 | 4.65504336 |
| **H** | 6.77310608 | 1.63405578 | 3.68578965 |
| **C** | 5.11925689 | 1.97360552 | 5.0196077 |
| **H** | 4.39000574 | 1.56268554 | 4.32919315 |
| **C** | 1.96648878 | 2.32712335 | 5.29370751 |
| **C** | 1.73172049 | 1.106031 | 4.64385491 |
| **H** | 2.13046964 | 0.18547083 | 5.05994135 |

| | | | |
|---|---|---|---|
| **C** | 0.98307842 | 1.06202234 | 3.46738264 |
| **H** | 0.80380155 | 0.1089064 | 2.97801875 |
| **C** | 0.46361047 | 2.23745379 | 2.92217934 |
| **H** | -0.12049415 | 2.20137915 | 2.00724725 |
| **C** | 0.68870768 | 3.45707154 | 3.5616222 |
| **H** | 0.27901682 | 4.37382425 | 3.14780886 |
| **C** | 1.42821226 | 3.49999645 | 4.74360462 |
| **H** | 1.58038394 | 4.44931108 | 5.24988183 |
| **N** | -0.47408194 | 0.65734712 | 8.73864879 |
| **N** | 0.47870729 | 1.28779708 | 8.09064414 |
| **N** | 1.58480114 | 0.49995492 | 8.1535443 |
| **P** | 2.94265816 | 2.51271005 | 6.85257511 |

# Crystal Structure Analysis

## Compound 4a)

*Crystal data*

| | |
|---|---|
| $C_{19}H_{16}N_3P$ | $F(000)$ = 664 |
| $M_r$ = 317.32 | |
| Triclinic, $P\bar{1}$ | $D_x$ = 1.292 Mg m$^{-3}$ |
| Hall symbol: -P 1 | |
| $a$ = 11.7432 (4) Å | Mo $K\alpha$ radiation, λ = 0.71073 Å |
| $b$ = 12.4966 (4) Å | Cell parameters from 9832 reflections |
| $c$ = 13.3411 (5) Å | θ = 1.0–27.5° |
| α = 79.341 (2)° | μ = 0.17 mm$^{-1}$ |
| β = 66.710 (2)° | $T$ = 173 K |
| γ = 65.127 (2)° | Block, colorless |
| $V$ = 1631.06 (10) Å$^3$ | 0.25 × 0.25 × 0.15 mm |
| $Z$ = 4 | |

*Data collection*

| | |
|---|---|
| KappaCCD diffractometer | 5023 reflections with $I > 2\sigma(I)$ |

| | |
|---|---|
| Radiation source: fine-focus sealed tube | $R_{int}$ = 0.055 |
| graphite | $\theta_{max}$ = 27.5°, $\theta_{min}$ = 1.7° |
| Detector resolution: ? pixels $mm^{-1}$ | $h$ = −15→12 |
| phi and ω scans | $k$ = −16→13 |
| 18652 measured reflections | $l$ = −17→17 |
| 7470 independent reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.050 | H-atom parameters constrained |
| $wR(F^2)$ = 0.171 | $w = 1/[\sigma^2(F_o^2) + (0.0966P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S$ = 1.07 | |
| 7470 reflections | $\Delta\rho_{max}$ = 0.40 e $Å^{-3}$ |
| 417 parameters | $\Delta\rho_{min}$ = −0.47 e $Å^{-3}$ |
| 0 restraints | Extinction correction: none |
| ? constraints | Extinction coefficient: ? |
| Primary atom site location: structure-invariant direct methods | |

Refinement of $F^2$ against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on $F^2$, conventional *R*-factors *R* are based on F, with F set to zero for negative $F^2$. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.6124 (2) | −0.3827 (2) | 1.3422 (2) | 0.0395 (6) |
| C2 | 0.6151 (2) | −0.2723 (2) | 1.30640 (19) | 0.0312 (5) |
| C3 | 0.5773 (2) | −0.1859 (2) | 1.2284 (2) | 0.0372 (6) |
| H3 | 0.5443 | −0.2003 | 1.1799 | 0.045* |
| C4 | 0.5894 (3) | −0.0818 (2) | 1.2242 (2) | 0.0404 (6) |
| H4 | 0.5608 | −0.0216 | 1.1742 | 0.049* |
| C5 | 0.6439 (2) | −0.0609 (2) | 1.2930 (2) | 0.0353 (6) |
| H5 | 0.6529 | 0.0123 | 1.2868 | 0.042* |
| C6 | 0.6837 (2) | −0.1435 (2) | 1.36790 (19) | 0.0300 (5) |
| C7 | 0.5641 (3) | −0.4536 (3) | 1.3018 (3) | 0.0577 (8) |
| H7A | 0.6373 | −0.4997 | 1.2393 | 0.087* |
| H7B | 0.4884 | −0.4005 | 1.2794 | 0.087* |
| H7C | 0.5351 | −0.5071 | 1.3603 | 0.087* |
| C8 | 0.9138 (2) | −0.23732 (19) | 1.43027 (19) | 0.0294 (5) |
| C9 | 0.9791 (2) | −0.30585 (19) | 1.33780 (19) | 0.0313 (5) |

| | | | | |
|---|---|---|---|---|
| H9 | 0.9366 | −0.2926 | 1.2865 | 0.038* |
| C10 | 1.1066 (2) | −0.39377 (19) | 1.3202 (2) | 0.0339 (6) |
| H10 | 1.1507 | −0.4403 | 1.2569 | 0.041* |
| C11 | 1.1696 (2) | −0.4140 (2) | 1.3942 (2) | 0.0350 (6) |
| H11 | 1.2555 | −0.4757 | 1.3828 | 0.042* |
| C12 | 1.1071 (2) | −0.3442 (2) | 1.4846 (2) | 0.0378 (6) |
| H12 | 1.1511 | −0.3559 | 1.5344 | 0.045* |
| C13 | 0.9803 (2) | −0.2571 (2) | 1.5022 (2) | 0.0360 (6) |
| H13 | 0.9376 | −0.2097 | 1.5649 | 0.043* |
| C14 | 0.7714 (2) | 0.0111 (2) | 1.41206 (19) | 0.0316 (5) |
| C15 | 0.8758 (3) | 0.0154 (2) | 1.3173 (2) | 0.0395 (6) |
| H15 | 0.9396 | −0.0555 | 1.2801 | 0.047* |
| C16 | 0.8890 (3) | 0.1216 (2) | 1.2756 (2) | 0.0450 (7) |
| H16 | 0.9607 | 0.1237 | 1.2100 | 0.054* |
| C17 | 0.7963 (3) | 0.2244 (2) | 1.3308 (2) | 0.0445 (7) |
| H17 | 0.8041 | 0.2976 | 1.3025 | 0.053* |
| C18 | 0.6937 (3) | 0.2215 (2) | 1.4256 (2) | 0.0464 (7) |
| H18 | 0.6312 | 0.2924 | 1.4632 | 0.056* |
| C19 | 0.6804 (2) | 0.1150 (2) | 1.4672 (2) | 0.0385 (6) |

| | | | | |
|---|---|---|---|---|
| H19 | 0.6092 | 0.1133 | 1.5333 | 0.046* |
| C20 | 0.2010 (2) | 0.34932 (19) | 1.1430 (2) | 0.0311 (5) |
| C21 | 0.3104 (2) | 0.32443 (18) | 1.17410 (18) | 0.0278 (5) |
| C22 | 0.3364 (2) | 0.30972 (19) | 1.27189 (19) | 0.0324 (5) |
| H22 | 0.2663 | 0.3176 | 1.3410 | 0.039* |
| C23 | 0.4637 (2) | 0.2842 (2) | 1.2643 (2) | 0.0350 (6) |
| H23 | 0.4830 | 0.2727 | 1.3292 | 0.042* |
| C24 | 0.5687 (2) | 0.2742 (2) | 1.16134 (19) | 0.0333 (6) |
| H24 | 0.6565 | 0.2574 | 1.1590 | 0.040* |
| C25 | 0.5470 (2) | 0.28808 (18) | 1.06581 (19) | 0.0275 (5) |
| C26 | 0.0580 (3) | 0.3755 (2) | 1.2121 (2) | 0.0430 (6) |
| H26A | 0.0003 | 0.4385 | 1.1772 | 0.065* |
| H26B | 0.0402 | 0.4010 | 1.2839 | 0.065* |
| H26C | 0.0390 | 0.3044 | 1.2209 | 0.065* |
| C27 | 0.8137 (2) | 0.26614 (19) | 0.95121 (18) | 0.0295 (5) |
| C28 | 0.8276 (3) | 0.3614 (2) | 0.9784 (2) | 0.0389 (6) |
| H28 | 0.7554 | 0.4364 | 0.9895 | 0.047* |
| C29 | 0.9449 (3) | 0.3482 (2) | 0.9895 (2) | 0.0463 (7) |
| H29 | 0.9522 | 0.4135 | 1.0094 | 0.056* |

| | | | | |
|---|---|---|---|---|
| C30 | 1.0513 (3) | 0.2405 (3) | 0.9717 (2) | 0.0471 (7) |
| H30 | 1.1327 | 0.2320 | 0.9776 | 0.057* |
| C31 | 1.0393 (3) | 0.1452 (2) | 0.9452 (2) | 0.0414 (6) |
| H31 | 1.1124 | 0.0708 | 0.9336 | 0.050* |
| C32 | 0.9210 (2) | 0.1571 (2) | 0.93543 (19) | 0.0335 (5) |
| H32 | 0.9133 | 0.0907 | 0.9179 | 0.040* |
| C33 | 0.6950 (2) | 0.16067 (19) | 0.86868 (18) | 0.0275 (5) |
| C34 | 0.7543 (2) | 0.1502 (2) | 0.75569 (19) | 0.0333 (5) |
| H34 | 0.7767 | 0.2126 | 0.7118 | 0.040* |
| C35 | 0.7809 (3) | 0.0491 (2) | 0.7067 (2) | 0.0399 (6) |
| H35 | 0.8224 | 0.0422 | 0.6297 | 0.048* |
| C36 | 0.7470 (3) | −0.0413 (2) | 0.7698 (2) | 0.0390 (6) |
| H36 | 0.7643 | −0.1099 | 0.7361 | 0.047* |
| C37 | 0.6880 (2) | −0.0322 (2) | 0.8819 (2) | 0.0375 (6) |
| H37 | 0.6644 | −0.0944 | 0.9252 | 0.045* |
| C38 | 0.6632 (2) | 0.0678 (2) | 0.9310 (2) | 0.0334 (5) |
| H38 | 0.6241 | 0.0730 | 1.0083 | 0.040* |
| N1 | 0.6568 (2) | −0.41861 (18) | 1.42655 (19) | 0.0437 (6) |
| N2 | 0.6899 (2) | −0.33688 (17) | 1.44728 (18) | 0.0393 (5) |

| | | | | |
|---|---|---|---|---|
| N3 | 0.66415 (18) | −0.24727 (16) | 1.37373 (15) | 0.0303 (4) |
| N4 | 0.24543 (19) | 0.34829 (16) | 1.03269 (16) | 0.0325 (5) |
| N5 | 0.37644 (19) | 0.32475 (16) | 0.99009 (16) | 0.0308 (4) |
| N6 | 0.41582 (18) | 0.31090 (15) | 1.07653 (15) | 0.0269 (4) |
| P1 | 0.74245 (6) | −0.12461 (5) | 1.46897 (5) | 0.03111 (18) |
| P2 | 0.66007 (6) | 0.29830 (5) | 0.92617 (5) | 0.02817 (17) |

Atomic displacement parameters (Å$^2$)

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0320 (13) | 0.0374 (14) | 0.0472 (16) | −0.0097 (11) | −0.0172 (13) | 0.0011 (11) |
| C2 | 0.0229 (12) | 0.0387 (13) | 0.0291 (13) | −0.0088 (10) | −0.0090 (10) | −0.0024 (10) |
| C3 | 0.0315 (13) | 0.0546 (16) | 0.0282 (13) | −0.0174 (12) | −0.0139 (11) | 0.0027 (11) |
| C4 | 0.0389 (14) | 0.0525 (16) | 0.0349 (15) | −0.0213 (12) | −0.0216 (12) | 0.0162 (12) |
| C5 | 0.0326 (13) | 0.0400 (14) | 0.0355 (14) | −0.0170 (11) | −0.0154 (12) | 0.0088 (11) |
| C6 | 0.0221 (11) | 0.0355 (13) | 0.0282 (13) | −0.0086 (9) | −0.0074 (10) | −0.0008 (10) |
| C7 | 0.064 (2) | 0.0486 (17) | 0.077 (2) | −0.0233 (15) | −0.0406 (19) | 0.0013 (15) |
| C8 | 0.0305 (12) | 0.0314 (12) | 0.0255 (12) | −0.0114 (10) | −0.0106 (10) | 0.0015 (9) |
| C9 | 0.0327 (13) | 0.0324 (12) | 0.0303 (13) | −0.0106 (10) | −0.0147 (11) | −0.0006 (10) |
| C10 | 0.0328 (13) | 0.0298 (12) | 0.0351 (14) | −0.0095 (10) | −0.0080 (11) | −0.0073 (10) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C11 | 0.0293 (13) | 0.0311 (12) | 0.0398 (15) | −0.0070 (10) | −0.0133 (11) | 0.0007 (10) |
| C12 | 0.0366 (14) | 0.0439 (14) | 0.0358 (14) | −0.0120 (11) | −0.0201 (12) | 0.0005 (11) |
| C13 | 0.0355 (14) | 0.0417 (14) | 0.0298 (13) | −0.0097 (11) | −0.0142 (11) | −0.0052 (10) |
| C14 | 0.0263 (12) | 0.0351 (13) | 0.0304 (13) | −0.0069 (10) | −0.0111 (11) | −0.0042 (10) |
| C15 | 0.0333 (14) | 0.0385 (14) | 0.0388 (15) | −0.0104 (11) | −0.0055 (12) | −0.0088 (11) |
| C16 | 0.0381 (15) | 0.0454 (16) | 0.0487 (17) | −0.0188 (12) | −0.0099 (13) | −0.0009 (13) |
| C17 | 0.0404 (15) | 0.0368 (14) | 0.063 (2) | −0.0151 (12) | −0.0257 (15) | 0.0016 (13) |
| C18 | 0.0365 (15) | 0.0357 (14) | 0.0597 (19) | −0.0050 (11) | −0.0150 (15) | −0.0114 (13) |
| C19 | 0.0303 (13) | 0.0401 (14) | 0.0368 (15) | −0.0056 (11) | −0.0091 (12) | −0.0086 (11) |
| C20 | 0.0335 (13) | 0.0293 (12) | 0.0337 (14) | −0.0148 (10) | −0.0122 (11) | −0.0007 (10) |
| C21 | 0.0310 (12) | 0.0218 (11) | 0.0282 (12) | −0.0104 (9) | −0.0075 (11) | −0.0016 (9) |
| C22 | 0.0368 (14) | 0.0308 (12) | 0.0256 (13) | −0.0118 (10) | −0.0081 (11) | −0.0017 (10) |
| C23 | 0.0397 (14) | 0.0373 (13) | 0.0274 (13) | −0.0121 (11) | −0.0146 (12) | 0.0002 (10) |
| C24 | 0.0328 (13) | 0.0363 (13) | 0.0324 (14) | −0.0103 (10) | −0.0152 (11) | −0.0032 (10) |
| C25 | 0.0278 (12) | 0.0244 (11) | 0.0310 (13) | −0.0086 (9) | −0.0112 (10) | −0.0043 (9) |
| C26 | 0.0355 (14) | 0.0497 (15) | 0.0439 (16) | −0.0198 (12) | −0.0117 (13) | 0.0017 (12) |
| C27 | 0.0321 (12) | 0.0327 (12) | 0.0253 (12) | −0.0161 (10) | −0.0082 (10) | −0.0005 (9) |
| C28 | 0.0475 (16) | 0.0343 (13) | 0.0437 (16) | −0.0207 (11) | −0.0206 (13) | 0.0013 (11) |
| C29 | 0.0613 (19) | 0.0518 (16) | 0.0471 (17) | −0.0350 (14) | −0.0281 (15) | 0.0038 (13) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C30 | 0.0435 (16) | 0.0662 (19) | 0.0463 (17) | −0.0319 (14) | −0.0225 (14) | 0.0072 (14) |
| C31 | 0.0335 (14) | 0.0472 (15) | 0.0431 (16) | −0.0134 (11) | −0.0166 (13) | 0.0015 (12) |
| C32 | 0.0326 (13) | 0.0367 (13) | 0.0333 (14) | −0.0168 (10) | −0.0096 (11) | −0.0021 (10) |
| C33 | 0.0258 (12) | 0.0317 (12) | 0.0266 (12) | −0.0110 (9) | −0.0109 (10) | −0.0011 (9) |
| C34 | 0.0342 (13) | 0.0394 (13) | 0.0279 (13) | −0.0177 (11) | −0.0089 (11) | −0.0008 (10) |
| C35 | 0.0373 (14) | 0.0476 (15) | 0.0325 (14) | −0.0139 (12) | −0.0071 (12) | −0.0141 (12) |
| C36 | 0.0385 (14) | 0.0352 (13) | 0.0448 (16) | −0.0113 (11) | −0.0146 (13) | −0.0122 (11) |
| C37 | 0.0383 (14) | 0.0290 (12) | 0.0449 (16) | −0.0136 (10) | −0.0138 (13) | −0.0008 (11) |
| C38 | 0.0392 (14) | 0.0329 (13) | 0.0263 (13) | −0.0144 (10) | −0.0093 (11) | −0.0006 (10) |
| N1 | 0.0413 (13) | 0.0394 (12) | 0.0567 (15) | −0.0163 (10) | −0.0270 (12) | 0.0087 (10) |
| N2 | 0.0393 (12) | 0.0377 (12) | 0.0435 (13) | −0.0145 (9) | −0.0231 (11) | 0.0114 (10) |
| N3 | 0.0263 (10) | 0.0340 (10) | 0.0296 (11) | −0.0096 (8) | −0.0136 (9) | 0.0048 (8) |
| N4 | 0.0313 (11) | 0.0334 (11) | 0.0364 (12) | −0.0142 (8) | −0.0135 (10) | −0.0013 (9) |
| N5 | 0.0323 (11) | 0.0337 (10) | 0.0305 (11) | −0.0131 (8) | −0.0138 (9) | −0.0029 (8) |
| N6 | 0.0300 (10) | 0.0268 (9) | 0.0266 (10) | −0.0112 (8) | −0.0117 (9) | −0.0020 (8) |
| P1 | 0.0272 (3) | 0.0355 (3) | 0.0261 (3) | −0.0079 (3) | −0.0091 (3) | −0.0014 (3) |
| P2 | 0.0303 (3) | 0.0282 (3) | 0.0269 (3) | −0.0116 (2) | −0.0105 (3) | −0.0013 (2) |

Geometric parameters (Å, °)

| | | | |
|---|---|---|---|
| C1—N1 | 1.350 (3) | C20—C26 | 1.484 (4) |
| C1—C2 | 1.383 (3) | C21—N6 | 1.374 (3) |
| C1—C7 | 1.495 (4) | C21—C22 | 1.417 (3) |
| C2—N3 | 1.379 (3) | C22—C23 | 1.356 (3) |
| C2—C3 | 1.411 (3) | C22—H22 | 0.9500 |
| C3—C4 | 1.356 (4) | C23—C24 | 1.421 (3) |
| C3—H3 | 0.9500 | C23—H23 | 0.9500 |
| C4—C5 | 1.420 (3) | C24—C25 | 1.363 (3) |
| C4—H4 | 0.9500 | C24—H24 | 0.9500 |
| C5—C6 | 1.365 (3) | C25—N6 | 1.396 (3) |
| C5—H5 | 0.9500 | C25—P2 | 1.830 (2) |
| C6—N3 | 1.393 (3) | C26—H26A | 0.9800 |
| C6—P1 | 1.828 (2) | C26—H26B | 0.9800 |
| C7—H7A | 0.9800 | C26—H26C | 0.9800 |
| C7—H7B | 0.9800 | C27—C32 | 1.393 (3) |
| C7—H7C | 0.9800 | C27—C28 | 1.396 (3) |
| C8—C9 | 1.391 (3) | C27—P2 | 1.828 (2) |
| C8—C13 | 1.391 (3) | C28—C29 | 1.381 (4) |
| C8—P1 | 1.834 (2) | C28—H28 | 0.9500 |

| | | | |
|---|---|---|---|
| C9—C10 | 1.392 (3) | C29—C30 | 1.377 (4) |
| C9—H9 | 0.9500 | C29—H29 | 0.9500 |
| C10—C11 | 1.383 (3) | C30—C31 | 1.379 (4) |
| C10—H10 | 0.9500 | C30—H30 | 0.9500 |
| C11—C12 | 1.380 (3) | C31—C32 | 1.390 (3) |
| C11—H11 | 0.9500 | C31—H31 | 0.9500 |
| C12—C13 | 1.383 (3) | C32—H32 | 0.9500 |
| C12—H12 | 0.9500 | C33—C38 | 1.393 (3) |
| C13—H13 | 0.9500 | C33—C34 | 1.393 (3) |
| C14—C15 | 1.382 (3) | C33—P2 | 1.833 (2) |
| C14—C19 | 1.391 (3) | C34—C35 | 1.390 (3) |
| C14—P1 | 1.836 (3) | C34—H34 | 0.9500 |
| C15—C16 | 1.388 (4) | C35—C36 | 1.380 (4) |
| C15—H15 | 0.9500 | C35—H35 | 0.9500 |
| C16—C17 | 1.385 (4) | C36—C37 | 1.380 (4) |
| C16—H16 | 0.9500 | C36—H36 | 0.9500 |
| C17—C18 | 1.366 (4) | C37—C38 | 1.387 (3) |
| C17—H17 | 0.9500 | C37—H37 | 0.9500 |
| C18—C19 | 1.392 (4) | C38—H38 | 0.9500 |

| | | | |
|---|---|---|---|
| C18—H18 | 0.9500 | N1—N2 | 1.339 (3) |
| C19—H19 | 0.9500 | N2—N3 | 1.361 (3) |
| C20—N4 | 1.354 (3) | N4—N5 | 1.329 (3) |
| C20—C21 | 1.399 (3) | N5—N6 | 1.362 (2) |
| N1—C1—C2 | 108.7 (2) | C21—C22—H22 | 120.8 |
| N1—C1—C7 | 122.9 (2) | C22—C23—C24 | 121.3 (2) |
| C2—C1—C7 | 128.3 (2) | C22—C23—H23 | 119.4 |
| N3—C2—C1 | 104.09 (19) | C24—C23—H23 | 119.4 |
| N3—C2—C3 | 118.3 (2) | C25—C24—C23 | 121.8 (2) |
| C1—C2—C3 | 137.5 (2) | C25—C24—H24 | 119.1 |
| C4—C3—C2 | 118.5 (2) | C23—C24—H24 | 119.1 |
| C4—C3—H3 | 120.8 | C24—C25—N6 | 115.4 (2) |
| C2—C3—H3 | 120.8 | C24—C25—P2 | 129.04 (18) |
| C3—C4—C5 | 121.3 (2) | N6—C25—P2 | 115.11 (15) |
| C3—C4—H4 | 119.3 | C20—C26—H26A | 109.5 |
| C5—C4—H4 | 119.3 | C20—C26—H26B | 109.5 |
| C6—C5—C4 | 121.6 (2) | H26A—C26—H26B | 109.5 |
| C6—C5—H5 | 119.2 | C20—C26—H26C | 109.5 |
| C4—C5—H5 | 119.2 | H26A—C26—H26C | 109.5 |

| | | | |
|---|---|---|---|
| C5—C6—N3 | 115.7 (2) | H26B—C26—H26C | 109.5 |
| C5—C6—P1 | 126.41 (19) | C32—C27—C28 | 118.4 (2) |
| N3—C6—P1 | 117.60 (16) | C32—C27—P2 | 124.74 (18) |
| C1—C7—H7A | 109.5 | C28—C27—P2 | 116.55 (17) |
| C1—C7—H7B | 109.5 | C29—C28—C27 | 120.9 (2) |
| H7A—C7—H7B | 109.5 | C29—C28—H28 | 119.6 |
| C1—C7—H7C | 109.5 | C27—C28—H28 | 119.6 |
| H7A—C7—H7C | 109.5 | C30—C29—C28 | 120.2 (3) |
| H7B—C7—H7C | 109.5 | C30—C29—H29 | 119.9 |
| C9—C8—C13 | 118.4 (2) | C28—C29—H29 | 119.9 |
| C9—C8—P1 | 125.26 (17) | C29—C30—C31 | 119.7 (2) |
| C13—C8—P1 | 116.27 (18) | C29—C30—H30 | 120.1 |
| C8—C9—C10 | 120.1 (2) | C31—C30—H30 | 120.1 |
| C8—C9—H9 | 119.9 | C30—C31—C32 | 120.5 (2) |
| C10—C9—H9 | 119.9 | C30—C31—H31 | 119.7 |
| C11—C10—C9 | 120.5 (2) | C32—C31—H31 | 119.7 |
| C11—C10—H10 | 119.7 | C31—C32—C27 | 120.2 (2) |
| C9—C10—H10 | 119.7 | C31—C32—H32 | 119.9 |
| C12—C11—C10 | 119.7 (2) | C27—C32—H32 | 119.9 |

| | | | |
|---|---|---|---|
| C12—C11—H11 | 120.2 | C38—C33—C34 | 118.5 (2) |
| C10—C11—H11 | 120.2 | C38—C33—P2 | 123.89 (18) |
| C11—C12—C13 | 119.7 (2) | C34—C33—P2 | 117.61 (17) |
| C11—C12—H12 | 120.1 | C35—C34—C33 | 120.5 (2) |
| C13—C12—H12 | 120.1 | C35—C34—H34 | 119.8 |
| C12—C13—C8 | 121.4 (2) | C33—C34—H34 | 119.8 |
| C12—C13—H13 | 119.3 | C36—C35—C34 | 120.1 (2) |
| C8—C13—H13 | 119.3 | C36—C35—H35 | 119.9 |
| C15—C14—C19 | 119.0 (2) | C34—C35—H35 | 119.9 |
| C15—C14—P1 | 123.71 (18) | C37—C36—C35 | 120.1 (2) |
| C19—C14—P1 | 117.30 (19) | C37—C36—H36 | 119.9 |
| C14—C15—C16 | 121.1 (2) | C35—C36—H36 | 119.9 |
| C14—C15—H15 | 119.5 | C36—C37—C38 | 119.9 (2) |
| C16—C15—H15 | 119.5 | C36—C37—H37 | 120.1 |
| C17—C16—C15 | 119.1 (3) | C38—C37—H37 | 120.1 |
| C17—C16—H16 | 120.4 | C37—C38—C33 | 120.9 (2) |
| C15—C16—H16 | 120.4 | C37—C38—H38 | 119.5 |
| C18—C17—C16 | 120.6 (3) | C33—C38—H38 | 119.5 |
| C18—C17—H17 | 119.7 | N2—N1—C1 | 110.3 (2) |

| | | | |
|---|---|---|---|
| C16—C17—H17 | 119.7 | N1—N2—N3 | 105.79 (19) |
| C17—C18—C19 | 120.3 (2) | N2—N3—C2 | 111.09 (19) |
| C17—C18—H18 | 119.9 | N2—N3—C6 | 124.42 (19) |
| C19—C18—H18 | 119.9 | C2—N3—C6 | 124.48 (18) |
| C14—C19—C18 | 120.0 (2) | N5—N4—C20 | 110.82 (19) |
| C14—C19—H19 | 120.0 | N4—N5—N6 | 105.73 (18) |
| C18—C19—H19 | 120.0 | N5—N6—C21 | 111.64 (17) |
| N4—C20—C21 | 108.1 (2) | N5—N6—C25 | 123.53 (19) |
| N4—C20—C26 | 122.5 (2) | C21—N6—C25 | 124.82 (19) |
| C21—C20—C26 | 129.3 (2) | C6—P1—C8 | 102.22 (10) |
| N6—C21—C20 | 103.66 (19) | C6—P1—C14 | 98.57 (10) |
| N6—C21—C22 | 118.2 (2) | C8—P1—C14 | 102.27 (11) |
| C20—C21—C22 | 138.1 (2) | C27—P2—C25 | 100.09 (10) |
| C23—C22—C21 | 118.4 (2) | C27—P2—C33 | 102.77 (10) |
| C23—C22—H22 | 120.8 | C25—P2—C33 | 101.79 (10) |
| N1—C1—C2—N3 | 0.5 (3) | P2—C33—C38—C37 | 177.59 (18) |
| C7—C1—C2—N3 | 177.9 (3) | C2—C1—N1—N2 | −0.6 (3) |
| N1—C1—C2—C3 | −176.1 (3) | C7—C1—N1—N2 | −178.2 (3) |
| C7—C1—C2—C3 | 1.3 (5) | C1—N1—N2—N3 | 0.4 (3) |

| | | | |
|---|---|---|---|
| N3—C2—C3—C4 | −0.9 (3) | N1—N2—N3—C2 | −0.1 (3) |
| C1—C2—C3—C4 | 175.4 (3) | N1—N2—N3—C6 | 179.3 (2) |
| C2—C3—C4—C5 | 2.7 (4) | C1—C2—N3—N2 | −0.2 (3) |
| C3—C4—C5—C6 | −1.5 (4) | C3—C2—N3—N2 | 177.2 (2) |
| C4—C5—C6—N3 | −1.5 (3) | C1—C2—N3—C6 | −179.7 (2) |
| C4—C5—C6—P1 | −174.67 (19) | C3—C2—N3—C6 | −2.3 (3) |
| C13—C8—C9—C10 | 1.6 (4) | C5—C6—N3—N2 | −176.0 (2) |
| P1—C8—C9—C10 | −176.15 (18) | P1—C6—N3—N2 | −2.2 (3) |
| C8—C9—C10—C11 | 0.0 (4) | C5—C6—N3—C2 | 3.4 (3) |
| C9—C10—C11—C12 | −1.9 (4) | P1—C6—N3—C2 | 177.21 (17) |
| C10—C11—C12—C13 | 2.0 (4) | C21—C20—N4—N5 | −0.2 (3) |
| C11—C12—C13—C8 | −0.4 (4) | C26—C20—N4—N5 | 178.8 (2) |
| C9—C8—C13—C12 | −1.4 (4) | C20—N4—N5—N6 | −0.2 (2) |
| P1—C8—C13—C12 | 176.5 (2) | N4—N5—N6—C21 | 0.6 (2) |
| C19—C14—C15—C16 | −1.5 (4) | N4—N5—N6—C25 | −178.23 (18) |
| P1—C14—C15—C16 | 177.03 (19) | C20—C21—N6—N5 | −0.7 (2) |
| C14—C15—C16—C17 | 0.5 (4) | C22—C21—N6—N5 | 178.53 (18) |
| C15—C16—C17—C18 | 0.5 (4) | C20—C21—N6—C25 | 178.11 (19) |
| C16—C17—C18—C19 | −0.7 (4) | C22—C21—N6—C25 | −2.7 (3) |

| | | | |
|---|---|---|---|
| C15—C14—C19—C18 | 1.3 (4) | C24—C25—N6—N5 | −178.59 (19) |
| P1—C14—C19—C18 | −177.26 (19) | P2—C25—N6—N5 | 8.3 (3) |
| C17—C18—C19—C14 | −0.3 (4) | C24—C25—N6—C21 | 2.7 (3) |
| N4—C20—C21—N6 | 0.5 (2) | P2—C25—N6—C21 | −170.40 (16) |
| C26—C20—C21—N6 | −178.4 (2) | C5—C6—P1—C8 | −118.9 (2) |
| N4—C20—C21—C22 | −178.4 (2) | N3—C6—P1—C8 | 68.07 (19) |
| C26—C20—C21—C22 | 2.6 (5) | C5—C6—P1—C14 | −14.2 (2) |
| N6—C21—C22—C23 | 0.6 (3) | N3—C6—P1—C14 | 172.70 (17) |
| C20—C21—C22—C23 | 179.5 (3) | C9—C8—P1—C6 | 6.7 (2) |
| C21—C22—C23—C24 | 1.1 (3) | C13—C8—P1—C6 | −171.11 (19) |
| C22—C23—C24—C25 | −1.0 (4) | C9—C8—P1—C14 | −95.1 (2) |
| C23—C24—C25—N6 | −0.9 (3) | C13—C8—P1—C14 | 87.2 (2) |
| C23—C24—C25—P2 | 171.12 (18) | C15—C14—P1—C6 | −71.7 (2) |
| C32—C27—C28—C29 | 0.0 (4) | C19—C14—P1—C6 | 106.78 (19) |
| P2—C27—C28—C29 | −174.3 (2) | C15—C14—P1—C8 | 32.9 (2) |
| C27—C28—C29—C30 | 1.2 (4) | C19—C14—P1—C8 | −148.64 (18) |
| C28—C29—C30—C31 | −1.5 (4) | C32—C27—P2—C25 | 100.3 (2) |
| C29—C30—C31—C32 | 0.6 (4) | C28—C27—P2—C25 | −85.8 (2) |
| C30—C31—C32—C27 | 0.7 (4) | C32—C27—P2—C33 | −4.3 (2) |

| | | | |
|---|---|---|---|
| C28—C27—C32—C31 | −0.9 (4) | C28—C27—P2—C33 | 169.56 (19) |
| P2—C27—C32—C31 | 172.85 (19) | C24—C25—P2—C27 | 6.8 (2) |
| C38—C33—C34—C35 | 0.0 (3) | N6—C25—P2—C27 | 178.79 (16) |
| P2—C33—C34—C35 | −178.66 (18) | C24—C25—P2—C33 | 112.2 (2) |
| C33—C34—C35—C36 | 0.9 (4) | N6—C25—P2—C33 | −75.76 (17) |
| C34—C35—C36—C37 | −0.7 (4) | C38—C33—P2—C27 | 90.6 (2) |
| C35—C36—C37—C38 | −0.2 (4) | C34—C33—P2—C27 | −90.79 (19) |
| C36—C37—C38—C33 | 1.1 (4) | C38—C33—P2—C25 | −12.7 (2) |
| C34—C33—C38—C37 | −1.0 (3) | C34—C33—P2—C25 | 165.86 (17) |

All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

## Compound 4b

*Crystal data*

| | |
|---|---|
| $C_{18}H_{14}N_3P$ | |
| $M_r$ = 303.29 | $D_x$ = 1.348 Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | |
| Hall symbol: -P 2ybc | Mo $K\alpha$ radiation, λ = 0.71073 Å |
| $a$ = 9.4104 (5) Å | Cell parameters from 8238 reflections |
| $b$ = 16.0595 (10) Å | θ = 1.0–27.5° |
| $c$ = 10.0214 (5) Å | μ = 0.18 mm$^{-1}$ |
| β = 99.277 (3)° | $T$ = 173 K |
| $V$ = 1494.69 (14) Å$^3$ | Block, colorless |
| $Z$ = 4 | 0.35 × 0.30 × 0.25 mm |
| $F$(000) = 632 | |

*Data collection*

| | |
|---|---|
| KappaCCD diffractometer | 2517 reflections with $I > 2\sigma(I)$ |
| Radiation source: fine-focus sealed tube | $R_{int}$ = 0.065 |
| graphite | $\theta_{max}$ = 27.5°, $\theta_{min}$ = 2.2° |

| | |
|---|---|
| Detector resolution: ? pixels $mm^{-1}$ | $h$ = −12→11 |
| phi and ω scans | $k$ = −18→20 |
| 10729 measured reflections | $l$ = −10→13 |
| 3414 independent reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.057 | H-atom parameters constrained |
| $wR(F^2)$ = 0.172 | $w = 1/[\sigma^2(F_o^2) + (0.1011P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S$ = 1.15 | |
| 3414 reflections | $\Delta\rho_{max}$ = 0.79 e Å$^{-3}$ |
| 200 parameters | $\Delta\rho_{min}$ = −0.47 e Å$^{-3}$ |
| 0 restraints | Extinction correction: *SHELXL*, $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$ |
| ? constraints | Extinction coefficient: 0.079 (7) |
| Primary atom site location: structure-invariant direct methods | |

Refinement of $F^2$ against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on $F^2$, conventional *R*-factors *R* are based on F, with F set to zero for negative $F^2$. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on F,

and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.1774 (2) | −0.02780 (15) | 0.9538 (2) | 0.0363 (6) |
| H1 | 0.1360 | −0.0660 | 1.0090 | 0.044* |
| C2 | 0.3027 (2) | −0.04111 (14) | 0.90204 (19) | 0.0294 (5) |
| C3 | 0.4100 (2) | −0.10257 (14) | 0.9036 (2) | 0.0327 (5) |
| H3 | 0.4035 | −0.1539 | 0.9494 | 0.039* |
| C4 | 0.5228 (2) | −0.08696 (14) | 0.8382 (2) | 0.0330 (5) |
| H4 | 0.5963 | −0.1276 | 0.8393 | 0.040* |
| C5 | 0.5328 (2) | −0.01094 (13) | 0.7683 (2) | 0.0287 (5) |
| H5 | 0.6136 | −0.0017 | 0.7243 | 0.034* |
| C6 | 0.4300 (2) | 0.04907 (13) | 0.7624 (2) | 0.0261 (5) |
| C7 | 0.6009 (2) | 0.15623 (12) | 0.6324 (2) | 0.0256 (5) |
| C8 | 0.7198 (2) | 0.16825 (14) | 0.7332 (2) | 0.0342 (5) |
| H8 | 0.7061 | 0.1715 | 0.8249 | 0.041* |
| C9 | 0.8573 (3) | 0.17556 (16) | 0.7023 (3) | 0.0414 (6) |
| H9 | 0.9374 | 0.1822 | 0.7724 | 0.050* |
| C10 | 0.8775 (3) | 0.17320 (15) | 0.5689 (3) | 0.0395 (6) |

| | | | | |
|---|---|---|---|---|
| H10 | 0.9716 | 0.1788 | 0.5471 | 0.047* |
| C11 | 0.7620 (3) | 0.16281 (14) | 0.4679 (3) | 0.0363 (6) |
| H11 | 0.7766 | 0.1618 | 0.3762 | 0.044* |
| C12 | 0.6230 (2) | 0.15367 (13) | 0.4983 (2) | 0.0302 (5) |
| H12 | 0.5438 | 0.1457 | 0.4277 | 0.036* |
| C13 | 0.2975 (2) | 0.13885 (13) | 0.5317 (2) | 0.0262 (5) |
| C14 | 0.2260 (2) | 0.06419 (14) | 0.4937 (2) | 0.0319 (5) |
| H14 | 0.2431 | 0.0168 | 0.5507 | 0.038* |
| C15 | 0.1303 (3) | 0.05872 (15) | 0.3730 (2) | 0.0381 (6) |
| H15 | 0.0809 | 0.0080 | 0.3487 | 0.046* |
| C16 | 0.1068 (2) | 0.12726 (16) | 0.2881 (2) | 0.0383 (6) |
| H16 | 0.0427 | 0.1232 | 0.2048 | 0.046* |
| C17 | 0.1764 (2) | 0.20137 (16) | 0.3246 (2) | 0.0382 (6) |
| H17 | 0.1610 | 0.2482 | 0.2660 | 0.046* |
| C18 | 0.2688 (2) | 0.20751 (14) | 0.4464 (2) | 0.0326 (5) |
| H18 | 0.3134 | 0.2594 | 0.4724 | 0.039* |
| N1 | 0.1226 (2) | 0.04725 (13) | 0.9146 (2) | 0.0398 (5) |
| N2 | 0.20675 (19) | 0.08462 (13) | 0.83903 (19) | 0.0357 (5) |
| N3 | 0.31655 (18) | 0.03144 (11) | 0.83112 (17) | 0.0268 (4) |

| | | | | |
|---|---|---|---|---|
| P1 | 0.42520 (6) | 0.15362 (4) | 0.68810 (5) | 0.0270 (2) |

Atomic displacement parameters (Å$^2$)

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0326 (12) | 0.0424 (15) | 0.0353 (12) | −0.0060 (11) | 0.0102 (10) | 0.0050 (11) |
| C2 | 0.0324 (11) | 0.0314 (12) | 0.0247 (10) | −0.0070 (9) | 0.0051 (9) | 0.0001 (9) |
| C3 | 0.0408 (13) | 0.0295 (12) | 0.0275 (11) | −0.0031 (10) | 0.0049 (10) | 0.0009 (9) |
| C4 | 0.0370 (12) | 0.0337 (13) | 0.0284 (11) | 0.0088 (10) | 0.0058 (9) | 0.0002 (9) |
| C5 | 0.0289 (11) | 0.0305 (12) | 0.0277 (10) | 0.0007 (9) | 0.0078 (9) | −0.0016 (9) |
| C6 | 0.0264 (10) | 0.0297 (12) | 0.0233 (10) | −0.0034 (9) | 0.0073 (9) | −0.0020 (8) |
| C7 | 0.0287 (11) | 0.0199 (10) | 0.0294 (11) | −0.0020 (8) | 0.0080 (9) | 0.0000 (8) |
| C8 | 0.0336 (12) | 0.0368 (13) | 0.0329 (12) | −0.0065 (10) | 0.0075 (10) | 0.0008 (10) |
| C9 | 0.0287 (12) | 0.0466 (16) | 0.0477 (14) | −0.0087 (11) | 0.0022 (11) | 0.0002 (12) |
| C10 | 0.0284 (12) | 0.0382 (14) | 0.0550 (15) | −0.0046 (10) | 0.0160 (11) | 0.0019 (12) |
| C11 | 0.0379 (13) | 0.0349 (13) | 0.0408 (13) | 0.0030 (10) | 0.0205 (11) | 0.0009 (10) |
| C12 | 0.0305 (11) | 0.0296 (12) | 0.0314 (11) | −0.0011 (9) | 0.0076 (9) | −0.0010 (9) |
| C13 | 0.0216 (10) | 0.0259 (11) | 0.0329 (11) | 0.0029 (8) | 0.0099 (9) | 0.0013 (8) |
| C14 | 0.0330 (12) | 0.0250 (12) | 0.0385 (12) | 0.0020 (9) | 0.0084 (10) | 0.0004 (9) |
| C15 | 0.0357 (12) | 0.0332 (14) | 0.0448 (14) | −0.0033 (10) | 0.0048 (11) | −0.0046 (10) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C16 | 0.0295 (11) | 0.0477 (15) | 0.0366 (13) | 0.0004 (11) | 0.0016 (10) | 0.0009 (11) |
| C17 | 0.0293 (12) | 0.0433 (15) | 0.0422 (13) | 0.0009 (10) | 0.0063 (10) | 0.0101 (11) |
| C18 | 0.0255 (10) | 0.0275 (12) | 0.0445 (13) | −0.0024 (9) | 0.0044 (10) | 0.0043 (10) |
| N1 | 0.0310 (10) | 0.0495 (13) | 0.0415 (11) | −0.0016 (9) | 0.0141 (9) | 0.0049 (10) |
| N2 | 0.0295 (10) | 0.0375 (12) | 0.0431 (11) | 0.0033 (8) | 0.0154 (9) | 0.0038 (9) |
| N3 | 0.0241 (9) | 0.0294 (10) | 0.0279 (9) | −0.0005 (7) | 0.0070 (7) | 0.0001 (7) |
| P1 | 0.0265 (3) | 0.0257 (4) | 0.0302 (3) | −0.0008 (2) | 0.0088 (2) | −0.0014 (2) |

Geometric parameters (Å, °)

| | | | |
|---|---|---|---|
| C1—N1 | 1.344 (3) | C10—C11 | 1.372 (4) |
| C1—C2 | 1.379 (3) | C10—H10 | 0.9500 |
| C1—H1 | 0.9500 | C11—C12 | 1.398 (3) |
| C2—N3 | 1.382 (3) | C11—H11 | 0.9500 |
| C2—C3 | 1.411 (3) | C12—H12 | 0.9500 |
| C3—C4 | 1.358 (3) | C13—C18 | 1.395 (3) |
| C3—H3 | 0.9500 | C13—C14 | 1.398 (3) |
| C4—C5 | 1.418 (3) | C13—P1 | 1.830 (2) |
| C4—H4 | 0.9500 | C14—C15 | 1.389 (3) |
| C5—C6 | 1.360 (3) | C14—H14 | 0.9500 |

| | | | |
|---|---|---|---|
| C5—H5 | 0.9500 | C15—C16 | 1.387 (3) |
| C6—N3 | 1.390 (2) | C15—H15 | 0.9500 |
| C6—P1 | 1.834 (2) | C16—C17 | 1.379 (3) |
| C7—C12 | 1.394 (3) | C16—H16 | 0.9500 |
| C7—C8 | 1.395 (3) | C17—C18 | 1.383 (3) |
| C7—P1 | 1.828 (2) | C17—H17 | 0.9500 |
| C8—C9 | 1.384 (3) | C18—H18 | 0.9500 |
| C8—H8 | 0.9500 | N1—N2 | 1.325 (3) |
| C9—C10 | 1.380 (4) | N2—N3 | 1.353 (2) |
| C9—H9 | 0.9500 | | |
| N1—C1—C2 | 109.88 (19) | C10—C11—H11 | 119.7 |
| N1—C1—H1 | 125.1 | C12—C11—H11 | 119.7 |
| C2—C1—H1 | 125.1 | C7—C12—C11 | 119.8 (2) |
| C1—C2—N3 | 102.72 (19) | C7—C12—H12 | 120.1 |
| C1—C2—C3 | 139.3 (2) | C11—C12—H12 | 120.1 |
| N3—C2—C3 | 117.94 (18) | C18—C13—C14 | 118.3 (2) |
| C4—C3—C2 | 118.7 (2) | C18—C13—P1 | 117.27 (17) |
| C4—C3—H3 | 120.7 | C14—C13—P1 | 124.46 (17) |
| C2—C3—H3 | 120.7 | C15—C14—C13 | 120.5 (2) |

| | | | |
|---|---|---|---|
| C3—C4—C5 | 121.1 (2) | C15—C14—H14 | 119.7 |
| C3—C4—H4 | 119.5 | C13—C14—H14 | 119.7 |
| C5—C4—H4 | 119.5 | C16—C15—C14 | 120.0 (2) |
| C6—C5—C4 | 121.89 (19) | C16—C15—H15 | 120.0 |
| C6—C5—H5 | 119.1 | C14—C15—H15 | 120.0 |
| C4—C5—H5 | 119.1 | C17—C16—C15 | 120.0 (2) |
| C5—C6—N3 | 115.60 (19) | C17—C16—H16 | 120.0 |
| C5—C6—P1 | 129.58 (16) | C15—C16—H16 | 120.0 |
| N3—C6—P1 | 114.64 (15) | C16—C17—C18 | 120.0 (2) |
| C12—C7—C8 | 118.4 (2) | C16—C17—H17 | 120.0 |
| C12—C7—P1 | 125.20 (17) | C18—C17—H17 | 120.0 |
| C8—C7—P1 | 116.22 (15) | C17—C18—C13 | 121.1 (2) |
| C9—C8—C7 | 121.3 (2) | C17—C18—H18 | 119.4 |
| C9—C8—H8 | 119.3 | C13—C18—H18 | 119.4 |
| C7—C8—H8 | 119.3 | N2—N1—C1 | 109.67 (18) |
| C10—C9—C8 | 119.6 (2) | N1—N2—N3 | 106.28 (18) |
| C10—C9—H9 | 120.2 | N2—N3—C2 | 111.45 (16) |
| C8—C9—H9 | 120.2 | N2—N3—C6 | 123.76 (18) |
| C11—C10—C9 | 120.1 (2) | C2—N3—C6 | 124.78 (17) |

| | | | |
|---|---|---|---|
| C11—C10—H10 | 119.9 | C7—P1—C13 | 104.06 (9) |
| C9—C10—H10 | 119.9 | C7—P1—C6 | 100.39 (9) |
| C10—C11—C12 | 120.7 (2) | C13—P1—C6 | 101.48 (10) |
| N1—C1—C2—N3 | 0.3 (2) | C2—C1—N1—N2 | −0.2 (3) |
| N1—C1—C2—C3 | 179.5 (3) | C1—N1—N2—N3 | 0.0 (3) |
| C1—C2—C3—C4 | −177.7 (2) | N1—N2—N3—C2 | 0.2 (2) |
| N3—C2—C3—C4 | 1.4 (3) | N1—N2—N3—C6 | −178.48 (18) |
| C2—C3—C4—C5 | −0.7 (3) | C1—C2—N3—N2 | −0.3 (2) |
| C3—C4—C5—C6 | −0.6 (3) | C3—C2—N3—N2 | −179.70 (18) |
| C4—C5—C6—N3 | 1.0 (3) | C1—C2—N3—C6 | 178.37 (18) |
| C4—C5—C6—P1 | 175.79 (16) | C3—C2—N3—C6 | −1.0 (3) |
| C12—C7—C8—C9 | −1.5 (3) | C5—C6—N3—N2 | 178.32 (19) |
| P1—C7—C8—C9 | −176.67 (19) | P1—C6—N3—N2 | 2.8 (3) |
| C7—C8—C9—C10 | 1.8 (4) | C5—C6—N3—C2 | −0.2 (3) |
| C8—C9—C10—C11 | −0.7 (4) | P1—C6—N3—C2 | −175.77 (16) |
| C9—C10—C11—C12 | −0.6 (4) | C12—C7—P1—C13 | 4.4 (2) |
| C8—C7—C12—C11 | 0.2 (3) | C8—C7—P1—C13 | 179.12 (16) |
| P1—C7—C12—C11 | 174.87 (17) | C12—C7—P1—C6 | 109.10 (18) |
| C10—C11—C12—C7 | 0.9 (3) | C8—C7—P1—C6 | −76.14 (17) |

| | | | |
|---|---|---|---|
| C18—C13—C14—C15 | 0.7 (3) | C18—C13—P1—C7 | −75.14 (18) |
| P1—C13—C14—C15 | 179.76 (15) | C14—C13—P1—C7 | 105.81 (18) |
| C13—C14—C15—C16 | 1.1 (3) | C18—C13—P1—C6 | −179.06 (16) |
| C14—C15—C16—C17 | −1.2 (3) | C14—C13—P1—C6 | 1.89 (19) |
| C15—C16—C17—C18 | −0.5 (3) | C5—C6—P1—C7 | −2.8 (2) |
| C16—C17—C18—C13 | 2.5 (3) | N3—C6—P1—C7 | 171.98 (15) |
| C14—C13—C18—C17 | −2.5 (3) | C5—C6—P1—C13 | 104.0 (2) |
| P1—C13—C18—C17 | 178.37 (16) | N3—C6—P1—C13 | −81.21 (16) |

All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

## Compound 4c

*Crystal data*

| | |
|---|---|
| $C_{24}H_{18}N_3P$ | |
| $M_r$ = 379.38 | $D_x$ = 1.328 Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | |
| Hall symbol: -P 2ybc | Mo $K\alpha$ radiation, λ = 0.71073 Å |
| $a$ = 6.0164 (2) Å | Cell parameters from 14158 reflections |
| $b$ = 28.2297 (13) Å | θ = 1.0–27.5° |
| $c$ = 11.5981 (5) Å | μ = 0.16 mm$^{-1}$ |
| β = 105.641 (2)° | $T$ = 173 K |
| $V$ = 1896.89 (14) Å$^3$ | Block, pale yellow |
| $Z$ = 4 | 0.30 × 0.12 × 0.10 mm |
| $F$(000) = 792 | |

*Data collection*

| | |
|---|---|
| KappaCCD diffractometer | 2730 reflections with $I > 2\sigma(I)$ |
| Radiation source: fine-focus sealed tube | $R_{int}$ = 0.063 |
| graphite | $\theta_{max}$ = 27.5°, $\theta_{min}$ = 1.4° |

| | |
|---|---|
| Detector resolution: ? pixels $mm^{-1}$ | $h$ = −7→7 |
| phi and ω scans | $k$ = −33→36 |
| 11043 measured reflections | $l$ = −9→15 |
| 4333 independent reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.065 | H-atom parameters constrained |
| $wR(F^2)$ = 0.201 | $w = 1/[\sigma^2(F_o^2) + (0.0875P)^2 + 0.8647P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S$ = 1.14 | |
| 4333 reflections | $\Delta\rho_{max}$ = 0.69 e Å$^{-3}$ |
| 253 parameters | $\Delta\rho_{min}$ = −0.43 e Å$^{-3}$ |
| 0 restraints | Extinction correction: none |
| ? constraints | Extinction coefficient: ? |
| Primary atom site location: structure-invariant direct methods | |

Refinement of $F^2$ against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on $F^2$, conventional *R*-factors *R* are based on F, with F set to zero for negative $F^2$. The threshold expression of $F^2 > 2sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on F,

and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| P1 | 0.64321 (14) | −0.05760 (3) | 0.69096 (8) | 0.0313 (3) |
| N1 | 0.5721 (4) | −0.17367 (9) | 0.4432 (2) | 0.0293 (6) |
| N2 | 0.6147 (4) | −0.13901 (9) | 0.5239 (2) | 0.0303 (6) |
| N3 | 0.4129 (4) | −0.11505 (9) | 0.5080 (2) | 0.0257 (6) |
| C1 | 0.3486 (5) | −0.17256 (11) | 0.3786 (3) | 0.0256 (7) |
| C2 | 0.2409 (5) | −0.13474 (11) | 0.4174 (3) | 0.0257 (7) |
| C3 | 0.0203 (5) | −0.11307 (11) | 0.3868 (3) | 0.0296 (7) |
| H3 | −0.1024 | −0.1256 | 0.3246 | 0.036* |
| C4 | −0.0111 (5) | −0.07393 (12) | 0.4489 (3) | 0.0318 (7) |
| H4 | −0.1568 | −0.0585 | 0.4284 | 0.038* |
| C5 | 0.1709 (5) | −0.05562 (11) | 0.5441 (3) | 0.0313 (7) |
| H5 | 0.1424 | −0.0286 | 0.5868 | 0.038* |
| C6 | 0.3841 (5) | −0.07574 (11) | 0.5753 (3) | 0.0281 (7) |
| C7 | 0.2514 (5) | −0.20873 (10) | 0.2877 (3) | 0.0265 (7) |
| C8 | 0.0434 (5) | −0.23153 (12) | 0.2864 (3) | 0.0307 (7) |
| H8 | −0.0407 | −0.2222 | 0.3412 | 0.037* |

| | | | | |
|---|---|---|---|---|
| C9 | −0.0398 (5) | −0.26773 (12) | 0.2051 (3) | 0.0328 (7) |
| H9 | −0.1799 | −0.2833 | 0.2050 | 0.039* |
| C10 | 0.0808 (6) | −0.28132 (12) | 0.1241 (3) | 0.0344 (8) |
| H10 | 0.0239 | −0.3061 | 0.0686 | 0.041* |
| C11 | 0.2844 (6) | −0.25843 (12) | 0.1247 (3) | 0.0362 (8) |
| H11 | 0.3662 | −0.2675 | 0.0686 | 0.043* |
| C12 | 0.3709 (5) | −0.22252 (11) | 0.2060 (3) | 0.0307 (7) |
| H12 | 0.5117 | −0.2073 | 0.2059 | 0.037* |
| C13 | 0.6642 (5) | −0.10648 (11) | 0.7987 (3) | 0.0308 (7) |
| C14 | 0.4807 (6) | −0.13529 (12) | 0.8045 (3) | 0.0354 (8) |
| H14 | 0.3320 | −0.1295 | 0.7523 | 0.043* |
| C15 | 0.5116 (7) | −0.17237 (12) | 0.8853 (3) | 0.0414 (9) |
| H15 | 0.3842 | −0.1918 | 0.8882 | 0.050* |
| C16 | 0.7249 (7) | −0.18113 (14) | 0.9613 (3) | 0.0477 (10) |
| H16 | 0.7459 | −0.2068 | 1.0161 | 0.057* |
| C17 | 0.9092 (7) | −0.15262 (15) | 0.9581 (4) | 0.0525 (11) |
| H17 | 1.0565 | −0.1584 | 1.0118 | 0.063* |
| C18 | 0.8805 (6) | −0.11542 (14) | 0.8766 (3) | 0.0411 (9) |
| H18 | 1.0085 | −0.0961 | 0.8742 | 0.049* |

| | | | | |
|---|---|---|---|---|
| C19 | 0.5286 (5) | −0.00896 (11) | 0.7624 (3) | 0.0308 (7) |
| C20 | 0.3595 (6) | −0.01362 (13) | 0.8239 (3) | 0.0413 (9) |
| H20 | 0.2895 | −0.0436 | 0.8270 | 0.050* |
| C21 | 0.2930 (7) | 0.02466 (14) | 0.8801 (3) | 0.0469 (9) |
| H21 | 0.1754 | 0.0209 | 0.9201 | 0.056* |
| C22 | 0.3946 (7) | 0.06829 (14) | 0.8792 (3) | 0.0469 (10) |
| H22 | 0.3496 | 0.0943 | 0.9196 | 0.056* |
| C23 | 0.5619 (7) | 0.07396 (13) | 0.8194 (3) | 0.0473 (10) |
| H23 | 0.6313 | 0.1041 | 0.8175 | 0.057* |
| C24 | 0.6294 (6) | 0.03537 (12) | 0.7616 (3) | 0.0384 (8) |
| H24 | 0.7458 | 0.0394 | 0.7210 | 0.046* |

Atomic displacement parameters (Å$^2$)

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| P1 | 0.0311 (4) | 0.0290 (5) | 0.0337 (5) | −0.0042 (4) | 0.0086 (3) | −0.0037 (4) |
| N1 | 0.0284 (13) | 0.0287 (14) | 0.0304 (14) | −0.0002 (11) | 0.0069 (11) | −0.0018 (12) |
| N2 | 0.0259 (13) | 0.0318 (15) | 0.0341 (15) | 0.0020 (12) | 0.0094 (11) | −0.0031 (12) |
| N3 | 0.0265 (13) | 0.0242 (13) | 0.0265 (14) | 0.0004 (11) | 0.0076 (10) | −0.0014 (11) |
| C1 | 0.0258 (15) | 0.0274 (16) | 0.0246 (16) | 0.0024 (13) | 0.0087 (12) | 0.0039 (13) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C2 | 0.0265 (15) | 0.0252 (16) | 0.0256 (15) | −0.0010 (13) | 0.0075 (12) | 0.0012 (13) |
| C3 | 0.0273 (16) | 0.0300 (17) | 0.0299 (17) | −0.0026 (14) | 0.0050 (13) | 0.0014 (14) |
| C4 | 0.0286 (16) | 0.0287 (17) | 0.0386 (19) | 0.0052 (14) | 0.0101 (14) | 0.0036 (14) |
| C5 | 0.0330 (17) | 0.0248 (16) | 0.0371 (19) | 0.0008 (14) | 0.0112 (14) | −0.0015 (14) |
| C6 | 0.0357 (17) | 0.0229 (16) | 0.0278 (17) | −0.0024 (14) | 0.0120 (13) | −0.0018 (13) |
| C7 | 0.0276 (16) | 0.0241 (16) | 0.0264 (16) | 0.0045 (13) | 0.0051 (12) | 0.0025 (12) |
| C8 | 0.0282 (16) | 0.0337 (18) | 0.0294 (17) | 0.0026 (14) | 0.0066 (13) | 0.0010 (14) |
| C9 | 0.0268 (16) | 0.0346 (18) | 0.0335 (18) | −0.0006 (14) | 0.0022 (13) | −0.0020 (15) |
| C10 | 0.0354 (18) | 0.0340 (19) | 0.0273 (18) | 0.0033 (15) | −0.0029 (13) | −0.0053 (14) |
| C11 | 0.0385 (19) | 0.040 (2) | 0.0302 (18) | 0.0077 (16) | 0.0098 (14) | −0.0054 (15) |
| C12 | 0.0278 (16) | 0.0325 (18) | 0.0311 (18) | 0.0030 (14) | 0.0065 (13) | −0.0004 (14) |
| C13 | 0.0326 (17) | 0.0281 (17) | 0.0308 (18) | −0.0002 (14) | 0.0068 (13) | −0.0051 (14) |
| C14 | 0.0366 (18) | 0.0340 (19) | 0.0331 (19) | −0.0023 (15) | 0.0048 (14) | −0.0027 (15) |
| C15 | 0.058 (2) | 0.0296 (19) | 0.037 (2) | −0.0036 (17) | 0.0125 (17) | −0.0025 (15) |
| C16 | 0.070 (3) | 0.038 (2) | 0.036 (2) | 0.016 (2) | 0.0155 (19) | 0.0056 (16) |
| C17 | 0.047 (2) | 0.062 (3) | 0.045 (2) | 0.022 (2) | 0.0056 (17) | 0.004 (2) |
| C18 | 0.0318 (18) | 0.048 (2) | 0.042 (2) | 0.0025 (17) | 0.0073 (15) | −0.0012 (17) |
| C19 | 0.0331 (17) | 0.0283 (17) | 0.0298 (17) | −0.0006 (14) | 0.0066 (13) | −0.0013 (14) |
| C20 | 0.044 (2) | 0.0350 (19) | 0.048 (2) | −0.0066 (17) | 0.0185 (17) | −0.0083 (17) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C21 | 0.049 (2) | 0.051 (2) | 0.042 (2) | 0.0053 (19) | 0.0144 (17) | −0.0058 (18) |
| C22 | 0.063 (2) | 0.037 (2) | 0.036 (2) | 0.0104 (19) | 0.0041 (18) | −0.0066 (16) |
| C23 | 0.065 (3) | 0.0285 (19) | 0.046 (2) | −0.0033 (18) | 0.0094 (19) | −0.0027 (17) |
| C24 | 0.046 (2) | 0.0298 (19) | 0.039 (2) | −0.0066 (16) | 0.0096 (16) | −0.0003 (15) |

Geometric parameters (Å, °)

| | | | |
|---|---|---|---|
| P1—C19 | 1.832 (3) | C11—C12 | 1.387 (5) |
| P1—C6 | 1.834 (3) | C11—H11 | 0.9500 |
| P1—C13 | 1.843 (3) | C12—H12 | 0.9500 |
| N1—N2 | 1.330 (4) | C13—C14 | 1.387 (5) |
| N1—C1 | 1.352 (4) | C13—C18 | 1.393 (5) |
| N2—N3 | 1.358 (3) | C14—C15 | 1.384 (5) |
| N3—C2 | 1.378 (4) | C14—H14 | 0.9500 |
| N3—C6 | 1.394 (4) | C15—C16 | 1.369 (5) |
| C1—C2 | 1.385 (4) | C15—H15 | 0.9500 |
| C1—C7 | 1.471 (4) | C16—C17 | 1.378 (6) |
| C2—C3 | 1.417 (4) | C16—H16 | 0.9500 |
| C3—C4 | 1.359 (4) | C17—C18 | 1.392 (5) |
| C3—H3 | 0.9500 | C17—H17 | 0.9500 |

| | | | |
|---|---|---|---|
| C4—C5 | 1.426 (5) | C18—H18 | 0.9500 |
| C4—H4 | 0.9500 | C19—C24 | 1.392 (4) |
| C5—C6 | 1.360 (4) | C19—C20 | 1.398 (5) |
| C5—H5 | 0.9500 | C20—C21 | 1.376 (5) |
| C7—C12 | 1.391 (4) | C20—H20 | 0.9500 |
| C7—C8 | 1.404 (4) | C21—C22 | 1.377 (5) |
| C8—C9 | 1.389 (5) | C21—H21 | 0.9500 |
| C8—H8 | 0.9500 | C22—C23 | 1.377 (6) |
| C9—C10 | 1.387 (5) | C22—H22 | 0.9500 |
| C9—H9 | 0.9500 | C23—C24 | 1.396 (5) |
| C10—C11 | 1.384 (5) | C23—H23 | 0.9500 |
| C10—H10 | 0.9500 | C24—H24 | 0.9500 |
| C19—P1—C6 | 101.00 (14) | C12—C11—H11 | 119.5 |
| C19—P1—C13 | 102.68 (15) | C11—C12—C7 | 120.0 (3) |
| C6—P1—C13 | 100.13 (14) | C11—C12—H12 | 120.0 |
| N2—N1—C1 | 110.3 (2) | C7—C12—H12 | 120.0 |
| N1—N2—N3 | 106.0 (2) | C14—C13—C18 | 118.6 (3) |
| N2—N3—C2 | 111.3 (2) | C14—C13—P1 | 124.2 (2) |
| N2—N3—C6 | 124.2 (2) | C18—C13—P1 | 117.2 (3) |

| | | | |
|---|---|---|---|
| C2—N3—C6 | 124.6 (3) | C15—C14—C13 | 120.9 (3) |
| N1—C1—C2 | 108.7 (3) | C15—C14—H14 | 119.6 |
| N1—C1—C7 | 121.7 (3) | C13—C14—H14 | 119.6 |
| C2—C1—C7 | 129.5 (3) | C16—C15—C14 | 120.2 (4) |
| N3—C2—C1 | 103.7 (2) | C16—C15—H15 | 119.9 |
| N3—C2—C3 | 118.5 (3) | C14—C15—H15 | 119.9 |
| C1—C2—C3 | 137.8 (3) | C15—C16—C17 | 119.9 (4) |
| C4—C3—C2 | 118.2 (3) | C15—C16—H16 | 120.0 |
| C4—C3—H3 | 120.9 | C17—C16—H16 | 120.0 |
| C2—C3—H3 | 120.9 | C16—C17—C18 | 120.4 (3) |
| C3—C4—C5 | 121.2 (3) | C16—C17—H17 | 119.8 |
| C3—C4—H4 | 119.4 | C18—C17—H17 | 119.8 |
| C5—C4—H4 | 119.4 | C17—C18—C13 | 120.0 (3) |
| C6—C5—C4 | 121.8 (3) | C17—C18—H18 | 120.0 |
| C6—C5—H5 | 119.1 | C13—C18—H18 | 120.0 |
| C4—C5—H5 | 119.1 | C24—C19—C20 | 117.8 (3) |
| C5—C6—N3 | 115.7 (3) | C24—C19—P1 | 116.9 (3) |
| C5—C6—P1 | 129.3 (2) | C20—C19—P1 | 125.1 (3) |
| N3—C6—P1 | 115.0 (2) | C21—C20—C19 | 120.8 (3) |

| | | | |
|---|---|---|---|
| C12—C7—C8 | 119.2 (3) | C21—C20—H20 | 119.6 |
| C12—C7—C1 | 120.3 (3) | C19—C20—H20 | 119.6 |
| C8—C7—C1 | 120.5 (3) | C20—C21—C22 | 120.8 (4) |
| C9—C8—C7 | 120.1 (3) | C20—C21—H21 | 119.6 |
| C9—C8—H8 | 120.0 | C22—C21—H21 | 119.6 |
| C7—C8—H8 | 120.0 | C21—C22—C23 | 119.7 (4) |
| C10—C9—C8 | 120.3 (3) | C21—C22—H22 | 120.2 |
| C10—C9—H9 | 119.8 | C23—C22—H22 | 120.2 |
| C8—C9—H9 | 119.8 | C22—C23—C24 | 119.9 (3) |
| C11—C10—C9 | 119.4 (3) | C22—C23—H23 | 120.1 |
| C11—C10—H10 | 120.3 | C24—C23—H23 | 120.1 |
| C9—C10—H10 | 120.3 | C19—C24—C23 | 121.0 (3) |
| C10—C11—C12 | 120.9 (3) | C19—C24—H24 | 119.5 |
| C10—C11—H11 | 119.5 | C23—C24—H24 | 119.5 |
| C1—N1—N2—N3 | −1.0 (3) | C1—C7—C8—C9 | −175.9 (3) |
| N1—N2—N3—C2 | 0.4 (3) | C7—C8—C9—C10 | −0.6 (5) |
| N1—N2—N3—C6 | −179.9 (3) | C8—C9—C10—C11 | −0.1 (5) |
| N2—N1—C1—C2 | 1.2 (3) | C9—C10—C11—C12 | 0.7 (5) |
| N2—N1—C1—C7 | −176.4 (3) | C10—C11—C12—C7 | −0.6 (5) |

| | | | |
|---|---|---|---|
| N2—N3—C2—C1 | 0.3 (3) | C8—C7—C12—C11 | −0.1 (5) |
| C6—N3—C2—C1 | −179.4 (3) | C1—C7—C12—C11 | 176.5 (3) |
| N2—N3—C2—C3 | −178.2 (3) | C19—P1—C13—C14 | 82.4 (3) |
| C6—N3—C2—C3 | 2.1 (4) | C6—P1—C13—C14 | −21.4 (3) |
| N1—C1—C2—N3 | −0.9 (3) | C19—P1—C13—C18 | −99.4 (3) |
| C7—C1—C2—N3 | 176.4 (3) | C6—P1—C13—C18 | 156.8 (3) |
| N1—C1—C2—C3 | 177.1 (4) | C18—C13—C14—C15 | −0.4 (5) |
| C7—C1—C2—C3 | −5.5 (6) | P1—C13—C14—C15 | 177.8 (3) |
| N3—C2—C3—C4 | −0.2 (4) | C13—C14—C15—C16 | 0.1 (5) |
| C1—C2—C3—C4 | −178.1 (3) | C14—C15—C16—C17 | 0.7 (6) |
| C2—C3—C4—C5 | −1.4 (5) | C15—C16—C17—C18 | −1.1 (6) |
| C3—C4—C5—C6 | 1.4 (5) | C16—C17—C18—C13 | 0.8 (6) |
| C4—C5—C6—N3 | 0.4 (5) | C14—C13—C18—C17 | 0.0 (5) |
| C4—C5—C6—P1 | 178.4 (2) | P1—C13—C18—C17 | −178.4 (3) |
| N2—N3—C6—C5 | 178.2 (3) | C6—P1—C19—C24 | −120.6 (3) |
| C2—N3—C6—C5 | −2.1 (4) | C13—P1—C19—C24 | 136.3 (3) |
| N2—N3—C6—P1 | −0.1 (4) | C6—P1—C19—C20 | 63.7 (3) |
| C2—N3—C6—P1 | 179.6 (2) | C13—P1—C19—C20 | −39.4 (3) |
| C19—P1—C6—C5 | 5.5 (3) | C24—C19—C20—C21 | 0.9 (5) |

| | | | |
|---|---|---|---|
| C13—P1—C6—C5 | 110.7 (3) | P1—C19—C20—C21 | 176.6 (3) |
| C19—P1—C6—N3 | −176.5 (2) | C19—C20—C21—C22 | −1.3 (6) |
| C13—P1—C6—N3 | −71.3 (2) | C20—C21—C22—C23 | 1.2 (6) |
| N1—C1—C7—C12 | −45.7 (4) | C21—C22—C23—C24 | −0.8 (6) |
| C2—C1—C7—C12 | 137.2 (3) | C20—C19—C24—C23 | −0.6 (5) |
| N1—C1—C7—C8 | 130.9 (3) | P1—C19—C24—C23 | −176.6 (3) |
| C2—C1—C7—C8 | −46.2 (5) | C22—C23—C24—C19 | 0.5 (6) |
| C12—C7—C8—C9 | 0.7 (5) | | |

All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

## Compound 5a

*Crystal data*

| | |
|---|---|
| $C_{19}H_{28}N_3P$ | $F(000)$ = 712 |
| $M_r$ = 329.41 | |
| Triclinic, $P\bar{1}$ | $D_x$ = 1.189 Mg m$^{-3}$ |
| Hall symbol: -P 1 | |
| $a$ = 11.1873 (7) Å | Mo $K\alpha$ radiation, λ = 0.71073 Å |
| $b$ = 11.4055 (7) Å | Cell parameters from 16205 reflections |
| $c$ = 16.9232 (8) Å | θ = 1.0–27.5° |
| α = 100.619 (3)° | μ = 0.15 mm$^{-1}$ |
| β = 90.506 (3)° | $T$ = 173 K |
| γ = 119.238 (2)° | Block, colorless |
| $V$ = 1839.63 (18) Å$^3$ | 0.22 × 0.20 × 0.12 mm |
| $Z$ = 4 | |

*Data collection*

| | |
|---|---|
| KappaCCD diffractometer | 4333 reflections with $I > 2\sigma(I)$ |
| Radiation source: fine-focus sealed tube | $R_{int}$ = 0.084 |

| | |
|---|---|
| graphite | $\theta_{max}$ = 27.4°, $\theta_{min}$ = 1.2° |
| Detector resolution: ? pixels $mm^{-1}$ | *h* = −14→10 |
| phi and ω scans | *k* = −14→14 |
| 19790 measured reflections | *l* = −21→21 |
| 8370 independent reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.071 | H-atom parameters constrained |
| $wR(F^2)$ = 0.221 | $w = 1/[\sigma^2(F_o^2) + (0.1076P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| *S* = 1.05 | |
| 8370 reflections | $\Delta\rho_{max}$ = 0.38 e $Å^{-3}$ |
| 417 parameters | $\Delta\rho_{min}$ = −0.53 e $Å^{-3}$ |
| 0 restraints | Extinction correction: none |
| ? constraints | Extinction coefficient: ? |
| Primary atom site location: structure-invariant direct methods | |

Refinement of $F^2$ against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on $F^2$, conventional *R*-factors *R* are based on F, with F set to zero for negative $F^2$. The threshold expression

of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.5325 (3) | 0.2621 (3) | 0.19165 (18) | 0.0353 (8) |
| C2 | 0.6244 (3) | 0.2740 (3) | 0.13523 (19) | 0.0355 (8) |
| C3 | 0.6516 (4) | 0.1852 (4) | 0.0795 (2) | 0.0519 (10) |
| H3 | 0.6026 | 0.0889 | 0.0770 | 0.062* |
| C4 | 0.7485 (4) | 0.2383 (4) | 0.0297 (3) | 0.0666 (12) |
| H4 | 0.7664 | 0.1796 | −0.0097 | 0.080* |
| C5 | 0.8240 (4) | 0.3843 (4) | 0.0368 (2) | 0.0578 (11) |
| H5 | 0.8920 | 0.4198 | 0.0013 | 0.069* |
| C6 | 0.8045 (3) | 0.4746 (3) | 0.0910 (2) | 0.0408 (8) |
| C7 | 0.4229 (4) | 0.1332 (3) | 0.2129 (2) | 0.0480 (9) |
| H7A | 0.3687 | 0.1559 | 0.2516 | 0.072* |
| H7B | 0.4658 | 0.0891 | 0.2371 | 0.072* |
| H7C | 0.3622 | 0.0703 | 0.1638 | 0.072* |
| C8 | 0.8036 (3) | 0.7298 (3) | 0.09065 (18) | 0.0375 (8) |
| H8 | 0.7499 | 0.7239 | 0.1381 | 0.045* |
| C9 | 0.7045 (4) | 0.6470 (3) | 0.0132 (2) | 0.0520 (10) |

| | | | | |
|---|---|---|---|---|
| H9A | 0.7584 | 0.6416 | −0.0320 | 0.062* |
| H9B | 0.6423 | 0.5521 | 0.0199 | 0.062* |
| C10 | 0.6185 (4) | 0.7079 (4) | −0.0085 (2) | 0.0600 (11) |
| H10A | 0.5534 | 0.6994 | 0.0322 | 0.072* |
| H10B | 0.5637 | 0.6549 | −0.0617 | 0.072* |
| C11 | 0.7061 (4) | 0.8584 (3) | −0.0123 (2) | 0.0479 (9) |
| H11A | 0.7620 | 0.8663 | −0.0582 | 0.057* |
| H11B | 0.6454 | 0.8961 | −0.0216 | 0.057* |
| C12 | 0.8005 (4) | 0.9407 (3) | 0.0656 (2) | 0.0559 (11) |
| H12A | 0.7446 | 0.9401 | 0.1107 | 0.067* |
| H12B | 0.8600 | 1.0373 | 0.0610 | 0.067* |
| C13 | 0.8896 (4) | 0.8808 (4) | 0.0836 (2) | 0.0583 (11) |
| H13A | 0.9500 | 0.9360 | 0.1349 | 0.070* |
| H13B | 0.9494 | 0.8869 | 0.0399 | 0.070* |
| C14 | 0.9780 (3) | 0.7107 (3) | 0.2150 (2) | 0.0422 (9) |
| H14 | 0.8949 | 0.6710 | 0.2446 | 0.051* |
| C15 | 1.0667 (6) | 0.6483 (5) | 0.2302 (3) | 0.0936 (18) |
| H15A | 1.1406 | 0.6757 | 0.1942 | 0.112* |
| H15B | 1.0091 | 0.5468 | 0.2158 | 0.112* |

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|---|---|---|---|---|
| C16 | 1.1323 (6) | 0.6917 (4) | 0.3174 (3) | 0.0915 (18) |
| H16A | 1.0591 | 0.6532 | 0.3529 | 0.110* |
| H16B | 1.1940 | 0.6533 | 0.3219 | 0.110* |
| C17 | 1.2137 (4) | 0.8455 (4) | 0.3454 (2) | 0.0539 (10) |
| H17A | 1.2488 | 0.8698 | 0.4034 | 0.065* |
| H17B | 1.2938 | 0.8835 | 0.3143 | 0.065* |
| C18 | 1.1249 (4) | 0.9068 (4) | 0.3337 (2) | 0.0588 (11) |
| H18A | 1.1817 | 1.0084 | 0.3491 | 0.071* |
| H18B | 1.0516 | 0.8772 | 0.3701 | 0.071* |
| C19 | 1.0585 (4) | 0.8647 (4) | 0.2465 (2) | 0.0593 (11) |
| H19A | 0.9959 | 0.9023 | 0.2432 | 0.071* |
| H19B | 1.1316 | 0.9060 | 0.2113 | 0.071* |
| C20 | 0.5176 (4) | −0.2354 (3) | 0.2335 (2) | 0.0471 (9) |
| C21 | 0.6151 (3) | −0.2013 (3) | 0.2971 (2) | 0.0415 (8) |
| C22 | 0.6613 (4) | −0.2707 (4) | 0.3385 (2) | 0.0498 (10) |
| H22 | 0.6215 | −0.3678 | 0.3233 | 0.060* |
| C23 | 0.7632 (4) | −0.1966 (4) | 0.4001 (2) | 0.0522 (10) |
| H23 | 0.7974 | −0.2415 | 0.4276 | 0.063* |
| C24 | 0.8197 (4) | −0.0526 (4) | 0.4243 (2) | 0.0451 (9) |

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|---|---|---|---|---|
| H24 | 0.8886 | −0.0041 | 0.4695 | 0.054* |
| C25 | 0.7799 (3) | 0.0204 (3) | 0.38573 (19) | 0.0381 (8) |
| C26 | 0.4180 (4) | −0.3744 (4) | 0.1832 (2) | 0.0614 (11) |
| H26A | 0.3447 | −0.4252 | 0.2152 | 0.092* |
| H26B | 0.4665 | −0.4251 | 0.1663 | 0.092* |
| H26C | 0.3776 | −0.3638 | 0.1353 | 0.092* |
| C27 | 0.7250 (3) | 0.2497 (3) | 0.40928 (19) | 0.0370 (8) |
| H27 | 0.6939 | 0.2272 | 0.3501 | 0.044* |
| C28 | 0.6028 (3) | 0.1649 (3) | 0.4533 (2) | 0.0434 (9) |
| H28A | 0.5619 | 0.0662 | 0.4274 | 0.052* |
| H28B | 0.6368 | 0.1774 | 0.5102 | 0.052* |
| C29 | 0.4914 (4) | 0.2049 (4) | 0.4524 (2) | 0.0493 (9) |
| H29A | 0.4487 | 0.1811 | 0.3961 | 0.059* |
| H29B | 0.4187 | 0.1515 | 0.4848 | 0.059* |
| C30 | 0.5493 (4) | 0.3578 (4) | 0.4866 (2) | 0.0568 (10) |
| H30A | 0.4758 | 0.3813 | 0.4813 | 0.068* |
| H30B | 0.5821 | 0.3800 | 0.5448 | 0.068* |
| C31 | 0.6677 (4) | 0.4419 (4) | 0.4416 (2) | 0.0539 (10) |
| H31A | 0.7072 | 0.5408 | 0.4664 | 0.065* |

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|---|---|---|---|---|
| H31B | 0.6323 | 0.4266 | 0.3847 | 0.065* |
| C32 | 0.7814 (4) | 0.4041 (3) | 0.4435 (2) | 0.0459 (9) |
| H32A | 0.8236 | 0.4286 | 0.5000 | 0.055* |
| H32B | 0.8541 | 0.4581 | 0.4113 | 0.055* |
| C33 | 0.9860 (3) | 0.2775 (3) | 0.35008 (19) | 0.0395 (8) |
| H33 | 1.0233 | 0.3792 | 0.3631 | 0.047* |
| C34 | 1.1082 (4) | 0.2563 (4) | 0.3662 (2) | 0.0543 (10) |
| H34A | 1.1453 | 0.2949 | 0.4240 | 0.065* |
| H34B | 1.0754 | 0.1564 | 0.3553 | 0.065* |
| C35 | 1.2233 (4) | 0.3239 (4) | 0.3145 (2) | 0.0578 (10) |
| H35A | 1.2629 | 0.4249 | 0.3290 | 0.069* |
| H35B | 1.2975 | 0.3034 | 0.3254 | 0.069* |
| C36 | 1.1694 (4) | 0.2718 (4) | 0.2253 (2) | 0.0511 (10) |
| H36A | 1.1377 | 0.1722 | 0.2095 | 0.061* |
| H36B | 1.2445 | 0.3203 | 0.1928 | 0.061* |
| C37 | 1.0508 (4) | 0.2959 (4) | 0.2081 (2) | 0.0530 (10) |
| H37A | 1.0145 | 0.2581 | 0.1501 | 0.064* |
| H37B | 1.0850 | 0.3962 | 0.2193 | 0.064* |
| C38 | 0.9342 (3) | 0.2283 (4) | 0.25961 (19) | 0.0465 (9) |

| | | | | |
|---|---|---|---|---|
| H38A | 0.8933 | 0.1271 | 0.2442 | 0.056* |
| H38B | 0.8612 | 0.2504 | 0.2487 | 0.056* |
| N1 | 0.5533 (3) | 0.3883 (3) | 0.22524 (15) | 0.0392 (7) |
| N2 | 0.6560 (3) | 0.4832 (3) | 0.19351 (15) | 0.0361 (6) |
| N3 | 0.7000 (3) | 0.4150 (2) | 0.13905 (15) | 0.0330 (6) |
| N4 | 0.5244 (3) | −0.1185 (3) | 0.22048 (17) | 0.0489 (8) |
| N5 | 0.6203 (3) | −0.0100 (3) | 0.27317 (17) | 0.0447 (7) |
| N6 | 0.6763 (3) | −0.0591 (2) | 0.32034 (16) | 0.0368 (7) |
| P1 | 0.92062 (9) | 0.66163 (9) | 0.10451 (5) | 0.0399 (3) |
| P2 | 0.86205 (9) | 0.20712 (9) | 0.42435 (5) | 0.0389 (3) |

Atomic displacement parameters (Å$^2$)

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0360 (19) | 0.0323 (18) | 0.0372 (18) | 0.0174 (15) | −0.0013 (14) | 0.0059 (14) |
| C2 | 0.0351 (18) | 0.0242 (16) | 0.0432 (18) | 0.0132 (14) | −0.0008 (15) | 0.0034 (14) |
| C3 | 0.046 (2) | 0.0279 (18) | 0.076 (3) | 0.0168 (17) | 0.0106 (19) | 0.0015 (18) |
| C4 | 0.064 (3) | 0.037 (2) | 0.086 (3) | 0.023 (2) | 0.025 (2) | −0.009 (2) |
| C5 | 0.046 (2) | 0.038 (2) | 0.074 (3) | 0.0131 (18) | 0.0233 (19) | −0.0019 (19) |
| C6 | 0.0362 (19) | 0.0321 (18) | 0.047 (2) | 0.0140 (15) | 0.0098 (15) | 0.0016 (15) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C7 | 0.047 (2) | 0.040 (2) | 0.056 (2) | 0.0174 (17) | 0.0070 (17) | 0.0232 (17) |
| C8 | 0.0386 (19) | 0.0320 (17) | 0.0347 (17) | 0.0122 (15) | 0.0044 (14) | 0.0070 (14) |
| C9 | 0.054 (2) | 0.0261 (18) | 0.054 (2) | 0.0060 (17) | −0.0141 (18) | 0.0019 (16) |
| C10 | 0.056 (2) | 0.041 (2) | 0.067 (3) | 0.0125 (19) | −0.0176 (19) | 0.0104 (19) |
| C11 | 0.058 (2) | 0.0352 (19) | 0.044 (2) | 0.0199 (18) | −0.0051 (17) | 0.0062 (16) |
| C12 | 0.072 (3) | 0.0323 (19) | 0.052 (2) | 0.0216 (19) | −0.0142 (19) | −0.0015 (17) |
| C13 | 0.060 (3) | 0.034 (2) | 0.067 (3) | 0.0180 (19) | −0.017 (2) | −0.0007 (18) |
| C14 | 0.0358 (19) | 0.0270 (17) | 0.054 (2) | 0.0091 (15) | −0.0005 (15) | 0.0064 (15) |
| C15 | 0.138 (5) | 0.062 (3) | 0.092 (3) | 0.070 (3) | −0.041 (3) | −0.015 (3) |
| C16 | 0.134 (4) | 0.054 (3) | 0.090 (3) | 0.054 (3) | −0.042 (3) | 0.004 (2) |
| C17 | 0.049 (2) | 0.056 (2) | 0.054 (2) | 0.0256 (19) | −0.0079 (17) | 0.0099 (19) |
| C18 | 0.064 (3) | 0.041 (2) | 0.066 (3) | 0.029 (2) | −0.019 (2) | −0.0056 (18) |
| C19 | 0.068 (3) | 0.036 (2) | 0.064 (2) | 0.0219 (19) | −0.023 (2) | 0.0001 (18) |
| C20 | 0.041 (2) | 0.0295 (18) | 0.061 (2) | 0.0135 (16) | 0.0150 (18) | −0.0011 (16) |
| C21 | 0.043 (2) | 0.0243 (17) | 0.055 (2) | 0.0162 (15) | 0.0179 (17) | 0.0050 (15) |
| C22 | 0.066 (3) | 0.0311 (19) | 0.062 (2) | 0.0275 (19) | 0.032 (2) | 0.0186 (18) |
| C23 | 0.071 (3) | 0.046 (2) | 0.060 (2) | 0.040 (2) | 0.022 (2) | 0.0240 (19) |
| C24 | 0.051 (2) | 0.045 (2) | 0.049 (2) | 0.0295 (18) | 0.0106 (16) | 0.0141 (17) |
| C25 | 0.041 (2) | 0.0328 (18) | 0.0453 (19) | 0.0216 (16) | 0.0081 (15) | 0.0105 (15) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C26 | 0.055 (2) | 0.032 (2) | 0.074 (3) | 0.0102 (18) | 0.007 (2) | −0.0057 (18) |
| C27 | 0.047 (2) | 0.0247 (16) | 0.0387 (18) | 0.0184 (15) | 0.0013 (15) | 0.0039 (14) |
| C28 | 0.048 (2) | 0.0328 (18) | 0.050 (2) | 0.0205 (16) | 0.0084 (16) | 0.0095 (16) |
| C29 | 0.051 (2) | 0.045 (2) | 0.057 (2) | 0.0297 (18) | 0.0080 (17) | 0.0066 (18) |
| C30 | 0.066 (3) | 0.049 (2) | 0.065 (2) | 0.039 (2) | 0.010 (2) | 0.0045 (19) |
| C31 | 0.074 (3) | 0.0328 (19) | 0.060 (2) | 0.0331 (19) | −0.001 (2) | 0.0043 (17) |
| C32 | 0.056 (2) | 0.0267 (17) | 0.048 (2) | 0.0173 (17) | 0.0042 (17) | 0.0038 (15) |
| C33 | 0.043 (2) | 0.0273 (17) | 0.0452 (19) | 0.0166 (15) | 0.0026 (15) | 0.0029 (14) |
| C34 | 0.046 (2) | 0.064 (3) | 0.054 (2) | 0.029 (2) | −0.0004 (17) | 0.0100 (19) |
| C35 | 0.041 (2) | 0.059 (3) | 0.067 (3) | 0.023 (2) | 0.0051 (18) | 0.006 (2) |
| C36 | 0.050 (2) | 0.034 (2) | 0.060 (2) | 0.0157 (17) | 0.0138 (18) | 0.0041 (17) |
| C37 | 0.059 (2) | 0.040 (2) | 0.048 (2) | 0.0145 (18) | 0.0069 (18) | 0.0107 (17) |
| C38 | 0.042 (2) | 0.045 (2) | 0.048 (2) | 0.0187 (17) | 0.0014 (16) | 0.0103 (17) |
| N1 | 0.0394 (16) | 0.0344 (15) | 0.0422 (15) | 0.0173 (13) | 0.0068 (12) | 0.0080 (13) |
| N2 | 0.0377 (16) | 0.0320 (15) | 0.0372 (15) | 0.0181 (13) | 0.0071 (12) | 0.0018 (12) |
| N3 | 0.0328 (15) | 0.0256 (13) | 0.0379 (14) | 0.0142 (12) | 0.0018 (11) | 0.0015 (11) |
| N4 | 0.0418 (18) | 0.0345 (16) | 0.0601 (19) | 0.0167 (14) | −0.0038 (14) | −0.0060 (14) |
| N5 | 0.0438 (17) | 0.0320 (15) | 0.0536 (17) | 0.0188 (14) | −0.0036 (14) | −0.0002 (13) |
| N6 | 0.0386 (16) | 0.0244 (14) | 0.0482 (16) | 0.0167 (12) | 0.0059 (13) | 0.0073 (12) |

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|---|---|---|---|---|---|---|
| P1 | 0.0356 (5) | 0.0286 (5) | 0.0453 (5) | 0.0102 (4) | 0.0070 (4) | 0.0020 (4) |
| P2 | 0.0421 (5) | 0.0303 (5) | 0.0424 (5) | 0.0180 (4) | 0.0014 (4) | 0.0038 (4) |

Geometric parameters (Å, °)

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| C1—N1 | 1.348 (4) | C20—C26 | 1.496 (5) |
| C1—C2 | 1.384 (4) | C21—N6 | 1.388 (4) |
| C1—C7 | 1.495 (4) | C21—C22 | 1.408 (5) |
| C2—N3 | 1.392 (4) | C22—C23 | 1.346 (5) |
| C2—C3 | 1.401 (5) | C22—H22 | 0.9500 |
| C3—C4 | 1.347 (5) | C23—C24 | 1.414 (5) |
| C3—H3 | 0.9500 | C23—H23 | 0.9500 |
| C4—C5 | 1.432 (5) | C24—C25 | 1.368 (4) |
| C4—H4 | 0.9500 | C24—H24 | 0.9500 |
| C5—C6 | 1.351 (5) | C25—N6 | 1.404 (4) |
| C5—H5 | 0.9500 | C25—P2 | 1.837 (3) |
| C6—N3 | 1.391 (4) | C26—H26A | 0.9800 |
| C6—P1 | 1.843 (3) | C26—H26B | 0.9800 |
| C7—H7A | 0.9800 | C26—H26C | 0.9800 |
| C7—H7B | 0.9800 | C27—C28 | 1.534 (4) |

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| C7—H7C | 0.9800 | C27—C32 | 1.539 (4) |
| C8—C9 | 1.527 (4) | C27—P2 | 1.849 (3) |
| C8—C13 | 1.538 (4) | C27—H27 | 1.0000 |
| C8—P1 | 1.852 (4) | C28—C29 | 1.523 (5) |
| C8—H8 | 1.0000 | C28—H28A | 0.9900 |
| C9—C10 | 1.512 (5) | C28—H28B | 0.9900 |
| C9—H9A | 0.9900 | C29—C30 | 1.521 (5) |
| C9—H9B | 0.9900 | C29—H29A | 0.9900 |
| C10—C11 | 1.520 (4) | C29—H29B | 0.9900 |
| C10—H10A | 0.9900 | C30—C31 | 1.516 (5) |
| C10—H10B | 0.9900 | C30—H30A | 0.9900 |
| C11—C12 | 1.511 (5) | C30—H30B | 0.9900 |
| C11—H11A | 0.9900 | C31—C32 | 1.531 (5) |
| C11—H11B | 0.9900 | C31—H31A | 0.9900 |
| C12—C13 | 1.514 (5) | C31—H31B | 0.9900 |
| C12—H12A | 0.9900 | C32—H32A | 0.9900 |
| C12—H12B | 0.9900 | C32—H32B | 0.9900 |
| C13—H13A | 0.9900 | C33—C34 | 1.530 (5) |
| C13—H13B | 0.9900 | C33—C38 | 1.531 (4) |

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| C14—C19 | 1.510 (4) | C33—P2 | 1.861 (3) |
| C14—C15 | 1.520 (6) | C33—H33 | 1.0000 |
| C14—P1 | 1.861 (3) | C34—C35 | 1.523 (5) |
| C14—H14 | 1.0000 | C34—H34A | 0.9900 |
| C15—C16 | 1.522 (6) | C34—H34B | 0.9900 |
| C15—H15A | 0.9900 | C35—C36 | 1.516 (5) |
| C15—H15B | 0.9900 | C35—H35A | 0.9900 |
| C16—C17 | 1.502 (5) | C35—H35B | 0.9900 |
| C16—H16A | 0.9900 | C36—C37 | 1.517 (5) |
| C16—H16B | 0.9900 | C36—H36A | 0.9900 |
| C17—C18 | 1.497 (5) | C36—H36B | 0.9900 |
| C17—H17A | 0.9900 | C37—C38 | 1.530 (5) |
| C17—H17B | 0.9900 | C37—H37A | 0.9900 |
| C18—C19 | 1.527 (5) | C37—H37B | 0.9900 |
| C18—H18A | 0.9900 | C38—H38A | 0.9900 |
| C18—H18B | 0.9900 | C38—H38B | 0.9900 |
| C19—H19A | 0.9900 | N1—N2 | 1.338 (3) |
| C19—H19B | 0.9900 | N2—N3 | 1.347 (4) |
| C20—N4 | 1.357 (4) | N4—N5 | 1.325 (4) |

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| C20—C21 | 1.383 (5) | N5—N6 | 1.357 (4) |
| N1—C1—C2 | 109.1 (3) | C21—C22—H22 | 120.7 |
| N1—C1—C7 | 123.2 (3) | C22—C23—C24 | 120.6 (3) |
| C2—C1—C7 | 127.7 (3) | C22—C23—H23 | 119.7 |
| C1—C2—N3 | 103.6 (3) | C24—C23—H23 | 119.7 |
| C1—C2—C3 | 137.1 (3) | C25—C24—C23 | 123.2 (3) |
| N3—C2—C3 | 119.3 (3) | C25—C24—H24 | 118.4 |
| C4—C3—C2 | 119.0 (3) | C23—C24—H24 | 118.4 |
| C4—C3—H3 | 120.5 | C24—C25—N6 | 114.8 (3) |
| C2—C3—H3 | 120.5 | C24—C25—P2 | 118.3 (3) |
| C3—C4—C5 | 119.2 (4) | N6—C25—P2 | 126.9 (2) |
| C3—C4—H4 | 120.4 | C20—C26—H26A | 109.5 |
| C5—C4—H4 | 120.4 | C20—C26—H26B | 109.5 |
| C6—C5—C4 | 124.1 (3) | H26A—C26—H26B | 109.5 |
| C6—C5—H5 | 118.0 | C20—C26—H26C | 109.5 |
| C4—C5—H5 | 118.0 | H26A—C26—H26C | 109.5 |
| C5—C6—N3 | 114.8 (3) | H26B—C26—H26C | 109.5 |
| C5—C6—P1 | 121.0 (3) | C28—C27—C32 | 109.7 (3) |
| N3—C6—P1 | 123.9 (2) | C28—C27—P2 | 109.2 (2) |

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| C1—C7—H7A | 109.5 | C32—C27—P2 | 109.5 (2) |
| C1—C7—H7B | 109.5 | C28—C27—H27 | 109.5 |
| H7A—C7—H7B | 109.5 | C32—C27—H27 | 109.5 |
| C1—C7—H7C | 109.5 | P2—C27—H27 | 109.5 |
| H7A—C7—H7C | 109.5 | C29—C28—C27 | 112.9 (3) |
| H7B—C7—H7C | 109.5 | C29—C28—H28A | 109.0 |
| C9—C8—C13 | 108.7 (3) | C27—C28—H28A | 109.0 |
| C9—C8—P1 | 110.1 (2) | C29—C28—H28B | 109.0 |
| C13—C8—P1 | 109.2 (2) | C27—C28—H28B | 109.0 |
| C9—C8—H8 | 109.6 | H28A—C28—H28B | 107.8 |
| C13—C8—H8 | 109.6 | C30—C29—C28 | 111.8 (3) |
| P1—C8—H8 | 109.6 | C30—C29—H29A | 109.3 |
| C10—C9—C8 | 113.3 (3) | C28—C29—H29A | 109.3 |
| C10—C9—H9A | 108.9 | C30—C29—H29B | 109.3 |
| C8—C9—H9A | 108.9 | C28—C29—H29B | 109.3 |
| C10—C9—H9B | 108.9 | H29A—C29—H29B | 107.9 |
| C8—C9—H9B | 108.9 | C31—C30—C29 | 110.3 (3) |
| H9A—C9—H9B | 107.7 | C31—C30—H30A | 109.6 |
| C9—C10—C11 | 112.4 (3) | C29—C30—H30A | 109.6 |

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| C9—C10—H10A | 109.1 | C31—C30—H30B | 109.6 |
| C11—C10—H10A | 109.1 | C29—C30—H30B | 109.6 |
| C9—C10—H10B | 109.1 | H30A—C30—H30B | 108.1 |
| C11—C10—H10B | 109.1 | C30—C31—C32 | 112.1 (3) |
| H10A—C10—H10B | 107.9 | C30—C31—H31A | 109.2 |
| C12—C11—C10 | 110.6 (3) | C32—C31—H31A | 109.2 |
| C12—C11—H11A | 109.5 | C30—C31—H31B | 109.2 |
| C10—C11—H11A | 109.5 | C32—C31—H31B | 109.2 |
| C12—C11—H11B | 109.5 | H31A—C31—H31B | 107.9 |
| C10—C11—H11B | 109.5 | C31—C32—C27 | 111.7 (3) |
| H11A—C11—H11B | 108.1 | C31—C32—H32A | 109.3 |
| C11—C12—C13 | 110.7 (3) | C27—C32—H32A | 109.3 |
| C11—C12—H12A | 109.5 | C31—C32—H32B | 109.3 |
| C13—C12—H12A | 109.5 | C27—C32—H32B | 109.3 |
| C11—C12—H12B | 109.5 | H32A—C32—H32B | 107.9 |
| C13—C12—H12B | 109.5 | C34—C33—C38 | 109.7 (3) |
| H12A—C12—H12B | 108.1 | C34—C33—P2 | 108.5 (2) |
| C12—C13—C8 | 112.3 (3) | C38—C33—P2 | 119.1 (2) |
| C12—C13—H13A | 109.1 | C34—C33—H33 | 106.3 |

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| C8—C13—H13A | 109.1 | C38—C33—H33 | 106.3 |
| C12—C13—H13B | 109.1 | P2—C33—H33 | 106.3 |
| C8—C13—H13B | 109.1 | C35—C34—C33 | 112.8 (3) |
| H13A—C13—H13B | 107.9 | C35—C34—H34A | 109.0 |
| C19—C14—C15 | 109.8 (3) | C33—C34—H34A | 109.0 |
| C19—C14—P1 | 112.7 (2) | C35—C34—H34B | 109.0 |
| C15—C14—P1 | 108.0 (3) | C33—C34—H34B | 109.0 |
| C19—C14—H14 | 108.8 | H34A—C34—H34B | 107.8 |
| C15—C14—H14 | 108.8 | C36—C35—C34 | 110.8 (3) |
| P1—C14—H14 | 108.8 | C36—C35—H35A | 109.5 |
| C14—C15—C16 | 113.6 (4) | C34—C35—H35A | 109.5 |
| C14—C15—H15A | 108.8 | C36—C35—H35B | 109.5 |
| C16—C15—H15A | 108.8 | C34—C35—H35B | 109.5 |
| C14—C15—H15B | 108.8 | H35A—C35—H35B | 108.1 |
| C16—C15—H15B | 108.8 | C35—C36—C37 | 110.3 (3) |
| H15A—C15—H15B | 107.7 | C35—C36—H36A | 109.6 |
| C17—C16—C15 | 111.9 (3) | C37—C36—H36A | 109.6 |
| C17—C16—H16A | 109.2 | C35—C36—H36B | 109.6 |
| C15—C16—H16A | 109.2 | C37—C36—H36B | 109.6 |

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| C17—C16—H16B | 109.2 | H36A—C36—H36B | 108.1 |
| C15—C16—H16B | 109.2 | C36—C37—C38 | 111.8 (3) |
| H16A—C16—H16B | 107.9 | C36—C37—H37A | 109.3 |
| C18—C17—C16 | 110.2 (3) | C38—C37—H37A | 109.3 |
| C18—C17—H17A | 109.6 | C36—C37—H37B | 109.3 |
| C16—C17—H17A | 109.6 | C38—C37—H37B | 109.3 |
| C18—C17—H17B | 109.6 | H37A—C37—H37B | 107.9 |
| C16—C17—H17B | 109.6 | C37—C38—C33 | 111.6 (3) |
| H17A—C17—H17B | 108.1 | C37—C38—H38A | 109.3 |
| C17—C18—C19 | 112.4 (3) | C33—C38—H38A | 109.3 |
| C17—C18—H18A | 109.1 | C37—C38—H38B | 109.3 |
| C19—C18—H18A | 109.1 | C33—C38—H38B | 109.3 |
| C17—C18—H18B | 109.1 | H38A—C38—H38B | 108.0 |
| C19—C18—H18B | 109.1 | N2—N1—C1 | 109.9 (3) |
| H18A—C18—H18B | 107.8 | N1—N2—N3 | 106.6 (2) |
| C14—C19—C18 | 113.3 (3) | N2—N3—C6 | 125.6 (3) |
| C14—C19—H19A | 108.9 | N2—N3—C2 | 110.9 (2) |
| C18—C19—H19A | 108.9 | C6—N3—C2 | 123.5 (3) |
| C14—C19—H19B | 108.9 | N5—N4—C20 | 110.3 (3) |

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| C18—C19—H19B | 108.9 | N4—N5—N6 | 106.3 (3) |
| H19A—C19—H19B | 107.7 | N5—N6—C21 | 111.1 (3) |
| N4—C20—C21 | 108.9 (3) | N5—N6—C25 | 125.6 (3) |
| N4—C20—C26 | 122.3 (3) | C21—N6—C25 | 123.3 (3) |
| C21—C20—C26 | 128.9 (3) | C6—P1—C8 | 104.22 (15) |
| C20—C21—N6 | 103.5 (3) | C6—P1—C14 | 100.94 (14) |
| C20—C21—C22 | 137.2 (3) | C8—P1—C14 | 106.00 (16) |
| N6—C21—C22 | 119.3 (3) | C25—P2—C27 | 105.17 (14) |
| C23—C22—C21 | 118.6 (3) | C25—P2—C33 | 102.82 (15) |
| C23—C22—H22 | 120.7 | C27—P2—C33 | 107.04 (14) |
| N1—C1—C2—N3 | 0.5 (3) | P2—C33—C38—C37 | −179.3 (3) |
| C7—C1—C2—N3 | 178.7 (3) | C2—C1—N1—N2 | −0.4 (3) |
| N1—C1—C2—C3 | −177.0 (4) | C7—C1—N1—N2 | −178.7 (3) |
| C7—C1—C2—C3 | 1.2 (6) | C1—N1—N2—N3 | 0.1 (3) |
| C1—C2—C3—C4 | 175.7 (4) | N1—N2—N3—C6 | 178.8 (3) |
| N3—C2—C3—C4 | −1.5 (5) | N1—N2—N3—C2 | 0.2 (3) |
| C2—C3—C4—C5 | 2.1 (6) | C5—C6—N3—N2 | −175.6 (3) |
| C3—C4—C5—C6 | −0.2 (7) | P1—C6—N3—N2 | 10.1 (4) |
| C4—C5—C6—N3 | −2.1 (6) | C5—C6—N3—C2 | 2.8 (5) |

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| C4—C5—C6—P1 | 172.3 (3) | P1—C6—N3—C2 | −171.6 (2) |
| C13—C8—C9—C10 | −52.6 (4) | C1—C2—N3—N2 | −0.5 (3) |
| P1—C8—C9—C10 | −172.2 (2) | C3—C2—N3—N2 | 177.6 (3) |
| C8—C9—C10—C11 | 53.3 (4) | C1—C2—N3—C6 | −179.1 (3) |
| C9—C10—C11—C12 | −54.0 (5) | C3—C2—N3—C6 | −1.0 (5) |
| C10—C11—C12—C13 | 56.3 (4) | C21—C20—N4—N5 | −0.8 (4) |
| C11—C12—C13—C8 | −58.6 (4) | C26—C20—N4—N5 | 179.7 (3) |
| C9—C8—C13—C12 | 55.4 (4) | C20—N4—N5—N6 | 0.4 (4) |
| P1—C8—C13—C12 | 175.5 (3) | N4—N5—N6—C21 | 0.1 (4) |
| C19—C14—C15—C16 | 51.3 (5) | N4—N5—N6—C25 | −178.3 (3) |
| P1—C14—C15—C16 | 174.5 (4) | C20—C21—N6—N5 | −0.5 (4) |
| C14—C15—C16—C17 | −54.6 (6) | C22—C21—N6—N5 | 179.1 (3) |
| C15—C16—C17—C18 | 55.0 (6) | C20—C21—N6—C25 | 177.9 (3) |
| C16—C17—C18—C19 | −55.1 (5) | C22—C21—N6—C25 | −2.5 (5) |
| C15—C14—C19—C18 | −50.9 (5) | C24—C25—N6—N5 | 179.9 (3) |
| P1—C14—C19—C18 | −171.2 (3) | P2—C25—N6—N5 | 1.2 (5) |
| C17—C18—C19—C14 | 54.5 (5) | C24—C25—N6—C21 | 1.7 (4) |
| N4—C20—C21—N6 | 0.8 (4) | P2—C25—N6—C21 | −177.0 (2) |
| C26—C20—C21—N6 | −179.8 (3) | C5—C6—P1—C8 | 126.0 (3) |

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| N4—C20—C21—C22 | −178.7 (4) | N3—C6—P1—C8 | −60.1 (3) |
| C26—C20—C21—C22 | 0.7 (7) | C5—C6—P1—C14 | −124.2 (3) |
| C20—C21—C22—C23 | −180.0 (4) | N3—C6—P1—C14 | 49.7 (3) |
| N6—C21—C22—C23 | 0.6 (5) | C9—C8—P1—C6 | −49.5 (2) |
| C21—C22—C23—C24 | 1.9 (5) | C13—C8—P1—C6 | −168.8 (2) |
| C22—C23—C24—C25 | −2.7 (6) | C9—C8—P1—C14 | −155.5 (2) |
| C23—C24—C25—N6 | 0.9 (5) | C13—C8—P1—C14 | 85.2 (3) |
| C23—C24—C25—P2 | 179.7 (3) | C19—C14—P1—C6 | −170.9 (3) |
| C32—C27—C28—C29 | 53.4 (4) | C15—C14—P1—C6 | 67.7 (3) |
| P2—C27—C28—C29 | 173.4 (2) | C19—C14—P1—C8 | −62.5 (3) |
| C27—C28—C29—C30 | −55.1 (4) | C15—C14—P1—C8 | 176.2 (3) |
| C28—C29—C30—C31 | 55.0 (4) | C24—C25—P2—C27 | −144.7 (3) |
| C29—C30—C31—C32 | −56.0 (4) | N6—C25—P2—C27 | 34.0 (3) |
| C30—C31—C32—C27 | 56.2 (4) | C24—C25—P2—C33 | 103.4 (3) |
| C28—C27—C32—C31 | −53.5 (4) | N6—C25—P2—C33 | −77.9 (3) |
| P2—C27—C32—C31 | −173.3 (2) | C28—C27—P2—C25 | 57.3 (2) |
| C38—C33—C34—C35 | 54.5 (4) | C32—C27—P2—C25 | 177.4 (2) |
| P2—C33—C34—C35 | −173.9 (3) | C28—C27—P2—C33 | 166.1 (2) |
| C33—C34—C35—C36 | −56.5 (4) | C32—C27—P2—C33 | −73.7 (2) |

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| C34—C35—C36—C37 | 56.4 (4) | C34—C33—P2—C25 | −74.8 (2) |
| C35—C36—C37—C38 | −56.8 (4) | C38—C33—P2—C25 | 51.5 (3) |
| C36—C37—C38—C33 | 56.0 (4) | C34—C33—P2—C27 | 174.7 (2) |
| C34—C33—C38—C37 | −53.6 (4) | C38—C33—P2—C27 | −59.1 (3) |

All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

## Compound 5b

*Crystal data*

| | |
|---|---|
| $C_{18}H_{26}N_3P$ | |
| $M_r$ = 315.39 | $D_x$ = 1.186 Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | |
| Hall symbol: -P 2ybc | Mo $K\alpha$ radiation, λ = 0.71073 Å |
| $a$ = 15.9046 (10) Å | Cell parameters from 14773 reflections |
| $b$ = 11.0103 (5) Å | θ = 1.0–27.5° |
| $c$ = 10.0953 (7) Å | μ = 0.16 mm$^{-1}$ |
| β = 91.701 (3)° | $T$ = 173 K |
| $V$ = 1767.05 (18) Å$^3$ | Prism, colorless |
| $Z$ = 4 | 0.30 × 0.28 × 0.25 mm |
| $F$(000) = 680 | |

*Data collection*

| | |
|---|---|
| KappaCCD diffractometer | 3024 reflections with $I > 2\sigma(I)$ |
| Radiation source: fine-focus sealed tube | $R_{int}$ = 0.053 |
| graphite | $\theta_{max}$ = 27.5°, $\theta_{min}$ = 1.3° |

| | |
|---|---|
| Detector resolution: ? pixels $mm^{-1}$ | $h$ = −20→15 |
| phi and ω scans | $k$ = −14→13 |
| 10149 measured reflections | $l$ = −10→13 |
| 4040 independent reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.082 | H-atom parameters constrained |
| $wR(F^2)$ = 0.253 | $w = 1/[\sigma^2(F_o^2) + (0.1036P)^2 + 3.1152P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S$ = 1.17 | |
| 4040 reflections | $\Delta\rho_{max}$ = 0.59 e Å$^{-3}$ |
| 200 parameters | $\Delta\rho_{min}$ = −0.50 e Å$^{-3}$ |
| 0 restraints | Extinction correction: *SHELXL*, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$ |
| ? constraints | Extinction coefficient: 0.037 (5) |
| Primary atom site location: structure-invariant direct methods | |

Refinement of $F^2$ against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on $F^2$, conventional *R*-factors *R* are based on F, with F set to zero for negative $F^2$. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on $F^2$ are statistically about twice as large as those based on F,

and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| P1 | 0.28814 (6) | −0.58726 (8) | 0.37145 (9) | 0.0294 (3) |
| N1 | 0.1852 (2) | −0.2416 (3) | 0.5489 (3) | 0.0340 (7) |
| N2 | 0.2178 (2) | −0.3330 (3) | 0.4805 (3) | 0.0344 (7) |
| N3 | 0.23996 (19) | −0.4196 (3) | 0.5717 (3) | 0.0284 (7) |
| C1 | 0.1866 (2) | −0.2677 (4) | 0.6775 (4) | 0.0322 (8) |
| H1 | 0.1666 | −0.2162 | 0.7451 | 0.039* |
| C2 | 0.2220 (2) | −0.3822 (4) | 0.6980 (4) | 0.0313 (8) |
| C3 | 0.2422 (3) | −0.4586 (4) | 0.8055 (4) | 0.0369 (9) |
| H3 | 0.2304 | −0.4351 | 0.8936 | 0.044* |
| C4 | 0.2793 (3) | −0.5677 (4) | 0.7803 (4) | 0.0380 (9) |
| H4 | 0.2944 | −0.6203 | 0.8517 | 0.046* |
| C5 | 0.2955 (2) | −0.6032 (4) | 0.6482 (4) | 0.0345 (9) |
| H5 | 0.3211 | −0.6798 | 0.6337 | 0.041* |
| C6 | 0.2757 (2) | −0.5317 (3) | 0.5412 (3) | 0.0291 (8) |
| C7 | 0.1765 (2) | −0.5701 (3) | 0.3100 (4) | 0.0304 (8) |
| H7 | 0.1578 | −0.4858 | 0.3312 | 0.037* |

| | | | | |
|---|---|---|---|---|
| C8 | 0.1206 (3) | −0.6586 (5) | 0.3829 (4) | 0.0510 (12) |
| H8A | 0.1400 | −0.7426 | 0.3674 | 0.061* |
| H8B | 0.1253 | −0.6424 | 0.4793 | 0.061* |
| C9 | 0.0290 (3) | −0.6467 (7) | 0.3364 (5) | 0.0684 (17) |
| H9A | −0.0051 | −0.7081 | 0.3823 | 0.082* |
| H9B | 0.0079 | −0.5653 | 0.3607 | 0.082* |
| C10 | 0.0182 (3) | −0.6639 (6) | 0.1882 (5) | 0.0589 (14) |
| H10A | −0.0412 | −0.6495 | 0.1608 | 0.071* |
| H10B | 0.0326 | −0.7486 | 0.1647 | 0.071* |
| C11 | 0.0746 (3) | −0.5767 (5) | 0.1148 (4) | 0.0461 (11) |
| H11A | 0.0553 | −0.4924 | 0.1293 | 0.055* |
| H11B | 0.0699 | −0.5937 | 0.0186 | 0.055* |
| C12 | 0.1663 (2) | −0.5879 (4) | 0.1612 (4) | 0.0384 (9) |
| H12A | 0.1877 | −0.6692 | 0.1372 | 0.046* |
| H12B | 0.2002 | −0.5264 | 0.1153 | 0.046* |
| C13 | 0.3440 (2) | −0.4614 (3) | 0.2895 (3) | 0.0299 (8) |
| H13 | 0.3029 | −0.3941 | 0.2716 | 0.036* |
| C14 | 0.4173 (3) | −0.4110 (4) | 0.3755 (4) | 0.0382 (9) |
| H14A | 0.3957 | −0.3814 | 0.4607 | 0.046* |

| | | | | |
|---|---|---|---|---|
| H14B | 0.4583 | −0.4767 | 0.3951 | 0.046* |
| C15 | 0.4612 (3) | −0.3066 (5) | 0.3043 (5) | 0.0508 (12) |
| H15A | 0.4216 | −0.2377 | 0.2933 | 0.061* |
| H15B | 0.5098 | −0.2785 | 0.3596 | 0.061* |
| C16 | 0.4915 (3) | −0.3448 (5) | 0.1693 (5) | 0.0506 (12) |
| H16A | 0.5370 | −0.4056 | 0.1809 | 0.061* |
| H16B | 0.5149 | −0.2734 | 0.1236 | 0.061* |
| C17 | 0.4202 (3) | −0.3988 (4) | 0.0845 (4) | 0.0429 (10) |
| H17A | 0.4425 | −0.4284 | −0.0002 | 0.051* |
| H17B | 0.3778 | −0.3352 | 0.0638 | 0.051* |
| C18 | 0.3786 (3) | −0.5038 (4) | 0.1564 (4) | 0.0354 (9) |
| H18A | 0.4202 | −0.5694 | 0.1725 | 0.042* |
| H18B | 0.3320 | −0.5370 | 0.1001 | 0.042* |

Atomic displacement parameters (Å$^2$)

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| P1 | 0.0340 (5) | 0.0279 (5) | 0.0261 (5) | 0.0015 (4) | −0.0008 (4) | −0.0012 (4) |
| N1 | 0.0410 (18) | 0.0297 (16) | 0.0316 (16) | 0.0020 (13) | 0.0027 (13) | −0.0036 (13) |
| N2 | 0.0451 (19) | 0.0302 (16) | 0.0277 (16) | 0.0042 (14) | −0.0006 (13) | 0.0029 (13) |

| | | | | | | |
|---|---|---|---|---|---|---|
| N3 | 0.0326 (15) | 0.0283 (15) | 0.0241 (14) | −0.0015 (12) | 0.0000 (12) | 0.0016 (12) |
| C1 | 0.0350 (19) | 0.036 (2) | 0.0255 (17) | −0.0056 (15) | 0.0052 (14) | −0.0061 (15) |
| C2 | 0.0319 (18) | 0.0361 (19) | 0.0259 (18) | −0.0085 (15) | −0.0002 (14) | −0.0029 (15) |
| C3 | 0.043 (2) | 0.045 (2) | 0.0225 (17) | −0.0063 (18) | 0.0015 (15) | 0.0019 (17) |
| C4 | 0.044 (2) | 0.039 (2) | 0.0303 (19) | −0.0057 (17) | −0.0043 (16) | 0.0081 (16) |
| C5 | 0.039 (2) | 0.034 (2) | 0.0302 (19) | −0.0014 (16) | −0.0038 (15) | 0.0019 (16) |
| C6 | 0.0320 (18) | 0.0278 (18) | 0.0273 (17) | −0.0025 (14) | −0.0013 (14) | 0.0015 (14) |
| C7 | 0.0318 (18) | 0.0318 (19) | 0.0278 (18) | 0.0009 (14) | 0.0008 (14) | −0.0029 (15) |
| C8 | 0.040 (2) | 0.076 (3) | 0.037 (2) | −0.014 (2) | −0.0036 (18) | 0.013 (2) |
| C9 | 0.036 (2) | 0.120 (5) | 0.050 (3) | −0.020 (3) | 0.002 (2) | 0.014 (3) |
| C10 | 0.040 (2) | 0.087 (4) | 0.050 (3) | −0.016 (2) | −0.008 (2) | 0.000 (3) |
| C11 | 0.035 (2) | 0.069 (3) | 0.034 (2) | 0.003 (2) | −0.0050 (16) | −0.002 (2) |
| C12 | 0.035 (2) | 0.053 (2) | 0.0278 (19) | 0.0036 (18) | −0.0007 (15) | −0.0005 (18) |
| C13 | 0.0323 (18) | 0.0295 (18) | 0.0278 (17) | 0.0017 (15) | 0.0017 (14) | 0.0004 (15) |
| C14 | 0.039 (2) | 0.044 (2) | 0.032 (2) | −0.0077 (17) | 0.0001 (16) | −0.0058 (17) |
| C15 | 0.045 (2) | 0.057 (3) | 0.050 (3) | −0.020 (2) | 0.009 (2) | −0.011 (2) |
| C16 | 0.045 (2) | 0.060 (3) | 0.047 (3) | −0.014 (2) | 0.012 (2) | −0.005 (2) |
| C17 | 0.039 (2) | 0.053 (3) | 0.037 (2) | 0.0026 (19) | 0.0093 (17) | 0.0039 (19) |
| C18 | 0.0352 (19) | 0.040 (2) | 0.0314 (19) | 0.0019 (16) | 0.0023 (15) | −0.0038 (17) |

Geometric parameters (Å, °)

| | | | |
|---|---|---|---|
| P1—C6 | 1.836 (4) | C10—C11 | 1.521 (7) |
| P1—C13 | 1.854 (4) | C10—H10A | 0.9900 |
| P1—C7 | 1.872 (4) | C10—H10B | 0.9900 |
| N1—C1 | 1.330 (5) | C11—C12 | 1.523 (5) |
| N1—N2 | 1.334 (4) | C11—H11A | 0.9900 |
| N2—N3 | 1.365 (4) | C11—H11B | 0.9900 |
| N3—C2 | 1.378 (5) | C12—H12A | 0.9900 |
| N3—C6 | 1.397 (5) | C12—H12B | 0.9900 |
| C1—C2 | 1.393 (6) | C13—C14 | 1.536 (5) |
| C1—H1 | 0.9500 | C13—C18 | 1.539 (5) |
| C2—C3 | 1.404 (5) | C13—H13 | 1.0000 |
| C3—C4 | 1.365 (6) | C14—C15 | 1.536 (6) |
| C3—H3 | 0.9500 | C14—H14A | 0.9900 |
| C4—C5 | 1.420 (5) | C14—H14B | 0.9900 |
| C4—H4 | 0.9500 | C15—C16 | 1.519 (6) |
| C5—C6 | 1.366 (5) | C15—H15A | 0.9900 |
| C5—H5 | 0.9500 | C15—H15B | 0.9900 |
| C7—C12 | 1.519 (5) | C16—C17 | 1.522 (6) |

| | | | |
|---|---|---|---|
| C7—C8 | 1.523 (6) | C16—H16A | 0.9900 |
| C7—H7 | 1.0000 | C16—H16B | 0.9900 |
| C8—C9 | 1.523 (6) | C17—C18 | 1.526 (6) |
| C8—H8A | 0.9900 | C17—H17A | 0.9900 |
| C8—H8B | 0.9900 | C17—H17B | 0.9900 |
| C9—C10 | 1.513 (7) | C18—H18A | 0.9900 |
| C9—H9A | 0.9900 | C18—H18B | 0.9900 |
| C9—H9B | 0.9900 | | |
| C6—P1—C13 | 103.54 (16) | H10A—C10—H10B | 108.1 |
| C6—P1—C7 | 98.54 (16) | C10—C11—C12 | 111.8 (4) |
| C13—P1—C7 | 103.81 (17) | C10—C11—H11A | 109.3 |
| C1—N1—N2 | 110.2 (3) | C12—C11—H11A | 109.3 |
| N1—N2—N3 | 106.0 (3) | C10—C11—H11B | 109.3 |
| N2—N3—C2 | 111.0 (3) | C12—C11—H11B | 109.3 |
| N2—N3—C6 | 124.6 (3) | H11A—C11—H11B | 107.9 |
| C2—N3—C6 | 124.4 (3) | C7—C12—C11 | 111.5 (3) |
| N1—C1—C2 | 109.7 (3) | C7—C12—H12A | 109.3 |
| N1—C1—H1 | 125.2 | C11—C12—H12A | 109.3 |
| C2—C1—H1 | 125.2 | C7—C12—H12B | 109.3 |

| | | | |
|---|---|---|---|
| N3—C2—C1 | 103.1 (3) | C11—C12—H12B | 109.3 |
| N3—C2—C3 | 119.1 (4) | H12A—C12—H12B | 108.0 |
| C1—C2—C3 | 137.7 (4) | C14—C13—C18 | 108.5 (3) |
| C4—C3—C2 | 118.3 (4) | C14—C13—P1 | 112.5 (3) |
| C4—C3—H3 | 120.9 | C18—C13—P1 | 110.5 (3) |
| C2—C3—H3 | 120.9 | C14—C13—H13 | 108.4 |
| C3—C4—C5 | 120.6 (4) | C18—C13—H13 | 108.4 |
| C3—C4—H4 | 119.7 | P1—C13—H13 | 108.4 |
| C5—C4—H4 | 119.7 | C15—C14—C13 | 110.7 (3) |
| C6—C5—C4 | 122.7 (4) | C15—C14—H14A | 109.5 |
| C6—C5—H5 | 118.7 | C13—C14—H14A | 109.5 |
| C4—C5—H5 | 118.7 | C15—C14—H14B | 109.5 |
| C5—C6—N3 | 114.9 (3) | C13—C14—H14B | 109.5 |
| C5—C6—P1 | 121.2 (3) | H14A—C14—H14B | 108.1 |
| N3—C6—P1 | 123.8 (3) | C16—C15—C14 | 111.9 (4) |
| C12—C7—C8 | 110.4 (3) | C16—C15—H15A | 109.2 |
| C12—C7—P1 | 112.8 (3) | C14—C15—H15A | 109.2 |
| C8—C7—P1 | 109.7 (3) | C16—C15—H15B | 109.2 |
| C12—C7—H7 | 107.9 | C14—C15—H15B | 109.2 |

| | | | |
|---|---|---|---|
| C8—C7—H7 | 107.9 | H15A—C15—H15B | 107.9 |
| P1—C7—H7 | 107.9 | C15—C16—C17 | 111.2 (4) |
| C9—C8—C7 | 111.3 (4) | C15—C16—H16A | 109.4 |
| C9—C8—H8A | 109.4 | C17—C16—H16A | 109.4 |
| C7—C8—H8A | 109.4 | C15—C16—H16B | 109.4 |
| C9—C8—H8B | 109.4 | C17—C16—H16B | 109.4 |
| C7—C8—H8B | 109.4 | H16A—C16—H16B | 108.0 |
| H8A—C8—H8B | 108.0 | C16—C17—C18 | 110.8 (4) |
| C10—C9—C8 | 111.9 (4) | C16—C17—H17A | 109.5 |
| C10—C9—H9A | 109.2 | C18—C17—H17A | 109.5 |
| C8—C9—H9A | 109.2 | C16—C17—H17B | 109.5 |
| C10—C9—H9B | 109.2 | C18—C17—H17B | 109.5 |
| C8—C9—H9B | 109.2 | H17A—C17—H17B | 108.1 |
| H9A—C9—H9B | 107.9 | C17—C18—C13 | 110.9 (3) |
| C9—C10—C11 | 110.6 (4) | C17—C18—H18A | 109.5 |
| C9—C10—H10A | 109.5 | C13—C18—H18A | 109.5 |
| C11—C10—H10A | 109.5 | C17—C18—H18B | 109.5 |
| C9—C10—H10B | 109.5 | C13—C18—H18B | 109.5 |
| C11—C10—H10B | 109.5 | H18A—C18—H18B | 108.0 |

| | | | |
|---|---|---|---|
| C1—N1—N2—N3 | 0.3 (4) | C6—P1—C7—C12 | 169.8 (3) |
| N1—N2—N3—C2 | −0.6 (4) | C13—P1—C7—C12 | 63.5 (3) |
| N1—N2—N3—C6 | 179.0 (3) | C6—P1—C7—C8 | −66.6 (3) |
| N2—N1—C1—C2 | 0.1 (4) | C13—P1—C7—C8 | −172.9 (3) |
| N2—N3—C2—C1 | 0.7 (4) | C12—C7—C8—C9 | −55.5 (5) |
| C6—N3—C2—C1 | −179.0 (3) | P1—C7—C8—C9 | 179.5 (4) |
| N2—N3—C2—C3 | −178.6 (3) | C7—C8—C9—C10 | 56.0 (7) |
| C6—N3—C2—C3 | 1.8 (5) | C8—C9—C10—C11 | −54.9 (7) |
| N1—C1—C2—N3 | −0.4 (4) | C9—C10—C11—C12 | 54.6 (6) |
| N1—C1—C2—C3 | 178.6 (4) | C8—C7—C12—C11 | 55.4 (5) |
| N3—C2—C3—C4 | 0.1 (5) | P1—C7—C12—C11 | 178.5 (3) |
| C1—C2—C3—C4 | −178.8 (4) | C10—C11—C12—C7 | −55.5 (5) |
| C2—C3—C4—C5 | −1.1 (6) | C6—P1—C13—C14 | 44.9 (3) |
| C3—C4—C5—C6 | 0.3 (6) | C7—P1—C13—C14 | 147.4 (3) |
| C4—C5—C6—N3 | 1.4 (5) | C6—P1—C13—C18 | 166.4 (3) |
| C4—C5—C6—P1 | −174.0 (3) | C7—P1—C13—C18 | −91.1 (3) |
| N2—N3—C6—C5 | 178.0 (3) | C18—C13—C14—C15 | 57.7 (4) |
| C2—N3—C6—C5 | −2.4 (5) | P1—C13—C14—C15 | −179.6 (3) |
| N2—N3—C6—P1 | −6.9 (5) | C13—C14—C15—C16 | −56.1 (5) |

| | | | |
|---|---|---|---|
| C2—N3—C6—P1 | 172.8 (3) | C14—C15—C16—C17 | 54.1 (6) |
| C13—P1—C6—C5 | −132.4 (3) | C15—C16—C17—C18 | −55.0 (5) |
| C7—P1—C6—C5 | 121.1 (3) | C16—C17—C18—C13 | 58.5 (4) |
| C13—P1—C6—N3 | 52.8 (3) | C14—C13—C18—C17 | −59.5 (4) |
| C7—P1—C6—N3 | −53.8 (3) | P1—C13—C18—C17 | 176.7 (3) |

All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.