Supplementary Material (ESI) for Chemical Communications

A Persistent *P,N*-heterocyclic Carbene

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SUPPORTING INFORMATION

Synthesis and Spectroscopic Data

All experiments were carried out under a dry argon atmosphere using standard Schlenk or dry box techniques. Solvents were dried by standard methods and distilled under argon. ^{1}H (300, 500, 600 MHz), ^{13}C-NMR (75, 125, 150 MHz), and ^{31}P-NMR (121, 161, 243 MHz) spectra were recorded on a Bruker (Billerica, MA) Avance 300 or 600, or Varian 500 MHz spectrometer, and referenced to the residual ^{1}H and ^{13}C signals of the solvents, or to H_3PO_4 as an internal standard. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, sept. = septet, m = multiplet, br = broad signal. Coupling constants *J* are given in Hz. Mass spectra were performed at the UC Riverside Mass Spectrometry Laboratory. Melting points were measured with a Büchi melting point apparatus system.

Synthesis of *N*-(2,4,6-trimethylphenyl)-*P*-(2,4,6-tri-*tert*-butylphenyl)-phosphaformamidine

n-BuLi (2.5 M solution in *n*-hexane, 7.9 mL, 19.8 mmol) was added at –78 ºC to a solution of (2,4,6-tri-*tert*-butylphenyl)phosphine (4.6 g, 16.52 mmol) in Et_2O (50 mL). After 1 h at low temperature, a diethyl ether solution (10 mL) of ethyl *N*-2,4,6-trimethylphenyl formimidate (3.1 g, 16.52 mmol) was added dropwise to the solution. The reaction mixture was stirred at -78 ºC for 3 h, and then at room temperature for an additional 16h. The volatiles were removed under vacuum and the residue was extracted twice with hexane (2 x 10 mL). Successive crystallization in distilled EtOH at –30 ºC afforded *N*-(2,4,6-trimethylphenyl)-*P*-(2,4,6-tri-*tert*-butylphenyl)phosphaformamidine as light yellow crystals (3.0 g, 43 %). δ_H(300 MHz, CD_3CN, 25°C) 1.32 (s, 9H, CCH_3), 1.60 (d, 18H, $^{5}J_{PH}$ = 0.9 Hz, CCH_3), 1.91 (s, 6H, Ar-CH_3), 2.12 (s, 3H, Ar-CH_3), 4.93 (d, 1H, $^{3}J_{HH}$ = 13.8 Hz, N*H*), 6.72 (s, 2H, CH_{aro}), 7.52 (d, 2H, $^{4}J_{PH}$ = 1.2 Hz, CH_{aro}), 7.50 (dd, 1H, $^{3}J_{HH}$ = 13.8 Hz, $^{2}J_{PH}$ = 44.7 Hz, NC*H*P); δ_C(75 MHz, CD_3CN, 25°C) 19.4 (*C*H_3), 20.9 (*C*H_3), 32.0 (C*C*H_3), 33.3 (d, $^{4}J_{PC}$ = 7.5Hz, C*C*H_3), 34.3 (*C*CH_3), 39.4 (*C*CH_3), 120.9 (*C*$_{aro}$), 123.5 (*C*H$_{aro}$), 124.9 (*C*$_{aro}$), 129.8 (d, $^{1}J_{PC}$ = 45.1Hz, *C*$_{aro}$), 131.1 (*C*H$_{aro}$), 134.1 (*C*$_{aro}$), 151.1 (*C*$_{aro}$), 157.2 (*C*$_{aro}$), 166.9 (d, $^{1}J_{PC}$ = 63.9Hz, N*C*HP); δ_P(121 MHz, CD_3CN, 25°C) 77.3. EI+/MS: m/z [M^+] Calcd for $C_{28}H_{41}NP^+$ 422.61, found 423.

Synthesis of compound 3a

1,3-dibromopropane (1.49 g, 7.36 mmol) was added at room temperature to an Et_2O (10 ml) solution of **1a** (0.78 g, 1.81 mmol), prepared in situ by addition of a stoichiometric amount of BuLi in hexanes to the phosphaformamidine synthesized as described above [δ_P(121 MHz, THF, 25°C) 53.0, 46.6]. The solution was stirred for 14 h and the solvent was removed under vacuum. After extraction with hexane, the volatiles were removed under vacuum to yield compound **2a** in 90% [δ_P(Et_2O, 25°C) -11.1 ppm (d, $^2J_{PH}$ = 47.5 Hz)]. A solution of **2a** in THF (10 ml) was heated at 40°C for 18 h. All volatiles were removed afterwards under vacuum. The residue was washed three times with hexane to afford the cyclic phosphino iminium salt **3a** as a white powder in 85% yield (0.84 g). δ_H(300 MHz, $CDCl_3$, 25°C) 1.31 (s, 9H, C(CH_3)$_3$), 1.60 (s, 18H, C(CH_3)$_3$), 2.21 (s, 6H, CH_3), 2.27 (s, 3H, CH_3), 2.72 (m, 2H, CH_2), 3.29 (t, 2H, ^3J = 6.8 Hz, CH_2), 4.29 (m, 2H, CH_2), 6.91 (s, 2H, CH_{aro}), 7.56 (d, 2H, $^4J_{PH}$ = 4.2 Hz, CH_{aro}), 8.32 (d, 1H, $^2J_{PH}$ = 6.9 Hz, NC*H*P); δ_C(75 MHz, $CDCl_3$, 25°C) 17.8 (s, *C*H_3), 18.7 (s, CH_2), 21.0 (s, *C*H_3), 24.5 (d, J_{PC} = 12.7 Hz, *C*H_2), 30.9 (s, C*C*H_3), 34.1 (s, C*C*H_3), 35.4 (s, *C*CH_3), 39.0 (d, J_{PC} = 3.6 Hz, *C*CH_3), 54.7 (d, J_{PC} = 2.6 Hz, *C*H_2), 114.2 (s, C_{aro}), 124.5 (d, J_{PC} = 11.4 Hz, *C*H_{aro}), 130.3 (s, *C*H_{aro}), 132.5 (d, J_{PC} = 10.1 Hz, C_{aro}), 140.5 (s, C_{aro}), 142.2 (d, J_{PC} = 3.9 Hz, C_{aro}), 155.6 (d, J_{PC} = 3.6 Hz, C_{aro}), 160.5 (d, J_{PC} = 12.0 Hz, C_{aro}), 178.4 (d, J_{PC} = 2.9 Hz, NCHP); δ_P(121 MHz, $CDCl_3$, 25°C) -5.3. FAB+/MS: m/z [M^+] Calcd for $C_{31}H_{47}NP^+$ 464.69, found 464.

Synthesis of compound 4a

To a mixture of iminium salt **3a** (0.350 g, 0.643 mmol) and lithium diisopropylamide (0.069 g, 0.643 mmol) was slowly added THF (10 ml) at -78°C. The reaction mixture was warmed to room temperature and stirred for 1 h. The solvent was removed under vacuum and the resulting residue was extracted with hexane (10 mL). Evaporation of hexane gave alkene **4a** as a white solid in 75% yield (0.224 g). δ_H(300 MHz, C_6D_6, 25°C) 1.20 (s, 9H, C(CH_3)$_3$), 1.51 (s, 18H, C(CH_3)$_3$), 1.98 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.90 (dd, 1H, $^2J_{PH}$ = 15.6 Hz, *J* = 1.8 Hz, PCH_2), 3.71 (d, 1H, *J* = 12.3 Hz, PCH_2), 4.35 (dtd, 1H, *J* = 15.3 Hz, *J* = 7.8 Hz, *J* = 2.4 Hz, NCH=C*H*), 5.87 (d, 1H, $^3J_{PH}$ = 8.4 Hz, NC*H*=CH), 6.62 (d, 2H, $^1J_{PH}$ = 15.0 Hz, NCH_2P), 7.09 (s, 2H, CH_{aro}), 7.38 (d, 2H, $^3J_{PH}$ = 2.4 Hz, CH_{aro}); δ_C(75 MHz, d^8-THF, 25°C) 18.4 (s, *C*H_3), 19.1 (s, *C*H_3), 21.1 (s, *C*H_3), 27.3

(d, J_{PC} = 28.3 Hz, PCH_2CH), 31.7 (s, CCH_3), 34.4 (d, J_{PC} = 8.3 Hz, CCH_3), 35.2 (s, CCH$_3$), 39.7 (s, CCH$_3$), 51.8 (d, J_{PC} = 20.8 Hz, NCH_2P), 89.4 (s, NCH=CH), 123.0 (s, CH$_{aro}$), 130.0 (d, J_{PC} = 14.6 Hz, CH$_{aro}$), 136.3 (d, J_{PC} = 8.2 Hz, NCH=CH), 136.5 (s, C_{aro}), 136.8 (s, C_{aro}), 136.9 (s, C_{aro}), 144.9 (s, C_{aro}), 148.8 (s, C_{aro}), 152.6 (d, J_{PC} = 6.2 Hz, C_{aro}); δ_P(121 MHz, C_6D_6, 25°C) -46.9.

Synthesis of compound 5a

THF (1.5 ml) was added slowly to the solid mixture of iminium salt **3a** (0.350 g, 0.643 mmol) and lithium hexamethyldisilylazide (0.107 g, 0.643 mmol) at -78 °C in a NMR tube. The reaction was monitored by VT-NMR. The cyclic azomethine ylide intermediate **5a** was observed at -60°C. ^{13}C NMR (THF, -60°C) δ = 17.7 (s, CH$_3$), 20.4 (d, $^1J_{PC}$ = 15.1 Hz, PCH_2), 21.2 (s, CH$_3$), 23.5 (s, PCH$_2$$CH_2$), 31.8 (s, C$CH_3$), 33.9 (s, C$CH_3$), 34.9 (s, CCH$_3$), 39.6 (s, CCH$_3$), 89.7 (d, $^1J_{PC}$ = 26.9 Hz, PCHN), 103.8 (s, NCHCH$_2$), 122.0 (s, CH$_{aro}$), 129.7 (d, $^3J_{PC}$ = 14.6 Hz, CH$_{aro}$), 132.6 (d, $^2J_{PC}$ = 29.1 Hz, C_{aro}), 136.5 (d, $^3J_{PC}$ = 20.8 Hz, C_{aro}), 137.8 (s, C_{aro}), 146.6 (d, $^4J_{PC}$ = 8.3 Hz, C_{aro}), 151.4 (d, $^1J_{PC}$ = 66.4 Hz, C_{aro}), 155.6 (s, C_{aro}); ^{31}P NMR (THF, -60°C) δ = -30.6 ppm. The reaction mixture was warmed to room temperature and stirred for 1 h. The solvent was removed under vacuum and the resulting residue was extracted with hexane (10 mL) affording alkene **4a**.

Synthesis of compound 3b

At room temperature, 1,3-dibromobutane (1.86 g, 8.60 mmol) was added to a solution of **1a** (1.00 g; 2.16 mmol) in 20 ml Et_2O. The solution was stirred for 14 h and the solvent was then removed under vacuum. The resulting residue was extracted with 15 mL hexane. Evaporation of hexane under vacuum afforded product **2b** as a light yellow oil in 80% yield (1.04 g). ^{31}P NMR (Et_2O, 25°C) δ = -10.8, -12.3 ppm. The THF (10 ml) solution of **2b** was heated at 70°C for 6 h. All volatiles were removed under vacuum and the residue was washed three times with hexane (10 mL). The cyclic phosphino iminium salt **3b** was obtained as a yellow powder in 60% overall yield (0.78 g). δ_H(300 MHz, $CDCl_3$, 25°C) 1.31 (s, 9H, C(CH_3)$_3$), 1.41 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CHCH_3), 1.59 (s, 18H, C(CH_3)$_3$), 2.18 (s, 3H, ArCH_3), 2.22 (s, 3H, ArCH_3), 2.28 (s, 3H, ArCH_3), 2.62 (m, 1H, CH_2), 2.86 (m, 1H, CH_2), 3.08 (m, 1H, CH_2), 3.51 (m, 1H, CH_2), 4.54 (m, 1H, NCHCH$_3$), 6.93 (s, 2H, C$H$$_{aro}$), 7.56 (d, 2H, $^4J_{PH}$ = 4.2 Hz, C$H$$_{aro}$), 8.28 (d, 1H, $^2J_{PH}$ = 6.0 Hz, NCHP); δ_C(75 MHz,

$CDCl_3$, 25°C) 15.7 (s, NCH*C*H_3), 18.4 (s, Ar*C*H_3), 18.8 (s, Ar*C*H_3), 21.2 (s, Ar*C*H_3), 23.9 (d, J_{PC} = 10.7 Hz, *C*H_2), 26.1 (s, CH_2), 31.2 (s, C*C*H_3), 34.4 (s, C*C*H_3), 35.6 (s, *C*CH_3), 39.2 (d, J_{PC} = 4.8 Hz, *C*CH_3), 60.8 (d, J_{PC} = 5.1 Hz, N*C*HCH_3), 114.5 (s, C_{aro}), 124.7 (d, J_{PC} = 12.0 Hz, *C*H_{aro}), 130.4 (s, *C*H_{aro}), 130.8 (s, *C*H_{aro}), 132.8 (s, C_{aro}), 133.4 (d, J_{PC} = 57.3 Hz, C_{aro}), 133.9 (s, C_{aro}), 140.7 (s, C_{aro}), 155.8 (s, C_{aro}), 160.7 (d, J_{PC} = 12.0 Hz, C_{aro}), 177.9 (d, J_{PC} = 3.1 Hz, N*C*HP); δ_P(121 MHz, $CDCl_3$, 25°C) -6.5. FAB+/MS: m/z [M^+] Calcd for $C_{32}H_{49}NP$ 478.36; found 478.

Synthesis of compound 4b

To a mixture of iminium salt **3b** (0.300 g, 0.537 mmol) and lithium diisopropylamide (0.058 g, 0.542 mmol) was slowly added THF (10 ml) at -78°C. The reaction mixture was warmed to room temperature and stirred for 1 h. The solvent was removed under vacuum and the resulting residue was extracted with hexane (10 mL). Evaporation of hexane gave alkene **4b** as a white solid in 65% yield (0.167 g). δ_C(125 MHz, THF, 25°C) 15.7 (s, NC*C*H_3), 16.2 (s, Ar*C*H_3), 19.2 (s, Ar*C*H_3), 19.3 (s, Ar*C*H_3), 28.4 (d, J_{PC} = 38.4 Hz, P*C*H_2), 29.7 (s, CH_3), 30.2 (s, *C*$(CH_3)_3$), 32.3 (s, CH_3), 32.4 (s, CH_3), 33.0 (s, *C*$(CH_3)_3$), 52.7 (d, J_{PC} = 30.8 Hz, P*C*H_2N), 88.1 (s, PCH_2*C*H), 120.9 (CH), 127.9 (s, *C*H_{Mes}), 134.5 (C^q), 135.4 (d, J_{PC} = 13.3 Hz, PC^q), 139.0 (s, C^q), 141.2 (s, C^q), 146.2 (s, C^q), 154.0 (s, C^q); δ_P(121 MHz, THF, 25°C) -45.7;

Synthesis of compound 2c

To a solution of **1c** (2.53 g, 5.4 mmol) in Et_2O (50 ml) was added 1,3-dibromobutane (4.63 g, 21.4 mmol) at room temperature. The solution was stirred for 14 h at room temperature, and then all volatiles were removed under vacuum. The resulting residue was extracted twice with hexane (10 mL). Removal of the volatiles under vacuum afforded compound **2c** as a yellow solid in 86% yield (2.77 g). Melting point: 101-103°C. δ_H(300 MHz, C_6D_6, 25°C) 1.23 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3)_2$), 1.25 (d, 6H, $^3J_{HH}$ = 6.8 Hz, CH(C*H*$_3)_2$), 1.30 (s, 9H, C(C*H*$_3)_3$), 1.38 (m, 2H), 1.58 (m, 3H), 1.67 (s, 18H, C(C*H*$_3)_3$), 1.83 (m, 2H), 3.40 (sept, 2H, $^3J_{HH}$ = 6.8 Hz, C*H*$(CH_3)_2$), 3.79 (br. m, 1H, C*H*Br), 7.14-7.34 (m, 3H), 7.62 (d, 2H, $^4J_{PH}$ = 2.2 Hz, C*H*$_{aro}$), 8.78 (d, 1H, $^2J_{PH}$ = 46.7 Hz, NC*H*P); δ_C(75 MHz, C_6D_6, 25°C) 24.8 (s, *C*H_3), 26.5 (s, *C*H), 28.4 (s, *C*H_3), 31.4 (s, *C*H_3), 32.1 (d, $^3J_{PC}$ = 13.5 Hz, *C*HBr), 34.6 (s, *C*H_3), 34.7 (s, *C*H_3), 35.4 (s, *C*$(CH_3)_3$), 35.6 (*C*H_2), 39.8 (s,

C(CH_3)$_3$), 40.6 (d, J_{PC} = 29.9 Hz, P*C*H$_2$), 123.9 (s, *C*H$_{aro}$), 124.1 (s, *C*H$_{aro}$), 125.0 (s, *C*H$_{aro}$), 127.6 (d, J_{PC} = 24.6 Hz, *C$_{aro}$*), 138.7 (d, J_{PC} = 4.2 Hz, *C*$_{aro}$), 151.6 (d, J_{PC} = 9.7 Hz, *C$_{aro}$*), 151.9 (s, *C$_{aro}$*), 160.0 (d, J_{PC} = 13.5 Hz, *C$_{aro}$*), 177.0 (d, J_{PC} = 18.9 Hz, N*C*HP); δ_P(121 MHz, C_6D_6, 25°C) -11.2, -12.4 (1:1). FAB-HRMS calcd for $C_{35}H_{56}NBrP$ $[M+H]^+$: *m/z* 600.3334; found 600.3331.

Synthesis of compound 3c

A solution of compound **2c** (2.77 g; 4.61 mmol) in THF (25ml) was heated at 50°C for 48 h. All volatiles were removed under high vacuum. The residue was washed three times with hexane and dried under vacuum to obtain the cyclic phosphino iminium salt **3c** as a light yellow powder in 89% yield (2.47 g). From a THF solution suitable single crystals for X-ray diffraction studies were obtained by slow evaporation of the solvent. Melting point: 133-135°C. δ_H(400 MHz, $CDCl_3$, 25°C) 1.03 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CHC*H*$_3$), 1.05 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CHC*H*$_3$), 1.21 (s, 9H, C(C*H*$_3$)$_3$), 1.25 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CHC*H*$_3$), 1.34 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CHC*H*$_3$), 1.52 (s, 18H, C(C*H*$_3$)$_3$), 2.50 (m, 1H, *J* = 6.9 Hz, C*H*), 2.62 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, C*H*CH$_3$), 2.80 (m, 1H, C*H*$_2$), 3.07 (m, 1H, *J* = 15.3 Hz, $^3J_{HH}$ = 6.5 Hz, C*H*$_2$), 3.42 (dt, 1H, *J* = 15.3 Hz, $^3J_{HH}$ = 6.5 Hz, C*H*$_2$), 4.18 (m, 1H, NC*H*CH$_3$), 7.14 (d, 2H, $^3J_{HH}$ = 7.8 Hz, C*H*$_{aro}$), 7.34 (t, 1H, $^3J_{HH}$ = 7.7 Hz, C*H*$_{aro}$), 7.49 (d, 2H, $^4J_{PH}$ = 4.2 Hz, C*H*$_{aro}$), 8.20 (d, 1H, $^2J_{PH}$ = 5.4 Hz, NC*H*P); δ_C(100 MHz, $CDCl_3$, 25°C) 14.8 (s, NCH*C*H$_3$), 23.0 (d, J_{PC} = 6.0 Hz, *C*H$_2$), 23.2 (s, CH*C*H$_3$), 23.9 (s, CH*C*H$_3$), 24.5 (s, CH*C*H$_3$), 25.4 (s, CH*C*H$_3$), 25.5 (s, *C*H$_2$), 28.7 (s, *C*HCH$_3$), 30.4 (s, C*C*H$_3$), 33.7 (s, C*C*H$_3$), 34.9 (s, *C*CH$_3$), 38.5 (s, *C*CH$_3$), 61.0 (d, J_{PC} = 4.8 Hz, N*C*HCH$_3$), 113.0 (s, *C$_{aro}$*), 123.9 (d, J_{PC} = 9.5 Hz, *C*H$_{aro}$), 125.0 (s, *C*H$_{aro}$), 125.2 (s, *C*H$_{aro}$), 130.7 (s, *C*H$_{aro}$), 138.9 (s, *C$_{aro}$*), 143.9 (d, J_{PC} = 9.5 Hz, *C$_{aro}$*), 144.1 (d, J_{PC} = 9.5 Hz, *C$_{aro}$*), 155.6 (s, *C*$_{aro}$), 159.8 (d, J_{PC} = 9.5 Hz, *C$_{aro}$*), 176.0 (s, N*C*HP); δ_P(121 MHz, $CDCl_3$, 25°C) -3.8. FAB-HRMS calcd for $C_{35}H_{55}NP$ $[M]^+$: *m/z* 520.4072; found 520.4078.

Synthesis of compound 3c'

A THF (40 ml) solution of **1c** (3.02 g, 6.40 mmol) was added to a THF (15 ml) solution of 1,3-dibromobutane (4.45 g, 20.6 mmol) at room temperature. The solution was stirred at room temperature for 14 h. The solvent was removed under vacuum, and the resulting residue was extracted with hexane (10 mL). The resulting solid was disolved in THF (40

ml) and heated to 70°C for 72 h. Afterwards all volatiles were removed under vacuum at room temperature. The residue was washed three times with hexane (5 mL) to obtain the cyclic phosphino iminium salts **3c** and **3c′** as a 40/60 mixture in 63% yield (2.42 g)**.** Suitable single crystals for X-ray diffraction studies were obtained from iminium salt **3c′** from a THF/hexane solution at -30°C. δ_H(300 MHz, CD_3CN, 25°C) 1.19 (d, 6H, $^3J_{HH}$ = 6.7 Hz, CHC*H*$_3$), 1.27 (d, 6H, $^3J_{HH}$ = 6.2 Hz, CHC*H*$_3$), 1.30 (s, 9H, C(C*H*$_3$)$_3$), 1.58 (s, 18H, C(C*H*$_3$)$_3$), 2.43 (m, 2H, C*H*$_2$), 2.72 (sept, 1H, $^3J_{HH}$ = 6.7 Hz, C*H*CH$_3$), 2.80 (sept, 1H, $^3J_{HH}$ = 6.7 Hz, C*H*CH$_3$), 3.14 (m, 1H, *J* = 17.1 Hz, J_{HH} = 6.5 Hz, PC*H*), 3.89 (m, 1H, NC*H*$_2$), 4.29 (m, 1H, NC*H*$_2$), 7.34 (d, 2H, $^3J_{HH}$ = 7.5 Hz, C*H*$_{aro}$), 7.48 (t, 1H, $^3J_{HH}$ = 7.5 Hz, C*H*$_{aro}$), 7.64 (d, 2H, $^4J_{PH}$ = 3.9 Hz, C*H*$_{aro}$), 9.64 (d, 1H, $^2J_{PH}$ = 9.3 Hz, NC*H*P); δ_C(75 MHz, $CDCl_3$, 25°C) 18.8 (d, J_{PC} = 18.4 Hz, PCH*C*H$_3$), 24.8 (s, CH*C*H$_3$), 26.2 (s, CH*C*H$_3$), 28.9 (s, *C*HCH$_3$), 29.0 (s, *C*HCH$_3$), 30.9 (s, C*C*H$_3$), 34.1 (s, C*C*H$_3$), 35.5 (s, *C*CH$_3$), 38.9 (s, *C*CH$_3$), 43.2 (s, *C*H$_2$), 48.7 (s, P*C*H), 56.5 (s, NCH$_2$), 113.5 (s, *C*$_{aro}$), 124.0 (d, J_{PC} = 27.2 Hz, *C*H$_{aro}$), 125.6 (s, *C*H$_{aro}$), 131.2 (s, *C*H$_{aro}$), 139.4 (s, *C*$_{aro}$), 141.4 (s, *C*$_{aro}$), 143.2 (d, J_{PC} = 8.2 Hz, *C*$_{aro}$), 143.9 (d, J_{PC} = 8.2 Hz, *C*$_{aro}$), 155.8 (s, *C*$_{aro}$), 181.7 (d, J_{PC} = 19.2 Hz, NCHP); δ_P(121 MHz, CD_3CN, 25°C) 8.6. FAB-HRMS calcd for $C_{35}H_{55}NP$ $[M]^+$: *m/z* 520.4072; found 520.4069.

Synthesis of compound 4c

Diethyl ether (5 ml) was added slowly to a mixture of **3c** (220 mg, 0.366 mmol) and LiTMP (54 mg, 0.367 mmol) at -78 °C. The reaction mixture was stirred at low temperature for 1 h and afterwards at room temperature for 30 min. The volatiles were removed under vacuum, and the resulting residue was extracted with hexane (6 mL). After evaporation of the solvents, product **4c** was obtained as a light yellow powder in 76% yield (145 mg). δ_H(300 MHz, $CDCl_3$, 25°C) 1.16 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CHC*H*$_3$), 1.23 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CHC*H*$_3$), 1.27 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CHC*H*$_3$), 1.29 (d, 3H, $^3J_{HH}$ = 6.7 Hz, CHC*H*$_3$), 1.33 (s, 9H, C(C*H*$_3$)$_3$), 1.50 (m, 3H, NCC*H*$_3$), 1.56 (s, 18H, C(C*H*$_3$)$_3$), 2.82 (br, 1H, C*H*$_2$P), 3.02 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, C*H*CH$_3$), 3.34 (m, 1H, C*H*$_2$), 3.52 (m, 1H, C*H*$_2$), 3.55 (sept, 2H, $^3J_{HH}$ = 6.9 Hz, C*H*CH$_3$), 4.32 (br. m, 1H, C*H*), 7.14 (d, 1H, J_{PH} = 7.5 Hz, C*H*$_{aro}$), 7.19 (d, 1H, J_{PH} = 7.5 Hz, C*H*$_{aro}$), 7.31-7.27 (m, 3H, C*H*$_{aro}$); δ_C(75 MHz, $CDCl_3$, 25°C) 22.1 (s, NC*C*H$_3$), 23.9 (s, CH*C*H$_3$), 24.6 (s, CH*C*H$_3$), 25.5 (s, CH*C*H$_3$), 25.9 (s, CH*C*H$_3$), 27.9 (s, *C*HCH$_3$), 28.5 (d, J_{PC} = 21.8 Hz, P*C*H$_2$), 31.5 (s, C*C*H$_3$), 34.1 (d, J_{PC}

= 8.4 Hz, C*C*H$_3$), 34.7 (s, *C*CH$_3$), 39.3 (s, *C*CH$_3$), 54.3 (d, J_{PC} = 17.8 Hz, NCH$_2$P), 87.2 (d, J_{PC} = 3.8 Hz, *C*HCH$_2$), 122.2 (s, *C*H$_{aro}$), 124.1 (s, *C*H$_{aro}$), 124.3 (s, *C*H$_{aro}$), 127.8 (s, *C*H$_{aro}$), 136.6 (d, J_{PC} = 52.0 Hz, C_{aro}), 142.0 (d, $^4J_{PC}$ = 7.6 Hz, C_{aro}), 142.5 (d, J_{PC} = 6.0 Hz, NCCH), 148.2 (s, C_{aro}), 148.6 (s, C_{aro}), 156.0 (d, J_{PC} = 6.9Hz, C_{aro}); δ_P(121 MHz, $CDCl_3$, 25°C) -48.3.

Synthesis of compound 6c

A solution of salt **3c** (600 mg, 1.02 mmol) in diethyl ether (5 mL) was cooled to -78 °C. A solution of LDA (107 mg, 1.00 mmol) in 4 mL diethyl ether was slowly added at -78 °C. Immediately after addition, the reaction mixture was warmed to -30 °C and kept for an additional 30 min at this temperature. During this time the colour changed from colourless to red. The reaction mixture was warmed to room temperature and the colour faded to yellowish. The solvent was removed in vacuum and the residue was extracted twice with *n*-hexane (6 mL). Evaporation of the volatiles afforded **6c** as light yellow crystals in 84% (435 mg) yield, as a 70/30 mixture of diastereomers. Single crystals suitable for X-ray diffraction studies were obtained by slow evaporation of a *n*-hexane solution of the major isomer. Minor isomer is given in brackets. δ_C(75 MHz, C_6D_6, 25°C) [20.5 (CH*C*H$_3$)], 20.8 (CH*C*H$_3$), [24.5 (CH(*C*H$_3$)$_2$)], 25.1 (CH(*C*H$_3$)$_2$), 25.6 (d, J_{PC} = 28.2 Hz, *C*HP), [25.8 (d, J_{PC} = 30.0 Hz, *C*HP)], 27.9 (*C*H(CH$_3$)$_2$), 28.0 (CH(*C*H$_3$)$_2$), [28.4 (*C*H(CH$_3$)$_2$)], [28.6 (*C*H(CH$_3$)$_2$)], 28.8 (*C*H(CH$_3$)$_2$), 29.3 (*C*H(CH$_3$)$_2$), 29.5 (*C*H(CH$_3$)$_2$), 31.8 (*C*H$_3$), [32.2 (*C*H$_3$)], 34.2 (d, J_{PC} = 7.6 Hz, *C*H$_3$), 34.6 (d, J_{PC} = 7.6 Hz, *C*H$_3$), [37.6 (*C*H$_2$)], 37.8 (*C*H$_2$), 39.9 (d, J_{PC} = 23.3 Hz, C_q), [39.9 (d, J_{PC} = 23.0 Hz, C_q)], 39.9 (C_q), [56.4 (NCH)], 56.5 (NCH), [65.5 (d, J_{PC} = 36.2 Hz, PCHN)], 67.0 (d, J_{PC} = 43.3 Hz, PCHN), [122.7 (d, J_{PC} = 116.0 Hz, *C*H$_{aro}$)], 122.5 (d, J_{PC} = 95.7 Hz, *C*H$_{aro}$), 124.6 (d, J_{PC} = 22.7 Hz, *C*H$_{aro}$), [124.9 (d, J_{PC} = 27.7 Hz, *C*H$_{aro}$)], 127.8 (*C*H$_{aro}$), [128.1 (*C*H$_{aro}$)], 138.7 (C_q), [140.1 (C_q)], 148.4 (C_q), [148.5 (C_q)], 150.0 (d, J_{PC} = 12.5 Hz, C_q), 151.9 (C_q), 156.5 (d, J_{PC} = 21.0 Hz, C_q); δ_P(121 MHz, C_6D_6, 25°C) -151.4, -175.6 (30/70 ratio). FAB-HRMS calcd for $C_{35}H_{55}NP$ $[M+H]^+$: *m/z* 520.4072; found 520.4073.

Synthesis of compounds 7c and 8c

LDA (7.5 mg, 0.07 mmol) and compound **3c** (42 mg, 0.07 mmol) were mixed as solids in a NMR tube. The tube was placed at -80 °C and d_{10}-diethyl ether (0.4 mL) was added.

The mixture was kept for 2 min at this temperature, and warmed to room temperature. The yield of the free carbene **7c** was >90% according to ^{31}P-NMR. δ_H(600 MHz, d_{10}-Et_2O, -35°C) 1.06 (s, 9H, C(CH_3)$_3$), 1.12 (d, 3H, $^3J_{HH}$ = 7.2 Hz, CHCH_3), 1.16 (d, 3H, $^3J_{HH}$ = 7.2 Hz, CHCH_3), 1.21-1.24 (m, 3H), 1.26 (d, 3H, $^3J_{HH}$ = 6.8 Hz, CHCH_3), 1.28-1.36 (7H, m), 1.65 (s, 18H, C(CH_3)$_3$), 3.05 (sept, 1H, $^3J_{HH}$ = 6.8 Hz, CHCH$_3$), 3.16 (sept, 1H, $^3J_{HH}$ = 6.8 Hz, CHCH$_3$), 3.34 (m, 1H, CH), 7.04-7.18 (m, 3H, CH_{aro}), 7.52 (d, 2H, J_{PH} = 3.2 Hz, CH_{aro}); δ_C(150 MHz, d_{10}-Et_2O, -35°C) 14.5 (s, NCHCH_3), 22.1 (d, J_{PC} = 29.9 Hz, CH_2), 23.6 (CHCH_3), 25.9 (CHCH_3), 26.4 (CHCH_3), 27.2 (CH_2), 29.3 (d, J_{PC} = 14.3 Hz, CH_3), 31.6 ($CHCH_3$), 34.2 (CCH_3), 35.6 (CCH_3), 39.7 (CCH_3), 59.2 (d, J_{PC} = 32.3 Hz, N$CHCH_3$), 124.4 (CH_{aro}), 124.7 (CH_{aro}), 127.7 (CH_{aro}), 130.7 (C_{aro}), 144.0 (C_{aro}), 146.0 (C_{aro}), 148.5 (d, J_{PC} = 15.2 Hz, C_{aro}), 151.1 (C_{aro}), 313.6 (d, J_{PC} = 122.7 Hz, NCP); δ_P(161 MHz, d_{10}-Et_2O, 25°C) -32.8. All volatile compounds were removed under vacuum. The solid was dissolved in hexane, and after 2 days at -30 °C, compound **8c** was obtained as single crystals suitable for an X-ray diffraction study. δ_P(121 MHz, C_6D_6, 25°C) -68.4. FAB-HRMS calcd for $C_{35}H_{55}NP$ $[M+H]^+$: *m/z* 520.4072; found 520.4070.

Crystal Structure Determination of compounds 3c, 3c', 6c, 8c :

The Bruker X8-APEX (**ref. 1**) X-ray diffraction instrument with Mo-radiation was used for data collection**.** All data frames were collected at low temperatures (T = 100 K) using an ω, φ-scan mode (0.5° ω-scan width, hemisphere of reflections) and integrated using a Bruker SAINTPLUS software package (**ref. 2**). The intensity data were corrected for Lorentzian polarization. Absorption corrections were performed using the SADABS program (**ref. 3**). The SIR97 (**ref. 4**) was used for direct methods of phase determination, and Bruker SHELXTL software package (**ref. 5**) for structure refinement and difference Fourier maps. Atomic coordinates, isotropic and anisotropic displacement parameters of all the non-hydrogen atoms of two compounds were refined by means of a full matrix least-squares procedure on F^2. All H-atoms were included in the refinement in calculated positions riding on the C atoms. Drawings of molecules were performed using Ortep 3 (**ref. 6**).

Crystal and structure parameters of 3c **:** size 0.20 x 0.18 x 0.13 mm^3, monoclinic, space group P 2(1)/n, **a** = 13.146(3) Å, **b** = 17.956(3) Å, **c** = 17.575(3) Å, α = 90.0° **,** β = 95.959(3)° , γ = 90.0°, V = 4126.0(14) $Å^3$, ρ_{calcd} = 1.319 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K , reflections collected = 23150, independent reflections = 5896 (R_{int} = 0.0639), absorption coefficient μ = 1.319 mm^{-1}; max/min transmission = 0.8169 and 0.4459, 485 parameters were refined and converged at R1 = 0.0607, wR2 = 0.1521 R1 = 0.0607, wR2 = 0.1521, with intensity I>2σ(I), the final difference map was 0.859 and -0.449 e.$Å^{-3}$.

Crystal and structure parameters of 3c' **:** size 0.17 x 0.12 x 0.03 mm^3, triclinic, space group P -1, **a** = 10.9613(13) Å, **b** = 14.7848(18) Å, **c** = 16.2547(19) Å, α = 99.990(2)°, β = 108.109(2)°, γ = 97.624(2)°, V = 2416.3(5) $Å^3$, ρ_{calcd} = 1.748 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 14058, independent reflections = 6875 (R_{int} = 0.0617), absorption coefficient μ = 1.748 mm^{-1}; max/min transmission = 0.9884 and 0.9810, 555 parameters were refined and converged at R1 = 0.0554, wR2 = 0.1185, with intensity I>2σ(I), the final difference map was 0.381 and -0.335 e.$Å^{-3}$.

Crystal and structure parameters of 6c **:** size 0.10 x 0.08 x 0.06 mm^3, triclinic, space group P 2(1)/c, **a** = 11.330(13) Å, **b** = 17.35(2) Å, **c** = 15.903(19) Å, α = 90.0° , β = 93.133(16)° , γ = 90.0°, V = 3122(6) $Å^3$, ρ_{calcd} = 1.106 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 14462, independent reflections = 3467 (R_{int} = 0.2413), absorption coefficient μ = 0.111 mm^{-1}; max/min transmission = 0.9934 and 0.9890, 349 parameters were

refined and converged at R1 = 0.0844, wR2 = 0.1635, with intensity I>2σ(I), the final difference map was 0.336 and -0.261 e.Å^{-3}.

Crystal and structure parameters of 8c **:** size 0.32 x 0.13 x 0.11 mm^3, triclinic, space group P 2(1)/c, **a** = 17.676(3) Å, **b** = 17.298(3) Å, **c** = 15.2989(196 Å, α = 90.0°, β = 91.407(2)° , γ = 90.0°, V = 3148.1(9) Å^3, ρ_{calcd} = 1.097 g/cm^3, Mo-radiation (λ = 0.71073 Å), T = 100(2) K, reflections collected = 19438, independent reflections = 348 (R_{int} = 0.0488), absorption coefficient μ = 0.110 mm^{-1}; max/min transmission = 0.9880 and 0.9656, 348 parameters were refined and converged at R1 = 0.0501, wR2 = 0.1207, with intensity I>2σ(I), the final difference map was 0.653 and -0.354 e.Å^{-3}.

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Table S1. Crystal data and structure refinement for 3c.

Empirical formula	$C_{37}H_{59}BrCl_4NP$	
Formula weight	770.53	
Temperature	160(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.146(3) Å	α= 90°
	b = 17.956(3) Å	β= 95.959(3)°
	c = 17.575(3) Å	γ = 90°
Volume	4126.0(14) $Å^3$	
Z	4	
Density (calculated)	1.240 Mg/m^3	
Absorption coefficient	1.319 mm^{-1}	
F(000)	1624	
Crystal size	0.20 x 0.18 x 0.13 mm^3	
Theta range for data collection	1.63 to 23.26°	
Index ranges	-14<=h<=14, -19<=k<=19, -15<=l<=19	
Reflections collected	23150	
Independent reflections	5896 [R(int) = 0.0639]	
Completeness to theta = 23.26°	99.4 %	
Absorption correction	Sadabs	
Max. and min. transmission	0.8483 and 0.7802	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5896 / 49 / 485	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0607, wR2 = 0.1521	
R indices (all data)	R1 = 0.0773, wR2 = 0.1607	
Extinction coefficient	0.0015(4)	
Largest diff. peak and hole	0.859 and -0.449 $e.Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 3c. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	8436(1)	8635(1)	1622(1)	52(1)
P(1)	7559(1)	5556(1)	1894(1)	42(1)
N(1)	6691(3)	6102(2)	3092(2)	38(1)
C(1)	6979(3)	5505(2)	2752(3)	35(1)
C(2A)	6972(7)	6831(4)	2743(6)	37(3)
C(17A)	6717(6)	7494(4)	3230(5)	56(2)
C(2B)	7112(11)	6881(5)	3058(12)	37(7)
C(17B)	6362(13)	7237(10)	2441(12)	67(6)
C(3)	8148(4)	6838(3)	2706(3)	55(1)
C(4)	8405(4)	6370(3)	2038(3)	51(1)
C(5)	8260(3)	4723(2)	1652(3)	39(1)
C(6)	7846(3)	4379(3)	963(3)	41(1)
C(7)	8495(3)	3982(3)	542(3)	44(1)
C(8)	9524(4)	3897(3)	760(3)	44(1)
C(9)	9882(3)	4163(3)	1471(3)	44(1)
C(10)	9284(3)	4552(2)	1949(3)	38(1)
C(11)	5961(3)	6043(2)	3662(3)	39(1)
C(12)	6324(4)	6042(2)	4432(3)	43(1)
C(13)	5611(4)	5989(3)	4959(3)	53(1)
C(14)	4585(4)	5929(3)	4728(4)	56(1)
C(15)	4244(4)	5926(3)	3963(3)	53(1)
C(16)	4919(3)	5984(2)	3405(3)	45(1)
C(18)	6702(3)	4406(3)	634(3)	51(1)
C(19)	5964(4)	4369(3)	1249(3)	61(2)
C(20)	6418(5)	3728(4)	116(5)	98(3)
C(21)	6507(4)	5096(4)	132(3)	67(2)
C(22)	10252(4)	3515(3)	257(3)	53(1)
C(23)	9700(6)	3222(5)	-492(5)	104(3)
C(24)	10728(6)	2844(4)	663(5)	104(3)
C(25)	11048(5)	4066(4)	65(4)	86(2)

	x	y	z	U(eq)
C(26)	9799(3)	4668(3)	2770(3)	48(1)
C(27)	9127(4)	4985(3)	3351(3)	56(1)
C(28)	10110(4)	3889(3)	3091(3)	62(2)
C(29)	10751(4)	5157(3)	2763(4)	66(2)
C(30)	7459(4)	6085(3)	4706(3)	48(1)
C(31)	7708(5)	6713(3)	5280(4)	72(2)
C(32)	7833(4)	5330(3)	5042(3)	62(2)
C(33)	4521(4)	5975(3)	2574(3)	60(2)
C(34)	3804(6)	6636(5)	2368(4)	112(3)
C(35)	4002(5)	5236(5)	2351(5)	103(3)

	x	y	z	U(eq)
C(10A)	6548(11)	8035(11)	121(18)	138(13)
Cl(1A)	5592(9)	8592(6)	-316(7)	142(4)
Cl(2A)	6096(9)	7261(5)	537(4)	137(4)
C(10B)	6551(9)	8109(8)	29(15)	56(7)
Cl(1B)	5475(7)	8632(6)	-248(5)	68(2)
Cl(2B)	6325(9)	7184(5)	155(6)	129(4)
C(10C)	951(6)	8121(5)	2575(8)	87(3)
Cl(3A)	911(3)	7243(3)	2920(4)	163(2)
Cl(4A)	2099(2)	8429(2)	2358(2)	113(1)
C(10D)	732(12)	7851(15)	3020(14)	88(7)
Cl(3B)	1041(8)	7316(6)	2261(8)	161(4)
Cl(4B)	1666(9)	8431(5)	3393(8)	218(8)

Table S3. Bond lengths [Å] and angles [°] for 3c .

P(1)-C(1)	1.761(5)	P(1)-C(5)	1.829(4)
P(1)-C(4)	1.838(5)	N(1)-C(1)	1.302(6)
N(1)-C(11)	1.461(6)	N(1)-C(2A)	1.508(7)
N(1)-C(2B)	1.509(8)	C(2A)-C(17A)	1.524(10)
C(2A)-C(3)	1.555(9)	C(2B)-C(17B)	1.528(15)
C(2B)-C(3)	1.555(14)	C(3)-C(4)	1.511(8)
C(5)-C(6)	1.418(7)	C(5)-C(10)	1.427(6)
C(6)-C(7)	1.384(7)	C(6)-C(18)	1.554(6)
C(7)-C(8)	1.375(6)	C(8)-C(9)	1.375(7)
C(8)-C(22)	1.531(7)	C(9)-C(10)	1.395(7)
C(10)-C(26)	1.542(7)	C(11)-C(12)	1.388(7)
C(11)-C(16)	1.400(6)	C(12)-C(13)	1.389(7)
C(12)-C(30)	1.521(7)	C(13)-C(14)	1.372(8)
C(14)-C(15)	1.372(8)	C(15)-C(16)	1.392(7)
C(16)-C(33)	1.500(8)	C(18)-C(19)	1.526(7)
C(18)-C(21)	1.527(8)	C(18)-C(20)	1.543(8)
C(22)-C(25)	1.504(7)	C(22)-C(24)	1.504(8)
C(22)-C(23)	1.529(10)	C(26)-C(27)	1.529(7)
C(26)-C(29)	1.529(7)	C(26)-C(28)	1.549(7)
C(30)-C(31)	1.525(8)	C(30)-C(32)	1.538(7)
C(33)-C(35)	1.523(8)	C(33)-C(34)	1.536(8)
C(10A)-Cl(2A)	1.705(10)	C(10A)-Cl(1A)	1.723(9)
C(10B)-Cl(2B)	1.706(10)	C(10B)-Cl(1B)	1.725(8)
C(10C)-Cl(4A)	1.688(8)	C(10C)-Cl(3A)	1.693(7)
C(10D)-Cl(4B)	1.690(11)	C(10D)-Cl(3B)	1.726(10)

C(1)-P(1)-C(5)	115.5(2)	C(1)-P(1)-C(4)	103.4(2)
C(5)-P(1)-C(4)	111.7(2)	C(1)-N(1)-C(11)	119.9(4)
C(1)-N(1)-C(2A)	115.6(5)	C(11)-N(1)-C(2A)	123.2(4)
C(1)-N(1)-C(2B)	128.3(7)	C(11)-N(1)-C(2B)	111.3(7)
N(1)-C(1)-P(1)	121.5(3)	N(1)-C(2A)-C(17A)	111.9(7)
N(1)-C(2A)-C(3)	108.1(5)	C(17A)-C(2A)-C(3)	107.2(6)
N(1)-C(2B)-C(17B)	101.7(12)	N(1)-C(2B)-C(3)	108.1(8)

C(17B)-C(2B)-C(3)	105.4(13)	C(4)-C(3)-C(2A)	109.3(5)
C(4)-C(3)-C(2B)	127.8(7)	C(3)-C(4)-P(1)	111.6(3)
C(6)-C(5)-C(10)	118.9(4)	C(6)-C(5)-P(1)	113.4(3)
C(10)-C(5)-P(1)	124.8(4)	C(7)-C(6)-C(5)	118.5(4)
C(7)-C(6)-C(18)	116.4(4)	C(5)-C(6)-C(18)	125.1(4)
C(8)-C(7)-C(6)	123.4(5)	C(9)-C(8)-C(7)	116.7(4)
C(9)-C(8)-C(22)	120.3(5)	C(7)-C(8)-C(22)	123.0(5)
C(8)-C(9)-C(10)	124.0(4)	C(9)-C(10)-C(5)	117.2(4)
C(9)-C(10)-C(26)	114.3(4)	C(5)-C(10)-C(26)	128.2(4)
C(12)-C(11)-C(16)	122.7(4)	C(12)-C(11)-N(1)	118.9(4)
C(16)-C(11)-N(1)	118.3(4)	C(11)-C(12)-C(13)	117.6(5)
C(11)-C(12)-C(30)	122.5(4)	C(13)-C(12)-C(30)	120.0(5)
C(14)-C(13)-C(12)	121.3(5)	C(13)-C(14)-C(15)	120.1(5)
C(14)-C(15)-C(16)	121.5(5)	C(15)-C(16)-C(11)	116.9(5)
C(15)-C(16)-C(33)	120.1(5)	C(11)-C(16)-C(33)	123.1(4)
C(19)-C(18)-C(21)	111.4(4)	C(19)-C(18)-C(20)	104.5(5)
C(21)-C(18)-C(20)	106.5(6)	C(19)-C(18)-C(6)	113.4(4)
C(21)-C(18)-C(6)	109.7(4)	C(20)-C(18)-C(6)	111.1(4)
C(25)-C(22)-C(24)	111.7(5)	C(25)-C(22)-C(23)	108.2(6)
C(24)-C(22)-C(23)	105.6(6)	C(25)-C(22)-C(8)	109.1(4)
C(24)-C(22)-C(8)	109.8(5)	C(23)-C(22)-C(8)	112.5(5)
C(27)-C(26)-C(29)	108.8(4)	C(27)-C(26)-C(10)	116.6(4)
C(29)-C(26)-C(10)	110.5(4)	C(27)-C(26)-C(28)	104.0(5)
C(29)-C(26)-C(28)	109.6(4)	C(10)-C(26)-C(28)	107.0(4)
C(12)-C(30)-C(31)	112.5(4)	C(12)-C(30)-C(32)	110.0(4)
C(31)-C(30)-C(32)	111.1(5)	C(16)-C(33)-C(35)	111.2(6)
C(16)-C(33)-C(34)	111.4(5)	C(35)-C(33)-C(34)	111.4(6)

Cl(2A)-C(10A)-Cl(1A)	113.2(8)	Cl(2B)-C(10B)-Cl(1B)	114.7(8)
Cl(4A)-C(10C)-Cl(3A)	116.6(5)	Cl(4B)-C(10D)-Cl(3B)	115.1(9)

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 3c. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	64(1)	44(1)	48(1)	4(1)	5(1)	3(1)
P(1)	38(1)	41(1)	48(1)	5(1)	6(1)	6(1)
N(1)	36(2)	30(2)	49(2)	-1(2)	6(2)	3(2)
C(1)	31(2)	31(2)	42(3)	4(2)	0(2)	5(2)
C(2A)	49(6)	28(5)	34(6)	-2(4)	0(4)	3(4)
C(17A)	71(5)	42(5)	57(5)	-2(4)	18(4)	4(4)
C(2B)	28(9)	25(10)	57(18)	-12(8)	-4(10)	-1(7)
C(17B)	55(11)	46(10)	102(17)	18(11)	28(11)	15(9)
C(3)	50(3)	34(3)	81(4)	4(3)	15(3)	-1(2)
C(4)	48(3)	43(3)	64(4)	10(3)	11(3)	0(2)
C(5)	33(2)	35(2)	51(3)	6(2)	9(2)	3(2)
C(6)	31(2)	42(3)	50(3)	7(2)	8(2)	2(2)
C(7)	38(3)	46(3)	49(3)	3(2)	9(2)	0(2)
C(8)	43(3)	32(2)	58(4)	1(2)	18(2)	0(2)
C(9)	29(2)	37(3)	67(4)	10(3)	7(2)	3(2)
C(10)	30(2)	32(2)	53(3)	6(2)	3(2)	1(2)
C(11)	41(3)	28(2)	49(3)	-2(2)	10(2)	3(2)
C(12)	49(3)	30(2)	50(3)	7(2)	6(2)	7(2)
C(13)	71(4)	37(3)	52(3)	5(2)	13(3)	-1(2)
C(14)	59(4)	38(3)	75(4)	-1(3)	29(3)	-2(2)
C(15)	42(3)	42(3)	75(4)	-11(3)	10(3)	1(2)
C(16)	40(3)	34(3)	61(3)	-7(2)	12(2)	2(2)
C(18)	31(2)	62(3)	58(3)	-4(3)	2(2)	1(2)
C(19)	37(3)	85(4)	58(4)	8(3)	-4(3)	-9(3)
C(20)	51(4)	117(6)	123(7)	-60(5)	-7(4)	-4(4)
C(21)	43(3)	102(5)	55(4)	25(3)	-3(3)	5(3)
C(22)	50(3)	38(3)	75(4)	2(3)	30(3)	1(2)
C(23)	85(5)	119(6)	114(7)	-47(5)	45(5)	-11(4)
C(24)	124(6)	61(4)	141(7)	10(4)	75(6)	36(4)
C(25)	83(5)	70(4)	115(6)	-9(4)	66(4)	-6(3)

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(26)	36(3)	46(3)	61(3)	1(2)	-6(2)	6(2)
C(27)	51(3)	58(3)	55(4)	-1(3)	-11(3)	6(3)
C(28)	65(3)	55(3)	62(4)	6(3)	-8(3)	13(3)
C(29)	45(3)	72(4)	79(4)	-4(3)	-3(3)	-9(3)
C(30)	50(3)	45(3)	47(3)	7(2)	0(2)	2(2)
C(31)	76(4)	58(4)	78(5)	-5(3)	-11(3)	0(3)
C(32)	60(3)	55(3)	67(4)	15(3)	-4(3)	4(3)
C(33)	37(3)	76(4)	67(4)	-19(3)	-2(3)	7(3)
C(34)	108(6)	144(7)	77(5)	-26(5)	-30(4)	72(5)
C(35)	72(4)	127(7)	114(6)	-64(5)	26(4)	-39(4)

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(10A)	140(20)	100(20)	150(20)	30(16)	-90(16)	-14(15)
Cl(1A)	155(8)	92(6)	166(8)	7(5)	-39(6)	21(5)
Cl(2A)	205(9)	73(3)	118(5)	15(3)	-53(5)	-39(4)
C(10B)	34(10)	43(11)	91(17)	-7(10)	9(11)	-2(8)
Cl(1B)	61(3)	70(4)	70(4)	-14(3)	-8(3)	21(3)
Cl(2B)	113(4)	56(3)	213(12)	19(6)	-13(7)	-8(3)
C(10C)	55(5)	63(6)	141(10)	42(6)	2(6)	-3(4)
Cl(3A)	100(3)	134(3)	244(6)	106(4)	-38(3)	-39(2)
Cl(4A)	64(2)	112(2)	168(3)	44(2)	32(2)	2(1)
C(10D)	84(10)	63(10)	118(11)	-21(9)	15(9)	28(8)
Cl(3B)	109(6)	109(7)	258(13)	-28(8)	-21(8)	24(5)
Cl(4B)	230(12)	101(6)	280(17)	-41(7)	-177(13)	51(7)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 3c

	x	y	z	U(eq)
H(1)	6875	5032	2973	42
H(2A)	6610	6880	2216	45
H(17A)	6892	7957	2979	84
H(17B)	7111	7460	3734	84
H(17C)	5985	7491	3292	84
H(2B)	7158	7149	3560	44
H(17D)	5665	7197	2589	100
H(17E)	6401	6978	1954	100
H(17F)	6537	7763	2385	100
H(3A)	8386	7355	2645	66
H(3B)	8499	6635	3188	66
H(4A)	9123	6200	2130	62
H(4B)	8339	6678	1568	62
H(7)	8216	3756	78	53
H(9)	10580	4077	1648	53
H(13)	5838	5994	5490	64
H(14)	4109	5889	5098	67
H(15)	3532	5884	3810	64
H(19A)	5932	4856	1496	73
H(19B)	6205	3995	1632	73
H(19C)	5282	4231	1013	73
H(20A)	5699	3765	-93	118
H(20B)	6522	3270	417	118
H(20C)	6853	3720	-304	118
H(21A)	5798	5091	-105	81
H(21B)	6974	5096	-268	81
H(21C)	6623	5545	447	81
H(23A)	9180	2859	-378	124
H(23B)	10196	2981	-792	124
H(23C)	9372	3637	-784	124
H(24A)	11155	3003	1124	125

	x	y	z	U(eq)
H(24B)	11150	2579	323	125
H(24C)	10187	2512	806	125
H(25A)	10713	4492	-204	103
H(25B)	11511	3827	-264	103
H(25C)	11440	4238	537	103
H(27A)	9507	4979	3862	67
H(27B)	8508	4681	3354	67
H(27C)	8935	5498	3212	67
H(28A)	10611	3667	2782	74
H(28B)	9504	3569	3071	74
H(28C)	10412	3937	3622	74
H(29A)	11099	5192	3282	79
H(29B)	10549	5655	2578	79
H(29C)	11215	4935	2424	79
H(30)	7834	6187	4251	57
H(31A)	7414	7180	5069	86
H(31B)	8451	6765	5382	86
H(31C)	7418	6597	5758	86
H(32A)	7514	5232	5511	74
H(32B)	8578	5342	5159	74
H(32C)	7646	4935	4669	74
H(33)	5121	6027	2272	72
H(34A)	3206	6600	2655	135
H(34B)	3581	6627	1818	135
H(34C)	4168	7103	2499	135
H(35A)	4485	4827	2472	124
H(35B)	3781	5236	1801	124
H(35C)	3406	5171	2636	124
H(10A)	7004	7879	-264	166
H(10B)	6961	8330	517	166
H(10C)	7036	8164	-362	67
H(10D)	6886	8315	515	67

	x	y	z	U(eq)
H(10E)	462	8154	2108	105
H(10F)	706	8464	2957	105
H(10G)	120	8151	2848	106
H(10H)	548	7514	3430	106

Table S6. Crystal data and structure refinement for 3c'.

Empirical formula	$C_{47}H_{79}Br_2LiNO_3P$	
Formula weight	903.84	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.9613(13) Å	α= 99.990(2)°
	b = 14.7848(18) Å	β= 108.109(2)°
	c = 16.2547(19) Å	γ = 97.624(2)°
Volume	2416.3(5) $Å^3$	
Z	2	
Density (calculated)	1.242 Mg/m^3	
Absorption coefficient	1.748 mm^{-1}	
F(000)	960	
Crystal size	0.17 x 0.12 x 0.03 mm^3	
Theta range for data collection	1.35 to 23.26°	
Index ranges	-12<=h<=11, -16<=k<=16, -18<=l<=18	
Reflections collected	14058	
Independent reflections	6875 [R(int) = 0.0617]	
Completeness to theta = 23.26°	99.0 %	
Absorption correction	Sadabs	
Max. and min. transmission	0.9494 and 0.7554	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6875 / 9 / 555	
Goodness-of-fit on F^2	0.999	

Final R indices [I>2sigma(I)]	R1 = 0.0537, wR2 = 0.1057
R indices (all data)	R1 = 0.1172, wR2 = 0.1264
Extinction coefficient	0.0015(5)
Largest diff. peak and hole	0.381 and -0.335 e.Å^{-3}

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 3c'. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1A)	2207(6)	7335(3)	10216(3)	34(1)
Br(2A)	2321(7)	6347(6)	7583(5)	67(2)
Br(1B)	2106(6)	7300(4)	10205(3)	53(2)
Br(2B)	2149(6)	6385(6)	7547(5)	41(1)
P(1A)	2484(2)	2917(1)	3289(1)	21(1)
C(1A)	1484(5)	1817(3)	2958(3)	24(1)
C(2A)	1345(8)	3619(5)	2741(4)	32(2)
C(3A)	811(8)	3024(5)	1769(4)	34(2)
C(4A)	-117(10)	2074(5)	1596(6)	40(3)
C(35A)	1928(8)	4597(4)	2802(5)	47(2)
N(1A)	544(4)	1495(3)	2196(3)	26(1)
P(1B)	1858(10)	3015(4)	3490(4)	39(2)
C(1B)	1484(5)	1817(3)	2958(3)	24(1)
C(2B)	1890(30)	3580(20)	2569(14)	27(9)
C(3B)	400(30)	3220(20)	2060(30)	77(16)
C(4B)	330(30)	2182(17)	1619(17)	0(9)
C(35B)	930(40)	2140(30)	1020(30)	89(13)
N(1B)	544(4)	1495(3)	2196(3)	26(1)
C(11)	3244(5)	3113(3)	4509(3)	26(1)
C(5)	-4(6)	485(3)	1872(3)	30(1)
C(6)	-1255(6)	148(4)	1871(3)	29(1)
C(7)	-1720(6)	-810(4)	1553(4)	40(2)
C(8)	-969(6)	-1384(4)	1265(4)	39(2)

	x	y	z	U(eq)
C(9)	256(6)	-1033(4)	1269(3)	35(2)
C(10)	792(5)	-76(4)	1568(3)	27(1)
C(12)	4591(6)	3110(3)	4753(3)	27(1)
C(13)	5239(5)	3013(3)	5620(3)	26(1)
C(14)	4637(6)	2954(3)	6244(3)	26(1)
C(15)	3331(6)	3023(3)	5996(3)	30(1)
C(16)	2587(5)	3109(3)	5153(3)	28(1)
C(17)	-2075(6)	758(4)	2197(4)	39(2)
C(18)	-3311(6)	802(4)	1437(4)	47(2)
C(19)	-2448(6)	457(4)	2955(4)	52(2)
C(20)	2129(5)	300(4)	1558(3)	29(1)
C(21)	2212(6)	41(4)	628(3)	42(2)
C(22)	3178(6)	-65(4)	2201(4)	40(2)
C(23)	1181(5)	3249(4)	5014(3)	32(1)
C(24)	851(6)	3313(5)	5869(4)	66(2)
C(25)	1036(7)	4195(4)	4774(4)	58(2)
C(26)	140(6)	2450(4)	4302(4)	57(2)
C(27)	5458(6)	3241(4)	4166(3)	31(1)
C(28)	5313(5)	4142(4)	3822(3)	35(2)
C(29)	5227(7)	2381(4)	3422(4)	52(2)
C(30)	6925(6)	3394(4)	4694(4)	49(2)
C(31)	5354(5)	2845(4)	7172(3)	29(1)
C(32)	6760(6)	2724(4)	7298(4)	42(2)
C(33)	5397(6)	3706(4)	7846(3)	49(2)
C(34)	4656(6)	1973(4)	7351(4)	51(2)

	x	y	z	U(eq)
O(1)	4660(4)	6372(3)	9705(2)	41(1)
C(101)	5461(6)	7291(4)	9986(4)	57(2)
C(102)	5957(7)	7388(4)	9237(4)	57(2)
C(103)	6078(8)	6410(5)	8894(5)	67(2)
C(104)	5268(6)	5785(4)	9227(4)	53(2)

	x	y	z	U(eq)
O(2)	2113(4)	4924(3)	9099(2)	48(1)
C(201)	1886(7)	4172(4)	8349(4)	54(2)
C(202)	510(7)	3740(5)	8057(5)	70(2)
C(203)	171(10)	3989(7)	8873(6)	151(6)
C(204)	1168(7)	4689(5)	9494(4)	64(2)

	x	y	z	U(eq)
Li(1)	2767(10)	6247(7)	9143(6)	38(2)
O(3)	1623(5)	10358(3)	4149(3)	59(1)
C(301)	2789(7)	10466(5)	4879(4)	62(2)
C(302)	3165(7)	9530(5)	4791(5)	62(2)
C(303)	1881(7)	8875(5)	4382(5)	68(2)
C(304)	972(8)	9412(4)	3906(5)	76(3)

Table S8. Bond lengths [Å] and angles [°] for 3c'.

Br(1A)-Li(1)	2.441(10)	Br(2A)-Li(1)	2.465(12)
Br(1B)-Li(1)	2.464(9)	Br(2B)-Li(1)	2.522(12)
P(1A)-C(1A)	1.730(5)	P(1A)-C(2A)	1.845(6)
P(1A)-C(11)	1.851(5)	C(1A)-N(1A)	1.302(6)
C(2A)-C(35A)	1.473(9)	C(2A)-C(3A)	1.555(6)
C(3A)-C(4A)	1.548(6)	C(4A)-N(1A)	1.490(7)
N(1A)-C(5)	1.470(6)	P(1B)-C(11)	1.835(10)
P(1B)-C(2B)	1.845(8)	C(2B)-C(3B)	1.553(7)
C(3B)-C(4B)	1.552(7)	C(4B)-C(35B)	1.33(4)
C(11)-C(12)	1.406(7)	C(11)-C(16)	1.442(7)
C(5)-C(6)	1.394(7)	C(5)-C(10)	1.418(7)
C(6)-C(7)	1.387(7)	C(6)-C(17)	1.499(7)
C(7)-C(8)	1.380(7)	C(8)-C(9)	1.371(7)
C(9)-C(10)	1.396(7)	C(10)-C(20)	1.503(7)
C(12)-C(13)	1.409(7)	C(12)-C(27)	1.559(7)
C(13)-C(14)	1.380(6)	C(14)-C(15)	1.384(7)
C(14)-C(31)	1.517(7)	C(15)-C(16)	1.398(7)
C(16)-C(23)	1.534(7)	C(17)-C(19)	1.529(7)
C(17)-C(18)	1.542(8)	C(20)-C(22)	1.523(7)
C(20)-C(21)	1.527(6)	C(23)-C(25)	1.532(8)
C(23)-C(24)	1.532(7)	C(23)-C(26)	1.545(8)
C(27)-C(29)	1.527(7)	C(27)-C(30)	1.533(8)
C(27)-C(28)	1.539(7)	C(31)-C(33)	1.514(7)
C(31)-C(32)	1.529(7)	C(31)-C(34)	1.529(7)
O(1)-C(104)	1.429(6)	O(1)-C(101)	1.430(7)
O(1)-Li(1)	1.958(11)	C(101)-C(102)	1.500(8)
C(102)-C(103)	1.496(8)	C(103)-C(104)	1.480(8)
O(2)-C(204)	1.416(6)	O(2)-C(201)	1.432(6)
O(2)-Li(1)	1.972(10)	C(201)-C(202)	1.450(9)
C(202)-C(203)	1.486(9)	C(203)-C(204)	1.391(9)
O(3)-C(304)	1.411(7)	O(3)-C(301)	1.416(8)
C(301)-C(302)	1.492(8)	C(302)-C(303)	1.481(9)
C(303)-C(304)	1.472(9)		

C(1A)-P(1A)-C(2A)	101.3(3)	C(1A)-P(1A)-C(11)	104.9(2)
C(2A)-P(1A)-C(11)	123.5(3)	N(1A)-C(1A)-P(1A)	124.9(4)
C(35A)-C(2A)-C(3A)	112.4(6)	C(35A)-C(2A)-P(1A)	115.9(6)
C(3A)-C(2A)-P(1A)	100.7(4)	C(4A)-C(3A)-C(2A)	116.4(7)
N(1A)-C(4A)-C(3A)	109.7(6)	C(1A)-N(1A)-C(5)	120.6(4)
C(1A)-N(1A)-C(4A)	125.7(5)	C(5)-N(1A)-C(4A)	113.6(5)
C(11)-P(1B)-C(2B)	125.9(10)	C(3B)-C(2B)-P(1B)	93(2)
C(4B)-C(3B)-C(2B)	103(3)	C(35B)-C(4B)-C(3B)	111(3)
C(12)-C(11)-C(16)	120.8(5)	C(12)-C(11)-P(1B)	137.9(5)
C(16)-C(11)-P(1B)	101.0(5)	C(12)-C(11)-P(1A)	110.8(4)
C(16)-C(11)-P(1A)	127.5(4)	P(1B)-C(11)-P(1A)	27.2(3)
C(6)-C(5)-C(10)	124.8(5)	C(6)-C(5)-N(1A)	118.8(5)
C(10)-C(5)-N(1A)	116.4(5)	C(7)-C(6)-C(5)	116.1(5)
C(7)-C(6)-C(17)	120.3(5)	C(5)-C(6)-C(17)	123.6(5)
C(8)-C(7)-C(6)	121.1(6)	C(9)-C(8)-C(7)	121.7(5)
C(8)-C(9)-C(10)	120.9(5)	C(9)-C(10)-C(5)	115.5(5)
C(9)-C(10)-C(20)	120.3(5)	C(5)-C(10)-C(20)	124.2(5)
C(11)-C(12)-C(13)	117.4(5)	C(11)-C(12)-C(27)	126.2(5)
C(13)-C(12)-C(27)	116.3(5)	C(14)-C(13)-C(12)	123.8(5)
C(13)-C(14)-C(15)	116.9(5)	C(13)-C(14)-C(31)	122.8(5)
C(15)-C(14)-C(31)	120.3(5)	C(14)-C(15)-C(16)	124.3(5)
C(15)-C(16)-C(11)	116.5(5)	C(15)-C(16)-C(23)	117.2(5)
C(11)-C(16)-C(23)	126.1(5)	C(6)-C(17)-C(19)	112.4(5)
C(6)-C(17)-C(18)	111.8(4)	C(19)-C(17)-C(18)	110.4(5)
C(10)-C(20)-C(22)	110.9(4)	C(10)-C(20)-C(21)	111.7(5)
C(22)-C(20)-C(21)	109.2(4)	C(25)-C(23)-C(24)	104.5(5)
C(25)-C(23)-C(16)	109.5(5)	C(24)-C(23)-C(16)	112.2(5)
C(25)-C(23)-C(26)	110.4(5)	C(24)-C(23)-C(26)	106.8(5)
C(16)-C(23)-C(26)	113.0(4)	C(29)-C(27)-C(30)	103.5(5)
C(29)-C(27)-C(28)	112.8(4)	C(30)-C(27)-C(28)	103.9(4)
C(29)-C(27)-C(12)	113.4(4)	C(30)-C(27)-C(12)	112.5(4)
C(28)-C(27)-C(12)	110.2(4)	C(33)-C(31)-C(14)	109.3(4)
C(33)-C(31)-C(32)	108.3(5)	C(14)-C(31)-C(32)	112.3(4)
C(33)-C(31)-C(34)	109.8(5)	C(14)-C(31)-C(34)	110.1(4)
C(32)-C(31)-C(34)	106.9(5)		

C(104)-O(1)-C(101)	107.0(4)	C(104)-O(1)-Li(1)	115.7(4)
C(101)-O(1)-Li(1)	118.1(5)	O(1)-C(101)-C(102)	104.4(5)
C(103)-C(102)-C(101)	102.9(5)	C(104)-C(103)-C(102)	106.5(5)
O(1)-C(104)-C(103)	106.6(5)	C(204)-O(2)-C(201)	107.1(5)
C(204)-O(2)-Li(1)	120.3(5)	C(201)-O(2)-Li(1)	123.7(4)
O(2)-C(201)-C(202)	106.4(5)	C(201)-C(202)-C(203)	102.9(6)
C(204)-C(203)-C(202)	109.1(6)	C(203)-C(204)-O(2)	107.7(5)
O(1)-Li(1)-O(2)	101.9(5)	O(1)-Li(1)-Br(1A)	103.0(4)
O(2)-Li(1)-Br(1A)	112.6(4)	O(1)-Li(1)-Br(1B)	105.1(4)
O(2)-Li(1)-Br(1B)	110.7(4)	Br(1A)-Li(1)-Br(1B)	2.5(3)
O(1)-Li(1)-Br(2A)	108.1(4)	O(2)-Li(1)-Br(2A)	105.5(4)
Br(1A)-Li(1)-Br(2A)	123.5(4)	Br(1B)-Li(1)-Br(2A)	123.4(4)
O(1)-Li(1)-Br(2B)	112.1(4)	O(2)-Li(1)-Br(2B)	105.8(4)
Br(1A)-Li(1)-Br(2B)	120.1(4)	Br(1B)-Li(1)-Br(2B)	119.8(4)
Br(2A)-Li(1)-Br(2B)	4.4(2)	C(304)-O(3)-C(301)	108.5(5)
O(3)-C(301)-C(302)	105.3(5)	C(303)-C(302)-C(301)	102.7(6)
C(304)-C(303)-C(302)	105.6(6)	O(3)-C(304)-C(303)	107.6(6)

Table S9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 3c'. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1A)	32(2)	42(2)	24(2)	18(2)	1(2)	4(2)
Br(2A)	91(4)	73(3)	28(2)	14(2)	13(3)	-2(3)
Br(1B)	71(4)	74(3)	21(2)	0(2)	18(2)	48(3)
Br(2B)	26(1)	76(3)	27(2)	12(2)	13(1)	27(2)
P(1A)	24(1)	22(1)	16(1)	1(1)	6(1)	5(1)
C(1A)	23(3)	33(3)	16(3)	5(2)	6(3)	6(3)
C(2A)	35(5)	34(5)	32(4)	9(4)	11(4)	15(4)
C(3A)	41(5)	39(5)	23(4)	15(3)	5(4)	8(4)
C(4A)	32(7)	42(6)	30(5)	10(4)	-8(5)	-2(5)
C(35A)	66(6)	25(5)	59(5)	17(4)	28(5)	15(4)

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1A)	27(3)	29(3)	21(3)	7(2)	6(2)	5(2)
P(1B)	61(8)	22(5)	27(5)	7(4)	4(5)	11(5)
C(1B)	23(3)	33(3)	16(3)	5(2)	6(3)	6(3)
N(1B)	27(3)	29(3)	21(3)	7(2)	6(2)	5(2)
C(11)	30(4)	20(3)	21(3)	1(2)	2(3)	4(3)
C(5)	45(4)	18(3)	13(3)	-6(2)	-1(3)	-3(3)
C(6)	28(4)	23(3)	25(3)	2(2)	2(3)	-4(3)
C(7)	31(4)	41(4)	36(4)	0(3)	5(3)	-5(3)
C(8)	42(4)	28(4)	36(4)	-7(3)	11(3)	-4(3)
C(9)	31(4)	32(4)	34(3)	-4(3)	6(3)	3(3)
C(10)	34(4)	25(3)	14(3)	0(2)	1(3)	5(3)
C(12)	34(4)	20(3)	21(3)	3(2)	3(3)	4(3)
C(13)	20(3)	29(3)	26(3)	4(2)	4(3)	4(3)
C(14)	32(4)	21(3)	19(3)	1(2)	6(3)	-2(3)
C(15)	32(4)	33(3)	23(3)	1(3)	10(3)	2(3)
C(16)	22(4)	22(3)	28(3)	2(2)	-3(3)	0(3)
C(17)	30(4)	36(4)	43(4)	-3(3)	9(3)	0(3)
C(18)	31(4)	54(4)	44(4)	-3(3)	1(3)	14(3)
C(19)	49(5)	62(5)	44(4)	3(3)	21(4)	8(4)
C(20)	32(4)	24(3)	26(3)	0(2)	9(3)	0(3)
C(21)	54(5)	41(4)	32(3)	5(3)	20(3)	8(3)
C(22)	40(4)	39(4)	38(4)	4(3)	12(3)	8(3)
C(23)	23(4)	34(4)	35(3)	4(3)	5(3)	8(3)
C(24)	30(4)	113(6)	63(5)	20(4)	21(4)	29(4)
C(25)	55(5)	56(5)	61(5)	8(4)	14(4)	24(4)
C(26)	25(4)	48(4)	76(5)	-11(4)	4(4)	-4(3)
C(27)	38(4)	28(3)	22(3)	1(3)	10(3)	-1(3)
C(28)	27(4)	36(4)	33(3)	9(3)	0(3)	-6(3)
C(29)	71(5)	34(4)	47(4)	-3(3)	27(4)	-1(4)
C(30)	46(5)	68(5)	52(4)	30(4)	29(4)	22(4)
C(31)	27(4)	39(4)	19(3)	8(3)	6(3)	4(3)
C(32)	39(4)	55(4)	32(3)	15(3)	9(3)	14(3)

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(33)	58(5)	56(4)	21(3)	-1(3)	-2(3)	19(4)
C(34)	36(4)	74(5)	34(4)	25(3)	-1(3)	-2(4)
O(1)	35(3)	43(3)	38(2)	-3(2)	9(2)	2(2)
C(101)	35(4)	54(5)	56(5)	-20(4)	6(4)	-13(4)
C(102)	48(5)	48(5)	59(5)	20(4)	0(4)	-9(4)
C(103)	79(6)	76(6)	57(5)	16(4)	37(5)	14(5)
C(104)	44(5)	51(4)	61(4)	-5(4)	25(4)	3(4)
O(2)	45(3)	54(3)	39(2)	-3(2)	17(2)	-7(2)
C(201)	59(5)	48(4)	52(4)	-3(3)	27(4)	1(4)
C(202)	64(6)	59(5)	76(5)	-12(4)	30(5)	-4(4)
C(203)	134(10)	164(10)	113(8)	-79(7)	94(8)	-93(8)
C(204)	48(5)	93(6)	54(5)	17(4)	29(4)	-7(4)
Li(1)	41(7)	44(6)	28(5)	-2(4)	12(5)	14(5)
O(3)	78(4)	40(3)	44(3)	17(2)	-1(3)	8(3)
C(301)	75(6)	50(5)	45(4)	12(3)	5(4)	1(4)
C(302)	66(6)	54(5)	72(5)	30(4)	23(5)	14(4)
C(303)	69(6)	41(5)	106(6)	24(4)	40(5)	22(4)
C(304)	91(7)	42(5)	71(5)	30(4)	-3(5)	-19(5)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 3c'.

	x	y	z	U(eq)
H(2A)	614	3614	2987	39
H(3A1)	340	3404	1380	41
H(3A2)	1568	2902	1588	41
H(4A1)	-931	2182	1706	48
H(4A2)	-355	1737	969	48
H(35A)	2586	4604	2509	70
H(35B)	2344	4923	3429	70

	x	y	z	U(eq)
H(35C)	1240	4913	2509	70
H(2B1)	2141	4272	2756	32
H(2B2)	2446	3330	2240	32
H(3B1)	-96	3252	2477	93
H(3B2)	62	3576	1612	93
H(4B)	-617	1967	1243	0
H(35D)	1871	2361	1324	134
H(35E)	593	2536	612	134
H(35F)	754	1490	687	134
H(7)	-2570	-1075	1532	48
H(8)	-1309	-2038	1059	47
H(9)	747	-1448	1065	42
H(13)	6142	2987	5784	31
H(15)	2914	3011	6427	36
H(17)	-1536	1407	2436	47
H(18A)	-3053	1068	990	71
H(18B)	-3829	1197	1676	71
H(18C)	-3837	168	1162	71
H(19A)	-3024	-163	2733	78
H(19B)	-2904	911	3186	78
H(19C)	-1653	430	3432	78
H(20)	2309	999	1752	34
H(21A)	3061	353	632	63
H(21B)	1508	244	206	63
H(21C)	2121	-639	450	63
H(22A)	3106	79	2794	60
H(22B)	4045	236	2227	60
H(22C)	3056	-745	1995	60
H(24A)	866	2713	6046	99
H(24B)	-23	3460	5765	99
H(24C)	1499	3809	6343	99
H(25A)	113	4248	4608	87

	x	y	z	U(eq)
H(25B)	1340	4241	4273	87
H(25C)	1561	4703	5287	87
H(26A)	312	1844	4425	86
H(26B)	179	2483	3713	86
H(26C)	-733	2515	4315	86
H(28A)	5521	4676	4327	53
H(28B)	4411	4079	3427	53
H(28C)	5915	4243	3495	53
H(29A)	5874	2474	3128	77
H(29B)	4344	2289	2988	77
H(29C)	5314	1826	3674	77
H(30A)	7120	2828	4901	73
H(30B)	7162	3924	5207	73
H(30C)	7431	3528	4312	73
H(32A)	6751	2168	6868	62
H(32B)	7180	2649	7902	62
H(32C)	7249	3279	7205	62
H(33A)	5849	4262	7731	74
H(33B)	5867	3639	8446	74
H(33C)	4501	3774	7798	74
H(34A)	3783	2056	7348	76
H(34B)	5165	1880	7933	76
H(34C)	4574	1424	6888	76
H(10A)	6196	7351	10545	68
H(10B)	4941	7773	10080	68
H(10C)	5329	7614	8773	68
H(10D)	6816	7824	9454	68
H(10E)	5759	6253	8235	81
H(10F)	7004	6343	9112	81
H(10G)	4597	5318	8726	64
H(10H)	5822	5449	9624	64
H(20A)	2439	3711	8521	64

	x	y	z	U(eq)
H(20B)	2095	4414	7868	64
H(20C)	374	3052	7849	84
H(20D)	-17	3999	7573	84
H(20E)	-666	4212	8728	181
H(20F)	65	3430	9122	181
H(20G)	1571	4462	10035	77
H(20H)	812	5246	9665	77
H(30D)	2634	10650	5448	74
H(30E)	3486	10951	4856	74
H(30F)	3703	9464	4403	74
H(30G)	3656	9425	5379	74
H(30H)	1939	8322	3965	81
H(30I)	1586	8659	4845	81
H(30J)	713	9171	3256	92
H(30K)	172	9353	4070	92
H(1)	1554	1264	3320	92

Table S10. Crystal data and structure refinement for 6c.

Empirical formula	$C_{35}H_{54}NP$	
Formula weight	519.76	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 11.330(13) Å	α= 90°
	b = 17.35(2) Å	β= 93.133(16)°
	c = 15.903(19) Å	γ = 90°
Volume	3122(6) $Å^3$	
Z	4	
Density (calculated)	1.106 Mg/m^3	
Absorption coefficient	0.111 mm^{-1}	
F(000)	1144	
Crystal size	0.10 x 0.08 x 0.06 mm^3	
Theta range for data collection	1.74 to 21.26°	
Index ranges	-11<=h<=11, -17<=k<=17, -15<=l<=16	
Reflections collected	14462	
Independent reflections	3467 [R(int) = 0.2413]	
Completeness to theta = 21.26°	99.9 %	
Absorption correction	Sadabs	
Max. and min. transmission	0.9934 and 0.9890	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3467 / 0 / 349	
Goodness-of-fit on F^2	0.958	
Final R indices [I>2sigma(I)]	R1 = 0.0844, wR2 = 0.1635	
R indices (all data)	R1 = 0.2035, wR2 = 0.2199	
Extinction coefficient	0.0044(10)	
Largest diff. peak and hole	0.336 and -0.261 $e.Å^{-3}$	

Table S11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 6c. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	5015(2)	1667(1)	8008(1)	37(1)
N(1)	2548(5)	1941(3)	7790(4)	35(2)
C(1)	3602(7)	2192(4)	8246(4)	34(2)
C(2)	2326(9)	1145(6)	7975(7)	91(4)
C(3)	2993(7)	968(4)	8781(5)	39(2)
C(4)	3954(7)	1582(4)	8859(5)	35(2)
C(5)	6142(7)	2247(4)	8620(4)	31(2)
C(6)	6872(7)	1863(4)	9251(5)	29(2)
C(7)	7418(7)	2298(4)	9883(5)	29(2)
C(8)	7367(7)	3090(4)	9910(5)	33(2)
C(9)	6802(6)	3446(4)	9220(4)	30(2)
C(10)	6218(7)	3057(4)	8553(5)	32(2)

	x	y	z	U(eq)
C(11)	2076(7)	2363(4)	7074(5)	32(2)
C(12)	2345(7)	2183(4)	6244(5)	36(2)
C(13)	1854(7)	2621(5)	5581(5)	38(2)
C(14)	1154(7)	3252(5)	5740(5)	44(2)
C(15)	910(7)	3431(4)	6554(5)	41(2)
C(16)	1364(7)	3000(4)	7244(5)	33(2)
C(17)	1111(7)	844(4)	7838(5)	48(3)
C(18)	3146(7)	1510(4)	6020(5)	35(2)
C(19)	4051(7)	1728(5)	5384(5)	49(3)
C(20)	2438(7)	814(4)	5703(5)	49(3)
C(21)	1018(7)	3202(4)	8114(5)	36(2)
C(22)	1011(8)	4062(4)	8279(5)	59(3)
C(23)	-179(7)	2844(5)	8308(5)	58(3)
C(24)	7156(7)	982(4)	9230(5)	36(2)
C(25)	6130(7)	463(4)	9499(5)	46(3)

C(26)	8207(7)	779(4)	9850(5)	48(3)
C(27)	7529(7)	745(4)	8364(5)	39(2)
C(28)	7939(7)	3570(4)	10640(5)	35(2)
C(29)	8418(7)	3077(4)	11371(4)	40(2)
C(30)	8962(7)	4040(4)	10313(5)	42(2)
C(31)	7015(7)	4142(4)	10976(4)	40(2)
C(32)	5815(7)	3575(4)	7795(5)	36(2)
C(33)	6921(7)	3998(4)	7509(5)	52(3)
C(34)	4921(8)	4189(4)	8059(5)	51(3)
C(35)	5305(7)	3164(4)	6997(5)	48(3)

Table S11. Bond lengths [Å] and angles [°] for 6c.

P(1)-C(5)	1.858(7)	P(1)-C(4)	1.866(8)
P(1)-C(1)	1.898(8)	N(1)-C(1)	1.430(8)
N(1)-C(11)	1.433(9)	N(1)-C(2)	1.437(10)
C(1)-C(4)	1.479(9)	C(2)-C(17)	1.478(11)
C(2)-C(3)	1.485(10)	C(3)-C(4)	1.523(10)
C(5)-C(10)	1.414(9)	C(5)-C(6)	1.429(9)
C(6)-C(7)	1.377(9)	C(6)-C(24)	1.563(10)
C(7)-C(8)	1.377(9)	C(8)-C(9)	1.385(9)
C(8)-C(28)	1.543(10)	C(9)-C(10)	1.393(9)
C(10)-C(32)	1.552(10)	C(11)-C(16)	1.402(10)
C(11)-C(12)	1.406(10)	C(12)-C(13)	1.390(10)
C(12)-C(18)	1.533(10)	C(13)-C(14)	1.384(10)
C(14)-C(15)	1.373(10)	C(15)-C(16)	1.403(10)
C(16)-C(21)	1.501(10)	C(18)-C(20)	1.520(9)
C(18)-C(19)	1.526(11)	C(21)-C(22)	1.515(10)
C(21)-C(23)	1.538(10)	C(24)-C(27)	1.519(10)
C(24)-C(26)	1.545(9)	C(24)-C(25)	1.549(11)

C(28)-C(29)	1.519(9)	C(28)-C(30)	1.532(10)
C(28)-C(31)	1.557(10)	C(32)-C(35)	1.542(10)
C(32)-C(33)	1.542(10)	C(32)-C(34)	1.544(10)

C(5)-P(1)-C(4)	96.6(4)	C(5)-P(1)-C(1)	101.5(3)
C(4)-P(1)-C(1)	46.3(3)	C(1)-N(1)-C(11)	120.8(6)
C(1)-N(1)-C(2)	109.8(6)	C(11)-N(1)-C(2)	126.3(6)
N(1)-C(1)-C(4)	107.7(6)	N(1)-C(1)-P(1)	116.3(5)
C(4)-C(1)-P(1)	65.7(4)	N(1)-C(2)-C(17)	118.8(8)
N(1)-C(2)-C(3)	106.8(7)	C(17)-C(2)-C(3)	118.7(8)
C(2)-C(3)-C(4)	104.6(7)	C(1)-C(4)-C(3)	106.4(6)
C(1)-C(4)-P(1)	68.0(4)	C(3)-C(4)-P(1)	118.9(6)
C(10)-C(5)-C(6)	118.8(6)	C(10)-C(5)-P(1)	122.8(5)
C(6)-C(5)-P(1)	118.0(6)	C(7)-C(6)-C(5)	118.5(7)
C(7)-C(6)-C(24)	117.8(6)	C(5)-C(6)-C(24)	123.6(6)
C(8)-C(7)-C(6)	123.5(7)	C(7)-C(8)-C(9)	116.1(7)
C(7)-C(8)-C(28)	123.1(7)	C(9)-C(8)-C(28)	120.8(7)
C(8)-C(9)-C(10)	124.5(7)	C(9)-C(10)-C(5)	117.0(7)
C(9)-C(10)-C(32)	114.7(7)	C(5)-C(10)-C(32)	128.2(7)
C(16)-C(11)-C(12)	120.8(7)	C(16)-C(11)-N(1)	116.3(7)
C(12)-C(11)-N(1)	122.8(7)	C(13)-C(12)-C(11)	119.5(8)
C(13)-C(12)-C(18)	117.2(7)	C(11)-C(12)-C(18)	123.3(7)
C(14)-C(13)-C(12)	120.2(8)	C(15)-C(14)-C(13)	119.9(8)
C(14)-C(15)-C(16)	122.2(8)	C(11)-C(16)-C(15)	117.3(8)
C(11)-C(16)-C(21)	123.0(7)	C(15)-C(16)-C(21)	119.6(7)
C(20)-C(18)-C(19)	109.8(6)	C(20)-C(18)-C(12)	112.0(7)
C(19)-C(18)-C(12)	113.1(7)	C(16)-C(21)-C(22)	113.2(7)
C(16)-C(21)-C(23)	111.6(6)	C(22)-C(21)-C(23)	110.5(7)
C(27)-C(24)-C(26)	105.9(7)	C(27)-C(24)-C(25)	110.1(6)
C(26)-C(24)-C(25)	104.7(6)	C(27)-C(24)-C(6)	110.6(6)
C(26)-C(24)-C(6)	111.2(6)	C(25)-C(24)-C(6)	113.8(7)
C(29)-C(28)-C(30)	108.3(6)	C(29)-C(28)-C(8)	112.9(6)
C(30)-C(28)-C(8)	109.0(7)	C(29)-C(28)-C(31)	108.4(7)
C(30)-C(28)-C(31)	108.3(6)	C(8)-C(28)-C(31)	109.9(6)
C(35)-C(32)-C(33)	104.5(7)	C(35)-C(32)-C(34)	108.7(6)
C(33)-C(32)-C(34)	107.9(6)	C(35)-C(32)-C(10)	116.9(6)
C(33)-C(32)-C(10)	107.2(6)	C(34)-C(32)-C(10)	111.0(7)

Table S11. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 6c. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	34(2)	36(1)	39(1)	1(1)	-5(1)	-1(1)
N(1)	35(5)	20(4)	49(5)	3(3)	-22(4)	0(3)
C(1)	32(6)	33(5)	36(5)	-7(4)	-4(5)	3(4)
C(2)	62(8)	87(9)	118(10)	48(7)	-59(7)	-43(6)
C(3)	40(6)	35(5)	42(6)	0(4)	-2(5)	2(5)
C(4)	47(6)	29(5)	27(5)	1(4)	-1(4)	2(4)
C(5)	31(6)	32(5)	29(5)	0(4)	-2(4)	-1(4)
C(6)	27(5)	31(5)	30(5)	6(4)	-1(4)	-3(4)
C(7)	29(6)	24(5)	36(5)	6(4)	-1(4)	-4(4)
C(8)	24(5)	34(6)	41(5)	2(4)	-8(5)	-10(4)
C(9)	33(6)	22(5)	34(5)	-1(4)	-4(5)	2(4)
C(10)	22(5)	41(6)	33(5)	-2(4)	3(4)	0(4)
C(11)	29(6)	24(5)	42(6)	-1(5)	-8(5)	3(4)
C(12)	35(6)	40(6)	32(6)	-7(5)	8(5)	-5(5)
C(13)	41(6)	44(6)	29(5)	4(5)	-7(5)	3(5)
C(14)	42(6)	51(6)	39(6)	9(5)	-6(5)	7(5)
C(15)	44(6)	36(5)	43(6)	0(5)	1(5)	4(4)
C(16)	27(6)	37(5)	34(6)	-1(5)	-3(5)	-2(4)
C(17)	34(6)	49(6)	61(6)	8(5)	-5(5)	-10(5)
C(18)	38(6)	38(5)	28(5)	-6(4)	0(5)	5(5)
C(19)	27(6)	54(6)	66(6)	-3(5)	3(5)	7(5)
C(20)	57(7)	41(6)	47(6)	-4(5)	-10(5)	12(5)
C(21)	33(6)	35(6)	41(6)	-6(4)	1(5)	6(4)
C(22)	82(8)	46(6)	50(6)	-6(5)	6(6)	13(5)
C(23)	43(7)	71(7)	63(7)	-34(5)	25(6)	-14(5)
C(24)	45(6)	21(5)	39(6)	5(4)	-7(5)	-3(4)
C(25)	49(7)	36(5)	53(6)	9(5)	-13(5)	4(5)
C(26)	46(6)	26(5)	70(6)	6(5)	-22(5)	-7(4)
C(27)	37(6)	32(5)	50(6)	2(4)	3(5)	7(4)
C(28)	29(6)	34(5)	41(5)	-5(4)	2(5)	-5(5)

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(29)	48(6)	35(5)	35(5)	6(4)	-8(5)	-7(4)
C(30)	43(6)	36(5)	46(6)	-5(4)	-13(5)	0(5)
C(31)	44(6)	48(6)	29(5)	-4(4)	7(5)	1(5)
C(32)	39(6)	29(5)	41(5)	10(4)	4(5)	1(4)
C(33)	52(7)	43(6)	59(6)	8(5)	-1(6)	-11(5)
C(34)	62(7)	35(5)	54(6)	5(5)	-13(5)	16(5)
C(35)	62(7)	44(6)	38(5)	10(5)	-3(5)	-9(5)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 6c

	x	y	z	U(eq)
H(1)	3655	2730	8429	41
H(2)	2767	868	7556	110
H(3A)	3338	456	8767	47
H(3B)	2482	997	9250	47
H(4)	4226	1744	9427	41
H(7)	7845	2043	10315	35
H(9)	6814	3982	9201	36
H(13)	1997	2489	5029	46
H(14)	848	3554	5297	53
H(15)	428	3852	6650	49
H(17A)	620	1055	8254	72
H(17B)	1121	292	7884	72
H(17C)	801	989	7287	72
H(18)	3587	1354	6539	42
H(19A)	4593	1310	5326	73
H(19B)	4477	2178	5579	73
H(19C)	3651	1835	4849	73
H(20A)	2047	933	5168	73
H(20B)	1860	686	6099	73

	x	y	z	U(eq)
H(20C)	2960	385	5641	73
H(21)	1614	2976	8510	44
H(22A)	1724	4286	8091	89
H(22B)	962	4153	8872	89
H(22C)	341	4291	7979	89
H(23A)	-787	3050	7929	87
H(23B)	-355	2962	8878	87
H(23C)	-142	2295	8240	87
H(25A)	6390	-63	9527	70
H(25B)	5473	509	9095	70
H(25C)	5893	623	10043	70
H(26A)	7975	842	10418	72
H(26B)	8860	1114	9754	72
H(26C)	8439	254	9764	72
H(27A)	8197	1047	8217	59
H(27B)	6886	828	7956	59
H(27C)	7741	209	8371	59
H(29A)	7783	2791	11596	60
H(29B)	8774	3403	11802	60
H(29C)	8999	2727	11176	60
H(30A)	9550	3697	10113	63
H(30B)	9307	4352	10760	63
H(30C)	8671	4366	9860	63
H(31A)	6671	4439	10516	60
H(31B)	7398	4481	11383	60
H(31C)	6406	3857	11236	60
H(33A)	7439	3634	7262	78
H(33B)	7325	4239	7986	78
H(33C)	6688	4383	7100	78
H(34A)	4703	4512	7586	76
H(34B)	5274	4499	8506	76
H(34C)	4229	3939	8251	76

	x	y	z	U(eq)
H(35A)	5256	3522	6535	72
H(35B)	4529	2972	7094	72
H(35C)	5810	2743	6863	72

Table S12. Crystal data and structure refinement for 8c

Empirical formula	$C_{35}H_{54}NP$	
Formula weight	519.76	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 17.676(3) Å	α= 90°
	b = 17.298(3) Å	β= 91.407(2)°
	c = 10.2989(16) Å	γ = 90°
Volume	3148.1(9) $Å^3$	
Z	4	
Density (calculated)	1.097 Mg/m^3	
Absorption coefficient	0.110 mm^{-1}	
F(000)	1144	
Crystal size	0.32 x 0.13 x 0.11 mm^3	
Theta range for data collection	1.65 to 24.71°	
Index ranges	-20<=h<=20, -20<=k<=20, -12<=l<=10	
Reflections collected	19438	
Independent reflections	5359 [R(int) = 0.0488]	
Completeness to theta = 24.71°	99.8 %	
Absorption correction	Sadabs	
Max. and min. transmission	0.9880 and 0.9656	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5359 / 0 / 348	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0501, wR2 = 0.1207	
R indices (all data)	R1 = 0.0710, wR2 = 0.1340	

Extinction coefficient	0.0002(4)
Largest diff. peak and hole	0.653 and -0.354 e.Å^{-3}

Table S13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 8c. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	8228(1)	83(1)	2676(1)	17(1)
N(1)	7804(1)	-976(1)	868(2)	18(1)
C(1)	7693(1)	642(1)	3897(2)	16(1)
C(2)	8086(1)	1169(1)	4742(2)	17(1)
C(3)	7697(1)	1476(1)	5791(2)	18(1)
C(4)	6946(1)	1316(1)	6031(2)	17(1)
C(5)	6559(1)	863(1)	5123(2)	19(1)
C(6)	6908(1)	533(1)	4056(2)	17(1)
C(7)	6387(1)	139(1)	3029(2)	19(1)
C(8)	6760(1)	-537(1)	2326(2)	19(1)
C(9)	7468(1)	-334(1)	1600(2)	18(1)
C(10)	7616(1)	-993(1)	-498(2)	18(1)
C(11)	6968(1)	-1379(1)	-1010(2)	20(1)
C(12)	6810(1)	-1329(1)	-2341(2)	24(1)
C(13)	7258(1)	-908(1)	-3159(2)	27(1)
C(14)	7898(1)	-542(1)	-2658(2)	24(1)
C(15)	8091(1)	-584(1)	-1341(2)	21(1)
C(16)	8072(1)	-1667(1)	1582(2)	22(1)
C(17)	8663(1)	-1446(1)	2624(2)	23(1)
C(18)	8411(1)	-828(1)	3586(2)	21(1)
C(19)	8418(1)	-2252(1)	665(2)	27(1)
C(20)	6148(1)	767(1)	2035(2)	25(1)
C(21)	5664(1)	-194(1)	3617(2)	28(1)
C(22)	8913(1)	1446(1)	4539(2)	18(1)
C(23)	8982(1)	1830(1)	3200(2)	23(1)

	x	y	z	U(eq)
C(24)	9487(1)	785(1)	4696(2)	21(1)
C(25)	9163(1)	2061(1)	5543(2)	24(1)
C(26)	6534(1)	1618(1)	7229(2)	22(1)
C(27)	7017(1)	2181(1)	8042(2)	28(1)
C(28)	6333(1)	925(1)	8091(2)	27(1)
C(29)	5805(1)	2039(1)	6793(2)	26(1)
C(30)	6424(1)	-1836(1)	-184(2)	23(1)
C(31)	6370(1)	-2688(1)	-606(2)	28(1)
C(32)	5629(1)	-1478(1)	-240(3)	30(1)
C(33)	8814(1)	-191(1)	-852(2)	24(1)
C(34)	8753(2)	694(1)	-961(3)	36(1)
C(35)	9500(1)	-485(2)	-1568(3)	38(1)

Table S14. Bond lengths [Å] and angles [°] for 8c.

P(1)-C(18)	1.858(2)	P(1)-C(1)	1.861(2)
P(1)-C(9)	1.865(2)	N(1)-C(10)	1.438(3)
N(1)-C(16)	1.475(3)	N(1)-C(9)	1.477(3)
C(1)-C(6)	1.413(3)	C(1)-C(2)	1.430(3)
C(2)-C(3)	1.400(3)	C(2)-C(22)	1.557(3)
C(3)-C(4)	1.385(3)	C(4)-C(5)	1.387(3)
C(4)-C(26)	1.539(3)	C(5)-C(6)	1.395(3)
C(6)-C(7)	1.544(3)	C(7)-C(8)	1.533(3)
C(7)-C(21)	1.540(3)	C(7)-C(20)	1.544(3)
C(8)-C(9)	1.514(3)	C(10)-C(15)	1.413(3)
C(10)-C(11)	1.416(3)	C(11)-C(12)	1.395(3)
C(11)-C(30)	1.521(3)	C(12)-C(13)	1.379(3)
C(13)-C(14)	1.384(3)	C(14)-C(15)	1.393(3)
C(15)-C(33)	1.522(3)	C(16)-C(19)	1.522(3)
C(16)-C(17)	1.528(3)	C(17)-C(18)	1.531(3)
C(22)-C(24)	1.534(3)	C(22)-C(23)	1.539(3)
C(22)-C(25)	1.542(3)	C(26)-C(27)	1.531(3)
C(26)-C(29)	1.538(3)	C(26)-C(28)	1.539(3)

C(30)-C(32)	1.535(3)	C(30)-C(31)	1.538(3)
C(33)-C(35)	1.523(3)	C(33)-C(34)	1.537(3)

C(18)-P(1)-C(1)	100.66(9)	C(18)-P(1)-C(9)	94.93(10)
C(1)-P(1)-C(9)	103.41(9)	C(10)-N(1)-C(16)	122.37(16)
C(10)-N(1)-C(9)	115.38(16)	C(16)-N(1)-C(9)	118.89(17)
C(6)-C(1)-C(2)	118.55(19)	C(6)-C(1)-P(1)	121.71(15)
C(2)-C(1)-P(1)	119.67(15)	C(3)-C(2)-C(1)	118.12(19)
C(3)-C(2)-C(22)	117.92(18)	C(1)-C(2)-C(22)	123.93(18)
C(4)-C(3)-C(2)	123.61(19)	C(3)-C(4)-C(5)	116.83(19)
C(3)-C(4)-C(26)	123.35(19)	C(5)-C(4)-C(26)	119.83(19)
C(4)-C(5)-C(6)	122.9(2)	C(5)-C(6)-C(1)	119.41(19)
C(5)-C(6)-C(7)	116.91(18)	C(1)-C(6)-C(7)	123.33(19)
C(8)-C(7)-C(21)	105.73(17)	C(8)-C(7)-C(6)	113.81(17)
C(21)-C(7)-C(6)	112.50(18)	C(8)-C(7)-C(20)	109.68(18)
C(21)-C(7)-C(20)	107.91(18)	C(6)-C(7)-C(20)	107.08(16)
C(9)-C(8)-C(7)	115.27(17)	N(1)-C(9)-C(8)	115.22(16)
N(1)-C(9)-P(1)	107.56(14)	C(8)-C(9)-P(1)	112.82(15)
C(15)-C(10)-C(11)	119.7(2)	C(15)-C(10)-N(1)	117.60(18)
C(11)-C(10)-N(1)	122.67(19)	C(12)-C(11)-C(10)	118.5(2)
C(12)-C(11)-C(30)	117.85(19)	C(10)-C(11)-C(30)	123.6(2)
C(13)-C(12)-C(11)	121.9(2)	C(12)-C(13)-C(14)	119.3(2)
C(13)-C(14)-C(15)	121.2(2)	C(14)-C(15)-C(10)	119.2(2)
C(14)-C(15)-C(33)	118.9(2)	C(10)-C(15)-C(33)	121.9(2)
N(1)-C(16)-C(19)	110.98(18)	N(1)-C(16)-C(17)	110.66(17)
C(19)-C(16)-C(17)	108.97(18)	C(16)-C(17)-C(18)	115.11(18)
C(17)-C(18)-P(1)	108.41(15)	C(24)-C(22)-C(23)	110.50(17)
C(24)-C(22)-C(25)	105.44(18)	C(23)-C(22)-C(25)	105.93(17)
C(24)-C(22)-C(2)	112.16(16)	C(23)-C(22)-C(2)	110.42(17)
C(25)-C(22)-C(2)	112.12(17)	C(27)-C(26)-C(29)	108.09(18)
C(27)-C(26)-C(28)	108.33(19)	C(29)-C(26)-C(28)	109.50(18)
C(27)-C(26)-C(4)	112.70(18)	C(29)-C(26)-C(4)	109.62(18)
C(28)-C(26)-C(4)	108.55(17)	C(11)-C(30)-C(32)	111.12(18)
C(11)-C(30)-C(31)	112.04(18)	C(32)-C(30)-C(31)	109.02(18)
C(15)-C(33)-C(35)	111.3(2)	C(15)-C(33)-C(34)	111.41(19)
C(35)-C(33)-C(34)	110.6(2)		

Table S15. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 8c. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	23(1)	12(1)	17(1)	-2(1)	3(1)	0(1)
N(1)	28(1)	10(1)	16(1)	-1(1)	1(1)	3(1)
C(1)	25(1)	10(1)	15(1)	3(1)	1(1)	2(1)
C(2)	25(1)	11(1)	16(1)	2(1)	0(1)	3(1)
C(3)	27(1)	10(1)	17(1)	-1(1)	-2(1)	1(1)
C(4)	24(1)	11(1)	18(1)	1(1)	2(1)	3(1)
C(5)	22(1)	13(1)	22(1)	2(1)	2(1)	-1(1)
C(6)	26(1)	9(1)	17(1)	2(1)	2(1)	1(1)
C(7)	23(1)	15(1)	18(1)	-2(1)	1(1)	0(1)
C(8)	24(1)	13(1)	20(1)	-2(1)	1(1)	-1(1)
C(9)	25(1)	10(1)	18(1)	-1(1)	2(1)	3(1)
C(10)	26(1)	12(1)	17(1)	-3(1)	2(1)	5(1)
C(11)	26(1)	13(1)	20(1)	-4(1)	3(1)	4(1)
C(12)	31(1)	16(1)	25(1)	-6(1)	-3(1)	0(1)
C(13)	42(2)	20(1)	18(1)	-1(1)	1(1)	5(1)
C(14)	36(1)	17(1)	22(1)	1(1)	6(1)	2(1)
C(15)	29(1)	14(1)	19(1)	0(1)	4(1)	5(1)
C(16)	31(1)	14(1)	20(1)	1(1)	4(1)	2(1)
C(17)	33(1)	15(1)	22(1)	1(1)	1(1)	7(1)
C(18)	25(1)	16(1)	20(1)	1(1)	1(1)	2(1)
C(19)	34(1)	19(1)	27(1)	-4(1)	0(1)	5(1)
C(20)	32(1)	18(1)	26(1)	-3(1)	-4(1)	7(1)
C(21)	27(1)	26(1)	32(2)	-12(1)	5(1)	-5(1)
C(22)	23(1)	14(1)	19(1)	-1(1)	3(1)	0(1)
C(23)	25(1)	17(1)	26(1)	3(1)	3(1)	-2(1)
C(24)	24(1)	17(1)	23(1)	2(1)	2(1)	0(1)
C(25)	26(1)	20(1)	26(1)	-6(1)	4(1)	-4(1)

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(26)	25(1)	18(1)	22(1)	-5(1)	4(1)	0(1)
C(27)	28(1)	30(1)	25(1)	-11(1)	5(1)	0(1)
C(28)	33(1)	26(1)	23(1)	-1(1)	8(1)	0(1)
C(29)	29(1)	21(1)	29(1)	-7(1)	5(1)	3(1)
C(30)	28(1)	18(1)	22(1)	-4(1)	1(1)	-1(1)
C(31)	40(1)	18(1)	27(1)	-2(1)	1(1)	-4(1)
C(32)	31(1)	27(1)	33(2)	-6(1)	2(1)	-1(1)
C(33)	30(1)	23(1)	21(1)	2(1)	4(1)	-4(1)
C(34)	43(2)	24(1)	41(2)	6(1)	-3(1)	-8(1)
C(35)	33(1)	51(2)	30(2)	3(1)	7(1)	-1(1)

Table S16. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 8c

	x	y	z	U(eq)
H(3)	7963	1812	6371	21
H(5)	6035	773	5233	23
H(8A)	6889	-942	2973	23
H(8B)	6386	-760	1701	23
H(9)	7323	75	954	22
H(12)	6380	-1592	-2694	29
H(13)	7130	-870	-4058	32
H(14)	8210	-258	-3223	29
H(16)	7632	-1913	2012	26
H(17A)	9121	-1257	2190	28
H(17B)	8807	-1917	3118	28
H(18A)	8811	-744	4261	25
H(18B)	7945	-998	4019	25
H(19A)	8037	-2408	8	40
H(19B)	8587	-2707	1160	40
H(19C)	8851	-2018	238	40

	x	y	z	U(eq)
H(20A)	5834	533	1343	38
H(20B)	6600	996	1660	38
H(20C)	5858	1169	2471	38
H(21A)	5387	-497	2957	42
H(21B)	5343	230	3913	42
H(21C)	5801	-527	4356	42
H(23A)	9506	1995	3081	34
H(23B)	8647	2282	3147	34
H(23C)	8836	1460	2518	34
H(24A)	10001	995	4676	32
H(24B)	9413	414	3985	32
H(24C)	9412	524	5527	32
H(25A)	9162	1836	6416	36
H(25B)	8812	2500	5499	36
H(25C)	9674	2240	5351	36
H(27A)	7469	1914	8380	41
H(27B)	6722	2374	8768	41
H(27C)	7168	2617	7498	41
H(28A)	6012	564	7592	41
H(28B)	6060	1107	8849	41
H(28C)	6798	661	8380	41
H(29A)	5932	2473	6226	39
H(29B)	5545	2234	7556	39
H(29C)	5472	1678	6317	39
H(30)	6615	-1820	737	27
H(31A)	6179	-2716	-1506	43
H(31B)	6024	-2963	-39	43
H(31C)	6873	-2925	-541	43
H(32A)	5663	-926	-32	45
H(32B)	5309	-1736	392	45
H(32C)	5407	-1543	-1114	45
H(33)	8887	-323	88	29

	x	y	z	U(eq)
H(34A)	9226	930	-642	54
H(34B)	8333	876	-438	54
H(34C)	8662	838	-1871	54
H(35A)	9439	-370	-2496	56
H(35B)	9547	-1045	-1446	56
H(35C)	9957	-230	-1222	56