Supporting Information for:

Phosphorus–Bismuth *peri*-Substituted Acenaphthenes: A Synthetic, Structural and Computational Study

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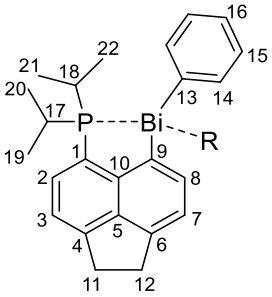
Experimental

General Considerations

All reactions and manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques or under an argon atmosphere in a Saffron glove box. Dry solvents were either collected from an MBraun Solvent Purification System, or dried and stored according to common procedures.[1] Acenap(P*i*Pr$_2$)Li, **1**, was prepared *in situ* by reacting 5-bromo-6-diisopropylphosphinoacenaphthene Acenap(P*i*Pr$_2$)Br with *n*BuLi, as described in the relevant synthetic methods section. Acenap(P*i*Pr$_2$)Br,[2] $BiPh_3$, Ph_2BiCl and $PhBiCl_2$[3-4] were synthesised as reported in the literature. All novel compounds were characterised by ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR, including measurement of ^{1}H{^{31}P}, H–H DQF COSY, H–C HSQC, H–C HMBC and H–P HMBC where possible. ^{13}C{^{1}H} NMR spectra were recorded using the DEPT-Q-135 pulse sequence with broadband proton decoupling. Measurements were performed at 25 °C (unless specified otherwise) using a Bruker Avance III 500 (MHz) spectrometer or a Bruker Avance II 400 MHz spectrometer. 85% H_3PO_4 was used as an external standard for ^{31}P NMR; ^{1}H and ^{13}C NMR shifts are relative to Me_4Si, residual solvent peaks were used for calibration ($CHCl_3$ δ_H 7.26, δ_C 77.2 ppm). Elemental analysis (C, H and N) was performed at London Metropolitan University. Mass Spectra were acquired in the EPSRC UK National Mass Spectrometry Facility (NMSF) at Swansea University. Infrared and Raman spectra were collected on a Perkin Elmer 2000 NIR FT spectrometer. "*In vacuo*" refers to a pressure of *ca.* 2×10^{-2} mbar.



2 R = Ph
3 R = Acenap(P*i*Pr$_2$)
5 R = [BF$_4$]$^-$
6 R = Cl
7 R = Br
8 R = I
10 R = SPh

Figure S1: NMR numbering scheme for compounds **2**, **3**, **5**-**8** and **10**.

Synthetic Methods

Acenap(P*i*Pr$_2$)(BiPh$_2$), 2

*n*BuLi (1.14 mL, 2.5 M solution in hexanes, 2.86 mmol) was added to a stirred solution of Acenap(P*i*Pr$_2$)Br (1.00 g, 2.86 mmol) in THF (30 mL) at −78 °C over 30 mins. The reaction was stirred for 3 h at this temperature. A suspension of BiPh$_2$Cl (1.14 g, 2.86 mmol) in THF (30 mL) was added in portions over 1 h. The reaction was warmed to room temperature and stirred overnight. The volatiles were removed *in vacuo* and diethyl ether (70 mL) was added. The organic layer was washed with degassed water. The aqueous layer was extracted further with diethyl ether (2 x 15 mL) and the combined organic fractions dried over magnesium sulfate. The volatiles were removed *in vacuo* to afford a sticky solid. Addition of MeCN caused the product to solidify, this was collected by filtration. Recrystallisation from hot MeCN afforded **2** as an off white solid (1.09 g, 1.72 mmol, 60%) m.p. 144.6−146.1 °C (decomp.). Crystals suitable for X-ray diffraction were obtained from hot MeCN.

Anal. calcd. for $C_{30}H_{32}BiP{\cdot}CH_3CN$ (673.58 g mol^{-1}): C, 57.04; H, 5.24; N, 2.07. Found C, 56.95; H, 5.30; N 1.97.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, $^3J_{HH}$ = 7.0 Hz, 1 H, H8), 7.85−7.81 (m, 4 H, H14), 7.63 (dd, $^3J_{HH}$ = 7.1, $^3J_{HP}$ = 3.8 Hz, 1 H, H2), 7.37−7.31 (m, 5 H, H3 and H15), 7.29−7.24 (m, 2 H, H16), 7.18 (d, $^3J_{HH}$ = 7.0 Hz, 1 H, H7), 3.44−3.35 (m, 4 H, H11 and H12), 2.13−2.00 (m, 2 H, H17 and H18), 1.07 (dd, $^3J_{HP}$ = 15.3, $^3J_{HH}$ = 6.9 Hz, 6 H, H19 and H21), 0.61 (dd, $^3J_{HP}$ = 12.2, $^3J_{HH}$ = 7.0 Hz, 6 H, H20 and H22).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.3 (d, $^{5ts}J_{CP}$ = 42.2 Hz, C_q, C13), 153.4 (C_q, C9), 149.3 (C_q, C4), 146.5 (d, $^4J_{CP}$ = 1.4 Hz, C_q, C6), 143.7 (C_q, C10), 142.8 (CH, C8), 141.4 (C_q, C5), 138.3 (CH, C14), 133.9 (d, $^2J_{CP}$ = 2.8 Hz, CH, C2), 131.3 (d, $^1J_{CP}$ = 14.8 Hz, C_q, C1), 130.2 (CH, C15), 126.7 (CH, C16), 123.0 (CH, C7), 118.9 (CH, C3), 30.2 (CH_2, C11 and C12), 25.9 (d, $^1J_{CP}$ = 12.0 Hz, CH, C17 and C18), 20.4 (d, $^2J_{CP}$ = 17.7 Hz, CH_3, C19 and C21), 19.2 (d, $^2J_{CP}$ = 8.9 Hz, CH_3, C20 and C22).

^{31}P NMR (162 MHz, $CDCl_3$): δ −23.7 (complex m (≈ br s)).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ −23.7 (s).

HRMS (APCI$^+$) *m/z* (%) 555.16 (100) [M−Ph]$^+$, 271.16 (70).

IR (KBr disc) ν_{max}/cm^{-1} 3053w (ν_{Ar-H}), 2921m (ν_{C-H}), 1425m, 841m, 724s, 696s, 447m.

Raman (glass capillary) ν_{max}/cm^{-1} 3034w (ν_{Ar-H}), 2924w (ν_{C-H}), 1328m, 999s, 641m, 208m, 177s.

(Acenap(P*i*Pr$_2$))$_2$BiPh **3**

Method 1 (impure 3 produced)

*n*BuLi (1.25 mL, 2.5 M solution in hexanes, 3.15 mmol) was added to a stirred solution of Acenap(P*i*Pr$_2$)Br (1.09 g, 3.15 mmol) in THF (30 mL) at −78 °C over 30 mins. The reaction was stirred for 3 h at this temperature. A suspension of $BiPhCl_2$ (0.56 g, 1.57 mmol) in THF (35 mL) was added in portions over 1 h. The reaction was warmed to room temperature and stirred overnight. The volatiles were removed *in vacuo* and diethyl ether (70 mL) was added. The organic layer was washed with degassed water. The aqueous layer was extracted further with diethyl ether (2 x 15 mL) and the combined organic fractions dried over magnesium sulfate. The volatiles were removed *in vacuo* to afford a sticky solid. Addition of MeCN caused the compound to solidify. Compound **3** was obtained as an off white solid (1.23 g) after filtration. No yield is reported due to contamination with **2** and **11**. Crystals suitable for X-ray diffraction were obtained from hot MeCN.

Method 2 (pure 3 produced)

*n*BuLi (1.40 mL, 2.5 M solution in hexanes, 3.34 mmol) was added to a stirred solution of Acenap(P*i*Pr$_2$)Br (1.18 g, 3.34 mmol) in THF (70 mL) at −78 °C over 15 mins. The reaction was left to stir at this temperature for 2 h. A suspension of Acenap(P*i*Pr$_2$)BiPhCl , **6**, (2.00 g, 3.34 mmol) in THF (30 mL) was added portion wise over 30 minutes at −78 °C. The reaction mixture was left to warm up to room temperature and stirred overnight. The volatiles were removed *in vacuo* and diethyl ether (120 mL) was added, the suspension was filtered through celite which was then washed with diethyl ether (30 mL). The volatiles were removed *in vacuo* and the product recrystallised from hot MeCN to afford **3** as an off white solid (1.69 g, 2.06 mmol, 62%), m.p. 169.5−171.9 °C. Crystals suitable for X-ray diffraction were obtained from hot MeCN.

Anal. calcd. for $C_{42}H_{49}BiP_2$ (824.31 g mol^{-1}): C, 61.14; H, 5.99. Found: C, 61.21; H, 6.06.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (d, $^3J_{HH}$ = 6.8 Hz, 2 H, H8), 7.89 (d, $^3J_{HH}$ = 7.3 Hz, 2H, H14), 7.65 (dd, $^3J_{HH}$ = 7.2, $^3J_{HP}$ = 2.8 Hz, 2 H, H2), 7.34 (d, $^3J_{HH}$ = 7.2 Hz, 2 H, H3), 7.28 (*p*t, $^3J_{HH}$ = 7.4 Hz, 2 H, H15), 7.21 (t, $^3J_{HH}$ = 7.1 Hz, 1 H, H16), 7.02 (d, $^3J_{HH}$ = 7.0 Hz, 2 H, H7), 3.44−3.38 (m, 4 H, 2 × CH_2, H11), 3.37−3.29 (m, 4 H, 2 × CH_2, H12), 2.15−1.99 (m, 4 H, H17 and H18), 1.06 (dd, $^3J_{HP}$ = 14.6, $^3J_{HH}$ = 6.8 Hz, 6 H, H19 or H20 or H21 or H22, 2 × CH_3), 1.03−0.95 (br m, 6 H, H19 or H20 or H21 or H22, 2 × CH_3), 0.69 (br s, 6 H, H19 or H20 or H21 or H22, 2 × CH_3), 0.58 (br s, 6 H, H19 or H20 or H21 or H22, 2 × CH_3).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 175.5 (t, $^{5ts}J_{CP}$ = 34.7 Hz, C_q, C13), 149.3 (C_q), 145.5 (C_q), 144.4 (C_q), 144.3 (CH, C8), 144.0 (C_q), 141.2 (d, $^3J_{CP}$ = 9.3 Hz, C_q, C5), 139.2 (CH, C14), 133.5 (CH, C2), 131.8 (d, $^1J_{CP}$ = 16.4 Hz, C_q, C1), 129.8 (CH, C15), 125.9 (CH, C16), 123.1 (CH, C7), 118.5 (CH, C3), 30.1 (2 × CH_2, C11), 30.0 (2 × CH_2, C12), 26.2 (d, $^1J_{CP}$ = 13.0 Hz, 2 × CH, C17 or C18), 25.8 (d, $^1J_{CP}$ = 12.3 Hz, 2 × CH, C17 or C18), 20.6−20.1 (m, 4 × CH_3, C19 or C20 or C21 or C22), 19.6 (d, $^2J_{CP}$ = 8.7 Hz, C19 or C20 or C21 or C22, 2 × CH_3), 18.9 (d, $^2J_{CP}$ = 8.0 Hz, C19 or C20 or C21 or C22, 2 × CH_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ −22.9 (br s).

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ −22.9 (s).

HRMS (APCI$^+$) *m/z* (%) 825.3192 (17) $[M+H]^+$, 747.2752 (100) $[M-Ph]^+$, 556.1728 (80) $[M-C_{18}H_{21}P]^+$.

IR (KBr disc) ν_{max}/cm^{-1} 3048w (ν_{Ar-H}), 2926m (ν_{C-H}), 1424m, 841m, 723s, 695s, 444m.

[Acenap(P*i*Pr$_2$)(BiPh)]$^+$[BF$_4$]$^-$ 5

$BF_3{\cdot}Et_2O$ (0.15 mL, 1.18 mmol) was added to a stirred solution of Acenap(P*i*Pr$_2$)(BiPh$_2$) **2** (0.50 g, 0.79 mmol) in diethyl ether (20 mL) at 0 °C; immediately a white precipitate formed. The reaction mixture was warmed to room temperature and stirred for 3 h. The solid was collected by filtration and washed with diethyl ether (10 mL). Compound **5** was obtained as a white powder (326 mg, 0.51 mmol, 86% with $BF_3{\cdot}Et_2O$ limiting), m.p. 218.9−220.2 °C (decomp.). Crystals suitable for X-ray diffraction were obtained by diffusion of diethyl ether into a CH_2Cl_2 solution of **5**.

Anal. calcd. for $C_{24}H_{27}BBiF_4P$ (642.24 g mol^{-1}): C, 44.88; H, 4.24. Found: C, 44.97; H, 4.19.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28 (d, $^3J_{HH}$ = 7.0 Hz, 1 H, H8), 7.96−7.93 (m, 2 H, H14), 7.79 (d, $^3J_{HH}$ = 7.0 Hz, 1 H, H7), 7.70 (dd, $^3J_{HP}$ = 8.5, $^3J_{HH}$ = 7.3 Hz, 1 H, H2), 7.48 (d, $^3J_{HH}$ = 7.3 Hz, 1 H, H3), 7.37 (*p*t, $^3J_{HH}$ = 7.6 Hz, 2 H, H15), 7.27−7.23 (m, 1 H, H16), 3.64−3.45 (m, 4 H, H11 and H12), 3.12−3.01 (m, 1 H, H17), 3.00−2.91 (m, 1 H, H18), 1.28−1.19 (m, 6 H, H19 and H21), 1.12 (dd, $^3J_{HP}$ = 20.1, $^3J_{HH}$ = 7.0 Hz, 3 H, H22), 0.53 (dd, $^3J_{HP}$ = 18.3, $^3J_{HH}$ = 7.2 Hz, 3 H, H20).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 165.7 (C_q, C9), 154.3 (d, $^4J_{CP}$ = 2.0 Hz, C_q, C4), 154.2 (d, $^2J_{CP}$ = 12.8 Hz, C_q, C13), 152.9 (d, $^2J_{CP}$ = 21.5 Hz, C_q, C10), 147.5 (C_q, C6), 144.5 (d, $^3J_{CP}$ = 11.2, C_q, C5), 139.5 (CH, C14), 139.0 (d, $^2J_{CP}$ = 5.2 Hz, CH, C2), 136.5 (CH, C8), 131.4 (d, $^4J_{CP}$ = 1.5 Hz, CH, C15), 129.2 (CH, C16), 127.2 (d, $^1J_{CP}$ = 36.7 Hz, C_q, C1), 124.4 (CH, C7), 121.4 (d, $^3J_{CP}$ = 7.5 Hz, CH, C3), 30.8 (CH_2, C11), 30.7 (CH_2, C12), 27.8 (d, $^1J_{CP}$ = 17.4 Hz, CH, C17), 25.3 (d, $^1J_{CP}$ = 20.4 Hz, CH, C18), 19.9 (CH_3, C22), 18.1 (CH_3, C19 or C21), 17.7 (CH_3, C20), 17.1 (d, $^2J_{CP}$ = 5.4 Hz, CH_3, C19 or C21).

^{31}P NMR (202 MHz, $CDCl_3$): δ 56.6 (br s).

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 56.6 (s).

HRMS (ASAP$^+$) *m/z* (%) 555.1661 (100) [M-BF_4]$^+$.

IR (KBr disc) ν_{max}/cm^{-1} 3042w (ν_{Ar-H}), 2927w (ν_{C-H}), 1592w, 1084s, 1056s, 1008s, 852m, 731m.

Acenap(P*i*Pr$_2$)(BiPhCl) 6

A solution of NaCl (0.29 g, 5.0 mmol) in degassed water (10 mL) was added to [Acenap(P*i*Pr$_2$)(BiPh)][BF$_4$] **5** (326 mg, 0.51 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred vigorously for 15 mins. The CH_2Cl_2 layer was removed and the aqueous layer extracted with CH_2Cl_2 (15 mL). The combined organic fractions were dried over magnesium sulfate. Removal of the solvent *in vacuo* afforded **6** as an off white solid (259 mg, 0.44 mmol, 86%), m.p. 210.4−211.8 °C (decomp.). Crystals suitable for X-ray diffraction were obtained by diffusion of diethyl ether into a CH_2Cl_2 solution of **6**.

Anal. calcd. for $C_{24}H_{27}BiClP$ (590.87 g mol^{-1}): C, 48.78; H, 4.60. Found: C, 48.71; H, 4.59.

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.32 (d, $^3J_{HH}$ = 7.0 Hz, 1 H, H8), 7.98 (d, $^3J_{HH}$ = 7.3 Hz, 2 H, H14), 7.69 (d, $^3J_{HH}$ = 7.0 Hz, 1 H, H7), 7.53 (t, $^3J_{HP}$ = 7.0, $^3J_{HH}$ = 7.0 Hz, 1 H, H2), 7.36−7.30 (m, 3 H, H3 and H15), 7.17 (t, $^3J_{HH}$ = 7.3 Hz, 1 H, H16), 3.50−3.38 (m, 4 H, H11 and H12), 2.50−2.31 (m, 2 H, H17 and H18), 1.11

(dd, $^{3}J_{HP}$ = 17.7, $^{3}J_{HH}$ = 7.0 Hz, 3 H, H20), 1.06 (dd, $^{3}J_{HP}$ = 13.7, $^{3}J_{HH}$ = 7.0 Hz, 3 H, H19), 0.95 (dd, $^{3}J_{HP}$ = 18.3, $^{3}J_{HH}$ = 6.7 Hz, 3 H, H21), 0.35 (dd, $^{3}J_{HP}$ = 16.1, $^{3}J_{HH}$ = 6.7 Hz, 3 H, H22).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 165.1 (C_q, C9), 160.7 (d, $^{5ts}J_{CP}$ = 8.4 Hz, C_q, C13), 152.5 (C_q, C4), 150.4 (d, $^{2}J_{CP}$ = 28.1 Hz, C_q, C10), 147.0 (C_q, C6), 143.7 (d, $^{3}J_{HH}$ = 11.4 Hz, C_q, C5), 141.0 (CH, C8), 138.8 (CH, C14), 134.7 (d, $^{2}J_{CP}$ = 3.2 Hz, CH, C2), 131.0 (CH, C15), 128.1 (d, $^{1}J_{CP}$ = 21.0 Hz, C_q, C1), 128.0 (CH, C16), 124.5 (CH, C7), 120.0 (d, $^{3}J_{CP}$ = 4.7 Hz, CH, C3), 30.7 (CH_2, C11 or C12), 30.5 (CH_2, C11 or C12), 26.0 (d, $^{1}J_{CP}$ = 5.8 Hz, CH, C17), 24.7 (d, $^{1}J_{CP}$ = 10.9 Hz, CH, C18), 20.3 (d, $^{2}J_{CP}$ = 6.2 Hz, CH_3, C20), 18.5 (d, $^{2}J_{CP}$ = 8.0 Hz, CH_3, C19), 18.0 (CH_3, C21), 17.6 (CH_3, C22).

^{31}P NMR (202 MHz, $CDCl_3$): δ 18.8 (br s).

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 18.8 (s).

HRMS (APCI^{+}) *m/z* (%) 555.1661 (100) $[M-Cl]^{+}$.

IR (KBr disc) ν_{max}/cm^{-1} 3044w (ν_{Ar-H}), 2925s (ν_{C-H}), 1591s, 1443s, 1254s, 847vs, 739s, 443m.

Acenap(P*i*Pr$_2$)(BiPhBr) **7**

A saturated KBr(aq) solution (25 mL) was added to [Acenap(P*i*Pr$_2$)(BiPh)][BF_4] **5** (294 mg, 0.45 mmol) dissolved in CH_2Cl_2 (30 mL). The reaction mixture was stirred vigorously for 50 mins. The CH_2Cl_2 layer was removed and the aqueous layer extracted with CH_2Cl_2 (15 mL). The combined organic fractions were dried over magnesium sulfate. Removal of the solvent *in vacuo* afforded **7** as a white solid (241 mg, 0.38 mmol, 83%), m.p. 215.6–217.0 °C (decomp.). Crystals suitable for X-ray diffraction were obtained from MeCN by slow evaporation.

Anal. calcd. for $C_{24}H_{27}BiBrP$ (635.34 g mol^{-1}): C, 45.37; H, 4.28. Found: C, 45.50; H, 4.35.

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.47 (d, $^{3}J_{HH}$ = 7.2 Hz, 1 H, H8), 7.99 (d, $^{3}J_{HH}$ = 7.7 Hz, 2 H, H14), 7.68 (d, $^{3}J_{HH}$ = 7.2 Hz, 1 H, H7), 7.54 (t, $^{3}J_{HH}$ = 6.9, $^{3}J_{HP}$ = 6.9 Hz, 1 H, H2), 7.34 (d, $^{3}J_{HH}$ = 6.9 Hz, 1 H, H3), 7.31 (t, $^{3}J_{HH}$ = 7.7 Hz, 2 H, H15), 7.17 (t, $^{3}J_{HH}$ = 7.4 Hz, 1 H, H16), 3.51−3.42 (m, 4 H, H11 and H12), 2.49−2.34 (m, 2 H, H17 and H 18), 1.13 (dd, $^{3}J_{HP}$ = 17.7, $^{3}J_{HH}$ = 7.0 Hz, 3 H, H20), 1.07 (dd, $^{3}J_{HP}$ = 13.6, $^{3}J_{HH}$ = 7.0 Hz, 3 H, H19), 0.97 (dd, $^{3}J_{HP}$ = 17.9, $^{3}J_{HH}$ = 7.0 Hz, 3 H, H21), 0.36 (dd, $^{3}J_{HP}$ = 15.9, $^{3}J_{HH}$ = 7.0 Hz, 3 H, H22).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 162.8 (C_q, C9), 158.6 (d, $^{5ts}J_{CP}$ = 7.3 Hz, C_q, C13), 152.5 (d, $^{4}J_{CP}$ = 1.7 Hz, C_q, C4), 150.5 (d, $^{2}J_{CP}$ = 27.6 Hz, C_q, C10), 147.0 (C_q, C6), 143.5 (d, $^{3}J_{CP}$ = 11.1 Hz, C_q, C5), 142.9 (CH, C8), 139.0 (CH, C14), 134.5 (d, $^{2}J_{CP}$ = 3.4 Hz, CH, C2), 131.0 (CH, C15), 128.0 (CH, C16), 127.7 (d $^{1}J_{CP}$ = 19.9 Hz, C_q, C1), 124.9 (CH, C7), 120.1 (d, $^{3}J_{CP}$ = 5.0 Hz, CH, C3), 30.7 (CH_2, C11 or C12), 30.6 (CH_2, C11 or C12), 26.1 (d, $^{1}J_{CP}$ = 5.7 Hz, CH, C17), 24.8 (d, $^{1}J_{CP}$ = 10.8, CH, C18), 20.2 (d, $^{2}J_{CP}$ = 6.6 Hz, CH_3, C19), 18.6 (d, $^{2}J_{CP}$ = 7.5 Hz, CH_3, C20), 18.0 (CH_3, C21), 17.7 (CH_3, C22).

^{31}P NMR (202 MHz, $CDCl_3$): δ 15.4 (br s).

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 15.4 (s).

HRMS (APCI^{+}) *m/z* (%) 635.0916 (^{79}Br) $[M+H]^{+}$ (<1%), 637.0898 (^{81}Br) (<1%) $[M+H]^{+}$, 555.1789 (100) $[M-Br]^{+}$.

IR (KBr disc) ν_{max}/cm^{-1} 3042w (ν_{Ar-H}), 2958s (ν_{C-H}), 1592s, 1443s, 1254s, 847vs, 735s, 443m.

Acenap(P*i*Pr$_2$)(BiPhI) 8

A saturated NaI(aq) solution (25 mL) was added to [Acenap(P*i*Pr$_2$)(BiPh)][BF_4] **5** (323 mg, 0.51 mmol) dissolved in CH_2Cl_2 (25 mL). The reaction mixture was stirred vigorously for 50 mins. The CH_2Cl_2 layer was removed and the aqueous layer extracted with CH_2Cl_2 (15 mL). The combined organic fractions were dried over magnesium sulfate. Removal of the solvent *in vacuo* afforded **8** as a yellow solid (265 mg, 0.39 mmol, 77%), m.p. 221.6−223.1 °C (decomp.). Crystals of **8** suitable for X-ray diffraction were obtained from MeCN by slow evaporation. On one occasion a crystal of **9**·$CHCl_3$ was obtained from $CHCl_3$ solution of the crude material.

Anal. calcd. for $C_{24}H_{27}BiPI$ (682.33 g mol^{-1}): C, 42.25; H, 3.99. Found: C, 42.25; H, 3.89.

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.61 (d, $^3J_{HH}$ = 7.2 Hz, 1 H, H8), 8.01 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, H14), 7.63 (d, $^3J_{HH}$ = 7.2 Hz, 1 H, H7), 7.56 (t, $^3J_{HH}$ = 7.2, $^3J_{HP}$ = 7.2 Hz, 1 H, H2), 7.36 (d, $^3J_{HH}$ = 7.2 Hz, 1 H, H3), 7.29 (t, $^3J_{HH}$ = 7.7 Hz, 2 H, H15), 7.18 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, H16), 3.52−3.44 (m, 4 H, H11 and H12), 2.49−2.37 (m, 2 H, H17 and H18), 1.11 (dd, $^3J_{HP}$ = 17.8, $^3J_{HH}$ = 7.1 Hz, 3 H, H20), 1.08 (dd, $^3J_{HP}$ = 13.6, $^3J_{HH}$ = 7.0 Hz, 3 H, H19), 1.00 (dd, $^3J_{HP}$ = 18.1, $^3J_{HH}$ = 7.0 Hz, 3 H, H21), 0.3 (dd, $^3J_{HP}$ = 16.0, $^3J_{HH}$ = 7.0 Hz, 3 H, H22).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 159.5 (C_q, C9), 155.1 (d, $^{5ts}J_{CP}$ = 6.2 Hz, C_q, C13), 152.7 (C_q, C4), 150.9 (d, $^2J_{CP}$ = 28.0 Hz, C_q, C10), 147.2 (C_q, C6), 146.1 (CH, C8), 143.2 (d, $^3J_{CP}$ = 11.3 Hz, C_q, C5), 139.6 (CH, C14), 134.4 (d, $^2J_{CP}$ = 3.7 Hz, CH, C2), 131.0 (CH, C15), 128.0 (CH, C16), 127.7 (d, $^1J_{CP}$ = 20.4 Hz, C_q, C1), 125.4 (CH, C7), 120.2 (d, $^3J_{CP}$ = 5.1 Hz, CH, C3), 30.7 (CH_2, C11 or C12), 30.7 (CH_2, C11 or C12), 26.1 (d, $^1J_{CP}$ = 5.2 Hz, CH, C17), 24.8 (d, $^1J_{CP}$ = 11.0 Hz, CH, C18), 20.3 (d, $^2J_{CP}$ = 5.8 Hz, CH_3, C21), 18.6 (d, $^2J_{CP}$ = 7.2 Hz, CH_3, C19), 17.9 (CH_3, C22), 17.7 (CH_3, C20).

^{31}P NMR (202 MHz, $CDCl_3$): δ 12.9 (br s).

^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 12.9 (s).

HRMS (APCI$^+$) *m/z* (%) 555.1758 (100) $[M-I]^+$.

IR (KBr disc) ν_{max}/cm^{-1} 3034w (ν_{Ar-H}), 2924s (ν_{C-H}), 1591s, 1442s, 1252s, 844vs, 735s, 444m.

Acenap(P*i*Pr$_2$)(BiI_2) 9

Method 1:

*n*BuLi (1.14 mL, 2.5 M solution in hexanes, 2.86 mmol) was added to a stirred solution of Acenap(P*i*Pr$_2$)Br (1.00 g, 2.86 mmol) in THF (20 mL) at −78 °C, over 30 mins. The reaction mixture was stirred for 2 h at this temperature, before being added to a solution of BiI_3 (1.69 g, 2.86 mmol) in THF (100 mL) in small batches over 30 minutes, at the same temperature. The resulting suspension was allowed to warm to room temperature overnight with stirring. The volatiles were removed *in vacuo* to give a brown oil which was washed with water (20 mL). After removal of the water, the residue was dried *in vacuo* to give a brown solid. Addition of CH_2Cl_2 (80 mL) gave a suspension from which the insoluble solid product was collected by filtration, thoroughly washed with CH_2Cl_2 (3 x 10 mL) and dried *in vacuo*.

Crystals of **9**·CH_2Cl_2 and **9**·THF suitable for X-ray diffraction were obtained from CH_2Cl_2 and THF, respectively.

Extremely low solubility of the solid product prevented collection of the solution state NMR spectra.

$^{31}P\{^1H\}$ SS DP MAS NMR (162 MHz): δ 61 (br s), 39 (br s), 13 (br s).

MS (EI) *m/z* (%) 605.0 (11) $[M-I]^+$, 589.7 (100) $[BiI_3]^+$, 478.1 (8) $[M-I_2]^+$, 462.8 (54) $[BiI_2]^+$, 435.0 (4) [Acenap(P*i*Pr)Bi]$^+$, 335.9 (57) $[BiI]^+$, 270.1 (19) [Acenap(P*i*Pr$_2$)H]$^+$.

HRMS (EI) *m/z* calcd. for $C_{18}H_{22}BiIP$ $[M-I]^+$: 605.0302, found 605.0304.

HRMS (ASAP) *m/z* (%) 748.9366 (32) $[M+O+H]^+$, 732.9418 (<1) $[M+H]^+$, 495.1268 (100) $[M-I_2+O+H]^+$, 462.7875 (52) $[BiI_2]^+$, 335.9 (47) $[BiI]^+$, 287.1556 (76) [Acenap(P(=O)*i*Pr$_2$)H + H$^+$], 270.1531 (6) [Acenap(P*i*Pr$_2$)H]$^+$.

HRMS (ASAP) *m/z* calcd. for $C_{18}H_{23}BiI_2P$ $[M+H]^+$: 732.9425, found 732.9418.

Method 2:

A solution of I_2 (0.15 g, 0.58 mmol) in diethyl ether (10 mL) was added dropwise to a suspension of Acenap(P*i*Pr$_2$)($BiPh_2$) **2** (0.18 g, 0.29 mmol) in diethyl ether (20 mL) over 30 minutes, followed by stirring overnight. The resulting suspension was filtered to give a red solid which was thoroughly washed with diethyl ether (3 x 10 mL).

Extremely low solubility of the solid product prevented collection of solution state NMR spectra.

Crystals of **9**·$CHCl_3$ suitable for X-ray diffraction were repeatedly obtained from extracts of the material with $CDCl_3$.

$^{31}P\{^1H\}$ SS DP MAS NMR (162 MHz): δ 103 (br s), 56 (br s), 21 (br s).

MS (ASAP) *m/z* (%) 748.9364 (<1) $[M+O+H]^+$, 605.0284 (9) $[M-I]^+$, 494.1187 (3) $[M-I_2+O]^+$, 478.1238 (41) $[M-I_2]^+$, 435.0694 (100) [Acenap(P*i*Pr)Bi]$^+$, 393.0227 (42) [Acenap(PH)Bi]$^+$, 287.1555 (20) [Acenap(P(=O)*i*Pr$_2$)H + H$^+$].

HRMS (ASAP) *m/z* calcd. for $C_{18}H_{23}OBiI_2P$ $[M+O+H]^+$: 748.9374, found 748.9364.

Further reaction: PhLi (0.15 mL, 1.9 M solution in di-*n*butylether, 0.27 mmol) was added slowly to the solid material obtained from Method 2 (0.095 g, 0.13 mmol (assumed)), suspended in THF (20 mL) at –78 °C. $^{31}P\{^1H\}$ NMR of the mixture after reaction indicated a *ca.* 50% conversion to **2** was achieved.

Acenap(P*i*Pr2)(BiPh(SPh)) 10

*n*BuLi (0.27 mL, 2.5 M solution in hexanes, 0.69 mmol) was added dropwise to a stirred solution of thiophenol (0.07 mL, 0.69 mmol) in THF (10 mL), cooled to −78 °C. The resulting solution was stirred at this temperature for 1 h. The cold thiolate solution was added in one batch to a suspension of **6** (0.36 g, 0.60 mmol) in THF (10 mL) also cooled to −78 °C. The resulting yellow solution was stirred at −78 °C for 1 h and then allowed to warm to room temperature overnight with stirring. Volatiles were

removed *in vacuo* to give a yellow oil. Toluene (20mL) was added and the resulting suspension was filtered. Volatiles were removed from the filtrate *in vacuo*. The resulting yellow oil was purified via recrystallisation from hot acetonitrile to yield **10** as yellow crystals (0.18 g, 0.31 mmol, 62%), m.p. 134–136 °C. The crystals obtained were suitable for X-ray diffraction.

Anal. calcd. for $C_{24}H_{27}BiPI$ (682.33 g mol^{-1}): C, 54.22; H, 4.85. Found: C, 54.05; H, 4.74.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ 9.43 (d, $^{3}J_{HH}$ = 7.0 Hz, 1 H, H8), 7.95 (d, $^{3}J_{HH}$ = 7.0 Hz, 2 H, H14), 7.63 (d, $^{3}J_{HH}$ = 6.9 Hz, 1 H, H7), 7.52 (dd, $^{3}J_{HH}$ = 7.1, $^{3}J_{HP}$ = 5.5 Hz, 1 H, H2), 7.44−7.38 (m, 2 H, -S-*o*-Ph), 7.31−7.27 (m, 3 H, H3 and H15), 7.21−7.15 (m, 1 H, H16), 7.14−7.08 (m, 2 H, -S-*m*-Ph), 7.01−6.95 (m, 1 H, -S-*p*-Ph), 3.44 (s, 4 H, H11 and H12), 3.47−3.42 (m, 2 H, H17 and H18), 1.10 (dd, $^{3}J_{HP}$ = 16.3, $^{3}J_{HH}$ = 7.0 Hz, 3 H, H22) 1.01 (dd, $^{3}J_{HP}$ = 12.2, $^{3}J_{HH}$ = 7.0 Hz, 3 H, H21), 0.90 (dd, $^{3}J_{HP}$ = 17.0, $^{3}J_{HH}$ = 6.9 Hz, 3 H, H20), 0.22 (dd, $^{3}J_{HP}$ = 14.7, $^{3}J_{HH}$ = 7.1 Hz, 3 H, H19).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 161.3 (C_q, C6), 160.6 (C_q, C13), 151.2 (C_q, C4), 147.8 (d, $^{2}J_{CP}$ = 28.8 Hz, C_q, C10), 147.0 (d, $^{3}J_{CP}$ = 1.5 Hz, C_q, C9), 143.0 (d, $^{3}J_{CP}$ = 10.1 Hz, C_q, C5), 142.1 (CH, C8), 141.4 (C_q, -S-*ipso*-Ph), 138.8 (CH, C14), 134.5 (CH, -S-*o*-Ph), 134.0 (d, $^{2}J_{CP}$ = 3.8 Hz, CH, C2), 130.9 (CH, C15), 129.5 (d, $^{1}J_{CP}$ = 4.8 Hz, C_q, C1), 128.2 (CH, -S-*m*-Ph), 127.5 (CH, C16), 124.6 (CH, C7), 123.9 (CH, -S-*p*-Ph), 119.6 (d, $^{3}J_{CP}$ = 2.9 Hz, CH, C3), 30.6 (CH_2, C11), 30.5 (CH_2, C12), 25.6 (d, $^{1}J_{CP}$ = 4.0 Hz, CH, C17), 25.3 (CH, C18), 20.7 (d, $^{2}J_{CP}$ = 9.8 Hz, CH_3, C22), 19.1 (d, $^{2}J_{CP}$ = 13.1 Hz, CH_3, C20), 18.7 (CH_3, C21), 18.0 (d, $^{2}J_{CP}$ = 5.7 Hz, CH_3, C19).

^{31}P NMR (162.0 MHz, $CDCl_3$): δ −14.0 (br s).

^{31}P{^{1}H} NMR (162.0 MHz, $CDCl_3$): δ −14.0 (s).

MS (ASAP+) *m/z* (%) 665.18 (3) [M+H$^+$], 633.21 (7) [M−S+H$^+$], 555.17 (100) [M−SPh]$^+$, 479.13 (4) [M−SPh−Ph+H$^+$], 435.07 (2) [M−SPh−Ph−*i*Pr]$^+$, 395.03 (3) [Bi(SPh)Ph]$^+$, 363.06 (13) [AcenapBiH_2]$^+$, 287.16 (3) [BiPhH]$^+$, 271.16 (2) [Acenap(P*i*Pr$_2$)H + H$^+$], 208.98 (4) [Bi].

HRMS (ASAP+) *m/z* calcd. for $C_{30}H_{33}BiPS$ [M+H$^+$]: 665.1844, found 665.1849; calcd. for $C_{24}H_{27}BiP$ [M−SPh+H$^+$]: 555.1654, found 555.1671.

Raman (glass capillary) ν_{max}/cm^{-1} 3041s (ν_{Ar-H}), 2920s (ν_{C-H}), 1580s, 1438m, 1334s, 1085m, 1001s, 579m, 417s, 300m, 259vs, 179vs.

Exploration of rational synthetic routes to diiodobismuthine 9

Two different routes to **9** were investigated as shown in Scheme 2 (main text). The first synthesis used slow addition of **1** to one equivalent of BiI_3 at –78 °C. The brown solid obtained after work-up was barely soluble in common organic solvents, which ruled out its analysis by solution state NMR. The solid state ^{31}P{^{1}H} DP NMR spectrum of the material revealed three major broad resonances centred at δ_P 61, 39 and 13 ppm, indicating several phosphorus containing species were present (Figure S2). Mass spectra (both ASAP and EI) confirmed the presence of **9** in the solid material through observation of intense (M+O+H)$^+$ and (M–I)$^+$ peaks. In addition, attempts to recrystallise the solid from warm THF and dichloromethane reproducibly gave a very small amount of crystals, which were shown to be **9**·THF and **9**·CH_2Cl_2, respectively, by single crystal X-ray diffraction.

Our second attempt for the rational synthesis of **9** utilised a double dearylation reaction with iodine (Scheme 2, main text). We postulated this reactivity based on a literature precedent, in which a tolyl group was displaced from a bismuth atom using iodine to generate a Bi–I motif and 4-iodotoluene.[5] The reaction of **2** with iodine yielded a red solid, whose insoluble nature prevented analysis by solution state NMR. High resolution mass spectra (ASAP) confirmed the presence of **9** in the solid material through observation of low intensity $(M+O+H)^+$ and also intense $(M–I)^+$ peaks. The solid state $^{31}P\{^1H\}$ DP NMR spectrum of the material revealed three major broad resonances centred at δ_P 107, 56 and 21 ppm, indicating several phosphorus containing species were present (Figure S2). Attempts to purify the barely soluble material by recrystallisation repeatedly led to formation of a very small amount of crystals, which were shown to be **9**·$CHCl_3$ by single crystal X-ray diffraction. Furthermore, reaction of the solid product with PhLi in THF gave **2** with a *ca*. 50% conversion (as judged by $^{31}P\{^1H\}$ NMR), indicating at least 50% of the crude material was **9**.

Neither of the two synthetic routes produces **9** in good purity, nevertheless **9** appears to be one of the major products in both these syntheses. Comparison of the two SS $^{31}P\{^1H\}$ DP NMR spectra in Figure S2 indicates the signals centred at *ca*. 18 and 60 ppm appear in both of these; it is hence likely that one of these resonances belongs to **9**.

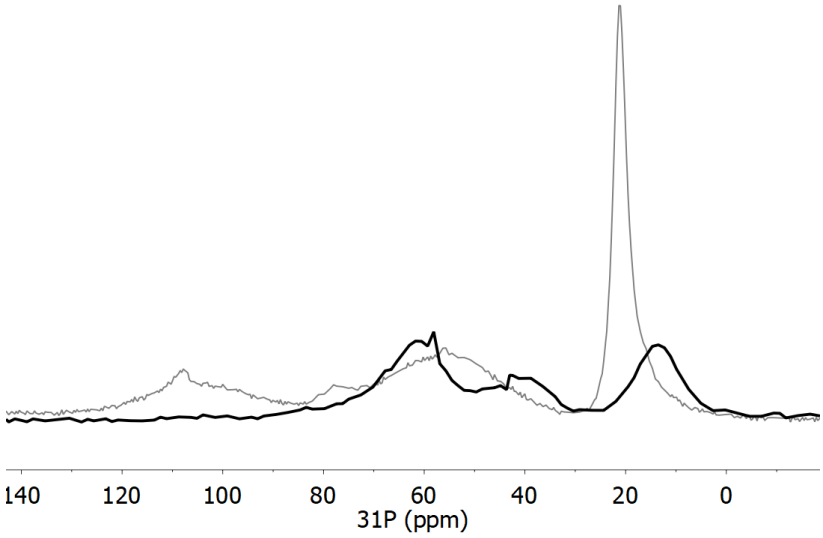


Figure S2: Solid state $^{31}P\{^1H\}$ DP NMR spectra of products obtained in preparations of **9**. Black trace: product of the reaction of **1** with BiI_3, grey trace: product of the reaction of **2** with I_2.

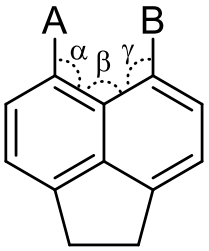
X-ray Diffraction

CCDC 1948146-1948155 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/structures. Selected crystallographic data are presented in Table S2.

The crystallographic data for **2, 3** and **5**–**8**, **9**·$CHCl_3$, **9**·CH_2Cl_2, **9**·THF and **10** were collected using a Rigaku FR-X Ultrahigh Brilliance Microfocus RA generator/confocal optics with a Rigaku XtaLAB P200 diffractometer with multi-layer mirror monochromated Mo-Kα radiation (λ = 0.71073 Å) at –180(±1) °C (**2**, **3**, **5**–**8**, **9**·$CHCl_3$) or at –100(±1) °C (**9**·CH_2Cl_2, **9**·THF and **10**).

All intensity data were collected (CrystalClear[6]) using ω steps accumulating area detector frames spanning at least a hemisphere of reciprocal space, and were corrected for Lorentz, polarisation and long-term intensity fluctuations. Absorption effects were corrected on the basis of multiple equivalent reflections using either CrystalClear[6] or CrysAlisPro.[7] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

The crystal structures of **5**, **7**, **8**, **9**·THF and **10** were solved using heavy-atom Patterson methods (PATTY),[8] those of **8**, **9**·THF and **10** using dual-space methods (SHELXT),[9] and all other structures were solved using direct methods (SIR2011).[10] All structures were refined by full-matrix least-squares against F^2 (SHELXL-2018/3).[9] Five of the structures (**2**, **3**, **6**, **7** and **9**·DCM) showed higher than expected electron density peaks in close proximity to the heavy bismuth atom. This arises from somewhat lower than ideal crystal quality, and possibly from minor errors in absorption correction. In all cases this electron density is under 6 % of the electron count of bismuth, so is likely to be statistically insignificant. All calculations were performed using the CrystalStructure crystallographic software package.[11] Images of crystal structures were obtained using Olex2.[12]



Splay angle = $\Sigma_{\alpha\beta\gamma} - 360$

Figure S3 Definition of the splay angle.

Table S1 Selected distances [Å] and bond angles and torsion angles [°] in various solvates of **9**.

	9·$CHCl_3$	**9**·CH_2Cl_2	**9**·THF
Distances			
P9–Bi1	2.7366(6)	2.746(3)	2.733(1)
Bi1–$I_{terminal}$	3.0295(3)	2.9523(9)	2.9774(5)
Bi1–$I_{bridging}$	3.1175(3)	3.2115(8)	3.0966(4)
Bi1–I' (secondary contact)	3.4723(5)	3.3966(9)	3.5013(4)
Angles			
P9–Bi1–I2'	174.6(3)	169.4(3)	173.7(3)
I1–Bi1–I2	172.17(1)	179.39(2)	171.70(1)
peri-region torsion angle Bi1–C1···C9–P9	1.6(3)	0.6(3)	4.6(3)
Splay angle[a]	3.6(3)	4(1)	3.7(6)

[a] Splay angle: the sum of the bay region angles − 360° (see **Figure S3**).

Table S2 Crystal and structure refinement data.

	2·**MeCN**	3	5	6
Formula	$C_{32}H_{35}BiNP$	$C_{42}H_{49}BiP$	$C_{24}H_{27}BBiF_4P$	$C_{24}H_{27}BiClP$
M_r	673.59	824.78	642.24	590.88
Colour/Habit	Colourless/prism	Colourless/prism	Colourless/prism	Yellow/prism
Crystal Dimensions [mm]	0.05×0.05×0.05	0.12×0.10×0.05	0.15×0.08×0.08	0.10×0.10×0.10
Crystal System	triclinic	triclinic	tetragonal	triclinic
Space Group	$P\bar{1}$	$P\bar{1}$	$I\bar{4}$	$P\bar{1}$
a [Å]	11.4076(6)	9.3657(13)	19.774(3)	8.2875(19)
b [Å]	11.4253(7)	11.2663(13)	19.774(3)	9.345(2)
c [Å]	12.0918(7)	18.712(2)	12.2188(18)	15.998(4)
α [°]	67.059(6)	75.478(7)	90	103.437(5)
β [°]	85.656(5)	85.310(9)	90	91.451(3)
γ [°]	73.633(5)	77.042(7)	90	110.982(4)
V [Å^3]	1391.49(16)	1862.0(4)	4777.7(12)	1117.1(5)
Z	2	2	8	2
$\rho_{calcd.}$ [g cm^{-3}]	1.608	1.471	1.786	1.757
μ [cm^{-1}]	6.402	4.839	7.474	8.075
$2\theta_{max}$	60.8	50.7	50.6	50.8
F_{000}	664.00	828.00	2480.00	572.00
Measured refln.	21401	18916	11827	14350
Unique refln. (R_{int})	7393 (0.0979)	6707 (0.0839)	4279 (0.0364)	4064 (0.1132)
R [I>2σ(I)]	0.0660	0.0619	0.0210	0.0531
wR_2	0.1670	0.1444	0.0410	0.1018
Goodness of Fit	1.027	1.037	0.740	0.996
Largest peak/hole [e Å^{-3}]	5.0/–3.26	1.81/–2.20	0.68/–0.55	2.51/–2.81

	7	**8**	**9**·$CHCl_3$	**9**·CH_2Cl_2
Formula	$C_{24}H_{27}BiBrP$	$C_{24}H_{27}BiIP$	$C_{19}H_{23}BiCl_3I_2P$	$C_{19}H_{24}BiCl_2I_2P$
M_r	635.34	682.34	851.51	817.07

Colour/Habit	Colourless/prism	Colourless/prism	Yellow/prism	Yellow/plate
Crystal Dimensions [mm]	0.10×0.08×0.05	0.20×0.05×0.05	0.03×0.03×0.03	0.04×0.03×0.01
Crystal System	triclinic	monoclinic	monoclinic	triclinic
Space Group	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a [Å]	7.899(3)	13.519(3)	10.4168(10)	9.2102(7)
b [Å]	10.340(3)	9.5435(18)	17.549(2)	11.6401(7)
c [Å]	15.648(5)	17.901(4)	13.3351(15)	12.2333(9)
α [°]	105.173(5)	90	90	68.221(6)
β [°]	91.407(5)	98.241(3)	93.355(3)	87.750(6)
γ [°]	110.229(4)	90	90	79.801(5)
V [Å^3]	1148.0(7)	2285.7(8)	2433.5(5)	1198.14(16)
Z	2	4	4	2
$\rho_{calcd.}$ [g cm^{-3}]	1.838	1.983	2.324	2.265
μ [cm^{-1}]	9.486	9.127	10.168	10.213
$2\theta_{max}$	51.0	54.8	50.7	58.2
F_{000}	608.00	1288.00	1568.00	752.00
Measured refln.	11285	14651	33835	25528
Unique refln. (R_{int})	4189 (0.0747)	4150 (0.0532)	4443 (0.0248)	5521 (0.0992)
R [I>2σ(I)]	0.0680	0.0256	0.0115	0.0744
wR_2	0.1807	0.0601	0.0274	0.1666
Goodness of Fit	1.078	0.988	1.059	1.110
Largest peak/hole [e Å^{-3}]	1.60/–2.05	2.08/–1.05	0.66/–0.32	2.70/-1.83

	9·THF	**10**
Formula	$C_{22}H_{30}BiI_2OP$	$C_{30}H_{32}BiPS$
M_r	804.24	664.60
Colour/Habit	Yellow/prism	Yellow/prism
Crystal Dimensions [mm]	0.04×0.03×0.03	0.16×0.12×0.10
Crystal System	monoclinic	monoclinic
Space Group	$P2_1/c$	$P2_1/n$

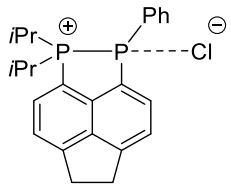
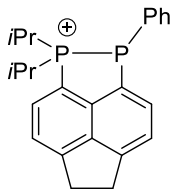
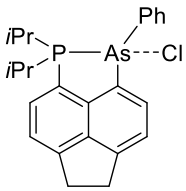
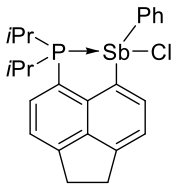
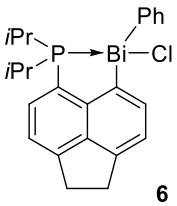
a [Å]	10.4445(2)	10.6281(14)
b [Å]	17.3541(4)	12.7934(16)
c [Å]	13.3809(3)	19.749(3)
α [°]	90	90
β [°]	92.068(2)	101.804(3)
γ [°]	90	90
V [Å^3]	2423.77(9)	2628.5(6)
Z	4	4
$\rho_{calcd.}$ [g cm^{-3}]	2.204	1.679
μ [cm^{-1}]	9.886	6.852
$2\theta_{max}$	58.1	50.8
F_{000}	1496.00	1304.00
Measured refln.	30554	31603
Unique refln. (R_{int})	5542 (0.0260)	4805 (0.0227)
R [I>2σ(I)]	0.0253	0.0124
wR_2	0.0682	0.0301
Goodness of Fit	1.132	1.044
Largest peak/hole [e Å^{-3}]	1.37/-1.57	0.59/-0.40

Computational details

Molecular calculations

Geometries were fully optimized at the B3LYP/6-31G* level[13-14] of density functional theory (DFT), together with a fine integration grid (75 radial shells with 302 angular points per shell); Sb and Bi were described with relativistically adjusted effective core potentials from the Stuttgart-Dresden (SDD) groups along with their associated polarised double-zeta valence basis[15-16] (d-exponent for Sb: 0.211); As was described with Curtis and Binning's 962(d) basis.[17] Because negative charge is expected to build up on the halogens, their basis sets were augmented with sets of diffuse s and p basis functions, i.e. 6-31+G* basis for F and Cl, the 962+(d) basis on Br, and the SDD effective core potential on I[18] along with its split-valence basis augmented with diffuse s and p functions and a d-polarisation functions with exponent 0.241.[19] Solid state structures were used as starting points for the optimisations. The nature of the minima was verified by computations of the harmonic frequencies at the same level of theory. Geometries were reoptimised using the polarizable conductor calculation model (CPCM)[20-21] with the parameters of chloroform, denoted CPCM. WBIs[22] were obtained in NBO analyses[23] *in vacuo* and in chloroform using the corresponding basis sets. To probe for the effect of dispersion the structures were reoptimized at the B3LYP-D3/CPCM level, i.e. including the empiricial correction from Grimme[24-25] with Becke-Johnson damping.[26-27] These computations were performed using the Gaussian09 suite of programs.[28]

Table S3 Salient bond distances [Å], observed in the solid (single crystal X-ray diffraction) and calculated at the B3LYP/SDD/6-31(+)G*/CPCM($CHCl_3$) level for the series of compounds in Figure 2 in the main paper [in brackets: Wiberg bond indices obtained at the same level].

					
					6
d(iPr$_2$)P–E $_{X\text{-}Ray}$	*2.2347(9)*	*n.a.*	*2.4239(7)*	*2.7104(8)*	*2.816(2)*
d(*i*Pr$_2$)P–E $_{calc}$	2.290 [0.88]	2.279 [0.90]	2.502 [0.71]	2.800 [0.50]	2.887 [0.44]
d E–Cl $_{X\text{-}Ray}$	*3.87*	*n.a.*	*2.9016(8)*	*2.6798(8)*	*2.768(2)*
d E–Cl $_{calc}$	3.639 [0.03]	n.a.	2.919 [0.21]	2.752 [0.37]	2.799 [0.35]

Optimised coordinates (in Å, xyz format) for all compounds studied computationally (B3LYP/SDD/6-31(+)G*/CPCM($CHCl_3$) level).

64
compound **2**
Bi 2.9586962163 0.844013305 0.2099757297
P 3.6280357893 -0.8134484696 2.9469159453
C 1.2348001672 1.1656682477 1.7117894053
C 0.1736518031 1.9276619378 1.2323968356
H 0.2228514499 2.3150970615 0.2195803559
C -0.983068044 2.2565678927 1.9886620459
H -1.7680590837 2.8579646686 1.5361088324
C -1.0628992184 1.8126859891 3.284829846
C 0.0000570193 1.0331860813 3.8026180194
C -0.2386186813 0.685245867 5.1532643329
C 0.697678228 -0.0659114889 5.8240373143
H 0.5698931645 -0.3510964015 6.8652100416
C 1.8518395848 -0.4806630562 5.1175139492
H 2.5744687605 -1.0809082756 5.6605678583
C 2.1076639128 -0.1656962444 3.7830449987
C 1.163414261 0.6591190532 3.0628024802
C -2.127186799 2.0017643715 4.3488635119
H -3.086650826 1.5761851881 4.0311754436
H -2.3107358056 3.0638886266 4.5492260369
C -1.564036155 1.2659664248 5.6072249443
H -1.426506272 1.9550813908 6.4491497621
H -2.2449436463 0.4813539572 5.9577924102
C 2.0937493573 2.2677610208 -1.4065110392
C 1.4531362726 1.6691745679 -2.5047807435
H 1.3290038776 0.5868224561 -2.5434509707
C 0.9599894317 2.4352976663 -3.5672007352
H 0.4647712871 1.9493823915 -4.4050094728
C 1.1067047 3.8242899164 -3.5505472626
H 0.7281086913 4.4241637158 -4.3744307625
C 1.7471853769 4.4381370114 -2.4703326051
H 1.867053366 5.5192994489 -2.4529932961
C 2.2354463943 3.6653359853 -1.4111287955
H 2.7305613334 4.1642622398 -0.5810273366
C 4.3266639221 2.4362544295 1.0942355993
C 5.6863108119 2.4186231703 0.7473110826
H 6.0730944758 1.6558655561 0.0732808422
C 6.5703371504 3.374759145 1.2594070264
H 7.620891818 3.3462172795 0.9798535984
C 6.1032574425 4.3641922698 2.1284577362
H 6.7880369 5.1077325953 2.5281613057
C 4.7515983942 4.3926067851 2.4810802063
H 4.381749285 5.1598264755 3.1574399709
C 3.8704852771 3.4339779932 1.9681203425
H 2.8229312258 3.4673839252 2.2576922265
C 3.2867388414 -2.6727212254 2.7546304441

H 4.2084347586 -3.0416409846 2.2834531198
C 3.047235284 -3.4812045515 4.0367677516
H 2.9396336502 -4.5452467515 3.788380885
H 2.1270823 -3.1660692836 4.5399265307
H 3.8736699534 -3.3937474357 4.7501013268
C 2.1377079762 -2.8855572253 1.7543190235
H 1.1919139359 -2.4947744469 2.1475437879
H 1.9991875608 -3.9565746553 1.5603410543
H 2.3342447937 -2.394310985 0.7950402211
C 4.9618003415 -0.738660258 4.279868872
H 4.6297445903 -1.2927388463 5.1667981268
C 5.2269407652 0.7191415082 4.6881793222
H 5.5711415603 1.3137400586 3.8344095294
H 6.0061810933 0.7551156269 5.4601369024
H 4.3299951268 1.1979003273 5.093421938
C 6.2490944553 -1.3991920822 3.7562580507
H 7.0407296698 -1.3268146607 4.5124645065
H 6.6094131957 -0.8994324269 2.8487496785
H 6.1107075309 -2.4608438737 3.5253419123

94
compound **3**
Bi 6.4642968456 7.3320178274 12.4007048069
P 8.9073356336 5.0915689089 12.4219175822
P 6.4184275627 9.0297074702 15.2351981697
C 6.1540126233 5.7788407357 10.6508706039
C 5.050314898 6.028631974 9.8374960123
H 4.3909782105 6.8529384926 10.0912232503
C 4.7010827343 5.2709556214 8.6868837878
H 3.8180336906 5.5409037176 8.1115765048
C 5.4920858596 4.2035380768 8.3440793582
C 6.6238392684 3.9148115247 9.1450534189
C 7.3038442167 2.7709513786 8.6635855019
C 8.422406271 2.3303324989 9.3305195238
H 8.9760457317 1.4509434637 9.0108549574
C 8.8550391379 3.0613774682 10.462688419
H 9.7424788199 2.700565905 10.9719840888
C 8.2139922397 4.1997082946 10.952070035
C 7.0129686628 4.6696350948 10.2948608736
C 5.3925632973 3.1995224537 7.2111653346
H 5.4524838686 3.6936707566 6.2338645245
H 4.4348038076 2.6659869445 7.2296222765
C 6.5967835615 2.2292266015 7.4359585531
H 6.259581426 1.1978060498 7.5948104174
H 7.2662059788 2.2050753075 6.5677381372
C 10.4991274959 5.8915249447 11.7561156157
H 10.905559792 6.3970334585 12.6432865197
C 10.1426554417 6.9781903451 10.7272165537
H 9.6866437097 6.5415134433 9.8309466728

H 11.0481533732 7.5121328182 10.4124532096
H 9.4440290098 7.7159350976 11.1361756991
C 11.5814472167 4.9572841758 11.1994472896
H 12.4693177194 5.5416740818 10.924046043
H 11.2356966518 4.4399933379 10.298234691
H 11.9001456118 4.2022379711 11.9256066657
C 9.5423427895 3.7061949349 13.5381062734
H 10.2309164226 3.0591275129 12.9799955795
C 8.3691829328 2.8451084263 14.0332127185
H 7.6494193471 3.4433217891 14.603301679
H 8.7399345949 2.0478199902 14.6900764144
H 7.8317442102 2.3748532003 13.2036331002
C 10.3133811421 4.307989221 14.7255184678
H 10.6468813091 3.5086577306 15.3992682152
H 9.6792814351 4.9888121198 15.3061773345
H 11.2024997023 4.8634271529 14.4084480156
C 5.4437928057 6.0424344871 14.0218310129
C 4.9325071245 4.8263468203 13.5786759977
H 4.9809196589 4.5937491329 12.5189249108
C 4.3514030613 3.8432056759 14.424931781
H 3.9720400436 2.9194582835 13.9939255385
C 4.3003693034 4.0903402422 15.7739543174
C 4.8025430967 5.3233736114 16.2569745264
C 4.6640895856 5.4115002632 17.6621939286
C 5.0855466966 6.5523679452 18.3050535183
H 5.0023286508 6.6714817307 19.3824527109
C 5.625412395 7.5981144472 17.5194787344
H 5.9247366719 8.5053089603 18.0384700631
C 5.7710134665 7.5402544857 16.1341021142
C 5.3662745659 6.3453319432 15.4320093634
C 3.7741062224 3.2616758443 16.930677513
H 4.2873563534 2.2951556109 16.998059213
H 2.7075118066 3.0382953464 16.8081335018
C 4.0330491321 4.1404226247 18.1971738202
H 3.1046630802 4.35303153 18.7404702646
H 4.6987884517 3.6363349518 18.9081274641
C 5.3073538688 10.4432394109 15.8582716767
H 5.6441966411 10.7240567473 16.866624976
C 5.457887828 11.6585772009 14.922729922
H 4.8785099776 12.5053929553 15.3127604341
H 5.0757551435 11.4238238628 13.9225322039
H 6.4944328247 11.9890306333 14.8124331816
C 3.8266733302 10.0359958116 15.9279681467
H 3.4665061609 9.6845390576 14.9536514468
H 3.219243072 10.9052759572 16.2113350247
H 3.6475274086 9.2451388614 16.6604239393
C 8.0435106304 9.3061483406 16.1743211707
H 7.8132075277 9.3046528763 17.2483390557
C 8.7055047287 10.6485033981 15.827993159

H 8.874900215 10.7484933971 14.7486216948
H 9.6821953528 10.719123942 16.3236976251
H 8.1080382995 11.502493457 16.1602062991
C 9.0036330775 8.1418589998 15.8827751597
H 9.9292088171 8.2612604631 16.4602966177
H 9.2757824494 8.1098359989 14.8205992213
H 8.5647679906 7.1746306309 16.1483403048
C 4.5275492635 8.5148311147 11.9124502344
C 4.6584872683 9.697454281 11.1655012488
H 5.6383988411 10.0141549466 10.8084271171
C 3.5473481336 10.4921437778 10.8588283568
H 3.6735313784 11.4023726848 10.2766103022
C 2.2767805134 10.1141202188 11.3000475711
H 1.4109105256 10.7280612665 11.0648947312
C 2.1261636396 8.9411287312 12.0451135147
H 1.139487929 8.6397827422 12.3905835122
C 3.2424756893 8.1521616882 12.3472954732
H 3.1043350478 7.2415042904 12.9260434886

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compound **4**
Bi 2.6091867834 1.9678314461 3.3025698589
P 3.6327914086 4.7754424171 3.3862394775
C 3.5715013528 2.2209609111 5.3592527443
C 3.5504101569 1.1256796253 6.2138341815
H 3.1216426435 0.1941970182 5.8539370604
C 4.0621715342 1.1599075297 7.5422240736
H 4.0170632194 0.263108193 8.1554777808
C 4.5977963216 2.3349385702 8.0160673046
C 4.6222065456 3.4613935521 7.1609334029
C 5.1952058924 4.5890610761 7.789882555
C 5.2882608178 5.7708983394 7.0858861683
H 5.7176672025 6.6679450445 7.5241969407
C 4.8087049726 5.8032716547 5.7522042633
H 4.8933319857 6.7408330535 5.20769898
C 4.2476786179 4.6980329677 5.1162230206
C 4.1290404175 3.4566514796 5.8285715773
C 5.2086605901 2.711125078 9.3542071929
H 6.0801010428 2.0872626344 9.5852742242
H 4.4962375145 2.5646426537 10.174514796
C 5.6068392134 4.2182811704 9.2027034539
H 5.097526003 4.8465548103 9.9429568641
H 6.6819796489 4.3691624726 9.3558779494
C 2.3526123041 6.1595819453 3.4858791081
H 2.8600541321 7.0112475934 3.9594566285
C 1.1877193143 5.7229076876 4.3888543738
H 0.6312802645 4.8894488355 3.9433208415
H 0.4865974388 6.5561587361 4.5189637437
H 1.5293314849 5.4143837734 5.3817665541

C 1.8395673861 6.6044691835 2.1082090351
H 1.053224425 7.3580701876 2.2378445037
H 1.4052315973 5.7672565713 1.5486409589
H 2.6268151895 7.0554268687 1.4972129115
C 5.0433753949 5.4808310162 2.341336465
H 5.0258220962 6.5705698105 2.4820836516
C 6.4167737964 4.946797731 2.7789909294
H 7.1905445978 5.3567623637 2.118213075
H 6.4606861932 3.8543590903 2.7042420313
H 6.6643016042 5.2283260665 3.8053711344
C 4.8058029547 5.1625013518 0.8528283715
H 4.8712834426 4.0838967123 0.6736233464
H 5.5761380743 5.6522415877 0.244453227
H 3.8316976159 5.5042797379 0.4927159522
C 4.5008290035 1.3103210824 2.2172132605
C 4.4587082583 1.1937499958 0.8194905345
H 3.5598245507 1.4669330025 0.2691270663
C 5.5672710717 0.7212814742 0.1080204786
H 5.5199447588 0.6352456195 -0.9748092399
C 6.7303224991 0.3562996529 0.7901487054
H 7.5920312546 -0.0126355287 0.2400032367
C 6.7803923955 0.4625199289 2.1828063038
H 7.682220692 0.175229246 2.7181662872
C 5.6715415895 0.936604611 2.8921572373
H 5.7229801406 1.0083481245 3.975693469
F 2.1794311238 -0.1243678171 3.799281947

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compound **5**
Bi 13.1555909113 15.2630847075 0.2377695228
P 10.531514101 15.083001276 -0.5863795805
F 15.4090525413 15.3029859606 1.6309996011
F 16.5178511966 13.7758807106 2.9653288975
F 17.489964917 14.5082311956 1.00238112
F 15.6433983256 13.1207298421 0.929669867
C 12.1000260087 14.5201223741 2.1103531964
C 12.8010977853 14.2499936745 3.2791760326
H 13.8747537149 14.4077412061 3.3091000453
C 12.174162748 13.7714476374 4.4651706596
H 12.7818779223 13.5809436322 5.3457297574
C 10.8128351938 13.5677674263 4.4646502473
C 10.0898046681 13.8372736054 3.280380325
C 8.7060365215 13.6017489326 3.4334349181
C 7.8648885591 13.8382041811 2.3654141532
H 6.7920613927 13.6822551496 2.4346954456
C 8.4240457249 14.2983740749 1.1465520531
H 7.7464838399 14.4866407183 0.3188460706
C 9.7905651897 14.5209921019 0.9822392435
C 10.6853558927 14.3047165871 2.0830662419

C 9.8482417767 13.0871912146 5.5336575281
H 9.877432584 13.7338838463 6.4180524663
H 10.1053928718 12.0785836123 5.8771151566
C 8.4405368956 13.116967031 4.846222615
H 7.9707778797 12.1265505083 4.8429562764
H 7.749009302 13.7866827035 5.3705603835
C 13.0848685412 17.4701992973 0.7624439489
C 12.6383966414 17.9492430387 2.0016553265
H 12.2513794276 17.2611371488 2.7481357607
C 12.6905090208 19.3169201764 2.288541924
H 12.3432727954 19.6796189143 3.2526967737
C 13.18871316 20.2152195358 1.3409282641
H 13.2283351811 21.2775762771 1.5661055539
C 13.6418416831 19.7445712595 0.106287621
H 14.0369694509 20.4384886022 -0.6311329207
C 13.5943952395 18.3762943176 -0.1803174811
H 13.9620881886 18.0275431927 -1.1436106997
C 9.5523597932 16.5474466481 -1.2212912056
H 8.550667668 16.1554448024 -1.440468423
C 10.1687536685 17.0855146533 -2.5238900424
H 11.1777873601 17.4764353245 -2.3520075434
H 9.5521919649 17.9092059938 -2.9012295697
H 10.2224901705 16.3264309691 -3.3109688732
C 9.4202618673 17.6479849545 -0.1577335357
H 8.7870899468 18.4505922773 -0.5533233919
H 10.3930516573 18.0774059271 0.0967117262
H 8.9580298706 17.2751236924 0.7608171432
C 10.3697845996 13.7116548781 -1.8634353375
H 10.9324718201 14.0944598009 -2.7248236766
C 8.9261895078 13.4259661058 -2.305076597
H 8.3238445569 13.0404890901 -1.4760482146
H 8.9384253088 12.6587677621 -3.087939433
H 8.4276258425 14.3079101848 -2.7180222569
C 11.0605890119 12.4305207994 -1.3664068743
H 11.0153787742 11.6673531558 -2.1512305203
H 10.5634190592 12.0282525753 -0.4774506804
H 12.1173523651 12.5893044678 -1.1262402715
B 16.2951273931 14.1523302669 1.6352912631

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compound **5a**
Bi 13.0181686666 15.2208551237 0.1467415904
P 10.4381802635 15.0455252691 -0.6056229436
C 12.0527791121 14.4829408085 2.0572496856
C 12.7808202251 14.211586873 3.2086034605
H 13.8577830511 14.3624139125 3.215380519
C 12.1770853759 13.7440678772 4.4107097417
H 12.8007637856 13.5531148856 5.2796596623
C 10.8128463478 13.5536480439 4.4407803936

C 10.0660317249 13.8235405228 3.2717192281
C 8.6834517432 13.6029741335 3.4535027337
C 7.8239886989 13.8422239525 2.3997466906
H 6.7516883522 13.6965276742 2.4904070576
C 8.361074888 14.291859583 1.1673058168
H 7.6685318666 14.4812573798 0.3524849631
C 9.7270452231 14.5012425276 0.9781767237
C 10.6389281773 14.2797853403 2.0615618
C 9.8655710651 13.0912835063 5.5326182157
H 9.9198772278 13.7455123783 6.410036289
H 10.1201960726 12.0833615114 5.8794857122
C 8.4440653803 13.1295314704 4.8742347536
H 7.9655489824 12.1436709823 4.886793479
H 7.7697421683 13.8089928083 5.4078757317
C 13.0639788892 17.4141088542 0.7088440072
C 12.6505534166 17.8870068624 1.9617683312
H 12.2241552919 17.2073044815 2.6941736756
C 12.7843937928 19.2423013229 2.2779735625
H 12.4613238723 19.6032651458 3.250830055
C 13.3306266058 20.1306683463 1.3474920618
H 13.4325764339 21.1833646693 1.5959168582
C 13.7509872487 19.6633174554 0.1000559977
H 14.1812797413 20.3499425135 -0.6239805951
C 13.6233979652 18.3074746456 -0.2178165633
H 13.964176701 17.9600591039 -1.1911547682
C 9.5204281594 16.5507731203 -1.2299508494
H 8.512845178 16.1779786634 -1.455642729
C 10.1512309561 17.0855662434 -2.5270923453
H 11.1572062941 17.479368725 -2.3466215764
H 9.5362538269 17.9085244697 -2.9072510218
H 10.2108373043 16.3280550526 -3.314703264
C 9.4049757349 17.6422430548 -0.1548539615
H 8.7796655267 18.4530029737 -0.5451612686
H 10.38241944 18.0612272748 0.0998446005
H 8.9383058818 17.2685182245 0.7609039569
C 10.2689252184 13.68415594 -1.8862373232
H 10.8295757688 14.066234758 -2.7486861439
C 8.8150903963 13.4250082082 -2.3154792455
H 8.2150856719 13.0352398269 -1.4868453467
H 8.8131362116 12.6679925782 -3.1076979154
H 8.3238666259 14.3171117234 -2.7150271803
C 10.9439726196 12.3913378311 -1.3980547448
H 10.8714302305 11.6319831935 -2.183936785
H 10.4530919423 11.9966554338 -0.5024253296
H 12.0077386556 12.5306627396 -1.1771354535

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compound **6**
Bi 2.6336983772 2.0895044838 3.269723671

Cl 1.7992776289 -0.5557828023 3.6461534198
P 3.6595515817 4.7851561217 3.4024304018
C 3.5679593765 2.2367026131 5.3552694503
C 3.5270486168 1.141166867 6.2079775205
H 3.0884846483 0.2128821279 5.851885149
C 4.0322305454 1.1663170904 7.5389634867
H 3.9692573425 0.2686493904 8.1489451411
C 4.5834835159 2.3318118 8.0184001256
C 4.6302394488 3.4579366095 7.164561708
C 5.2173016851 4.5767661658 7.7960959632
C 5.331747758 5.7582708161 7.0938867786
H 5.7727764913 6.6478691458 7.5352593413
C 4.8574865269 5.8006694419 5.7589676684
H 4.957324193 6.7378707758 5.2161885574
C 4.282523852 4.7022586166 5.1232627594
C 4.1430408736 3.4621522634 5.8309870495
C 5.1913560598 2.698361968 9.3600599581
H 6.0499097686 2.0595878365 9.5978245112
H 4.4700024675 2.5650072694 10.1746545769
C 5.6161466293 4.1983748424 9.2103387509
H 5.1147224418 4.8358360125 9.9479981912
H 6.6930482721 4.3307144976 9.3676347069
C 2.3504344339 6.1369024615 3.4947651505
H 2.8549711721 7.0006447189 3.9486571191
C 1.2054979403 5.6981484509 4.4221735609
H 0.6526694254 4.8509255981 3.9988936155
H 0.4966648999 6.5252934314 4.5462932653
H 1.5648613709 5.4116276394 5.4151443436
C 1.8142245854 6.5518892156 2.1165786246
H 1.0201765376 7.2971105651 2.2459590193
H 1.3832280102 5.7002172756 1.5768595004
H 2.5868572621 7.003784676 1.488176469
C 5.0441255058 5.4783187552 2.3211261825
H 5.0153280426 6.5685850483 2.4558050403
C 6.4280529761 4.9617172144 2.7466771939
H 7.1866183187 5.3715856701 2.0689235792
H 6.481488854 3.8693654489 2.6853245547
H 6.687645574 5.2597552935 3.7652415481
C 4.7868502323 5.1490518049 0.838401571
H 4.8573167154 4.0705420384 0.6632125744
H 5.5480027379 5.6403150482 0.2203954905
H 3.8075121646 5.485763732 0.487920135
C 4.5177484534 1.3587173236 2.2184162468
C 4.4657131678 1.1753293482 0.8283523872
H 3.5608678565 1.412047524 0.2716542181
C 5.5748300166 0.6788139263 0.1347296641
H 5.5217356642 0.5400263398 -0.9421816988
C 6.7453423711 0.3583325345 0.8263700794
H 7.60680978 -0.0294225353 0.2891744662

C 6.803246282 0.5322530346 2.2116310155
H 7.7103430687 0.2788016248 2.7548298878
C 5.6944637105 1.029760415 2.905032711
H 5.7512847689 1.1538524249 3.9832335985

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compound **7**
Bi 4.242255226 9.8736952922 4.4619588148
Br 5.0536113882 12.7326630485 3.9932329018
P 3.3772228902 7.1491562924 4.4062969353
C 3.3416983214 9.6100393061 2.3722204071
C 3.3544552554 10.6682159854 1.4727266859
H 3.7895508518 11.6153665892 1.7818309271
C 2.8154027424 10.5834693981 0.1577716815
H 2.8582073858 11.454175487 -0.4918997819
C 2.2461791114 9.3998581432 -0.2515320089
C 2.2277241242 8.3117090869 0.6512662904
C 1.5958362314 7.1757614983 0.0979205772
C 1.4825934119 6.0335447563 0.8620576477
H 0.996531548 5.1374049134 0.4861975606
C 2.020042292 6.0391148322 2.1736800684
H 1.9191791315 5.1338128228 2.7652925179
C 2.6567959664 7.1490766889 2.726768191
C 2.7665976251 8.3608707809 1.9632476744
C 1.5836815501 8.980188389 -1.5509380597
H 2.2775663189 9.0605070236 -2.3958803305
H 0.7280892605 9.622428474 -1.7896187186
C 1.1402803623 7.4970546904 -1.3132429122
H 0.0550868678 7.3792763885 -1.415077253
H 1.5958161496 6.8165725282 -2.0420676381
C 2.3113349176 10.5396994839 5.464358183
C 1.164405346 10.8987617384 4.7441964942
H 1.1562149235 10.8347487316 3.6590369126
C 0.0190905302 11.3411435824 5.4141551189
H -0.8658953736 11.6171231301 4.8459767888
C 0.0097150409 11.4269047156 6.8091037439
H -0.8813934249 11.7697799127 7.3281561226
C 1.1506212217 11.0747204428 7.5342616277
H 1.1508443943 11.1432335787 8.6192570316
C 2.2976019218 10.636210966 6.8638468522
H 3.1782493741 10.3723601029 7.4469998863
C 4.8621206525 5.9867677134 4.3893627414
H 5.2813816211 6.0948329142 5.3984389778
C 4.5291337739 4.5056163602 4.1547948121
H 5.4481400464 3.9124638243 4.2345395028
H 4.1184748631 4.3426483849 3.152875941
H 3.8197541982 4.1110638759 4.8886270291
C 5.9122417822 6.4811168307 3.3799179325
H 5.5262948458 6.4467161978 2.3552699969

H 6.7976225361 5.8366697551 3.4265422267
H 6.2403786092 7.5052874711 3.5882230094
C 2.1219684302 6.371598534 5.5645878649
H 1.9833460957 5.3374577171 5.223803989
C 2.6727835128 6.3485026709 7.000606667
H 1.9448784164 5.8668553487 7.6638903456
H 2.8420098677 7.3652302775 7.3729586418
H 3.6121698459 5.7920327631 7.083164805
C 0.7654801131 7.089639935 5.4956442957
H 0.8435068904 8.1253638362 5.8388106626
H 0.0503961511 6.5698550935 6.1444757816
H 0.3573448645 7.0936016958 4.4806138372

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compound **8**
Bi 2.0162303641 1.1443324335 0.6886622339
I 1.8944820513 -1.0411620528 -1.6596501801
P 2.4596482117 3.2367946303 2.6075445012
C 4.2309111767 1.6808693374 0.4238099591
C 5.0019777572 1.0287053452 -0.5299039622
H 4.551040868 0.2393784696 -1.1260519869
C 6.3697563903 1.3375099156 -0.7768217891
H 6.9107843946 0.7818026664 -1.5385656067
C 6.9685030266 2.3355988844 -0.043866797
C 6.1974299208 3.0143829397 0.9275980591
C 6.9434870887 4.0140089501 1.590777013
C 6.3290154953 4.7740889157 2.5637319022
H 6.8579119521 5.557266063 3.0999600654
C 4.9680274572 4.5171619558 2.8629970419
H 4.4955133939 5.1230199126 3.6325478849
C 4.2246282583 3.5286657346 2.2215818588
C 4.8342370302 2.7262147728 1.2006966025
C 8.3734009192 2.9098885584 -0.055528388
H 8.6305799395 3.3154022771 -1.0409873111
H 9.1213014527 2.1404584844 0.1686470001
C 8.3566850871 4.0300112163 1.0388892614
H 9.0922468488 3.8346100402 1.8280020528
H 8.6069847229 5.0106593554 0.6175756395
C 2.3708273035 -0.4661424131 2.262552115
C 1.2491546137 -1.0946993264 2.8241206486
H 0.243397255 -0.7986108373 2.5320031629
C 1.4049204581 -2.1199677223 3.763097941
H 0.5279854747 -2.6002286208 4.1898479011
C 2.6846748799 -2.5283339836 4.1462417203
H 2.8071196056 -3.3266094876 4.8734211328
C 3.8067014869 -1.9120406361 3.5862055642
H 4.8048282202 -2.2311554942 3.876097524
C 3.6511264607 -0.8859642941 2.6477762825
H 4.5332699771 -0.4226221881 2.2139522889

C 1.6508309266 4.8838231407 2.1854358856
H 2.2133063622 5.6369063486 2.7543981376
C 1.8144502041 5.1812775379 0.6860874299
H 2.8615572208 5.1521430332 0.370137949
H 1.2500016867 4.4668286569 0.0750421976
H 1.424444609 6.1822380803 0.4673074609
C 0.1739972449 4.9562677605 2.6024170787
H 0.0434616769 4.8970442229 3.6865499042
H -0.2472490531 5.9137411518 2.2736765741
H -0.4170138783 4.1582031154 2.1376313054
C 2.2937786432 3.0320193129 4.4760505592
H 2.2745191743 4.0495372574 4.8905523676
C 3.4807318437 2.2689580185 5.0859817852
H 4.4296967864 2.7912281692 4.9431494733
H 3.3146775551 2.1548370335 6.1639800425
H 3.572620944 1.2662470947 4.6547709864
C 0.9714235168 2.3225555483 4.8239469747
H 0.0943363559 2.8173823264 4.3986173827
H 0.9832818079 1.287276417 4.4678393337
H 0.8465468305 2.3020319718 5.9131958359

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compound **9** (dimer)
Bi -2.3079243988 0.9868585381 -0.0012838343
I -3.6070903883 2.9119300955 -2.0088878149
I -0.5510662429 -0.9395239229 1.9576203091
P -4.6678279402 0.7283293102 1.4806635993
C -3.300591887 -0.8342159691 -0.9398355831
C -2.7167435701 -1.4906269891 -2.0154773133
H -1.7831901136 -1.1162658229 -2.4272418909
C -3.2827182884 -2.6487198258 -2.6166964913
H -2.7753286044 -3.1136188414 -3.457986058
C -4.4580971804 -3.1539336182 -2.108469197
C -5.0608933945 -2.4949013807 -1.0126991044
C -6.2469494209 -3.1367305996 -0.5940746379
C -6.9457114255 -2.6168134253 0.4752304053
H -7.8582325836 -3.0769930787 0.8435373214
C -6.4529380896 -1.447268561 1.1052872365
H -7.015366029 -1.054406279 1.9463616885
C -5.2886523895 -0.798517148 0.6942646263
C -4.5297281428 -1.3315396407 -0.4006711137
C -5.3058650455 -4.3520604986 -2.4939533608
H -4.731021828 -5.2834740236 -2.4360689348
H -5.6630080598 -4.2700632576 -3.5271448576
C -6.4951096387 -4.3460830755 -1.474949325
H -7.4636560989 -4.2741890659 -1.983188692
H -6.5228504973 -5.267517246 -0.8817180229
C -5.896962517 2.1106427559 1.1270915254
H -5.8403242668 2.2063016886 0.0364092737

C -5.4389811351 3.4423320622 1.7465088788
H -4.4087199824 3.697568378 1.4796305171
H -6.0846499899 4.2452421879 1.3733563552
H -5.5260059778 3.4326262604 2.8380727987
C -7.3485292221 1.7898140431 1.5148395983
H -7.7345669419 0.9177242976 0.9823373737
H -7.4647583095 1.6237018792 2.5922496798
H -7.9786687531 2.6465808859 1.2476956231
C -4.5788743732 0.5239444961 3.3540472393
H -5.5614816243 0.8520682742 3.7169446062
C -3.5017531237 1.4520221535 3.9475822342
H -3.6314045461 2.4968067528 3.6533615904
H -3.5527839741 1.4048804374 5.0415489781
H -2.4993830196 1.1311317937 3.6451043982
C -4.3512640745 -0.9297972538 3.7958133556
H -5.1569228214 -1.5950035837 3.4775413885
H -3.4066650124 -1.3247650978 3.408234488
H -4.3012704775 -0.9588954832 4.8906790416
Bi 2.3079243988 -0.9868585381 0.0012838343
I 3.6070903883 -2.9119300955 2.0088878149
I 0.5510662429 0.9395239229 -1.9576203091
P 4.6678279402 -0.7283293102 -1.4806635993
C 3.300591887 0.8342159691 0.9398355831
C 2.7167435701 1.4906269891 2.0154773133
H 1.7831901136 1.1162658229 2.4272418909
C 3.2827182884 2.6487198258 2.6166964913
H 2.7753286044 3.1136188414 3.457986058
C 4.4580971804 3.1539336182 2.108469197
C 5.0608933945 2.4949013807 1.0126991044
C 6.2469494209 3.1367305996 0.5940746379
C 6.9457114255 2.6168134253 -0.4752304053
H 7.8582325836 3.0769930787 -0.8435373214
C 6.4529380896 1.447268561 -1.1052872365
H 7.015366029 1.054406279 -1.9463616885
C 5.2886523895 0.798517148 -0.6942646263
C 4.5297281428 1.3315396407 0.4006711137
C 5.3058650455 4.3520604986 2.4939533608
H 4.731021828 5.2834740236 2.4360689348
H 5.6630080598 4.2700632576 3.5271448576
C 6.4951096387 4.3460830755 1.474949325
H 7.4636560989 4.2741890659 1.983188692
H 6.5228504973 5.267517246 0.8817180229
C 5.896962517 -2.1106427559 -1.1270915254
H 5.8403242668 -2.2063016886 -0.0364092737
C 5.4389811351 -3.4423320622 -1.7465088788
H 4.4087199824 -3.697568378 -1.4796305171
H 6.0846499899 -4.2452421879 -1.3733563552
H 5.5260059778 -3.4326262604 -2.8380727987
C 7.3485292221 -1.7898140431 -1.5148395983

H 7.7345669419 -0.9177242976 -0.9823373737
H 7.4647583095 -1.6237018792 -2.5922496798
H 7.9786687531 -2.6465808859 -1.2476956231
C 4.5788743732 -0.5239444961 -3.3540472393
H 5.5614816243 -0.8520682742 -3.7169446062
C 3.5017531237 -1.4520221535 -3.9475822342
H 3.6314045461 -2.4968067528 -3.6533615904
H 3.5527839741 -1.4048804374 -5.0415489781
H 2.4993830196 -1.1311317937 -3.6451043982
C 4.3512640745 0.9297972538 -3.7958133556
H 5.1569228214 1.5950035837 -3.4775413885
H 3.4066650124 1.3247650978 -3.408234488
H 4.3012704775 0.9588954832 -4.8906790416

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compound **10**
Bi -0.2542025972 2.5519072409 8.5875045343
S 1.6601488652 4.212608989 9.6350069655
P -2.1291068403 0.8274057691 6.9854051426
C 0.1477422856 1.5018732274 5.4640189454
C -3.9012119707 1.1555503263 6.4458646318
C 2.4487482548 3.070946918 10.7724896636
C 0.4479472164 0.7735440766 3.0841536372
C 2.1693366357 2.0125887164 4.0719428076
C 0.8944956495 1.4270469715 4.2554075523
C 2.7887030444 2.2582819279 13.0442440813
C 2.1628161142 3.1277833282 12.1485566916
C 2.7305388903 2.70641568 5.1172834198
C 2.6569724367 1.7268579542 2.6635474936
C -2.1248764016 -0.9556593225 7.6143177419
C 3.3770508878 2.114565113 10.321480066
C -2.7860179401 -1.9950037549 6.6978466716
C -4.8436733503 1.0817660093 7.6594629404
C -1.4587255352 4.3834781584 7.978653578
C -0.6927820081 -1.3798187464 7.9815117149
C 0.7486370053 2.248995187 6.5363431775
C -3.208176888 5.9780459881 8.5481496625
C -1.9844321102 6.2232371668 6.4782476004
C -1.1245374943 0.8284159835 5.4484429393
C 1.4993067297 0.9098813158 1.9989728313
C -4.0168082342 2.5139256748 5.7369585397
C 2.0011081653 2.8152316114 6.3339222272
C -2.4516290055 4.8428031373 8.8575846578
C -1.553693294 0.2009727291 4.2797474462
C -1.231004372 5.0852722399 6.7869410287
C 3.7066933114 1.3100114551 12.585029785
C -2.9752330145 6.6694142306 7.3564395066
C -0.7870208491 0.1633799041 3.0887409151
C 3.9959305171 1.2423218386 11.2197605288

H -2.5251264736 -0.2840288679 4.2661980298
H -1.1814488902 -0.3425218689 2.2114866776
H 1.8434527028 -0.0716766768 1.6524864602
H 1.0958286037 1.4248657262 1.1190948893
H 3.5941931065 1.1579124938 2.6742124741
H 2.8630300519 2.6534351703 2.1151922874
H 3.7063413282 3.1791013775 5.0348393323
H 2.4539321995 3.3855787662 7.1415246345
H -4.1866290585 0.3687443757 5.7357414518
H -2.7061416024 -0.8927859526 8.5442295205
H -4.5811069874 1.8356731794 8.410930291
H -5.87407503 1.2767277824 7.3386770724
H -4.8298732323 0.0993041833 8.1429638416
H -3.3723407925 2.5689029958 4.8542629457
H -5.0519655991 2.6680309589 5.4083040517
H -3.7482354309 3.3372112192 6.4067204694
H -2.2280856029 -2.1137341978 5.7631235704
H -2.7980294599 -2.9702577532 7.2005041272
H -3.8214672243 -1.74020858 6.4507810136
H -0.237863708 -0.7052616463 8.7150770629
H -0.7034324181 -2.3853369077 8.4188967789
H -0.0468844341 -1.4078262948 7.0966352362
H -2.6462587253 4.3212927159 9.7931546281
H -3.9756229554 6.3216645493 9.2374126919
H -3.5609513824 7.5525468884 7.1150363439
H -1.7972915347 6.7595573771 5.5510240967
H -0.4674396317 4.7480994789 6.090703893
H 1.4469078858 3.8597224562 12.5118823114
H 2.5545530953 2.3215624026 14.1040852939
H 4.1914093846 0.6326807174 13.2828405186
H 4.709375331 0.5102245994 10.8493728615
H 3.6145733604 2.0594384477 9.2628446768

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(Acenap)(P*i*Pr$_2$)(PPhCl)

P 8.9341866447 8.335028533 10.4701930879
C 8.1451229297 6.7259019234 10.0079427331
C 8.7770956896 5.4908590228 10.1147509339
H 9.7874677955 5.4517233527 10.5158599747
C 8.1450590473 4.280048442 9.7072208408
H 8.6875413027 3.3454865253 9.8201653353
C 6.8696823028 4.3166588424 9.1791435621
C 6.2359358364 5.5704619297 9.0590902869
C 4.9382611091 5.4953586549 8.5165252826
C 4.213160726 6.6640782176 8.3586520852
H 3.2071008227 6.6591095576 7.9495280811
C 4.7963985417 7.903490192 8.7372830691
H 4.2095319615 8.8078027265 8.6056017267
C 6.0825704827 7.9715116208 9.2684362688

C 6.8358712874 6.7771243587 9.4533355078
P 7.0516451788 9.4197287865 9.7459819125
C 5.9197329014 3.2521219804 8.6573671192
H 5.6927379889 2.5065261613 9.42776901
H 6.3578916994 2.7058317644 7.8143513401
C 4.6303823794 4.0378470682 8.2216225357
H 4.406832135 3.8874576188 7.1592218432
H 3.7470561189 3.700284588 8.7758407324
C 8.7852426224 8.402219873 12.3111761697
C 8.0314602883 7.498107704 13.0754152318
H 7.4530832711 6.7215459935 12.5852053201
C 8.0290585029 7.5883939892 14.4683561818
H 7.445219385 6.8819674843 15.0518103282
C 8.7748255739 8.5808619173 15.110845978
H 8.771283254 8.6469919867 16.1951315971
C 9.5360652135 9.477927252 14.3577484216
H 10.1308094278 10.2404114975 14.8523234232
C 9.5499407617 9.3833327682 12.9650000649
H 10.1702965056 10.0624822521 12.3857810552
C 6.0969125007 10.5595637139 10.8752053237
H 5.31757611 10.9585779053 10.2122449359
C 5.4052210284 9.8145721491 12.027038212
H 4.7612197409 10.5228709339 12.5601177602
H 6.1266475285 9.4088279539 12.7401598324
H 4.7770346853 8.9957403726 11.664588048
C 6.9657188813 11.7304127644 11.3671369692
H 6.3334099012 12.4248512745 11.930856819
H 7.4215281753 12.2912047985 10.5451640471
H 7.7608157511 11.3843539662 12.0339694373
C 7.5674763771 10.3910732267 8.2351158704
H 8.3133397551 11.0995828246 8.6178109408
C 8.2484534856 9.473164608 7.2050379093
H 8.6107880669 10.0863026213 6.3729958016
H 7.5462486046 8.7367725191 6.800872173
H 9.1091171467 8.9425057435 7.6232462279
C 6.4032093642 11.1736324641 7.6052861542
H 6.7766407772 11.7101527167 6.726241679
H 5.9732990254 11.9158274199 8.283932469
H 5.6047114105 10.5040238875 7.2672074305
Cl 12.0924273262 6.6174779112 11.0330106591

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(Acenap)(P*i*Pr$_2$)(PPh)$^+$

P 8.9612749869 8.2630152656 10.4950370216
C 8.1596291932 6.6575156611 10.0656916262
C 8.7551774546 5.4100391856 10.2235267106
H 9.7432063832 5.3378688533 10.6703806776
C 8.1112319954 4.2034279776 9.8255474038
H 8.624514501 3.2592667909 9.9830464205

C 6.8566497689 4.2588573799 9.2495540029
C 6.2594395165 5.5241169113 9.0767161972
C 4.9797862383 5.466288282 8.4900193382
C 4.2898772442 6.6482087994 8.2819040132
H 3.2993446964 6.6583247628 7.837109943
C 4.8869174561 7.8817689298 8.6573727504
H 4.3245876508 8.7947934554 8.4863470242
C 6.1551312751 7.9322159437 9.2326715132
C 6.8730411747 6.7251252954 9.464730068
P 7.1223446445 9.3741795285 9.7340939109
C 5.8985600186 3.2049937732 8.7223708921
H 5.6237786581 2.4893651793 9.5054057087
H 6.3530856833 2.6224424594 7.913205442
C 4.6478270337 4.0106946725 8.2166731
H 4.4643066064 3.8413400074 7.1496712517
H 3.7345385065 3.7081074859 8.7412368753
C 8.8820377737 8.351058136 12.3355692386
C 8.1178772151 7.4871645679 13.137134838
H 7.4765066877 6.7417667744 12.6778649392
C 8.1852288306 7.5803413918 14.5277348547
H 7.5929854363 6.9071961683 15.1408921743
C 9.0096089905 8.5352674892 15.1307486607
H 9.0582106509 8.6040294184 16.2135944696
C 9.7799025723 9.3917394875 14.3408826093
H 10.4319518731 10.1257931856 14.8049623131
C 9.7256861793 9.2937632446 12.9493613595
H 10.3473547971 9.9447281009 12.3396609542
C 6.1702780702 10.4990311286 10.8768751484
H 5.4036722678 10.9167651563 10.2107290404
C 5.4585786754 9.7365407177 12.0047200832
H 4.8070984324 10.4382995455 12.5368199031
H 6.1680664921 9.3219005493 12.7245312275
H 4.8353356509 8.9237499934 11.6212833333
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H 6.4128315836 12.3378063122 11.9732410503
H 7.5123478174 12.2258692295 10.5952288201
H 7.8308652336 11.2845709448 12.068284933
C 7.6890025398 10.3584686265 8.2517799102
H 8.449128414 11.0374939031 8.6594701849
C 8.3551700766 9.4411581376 7.2117209556
H 8.7472704289 10.0604937637 6.3982113131
H 7.6364317483 8.735683602 6.7826619818
H 9.1938685586 8.8753812332 7.6290584597
C 6.554054115 11.1884584764 7.6269989073
H 6.9560608381 11.7364341776 6.7681606478
H 6.1358415797 11.9244128377 8.3194026739
H 5.7426336873 10.5510818667 7.259662814

54

(Acenap)(P*i*Pr$_2$)(AsPhCl)

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Cl 2.2513591549 -0.4341844157 4.8936082188
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C 3.0389535709 1.1990234812 8.0784858472
C 4.1474486919 1.2338319676 7.2412389524
C 5.4160532846 1.7267122582 7.6621392078
C 5.569467674 2.1870961901 8.951849044
C 4.4498970486 2.1487362865 9.8106677199
C 4.7286921645 2.6606436284 11.0953229772
C 3.7166235283 2.6976412517 12.0354555287
C 2.4303881864 2.2143158262 11.6800718819
C 2.1558883444 1.7026944467 10.413638585
C 3.1824808365 1.6660168074 9.4214468855
C 6.7468564708 2.7705773774 9.7125384031
C 6.18349132 3.0916944096 11.1412091023
C 0.4587765542 1.985710988 6.6089553915
C 1.1008477803 3.2162229626 6.4241775248
C 0.4593199496 4.2444913408 5.7279210981
C -0.8264059739 4.0528112867 5.2154407674
C -1.4683175605 2.8241906888 5.391239342
C -0.8257641308 1.7921094072 6.0794595662
C -0.8015832401 2.2339242561 10.2566056717
C -0.500718421 3.6627591187 9.7789967994
C -2.1573211363 1.7260091195 9.7365627392
C 0.2059858608 -0.5746920263 10.7135044378
C -0.1973903393 -0.3981766763 12.1865112384
C 1.3893487337 -1.5480737753 10.5756130367
H 4.0438378683 0.8686164705 6.2243556382
H 6.2392700891 1.7295602174 6.9526656369
H 3.8799477638 3.0880375028 13.0359339261
H 1.6434948847 2.2577529019 12.4278867844
H 7.1328837165 3.6713948681 9.221862526
H 7.580986865 2.0612174419 9.7616377417
H 6.7324613041 2.5524240103 11.9217936216
H 6.2728257869 4.158033668 11.3790456941
H 2.1001019969 3.3746802682 6.8177143986
H 0.9659960822 5.1955293943 5.586725706
H -1.3227092411 4.8541461057 4.6750843644
H -2.4638623299 2.6644355359 4.9861916965
H -1.3253762477 0.8324484709 6.1919894539
H -0.8258186743 2.2386909094 11.3542852691
H -1.2907760245 4.3294985558 10.1434130362
H -0.4778044664 3.7283268609 8.6882450553
H 0.454325293 4.0295113476 10.1666637967
H -2.1769430858 1.7024049207 8.6424674505
H -2.9474243821 2.4078254517 10.0707808512
H -2.4043785925 0.7265284236 10.1087819716
H -0.6465524155 -0.9875015845 10.1582498722

H 0.6191260606 0.0323294921 12.776433781
H -0.427213391 -1.3814214966 12.6129161304
H -1.0848526574 0.2291254135 12.3118581269
H 1.1187070571 -2.5079155541 11.0292817177
H 2.2772610824 -1.169254382 11.0927229145
H 1.652459157 -1.7386345391 9.5304467211

54

(Acenap)(P*i*Pr$_2$)(SbPhCl)

Sb 4.3327718253 -2.188986717 3.3509055854
Cl 3.5768603455 -4.8198744826 3.6416185741
P 5.3531201267 0.417247965 3.4260189622
C 5.1997830321 -2.0856894703 5.3645676881
C 5.1176828561 -3.174386845 6.2257832361
C 5.6076991843 -3.1571718339 7.5617285423
C 6.1879696805 -2.0073028344 8.0450357129
C 6.2743639312 -0.8871308653 7.1876130444
C 6.8866770087 0.2184735342 7.8180920425
C 7.0387661757 1.3934179493 7.1111224374
C 6.5759578465 1.4429783389 5.7724491941
C 5.9787568424 0.3550634661 5.1400350692
C 5.802022264 -0.8762667229 5.8506224754
C 6.7939938635 -1.6518192858 9.3901430776
C 7.2638100045 -0.1653035707 9.2369166613
C 6.1076661491 -2.8877208677 2.3020247058
C 7.3035238591 -3.2209757874 2.9549662281
C 8.3920451812 -3.7181830605 2.2311915929
C 8.2978393805 -3.8888884193 0.8476274776
C 7.1093136471 -3.5657798832 0.1886861567
C 6.0204306316 -3.0701981368 0.9125042941
C 6.7202982958 1.106986608 2.3220631326
C 8.1128030634 0.6034085389 2.7349133896
C 6.4515972261 0.7730063465 0.8423948316
C 4.0248110025 1.7500688675 3.5029449823
C 3.4466750069 2.1146902933 2.1269036984
C 2.9077661081 1.3318989133 4.4734979752
H 4.6586041718 -4.0910278846 5.868959817
H 5.5112072019 -4.0510593686 8.1726643436
H 7.499907149 2.2728390651 7.5521723144
H 6.7011631387 2.3745017895 5.2255686535
H 7.6311713718 -2.314397918 9.6386358483
H 6.061662954 -1.7601311371 10.1985943155
H 6.776467545 0.4897539528 9.9684456463
H 8.343084095 -0.0645044531 9.4009717327
H 7.3890736471 -3.102008772 4.0315199975
H 9.3121568455 -3.974611655 2.7502406772
H 9.144074045 -4.2768640648 0.2870658176
H 7.0261619766 -3.7026253791 -0.8863774795
H 5.100155942 -2.8326439355 0.3826993929

H 6.6830471286 2.1972161158 2.4549795233
H 8.8604533899 1.0286923577 2.054628022
H 8.1788078655 -0.4873782907 2.6631179512
H 8.3775463414 0.8962645314 3.7536952654
H 6.5226550812 -0.3052756355 0.6684911316
H 7.207754 1.2650883354 0.2191110197
H 5.4698122404 1.1076961327 0.4978019813
H 4.5322478537 2.6333059255 3.9148747223
H 2.6428401809 2.8489962984 2.2573177352
H 3.0170024897 1.2406367403 1.6238508498
H 4.1935198129 2.5629145029 1.4658343603
H 2.3535008391 0.4662405225 4.0928275556
H 2.1953790169 2.1577269702 4.5848302711
H 3.2928191379 1.0840932158 5.4671077664

Periodic calculations

Periodic planewave DFT calculations were performed using CASTEP version 18.1[29-30] using the PBE exchange correlation functional[31] with Tkatchenko-Scheffler (TS) dispersion corrections.[32] Pseudopotentials were generated using the CASTEP 18.1 on-the-fly generator with ZORA relativistic effects.[33] A planewave cut-off energy of 50 Ry and Monkhorst-Pack grid[34] k-point spacing of 0.04 2π/Å were found to be well converged for the present systems. Geometry optimization was performed using the experimentally derived structure of **3** allowing atomic positions and unit cell parameters to vary under quantum mechanical forces and stresses to produce model structure **3'$_{solid}$**. The molecular geometry of **3** was then extracted and placed in a 30 Å cubic unit cell and geometry optimized with the cell fixed to produce model **3'$_{isol}$**. Selected distances from **3'$_{isol}$** and **3'$_{solid}$**, are given in Table S4. **3'$_{solid}$** exhibits a P···P distance of 5.367 Å and P···Bi distances of 3.197 Å (P9···Bi1) and 3.196 Å (P29···Bi1). The computed quasi-linear P9···Bi1–C41 angle is 163.9°. This, together with the *peri*-region torsion angles and splay angles, was found to be in good agreement with experimental single crystal X-ray diffraction data, as well as computed structures in the gas phase and under implicit solvation (see Table 1 in the main text). The isolated structure, **3'$_{isol}$**, features a shorter P···P interatomic distance than **3'$_{solid}$**, likely due to the use of a dispersion correction with the lack of a crystal environment.

J-coupling calculations[33] were tested for supercell size convergence, where a 2 × 2 × 1 supercell was converged for **3'$_{solid}$** and the unit cell was converged for **3'$_{isol}$** (*i.e.*, the computed total isotropic *J* values did not vary by further increasing the supercell size). Isotropic *J*-coupling values, including their full decompositions, for **3'$_{isol}$** and **3'$_{solid}$** are given in

Table S5. These show the total isotropic *J* couplings are dominated by the Fermi-contact mechanism.

Table S4. Selected geometrical parameters computed for **3'$_{isol}$** and **3'$_{solid}$**.

	3'$_{isol}$	**3'$_{solid}$**
Distances [Å]		
P···Bi	3.201	3.197
	3.169	3.196
Bi–C(Ph)	2.330	2.330
P···P	5.251	5.367
Angles [°]		
P–Bi–C41	162.5	163.9
Peri-region torsion	3.1	0.3
angles [°]	8.3	8.8
Splay angles [°]	14.9	14.7
	14.1	14.4

Table S5 A breakdown of the computed isotropic *J* couplings in **3'$_{solid}$** and **3'$_{isol}$** into components of Fermi-contact (J_{isoFC}), spin-dipolar (J_{isoSD}), diamagnetic spin-orbit coupling (J_{isoDSO}) and paramagnetic spin-orbit coupling (J_{isoPSO}) mechanisms.

	d_{AB} / Å	J_{iso} / Hz	J_{isoFC} / Hz	J_{isoSD} / Hz	J_{isoDSO} / Hz	J_{isoPSO} / Hz
3'$_{solid}$						
J_{PP}	5.37	17.7	17.46	−0.01	0.02	0.25
$J_{PC(Ph)}$	5.46	70.7	70.91	−0.25	−0.03	0.10
J_{PBi}	3.20	1360	1363	1.05	0.07	−7.33
3'$_{isol}$						
J_{PP}	5.25	34.7	34.80	−0.40	0.19	0.07
$J_{PC(Ph)}$	5.48	75.2	74.91	0.23	0.06	0.03
J_{PBi}	3.21	1520	1525	0.91	−7.12	0.08

Optimized structures (SHELX format)

3'$_{solid}$

```
TITL  3 prime solid
CELL  1.54180   9.082168   11.11768   18.59197    75.8037   85.60284   78.22942
LATT -1
SFAC H C P Bi
H     1  0.2814430000000  0.4235160000000  0.5489090000000 1.0
H     1  0.7185570000000  0.5764840000000  0.4510910000000 1.0
H     1  0.2607930000000  0.3577820000000  0.4343410000000 1.0
H     1  0.7392070000000  0.6422180000000  0.5656590000000 1.0
H     1  0.8831150000000  0.9194600000000  0.5009900000000 1.0
H     1  0.1168850000000  0.0805400000000  0.4990100000000 1.0
H     1  0.9262430000000  0.9792150000000  0.6149410000000 1.0
H     1  0.0737570000000  0.0207850000000  0.3850590000000 1.0
H     1  0.9480970000000  0.3068820000000  0.7025450000000 1.0
H     1  0.0519030000000  0.6931180000000  0.2974550000000 1.0
H     1  0.9737650000000  0.9841140000000  0.7214750000000 1.0
H     1  0.0262350000000  0.0158860000000  0.2785250000000 1.0
H     1  0.4214490000000  0.1257240000000  0.6922150000000 1.0
H     1  0.5785510000000  0.8742760000000  0.3077850000000 1.0
H     1  0.3624850000000  0.9312250000000  0.7728400000000 1.0
H     1  0.6375150000000  0.0687750000000  0.2271600000000 1.0
H     1  0.2974020000000  0.1714500000000  0.0707140000000 1.0
H     1  0.7025980000000  0.8285500000000  0.9292860000000 1.0
H     1  0.3549260000000  0.3737440000000  0.9966490000000 1.0
H     1  0.6450740000000  0.6262560000000  0.0033510000000 1.0
H     1  0.2973720000000  0.6249730000000  0.9179050000000 1.0
H     1  0.7026280000000  0.3750270000000  0.0820950000000 1.0
H     1  0.5526260000000  0.4948270000000  0.9412870000000 1.0
H     1  0.4473740000000  0.5051730000000  0.0587130000000 1.0
H     1  0.3139160000000  0.6467650000000  0.5785960000000 1.0
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H     1  0.0725830000000  0.7955790000000  0.5661150000000 1.0
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H     1  0.8519660000000  0.7433210000000  0.6485530000000 1.0
H     1  0.1480340000000  0.2566790000000  0.3514470000000 1.0
H     1  0.8782370000000  0.5366680000000  0.7410720000000 1.0
H     1  0.1217630000000  0.4633320000000  0.2589280000000 1.0
H     1  0.1226650000000  0.3869550000000  0.7543310000000 1.0
H     1  0.8773350000000  0.6130450000000  0.2456690000000 1.0
H     1  0.5000050000000  0.2333590000000  0.3329870000000 1.0
H     1  0.4999950000000  0.7666410000000  0.6670130000000 1.0
H     1  0.3936220000000  0.1181040000000  0.3774960000000 1.0
H     1  0.6063780000000  0.8818960000000  0.6225040000000 1.0
H     1  0.6182970000000  0.9646950000000  0.3998040000000 1.0
H     1  0.3817030000000  0.0353050000000  0.6001960000000 1.0
H     1  0.7242550000000  0.0808440000000  0.3570560000000 1.0
H     1  0.2757450000000  0.9191560000000  0.6429440000000 1.0
```

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C 2 0.6296570000000 0.6510000000000 0.4640220000000 1.0
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