Supporting information

Highly functionalised (γ-azido/γ-fluoro-β-iodo)vinyl derivatives from phosphorus based allenes or allenoates: I•••O halogen bonding interactions

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**Figure S1.** ORTEP diagram of compound 6 (probability ellipsoid at 30%). CCDC 1905975.

**Figure S2.** ORTEP diagram of compound 17 (probability ellipsoid at 30%). Hydrogen atoms are omitted for clarity. CCDC 1905976.
Figure S3. ORTEP diagram of compound 18 (probability ellipsoid at 30%). Hydrogen atoms are omitted for clarity. CCDC 1905977.

Figure S4. ORTEP diagram of compound 19 (probability ellipsoid at 30%). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] with esds are given in parentheses: Compound 16 P1-C13 1.844(6), C13-C14 1.329(8), C14-C15 1.516(9), N1-C15 1.485(10), N1-N2 1.244(11), N2-N3 1.119(12), I1-C14 2.112(5), C13-C16 1.488(8). CCDC 1905978.
Figure S5: ORTEP diagram of compound 20 (probability ellipsoid at 30%). Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] with esds are given in parentheses: P1-C13 1.822(13), I1-C14 2.102(12), C13-C14 1.315(18), N1-C15 1.50(2), N1-N2 1.23(2), N2-N3 1.12(2), C16-C13 1.521(19). CCDC 1905979.

Figure S6: ORTEP diagram of compound 25 (probability ellipsoid at 30%). Hydrogen atoms are omitted for clarity. CCDC 1905980.
Figure S7: ORTEP diagram of compound 27 (probability ellipsoid at 30%). Hydrogen atoms are omitted for clarity. CCDC 1905981.

Figure S8: ORTEP diagram of compound 29 (probability ellipsoid at 30%). Hydrogen atoms are omitted for clarity. CCDC 1905982.
**Figure S9:** ORTEP diagram of compound 30 (probability ellipsoid at 30%). Hydrogen atoms are omitted for clarity. CCDC 1905983.

**Figure S10:** ORTEP diagram of compound 31 (probability ellipsoid at 30%). Hydrogen atoms are omitted for clarity. CCDC 1905984.
**Figure S11**: ORTEP diagram of compound 32 (probability ellipsoid at 30%). Hydrogen atoms are omitted for clarity. CCDC 1905985.

**X-ray data:**

Crystallographic data were collected on a Bruker APX-II-SMART using Mo-Kα radiation (λ = 0.71073 Å) and have been deposited at the Cambridge Crystallographic Data Center (CCDC). Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

**Compound 6**: C22H19I2OP, \( M = 584.14 \), Orthorhombic, Space group \( p_{n\_a\_21} \), \( a = 19.5490(16) \), \( b = 9.8719(8) \), \( c = 10.8488(8) \) Å, \( V = 2093.7(3) \) Å³, \( \alpha = 90 \), \( \beta = 90 \), \( \gamma = 90 \), \( Z = 4 \), \( \mu = 3.089 \) mm⁻¹, data/restraints/parameters: 3647/1/237, R indices \( (I > 2\sigma(I)) \) R1 = 0.0347, wR2 (all data) = 0.1021. CCDC No. 1905975.

**Compound 17**: C21H17I3OP, \( M = 485.25 \), Monoclinic, Space group \( P 1 21/c 1 \), \( a = 9.1543(3) \), \( b = 10.0610(4) \), \( c = 22.0753(9) \) Å, \( V = 2032.48(13) \) Å³, \( \beta = 91.464(3) \), \( Z = 4 \), \( \mu = 13.245 \) mm⁻¹, data/restraints/parameters: 3907/0/244, R indices \( (I > 2\sigma(I)) \) R1 = 0.0726, wR2 (all data) = 0.1985. CCDC No. 1905976.

**Compound 18**: C22H19I3OP, \( M = 499.27 \), Monoclinic, Space group \( P2(1)/c \), \( a = 8.209(3) \), \( b = 16.624(7) \), \( c = 15.715(6) \) Å, \( V = 2142.9(14) \) Å³, \( \beta = 92.215(6) \), \( Z = 4 \), \( \mu = 1.586 \) mm⁻¹,
data/restraints/parameters: 3686/0/254, R indices (I > 2σ(I)) R1 = 0.0268, wR2 (all data) = 0.0698. CCDC No. 1905977.

**Compound 19:** C$_2$H$_{19}$In$_3$O$_2$P, $M = 515.27$, Orthorhombic, Space group $P 21 21 21$, $a = 8.3026(2)$, $b = 8.5630(2)$, $c = 30.1250(8)$ Å, $V = 2141.75(10)$ Å$^3$, $α = 90$, $β = 90$, $γ = 90$, $Z = 4$, $μ = 12.643$ mm$^{-1}$, data/restraints/parameters: 3737 /0/263, R indices (I > 2σ(I)) R1 = 0.0476, wR2 (all data) = 0.1264. CCDC No. 1905978.

**Compound 20:** C$_{21}$H$_{16}$ClIN$_3$OP, $M = 519.69$, Orthorhombic, Space group $P_21 21 21$, $a = 29.548(4)$, $b = 8.3033(8)$, $c = 8.5609(11)$ Å, $V = 2100.4(4)$ Å$^3$, $α = 90$, $β = 90$, $γ = 90$, $Z = 4$, $μ = 1.745$ mm$^{-1}$, data/restraints/parameters: 3693/0/253, R indices (I > 2σ(I)) R1 = 0.0780, wR2 (all data) = 0.2136. CCDC No. 1905979.

**Compound 25:** C$_{30}$H$_{25}$IN$_3$OP, $M = 601.40$, Triclinic, Space group $P-1$, $a = 8.9643(4)$, $b = 11.6596(6)$, $c = 14.2643(7)$ Å, $V = 1324.64(11)$ Å$^3$, $α = 69.832(2)$, $β = 71.872(2)$, $γ = 79.193(2)$, $Z = 2$, $μ = 1.297$ mm$^{-1}$, data/restraints/parameters: 3554/1/235, R indices (I > 2σ(I)) R1 = 0.0308, wR2 (all data) = 0.0875. CCDC No. 1905980.

**Compound 27:** C$_{15}$H$_{17}$Cl$_2$O$_3$P, $M = 530.06$, Monoclinic, Space group $P 21/n$, $a = 9.1150(7)$, $b = 10.3990(10)$, $c = 19.1186(18)$ Å, $V = 1810.7(3)$ Å$^3$, $β = 92.325(4)$, $Z = 4$, $μ = 3.568$ mm$^{-1}$, data/restraints/parameters: 3140/0/194, R indices (I > 2σ(I)) R1 = 0.0869, wR2 (all data) = 0.2603. CCDC No. 1905981.

**Compound 29:** C$_{22}$H$_{19}$FIO, $M = 476.24$, Monoclinic, Space group $P2(1)$, $a = 9.6921(13)$, $b = 9.8549(12)$, $c = 11.1815(15)$ Å, $V = 1015.7(2)$ Å$^3$, $θ = 107.996(4)$, $Z = 2$, $μ = 1.671$ mm$^{-1}$, data/restraints/parameters: 11020/2/733, R indices (I > 2σ(I)) R1 = 0.0308, wR2 (all data) = 0.0944. CCDC No. 1905982.

**Compound 30:** C$_{22}$H$_{19}$FIO$_2$P, $M = 492.24$, Monoclinic, Space group $Pn$, $a = 8.2948(19)$, $b = 26.144(6)$, $c = 14.533(3)$ Å, $V = 3142.3(12)$ Å$^3$, $θ = 94.408(4)$, $Z = 6$, $μ = 1.627$ mm$^{-1}$, data/restraints/parameters: 3554/1/235, R indices (I > 2σ(I)) R1 = 0.0724, wR2 (all data) = 0.1884. CCDC No. 1905983.

**Compound 31:** C$_{22}$H$_{16}$ClFIOP, $M = 496.66$, Monoclinic, Space group $P2(1)/c$, $a = 8.2639(11)$, $b = 8.5040(13)$, $c = 29.114(5)$ Å, $V = 2030.9(5)$ Å$^3$, $θ = 96.974(5)$, $Z = 4$, $μ = 1.803$ mm$^{-1}$,
Compound 32: $C_{14}H_{17}FIO_{3}P$, $M = 410.15$, Monoclinic, Space group $P2(1)/c$, $a = 16.7231(17)$, $b = 7.8520(8)$, $c = 12.4005(17)$ Å, $V = 1582.0(3)$ Å$^3$, $\beta = 103.700(13)$, $Z = 4$, $\mu = 2.139$ mm$^{-1}$, data/restraints/parameters: $2789/0/183$, R indices ($I > 2\sigma(I)$) $R_1 = 0.0536$, $wR_2$ (all data) = 0.1714. CCDC No. 1905985.

Figure S12. H-coupled $^{19}$F NMR spectrum of compound 28 showing triplet of doublet.
Figure S13. $^1$H NMR spectrum of compound 5

Figure S14. $^1$H NMR spectrum of compound 6
**Figure S15.** $^1$H NMR spectrum Expansion of compound 6

**Figure S16.** $^{13}$C NMR spectrum of compound 6
Figure S17. $^1$H NMR spectrum of compound 7

Figure S18. $^{13}$C NMR spectrum of compound 7
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Figure S24. $^1$H NMR spectrum of compound 11
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