Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Catalyst-free synthesis of α^1-oxindole-α-hydroxyphosphonates *via* phospha-aldol reaction of isatins employing *N*-heterocyclic phosphine (NHP)-thiourea

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Supporting information

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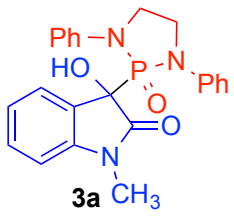
1. General Information

All reactions were carried out under an argon atmosphere in oven-dried glassware with magnetic stirring bar. Dry solvents (THF, toluene, and DCM) were obtained by solvent purification system under argon. All commercially available reagents and istains (**1e-o**) were used as received without further purification. Starting materials NHP reagents and isatins (**1a,p-r**) were prepared by earlier reported methods.[1,2] Purification of reaction products was carried out by flash column chromatography using silica gel 60 (230-400 mesh). Analytical thin layer chromatography was performed on 0.25 mm aluminum-backed silica gel 60-F plates. Visualization was accompanied with UV light and $KMnO_4$ solution. Concentration under reduced pressure refers to the removal of volatiles using a rotary evaporator attached to a dry diaphragm pump (10-15 mm Hg) followed by pumping to a constant weight with an oil pump (<300 mTorr). Infrared (IR) spectra were recorded on an IR spectrometer with KBr wafers or a film on KBr plate. High-resolution mass spectra (HRMS) were recorded on LCMS-IT-TOF mass spectrometer using ESI (electrospray ionization) or APCI (Atmospheric Pressure Chemical Ionization). ^{1}H NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on 400 MHz NMR spectrometer. The ^{1}H chemical shifts are referenced to residual solvent signals at δ 7.26 ($CHCl_3$) or δ 0.00 (TMS). ^{1}H NMR coupling constants (*J*) are reported in Hertz (Hz) and multiplicities are indicated as follows: s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet). ^{13}C NMR spectra were proton decoupled and recorded in $CDCl_3$ or DMSO-d_6 on 100.5 MHz NMR spectrometer. The ^{13}C chemical shifts are referenced to solvent signals at δ 77.16

($CDCl_3$). ^{31}P NMR spectra were proton decoupled and recorded in $CDCl_3$ or DMSO-d_6 on 162 MHz NMR spectrometer. ^{31}P chemical shifts are reported relative to 85% H_3PO_4 (0.00 ppm) as an external standard.

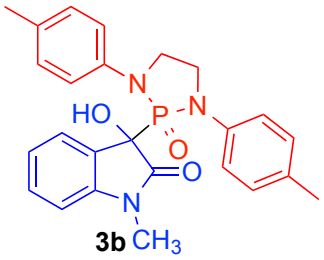
2. Experimental procedure and characterization data: Isatin **1** (0.1 mmol) and NHP-thiourea **2** (0.15 mmol) were dissolved in $CHCl_3$ (1 mL) in a two-dram vial with a closed cap and PTFE at room temperature. The resulting reaction mixture was stirred at 61 °C for 15 h. After stirring for 15 h at 61 °C, the reaction mixture was cooled down to room temperature. The volatiles were removed under reduced pressure. The residue was subjected to column chromatography on silica gel (gradient eluent of DCM:EtOAc 9/1) to give the product **3**.



3a

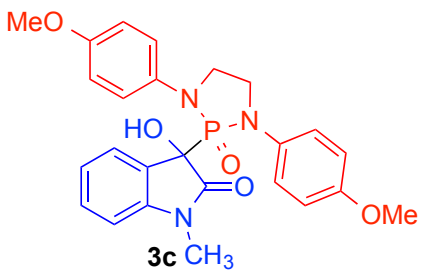
3-Hydroxy-1-methyl-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)indolin-2-one (3a): White solid **3a** (41.5 mg, 99%). R_f = 0.22 (Hexanes:EtOAc = 1:1); mp: 165 °C (decomp.) IR (KBr, cm^{-1}): 3433, 3057, 2941, 2881, 1724, 1616, 1491, 1259, 1008; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49 – 7.47 (m, 2H), 7.40 – 7.30 (m, 6H), 7.24 – 7.22 (m, 1H), 7.11 – 7.05 (m, 2H), 6.90 (td, *J* = 7.6, 0.8 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 7.2 Hz, 1H), 5.62 (d, *J* = 7.6 Hz, 1H), 3.82- 3.73 (m, 4H), 3.06 (s, 3H); **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 171.8 (d, *J* = 5.2 Hz), 144.1, 140.7 (dd, *J* = 26.9, 5.9 Hz), 130.2, 129.3 (d, *J* = 10.4 Hz), 125.5, 124.1 (d, *J* = 3.7 Hz), 122.8 (d, *J* = 1.5 Hz), 122.4,

118.1 (d, J = 75.5, 4.4 Hz), 108.1, 72.8 (d, J = 8.2 Hz), 42.6 (d, J = 13.3 Hz), 42.4 (d, J = 12.6 Hz), 26.2; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 12.26 ppm; **HRMS** (ESI) calcd for $C_{22}H_{22}N_3O_3P$ [M+Na]$^+$: 442.1291; found: 442.1294.



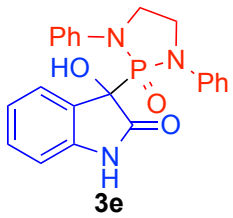
3b

3-Hydroxy-1-methyl-3-(2-oxido-1,3-di-p-tolyl-1,3,2-diazaphospholidin-2-yl)indolin-2-one (3b): White solid **3b** (38 mg, 85%). R_f = 0.40 (CH_2Cl_2:EtOAc = 9:1); mp: 180 °C (decomp.); IR (KBr, cm^{-1}): 3425, 3059, 2864, 1724, 1614, 1512, 1469, 1265, 1024; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.37 (d, J = 8.4 Hz, 2H), 7.27 – 7.13 (m, 7H), 6.78 (td, J = 7.2, 0.8 Hz, 1H), 6.68 (d, J = 7.6 Hz, 1H), 6.55 (d, J = 7.6 Hz, 1H), 5.61 (d, J = 12.8 Hz, 1H), 3.86 – 3.68 (m, 4H), 3.07 (s, 3H), 2.33 (s, 3H), 2.31 (s, 3H); **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 172.0 (d, J = 5.2 Hz), 144.0 , 138.2 (dd, J = 21.0, 6.0 Hz), 132.0 (d, J = 50.8 Hz), 130.1, 129.8 (d, J = 7.5 Hz), 125.6, 124.3 (d, J = 5.2 Hz), 122.7, 118.4 (dd, J = 84.5, 4.5 Hz), 108.0, 72.7 (d, J = 7.4 Hz), 42.8 (d, J = 13.4 Hz), 42.7 (d, J = 12.6 Hz), 26.2, 20.6; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 12.49 ppm; **HRMS** (ESI) calcd for $C_{25}H_{26}N_3O_3P$ [M+Na]$^+$: 470.1604; found: 470.1614.



3c

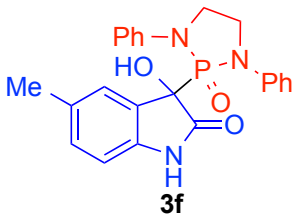
3-(1,3-Bis(4-methoxyphenyl)-2-oxido-1,3,2-diazaphospholidin-2-yl)-3-hydroxy-1-methylindolin-2-one (3c): White solid **3c** (44.1 mg, 92%). R_f = 0.3 (CH_2Cl_2:EtOAc = 8:2); mp: 185 °C (decomp.); IR (KBr, cm^{-1}): 3425, 3061, 2872, 1728, 1612, 1512, 1464, 1261, 1026; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.8 Hz, 2H), 7.29 (dd, *J* = 8.8, 0.8 Hz, 2H), 7.24 – 7.20 (m, 1H), 6.94 – 6.87 (m, 4H), 6.80 – 6.76 (m, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 6.56 (d, *J* = 7.6 Hz, 1H), 5.59 (d, *J* = 12.8 Hz, 1H), 3.83 – 3.75 (m, 4H), 3.80 (s, 6H), 3.09 (s, 3H); **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 172.2 (d, *J* = 6.0 Hz), 155.9, 155.5, 144.0, 133.9 (dd, *J* = 10.4, 5.2 Hz), 125.6, 124.4 (d, *J* = 3.7 Hz), 122.7, 120.7 (dd, *J* = 95.6, 4.5 Hz), 114.7 (d, *J* = 5.2 Hz), 108.0, 72.7 (d, *J* = 7.5 Hz), 55.5 (d, *J* = 8.2 Hz), 43.7 (d, *J* = 13.4 Hz), 43.5 (d, *J* = 13.4 Hz), 26.2; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 12.96 ppm; **HRMS** (ESI) calcd for $C_{25}H_{26}N_3O_5P$ $[M+H]^+$: 480.1683; found: 480.1675.



3e

3-Hydroxy-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)indolin-2-one (3e): White solid **3e** (39.7 mg, 98%). R_f = 0.36 (Hexanes:EtOAc = 1:2); mp: 177 °C (decomp.); IR (KBr, cm^{-1}): 3427, 3155, 3072, 2829, 1722, 1624, 1599, 1475, 1271,

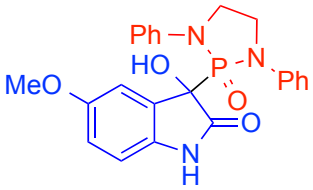
1041; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.47 – 7.45 (m, 2H), 7.41 – 7.34 (m, 6H), 7.17 – 7.04 (m, 3H), 6.78 – 6.73 (m, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.50 (d, *J* = 7.6 Hz, 1H), 5.62 (d, *J* = 13.2 Hz, 1H), 3.89 – 3.75 (m, 4H); **^{13}C NMR** (100.5 MHz, DMSO-d_6): δ 173.3 (d, *J* = 4.4 Hz), 143.1, 141.3 (dd, *J* = 29.1, 6.7 Hz), 130.6, 129.5 (d, *J* = 4.4 Hz), 125.3, 125.0 (d, *J* = 4.5 Hz), 122.2 (d, *J* = 32.1 Hz), 121.9, 117.3 (dd, *J* = 71.7, 4.4 Hz), 110.3, 73.3 (d, *J* = 8.2 Hz), 42.3 (d, *J* = 12.7 Hz), 42.1 (d, *J* = 12.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 12.14 ppm; **HRMS** (ESI) calcd for $C_{22}H_{20}N_3O_3P$ $[M+Na]^+$: 428.1134; found: 428.1146.



3f

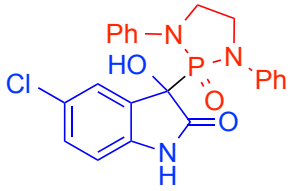
3-Hydroxy-5-methyl-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)indolin-2-one (3f): White solid **3f** (37.7 mg, 90%). R_f = 0.26 (CH_2Cl_2:EtOAc = 8:2); mp: 162 °C (decomp.); IR (KBr, cm^{-1}): 3348, 3163, 3130, 2953, 1736, 1599, 1492, 1271, 1037; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 10.33 (s, 1H), 7.44 – 7.34 (m, 8H), 7.11 – 7.03 (m, 2H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 5.82 (s, 1H), 5.58 (d, *J* = 14.0 Hz, 1H), 3.86 – 3.80 (m, 4H), 1.92 (s, 3H); **^{13}C NMR** (100.5 MHz, DMSO-d_6): δ 173.4 (d, *J* = 5.2 Hz), 141.4 (dd, *J* = 27.7, 6.0 Hz), 140.6, 130.8, 130.6, 129.5 (d, *J* = 13.4 Hz), 126.2, 125.1 (d, *J* = 4.5 Hz), 122.2 (d, *J* = 54.5 Hz), 117.4 (dd, *J* = 94.1, 4.4 Hz), 109.9, 73.4 (d, *J* = 8.2 Hz), 42.4 (d, *J* = 11.9 Hz), 42.1 (d, *J* = 12.7 Hz), 20.7.; **^{31}P NMR** (162 MHz,

DMSO-d_6): δ 7.86 ppm; **HRMS** (ESI) calcd for $C_{23}H_{22}N_3O_3P$ [M+Na]$^+$: 442.1291; found: 442.1292.



3g

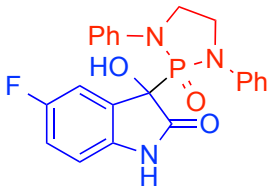
3-Hydroxy-5-methoxy-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)indolin-2-one (3g): White solid **3g** (34.8 mg, 80%). R_f = 0.17 (CH_2Cl_2:EtOAc = 8:2); mp: 180 °C (decomp.); IR (KBr, cm^{-1}): 3410, 3180, 3059, 2955, 1736, 1736, 1599, 1492, 1261, 1033; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 10.25 (s, 1H), 7.44 – 7.34 (m, 8H), 7.06 – 7.04 (m, 2H), 6.74 – 6.65 (m, 2H), 6.01 (s, 1H), 5.59 (d, *J* = 14.0 Hz, 1H), 3.87 – 3.85 (m, 4H), 3.37 (s, 3H); **^{13}C NMR** (100.5 MHz, DMSO-d_6): δ 173.2 (d, *J* = 4.5 Hz), 155.1, 141.3 (dd, *J* = 32.8, 6.7 Hz), 136.2, 129.5, 126.0 (d, *J* = 4.5 Hz), 122.1 (d, *J* = 20.9 Hz), 117.2 (dd, *J* = 46.3, 5.2 Hz), 116.3, 111.4, 110.9, 73.6 (d, *J* = 7.4 Hz), 55.8, 42.3 (d, *J* = 12.7 Hz), 42.1 (d, *J* = 12.6 Hz); **^{31}P NMR** (162 MHz, DMSO-d_6): δ 7.62 ppm; **HRMS** (ESI) calcd for $C_{23}H_{22}N_3O_4P$ [M+Na]$^+$: 458.1240; found: 458.1240.



3h

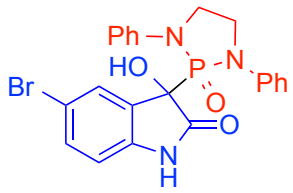
5-Chloro-3-hydroxy-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)indolin-2-one (3h): White solid **3h** (43.1 mg, 98%). R_f = 0.24 (CH_2Cl_2:EtOAc = 8:2); mp: 176 °C

(decomp.); IR (KBr, cm^{-1}): 3414, 3169, 3057, 2872, 1726, 1622, 1452, 1259, 1049; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 10.57 (s, 1H), 7.44 – 7.34 (m, 8H), 7.20 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.11 – 7.04 (m, 2H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.95 (s, 1H), 5.67 (d, *J* = 14.0 Hz, 1H), 3.87 – 3.82 (m, 4H); **^{13}C NMR** (100.5 MHz, DMSO-d_6): δ 173.2 (d, *J* = 5.2 Hz), 142.0, 141.2 (dd, *J* = 26.9, 5.9 Hz), 130.3, 129.6 (d, *J* = 15.6 Hz), 127.0 (d, *J* = 4.5 Hz), 126.1, 125.4, 122.5 (d, *J* = 55.3 Hz), 117.9 (dd, *J* = 81.5, 4.5 Hz), 111.7, 73.1 (d, *J* = 7.4 Hz), 42.4 (d, *J* = 12.7 Hz), 42.2 (d, *J* = 12.6 Hz); **^{31}P NMR** (162 MHz, DMSO-d_6): δ 8.16 ppm; **HRMS** (ESI) calcd for $C_{22}H_{19}N_3O_3PCl$ $[M+Na]^+$: 462.0745; found: 462.0745.



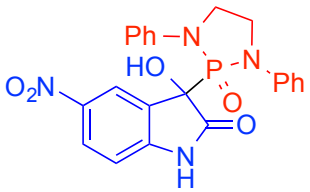
3i

5-Fluoro-3-hydroxy-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)indolin-2-one (3i): White solid **3i** (41.5 mg, 98%). R_f = 0.20 (CH_2Cl_2:EtOAc = 8:2); mp: 157 °C (decomp.); IR (KBr, cm^{-1}): 3423, 3186, 2885, 1734, 1599, 1475, 1267, 1043; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 10.46 (s, 1H), 7.43 – 7.34 (m, 8H), 7.10 – 6.96 (m, 3H), 6.74 – 6.71 (m, 1H), 5.79 – 5.75 (m, 1H), 5.65 (d, *J* = 14.4 Hz, 1H), 3.85 – 3.82 (m, 4H); **^{13}C NMR** (100.5 MHz, DMSO-d_6): δ 173.4 (d, *J* = 5.9 Hz), 159.1, 156.8, 141.2 (dd, *J* = 29.1, 6.7 Hz), 139.3, 129.6 (d, *J* = 12.7 Hz), 126.6, 122.4 (d, *J* = 48.6 Hz), 117.5 (dd, *J* = 82.3, 4.5 Hz), 112.9 (d, *J* = 25.4 Hz), 111.1 (d, *J* = 7.5 Hz), 73.3 (d, *J* = 7.5 Hz), 42.4 (d, *J* = 12.7 Hz), 42.1 (d, *J* = 11.9 Hz); **^{31}P NMR** (162 MHz, DMSO-d_6): δ 7.98 ppm; **HRMS** (ESI) calcd for $C_{22}H_{19}N_3O_3FP$ $[M+Na]^+$: 446.1040; found: 446.1040.



3j

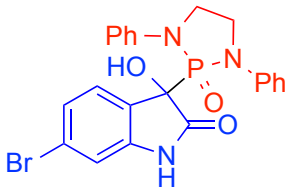
5-Bromo-3-hydroxy-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)indolin-2-one (3j): White solid **3j** (39.7 mg, 82%). R_f = 0.25 (CH_2Cl_2:EtOAc = 8:2); mp: 158 °C (decomp.); IR (KBr, cm^{-1}): 3412, 3169, 3055, 2868, 1728, 1618, 1257, 1045; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 10.58 (s, 1H), 7.44 – 7.32 (m, 9H), 7.11 – 7.04 (m, 2H), 6.70 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.10 (bs, 1H), 5.68 (d, *J* = 13.6 Hz, 1H), 3.86 – 3.81 (m, 4H); **^{13}C NMR** (100.5 MHz, DMSO-d_6): δ 173.0 (d, *J* = 5.2 Hz), 142.4, 141.2 (dd, *J* = 26.9, 7.2 Hz), 133.2, 129.5 (d, *J* = 8.9 Hz), 128.2, 127.4 (d, *J* = 4.5 Hz), 122.5 (d, *J* = 53.8 Hz), 117.4 (dd, *J* = 75.5, 4.5 Hz) 113.7, 112.2, 73.0 (d, *J* = 8.2 Hz), 42.4 (d, *J* = 12.6 Hz), 42.1 (d, *J* = 12.6 Hz); **^{31}P NMR** (162 MHz, DMSO-d_6): δ 8.12 ppm; **HRMS** (ESI) calcd for $C_{22}H_{19}N_3O_3P$ Br[M+Na]$^+$: 506.0240; found: 506.0240.



3k

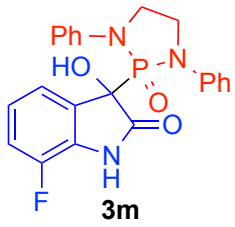
3-Hydroxy-5-nitro-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)indolin-2-one (3k): Light brown solid **3k** (40.0 mg, 89%). R_f = 0.20 (CH_2Cl_2:EtOAc = 8:2); mp: 210 °C (decomp.); IR (KBr, cm^{-1}): 3433, 3068, 2883, 1739, 1529, 1257, 1087, 1053; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 11.15 (s, 1H), 8.10 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.40– 7.25 (m,

9H), 7.05 – 6.98 (m, 2H), 6.93 (d, *J* = 8.4 Hz, 1H), 5.75 (d, *J* = 16.0 Hz, 1H), 3.90 – 3.83 (m, 4H); **^{13}C NMR** (100.5 MHz, DMSO-d_6): δ 173.2 (d, *J* = 4.4 Hz), 149.0, 141.8, 140.5 (dd, *J* = 15.8, 6.7 Hz), 129.0 (d, *J* = 10.4 Hz), 127.1, 125.5 (d, *J* = 3.7 Hz), 121.8 (d, *J* = 29.9 Hz), 120.6, 116.9 (dd, *J* = 38.2, 4.5 Hz), 109.9, 71.9 (d, *J* = 7.5 Hz), 41.9 (d, *J* = 12.7 Hz), 41.7 (d, *J* = 12.6 Hz); **^{31}P NMR** (162 MHz, DMSO-d_6): δ 7.92 ppm; **HRMS** (ESI) calcd for $C_{22}H_{19}N_4O_5P$ [M+Na]$^+$: 473.0985; found: 473.0982.



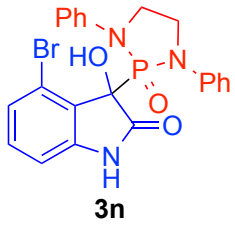
3l

6-Bromo-3-hydroxy-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)indolin-2-one (3l): White solid **3l** (40.2 mg, 83%). R_f = 0.23 (CH_2Cl_2:EtOAc = 17:3); mp: 144 °C (decomp.); IR (KBr, cm^{-1}): 3421, 3173, 3030, 2883, 1732, 1618, 1498, 1267, 1058; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 10.53 (s, 1H), 7.35 – 7.28 (m, 8H), 7.03 – 6.98 (m, 2H), 6.84 (d, *J* = 2.0 Hz, 1H), 6.77– 6.75 (m, 1H), 6.09 (d, *J* = 8.0 Hz, 1H), 5.54 (d, *J* = 14.0 Hz, 1H), 3.82 – 3.77 (m, 4H); **^{13}C NMR** (100.5 MHz, DMSO-d_6): δ 173.2 (d, *J* = 4.5 Hz), 144.8, 141.2 (dd, *J* = 21.7, 5.9 Hz), 129.5 (d, *J* = 7.5 Hz), 127.0, 124.5, 124.3 (d, *J* = 4.5 Hz), 123.2, 122.3 (d, *J* = 37.3 Hz), 117.7 (dd, *J* = 69.5, 4.4 Hz), 113.1, 72.8 (d, *J* = 7.5 Hz), 42.4 (d, *J* = 12.7 Hz), 42.1 (d, *J* = 11.9 Hz); **^{31}P NMR** (162 MHz, DMSO-d_6): δ 7.83 ppm; **HRMS** (ESI) calcd for $C_{22}H_{19}N_3O_3PBr$ [M-H]$^-$: 482.0275; found: 482.0259.



3m

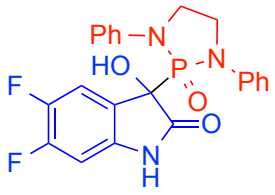
7-Fluoro-3-hydroxy-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)indolin-2-one (3m): White solid **3m** (30.9 mg, 73%). R_f = 0.41 (DCM:EtOAc = 8:2); mp: 170 °C (decomp.); IR (KBr, cm^{-1}): 3483, 3128, 2924, 1753, 1645, 1599, 1498, 1267, 1055, 989; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 10.96 (s, 1H), 7.42 – 7.34 (m, 8H), 7.12 – 7.03 (m, 3H), 6.69 – 6.64 (m, 1H), 6.09 (d, *J* = 7.2 Hz, 1H), 5.68 (d, *J* = 14.0 Hz, 1H), 3.88 – 3.83 (m, 4H); **^{13}C NMR** (100.5 MHz, DMSO-d_6): δ 173.2 (d, *J* = 3.7 Hz), 147.8, 145.4, 141.2 (dd, *J* = 27.8, 6.7 Hz), 130.3 (d, *J* = 12.7 Hz), 129.5 d, *J* = 5.9 Hz), 127.9 (d, *J* = 4.4 Hz), 122.8 (d, *J* = 6.0 Hz), 122.3 (d, *J* = 32.9 Hz), 121.3 (d, *J* = 3.7 Hz), 117.4(dd, *J* = 69.5, 5.2 Hz), 105.0, 73.2 (d, *J* = 3.0 Hz), 42.4 (d, *J* = 12.6 Hz), 42.1 (d, *J* = 12.7 Hz); **^{31}P NMR** (162 MHz, DMSO-d_6): δ 7.78 ppm; **HRMS** (ESI) calcd for $C_{22}H_{19}N_3O_3FP$ $[M+Na]^+$: 446.1040; found: 446.1040.



3n

4-Bromo-3-hydroxy-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)indolin-2-one (3n): White solid **3n** (27.1 mg, 56%). R_f = 0.20 (CH_2Cl_2:EtOAc = 8:2); mp: 169 °C (decomp.); IR (KBr, cm^{-1}): 3448, 3169, 2931, 1743, 1589, 1275, 1043; **^{1}H NMR** (400

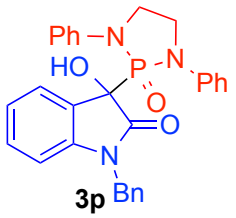
MHz, DMSO-d_6): δ 10.60 (s, 1H), 7.36 – 7.28 (m, 4H), 7.18 – 7.16 (m, 2H), 7.12 – 7.08 (m, 2H), 7.03 – 6.96 (m, 2H), 6.88 (t, *J* = 7.2 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.66 – 6.63 (m, 1H), 5.38 (d, *J* = 21.6 Hz, 1H), 3.94 – 3.78 (m, 4H); **^{13}C NMR** (100.5 MHz, DMSO-d_6): δ 172.2, 145.1, 141.6 (dd, *J* = 14.2, 7.4 Hz), 132.5, 129.0 (d, *J* = 44.1 Hz), 125.3, 124.7 (d, *J* = 4.5 Hz), 121.5 (d, *J* = 8.2 Hz), 120.6, 117.2 (dd, *J* = 65.8, 4.5 Hz), 109.2, 73.7 (d, *J* = 8.2 Hz), 42.6 (d, *J* = 13.4 Hz), 42.0 (d, *J* = 12.7 Hz); **^{31}P NMR** (162 MHz, DMSO-d_6): δ 5.37 ppm; **HRMS** (ESI) calcd for $C_{22}H_{19}N_3O_3PBr$ $[M+Na]^+$: 506.0240; found: 506.0245.



3o

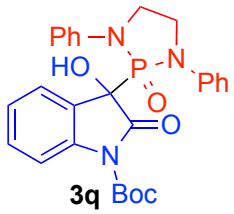
5,6-Difluoro-3-hydroxy-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)indolin-2-one (3o): White solid **3o** (38.4 mg, 87%). R_f = 0.27 (DCM:EtOAc = 8:2); mp: 169 °C (decomp.); IR (KBr, cm^{-1}): 3433, 3155, 2943, 1739, 1600, 1496, 1257, 10454; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 10.60 (s, 1H), 7.40 – 7.30 (m, 8H), 7.11 – 7.03 (m, 2H), 6.81 – 6.76 (m, 1H), 5.92 – 5.88 (m, 1H), 5.61 (d, *J* = 14.4 Hz, 1H), 3.88 – 3.79 (m, 4H); **^{13}C NMR** (100.5 MHz, DMSO-d_6): δ 173.5 (d, *J* = 5.2 Hz), 152.1 (d, *J* = 14.2 Hz), 149.6 (d, *J* = 14.2 Hz), 146.4 (d, *J* = 12.6 Hz), 144.0 (d, *J* = 10.5 Hz), 141.2 (dd, *J* = 23.9, 6.0 Hz), 140.1 (d, *J* = 10.5 Hz), 129.6 (d, *J* = 16.5 Hz), 122.4 (d, *J* = 52.3 Hz), 121.0, 117.5 (dd, *J* = 83.7, 4.4 Hz), 114.8 (d, *J* = 21.0 Hz), 100.3 (d, *J* = 22.5 Hz), 72.7 (d, *J* = 7.4 Hz), 42.4 (d, *J* = 12.7 Hz), 42.2 (d, *J* = 11.9 Hz); **^{31}P NMR** (162 MHz, DMSO-

d_6): δ 7.91 ppm; **HRMS** (ESI) calcd for $C_{22}H_{18}N_3O_3F_2P$ $[M+Na]^+$: 464.0946; found: 464.0938.



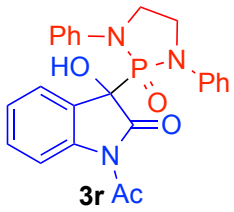
3p

1-Benzyl-3-hydroxy-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)indolin-2-one (3p): White solid **3p** (46.1 mg, 93%). R_f = 0.38 (Hexanes:EtOAc = 1:1); mp: 178-180 °C. IR (KBr, cm^{-1}): 3448, 3065, 2887, 1734, 1612, 1597, 1492, 1261, 1074, 1020; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 – 7.41 (m, 2H), 7.40 – 7.34 (m, 6H), 7.27 – 7.19 (m, 5H), 7.11 – 7.05 (m, 3H), 6.76 – 6.72 (m, 1H), 6.56 (d, *J* = 7.6 Hz, 1H), 6.52 (d, *J* = 6.8 Hz, 1H), 5.72 (d, *J* = 12.8 Hz, 1H), 4.83 – 4.69 (m, 2H), 3.94 – 3.73 (m, 4H); **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 171.9 (d, *J* = 5.2 Hz), 143.2, 140.8 (dd, *J* = 28.4, 6.0 Hz), 135.1, 130.1, 129.4 (d, *J* = 10.4 Hz), 128.7, 127.6, 127.2, 125.5, 124.1 (d, *J* = 4.5 Hz), 122.8 (d, *J* = 6.7 Hz), 122.4, 117.6 (dd, *J* = 76.9, 4.5 Hz),109.2, 72.9 (d, *J* = 7.4 Hz), 43.8, 42.6 (d, *J* = 13.4 Hz), 42.4 (d, *J* = 13.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 12.4 ppm; **HRMS** (ESI) calcd for $C_{29}H_{26}N_3O_3P$ $[M+Na]^+$: 518.1604; found: 518.1603.



3q

***Tert*-butyl 3-hydroxy-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)-2-oxoindoline-1-carboxylate (3q):** White solid **3q** (30.3 mg, 60%). R_f = 0.35 (DCM:EtOAc = 19:1); mp: 190 °C (decomp.) IR (KBr, cm^{-1}): 3394, 3045, 2928, 1784, 1709, 1599, 1498, 1271, 1168, 1064, 1035; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.39 – 7.28 (m, 6H), 7.28 – 7.23 (m, 1H), 7.10 – 7.05 (m, 2H), 6.92 – 6.87 (m, 1H), 6.69 – 6.67 (m, 1H), 5.67 (d, *J* = 12.4 Hz, 1H), 3.87 – 3.73 (m, 4H), 1.57 (s, 9H); **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 169.9 (d, *J* = 6.0 Hz), 148.6, 140.6 (dd, *J* = 17.9, 5.9 Hz), 140.1, 130.4, 129.4 (d, *J* = 8.2 Hz), 125.5, 124.6, 123.1 (d, *J* = 4.5 Hz), 122.8 (d, *J* = 35.8 Hz), 117.6 (dd, *J* = 68.0, 4.5 Hz), 114.9, 84.9, 72.7 (d, *J* = 7.4 Hz), 42.7 (d, *J* = 13.4 Hz), 42.5 (d, *J* = 12.7 Hz), 28.0; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 12.4 ppm; **HRMS** (ESI) calcd for $C_{27}H_{28}N_3O_5P$ $[M+Na]^+$: 528.1659; found: 528.1663.



3r

1-Acetyl-3-hydroxy-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)indolin-2-one (3r): Pale brown solid **3r** (20.1 mg, 45%). R_f = 0.33 (DCM:EtOAc = 19:1); mp: 180 °C (decomp.); IR (KBr, cm^{-1}): 3427, 3059, 2930, 1793, 1724, 1599, 1269, 1097, 1004; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.0 Hz, 1H), 7.44 – 7.35 (m, 8H), 7.30 –

7.25 (m, 1H), 7.15 – 7.06 (m, 2H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 5.76 (d, *J* = 13.6 Hz, 1H), 3.86 – 3.75 (m, 4H), 2.54 (s, 3H); **^{13}C NMR** (100.5 MHz, $CDCl_3$): δ 172.3 (d, *J* = 4.5 Hz), 170.3, 140.5 (dd, *J* = 18.7, 5.9 Hz), 130.6, 129.5, 129.3, 125.3 (d, *J* = 10.5 Hz), 123.3 (d, *J* = 3.8 Hz, 1H), 123.1, 122.7, 117.8 (dd, *J* = 65.0, 5.2 Hz), 116.5, 72.9 (d, *J* = 7.4 Hz), 42.7 (d, *J* = 14.1 Hz), 42.4 (d, *J* = 13.4 Hz), 26.4; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 12.40 ppm; **HRMS** (ESI) calcd for $C_{24}H_{22}N_3O_4P$ $[M+Na]^+$: 470.1240; found: 470.1240.

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