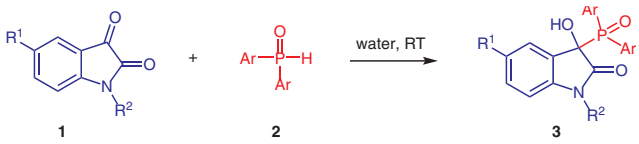
Room Temperature, Open-Flask C–P Bond-Formation on Water under Catalyst-Free Conditions

Rakhee Choudhary‡
Rekha Bai‡
Pratibha Singh‡
Mahesh C. Sharma
Satpal Singh Badsara*

MFOS Laboratory, Department of Chemistry (Centre of Advanced Study), University of Rajasthan, JLN Marg, Jaipur, Rajasthan-302004, India
badsarass4@uniraj.ac.in
sattubhu2005@gmail.com

‡Authors contributed equally



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Abstract A catalyst-free C–P bond-formation in an open flask at room temperature between isatin derivatives and phosphorus surrogates on water is described. Isatin derivatives possessing different substitutes underwent C–P coupling reaction with a variety of phosphine oxides under the reaction conditions employed, providing the desired products in up to quantitative yields.

Key words catalyst-free, C–P bond formation, isatin

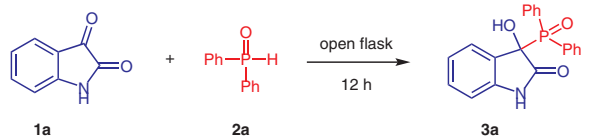
Organophosphorus compounds play important roles in organic synthesis,[1] organometallic chemistry,[2] medicinal chemistry,[3] chemical biology,[4] and material science.[5] More specifically, α-hydroxy- and α-aminophosphonic acids have roles as biophosphate mimics, antibiotics, antivirals, and antitumor agents.[6] Nucleophilic substitution of toxic phosphinoyl halides with organometallic reagents has been the traditional method for the synthesis of these compounds.[1d] Subsequently, the Hirao transition-metal-catalysed phosphonation of organohalides has emerged as a facile alternative.[7] Use of toxic phosphorus halides, high catalyst loading, harsh reaction conditions or poor functional group tolerance are drawbacks of these approaches.

Oxindole frameworks bearing a C-3 quaternary stereocenter are important constituents of many natural products and biologically active molecules.[8] These molecules are often synthesized via aldol reactions of aldehydes or ketones or other nucleophilic species to the 3-carbonyl of isatins.[9]

In recent years, organophosphorus compounds have been mostly synthesized via cross-coupling reactions,[10] C–H activation,[11] and dehydrogenative coupling reactions.[12] Several catalytic systems such as the NHC/Icy.CO_2 precatalyst, organocatalysts, and palladium pincer complexes have been employed for phospha-Michael additions to activated alkenes and alkynes.[13] Recently, Cai and co-workers disclosed a copper catalyst with fluorous bis(oxazoline) as a ligand for the asymmetric α-hydrophosphonylation of isatins.[14a] Swamy and co-workers have reported a catalyst-free addition of allenyl or alkynyl-phosphonates and phosphine oxides.[14b] Although various synthetic pathways using different catalytic systems have been developed for the preparation of α1-oxindole-α-hydroxy phosphonates,[15,16] the synthesis of oxindoles containing α-hydroxy phosphinoyl compounds under mild conditions remains a major goal. As a part of our ongoing project to develop metal-free organic transformations,[17] we have developed a facile and efficient synthetic protocol for preparation of oxindoles containing an α-hydroxyphosphinoyl group by a catalyst-free C–P bond formation between isatins and phosphine oxides or phosphites.

For optimization studies, we choose isatin **1a** and diphenylphosphine oxide **2a** as model substrates. Initially, the C–P coupling was carried out in toluene at 100 °C to afford the desired α-hydroxyphosphinoyl oxindole **3a** in 95% yield after 12 h (Table 1, entry 1). When the reaction was carried out at room temperature in toluene no improvement in yield was observed (entry 2). A slight improvement in yield (96%) was observed when the reaction was carried out in isopropanol as the solvent (entry 3), whereas C–P coupling reaction in the absence of solvent at ambient or elevated temperature led to lower yields (entries 4 and 5). Remarkably, the reaction between **1a** and **2a** proceeded smoothly and efficiently in water at room temperature, affording **3a** in excellent yield (98%).

Table 1 Optimization of Reaction Conditions for C–P Bond Formation between Isatin **1a** and Diphenylphosphine Oxide **2a**[a]



1a **2a** **3a**

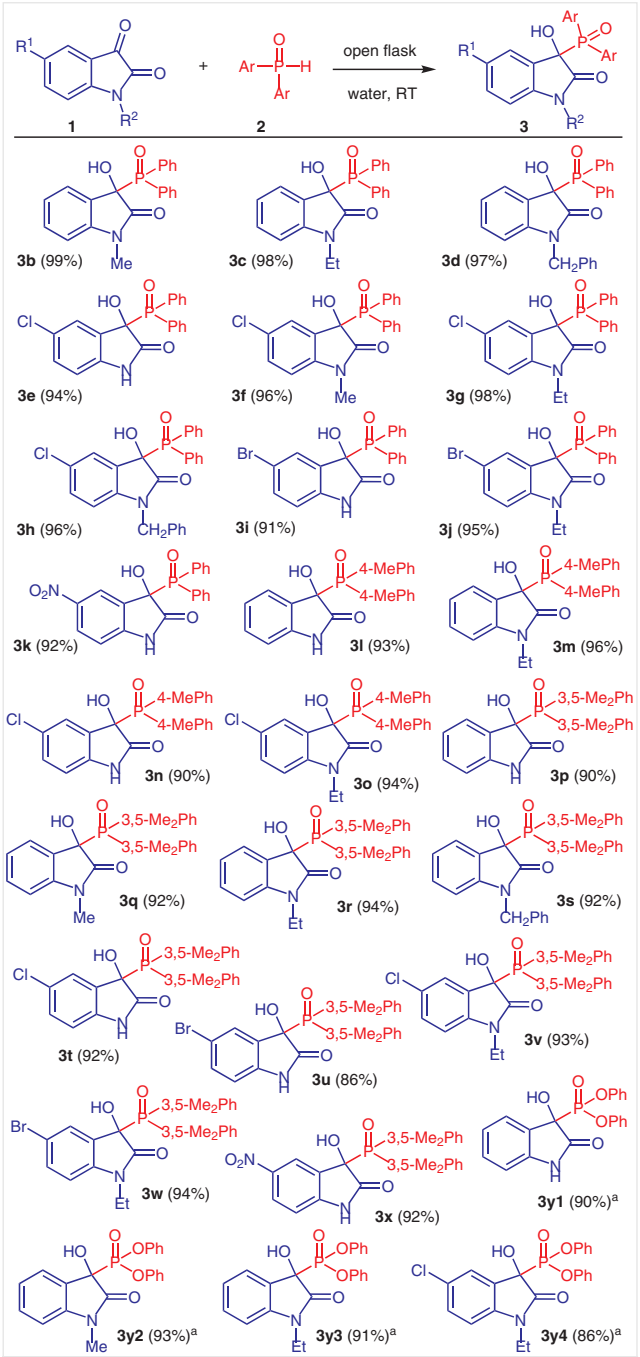
Entry	Solvent	Temperature (°C)	Time (h)	Yield (%)[b]
1	toluene	100	12	95
2	toluene	RT	24	90
3	*i*-PrOH	RT	12	96
4	neat	100	24	74
5	neat	RT	24	58
6	water	RT	12	98

[a] Reaction conditions: Isatin **1a** (0.5 mmol), diphenylphosphine oxide **2a** (0.5 mmol), solvent or neat, r.t. to 100 °C.
[b] Isolated yields based on **1a**.

After optimization studies, we then turned our attention to study the substrate scope of this intriguing C–P bond formation. For this, isatin **1a** and N-alkylated isatins **1b–k** (prepared by following a known procedure[18]) were employed for the C–P cross-coupling reaction with diphenylphosphine oxide **2a** on water under the optimized reaction conditions. The corresponding oxindole containing α-hydroxyphosphinoyl compounds **3b–k** were obtained in 91–99% yields (Scheme 1). Other phosphine oxides **2b** and **2c** also reacted well with different isatins to provide the desired products **3l–x** in 86–96% yields. The structures of all the compounds **3a–x** were established based on ^{1}H NMR, ^{13}C NMR, ^{31}P NMR spectroscopy and HRMS analysis.

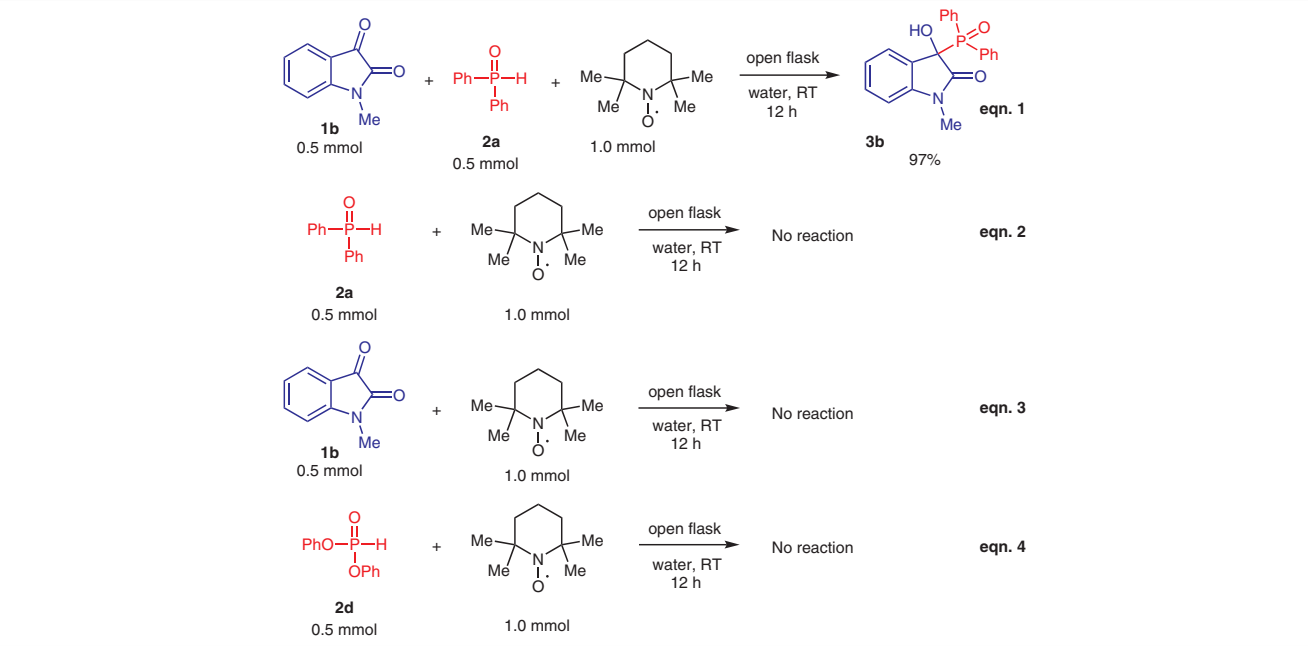
We next attempted the synthesis of α1-oxindole-α-hydroxyphosphonates using this interesting C–P bond-formation methodology. Accordingly, we employed diphenyl phosphite **2d** for C–P bond formation with isatin derivatives **1a–c** and **1g** under neat conditions at room temperature. Under these conditions, efficient coupling provided the desired α1-oxindole-α-hydroxyphosphonates **3y1–3y4** in 86–93% yields (Scheme 1).

To elucidate the reaction mechanism, we performed several control experiments as shown in Scheme 2. Initially, assuming that the reaction with diphenylphosphine oxide proceeded following a radical pathway,[13] the reaction between **1b** and **2a** was carried out in the presence of the free radical quencher 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO; Scheme 2, equiv 1), but we found that there was no effect on the reaction as the desired product **3a** was obtained in 97% yield. We also performed the reaction between TEMPO and **2a** (Scheme 2, equiv 2), TEMPO and **1b** (Scheme 1, equiv 3) and TEMPO and **2d** (Scheme 2, equiv 4). However, no coupled product was observed in these cases. These results clearly rule out the possibility of a radical pathway during the formation of products **3**.



Scheme 1 C–P bond formation between isatins **1** and phosphine oxides **2**. *Reaction conditions*: Isatin **1** (0.5 mmol), diphenylphosphine oxide **2** (0.5 mmol), water (1.0 mL), r.t., 12 h. Isolated yields are based on **1**. [a] Reaction conditions: Isatin **1** (1.0 mmol), diphenyl phosphite **2d** (0.2 mL), neat, r.t., 12 h.

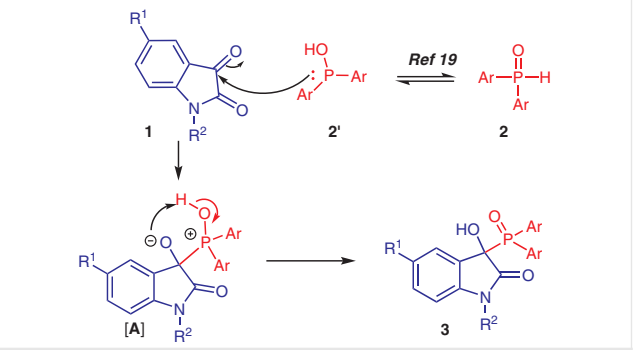
A literature survey revealed that diarylphosphine oxides **2** in the presence of air can undergo tautomerism to generate the corresponding phosphinous acid **2′**.[19] On this basis, a plausible reaction mechanism for this interesting catalyst-



Scheme 2 Control experiments

free C–P bond formation is depicted in Scheme 3 for the reaction between **1** and **2**. Initially phosphine oxide **2** converts into its tautomer **2′**. Then **2′** attacks the electrophilic C=O of isatin **1** to generate intermediate **A**, which is subsequently converted into the product **3**.

In conclusion, we have reported a convenient protocol for the synthesis of oxindole α-hydroxyphosphinoyl compounds and α1-oxindole-α-hydroxyphosphonates via a catalyst-free C–P bond formation between isatins and phosphine oxides or phosphites on aqueous medium. The corresponding products were obtained in excellent yields.



Scheme 3 Plausible reaction mechanism for C–P bond formation between isatin and diphenyl phosphine oxide

All chemicals were purchased from commercial suppliers and used without further purification. NMR spectra were recorded with a JEOL Ressonance-400 instrument using $CDCl_3$ or DMSO-d_6 as solvent. In some cases, one drop of DMSO-d_6 was added to $CDCl_3$ to improve solubility. Chemical shifts are reported in parts per million (ppm) and referenced to the residual solvent resonance. Coupling constants (*J*) are reported in Hertz (Hz). Standard abbreviations indicating multiplicity are used as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, dt = double triplet, q = quartet, m = multiplet. HRMS data were collected with a Waters - Xevo G2S QTof LC-MS with UPLC.

General Procedure for Table 1

3-(Diphenyl-phosphinoyl)-3-hydroxy-indolin-2-one (3a)

Diphenylphosphine oxide **2a** (0.5 mmol, 101 g) was added to stirred isatin **1a** (0.5 mmol, 0.073 g) in an open flask in solvent (1.0 mL) or neat and then the reaction mixture was stirred at the given temperature. The mixture was then diluted with EtOAc (10 mL). After usual workup, the organic layer was dried over Na_2SO_4, filtered, EtOAc was evaporated, and the crude product thus obtained was purified by crystallization (EtOAc) to afford the corresponding product **3a** as a white solid. Yield: 0.171 g (98%); mp 142 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.38 (d, *J* = 7.2 Hz, 1 H), 6.72 (s, 1 H), 6.75 (dd, *J* = 3.2, 7.6 Hz, 1 H), 7.18 (t, *J* = 7.6 Hz, 1 H), 7.25–7.32 (m, 1 H), 7.41–7.59 (m, 5 H), 7.63 (t, *J* = 7.6 Hz, 1 H), 7.85–8.02 (m, 4 H), 10.49 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 79.8 (d, J_{C-P} = 82.1 Hz), 109.5, 121.0, 125.5, 126.8, 127.8 (d, J_{C-P} = 11.5 Hz), 128.1 (d, J_{C-P} = 11.3 Hz), 129.8, 130.5 (d, J_{C-P} = 95.0 Hz), 130.7 (d, J_{C-P} = 95.2 Hz), 131.6, 132.1, 132.3 (d, J_{C-P} = 8.5 Hz), 142.9 (d, J_{C-P} = 5.9 Hz), 175.3.

^{31}P NMR (162 MHz, DMSO-d_6): δ = 28.8.

HRMS: *m*/*z* [M + H] calcd. for $C_{20}H_{16}NO_3P$ + H: 350.0946; found: 350.0941.

General Procedure for Scheme 1

Phosphine oxide **2** (0.5 mmol) was added to a stirred mixture of isatin **1b–x** (0.5 mmol) in water (1.0 mL) in an open flask at r.t. The stirring was continued for 12 h, then the reaction mixture was diluted with EtOAc (10 mL). After usual workup, the organic layer was dried over Na_2SO_4, filtered, the EtOAc was evaporated and the crude product thus obtained was purified by crystallization (EtOAc or EtOAc/methanol) to afford the corresponding products **3b–x**.

For Compounds 3y1–y4

Isatin **1** (1.0 mmol) and diphenyl phosphite **2d** (0.2 mL) were reacted neat in an open flask at r.t. for 12 h and the reaction mixture was then diluted with EtOAc (10 mL). After usual workup, the organic layer was dried over Na_2SO_4, filtered, the EtOAc was evaporated and the crude product thus obtained was purified by column chromatography (EtOAc/hexanes, 1:1) to afford the corresponding products **3y1–y4**.

3-(Diphenyl-phosphinoyl)-3-hydroxy-1-methylindolin-2-one (3b)

The title compound was prepared by following the general procedure for Scheme 1, using *N*-methylisatin **1b** (0.5 mmol, 0.080 g) and diphenylphosphine oxide **2a** (0.5 mmol, 0.101 g), providing **3b** as a white solid. Yield: 0.179 g (99%); mp 130 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.99 (s, 3 H), 6.52 (d, *J* = 7.6 Hz, 1 H), 6.85 (t, *J* = 7.6 Hz, 1 H), 6.92 (d, *J* = 7.6 Hz, 1 H), 7.29 (t, *J* = 7.6 Hz, 1 H), 7.42–7.49 (m, 2 H), 7.51–7.59 (m, 3 H), 7.65 (t, *J* = 7.6 Hz, 1 H), 7.83 (d, *J* = 7.6 Hz, 1 H), 7.86 (d, *J* = 7.6 Hz, 1 H), 7.97 (d, *J* = 7.6 Hz, 1 H), 7.99 (d, *J* = 7.6 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 26.2, 79.7 (d, J_{C-P} = 81.3 Hz), 108.4, 121.8, 125.2 (d, J_{C-P} = 2.7 Hz), 126.0, 127.8 (d, J_{C-P} = 11.5 Hz), 128.3 (d, J_{C-P} = 11.3 Hz), 129.8, 130.0, 130.7, 131.8 (d, J_{C-P} = 1.6 Hz), 132.2 (d, J_{C-P} = 8.8 Hz), 132.4 (d, J_{C-P} = 8.7 Hz), 144.0 (d, J_{C-P} = 5.6 Hz), 173.7.

^{31}P NMR (162 MHz, $CDCl_3$/ DMSO-d_6): δ = 30.3.

HRMS: *m*/*z* [M + H] calcd. for $C_{21}H_{18}NO_3P$ + H: 364.1103; found: 364.1109.

3-(Diphenyl-phosphinoyl)-3-hydroxy-1-ethylindolin-2-one (3c)

The title compound was prepared by following the general procedure for Scheme 1, using N-ethylisatin **1c** (0.5 mmol, 0.087 g) and diphenylphosphine oxide **2a** (0.5 mmol, 0.101 g), providing **3c** as a white solid. Yield: 0.184 g (98%); mp 120 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.2 Hz, 3 H), 3.28–3.33 (m, 1 H), 3.52–3.57 (m, 1 H), 5.41 (d, *J* = 4.0 Hz, 1 H), 6.62 (d, *J* = 7.6 Hz, 1 H), 6.87 (t, *J* = 7.6 Hz, 1 H), 7.10 (d, *J* = 7.6 Hz, 1 H), 7.26 (t, *J* = 7.6 Hz, 1 H), 7.31–7.39 (m, 2 H), 7.41–7.54 (m, 3 H), 7.55–7.71 (m, 3 H), 7.97 (d, *J* = 7.6 Hz, 1 H), 8.00 (d, *J* = 7.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.0, 34.9, 80.2 (d, J_{C-P} = 71.3 Hz), 108.1, 122.6, 124.6, 127.1, 128.0 (d, J_{C-P} = 11.8 Hz), 128.2, 128.4 (d, J_{C-P} = 11.9 Hz), 129.1, 130.3, 132.4 (d, J_{C-P} = 9.1 Hz), 132.6, 133.1 (d, J_{C-P} = 8.8 Hz), 143.2 (d, J_{C-P} = 5.7 Hz), 173.5.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 30.3.

HRMS: *m*/*z* [M + H] calcd. for $C_{22}H_{20}NO_3P$ + H: 378.1259; found: 378.1245.

3-(Diphenyl-phosphinoyl)-3-hydroxy-1-benzylindolin-2-one (3d)

The title compound was prepared by following the general procedure for Scheme 1, using *N*-benzylisatin **1d** (0.5 mmol, 0.118 g) and diphenylphosphine oxide **2a** (0.5 mmol, 0.101 g), providing **3d** as a white solid. Yield: 0.213 g (97%); mp 142 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.53 and 4.79 (ABq, *J* = 15.6 Hz, 2 H), 4.66 (bs, 1 H), 6.55 (d, *J* = 7.6 Hz, 1 H), 6.85 (t, *J* = 7.6 Hz, 1 H), 6.93 (d, *J* = 7.6 Hz, 1 H), 7.06–7.10 (m, 2 H), 7.17 (t, *J* = 7.6 Hz, 1 H), 7.20–7.26 (m, 3 H), 7.32–7.65 (m, 6 H), 7.76 (d, *J* = 8.4 Hz, 1 H), 7.79 (d, *J* = 8.4 Hz, 1 H), 7.97 (d, *J* = 8.4 Hz, 1 H), 7.99 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 42.9, 79.6 (d, J_{C-P} = 81.9 Hz), 109.1, 121.8, 125.2, 126.2, 127.1, 127.2, 127.8 (d, J_{C-P} = 11.5 Hz), 128.2 (d, J_{C-P} = 11.4 Hz), 128.4, 129.8, 130.2 (d, J_{C-P} = 95.5 Hz), 130.4 (d, J_{C-P} = 95.7 Hz), 131.7, 132.4 (d, J_{C-P} = 8.6 Hz), 135.6, 143.2 (d, J_{C-P} = 5.6 Hz), 173.9.

^{31}P NMR (162 MHz, DMSO-d_6): δ = 28.1.

HRMS: *m*/*z* [M + H] calcd. for $C_{27}H_{22}NO_3P$ + H; 440.1416; found: 440.1422.

5-Chloro-3-(diphenyl-phosphinoyl)-3-hydroxy-indolin-2-one (3e)

The title compound was prepared by following the general procedure for Scheme 1, using 5-chloroisatin **1e** (0.5 mmol, 0.091 g) and diphenylphosphine oxide **2a** (0.5 mmol, 0.101 g), providing **3e** as a white solid. Yield: 0.180 g (94%); mp 128 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.23 (s, 1 H), 6.77 (d, *J* = 8.4 Hz, 1 H), 7.25 (d, *J* = 8.4 Hz, 1 H), 7.45–7.54 (m, 3 H), 7.55–7.63 (m, 3 H), 7.68 (t, *J* = 7.2 Hz, 1 H), 7.85–8.04 (m, 4 H), 10.65 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 79.9 (d, J_{C-P} = 80.5 Hz), 111.0, 125.0 (d, J_{C-P} = 2.5 Hz), 125.5 (d, J_{C-P} = 2.8 Hz), 128.0 (d, J_{C-P} = 11.5 Hz), 128.3 (d, J_{C-P} = 11.3 Hz), 128.7, 129.6, 129.9 (d, J_{C-P} = 95.6 Hz), 130.1 (d, J_{C-P} = 92.8 Hz), 131.9, 132.4 (d, J_{C-P} = 8.6 Hz), 132.5, 141.7 (d, J_{C-P} = 6.1 Hz), 175.1.

^{31}P NMR (162 MHz, $CDCl_3$/DMSO-d_6): δ = 29.0.

HRMS: *m*/*z* [M + H] calcd. for $C_{20}H_{15}ClNO_3P$ + H: 384.0556; found: 384.0540.

5-Chloro-3-(diphenyl-phosphinoyl)-3-hydroxy-1-methylindolin-2-one (3f)

The title compound was prepared by following the general procedure for Scheme 1, using 5-chloro-1-methylisatin **1f** (0.5 mmol, 0.098 g) and diphenylphosphine oxide **2a** (0.5 mmol, 0.101 g), providing **3f** as a white solid. Yield: 0.190 g (96%); mp 136 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.87 (s, 3 H), 5.35 (bs, 1 H), 6.53 (d, *J* = 8.4 Hz, 1 H), 6.94 (s, 1 H), 7.23 (d, *J* = 8.4 Hz, 1 H), 7.37–7.43 (m, 2 H), 7.48–7.51 (m, 3 H), 7.61 (d, *J* = 7.2 Hz, 1 H), 7.72 (d, *J* = 8.0 Hz, 1 H), 7.75 (d, *J* = 8.0 Hz, 1 H), 7.98 (d, *J* = 8.0 Hz, 1 H), 8.01 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.4, 80.5 (d, J_{C-P} = 70.4 Hz), 109.1, 126.4, 126.9 (d, J_{C-P} = 3.2 Hz), 127.4, 127.5 (d, J_{C-P} = 96.9 Hz), 128.1 (d, J_{C-P} = 12.2 Hz), 128.5 (d, J_{C-P} = 12.1 Hz), 128.9, 130.2, 130.7, 132.4 (d, J_{C-P} = 9.2 Hz), 132.6 (d, J_{C-P} = 2.3 Hz), 132.8 (d, J_{C-P} = 2.5 Hz), 133.4 (d, J_{C-P} = 9.0 Hz), 142.4, 173.8.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.5.

HRMS: *m*/*z* [M + H] calcd. for $C_{21}H_{17}ClNO_3P$ + H: 398.0713; found: 398.0719.

5-Chloro-3-(diphenyl-phosphinoyl)-3-hydroxy-1-ethylindolin-2-one (3g)

The title compound was prepared by following the general procedure for Scheme 1, using 5-chloro-1-ethylisatin **1g** (0.5 mmol, 0.105 g) and diphenylphosphine oxide **2a** (0.5 mmol, 0.101 g), providing **3g** as a white solid. Yield: 0.201 g (98%); mp 120 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7.2 Hz, 3 H), 3.28–3.33 (m, 1 H), 3.52–3.57 (m, 1 H), 5.53 (s, 1 H), 6.56 (d, *J* = 8.0 Hz, 1 H), 7.02 (s, 1 H), 7.24 (d, *J* = 8.0 Hz, 1 H), 7.34–7.44 (m, 2 H), 7.45–7.55 (m, 3 H), 7.61 (t, *J* = 8.4 Hz, 1 H), 7.68 (d, *J* = 7.6 Hz, 1 H), 7.71 (d, *J* = 7.6 Hz, 1 H), 7.95 (d, *J* = 7.6 Hz, 1 H), 7.98 (d, *J* = 7.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.0, 35.1, 80.1 (d, J_{C-P} = 70.3 Hz), 109.0, 126.5, 126.8, 127.3, 127.6, 127.7, 128.0 (d, J_{C-P} = 2.6 Hz), 128.2 (d, J_{C-P} = 11.9 Hz), 128.5 (d, J_{C-P} = 11.9 Hz), 130.2, 132.4 (d, J_{C-P} = 9.3 Hz), 132.7 (d, J_{C-P} = 2.1 Hz), 132.8 (d, J_{C-P} = 2.4 Hz), 133.0 (d, J_{C-P} = 9.0 Hz), 141.7 (d, J_{C-P} = 5.8 Hz), 173.1.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 30.9.

HRMS: *m*/*z* [M + H] calcd. for $C_{22}H_{19}ClNO_3P$ + H: 412.0869; found: 412.0855.

5-Chloro-3-(diphenyl-phosphinoyl)-3-hydroxy-1-benzylindolin-2-one (3h)

The title compound was prepared by following the general procedure for Scheme 1, using 5-chloro-1-benzylisatin **1h** (0.5 mmol, 0.135 g) and diphenylphosphine oxide **2a** (0.5 mmol, 0.101 g), providing **3h** as a white solid. Yield: 0.227 g (96%); mp 138 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.69–4.78 (m, 2 H), 6.47 (d, *J* = 8.4 Hz, 1 H), 6.68 (s, 1 H), 7.09 (d, *J* = 8.4 Hz, 1 H), 7.18–7.31 (m, 5 H), 7.37–7.45 (m, 2 H), 7.47–7.50 (m, 3 H), 7.63 (t, *J* = 8.4 Hz, 1 H), 7.95 (d, *J* = 8.0 Hz, 1 H), 7.98 (d, *J* = 8.0 Hz, 1 H), 8.10 (d, *J* = 8.0 Hz, 1 H), 8.13 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6): δ = 43.4, 79.6 (d, J_{C-P} = 78.7 Hz), 109.4, 110.0, 125.8, 126.7, 126.9, 127.0, 127.4 (d, J_{C-P} = 12.3 Hz), 127.6 (d, J_{C-P} = 11.7 Hz), 128.0, 128.2, 128.4, 129.1, 130.2 (d, J_{C-P} = 91.2 Hz), 131.5, 131.9, 132.2 (d, J_{C-P} = 8.9 Hz), 132.4 (d, J_{C-P} = 8.6 Hz), 134.3, 141.3 (d, J_{C-P} = 5.7 Hz), 173.6.

^{31}P NMR (162 MHz, $CDCl_3$/DMSO-d_6): δ = 28.1.

HRMS: *m*/*z* [M + H] calcd. for $C_{27}H_{21}ClNO_3P$ + H: 474.1026; found: 474.1036.

5-Bromo-3-(diphenyl-phosphinoyl)-3-hydroxy-indolin-2-one (3i)

The title compound was prepared by following the general procedure for Scheme 1, using 5-bromoisatin **1i** (0.5 mmol, 0.113 g) and diphenylphosphine oxide **2a** (0.5 mmol, 0.101 g), providing **3i** as a white solid. Yield: 0.194 g (91%); mp 158 °C.

^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6): δ = 6.58 (s, 1 H), 6.67 (d, *J* = 8.4 Hz, 1 H), 7.10–7.15 (m, 1 H), 7.27 (d, *J* = 8.0 Hz, 1 H), 7.37–7.70 (m, 6 H), 7.90–8.10 (m, 4 H), 10.34 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6): δ = 79.3 (d, J_{C-P} = 79.3 Hz), 110.3, 112.4, 126.8 (d, J_{C-P} = 11.9 Hz), 127.0 (d, J_{C-P} = 11.7 Hz), 127.8, 128.0 (d, J_{C-P} = 2.5 Hz), 128.4 (d, J_{C-P} = 96.5 Hz), 128.7 (d, J_{C-P} = 96.3 Hz), 130.8 (d, J_{C-P} = 2.1 Hz), 131.3, 131.6 (d, J_{C-P} = 9.2 Hz), 131.8 (d, J_{C-P} = 8.9 Hz), 140.9 (d, J_{C-P} = 6.0 Hz), 174.4.

^{31}P NMR (162 MHz, $CDCl_3$/DMSO-d_6): δ = 28.3.

HRMS: *m*/*z* [M + H] calcd. for $C_{20}H_{15}BrNO_3P$ + H: 428.0051; found: 428.0041.

5-Bromo-3-(diphenyl-phosphinoyl)-3-hydroxy-1-ethylindolin-2-one (3j)

The title compound was prepared by following the general procedure for Scheme 1, using 5-bromo-1-ethylisatin **1j** (0.5 mmol, 0.127 g) and diphenylphosphine oxide **2a** (0.5 mmol, 0.101 g), providing **3j** as a white solid. Yield: 0.216 g (95%); mp 132 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 0.93 (t, *J* = 7.2 Hz, 3 H), 3.49–3.56 (m, 2 H), 6.60 (s, 1 H), 6.96 (d, *J* = 8.4 Hz, 1 H), 7.42–7.62 (m, 7 H), 7.69 (t, *J* = 7.2 Hz, 1 H), 7.76 (d, *J* = 7.6 Hz, 1 H), 7.79 (d, *J* = 7.2 Hz, 1 H), 7.98 (d, *J* = 8.0 Hz, 1 H), 8.01 (d, *J* = 7.2 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 12.0, 34.4, 79.6 (d, J_{C-P} = 79.3 Hz), 110.5, 113.3, 128.0 (d, J_{C-P} = 11.5 Hz), 128.3 (d, J_{C-P} = 11.0 Hz), 128.5 (d, J_{C-P} = 2.4 Hz), 129.6 (d, J_{C-P} = 96.3 Hz), 129.8 (d, J_{C-P} = 95.6 Hz), 132.0, 132.1 (d, J_{C-P} = 8.9 Hz), 132.5 (d, J_{C-P} = 8.7 Hz), 142.3 (d, J_{C-P} = 5.5 Hz), 172.9.

^{31}P NMR (162 MHz, DMSO-d_6): δ = 28.1.

HRMS: *m*/*z* [M + H] calcd. for $C_{22}H_{19}BrNO_3P$ + H: 456.0364; found: 456.0370.

3-(Diphenyl-phosphinoyl)-3-hydroxy-5-nitro-indolin-2-one (3k)

The title compound was prepared by following the general procedure for Scheme 1, using 5-nitroisatin **1k** (0.5 mmol, 0.096 g) and diphenylphosphine oxide **2a** (0.5 mmol, 0.101 g), providing **3k** as a white solid. Yield: 0.181 g (92%); mp 142 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 6.97 (d, *J* = 8.8 Hz, 1 H), 7.09 (s, 1 H), 7.48–7.52 (m, 2 H), 7.55–7.75 (m, 5 H), 7.90–8.00 (m, 4 H), 8.18 (dd, *J* = 8.8, 1.2 Hz, 1 H), 11.2 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 79.7 (d, J_{C-P} = 79.2 Hz), 109.8, 120.8, 127.0, 127.7, 128.1 (d, J_{C-P} = 11.5 Hz), 128.4 (d, J_{C-P} = 11.5 Hz), 129.3 (d, J_{C-P} = 96.1 Hz), 129.5 (d, J_{C-P} = 96.4 Hz), 132.1, 132.3 (d, J_{C-P} = 2.0 Hz), 132.4 (d, J_{C-P} = 2.5 Hz), 132.7, 141.4, 149.1 (d, J_{C-P} = 5.5 Hz), 175.8.

^{31}P NMR (162 MHz, DMSO-d_6): δ = 27.7.

HRMS: *m*/*z* [M + H] calcd. for $C_{20}H_{15}N_2O_5P$ + H: 395.0797; found: 395.0785.

3-(Di(4-methylphenyl)phosphinoyl)-3-hydroxy-indolin-2-one (3l)

The title compound was prepared by following the general procedure for Scheme 1, using isatin **1a** (0.5 mmol, 0.073 g) and di(*p*-tolyl)phosphine oxide **2b** (0.5 mmol, 0.115 g), providing **3l** as a white solid. Yield: 0.175 g (93%); mp 152 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.32 (s, 3 H), 2.38 (s, 3 H), 6.44 (d, *J* = 7.6 Hz, 1 H), 6.71–6.77 (m, 2 H), 7.11–7.29 (m, 4 H), 7.34 (s, 1 H), 7.36 (s, 1 H), 7.66–7.91 (m, 4 H), 10.4 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.1, 21.2, 79.8 (d, J_{C-P} = 81.8 Hz), 109.4, 121.0, 125.6, 127.0, 127.4 (d, J_{C-P} = 97.7 Hz), 127.6 (d, J_{C-P} = 97.7 Hz), 128.4 (d, J_{C-P} = 11.8 Hz), 128.7 (d, J_{C-P} = 11.7 Hz), 129.7, 132.3 (d, J_{C-P} = 9.0 Hz), 141.5, 142.0, 142.8 (d, J_{C-P} = 5.8 Hz), 175.4.

^{31}P NMR (162 MHz, DMSO-d_6): δ = 27.9.

HRMS: *m*/*z* [M + H] calcd. for $C_{22}H_{20}NO_3P$ + H: 378.1259; found: 378.1265.

3-(Di(4-methylphenyl)phosphinoyl)-3-hydroxy-1-ethylindolin-2-one (3m)

The title compound was prepared by following the general procedure for Scheme 1, using 1-ethylisatin **1c** (0.5 mmol, 0.087 g) and di(*p*-tolyl)phosphine oxide **2b** (0.5 mmol, 0.115 g), providing **3m** as a white solid. Yield: 0.194 g (96%); mp 140 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.2 Hz, 3 H), 2.36 (s, 3 H), 2.41 (s, 3 H), 3.32–3.37 (m, 1 H), 3.57–3.63 (m, 1 H), 4.58 (bs, 1 H), 6.66 (d, *J* = 8.0 Hz, 1 H), 6.89 (t, *J* = 7.6 Hz, 1 H), 6.98 (d, *J* = 7.6 Hz, 1 H), 7.170 (d, *J* = 8.0 Hz, 1 H), 7.176 (d, *J* = 8.0 Hz, 1 H), 7.26–7.29 (m, 3 H), 7.57 (d, *J* = 8.0 Hz, 1 H), 7.60 (d, *J* = 8.0 Hz, 1 H), 7.75 (d, *J* = 8.0 Hz, 1 H), 7.78 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.0, 21.7, 34.9, 79.8 (d, J_{C-P} = 70.8 Hz), 108.2, 122.6, 124.0 (d, J_{C-P} = 98.4 Hz), 124.5, 125.4 (d, J_{C-P} = 99.9 Hz), 126.8 (d, J_{C-P} = 3.0 Hz), 128.9 (d, J_{C-P} = 12.3 Hz), 129.1 (d, J_{C-P} = 11.9 Hz), 130.3, 132.4 (d, J_{C-P} = 9.5 Hz), 132.9 (d, J_{C-P} = 8.9 Hz), 143.0 (d, J_{C-P} = 2.4 Hz), 143.2 (d, J_{C-P} = 2.7 Hz), 143.5 (d, J_{C-P} = 5.4 Hz), 173.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 30.9.

HRMS: *m*/*z* [M + H] calcd. for $C_{24}H_{24}NO_3P$ + H: 406.1572; found: 406.1574.

5-Chloro-3-(di(4-methylphenyl)phosphinoyl)-3-hydroxy-indolin-2-one (3n)

The title compound was prepared by following the general procedure for Scheme 1, using 5-chloroisatin **1e** (0.5 mmol, 0.090 g) and di(*p*-tolyl)phosphine oxide **2b** (0.5 mmol, 0.115 g), providing **3n** as a white solid. Yield: 0.185 g (90%); mp 138 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.32 (s, 3 H), 2.39 (s, 3 H), 6.33 (s, 1 H), 6.75 (d, *J* = 8.4 Hz, 1 H), 7.23–7.42 (m, 6 H), 7.73 (d, *J* = 8.0 Hz, 1 H), 7.75 (d, *J* = 8.0 Hz, 1 H), 7.81 (d, *J* = 8.4 Hz, 1 H), 7.84 (d, *J* = 8.4 Hz, 1 H), 10.6 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.1, 22.2, 80.0 (d, J_{C-P} = 80.2 Hz), 110.8, 124.9 (d, J_{C-P} = 2.4 Hz), 125.6, 126.8 (d, J_{C-P} = 98.3 Hz), 127.0 (d, J_{C-P} = 98.5 Hz), 128.5 (d, J_{C-P} = 11.8 Hz), 128.8 (d, J_{C-P} = 11.9 Hz), 128.9, 129.5, 132.3 (d, J_{C-P} = 9.2 Hz), 132.5 (d, J_{C-P} = 9.1 Hz), 141.6 (d, J_{C-P} = 5.2 Hz), 141.8, 142.4, 175.2.

^{31}P NMR (162 MHz, DMSO-d_6): δ = 28.3.

HRMS: *m*/*z* [M + H] calcd. for $C_{22}H_{19}ClNO_3P$ + H: 412.0869; found: 412.0875.

5-Chloro-3-(di(4-methylphenyl)phosphinoyl)-3-hydroxy-1-ethylindolin-2-one (3o)

The title compound was prepared by following the general procedure for Scheme 1, using 5-chloro-1-ethylisatin **1g** (0.5 mmol, 0.105 g) and di(*p*-tolyl)phosphine oxide **2b** (0.5 mmol, 0.115 g), providing **3o** as a white solid. Yield: 0.206 g (94%); mp 122 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 7.2 Hz, 3 H), 2.34 (s, 3 H), 2.42 (s, 3 H), 3.26–3.32 (m, 1 H), 3.49–3.54 (m, 1 H), 6.13 (bs, 1 H), 6.51 (d, *J* = 8.4 Hz, 1 H), 7.10–7.16 (m, 3 H), 7.21 (d, *J* = 8.0 Hz, 1 H), 7.23–7.30 (m, 2 H), 7.51 (d, *J* = 8.0 Hz, 1 H), 7.54 (d, *J* = 8.0 Hz, 1 H), 7.83 (d, *J* = 8.0 Hz, 1 H), 7.86 (d, *J* = 8.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.9, 21.6, 21.7, 35.0, 80.3 (d, J_{C-P} = 70.8 Hz), 108.8, 124.2 (d, J_{C-P} = 99.8 Hz), 124.9 (d, J_{C-P} = 99.9 Hz), 127.0, 127.4 (d, J_{C-P} = 2.6 Hz), 127.9 (d, J_{C-P} = 2.6 Hz), 128.8 (d, J_{C-P} = 12.3 Hz), 129.1 (d, J_{C-P} = 12.4 Hz), 129.9, 132.4 (d, J_{C-P} = 9.6 Hz), 133.0 (d, J_{C-P} = 9.5 Hz), 141.6 (d, J_{C-P} = 5.7 Hz), 143.0 (d, J_{C-P} = 2.6 Hz), 143.2 (d, J_{C-P} = 2.4 Hz), 173.2 (d, J_{C-P} = 5.2 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.8.

HRMS: *m*/*z* [M + H] calcd. for $C_{24}H_{23}ClNO_3P$ + H: 440.1182; found: 440.1195.

3-(Bis(3,5-dimethylphenyl)phosphinoyl)-3-hydroxy-indolin-2-one (3p)

The title compound was prepared following the general procedure for Scheme 1, using isatin **1a** (0.5 mmol, 0.073 g) and bis (3,5-dimethylphenyl)phosphine oxide **2c** (0.5 mmol, 0.129 g), providing **3p** as a white solid. Yield: 0.182 g (90%); mp 178 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.29 (s, 6 H), 2.31 (s, 6 H), 5.31 (d, *J* = 6.4 Hz, 1 H), 6.65 (d, *J* = 7.2 Hz, 1 H), 6.69 (d, *J* = 7.6 Hz, 1 H), 7.79 (t, *J* = 7.6 Hz, 1 H), 7.11–7.23 (m, 3 H), 7.44 (s, 1 H), 7.46 (s, 1 H), 7.48 (s, 1 H), 7.51 (s, 1 H), 9.31 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6): δ = 21.3, 80.2 (d, J_{C-P} = 72.7 Hz), 110.2, 122.0, 125.3, 126.3 (d, J_{C-P} = 2.3 Hz), 127.4 (d, J_{C-P} = 91.9 Hz), 128.1, 128.4 (d, J_{C-P} = 95.6 Hz), 130.1 (d, J_{C-P} = 8.5 Hz), 130.3 (d, J_{C-P} = 9.2 Hz), 134.1 (d, J_{C-P} = 2.4 Hz), 134.2 (d, J_{C-P} = 2.5 Hz), 137.6 (d, J_{C-P} = 12.6 Hz), 137.8 (d, J_{C-P} = 12.3 Hz), 142.4 (d, J_{C-P} = 6.1 Hz), 175.9.

^{31}P NMR (162 MHz, $CDCl_3$/DMSO-d_6): δ = 30.8.

HRMS: *m*/*z* [M + H] calcd. for $C_{24}H_{24}NO_3P$ + H: 406.1572; found: 406.1582.

3-(Bis(3,5-dimethylphenyl)phosphinoyl)-3-hydroxy-1-methylindolin-2-one (3q)

The title compound was prepared by following the general procedure for Scheme 1, using 1-methylisatin **1b** (0.5 mmol, 0.080 g) and bis (3,5-dimethylphenyl)phosphine oxide **2c** (0.5 mmol, 0.129 g), providing **3q** as a white solid. Yield: 0.192 g (92%); mp 138 °C.

^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6): δ = 2.27 (s, 6 H), 2.34 (s, 6 H), 2.94 (s, 3 H), 6.65 (d, *J* = 8.0 Hz, 1 H), 6.75 (bs, 1 H), 6.85–6.95 (m, 2 H), 7.10 (s, 1 H), 7.19 (s, 1 H), 7.26 (t, *J* = 7.6 Hz, 1 H), 7.36 (s, 1 H), 7.39 (s, 1 H), 7.57 (s, 1 H), 7.60 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6): δ = 20.7, 20.8, 25.6, 80.0 (d, J_{C-P} = 75.5 Hz), 107.2, 121.7, 125.1, 125.8, 128.0 (d, J_{C-P} = 95.6 Hz), 128.4 (d, J_{C-P} = 95.6 Hz), 129.4 (d, J_{C-P} = 8.7 Hz), 129.8 (d, J_{C-P} = 8.9 Hz), 133.1, 133.3, 136.7 (d, J_{C-P} = 12.5 Hz), 137.0 (d, J_{C-P} = 12.4 Hz), 143.4 (d, J_{C-P} = 5.7 Hz), 173.5.

^{31}P NMR (162 MHz, $CDCl_3$/DMSO-d_6): δ = 30.4.

HRMS: *m*/*z* [M + H] calcd. for $C_{25}H_{26}NO_3P$ + H: 420.1729; found: 420.1737.

3-(Bis(3,5-dimethylphenyl)phosphinoyl)-3-hydroxy-1-ethylindolin-2-one (3r)

The title compound was prepared by following the general procedure for Scheme 1, using 1-ethylisatin **1c** (0.5 mmol, 0.087 g) and bis (3,5-dimethylphenyl)phosphine oxide **2c** (0.5 mmol, 0.129 g), providing **3r** as a white solid. Yield: 0.203 g (94%); mp 132 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83 (t, *J* = 7.2 Hz, 3 H), 2.26 (s, 6 H), 2.31 (s, 6 H), 3.29–3.35 (m, 1 H), 3.51–3.62 (m, 1 H), 4.57 (s, 1 H), 6.66 (d, *J* = 7.6 Hz, 1 H), 6.91 (t, *J* = 7.6 Hz, 1 H), 6.99 (d, *J* = 7.2 Hz, 1 H), 7.12 (s, 1 H), 7.19 (s, 1 H), 7.24–7.34 (m, 3 H), 7.39 (s, 1 H), 7.42 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.0, 21.36, 21.39, 34.8, 79.8 (d, J_{C-P} = 69.4 Hz), 107.9, 122.5, 124.4, 126.8 (d, J_{C-P} = 95.7 Hz), 127.1, 128.1, 128.2, 128.4 (d, J_{C-P} = 96.2 Hz), 129.9 (d, J_{C-P} = 9.2 Hz), 130.3 (d, J_{C-P} = 8.4 Hz), 134.2 (d, J_{C-P} = 1.8 Hz), 134.3 (d, J_{C-P} = 2.5 Hz), 137.8 (d, J_{C-P} = 12.7 Hz), 138.0 (d, J_{C-P} = 12.4 Hz), 143.7 (d, J_{C-P} = 5.9 Hz), 173.6.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.3.

HRMS: *m*/*z* [M + H] calcd. for $C_{26}H_{28}NO_3P$ + H: 434.1885; found: 434.1872.

3-(Bis(3,5-dimethylphenyl)phosphinoyl)-3-hydroxy-1-benzylindolin-2-one (3s)

The title compound was prepared by following the general procedure for Scheme 1, using 1-benzylisatin **1d** (0.5 mmol, 0.118 g) and bis (3,5-dimethylphenyl)phosphine oxide **2c** (0.5 mmol, 0.129 g), providing **3s** as a white solid. Yield: 0.227 g (92%); mp 134 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 6 H), 2.26 (s, 6 H), 4.45 and 4.79 (ABq, *J* = 16.0 Hz, 2 H), 6.52 (d, *J* = 7.6 Hz, 1 H), 6.87 (t, *J* = 7.6 Hz, 1 H), 6.92–6.97 (m, 2 H), 7.00 (d, *J* = 7.6 Hz, 1 H), 7.13–7.22 (m, 6 H), 7.28 (s, 1 H), 7.31 (s, 1 H), 7.42 (s, 1 H), 7.45 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.36, 21.38, 44.3, 79.8 (d, J_{C-P} = 70.3 Hz), 109.1, 122.8, 124.7, 126.8 (d, J_{C-P} = 95.3 Hz), 126.9, 127.0, 127.4 (d, J_{C-P} = 93.0 Hz), 127.5, 128.7, 128.82, 128.86, 130.1 (d, J_{C-P} = 9.3 Hz), 130.3 (d, J_{C-P} = 9.0 Hz), 134.3 (d, J_{C-P} = 2.7 Hz), 134.5, 135.0, 137.8 (d, J_{C-P} = 12.6 Hz), 138.0 (d, J_{C-P} = 12.4 Hz), 143.8 (d, J_{C-P} = 5.8 Hz), 174.4.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.6.

HRMS: *m*/*z* [M + H] calcd. for $C_{31}H_{30}NO_3P$ + H: 496.2042; found: 496.2051.

3-(Bis(3,5-dimethylphenyl)phosphinoyl)-5-chloro-3-hydroxy-indolin-2-one (3t)

The title compound was prepared by following the general procedure for Scheme 1, using 5-chloroisatin **1e** (0.5 mmol, 0.090 g) and bis (3,5-dimethylphenyl)phosphine oxide **2c** (0.5 mmol, 0.129 g), providing **3t** as a white solid. Yield: 0.202 g (92%); mp 208 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.28 (s, 6 H), 2.33 (s, 6 H), 6.21 (s, 1 H), 6.76 (d, *J* = 8.4 Hz, 1 H), 7.18 (s, 1 H), 7.24–7.33 (m, 3 H), 7.46 (s, 1 H), 7.49 (s, 1 H), 7.53 (s, 1 H), 7.56 (s, 1 H), 10.60 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.94, 20.98, 80.0 (d, J_{C-P} = 79.7 Hz), 110.7, 124.8 (d, J_{C-P} = 2.4 Hz), 125.6 (d, J_{C-P} = 2.1 Hz), 128.9, 129.4, 129.83 (d, J_{C-P} = 94.4 Hz), 129.88 (d, J_{C-P} = 8.2 Hz), 129.9 (d, J_{C-P} = 5.9 Hz), 130.0 (d, J_{C-P} = 94.8 Hz), 133.2, 133.6, 136.8 (d, J_{C-P} = 12.3 Hz), 137.2 (d, J_{C-P} = 12.0 Hz), 141.6 (d, J_{C-P} = 5.7 Hz), 175.0.

^{31}P NMR (162 MHz, DMSO-d_6): δ = 27.9.

HRMS: *m*/*z* [M + H] calcd. for $C_{24}H_{23}ClNO_3P$ + H: 440.1182; found: 440.1172.

3-(Bis(3,5-dimethylphenyl)phosphinoyl)-5-bromo-3-hydroxy-indolin-2-one (3u)

The title compound was prepared by following the general procedure for Scheme 1, using 5-bromoisatin **1i** (0.5 mmol, 0.113 g) and bis (3,5-dimethylphenyl)phosphine oxide **2c** (0.5 mmol, 0.129 g), providing **3u** as a white solid. Yield: 0.207 g (86%); mp 178 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.24 (s, 6 H), 2.28 (s, 6 H), 5.55 (d, *J* = 11.6 Hz, 1 H), 6.74 (d, *J* = 8.0 Hz, 1 H), 7.19 (s, 1 H), 7.23 (s, 1 H), 7.27 (s, 1 H), 7.30 (s, 1 H), 7.35 (s, 1 H), 7.39 (d, *J* = 8.4 Hz, 1 H), 7.51 (s, 1 H), 7.54 (s, 1 H), 10.7 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.2, 69.9 (d, J_{C-P} = 6.0 Hz,), 111.5, 112.8, 127.1, 128.1 (d, J_{C-P} = 8.3 Hz), 129.5 (d, J_{C-P} = 3.2 Hz), 130.7 (d, J_{C-P} = 10.0 Hz), 132.3, 132.6, 133.5, 137.6 (d, J_{C-P} = 14.0 Hz), 141.7, 172.4.

^{31}P NMR (162 MHz, DMSO-d_6): δ = 35.6.

HRMS: *m*/*z* [M + H] calcd. for $C_{24}H_{23}BrNO_3P$ + H: 484.0677; found: 484.0689.

3-(Bis(3,5-dimethylphenyl)phosphinoyl)-5-chloro-3-hydroxy-1-ethylindolin-2-one (3v)

The title compound was prepared by following the general procedure for Scheme 1, using 5-chloro-1-ethylisatin **1g** (0.5 mmol, 0.105 g) and bis (3,5-dimethylphenyl)phosphine oxide **2c** (0.5 mmol, 0.129 g), providing **3v** as a white solid. Yield: 0.217 g (93%); mp 138 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.2 Hz, 3 H), 2.29 (s, 6 H), 2.33 (s, 6 H), 3.32–3.37 (m, 1 H), 3.56–3.61 (m, 1 H), 4.75 (d, *J* = 3.6 Hz, 1 H), 6.60 (d, *J* = 8.4 Hz, 1 H), 6.85–6.90 (m, 1 H), 7.15 (s, 1 H), 7.21 (s, 1 H), 7.25–7.27 (m, 2 H), 7.30 (s, 1 H), 7.33 (s, 1 H), 7.42 (s, 1 H), 7.45 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.0, 21.3, 21.4, 35.0, 79.7 (d, J_{C-P} = 68.0 Hz), 108.8, 126.2, 126.4, 127.5 (d, J_{C-P} = 2.7 Hz), 127.9 (d, J_{C-P} = 2.6 Hz), 128.2, 128.6, 130.0 (d, J_{C-P} = 9.4 Hz), 130.2 (d, J_{C-P} = 8.8 Hz), 134.5 (d, J_{C-P} = 2.4 Hz), 134.6 (d, J_{C-P} = 2.5 Hz), 137.9 (d, J_{C-P} = 12.6 Hz), 138.2 (d, J_{C-P} = 12.5 Hz), 142.1 (d, J_{C-P} = 5.6 Hz), 173.3.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.4.

HRMS: *m*/*z* [M + H] calcd. for $C_{26}H_{27}ClNO_3P$ + H: 468.1495; found: 468.1480.

3-(Bis(3,5-dimethylphenyl)phosphinoyl)-5-bromo-3-hydroxy-1-ethylindolin-2-one (3w)

The title compound was prepared by following the general procedure for Scheme 1, using 5-bromo-1-ethylisatin **1j** (0.5 mmol, 0.127 g) and bis (3,5-dimethylphenyl)phosphine oxide **2c** (0.5 mmol, 0.129 g), providing **3w** as a white solid. Yield: 0.240 g (94%); mp 132 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 7.2 Hz, 3 H), 2.29 (s, 6 H), 2.33 (s, 6 H), 3.30–3.36 (m, 1 H), 3.54–3.60 (m, 1 H), 5.14 (s, 1 H), 6.55 (d, *J* = 8.4 Hz, 1 H), 7.01 (s, 1 H), 7.15 (s, 1 H), 7.26 (s, 1 H), 7.31 (s, 1 H), 7.34 (s, 1 H), 7.41–7.51 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.0, 21.3, 21.4, 35.0, 79.8 (d, J_{C-P} = 68.3 Hz), 109.2, 115.0, 126.2, 126.8, 127.6 (d, J_{C-P} = 96.3 Hz), 130.0 (d, J_{C-P} = 9.2 Hz), 130.3 (d, J_{C-P} = 9.1 Hz), 132.9, 134.4 (d, J_{C-P} = 2.4 Hz), 134.5 (d, J_{C-P} = 2.5 Hz), 137.9 (d, J_{C-P} = 12.9 Hz), 138.1 (d, J_{C-P} = 12.5 Hz), 142.5 (d, J_{C-P} = 5.9 Hz), 173.2.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.5.

HRMS: *m*/*z* [M + H] calcd. for $C_{26}H_{27}BrNO_3P$ + H: 512.0990; found: 512.0982.

3-(Bis(3,5-dimethylphenyl)phosphinoyl)-3-hydroxy-5-nitro-indolin-2-one (3x)

The title compound was prepared by following the general procedure for Scheme 1, using 5-nitroisatin **1k** (0.5 mmol, 0.096 g) and bis (3,5-dimethylphenyl)phosphine oxide **2c** (0.5 mmol, 0.129 g), providing **3x** as a white solid. Yield: 0.207 g (92%); mp 184 °C.

^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6): δ = 2.36 (s, 12 H), 6.80–6.95 (m, 2 H), 7.18 (s, 1 H), 7.27 (s, 1 H), 7.28–7.35 (m, 1 H),7.50–7.60 (m, 2 H), 7.68 (s, 1 H), 7.71 (s, 1 H), 8.08 (t, *J* = 7.2 Hz, 1 H), 10.7 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 20.9, 21.0, 79.7 (d, J_{C-P} = 78.4 Hz), 109.7, 121.0, 126.9, 127.8, 129.0, 129.2 (d, J_{C-P} = 94.9 Hz), 129.9 (d, J_{C-P} = 8.7 Hz), 133.5, 133.9, 137.1 (d, J_{C-P} = 12.3 Hz), 137.5 (d, J_{C-P} = 12.2 Hz), 141.3, 149.1 (d, J_{C-P} = 5.3 Hz), 175.8.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.4.

HRMS: *m*/*z* [M + H] calcd. for $C_{24}H_{23}N_2O_5P$ + H: 451.1423; found: 451.1430.

3-Diphenylphosphoryl-3-hydroxy-indolin-2-one (3y1)[20]

The title compound was prepared by following the general procedure for Scheme 1, using isatin **1a** (1.0 mmol, 0.147 g) and diphenyl phosphite **2d** (1.0 mmol, 0.234 g, 0.2 mL), providing **3y1** as a white solid. Yield: 0.343 g (90%); mp 130 °C.

^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6): δ = 6.25 (bs, 1 H), 6.84–6.93 (m, 3 H), 7.02–7.10 (m, 2 H), 7.13–7.33 (m, 8 H), 7.65 (d, *J* = 7.6 Hz, 1 H), 9.85 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6): δ = 75.5, 110.3, 120.4 (d, J_{C-P} = 3.8 Hz), 120.9 (d, J_{C-P} = 3.9 Hz), 122.4, 125.0 (d, J_{C-P} = 9.2 Hz), 125.2, 126.8 (d, J_{C-P} = 3.4 Hz), 129.3 (d, J_{C-P} = 8.3 Hz), 130.5, 142.4 (d, J_{C-P} = 9.1 Hz), 150.1 (d, J_{C-P} = 10.2 Hz), 150.4 (d, J_{C-P} = 10.4 Hz), 174.6 (d, J_{C-P} = 4.9 Hz).

^{31}P NMR (162 MHz, $CDCl_3$/DMSO-d_6): δ = 9.1.

HRMS: *m*/*z* [M + Na] calcd. for $C_{20}H_{16}NO_5P$ + Na: 404.0664; found: 404.0622.

3-Diphenylphosphoryl-3-hydroxy-1-methylindolin-2-one (3y2)

The title compound was prepared by following the general procedure for Scheme 1, using *N*-methylisatin **1b** (1.0 mmol, 0.161 g) and diphenyl phosphite **2d** (1.0 mmol, 0.234 g, 0.2 mL), providing **3y2** as a white solid. Yield: 0.367 g (93%); mp 106 °C.

^{1}H NMR (400 MHz, $CDCl_3$/DMSO-d_6): δ = 3.22 (s, 3 H), 6.82–6.90 (m, 3 H), 7.07–7.12 (m, 2 H), 7.15–7.25 (m, 5 H), 7.27–7.35 (m, 2 H), 7.36–7.42 (m, 1 H), 7.67 (d, *J* = 7.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$/DMSO-d_6): δ = 26.8, 75.2, 108.8, 120.4 (d, J_{C-P} = 3.9 Hz), 120.7 (d, J_{C-P} = 4.1 Hz), 123.5 (d, J_{C-P} = 2.5 Hz), 125.5 (d, J_{C-P} = 11.4 Hz), 126.9 (d, J_{C-P} = 3.4 Hz), 129.7 (d, J_{C-P} = 13.4 Hz), 131.1, 144.4 (d, J_{C-P} = 8.8 Hz), 150.1 (d, J_{C-P} = 9.8 Hz), 150.3 (d, J_{C-P} = 10.3 Hz), 173.0 (d, J_{C-P} = 6.0 Hz).

^{31}P NMR (162 MHz, $CDCl_3$/DMSO-d_6): δ = 8.8.

HRMS: *m*/*z* [M + H] calcd. for $C_{21}H_{18}NO_5P$ + H: 396.1001; found: 396.0989.

3-Diphenylphosphoryl-3-hydroxy-1-ethylindolin-2-one (3y3)

The title compound was prepared by following the general procedure for Scheme 1, using *N*-ethylisatin **1c** (1.0 mmol, 0.175 g) and diphenyl phosphite **2d** (1.0 mmol, 0.234 g, 0.2 mL), providing **3y3** as a colorless viscous liquid. Yield: 0.372 g (91%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.27 (t, *J* = 7.2 Hz, 3 H), 3.73–3.76 (m, 2 H), 5.78 (d, *J* = 12.0 Hz, 1 H), 6.83 (d, *J* = 8.0 Hz, 1 H), 6.98 (t, *J* = 7.6 Hz, 1 H), 7.18–7.24 (m, 5 H), 7.25–7.47 (m, 7 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.5, 35.0, 73.6 (d, J_{C-P} = 6.0 Hz), 108.7, 120.50 (d, J_{C-P} = 4.7 Hz), 120.59 (d, J_{C-P} = 4.7 Hz), 123.0, 123.6 (d, J_{C-P} = 3.2 Hz), 125.6, 126.3, 129.8, 130.9, 143.4, 150.3 (d, J_{C-P} = 7.3 Hz), 150.5 (d, J_{C-P} = 7.4 Hz), 170.7.

^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.7.

HRMS: *m*/*z* [M + H] calcd. for $C_{22}H_{20}NO_5P$ + H: 410.1157; found: 410.1168.

3-Diphenylphosphoryl-5-chloro-3-hydroxy-1-methylindolin-2-one (3y4)

The title compound was prepared by following the general procedure for Scheme 1, using 5-chloro-1-ethylisatin **1g** (1.0 mmol, 0.209 g) and diphenyl phosphite **2d** (1.0 mmol, 0.234 g, 0.2 mL), providing **3y4** as a colorless viscous liquid. Yield: 0.381 g (86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.2 Hz, 3 H), 3.69–3.75 (m, 2 H), 5.73 (d, *J* = 12.4 Hz, 1 H), 6.74 (d, *J* = 8.4 Hz, 1 H), 7.06–7.08 (m, 1 H), 7.23–7.26 (m, 5 H), 7.27–7.47 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.4, 35.2, 73.1 (d, J_{C-P} = 5.9 Hz), 109.6, 120.6 (d, J_{C-P} = 3.0 Hz), 125.1 (d, J_{C-P} = 2.9 Hz), 125.9 (d, J_{C-P} = 18.6 Hz), 126.7, 128.4, 129.9 (d, J_{C-P} = 3.2 Hz), 130.7, 141.9, 150.1 (d, J_{C-P} = 7.2 Hz), 150.4 (d, J_{C-P} = 7.6 Hz), 170.4 (d, J_{C-P} = 6.8 Hz).

^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.6.

HRMS: *m*/*z* [M + Na] calcd. for $C_{22}H_{19}ClNO_5P$ + Na: 466.0587; found: 466.0542.

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Supporting Information

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