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Palladium-Catalyzed Oxidative Cyclization for the Synthesis of Indolyl/Pyrrolyl 3-Phosphonates

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Abstract: Imino-/enaminophosphonates derived from amines and diethyl phenacyl phosphonates undergo oxidative cyclization *via* C–H bond activation catalyzed by palladium chloride to provide a convenient route for the synthesis of substituted indol-3-yl and pyrrol-3-yl phosphonates.

Keywords: C–H bond activation; imine-enamines; indoles; ketophosphonates; phosphonates; pyrroles

The ubiquitous presence of indole and pyrrole skeletons in various natural products, pharmaceuticals and synthetic materials make them immensely valuable heterocycles.[1] Hence development of new and efficient methods for their synthesis and derivatization assumes high significance.[2] Ketones, hydrazines, arylamines and their derivatives are the most common and easily accessible starting materials for the synthesis of various azaheterocycles.[3] Over the past decades, a plethora of methods through C–H/C–X functionalization have been developed for the synthesis of indoles, pyrroles and carbazoles.[4] In this context, the Glorius and Yoshikai groups have developed a concept of palladium-catalyzed oxidative cyclization of α-arylenamine/imines independently.[5] On the other hand, significant attention has also been devoted to synthesize biologically active[6] (Figure 1) and synthetically important organophosphorus molecules,[7] including conventional methods and direct C–P bond formation reactions.[8]

Recently, 3-phosphinoylindoles have been synthesized employing direct C–H/C–P bond formation approaches [Scheme 1, Eq. (1) and Eq. (2)].[9]

However, the synthesis of indolyl 3-phosphonates using transition metal-catalyzed oxidative cyclization of imines or enamines remains untouched. Encouraged by the recent reports on the synthesis of phosphonate-containing heterocycles, we sought to find a catalytic method for indolyl 3-phosphonates *via* oxi-

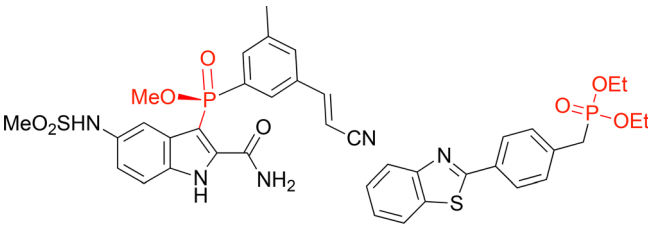
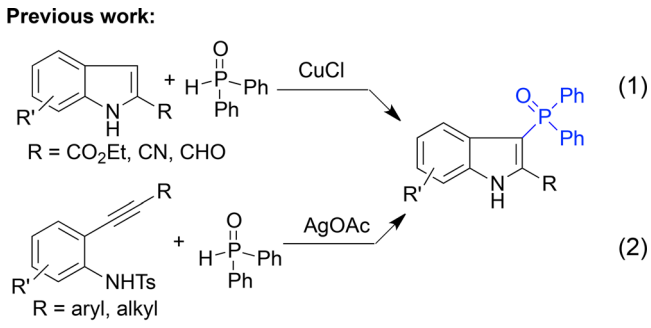


Figure 1. Bioactive phosphonates.



Scheme 1. Strategy for indolyl-phosphine derivatives.

dative cyclization of enamines/imines derived from β-ketophosphonates and amines [Eq. (3)].[10] Herein, we disclose a $PdCl_2/Cu(OAc)_2$-catalyzed oxidative cyclization approach for the synthesis of indolyl 3-phosphonates starting from *N*-arylimines/enamines, prepared from arylamines and β-ketophosphonates [Eq. (3)].

We commenced our study using the freshly prepared mixture of imine-enamine **1a/2a**,[10] obtained from aniline and diethyl phenacylphosphonate, as substrate. Screening of various palladium catalysts led us to find that the combination of $PdCl_2$ (10 mol%) and $Cu(OAc)_2$ (1 equiv.) in DMSO serves as an efficient catalytic system to obtain indolyl 3-phosphonate **3a** in 82% yield at 100 °C or 60 °C (Table 1, entries 8 and 12). The use of several other palladium sources resulted in lower yields (Table 1). Replacement of $Cu(OAc)_2$ with other oxidants also proved less effective or not effective at all. Even the use of various solvents (DMF, DMA and MeCN) other than DMSO resulted in poor conversion.

Increasing the amount of $Cu(OAc)_2$ to 2 equiv. did not improve the yield of the product, while 0.5 equiv. of $Cu(OAc)_2$ proved less efficient (65%). Lowering the catalyst loading ($PdCl_2$, 5 mol%) also proved less satisfactory (Table 1, entries 3 and 14). Complete hydrolysis of the starting material was observed in the presence of 1 equiv. of $PdCl_2$ (Table 1, entry 19). Addition of different bases such as Ag_2CO_3, K_2CO_3, DBU, DIPEA, etc. as additives remained ineffective. The yield could not be improved either by extending the reaction time or increasing the reaction temperature. However, to make this method general, we have chosen 100 °C as the optimized reaction temperature. Using the optimized reaction conditions (Table 1, entry 8), we expanded the scope of indole formation from the corresponding enamines.

Employing the $PdCl_2/Cu(OAc)_2$ catalytic combination, an array of 2-substituted indolyl 3-phosphonates was synthesized in good to excellent yields from the corresponding imine/enamine mixtures, derived from substituted anilines and β-ketophosphonates with tolerance of a broad range of functional groups as illustrated in Table 2. The effect of substituents on the aromatic ring undergoing indole formation was tested using imines/enamines **1/2** derived from anilines and β-ketophosphonates (Table 2).

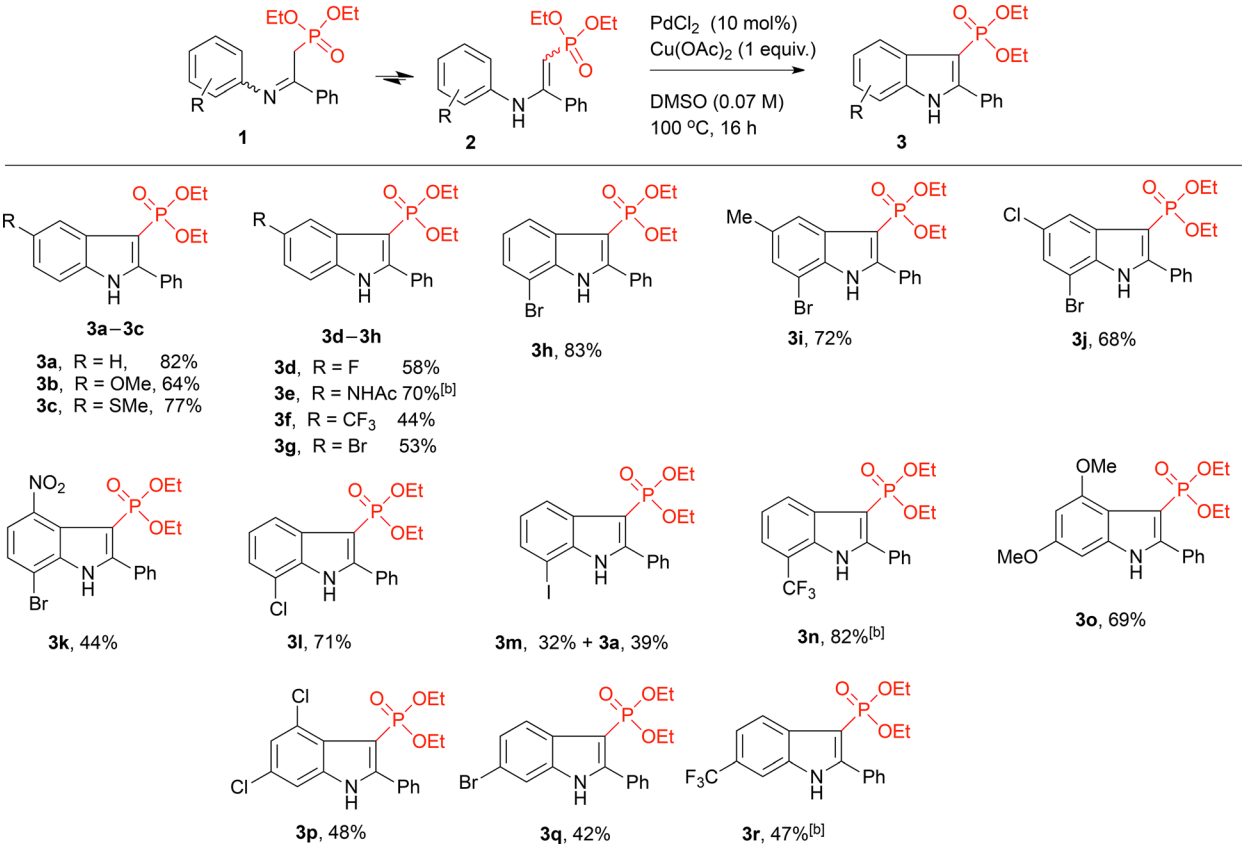
Substrates bearing electron-donating (methoxy, S-methyl) or electron-withdrawing groups on the *para* position of the arene underwent cyclization and readily afforded the products in moderate to good yields (**3a–3g**). Interestingly, substrates containing a halogen (F, Cl or Br) at *ortho*, *meta* and *para* positions provided the indoles in good to excellent yields (**3d**, **3g**-**3l**). On the other hand for iodo-containing substrate **2m**, the desired product **3m** was obtained in 32% yield along with deiodinated parent indole **3a** (39% yield). We observed that the substrates **2f**, **2k**, **2p** and **2r**

Table 1. Optimization of the reaction conditions for the cyclization of imine-enamines.[a]

Entry	Catalyst (mol%)	Additive	Solvent	Temp. [°C]	Yield [%][b]
1	$Pd(OAc)_2$ (10)	O_2/TBAB	DMSO	60	62[c]
2	$Pd(OAc)_2$ (5)	$Cu(OAc)_2$	DMSO	100	52
3	$PdCl_2$ (5)	$Cu(OAc)_2$	DMSO	100	58
4	$Pd(MeCN)_2Cl_2$ (5)	$Cu(OAc)_2$	DMSO	100	52
5	Pd(xanthphos)Cl_2 (5)	$Cu(OAc)_2$	DMSO	100	54
6	Pd(dppf)Cl_2 (5)	$Cu(OAc)_2$	DMSO	100	56
7	$Pd[P(O\text{-tol})_3]_2Cl_2$ (5)	$Cu(OAc)_2$	DMSO	100	28
8	**$PdCl_2$ (10)**	**$Cu(OAc)_2$**	**DMSO**	**100**	**82**
9	$PdCl_2$ (10)	O_2/TBAB	DMSO	100	–[d]
10	$PdCl_2$ (10)	$CuCl_2$	DMSO	100	58
11	$PdCl_2$ (10)	$Cu(OAc)_2$	DMSO	120	68
12	**$PdCl_2$ (10)**	**$Cu(OAc)_2$**	**DMSO**	**60**	**82**
13	$PdCl_2$ (10)	$Cu(OAc)_2$	DMSO	60	65[e]
14	$PdCl_2$ (5)	$Cu(OAc)_2$	DMSO	60	55
15	$PdCl_2$ (10)	$Cu(OAc)_2$	DMF	60	38
16	$PdCl_2$ (10)	$Cu(OAc)_2$	DMA	60	39
17	$PdCl_2$ (10)	$Cu(OAc)_2$	CH_3CN	60	73
18	–	$Cu(OAc)_2$	DMSO	60	nr
19	$PdCl_2$ (100)	–	DMSO	60	–[d]

[a] *Reaction conditions:* unless otherwise mentioned all reactions performed with mixture of **1a** and **2a** (0.2 mmol), $PdCl_2$ (10 mol%), $Cu(OAc)_2$ (1 equiv.), DMSO (0.07 M), 60–100 °C, N_2, 16 h.
[b] Isolated yield; nr = no reaction.
[c] 2.0 equiv of tetrabutylammonium bromide (TBAB).
[d] Hydrolysis of **1a**/**2a** was observed.
[e] 0.5 equiv. of $Cu(OAc)_2$.

Table 2. Scope of palladium-catalyzed oxidative cyclization of imine-enamines.[a]



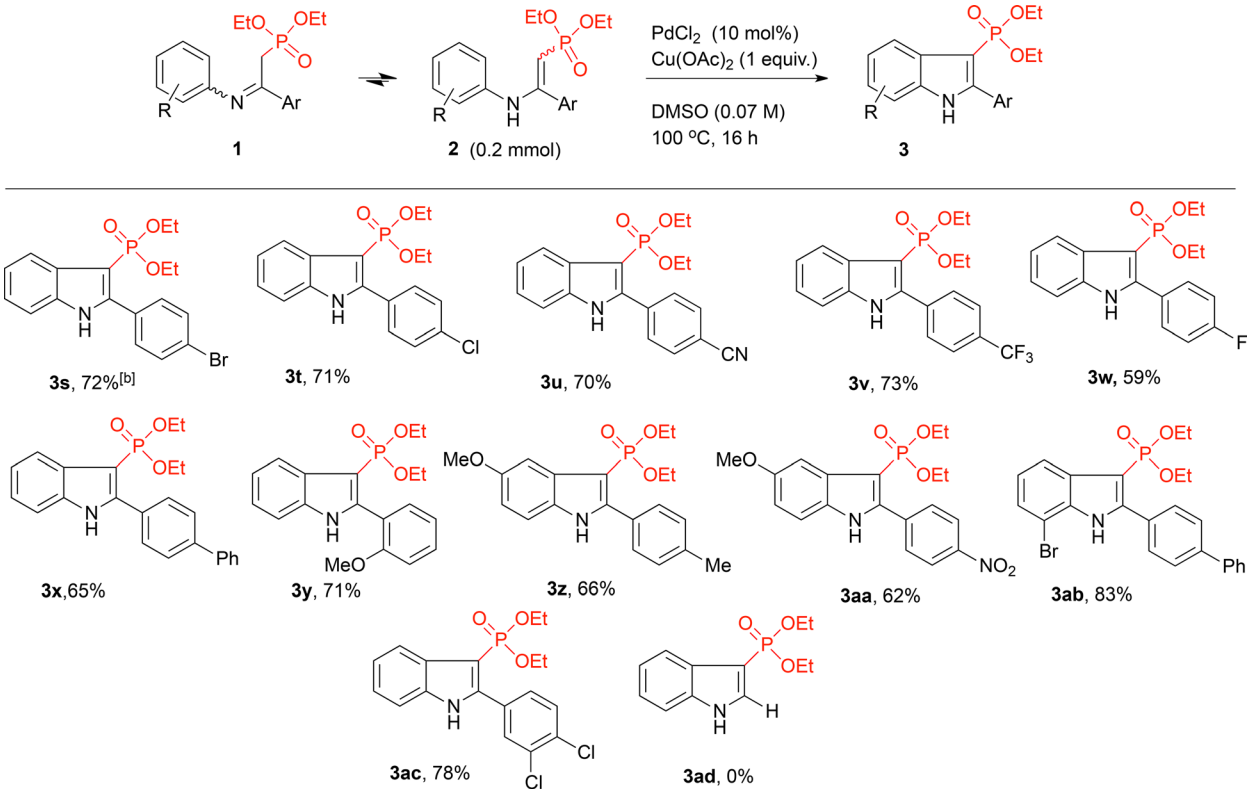
[a] *Reaction conditions:* mixture of **1** and **2** (0.2 mmol), $PdCl_2$ (10 mol%), $Cu(OAc)_2$ (1 equiv.), DMSO (2.8 mL), 100 °C, 16 h, N_2. Yields refer to isolated products.
[b] At 60 °C.

bearing electron-withdrawing group(s) on *para* and *meta* positions of the amine provided relatively lower yields, which may be due to the rapid decomposition of starting material **1/2**. However, the presence of an electron-withdrawing group at an *ortho* position of the amine provided the products **3l** and **3n** in excellent yields. Next, we turned our attention of using the enamines, derived from substituted diethyl phenacylphosphonates for cyclization. Under the optimized conditions employed, the enamines **2s–2ac** derived from substituted ketophosphonates and aniline as well as their *p*-substituted derivatives were successfully converted to indoles **3s–3x** and **3aa–3ac** in good to excellent yields (Table 3).

It should be noted that the nature of the substituents on the second aryl rings of phosphonates **2s–2ac** has a minor effect on the yields. Electron-withdrawing groups (F, CF_3, CN, NO_2) on phosphonates worked well to provide the desired products **3t**, **3u**, **3v** and **3aa** in good to excellent yields. Unfortunately, the reaction remained unsuccessful when pinacolonyl phosphonate and acetonyl phosphonate were used for the preparation of the corresponding enamines. However, the imine-enamine derived from bromoacetaldehyde diethyl acetal and aniline did not afford the desired indole **3ad**. The structures of all the products were deduced by spectroscopic studies (see the Supporting Information). A single-crystal X-ray study of **3e** and **3i** further confirmed the structures (see the Supporting Information).[11] To determine the scalability of the cyclization process, we conducted a gram-scale experiment using the mixture of imine and enamine (**1a**+**2a**) (1 g, 3 mmol) at 60 °C and obtained the product in 79% yield (0.78 g) (Scheme 2a). In a one-pot variation, where the crude imine/enamine, prepared from the corresponding amine and ketone was subjected to cyclization without further purification, the indole **3a** was obtained in 60% yield (Scheme 2b).

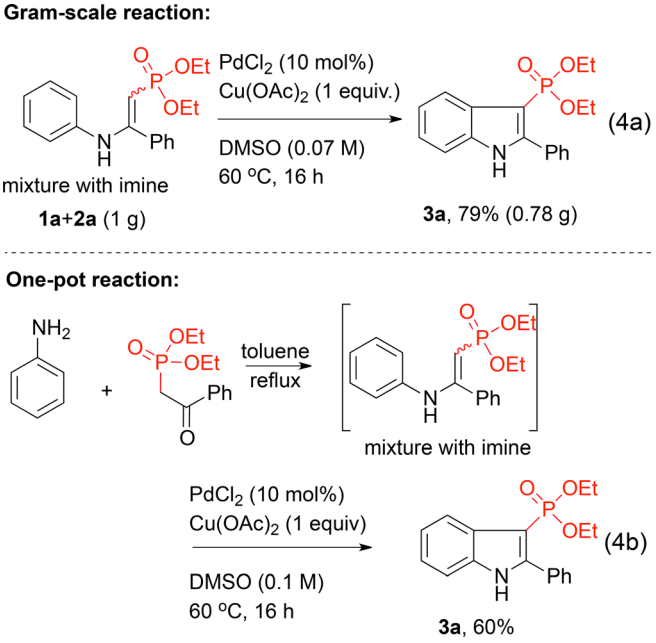
This result encouraged us to extend the methodology and explore whether phosphonate-functionalized pyrroles could also be synthesized from enamines derived from ketophosphonates and allylamine *via* palladium-catalyzed dehydrogenative cyclization,[12] in order to broaden the synthetic utility of this process. After thorough optimization, we found that under modified conditions employing $PdCl_2$ (20 mol%) in the presence of $Cu(OAc)_2$, enamine **4a** also participated in the reaction and afforded the pyrrolyl 3-phos-

Table 3. Scope of palladium-catalyzed oxidative cyclization of imine-enamines.[a]

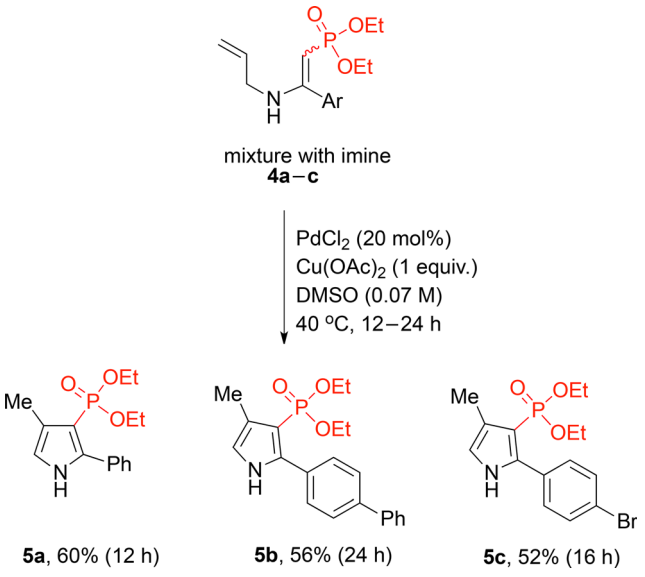


[a] *Reaction conditions:* mixture of **1** and **2** (0.2 mmol), $PdCl_2$ (10 mol%), $Cu(OAc)_2$ (1 equiv.), DMSO (2.8 mL), 100 °C, 16 h, N_2. Yields refer to isolated products.
[b] At 60 °C.

phonate **5a** in 60% yield (Scheme 3). β-Ketophosphonates bearing 4-phenylaryl and 4-bromoaryl substituents underwent smooth cyclization to provide the desired products **5b** and **5c** in 56% and 52% yields, respectively (Scheme 3).

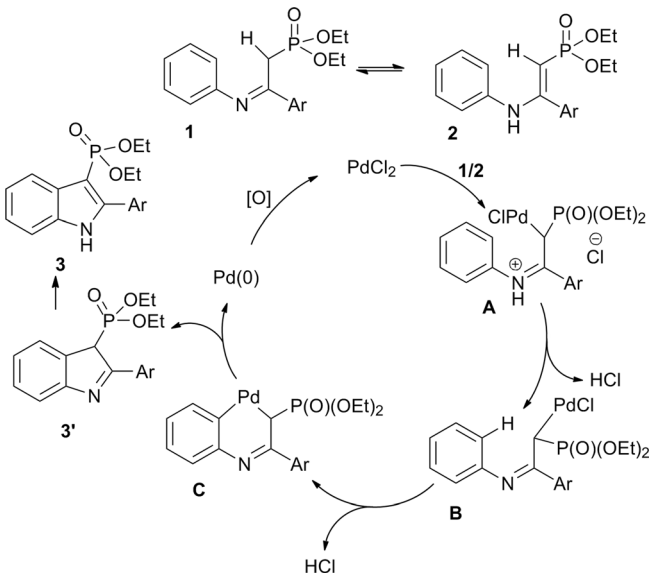


Scheme 2. Gram-scale and one-pot reactions.



Scheme 3. Scope for synthesis of pyrroles *via* dehydrogenative cyclization.

We believe that the indole formation reaction is likely to involve oxidative addition of the enamine C–H bond to Pd(II), followed by second C–H bond palladation and reductive elimination of the resulting indole (Scheme 4).[5b,d,4f,13]



Scheme 4. A plausible mechanism for indole formation.

Conclusions

In summary, we have demonstrated that a $PdCl_2$/$Cu(OAc)_2$ catalytic system allows the formation of indolyl 3-phosphonates and pyrrolyl 3-phosphonates in good to excellent yields *via* oxidative cyclization of the corresponding imino/enaminophosphonates with a broad range of substrates.

Experimental Section

General Procedure for Synthesis of Indolyl 3-Phosphonates

In a 10-mL, oven-dried, two-necked round-bottom flask a mixture of 0.2 mmol of imine-enamine, $Cu(OAc)_2$ (1 equiv.) and $PdCl_2$ (10 mol%) were charged. To that 2.8 mL of anhydrous DMSO were added. The reaction flask was quickly evacuated and backfilled with nitrogen (this process was repeated three times). Then it was slowly heated to 100 °C or 60 °C (bath temperature) while stirring in an oil bath. After 16 h the reaction was stopped and was allowed to cool to room temperature. Then the reaction mixture was passed through a short pad of celite and was washed with 5 mL of ethyl acetate. To that 20 mL of water were added and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (3×) and the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography on neutral alumina using petroleum ether/ethyl acetate as eluent to obtain the desired product.

Full characterization data and copies of relevant spectra of all new products are provided in the Supporting Information.

General Procedure for Synthesis of Pyrrolyl 3-Phosphonates

In a 10-mL, oven-dried, two-necked round bottom flask a mixture of 0.2 mmol of imine-enamine, $Cu(OAc)_2$ (1 equiv.) and $PdCl_2$ (20 mol%) were charged. To that 2.8 mL of anhydrous DMSO were added. The reaction flask was quickly evacuated and backfilled with nitrogen (this process was repeated three times). Then it was slowly heated to 40 °C (bath temperature) while stirring in an oil bath. After the mentioned time the reaction was stopped and allowed to cool to room temperature. Then the reaction mixture was passed through a short pad of celite and washed with 5 mL of ethyl acetate. To that 20 mL of water were added and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (3×) and the combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was purified by column chromatography on neutral alumina using petroleum ether/ethyl acetate as eluent to obtain the desired product.

Full characterization data and copies of relevant spectra of all new products are provided in the Supporting Information.

Acknowledgements

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References

[1] a) R. J. Sundberg, *Indoles*, Academic Press, San Diego, **1996**; b) M. d'Ischia, A. Napolitano, A. Pezzella, in: *Comprehensive Heterocyclic Chemistry III*, (Eds.: A. R. Katritzky, C. A. Ramsden, E. F. V. Scriven, R. J. K. Taylor), Elsevier, Oxford, **2008**; Vol. 3, pp 353–388; c) B. P. Smart, R. C. Oslund, L. A. Walsh, M. H. Gelb, *J. Med. Chem.* **2006**, *49*, 2858, and references cited therein.

[2] Synthesis of indoles, see: a) E. Fischer, F. Jourdan, *Ber. Dtsch. Chem. Ges.* **1883**, *16*, 2241; b) L. S. Hegedus, *Angew. Chem.* **1988**, *100*, 1147; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1113; c) R. C. Larock, E. K. Yum, *J. Am. Chem. Soc.* **1991**, *113*, 6689; d) R. C. Larock, E. K. Yum, M. D. Refvik, *J. Org. Chem.* **1998**, *63*, 7652; e) J. L. Rutherford, M. P. Rainka, S. L. Buchwald, *J. Am. Chem. Soc.* **2002**, *124*, 15168; f) L. Ackermann, *Org. Lett.* **2005**, *7*, 439; g) M. P. Huestis, L. Chan, D. R.

Stuart, K. Fagnou, *Angew. Chem.* **2011**, *123*, 1374; *Angew. Chem. Int. Ed.* **2011**, *50*, 1338.
[3] For reviews, see: a) G. W. Gribble, *J. Chem. Soc. Perkin Trans. 1* **2000**, 1045; b) G. R. Humphrey, J. T. Kuethe, *Chem. Rev.* **2006**, *106*, 2875; c) G. Zeni, R. C. Larock, *Chem. Rev.* **2006**, *106*, 4644; d) N. Yoshikai, Y. Wei, *Asian J. Org. Chem.* **2013**, *2*, 466; e) R. Bernini, G. Fabrizi, A. Sferrazza, S. Cacchi, *Angew. Chem.* **2009**, *121*, 8222; *Angew. Chem. Int. Ed.* **2009**, *48*, 8078; f) S. Cacchi, G. Fabrizi, *Chem. Rev.* **2011**, *111*, PR215.
[4] For selected examples, see: a) Y. Du, R. Liu, G. Linn, K. Zhao, *Org. Lett.* **2006**, *8*, 5919; b) D. R. Stuart, M. Bertrand-Laperle, K. M. N. Burgess, K. Fagnou, *J. Am. Chem. Soc.* **2008**, *130*, 16474; c) Z. Shi, C. Zhang, S. Li, D. Pan, S. Ding, Y. Cui, N. Jiao, *Angew. Chem.* **2009**, *121*, 4642; *Angew. Chem. Int. Ed.* **2009**, *48*, 4572; d) W. Yu, Y. Du, K. Zhao, *Org. Lett.* **2009**, *11*, 2417; e) D. R. Stuart, P. Alsabeh, M. Kuhn, K. Fagnou, *J. Am. Chem. Soc.* **2010**, *132*, 18326; f) Z. H. Guan, Z. Y. Yan, Z. H. Ren, X. Y. Liua, Y. M. Liang, *Chem. Commun.* **2010**, *46*, 2823; g) Z. He, H. Li, Z. Li, *J. Org. Chem.* **2010**, *75*, 4296; h) S. Cacchi, G. Fabrizi, A. Goggiamani, *Org. Biomol. Chem.* **2011**, *9*, 641; i) M. Ali, T. Punniyamurthy, *Synlett* **2011**, 623; j) L. Ackermann, A. V. Lygin, *Org. Lett.* **2012**, *14*, 764; k) A. Gogoi, S. Guin, S. K. Rout, B. K. Patel, *Org. Lett.* **2013**, *15*, 1802; l) H. H. Nguyen, M. J. Kurth, *Org. Lett.* **2013**, *15*, 362; m) X. Ji, H. Huang, W. Wu, X. Li, H. Jiang, *J. Org. Chem.* **2013**, *78*, 11155; n) U. Sharma, R. Kancherla, T. Naveen, S. Agasti, D. Maiti, *Angew. Chem.* **2014**, *126*, 12089; *Angew. Chem. Int. Ed.* **2014**, *53*, 11895; o) R. Nallagonda, M. Rehan, P. Ghorai, *Org. Lett.* **2014**, *16*, 4786; p) X.-L. Lian, Z.-H. Ren, Y.-Y. Wang, Z.-H. Guan, *Org. Lett.* **2014**, *16*, 3360; q) A. P. Kale, G. S. Kumar, M. Kapur, *Org. Biomol. Chem.* **2015**, *13*, 10995; r) M. K. Manna, A. Hossian, R. Jana, *Org. Lett.* **2015**, *17*, 672.
[5] a) S. Würtz, S. Rakshit, J. J. Neumann, T. Dröge, F. Glorius, *Angew. Chem.* **2008**, *120*, 7340; *Angew. Chem. Int. Ed.* **2008**, *47*, 7230; b) J. J. Neumann, S. Rakshit, T. Dröge, S. Würtz, F. Glorius, *Chem.* Eur. *J.* **2011**, 17, 7298; c) S. Rakshit, F. W. Patureau, F. Glorius, *J. Am. Chem. Soc.* **2010**, *132*, 9585; d) Y. Wei, I. Deb, N. Yoshikai, *J. Am. Chem. Soc.* **2012**, *134*, 9098.
[6] a) K. Yoshino, T. Kohno, T. Morita, G. Tsukamoto, *J. Med. Chem.* **1989**, *32*, 1528; b) M. D. Sørensen, L. K. A. Blæhr, M. K. Christensen, T. Høyer, S. Latini, P. J. V. Hjarnaa, F. Björkling, *Bioorg. Med. Chem.* **2003**, *11*, 5461; c) W. Jiang, G. Allan, J. J. Fiordeliso, O. Linton, P. Tannenbaum, J. Xu, P. Zhu, J. Gunnet, K. Demarest, S. Lundeen, Z. Sui, *Bioorg. Med. Chem.* **2006**, *14*, 6726; d) Q. Dang, S. R. Kasibhatla, T. Jiang, K. Fan, Y. Liu, F. Taplin, W. Schulz, D. K. Cashion, P. D. V. Poelje, J. M. Fujitaki, S. C. Potter, M. D. Erion, *J. Med. Chem.* **2008**, *51*, 4331; e) P. Lassaux, M. Hamel, M. Gulea, H. Delbrück, P. S. Mercuri, L. Horsfall, D. Dehareng, M. Kupper, J. M. Frère, K. Hoffmann, M. Galleni, C. Bebrone, *J. Med. Chem.* **2010**, *53*, 4862; f) C. Queffélec, M. Petit, P. Janvier, D. A. Knight, B. Bujoli, *Chem. Rev.* **2012**, *112*, 3777; g) A. Sokolsky, A. B. Smith, *Org. Lett.* **2012**, *14*, 4470.
[7] a) B. C. Chary, S. Kim, *Org. Biomol. Chem.* **2013**, *11*, 6879; b) L. C. Chan, L. Cheong, S. Kim, *Org. Lett.* **2013**, *15*, 2186; c) R.-B. Hu, H. Zhang, X.-Y. Zhang, S.-D. Yang, *Chem. Commun.* **2014**, *50*, 2193.
[8] a) W. A. Abdou, A. A. Kamel, M. D. Khidre, *Heteroat. Chem.* **2004**, *15*, 77; b) S. Thielges, E. Meddah, P. Bisseret, J. Eustache, *Tetrahedron Lett.* **2004**, *45*, 907; c) X. J. Mu, J. P. Zou, Q. F. Qian, W. Zhang, *Org. Lett.* **2006**, *8*, 5291; d) M. Kalek, A. Ziadi, J. Stawinski, *Org. Lett.* **2008**, *10*, 4637; e) S. H. Cho, J. Y. Kim, S. Y. Lee, S. Chang, *Angew. Chem.* **2009**, *121*, 9291; *Angew. Chem. Int. Ed.* **2009**, *48*, 9127; f) D. S. Wang, Q. A. Chen, Y. G. Zhou, X. M. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 8909; g) H. Wang, X. Li, F. Wu, B. Wan, *Synthesis* **2012**, *44*, 941; h) S. H. Kim, S. H. Kim, J. N. Kim, *Tetrahedron Lett.* **2013**, *54*, 1697; i) S. H. Kim, K. H. Kim, J. W. Lim, J. N. Kim, *Tetrahedron Lett.* **2014**, *55*, 531; j) W. C. Fu, C. M. So, F. Y. Kwong, *Org. Lett.* **2015**, *17*, 5906; k) Q. Chen, X. Yan, Z. Du, K. Zhang, C. Wen, *J. Org. Chem.* **2016**, *81*, 276; l) M. Yadav, S. Dara, V. Saikam, M. Kumar, S. K. Aithagani, S. Paul, R. A. Vishwakarma, P. P. Singh, *Eur. J. Org. Chem.* **2015**, 6526.
[9] a) A.-X. Zhou, L.-L. Mao, G.-W. Wang, S.-D. Yang, *Chem. Commun.* **2014**, *50*, 8529; b) Y. Gao, G. Lu, P. Zhang, L. Zhang, G. Tang, Y. Zhao, *Org. Lett.* **2016**, DOI: 10.1021/acs.orglett.6b00056 (this cascade approach for the synthesis of 3-phosphinoylindole was published during preparation of our manuscript).
[10] a) F. Palacios, A. M. O. de Retana, J. Oyarzabal, *Tetrahedron* **1999**, *55*, 5947; b) W. Debrouwer, T. S. A. Heugebaert, K. V. Hecke, C. V. Stevens, *J. Org. Chem.* **2013**, *78*, 8232.
[11] CCDC 1455258 (**3e**) and 1455259 (**3i**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.
[12] a) Y. Izawa, D. Pun, S. S. Stahl, *Science* **2011**, *333*, 209; b) A. Hazra, Y. Wei, N. Yoshikai, *Org. Lett.* **2012**, *14*, 5488; c) Z. Chen, B. Lu, Z. Ding, K. Gao, N. Yoshikai, *Org. Lett.* **2013**, *15*, 1966.
[13] a) B. Liu, J. Li, F. Song, J. You, *Chem. Eur. J.* **2012**, *18*, 10830; b) F. Jafarpour, M. B. A. Olia, H. Hazrati, *Adv. Synth. Catal.* **2013**, *355*, 3407.

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