

ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

COMMUNICATION

Palladium-catalysed decarboxylative nitrile insertion via C-H activation or self-coupling of indole-2-carboxylic acids: A new route to indolocarbolines and triindoles

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

R. N. Prasad Tulichala and K. C. Kumara Swamy*

Palladium catalysed-reaction of indole carboxylic acids with nitriles in the presence of Ag_2CO_3 proceeds via decarboxylative dual C-H activation leading to the nitrile insertion products, triazaindeno-fluorenes (indolocarbolines); in the absence of nitrile, diindolocarbazoles (heptacyclic triindoles, triazatruxenes) are formed.

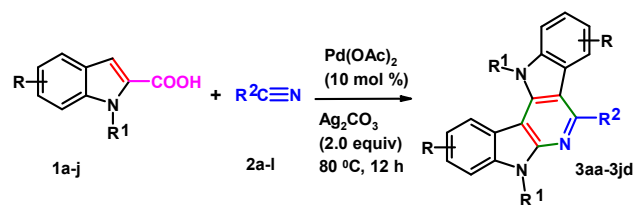
Development of methods for the direct conversion of C-H bonds to C-C and C-N bonds has received significant attention in organic chemistry.¹ Palladium-based and other transition metal catalytic systems are widely used for such transformations and are important tools to construct and convert the indole core motif into more complex structures.²⁻³ In such cases, the nitrile group is considered to be inert and thus acetonitrile is a commonly used solvent.⁴ To our knowledge, there is hardly any report on the nitrile insertion directly into a cyclic structure.⁵⁻⁶ Such reactions utilizing the indole system could lead to carbolines⁷ that are again another important class of medicinally useful products (cf. Figure S1).⁸ This is the first point that we would like to address in this paper.

Another component/additive that is often used in [Pd]-catalysis as an oxidant is Ag_2CO_3 . Quite often, decarboxylation in conjunction with C-H activation is the observed phenomenon.⁹ A few examples utilizing indole carboxylic acids are known.¹⁰ Although it is possible that intermediates formed in such decarboxylations undergo self-association leading to multiply fused indoles, to this date, reports of this kind are absent in the literature. In the course of our investigations on such a system we have discovered that indole-2-carboxylic acids lead to triindoles (diindolocarbazoles) that constitute the hot area of organic electronic materials (cf. Figure S2).¹¹ Despite the fact that both acetonitrile and Ag_2CO_3 have been utilized in several [Pd]-catalysed reactions involving indoles,^{9h,10a,12} rather surprisingly, formation of triindoles (albeit in only moderate yield) is not mentioned in earlier reports.¹³ This is the second point that we wish to highlight in this work.

This work began with a serendipitous observation that a blank reaction of 1-methyl-indole-2-carboxylic acid (**1a**) with CH_3CN (**2a**, used actually as a solvent!) in the presence of $\text{Pd}(\text{OAc})_2 / \text{Ag}_2\text{CO}_3$ afforded indole fused α -carboline **3aa** as one of the products.¹³ We then surmised that it may be possible to construct indole fused α -carbolines by treating **1a-j** with various nitriles under [Pd] catalysis.

The best conditions for the reaction of **1a** with **2b** (see ESI, Table S1) were: 10 mol % of $\text{Pd}(\text{OAc})_2$ as catalyst, Ag_2CO_3 (2.0 equiv) as oxidant at 80 °C for 12 h (65% yield; entry 4). The scope of this decarboxylative [Pd]-catalysed reaction was then examined with respect to both indole-2-carboxylic acids **1** and nitriles **2** (Table 1). Gratifyingly, this protocol was general to a wide range of indole carboxylic acids and nitriles (48-65 %) except in the case of **3aa** where formation of triindoles was significant (*vide infra*). Compounds of type **4-5** were not obtained in other cases (*viz.* entries 2-22). The yield of the isolated product was moderate probably because of the formation of insoluble silver carboxylate salt (X-ray powder diffraction). A variety of substrates including cinnamyl nitrile afforded the expected products **3ab-3jd** in good yield. Nitrile attached to heterocyclic moiety or a functional group like CHO attached to phenyl moiety of nitrile were perfectly tolerated (products **3aj-3ak**). X-ray structures of compounds **3aa** (Figure S3) and **3ac** (Figure S4) have been determined.¹⁴ The new carbolines exhibit fairly strong fluorescence emission spectra in the visible region (see ESI).

Table 1. Formation of indole fused α -carbolines **3^a**



entry	R, R ¹	R ²	product	yield [%] ^b
1 ^c	H, Me (1a)	Me (2a)	3aa	38 (see text) ^d
2	1a	Ph (2b)	3ab	65
3 ^c	1a	3-Me-C ₆ H ₄ (2c)	3ac	61
4	1a	4-Me-C ₆ H ₄ (2d)	3ad	57

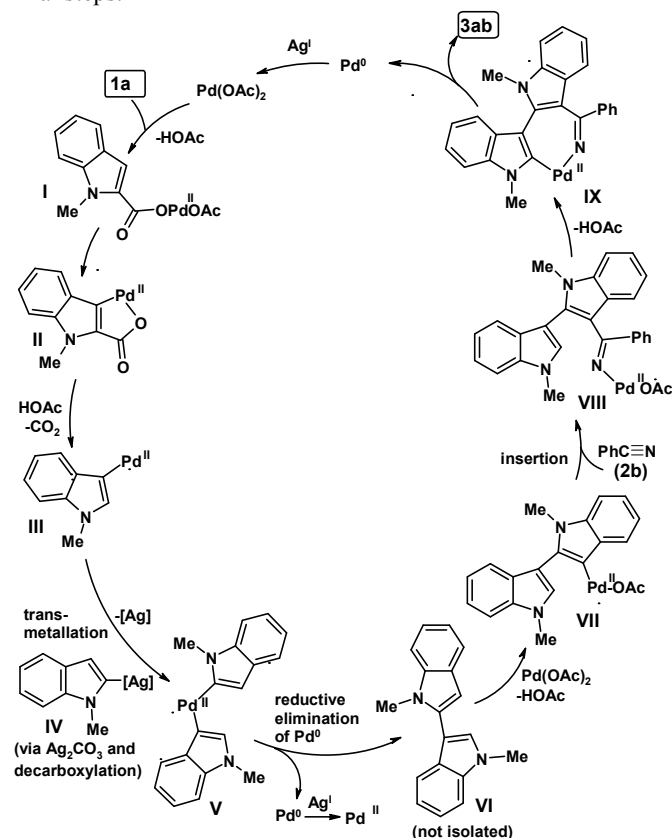
5 ^e	1a	4-MeO-C ₆ H ₄ (2e)	3ae	59
6	1a	C ₃ H ₇ (2f)	3af	56
7	1a	C ₄ H ₉ (2g)	3ag	53
8	1a	CH ₂ Ph (2h)	3ah	60
9	1a	CH ₂ (4-MeO-C ₆ H ₄) (2i)	3ai	55
10	1a	2-thiophenyl (2j)	3aj	59
11 ^e	1a	3-OHC-C ₆ H ₄ (2k)	3ak	60
12 ^f	1a	cinnamyl (2l)	3al	63
13	5-OMe, Me (1b)	2d	3bd	58
14	5-OCH ₂ Ph, Me (1c)	2b	3cb	64
15	5-F, Me (1d)	2b	3db	51
16	5,6-dimethyl, Me (1e)	2b	3eb	62
17	7-Cl, Me (1f)	2b	3fb	56
18	H, Et (1g)	2f	3gf	55
19	1g	2d	3gd	55
20	H, Bn (1h)	2b	3hb	57
21	H, EOM (1i)	2b	3ib	50
22	H, MOM (1j)	2d	3jd	48

^a Reaction conditions: indole-2-carboxylic acid (1.0 mmol), nitrile (20 mmol), Pd(OAc)₂ (10 mol %), Ag₂CO₃ (2.0 mmol) under N₂ atmosphere. ^b Yield of isolated products. ^c X-ray structures of **3aa** and **3ac** determined. ^d In this reaction, we isolated the triindoles (**4a** and **5a**, see Table 2 also) in ca 28% yield. ^e 2.5 mmol of **2e** and **2k** were used. ^f Acrylonitrile gave a decarboxylated 3-substituted product (see ESI).

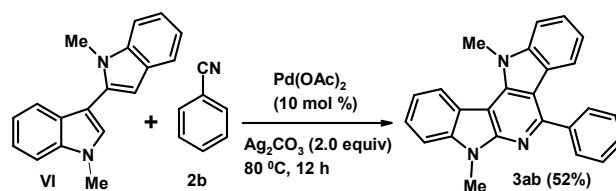
The intermediate palladium(II) carboxylate species **I** (Scheme 1) is formed first. This proposal is consistent with the fact that **1a** reacts with Pd(OAc)₂ (1:1 stoichiometry) even at room temperature (25 °C) within 15 min with the complete consumption of **1a**. Species **I** undergoes carbo-palladation at the 3-position affording the key palladacycle intermediate **II**.^{9g,10a,15} Decarboxylation of **II** results in the metallated species **III**. Meanwhile, **1a** undergoes decarboxylation in presence of silver carbonate affording the aryl metal species **IV**,^{9f} which on transmetalation with the Pd^{II} species **III** gives the biaryl Pd^{II} species **V**.^{9d,f,g,16} Intermediate **V** gives the biindolyl **VI** (also see Scheme 2 below) and Pd⁰ by reductive elimination. This Pd⁰ species may be oxidized in the presence of Ag^I salt to regenerate active Pd^{II} species. The *in situ* produced biindolyl **VI** undergoes palladation to give **VII**. This species has been proposed earlier by Liang et al.¹⁷ Species **VII** upon nitrile insertion produces **VIII**.^{6b,18,19} Upon intramolecular C-H activation, **VIII** leads to the palladacycle **IX** that by reductive elimination affords indole fused α -carboline **3ab**. Again, Pd⁰ is reoxidized to Pd^{II} via Ag^I, thus closing the catalytic cycle.

As mentioned above, the pathway for the formation of indole fused α -carboline (e.g., **3ab**) is assumed to take place via biindolyl intermediate by dual C-H activation.^{20a} To confirm this, we performed a reaction between biindolyl **VI**^{17,20b} and benzonitrile. Satisfyingly, this reaction afforded α -carboline **3ab** in 52% yield (Scheme 2) vindicating our proposal. Formation of **3ab** from **VI** is not a simple [4+2] cycloaddition,

since in the absence of the catalyst, the reaction did not take place. Also, dimethylacetylene dicarboxylate (DMAD) did not undergo [4+2] cycloaddition with **VI**. These results are also consistent with the involvement of palladium catalyst in the final steps.



Scheme 1 Plausible pathway for decarboxylative coupling of **1a** and nitrile **2b**.



Scheme 2 Double C-H Activation of biindolyl with **2b**

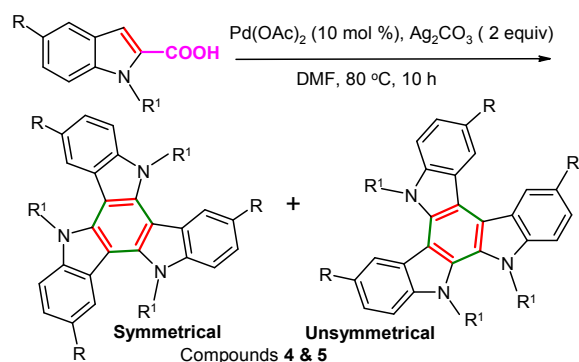
The reaction of 1-methyl-indole-2-carboxylic acid **1a** with benzonitrile **2b** using of Pd(OAc)₂ [10 mol %]/ Ag₂CO₃ [2 equiv] in DMF at 80-90 °C afforded three products. One was indole fused α -carboline (**3ab**; ~10 %); the other two the heptacyclic triindoles (diindolocarbazoles). After careful chromatography, both symmetrical and unsymmetrical triindoles (overall yield 35%) were isolated thus revealing a new type of reaction in indole chemistry. Such products must have been formed in several reactions of indole substrates (albeit in small quantities) where Pd(OAc)₂/Ag₂CO₃ system is utilized, but to our knowledge, are not reported thus far.

In the above reaction, benzonitrile is not required for the formation of triindoles. Even a blank reaction of **1a** with Pd(OAc)₂/ Ag₂CO₃ in DMF led to the symmetrical and unsymmetrical triindole in an overall yield of 48 % (Table S2, entry 4).²¹ Inspired by this, we synthesized triindoles **4a,i,k,l** and **5a,b,h,i,l** using the protocol: Pd(OAc)₂ (10 mol %)/

Ag₂CO₃ (2.0 equiv) in DMF at 80 °C for 10 h (48% overall yield; Table S2, entry 4).

Because of the closeness in the R_f values of the symmetrical and unsymmetrical triindoles, we were able to separate both the isomers only in selected cases. Overall, four symmetrical triindoles (**4a**, **4i**, **4k**, and **4l**) and five unsymmetrical triindoles (**5a-b**, **5h**, **5i**, and **5l**) have been obtained in a pure state.²¹ Quite pleasingly, the yield (after isolation) and selectivity of **5a** was dramatically increased to 50% by keeping the reaction for 12 h at 30 °C and then slowly raising the temperature to 50 °C during 12 h (Table 2, entry 2). This observation may be related to kinetic/steric parameters. Inspired by this, we prepared compound **5h** also in 42% yield (entry 5). In other cases, both the isomers were formed under these conditions. The structures of **5b** and **4k** were confirmed by single crystal X-ray analysis (Figures S5 and S6);¹⁴ fluorescence spectra for selected compounds are provided as ESI.

Table 2. Synthesis of triindoles (diindolocarbazoles) **4** and **5**^a



entry	substrate	R, R ¹	triindole ^b		overall yield (%)
			sym	unsym	
1	1a	H, Me	4a (20%)	5a (28%)	48
2 ^c	1a	H, Me	-	5a (50%)	50
3 ^d	1b	OMe, Me	Not isolated	5b (30%)	45
4 ^d	1h	H, Bn	Not isolated	5h (32%)	43
5 ^c	1h	H, Bn	-	5h (42%)	42
6	1i	H, EOM	4i (21%)	5i (31%)	52
7 ^d	1k	OMe, Bn	4k (35%)	Not isolated	44
8	1l	H, Bu	4l (20%)	5l (30%)	50

^a Reaction conditions: indole-2-carboxylic acid (1.0 mmol)/ Pd(OAc)₂ (10 mol %)/ Ag₂CO₃ (2.0 mmol)/ DMF (5 mL) under N₂ atmosphere. ^b Isolated yield. ^c Reactions were performed at rt for 12 h and then heated to 50 °C (oil bath) for 12 h. ^d In these cases, only one isomer was isolated in a pure state. The other isomer was eluted along with the first one (very close R_f values); this was obtained only as the isomeric mixture. The combined weight (isomeric mixture + pure isomer) corresponds to the total yield.

Formation of triindoles is possible through the biindolyl and an *in situ* formed *N*-methylindole *via* cycloaddition followed by aromatization. At least in the reaction of biindolyl **VI** with **1a** or *N*-methylindole, we have been able to isolate the symmetrical triindole **4a**, albeit in 25% yield, but this could also be due to self-reaction involving **1a** or *N*-methylindole.

In summary, a new [Pd]-catalysed cyclization reaction of indole carboxylic acids with a nitrile (e.g., acetonitrile or benzonitrile) involving *nitrile insertion* and leading to fluorescence active indolocarbazoles, is discovered. This result is significant because acetonitrile or benzonitrile is often used as a solvent in [Pd]-catalysed reactions involving indoles. In the absence of the nitrile, triindoles are obtained. This observation acts as a caveat while using the common [Pd]-catalyst/Ag₂CO₃ system in similar reactions. To our knowledge, there is no such previously recorded report.

We thank DST and UGC (New Delhi) for financial support and equipment. RNPT thanks UGC, New Delhi for a fellowship; he also thanks M. Ramu Sagar and K Suresh for help in recording fluorescence spectra. KCK thanks DST for the J. C. Bose fellowship and UGC for a one-time grant.

Notes and references

School of Chemistry, University of Hyderabad, Hyderabad 500 046, Telangana, India. E-mail: kcksse@uohyd.ernet.in, kcksse@yahoo.com; Fax: (+91)-40-23012460; Tel: (+91)-40-231348560

Electronic Supplementary Information (ESI) available: Experimental details including Tables S1-S4, structures showing the importance of α -carbolines/ triindoles (Figures S1-S2), Structures of **3aa**, **3ac**, **4k**, **5b** and **A** (Figure S3-S7), fluorescence spectra (Figures S8-S22), CIF file and ¹H/¹³C NMR spectra. See DOI:10.1039/c000000x/

- Reviews: a) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem. Int. Ed.*, 2009, **48**, 5094; b) L. Ackermann, R. Vicente, A. R. Kapdi, *Angew. Chem. Int. Ed.*, 2009, **48**, 9792; c) C.-L. Sun, B.-J. Li, Z.-J. Shi, *Chem. Commun.*, 2010, **46**, 677; d) T. W. Lyons, M. S. Sanford, *Chem. Rev.*, 2010, **110**, 1147; e) C. S. Yeung, V. M. Dong, *Chem. Rev.*, 2011, **111**, 1215; f) C. Liu, H. Zhang, W. Shi, A. Lei, *Chem. Rev.*, 2011, **111**, 1780.
- For reviews see: a) E. M. Beccalli, G. Broggini, M. Martinelli, S. Sottocornola, *Chem. Rev.*, 2007, **107**, 5318; b) M. Bandini, A. Eichholzer, *Angew. Chem. Int. Ed.*, 2009, **48**, 9608; c) S. Cacchi; G. Fabrizi, *Chem. Rev.*, 2011, **111**, PR215; d) G. Broggini, E. M. Beccalli, A. Fasana, S. Gazzola, *Beilstein J. Org. Chem.*, 2012, **8**, 1730; e) M. Platon, R. Armadeil, L. Djakovitch, J. C. Hierro, *Chem. Soc. Rev.*, 2012, **41**, 3929; f) M. Shiri, *Chem. Rev.*, 2012, **112**, 3508.
- Selected recent references: a) N. Chernyak, D. Tilly, Z. Li, V. Gevorgyan, *Chem. Commun.*, 2010, **46**, 150; b) S. Potavathi, K. C. Pereira, S. I. Gorelsky, A. Pike, A. P. LeBris, B. DeBoef, *J. Am. Chem. Soc.*, 2010, **132**, 14676; c) J. Lei, T. Bach, *J. Am. Chem. Soc.*, 2011, **133**, 12990; d) M. V. Leskinen, K.-T. Yip, A. Valkonen, P. M. Pihko, *J. Am. Chem. Soc.*, 2012, **134**, 5750; e) L. Du, P. Cao, J. Xing, Y. Lou, L. Jiang, L. Li, J. Liao, *Angew. Chem. Int. Ed.*, 2013, **52**, 4207; f) R. Y. Nimje, M. V. Leskinen, P. M. Pihko, *Angew. Chem. Int. Ed.*, 2013, **52**, 4818; g) C. Wang, L. Zhang, A. Ren, P. Lu, Y. Wang, *Org. Lett.*, 2013, **15**, 2982. h) Y. Xing, G. Sheng, J. Wang, P. Lu, Y. Wang, *Org. Lett.*, 2014, **16**, 1244. i) R.-D. Gao, C. Liu, L.-X. Dai, W. Zhang, S.-L. You, *Org. Lett.*, 2014, **16**, 3919; j) Y. Duan, L. Li, M.-W. Chen, C.-B. Yu, H.-J. Fan, Y.-G. Zhou, *J. Am. Chem. Soc.*, 2014, **136**, 7688; k) M. V. Leskinen, A. Madarász, K.-T. Yip, A.

- Vuorinen, I. Pápai, A. J. Neuvonen, P. M. Pihko, *J. Am. Chem. Soc.*, 2014, **136**, 6453; l) G. Gangadhararao, A. Uruvakilli, K. C. Kumara Swamy, *Org. Lett.*, 2014, **16**, 6060.
- 4 a) J. Tsuji, *Palladium Reagents and Catalysts: New perspectives for the 21st Century*; John Wiley: Japan, 2004.; b) M. R. Luzung, C. A. Lewis, P. S. Baran, *Angew. Chem. Int. Ed.*, 2009, **48**, 7025; c) Z. Shi, B. Zhang, Y. Cui, N. Jiao, *Angew. Chem. Int. Ed.*, 2010, **49**, 4036; d) E. M. Beccalli, A. Bernasconi, E. Borsini, G. Broggini, M. Rigamonti, G. Zecchi, *J. Org. Chem.*, 2010, **75**, 6923; e) M.-J. Zhong, X.-C. Wang, H.-T. Zhu, J. Hu, L. Liu, X.-Y. Liu, *J. Org. Chem.*, 2012, **77**, 10955; f) R.-Y. Tang, X.-K. Guo, J.-N. Xiang, J.-H. Li, *J. Org. Chem.*, 2012, **78**, 11163; g) R.-Y. Tang, X.-K. Guo, J.-N. Xiang, J.-H. Li, *J. Org. Chem.*, 2013, **78**, 11163; h) L. Yu, P. Li, L. Wang, *Chem. Commun.*, 2013, **49**, 2368.
- 5 L. S. Hegedus, T. A. Mulhern, H. Asada, *J. Am. Chem. Soc.*, 1986, **108**, 6224.
- 6 a) A. A. Pletnev, R. C. Larock, *J. Org. Chem.*, 2002, **67**, 9428; b) A. A. Pletnev, Q. Tian, R. C. Larock, *J. Org. Chem.*, 2002, **67**, 9276; c) T.-S. Jiang, G.-W. Wang, *Org. Lett.*, 2013, **15**, 788; d) Y. Ma, J. You, F. Song, *Chem. Eur. J.*, 2013, **19**, 1189; e) J.-C. Wan, J.-M. Huang, Y.-H. Jhan, J.-C. Hsieh, *Org. Lett.*, 2013, **15**, 2742.
- 7 Selected recent reports on α -carboline: a) S. Hostyn, G. Van Baelen, G. L. F. Lemiere, B. U. W. Maes, *Adv. Synth. Catal.*, 2008, **350**, 2653; b) J. K. Laha, P. Petrou, G. D. Cuny, *J. Org. Chem.*, 2009, **74**, 3152; c) S. Majumder, P. J. Bhuyan, *Synlett.*, 2011, **11**, 1547; d) S. Gupta, B. Kumar, B. Kundu, *J. Org. Chem.*, 2011, **76**, 10154; e) A. S. Kumar, R. Nagarajan, *Org. Lett.*, 2011, **13**, 1398; f) A. L. Pumphrey, H. Dong, T. G. Driver, *Angew. Chem. Int. Ed.*, 2012, **51**, 5920; g) S. J. Markey, W. Lewis, C. J. Moody, *Org. Lett.*, 2013, **15**, 6306; h) A. K. Yadav, S. Verbeeck, S. Hostyn, P. Franck, S. Sergeev, B. U. W. Maes, *Org. Lett.*, 2013, **15**, 1060; i) R. K. Arigela, R. Kumar, S. Samala, S. Gupta, B. Kundu, *Eur. J. Org. Chem.*, 2014, 6057.
- 8 a) T. Choshi, S. Yamada, E. Sugino, T. Kuwada, S. Hibino, *J. Org. Chem.*, 1995, **60**, 5899; b) S. Achab, M. Guyot, P. Potier, *Tetrahedron Lett.*, 1995, **36**, 2615; c) F. Y. Miyake, K. Yakushijin, D. A. Horne, *Angew. Chem. Int. Ed.*, 2005, **44**, 3280; d) C. Moquin-Patey, M. Guyot, *Tetrahedron.*, 1989, **45**, 3445; e) D. Bolton, I. T. Forbes, C. J. Hayward, D. C. Piper, D. R. Thomas, M. Thompson, N. Upton, *Bioorg. Med. Chem. Lett.*, 1993, **3**, 1941; f) G. P. Carlo, B. Joseph, M. Luca, S. Leonardo, B. William, A. Shaheen, G. Peter, T. Sébastien, O. Alexandre, G. David, Alpha-carbolines for the treatment of cancer. EP Patent 2662372 A1, 2013.
- 9 a) A. G. Myers, D. Tanaka, M. R. Mannion, *J. Am. Chem. Soc.*, 2002, **124**, 11250; b) D. Tanaka, S. P. Romeril, A. G. Myers, *J. Am. Chem. Soc.*, 2005, **127**, 10323; c) A. Voutchkova, A. Coplin, N. E. Leadbeater, R. H. Crabtree, *Chem. Commun.*, 2008, 6312; d) L. J. Goossen, N. Rodriguez, K. Goossen, *Angew. Chem. Int. Ed.*, 2008, **47**, 3100; e) C. Wang, I. Piel, F. Glorius, *J. Am. Chem. Soc.*, 2009, **131**, 4194; f) J. Cornella, P. Lu, I. Larrosa, *Org. Lett.*, 2009, **11**, 5506; g) C. Wang, S. Rakshit, F. Glorius, *J. Am. Chem. Soc.*, 2010, **132**, 14006; h) J. Zhou, P. Hu, M. Zhang, S. Huang, M. Wang, W. Su, *Chem. Eur. J.*, 2010, **16**, 5876.
- 10 a) M. Yamashita, H. Horiguchi, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.*, 2009, **74**, 7481; b) L. Huang, J. Qi, X. Wu, K. Huang, H. Jiang, *Org. Lett.*, 2013, **15**, 2330.
- 11 a) A. R. Mount, A. D. Thomson, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 553; b) W. Y. Lai, Q. Y. He, R. Zhu, Q. Q. Chen, W. Huang, *Adv. Funct. Mater.*, 2008, **18**, 265; c) E. M. García-Frutos, E. Gutierrez-Puebla, M. A. Monge, R. Remírez, P. Andrés, A. Andrés, R. Ramirez, B. Gómez-Lor, *Org. Electron.*, 2009, **10**, 643; d) E. M. García-Frutos, U. P. Pandey, R. Termine, A. Omenat, J. Barberá, J. L. Serrano, A. Golemme, B. Gómez-Lor, *Angew. Chem. Int. Ed.*, 2011, **50**, 7399; e) C. Ruiz, E. M. García-Frutos, D. A. da Silva Filho, J. T. López Navarrete, M. C. R. Delgado, B. Gómez-Lor, *J. Phys. Chem. C* 2014, **118**, 5470.
- 12 a) L. Yu, P. Li, L. Wang, *Chem. Commun.*, 2013, **49**, 2368; b) C. Pan, H. Jin, X. Liu, Y. Cheng, C. Zhu, *Chem. Commun.*, 2013, **49**, 2933; c) L. Jiao, E. Herdtweck, T. Bach, *J. Am. Chem. Soc.*, 2012, **134**, 14563; d) M.-J. Zhong, X.-C. Wang, H.-T. Zhu, J. Hu, L. Liu, X.-Y. Liu, *J. Org. Chem.*, 2012, **77**, 10955; e) Z. Shi, B. Zhang, Y. Cui, N. Jiao, *Angew. Chem. Int. Ed.*, 2010, **49**, 4036; f) G. Yan, C. Kuang, Y. Zhang, J. Wang, *Org. Lett.*, 2010, **12**, 1052; g) Z. Liang, B. Yao, Y. Zhang, *Org. Lett.*, 2010, **12**, 3185; h) M. Miyasaka, A. Fukushima, T. Satoh, K. Hirano, M. Miura, *Chem. Eur. J.*, 2009, **15**, 3674.
- 13 We observed a small quantity of such triindoles in the reaction between allenes and indole carboxylic acids, but could not identify them earlier. An indolocarboline, though, was identified. See: R. Rama Suresh, K. C. Kumara Swamy, *J. Org. Chem.*, 2012, **77**, 6959.
- 14 (a) Crystallographic data for the structures **3aa**, **3ac**, **5b**, **4k** and **A** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 1029448-1029452.
- 15 A. Maehara, H. Tsurugi, T. Satoh, M. Miura, *Org. Lett.*, 2008, **10**, 1159.
- 16 a) S. M. Bonesi, M. Fagnoni, A. Albini, *Angew. Chem. Int. Ed.*, 2008, **47**, 10022 (review); b) J. Cornella, C. Sanchez, D. Banawa, I. Larrosa, *Chem. Commun.*, 2009, 7176.
- 17 Z. Liang, J. Zhao, Y. Zhang, *J. Org. Chem.*, 2010, **75**, 170.
- 18 a) T.-S. Jiang, G.-W. Wang, *Org. Lett.*, 2013, **15**, 788; b) D. Leow, G. Li, T.-S. Mei, J.-Q. Yu, *Nature* 2012, **486**, 518.
- 19 Coordination by (terminal) nitrile nitrogen may also be relevant, because compound **1a** did not react with benzaldehyde, *t*-butyl isocyanate or phenylisothiocyanate.
- 20 a) Z. Shi, S. Ding, Y. Cui, N. Jiao, *Angew. Chem. Int. Ed.*, 2009, **48**, 7895; b) Y.-X. Li, K.-G. Ji, H.-X. Wang, S. Ali, Y.-M. Liang, *J. Org. Chem.*, 2011, **76**, 744.
- 21 Some of these are reported, but the methods are different. See: a) J. Bergman, N. Eklund, *Tetrahedron.*, 1980, **36**, 1445; b) L. Greci, G. Tommasi, R. Petrucci, G. Marrosu, A. Trazza, P. Sgarabotto, L. Righi, A. Alberti, *J. Chem. Soc., Perkin Trans.*, 2, 2000, 2337; c) M. S. Yaun, T. B. Li, W. J. Wang, Z. T. Du, J. R. Wang, Q. Fang, *Spectrochim. Acta, Part A* 2012, **96**, 1020; d) E. M. García-Frutos, B. Gómez-Lor, A. Monge, E. Gutierrez-Puebla, I. Alkorta, J. Elguero, *Chem. Eur. J.*, 2008, **14**, 8555.