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ADDENDUM/CORRECTION

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Synthesis of Tetrahydrodibenzofuran and Tetrahydrophenanthridinone Skeletons by Intramolecular Nucleopalladation/Oxidative Heck Cascades

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Keywords: Nitrogen heterocycles / Fused ring systems / Palladium / Cascade reactions / Heck reaction

The structures of products **10** shown in the schemes of Tables 3 and 4 of the original article[1] are incorrect. We have now found, based on X-ray diffraction analysis[2] (Figure 1), that those reactions proceed via *O*-cyclization and not through the *N*-cyclization pathway originally reported. However, the conclusions of the paper do not change.

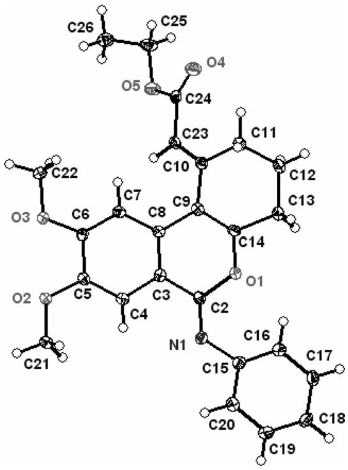


Figure 1. ORTEP diagram of **10b** with thermal ellipsoids at 50% probability.

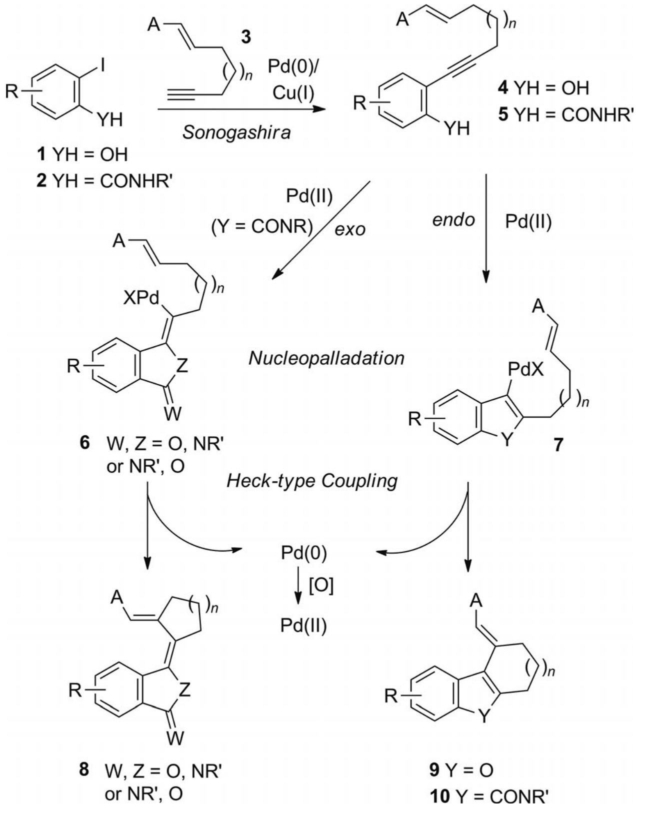
As a result, the following corrections are needed:

1. Page 100, left column, lines 11–12: "... the corresponding isoindolone- (**8**) or phenanthridinone-type (**10**) structures ..." is replaced by "... the corresponding five- (**8**) or six-membered (**10**) heterocyclic structures ...".

2. The term "phenanthridinone" is replaced by "benzo[*c*]chromen-6-imine" throughout the rest of the paper.

3. Reference [19] is removed.

4. Revised versions of Scheme 1 and Tables 3 and 4 are given here.



Scheme 1. General outline of the consecutive Sonogashira and oxidative intramolecular nucleopalladation/Heck coupling cascade.

5. Revised names for compounds **10** are provided here (the structure drawings accompanying their spectra have been correspondingly corrected in the Supporting Information): Ethyl (*E*)-2-[(*Z*)-6-(phenylimino)-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-1-ylidene]acetate (**10a**), ethyl (*E*)-2-[(*Z*)-8,9-dimethoxy-6-(phenylimino)-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-1-ylidene]acetate (**10b**), ethyl (*E*)-2-{(*Z*)-6-[(4-methoxyphenyl)imino]-2,3,4,6-tetrahydro-

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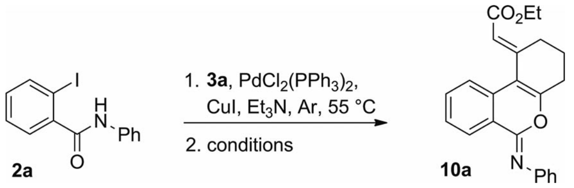
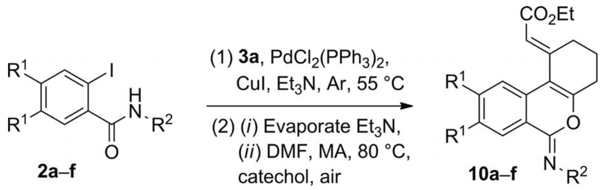
Table 3. Survey of reaction conditions for consecutive Sonogashira/cyclization/intramolecular Heck coupling cascade of benzamide **2a**.[a]



Entry	Conditions for step 2	Yield [%]
1[b]	MA, air, 80 °C	47
2	(i) Evaporate Et_3N; (ii) MA, DMF, air, 80 °C	60
3	(i) Evaporate Et_3N; (ii) Et_3N,[c] MA, DMF, air, 80 °C	22
4[b]	(i) Evaporate Et_3N; (ii) DMF, air, 80 °C	37
5[b]	(i) Evaporate Et_3N; (ii) ethyl acrylate,[d] DMF, air, 80 °C	37
6	(i) Evaporate Et_3N; (ii) MA, DMF, catechol, air, 80 °C	70

[a] Relative amounts of reagents: $PdCl_2(PPh_3)_2$ (5 mol-%), CuI (1 mol-%), Et_3N, 55 °C, MA (1 mol-equiv.), catechol (2 mol-%). [b] Yield in the crude as determined by ^1H NMR using (3,4-dimethoxyphenyl)acetonitrile as internal standard. [c] 5 mol-equiv. of Et_3N were used. [d] 1 mol-equiv. of ethyl acrylate was used.

Table 4. Preparation of 1-methylene-3,4-dihydro-1*H*-benzo[*c*]chromen-6(2*H*)-imines **10**.



Entry	2	R^1	R^2	10, Yield [%]
1	**2a**	H	Ph	**10a**, 70
2	**2b**	OMe	Ph	**10b**, 56
3	**2c**	H	*p*$MeOC_6H_4$	**10c**, 49
4	**2d**	H	*p*MeC_6H_4	**10d**, 76
5	**2e**	H	*p*ClC_6H_4	**10e**, 66
6	**2f**	H	*n*Bu	**10f**, 67

1*H*-benzo[*c*]chromen-1-ylidene}acetate (**10c**), ethyl (*E*)-2-[(*Z*)-6-(*p*-tolylimino)-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-1-ylidene]acetate (**10d**), ethyl (*E*)-2-{(*Z*)-6-[(4-chlorophenyl)imino]-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-1-ylidene}acetate (**10e**), ethyl (*E*)-2-[(*Z*)-6-(butylimino)-2,3,4,6-tetrahydro-1*H*-benzo[*c*]chromen-1-ylidene]acetate (**10f**).

Additional Discussion

Palladium-catalyzed cycloisomerization reactions of 2-alkynylbenzamides have been shown in various instances to proceed with formation of isoindolone or isoquinolone products via 5-*exo*- or 6-*endo-dig-N*-cyclizations, respectively.[3] Recently, the alternative 5-*exo-dig-O*-cyclization mode has also been observed, resulting in the regioselective formation of iminoisobenzofuran derivatives via Pd^0-catalyzed cyclization/coupling with aryl halides[4] or cyclizative dimerization using Cu^{II} as both stoichiometric oxidant and cocatalyst.[5] In the present case, the initial heterocyclization of Sonogashira adducts **5** derived from **2** and **3** is followed by an oxidative intramolecular Heck-type coupling (Schemes 1 and 2, where Y = –CONR) leading to 3,4-dihydro-1*H*-benzo[*c*]chromen-6(2*H*)-imine derivatives (**10**). Incidentally, products **10** contain an isochromen-1-imine core structure, the derivatives of which have attracted significant recent synthetic attention[6] not only for being the nitrogen analogues of the biologically important isocoumarins but also because of their own interesting properties.[6a,6d] Isochromen-1-imines are also the products obtained when the Heck-type coupling is performed *inter*molecularly.[7,8] In any event, in common with the processes leading to iminoisobenzofurans mentioned above,[4,5] the Pd-catalyzed formation of **10** from 2-alkynylbenzamides also follows an initial *O*-cyclization pathway, albeit of the 6-*endo-dig* type, therefore giving rise to a regiochemically different family of products. An even more fundamental difference arises in the nature of the catalytic cycle, which is shared by products **9** and **10** and incorporates a coupling with a tethered alkene, thus providing a new strategic element in the synthesis of various heterocyclic motifs.

Supporting Information (see footnote on the first page of this article): Reproduction of NMR spectra with the corrected structures for compounds **10a**–**f**.

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