Correction to Route to Benzo- and Pyrido-Fused 1,2,4-Triazinyl Radicals via N'-(Het)aryl-N'-[2-nitro(het)aryl]hydrazides

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Supporting Information

T he structure of compound 10, which has the unexpected cyclic voltammogram showing an additional oxidation peak (see Table 4 in original article), has now been shown by single-crystal X-ray diffractometry (CCDC-1419062) to be a dimeric species (Figure 1). A new analysis of the MALDI-TOF mass spectrum also supported a parent ion of m/z 708 (MH⁺, 100%).



Figure 1. ORTEP (ellipsoids at 50% probability) view of the X-ray structure of 10; hydrogen atoms omitted for clarity.

As such, Scheme 7 in the original article should now be as follows:

Furthermore, the Experimental Section (section 4.7.2) now becomes:

4.7.2. 5 - [1,3-Di(pyrid-2-yl)-7-(trifluoromethyl)-1,4dihydrobenzo[e][1,2,4]triazin-4-yl]-1,3-di(pyrid-2-yl)-7-(trifluoromethyl)-1,4-dihydro-1,2,4-benzotriazin-4-yl (**10**). To a stirred solution of 1,3-di(pyrid-2-yl)-7-(trifluoromethyl)-1,4-dihydro-1,2,4-benzotriazine (**23c**) (355 mg, 1.0 mmol) in DCM (10 mL) at ca. 20 °C was added MnO₂ (869 mg, 10.0 mmol). After 2 days, the reaction mixture was filtered through Celite and rinsed with additional DCM, and volatiles were removed in vacuo. The residue was chromatographed on basic alumina (DCM/t-BuOMe, 1:1) to give the title compound **10** (173 mg, 49%) as black needles. Mp (DSC) onset 218.1 °C, peak max 222.9 °C (from MeCN); R_f 0.49 (Al₂O₃, DCM); (found C, 60.93; H, 3.07; N, 19.89. $C_{36}H_{21}F_6N_{10}\bullet$ requires C, 61.11; H, 2.99; N, 19.79%); $\lambda_{max}(DCM)/nm$ 236 (log ε 4.56), 267

Scheme 7. MnO₂ Oxidation of 1,3-Bis(pyrid-2yl)benzotriazines 23b and 23c



(4.66), 282 inf (4.63), 328 inf (4.36), 436 (3.78), 510 (3.31); $\nu_{\rm max}/{\rm cm}^{-1}$ 3061w and 3011w (Ar CH), 1585m, 1568w, 1514w, 1466m, 1429s, 1402m, 1375m, 1344s, 1325s, 1290m, 1271s, 1233w, 1190w, 1161s, 1115s, 1088m, 1061m, 1043w, 991w, 947w, 912m, 878m, 822m, 800m, 775m, 743m, 733w; MALDI-TOF (m/z) 709 (MH⁺ + 1, 39%), 708 (MH⁺, 100), 696 (24), 630 (8), 617 (20), 603 (9), 588 (17), 354 (8), 342 (9), 339 (6).

The structures of the remaining radicals have been rechecked, and their structures are correct. From a brief initial study, it appears that the higher basicity of the dipyridyl **10** is partly responsible for this unexpected dimerization, and we have been unable to find conditions to oxidize the precursor triazine **23c** that do not give the dimeric species **10**. This dimerization is now under study, and we plan to provide a full report on this reaction in the very near future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01915.

X-ray data for 10 (CIF)

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