JOC The Journal of Organic Chemistry

Article

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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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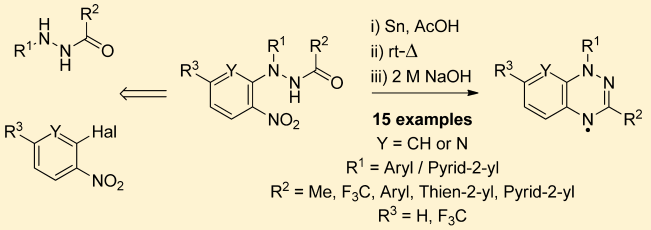
Supporting Information

ABSTRACT: A two-step route to 1,3-disubstituted benzo- and pyrido-fused 1,2,4-triazinyl radicals is presented. The route involves the *N*′-(2-nitroarylation) of easily prepared *N*′-(het)arylhydrazides via nucleophilic aromatic substitution of 1-halo-2-nitroarenes, which in most cases gives *N*′-(het)aryl-*N*′-[2-nitro(het)aryl]hydrazides in good yields. Mild reduction of the nitro group followed by an acid-mediated cyclodehydration gives the fused triazines, which upon alkali treatment afford the desired radicals. Fifteen examples of radicals are presented bearing a range of substituents at N-1, C-3, and C-7, including the pyrid-2-yl and 8-aza analogues. This route to the *N*′-(het)aryl-*N*′-[2-nitro(het)aryl]hydrazides, which works well with benzo- and picolinohydrazides, required a modification for aceto- and trifluoroacetohydrazides that involved a multistep synthesis of asymmetrically 1,1-diaryl-substituted hydrazines.



A flexible route to fused triazinyl radicals that avoids the preparation of amidrazone

1. INTRODUCTION

Stable organic radicals are of interest as building blocks for multifunctional molecular materials because of their unique physical properties.[1] These materials can combine optical, transport, and magnetic properties that can be tuned by introducing subtle structural changes at the molecular level.[2a] Control over their solid-state packing and therefore their macroscopic properties remains a challenge, and progress in this area is expected to provide useful structure−property relationships.[2]

We recently developed new synthetic routes[3] to the air- and moisture-stable benzo[1,2,4]triazinyls **1** (Blatter radicals) in an effort to identify structure−magnetism correlations, and in the process we elucidated a range of 1D magnetic behaviors.[4] During our studies we also discovered a high-yield route to the useful benzotriazinone **2**,[3a,4a] which is the oxidation product of the Blatter radical **1** (R^3 = H). New radical entities were prepared from benzotriazinone **2**, such as the π-extended fused imidazolo-, oxazolo-, and thiazolobenzotriazinyls **3**−**5** (Figure 1).[5] Blatter radicals **1** also mediate the controlled polymerization of styrene.[6]

The classical route to 1,3-disubstituted 1,2,4-benzotriazinyls **1** involves oxidation of the amidrazones **6** *in situ* to give the 1,2,4-triazabutadienes **7**, which then undergo an electrocyclic ring closure to afford benzotriazines that further oxidize to the desired 1,2,4-benzotriazinyls **1** (Scheme 1). The oxidative cyclization sequence has been accelerated using a variety of oxidants, including HgO,[7a−c] Ag_2O,[7d] Pd−C/air/DBU,[3a] $RuCl_3$,[7e] and potassium ferricyanide $K_3[Fe(CN)_6]$.[7f]

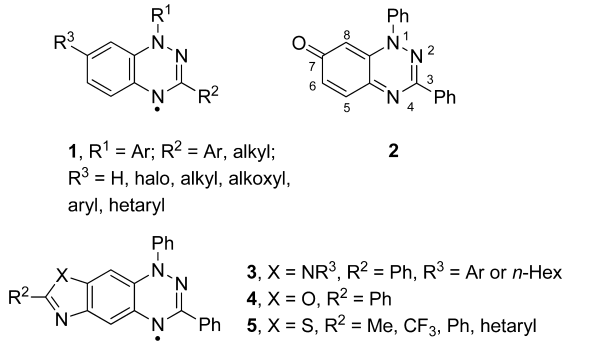
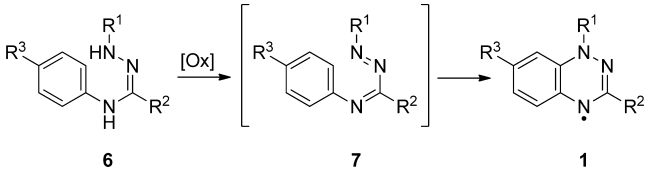


Figure 1. General structures of the benzotriazinyl radicals **1**, benzotriazinone **2**, and the imidazolo-, oxazolo-, and thiazolo-fused benzotriazinyl radicals **3**−**5**.

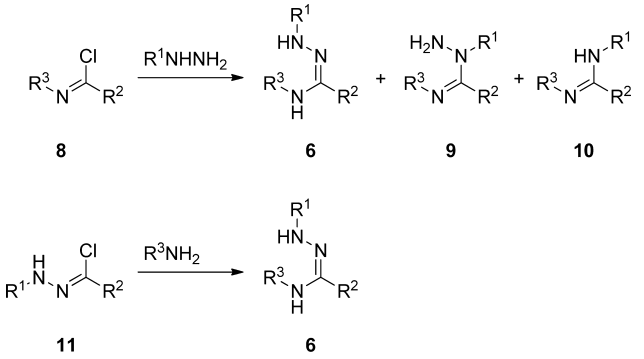
Scheme 1. Classical Route to Benzotriazinyl Radicals 1 via Amidrazones 6



Received: November 8, 2013
Published: December 12, 2013

These reactions afford the desired products in quite variable yields, and our experience has demonstrated that this is highly dependent on the purity of the starting amidrazone **6**. When the amidrazone has been purified by recrystallization, the yield can be gratifyingly high (>90%).[3a] However, problems arise because not all amidrazones are easily crystallized, and in particular, electron-rich analogues rapidly oxidize upon storage. Further difficulties arise during the synthesis of the desired amidrazones. Two routes are commonly used (Scheme 2): The

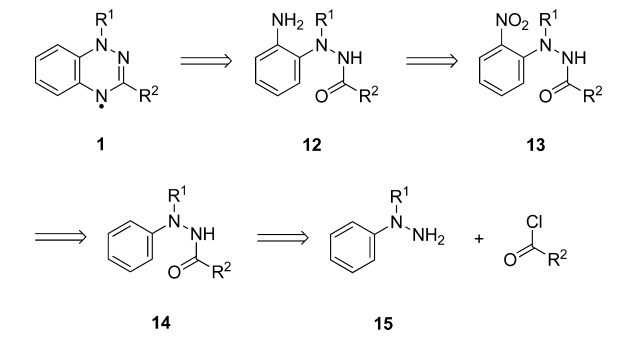
Scheme 2. Routes to Amidrazones 6 via Imidoyl Chlorides 8 and Hydrazonyl Chlorides 11



first method involves the preparation of an *N*-arylimidoyl chloride **8**, which upon treatment with arylhydrazine gives a mixture of three products (**6**, **9**, and **10**) since the hydrazine can attack via both the α and β nitrogens. Thus, the amidrazone **6** needs to be isolated from this mixture by a careful extraction sequence.[8] The second method, which involves the formation of the *N*-arylhydrazonyl chloride **11**[9] and subsequent condensation with a primary aniline, avoids the formation of mixtures and is currently the preferred route.[10]

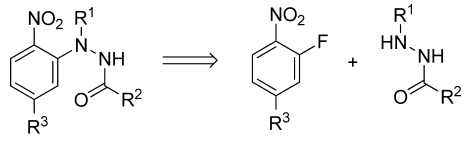
As part of our ongoing studies on 1,2,4-benzotriazines, we required a reliable general route to benzotriazinyl radicals **1** that supported variation of the substituents at N-1 and C-3 and on the benzo-fused moiety. Herein we present a synthesis that avoids the formation of any unstable (highly reactive) intermediates such as the amidrazones **6** or the imidoyl/hydrazonyl chlorides **8** and **11**. Our strategy was inspired by an early synthesis of benzotriazinyl radical developed by Blatter,[11] which involved the preparation of the nitro-substituted intermediate **13** from a 1,1-diarylated hydrazine **15**, followed by reduction of the nitro group to give amine **12** and subsequent cyclodehydration (Scheme 3).

Scheme 3. Blatter's Route to Benzotriazinyl Radical 1 via Hydrazide 14



Unlike Blatters' method, which introduces the nitro group at a latter stage of the synthesis via nitration of hydrazide **14**, we chose to construct intermediate **13** starting from 1-halo-2-nitroarenes **18** and readily prepared *N*′-(het)arylhydrazides **19** (Scheme 4).

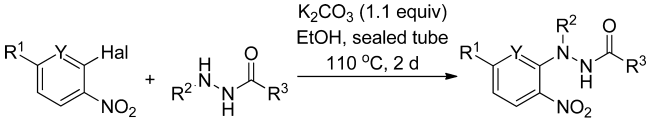
Scheme 4. Modified Synthesis of *N*′-(Het)aryl-*N*′-[2-nitro(het)aryl]hydrazides 13



2. RESULTS AND DISCUSSION

2.1. Synthesis of *N*′-(Het)aryl-*N*′-[2-nitro(het)aryl]-hydrazides 13. The first step in the preparation of the Blatter radical **1a** ($R^1 = R^2 = Ph$, $R^3 = H$) involved condensation of 1-fluoro-2-nitrobenzene (**18a**) with readily available *N*′-phenylbenzohydrazide (**19a**) to give *N*′-(2-nitrophenyl)-*N*′-phenylbenzohydrazide (**13a**) (Table 1). The reaction worked well in a

Table 1. Reaction of 1-Halo-2-nitroarenes 18 with Hydrazides 19



entry	Y	Hal	R^1	R^2	R^3	**13** (% yield)
1	CH	F	H	Ph	Ph	**13a** (62)
2	CH	F	F_3C	Ph	Ph	**13b** (60)[a]
3	CH	F	H	Ph	4-FC_6H_4	**13c** (63)
4	CH	F	H	Ph	thien-2-yl	**13d** (61)
5	CH	F	H	Ph	pyrid-2-yl	**13e** (85)
6	CH	F	H	Ph	Me	**13f** (23)
7	CH	F	F_3C	Ph	Me	**13g** (19)[a]
8	CH	F	H	Ph	F_3C	**13h** (17)
9	CH	F	F_3C	Ph	F_3C	**13i** (35)[a]
10	CH	F	H	4-NCC_6H_4	Ph	**13j** (64)
11	CH	F	H	4-NCC_6H_4	thien-2-yl	**13k** (57)
12	CH	F	H	pyrid-2-yl	Ph	**13l** (77)
13	CH	F	H	pyrid-2-yl	pyrid-2-yl	**13m** (75)
14	CH	F	F_3C	pyrid-2-yl	pyrid-2-yl	**13n** (86)[a]
15	N	Cl	H	Ph	Ph	**13o** (84)[a]
16	N	Cl	H	pyrid-2-yl	pyrid-2-yl	**13p** (81)[a]

[a]Reaction run for 1 day only.

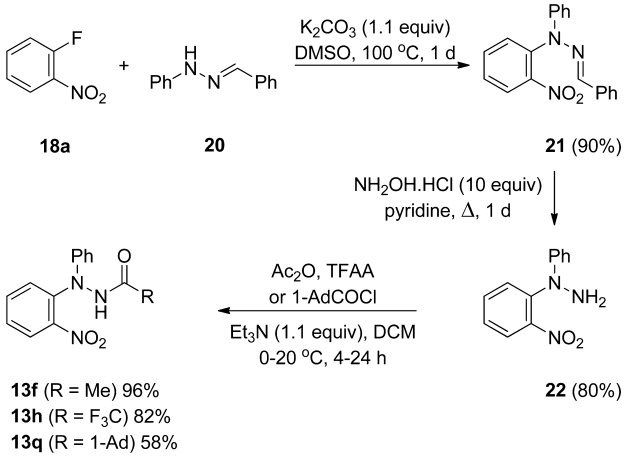
range of alcoholic solvents ROH (R = Me, Et, *i*-Pr, *s*-Bu), and the optimum yield was obtained using K_2CO_3 (1.1 equiv) as the base in EtOH upon heating to ca. 110 °C (sealed tube) for 2 days, which gave the desired product **13a** in 62% yield (Table 1, entry 1). The use of the higher-boiling solvent *s*-BuOH (bp 98−100 °C) avoided the need for a sealed reaction vessel without affecting the product yield (61%), but we proceeded to prepare the other analogues using the EtOH/sealed tube protocol because it was easier to remove EtOH from the reaction mixture during the workup.

dx.doi.org/10.1021/jo402481t | J. Org. Chem. 2014, 79, 314−327

The reaction tolerated hydrazides bearing benzonitrile (Table 1, entries 10 and 11), pyrid-2-yl (Table 1, entries 5, 12−14, and 16), and thien-2-yl (Table 1, entries 4 and 11) substituents and also worked when the 1-fluoro-2-nitrobenzene (**18a** or **18b**) was replaced with 2-chloro-3-nitropyridine (**18c**) (Table 1, entries 15 and 16). Interestingly, the reaction with either 2-fluoro-1-nitro-4-(trifluoromethyl)benzene (**18b**) or the chloronitropyridine **18c** required less time (1 vs 2 days) than those with the fluoronitrobenzene **18a**; longer reaction times (2 days) led to a drop in product yield, suggesting that the products were not stable under the reaction conditions. Disappointingly, the use of aceto- or trifluoroacetohydrazide (**19f** or **19g**, respectively) gave low to moderate yields (17−35%) of the desired 1-phenyl-1-(2-nitroaryl)aceto- and -trifluoroacetohydrazides **13f−i** (Table 1, entries 6−9), identifying a limitation for the protocol.

Nevertheless, this limitation was partly overcome via an alternative multistep route that invoked the use of readily available 1-benzylidene-2-phenylhydrazine (**20**) (Scheme 5).

Scheme 5. Stepwise Route to *N*′-(2-Nitrophenyl)-*N*′-phenylacetohydrazide (13f), *N*′-(2-Nitrophenyl)-*N*′-phenyltrifluoroacetohydrazide (13h), and *N*′-(2-Nitrophenyl)-*N*′-phenyl-1-adamantanecarbohydrazide (13q)

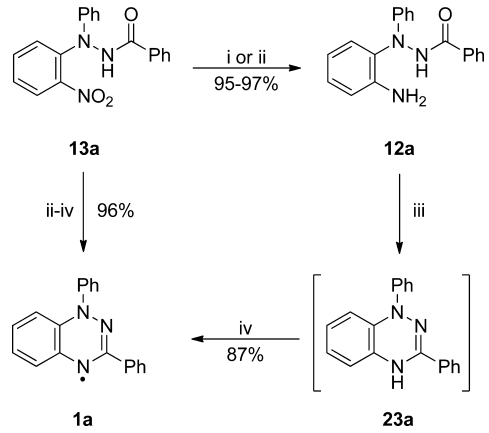


Heating of **20** with 1-fluoro-2-nitrobenzene (**18a**) and K_2CO_3 (1.1 equiv) in DMSO at ca. 100 °C for 1 day gave 2-benzylidene-1-(2-nitrophenyl)-1-phenylhydrazine (**21**) in 90% yield, which upon treatment with excess $NH_2OH{\cdot}HCl$ (10 equiv) in pyridine and heating to ca. 80 °C for 1 day released 1-(2-nitrophenyl)-1-phenylhydrazine (**22**) in 80% yield together with some recovered starting material **21** (17%). While we were unable to drive this reaction to completion, it was suitable to provide multigram quantities of the desired asymmetrically 1,1-diaryl substituted hydrazine **22**, which was then readily acylated or trifluoracetylated to give the desired *N*′-(2-nitrophenyl)-*N*′-phenylaceto- and -trifluoroacetohydrazides **13f** and **13h** in good overall yields (69 and 59%, respectively). The procedure also worked for the preparation of adamantane analogue **13q** (Scheme 5).

Additional optimization efforts for this multistep procedure to broaden its scope are currently underway in our laboratory. However, it is worthy of note that only a few methods for the preparation of asymmetrically 1,1-diarylated hydrazines have been reported, namely, the reduction of the corresponding nitrosamines,[12] the Hofmann rearrangement of the corresponding ureas,[13] and more recently the transition-metal-catalyzed *N*-arylation of protected 1-arylhydrazines.[14] However, these methods are limited because they cannot readily be performed on multigram scales. Furthermore, the classical methods require harsh reaction conditions and complicated workups and have limited functional group tolerance and low yields,[14a] while the transition-metal-catalyzed couplings do not tolerate well the presence of *o*-nitro-substituted haloarenes.[14b,c]

2.2. Reduction and Cyclodehydration of *N*′-(Het)aryl-*N*′-[2-nitro(het)aryl]hydrazides 13 To Give Benzo- and Pyrido-Fused Triazinyl Radicals 1. The second key step of the synthesis of the Blatter radical **1a** required the mild reduction of the nitro group of *N*′-(2-nitrophenyl)-*N*′-phenylbenzohydrazide (**13a**). This was achieved using either Pd−C/H_2 in EtOH or In powder (4 equiv) in AcOH at ca. 20 °C, which gave *N*′-(2-aminophenyl)-*N*′-phenylbenzohydrazide (**12a**) in high yield (95−97%) (Scheme 6). Interestingly,

Scheme 6. Synthesis of 1a from 13a[a]



[a]Reagents and conditions: (i) Pd−C (5 mol %), H_2(g), EtOH, ca. 20 °C, 4 h (97%); (ii) In (4 equiv), AcOH, ca. 20 °C, 0.5 h (95%); (iii) AcOH, ca. 118 °C, 10 min; (iv) 2 M NaOH, ca. 20 °C, 3 h.

benzohydrazide **12a** was also recently prepared via the copper-catalyzed coupling of 2-iodoaniline with *N*′-phenylbenzohydrazide (**19a**),[14b] providing an alternative route to this useful intermediate.

Heating of *N*′-(2-aminophenyl)benzohydrazide **12a** in AcOH at ca. 118 °C (reflux) for 10 min led to cyclodehydration and formation of the benzotriazine **23a**, which was oxidatively unstable and rapidly gave a mixture containing the Blatter radical **1a**. In light of this, during the workup we treated the reaction mixture with 2 M NaOH at ca. 20 °C for 3 h, which converted benzotriazine **23a** into the Blatter radical **1a** in high yield (87%). Fortunately, when In powder (4 equiv) was used in AcOH, the reduction of the nitro group and the cyclodehydration could be performed in one pot, and after the alkali workup the radical was obtained directly in 91% yield (Table 2, entry 1). Because of the high cost of In powder, we examined the use of cheaper Sn and Fe (Table 2, entries 2 and 3). While the use of Fe powder required a large excess (10 equiv) to drive the reduction to completion and gave the radical in only 68% yield (Table 2, entry 3), the use of Sn (4 equiv) gave the radical in an excellent 96% yield (Table 2, entry 2). Interestingly, the three-step procedure did not tolerate the use of stronger reducing metals such as Zn or Cu, which cause reductive ring contraction of benzotriazines to benzimidazoles.[15] Furthermore, the use of less than 4 equiv of Sn powder

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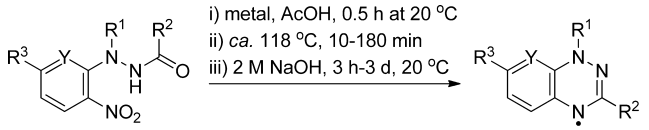
Table 2. Reduction and *In Situ* Cyclodehydration To Give Benzotriazinyls 1



13 **1**

entry	Y	R^1	R^2	R^3	metal (equiv)	time at Δ (min)	product (% yield)
1	CH	Ph	Ph	H	In (4)	10	**1a** (91)
2	CH	Ph	Ph	H	Sn (4)	10	**1a** (96)
3	CH	Ph	Ph	H	Fe (10)	10	**1a** (68)
4	CH	Ph	Ph	F_3C	Sn (4)	10	**1b** (81)
5	CH	Ph	4-FC_6H_4	H	Sn (4)	10	**1c** (88)
6	CH	Ph	thien-2-yl	H	Sn (4)	10	**1d** (87)
7	CH	Ph	pyrid-2-yl	H	Sn (4)	10	**1e** (82)[a]
8	CH	Ph	Me	H	Sn (4)	10	**1f** (63)
9	CH	Ph	Me	F_3C	Sn (4)	10	**1g** (64)
10	CH	Ph	F_3C	H	Sn (4)	10	**1h** (63)
11	CH	Ph	F_3C	F_3C	Sn (4)	10	**1i** (83)
12	CH	Ph	1-Ad	H	Sn (4)	10	**1j** (79)
13	CH	4-NCC_6H_4	Ph	H	Sn (4)	10	**1k** (85)
14	CH	4-NCC_6H_4	thien-2-yl	H	Sn (4)	10	**1l** (71)
15	CH	pyrid-2-yl	Ph	H	Sn (4)	10	**1m** (77)
16	CH	pyrid-2-yl	pyrid-2-yl	H	Sn (3)	0	**12b** (78)[b,c]
17	CH	pyrid-2-yl	pyrid-2-yl	H	Sn (4)	0	**12b** (98)[b,c]
18	CH	pyrid-2-yl	pyrid-2-yl	H	Sn (4)	10	**12b** (22)/**23b** (66)[c]
19	CH	pyrid-2-yl	pyrid-2-yl	H	Sn (4)	180	**23b** (82)[c]
20	CH	pyrid-2-yl	pyrid-2-yl	F_3C	Sn (4)	180	**23c** (88)[c]
21	N	Ph	Ph	H	Sn (4)	60	**1n** (77)
22	N	pyrid-2-yl	pyrid-2-yl	H	Sn (4)	60	**23d** (91)[c]

[a]2 M NaOH, 3 days, 20 °C. [b]Reaction time at ca. 20 °C was 2 h. [c]No alkali workup.

led to slow or incomplete reactions, while increasing the amount of Sn or replacing AcOH with formic acid led to lower yields. Therefore, the use of Sn (4 equiv) in AcOH was chosen for the reduction of analogues **13b–q** (Table 2, entries 4–22).

Interestingly, the Sn/AcOH-mediated reduction of the *N*′-(pyrid-2-yl)picolinohydrazides **13m**, **13n**, and **13p** followed by the alkali workup (2 M NaOH) gave only traces of the expected benzo- and pyrido-fused triazinyl radicals (by TLC) and mainly afforded the reduced *leuco* forms **23b–d**, respectively. Thus, for these examples we chose to maximize the yields of the *leuco* forms **23b–d** by avoiding the alkali workup (Table 2, entries 18–20 and 22). Furthermore, the *N*′-phenylpicolinohydrazide **13e** was reduced and cyclodehydrated to give the benzotriazine after only 10 min of heating (by TLC) but required extended treatment (3 days) with 2 M NaOH for full conversion into the desired radical **1e** (82%; Table 2, entry 7), while the *N*′-(pyrid-2-yl)benzohydrazide **13l** was converted without any difficulty into the radical **1m** (77%; Table 2, entry 15). This suggests that the 3-(pyrid-2-yl) substituent had a more significant effect on the transformation than the 1-(pyrid-2-yl) substituent. The *N*′-(pyrid-2-yl)picolinohydrazides **13m**, **13n**, and **13p** notably all required longer heating times (1–3 h; Table 2, entries 19, 20, and 22). For the *N*′-(pyrid-2-yl)picolinohydrazide **13m**, shorter heating times (Table 2, entry 18) led to a mixture of the *leuco* form **23b** (66%) and the noncyclized amine **12b** (22%), both of which were sufficiently stable to be isolated and characterized. Interestingly, the reduction of the *N*′-(pyrid-2-yl)picolinohydrazide **13m** at ca. 20 °C required a minimum of 3 equiv of Sn powder to give amine **12b** in 78% yield after only 2 h (Table 2, entry 16), whereas the use of 2.2 equiv of Sn powder led to an incomplete reaction after 12 h (data not shown) and the use of 4 equiv led to quantitative (98%) conversion in only 0.5 h (Table 2, entry 17).

Since the alkali treatment of the 1,3-bis(pyrid-2-yl)-substituted benzo- and pyrido-fused triazines **23b–d** failed to give reasonable yields of the desired radicals, we attempted to prepare the radicals via oxidation. Treatment of triazines **23b–d** with HgO (10 equiv) in DCM at ca. 20 °C for 1 day led to no reaction. The use of Pd–C (1.6 mol %) with DBU (0.1–1 equiv) in DCM at ca. 20 °C for 1 day gave for benzotriazines **23b** and **23c** mainly unreacted starting material and traces of what might be radical (by TLC), while pyridotriazine **23d** gave a complex reaction mixture that was not investigated further. Therefore, we treated the benzo- and pyrido-fused triazines **23b–d** with the stronger oxidizing agent MnO_2 (10 equiv) in DCM, upon which benzotriazine **23b** gave the purple-colored benzotriazinone **24** in 53% yield while the 7-trifluorobenzotriazine **23c** fortunately gave the desired radical **1o** in a moderate 49% yield (Scheme 7). Trifluoromethyl substitution at C-7 has previously been shown to prevent the oxidation of Blatter radicals to the benzotriazinones.[4a] Treating the pyrido-fused triazine **23d** with MnO_2 gave neither radical nor quinone, and the reaction remains under investigation.

The pyrid-2-yl-substituted benzotriazinyl radicals **1e**, **1m**, and **1o** and the 3-(pyrid-2-yl)-substituted benzotriazinone **24** promise to be interesting compounds for metal coordination studies, and this work is currently under investigation. Several 1,3-diphenylbenzotriazinones have also been shown to inhibit both AChE and β-amyloid aggregation, and therefore, access to

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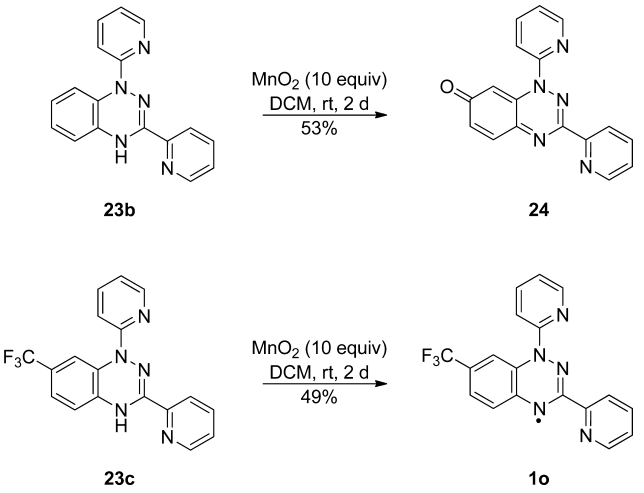
Scheme 7. MnO_2 Oxidation of 1,3-Bis(pyrid-2-yl)benzotriazines 23b and 23c



new pyridyl analogues can lead to inhibitors with improved properties.[16]

2.3. EPR Spectroscopy. Previous EPR studies of 1,2,4-benzotriazinyl radicals showed that the spin density is mainly delocalized on the amidrazonyl fragment of the 1,2,4-triazinyl cycle.[7a,c,d,17,18] The largest hyperfine coupling constant (hfcc) is observed on the N-1 atom (~7.5 G), whereas the N-2 and N-4 coupling constants are smaller and approximately equal to each other (~5.1 G). These two coupling constants were separately measured with further EPR and ENDOR studies by Neugebauer on ^{15}N-labeled derivatives and found to be 4.9 G for N-2 and 5.2 G for N-4 ($a_{N\text{-}1} \gg a_{N\text{-}4} > a_{N\text{-}2}$).[18b]

Room-temperature solid-state EPR studies of the new radicals **1c–o** (Figures S1–S13 in the Supporting Information) all revealed essentially isotropic singlet EPR spectra ($2.0040 < g < 2.0060$; Table 3), consistent with organic radicals with small spin–orbit couplings. Some variation in line width was also observed and presumably results from dipolar line broadening in the solid state, which exhibits a $1/r^n$ dependence. The g factors for radicals **1c–o** in solution ($2.0035 < g < 2.0050$; Table 3) were similar to those observed in the solid state, but the lower concentrations permitted the resolution of the ^{14}N hyperfine coupling to the three chemically distinct N atoms of the triazinyl ring. The solution EPR spectra of these radicals (Figures S1–S13 in the Supporting Information) are similar to those observed for other benzotriazinyls.[3–5,17,18] The seven-line spectra are consistent with the coupling of the unpaired electron with three similar but slightly nonequivalent ^{14}N nuclei. EPR spectra of radicals containing F (**1c**) and F_3C (**1g–i** and **1o**) show additional coupling to ^{19}F atoms (Figures S1, S5–S7, and S13, respectively, in the Supporting Information). In radicals **1g** and **1h**, the F_3C group causes further splitting of the EPR signals into quartets, implying rotational averaging of the three fluorine nuclei. The hfcc from ^{19}F is likely to result mostly from spin polarization for radicals **1c** (R^2 = 4-FC_6H_4) and **1h** (R^2 = F_3C), where the F-containing groups are connected to a nodal carbon (C-3), whereas the connection of the F_3C group via C-7 in radicals **1g**, **1i**, and **1o** (R^3 = F_3C) causes a slightly larger hfcc as a result of the mesomeric influence of the F lone pairs. However, fluorine has a large atomic hyperfine parameter,[19] and therefore, coupling to F does not represent a large spin density at F. The EPR spectrum of pyridotriazinyl radical **1n** (Figure 2) appears as a binomial nonet arising from coupling of the unpaired electron with four chemically distinct ^{14}N atoms.

The EPR spectra were simulated to determine the g factors and hfcc values. For radicals **1c**, **1g–i**, **1n**, and **1o**, additional simulations of the second derivatives were necessary because of the low resolution of the first-derivative spectra. Assignments of the hfcc values are given according to Neugebauer's

Table 3. Fitting Parameters of Simulated Spectra for Radicals 1a–o

	g		a (G)					
radical	solid state	DCM	N-1	N-2	N-4	F-3	F-7	other
1a[a]		2.0033	7.50	4.77	5.05			
1b[b]		2.0036	7.62	4.56	4.95		3.46	
1c	2.0041	2.0040	7.68	4.84	4.90			0.54[d]
1c[c]			7.69	4.75	5.00			0.73[d]
1d	2.0040	2.0040	7.81	4.83	5.07			
1e	2.0060	2.0040	7.69	4.57	5.13			
1f	2.0042	2.0041	7.82	4.94	4.95			
1g	2.0042	2.0035	7.97	4.23	5.03		3.14	
1g[c]			7.97	4.37	5.36		3.02	
1h	2.0042	2.0050	8.07	4.21	5.36	1.89		
1h[c]			8.07	4.19	5.31	1.26		
1i	2.0047	2.0042	6.64	4.38	4.38	4.39	4.44	
1i[c]			8.13	2.70	3.62	4.02	4.75	
1j	2.0046	2.0040	7.51	4.94	5.13			
1k	2.0040	2.0040	6.89	4.95	5.08			
1l	2.0040	2.0040	7.12	4.89	5.26			
1m	2.0046	2.0040	6.74	4.88	4.93			
1n	2.0050	2.0040	6.88	4.81	4.81			2.00[e]
1n[c]			7.12	4.81	5.13			1.94[e]
1o	2.0040	2.0040	6.88	4.20	4.44		4.38	
1o[c]			6.88	4.25	4.32		4.32	

[a]Reference 18b. [b]Reference 4a. [c]Simulated second-derivative EPR spectrum. [d]a_F for 4-FC_6H_4. [e]$a_{N\text{-}8}$.

dx.doi.org/10.1021/jo402481t | J. Org. Chem. 2014, 79, 314–327

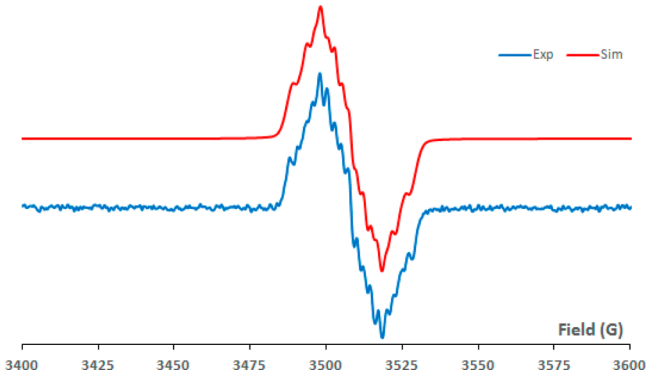


Figure 2. Experimental (blue) and simulated (red) solution EPR spectra of pyridotriazinyl radical **1n** in DCM at ca. 20 °C. Fitting parameters are shown in Table 3

observations: the largest hfcc is on the N-1 atom (6.64−8.13 G), followed by that on N-4 (3.62−5.36 G), which is slightly larger than that on N-2 (2.70−4.95 G). Electron-withdrawing groups directly attached to the N-1 atom (**1k**, **1m**, and **1o**) have the biggest impact on the electron distribution over the amidrazonyl fragment, reducing the electron density on the three triazinyl N atoms. The pyrido-fused ring in **1n** has the same effect, shifting electron density from the amidrazonyl unit and resulting in smaller hfcc values (Table 3).

On the basis of the estimated hfcc values, we employed the McConnell equation[20,21] to calculate the spin density distribution around the benzotriazinyl ring (Table T1 in the Supporting Information). Atomic spin densities of the benzo-fused rings in radicals **1c−n** could not be experimentally determined since line-broadening of the spectra resulted in poor resolution of the hfcc. It is clear from Table T1 that most of the spin density is mainly delocalized over the 1,2,4-triazinyl ring, indicating the importance of this part of the molecule in the solid-state packing and therefore in the transport and magnetic properties of the radicals. However, the introduction of electron-withdrawing or electron-donating groups directly on N-1 can significantly alter this distribution.

2.4. Cyclic Voltammetry. The electrochemical behavior of 1 mM DCM solutions of the radicals **1c−o** was probed by cyclic voltammetry using *n*-Bu_4NBF_4 as a supporting electrolyte and the ferrocene/ferrocenium (Fc/Fc^+) couple as an internal reference (Table 4 and Figures S14−S26 in the Supporting Information). The redox behavior of radicals **1c−o** is typical of 1,2,4-benzotriazinyls: two fully reversible waves that correspond to −1/0 and 0/+1 processes. While substitution at C3 (the nodal carbon) did not significantly alter the halfway oxidation and reduction potentials (**1c−f** and **1h**; Table 4), the 4-cyanophenyl and pyrid-2-yl substituents at N-1, which are less electron-releasing than phenyl, moderately facilitated the reduction of the radicals (**1k−m**; Table 4).

Interestingly, the introduction of a strongly electron-withdrawing F_3C group at either C-3 (**1h**) or C-7 (**1b**) did not cause a notable change in the redox potential; however, when two such groups were combined, as in the 3,7-bis(trifluoromethyl) radical **1i**, they worked in a synergistic manner and dramatically reduced the reduction potential to −0.58 V and increased the oxidation potential to 0.66 V. A similar effect was observed when pyrid-2-yl groups were placed at N-1 and C-3 in the presence of a F_3C group at C-7 (radical **1o**). For the latter, an additional oxidation peak was also observed at $E_{1/2}^{+1/+2}$ = 0.77 V.

Table 4. Cyclic Voltammetry Data for Radicals 1a−o[a]

radical	$E_{1/2}^{-1/0}$ (V)	$E_{1/2}^{0/+1}$ (V)	$E_{1/2}^{+1/+2}$ (V)	E_{cell} (V)[b]
1a[c]	−0.96	0.10		1.06
1b[c]	−0.84	0.36		1.20
1c	−0.97	0.19		1.16
1d	−0.93	0.19		1.12
1e	−0.96	0.21		1.17
1f	−1.06	0.26		1.32
1g	−0.84	0.35		1.19
1h	−0.89	0.25		1.14
1i	−0.58	0.66		1.24
1j	−1.06	0.08		1.14
1k	−0.78	0.28		1.06
1l	−0.67	0.33		1.00
1m	−0.82	0.24		1.06
1n	−0.83	0.35		1.18
1o	−0.54	0.61	0.77	1.15

[a]The concentration of radicals used was 1 mM in DCM containing *n*-Bu_4NBF_4 (0.1 M) as an electrolyte. Reference electrode = Ag/AgCl; scan rate = 50 mV s^{-1}; temperature = 20 °C. Fc/Fc^+ (0.352 V) was used as an internal reference.[22] [b]$E_{cell} = E_{1/2}^{0/+1} - E_{1/2}^{-1/0}$. [c]Reference 4a.

The above data indicate that the redox potentials of 1,2,4-benzotriazinyls can be tailored by strategic substitution. Customizing the redox potentials of 1,2,4-benzotriazinyls can enable their broader application in the material sciences. Nonetheless, the presence of more than one substituent was needed to alter the electron density distribution and thus the redox potential significantly.

3. CONCLUSIONS

A route to benzo- and pyrido-fused triazinyl radicals has been developed that avoids the formation of unstable or highly reactive intermediates, such as amidrazones or imidoyl chlorides. The synthesis involves the preparation of 1-(2-nitroaryl)-1-arylhydrazides from 1-halo-2-nitroarenes and 1-arylhydrazides. Subsequent reduction of the nitro group using a mild reducing agent (e.g., In or Sn powder) followed by *in situ* acid-catalyzed cyclodehydration and finally an alkali workup affords the desired radicals. For 3-alkyl-substituted benzotriazinyl radicals, an alternative multistep route that involves the preparation of asymmetrically 1,1-diaryl-substituted hydrazines provides overall higher yields. In this manner, 15 radicals with varying substitution at the N-1, C-3, and C-7 positions were prepared.

4. EXPERIMENTAL SECTION

4.1. General Methods. Anhydrous Na_2SO_4 was used to dry organic extracts, and all volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by thin-layer chromatography (TLC) using commercial glass-backed TLC plates (Kieselgel 60 F_{254} or, where stated, aluminum oxide 60 F_{254} neutral). The plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography was used throughout for all non-TLC-scale chromatographic separations and employed either silica gel 60 (<0.063 mm) or, where stated, aluminum oxide 60 G neutral (type E). Melting and decomposition points were determined using either a Kofler hot-stage microscope apparatus or a DSC with samples hermetically sealed in aluminum pans under an argon atmosphere, using heating rates of 5 °C/min. The solvent used for recrystallization is indicated after each melting point. UV spectra were obtained using a UV/vis spectrophotometer, and inflections are identified by the abbreviation "inf". IR spectra were recorded on an FTIR-NIR spectrometer with a Ge ATR accessory, and strong,

dx.doi.org/10.1021/jo402481t | J. Org. Chem. 2014, 79, 314−327

medium, and weak peaks are represented by "s", "m", and "w", respectively. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, or at 500 and 125 MHz, respectively. Deuterated solvents were used for homonuclear lock, and the signals are referenced to the deuterated solvent peaks. Low-resolution (EI) mass spectra were recorded on a GC/MS with direct inlet probe. MALDI-TOF MS was conducted on a time-of-flight (TOF) mass spectrometer. Cyclic voltammetry (CV) measurements were performed on a Princeton Applied Research 263A potentiostat/galvanostat apparatus. The concentration of the benzotriazinyl radical used was 1 mM in DCM containing tetra-*n*-butylammonium tetrafluoroborate (*n*-Bu_4NBF_4) (0.1 M) as the electrolyte. The reference electrode was Ag/AgCl, and the scan rate was 50 mV/s. The Fc/Fc$^+$ couple, for which $E^{ox}_{1/2}$ = 0.352 V in this system, was used as an internal reference.[22] EPR spectra were recorded on an X-band EPR spectrometer at room temperature on solid-state samples of the benzotriazinyls and on dilute solutions in DCM. For the dilute-solution spectra, the microwave power was in the region 5−70 mW with a modulation frequency of 50 or 100 kHz and a modulation amplitude of 0.5−1.0 G_{pp}. Simulations of the solution spectra were made using WinSim.[23] The nearly isotropic nature of most of the benzotriazinyl radical samples meant that the majority of the solid-state samples could be initially modeled with an isotropic spectrum using WinSim. *N*′-Phenylbenzohydrazide (**19a**),[24] 4-fluoro-*N*′-phenylbenzohydrazide (**19b**),[25] *N*′-phenylthiophene-2-carbohydrazide (**19c**),[26] *N*′-phenylpicolinohydrazide (**19d**),[27] *N*′-phenylacetohydrazide (**19e**),[28] 2,2,2-trifluoro-*N*′-phenylacetohydrazide (**19f**),[29] *N*′-(pyrid-2-yl)benzohydrazide (**19i**)[30] *N*′-(pyrid-2-yl)picolinohydrazide (**19j**),[31] and 1-benzylidene-2-phenylhydrazine (**20**)[32] were prepared according to literature procedures.

4.2. Synthesis of *N*′-(4-Cyanophenyl)hetarylhydrazides 19g and 19h. *4.2.1. N′-(4-Cyanophenyl)benzohydrazide (19g) (Typical Procedure).* Hydrazin-4-ylbenzonitrile hydrochloride (0.509 g, 3 mmol) was suspended in DCM (5 mL), and Et_3N (0.668 g, 6.6 mmol) was added. The mixture was immersed in an ice−salt bath (ca. −5 °C), and benzoyl chloride (0.422 g, 3 mmol) was added dropwise under vigorous stirring. The reaction mixture was allowed to slowly (12 h) warm to ca. 20 °C, diluted with DCM (50 mL), and washed with water (2 × 50 mL). The organic phase was separated and dried (Na_2SO_4), and the volatiles were removed in vacuo. Trituration of the residue with PhH (10 mL) precipitated the title compound **19g** as colorless needles (0.513 g, 72%). Mp 187−188 °C (from PhH); R_f 0.88 (*t*-BuOMe); (anal. found: C, 70.91; H, 4.61; N, 17.60. $C_{14}H_{11}N_3O$ requires C, 70.87; H, 4.67; N, 17.71%); λ_{max}(DCM)/nm (log ε) 232 (3.60), 267 (4.00); ν_{max}/cm^{-1} 3316w and 3260m (NH), 2216s (C≡N), 1628s, 1607s, 1578m, 1541m, 1512s, 1481m, 1447w, 1346w, 1296m, 1267m, 1176m, 1167m, 1157m, 1069w, 1024m, 1002w, 914w, 831s, 818m, 799m; δ_H (500 MHz, DMSO-d_6) 10.53 (1H, s), 8.78 (1H, s), 7.91 (2H, d, *J* = 7.5 Hz), 7.60 (1H, dd, *J* = 7.5, 7.5 Hz), 7.56 (2H, d, *J* = 8.5 Hz), 7.51 (2H, dd, *J* = 7.5, 7.5 Hz), 6.83 (2H, d, *J* = 9.0 Hz); δ_C (125 MHz, DMSO-d_6) 166.5 (s), 153.1 (s), 133.6 (d), 132.6 (s), 132.1 (d), 128.7 (d), 127.5 (d), 120.2 (s), 111.9 (d), 99.1 (s); MALDI-TOF *m*/*z* (%): 238 (M$^+$, 41), 220 (15), 195 (8), 117 (10), 105 (100).

4.2.2. N′-(4-Cyanophenyl)thiophene-2-carbohydrazide (19h). Similar treatment of 4-hydrazinylbenzonitrile hydrochloride (0.509 g, 3 mmol) with Et_3N (0.668 g, 6.6 mmol) and dropwise addition of thiophene-2-carbonyl chloride (0.440 g, 320.8 μL, 3 mmol) gave the title compound **19h** as colorless plates (0.511 g, 70%). Mp (DSC) onset 236.3 °C, peak max 237.5 °C (from PhH); R_f 0.63 (*t*-BuOMe); (anal. found: C, 59.47; H, 3.69; N, 17.42. $C_{12}H_9N_3OS$ requires C, 59.24; H, 3.73; N, 17.27%); λ_{max}(DCM)/nm (log ε) 230 (3.52), 268 (4.03); ν_{max}/cm^{-1} 3207w and 3113w (NH), 2984w, 2224m (C≡N), 1663s (C═O), 1632s, 1601w, 1530m, 1497s, 1414s, 1358s, 1337m, 1325w, 1302s, 1267m, 1221w, 1171w, 1101w, 1072w, 1040w, 1040w, 961w, 889s, 862s, 840w, 814w, 756s, 739s; δ_H (500 MHz, DMSO-d_6) 10.55 (1H, s), 8.79 (1H, s), 7.88 (1H, d, *J* = 4.0 Hz), 7.85 (1H, d, *J* = 5.0 Hz), 7.56 (2H, d, *J* = 9.0 Hz), 7.21 (1H, dd, *J* = 4.5, 4.5 Hz), 6.80 (2H, d, *J* = 8.5 Hz); δ_C (125 MHz, DMSO-d_6) 161.5 (s), 153.0 (s), 137.6 (s), 133.6 (d), 131.9 (s), 129.1 (d), 128.3 (d), 120.1 (s), 111.9 (d), 99.2 (s); MALDI-TOF *m*/*z* (%): 244 (MH$^+$, 30), 242 (M$^+$ − 1, 30), 231 (96), 225 (11), 199 (20), 158 (6), 133 (8), 115 (9), 109 (100).

4.3. 2-Nitrophenylation of Hydrazides 19 with 1-Halo-2-nitro(het)arenes 18. *4.3.1. N′-(2-Nitrophenyl)-N′-phenylbenzohydrazide (13a) (Typical Procedure).* To a stirred solution of *N*′-phenylbenzohydrazide (**19a**) (1.167 g, 5.5 mmol) and 1-fluoro-2-nitrobenzene (**18a**) (0.527 mL, 5.0 mmol) in EtOH (4 mL) at ca. 20 °C was added powdered K_2CO_3 (0.760 g, 5.5 mmol). The reaction mixture was then sealed in a glass pressure tube and heated at ca. 110 °C for 2 days, allowed to cool to ca. 20 °C, diluted with DCM (10 mL), filtered through Celite, and rinsed with additional DCM, and the volatiles were removed in vacuo. The residue was dissolved in DCM (2 mL) and chromatographed (DCM) to give the title compound **13a** as yellow needles (1.667 g, 62%). Mp 170−172 °C (from EtOH) (lit.[33] 171−172 °C); R_f 0.27 (DCM); ν_{max}/cm^{-1} 3283w (NH), 3082w, 3059w and 3040w (Ar CH), 1657s (C═O), 1593m, 1530s, 1487s, 1477m, 1456w, 1447w, 1352s, 1306m, 1263m, 1248m, 1167w, 1155w, 1097w, 1076w, 1061w, 1026w, 980w, 932w, 893m, 853m, 804w, 773m; δ_H (300 MHz, $CDCl_3$) 8.65 (1H, br s), 8.05 (1H, dd, *J* = 8.2, 1.4 Hz), 7.93 (1H, dd, *J* = 8.1, 1.1 Hz), 7.88−7.79 (2H, m), 7.68 (1H, ddd, *J* = 7.9, 7.9, 1.5 Hz), 7.57 (1H, ddd, *J* = 7.3, 7.3, 1.3 Hz), 7.53−7.37 (3H, m), 7.25−7.19 (3H, m), 6.95 (1H, dd, *J* = 7.4, 7.4 Hz), 6.90−6.82 (2H, m); δ_C (75 MHz, $CDCl_3$) 166.5 (s), 145.7 (s), 145.0 (s), 138.8 (s), 134.7 (d), 132.5 (d), 131.8 (s), 131.1 (d), 129.2 (d), 128.8 (d), 127.3 (d), 127.1 (d), 126.2 (d), 121.7 (d), 114.9 (d); identical to an authentic sample.

4.3.2. N′-[2-Nitro-5-(trifluoromethyl)phenyl]-N′-phenylbenzohydrazide (13b). Similar treatment of *N*′-phenylbenzohydrazide (**19a**) (1.167 g, 5.5 mmol) with 2-fluoro-1-nitro-4-(trifluoromethyl)benzene (**18b**) (0.700 mL, 5.0 mmol) and K_2CO_3 (0.760 g, 5.5 mmol) in EtOH (4 mL) in a thick-walled glass tube that was sealed and heated at ca. 110 °C for 1 day gave upon chromatography (DCM) the title compound **13b** as yellow needles (1.203 g, 60%). Mp (DSC) onset 165.3 °C, peak max 166.2 °C (from MeOH); R_f 0.59 (DCM); (anal. found: C, 60.00; H, 3.41; N, 10.58. $C_{20}H_{14}F_3N_3O_3$ requires C, 59.85; H, 3.52; N, 10.47%); λ_{max}(DCM)/nm (log ε) 234 (3.44), 263 (3.13), 410 (2.37); ν_{max}/cm^{-1} 3215m (NH), 3063w (Ar CH), 1670s (C═O), 1618m, 1589m, 1524s, 1499m, 1487m, 1431m, 1371m, 1346s, 1323m, 1306s, 1294s, 1265m, 1234m, 1179s, 1163m, 1155m, 1123s, 1103m, 1076m, 1065m, 1028m, 962m, 895m, 872m, 849m, 833s, 800m, 779m, 756w, 735m; δ_H (500 MHz, DMSO-d_6) 11.51 (1H, s), 8.07 (1H, d, *J* = 8.5 Hz), 7.87 (2H, dd, *J* = 8.5, 1.3 Hz), 7.71 (1H, s), 7.67−7.60 (2H, m), 7.53 (2H, dd, *J* = 7.6, 7.6 Hz), 7.33 (2H, dd, *J* = 8.0, 8.0 Hz), 7.12−7.04 (3H, m); δ_C (125 MHz, DMSO-d_6) 165.9 (s), 144.4 (s), 144.0 (s), 139.3 (s), 133.0 (q, $^2J_{FC}$ = 32.2 Hz), 132.4 (d), 131.5 (s), 129.3 (d), 128.6 (d), 127.6 (d), 126.8 (d), 123.7 (d), 122.9 (q, $^1J_{FC}$ = 272.9 Hz), 120.4 (q, $^3J_{FC}$ = 2.7 Hz), 120.2 (q, $^3J_{FC}$ = 3.6 Hz), 118.3 (d); MALDI-TOF *m*/*z* (%): 402 (MH$^+$, 25), 354 (16), 297 (21), 280 (53), 235 (28), 104 (100).

4.3.3. 4-Fluoro-N′-(2-nitrophenyl)-N′-phenylbenzohydrazide (13c). Similar treatment of 4-fluoro-*N*′-phenylbenzohydrazide (**19b**) (1.266 g, 5.5 mmol) with 1-fluoro-2-nitrobenzene (**18a**) (0.527 mL, 5.0 mmol) and K_2CO_3 (0.760 g, 5.5 mmol) in EtOH (4 mL) in a thick-walled glass tube that was sealed and heated at ca. 110 °C for 2 days gave upon chromatography (DCM) the title compound **13c** as yellow needles (1.106 g, 63%). Mp (DSC) onset 169.9 °C, peak max 170.8 °C (from EtOH); R_f 0.39 (DCM); (anal. found: C, 65.08; H, 3.95; N, 12.13. $C_{19}H_{14}FN_3O_3$ requires C, 64.95; H, 4.02; N, 11.96%); λ_{max}(DCM)/nm (log ε) 235 (3.44), 265 (3.18), 407 (2.27); ν_{max}/cm^{-1} 3269w (NH), 1659s (C═O), 1605m, 1595m, 1530s, 1497s, 1477m, 1456w, 1408w, 1352s, 1329w, 1300w, 1263m, 1252m, 1238m, 1159m, 1155m, 1094w, 1059w, 1013w, 970w, 930w, 897m, 854m, 849m, 814w, 773s, 764m, 750s, 731m; δ_H (500 MHz, DMSO-d_6) 11.36 (1H, s), 7.95 (2H, dd, *J* = 8.8, 5.5 Hz), 7.87 (1H, dd, *J* = 8.2, 1.3 Hz), 7.68 (1H, ddd, *J* = 7.8, 7.8, 1.3 Hz), 7.57 (1H, d, *J* = 7.4 Hz), 7.40−7.31 (3H, m), 7.26 (2H, dd, *J* = 8.0, 8.0 Hz), 6.98 (1H, dd, *J* = 7.3, 7.3 Hz), 6.91 (2H, d, *J* = 8.0 Hz); δ_C (125 MHz, DMSO-d_6) 164.8 (s), 164.3 (q, $^1J_{FC}$ = 249.8 Hz), 145.6 (s), 143.1 (s), 138.2 (s), 133.9 (d), 130.3 (d, $^3J_{FC}$ = 9.1 Hz), 129.0 (d), 128.4 (d, $^4J_{FC}$ = 2.7 Hz), 125.1 (d), 124.8

dx.doi.org/10.1021/jo402481t | J. Org. Chem. 2014, 79, 314−327

(d), 122.1 (d), 116.8 (d), 115.6 (d, $^2J_{FC}$ = 21.8 Hz); MALDI-TOF *m*/*z* (%): 352 (MH^+, 53), 334 (14), 324 (14), 304 (49), 212 (100), 184 (10), 167 (32), 122 (27).

4.3.4. N′-(2-Nitrophenyl)-N′-phenyl-2-thiophenecarbohydrazide (13d). Similar treatment of *N′*-phenylthiophene-2-carbohydrazide (**19c**) (1.200 g, 5.5 mmol) with 1-fluoro-2-nitrobenzene (**18a**) (0.527 mL, 5.0 mmol) and K_2CO_3 (0.760 g, 5.5 mmol) in EtOH (4 mL) in a thick-walled glass tube that was sealed and heated at ca. 110 °C for 2 days gave upon chromatography (DCM) the title compound **13d** as yellow needles (1.034 g, 61%). Mp (DSC) onset 170.8 °C, peak max 171.7 °C (from 2-PrOH); R_f 0.20 (DCM); (anal. found: C, 60.11; H, 3.89; N, 12.31. $C_{17}H_{13}N_3O_3S$ requires C, 60.17; H, 3.86; N, 12.38%); λ_{max}(DCM)/nm (log ε) 239 (3.43), 264 inf (3.37), 410 (2.06); ν_{max}/cm^{-1} 3262w (NH), 3084w (Ar CH), 1645s (C═O), 1609w, 1593m, 1526s, 1495m, 1477m, 1456w, 1449w, 1416m, 1352s, 1323m, 1304m, 1265m, 1244m, 1167w, 1146w, 1092w, 1061w, 1030w, 928w, 903w, 876m, 849s, 773m, 745s, 729m; δ_H (300 MHz, DMSO-d_6) 11.36 (1H, s), 7.94 (1H, d, *J* = 3.6 Hz), 7.91−7.85 (2H, m), 7.70 (1H, ddd, *J* = 7.9, 7.9, 1.3 Hz), 7.58 (1H, d, *J* = 7.4 Hz), 7.35 (1H, ddd, *J* = 7.8, 7.8, 0.8 Hz), 7.31−7.18 (3H, m), 6.97 (1H, dd, *J* = 7.3, 7.3 Hz), 6.89 (2H, d, *J* = 7.9 Hz); δ_C (75 MHz, DMSO-d_6) 160.8 (s), 145.7 (s), 143.1 (s), 138.2 (s), 136.3 (s), 134.0 (d), 132.3 (d), 129.6 (d), 129.0 (d), 128.2 (d), 125.3 (d), 125.2 (d), 125.0 (d), 122.1 (d), 116.6 (d); MALDI-TOF *m*/*z* (%): 340 (MH^+, 28), 339 (M^+, 100), 322 (12), 287 (21), 256 (55), 228 (17), 216 (31), 212 (18), 181 (8), 167 (5).

4.3.5. N′-(2-Nitrophenyl)-N′-phenylpicolinohydrazide (13e). Similar treatment of *N′*-phenylpicolinohydrazide (**19d**) (1.173 g, 5.5 mmol) with 1-fluoro-2-nitrobenzene (**18a**) (0.527 mL, 5.0 mmol) and K_2CO_3 (0.760 g, 5.5 mmol) in EtOH (4 mL) in a thick-walled glass tube that was sealed and heated at ca. 110 °C for 2 days gave upon chromatography (DCM) the title compound **13e** as yellow needles (1.420 g, 85%). Mp (DSC) onset 178.3 °C, peak max 182.8 °C (from EtOAc/*n*-pentane); R_f 0.70 (*t*-BuOMe); (anal. found: C, 64.80; H, 4.29; N, 16.89. $C_{18}H_{14}N_4O_3$ requires C, 64.66; H, 4.22; N, 16.76%); λ_{max}(DCM)/nm (log ε) 234 (3.32), 261 inf (2.99), 266 (3.03), 273 inf (2.99); ν_{max}/cm^{-1} 3233m (NH), 3059w and 3009w (Ar CH), 1659s (C═O), 1603m, 1589m, 1570w, 1537m, 1495s, 1466m, 1431m, 1323w, 1308w, 1290w, 1256w, 1244m, 1177w, 1101w, 1090w, 1049w, 999m, 970w, 918m, 872m, 818m, 758s, 743s; δ_H (500 MHz, acetone-d_6) 10.46 (1H, s), 8.68 (1H, d, *J* = 4.5 Hz), 8.13 (1H, d, *J* = 8.0 Hz), 8.06−8.03 (2H, m), 7.89 (1H, d, *J* = 8.0 Hz), 7.81 (1H, dd, *J* = 8.0, 8.0 Hz), 7.68−7.66 (1H, m), 7.54 (1H, dd, *J* = 7.5, 7.5 Hz), 7.23 (2H, dd, *J* = 8.5, 8.5 Hz), 6.92 (1H, d, *J* = 7.5, 7.5 Hz), 6.87 (2H, d, *J* = 8.0 Hz); δ_C (75 MHz, acetone-d_6) 163.8 (s), 150.0 (s), 149.6 (d), 147.3 (s), 146.3 (s), 139.2 (s), 138.7 (d), 135.4 (d), 130.6 (d), 129.9 (d), 128.2 (d), 128.0 (d), 126.7 (d), 123.3 (d), 122.2 (d), 115.8 (d); MALDI-TOF *m*/*z* (%): 335 (MH^+, 22), 334 (M^+, 100), 317 (60), 288 (43).

4.3.6. N′-(2-Nitrophenyl)-N′-phenylacetohydrazide (13f). Similar treatment of *N′*-phenylacetohydrazide (**19e**) (0.826 g, 5.5 mmol) with 1-fluoro-2-nitrobenzene (**18a**) (0.527 mL, 5.0 mmol) and K_2CO_3 (0.760 g, 5.5 mmol) in EtOH (4 mL) in a thick-walled glass tube that was sealed and heated at ca. 110 °C for 2 days gave upon chromatography (DCM/*t*-BuOMe, 1:1) the title compound **13f** as yellow needles (0.312 g, 23%). Mp (DSC) onset 140.9 °C, peak max 141.7 °C (from 2-PrOH); R_f 0.45 (*t*-BuOMe); (anal. found: C, 62.11; H, 4.76; N, 15.56. $C_{14}H_{13}N_3O_3$ requires C, 61.99; H, 4.83; N, 15.49%); λ_{max}(DCM)/nm (log ε) 236 (3.38), 264 (3.22), 404 (2.32); ν_{max}/cm^{-1} 3256w (NH), 3084w and 3026w (Ar CH), 1697w, 1672s (C═O), 1595m, 1574w, 1526s, 1495s, 1479m, 1458w, 1354s, 1329m, 1317m, 1302m, 1258w, 1234m, 1182w, 1165w, 1132w, 1082w, 1040w, 1032w, 997w, 957w, 899w, 874w, 853w, 777s, 752m; δ_H (500 MHz, DMSO-d_6) mixture of major and minor prototautomers: major 10.54 (1H, s), 7.87 (1H, d, *J* = 8.0 Hz), 7.68 (1H, dd, *J* = 7.7, 7.7 Hz), 7.54 (1H, d, *J* = 7.9 Hz), 7.36 (1H, dd, *J* = 7.6, 7.6 Hz), 7.22 (2H, dd, *J* = 7.9, 7.9 Hz), 6.91 (1H, dd, *J* = 7.3, 7.3 Hz), 6.77 (2H, d, *J* = 8.0 Hz), 1.91 (3H, s); minor 10.12 (1H, s), 7.93 (1H, d, *J* = 8.0 Hz), 7.78 (1H, dd, *J* = 7.7, 7.7 Hz), 7.59 (1H, d, *J* = 8.2 Hz), 7.41 (1H, dd, *J* = 7.6, 7.6 Hz), 7.29 (2H, dd, *J* = 7.9, 7.9 Hz), 7.03 (1H, dd, *J* = 7.3, 7.3 Hz), 6.83 (2H, d, *J* = 8.0 Hz), 1.96 (3H, s); δ_C (125 MHz, DMSO-d_6) mixture of major and minor prototautomers: major 169.3 (s), 145.7 (s), 143.7 (s), 138.2 (s), 134.2 (d), 129.1 (d), 126.6 (d), 125.6 (d), 125.3 (d), 121.6 (d), 115.7 (d), 20.3 (q); minor 174.6 (s), 146.7 (s), 142.9 (s), 138.6 (s), 134.8 (d), 129.4 (d), 125.8 (d), 125.5 (d), 124.7 (d), 123.3 (d), 117.2 (d), 19.4 (q); MS (EI) *m*/*z* (%): 271 (M^+, 55), 229 (100), 212 (58), 196 (4), 181 (62), 167 (92), 152 (18), 140 (9), 128 (9), 115 (5), 105 (6), 77 (74), 65 (7), 51 (29).

4.3.7. N′-[2-Nitro-5-(trifluoromethyl)phenyl]-N′-phenylacetohydrazide (13g). Similar treatment of *N′*-phenylacetohydrazide (**19e**) (0.826 g, 5.5 mmol) with 2-fluoro-1-nitro-4-(trifluoromethyl)benzene (**18b**) (0.700 mL, 5.0 mmol) and K_2CO_3 (0.760 g, 5.5 mmol) in EtOH (4 mL) in a thick-walled glass tube that was sealed and heated at ca. 110 °C for 1 day gave upon chromatography (DCM/*t*-BuOMe) the title compound **13g** as yellow needles (0.322 g, 19%). Mp (DSC) onset 156.3 °C, peak max 157.2 °C (from *c*-hexane); R_f 0.16 (DCM); (anal. found: C, 52.89; H, 3.39; N, 12.22. $C_{15}H_{12}F_3N_3O_3$ requires C, 53.10; H, 3.57; N, 12.39%); λ_{max}(DCM)/nm (log ε) 236 (3.13), 267 inf (2.94), 407 (2.24); ν_{max}/cm^{-1} 3167w (NH), 2994w, 1663m (C═O), 1614w, 1591m, 1537m, 1493m, 1458w, 1429m, 1371m, 1344s, 1312s, 1300s, 1256m, 1233w, 1177s, 1167s, 1128s, 1094m, 1070m, 1026w, 1003w, 976w, 872m, 854m, 837w, 829m, 820m, 772m, 752w; δ_H (500 MHz, DMSO-d_6) mixture of major and minor prototautomers: major 10.78 (1H, s), 8.07 (1H, d, *J* = 8.4 Hz), 7.69 (1H, s), 7.65 (1H, d, *J* = 8.7 Hz), 7.29 (2H, dd, *J* = 7.9, 7.9 Hz), 7.03 (1H, dd, *J* = 7.3, 7.3 Hz), 6.97 (2H, d, *J* = 8.2 Hz), 1.93 (3H, s); minor 10.23 (1H, s), 8.15 (1H, d, *J* = 8.4 Hz), 7.90 (1H, s), 7.76 (1H, d, *J* = 8.5 Hz), 7.33 (2H, d, *J* = 8.0 Hz), 7.11 (1H, dd, *J* = 7.4, 7.4 Hz), 2.01 (3H, s); δ_C (125 MHz, DMSO-d_6) mixture of major and minor prototautomers: major 144.5 (s), 144.3 (s), 169.2 (s), 139.1 (s), 133.0 (q, $^2J_{FC}$ = 32.2 Hz), 129.2 (d), 126.8 (d), 123.2 (d), 122.9 (q, $^1J_{FC}$ = 273.4 Hz), 121.1 (q, $^3J_{FC}$ = 3.6 Hz), 120.8 (q, $^3J_{FC}$ = 3.6 Hz), 117.4 (d), 20.1 (q); minor (five C signals missing) 174.2 (s), 145.7 (s), 139.3 (s), 129.4 (d), 127.0 (d), 124.3 (d), 118.2 (d), 19.3 (q); MALDI-TOF *m*/*z* (%): 340 (MH^+, 44), 297 (100), 280 (29), 235 (23).

4.3.8. 2,2,2-Trifluoro-N′-(2-nitrophenyl)-N′-phenylacetohydrazide (13h). Similar treatment of 2,2,2-trifluoro-*N′*-phenylacetohydrazide (**19f**) (1.123 g, 5.5 mmol) with 1-fluoro-2-nitrobenzene (**18a**) (0.527 mL, 5.0 mmol) and K_2CO_3 (0.760 g, 5.5 mmol) in EtOH (4 mL) in a thick-walled glass tube that was sealed and heated at ca. 110 °C for 2 days gave upon chromatography (DCM) the title compound **13h** as yellow needles (0.276 g, 17%). Mp (DSC) onset 90.5 °C, peak max 91.5 °C (from *n*-hexane); R_f 0.61 (DCM); (anal. found: C, 51.69; H, 3.16; N, 12.82. $C_{14}H_{10}F_3N_3O_3$ requires C, 51.70; H, 3.10; N, 12.92%); λ_{max}(DCM)/nm (log ε) 231 (3.34), 259 inf (3.13), 325 (2.51), 382 (2.07); ν_{max}/cm^{-1} 3319w (NH), 3103w and 3044w (Ar CH), 1740s (C═O), 1595w, 1578w, 1514m, 1497s, 1456w, 1350m, 1310m, 1298m, 1254w, 1207s, 1192m, 1175s, 1163s, 1113w, 1099w, 1067w, 934w, 901m, 878w, 853w, 793m, 775w, 766w, 741s; δ_H (300 MHz, DMSO-d_6) 12.46 (1H, s), 7.95 (1H, dd, *J* = 7.9, 1.1 Hz), 7.76 (1H, ddd, *J* = 8.4, 7.2, 1.1 Hz), 7.55−7.41 (2H, m), 7.31 (2H, dd, *J* = 7.9, 7.9 Hz), 7.04 (1H, dd, *J* = 7.4, 7.4 Hz), 6.84 (2H, d, *J* = 7.9 Hz); δ_C (75 MHz, DMSO-d_6) 155.6 (q, $^2J_{FC}$ = 36.5 Hz), 144.9 (s), 144.2 (s), 136.9 (s), 134.4 (d), 129.2 (d), 126.5 (d), 126.7 (d), 125.3 (d), 122.8 (d), 116.8 (d), 115.5 (q, $^1J_{FC}$ = 289.0 Hz); MS (EI) *m*/*z* (%): 325 (M^+, 23), 278 (41), 228 (18), 207 (6), 181 (46), 167 (29), 154 (40), 140 (10), 128 (8), 115 (4), 105 (7), 91 (7), 77 (100), 69 (22), 63 (13), 51 (83).

4.3.9. 2,2,2-Trifluoro-N′-[2-nitro-5-(trifluoromethyl)phenyl]-N′-phenylacetohydrazide (13i). Similar treatment of 2,2,2-trifluoro-*N′*-phenylacetohydrazide (**19f**) (1.123 g, 5.5 mmol) with 2-fluoro-1-nitro-4-(trifluoromethyl)benzene (**18b**) (0.700 mL, 5.0 mmol) and K_2CO_3 (0.760 g, 5.5 mmol) in EtOH (4 mL) in a thick-walled glass tube that was sealed and heated at ca. 110 °C for 1 day gave upon chromatography the title compound **13i** as yellow needles (0.688 g, 35%). Mp (DSC) onset 106.1 °C, peak max 107.5 °C (from *n*-hexane); R_f 0.61 (DCM); (anal. found: C, 45.70; H, 2.29; N, 10.60. $C_{15}H_9F_6N_3O_3$ requires C, 45.81; H, 2.31; N, 10.69%); λ_{max}(DCM)/nm (log ε) 232 (3.06), 249 inf (2.94), 389 (2.05); ν_{max}/cm^{-1} 3204w (NH), 3036w (Ar CH), 1713s (C═O), 1614w, 1591m, 1541m,

dx.doi.org/10.1021/jo402481t | *J. Org. Chem.* 2014, 79, 314−327

1493m, 1458w, 1427m, 1352m, 1331m, 1314m, 1296m, 1271m, 1250m, 1217s, 1161s, 1142s, 1130s, 1109w, 1084s, 1072m, 1028w, 1005w, 951w, 905w, 878m, 851m, 827m, 810w, 770m, 754w, 745w; δ_H (300 MHz, DMSO-d_6) 12.59 (1H, s), 8.15 (1H, d, J = 8.5 Hz), 7.80 (1H, d, J = 8.9 Hz), 7.72 (1H, s), 7.36 (2H, dd, J = 7.9, 7.9 Hz), 7.13 (1H, dd, J = 7.4, 7.4 Hz), 6.98 (2H, d, J = 7.7 Hz); δ_C (75 MHz, DMSO-d_6) 155.8 (q, $^2J_{FC}$ = 36.8 Hz), 145.2 (s), 143.9 (s), 137.8 (s), 133.4 (q, $^2J_{FC}$ = 32.9 Hz), 129.5 (d), 126.9 (d), 124.3 (d), 122.7 (q, $^1J_{FC}$ = 273.4 Hz), 122.5 (q, $^3J_{FC}$ = 3.6 Hz), 121.1 (q, $^3J_{FC}$ = 3.6 Hz), 118.2 (d), 115.4 (q, $^1J_{FC}$ = 288.2 Hz); MS (EI) m/z (%): 393 (M^+, 33), 346 (9), 296 (22), 279 (6), 249 (53), 235 (15), 154 (13), 145 (8), 77 (100), 69 (19), 63 (10), 51 (54).

*4.3.10. N′-(4-Cyanophenyl)-N′-(2-nitrophenyl)benzohydrazide (**13j**).* Similar treatment of *N′*-(4-cyanophenyl)benzohydrazide (**19j**) (1.305 g, 5.5 mmol) with 1-fluoro-2-nitrobenzene (**18a**) (0.527 mL, 5.0 mmol) and K_2CO_3 (0.760 g, 5.5 mmol) in EtOH (4 mL) in a thick-walled glass tube that was sealed and heated at ca. 110 °C for 2 days gave upon chromatography (DCM) the title compound **13j** as yellow needles (1.150 g, 64%). Mp (DSC) decomp. onset 260.7 °C, peak max 262.7 °C (from *c*-hexane); R_f 0.30 (DCM); (anal. found: C, 67.12; H, 4.08; N, 15.53. $C_{20}H_{14}N_4O_3$ requires C, 67.03; H, 3.94; N, 15.63%); λ_{max}(DCM)/nm (log ε) 232 (3.27), 270 (3.48), 374 (2.33); ν_{max}/cm^{-1} 3289w (NH), 3067w (Ar CH), 2220m (C≡N), 1686m (C═O), 1667m, 1597s, 1526s, 1504s, 1483m, 1342s, 1300m, 1285m, 1260m, 1246m, 1179m, 1148w, 1078w, 1059w, 1026w, 928w, 893w, 851m, 827m, 800w, 783m; δ_H (500 MHz, DMSO-d_6) 11.46 (1H, s), 8.05 (1H, d, J = 7.9 Hz), 7.88 (2H, d, J = 7.3 Hz), 7.83 (1H, ddd, J = 7.9, 7.9, 1.0 Hz), 7.79 (1H, d, J = 7.1 Hz), 7.67 (2H, d, J = 8.8 Hz), 7.64−7.56 (2H, m), 7.52 (2H, dd, J = 7.6, 7.6 Hz), 6.86 (2H, d, J = 8.8 Hz); δ_C (125 MHz, DMSO-d_6) 165.9 (s), 150.1 (s), 145.7 (s), 136.1 (s), 134.8 (d), 133.4 (d), 132.4 (d), 131.5 (s), 128.8 (d), 128.5 (d), 128.3 (d), 127.7 (d), 125.3 (d), 119.3 (s), 114.4 (d), 101.7 (s); MALDI-TOF m/z (%): 359 (MH^+, 72), 343 (20), 331 (45), 239 (37), 208 (30), 105 (100).

*4.3.11. N′-(4-Cyanophenyl)-N′-(2-nitrophenyl)thiophene-2-carbohydrazide (**13k**).* Similar treatment of *N′*-(4-cyanophenyl)-thiophene-2-carbohydrazide (**19i**) (1.340 g, 5.5 mmol) with 1-fluoro-2-nitrobenzene (**18a**) (0.527 mL, 5.0 mmol) and K_2CO_3 (0.760 g, 5.5 mmol) in EtOH (4 mL) in a thick-walled glass tube that was sealed and heated at ca. 110 °C for 2 days gave upon chromatography (DCM) the title compound **13k** as yellow needles (1.04 g, 57%). Decomp. (DSC) onset 266.7 °C, peak max 267.5 °C (from *c*-hexane); R_f 0.30 (DCM); (anal. found: C, 59.45; H, 3.17; N, 15.28. $C_{18}H_{12}N_4O_3S$ requires C, 59.33; H, 3.32; N, 15.38%); λ_{max}(DCM)/nm (log ε) 271 (3.58), 374 (2.21); ν_{max}/cm^{-1} 3281w (NH), 3092w (Ar CH), 2220m (C≡N), 1672m and 1666m (C═O), 1597s, 1526s, 1508s, 1480m, 1416m, 1352s, 1287m, 1260m, 1246m, 1202w, 1177m, 1144w, 1080m, 1065w, 1020w, 849s, 827m, 781m, 754w; δ_H (500 MHz, DMSO-d_6) 11.49 (1H, s), 8.05 (1H, dd, J = 8.2, 1.3 Hz), 7.94 (1H, d, J = 3.3 Hz), 7.91 (1H, d, J = 4.9 Hz), 7.84 (1H, ddd, J = 8.0, 8.0, 1.3 Hz), 7.77 (1H, dd, J = 8.1, 1.0 Hz), 7.67 (2H, d, J = 9.0 Hz), 7.59 (1H, ddd, J = 8.0, 8.0, 1.3 Hz), 7.22 (1H, dd, J = 4.3, 4.3 Hz), 6.84 (2H, d, J = 9.0 Hz); δ_C (125 MHz, DMSO-d_6) 160.8 (s), 150.0 (s), 145.6 (s), 136.0 (s), 135.8 (s), 134.9 (d), 133.4 (d), 132.7 (d), 130.0 (d), 128.9 (d), 128.4 (d), 128.3 (d), 125.4 (d), 119.3 (s), 114.3 (d), 101.8 (s); MALDI-TOF m/z (%): 364 (M^+, 11), 325 (26), 271 (5).

*4.3.12. N′-(2-Nitrophenyl)-N′-(pyrid-2-yl)benzohydrazide (**13l**).* Similar treatment of *N′*-(pyrid-2-yl)benzohydrazide (**19j**) (1.170 g, 5.5 mmol) with 1-fluoro-2-nitrobenzene (**18a**) (0.527 mL, 5.0 mmol) and K_2CO_3 (0.760 g, 5.5 mmol) in EtOH (4 mL) in a thick-walled glass tube that was sealed and heated at ca. 110 °C for 2 days gave upon chromatography (*t*-BuOMe) the title compound **13l** as yellow needles (1.290 g, 77%). Mp (DSC) onset 178.6 °C, peak max 180.3 °C (from PhH); R_f 0.76 (*t*-BuOMe); (anal. found: C, 64.86; H, 4.33; N, 16.87. $C_{18}H_{14}N_4O_3$ requires C, 64.66; H, 4.22; N, 16.76%); λ_{max}(DCM)/nm (log ε) 233 (4.72), 259 inf (4.47), 278 inf (4.39) 288 (4.33); ν_{max}/cm^{-1} 3269m (NH), 1660s (C═O), 1589s, 1522s, 1487w, 1464s, 1433s, 1343s, 1300m, 1287m, 1262s, 1153w, 1078w, 1022w, 986w, 932w, 897w, 849w, 802w, 785m, 775m, 762s, 743w, 732w; δ_H (500 MHz, $CDCl_3$) 8.88 (1H, s), 8.08 (1H, dd, J = 5.0, 1.0 Hz), 8.06 (1H, dd, J = 8.0, 1.5 Hz), 8.01 (1H, dd, J = 8.0, 1.5 Hz), 7.88 (2H, dd, J = 7.0, 1.5 Hz), 7.72 (1H, ddd, J = 7.8, 7.8, 1.5 Hz), 7.58−7.52 (2H, m), 7.50−7.46 (3H, m), 6.84 (1H, d, J = 8.0 Hz), 6.79 (1H, dd, J = 7.0, 5.0 Hz); δ_C (500 MHz, $CDCl_3$) 166.8 (s), 156.9 (s), 147.8 (d), 146.1 (s), 138.1 (d), 137.1 (s), 134.9 (d), 132.58 (d), 132.56 (d), 131.9 (s), 128.8 (d), 128.4 (d), 127.4 (d), 125.6 (d), 116.4 (d), 107.2 (d); MALDI-TOF m/z (%): 336 (MH^+ + 1, 10), 335 (MH^+, 89), 317 (12), 288 (100), 200 (27), 174 (11).

*4.3.13. N′-(2-Nitrophenyl)-N′-(pyrid-2-yl)picolinohydrazide (**13m**).* Similar treatment of *N′*-(pyrid-2-yl)picolinohydrazide (**19k**) (1.180 g, 5.5 mmol) with 1-fluoro-2-nitrobenzene (**18a**) (0.527 mL, 5.0 mmol) and K_2CO_3 (0.760 g, 5.5 mmol) in EtOH (4 mL) in a thick-walled glass tube that was sealed and heated at ca. 110 °C for 2 days gave upon chromatography (*t*-BuOMe/*n*-hexane, 1:1) the title compound **13m** as yellow needles (1.260 g, 75%). Mp (DSC) decomp. onset 256.6 °C, peak max 297.4 °C (from *c*-hexane); R_f 0.44 (*t*-BuOMe); (anal. found: C, 61.01; H, 3.84; N, 20.76. $C_{17}H_{13}N_5O_3$ requires C, 60.89; H, 3.91; N, 20.89%); λ_{max}(DCM)/nm (log ε) 230 (3.41), 259 (3.24), 288 inf (2.99), 376 (2.14); ν_{max}/cm^{-1} 3341w (NH), 1703m (C═O), 1589s, 1572m, 1526s, 1485m, 1468s, 1433s, 1352m, 1300w, 1281w, 1236w, 1152w, 1107w, 1088w, 1069w, 1040w, 997w, 988w, 903w, 853w, 820w, 779m, 770m; δ_H (300 MHz, $CDCl_3$) 10.34 (1H, s), 8.63 (1H, d, J = 4.7 Hz), 8.22 (1H, d, J = 7.9 Hz), 8.11−8.04 (2H, m), 8.01 (1H, dd, J = 8.0, 1.2 Hz), 7.89 (1H, ddd, J = 7.7, 7.7, 1.6 Hz), 7.72 (1H, ddd, J = 7.7, 7.7, 1.3 Hz), 7.59−7.44 (3H, m), 6.88 (1H, d, J = 8.1 Hz), 6.78 (1H, dd, J = 7.2, 4.9 Hz); δ_C (75 MHz, acetone-d_6) 164.2 (s), 158.0 (s), 149.9 (s), 149.6 (d), 148.1 (d), 146.9 (s), 139.0 (d), 138.7 (d), 138.0 (s), 135.3 (d), 130.9 (d), 128.5 (d), 128.2 (d), 125.9 (d), 123.4 (d), 117.2 (d), 108.5 (d); MS (EI) m/z (%): 335 (M^+, 27), 318 (22), 289 (87), 271 (6), 257 (27), 210 (4), 197 (16), 185 (17), 168 (43), 154 (7), 106 (22), 78 (100), 51 (22).

*4.3.14. N′-[2-Nitro-5-(trifluoromethyl)phenyl]-N′-(pyrid-2-yl)-picolinohydrazide (**13n**).* Similar treatment of *N′*-(pyrid-2-yl)-picolinohydrazide (**19k**) (1.178 g, 5.5 mmol) with 2-fluoro-1-nitro-4-(trifluoromethyl)benzene (**18b**) (0.700 mL, 5.0 mmol) and K_2CO_3 (0.760 g, 5.5 mmol) in EtOH (4 mL) in a thick-walled glass tube that was sealed and heated at ca. 110 °C for 1 day gave upon chromatography (DCM) the title compound **13n** as yellow needles (1.733 g, 86%). Mp (DSC) decomp. onset 197.7 °C, peak max 226.1 °C (from *c*-hexane); R_f 0.60 (*t*-BuOMe); (anal. found: C, 53.75; H, 2.94; N, 17.27. $C_{18}H_{12}F_3N_5O_3$ requires C, 53.60; H, 3.00; N, 17.36%); λ_{max}(DCM)/nm (log ε) 230 (3.47), 261 (3.29), 273 inf (3.23), 291 inf (3.04), 379 (2.28); ν_{max}/cm^{-1} 3343w (NH), 3061w (Ar CH), 1701m (C═O), 1591m, 1572w, 1535s, 1483m, 1468s, 1437s, 1337s, 1310s, 1263w, 1256w, 1236m, 1206w, 1177s, 1152s, 1132s, 1099m, 1065m, 1040w, 997w, 988w, 964w, 908w, 858m, 847w, 841w, 820w, 804w, 773m; δ_H (500 MHz, DMSO-d_6) 11.94 (1H, s), 8.77 (1H, d, J = 4.7 Hz), 8.19 (1H, d, J = 8.4 Hz), 8.11−8.06 (2H, m), 8.01 (1H, dd, J = 4.9, 1.1 Hz), 7.96 (1H, d, J = 1.6 Hz), 7.77 (1H, dd, J = 8.6, 1.6 Hz), 7.75−7.69 (2H, m), 6.99 (1H, d, J = 8.5 Hz), 6.95 (1H, dd, J = 7.0, 5.1 Hz); δ_C (125 MHz, DMSO-d_6) one C (d) signal missing, 163.8 (s), 155.6 (s), 148.9 (d), 148.6 (s), 146.6 (d), 145.6 (s), 138.8 (d), 138.0 (d), 137.1 (s), 133.3 (q, $^2J_{FC}$ = 32.7 Hz), 127.6 (d), 126.2 (d), 122.83 (d), 122.75 (q, $^1J_{FC}$ = 273.4 Hz), 122.0 (q, $^3J_{FC}$ = 3.6 Hz), 117.7 (d), 109.5 (d); MS (EI) m/z (%): 403 (M^+, 9), 386 (7), 357 (36), 325 (10), 253 (8), 236 (14), 197 (6), 106 (21), 78 (100), 51 (23).

*4.3.15. N′-(3-Nitropyrid-2-yl)-N′-phenylbenzohydrazide (**13o**).* Similar treatment of *N′*-phenylbenzohydrazide (**19a**) (1.167 g, 5.5 mmol) with 2-chloro-3-nitropyridine (**18c**) (0.793 g, 5.0 mmol) and K_2CO_3 (0.760 g, 5.5 mmol) in EtOH (4 mL) in a thick-walled glass tube that was sealed and heated at ca. 110 °C for 1 day gave upon chromatography (*t*-BuOMe) the title compound **13o** as yellow needles (1.400 g, 84%). Mp (DSC) onset 205.1 °C, peak max 206.3 °C (from PhH); R_f 0.8 (*t*-BuOMe); (anal. found: C, 64.77; H, 4.28; N, 16.66. $C_{18}H_{14}N_4O_3$ requires C, 64.66; H, 4.22; N, 16.76%); λ_{max}(DCM)/nm (log ε) 232 (4.32), 278 inf (4.17), 395 (3.36); ν_{max}/cm^{-1} 3250m (NH), 1663s (C═O), 1589s, 1564m, 1559m, 1518s, 1491s, 1449s, 1431s, 1356s, 1341m, 1321m, 1300w, 1275m, 1258s, 1146w, 1098w, 1028m, 930w, 907m, 856s, 851m, 804m, 773w, 752s; δ_H (500 MHz,

dx.doi.org/10.1021/jo402481t | J. Org. Chem. 2014, 79, 314−327

$CDCl_3$) 8.58 (1H, s), 8.45 (1H, dd, J = 3.5, 1.0 Hz), 8.13 (1H, dd, J = 8.0, 1.5 Hz), 7.81 (2H, d, J = 7.5 Hz), 7.57 (1H, dd, J = 7.5, 7.5 Hz), 7.47 (2H, dd, J = 7.5, 7.5 Hz), 7.38−7.32 (4H, m), 7.20 (1H, dd, J = 7.0, 7.0 Hz), 7.05 (1H, dd, J = 8.0, 5.0 Hz); δ_C (500 MHz, $CDCl_3$) 166.5 (s), 151.9 (d), 150.3 (s), 143.6 (s), 135.1 (s), 135.0 (d), 132.6 (d), 131.5 (s), 129.3 (d), 128.9 (d), 127.4 (d), 126.0 (d), 122.1 (d), 117.5 (d); MALDI-TOF m/z (%): 336 (MH^+ + 1, 6), 335 (MH^+, 82), 317 (9), 288 (100), 200 (26), 174 (12).

4.3.16. N′-(3-Nitropyrid-2-yl)-N′-(pyrid-2-yl)picolinohydrazide (13p). Similar treatment of N′-(pyrid-2-yl)picolinohydrazide (**19j**) (1.180 g, 5.5 mmol) with 2-chloro-3-nitropyridine (**18c**) (0.793 g, 5.0 mmol) and K_2CO_3 (0.760 g, 5.5 mmol) in EtOH (4 mL) in a thick-walled glass tube that was sealed and heated at ca. 110 °C for 1 day gave upon chromatography (DCM/THF, 8:2) the title compound **13p** as yellow flakes (1.360 g, 81%). Mp (DSC) decomp. onset 220.3 °C, peak max 254.2 °C (from PhH); R_f 0.74 (THF); (anal. found: C, 57.26; H, 3.64; N, 24.88. $C_{16}H_{12}N_6O_3$ requires C, 57.14; H, 3.60; N, 24.99%); λ_{max}(DCM)/nm (log ε) 232 (4.49), 246 inf (4.39), 273 (4.32), 297 (4.32), 374 (3.52); ν_{max}/cm^{-1} 3334w (NH), 3076w (Ar CH), 1701m (C═O), 1589s, 1574m, 1526s, 1487m, 1472m, 1427s, 1356s, 1329m, 1279w, 1238m, 1148w, 1109w, 1090w, 1040w, 997w, 962w, 907w, 858m, 818w, 787w, 772w, 752m; δ_H (500 MHz, DMSO-d_6) 11.71 (1H, s), 8.74 (1H, d, J = 4.5 Hz), 8.56 (1H, dd, J = 4.5, 1.5 Hz), 8.37 (1H, dd, J = 8.0, 1.5 Hz), 8.07−8.03 (2H, m), 7.99 (1H, dd, J = 4.5, 1.0 Hz), 7.75 (1H, ddd, J = 7.8, 7.8, 1.5 Hz), 7.69 (1H, ddd, J = 9.0, 5.0, 2.5 Hz), 7.34 (1H, dd, J = 8.5, 5.0 Hz), 7.14 (1H, d, J = 8.5 Hz), 6.99 (1H, dd, J = 6.5, 5.0 Hz); δ_C (125 MHz, DMSO-d_6) 163.8 (s), 155.4 (s), 151.9 (d), 149.1 (s), 148.9 (d), 146.4 (d), 145.8 (s), 138.9 (d), 138.0 (d), 137.6 (s), 134.1 (d), 127.4 (d), 122.8 (d), 119.5 (d), 118.9 (d), 112.0 (d); MALDI-TOF m/z (%): 337 (MH^+, 94), 328 (16), 312 (15), 290 (100), 271 (13).

4.4. Multistep Route to Hydrazides 13f, 13h, and 13q. *4.4.1. 2-Benzylidene-1-(2-nitrophenyl)-1-phenylhydrazine (21).* A stirred mixture of 2-benzylidene-1-phenylhydrazine (**20**) (5.00 g, 25.48 mmol), 1-fluoro-2-nitrobenzene (**18a**) (2.70 mL, 28.03 mmol), and K_2CO_3 (3.87 g, 28.03 mmol) in DMSO (25 mL) was heated at ca. 100 °C for 15 h and then cooled to ca. 20 °C, diluted with t-BuOMe (200 mL), and washed with water (200 mL), 10% HCl (2 × 100 mL), 2 M NaOH (2 × 100 mL), and brine. The organic phase was then separated and dried (Na_2SO_4), and the volatiles were removed in vacuo. The residue was dissolved in DCM (10 mL) and chromatographed (DCM/n-hexane, 1:1) to give the title compound **21** as yellow needles (7.27 g, 90%). Mp (DSC) onset 102.6 °C, peak max 104.8 °C (from EtOH); R_f 0.40 (DCM/n-hexane, 1:1); (anal. found: C, 72.04; H, 4.84; N, 13.26. $C_{19}H_{15}N_3O_2$ requires C, 71.91; H, 4.76; N, 13.24%); λ_{max}(DCM)/nm (log ε) 239 (3.35), 296 inf (3.18), 326 (3.38), 438 inf (1.83); ν_{max}/cm^{-1} 3063w (Ar CH), 1603m, 1593m, 1566w, 1526s, 1493s, 1445m, 1381w, 1368m, 1329w, 1319w, 1296m, 1281m, 1229m, 1206m, 1163w, 1105w, 1086m, 1069m, 1038w, 1024w, 1003w, 955w, 934w, 905w, 864w, 847m, 781w, 758s, 739s; δ_H (300 MHz, DMSO-d_6) 8.16 (1H, dd, J = 8.1, 1.3 Hz), 7.87 (1H, ddd, J = 7.7, 7.7, 1.3 Hz), 7.68 (1H, ddd, J = 7.8, 7.8, 1.2 Hz), 7.64−7.57 (2H, m), 7.43−7.30 (6H, m), 7.19 (1H, s), 7.14−7.06 (3H, m); δ_C (75 MHz, DMSO-d_6) 146.3 (s), 143.9 (s), 136.8 (d), 135.0 (d), 134.9 (s), 133.8 (s), 129.54 (d), 129.47 (d), 128.68 (d), 128.58 (d), 128.55 (d), 126.3 (d), 125.8 (d), 123.1 (d), 118.3 (d); MALDI-TOF m/z (%): 318 (MH^+, 22), 317 (M^+, 100), 299 (2), 286 (11), 271 (29), 214 (2), 195 (4), 180 (68), 167 (2).

4.4.2. N′-(2-Nitrophenyl)-N′-phenylhydrazine (22). A stirred mixture of 2-benzylidene-1-(2-nitrophenyl)-1-phenylhydrazine (**21**) (1.59 g, 5.0 mmol) and $H_2NOH{\cdot}HCl$ (3.47 g, 50.0 mmol) in pyridine (20 mL) was heated at ca. 80 °C for 1 day. Upon cooling to ca. 20 °C, the pyridine was removed in vacuo. The residue was suspended in DCM, and excess $H_2NOH{\cdot}HCl$ was separated by filtration. The filtrate was diluted with DCM (100 mL) and washed with 2 M NaOH (2 × 100 mL), 10% HCl (2 × 100 mL), and water (100 mL). The organic phase was separated and dried (Na_2SO_4), and the volatiles were removed in vacuo. The residue was dissolved in DCM (5 mL) and chromatographed (DCM) to give recovered starting material **21** (0.27 g, 17%). Mp (DSC) onset 102.6 °C, peak max 104.8 °C (from EtOH); R_f 0.40 (DCM/n-hexane, 1:1); identical to that described above. Further elution gave the title compound **22** as red plates (0.920 g, 80%). Mp (DSC) onset 74.9 °C, peak max 76.5 °C (from MeOH); R_f 0.23 (DCM/n-hexane, 1:1); (anal. found: C, 62.93; H, 4.70; N, 18.28. $C_{12}H_{11}N_3O_2$ requires C, 62.87; H, 4.84; N, 18.33%); λ_{max}(DCM)/nm (log ε) 242 (3.17), 274 (3.13), 288 inf (3.09), 419 (2.25); ν_{max}/cm^{-1} 3346w (NH), 3065w (Ar CH), 2918w, 2849w, 1589s, 1574w, 1518s, 1493s, 1456w, 1443w, 1358m, 1292m, 1265m, 1248m, 1163w, 1146w, 1113w, 1072w, 1040w, 941w, 864m, 843m, 775m, 758s, 746s, 729w; δ_H (300 MHz, DMSO-d_6) 7.81 (1H, d, J = 8.1 Hz), 7.58 (1H, ddd, J = 8.1, 8.1, 0.9 Hz), 7.50 (1H, d, J = 7.5 Hz), 7.28−7.17 (3H, m), 7.04 (2H, d, J = 7.9 Hz), 6.88 (1H, dd, J = 7.3, 7.3 Hz), 5.16 (2H, s); δ_C (75 MHz, $CDCl_3$) 148.3 (s), 144.3 (s), 142.3 (s), 133.2 (d), 129.2 (d), 126.8 (d), 126.0 (d), 124.4 (d), 121.4 (d), 115.9 (d); MALDI-TOF m/z (%): 230 (MH^+, 14), 229 (M^+, 100), 228 (80), 212 (61), 181 (7).

4.4.3. N′-(2-Nitrophenyl)-N′-phenylacetohydrazide (13f). To a stirred solution of 1-(2-nitrophenyl)-1-phenylhydrazine (**22**) (0.500 g, 2.183 mmol) and Et_3N (0.340 mL, 2.401 mmol) in DCM (10 mL) at ca. −5 °C was added dropwise acetic anhydride (0.170 mL, 2.401 mmol). Over the next 4 h the reaction mixture was left to warm to ca. 20 °C, and then after a further 8 h the mixture was diluted with t-BuOMe (30 mL) and washed with water (2 × 50 mL). The organic phase was dried (Na_2SO_4) and concentrated in vacuo. The residue was dissolved in DCM (1 mL) and chromatographed (DCM/t-BuOMe, 1:1) to give the title compound **13f** as yellow needles (0.57 g, 96%). Mp (DSC) onset 140.9 °C, peak max 141.7 °C (from 2-PrOH); R_f 0.45 (t-BuOMe); identical to that described above.

4.4.4. 2,2,2-Trifluoro-N′-(2-nitrophenyl)-N′-phenylacetohydrazide (13h). Similar treatment of 1-(2-nitrophenyl)-1-phenylhydrazine (**22**) (0.500 g, 2.183 mmol) with Et_3N (0.340 mL, 2.401 mmol) and trifluoroacetic anhydride (0.34 mL, 2.401 mmol) in DCM (10 mL) gave upon chromatography (DCM) the title compound **13h** as yellow needles (0.582 g, 82%). Mp (DSC) onset 90.5 °C, peak max 91.5 °C (from n-hexane); R_f 0.61 (DCM); identical to that described above.

4.4.5. N′-(2-Nitrophenyl)-N′-phenyl-1-adamantanecarbohydrazide (13q). Similar treatment of 1-(2-nitrophenyl)-1-phenylhydrazine (**22**) (0.500 g, 2.183 mmol) with Et_3N (0.340 mL, 2.401 mmol) and 1-adamantanecarbonyl chloride (0.34 mL, 2.401 mmol) in DCM (10 mL) gave upon chromatography (DCM) the title compound **13q** as yellow needles (0.50 g, 58%). Mp (DSC) onset 161.0 °C, peak max 162.8 °C (from c-hexane); R_f 0.24 (DCM); (anal. found: C, 70.62; H, 6.40; N, 10.66. $C_{23}H_{25}N_3O_3$ requires C, 70.57; H, 6.44; N, 10.73%); λ_{max}(DCM)/nm (log ε) 240 (2.98), 268 (2.89), 413 (2.07); ν_{max}/cm^{-1} 3314w and 3265w (NH), 2905m and 2851w (CH_2), 1659s (C═O), 1593s, 1574w, 1535s, 1526s, 1493s, 1477m, 1452m, 1350m, 1315w, 1300m, 1254w, 1227m, 1182w, 1165w, 1107w, 1086w, 1059w, 1049w, 916w, 853m, 831w, 781m, 741s, 731m; δ_H (500 MHz, DMSO-d_6) 10.40 (1H, s), 7.81 (1H, d, J = 8.0 Hz), 7.63 (1H, dd, J = 7.8, 7.8 Hz), 7.43 (1H, d, J = 8.4 Hz), 7.30−7.18 (3H, m), 6.94 (1H, dd, J = 7.2, 7.2 Hz), 6.82 (2H, d, J = 8.0 Hz), 1.98 (3H, s), 1.84 (6H, s), 1.67 (6H, s); δ_C (125 MHz, DMSO-d_6) one C (s) signal missing, 175.7 (s), 145.6 (s), 142.4 (s), 138.6 (s), 133.7 (d), 128.8 (d), 125.1 (d), 124.5 (d), 124.0 (d), 121.9 (d), 116.7 (d), 39.6 (s), 38.0 (t), 35.9 (t), 27.4 (d); MALDI-TOF m/z (%): 392 (MH^+, 68), 391 (M^+, 6), 374 (7), 358 (11), 353 (6), 346 (53), 330 (8), 212 (100), 196 (6), 181 (31), 167 (38).

4.5. Reduction of Benzohydrazide 13a and Picolinohydrazides 13m, 13n, and 13p. *4.5.1. N′-(2-Aminophenyl)-N′-phenylbenzohydrazide (12a). 4.5.1.1. Method 1: Using Pd−C/H_2 in EtOH.* To a solution of N′-(2-nitrophenyl)-N′-phenylbenzohydrazide (**13a**) (0.333 g, 1.0 mmol) in EtOH (10 mL) at ca. 20 °C was added Pd/C (10 mol %) (33 mg) in one portion. The reaction mixture was evacuated and flushed with H_2 (3×), filled with H_2 (3 bar), and left to stir for 4 h. During that time the yellow color of the reaction mixture disappeared and consumption of H_2 ceased. The mixture was filtered through a short pad of Celite, and the volatiles were removed in vacuo. Chromatography (Et_2O/n-hexane, 1:1) of the residue gave the title compound **12a** as colorless needles (0.264 g, 97%). Mp (DSC) onset 176.6 °C, peak max 178.2 °C (from Et_2O); R_f 0.71 (n-hexane/Et_2O, 1:1); λ_{max}(DCM)/nm (log ε) 239 (3.80), 294 (3.19); ν_{max}/cm^{-1}

dx.doi.org/10.1021/jo402481t | J. Org. Chem. 2014, 79, 314−327

3387w and 3219w (NH), 3057w (Ar CH), 1651s (C═O), 1612m, 1593m, 1582m, 1530m, 1460w, 1310m, 1256m, 1157w, 1136w, 1024w, 939w, 924w, 893w, 849w, 802w, 746s; δ_H (500 MHz, $CDCl_3$) 8.15 (1H, s), 7.85 (2H, d, J = 7.5 Hz), 7.56 (1H, dd, J = 7.5, 7.5 Hz), 7.46 (2H, dd, J = 7.5, 7.5 Hz), 7.23 (2H, dd, J = 7.0, 7.0 Hz), 7.14 (2H, dd, J = 7.5, 7.5 Hz), 6.88 (1H, dd, J = 7.0, 7.0 Hz), 6.81 (1H, dd, J = 8.5, 1.0 Hz), 6.78 (2H, d, J = 8.0 Hz), 6.73 (1H, ddd, J = 7.5, 7.5, 1.5 Hz), 4.72 (2H, br s); δ_C (125 MHz, $CDCl_3$) 167.4 (s), 147.0 (s), 145.9 (s), 132.4 (d), 132.2 (s), 130.4 (s), 129.2 (d), 129.1 (d), 128.8 (d), 128.0 (d), 127.3 (d), 120.2 (d), 118.4 (d), 116.6 (d), 113.3 (d); identical to an authentic sample.[14b]

4.5.1.2. Method 2: Using In in AcOH. To a vigorously stirred suspension of *N*′-(2-nitrophenyl)-*N*′-phenylbenzohydrazide (**13a**) (0.333 g, 1.0 mmol) in AcOH (5 mL) was added In powder (0.459 g, 4.0 mmol) in one portion, and the mixture was stirred at ca. 20 °C for 0.5 h, filtered, and washed with Et_2O. The organic phase was washed with water (2 × 50 mL) and dried (Na_2SO_4), and the volatiles were removed in vacuo. Chromatography (Et_2O/*n*-hexane, 1:1) of the residue gave the title compound **12a** as colorless needles (0.264 g, 95%). Mp (DSC) onset 176.6 °C, peak max 178.2 °C (from Et_2O); R_f 0.71 (*n*-hexane/Et_2O, 1:1); δ_H (500 MHz, $CDCl_3$) 8.15 (1H, s), 7.85 (2H, d, J = 7.5 Hz), 7.56 (1H, dd, J = 7.5, 7.5 Hz), 7.46 (2H, dd, J = 7.5, 7.5 Hz), 7.23 (2H, dd, J = 7.0, 7.0 Hz), 7.14 (2H, dd, J = 7.5, 7.5 Hz), 6.88 (1H, dd, J = 7.0, 7.0 Hz), 6.81 (1H, dd, J = 8.5, 1.0 Hz), 6.78 (2H, d, J = 8.0 Hz), 6.73 (1H, ddd, J = 7.5, 7.5, 1.5 Hz), 4.72 (2H, br s, NH_2); identical to that described above.

*4.5.2. N′-(2-Aminophenyl)-N′-(pyrid-2-yl)picolinohydrazide (**12b**).* Similar treatment of *N*′-(2-nitrophenyl)-*N*′-(pyrid-2-yl)-picolinohydrazide (**13m**) (0.335 g, 1.0 mmol) in AcOH (5 mL) with Sn powder (0.475 g, 4.0 mmol) gave upon chromatography ($CHCl_3$/MeOH, 10:1) the title compound **12b** (0.300 g, 98%) as colorless flakes. Mp (DSC) onset 138.0 °C, peak max 144.2 °C (from *c*-hexane); R_f 0.28 ($CHCl_3$/MeOH, 10:1); (anal. found: C, 66.82; H, 5.06; N, 22.85. $C_{17}H_{15}N_5O$ requires C, 66.87; H, 4.95; N, 22.94%); λ_{max}(DCM)/nm (log ε) 233 (3.42), 260 inf (3.06), 294 (3.01); ν_{max}/cm^{-1} 3451w and 3341w (NH), 3059w and 3009w (Ar CH), 1695m, 1680m, 1620m, 1589s, 1566m, 1530m, 1503s, 1470s, 1429s, 1342m, 1337m, 1308m, 1285m, 1240m, 1152m, 1040m, 997m, 986m, 903m, 885m, 860m, 818m, 773m, 748s; δ_H (500 MHz, DMSO-d_6) 11.25 (1H, s), 8.71 (1H, d, J = 4.6 Hz), 8.10−8.00 (3H, m), 7.67 (1H, ddd, J = 5.9, 5.9, 1.9 Hz), 7.50 (1H, ddd, J = 8.0, 8.0, 1.7 Hz), 7.39 (1H, dd, J = 7.9, 1.4 Hz), 7.05 (1H, ddd, J = 7.7, 7.7, 1.6 Hz), 6.78−6.70 (2H, m), 6.56 (1H, ddd, J = 8.0, 8.0, 1.3 Hz), 6.36 (1H, d, J = 8.5 Hz), 5.49 (2H, s, NH_2); δ_C (125 MHz, DMSO-d_6) 164.2 (s), 157.1 (s), 149.2 (s), 148.6 (d), 147.4 (d), 146.6 (s), 137.9 (d), 137.3 (d), 130.1 (d), 128.7 (d), 127.8 (s), 127.1 (d), 122.5 (d), 116.0 (d), 115.4 (d), 114.4 (d), 107.1 (d); MALDI-TOF m/z (%): 305 (M^+, 3), 303 ($M^+ - 2$, 100), 198 (49), 183 (95), 105 (9).

*4.5.3. 1,3-Bis(pyrid-2-yl)-1,4-dihydro-1,2,4-benzotriazine (**23b**).* Similar treatment of *N*′-(2-nitrophenyl)-*N*′-(pyrid-2-yl)-picolinohydrazide (**13m**) (0.335 g, 1.0 mmol) with Sn powder (0.475 g, 4.0 mmol) in AcOH (5 mL) at ca. 20 °C for 0.5 h and then at ca. 118 °C for 3 h gave upon chromatography (*t*-BuOMe) the title compound **23b** (0.234 g, 82%) as yellow needles. Mp (DSC) onset 118.5 °C, peak max 119.3 °C (from EtOH); R_f 0.24 (Et_2O); (anal. found: C, 71.15; H, 4.44; N, 24.31. $C_{17}H_{13}N_5$ requires C, 71.06; H, 4.56; N, 24.37%); λ_{max}(DCM)/nm (log ε) 232 (3.36), 273 (3.37), 342 (3.12), 426 (2.42); ν_{max}/cm^{-1} 3352w (NH), 3055w and 3009w (Ar CH), 1585m, 1562w, 1503m, 1476m, 1460m, 1431s, 1416m, 1368m, 1310m, 1294m, 1269w, 1247w, 1192w, 1150m, 1105w, 1057w, 1042w, 995m, 980w, 930w, 891w, 853w, 800m, 762m, 745m; δ_H (300 MHz, DMSO-d_6) 9.17 (1H, s), 8.69 (1H, d, J = 4.7 Hz), 8.27−8.15 (2H, m), 7.97 (1H, ddd, J = 7.7, 7.7, 1.7 Hz), 7.80−7.66 (2H, m), 7.63−7.52 (2H, m), 7.03 (1H, dd, J = 7.4, 1.7 Hz), 6.96−6.75 (3H, m); δ_C (75 MHz, DMSO-d_6) 155.5 (s), 148.5 (s), 148.3 (d), 147.7 (s), 146.6 (d), 138.0 (d), 137.3 (d), 133.9 (s), 128.6 (s), 125.5 (d), 124.2 (d), 122.6 (d), 120.9 (d), 117.3 (d), 116.0 (d), 114.6 (d), 109.9 (d); MS (EI) m/z (%): 287 (M^+, 83), 209 (100), 181 (9), 154 (5), 143 (4), 127 (4), 105 (14), 78 (34), 51 (13).

*4.5.4. 1,3-Bis(pyrid-2-yl)-7-(trifluoromethyl)-1,4-dihydro-1,2,4-benzotriazine (**23c**).* Similar treatment of *N*′-[2-nitro-5-(trifluoromethyl)phenyl]-*N*′-(pyrid-2-yl)picolinohydrazide (**13n**) (403 mg, 1.0 mmol) with Sn powder (475 mg, 4.0 mmol) in AcOH (5 mL) at ca. 20 °C for 0.5 h and then at ca. 118 °C for 3 h gave upon chromatography (*t*-BuOMe) the title compound **23c** as yellow needles (313 mg, 88%). Mp (DSC) onset 132.6 °C, peak max 133.6 °C (from *n*-hexane); R_f 0.20 (DCM); (anal. found: C, 60.81; H, 3.51; N, 19.68. $C_{18}H_{12}F_3N_5$ requires C, 60.85; H, 3.40; N, 19.71%); λ_{max}(DCM)/nm (log ε) 233 (3.32), 266 (3.40), 326 (3.15), 429 (2.26); ν_{max}/cm^{-1} 3358w (NH), 3076w, 3059w and 3013w (Ar CH), 1661w, 1585m, 1568m, 1528w, 1518w, 1481w, 1470m, 1462m, 1433s, 1414s, 1368m, 1327s, 1315s, 1306m, 1300m, 1287m, 1267w, 1161s, 1152s, 1136w, 1111s, 1076m, 1055m, 1045w, 1038m, 999w, 986w, 966w, 930w, 910m, 872m, 856w, 820m, 814m, 791m, 777s, 750w, 743w, 735m, 727w; δ_H (500 MHz, DMSO-d_6) 9.60 (1H, s), 8.71 (1H, d, J = 4.6 Hz), 8.26 (1H, dd, J = 4.7, 1.1 Hz), 8.22 (1H, d, J = 7.9 Hz), 8.09 (1H, s), 7.99 (1H, ddd, J = 8.4, 8.4, 1.5 Hz), 7.80 (1H, ddd, J = 7.8, 7.8, 1.9 Hz), 7.65−7.58 (2H, m), 7.20 (1H, d, J = 8.4 Hz), 7.14 (1H, d, J = 8.2 Hz), 7.00 (1H, dd, J = 6.8, 5.2 Hz); δ_C (125 MHz, DMSO-d_6) 155.2 (s), 148.3 (d), 147.8 (s), 147.2 (s), 146.5 (d), 138.2 (d), 137.7 (s), 137.3 (d), 129.3 (s), 125.7 (d), 124.3 (q, $^1J_{FC}$ = 271.6 Hz), 122.8 (q, $^2J_{FC}$ = 31.8 Hz), 121.5 (q, $^3J_{FC}$ = 3.6 Hz), 120.9 (d), 116.9 (d), 114.4 (d), 113.2 (q, $^3J_{FC}$ = 3.6 Hz), 110.3 (d); MALDI-TOF m/z (%): 356 (MH^+, 18), 355 (M^+, 10), 354 (51), 343 (17), 342 (100).

*4.5.5. 1,3-Bis(pyrid-2-yl)-1,4-dihydro-1,2,4-pyridotriazine (**23d**).* Similar treatment of *N*′-(3-nitropyridin-2-yl)-*N*′-(pyridin-2-yl)-picolinohydrazide (**13p**) (0.336 g, 1.0 mmol) with Sn powder (0.475 g, 4.0 mmol) in AcOH (5 mL) at ca. 20 °C for 2 h and then at ca. 118 °C for 3 h gave upon chromatography (EtOAc/THF, 9:1) the title compound **23d** as orange needles (0.262 g, 91%). Mp (DSC) onset 152.2 °C, peak max 154.9 °C (from PhH); R_f 0.20 (EtOAc); (anal. found: C, 66.57; H, 4.37; N, 29.02. $C_{16}H_{12}N_6$ requires C, 66.66; H, 4.20; N, 29.15%); λ_{max}(DCM)/nm (log ε) 239 (4.14), 267 (4.09), 312 (3.95); ν_{max}/cm^{-1} 3343w (NH), 3053w and 3012w (Ar CH), 1585m, 1566m, 1547w, 1487w, 1464s, 1418s, 1360w, 1304m, 1288m, 1225m, 1192w, 1150w, 1096w, 1069w, 1049w, 997m, 893w, 853w, 783s, 760m, 743m; δ_H (500 MHz, $CDCl_3$) 8.53 (1H, d, J = 5.0 Hz), 8.49 (1H, dd, J = 3.5, 1.5 Hz), 8.19 (1H, d, J = 8.0 Hz), 7.76−7.69 (3H, m), 7.65 (1H, dd, J = 5.0, 1.5 Hz), 7.62 (1H, d, J = 8.5 Hz), 7.34 (1H, dd, J = 5.0, 1.5 Hz), 7.03 (1H, dd, J = 5.0, 1.5 Hz), 6.68−6.63 (2H, m); δ_C (125 MHz, $CDCl_3$) 154.1 (s), 147.8 (d), 147.8 (d), 147.2 (s), 145.2 (s), 145.2 (s), 141.4 (d), 137.4 (d), 136.6 (d), 128.3 (s), 124.9 (d), 121.0 (d), 119.3 (d), 119.2 (d), 118.8 (d), 116.3 (d); MALDI-TOF m/z (%): 290 (MH^+, 13), 289 (M^+, 100), 247 (6), 210 (22), 185 (100), 170 (30), 155 (4).

4.6. Preparation of Benzo- and Pyrido-Fused Triazinyl Radicals 1a−n. *4.6.1. 1,3-Diphenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (**1a**) (Typical Procedure).* To a vigorously stirred mixture of *N*′-(2-nitrophenyl)-*N*′-phenylbenzohydrazide (**13a**) (0.333 g, 1.0 mmol) in AcOH (5 mL) at ca. 20 °C was added in one portion Sn powder (0.475 g, 4.0 mmol), and after 0.5 h the mixture was heated at ca. 118 °C for 10 min. The mixture was then allowed to cool to ca. 20 °C, diluted with DCM (50 mL), and washed with 2 M NaOH (2 × 50 mL), and the organic phase was separated. To the organic phase was added 2 M NaOH (50 mL), and the biphasic mixture was stirred at ca. 20 °C for 12 h. The organic phase was separated, washed with water, filtered (Celite), and rinsed with additional DCM, and the volatiles were removed in vacuo. Chromatography of the residue (basic alumina, DCM) gave the title compound **1a** as black needles (0.274 g, 96%). Mp 109−111 °C (from EtOH) (lit.[3a] 109−110 °C); R_f 0.56 (Al_2O_3, DCM/*n*-hexane, 1:1); λ_{max}(DCM)/nm (log ε) 271 (3.63), 322 (2.93), 372 (2.82), 429 (2.56), 494 (2.17); ν_{max}/cm^{-1} 3061w and 3003w (Ar CH), 1585w, 1481w, 1450m, 1395s, 1317w, 1252w, 1206w, 1175w, 1082w, 1065w, 1024w, 984w, 916w, 880w, 841w, 785m, 750s; identical to an authentic sample.

*4.6.2. 1,3-Diphenyl-7-(trifluoromethyl)-1,4-dihydro-1,2,4-benzotriazin-4-yl (**1b**).* Similar treatment of *N*′-[2-nitro-5-(trifluoromethyl)-phenyl]-*N*′-phenylbenzohydrazide (**13b**) (0.401 g, 1.0 mmol) with Sn powder (0.475 g, 4.0 mmol) in AcOH (5 mL) at ca. 20 °C for 0.5 h

dx.doi.org/10.1021/jo402481t | J. Org. Chem. 2014, 79, 314−327

and at ca. 118 °C for 10 min followed by stirring with 2 M NaOH (50 mL) for 12 h gave upon chromatography (basic alumina, DCM) the title compound **1b** as black needles (0.286 g, 81%). Mp 149−152 °C (from *c*-hexane) (lit.[3a] 149−153 °C); R_f 0.56 (Al_2O_3, DCM/*n*-hexane, 1:1); λ_{max}(DCM)/nm (log ε) 259 inf (4.04), 273 (4.21), 284 inf (4.03), 323 (3.55), 373 (3.40), 431 (3.17), 495 (284); ν_{max}/cm^{-1} 1593w, 1506w, 1489m, 1452w, 1422m, 1395m, 1356m, 1337w, 1314m, 1281w, 1261m, 1248w, 1204w, 1150m, 1117s, 1063m, 1024w, 905m, 870m, 841m, 793w, 781m, 768m; identical to an authentic sample.

*4.6.3. 3-(4-Fluorophenyl)-1-phenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (**1c**).* Similar treatment of 4-fluoro-*N*′-(2-nitrophenyl)-*N*′-phenylbenzohydrazide (**13c**) (0.351 g, 1.0 mmol) with Sn powder (0.475 g, 4.0 mmol) in AcOH (5 mL) at ca. 20 °C for 0.5 h and at ca. 118 °C for 10 min followed by stirring with 2 M NaOH (50 mL) for 12 h gave upon chromatography (basic alumina, DCM) the title compound **1c** as black needles (0.266 g, 88%). Mp (DSC) onset 112.5 °C, peak max 113.1 °C (from *c*-hexane); R_f 0.69 (Al_2O_3, DCM); (anal. found: C, 75.31; H, 4.28; N, 13.91. $C_{19}H_{13}FN_3$ requires C, 75.48; H, 4.33; N, 13.90%); λ_{max}(DCM)/nm (log ε) 271 (3.67), 282 inf (3.47), 323 (2.99), 372 (2.87), 426 (2.62), 494 (2.24); ν_{max}/cm^{-1} 3055w (Ar CH), 1601w, 1582w, 1508w, 1481m, 1450w, 1416w, 1393s, 1325w, 1292w, 1246w, 1215m, 1155m, 1096w, 1082w, 1065w, 1042w, 1024w, 1016w, 1001w, 984w, 924w, 918w, 881w, 841m, 810w, 775m, 762s, 746m, 729s; MALDI-TOF *m*/*z* (%): 303 (MH$^+$, 11), 302 (M$^+$, 100), 290 (2).

*4.6.4. 1-Phenyl-3-(thien-2-yl)-1,4-dihydro-1,2,4-benzotriazin-4-yl (**1d**).* Similar treatment of *N*′-(2-nitrophenyl)-*N*′-phenyl-2-thiophenecarbohydrazide (**13d**) (0.339 g, 1.0 mmol) with Sn powder (0.475 g, 4.0 mmol) in AcOH (5 mL) at ca. 20 °C for 0.5 h and at ca. 118 °C for 10 min followed by stirring with 2 M NaOH (50 mL) for 12 h gave upon chromatography (basic alumina, DCM) the title compound **1d** as dark-green needles (0.253 g, 87%). Mp (DSC) onset 133.7 °C, peak max 134.6 °C (from EtOH); R_f 0.63 (Al_2O_3, DCM); (anal. found: C, 70.52; H, 4.24; N, 14.29. $C_{17}H_{12}N_3S$ requires C, 70.32; H, 4.17; N, 14.47%); λ_{max}(DCM)/nm (log ε) 231 (3.35), 259 inf (3.38), 290 (3.74), 303 inf (3.57), 380 (2.85), 409 inf (2.77), 507 (2.34); ν_{max}/cm^{-1} 3103w, 3071w, 3063w, 3055w (Ar CH), 1533m, 1493m, 1479s, 1452s, 1435s, 1389s, 1360w, 1350w, 1327w, 1287m, 1252w, 1219m, 1206m, 1148w, 1121w, 1076m, 1055w, 1036w, 1024w, 1003w, 972w, 934w, 916w, 847m, 839m, 831m, 814w, 770m, 752s, 743s; MALDI-TOF *m*/*z* (%): 291 (MH$^+$, 18), 290 (M$^+$, 100), 272 (6).

*4.6.5. 1-Phenyl-3-(pyrid-2-yl)-1,4-dihydro-1,2,4-benzotriazin-4-yl (**1e**).* Similar treatment of *N*′-(2-nitrophenyl)-*N*′-phenyl-2-pyridinecarbohydrazide (**13e**) (0.334 g, 1.0 mmol) with Sn powder (0.475 g, 4.0 mmol) in AcOH (5 mL) at ca. 20 °C for 0.5 h and at ca. 118 °C for 10 min followed by stirring with 2 M NaOH (50 mL) for 3 days gave upon chromatography (basic alumina, DCM/*t*-BuOMe) the title compound **1e** as black needles (0.235 g, 82%). Mp (DSC) onset 179.7 °C, peak max 181.7 °C (from PhH); R_f 0.40 (Al_2O_3, DCM); (anal. found: C, 75.89; H, 4.44; N, 19.58. $C_{18}H_{13}N_4$ requires C, 75.77; H, 4.59; N, 19.64%); λ_{max}(DCM)/nm (log ε) 257 inf (3.31), 276 (3.39), 320 (2.79), 363 (2.74), 424 (2.43), 493 (2.08); ν_{max}/cm^{-1} 3065w, 3044w and 3036w (Ar CH), 1587m, 1580m, 1570m, 1562m, 1495m, 1481m, 1474m, 1454m, 1435m, 1385s, 1331m, 1308m, 1260m, 1211m, 1163m, 1099m, 1082m, 1072m, 1047m, 1026m, 995m, 937m, 891m, 881m, 845m, 837m, 797m, 789s, 758s, 739s; MALDI-TOF *m*/*z* (%): 286 (MH$^+$, 35), 285 (M$^+$, 100), 267 (1), 185 (1).

*4.6.6. 3-Methyl-1-phenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (**1f**).* Similar treatment of *N*′-(2-nitrophenyl)-*N*′-phenylacetohydrazide (**13f**) (0.271 g, 1.0 mmol) with Sn powder (0.475 g, 4.0 mmol) in AcOH (5 mL) at ca. 20 °C for 0.5 h and at ca. 118 °C for 10 min followed by stirring with 2 M NaOH (50 mL) for 12 h gave upon chromatography (basic alumina, DCM) the title compound **1f** as a deep-red oil (0.140 g, 63%); R_f 0.56 (Al_2O_3, DCM); (anal. found: C, 75.56; H, 5.32; N, 18.92. $C_{14}H_{12}N_3$ requires C, 75.65; H, 5.44; N, 18.91%); λ_{max}(DCM)/nm (log ε) 241 (3.22), 259 inf (2.93), 286 (2.61), 318 (2.73), 348 (2.69), 424 (2.23), 548 inf (1.81); ν_{max}/cm^{-1} 3061w (Ar CH), 2924w (CH_3), 1659w, 1585m, 1489s, 1452m, 1406m, 1327m, 1294m, 1271m, 1202w, 1171w, 1157w, 1124w, 1074w, 1026w, 999w, 935w, 912w, 853w, 746s; MALDI-TOF *m*/*z* (%): 223 (MH$^+$, 69), 222 (M$^+$, 100), 210 (4), 181 (5).

*4.6.7. 3-Methyl-1-phenyl-7-(trifluoromethyl)-1,4-dihydro-1,2,4-benzotriazin-4-yl (**1g**).* Similar treatment of *N*′-[2-nitro-5-(trifluoromethyl)phenyl]-*N*′-phenylacetohydrazide (**13g**) (0.339 g, 1.0 mmol) with Sn powder (0.475 g, 4.0 mmol) in AcOH (5 mL) at ca. 20 °C for 0.5 h and at ca. 118 °C for 10 min followed by stirring with 2 M NaOH (50 mL) for 12 h gave upon chromatography (basic alumina, DCM) the title compound **1g** as dark-red needles (0.186 g, 64%). Mp (DSC) onset 120.9 °C, peak max 121.6 °C (from *n*-hexane); R_f 0.57 (Al_2O_3, DCM); (anal. found: C, 62.18; H, 3.76; N, 14.59. $C_{15}H_{11}F_3N_3$ requires C, 62.07; H, 3.82; N, 14.48%); λ_{max}(DCM)/nm (log ε) 241 (3.40), 259 inf (3.04), 285 (2.71), 318 (2.81), 346 (2.76), 428 (2.33), 528 inf (1.86); ν_{max}/cm^{-1} 3103w (Ar CH), 2982w and 2928w (CH_3), 1678w, 1591m, 1504m, 1491m, 1418s, 1371m, 1356m, 1337m, 1315s, 1265s, 1256m, 1198m, 1163s, 1157s, 1128s, 1103s, 1072s, 1028w, 1001m, 926w, 918m, 870m, 816s, 779w, 762m, 733w; MALDI-TOF *m*/*z* (%): 291 (MH$^+$, 40), 290 (M$^+$, 100), 277 (4), 132 (9).

*4.6.8. 1-Phenyl-3-(trifluoromethyl)-1,4-dihydro-1,2,4-benzotriazin-4-yl (**1h**).* Similar treatment of 2,2,2-trifluoro-*N*′-(2-nitrophenyl)-*N*′-phenylacetohydrazide (**13h**) (0.325 g, 1.0 mmol) with Sn powder (0.475 g, 4.0 mmol) in AcOH (5 mL) at ca. 20 °C for 0.5 h and then at ca. 118 °C for 10 min followed by stirring with 2 M NaOH (50 mL) for 12 h gave upon chromatography (basic alumina, DCM) the title compound **1h** (0.273 g, 99%) as dark-red needles. Mp (DSC) onset 109.7 °C, peak max 110.8 °C (from *n*-pentane); R_f 0.46 (*t*-BuOMe/*n*-hexane, 1:1); (anal. found: C, 61.03; H, 3.35; N, 15.08. $C_{14}H_9F_3N_3$ requires C, 60.87; H, 3.28; N, 15.21%); λ_{max}(DCM)/nm (log ε) 245 (3.50), 296 inf (2.65), 314 (2.98), 345 (2.92), 414 (2.38), 481 (2.19), 543 inf (1.84); ν_{max}/cm^{-1} 3075w (Ar CH), 1587w, 1570w, 1489w, 1462w, 1452w, 1422w, 1371w, 1333w, 1323w, 1300w, 1287w, 1260m, 1194s, 1175s, 1159m, 1132s, 1094s, 1070w, 1032w, 993m, 945w, 926w, 887w, 858w, 839w, 775s, 760s, 752s; MALDI-TOF *m*/*z* (%): 277 (MH$^+$, 14), 276 (M$^+$, 91), 264 (32), 222 (100), 181 (5).

*4.6.9. 1-Phenyl-3,7-bis(trifluoromethyl)-1,4-dihydro-1,2,4-benzotriazin-4-yl (**1i**).* Similar treatment of 2,2,2-trifluoro-*N*′-[2-nitro-5-(trifluoromethyl)phenyl]-*N*′-phenylacetohydrazide (**13i**) (0.393 g, 1.0 mmol) with Sn powder (0.475 g, 4.0 mmol) in AcOH (5 mL) at ca. 20 °C for 0.5 h and at ca. 118 °C for 10 min followed by stirring with 2 M NaOH (50 mL) for 12 h gave upon chromatography (basic alumina, DCM) the title compound **1i** as dark-red needles (0.286 g, 83%). Mp (DSC) onset 126.0 °C, peak max 127.5 °C (from *n*-hexane); R_f 0.61 (Al_2O_3, DCM/*n*-hexane, 1:1); (anal. found: C, 52.46; H, 2.32; N, 12.15. $C_{15}H_8F_6N_3$ requires C, 52.34; H, 2.34; N, 12.21%); λ_{max}(DCM)/nm (log ε) 244 (3.44), 261 inf (3.07), 318 (2.87), 340 (2.76), 414 (2.38), 478 (2.21); ν_{max}/cm^{-1} 3067w (Ar CH), 1591w, 1493w, 1456w, 1441w, 1416w, 1379w, 1341m, 1317m, 1275s, 1198s, 1175m, 1165m, 1150s, 1128s, 1096m, 1065s, 1026w, 999w, 910s, 870w, 862m, 835m, 802w, 768m, 737m; MALDI-TOF *m*/*z* (%): 345 (MH$^+$, 10), 344 (M$^+$, 86), 316 (4), 290 (100).

*4.6.10. 3-(Adamant-1-yl)-1-phenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (**1j**).* Similar treatment of *N*′-(2-nitrophenyl)-*N*′-phenyl-1-adamantanecarbohydrazide (**13q**) (0.391 g, 1.0 mmol) with Sn powder (0.475 g, 4.0 mmol) in AcOH (5 mL) at ca. 20 °C for 0.5 h and at ca. 118 °C for 10 min followed by stirring with 2 M NaOH (50 mL) for 12 h gave upon chromatography (basic alumina, DCM/*t*-BuOMe) the title compound **1j** as dark-red needles (0.271 g, 79%). Mp (DSC) onset 171.0 °C, peak max 172.1 °C (from MeOH); R_f 0.71 (Al_2O_3, DCM); (anal. found: C, 80.58; H, 7.17; N, 12.18. $C_{23}H_{24}N_3$ requires C, 80.67; H, 7.06; N, 12.27%); λ_{max}(DCM)/nm (log ε) 242 (3.40), 320 (2.87), 348 (2.84), 429 (2.48), 538 inf (1.74); ν_{max}/cm^{-1} 3092w, 3075w and 3038w (Ar CH), 1597w, 1591w, 1533s, 1487m, 1456w, 1368m, 1344w, 1333w, 1315w, 1298m, 1287m, 1256w, 1188w, 1175w, 1157w, 1113s, 1084w, 1076m, 1030w, 962w, 945w, 910w, 901w, 876w, 853m, 829w, 781m, 762w, 750m, 727w; MALDI-TOF *m*/*z* (%): 343 (MH$^+$, 20), 342 (M$^+$, 100).

*4.6.11. 1-(4-Cyanophenyl)-3-phenyl-1,4-dihydro-1,2,4-benzotriazin-4-yl (**1k**).* Similar treatment of *N*′-(4-cyanophenyl)-*N*′-(2-nitrophenyl)benzohydrazide (**13j**) (0.358 g, 1.0 mmol) with Sn

dx.doi.org/10.1021/jo402481t | J. Org. Chem. 2014, 79, 314−327

powder (0.475 g, 4.0 mmol) in AcOH (5 mL) at ca. 20 °C for 0.5 h and at ca. 118 °C for 10 min followed by stirring with 2 M NaOH (50 mL) for 3 days gave upon chromatography (basic alumina, DCM) the title compound **1k** as dark-green needles (0.263 g, 85%). Mp (DSC) onset 137.5 °C, peak max 140.0 °C (from *n*-hexane); R_f 0.64 (Al_2O_3, DCM/*n*-hexane, 1:1); (anal. found: C, 77.52; H, 4.26; N, 17.95. $C_{20}H_{13}N_4$ requires C, 77.65; H, 4.24; N, 18.11%); λ_{max}(DCM)/nm (log ε) 233 (3.33), 270 (3.59), 345 (3.05), 370 (2.91), 461 (2.8), 503 inf (2.38); ν_{max}/cm^{-1} 3061w and 3028w (Ar CH), 2222m (C≡N), 1597m, 1501m, 1483s, 1450m, 1414w, 1398s, 1327w, 1315m, 1296w, 1288w, 1252w, 1206w, 1175m, 1152w, 1126w, 1065w, 1024w, 984w, 928w, 880w, 845m, 837m, 781w, 758s, 741m; MALDI-TOF *m*/*z* (%): 310 (MH^+, 15), 309 (M^+, 100), 297 (2).

*4.6.12. 1-(4-Cyanophenyl)-3-(thien-2-yl)-1,4-dihydro-1,2,4-benzotriazin-4-yl (**1l**).* Similar treatment of *N*′-(4-cyanophenyl)-*N*′-(2-nitrophenyl)-2-thiophenecarbohydrazide (**13k**) (0.364 g, 1.0 mmol) with Sn powder (0.475 g, 4.0 mmol) in AcOH (5 mL) at ca. 20 °C for 0.5 h and at ca. 118 °C for 10 min followed by stirring with 2 M NaOH (50 mL) for 3 days gave upon chromatography (basic alumina, DCM) the title compound **1l** as dark-green needles (0.223 g, 71%). Mp (DSC) onset 166.8 °C, peak max 168.8 °C (from EtOH); R_f 0.67 (Al_2O_3, DCM/*n*-hexane, 1:1); (anal. found: C, 68.42; H, 3.56; N, 17.68. $C_{18}H_{11}N_4S$ requires C, 68.55; H, 3.52; N, 17.77%); λ_{max}(DCM)/nm (log ε) 231 (3.28), 292 (3.52), 346 (3.00), 378 inf (2.80), 396 inf (2.71), 469 (2.74), 499 inf (2.49), 602 (1.84); ν_{max}/cm^{-1} 3088w and 3063w (Ar CH), 2226m (C≡N), 1599m, 1585w, 1533m, 1501m, 1481s, 1456w, 1433s, 1391s, 1331m, 1288m, 1254w, 1217w, 1207w, 1180w, 1152m, 1115w, 1094w, 1055w, 1038w, 1018w, 970w, 932w, 851m, 841s, 829m, 750m, 743s, 729s; MALDI-TOF *m*/*z* (%): 316 (MH^+, 15), 315 (M^+, 100), 303 (8), 123 (9).

*4.6.13. 3-Phenyl-1-(pyrid-2-yl)-1,4-dihydro-1,2,4-benzotriazin-4-yl (**1m**).* Similar treatment of *N*′-(2-nitrophenyl)-*N*′-(pyrid-2-yl)-benzohydrazide (**13l**) (0.334 g, 1.0 mmol) with Sn powder (0.475 g, 4.0 mmol) in AcOH (5 mL) at ca. 20 °C for 0.5 h and at ca. 118 °C for 10 min followed by stirring with 2 M NaOH (50 mL) for 12 h gave upon chromatography (basic alumina, DCM) the title compound **1m** as dark-green needles (0.220 g, 77%). Mp (DSC) onset 146.7 °C, peak max 147.4 °C (from *n*-hexane/*n*-heptane, 1:1); R_f 0.71 (Al_2O_3, DCM/*n*-hexane, 1:1); (anal. found: C, 75.62; H, 4.60; N, 19.48. $C_{18}H_{13}N_4$ requires C, 75.77; H, 4.59; N, 19.64%); λ_{max}(DCM)/nm (log ε) 232 inf (4.22), 273 (4.68), 315 (4.10), 380 (3.94), 429 (3.79); ν_{max}/cm^{-1} 3065w, 1584m, 1568w, 1485m, 1466m, 1449m, 1433s, 1398s, 1333w, 1314m, 1275w, 1256w, 1200w, 1175w, 1161w, 1150m, 1121w, 1028w, 989w, 922w, 863w, 849w, 785s, 772m, 760m, 752s, 745s, 737m, 731m; MALDI-TOF *m*/*z* (%): 286 (MH^+, 22), 285 (M^+, 100).

*4.6.14. 1,3-Diphenyl-1,4-dihydro-1,2,4-pyridotriazin-4-yl (**1n**).* Similar treatment of *N*′-(3-nitropyrid-2-yl)-*N*′-phenylbenzohydrazide (**13o**) (0.334 g, 1.0 mmol) with Sn powder (0.475 g, 4.0 mmol) in AcOH (5 mL) at ca. 20 °C for 0.5 h and at ca. 118 °C for 1 h followed by stirring with 2 M NaOH (50 mL) for 3 h gave upon chromatography (basic alumina, DCM) the title compound **1n** as dark-maroon needles (0.220 g, 77%). Mp (DSC) onset 147.8 °C, peak max 141.4 °C (from *n*-hexane/*n*-heptane, 1:1); R_f 0.66 (Al_2O_3, DCM/*n*-hexane, 1:1); (anal. found: C, 75.78; H, 4.63; N, 19.49. $C_{18}H_{13}N_4$ requires C, 75.77; H, 4.59; N, 19.64%); λ_{max}(DCM)/nm (log ε) 265 (4.49), 303 inf (4.17), 329 inf (4.01), 367 (3.87), 432 (3.83); ν_{max}/cm^{-1} 3061w (Ar CH), 1643m, 1624w, 1591w, 1541w, 1489m, 1468m, 1445m, 1423s, 1383m, 1319m, 1306m, 1283m, 1263m, 1242m, 1179w, 1109w, 1026w, 980w, 926w, 887w, 849w, 800m, 766m, 741m; MALDI-TOF *m*/*z* (%): 286 (MH^+, 20), 285 (M^+, 100).

4.7. MnO_2 Oxidation of 1,3-Bis(pyrid-2-yl)benzotriazines 23b and 23c. *4.7.1. 1,3-Bis(pyrid-2-yl)-1,2,4-benzotriazin-7(1H)-one (**24**).* To a stirred solution of 1,3-bis(pyrid-2-yl)-1,4-dihydro-1,2,4-benzotriazine (**23b**) (287 mg, 1.0 mmol) in DCM (10 mL) at ca. 20 °C was added MnO_2 (869 mg, 10.0 mmol). After 2 days the reaction mixture was filtered through Celite and rinsed with additional DCM, and the volatiles were removed in vacuo. The residue was chromatographed on a short pad of silica (acetone) to give the title compound **24** (159 mg, 53%) as blue flakes. Mp (DSC) decomp. onset 175.9 °C, peak max 197.7 °C (from acetone); R_f 0.65 ($CHCl_3$/MeOH, 5:1); (anal. found: C, 67.70; H, 3.71; N, 23.12. $C_{17}H_{11}N_5O$ requires C, 67.77; H, 3.68; N, 23.24%); λ_{max}(DCM)/nm (log ε) 243 (3.22), 298 (3.54), 308 inf (3.45), 342 (3.04), 355 inf (3.03), 489 inf (2.56), 536 (2.72), 575 (2.66), 623 inf (2.33); ν_{max}/cm^{-1} 3071w (Ar CH), 1626m, 1614m, 1601m, 1585s, 1570m, 1545s, 1470m, 1427m, 1396w, 1339w, 1292w, 1234m, 1198w, 1153w, 1117w, 1101w, 1090w, 1078w, 1049w, 997w, 974w, 908w, 851s, 822w, 793m, 764w, 741w; δ_H (500 MHz, $CDCl_3$) 8.83 (1H, d, *J* = 4.4 Hz), 8.65 (1H, d, *J* = 3.8 Hz), 8.30 (1H, d, *J* = 8.0 Hz), 8.03 (1H, ddd, *J* = 7.9, 7.9, 1.5 Hz), 7.86 (1H, ddd, *J* = 7.9, 7.9, 1.3 Hz), 7.84−7.79 (2H, m), 7.49 (1H, dd, *J* = 7.3, 5.0 Hz), 7.41 (1H, dd, *J* = 7.1, 5.0 Hz), 7.29 (1H, d, *J* = 1.9 Hz), 6.68 (1H, d, *J* = 1.9 Hz); δ_C (125 MHz, $CDCl_3$) 183.2 (s), 156.8 (s), 154.1 (s), 151.5 (s), 150.2 (d), 149.2 (s), 148.8 (d), 141.7 (d), 139.7 (d), 137.1 (d), 134.5 (s), 133.0 (d), 124.8 (d), 124.7 (d), 122.4 (d), 120.4 (d), 100.2 (d); MALDI-TOF *m*/*z* (%): 304 (MH^+ + 2, 9), 303 (MH^+ + 1, 33), 302 (MH^+, 100), 301 (M^+, 40), 299 (31), 288 (6), 274 (47).

*4.7.2. 1,3-Bis(pyrid-2-yl)-7-(trifluoromethyl)-1,4-dihydro-1,2,4-benzotriazin-4-yl (**1o**).* Similar treatment of 1,3-bis(pyrid-2-yl)-7-(trifluoromethyl)-1,4-dihydro-1,2,4-benzotriazine (**23c**) (355 mg, 1.0 mmol) in DCM (10 mL) with MnO_2 (869 mg, 10.0 mmol) at ca. 20 °C for 2 days gave upon chromatography (basic alumina, DCM/*t*-BuOMe, 1:1) the title compound **1o** (173 mg, 49%) as black needles. Mp (DSC) onset 218.1 °C, peak max 222.9 °C (from MeCN); R_f 0.49 (Al_2O_3, DCM); (anal. found: C, 60.93; H, 3.07; N, 19.89. $C_{18}H_{11}F_3N_5$ requires C, 61.02; H, 3.13; N, 19.77%); λ_{max}(DCM)/nm (log ε) 236 (3.16), 267 (3.29), 282 inf (3.26), 328 inf (2.96), 436 (2.41), 510 (1.95); ν_{max}/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* (%): 355 (MH^+, 10), 354 (M^+, 86), 342 (100), 339 (63), 182 (6), 78 (4).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and simulated EPR data for all new radicals **1c−o**, cyclic voltammograms for radicals **1c−o**, and ^{1}H and ^{13}C NMR spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the University of Cyprus (medium-size grants) and the Cyprus Research Promotion Foundation (Grants ΥΓΕΙΑ/ΒΙΟΣ/0308(ΒΙΕ)/13, ΝΕΚΥΠ/0308/02, and ΑΝΑΒΑΘΜΙΣΗ/0308/32) for support and the following organizations in Cyprus for generous donations of chemicals and glassware: the State General Laboratory, the Agricultural Research Institute, and the Ministry of Agriculture and Biotronics Ltd. Furthermore, we thank the A. G. Leventis Foundation for helping to establish the NMR facility at the University of Cyprus.

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