JOC The Journal of Organic Chemistry

Article

Preparation of Blatter Radicals via Aza-Wittig Chemistry: The Reaction of N Aryliminophosphoranes with 1-(Het)aroyl-2-aryldiazenes

Anastasia C. Savva, Styliana I. Mirallai, Georgia A. Zissimou, Andrey A. Berezin, Marina Demetriades, Andreas Kourtellaris, Christos P. Constantinides, Constantinos Nicolaides, Theodossis Trypiniotis, and Panayiotis A. Koutentis

J. Org. Chem., **Just Accepted Manuscript** • Publication Date (Web): 19 Jun 2017

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

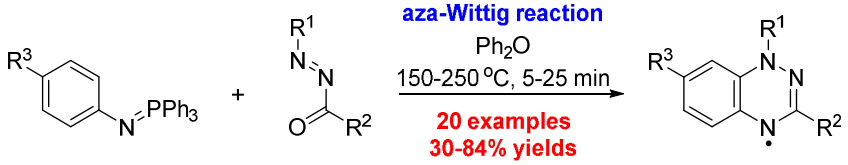
Preparation of Blatter Radicals *via* Aza-Wittig Chemistry: The Reaction of *N*-Aryliminophosphoranes with 1-(Het)aroyl-2-aryldiazenes

Anastasia C. Savva,[1] Styliana I. Mirallai,[1] Georgia A. Zissimou,[1] Andrey A. Berezin,[1] Marina Demetriades,[1] Andreas Kourtellaris,[1] Christos P. Constantinides,[1] Constantinos Nicolaides,[2] Theodossis Trypiniotis,[2] Panayiotis A. Koutentis*,[1]

[1] Department of Chemistry, University of Cyprus, P. O. Box 20537, 1678 Nicosia, Cyprus

[2] Department of Physics, University of Cyprus, P. O. Box 20537, 1678 Nicosia, Cyprus

e-mail: koutenti@ucy.ac.cy



Abstract. Reacting *N*-aryliminophosphoranes with 1-(het)aroyl-2-aryldiazenes in preheated diphenyl ether at *ca.* 150-250 °C for 5-25 min, affords in most cases the 1,3-diaryl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yls (aka Blatter radicals) in moderate to good yields. All new compounds are fully characterized, including for the radicals EPR and CV studies. Single crystal x-ray structures of 1-benzoyl-2-(perfluorophenyl)diazene and 1-(perfluorophenyl)-3-phenyl-1,4-dihydrobenzo[e][1,2,4]triazinyl are also presented.

Keywords: Stable organic radicals; Aza-Wittig reaction; Nitrogen heterocycles; Blatter radicals; Pentafluorophenyl.

1. INTRODUCTION

Blatter radical (**1a**), also known as 1,3-diphenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl, is an air and moisture stable neutral organic radical, first reported in 1968, that shows reversible redox behavior (Figure 1).[1] In the presence of strongly oxidizing agents (*e.g.*, MnO_2 or $KMnO_4$) it gives the useful benzotriazinone **2**,[2] several analogues of which have interesting biological properties,[3] while with strongly reducing agents (*e.g.*, Zn in AcOH) it gives 1,2-diphenylbenzimidazole (**3**).[4] Aside from an extensive EPR studies by Neugebauer,[5] and later by Kadirov,[6] little else was reported until Wudl reignited interest by preparing a pressure sensitive semiconducting charge transfer complex of Blatter radical **1a** with 7,7,8,8-tetracyanoquinodimethane (**TCNQ**)[7] and the unusual zwitterionic tetraphenylhexaazaanthracene (**TPHA**) (Figure 1).[8]

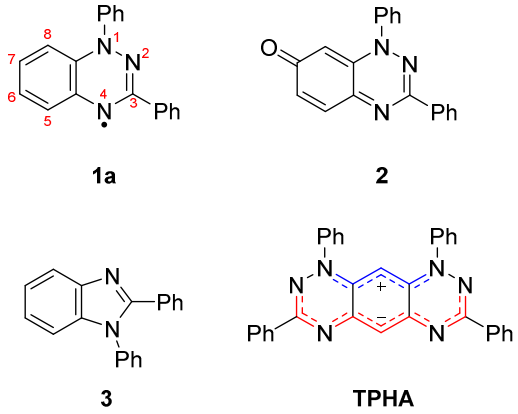


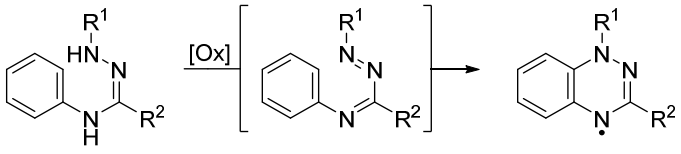
Figure 1. Structures of Blatter radical **1a** with IUPAC numbering (in red), benzotriazinone **2**, 1,2-diphenylbenzimidazole **3** and Wudl's **TPHA**.

Since then, extensive studies have been reported on their interesting magnetic properties[9] and several new applications of Blatter-type radicals have appeared, *e.g.*, as ligands for metal coordination,[10] as polymerization initiators,[11] as pH sensors,[12] as discotic liquid crystals,[13] as components of organic radical batteries,[14] as high-spin diradicals[15] and biradicaloids.[16] Fur-

thermore, stable thin films composed of Blatter-type radicals have been prepared highlighting their potential as new materials in electronic devices.[17]

Future development of Blatter radical chemistry and applications will benefit from improved syntheses. Up until recently, the most commonly used synthesis of Blatter radicals involved the oxidative cyclisation of amidrazones **4** *via* the intermediate 1,2,4-triazabutadienes **5** (Scheme 1),[5] however, yields are highly dependent on the purity of the starting amidrazone **4** which can often be difficult to access and purify.

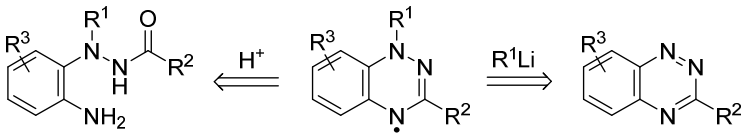
Scheme 1. Neugebauer's Classical Synthesis of Blatter Radicals 1



4 **5** **1**

Syntheses that avoid the need to prepare amidrazones **4** include: the cyclodehydration of *N*′-(2-aminophenyl)-*N*′-arylbenzohydrazides **6**, prepared from *N*-arylbenzohydrazides and either 1-halo-2-nitroarenes *via* nucleophilic aromatic substitution followed by reduction of the nitro group[18] or from 2-haloanilines *via* a Cu-mediated C-N coupling protocol[9b] and the regioselective addition of aryllithium agents to preformed benzo[*e*][1,24]triazines **7**[19] (Scheme 2).

Scheme 2. Routes to Blatter Radicals 1 that Avoid the Need to Prepare Amidrazones 4

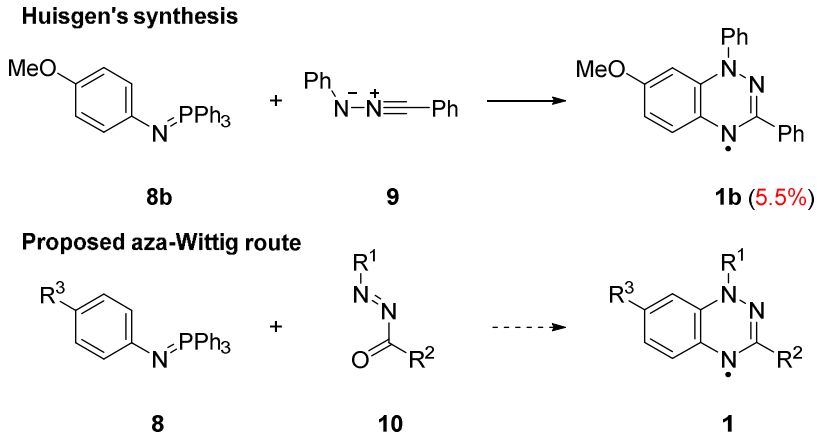


6 **1** **7**

While these syntheses are advantageous as they avoid difficult to purify and oxidatively unstable amidrazones **4**, both require often costly starting 1-halo-2-nitroarenes, particularly when $R^3 \neq H$, and the use of organolithium reagents can be problematic when sensitive functional groups (*e.g.*, halogens) are present. Recently, a fascinating ring transformation of the analytical reagent Nitron to a 3-amido-substituted benzotriazinyl[20] and a route to planar Blatter-type radicals[21] have also been described, but these syntheses have been limited to just a few analogues and the synthetic usefulness of these new routes remains to be tested.

Considering the above, we continue to develop routes to Blatter-type radicals that offer advantages such as ease of access to cheap starting materials, speed, overall yield and applicability. Herein, we report an aza-Wittig-mediated[22] synthesis of Blatter radicals **1** starting from *N*-aryliminophosphoranes **8** and 1-(het)aroyl-2-diazenes **10** that was inspired by Huisgen's 1969 low yielding (5.5%)[23] synthesis of 7-methoxy-1,3-diphenyl-1,4-dihydrobenzo[*e*][1,2,4]-triazin-4-yl (**1b**) starting from *N*-(4-methoxyphenyl)iminophosphorane **8b** and diphenylnitrylimine **9** (Scheme 3).

Scheme 3. The Proposed Aza-Wittig-mediated Synthesis of Blatter Radicals 1 and Huisgen's Synthesis *via* *N*-(4-Methoxyphenyl)iminophosphorane 8b and Diphenylnitrylimine 9

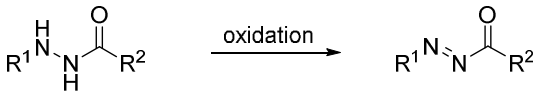


2. RESULTS AND DISCUSSION

Initially, efforts focused on the aza-Wittig coupling of *N′* -phenylbenzohydrazide (**11a**) and *N*-phenyliminophosphorane **8a** but these failed. Amides are heavily deactivated towards aza-Wittig reactions owing to the strong electron release from the amide nitrogen to the carbonyl. To the best of our knowledge, only a few examples of intramolecular aza-Wittig reactions have been reported.[24] Nevertheless, *α,β*-unsaturated ketones or aldehydes can undergo intermolecular aza-Wittig reactions with relative ease to give the *α,β*-unsaturated imines,[25] and based on this we considered oxidizing the *N′* -aryl(het)arenohydrazides **11** to 1-(het)aroyl-2-aryldiazenes **10** in the hope that these would be more reactive.

The proposed aza-Wittig reaction protocol for preparing Blatter-type radicals required access to *N*-aryliminophosphoranes **8** and 1-(het)aroyl-2-aryldiazenes **10**. The former were readily prepared in one-pot either from the Staudinger reaction[26a] *via* the azide, or the Kirsanov reaction,[26b] that involves the *in situ* preparation of triphenyldibromophosphorane, or *via* direct halogenation of *N*-phenyliminophosphorane **8a**.[26c] The latter were prepared *via* the mild oxidation of readily available *N′* -aryl(het)arenohydrazides **11**. Three methods are commonly used for this oxidation and involve the use of HgO,[27a] $NaNO_2/Ac_2O$[27b] or NBS[27c] (Table 1).

Table 1. Oxidation of *N′* -Aryl(het)arenohydrazides 11 to 1-(Het)aroyl-2-diazenes 10.



11 **10**

entry	R^1	R^2	reagents (equiv)	solvent	temp (°C)	time (h)	yields **10** (%)
1	Ph	Ph	HgO (1)	*n*-hexane	20	3	**10a** (93)
2	Ph	Ph	$NaNO_2$ (3)/Ac_2O (3)	acetone	20	5	**10a** (82)
3	Ph	Ph	NBS (1)/pyridine (1.1)	CH_2Cl_2	0-20	0.5	**10a** (84)
4	Ph	4-Tol	HgO (1)	*n*-hexane	20	3	**10b** (99)
5	Ph	4-FC_6H_4	HgO (1)	*n*-hexane	20	3	**10c** (96)
6	Ph	4-$O_2NC_6H_4$	NBS (1)/pyridine (1.1)	CH_2Cl_2	0-20	0.5	**10d** (94)
7	Ph	thien-2-yl	$NaNO_2$ (3)/Ac_2O (3)	acetone	20	5	**10e** (95)
8	C_6F_5	Ph	$NaNO_2$ (3)/Ac_2O (3)	acetone	20	5	**10f** (73)
9	C_6F_5	thien-2-yl	$NaNO_2$ (3)/Ac_2O (3)	acetone	20	5	**10g** (52)

Initially, all three oxidation protocols were screened for the conversion of *N*′-phenyl-benzohydrazide (**11a**) into 1-benzoyl-2-phenyldiazene (**10a**) (Table 1, entries 1-3), and in our hands, the use of powdered yellow HgO (1 equiv) in *n*-hexane at *ca.* 20 °C for 3 h gave the desired diazene **10a** in the highest yield of 93% (Table 1, entry 1). These conditions also worked well for the 4-tolyl and 4-fluorophenyl analogues affording the diazenes **10b** and **10c** in 99 and 96% yields, respectively (Table 1, entries 4 & 5). However, for hydrazide **11d** (R^2 = 4-$O_2NC_6H_4$) the use of either HgO (1 equiv) or $NaNO_2$ (3 equiv)/Ac_2O (3 equiv) failed. Fortunately, oxidation of this hydrazide was achieved using NBS (1 equiv) and pyridine (1.1 equiv) in CH_2Cl_2 at *ca.* 0-20 °C in 0.5-2 h to afford the desired diazene **10d** in 94% yield (Table 1, entry 6). The use of HgO (1 equiv) also failed to oxidize hydrazides bearing either thien-2-yl groups at the carbonyl (*e.g.*, hydrazides **11e** & **11g**) or *N*-pentafluorophenyl groups (*e.g.*, hydrazides **11f** & **11g**) but, in these cases, oxidation with $NaNO_2$ (3 equiv) in Ac_2O (3 equiv) in acetone at 20 °C for 5 h gave the desired 1-hetaroyl-2-aryldiazenes **10e-g** in 95, 73 and 52% yield, respectively (Table 1, entries 7-9). Attempts to oxidize hydrazides bearing methyl, trifluoromethyl or pyrid-2-yl groups at the carbonyl using these three protocols led to complex reaction mixtures from which no diazene could be isolated (data not shown).

Interestingly, a single crystal X-ray structure was obtained for one of the crystalline analogues 1-benzoyl-2-(perfluorophenyl)diazene (**10f**) (Figure 2). For the following discussion on the geometry the crystallographic numbering is used.

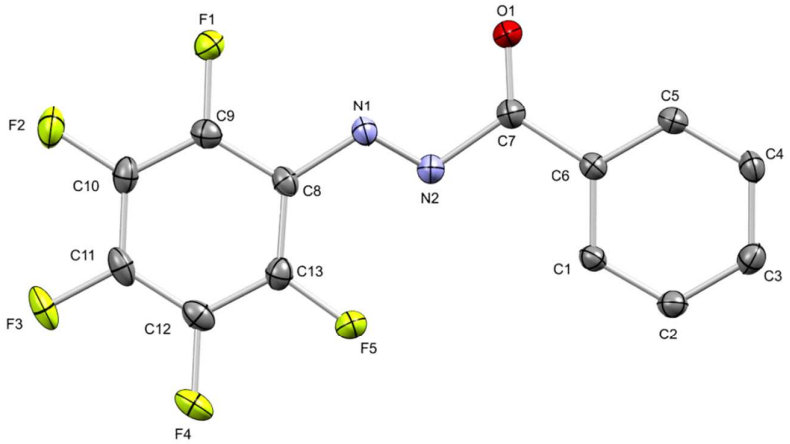


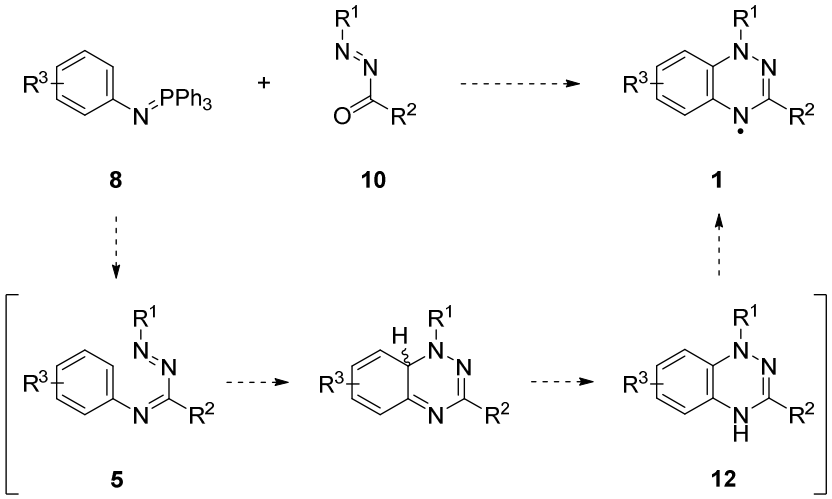
Figure 2. ORTEP view of 1-benzoyl-2-(perfluorophenyl)diazene (**10f**) (CCDC 1551626). Crystallographic atom numbering showing. Hydrogens omitted for clarity. Ellipsoids at 50% probability.

The structure, which was surprisingly non planar (torsion angle C6-C7-N2-N1 = 153.8°), supported a *trans* (*E*) geometry for the diazene [$d_{(N=N)}$ 1.238(2) Å] and a short carbonyl bond of $d_{(C=O)}$ 1.199(3) Å which was typical of highly electrophilic non resonance stabilized carbonyls [*cf.* cyclobutanone $d_{(C=O)}$ 1.198(1) Å][28] and dissimilar to typical *α,β*-unsaturated carbonyl compounds [*cf.* C=C-C=O $d_{(C=O)}$ 1.222 Å].[28] The short C=O bond length suggested the diazenes **10** would be suitable partners for the proposed aza-Wittig reaction.

The anticipated reaction sequence for the aza-Wittig-mediated synthesis of Blatter radicals **1** was expected to proceed *via* an initial aza-Wittig reaction to give the iminodiazenes **5**, which under the high reaction temperatures cyclize and prototautomerize to afford the benzotria-

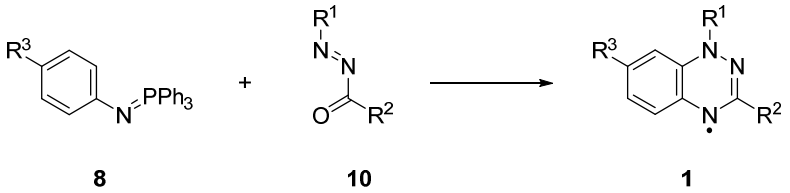
zines **12**. These, on air oxidation or on treatment with alkali in air, should afford the desired radicals **1** (Scheme 4).

Scheme 4. Proposed Reaction Sequence for the Aza-Wittig-mediated Synthesis of Blatter Radicals 1



As predicted, the treatment of 1-(het)aroyl-2-aryldiazenes **10** (1 equiv) with the corresponding *N*-aryliminophosphorane **8** (1 equiv) in preheated Ph_2O (*ca.* 150-200 °C) for 5-25 min led in most cases to the desired benzotriazinyls **1** (Table 2).

Table 2. Preparation of Blatter Radicals 1 *via* the Aza-Wittig Reaction.



8 **10** **1**

entry	R^1	R^2	R^3	**8**/**10** mol ratio	temp. (°C)	time (min)	yields **1** (%)
1	Ph	Ph	H	1:1	200	10	**1a** (80)
2	Ph	Ph	MeO	2:1	200	10	**1b** (-)[a,b]
3	Ph	Ph	Me	1:1	200	10	**1c** (84)
4	Ph	Ph	F_3C	1:1	200	20	**1d** (76)
5	Ph	Ph	NC	1:1	200	25	**1e** (48)
6	Ph	Ph	O_2N	2:1	200	10	**1f** (-)[a,b]
7	Ph	Ph	F	2:1	200	15	**1g** (71)[a]
8	Ph	Ph	Cl	2:1	200	10	**1h** (62)[a]
9	Ph	Ph	Br	2:1	200	5	**1i** (57)[a]
10	Ph	Ph	I	2:1	160	5	**1j** (52)[a]
11	Ph	4-$O_2NC_6H_4$	H	2:1	200	10	**1k** (75)[a]
12	Ph	4-Tol	F_3C	1:1	200	10	**1l** (77)
13	Ph	4-Tol	I	2:1	160	10	**1m** (57)[a]
14	Ph	4-FC_6H_4	F_3C	1:1	250	10	**1n** (74)
15	Ph	4-FC_6H_4	I	2:1	160	10	**1o** (55)[a]
16	Ph	thien-2-yl	H	1:1	200	20	**1p** (65)
17	Ph	thien-2-yl	F_3C	1:1	200	5	**1q** (82)
18	Ph	thien-2-yl	CN	2:1	200	20	**1r** (81)[a]
19	Ph	thien-2-yl	I	2:1	160	10	**1s** (54)[a]
20	C_6F_5	Ph	H	2:1	150	10	**1t** (61)
21	C_6F_5	Ph	F_3C	2:1	150	5	**1u** (70)
22	C_6F_5	thien-2-yl	F_3C	2:1	150	5	**1v** (30)

[a] Under Ar atmosphere. [b] Decomposition; mainly 1,3-diphenyl-benzo[*e*][1,2,4]triazin-7(*H*)-one (**2**) observed by TLC.

Several attempts were made to improve the product yields. According to recent work by Kaszynski *et al.*,[29] the ring closure should be facilitated by acid catalysis, as such, we carried out the reaction in the presence of both Brønsted *e.g.*, AcOH, TsOH and Lewis acids *e.g.*, $Cu(OTf)_2$ in catalytic (5 mol %) and stoichiometric (100 mol %) amounts but in our hands, there was no improvement in either yield or reaction time. In several cases, minor modifications of the reaction conditions did improve the yields but these were substrate specific. For example, in most cases where the yields of radical were low owing to the formation of over oxidation products such as the purple colored benzotriazinone **2**,[2] the yields of radicals were improved by performing the reactions under an argon atmosphere (*e.g.*, the

7-halobenzotriazinyls **1g-j**, **1m**, **1o**, and **1s**; Table 2, entries 7-10, 13, 15 and 19). Exceptions included the reaction of 4-methoxyphenyl- (**8b**) and 4-nitrophenyliminophosphoranes (**8f**) with 1-benzoyl-2-phenyldiazene **10a** (Table 2, entries 2 and 6, respectively) that gave no radical; mainly benzotriazinone **2** (by TLC). A further modification that worked was to increase the equivalents of iminophosphorane **8** (from 1-2 equiv). Tentatively, in these cases, decomposition of the diazene **10** under the reaction conditions competed with the desired aza-Wittig reaction; evidenced by the disappearance of diazene by TLC (*e.g.*, the pentafluorophenyl-substituted diazene, Table 2, entries 20-22). Worthy of note was that differential scanning colorimetry (DSC) studies on selected diazenes **10** indicated decomposition onset temperatures at low as 189.3 °C (*e.g.*, diazene **10g**) and as high as 251.7 °C (*e.g.*, diazene **10c**). Increasing the equivalents of the iminophosphorane **8** (up to 2 equiv) enabled a better consumption of the diazene **10** and improved the yield of desired radicals. Interestingly, this was more successful than increasing the equivalents of diazene **10** and fortunately, unlike the diazene, unreacted iminophosphorane **8** was also recoverable (by chromatography) after the reaction. Furthermore, attempts to use microwave irradiation to facilitate the heating rate and shorten the reaction times were less successful. Finally, the above modifications could be combined to enable the yield of radical to be maximized.

The aza-Wittig reaction sequence for preparing Blatter radicals is simple, cheap and fast affording radicals in moderate to good yields. Limitations include: the difficulty in preparing 1-acyl-2-aryldiazenes which prevent the preparation of 3-alkyl-substituted radicals, and the poor stability at the elevated reaction temperatures of Blatter radicals that have labile substituents such as methoxy or nitro groups at the C7 position.

EPR Spectroscopy

EPR studies on the new benzo[*e*][1,2,4]triazin-4-yls (**1e**,**g**,**k-o**,**q-v**) show that the unpaired electron was mainly delocalized on the amidrazonyl moiety.[5,6,18,23] Most of the spin density is located on the N1 atom (a_{N1} ~7.7 G), with N2 and N4 bearing smaller but similar spin densities (a_{N2} ~4.4 G and a_{N4} ~5.3 G) (Table 3). Elegant EPR and ENDOR studies by Neugebauer on ^{15}N-labelled derivatives reveal the coupling constants to be 4.9 G for N2 and 5.2 G for N4 ($a_{N1} >> a_{N4} > a_{N2}$).[5c]

Table 3. Fitting Parameters of Simulated Spectra for the New Radicals 1e,g,k-o,q-v.

entry	radical	*g*	*α* (G)						
			N1	N2	N4	/X	/X	/X	/X
1	**1e**[a]	2.0036	8.26	4.53	5.29	0.98/N			
2	**1g**	2.0041	7.67	4.53	4.94				
3	**1k**	2.0048	7.63	4.46	5.19				
4	**1l**[b]	2.0077	8.05	3.52	5.10	3.70/F			
5	**1l**[c]	2.0078	7.80	3.52	4.94	3.70/F			
6	**1m**	2.0042	7.62	4.91	5.02				
7	**1n**[b]	2.0036	7.84	3.36	5.22	3.27/F			
8	**1n**[c]	2.0038	7.84	3.38	5.21	3.26/F			
9	**1o**	2.0041	7.74	4.75	5.07				
10	**1q**[b]	2.0037	8.65	3.81	5.59	3.66/F			
11	**1q**[c]	2.0038	8.24	3.62	5.42	3.46/F			
12	**1r**	2.0037	8.19	4.49	5.16	1.02/N			
13	**1s**	2.0043	7.48	5.07	5.30				
14	**1t**	2.0039	6.18	4.79	5.68				
15	**1u**[b]	2.0056	7.37	4.85	5.34	4.90/F	4.25/F	3.18/F	1.91/F
16	**1u**[c]	2.0057	7.15	4.74	5.36	4.95/F	4.22/F	3.22/F	2.04/F
17	**1v**[b]	2.0040	7.27	5.32	5.44	4.96/F	4.24/F	3.18/F	1.96/F
18	**1v**[c]	2.0041	7.22	5.26	5.50	5.02/F	4.26/F	3.12/F	2.02/F

[a] Radical **1e** is known (ref 11b), but no EPR data has been reported, as such, it is included. [b] First derivative. [c] Second derivative.

Solution EPR spectra of radicals **1e**,**g**,**k-o**,**q-v** [Sect. S1. in the Supporting Information (SI)] are typical of benzo[*e*][1,2,4]triazin-4-yls,[5,6,18,23] and exhibit a seven-line spectrum arising from the coupling of the unpaired electron with three similar but slightly nonequivalent ^{14}N nuclei. EPR spectra of F_3C containing radicals (**1l**, **1n** and **1q**) show additional coupling to ^{19}F atoms (Figures S1.4., S1.6. and S1.8. in the SI). In these radicals, the F_3C group causes further splitting of the EPR signals into quartets, implying rotational averaging of the three

fluorine nuclei. The hyperfine coupling constants, in radicals with F_3C group attached on C7, are slightly larger because of the mesomeric influence of F lone pairs.

Table 4. Spin Densities (ρ) of New Radicals 1e,g,k-o,q-v Estimated from Hyperfine Coupling Constants using McConnell's equation.[30]

entry	radical	N1	N2	N4
4	**1e**[a]	0.330	0.214	0.250
5	**1g**	0.305	0.214	0.233
6	**1k**	0.305	0.210	0.245
7	**1l**[b]	0.322	0.166	0.240
8	**1l**[c]	0.312	0.166	0.233
9	**1m**	0.305	0.232	0.237
10	**1n**[b]	0.314	0.158	0.246
11	**1n**[c]	0.314	0.159	0.246
12	**1o**	0.310	0.224	0.239
13	**1q**[b]	0.346	0.180	0.264
14	**1q**[c]	0.330	0.171	0.256
15	**1r**	0.328	0.212	0.243
16	**1s**	0.299	0.239	0.250
17	**1t**	0.277	0.238	0.299
18	**1u**[b]	0.295	0.229	0.252
19	**1u**[c]	0.286	0.226	0.253
20	**1v**[b]	0.291	0.251	0.257
21	**1v**[c]	0.289	0.248	0.259

[a] Radical **1e** is known (ref 11b), but no EPR data has been reported, as such, it is included. [b] First derivative. [c] Second derivative. $A_N = Q_N . \rho_N$ where A_N is the hyperfine coupling constant in Gauss; Q_N = 21.2 G (for N2, N4) and Q_N = 25 G (for N1).[31]

The McConnell equation was used to calculate the spin density distribution based on the estimated hyperfine coupling constants (Table 4). Spin density on F atoms is small due to the large atomic hyperfine parameter of fluorine.[32] The F_3C group leads to a noticeable consistent decrease of the spin density on N2 to ~0.17 in radicals **1l**, **1n** and **1q**. The perfluorophenyl substituent in radicals **1t-v** decreases slightly the spin density on N1 to ~0.29. Despite these subtle changes in the spin density distribution, our study supports that most of the spin density remains mainly delocalized over the 1,2,4-triazinyl ring denoting its importance in the transport and magnetic properties of these radicals.

Cyclic Voltammetry

In most cases, the cyclic voltammograms of radicals **1a**,**c-e**,**g-v** have one reversible reduction and one reversible oxidation, typical of 1,2,4-benzotriazinyl radicals (see SI, Sect. S2, Figures S2.1-S2.20).[18] The exception was the 3-(4-nitrophenyl)-substituted radical **1k**, which presents two reversible reductions and one reversible oxidation (Table 5, entry 9; SI, Figure S2.9). We have seen in only one other case an unusual deviation in the redox behavior which was attributed to an oxidatively dimerized Blatter radical that gave two reversible oxidations,[18,33] as such, to remove any ambiguity in the structure of radical **1k** it was reduced *in situ* to the corresponding 1,4-dihydrobenzotriazine (**12a**) with ascorbic acid (1 equiv) in DMSO-d_6 and had its ^{1}H-NMR spectrum recorded (see SI, Sect. S3), that gratifyingly supported the monomeric structure. The second reversible reduction ($E_{1/2} \approx -1.185$ V *vs* Fc) was therefore attributed to the reduction of the nitro group[34] on the C3-phenyl.

Table 5. Overview of Electrochemical Characteristics of Radicals 1a,c-e,g-v.

entry	radical	$E_{1/2}^{ox}$ (V)	$E_{1/2}^{red}$ (V)	$E_{1/2}^{red_2}$ (V)	E_{cell} (V)	E_{HOMO} (eV)	E_{LUMO} (eV)
1	**1a**	0.288	-0.864		1.152	-5.272	-6.424
2	**1c**	0.193	-0.936		1.129	-5.367	-6.496
3	**1d**	0.476	-0.700		1.176	-5.084	-6.260
4	**1e**	0.543	-0.627		1.170	-5.017	-6.187
5	**1g**	0.281	-0.851		1.132	-5.279	-6.411
6	**1h**	0.361	-0.799		1.160	-5.199	-6.359
7	**1i**	0.380	-0.772		1.152	-5.180	-6.332
8	**1j**	0.366	-0.767		1.133	-5.194	-6.327
9	**1k**	0.365	-0.811	-1.185	1.176	-5.195	-6.371
10	**1l**	0.462	-0.710		1.172	-5.098	-6.270
11	**1m**	0.350	-0.783		1.133	-5.210	-6.343
12	**1n**	0.474	-0.704		1.178	-5.086	-6.264
13	**1o**	0.356	-0.781		1.137	-5.204	-6.341
14	**1p**	0.321	-0.823		1.144	-5.239	-6.383
15	**1q**	0.488	-0.680		1.153	-5.005	-6.158
16	**1r**	0.555	-0.598		1.168	-5.072	-6.240
17	**1s**	0.420	-0.703		1.123	-5.140	-6.263
18	**1t**	0.565	-0.757		1.322	-4.995	-6.317
19	**1u**	0.796	-0.522		1.318	-4.764	-6.082
20	**1v**	0.817	-0.480		1.297	-4.743	-6.040

Strong electron withdrawing groups, such as $–CF_3$ (σ_{meta} 0.43; σ_{para} 0.54),[35] and –C≡N (σ_{meta} 0.56; σ_{para} 0.66),[35] at the C7 position of the Blatter radical, increase both the oxidation and the reduction half-wave potentials, by ~200 mV (Table 5, entries 3-4). While the introduction of either electron withdrawing or donating groups at the benzotriazinyl C3 position did not significantly alter the redox potentials, as has been observed previously.[18] Notable changes occur when the pentafluorophenyl ($-C_6F_5$) group (σ_{meta} 0.26; σ_{para} 0.27)[35] occupies the N1 position (Table 5, entries 18-20). While the C_6F_5 is clearly not as powerful at electron withdrawing group as either CF_3 and C≡N groups, it nevertheless resides on the spin rich N1 position (see Table 3, a_{N1} ~7.7 G). As such, its ability to influence the radical's redox properties is enhanced, increasing (more +ve) both the oxidation and reduction potentials. Differences up to ~530 mV are observed for the oxidation half-wave potentials and up to ~380 mV for the reduction half-wave potentials, when synergistic effects with strong electron withdrawing groups at the C7 position are in place (Table 5, entries 19-20).

The above data supports the use of pentafluorophenyl at N1 and/or trifluoromethyl and cyano groups at C7 to significantly moderate the redox potentials of 1,2,4-benzotriazinyls. The effects of multiple substitutions appear to be somewhat additive further suggesting that customizing the redox potentials of 1,2,4-benzotriazinyls is possible and can enable their broader application in the material sciences

Crystallography

In light of the electron withdrawing influence of the pentafluorophenyl group at N1 which leads to a significant shift in the redox behaviors of radicals **1t-v**, we looked at the geometry on one of these Blatter radicals. Single crystals of 1-pentafluorophenyl radical **1t** were grown *via* bulk recrystallization from *c*-hexane and X-ray crystallography was carried out to better

understand the substituents effect on the geometry of the benzotriazinyl moiety (Figure 3); the crystallographic numbering shown is used for the subsequent discussion.

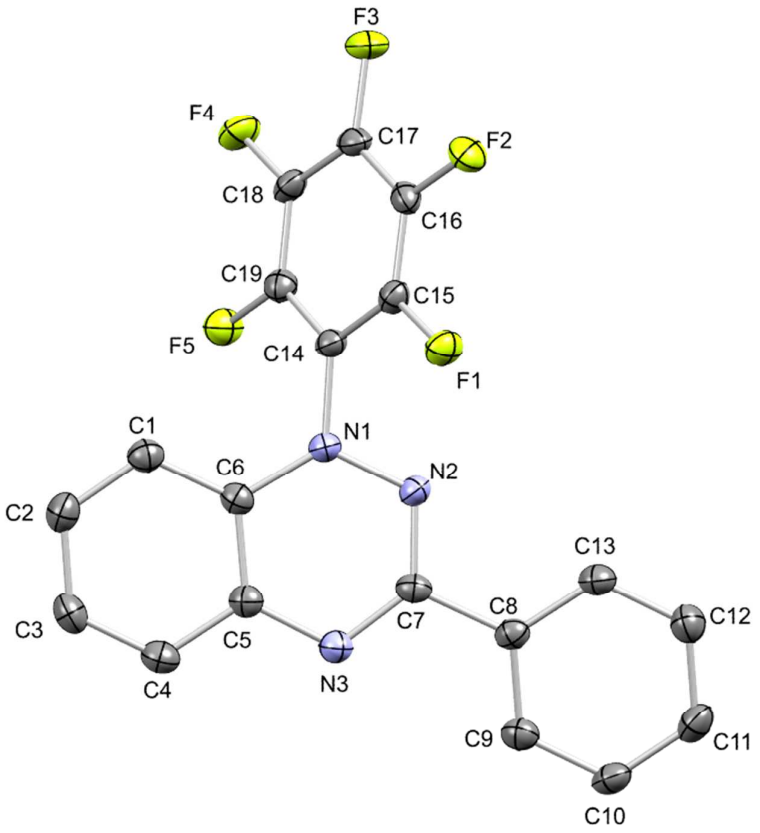


Figure 3. Intramolecular geometry of radical **1t** (CCDC 1551625) along with the crystallographic atom numbering (hydrogens are omitted for clarity reasons and ellipsoid at 50% probability).

Radical **1t** crystalized in the monoclinic $P\ 2_1/c$ space group with one molecule in the asymmetric unit cell. The C7-N2 and C7-N3 bond lengths [1.333(2) Å and 1.334(2) Å] are intermediate of single and double C-N bonds indicating strong conjugation in the amidrazonyl moiety of the heterocycle. This was further supported by the decrease in the C7-N3-C5 and C7-N2-N1 bond angles [115.9(2)° and 115.5(1)°, respectively] typical of sp^2-hybridized pyridine nitrogen atoms coordinated to metals.[36] Overall the benzotriazinyl moiety was planar, with a maximum deviation from the plane no greater than 0.047 Å. The phenyl

substituent at C7 is almost coplanar with the benzotriazinyl moiety as the torsion angle about the C7-C8 bond is only 7.4° (*cf.* for Blatter radical **1a** the analogous torsion[37] is 10.4°). The N1 perfluorophenyl substituent is comfortably out of the benzotriazinyl plane with a torsion angle of 52.6° (defined by the angle between the mean planes of the benzotriazine and the N1 aryl ring), but it is not significantly different from the analogous torsion angle of the parent Blatter radical **1a** (53.8°)[37] suggesting a negligible steric effect owing to the presence of the fluorine atoms. This torsion angle also falls comfortably within the range of N1-Ar torsion angles of 38–82° observed in other benzo[*e*][1,2,4]triazin-4-yls.[9c,38] The N1-C14 bond length of 1.418(2) Å, however, was marginally shorter by ~0.01 Å than the analogous bond in Blatter radical **1a** [1.427(2) Å],[37] tentatively suggesting a small degree additional electron release from N1 (or the triazine) to the pentafluorophenyl group.

3. CONCLUSION

A short synthesis of Blatter radicals has been developed that invokes the aza-Wittig reaction between readily available *N*-aryliminophosphoranes and 1-(het)aroyl-2-aryldiazenes. The low cost synthesis avoids the formation of either moisture sensitive imidoyl chlorides, oxidatively unstable amidrazones, expensive reagents or organolithium bases. As such, it offers the above advantages to the known syntheses of Blatter radicals.

4 EXPERIMENTAL SECTION

4.1 General methods and materials

All chemicals were commercially sourced except those whose synthesis is described. CH_2Cl_2 was freshly distilled from CaH_2 under argon. Reactions were protected from atmospheric moisture by $CaCl_2$ drying tubes or argon atmosphere was used where stated. Anhydrous Na_2SO_4 was used to dry organic extracts, and all volatiles were removed under reduced pres-

sure. All reaction mixtures and column eluents were monitored by thin-layer chromatography (TLC) using commercial aluminum-backed TLC plates (Merck Kieselgel 60 F_{254} or, where stated, aluminum oxide 60 F_{254} neutral). TLC plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography[39] 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 (type E). Melting and decomposition points were determined using either a PolyTherm-A, Wagner & Munz, Kofler hot-stage microscope apparatus or a TA Instruments DSC Q1000 differential scanning calorimeter (DSC) with samples hermetically sealed in aluminum pans under an argon atmosphere, using heating rates of 5 °C/min (DSC mp and decomp. points are listed by onset and peak max values). The solvent used for recrystallization is indicated after each melting point. UV/vis spectra were obtained using a Perkin-Elmer Lambda-25 UV/vis spectrophotometer, and inflections are identified by the abbreviation "inf". IR spectra were recorded on Shimadzu FTIR-NIR Prestige-21 spectrometer with a Pike Miracle Ge ATR accessory; strong, medium, and weak peaks are represented by "s", "m", and "w", respectively. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 500 machine at 500 and 125 MHz, respectively. Deuterated solvents were used for homonuclear lock, and the signals are referenced to the deuterated solvent peaks. APT NMR studies identified quaternary, tertiary, secondary and primary carbons, which are indicated by (s), (d), (t) and (q) notations, respectively. Low-resolution (EI) mass spectra were recorded on a Shimadzu GC-MS QP2010 with direct inlet probe. MALDI-TOF mass spectra were recorded on a on a Bruker Autoflex III Smartbeam instrument while ESI-APCI^{+} mass spectra were recorded on a Model 6110 Quadrupole MSD, Agilent Technologies. Elemental analysis was performed on a Perkin Elmer 2400 Series Elemental Analyzer by Stephen Boyer of London Metropolitan University. *N*-Phenyl(triphenyl)iminophosphorane (**8a**),[40] *N*-(4-methoxyphenyl)(triphenyl)iminophosphorane (**8b**),[41] *N*-(4-tolyl)(triphenyl)-

iminophosphorane (**8c**),[40] *N*-(4-trifluoromethylphenyl)(triphenyl)iminophosphorane (**8d**),[42] *N*-(4-cyanophenyl)(triphenyl)iminophosphorane (**8e**),[43] *N*-(4-nitrophenyl)(triphenyl)imino-phosphorane (**8f**),[41] *N*-(4-fluorophenyl)(triphenyl)iminophosphorane (**8g**),[43] *N*-(4-chloro-phenyl)(triphenyl)iminophosphorane (**8h**),[40] *N*-(4-bromophenyl)(triphenyliminophosphorane (**8i**),[44] *N*-(4-iodophenyl)(triphenyl)iminophosphorane (**8j**)[45] *N*′-phenylbenzohydrazide (**11a**),[46] 4-methyl-*N*′-phenylbenzohydrazide (**11b**),[47] 4-fluoro-*N*′-phenylbenzohydrazide (**11c**),[46] 4-nitro-*N*′-phenylbenzohydrazide (**11d**),[48] *N*′-phenylthiophene-2-carbohydrazide (**11e**),[46] and *N*′-pentafluorophenylbenzohydrazide (**11f**)[49] were prepared according to the literature.

4.2 EPR Spectroscopy

EPR spectra were recorded on an X-band EPR spectrometer (Adani CMS 8400) at room temperature on dilute solutions of the benzotriazinyls **1** in CH_2Cl_2. For the dilute solution spectra, the microwave power was in the region 0.5−7.0 mW with a modulation frequency of 100 kHz and a modulation amplitude of 1.0 Gpp. Simulations of the solution spectra were made using EasySpin.[50] The nearly isotropic nature of most of the benzotriazinyl radical samples meant that most of the solid-state samples could be initially modeled with an isotropic spectrum using EasySpin.

4.3 Cyclic Voltammetry

Cyclic voltammetry studies were performed on a Princeton Applied Research Potentiostat/Galvanostat 263A. The concentrations of radicals **1** used were 1 mM in CH_2Cl_2 containing *n*-Bu_4NPF_6 (0.1 M) as an electrolyte. A three electrode electrochemical cell was used with glassy carbon disk as working electrode, Pt wire as counter electron and Ag/AgCl (1 M KCl) as reference electrode. Scan rate 50 mV s^{-1}. Temperature = 20 °C. Fc/Fc^+ ($E_{Fc/Fc+}$ = 0.460 V *vs* SCE) was used as an internal reference.[51]

CH_2Cl_2 was distilled over CaH_2. Samples were deaerated by passing argon through the solvent, prior to measuring the cyclic voltammogram of each radical. For all measurements, blank samples (only electrolyte in the system) were taken to ensure the correct operation of the electrochemical cell. Upon each measurement, ferrocene was added and the cyclic voltammogram was taken again. All redox potentials ($E_{1/2}$) are referenced according to the ferrocene's value ($E_{\mathrm{Fc/Fc^+}} = 0.460\ V\ vs$ SCE).

The following equations were used to calculate the E_{cell}, E_{HOMO} and E_{LUMO}:

$$E_{cell} = E_{1/2}^{ox} - E_{1/2}^{red}$$

$$E_{\mathrm{HOMO}} = -\left[\left(E_{1/2}^{ox} - E_{\mathrm{Fc/Fc^+}}\right) - 5.1\right]\mathrm{eV}$$

$$E_{\mathrm{LUMO}} = -\left[\left(E_{1/2}^{red} - E_{\mathrm{Fc/Fc^+}}\right) - 5.1\right]\mathrm{eV}$$

4.4 X-Ray Crystallography

Data were collected on an Oxford-Diffraction Supernova diffractometer, equipped with a CCD area detector utilizing Mo-Kα radiation (λ = 0.7103 Å). A suitable crystal was attached to glass fibers using paratone-N oil and transferred to a goniostat where they were cooled for data collection. Unit cell dimensions were determined and refined by using 1464 ($3.76 \leq \theta \leq 28.77°$) and 2149 ($3.03 \leq \theta \leq 24.99°$) reflections for **10f** and **1t**, respectively. Empirical absorption corrections (multi-scan based on symmetry-related measurements) were applied using CrysAlis RED software.[52] The structures were solved by direct methodand refined on F^2 using full-matrix least squares using SHELXL97.[53] Software packages used: CrysAlis CCD[52] for data collection, CrysAlis RED[52] for cell refinement and data reduction, WINGX for geometric calculations,[54] and DIAMOND[55] for molecular graphics. The non-H atoms

were treated anisotropically. The hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms.

Crystal refinement data for compound **10f** (CCDC 1551626): $C_{13}H_5F_5N_2O$, M = 300.19, triclinic, space group *P-1*, a = 7.3520(5) Å, b = 7.894(5) Å, c = 10.285(5) Å, α = 80.949(5)°, β = 79.134(5)°, γ = 78.079(5)°, V = 567.60(7) Å^3, Z = 2, T = 100(2) K, ρ_{calcd} = 1.747 g cm^{-3}, $2\theta_{max}$ = 25. Refinement of 190 parameters on 2008 independent reflections out of 4627 measured reflections (R_{int} = 0.0398) led to R_1 = 0.0484 [I > 2s(I)], wR_2 = 0.1243 (all data), and S = 1.042 with the largest difference peak and hole of 0.245 and -0.313 e^{-3}, respectively.

Crystal refinement data for compound **1t** (CCDC 1551625): $C_{19}H_9F_5N_3$, M = 374.29, monoclinic, space group $P2_1c$, a = 15.6557(10) Å, b = 7.5132(4) Å, c = 13.4325(7) Å, α = 90°, β = 105.036(6)°, γ = 90°, V = 1525.90(15) Å^3, Z = 4, T = 100(2) K, ρ_{calcd} = 1.629 gcm^{-3}, $2\theta_{max}$ = 25. Refinement of 244 parameters on 2673 independent reflections out of 3230 measured reflections (R_{int} = 0.0474) led to R_1 = 0.0426 [I > 2s(I)], wR_2 = 0.1146 (all data), and S = 1.073 with the largest difference peak and hole of 0.218 and -0.227 e^{-3}, respectively.

4.5 Synthesis of Hydrazides

4.5.1 N'-*(Perfluorophenyl)thiophene-2-carbohydrazide (**11g**):* To a stirred solution of (perfluorophenyl)hydrazine (3.011 g, 15.20 mmol) in pyridine (10 mL) at *ca*. 0 °C, was added dropwise 2-thiophenecarbonyl chloride (1.63 mL, 15.20 mmol). The reaction mixture was then allowed to warm to *ca*. 20 °C and left to stir for 16 h, after which time it was poured into a stirred aqueous solution of 4.3 M H_2SO_4 (50 mL) and left to stir for an additional 2 h. The formed precipitate was collected by filtration, washed (H_2O) and recrystallized to afford the *title compound* **11g** (2.910 g, 62%) as colorless needles, mp (hot-stage) 181.4-183.8 °C (EtOH), mp (DSC) onset: 185.3 °C, peak max: 186.4 °C; decomp. onset: 239.7 °C, peak max: 255.5 °C (EtOH); R_f 0.40 (*n*-hexane/Et_2O, 50:50); Anal. Calcd for $C_{11}H_5F_5N_2OS$: C, 42.86;

H, 1.64; N, 9.09. Found: C, 42.79; H, 1.57; N, 8.91; $\lambda_{max}(CH_2Cl_2)$/nm 271 inf (log ε 3.49), 317 inf (2.75), 364 (2.57); ν_{max}/cm^{-1} 3285w (N-H), 1624m (C=O), 1518s, 1503w, 1464w, 1418w, 1356w, 1321w, 1302w, 1237w, 1200w, 1128w, 1088w, 1067w, 1022m, 962m, 880w, 858m, 806m, 719s; δ_H(500 MHz, DMSO-d_6) 10.75 (1H, d, *J* 1.5, N*H*), 8.24 (1H, d, *J* 1.5, N*H*), 7.84-7.83 (2H, m, thienyl *H*), 7.19 (1H, dd, *J* 4.5, 4.5, thienyl *H*); δ_C(125 MHz, $CDCl_3$) one C (s) resonance missing, 161.4 (s), 137.4 (dm $^1J_{CF}$ 242.5, overlapping Ar *C*Fs), 136.7 (s), 133.7 (dt, $^1J_{CF}$ 241.3, $^2J_{CF}$ 13.8, Ar *C*F), 131.6 (d), 128.9 (d), 128.1 (d), 124.6 (t, $^2J_{CF}$ 9.4, Ar *C*); *m/z* (MALDI-TOF) 309 (MH^+, 14%), 111 (100).

4.6 Synthesis of 1-(Het)aroyl-2-aryldiazenes 10 (see Table 1)

*4.6.1 1-Benzoyl-2-phenyldiazene (**10a**) (Method A, Typical Procedure):* To a stirred solution of *N'*-phenylbenzohydrazide (**11a**) (1.061 g, 5.00 mmol) in *n*-hexane (30 mL) at *ca*. 20 °C was added yellow HgO (1.083 g, 5.00 mmol). After 3 h the mixture was passed through thin layer of silica, which was subsequently rinsed with CH_2Cl_2 (50 mL). The combined filtrate was concentrated *in vacuo* at *ca*. 20 °C and recrystallized at *ca*. -20 °C to give the *title compound* **10a** (1.130 g, 93%) as red needles, mp (hot-stage) 23.5-25.4 °C (*n*-pentane/CH_2Cl_2, 90:10 at *ca*. -20 °C), (lit.,[27a] 28-29 °C); R_f 0.61 (*n*-hexane/CH_2Cl_2, 50:50); $\lambda_{max}(CH_2Cl_2)$/nm 297 (log ε 3.83), 450 (2.47); ν_{max}/cm^{-1} 3065w (aryl C-H), 1709s (C=O), 1599m, 1582w, 1501s, 1450s, 1314m, 1256s, 1194m, 1177m, 1148s, 1072w, 1032m, 1007s, 997s, 928w, 787w, 762s, 712s; δ_H(500 MHz, $CDCl_3$) 8.07 (2H, dd, *J* 8.3, 1.3, Ar *H*), 8.01 (2H, dd, *J* 8.3, 1.8, Ar *H*), 7.67 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.61-7.56 (3H, m, Ar *H*), 7.53 (2H, dd, *J* 7.8, 7.8, Ar *H*); δ_C(125 MHz, $CDCl_3$) 182.0 (s), 152.0 (s), 134.5 (d), 133.4 (d), 130.8 (s), 130.5 (d), 129.3 (d), 128.9 (d), 123.6 (d); *m/z* (APCI) 211 (MH^+, 30%), 168 (13), 105 (13).

*4.6.2 1-(4-Methylbenzoyl)-2-phenyldiazene (**10b**) (Method A):* Similar treatment of 4-methyl-*N*′-phenylbenzohydrazide (**11b**) (1.131 g, 5.00 mmol) with yellow HgO (1.083 g, 5.00 mmol) gave the *title compound* **10b** (1.110 g, 99%) as red needles, mp (hot-stage) 38.2-40.1 °C (*n*-pentane/CH_2Cl_2, 90:10 at *ca*. -20 °C), (lit.,[56] bp 130-133 °C at 0.2 Torr); mp (DSC) onset: 40.6 °C, peak max: 42.9 °C; decomp. onset: 238.5 °C, peak max: 255.7 °C (*n*-pentane/CH_2Cl_2, 90:10 at *ca*. -20 °C); R_f 0.62 (*n*-hexane/Et_2O, 50:50); $\lambda_{max}(CH_2Cl_2)$/nm 246 (log ε 4.21), 289 (4.37), 444 (2.59); ν_{max}/cm^{-1} 3065w (aryl C-H), 2934w (alkyl C-H), 1701s (C=O), 1605m, 1503m, 1452m, 1310w, 1296w, 1261s, 1244m, 1209w, 1194w, 1179m, 1146m, 1119w, 1072w, 1026m, 1009s, 999m, 930w, 912w, 829m, 775s, 760s, 733m; δ_H(500 MHz, $CDCl_3$) 7.99 (2H, dd, *J* 8.5, 1.5, Ar *H*), 7.95 (2H, d, *J* 8.5, Ar *H*), 7.62-7.55 (3H, m, Ar *H*), 7.32 (2H, d, *J* 8.0, Ar *H*), 2.45 (3H, s, C*H*$_3$); δ_C(125 MHz, $CDCl_3$) 181.9 (s), 152.1 (s), 145.7 (s), 133.3 (d), 130.6 (d), 129.6 (d), 129.3 (d), 128.2 (s), 123.6 (d), 21.9 (q); *m/z* (APCI) 225 (MH^+, 100%), 215 (11), 119 (28).

*4.6.3 1-(4-Fluorobenzoyl)-2-phenyldiazene (**10c**) (Method A):* Similar treatment of 4-fluoro-*N*′-phenylbenzohydrazide (**11c**) (1.151 g, 5.00 mmol) with yellow HgO (1.083 g, 5.00 mmol) gave the *title compound* **10c** (1.095 g, 96%) as red needles, mp (hot-stage) 32.1-34.9 °C (*n*-pentane/CH_2Cl_2, 90:10 at *ca*. -20 °C), mp (DSC) onset: 36.6 °C, peak max: 39.1 °C; decomp. onset: 251.7 °C, peak max: 262.7 °C (*n*-pentane/CH_2Cl_2, 90:10 at *ca*. -20 °C); R_f 0.68 (*n*-hexane/Et_2O, 50:50); Anal. Calcd for $C_{13}H_9FN_2O$: C, 68.42; H, 3.98; N, 12.27. Found: C, 68.35; H, 3.89; N, 12.14; $\lambda_{max}(CH_2Cl_2)$/nm 294 (log ε 4.04), 450 (2.30); ν_{max}/cm^{-1} 3065w (aryl C-H), 1707s (C=O), 1595m, 1503m, 1497m, 1452m, 1410w, 1312w, 1302w, 1290w, 1261s, 1238m, 1223m, 1198m, 1148s, 1094w, 1072w, 1009s, 997s, 928w, 918w, 847m, 820w, 779m, 770s, 743m; δ_H(500 MHz, $CDCl_3$) 8.14-8.10 (2H, m, Ar *H*), 8.02-7.99 (2H, m, Ar *H*), 7.64-7.61 (1H, m, Ar *H*), 7.60-7.56 (2H, m, Ar *H*), 7.20 (2H, dd, *J* 8.5, 8.5, Ar *H*); δ_C(125 MHz, $CDCl_3$) 180.5 (s), 166.6 (d, $^1J_{CF}$ 256.3), 152.0 (s), 133.6 (d), 133.4 (d, $^3J_{CF}$

10.0), 129.4 (d), 127.4 (d, $^{4}J_{CF}$ 2.5), 123.7 (d), 116.2 (d, $^{2}J_{CF}$ 21.3); *m/z* (APCI) 229 (MH^+, 100%), 123 (30).

*4.6.4 1-(4-Nitrobenzoyl)-2-phenyldiazene (**10d**) (Method C, Typical Procedure):* To a stirred solution of 4-nitro-*N*′-phenylbenzohydrazide (**11d**) (1.286 g, 5.00 mmol) in CH_2Cl_2 (20 mL) at *ca.* 20 °C was added pyridine (0.443 mL, 5.50 mmol). The reaction mixture was then cooled to *ca*. 0 °C and portionwise was added NBS (0.890 g, 5.00 mmol). After the addition, the mixture was allowed to warm to *ca.* 20 °C and left to stir for 0.5 h. The reaction mixture was then extracted with 1.65 M HCl (2 × 20 mL). The organic phase was separated and sequentially washed first with 0.1 M aq. $Na_2S_2O_3 \cdot 5H_2O$ (20 mL), then with saturated aq. $NaHCO_3$ (20 mL) and finally with brine (20 mL), dried (Na_2SO_4) and filtered. The volatiles were then removed *in vacuo* at *ca*. 20 °C to give the *title compound* **10d** (1.200 g, 94%) as red needles, mp (hot-stage) 128.9-132.1 °C (CH_2Cl_2), (lit.,[57] 136 °C); mp (DSC) onset: 131.1 °C, peak max: 134.5 °C; decomp. onset: 191.7 °C, peak max: 226.1 °C (CH_2Cl_2); R_f 0.72 (*n*-hexane/Et_2O, 50:50); $\lambda_{max}(CH_2Cl_2)$/nm 264 (log ε 4.15), 300 (4.20), 446 (3.02); ν_{max}/cm^{-1} 3057w (aryl C-H), 1709s (C=O), 1703m, 1605m, 1524s, 1499m, 1450m, 1346s, 1321w, 1302w, 1248m, 1240m, 1229m, 1190m, 1180m, 1148m, 1111w, 1074w, 1020m, 1008s, 997s, 935w, 922w, 880w, 860w, 854s, 816w, 783s, 758s, 720s; δ_H(500 MHz, $CDCl_3$) 8.38 (2H, d, *J* 8.5, Ar *H*), 8.28 (2H, d, *J* 9.0, Ar *H*), 8.04-8.02 (2H, m, Ar *H*), 7.66 (1H, dd, *J* 7.3, 7.3, Ar *H*), 7.60 (2H, dd, *J* 7.3, 7.3, Ar *H*); δ_C(125 MHz, $CDCl_3$) 179.7 (s), 152.0 (s), 151.1 (s), 136.0 (s), 134.3 (d), 131.6 (d), 129.5 (d), 124.0 (d), 123.9 (d); *m/z* (APCI) 256 (MH^+, 100%), 150 (20).

*4.6.5 1-Phenyl-2-(2-thienylcarbonyl)diazene (**10e**) (Method B, Typical Procedure):* To a stirred solution of *N*′-phenylthiophene-2-carbohydrazide (**11e**) (1.091 g, 5.00 mmol) in acetone (50 mL) at *ca*. 20 °C was added acetic anhydride (1.42 mL, 15.00 mmol) and sodium

nitrite (1.035 g, 15.00 mmol). After 5 h the reaction mixture was diluted with H_2O (100 mL) and extracted with CH_2Cl_2 (2 × 50 mL). The organic phase was then washed with 1% aq. Na_2CO_3 (50 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo* at *ca*. 20 °C to give the *title compound* **10e** (1.027 g, 95%) as a red oil, (lit.,[58] no data provided); R_f 0.79 (*n*-hexane/Et_2O, 50:50); Anal. Calcd for $C_{11}H_8N_2OS$: C, 61.09; H, 3.73; N: 12.95. Found: C, 61.19; H, 3.70; N, 12.86; $\lambda_{max}(CH_2Cl_2)$/nm 237 (log ε 4.18), 312 (3.75), 442 inf (2.82); ν_{max}/cm^{-1} 3096w (aryl C-H), 1788w, 1692s (C=O), 1585w, 1514m, 1497s, 1474w, 1452m, 1408s, 1358s, 1311m, 1250s, 1192s, 1148s, 1082m, 1070w, 1045m, 1020m, 976m, 952m, 928m, 858s, 775s, 754w, 725s; δ_H(500 MHz, $CDCl_3$) 8.05-8.02 (2H, m, Ar *H*), 7.95 (1H, dd, *J* 3.8, 1.3, thienyl *H*), 7.85 (1H, dd, *J* 5.0, 1.0, thienyl *H*), 7.63 (1H, dd, *J* 7.8, 7.8, Ar *H*), 7.58 (2H, dd, *J* 7.6, 7.6, Ar *H*), 7.24 (1H, dd, *J* 4.8, 3.8, thienyl *H*); δ_C(125 MHz, $CDCl_3$) 174.7 (s), 151.9 (s), 136.5 (d), 136.3 (d), 135.8 (s), 133.8 (d), 129.4 (d), 128.7 (d), 123.9 (d).

*4.6.6 1-Benzoyl-2-(perfluorophenyl)diazene (**10f**) (Method B):* Similar treatment of *N'*-perfluorophenylbenzohydrazide (**11f**) (1.511 g, 5.00 mmol) with acetic anhydride (1.42 mL, 15.0 mmol) and sodium nitrite (1.035 g, 15.00 mmol) gave the *title compound* **10f** (1.096 g, 73%) as orange microneedles, mp (hot-stage) 118.6-121.2 °C (*n*-pentane/CH_2Cl_2, 90:10), mp (DSC) onset: 121.0 °C, peak max: 121.9 °C; decomp. onset: 200.1 °C, peak max: 225.2 °C (*n*-pentane/CH_2Cl_2, 90:10); R_f 0.77 (*n*-hexane/Et_2O, 50:50); Anal. Calcd for $C_{13}H_5F_5N_2O$: C, 52.02; H, 1.68; N, 9.33. Found: C, 52.11; H, 1.54; N, 9.46; $\lambda_{max}(CH_2Cl_2)$/nm 240 (log ε 4.29), 282 (4.37), 454 (2.13); ν_{max}/cm^{-1} 3071w (aryl C-H), 1721s (C=O), 1645w, 1595w, 1518s, 1514s, 1497m, 1487m, 1450m, 1406w, 1314m, 1244s, 1177w, 1150m, 1136m, 1020s, 1003s, 997s, 955m, 883w, 800w, 735m, 708s; δ_H(500 MHz, $CDCl_3$) 8.05 (2H, dd, *J* 8.3, 1.3, Ar *H*), 7.71 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.56 (2H, dd, *J* 7.8, 7.8, Ar *H*); δ_C(125 MHz, $CDCl_3$) one C (s) resonance is missing, 180.1 (s), 144.4-144.2 and 142.4-142.1 (m, *C*F), 142.9-142.8 and 140.8-140.6 (m, *C*F), 139.2-138.9 and 137.1-136.9 (m, *C*F), 135.1 (d), 130.7 (d), 129.8 (s),

129.1 (d); *m/z* (MALDI) 303 (MH^++2, 54%), 302 (MH^++1, 10), 301 (MH^+,13), 300 (M^+, 16), 299 (52), 298 (100).

*4.6.7 1-(Perfluorophenyl)-2-(2-thienylcarbonyl)diazene (**10g**) (Method B):* Similar treatment of *N'*-(perfluorophenyl)thiophene-3-carbohydrazide (**11g**) (1.541 g, 5.00 mmol) with acetic anhydride (1.42 mL, 15.0 mmol) and sodium nitrite (1.035 g, 15.00 mmol) gave the *title compound* **10g** (0.796 g, 52%) as orange needles, mp (hot-stage) 78.8-80.5 °C (*n*-pentane/CH_2Cl_2, 90:10), mp (DSC) onset: 85.4 °C, peak max: 89.2 °C; decomp. onset: 189.3 °C, peak max: 237.6 °C (*n*-pentane/CH_2Cl_2, 90:10); R_f 0.80 (*n*-hexane/Et_2O, 50:50); Anal. Calcd for $C_{11}H_3F_5N_2OS$: C, 43.15; H, 0.99; N, 9.15. Found: C, 43.10; H, 1.08; N, 9.11; $\lambda_{max}(CH_2Cl_2)$/nm 259 inf (log ε 4.42), 288 (4.51), 465 (2.56); ν_{max}/cm^{-1} 3119w (aryl C-H), 1792w, 1697s (C=O), 1643w, 1512s, 1487m, 1408m, 1356m, 1317w, 1258m, 1248m, 1182w, 1155w, 1138m, 1084w, 1059m, 1047w, 1024s, 984m, 951m, 922w, 862w, 845w, 756m, 712w; δ_H(500 MHz, $CDCl_3$) 7.95 (1H, dd, *J* 4.0, 1.0, thienyl *H*), 7.91 (1H, dd, *J* 4.8, 1.3, thienyl *H*), 7.24 (1H, dd, *J* 4.5, 4.5, thienyl *H*); δ_C(125 MHz, $CDCl_3$) one C (s) resonance is missing, 172.8 (s), 144.6-144.4 and 143.0-142.9 (m, *C*F), 142.5-142.3 (m, *C*F), 140.9-140.7 and 139.2-139.0 (m, *C*F), 137.5 (d), 137.1 (d), 134.8 (s), 129.0 (d); *m/z* (APCI) 307 (MH^+, 100%), 285 (18), 143 (38), 129 (11), 111 (53).

4.7 Synthesis of Benzotriazinyl Radicals

*4.7.1 1,3-Diphenyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (**1a**) (Typical Procedure):* To a stirred solution of 1-benzoyl-2-phenyldiazene (**10a**) (105.0 mg, 0.50 mmol) in diphenyl ether (1 mL) at *ca*. 20 °C was added *N*-phenyl(triphenyl)iminophosphorane (**8a**) (176.7 mg, 0.50 mmol). The stirred reaction mixture was then immersed into a preheated (*ca.* 200 °C) Wood's metal bath for 10 min and then cooled to *ca.* 20 °C. Dilution of the reaction mixture in CH_2Cl_2 (2 mL), followed by chromatography (neutral Al_2O_3, *n*-hexane/CH_2Cl_2, 50:50) gave

the *title compound* **1a** (113.7 mg, 80%) as black needles, mp (hot-stage) 109.2-111.3 °C (EtOH) (lit.,[18] 109-111 °C); R_f 0.67 (neutral Al_2O_3, *n*-hexane/CH_2Cl_2, 50:50); $\lambda_{max}(CH_2Cl_2)$/nm 271 (log ε 3.63), 322 (2.93), 372 (2.82), 429 (2.56), 494 (2.17); ν_{max}/cm^{-1} 3061w and 3003w (aryl C-H), 1585w, 1481w, 1450m, 1395s, 1317w, 1252w, 1206w, 1175w, 1082w, 1065w, 1024w, 984w, 916w, 880w, 841w, 785m, 750s; identical to an authentic sample.

*4.7.2 7-Methyl-1,3-diphenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1c**):* Similar treatment of 1-benzoyl-2-phenyldiazene (**10a**) (105.0 mg, 0.50 mmol) in diphenyl ether (1 mL) with *N*-(4-tolyl)(triphenyl)iminophosphorane (**8c**) (183.7 mg, 0.50 mmol) at *ca.* 200 °C for 10 min gave on chromatography (neutral Al_2O_3, *n*-hexane/CH_2Cl_2, 50:50) the *title compound* **1c** (125.0 mg, 84%) as black needles, mp (hot-stage) 159.8-163.2 °C (*c*-hexane) (lit.,[59] 160-163 °C); R_f 0.42 (neutral Al_2O_3, *n*-hexane/CH_2Cl_2, 50:50); $\lambda_{max}(CH_2Cl_2)$/nm 275 (log ε 4.21), 283 inf (4.10), 322 (3.55), 373 (3.35), 433 (2.95), 481 inf (1.58); ν_{max}/cm^{-1} 3063w (aryl C-H), 2920w (alkyl C-H), 1684w, 1653w, 1592m, 1559w, 1539w, 1503m, 1490m, 1459w, 1452m, 1420w, 1394s, 1327m, 1279w, 1257w, 1170m, 1087w, 1067w, 1024m, 1002w, 929w, 917w, 862w, 849w, 844w, 803s, 780s, 759s, 712m; identical to an authentic sample.

*4.7.3 1,3-Diphenyl-7-(trifluoromethyl)-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1d**):* Similar treatment of 1-benzoyl-2-phenyldiazene (**10a**) (105.0 mg, 0.50 mmol) in diphenyl ether (1 mL) with *N*-(4-trifluoromethylphenyl)(triphenyl)iminophosphorane (**8d**) (210.7 mg, 0.50 mmol) at *ca.* 200 °C for 20 min gave on chromatography (neutral Al_2O_3, *n*-hexane/CH_2Cl_2, 50:50) the *title compound* **1d** (133.9 mg, 76%) as black needles, mp (hot-stage) 148.7-150.3 °C (*c*-hexane) (lit.,[59] 149-153 °C); R_f 0.78 (neutral Al_2O_3, *n*-hexane/CH_2Cl_2, 50:50); $\lambda_{max}(CH_2Cl_2)$/nm 259 inf (log ε 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.

*4.7.4 7-Cyano-1,3-diphenyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (**1e**):* Similar treatment of 1-benzoyl-2-phenyldiazene (**10a**) (105.0 mg, 0.50 mmol) in diphenyl ether (1 mL) with *N*-(4-cyanophenyl)(triphenyl)iminophosphorane (**8e**) (189.2 mg, 0.50 mmol) at *ca.* 200 °C, stirred for 25 min, gave on chromatography (neutral Al_2O_3, *n*-hexane/Et_2O, 50:50) the *title compound* **1e** as black needles (74.2 mg, 48%), mp (hot-stage) 213.7-216.6 °C (*c*-hexane) (lit.,[11b] no data provided); mp (DSC) onset: 219.2 °C, peak max: 220.9 °C; decomp. onset: 276.1 °C, peak max: 337.2 °C (*c*-hexane); R_f 0.83 (neutral Al_2O_3, *n*-hexane/*t*-BuOMe, 50:50); Anal. Calcd for $C_{20}H_{13}N_4$: C, 77.65; H, 4.24; N, 18.11. Found: C, 77.43; H, 4.46; N, 17.92; $\lambda_{max}(CH_2Cl_2)$/nm 262 (log ε 4.03), 294 (4.20), 323 (3.60), 378 (3.55), 441 (3.38), 461 inf (3.30), 510 (3.18); ν_{max}/cm^{-1} 3082w (aryl C-H), 2222m (C≡N), 1587w, 1485m, 1450w, 1400s, 1313,, 1277w, 1254w, 1194m, 1179w, 1142w, 1126w, 1065w, 1028m, 916w, 887m, 847w, 829s, 754s, 702m; *m/z* (MALDI-TOF) 310 (MH^+, 24%), 309 (M^+, 100).

*4.7.5 7-Fluoro-1,3-diphenyl-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl (**1g**):* Similar treatment of 1-benzoyl-2-phenyldiazene (**10a**) (105.0 mg, 0.50 mmol) in diphenyl ether (1 mL) with *N*-(4-fluorophenyl)(triphenyl)iminophosphorane (**8g**) (371.4 mg, 1.00 mmol), deaerated and under Ar atmosphere at *ca.* 20 °C, and immersed into a preheated Wood's metal bath at *ca.* 200 °C for 15 min gave on chromatography (neutral Al_2O_3, *n*-hexane/Et_2O, 50:50) the *title compound* **1g** (107.3 mg, 71%) as olive green needles, mp (hot-stage) 119.0-123.7 °C (*n*-pentane/CH_2Cl_2, 90:10); R_f 0.60 (*n*-hexane/*t*-BuOMe, 50:50); Anal. Calcd for $C_{19}H_{13}FN_3$: C, 75.48; H, 4.33; N, 13.90. Found: C, 75.31; H, 4.26; N, 13.97; $\lambda_{max}(CH_2Cl_2)$/nm 272 (log ε 3.66), 284 inf (3.43), 322 (2.98), 372 (2.87), 427 (2.61), 493 (2.28), 515 inf (3.63); ν_{max}/cm^{-1} 3065w (aryl C-H), 1599w, 1479m, 1450w, 1414w, 1395s, 1325w, 1292w, 1246w, 1217m,

1155m, 1096w, 1082w, 1065w, 1016w, 928w, 922w, 910w, 881w, 841m, 812w, 762s, 746m, 729s, 714m, 706m; *m/z* (MALDI-TOF) 302 (M^+, 21%), 301 (100), 279 (18).

*4.7.6 7-Chloro-1,3-diphenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1h**):* Similar treatment of 1-benzoyl-2-phenyldiazene (**10a**) (105.0 mg, 0.50 mmol) in diphenyl ether (1 mL) with *N*-(4-chlorophenyl)(triphenyl)iminophosphorane (**8h**) (387.8 mg, 1.00 mmol), deaerated under Ar atmosphere at *ca.* 20 °C, and immersed into a preheated Wood's metal bath at *ca.* 200 °C for 10 min gave on chromatography (silica, *n*-hexane/CH_2Cl_2, 50:50) the *title compound* **1h** (99.0 mg, 62%) as black needles, mp (hot-stage) 149.0−151.2 °C (*c*-hexane) (lit.,[59] 149–152 °C); R_f 0.24 (silica, *n*-hexane/CH_2Cl_2, 50:50); $\lambda_{max}(CH_2Cl_2)$/nm 275 (log ε 3.55), 322 (2.81), 374 (2.72), 436 (2.48), 480 inf (2.05); ν_{max}/cm^{-1} 3069w (aryl C-H), 1614w, 1591w, 1474s, 1449w, 1394m, 1356w, 1317w, 1294w, 1265w, 1242w, 1192w, 1150w, 1092w, 1082w, 1024w, 897m, 846w, 829m, 779m; identical to an authentic sample.

*4.7.7 7-Bromo-1,3-diphenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1i**)*: Similar treatment of 1-benzoyl-2-phenyldiazene (**10a**) (105.0 mg, 0.50 mmol) in diphenyl ether (1 mL) with *N*-(4-bromophenyl)(triphenyl)iminophosphorane (**8i**) (432.3 mg, 1.00 mmol), deaerated under Ar atmosphere at *ca.* 20 °C, and immersed into a preheated Wood's metal bath at *ca.* 200 °C for 5 min gave on chromatography (silica, *n*-hexane/CH_2Cl_2, 50:50) the *title compound* **1i** (103.4 mg, 57%) as black needles, mp (hot-stage) 160.1-162.3 °C (*c*-hexane) (lit.,[59] 160-162 °C); R_f 0.26 (silica, *n*-hexane/CH_2Cl_2, 50:50); $\lambda_{max}(CH_2Cl_2)$/nm 277 (log ε 3.62), 322 (2.87), 376 (2.84), 434 (2.59), 498 (2.08); ν_{max}/cm^{-1} 3069w (aryl C-H), 1591w, 1566w, 1476s, 1449m, 1393s, 1317w, 1265w, 1242w, 1196w, 1130w, 1070w, 1061w, 1022w, 926w, 889m, 827m, 777s, 758w, 740w; identical to an authentic sample.

*4.7.8 7-Iodo-1,3-diphenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1j**):* Similar treatment of 1-benzoyl-2-phenyldiazene (**10a**) (105.0 mg, 0.50 mmol) in diphenyl ether (1 mL) with *N*-

(4-iodophenyl)(triphenyl)iminophosphorane (**8j**) (479.3 mg, 1.00 mmol), deaerated under Ar atmosphere at *ca.* 20 °C and immersed into a preheated Wood's metal bath at *ca.*at *ca.* 160 °C for 5 min gave upon chromatography (silica, *n*-hexane/CH_2Cl_2, 50:50) the title compound **1j** (106.7 mg, 52%) as black needles, mp (hot-stage) 150.4-151.8 °C (*c*-hexane) (lit.,[59] 149–152 °C); R_f 0.26 (silica, *n*-hexane/CH_2Cl_2, 50:50); $\lambda_{max}(CH_2Cl_2)$/nm 280 (log ε 3.37), 323 (2.77), 377 (2.71), 438 (2.37), 481 inf (1.72); ν_{max}/cm^{-1} 3065w (aryl C-H), 1591w, 1487m, 1477s, 1458w, 1450m, 1393s, 1315m, 1267w, 1246w, 1194w, 1175w, 1067w, 1057w, 1024m, 883s, 827s, 781s, 773s, 739m; identical to an authentic sample.

*4.7.9 3-(4-Nitrophenyl)-1-phenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1k**):* Similar treatment of 1-(4-nitrobenzoyl)-2-phenyldiazene (**10d**) (127.6 mg, 0.50 mmol) in diphenyl ether (1 mL) with *N*-phenyl(triphenyl)iminophosphorane (**8a**) (353.4 mg, 1.00 mmol), deaerated under Ar atmosphere at *ca.* 20 °C and immersed into a preheated Wood's metal bath at *ca.* 200 °C for 10 min gave on chromatography (silica, *n*-hexane/Et_2O, 50:50) the *title compound* **1k** (123.5 mg, 75%) as dark brown needles, mp (hotstage) 195.9-197.8 °C (*c*-hexane), mp (DSC) onset: 189.5 °C, peak max: 192.7 °C; decomp. onset: 272.0 °C, peak max: 317.5 °C (*c*-hexane); R_f 0.60 (*n*-hexane/Et_2O, 50:50); Anal. Calcd for $C_{19}H_{13}N_4O_2$: C, 69.29; H, 3.98; N, 17.01. Found: C, 69.12; H, 4.04; N, 16.98; $\lambda_{max}(CH_2Cl_2)$/nm 244 (log ε 4.28), 311 (4.43), 353 inf (3.82), 425 (3.44), 460 inf (3.24), 509 (3.14); ν_{max}/cm^{-1} 1599w, 1522s, 1483m, 1450w, 1383w, 1344s, 1323w, 1314w, 1302w, 1252w, 1206w, 1175w, 1161w, 1152w, 1107w, 1099w, 1080w, 1067w, 1026w, 1013w, 986w, 864m, 850m, 841w, 756s, 737m, 702m; *m/z* (MALDI-TOF) 330 (MH^+, 19%), 329 (M^+, 100), 284 (7). *In situ* reduction of 3-(4-nitrophenyl)-1-phenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1k**) using L-ascorbic acid (1.8 mg, 0.01 mmol) in DMSO-d_6 (0.6 mL) at *ca.* 20 °C for 2 min, gave the NMR spectra of 3-(4-nitrophenyl)-1-phenyl-1,4-dihydrobenzo[*e*][1,2,4]triazine (**12a**): δ_H(500 MHz, DMSO-d_6) 8.98 (1H, s, N*H*), 8.32 (2H, dd, *J* 7.0, 2.0, Ar *H*), 8.10 (2H, dd, *J* 7.0, 2.0 Ar

H), 7.46-7.40 (4H, m, Ar *H*), 7.14 (1H, dd, *J* 7.0, 7.0, Ar *H*), 6.79-6.75 (2H, m, Ar *H*), 6.71-6.68 (1H, m, Ar *H*), 6.38 (1H, d, *J* 8.0, Ar *H*); δ_C(125 MHz, DMSO-d_6) 148.0 (s), 145.8 (s), 143.3 (s), 137.1 (s), 133.4 (s), 133.3 (s), 129.0 (d), 126.8 (d), 123.8 (d), 123.6 (d), 123.5 (d), 123.4 (d), 121.4 (d), 113.9 (d), 111.3 (d).

*4.7.10 1-Phenyl-3-(4-tolyl)-7-(trifluoromethyl)-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1l**):* Similar treatment of 1-(4-methylbenzoyl)-2-phenyldiazene (**10b**) (112.1 mg, 0.50 mmol) in diphenyl ether (1 mL) with *N*-(4-(trifluoromethylphenyl)(triphenyl)iminophosphorane (**8d**) (210.7 mg, 0.50 mmol) at *ca.* 200 °C for 10 min gave on chromatography (neutral Al_2O_3, CH_2Cl_2) the *title compound* **1l** (141.1 mg, 77%) as brown needles; mp (hot-stage) 138.9-142.2 °C (*c*-hexane); mp (DSC) onset: 144.3 °C, peak max: 148.0 °C (*c*-hexane), R_f 0.43 (neutral Al_2O_3, *n*-hexane/CH_2Cl_2, 50:50); Anal. Calcd for $C_{21}H_{15}F_3N_3$: C, 68.85; H, 4.13; N, 11.47. Found: C, 68.96; H, 3.99; N, 11.46; $\lambda_{max}(CH_2Cl_2)$/nm 259 inf (log ε 3.51), 278 (3.76), 292 inf (3.53), 324 (3.01), 378 (2.84), 431 (2.67), 498 (2.32); ν_{max}/cm^{-1} 3049w (aryl C-H), 2924w (alkyl C-H), 1611w, 1591w, 1489w, 1454w, 1422m, 1396s, 1354s, 1335w, 1314s, 1263s, 1202w, 1163m, 1150m, 1115s, 1070m, 1061m, 1018w, 905m, 870w, 843w, 827m, 766m, 754w; *m/z* (EI) 366 (M^+, 100%), 351 (6), 260 (5), 183 (9), 116 (6), 90 (5), 77 (23), 51 (8).

*4.7.11 7-Iodo-1-phenyl-3-(4-tolyl)-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1m**):* Similar treatment of 1-(4-methylbenzoyl)-2-phenyldiazene (**10b**) (112.1 mg, 0.50 mmol) in diphenyl ether (1 mL) with *N*-(4-iodophenyl)(triphenyl)iminophosphorane (**8j**) (479.3 mg, 1.00 mmol), deaerated under Ar atmosphere at *ca.* 20 °C and immersed into a preheated Wood's metal bath at *ca.* 160 °C for 10 min gave on chromatography (neutral Al_2O_3, CH_2Cl_2/*n*-hexane, 50:50) the *title compound* **1m** (121.0 mg, 57%) as brown needles; mp (hot-stage) 148.4-150.6 °C (*c*-hexane); mp (DSC) decomp. onset: 147.8 °C, peak max: 151.2 °C (*c*-hexane); R_f 0.35

(*n*-hexane/CH_2Cl_2, 50:50); Anal. Calcd for $C_{20}H_{15}IN_3$: C, 56.62; H, 3.56; N, 9.90. Found: C, 56.71; H, 3.49; N, 9.85; $\lambda_{max}(CH_2Cl_2)$/nm 261 inf (log ε 3.53), 284 (3.80), 295 inf (3.73), 322 (3.07), 346 inf (2.90), 381 (3.02), 438 (2.77), 503 (2.34); ν_{max}/cm^{-1} 3067w (aryl C-H), 2928w and 2849w (alkyl C-H), 1614w, 1593w, 1564w, 1545w, 1514w, 1493m, 1474s, 1393s, 1319w, 1312w, 1294w, 1267w, 1244m, 1196w, 1177m, 1150w, 1109w, 1070w, 1055w, 1018m, 986w, 914w, 885m, 847w, 829s, 799m, 772m; *m/z* (EI) 424 (M^+, 100%), 297 (44), 212 (8), 192 (12), 179 (12), 152 (9), 116 (6), 103 (6), 91 (6), 77 (21), 75 (27), 51 (11).

*4.7.12 3-(4-Fluorophenyl)-1-phenyl-7-(trifluoromethyl)-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1n**):* Similar treatment of 1-(4-fluorobenzoyl)-2-phenyldiazene (**10c**) (114.1 mg, 0.50 mmol) in diphenyl ether (1 mL) with *N*-(4-trifluoromethylphenyl)(triphenyl)iminophosphorane (**8d**) (210.7 mg, 0.50 mmol) at *ca.* 250 °C for 10 min gave on chromatography (neutral Al_2O_3, CH_2Cl_2) the *title compound* **1n** (137.0 mg, 74%) as brown needles, mp (hot-stage) 147.5-149.9 °C (*c*-hexane); mp (DSC) onset: 154.9 °C, peak max: 155.5 °C (*c*-hexane), R_f 0.47 (*n*-hexane/CH_2Cl_2, 50:50); Anal. Calcd for $C_{20}H_{12}F_4N_3$: C, 64.87; H, 3.27; N, 11.35. Found: C, 64.66; H, 3.45; N, 11.29; $\lambda_{max}(CH_2Cl_2)$/nm 257 inf (log ε 3.48), 274 (3.67), 286 inf (3.48), 324 (2.97), 373 (2.83), 429 (2.61), 495 (2.29); ν_{max}/cm^{-1} 3086w (aryl C-H), 1601w, 1510w, 1491w, 1423w, 1395s, 1354m, 1337w, 1312m, 1292w, 1263m, 1221m, 1202w, 1167w, 1152m, 1117s, 1070w, 1061m, 1013w, 905m, 872w, 845m, 781m, 768w, 756w; *m/z* (EI) 370 (M^+, 100%), 265 (7), 198 (7), 185 (6), 121 (6), 77 (31), 51 (10).

*4.7.13 3-(4-Fluorophenyl)-7-iodo-1-phenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1o**):* Similar treatment of 1-(4-fluorobenzoyl)-2-phenyldiazene (**10c**) (114.1 mg, 0.50 mmol) in diphenyl ether (1 mL) with *N*-(4-iodophenyl)(triphenyl)iminophosphorane (**8j**) (479.3 mg, 1.00 mmol), deaerated under Ar atmosphere at *ca.* 20 °C, and immersed into a preheated Wood's metal bath at *ca.* 160 °C for 10 min gave on chromatography (neutral Al_2O_3, *n*-

hexane/CH_2Cl_2, 50:50) the *title compound* **1o** (118.0 mg, 55%) as brown needles; mp (hot-stage) 147.2-150.9 °C (*n*-hexane); mp (DSC) decomp. onset: 157.7 °C, peak max: 160.1 °C (*n*-hexane); R_f 0.42 (*n*-hexane/CH_2Cl_2, 50:50); Anal. Calcd for $C_{19}H_{12}FIN_3$: C, 53.29; H, 2.82; N, 9.81. Found: C, 53.31; H, 2.73; N, 9.75; $\lambda_{max}(CH_2Cl_2)$/nm 280 (log ε 3.73), 290 inf (3.66), 322 (2.99), 378 (3.04), 433 (2.68), 500 (2.18); ν_{max}/cm^{-1} 3053w (aryl C-H), 1599m, 1566w, 1545w, 1506m, 1491m, 1477s, 1456w, 1393s, 1310w, 1288w, 1267w, 1223m, 1190w, 1146m, 1094w, 1084w, 1070w, 1055w, 1026w, 1013w, 951w, 908w, 885m, 837m, 818s, 764s; *m/z* (EI) 428 (M^+, 100%), 301 (53), 214 (10), 196 (9), 179 (13), 152 (12), 103 (8), 77 (27), 75 (43), 51 (19).

*4.7.14 1-Phenyl-3-(thien-2-yl)-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1p**):* Similar treatment of 1-phenyl-2-(2-thienylcarbonyl)diazene (**10e**) (108.1 mg, 0.50 mmol) in diphenyl ether (1 mL) with *N*-phenyl(triphenyl)iminophosphorane (**8a**) (176.7 mg, 0.50 mmol) at *ca.* 200 °C for 20 min gave on chromatography (neutral Al_2O_3, CH_2Cl_2) the *title compound* **1p** as dark-green needles (94.5 mg, 65%); mp (hot-stage) 133.1-134.8 °C (*c*-hexane) (lit.[18] (DSC) onset 133.7 °C, peak max 134.6 °C); R_f 0.63 (neutral Al_2O_3, CH_2Cl_2); $\lambda_{max}(CH_2Cl_2)$/nm 259 inf (log ε 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 and 3055w (aryl C-H), 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; identical to an authentic sample.

*4.7.15 1-Phenyl-3-(thien-2-yl)-7-(trifluoromethyl)-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1q**), (Method A):* Similar treatment of 1-phenyl-2-(2-thienylcarbonyl)diazene (**10e**) (108.1 mg, 0.50 mmol) in diphenyl ether (1 mL) with *N*-(4-trifluoromethylphenyl)(triphenyl)iminophosphorane (**8d**) (210.7 mg, 0.50 mmol) at *ca.* 200 °C for 5 min gave on chromatography

(neutral Al_2O_3, CH_2Cl_2) the *title compound* **1q** (147.0 mg, 82%) as brown needles; mp (hot-stage) 182.6-184.3 °C (*c*-hexane); mp (DSC) onset: 183.5 °C, peak max: 185.7 °C (*c*-hexane), R_f 0.38 (*n*-hexane/CH_2Cl_2, 50:50); Anal. Calcd for $C_{18}H_{11}F_3N_3S$: C, 60.33; H, 3.09; N, 11.73. Found: C, 60.48; H, 2.89; N, 11.68; $\lambda_{max}(CH_2Cl_2)$/nm 260 (log ε 3.18), 293 (3.59), 307 inf (3.42), 383 (2.67), 421 (2.64), 512 (2.30); ν_{max}/cm^{-1} 3086w and 3071w (aryl C-H), 1591w, 1531w, 1491w, 1437m, 1420w, 1387m, 1356m, 1344m, 1312m, 1287w, 1267m, 1246w, 1219w, 1202w, 1163w, 1148w, 1117s, 1070m, 1057m, 1028w, 897w, 889w, 870m, 851w, 841m, 773w, 764w, 752w; *m/z* (EI) 358 (M^+, 100%), 325 (6), 253 (5), 186 (6), 179 (8), 109 (7), 77 (28), 51 (10).

*4.7.16 7-Cyano-1-phenyl-3-(thien-2-yl)-1,4-dihydrobenzo[e][1,2,4]triazin-4-yl **(1r)**:* Similar treatment of 1-phenyl-2-(2-thienylcarbonyl)diazene (**10e**) (108.1 mg, 0.50 mmol) with *N*-(4-cyanophenyl)(triphenyl)iminophosphorane (**8e**) (378.4 mg, 1.00 mmol), deaerated under Ar atmosphere at *ca.* 20 °C and immersed into a preheated Wood's metal bath at *ca.* 200 °C for 20 min gave on chromatography (silica, *n*-hexane/Et_2O, 50:50) the *title compound* **1r** as black needles (127.8 mg, 81%), mp (hot-stage) 227.8-229.2 °C (*c*-hexane); mp (DSC) onset: 234.4 °C, peak max: 236.5 °C; decomp. onset: 278.5 °C, peak max: 329.1 °C (*c*-hexane); R_f 0.56 (silica, *n*-hexane/Et_2O, 50:50); Anal. Calcd for $C_{18}H_{11}N_4S$: C, 68.55; H, 3.52; N, 17.77. Found: C, 68.34; H, 3.73; N, 17.68; $\lambda_{max}(CH_2Cl_2)$/nm 245 (log ε 4.15), 259 (4,14), 306 (4.50), 319 inf (4.37), 394 (3.60), 435 (3.60), 530 (3,47); ν_{max}/cm^{-1} 2222m (C≡N), 1589w, 1547w, 1531w, 1497m, 1487s, 1437s, 1414w, 1389m, 1344w, 1327w, 1312w, 1279w, 1256w, 1217w, 1194m, 1171w, 1140w, 1115w, 1076w, 1061w, 1051w, 1032w, 1026w, 1005w, 905w, 878w, 856w, 839w, 831w, 758w, 716w, 710w, 702s; *m/z* (MALDI-TOF) 316 (MH^+, 25%), 315 (M^+, 100).

*4.7.17 7-Iodo-1-phenyl-3-(thien-2-yl)-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1s**):* Similar treatment of 1-phenyl-2-(2-thienylcarbonyl)diazene (**10e**) (108.1 mg, 0.50 mmol) in diphenyl ether (1 mL) with *N*-(4-iodophenyl)(triphenyl)iminophosphorane (**8j**) (479.3 mg, 1.00 mmol) at *ca.* 160 °C for 10 min gave on chromatography (silica, *n*-hexane/CH_2Cl_2, 50:50) the *title compound* **1s** (112.4 mg, 54%) as brown needles; mp (hot-stage) 179.8-182.7 °C (*c*-hexane); mp (DSC) decomp. onset: 181.4 °C, peak max: 186.1 °C (*c*-hexane); R_f 0.31 (*n*-hexane/CH_2Cl_2, 50:50); Anal. Calcd for $C_{17}H_{11}IN_3S$: C, 49.05; H, 2.66; N, 10.09. Found: C, 49.13; H, 2.60; N, 9.89; $\lambda_{max}(CH_2Cl_2)$/nm 259 inf (log ε 3.13), 292 inf (3.55), 303 (3.62), 355 (2.67), 388 (2.71), 422 (2.61), 442 inf (2.57), 516 (2.21); ν_{max}/cm^{-1} 3096w and 3067w (aryl C-H), 1591w, 1568w, 1530w, 1491m, 1472s, 1450w, 1435s, 1404w, 1383s, 1344w, 1335w, 1321w, 1287w, 1273w, 1244w, 1215m, 1194w, 1150w, 1124w, 1078w, 1047w, 1026w, 1003w, 972w, 912w, 868m, 851s, 831s, 770m; *m/z* (EI) 416 (M^+, 100%), 289 (33), 208 (9), 184 (8), 179 (11), 152 (8), 77 (25), 75 (26), 51 (16).

*4.7.18 1-(Perfluorophenyl)-3-phenyl-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1t**):* Similar treatment of 1-benzoyl-2-(perfluorophenyl)diazene (**10f**) (150.1 mg, 0.50 mmol) in diphenyl ether (1 mL) with *N*-phenyl(triphenyl)iminophosphorane (**8a**) (353.4 mg, 1.00 mmol) at *ca.* 150 °C for 10 min gave on chromatography (neutral Al_2O_3, *n*-hexane/Et_2O, 50:50) the *title compound* **1t** (114.1 mg, 61%) as black prisms, mp (hot-stage) 188.6-190.1 °C (*c*-hexane); mp (DSC) onset: 190.4 °C, peak max: 191.6 °C; decomp. onset: 281.8 °C, peak max: 308.5 °C (*c*-hexane); R_f 0.83 (Al_2O_3, *n*-hexane/Et_2O, 50:50); Anal. Calcd for $C_{19}H_9F_5N_3$: C, 60.97; H, 2.42; N, 11.23. Found: C, 60.95; H, 2.31; N, 11.14; $\lambda_{max}(CH_2Cl_2)$/nm 268 (log ε 4.61), 322 (3.66), 375 (3.76), 423 inf (3.40), 455 inf (3.17), 486 (3.10), 565 inf (2.78); ν_{max}/cm^{-1} 1514s, 1491w, 1450w, 1391m, 1310w, 1298w, 1244w, 1198w, 1177w, 1146w, 1121w, 1076m, 1069w, 1036w, 1028m, 989s, 928m, 783m, 760m, 735m, 723w; *m/z* (MALDI-TOF) 375 (MH^+, 25%), 374 (M^+, 100).

*4.7.19 1-(Perfluorophenyl)-3-phenyl-7-(trifluoromethyl)-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1u**):* Similar treatment of 1-benzoyl-2-(perfluorophenyl)diazene (**10f**) (150.1 mg, 0.50 mmol) in diphenyl ether (1 mL) with *N*-(4-trifluoromethylphenyl)(triphenyl)iminophosphorane (**8d**) (421.4 mg, 1.00 mmol) at *ca.* 150 °C for 5 min gave on chromatography (neutral Al_2O_3, *n*-hexane/Et_2O, 50:50) the *title compound* **1u** (154.8 mg, 70%) as black needles, mp (hot-stage) 155.3-158.8 °C (*c*-hexane); mp (DSC) onset: 163.0 °C, peak max: 166.3 °C; decomp. onset: 279.3 °C, peak max: 327.1 °C (*c*-hexane); R_f 0.89 (neutral Al_2O_3, *n*-hexane/Et_2O, 60:40); Anal. Calcd for $C_{20}H_8F_8N_3$: C, 54.31; H, 1.82; N, 9.50. Found: C, 54.12; H, 1.74; N, 9.51; $\lambda_{max}(CH_2Cl_2)$/nm 271 (log ε 4.61), 323 inf (3.49), 380 (3.62), 428 inf (3.33), 459 inf (3.11), 488 (3.15), 575 (2.86); ν_{max}/cm^{-1} 1524m, 1510s, 1454w, 1431m, 1395s, 1358m, 1331m, 1319s, 1269m, 1236w, 1194m, 1175w, 1167m, 1134s, 1121s, 1084w, 1065m, 1026m, 991s, 930m, 897m, 866m, 833m, 806w, 783m, 754w, 730m, 700s; *m/z* (MALDI-TOF) 443 (MH^+, 41%), 442 (M^+, 100), 247 (30).

*4.7.20 1-(Perfluorophenyl)-3-(thien-2-yl)-7-(trifluoromethyl)-1,4-dihydrobenzo[*e*][1,2,4]triazin-4-yl (**1v**):* Similar treatment of 1-(perfluorophenyl)-2-(2-thienylcarbonyl)diazene (**10g**) (153.1 mg, 0.50 mmol) in diphenyl ether (1 mL) with *N*-(4-trifluoromethylphenyl)(triphenyl)iminophosphorane (**8d**) (421.4 mg, 1.00 mmol) at *ca.* 150 °C for 5 min gave on chromatography (neutral Al_2O_3, *n*-hexane/Et_2O, 50:50) the *title compound* **1v** (67.2 mg, 30%) as olive green needles, mp (hot-stage) 198.7-201.2 °C (*c*-hexane); mp (DSC) onset: 207.5 °C, peak max: 209.8 °C; decomp. onset: 316.8 °C, peak max: 350.5 °C (*c*-hexane); R_f 0.83 (neutral Al_2O_3, *n*-hexane/Et_2O, 50:50); Anal. Calcd for $C_{18}H_6F_8N_3S$: C, 48.22; H, 1.35; N, 9.37. Found: C, 48.16; H, 1.12; N, 9.45; $\lambda_{max}(CH_2Cl_2)$/nm (log ε) 265 inf (4.56), 293 (4.75), 314 inf (4.39), 379 inf (3.63), 413 (3.75), 475 inf (3.23), 508 (3.36), 591 (2.93); ν_{max}/cm^{-1} 3102w (aryl C-H), 1559w, 1522m, 1514s, 1437m, 1389m, 1364w, 1352w, 1327m, 1294w, 1273m, 1240w, 1213w, 1192w, 1157w, 1140w, 1125s, 1082w, 1070w, 1057m, 1032w,

1020w, 993s, 907w, 895w, 868w, 856w, 837w, 734w, 718s; *m/z* (MALDI-TOF) 449 (MH^+, 33%), 448 (M^+, 100), 404 (78), 253 (43).

ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR for all 1-(het)aroyl-2-aryldiazenes; experimental and simulated EPR spectra for all new radicals; cyclic voltammograms and FTIR spectra for all radicals (PDF). Crystallographic data for radicals **10f** and **1t** (CIF), which have also been deposited with the Cambridge Crystallographic Data Centre with deposit nos. CCDC 1551626 and 1551625, respectively and can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; Fax: + 441223336033; E-mail: deposit@ccdc.cam.ac.uk.

AUTHOR INFORMATION

Corresponding Author

*E-mail: Koutenti@ucy.ac.cy.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank the Cyprus Research Promotion Foundation (Grant: NEKYP/0308/02) and the following organizations and companies in Cyprus for generous donations of chemicals and glassware: the State General Laboratory, the Agricultural Research Institute, the Ministry of Agriculture, MedoChemie Ltd, Medisell Ltd and Biotronics Ltd. Furthermore, we thank

the A. G. Leventis Foundation for helping to establish the NMR facility at the University of Cyprus.

REFERENCES

1. Blatter, H. M.; Lukaszewski, H. *Tetrahedron Lett.* **1968**, *9*, 2701–2705.

2. Koutentis, P. A.; Krassos, H.; Lo Re, D. *Org. Biomol. Chem*. **2011**, *9*, 5228–5237.

3. (a) Sweeney, M.; Coyle, R.; Kavanagh, P.; Berezin, A. A.; Lo Re, D.; Zissimou, G. A.; Koutentis, P. A.; Carty, M. P.; Aldabbagh, F. *Bioorg. Med. Chem.* **2016**, *24*, 3565–3570. (b) Catto, M.; Berezin, A. A.; Lo Re, D.; Loizou, G.; Demetriades, M.; De Stradis, A.; Campagna, F.; Koutentis, P. A.; Carotti, A. *Eur. J. Med. Chem.* **2012**, *58*, 84–97.

4. Berezin, A. A.; Koutentis, P. A. *Org. Biomol. Chem.* **2014**, *12*, 1641–1648.

5. (a) Neugebauer, F. A.; Umminger, I. *Chem. Ber.* **1980**, *113*, 1205-1225. (b) Neugebauer, F. A.; Umminger, I. *Chem. Ber.* **1981**, *114*, 2423–2430. (c) Neugebauer, F. A.; Rimmler, G. *Magn. Reson. Chem.* **1988**, *26*, 595-600. (d) Mukai, K.; Inoue, K.; Achiwa, N.; Jamali, J. B.; Krieger, C.; Neugebauer, F. A. *Chem. Phys. Lett.* **1994**, *224*, 569-575.

6. (a) Kadirov, M. K.; Il'yasov, A. V.; Vafina, A. A.; Buzykin, B. I.; Gazetdinova, N. G.; Kitaev, Yu. P. *Izv. Akad. Nauk SSSR*, *Ser. Khim.* **1984**, *33*, 649-650. (b) Kadirov, M. K.; Buzykin, B. I.; Gazetdinova, N. G. *Russ. Chem. Bull.* **2002**, *51*, 1796–1799.

7. Hutchison, K. A.; Srdanov, G.; Menon, R.; Gabriel, J.-C. P.; Knight, B.; Wudl, F. *J. Am. Chem. Soc.* **1996**, *118*, 13081–13082.

8. (a) Hutchison, K.; Srdanov, G.; Hicks, R.; Yu, H.; Wudl, F.; Strassner, T.; Nendel, M.; Houk, K. N. *J. Am. Chem. Soc.* **1998**, *120*, 2989–2990. (b) Constantinides, C. P.; Zissimou, G. A.; Berezin, A. A.; Ioannou, T. A.; Manoli, M.; Tsokkou, D.; Theodorou, E.; Hayes, S. C.; Koutentis, P. A. *Org. Lett.* **2015**, *17*, 4026-4029.

9. (a) Yan, B.; Cramen, J.; McDonald, R.; Frank, N. L. *Chem. Commun.* **2011**, *47*, 3201-3203. (b) Constantinides, C. P.; Berezin, A. A.; Zissimou, G. A.; Manoli, M.; Leitus, G. M.; Bendikov, M.; Probert, M. R.; Rawson, J. M.; Koutentis, P. A. *J. Am. Chem. Soc.* **2014**, *136*, 11906–11909. (c) Constantinides, C. P.; Berezin, A. A.; Manoli, M.; Leitus, G. M.; Zissimou, G. A.; Bendikov, M.; Rawson, J. M.; Koutentis, P. A. *Chem.-Eur. J.* **2014**, *20*, 5388–5396. (d) Takahashi, Y.; Miura, Y.; Yoshioka, N. *Chem. Lett.* **2014**, *43*, 1236-1238. (e) Fumanal, M.; Vela, S.; Novoa, J. J.; Ribas-Arino, J. *Chem. Commun.* **2015**, *51*, 15776-15779.

10. (a) Morgan, I. S.; Peuronen, A.; Hänninen, M. M.; Reed, R. W.; Clérac, R.; Tuononen, H. M. *Inorg. Chem.* **2014**, *53*, 33–35. (b) Morgan, I. S.; Mansikkamäki, A.; Zissimou, G. A.; Koutentis, P. A.; Rouzières, M.; Clérac, R.; Tuononen, H. M. *Chem.-Eur. J.* **2015**, *21*, 15843–15853.

11. (a) Demetriou, M.; Berezin, A. A.; Koutentis, P. A.; Krasia-Christoforou, T. *Polym. Int.* **2014**, *63*, 674–679. (b) Areephong, J.; Treat, N.; Kramer, J. W.; Christianson, M. D.; Hawker, C. J.; Collins, H. A. *WO Pat.* 2015/061189 A1, 2015. (c) Areephong, J.; Mattson, K. M.; Treat, N. J.; Poelma, S. O.; Kramer, J. W.; Sprafke, H. A.; Latimer, A. A.; Read de Alaniz, J.; Hawker, C. J. *Polym. Chem.* **2016**, *7*, 370-374.

12. Zheng, Y.; Miao, M.-s.; Kemei, M. C.; Seshadri, R.; Wudl, F. *Isr. J. Chem.* **2014**, *54*, 774–778.

13. Jasiński, M.; Szczytko, J.; Pociecha, D.; Monobe, H.; Kaszyński, P. *J. Am. Chem. Soc.* **2016**, *138*, 9421–9424.

14. Muench, S.; Wild, A.; Friebe, C.; Häupler, B.; Janoschka, T.; Schubert, U. S. *Chem. Rev.* **2016**, *116*, 9438–9484.

15. Gallagher, N. M.; Bauer, J. J.; Pink, M.; Rajca, S.; Rajca, A. *J. Am. Chem. Soc.* **2016**, *138*, 9377–9380.

16. (a) Zheng, Y.; Miao, M.-s.; Dantelle, G.; Eisenmenger, N. D.; Wu, G.; Yavuz, I.; Chabinyc, M. L.; Houk, K. N.; Wudl, F. *Adv. Mater. (Weinheim, Ger.)* **2015**, *27*, 1718–1723. (b) Zhang, Y.; Zheng, Y.; Zhou, H.; Miao, M.-s.; Wudl, F.; Nguyen, T.-Q. *Adv. Mater. (Weinheim, Ger.)* **2015**, *27*, 7412–7419.

17. Ciccullo, F.; Gallagher, N. M.; Geladari, O.; Chassé, T.; Rajca, A.; Casu, M. B. *ACS Appl. Mater. Interfaces* **2016**, *8*, 1805–1812.

18. Berezin, A. A.; Zissimou, G.; Constantinides, C. P.; Beldjoudi, Y.; Rawson, J. M.; Koutentis, P. A. *J. Org. Chem.* **2014**, *79*, 314–327.

19. Constantinides, C. P.; Obijalska, E.; Kaszyński, P. *Org. Lett.* **2016**, *18*, 916–919.

20. Grant, J. A.; Lu, Z.; Tucker, D. E.; Hockin, B. M.; Yufit, D. S.; Fox, M. A.; Kataky, R.; Chechik, V.; O'Donoghue, A. C. *Nat. Commun.* **2017**, *8*, No. 15088.

21. Kaszyński, P.; Constantinides, C. P.; Young, V. G. Jr. *Angew. Chem., Int. Ed.* **2016**, *55*, 11149–11152.

22. (a) Eguchi, S.; Matsushita, Y.; Yamashita, K. *Org. Prep. Proced. Int.* **1992**, *24*, 209-243.

23. Huisgen, R.; Wulff, J. *Chem. Ber*. **1969**, *102*, 1848-1858.

24. (a) Gololobov, Y. G.; Gusar', N. I.; Chaus, M. P. *Tetrahedron* **1985**, *41*, 793-799. (b) Luheshi, A.-B. N.; Salem, S. M.; Smalley, R. K.; Kennewell, P. D.; Westwood, R. *Tetrahedron Lett.* **1990**, *31*, 6561-6564. (c) Fresneda, P. M.; Molina, P.; Delgado, S. *Tetrahedron* **2001**, *57*, 6197-6202. (d) Barthélémy, S.; Schneider, S.; Bannwarth, W. *Tetrahedron Lett.* **2002**, *43*, 807-810. (e) Zhong, Y.; Wang, L.; Ding, M.-W. *Tetrahedron* **2011**, *67*, 3714-3723.

25. (a) Kanomata, N.; Kawaji, H.; Nitta, M. *J. Org. Chem.* **1992**, *57*, 618-625. (b) Palacios, F.; Rubiales, G. *Tetrahedron Lett.* **1996**, *37*, 6379-6382. (c) Anwar, B.; Grimsey, P.; Hemming, K.; Krajniewski, M.; Loukou, C. *Tetrahedron Lett.* **2000**, *41*, 10107-10110. (d) Bonini, C.; D'Auria, M.; Funicello, M.; Romaniello, G. *Tetrahedron* **2002**, *58*, 3507-3512. (e) Palacios, F.; Herrán, E.; Alonso, C.; Rubiales, G. *Tetrahedron* **2006**, *62*, 7661-7666. (f) Palacios, F.; Herrán, E.; Alonso, C.; Rubiales, G.; Lecea, B.; Ayerbe, M.; Cossío, F. P. *J. Org. Chem.* **2006**, *71*, 6020-6030. (g) Nagy, I.; Hajós, G.; Riedl, Z.; Egyed, O.; Pápai, I. *Tetrahedron* **2007**, *63*, 4730-4736. (h) Vicario, J.; Aparicio, D.; Palacios, F. *J. Org. Chem.* **2009**, *74*, 452-455.

26. (a) Staudinger, H.; Meyer, J. *Helv. Chim. Acta* **1919**, *2*, 635-646. (b) Kirsanov, A. V. *IzV. Akad. Nauk. SSSR, Otd. Khim. Nauk.* **1950**, 426-431. (c) Kostina, v. G.; Feshchenko, N. G.; Rutkovskii, E. K.; *Zh. Obshch. Khim*. **1983**, *53,* 1223-1226.

27. (a) Cohen, S. G.; Nicholson, J. *J. Org. Chem.* **1965**, *30*, 1162-1168. (b) Li, J.-P.; Liu, P.; Xue, W.-X.; Wang, Y.-L. *J. Chin. Chem. Soc.* **2003**, *50*, 433-435. (c) Bowman, W. R.; Forshaw, J. A.; Hall, K. P.; Kitchin, J. P.; Mott, A. W. *Tetrahedron* **1996***, 52,* 3961-3972.

28. Lide, D. R. *CRC Handbook of Chemistry and Physics: A Ready-Reference Book of Chemical and Physical Data*. Boca Raton: CRC Press, 2004.

29. Bodzioch, A.; Zheng, M.; Kaszyński, P.; Utecht, G. *J. Org. Chem.* **2014**, *79*, 7294−7310.

30. McConnell, H. M. *J. Chem. Phys.* **1958**, *28*, 1188-1192.

31. (a) Singel, D. J.; van der Poel, W. A. J. A.; Schmidt, J.; van der Waals, J. H.; de Beer, R. *J. Chem. Phys.* **1984**, *81*, 5453-5461. (b) Stoll, S.; NejatyJahromy, Y.; Woodward, J. J.; Ozarowski, A.; Marletta, M. A.; Britt, R. D. *J. Am. Chem. Soc.* **2010**, *132*, 11812-11823. (c) Luzon, J.; Campo, J.; Palacio, F.; McIntyre, G. J.; Rawson, J. M.; Less, R. J.; Pask, C. M.; Alberola, A.; Farley, R. D.; Murphy, D. M.; Goeta, A. E. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *81*, No. 144429.

32. Morton, J. R.; Preston, K. F. *J. Magn. Reson. (1969-1992)* **1978**, *30*, 577-582.

33. Berezin, A. A.; Zissimou, G.; Constantinides, C. P.; Beldjoudi, Y.; Rawson, J. M.; Koutentis, P. A. *J. Org. Chem.* **2015**, *80*, 8943–8944.

34. (a) Jannakoudakis, P. D.; Karabinas, P.; Theodoridou, E. *Z. Phys. Chem. (Muenchen, Ger.)* **1982**, *131*, 89-100. (b) Bu, J.; Lilienthal, N. D.; Woods, J. E.; Nohrden, C. E.; Hoang, K. T.; Truong, D.; Smith, D. K. *J. Am. Chem. Soc.* **2005**, *127*, 6423-6429.

35. Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165-195.

36. (a) Gainsford, G. J.; Woolhouse, A. D. *Aust. J. Chem.* **1980**, *33*, 2447–2454. (b) Schmidt, R. R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 581–591. (c) Butler, R. N.; Evans, A. M.; McNeela, E. M.; O'Halloran, G. A.; O'Shea, P. D.; Cunningham, D.; McArdle, P. *J. Chem. Soc.*, *Perkin Trans. 1* **1990**, 2527–2536.

37. Krieger, C.; Neugebauer, F. A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1996**, *52*, 3124-3126.

38. Takahashi, Y.; Miura, Y.; Yoshioka, N. *New J. Chem.* **2015**, *39*, 4783–4789.

39. Harwood, L. M. *Aldrichimica Acta* **1985**, *18*, 25-25.

40. Katritzky, A. R.; Khashab, N. M.; Bobrov, S. *Helv. Chim. Acta* **2005**, *88*, 1664-1675.

41. Johnson, A. W.; Wong, S. C. K. *Can. J. Chem*. **1966**, *44*, 2793-2803.

42. (a) Zhmurova, I. N.; Yurchenko, R. I. *J. Gen. Chem. USSR (Engl. Transl.)* **1968**, *38*, 613. (b) Zhmurova, I. N.; Kirsanov, A. V. *Zh. Obshch. Khim.* **1966**, *36*, 1248-1254.

43. Leffler, J. E.; Temple, R. D. *J. Am. Chem. Soc.* **1967**, *89*, 5235-5246.

44. Lambrecht, J.; Gambke, B.; von Seyerl, J.; Huttner, G.; von Nell, G. K.; Herzberger, S.; Jochims, J. C. *Chem. Ber.* **1981**, *114*, 3751-3771.

45. Zbiral, E. *Tetrahedron Lett.* **1966**, *7*, 2005-2008.

46. Garve, L. K. B.; Petzold, M.; Jones, P. G.; Werz, D. B. *Org. Lett.* **2016**, *18*, 564–567.

47. Zhang, C.-Y.; Liu, X.-H.; Wang, B.-L.; Wang, S.-H.; Li, Z.-M. *Chem*. *Biol*. *Drug Des*. **2010**, *75*, 489-493.

48. Lockemann, G. *Ber. Dtsch. Chem. Ges.* **1942**, *75*, 1911–1921.

49. Herkes, F. E. *J. Fluorine Chem.* **1979**, *13*, 1–21.

50. Stoll, S.; Schweiger, A. *J. Magn. Reson.* **2006**, *178*, 42-55.

51. Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877-910.

52. *CrysAlis CCD and CrysAlis RED*, version 1.171.32.15; Oxford Diffraction Ltd: Abingdon, Oxford, England, 2008.

53. Sheldrick, G. M. *SHELXL-97: A Program for the Refinement of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1997.

54. Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837−838.

55. Brandenburg, K. *DIAMOND*, version 3.1d; Crystal Impact GbR: Bonn, Germany, 2006.

56. McNab, H.; Murray, M. E.-A. *J. Chem. Soc.*, *Perkin Trans. 1* **1989**, 583-587.

57. Gastaldi, C. *Gazz. Chim. Ital.* **1912**, *41*, 319-324.

58. Yang, L.; Wang, F.; Lee, R.; Lv, Y.; Huang, K.-W.; Zhong, G. *Org. Lett*. **2014**, *16,* 3872-3875.

59. Koutentis, P. A.; Lo Re, D. *Synthesis* **2010**, 2075–2079.