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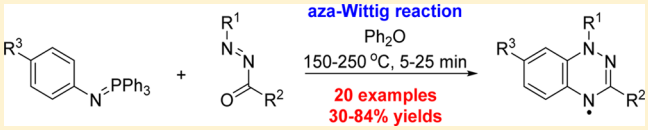
Preparation of Blatter Radicals via Aza-Wittig Chemistry: The Reaction of *N*-Aryliminophosphoranes with 1-(Het)aroyl-2-aryldiazenes

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*[,†]

[†]Department of Chemistry and [‡]Department of Physics, University of Cyprus, P.O. Box 20537, 1678 Nicosia, Cyprus

Supporting Information

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 EPR and CV studies for the radicals. 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.



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] whereas 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]

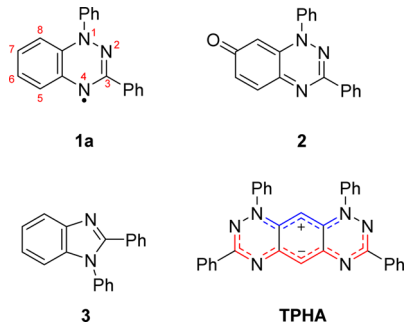
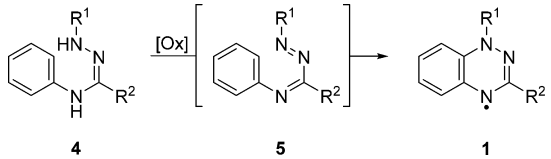


Figure 1. Structures of Blatter radical **1a** with IUPAC numbering (in red), benzotriazinone **2**, 1,2-diphenylbenzimidazole **3**, and Wudl's TPHA.

Since then, extensive studies have been reported on their interesting magnetic properties,[9] and several new applications of Blatter-type radicals have appeared, for example, 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] and as high-spin diradicals[15] and biradicaloids.[16] Furthermore, 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. Until recently, the most commonly used synthesis of Blatter radicals involved the oxidative cyclization 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



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

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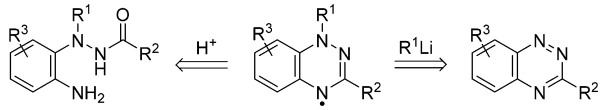
protocol[9b] and the regioselective addition of aryllithium agents to preformed benzo[*e*][1,2,4]triazines **7**[19] (Scheme 2).

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

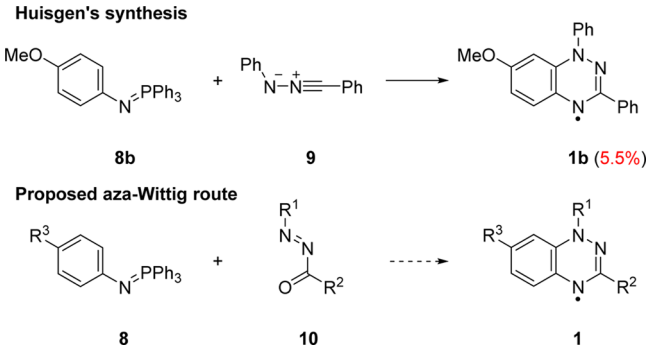


6 **1** **7**

Although 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 information, 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. 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 toward 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 from 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).

Initially, all three oxidation protocols were screened for the conversion of *N*′-phenylbenzohydrazide (**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 and 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** and **11g**) or *N*-pentafluorophenyl groups (e.g., hydrazides **11f** and **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.

The structure, which was surprisingly nonplanar (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 benzotriazines **12**. These, on air oxidation or on treatment with alkali in air, should afford the desired radicals **1** (Scheme 4).

As predicted, the treatment of 1-(het)aroyl-2-aryldiazenes **10** (1 equiv) with the corresponding *N*-aryliminophosphorane **8**

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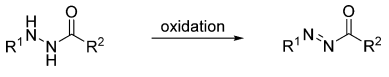
Table 1. Oxidation of *N*′-Aryl(het)arenohydrazides 11 to 1-(Het)aroyl-2-diazenes 10



11 10

entry	R^1	R^2	reagents (equiv)	solvent	temp (°C)	time (h)	yield of **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)

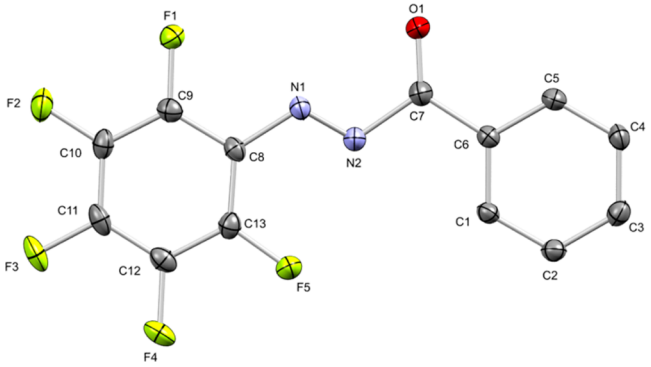
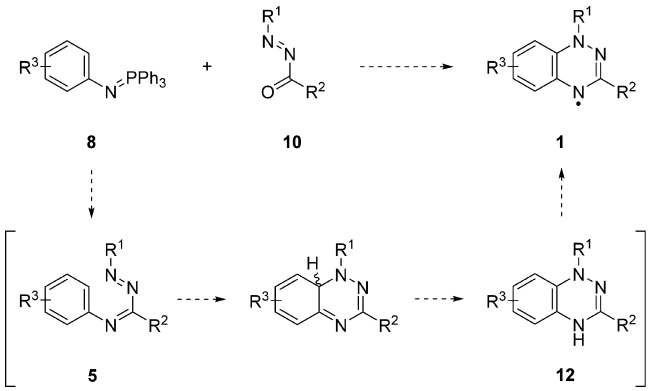


Figure 2. ORTEP view of 1-benzoyl-2-(perfluorophenyl)diazene (**10f**) (CCDC 1551626). Crystallographic atom numbering shown. Hydrogens omitted for clarity. Ellipsoids at 50% probability.

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



(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).

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, and 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 due 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-nitrophenyl-iminophosphoranes (**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 to 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 calorimetry (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 the 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 prevents 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.

2.1. 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} ~ 7.5 G), with N2 and N4 bearing smaller but similar spin densities (a_{N2} ~ 4.8 G and a_{N4} ~ 5.2 G) (Table 3). Elegant EPR and ENDOR studies by Neugebauer on ^{15}N-labeled derivatives reveal the coupling constants to be 4.9 G for N2 and 5.2 G for N4 ($a_{N1} \gg a_{N4} > a_{N2}$).[5c]

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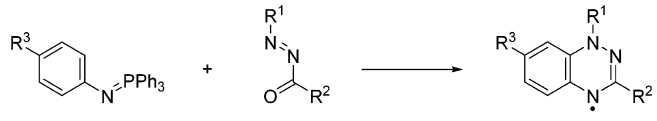
Table 2. Preparation of Blatter Radicals 1 via the Aza-Wittig Reaction



8 10 1

entry	R^1	R^2	R^3	8/10 mol ratio	temp (°C)	time (min)	yield of 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-diphenylbenzo[*e*][1,2,4]triazin-7(*H*)-one (**2**) observed by TLC.

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

			α (G)			
entry	radical	*g*	N1	N2	N4	/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**	2.0077	7.41	4.52	4.52	3.41/F[c]
5	**1l**[b]	2.0077	7.36	4.51	4.52	3.42/F[c]
6	**1m**	2.0042	7.62	4.91	5.02	
7	**1n**	2.0036	8.05	4.98	5.05	3.21/F[c]
8	**1n**[b]	2.0037	7.71	4.91	4.91	3.18/F[c]
9	**1o**	2.0041	7.74	4.75	5.07	
10	**1q**	2.0037	8.12	4.66	5.32	3.17/F[c]
11	**1q**[b]	2.0038	7.85	4.56	5.04	3.24/F[c]
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	6.57	5.20	5.26	2.11/F[d]
15	**1t**[b]	2.0040	6.70	5.17	5.30	2.11/F[d]
16	**1u**	2.0056	7.17	5.26	5.74	3.59/F[c]
17	**1u**[b]	2.0057	6.86	5.09	5.48	3.60/F[c]
18	**1v**	2.0040	6.97	5.19	5.54	3.56/F[c]
19	**1v**[b]	2.0040	6.93	5.15	5.50	3.59/F[c]

[a]Radical **1e** is known (ref 11b), but no EPR data have been reported; as such, it is included. [b]Second derivative. [c]Three equivalent F atoms (CF_3). [d]Two equivalent *ortho* F atoms (C_6F_5).

Solution EPR spectra of radicals **1e,g,k–o,q–v** [section 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 non-equivalent ^{14}N nuclei. EPR spectra of F_3C-containing radicals (**1l**, **1n**, **1q**, **1u**, and **1v**) show additional coupling to ^{19}F atoms (Figures S1.4, S1.6, S1.8, S1.12, and S1.13 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 the F_3C group attached on C7, are slightly larger because of the mesomeric influence of F lone pairs.

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 perfluorophenyl substituent in radicals **1t–v** decreases slightly the spin density on N1 to ~0.27. 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.

2.2. 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, section 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

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Table 4. Spin Densities (ρ_N) of New Radicals 1e,g,k−o,q−v Estimated from Hyperfine Coupling Constants Using McConnell's Equation[30]

entry	radical	N1	N2	N4
1	**1e**[a]	0.330	0.214	0.250
2	**1g**	0.307	0.214	0.233
3	**1k**	0.305	0.210	0.245
4	**1l**	0.296	0.213	0.213
5	**1l**[b]	0.294	0.213	0.213
6	**1m**	0.305	0.232	0.237
7	**1n**	0.322	0.235	0.238
8	**1n**[b]	0.308	0.232	0.232
9	**1o**	0.310	0.224	0.239
10	**1q**	0.346	0.220	0.251
11	**1q**[b]	0.314	0.215	0.237
12	**1r**	0.328	0.212	0.243
13	**1s**	0.299	0.239	0.250
14	**1t**	0.263	0.245	0.248
15	**1t**[b]	0.268	0.244	0.250
16	**1u**	0.287	0.248	0.270
17	**1u**[b]	0.274	0.240	0.258
18	**1v**	0.279	0.245	0.261
19	**1v**[b]	0.277	0.243	0.259

[a]Radical **1e** is known (ref 11b), but no EPR data have been reported; as such, it is included. [b]Second derivative. $A_N = Q_N \cdot \rho_N$ 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]

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, section S4), which 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.

Strong electron-withdrawing groups, such as $-CF_3$ (σ_{meta} 0.43; σ_{para} 0.54),[35] and $-C\equiv N$ (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 and 4). 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). Whereas the C_6F_5 is clearly not as powerful as an electron-withdrawing group as either CF_3 and $C\equiv N$ 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 and 20).

The above data support 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 materials science.

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

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

entry	radical	$E^{ox}_{1/2}$ (V)	$E^{red}_{1/2}$ (V)	$E^{red2}_{1/2}$ (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

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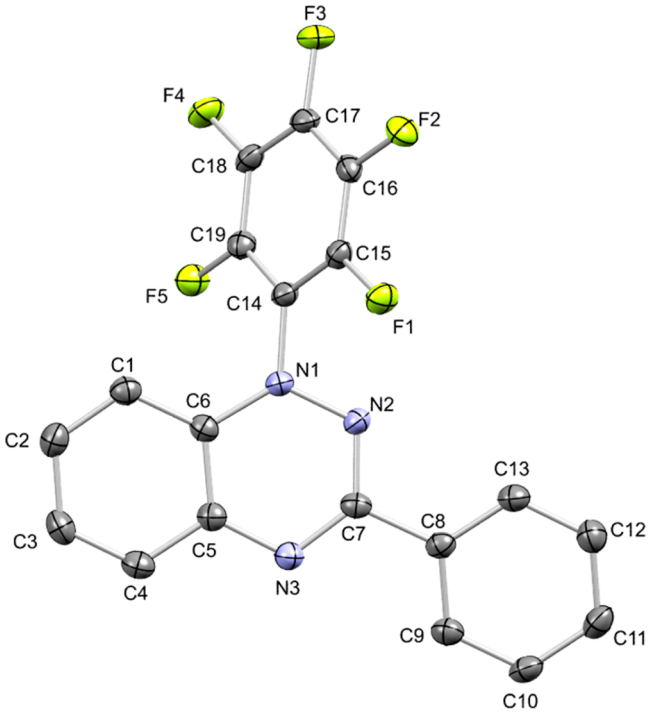

Figure 3. Intramolecular geometry of radical **1t** (CCDC 1551625) along with the crystallographic atom numbering (hydrogens are omitted for clarity reasons, and ellipsoids are at 50% probability).

Radical **1t** crystallized in the monoclinic $P2_1/c$ space group with one molecule in the asymmetric unit cell. The C7−N2 and C7−N3 bond lengths [1.333(2) 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 pressure. 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 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 PerkinElmer 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 the 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, and ESI-APCI$^+$ mass spectra were recorded on a model 6110 Quadrupole MSD, Agilent Technologies. Elemental analysis was performed on a PerkinElmer 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)iminophosphorane (**8f**),[41] *N*-(4-fluorophenyl)(triphenyl)iminophosphorane (**8g**),[43] *N*-(4-chlorophenyl)(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 of 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

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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 was 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_{Fc/Fc^+} = 0.460 V vs SCE).

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

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

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

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

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 ($3.76 \le \theta \le 28.77°$) and 2149 ($3.03 \le \theta \le 24.99°$) reflections for **10f** and **1t**, respectively. Empirical absorption corrections (multiscan based on symmetry-related measurements) were applied using CrysAlis RED software.[52] The structures were solved by direct method and 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 $P\bar{1}$, 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 [$I > 2\sigma(I)$], 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 [$I > 2\sigma(I)$], 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; λ_{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 CF), 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 a 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); λ_{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); λ_{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; λ_{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, $^4J_{CF}$ 2.5), 123.7 (d), 116.2 (d, $^2J_{CF}$ 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

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then extracted with 1.65 M HCl (2 × 20 mL). The organic phase was separated and sequentially washed first with 0.1 M aqueous $Na_2S_2O_3 \cdot 5H_2O$ (20 mL), then with saturated aqueous $NaHCO_3$ (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); λ_{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 were 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% aqueous 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; λ_{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; λ_{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; λ_{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); λ_{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); λ_{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); λ_{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; λ_{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).

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*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; λ_{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); λ_{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); λ_{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); λ_{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; λ_{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; λ_{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; λ_{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)-iminophosphor-ane (**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; λ_{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).

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*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; λ_{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); λ_{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)-imino-phosphorane (**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; λ_{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; λ_{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; λ_{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; λ_{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)-imino-phosphorane (**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; λ_{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; λ_{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).

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■ ASSOCIATED CONTENT

Supporting Information

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^{1}H 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 **10f** (CIF)

Crystallographic data for **1t** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

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

ORCID

Christos P. Constantinides: 0000-0001-6364-1102

Panayiotis A. Koutentis: 0000-0002-4652-7567

Notes

The authors declare no competing financial interest.

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