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Synthesis of Benzotriazine and Aryltriazene Derivatives Starting from 2-Azidobenzonitrile Derivatives

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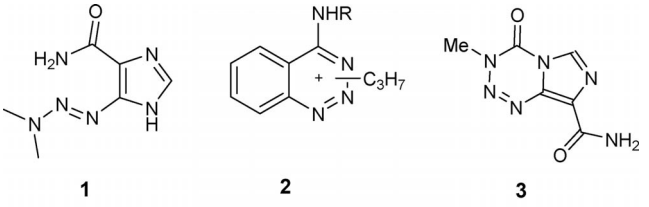
3-Substituted 3,4-dihydro-4-imino-1,2,3-benzotriazine derivatives **7** were formed from 2-azidobenzonitriles **4** as starting materials on treatment with Grignard or lithium organic reagents. In some cases these procedures gave aryltriazenes **10** and **11** as products. All compounds were identified by NMR spectroscopy and the structures of three products, namely **7a**, **10a** and **11i**, were corroborated by X-ray crystallography.

Introduction

Compounds with NNN linkages in either acyclic (e.g., triazenes) or cyclic (e.g., 1,2,3-triazines) arrangements embrace a wide variety of biological activity. A series of triazene derivatives has been reported to have interesting pharmacological properties.[1,2] One of them, namely dacarbazine (**1**),[2–5] is used in the treatment of various cancers, among them leukaemia and malignant melanoma.



Benzotriazine derivatives are another interesting class of compounds and compounds containing this nucleus have shown biological and pharmacological activity. The quaternary 4-arylamino-1,2,3-benzotriazines **2** exhibit a local anaesthetic effect[6] as well as anti-arrhythmic activity.[7] Furthermore, the successful antitumour drug temozolomide (**3**) also features the triazine ring system.[8–10]

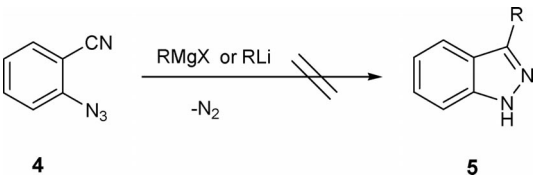
The first synthesis of temozolomide (**3**) used methyl isocyanate (MIC) as a reagent, which afforded both high purity and excellent yields. Unfortunately, due to the high toxicity of MIC and difficulties in handling it on an industrial scale, this is a less than desirable method to use.[11] More recently an improvement of the synthesis of temozolomide has been claimed.[12]

There have been several approaches to the preparation of benzotriazine and its derivatives, primarily by Stevens et al.[13–17] One of the most common methods for the preparation of 3-substituted 3,4-dihydro-4-oxo-1,2,3-benzotriazines involves the cyclization of diazotized starting materials.[18,19] The 4-imino derivatives of 3-substituted 1,2,3-benzotriazine have been prepared by the cyclization of the appropriate *o*-cyanophenyltriazenes.[13]

In this paper we describe a facile and efficient route towards various *o*-cyanophenyltriazene derivatives and also 3-substituted 3,4-dihydro-4-imino-1,2,3-benzotriazine derivatives using 2-azidobenzonitrile derivatives as starting materials. The reactions of different Grignard or organolithium reagents with 2-azidobenzonitrile derivatives have been investigated and the mechanisms studied.

Results and Discussion

The initial strategy of this project was to investigate the possibility of synthesizing 3-substituted indazoles **5** in one step by using 2-azidobenzonitrile (**4**) as a readily available starting material. The anticipated transformation to 3-substituted indazole **5** was based on the treatment of 2-azidobenzonitrile (**4**) with Grignard or lithium reagents (Scheme 1).



Scheme 1.

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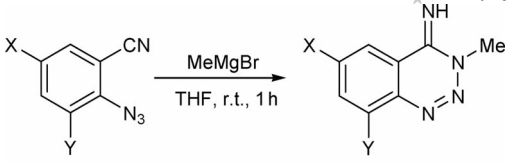
Initially we used the standard conditions developed for the synthesis of 2-azidobenzonitrile (**4**) from 2-aminobenzonitrile (**6**).[20] Exposure of 2-azidobenzonitrile (**4**) to methylmagnesium bromide in THF or diethyl ether at room temperature gave, after work-up, a white solid material in 78% yield, the LC–MS data of which indicated the same mass as 3-methylindazole. However, because NMR and IR analysis did not give clear-cut information about the structure, the molecule was subjected to an X-ray analysis which gave conclusive evidence for 3,4-dihydro-4-imino-3-methyl-1,2,3-benzotriazine (**7a**; Scheme 2, Table 1, entry 1). Details of the X-ray analysis are given in the Exp. Sect. and an ORTEP representation of the molecular structure is shown in Figure 1.

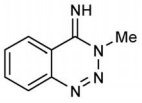
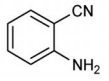
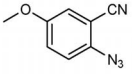
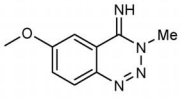
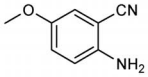
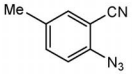
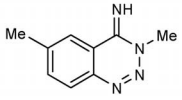
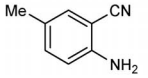
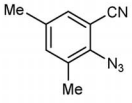
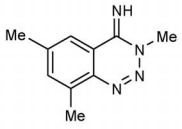
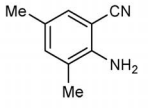
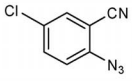
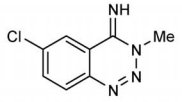
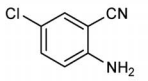
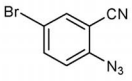
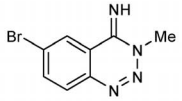
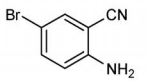
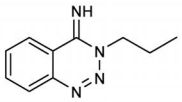
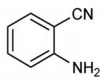
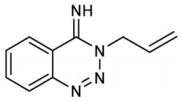
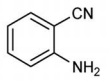


Y = H; X = H, OMe, Me, Cl, Br
Y = X = Me

Scheme 2.

The crystal structure shows that the amine hydrogen N(12)H links the molecules together into weak infinite hydrogen-bonded chains along the crystallographic *b* axis. The packing coefficient (percent filled van der Waals space in the unit cell) is high, 70.5%, which indicates an almost close-packed molecular framework in the solid state. The tight molecular packing is without doubt facilitated by aro-

Table 1. Formation of 3,4-dihydro-4-imino-3-methyl-1,2,3-benzotriazine derivatives **7**.

Entry	Starting compound		Reagent	Product		Yield (%)	By-product		Yield (%)
1		**4a** [20]	MeMgBr		**7a**	78		**6a**	-
2		**4b**	MeMgBr		**7b**	71		**6b** [27]	14
3		**4c** [20]	MeMgBr		**7c**	49		**6c** [28]	34
4		**4d**	MeMgBr		**7d**	56		**6d** [29]	12
5		**4e** [20]	MeMgBr		**7e**	31		**6e** [30]	29
6		**4f**	MeMgBr		**7f**	30		**6f** [31]	50
7		**4a**	propyl-MgBr		**7g**	21		**6a**	40
8		**4a**	allyl-MgCl		**7h**	18		**6a**	38

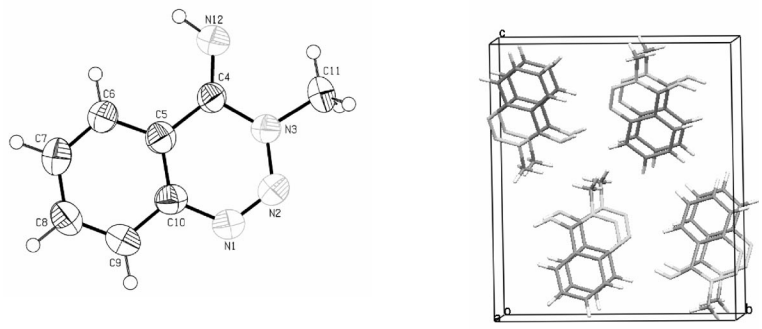


Figure 1. The molecular and crystal structure of 3,4-dihydro-4-imino-3-methyl-1,2,3-benzotriazine (**7a**).

matic π–π stacking. The distance between the planes of two adjacent aromatic moieties is approximately 3.5 Å. It is notable that 3,4-dihydro-4-imino-3-methyl-1,2,3-benzotriazine crystallizes in the chiral space group $P2_12_12_1$.

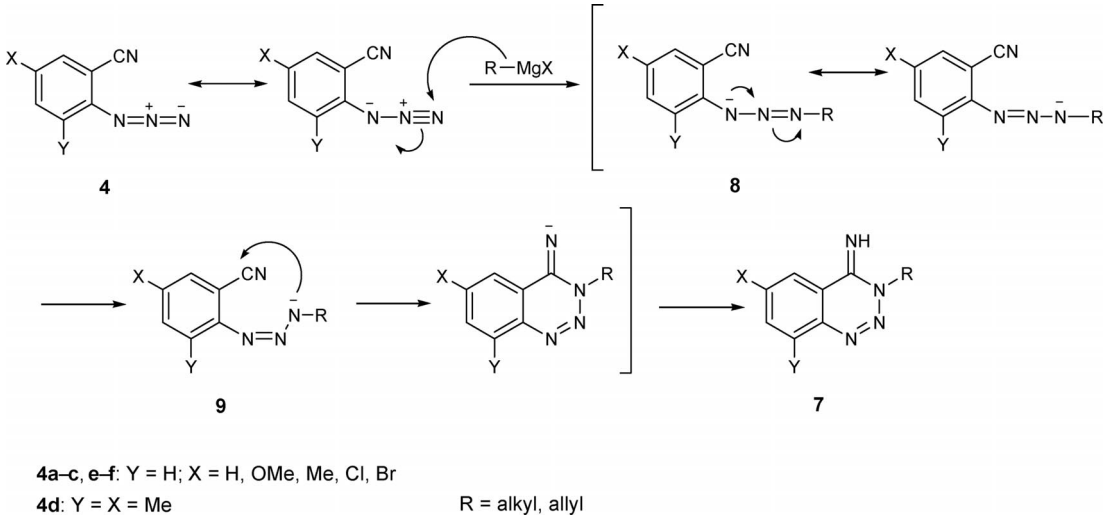
Evidently benzotriazine derivatives readily undergo elimination of nitrogen gas,[21] which explains the LC–MS data of 3,4-dihydro-4-imino-3-methyl-1,2,3-benzotriazine (**7a**), as the recorded mass for **7a** is equal to that of 3-methylindazole. Treatment of 2-azidobenzonitrile derivatives **4** with methylmagnesium bromide delivered the same type of compounds, 3,4-dihydro-4-imino-3-methyl-1,2,3-benzotriazine derivatives **7** (Scheme 2, Table 1, entries 1–6).

It should be noted that simple aromatic azides, for example, 1-azidobenzene, are known[22–24] to add nucleophilic reagents (including Grignard and organolithium reagents[25,26]) and with *o*-azidobenzonitriles clearly the azido function is more attractive than the nitrile function for the Grignard reagent.

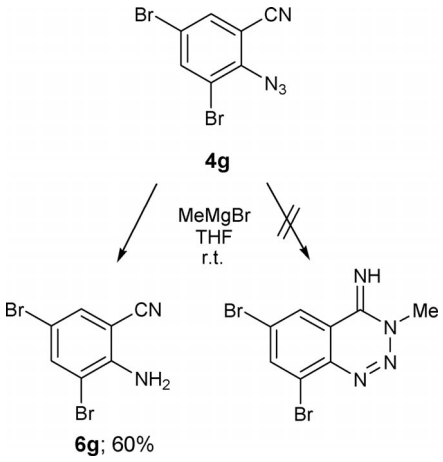
Scheme 3 shows a plausible mechanism for the formation of the 3,4-dihydro-4-imino-3-methyl-1,2,3-benzotriazine derivatives **7a**–**h**. Nucleophilic attack of the Grignard or the lithium reagent on the azide group **4** would give an intermediate of structure **8**. Intramolecular cyclization by a second nucleophilic attack from the nitrogen to the carbon atom of the cyano group (arrow on **9**) will lead to **7** after work-up.

The results shown in Table 1 led us to postulate that the type of products and the yields depend on the substituents on the 2-azidobenzonitrile derivatives **4**. When 2-azidobenzonitriles **4a**–**d** having electron-donating substituents were used as starting materials, 3,4-dihydro-4-imino-3-methyl-1,2,3-benzotriazine derivatives **7a**–**d** were isolated in good yields. On the other hand, when the substituents were electron-withdrawing the yields of the expected products, 3,4-dihydro-4-imino-3-methyl-1,2,3-benzotriazines **7e**–**f**, were lower (Table 1, entries 5 and 6). Because the Grignard reagent works largely as a reducing agent, 2-aminobenzonitrile derivatives **6b**–**f** were also isolated. In analogy with the postulated mechanism outlined in Scheme 3, when other types of aliphatic Grignard reagents were used, the yields of the isolated products, 3-substituted 3,4-dihydro-4-imino-1,2,3-benzotriazines **7g** and **7h** (Table 1, entries 7 and 8), were low (≤20%).

In contrast, when 2-azido-3,5-dibromobenzonitrile (**4g**)[32] was used as the starting material, only one isolable product was obtained in high yield, namely the reduced product 2-amino-3,5-dibromobenzonitrile (**6g**;[33] Scheme 4).



Scheme 3.



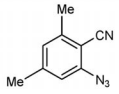
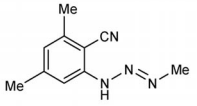
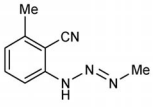
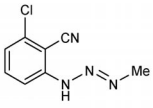
Scheme 4.

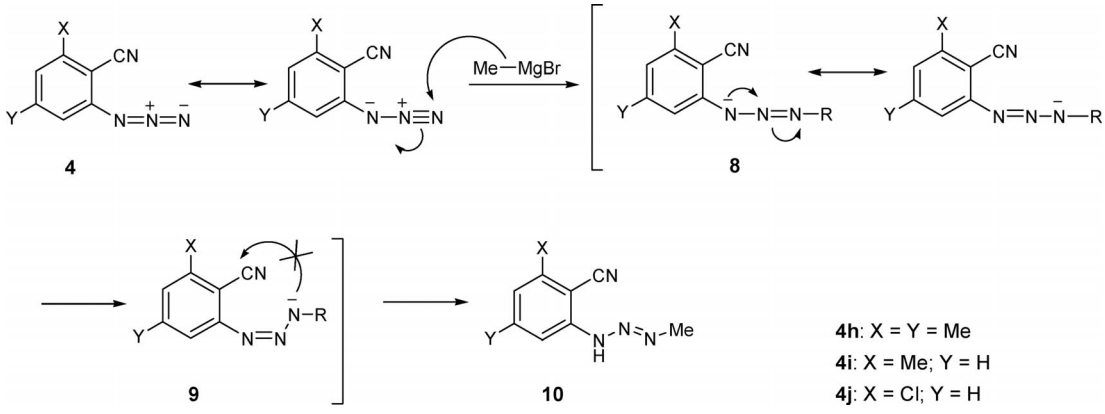
Much to our surprise, when the same reagent (methylmagnesium bromide) was treated with 2-azido-4,6-dimethylbenzonitrile (**4h**) in the same manner, only one isolable product was obtained in 77% yield, 3-methyl-1-(2-cyano-3,5-dimethylphenyl)triazene (**10a**; Table 2, entry 1).

In comparison with the mechanism shown in Scheme 3, we postulate that the 2-azidobenzonitriles **4h**–**j** having a substituent at the 6-position are more hindered with respect to a second nucleophilic attack from the nitrogen to the carbon atom of the cyano group (arrow on **9**). Under these conditions, intramolecular cyclization did not occur, which resulted in the isolation of products **10a**–**c** (Scheme 5, Table 2).

The structure of **10a** was confirmed by X-ray analysis, the details of which are given in the Exp. Sect. and an ORTEP representation of the molecular structure is shown in Figure 2.

Table 2. Reaction of 6-substituted 2-azidobenzonitriles **4** with methylmagnesium bromide.

Entry	Starting compound		Reagent	Product		Yield (%)
1		**4h**	MeMgBr		**10a**	77
2		**4i**	MeMgBr		**10b**	60
3		**4j**[34]	MeMgBr		**10c**	80



Scheme 5.

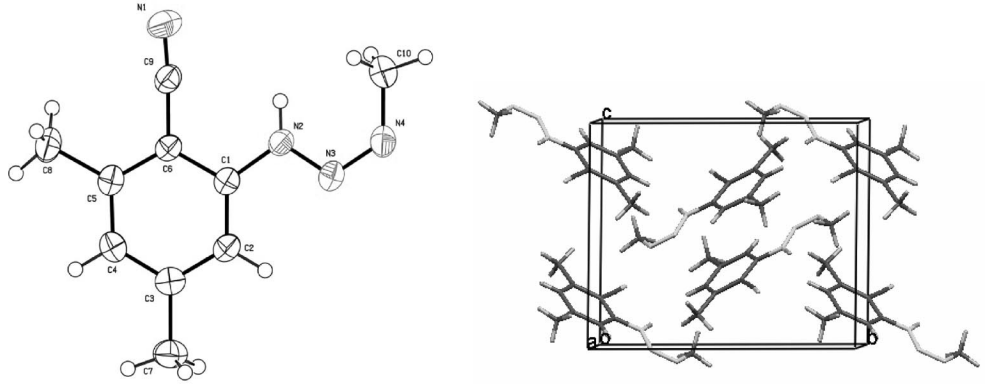
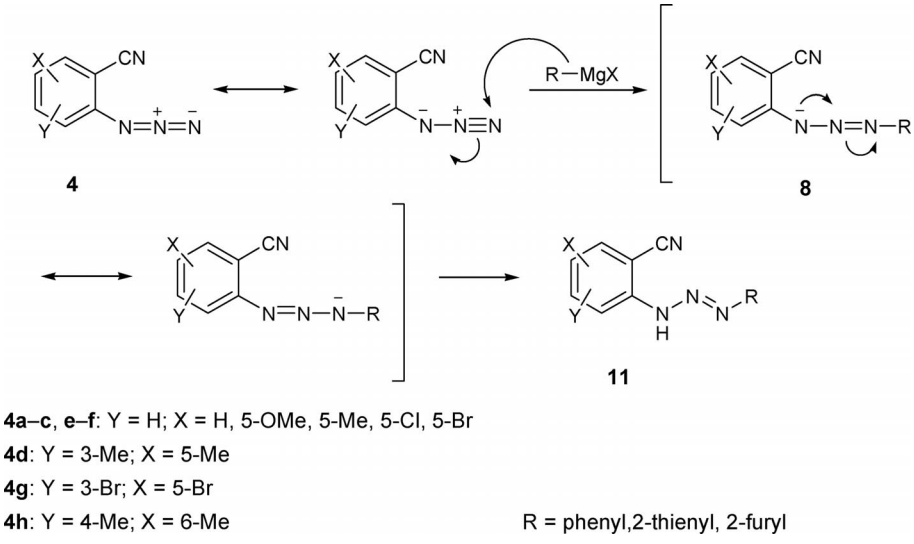


Figure 2. The molecular and crystal structure of 3-methyl-1-(2-cyano-3,5-dimethylphenyl)triazene (**10a**).

There are several features of the crystal structure that merit comment. The hydrogen of the amine N(2)H is positioned *cis* relative to the terminal methyl group C(10). The N(2)H hydrogen is not involved in any classical hydrogen bonding, which is probably due to steric reasons. The molecular energy difference between the *cis* and *trans* conformers is 26 kJ/mol [PW91/6-31++G(2d,2p)]. This indicates that the *trans* conformer should be significantly more stable in vacuo than the *cis* conformer. In the CSD database (CSD 5.30, November 2008) no similar *cis* triazene configuration has been reported. The *cis* conformer is most likely more favourable than the *trans* conformer in the solid state, depending on crystal structure packing effects. Interactions between the nitrile nitrogen N(1) and N(4) lead to an infinite chain approximately along the crystallographic *a* axis direction. The packing coefficient, 67.2%, indicates an efficiently packed molecular framework in the solid state.

When aryl Grignard or lithium reagents were used, the reaction also stopped at intermediate **8** and compounds **11** were isolated (Scheme 6, Table 3). This is presumably due to the stability of the conjugated system between the benzene ring and the aryl groups. The structure of 3-(2-thienyl)-1-(2-cyanophenyl)triazene (**11i**; Table 3, entry 9) was confirmed by X-ray analysis, the details of which are given in the Exp. Sect. and an ORTEP representation of the molecular structure is shown in Figure 3. Although the molecule is non-chiral the compound crystallizes in the non-centrosymmetric chiral space group $P2_12_12_1$ with two independent molecules (A and B) in the unit cell. The molecules are linked into infinite A···B···A···B screw chains running along the crystallographic *a* axis. The packing coefficient, 66.7%, indicates an efficiently packed molecular framework in the solid state.

As expected, when compound **11a** was heated at reflux in alcoholic solvents, cyclization occurred and compound **7i**[13] was isolated without further purification. Many compounds of this structure have previously been prepared and studied.[13,15–17,31,35,36] However, attempts now to extend this chemistry (cyclization of aryltriazenes to benzotriazines) by using the sensitive compounds **11i** and **11j** gave



Scheme 6.

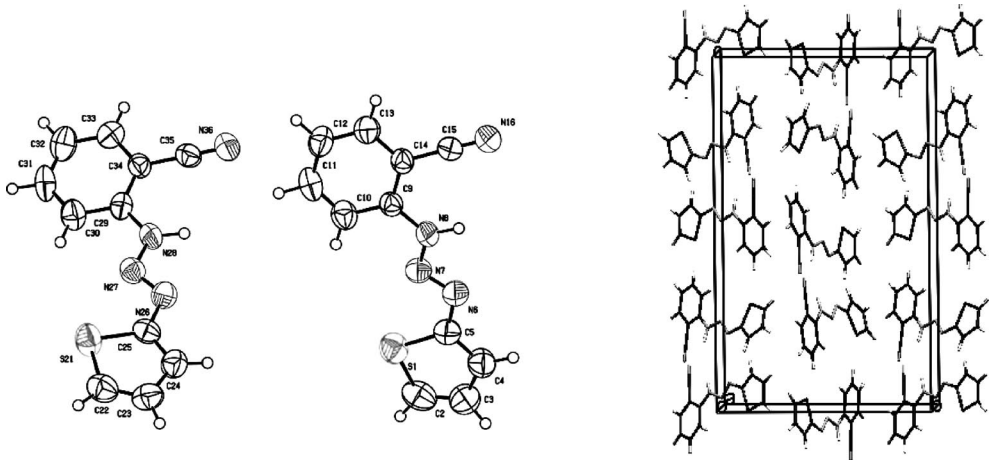
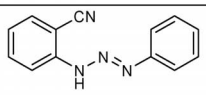
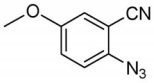
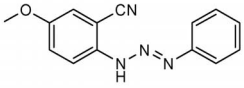
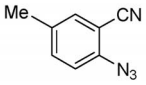
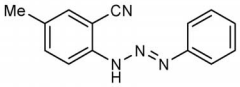
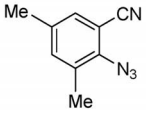
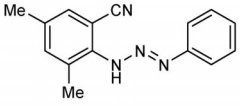
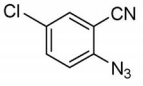
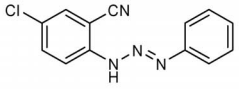
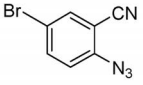
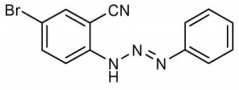
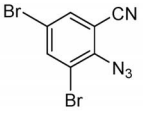
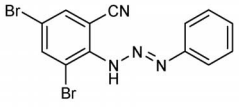
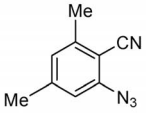
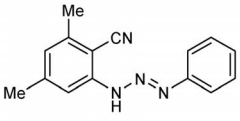
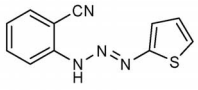
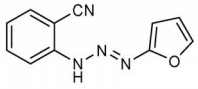


Figure 3. The molecular and crystal structure of 3-(2-thienyl)-1-(2-cyanophenyl)triazene (**11i**).

Table 3. Formation of aryltriazene derivatives **11**.

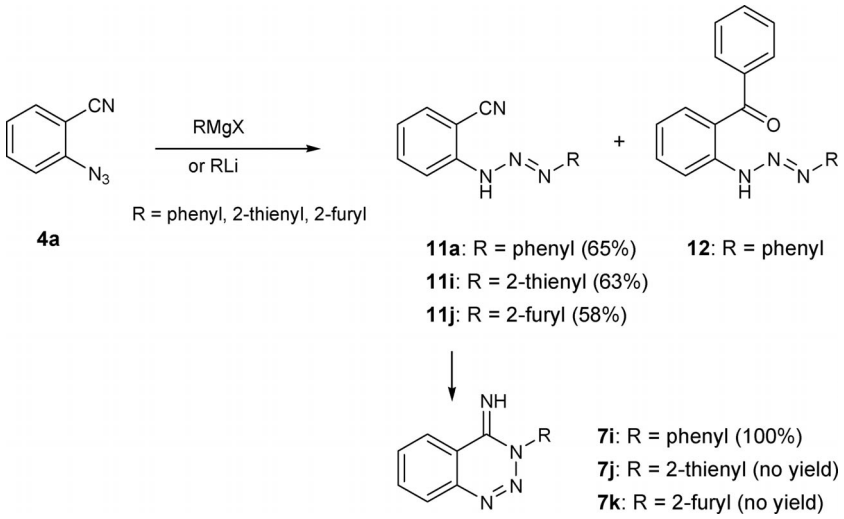
Entry	Starting compound		Reagent	Product		Yield (%)
1		**4a**	PhMgBr		**11a**[13]	65
2		**4b**	PhMgBr		**11b**	49
3		**4c**	PhMgBr		**11c**	70
4		**4d**	PhMgBr		**11d**	56
5		**4e**	PhMgBr		**11e**	71
6		**4f**	PhMgBr		**11f**	63
7		**4g**	PhMgBr		**11g**	54
8		**4h**	PhMgBr		**11h**	54
9		**4a**	(2-thienyl) MgBr		**11i**	63
10		**4a**	(2-furyl)MgBr		**11j**	58

erratic results. Moreover, when 2-azidobenzonitrile (**4a**) was treated with additional equivalents of phenylmagnesium bromide, an additional compound of type **12** was isolated in low yield (Scheme 7).

Conclusions

We have described a simple and efficient synthesis of 3-alkyl-4-imino-1,2,3-benzotriazines by treating 2-azidobenzonitrile derivatives with Grignard or lithium reagents. It has been shown that the effects of electron-withdrawing and -donating substituents on the 2-azidobenzonitriles have a clear impact on the formation of products and their yields. Furthermore, when aryl Grignard or lithium reagents were used the only isolable products were aryltriazene derivatives. However, attempts to achieve the cyclization of aryltriazenes **11i** and **11j** by already reported routes failed.

Finally, we would like to emphasize that the crystal structure of **10a** revealed that the molecular structure in the solid state has an unusual *cis* conformation. This in vacuo energetically unfavourable conformation probably exists in the solid state as a result of crystal structure packing effects.



Scheme 7.

Experimental Section

General: NMR spectroscopic data were recorded with a Bruker DPX 300 instrument operating at 300.1 MHz for ^{1}H and 75.5 MHz for ^{13}C using the residual solvent signal as reference. Assignments were made on the basis of standard ^{1}H, ATP, ^{13}C high-power decoupling (HPDEC) and 1D NOE-DIFF experiments. IR spectra were acquired with a Thermo Nicolet Avatar 330 FT-IR instrument. Melting points were determined with a Leica Kofler hot stage or a Büchi B-545 capillary melting point apparatus. Chromatographic separations were performed on silica gel 60 (40–63 μm). Elemental analyses were performed by H. Kolbe Mikroanalytisches Laboratorium, Mülheim an der Ruhr, Germany, and LSM Lab, Uppsala, Sweden. HRMS (FAB and ESI) was performed by Einar Nilsson, University of Lund, Sweden. Chemicals and solvents were obtained from commercial sources and used as received with the exception of THF, which was distilled from sodium and benzophenone and Et_2O, which were stored over sodium.

CAUTION: A buffered sodium acetate solution containing sodium azide minimizes the formation of toxic hydrazoic acid during reaction. Azides and triazenes are potentially explosive and they are also toxic. These compounds should hence be handled with great care. Use of explosion shields and storage in a refrigerator is necessary.

Single-Crystal X-ray Analysis: X-ray structures were recorded with a Kappa-CCD diffractometer with graphite-monochromated Mo-K_α radiation. Lattice parameters were obtained by least-squares fits to the scattering angles of reflections observed in several pre-scans. The intensity data was collection by ω and ϕ scans. All raw data were corrected for Lorentzian and polarization effects. The structures were solved by direct methods and refined by full-matrix least-squares analysis with anisotropic temperature factors for all atoms except hydrogen atoms. Hydrogen positions were calculated by using known molecular geometries refined in the riding mode with fixed isotropic temperature factors.

CCDC-728275 (for **7a**), -728276 (for **10a**) and -728274 (for **11i**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DFT Geometry Optimization Calculations: The geometries of the *cis* and *trans* conformers of 3-methyl-1-(2-cyano-3,5-dimethylphenyl)triazene (**10a**) were optimized at the PW91/6-31++G(2d,2p) level of theory. The calculations were performed with the Gaussian 03 package.[37]

2-Azidobenzonitrile (4a):[20,38] 2-Aminobenzonitrile (**6a**; 10.0 g, 84.6 mmol) was dissolved by heating in concentrated hydrochloric acid (75 mL) and water (25 mL). The solution obtained was then cooled to 0 °C and diazotized over 0.5 h at 0–5 °C with sodium nitrite (6.54 g, 94.8 mmol) dissolved in a minimum volume of water. The contents were stirred for 15 min, filtered rapidly and the filtrate was added slowly to a solution of sodium azide (5.50 g, 84.6 mmol), sodium acetate (8.2 g, 100 mmol), water (120 mL) and some ice. After a further 0.5 h of stirring at 0–5 °C, the solid product was collected and then washed with water and dried at room temperature in the air to yield **4a** (9.90 g, 81%) as a yellow solid, m.p. 52–53 °C (ref.[38] 58 °C). IR (neat): $\tilde{\nu}$ = 2224, 2138, 2110, 1487, 1445, 1307, 1166, 757 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 7.88–7.70 (m, 2 H), 7.54 (d, J = 8.24 Hz, 1 H), 7.33 (t, J = 7.5 Hz, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 143.0 (s), 134.8 (d), 133.9 (d), 125.4 (d), 119.9 (d), 115.8 (s), 102.5 (s) ppm.

2-Azido-5-methoxybenzonitrile (4b): This compound was prepared from 2-amino-5-methoxybenzonitrile (**6b**;[27] 1.0 g, 6.75 mmol) according to the procedure given for compound **4a**. The product was obtained as a pale-yellow solid (0.80 g, 68%), m.p. 93–94 °C. IR (neat): $\tilde{\nu}$ = 2225, 2135, 2087, 1496, 1300, 1244, 1027, 821 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 7.48–7.39 (m, 2 H), 7.32 (dd, J = 8.98, 2.98 Hz, 1 H), 3.79 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 156.2 (s), 135.3 (s), 121.7 (d), 121.2 (d), 117.6 (d), 115.6 (s), 103.1 (s), 56.0 (q) ppm. HRMS (FAB): calcd. for $C_8H_6N_4O$ [M + H]$^+$ 175.0620; found 175.0608.

2-Azido-5-methylbenzonitrile (4c):[20] This compound was prepared from 2-amino-5-methylbenzonitrile (**6c**;[28] 3.40 g, 25.5 mmol) according to the procedure given for compound **4a**. The product was obtained as a yellow solid (3.65 g, 91%), m.p. 58–61 °C (ref.[20] 61–62 °C). IR (neat): $\tilde{\nu}$ = 2928, 2227, 2120, 2082, 1491, 1298, 1280, 818 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 7.64–7.61 (m, 1 H), 7.58–7.52 (m, 1 H), 7.41 (d, J = 8.68 Hz, 1 H), 2.30 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 140.1 (s), 135.4 (d), 135.2 (s), 133.7 (d), 119.6 (d), 115.8 (s), 102.3 (s), 19.8 (q) ppm.

2-Azido-3,5-dimethylbenzonitrile (4d): This compound was prepared from 2-amino-3,5-dimethylbenzonitrile (**6d**;[29] (0.85 g, 5.8 mmol) according to the procedure given for compound **4a**. The product was obtained after extraction with EtOAc (3 × 20 mL) followed by evaporation which resulted in a yellow oil (0.92 g, 91%). IR (neat): $\tilde{\nu}$ = 2228, 2122, 2091, 1472, 1434, 1319, 1277, 863 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 7.47 (s, 1 H), 7.39 (s, 1 H), 2.30 (s, 3 H), 2.27 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 137.0 (d), 136.6 (s), 135.8 (s), 132.5 (s), 131.8 (d), 115.9 (s), 104.9 (s), 19.8 (q), 17.2 (q) ppm. HRMS (ESI): calcd. for $C_9H_8N_4$ $[M]^+$ 172.0749; found 172.0740.

2-Azido-5-chlorobenzonitrile (4e):[20] This compound was prepared from 2-amino-5-chlorobenzonitrile (**6e**;[30] 2.85 g, 18.7 mmol) according to the procedure given for compound **4a**. The product was obtained as a yellow solid (2.40 g, 72%), m.p. 86–88 °C (ref.[20] 85 °C). IR (neat): $\tilde{\nu}$ = 3069, 2922, 2233, 2126, 2088, 1486, 1301, 833 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 8.02 (d, J = 2.46 Hz, 1 H), 7.80 (dd, J = 8.82, 2.46 Hz, 1 H), 7.56 (d, J = 8.82 Hz, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 142.2 (s), 134.6 (d), 133.1 (d), 128.9 (s), 121.8 (d), 114.6 (s), 103.9 (s) ppm.

2-Azido-5-bromobenzonitrile (4f): This compound was prepared from 2-amino-5-bromobenzonitrile (**6f**;[31] 5.0 g, 25.5 mmol) according to the procedure given for compound **4a**. The product was obtained as a yellow solid (4.50 g, 79%), m.p. 94–97 °C. IR (neat): $\tilde{\nu}$ = 3064, 2231, 2124, 1483, 1465, 1303, 1112, 831 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 8.12 (d, J = 2.3 Hz, 1 H), 7.92 (dd, J = 8.8, 2.3 Hz, 1 H), 7.50 (d, J = 8.8 Hz, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 142.6 (s), 137.4 (d), 135.8 (d), 122.0 (d), 116.5 (s), 114.4 (s), 104.3 (s) ppm. HRMS (FAB): calcd. for $C_7H_3BrN_4$ $[M]^+$ 221.9541; found 221.9539.

2-Azido-3,5-dibromobenzonitrile (4g):[32] This compound was prepared from 2-amino-3,5-dibromobenzonitrile (**6g**;[33] 4.50 g, 16.4 mmol) according to ref.[32] The product was obtained as a pale-yellow solid (4.70 g, 95%), m.p. 60–63 °C (ref.[32] 59–60 °C).[32] IR (neat): $\tilde{\nu}$ = 3048, 2228, 2106, 1432, 1324, 1257, 1171, 874 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 8.28 (d, J = 2.2 Hz, 1 H), 8.20 (d, J = 2.2 Hz, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 140.5 (d), 139.0 (s), 135.7 (d), 118.2 (s), 117.9 (s), 113.9 (s), 108.7 (s) ppm.

2-Azido-4,6-dimethylbenzonitrile (4h): This compound was prepared from 2-amino-4,6-dimethylbenzonitrile (**6h**;[39] 4.0 g, 27.4 mmol) according to ref.[32] The product was obtained as a yellow solid (3.56 g, 76%), m.p. 68–69 °C. IR (neat): $\tilde{\nu}$ = 2224, 2144, 2134, 2107, 1312, 1253, 1196, 856 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 7.18 (s, 1 H), 7.05 (s, 1 H), 2.39 (s, 3 H), 2.35 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 145.0 (s), 143.1 (s), 143.0 (s), 127.3 (d), 117.3 (d), 115.1 (s), 100.4 (s), 21.1 (q), 19.9 (q) ppm. HRMS (ESI): calcd. for $C_9H_8N_4$ $[M + H]^+$ 173.0827; found 173.0828.

2-Azido-6-methylbenzonitrile (4i): This compound was prepared from 2-amino-6-methylbenzonitrile (**6i**;[40,41] 0.47 g, 3.6 mmol) according to the procedure given for compound **4a**. The product was obtained as a pale-yellow solid (0.46 g, 81%), m.p. 101–103 °C. IR (neat): $\tilde{\nu}$ = 2221, 2127, 2108, 1595, 1463, 1303, 1162, 779 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 7.62 (t, J = 7.9 Hz, 1 H), 7.34 (d, J = 7.9 Hz, 1 H), 7.23 (d, J = 7.9 Hz, 1 H), 2.45 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 143.5 (s), 143.1 (s), 134.0 (d), 126.3 (d), 116.9 (d), 114.8 (s), 103.2 (s), 20.0 (q) ppm. HRMS (FAB): calcd. for $C_8H_6N_4$ $[M]^+$ 158.0592; found 158.0593.

2-Azido-6-chlorobenzonitrile (4j):[34] This compound was prepared from 2-amino-6-chlorobenzonitrile (**6j**;[41] 4.70 g, 30.8 mmol) according to ref.[34] The product was obtained as a pale-yellow solid (3.90 g, 71%), m.p. 99–101 °C (ref.[34] 101–102 °C). IR (neat): $\tilde{\nu}$ = 2230, 2168, 2121, 1579, 1569, 1444, 1297, 786 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 7.73 (t, J = 8.2 Hz, 1 H), 7.56–7.45 (m, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 145.4 (s), 136.6 (s), 135.3 (d), 125.6 (d), 118.7 (d), 113.1 (s), 103.2 (s) ppm.

2-Amino-5-methoxybenzonitrile (6b):[27] Compound **6b** was prepared in four steps as follows.

2-(Hydroxyimino)-*N*-(4-methoxyphenyl)acetamide: A solution of *p*-anisidine (12.3 g, 0.1 mol) in water (60 mL) and conc. HCl (8.7 mL) were added to a solution of chloral hydrate (18.02 g, 0.109 mol) and sodium sulfate (126.8 g, 0.893 mol) in water (390 mL). The reaction mixture was stirred at room temperature, a solution of hydroxylamine hydrochloride (13.9 g, 0.2 mol) in water (50 mL) was added and the mixture was gently heated at reflux for 1 h. Upon cooling to room temperature and later on ice, brown crystals precipitated from the reaction solution. These crystals were collected by filtration, washed with water and dried at room temperature to afford 2-(hydroxyimino)-*N*-(4-methoxyphenyl)acetamide (16.4 g, 85%), m.p. 185 °C (ref.[42] 184–185 °C). IR (neat): $\tilde{\nu}$ = 3193, 2835, 1728, 1476, 1196, 1032, 1016, 806 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 12.11 (s, 1 H), 10.06 (s, 1 H), 7.66–7.54 (m, 3 H), 6.94–6.85 (m, 2 H), 3.72 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 159.9 (s), 155.7 (s), 144.2 (d), 131.6 (s), 2 × 121.4 (d), 2 × 113.9 (d), 55.2 (q) ppm.

5-Methoxyisatin:[27] 2-(Hydroxyimino)-*N*-(4-methoxyphenyl)acetamide (16.3 g, 84.0 mmol) was added with stirring to 90% sulfuric acid (100 mL) in small portions. When the addition was complete the solution was gently heated to 45 °C at which point the temperature abruptly rose to 110 °C and was maintained for 5 min. The reaction mixture was then cooled, poured onto 10 times its volume of cracked ice and stirred for 1 h. The brownish product was collected by filtration, washed with water and dried at room temperature to afford 5-methoxyisatin as a red solid (10.6 g, 71%), m.p. 201 °C (ref.[43] 201 °C). IR (neat): $\tilde{\nu}$ = 3185, 3102, 1745, 1729, 1489, 1198, 1030, 823 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 10.84 (s, 1 H), 7.17 (dd, J = 8.5, 2.7 Hz, 1 H), 7.05 (d, J = 2.7 Hz, 1 H), 6.84 (d, J = 8.5 Hz, 1 H), 3.74 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 184.7 (s), 159.6 (s), 155.3 (s), 144.7 (s), 124.9 (d), 118.1 (s), 113.3 (d), 108.8 (d), 55.8 (q) ppm.

3-(Hydroxyimino)-5-methoxyisatin:[27] A solution of 5-methoxyisatin (0.9 g, 5.08 mmol) in acetic acid (30 mL) was added to a solution of hydroxylamine (0.35 g, 5.08 mmol) and sodium acetate (0.42 g, 5.12 mmol) in water (30 mL). The solution was stirred at room temperature overnight and the brown precipitate was collected by filtration. The solid was dried at room temperature to afford pure 3-(hydroxyimino)-5-methoxyisatin as a yellow solid (0.54 g, 55%), m.p. 253 °C (ref.[44] 248 °C). IR (neat): $\tilde{\nu}$ = 3193, 2835, 1728, 1476, 1196, 1032, 1016, 806 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 13.33 (s, 1 H), 10.51 (s, 1 H), 7.53 (d, J = 2.7 Hz, 1 H), 6.94 (dd, J = 8.5, 2.7 Hz, 1 H), 6.79 (d, J = 8.5 Hz, 1 H), 3.71 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 164.5 (s), 154.7 (s), 144.5 (s), 136.2 (s), 117.5 (d), 116.4 (s), 112.9 (d), 110.8 (d), 55.6 (q) ppm.

Solid sodium carbonate (0.17 g, 1.56 mmol) was added to a solution of 3-(hydroxyimino)-5-methoxyisatin (0.2 g, 1.04 mmol) in DMF (10 mL) and the reaction mixture was heated to 130 °C. The solution was stirred at this temperature for 2 h, allowed to cool to room temperature and poured into water. The reaction mixture was extracted with diethyl ether (3 × 50 mL). The combined organic solvents were washed several times with water, dried (Na_2SO_4) and evaporated to afford 2-amino-5-methoxybenzonitrile (**6b**; 0.14 g, 89%) as a dark-brown oil. IR (neat): $\tilde{\nu}$ = 3457, 3362, 3233, 2213, 1634, 1499, 1248, 1032 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 6.93 (dd, J = 9.0, 2.9 Hz, 1 H), 6.80 (d, J = 2.9 Hz, 1 H), 6.67 (d, J = 9.0 Hz, 1 H), 4.21 (br. s, 2 H), 3.69 (s, 3 H) ppm. ^{13}C NMR ($CDCl_3$): δ =

151.5 (s), 144.4 (s), 122.7 (d), 117.7 (s), 117.1 (d), 114.5 (d), 95.9 (s), 55.8 (q) ppm.

2-Amino-5-methylbenzonitrile (6c):[28] This compound was prepared from *p*-toluidine in two steps according to ref.[28] The total yield of the desired product was (83%). IR (neat): $\tilde{\nu}$ = 3456, 3364, 3240, 2210, 1630, 1504, 1260, 807 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 7.17–7.08 (m, 2 H), 6.71 (d, J = 8.4 Hz, 1 H), 5.78 (br. s, 2 H), 2.12 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 149.5 (s), 135.0 (d), 131.6 (d), 124.7 (s), 118.2 (s), 115.4 (d), 93.4 (s), 19.4 (q) ppm.

2-Amino-3,5-dimethylbenzonitrile (6d):[29] This compound was prepared from 2,4-dimethylaniline (9.8 g, 80.9 mmol) in two steps according to ref.[29] The product was obtained as a dark-brown oil (4.8 g, 41%). IR (neat): $\tilde{\nu}$ = 3428, 3347, 2215, 1625, 1483, 1286, 1248, 855 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 7.04 (s, 1 H), 5.48 (s, 1 H), 2.11 (s, 3 H), 2.07 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 147.4 (s), 135.9 (d), 129.3 (d), 124.8 (s), 123.0 (s), 118.6 (s), 93.4 (s), 19.5 (q), 17.5 (q) ppm.

2-Amino-5-chlorobenzonitrile (6e):[30] This compound was prepared from 2-aminobenzonitrile (**6a**; 5.0 g, 42.4 mmol) and *N*-chlorosuccinimide (NCS; 5.93 g, 44.4 mmol) according to ref.[30] The product was obtained as a pale-yellow solid (4.3 g, 67%), m.p. 95–96 °C (ref.[45] 95.0–96.3 °C). IR (neat): $\tilde{\nu}$ = 3449, 3356, 2218, 1615, 1488, 1411, 878, 816 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 7.48 (d, J = 2.5 Hz, 1 H), 7.31 (dd, J = 9.0, 2.5 Hz, 1 H), 6.79 (d, J = 9.0 Hz, 1 H), 6.23 (br. s, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 150.7 (s), 134.0 (d), 131.1 (d), 118.5 (s), 117.0 (d), 116.9 (s), 94.3 (s) ppm.

2-Amino-5-bromobenzonitrile (6f):[31] This compound was prepared from 2-aminobenzonitrile (**6a**; 5.0 g, 42.4 mmol) and bromine (2.26 mL, 43.8 mmol) according to ref.[31] The product was obtained as a white solid (5.68 g, 68%), m.p. 94–95 °C (ref.[46] 96–97 °C). IR (neat): $\tilde{\nu}$ = 3434, 3351, 2218, 1629, 1485, 1303, 1255, 828 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 7.58 (d, J = 2.4 Hz, 1 H), 7.41 (dd, J = 9.0, 2.4 Hz, 1 H), 6.74 (d, J = 9.0 Hz, 1 H), 6.26 (br. s, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 151.0 (s), 136.7 (d), 133.9 (d), 117.3 (d), 116.8 (s), 105.2 (s), 95.0 (s) ppm.

2-Amino-3,5-dibromobenzonitrile (6g):[33] Bromine (6.5 mL, 127.1 mmol) was added dropwise to a solution of 2-aminobenzonitrile (**6a**; 5.0 g, 42.4 mmol) in acetic acid (100 mL). The reaction mixture was stirred at room temperature overnight and the white precipitate was collected by filtration. The solid was dried at room temperature to afford the title product **6g** (11.4 g, 98%), m.p. 156 °C (ref.[33] 156–156.5 °C). IR (neat): $\tilde{\nu}$ = 3470, 3359, 2225, 1635, 1470, 1237, 1174, 870 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 7.88 (d, J = 2.3 Hz, 1 H), 7.74 (d, J = 2.3 Hz, 1 H), 6.27 (br. s, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 147.5 (s), 139.0 (d), 134.2 (d), 115.9 (s), 109.3 (s), 105.6 (s), 96.6 (s) ppm.

2-Amino-4,6-dimethylbenzonitrile (6h):[39] This compound was prepared according to ref.[39], m.p. 64–65 °C (ref.[39] 62–63 °C). IR (neat): $\tilde{\nu}$ = 3446, 3365, 3351, 2201, 1636, 1610, 1294, 837 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 6.41 (s, 1 H), 6.31 (s, 1 H), 5.83 (s, 2 H), 2.26 (s, 3 H), 2.14 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 151.9 (s), 143.5 (s), 141.0 (s), 118.3 (d), 117.5 (s), 112.5 (d), 92.0 (s), 21.4 (q), 20.2 (q) ppm.

2-Amino-6-methylbenzonitrile (6i):[40,41] This compound was prepared from 2-methyl-6-nitrobenzonitrile (2.0 g, 12.3 mmol) as according to ref.[40] The product was obtained as a yellow solid (1.04 g, 64%), m.p. 125–127 °C (ref.[40] 127–129 °C). IR (neat): $\tilde{\nu}$ = 3403, 3338, 3232, 2211, 1645, 1474, 1167, 778 cm^{-1}. ^1H NMR ([D$_6$]-DMSO): δ = 7.15 (t, J = 7.9 Hz, 1 H), 6.60 (d, J = 8.3 Hz, 1 H), 6.47 (d, J = 7.9 Hz, 1 H), 5.90 (br. s, 2 H), 2.31 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 151.9 (s), 141.2 (s), 133.2 (d), 117.1 (s), 116.8 (d), 112.4 (d), 94.6 (s), 20.3 (q) ppm.

2-Amino-6-chlorobenzonitrile (6j):[41] This compound was prepared from 2-chloro-6-nitrobenzonitrile (6.57 g, 36.0 mmol) according to ref.[41] The product was obtained as a yellow solid (5.04 g, 92%), m.p. 132–134 °C (ref.[41] 132–136 °C). IR (neat): $\tilde{\nu}$ = 3402, 3335, 3230, 2219, 1646, 1598, 1471, 777 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 7.26 (t, J = 8.2 Hz, 1 H), 6.78–6.66 (m, 2 H), 6.40 (s, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 153.6 (s), 135.0 (s), 134.4 (d), 115.8 (d), 115.3 (s), 113.8 (d), 93.8 (s) ppm.

3,4-Dihydro-4-imino-3-methyl-1,2,3-benzotriazine (7a): 2-Azidobenzonitrile (**4a**; 1.0 g, 6.94 mmol) was dissolved in dry THF (20 mL) and methylmagnesium bromide (3.0 M, 13.89 mmol) was added dropwise at room temperature. After stirring for 1 h, the reaction mixture was quenched with NH_4Cl (20% aq.) and the mixture was stirred for 20 min. The solvent was separated and the aqueous phase extracted with diethyl ether (3 × 50 mL). The combined organic solvents were dried (Na_2SO_4), evaporated and the crude product was purified by column chromatography on silica (heptane/EtOAc) to give of product **7a** (0.87 g, 78%) as a pale-yellow solid, m.p. 108.9–111.7 °C. IR (neat): $\tilde{\nu}$ = 3313, 3031, 1609, 1454, 1250, 1169, 1009, 769 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 8.72 (br. s, 1 H), 8.30 (d, J = 7.47 Hz, 1 H), 7.89–7.85 (m, 1 H), 7.83–7.77 (m, 1 H), 7.75–7.68 (m, 1 H), 3.82 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 149.6 (s), 140.1 (s), 133.1 (d), 131.7 (d), 127.6 (d), 123.5 (d), 117.9 (s), 38.6 (q) ppm. $C_8H_8N_4$ (160.07): calcd. C 59.99, H 5.03, N 34.98; found C 60.4, H 5.5, N 35.0.

3,4-Dihydro-4-imino-6-methoxy-3-methyl-1,2,3-benzotriazine (7b): This compound was prepared from 2-azido-5-methoxybenzonitrile (**4b**; 0.50 g, 2.87 mmol) and methylmagnesium bromide (3.0 M, 5.74 mmol) according to the procedure given for compound **7a**. The crude product was purified by column chromatography on silica (heptane/EtOAc) to yield the product **7b** (0.39 g, 71%) as a yellow solid, m.p. 169.7–172–8 °C. IR (neat): $\tilde{\nu}$ = 3282, 3033, 1607, 1487, 1361, 1245, 1009, 738 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 8.58 (br. s, 1 H), 7.85–7.72 (m, 2 H), 7.34 (dd, J = 8.83, 2.55 Hz, 1 H), 3.90 (s, 3 H), 3.79 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 161.7 (s), 149.6 (s), 135.0 (s), 129.8 (d), 121.4 (d), 119.5 (s), 104.9 (d), 56.2 (q), 38.5 (q) ppm. HRMS (ESI): calcd. for $C_9H_{10}N_4O$ [M + H]$^+$ 191.0933; found 191.0931.

3,4-Dihydro-4-imino-3,6-dimethyl-1,2,3-benzotriazine (7c): This compound was prepared from 2-azido-5-methylbenzonitrile (**4c**; 0.50 g, 3.16 mmol) and methylmagnesium bromide (3.0 M, 6.33 mmol) according to the procedure given for compound **7a**. The crude product was purified by column chromatography on silica (heptane/EtOAc) to yield the product **7c** (0.27 g, 49%) as a yellow solid, m.p. 101.6–103.8 °C. IR (neat): $\tilde{\nu}$ = 3282, 1608, 1572, 1246, 1227, 1023, 998, 833 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 8.55 (br. s, 1 H), 8.11 (s, 1 H), 7.75 (d, J = 8.19 Hz, 1 H), 7.60 (dd, J = 8.19, 1.27 Hz, 1 H), 3.80 (s, 3 H), 2.44 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 149.7 (s), 142.2 (s), 138.3 (s), 134.0 (d), 127.6 (d), 123.0 (d), 117.6 (s), 38.6 (q), 21.3 (q) ppm. HRMS (ESI): calcd. for $C_9H_{10}N_4$ [M + H]$^+$ 175.0984; found 175.0981.

3,4-Dihydro-4-imino-3,6,8-trimethyl-1,2,3-benzotriazine (7d): This compound was prepared from 2-azido-3,5-dimethylbenzonitrile (**4d**; 0.45 g, 2.61 mmol) and methylmagnesium bromide (3.0 M, 5.23 mmol) according to the procedure given for compound **7a**. The crude product was purified by column chromatography on silica (heptane/EtOAc) to yield the product **7d** (0.27 g, 56%) as a yellow solid, m.p. 83.7–85.0 °C. IR (neat): $\tilde{\nu}$ = 3260, 2920, 1606, 1578, 1464, 1227, 974, 773 cm^{-1}. ^1H NMR ([D$_6$]DMSO): δ = 8.26 (br. s, 1 H), 7.90 (s, 1 H), 7.42 (s, 1 H), 3.79 (s, 3 H), 2.56 (s, 3 H),

2.39 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 149.2 (s), 141.6 (s), 136.5 (s), 136.4 (s), 134.9 (d), 120.6 (d), 117.7 (s), 38.5 (q), 21.2 (q), 16.5 (q) ppm. HRMS (FAB): calcd. for $C_{10}H_{12}N_4$ [M + H]$^+$ 189.114; found 189.1144.

6-Chloro-3,4-dihydro-4-imino-3-methyl-1,2,3-benzotriazine (7e): This compound was prepared from 2-azido-5-chlorobenzonitrile (**4e**; 0.53 g, 2.98 mmol) and methylmagnesium bromide (3.0 M, 5.95 mmol) according to the procedure given for compound **7a**. The crude product was purified by column chromatography on silica (heptane/EtOAc) to yield the product **7e** (0.18 g, 31%) as a yellow solid, m.p. 144.6–147.6 °C. IR (neat): $\tilde{\nu}$ = 3280, 1605, 1563, 1461, 1249, 1204, 1009, 840 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 8.93 (br. s, 1 H), 8.50 (s, 1 H), 7.90 (d, J = 8.6 Hz, 1 H), 7.84 (dd, J = 8.6, 2.1 Hz, 1 H), 3.81 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 148.5 (s), 138.8 (s), 136.2 (s), 133.2 (d), 129.8 (d), 123.3 (d), 119.4 (s), 38.8 (q) ppm. HRMS (ESI): calcd. for $C_8H_7ClN_4$ [M + H]$^+$ 195.0437; found 195.0434.

6-Bromo-3,4-dihydro-4-imino-3-methyl-1,2,3-benzotriazine (7f): This compound was prepared from 2-azido-5-bromobenzonitrile (**4f**; 1.0 g, 4.50 mmol) and methylmagnesium bromide (3.0 M, 9.01 mmol) according to the procedure given for compound **7a**. The crude product was purified by column chromatography on silica (heptane/EtOAc) to yield the product **7f** (0.32 g, 30%) as a yellow solid, m.p. 148.8–152.9 °C. IR (neat): $\tilde{\nu}$ = 3262, 2938, 1619, 1457, 1257, 1198, 1011, 819 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 8.95 (br. s, 1 H), 8.61 (s, 1 H), 7.97 (dd, J = 8.6, 2.1 Hz, 1 H), 7.80 (d, J = 8.6 Hz, 1 H), 3.80 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 148.3 (s), 139.1 (s), 136.1 (d), 129.8 (d), 126.4 (d), 124.9 (s), 119.6 (s), 38.9 (q) ppm. HRMS (ESI): calcd. for $C_8H_7BrN_4$ [M + H]$^+$ 238.9932; found 238.9938.

3,4-Dihydro-4-imino-3-propyl-1,2,3-benzotriazine (7g): This compound was prepared according to the procedure given for compound **7a** using 2-azidobenzonitrile (**4a**; 1.0 g, 6.94 mmol) and freshly prepared propylmagnesium bromide (13.89 mmol) in dry THF (30 mL). The resulting mixture was stirred at room temp. for 1 h and thereafter heated at reflux for 3 h. The crude product was purified by column chromatography on silica (heptane/EtOAc) to yield the product **7g** (0.28 g, 21%) as a brown oil. IR (neat): $\tilde{\nu}$ = 3289, 2963, 2874, 1612, 1463, 1172, 1043, 769 cm^{-1}. ^{1}H NMR ([D$_6$]-DMSO): δ = 8.70 (br. s, 1 H), 8.31 (d, J = 7.84 Hz, 1 H), 7.91–7.68 (m, 3 H), 4.30 (t, J = 7.19 Hz, 2 H), 1.91–1.74 (m, 2 H), 0.92 (t, J = 7.43 Hz, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 150.0 (s), 140.7 (s), 134.0 (d), 132.6 (d), 128.5 (d), 124.5 (d), 118.8 (s), 52.6 (t), 21.5 (t), 11.9 (q) ppm.

3-Allyl-3,4-dihydro-4-imino-1,2,3-benzotriazine (7h): This compound was prepared according to the procedure given for compound **7a** using 2-azidobenzonitrile (**4a**; 1.0 g, 6.94 mmol) and allylmagnesium chloride (2.0 M, 13.89 mmol) in dry THF (30 mL). The resulting mixture was stirred at room temp. for 1 h and thereafter heated at reflux for 3 h. The crude product was purified by column chromatography on silica (heptane/EtOAc) to yield the product **7h** (0.23 g, 18%) as a brown oil. IR (neat): $\tilde{\nu}$ = 3179, 3078, 2904, 1621, 1497, 1346, 913, 738 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 12.74 (br. s, 1 H), 7.74–7.65 (m, 1 H), 7.53–7.44 (m, 1 H), 7.38–7.27 (m, 1 H), 7.12–7.02 (m, 1 H), 6.16–5.98 (m, 1 H), 5.24–4.99 (m, 2 H), 3.70 (d, J = 6.50 Hz, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 142.9 (s), 140.9 (s), 135.9 (d), 125.8 (d), 121.5 (s), 120.0 (d), 119.5 (d), 116.0 (t), 110.0 (d), 31.3 (t) ppm.

1-(2-Cyano-3,5-dimethylphenyl)-3-methyltriazene (10a): This compound was prepared from 2-azido-4,6-dimethylbenzonitrile (**4h**; 0.50 g, 2.91 mmol) and methylmagnesium bromide (3.0 M, 5.81 mmol) according to the procedure given for compound **7a**. The crude product was purified by column chromatography on silica (heptane/EtOAc) to yield the product **10a** (0.42 g, 77%) as an orange crystalline solid, m.p. 124.0–125.3 °C. IR (neat): $\tilde{\nu}$ = 3316, 3073, 2221, 1603, 1430, 1365, 1246, 859 cm^{-1}. ^{1}H NMR ([D$_6$]-DMSO): δ = 10.97 (br. s, 1 H), 7.13 (s, 1 H), 6.97 (s, 1 H), 3.06 (d, J = 3.42 Hz, 3 H), 2.41 (s, 3 H), 2.30 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 153.5 (s), 143.3 (s), 141.8 (s), 127.1 (d), 116.7 (s), 114.8 (d), 104.7 (s), 30.6 (q), 21.4 (q), 19.9 (q) ppm. $C_{10}H_{12}N_4$ (188.11): calcd. C 63.81, H 6.43, N 29.77; found C 64.04, H 6.09, N 29.54.

1-(2-Cyano-3-methylphenyl)-3-methyltriazene (10b): This compound was prepared from 2-azido-6-methylbenzonitrile (**4i**; 0.20 g, 1.26 mmol) and methylmagnesium bromide (3.0 M, 2.53 mmol) according to the procedure given for compound **7a**. The crude product was recrystallized from 2-propanol to give **10b** (0.13 g, 60%) as a yellow solid, m.p. 85–86 °C. IR (neat): $\tilde{\nu}$ = 3318, 3069, 2219, 1589, 1431, 1356, 1252, 1237 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 11.03 (br. s, 1 H), 7.52–7.44 (m, 1 H), 7.34–7.30 (m, 1 H), 7.18–7.13 (m, 1 H), 3.08 (d, J = 4.0 Hz, 3 H), 2.47 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 153.6 (s), 142.1 (s), 133.0 (d), 126.2 (d), 116.4 (s), 114.3 (d), 107.4 (s), 30.7 (q), 20.0 (q) ppm. HRMS (ESI): calcd. for $C_9H_{10}N_4$ [M]$^+$ 174.0905; found 174.0908.

1-(2-Cyano-3-chlorophenyl)-3-methyltriazene (10c): This compound was prepared from 2-azido-6-chlorobenzonitrile (**4j**; 1.0 g, 5.60 mmol) and methylmagnesium bromide (3.0 M, 11.2 mmol) according to the procedure given for compound **7a**. The product was obtained without further purification as a yellowish solid (0.87 g, 80%), m.p. 102–103.5 °C. IR (neat): $\tilde{\nu}$ = 3357, 2231, 1585, 1428, 1362, 1243, 1163, 793 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 11.34 (br. s, 1 H), 7.64–7.56 (m, 1 H), 7.52–7.46 (m, 1 H), 7.44–7.39 (m, 1 H), 3.10 (d, J = 3.9 Hz, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 155.4 (s), 135.8 (s), 134.5 (d), 125.3 (d), 115.7 (d), 114.5 (s), 107.0 (s), 31.0 (q) ppm. HRMS (ESI): calcd. for $C_8H_7N_4$ [M]$^+$ 194.0359; found 194.0359.

1-(2-Cyanophenyl)-3-phenyltriazene (11a):[13] This compound was prepared from freshly prepared phenylmagnesium bromide (15.3 mmol) and 2-azidobenzonitrile (**4a**; 1.0 g, 6.94 mmol) in dry THF (40 mL) according to the procedure given for compound **7a**. The crude product was recrystallized from benzene and light petroleum ether to give **11a** (1.0 g, 65%) as a yellow solid, m.p. 108.3–109.2 °C (ref.[13] 107–108 °C). IR (neat): $\tilde{\nu}$ = 3270, 2226, 1602, 1513, 1439, 1405, 1252, 740 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 13.07 (br. s, 1 H), 7.88–7.64 (m, 3 H), 7.52–7.31 (m, 5 H), 7.17–7.05 (m, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 152.2 (s), 140.9 (s), 2 × 134.0 (d), 133.7 (d), 2 × 129.4 (d), 126.8 (d), 123.6 (d), 118.3 (d), 117.7 (s), 114.9 (d), 106.6 (s) ppm.

1-(2-Cyano-4-methoxyphenyl)-3-phenyltriazene (11b): This compound was prepared from freshly prepared phenylmagnesium bromide (6.32 mmol) and 2-azido-5-methoxybenzonitrile (**4b**; 0.50 g, 2.87 mmol) in dry THF (30 mL) according to the procedure given for compound **7a**. The crude product was recrystallized from methanol to give **11b** (0.35 g, 49%) as yellow needles, m.p. 152–154 °C. IR (neat): $\tilde{\nu}$ = 3219, 2226, 1596, 1488, 1458, 1248, 1186, 763 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 12.82 (br. s, 1 H), 7.75 (d, J = 9.1 Hz, 1 H), 7.45–7.31 (m, 5 H), 7.28 (dd, J = 9.1, 2.9 Hz, 1 H), 7.05 (t, J = 6.9 Hz, 1 H), 3.83 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 157.6 (s), 146.1 (s), 141.2 (s), 2 × 129.4 (d), 123.0 (d), 121.3 (d), 119.5 (d), 117.5 (s), 116.6 (d), 2 × 114.6 (d), 107.4 (s), 55.9 (q) ppm. $C_{14}H_{12}N_4O$ (252.10): calcd. C 66.65, H 4.79, N 22.21; found C 66.85, H 5.19, N 22.21.

1-(2-Cyano-4-methylphenyl)-3-phenyltriazene (11c): This compound was prepared from freshly prepared phenylmagnesium bromide (6.96 mmol) and 2-azido-5-methylbenzonitrile (**4c**; 0.50 g,

3.16 mmol) in dry THF (30 mL) according to the procedure given for compound **7a**. The crude product was recrystallized from methanol to give **11c** (0.52 g, 70%) as yellow needles, m.p. 147.3–149.6 °C. IR (neat): $\tilde{\nu}$ = 3223, 2231, 1600, 1456, 1247, 1234, 1198, 753 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 12.95 (br. s, 1 H), 7.75–7.60 (m, 2 H), 7.55–7.31 (m, 5 H), 7.15–7.03 (m, 1 H), 2.34 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 150.0 (s), 141.0 (s), 136.8 (s), 134.8 (d), 133.4 (d), 2 × 129.4 (d), 123.3 (d), 118.1 (d), 117.8 (s), 2 × 114.8 (d), 106.4 (s), 20.1 (q) ppm. $C_{14}H_{12}N_4$ (236.11): calcd. C 71.17, H 5.12, N 23.71; found C 71.16, H 5.08, N 23.65.

1-(2-Cyano-4,6-dimethylphenyl)-3-phenyltriazene (11d): This compound was prepared from freshly prepared phenylmagnesium chloride (2.0 M, 5.68 mmol) and 2-azido-3,5-dimethylbenzonitrile (**4d**; 0.44 g, 2.58 mmol) in dry THF (20 mL) according to the procedure given for compound **7a**. The crude product was purified by column chromatography on silica (heptane/EtOAc) to yield the product **11d** (0.36 g, 56%) as a yellow solid, m.p. 81–82 °C. IR (neat): $\tilde{\nu}$ = 3214, 2216, 1601, 1517, 1452, 1242, 1172, 745 cm^{-1}. ^{1}H NMR ([D$_6$]-DMSO): δ = 12.81 (br. s, 1 H), 7.52–7.31 (m, 6 H), 7.06 (t, J = 7.0 Hz, 1 H), 2.37 (s, 3 H), 2.30 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]-DMSO): δ = 147.8 (s), 141.1 (s), 136.4 (d), 136.0 (s), 133.1 (s), 132.3 (d), 2 × 129.4 (d), 123.1 (d), 119.1 (s), 2 × 114.5 (d), 102.1 (s), 20.0 (q), 18.2 (q) ppm. HRMS (FAB): calcd. for $C_{15}H_{14}N_4$ [M + H]$^+$ 251.1297; found 251.1298.

1-(4-Chloro-2-cyanophenyl)-3-phenyltriazene (11e): This compound was prepared from freshly prepared phenylmagnesium bromide (4.82 mmol) and 2-azido-5-chlorobenzonitrile (**4e**; 0.39 g, 2.19 mmol) in dry THF (30 mL) according to the procedure given for compound **7a**. The crude product was purified by column chromatography on silica (heptane/EtOAc) to yield the product **11e** (0.40 g, 71%) as a yellow solid, m.p. 142.5–143.9 °C. IR (neat): $\tilde{\nu}$ = 3208, 2236, 1598, 1452, 1383, 1253, 1211, 831 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 13.20 (s, 1 H), 7.99 (d, J = 2.1 Hz, 1 H), 7.81 (d, J = 8.9 Hz, 1 H), 7.72 (dd, J = 8.9, 2.1 Hz, 1 H), 7.52–7.33 (m, 4 H), 7.11 (t, J = 7.0 Hz, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 151.3 (s), 140.7 (s), 134.1 (d), 132.7 (d), 130.5 (s), 2 × 129.4 (d), 123.8 (d), 119.8 (d), 116.4 (s), 2 × 115.1 (d), 108.0 (s) ppm. HRMS (ESI): calcd. for $C_{13}H_9ClN_4$ [M + H]$^+$ 257.0594; found 257.0592.

1-(4-Bromo-2-cyanophenyl)-3-phenyltriazene (11f): This compound was prepared from freshly prepared phenylmagnesium bromide (4.96 mmol) and 2-azido-5-bromobenzonitrile (**4f**; 0.50 g, 2.25 mmol) in dry THF (30 mL) according to the procedure given for compound **7a**. The crude product was purified by column chromatography on silica (heptane/EtOAc) to yield the product **11f** (0.42 g, 63%) as a yellow solid, m.p. 137.5–138.7 °C. IR (neat): $\tilde{\nu}$ = 3186, 2223, 1603, 1530, 1448, 1394, 1212, 826 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 13.21 (s, 1 H), 8.12 (s, 1 H), 7.87 (dd, J = 8.9, 2.3 Hz, 1 H), 7.75 (d, J = 8.9 Hz, 1 H), 7.52–7.33 (m, 4 H), 7.19–7.07 (m, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 151.6 (s), 140.7 (s), 137.0 (d), 135.6 (d), 2 × 129.5 (d), 123.9 (d), 120.0 (d), 118.4 (s), 116.3 (s), 2 × 115.1 (d), 108.3 (s) ppm. HRMS (ESI): calcd. for $C_{13}H_9BrN_4$ [M + H]$^+$ 301.0089; found 301.0098.

1-(4,6-Dibromo-2-cyanophenyl)-3-phenyltriazene (11g): This compound was prepared from freshly prepared phenylmagnesium bromide (3.68 mmol) and 2-azido-3,5-dibromobenzonitrile (**4g**; 0.50 g, 1.67 mmol) in dry THF (30 mL) according to the procedure given for compound **7a**. The crude product was purified by column chromatography on silica (heptane/EtOAc) to yield the product **11g** (0.34 g, 54%) as a yellow solid, m.p. 128.2–128.6 °C. IR (neat): $\tilde{\nu}$ = 3221, 2215, 1602, 1518, 1405, 1249, 1220, 1203 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 13.43 (s, 1 H), 8.28 (d, J = 2.0 Hz, 1 H), 8.17 (d, J = 2.0 Hz, 1 H), 7.54–7.32 (m, 4 H), 7.14 (t, J = 7.0 Hz, 1 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 149.0 (s), 140.5 (s), 140.0 (d), 136.4 (d), 2 × 129.5 (d), 124.4 (d), 120.2 (s), 118.2 (s), 116.7 (s), 2 × 115.3 (d), 104.8 (s) ppm. $C_{13}H_8Br_2N_4$ (377.91): calcd. C 41.09, H 2.12, N 14.74; found C 41.27, H 2.43, N 14.44.

1-(2-Cyano-3,5-dimethylphenyl)-3-phenyltriazene (11h): This compound was prepared from freshly prepared phenylmagnesium bromide (6.40 mmol) and 2-azido-4,6-dimethylbenzonitrile (**4h**; 0.50 g, 2.90 mmol) in dry THF (30 mL) according to the procedure given for compound **7a**. The crude product was recrystallized from methanol to give **11h** (0.39 g, 54%) as a yellow solid, m.p. 168.4–169.5 °C. IR (neat): $\tilde{\nu}$ = 3189, 2223, 1600, 1523, 1403, 1238, 1207, 740 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 12.96 (br. s, 1 H), 7.50–7.32 (m, 5 H), 7.15–7.05 (m, 2 H), 2.45 (s, 3 H), 2.37 (s, 3 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 152.6 (s), 143.8 (s), 142.3 (s), 141.0 (s), 2 × 129.4 (d), 128.7 (d), 123.4 (d), 116.8 (s), 115.5 (d), 2 × 114.8 (d), 104.9 (s), 21.3 (q), 20.0 (q) ppm. $C_{15}H_{14}N_4$ (250.12): calcd. C 71.98, H 5.64, N 22.38; found C 71.89, H 5.96, N 22.04.

1-(2-Cyanophenyl)-3-(2-thienyl)triazene (11i): This compound was prepared from freshly prepared 2-thienylmagnesium bromide (15.27 mmol) and 2-azidobenzonitrile (**4a**; 1.0 g, 6.94 mmol) in dry THF (30 mL) according to the procedure given for compound **7a**. The crude product was purified by column chromatography on silica (heptane/EtOAc) to yield the product **11i** (1.0 g, 63%) as an orange solid, m.p. 107–108 °C. IR (neat): $\tilde{\nu}$ = 3204, 2232, 1583, 1513, 1455, 1250, 1153, 751 cm^{-1}. ^{1}H NMR ([D$_6$]acetone): δ = 11.22 (br. s, 1 H), 7.70–7.64 (m, 2 H), 7.59 (d, J = 8.4 Hz, 1 H), 7.32 (dd, J = 5.4, 1.3 Hz, 1 H), 7.26–7.17 (m, 2 H), 7.07–7.01 (m, 1 H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 155.2 (s), 144.4 (s), 135.1 (d), 134.9 (d), 127.4 (d), 2 × 124.7 (d), 124.0 (d), 117.4 (s), 117.2 (d), 99.7 (s) ppm. $C_{11}H_8N_4S$ (228.05): calcd. C 57.88, H 3.53, N 24.54, S 14.05; found C 58.5, H 3.5, N 24.5, S 14.1.

1-(2-Cyanophenyl)-3-(2-furyl)triazene (11j): This compound was prepared from freshly prepared furylmagnesium bromide (7.64 mmol) and 2-azidobenzonitrile (**4a**; 0.50 g, 3.47 mmol) in dry THF (30 mL) according to the procedure given for compound **7a**. The crude product was purified by column chromatography on silica (heptane/EtOAc) to yield the product **11j** (0.43 g, 58%) as an orange solid, m.p. 73.9–76.1 °C. IR (neat): $\tilde{\nu}$ = 3314, 2213, 1603, 1585, 1505, 1162, 753, 731 cm^{-1}. ^{1}H NMR ([D$_6$]acetone): δ = 10.41 (br. s, 1 H), 7.82–7.54 (m, 4 H), 7.28 (t, J = 7.30 Hz, 1 H), 6.71–6.61 (m, 2 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 157.5 (s), 142.7 (s), 141.1 (d), 134.8 (d), 134.2 (d), 123.0 (d), 117.8 (s), 117.4 (d), 112.7 (d), 99.9 (d), 97.7 (s) ppm. $C_{11}H_8N_4O$ (212.07): calcd. C 62.26, H 3.80, N 26.40; found C 62.42, H 4.34, N 26.25.

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