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1-Aryl-3,3-diisopropyltriazenes: An Easily Accessible and Particularly Stable Class of Triazenes Towards Strong Basic and Lewis Acid Conditions

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The stability of various substituted aryl-3,3-dialkyltriazenes, valuable synthetic intermediates, under several reaction conditions has been evaluated. To do so, anthranilonitrile and 2-amino-6-(trifluoromethyl)benzonitrile have been reacted in the presence of different secondary amines to the corresponding 1-(2-R-phenyl)-3,3-dialkyltriazenes. These compounds have been submitted to a series of different reaction conditions with special emphasis on strong basic and metal/acid reductive conditions in order to test the stability of the triazene moiety under these circumstances. Generally, triazenes are unstable in metal/acid reducing conditions. A lot of 1-aryl-3,3-dialkyltriazenes are known to undergo deprotonation in α-position of N-3 in the presence of strong bases, thus limiting the scope of action of this class of compounds. Among the tested substances, most triazenes were stable in the presence of titanium isopropoxide and/or strong nucleophiles. 1-(2-R-phenyl)-3,3-diisopropyltriazenes turned out to be particularly stable under strong basic conditions. 1,2-addition reactions in the presence of Grignard reagents or lithiated compounds, showed in most cases no side products resulting from a degradation of the triazene function. The same was true for the titanium-catalyzed Kulinkovich–de Meijere cyclopropanation or for reductive amination. In both cases, no triazene degradation products could be detected. 1-(2-R-phenyl)-3,3-diisopropyltriazenes were even stable in the presence of strong Lewis acids like trimethylaluminium.
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Introduction

Triazenes, especially 1-aryl-3,3-dialkyltriazenes, make up a very versatile and useful class of compounds.[1] They are stable during palladium-mediated cross-coupling reactions[2] and act as ligands in organometallic syntheses.[3] They can easily be converted into iodoarenes and are regularly used to prepare extended phenylacetylene systems.[3] Triazenes have found application in total synthesis[4] and are extensively used in solid phase chemistry as traceless linker.[5] Above all, they commonly act as amine and/or diazonium salt protecting groups[6] and azide precursors.[7] Triazenes tend to be acid-labile and generally decompose in the presence of Brønsted or Lewis acids to the corresponding amines and diazonium salts. This acid-catalyzed degradation yielding reactive diazonium ions which occurs as well under physiological conditions, is at least partially responsible for the potent biological activities of triazenes.[8] Aside, diazonium salts play an important role in the syntheses of N-heterocycles. This huge class of compounds is part of innumerable natural products.[3,5a] Thus, triazenes as protected diazonium ions are valuable synthetic intermediates. Triazenes can also be readily converted to azides, another widely used functional group. We have developed a one pot synthesis of aryl azides via post-cleavage modification of polymer-bound triazenes.[7a,7b] Recently, Knochel et al. reported a method starting from triazenes and inorganic sodium azide in the presence of $KHSO_4$ or $BF_3{\cdot}OEt_2$/TFA.[7c] All in all, triazenes represent a versatile and easily accessible class of compounds.

There are however some major drawbacks which considerably limit the use of 1-aryl-3,3-dialkyltriazenes as synthetic intermediates. First of all, most triazenes readily decompose under metal/acid reducing conditions.[9] Secondly, triazenes tend to be deprotonated at the α-position of N-3 in strongly basic conditions which normally goes along with a fragmentation of the triazene moiety.[10] In some cases, this base liability was used to react the formed anions with electrophiles resulting in a triazene containing a modified alkyl group on N-3.[11] In most cases, it is however seriously limiting the use of 1-aryl-3,3-dialkyltriazenes as synthetic intermediates.

Here we report on the syntheses of a series of 1-(2-R-phenyl)-3,3-dialkyltriazenes having different alkyl groups on N-3 and two different aryl substituents on N-1. We then investigated the stability of the triazene moiety under

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strongly basic, metal/acid reductive conditions. Some compounds were even reacted in the presence of strong Lewis acids. It turned out that the most stable triazenes bear isopropyl groups as substituents on N-3. In most cases, no triazene fractioning or alkylation of an isopropyl group could be detected in the presence of strong bases or electrophiles and the prepared diisopropyltriazenes were even stable in the presence of strong Lewis acids. Some of these findings might have been predictable and one may find an explanation in the pK_b values of the different substituents. It is nevertheless remarkable that to the best of our knowledge there are no examples in the literature about the use of 1-(2-R-phenyl)-3,3-diisopropyltriazenes as synthetic intermediates.

Results and Discussion

1-(2-R-phenyl)-3,3-dialkyltriazenes are useful intermediates which can easily be prepared in multigram quantities from the corresponding aniline derivatives and secondary amines. A lot of trisubstituted triazenes are however known to be unstable in the presence of strong bases. Figure 1 shows commonly used compounds **1**–**6** whose triazene function is deprotonated in α-position of N-3 under strong basic conditions.

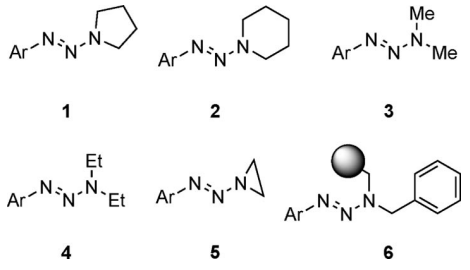


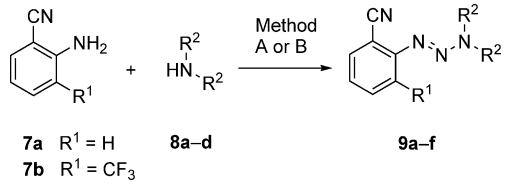
Figure 1. Triazenes known to undergo deprotonation in α-position of N-3 under strong basic conditions.[10,11]

Most importantly, to avoid this deprotonation is of course the choice of suitable alkyl substituents on N-3. The aryl substituent on N-1 on the other hand, should also have its significance as it is also known to influence the acid-catalyzed cleavage of triazenes.[12]

In order to evaluate the stability of differently trisubstituted triazenes, we prepared a sequence of compounds which were subsequently submitted to reactions employing strong basic as well as acid/metal reducing conditions. Synthesized 3,3-diisopropyltriazenes were even reacted in the presence of a strong Lewis acid without altering the triazene function.

Design and Synthesis of the Triazenes

Bearing the above mentioned considerations in mind, we prepared triazenes **9a**–**f** reacting either anthranilonitrile (**7a**) or its more electron-withdrawing fluorinated analog 2-amino-3-(trifluoromethyl)benzonitrile (**7b**) with respectively pyrrolidine (**8a**), piperidine (**8b**), diethyl- (**8c**) or diisopropylamine (**8d**) (Scheme 1, Table 1).



Scheme 1. Syntheses of the different triazenes via Method A: 1. $HCl_{aq.}$, $NaNO_2$; 2. amine, $KOH_{aq.}$, 0 °C or Method B: 1. $BF_3{\cdot}Et_2O$, *tert*-BuONO, THF; 2. amine, pyridine, CH_3CN, –20 °C.

Table 1. Yields of the different triazene syntheses.

Entry	Method	R^1	Amine	Product	Yield (%)
1	A	H	pyrrolidine	**9a**	40
2	A	H	piperidine	**9b**	55
3	A	H	diethylamine	**9c**	59
4	A	H	diisopropylamine	**9d**	26
5	B	H	diisopropylamine	**9d**	75
6	B	CF_3	diisopropylamine	**9e**	77
7	B	CF_3	diethylamine	**9f**	48

Triazenes **9a**–**c** have been obtained using method A, that is, preparation of the diazonium salt starting from **7a** in the presence of HCl, $NaNO_2$ followed by its addition to an aqueous solution of amines **8a**–**d** respectively and KOH (entries 1–3).[13] If diisopropylamine (**8d**) was treated with **7a**, the classic conditions delivered the desired triazene **9d** in only poor yield along with a lot of unreacted starting material (entry 4). The same was true when aniline derivative **7b** and amine **8d** were reacted following method A (data not shown).

This problem could however be overcome using method B (Scheme 1, Table 1). Starting from **7a**,**b**, the respective diazonium ion was obtained in the presence of boron trifluoride–diethyl ether and *tert*-butyl nitrite in THF. It was then added to a solution of pyridine and amines **8c**,**d** respectively in acetonitrile which provided triazenes **9d**–**f** in moderate to excellent yields (entries 5–7).[14] With all the different triazenes **9a**–**f** in hand, we started investigating their stability towards different reaction conditions.

Figure 2 shows the molecular structures of compounds **9a**,**d**,**e**. One can see that at least in the solid state, the triazene moiety and the nitrile function of compounds **9a**,**d** are oriented in order to minimize joint steric hindrance (Figure 2 top and middle). This changes when another substituent is added.

Comparing compounds **9d** and **9e** which differ by an additional CF_3 substituent Figure 2 (middle and bottom), reveals that the triazene in **9e** is shielding the nitrile function. This could result in a reduced reactivity of the latter. On the other hand, one could state that this engenders a more stable triazene moiety.

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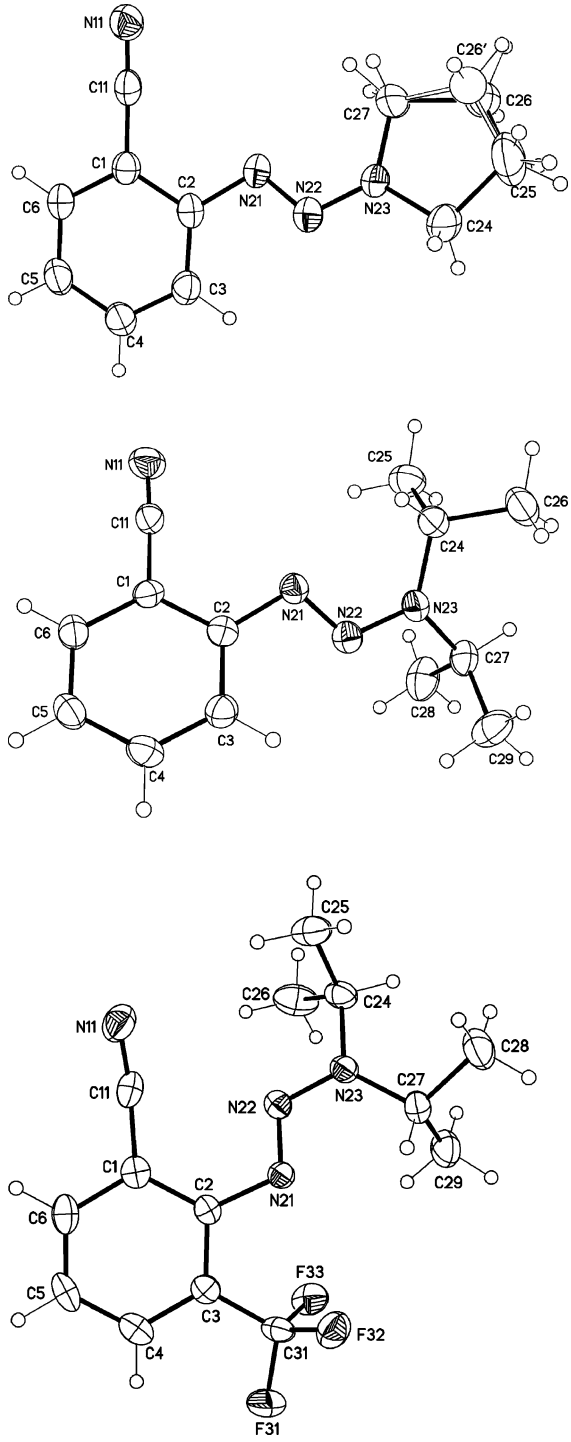
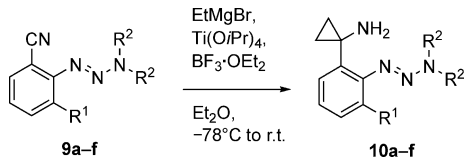


Figure 2. Top: Molecular structure of **9a**. Displacement parameters are drawn at 50% probability level. Middle: Molecular structure of **9d**. Displacement parameters are drawn at 50% probability level. Bottom: Molecular structure of **9e**. Displacement parameters are drawn at 50% probability level.

Titanium-Catalyzed Kulinkovich–de Meijere Cyclopropanation

1-(2-R-phenyl)cyclopropylamines **10a**–**f** were prepared from arylnitriles **9a**–**f** in the presence of titanium isopropoxide, boron trifluoride–diethyl ether and ethylmagnesium bromide in ether in poor to modest yields (Scheme 2, Table 2).[15,16]



Scheme 2. Kulinkovich–de Meijere cyclopropanation.

Table 2. Yields of the different cyclopropanation reactions.

Entry	Reactant	Product	Yield (%)
1	**9a**	**10a**	26
2	**9b**	**10b**	5
3	**9c**	**10c**	37
4	**9d**	**10d**	30
5	**9e**	**10e**	39
6	**9f**	**10f**	35

Cyclic substituents on N-3 (entries 1,2) lead to even lower yields than the ones obtained with acyclic groups (entries 3–6). No notable differences between the two aryl substituents were observed (entries 1–4 and 5–6). The moderate yields observed can in part be explained because reactions did not go to completion; no substantial triazene decomposition products could however be detected. One can further add that to the best of our knowledge this is the first time that a Kulinkovich–de Meijere cyclopropanation reaction has been reported on triazene containing compounds and that if applied to other substrates, comparable yields have already been reported.

1,2-Addition

Arylnitriles **9a**,**c**–**e** were submitted to either methylmagnesium bromide or a number of lithiated compounds (MeLi, BuLi, PhLi) under various reaction conditions (Scheme 3, Table 3). Even with a large excess of nucleophile, reactions did not always go to completion. In general term, no double addition to the nitrile function of compounds **9a**,**c**–**e** could be detected. In nearly all cases, the formation of the corresponding imines was observed on TLC. Latter was stable during the work up procedure as determined by TLC, hydrolyzed however most of the time at some stage during the silica column chromatography (entries 3–6). It is only by using nitrile derivative **9e** bearing an additional electron-withdrawing trifluoromethyl group on the aromatic nucleus, that some corresponding imines were stable enough to be isolated in high yields after simple aqueous workup (entries 7–9). If they were however to be purified on a silica column, they still did, at least partially, hydrolyze to give the corresponding ketones.

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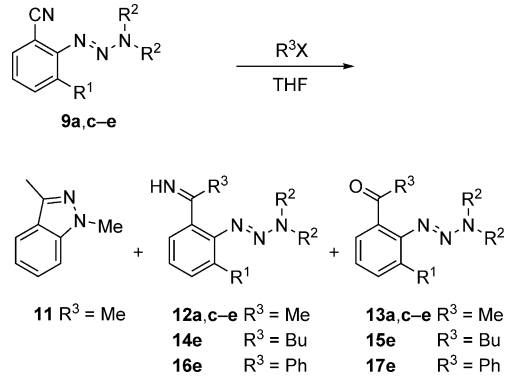


Scheme 3. Reaction of triazenes **9a**,**c**–**e** with MeMgBr or different lithiated compounds.

Table 3. Results of the different 1,2-addition reactions.

Entry	Reactant	R^3X	Temperature[a]	Products	Yield (%)
1	**9a**	MeMgBr	0 °C, reflux	**11**	12
2	**9a**	MeLi	–65 °C to r.t.	**13a**	traces
3	**9a**	MeLi	–65 °C to r.t., $CeCl_3$	**13a**[b]	23
4	**9c**	MeMgBr	reflux	**13c**[b]	62
5	**9d**	MeMgBr	reflux	**13d**[b]	68
6	**9d**	MeLi	0 °C to r.t.	**13d**[b]	67
7	**9e**	MeLi	0 °C to r.t.	**13e**[b]	78
8	**9e**	BuLi	–20 °C to r.t.	**14e**	80
9	**9e**	PhLi	–20 °C to r.t.	**16e**	95

[a] All reactions were carried out in THF. [b] The corresponding imine could be observed on TLC even after an aqueous work up but hydrolyzed during silica column chromatography.

The substituents on N-3 of the triazene function were crucial for the outcome of the 1,2-addition reactions. If compound **9a**, containing a pyrrolidine group, was used, no 1,2-addition product or derivative could be isolated, no matter what nucleophile (entries 1, 2) or which conditions were used (entries 2, 3). TLC analysis showed multiple spots, the corresponding compounds of which were not characterized. If methylmagnesium bromide was employed under reflux for several hours, an unexpected side product, 1,3-dimethyl-1*H*-indazole (**11**), could be isolated as major compound in poor yield (entry 1). There are ongoing studies to improve the yield and to elucidate the mechanism of this reaction. Ethyl or isopropyl groups on N-3 delivered the corresponding ketones **13c** and **13d** in satisfactory yields (entries 4–6) which were slightly higher for the bulkier substituents (entries 5, 6). Figure 3 shows the molecular structure of **13d**. The carbonyl function seems, at least in the solid state, to be shielded from a 1,2-addition by the triazene group (Bürgi–Dunitz).

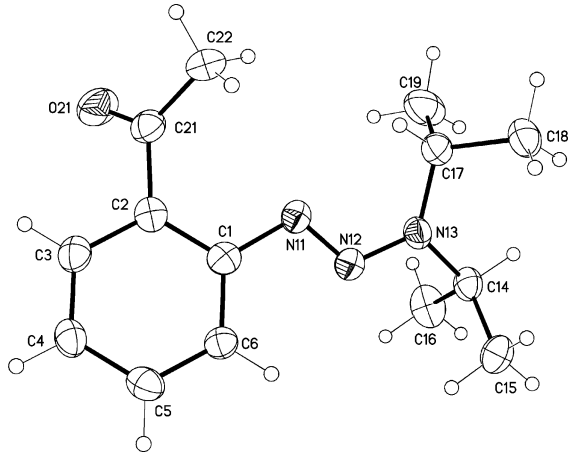
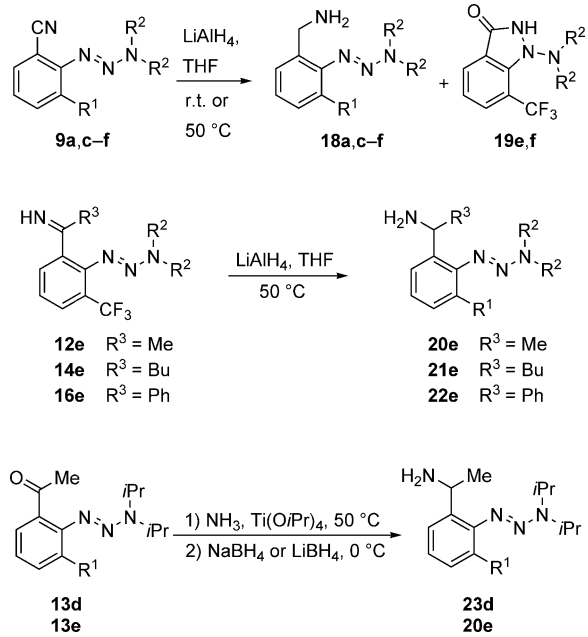


Figure 3. Molecular structure of **13d**, one of the two crystallographic independent molecules is shown. Displacement parameters are drawn at 50% probability level.

Considering the above mentioned results, only triazene **9e** bearing two isopropyl groups, was tested in the series of the fluorinated aryl substituent (entries 7–9). **9e** was treated with different lithiated compounds, e.g. methyl-, butyl- or phenyllithium and delivered the corresponding crude imines **12e**, **14e** and **16e** respectively in good to excellent yields after aqueous workup.

Reductions Using $LiAlH_4$

Because some triazenes are known to be sensitive towards metal-acid reducing conditions,[9] attempts were made to investigate the reduction of the nitrile function of **9a**,**c**–**f**, as well as the reduction of imines **12e**, **14e** and **16e** (Scheme 4, Table 4, entries 1–8). The reduction of nitriles **9a**,**c**,**d** to the corresponding primary amines **18a**,**c**,**d** was achieved in the presence of lithium aluminium hydride in THF with excellent yields (entries 1–3). On the other hand, in the case of arylnitriles **9e** and **9f** containing an additional electron-withdrawing trifluoromethyl substituent, the expected amines **18e**,**f** could only be obtained in poor to modest yields after heating for several hours at 50 °C (entries 4,5).



Scheme 4. Reductions of nitriles **9a**,**c**–**f**, imines **12e**, **14e** and **16e** as well as reductive aminations of ketones **13d**,**e**.

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Table 4. Conditions and yields of the different reductions and reductive aminations.

Entry	Reactant	Conditions	Products	Yield (%)
1	**9a**	$LiAlH_4$, THF, r.t.	**18a**	76–90[b]
2	**9c**	$LiAlH_4$, THF, r.t.	**18c**	86–93[b]
3	**9d**	$LiAlH_4$, THF, r.t.	**18d**	quant.
4	**9e**	$LiAlH_4$, THF, 50 °C	**18e/19e**	57/traces[c]
5	**9f**	$LiAlH_4$, THF, 50 °C	**18f/19f**	25/21[c]
6	**12e**	$LiAlH_4$, THF, 50 °C	**20e**	48[d]
7	**14e**	$LiAlH_4$, THF, 50 °C	**21e**	51[d]
8	**16e**	$LiAlH_4$, THF, 50 °C	**22e**	30[d]
9	**13d**	1) NH_3, $Ti(OiPr)_4$[a] 2) $NaBH_4$, 0 °C	**23d**	39
10	**13e**	1) NH_3, $Ti(OiPr)_4$[a] 2) $LiBH_4$, 0 °C	**20e**	65

[a] Heated at 50 °C. [b] Depending on the reaction scale. [c] Accompanied by recovery of about 40% starting material. [d] Yield over two steps (1,2-addition plus reduction).

Even after longer reaction times (several days) at this temperature, we were still able to isolate about 40% of starting material. Besides, amine **18f** was accompanied by a side product, 1-(diethylamino)-7-(trifluoromethyl)-1*H*-indazol-3(2*H*)-one (**19f**), resulting from reaction of the triazene moiety (entry 5). In the case of amine **18e**, the corresponding side product **19e** could only be isolated as traces (entry 4). Reduction of imines **12e**, **14e** and **16e** delivered amines **20e**, **21e** and **22e** respectively in poor to moderate yields determined over two steps (1,2-addition and reduction) (entries 6–8). Considering that the 1,2-addition reactions are high yielding (Table 3, entries 7–9), the low overall yields are probably due to the subsequent reduction and seem to be correlated to the R^3 substituent.

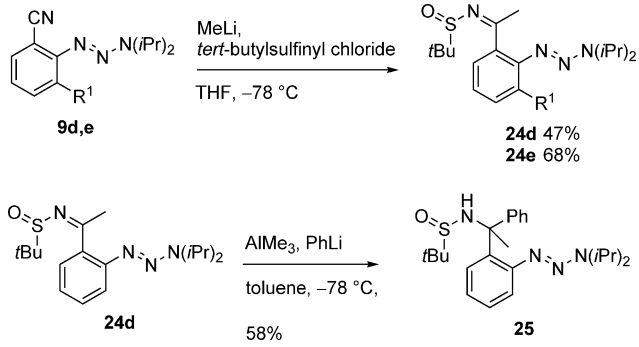
Reductive Aminations

The previously synthesized triazenyl ketones **13d** and **13e** were treated with ammonia and titanium isopropoxide in THF at 50 °C followed by addition of sodium or lithium borohydride after cooling to 0 °C (Scheme 4, Table 4, entries 9,10). The yield of the reaction is dependent on the aryl substituent on N-1. A more electron-withdrawing aryl group resulted in a clearly enhanced yield (entry 10).

1,2-Addition Reactions in the Presence of Trimethylaluminium

1-(2-R-Phenyl)-3,3-diisopropyltriazenes had proven to be stable in strong basic conditions and to tolerate acid/metal reductive conditions. In order to test their stability towards strong Lewis acids, triazenes **9d**,**e** were first converted to *N*-*tert*-sulfinylamides **24d**,**e** in the presence of butyllithium and *tert*-butylsulfinyl chloride in THF at low temperature (Scheme 5).[17]

Subsequent 1,2-addition of phenyllithium on activated imine **24d** in the presence of trimethylaluminium provided *N*-*tert*-butylsulfinylamine **25** in good yield. When the same reaction sequence was performed on the fluorinated analog



Scheme 5. 1,2-Addition in the presence of a strong Lewis acid.

9e, the corresponding *N*-*tert*-butylsulfinylamine **24e** obtained in 68% yield (Scheme 5), did not react during the 1,2-addition conditions (data not shown). It was only when the temperature was risen, that triazene **24e** started decomposing. The fact that the 3,3-diisopropyl-substituted compounds are by far the most stable triazenes in strong basic conditions might in part be explained by the pK_b value of the isopropyl group. Another part of the explanation may lie in the bulkiness of this group. This system is probably so hindered that the α-position of N-3 cannot be easily deprotonated. This steric hindrance would also account for the unprecedented resistance towards strong Lewis acids as it would shield the lone pair for N-3. Finally, there is the influence of the 1-aryl substituent on the stability of the different triazenes. This is however not to be confused with the expectable and observed changes of reactivity of the other functionalities of the molecule. It is known that modifications in the electron-withdrawing properties of a 1-aryl group affect the rotational barrier around the N-2–N-3 linkage.[18] Different aryl substituents may though lead to more or less stable triazenes. In our study, we could however conclude that a change of the electron density on the aryl substituent did not significantly modify the stability of the triazene functions.

Conclusions

1-(2-Substituted phenyl)-3,3-diisopropyltriazenes have proven to be valuable synthetic intermediates because they are stable towards strong bases, tolerate metal/acid reductive conditions and most unexpected, stand strong Lewis acids at low temperatures. Thus, 3,3-diisopropyltriazenes have the potential to substantially extend the already broad application spectra of triazenes. The remarkable stability towards strong Lewis acids needs further studies and is currently being investigated in our group. In the same context, 3,3-diisopropyltriazenes containing differently substituted aryl moieties are at this time being prepared in order to study the stability of 1-aryl-3,3-diisopropyltriazenes in general.

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Experimental Section

General: ^{1}H NMR spectra were recorded on a Bruker AM 400 (400 MHz) spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to $CHCl_3$ (δ = 7.26 ppm) as internal standard. All couplings constants J are absolute values (Hz). Description of signals: s singlet, br. s broad singlet, d doublet, t triplet, q quartet, m multiplet, dd doublet of doublets, ddd doublet of dd, dt doublet of triplets, ddt doublet of dt, tt triplet of triplets, quin quintet, qdd quartet of dd and sept septet. The spectra were analyzed according to first order. The signal abbreviations include: Ar-H for aromatic proton. ^{13}C NMR spectra were recorded on a Bruker AM 400 (100 MHz) spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to $CHCl_3$ (δ = 77.4 ppm) as internal standard. The signal structure was analyzed by DEPT and is described as follows: + denotes a primary or tertiary C-atom (positive signal), – denotes a secondary C-atom (negative signal), and q stands for a quaternary C-atom (no signal). MS (EI) (electron-impact mass spectrometry): Finnigan MAT 90 (70 eV). The molecular fragments are quoted as the relation between mass and charge (m/z), the intensities as a percentaged value relative to the intensity of the base signal (100%). The abbreviation [M^+] refers to the molecular ion. IR (infrared spectroscopy): FT-IR Bruker IFS 88. IR spectra of solids were recorded in KBr, and as thin films on KBr for oils and liquids. The deposit of the absorption band was given in wave numbers $\tilde{\nu}$ in cm^{-1}. The forms and intensities of the bands were characterized as follows: vs very strong 0–10% T, s strong 10–40% T, m medium 40–70% T, w weak 70–90% T, vw very weak 90–100% T, br. broad. Elemental analysis: Elementar Vario Microcube. Descriptions without nominated temperature were done at room temperature (r.t.), and the following abbreviations were used: calcd. (theoretical value), found (measured value). Information is given in masspercent. Triazenes have proven to easily lose molecular nitrogen during elemental analysis which often gives diminished nitrogen content.[19] Routine monitoring of reactions were performed using Silica gel coated aluminium plates (Merck, silica gel 60, F_{254}), which were analyzed under UV light (λ = 254 nm) and/or dipped into a solution of molybdatophosphate (5% phosphor molybdic acid in ethanol, dipping solution) and ninhydrine solution (3 g of ninhydrine in 100 mL of ethanol) and heated with a heat gun. Solvent mixtures are understood as volume/volume. Solid materials were powdered. Solvents, reagents and chemicals were purchased from Aldrich, Fluka and Acros. Tetrahydrofuran was distilled from sodium/benzophenone under argon prior use. Dichloromethane, ethyl acetate and diethyl ether were distilled from calcium hydride. All reactions involving moisture sensitive reactants were executed under an argon atmosphere using oven dried and/or flame dried glassware. All other solvents, reagents and chemicals were used as purchased unless stated otherwise.

General Procedure A. Synthesis of 2-Triazenylbenzonitriles 9a–c: A solution of sodium nitrite (50.8 mmol) in cold H_2O (5 mL) was added over 30 to 40 min to a suspension of anthranilonitrile (50.8 mmol) in concd. HCl (10 mL) at 0 °C. After complete addition, the resulting mixture was stirred for additional 10 min at 0 °C and then added all at once to a solution of KOH (50.8 mmol) and amine (50.8 mmol) in H_2O (50 mL) cooled to –20 °C. After 10 min, the resulting solid was filtered off, dried and purified by flash column chromatography to afford a slightly yellow solid.

General Procedure B. Synthesis of 2-Triazenylbenzonitriles 9d–f: $BF_3{\cdot}OEt_2$ (203 mmol) was slowly added to a solution of anthranilonitrile or 2-amino-3-(trifluoromethyl)benzonitrile (50.8 mmol) in dry THF (70 mL) cooled to –20 °C. Then, *tert*-BuONO (178 mmol) was added over 35 min, a precipitate formed during addition. After the addition was completed, stirring was continued at –20 °C for 30 min, then dry Et_2O (20 mL) was added and the mixture was stirred at 0 °C. After 1 h, the precipitated diazonium salt was filtered off, washed with Et_2O (3 × 100 mL) and dried under vacuum.

Pyridine (7 mL) was added to a solution of amine (50.8 mmol) in CH_3CN (50 mL) cooled to 0 °C. The diazonium salt was added portionwise to this solution which was then warmed to room temp. overnight. H_2O (150 mL) was added and the aqueous phase was extracted with CH_2Cl_2 (3 × 150 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by column chromatography to afford a white solid.

General Procedure C. Kulinkovich–de Meijere Cyclopropanation of 2-Triazenylbenzonitriles 9d–f: A solution of EtMgBr (3 M in Et_2O, 4.00 mmol) was slowly added to a solution of triazene (2.00 mmol) and titanium(IV) isopropoxide (2.40 mmol) in dry Et_2O at –78 °C. After stirring for 10 min at this temperature, the mixture was warmed to room temp. within 2 h. Then $BF_3{\cdot}OEt_2$ (4.00 mmol) was added and after additional stirring for 2 h at room temp. a 10% aqueous solution of NaOH (20 mL) was added and the aqueous phase was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine, dried with Na_2SO_4 and purified by flash column chromatography to afford a slightly yellow oil.

General Procedure D. Reaction of 2-Triazenylbenzonitriles with Methylmagnesium Bromide or Different Lithiated Compounds: A solution of Grignard or lithiated compound (1.60 mmol) was slowly added to a solution of triazene (1.00 mmol) in dry THF cooled to 0 °C. The resulting mixture was warmed to room temp. After 3 h, a saturated solution of NH_4Cl was added and the aqueous phase was extracted with EtOAc. The combined organic layers were dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography to afford a white solid.

General Procedure E. Reduction of Nitriles 9a,c–d: $LiAlH_4$ (2.00 mmol) was added portionwise to a solution of triazene (1.00 mmol) in dry THF (7 mL) cooled to 0 °C. The resulting mixture was warmed to room temp. After 3 h, a saturated solution of sodium/potassium tartrate (100 mL) was added and the aqueous phase was extracted with EtOAc (4 × 100 mL). The combined organic layers were dried with $MgSO_4$, filtered and concentrated in vacuo to give a slightly yellow oil that was used without further purification.

General Procedure F. Reduction of Nitriles 9e,f and Imines 12e, 14e and 16e with Lithium Aluminium Hydride: A solution of $LiAlH_4$ (1 M in THF, 2.00 mmol) was added portionwise to a solution of triazene (1.00 mmol) in dry THF (7 mL) cooled to 0 °C. The resulting mixture was heated at 50 °C. After 16 h, the reaction mixture was cooled to room temp. and a saturated solution of sodium/potassium tartrate (100 mL) was added and the aqueous phase was extracted with EtOAc (4 × 100 mL). The combined organic layers were dried with $MgSO_4$, filtered, concentrated in vacuo. The residue was purified by flash column chromatography to give a slightly yellow oil.

General Procedure G. Reductive Amination of Triazenyl Ketones 13d,e: A mixture of triazenyl ketone (1.00 mmol), a solution of ammonia (2 M in MeOH, 5.00 mmol) and titanium(IV) isopropoxide

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(2.00 mmol) was stirred for 6 h at 50 °C under a dry argon atmosphere. After cooling to 0 °C, a solution of $LiBH_4$ (2 M in THF, 1.50 mmol) was added and stirring at this temperature was continued for 3 h. The solution was put into an aqueous solution of NH_4OH (2 M) and after additional stirring of 1 h, the aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried with $MgSO_4$, filtered, concentrated in vacuo. The residue was purified by flash column chromatography to give a slightly yellow oil.

Synthesis and Characterization of Compounds

(*E*)-2-(Pyrrolidin-1-yldiazenyl)benzonitrile 9a: Following general procedure A, anthranilonitrile (**7a**) (6.00 g, 50.8 mmol) was treated with sodium nitrite (3.50 g, 50.7 mmol) and pyrrolidine (**8a**) (3.97 g, 55.8 mmol) to yield 4.06 g (20.3 mmol, 40%) as a light yellow solid after column chromatography on silica (*n*-pentane/diethyl ether, 2:1). R_f (*n*-pentane/diethyl ether, 2:1) = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (ddd, J = 7.7, J = 1.4, J = 0.5 Hz, 1 H, Ar-H^6), 7.53 (ddd, J = 8.3, J = 0.7 Hz, 1 H, Ar-H^3), 7.46 (ddd, J = 7.2, J = 1.5 Hz, 1 H, Ar-H^4), 7.11 (ddd, J = 7.3, J = 1.2 Hz, 1 H, Ar-H^5), 3.96 (t, J = 6.4 Hz, 2 H, NCH_2), 3.76 (t, J = 6.4 Hz, 2 H, NCH_2), 2.11–1.99 (m, 4 H, 2×CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.90 (C_q, C^2-Ar), 133.33 (+, C^6-Ar), 133.06 (+, C^4-Ar), 124.59 (+, C^5-Ar), 118.15 (C_q, CN), 117.33 (+, C^3-Ar), 107.20 (C_q, C^1-Ar), 51.34 (–, NCH_2), 47.11 (–, NCH_2), 23.98 (–, CH_2), 23.44 (–, CH_2) ppm. IR (KBr): $\tilde{\nu}$ = 3813 (w), 3402 (w), 3072 (m) [=C–H valence], 2976 (s), 2889 (s) [–C–H valence], 2759 (m), 2498 (w), 2222 (s) [CN], 1976 (w), 1724 (w), 1591 (m), 1571 (m), 1393 (s), 1277 (s) [–C–N valence], 1227 (s), 1159 (s), 762 (s), 679 (m), 515 (m) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 200 (24) [M$^+$], 130 (35) [$C_7H_4N_3^+$], 102 (100) [$C_7H_4N^+$], 76 (7) [$C_6H_4^+$], 70 (5) [$C_4H_8N^+$], 51 (5) [$C_4H_3^+$], 41 (8). HR-EIMS ($C_{11}H_{12}N_4$): calcd. 200.1062; found 200.1059 ($C_{11}H_{12}N_4$): calcd. C 65.98, H 6.04, N 27.98; found C 66.06, H 6.03, N 26.97.

(*E*)-2-(Piperidin-1-yldiazenyl)benzonitrile (9b): Following general procedure A, anthranilonitrile (**7a**) (6.00 g, 50.8 mmol) was treated with sodium nitrite (3.50 g, 50.7 mmol) and piperidine (**8b**) (4.33 g, 50.8 mmol) to yield 6.02 g (28.1 mmol, 55%) as a yellow solid after column chromatography on silica (*n*-pentane/diethyl ether, 3:1). R_f (*n*-pentane/diethyl ether, 3:1) = 0.76. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60–7.56 (m, 2 H, Ar-H^6, Ar-H^3), 7.47 (ddd, J = 7.3, J = 1.5 Hz, 1 H, Ar-H^4), 7.13 (ddd, J = 7.5, J = 1.2 Hz, 1 H, Ar-H^5), 3.90 [bd, 4 H, $N(CH_2)_2$], 1.77–1.71 [m, 6 H, $(CH_2)_3$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.36 (C_q, C^2-Ar), 133.09 (+, C^6-Ar), 132.79 (+, C^4-Ar), 124.93 (+, C^5-Ar), 118.14 (C_q, CN), 117.31 (+, C^3-Ar), 107.40 (C_q, C^1-Ar), 53.22 (–, *o*-CH_2), 26.43 (–, *p*-CH_2), 24.18 (–, *m*-CH_2). IR (KBr): $\tilde{\nu}$ = 3067 (w) [=C–H valence], 2953 (m), 2859 (m) [–CH_2 valence], 2224 (m) [CN], 1973 (w), 1832 (w), 1589 (m), 1406 (s), 1298 (m) [–C–N valence], 765 (m) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 214 (24) [M$^+$], 130 (49) [$C_7H_4N_3^+$], 102 (100) [$C_7H_4N^+$], 84 (16) [$C_5H_{10}N^+$], 76 (6) [$C_6H_4^+$], 56 (5) [$C_3H_6N^+$], 42 (8) [$C_2H_4N^+$]. HR-EIMS ($C_{11}H_{12}N_4$): calcd. 200.1062; found 200.1059. ($C_{12}H_{14}N_4$): calcd. C 67.27, H 6.59, N 26.15; found C 67.35, H 6.42, N 24.87.

(*E*)-2-(3,3-Diethyltriaz-1-enyl)benzonitrile (9c): Following general procedure A, anthranilonitrile (**7a**) (6.00 g, 50.8 mmol) was treated with sodium nitrite (3.50 g, 50.7 mmol) and diethylamine (**8c**) (3.70 g, 50.8 mmol) to yield 6.04 g (29.9 mmol, 59%) as a light yellow solid after column chromatography on silica (*n*-pentane/diethyl ether, 3:1). R_f (*n*-pentane/diethyl ether, 3:1) = 0.28. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (ddd, J = 7.7, J = 1.4, J = 0.4 Hz, 1 H, Ar-H^6), 7.53 (ddd, J = 8.3, J = 1.1, J = 0.3 Hz, 1 H, Ar-H^3), 7.46 (ddd, J = 7.2, J = 1.5 Hz, 1 H, Ar-H^4), 7.11 (ddd, J = 7.6, J = 1.2 Hz, 1 H, Ar-H^5), 3.82 [quin, J = 7.3 Hz, 4 H, $N(CH_2)_2$], 1.35 (t, J = 7.2 Hz, 3 H, CH_3), 1.28 (t, J = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.76 (C_q, C^2-Ar), 133.03 (+, C^6-Ar), 132.80 (+, C^4-Ar), 124.58 (+, C^5-Ar), 118.20 (C_q, CN), 117.40 (+, C^3-Ar), 107.28 (C_q, C^1-Ar), 49.50 (–, CH_2), 42.24 (–, CH_2), 14.41 (+, CH_3), 10.85 (+, CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3470 (vw), 3070 (vw) [=C–H valence], 2977 (m), 2936 (m) [–C–H valence], 2875 (w), 2224 (m) [CN], 1592 (m), 1573 (w), 1468 (m), 1445 (m), 1400 (m), 1330 (m), 1276 (m) [–C– *N* valence], 1241 (m), 1094 (m), 761 (m) 520 (w) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 202 (77) [M$^+$], 130 (46) [$C_7H_4N_3^+$], 103 (51), 102 (100) [$C_7H_4N^+$], 76 (18) [$C_6H_4^+$], 72 (10) [$C_4H_{10}N^+$], 51 (6) [$C_4H_3^+$]. HR-EIMS ($C_{11}H_{14}N_4$): calcd. 202.1218; found 202.1220; elemental analysis ($C_{11}H_{14}N_4$): calcd. C 65.32, H 6.98, N 27.70; found C 65.63, H 7.03, N 25.95.

(*E*)-2-(3,3-Diisopropyltriaz-1-enyl)benzonitrile (9d): Following general procedure B, anthranilonitrile (**7a**) (6.00 g, 50.8 mmol) was treated with BF_3·OEt_2 (28.8 g, 203 mmol), *tert*-BuONO (20.4 g, 177 mmol) and diisopropylamine (**8d**) (5.13 g, 50.7 mmol) to yield 8.81 g (43.6 mmol, 75%) as a slightly yellow solid after column chromatography on silica (*n*-pentane/diethyl ether, 55:15). R_f (*n*-pentane/diethyl ether, 3:1) = 0.29. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (ddd, J = 7.7, J = 1.1 Hz, 1 H, Ar-H^6), 7.53 (ddd, J = 8.4, J = 0.7 Hz, 1 H, Ar-H^3), 7.46 (ddd, J = 7.2, J = 1.5 Hz, 1 H, Ar-H^4), 7.10 (ddd, J = 7.7, J = 1.2, J = 0.8 Hz, 1 H, Ar-H^5), 5.29 (sept, J = 6.8 Hz, 1 H, CH), 4.07 (sept, J = 6.6 Hz, 1 H, CH), 1.40 (d, J = 6.6 Hz, 6 H, 2×CH_3), 1.30 (d, J = 6.8 Hz, 6 H, 2×CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.30 (C_q, C^2-Ar), 133.09 (+, C^6-Ar), 132.97 (+, C^4-Ar), 124.24 (+, C^5-Ar), 118.48 (C_q, CN), 117.31 (+, C^3-Ar), 106.96 (C_q, C^1-Ar), 50.27 (+, CH), 47.75 (+, CH), 23.69 (+, 2×CH_3), 19.10 (+, 2×CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3404 (vw), 3099 (w), 3058 [=C–H valence] (w), 2973 (m), 2932 (m) [-C–H valence], 2872 (w), 2627 (w), 2424 (vw), 2222 (m) [CN], 1983 (w), 1950 (w), 1837 (w), 1591 (m), 1468 (m), 1396 (m), 1270 (m) [–C–*N* valence], 1229 (m), 1156 (m), 1030 (m), 798 (m), 772 (m), 638 (w), 544 (m) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 230 (100) [M$^+$], 130 (27) [$C_7H_4N_3^+$], 102 (59) [$C_7H_4N^+$], 100 (31) [$C_6H_{14}N^+$], 58 (24) [$C_3H_8N^+$], 43 (8) [$C_3H_7^+$]. HR-EIMS ($C_{11}H_{12}N_4$): calcd. 200.1062; found 200.1059; elemental analysis ($C_{13}H_{18}N_4$): calcd. C 67.80, H 7.88, N 24.33; found C 67.72, H 7.79, N 22.67.

(*E*)-2-(3,3-Diisopropyltriaz-1-enyl)-3-(trifluoromethyl)benzonitrile (9e): Following general procedure B, 2-amino-3-(trifluoromethyl)-benzonitrile (**7b**) (1.84 g, 9.90 mmol) was treated with BF_3·OEt_2 (5.68 g, 40.0 mmol), *tert*-BuONO (3.60 g, 35.0 mmol) and of diisopropylamine (**8d**) (1.01 g, 10.0 mmol) to yield 2.30 g (7.70 mmol, 77%) as a slightly yellow solid after column chromatography on silica (*n*-pentane/diethyl ether, 5:1). R_f (*n*-pentane/diethyl ether, 3:1) = 0.60. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (dd, J = 7.8, J = 0.8 Hz, 1 H, Ar-H^4), 7.76 (dd, J = 7.8, J = 1.0 Hz, 1 H, Ar-H^6), 7.19 (dt, J = 7.8, J = 0.6 Hz, 1 H, Ar-H^5), 5.17 (sept, J = 6.8 Hz, 1 H, CH), 4.13 (sept, J = 6.7 Hz, 1 H, CH), 1.47 (d, J = 6.7 Hz, 6 H, 2×CH_3), 1.32 (d, J = 6.8 Hz, 6 H, 2×CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.45 (C_q, C^2-Ar), 138.12 (+, C^6-Ar), 130.45 (+, J = 5.5 Hz, q, C^4-Ar), 124.76 (+, q, C^5-Ar, J = 30.4 Hz), 123.28 (C_q, CN), 123.43 (+, q, CF_3, J = 273.6 Hz), 118.97 (+, C^3-Ar), 103.13 (C_q, C^1-Ar), 51.30 (+, CH), 48.41 (+, CH), 23.17 (+, CH_3), 18.95 (+, CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3090 (m) [=C–H valence], 2977 (m), 2938 (m) [–C–H valence], 2877 (m), 2469 (w), 2221 (m) [CN], 1980 (w), 1954 (w), 1913 (w), 1581 (m), 1472 (m), 1396 (s), 1380 (s) [–C–N valence], 1318 (m), 1294 (m), 1235 (s), 1141 (s) [CF_3], 1026 (m), 870 (m), 839 (m), 764 (m), 723 (m), 520 (m), 405 (w) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 298 (43) [M$^+$], 198 (37) [$C_8H_3F_3N_3^+$], 170 (100) [$C_8H_3F_3N^+$], 100 (23) [$C_6H_{14}N^+$], 84 (5) [$C_3H_6N_3^+$], 58 (22) [$C_3H_8N^+$], 43 (16) [$C_3H_7^+$]. HR-EIMS

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($C_{14}H_{17}F_3N_4$): calcd. 298.1405; found 298.1400; elemental analysis ($C_{14}H_{17}F_3N_4$): calcd. C 56.37, H 5.74, N 18.78; found C 56.52, H 5.63, N 17.09.

(*E*)-2-(3,3-Diethyltriaz-1-enyl)-3-(trifluoromethyl)benzonitrile (9f): Following general procedure B, 2-amino-3-(trifluoromethyl)benzonitrile (**7b**) (1.84 g, 9.90 mmol) was treated with $BF_3{\cdot}OEt_2$ (5.68 g, 40.0 mmol), of *tert*-BuONO (3.60 g, 35.0 mmol) and diethylamine (**8c**) (0.73 g, 10.0 mmol) to yield 1.30 g (4.81 mmol, 48%) as a slightly yellow solid after column chromatography on silica (*n*-pentane/diethyl ether, 3:1). R_f (*n*-pentane/diethyl ether, 3:1) = 0.23. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (dd, J = 7.8, J = 0.8 Hz, 1 H, Ar-H^4), 7.75 (dd, J = 7.8, J = 1.0 Hz, 1 H, Ar-H^6), 7.21 (dt, J = 7.8, J = 0.6 Hz, 1 H, Ar-H^5), 3.88 (q, J = 7.3 Hz, 2 H, CH_2), 3.82 (q, J = 7.1 Hz, 2 H, CH_2), 1.42 (t, J = 7.3 Hz, 3 H, CH_3), 1.27 (t, J = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.03 (C_q, C^2-Ar), 137.86 (+, C^6-Ar), 130.46 (+, q, C^4-Ar, J = 5.5 Hz), 124.79 (+, q, C^5-Ar, J = 30.7 Hz), 123.61 (C_q, CN), 123.33 (+, q, CF_3, J = 273.7 Hz), 118.43 (+, C^3-Ar), 103.85 (C_q, C^1-Ar), 49.82 (–, CH_2), 42.63 (–, CH_2), 14.15 (+, CH_3), 10.78 (+, CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3405 (vw), 2981 (w) [=C–H valence], 2940 (w), 2878 (vw), 2224 (w) [CN], 1638 (w), 1586 (w), 1397 (s), 1340 (m) [–C–N valence], 1318 (m), 1244 (m), 1203 (m), 1139 (s) [CF_3], 1077 (m), 752 (w), 726 (w) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 270 (28) [M$^+$], 198 (36) [$C_8H_3F_3N_3^+$], 170 (100) [$C_8H_3F_3N^+$], 72 (16) [$C_4H_{10}N^+$], 44 (5) [$C_2H_6N^+$], 42 (4) [$CH_2N_2^+$]. HR-EIMS ($C_{12}H_{13}F_3N_4$): calcd. 270.1092; found 270.1095; elemental analysis ($C_{12}H_{13}F_3N_4$): calcd. C 53.33, H 4.85, N 20.73; found C 53.72, H 5.07, N 19.67.

(*E*)-1-[2-(Pyrrolidin-1-yldiazenyl)phenyl]cyclopropanamine (10a): Following general procedure C, compound **9a** (300 mg, 1.50 mmol) was treated with titanium(IV) isopropoxide (0.53 mL, 1.80 mmol), EtMgBr (3 M in diethyl ether, 1.0 mL, 3.0 mmol) and $BF_3{\cdot}OEt_2$ (0.38 mL, 3.0 mmol). After aqueous work up, column chromatography (0.2% triethylamine in diethyl ether) on silica yielded 89 mg (0.39 mmol, 26%) as an oil. R_f (0.2% triethylamine in diethyl ether) = 0.12. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (ddd, J = 8.0, J = 1.2 Hz, 1 H, Ar-H^3), 7.25 (ddd, J = 7.5, J = 1.4 Hz, 1 H, Ar-H^6), 7.20 (ddd, J = 7.4, J = 1.5 Hz, 1 H, Ar-H^5), 7.04 (ddd, J = 7.4, J = 1.3 Hz, 1 H, Ar-H^4), 3.93–3.13 [m, 4 H, $N(CH_2)_2$], 3.15 (br. s, 2 H, NH_2), 2.05 [br. s, 4 H, $(CH_2)_2$], 1.01–0.94 (m, 2 H, CH_2, [cyclopropane]), 0.90–0.84 (m, 2 H, CH_2, [cyclopropane]) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.76 (C_q, C^2-Ar), 138.41 (C_q, C^1-Ar), 127.53 (+, C^4-Ar), 126.48 (+, C^6-Ar), 124.93 (+, C^5-Ar), 116.72 (+, C^3-Ar), 53.98 [–, $N(CH_2)_2$], 36.23 (C_q, CNH_2), 23.77 (–, 2×*m*-CH_2), 14.06 (–, 2×CH_2, [cyclopropane]) ppm. IR (KBr): $\tilde{\nu}$ = 3360 (w) [NH_2], 3085 (w) [=C–H valence], 3062 (w) [cyclopropane], 2973 (m), 2870 (m) [–C–H valence], 1574 (w), 1480 (m), 1414 (m), 1318 (m), 1290 (m) [–C–N valence], 1187 (m), 1107 (m), 1085 (m), 1017 (m), 762 (m) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 230 (60) [M$^+$], 215 (16) [$C_{13}H_{17}N_3^+$], 202 (36) [$C_{11}H_{14}N_4^+$], 201 (100) [$C_{11}H_{13}N_4^+$], 187 (37) [$C_{11}H_{13}N_3^+$], 185 (12) [$C_{11}H_{11}N_3^+$], 174 (20) [$C_{10}H_{12}N_3^+$]. HR-EIMS ($C_{13}H_{18}N_4$): calcd. 230.1531; found 230.1529; elemental analysis ($C_{13}H_{18}N_4$): calcd. C 67.80, H 7.88, N 24.33; found C 68.18, H 7.88, N 24.06.

(*E*)-1-[2-(Piperidin-1-yldiazenyl)phenyl]cyclopropanamine (10b): Following general procedure C, compound **9b** (529 mg, 2.47 mmol) was treated with titanium(IV) isopropoxide (0.65 mL, 5.44 mmol), EtMgBr (3 M in diethyl ether, 1.80 mL, 5.22 mmol) and $BF_3{\cdot}OEt_2$ (0.63 mL, 4.94 mmol). After aqueous work up, column chromatography (0.2% triethylamine in diethyl ether) on silica yielded 30.2 mg (0.12 mmol, 5%) as an oil. R_f (0.2% triethylamine in diethyl ether) = 0.10. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.39 (ddd, J = 8.0, J = 1.1 Hz, 1 H, Ar-H^3), 7.28 (ddd, J = 7.5, J = 1.4 Hz, 1 H, Ar-H^6), 7.20 (ddd, J = 7.3, J = 1.6 Hz, 1 H, Ar-H^5), 7.08 (ddd, J = 7.4, J = 1.3 Hz, 1 H, Ar-H^4), 3.82–3.80 [m, 4 H, $N(CH_2)_2$], 2.13 (br. s, 2 H, NH_2), 1.72 [br. s, 6 H, $(CH_2)_3$], 0.96–0.93 (m, 2 H, CH_2, [cyclopropane]), 0.85–0.82 (m, 2 H, CH_2, [cyclopropane]) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.35 (C_q, C^2-Ar), 138.61 (+, C^4-Ar), 126.66 (+, C^6-Ar), 126.45 (C_q, C^1-Ar), 124.52 (+, C^5-Ar), 116.02 (+, C^3-Ar), 77.24 [–, $N(CH_2)_2$], 52.92 (C_q, CNH_2), 24.43 (–, *p*-CH_2), 14.43 (–, 2×*m*-CH_2), 8.08 (–, CH_2, [cyclopropane]) ppm. IR (KBr): $\tilde{\nu}$ = 3360 (w) [NH_2], 3064 (w) [cyclopropane], 2938 (m), 2855 (m) [–C–H valence], 1480 (m), 1430 (m), 1356 (m) 1294 (m) [–C–N valence], 1259 (m), 1180 (m), 1105 (m), 1084 (m), 1016 (m), 760 (m) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 244 (3) [M$^+$], 159 (12) [$C_9H_9N_3^+$], 147 (17), 146 (40) [$C_9H_{10}N_2^+$], 145 (100) [$C_8H_7N_3^+$], 132 (16) [$C_9H_{10}N^+$], 131 (24) [$C_7H_5N_3^+$], 130 (48), 117 (21) [$C_9H_9^+$], 115 (10) [$C_9H_7^+$], 104 (10) [$C_7H_6N^+$], 103 (10) [$C_7H_5N^+$], 99 (80), 91 (10) [$C_6H_5N^+$], 42 (12) [$C_3H_6^+$]. HR-EIMS ($C_{14}H_{20}N_4$): calcd. 244.1688; found 244.1691.

(*E*)-1-[2-(3,3-Diethyltriaz-1-enyl)phenyl]cyclopropanamine (10c): Following general procedure C, compound **9c** (500 mg, 2.47 mmol) was treated with titanium(IV) isopropoxide (0.65 mL, 5.44 mmol), EtMgBr (3 M in diethyl ether, 1.80 mL, 5.22 mmol) and $BF_3{\cdot}OEt_2$ (0.63 mL, 4.94 mmol). After aqueous work up, column chromatography (0.2% triethylamine in diethyl ether) on silica yielded 210 mg (0.90 mmol, 37%) as an oil. R_f (0.2% triethylamine in diethyl ether) = 0.09. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (ddd, J = 8.0, J = 1.1 Hz, 1 H, Ar-H^3), 7.26 (ddd, J = 7.5, J = 1.4 Hz, 1 H, Ar-H^6), 7.20 (ddd, J = 7.3, J = 1.6 Hz, 1 H, Ar-H^5), 7.05 (ddd, J = 7.4, J = 1.3 Hz, 1 H, Ar-H^4), 3.80 [q, J = 7.1 Hz, 4 H, $N(CH_2)_2$], 1.31–1.27 (br. s, 2 H, NH_2), 1.23 (t, 6 H, 2×CH_3), 1.01–0.98 (m, 2 H, CH_2, [cyclopropane]), 0.86–0.83 (m, 2 H, CH_2, [cyclopropane]) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.59 (C_q, C^2-Ar), 131.68 (+, C^4-Ar), 127.63 (+, C^6-Ar), 125.11 (C_q, C^1-Ar), 118.28 (+, C^5-Ar), 103.98 (+, C^3-Ar), 63.84 [–, $N(CH_2)_2$], 36.21 (C_q, CNH_2), 118.24 (–, 2×CH_2, [cyclopropane]), 14.07 (+, 2×CH_3) ppm. MS (70 eV, EI): *m*/*z* (%): 232 (5) [M$^+$], 158 (12) [$C_9H_8N_3^+$], 147 (18), 146 (25) [$C_9H_{10}N_2^+$], 145 (51) [$C_9H_9N_2^+$], 132 (15) [$C_9H_{10}N^+$], 131 (18) [$C_7H_5N_3^+$], 130 (51) [$C_9H_8N^+$], 117 (33) [$C_9H_9^+$], 115 (15) [$C_9H_7^+$], 106 (11), 104 (13) [$C_7H_6N^+$], 103 (16) [$C_7H_5N^+$], 91 (15), 87 (100) [$C_4H_{11}N_2^+$], 77 (17) [$C_6H_5^+$], 57 (20) [$C_3H_7N^+$], 45 (10), 43 (21) [$C_2H_5N^+$]. HR-EIMS ($C_{12}H_{20}N_4$): calcd.232.1688; found 232.1685.

(*E*)-1-[2-(3,3-Diisopropyltriaz-1-enyl)phenyl]cyclopropanamine 10d): Following general procedure C, compound **9d** (500 mg, 2.17 mmol) was treated with titanium(IV) isopropoxide (0.77 mL, 2.61 mmol), EtMgBr (3 M in diethyl ether, 1.74 mL, 5.21 mmol) and $BF_3{\cdot}OEt_2$ (0.55 mL, 4.34 mmol). After aqueous work up, column chromatography (0.2% triethylamine in diethyl ether) on silica yielded 170 mg (0.65 mmol, 30%) as an oil. R_f (0.2% triethylamine in diethyl ether) = 0.09. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (ddd, J = 8.0, J = 1.1 Hz, 1 H, Ar-H^6), 7.27 (ddd, J = 7.7, J = 1.4 Hz, 1 H, Ar-H^3), 7.21 (ddd, J = 7.3, J = 1.6 Hz, 1 H, Ar-H^5), 7.04 (ddd, J = 7.4, J = 1.3 Hz, 1 H, Ar-H^4), 5.19 (br. s, 1 H, CH), 4.05 (br. s, 1 H, CH), 2.68 (br. s, 2 H, NH_2), 1.38–1.23 (m, 12 H, 4×CH_3), 0.97–0.95 (m, 2 H, CH_2, [cyclopropane]), 0.87–0.84 (m, 2 H, CH_2, [cyclopropane]) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.10 (C_q, C^2-Ar), 139.12 (+, C^4-Ar), 127.57 (+, C^6-Ar), 127.42 (C_q, C^1-Ar), 124.62 (+, C^5-Ar), 116.59 (+, C^3-Ar), 49.34 (+, CH), 46.65 (+, CH), 36.28 (C_q, CNH_2), 23.91 (+, 2×CH_3), 19.31 (+, 2×CH_3), 14.30 (–, 2×CH_2, [cyclopropane]). IR (KBr): $\tilde{\nu}$ = 3363 (vw) [NH_2], 3086 (vw) [=C–H valence], 3062 (vw) [cyclopropane], 2973 (m), 2931 (m), 2931 (m), 2872 (w) [–C–H valence], 1479 (w), 1420 (w), 1364 (w), 1281 (m) [–C–N valence], 1254 (m), 1193 (m),

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1098 (m), 1031 (m), 752 (m) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 261 (2) [M + 1], 260 (7) [M^+], 189 (21) [$C_{11}H_{15}N_3^+$], 159 (10) [$C_9H_9N_3^+$], 147 (100) [$C_8H_9N_3^+$], 145 (55) [$C_8H_7N_3^+$], 132 (30) [$C_9H_{10}N^+$], 130 (87) [$C_9H_8N^+$], 117 (24) [$C_9H_9^+$], 115 (85) [$C_9H_7^+$], 106 (24) [$C_6H_6N_2^+$], 91 (14) [$C_6H_5N^+$], 77 (13) [$C_6H_5^+$], 73 (21), 43 (62) [$C_3H_7^+$]. HR-EIMS ($C_{15}H_{24}N_4$): calcd. 260.2001; found 260.2004; elemental analysis ($C_{15}H_{24}N_4$): calcd. C 69.19, H 9.29, N 21.52; found C 69.26, H 9.55, N 20.68.

(*E*)-1-[2-(3,3-Diisopropyltriaz-1-enyl)-3-(trifluoromethyl)phenyl]cyclopropanamine (10e): Following general procedure C, compound **9e** (597 mg, 2.00 mmol) was treated with titanium(IV) isopropoxide (0.71 mL, 2.40 mmol), EtMgBr (3 M in diethyl ether, 1.60 mL, 4.80 mmol) and $BF_3{\cdot}OEt_2$ (0.51 mL, 4.00 mmol). After aqueous work up, column chromatography (diethyl ether) on silica yielded 255 mg (0.78 mmol, 39%) as an oil. R_f (diethyl ether) = 0.18. ^{1}H NMR (400 MHz, $CDCl_3$) = δ = 7.56–7.53 (m, 2 H, Ar-H^6, Ar-H^4), 7.14 (dt, J = 7.8, J = 0.7 Hz, 1 H, Ar-H^5), 5.20 (sept, J = 6.8 Hz, 1 H, CH), 4.05 (sept, J = 6.7 Hz, 1 H, CH), 2.16 (br. s, 2 H, NH_2), 1.37 (d, J = 6.7 Hz, 6 H, 2×CH_3), 1.31 (d, J = 6.8 Hz, 6 H, 2×CH_3), 0.91–0.88 (m, 2 H, CH_2, [cyclopropane]), 0.72–0.69 (m, 2 H, CH_2, [cyclopropane]) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.46 (C_q, C^2-Ar), 139.30 (+, C^6-Ar), 132.93 (C_q, C^1-Ar), 125.22 (+, J = 5.5 Hz, q, C^4-Ar), 124.16 (+, q, CF_3, J = 273.4 Hz), 124.00 (+, C^5-Ar), 123.67 (+, q, C^3-Ar, J = 29.6 Hz), 49.46 (+, CH), 45.98 (+, CH), 35.71 (C_q, CNH_2), 23.33 (+, 2×CH_3), 19.27 (+, 2×CH_3), 15.27 (–, 2×CH_2 [cyclopropane]) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –58.6 (m, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3369 (vw) [NH_2], 3087 (vw) [cyclopropane], 2976 (m) [–C–H valence], 2935 (w), 1585 (w), 1469 (w), 1431 (m), 1404 (m), 1368 (m), 1333 (m), 1306 (m), 1228 (m) [–C–N valence], 1158 (m), 1130 (s) [CF_3], 1093 (m), 844 (w), 768 (w) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 328 (4) [M^+], 257 (11) [$C_{12}H_{14}F_3N_3^+$], 216 (11), 215/214 (100/13), [$C_9H_8F_3N_3^+$], 200 (16) [$C_{10}H_9F_3N^+$], 198 (19) [$C_8H_3F_3N_3^+$], 130 (10) [$C_7H_4N_3^+$], 115 (29) [$C_6H_{15}N_2^+$], 73 (16) [$C_4H_{11}N^+$], 43 (51) [$C_2H_5N^+$], 42 (12) [$C_2H_4N^+$]. HR-EIMS ($C_{16}H_{23}F_3N_4$): calcd. 328.1875; found 328.1873.

(*E*)-1-[2-(3,3-Diethyltriaz-1-enyl)-3-(trifluoromethyl)phenyl]cyclopropanamine (10f): Following general procedure C, compound **9f** (540 mg, 2.00 mmol) was treated with titanium(IV) isopropoxide (0.71 mL, 2.40 mmol), EtMgBr (3 M in diethyl ether, 1.60 mL, 4.80 mmol) and $BF_3{\cdot}OEt_2$ (0.51 mL, 4.00 mmol). After aqueous work up, column chromatography (ethyl acetate) on silica yielded 210 mg (0.70 mmol, 35%) as an oil. R_f (ethyl acetate) = 0.11. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58 (dd, J = 7.6 Hz, 1 H, Ar-H^6), 7.54 (dd, J = 7.8, J = 1.0 Hz, 1 H, Ar-H^4), 7.14 (dt, J = 7.7, J = 0.6 Hz, 1 H, Ar-H^5), 3.80 [quin, J = 6.9 Hz, 4 H, $N(CH_2)_2$], 2.18 (br. s, 2 H, NH_2), 1.34 (t, J = 7.1 Hz, 3 H, CH_3), 1.27 (t, J = 6.9 Hz, 3 H, CH_3), 0.91–0.88 (m, 2 H, CH_2, [cyclopropane]), 0.68–0.66 (m, 2 H, CH_2, [cyclopropane]) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.54 (C_q, C^2-Ar), 138.98 (+, C^6-Ar), 133.68 (C_q, C^1-Ar), 125.15 (+, J = 5.6 Hz, q, C^4-Ar), 124.16 (+, C^5-Ar), 124.16 (+, J = 273.5 Hz, q, CF_3), 123.74 (+, q, C^3-Ar, J = 29.5 Hz), 48.98 (–, NCH_2), 41.02 (–, NCH_2), 35.82 (C_q, CNH_2), 15.77 (–, 2×CH_2, [cyclopropane]), 14.50 (+, CH_3), 11.24 (+, CH_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –58.9 (m, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3370 (vw) [NH_2], 3086 (vw) [cyclopropane], 2978 (w), 2938 (w) [–C–H valence], 2876 (w), 1584 (w), 1469 (w), 1435 (m), 1339 (m), 1305 (m) [–C–N valence], 1160 (m), 1130 (m) [CF_3], 1092 (m), 1078 (m) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 300 (4) [M^+], 243 (12), 215 (26) [$C_{10}H_{10}F_3N_2^+$], 214 (18) [$C_{10}H_9F_3N_2^+$], 213 (19) [$C_{10}H_8F_3N_2^+$], 200 (15) [$C_{10}H_9F_3N^+$], 199 (14) [$C_{10}H_8F_3N^+$], 198 (39) [$C_{10}H_7F_3N^+$], 172 (10) [$C_8H_5F_3N^+$], 170 (11) [$C_8H_3F_3N^+$], 130 (18), 87 (100) [$C_4H_{11}N_2^+$], 86 (16) [$C_4H_{10}N_2^+$], 58 (12), 57 (15) [$C_3H_7N^+$]. HR-EIMS ($C_{14}H_{19}F_3N_4$): calcd. 300.1562; found 300.1558.

1,3-Dimethyl-1H-indazole (11): Following general procedure D, compound **9a** (500 mg, 2.50 mmol) was treated with MeMgBr (3 M in Et_2O, 3.33 mL, 9.98 mmol) in THF (8 mL). Column chromatography (EtOAc) on silica yielded 44.0 mg (0.30 mmol, 12%) of a white solid. R_f (EtOAc) = 0.29. ^{1}H NMR (400 MHz, $CDCl_3$): δ = δ = 7.61 (td, J = 8.7, J = 0.9 Hz, 1 H, Ar-H^6), 7.54 (td, J = 8.4, J = 1.0 Hz, 1 H, Ar-H^7), 7.25 (ddd, J = 6.6, J = 1.0 Hz, 1 H, Ar-H^8), 7.01 (ddd, J = 6.6, J = 0.8 Hz, 1 H, Ar-H^5), 4.08 (s, 3 H, NCH_3), 2.59 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.77 (C_q, C^9-Ar), 131.36 (C_q, C^3-Ar), 125.98 (C_q, C^4-Ar), 121.08 (+, C^5-Ar), 120.31 (+, C^7-Ar), 119.56 (+, C^6-Ar), 116.89 (+, C^8-Ar), 37.31 (+, NCH_3), 9.93 (+, CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3048 (m), 2946 (m) [=C–H valence], 2923 (m) [–CH_3 valence], 2738 (w), 2565 (w), 1937 (w), 1912 (w), 1809 (w), 1788 (w), 1688 (w), 1629 (m) [–C=N valence], 1504 (m), 1453 (m), 1367 (m) 1286 (m) [–C–N valence], 1031 (m), 854 (m), 762 (m), 744 (s), 718 (m) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 146 (100) [M^+], 145 (64) [$C_9H_9N_2^+$], 117 (5) [$C_4H_5N^{2+}$], 103 (47) [$C_7H_5N^+$], 91 (10) [C_7H_{7+}], 77 (20) [$C_6H_5^+$], 51 (10) [$C_4H_3^+$]. HR-EIMS ($C_9H_{10}N_2$): calcd. 146.0844; found 146.0846.

(*E*)-1-[2-(Pyrrolidin-1-yldiazenyl)phenyl]ethanone (13a): $CeCl_3{\cdot}7H_2O$ was dried in high vacuum at 150 °C for 5 h while stirring. After cooling down the anhydrous $CeCl_3$ (1.15 g, 4.67 mmol) was suspended in dry THF (8 mL). At –50 °C, methyllithium (1.6 M in diethyl ether, 1.94 mL, 3.10 mmol) was added. After 30 min compound **9a** (200 mg, 1.00 mmol) dissolved in THF (2 mL) was added at –65 °C. The resulting violet mixture was stirred for 7 h at this temperature before a NH_4OH solution (25% in water, 2.50 mL) was added and the reaction was warmed to room temp. within 16 h. The residue was filtered off over celite® 545, washed with dichloromethane and the filtrate was concentrated in vacuo. Column chromatography on silica (*n*-pentane/diethyl ether, 3:1) yielded 50.0 mg (0.23 mmol, 23%) as a white solid. R_f (*n*-pentane/diethyl ether, 3:1) = 0.16. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.54 (ddd, J = 7.7, J = 1.4 Hz, 1 H, Ar-H^6), 7.47 (ddd, J = 8.2, J = 1.4 Hz, 1 H, Ar-H^3), 7.39 (ddd, J = 7.2, J = 1.6 Hz, 1 H, Ar-H^4), 7.14 (ddd, J = 7.2, J = 1.4 Hz, 1 H, Ar-H^5), 3.81 (bd, 4 H, 2×NCH_2), 2.62 (s, 3 H, CH_3), 2.05 (br. s, 4 H, 2×CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.15 (C_q, C=O), 153.83 (C_q, C^2-Ar), 132.30 (+, C^6-Ar), 124.53 (+, C^3-Ar), 118.08 (+, C^5-Ar), 117.27 (C_q, C^1-Ar), 107.15 (+, C^2-Ar), 51.28 (–, 2×NCH_2), 47.05 (+, CO-*C*H$_3$), 23.92 (–, CH_2), 23.38 (–, CH_2) ppm. IR (KBr): $\tilde{\nu}$ = 3304 (w), 3053 (w), 2974 (m), 2924 (m) [C–H valence], 2875 (m) [–CH_3 valence], 2702 (w), 1953 (w), 1668 (m) [C=O], 1589 (m), 1568 (m), 1471 (m), 1442 (m), 1406 (s), 1353 (m), 1281 (m) [–C–N valence], 1155 (m), 967 (m), 774 (m), 596 (m), 540 (m) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 217 (11) [M^+], 147 (74) [$C_8H_7N_2O^+$], 119 (13) [$C_8H_7O^+$], 91 (100) [$C_7H_7^+$], 77 (9) [$C_6H_5^+$], 70 (6) [$C_4H_8N^+$], 43 (22) [$C_2H_5N^+$]. HR-EIMS ($C_{12}H_{15}N_3O$): calcd. 217.1215; found 217.1218; elemental analysis ($C_{12}H_{15}N_3O$): calcd. C 66.34, H 6.96, N 19.34; found C 66.46, H 6.90, N 18.46.

(*E*)-1-[2-(3,3-Diethyltriaz-1-enyl)phenyl]ethanone (13c): Following general procedure D, methylmagnesium bromide (3 M in diethyl ether, 6.70 mL, 20.0 mmol) was added to a solution of compound **9c** (404 mg, 2.00 mmol) in dry THF (5 mL) and the mixture was heated to 60 °C for 7 h. After cooling down to room temp. the reaction was quenched with water (10 mL) and the aqueous layer was extracted with diethyl ether (3×30 mL). Column chromatography on silica (*n*-pentane/diethyl ether, 4:1) gave 273 mg (1.24 mmol, 62%) of a yellow oil. R_f (*n*-pentane/diethyl ether, 4:1)

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= 0.18. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (ddd, J = 7.7, J = 1.4 Hz, 1 H, Ar-H^6), 7.47 (ddd, J = 8.1, J = 0.9 Hz, 1 H, Ar-H^3), 7.39 (ddd, J = 7.2, J = 1.6 Hz, 1 H, Ar-H^4), 7.14 (ddd, J = 7.4, J = 1.2 Hz, 1 H, Ar-H^5), 3.77 (q, J = 6.8 Hz, 4 H, 2×CH_2), 2.57 (s, 3 H, CH_3), 1.30–1.23 (m, 6 H, 2×CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.89 (C_q, C=O), 149.39 (C_q, C^2-Ar), 134.88 (+, C^6-Ar), 131.50 (+, C^4-Ar), 128.24 (+, C^5-Ar), 124.85 (C_q, C^1-Ar), 118.48 (+, C^3-Ar), 48.99 (–, CH_2), 41.58 (–, CH_2), 32.08 (+, CO-*C*H$_3$), 14.51 (+, CH_3), 11.24 (+, CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3471 (vw), 3065 (vw), 2977 (m) [–C–H valence], 2935 (w), 2875 (w) [–CH_3 valence], 1681 (m) [C=O], 1593 (w), 1467 (m), 1407 (m), 1352 (m) 1282 (m) [–C–N valence], 1246 (m), 1104 (m), 762 (m), 595 (w) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 219 (18) [M$^+$], 147 (36) [$C_8H_7N_2O^+$], 119 (11) [$C_8H_7O^+$], 91 (100) [$C_7H_7^+$], 77 (6) [$C_6H_5^+$], 43 (12) [$C_2H_5N^+$]. HR-EIMS ($C_{12}H_{17}N_3O$): calcd. 219.1372; found 219.1375; elemental analysis ($C_{12}H_{17}N_3O$): calcd. C 65.73, H 7.81, N 19.16; found C 65.98, H 7.70, N 18.06.

(*E*)-1-[2-(3,3-Diisopropyltriaz-1-enyl)phenyl]ethanone (13d): Following general procedure D, compound **9d** (230 mg, 1.00 mol) was treated with MeMgBr (3 M in Et_2O, 1.00 mL, 1.60 mmol) in THF (10 mL). Column chromatography (*n*-pentane/diethyl ether, 4:1) on silica yielded 168 mg (0.68 mmol, 68%) of a white solid. R_f (*n*-pentane/diethyl ether, 4:1) = 0.18. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (ddd, J = 7.7, J = 1.1 Hz, 1 H, Ar-H^6), 7.47 (ddd, J = 8.2, J = 1.2, J = 0.8 Hz, 1 H, Ar-H^3), 7.39 (ddd, J = 7.1, J = 1.5 Hz, 1 H, Ar-H^4), 7.13 (ddd, J = 7.7, J = 1.2, J = 0.5 Hz, 1 H, Ar-H^5), 5.25 (br. s, 1 H, CH), 4.02 (br. s, 1 H, CH), 2.57 (s, 3 H, CH_3), 1.39 (d, J = 4.8 Hz, 6 H, 2×CH_3), 1.26 (bd, 6 H, 2×CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.01 (C_q, C=O), 150.00 (C_q, C^2-Ar), 134.73 (+, C^6-Ar), 131.45 (+, C^4-Ar), 128.48 (+, C^5-Ar), 124.53 (C_q, C^1-Ar), 118.49 (+, C^3-Ar), 49.16 (+, CH), 41.58 (–, CH_2), 46.68 (+, CH), 32.21 (+, CO-*C*H$_3$), 23.92 (+, CH_3), 19.41 (+, CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3335 (w), 3067 (m), 2977 (m) [–C–H valence], 1952 (w), 1923 (w), 1676 (m) [C=O], 1591 (m), 1472 (m), 1403 (s), 1368 (m), 1285 (m) [–C–N valence], 1238 (m), 1220 (m), 1156 (m), 753 (m) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 247 (15) [M$^+$], 147 (15) [$C_8H_7N_2O^+$], 120 (9) [$C_8H_7O^+$], 119 (25) [$C_8H_7O^+$], 105 (27) [$C_7H_5O^+$], 100 (36) [$C_6H_{14}N^+$], 92 (8), 91 (100) [$C_6H_5N^+$], 77 (6) [$C_6H_5^+$], 58 (6) [$C_3H_8N^+$], 43 (20) [$C_3H_7^+$]. HR-EIMS ($C_{14}H_{21}N_3O$): calcd. 247.1685; found 247.1683; elemental analysis ($C_{14}H_{21}N_3O$): calcd. C 67.98, H 8.56, N 16.99; found C 67.62, H 8.34, N 16.93.

(*E*)-1-[2-(3,3-Diisopropyltriaz-1-enyl)-3-(trifluoromethyl)phenyl]ethanone (13e): Following general procedure D, compound **9e** (597 mg, 2.00 mmol) was treated with MeMgBr (3 M in Et_2O, 2.00 mL, 3.20 mmol) in THF (15 mL). Column chromatography on silica (*n*-pentane/diethyl ether, 3:1) yielded 493 mg (1.56 mmol, 78%) of a white solid. R_f (*n*-pentane/diethyl ether, 3:1) = 0.35. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (dd, J = 7.8, J = 0.9 Hz, 1 H, Ar-H^6), 7.40 (dd, J = 7.1 Hz, 1 H, Ar-H^4), 7.18 (dt, J = 7.7, J = 0.6 Hz, 1 H, Ar-H^5), 5.13 (sept, J = 6.8 Hz, 1 H, CH), 4.00 (sept, J = 6.6 Hz, 1 H, CH), 2.12 (s, 3 H, CH_3), 1.31 (d, J = 6.6 Hz, 6 H, 2×CH_3), 1.28 (d, J = 6.8 Hz, 6 H, 2×CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 202.46 (C_q, C=O), 179.29 (C_q, C^2-Ar), 131.62 (+, C^6-Ar), 128.02 (+, J = 5.4 Hz, q, C^4-Ar), 126.77 (+, q, C^1-Ar, J = 5.4 Hz), 124.08 (+, q, *C*CF$_3$, J = 29.8 Hz), 124.03 (+, q, CF_3, J = 273.5 Hz), 123.82 (+, C^5-Ar), 50.11 (+, CH), 47.15 (+, CH), 23.42 (+, CO*C*H$_3$), 19.18 (+, 4×CH_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –58.2 (m, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2976 (w), 2935 (w), 1694 (w) [C=O], 1629 (w), 1583 (w), 1405 (m), 1368 (m), 1312 (s), 1229 (m) [–C–N valence], 1133 (s) [CF_3] cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 315 (18) [M$^+$], 215 (8) [$C_9H_6F_3N_2O^+$], 201 (39) [$C_9H_6F_3NO^+$], 187 (28) [$C_9H_6F_3O^+$], 173 (22) [$C_7H_4F_3N_2^+$], 172 (15) [$C_8H_3F_3O^+$], 166 (54), 159 (100) [$C_7H_4F_3N^+$], 145 (11) [$C_7H_4F_3^+$], 100 (51) [$C_6H_{14}N^+$], 58 (25) [$C_3H_8N^+$], 43 (56) [$C_3H_7^+$]. HR-EIMS ($C_{15}H_{20}F_3N_3O$): calcd. 315.1558; found 315.1556; elemental analysis ($C_{15}H_{20}F_3N_3O$): calcd. C 57.13, H 6.39, N 13.33; found C 56.89, H 6.17, N 14.17.

(*E*)-1-[2-(3,3-Diisopropyltriaz-1-enyl)-3-(trifluoromethyl)phenyl]pentan-1-imine (14e): To a solution of compound **9e** (597 mg, 2.00 mmol) in dry THF (15 mL) was added *n*-butyllithium (1.6 M in hexane, 2.00 mL, 3.20 mmol) dropwise at 0 °C. After stirring at room temp. for 2.5 h, no starting material could be detected via TLC and the reaction was quenched with saturated NH_4Cl solution (7 mL). The aqueous phase was extracted with EtOAc (3×30 mL), the organic phase was washed with brine (20 mL) and dried with Na_2SO_4. Column chromatography on silica (cyclohexane/ethyl acetate, 1:1) yielded 570 mg (1.60 mmol, 80%) of the product. R_f (cyclohexane/ethyl acetate, 1:1) = 0.29. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.26 (br. s, 1 H, NH), 7.64 (dd, J = 7.8, J = 1.0 Hz, 1 H, Ar-H^6), 7.35 (dd, J = 7.5 Hz, 1 H, Ar-H^4), 7.18 (dt, J = 7.7, J = 0.5 Hz, 1 H, Ar-H^5), 5.09 (sept, J = 6.8 Hz, 1 H, CH), 3.99 (sept, J = 6.6 Hz, 1 H, CH), 2.34 (t, J = 7.9 Hz, 2 H, C*H*$_2$C=NH), 1.48–1.40 (m, 2 H, CH_2), 1.33–1.21 (m, 2 H, CH_2), 1.29 (d, J = 6.6 Hz, 6 H, 2×CH_3), 1.27 (d, J = 6.8 Hz, 6 H, 2×CH_3), 0.85 (t, J = 7.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.88 (C_q, C=NH), 135.38 (C_q, C^2-Ar), 134.66 (+, C^1-Ar), 132.06 (+, C^6-Ar), 126.68 (+, q, C^4-Ar, J = 5.6 Hz), 124.04 (+, q, CF_3, J = 273.5 Hz), 123.88 (+, q, *C*CF$_3$, J = 29.7 Hz), 123.77 (+, C^5-Ar), 50.11 (+, CH), 47.00 (+, CH), 39.48 (–, *C*H$_2$C=NH), 28.42 (–, CH_2), 23.34 (+, 2×CH_3), 22.45 (–, CH_2), 19.15 (+, 2×CH_3), 13.83 (+, CH_3). ^{19}F NMR (376 MHz, $CDCl_3$): δ = –59.4 (m, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 2972 (m) 2934 (m) [–C–H valence], 2873 (w), 1691 (w) [C=NH], 1626 (w), 1584 (w), 1405 (s), 1315 (m), 1229 (m) [–C–N valence], 1134 (s) [CF_3], 1032 (w), 775 (w), 753 (w) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 356 (28) [M$^+$], 299 (26) [$C_{14}H_{18}F_3N_4^+$], 285 (9) [$C_{14}H_{18}F_3N_3$ +], 243 (100) [$C_{11}H_{12}F_3N_3^+$], 228 (14) [$C_{12}H_{13}F_3N^+$], 223 (28), 208 (11), 201 (42) [$C_{11}H_{13}N_4^+$], 200 (38) [$C_8H_5F_3N_3^+$], 188 (10) [$C_{10}H_{12}N_4^+$], 187 (13) [$C_{10}H_{11}N_4^+$], 173 (37) [$C_7H_4F_3N_2^+$], 172 (81) [$C_8H_5F_3N^+$], 166 (17), 145 (12) [$C_7H_4F_3^+$], 100 (16) [$C_6H_{14}N^+$], 84 (12) [$C_5H_{10}N^+$], 58 (16) [$C_3H_8N^+$], 43 (52) [$C_3H_7^+$]. HR-EIMS ($C_{18}H_{27}F_3N_4$): calcd. 356.2188; found 356.2186.

(*E*)-[2-(3,3-Diisopropyltriaz-1-enyl)-3-(trifluoromethyl)phenyl](phenyl)methanimine (16e): To a solution of compound **9e** (597 mg, 2.00 mol) in dry THF (15 mL) was added phenyllithium (2.0 M in dibutyl ether, 1.60 mL, 3.20 mmol) dropwise at 0 °C. After stirring at room temp. for 2.5 h, no starting material could be detected via TLC and the reaction was quenched with saturated NH_4Cl solution (7 mL). The aqueous phase was extracted with EtOAc (3×30 mL), the organic phase was washed with brine (20 mL) and dried with Na_2SO_4. Column chromatography on silica (cyclohexane/ethyl acetate, 3:1) yielded 734 mg (1.95 mmol, 95%) of the product. R_f (cyclohexane/ethyl acetate, 1:1) = 0.56. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.52 (br. s, 1 H, NH), 7.73 (dd, J = 7.8, J = 1.0 Hz, 1 H, Ar-H^4), 7.62 (d, J = 7.3 Hz, 2 H, Ar$_o$-H), 7.42 (d, J = 7.5 Hz, 1 H, Ar$_p$-H), 7.39–7.35 (m, 1 H, Ar-H^6), 7.33–7.28 (m, 2 H, Ar$_m$-H) 7.23 (dt, J = 7.7, J = 0.5 Hz, 1 H, Ar-H^5), 4.63 (sept, J = 6.8 Hz, 1 H, CH), 3.77 (sept, J = 6.6 Hz, 1 H, CH), 1.03 (d, J = 6.7 Hz, 6 H, 2×CH_3), 1.00 (d, J = 6.8 Hz, 6 H, 2×CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.33 (C_q, C=NH), 148.22 (C_q, C^2-Ar), 137.75 (+, C$_i$-Ar), 133.38 (+, C$_o$-Ar), 133.05 (+, C^6-Ar), 130.24 (+, C$_p$-Ar), 128.08 (+, C^1-Ar), 127.99 (+, C$_m$-Ar), 127.08 (+, J = 5.5 Hz, q, C^4-Ar), 124.07 (+, q, CF_3, J = 273.5 Hz), 124.00 (+, q, *C*CF$_3$, J = 29.6 Hz), 123.64 (+, C^5-Ar), 50.47 (+, CH), 47.18 (+, CH), 22.81 (+, CH_3), 18.71 (+, CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 2975 (m), 2935 (w) [–C–H valence], 1603 (w) [C=NH], 1405 (s), 1367 (m),

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1316 (s), 1278 (m) [–C–N valence], 1133 (s) [CF_3], 1031 (w), 939 (w), 883 (w), 768 (w), 698 (m) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 376/377 (65/15) [M^+], 305 (8) [$C_{19}H_{21}N_4^+$], 263/264 (57/9) [$C_{14}H_{10}F_3N_2^+$], 248/249 (100/17) [$C_{14}H_9F_3N^+$], 243 (22)[$C_{11}H_{12}F_3N_3^+$], 228 (29) [$C_{10}H_8F_3N_3^+$], 104 (10), 100 (24) [$C_6H_{14}N^+$], 74 (14) [$C_4H_{12}N^+$], 59 (31) [$C_3H_9N_+$], 43 (20) [$C_3H_7^+$]. HR-EIMS ($C_{20}H_{23}F_3N_4$): calcd. 376.175; found 376.1877; elemental analysis ($C_{20}H_{23}F_3N_4$): calcd. C 63.82, H 6.16, N 14.88; found C 63.88, H 6.06, N 14.65.

(*E*)-[2-(Pyrrolidin-1-yldiazenyl)phenyl]methanamine (18a): Following general procedure E, compound **9a** (200 mg, 1.00 mol) was reduced by $LiAlH_4$ (76.0 mg, 2.00 mmol) to yield 183 mg (0.90 mmol, 90%) of a yellow oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42 (ddd, *J* = 7.2, *J* = 1.4, *J* = 0.9 Hz, 1 H, Ar-H^3), 7.22–7.19 (m, 2 H, Ar-H^4, Ar-H^5), 7.07 (ddt, *J* = 7.4, *J* = 1.2 Hz, 1 H, Ar-H^6), 3.96 (s, 2 H, C*H*$_2$-NH_2), 3.80 [br. s, 4 H, $N(CH_2)_2$], 2.28 (br. s, 2 H, NH_2), 2.05–2.01 (m, 4 H, 2×CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.85 (C_q, C^2-Ar), 137.16 (+, C^4-Ar), 128.54 (+, C^6-Ar), 127.66 (C_q, C^1-Ar), 125.28 (+, C^5-Ar), 116.48 (+, C^3-Ar), 77.27 [–, $N(CH_2)_2$], 44.45 (–, CH_2–NH_2), 23.79 (–, 2×CH_2). IR (KBr): $\tilde{\nu}$ = 3299 (vw) [NH_2], 3063 (w), 3028 (w), 2971 (m), 2870 (m) [–C–H valence], 1712 (w), 1662 (m) [NH_2], 1595 (w), 1580 (w), 1480 (m), 1413 (m), 1318 (m), 1222 (m) [–C–N valence], 1161 (w), 1104 (w), 761 (m), 561 (w) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 204 (8) [M^+], 148 (8) [$C_7H_8N_4^+$], 133 (19) [$C_7H_7N_3^+$], 106 (100) [$C_7H_8N^+$], 105 (9) [$C_7H_7N^+$], 104 (11) [$C_7H_6N^+$], 84 (15) [$C_4H_8N_2^+$], 77 (24) [$C_6H_5^+$], 70 (8) [$C_4H_8N^+$], 56 (5) [$C_3H_6N^+$], 43 (11) [$C_2H_5N^+$]. HR-EIMS ($C_{11}H_{16}N_4$): calcd. 204.1375; found 204.1378.

(*E*)-[2-(3,3-Diethyltriaz-1-enyl)phenyl]methanamine (18c): Following general procedure E, compound **9c** (500 mg, 2.47 mmol) was reduced by $LiAlH_4$ (190 mg, 5.01 mmol) to yield 478 mg (2.32 mmol, 93%) of a yellow oil. R_f (1% triethylamine in methanol) = 0.14. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47 (ddd, *J* = 7.2 Hz, 1 H, Ar-H^3), 7.28–7.24 (m, 2 H, Ar-H^4, Ar-H^5), 7.13 (dt, *J* = 7.3, *J* = 1.2 Hz, 1 H, Ar-H^6), 4.02 (s, 2 H, C*H*$_2$-NH_2), 3.81 [q, *J* = 7.2 Hz, 4 H, $N(CH_2)_2$], 2.00 (br. s, 2 H, NH_2), 1.32 (t, *J* = 6.7 Hz, 6 H, 2×CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.57 (C_q, C^2-Ar), 137.45 (+, C^4-Ar), 128.46 (+, C^6-Ar), 127.59 (C_q, C^1-Ar), 126.17 (+, C^5-Ar), 117.47 (+, C^3-Ar), 44.39 [–, $N(CH_2)_2$], 22.63 (–, CH_2–NH_2), 12.11 (+, 2×CH_3). IR (KBr): $\tilde{\nu}$ = 3367 (w) [NH_2], 3064 (w), 2974 (m), 2933 (m) [–C–H valence], 2871 (m), 1581 (w), 1412 (s), 1380 (s), 1342 (s), 1281 (m) [–C–N valence], 1239 (s), 1201 (m), 1086 (s), 902 (w), 760 (s), 639 (w), 572 (w) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 206 (36) [M^+], 190 (47) [$C_{11}H_{16}N_3^+$], 149 (16) [$C_7H_9N_4^+$], 134 (8) [$C_7H_8N_3^+$], 132 (19) [$C_7H_6N_3^+$], 106 (100) [$C_7H_8N^+$], 105 (13) [$C_7H_7N^+$], 104 (10) [$C_7H_6N^+$], 77 (24) [$C_6H_5^+$]. HR-EIMS ($C_{12}H_{13}F_3N_4$): calcd. 206.1531; found 206.1533; elemental analysis ($C_{11}H_{18}N_4$): calcd. C 64.05, H 8.79, N 27.16; found C 64.04, H 8.46, N 26.65.

(*E*)-[2-(3,3-Diisopropyltriaz-1-enyl)phenyl]methanamine (18d): Following general procedure E, compound **9d** (500 mg, 2.17 mmol) was reduced by $LiAlH_4$ (170 mg, 4.48 mmol) to yield 506 mg (2.16 mmol, quant.) of a yellow oil. R_f (1% triethylamine methanol) = 0.14. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.49 (m, 1 H, Ar-H^3), 7.30–7.24 (m, 2 H, Ar-H^4, Ar-H^5), 7.11 (ddd, *J* = 7.4, *J* = 1.3 Hz, 1 H, Ar-H^6), 5.22 (br. s, 1 H, CH), 4.07 (br. s, 1 H CH), 2.00 (br. s, 2 H, CH_2), 1.37 (bd, 12 H, 4×CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.02 (C_q, C^2-Ar), 137.28 (+, C^4-Ar), 128.46 (+, C^6-Ar), 127.55 (C_q, C^1-Ar), 124.91 (+, C^5-Ar), 116.57 (+, C^3-Ar), 51.98 (+, 2×CH), 44.50 (–, CH_2–NH_2), 20.65 (+, 4×CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3371 (w) [NH_2], 3063 (w), 2973 (m), 2931 (m) [–C–H valence], 2869 (m), 1580 (w), 1418 (s), 1365 (s) 1283 (m) [–C–N valence], 1228 (s), 1151 (m), 1030 (m), 898 (w), 760 (s), 640 (w), 542 (w) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 234 (100) [M^+], 218 (3) [$C_{13}H_{20}N_4^+$], 134 (6) [$C_7H_8N_3$]. HR-EIMS ($C_{13}H_{22}N_4$): calcd. 234,1844; found 234.1841; elemental analysis ($C_{13}H_{22}N_4$): calcd. C 66.63, H 9.46, N 23.91; found C 66.26, H 9.27, N 23.36.

(*E*)-[2-(3,3-Diisopropyltriaz-1-enyl)-3-(trifluoromethyl)phenyl]-methanamine (18e): Following general procedure F, compound **9e** (2.22 g, 7.44 mmol) was reduced by a $LiAlH_4$ solution (1 M in THF, 14.9 mL, 14.9 mmol) to yield 1.28 g (4.23 mmol, 57%) of a yellow oil after column chromatography on silica (CH_2Cl_2/methanol with 1% of triethylamine, 19:1). R_f (CH_2Cl_2/methanol with 1% of triethylamine, 9:1) = 0.33. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.57 (dd, *J* = 7.8, *J* = 0.9 Hz, 1 H, Ar-H^4), 7.50 (dd, *J* = 7.6 Hz, 1 H, Ar-H^6), 7.17 (dt, *J* = 7.6 Hz, 1 H, Ar-H^5), 5.19 (sept, *J* = 6.8 Hz, 1 H, CH), 4.03 (sept, *J* = 6.7 Hz, 1 H, CH), 3.75 (s, 2 H, CH_2), 2.33 (br. s, 2 H, NH_2), 1.35 (d, *J* = 6.7 Hz, 6 H, 2×CH_3), 1.28 (d, *J* = 6.8 Hz, 6 H, 2×CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.06 (C_q, C^2-Ar), 136.10 (+, C^5-Ar), 132.54 (+, C^6-Ar), 125.46 (+, q, C^5-Ar, *J* = 5.6 Hz), 124.23 (+, C^4-Ar), 124.19 (+, q, CF_3, *J* = 273.6 Hz), 123.35 (+, q, C^3-Ar, *J* = 29.7 Hz), 49.25 (+, CH), 46.22 (+, CH), 43.43 (–, CH_2), 23.36 (+, CH_3), 19.19 (+, CH_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –58.6 (m, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3363 (w) [NH_2], 3074 (w), 2976 (m), 2935 (m) [–C–H valence], 2874 (m) [CH_2 valence], 1639 (w) [NH_2], 1596 (m), 1426 (m), 1405 (m), 1367 (m), 1318 (m) [–C–N valence], 1129 (m) [CF_3], 779 (m) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 302 (8) [M^+], 215 (28), 201 (16) [$C_8H_6F_3N_3^+$], 189 (57) [$C_8H_8F_3N_2^+$], 188 (17) [$C_8H_7F_3N_2^+$], 174 (29) [$C_8H_7F_3N^+$], 172 (11) [$C_8H_5F_3N^+$], 145 (12) [$C_7H_4F_3^+$], 100 (12) [$C_6H_{14}N^+$], 58 (25) [$C_3H_8N^+$], 43 (51) [$C_3H_7^+$]. HR-EIMS ($C_{14}H_{21}F_3N_4$): calcd. 302.1718; found 302.1716.

(*E*)-[2-(3,3-Diethyltriaz-1-enyl)-3-(trifluoromethyl)phenyl]methanamine (18f): Following general procedure F, compound **9f** (270 mg, 1.00 mmol) was reduced by a $LiAlH_4$ solution (1 M in THF, 2.0 mL, 2.00 mmol) to yield 68.0 mg (0.25 mmol, 25%) of a yellow oil. R_f (1% triethylamine methanol) = 0.26. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 (dd, *J* = 7.9, *J* = 0.9 Hz, 1 H, Ar-H^4), 7.48 (dd, *J* = 7.6 Hz, 1 H, Ar-H^6), 7.18 (dt, *J* = 7.6, *J* = 0.5 Hz, 1 H, Ar-H^5), 3.77 [q, *J* = 6.7 Hz, 4 H, $N(CH_2)_2$], 3.70 (s, 2 H, CH_2), 1.62 (br. s, 2 H, NH_2), 1.32–1.25 (m, 6 H, 2×CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.64 (C_q, C^2-Ar), 136.99 (+, C^6-Ar), 132.69 (C_q, C^1-Ar), 125.27 (+, q, C^4-Ar, *J* = 5.5 Hz), 124.44 (+, C^5-Ar), 124.17 (+, q, CF_3, *J* = 273.5 Hz), 123.51 (+, q, C^3-Ar, *J* = 29.6 Hz), 48.99 (–, *C*H_2CH$_3$), 43.70 (–, *C*H_2NH$_2$), 41.13 (–, *C*H_2CH$_3$), 14.44 (+, CH_3), 11.13 (+, CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3440 (br.) [NH_2], 2977 (vw), 2937 (vw) [–CH_2 valence], 1587 (vw), 1449 (w), 1317 (w) [–C–N valence], 1129 (w) [CF_3], 773 (vw), 752 (vw) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 274 (9) [M^+], 200 (10) [$C_8H_5F_3N_3^+$], 189 (8) [$C_8H_8F_3N_2^+$], 174 (13) [$C_8H_7F_3N_+$], 173 (10) [$C_8H_6F_3N^+$], 172 (10) [$C_8H_5F_3N^+$], 134 (13) [$C_7H_8N_3^+$], 127 (20), 87 (14) [$C_7H_3^+$], 86 (24), 74 (8) [$C_4H_{12}N^+$], 57 (9) [$C_3H_7N^+$]. HR-EIMS ($C_{12}H_{17}F_3N_4$): calcd. 274.1405; found 274.1396.

1-(Diethylamino)-7-(trifluoromethyl)-1H-indazol-3(2H)-one (19f): ^1H NMR (400 MHz, $CDCl_3$): δ = 7.62 (dd, *J* = 8.3 Hz, 1 H, Ar-H^{10}), 7.52 (qdd, *J* = 7.0, *J* = 1.0 Hz, 1 H, Ar-H^8), 6.83 (ddt, *J* = 7.1, *J* = 0.6 Hz, 1 H, Ar-H^9), 4.51 (br. s, 1 H, NH), 3.56 (q, *J* = 4.8 Hz, 2 H, NCH_2), 3.10 (q, *J* = 4.5 Hz, 2 H, NCH_2), 0.85 (t, *J* = 7.1 Hz, 6 H, 2×CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.38 (C_q, C=O), 140.82 (C_q, C^6-Ar), 139.63 (+, C^8-Ar), 125.20 (+, q, C^9-Ar, *J* = 5.4 Hz), 124.21 (+, C^{10}-Ar), 124.21 (+, q, CF_3, *J* = 271.8 Hz), 117.25 (C_q, q, *C*CF_3, *J* = 32.2 Hz), 115.54 (C_q, C^5-Ar), 51.74 (–, 2×CH_2), 12.15 (+, 2×CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3465

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(vw) [N–H], 3154 (w), 3110 (w), 2974 (w) [–C–H valence], 2875 (vw), 1639 (w) (C=O), 1614 (w), 1309 (w), 1248 (w) [–C–N valence], 1111 (w), 753 (w) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 273 (7) [M^+], 272 (63) [$M^+ - 1$], 253 (8), 201 (18) [$C_8H_4F_3N_2O^+$], 172 (9) [$C_8H_3F_3O^+$], 151 (9), 73 (18) [$C_4H_{11}N^+$], 72 (22) [$C_4H_{10}N^+$], 58 (100) [$C_3H_8N^+$]. HR-EIMS ($C_{12}H_{14}N_3F_4O$): calcd. 273.1089; found 273.1084; elemental analysis ($C_{12}H_{14}N_3F_4O$): calcd. C 52.75, H 5.16, N 15.38; found C 52.28, H 5.01, N 17.77.

(*E*)-1-[2-(3,3-Diisopropyltriaz-1-enyl)-3-(trifluoromethyl)phenyl]-ethanamine (20e): Following general procedure G, compound **13e** (140 mg, 0.44 mmol) was reduced with ammonia (2 M in methanol, 1.11 mL, 2.22 mmol), Ti(O*i*Pr)$_4$ (0.20 mL, 0.89 mmol) and $LiBH_4$ (2 M in THF, 0.30 mL, 0.67 mmol). Column chromatography (*n*-pentane/diethyl ether + 10% triethylamine, 3:1) on silica yielded 80.0 mg (0.25 mmol, 57%) of a yellow oil. R_f (*n*-pentane/diethyl ether + 10% triethylamine, 3:1) = 0.12. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66 (dd, J = 6.9 Hz, 1 H, Ar-H^6), 7.53 (dd, J = 7.7, J = 1.0 Hz, 1 H, Ar-H^4), 7.22 (dt, J = 7.8 Hz, 1 H, Ar-H^5), 5.19 (sept, J = 6.8 Hz, 1 H, CH), 4.23 (q, J = 6.7 Hz, 1 H, NH_2CH), 4.00 (sept, J = 6.6 Hz, 1 H, CH), 1.54 (br. s, 2 H, NH_2), 1.34 [d, J = 6.7 Hz, 6 H, $CH(CH_3)_2$], 1.33 (d, J = 6.6 Hz, 3 H, CH_3), 1.28 [d, J = 6.8 Hz, 6 H, $CH(CH_3)_2$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.77 (C_q, C^2-Ar), 148.88 (+, C^6-Ar), 141.74 (C_q, C^1-Ar), 128.90 (+, C^4-Ar), 124.86 (+, q, C^5-Ar, J = 5.5 Hz), 124.22 (+, q, CF_3, J = 273.5 Hz), 122.81 (C_q, q, C^3-Ar, J = 29.6 Hz), 49.01 (+, CH), 45.91 (+, CH), 45.49 (+, NH_2CH), 23.99 (+, $CHCH_3$), 23.42 (+, 2×CH_3), 19.31 (+, 2×CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3373 (br.) [NH_2], 3074 (vw), 2975 (m), 2933 (m) [–C–H valence], 2871 (w) [–CH_3 valence], 1947 (vw), 1668 (w), 1596 (w), 1430 (m), 1403 (m), 1367 (m), 1317 (m) 1226 (m) [–C–N valence], 1128 (m) [CF_3], 1031 (w), 922 (vw), 778 (w), 741 (w) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 316 (0.5) [M^+], 228 (21) [$C_{10}H_9F_3N_3^+$], 203 (100) [$C_{12}H_{17}N_3^+$], 186 (80) [$C_9H_7F_3N^+$], 168 (48), 115 (44) [$C_6H_{15}N_2^+$], 100 (16) [$C_6H_{14}N^+$], 73 (26) [$C_4H_{11}N^+$], 43 (54) [$C_3H_7^+$]; elemental analysis ($C_{15}H_{23}F_3N_4$): calcd. C 56.95, H 7.33, N 17.71; found C 56.79, H 7.22, N 13.79.

(*E*)-1-[2-(3,3-Diisopropyltriaz-1-enyl)-3-(trifluoromethyl)phenyl]-pentan-1-amine (21e): A solution of compound **14e** (170 mg, 0.48 mmol) in dry THF (5 mL) was cooled down to 0 °C. At this temperature lithium borohydride (0.36 mL, 0.72 mmol) was added dropwise. The resulting solution was heated up to room temp. and stirred for 6 h until no more starting material could be detected via TLC. Then water (5 mL) was added and the aqueous layer was extracted with EtOAc (3 × 15 mL), the organic layer was washed with brine (15 mL) and dried with Na_2SO_4. Column chromatography on silica (*n*-pentane/diethyl ether, 5:1 + 0.2% of triethylamine) gave 88.0 mg (0.25 mmol, 51%) of a yellow oil. R_f (*n*-pentane/diethyl ether, 5:1 + 0.2% of triethylamine) = 0.21. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (dd, J = 7.7 Hz, 1 H, Ar-H^6), 7.52 (dd, J = 7.9 Hz, 1 H, Ar-H^4), 7.21 (dt, J = 7.8 Hz, 1 H, Ar-H^5), 5.18 (sept, J = 6.8 Hz, 1 H, CH), 4.04 (m, 1 H, $CHNH_2$), 3.99 (sept, J = 6.6 Hz, 1 H, CH), 1.69–1.54 (m, 2 H, $CHCH_2$), 1.50 (br. s, 2 H, NH_2), 1.36–1.23 (m, 16 H, 2×CH_2, 4×CH_3), 0.85 (t, J = 7.2 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.66 (C_q, C^2-Ar), 138.59 (+, C^6-Ar), 130.17 (C_q, C^1-Ar), 125.76 (+, q, C^4-Ar, J = 5.6 Hz), 124.30 (+, C^5-Ar), 124.18 (+, q, CF_3, J = 273.5 Hz), 122.84 (+, q, CCF_3, J = 29.9 Hz), 49.29 (+, CH), 46.20 (+, CH), 37.10 (+, $CHNH_2$), 28.47 (–, $CHCH_2$), 23.28 (–, CH_2), 23.20 (–, CH_2), 22.65 (+, 2×CH_3), 19.27 (+, 2×CH_3), 14.02 (+, CH_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –59.9 (m, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3404 (br.) [NH_2], 3076 (w), 2973 (m), 2934 (m) [–C–H valence], 2873 (m), 1597 (w), 1431 (m), 1367 (m), 1318 (m), 1266 (m) [–C–N valence], 1226 (m), 1193 (m), 1129 (m) [CF_3], 1098 (m), 1031 (w), 780 (w), 671 (w) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 359/360 (100) [M + 1], 340 (13) [$C_{17}H_{23}F_3N_4^+$], 302 (23) [$C_{14}H_{21}F_3N_4^+$], 259 (7) [$C_{11}H_{14}F_3N_4^+$], 246 (19) [$C_{11}H_{15}F_3N_3^+$], 185 (14) [$C_8H_4F_3N_2^+$], 175 (63), 173 (16) [$C_7H_4F_3N_2^+$], 159 (8) [$C_8H_6F_3^+$], 155 (26), 127 (15) [$C_6H_{13}N_3^+$], 115 (27) [$C_5H_{13}N_3^+$], 100 (40) [$C_6H_{14}N^+$]; elemental analysis ($C_{18}H_{29}F_3N_4$): calcd. C 60.31, H 8.15, N 15.63; found C 60.45, H 8.00, N 15.56.

(*E*)-[2-(3,3-Diisopropyltriaz-1-enyl)-3-(trifluoromethyl)phenyl]-(phenyl)methanamine (22e): A solution of compound **16e** (347 mg, 0.92 mmol) in dry THF (5 mL) was cooled down to 0 °C. At this temperature lithium borohydride (0.69 mL, 1.38 mmol) was added dropwise. The resulting solution was heated up to room temp. and stirred for 6 h until no more starting material could be detected via TLC. Then water (5 mL) was added and the aqueous layer was extracted with EtOAc (3 × 15 mL), the organic layer washed with brine (15 mL) and dried with Na_2SO_4. Column chromatography on silica (*n*-pentane/diethyl ether, 1:2 + 0.2% of triethylamine) gave 100 mg (0.26 mmol, 30%) of a yellow oil. R_f (*n*-pentane/diethyl ether, 1:2 + 0.2% of triethylamine) = 0.15. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (dd, J = 7.8, J = 1.1 Hz, 1 H, Ar-H^4), 7.46 (dd, J = 7.7 Hz, 1 H, Ar-H^6), 7.33–7.27 (m, 4 H, Ar$_o$-H, Ar$_m$-H), 7.22–7.15 (m, 2 H, Ar$_p$-H, Ar-H^5), 5.40 (s, 1 H, CH), 5.17 (sept, J = 6.8 Hz, 1 H, CH), 3.94 (sept, J = 6.6 Hz, 1 H, CH), 1.81 (br. s, 2 H, NH_2), 1.24 (dd, J = 34.7, J = 6.8 Hz, 6 H, 2×CH_3), 1.24 (dd, J = 6.8, J = 2.3 Hz, 6 H, 2×CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.37 (C_q, C^2-Ar), 144.48 (+, C$_i$-Ar), 140.23 (+, C^6-Ar), 131.26 (+, C^1-Ar), 128.33 (+, C$_o$-Ar), 127.06 (+, C$_p$-Ar), 126.58 (+, C$_m$-Ar), 125.35 (+, q, C^4-Ar, J = 5.5 Hz), 124.30 (+, C^5-Ar), 124.20 (+, q, CF_3, J = 273.6 Hz), 122.73 (+, q, $CCF3$, J = 29.8 Hz), 53.72 (+, $CHNH_2$), 48.93 (+, CH), 45.83 (+, CH), 23.31 (+, CH_3), 19.27 (+, CH_3) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = –57.8 (m, CF_3) ppm. IR (KBr): $\tilde{\nu}$ = 3376 (br.) [NH_2], 3310 (vw), 2976 (vw), 2930 (vw) [–C–H valence], 1736 (vw), 1493 (vw), 1428 (w), 1367 (w), 1317 (w), 1271 (w) [–C–*N* valence], 1226 (w), 1150 (w), 1127 (w) [CF_3], 1082 (w), 1030 (vw), 781 (vw), 739 (vw), 700 (w), 672 (vw) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 378 (84) [M^+], 362 (90) [$C_{20}H_{23}F_3N_3^+$], 341 (13), 281 (17), 227 (17) [$C_{10}H_7F_3N_3$ +], 178 (19) [$C_{13}H_8N^+$], 153 (17), 127 (21), 100 (27) [$C_6H_{14}N^+$], 86 (48) [$C_5H_{12}N^+$], 84 (100) [$C_5H_{10}N^+$], 77 (35) [$C_6H_5^+$], 44 (35), 43 (40) [$C_2H_5N^+$], 41 (60) [$C_2H_3N^+$]. HR-EIMS ($C_{20}H_{25}F_3N_4$): calcd. 378.2031; found 378.2030; elemental analysis ($C_{20}H_{25}F_3N_4$): calcd. C 63.48, H 6.66, N 14.80; found C 62.52, H 6.72, N 13.72.

(*E*)-1-[2-(3,3-Diisopropyltriaz-1-enyl)phenyl]ethanamine (23d): Following general procedure G, compound **13d** (150 mg, 0.61 mmol) was reduced with ammonia (2 M in methanol, 1.50 mL, 3.03 mmol), Ti(O*i*Pr)$_4$ (0.40 mL, 1.21 mmol) and $LiBH_4$ (2 M in THF, 0.50 mL, 0.91 mmol). Column chromatography (*n*-pentane/diethyl ether, 1:1) on silica yielded 59.1 mg (0.24 mmol, 39%) of a yellow oil. R_f (*n*-pentane/diethyl ether, 1:1) = 0.15. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (ddd, J = 7.9, J = 1.2 Hz, 1 H, Ar-H^3), 7.35 (ddd, J = 7.6, J = 1.5 Hz, 1 H, Ar-H^6), 7.24–7.21 (m, 1 H, Ar-H^5), 7.11 (dt, J = 7.0, J = 1.9 Hz, 1 H, Ar-H^4), 5.14 (br. s, 2 H, 2×CH), 4.62 (q, J = 6.8 Hz, 1 H, $CHNH_2$), 1.45 (d, J = 6.8 Hz, 3 H, CH_3), 1.33–1.29 (m, 14 H, NH_2, 4×CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.31 (C_q, C^2-Ar), 128.86 (C_q, C^1-Ar), 127.01 (+, C^6-Ar), 125.24 (+, C^4-Ar), 124.96 (+, C^5-Ar), 116.45 (+, C^3-Ar), 56.71 (+, CH), 50.74 (+, CH), 47.41 (+, NH_2CH), 23.52 (+, CH-CH_3), 17.46 (+, 4×CH_3) ppm. IR (KBr): $\tilde{\nu}$ = 3064 (w), 2973 (m) 2931 (m) [–C–H valence], 2871 (w) [–CH_3 valence], 2361 (w), 2315 (w), 1467 (w), 1416 (s), 1364 (m) 1226 (m) [–C–N valence], 1154 (m), 1030 (w), 757 (w), 547 (vw) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 248 (10) [M^+], 232 (99) [$C_{14}H_{22}N_3^+$], 177 (55) [$C_{10}H_{15}N_3^+$], 160 (35) [$C_9H_{10}N_3^+$],

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135 (97) [$C_8H_{11}N_2^+$], 120 (78) [$C_8H_{10}N^+$], 118 (100) [$C_8H_8N^+$], 115 (28) [$C_6H_{15}N_2^+$], 103 (47) [$C_7H_5N^+$], 91 (21) [$C_7H_7^+$], 77 (20) [$C_6H_5^+$], 43 (41) [$C_3H_7^+$]. HR-EIMS ($C_{14}H_{24}N_4$): calcd. 248.2001; found 248.2004.

(*E*)-*N*-(1-{2-[(*E*)-3,3-Diisopropyltriaz-1-enyl]phenyl}ethylidene)-2-methylpropane-2-sulfinamide (24d): To a solution of compound **9d** (500 mg, 2.17 mmol) in dry THF (5 mL), methyllithium (1.6 M in diethyl ether, 1.76 mL, 2.82 mmol) was added at 0 °C. After stirring for 30 min at this temperature, the mixture was cooled down to –78 °C and *tert*-butylsulfinyl chloride (638 mg, 4.54 mmol) was added at once. After 10 min the reaction was warmed to 0 °C with the help of an ice bath and saturated NH_4Cl solution (50 mL) was added after 60 min at this temperature. The aqueous phase was extracted with EtOAc (3 × 40 mL), the organic phase washed with brine (30 mL) and dried with $MgSO_4$. The crude product was purified via column chromatography on silica (*n*-pentane/ethyl acetate, 7:3) to give 360 mg (1.03 mmol, 47%) of a yellow oil. R_f (*n*-pentane/ethyl acetate, 3:1) = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.47 (m, 1 H, Ar-H^3), 7.39–7.32 (m, 2 H, Ar-H^4, Ar-H^5), 7.10 (ddd, J = 7.4 Hz, 1 H, Ar-H^6), 5.18 (br. s, 1 H, CH), 4.00 (br. s, 1 H, CH), 2.69 (s, 3 H, NC-CH_3), 1.38 (s, 9 H, *t*Bu-H), 1.30 (m, 6 H, 2 CH_3), 1.14 (m, 6 H, 2×CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.39 (C_q, C=N), 147.93 (C_q, C^2-Ar), 135.11 (+, C^4-Ar), 129.19 (C_q, C^1-Ar), 127.49 (+, C^6-Ar), 123.43 (+, C^5-Ar), 116.55 (+, C^3-Ar), 60.41 [C_q, $C(CH_3)_3$], 48.15 (+, CH), 45.49 (+, CH), 22.92 [+, C(CH_3)$_3$], 21.76 (+, NC-CH_3), 18.37 [+, CH(CH_3)$_2$], 13.18 [+, CH(CH_3)$_2$] ppm. IR (KBr): $\tilde{\nu}$ = 3442 (br.), 3063 (vw), 2974 (m), 2929 (m) [–C–H valence], 1607 (m) [–C=N], 1475 (m), 1408 (s), 1364 (m) [*tert*-butyl], 1222 (s), 1158 (m) [CF_3], 1082 (m) [S=O], 758 (m) [–C–S valence] cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 350 (10) [M$^+$], 295 (15), 294 (100) [$C_{14}H_{22}N_4OS^+$], 293 (17) [$C_{14}H_{21}N_4OS^+$], 167 (13) [$C_8H_9NOS^+$], 166 (10) [$C_8H_8NOS^+$], 165 (34) [$C_8H_7NOS^+$], 146 (29), 137 (11), 133 (51) [$C_7H_3NS^+$], 132 (11), 123 (13), 119 (22), 118 (26), 117 (13) [$C_8H_7N^+$], 115 (12) [$C_5H_{13}N_3^+$], 100 (14) [$C_6H_{14}N^+$], 96 (11), 91 (19) [$C_7H_7^+$], 57 (25) [$C_4H_9^+$], 43 (42) [$C_2H_5N^+$], 41 (12) [$C_3H_5^+$]. HR-EIMS ($C_{18}H_{30}N_4OS$): calcd. 350.2140; found 350.2138.

(*E*)-*N*-(1-{2-[(*E*)-3,3-Diisopropyltriaz-1-enyl]-3-(trifluoromethyl)-phenyl}ethylidene)-2-methylpropane-2-sulfinamide (24e): To a solution of compound **9e** (895 mg, 3.00 mmol) in dry THF (10 mL), methyllithium (1.6 M in diethyl ether, 2.40 mL, 3.90 mmol) was added at 0 °C. After stirring for 30 min at this temperature the mixture was cooled down to –78 °C and *tert*-butylsulfinyl chloride (844 mg, 6.00 mmol) was added at once. After 10 min the reaction was warmed to 0 °C with the help of an ice bath and saturated NH_4Cl solution (50 mL) was added after 60 min at this temperature. The aqueous phase was extracted with EtOAc (3 × 40 mL), the organic phase washed with brine (30 mL) and dried with $MgSO_4$. The crude product was purified via column chromatography on silica (*n*-pentane/diethyl ether, 3:1) to give 854 mg (2.04 mmol, 68%) of a yellow oil. R_f (*n*-pentane/diethyl ether, 3:1) = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (dd, J = 7.6 Hz, 1 H, Ar-H^4), 7.52 (dd, J = 7.7 Hz, 1 H, Ar-H^6), 7.19 (dt, J = 7.7 Hz, 1 H, Ar-H^5), 5.00 (sept, J = 6.7 Hz, 1 H, CH), 4.05 (sept, J = 6.6 Hz, 1 H, CH), 2.31 (s, 3 H, NC-CH_3), 1.31 (s, 9 H, *t*Bu-H), 1.20 (m, 6 H, 2×CH_3), 1.14 (m, 6 H, 2×CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.29 (C_q, C=N), 148.45 (C_q, C^2-Ar), 134.71 (C_q, C^1-Ar), 133.11 (+, C^6-Ar), 127.69 (+, q, C^4-Ar, J = 5.0 Hz), 123.97 (+, q, CF_3, J = 273.5 Hz), 123.53 (+, C^5-Ar), 124.39 (+, q, C^3-Ar, J = 29.8 Hz), 60.37 [C_q, $C(CH_3)_3$], 51.00 (+, CH), 48.07 (+, CH), 23.45 [+, C(CH_3)$_3$], 21.03 (+, NC-CH_3), 19.12 [+, CH(CH_3)$_2$], 14.17 [+, CH(CH_3)$_2$] ppm. IR (KBr): $\tilde{\nu}$ = 3451 (vw), 3189 (br.), 2975 (m) [–CH_3 valence], 2931 (w), 1739 (w), 1587 (w), 1525 (w), 1404 (m), 1364 (m) [*tert*-butyl], 1322 (m), 1272 (m) [–C–*N* valence], 1158 (m), 1130 (m) [CF_3], 1082 (m) [S=O] cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 418/419 (12/3) [M$^+$], 362/363 (100/18) [$C_{15}H_{21}F_3N_4OS^+$], 361 (15) [$C_{15}H_{20}F_3N_4OS^+$], 261 (22) [$C_9H_6F_3N_3OS^+$], 233/234 (80/13) [$C_9H_6F_3NOS^+$], 214 (11) [$C_9H_6F_3N_3^+$], 213 (15) [$C_9H_6F_3N_3^+$], 200 (12) [$C_9H_7F_3N_2^+$], 187 (11) [$C_7H_4F_3N_3^+$], 186 (17) [$C_7H_3F_3N_3^+$], 181 (15), 166 (12), 100 (13) [$C_6H_{14}N^+$]. HR-EIMS ($C_{19}H_{29}F_3N_4OS$): calcd. 418.2014; found 418.2011; elemental analysis ($C_{19}H_{29}F_3N_4OS$): calcd. C 54.53, H 6.98, N 13.39; found C 54.28, H 6.72, N 13.12.

(*E*)-*N*-{1-[2-(3,3-Diisopropyltriaz-1-enyl)phenyl]-1-phenylethyl}-2-methylpropane-2-sulfinamide (25): To a solution of compound **24d** (165 mg, 0.47 mmol) in toluene (2 mL), a $AlMe_3$ solution (2 M in toluene, 0.26 mL, 0.52 mmol) was added at –78 °C and the resulting mixture was stirred for 5 min. The mixture was then added to a solution of phenyllithium (2 M in dibutyl ether, 0.52 mL, 0.26 mmol) in toluene (1.5 mL) and also cooled to –78 °C within 10 to 15 min. The reaction was stirred for 3.5 h at this temperature, warmed to 0 °C and saturated Na_2SO_4 solution (2 mL) was added. The aqueous phase was separated and the organic phase was dried with $MgSO_4$. Purification of the crude product on silica (*n*-pentane/ethyl acetate, 2:1) gave 116 mg (0.27 mmol, 58%) of a yellow solid. R_f (*n*-pentane/ethyl acetate, 2:1) = 0.15. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.49 (m, 1 H, Ar-H^3), 7.36–7.25 (m, 4 H, Ar-H^6, Ar-H^5, Ar-H$_o$), 7.18–7.11 (m, 3 H, Ar-H$_m$, Ar-H$_p$), 7.03 (tt, J = 7.3, J = 1.2 Hz, 1 H, Ar-H^4), 4.62 (sept, J = 6.6 Hz, 1 H, CH), 3.74 (sept, J = 6.4 Hz, 1 H, CH), 2.01 (s, 3 H, NC-CH_3), 1.81 (br. s, 1 H, NH), 1.28 (d, 3 H, CH_3), 1.09 (d, J = 6.4 Hz, 3 H, CH_3), 1.07 (s, 9 H, *t*Bu-H), 1.03 (d, J = 6.8 Hz, 3 H, CH_3), 0.67 (d, J = 6.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.80 (C_q, C^2-Ar), 139.42 (C_q, C$_i$-Ar), 131.14 (+, C$_o$-Ar), 127.96 (+, C^4-Ar), 127.75 (+, C^6-Ar), 126.31 (+, C$_p$-Ar), 125.73 (+, C$_m$-Ar), 125.05 (C_q, C^1-Ar), 124.30 (+, C^5-Ar), 118.31 (+, C^3-Ar), 64.68 (C_q, CNH), 60.41 [C_q, $C(CH_3)_3$], 55.76 (+, CH), 45.83 (+, CH), 29.03 (+, NC-CH_3), 22.79 [+, C(CH_3)$_3$], 19.53 [+, CH(CH_3)$_2$] 14.41 [+, CH(CH_3)$_2$] ppm. IR (KBr): $\tilde{\nu}$ = 3318 (w), 3062 (w) [–N–H valence], 2978 (w), 1598 (vw), 1416 (m), 1284 (w), 1228 (m) [–C–N valence], 1151 (w), 1072 (m) [S=O], 955 (w), 835 (w), 766 (w) [–C–S valence], 709 (w), 545 (w) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 429 (0.11) [M + 1], 371/372 (89/18) [$C_{20}H_{27}N_4OS^+$], 309 (20) [$C_{20}H_{27}N_3^+$], 308 (100) [$C_{20}H_{26}N_3^+$], 194 (11) [$C_{14}H_{12}N^+$], 179 (15) [$C_{14}H_{11}^+$], 165 (9) [$C_8H_7NOS^+$], 118 (2) [$C_8H_8N^+$], 103 (2) [$C_7H_5N^+$], 100 (2) [$C_6H_{14}N^+$], 77 (1) [$C_6H_5^+$], 57 (4) [$C_4H_9^+$], 43 (8) [$C_2H_5N^+$], 41 (2) [$C_3H_5^+$]. HR-EIMS ($C_{20}H_{27}N_4OS$): calcd. 371.1906; found 371.1903 (M – *t*Bu).

Crystal Structure Studies: Single-crystal X-ray diffraction studies were carried out either on a Nonius Kappa-CCD diffractometer (for **9a**, **13d**) or a Bruker–Nonius APEXII diffractometer (for **9d**, **9e**) at 123(2) K using Mo-K_α radiation (λ = 0.71073 Å). Direct Methods (SHELXS-97[20]) were used for structure solution and refinement (SHELXL-97,[21] full-matrix least-squares on F^2). The absolute structure could not be determined reliably [refinement of Flack's x parameter x = –2(4) (for **9d**) and x = –0.6(7) (for **9e**)],[22] and H atoms were refined using a riding model. In **9a** the pyrrolidine is disordered. **13d** is a non-merohedral twin with 3 domains.[23] Important data on the data collection and structure solution and refinement are listed in Table 5.

CCDC-670842 (for **9a**), -670843 (for **9d**), -670844 (for **9e**), and -670845 (for **13d**) 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.

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Table 5. Crystallographic data, structure solution and refinement of **9a**, **9d**, **9e**, **13d**.

	9a	**9d**	**9e**	**13d**
Empirical formula	$C_{11}H_{12}N_4$	$C_{13}H_{18}N_4$	$C_{14}H_{17}F_3N_4$	$C_{14}H_{21}N_3O$
Formula weight	200.25	230.31	298.32	247.34
Temperature [K]	123(2)	123(2)	123(2)	123(2)
Crystal system	monoclinic	monoclinic	orthorhombic	triclinic
Space group	$P2_1/c$ (No. 14)	$P2_1$ (No. 4)	$P2_12_12_1$ (No. 19)	$P\bar{1}$ (No. 2)
a [Å]	8.9317(6)	7.7651(5)	9.0195(2)	7.8841(6)
b [Å]	11.2714(4)	10.6314(8)	10.2052(3)	12.0150(8)
c [Å]	10.9547(8)	8.2078(6)	16.3904(4)	15.0091(13)
α [°]	90	90	90	88.366(5)
β [°]	109.731(3)	100.803(4)	90	87.199(4)
γ [°]	90	90	90	89.964(5)
V [Å^3]	1038.09(11)	665.58(8)	1508.67(7)	1419.50(9)
Z	4	2	4	4
$D_{calcd.}$ [g cm^{-3}]	1.281	1.149	1.313	1.157
Abs. coeff. [mm^{-1}]	0.082	0.072	0.107	0.075
F[000]	424	248	624	536
Crystal size [mm]	0.40 × 0.30 × 0.15	0.40 × 0.05 × 0.05	0.20 × 0.15 × 0 × 10	0.40 × 0.30 × 0.20
θ range for data collection [°]	3.02 to 25.03	3.17 to 24.98	3.01 to 25.02	2.98 to 25.03
Limiting indices	$-9 \le h \le 10$, $-13 \le k \le 13$ $-13 \le l \le 12$	$-9 \le h \le 9$ $-12 \le k \le 12$ $-9 \le l \le 9$	$-10 \le h \le 10$ $-12 \le k \le 12$ $-19 \le l \le 19$	$-9 \le h \le 9$ $-14 \le k \le 14$ $-17 \le l \le 17$
Reflections collected	6607	10686	22862	4907
Unique reflections	1828	2342	2665	4907
R_{int}	0.0272	0.0692	0.0476	0.0000
Data/restraints/parameters	1828/17/135	2342/1/154	2665/0/190	4907/0/330
GOF on F^2	1.036	1.176	1.137	0.998
R_1 [$I > 2\sigma(I)$]	0.0536	0.0508	0.0355	0.1200
wR_2 (all data)	0.1473	0.1046	0.0708	0.4303
Largest difference map peak/ hole [e Å^{-3}]	0.389/ –0.316	0.160/ –0.180	0.127/ –0.156	0.680/ –0.640

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