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Formation of benzylamines from triazene compounds via a 1,2-proton shift

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Abstract—A new approach to benzylamines using triazene compounds has been developed that is facilitated by the lithiation of aryltriazenes followed by treatment with an electrophile. The regioselectivity of the reaction can be controlled by means of the substituents in the aryl group. The reaction contains the following steps: intramolecular carbon–carbon bond formation involving lithiation of an alkyl group on a 3-nitrogen atom; a 1,2-proton shift; and the subsequent release of nitrogen gas. Through the use of a deuterated triazene, we were able to determine that the reaction proceeds through a 1,2-proton shift.

1. Introduction

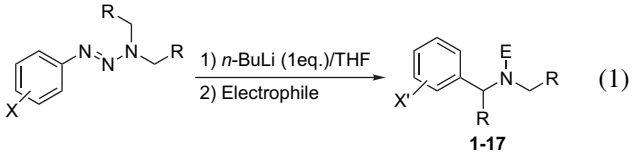
Benzylamines are very important intermediates of fine chemical derivatives such as biologically active compounds and material chemicals. The methods of forming benzylamines are well-known, for example, the condensation of benzyl halide with amine derivatives and the reduction of the benzonitriles etc. In the case of phenols and arylamines as substrates, functionalized benzylamines were created using the bimolecular aromatic Mannich reaction with iminium salt.[1] 1-Aryl-3,3-dialkyltriazenes are also used in many ways in organic syntheses, including the following:[2] as protective groups for aniline derivatives;[3] as substrates of benzyne generation;[4] in diazo coupling;[5] in the Sandmeyer–Gattermann reaction;[6] and in the hydroxylation of positive ion exchange resins.[7] Nicolaou et al. showed that aryltriazenes are used in the construction of aryl ethers and applied these results for the synthesis of vancomycin.[8] In combinatorial chemistry, triazenes are used as linkers in solid-phase synthesis[9] and as alkylating polymers in solution-phase synthesis.[10] Recently, Haley's group has reported the cyclization of 2-alkynylphenyl triazenes.[11]

We have previously reported the preliminary results of a unique transformation of 3,3-dialkyl-1-aryltriazenes into benzylamines.[12] We now report the results of our further investigations into the transformation of triazenes to benzylamines. In fact, that reaction proceeded via a 1,2-proton shift. Since a 1,2-proton shift on an aromatic ring has never been reported, we demonstrated the phenomenon using NMR, mass spectrometry, and computational chemistry.

2. Results and discussion

2.1. Formation of benzylamines

The alkyltriazenes were prepared from arylamines in good yields according to the standard conditions ($NaNO_2$–HCl, then the addition of respective amines).[13] And trimethylsilylphenyltriazenes were synthesized by way of the halogen–metal exchange reaction from the corresponding bromophenyltriazenes according to Welch's procedure.[3a] The general procedure for the transformation of triazenes into benzylamines is as follows: the alkyltriazenes were treated with *n*-BuLi (1 equiv) in THF at 0 °C for 1 h, followed by the addition of electrophiles to produce the corresponding benzylamine derivatives (Eq. 1).



1-17 (1)

The aminoalkyl group of the benzylamines connected to *ortho* position of the original triazenyl group was derived

Keywords: C–C bond forming; Dearomatization; Nucleophilic addition; 1,2-Proton shift; Triazene.
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Table 1. Results of transformation reaction of triazenes into benzylamines

Entry	Substrates			Products			Yield (%)
	X	R	Electrophile	X′[a]		E	
1	H	H	H_2O	**1**	H	H	57
2	H	H	*n*-BuBr	**2**	H	*n*-Bu	78
3	H	H	$(Boc)_2O$	**3**	H	Boc	81
4	H	Me	$(Boc)_2O$	**4**	H	Boc	47
5	H	$-(CH_2)_2-$	$(Boc)_2O$	**5**	H	Boc	69
6	*o*-Me	H	H_2O	**6**	*m*-Me	H	74
7	*m*-Me	H	H_2O	**7**	*o*,*p*-Me (2:1)	H	71
8	*m*-Me	H	$(Boc)_2O$	**8**	*o*,*p*-Me (2:1)	Boc	90
9	*p*-Me	H	H_2O	**6**	*m*-Me	H	95
10	*p*-Me	H	$(Boc)_2O$	**9**	*m*-Me	Boc	95
11	*m*-MeO	H	$(Boc)_2O$	**10**	*o*-MeO	Boc	70
12	*p*-MeO	H	$(Boc)_2O$	**11**	*m*-MeO	Boc	65
13	*o*-F	H	$(Boc)_2O$	**12**	*m*-F	Boc	Trace
14	*m*-F	H	$(Boc)_2O$	**13**	*o*-F	Boc	41
15	*p*-F	H	$(Boc)_2O$	**12**	*m*-F	Boc	89
16	*o*-Cl	H	$(Boc)_2O$	**14**	*m*-Cl	Boc	29
17	*m*-Cl	H	$(Boc)_2O$	**15**	*o*,*p*-Cl (1:1)	Boc	45
18	*p*-Cl	H	$(Boc)_2O$	**14**	*m*-Cl	Boc	54
19	*o*-TMS	H	$(Boc)_2O$	**16**	*m*-TMS	Boc	68
20	*m*-TMS	H	$(Boc)_2O$	**17**	*p*-TMS	Boc	81
21	*p*-TMS	H	$(Boc)_2O$	**16**	*m*-TMS	Boc	70

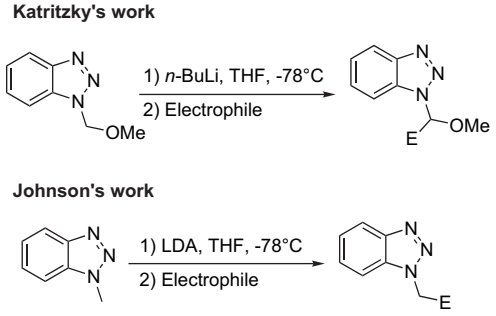
[a] The ratio of diastereomers was determined by ^1H NMR.

from the alkyl group on 3-nitrogen of the triazenyl group. The results of transformation of the triazenes to benzylamines are summarized in Table 1. The 3,3-dimethyl-1-phenyltriazene was transformed to benzylmethylamine (**1**) at a 57% yield, by treating first with *n*-BuLi and then with H_2O. The addition of $(Boc)_2O$ instead of H_2O as an electrophile greatly increased the isolated yield of **3** (81%) (entries 1 and 3). When *o*- and *p*-methylphenyltriazenes were treated as above, *m*-methylbenzylamines (**6** and **9**) were formed in both cases, but the yield of the product was superior in the latter case (entries 6, 9, and 10).

Other *o*- and *p*-substituted triazenes also gave *m*-substituted benzylamine derivatives (**11**, **12**, **14**, and **16**) (entries 12, 13, 15, 16, 18, 19, and 21). In entry 13, the desired product was obtained in trace amount and the most of substrate was remained. In the case of the *m*-methyl- and *m*-chlorophenyltriazenes, the mixtures of *o*- and *p*-substituted benzylamine derivatives (**7**, **8**, and **15**) were obtained (entries 7, 8, and 17). In contrast, *m*-methoxy- and *m*-fluorophenyltriazenes created the *o*-substituted benzylamines (**10** and **13**) exclusively in moderate to good yields, and *m*-trimethylsilylphenyltriazene gave *p*-trimethylsilylbenzylamine (**17**) as the sole product (entries 11, 14, and 20). When *o*-, *m*-, and *p*-bromophenyltriazenes were treated with *n*-BuLi (1 equiv) as above, non-substituted triazene was obtained at yields of 60, 32, and 41%, respectively. Similarly, trimethylsilylphenyltriazenes were obtained from bromophenyltriazenes, when chlorotrimethylsilane was used as an electrophile. It seemed that these reactions proceeded via transmetallation and then protonation, or trimethylsilylation.

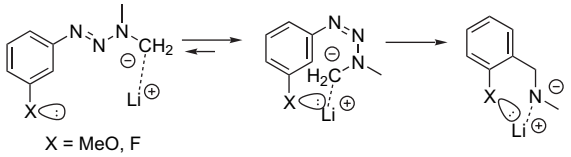
In order to explain the interesting results above, we tried to confirm the place of the first triazene deprotonations. When 3,3-dimethyl-1-phenyltriazene was treated with LDA (1 equiv) at 0 °C in the presence of chlorotrimethylsilane (1 equiv), 3-monosilylated- and 3,3-disilylated triazenes (**18** and **19**) were obtained at yields of 16 and 10%, respectively (Scheme 1). We did not observe any silylated products of the phenyl group, which are generated by the neighboring effects of nitrogen atoms. In the absence of chlorotrimethylsilane, the same procedure created benzylmethylamine at a yield of 48%. These results indicate that deprotonation of the triazene with LDA occurred at the alkyl group on the 3-nitrogen atom[14] and that the successive nucleophilic attack of the carbanion to complete the reaction proceeded on the aromatic ring.

We should also note that both Katritzky's group[15] and Johnson's group[16] reported that 1-alkylated benzotriazoles introduced some electrophiles on the 1-alkyl group via deprotonation with the base (Scheme 2). These reports support our results.



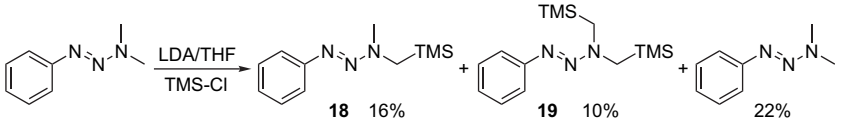
Scheme 2. Deprotonation position of 1-alkylated benzotriazoles.

As mentioned above, *m*-methoxy- and *m*-fluorophenyltriazenes exclusively created the *o*-substituted benzylamines (**10** and **13**). These results can be accounted for by the chelation control as shown in Scheme 3.

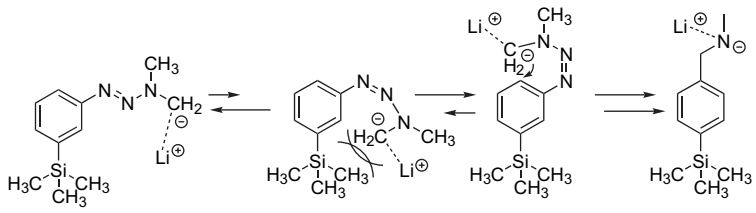


Scheme 3. Chelation control by substituents on the aromatic ring.

Conversely, the observation that *m*-trimethylsilylphenyltriazene provided *p*-trimethylsilylbenzylamine (**17**) was attributed to the steric bulk of trimethylsilyl group (Scheme 4). The regioselectivities of the carbon–carbon bond formation were attributed to the electronic and steric features of the substituents on the aromatic rings.



Scheme 1. Deprotonation position.



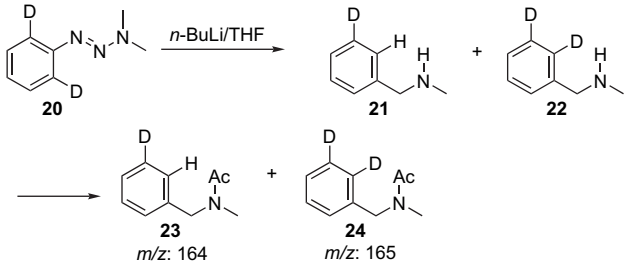
Scheme 4. Steric control by substituents on the aromatic ring.

When the substituents on the benzene ring were the strongly electron-withdrawing group like nitro group and trifluoromethyl groups, the reactions did not produce good results. In the case of the nitro and trifluoromethyl groups, the triazene reactions created complex mixtures containing unidentified polymerized products. On the other hand, the fluoro- and chlorophenyltriazenes were transformed to the corresponding benzylamines in good to moderate yields.

Also, silyl substituted benzenes are very important intermediates in organic synthesis, because the benzene nuclei are easily transformed to various electron-withdrawing groups by aromatic electrophilic *ipso*-desilylation.[17] Consequently, in order to get benzylamines, which are substituted with electron-withdrawing groups, the silyl substituted products (**16** and **17**) may become valuable compounds.

2.2. Proton source

To reveal the proton source of the products, 1-(2,6-dideuteriophenyl)-3,3-dimethyltriazene (**20**) was treated with base (Scheme 5). The ^{1}H NMR spectra of the products (**21**+**22**) indicated that the integrated value of peaks of the phenyl protons is 3.6, while that of the methyl group protons is 3 (Fig. 1). This result indicated that the products involved one or two deuterium atoms and one deuterium atom was abstracted. The MS spectra of the benzylmethylamine and the reaction products gave an (M^+-1) peak as the standard peak and the parent peaks did not appear clearly. Therefore, the amines were treated with acetic anhydride to provide the amides. The MS spectra of the acetylated compounds (**23**+**24**) and *N*-benzyl-*N*-methylacetamide are shown in Figure 2. In the former case, the parent peaks appeared at *m*/*z*=164 and 165, indicating that one or two deuterium atoms remained in the products. This suggests that the proton, located on the *ipso* position of the triazenyl group in the product, shifted from the *o*-position of the triazenyl group and/or was abstracted by the THF of the solvent.



Scheme 5. Reaction of dideuterated triazene.

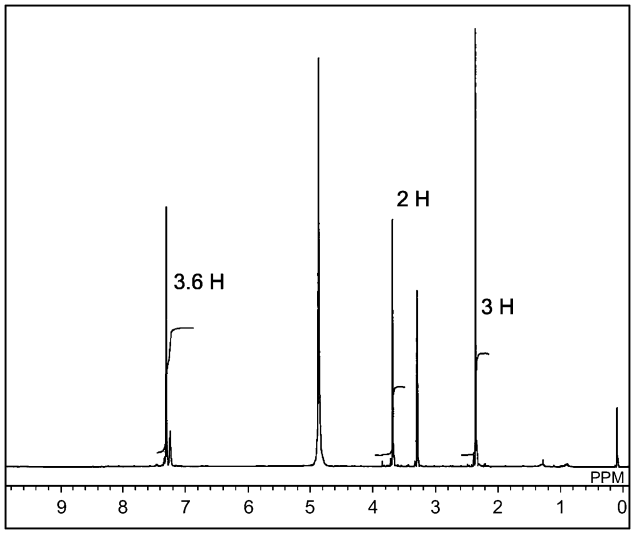


Figure 1. ^{1}H NMR spectrum of the products obtained from **20**.

2.3. Computational studies

The 1,2-proton shift on aromatic ring was proposed and verified by a computational study, because it had not yet been reported. Semiempirical PM3 optimization, as demonstrated in the WinMOPAC 2.0 program (Fujitsu Limited), was used during the preliminary studies.[18] We confirmed the reasonable reaction coordinates by searching through the transition states and conducting vibrational frequency analysis (Fig. 3). The first anion of the molecule was located on the methyl group of near side to N1–N2 double bond. In the case where the anion stayed on another methyl group, the transition state 1 (**TS1**) had no negative frequencies. When the new carbon–carbon bond formed (**I**), the configuration of methyl group and the proton of new ring junction was *syn*. When the two methyl groups were *anti* configured, we could not achieve the required optimized structure for the **TS1**. The second transition state (**TS2**) contained reasonable coordinates among the intermediate (**I**) to the product (**P**) that possessed only one negative vibrational frequency: $-2303.5\ \mathrm{cm}^{-1}$.

We performed precise ab initio calculations for the PM3 results using HyperChem software.[19] We obtained the energies (including electron correlation effects) from single point calculations using second order perturbation theory according to Møller and Plesset 2 (MP2/6-31G*).[20] The nature of each stationary point was verified by vibrational frequency analysis. As this reaction was conducted in the hexane solution, we did not consider the solvent effect. In Figure 4, the vertical line represents relative energy, and the abscissa axis is the transition of the reaction. Unexpectedly, the

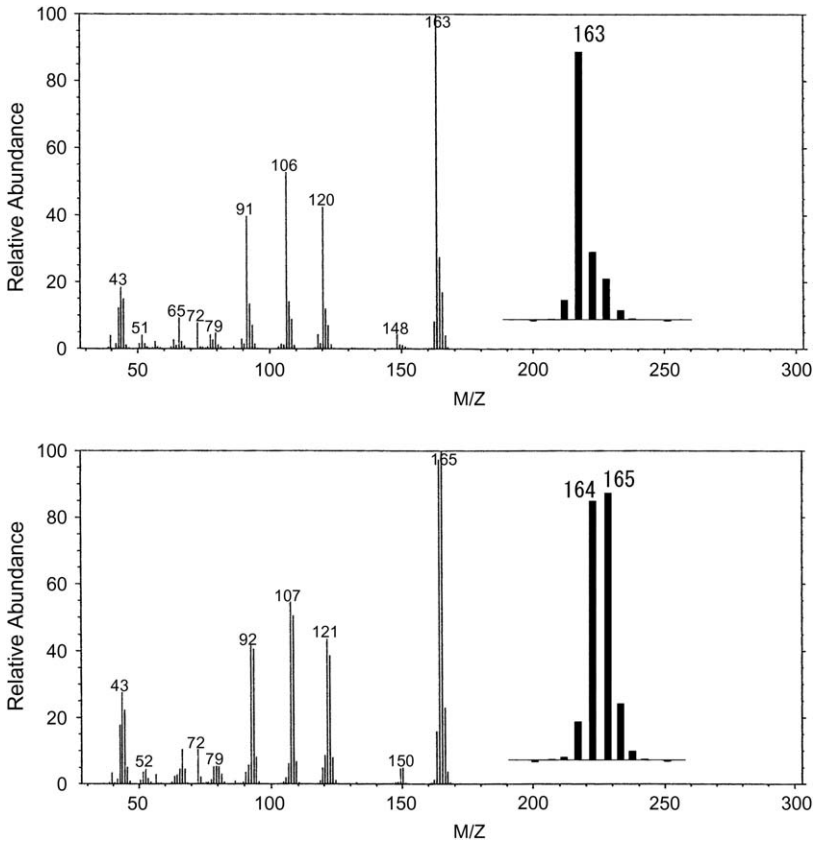


Figure 2. MS spectra of *N*-benzyl-*N*-methylacetamide (upper) and the mixture of **23** and **24** (lower).

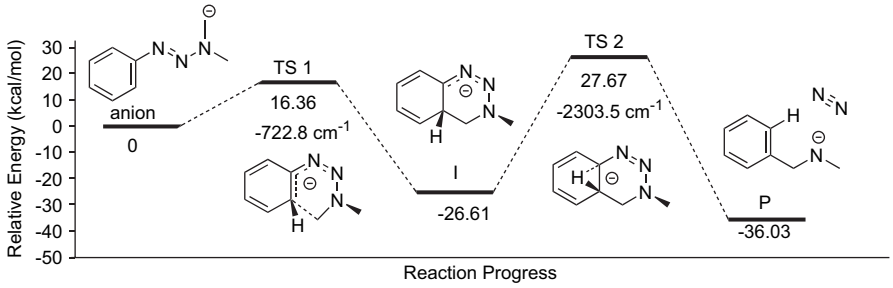


Figure 3. Potential energy correlation diagram and vibrational frequency analysis of reaction. Energy values are given in kcal/mol relative to isolated reactants.

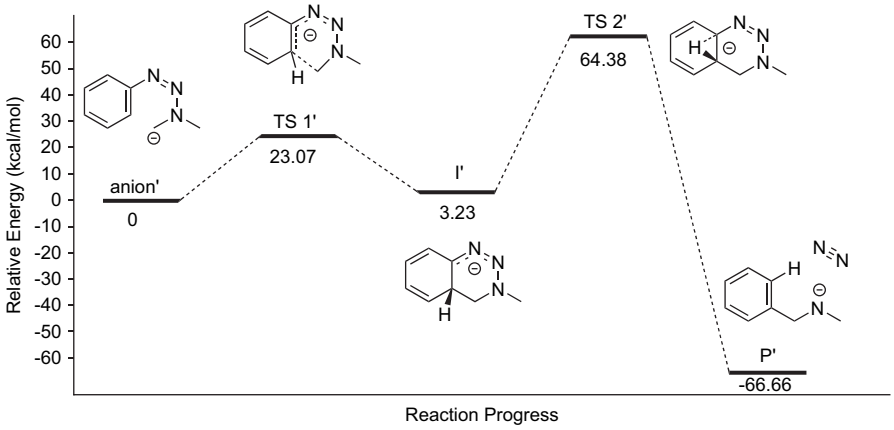
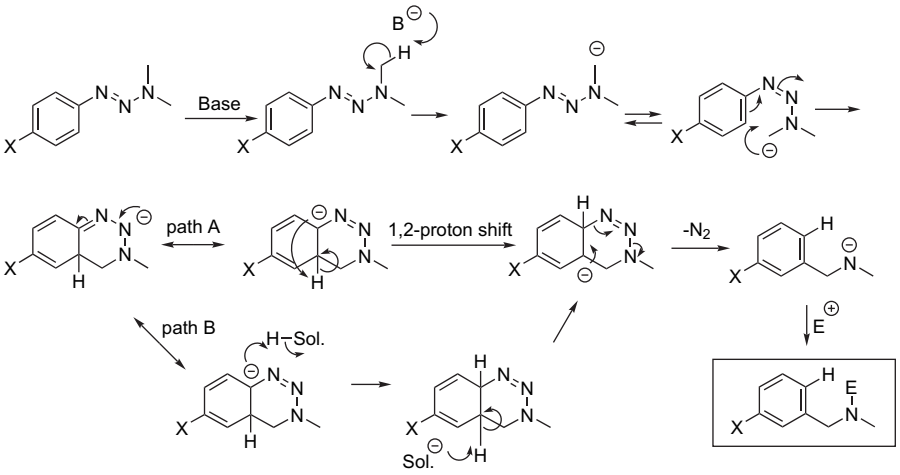


Figure 4. Potential energy surface calculated for the reaction of triazene and base via a mechanism involving 1,2-proton shift. Energy values are given in kcal/mol relative to isolated reactants.



Scheme 6. The proposed reaction mechanism.

intermediate (**I′**) was 3.23 kcal/mol higher than the starting anion, which suggests that the dearomatized compound was comparatively stable. Although the second transition state (**TS2′**) needs extremely high energy (61.15 kcal/mol) to activate **I′**, it had one negative vibration and the 1,2-shift of the proton reflected this experimental result. The release of nitrogen was the driving force of this reaction.

2.4. Reaction mechanism

Considering the above results, we proposed the reaction mechanism shown in Scheme 6. Deprotonation occurred on the α-carbon of the 3-nitrogen. This anion took place in a nucleophilic attack at the *o*-position to the triazenyl group on the aryl group, similar to the Sommelet–Hauser rearrangement[21] and formed a dearomatized intermediate like the Meisenheimer complex. For further reactions, two possible routes were considered. In path A, a 1,2-proton shift occurred. In path B, the solvent was involved in the reaction. The proton that originated from the solvent was incorporated into the anion. This was followed by the abstraction of the proton with the anion derived from the solvent. The carbanion formed a double bond to reconstruct the benzene nuclei, which released nitrogen gas continuously.

3. Conclusion

We discovered a benzylamine forming reaction from 1-aryl-3,3-dialkyltriazene. It contained an intramolecular carbon–carbon bond forming reaction. This reaction was proceeded by an unusual 1,2-proton shift, which was revealed using the deuterated triazene. In the case where the aryl group possessed a strong electron-withdrawing group as nitro or trifluoromethyl, this reaction was not permitted. These reactions provide an alternative method for the preparation of benzylamine derivatives and the new cleavage of triazenyl linkers in the solid-phase synthesis.

4. Experimental

4.1. General methods

NMR spectra were recorded on JEOL GSX-270 (^{1}H 270 MHz, ^{13}C 67.5 MHz) or JEOL GX-500 (^{1}H 500 MHz, ^{13}C 125 MHz) spectrometers in $CDCl_3$ or CD_3OD with TMS as an internal standard. Mass spectra (EI) were recorded on a JMS-HX100 spectrometer. Infrared spectra were recorded on a Shimadzu IR-435 spectrophotometer. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was freshly distilled under nitrogen from sodium benzophenone ketyl prior to use.

4.2. Preparation of triazenes

Most 1-aryl-3,3-dialkyltriazene was synthesized according to the method described in the literature.[13] And the trimethylsilylphenyltriazenes were synthesized by way of the halogen–metal exchange reaction from the corresponding bromophenyltriazene according to Welch's procedure.[3a]

4.2.1. Registry numbers of triazenes.

3,3-Dimethyl-1-phenyltriazene	7227-91-0
3,3-Diethyl-1-phenyltriazene	13056-98-9
1-(Phenylazo)pyrrolidine	36719-71-8
3,3-Dimethyl-1-(2-methylphenyl)triazene	20240-98-6
3,3-Dimethyl-1-(3-methylphenyl)triazene	20241-03-6
3,3-Dimethyl-1-(4-methylphenyl)triazene	7203-89-6
3,3-Dimethyl-1-(3-methoxyphenyl)triazene	20241-03-6
3,3-Dimethyl-1-(4-methoxyphenyl)triazene	7203-92-1
1-(2-Fluorophenyl)-3,3-dimethyltriazene	52010-51-2
1-(3-Fluorophenyl)-3,3-dimethyltriazene	52010-52-3
1-(4-Fluorophenyl)-3,3-dimethyltriazene	23456-94-2
1-(2-Chlorophenyl)-3,3-dimethyltriazene	20241-00-3
1-(3-Chlorophenyl)-3,3-dimethyltriazene	20241-05-8
1-(4-Chlorophenyl)-3,3-dimethyltriazene	7203-90-9
1-(2-Bromophenyl)-3,3-dimethyltriazene	52010-61-4
1-(4-Bromophenyl)-3,3-dimethyltriazene	7239-21-6
1-(3-Bromophenyl)-3,3-dimethyltriazene	29878-94-2

4.2.2. 3,3-Dimethyl-1-(2-trimethylsilylphenyl)triazene. To a solution of 1-(2-bromophenyl)-3,3-dimethyltriazene (3.68 g, 16.1 mmol) in dry THF (16 mL) was added dropwise a solution of *n*-BuLi (10.0 mL, 1.72 mmol, 1.72 M in hexane) at −84 °C. After stirring for 5 min, chlorotrimethylsilane (2.08 mL, 16.4 mmol) was added dropwise, and the mixture was stirred for 30 min at room temperature. The reaction was quenched with water. Extractive work-up and subsequent flash silica gel chromatography (hexane)

afforded the title compound as an oil (1.78 g, 8.03 mmol, 50%); ^{1}H NMR ($CDCl_3$) δ: 7.48 (dd, J=7.0, 1.5 Hz, 1H), 7.43 (dd, J=8.0, 1.0 Hz, 1H), 7.32 (ddd, J=8.0, 7.0, 1.5 Hz, 1H), 7.12 (dd, J=7.0, 1.0 Hz, 1H), 3.35 (br s, 6H), 0.31 (s, 9H); ^{13}C NMR ($CDCl_3$) δ: 155.59, 134.38, 129.90, 124.82, 115.46, 41.26, 39.39, −0.22; IR (neat) cm^{-1}: 2900 (s), 1580 (m), 1460 (s), 1400 (m), 1320 (s), 1250 (s), 1060 (s), 830 (s), 750 (s); Low-MS (EI) (*m*/*z*, %): 221 (M^+, 27), 206 (21), 178 (5), 163 (16), 149 (100), 135 (9), 121 (78), 105 (5.0), 91 (5.1), 73 (7.0), 59 (3.0), 43 (8.1); HRMS: 221.1354 (Calcd for $C_{11}H_{19}N_3Si$, 221.1349).

4.2.3. 3,3-Dimethyl-1-(3-trimethylsilylphenyl)triazene. To a solution of 1-(3-bromophenyl)-3,3-dimethyltriazene (3.75 g, 16.4 mmol) in dry THF (16 mL) was added dropwise a solution of *n*-BuLi (10.0 mL, 1.72 mmol, 1.72 M in hexane) at −84 °C. After stirring for 5 min, chlorotrimethylsilane (2.10 mL, 16.6 mmol) was added dropwise, and the mixture was stirred for 30 min at room temperature. The reaction was quenched with water. Extractive work-up and subsequent flash silica gel chromatography (hexane/EtOAc=19/1 as eluents) afforded the title compound as an oil (3.04 g, 13.7 mmol, 84%); ^{1}H NMR ($CDCl_3$) δ: 7.55 (m, 1H), 7.40 (m, 1H), 7.34 (dd, J=7.0, 0.8 Hz, 1H), 7.30 (dt, J=3.0, 1.0 Hz, 1H), 3.34 (s, 6H), 0.28 (s, 9H); ^{13}C NMR ($CDCl_3$) δ: 150.13, 141.09, 130.42, 128.27, 126.00, 120.33, 39.09, −1.08; IR (neat) cm^{-1}: 2900 (m), 1570 (w), 1440 (s), 1380 (s), 1300 (s), 1240 (s), 1070 (s), 820 (s), 740 (s); Low-MS (EI) (*m*/*z*, %): 221 (M^+, 26), 206 (10), 177 (5), 149 (100), 135 (5), 121 (28), 105 (3.0), 88 (5.0), 73 (45), 67 (3.0), 45 (4.0); HRMS: 221.1367 (Calcd for $C_{11}H_{19}N_3Si$, 221.1349).

4.2.4. 3,3-Dimethyl-1-(4-trimethylsilylphenyl)triazene. To a solution of 1-(4-bromophenyl)-3,3-dimethyltriazene (3.66 g, 16.0 mmol) in dry THF (16 mL) was added dropwise a solution of *n*-BuLi (10.0 mL, 1.72 mmol, 1.72 M in hexane) at −84 °C. After stirring for 5 min, chlorotrimethylsilane (2.10 mL, 16.6 mmol) was added dropwise, and the mixture was stirred for 30 min at room temperature. The reaction was quenched with water. Extractive work-up and subsequent flash silica gel chromatography (hexane/$CHCl_3$=4/1 as eluents) afforded the title compound as an oil (2.68 g, 12.1 mmol, 76%); ^{1}H NMR ($CDCl_3$) δ: 7.48 (dd, J=8.0, 3.0 Hz, 2H), 7.39 (dd, J=8.0, 3.0 Hz, 2H), 3.34 (br s, 6H), 0.26 (s, 9H); ^{13}C NMR ($CDCl_3$) δ: 151.39, 136.93, 133.95, 119.86, 41.29, 37.36, −1.00; IR (neat) cm^{-1}: 2950 (s), 1590 (s), 1450 (s), 1410 (s), 1380 (s), 1320 (s), 1250 (s), 1070 (s), 820 (s), 750 (s); Low-MS (EI) (*m*/*z*, %): 221 (M^+, 28), 206 (10), 178 (5.1), 149 (100), 135 (3.0), 121 (28), 73 (15); HRMS: 221.1357 (Calcd for $C_{11}H_{19}N_3Si$, 221.1349).

4.3. General procedure for transformation of triazenes into benzylamines

To a solution (0.5–1 M) of triazene in dry THF was added dropwise a solution of *n*-BuLi/hexane (1.0 equiv) at 0 °C. After stirring for 1 h, the reaction mixture was quenched with water or each electrophile (1.5 equiv). Extractive work-up and the subsequent purification afforded benzylamine derivatives.

4.3.1. Benzylmethylamine (1). Oil, 57%; ^{1}H NMR ($CDCl_3$) δ: 7.26 (m, 5H), 4.42 (s, 2H), 2.82 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 139.90, 127.97, 127.76, 126.52, 55.72, 35.65; IR (neat) cm^{-1}: 3500 (m), 3000 (m), 1680 (s), 1440 (m), 1380 (m), 1250 (m), 1140 (m), 870 (m), 680 (m); Low-MS (EI) (*m*/*z*, %): 121 (M^+, 86), 120 (100), 104 (5.0), 91 (69), 77 (11), 65 (18), 51 (11), 41 (61); HRMS: 121.0897 (Calcd for $C_8H_{11}N$, 121.0892).

4.3.2. *N*-Benzyl-*N*-*n*-butylmethylamine (2). Oil, 78%; ^{1}H NMR ($CDCl_3$) δ: 7.33–7.19 (m, 5H), 3.48 (s, 2H), 2.36 (t, J=7.5 Hz, 2H), 2.18 (s, 3H), 1.50 (m, 2H), 1.33 (m, 3H), 0.90 (t, J=7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 139.20, 129.05, 128.18, 62.69, 57.27, 42.20, 29.54, 20.60, 14.05; IR (neat) cm^{-1}: 2950 (s), 2920 (s), 2850 (s), 1640 (br m), 1475 (br m), 1380 (m), 1260 (m); Low-MS (EI) (*m*/*z*, %): 177 (M^+, 8.8), 134 (84), 91 (100), 65 (6.3), 42 (5.0); HRMS: 177.1508 (Calcd for $C_{12}H_{19}N$, 177.1517).

4.3.3. *N*-Benzyl-*N*-(*t*-butoxycarbonyl)methylamine (3). Oil, 81%; ^{1}H NMR ($CDCl_3$) δ: 7.38–7.18 (m, 5H), 4.42 (s, 2H), 2.82 (s, 3H), 1.48 (s, 9H); ^{13}C NMR ($CDCl_3$) δ: 155.87, 138.08, 128.47, 127.14, 79.62, 52.26, 33.86, 28.42; IR (neat) cm^{-1}: 3000 (m), 1680 (s), 1440 (m), 1380 (m), 1250 (m), 1140 (m), 870 (m), 680 (m); Low-MS (EI) (*m*/*z*, %): 221 (M^+, 0.38), 165 (100), 140 (6.3), 120 (48), 91 (57), 77 (2.8), 65 (5.6), 57 (57), 51 (1.9), 41 (11); HRMS: 221.1443 (Calcd for $C_{13}H_{19}NO_2$, 221.1416).

4.3.4. *N*-(*t*-Butoxycarbonyl)-*N*-methyl(α-methylbenzyl)amine (4). Oil, 47%; ^{1}H NMR ($CDCl_3$) δ: 7.48–7.28 (m, 5H), 5.42 (br s, 1H), 3.10 (br m, 1H), 2.93 (br m, 1H), 1.52 (d, J=2.0 Hz, 3H), 1.46 (s, 9H), 0.98 (t, J=2.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ: 155.80, 142.18, 128.21, 127.04, 126.93, 53.10, 38.13, 28.51, 17.49, 15.24; IR (neat) cm^{-1}: 2950 (m), 1680 (s), 1450 (s), 1400 (s), 1280 (s), 1130 (m), 760 (m), 700 (m); Low-MS (EI) (*m*/*z*, %): 249 (M^+, 0.63), 234 (0.44), 193 (100), 178 (75), 164 (10), 148 (14), 134 (72), 120 (7.5), 105 (87), 91 (5), 77 (15), 72 (6), 57 (78), 51 (3.5), 41 (16); HRMS: 249.1715 (Calcd for $C_{15}H_{23}NO_2$, 249.1729).

4.3.5. 1-(*t*-Butoxycarbonyl)-2-phenylpyrrolidine (5). Oil, 69%; ^{1}H NMR ($CDCl_3$) δ: 7.12–7.34 (m, 5H), 4.95 and 4.75 (br s, 1H), 3.61 (d, 3H), 2.30 (br s, 1H), 1.87 (m, 3H), 1.45 (s, 3H), 1.18 (s, 6H); ^{13}C NMR ($CDCl_3$) δ: 160.95, 152.44, 137.77, 131.16, 125.96, 121.09, 81.66, 63.96, 40.11, 33.69, 28.24, 26.93, 16.54; IR (neat) cm^{-1}: 2950 (m), 1680 (s), 1600 (w), 1480 (m), 1450 (m), 1380 (s), 1250 (m), 1150 (m), 900 (m), 730 (m); Low-MS (EI) (*m*/*z*, %): 247 (M^+, 0.23), 191 (100), 174 (27.5), 163 (4.4), 146 (85), 131 (24), 119 (37), 104 (12), 91 (23), 77 (88), 70 (21), 65 (2.5), 57 (72), 51 (3.1), 41 (20); HRMS: 247.1589 (Calcd for $C_{15}H_{21}NO_2$, 247.1572).

4.3.6. Methyl(*m*-methylbenzyl)amine (6). Oil, 74% from *o*-methylphenyltriazene, 95% from *m*-methylphenyltriazene; ^{1}H NMR ($CDCl_3$) δ: 7.05–7.24 (m, 4H), 3.71 (s, 2H), 2.45 (s, 3H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$) δ: 158.21, 156.21, 147.15, 146.46, 145.89, 143.40, 74.24, 54.22, 39.55; IR (neat) cm^{-1}: 3315 (m), 2923 (s), 2790 (s), 1608 (s), 1444 (s), 1379 (w), 1351 (w); Low-MS (EI) (*m*/*z*, %): 135 (M^+, 31), 134 (58), 120 (25), 106 (19), 91 (36), 77

(31), 44 (100); HRMS: 135.1039 (Calcd for $C_9H_{13}N$, 135.1048).

4.3.7. A mixture of methyl(*o*-methylbenzyl)amine and methyl(*p*-methylbenzyl)amine (7). Oil, *o*/*p*=2/1, 71%; mixture: ^{13}C NMR ($CDCl_3$) δ: 137.95, 136.78, 136.60, 136.21, 130.23, 129.06, 128.36, 128.17, 126.97, 125.88, 55.65, 53.55, 36.30, 35.80, 21.06, 18.89; IR (neat) cm^{-1}: 3318 (m), 3019 (m), 2934 (s), 2789 (s), 1513 (w), 1460 (s), 1379 (w), 1354 (w), 1131 (w), 1096 (m), 804 (m), 743 (s).

Major product (o-isomer): ^1H NMR ($CDCl_3$) δ: 7.27–7.30 (m, 1H), 7.15–7.18 (m, 3H), 3.74 (s, 2H), 2.50 (s, 3H), 2.35 (s, 3H), 1.87 (br s, 1H); IR (neat) cm^{-1}: 3318 (m), 3019 (m), 2934 (s), 2789 (s), 1513 (w), 1460 (s), 1379 (w), 1354 (w), 1131 (w), 1096 (m), 804 (m), 743 (s); Low-MS (EI) (*m*/*z*, %): 135 (M^+, 36), 134 (14), 120 (11), 104 (100), 91 (19), 77 (28), 51 (17), 44 (67); HRMS: 135.1053 (Calcd for $C_9H_{13}N$, 135.1048).

Minor product (p-isomer): ^1H NMR ($CDCl_3$) δ: 7.20 (d, *J*=8.0 Hz, 2H), 7.13 (d, *J*=8.0 Hz, 2H), 3.71 (s, 2H), 2.44 (s, 3H), 2.33 (s, 3H), 1.87 (br s, 1H); Low-MS (EI) (*m*/*z*, %): 135 (M^+, 35), 134 (56), 120 (27), 105 (56), 91 (36), 77 (33), 51 (25), 44 (86), 42 (100); HRMS: 135.1032 (Calcd for $C_9H_{13}N$, 135.1048).

4.3.8. A mixture of *N*-(*t*-butoxycarbonyl)-*N*-methyl (*o*-methylbenzyl)amine and *N*-(*t*-butoxycarbonyl)-*N*-methyl(*p*-methylbenzyl)amine (8). Oil, *o*/*p*=2/1, 90%; ^1H NMR ($CDCl_3$) δ (*major product*): 7.14 (m, 4H), 4.44 (2H), 2.79 (br s, 3H), 2.28 (2H), 1.53 (s, 9H); (*minor product*): 7.14 (m, 4H), 3.38 (2H), 2.79 (br s, 3H), 2.34 (2H), 1.48 (s, 9H); ^{13}C NMR ($CDCl_3$) δ: 155.91, 136.77, 135.00, 129.16, 127.10, 125.96, 79.59, 49.84, 28.45, 28.41, 27.40, 18.98; IR (neat) cm^{-1}: 2950 (m), 1780 (br s), 1690 (s), 1460 (s), 1370 (s), 1280 (s), 1250 (s), 840 (m), 760 (m).

4.3.9. *N*-(*t*-Butoxycarbonyl)-*N*-methyl(*m*-methylbenzyl)amine (9). Oil, 95%; ^1H NMR ($CDCl_3$) δ: 7.22 (t, *J*=8.0 Hz, 1H), 7.10–6.97 (m, 3H), 4.39 (br s, 2H), 2.81 (br s, 3H), 2.34 (s, 3H), 1.48 (s, 9H); ^{13}C NMR ($CDCl_3$) δ: 155.98, 138.08, 137.98, 128.36, 127.86, 124.34, 79.55, 52.47, 33.83, 28.42, 21.38; IR (neat) cm^{-1}: 2900 (m), 1680 (s), 1650 (m), 1380 (br s), 1250 (s), 1120 (br s), 870 (m), 760 (m), 730 (m); Low-MS (EI) (*m*/*z*, %): 235 (M^+, 1.3), 179 (100), 164 (7.5), 146 (3.0), 134 (46), 120 (15), 105 (75), 91 (11), 77 (13), 65 (5.0), 57 (74), 51 (2.5), 41 (20); HRMS: 235.1581 (Calcd for $C_{14}H_{21}NO_2$, 235.1572).

4.3.10. *N*-(*t*-Butoxycarbonyl)-*N*-methyl(*o*-methoxybenzyl)amine (10). Oil, 70%; ^1H NMR ($CDCl_3$) δ: 7.23 (br t, *J*=7.9 Hz, 1H), 7.14 (br d, *J*=7.0 Hz, 1H), 6.93 (dt, *J*=1.0, 8.0 Hz, 1H), 6.88 (d, *J*=8.0 Hz, 1H), 4.44 (s, 2H), 3.82 (s, 3H), 2.85 (br s, 3H), 1.45 (s, 9H); ^{13}C NMR ($CDCl_3$) δ: 157.30, 156.17, 128.05, 126.16, 120.43, 113.87, 110.14, 79.34, 55.19, 47.34, 34.30, 28.43; IR (neat) cm^{-1}: 2950 (m), 1690 (s), 1600 (m), 1460 (s), 139 (s), 1250 (s), 1140 (s), 1020 (m), 880 (m), 750 (m); Low-MS (EI) (*m*/*z*, %): 251 (M^+, 2.5), 195 (61), 180 (1.9), 150 (100), 136 (39), 121 (58), 108 (3.1), 91 (40), 78 (8.1), 65 (8.8), 57 (56), 51 (3.8), 41 (11); HRMS: 251.1506 (Calcd for $C_{14}H_{21}NO_3$, 251.1521).

4.3.11. *N*-(*t*-Butoxycarbonyl)-*N*-methyl(*m*-methoxybenzyl)amine (11). Oil, 96%; ^1H NMR ($CDCl_3$) δ: 7.24 (t, *J*=7.8 Hz, 1H), 7.24 (m, 3H), 4.40 (s, 2H), 3.80 (s, 3H), 2.82 (br s, 3H), 1.48 (s, 9H); ^{13}C NMR ($CDCl_3$) δ: 159.82, 139.75, 129.47, 119.59, 112.94, 112.56, 79.62, 55.13, 52.48, 33.88, 28.43; IR (neat) cm^{-1}: 2900 (m), 1680 (s), 1600 (s), 1420 (br s), 1280 (br s), 1040 (m), 870 (m), 760 (m); Low-MS (EI) (*m*/*z*, %): 251 (M^+, 5.0), 195 (100), 170 (6.3), 150 (35), 136 (5.0), 122 (58), 107 (2.5), 91 (10), 78 (63), 57 (44), 41 (10); HRMS: 251.1503 (Calcd for $C_{14}H_{21}NO_3$, 251.1521).

4.3.12. *N*-(*t*-Butoxycarbonyl)-*N*-methyl(*m*-fluorobenzyl)amine (12). Oil, trace from *o*-fluorophenyltriazene, from 89% *p*-fluorophenyltriazene; ^1H NMR ($CDCl_3$) δ: 7.29 (dt, *J*=6.0, 7.8 Hz, 1H), 6.89–7.03 (m, 3H), 4.41 (br s, 2H), 2.83 (br s, 3H), 1.48 (s, 9H); ^{13}C NMR ($CDCl_3$) δ: 163.26 (d, J_{CF}=246 Hz), 155.70, 146.80, 140.82 (d, J_{CF}=7.2 Hz), 129.96 (d, J_{CF}=8.3 Hz), 122.89 (d, J_{CF}=20.8 Hz), 114.02 (d, J_{CF}=20.8 Hz), 79.84, 52.24, 52.17, 34.02, 28.36; IR (neat) cm^{-1}: 3020 (m), 2930 (m), 1690 (s), 1620 (w), 1590 (m), 1490 (m), 1450 (m), 1390 (s), 1370 (m), 1295 (w), 1250 (m), 1170 (m), 1145 (m), 1070 (m), 980 (w), 870 (w); Low-MS (EI) (*m*/*z*, %): 239 (M^+, 0.57), 183 (98), 166 (8.6), 138 (43), 109 (80), 83 (14), 57 (100), 41 (41); HRMS: 239.1331 (Calcd for $C_{13}H_{18}FNO_2$, 239.1322).

4.3.13. *N*-(*t*-Butoxycarbonyl)-*N*-methyl(*o*-fluorobenzyl)amine (13). Oil, 41%; ^1H NMR ($CDCl_3$) δ: 7.24 (m, 1H), 7.12 (dd, *J*=7.5, 1.5 Hz, 1H), 6.99–7.09 (m, 2H), 4.48 (br s, 2H), 2.87 (br s, 3H), 1.47 (s, 9H); ^{13}C NMR ($CDCl_3$) δ: 160.67 (d, J_{CF}=246 Hz), 155.80, 129.48 (d, J_{CF}=32.2 Hz), 128.77 (d, J_{CF}=8.3 Hz), 124.94 (d, J_{CF}=15.6 Hz), 124.11, 115.21 (d, J_{CF}=21.8 Hz), 79.71, 46.18, 45.33, 34.13, 28.35; IR (neat) cm^{-1}: 2990 (m), 2930 (m), 1710 (s), 1690 (s), 1620 (w), 1590 (m), 1490 (m), 1445 (m), 1395 (m), 1370 (m), 1250 (m), 1225 (m), 1175 (m), 1145 (m), 1050 (w), 1025 (w), 875 (w), 830 (w), 750 (m); Low-MS (EI) (*m*/*z*, %): 239 (M^+, 0.28), 183 (98), 166 (6.0), 138 (57), 109 (86), 83 (13), 57 (100), 41 (37); HRMS: 239.1346 (Calcd for $C_{13}H_{18}FNO_2$, 239.1322).

4.3.14. *N*-(*t*-Butoxycarbonyl)-*N*-methyl(*m*-chlorophenylmethyl)amine (14). Oil, 29% from *o*-chlorophenyltriazene; 54% from *p*-chlorophenyltriazene; ^1H NMR ($CDCl_3$) δ: 7.22 (m, 4H), 4.40 (s, 2H), 2.86 (s, 3H), 1.48 (s, 9H); ^{13}C NMR ($CDCl_3$) δ: 155.62, 140.21, 134.36, 129.74, 128.43, 127.31, 125.28, 79.87, 52.09, 34.02, 28.35; IR (neat) cm^{-1}: 2900 (m), 1680 (s), 1600 (m), 1580 (m), 1420 (br m), 1250 (s), 1140 (s), 880 (m), 780 (m), 680 (m); Low-MS (EI) (*m*/*z*, %): 255 (M^+, 0.23), 199 (82), 182 (8.8), 164 (5.0), 154 (33), 125 (70), 111 (3.1), 99 (5.0), 89 (15), 77 (3.5), 57 (100), 51 (2.5), 41 (26); HRMS: 255.1031 (Calcd for $C_{13}H_{18}ClNO_2$, 255.1026).

4.3.15. A mixture of *N*-(*t*-butoxycarbonyl)-*N*-methyl (*o*-chlorobenzyl)amine and *N*-(*t*-butoxycarbonyl)-*N*-methyl(*p*-chlorobenzyl)amine (15). Oil, *o*/*p*=1/1, 45%; ^1H NMR ($CDCl_3$) δ: 7.27 (m, 4H), 4.55 (d, 2H), 2.87 (d, 3H), 1.46 (m, 9H); ^{13}C NMR ($CDCl_3$) δ: 155.95, 135.44, 129.50, 128.47, 128.23, 127.75, 126.91, 79.82, 50.18, 34.38, 28.36; IR (neat) cm^{-1}: 2950 (m), 1680 (s), 1480 (br s), 1390 (s), 1250 (s), 1140 (br s), 1040 (m), 880 (m), 740 (m).

4.3.16. *N*-(*t*-Butoxycarbonyl)-*N*-methyl(*m*-trimethylsilylbenzyl)amine (16). Oil, 67% from *o*-trimethylsilylphenyltriazene, 70% from *p*-trimethylsilylphenyltriazene; ^{1}H NMR ($CDCl_3$) δ: 7.31 (m, 4H), 4.42 (br s, 2H), 2.81 (br s, 3H), 1.48 (s, 9H), 0.26 (s, 9H); ^{13}C NMR ($CDCl_3$) δ: 155.82, 140.78, 137.21, 132.17, 127.86, 79.63, 52.79, 33.91, 28.45, −1.15; IR (neat) cm^{-1}: 2950 (m), 1690 (s), 1460 (s), 1390 (s), 1250 (s), 1150 (s), 820 (s), 750 (s); Low-MS (EI) (*m*/*z*, %): 293 (M^+, 0.13), 237 (100), 222 (48), 206 (3.5), 192 (28), 178 (23), 163 (39), 149 (13), 135 (5.0), 120 (37), 103 (13), 91 (3.8), 86 (9.4), 73 (21), 57 (68), 41 (10); HRMS: 293.1817 (Calcd for $C_{16}H_{27}NO_2Si$, 293.1811).

4.3.17. *N*-(*t*-Butoxycarbonyl)-*N*-methyl(*p*-trimethylsilylbenzyl)amine (17). Oil, 81%; ^{1}H NMR ($CDCl_3$) δ: 7.49 (d, J=7.5 Hz, 2H), 7.21 (d, J=7.5 Hz, 2H), 4.42 (s, 2H), 2.82 (br s, 3H), 1.48 (s, 9H), 0.26 (s, 9H); ^{13}C NMR ($CDCl_3$) δ: 155.91, 139.20, 138.63, 133.54, 79.63, 52.54 (d), 33.91, 28.45, 28.07, −1.13; IR (neat) cm^{-1}: 2950 (m), 1690 (s), 1470 (s), 1350 (s), 1130 (m), 830 (s), 750 (m); Low-MS (EI) (*m*/*z*, %): 293 (M^+, 0.44), 237 (97), 222 (100), 206 (2.5), 192 (25), 178 (28), 163 (31), 147 (12), 135 (15), 120 (27), 103 (7.5), 91 (3.5), 73 (14), 57 (51), 41 (8.8); HRMS: 293.1806 (Calcd for $C_{16}H_{27}NO_2Si$, 293.1811).

4.3.18. 3-Methyl-1-phenyl-3-(trimethylsilylmethyl)triazene (18) and 1-phenyl-3,3-bis-(trimethylsilylmethyl)-triazene (19). To a solution of lithium diisopropylamide [prepared from diisopropylamine (0.14 mL, 1.00 mmol) and *n*-BuLi (0.64 mL, 1.01 mmol, 1.58 M in hexane)] in dry THF (1 mL) was added chlorotrimethylsilane (0.13 mL, 1.03 mmol). 3,3-Dimethyl-1-phenyltriazene (0.147 mg, 0.99 mmol) was added dropwise to the above solution at 0 °C. The mixture was stirred for 30 min and warmed up to room temperature. The reaction was quenched with water. Extractive work-up and subsequent flash silica gel chromatography (hexane/EtOAc=99/1 as eluents) afforded **18** (0.034 g, 16%) and **19** (0.029 g, 10%).

18: ^{1}H NMR ($CDCl_3$) δ: 7.32–7.15 (m, 4H), 7.00 (tt, J=8.2, 1.8 Hz, 1H), 3.00–3.50 (envelope, 5H), 0.04 (s, 9H); ^{13}C NMR ($CDCl_3$) δ: 151.09, 128.77, 124.70, 120.28, 39.97, 11.7, −1.05; IR (neat) cm^{-1}: 2952 (s), 1594 (s), 1457 (s), 1436 (s), 1387 (s), 1346 (s), 852 (s); Low-MS (EI) (*m*/*z*, %): 221 (M^+, 6.1), 153 (6.9), 135 (8.3), 105 (40), 77 (100), 73 (93), 59 (15), 51 (23), 43 (31); HRMS: 221.1330 (Calcd for $C_{11}H_{19}N_3Si$, 221.1348).

19: ^{1}H NMR ($CDCl_3$) δ: 7.31–6.95 (m, 5H), 3.24 (s, 2H), 3.10 (s, 2H), 0.11 (s, 9H), 0.01 (s, 9H); ^{13}C NMR ($CDCl_3$) δ: 151.22, 128.75, 124.06, 120.09, 49.13, 44.96, −0.52, −1.29; IR (neat) cm^{-1}: 3065 (s), 2897 (m), 1595 (m), 1482 (m), 1455 (s), 1415 (s), 1388 (s), 1358 (s), 1248 (s), 1183 (s), 853 (s); Low-MS (EI) (*m*/*z*, %): 293 (M^+, 0.4), 278 (0.9), 188 (18), 105 (27), 73 (100), 69 (25), 59 (28), 45 (29); HRMS: 293.1730 (Calcd for $C_{14}H_{27}N_3Si_2$, 293.1776).

4.3.19. 1-(2,6-Dideuteriophenyl)-3,3-dimethyltriazene (20). To a solution of 1-(2,6-dibromophenyl)-3,3-dimethyltriazene (1.08 g, 3.50 mmol) in dry THF (2.9 mL) was added dropwise a solution of *n*-BuLi (3.50 mL, 5.10 mmol, 1.45 M in hexane) at −80 °C. After stirring for an additional 1 h, MeOD (0.29 mL, 7.00 mmol) was added and the mixture was stirred for 30 min at room temperature. The reaction was quenched with water and extracted with ether. The extracts were dried over sodium sulfate, filtered, and concentrated in vacuo. To a solution of the residue in dry THF (2.9 mL) was added dropwise a solution of *n*-BuLi (3.50 mL, 5.10 mmol, 1.45 M in hexane) at −80 °C. After stirring for an additional 1 h, MeOD (0.29 mL, 7.00 mmol) was added and the mixture was stirred for 30 min at room temperature. The reaction was quenched with water. Extractive work-up and subsequent flash silica gel chromatography (hexane/EtOAc=19/1 as eluents) afforded **20** (0.312 g, 59%); ^{1}H NMR ($CDCl_3$) δ: 7.33 (d, J=7.2 Hz, 2H), 7.105–7.165 (t, J=7.2 Hz, 1H), 3.33 (br s, 6H); ^{13}C NMR ($CDCl_3$) δ: 150.81, 128.77, 128.67, 125.34, 120.5, 120.20 (t, J_{CD}=23.9 Hz), 120.0, 41.13; IR (neat) cm^{-1}: 760 (s), 640 (w), 610 (m), 560 (w); Low-MS (EI) (*m*/*z*, %): 151 (M^+, 28), 107 (50), 79 (100), 52 (10), 42 (4); HRMS: 151.1050 (Calcd for $C_8H_9N_3D_2$, 151.1076).

4.3.20. *N*-Benzyl-*N*-methylacetamide. To a solution of *N*-methylbenzylamine (0.121 g, 1.00 mmol) in Et_3N (1 mL) was added dropwise Ac_2O (0.15 mL, 2.00 mmol) at 0 °C. After stirring for 1 h, the reaction was quenched with water. Extractive work-up and subsequent flash silica gel chromatography (hexane/EtOAc=3/2 as eluents) afforded the title compound (0.123 g, 76%); ^{1}H NMR (500 MHz; CD_3OD) δ: 7.19–7.37 (m, 5H), 4.61 and 4.57 (2H), 2.97 and 2.97 (3H), 2.16 and 2.15 (3H); ^{13}C NMR (125 MHz; $CDCl_3$) δ: 170.92, 170.61, 137.15, 136.36, 128.78, 128.41, 127.83, 127.46, 127.17, 126.13, 54.06, 50.41, 35.35, 33.56, 21.63, 21.25; Low-MS (EI) (*m*/*z*, %): 163 (M^+, 100), 148 (5), 120 (43), 106 (53), 91 (40), 79 (5), 72 (8), 65 (10), 51 (5), 43 (20).

4.3.21. A mixture of *N*-methyl-(3-deuteriobenzyl)amine (21) and *N*-methyl-(2,3-dideuteriobenzyl)amine (22). To a solution of 1-(2,6-dideuteriophenyl)-3,3-dimethyltriazene (**20**) (0.324 g, 2.14 mmol) in dry THF (2.1 mL) was added dropwise a solution of *n*-BuLi (1.47 mL, 2.14 mmol, 1.45 M in hexane) at 0 °C. After stirring for 1 h, the reaction was quenched with water. Extractive work-up and subsequent short path distillation (0.77 mmHg) afforded the mixture of title compounds (0.099 g); ^{1}H NMR (500 MHz; CD_3OD) δ: 7.34–7.21 (m, 4H), 3.68 (s, 2H), 2.36 (s, 3H); Low-MS (EI) (*m*/*z*, %): 124 (12.5), 123 (M^+, 37), 122 (100), 105 (5), 93 (34), 92 (55), 78 (10), 66 (10), 51 (8), 44 (58); HRMS: 123.1025 (Calcd for $C_8H_9ND_2$, 123.1025).

4.3.22. A mixture of *N*-(3-deuteriobenzyl)-*N*-methylacetamide (23) and *N*-(2,3-dideuteriobenzyl)-*N*-methylacetamide (24). To a solution of a mixture of *N*-methyl (3-deuteriobenzyl)amine and *N*-methyl(2,3-dideuteriobenzyl)amine (0.220 g) in Et_3N (1.78 mL) was added dropwise Ac_2O (0.19 mL, 2.00 mmol) at 0 °C. After stirring for 1 h, the reaction was quenched with water. Extractive work-up and subsequent flash silica gel chromatography (hexane/EtOAc=3/2 as eluents) afforded the title compounds (0.065 g); ^{1}H NMR (500 MHz; CD_3OD) δ: 7.20–7.40 (m, 4H), 4.59 and 4.53 (s, 2H), 2.95 and 2.92 (s, 3H), 2.163 and 2.158 (s, 3H); ^{13}C NMR (125 MHz; $CDCl_3$) δ: 170.92,

170.62, 137.23, 137.16, 136.44, 136.35, 128.82, 128.53, 128.45, 128.34, 128.17, 127.88, 127.76, 127.41, 127.21, 127.11, 126.19, 126.08, 54.14, 54.09, 50.46, 50.42, 35.40, 33.60, 24.03, 21.70, 21.31, 13.56; Low-MS (%) 167 (3.5), 166 (22), 165 (M^+, 100), 164 (M^+, 98), 163 (16), 150 (5), 122 (38), 121 (43), 108 (50), 107 (54), 93 (39), 92 (41), 79 (5), 72 (10), 52 (5), 43 (27).

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