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Radical Carbodiazenylation – A Convenient and Effective Method to Achieve Carboamination of Non-Activated Olefins

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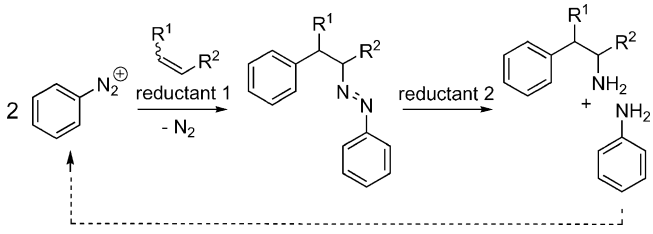
The regioselective addition of aryl and aryldiazenyl substituents to olefinic substrates can be described as carbodiazenylation. In this report we present our final results relating to this unique type of radical functionalization reaction, which has now been developed into a convenient, versatile and highly effective synthetic method. Starting from an investigation into rate constants for the addition of aryl radicals to monosubstituted, non-activated olefins, this key step is shown to be both fast and selective in mixtures of dimethyl sulfoxide and water. The by-products obtained in earlier reactions reveal that the main complication of carbodiazenylation is the formation of biaryl azo compounds. A careful adjustment of the carbodiazenylation procedure led to significantly improved results and now permits the synthesis of previously inaccessible products. New applications of carbodiazenylation such as the synthesis of 1,2-diazabutadienes, tetrahydropyridazines and substituted tricyclanes were investigated. Apart from this, we describe a convenient two-step sequence for intermolecular carboamination.

Introduction

Several synthetic efforts to achieve carboamination of non-activated olefins have been reported in the last few years. Among the organometallic methods, olefinic amines have been cyclized to give pyrrolidines,[1] isoxazolidines,[2] piperidines[3] and piperazines[4] through palladium catalysis. 2-Alkynyl-substituted anilines[5] and isocyanates[6] have served as precursors for indoles in the presence of transition metals, and imines have been induced to react with alkynes in the presence of zirconium[7] and titanium[8] catalysts. All these approaches have in common the fact that two of three basic components – carbon equivalent, olefin and amine equivalent – are linked, so that the overall reaction is partially intramolecular.[9] Radical chemistry, in contrast, is not limited in this way, and less complex starting materials can be used. In a three component mixture, carbon-centred radicals add to olefins, and the resulting adduct radicals are subsequently trapped by a nitrogen-centred scavenger. The best studied radical reaction of this type is carboazidation.[10] In this case, sulfonyl azides are employed as nitrogen equivalents, and carboamination products can be obtained from the alkyl azides by simple reductive workup.[11] Our approaches to achieve carboamination are based on the capability of arenediazonium salts to act as highly efficient scavengers for nucleophilic, carbon-centred radicals.[12,13] In analogy to carboazidation, the overall reaction can be described as carbodiazenylation. The first examples of carbodiazenylation were reported by Levisalles and Rudler[14] in relation to mechanistic studies of the Meerwein arylation.[15] A few reactions with activated olefins were later published by Citterio and Minisci.[16] All of these early carbodiazenylation reactions were already taking advantage of the fact that arenediazonium salts can act as a source of aryl radicals,[17] or as radical scavengers when reductive conditions are applied. In this way, β-arylazo compounds can be obtained in a simple one-step procedure from readily available olefins and diazonium salts (Scheme 1). The azo compounds accessible by carbodiazenylation are of particular interest since suitable further reductive treatment leads to biologically active β-arylamines and recovery of one aniline equivalent, which can be reused for the synthesis of the diazonium salt.



Scheme 1. Carboamination of olefins by a carbodiazenylation/reduction sequence.

Although this strategy for olefin functionalization appears both simple and powerful, for a long time it was not developed into a bona fide synthetic method. This is probably due to the fact that non-activated olefins, which repre-

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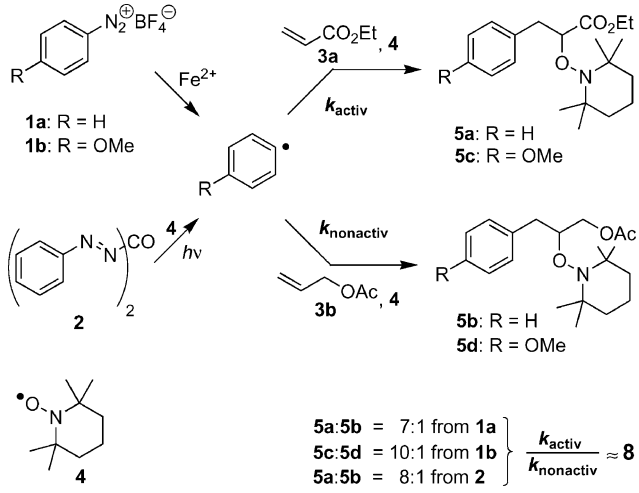
sent the largest group of potential substrates, were believed to possess insufficient reactivity for aryl radical additions. These circumstances are reflected to some degree in the wide range of rate constants that have been published for addition steps of aryl radicals to non-activated olefins.[18] Synthetic applications of aryl radicals involving olefinic substrates therefore remained practically limited to the well known Meerwein reactions in which activated (vinylic, donor- or acceptor-substituted) alkenes are commonly used.[19] Successful, high-yielding additions to non-activated olefins were almost exclusively observed in intramolecular cyclization reactions.[20–22] Remarkable exceptions are Raucher's indole synthesis, employing vinyl bromide,[23] Gorbovoi's chloroarylation of allylic alcohols[24] and the allylation reactions with allyl bromide reported by Frejd.[25]

Results and Discussion

Starting from our initial results on carbodiazenylation[26a] of non-activated olefins, we turned our attention and efforts towards the development of reaction conditions that would allow the functionalization of a broad range of olefinic substrates with a large variety of diazonium salts. Since the presence of water appeared to be a key element for successful carbodiazenylations, we tried to find a suitable co-solvent to achieve sufficient solubilities for lipophilic alkenes. In this case, we were happy to see that a decrease in the water content in dimethyl sulfoxide down to two percent still gave satisfactory results.[26b] This particular mixture now allowed the conversion of lipophilic olefins such as oct-1-ene and was luckily not troubled by side-reactions involving the solvent. As our first carbodiazenylation procedure, which had employed titanium(III) chloride as reductant, was also limited in the sense that only acceptor-substituted arenediazonium salts were reduced in reasonable reaction times,[26a,26c,26d] we changed to iron(II) sulfate as reducing agent.[26b] With respect to the pH-dependent reduction potential of iron(II) ions, the quasi-neutral mixtures of dimethyl sulfoxide and water described above turned out to be perfect solvents, since the reductive power of iron(II) rapidly decreases under acidic conditions. Even weak acids such as acetic acid no longer allow the iron(II)-mediated reduction of donor-substituted (e.g., 4-methoxy) arenediazonium salts at room temperature.[27]

The fact that synthetically useful yields (50 to 65%) of carbodiazenylation products can be obtained with a relatively low excess of olefin (3 to 5 equiv.) shows that the aryl radical addition to the non-activated olefin, which is the crucial key step of the reaction, has to be efficient. The fastest rate constants ever reported for this type of radical reaction were determined by Ingold and Lusztyk in water as sole solvent.[18a] Aryl radicals generated from sodium 4-iodophenylsulfonate by laser flash photolysis reacted with non-activated olefins at rates of $k \approx 2–3 \times 10^7$ M^{-1} s^{-1}, and the authors pointed out that the fast and selective aryl radical addition was largely due to the aqueous solvent. For comparison, rate constants as low as $k \approx 5 \times 10^5$ M^{-1} s^{-1} were derived in earlier experiments conducted in tetrachlorocarbon.[17] Bearing in mind this significant dependence of aryl radical reactivity on the solvent, we became interested in which way our optimized mixture of dimethyl sulfoxide and water would affect aryl radical additions to olefins. We therefore set up a competition experiment in which we compared the reactive, electron-deficient olefin ethyl acrylate with the non-activated olefin allyl acetate. Rate constants for aryl radical additions to various α,β-unsaturated carbonyls are known in the literature,[12b] since these types of alkenes have served numerous times as reactants in Meerwein arylations. For the trapping of the radical adduct and to prevent oligomerization, we added tetramethylpiperdine-1-oxyl (TEMPO) to the reaction mixture.[28] The results obtained in three different experiments are summarized in Scheme 2. In the first attempts, we generated aryl radicals from the diazonum salts **1a** and **1b** in a mixture of dimethyl sulfoxide and water (5:1). The third experiment was conducted in dichloromethane, and carbodiazone **2** was used as precursor for the aryl radicals in a photochemical reaction.[29] In all cases, ten equivalents of each olefin **3a** and **3b** were added to maintain nearly constant olefin concentrations throughout the course of the reaction.

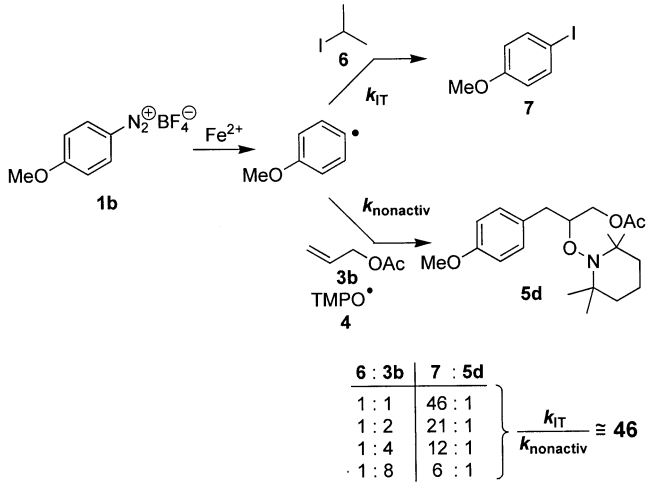


Scheme 2. Determination of relative rate constants for the addition of aryl radicals to the activated olefin ethyl acrylate (**3a**, k_{activ}) and the non-activated olefin allyl acetate (**3b**, $k_{nonactiv}$).

The relative addition rates of the aryl radicals to ethyl acrylate (**3a**) and to allyl acetate (**3b**) can be calculated from the ratios of the products **5a/5b** and **5c/5d**, which were determined by proton NMR analysis of the crude reaction mixtures. Firstly, the observation that all three reactions give similar product ratios is one more piece of evidence for the aryl radical as common intermediate. Secondly, the experiments show that aryl radical addition to non-activated olefins is only eight times slower (averaged from the three experiments) than that to activated acrylates. From the known literature[12b] rate of addition to an activated substrate ($k_{activ} \approx 2 \times 10^8$ M^{-1} s^{-1}, determined for vinyl methyl ketone) one can estimate a rate constant of $k_{nonactiv}$

$\cong 7.3 \times 10^7\ M^{-1}s^{-1}$, which is in good agreement with the value found by Ingold and Lusztyk.[18a] Although the significant change in the nature of the solvent, from aqueous dimethyl sulfoxide to dichloromethane in the photochemical experiments, does not remarkably affect the product ratio, there is a significant difference in the overall outcome in the two reaction types. Combined yields of up to 75% (**5a** and **5b**) were obtained from the iron(II)-mediated process, whereas the photochemical reaction furnished products **5a** and **5b** in only 40% total yield. These results can be explained by the reduced reactivity of the TEMPO radical in polar solvents.[30] Aryl radical trapping by TEMPO therefore occurs to a decreased extent in aqueous dimethyl sulfoxide, which in turn raises the effectiveness of olefin addition. We recently used this finding for the development of a novel intermolecular carbohydroxylation process.[31]

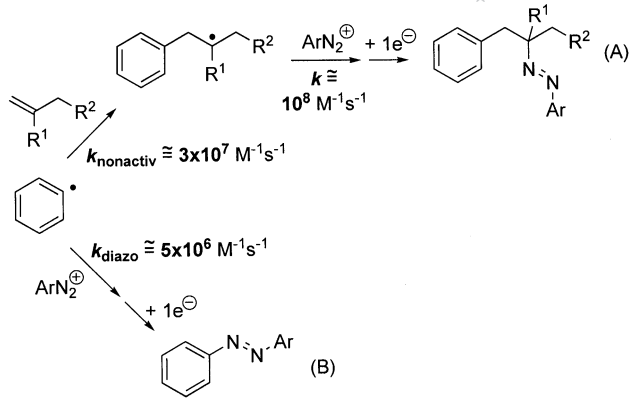
In contrast with the rather slow recombination with TEMPO in polar solvents, aryl radicals readily abstract iodine atoms from alkyl iodides at practically diffusion-controlled rates ($k_{IT} \approx 10^9\ M^{-1}s^{-1}$).[32] The result of a second competition experiment comparing aryl radical reactivity towards 2-iodopropane (**6**) and allyl acetate (**3b**) by examination of the product ratio of 4-iodoanisole (**7**) and olefin adduct **5d** at low conversions led to a ratio of the rate constants $k_{IT}/k_{nonactiv}$ = 46:1 (Scheme 3). From this result and from the value of k_{IT} discussed above, a rate constant of $k_{nonactiv} \approx 2 \times 10^7\ M^{-1}s^{-1}$ (comparable to the one determined before; see Scheme 2) can be derived.[33]



Scheme 3. Determination of relative rate constants for iodine transfer (k_{IT}) to the aryl radical and addition to the non-activated olefin allyl acetate ($k_{nonactiv'}$).

Literature data,[12b,12c] combined with the rate constants determined for the aryl radical addition to non-activated olefins ($k \approx 7.3 \times 10^7\ M^{-1}s^{-1}$, see Scheme 2 and Scheme 3), lead to an overview over the main steps occurring in a carbodiazenylation reaction (Scheme 4).

From a comparison of the rate constants $k_{nonactiv}$ and k_{diazo} it is obvious that azo coupling to biaryl azo compounds (Scheme 4, Path B) remains a competing process in

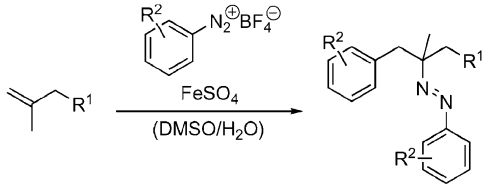


Scheme 4. Key steps of the carbodiazenylation process.

a carbodiazenylation reaction. Indeed, biaryl azo compounds were found in significant amounts in the reactions conducted according to the procedures developed so far. The only practicable solution to circumvent this undesired side-reaction would be to reduce the concentration of the diazonium salt in the reaction mixture. On the other hand, this modification could negatively affect the trapping of the alkyl radicals by the arenediazonium salts in the second stage of the desired radical pathway (Scheme 4, Path A).

To find out in which way lower concentrations of the diazonium ions would influence the overall outcome, we carried out a number of experiments in which we added the salts slowly to the reaction mixture. In the first set of experiments, we examined the behaviour of the 1,1-disubstituted olefins β-methallyl alcohol (**3c**) and β-methallyl acetate (**3d**). To obtain an insight into the influence of the substitution pattern on the aromatic ring of the diazonium salts, we included the donor-substituted *para*-methoxy salt **1b**, the more or less neutral *para*-fluoro salt **1c** and the more reactive acceptor-substituted *ortho*-methoxycarbonyl diazonium salt **1d** in our study. The results are summarized in Table 1. Comparison with earlier experiments (Table 1, En-

Table 1. Carbodiazenylation of 1,1-disubstituted olefins **3c** and **3d**.



3c: R^1 = OH
3d: R^1 = OAc

1b: R^2 = *p*-OMe
1c: R^2 = *p*-F
1d: R^2 = *o*-CO_2Me

8a-c (from **3c**)
8d-f (from **3d**)

	Olefin **3** R^1	Arenediazonium salt **1** R^2	% Yield[a] **8**	% Yield[b] **8**
1	OH (**3c**)	*p*-OMe (**1b**)	77 (**8a**)	63 (**8a**)
2	OH (**3c**)	*p*-F (**1c**)	66 (**8b**)	–
3	OH (**3c**)	*o*-CO_2Me (**1d**)	70 (**8c**)	–
4	OAc (**3d**)	*p*-OMe (**1b**)	78 (**8d**)	60 (**8d**)
5	OAc (**3d**)	*p*-F (**1c**)	91 (**8e**)	–
6	OAc (**3d**)	*o*-CO_2Me (**1d**)	83 (**8f**)	–

[a] Yields by improved procedure. [b] Yields obtained from earlier procedures; see ref.[26b].

tries 1 and 4) shows that the modified procedure is superior to the previous protocol, in which the diazonium salt was added all at once at the beginning. Only traces of biaryl azo compounds were found in the crude product mixture, which indicated that the slow addition of the diazonium salt had indeed had the desired effect. Apparently, the highly effective alkyl radical trapping ($k \approx 1 \times 10^8$ M^{-1} s^{-1}) in the second stage of the carbodiazenylation reaction does not suffer as a result of the lowered concentrations of diazonium salt (Scheme 4, Path A). Among the three different diazonium salts **1b**–**1d** no specific trends became apparent. As far as the olefins are concerned, β-methallyl acetate (**3d**, Entries 4–6) gave slightly better yields, which is most probably due to decreased hydrogen abstraction from the olefin (see also Figure 1).

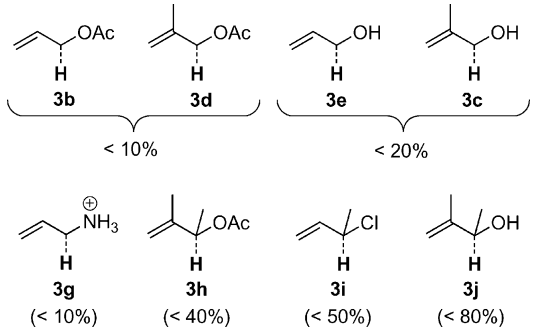
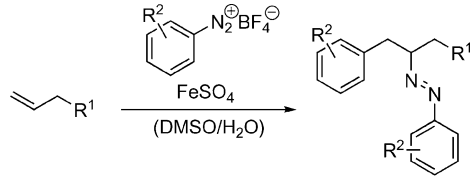


Figure 1. Degree of hydrogen abstraction from olefinic substrates **3b**–**e** and **3g**–j given in percentages of total yields based on aryl radical precursors.

Since the effectiveness of alkyl radical trapping by diazonium salts is known to depend on the nucleophilicity of the alkyl radical (Scheme 1, Path A, R^1 = H),[12b] we expected difficulties in reactions that pass through less nucleophilic secondary rather than tertiary alkyl radicals. For this second series of experiments (Table 2), we used allyl acetate (**3b**), allyl alcohol (**3e**) and but-3-en-1-ol (**3f**) as substrates. Given this less favourable background, we were surprised to obtain better results than in the previous procedure. In addition to increased yields, further advantages of the slow diazonium salt addition turned out to be the cleanness and the mildness of the reaction. Most products were obtained in purities that could not be further improved by column chromatography. The content of biaryl azo compounds was again reduced to trace amounts. Carbodiazenylation products of allyl alcohol (Entries 4–6), which easily undergo isomerization to the corresponding hydrazones and subsequent hydrolysis to the hydroxyketones, could not be obtained by earlier procedures. In all of the second set of reactions (Table 2), the rate of addition of diazonium salt to the reaction mixture turned out to be the critical element. Reactive diazonium salts (e.g., the acceptor-substituted salt **1d**), for example, are reduced more rapidly by iron(II) ions and thus have to be added over a shorter overall period to maintain the ideal concentration. Our standard procedure (addition of the diazonium salt over 10 min) was adjusted in a way to give more than 65% yields of the carbodiazenylation products reliably with any type of diazonium salt and monosubstituted, non-activated olefin. The maximum yields achieved by variation of the rate of addition are reported in order to demonstrate the potential of the reaction. In our optimization attempts, we also found that the diazonium salt can be added either as a solid in small portions or dropwise in solution without significant negative or positive effects.

Table 2. Carbodiazenylation of monosubstituted olefins **3b**, **3e** and **3f**.

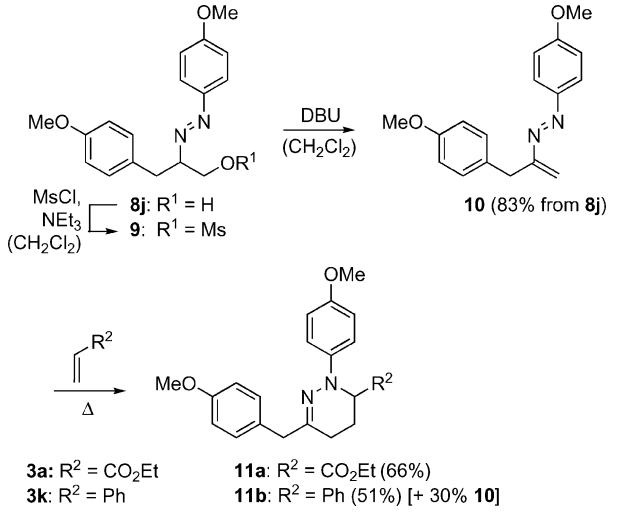


	Olefin **3**	Arenediazonium salt **1**	Maximum % yield[a]	% Yield[b]
	R^1	R^2	**8**	**8**
1	OAc (**3b**)	*p*-OMe (**1b**)	80 (**8 g**)	58 (**8 g**)
2	OAc (**3b**)	*p*-F (**1c**)	81 (**8h**)	–
3	OAc (**3b**)	*o*-CO_2Me (**1d**)	78 (**8i**)	64 (**8 g**)
4	OH (**3e**)	*p*-OMe (**1b**)	83 (**8j**)	–
5	OH (**3e**)	*p*-F (**1c**)	80 (**8k**)	–
6	OH (**3e**)	*o*-CO_2Me (**1d**)	65[c] (**8l**)	–
7	CH_2OH (**3f**)	*p*-OMe (**1b**)	76 (**8m**)	56 (**8 g**)

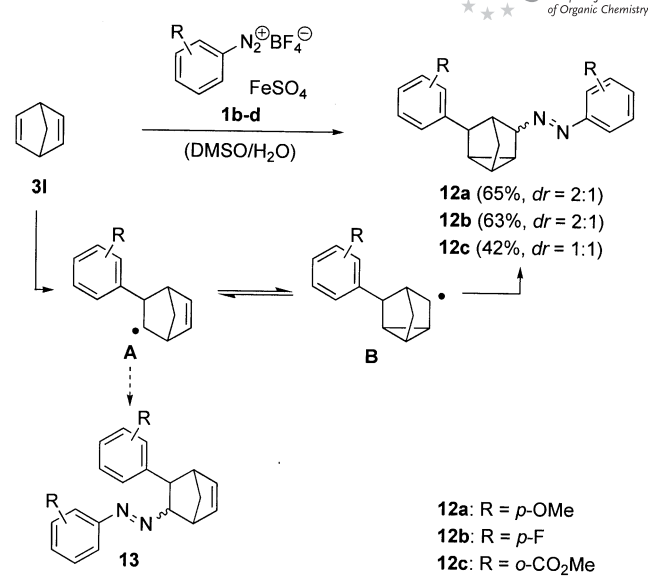
[a] Yields by improved procedure. [b] Yields obtained from earlier procedures; see ref.[26b]. [c] Product **8l** easily undergoes isomerization to the corresponding hydrazone.

As well as biaryl azo coupling, which can successfully be suppressed by the protocol described above, another undesired side-reaction is hydrogen abstraction from the olefinic substrate. From the results of numerous carbodiazenylation experiments conducted in aqueous dimethyl sulfoxide, we have collected experimental data for the degree of hydrogen abstraction for a series of common types of olefin. The maximum values given in Figure 1 are helpful for predicting complications in experiments with unknown substrates.[34] The maximum value of 10% for allyl acetate (**3b**) indicates that usually more than 90% of the aryl radicals undergo addition to the double bond and that less than 10% are reduced by hydrogen abstraction from the allylic position from the olefin. In contrast, as few as 20% of the aryl radicals add to α,β-dimethallyl alcohol (**3j**) and up to 80% stabilize themselves by hydrogen abstraction.

As a first new application of the now readily available β-hydroxyazo compounds (Table 2, Entries 4–6) we investigated the synthesis of vinyldiazenes. Mesylation of the alcohol **8j**, followed by DBU-mediated elimination of **9**, gave the desired diazabutadiene **10** as a yellow solid in 83% yield (Scheme 5).[35]



Scheme 5. Synthesis of vinyldiazene **10** and tetrahydropyridazines **11a** and **11b**.

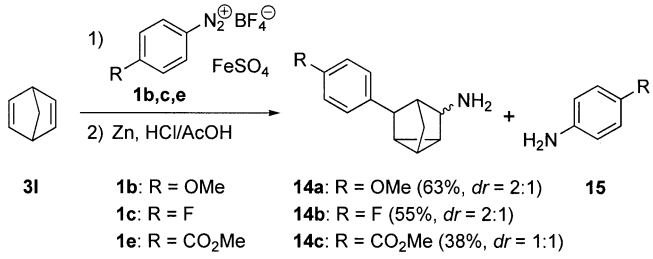


Scheme 6. Carbodiazenylation of norborna-1,4-diene (**3l**).

In view of recently growing interest in photoswitchable compounds,[36] we irradiated the vinyldiazene **10** in deuteriobenzene at wavelengths of 419, 350 and 300 nm and found photochemical *E*/*Z* equilibria of 10:1, 2:3 and 3:1, respectively. During the isomerization experiments no degradation of the azo compound **10** was observed. The decay of the *Z* isomer occurred with a half-life of t_h = 205 min at 23 °C in deuteriobenzene. Since the vinyldiazene **10** is also a potential substrate for hetero-Diels–Alder reactions, we treated **10** in three separate attempts with the dienophiles ethyl acrylate (**3a**), styrene (**3k**) and furan. After heating for 18 h at 60 °C the tetrahydropyridazines **11a** and **11b** had formed, whereas only unchanged starting material was isolated from the reaction mixture containing furan.[37,38]

Carbodiazenylation of olefins such as norborna-1,4-diene (**3l**) by our early procedures would have been difficult because of the low solubility of the substrate in aqueous solvents. Moreover, we chose this norbornadiene **3l** because of its particular behaviour in radical reactions. It is known that after radical addition to the first double bond an equilibrium between two secondary alkyl radicals A and B is established (Scheme 6). Although literature precedence[39] for the trapping of both intermediates exists, the arenediazonium salts **1b**–**d** react preferably with intermediate **B** to give tricyclanes **12a**–**c**.[40] Only in the attempt with the most electrophilic diazonium salt **1d** were traces of azo compound **13** found in the crude product mixture.

The products from the three experiments vary only in the sense that a 1:1 diastereomeric ratio of **12c** is obtained from the electrophilic diazonium salt **1d**, whereas a ratio of 2:1 was found for both **12a** and **12b**. Given the good yields and selective formation of product type **12**, we decided also to use norborna-1,4-diene (**3l**) in the search for an improved, more convenient carboamination procedure. Our previously reported protocol[26a,26c,26d] for reductive cleavage of the N–N bond by hydrogenation in the presence of Raney nickel later turned out not to be the best choice. High pressures (up to 100 bar) were sometimes necessary to achieve complete conversion.[41] Moreover, different commercially available batches of catalyst gave varying outcomes, and workup and isolation of very hydrophilic products was often troubled by the formation of complexes with aluminium ions from the catalyst. Initial experiments with zinc as reductant appeared more promising, and the search for a suitable solvent led us to a mixture of acetic acid and dilute hydrochloric acid. Under these conditions, the azo compounds **12** were cleanly converted into mixtures of amines **14** and anilines **15** (Scheme 7).[42]



Scheme 7. Synthesis of 5-aryl-3-tricycloheptylamines **14a**–**c** by carboamination of norborna-1,4-diene (**3l**).

Tricycloheptylamines of type **14** have so far not been described. One possible route by reductive amination of the literature-known 5-aryltricycloheptan-3-ones would result in a far more complicated procedure.[43] Because of the unique structure, in combination with the defined steric demand, these amines could be valuable building blocks for the synthesis of new biologically active compounds.[44] The developed carbodiazenylation/hydrogenation sequence offers efficient, quick and variable access (with respect to the aromatic moiety) to this new class of compounds.

Conclusions

In summary, we have shown that radical carbodiazenylation can be developed into a versatile and effective synthetic method. The readily available starting materials and the use of non-toxic iron salts are favourable both for laboratory and for large-scale applications.[19] The β-arylazo compounds, which are accessible from aryldiazonium salts and olefins under simple reaction conditions, give quick access to numerous further products including β-arylamines, amino acids and heterocycles.

Experimental Section

General Remarks: Solvents and reagents were degassed with argon prior to use in radical reactions. ^{1}H NMR spectra were recorded on 250, 360 and 500 MHz spectrometers in $CDCl_3$, CD_3OD, CD_3CN and C_6D_6 as solvents and referenced to TMS (δ = 0 ppm), $CHCl_3$ (δ = 7.26 ppm), CHD_2OD (δ = 3.31 ppm), CHD_2CN (δ = 1.94 ppm) or C_6HD_5 (δ = 7.15 ppm). Chemical shifts are reported in parts per million (ppm). Coupling constants J are given in Hertz (Hz). The following abbreviations are used for the description of signals: s (singlet), d (doublet), dd (double doublet), t (triplet), q (quadruplet), m (multiplet). ^{13}C NMR spectra were recorded at 62.9 and 90.6 MHz in $CDCl_3$, CD_3OD, CD_3CN and C_6D_6 with $CDCl_3$ (δ = 77.0 ppm), CD_3OD (δ = 49.5 ppm), CD_3CN (δ = 1.24 ppm) and C_6D_6 (δ = 128.0 ppm) as standards. Chemical shifts are given in parts per million (ppm). ^{19}F NMR spectra were recorded at 235.3 MHz with $CFCl_3$ (δ = 0 ppm) as standard. Analytical TLC was carried out on Merck silica gel plates with use of short-wave UV light (254 nm) to visualize components. Silica gel (Kieselgel 60, 40–63 μm, Merck) was used for flash column chromatography. Arenediazonium tetrafluoroborates were prepared by previously reported procedures.[45]

Competition Experiment Comparing Aryl Radical Addition to Ethyl Acrylate and to Allyl Acetate: The arenediazonium salts **1a** and **1b** (1.00 mmol) were decomposed with $FeSO_4 \cdot 7H_2O$ (3.00 mmol) in the presence of ethyl acrylate (10.0 mmol), allyl acetate (10.0 mmol) and TEMPO (3.00 mmol) in DMSO/water (5:1, 10.0 mL). After addition of ascorbic acid (3 mmol), aqueous workup, extraction with diethyl ether and removal of excess olefin under reduced pressure, the product mixture was analysed by ^{1}H NMR spectroscopy. In the photochemical experiment, a solution of carbodiazone **2** (120 mg, 0.500 mmol) and TEMPO (1.50 mmol) in dichloromethane (5 mL), ethyl acrylate (1.00 mL, 10.0 mmol) and allyl acetate (1.00 mL, 10.0 mmol) was irradiated at 350 nm (Rayonet photoreactor) for 120 min. After addition of ascorbic acid (3 mmol), aqueous workup, extraction with diethyl ether and removal of excess olefin under reduced pressure, the product mixture was analysed by ^{1}H NMR spectroscopy.

Ethyl 3-Phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propionate (5a): For analytical data, see ref.[31]

3-Phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propyl Acetate (5b): For analytical data, see ref.[31]

Ethyl 3-(4-Methoxyphenyl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)-propionate (5c): For analytical data, see ref.[31]

3-(4-Methoxyphenyl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propyl Acetate (5d): For analytical data, see ref.[31]

Competition Experiment Comparing Iodine Transfer and Aryl Radical Addition to Allyl Acetate: The arenediazonium salt **1b** (0.500 mmol) was decomposed by $FeSO_4$ (1.50 mmol) in the presence of 2-iodopropane (**6**, 5.00 mmol), allyl acetate (**3b**, 5.00, 10.0, 20.0, 40.0 mmol) and TEMPO (**4**, 2.00 mmol) in DMSO/water (10:1, v/v, 10.0 mL). After the system had been stirred at room temp. for 10 min, ascorbic acid (3.0 mmol) was added and stirring was continued for a further 10 min. Aqueous workup followed by extraction with diethyl ether and removal of excess olefin and iodopropane under reduced pressure gave a product mixture, which was analysed by ^{1}H NMR spectroscopy.

4-Iodoanisole (7): R_f = 0.85 (petroleum ether/EtOAc, 4:1). ^{1}H NMR (250 MHz, C_6D_6): δ = 3.09 (s, 3 H), 6.30 (d, J = 9.0 Hz, 2 H), 7.34 (d, J = 9.0 Hz, 2 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 54.7 (CH_3), 82.9 (C_q), 116.6 (2 × CH), 138.5 (2 × CH), 159.8 (C_q) ppm. GC-MS (EI): m/z (%) = 234 $[M]^+$ (100), 219 (30), 191 (12), 92 (11).

General Procedure for Carbodiazenylation: $DMSO/H_2O$ (6.0 mL, 5:2, v/v, mixture, previously degassed with argon), olefin (12.0 mmol, 6 equiv.) and $FeSO_4 \cdot 7H_2O$ (1.67 g, 6.00 mmol, 3 equiv.) were introduced into an argon-filled 50 mL Schlenk flask fitted with argon balloon and rubber septum. A solution of the diazonium salt (2.00 mmol, 1 equiv.) in $DMSO/H_2O$ (3.0 mL, 5:2, v/v, mixture, previously degassed with argon) was added dropwise by syringe over a period of 10 min. The reaction mixture was stirred for 10 more min at room temp., and was then diluted with water (50 mL) and extracted with Et_2O (3 × 50 mL). The combined ethereal extracts were washed with satd. aq. NaCl and dried with Na_2SO_4. Careful evaporation of the solvent gave the carbodiazenylation products as yellow oils, which were further purified by column chromatography.

Among the carbodiazenylation products, the β-hydroxy azo compounds arising from β-methallyl alcohol (Table 1, Entries 1–3) and allyl alcohol (Table 2, Entries 4–6) are particularly labile since they can decompose by fragmentation and isomerization. To prevent these side reactions, the crude product mixture should be heated in the water bath as briefly as possible during evaporation of the solvents and the silica gel used for column chromatography should be deactivated prior to use with triethylamine. Both isomerization and fragmentation occur especially quickly when the diazonium salts bear electron-withdrawing substituents.

3-(4-Methoxyphenyl)-2-(4-methoxyphenylazo)-2-methylpropan-1-ol (8a): Yield 242 mg (0.77 mmol, 77%). For analytical data, see ref.[26b]

3-(4-Fluorophenyl)-2-(4-fluorophenylazo)-2-methylpropan-1-ol (8b): Yield 192 mg (0.66 mmol, 66%). Yellow oil. R_f = 0.50 (petroleum ether/EtOAc, 4:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.22 (s, 3 H), 3.00 (d, J = 11.8 Hz, 1 H), 3.13 (d, J = 11.8 Hz, 1 H), 3.71 (d, J = 11.8 Hz, 1 H), 3.79 (d, J = 11.8 Hz, 1 H), 6.95 (dd, $J_{H,F}$ = 8.9, J = 8.9 Hz, 2 H), 7.11–7.21 (m, 4 H), 7.71 (dd, $J_{H,F}$ = 5.2, J = 8.9 Hz, 2 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 19.5 (CH_3), 40.5 (CH_2), 66.8 (CH_2), 73.7 (C_q), 114.8 (d, $^2J_{C,F}$ = 21.1 Hz, 2 × CH), 115.9 (d, $^2J_{C,F}$ = 22.8 Hz, 2 × CH), 124.1 (d, $^3J_{C,F}$ = 8.9 Hz, 2 × CH), 132.1 (d, $^3J_{C,F}$ = 7.9 Hz, 2 × CH), 132.5 (d, $^4J_{C,F}$ = 3.3 Hz, 2 × C_q), 148.0 (d, $^4J_{C,F}$ = 3.0 Hz, 2 × C_q), 161.7 (d, $^1J_{C,F}$ = 244.5 Hz, 2 × C_q), 164.2 (d, $^1J_{C,F}$ = 251.4 Hz, 2 × C_q) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –110.2, –117.2 ppm. MS (ESI): m/z (%) = 291 $[M + H]^+$. HRMS (ESI): calcd. for $C_{16}H_{17}N_2OF_2$ $[M + H]^+$: 291.1303; found 291.1305.

Methyl 2-[1-Hydroxymethyl-2-(2-methoxycarbonylphenyl)-1-methylethylazo]benzoate (8c): Yield 260 mg (0.70 mmol, 70%). Yellow oil. R_f = 0.30 (petroleum ether/EtOAc, 3:1). ^{1}H NMR (250 MHz,

$CDCl_3$): δ = 1.12 (s, 3 H), 3.37 (d, J = 13.4 Hz, 1 H), 3.60–3.75 (m, 2 H), 3.63 (s, 3 H), 3.76 (s, 3 H), 3.83 (d, J = 13.4 Hz, 1 H), 7.00 (dd, J = 1.4, J = 7.9 Hz, 1 H), 7.11–7.37 (m, 4 H), 7.41–7.48 (m, 1 H), 7.71 (dd, J = 1.1, J = 7.8 Hz, 1 H), 7.82 (dd, J = 1.4, J = 7.7 Hz, 1 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 19.3 (CH_3), 37.8 (CH_2), 51.8 (CH_3), 52.6 (CH_3), 66.3 (CH_2), 75.8 (C_q), 117.8 (CH), 126.0 (C_q), 126.3 (CH), 129.2 (CH), 130.3 (CH), 130.4 (CH), 131.1 (CH), 131.7 (C_q), 133.0 (CH), 133.3 (CH), 138.1 (C_q), 152.5 (C_q), 166.7 (C_q), 168.6 (C_q) ppm. MS (ESI): m/z (%) = 371 [M + H]$^+$. HRMS (ESI): calcd. for $C_{20}H_{23}N_2O_5$ [M + H]$^+$: 371.1602; found 371.1605.

3-(4-Methoxyphenyl)-2-(4-methoxyphenylazo)-2-methylpropyl Acetate (8d): Yield 276 mg (0.78 mmol, 78%). For analytical data, see ref.[26b]

3-(4-Fluorophenyl)-2-(4-fluorophenylazo)-2-methylpropyl Acetate (8e): Yield 302 mg (0.91 mmol, 91%). Yellow oil. R_f = 0.80 (petroleum ether/EtOAc, 4:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.24 (s, 3 H), 2.05 (s, 3 H), 3.10 (d, J = 15.4 Hz, 1 H), 3.16 (d, J = 15.4 Hz, 1 H), 4.32 (d, J = 11.2 Hz, 1 H), 4.37 (d, J = 11.2 Hz, 1 H), 6.91 (d, $J_{H,F}$ = 8.7, J = 8.7 Hz, 2 H), 7.04 (dd, $J_{H,F}$ = 5.5, J = 8.7 Hz, 2 H), 7.13 (dd, $J_{H,F}$ = 8.7, J = 8.7 Hz, 2 H), 7.68 (dd, $J_{H,F}$ = 5.2, J = 8.7 Hz, 2 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 19.8 (CH_3), 20.8 (CH_3), 41.3 (CH_2), 67.8 (CH_2), 72.1 (C_q), 114.8 (d, $^2J_{C,F}$ = 21.2 Hz, 2×CH), 115.8 (d, $^2J_{C,F}$ = 22.8 Hz, 2×CH); 124.1 (d, $^3J_{C,F}$ = 8.9 Hz, 2×CH), 132.0 (d, $^3J_{C,F}$ = 7.9 Hz, 2×CH), 132.1 (d, $^4J_{C,F}$ = 3.3 Hz, 2×C_q); 148.2 (d, $^4J_{C,F}$ = 3.1 Hz, 2×C_q); 161.7 (d, $^1J_{C,F}$ = 244.8 Hz, 2×C_q), 164.1 (d, $^1J_{C,F}$ = 251.0 Hz, 2×C_q), 170.7 (C_q) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –110.7, –117.0 ppm. MS (ESI): m/z (%) = 333 [M + H]$^+$. HRMS (ESI): calcd. for $C_{18}H_{19}N_2O_2F_2$ [M + H]$^+$: 333.1409; found 333.1411.

Methyl 2-[1-Acetoxymethyl-2-(2-methoxycarbonylphenyl)-1-methylethylazo]benzoate (8f): Yield 340 mg (0.83 mmol, 83%). Yellow oil. R_f = 0.50 (petroleum ether/EtOAc, 4:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.14 (s, 3 H), 1.95 (s, 3 H), 3.65 (s, 3 H), 3.65 (d, J = 13.6 Hz, 1 H), 3.67 (s, 3 H), 3.74 (d, J = 13.6 Hz, 1 H), 4.26 (d, J = 11.2 Hz, 1 H), 4.33 (d, J = 11.2 Hz, 1 H), 7.06–7.13 (m, 2 H), 7.15–7.22 (m, 1 H), 7.24–7.31 (m, 1 H), 7.32–7.40 (m, 1 H), 7.42–7.50 (m, 1 H), 7.71 (dd, J = 1.7, J = 7.5 Hz, 1 H), 7.73 (dd, J = 1.6, J = 7.3 Hz, 1 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 19.2 (CH_3), 20.8 (CH_3), 38.2 (CH_2), 51.8 (CH_3), 52.1 (CH_3), 68.1 (CH_2), 73.6 (C_q), 118.0 (CH), 126.5 (CH), 127.8 (C_q), 129.2 (CH), 129.7 (CH), 130.3 (CH), 131.1 (CH), 131.7 (C_q), 132.1 (CH), 133.0 (CH), 137.6 (C_q), 151.6 (C_q), 167.4 (C_q), 168.4 (C_q), 170.7 (C_q) ppm. MS (ESI): m/z (%) = 413 [M + H]$^+$. HRMS (ESI): calcd. for $C_{22}H_{25}N_2O_6$ [M + H]$^+$: 413.1708; found 413.1706.

3-(4-Methoxyphenyl)-2-(4-methoxyphenylazo)propyl Acetate (8 g): Yield 273 mg (0.80 mmol, 80%). For analytical data, see ref.[26b]

3-(4-Fluorophenyl)-2-(4-fluorophenylazo)propyl Acetate (8h): Yield 258 mg (0.81 mmol, 81%). Yellow oil. R_f = 0.65 (petroleum ether/EtOAc, 4:1). ^{1}H NMR (360 MHz, C_6D_6): δ = 1.57 (s, 3 H), 2.75 (dd, J = 6.5, J = 14.0 Hz, 1 H), 2.90 (dd, J = 7.6, J = 14.0 Hz, 1 H), 4.14–4.20 (m, 1 H), 4.35 (dd, J = 3.8, J = 11.5 Hz, 1 H), 4.54 (dd, J = 8.1, J = 11.5 Hz, 1 H), 6.67–6.74 (m, 6 H), 7.53 (dd, $J_{H,F}$ = 5.2, J = 9.0 Hz, 2 H) ppm. ^{13}C NMR (91 MHz, C_6D_6): δ = 20.2 (CH_3), 35.9 (CH_2), 64.6 (CH_2), 77.1 (CH), 115.5 (d, $^2J_{C,F}$ = 21.2 Hz, 2×CH), 116.1 (d, $^2J_{C,F}$ = 22.9 Hz, 2×CH), 124.8 (d, $^3J_{C,F}$ = 8.9 Hz, 2×CH), 131.2 (d, $^3J_{C,F}$ = 7.8 Hz, 2×CH), 133.2 (d, $^4J_{C,F}$ = 3.3 Hz, C_q), 148.7 (d, $^4J_{C,F}$ = 3.0 Hz, C_q), 162.1 (d, $^1J_{C,F}$ = 244.6 Hz, C_q), 164.5 (d, $^1J_{C,F}$ = 251.1 Hz, C_q), 169.9 (C_q) ppm. ^{19}F NMR (235 MHz, C_6D_6): δ = –109.7, –116.3 ppm. MS (ESI): m/z (%) = 319 [M + H]$^+$. HRMS (ESI): calcd. for $C_{17}H_{17}N_2O_2F_2$ [M + H]$^+$: 319.1253; found 319.1254.

Methyl 2-[3-Acetoxy-2-(2-methoxycarbonylphenylazo)propyl]benzoate (8i): Yield 310 mg (0.78 mmol, 78%). For analytical data, see ref.[26b]

3-(4-Methoxyphenyl)-2-(4-methoxyphenylazo)propan-1-ol (8j): Yield 248 mg (0.83 mmol, 83%). Yellow oil. R_f = 0.30 (petroleum ether/EtOAc, 2:1). ^{1}H NMR (360 MHz, C_6D_6): δ = 3.03 (dd, J = 7.3, J = 14.0 Hz, 1 H), 3.15 (dd, J = 6.8, J = 14.0 Hz, 1 H), 3.20 (s, 3 H), 3.29 (s, 3 H), 3.83 (dd, J = 3.6, J = 11.3 Hz, 1 H), 3.93 (dd, J = 6.6, J = 11.3 Hz, 1 H), 4.12–4.19 (m, 1 H), 6.70 (d, J = 9.1 Hz, 2 H), 6.73 (d, J = 9.5 Hz, 2 H), 7.05 (d, J = 9.5 Hz, 2 H), 7.79 (d, J = 9.1 Hz, 2 H) ppm. ^{13}C NMR (91 MHz, C_6D_6): δ = 35.9 (CH_2), 54.7 (CH_3), 55.0 (CH_3), 63.7 (CH_2), 79.9 (CH), 114.3 (2×CH), 114.4 (2×CH), 124.6 (2×CH), 130.6 (C_q), 130.9 (2×CH), 146.8 (C_q), 158.8 (C_q), 162.2 (C_q) ppm. MS (ESI): m/z (%) = 301 [M + H]$^+$. HRMS (ESI): calcd. for $C_{17}H_{21}N_2O_3$ [M + H]$^+$: 301.1547; found 301.1553.

3-(4-Fluorophenyl)-2-(4-fluorophenylazo)propan-1-ol (8k): Yield 221 mg (0.80 mmol, 80%). Yellow oil. R_f = 0.60 (petroleum ether/EtOAc, 2:1). ^{1}H NMR (360 MHz, C_6D_6): δ = 2.92 (dd, J = 6.8, J = 14.0 Hz, 1 H), 3.00 (dd, J = 7.4, J = 14.0 Hz, 1 H), 3.75 (dd, J = 4.1, J = 11.3 Hz, 1 H), 3.85 (dd, J = 6.7, J = 11.3 Hz, 1 H), 3.99–4.04 (m, 1 H), 6.70–6.76 (m, 4 H), 6.84 (dd, $J_{H,F}$ = 5.5, J = 8.6 Hz, 2 H), 7.53 (dd, $J_{H,F}$ = 5.2, J = 8.9 Hz, 2 H) ppm. ^{13}C NMR (91 MHz, C_6D_6): δ = 35.5 (CH_2), 63.3 (CH_2), 79.8 (CH), 115.4 (d, $^2J_{C,F}$ = 21.1 Hz, 2×CH), 116.1 (d, $^2J_{C,F}$ = 22.8 Hz, 2×CH), 124.7 (d, $^3J_{C,F}$ = 8.9 Hz, 2×CH), 131.3 (d, $^3J_{C,F}$ = 7.6 Hz, 2×CH), 134.1 (d, $^4J_{C,F}$ = 3.3 Hz, C_q), 148.7 (d, $^4J_{C,F}$ = 3.0 Hz, C_q), 162.1 (d, $^1J_{C,F}$ = 244.2 Hz, C_q), 164.5 (d, $^1J_{C,F}$ = 251.1 Hz, C_q) ppm. MS (ESI): m/z (%) = 277 [M + H]$^+$. HRMS (ESI): calcd. for $C_{15}H_{15}N_2OF_2$ [M + H]$^+$: 277.1147; found 277.1148.

Methyl 2-[2-(2-Methoxycarbonylphenyl)-1-hydroxymethylethylazo]-benzoate (8l): Yield 231 mg (0.65 mmol, 65%). Yellow oil. R_f = 0.50 (petroleum ether/EtOAc, 2:1). ^{1}H NMR (360 MHz, C_6D_6): δ = 3.41 (s, 3 H), 3.45 (s, 3 H), 3.63 (dd, J = 6.6, J = 13.2 Hz, 1 H), 3.83 (dd, J = 7.4, J = 13.2 Hz, 1 H), 4.05–4.14 (m, 2 H), 4.61–4.69 (m, 1 H), 6.87–6.97 (m, 2 H), 7.02–7.08 (m, 3 H), 7.18 (dd, J = 1.0, J = 7.7 Hz, 1 H), 7.63 (d, J = 6.6 Hz, 1 H), 7.90 (d, J = 1.2, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR (91 MHz, C_6D_6): δ = 34.7 (CH_2), 51.5 (CH_3), 52.1 (CH_3), 63.0 (CH_2), 80.5 (CH), 119.2 (CH), 126.3 (C_q), 126.6 (CH), 128.8 (CH), 130.3 (CH), 130.5 (C_q), 131.3 (CH), 132.0 (CH), 132.7 (CH), 132.9 (CH), 141.2 (C_q), 153.8 (C_q), 166.9 (C_q), 167.7 (C_q) ppm. MS (ESI): m/z (%) = 357 [M + H]$^+$. HRMS (ESI): calcd. for $C_{19}H_{21}N_2O_5$ [M + H]$^+$: 357.1445; found 357.1446.

4-(4-Methoxyphenyl)-3-(4-methoxyphenylazo)butan-1-ol (8m): Yield 238 mg (0.76 mmol, 76%). For analytical data, see ref.[26b]

Synthesis of Vinyldiazene 10 By Mesylation of 8j and Elimination from 9: Mesyl chloride (0.39 mL, 0.57 g, 5.0 mmol, 2.5 equiv.) and NEt_3 (1.1 mL, 0.81 g, 8.0 mmol, 4.0 equiv.) were added at 0 °C to a solution of **8j** (0.601 g, 2.00 mmol) in CH_2Cl_2 (20 mL). The resulting mixture was stirred at room temp. over 2 h, and was then washed with satd. aq. $KHSO_4$ and $NaHCO_3$. After the system had been dried over Na_2SO_4 and filtered, DBU (0.60 mL, 4.0 mmol, 2.0 equiv.) was added at 0 °C to the solution of **9**, and the resulting mixture was left to come to room temp. over 2 h. After washing with satd. aq. $KHSO_4$ the organic phase was dried with Na_2SO_4 and quickly concentrated under reduced pressure. Immediate purification by column chromatography gave **10** as a yellow solid (468 mg, 1.66 mmol, 83%). Compound **10** is stable in the pure state when stored below 0 °C. The crude product decomposes in concentrated solution within several hours.

3-(4-Methoxyphenyl)-2-(4-methoxyphenylazo)propyl Methanesulfonate (9): Yellow oil. R_f = 0.40 (petroleum ether/EtOAc, 2:1). ^{1}H

NMR (360 MHz, C_6D_6): δ = 2.11 (s, 3 H), 2.86 (dd, J = 7.0, J = 13.7 Hz, 1 H), 2.98 (dd, J = 7.3, J = 13.7 Hz, 1 H), 3.18 (s, 3 H), 3.25 (s, 3 H), 4.22 (m, 1 H), 4.36 (dd, J = 3.7, J = 10.6 Hz, 1 H), 4.57 (dd, J = 7.3, J = 10.6 Hz, 1 H), 6.67 (d, J = 9.0 Hz, 2 H), 6.68 (d, J = 8.7 Hz, 2 H), 6.91 (d, J = 8.7 Hz, 2 H), 7.78 (d, J = 9.0 Hz, 2 H) ppm. MS (EI): m/z (%) = 378 $[M]^+$ (1), 348 (1), 312 (8), 320 (37), 319 (19), 305 (10), 279 (13), 244 (11), 189 (13), 148 (23), 147 (26), 136 (16), 135 (41), 123 (43), 121 (88), 109 (81), 108 (46), 107 (34), 97 (27), 80 (25), 79 (100), 77 (25).

(*E*)-[1-(4-Methoxybenzyl)vinyl](4-methoxyphenyl)diazene [(*E*)-10]: Yellow solid, m.p. 78–81 °C, R_f = 0.80 (petroleum ether/EtOAc, 3:1). ^{1}H NMR (360 MHz, C_6D_6): δ = 3.19 (s, 3 H), 3.31 (s, 3 H), 3.85 (s, 2 H), 5.55 (s, 1 H), 6.27 (s, 1 H), 6.72 (d, J = 9.0 Hz, 2 H), 6.76 (d, J = 8.5 Hz, 2 H), 7.08 (d, J = 8.5 Hz, 2 H), 7.97 (d, J = 9.0 Hz, 2 H) ppm. ^{13}C NMR (91 MHz, C_6D_6): δ = 34.8 (CH_2), 54.7 (CH_3), 54.9 (CH_3), 114.2 (2×CH), 114.5 (2×CH), 124.2 (CH_2), 125.0 (2×CH), 130.7 (2×CH), 131.2 (C_q), 147.1 (C_q), 158.7 (C_q), 162.4 (C_q), 162.8 (C_q) ppm. MS (ESI): m/z (%) = 283 $[M + H]^+$. HRMS (ESI): calcd. for $C_{17}H_{18}N_2O_2$ $[M + H]^+$: 283.1441; found 283.1446.

Photochemical Isomerization of Vinyldiazene 10: Photoisomerization (solutions in C_6D_6) was carried out in Rayonet photoreactors at 419, 350 and 300 nm. The *E*/*Z* ratios were determined by ^{1}H NMR spectroscopy.

(*Z*)-[1-(4-Methoxybenzyl)vinyl](4-methoxyphenyl)diazene [(*Z*)-10]: ^{1}H NMR (250 MHz, C_6D_6): δ = 3.17 (s, 3 H), 3.26 (s, 3 H), 3.36 (br. s, 2 H), 4.25 (t, J = 1.5 Hz, 1 H), 4.35 (t, J = 0.8 Hz, 1 H), 6.58 (d, J = 9.0 Hz, 2 H), 6.71 (d, J = 8.8 Hz, 2 H), 6.92 (d, J = 8.8 Hz, 2 H), 6.96 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (91 MHz, C_6D_6): δ = 38.2 (CH_2), 54.7 (CH_3), 54.9 (CH_3), 101.9 (CH_2), 113.9 (2×CH), 114.3 (2×CH), 122.2 (2×CH), 130.7 (2×CH), 130.8 (C_q), 147.9 (C_q), 159.1 (C_q), 159.4 (C_q), 162.3 (C_q) ppm.

Diels–Alder Reactions of Vinyldiazene 10: A mixture of vinyldiazene **10** (0.141 g, 0.500 mmol) and the dienophile (3.0 mL) was warmed to 60 °C for 18 h. The reaction with ethyl acrylate (**3a**) was complete at that time, the mixture with styrene (**3k**) showed ca. 30% of unreacted starting material, and the attempt with furan remained unsuccessful. Excess dienophile was removed under reduced pressure and the residue was purified by column chromatography.

Ethyl 6-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-2,3,4,5-tetrahydropyridazine-3-carboxylate (11a): Yield 126 mg (0.33 mmol, 66%). Colourless oil. R_f = 0.60 (petroleum ether/EtOAc, 3:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.17 (t, J = 7.1 Hz, 3 H), 1.98–2.08 (m, 3 H), 2.26–2.33 (m, 1 H), 3.54 (s, 2 H), 3.78 (m, 3 H), 3.79 (m, 3 H), 4.13 (dq, J = 1.0, J = 7.1 Hz, 2 H), 4.52–4.58 (m, 1 H), 6.84 (d, J = 8.8 Hz, 2 H), 6.86 (d, J = 9.3 Hz, 2 H), 7.14 (d, J = 9.3 Hz, 2 H), 7.20 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 14.1 (CH_3), 20.2 (CH_2), 21.1 (CH_2), 43.7 (CH_2), 54.6 (CH), 55.2 (CH_3), 55.6 (CH_3), 61.1 (CH_2), 113.8 (2×CH), 114.3 (2×CH), 115.1 (2×CH), 129.8 (2×CH), 130.3 (C_q), 141.6 (C_q), 143.5 (C_q), 153.5 (C_q), 158.2 (C_q), 171.7 (C_q) ppm. MS (EI): m/z (%) = 382 $[M]^+$ (20), 309 (38), 262 (7), 206 (17), 122 (14), 121 (100). HRMS (EI): calcd. for $C_{22}H_{26}N_2O_4$ $[M]^+$: 382.1893; found 390.1892.

3-(4-Methoxybenzyl)-1-(4-methoxyphenyl)-6-phenyl-1,4,5,6-tetrahydropyridazine (11b): Yield 98 mg, 0.26 mmol, 51%. Colourless oil. R_f = 0.70 (petroleum ether/EtOAc, 4:1). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.61–1.76 (m, 1 H), 1.86–1.98 (m, 1 H), 2.05–2.15 (m, 2 H), 3.57 (s, 2 H), 3.74 (s, 3 H), 3.79 (s, 3 H), 5.06 (t, J = 3.3 Hz, 1 H), 6.81 (d, J = 9.3 Hz, 2 H), 6.84 (d, J = 9.0 Hz, 2 H), 7.09–7.33 (m, 9 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$): δ = 19.4 (CH_2), 25.2 (CH_2), 43.8 (CH_2), 55.2 (CH_3), 55.4 (CH), 55.6 (CH_3), 113.7 (2×CH), 114.3 (2×CH), 114.4 (2×CH), 126.1 (2×CH), 126.8 (CH), 128.5 (2×CH), 129.7 (2×CH), 130.5 (C_q), 141.4 (C_q), 141.5 (C_q), 143.3 (C_q), 152.9 (C_q), 158.1 (C_q) ppm. MS (EI): m/z (%) = 386 (4) $[M]^+$, 288 (6), 267 (7), 250 (6), 161 (19), 152 (42), 135 (100), 122 (23), 121 (26), 107 (17), 105 (85), 77 (57). HRMS (EI): calcd. for $C_{25}H_{26}N_2O_2$ $[M]^+$: 386.1994; found 390.1999.

(4-Methoxyphenyl)[5-(4-methoxyphenyl)tricyclo[2.2.1.0^{2,6}]hept-3-yl]-diazene (12a): This compound was isolated as a 2:1 mixture of diastereoisomers. Yield 217 mg (0.65 mmol, 65%). Yellow oil. R_f = 0.50 (petroleum ether/EtOAc, 10:1). ^{1}H NMR (500 MHz, C_6D_6, major isomer): δ = 1.35–1.55 (m, 4 H), 2.20–2.23 (m, 2 H), 2.94 (br. s, 1 H), 3.20 (s, 3 H), 3.36 (s, 3 H), 4.14 ("t", J = 1.5 Hz, 1 H), 6.74 (d, J = 9.0 Hz, 2 H), 6.82 (d, J = 8.5 Hz, 2 H), 7.08 (d, J = 8.5 Hz, 2 H), 7.91 (d, J = 9.0 Hz, 2 H) ppm. ^{1}H NMR (500 MHz, C_6D_6, major isomer): δ = 1.19 (d, J = 10.8 Hz, 1 H), 1.30 ("t", J = 5.1 Hz, 1 H), 1.45–1.60 (m, 3 H), 2.26 (br. s, 1 H), 3.20 (s, 3 H), 3.35 (s, 3 H), 4.12 ("t", J = 1.5 Hz, 1 H), 4.17 (br. s, 1 H), 6.75 (d, J = 9.0 Hz, 2 H), 6.82 (d, J = 8.6 Hz, 2 H), 7.16 (m, 2 H), 7.95 (d, J = 9.0 Hz, 2 H) ppm. ^{13}C NMR (63 MHz, C_6D_6, major isomer): δ = 11.8 (CH), 16.9 (CH), 17.5 (CH), 26.6 (CH_2), 42.0 (CH), 48.0 (CH), 54.8 (CH_3), 54.9 (CH_3), 82.8 (CH), 113.9 (2×CH), 114.3 (2×CH), 124.6 (2×CH), 129.1 (2×CH), 133.3 (C_q), 147.2 (C_q), 158.8 (C_q), 161.9 (C_q) ppm. ^{13}C NMR (63 MHz, C_6D_6, minor isomer): δ = 13.8 (CH), 15.3 (CH), 17.7 (CH), 29.1 (CH_2), 42.2 (CH), 45.9 (CH), 54.8 (CH_3), 54.9 (CH_3), 83.5 (CH), 113.9 (2×CH), 114.4 (2×CH), 124.7 (2×CH), 129.3 (2×CH), 134.0 (C_q), 147.3 (C_q), 158.7 (C_q), 162.0 (C_q) ppm. MS (EI): m/z (%) = 334 (44) $[M]^+$, 242 (23), 214 (18), 212 (19), 199 (71), 184 (14), 171 (13), 158 (12), 139 (12), 135 (55), 122 (26), 121 (100), 107 (78), 91 (44), 77 (34). HRMS (EI): calcd. for $C_{21}H_{22}N_2O_2$: 334.1681; found 334.1676.

(4-Fluorophenyl)[5-(4-fluorophenyl)tricyclo[2.2.1.0^{2,6}]hept-3-yl]diazene (12b): This compound was isolated as a 2:1 mixture of diastereoisomers. Yield 196 mg (0.63 mmol, 63%). Yellow oil. R_f = 0.80 (petroleum ether/EtOAc, 10:1). ^{1}H NMR (500 MHz, C_6D_6, major isomer): δ = 1.22–1.40 (m, 4 H), 2.02–2.06 (m, 2 H), 2.76 (s, 1 H), 3.99 (br. s, 1 H), 6.73–6.97 (m, 6 H), 7.65 (dd, $J_{H,F}$ = 5.2, J = 8.9 Hz, 2 H) ppm. ^{1}H NMR (500 MHz, C_6D_6, minor isomer): δ = 1.10 (td, J = 1.3, J = 10.9 Hz, 1 H), 1.22–1.40 (m, 4 H), 2.08 (s, 1 H), 3.92 (s, 1 H), 3.98 (br. s, 1 H), 6.73–6.90 (m, 4 H), 6.95 (ddd, J = 0.7, $J_{H,F}$ = 5.5, J = 8.8 Hz, 2 H), 7.69 (dd, $J_{H,F}$ = 5.2, J = 9.0 Hz, 2 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$, major isomer): δ = 11.6 (CH), 16.7 (CH), 17.4 (CH), 26.4 (CH_2), 41.8 (CH), 47.8 (CH), 82.8 (CH), 115.0 (d, $^2J_{C,F}$ = 21.0 Hz, 2×CH), 116.0 (d, $^2J_{C,F}$ = 22.8 Hz, 2×CH), 124.7 (d, $^3J_{C,F}$ = 8.8 Hz, 2×CH), 129.5 (d, $^3J_{C,F}$ = 7.8 Hz, 2×CH), 136.7 (d, $^4J_{C,F}$ = 3.2 Hz, C_q), 149.1 (d, $^4J_{C,F}$ = 3.1 Hz, C_q), 162.0 ($^1J_{C,F}$ = 243.8 Hz, C_q), 164.3 (d, $^1J_{C,F}$ = 250.4 Hz, C_q) ppm. ^{13}C NMR (63 MHz, $CDCl_3$, minor isomer): δ = 13.7 (CH), 15.0 (CH), 17.6 (CH), 28.9 (CH_2), 42.0 (CH), 45.8 (CH), 83.5 (CH), 114.9 (d, $^2J_{C,F}$ = 21.0 Hz, 2×CH), 116.1 (d, $^2J_{C,F}$ = 22.8 Hz, 2×CH), 124.8 (d, $^3J_{C,F}$ = 8.7 Hz, 2×CH), 129.6 (d, $^3J_{C,F}$ = 7.6 Hz, 2×CH), 137.4 (d, $^4J_{C,F}$ = 3.2 Hz, C_q), 149.2 (d, $^4J_{C,F}$ = 3.0 Hz, C_q), 161.9 (d, $^1J_{C,F}$ = 243.4 Hz, C_q), 164.4 (d, $^1J_{C,F}$ = 250.5 Hz, C_q) ppm. MS (EI): m/z (%) = 310 (19) $[M]^+$, 234 (4), 220 (5), 218 (11), 205 (9), 200 (10), 190 (20), 188 (14), 187 (35), 172 (6), 159 (16), 146 (6), 123 (16), 109 (100), 107 (14), 95 (44), 91 (19), 79 (21). HRMS (EI): calcd. for $C_{19}H_{16}F_2N_2$: 310.1281; found 310.1280.

Methyl 2-[5-(2-Methoxycarbonylphenyl)tricyclo[2.2.1.0^{2,6}]hept-3-yl-azo]benzoate (12c): This compound was isolated as a 1:1 mixture of diastereoisomers. Yield 164 mg (0.42 mmol, 42%). Yellow oil. R_f

= 0.30 (petroleum ether/EtOAc, 10:1). ^{1}H NMR (360 MHz, C_6D_6, mixture of diastereoisomers): δ = 1.09 (d, J = 11.3 Hz, 1 H), 1.26–1.34 (m, 4 H), 1.38–1.54 (m, 4 H), 2.07 (d, J = 10.9 Hz, 1 H), 2.40 (br. s, 1 H), 2.66 (br. s, 1 H), 3.41 (s, 3 H), 3.47 (s, 3 H), 3.55 (s, 3 H), 3.57 (s, 3 H), 3.97 (br. s, 1 H), 4.12 ("t", J = 1.4 Hz, 1 H), 4.35 ("t", J = 1.6 Hz, 1 H), 4.80 (br. s, 1 H), 6.88–7.04 (m, 5 H), 7.10–7.21 (m, 3 H), 7.26 (dd, J = 1.1, J = 7.7 Hz, 1 H), 7.38–7.49 (m, 2 H), 7.56–7.69 (m, 3 H), 7.88 (dd, J = 1.5, J = 8.0 Hz, 1 H), 7.91 (dd, J = 1.4, J = 7.8 Hz, 1 H) ppm. ^{13}C NMR (90 MHz, C_6D_6, mixture of diastereoisomers): δ = 12.5 (CH), 14.4 (CH), 15.5 (CH), 17.1 (CH), 17.2 (CH), 17.3 (CH), 26.6 (CH_2), 29.1 (CH_2), 41.6 (CH), 42.1 (CH), 44.5 (CH), 46.7 (CH), 51.5 (CH_3), 51.6 (CH_3), 51.8 (CH_3), 51.9 (CH_3), 83.8 (CH), 84.5 (CH), 119.5 (CH), 120.3 (CH), 126.3 (CH), 126.5 (CH), 128.2 (C_q), 128.9 (C_q), 129.0 (CH), 129.1 (CH), 129.2 (CH), 129.3 (CH), 129.7 (CH), 129.8 (CH), 130.2 (C_q), 130.8 (CH), 131.1 (CH), 131.2 (C_q), 131.3 (CH), 131.5 (CH), 131.6 (CH), 131.9 (CH), 142.7 (C_q), 142.8 (C_q), 152.7 (C_q), 152.8 (C_q), 167.5 (C_q), 167.6 (C_q), 167.7 (C_q), 168.2 (C_q) ppm. MS (EI): m/z (%) = 391 (8) $[M + H]^+$, 390 (23) $[M]^+$, 359 (4), 298 (8), 240 (7), 227 (44), 196 (17), 195 (100), 177 (27), 167 (28), 165 (22), 163 (18), 161 (58), 152 (21), 149 (15), 135 (36), 109 (10), 105 (12), 91 (18), 85 (15), 77 (22). HRMS (EI): calcd. for $C_{23}H_{22}N_2O_4$: 390.1580; found 390.1577.

Carboamination of Norborna-1,4-diene (3l) by a Carbodiazenylation/Hydrogenation Sequence: The crude carbodiazenylation product obtained from the arenediazonium tetrafluoroborate (2.00 mmol, 1 equiv.), norborna-1,4-diene (**3l**, 1.22 mL, 1.10 g, 6 equiv.) and $FeSO_4$ (1.67 g, 6.00 mmol, 3 equiv., see general procedure described above) were dissolved in AcOH (10 mL). Zn dust (1.0 g) and aq. HCl (6 M, 10 mL) were added to this solution, and the resulting mixture was stirred for 4 h at room temp. After dilution with H_2O and addition of aq. NaOH (3 M) to pH > 12, the aqueous phase was extracted with Et_2O (3 × 30 mL). The combined extracts were dried with Na_2SO_4 and concentrated under reduced pressure. Purification by column chromatography (silica gel previously deactivated with NEt_3) gave the anilines **15** followed by the amines **14**.

5-(4-Methoxyphenyl)tricyclo[2.2.1.0^{2,6}]hept-3-ylamine (14a): This compound was isolated as a 2:1 mixture of diastereoisomers. Yield 135 mg (0.63 mmol, 63%). Colourless oil. R_f = 0.50 ($CHCl_3$/MeOH = 10:1). ^{1}H NMR (250 MHz, $CDCl_3$, major isomer): δ = 1.15–1.45 (m, 5 H), 1.73 (br. s, 1 H), 2.83 (br. s, 1 H), 3.10 (br. s, 1 H), 3.78 (s, 3 H), 6.83 (d, J = 8.8 Hz, 2 H), 7.13 (d, J = 8.8 Hz, 2 H) ppm. ^{1}H NMR (250 MHz, $CDCl_3$, minor isomer): δ = 1.15–1.45 (m, 5 H), 1.69 (br. s, 1 H), 2.89 (br. s, 1 H), 3.26 (br. s, 1 H), 3.79 (s, 3 H), 6.84 (d, J = 8.6 Hz, 2 H), 7.21 (d, J = 8.8 Hz, 2 H) ppm. ^{13}C NMR (63 MHz, $CDCl_3$, major isomer): δ = 10.5 (CH), 16.4 (CH), 17.3 (CH), 24.9 (CH_2), 41.4 (CH), 46.8 (CH), 55.2 (CH_3), 57.3 (CH), 113.4 (2 × CH), 128.5 (2 × CH), 133.0 (C_q), 158.0 (C_q) ppm. ^{13}C NMR (63 MHz, $CDCl_3$, minor isomer): δ = 13.3 (CH), 14.1 (CH), 14.8 (CH), 28.3 (CH_2), 41.4 (CH), 44.1 (CH), 55.2 (CH_3), 58.2 (CH), 113.4 (2 × CH), 128.7 (2 × CH), 133.0 (C_q), 157.9 (C_q) ppm. MS (ESI): m/z = 216 $[M + H]^+$. HRMS (ESI): calcd. for $C_{14}H_{18}NO$ $[M + H]^+$: 216.1383; found 216.1383.

5-(4-Fluorophenyl)tricyclo[2.2.1.0^{2,6}]hept-3-ylamine (14b): This compound was isolated as a 2:1 mixture of diastereoisomers. Yield 112 mg (0.55 mmol, 55%). Colourless oil. R_f = 0.80 (petroleum ether/EtOAc, 2:1, TLC plate deactivated with NEt_3). ^{1}H NMR (360 MHz, $CDCl_3$, major isomer): δ = 1.10–1.90 (m, 8 H), 2.87 (br. s, 1 H), 3.15 (br. s, 1 H), 6.95 (dd, $J_{H,F}$ = 8.4, J = 8.4 Hz, 2 H), 7.15 (dd, $J_{H,F}$ = 5.6, J = 8.4 Hz, 2 H) ppm. ^{1}H NMR (360 MHz, $CDCl_3$, minor isomer): δ = 1.10–2.00 (m, 8 H), 3.15 (br. s, 1 H), 3.29 (br. s, 1 H), 6.95 (dd, $J_{H,F}$ = 8.4, J = 8.4 Hz, 2 H), 7.23 (m, 2 H) ppm. ^{13}C NMR (91 MHz, $CDCl_3$, major isomer): δ = 10.3 (CH), 16.7 (CH), 18.6 (CH), 24.8 (CH_2), 42.8 (CH), 47.0 (CH), 58.6 (CH), 115.1 (d, $^2J_{C,F}$ = 21.0 Hz, 2 × CH), 129.4 (d, $^3J_{C,F}$ = 7.7 Hz, 2 × CH), 137.6 (d, $^4J_{C,F}$ = 3.1 Hz, C_q), 161.8 (d, $^1J_{C,F}$ = 243.7 Hz, C_q) ppm. ^{13}C NMR (91 MHz, $CDCl_3$, minor isomer): δ = 13.6 (CH), 14.0 (CH), 18.8 (CH), 28.4 (CH_2), 42.8 (CH), 44.2 (CH), 59.3 (CH), 115.1 (d, $^2J_{C,F}$ = 21.0 Hz, 2 × CH), 129.6 (d, $^3J_{C,F}$ = 7.7 Hz, 2 × CH), 137.7 (d, $^4J_{C,F}$ = 3.1 Hz, C_q), 161.7 (d, $^1J_{C,F}$ = 243.7 Hz, C_q) ppm. MS (EI): m/z (%) = 203 (16) $[M]^+$, 187 (15), 186 (100), 185 (34), 171 (11), 160 (12), 159 (12), 146 (7), 137 (8), 133 (8), 120 (7), 11 (14), 109 (12), 107 (10), 94 (7), 66 (49). HRMS (EI): calcd. for $C_{13}H_{14}FN$: 203.1110; found 203.1106.

Methyl 4-(5-Aminotricyclo[2.2.1.0^{2,6}]hept-3-yl)benzoate (14c): This compound was isolated as a 1:1 mixture of diastereoisomers. Yield 92 mg (0.38 mmol, 38%). Colourless oil. R_f = 0.30 ($CHCl_3$/MeOH = 20:1, TLC plate deactivated with NEt_3). ^{1}H NMR (500 MHz, $CDCl_3$, mixture of diastereoisomers): δ = 1.10–1.70 (m, 10 H), 2.18–2.21 (m, 2 H), 2.98 (br. s, 1 H), 3.31 (br. s, 1 H), 3.34 (br. s, 1 H), 3.58 (br. s, 1 H), 3.88 (s, 3 H), 3.89 (s, 3 H), 7.24 (d, J = 8.4 Hz, 2 H), 7.34 (d, J = 8.3 Hz, 2 H), 7.89 (d, J = 8.3 Hz, 2 H), 7.93 (d, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR (90 MHz, $CDCl_3$, mixture of diastereoisomers): δ = 10.8 (CH), 13.4 (CH), 14.0 (CH), 16.1 (CH), 16.7 (CH), 16.9 (CH), 25.4 (CH_2), 28.3 (CH_2), 40.5 (CH), 40.6 (CH), 45.4 (CH), 47.6 (CH), 51.9 (CH_3), 52.0 (CH_3), 57.4 (CH), 58.2 (CH), 127.6 (2 × CH), 127.8 (2 × CH), 128.1 (C_q), 128.3 (C_q), 129.2 (2 × CH), 129.3 (2 × CH), 145.9 (C_q), 146.3 (C_q), 166.9 (C_q), 167.0 (C_q) ppm. MS (EI): m/z (%) = 243 (14) $[M]^+$, 226 (68), 195 (15), 167 (62), 151 (57), 120 (100), 107 (23), 92 (34), 86 (26), 66 (79), 59 (89). HRMS (EI): calcd. for $C_{15}H_{17}NO_2$: 243.1259; found 243.1257.

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