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Substitution of a nitro group by diazonium salts in σ^H-Adducts of carbanions to mono-nitrobenzenes. Formation of substituted azobenzenes and indazoles

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ABSTRACT

σ^H-Adducts formed at low temperature from nitrobenzene derivatives and carbanions stabilized by cyano, alkoxycarbonyl or sulfonyl groups react with benzenediazonium salts as nucleophiles, forming a new C–N bond preferentially at carbon atom bearing the nitro group. The so-formed intermediates eliminate HNO_2 molecule under action of base, yielding substituted azobenzenes. Adducts of secondary carbanions, stabilized by cyano or sulfonyl groups to the *ortho* positions of nitrobenzenes, cyclize *in situ* to substituted indazoles. Some *ortho* σ^H-adducts of 1-chloroethyl phenyl sulfone carbanion add diazonium cations at *meta* position to the nitro group. In this case, the subsequent elimination of HCl leads to azo compounds retaining the nitro group in its original position.

1. Introduction

Addition of nucleophilic species to the aromatic ring of electron-poor arenes is one of the elementary processes fundamental to the chemistry of aromatic compounds. It was convincingly proved that the addition of typical nucleophilic reagents, namely carbon, oxygen or nitrogen anions to electrophilic arenes, proceeds preferentially in activated, unsubstituted positions giving σ^H-adducts [1,2]. The addition is essentially reversible, so unless the equilibrium is shifted strongly to the right or any subsequent transformation leading to a stable product is not fast enough, the σ^H-adduct formation may go unnoticed, giving other processes a chance to proceed. Stable σ^H-adducts formed from polynitrobenzenes or strongly electrophilic heterocyclic compounds are well known and also investigated presently [3]. The study of transformations of σ^H-adducts formed as intermediates in the reactions of nucleophiles with less reactive mononitroarenes has a much shorter history, but several reviews and chapters in monographs have been devoted to them [1,3]. It has been found that these unstable adducts can be converted into stable products in several synthetically significant ways (Scheme 1).

Oxidation of σ^H-adducts with external oxidants, sometimes also spontaneously, leads to products of the oxidative substitution of hydrogen (ONSH) [4]. Nucleophiles containing X-leaving groups in the nucleophilic center enable β-elimination of HX from σ^H-adducts to give products of Vicarious Nucleophilic Substitution (VNS) [1,3,5]. Intramolecular redox process involving vicinal adjacent nitro group is often followed by subsequent transformations [6a-d]. In case of the *ortho* addition of anilide nucleophiles it leads to substitution of hydrogen along with the formation of substituted 2-nitrosodiarylamines [6e]. Nitroso compounds were also produced after acidic workup of irreversibly formed σ^H-adducts of mononitroarenes with some organolithium and Grignard reagents [7]. Less common transformations are *cine* and *tele* substitutions which have been reviewed [8].

σ^H-Adducts of carbon nucleophiles to nitroarenes are negatively charged species with a charge spread on the nitro group and conjugate carbon atoms of the ring. This makes them weakly basic and nucleophilic molecules that are prone to react with external or internal electrophilic reagents. Intramolecular trapping of a negatively charged carbon atom of the ring by a side chain isonitrile group is an interesting way for the synthesis of isoindoles [9]. Recently a report on intramolecular S_N2 substitution of phenylselenone group with a carbon atom forming cyclopropane ring on the C1–C2 bond of 1-nitronaphtalene was reported [10].

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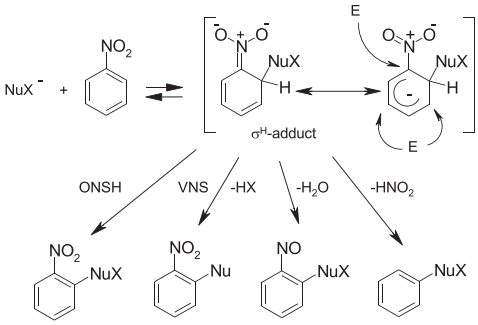


Scheme 1. Principal transformations of σ^H-adducts of mononitroarenes and possible interactions with electrophiles.

The reaction of σ^H-adduct with an external electrophilic reagent requires that the adduct is stable under the reaction conditions and formed in high concentration so that the starting, stronger nucleophile does not compete with the adduct. Those requirements are met for adducts formed irreversibly by addition of Grignard reagents or silyl enol ethers in which case *O*-silylated adducts are formed. Both types of adducts easily react with bromine giving geminal bromonitrocyclohexadiene intermediates susceptible to elimination of HBr or HNO_2 [11]. For typical, stabilized carbanions or their hetero analogues, the requirements are easily satisfied with strongly electrophilic arenes such as polynitrobenzenes or nitro compounds of low aromaticity. It was found, however, that equilibrium of the addition of some carbanions to mononitrobenzene derivatives, when carried out in polar solvents at low temperature, lies shifted strongly to the right and σ^H-adducts are formed in high concentration [4]. This finding was successfully exploited in the ONSH reactions mentioned above [4] and in the *cine* substitution of the nitro group with some sulfone-stabilized carbanions [12]. According to our best knowledge, no other electrophiles than proton or halogens have been successfully used for trapping σ^H-adducts of carbanions to regular mononitrobenzenes. Our goal was to find other external electrophiles which would take advantage of the nucleophilic feature of the ring carbon atoms of such σ^H-adducts to form a new stable bond. The most promising electrophiles seemed to be benzenediazonium salts which were found earlier to add to nitronate anions [13] and stable adducts formed from hydride, alkoxylate or enolate anions and polynitroarenes[14a–c] or 9-nitroantracene [14d] that could be finally transformed to azo compounds [14]. This proved their high reactivity to such type of weak nucleophiles.

2. Results and discussion

As a model σ^H-adduct, a product of the addition of 2-phenylpropionitrile anion (**1a**$^-$ generated from **1a** using *t*-BuOK) to nitrobenzene (**2a**) was chosen. 4-Bromobenzenediazonium salt (**3a**) was used in preliminary experiments and found to be a potentially effective electrophilic agent in the intended reaction. The reaction was completed with the addition of a second base to form the substituted azobenzene final product (Scheme 2).

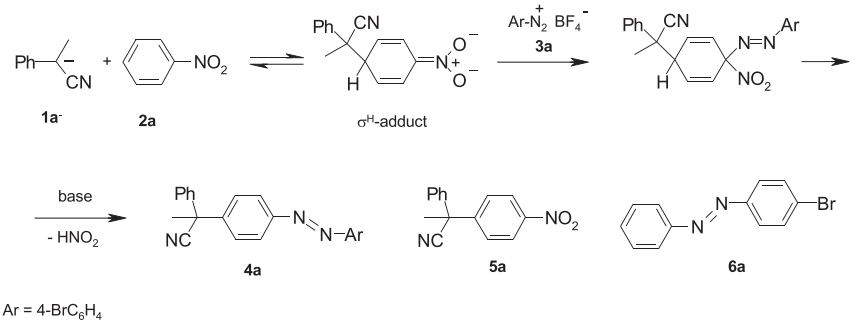
To find the best reaction conditions, a short series of scrutinizing experiments were performed. The reaction was carried out under various conditions which differed in the solvent, temperature and base added (Table 1).

In all the cases, a solution of nitrobenzene and the nitrile was added into a cooled solution of *t*-BuOK. This should result in formation of a σ^H-adduct of the carbanion at position 4 of nitrobenzene. Then the diazonium salt was added, followed by addition of the base (1 equiv. of *t*-BuOK in THF or an excess of neat Et_3N). The reaction was quenched with aqueous NH_4Cl at the reaction temperature or, after removing the cooling bath, at room temperature. In all the reactions, the desired product (**4a**) was formed, although in rather low to moderate yield. Depending on the reaction conditions, **4a** was accompanied by numerous side-products, mainly **5a** and **6a** as shown in Fig. 1. Thus, under unsuitable conditions, the reaction course was quite complicated. The best results were obtained when the reaction was carried out in a solvent of low polarity (THF) and a strong base was used, even at low temperature (conditions A, G, H). A weak base (Et_3N) is not effective under these conditions and requires higher temperature reached before the quench (condition F).

Those reaction conditions were then applied for the reactions of selected carbanions stabilized by CN, COOR and $ArSO_2$ groups. At first, tertiary compounds were chosen since they are known to add to nitrobenzenes selectively at *para* position, if available, thus the formation of isomeric *ortho* adducts was avoided (Table 2).

tert-Butyl ester of phenylacetic acid was expected to react at *para* position, similarly to the tertiary nitriles, due to its bulkiness. However, while under condition F, the reactions gave multicomponent mixtures. Positive results were achieved when they were carried out in DMF with Et_3N or *t*-BuOK used as a base (condition C or D). These conditions were found rather unfavorable for the nitriles (Table 1). The addition proceeded at position *para* to the nitro group and the products, azo compounds **4i** and **4j**, were isolated in relatively good yield (Table 2, entries 10 and 11). Also, tertiary benzyl sulfones reacted better in DMF (condition C) than in THF. Thus, it is apparent that there are no optimal reaction conditions for every class of CH-acids and particular reactions were not further optimized. The yields obtained were rather low due to the several by-products, which only in a few cases were formed individually in sufficient amounts for identification (Table 2, entries 4 and 5).

The results show the crucial role of the added base. In the absence of base or when a weak base is operating at low temperature, other processes take place in parallel and they can dominate over the main course (Table 1). The formation of substituted

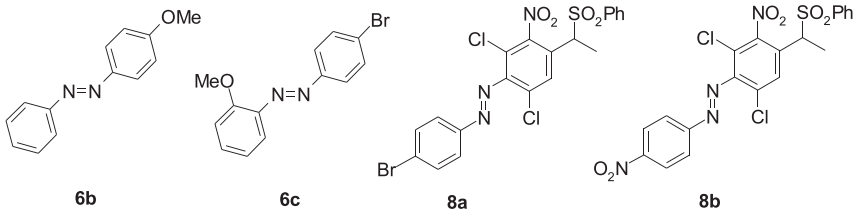


Scheme 2. The model reaction of the σH-adduct of 1a and 2a with diazonium salt 3a.

Table 1
Screening of the reaction conditions[a].

Entry	Solvent	Temperature °C	Base	Final temperature °C	Condition	4a %	5a %	6a %
1	THF	−100	*t*-BuOK	−100	A	53[b]	–	–
2	THF	−100	none	−100	B	*26*	*29*	*2*
3	DMF	−60	*t*-BuOK	r.t.	C	*25*	*13*	*20*
4	DMF	−60	Et_3N	r.t.	D	*20*	*12*	*19*
5	THF	−78	Et_3N	−78	E	*20*	*30*	*5*
6	THF	−78	Et_3N	r.t.	F	*59*	*<2*	*<2*
7	THF	−78	*t*-BuOK	−78	G	*55*	*2*	*6*
8	THF	−78	*t*-BuOK	r.t.	H	*60*	*<2*	*<2*

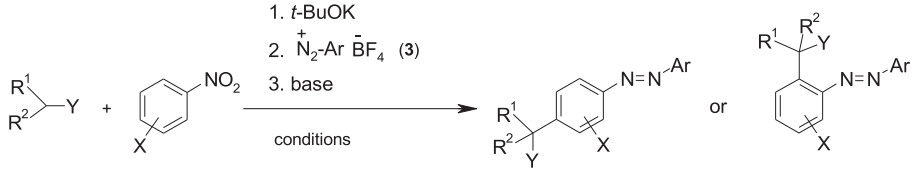
[a] Yields measured by GC. [b] Isolated yield



6b 6c 8a 8b

Fig. 1. The identified by-products in the reactions of diazonium salts with σ^H-adducts of **1a**-**e** and **2a**-**h** (Table 2).

Table 2
Formation of σ^H-adducts and their reactions with diazonium salts **3**.



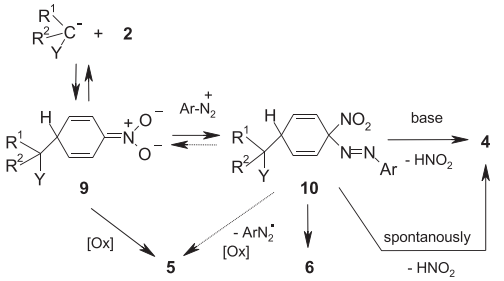
1 2 4 7

Entry	CH-Acid				Nitroarene		Diazonium salt		Product		
	Y	R^1	R^2	1	X	2	Z	3	Condition[a]	No	Yield[b] %
1	CN	Ph	Me	**1a**	H	**2a**	4-Br	**3a**	A	**4a**	53
2	CN	Ph	Me	**1a**	H	**2a**	4-NO_2	**3b**	F	**4b**	42
3	CN	Ph	Me	**1a**	H	**2a**	3-NO_2	**3c**	F	**4c**	47
4	CN	Ph	Me	**1a**	H	**2a**	4-OMe	**3d**	F	**4d**	31[c]
5	CN	Ph	Me	**1a**	2-OMe	**2b**	4-Br	**3a**	F	**4e**	21[d]
6	CN	Ph	Me	**1a**	2-OMe	**2b**	4-Br	**3a**	H	**4e**	42
7	CN	Ph	Me	**1a**	3-Cl	**2c**	4-Br	**3a**	F	**4f**	31
8	CN	Ph	*i*-Pr	**1b**	H	**2a**	4-Br	**3a**	H	**4g**	34
9	CN	Ph	Me	**1a**	2-Cl	**2d**	4-Br	**3a**	H	**4h**	20
10	CO_2t-Bu	Ph	H	**1c**	H	**2a**	4-Br	**3a**	D	**4i**	51
11	CO_2t-Bu	Ph	H	**1c**	2-Cl	**2d**	4-Br	**3a**	C	**4j**	41
12	SO_2Ph	4-ClC_6H_4	Me	**1d**	H	**2a**	4-Br	**3a**	F	**4k**	31
13	SO_2Ph	Cl	Me	**1e**	2,4-Cl_2	**2e**	4-Br	**3a**	I	**7a**	30[e]
14	SO_2Ph	Cl	Me	**1e**	2,4-Cl_2	**2e**	4-NO_2	**3b**	I	**7b**	27[f]
15	SO_2Ph	Cl	Me	**1e**	4-CF_3	**2f**	4-Br	**3a**	I	**7c**	39
16	SO_2Ph	Cl	Me	**1e**	4-Cl	**2g**	4-Br	**3a**	I	**7d**	32
17	SO_2Ph	Cl	Me	**1e**	4-F	**2h**	4-Br	**3a**	I	**7e**	30

[a] Reaction conditions as in Table 1. Condition I: same as D except that the initial temperature was −40 °C.
[b] Isolated yield.
[c] 4-Methoxyazobenzene (**6b**) was isolated in 10% yield.
[d] 4-Bromo-2′-methoxyazobenzene (**6c**) was isolated in 26% yield.
[e] Additionally **8a** (Fig. 1) was formed in 33% yield.
[f] Additionally **8b** (Fig. 1) was formed in 26% yield.

azobenzenes **4** and **7** is believed to proceed according to the intended reaction scheme (Scheme 2). However, additional noteworthy observations can be made. First, azo compound **4a** is formed in a considerable amount even in the absence of a concluding base, or when a weak base is used at low temperature. Second, the product of the oxidative substitution of hydrogen **5a** is a major reaction product under such conditions (Table 1, entries 2 and 5).

Oxidation of the σ^H-adduct is a common process which often accompanies these reactions when potentially oxidizing reagents are present in the reaction mixture. In this case, there are starting nitroarenes and, particularly, diazonium salts which can play the role of a powerful electron acceptor [15]. The fact that this process is remarkably efficient when the base is absent or operates ineffectively could be explained by the assumption of reversibility of the formation of **10** (Scheme 3), which means that it dissociates to form **9** and the diazonium cation. Alternatively, intermediate **10** could be believed to form irreversibly, as an unstable, not isolable

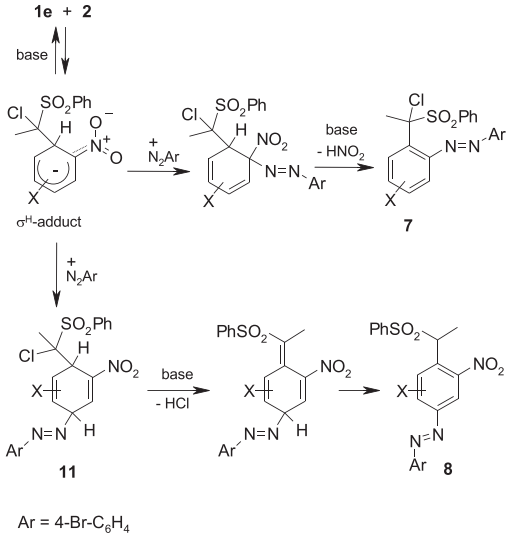


Scheme 3. Plausible routes of the formation of **4**, **5** and **6** from σ^H-adduct of **1** and **2**.

compound that at higher temperature (up to room temperature) or during workup undergoes energetically favored rearomatization. This is possible to take place via several plausible routes. The most obvious is spontaneous elimination of HNO_2 leading to **4** without action of base. On the other hand, homolytic fragmentation of **10** by departure of the ArN_2 radical would allow the nitrocyclohexadiene radical to rearomatize yielding **5** [15]. Side products **6** were formed in considerable amounts in the model reaction conducted in DMF (**6a**, Table 1, entries 2 and 3) and unexpectedly also in two cases of the reaction carried out in THF when the nitroarene (**2b**) or diazonium salt (**3d**) bear OMe substituent in the benzene ring (**6b** and **6c**, Table 2, entries 4 and 5).

In both reactions, Et_3N was used as a base that was allowed to act up to room temperature (condition F). For the model reaction, these conditions were equally efficient as those with *t*-BuOK used as a base (condition H). In the cases of the methoxy-substituted reagents, changing the reaction conditions from F to H allowed to suppress the side process and to increase the yields of the desired products significantly. This fact and the structure of azo compounds **6**, lacking both carbon substituent and a nitro group, suggest that the way of its formation from intermediate **10** is rather complex and may involve some radical processes [15]. Thus, additional research would be necessary to propose a reasonable mechanistic scheme for this transformation.

Some sterically undemanding tertiary sulfone-stabilized carbanions readily add to nitroarene ring at both *para* and *ortho* positions. They form σ^H-adducts which, in the presence of strong base, undergo elimination of HCl (VNS) [5]. On the other hand, the *ortho* σ^H-adducts formed from carbanions such as 1-chloroethyl phenyl sulfone (**1e**) eliminate HCl relatively slowly. Additionally, when generated at low temperature, they can be protonated with aqueous strong acids at position bearing NO_2 group, followed by spontaneous elimination of HNO_2 leading to the *cine* substitution of nitro group [12]. It was expected that diazonium salt would capture such *ortho* σ^H-adducts when added prior to base, although further effect of the base added was difficult to predict. For the reaction of **1e** with 4-substituted nitrobenzenes **2**, initially applied condition F was found to be ineffective and complex mixtures of products were obtained. Better results were achieved when the reactions were carried out in DMF at −40 °C and, after addition of Et_3N, finished at room temperature (Table 2, condition I). A short series of reactions showed that the expected products **7** were formed and the VNS process did not occur to a noticeable extent. However, in some cases another unpredicted product **8** (Fig. 1) was created in a quantity comparable to main product **7** (Scheme 4). Addition of the diazonium cation to the σ^H-adduct can occur at the partially negatively charged position *ipso* or *meta* to the nitro group. In the former case, the subsequent elimination of HNO_2 but not HCl took place yielding **7**. This demonstrates that rearomatization of the ring, as a result of NO_2 anion departure, is energetically more favorable than formation of exo-double bond by elimination of HCl.

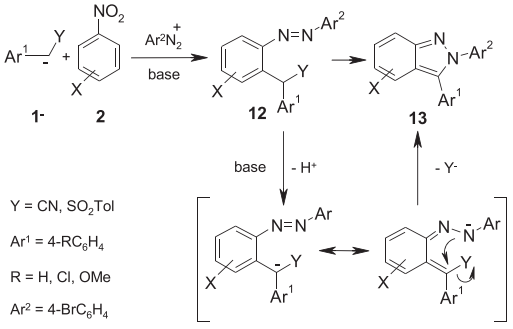


Scheme 4. Two pathways of the reaction of diazonium salt 3a with σH-adducts of 1-chloroethyl phenyl sulfone (1e) and nitroarenes 2.

The addition of ArN_2^+ at *meta* position results in formation of compound **11**, which transforms into **8** by abstraction of two protons and departure of Cl^- (steps shown in Scheme 4) or vice versa. The formation of **8** was observed only in case of *ortho*-substituted nitroarene **2e**, thus, it can be attributed to the sterically crowded position occupied by the nitro group. It should be noted that the conceivable course of the reaction via initially formed VNS product, followed by its reaction with **3a**, was excluded in the separate experiment. The VNS product obtained from **1e** and **2e** was subjected to the reaction with **3a** under the reaction conditions. The reaction did not result in **7a**, only some unidentified products were observed.

Anions of secondary, less crowded CH-acids are known to form σ^H-adducts in both *ortho* and *para* positions of nitroarenes. To avoid formation of a mixture of isomeric products, 4-substituted nitrobenzenes were then selected and reacted with arylacetonitriles and diazonium salts under condition H, which was most effective in the reactions of 2-arylpropionitriles. However, the main or exclusive products of the reactions were not the expected azo compounds **12** but 2,3-diaryl-2*H*-indazole derivatives **13** (Scheme 5, Table 3).

Apparently, the initially formed azo compounds **12** underwent base-induced cyclization together with the departure of cyanide ion. The arylsulfonyl group can also play a role of a leaving group in the cyclization step (entry 5). The process seems to be analogous to the cyclization of (2-nitrosophenyl)acetonitriles leading to 2,1-benzisoxazoles (anthranils) [6a,c,16] (Scheme 5).



Scheme 5. Formation of indazoles **13** from nitroarenes **1** and diazonium salts **3**.

Table 3
Reaction of secondary carbanions with nitroarenes and **3a** under condition H[a].

Entry	CH-acid			Nitroarene		Indazole 13	
	Y	R	1	X	2		Yield[b] %
1	CN	H	**1f**	H	**2a**	**13a**	23
2	CN	H	**1f**	4-Cl	**2g**	**13b**	52
3	CN	H	**1f**	4-CF_3	**2f**	**13c**	15
4	CN	4-OMe	**1g**	2,4-Cl_2	**2e**	**13d**	36
5	$TolSO_2$	H	**1h**	4-Cl	**2g**	**13b**	32

[a] See Table 1.
[b] Isolated yield.

When in the reaction of **1f** with **2g** using weaker base Et_3N (condition F), the intermediate azo compound **12b** (X = 4-Cl, Ar^1 = Ph, Ar^2 [] = 4-BrC_6H_4) was isolated in 35% yield. Then, it was successfully cyclized to **13b** in almost quantitative yield under action of *t*-BuOK, analogously to condition H.

To our best knowledge, such a transformation is unknown in the literature so far, thus, it becomes a novel route for the synthesis of aryl-substituted indazole scaffold.

3. Conclusion

The nucleophilic reactivity of unstable σ^H-adducts formed from stabilized carbanions and substituted nitrobenzenes, so far limited to reactions with protons and bromine, has been extended to the reactions with diazonium salts forming new C–N bonds. The coupling takes place preferentially at carbon atom bearing the nitro group or, in certain cases, also at other conjugated position. Less crowded adducts of secondary carbanions stabilized by cyano or sulfonyl groups are formed at *ortho* positions of nitrobenzenes and cyclize to substituted indazoles as a result of departure of those stabilizing groups. Carbanion generated from 1-chloroethyl phenyl sulfone, suitable for the VNS reaction with nitrobenzenes, forms *ortho* σ^H-adducts that add diazonium cations at carbon bearing the nitro group and, in case of *ortho*-substituted nitrobenzenes, also at the conjugated *meta* position. The subsequent elimination of HCl leads to azo compounds retaining the nitro group in its original position.

4. Experimental section

4.1. General remarks

Melting points were recorded in open capillary and are uncorrected. The ^1H and ^{13}C NMR spectra of all compounds studied were measured at temperature 298 K in $CDCl_3$ or deuterated dimethyl sulfoxide (DMSO-d_6) solutions with a Varian vnmrs-600 or Varian vnmrs-500 using tetramethylsilane (TMS) as the internal standard. Mass spectra (EI, 70 eV) were obtained on an AutoSpec Premier (Waters) spectrometer. For ESI+ and ESI- measurements, a Maldi SYNAPT G2-S HDMS (Waters) was used. Accurate mass measurements were obtained using magnetic sector mass analyzer (EI) or TOF analyzer (ESI). Silica gel Merck 60 (230–400 mesh) was used for column chromatography. GC analyses were performed on a Hewlett Packard HP6890 GC system with HP5 column and FID (carrier gas – helium) THF was distilled from sodium/benzophenone ketyl prior to use. DMF was dried over CaH_2, distilled and stored over molecular sieves.

Sulfone **1d** [17] and **1e** [18] were obtained following published procedures. Remaining compounds **1**, nitroarenes **2** and diazonium salts **3** were commercial reagents and were used without additional purification.

The known by-products: 2-(4-nitrophenyl)-2-phenylpropanenitrile (**5a**) [4b], 1-(4-bromophenyl)-2-phenyldiazene (**6a**) [19] and 1-(4-bromophenyl)-2-(2-methoxyphenyl)diazene (**6b**) [19] were identified on the basis of the published ^1H NMR and MS spectra which were matching.

4.2. General procedure for the reactions of CH-acids 1 with nitroarenes 2 and diazonium salts 3

The initial and final temperatures, solvents and the added base are given in Table 1.

A solution of *t*-BuOK (112 mg, 1.0 mmol) in dry THF (10.0 mL) or in dry DMF (6.0 mL) was cooled down under nitrogen to the temperature specified for a particular variant. To that mixture, a solution of the carbanion precursor **1** (1.0 mmol) in THF (1.0 mL) or DMF (1.0 mL) was added dropwise, followed by the addition of the nitroarene **2** (1.0 mmol) in the same manner. The mixture was stirred at that temperature for 5 min, then a solution of diazonium tetrafluoroborate **3** (1.2 mmol) in cold *N*-methylpyrrolidone (1.0 mL) was added over ca 3–4 s. The mixture was stirred for 5 min, then neat Et_3N (0.5 mL) or a solution of *t*-BuOK (112 mg, 1.0 mmol) in THF (2.0 mL) was added. After 5 min the reaction was quenched by pouring the mixture into saturated aqueous NH_4Cl (50 mL) or, prior to that, the cooling bath was removed and the mixture was allowed to reach room temperature. After the quench, the resulting mixture was diluted with water (200 mL) and extracted with EtOAc (3 × 50 mL). The extracts were washed with water (3 × 100 mL) and dried with Na_2SO_4. For the results shown in Table 1, to a 1/10 part of the products solution was added an appropriate amount of diphenylmethyl phenyl sulfone as an internal standard and the GC analysis was performed. For preparative purposes, the dried solution was evaporated and the residue was separated by column chromatography (SiO_2, hexane/DCM). For analytical purposes, the solid products were recrystallized from *i*-PrOH or hexane/EtOAc.

4.2.1. 2-{4-[(4-Bromophenyl)diazenyl]phenyl}-2-phenylpropanenitrile 4a

Obtained from **1a**, **2a** and **3a**, condition A. Yield: 207 mg (53%); orange crystals, mp. 132–133 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 2.15 (s, 3H), 7.31–7.43 (m, 5H), 7.52–7.55 (m, 2H), 7.63–7.67 (m, 2H), 7.78–7.81 (m, 2H), 7.88–7.91 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1, 46.1, 123.0, 123.3, 124.4, 125.7, 126.6, 127.5, 128.2, 129.0, 132.4, 140.7, 144.2, 151.2, 151.8; MS (EI) *m/z* 392 (18), 391 (55), 390 (17), 389 (55, $[M]^+$), 206 (100), 190 (38), 155 (51), 157 (50); HRMS (EI) *m/z* calcd for $C_{21}H_{16}N_3^{79}Br$ 389.0528; found, 389.0526.

4.2.2. 2-{4-[(4-Nitrophenyl)diazenyl]phenyl}-2-phenylpropanenitrile 4b

Obtained from **1a**, **2a** and **3b**, condition F. Yield: 150 mg (42%); orange crystals, mp. 145–146 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 2.16 (s, 3H). 7.33–7.44 (m, 5H), 7.56–7.60 (m, 2H), 7.95–7.98 (m, 2H), 8.02–8.05 (m, 2H), 8.37–8.41 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0, 48.2, 122.8, 123.5, 123.8, 124.7, 126.6, 127.7, 128.3, 129.1, 140.5, 145.4, 148.9, 151.7, 155.5; MS (EI) *m/z* 356 (67, $[M]^+$), 206 (100), 190 (28); HRMS (EI) *m/z* calcd for $C_{21}H_{16}N_4O_2$ 356.1273; found, 356.1273.

4.2.3. 2-{4-[(3-Nitrophenyl)diazenyl]phenyl}-2-phenylpropanenitrile 4c

Obtained from **1a**, **2a** and **3c**, condition F. Yield: 167 mg (47%); red oil. ^1H NMR (500 MHz, $CDCl_3$) δ 2.16 (s, 3H), 7.32–7.44 (m, 5H), 7.56–7.59 (m, 2H), 7.72 (t, *J* = 8.1 Hz, 1H), 7.95–7.97 (m, 2H), 8.24–8.27 (m, 1H), 8.32–8.35 (m, 1H), 8.73 (t, *J* = 2.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0, 46.2, 117.1, 122.9, 123.7, 125.2, 126.6, 127.7, 128.2, 129.1, 129.3, 130.0, 140.5, 145.1, 149.0, 151.4, 152.9; MS

(EI) *m/z* 356 (59, $[M]^+$), 206 (100), 190 (35); HRMS (EI) *m/z* calcd for $C_{21}H_{16}N_4O_2$ 356.1273; found, 356.1278.

4.2.4. 2-{4-[(4-Methoxyphenyl)diazenyl]phenyl}-2-phenylpropanenitrile 4d

Obtained from **1a**, **2a** and **3d**, condition F. Yield: 106 mg (31%); orange crystals, mp. 98–100 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (s, 3H), 3.89 (s, 3H), 6.99–7.03 (m, 2H), 7.31–7.35 (m, 1H), 7.36–7.42 (m, 4H), 7.50–7.53 (m, 2H), 7.84–7.88 (m, 2H), 7.90–7.93 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1, 46.1, 55.6, 114.3, 122.9, 123.1, 124.9, 126.6, 127.4, 128.1, 129.0, 140.9, 143.1, 146.9, 151.1, 162.3. HRMS (ESI) *m/z* calcd for $C_{22}H_{20}N_3O$, $[M+H]^+$ 342.1606; found, 342.1608.

4.2.5. 2-{4-[(4-Bromophenyl)diazenyl]-3-methoxyphenyl}-2-phenylpropanenitrile 4e

Obtained from **1a**, **2b** and **3a**, condition H. Yield: 176 mg (42%); orange crystals, mp. 121–122 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.13 (s, 3H), 3.98 (s, 3H), 6.98 (dd, J = 8.4, 2.0 Hz, 1H), 7.13 (d, J = 1.8 Hz, 1H), 7.31–7.35 (m, 1H), 7.36–7.42 (m, 4H), 7.60–7.63 (m, 3H), 7.75–7.78 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 28.0, 46.4, 56.5, 111.6, 117.4, 119.0, 122.9, 124.5, 125.4, 126.6, 128.2, 129.0, 132.3, 140.5, 141.4, 145.8, 151.7, 157.1; MS (EI) *m/z* 421 (50), 419 (49, $[M]^+$), 264 (35), 249 (40), 206 (100); HRMS (EI) *m/z* calcd for $C_{22}H_{18}N_3^{79}Br$ 419.0633; found, 419.0637.

4.2.6. 2-{4-[(4-Bromophenyl)diazenyl]-2-chlorophenyl}-2-phenylpropanenitrile 4f

Obtained from **1a**, **2c** and **3a**, condition F. Yield: 132 mg (31%); orange crystals, mp. 134–135 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.20 (s, 3H), 7.29 (m, 5H), 7.67–7.68 (m, 2H), 7.81–7.84 (m, 3H), 7.93–7.96 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 29.3, 45.6, 121.3, 122.4, 124.6, 124.9, 126.4, 127.8, 128.8, 128.9, 132.5, 135.5, 138.9, 140.4, 151.0, 152.7; MS (EI) *m/z* 425c(78), 423 (66, $[M]^+$), 240 (73), 190 (60), 183 (69), 155 (100); HRMS (ESI) *m/z* calcd for $C_{21}H_{15}N_3^{79}Br^{35}Cl$ 423.0138; found, 423.0137.

4.2.7. 2-{4-[(4-Bromophenyl)diazenyl]phenyl}-3-methyl-2-phenylbutanenitrile 4g

Obtained from **1a**, **2e** and **3a**, condition H. Yield: 142 mg (34%); orange oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.11 (d, J = 1.7 Hz, 3H), 1.12 (d, J = 1.7 Hz, 3H), 2.97 (sep, J = 1.7 H, 1H), 7.26–7.29 (m, 1H), 7.33–7.38 (m, 2H), 7.51–7.54 (m, 2H), 7.62–7.67 (m, 4H), 7.75–7.79 (m, 2H), 7.85–7.89 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.1, 34.9, 59.1, 120.4, 123.3, 124.4, 125.7, 126.7, 127.5, 127.8, 129.0, 132.3, 139.2, 124.9, 151.2, 151.5; MS (EI) *m/z* 419 (53), 417 (53, $[M]^+$), 377 (99), 375 (100), 192 (91)190 (72); HRMS (EI) *m/z* calcd for $C_{23}H_{20}N_3^{79}Br$ 417.0841; found, 417.0840.

4.2.8. 2-{4-[(4-Bromophenyl)diazenyl]-3-chlorophenyl}-2-phenylpropanenitrile 4h

Obtained from **1b**, **2a** and **3a**, condition H. Yield: 86 mg (20%); orange crystals, mp. 90–92 °C (*i*-PrOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.13 (s, 3H), 7.33–7.38 (m, 2H), 7.39–7.42 (m, 4H), 7.85 (d, J = 2.1 Hz, 1H), 7.64–7.69 (m, 3H), 7.82–7.85 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.9, 45.9, 118.0, 122.5, 124.8, 125.9, 126.5, 128.4, 128.9, 129.2, 132.5, 135.9, 140.0, 145.3, 147.9, 151.4; MS (EI) *m/z* 425 (85), 423 (67, $[M]^+$), 240 (66), 183 (71), 155 (100); HRMS (EI) *m/z* calcd for $C_{21}H_{15}N_3^{79}Br^{35}Cl$ 423.0138; found, 423.0134.

4.2.9. tert-Butyl {4-[(4-bromophenyl)diazenyl]phenyl}(phenyl) acetate 4i

Obtained from **1c**, **2a** and **3a**, condition D. Yield: 209 mg (51%); orange crystals, mp. 112–114 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46 (s, 9H), 4.99 (s, 1H), 7.26–7.29 (m, 1H), 7.31–7.35 (m, 4H), 7.44–7.47 (m, 2H), 7.62–7.65 (m, 2H), 7.76–7.79 (m, 2H), 7.84–7.88 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0, 57.9, 81.7, 123.0, 124.3, 125.3, 127.2, 128.5, 128.6, 129.4, 132.3, 138.7, 142.6, 151.36, 151.41, 171.15; MS (EI) *m/z* 452 (13), 450 (13, $[M]^+$), 351 (64), 349 (62), 165 (60), 57 (100); HRMS (ESI) *m/z* calcd for $C_{24}H_{23}^{79}BrN_2O_2$, $[M]^+$ 4500943; found, 450.0939.

4.2.10. tert-Butyl {4-[(4-bromophenyl)diazenyl]-3-chlorophenyl}(phenyl)acetate 4j

Obtained from **1c**, **2d** and **3a**, condition C. Yield: 199 mg (41%); red oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.51 (s, 9H), 4.98 (s, 1H), 7.32–7.42 (6H), 7.56–7.57 (m, 1H), 7.67–7.71 (m, 3H), 7.85–7.88 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.0, 57.6, 82.0, 117.4, 124.7, 126.0, 127.5, 127.7, 128.5, 128.8, 130.9, 132.4, 135.7, 138.0, 143.7, 147.4, 151.5, 170.6; MS (EI) *m/z* 486 (7), 484 (5, $[M]^+$), 351 (64), 385 (100), 383 (83), 165 (50); HRMS (ESI) *m/z* calcd for $C_{24}H_{22}^{79}Br^{35}ClN_2O_2$, $[M]^+$ 484.0553; found, 484.0544.

4.2.11. 1-(4-Bromophenyl)-2-{4-[1-(4-chlorophenyl)-1-(phenylsulfonyl)ethyl]phenyl}diazene 4k

Obtained from **1d**, **2a** and **3a**, condition F. Yield: 167 mg (31%); orange crystals, mp. 149–150 °C (hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.12 (s, 3H), 7.27–7.32 (m, 4H), 7.38 (d, J = 7.4 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.62–7.67 (m, 4H), 7.80–7.83 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.0, 74.6, 122.5, 124.4, 125.8, 128.2, 128.3, 130.3, 130.9, 132.4, 133.6, 134.5, 136.1, 137.5, 141.9, 151.2, 151.8; HRMS (ESI) *m/z* calcd for $C_{26}H_{20}^{79}Br^{35}ClN_2O_2SNa$ $[M+Na]^+$ 561.0015; found, 561.0044.

4.2.12. 1-(4-Bromophenyl)-2-(2-methoxyphenyl)diazene 6c

Obtained from **1a**, **2b** and **3a**, condition F, as by-product along with **4e**. Yield 75 mg (26%); orange crystals, mp. 80–81 °C. (lit[21] 81.5–82.5 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.02 (s, 3H), 7.01 (ddd, J = 8.0, 7.3, 1.2 Hz, 1H), 7.10 (dd, J = 8.4, 1.2 Hz, 1H), 7.46 (dd, J = 8.4, 7.3, 1.7 Hz, 1H), 7.61–7.64 (m, 2H), (dd, J = 8.0, 1.7 Hz, 1H), 7.77–7.80 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 56.3, 112.8, 116.9, 120.8, 124.4, 125.1, 132.2, 132.9, 142.1, 151.8, 157.1; MS (EI) *m/z* 292 (30), 290 (31, $[M]^+$), 186 (20), 185 (29), 184 (22), 183 (29), 157 (40), 155 (41), 135 (48), 77 (100); HRMS (ESI) *m/z* calcd for$C_{13}H_{11}^{79}BrN_2O$ $[M]^+$ 290.0055; found, 290.0065.

4.3. General procedure for the reaction of 1-chloroethyl phenyl sulfone (1e) or phenylacetonitrile (1f) with nitroarenes 2 and diazonium salts 3

A solution of *t*-BuOK (56 mg, 0.55 mmol) in dry DMF (6.0 mL) was cooled down under nitrogen to −40 °C. To that mixture, a solution of **1e** (102 mg, 0.5 mmol) in DMF (1.0 mL) was added, followed by the addition of the nitroarene **2** (1.0 mmol) in DMF (1.0 mL). The mixture was stirred at that temperature for 2 min then a solution of diazonium tetrafluoroborate **3** (1.2 mmol) in cold *N*-methylpyrrolidone (1.0 mL) was added over ca 3–4 s. Neat Et_3N (0.5 mL) was added, the cooling bath was removed and the mixture was allowed to reach room temperature. The reaction was quenched by pouring the mixture into saturated aqueous NH_4Cl (50 mL), the resulted mixture was diluted with water (100 mL), extracted with EtOAc (3 × 30 mL). The extracts were washed with water (3 × 70 mL) and dried with Na_2SO_4. The solution was evaporated and the residue was separated by column chromatography on SiO_2 using hexane/EtOAc mixtures as eluent.

4.3.1. 1-(4-Bromophenyl)-2-{2,4-dichloro-6-[1-chloro-1-(phenylsulfonyl)ethyl]phenyl}diazene 7a

Obtained from **1e**, **2e** and **3a** along with **8a**. Yield: 79 mg (30%); orange crystals, mp. 133–134 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.18

(s, 3H), 7.48 (ddd J = 8.3, 7.0, 0.5 Hz, 2H), 7.56 (dd, J = 2.2, 0.5 Hz, 1H), 7.59 (dd, J = 2.2, 0.5 Hz, 1H), 7.65–7.68 (m, 3H), 7.68–7.70 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.3, 86.0, 123.9, 124.6, 127.6, 128.6, 130.1, 131.5, 131.7, 132.3, 132.4, 132.7, 132.9, 134.7, 150.0, 150.6; HRMS (ESI) *m/z* calcd for $C_{20}H_{14}^{79}Br^{35}Cl_3N_2O_2SNa$, $[M+Na]^+$ 552.8923; found, 552.8897.

4.4. 1-(4-Bromophenyl)-2-{2,6-dichloro-3-nitro-4-[1-(phenylsulfonyl)ethyl]phenyl}diazene 8a

Obtained from **1e**, **2e** and **3a** along with **7a**. Yield: 90 mg (33%); orange crystals, mp. 132–133 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.79 (d, J = 7.0 Hz, 3H), 4.21 (q. J = 7.0 Hz, 1H), 7.54–7.58 (m, 2H), 7.68–7.74 (m, 5H), 7.83–7.85 (m, 2H), 7.93 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.6, 59.7, 118.8, 124.8, 127.7, 128.4, 128.91, 128.94, 129.4, 129.5, 132.8, 134.6, 136.5, 149.0, 149.1, 150.7; HRMS (ESI) *m/z* calcd for $C_{20}H_{14}^{79}Br^{35}Cl_2N_3O_4SNa$, $[M+Na]^+$ 563.9163; found, 563.9150.

4.5. 1-{2,4-Dichloro-6-[1-chloro-1-(phenylsulfonyl)ethyl]phenyl}-2-(4-nitrophenyl)diazene 7b

Obtained from **1e**, **2e** and **3b** along with **8b**. Yield: 68 mg (27%); red crystals, mp. 186–187 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.25 (s, 3H), 7.47–7.51 (m, 2H), 7.56 (d, J = 2.2 Hz, 1H), 7.59 (d, J = 2.2 Hz, 1H), 7.65–7.71 (m, 3H), 7.96–7.99 (m, 2H), 8.42–8.44 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.8, 85.8, 123.6, 123.8, 124.9, 128.6, 130.6, 131.5, 131.6, 132.6, 132.8, 133.1, 134.8, 149.7, 149.8, 154.7; MS (EI) *m/z* (%) 499 (2), 497 (2), 358 (55), 356 (56), 323 (75), 321 (100); HRMS (EI) *m/z* calcd for $C_{20}H_{14}^{79}Br^{35}Cl_3N_3O_4S$, $[M]^+$ 496.9771; found,496.9775.

4.5.1. 1-{2,6-Dichloro-3-nitro-4-[1-(phenylsulfonyl)ethyl]phenyl}-2-(4-nitrophenyl)diazene 8b

Obtained from **1e**, **2e** and **3b** along with **7b**. Yield: 66 mg (26%); orange crystals, mp. 180–182 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.79 (d, J = 2.2 Hz, 3H), 4.23 (q. J = 7.0 Hz, 1H), 7.55–7.59 (m, 2H), 7.69–7.77 (m, 3H), 7.97 (s, 1H), 8.09–8.12 (m, 2H), 8.43–8.46 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.6, 59.7, 119.0, 124.0, 124.9, 128.5, 128.94, 128.95 129.5, 129.7, 134.7, 136.5, 148.4, 149.2, 150.1, 154.6; MS (EI) *m/z* (%) 508 (5), 369 (75), 367 (100), 122 (54); HRMS (EI) *m/z* calcd for $C_{20}H_{14}^{35}Cl_2N_4O_6S$, $[M]^+$ 508.0011; found, 508.0023.

4.6. 1-(4-Bromophenyl)-2-[2-[1-chloro-1-(phenylsulfonyl)ethyl]-4-(trifluoromethyl)phenyl]diazene 7c

Obtained from **1e**, **2f** and **3a.** Yield: 104 mg (39%); orange crystals, mp. 146–147 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.72 (s, 3H), 7.35–7.39 (m, 2H), 7.53–7.63 (m, 4H), 7.68–7.76 (m, 5H), 7.86 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.1, 87.6, 118.1, 123.3 (q, J_{FC} = 273 Hz), 125.2, 126.9, 127.7 (q, J_{FC} = 3.5 Hz), 128.4, 130.1 (q, J_{FC} = 3.5 Hz), 131.2, 131.3 (q, J_{FC} = 32.9 Hz), 132.2, 132.7, 132.9, 134.5, 151.3, 153.8; HRMS (EI) *m/z* calcd for $C_{21}H_{15}^{79}Br\ ^{35}Cl_2F_3N_2O_2SNa$, $[M+Na]^+$ 552.9576; found, 552.9562.

4.7. 1-(4-Bromophenyl)-2-{4-chloro-2-[1-chloro-1-(phenylsulfonyl)ethyl]phenyl}diazene 7d

Obtained from **1e**, **2g** and **3a.** Yield: 79 mg (32%); orange crystals, mp. 181–184 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.69 (s, 3H), 7.35–7.39 (m, 2H), 7.45 (dd, J = 8.7, 2.2 Hz, 1H), 7.53–7.59 (m, 4H), 7.66 (s, 4H), 7.73 (d, J = 2.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.7, 87.6, 118.3, 125.0, 126.3, 128.4, 130.9, 131.3, 132.5, 133.0, 133.2, 133.4, 134.5, 136.3, 150.0, 151.2; MS (EI) *m/z* (%) 498 (2), 496 (1), 359 (45), 357 (92), 355 (60), 322 (100), 320 (80); HRMS (EI) *m/z* calcd for $C_{20}H_{15}^{79}Br\ ^{35}Cl_2N_2O_2S$, $[M]^+$ 495.9415; found, 495.9417.

4.8. 1-(4-Bromophenyl)-2-{2-[1-chloro-1-(phenylsulfonyl)ethyl]-4-fluorophenyl}diazene 7e

Obtained from **1e**, **2h** and **3a.** Yield: 73 mg (30%); orange crystals, mp. 112–113 °C**;** ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.70 (s, 3H), 7.18 (ddd, J = 9.2, 6.9, 2.7 Hz, 1H), 7.33–7.37 (m, 2H), 7.51–7.55 (m, 2H), 7.57–7.60 (m, 2H), 7.62–7.67 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ28.8, 87.8, 117.9 (d, J_{FC} = 22.5 Hz), 119.1 (d, J_{FC} = 8.7 Hz), 120.1 (d, J_{FC} = 26.6), 124.9, 126.0, 128.4, 131.2, 132.5, 133.4, 134.4, 134.5, 148.1 (d, J_{FC} = 3.5 Hz), 151.2, 163.1 (d, J_{FC} = 252 Hz); MS (EI) *m/z* (%) 482 (4), 480 (3), 343 (39), 341 (100), 339 (84), 304 (100), 224 (54); HRMS (EI) *m/z* calcd for $C_{20}H_{15}^{79}Br\ ^{35}ClFN_2O_2S$, $[M]^+$ 479.9710; found, 479.9711.

4.9. {2-[(4-Bromophenyl)diazenyl]-5-chlorophenyl}(phenyl) acetonitrile 12b

Obtained from **1f**, **2g** and **3a**, condition F. Yield: 143 mg (35%); orange crystals, mp. 142–143 °C (*i*-PrOH); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.41 (s, 1H), 7.30–7.34 (m, 1H), 7.35–7.40 (m, 4H), 7.44 (dd, J = 8.8, 1.8 Hz, 1H), 7.59 (d, J = 1.8 Hz, 1H), 7.67–7.70 (m, 2H), 7.75–7.80 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 36.8, 117.5, 119.3, 124.7, 126.6, 127.6, 128.3, 129.2, 129.3, 129.7, 132.6, 135.2, 137.6, 138.4, 146.6, 151.2; MS (EI) *m/z* 410 (70), 408 (50, $[M]^+$), 384 (29), 334 (32), 239 (100), 190 (82), 155 (51); HRMS (EI) *m/z* calcd for $C_{20}H_{13}N_3^{79}Br^{35}Cl$ 408.9981; found, 408.9981.

4.10. ***2-(4-Bromophenyl)-3-phenyl-2H-indazole 13a***

Obtained from **1f**, **2a** and **3a**, condition H. Yield: 80 mg (23%); red solid, mp. 121–122 °C (*i*-PrOH) (lit [20] 118.6–119.3 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (ddd, J = 8.5, 6.6, 0.8 Hz, 1H), 7.31–7.45 (m, 8H), 7.49–7.53 (m, 2H), 7.69 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 8.7 Hz, 1H); MS (EI) *m/z* 350 (98), 348 (100, $[M]^+$), 268 (63), 134 (37); HRMS (EI) *m/z* calcd for $C_{19}H_{13}^{79}BrN_2$, $[M]^+$ 348.0262; found, 348.0255.

4.11. 2-(4-Bromophenyl)-5-chloro-3-phenyl-2H-indazole 13b

Obtained from **1f**, **2g** and **3a**, condition H, yield 199 mg (52%), and from **1h**, **2g** and **3a**, condition H; yield 123 mg (32%); creamy crystals, mp. 178–179 °C (*i*-PrOH). Obtained also by separate cyclization of **12b** according to the following procedure:

To a cooled solution of azo compound **12b** (41 mg, 0.1 mmol) in dry THF (1.0 mL) was added at −78 °C under nitrogen a solution of *t*-BuOK (12 mg, 0.11 mmol) in dry THF (1.0 mL). The cooling bath was then removed and the mixture was allowed to reach room temperature. The mixture was poured into aqueous NH_4Cl and extracted with EtOAc (3 × 20 mL). The extract was washed with water and brine and dried with Na_2SO_4. The solvent was evaporated to dryness to obtain **13b** (33 mg, 95%) as a pale pink solid, pure by TLC and GC, identical with that obtained from **1f**, **2g** and **3a**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.34 (m, 5H), 7.39–7.46 (m, 3H), 7.50–7.53 (m, 2H), 7.66 (d, J = 1.4 Hz, 1H), 7.72 (d, J = 9.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 119.2, 119.3, 122.3, 122.4, 127.2, 128.4, 128.7, 128.9, 129.0, 129.1, 129.5, 132.2, 135.2, 138.9, 147.4; MS (EI) 5 *z* 384 (100), 382 (83, $[M]^+$), 302 (22), 268 (26), 267 (26); HRMS (EI) *m/z* calcd for $C_{19}H_{12}^{79}Br^{35}ClN_2$, $[M]^+$ 381.9872; found, 381.9869.

4.12. 2-(4-Bromophenyl)-3-phenyl-5-(trifluoromethyl)-2H-indazole 13c

Obtained from **1f**, **2f** and **3a**, condition H. Yield: 63 mg (15%); creamy crystals, mp. 155–157 °C (*i*-PrOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.38 (m, 4H), 7.44–7.49 (m, 3H), 7.51–7.56 (m, 3H), 7.87 (d, J = 9.2 Hz, 1H), 8.01 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 118.9, 119.6 (q, J = 5 Hz), 120.6, 122.7, 123,2 (q, J = 3 Hz), 124,6 (q, 272 Hz), 124.9, (q, J = 32 Hz), 125.0, 127.3, 128.6, 129.3, 129.6, 132.3, 137.6, 138.7, 149.3; MS (EI) *m/z* 486 (7), 484 (5, $[M]^+$), 385 (100), 383 (84), 165 (50); HRMS (ESI) *m/z* calcd for $C_{20}H_{12}^{79}Br^{35}F_3N_2$, $[M]^+$ $[M]^+$ 416.0136; found, 416.0139.

4.13. 2-(4-Bromophenyl)-5,7-dichloro-3-(4-methoxyphenyl)-2H-indazole 13d

Obtained from **1g**, **2e** and **3a**, condition H. Yield: 162 mg (36%); creamy crystals, mp. 190–191 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.86 (s, 3H), 6.94–6.97 (m, 2H), 7.21–7.24 (m, 2H), 7.32–7.35 (m, 2H), 7.37 (d, J = 1.7 Hz, 1H), 7.51–7.54 (m, 2H), 7.55 (d, J = 1.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 55.4, 114.7, 118.3, 120.7, 122.65, 122.66, 124.1, 127.4, 127.46, 127.47, 130.9, 132.3, 136.6, 138.7, 145.2, 160.2; MS (EI) *m/z* (%) 450 (46), 448 (100), 446 (61); HRMS (ESI) *m/z* calcd for $C_{20}H_{13}^{79}Br^{35}Cl_2N_2O$, $[M]^+$ 445.9588; found, 445.9590.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.132186.

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