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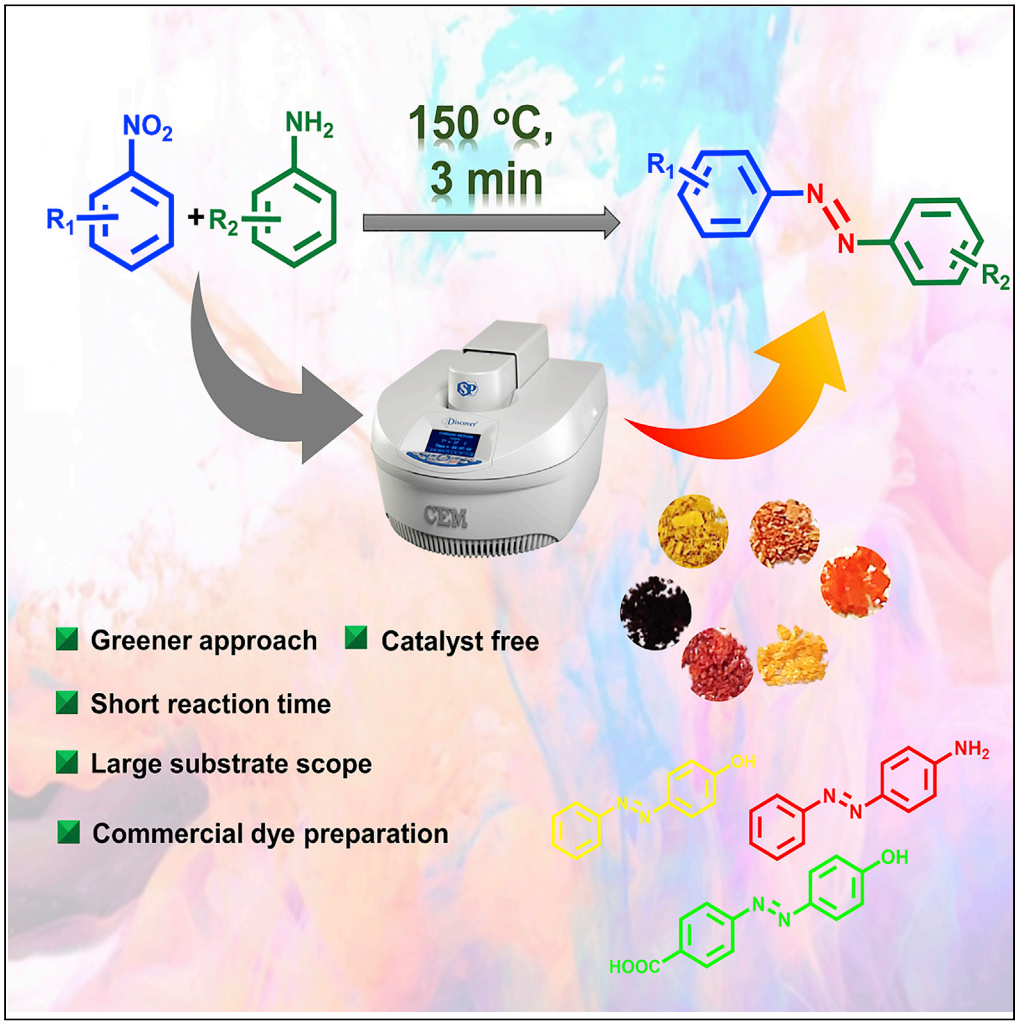

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Highlights

Microwave-based green synthesis of unsymmetrical azo dyes

Catalyst-free, rapid synthesis

Gram-scale synthesis of commercial dyes

Efficient synthesis of water-soluble dyes

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Microwave-assisted rapid and sustainable synthesis of unsymmetrical azo dyes by coupling of nitroarenes with aniline derivatives

Ankit Thakuri,[1] Mainak Banerjee,[1,*] and Amrita Chatterjee[1,2,*]

SUMMARY

Aromatic azo dyes are of immense commercial importance, and the development of greener routes for their synthesis is imperative due to current environmental concerns. In the present study, a microwave-assisted route has been developed for rapid and convenient synthesis of unsymmetrical azo dyes in a single step. In a metal-catalyst-free approach, an aromatic amine was used as an *in situ* reductant to affect its direct cross-condensation with nitroarenes to afford a variety of dispersed and water-soluble azo dyes. The electronic and substituent effects were thoroughly understood by placing suitable substituents in both nitroarenes and aniline derivatives in competitive reactions. The microwave (MW) method worked better with aniline or electron-rich aromatic amines to prepare a range of unsymmetrical azo dyes in up to 97% yields within a few minutes. The method worked well in the gram-scale synthesis of commercial dye, solvent yellow 7.

INTRODUCTION

Humans' love for color continues from the prehistoric ages, and with modernization, a full rainbow of colors has been used by people in their clothes, other textiles, paints, etc. Aromatic azo compounds, with a characteristic Ar–N=N–Ar chromophore unit, are known for their intense color, possess good photostability, and therefore, exhibit excellent dyeing properties (Merino, 2011; Benkhaya et al., 2020). Accounting for more than 50% of the commercial dyes, azo dyes are involved in nearly all dye groups, such as direct, reactive, and disperse dyes (Gordon and Gregory, 1987; Hunger, 2002; Qiu et al., 2019). Different classes of azo dyes are used by different industrial sectors such as textile, cosmetic, leather, paint, and printing industries (Griffiths, 2013). For example, water-soluble Congo red is used as a direct dye for cotton, whereas, Tartrazine and Allura Red AC are used as regulated food coloring agents (Chattopadhayay, 2011; Yamjala et al., 2016). Lithol red, an azo disperse dye, is extensively used as a pigment in the paint industry. Apart from being coloring agents, azobenzenes have displayed versatile applications in the fields like biomedicine (Cheng et al., 2021), chemosensors (DiCesare and Lakowicz, 2001), nonlinear optics (Ishow et al., 2003; Qiu et al., 2007), optical storage media (Li, 2010), photochemical switches (Beharry and Woolley, 2011), and electronics (Yu et al., 2006; Türel and Valiyaveettil, 2020). Thus, the development of suitable methods for aromatic azo compounds has garnered significant research attention over the years.

Traditionally, azo dyes are synthesized by coupling between a diazonium salt and electron-rich aromatic systems such as anilines, phenols, etc. (Zollinger, 1994; Haghbeen and Tan, 1998; Hamon et al., 2009; Shah et al., 2021). Catalytic oxidation of aromatic amines using lead tetraacetate (Baer and Tosoni, 1956), manganese dioxide (Hombrecher and Lüdtke, 1993; Kumari et al., 2014), or metal catalysts such as copper(I) (Zhang and Jiao, 2010; Zhu and Shi, 2013) or gold(0) (Grirrane et al., 2008) have been employed to make symmetrical azo compounds (Orito et al., 1998; Patel and Mishra, 2004; Cai et al., 2013). On the other hand, reduction of nitroaromatics by reducing agents such as $LiAlH_4$ (Nystorm and Brown, 1948; Hutchins et al., 1971), Zn/NaOH (Khan and Hecht, 2006), or metal catalysts including AuNPs or FeNPs (Moglie et al., 2008; Zhu et al., 2010a) offer the synthesis of symmetrical azo dyes. However, most of the commercial azo dyes possess an unsymmetrical skeleton across the azo bond. Other than diazotization, Mill's reaction by coupling aniline derivatives and aromatic nitroso compounds is a common way for the synthesis of unsymmetrical azoarenes (Ueno and Akiyoshi, 1954; Zhu and Espenson, 1995; Priewisch and Rück-Braun, 2005; Tie et al., 2006) (Scheme 1). In recent years, various other methods have been developed for the synthesis of unsymmetrical azobenzenes in conventional media (Zhao et al., 2011; Takeda et al., 2012; Monir et al., 2013; de Souza et al., 2018; Shen et al., 2021; Wang et al., 2021). For example, Zhao et al.

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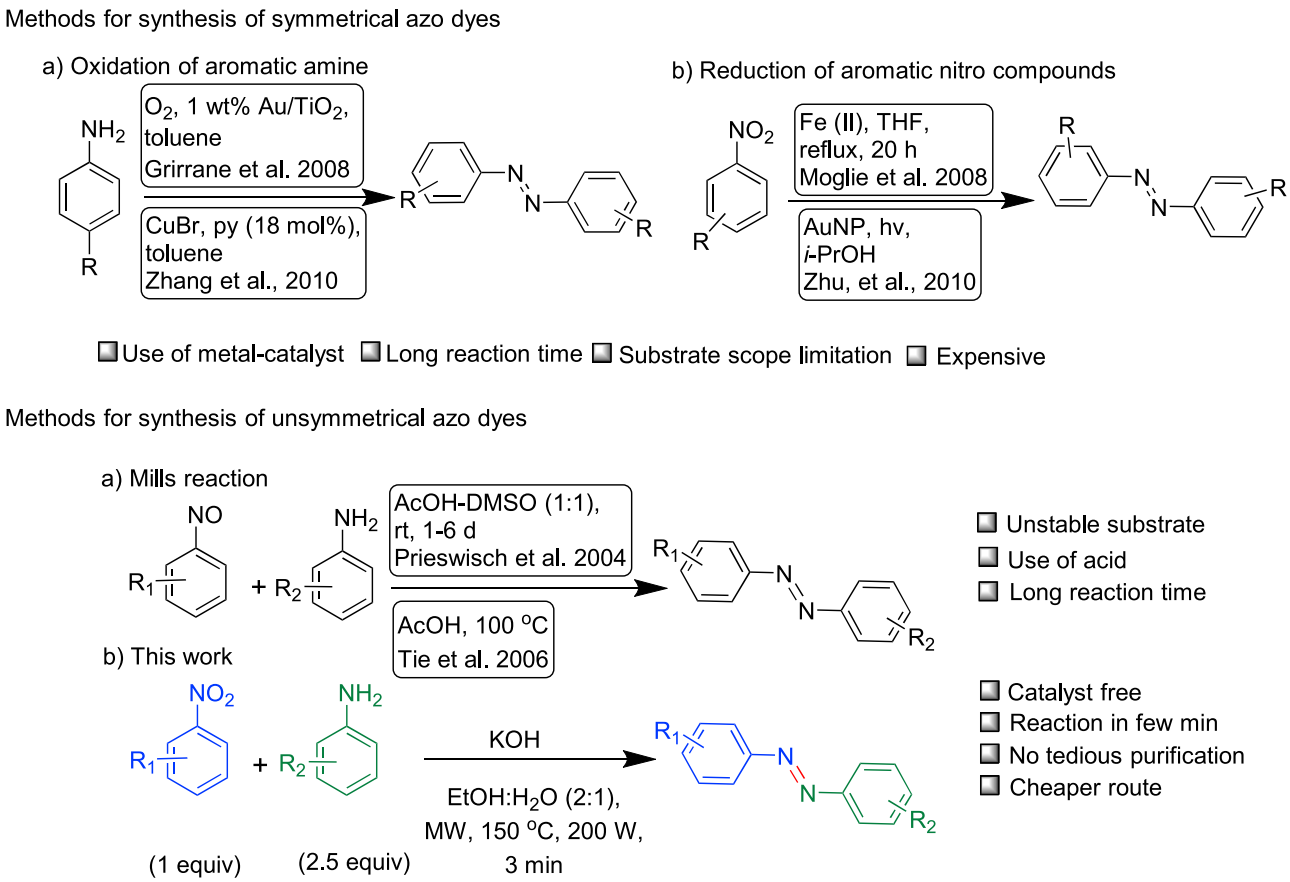


Scheme 1. Different routes for the synthesis of aromatic azo arenes

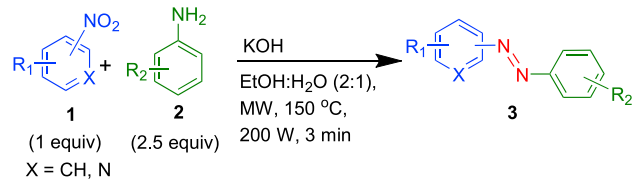
used aniline as the reductant of nitroaromatics and the coupling substrate to afford unsymmetrical azo dyes. This method requires the use of toxic DMF as the solvent, high temperature, long reaction time, tedious work-up, and purification, and thus not suitable for batch processes (Zhao et al., 2011). In recent times, the stringent environmental concerns have instigated the development of various alternative and greener strategies for the synthesis of azo dyes that include diazo coupling on clay, polymer, or resin-supported diazonium salts (Caldarelli et al., 2000; Merrington et al., 2002; Dabbagh et al., 2008; Kollarigowda and Braun, 2021), and use of grindstone chemistry (Eissa and Mohamed, 2018). Besides, a few continuous flow methods are also developed for diazo coupling (Wang et al., 2019; Shukla et al., 2021). Although these methods click several greener aspects, the concerns on stability of diazonium salts or substrate limitation are always associated with diazo coupling.

The use of microwave (MW) irradiation for chemical transformations under solvent-*less* conditions for quick access to a large variety of compounds has received substantial attention in recent years (Gawande et al., 2014; Hoz et al., 2016; Kumar et al., 2020) and is recognized as one of the world-changing technologies to achieve sustainability (Gomollon-Bel, 2019). MW irradiation has been occasionally employed for the synthesis or modifications of dye scaffolds that include the synthesis of cyanine and hemicyanine dyes by a condensation reaction (Wang et al., 2004; Winstead et al., 2010), azo-imidazoles synthesis from azo dyes by multi-component reactions, (Mahmoodi et al., 2017), etc. Herein, we present a method for catalyst-free, microwave-assisted cross-coupling of nitroarenes with aniline derivatives for rapid access to unsymmetrical azo dyes in a single pot (Scheme 2).

RESULTS AND DISCUSSION

Reaction development

We initiated our investigation with the identification of the optimal microwave conditions for azo coupling using a model reaction between nitrobenzene (1a) and 4-aminophenol (2a) in a microwave reactor (Table1). As the aniline



R_1 = H (**1a**), 4-OH (**1b**), 4-Me (**1c**), 4-OMe (**1d**), 4-Cl (**1g**), 4-Br (**1h**), 2-Cl (**1j**),4-I (**1l**), 3-NO_2-py (**1r**), 2-Me-6NO_2-py (**1s**), 2-HO-5-NO_2-py (**1t**), 3-SO_3H (**1u**), 4-SO_3H (**1v**), 4-COOH (**1w**),
R_2 = 4-OH (**2a**), H (**2b**), 4-Me (**2c**), 4-OMe (**2d**), 2-OMe (**2f**), 4-Cl (**2g**), 4-Br (**2h**), 2-C_6H_5 (**2n**), 8-quinoline (**2o**), 4-NH_2 (**2p**), 4-NMe_2 (**2q**), 4-COOH (**2x**)

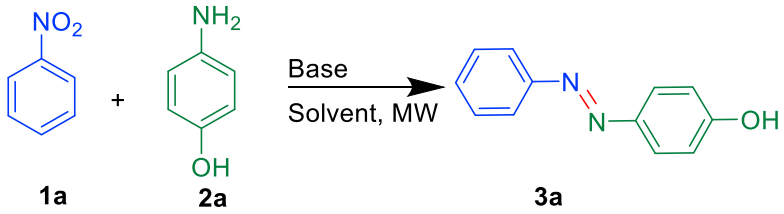
Scheme 2. General scheme for microwave-assisted synthesis of azo dyes (3)

derivative was expected to act as a reductant, 2.5 equiv of it was used for the reaction. In the very first attempt, water was considered as the green solvent, and the "on water" reaction, considering liquid nitrobenzene (1a) has limited aqueous solubility, was attempted taking KOH as the base for the expected conversion (Table 1, entry 1). However, the expected azo dye (3a) was not isolated. Next, the reaction was conducted in EtOH, taking 10 M aqueous KOH in a 2:1 ratio for the same conversion (Table 1, entry 2). The reaction mixture was microwaved at 200 W for 3 min (temperature was fixed at 150°C). To our delight, the azo dye, (*E*)-4-(phenyldiazenyl)phenol (3a), a commercial dye named solvent yellow 7, was obtained within 3 min in 97% yield. After completion, the reaction mixture was concentrated in vacuum, and in the remaining aqueous part, 6 N HCl was added when solid azo dye separated out. The crude dye was filtered, and after water wash, the dye was found sufficiently pure in NMR spectroscopy. Next, the reaction media was varied, keeping other conditions the same. It was noticed that increasing the volume of water in the aqueous ethanolic mixtures lowers the yield of 3a (Table 1, entries 3,4). Reaction in pure EtOH, THF, or ACN with solid KOH did not work better (Table 1, entries 5–7). In another attempt, PEG-400 was used as the green solvent, and the reaction went well to afford azo dye, 3a in 88% yield, but purification was tedious as a pasty mass of the dye was obtained upon acidification which requires extraction by solvent and column purification (Table 1, entry 8). Next, the attempts to use milder bases like K_2CO_3 or Et_3N did not show any significant conversion (Table 1, entries 9–11), and with NaOH, the final yield dropped to some extent (Table 1, entry 12). The use of a strong base was vital for the azo coupling as without a base, no conversion was observed (Table 1, entry 14). Lowering the temperature of the reaction proved detrimental to the yield of the product (Table 1, entries 15,16). As 1 equiv of amine (2a) was expected to be used up in the reduction of nitrobenzene (3a), a gradual reduction of the amount of 2a led to a substantial drop in the product yield (Table 1, entries 17–19). So, the optimum condition was set as 2.5 mmol of aniline derivative per mmol of nitroarenes with KOH as the base and EtOH-H_2O as the reaction media and MW irradiation at 150°C for 3 min for better yields of azo dyes (3).

Scope

With the optimal conditions in hand, we focused our attention on exploring the substrate scope using various nitroarenes and aniline derivatives (Scheme 3). The reaction mixtures were microwaved at 150°C for 3 min, cooled to room temperature, and acidified with 6 N HCl. The solid precipitate was filtered, washed with water, and recrystallized further from EtOH-H_2O. In all cases, the spectral data of newly synthesized azo dyes matched well with the reported values indicating the formation of *E*-isomers (Leriche et al., 2010; Zhao et al., 2011; Lv et al., 2019; Chen et al., 2021). The reaction between nitrobenzene (1a) and aniline (2b) afforded the azo dye 3b in 93% yield, indicating the scope of the synthesis of some symmetrical azo dyes by coupling nitroarenes and anilines having the same substituents in them. With a focus on unsymmetrical azo dye synthesis, anilines with electron-donating groups (EDGs) in the ring were taken and coupled with nitrobenzene (1a) to afford the corresponding azo dyes (3c-f) in high to excellent yields (Scheme 3, case A, entries 3c-f). In an alternate approach, the substituents in aniline derivatives were exchanged with nitroarenes (such as 4-nitrotoluene (1c) and aniline (2b) to see a significant drop in the yield after 3 min of microwave irradiation (Scheme 3, case B, entry 3c). In the case of the reaction between 4-nitroanisole (1 day) and aniline (2b), only a trace amount of the desired product was observed after 3 min (Scheme 3, case B, entry 3days). It seems the nitroarenes with a strong electron-donating group (-OMe) are not sufficiently reactive to get reduced by aniline at the optimized microwave condition. In a similar way, nitroarenes having electron-withdrawing groups (EWGs) such as Cl and Br were used for azo dye synthesis (Scheme 3, case A, entries 3g,h). However, in the case of the reaction between

Table 1. Optimization of reaction conditions

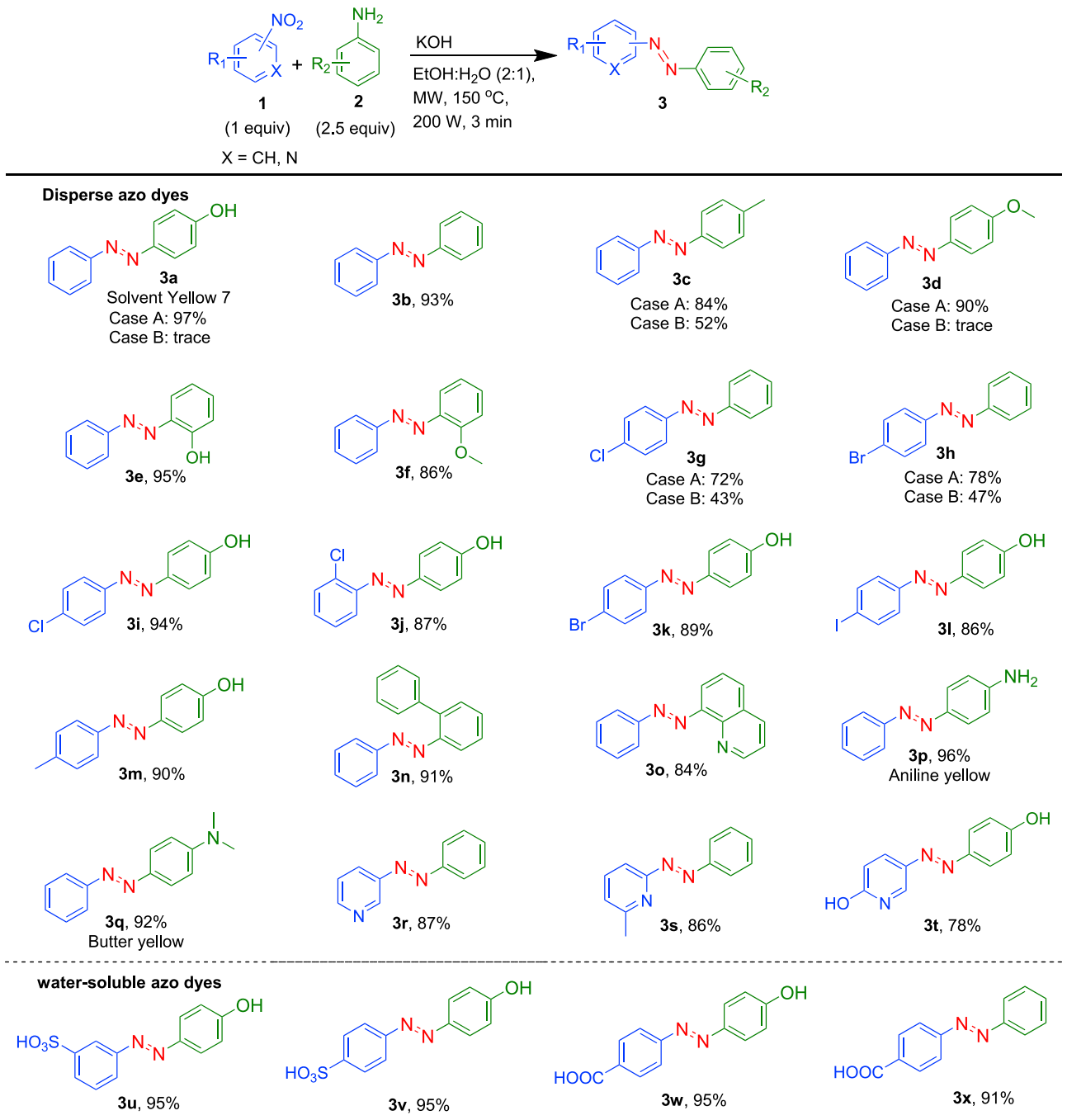


1a 2a 3a

Entry	Solvent	Base	Equiv of 2[c]	Temperature (°C)	Tim[c] (min)	Yield (%)[a,b]
1	H_2O	KOH	2.5	150	10	ND
2	EtOH: H_2O (2:1)	KOH	2.5	150	3	97
3	EtOH: H_2O (1:1)	KOH	2.5	150	3	72
4	EtOH: H_2O (1:2)	KOH	2.5	150	3	47
5	EtOH	KOH[c]	2.5	120	5	21
6	THF	KOH[c]	2.5	100	5	ND
7	CAN	KOH[c]	2.5	120	5	Trace
8	PEG-400	KOH[c]	2.5	150	3	88
9	EtOH: H_2O (2:1)	K_2CO_3	2.5	150	5	ND
10	EtOH: H_2O (2:1)	Et_3N	2.5	150	5	ND
11	EtOH: H_2O (2:1)	Pyridine	2.5	150	5	ND
12	EtOH: H_2O (2:1)	NaOH	2.5	150	3	83
13	EtOH: H_2O (2:1)	NaOEt	2.5	150	3	49
14	EtOH: H_2O (2:1)	No base	2.5	150	5	0
15	EtOH: H_2O (2:1)	KOH	2.5	110	3	Trace
16	EtOH: H_2O (2:1)	KOH	2.5	130	3	43
17	EtOH: H_2O (2:1)	KOH	2.2	150	3	84
18	EtOH: H_2O (2:1)	KOH	2.0	150	3	67
19	EtOH: H_2O (2:1)	KOH	1.0	150	3	35

[a]Unless specified, all reactions were carried out with 1.0 mmol of 1a and 2.5 mmol of 2a in 2 mL of ethanol with 1 mL of 10 M KOH in a microwave reactor at 150°C and power was set as 200 W.
[b]All are isolated yields.
[c]5 equiv of solid KOH was used.

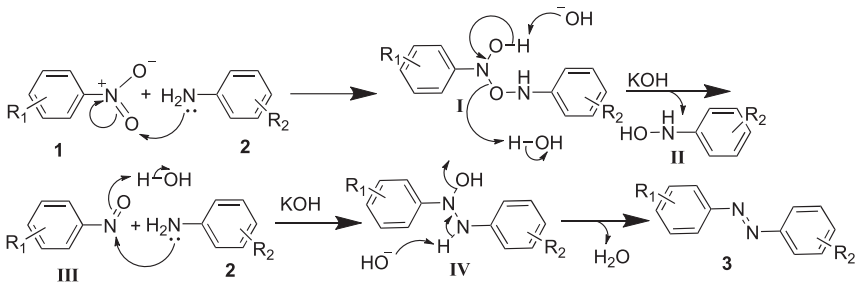
4-chloronitrobenzene (1g) and aniline (2b), the desired azo dye, 3g was obtained as ~70% yield. The presence of 3a was also seen as a minor spot in TLC. In this case, both the products were purified by column chromatography and confirmed by NMR spectroscopy. Thus, microwave irradiation caused partial nucleophilic substitution of –Cl by $–OH^-$ during the course of the reaction and about 72% yield of 3g was obtained along with 12% of 3a as the side product (Scheme 3, entry 3g Dalmann and Neumann, 1968). Variation in time and temperature could not prevent the formation of 3a and the optimized time was found to be 3 min in this case as well to get a better yield of (*E*)-1-(4-chlorophenyl)-2-phenyldiazene (3g). In the case of 4-bromonitrobenzene, only 5% of 3a was isolated and the yield of the desired dye (3h) improved to 78% (Scheme 3, entry 3h). However, for electron-rich aniline derivatives (2a), the nucleophilic substitution was not observed or was negligible, and the azo dyes were obtained in excellent yields (Scheme 3, entries 3i,j). It may be presumed that azo dye formation is kinetically favorable than a simple nucleophilic halide exchange by $–OH^-$ to afford the halo-substituted azo dyes as the major product under the prevailing microwave condition (Scheme 3, entries 3g-l). With a reasonable understanding of the substituent effect, more azo dyes were synthesized in high to excellent yields (Scheme 3, entries 3m-q). Notably, commercially important azo dyes, Aniline yellow (3p) and Butter yellow (3q), were synthesized by this method in 96% and 92% yields, respectively. To further extend the methodology on heteroaromatic systems with nitro group, a few pyridyl derivatives were selected and reacted with aromatic amines. The methodology worked equally well as the corresponding heteroaromatic azo dyes were formed within 3 min in high yields (Scheme 3,



Scheme 3. Substrate scope for nitrobenzene and aniline derivatives in the formation of azo dyes (3). In case A, EDG is placed in aniline, EWG in nitroarenes (e.g. 4-chloronitrobenzene (1e) and aniline (2b) for azo dye 3f), and in case B, the substituents are interchanged in the substrates. In all other cases, reactions were conducted placing EDG in aniline (green color represents aniline part in azo dyes)

entries 3r–t). Encouraged by this, a short series of water-soluble azo dyes were also synthesized, taking $-SO_3H$ and –COOH in the nitroarenes, and the corresponding dyes were obtained in more than 90% yields (Scheme 3, entries 3u–x).

Finally, several reactions were carried out under conventional heating conditions to access the advantage of the microwave-based method over the conventional solution-based method (Table S1, supplementary information).



Scheme 4. Plausible mechanism of azo dye synthesis by reductive cross-coupling of nitroarene and aniline

The thermal reactions were carried out under two conditions: a) by refluxing in EtOH:H_2O (2:1) in the presence of KOH, a condition which is similar to microwave condition and b) by heating in DMF at 150°C in the presence of KOH, the condition developed by Zhao et al. (Zhao et al., 2011). The reactions were monitored up to 36 h and the desired products and unreacted starting nitroarenes were isolated. The reactions were found sluggish in EtOH-H_2O and did not go to completion in all cases (Table S1, supplementary information). For example, the isolated yields of solvent yellow 7 (3a) and aniline yellow (3p) were found to be only 39% and 37%, respectively. However, in DMF, the reactions took 18–24 h for completion affording marginally lower yields of corresponding azo dyes (3a, 3b, 3d, 3p, and 3w) (Table S1, supplementary information). Overall, MW method is superior to the conventional heating methods in terms of time- and cost-effectiveness, and the use of benign solvents.

Plausible mechanism

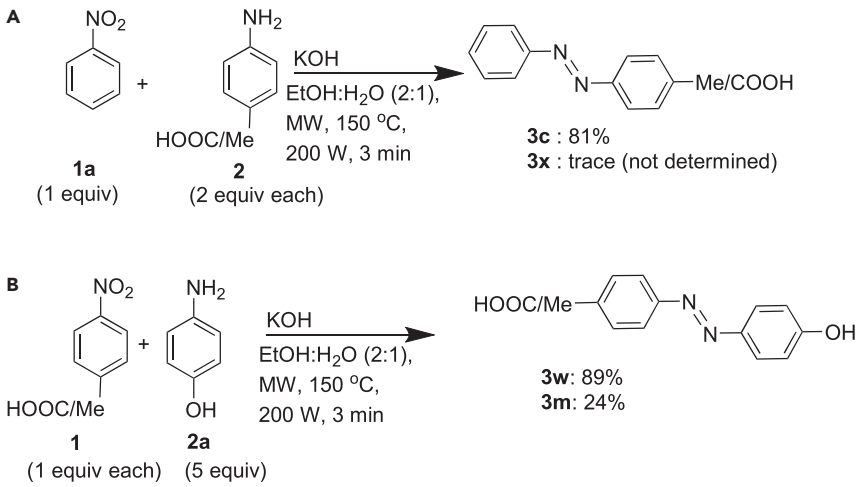
As per the strategy, excess of aniline derivative was used for the cross-coupling of nitroarenes with anilines considering 1 equiv of amine will be used up in the reduction of the nitro group. It was presumed that aniline will reduce the nitro group to nitroso, which will subsequently react with the remaining amine via Mill's reaction to form the azo dye. The plausible mechanism is depicted in scheme 4. To prove the formation of intermediate hydroxylamine (II) from aniline and to confirm the presence of nitroso-intermediate (III), a reaction mixture of nitrobenzene (1a) and aniline (2b) was microwaved at 150°C for 1 min and the resultant reaction mixture was directly subjected to LC-MS analysis. The presence of peaks at *m/z* 108 (III + H) and *m/z* 110 (II + H) along with a distinct peak at *m/z* 183 (3b + H) confirmed the formation of nitroso-intermediate (see supplementary information) and thus, indicating the proposed mechanism as the most likely pathway for the formation of azo dyes (3). To further understand the mechanistic pathway, we carried out a Mill's reaction between stoichiometric amounts of freshly synthesized nitrosobenzene (Coleman et al., 1945) and aniline at the optimized microwave condition in the presence of KOH as the base to obtain the corresponding azo dye, 3b in 52% yield. Thus, aniline derivatives could act as *in situ* reductant for the smooth cross-coupling of nitroarenes and anilines leading to a variety of azo dyes.

Substituent effect

To get a better insight into the substituent effect on product formation, couple of kinetic experiments were performed by challenging an electron-donating group (-Me) with an electron-withdrawing group, –COOH both in nitrobenzene and aniline. Stoichiometric amounts of the competing substrates were taken and the reactions were carried out under optimized conditions by MW irradiation for 3 min (Scheme 4). TLC revealed the complete conversion of the limiting substrates. From the isolated yields of products, it can be understood that the presence of an electron-donating group in aromatic amines could facilitate the azo dye formation at a faster rate and the corresponding dye (3c) formed as the sole product, whereas, the other possible product (3t) was not isolated (Scheme 5A). It may be presumed that the presence of an EWG in aniline (e.g. –COOH, 2k) significantly lowers its reducing ability. Similarly, a strong electron-withdrawing group in the nitroarene facilitates a faster reaction and the corresponding product, 3s formed in 89% yield, whereas, only a small amount of 3l (24%) was isolated from the reaction mixture (Scheme 5B). The competitive experiment revealed that the placement of electron-rich substituents in aromatic amines and electron-deficient substituents in nitroarenes is more suitable for the synthesis of unsymmetrical push-pull type azo dyes.

Gram-scale synthesis

The scalability is an important attribute of any synthetic methodology from an industrial perspective and the availability of bigger microwave reactors makes the scale-up from the laboratory scale to the pilot-scale



Scheme 5. Substituent effect on the reaction kinetics of cross-coupling of amines and nitroarenes

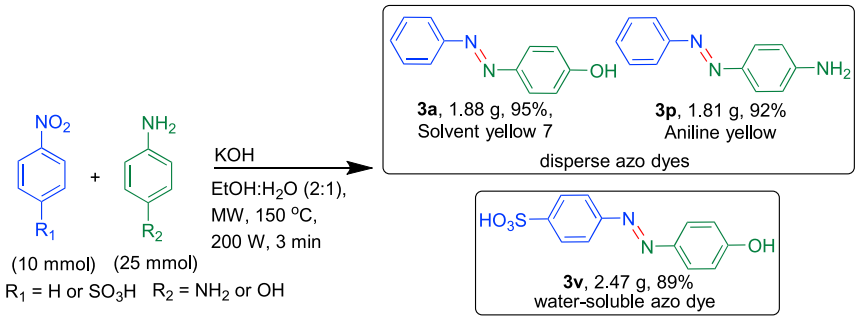
(A) Substituent on aromatic amine.

(B) Substituent on nitroarene.

feasible (Scheme 6). For the gram-scale synthesis of 3a, 10 mmol of 1a and 25 mmol of 2a were taken in a 35 mL microwave vessel and this time the volume of solvent was reduced to 6 mL of EtOH-H_2O (2:1) and the reaction mixture was microwaved at 150°C for 3 min. After acidification and washing steps, 1.88 g of commercial dye, solvent yellow 7 (3a) was obtained. The yield (95%) is similar to that of smaller batches (97%). Thus, 5-folds reduction in solvent volume hardly affects the yield or reaction time. Encouraged by this, one more dispersed dye, 3p (aniline yellow) and another water-soluble dye 3v were synthesized in gram-scale. This short study revealed that the microwave protocol can be scaled up to several grams indicating its potential for the synthesis of azo dyes at a commercial scale.

Conclusion

In conclusion, we have developed a microwave-assisted sustainable method for the synthesis of unsymmetrical azo dyes by coupling nitroarenes with aromatic amines in a single step. In this approach, the aromatic amines act as a reductant for the conversion of nitroarenes to nitrosoarenes which subsequently couple with the same aromatic amine to form a series of dispersed and water-soluble azo dyes in high yields. Thus, cheaper aniline derivatives perform a dual role of reductant and the coupling substrate omitting the use of any toxic and costly metals in the process. The use of microwave irradiation greatly enhanced the reaction rates and the aromatic azo compounds were formed within just a few minutes. In most cases, solid azo dyes were isolated in sufficiently pure form by simple filtration avoiding tedious column purification. A broad substrate scope was established by varying substituents in both nitroarenes and aniline derivatives as well as heteroaromatic nitro derivatives. The competitive reactions with suitable EDG and EWG in anilines and nitroarenes revealed that electron-rich aromatic amines react faster with electron-deficient nitroarenes to afford the corresponding azo dyes as the major product and other possibilities are almost ceased. The MW method worked well in the gram-scale synthesis of



Scheme 6. Gram-scale synthesis of azo dyes

several dyes with no drop in the yield. The current method is superior to several other existing methods of azo dye synthesis because of fast reaction, catalyst-free condition, devoid of work-up and purification steps, use of greener media, and high yields.

Limitations of the study

The synthesis of azo dyes with stronelectron-donating groups on both the aromatic rings through this methodology remains a challenge. For e.g., the reaction between 4-nitrophenol (1b) and 4-aminophenol (2a) did not yield the expected azo product as well as the reaction between 4-methoxynitrobenzene (1c) and 4-aminophenol (2a).

STAR★METHODS

Detailed methods are provided in the online version of this paper and include the following:

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  - Materials availability
  - Data and code availability
- METHOD DETAILS
  - General procedure: Preparation of (*E*)-4-(phenyldiazenyl)phenol (3a)
  - A typical procedure for case B
  - Spectroscopic details

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.isci.2022.104497.

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AUTHOR CONTRIBUTIONS

Methodology, Investigation; A.T. and A.C.; Writing- Orignal Draft, Review and Editing; A.T., M.B., and A.C.; NMR Spectrscopic analysis; A.T., A.C., and M.B.; Supervision; M.B. and A.C.

DECLARATION OF INTEREST

The authors declare no competing interests.

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STAR★METHODS

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
Nitrobenzene	Sigma-Aldrich	Cat#8.06770
Aniline	Sigma-Aldrich	Cat#8.22256
4-aminophenol	Sigma-Aldrich	Cat# 8.00421
4-nitrophenol	Sigma-Aldrich	Cat# 241,326
p-toluidine	Sigma-Aldrich	Cat# 461,121
4-nitrotoulene	Sigma-Aldrich	Cat# N27322
p-anisidine	Sigma-Aldrich	Cat# 8.00458
4-nitroanisole	Sigma-Aldrich	Cat# 103,543
2-aminophenol	Sigma-Aldrich	Cat# 8.00419
2-anisidine	Sigma-Aldrich	Cat# A88182
4-chloronitrobenzene	Sigma-Aldrich	Cat# C59122
2-chloronitrobenzene	Sigma-Aldrich	Cat# 185,760
4-bromonitrobenzene	Sigma-Aldrich	Cat# 167,150
4-iodonitrobenzene	Sigma-Aldrich	Cat# I9805
4-chloroaniline	Sigma-Aldrich	Cat# 8.02613
4-bromoaniline	Sigma-Aldrich	Cat# 8.01600
1,4-diaminobenzene	Sigma-Aldrich	Cat# P6001
4-nitrobenzoic aicd	Sigma-Aldrich	Cat# 461,091
2-methyl-6-nitropyridine	Sigma-Aldrich	Cat# AMBH2D702D84
3-nitropydine	Sigma-Aldrich	Cat# 736,090
2-hydroxy-4-nitropyridine	Sigma-Aldrich	Cat# H48808
2-aminobiphenyl	Alfa Aesar	Cat# L05728
8-aminoquinoline	Alfa Aesar	Cat# A16752
N,N-Dimethyl-1,4-phenylenediamine	TCI	Cat# D0779
3-nitrobenzenesulfonic acid	TCI	Cat# N0138
4-nitrobenzenesulfonate	TCI	Cat# N0140
Software and algorithms		
ChemDraw Professional 18.0	PerkinElmer	https://www.perkinelmer.com/category/chemdraw
Other		
CEM SP Discover Microwave	CEM	https://cem.com/media/contenttype/media/literature/b087v8-cem.pdf

RESOURCE AVAILABILITY

Lead contact

Further information and requests for reagents may be directed to and will be fulfilled by the corresponding author Amrita Chatterjee, amrita@goa.bits-pilani.ac.in.

Materials availability

The study did not generate any new materials. All materials used in the work were sourced from commercial resources as described under STAR Methods.

Data and code availability

- All data reported in this paper will be shared by the lead contact upon request.
- This paper does not report original code.

- Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.

METHOD DETAILS

All the fine chemicals were procured from Sigma-Aldrich, Alfa Aesar, or TCI chemicals and used directly. Other common reagents and solvents of AR grade were obtained from local suppliers and used without further purification. A CEM Discover SP microwave oven was used for all the reactions. Thin-layer chromatography (TLC) of 0.25 mm silica gel aluminum plates (60F-254) was used to monitor the progress of the reaction, and visualization was done using UV light (254 or 365 nm). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE (400 and 500 MHz) instrument with $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane as the internal standard. The chemical shifts are reported in parts per million (δ) units, and the multiplicity of NMR peaks is represented using standard abbreviation.

General procedure: Preparation of (*E*)-4-(phenyldiazenyl)phenol (3a)

Nitrobenzene (1a, 1 mmol) and 4-aminophenol (2a, 2.5 mmol) were dissolved in 2 mL of ethanol in a 10 mL microwave reactor vessel, 1 mL of 10 M aqueous KOH was added to it, closed with a cap and the reaction mixture was placed in a microwave reactor and exposed to microwave irridation at 150°C (200 W power) for 3 min. After completion of reaction (monitored by TLC) the mixture was acidified with 6 N HCl. The precipitate formed was collected, washed with water and air dried to obtain the sufficiently pure azo dye, 3a (solvent yellow 7, 190 mg, 97%). The azo compounds were further purified by recrystallization from 20% EtOH-water mixture.

A typical procedure for case B

4-Nitrophenol (1a, 1 mmol) and aniline (2a, 2.5 mmol) were dissolved in 2 mL of ethanol in a 10 mL microwave reactor vessel, 1 mL of 10 M aqueous KOH was added to it, closed with a cap and the reaction mixture was placed in a microwave reactor and exposed to microwave irradiation at 150°C (200 W power) for 3 min. The reaction was monitored through TLC.

Spectroscopic details

(*E*)-4-(Phenyldiazenyl)phenol, 3a: (Chen et al., 2021) bright yellow solid, 97%, m.p. 152–153°C [Lit. m.p. 149–151°C]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.86 (m, 4H), 7.53–7.42 (m, 3H), 6.94 (d, *J* = 8.0, 2H), 5.32 (s, 1H, exchangeable); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 152.7, 147.2, 130.5, 129.1, 125.0, 122.6, 115.8; Elemental analysis calcd (%) for $C_{12}H_{10}N_2O$: C, 75.16; H, 4.91; N, 16.23; found: C 74.78, H 4.84, N 16.03.

(*E*)-1,2-Diphenyldiazene, 3b: (Lv et al., 2019) yellow-orange solid, 93%, m.p. 65–67°C [Lit. m.p.. 66–68°C]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95–7.93 (m, 4H), 7.59–7.44 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 131.0, 129.1, 122.9; Elemental analysis calcd (%) for $C_{12}H_{10}N_2$: C, 79.10; H, 5.53; N, 15.37; found: C 78.98, H 5.64, N 15.23.

(*E*)-1-Phenyl-2-(*p*-tolyl)diazene, 3c (Lv et al., 2019), orange solid, 84%, m.p. 66–68°C [Lit. m.p. 65–67°C]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94–7.89 (m, 2H), 7.86–7.80 (m, 2H), 7.55–7.44 (m, 3H), 7.32 (d, *J* = 8 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.8, 150.8, 141.6, 130.7, 129.8, 129.7, 129.1, 122.9, 122.7, 21.5; Elemental analysis calcd (%) for $C_{13}H_{12}N_2$: C, 79.56; H, 6.16; N, 14.27; found: C 79.88, H 6.14, N 14.23.

(*E*)-1-(4-Methoxyphenyl)-2-phenyldiazene, 3days: (Zhao et al., 2011), orange solid, 90%, m.p. 53–55°C [Lit. m.p. 52–54°C]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.0, 2H), 7.89 (d, *J* = 8.0, 2H), 7.53–7.42 (m, 3H), 7.02 (d, *J* = 8.0, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.1, 152.8, 147.1, 130.4, 129.0, 124.8, 122.6, 114.2, 55.6; Elemental analysis calcd (%) for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20; found: C 73.75, H 5.74, N 13.35.

(*E*)-2-(Phenyldiazenyl)phenol, 3e: (Nguyen et al., 2016), red solid, 95%, m.p. 82–84°C [Lit. m.p. 81–82°C]; ^{1}H NMR (500 MHz, $CDCl_3$): δ 12.94 (s, 1H, exchangeable), 7.96 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.55–7.47 (m, 3H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.7, 150.5, 137.3, 133.2, 133.2, 131.1, 129.3, 122.2, 119.9, 118.2. Elemental analysis calcd (%) for $C_{12}H_{10}N_2O$: C, 72.71; H, 5.09; N, 14.13; found: C 72.64, H 5.17, N 14.21.

(*E*)-1-(2-Methoxyphenyl)-2-phenyldiazene, 3f: (Zhao et al., 2011) 86%, orange semisolid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.89 (m, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.53–7.43 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 1H),

7.02 (td, *J* = 8.0, 1.2 Hz, 1H), 6.75–6.71 (m, 1H), 4.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 153.2, 142.4, 132.5, 130.8, 129.0, 123.0, 121.1, 120.8, 117.0, 56.4; Elemental analysis calcd (%) for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20; found: C 73.34, H 5.79, N 13.32.

(*E*)-1-(4-Chlorophenyl)-2-phenyldiazene, 3g: (Lv et al., 2019) 72%, yellow solid, m.p. 83–85°C. [Lit. m.p. 81–83°C]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.0 Hz, 2H), 8.16 (d, *J* = 8.0 Hz, 2H), 7.89–7.84 (m, 1H), 7.50–7.43 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.6, 144.0, 131.6, 130.9, 129.6, 129.0, 128.8, 128.7, 125.5, 122.8, 122.3; Elemental analysis calcd (%) for $C_{12}H_9ClN_2$: C, 66.52; H, 4.19; N, 12.93; found: C 66.74, H 4.13, N 13.12.

(*E*)-1-(4-Bromophenyl)-2-phenyldiazene, 3h: (Lv et al., 2019) pale orange solid, 78%, m.p. 90–91°C [Lit. m.p. 90–92°C]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.82–7.78 (m, 2H), 7.65 (d, *J* = 8.0, 2H), 7.55–7.46 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 151.4, 151.2, 132.4, 132.3, 131.3, 129.2, 125.8, 125.4, 124.4, 123.0; Elemental analysis calcd (%) for $C_{12}H_9BrN_2$: C, 55.20; H, 3.47; N, 10.73; found: C 55.61, H 3.39, N 10.62.

(*E*)-4-((4-Chlorophenyl)diazenyl)phenol, 3i: (Chen et al., 2021) red solid, 94%, m.p. 151–153°C [Lit. m.p. 150–152°C]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.41 (s, 1H, exchangeable); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 151.1, 147.0, 136.3, 129.3, 125.1, 123.9, 115.9; Elemental analysis calcd (%) for $C_{12}H_9ClN_2O$: C, 61.95; H, 3.90; N, 12.04; found: C 61.61, H 3.95, N 12.22.

(*E*)-4-((2-Chlorophenyl)diazenyl)phenol, 3j: (Kocaokutgen and Gumrukcuoglu, 1996) bright red solid, 87%, m.p. 90–92°C [Lit. m.p. 88°C]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.66 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.54 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.40–7.28 (m, 2H), 6.94 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 148.8, 147.4, 134.7, 131.1, 130.6, 127.3, 125.6, 117.6, 115.9; Elemental analysis calcd (%) for $C_{12}H_9ClN_2O$: C, 61.95; H, 3.90; N, 12.04; found: C 61.82, H 3.82, N 11.93.

(*E*)-4-((4-Bromophenyl)diazenyl)phenol, 3k: (Chen et al., 2021) pale orange solid, 89% m.p. 153–155°C [Lit. m.p. 153–155°C]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.40 (s, 1H, exchangeable); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 151.4, 147.0, 132.3, 125.2, 124.7, 124.1, 115.9; Elemental analysis calcd (%) for $C_{12}H_9BrN_2O$: C, 52.01; H, 3.27; N, 10.11; found: C 52.22, H 3.29, N 10.23.

(*E*)-4-((4-Iodophenyl)diazenyl)phenol, 3L: (Leriche et al., 2010) bright orange solid, 86%, m.p. 171–173°C [Lit. m.p. 170°C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 8.8, 2H), 7.61 (d, *J* = 8.8, 2H), 6.94 (d, *J* = 8.8 Hz 2H), 5.53 (s, 1H, exchangeable); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 152.0, 147.0, 138.3, 125.2, 124.2, 115.9, 96.8; Elemental analysis calcd (%) for $C_{12}H_9IN_2O$: C, 44.47; H, 2.80; N, 8.64; found: C 44.29, H 2.87, N 8.53.

(*E*)-4-(*p*-Tolyldiazenyl)phenol, 3m: (Zhu et al., 2010b) orange solid, 90%, m.p. 144–146°C [Lit. m.p. 146–148°C]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 5.59 (s, 1H, exchangeable), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 150.8, 147.2, 141.0, 129.7, 124.8, 122.6, 115.8, 21.5; Elemental analysis calcd (%) for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20; found: C 73.89, H 5.77, N 13.03.

(*E*)-1-([1,1′-Biphenyl]-2-yl)-2-phenyldiazene, 3n: (Hubrich et al., 2015), orange liquid, 91%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (dd, *J* = 8.0, 1.6 Hz, 2H), 8.19 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 8.0 Hz, 2H), 7.59–7.47 (m, 7H), 7.43–7.41 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 150.8, 142.2, 138.1, 137.2, 131.3, 129.4, 129.3, 129.2, 129.0, 127.1, 124.2, 124.1, 123.7, 122.9; Elemental analysis calcd (%) for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84; found: C 83.46, H 5.52, N 11.01.

(*E*)-8-(Phenyldiazenyl)quinoline, 3o: (Wang et al., 2017), orange liquid, 84%; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.92 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.70 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.58–7.43 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 152.7, 134.6, 131.0, 130.9, 129.3, 129.1, 128.8, 128.3, 127.6, 123.5, 123.3, 122.8; Elemental analysis calcd (%) for $C_{15}H_{11}N_3$: C, 77.23; H, 4.75; N, 18.01; found: C 76.99, H 4.82, N 18.09.

(*E*)-4-(Phenyldiazenyl)aniline, 3p: (Ohlsson et al., 2002), yellow solid, 96%, m.p. 125–127°C [Lit. m.p. 122–124°C]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87–7.81 (m, 4H), 7.52–7.39 (m, 3H), 6.74 (d, *J* = 8.0 Hz, 2H), 4.05 (s, 2H, exchangeable); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.9, 149.5, 145.5, 129.8, 128.9, 125.1, 122.3, 114.6; Elemental analysis calcd (%) for $C_{12}H_{11}N_3$: C, 73.07; H, 5.62; N, 21.30; found: C 72.92, H 5.70, N 21.24.

(*E*)-*N*,*N*-dimethyl-4-(phenyldiazenyl)aniline, 3q: (Zhang and Mellah, 2017), yellow solid, 92%, m.p. 111–112°C [Lit. m.p. 112–114°C]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.49–7.45 (m, 2H), 7.40–7.36 (m, 2H), 6.76 (d, *J* = 8.8 Hz, 2H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 152.4, 143.7, 132.5, 130.9, 129.4, 128.9, 128.8, 125.0, 122.2, 111.5, 40.3; Elemental analysis calcd (%) for $C_{14}H_{15}N_3$: C, 74.64; H, 6.71; N, 18.65; found: C 74.54, H 6.73, N 18.54.

(*E*)-3-(Phenyldiazenyl)pyridine, 3r: (Thies et al., 2012), red solid, 87%, m.p. 52–53°C [Lit. m.p. 53–54°C]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.18 (d, *J* = 2.9 Hz, 1H), 8.67 (d, *J* = 4.9 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 6.8 Hz, 2H), 7.56–7.46 (m, 3H), 7.40 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.3, 151.5, 147.7, 147.2, 131.6, 129.2, 126.8, 123.8, 123.0 Elemental analysis calcd (%) for $C_{11}H_9N_3$: C, 72.11; H, 4.95; N, 22.94; found: C 72.24, H 4.89, N 23.03.

(*E*)-2-Methyl-6-(phenyldiazenyl)pyridine, 3s: (Khatua et al., 2020) red solid, 86%, m.p. 160–162°C; ^{1}H NMR (500 MHz, $CDCl_3$): 8.02–8.00 (m, 2H), 7.76–7.71 (m, 1H); 7.56–7.46 (m, 3H); 7.27–7.18 (m, 2H); 2.27 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.6, 158.4, 152.2, 138.3, 131.9, 128.9, 124.8, 123.4, 110.6, 24.2; Elemental analysis calcd (%) $C_{12}H_{11}N_3$ Elemental Analysis: C, 73.07; H, 5.62; N, 21.30; found: C 73.15, H 5.69, N 21.24.

(*E*)-5-((4-Hydroxyphenyl)diazenyl)pyridin-2-ol, 3t: orange solid, 78%, m.p. 160–162°C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.34 (s, 1H), 8.96 (d, *J* = 2.8 Hz, 1H), 8.20 (dd, *J* = 9.3, 3.0 Hz, 1H), 7.41 (d, *J* = 8.7 Hz, 1H), 6.77 (d, *J* = 8.8 Hz, 2H), 6.74 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 159.9, 154.5, 146.9, 135.7, 132.8, 131.0, 128.4, 123.4, 115.9; Elemental analysis calcd (%) for $C_{11}H_9N_3O_2$: C, 61.39; H, 4.22; N, 19.53; found: C 61.44, H, 4.31, N 19.59.

(*E*)-3-((4-Hydroxyphenyl)diazenyl)benzenesulfonic acid, 3u: (Dodds et al., 2017), red solid, 95%, m.p. >260°C (charred); ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.36 (s, 1H), 7.72–7.64 (m, 2H), 7.48–7.50 (m, 2H), 7.44–7.37 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.4, 149.9, 147.7, 132.4, 132.0, 130.2, 129.11, 128.5, 123.7, 120.6; Elemental analysis calcd (%) for $C_{12}H_{10}N_2O_4S$: C, 51.79; H, 3.62; N, 10.07; found: C 52.01, H 3.70, N 10.22.

(*E*)-4-((4-Hydroxyphenyl)diazenyl)benzenesulfonic acid, 3v: (Leriche et al., 2010), red solid, 95%, m.p. >260°C (charred) [Lit. m.p. > 250 °C]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.16 (s, 1H, exchangeable), 7.73–7.64 (m, 4H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.4, 157.7, 132.1, 132.0, 129.1, 124.8, 122.8, 116.5; Elemental analysis calcd (%) for $C_{12}H_{10}N_2O_4S$: C, 51.79; H, 3.62; N, 10.07; found: C 51.91, H 3.67, N 10.02.

(*E*)-4-((4-Hydroxyphenyl)diazenyl)benzoic acid, 3w: (Leriche et al., 2010), reddish brown solid, 95%, m.p. 272–273°C [Lit. m.p. 273°C]; ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.16 (s, 1H, exchangeable), 10.48 (s, 1H, exchangeable), 8.11 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.4, 167.3, 162.1, 155.0, 145.8, 132.3, 131.0, 125.8, 122.6, 116.6; Elemental analysis calcd (%) for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16; N, 11.56; found: C 64.65, H 4.17, N 11.46.

(*E*)-4-(Phenyldiazenyl)benzoic acid, 3x: (Ohlsson et al., 2002), orange solid, 91%, m.p. 247–249°C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 13.33 (s, 1H, exchangeable), 8.37 (d, *J* = 8.0 Hz, 2H), 8.18–8.08 (m, 7H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.0, 166.6, 150.6, 146.9, 134.7, 131.8, 131.1, 130.9, 130.5, 125.4, 123.3, 123.0; Elemental analysis calcd (%) for $C_{13}H_{10}N_2O_2$: C, 69.02; H, 4.46; N, 12.38; found: C 68.88, H 4.57, N 12.26.

Further details can be found in the accompanying supplemental Information.