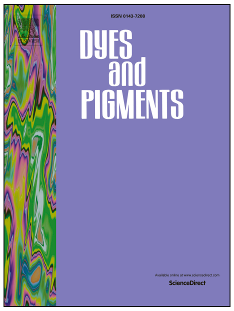

Convenient and rapid diazotization and diazo coupling reaction *via* aryl diazonium nanomagnetic sulfate under solvent-free conditions at room temperature

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Highlights

- Diazotization and diazo coupling are done *via* aryl diazonium nanomagnetic sulfate.
- Different anilines are converted to azo dyes with good to excellent yields.
- The advantages of this method are short reaction time, avoidance of harmful acids.

Convenient and rapid diazotization and diazo coupling reaction *via* aryl diazonium nanomagnetic sulfate under solvent-free conditions at room temperature

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ABSTRACT

For the first time, nanomagnetic-supported sulfonic acid is used for conversion of several types of aromatic amine, containing electron-withdrawing groups as well as electron-donating groups to the corresponding azo dyes in excellent yield. The synthesis of these compounds is described by the sequential diazotization–diazo coupling of various aromatic amines with sodium nitrite, nanomagnetic supported sulfonic acid and coupling agents under solvent-free conditions at room temperature. This new method offers several advantages including short reaction time, mild reaction conditions, avoidance of harmful acids, and simple work-up procedure. More importantly, aryldiazonium salts supported on magnetic nanoparticles (aryl diazonium nanomagnetic sulfate) were sufficiently stable to be kept at room temperature in the dry state.

Keywords Aryl diazonium nanomagnetic sulfate; Azobenzene; Diazo coupling; Nanomagnetic particles; Solvent-free condition

1. Introduction

Azobenzene, with two phenyl rings linked by N=N double bond, serves as the parent molecule for abroad class of aromatic azo compounds. The strong absorption of band these compounds can be tailored by ring substitution to fall anywhere from the ultraviolet to red-visible regions, allowing chemical fine-tuning of color. This property, combined with the fact that the azo groups are relatively robust and chemically stable, has prompted extensive study of azobenzene based structures as dyes [1]. Approximately 10,000 different dyes and pigments are used industrially, and over 0.7 million tones of synthetic dyes are produced annually worldwide [2]. Azoic dyes are the most important group of all synthetic dyes that are used extensively for textile dyeing [3], paper printing and color photography and as additives in petroleum products. In addition, azobenzene moiety is an important structural motif in biological systems [4]. The photo response of azo compounds modifies the activity of enzymes and polypeptides, also is used for more accurate diagnosis of Alzheimer' s disease [5]. Moreover, azobenzenes recently have been targeted for potential applications in areas of nonlinear optics [6], optical storage media [7], chemosensory [8, 9], liquid crystals [1], photochemical molecular switches [10], molecular shuttles [11], nanotubes [12], in the manufacture of protective eye glasses and filters [13] and as optical switch for in vivo experiments [14].

The synthesis of aromatic azo components has been attracting increasing interest over the past decade because of their utility in various applications. In recent years, several methods have been reported for synthesis of these components [15-17]. Although remarkable developments have been achieved in this field, the search for mild conditions could represent a useful tool in organic chemistry. The most important methods for the preparation of aromatic azo have focused on diazotization-azo coupling reaction. The main limitation of this process is their environmental incompatibility. Since, use of strong liquid acids for diazotization reaction (such as H_2SO_4, HCl) causes permanent damage to the environment and their use is contrary to the principles of green chemistry. In addition, these liquid acids require special processing in the form of neutralization, which involves costly and inefficient catalyst separation from homogeneous reaction mixture, and then results in an unrecyclable waste. The need for a “green” approach to chemical processing has stimulated the use of recyclable strong solid acids as replacements for unrecyclable liquid acid catalysts [18-21].

Magnetic nanoparticles have emerged as a highly valuable substrate for the attachment of homogeneous inorganic and organic containing catalysts. They have advantages such as readily available, high surface area and most importantly magnetically recoverable, which facilitates reaction work-up and rapid sample processing, and reduces solvent consumption [22, 23].

We have previously report synthesis of nanomagnetic-supported sulfonic acid (nano-γ-Fe_2O_3-SO_3H) and its applications as viable alternative to unrecyclable homogenous catalysts in organic synthesis [24-26]. Recently, we have used this catalyst for the synthesis of aryl iodides [27]. As part of our ongoing research program to explore catalytic properties of nanomagnetic-supported sulfonic acid, we herein report a new process for diazotization and diazo coupling reaction of aromatic amines using nano-γ-Fe_2O_3-SO_3H (Scheme 1).

Scheme 1.

2. Experimental

2.1. General

Nano-γ-Fe_2O_3-SO_3H was prepared by the reaction of chlorosulfonic acid with nano maghemite previously [24]. All reagents were purchased from Merck and Aldrich and used without further purification. Melting points were recorded on electro thermal 9100 apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained with a Bruker Avance spectrometer (^{1}H NMR 300, 400 MHz and ^{13}C NMR 75, 100 MHz) in pure deuteriated chloroform and DMSO using TMS as an internal standard. The IR spectra were recorded on a Perkin-Elmer model 783 spectrophotometer (Waltham, MA, USA). UV-Vis spectra were obtained as CH_2Cl_2 or DMSO solutions ($5*10^{-5}$ M) on a Shimadzu UV-1650PC spectrophotometer.

2.2. Typical procedure for the preparation of N,N-dimethyl-4-(phenyldiazenyl)aniline

Aniline (2 mmol, 0.1863 g), nanomagnetic-supported sulfonic acid (γ-Fe_2O_3-SO_3H) (1.3 g), $NaNO_2$ (4 mmol, 0.276 g) and 0.2 mL of H_2O were homogenized by grinding in a mortar with a pestle for a few minutes. The diazotization reaction lasted approximately 5-10 minutes. Dimethylaminobenzene (2 mmol, 0.2424 g) was added to the diazonium salt and grinding continued for 10 min. After completion of the reaction, the mixture was triturated with acetone (30 mL). In the presence of a magnetic stirrer bar, catalyst moved on to the stirrer bar steadily and the reaction mixture turned clear within 10 s. The catalyst was isolated by simple decantation. After evaporation of the solvent by rotary evaporator, the crude product was purified by recrystalization in EtOH/H_2O, 9:1. *N,N*-dimethyl-4-(phenyldiazenyl)aniline was obtained in 94% yield (0.423 g), mp 108–9 ºC, literature 107–9 ºC [28]. Recyclability of the catalyst was tested in this reaction, after completion of the reaction, the mixture was triturated with acetone and the catalyst was easily removed with an external magnet, after being washed with acetone and ethanol and dried at 70°C to be used in the next cycles. This process was repeated three times without significant loss of activity.

CAUTION! Although we did not experience any problems, diazonium salts are known to be explosive. Care must be exercised in handling them, especially when they are subjected to grinding.

2.3. The spectral data of some representative products

1-(*p*-tolyldiazenyl)naphthalen-2-ol (Table 2, **3a**): (0.225 g, 86%), as an orange red solid, (recrystallized from ethanol:water, 9:1). IR (KBr) cm^{-1}: 3433.06, 3030, 2920, 1620.09, 1496.66, 1265, 1203, 810, 748. UV (λ_{max} in CH_2Cl_2): 483 nm. ^{1}H NMR ($CDCl_3$): δ_H 15.98 (NH, s), 8.66 (1H, d, *J*=8.4 Hz), 7.79 (1H, d, *J*=9.2 Hz), 7.74 (1H, d, *J*=8 Hz), 7.69 (1H, d, *J*=8 Hz), 7.60 (1H, d, *J*=8.4 Hz), 7.44 (1H, d, *J*=8.4 Hz), 7.34 (2H, d, *J*=8 Hz), 6.96 (1H, d, *J*=9.2 Hz), 2.44 (CH_3, s). ^{13}C NMR: 21.3, 129.79, 168.4, 143.59, 130.19, 119.1, 138.36, 121.64, 124, 125.3, 128, 128.5, 128.6, 129.7, 130.1, 133.5, 138.36, 138.86, 143.59, 168.4. Anal. Calcd for $C_{17}H_{14}N_2O$: C, 77.84; H, 5.38; N, 10.68%. Found: C, 77.58; H, 5.48; N, 10.38%.

1-(phenyldiazenyl)naphthalen-2-ol (Table 2, **3e**): (0.196 g, 79%), (recrystallized from ethanol:water, 9:1). IR (KBr) cm^{-1}: 3434, 1617, 1447, 1261, 1207, 839, 751. ^{1}H NMR (Acetone-*d*$_6$): 16.05 (NH, s), 8.37 (1H, d, *J*=8 Hz), 7.58 (2H, d, *J*=8.4 Hz), 7.56 (1H, d, *J*=9.2 Hz), 7.42 (1H, d, *J*=8 Hz), 7.36 (1H, d, *J*=8 Hz) 7.21 (1H, d, *J*=8 Hz), 7.11 (2H, d, *J*=7.2 Hz), 6.68 (1H, d, *J*=9.2 Hz). ^{13}C NMR: 118.6, 121.73, 124.02, 125.7, 127.4, 128, 128.8, 129.5, 130.08, 133.4, 140, 144.8, 177.87. Anal. Calcd for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.87; N, 11.28%. Found: C, 77.25; H, 4.94; N, 11.18%.

1-((4-chlorophenyl)diazenyl)naphthalen-2-ol (Table 2, **3f**): (0.268 g, 95%), as a maroon solid, (recrystallized from ethanol:water, 9:1). IR (KBr) cm^{-1}: 3432, 1621, 1485.09, 1253.64, 1211.21, 1089.71, 819.69, 748.33. UV (λ_{max} in CH_2Cl_2): 480 nm. ^{1}H NMR ($CDCl_3$): 15.89 (NH, s), 8.55 (1H, d, *J*=8 Hz), 7.74 (1H, d, *J*=9.2 Hz), 7.69 (2H, t of d, *J*=6.8, 2 Hz), 7.62 (1H, d, *J*=8 Hz), 7.46-7.39 (2H, m), 6.89 (1H, d, *J*=9.2 Hz). ^{13}C NMR: 119.9, 121.7, 124.3, 125.8, 128.1, 128.69, 128.65, 128.9, 129.73, 130.22, 133, 133.36, 140.1, 164, 170. Anal. Calcd for $C_{16}H_{11}ClN_2O$: C, 67.97; H, 3.92; N, 9.91%. Found: C, 68.19; H, 3.90; N, 10.01%.

1-((4-bromophenyl)diazenyl)naphthalen-2-ol (Table 2, **3g**): (0.304 g, 93%), as a dark red solid, (recrystallized from ethanol:water, 9:1). IR (KBr) cm^{-1}: 3437, 1620.09, 1483.16, 1251.72, 1209.28, 1070.42, 817.76, 748.33. UV (λ_{max} in CH_2Cl_2): 483 nm. ^{1}H NMR ($CDCl_3$): 16.1 (NH, s), 8.54 (1H, d, *J*=7.2 Hz), 7.74 (1H, d, *J*=8.8 Hz), 7.61-7.57 (6H, m), 7.42 (1H, d, *J*=6.4 Hz), 6.87 (1H, d, *J*=9.2 Hz). ^{13}C NMR: 121.1, 121.9, 122.9, 125.6, 127.1, 129.3, 129.8, 130.1, 131.4, 133.8, 134.5, 141.4, 145.2, 172. Anal. Calcd for $C_{16}H_{11}BrN_2O$: C, 58.74; H, 3.39; N, 8.56%. Found: C, 58.40; H, 3.53; N, 8.5%.

4-((4-chlorophenyl)diazenyl)-N,N-dimethylaniline (Table 2, **3h**): (0.2337 g, 90%), (recrystallized from ethanol:water, 9:1). IR (KBr) cm^{-1}: 1598.88, 1519.80, 1365.51, 1135.99, 838.98. UV (λ_{max} in CH_2Cl_2): 421 nm. ^{1}H NMR ($CDCl_3$): 7.86 (2H, d, *J*=8), 7.78 (2H, t, *J*=7.6 Hz), 7.42 (2H, d, *J*=8 Hz), 6.75 (2H, d, *J*=8.8 Hz), 3.09 (6H, t, *J*=20 Hz). ^{13}C NMR: 40.2, 111.4, 123.4, 125, 129, 134.9, 152.5. Anal. Calcd for $C_{14}H_{14}ClN_3$: C, 64.74; H, 5.43; N, 16.18%. Found: C, 64.82; H, 5.41; N, 16.12%.

1-(4-((2,4-dihydroxyphenyl)diazenyl)phenyl)ethanone (Table 2, **3j**): (0.218 g, 85%), as a brown solid, (recrystallized from acetone). IR (KBr) cm^{-1}: 3263.33, 3178.47, 1658.67, 1596.95, 1481.23, 1249.79, 1118.64, 840.91. UV (λ_{max} in DMSO): 410 nm. ^{1}H NMR ($CDCl_3$): 13.85 (NH, s), 7.97-8.1 (3H, m), 7.83-7.87 (2H, m), 7.77 (1H, d, *J*=8.8 Hz), 6.6 (1H, d, *J*=8 Hz), 6.4 (OH, 1H) 2.5 (3H, s). ^{13}C NMR: 26.5, 108.8, 103.9, 117.7, 125.8, 129.1, 122.9, 138.9, 157, 153, 162.1, 197. Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93%. Found: C, 65.84; H, 4.78; N, 10.72%.

N,*N*-dimethyl-4-((2-(trifluoromethyl)phenyl)diazenyl)aniline (Table 2, **3k**): (0.267 g, 91%), (recrystallized from acetone). IR (KBr) cm^{-1}: 1604.66, 1521.73, 1402.15, 1373.22, 1317.29, 1309.58, 1265.22, 1153.35, 1137.92, 1126.35, 1103.21, 1051.13. UV (λ_{max} in CH_2Cl_2): 430 nm. ^{1}H NMR ($CDCl_3$): 7.92 (2H, d of d , *J*=7.2, 2 Hz), 7.87 (2H, t, *J*=8.4), 7.59 (1H, t, *J*=7.2 Hz), 7.42 (1H, t, *J*=7.4 Hz), 6.75 (2H, d of d, *J*=7.2, 2 Hz) 3.1 (6H, t, *J*=20). ^{13}C NMR: 40.23, 116.2, 122.8, 125.6, 125.8, 126.2, 128.4, 132.3, 144, 150.3, 152.9. Anal. Calcd for $C_{15}H_{14}F_3N_3$: C, 61.43; H, 4.81; N, 14.33%. Found: C, 61.64; H, 4.72; N, 14.23%.

Sodium 4-((2-hydroxynaphthalen-1-yl)diazenyl)benzenesulfonate (Table 2, **3n**): (0.2905 g, 83%), (recrystallized from acetone). IR (KBr) cm^{-1}: 3423.41, 1620.09, 1506.30, 1398.3, 1122.49. UV (λ_{max} in DMSO): 446 nm. ^{1}H NMR (DMSO-d_6): 15.8 (1H, s), 8.52 (1H, d, *J*=7.6), 7.93 (1H, d, *J*=9.2 Hz), 7.79-7.71 (5H, m), 7.60 (1H, d, *J*=6.4 Hz), 7.44 (1H, d, *J*=6.4 Hz), 6.88 (1H, d, *J*=8.4 Hz). ^{13}C NMR: 119.7, 123, 125.7, 127.5, 128.7, 129.4, 132.38, 130.5, 130.5, 130.8, 130.9, 134.3, 141.8, 149.1, 159, 171.5. Anal. Calcd for $C_{16}H_{11}N_2NaO_4S$: C, 54.86; H, 3.16; N, 8.01%. Found: C, 54.80; H, 3.17; N, 8.06%.

1-(4-((4-(dimethylamino)phenyl)diazenyl)phenyl)ethanone (Table 2, **3o**): (0.248 g, 93%), (recrystallized from acetone). IR (KBr) cm^{-1}: 2918.10, 1670.24, 1606.59, 1523.66, 1365.51, 1267.14, 1161.07, 946.98, 831.26, 821.62. UV (λ_{max} in CH_2Cl_2): 480 nm. ^{1}H NMR ($CDCl_3$): 8.06 (2H, d, *J*=8.4), 7.89 (4H, t, *J*=8.4 Hz), 6.76 (2H, d, *J*=9.2 Hz), 3.11 (6H, t, *J*=20 Hz) 2.64 (3H, s). ^{13}C NMR: 26.7, 40.2, 111.4, 122.1, 125.5, 129.3, 136.9, 143.7, 152.9, 155.9, 197.5. Anal. Calcd for $C_{16}H_{17}N_3O$: C, 71.89; H, 6.41; N, 15.72%. Found: C, 71.79; H, 6.78; N, 15.46%.

1-((4-hydroxyphenyl)diazenyl)naphthalen-2-ol (Table 2, **3p**): (0.2245 g, 85%), (recrystallized from ethanol:water, 9:1). IR (KBr) cm^{-1}: 3424, 1598, 1458, 1279, 1216, 844, 744. ^{1}H NMR (Acetone-*d*$_6$): 14.97 (NH, s), 9.22 (OH, s) 8.82 (1H, d, *J*=8.4 Hz), 7.95 (2H, d, *J*=8.8 Hz), 7.94 (1H, d, *J*=9.6 Hz), 7.86 (1H, d, *J*=7.6 Hz), 7.86 (1H, d, *J*=7.6 Hz), 7.63 (1H, d, *J*=7.6 Hz), 7.46 (2H, d, *J*=7.6 Hz), 7.15 (1H, d, *J*=9.6 Hz), 7.08 (1H, d, *J*=8.8 Hz). ^{13}C NMR: 116.37, 120.6, 121.45, 123.38, 124.5, 127.9, 128.3, 128.41, 132.38, 135.24, 143, 143.6, 155.61, 160.06, 172. Anal. Calcd for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.58; N, 10.60%. Found: C, 72.92; H, 4.38; N, 10.58%.

1-((4-nitrophenyl)diazenyl)naphthalen-2-ol (Table 2, **3q**): (0.258 g, 88%), as a dark red solid, (recrystallized from ethanol:water, 9:1). IR (KBr) cm^{-1}: 3384, 1632, 1516, 1448, 1352, 1245, 1205, 805, 749. ^{1}H NMR ($CDCl_3$): 16.15 (NH, s), 8.51 (1H, d, *J*=8 Hz), 8.39 (2H, d, *J*=9.2 Hz), 8.01 (2H, d, *J*=9.2 Hz), 7.93 (1H, d, *J*=8.8 Hz), 7.71 (1H, d, *J*=7.6 Hz) 7.62 (1H, d, *J*=8 Hz), 7.53 (1H, d, *J*=8 Hz), 6.72 (1H, d, *J*=8.8 Hz). Anal. Calcd for $C_{16}H_{11}N_3O_3$: C, 65.53; H, 3.78; N, 14.33%. Found: C, 65.60; H, 3.67; N, 14.34%.

2-((2-hydroxynaphthalen-1-yl)diazenyl)benzoic acid (Table 2, **3r**): (0.225 g, 77%), as an orange red solid, (recrystallized from acetone). IR (KBr) cm^{-1}: 1712.67, 1604.66, 1558.38, 1504.37, 1396.37, 1257.50, 1110.92, 748.33. UV (λ_{max} in DMSO): 483 nm. ^{1}H NMR ($CDCl_3$): 16.4 (NH, s), 8.28 (1H, d, *J*=8 Hz), 8.178 (1H, d, *J*=7.2 Hz), 7.96 (1H, d, *J*=8 Hz), 7.55-7.47 (3H, m), 7.40-7.34 (2H, m), 7.05 (1H, d of d, *J*=7.2, 7.6 Hz), 6.51 (1H, d, *J*=9.6). Anal. Calcd for $C_{17}H_{12}N_2O_3$: C, 69.86; H, 4.14; N, 9.58 %. Found: C, 69.66; H, 4.51; N, 9.38%.

2-((2,4-dihydroxyphenyl)diazenyl)-5-methylbenzoic acid (Table 2, **3s**): (0.250 g, 92%), as a dark red solid, (purified by short column chromatography using n-hexane and ethyl acetate, 8:2). IR (KBr) cm^{-1}: 2923.88, 1620.09, 1427.23, 1380.94, 1265.22, 1211.21. UV (λ_{max} in DMSO): 405 nm. ^{1}H NMR

($CDCl_3$): 7.85-7.81 (3H, m), 7.31-7.33 (2H, m), 6.47 (2H, br, s), 2.35 (3H, s). Anal. Calcd for $C_{14}H_{12}N_2O_4$: C, 61.76; H, 4.44; N, 10.29%. Found: C, 62.2; H, 4.67; N, 10%.

4-((4-nitrophenyl)diazenyl)benzene-1,3-diol (Table 2, **3t**): (0.225 g, 87%), as an orange red solid, (recrystallized from ethanol:water, 9:1). IR (KBr) cm^{-1}): 3467.92, 1602.42, 1526.61, 1503.24, 1342.03, 1271.31, 1140.41. UV (λ_{max} in DMSO): 428 nm. ^1H NMR ($CDCl_3$): 8.71 (1H, t, *J*= 1.8 Hz,), 8.28-8.32 (1H, m), 8.23 (1H, t, *J*= 7.2 Hz), 7.95 (2H, d, *J*= 8.7 Hz), 7.69, (1H, t, *J*= 8.1 Hz), 6.99 (2H, d, *J*= 8.7 Hz), 5.37 (OH, br, 1H). ^{13}C NMR: 163.66, 157.03, 150.97, 149.07, 132.82, 130.54, 127.19, 121.60, 109.81, 103.44. Anal. Calcd for $C_{16}H_{12}N_2O_4S$: C, 58.53; H, 3.68; N, 8.53%. Found: C, 58.38; H, 3.79; N, 8.66%.

3. Results and discussion

Arene diazonium salts are highly useful intermediates in organic synthesis due to their rich reactivity and diverse transformations. Usually, they are synthesized around 10 °C, and to avoid their decomposition, are handled below 0 °C. In this new method, diazotization and diazo coupling reaction of aniline derivatives with electron withdrawing groups as well as electron-donating groups were examined under solvent-free conditions at room temperature. First, in order to optimize the conditions, different ratios of aniline and sodium nitrite were studied in the presence of various quantities of nano-γ-Fe_2O_3-SO_3H as a catalyst (Table 1, Entries 1-7). The best amount of catalyst was 0.65 g (Table 1, Entry 6). It should be emphasized that the presence of the catalyst is critical to a successful outcome, since no product was formed in the absence of the catalyst (Table 1, Entry 8).

Table 1

The process was carried out in two steps: the aromatic amine (1 mmol), nanomagnetic-supported sulfonic acid (0.65 g), sodium nitrite (2 mmol), and 0.1 mL of water were homogenized by grinding in a mortar with a pestle for a few minutes. Then the reaction mixture is ground for 5–10 min until the gas evolution completely stops. Then, coupling reagent was added to the diazonium salt and grinding continued for 10 min. the whole process of diazotization and diazo coupling took 10–20 minutes. The crude product was extracted with acetone or ethanol, and after evaporation of the solvent, the crude product was purified by recrystallization or short column chromatography. It is important to mention that our new conditions also provide a fast and facile work-up; after completion of the reaction, the mixture was triturated with hot ethanol or acetone. Within a few seconds, after stirring was stopped, the reaction mixture turned clear and the catalyst was deposited on the magnetic bar, which was easily removed with an external magnet, after being washed with acetone and dried in air, the nano-γ-Fe_2O_3-SO_3H catalyst could be used at least three times without significant loss of activity. As is indicated in Table 2, electron-deficient, -neutral and -rich aryl amines were all successfully transformed to the corresponding azo dyes. Also, the various coupling reagents were employed in this reaction and high yields were obtained.

Table 2

The intrinsic instability of diazonium compounds limits the applications of them. So in order to investigate the stability of the diazonium salts prepared by this method, some aryldiazonium salts supported on nanomagnetic-supported sulfonic acid were stored in a desiccator at room temperature. After the specified times in Table 3, coupling reagent was added to each salt and the reaction mixture was ground at room temperature. The products were extracted and the yields of azo dyes compared with the product provided with the corresponding fresh diazonium salts. As shown in Table 3, aryl diazonium nanomagnetic sulfates with electron-withdrawing groups on the aromatic rings were more stable than those with electron-donating groups because of the instability of the resulting aryl cation.

Table 3

Table 4 compares the efficiency of our method with other published results. As indicated in Table 4, the main advantage of this research is the creation of diazonium salts that are relatively stable at room temperature (Compared with rows 1-7). Other benefits of this method are the fast reaction time, clean and environmentally benign catalyst. Furthermore, easy isolation of the catalyst from the reaction mixture was enabled by use of an external magnet.

Table 4

4. Conclusion

This synthetic method combines several advantages: 1) First, aryl diazonium nanomagnetic sulfate is easily prepared in large quantities from aniline derivatives; 2) both reaction steps (diazotization–azo coupling) take place at room temperature; 3) the leaving group N_2 does not interfere with the reaction mixture; 4) the coupling reaction proceed with high chemo selectivity. 5) Easy magnetic separation of the catalyst eliminates the requirement of catalyst filtration after completion of the reaction. In the absence of a magnetic field, the catalyst disperses in the same manner as any nanoparticle. However, in the presence of a magnetic field, it can be selectively precipitated. This property enables it to be readily removed from the reaction vessel by a simple magnetic separation and may enable it to be re-dispersed and re-used again. 6) The whole process of diazotization-diazo coupling reaction take 10-20 minutes, thus the time factor is another advantage. For these reasons, we wish to report an efficient, rapid, and one pot procedure for the synthesis of azo dyes employing aryl diazonium nanomagnetic sulfates in the presence of activated aromatic compounds at room temperature.

4. Acknowledgements

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Captions

Scheme 1. One-pot diazotiation-diazo coupling reaction of aryl amines *via* aryl diazonium nanomagnetic sulfate.

Table 1

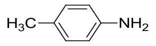
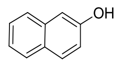
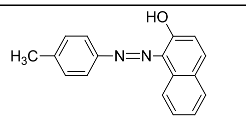
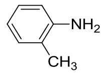
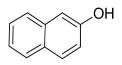
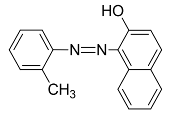
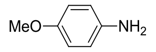
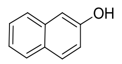
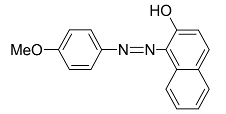
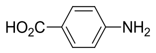
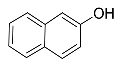
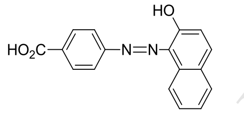
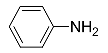
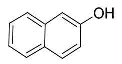
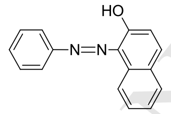
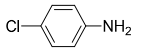
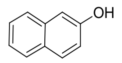
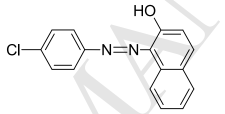
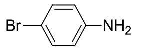
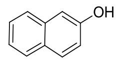
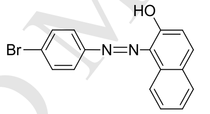
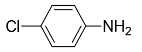
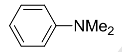
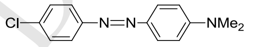
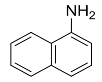
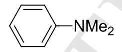
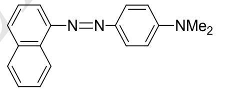
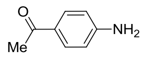
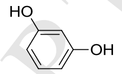
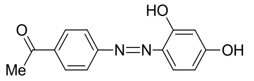
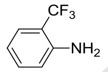
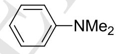
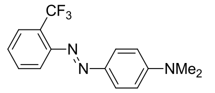
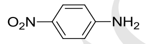
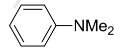
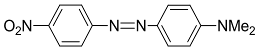
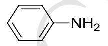
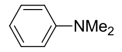
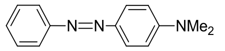
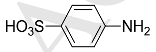
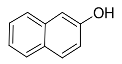
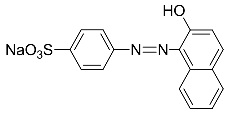
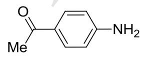
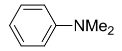
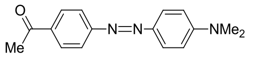
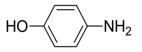
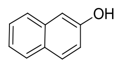
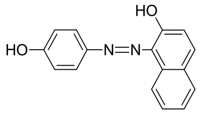
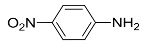
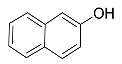
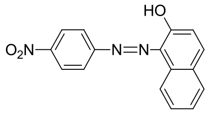
Effect of reagent and catalyst amounts on the synthesis of *N*,*N*-dimethyl-4-(phenyldiazenyl)aniline

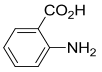
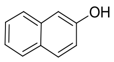
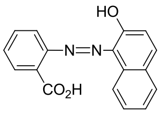
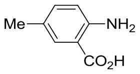
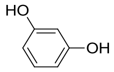
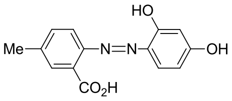
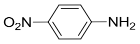
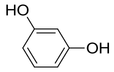
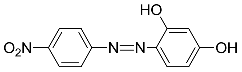
Entry	Sodium nitrite : aniline	γ-Fe_2O_3-SO_3H (g)	Yield (%)[a]
1	1:1	0.45	40
2	1:1	0.55	50
3	1:1	0.65	55
4	2:1	0.45	70
5	2:1	0.55	80
6	2:1	0.65	94
7	4:1	0.65	85
8	2:1	-	Trace

[a] Isolated yields.

Table 2

Diazotization and diazo coupling reaction of aromatic amines by nanomagnetic-supported sulfonic acid under solvent-free conditions at room temperature [a,b]

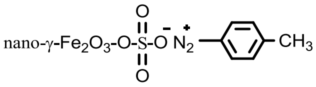
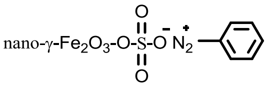
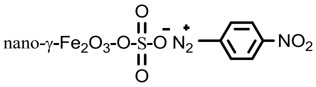
Entry	Substrate	Coupling reagent	Product	Product number	Time (min)	Yield (%)
1				**3a**	10	86
2				**3b**	20	81
3				**3c**	15	94
4				**3d**	20	85
5				**3e**	10	79
6				**3f**	15	95
7				**3g**	10	93
8				**3h**	10	90
9				**3i**	20	89
10				**3j**	10	85
11				**3k**	20	91
12				**3l**	10	90
13				**3m**	10	94
14				**3n**	20	83
15				**3o**	10	93
16				**3p**	20	85
17				**3q**	10	88

18				**3r**	20	77
19				**3s**	20	92
20				**3t**	10	87

[a] The yields refer to the isolated pure products.

[b] The products were characterized from their spectral data (IR, ^{1}H NMR, ^{13}C NMR, UV, CHN and mp) and compared with authentic samples [28-31].

Table 3 The stability of some aryl diazonium nano magnetic sulfates at room temperature[a,b]

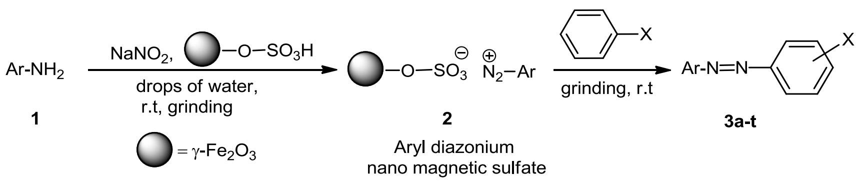
Diazonium salt	**Product**	**Yield (%)[a] after**			
		30 min	**1 day**	**2 days**	**3 days**
	**3a**	86	65	55	50
	**3e**	79	61	50	50
	**3q**	88	76	70	65

[a] The yields refer to the isolated pure products after adding 2-Naphthol into their corresponding diazonium salts within the specified time.

[b] Each yield of the product was compared with the product provided with the corresponding fresh diazonium salt.

Table 4 Comparison of diazotization of aromatic amines by nano-γ-Fe_2O_3-SO_3H with the reported values.

Entry	Condition	Time (min)	Yield (%)	Ref.
1	PTSA/MeCN/10-25 ºC	30	90	[32]
2	SiO_2-IL-ONO/HCl//0-5 ºC	20-40	74-92	[31]
3	IL-ONO/HCl/0-5 ºC	20-40	71-90	[30]
4	H_2SO_4/0-5 ºC	-	25-80	[33]
5	Activated clay with HCl /0-5 ºC	120	30-85	[34]
6	HCl(conc.)/0 ºC	45-60	65-85	[35]
7	Nano-BF_3.SiO_2/Solvent-free/r.t	6-7	77	[36]
8	$Fe(HSO_4)_3$/SiO_2/H_2O/r.t	3-20	80-97	[29]
9	wet SSA/Solvent-free/r.t	20-30	55-86	[37]
10	γ-Fe_2O_3-SO_3H/Solvent-free/ r.t	10-20	77-95	This work


Ar-NH2
NaNO2,
O—SO3H
drops of water,
r.t, grinding
1
= γ-Fe2O3
O—SO3
N2—Ar
2
Aryl diazonium
nano magnetic sulfate
X
grinding, r.t
Ar-N=N
X
3a-t