Reduction of Organic Azides to Amines using Reusable Fe$_3$O$_4$ Nanoparticles in Aqueous Medium

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1.0 Preparation of Fe₃O₄ Nanoparticle: Fe₃O₄ Nanoparticles were prepared following a literature procedure. A mixture of FeCl₃•6H₂O (2.074 g, 8 mmol) and FeCl₂•4H₂O (0.80 g, 4 mmol) were dissolved in degassed Millipore water (200 mL) under an inert atmosphere. A solution of ammonia hydroxide solution was slowly added to the mixture. Magnetic nanoparticles were precipitated at pH = 9.0. The resulting black suspension was stirred for 1 h. The black precipitate was washed with water for several times and centrifuged until neutral pH and then washed with 15 mL of ethanol and finally dried under vacuum.

Powder X-ray diffraction studies of Fe₃O₄:

Table S1: XRD data of magnetite nanoparticles

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<th>Plane</th>
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<th>(400)</th>
<th>(422)</th>
<th>(511)</th>
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<tr>
<td>2theta of Fe₃O₄</td>
<td>30.26</td>
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<td>43.18</td>
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<td>62.76</td>
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<tr>
<td>Interlayer spacings (d) of Fe₃O₄</td>
<td>0.295</td>
<td>0.252</td>
<td>0.209</td>
<td>0.171</td>
<td>0.161</td>
<td>0.148</td>
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<tr>
<td>2theta of recovered Fe₃O₄</td>
<td>30.20</td>
<td>35.62</td>
<td>43.26</td>
<td>53.74</td>
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<td>Interlayer spacings (d) of recovered Fe₃O₄</td>
<td>0.296</td>
<td>0.252</td>
<td>0.209</td>
<td>0.170</td>
<td>0.161</td>
<td>0.148</td>
</tr>
<tr>
<td>Standard Fe₃O₄ (d)</td>
<td>0.296</td>
<td>0.253</td>
<td>0.209</td>
<td>0.171</td>
<td>0.161</td>
<td>0.148</td>
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The XRD diffraction patterns of the prepared Fe₃O₄ and the recovered Fe₃O₄ were overlaps with those of standard JCPDS database for magnetite. The interlayer spacings (d) of the prepared Fe₃O₄ and the recovered Fe₃O₄ were calculated using Bragg’s equation and agree well with those of standard JCPDS database for magnetite. The average particle size for the prepared Fe₃O₄ was found to be 10.14 nm, which was calculated from the above XRD figure for magnetite, using the Debye-Scherrer equation on the full widths at half maximum of the strongest (100%) reflection at 2θ is 35.64 °. After 10 recycling experiments, the average size was found to be 11.04 nm calculated from the same peak value at 2θ = 35.62 °.
Atomic force microscopy images of Fe₃O₄:

Figure S1. Atomic force electron micrograph of Fe₃O₄ magnetic nanoparticles (a, b) and the height profile (c).

Figure S2. Atomic force electron micrograph of recovered Fe₃O₄ magnetic nanoparticles (a, b) and the height profile (c) after 10\textsuperscript{th} catalytic cycle.
2.0 Preparation of azides:

General procedure A (GP-A) for the preparation of azides from amines:

Aromatic amine 2 (10 mmol, 1.0 equiv) was suspended in 17% hydrochloric acid (65 mL) at room temperature. The solution was cooled to 0 °C using an ice bath. Then NaNO₂ (1.5 equiv) in 5 mL water was added in small portions. After stirring at 0 °C for 20-30 min, an aqueous solution of NaN₃ (1.5 equiv) was slowly added and the mixture was stirred for additional 2 h at room temperature. After completion, the reaction mixture was extracted with diethyl ether (3 x 40 mL). The combined organic fractions were washed with saturated NaHCO₃ solution (2 x 40 mL) and brine (2 x 40 mL). The organic fractions were dried over Na₂SO₄ and evaporated under reduced pressure to give the desired azides 1. The azides were used for the reduction reaction without further purification.

Phenyl azide 1d: Using GP-A, aniline 2d (3.0 g, 32.21 mmol) provided azide 1d (2.69 g, 70%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): 7.36 (t, J = 7.6 Hz, 2H), 7.15 (td, J = 7.6, 0.7 Hz, 1H), 7.04 (dd, J = 7.6, 0.7 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): 139.9, 129.7, 124.8, 119.0.

1-Azidonaphthalene 1e: Using GP-A, naphthalene-1-amine 2e (800 mg, 5.59 mmol) afforded the compound 1e (567 mg, 60%) as a yellow liquid. ¹H NMR (400 MHz, CDCl₃): 8.23-8.20 (m, 1H), 8.05-8.10 (m, 1H), 7.82-7.75 (d, J = 8.4 Hz, 1H), 7.52-7.42 (m, 3H), 7.23 (d, J = 7.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): 127.7, 126.9, 126.1, 125.6, 124.7, 122.5, 113.9.

1-Azido-4-bromobenzene 1f: Using GP-A, 4-bromo aniline 2f (700 mg, 4.07 mmol) provided 1f (733 mg, 91%) as a yellow oil. ¹H NMR (400 MHz, CDCl₃): 7.46-7.43 (m, 2H), 6.90-6.88 (d, 2H); ¹³C NMR (100 MHz, CDCl₃): 139.1, 132.7, 120.6, 117.7.

4-Azido-1-bromo-2-methylbenzene 1g: Using GP-A, 1-bromo 2-methyl aniline 2g (500 mg, 2.69 mmol) provided the azide 1g (513 mg, 90%) as a brown oil. ¹H NMR (400 MHz, CDCl₃): 7.46 (d, J = 10.6 Hz, 1H), 6.88 (d, J = 3.0 Hz, 1H), 6.72 (dd, J = 10.6, 3.6 Hz, 1H), 2.38 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 139.5, 139.1, 133.3, 121.1, 120.2, 117.9, 22.9; IR: 3306.0, 3224.1, 2954.7, 2504.0, 2425.3, 2324.3, 2241.2, 2110.0, 2065.3, 1602.2, 1474.2, 1380.2, 1304.7, 1202.3, 1149.4; HRMS (ESI) calcd for C₇H₇BrN₃ [M+H]⁺: 211.9823; Found: 211.9785.
2-Azido-1-bromo-4-fluorobenzene 1h.\textsuperscript{18f} Using GP-A, 1-bromo 5-fluoro aniline 2h (1.0 g, 5.26 mmol) afforded the compound 1h (966 mg, 85%) as a yellow solid. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): 7.49 (dd, \(J = 10.9, 7.1\) Hz, 1H), 6.90 (dd, \(J = 11.1, 3.0\) Hz, 1H), 6.75 (td, \(J = 10.5, 3.0\) Hz, 1H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): 163.6, 161.1, 140.2, 140.1, 134.7, 134.6, 113.4, 113.2, 108.3, 108.3, 107.2, 106.9.

Ethyl 4-azidobenzoate 1k: Using GP-A, ethyl 4-aminobenzoate 2k (500 mg, 3.03 mmol) provided the compound 1k (549 mg, 95%) as a yellow oil. \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}): 8.04-8.02 (m, 2H), 7.06-7.05 (m, 2H), 4.36 (q, \(J = 7.1\) Hz, 1H), 1.38 (t, \(J = 7.1\) Hz, 1H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}): 165.8, 144.6, 131.3, 127.1, 118.8, 61.0, 14.3.

5-Azidonaphthalen-1-ol 1o: Using GP-A, 5-aminonaphthalen-1-ol 2o (500 mg, 3.14 mmol) afforded the compound 1o (347.1 mg, 60%) as a yellowish brown solid. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): 7.99 (d, \(J = 10.7\) Hz, 1H), 7.68 (d, \(J = 10.5\) Hz, 1H), 7.49-7.45 (m, 1H), 7.34-7.27 (m, 2H), 6.86 (d, \(J = 9.4\) Hz, 1H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): 151.2, 136.3, 127.6, 126.1, 125.4, 124.9, 118.5, 115.1, 114.5, 109.5.

2-Azidothiazole 1q: Using GP-A, 2-amino thiazole 2q (500 mg, 4.99 mmol) provided the azide 1q (346 mg, 55%) as a light yellow solid. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): 7.43 (d, \(J = 4.6\) Hz, 1H), 6.98 (d, \(J = 4.4\) Hz, 1H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): 162.9, 140.4, 115.7.

General procedure B (GP-B) for the preparation of azides from amines: To a solution of the amines 2 (14.5 mmol) in 17% hydrochloric acid (40 mL), an aqueous solution of sodium nitrite (21.75 mmol in 5 mL, 1.5 equiv) was added slowly at 0 °C. After stirring for 30 min, an aqueous solution of sodium azide (21.75 mmol in 10 mL, 1.5 equiv) was added at the same temperature and the reaction was stirred additional one hour at room temperature. The reaction mixture was filtered and washed with water (3 x 20 mL) and dried under vaccum to give the desired azides 1 in quantitative yield.

4-Azidobenzoic acid 1i: Using GP-B, 4-amino benzoic acid 2i (1.0 g, 7.29 mmol) provided the compound 1i (927 mg, 78%) as light brown solid. \textsuperscript{1}H NMR (400 MHz DMSO-d\textsubscript{6}): 12.98 (s, 1H), 7.97-7.94 (m, 2H), 7.23-7.20 (m, 2H); \textsuperscript{13}C NMR: (125 MHz, DMSO-d\textsubscript{6}): 166.5, 143.9, 131.2, 127.3, 119.1.
3-Azidobenzoic acid 1j.\textsuperscript{18a} Using GP-B, 3-amino benzoic acid 2j (1.0 g, 7.29 mmol) afforded the azide 1j (952 mg, 80%) as a brownish yellow solid. \textsuperscript{1}H NMR (400 MHz DMSO-d$_6$): 13.2 (s$_{br}$, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.55-7.50 (m, 2H), 7.34 (d, J = 10.1 Hz, 1H); \textsuperscript{13}C NMR: (100 MHz, DMSO-d$_6$): 116.5, 139.9, 132.6, 130.4, 125.9, 123.5, 123.5, 119.4.

4-Nitrophenyl azide 1l:\textsuperscript{7h} Using GP-B, 4-nitro aniline 2l (800 mg, 5.79 mmol) afforded the azide 1l (902 mg, 95%) as a yellow solid. \textsuperscript{1}H NMR (400 MHz, CDCl$_3$): 8.23 (d, J = 9.0 Hz, 2H), 7.13 (d, J = 9.0 Hz, 2H); \textsuperscript{13}C NMR (100 MHz, CDCl$_3$): 146.8, 144.6, 125.6, 119.4.

General procedure C (GP-C) for the preparation of azides from bromides:\textsuperscript{17g} A mixture of bromide 3 (2 mmol), NaN$_3$ (4 mmol), sodium ascorbate (0.1 mmol), CuI (0.2 mmol), DMEDA 4 (0.3 mmol) in 5 mL EtOH–H$_2$O (7:3) were heated at 80 °C until the completion of the starting bromide 3 (monitored by TLC). The reaction mixture was cooled to RT, extracted with diethyl ether and purified by flash chromatography to give the corresponding azides 1.

4-Azidoaniline 1a:\textsuperscript{7j} Using GP-C, 4-bromo aniline 3a (500 mg, 2.9 mmol) afforded the azide 1a (291 mg, 75%) as a brown solid. \textsuperscript{1}H NMR (400 MHz, CDCl$_3$): 6.84 (d, J = 10.7 Hz, 2H), 6.67 (d, J = 10.9 Hz, 2H), 3.65 (s$_{br}$, 2H); \textsuperscript{13}C NMR (100 MHz, CDCl$_3$): 143.7, 130.0, 119.9, 116.2.

1-Azido-4-methoxybenzene 1b:\textsuperscript{7b} Using GP-C, 4-methoxy bromide 3b (1.0 g, 5.3 mmol) provided the azide 1b (773 mg, 97%) as a brown oil.\textsuperscript{1}H NMR (400 MHz, CDCl$_3$): 6.95 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl$_3$): 156.9, 132.2, 119.9, 115.0, 55.4.

2-Azidopyridine 1p:\textsuperscript{7m} Using GP-C, 2-bromo pyridine 3c (500 mg, 3.2 mmol) provided the compound 1p (262 mg, 69%) as a brown solid. \textsuperscript{1}H-NMR (400MHz, CDCl$_3$): 8.89 (dt, J = 7.0 Hz, 1.1 Hz, 1H), 8.07 (dt, J = 9.0 Hz, 1.1 Hz, 1H), 7.73 (ddd, J = 9.0 Hz, 7.0 Hz, 1.1 Hz, 1H), 7.30 (td, J = 6.9 Hz, 1.0 Hz, 1H); \textsuperscript{13}C-NMR (100 MHz, CDCl$_3$): 148.5, 131.9, 125.4, 116.6, 115.9.

General procedure D (GP-D) for the preparation of sulfonyl azides 1: A solution of sodium azide (39.3 mmol, 1.5 eq) in water (15 mL) was added drop wise over 1 h to a solution of sulphonyl chloride (26.2 mmol, 1.0 eq) in acetone (50 mL) at 0 °C. The reaction mixture was allowed to warm up to room temperature and stirred for 16 h. After completion of reaction (monitored by TLC) acetone was
removed under reduced pressure and the reaction mixture was extracted with ether (2 x 40 mL). The combined ether layers were washed with 5% Na₂CO₃ (2 x 20 mL) and water (2 x 20 mL), dried over Na₂SO₄ evaporated under reduced pressure to obtain the desired sulphonyl azide 1, which were used for the reduction reaction without further purification.

**Tosyl azide 1m**: Using GP-D, tosyl chloride 5a (500 mg, 2.62 mmol) afforded the azide 1m (460 mg, 89%) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃): 7.83 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 2.48 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): 143.6, 139.1, 129.7, 126.4, 21.5.

**Dansyl azide 1n**: Using GP-D, dansyl chloride 5b (100 mg, 0.37 mmol) afforded the azide 1n (80.9 mg, 79%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃): 8.67 (d, J = 8.4 Hz, 1H), 8.35-8.33 (m, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.66-7.56 (m, 2H), 7.24 (d, J = 7.9 Hz, 1H), 2.90 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): 152.1, 133.6, 132.6, 130.0, 129.6, 129.2, 122.9, 118.7, 115.8, 45.3.

**Synthesis of N-(4-azidophenyl)acetamide 1c**: To a solution of 4-azido aniline 1a (200 mg, 1.491 mmol, 1.0 equiv) in CH₂Cl₂ (4 mL) added acetic anhydride (0.168 mL, 1.789 mmol, 1.2 equiv). The reaction mixture was stirred at room temperature for 1 h. Then the reaction mixture was washed with a saturated solution of Na₂CO₃, the organic extracts were dried with Na₂SO₄ and removed under reduced pressure. The residue was purified by flash chromatography to afford the acetamide 1c (210 mg, 80%). ¹H NMR (400 MHz, DMSO-d₆): 10.01 (sbr, 1H), 7.61 (d, J = 11.2 Hz, 2H), 7.04 (d, J = 10.9 Hz, 2H), 2.03 (s, 3H); ¹³C NMR (100 MHz, DMSO-d₆): 168.2, 136.7, 133.5, 120.4, 119.4, 23.9.

**General procedure for the reduction of azides using Fe₃O₄**: To a solution of azide 1 (1 mmol, 1 equiv) in water (4.0 mL), Fe₃O₄ (116 mg, 0.5 mmol) and hydrazine monohydrate (0.243 mL, 5 mmol) were added to the mixture. The reaction mixture was refluxed or heated in a sealed tube at 120 °C under an argon atmosphere until completion, as monitored by TLC. The reaction was cooled and the Fe₃O₄-MNPs were separated using a magnet. The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic extracts were washed with water and brine, dried over Na₂SO₄ and evaporated under reduced pressure. The crude product was purified by flash chromatography (EtOAc/hexanes eluent) to afford the desired pure amine. Most of the amines were analytically pure.
before flash chromatography. The recovered catalyst was washed with methanol (2 x 5 mL), dried under vacuum, and reused for the next cycle of the reaction.

3.0 Analytic data of amines

**Benzene-1,4-diamine 1a:** Yield: 99%, obtained as a brown solid; $^1$H NMR (400 MHz, CDCl$_3$): 6.57 (s, 4H), 3.30 ($s_{br}$, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$): 137.8, 115.9.

**4-Methoxyaniline 2b:** Yield: 99%, obtained as a white solid; $^1$H NMR (400 MHz, CDCl$_3$): 6.75 (d, $J$ = 6.6 Hz, 2H), 6.64 (d, $J$ = 6.6 Hz, 2H), 3.75 (s, 3H), 3.39 ($s_{br}$, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): 152.7, 139.9, 116.3, 114.7, 55.6.

**N-(4-Aminophenyl)acetamide 2c:** Yield: 85%, obtained as a white solid; $^1$H NMR (400 MHz, DMSO-$d_6$): 9.47 (s, 1H), 7.18 (d, $J$ = 7.6 Hz, 2H), 6.47 (d, $J$ = 8.0 Hz, 2H), 4.82 (s, 2H), 1.94 (s, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$): 167.2, 144.6, 128.6, 120.8, 113.8, 23.7.

**Aniline 2d:** Yield: 90%; obtained as a colorless oil; $^1$H NMR (400 MHz, CDCl$_3$): 7.17 (m, 2H), 6.77 (t, $J$ = 9.2 Hz, 1H), 6.69 (m, 2H), 3.53 ($s_{br}$, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): 146.3, 129.2, 118.5, 115.1.

**Naphthalen-1-amine 2e:** Yield: 84%; obtained as a brown solid; $^1$H NMR (400 MHz, CDCl$_3$): 7.88-7.83 (m, 2H), 7.49-7.53 (m, 2H), 7.39-7.34 (m, 2H), 6.81 (dd, $J$ = 6.6, 1.5 Hz, 1H), 4.07 ($s_{br}$, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): 142.0, 134.2, 128.4, 126.3, 125.7, 124.7, 123.5, 120.7, 118.8, 109.6.

**4-Bromoaniline 2f:** Yield: 98%; obtained as a colorless solid; $^1$H NMR (400 MHz, CDCl$_3$): 7.22 (d, $J$ = 8.7 Hz, 2H), 6.54 (d, $J$ = 8.7 Hz, 2H), 3.52 ($s_{br}$, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): 145.3, 131.9, 116.6, 110.1.

**4-Bromo-3-methylaniline 2g:** Yield: 99%; obtained as a light brown solid; $^1$H NMR (400 MHz, CDCl$_3$): 7.26 (d, $J$ = 8.4 Hz, 1H), 6.57 (d, $J$ = 2.7 Hz, 1H), 6.39 (dd, $J$ = 2.7, 8.4 Hz, 1H), 3.59 ($s_{br}$, 2H), 2.29 (s, 3H); $^{13}$C NMR (400 MHz, CDCl$_3$): 145.6, 138.4, 132.7, 117.4, 114.2, 112.9, 22.9.

**2-Bromo-5-fluoroaniline 2h:** Yield: 81%; obtained as a yellow solid; $^1$H NMR (400 MHz, CDCl$_3$): 7.32 (dd, $J$ = 9.0, 6.0 Hz, 1H), 6.48 (d, $J$ = 10.0, 3.0 Hz, 1H), 6.36 (dd, $J$ = 9.0, 3.0 Hz, 1H), 4.18 ($s_{br}$, 3H).
2H); $^{13}$C NMR (100 MHz, CDCl$_3$): 164.1, 161.6, 145.4, 145.2, 133.3, 133.2, 106.4, 106.2, 103.4, 103.3, 102.5, 102.3.

4-Aminobenzoic acid 2i: Yield: 92%; obtained as a colorless solid; $^1$H NMR (400 MHz, DMSO-d$_6$): 11.96 (s, 1H), 7.61-7.65 (m, 2H), 6.54-6.58 (m, 2H), 5.86 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-d$_6$): 167.6, 153.2, 131.3, 117.0, 112.6.

3-Aminobenzoic acid 2j: Yield: 98%; obtained as a yellow solid; $^1$H NMR (400 MHz, DMSO-d$_6$): 7.18 (s, 1H), 7.09 (m, 2H), 5.61 (s, 1H); $^{13}$C NMR (100 MHz, DMSO-d$_6$): 168.0, 148.9, 131.4, 128.9, 118.0, 116.7, 114.5.

Ethyl 4-aminobenzoate (2k): Yield: 81%; obtained as a colorless solid; $^1$H NMR (400 MHz, CDCl$_3$): 7.85 (d, $J$ = 8.5 Hz, 2H), 6.62 (d, $J$ = 8.7 Hz, 2H), 4.30 (q, $J$ = 7.1 Hz, 2H), 4.08 (s, 2H), 1.35 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 166.7, 150.7, 131.5, 119.9, 113.7, 60.3, 14.4.

4-Methylbenzenesulfonamide 2m: Yield: 99%; obtained as a white solid; $^1$H NMR (400 MHz, CDCl$_3$): 7.80 (d, $J$ = 10.1 Hz, 2H), 7.30 (d, $J$ = 10.0 Hz, 2H), 4.97 (s$_{br}$, 1H), 2.42 (s, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): 146.2, 135.4, 130.2, 127.5, 21.7.

Dansyl amine 2n: Yield: 99%; obtained as a white solid; $^1$H NMR (400 MHz, DMSO-d$_6$): 8.41-8.40 (d, $J$ = 8.4 Hz, 1H), 8.23-8.21 (d, $J$ = 8.8 Hz, 1H), 8.10-8.09 (m, 1H), 7.60-7.57 (m, 4H), 7.23-7.22 (d, $J$ = 8.4 Hz), 2.78 (s, 6H); $^{13}$C NMR (DMSO-d$_6$, 100 MHz): 151.8, 139.8, 129.5, 129.4, 129.3, 128.3, 126.9, 124.1, 119.8, 115.6, 45.5.

5-Aminonaphthalen-1-ol 2o: Yield: 82%; obtained as a brown solid; $^1$H NMR (400 MHz, DMSO-d$_6$): 9.78 (s, 1H), 7.47 (d, $J$ = 10.6 Hz, 1H), 7.35 (d, $J$ = 10.3, 1H), 7.13 (m, 2H), 6.78 (d, $J$ = 9.18 Hz, 1H), 6.64 (d, $J$ = 9.2 Hz, 1H), 5.54 (s, 2H); $^{13}$C NMR (100 MHz, DMSO-d$_6$): 153.1, 144.3, 125.7, 125.2, 124.1, 123.9, 113.0, 109.7, 107.8.

Pyridin-2-amine 2p: Yield: 97%; obtained as a colourless solid; $^1$H NMR (400 MHz, CDCl$_3$): 8.04 (d, $J$ = 6.87 Hz, 1H), 7.41-7.37 (m, 1H), 6.63-6.59 (m, 1H), 6.47 (d, $J$ = 10. 6 Hz, 1H), 4.51 (s$_{br}$, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): 158.3, 148.0, 137.6, 113.9, 108.5.
**Thiazol-2-amine 2q:** \(^{18b}\) Yield: 99%; obtained as a light yellow solid; \(^1\)H NMR (400 MHz, CDCl\(_3\)): 7.05 (d, J = 4.59, 1H), 6.49 (d, J = 4.57, 1H), 5.4 (s\(_{br}\), 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 168.5, 138.6, 108.3.
4.0 NMR spectra of all the compounds

$^1$H-NMR and $^{13}$C-NMR of Compound 1a:
$^1$H-NMR and $^{13}$C-NMR of Compound 2a:
$^1$H-NMR and $^{13}$C-NMR of Compound 1b:
$^1$H-NMR and $^{13}$C-NMR of Compound 2b:
$^1$H-NMR and $^{13}$C-NMR of Compound 1c:
$^1$H-NMR and $^{13}$C-NMR of Compound 2c:
$^1$H-NMR and $^{13}$C-NMR of Compound 1d:
$^1$H-NMR and $^{13}$C-NMR of Compound 2d:
$^1$H-NMR and $^{13}$C-NMR of Compound 1e:
$^1$H-NMR and $^{13}$C-NMR of Compound 2e:
$^1$H-NMR and $^{13}$C-NMR of Compound 1f:
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$^1$H-NMR and $^{13}$C-NMR of Compound 1k:
$^1$H-NMR and $^{13}$C-NMR of Compound 2k:
$^1$H-NMR and $^{13}$C-NMR of Compound 11: 

![NMR Spectra of Compound 11]
$^1$H-NMR and $^{13}$C-NMR of Compound 1m:
$^1$H-NMR and $^{13}$C-NMR of Compound 2m:
$^1$H-NMR and $^{13}$C-NMR of Compound 1n:
$^1$H-NMR and $^{13}$C-NMR of Compound 2n:
$^{1}H$-NMR and $^{13}C$-NMR of Compound 10:
$^{1}H$-NMR and $^{13}C$-NMR of Compound 2o:
$^{1}$H-NMR and $^{13}$C-NMR of Compound 1p:
$^1$H-NMR and $^{13}$C-NMR of Compound 2p:
$^1$H-NMR and $^{13}$C-NMR of Compound 1q:
$^1$H-NMR and $^{13}$C-NMR of Compound 2q: