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Zinc-mediated efficient and selective reductive aza-Claisen rearrangement of *N*-allyl- and *N*-propargylaminoanthraquinones in ionic liquid

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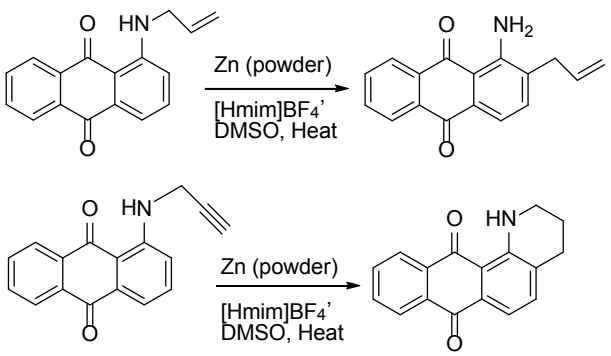
Graphical Abstract:



Abstract: An efficient method is described for the first time for reductive aza-Claisen rearrangement of 1-(*N*-allylamino) anthraquinones to 1-amino-2-(prop-2'-enyl)anthraquinones using zinc powder in 1-methylimidazolium tetrafluoroborate ([Hmim] BF_4) as an ionic liquid in good to excellent yields. Extending of this method on 1-(*N*-propargylamino)anthraquinones causes the production of 1,2,3,4-tetrahydronaphtho[2,3-*h*]quinoline-7,12-diones containing a newly synthesized six membered heterocyclic ring on anthraquinone core via performing this reductive [3,3] sigmatropic reaction followed by cyclization in a tandem manner. These rearrangements can be executed even in the presence of some other functional groups with excellent chemoselectivity.

Key words: *N*-Allylaminoanthraquinone, *N*-propargylaminoanthraquinone, zinc powder, reductive aza-Claisen rearrangement, ionic liquid

1. Introduction

Anthraquinone derivatives form a very important group in organic chemistry. These compounds have useful and important applications in different fields such as textile dyestuffs [1], colorimetric sensor systems [2,3], and pulp industry [4] and contain a lot of interesting and desired properties such as antioxidant [5], antifungal [6], enzyme inhibitor, and anti-Alzheimer [7], antiarthritic [8], antimalarial [9], hepatoprotective, neuroprotective, antidiabetes, and antiulcer [10], antimicrobial and antiviral [11], anticancer [12-16], laxative [17], and antiinflammatory [18]. Despite this importance, there are few ways for functionalization of anthraquinones. This is probably related to relative inertness of anthraquinone nucleus to perform electrophilic substitution reactions. Fortunately, the Claisen rearrangement [19] can be a solution for this matter and derivation of these valuable compounds. Despite different reports about this rearrangement on prop-2′-enyl(allyl)oxyanthraquinone derivatives [20, 21], as far as we know, there is no report about the aza-Claisen rearrangement [22-25] on anthraquinone systems. It must be noted that aza-Claisen rearrangement is generally less facile than its oxy-version, requires harsher reaction conditions, and affords lower yields of rearranged products [19, 25]. Now in the present work in continuation of our previous studies about this rearrangement [26-28] and also due to the importance of ionic

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liquids as environmentally friendly solvents in organic synthesis, we describe for the first time an efficient and selective method for the reductive aza-Claisen rearrangement of 1-(*N*-allylamino)anthraquinones to 1-amino-2-(prop-2′-enyl) anthraquinones using zinc powder in 1-methylimidazolium tetrafluoroborate ([Hmim] BF_4) [29] as an ionic liquid and a small amount of DMSO (Figure 1).

2. Experimental

Solvents, reagents, and chemicals were obtained from Merck, Fluka, or Aldrich chemical companies. Substrates and products were characterized by their physical and spectral data. Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer RXI spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded on Brucker Avance 300 and 400 spectrometers. Also, elemental analyses were performed using an Elementar vario EL III analyzer. Melting points were determined in open capillary tubes in an Electrothermal 9100 melting point apparatus. Thin layer chromatography (TLC) was carried out on silica gel 254 analytical sheets obtained from Fluka.

2.1. Typical procedure for the conversion of 1-aminoanthraquinone (3) to 1-(N-prop-2′-enylamino)anthraquinone (1)

Sodium hydroxide (1 mmol, 0.04 g) was added to a flask containing a solution of **3** (1 mmol, 0.22 g) in DMF (5 mL). The reaction mixture was stirred at 75 °C for 20 min so that its color changed from red to black. Next, allyl bromide (3 mmol, 0.26 mL) was added and stirring was continued for 6 h. Sodium hydroxide (0.5 mmol, 0.02 g) and then (after 15 min) allyl bromide (1 mmol, 0.09 mL) were added again and stirring was continued until TLC showed the completion of the reaction (30 h). The reaction mixture was cooled to room temperature and poured into distilled water (30 mL). The obtained precipitate was filtered and washed with distilled water (2 × 15 mL). **1** was obtained after column chromatography of this precipitate using a mixture of *n*-hexane and ethyl acetate (20:1) in 90% yield (0.24 g).

Similarly, 1-(*N*-prop-2′-ynylamino)anthraquinones were also synthesized from the reaction of 1-aminoanthraquinones with propargyl bromide via the above procedure.

2.2. Typical procedure for the reductive aza-Claisen rearrangement of 1-(*N*-prop-2′-enylamino)anthraquinone (1) to 1-amino-2-(prop-2′-enyl)anthraquinone (2)

Zinc powder (2 mmol, 0.13 g) was added to a flask containing a stirring solution of **1** (1 mmol, 0.26 g) in a mixture of [Hmim] BF_4 (0.25 g) and DMSO (2 drops) in an oil bath at 160 °C. The progress of the reaction was monitored by TLC. After completion of the reaction (1 h), the reaction mixture was cooled to room temperature. Dichloromethane (2 × 20 mL) was added to it and then filtered. The organic layer was washed with distilled water (2 × 30 mL), saturated $NaHCO_3$ (40 mL), and finally brine (40 mL) and evaporated after drying on calcium chloride. **2** was obtained after column chromatography of crude mixture on silica gel 60 using petroleum ether: ethyl acetate (40:1) as eluent in 90% yield (0.24 g) together with **3** in 6% yield (0.013 g).

Similarly, the reductive aza-Claisen rearrangement of 1-(*N*-prop-2′-ynylamino)anthraquinones were also carried out via this procedure except that the reaction temperature dropped to 140 °C.

2.3. Data

2.3.1. *N*-Allyl- and *N*-propargylaminoanthraquinones

1-(*N*-Prop-2′-enylamino)anthraquinone (1)

Dark red powder; mp = 122–124 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.96–4.00 (m, 2H), 5.23–5.26 (dd, 1H, *J* = 10.3, 1.2 Hz), 5.31–5.37 (dd, 1H, *J* = 17.2, 1.2 Hz), 5.92–6.05 (m, 1H), 6.98–7.01 (d, 1H, *J* = 8.4 Hz), 7.50–7.57 (m, 2H), 7.68–7.75 (m, 2H), 8.20–8.26 (m, 2H), 9.84 (s, br, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 45.1, 113.1, 115.8, 116.6, 118.1, 126.6, 132.91, 132.97, 133.6, 133.7, 133.8, 134.5, 134.9, 135.1, 151.5, 183.6, 185.0 ppm; IR (KBr): 3422 (br), 3070 (w), 2924 (m),

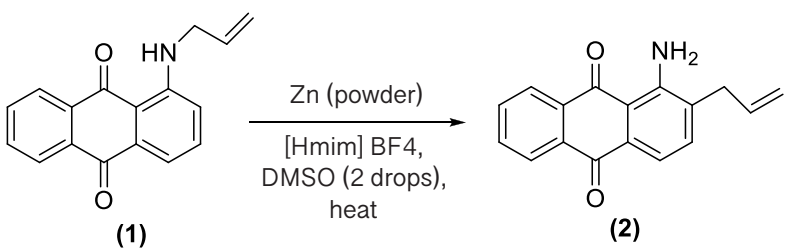


Figure 1. Reductive aza-Claisen rearrangement of 1-(*N*-allylamino)anthraquinone (**1**) to 1-amino-2-(prop-2′-enyl)anthraquinone (**2**) using zinc powder in ionic liquid.

2852 (w), 1651 (m), 1633 (m), 1628 (s), 1595 (s), 1303 (s), 1272 (s), 1071 (s), 802 (w), 735 (w), 708 (m) cm^{-1}; Anal. Calcd for $C_{17}H_{13}O_2N$: C, 77.56; H, 4.94; N, 5.32. Found: C, 77.01; H, 4.92; N, 4.96.

1-Amino-5-(*N*- prop-2′-enylamino)anthraquinone (4)

Pale red crystals; mp = 158 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.98 (s, 2H), 5.22–5.25 (d, 1H, *J* = 10.1 Hz), 5.31–5.36 (d, 1H, *J* = 17.1 Hz), 5.94–6.03 (m, 1H), 6.45–6.95 (m, 4H),7.39–7.61 (m, 4H), 9.83 (br, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 45.1, 113.3, 113.6, 115.1, 116.4, 116.5, 116.9, 121.6, 133.7, 134.5, 135.0, 135.9, 139.2, 150.6, 151.2, 185.4, 185.6 ppm; IR (KBr): 3415 (br), 3285 (br), 3012 (w), 2955 (w), 2865 (w), 1671 (s), 1650 (s), 1607 (s), 1533 (s), 1407 (s), 1366 (w), 1253 (s), 1090 (w), 893 (w), 793 (w), 722 (w) cm^{-1}; Anal. Calcd for $C_{17}H_{14}O_2N_2$: C, 73.38; H, 5.03; N, 10.07. Found: C, 73.28; H, 5.01; N, 10.01.

1,5-Bis(*N*- prop-2′-enylamino)anthraquinone (6)

Dark red powder; mp = 163–165 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.98 (s, br, 4H), 5.21–5.25 (d, 2H, *J* = 10.1 Hz), 5.30–5.36 (d, 2H, *J* = 17.2 Hz), 5.92–6.03 (m, 2H), 6.91–6.93 (d, 2H, *J* = 8.0 Hz), 7.46–7.57 (m, 4H), 9.82 (br, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 45.6, 115.4, 116.9, 117.1, 127.1, 134.2, 135.4, 136.5, 151.6, 185.9 ppm; IR (KBr): 3358 (br), 3083 (w), 3052 (w), 2957 (w), 2867 (w), 1648 (s), 1538 (m), 1401 (m), 1366 (w), 1251 (s), 1009 (w), 893 (w), 796 (w), 721 (w) cm^{-1}; Anal. Calcd for $C_{20}H_{18}O_2N_2$: C, 75.47; H, 5.66; N, 8.80. Found: C, 75.11; H, 5.96; N, 7.97.

1-Amino-4-(*N*- prop-2′-enylamino)anthraquinone (9)

Violet powder; mp = 132–134 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.00–4.03 (s, br, 2H), 5.21–5.24 (d, 1H, *J* = 10.2 Hz), 5.28–5.33 (d, 1H, *J* = 17.1 Hz), 5.91–6.04 (m, 1H), 6.91–7.11 (m, 4H), 7.66–7.70 (m, 2H), 8.30–8.34 (m, 2H), 10.72 (s, br, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 45.0, 109.8, 110.7, 116.5, 122.8, 126.13, 126.19, 128.1, 128.5, 132.1, 132.4, 134.2, 134.7, 144.4, 146.8, 182.7, 183.6 ppm; IR (KBr): 3375 (br), 3252 (br), 3069 (w), 2923 (s), 2853 (s), 1687 (m), 1650 (m), 1614 (s), 1597 (s), 1572 (s), 1535 (s), 1265 (s), 1169 (s), 813 (m), 794 (m), 725 (s) cm^{-1}; Anal. Calcd for $C_{17}H_{14}O_2N_2$: C, 73.38; H, 5.03; N, 10.07. Found: C, 73.18; H, 4.99; N, 9.98.

1,4-Bis(*N*- prop-2′-enylamino)anthraquinone (11)

Blue powder; mp = 140 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.04–4.07 (m, 4H), 5.21–5.35 (m, 4H), 5.95–6.04 (m, 2H), 7.16 (s, 2H), 7.69–7.72 (m, 2H), 8.33–8.36 (m, 2H), 10.82 (s, br, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 45.4, 110.6, 116.9, 124.0, 126.4, 127.1, 132.5, 134.7, 146.4, 183.2 ppm; IR (KBr): 3426 (br), 3073 (w), 3011 (w), 2919 (m), 2850 (m), 1639 (m), 1608 (s), 1592 (s), 1574 (s), 1554 (s), 1518 (s), 1275 (s), 1234 (s), 1170 (s), 1017 (s), 995 (s), 915 (m), 801 (m), 734 (s) cm^{-1}; Anal. Calcd for $C_{20}H_{18}O_2N_2$: C, 75.47; H, 5.66; N, 8.80. Found: C, 75.47; H, 5.66; N, 8.80.

1-(*N*-Methyl-*N*-prop-2′-enylamino)anthraquinone (13)

Dark red powder; mp = 155–157 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.98 (s, 3H), 4.11–4.14 (m, 2H), 5.14–5.23 (m, 2H), 5.88–5.97 (m, 1H), 7.19–7.73 (m, 5H), 8.17–8.38 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 29.6, 42.9, 114.8, 116.7, 117.8, 126.7, 126.8, 131.6, 132.9, 133.1, 133.7, 133.83, 133.89, 134.8, 134.9, 149.3, 183.3, 184.9 ppm; IR (KBr): 3012 (w), 2933 (m), 2855 (w), 1689 (s), 1671 (m), 1663 (s), 1651 (s), 1505 (m), 1388 (m), 1290 (s), 930 (m), 858 (m) cm^{-1}; Anal. Calcd for $C_{18}H_{15}O_2N$: C, 77.97; H, 5.41; N, 5.05. Found: C, 78.00; H, 5.11; N, 5.00.

1-(*N*-Methylamino)-5-(*N*′-prop-2′-enylamino)anthraquinone (15)

Red powder; mp = 187 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.96 (s, 3H), 4.31–4.34 (m, 2H), 5.14–5.23 (m, 2H), 5.86–6.00 (m, 1H), 7.30–7.73 (m, 5H), 8.17–8.23 (m, 1H), 8.71 (s, br, 1H), 8.84 (s, br, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.1, 53.8, 111.3, 116.7, 117.8, 126.5, 126.7, 131.6, 132.9, 133.1, 133.7, 133.83, 133.89, 134.8, 134.9, 149.6, 181.3, 185.4 ppm; IR (KBr): 3427 (br), 3270 (br), 3076 (w), 2923 (s), 2852 (m), 1661 (w), 1647 (w), 1621 (s), 1600 (s), 1572 (m), 1514 (m), 1397 (m), 1263 (s), 1076 (m), 768 (m), 708 (m) cm^{-1}; Anal. Calcd for $C_{18}H_{16}O_2N_2$: C, 73.97; H, 5.47; N, 9.58. Found: C, 73.87; H, 5.47; N, 9.07.

1-(*N*-Prop-2′-ynylamino)anthraquinone (17)

Orange crystals; mp = 182–183 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.29–2.30 (t, 1H, *J* = 2.4 Hz), 4.14–4.17 (dd, 2H, *J* = 5.7, 2.4 Hz), 7.14–7.18 (dd, 1H, *J* = 8.3, 1.0 Hz), 7.53–7.82 (m, 4H), 8.19–8.29 (m, 2H), 9.81 (br, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 32.4, 71.8, 79.4, 114.0, 116.5, 117.9, 126.7, 132.9, 133.1, 133.9, 134.6, 134.7, 135.3, 150.4, 183.5, 185.4 ppm; IR (KBr): 3441 (br), 3241 (s), 3075 (w), 2925 (m), 2853 (m), 2108 (w), 1671 (s), 1627 (s), 1592 (s), 1565 (s), 1507 (s), 1279 (s), 1229 (s), 1074 (s), 998 (s), 734 (s), 707 (s) cm^{-1}; Anal. Calcd for $C_{17}H_{11}O_2N$: C, 78.16; H, 4.21; N, 5.36. Found: C, 78.00; H, 4.38; N, 5.14.

1-Amino-5-(*N*- prop-2′-ynylamino)anthraquinone (19)

Red powder; mp = 180–182 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.27–2.29 (t, 1H, *J* = 2.4 Hz), 4.14 (d, 2H, *J* = 2.1 Hz), 6.73 (br, 2H), 6.88–6.91 (dd, 1H, *J* = 8.3, 0.9 Hz), 7.08–7.11 (dd, 1H, *J* = 8.2, 1.1 Hz), 7.41–7.47 (m, 1H), 7.57–7.67 (m, 3H), 9.80

(br, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 32.4, 71.7, 79.6, 115.8, 116.6, 116.7, 121.9, 128.7, 131.6, 134.6, 135.2, 135.7, 150.2, 150.6, 152.1, 185.4, 187.2 ppm; IR (KBr): 3420 (br), 3305 (br), 3070 (w), 2923 (s), 2852 (m), 2106 (w), 1665 (m), 1634 (s), 1602 (s), 1542 (s), 1503 (s), 1280 (s), 1166 (s), 1077 (s), 801 (m), 769 (m), 708 (s) cm^{-1}; Anal. Calcd for $C_{17}H_{12}O_2N_2$: C, 73.91; H, 4.34; N, 10.14. Found: C, 73.64; H, 4.69; N, 10.11.

1-Amino-4-(*N*- prop-2′-ynylamino)anthraquinone (21)

Violet powder; mp = 172 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.28 (s, 1H), 4.17 (s, 2H), 7.02–7.26 (m, 4H), 7.69–7.72 (m, 2H), 8.30–8.33 (m, 2H), 10.54 (br, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 32.3, 71.8, 79.9, 111.0, 122.5, 126.2, 128.31, 128.37, 132.4, 132.5, 134.1, 134.5, 134.6, 144.6, 145.5, 183.5, 183.6 ppm; IR (KBr): 3411 (br), 3355 (br), 3283 (br), 3055 (w), 2956 (w), 2866 (w), 2126 (w), 1659 (s), 1651 (s), 1539 (m), 1401 (m), 1251 (s), 1007 (w), 891 (w), 796 (w), 723 (w) cm^{-1}; Anal. Calcd for $C_{17}H_{12}O_2N_2$: C, 73.91; H, 4.34; N, 10.14. Found: C, 73.64; H, 4.68; N, 10.10.

2.3.2. Products

1-Amino-2-(prop-2′-enyl)anthraquinone (2)

Red powder; mp = 142–143 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.32–3.34 (d, 2H, *J* = 6.1 Hz), 5.14–5.23 (m, 2H), 5.88–5.97 (m, 1H), 7.06 (br, 2H), 7.30–7.32 (d, 1H, *J* = 7.5 Hz), 7.54–7.57 (d, 1H, *J* = 7.5 Hz), 7.64–7.73 (m, 2H), 8.17–8.24 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 36.1, 113.3, 116.8, 117.8, 126.5, 126.7, 131.6, 132.9, 133.1, 133.7, 133.81, 133.88, 134.8, 134.9, 149.6, 183.3, 185.4 ppm; IR (KBr): 3429 (s, br), 3295 (m, br), 3074 (w), 3007 (w), 2922 (w), 2852 (w), 1658 (s), 1634 (m), 1608 (s), 1591 (s), 1552 (s), 1425 (s), 1326 (s), 1279 (s), 747 (m), 712 (s) cm^{-1}; Anal. Calcd for $C_{17}H_{13}O_2N$: C, 77.56; H, 4.94; N, 5.32. Found: C, 76.90; H, 4.67; N, 5.11.

1,5-Diamino-2-(prop-2′-enyl)anthraquinone (5)

Pale red powder; mp = 155 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.38–3.40 (d, 2H, *J* = 6.0 Hz), 5.17–5.26 (m, 2H), 5.98 (m, 1H), 6.81 (br, 2H), 6.88–6.91 (dd, 1H, *J* = 8.3, 1.0 Hz), 7.05 (br, 2H), 7.37–7.46 (m, 2H), 7.60–7.64 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 37.0, 113.3, 116.1, 116.6, 117.7, 121.7, 130.4, 134.0, 134.5, 135.0, 135.8, 140.7, 149.4, 150.6, 153.0, 185.6, 185.9 ppm; IR (KBr): 3431 (br), 3306 (br), 3074 (w), 2924 (s), 2852 (s), 1636 (m), 1598 (s), 1548 (s), 1459 (m), 1262 (s), 771 (w), 724 (w) cm^{-1}; Anal. Calcd for $C_{17}H_{14}O_2N_2$: C, 73.38; H, 5.03; N, 10.07. Found: C, 73.14; H, 5.05; N, 10.07.

1-Amino-2-(prop-2′-enyl)-5-(N-prop-2′-enylamino)anthraquinone (7)

Pink powder; mp = 154–156 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.38–3.40 (d, 2H, *J* = 6.1 Hz), 3.98–4.02 (m, 2H), 5.22–5.34 (m, 4H), 5.91–6.05 (m, 2H), 6.94–6.97 (dd, 1H, *J* = 8.4, 1.1 Hz), 7.07 (br, 2H), 7.37–7.39 (d, 1H, *J* = 7.6 Hz), 7.51–7.54 (m, 1H), 7.58–7.77 (m, 2H), 9.84 (br, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 36.2, 45.2, 113.5, 115.3, 116.1, 116.6, 116.9, 117.7, 126.8, 128.7, 130.2, 130.8, 133.3, 133.8, 134.0, 135.1, 136.2, 149.4, 185.5, 186.0 ppm; IR (KBr): 3415 (br), 3285 (br), 3013 (w), 2955 (w), 2865 (w), 1671 (s), 1650 (s), 1607 (s), 1533 (s), 1407 (s), 1366 (w), 1253 (s), 1090 (w), 893 (w), 793 (w) cm^{-1}; Anal. Calcd for $C_{20}H_{18}O_2N_2$: C, 75.47; H, 5.66; N, 8.80. Found: C, 75.27; H, 5.16; N, 8.80.

1,5-Diamino-2,6-bis(prop-2′-enyl)anthraquinone (8)

Orange powder; mp = 161 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.39–3.41 (d, 4H, *J* = 6.0 Hz), 5.18–5.26 (m, 4H), 5.94–6.03 (m, 2H), 7.05 (br, 4H), 7.38–7.40 (d, 2H, *J* = 7.6 Hz), 7.62–7.65 (d, 2H, *J* = 7.6 Hz) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 36.2, 114.0, 116.2, 116.9, 117.7, 130.8, 134.0, 135.1, 149.4, 185.5 ppm; IR (KBr): 3487 (br), 3322 (br), 3059 (w), 3025 (m), 2922 (s), 2851 (s), 1632 (m), 1592 (s), 1550 (s), 1492 (s), 1452 (s), 1275 (s), 915 (m), 758 (s), 698 (s) cm^{-1}; Anal. Calcd for $C_{20}H_{18}O_2N_2$: C, 75.47; H, 5.66; N, 8.80. Found: C, 75.37; H, 5.56; N, 8.70.

1,4-Diamino-2-(prop-2′-enyl)anthraquinone (10)

Purple powder; mp = 152–154 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.12–3.15 (d, 2H, *J* = 11.7 Hz), 4.46 (s, br, 2H), 4.84 (s, br, 2H), 4.87–4.89 (d, 1H, *J* = 6.7 Hz), 5.13–5.16 (d, 1H, *J* = 13.1 Hz), 5.89–6.00 (m, 1H), 7.20 (s, 1H), 7.84–7.85 (m, 2H), 8.28–8.29 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 35.9, 110.0, 113.1, 115.9, 120.0, 126.7, 126.8, 129.6, 132.1, 133.62, 133.63, 136.5, 136.6, 139.7, 140.0, 185.70, 185.74 ppm; IR (KBr): 3402 (br), 3274 (br), 3029 (w), 2963 (w), 2870 (w), 1650 (s), 1630 (s), 1610 (s), 1536 (s), 1455 (s), 1367 (w), 1258 (m), 898 (w), 799 (w) cm^{-1}; Anal. Calcd for $C_{17}H_{14}O_2N_2$: C, 73.38; H, 5.03; N, 10.07. Found: C, 74.04; H, 4.59; N, 10.00.

1-Amino-2-(prop-2′-enyl)-4-(*N*-prop-2′-enylamino)anthraquinone (12)

Blue powder; mp = 149–151 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.21 (m, 2H), 3.94 (m, 2H), 4.76 (br, 2H), 4.87 (m, 1H), 5.12–5.33 (m, 3H), 5.74 (br, 1H), 5.82–6.02 (m, 2H), 7.16 (s, 1H), 7.85 (m, 2H), 8.29 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 35.9, 46.1, 107.6, 113.3, 115.9, 117.44, 117.47, 126.87, 126.89, 129.3, 132.10, 132.12, 133.6, 135.5, 136.5, 138.0, 139.7, 185.77, 185.79 ppm; IR (KBr): 3410 (br), 3275 (br), 3041 (w), 2955 (w), 2865 (w), 1649 (s), 1628 (s), 1605 (s), 1536 (s), 1407 (s), 1253 (m), 799 (w), 726 (w) cm^{-1}; Anal. Calcd for $C_{20}H_{18}O_2N_2$: C, 75.47; H, 5.66; N, 8.80. Found: C, 75.17; H, 5.46; N, 8.50.

1-(*N*-Methylamino)-2-(prop-2′-enyl)anthraquinone (14)
Dark red powder; mp = 170 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.98 (s, 3H), 3.31–3.34 (m, 2H), 5.14–5.23 (m, 2H), 5.88–5.97 (m, 1H), 6.77 (br, 1H), 7.30–7.32 (d, 1H, *J* = 7.5 Hz), 7.54–7.57 (d, 1H, *J* = 7.5 Hz), 7.63–7.73 (m, 2H), 8.17–8.24 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 29.8, 36.9, 113.8, 116.7, 117.8, 126.7, 126.8, 131.6, 132.9, 133.1, 133.7, 133.83, 133.89, 134.8, 134.9, 149.6, 183.5, 185.8 ppm; IR (KBr): 3418 (br), 3073 (w), 2923 (s), 2852 (s), 1666 (s), 1625 (m), 1592 (m), 1518 (m), 1464 (m), 1258 (s), 714 (s) cm^{-1}; Anal. Calcd for $C_{18}H_{15}O_2N$: C, 77.97; H, 5.41; N, 5.05. Found: C, 77.77; H, 5.31; N, 5.04.

1-Amino-5-(*N*-methylamino)-2-(prop-2′-enyl)anthraquinone (16)
Bright red powder; mp = 185–187 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.67 (s, 3H), 3.31–3.34 (m, 2H), 5.14–5.23 (m, 2H), 5.88–5.97 (m, 1H), 7.06 (br, 2H), 7.30–7.32 (d, 1H, *J* = 7.6 Hz), 7.54–7.57 (d, 1H, *J* = 7.5 Hz), 7.63–7.73 (m, 2H), 7.90–7.94 (m, 1H), 8.23 (br, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.6, 36.1, 113.3, 116.7, 117.8, 126.5, 126.7, 131.6, 132.9, 133.1, 133.7, 133.83, 133.89, 134.8, 134.9, 149.8, 182.3, 185.4 ppm; IR (KBr): 3414 (br), 3283 (br), 3084 (w), 2956 (w), 2866 (w), 1656 (s), 1646 (s), 1534 (m), 1401 (m), 1254 (s), 1007 (w), 798 (w), 726 (w) cm^{-1}; Anal. Calcd for $C_{18}H_{16}O_2N_2$: C, 73.97; H, 5.47; N, 9.58. Found: C, 73.77; H, 5.32; N, 9.48.

1,2,3,4-tetrahydronaphtho[2,3-*h*]quinoline-7,12-dione (18)
Orange powder; mp = 185–186 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.96–2.02 (m, 2H), 2.84–2.89 (m, 2H), 3.52–3.56 (m, 2H), 7.14–7.22 (m, 1H), 7.46–7.49 (d, 1H, *J* = 7.4 Hz), 7.61–7.77 (m, 2H), 8.21–8.28 (m, 2H), 9.81–9.94 (br, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 20.1, 29.6, 41.0, 115.6, 116.5, 117.9, 126.5, 126.6, 130.2, 132.6, 133.1, 133.6, 133.7, 135.3, 149.2, 183.6, 184.6 ppm; IR (KBr): 3286 (br), 3010 (w), 2926 (s), 2852 (s), 1663 (s), 1624 (s), 1591 (s), 1519 (s), 1323 (s), 1296 (s), 1271 (s), 1005 (s), 974 (s), 750 (m), 734 (m), 715 (s) cm^{-1}; Anal. Calcd for $C_{17}H_{13}O_2N$: C, 77.56; H, 4.94; N, 5.32. Found: C, 77.51; H, 5.00; N, 5.31.

8-Amino-1,2,3,4-tetrahydronaphtho[2,3-*h*]quinoline-7,12-dione (20)
Red powder; mp = 180–182 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.96–2.01 (m, 2H), 2.84–2.89 (m, 2H), 3.52–3.56 (m, 2H), 6.89 (br, 2H), 7.14–7.22 (m, 1H), 7.46–7.49 (d, 1H, *J* = 7.4 Hz), 7.67–7.74 (m, 2H), 8.23–8.26 (m, 1H), 9.81–9.94 (br, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 28.3, 29.6, 41.3, 115.6, 116.5, 117.9, 126.5, 130.2, 132.6, 133.1, 133.6, 133.7, 135.3, 149.7, 152.6, 183.2, 184.1 ppm; IR (KBr): 3328 (br), 3150 (br), 3054 (w), 2912 (w), 2830 (w), 1665 (s), 1632 (m), 1601 (s), 1517 (s), 1501 (s), 1495 (m), 1385 (m), 1308 (m), 1245 (s), 1115 (s), 833 (s), 763 (w) cm^{-1}; Anal. Calcd for $C_{17}H_{14}O_2N_2$: C, 73.38; H, 5.03; N, 10.07. Found: C, 73.38; H, 5.03; N, 10.07.

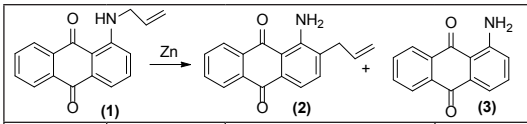
6-Amino-1,2,3,4-tetrahydronaphtho[2,3-*h*]quinoline-7,12-dione (22)
Purple powder; mp = 176–177 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.96 (m, 2H), 2.79 (m, 2H), 3.04 (m, 2H), 4.47 (br, 2H), 6.99 (br, 1H), 7.10 (s, 1H), 7.85 (m, 2H), 8.29 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz): δ 22.2, 27.0, 41.8, 110.77, 110.78, 119.3, 125.6, 126.88, 126.89, 132.11, 132.12, 133.62, 133.63, 138.0, 139.4, 185.7, 185.8 ppm; IR (KBr): 3340 (br), 3160 (br), 3066 (w), 2915 (w), 2822 (w), 1667 (s), 1632 (m), 1607 (s), 1518 (s), 1505 (s), 1388 (m), 1310 (m), 1246 (s), 1117 (s), 835 (s) 765 (w) cm^{-1}; Anal. Calcd for $C_{17}H_{14}O_2N_2$: C, 73.38; H, 5.03; N, 10.07. Found: C, 73.38; H, 5.03; N, 10.07.

3. Results and discussion

First, we tried to identify the optimized reaction conditions for this rearrangement via its operation on 1-(*N*-prop-2′-enylamino) anthraquinone **1** as a model compound. For this propose, zinc powder was used in different reaction conditions (Table 1).

As shown in Table 1, performing this reaction using zinc powder (2 equiv.) in solvents such as AcOH, DMF, and DMSO under heating up to 160 °C was unsuccessful so that the desired product **2** was formed in only 20%–30% yield with concomitant formation of the undesired deallylated product **3** in large amounts after 4.5–5 h (Table 1, entries 1–3). Surprisingly, the aza-rearranged product **2** was formed in excellent yield after 1.5 h only by exchanging of the solvent to [Hmim] BF_4 as an acidic ionic liquid (Table 1, entry 4). The best result was achieved with entering of only 2 drops of DMSO to the reaction medium which accelerate, to some extent, this rearrangement so that **2** was produced in 90% yield with concomitant formation of **3** in 6% yield after only 1 h (Table 1, entry 5). This reductive rearrangement was unsuccessful again using [EMIM]Br and [HexMIM]I as other ionic liquids or under solvent-free condition. In these cases, the starting material **1** completely remained after 5 h (Table 1, entries 6–8). On the other hand, decreasing of the reaction temperature caused a decrease in the yield of **2** so that **1** remained intact completely at room temperature after 6 h (Table 1, entries 9–13). However, the result did not improve with increasing of the reaction temperature (Table 1, entry 14). Also, decreasing or even increasing of the molar ratio of Zn caused a decrease in the yield of the desired rearranged product **2** (Table 1, entries 15 and 16). In addition, this rearrangement completely failed to run in the absence of zinc powder (thermally condition) indicating its reductive nature (Table 1, entry 17). Finally, with the above study, the conditions mentioned in the entry 5 of Table 1 were selected as optimized conditions for this rearrangement and applied for other 1-(*N*-prop-2′-enylamino) anthraquinones for their reductive aza-Claisen rearrangement to 1-amino-2-(prop-2′-enyl)anthraquinones. The results

Table 1. Reductive aza-Claisen rearrangement of 1-(*N*-prop-2′-enylamino)anthraquinone **1** to 1-amino-2-(prop-2′-enyl)anthraquinone **2** using zinc powder in different conditions.



Entry	Molar ratio of Zn	Solvent	Temp. (°C)	Time (h)	Yield (%) of **2**	Yield (%) of **3**[a]
1	2	AcOH	Reflux	4.5	20	80
2	2	DMF	Reflux	5	25	75
3	2	DMSO	160	5	30	70
4	2	[Hmim] BF_4	160	1.5	90	10
5	2	[Hmim] BF_4[b]	160	1	90	6
6	2	[EMIM]Br[c]	160	5	0	0
7	2	[HexMIM]I[d]	160	5	0	0
8	2	Solvent free	160	5	0	0
9	2	[Hmim] BF_4	140	4.5	65	10
10	2	[Hmim] BF_4	120	4.5	45	25
11	2	[Hmim] BF_4	100	5	35	25
12	2	[Hmim] BF_4	70	8	30	20
13	2	[Hmim] BF_4	rt	6	0	0
14	2	[Hmim] BF_4	180	1.5	85	15
15	1	[Hmim] BF_4	160	1.5	50	20
16	4	[Hmim] BF_4	160	1.5	80	20
17	0	[Hmim] BF_4	160	6	0	0

[a] **3** is deallylated product (1-aminoanthraquinone). [b] In this case, DMSO (2 drops) was added to the reaction mixture. [c] 1-Ethyl-3-methylimidazolium bromide. [d] 1-Hexyl-3-methylimidazolium iodide.

are shown in Table 2. All of these 1-(*N*-prop-2′-enylamino)anthraquinones were synthesized from the reaction of the corresponding 1-aminoanthraquinones with allyl bromide in the presence of sodium hydroxide in DMF as solvent at 75 °C with reaction times from 2.5 h up to 48 h.

As shown in Table 2, different 1-(*N*-prop-2′-enylamino)anthraquinones are converted to 1-amino-2-(prop-2′-enyl) anthraquinones via reductive aza-Claisen rearrangement in good to excellent yields using the present method. It is important to note that no anthracenone formation and also double bond isomerization or reduction was observed in this method. Also, in the case of 1,5-bis(*N*- prop-2′-enylamino)anthraquinone **6** with two *N*-allyl groups, the selective formation of mono- or double-rearranged product as main product can be easily controlled only with controlling of the molar ratio of zinc powder and reaction times (Table 2, entries 3 and 4). In addition, we found that it is possible to operate this rearrangement on **13** as a tertiary amine so that **14** was produced in good yield after 1.5 h (Table 2, entry 7). Also, extending of the present procedure on 1-(*N*-prop-2′-ynylamino)anthraquinones caused efficient production of 1,2,3,4-tetrahydronaphtho[2,3-*h*]quinoline-7,12-diones via a reductive aza-Claisen rearrangement followed by cyclization in a tandem manner. Of course, the reaction temperature was reduced to 140 °C for this type of substrates (Table 2, entries 9–11). These substrates were synthesized from the reaction of the corresponding 1-aminoanthraquinones with propargyl bromide in the presence of sodium hydroxide in DMF as solvent at 75 °C in 24 h. The aromatic aza-Claisen rearrangement of arylpropargylammonium salts to 2-propargylanilines in the first step and cyclization of the rearranged products with aluminum chloride to create a new five-membered ring affording indoles in the second step has been reported [24]. However, in our work, a new six-membered heterocyclic ring is created on anthraquinone system via spontaneous cyclization of the rearranged product affording 1,2,3,4-tetrahydronaphtho[2,3-*h*]quinoline-7,12-diones in a one-pot way. However, deallylated or depropargylated products are also created in low yields in these rearrangements.

Table 2. Reductive aza-Claisen rearrangement on anthraquinone structures using Zn powder (2 equiv.) in [Hmim] BF_4 at 160 °C.[a]

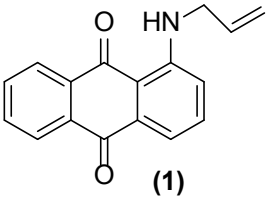
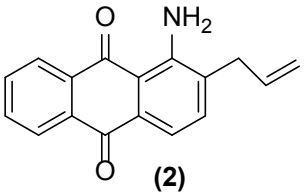
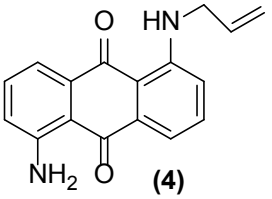
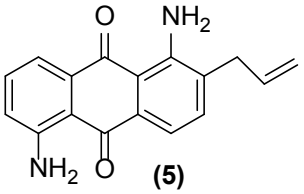
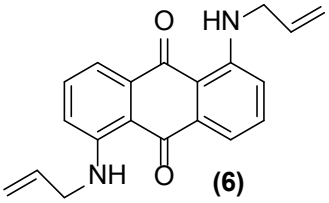
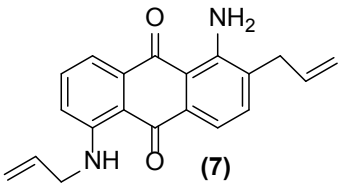
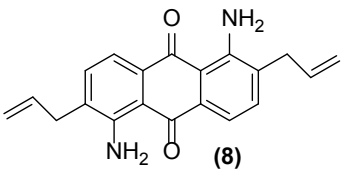
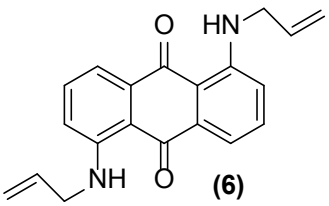
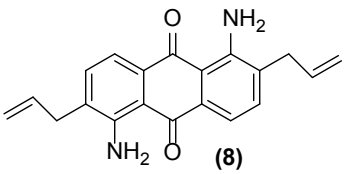
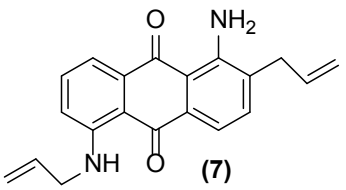
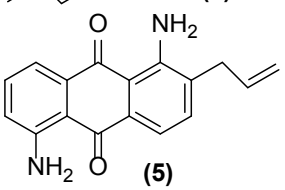
Entry no.	Substrate	Product	Time (h)	Yield (%)[b]
1	 (1)	 (2) Deallylated	1	90 6
2	 (4)	 (5) Deallylated	4.5	82 15
3	 (6)	 (7)  (8) Doubly deallylated	4.5	53 35 7
4[c]	 (6)	 (8)  (7)  (5) Doubly deallylated	10	64 14 10 5

Table 2. (Continued).

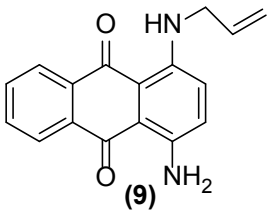
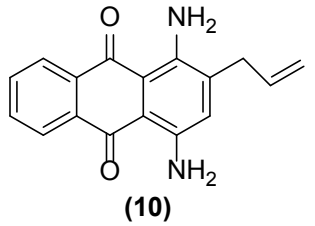
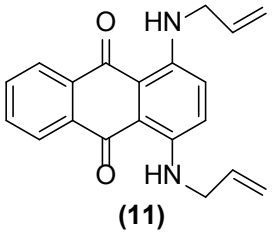
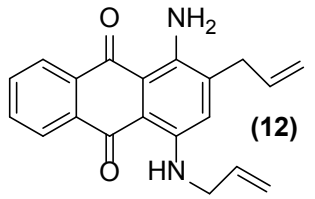
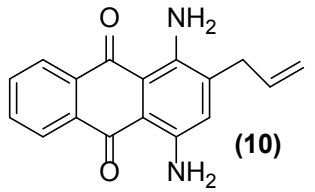
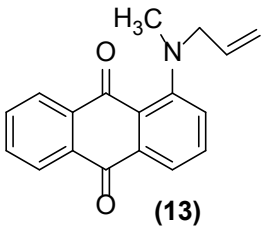
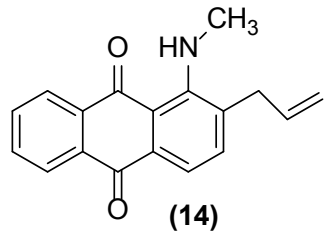
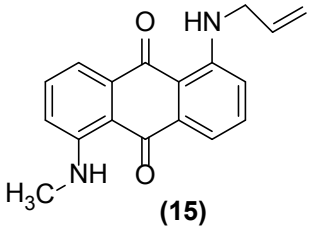
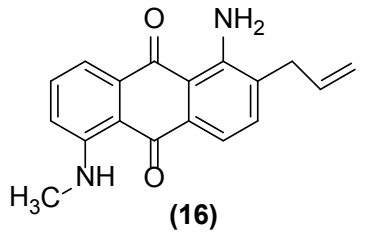
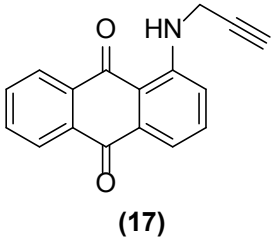
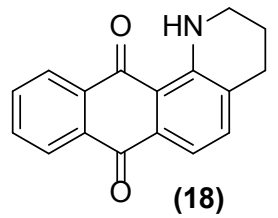
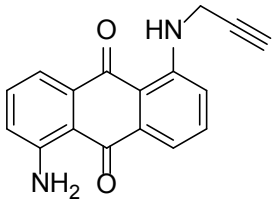
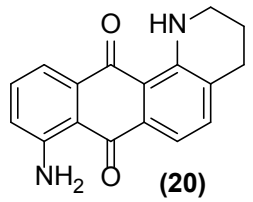
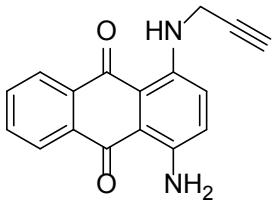
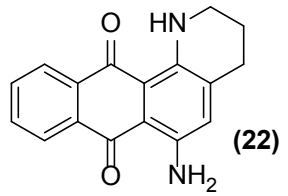
5	 **(9)**	 **(10)** Deallylated	4.5	67 27
6	 **(11)**	 **(12)**  **(10)** Doubly deallylated	6	61 15 20
7	 **(13)**	 **(14)** Deallylated	1.5	65 30
8	 **(15)**	 **(16)** Deallylated	2.5	76 15
9[d]	 **(17)**	 **(18)** Depropargylated	5.5	91 5

Table 2. (Continued).

10[d]	 **(19)**	 **(20)** Depropargylated	5.5	77 5
11[d]	 **(21)**	 **(22)** Depropargylated	5.5	73 6

[a] DMSO (2 drops) was added to the reaction medium in this rearrangement. [b] Isolated yields. [c] The molar ratio of substrate to Zn powder was adjusted to 1:3 in this case. [d] This rearrangement was carried out at 140 °C.

In order to better understand the efficiency and other aspects of selectivity of this method, different competitive reactions were designed and operated (Figure 2). In each of these reactions, Zn (2 equiv.) was treated with a mixture containing 1-(*N*-prop-2′-enylamino)anthraquinone **1** or 1-(*N*-prop-2′-ynylamino)anthraquinone **17** and another compound having a specified functional group (1:1) in [Hmim] BF_4/ DMSO (2 drops) at 160 °C for 1 h or 140 °C for 4.5 h, respectively.

As shown in Figure 2, this reductive rearrangement is executable on *N*-allyl (or *N*-propargyl)aminoanthraquinones in the presence of aldehyde, ketone, alcohol, ester, epoxide, carboxylic amide, phenolic, and nitro functional groups with excellent chemoselectivity. Also, surprisingly, it was found that the selectivity pathway for a binary mixture containing **1** and **17** is controlled by adjustment of the reaction temperature so that at 160 °C the rearranged product **2** and at 140 °C the rearranged product **18** was selectively formed as main product after 1 h and 4.5 h respectively (Figure 2, entries 10 and 11).As mentioned in Table 1, this reaction was unsuccessful in the absence of [Hmim] BF_4 or Zn powder (thermally conditions). In these cases, the desired rearranged product was produced in only 0%–30% yield. Thus, in the mechanism of this reaction, it is proposed that anthraquinone core is reduced by Zn powder in [Hmim] BF_4 as an acidic ionic liquid to its electron-rich hydroquinone type **A** which is more ready for this rearrangement (Figure 3).

Operation of this [3,3] sigmatropic reaction followed by enamine formation causes the creation of **C** which undergoes air oxidation to produce **2** as final rearranged product. It seems that the acidic nature of [Hmim] BF_4 facilitates this rearrangement. In the case of *N*-propargylaminoanthraquinones; the same reduction and [3,3] sigmatropic reaction followed by enamine formation are operated affording allenic intermediate **C**. However, in continuation, this intermediate is entered in cyclization reaction followed by enol-keto tautomerism affording the final product **18** needless to air oxidation. In accordance with these mechanisms, when the present procedure was applied on **1** and also **17** separately under N_2 atmosphere, no product formation was observed in the case of *N*-allyl (i.e. **1**) after 5 h while **18** was produced in 80% yield after the same reaction time indicating that air oxidation is necessary to produce rearranged product from *N*-allylaminoanthraquinones but not from *N*-propargylaminoanthraquinones.

4. Conclusion

In conclusion, the present study introduces, for the first time, reductive aza-Claisen rearrangement of 1-(*N*-allylamino) anthraquinones to 1-amino-2-(prop-2'-enyl)anthraquinones using zinc powder in [Hmim] BF_4 as an ionic liquid in good to excellent yields. No anthracenone formation and also double bond isomerization or reduction was observed in this method.

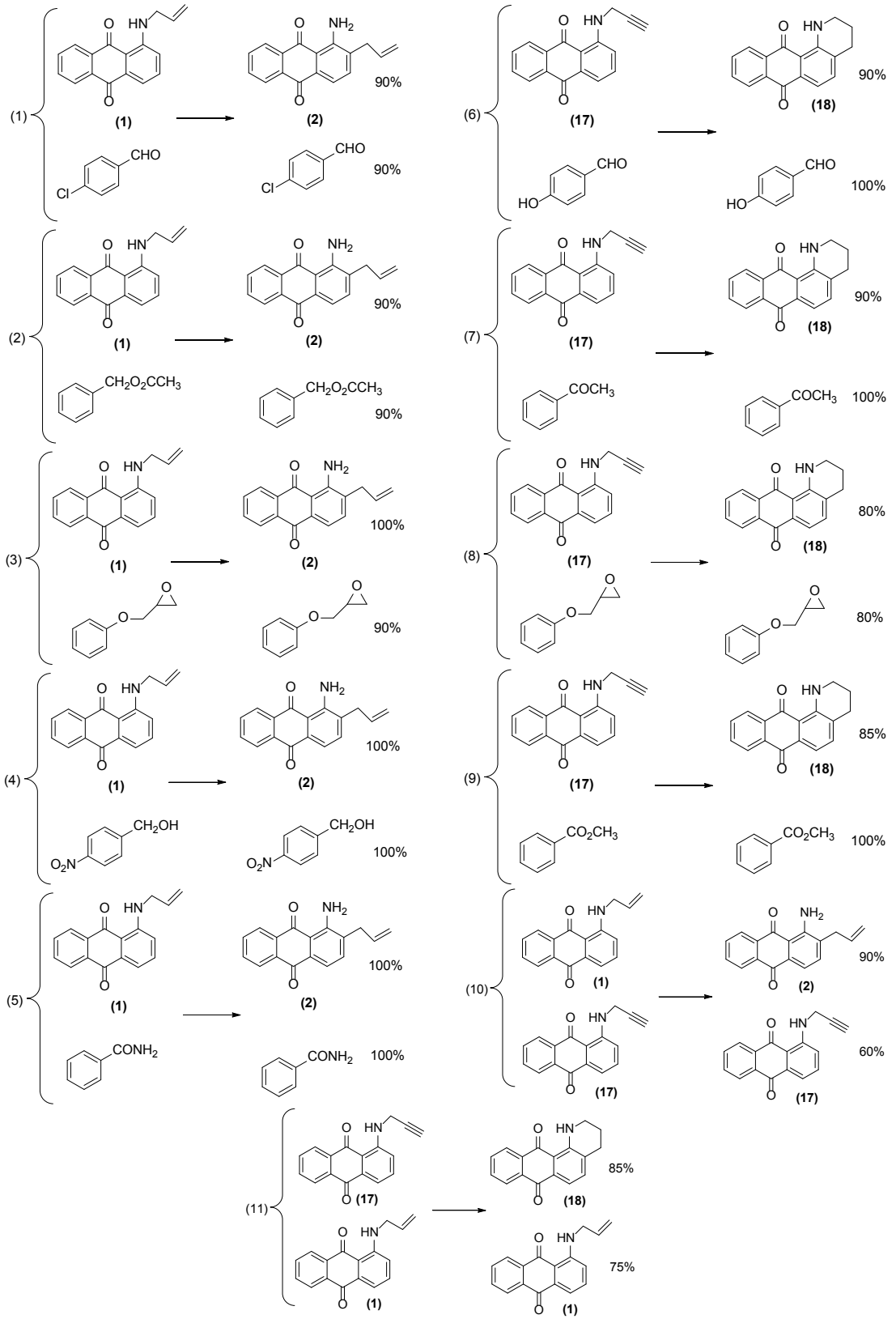


Figure 2. Various selectivities in the reductive aza-Claisen rearrangement of 1-(*N*-prop-2′-enylamino)anthraquinones or 1-(*N*-prop-2′-ynylamino)anthraquinones using zinc powder in [Hmim] BF_4/ DMSO at 160 °C after 1 h or 140 °C after 4.5 h, respectively.

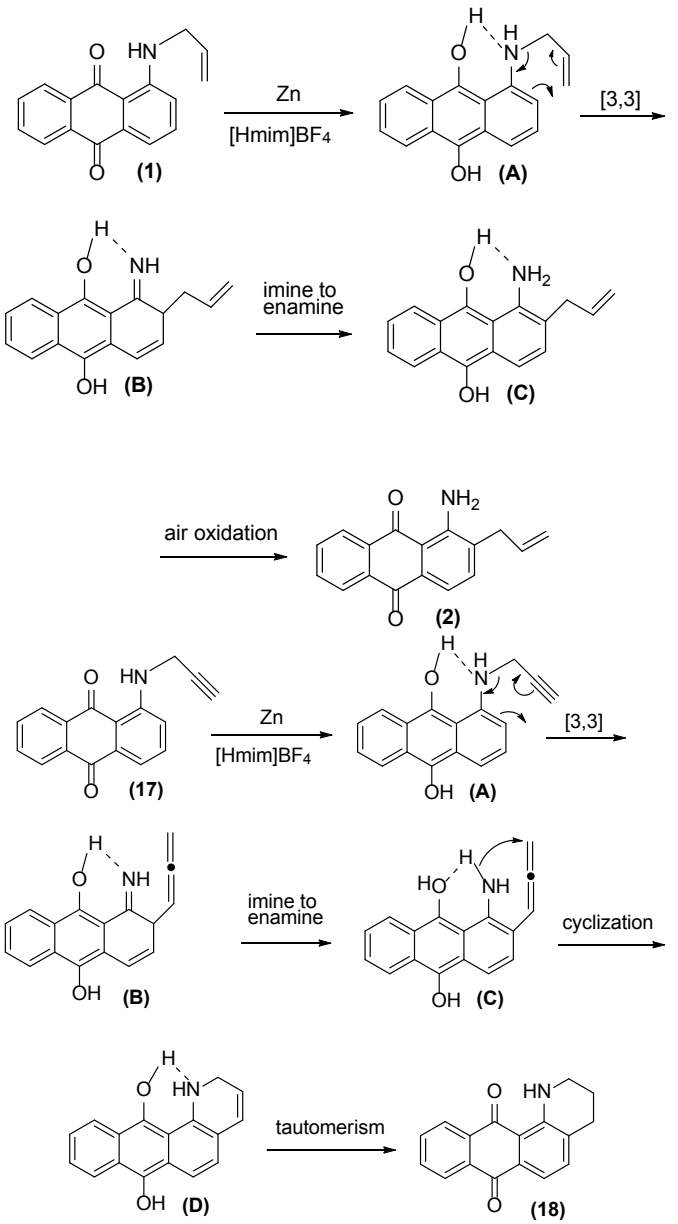


Figure 3. The suggested mechanism of the reductive aza-Claisen rearrangement of 1-(*N*-prop-2′-enylamino)anthraquinone and 1-(*N*-prop-2′-ynylamino)anthraquinone systems using zinc powder in [Hmim] BF_4.

N-propargyl rearrangement

Also, 1-(*N*-propargylamino)anthraquinones is converted to 1,2,3,4-tetrahydronaphtho[2,3-*h*]quinoline-7,12-diones containing a newly synthesized six-membered heterocyclic ring on anthraquinone core under these conditions via this [3,3] sigmatropic rearrangement followed by cyclization in a tandem manner. Surprisingly, with adjustment of the reaction temperature, it is possible to operate reductive aza-Claisen rearrangement of *N*-allylaminoanthraquinones in the presence of *N*-propargylaminoanthraquinones or vice versa with good selectivity. Moreover, some different other functional groups well tolerate this rearrangement so that it is executable with excellent chemoselectivity. In addition, operation in ionic liquid as environment-friendly solvent can be considered another advantage of the present method.

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