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Efficient reductive Claisen rearrangement of prop-2'-enyloxyanthraquinones and 2'-chloroprop-2'-enyloxyanthraquinones with iron powder in ionic liquids

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Abstract: A rapid and selective iron-mediated reductive Claisen rearrangement of various prop-2'-enyloxyanthraquinones and 2'-chloroprop-2'-enyloxyanthraquinones to 1-hydroxy-2-(prop-2'-enyl)anthraquinones and anthrafurandiones is presented. All reactions are carried out in a mixture of ionic liquids, [Bzmim]Cl (1-benzyl-3-methylimidazolium chloride) and [Hmim]BF_4 (1-methylimidazolium tetrafluoroborate), in short reaction times (5–35 min). Our study showed that 1-(prop-2'-enyloxy)anthraquinone is more active than 1-(2'-chloroprop-2'-enyloxy)anthraquinone to perform this rearrangement.

Key words: 2'-Chloroprop-2'-enyloxyanthraquinone, anthrafurandione, Claisen rearrangement, iron, ionic liquid

1. Introduction

Synthesis of anthraquinone (AQ) derivatives constitutes a very important field in organic chemistry due to their various desired properties such as antimicrobial and antiviral,[1] anticancer,[2–4] antiinflammatory,[5] antimalarial,[6] antifungal,[7] laxative,[8] antioxidant,[9] and antiarthritic,[10] and also their important industrial applications (e.g., textile dyestuffs,[11] pulping additives,[12] and colorimetric sensor systems[13,14]). In this regard, the reductive Claisen rearrangement of prop-2'-enyloxyanthraquinones has become a standard strategy for the functionalization of anthraquinones and synthesis of their desired derivatives.[15–19] This rearrangement has been performed using different reagents such as sodium dithionate[15] and glucose.[19] However, some described methods suffer from several disadvantages such as the formation of anthracenone derivatives as byproducts, loss of the methoxy group attached to the anthraquinone core, isomerization or even reduction of the allyl side chain double bond in rearranged products, and long reaction times.[15]

We previously performed this rearrangement on the allyloxyanthraquinones with silver/potassium iodide as a reagent in acetic acid.[20] Also, very recently we carried out this rearrangement on the propargyloxyanthraquinones affording anthrafurandiones.[21] Now with these descriptions and also with respect to our interest in applying ionic liquids in organic synthesis as environmentally friendly solvents,[22,23] we report an efficient and selective method for the reductive Claisen rearrangement of prop-2'-enyloxyanthraquinones and 2'-chloroprop-2'-enyloxyanthraquinones to 1-hydroxy-2-(prop-2'-enyl)anthraquinones and anthrafurandiones respectively using iron powder. All reactions are performed in a mixture of two ionic liquids containing 1-benzyl-3-methylimidazolium chloride [Bzmim]Cl and 1-methylimidazolium tetrafluoroborate [Hmim]BF_4[24] in short reaction times (Figure 1).

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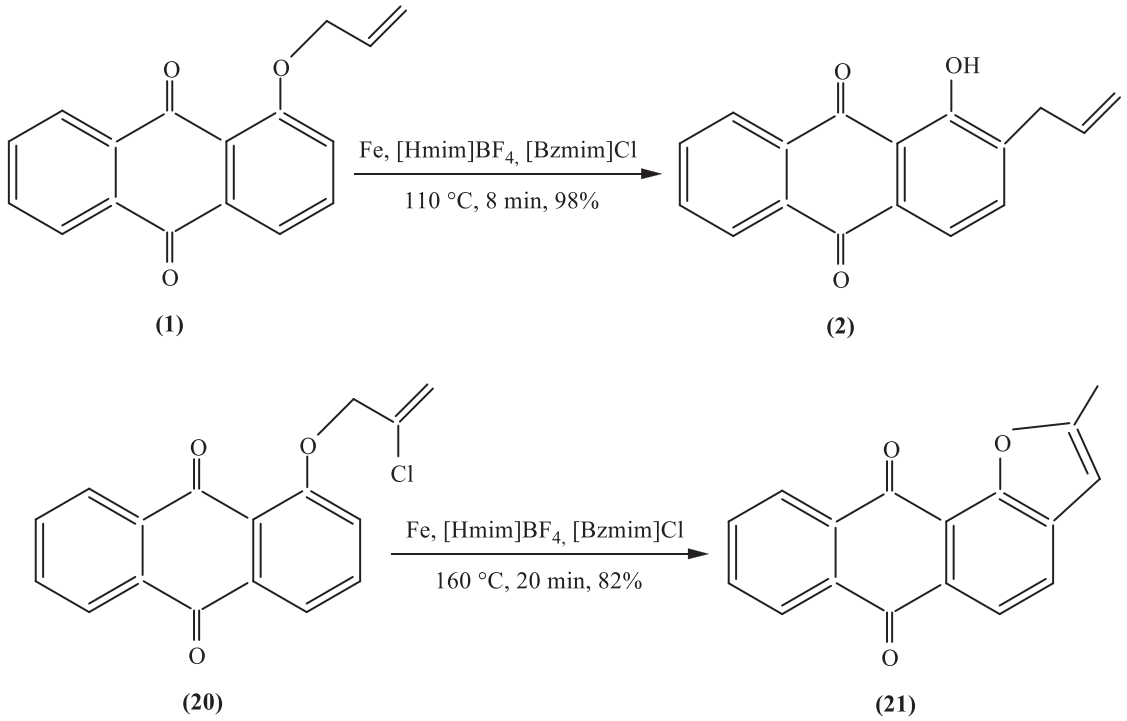


Figure 1. Reductive Claisen rearrangement of **1** and **20** to products **2** and **21** respectively using iron powder in a mixture of two ionic liquids, [Hmim]BF_4 and [Bzmim]Cl.

2. Results and discussion

We performed reductive Claisen rearrangement of 1-(prop-2'-enyloxy)anthraquinone (**1**) using iron powder (2 equiv.) in a mixture of two ionic liquids [Hmim]BF_4 and [Bzmim]Cl at 110 °C. Under these reaction conditions, 1-hydroxy-2-(prop-2'-enyl)anthraquinone (**2**) was produced in 98% yield after only 8 min. However, this reaction was unsuccessful in the absence of iron (i.e. thermal conditions), [Hmim]BF_4, or [Bzmim]Cl at 110 °C, affording the rearranged product (**2**) in less than 10% yields after 70 min. In addition, the yield of this reaction decreased to 50% at 90 °C. Also, when potassium chloride was used instead of [Bzmim]Cl in this rearrangement, the desired product (**2**) was formed in only 25% yield after 9 min. Therefore, we performed the reductive Claisen rearrangement of various prop-2'-enyloxyanthraquinones to their corresponding rearranged products using the above mentioned conditions. The results are shown in Table 1. These prop-2'-enyloxyanthraquinones were synthesized from the reaction of the related hydroxyanthraquinones with allyl bromide in the presence of anhydrous potassium carbonate in refluxing acetone as solvent.[16]

As shown in Table 1, the reductive Claisen rearrangement of the prop-2'-enyloxyanthraquinones was readily carried out in good to excellent yields (52%–98%) in short reaction times (5–35 min), affording the rearranged products 1-hydroxy-2-(prop-2'-enyl)anthraquinones. Most notably, no side chain double bond isomerization or reduction in the rearranged products, anthracenone formation, or loss of the methoxy group attached to the anthraquinone core was observed in this rearrangement. Moreover, it was possible to perform selectively mono or double Claisen rearrangements of bis(prop-2'-enyloxy)anthraquinone systems with controlling of the molar ratio of the reductant or reaction time (in Table 1, compare entries 3 with 4, 7 with 8, and 10 with 11).

With slight modification of the present procedure, we accomplished the reductive Claisen rearrangement

Table 1. Reductive Claisen rearrangement of prop-2'-enyloxyanthraquinones with iron in a mixture of two ionic liquids, [Hmim]BF_4 and [Bzmim]Cl, at 110 °C.

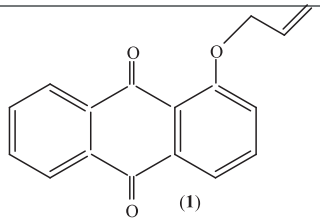
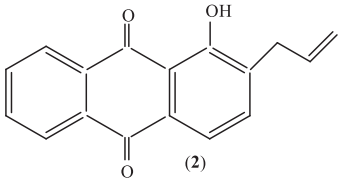
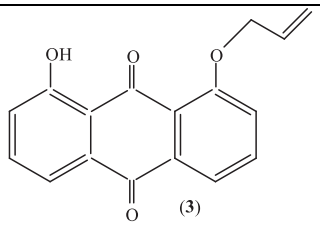
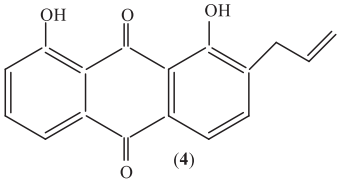
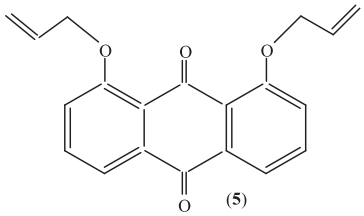
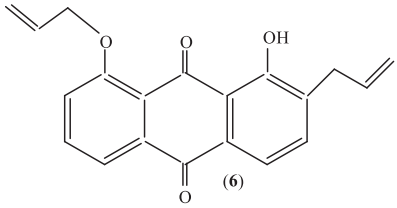
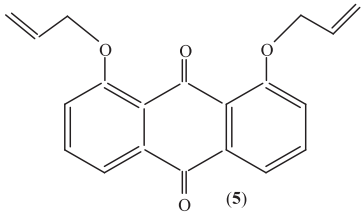
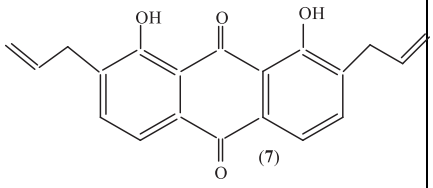
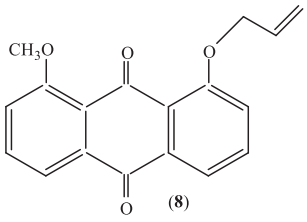
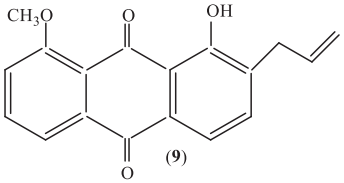
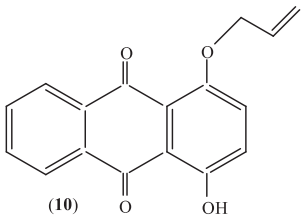
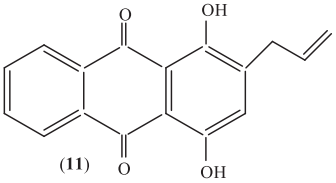
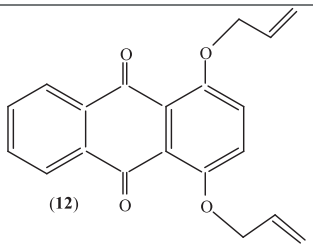
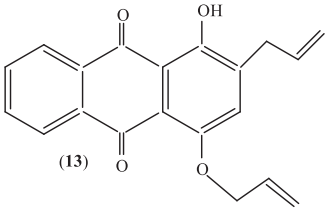
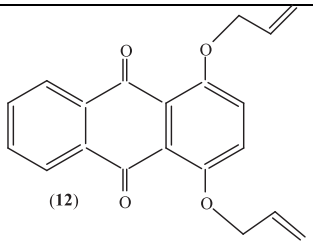
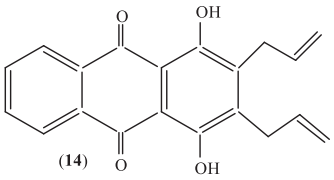
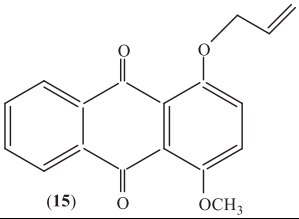
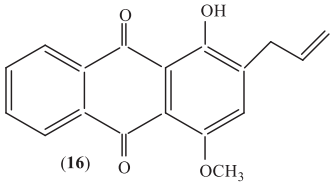
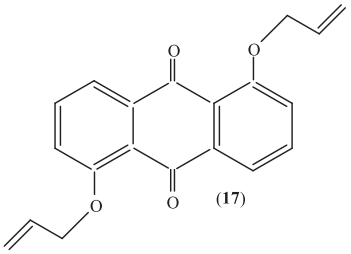
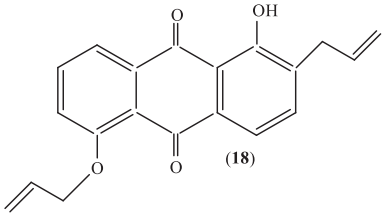
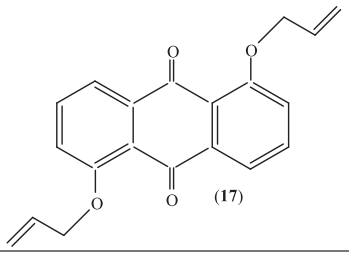
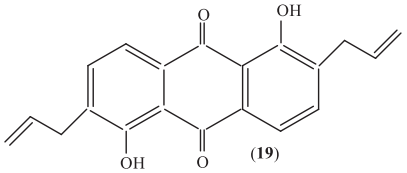
Entry no.	Substrate	Product	Molar ratio AQ: Fe	Time (min)	Yield (%)[a]
1	 (1)	 (2)	1:2	8	98
2	 (3)	 (4)	1:3	35	83
3	 (5)	 (6)	1:2	10	64
4	 (5)	 (7)	1:4	15	83
5	 (8)	 (9)	1:2	23	78
6	 (10)	 (11)	1:2	11	91

Table 1. Continued.

Entry no.	Substrate	Product	Molar ratio AQ: Fe	Time (min)	Yield (%)[a]
7	 (12)	 (13)	1:2	5	55
8	 (12)	 (14)	1:4	6	97
9	 (15)	 (16)	1:2	8	82
10	 (17)	 (18)	1:2	6	52
11	 (17)	 (19)	1:2	20	84

[a] Isolated yields.

of 2'-chloroprop-2'-enyloxyanthraquinones in short reaction times (7–25 min). All reactions produced anthrafurandiones as major products in moderate to good yields (Table 2) instead of the expected rearranged products, such as 2-(2'-chloroprop-2'-enyl)-1-hydroxyanthraquinone (**42**) (Figure 2).

In some reactions, we observed the formation of 1-hydroxyanthraquinone derivatives stemming from deprotection of starting anthraquinones. For example, in treatment of 1-(2'-chloroprop-2'-enyloxy)anthraquinone

Table 2. Reductive Claisen rearrangement of 2'-chloroprop-2'-enyloxyanthraquinones with iron in a mixture of two ionic liquids, [Hmim]BF_4 and [Bzmim]Cl, at 160 °C.

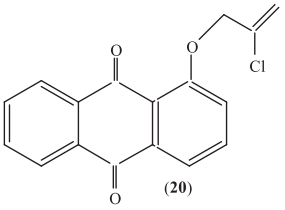
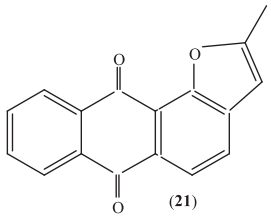
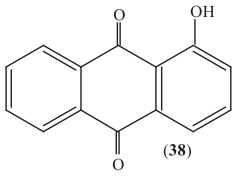
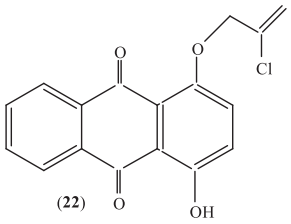
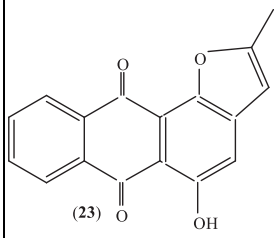
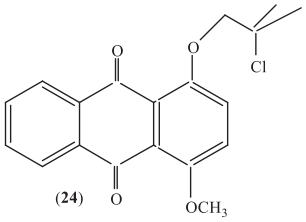
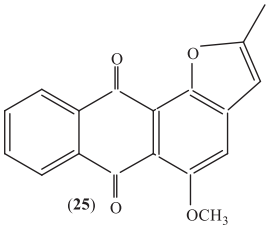
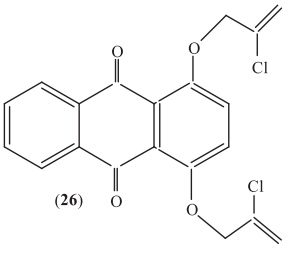
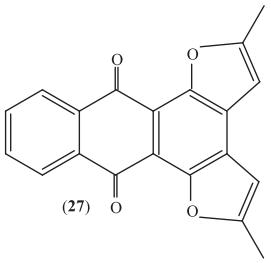
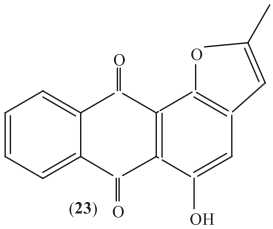
Entry no.	Substrate	Product	Molar ratio AQ : Fe	Time (min)	Yield (%)[a]
1	 (20)	 (21)  (38)	1:2	20	82 15
2	 (22)	 (23)	1:2	10	83
3	 (24)	 (25)	1:2	10	71
4	 (26)	 (27)  (23)	1:1	16	62 36

Table 2. Continued.

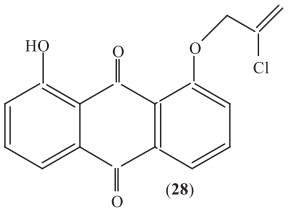
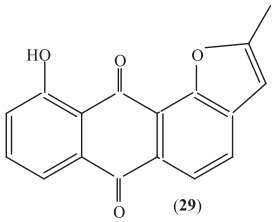
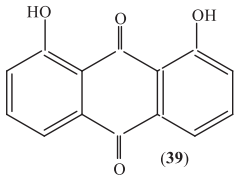
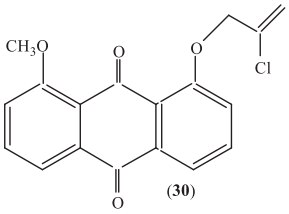
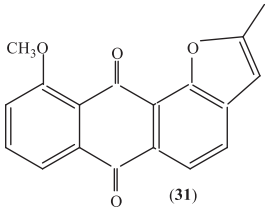
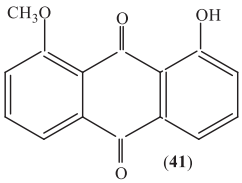
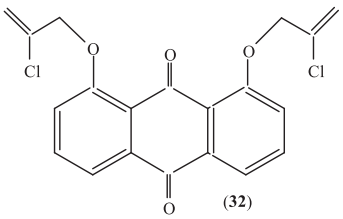
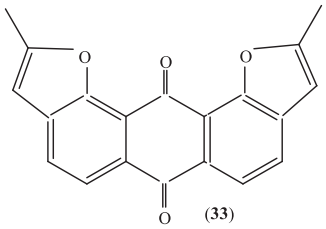
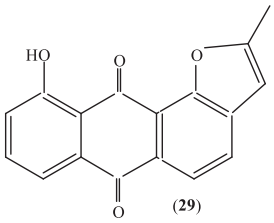
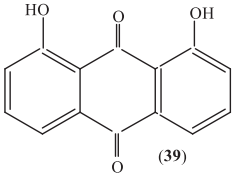
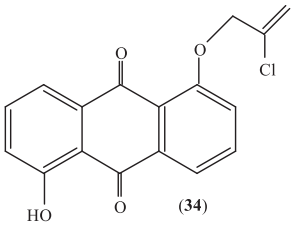
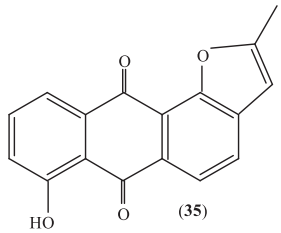
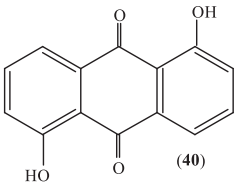
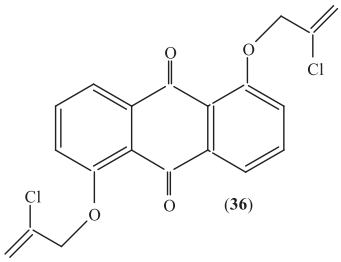
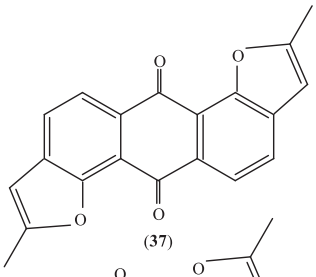
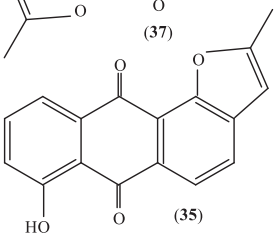
Entry no.	Substrate	Product	Molar ratio AQ : Fe	Time (min)	Yield (%) [a]
5	 (28)	 (29)  (39)	1:2	10	93 5
6	 (30)	 (31)  (41)	1:2	15	45 10
7	 (32)	 (33)  (29)  (39)	1:1	20	54 38 5

Table 2. Continued.

Entry no.	Substrate	Product	Molar ratio AQ : Fe	Time (min)	Yield (%) [a]
8	 (34)	 (35)  (40)	1:2	7	86 11
9	 (36)	 (37)  (35)	1:4	25	47 45

[a] Isolated yields.

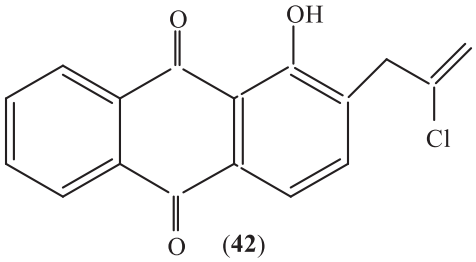

(42)

Figure 2. 2-(2'-Chloroprop-2'-enyl)-1-hydroxyanthraquinone (**42**).

(**20**) with iron powder (2 equiv.) in a mixture of [Hmim]BF_4 and [Bzmim]Cl at 160 °C, 2-methyl-6,11-dihydroanthra[1,2-b]furan-6,11-dione (**21**) was produced in 82% yield with concomitant formation of 1-hydroxyanthraquinone (**38**) in 15% yield after 20 min. However, this reaction was unsuccessful in the absence of iron (i.e. thermal conditions), [Hmim]BF_4, or [Bzmim]Cl at 160 °C again. In these attempts, **20** remained

completely intact after 2 h. Moreover, we did not observe the formation of an anthracenone derivative or loss of the methoxy group attached to the anthraquinone core (entry 6) in the reactions given in Table 2. Starting 2'-chloroprop-2'-enyloxyanthraquinones were easily synthesized by the reaction of the corresponding hydroxyanthraquinones with 2, 3-dichloroprop-1-ene in the presence of anhydrous potassium carbonate in DMF as solvent at 70 °C with reaction times up to 40 h.[25]

Then we decided to study the activity difference between prop-2'-enyloxy and 2'-chloroprop-2'-enyloxy groups in reductive Claisen rearrangement. For this purpose, reductive Claisen rearrangement of **1** was studied in the presence of **20** (1:1) at 110 °C via the present method. The result and conversion yield of this selective reaction is shown in Figure 3.

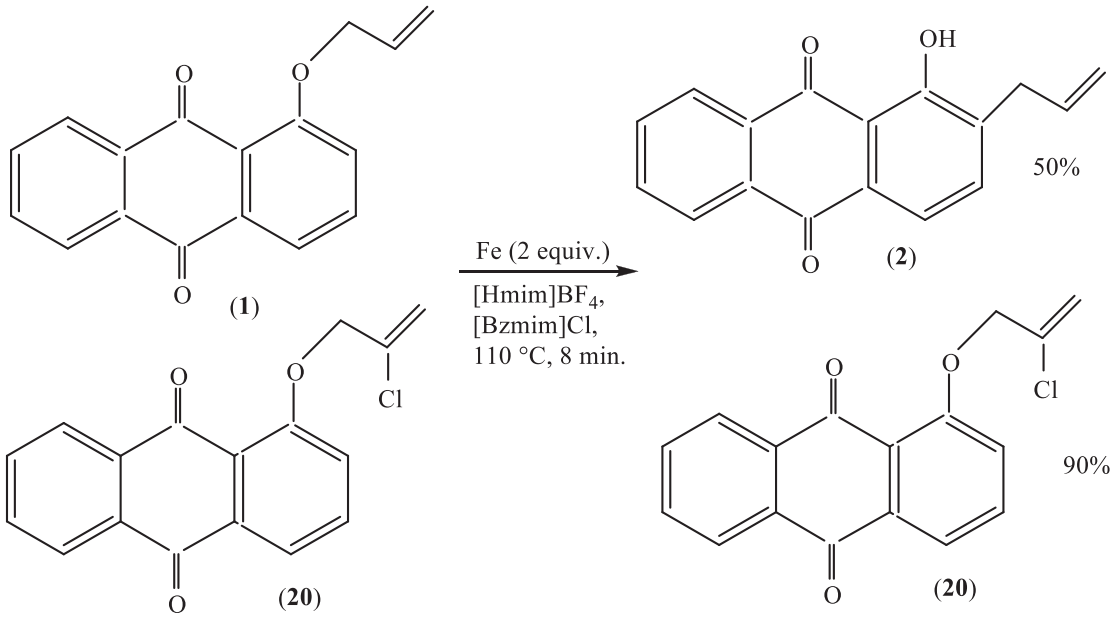


Figure 3. Selectivity between **1** and **20** in the reductive Claisen rearrangement using Fe/[Hmim]BF_4/[Bzmim]Cl at 110 °C.

As shown in this figure, reductive Claisen rearrangement of **1** is carried out in the presence of **20** in good selectivity, indicating that the prop-2'-enyloxy group is more active than the 2'-chloroprop-2'-enyloxy group in this rearrangement.

The proposed mechanism of these reactions is shown in Figure 4. First the anthraquinone core is reduced using iron powder in the presence of [Bzmim]Cl and [Hmim]BF_4 to its electron-rich hydroquinone intermediate **A** that easily performs this rearrangement. Intermediate **C** is formed after rearrangement followed by enolization. In this intermediate (if X = Cl), the OH group ortho to the allyl group is added to the double bond of this side chain, affording intermediate **D**. This internal cyclization in acidic media followed by HCl elimination leads to intermediate **E** containing furan moiety. Finally, product **2** or **21** is produced by air oxidation of intermediate **C** (X = H) or intermediate **E**, respectively. As mentioned above, these reactions were unsuccessful in the absence of iron (i.e. thermal conditions), [Hmim]BF_4, or [Bzmim]Cl. These results confirm the reductive nature of this rearrangement via electron transfer from iron to anthraquinone core (Figure 4, step 1), which is facilitated by theses ionic liquids. Also, when the rearrangement of **20** was performed under N_2 atmosphere via the present method, desired product **21** was produced in only 20% yield together with **38** in

40% yield after 20 min. This result also indicates the importance of air oxidation to produce the final product and is in accordance with the present mechanism (Figure 4, final step).

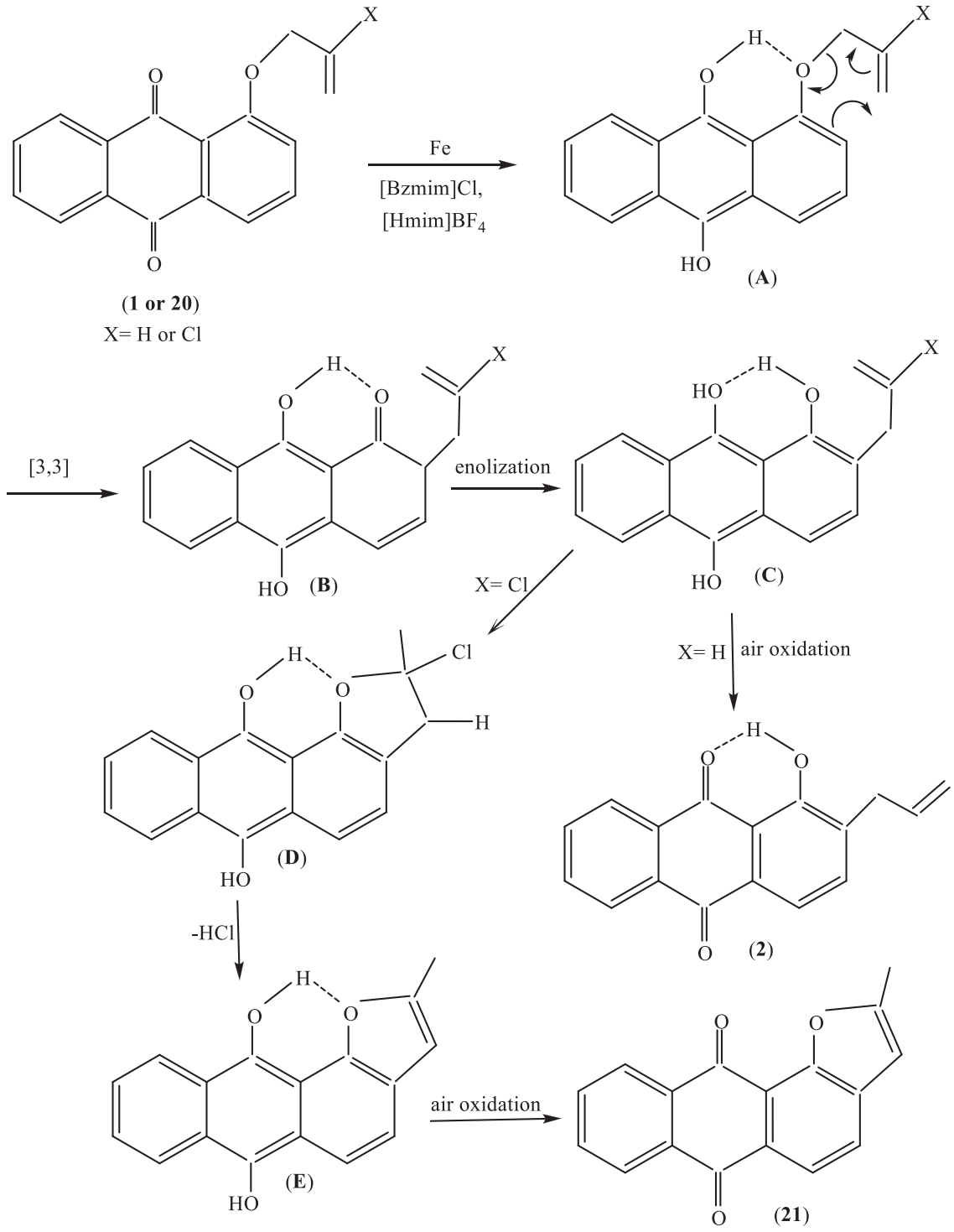


Figure 4. The proposed mechanism of the reductive Claisen rearrangement of prop-2'-enyloxyanthraquinones and 2'-chloroprop-2'-enyloxyanthraquinones using Fe/[Hmim]BF_4/[Bzmim]Cl.

In conclusion, the present investigation has demonstrated that prop-2'-enyloxyanthraquinones and also 2'-chloroprop-2'-enyloxyanthraquinones can be easily rearranged to their corresponding 1-hydroxy-2-(prop-2'-enyl)anthraquinones and anthrafurandiones respectively by the reductive Claisen rearrangement using iron powder. With respect to the important uses of ionic liquids in organic synthesis as environmentally friendly solvents, this rearrangement is carried out in [Bzmim]Cl under an acidic condition created by [Hmim]BF_4 in moderate to excellent yields and in short reaction times. Most notably, in contrast to some previous works,[15] no anthracenone formation or loss of methoxy group attached to the anthraquinone core was observed in these rearrangements. Also, it is possible to execute mono or double Claisen rearrangement selectively in bis(prop-2'-enyloxy)anthraquinone systems while controlling the molar ratio of the reductant or reaction time. In addition, it was found that the prop-2'-enyloxy group is more active than the 2'-chloroprop-2'-enyloxy group in this rearrangement via the present method.

3. Experimental

Solvents, reagents, and chemicals were obtained from Merck, Fluka, or Aldrich chemical companies. Some substrates and all products are known compounds[16,20,21,26–29] and were characterized by comparison of their physical or spectral data with authentic samples. Physical and spectral data for new substrates have been given below. Fourier transform-infrared spectra were recorded on a PerkinElmer RXI spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 300 and 500 spectrometer. UV/Vis spectra were obtained with an Analytik Jena SPECORD 205 spectrometer. Elemental analysis was 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.

3.1. Typical procedure for the reductive Claisen rearrangement of 1-(prop-2'-enyloxy)anthraquinone (1) to 1-hydroxy-2-(prop-2'-enyl)anthraquinone (2)

1-(Prop-2'-enyloxy)anthraquinone (**1**) (1 mmol, 0.264 g) and iron powder (2 mmol, 0.11 g) were added to a flask containing a mixture of two ionic liquids, 1-methylimidazolium tetrafluoroborate [Hmim]BF_4 (5 mmol, 0.85 g) and 1-benzyl-3-methylimidazolium chloride [Bzmim]Cl (3 mmol, 0.625 g), in an oil bath at 110 °C. The reaction mixture was stirred for 8 min in order to complete the reaction, as determined by TLC. The reaction mixture was cooled to room temperature and then filtered after addition of CH_2Cl_2 (2 × 20 mL). The organic layer was washed with water (50 mL), saturated $NaHCO_3$ (50 mL) and brine (50 mL). 1-Hydroxy-2-(prop-2'-enyl)anthraquinone (**2**) was obtained after drying and evaporation of the organic solvent in 98% yield (0.258 g); yellow needles (from acetone), mp = 121–122 °C (lit.[26] 120–120.5 °C).

3.2. Typical procedure for the reductive Claisen rearrangement of 1-(2'-chloroprop-2'-enyloxy) anthraquinone (20) to 2-methyl-6,11-dihydroanthra[1,2-b]furan-6,11-dione (21)

1-(2'-Chloroprop-2'-enyloxy)anthraquinone (**20**) (1 mmol, 0.3 g) and then iron powder (2 mmol, 0.11 g) were added to a flask containing a mixture of two ionic liquids, 1-methylimidazolium tetrafluoroborate [Hmim]BF_4 (5 mmol, 0.85 g) and 1-benzyl-3-methylimidazolium chloride [Bzmim]Cl (6 mmol, 1.25 g), in an oil bath at 160 °C. The reaction mixture was stirred for 20 min to complete the reaction, as determined by TLC. The reaction mixture was cooled to room temperature and then filtered after addition of CH_2Cl_2 (2 × 20 mL).

The organic layer was washed with water (50 mL), saturated $NaHCO_3$ (50 mL), and brine (50 mL). 2-Methyl-6,11-dihydroanthra[1,2-b]furan-6,11-dione (**21**) was isolated after evaporation of organic solvent and column chromatography of the crude mixture on silica gel 60 using n-hexane-ethyl acetate (30:1) as eluent in 82% yield (0.21 g); mp = 191–193 °C (lit.[29] 192–193 °C). Also, 1-hydroxyanthraquinone (**38**) was isolated using this column chromatography in 15% yield (0.034 g).

3.3. Data

3.3.1. 1-(2'-Chloroprop-2'-enyloxy)-4-methoxyanthraquinone (24)

Orange needles; mp = 142–144 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.94 (s, 3H), 4.64 (s, 2H), 5.46 (d, 1H, J= 1.1 Hz), 5.85 (d, 1H, J= 1.4 Hz), 7.26 (m, 2H), 7.64–7.66 (m, 2H), 8.09–8.11 (m, 2H), ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 57.10, 72.51, 114.59, 119.91, 123.13, 123.58, 124.22, 126.60, 126.71, 133.53, 133.65, 134.18, 134.39, 135.68, 152.05, 155.33, 183.24, 183.40 ppm; IR(KBr): 3125 (w), 2919 (w), 2848 (w), 1666 (s), 1646 (w), 1567 (w), 1435 (w), 1404 (w), 1322 (m), 1270 (s), 1251 (s), 1059 (m), 987 (m), 817 (w), 724 (m) cm^{-1}; UV (MeOH), λ_{max} (log ε): 204 (4.28), 221 (4.29), 251 (4.30), 412 (3.61) nm; Anal. Calcd for $C_{18}H_{13}O_4Cl$: C, 65.75; H, 3.95. Found: C, 64.88; H, 3.58.

3.3.2. 1-(2'-Chloroprop-2'-enyloxy)-8-hydroxyanthraquinone (28)

Yellow-orange powder; mp = 133–135 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.69 (s, 2H), 5.49–5.50 (d, 1H, J= 1.4 Hz), 5.95 (d, 1H, J= 1.65 Hz), 7.18–7.23 (m, 2H), 7.53–7.56 (m, 1H), 7.64–7.70 (m, 2H), 7.91–7.93 (m, 1H), 12.87 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 70.98, 114.40, 117.12, 119.08, 119.79, 121.18, 121.36, 124.97, 132.75, 134.66, 135.87, 135.96, 136.14, 158.82, 162.65, 182.63, 188.64 ppm; IR (KBr): 3422 (br), 3114 (w), 2924 (m), 2856 (w), 1669 (m), 1638 (s), 1587 (m), 1448 (m), 1289 (s), 1239 (s), 1025 (m), 843 (w), 744 (m) cm^{-1}; UV (MeOH), λ_{max} (log ε): 222 (4.48), 254 (4.30), 409 (3.83) nm; Anal. Calcd for $C_{17}H_{11}O_4Cl$: C, 64.86; H, 3.49. Found: C, 63.95; H, 3.19.

3.3.3. 1-(2'-Chloroprop-2'-enyloxy)-8-methoxyanthraquinone (30)

Yellow powder; mp = 138–140 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.94 (s, 3H), 4.69 (s, 2H), 5.44 (d, 1H, J= 1.1 Hz), 5.85 (d, 1H, J= 1.5 Hz), 7.18–7.25 (m, 2H), 7.54–7.60 (m, 2H), 7.77–7.83 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 56.78, 71.22, 114.27, 118.25, 119.21, 120.34, 120.46, 124.02, 124.80, 126.70, 133.99, 134.23, 134.93, 135.05, 157.56, 159.68, 182.57, 183.94 ppm; IR (KBr): 3018 (w), 2925 (w), 2856 (w), 1670 (s), 1647 (m), 1589 (m), 1325 (s), 1290 (s), 1240 (s), 1064 (m), 986 (s), 818 (w), 742 (m) cm^{-1}; UV (MeOH), λ_{max} (log ε): 222 (4.67), 256 (4.49), 382 (3.92) nm; Anal. Calcd for $C_{18}H_{13}O_4Cl$: C, 65.75; H, 3.95. Found: C, 65.62; H, 3.68.

3.3.4. 1,8- Bis(2'-chloroprop-2'-enyloxy)anthraquinone(32)

Yellow needles; mp = 161–163 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.72 (s, 4H), 5.51–5.52 (d, 2H, J= 1.38 Hz), 5.97–5.98 (d, 2H, J= 1.6 Hz), 7.24–7.27 (m, 2H), 7.60–7.65 (m, 2H), 7.86–7.89 (m, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 70.89, 113.81, 120.03, 120.09, 124.45, 133.92, 134.78, 134.80, 157.26, 181.85, 183.43 ppm; IR (KBr): 3094 (w), 3032 (w), 2909 (w), 2854 (w), 1665 (s), 1640 (m), 1588 (s), 1447 (m), 1322 (s), 1287 (s),

1238 (s), 1076 (m), 999 (m), 903 (m), 836 (w), 743 (m) cm^{-1}; UV (MeOH), λ_{max} (log ε): 286 (3.09), 376 (3.79) nm; Anal. Calcd for $C_{20}H_{14}O_4Cl_2$: C, 61.69; H, 3.60. Found: C, 61.36; H, 3.21.

3.3.5. 1-(2'-Chloroprop-2'-enyloxy)-5-hydroxyanthraquinone (34)

Yellow powder; mp = 140–143 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.77 (s, 2H), 5.57 (s, 1H), 6.03 (s, 1H), 7.25–7.33 (m, 2H), 7.66–7.80 (m, 3H), 8.03–8.05 (d, 1H, J= 7.75 Hz), 12.46 (s, 1H) ppm; ^{13}C NMR ($CDCl_3$, 125 MHz): δ 70.96, 114.27, 115.61, 119.41, 120.33, 120.53, 123.06, 123.15, 134.64, 134.90, 134.99, 135.52, 136.97, 158.43, 162.09, 181.31, 188.36 ppm; IR (KBr): 3415 (br), 3022 (w), 2925 (s), 2856 (s), 1656 (m), 1631 (m), 1621 (m), 1605 (m), 1587 (m), 1454 (m), 1288 (m), 1264 (s), 1103 (s), 1023 (s), 860 (w), 779 (w) cm^{-1}; UV (MeOH), λ_{max} (log ε): 294 (2.73), 402 (3.52) nm; Anal. Calcd for $C_{17}H_{11}O_4Cl$: C, 64.86; H, 3.50. Found: C, 63.79; H, 3.30.

Acknowledgment

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References

1. Wang, J.; Qin, X.; Chen, Z.; Ju, Z.; He, W.; Tan, Y.; Zhou, X.; Tu, Z.; Lu, F.; Liu, Y. *Phytochem. Lett.* **2016**, *15*, 13-15.
2. Choi, H. K.; Ryu, H.; Son, A.; Seo, B.; Hwang, S. G.; Song, J. Y.; Ahn, J. *Biomed. Pharmacother.* **2016**, *79*, 308-314.
3. Abu, N.; Akhtar, M. N.; Ho, W. Y.; Yeap, S. K.; Alitheen, N. B. *Molecules* **2013**, *18*, 10367-10377.
4. Zhang, Z.; Wu, X. H.; Sun, F. Q.; Shan, F.; Chen, J. C.; Chen, L. M.; Zhou, Y. S.; Mei, W. J. *Inorg. Chem. Acta* **2014**, *418*, 23-29.
5. Park, M. Y.; Kwon, H. J.; Sung, M. K. *Biosci. Biotechnol. Biochem.* **2009**, *73*, 828-832.
6. Hou, Y.; Cao, S.; Brodie, P. J.; Callmander, M. W.; Ratovoson, F.; Rakotobe, E. A.; Rasamison, V. E.; Ratsimbason, M.; Alumasa, J. N.; Roepe, P. D. et al. *Bioorg. Med. Chem.* **2009**, *17*, 2871-2876.
7. Wuthi-udomlert, M.; Kupittayanant, P.; Gritsanapan, W. *J. Health Res.* **2010**, *24*, 117-122.
8. van Gorkom, B. A. P.; de Veries, E. G. E.; Karrenbeld, A.; Kleibeuker, J. H. *Aliment. Pharmacol. Ther.* **1999**, *13*, 443-452.
9. Yen, G. C.; Duh, P. D.; Chuang, D. Y. *Food Chem.* **2000**, *70*, 437-441.
10. Davis, R.; Agnew, P.; Shapiro, E. *J. Am. Podiatr. Med. Assoc.* **1986**, *76*, 61-66.
11. Dauzonne, D.; Fouris, S. *Tetrahedron* **1993**, *49*, 8865-8876.
12. Karhunen, P.; Brunow, G. *Acta Chem. Scand.* **1991**, *45*, 945-948.
13. Ghosh, A.; Jose, D. A.; Kaushik, R. *Sens. Actuators B* **2016**, *229*, 545-560.
14. Langdon-Jones, E. E.; Pope, S. J. A. *Coord. Chem. Rev.* **2014**, *269*, 32-53.
15. Cambie, R. C.; Milbank, J. B. J.; Rutledge, P. S. *Org. Prep. Proced. Int.* **1997**, *29*, 365-407.
16. Cambie, R. C.; Howe, T. A.; Pausler, M. G.; Rutledge, P. S.; Woodgate, P. D. *Aust. J. Chem.* **1987**, *40*, 1063-1072.
17. Cambie, R. C.; Holroyd, S. E.; Larsen, D. S.; Rutledge, P. S.; Woodgate, P. D. *Aust. J. Chem.* **1992**, *45*, 1589-1610.
18. Boddy, I. K.; Boniface, P. J.; Cambie, R. C.; Craw, P. A.; Larsen, D. S.; McDonald, H.; Rutledge, P. S.; Woodgate, P. D. *Tetrahedron Lett.* **1982**, *23*, 4407-4408.

19. Murty, K. V. S. N.; Pal, R.; Datta, K.; Mal, D. *Synth. Commun.* **1994**, *24*, 1287-1292.
20. Sharghi, H.; Aghapour, G. *J. Org. Chem.* **2000**, *65*, 2813-2815.
21. Nadali, S.; Aghapour, G.; Rafieepour, Z. *Can. J. Chem.* **2017**, *95*, 1045-1051.
22. Welton, T. *Chem. Rev.* **1999**, *99*, 2071-2084.
23. Chiappe, C.; Pieraccini, D. *J. Phys. Org. Chem.* **2005**, *18*, 275-297.
24. Holbrey, J. D.; Seddon, K. R. *J. Chem. Soc. Dalton Trans.* **1999**, 2133-2139.
25. Pausler, M. G.; Rutledge, P. S. *Aust. J. Chem.* **1994**, *47*, 2149-2160.
26. Boddy, I. K.; Boniface, P. J.; Cambie, R. C.; Craw, P. A.; Huang, Z. D.; Larsen, D. S.; MacDonald, H.; Rutledge, P. S.; Woodgate, P. D. *Aust. J. Chem.* **1984**, *37*, 1511-1529.
27. Khalafy, J.; Bruce, J. M. *J. Sci. I. R. Iran* **1993**, *4*, 285-289.
28. Wong, C. M.; Singh, R,; Singh, K. *Can. J. Chem.* **1979**, *57*, 3304-3307.
29. Cambie, R. C.; Zhen-Dong, H.; Noall, W. I.; Rutledge, P. S.; Woodgate, P. D. *Aust. J. Chem.* **1981**, *34*, 819-828.