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# Amberlite IRA 402(OH): an efficient mediator for the exclusive synthesis of fused tricyclic oxaza quinolinium salts

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ABSTRACT

A high yielding green protocol for the synthesis of tricyclic oxaza quinolinium salts has been developed using Amberlite IRA 402(OH) in water. This method is more effective compared to previously reported phase-transfer catalytic (PTC) condition in terms of yield of the product, reaction time and ease of separation.

## 1. Introduction

The development of new methodologies that can afford products of greater structural complexity from relatively simple starting materials with fewer synthetic steps but ensuring high yield under mild reaction conditions is the prime challenge for organic chemists.[1] This challenge has become more pertinent nowadays due to global[2] environmental legislation that is coming into effect on chemical process industries. Thus, concerted efforts are being made for establishing organic reactions, which have no adverse effect on the environment.

Among the various manifestations, use of water as a solvent is assuming increasing relevance in many organic reactions[3] because it is abundant in nature, has virtually no cost and is safest among all available solvents, thus leading to environmentally benign chemical processes.[4] Also the use of heterogeneous catalysts such as ion exchange resins, clays and zeolites has received great impetus in different areas of organic synthesis[5] due to their low cost, ready availability, operative simplicity, greater selectivity, reusability, noncorrosiveness and overall environmental compatibility.[6]

New methods of ring formation in heterocyclic chemistry, particularly concerned with nitrogen heteroaromatic cations, are gaining significance due to their attractive biological properties of the products.[7] As a part of our ongoing investigation for the formation of newer heteroaromatics, very recently we have reported the synthesis of tri-, tetra- and penta-cyclic fused quinolones (**2**, **4**, **6**) and quinolinium cations (**1**, **3**, **5**) having six-, seven- and eight-membered ring systems (Fig 1) from easily available 8-hydroxyquinolines and 1,ω-dihaloalkanes/xylenes/methyl-quinoxalines in water–dichloromethane biphasic system using a phase-transfer catalyst (TBAB).[8] Although the reported method is effective, it suffers from some drawbacks such as long reaction time, involvement of hazardous solvent (DCM) and more specifically entails tedious separation of the complex mixtures of quinoliniums and quinolones, leaving scope for further development of the methodology towards the exclusive preparations of quinolinium cations without the formation of quinolones and vice versa. It is pertinent to mention that we have been successful in developing an effective methodology for the exclusive preparation of quinolones in an aqueous micellar system.[9] After a thorough and systematic study with different heterogeneous catalysts in an aqueous medium we have discovered that Amberlite IRA 402(OH) (type 1), an ion exchange resin based on cross-linked polystyrene having high regeneration efficiency and excellent rinse performance,[10] is an effective catalyst for the preparation of fused quinolinium cations. In this Letter, we wish to report a simple and truly green protocol for the exclusive synthesis of fused tricyclic oxaza quinolinium cations in short reaction time using Amberlite IRA 402(OH)® resin (Scheme 1). General applicability of the catalyst as well as its reusability has also been discussed.

## 2. Results and discussion

5-Chloro-8-hydroxy quinoline (**1a**) and dibromo ethane (**2a**) were employed as the model reactants in 1:3 molar ratios in the

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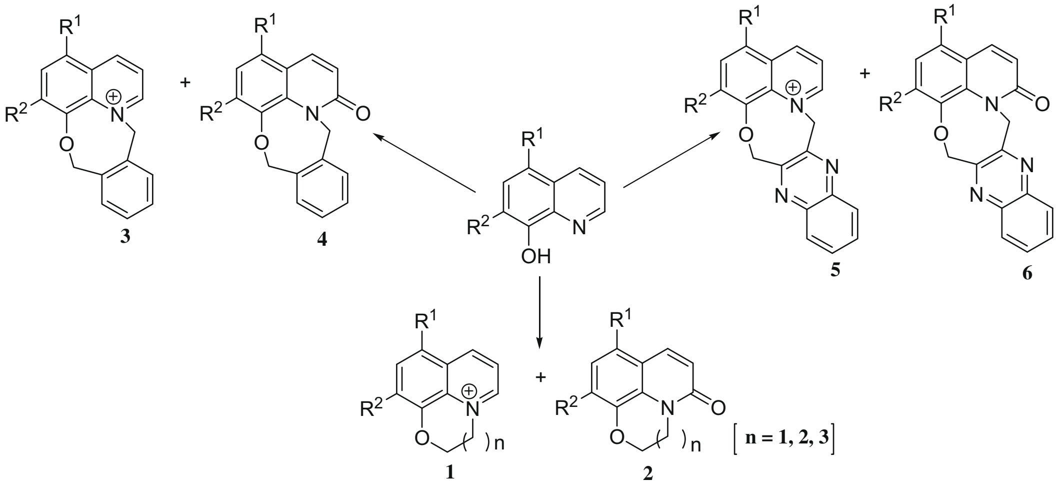
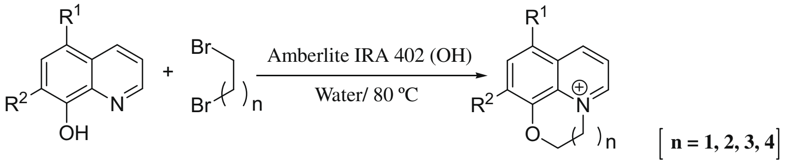


**Figure 1.** Tri-, tetra- and penta-cyclic quinolones and quinoliniums.



**Scheme 1.** General reaction scheme.

presence of Amberlite IRA 402(OH) in water. The reactions were performed for different time periods and at different temperatures, the progress being monitored by TLC studies. On carrying out the reactions at ambient temperature, not much change was observed even after 12 h (Table 1, entry 1). The same result was observed when the reaction was performed at 40 °C for 8 h (Table 1, entry 2). Successive reactions at 50, 60 and 70 °C indicated the formation of product **3a** on TLC studies but complete conversion was not observed even after 4 h of the reactions (Table 1, entries 3–5). However, when the temperature of the reaction mixture was increased to 80 °C, complete consumption of the substrate was observed within 2 h (Table 1, entry 6). The mixture was then filtered using sintered disc to remove the resins and the filtrate was then concentrated under reduced pressure.[11] Crystallization from methanol produced 93% of expected oxazino quinolinium salt, which displayed the expected signal of quaternary salt in its mass spectrum.[12] Other spectroscopic analyses like $^{1}$H NMR and $^{13}$C NMR were used for characterization of the product. It is noteworthy that earlier[8a] we were unable to isolate oxazinoquinolinium salt perhaps due to very quick conversion of quinoliniums to quinolones in that environment. In order to verify the effectiveness of Amberlite IRA 402(OH) a series of reactions were performed with different resins. It was found that although they are able to produce the product (**3a**), the yields are very low (31–52%), compared to that (93%) obtained using Amberlite IRA 402(OH) resin (Table 1, entries 6–13).

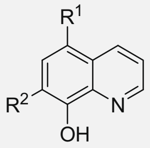
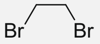
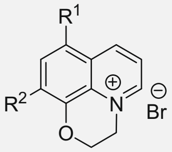
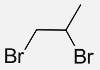
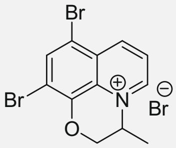
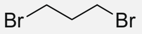
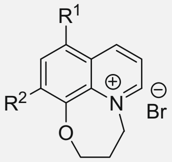
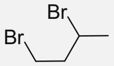
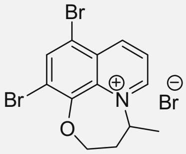
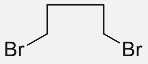
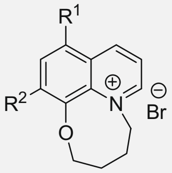
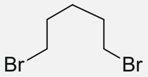
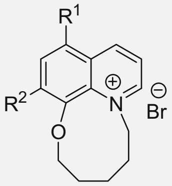
**Table 1**
Optimization of the reaction condition for the synthesis of tricyclic fused oxaza quinoliniums

| Entry | Resin[a] | Temp (°C) | Time (h) | Yield[b] (%) |
|---|---|---|---|---|
| 1 | Amberlite IRA 402(OH) | Rt | 12 | NR[c] |
| 2 | Amberlite IRA 402(OH) | 40 | 8 | NR |
| 3 | Amberlite IRA 402(OH) | 50 | 4 | 20 |
| 4 | Amberlite IRA 402(OH) | 60 | 4 | 30 |
| 5 | Amberlite IRA 402(OH) | 70 | 4 | 55 |
| 6 | Amberlite IRA 402(OH) | 80 | 2 | 93 |
| 7 | Amberlite IRA 402(OH) | 80 | 3 | 93 |
| 8 | Amberlite IRA 402(OH) | 85 | 4 | 93 |
| 9 | Amberlite IRA 402(Cl) | 45 | 12 | 23 |
| 10 | Amberlite IRA 402(Cl) | 75 | 12 | 39 |
| 11 | Amberlite IRA 402(Cl) | 85 | 12 | 39 |
| 12 | Amberlyst A-26 | 85 | 12 | 52 |
| 13 | Amberlyst A-27 | 85 | 12 | 31 |

[a] All the reactions were performed using **1a** and **2a**.
[b] Isolated yield.
[c] NR = No reaction.

Encouraged by the result obtained we turned our attention towards unsubstituted (**1b**) and differently substituted 8-hydroxy quinolines [5,7-dibromo (**1c**), 5-chloro-7-iodo (**1d**), 2-methyl (**1e**)] and reacted them with homologues of dibromoalkanes, like dibromo-propane (**2c**), -butane (**2e**) and -pentane (**2f**), to generalize the efficacy of this catalytic system. In most of the cases the reactions yielded the corresponding quinoliniums (**3a**, **3c**, **3d**, **4a**–**e**, **5a**–**d**) almost quantitatively (Table 2, entries 1–12) with no quinolones or dimers as byproducts, which were usually formed in our previous attempts. However, in case of the enhanced ring systems like oxazoninoquinoliniums (**6a**, **6b**, **6d**), low yields (5–25%) were observed (Table 2, entries 13–15) probably due to the formation of highly strained nine-membered rings. Fascinated by these observations we tried to explore the scope of this methodology using the secondary dibromides (**2b**, **2d**) and we were successful in synthesizing the corresponding tricyclic quinoliniums (**3e**, **4f**) with high yields (80–87%). Although theoretically there remains a possibility of the formation of two isomers, in the course of our studies we were able to isolate only one isomer. We presume that the quinoxide ion preferentially attacked at the more reactive primary bromide ($-CH_2Br$) end and then the cyclization occurred through the other end of the dibromide ($-CHBr$) and the corresponding fused quinolinium was produced exclusively. This presumption was supported by the inability of 5-chloro-8-hydroxy quinoline (**1a**) to couple with 2,3-dibromobutane (**2g**), when **1a** was reacted with **2g** under the optimal set of reaction conditions,

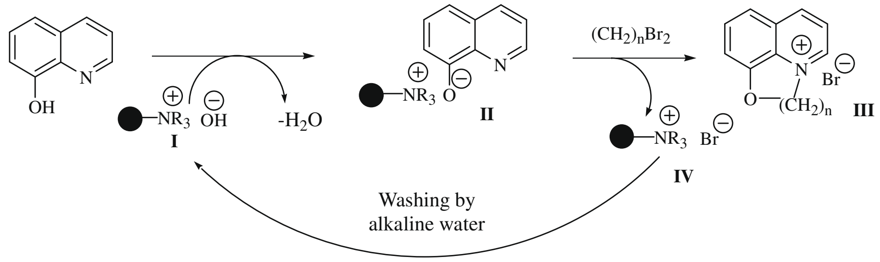
**Table 2**
Synthesis of tricyclic fused oxaza quinolinium salts using Amberlite IRA 402(OH)® catalyst

| Entry | 8-Hydroxy quinoline | Alkylating agent | Fused quinolinium[a] | Temp (°C) | Time (h) | Yields[b] (%) |
|---|---|---|---|---|---|---|
| |  |  |  | | | |
| 1 | **1a** (R$^1$ = Cl, R$^2$ = H) | **2a** | **3a** | 80 | 2 | 93 |
| 2 | **1c** (R$^1$ = R$^2$ = Br) | | **3c** | 80 | 3 | **97** |
| 3 | **1d** (R$^1$ = Cl, R$^2$ = I) | | **3d** | 80 | 3 | 90 |
| | |  |  | | | |
| 4 | **1c** (R$^1$ = R$^2$ = Br) | **2b** | **3e** | 80 | 3 | **80** |
| | |  |  | | | |
| 5 | **1a** | **2c** | **4a** | 80 | 3 | 89 |
| 6 | **1b** (R$^1$ = R$^2$ = H) | **2c** | **4b** | 80 | 3 | 94 |
| 7 | **1c** | **2c** | **4c** | 80 | 4 | 87 |
| 8 | **1d** | **2c** | **4d** | 80 | 3 | 84 |
| 9 | **1e** | **2c** | **4e** | 80 | 3 | 88 |
| | |  |  | | | |
| 10 | **1c** | **2d** | **4f** | 80 | 4 | 87 |
| | |  |  | | | |
| 9 | **1a** | **2e** | **5a** | 80 | 4 | 81 |
| 10 | **1b** | **2e** | **5b** | 80 | 4 | 88 |
| 11 | **1c** | **2e** | **5c** | 80 | 4 | 98 |
| 12 | **1d** | **2e** | **5d** | 80 | 4 | 87 |
| | |  |  | | | |
| 13 | **1a** | **2f** | **6a** | 80 | 8 | 20 |
| 14 | **1b** | **2f** | **6b** | 80 | 10 | 5 |
| 15 | **1d** | **2f** | **6d** | 80 | 10 | 25 |

[a] All the reactions are performed using water as solvent and in the presence of Amberlite IRA 402(OH) resin.
[b] Isolated yield.

and the starting materials were recovered unaltered. All the products were characterized by NMR and Mass spectral analyses, and also by comparison of the data with those reported in the literature.[8,12] It is remarkable that the reactions were confined to the formation of quinolinium cations exclusively even after enhanced time period (12 h). However, in the absence of the resin the reaction did not yield the desired product even after 24 h. In another attempt, we performed the reaction with the resin and added 10% of NaOH solution to the system, which produced the quinolones only. From this observation the inference can be drawn that lack of free hydroxyl ion in the system in the absence of NaOH prevents the conversion of quinoliniums to quinolones. To the best of our knowledge this is the first report of Amberlite IRA 402(OH) mediated fused quinolinium preparation.

Though the mechanism is not certain, the plausible pathway of the reaction is depicted in Scheme 2. It is presumed that the reaction is initiated by amberlite resin (**I**) converting the hydroxyquinoline to the quinoxide ion (**II**) and thus promoting it towards the



**Scheme 2.** Mechanistic pathway for Amberlite IRA 402(OH) mediated fused tricyclic oxaza quinolium salt formation.

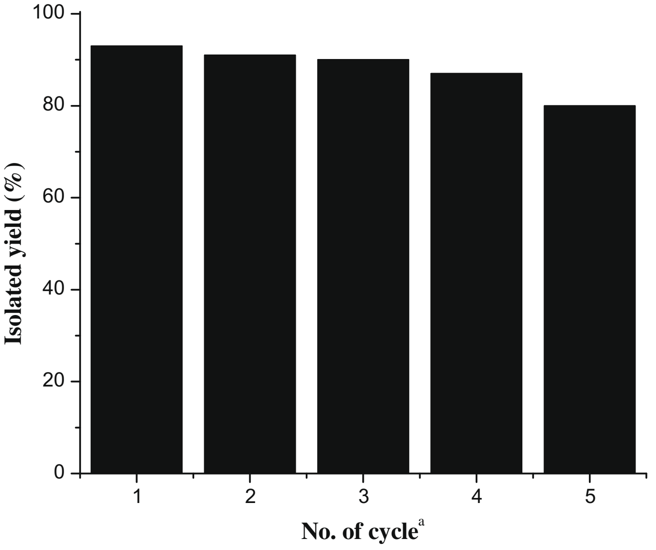


**Figure 2.** Reusability of the Amberlite IRA 402(OH) resin tested using **1a** and **2b**. [a]The reactions were performed with **1a** (3.3 mmol) and **2a** (10 mmol) successively using 400 mg. Amberlite IRA 402(OH) resin at 80 °C for 2 h.

organic layer (dibromoalkane) by acting as phase-transfer catalyst. Finally the resin bound quinoxide ion (**II**) reacts with dibromoalkane to furnish the desired quinolinium (**III**) through O, N-dialkylation.

After work-up of the reaction the resin was recovered by simple filtration, thoroughly washed first with ethanol and then with alkaline water. It was then dried at 80 °C under reduced pressure for 2 h and reused for subsequent runs. It was observed that after consecutive five-time use of the resin, there is a slight decrease in the conversion (93–80%) of the fused quinolinium products (Fig. 2).

## 3. Conclusion

In summary, we have described a simple, convenient and efficient green protocol for the synthesis of the expanded ring system of fused tricyclic oxaza quinolinium cations in a one-pot sequence using ion exchange resin, Amberlite IRA 402(OH). The notable features of this method are mild reaction conditions, greater selectivity, operational simplicity, cleaner reaction profile, low cost and reusability of the catalyst that makes it an attractive and useful process for the synthesis of newer heteroaromatics having potential biological activity.

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11. (a) *General reaction procedure for the synthesis of fused tricyclic quinolinium bromides* (**3**–**6 a**–**d**): Appropriate amount (3.3 mmol) of 8-hydroxyquinoline derivatives (**1a**–**e**) was taken in 50 mL of water in a 250 mL RB flask under inert atmosphere, 400 mg of Amberlite IRA 402 (OH) was added (after rinsing the resin properly with methanol) and the mixture was stirred at 30–40 °C till dissolution of the substrate. Then 10 mmol (1:3 molar ratios with respect to

the substrate) of dibromo alkane (**2a**–**f**) was added to the stirred solution of the reaction mixture and the stirring was continued for 30 min. The flask was placed in an oil bath and the stirring was continued for appropriate time at 80 °C. After completion of the reaction, the resin was recovered by simple filtration, thoroughly washed with ethanol and then with alkaline water. Finally it was dried at 80 °C under reduced pressure for 2 h and reused for subsequent runs. Then the filtrate was evaporated to dryness in a rotary evaporator under reduced pressure and the residue was crystallized from methanol, which yielded the respective fused quinolinium bromides (**3a**–**d**, **4a**–**e**, **5a**–**d**). In case of oxazoninoquinoliniums (**6a**–**d**) the residue obtained after evaporation of the filtrate was subjected to dianion column chromatography and the products were eluted with water and finally crystallized from methanol.

12. (a) *7-Chloro-2,3-dihydro-1-oxa-3a-azonia-phenalene; bromide* (**3a**): Quinolinium **3a** was obtained as white needles in 88% yield. Mp: 208–210 °C; $R_f$ (1% MeOH–CHCl$_3$) 0.36; IR (KBr, cm$^{-1}$) $\nu$ 1328, 1402, 3205; $^{1}$H NMR (300 MHz, CDCl$_3$): $\delta$ 4.80 (2H, m, CH$_2$), 5.20 (2H, m, CH$_2$), 7.71 (1H, d, $J$ = 8.7 Hz), 8.08 (1H, d, $J$ = 8.7 Hz), 8.27 (1H, m), 9.43 (2H, m); $^{13}$C NMR (CDCl$_3$, 75 MHz): 54.9 (CH$_2$), 65.0 (CH$_2$), 121.2 (CH), 124.0 (CH), 125.5 (C), 129.2 (C) 129.3 (C), 132.2 (CH), 144.9 (CH), 147.6 (C), 149.2 (CH). ESI-MS: *m*/*z* 206 [M−Br]$^+$, HRMS: calcd 206.0373 [M−Br]$^+$; found 206.0392; (b) *7,9-Dibromo-2,3-dihydro-1-oxa-3a-azonia-phenalene; bromide* (**3c**): Quinolinium **3c** was obtained as white needles in 91% yield. Mp: 212–214 °C; $R_f$ (1% MeOH–CHCl$_3$) 0.35; IR (KBr, cm$^{-1}$) $\nu$ 1272, 1532, 3015; $^{1}$H NMR (300 MHz, CDCl$_3$): $\delta$ 3.32 (2H, m, CH$_2$), 5.20 (2H, m, CH$_2$), 8.27 (1H, t, $J$ = 7.8 Hz), 8.56 (1H, s), 9.40 (2H, m). ESI-MS: *m*/*z* 330 [M−Br]$^+$, HRMS: calcd 327.8973 [M−Br]$^+$; found 327.8982; (c) *7-Chloro-9-iodo-2,3-dihydro-1-oxa-3a-azonia-phenalene; bromide* (**3d**): Quinolinium **3d** was obtained as white needles in 86% yield. Mp: 202–204 °C; $R_f$ (1% MeOH–CHCl$_3$) 0.38; IR (KBr, cm$^{-1}$) $\nu$ 1372, 1398, 3225; $^{1}$H NMR (300 MHz, CDCl$_3$): $\delta$ 3.32 (2H, m, CH$_2$), 5.16 (2H, m, CH$_2$), 8.25 (1H, m), 8.52 (1H, s), 9.40 (2H, m); $^{13}$C NMR (CDCl$_3$, 75 MHz): 53.1 (CH$_2$), 64.5 (CH$_2$), 91.2 (C), 123.3 (C), 123.4 (CH), 126.8 (C) 127.1 (C), 138.4 (CH), 143.2 (CH), 146.4 (C), 148.2 (CH); ESI-MS: *m*/*z* 332 [M−Br]$^+$, HRMS: calcd 331.9339 [M−Br]$^+$; found 331.9355; (d) *7,9-Dibromo-3-methyl-2,3-dihydro-1-oxa-3a-azonia-phenalene* (**3e**): Quinolinium **3e** was obtained as yellow needles in 80% yield. Mp: 218–220 °C; $R_f$ (1% MeOH–CHCl$_3$) 0.32; $^{1}$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 1.62 (3H, m), 2.96 (1H, m), 4.79 (2H, m), 8.33 (1H, s), 8.69 (1H, m), 9.28 (1H, m), 9.60 (1H, m); $^{13}$C NMR (DMSO-$d_6$, 75 MHz): 17.1 (CH$_3$), 59.5 (CH), 68.4 (CH$_2$), 113.0 (C), 113.7 (C), 123.8 (CH), 127.9 (C), 128.2 (C), 136.7 (CH), 144.2 (C), 145.9 (CH), 148.6 (CH); ESI-MS: *m*/*z* 344 [M−Br]$^+$, HRMS: calcd 341.9124 [M−Br]$^+$; found 341.9110; (e) *1,3-Dibromo-7-methyl-8,9-dihydro-7H-10-oxa-6a-azonia-cyclohepta[de]naphthalene* (**4f**): Quinolinium **4f** was obtained as yellow needles in 87% yield. Mp: 226–228 °C; $R_f$ (1% MeOH–CHCl$_3$) 0.33; $^{1}$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.60 (3H, m), 2.43 (1H, m), 4.65 (2H, m), 5.47 (2H, m), 8.28 (2H, m), 9.17 (1H, m), 10.24 (1H, m); $^{13}$C NMR (DMSO-$d_6$, 75 MHz): 19.9 (CH$_3$), 34.9 (CH$_2$), 68.0 (CH), 69.5 (CH$_2$), 117.2 (C), 122.4 (C), 124.0 (CH), 129.8 (C), 135.1 (C), 136.6 (CH), 146.1 (CH), 146.9 (C), 151.0 (CH); ESI-MS: *m*/*z* 358 [M−Br]$^+$, HRMS: calcd 355.9280 [M−Br]$^+$; found 355.9248; (f) *3-Chloro-1-iodo-7,8,9,10-tetrahydro-11-oxa-6a-azonia-cycloocta [de]naphthalene; bromide* (**5d**): Quinolinium **5d** was obtained as white needles in 83% yield. Mp: 210–212 °C; $R_f$ (1% MeOH–CHCl$_3$) 0.37; IR (KBr, cm$^{-1}$) $\nu$ 1362, 1508, 3265; $^{1}$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.83 (2H, m, CH$_2$), 2.43 (2H, m, CH$_2$), 4.48 (2H, m, CH$_2$), 4.64 (2H, m, CH$_2$), 8.23 (1H, m), 8.65 (1H, s), 9.46 (2H, m); $^{13}$C NMR (CDCl$_3$, 75 MHz): 22.5 (CH$_2$), 29.3 (CH$_2$), 63.8 (CH$_2$), 76.1 (CH$_2$), 104.4 (C), 124.9 (CH), 130.4 (C), 130.5 (C) 137.5 (C), 141.1 (CH), 145.9 (CH), 148.4 (C), 154.1 (CH). ESI-MS: *m*/*z* 360 [M−Br]$^+$, HRMS: calcd 359.9652 [M−Br]$^+$; found 359.9662; (g) *3-Chloro-1-iodo-8,9,10,11-tetrahydro-7H-12-oxa-6a-azonia-cyclonona[de]naphthalene; bromide* (**6d**): Quinolinium **6d** was obtained as white needles in 25% yield. Mp: 216–218 °C; $R_f$ (1% MeOH–CHCl$_3$) 0.36; IR (KBr, cm$^{-1}$) $\nu$ 1262, 1500, 3285; $^{1}$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.77 (2H, m, CH$_2$), 2.05 (2H, m, CH$_2$), 2.61 (2H, m, CH$_2$), 3.26 (2H, m, CH$_2$), 4.38 (2H, m, CH$_2$), 8.39 (3H, m), 9.10 (1H, s); ESI-MS: *m*/*z* 374 [M−Br]$^+$, HRMS: calcd 373.9809 [M−Br]$^+$; found 373.9811.