

Synthesis and spectroscopic characterization of new nonracemic quaternary ammonium salts derived from quinine and carbazole

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Abstract: In this paper, we report the synthesis and spectroscopic characterization of some representative *N*-alkylsubstituted quaternary ammonium salts derived from quinine using carbazole derivatives as alkylating agents.

Keywords: Quaternary ammonium salts, carbazole derivatives, quinine.

INTRODUCTION

Quaternary ammonium compounds are extensively used for clinical purposes such as preoperative disinfection of unbroken skin, application to mucous membranes, and disinfection of noncritical surfaces¹. The cationic properties of quaternary ammonium compounds contribute to a variety of applications as disinfectants, antiseptics, herbicides, spermicides, detergents, and sanitizing agents². Recent studies have also reported the application of quaternary ammonium compounds as Antimicrobial Surfactant³.

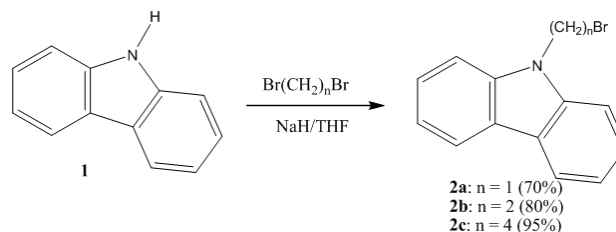
In organic syntheses, these compounds are used as phase transfer catalysts for a wide range of organic reactions involving immiscible solvent systems⁴⁻¹⁰.

Recently, a number of carbazole derivatives¹¹⁻¹⁷ have been used as organic materials, due to their well known charge-transport properties, luminescence, and high thermal stability. These advantageous properties provoked our interest in introducing the carbazole moiety into quaternary ammonium compounds.

Having the above subjects in mind and also in continuation of our previous studies on *N*-alkylation reactions¹⁸⁻¹⁹, we describe here our efforts toward the design and preparation of a series of novel chiral ammonium salts derived from quinine and carbazole.

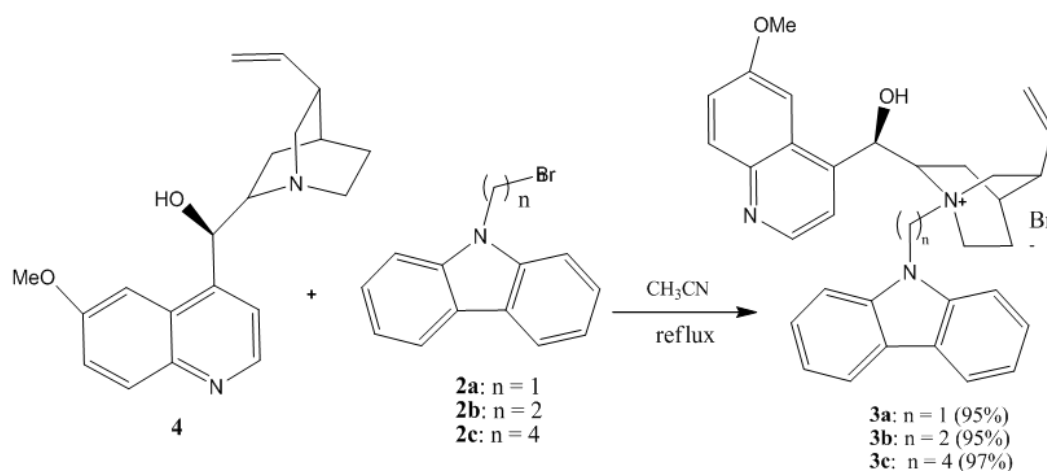
RESULTS AND DISCUSSION

Commercially available carbazole **1** was functionalized with variety of dibromoalkyl, in the presence of sodium hydride afforded a series of *N*-bromoalkyl carbazoles **2a-c**. An excess amount (greater than 10-fold equivalent to carbazole) of dibromoalkyl was added, the resulting carbazoles derivative **2a-c** was generally obtained in rather good yields, usually decreasing as the length of the *N*-alkyl chain decreases (see Experimental) and no quaternarization was observed. However, particularly for the compound **2c**, when two equimolar ratio of carbazole is used with dibromoalkyl, *N*-bromoalkyl carbazoles products were reduced and the dicarbazolalkyl, undesirable product, was apparent.²⁰ The synthesis of *N*-bromoalkyl carbazoles is shown in Scheme 1.



Scheme 1: synthesis of *N*-bromoalkyl carbazoles

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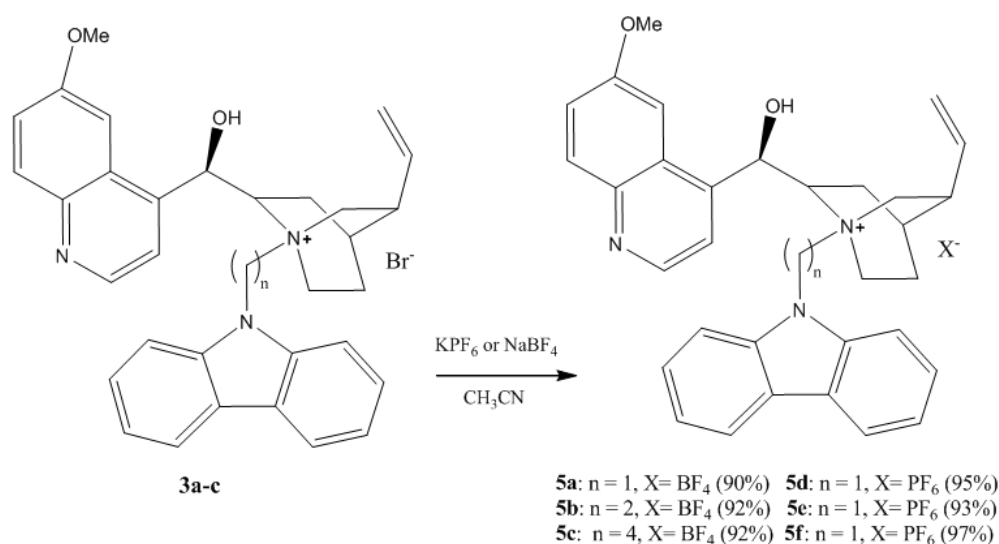
Scheme 2. Synthesis of quaternary ammonium salt bromide **3a-c**

To gain further insight into the nucleophilic properties of quinine, we reacted **4** with several primary alkyl halides **2a-c** using the Menshutkin reaction, i.e., *N*-alkylation of tertiary amines with haloalkyls. Compound **4** reacts with alkyl bromide in dry acetonitrile to produce mono *N*-alkyl ammonium quaternary salts (**3a-c**) (Scheme 2). The resulting salts were readily separated from the crude reaction mixtures by precipitation upon addition of diethyl ether. The alkylating procedure could be repeatedly applied to the mother liquors, each time previously freed of the precipitation solvent, in order to achieve convenient yields. According to NMR spectroscopy the products were of satisfactory purity and, therefore, no attempts at further purification by recrystallization were

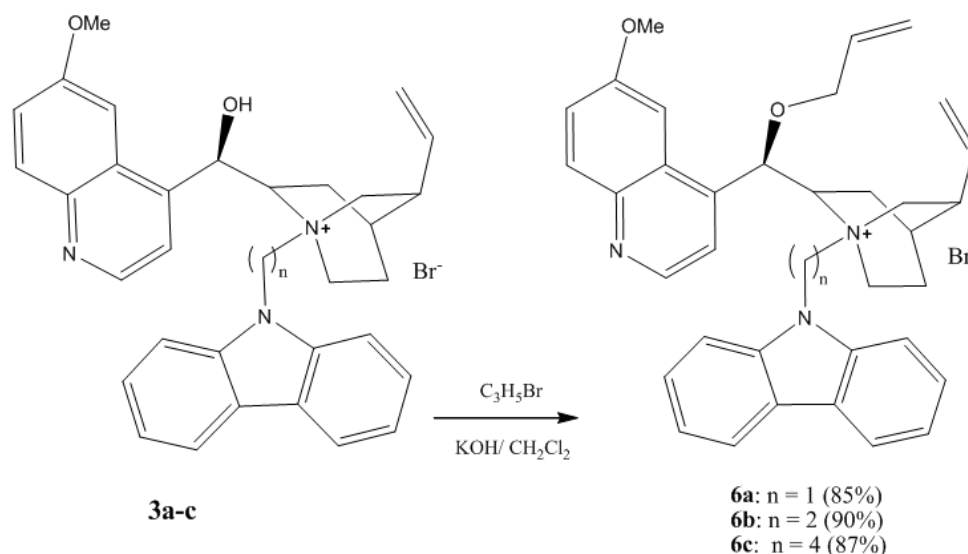
necessary.

Attending to different counter –anions for these types of salts, exchange of the bromide anions by the tetrafluoroborate and the hexafluorophosphate anions after reaction with sodium tetrafluoroborate or potassium hexafluorophosphate afforded salts **5a-c** and **5d-f** respectively (scheme 3).

In order to prepare diverse quaternary ammonium salt derivatives for various applications in asymmetric synthesis²¹⁻²⁴ we attempted the synthesis of *O*(9)-allylated bromide **6a-c**. Allylation of **3a-c** with allyl bromide in the biphasic system composed of 50% aqueous KOH and dichloromethane at room temperature afforded the allylated ammonium salts **6a-c** in 85–90% yields (Scheme 4)



Scheme 3. Synthesis of quaternary ammonium salts **5a-f**.



Scheme 4. Synthesis of O-allylated quinine-derived ammonium salts **6a-c**.

The bromine anion in the ammonium salts **6a-c** was exchanged by BF_4^- than PF_6^- in acetonitrile, at room temperature, leading to the nonracemic salts **7a-c** and **7d-f**, respectively.

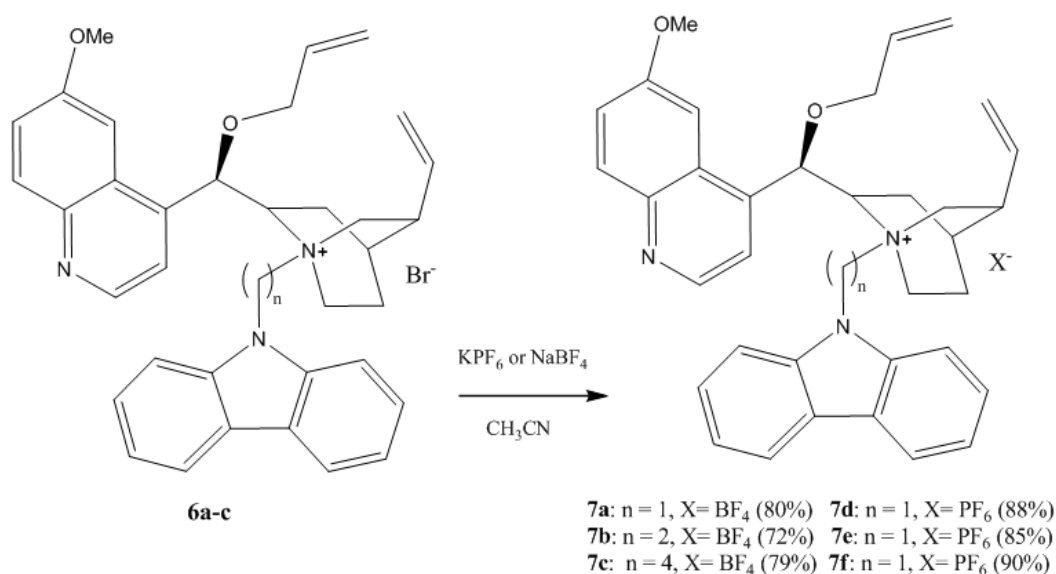
CONCLUSION

In summary, we have introduced the quaternary ammonium salts as efficient carbazole derivatives alkylating agents for *N*-alkylation of quinine. All this array of salts bearing different counter-anions will be employed as chiral PTC catalysts in different reaction.

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EXPERIMENTAL

All reactions were performed under an argon atmosphere and monitored by TLC Merck 60F-254 silica gel plates (layer thickness 0.25 mm). Column chromatography was performed on silica gel (70e 230 mesh) using ethyl acetate and cyclohexane mixture as eluents. Melting temperatures were determined on an Electrothermal 9002 apparatus



Scheme 5. Synthesis of quaternary ammonium salts **7a-f**.

and were reported uncorrected. NMR spectra were recorded on a Bruker AC-300 spectrometer at 300 MHz (^1H) and 75 MHz (^{13}C). All chemical shifts were reported as values (ppm) relative to internal tetramethylsilane. Electron impact (EI) mass spectra were determined on an ionizing voltage of 70 eV. Infra Red spectra were determined on BIO-RAD FTS-6000.

1. EXPERIMENTAL SECTION

General procedure A for the *N*-alkylation of carbazole

Carbazole **1** (6 mmol) was combined with an excess of sodium hydride (1.5eq.) and dissolved in 20 mL of anhydrous THF. A THF solution of dibromoalkane (1.5 mmol/mL, 50mL) was added dropwise to the carbazole solution, and the combined mixture was refluxed overnight. The solvent was removed, and the remaining solid was purified by column chromatography (silica gel, 9:1 cyclohexane / ethyl acetate).

Synthesis of 9-(Bromomethyl)-9*H*-carbazole **2a**.

It was prepared, in 70% yield as a white solid, from **1** and dibromomethane according to procedure A. Mp 140-142 °C; ^1H NMR (300 MHz, CDCl_3) : 6.05 (s, 2H); 7.35 (2H, dd, $J = 7.14$ Hz, 14.83 Hz); 7.45 (d, $J = 8.24$ Hz, 2H); 7.56 (dd, $J = 7.14$ Hz, 15.38 Hz, 2H); 8.19 (d, $J = 7.69$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) : 50.40, 109.12, 120.50, 121.20, 122.0, 126.60, 147.10. Anal. Calcd. for $\text{C}_{13}\text{H}_{10}\text{BrN}$: C, 60.02; H, 3.87. Found: C, 59.97; H, 3.82.

Synthesis of 9-(2-Bromoethyl)-9*H*-carbazole **2b**.

Compound **2b** was obtained in 80% yield, as a yellow solid, from **1** and 1,2- dibromoethane according to procedure A. Mp 148-150 °C; ^1H NMR (300 MHz, CDCl_3) : 3.99 (t, $J = 6.4$, 2H) ; 5.18 (t, $J = 6.4$, 2H) ; 7.18-7.22 (m, 2H) ; 7.49-7.44 (m, 4H) ; 8.15 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3) : 31.98 ; 47.33 ; 109.33 ; 118.62 ; 120.58 ; 122.77 ; 126.56 ; 138.11.

Synthesis of 9-(4-Bromobutyl)-9*H*-carbazole **2c**.

It was prepared, in 95% yield as a white solid, from **1** and 1,4-dibromobutane according to procedure A; Mp 138-140 °C; ^1H NMR (300 MHz, CDCl_3) : 8.19 (2H, d, $J = 7.69$ Hz); 7.56 (2H, dd, $J = 7.14$ Hz, 15.38 Hz); 7.45 (2H, d, $J = 8.24$); 7.35 (2H, dd, $J = 7.14$ Hz, 14.83 Hz); 4.36 (2H, t, $J = 7.14$ Hz); 3.40 (2H, t, $J = 6.59$ Hz); 2.11 (2H, m); 1.96 (2H, m). ^{13}C NMR (75 MHz, CDCl_3) : 140.4; 126.0; 123.1; 120.7; 119.2; 108.8; 42.5; 33.7; 30.6; 28.0. Anal. Calcd for $\text{C}_{16}\text{H}_{16}$ Br

N: C, 63.59; H, 5.34; Found: C, 63.52; H, 5.29.

General procedure B for the *N*-alkylation of quinine:

A mixture of the respective bromoalkylcarbazole derivative (1.1 equiv) and quinine (1 equiv) in refluxing toluene (25 mL) was stirred for 24h. After cooling the reaction mixture to room temperature, the solvent was removed and the crude solid was crystallized from dichloromethane. Experimental details and specific data for individual compounds are given below.

N-(*N*-carbazol)-methyl) quinine bromide **3a**

It was prepared, in 87% yield as a yellow solid, from **2a** (4.4 mmol) and quinine (4 mmol) according to procedure B; mp = 202-204 C; ^1H NMR (300 MHz, CDCl_3) : 1.48-1.52(m,2H), 1.71-1.81(m,3H) 2.30-2.35 (m,1H), 2.61-2.67(m,2H), 3.02-3.10(m,2H), 3.35-3.52(m,1H), 3.89(s,3H), 4.68(sl,1H), 4.89-4.99(m,2H), 5.49-5.50(m, 3H), 5.69-5.79(m,1H), 7.13 (d, $J = 9.3$ Hz,3H), 7.30-7.41(m,3H), 7.48,7.51(m,3H), 7.98-8.04(m, 3H), 8.65 (d, $J = 4.5$ Hz,1H). ^{13}C NMR (75 MHz, CDCl_3) : 30.02, 31.43, 33.38, 38.02, 56.63, 62.05, 66.30, 72.22, 72.94, 104.1, 109.05, 118.45, 120.70, 120.86, 121.07, 121.20, 122.10, 126.11, 126.11, 129.72, 131.36, 137.95, 139.61, 140.66, 147.24, 149.99, 159.82.

N-(*N*-carbazol)-ethyl) quinine bromide **3b**

It was prepared, in 93% yield as a yellow solid, from **2b** (4.4 mmol) and quinine (4 mmol) according to procedure B; mp = 210-212 C; ^1H NMR (300 MHz, CDCl_3) : 1.23-1.28 (m,1H), 1.6-1.7(m,3H), 2.04-2.14(m,1H), 2.60(m,3H), 2.75-2.79(m,1H), 3.25-3.43(m,2H), 3.95(s,3H), 4.45-4.51(m,2H), 4.90-4.98 (m,2H), 5.35-5.46(m,1H), 6.07-6.15 (m,2H), 7.17(d, $J = 8.5$, 3H), 7.35-7.41 (m,3H), 7.48,7.54 (m,3H), 7.98-8.02 (m, 3H), 8.67 (d, $J = 4.5$, 1H). ^{13}C NMR (75 MHz, CDCl_3) : 28.38, 29.60, 33.66, 38.44, 43.11,56.18, 56.63, 57.92, 61.90, 68.28, 74.04, 103.01, 109.20, 118.40, 119.0, 119.65, 120.85, 121.65, 122.55, 125.0, 128.94, 131.36, 138.40, 138.44, 139.92, 148.65, 149.99, 159.82.

N-(*N*-carbazol)-butyl) quinine bromide **3c**

Compound **3c** was obtained in 97% yield, as a brown solid, from 9-(4-Bromobutyl)-9*H*-carbazole **2c** (4.4 mmol) and quinine (4 mmol) according to procedure B; mp = 224-226 C; ^1H NMR (300 MHz, CDCl_3) : 1.20-1.27 (m,1H), 1.7-1.8 (m,3H), 2.03-2.12 (m,8H), 2.56 (s,1H), 2.74-2.78 (d,1H, $J=11.7$), 3.24-3.41 (m,3H), 3.83 (s,1H), 4.41-4.50 (m,3H), 4.88-4.96 (m,2H), 5.32-5.43



(m,1H), 6.04 (s,1H), 6.28 (s,1H), 7.12-7.18 (d,3H), 7.32-7.42 (m,3H), 7.49,7.52 (m,3H), 7.99-8.03 (t, 3H), 8.65-8.66 (d,1H). ^{13}C NMR (75 MHz, CDCl_3) : 20.65, 2.68, 25.27, 26.09, 26.35, 37.84, 42.33, 53.85, 56.54, 60.58, 61.70, 64.45, 67.52, 102.77, 109.47, 117.96, 119.56, 120.49, 120.69, 120.77, 123.13, 126.16, 126.38, 132.48, 136.75, 140.60, 143.39, 144.42, 147.97, 158.39.

General procedure C for the ion exchange reaction

To a suspension of the respective quinine-*N*-methylphenanthrene bromide derivative (1 equiv) in 10 mL of acetonitrile was added sodium tetrafluoroborate (5 equiv) or potassium hexafluorophosphate (5 equiv). The reaction mixture was stirred at room temperature for 24h. After removing the solvent, the mixture was diluted with water (10 mL) and extracted with dichloromethane. The combined organic extracts were dried over MgSO_4 and evaporated in vacuum to give a crude product, which was washed with water and Et_2O . Filtration and drying afforded the corresponding quaternary ammonium salt. Experimental details and specific data for individual compounds are given below.

N-(*N*-carbazol)-methyl) quinine tetrafluoroborate 5a

It was prepared in 90% yield by reacting **3a** with 5 equivalents of sodium tetrafluoroborate, according to procedure C; mp = 223-225°C. This new compound showed identical ^1H and ^{13}C NMR data to those of the corresponding parent bromide **3a**. $[\alpha]_D^{21} = -110$ (c 0.1, CHCl_3); IR (KBr): ν (cm^{-1}): 3430, 1611, 1514, 1076, 752.

N-(*N*-carbazol)-ethyl) quinine tetrafluoroborate 5b

It was prepared in 92% yield by reacting **3b** with 5 equivalents of sodium tetrafluoroborate, according to procedure C; mp = 235-237°C. This new compound showed identical ^1H and ^{13}C NMR data to those of the corresponding parent bromide **3b**. IR (KBr): ν (cm^{-1}): 3445, 1605, 1517, 1052, 763.

N-(*N*-carbazol)-butyl) quinine tetrafluoroborate 5c

It was prepared in 92% yield by reacting **3c** with 5 equivalents of sodium tetrafluoroborate, according to procedure C; mp = 215-217°C. This new compound showed identical ^1H and ^{13}C NMR data to those of the corresponding parent bromide **3c**. IR (KBr): ν (cm^{-1}): 3455, 1638, 1500, 1075, 754.

N-(*N*-carbazol)-methyl) quinine hexafluorophosphate 5d

It was prepared in 95% yield by reacting **3a** with 5 equivalents of potassium hexafluorophosphate, according to procedure C; mp = 214-216 °C. This new compound showed identical ^1H and ^{13}C NMR data to those of the corresponding parent bromide **3a**. IR (KBr): ν (cm^{-1}): 3540, 1635, 1526, 852, 570.

N-(*N*-carbazol)-ethyl) quinine hexafluorophosphate 5e

It was prepared in 93% yield by reacting **3b** with 5 equivalents of potassium hexafluorophosphate, according to procedure C; mp = 228-230 °C. This new compound showed identical ^1H and ^{13}C NMR data to those of the corresponding parent bromide **3b**. IR (KBr): ν (cm^{-1}): 3572, 1600, 1529, 873, 575.

N-(*N*-carbazol)-butyl) quinine hexafluorophosphate 5f

It was prepared in 97% yield by reacting **3c** with 5 equivalents of potassium hexafluorophosphate, according to procedure C; mp = 208-210 °C. This new compound showed identical ^1H and ^{13}C NMR data to those of the corresponding parent bromide **3c**. IR (KBr): ν (cm^{-1}): 3434, 1629, 1509, 1059, 864, 779, 545.

General procedure D for the *O*-allylation reaction:

To a suspension of the respective *N*-(*N*-carbazyl)-alkyl) quinine bromide derivative (1 equiv) in 10 mL of dichloromethane was added allyl bromide (6 equiv) and a KOH solution (50%, 10 equiv). The resulting mixture was stirred vigorously at room temperature for 4h. The mixture was then diluted with water and extracted with dichloromethane. The combined organic extracts were dried over MgSO_4 , filtered, and concentrated in vacuum. The crude solid was crystallized from a dichloromethane/hexane mixture to yield the corresponding product. Experimental details and specific data for individual compounds are given below.

O(9)-Allyl- *N*-(*N*-carbazol)-methyl) quinine bromide 6a

Compound **6a** was obtained in 85% yield, as a brown solid, from *N*-(*N*-carbazyl)-methyl) quinine bromide **3a** according to procedure D; mp = 212-214 °C; $[\alpha]_D^{21} = -280$ (c 0.2, CHCl_3); ^1H NMR (300 MHz, CDCl_3): 1.23-1.28(m,1H), 1.46-1.64 (m,2H), 1.99-2.05(m, 2H), 2.86-2.91 (m, 1H), 3.90 (s,3H), 3.98-4.02(m, 2H), 4.10-4.20 (m,2H), 4.40-4.51(m, 2H), 4.72-4.81 (m, 3H), 4.95-5.02(m,1H), 5.16-5.27 (m, 4H), 5.43-5.48 (m,2H), 5.82-5.89

(m,2H), 7.29-7.40 (m,4H), 7.62 (d, $J = 4.3$ Hz, 1H), 7.70-7.81 (m, 4H), 8.04 (d, $J = 7.5$ Hz, 1H), 8.22 (d, $J = 4.5$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3): 29.25, 31.47, 34.52, 38.22, 56.12, 62.44, 71.95, 72.52, 73.77, 78.52, 103.11, 109.15, 115.92, 118.45, 120.55, 120.70, 121.25, 122.12, 124.25, 126.14, 129.75, 132.54, 136.50, 138.17, 138.92, 139.50, 142.32, 149.87, 158.80. IR (KBr): ν (cm^{-1}): 1554, 1463, 737. Anal. Calcd. for $\text{C}_{36}\text{H}_{38}\text{BrN}_3\text{O}_2$: C, 69.22; H, 6.13. Found: C, 69.17; H, 5.08.

O(9)-Allyl- N-(N-carbazol)- ethyl quinine bromide 6b: $[\alpha]_D^{21}$

Compound **6b** was obtained in 90% yield, as a brown solid, form *N*-(*N*-carbazyl)- ethyl quinine bromide **3b** according to procedure **D**; mp = 220-222 °C; $[\alpha]_D^{21} = -190$ (c 0.2, CHCl_3); ^1H NMR (300 MHz, CDCl_3): 1.32-1.36(m, 1H), 1.50-1.61 (m,2H), 2.04-2.11 (m,2H), 2.91-2.96 (m,2H), 3.91 (s, 3H), 3.96-4.02 (m, 4H), 4.08- 4.19 (m, 4H), 4.83-4.85 (m, 1H), 5.10-5.16 (m, 3H), 5.25-5.31 (m, 3H), 5.78-5.88 (m, 2H), 7.14-7.18 (m, 2H), 7.36-7.38 (m, 2H), 7.49-7.53 (m, 2H), 7.59 (d, $J = 4.3$ Hz, 1H), 7.77-7.79 (m, 2H), 7.98-8.04 (m, 3H), 8.63-8.64 (m, 1H). ^{13}C NMR (75 MHz, CDCl_3): 29.05, 29.16, 34.85, 40.34, 46.06, 56.70, 57.10, 57.63, 62.92, 71.40, 71.80, 83.70, 102.48, 106.80, 116.02, 118.38, 118.45, 120.55, 120.80, 121.20, 124.57, 126.82, 128.48, 131.96, 135.09, 137.20, 138.54, 139.38, 139.74, 148.32, 155.31. IR (KBr): ν (cm^{-1}): 3080, 1514, 1463, 757.

O(9)-Allyl- N-(N-carbazol)- butyl quinine bromide 6c:

Compound **6c** was obtained in 87% yield, as a brown solid, form *N*-(*N*-carbazyl)- ethyl quinine bromide **3c** according to procedure **D**; mp = 250-252 °C; $[\alpha]_D^{21} = -200$ (c 0.25, CHCl_3); ^1H NMR (300 MHz, CDCl_3): δ (ppm): 1.32-1.35 (m, 1H), 1.62-1.73 (m, 2H), 1.90-2.03 (m, 4H), 2.12-2.18 (m,2H), 2.98-3.05 (m,1H), 3.25-3.36 (m, 2H), 3.62-3.69 (m, 2H), 3.90 (s,3H), 4.01-4.13 (m, 2H), 4.15-4.20 (m, 2H), 4.70-4.78 (m, 2H), 4.90-4.91 (m, 2H), 5.14-5.17 (m, 2H), 5.21-5.26 (m,2H), 5.78-5.90 (m,2H), 7.13-7.18 (m, 2H), 7.37-7.46 (m, 2H), 7.65 (d, $J = 4.3$ Hz, 1H), 7.90-7.94 (m, 2H), 8.01 (d, $J = 7.5$ Hz, 1H), 8.11-8.13 (m, 2H), 8.27 (d, $J = 4.5$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3): 22.45, 29.16, 29.42, 30.10, 35.42, 38.54, 47.40, 56.50, 57.15, 59.65, 65.43, 71.56, 72.82, 81.02, 102.41, 108.21, 116.40, 118.50, 119.02, 120.35, 120.72, 121.60, 123.83, 125.45, 129.58, 130.66, 134.19, 135.38, 138.40, 139.02, 139.70, 148.15,

156.31. Anal. Calcd. for $\text{C}_{39}\text{H}_{44}\text{BrN}_3\text{O}_2$: C, 70.26; H, 6.65. Found: C, 70.21; H, 6.60.

O(9)-Allyl- N-(N-carbazol)-methyl quinine tetrafluoroborate 7a

It was prepared in 80% yield by reacting **6a** with 5 equivalents of sodium tetrafluoroborate, according to procedure **C**; mp = 196-198°C; $[\alpha]_D^{21} = -130$ (c 0.15, CHCl_3). This new compound showed identical ^1H and ^{13}C NMR data to those of the corresponding parent bromide **6a**. IR (KBr): ν (cm^{-1}): 3090, 1510, 1405, 1125, 1065, 744.

O(9)-Allyl- N-(N-carbazol)- ethyl quinine tetrafluoroborate 7b

It was prepared in 80% yield by reacting **6b** with 5 equivalents of sodium tetrafluoroborate, according to procedure **C**; mp = 192-194°C; $[\alpha]_D^{21} = -120$ (c 0.24, CHCl_3). This new compound showed identical ^1H and ^{13}C NMR data to those of the corresponding parent bromide **6b**. IR (KBr): ν (cm^{-1}): 3087, 1518, 1425, 1120, 1062, 752.

O(9)-Allyl- N-(N-carbazol)- butyl quinine tetrafluoroborate 7c

It was prepared in 79% yield by reacting **6c** with 5 equivalents of sodium tetrafluoroborate, according to procedure **C**; mp = 187-189°C. This new compound showed identical ^1H and ^{13}C NMR data to those of the corresponding parent bromide **6c**. IR (KBr): ν (cm^{-1}): 3075, 1505, 1412, 1105, 1070, 732.

O(9)-Allyl- N-(N-carbazol)-methyl quinine hexafluorophosphate 7d

It was prepared in 88% yield by reacting **6a** with 5 equivalents of potassium hexafluorophosphate, according to procedure **C**; mp = 192-194 °C. This new compound showed identical ^1H and ^{13}C NMR data to those of the corresponding parent bromide **6a**.

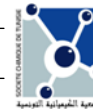
IR (KBr): ν (cm^{-1}): 3085, 1515, 1412, 875, 775.

O(9)-Allyl- N-(N-carbazol)- ethyl quinine hexafluorophosphate 7e

It was prepared in 85% yield by reacting **6b** with 5 equivalents of potassium hexafluorophosphate, according to procedure **C**; mp = 188-190 °C. This new compound showed identical ^1H and ^{13}C NMR data to those of the corresponding parent bromide **6b**. IR (KBr): ν (cm^{-1}): 3083, 1523, 1410, 843, 776.

O(9)-Allyl- N-(N-carbazol)- butyl quinine hexafluorophosphate 7f

It was prepared in 90% yield by reacting **6c** with 5 equivalents of potassium hexafluorophosphate, according to procedure **C**; mp = 182-184 °C. This



new compound showed identical ^1H and ^{13}C NMR data to those of the corresponding parent bromide **6c**. IR (KBr): ν (cm^{-1}): 3095, 1529, 1407, 853, 783.

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