Synthesis of [3-D_3]-, [3-^{13}C]-, and [1,2-$^{13}C_2$]Propynes and Their Use for the Synthesis of [5-D_3-Methyl]-, [5-^{13}C-Methyl]-, and [5,6-$^{13}C_2$-2,5-Cyclohexadienyl]ubiquinones 3

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Three selectively labeled propynes were prepared either with deuterium or carbon-13 at position 3 and doubly labeled with carbon-13 at positions 1 and 2 by an alkylation reaction from the corresponding labeled or unlabeled monolithio acetylides and dimethylsulfates. Their lithiation with *n*BuLi gave the corresponding propynyllithium derivatives which reacted with dimethyl squarate to afford the corresponding propargylic alcohols. These were thermolysed in *p*-xylene to furnish [5-D_3-methyl]-, [5-^{13}C-methyl]-, and [5,6-$^{13}C_2$-2,5-cyclohexadienyl]ubiquinone. The farnesyl side chain was introduced onto the labeled quinones with farnesyl trimethyltin under BF_3 catalysis to provide [5-D_3-methyl]-, [5-^{13}C-methyl]-, and [5,6-$^{13}C_2$-2,5-cyclohexadienyl]ubiquinone 3 (**6c**, **6b**, **6a**, respectively).

Introduction

Quinones are important molecules in biology where they play an essential role in oxido-reduction reactions taking place in respiratory and photosynthetic electron-transfer chains.[1] Photosynthetic bacterial reaction centers have two quinones in the Q_A and Q_B sites for which X-ray data have given structural information.[2] In these systems, the electronic properties (redox potential, semiquinone/quinol equilibrium) are governed not only by the chemical nature of the quinone itself, but also by the specific interactions with the protein. Complementary information can be obtained using specifically labeled quinones with various biophysical techniques such as FTIR,[3] ENDOR,[4] EPR,[5] and NMR spectroscopy.[6] Notably, using [1-^{13}C=O]- and [4-^{13}C=O]ubiquinone 3, FTIR differential spectroscopy showed that in the Q_A site of the reaction center strong hydrogen bonding occurs only at the 4-C=O group while in the Q_B site both carbonyls are weakly bonded.[3] We decided to extend our studies with the same technique by using ubiquinones specifically labeled on the methyl at position 5 and on the carbon atoms at positions 5 and 6. Here, we describe the synthesis of precursor propynes selectively labeled with ^2H or ^{13}C at position 3 and doubly labeled with ^{13}C at positions 1 and 2, and their use for the elaboration of the ubiquinones 3 labeled at previously selected positions. These compounds are useful probes to get information on the influence of the electronic density at the methyl and at the C(5)–C(6) double bond, and on the redox potential at the reaction center of the quinones.

Results and Discussion

In the framework of our program aimed at the characterization of the bacterial photosynthetic reaction centers by FTIR with labeled ubiquinones,[3] we describe a procedure for the synthesis of labeled propynes with deuterium and with carbon-13 from which [5-D_3-methyl]- (**6c**), [5-^{13}C-methyl]- (**6b**), and [5,6-$^{13}C_2$-2,5-cyclohexadienyl]ubiquinone 3 (**6a**) were prepared.

The method of Rüttimann and Lorenz, which uses methylsuccinic anhydride and trichloroethylene as precursors in a key Diels–Alder reaction,[7] was recently modified to incorporate ^{13}C isotopes into the quinonic ring.[8] Liebeskind and Moore have developed a more direct route to highly functionalized arenes based on the rearrangement of cyclobutenones substituted with unsaturated groups.[9] Thus, the addition of unsaturated lithium derivatives to 3,4-dimethoxy-3-cyclobutene-1,2-dione (dimethyl squarate) leads to 4-alkynyl or alkynyl-4-hydroxycyclobuten-1-one derivatives. The thermal rearrangement of these compounds gave various annelated hydroquinones and ubiquinones.[9a,9c,9e,9f] However, this approach has not been used until now to label quinones in the nucleus. We felt that the propyne was the precursor of choice for the preparation of quinones labeled at various positions. This route appeared to us to be very efficient for the selective introduction at the ubiquinone ring of either deuterium or carbon 13 at positions 5, 6, and at the methyl group at position 5. However, this method requires the preparation of propyne derivatives labeled at the appropriate positions. Here we report the synthesis of three labeled propynes [3-D_3], [3-^{13}C], [1,2-$^{13}C_2$] which were reacted further to form the corresponding labeled ubiquinones and ubiquinones 3 (**6a**, **6b**, **6c**, respectively).

The cost of labeled precursors and the millimolar scale generally employed in our laboratory excluded the transposition of classical methods, which have proved unsuitable for the synthesis of labeled propynes mainly because of the

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large amounts of acetylene required.[10] In addition, the low boiling point of propyne, which would be obtained after the alkylation reaction from the solutions of sodio- or lithioacetylide in liquid NH_3, creates difficulties for its recovery. An alternative route was the preparation of monosodioacetylide, followed by an alkylation reaction in organic solvents.[11] However, this procedure seemed difficult to handle on a millimolar scale. We therefore turned our attention to two other methods of labelling: methylation of monolithium acetylide with $^{14}CH_3I$,[12] and the use of a $Ca^{14}C_2/MgCl_2$ mixture at high temperature.[13] The first method affords only low yields whereas the second method seems difficult to adapt to the synthesis of specifically labeled propynes. This led us to develop an efficient method for the preparation of these labeled propynes. The most appropriate method was Midland's procedure, which yields monolithium acetylide under stoichiometric conditions (acetylene/*n*BuLi, THF, –78 °C).[14] This method furnished a fairly stable reagent which proved superior to the lithium acetylide/ethylenediamine complex. The latter needed stronger reaction conditions in the addition reaction with aldehydes or ketones and gave low yields of ethynyl carbinols.[15]

We generated metallated acetylene under these conditions and found that after optimization the alkylation reaction with dimethylsulfate at –40 °C led to better yields than with CH_3I.[16] The higher boiling point of dimethylsulfate allowed us to obtain a purer propyne, which was isolated by vacuum transfer from the reaction mixture and trapped on P_2O_5 at –196 °C. The amount of propyne obtained was quantified by an indirect method owing to the presence of THF and butane collected during the transfer. So, a second vacuum transfer of impure propyne was applied to an excess of *n*BuLi in a cooled THF solution. The propynyllithium formed was reacted with excess benzaldehyde to provide the corresponding propargylic alcohol. The quantity of the latter was determined by NMR spectroscopy of the crude reaction mixture after isolation by column chromatography.[14,17]

Acetylene was condensed in THF at –78 °C and *n*BuLi (1 equiv.) was added. After 30 min at –78 °C, dimethylsulfate (1.2 equiv.) was added and the reaction mixture was warmed to –40 °C and held there for 1 h 50 min. The temperature of the reaction mixture was then raised to –10 °C and propyne was vacuum-trapped on P_2O_5 at –196 °C to afford propyne in a yield of 70 to 90%. After trapping the propyne in THF at –78 °C, *n*BuLi (1 equiv.) was added and the reaction mixture was stirred for 30 min. The solution containing propynyllithium was transferred with a cannula to a solution of dimethyl squarate (1.2 equiv.) in THF at –78 °C and stirred for 45 min. The propargylic alcohol **4** was obtained in 35% yield after purification. It is noteworthy that the presence of LiBr (1.2 equiv.) in the reaction mixture increased the yield to 70% with commercial propyne and was superior to $MgBr_2$. LiBr allows activation of the carbonyl groups [18] and favors the solubilization of dimethyl squarate. It is also worth noting that the direct one-pot synthesis of compound **4** from acetylene by successive additions of the reagents failed. This result explains the need to operate on a vacuum line in order to isolate the propyne from the reaction mixture (see Figure 1).

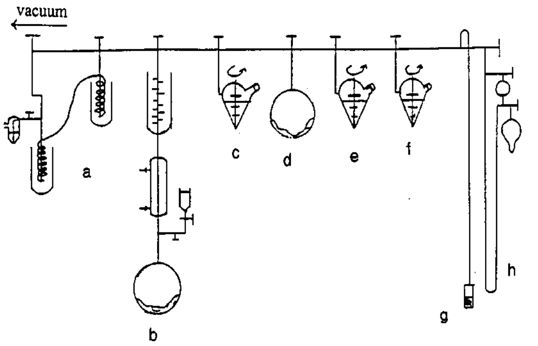
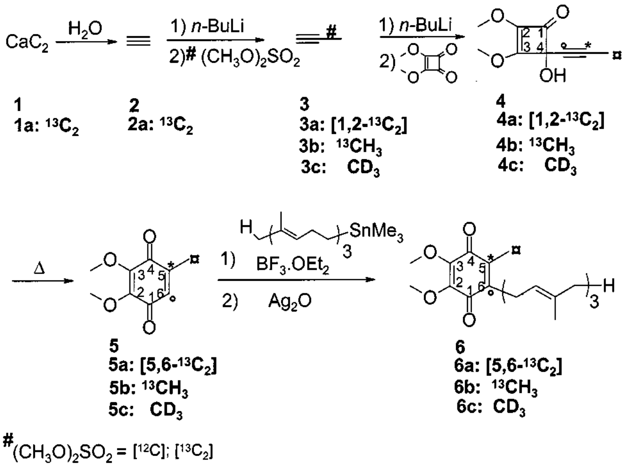


Figure 1. Vacuum line apparatus: (a) by-pass; (b) CaC_2/H_2O; (c) acetylene/*n*BuLi/$(CH_3O)_2SO_2$; (d) P_2O_5; (e) propyne/*n*BuLi; (f) dimethylsquarate/LiBr; (g) mercury manometer; (h) gauge

Unlabeled monolithium acetylide was methylated with [$^{13}C_2$]- and [D_6]dimethyl sulfate and monolithium [$^{13}C_2$]acetylide with unlabeled dimethylsulfate. The reaction conditions were the same as described previously and led to the corresponding labeled propynes **3a–c**. These were transferred into cooled THF and *n*BuLi (1 equiv.) was then added to give the corresponding propynyllithium derivatives. These mixtures were transferred to a solution of dimethyl squarate/LiBr in THF to furnish the corresponding propargylic alcohols **4a–c**. The purifications were conducted on silica gel columns. The thermolysis in *p*-xylene afforded quinones **5a–c** in 80–85% yields after purification. The farnesyl side chain was introduced using farnesyl trimethyltin in the presence of BF_3 as catalyst,[19] as previously described.[20] The hydroquinone intermediates were directly oxidized with Ag_2O, without isolation. to furnish **6a–c** in good yields (Scheme 1). Using the modified procedure of Rüttimann and Lorenz,[7] previous attempts showed that the introduction of the side chain on a millimolar scale gave the ubiquinone 3 in only poor yield. We have previously reported the synthesis of compound **6a** using this procedure and obtained only poor yields of **6**.[8d]



Scheme 1. General synthesis of labeled ubiquinones **3**

Conclusion

In this report we describe an efficient procedure to prepare [3-D_3]-, [3-^{13}C]-, and [1,2-$^{13}C_2$]propyne by an alkylation reaction of monolithium acetylide with [D_6]- or [$^{13}C_2$]dimethyl sulfate and monolithium [$^{13}C_2$]acetylide with unlabeled dimethyl sulfate. These labeled propynes were then incorporated into the framework of ubiquinones from their corresponding lithio derivatives. [5-D_3-methyl]-, [5-^{13}C-methyl]-, and [5,6-$^{13}C_2$-2,5-cyclohexadienyl]ubiquinone 3 (**6c**, **6b**, **6a**, respectively) could be efficiently obtained from the starting acetylene in seven steps and in 20% overall yields.

Experimental Section

General Remarks: [$^{13}C_2$]- and [D_6]dimethyl sulfate were from Eurisotop France (isotopic enrichment: 99 and 99.9%, respectively) and CaC_2 and dimethylsulfate from Aldrich. THF was distilled over Na/benzophenone under nitrogen. *n*BuLi (2.5 M in hexanes) was quantified before use. TLC: Silica Gel 60F$_{254}$ plates (Merck). – IR: Perkin–Elmer 2000. – HPLC analysis was performed on a Partisil column using a Merck system. – ^1H-NMR spectra were recorded at 300.13 MHz and ^{13}C NMR at 75.47 MHz on a Bruker AM 400 spectrometer with $CDCl_3$ as solvent. – MS: Finnegan-Mat 4600 (70 eV).

Acetylene (2): CaC_2 (**1**) (0.792 g, 10 mmol, 80% purity) was hydrolyzed with H_2O (flask b) to give acetylene **2** which was vacuum-trapped into a flask (d) containing P_2O_5 at –196 °C, dried at room temperature and used in the next step, without further purification (yield quantitative).

[1,2-$^{13}C_2$]Acetylene (2a): This compound was prepared using a modified version of Cox's method[21] in which [$^{13}C_2$]CaC_2 (**1a**) was obtained from $Ba^{13}CO_3$ (1.38 g, 7 mmol) and calcium (3.36 g, 84 mmol). The solid was hydrolyzed with H_2O (flask b) to give **2a** which was trapped through by-pass (a), dried over P_2O_5 (d) and used in the next step, without further purification.

Propyne (3): Compound **2** (3.5 mmol) was condensed into THF (10 mL) at –196 °C under vacuum (c). *n*BuLi (1.4 mL, 3.5 mmol) was then added at –78 °C under nitrogen. The reaction mixture was stirred for 30 min at –78 °C and dimethylsulfate was added dropwise. The solution was maintained for 1 h 50 min at –40 °C and for 40 min at –10 °C. Compound **3** was vacuum-transferred for 7 min (to avoid excessive THF transfer) to the flask (d) containing P_2O_5 at –196 °C. The flask (d) was removed from the vacuum line and warmed to room temperature and compound **3** used in the next step without further purification.

[1,2-$^{13}C_2$]Propyne (3a): This compound was prepared as described for **3**, from **2a** (3.5 mmol) and dimethylsulfate (4.2 mmol).

[3-^{13}C]Propyne (3b): This compound was prepared as described for **3**, from **2** (8.9 mmol) and [$^{13}C_2$]dimethylsulfate (10.7 mmol).

[3-D_3]Propyne (3c): This compound was prepared as described for **3**, from **2** (8.9 mmol) and [D_6]dimethylsulfate (10.7 mmol).

4-Hydroxy-2,3-dimethoxy-4-propynyl-2-cyclobuten-1-one (4): This procedure was adapted from ref.[9i] as follows: compound **3** was transferred into THF at –78 °C (flask e) and *n*BuLi (4.2 mmol) was added. The mixture was stirred for 30 min and transferred with a cannula to a solution of dimethyl squarate/LiBr (1:1: 4.2 mmol) in THF (30 mL) (flask f).The reaction mixture was maintained at –78 °C for 30 min and then a solution of 5% NH_4Cl (30 mL) and diethyl ether (50 mL) were added successively. The aqueous phase was extracted with diethyl ether (2 × 20 mL) and the combined organic extracts were evaporated. The crude product was purified on a silica gel column with CH_2Cl_2/ethyl acetate (95:5) as eluent to give 220 mg of **4**. (35% overall yield). – ^1H NMR: $\delta = 1.69$ (s, CH_3), 2.54 (s, OH), 3.96 (s, CH_3O), 4.18 (s, 2 CH_3O). – ^{13}C NMR: $\delta = 3.6$ CH_3, 58.3 CH_3O, 59.7 CH_3O, 73.5 C_4, 78.2 ($C_{2'}$), 85.8 (C_1)·, 135.5 (C_2), 166.1 (C_3), 182 (C_1). – IR (NaCl): $\tilde{\nu} = 3580$ cm^{-1}, 3350, 3000, 2960, 2240, 1780, 1640, 1470, 1430, 1350, 990, 830.

4-Hydroxy-2,3-dimethoxy-4-[1,2-$^{13}C_2$-propynyl]-2-cyclobuten-1-one (4a): This compound was prepared as described for **4**, from **3a** to give **4a** (337 mg, 53%). – ^1H NMR: $\delta = 1.8$ (m, $J = 30$ Hz, CH_3–C_3) (same spectrum as **4**). – IR ($CHCl_3$): $\tilde{\nu} = 3378$ cm^{-1}, 2956, 1780, 1635, 1470, 1435, 1343, 1146, 984, 833. – MS (CI/NH_3): *m*/*z* (%): 184 (100) [M^+]. – Isotopic enrichment: 94%.

4-Hydroxy-2,3-dimethoxy-4-[3-^{13}C-propynyl]-2-cyclobuten-1-one (4b): This compound was prepared as described for **4**, from **3b** (7 mmol), 331 mg of **4b** were obtained (yield: 26%). – ^1H NMR: $\delta = 1.69$ (t, $J = 66$ Hz, CH_3). – ^{13}C NMR: $\delta = 3.63$ ($C_{3'}$) (same spectrum as **4**). – IR (NaCl): $\tilde{\nu} = 3373$ cm^{-1}, 2955, 2242, 1779, 1634, 1471, 1434, 1034, 982, 833.

4-Hydroxy-2,3-dimethoxy-4-[3-D_3-propynyl]-2-cyclobuten-1-one (4c): This compound was prepared as described for **4**, from 0.93 g of **3c**, 0.935 g of **4c** was obtained (yield: 43%). – ^1H NMR: $\delta =$ 3.94 (s, CH_3O), 4.19 (s, CH_3O). – IR (KBr): $\tilde{\nu} = 3382$ cm^{-1}, 2956, 2246, 1778, 1634, 1471, 1434, 1346, 1033, 985, 828.

2,3-Dimethoxy-5-methyl-1,4-benzoquinone (UQ$_0$) (5): This procedure was adapted from ref.[9i] A solution of *p*-xylene (10 mL) containing **4** (0.61 g, 3.3 mmol) was refluxed for 20 min and then evaporated to dryness. The crude oil thus obtained was purified by flash chromatography with hexane/ethyl acetate (9:1) as eluent to give **5** (420 mg, 69%). – ^1H NMR: $\delta = 2.02$ (d, CH_3–C_5), 3.98 (s, CH_3O), 4.0 (s, CH_3O), 6.42 (m, H–C_6). – ^{13}C NMR: $\delta = 15.1$ (CH_3), 60.9 (CH_3O), 131 (C_6), 143.7 (C_5), 144.5, 144.7 (C_2, C_3), 183.8, 184.1 (C_1, C_4). – HPLC: (hexane/ethyl acetate, 9:1) $t_R = 15.18$ min.

2,3-Dimethoxy-5-methyl-[5,6-$^{13}C_2$]-1,4-benzoquinone ([5,6-$^{13}C_2$-cyclohexadienyl] UQ$_0$) (5a): This compound was prepared as described for **5**, from **4a** (0.15 g, 0.8 mmol), to give 110 mg of **5a** (yield: 73%). – ^1H NMR: $\delta = 6.42$ (dd, $J = 170$ Hz, H–C_6) (same spectrum as **5**). – ^{13}C NMR: $\delta = 131$ (d, $J = 66$ Hz, C_6), 143.7 (d, $J = 66$ Hz, C_5). – IR (KBr): $\tilde{\nu} = 2947$ cm^{-1}, 1658, 1604, 1461, 1380. – UV (MeOH): λ_{max} (lg ε) = 263 nm (4.10). – MS (CI/NH_3): *m*/*z* (%): 219 (49) [$M^+ + N_2H_5$], 202 (100) [$M^+ + NH_4$], 185 (9) [M^+ + H]. – $C_9H_{10}O_4$: calcd. 184.0645, found: 184.0623. – Isotopic enrichment: 94%.

2,3-Dimethoxy-5-[^{13}C-methyl]-1,4-benzoquinone ([5-^{13}C-methyl] UQ$_0$) (5b): This compound was prepared as described for **5,** from **4b** (331 mg), to give 210 mg of **5b** (yield: 64%). – ^1H NMR: $\delta =$ 2.00 (m, $J = 130$ Hz, CH_3–C_5), 3.98 (s, CH_3O), 4.00 (s, CH_3O), 6.41–6.43 (dd, H–C_6). – ^{13}C NMR: same spectrum as **5** – IR (KBr): $\tilde{\nu} = 3007$ cm^{-1}, 2947, 2839, 1671, 1603, 1467, 1431, 1320, 1281, 1220. – UV (MeOH): λ_{max} (lg ε) = 264 nm (4.08), 402 (2.85). – MS (CI/NH_3): *m*/*z* (%): 201 (100) [$M^+ + NH_4$], 184 (50) [M^+ + H]. – Isotopic enrichment: 86%.

2,3-Dimethoxy-5-[D_3-methyl]-1,4-benzoquinone ([5-D_3-methyl] UQ$_0$) (5c): This compound was prepared as described for **5**, from **4c** (0.935 g), to give 0.412 g of **5c** (yield: 55%). – ^1H NMR: $\delta = 3.98$, 4.0 (2s, 2 CH_3O); 6.4 (s, H–C_6). – ^{13}C NMR: same spectrum as **5**. – IR (KBr): $\tilde{\nu} = 3006$ cm^{-1}, 2951, 2840, 1660, 1604, 1465, 1432, 1320, 1281, 1218, 184. – UV (MeOH): λ_{max} (lg ε) = 264 nm (4.16), 400 (2.94). – MS (CI/NH_3): *m*/*z* (%): 203 (100) [M^+ + NH_4], 186 (19) [M^+ + H]. – $C_9H_{10}O_4$: calcd. 185.0765, found: 185.0764. – Isotopic enrichment: 96%.

6-(*all-E*)-2,3-Dimethoxy-3,7,11-trimethyl-2,6,10-dodecatrienyl-2,5-cyclohexadien-1,4-dione (Ubiquinone 3) (6): To a solution of 2,3-dimethoxy-1,4-benzoquinone (47 mg, 0.26 mmol) in CH_2Cl_2 (10 mL) at –78 °C was added $BF_3 \cdot OEt_2$ (0.1 mL, 0.78 mmol), followed by a solution of farnesyl trimethyltin[20] (100 mg, 0.27 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was stirred for 1 h, acidified with 2 M HCl (15 mL) and extracted with diethyl ether (3 × 30 mL). The combined organic extracts were washed with H_2O (15 mL) and with saturated brine (15 mL). The organic layer was treated with Ag_2O (100 mg) for 1 h at 20 °C and dried over $MgSO_4$, filtered and evaporated. The crude oil was purified on a silica gel column with hexane/ethyl acetate (85:15) as eluent to give **6** (220 mg, 61%). – ^1H NMR: (same spectra as in ref.[10c]) δ = 1.56 (s, CH_3–$C_{12'}$), 1.57 (s, CH_3–$C_{11'}$), 1.66 (s, CH_3–$C_{7'}$), 1.72 (s, CH_3–$C_{3'}$), 1.95–2.06 (m, 4 *allyl*–CH_2), 2.0 (s, CH_3–C_3), 3.16 (d, *J* = 7 Hz, CH_2–$C_{1'}$), 3.93, 3.98 (2s, 2 CH_3O), 4.9 (t, H–$C_{2'}$), 5.05 (m, H–$C_{5'}$, H–$C_{8'}$). – ^{13}C NMR: δ = 11.7 (C_3), 16.1 ($C_{12'}$), 25.1 ($C_{1'}$), 26.4 ($C_{13'}$), 39.4 (*allyl*–CH_2), 60.8 2 (CH_3O), 118.7 ($C_{2'}$), 123.6 (*allyl*–CH), 131 ($C_{11'}$), 134.9 ($C_{7'}$), 137.3 ($C_{3'}$), 138.6 (C_3), 141.4 (C_2), 144 (C_5), 144.1 (C_6), 163.6 (C_1), 164.5 (C_4). – IR (NaCl): $\tilde{\nu}$ = 2926 cm^{-1}, 2852, 1648, 1610, 1450, 1377, 1286, 1263, 1204. – HPLC: (heptane/diisopropyl ether: 5:2) *tR* = 14.24 min. – MS (CI/NH_3): *m*/*z* (%): 404 (100) [M^+ + NH_4], 387 (76) [M^+ + H].

6-(*all-E*)-2,3-Dimethoxy-5-methyl-3,7,11-trimethyl-2,6,10-dodecatrienyl-2,5-[5,6-$^{13}C_2$]cyclohexadien-1,4-dione ([5,6-$^{13}C_2$-2,5-cyclohexadienyl] Ubiquinone 3) (6a): This compound was prepared as described for **6**, from **5a** (26 mg, 0.15 mmol), to give 37 mg of **6a** (yield: 75%). – ^1H NMR: δ = 3.16 (dd, *J* = 11 Hz, CH_2–$C_{1'}$) (same spectra as **6**). – ^{13}C NMR: δ = 138.5 (d, *J* = 66 Hz, C_3), 141.4 (d, C_2). – IR (NaCl): $\tilde{\nu}$ = 2926 cm^{-1}, 2852, 1648, 1610, 1450, 1377, 1286, 1263, 1204. – $C_{24}H_{34}O_4$: calcd. 388.2522, found: 388.2501. – MS (CI/NH_3); *m*/*z* (%): 406 (94) [M^+ + NH_4], 389 (100) [M^+ + H]. – Isotopic enrichment: 94%.

6-(*all-E*)-2,3-Dimethoxy-5-[^{13}C-methyl]-3,7,11-trimethyl-2,6,10-dodecatrienyl-2,5-cyclohexadien-1,4-dione ([5-13C-methyl] Ubiquinone 3) (6b): This compound was prepared as described for **6**, from 70 mg of **5b**, to give 110 mg of **6b** (yield: 74%). – ^1H NMR and ^{13}C NMR: same spectra as **6**. – IR (NaCl): $\tilde{\nu}$ = 2926 cm^{-1}, 2852, 1648, 1610, 1450, 1377, 1286, 1263, 1204. – MS (CI/NH_3): *m*/*z* (%): 405 (53) [M^+ + NH_4], 388 (100) [M^+ + H]. – Isotopic enrichment: 87%.

6-(*all-E*)-2,3-Dimethoxy-5-[D_3-methyl]-3,7,11-trimethyl-2,6,10-dodecatrienyl-2,5-cyclohexadien-1,4-dione ([5-D_3-methyl] Ubiquinone 3) (6c): This compound was prepared as described for **6**, from 74 mg of **5c**, 129 mg of **6c** were obtained (yield: 83%). – ^1H NMR; ^{13}C NMR: same spectra as **6**. – IR (NaCl): $\tilde{\nu}$ = 2918 cm^{-1}, 2851, 1648, 1610, 1450, 1376, 1286, 1263, 1203. – MS (CI/NH_3); *m*/*z* (%): 407 (27) [M^+ + NH_4], 389 (100) [M^+ + H]. – Isotopic enrichment: 96%.

C.A. Nomenclature: [5,6-$^{13}C_2$] 2,5-cyclohexadiene-1,4-dione, 2,3-dimethoxy-5-methyl-6-(3,7,11-trimethyl-2,6,10-dodecatrienyl)-, (*E,E*)- [C.A. Registry Number: 1173–76–8].

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