

## **Supporting Information**

### **Sequence analysis and specificity of distinct types of menaquinone methyltransferases indicate the widespread potential of methylmenaquinone production in Bacteria and Archaea**

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## **Contents**

### **Additional experimental procedures**

**Table S1.** Taxonomic classification of 237 microbial species predicted to contain at least one protein of the MqnK/MenK/MenK2 family

**Table S2.** Taxonomic classification of 63 species for which the presence of MMK and/or DMMK has been demonstrated biochemically

**Table S3.** Nucleotide primers used in this study

**Table S4.** Accession numbers of sequences used in Fig. 2.

**Fig. S1.** Alignment of selected MqnK/MenK/MenK2 primary structures

**Fig. S2.** Immunodetection of Strep-tagged MenK and MenK2 homologues from *C. tanakaei* and *F. marina* using a Strep-Tactin-HRP conjugate

**Fig. S3.** Parts of 500 MHz <sup>1</sup>H-NMR spectra of MK<sub>8</sub>, 7-MMK<sub>8</sub>, 8-MMK<sub>8</sub>, 5,8-DMMK<sub>8</sub> and 7,8-DMMK<sub>8</sub>

**Fig. S4.** Mass spectra of DMK<sub>8</sub>, 7-MDMK<sub>8</sub>, 8-MDMK<sub>8</sub>, 5,8-DMDMK<sub>8</sub> and 5,8-DMMK<sub>8</sub>.

**Fig. S5.** Mass spectra of DMK<sub>7</sub>, 7-MDMK<sub>7</sub>, 8-MDMK<sub>7</sub> and 5,8-DMDMK<sub>7</sub>

**Fig. S6.** <sup>1</sup>H chemical shifts of spectra of MK<sub>8</sub>, 7-MMK<sub>8</sub>, 8-MMK<sub>8</sub>, 5,8-DMMK<sub>8</sub> and 7,8-DMMK<sub>8</sub> calibrated at the <sup>1</sup>H signal of residual protons in CDCl<sub>3</sub> at 7.20 ppm

**Fig. S7.** <sup>13</sup>C chemical shifts of spectra of MK<sub>8</sub>, 7-MMK<sub>8</sub>, 8-MMK<sub>8</sub>, 5,8-DMMK<sub>8</sub> and 7,8-DMMK<sub>8</sub> calibrated at the <sup>13</sup>C signal of CDCl<sub>3</sub> at 77.20 ppm

**Fig. S8.** Bootstrap consensus tree of 819 bacterial sequences from the MqnK/MenK/MenK2 cluster using 500 bootstrap replications (extension of data shown in Fig. 4).

### **References**

**Supplemental Excel file with accession numbers of MqnK/MenK/MenK2 cluster sequences.**

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## Additional experimental procedures

MqnK/MenK/MenK2 primary structures were aligned using ClustalOmega 1.2.2 command-line version.

One-dimensional SDS-PAGE was carried out with 50 µg of total cell protein applied to each lane. Proteins were transferred from polyacrylamide gel onto PVDF (polyvinylidene difluoride) membranes using the horizontal semi-dry electrophoretic system. Strep-tagged proteins were detected by ELISA using a Strep-Tactin-HRP conjugate (IBA Lifesciences).

Nuclear magnetic resonance spectroscopy (NMR). All NMR spectra were measured on a Bruker DRX 500 MHz spectrometer equipped with a room temperature 5 mm PABBO probe (Bruker Biospin, Karlsruhe, Germany) at 303 K using CDCl<sub>3</sub> (99.9% D from Sigma) as solvent. The concentrations of the samples were ~ 10<sup>-2</sup> mol l<sup>-1</sup>. The solvent signals were used for referencing the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra at 7.20 ppm and 77.20 ppm respectively. Chemical shift assignment was achieved with <sup>1</sup>H-, <sup>13</sup>C- and <sup>13</sup>C-DEPT-135 1D spectra, 2D <sup>1</sup>H-<sup>1</sup>H COSY (correlated spectroscopy), 2D <sup>1</sup>H-<sup>1</sup>H NOESY (nuclear overhauser enhancement correlated spectroscopy), 2D <sup>1</sup>H-<sup>13</sup>C HSQC (heteronuclear single quantum correlation) and 2D <sup>1</sup>H-<sup>13</sup>C HMBC (heteronuclear multiple-bond correlation) spectra, using the Bruker pulse sequences zg30, zgpg30, dept135, cosygpmf, noesygtp, invietgps and inv4gplrl2ndqf respectively. 1D spectra were recorded using an excitation pulse of 30° and a repetition time of 3.7 s (<sup>1</sup>H) and 1.5 s (<sup>13</sup>C). 128 scans (<sup>1</sup>H, 8.000 scans <sup>13</sup>C) were added and Fourier transformed with a final digital resolution of 0.08 Hz (<sup>1</sup>H, 0.26 Hz <sup>13</sup>C). The hetero-nuclear long-range correlation spectrum (HMBC) was recorded by a matrix of 1 k data points (f2, <sup>1</sup>H dimension) and 256 increments (data points in f1 <sup>13</sup>C dimension). 64 scans for every increment were added resulting in an experimental time of nearly 6 h. The spectrum has been optimized for a heteronuclear coupling constant of 9 Hz. Raw data were processed with Topspin (Bruker Biospin, Karlsruhe, Germany) and 2D data were analyzed using MestReNova 11.0.3 (Metrelab Research S.L.). Fig. S3 shows the <sup>1</sup>H-NMR spectra of MK<sub>8</sub>, 7-MMK<sub>8</sub>, 8-MMK<sub>8</sub>, 5,8-DMMK<sub>8</sub> and 7,8-DMMK<sub>8</sub>. Differences in the shift ranges of aromatic protons and of methyl groups are shown clearly. All <sup>1</sup>H- and <sup>13</sup>C NMR signals could be assigned completely (Figs S6 and S7).

Mass spectra were acquired by Alexander Schießler and Christiane Rudolph (Clemens Schöpf Institute, Department of Chemistry, Technical University of Darmstadt) on an Impact II quadrupole time-of-flight (QTOF) mass spectrometer (Bruker Daltonik) using atmospheric pressure chemical ionization (APCI) (5 kV corona discharge) as ion source. The samples were diluted in methanol.

**Table S1.** Taxonomic classification of 237 microbial species predicted to contain at least one protein of the MqnK/MenK/MenK2 family (see Fig. 3). Experimentally characterized MMK-producing species are shown in red.

<b>Bacteria</b>	<u>Campylobacter sp. P159</u>	<b>Betaproteobacteria</b>	<u>Shewanella sp. cp20</u>	<b>Eggerthellales</b>	<u>Desulfurobacterium indicum</u>
<b>Proteobacteria</b>	<u>Campylobacter sp. P160</u>	<b>Burkholderiales</b>	<u>Shewanella sp. GutCb</u>	<b>Eggerthellaceae</b>	<u>Desulfurobacterium sp. TC5-1</u>
<b>Epsilonproteobacteria</b>	<u>Campylobacter sp. P255</u>	<b>Sutterellaceae</b>	<u>Shewanella sp. HN-41</u>	<u>Adlercreutzia equolifaciens</u>	<b>Bacteroidetes</b>
<b>Campylobacterales</b>	<u>Campylobacter sp. RM12175</u>	<u>Dakarella massiliensis</u>	<u>Shewanella sp. MR-4</u>	<u>Arabia massiliensis</u>	<b>Bacteroidia</b>
<b>Campylobacteraceae</b>	<u>Campylobacter sp. RM16704</u>	<u>Duodenibacillus massiliensis</u>	<u>Shewanella sp. P1-14-1</u>	<u>Asaccharobacter celatus</u>	<b>Bacteroidales</b>
<u>Arcobacter canalis</u>	<u>Campylobacter sp. RM6137</u>	<u>Mesosutterella multiformis</u>	<u>Shewanella sp. Pdp11</u>	<u>Cryptobacterium curtum</u>	<b>Bacteroidaceae</b>
<u>Arcobacter halophilus</u>	<u>Campylobacter sp. RM8835</u>	<u>Parasutterella excrementihominis</u>	<u>Shewanella sp. R106</u>	<u>Denitrobacterium detoxificans</u>	<u>Bacteroides caecimuris</u>
<u>Arcobacter marinus</u>	<u>Campylobacter sp. RM8964</u>	<u>Sutterella megalosphaeroides</u>	<u>Shewanella sp. SACH</u>	<u>Eggerthella ienta</u>	<b>Deferribacteres</b>
<u>Campylobacter avium</u>	<u>Campylobacter sp. RM8965</u>	<u>Sutterella parvirubra</u>	<u>Shewanella sp. Shew256</u>	<u>Eggerthella sinensis</u>	<b>Deferribacteres</b>
<u>Campylobacter blaseri</u>	<u>Campylobacter sp. RM8966</u>	<u>Sutterella sp. AM11-39</u>	<u>Shewanella sp. UCD-FRSSP16_17</u>	<u>Eggerthella sp. AM16-19</u>	<b>Deferribacteres</b>
<u>Campylobacter coli</u>	<u>Campylobacter sp. RM8970</u>	<u>Sutterella sp. CAG:521</u>	<u>Shewanella sp. UCD-KL12</u>	<u>Eggerthella sp. YY7918</u>	<b>Deferribacteraceae</b>
<u>Campylobacter concisus</u>	<u>Campylobacter sp. RM9262</u>	<u>Sutterella wadsworthensis</u>	<u>Shewanella sp. UCD-KL21</u>	<u>Eggerthella timonensis</u>	<u>Denitrovibrio acetiphilus</u>
<u>Campylobacter corcagiensis</u>	<u>Campylobacter sp. S0112</u>	<u>Turicimonas muris</u>	<u>Shewanella sp. W3-18-1</u>	<u>Enterorhabdus caecimuris</u>	<u>Denitrovibrio sp.</u>
<u>Campylobacter curvus</u>	<u>Campylobacter sputorum</u>	<b>Gammaproteobacteria</b>	<u>Campylobacter sp. WE21</u>	<u>Enterorhabdus mucosicola</u>	<u>Flexistipes sinusarabici</u>
<u>Campylobacter fetus</u>	<u>Campylobacter subantarcticus</u>	<b>Alteromonadales</b>	<u>Shewanella vesiculosa</u>	<u>Enteroscripio rubneri</u>	<b>Firmicutes</b>
<u>Campylobacter geochelonis</u>	<u>Campylobacter upsaliensis</u>	<b>Shewanellaceae</b>	<u>Shewanella waksmanii</u>	<u>Gordonibacter massiliensis</u>	<b>Clostridia</b>
<u>Campylobacter gracilis</u>	<u>Campylobacter ureolyticus</u>	<u>Shewanella algae</u>	<u>Shewanella woodyi</u>	<u>Gordonibacter pamelaeeae</u>	<b>Thermoanaerobacteriales</b>
<u>Campylobacter helveticus</u>	<u>Campylobacter volucris</u>	<u>Shewanella algidipiscicola</u>	<u>Shewanella xiamenensis</u>	<u>Gordonibacter sp. 28C</u>	<b>Thermoanaerobacteraceae</b>
<u>Campylobacter hepaticus</u>	<u>Sulfurospirillum arcachonense</u>	<u>Shewanella amazonensis</u>	<b>Ferrimonadaceae</b>	<u>Gordonibacter sp. An230</u>	<u>Brockia lithotrophica</u>
<u>Campylobacter hominis</u>	<u>Sulfurospirillum arsenophilum</u>	<u>Shewanella baltica</u>	<u>Ferrimonas balearica</u>	<u>Gordonibacter sp. An232A</u>	<b>Clostridiales</b>
<u>Campylobacter hyointestinalis</u>	<u>Sulfurospirillum barnesii</u>	<u>Shewanella benthica</u>	<u>Ferrimonas futtsuensis</u>	<u>Gordonibacter urolithinifaciens</u>	<b>Peptococcaceae</b>
<u>Campylobacter iguanium</u>	<u>Sulfurospirillum cavolei</u>	<u>Shewanella carassii</u>	<u>Ferrimonas kyonanensis</u>	<u>Paraeggerthella hongkongensis</u>	<u>Desulfosporosinus infrequens</u>
<u>Campylobacter insulaenigræ</u>	<u>Sulfurospirillum deleyianum</u>	<u>Shewanella chilikensis</u>	<u>Ferrimonas marina</u>	<u>Raoultibacter massiliensis</u>	<u>Desulfosporosinus sp. Tol-M</u>
<u>Campylobacter jejuni</u>	<u>Sulfurospirillum halorespirans</u>	<u>Shewanella colwelliana</u>	<u>Ferrimonas sediminum</u>	<u>Raoultibacter timonensis</u>	<b>Peptostreptococcaceae</b>
<u>Campylobacter lanienae</u>	<u>Sulfurospirillum multivorans</u>	<u>Shewanella corallii</u>	<u>Ferrimonas senticii</u>	<u>Rubnerbacter badeniensis</u>	<u>Clostridioides difficile</u>
<u>Campylobacter lari</u>	<u>Sulfurospirillum sp. JPD-1</u>	<u>Shewanella fidelis</u>	<u>Paraferomonas halotius</u>	<u>Stackia equolifaciens</u>	<b>Clostridiaceae</b>
<u>Campylobacter mucosalis</u>	<u>Sulfurospirillum sp. MES</u>	<u>Shewanella frigidimarina</u>	<u>Paraferomonas sedimenticola</u>	<u>Stackia exigua</u>	<u>Clostridium cochlearium</u>
<u>Campylobacter ornithocola</u>	<u>Sulfurospirillum sp. SCADC</u>	<u>Shewanella halifaxensis</u>	<b>Oceanospirillales</b>	<u>Stackia faecianis</u>	<u>Clostridium formicaceticum</u>
<u>Campylobacter peloridis</u>	<u>Sulfurospirillum sp. SL2-1</u>	<u>Shewanella japonica</u>	<b>Saccharospirothaceae</b>	<u>Stackia heliotritinireducens</u>	<u>Clostridium tetani</u>
<u>Campylobacter pinnipediorum</u>	<u>Sulfurospirillum sp. UBA11407</u>	<u>Shewanella loihica</u>	<u>Reinekea blandensis</u>	<u>Stackia isoflavoniconvertens</u>	<u>Clostridium tetanomorphum</u>
<u>Campylobacter rectus</u>	<u>Sulfurospirillum sp. UBA12182</u>	<u>Shewanella mangrovi</u>	<b>Deltaproteobacteria</b>	<u>Stackia piriformis</u>	<b>Archaea</b>
<u>Campylobacter showae</u>	<u>Sulfurospirillum sp. UCH001</u>	<u>Shewanella marina</u>	<b>Syntrophobacteriales</b>	<u>Stackia sp. CM382</u>	<b>Crenarchaeota</b>
<u>Campylobacter sp. 10_1_50</u>	<b>Helicobacteraceae</b>	<u>Shewanella marisflavi</u>	<b>Syntrophobacteraceae</b>	<b>Chloroflexi</b>	<b>Thermoprotei</b>
<u>Campylobacter sp. 114</u>	<u>Helicobacter burdigaliensis</u>	<u>Shewanella morhuæ</u>	<u>Syntrophorhabdus aromaticivorans</u>	<b>Anaerolineae</b>	<b>Thermoproteales</b>
<u>Campylobacter sp. 251/13</u>	<u>Helicobacter canadensis</u>	<u>Shewanella oneidensis</u>	<b>Syntrophaceae</b>	<b>Anaerolineales</b>	<b>Thermoproteaceae</b>
<u>Campylobacter sp. 73/13</u>	<u>Helicobacter ganmani</u>	<u>Shewanella pealeana</u>	<u>Desulfomonile tiedjei</u>	<b>Anaerolineaceae</b>	<u>Thermoproteus sp. AZ2</u>
<u>Campylobacter sp. BCW_6462</u>	<u>Helicobacter macacae</u>	<u>Shewanella piezotolerans</u>	<u>Smithella sp. SDB</u>	<u>Anaerolinea thermolimos</u>	<u>Thermoproteus tenax</u>
<u>Campylobacter sp. P0087</u>	<u>Helicobacter pullorum</u>	<u>Shewanella psychrophila</u>	<u>Syntrophus aciditrophicus</u>	<u>Anaerolinea thermophila</u>	<b>Acidilobales</b>
<u>Campylobacter sp. P0094</u>	<u>Helicobacter rodentium</u>	<u>Shewanella putrefaciens</u>	<u>Syntrophus gentianis</u>	<u>Bellilinea caldifistulae</u>	<b>Acidilobaceae</b>
<u>Campylobacter sp. P0103</u>	<u>Helicobacter sp. 11-8110</u>	<u>Shewanella sediminis</u>	<u>Syntrophus sp. GWC2_56_31</u>	<u>Levilinea saccharolytica</u>	<u>Acidilobus saccharovorans</u>
<u>Campylobacter sp. P0106</u>	<u>Helicobacter sp. MIT 01-3238</u>	<u>Shewanella sp. 10N.286.48.A6</u>	<u>Syntrophus sp. RIFOXYC2_FULL_54_9</u>	<u>Longilinea arvoryzae</u>	<u>Acidilobus sp. 7A</u>
<u>Campylobacter sp. P0107</u>	<u>Helicobacter sp. MIT 05-5294</u>	<u>Shewanella sp. 10N.286.51.B7</u>	<b>Actinobacteria</b>	<b>Deinococcus-Thermus</b>	<u>Acidilobus sp. CIS</u>
<u>Campylobacter sp. P0136</u>	<u>Helicobacter sp. MIT 11-5569</u>	<u>Shewanella sp. 10N.286.52.B9</u>	<b>Coriobacteria</b>	<b>Deinococci</b>	<u>Acidilobus sp. JCHS</u>
<u>Campylobacter sp. P0138</u>	<u>Helicobacter valdiviensis</u>	<u>Shewanella sp. 10N.286.52.C2</u>	<b>Coriobacteriales</b>	<b>Thermales</b>	<b>Caldisphaeraceae</b>
<u>Campylobacter sp. P0139</u>	<u>Helicobacter winghamensis</u>	<u>Shewanella sp. 11B5</u>	<b>Coriobacteriaceae</b>	<b>Thermaceae</b>	<u>Caldisphaera lagunensis</u>
<u>Campylobacter sp. P0209</u>	<u>Sulfuricum sp. PD_MW2</u>	<u>Shewanella sp. 38A_GOM-205m</u>	<u>Collinsella tanakaei</u>	<u>Oceanithermus profundus</u>	<u>Caldisphaera sp.</u>
<u>Campylobacter sp. P0227</u>	<u>Wolinella succinogenes</u>	<u>Shewanella sp. Actino-trap-3</u>	<u>Collinsella vaginalis</u>	<b>Aquificae</b>	<b>Desulfurococcales</b>
<u>Campylobacter sp. P031</u>		<u>Shewanella sp. ALD9</u>	<u>Parvibacter caecicola</u>	<b>Aquificae</b>	<b>Pyrodictiaceae</b>
<u>Campylobacter sp. P148</u>		<u>Shewanella sp. Alg231_23</u>	<u>Senegalimassilia anaerobia</u>	<b>Desulfurobacteriales</b>	<u>Hyperthermus butylicus</u>
<u>Campylobacter sp. P155</u>		<u>Shewanella sp. Bq11-22</u>		<b>Desulfurobacteriaceae</b>	<u>Pyrodictium delaneyi</u>
<u>Campylobacter sp. P157</u>		<u>Shewanella sp. CG12</u>		<u>Desulfurobacterium atlanticum</u>	<u>Pyrodictium occultum</u>

**Table S2.** Taxonomic classification of 63 species for which the presence of MMK and/or DMMK has been demonstrated biochemically. Organisms for which MqnK/MenK/MenK2-encoding genes have been assigned are shown in red. Modified from Hein *et al.* (2017).

Organism	Major naphthoquinones	Reference (MMK identification)	Organism	Major naphthoquinones	Reference (MMK identification)
<b>Bacteria</b>			<b>Actinobacteria</b>		
<b>Proteobacteria</b>			<b>Coriobacteria</b>		
<b>Epsilonproteobacteria</b>			<b>Coriobacteriales</b>		
<b>Campylobacterales</b>			<b>Coriobacteriaceae</b>		
<b>Campylobacteraceae</b>			<i>Parvibacter caecicola</i> NR06		
<i>Campylobacter coli</i> LMG 23344	MK <sub>6</sub> , MMK <sub>6</sub>	Moss <i>et al.</i> 1990		MMK <sub>6</sub> , DMMK <sub>6</sub>	Clavel <i>et al.</i> 2013
<i>Campylobacter concisus</i> UNSWCD	MK <sub>6</sub> , MMK <sub>6</sub>	Moss <i>et al.</i> 1990	<b>Eggerthellales</b>		
<i>Campylobacter curvus</i> DSM 6644	MMK <sub>6</sub> , MK <sub>6</sub>	Fernandez and Collins 1987	<b>Eggerthellaceae</b>		
<i>Campylobacter faecalis</i>	MK <sub>6</sub> , MMK <sub>6</sub>	Moss <i>et al.</i> 1990	<i>Adiercreutzia equolifaciens</i> DSM 19450		
<i>Campylobacter fetus</i> subsp. fetus 82-40	MK <sub>6</sub> , MMK <sub>6</sub>	Carlone and Anet 1983		DMMK <sub>6</sub> , MMK <sub>6</sub>	Maruo <i>et al.</i> 2008, Hein <i>et al.</i> 2018
<i>Campylobacter fetus</i> subsp. Venerealis UM	MK <sub>6</sub> , MMK <sub>6</sub> , MK <sub>5</sub>	Moss <i>et al.</i> 1984		MMK <sub>6</sub> , MK <sub>6</sub>	Collins <i>et al.</i> 1985, Fernandez and Collins 1987, Maruo <i>et al.</i> 2008
<i>Campylobacter gracilis</i> RM 3268	MMK <sub>6</sub> , MK <sub>6</sub>	Fernandez and Collins 1987		MMK <sub>6</sub> , DMMK <sub>6</sub> , MK <sub>6</sub>	Maruo <i>et al.</i> 2008
<i>Campylobacter nyointestinalis</i> DSM 19053	MK <sub>6</sub> , MMK <sub>6</sub>	Moss <i>et al.</i> 1990		MMK <sub>6</sub> , DMMK <sub>6</sub>	Clavel <i>et al.</i> 2009
<i>Campylobacter jejuni</i> subsp. jejuni NCTC 11168	MK <sub>6</sub> , MMK <sub>6</sub>	Carlone and Anet 1983		MMK <sub>6</sub>	Clavel <i>et al.</i> 2009
<i>Campylobacter lari</i> NCTC 11845	MK <sub>6</sub> , MMK <sub>6</sub>	Moss <i>et al.</i> 1990		MK <sub>6</sub> , MMK <sub>6</sub> , DMMK <sub>6</sub>	Jin <i>et al.</i> 2014
<i>Campylobacter mucosalis</i> DSM 21682	MK <sub>6</sub> , MMK <sub>6</sub>	Moss <i>et al.</i> 1990		MK <sub>6</sub> , MMK <sub>6</sub> , DMMK <sub>6</sub>	Jin <i>et al.</i> 2014
<i>Campylobacter rectus</i> RM 3267	MK <sub>6</sub> , MMK <sub>6</sub>	Fernandez and Collins 1987		MMK <sub>6</sub> , DMMK <sub>6</sub> , MK <sub>6</sub>	Maruo <i>et al.</i> 2008
<i>Campylobacter sputorum</i> INTA 08/209	MK <sub>6</sub> , MMK <sub>6</sub> , MK <sub>5</sub>	Moss <i>et al.</i> 1990	<b>Actinobacteria</b>		
<i>Campylobacter upsaliensis</i> RM 3165	MK <sub>6</sub> , MMK <sub>6</sub>	Morotomi <i>et al.</i> 1990	<b>Micrococcales</b>		
<i>Campylobacter ureolyticus</i> ACS-301-VSch3b	MK <sub>6</sub> , MMK <sub>6</sub>	Vandamme <i>et al.</i> 2010	<b>Micrococcaceae</b>		
<i>Sulfurospirillum arcachonense</i> DSM 9755	MK <sub>6</sub> , MMK <sub>6</sub>	Finster <i>et al.</i> 1997	<i>Acaricomes phytoseili</i> DSM 14247		
<i>Sulfurospirillum deleyianum</i> DSM 6946	MK <sub>6</sub> , MMK <sub>6</sub> , MK <sub>5</sub>	Sikorski <i>et al.</i> 2010, Collins and Widdel 1986		MK <sub>10</sub> -(H <sub>2</sub> ), MMK <sub>10</sub> -(H <sub>2</sub> )	Pukall <i>et al.</i> 2006
<b>Helicobacteraceae</b>			<b>Archaea</b>		
<i>Wolinella succinogenes</i> DSM 1740	MK <sub>6</sub> , 8-MMK <sub>6</sub>	Collins and Fernandez 1984, Hein <i>et al.</i> 2017	<b>Crenarchaeota</b>		
<b>Nautiliales</b>			<b>Thermoprotei</b>		
<b>Nautiliaceae</b>			<b>Thermoproteales</b>		
<i>Celia pacifica</i> DSM 27783	MK <sub>7</sub> , MMK <sub>7</sub>	Grosche <i>et al.</i> 2015	<b>Thermoproteaceae</b>		
<b>Betaproteobacteria</b>			<i>Thermoproteus tenax</i> Kra 1		
<b>Burkholderiales</b>				MMK <sub>6</sub> , MMK <sub>5</sub> , MK <sub>6</sub> , MK <sub>5</sub> , MMK <sub>7</sub>	Thurl <i>et al.</i> 1985
<b>Sutterellaceae</b>			<b>Desulfurococcales</b>		
<i>Mesosutterella multiformis</i> DSM 106860	MMK <sub>6</sub> , MK <sub>6</sub>	Sakamoto <i>et al.</i> 2018	<b>Pyrodictiaceae</b>		
<i>Parasutterella excrementihominis</i> YIT 11859	MMK <sub>6</sub> , MK <sub>6</sub>	Nagai <i>et al.</i> 2009	<i>Pyrolobus fumarii</i> 1A		
<i>Parasutterella secunda</i> YIT 12071	MMK <sub>6</sub> , MK <sub>6</sub>	Morotomi <i>et al.</i> 2011		DMK <sub>6</sub> , MK <sub>6</sub> , DMK <sub>5</sub> , MTK <sub>6</sub> , MK <sub>5</sub> , MMK <sub>5</sub>	Elling <i>et al.</i> 2016
<i>Sutterella faecalis</i> KGMBO3119	MMK <sub>6</sub>	Oh <i>et al.</i> 2020	<b>Desulfurococcaceae</b>		
<i>Sutterella megalosphaeroides</i> DSM 106861	MMK <sub>6</sub> , MK <sub>6</sub>	Sakamoto <i>et al.</i> 2018	<i>Aeropyrum pernix</i> K1		
<i>Sutterella parvibrabra</i> YIT 11816	MMK <sub>6</sub>	Morotomi <i>et al.</i> 2011		DMK <sub>6</sub> , MK <sub>6</sub> , DMK <sub>5</sub> , MTK <sub>6</sub> , MK <sub>5</sub> , MMK <sub>5</sub>	Elling <i>et al.</i> 2016
<i>Sutterella stercoricanis</i> DSM 17807	MMK <sub>6</sub> , MK <sub>6</sub>	Morotomi <i>et al.</i> 2011	<i>Ignicoccus hospitalis</i> KIN4/1		
<i>Sutterella wadsworthensis</i> DSM 14016	MMK <sub>6</sub> , MK <sub>6</sub>	Morotomi <i>et al.</i> 2011		MMK <sub>6</sub> , MK <sub>6</sub> , MMK <sub>5</sub> , MK <sub>5</sub> , MK <sub>7</sub>	Elling <i>et al.</i> 2016
<b>Gammaproteobacteria</b>			<b>Euryarchaeota</b>		
<b>Alteromonadales</b>			<b>Thermoplasmata</b>		
<b>Shewanellaceae</b>			<b>Thermoplasmatales</b>		
<i>Shewanella aestuarii</i> JCM 17801			<b>Thermoplasmataceae</b>		
<i>Shewanella aigae</i> JCM 21037	MK <sub>7</sub> , MMK <sub>7</sub>	HY <i>et al.</i> 2013	<i>Thermoplasma acidophilum</i> 122-1B2		
<i>Shewanella arctica</i> KCTC 23109	MK <sub>7</sub> , MMK <sub>7</sub>	Bozal <i>et al.</i> 2002		MK <sub>7</sub> , MMK <sub>7</sub> , various MTKs	Elling <i>et al.</i> 2016
<i>Shewanella baltica</i> OS 185	MMK <sub>7</sub> , MK <sub>7</sub>	Hwang <i>et al.</i> 2019	<i>Thermoplasma acidophilum</i> HO-62		
<i>Shewanella colwelliana</i> ATCC 39565	MK <sub>7</sub> , MMK <sub>7</sub>	Bozal <i>et al.</i> 2002		8-MMK <sub>7</sub> , MK <sub>7</sub>	Collins 1985 and Shimada <i>et al.</i> 2001
<i>Shewanella fidelis</i> ATCC BAA-318	MK <sub>7</sub> , MMK <sub>7</sub>	Frolova <i>et al.</i> 2005	<b>Halobacteria</b>		
<i>Shewanella frigidimarina</i> NCIMB 400	MK <sub>7</sub> , MMK <sub>7</sub>	Bozal <i>et al.</i> 2002	<b>Natrialbales</b>		
<i>Shewanella gelidii</i> RZB5-4	MK <sub>7</sub> , MMK <sub>7</sub>	Frolova <i>et al.</i> 2005	<b>Natrialbaceae</b>		
<i>Shewanella litoralis</i> JCM 32306	MK <sub>7</sub> , MMK <sub>7</sub>	Frolova <i>et al.</i> 2005	<i>Natronobacterium gregoryi</i> SP 2		
<i>Shewanella maritima</i> JCM 33294	MK <sub>7</sub> , MMK <sub>7</sub>	Frolova <i>et al.</i> 2005		MK <sub>6</sub> , MK <sub>6</sub> (VIII-H <sub>2</sub> ), MMK <sub>6</sub> , MMK <sub>6</sub> (VIII-H <sub>2</sub> ), DMMK <sub>6</sub> , DMMK <sub>6</sub> (VIII-H <sub>2</sub> )	Collins and Tindall 1987
<i>Shewanella oneidensis</i> MR-1	MK <sub>7</sub> , MMK <sub>7</sub>	Wang <i>et al.</i> 2016	<b>Eukaryota</b>		
<i>Shewanella pacifica</i> KMM 3597	MK <sub>7</sub> , MMK <sub>7</sub>	Yun <i>et al.</i> 2018	<b>Evosea</b>		
<i>Shewanella profunda</i> DSM 157900	MMK <sub>7</sub> , MK <sub>7</sub> , MMK <sub>6</sub> , MK <sub>6</sub>	Yun <i>et al.</i> 2018	<b>Archamoebae</b>		
<i>Shewanella psychromarinicola</i> JCM 32090	MK <sub>7</sub> , MMK <sub>7</sub>	Bae <i>et al.</i> 2019	<b>Mastigamoebida</b>		
<i>Shewanella putrefaciens</i> IAM 12079	MK <sub>7</sub> , 8-MMK <sub>7</sub>	Venkateswaran <i>et al.</i> 1999	<b>Entamoebidae</b>		
<i>Shewanella saliphila</i> JCM 32304	MK <sub>7</sub> , MMK <sub>7</sub> , MK <sub>6</sub> , MMK <sub>6</sub>	Frolova <i>et al.</i> 2005	<i>Entamoeba histolytica</i> HM-1:IMSS		
<i>Shewanella uilleungensis</i> JCM 32305	MK <sub>7</sub> , MMK <sub>7</sub> , MMK <sub>6</sub> , MK <sub>6</sub>	Toffin <i>et al.</i> 2004		MMK <sub>7</sub>	Thurl <i>et al.</i> 1985
<i>Shewanella vesiculosa</i> M7	MK <sub>7</sub> , MMK <sub>7</sub>	Hwang <i>et al.</i> 2019			
		Itoh <i>et al.</i> 1985, Akagawa-Matsushita <i>et al.</i> 1992			
		Yun <i>et al.</i> 2018			
		Yun <i>et al.</i> 2018			
		Bozal <i>et al.</i> 2009			

**Table S3.** Nucleotide primers used in this study.

Primer	Sequence 5'→3'
PS_ubiE_F	GTATGTTTCAGGCGAACGCTGGTTTTAGAGCTAGAAATAGCAAG
PS_ubiE_R	CAGCGTTCGCCTGAACATACGTGCTCAGTATCTCTATCACTGA
CPEC2F	CGGCGTCACACTTTGCTAT
gamR	TTTATAACCTCCTTAGAGCTCGA
ubiE_FFA_F	AGCCGAATGATGAAGCTTATCAAC
ubiE_FFA_R	GGTTTAAAAGGCATTTCCGGTCTCCTGCTCAATGCCTGCTCATCAAAAAATTGTTCC
ubiE_RFA_F	GGAACAATTTTTTGGATGAGCAGGCATTGAGCAGGAGACCGGAAATGCCTTTTAAACC
ubiE_RFA_R	TGGCGTTCGCTGAACACCAGAATC
Ferri_975_I_F	GGAGATATACATATGGCTCAGGTTTCGCTTTC
Ferri_975_I_R	GCTCCATGCACTGGCGGCCTGCACCTCGATG
Ferri_975_O_F	GTGCAGGCCCGCCAGTGCATGGAGCCATCCG
Ferri_975_O_R	AACCTGAGCCATATGTATATCTCCTTCTTATAC
Ferri_647_I_F	AAGGAGATATACATATGTCATTAGCCGAACGC
Ferri_647_I_R	GGATGGCTCCATGCACTCATGTCCGACGCTTTG
Ferri_647_O_F	TCCGACATGAGTGCATGGAGCCATCCGCAGTTC
Ferri_647_O_R	TTCGGCTAATGACATATGTATATCTCCTTC
Colli_032_I_F	GAAGGAGATATACATATGCTATCCGAACGCCTACTTTTC
Colli_032_I_R	GCTCCATGCACTGAACATCTTGGCTCGCACTC
Colli_032_O_F	CGCAAGATGTTTCAGTGCATGGAGCCATCCGCAGTTC
Colli_032_O_R	GCGTTCGGATAGCATATGTATATCTCCTTC
Colli_643_I_F	ATAAGAAGGAGATATACATATGCTTTTCAGAAAGAATG
Colli_643_I_R	GCTCCATGCACTCTTCTGGGTGCCGTCGCCAAAGAGC
Colli_643_O_F	ACGGCACCCAGAAGAGTGCATGGAGCCATC
Colli_643_O_R	AGCATTCTTCTGAAAGCATATGTATATCTCCTTCTTATAC

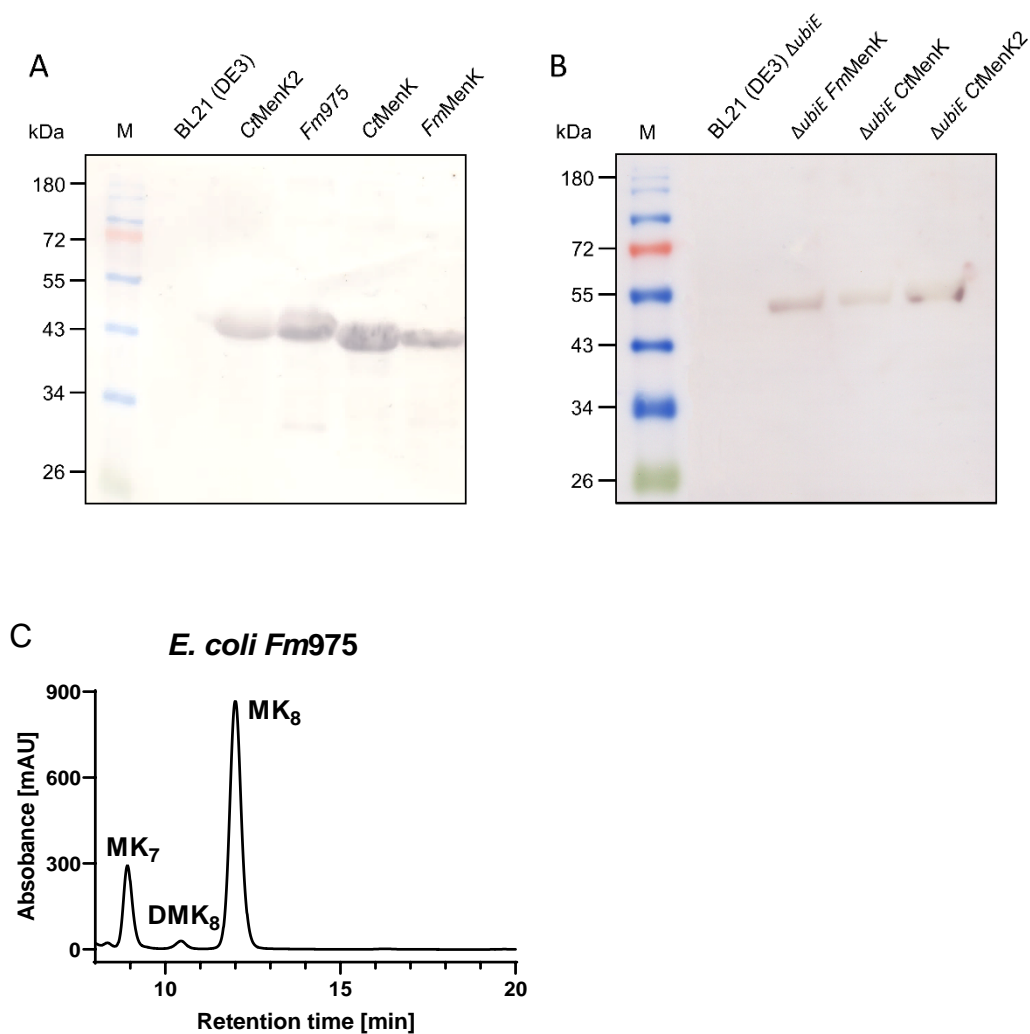
The primer pairs labelled Ferri (or Colli)\_xxx\_I\_F (or R) were used to amplify the (methyl)menaquinone methyltransferase genes, while the primer pairs Ferri (or Colli)\_xxx\_O\_F (or R) were used to amplify a suitable fragment of vector pACYCDuet-1.

**Table S4.** Accession numbers of sequences used in Fig. 2.

<b>Protein</b>	<b>Accession no.</b>	<b>Organism</b>
Blm-Orf8	AAG02372.1	<i>Streptomyces verticillus</i>
C10P	ARK19493.1	<i>Streptomyces zelensis</i>
ChuW	WP_000993317.1	<i>Escherichia coli</i>
ChuW	ASJ24187.1	<i>Laribacter hongkongensis</i>
HemN	AAN83245.1	<i>Escherichia coli</i>
HutW	WP_080284587.1	<i>Vibrio cholerae</i>
HutW	AIC83437.1	<i>Vibrio alginolyticus</i>
Jaw5	WP_120753176.1	<i>Streptomyces klenkii</i>
MenK	WP_022738066.1	<i>Adlercreutzia equolifaciens</i>
MenK	WP_011074137.1	<i>Shewanella oneidensis</i>
MenK2	WP_022739874.1	<i>Adlercreutzia equolifaciens</i>
MqnK	CAE09279.1	<i>Wolinella succinogenes</i>
NocN	ADR01089.1	<i>Nocardia</i> sp. ATCC 202099
NosN	AQM75227.1	<i>Streptomyces</i> sp.
NosN	ACR48343.1	<i>Streptomyces actuosus</i>
PbtM2	AGY49586.1	<i>Planobispora rosea</i>
PbtM3	AGY49595.1	<i>Planobispora rosea</i>
Tbtl	ADG87272.1	<i>Thermobispora bispora</i>
Tlm-Orf11	ABL74954.1	<i>Streptoalloteichus hindustanus</i>
TpdI	ACS83777.1	<i>Nonomuraea</i> sp. Bp3714-39
TpdL	ACS83774.1	<i>Nonomuraea</i> sp. WU8817
TpdU	ACS83765.1	<i>Nonomuraea</i> sp. WU8817
YtkT	WP_055490826.1	<i>Streptomyces</i> sp. TP-A0356
Zbm-Orf26	ACG60749.1	<i>Streptomyces flavoviridis</i>

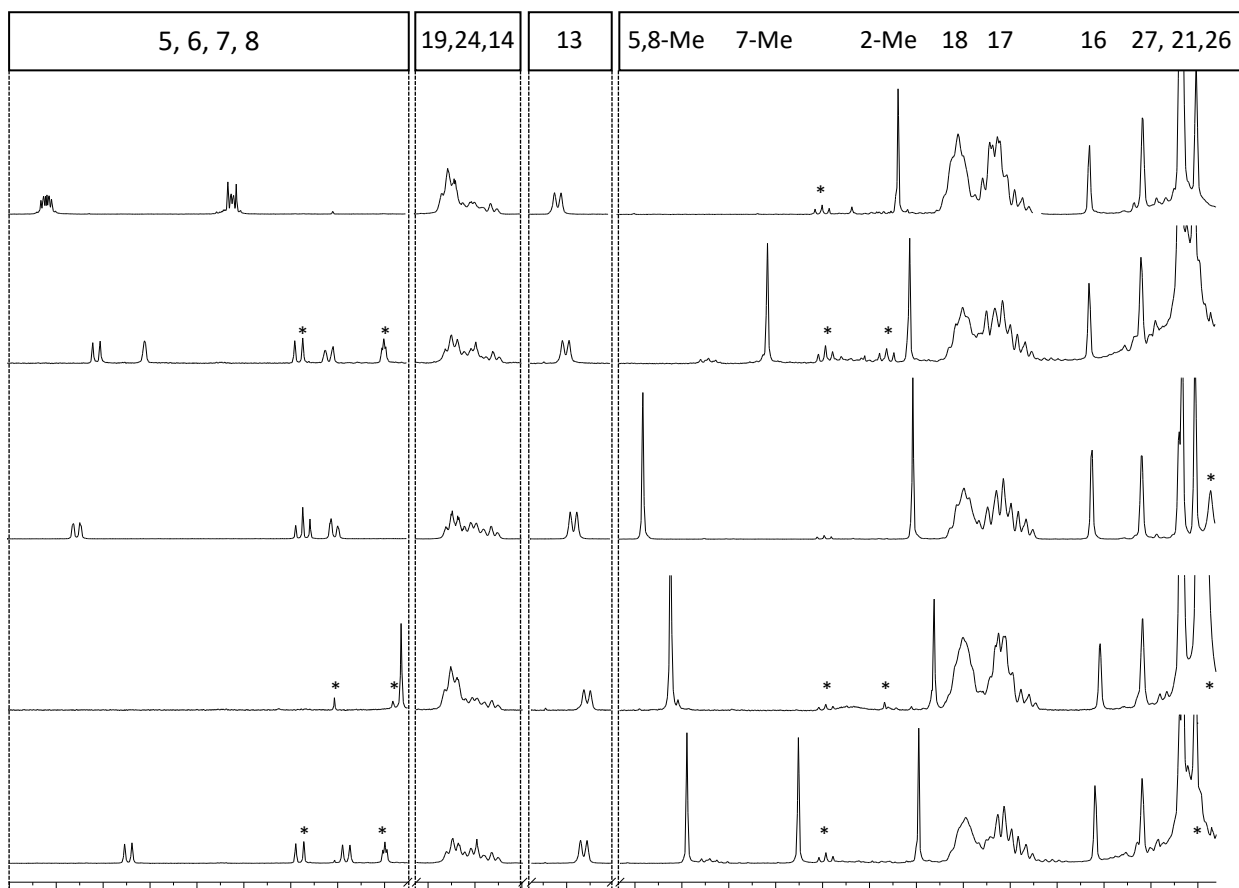
SoMenK	-----MSSVIQTLNGAIATPYQANITVPNWMLSSMERVMQYYVDKNLRLDLSAD--IMPAPVE	57
FmMenK	-----MSLAERALNNAAIHNAAEITTPKWMLSSMESLMQHYTKRHLKMDTRACD--AIPAPIE	56
WsMenK	MAEMKMKELMEGEGFSSPSCLLPFLSLEGLLEIKPGMLATRIVNRAMRQASGKYLRLPIDRD--RLPAPRE	68
AeMenK2	-----MLSERMLTTVVRAMTKTLTLHPVPEG--ALPDPVP	34
CtMenK2	-----MLSERMLTGVIKTMTKHELAMEPTTET--HLPGPKP	34
AeMenK	-----MLSERMLSKVVEACTANYLQKPCDEA--FMPSFNP	34
CtMenK	-----MLSERLLSKTVGIGARQLFRSKGECAR--TLPAPEA	34
Fm0975	-----MAQVRFPPQLSQALDYVMGGKIKSLLDLQQLSPGGYDLAELSG	43
	: : : :	
SoMenK	GKKYMLYAHVPFCHTLCSTYCTFHRFMFKEDKARAYFISLRKEMEMVKALGYDFESMYIGGGTTTVEDEL	127
FmMenK	GRKYTLYMHIPFCHTLCSTFCTHRRFLFKEEKARAYFASLRQEMHMAKALGYDFEELYIGGGTTTFLVDEL	126
WsMenK	GKHYYLYAHVPFCTSLCTYCTFNRFLEEEKARAYFRSLRQEMKMAVELGYRFDSDMYVGGGTTSLVDEL	138
AeMenK2	GRPYTLYVHVPFCERLCPYCSFNRFYREQRARDYFQALCQEMRMLAAQGYDFESVYVGGGTTPTVIDEL	104
CtMenK2	NMKYMLYMHIPFCQRLCPYCSFNRYPFREIARPYFANLRREMLMKDLGYDFESIYCGGGTTPTIMDEL	104
AeMenK	GQPYMLYMHVPFCERLCPYCSFNRFPFREARAPYFENMRREMLMKDLGYDFSDSYIGGGTTPTIMDEL	104
CtMenK	GHEYLIVHVPFCDVLCYCSFTRFPFEEAARAYFEALRRELKMIHDLGYQPPSAYIGGGTTPTIMDEL	104
Fm0975	KRVPTLYIHIPFCHTLCRFCSFRLKYDEAKAREYFKLLRQEVLELAQVGVQFDRLYIGGGTTTIESEL	113
	LY H PFC * C C E * * * Y F R E E L A Q V G V Q F D R L Y I G G G T T I E S E L **	
SoMenK	ARTIEHAKTLFPFIKEVSCSDPQHLDSPGFKQLKGLVDRMSIGVQSFNDDILKMTDRLEKFGTGGQTFD	197
FmMenK	AKTIELAKTLFPAIKQVSCSDPLHLSTEFMQLHGLVDRLSVGVQSFDRDILARTDRLEKFGGEEVVS	196
WsMenK	CATIDLARELFP-LKEVSCSDPNNDIKETMAHLKGRVDRISVGVQSFDDILKRVGRYKFGGGEETS	207
AeMenK2	CETIDLARDLFH-VKEVNSSETNPNIPEYLDKLGRIQRLSVGVQSFDDGLLRQMDRYEKYGSGEIIFE	173
CtMenK2	CETLDLARDLFS-IKEVSSSETNPNIPLPYLEKLGKRVQRLSVGVQSFDDSLLRQMDRYEKYGSQAEIFE	173
AeMenK	CETIDMARDLFS-IKEVSSSETNPNIHLEYLEKLGKRVQRLSVGVQSFDDDLRQMDRYEKYGSQGEILE	173
CtMenK	ERTIDYMRELFPFIKEVSSSETNPPLDRERLKRLSNMVQRFVSGVQSFDDTLKRMDRYNYGSAEIVE	174
Fm0975	IETIELIKSRFD-IQEVSCSDPIYFENSPLALKGLVDRFSIGIQSFDDIILKHSGRYKFGSGDAIAD	182
	* * * * * * R S G Q * F I * * * *	
SoMenK	FDKIMAAKELFPIINVDLIFGFRGQTEVIQHDLDMASRLDPRQITTYPLMITHQTR-----KSVGKGL	259
FmMenK	FEKLARAKENFPIINVDMIFGFDGQTEVLAQDMATLRKLNPRQITTYPLMVSDLTRHAATKIGTKANL	264
WsMenK	LSKLQALMGALPVVNIIDLIFNFPQTQDKMLRDLLEIKRLSPTQVTAYPLMSSPSVKS----LIKRSIG	270
AeMenK2	FERIGEAAPIYFESLNVDIMFNFPQTQEDILSDCEKIALCGCHQTTFSPLYQSHATTR----KMEQVLG-	236
CtMenK2	FERIGVAAPYFDILNVDMIFNFPQTEEVLRRIELIKECGCQTTFSPLYFSRATTR----KMLDTLG-	236
AeMenK	LERIQEASPIYFISMNADMIFNFPQTEDTLRDIEMVVASGASQTTFYPLMASPSVQR----SLAATVG-	236
CtMenK	VERIQSVHDMFDTFNVDIMFNFPQTPMEMVSRDIDVFRITGANQITTYPLMASPGSEK----LMQTCFHG	238
Fm0975	ADLSARAIAEFPTINLDMMGFNQTPDALTEDLMRASALKPQGITTYPLTLGVGKNR-----KKAKGL	244
	* * * * * Q T Y P L	
SoMenK	AAPQADMANQYRQILNSLNG-----QYNQLSAWAFGKA-----NDEGFDEYVIDEYLVGVSGS	314
FmMenK	ANINQDIRKDYALILNSLRG-----DYEQLTAWSFKS-----NDEGFDEYVNVNADYDLGLSGS	319
WsMenK	DISLDKEATLYRVILEELG-----EYNQISSWAFSK-----GDDIDEYVNVHDEYVGVGSGS	325
AeMenK2	RMDYDKERRFYHILDEILAG-----GDAPFFERRTLWTFNRDENLKRKQHELVDEYAVSYEECVIGSGS	302
CtMenK2	DPNYTREYIYKLLDHELAG-----GSDPAFERRTVWTFNRKGMDLHACGEVVPVDFPGVSYEYPAIGSGS	302
AeMenK	KVDYNRERRFYEICDILLGDLPGGQPLFELGSAWTFNRRGTGAAG-EDAMIDEYVVDYEEYPAIGSGG	305
CtMenK	QVDYINLEKDLNTLFDKMTAP-----VEKGGVGFYATDVYTFAKDRDAMI DEYVVDYGEYVAAGCGG	300
Fm0975	AGNPADLLGLYQTRNVLEPG-----YEREYAWTYRRAT-----GLPVEHDYVLDGEDCVGICGGA	300
	* * * * *	
SoMenK	FSFLNDTLYVNTFSLRKYQERIAAGKMGVEQQKNYKNDVMQYRFLLMFSGRLSRKYFRETFGNVLDTA	384
FmMenK	FSFLHDNLYVNSFSLRKYNEKIANGKMGVSSKAYDRKAVLQYRFLLSMFGGRLSKRYFKEGYDANLYTA	389
WsMenK	FSFLDGLVLYNTFSLKEYATRIESGKMGLSRARKYGRLSQMQRMLMVGLFGGGVHKESFSRQFKMPIEVG	395
AeMenK2	ITHLGDNLVNTFNLEEYGEVLRAGVTPLLGKTDLPRLDMRYKFLQLYSLRFDKHEFERDFGVSVERG	372
CtMenK2	VTHLDGTIYVNTFIREYNEAIESGRMSLMGKTKMGRDLMRYRMEQELYALRLDKNRFKDFGVSVERG	372
AeMenK	ITYLGENLYVNTFSVREYNATAIEAGHMSMMGKTFSLDRMRYRFMMQLFGLRLDKRQFERDFGMSVERG	375
CtMenK	YSFLGDDIYINDSSLDGYCRRIEEGTMSVASHISMGHANGKRYRMGRELFGLRLDNRAWRDFGKIYD	370
Fm0975	FGRIGNKFYLSFNLDYARRVKAGELSCSHKDLSTPLMRRYHLLMMVMKGLHLPNSVFEKLYGRSLYTA	370
	N F Y * *	
SoMenK	LFKEMTSMKLGAIKNDPTDPDNLIIITDNGKMMGLLMMKFEYAGMDNVRAQLRKLKPCDM-----	445
FmMenK	LTKEMAFMHAIGGLETPNDADKLQATPNGLMGLLMMKNFYTGMDNVRAELRRLKASDM-----	450
WsMenK	LFKELLFLRCAGAIKEKE---GVLYPTLKGKYLFLSMMKFEYIGMDTVREESRARLSSSDM-----	453
AeMenK2	LPVEMAFMRANGAFATDD--ADELTLTPAGRYLTVVLYRQYLAGLNNLRQARAKLPGDERDLLFGDGT	440
CtMenK2	LPVEMAFMRANGAFATDD--ADELTLTPKGRYTLVMQRQFLSGLNELRDQARAALTGPEHDLFGDGTQ	440
AeMenK	LPVEMGFMRACGAFATDN--ADELTLTPKGRYLVVMMRQFFIGVNNLRDQARAALTGEERELIFGDGK	443
CtMenK	MPVEYGYLAANGAFDKN--ADELTLTRKGRYLVVMMRQIFIGMNTDRDLRLLPECEKRMFADSAAK	438
Fm0975	LPAEMAFRLRHGAIVPSAC-GDGYRTPTEGFVALKMFSGFLAGMDWLREQAGSAEAAEQIARGQAIEVQ	439
	* * * * *	
SoMenK	-----	445
FmMenK	-----	450
WsMenK	-----	453
AeMenK2	K-----	441
CtMenK2	K-----	441
AeMenK	CGKVVAKPASADAVAAEIAREEAASAILDGTQAVASEE	481
CtMenK	QIAAKAADEAAGADQ-----	454
Fm0975	AA-----	441

**Fig. S1.** Alignment of selected MqnK/MenK/MenK2 primary structures. The N-terminal trip-wire (grey), the catalytic domain (green), the linker (orange) and the C-terminal HemN domain (blue) are highlighted. Cluster-specific motifs denoted in Table 1 are highlighted in red. \*, strictly conserved residue.

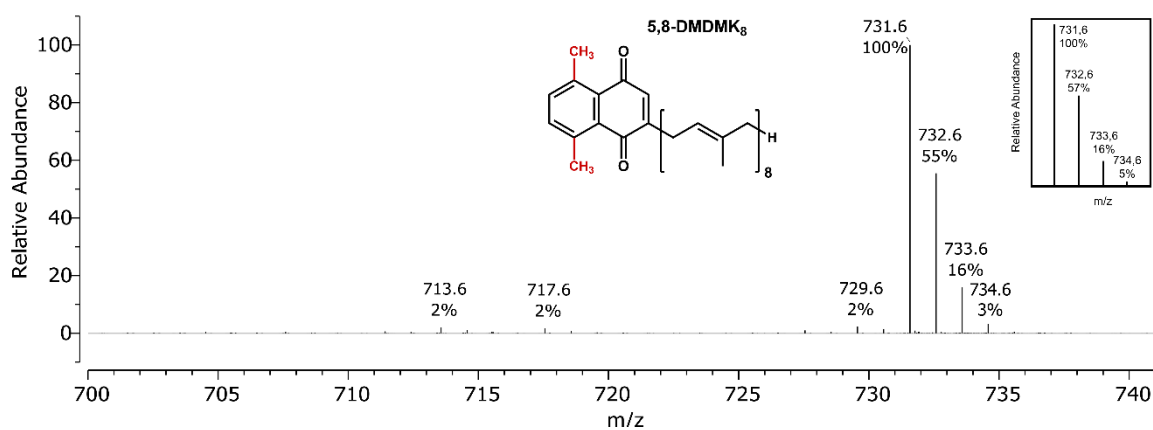
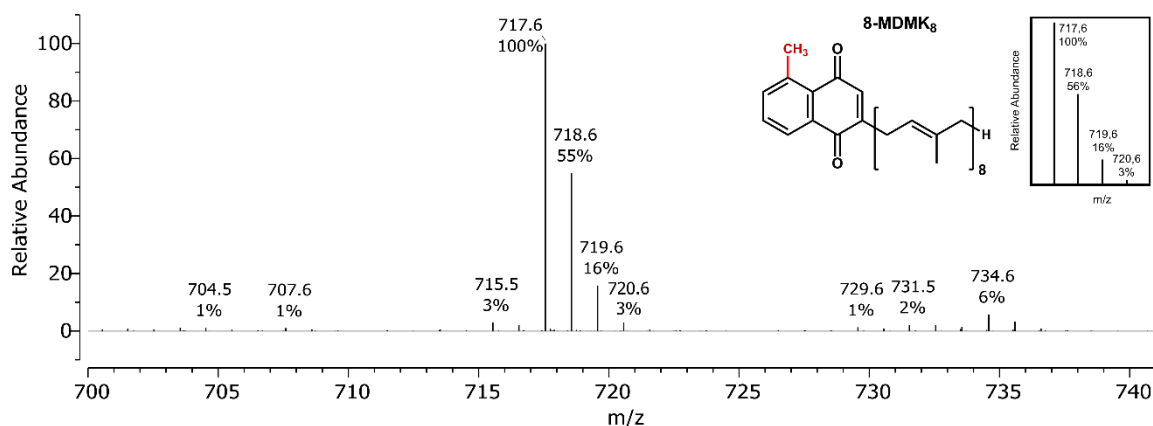
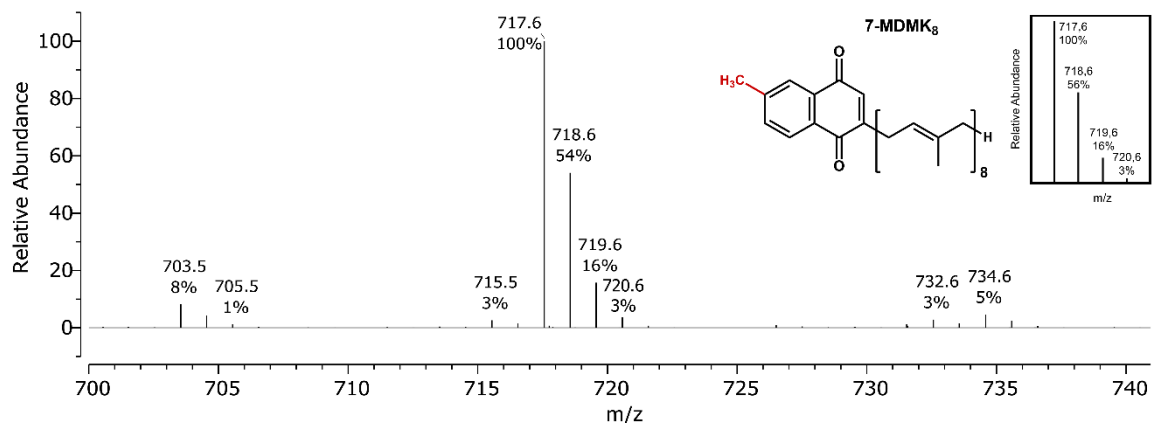
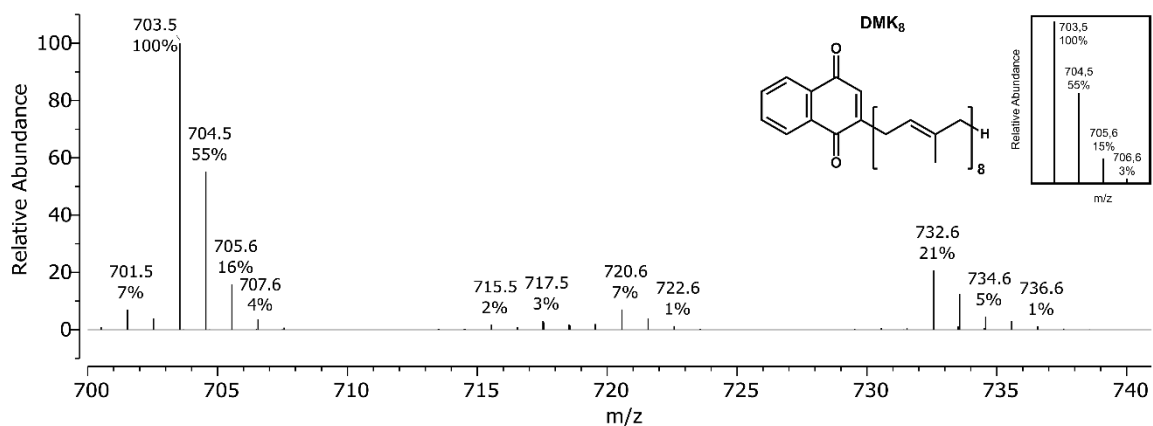


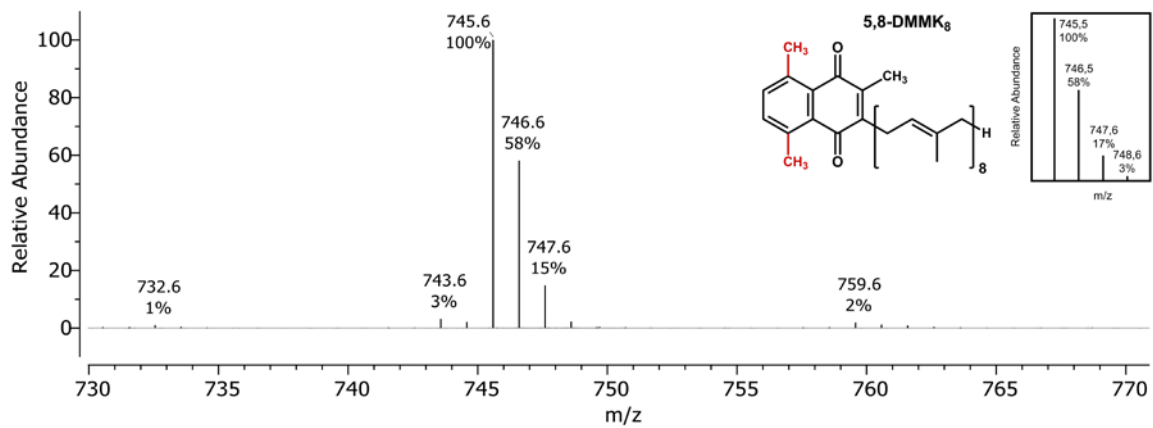
**Fig. S2.** (A,B) Immunodetection of Strep-tagged MenK and MenK2 homologues from *C. tanakaei* and *F. marina* using a Strep-Tactin-HRP conjugate (IBA Lifesciences). The proteins were produced in *Escherichia coli* BL21(DE3) (A) or *E. coli* BL21(DE3)  $\Delta$ ubiE (B). 50  $\mu$ g of total cell protein was applied to each lane. M, Color Prestained Protein Standard (NEB). *E. coli* BL21(DE3) or *E. coli* BL21(DE3)  $\Delta$ ubiE served as controls. Predicted protein masses are 52.1 kDa (CtMenK2), 52.3 kDa (Fm975), 51.2 kDa (CtMenK) and 50.3 (FmMenK). (C) HPLC chromatogram of purified quinones from *E. coli* Fm975.



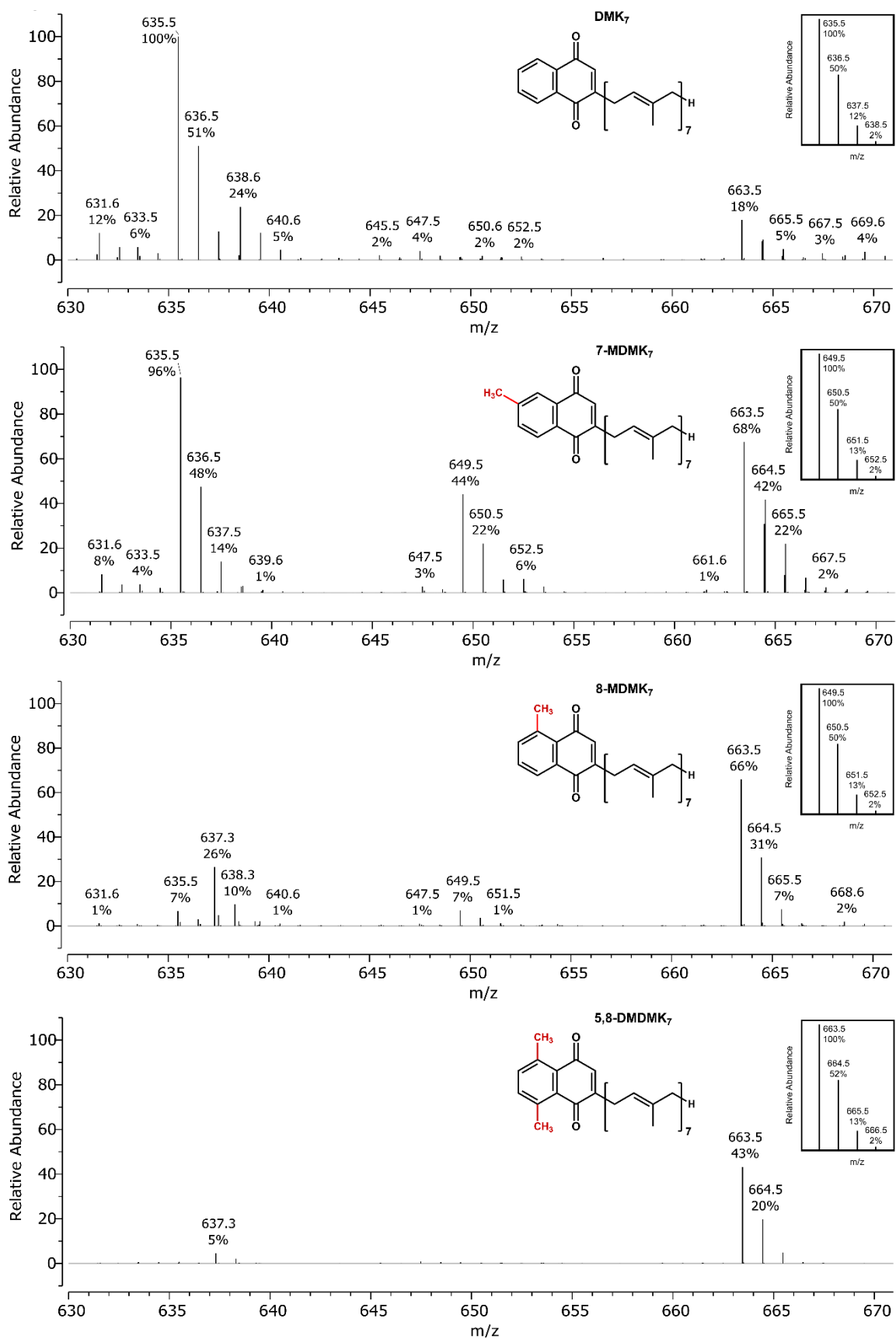


**Fig. S3.** Parts of 500 MHz  $^1\text{H-NMR}$  spectra of  $\text{MK}_8$ ,  $7\text{-MMK}_8$ ,  $8\text{-MMK}_8$ ,  $5,8\text{-DMMK}_8$  and  $7,8\text{-DMMK}_8$  (from top to bottom). All spectra were calibrated at the signal of residual protons in  $\text{CDCl}_3$  at 7.20 ppm. Asterisks mark small amounts of impurities. The signal assignments are given in the top line.

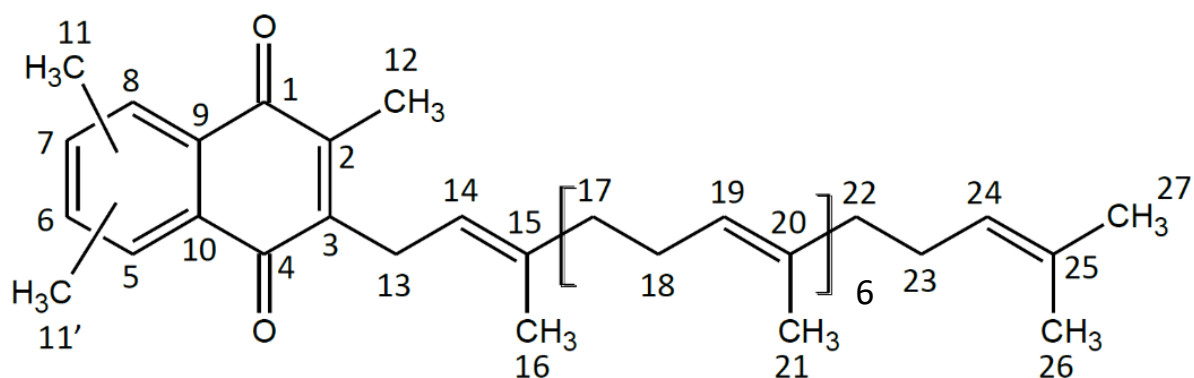




**Fig. S4.** Mass spectra of DMK<sub>8</sub>, 7-MDMK<sub>8</sub>, 8-MDMK<sub>8</sub>, 5,8-DMDMK<sub>8</sub> and 5,8-DMMK<sub>8</sub>. Insets show simulated isotopic distribution patterns.

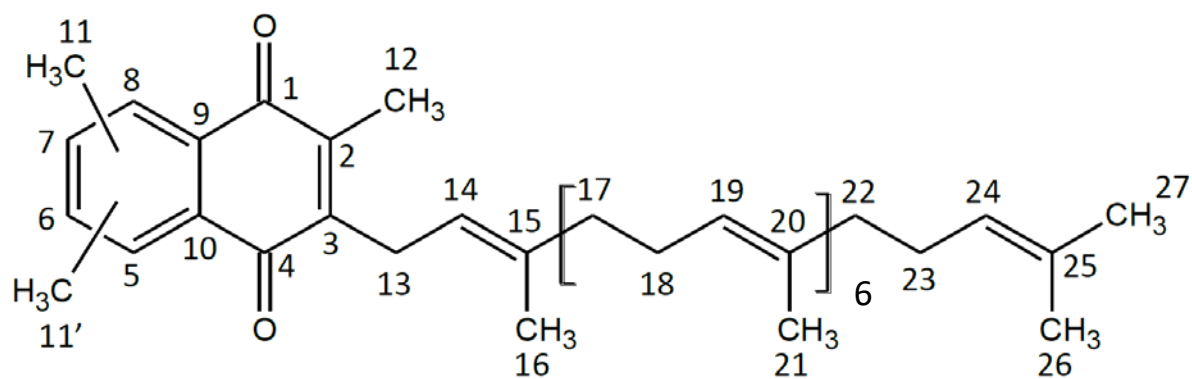


**Fig. S5.** Mass spectra of DMK<sub>7</sub>, 7-MDMK<sub>7</sub>, 8-MDMK<sub>7</sub> and 5,8-DMDMK<sub>7</sub>. Insets show simulated isotopic distribution patterns.



	MK <sub>8</sub>	7-MMK <sub>8</sub>	8-MMK <sub>8</sub>	5,8-DMMK <sub>8</sub>	7,8-DMMK <sub>8</sub>
1	-	-	-	-	-
2	-	-	-	-	-
3	-	-	-	-	-
4	-	-	-	-	-
5	7.61	7.89	7.93	-	7.84
6	8.02	7.39	7.45	7.26	7.37
7	8.02	-	7.39	7.26	-
8	7.61	7.80	-	-	-
9	-	-	-	-	-
10	-	-	-	-	-
11	-	2.40	2.67	2.62	2.35
11'	-	-	-	2.62	2.59
12	2.13	2.10	2.08	2.06	2.09
13	3.31	3.28	3.26	3.25	3.26
14	4.96	4.97	4.94	4.97	4.97
15	-	-	-	-	-
16	1.73	1.71	1.70	1.71	1.72
17	1.92	1.88	1.89	1.91	1.91
18	2.00	2.00	1.97	2.00	1.98
19	5.05	5.03	5.03	5.06	5.03
20	-	-	-	-	-
21	1.53	1.52	1.51	1.53	1.53
22	1.92	1.9	1.89	1.88	1.88
23	1.99	2.0	1.97	1.99	1.99
24	5.00	4.94	4.98	5.00	5.00
25	-	-	-	-	-
26	1.53	1.52	1.52	1.54	1.52
27	1.62	1.60	1.60	1.62	1.61

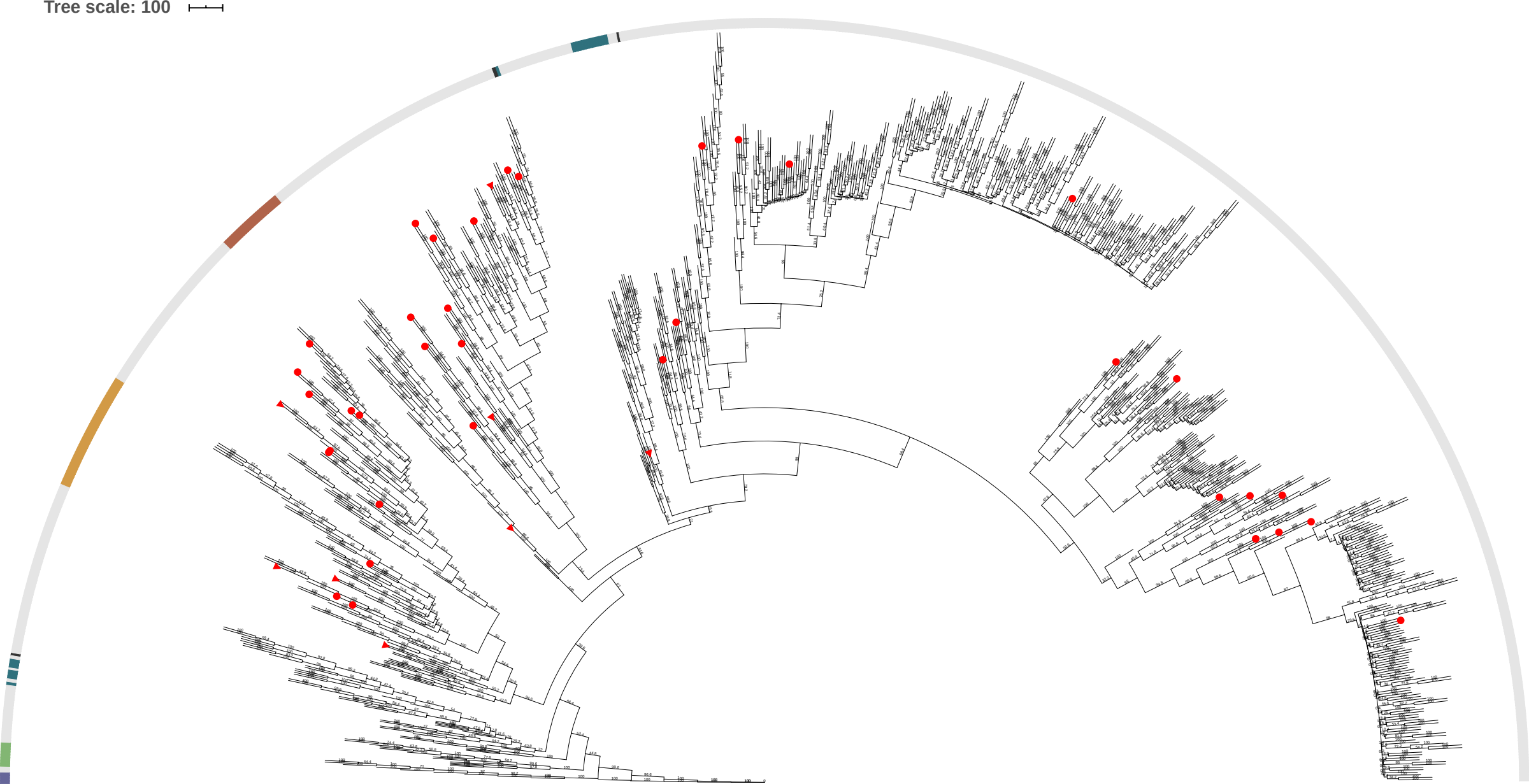
**Fig S6.** <sup>1</sup>H chemical shifts of spectra of MK<sub>8</sub>, 7-MMK<sub>8</sub>, 8-MMK<sub>8</sub>, 5,8-DMMK<sub>8</sub> and 7,8-DMMK<sub>8</sub> calibrated at the <sup>1</sup>H signal of residual protons in CDCl<sub>3</sub> at 7.20 ppm.



	MK <sub>8</sub>	7-MMK <sub>8</sub>	8-MMK <sub>8</sub>	5,8-DMMK <sub>8</sub>	7,8-DMMK <sub>8</sub>
1	185.4	185.7	186.4	188.3	188.3
2	143.3	143.0	143.5	142.8	143.9
3	146.1	146.0	143.6	145.8	145.1
4	184.4	184.4	183.9	187.4	184.7
5	133.6	126.3	124.2	139.1	124.6
6	126.6	133.9	131.4	136.6	134.2
7	126.6	144.0	136.2	136.6	144.2
8	133.6	126.2	139.7	139.1	139.1
9	133.1	132.0	128.9	131.5	130.5
10	133.1	130.2	132.7	136.6	132.0
11	-	21.6	21.8	23.3	21.4
11'	-	-	-	23.3	17.2
12	13.0	12.7	11.9	12.9	13.1
13	26.5	26.8	24.7	25.8	25.6
14	119.6	118.9	118.3	119.9	119.3
15	137.5	137.3	136.3	137.4	137.3
16	17.2	15.8	15.4	16.2	16.4
17	40.1	39.6	38.6	39.7	39.7
18	27.0	26.5	24.5	26.7	26.6
19	124.7	124.2	123.5	124.5	124.2
20	134.7	134.9	133.7	135.1	134.3
21	16.6	15.8	15.1	16.2	16.0
22	39.7	39.6	38.5	39.8	39.7
23	25.8	27.1	24.7	26.9	26.4
24	124.5	124.3	123.3	124.5	124.4
25	131.1	131.1	130.1	131.3	131.2
26	17.6	17.6	16.5	17.9	17.7
27	26.0	24.3	24.7	25.9	25.5

**Fig S7.** <sup>13</sup>C chemical shifts of spectra of MK<sub>8</sub>, 7-MMK<sub>8</sub>, 8-MMK<sub>8</sub>, 5,8-DMMK<sub>8</sub> and 7,8-DMMK<sub>8</sub> calibrated at the <sup>13</sup>C signal of CDCl<sub>3</sub> at 77.20 ppm.

Tree scale: 100



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