Regio- and Stereoselective Synthesis of Coenzymes Q_n (n = 2-10), Vitamin K, and Related Polyprenylquinones[1]

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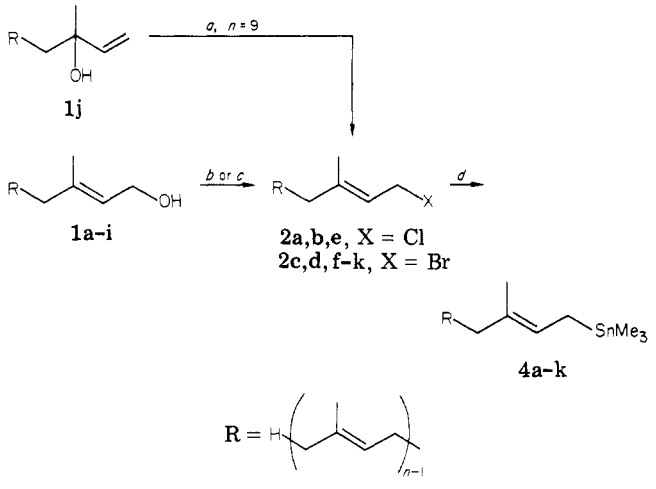
A new synthetic method for coenzyme Q_n (**13**; n = 2-10), vitamins $K_{2(10)}$ (**17a**) and K_1 (**17e**), and related polyprenylquinones is reported. The reaction of (trimethylstannyl)lithium with polyprenyl halides (**2**) regio- and stereoselectively gave the corresponding trimethylpolyprenylstannanes (**4a-k**) which coupled with 2,3-dimethoxy-5-methylbenzoquinone in the presence of BF_3-OEt_2. Mild oxidation of the coupling product gave coenzyme Q_n (isolated yields 25-93%, Table III). This method was similarly extended to the stereoselective synthesis of vitamins K_1 and K_2 and the related polyprenylbenzoquinones.

Polyprenylquinones are distributed ubiquitously in the majority of organisms from bacteria to higher plants and animals. Coenzyme Q_n (ubiquinone-n), vitamin K_1 (phylloquinone), and vitamin $K_{2(n)}$ (menadione-n) are well-known for their physiological and clinical activities:[2] coenzyme Q_n is involved in respiratory and photosynthetic electron-transport systems, and vitamins K_1 and K_2 are involved in normal blood clotting and oxidative phosphorylation. Especially coenzyme Q_{10} is known for its clinical activities.[3]

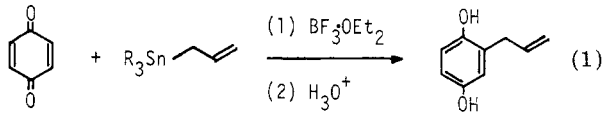
The requisites in the synthesis of these quinones are (a) a high yield based upon the prenyl component, (b) maintenance of all-trans stereochemistry in the polyprenyl chain, and (c) absence of side reactions, such as chromanol formation, side-chain cyclization, etc. Direct polyprenylations by Friedel-Crafts-type coupling have been reported in the synthesis of those quinones.[4,5] Although a lot of modifications of the method have appeared since then,[6] instability of allylic components restricts the wide application of them.[7] Other multistep methods containing organometallic intermediates (e.g., Grignard reagent,[8a] arylcuprate,[8b] and π-allylnickel complex[9]) satisfy all or a part of the above requisites.

Scheme I. Reactions Leading to Trimethylpolyprenylstannanes (4a-k) via Polyprenyl Halides (2a-k)[a]



[a] Compounds: **a**, n = 2; **b**, Δ^2-cis, n = 2; **c**, n = 3; **d**, n = 4; **e**, 6,7,10,11,14,15-hexahydro, n = 4; **f**, n = 5; **g**, n = 6; **h**, n = 7; **i**, n = 8; **j**, n = 9; **k**, n = 10. Reactions: *a*, PBr_3, Et_2O; *b*, MsCl, LiCl, *s*-collidine; *c*, PBr_3, Py; *d*, Me_3SnLi, THF.

We recently reported a preliminary work on the effective allylation of quinone with trialkylallylstannane (eq 1).[10]



(1)

This methodology was extended to the stereoselective synthesis of naturally occurring prenylquinones. The author wishes to report here (a) stereoselective synthesis of trimethylpolyprenylstannanes **4a-k** and (b) a new and effective synthesis of coenzyme Q_n (**13**; n = 2-10), vitamin $K_{2(10)}$ (**17a,b**), vitamin K_1 (**17e**), and other related polyprenylquinones.

Results and Discussion

Stereoselective Synthesis of Trimethylpolyprenylstannanes. The required side chains are obtained from either naturally occurring terpenes [geraniol (C_{10}), nerol (C_{10}), farnesol (C_{15}), phytol (C_{20}), or soranesol (C_{45})] or via the synthetic route shown in Scheme I.

(1) Synthesis of Naturally Occurring Quinones. Part 8. A part of this work has been published in a preliminary form: Naruta, Y.; Maruyama, K. *Chem. Lett.* **1979**, 881, 885. Part 7: see ref 10b.

(2) For reviews of quinones, see: (a) Wolsterholme, G. E. W.; O'Connor, C. M., Eds. "Ciba Foundation Symposium on Quinones in Electron Transport"; J. & E. Churchill: London, 1969; (b) Wagner, A. F.; Folkers, K. "Vitamins and Coenzymes"; Interscience: New York, 1964; (c) Morton, R. A., Ed. "Biochemistry of Quinones"; Academic Press: New York, 1965; (d) Harris, R. S.; Wool, I. G.; Loraine, J. A., Eds. "Vitamins and Hormons"; Academic Press: New York, 1966; Vol. 24; (e) Thomson, R. H. "Naturally Occurring Quinones", 2nd ed.; Academic Press: New York, 1971; (f) McCormick, D. B.; Wright, L. D., Eds. "Methods in Enzymology"; Academic Press: New York, 1971; Vol. 18, Part C, pp 137-562; (g) Morimoto, H.; Imada, I. "Methodicium Chimicum"; Korte, K., Ed.; Georg Thieme Verlag: Stuttgart, 1977; Vol. 11, Part 2, pp 69-145.

(3) (a) Littaru, G. P.; Ho, L.; Folkers, K. *Int. J. Vitam. Nutr. Res.* **1972**, *42*, 291, 413. (b) Yamagami, T.; Shibata, N.; Folkers, K. *Res. Commun. Chem. Pathol. Pharmacol.* **1976**, *14*, 271. (c) Imada, I.; Azuma, I.; Kishimoto, S.; Yamamura, Y.; Morimoto, H. *Int. Arch. Allergy Appl. Immunol.* **1972**, *43*, 898. (d) Heller, J. H. *Perspect. Biol. Med.* **1973**, *16*, 181. (e) Combs, A. B.; Acosta, D.; Folkers, K. *IRCS Med. Sci.: Libr. Compend.* **1976**, *4*, 403.

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(5) Ruegg, R.; Gloor, U.; Goel, R. N.; Ryser, G.; Wiss, O.; Isler, O. *Helv. Chim. Acta* **1959**, *52*, 2616.

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(9) The coupling reaction of protected haloquinols with the π-allylnickel complex was applied to the synthesis of vitamin K and coenzyme Q_n, although the selectivity of trans stereochemistry at the $\Delta^{2'}$ position is incomplete: Inoue, S.; Yamagami, R.; Saito, K. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 3098 and references cited therein.

(10) (a) Maruyama, K.; Naruta, Y. *J. Org. Chem.* **1978**, *43*, 3796. (b) Naruta, Y. *J. Am. Chem. Soc.* **1980**, *102*, 3774.

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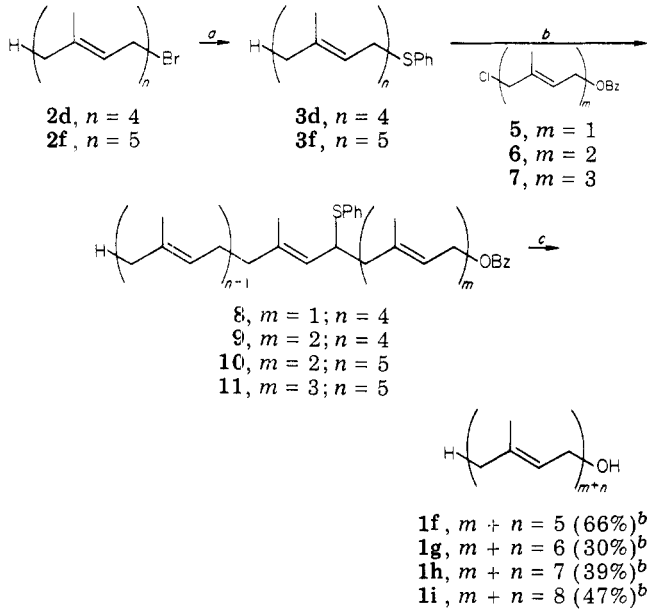
Table I. Synthesis of Trimethylpolyprenylstannanes 4a-k

polyprenyl halide (Δ^2 stereochemistry, trans/cis)[a]	reaction conditions		polyprenylstannane	
	T, °C	t, h	compd (yield,[b] %)	Δ^2 stereochemistry, trans/cis
2a (95/5)	−60 to +15	1.5	**4a** (70)	95/5[c]
2b (5/95)			**4b** (69)	6/94[c]
2c (96/4)			**4c** (59)	*d*
2d (98/2)			**4d** (59)	*d*
2e (100/0)			**4e** (87)	*d*
2f (99/1)	−78 to +15	1.5	**4f** (60)	*d*
2g (99/1)			**4g** (40)	*d*
2h (94/6)	−50 to 0	2.0	**4h** (61)	*d*
2i (89/11)			**4i** (49)	*d*
2j (100/0)			**4j** (92)	*d*
2k (82/18)			**4k** (80)	85/15[e]

[a] Determined by 220-MHz ^{1}H NMR (error ±1%). [b] Isolated yield. [c] Determined by GLC (10% silicon DC-550, 3 mm × 2 m, 180 °C). [d] The isomeric ratio was not precisely determined but was estimated to be trans/cis > 95/5 by NMR analysis. [e] Determined by 100-MHz NMR.

Scheme II. Synthesis of All-Trans Polyprenyl Alcohols (1f-i)[a]



2d, n = 4; **2f**, n = 5

3d, n = 4; **3f**, n = 5

5, m = 1; **6**, m = 2; **7**, m = 3

8, m = 1; n = 4; **9**, m = 2; n = 4; **10**, m = 2; n = 5; **11**, m = 3; n = 5

1f, $m + n$ = 5 (66%)[b]; **1g**, $m + n$ = 6 (30%)[b]; **1h**, $m + n$ = 7 (39%)[b]; **1i**, $m + n$ = 8 (47%)[b]

[a] *a*, PhSLi, THF; *b*, *n*-BuLi, THF; *c*, Li, $EtNH_2$. [b] Overall yield from **2**.

To synthesize all-trans polyprenyl alcohols **1f** (n = 5) through **1i** (n = 8), the elongation method of a polyprenyl chain employed by Altman et al.[11] was most applicable. All-trans geranylgeraniol (**1d**; n = 4) was chosen as the common starting material. The second component to be coupled with it was *trans*-4-chloro-3-methyl-2-butenyl benzyl ether (**5**; m = 1) and its higher homologues **6** and **7**. According to Scheme II, the repeated use of the coupling reaction provided pentaprenyl (**1f**) through octaprenyl (**1i**) alcohols.

In order to attain the stereoselective synthesis of all-trans polyprenylquinones, one should prepare all-trans polyprenylstannanes. For the establishment of regio- and stereoselective stannylation of polyprenyl halides, geranyl and neryl systems were examined.[12] Geranyl chloride (**2a**; isomeric purity 95% trans) was added to a THF solution of (trimethylstannyl)lithium at −78 °C, and then the reaction temperature was allowed to warm to room temperature. The stereochemistry at the Δ^2 position of the obtained geranyltrimethylstannane (**4a**) was estimated to be 95/5 trans/cis by GLC analysis. The cis isomer (**2b**; isomeric purity 95% cis) was also stannylated with perfect retention of the Δ^2 stereochemistry according to the above method. These coupling reactions consequently proceed via an S_N2 mechanism with retention of stereochemistry in moderate to high yields (40–92%). The other polyprenylstannanes, **4c–k**, were prepared from the corresponding halides as depicted in Scheme I. The stannylation of the higher homologues, **4h–k**, was performed at −50 °C to room temperature, because of their low solubility in THF below −55 °C. The results are summarized in Table I.

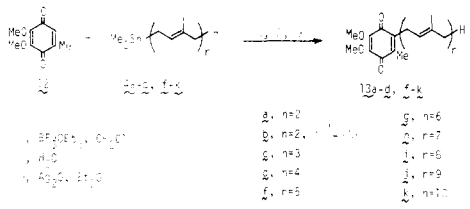
Table II. Synthesis of Coenzymes Q_{2-10} (13a-d,f-k)

polyprenylstannane (equiv)[e]	coenzyme Q_n	yield,[a] %	stereochemistry at $\Delta^{2'}$, trans/cis[b]
4a (1.2)	**13a** (Q_2)	90 (65)	>99/1
4b (1.2)	**13b** (cis Q_2)	79 (70)	12/88
4c (1.2)	**13c** (Q_3)	100 (93)	99/1
4d (1.2)	**13d** (Q_4)	88 (70)	99/1
4f (1.2)	**13f** (Q_5)	100 (94)	99/1
4g (1.2)	**13g** (Q_6)	60 (59)[d]	98/2
4h (1.2)	**13h** (Q_7)	(40)[d]	99/1
4i (0.85)	**13i** (Q_8)	(25)[c,d]	98/2
4j (0.85)	**13j** (Q_9)	(51)[c,d]	100/0
4k (0.85)	**13k** (Q_{10})	51 (51)[c,d]	86/14

[a] Yields in parentheses are of purified product after isolation based on quinone. All others are determined by ^{1}H NMR. [b] Determined by high-performance LC. [c] Yield based on polyprenylstannane. [d] Corresponding amount of the starting quinone was recovered. [e] Equivalents of polyprenylstannane per equivalent of **12**.

Synthesis of Polyprenylquinones. In the previous paper,[10] BF_3·OEt_2 (1 equiv to 1 equiv of the quinone) catalyzed allylation of quinones was reported, and coenzyme Q_1 was prepared in a high yield without any appreciable side reactions. This methodology was extended to the synthesis of the coenzyme Q_n (n = 2–10) series (eq 2). However, use of the reported conditions[10] in the reaction of 2,3-dimethoxy-5-methylbenzoquinone (**12**) with geranyltrimethylstannane (**4a**) was less suitable because of formation of a certain amount of unidentified side products; the yield was consequently suppressed. Use of an excess amount of BF_3·OEt_2 (3 equiv to 1 equiv of the

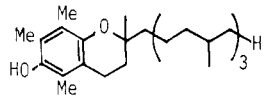
(11) Altman, L. J.; Ash, L.; Marson, S. *Synthesis* **1974**, 129.
(12) Stannylation of 2-butenyl chloride with stannyllithium has been reported to proceed with retention of the stereochemistry at the Δ^2 position.[13] This is the first example of allylic stannylation of trisubstituted olefins.
(13) Matarasso-Tchiroukhine, E.; Cadiot, P. *J. Organomet. Chem.* **1976**, *121*, 155.



(2)

quinone) and a lower reaction temperature (−78 to −60 °C) improved the yield (90%) without any undesirable side reactions. Each of the *cis*- and *trans*-coenzymes Q_2 can be assigned by the ^1H NMR chemical shifts (δ 1.71 and 1.76, respectively)[14] of the 3′-CH_3 and analyzed quantitatively by high-performance LC. The isomeric purity of **13a** at the $\Delta^{2'}$ position was determined to be >99/1 trans/cis. Starting with **4b** we obtained similarly *cis*-coenzyme Q_2 (**13b**) in 79% yield with retention of the original cis configuration (94%) at the $\Delta^{2'}$ position. Good to excellent yields of all-trans coenzymes Q_{3-10} (**13c–k**) were obtained by this simple manipulation. The results are summarized in Table II. A slight increase in trans ratio at the $\Delta^{2'}$ position in isolated coenzyme Q_n (n = 2–10) compared with those of the corresponding polyprenylstannanes was noticeable. The results indicate a preponderance of this method to fulfill the requisites for the synthesis of naturally occurring quinones.

Some other related quinones, plastquinone-2 (**14**), vitamin $K_{2(10)}$ (**17a**), and vitamin K_1 (**17e**), were successfully prepared in a similar fashion from the corresponding quinone (Table III). Trimethylbenzoquinone was converted to trimethylphytylbenzoquinone (**15**) (76%) without any formation of α-tocopherol (**16**). The latter is usually



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a major product in Lewis acid catalyzed prenylation of trimethylhydroquinone with phytol.[15] The reaction of 2-methyl-1,4-naphthoquinone with **4a**, **4b**, and **4e** and successive oxidation gave vitamin $K_{2(10)}$ (**17a**), *cis*-vitamin $K_{2(10)}$ (**17b**), and vitamin K_1 (**17e**), respectively. They were each accompanied with the corresponding regioisomers, **18a,b,e**.

Conclusively, the method described here opens the highly selective synthetic route to isoprenoid quinones by direct isoprenylation of mother quinones.

Experimental Section

All melting points are uncorrected. Infrared spectra were measured with JASCO-Al spectrometer. Nuclear magnetic resonance spectra were measured with a JEOL PS-100 or a Varian HA-220 NMR spectrometer with Me_4Si as internal standard. Mass spectra were measured with Hitachi M-52 mass spectrometer (20 eV). High-performance LC analysis was performed by using a Waters Model ALC 204 equipped with a silica gel column (8–10 μm, 4 mm × 30 cm and/or 7.9 mm × 30 cm). Preparative layer chromatography was performed by using Merck silica gel 60 plate F_{254}. Microanalyses were performed by Kyoto University Microanalysis Center.

Materials. Dichloromethane was distilled from calcium hydride and stored under a nitrogen atmosphere. THF and Et_2O were distilled from benzophenone ketyl and stored under a nitrogen atmosphere. Trimethylbenzoquinone was prepared by oxidation of trimethylhydroquinone. Other quinones were commercially available and purified by sublimation. Geraniol, nerol, farnesol, geranylgeraniol, and solanesol were commercially available and used without further purification. Isodecaprenol was prepared by the method of Isler.[5]

Geranyl Chloride (2a). Geranyl chloride was prepared from geraniol (**1a**, 95% trans) as reported.[16] The crude product was purified by distillation [60–62 °C (2 mm), lit.[17] 47–49 °C (0.4 mm)] to yield pure **2a** (84%, 95% Δ^2-trans by NMR): NMR (CCl_4) δ 1.60 (s, 3 H, terminal *trans*-CH_3), 1.68 (s, 3 H, terminal *cis*-CH_3), 1.73 (s, 3 H, *trans*-CH_3), 2.06 (br, 4 H, CH_2CH_2), 4.00 (d, 2 H, J = 8 Hz, $ClCH_2$), 5.04 (br, 1 H, CH=C), 5.40 (t, 1 H, J = 8 Hz, $ClCH_2CH$=).

Neryl Chloride (2b). Neryl chloride was prepared from nerol (95% cis) as reported.[16] The crude product was purified by distillation [81 °C (5 mm)] to give **2b** (86%, 95% Δ^2-cis by NMR): NMR (CCl_4) δ 1.60 (s, 3 H, terminal *trans*-CH_3), 1.68 (s, 3 H, terminal *cis*-CH_3), 1.77 (s, 3 H, *cis*-CH_3), 2.10 (m, 4 H, CH_2CH_2), 3.98 (d, 2 H, J = 8 Hz, $ClCH_2$), 5.04 (br, 1 H, CH=C), 5.36 (t, 1 H, J = 8 Hz, $ClCH_2CH$=C).

Phytyl Chloride (2e). Phytyl chloride was prepared from phytol (100% trans) as reported.[16] The crude product was purified by distillation [122–124 °C (0.03 mm)] to give pure **2e** (78%, 100% Δ^2-trans by NMR): NMR (CCl_4) δ 0.86 (d, 12 H, J = 7 Hz, 4 CH_3), 1.23 (m, 19 H, CH and CH_2), 1.71 (d, 3 H, J = 1 Hz, *trans*-CH_3), 2.00 (t, 2 H, J = 7 Hz, $CH_2(CH_3)C$=CH), 4.07 (d, 2 H, J = 8 Hz, CH_2Cl), 5.42 (t, 1 H, J = 8 Hz).

Polyprenyl Bromides (2c,d,f–k). The polyprenyl bromides **2c,d,f–i** were prepared from the corresponding polyprenyl alcohols (**1c,d,f–i**) according to the method of Isler.[18] Soranesyl bromide (**2j**) and decaprenyl bromide (**2k**) were prepared as reported.[5] The isomeric purity at the Δ^2 position was determined from the areas of two singlet peaks (δ 1.71–1.75, *trans*-CH_3; δ 1.63–1.68, *cis*-CH_3) by 220-MHz NMR. Yields and spectroscopic data are listed in Table IV.

Synthesis of Polyprenyl Alcohols. Polyprenyl alcohols **1f–i** were prepared by the method of Altman et al.[11]

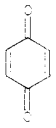
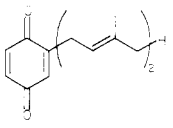
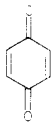
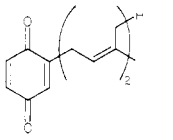
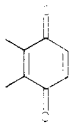
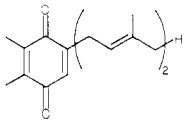
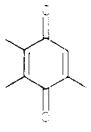
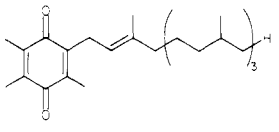
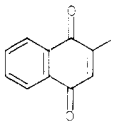
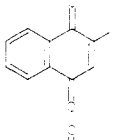
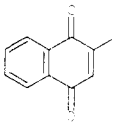
General Procedure. Polyprenyl Phenyl Thioethers 3d,f. To a THF solution (200 mL) of lithium thiophenoxide (40.5 mmol) was added polyprenyl halide (**2**, 40.5 mmol) slowly at 0 °C, and the solution was stirred for 8 h at room temperature. Addition of water was followed by extraction with three portions of hexane. The combined organic phase was washed with saturated sodium hydrogen carbonate solution and brine, dried over magnesium sulfate, and evaporated under reduced pressure to afford crude product. Chromatographic purification was accomplished by using silica gel and dichloromethane as eluent.

Biellmann Coupling. A THF solution (150 mL) of polyprenyl phenyl thioether (21 mmol) was treated with n-BuLi (21 mmol) at −78 °C, resulting in a yellow solution. After 3 h, the allyl chloride (**5–7**, 16.3 mmol) in THF (20 mL) was added, and the solution was stirred for an additional 1.5 h. The system was quenched at −78 °C with methanol (6 mL) and the solution allowed to warm to room temperature. The solution was treated with water and partitioned with ether. The aqueous phase was extracted twice with ether, and then the combined organic phase was washed with water and brine, dried over magnesium sulfate, filtered, and evaporated under reduced pressure. Chromatography on silica gel utilizing dichloromethane as eluent afforded pure coupled product (**8–11**).

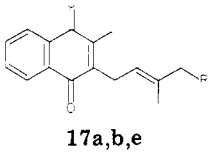
Polyprenyl Alcohols 1f–i. To dry ethylamine (100 g) at −78 °C was added lithium wire (with 1% sodium, 1.058 g). The reaction temperature was brought to 0 °C for 1.25 h to ensure dissolution and then decreased to −78 °C whereupon the coupled product (**8–11**, 5.0 mmol) in THF (50 mL) was added slowly and the resulting solution allowed to stir an additional 1.5 h. With the temperature maintained at −78 °C, isoprene was added until the blue color disappeared, and the resulting solution was then quenched with methanol until colorless. After the mixture warmed to room temperature, water was added until all the solids dissolved, and the volatiles were carefully evaporated under reduced pressure. The resulting solution was extracted four times with

(14) The configuration at the $\Delta^{2'}$ position was assigned to be cis (δ 1.67–1.70) and trans (δ 1.75–1.77) by 3′-CH_3 absorption; cf. ref 2d, p 371.
(15) See ref 2f, pp 241–403.
(16) Collington, E. W.; Meyers, A. I. *J. Org. Chem.* **1971**, *36*, 3044.
(17) Calzada, J. G.; Hooz, J. *Org. Synth.* **1974**, *54*, 63.
(18) Isler, O.; Ruegg, R.; Chopard-dit-Jean, L.; Wagner, H.; Bernhard, K. *Helv. Chim. Acta* **1956**, *39*, 897.

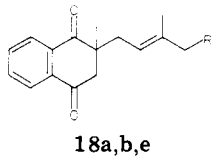
Table III. Synthesis of Polyprenylbenzoquinones and Vitamins K_1 and K_2 [a]

quinone	polyprenylstannane[f]	product[g]	yield,[b] %	stereochemistry at $\Delta^{2'}$, trans/cis[d]
	4a		73 (58)	98/2
	4b		74 (73)	23/77
	4a		(23)[c]	95/5
		14 (plastoquinone-2)		
	4e		(76)	95/5
		15		
	4a	17a (vitamin $K_{2(10)}$) 18a	46 (30)[c] (trace)[c]	95/5 *e*
	4b	17b 18b	(41)[c] (13)[c]	24/76 *e*
	4e	17e (vitamin K_1) 18e	(48) (14)	96/4 *e*

[a] The reactions were performed under the same conditions as those described in Table II. [b] Yields in parentheses are of purified products after isolation based on the amount of the quinone. All others are determined by ^1H NMR spectroscopy using *cis*-1,2-dichloroethylene as an internal standard. [c] The corresponding amount of the starting quinone was recovered. [d] Determined by high-performance LC. [e] Not determined. [f] 1.2 equiv/equiv of quinone in each case. [g] The structures of **17** and **18** are as follows:



17a,b,e



18a,b,e

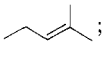
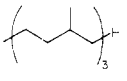
a, R =  ; b, $\Delta^{2'}$-*cis*, R =  ; e, R = 

Table IV. Synthesis of Polyprenyl Bromides 2c-d,f-k

halide	yield,[a] %	stereochemistry at Δ^2, trans/cis[b]	NMR (CCl_4),[c] δ *trans*-CH_3	terminal *cis*-CH_3	3-*trans*-CH_3	CH_2CH_2	$BrCH_2$	CH=C	$BrCH_2CH$
2c	99	96/4	1.58	1.65	1.72	2.07 (m)	3.91 (d, J = 8)	5.05 (br)	5.48 (t, J = 8)
2d	97	98/2	1.59	1.63	1.72	2.00 (m)	3.90 (d, J = 8)	5.04 (br)	5.48 (t, J = 8)
2f	93	99/1	1.55	1.63	1.71	1.95 (m)	3.88 (d, J = 8)	5.06 (br)	5.45 (t, J = 8)
2g	98	97/3	1.59	1.65	1.73	2.00 (m)	3.95 (d, J = 8)	5.11 (br)	5.53 (t, J = 8)
2h	90	94/6	1.58	1.67	1.75	1.99 (m)	3.92 (d, J = 8)	5.09 (br)	5.53 (t, J = 8)
2i	90	89/1	1.59	1.67	1.74	1.99 (m)	3.93 (d, J = 8)	5.07 (br)	5.52 (t, J = 8)
2j	86	100/0	1.60	1.67	1.73	2.04 (m)	4.01 (d, J = 8)	5.11 (br)	5.52 (t, J = 8)
2k	100	85/15	1.61	1.68	1.72	2.02 (m)	3.99 (d, J = 8)	5.10 (br)	5.52 (t, J = 8)

[a] Isolated yield. [b] Determined by 220-MHz NMR. [c] J values are given in hertz.

ether, and the combined organic layer was washed with water and brine, dried over magnesium sulfate, filtered, and evaporated under reduced pressure affording an oil. Chromatography on silica gel with 40% ether in hexane as eluent afforded the desired alcohol (**1f–i**). The obtained polyprenyl alcohol was contaminated (<5%) by one other component which was presumed to be the product from conjugate reduction of the phenyl thioether moiety (NMR analysis of the product showed aliphatic Me absorption at δ ~0.9 (d)).

Synthesis of 3,7,11,15,19-Pentamethyleicosa-2,6,10,14,18-pentaenol (1f). Step 1. Geranylgeranyl Phenyl Thioether (3d). To a THF solution (200 mL) of lithium thiophenoxide (40.5 mmol) was added **2d** (14.3 g, 40.5 mmol) slowly at 0 to −10 °C, and the solution was stirred for 8 h at room temperature. After the usual workup the resulting crude product was chromatographed on silica gel and afforded a pure product (**3d**): 13.2 g (85%); NMR (CCl_4) δ 1.57 (s, 12 H), 1.65 (s, 3 H), 1.99 (br, 12 H), 3.43 (d, 2 H, J = 7 Hz), 4.99 (br, 3 H), 5.20 (t, 1 H, J = 7 Hz), 7.0–7.4 (m, 6 H).

Step 2. 3,7,11,15,19-Pentamethyl-5-(phenylthio)eicosa-2,6,10,14,18-pentaenyl Benzyl Ether (8). A THF solution (150 mL) of **3d** (7.85 g, 21 mmol) was treated with *n*-BuLi (21 mmol) at −78 °C. After 3 h 4-chloro-3-methyl-2-butenyl benzyl ether[19] (**5**; 3.59 g, 16.3 mmol) in THF (20 mL) was added, and the solution was stirred for an additional 1.5 h. After the mixture was quenched with methanol at −78 °C, the reaction mixture was worked up as usual. Chromatography on silica gel afforded **8**: 15.0 mmol (92%); NMR (CCl_4) δ 1.34 (s, 3 H, CH_3), 1.57 (s, 12 H, CH_3), 1.64 (s, 3 H, CH_3), 1.80–2.50 (m, 14 H, CH_2), 3.90 (m, 3 H, C**H**SPh and =CHC**H**$_2$O), 4.36 (s, 2 H, OC**H**$_2$Ph), 5.02 (br, 4 H), 5.34 (t, 1 H, J = 6 Hz, =C**H**CH$_2$O), 7.0–7.5 (m, 10 H).

Step 3. 3,7,11,15,19-Pentamethyleicosa-2,6,10,14,18-pentaenol (1f). To an ethylamine solution (100 g) of lithium (with 1% sodium, 1.058 g) was added the coupling product (**8**; 2.775 g, 5.0 mmol) in THF (50 mL) at −78 °C, and the resulting solution was allowed to stir an additional 1.5 h at −78 °C. After addition of isoprene (the blue color disappeared), the resulting solution was quenched with methanol followed by the usual workup. Chromatography of the crude product on silica gel afforded **1f**: 1.55 g (87%); 94% Δ^2-trans by high-performance LC (0.5% 2-propanol–hexane); NMR (CCl_4) δ 1.56 (s, 12 H, *trans*-CH_3), 1.64 (s, 6 H, terminal *cis*-CH_3 and 3-*trans*-CH_3), 1.80–2.30 (m, 16 H, CH_2), 3.99 (d, 2 H, J = 6 Hz, OCH_2), 5.02 (m, 4 H), 5.30 (t, 1 H, J = 6 Hz); IR (neat) 3320 (s), 2925 (vs), 1670 (w), 1450 (s), 1390 (s), 1105 cm^{-1} (s).

Anal. Calcd for $C_{25}H_{42}O$: C, 83.73; H, 11.81. Found: C, 83.97; H, 11.06.

Synthesis of 3,7,11,15,19,23-Hexamethyltetracosa-2,6,10,14,18,22-hexaenol (1g). Step 1. 3,7,11,15,19,23-Hexamethyl-9-(phenylthio)tetracosa-2,6,10,14,18,22-hexamethyl Benzyl Ether (9). A THF solution (150 mL) of **3d** (7.85 g, 21 mmol) was treated with *n*-BuLi (21 mmol) at −78 °C. After 3 h, 8-chloro-3,7-dimethyl-2,6-octadienyl benzyl ether[11] (**6**; 4.54 g, 16.3 mmol) in THF (20 mL) was added, and the solution was stirred for an additional 1.5 h at −78 °C. After the usual workup chromatography of the crude product on silica gel afforded **9**: 4.20 g (41%); NMR (CCl_4) δ 1.32 (s, 3 H, CH_3), 1.57 (s, 15 H, CH_3), 1.64 (s, 3 H, CH_3), 1.80–2.38 (m, 18 H, CH_2), 3.89 (m, 3 H, C**H**SPh and =CHC**H**$_2$O), 4.36 (s, 2 H, OC**H**$_2$Ph), 4.98 (br, 5 H), 5.28 (t, 2 H, J = 6 Hz), 7.00–7.40 (m, 10 H).

Step 2. Synthesis of 1g. To an ethylamine solution (50 mL) of lithium (with 1% sodium, 1.587 g) was added the coupling product (**9**; 3.70 g, 5.94 mmol) in THF (75 mL) at −78 °C, and the resulting solution was allowed to stir an additional 2 h at −78 °C. After addition of isoprene, the resulting solution was quenched with methanol followed by the usual workup. Chromatography of the crude product on silica gel afforded **1g**: 2.26 g (89%); 94% Δ^2-trans by high-performance LC (0.5% 2-propanol–hexane); NMR (CCl_4) δ 1.58 (s, 15 H, CH_3), 1.64 (s, 6 H, terminal CH_3 and 3-*trans*-CH_3), 1.80–2.30 (m, 20 H, CH_2), 3.99 (d, 2 H, J = 6 Hz, CH_2O), 5.04 (m, 5 H), 5.32 (t, 1 H, J = 6 Hz); IR (neat) 3320 (vs), 2920 (vs), 1450 (vs), 1390 (vs), 1105 (s), 1100 cm^{-1} (vs).

Anal. Calcd for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found: C, 84.14; H, 11.98.

Synthesis of 3,7,11,15,19,23,27-Heptamethyloctacosa-2,6,10,14,18,22,26-heptaenol (1h). Step 1. 3,7,11,15,19-Pentamethyleicosa-2,6,10,14,18-pentaenyl Phenyl Thioether (3f). To a THF solution (30 mL) of lithium thiophenoxide (9.35 mmol) was added **2f** (3.21 g, 7.61 mmol) in THF (5 mL) at 0 to −10 °C, and the solution was stirred for 2 h at room temperature. After the usual workup the crude product was chromatographed on silica gel and afforded a pure product (**3f**): 2.81 g (82%); NMR (CCl_4) δ 1.58 (s, 12 H, CH_3), 1.64 (s, 6 H, CH_3), 1.98 (br, 16 H, CH_2), 3.44 (d, 2 H, J = 8 Hz, CH_2S), 5.02 (br, 4 H), 5.24 (t, 1 H, J = 8 Hz), 7.00–7.33 (m, 5 H).

Step 2. 3,7,11,15,19,23,27-Heptamethyl-9-(phenylthio)octacosa-2,6,10,14,18,22,26-heptaenyl Benzyl Ether (10). A THF solution (40 mL) of **3d** (2.78 g, 6.18 mmol) was treated with *n*-BuLi (6.18 mmol) at −78 °C. After 3 h, **6** (1.721 g, 6.18 mmol) in THF (8 mL) was added, and the solution was stirred for an additional 1.5 h at −78 °C. After the usual workup chromatography of the crude product on silica gel afforded **10**: 2.23 g (57%); NMR (CCl_4) δ 1.30 (s, 3 H, CH_3), 1.55 (s, 18 H, CH_3), 1.62 (s, 3 H, CH_3), 1.80–2.30 (m, 22 H, CH_2), 3.84 (m, 3 H), 4.31 (s, 2 H), 4.95 (br, 6 H), 5.23 (t, 1 H, J = 8 Hz), 7.00–7.30 (m, 10 H).

Step 3. Synthesis of 1h. To an ethylamine solution (30 mL) of lithium (with 1% sodium, 0.88 g) was added coupling product **10** (2.19 g, 3.17 mmol) in THF (5 mL) at −78 °C, and the resulting solution was allowed to stir an additional 2 h at −78 °C. After addition of isoprene, the resulting solution was quenched with methanol followed by the usual workup. Chromatography of the crude product on silica gel afforded **1h**: 1.33 g (83%); NMR (CCl_4) δ 1.59 (s, 18 H, CH_3), 1.66 (s, 6 H, CH_3), 1.8–2.3 (br, 24 H, CH_2), 4.02 (d, 2 H, J = 8 Hz, CH_2O), 5.06 (br, 6 H), 5.34 (t, 1 H, J = 8 Hz); IR (neat) 3300 (s), 2900 (vs), 1660 (m), 1435 (s), 1380 (s), 1100 (m), 995 cm^{-1} (s).

Anal. Calcd for $C_{35}H_{58}O$: C, 84.95; H, 11.82. Found: C, 85.16; H, 11.91.

Synthesis of 3,7,11,15,19,23,27,31-Octamethyldotriaconta-2,6,10,14,18,22,26,30-octaenol (1i). Step 1. 12-Chloro-3,7,11-trimethyldodeca-2,6,10-trienyl Benzyl Ether (7). To an ethanol solution (95%, 10 mL) of farnesyl benzyl ether (6.24 g, 20 mmol) was added selenium dioxide (1.17 g, 10 mmol) in ethanol (30 mL) dropwise within 1 h at 50–60 °C, and the solution was refluxed for additional 1.5 h. After removal of precipitated selenium, the solution was concentrated, and chromatography of the crude product on silica gel afforded the starting ether (2.0 g, 32%) and 12-hydroxyfarnesyl benzyl ether: 1.70 g (26%); NMR (CCl_4) δ 1.60 (s, 9 H, CH_3), 2.04 (br, 8 H, CH_2), 3.82 (s, 2 H, HOC**H**$_2$C=), 3.92 (d, 2 H, J = 7 Hz, =CHC**H**$_2$O), 4.20 (s, 2 H, C**H**$_2$Ph), 5.09 (br, 1 H), 5.30 (br, 2 H), 7.24 (m, 5 H); IR (neat) 3400 (s), 2920 (s), 2850 (s), 1665 (w), 1450 (vs), 1385 (s), 1070 (vs), 785 (s), 735 (s), 695 cm^{-1} (s).

By use of the reported method,[16] the obtained alcohol (1.37 g, 4.18 mmol) was chlorinated. Chromatographic purification on silica gel utilizing CH_2Cl_2 as eluent provided the desired chloride (**7**): 1.19 g (82%); NMR (CCl_4) δ 1.62 (s, 6 H, CH_3), 1.72 (s, 3 H, CH_3), 2.06 (br, 8 H, CH_2), 3.92 (s, 2 H, $ClCH_2$), 3.94 (d, 2 H, J = 7 Hz, C**H**$_2$OBz), 4.21 (s, 2 H, C**H**$_2$OPh), 5.08 (br, 1 H), 5.34 (t, 1 H, J = 7 Hz), 5.24 (br, 1 H), 7.24 (m, 5 H); IR (neat) 2910 (vs), 2840 (vs), 1660 (m), 1450 (vs), 1380 (m), 1360 (m), 1260 (vs), 1030 (vs), 1025 (s), 730 cm^{-1} (vs).

Step 2. 3,7,11,15,19,23,27,31-Octamethyl-9-(phenylthio)-octacosa-2,6,10,14,18,22,26-heptaenyl Benzyl Ether (11). A THF solution (30 mL) of **3f** (1.836 g, 4.08 mmol) was treated with *n*-BuLi (4.08 mmol) at −78 °C. After 3 h, **7** (1.16 g, 3.35 mmol) in THF (5 mL) was slowly added within 30 min, and the resulting solution was stirred for an additional 3 h at −78 °C. After the usual workup separation of the crude product by high-performance LC (silica gel, eluent 3% ether–hexane) afforded recovered **3f** (0.73 g, 1.62 mmol), recovered **7** (0.39 g, 1.13 mmol), and the coupling product (**11**): 1.07 g (32%); NMR (CCl_4) δ 1.32 (s, 3 H, CH_3), 1.59 (s, 21 H, CH_3), 1.64 (s, 3 H, CH_3), 1.80–2.40 (br, 26 H, CH_2), 3.93 (d, 2 H, J = 7 Hz), 4.40 (s, 2 H, C**H**$_2$Ph), 4.84–5.20 (br, 7 H), 5.32 (t, 1 H, =C**H**CH$_2$O), 7.24 (m, 10 H); IR (neat) 2900 (s), 2840 (s), 1660 (m), 1580 (m), 1450 and 1435 (vs), 1380 (s), 1190 and 1170

(19) Preparation of 4-chloro-3-methyl-2-butenyl benzyl ether was performed as follows. Prenyl benzyl ether was treated with SeO_2 in 95% EtOH as described,[11] and 4-hydroxy-3-methyl-2-butenyl benzyl ether was obtained in good yield. The obtained alcohol was chlorinated as reported[16] quantitatively to afford the desired chloride **5**.

Table V. Spectroscopic Properties of Trimethylpolyprenylstannanes 4a-k

compd	NMR (CCl_4),[d] δ	IR, cm^{-1}
4a[a,b]	0.06 (9 H, $J_{^{117}Sn-H}$ = 51, $J_{^{119}Sn-H}$ = 55, $(CH_3)_3Sn$), 1.51 (s, 3 H, Δ^2-*trans*-CH_3), 1.62 and 1.66 (each br s, 8 H, terminal CH_2 and CH_2Sn), 1.97 (m, 4 H, CH_2CH_2), 5.00 (br, 1 H), 5.24 (t, 1 H, $=CHCH_2Sn$, J = 8)	2960, 2900, 1645, 1440, 1375, 1115, 755
4b[a,c]	0.06 (9 H, J = 51, 54), 1.62 and 1.69 (each s, 11 H), 1.98 (m, 4 H), 5.09 (m, 1 H), 5.24 (t, 1 H, J = 7)	2960, 2900, 1445, 1370, 1185, 1105, 750
4c	0.06 (9 H, J = 50, 52), 1.52 (s, 3 H), 1.58 and 1.66 (each s, 11 H), 1.98 (m, 8 H), 5.04 (br, 2 H), 5.26 (t, 1 H, J = 9)	2980, 2925, 2860, 1450, 1390, 1120, 765
4d	0.06 (9 H, J = 50, 52), 1.52 (s, 3 H), 1.56 and 1.59 (each s, 14 H), 1.96 (br, 12 H), 5.02 (m, 3 H), 5.23 (t, 1 H, J = 9 Hz)	2970, 2920, 1445, 1385, 1120, 760
4e	0.07 (9 H, J = 50, 52), 0.88 (d, 12 H, J = 7, CH_3CH), 1.21 (m, 19 H, CH_2 and CH), 1.52 (s, 3 H), 1.64 (d, 2 H, J = 8, CH_2Sn), 1.93 (t, 2 H, J = 7, $CH_2(CH_3)C=C$), 5.24 (t, 1 H, J = 8)	2920, 1445, 1370, 1120, 760
4f	0.06 (9 H, J = 50, 53), 1.52 (s, 3 H), 1.56 and 1.65 (each s, 17 H), 1.80-2.30 (br, 16 H), 4.90-5.40 (m, 5 H)	2920, 1660, 1450, 1380, 1120, 760
4g	0.06 (9 H, J = 49.5, 51.5), 1.52 (s, 3 H), 1.58 and 1.65 (each s, 20 H), 1.80-2.30 (br, 20 H), 4.85-5.20 (m, 6 H)	2925, 2830, 1660, 1450, 1390, 1115, 765
4h	0.06 (9 H, J = 49, 51), 1.51 (s, 3 H), 1.56 and 1.63 (each s, 23 H), 1.80-2.30 (br, 24 H), 4.85-5.30 (br, 7 H)	2920, 1660, 1450, 1390, 1115, 765
4i	0.06 (9 H, J = 47, 50), 1.52 (s, 3 H), 1.60 and 1.66 (each s, 26 H), 1.80-2.30 (br, 28 H), 4.80-5.20 (br, 8 H)	2980, 2940, 1460, 1400, 1120, 780
4j	0.08 (9 H, J = 50, 52), 1.52 (s, 3 H), 1.62 and 1.68 (each s, 29 H), 1.80-2.30 (br, 32 H), 5.00-5.40 (br, 9 H)	2970, 2930, 2860, 1670, 1450, 1390, 1105, 765
4k	0.06 (9 H, J = 53, 57), 1.51 (s, 3 H), 1.61 and 1.66 (each s, 32 H), 1.80-2.30 (br, 36 H), 4.90-5.20 (br, 10 H)	2970, 2930, 2860, 1670, 1390, 1105, 765

[a] Satisfactory analytical data (±0.3% for C, H) were obtained. [b] Bp 105-107 °C (1 mm). [c] Bp 103-104 °C (2.5 mm). [d] J values are given in hertz.

(s), 1025 (s), 745 and 730 (s), 690 cm^{-1} (vs).

Step 3. Synthesis of 1i. To an ethylamine solution (25 mL) of lithium (with 1% sodium, 0.50 g) was added the coupling product **11** (1.04 g, 1.36 mmol) in THF (20 mL) at -78 °C, and the resulting solution was allowed to stir an additional 15 min at -78 °C. After addition of isoprene, the resulting solution was quenched with methanol followed by the usual workup. Chromatography of the crude product on silica gel afforded **1i**: 0.75 g (97%); NMR (CCl_4) δ 1.60 (s, 21 H, CH_3), 1.67 (s, 6 H, CH_3), 1.85-2.30 (br, 28 H, CH_2), 4.04 (d, 2 H, J = 6 Hz, CH_2OH), 4.92-5.20 (br, 7 H), 5.36 (t, 1 H, J = 6 Hz, $=CHCH_2OH$); IR (neat) 3300 (s), 2910 (vs), 1660 (m), 1440 (vs), 1380 (vs), 1000 (s), 830 cm^{-1} (m).

Anal. Calcd for $C_{40}H_{66}O$: C, 85.34; H, 11.82. Found: C, 85.47; H, 11.77.

Trimethylpolyprenylstannanes 4a-k (Table I). General Procedure. To a THF solution of (trimethylstannyl)lithium[13] was slowly added polyprenyl halide at -78 to -60 °C, and then the reaction mixture was allowed to warm to room temperature. Stannylation of halides **2i-k** was performed at -60 to -50 °C. The solution was cooled again below -20 °C, and cold saturated NaCl solution was added. The resulting mixture was partitioned between ether and saturated NaCl solution, the aqueous phase was washed with ether, and the combined organic extracts were washed with water and with saturated NaCl solution. After the ether layer was dried over anhydrous $MgSO_4$ and the solvent removed, NMR analysis of the residue showed it to be satisfactorily pure. Geranyl- (**4a**) and neryltrimethylstannane (**4b**) were purified by distillation in vacuo. Farnesyltrimethylstannane (**4c**) and higher homologues decomposed in the course of distillation even under high vacuum (0.01 mm) owing to their thermal instability. Purification by column chromatography on silica gel or Florisil also resulted in partial decomposition. Thus **4c-k** were used in the coupling reaction with quinone without further purification. The spectroscopic data of the polyprenylstannanes are summarized in Table V.

The configuration at the Δ^2 position was generally assigned to be trans by use of the 3-methyl absorption (δ 1.51-1.52) in the NMR, and the isomeric purity was determined by integration of the corresponding signal. The isomeric purity of **4a** and **4b** was determined by GLC analysis (10% silicon DC-550, 3 mm × 2 m, 180 °C).

General Reaction Procedure of Quinone with Polyprenylstannane. To a dichloromethane solution (20 mL) of a quinone (1.0 mmol) was added BF_3·OEt_2 (3.0 mmol) under N_2 at -78 °C. After a few minutes trimethylpolyprenylstannane (1.2 mmol) was added dropwise over a 5-min period, and then the temperature of the resulting solution was elevated to -65 °C within 1 h. The higher homologues of the stannyl reagent (**4h-k**) were added at -50 °C, and the temperature of the reaction mixture was maintained at -50 to -45 °C for 2 h instead of the above conditions. After addition of saturated NaCl solution, the resulting solution was partitioned between ether and saturated NaCl solution, the aqueous phase was extracted with ether, and the combined organic extracts were washed twice with ether and with saturated NaCl solution. After evaporation of the solvent, ether and an excess amount of Ag_2O were added to the residue, and the mixture was stirred for 30 min in the dark. The organic phase was dried over $MgSO_4$, and the crude mixture was purified by preparative TLC on silica gel (ether-hexane). The isomeric ratio at the $\Delta^{2'}$ position was determined by high-performance LC analysis (silica gel column, 4 mm × 60 cm, 7% ether-hexane).

Coenzyme Q_n (Table II). (a) *trans*-Coenzyme Q_2 (13a). The stannyl reagent (**4a**; 363 mg, 1.2 mmol) was added to 2,3-dimethoxy-5-methylbenzoquinone (**12**; 182 mg, 1.0 mmol) and BF_3·OEt_2 (3.0 mmol) in 20 mL of CH_2Cl_2 at -78 °C, following the general reaction procedure. The resulting product was chromatographed to afford *trans*-coenzyme Q_2 (**13a**): 207 mg (69%); >99% $\Delta^{2'}$-trans; red oil; NMR (CCl_4) δ 1.55 (s, 3 H, terminal *trans*-CH_3), 1.62 (s, 3 H, terminal *cis*-CH_3), 1.70 (s, 3 H, *trans*-CH_3 nearest ring), 1.94 (br, 7 H, CH_2 and ring CH_3), 3.11 (d, 2 H, J = 7 Hz, $ArCH_2$), 3.94 (s, 6 H, CH_3O), 4.88 (t, 1 H, J = 7 Hz, CH=C), 4.95 (br, 1 H, $CH{=}C(CH_3)_2$); IR (neat) 2920 (vs), 1640 (vs), 1605 (vs), 1445 (vs), 1260 (vs), 1202 (vs), 1150 (s), 1100 (s), 1004 (s), 940 (m), 734 cm^{-1} (s); mass spectrum, m/e (relative intensity) 318 (P, 65), 303 (27), 275 (36), 249 (base), 235 (69), 190 (55).

Anal. Calcd for $C_{19}H_{26}O_4$: C, 71.67; H, 8.23. Found: C, 71.73; H, 8.26.

(b) *cis*-Coenzyme Q_2 (13b). The stannyl reagent (**4b**; 363 mg, 1.2 mmol) was added to quinone **12** (182 mg, 1.0 mmol) and BF_3·OEt_2 (3.0 mmol) in 20 mL of CH_2Cl_2 at -78 °C, following the general reaction procedure. The resulting crude mixture was chromatographed to afford *cis*-coenzyme Q_2 (**13b**): 222 mg (70%); 88% $\Delta^{2'}$-cis; red oil; NMR ($CDCl_3$) δ 1.56 (s, terminal *trans*-CH_3), 1.61 (s, *cis*-CH_3), 1.66 (s, *trans*-CH_3 nearest ring of trans isomer), 2.3 (br, CH_2 and ring CH_3), 3.19 (d, J = 7 Hz, $ArCH_2$), 4.00 (s, CH_3O), 4.85-5.30 (m); IR (neat) 2960 (vs), 1640 (vs), 1605 (vs), 1445 (vs), 1375 (s), 1206 (vs), 1202 (s), 1150 (s), 1100 (s), 1075 (s), 1030 (s), 1010 (s), 940 (m), 735 cm^{-1} (m).

Anal. Calcd for $C_{19}H_{26}O_4$: C, 74.54; H, 8.87. Found: C, 74.65; H, 8.94.

(c) All-Trans Coenzyme Q_3 (13c). The stannyl reagent (**4c**; 442 mg, 1.2 mmol) was added to quinone **12** (182 mg, 1.0 mmol) and BF_3·OEt_2 (3.0 mmol) in 20 mL of CH_2Cl_2 at −78 °C, following the general reaction procedure. The resulting crude mixture was chromatographed to afford all-trans coenzyme Q_3 (**13c**): 343 mg (93%); 99% Δ^2-trans; red oil; NMR (CCl_4) δ 1.56 (s, 6 H, *trans*-CH_3), 1.64 (s, 3 H, terminal *cis*-CH_3), 1.72 (s, 3 H, *trans*-CH_3 nearest ring), 1.94 (br, 11 H, CH_2 and ring CH_3), 3.10 (d, 2 H, J = 8 Hz, $ArCH_2$), 3.87 (s, 6 H, CH_3O), 4.84 (t, 1 H, J = 8 Hz), 4.96 (m, 2 H); IR (neat) 2910 (s), 1640 (vs), 1600 (vs), 1445 (s), 1380 (m), 1285 (s), 1260 (vs), 1200 (s), 1150 (s), 1100 (s), 1020 (s), 780 cm^{-1} (s); mass spectrum, m/e (relative intensity) 388 (P + 2, 10), 387 (P + 1, 15), 386 (P, 54), 318 (10), 317 (13), 249 (48), 236 (26), 234 (base), 216 (19), 197 (57), 195 (42), 188 (32), 68 (63).

Anal. Calcd for $C_{24}H_{34}O_4$: C, 74.54; H, 8.87. Found: C, 74.61; H, 8.64.

(d) All-Trans Coenzyme Q_4 (13d). The stannyl reagent (**4d**; 524 mg, 1.2 mmol) was added to quinone **12** (182 mg, 1.0 mmol) and BF_3·OEt_2 (3.0 mmol) in 20 mL of CH_2Cl_2 at −78 °C, following the general reaction procedure. The resulting crude mixture was chromatographed to afford all-trans coenzyme Q_4 (**13d**): 318 mg (70%); 99% Δ^2-trans; red oil; NMR (CCl_4) δ 1.58 (s, 9 H, *trans*-CH_3), 1.64 (s, 3 H, terminal *cis*-CH_3), 1.72 (s, 3 H, *trans*-CH_3 nearest ring), 1.94 (br, 15 H, CH_2 and ring CH_3), 3.10 (d, 2 H, J = 8 Hz, $ArCH_2$), 3.90 (s, 6 H, CH_3O), 4.96 (m, 4 H); IR (neat) 2920 (vs), 1640 (vs), 1605 (vs), 1450 (s), 1380 (s), 1285 (s), 1260 (vs), 1205 (s), 1150 (s), 1100 (s), 1020 cm^{-1} (s); mass spectrum, m/e (relative intensity) m/e 456 (P + 2, 6), 455 (P + 1, 10), 454 (P, 23), 318 (12), 317 (12), 249 (33), 248 (35), 236 (49), 234 (66), 216 (15), 196 (79), 195 (38), 134 (21), 80 (55), 68 (base), 67 (64), 66 (61), 52 (41).

Anal. Calcd for $C_{29}H_{42}O_4$: C, 76.61; H, 9.31. Found: C, 76.22; H, 9.16.

(e) All-Trans Coenzyme Q_5 (13f). The stannyl reagent (**4f**; 1.2 mmol) was added to quinone **12** (182 mg, 1.0 mmol) and BF_3·OEt_2 (3.0 mmol) in 20 mL of CH_2Cl_2 at −78 °C, following the general reaction procedure. The resulting crude mixture was chromatographed to afford all-trans coenzyme Q_5 (**13f**): 490 mg (94%); 99% Δ^2-trans; red oil; NMR (CCl_4) δ 1.57 (s, 12 H, *trans*-CH_3), 1.64 (s, 3 H, terminal *cis*-CH_3), 1.72 (s, 3 H, trans CH_3 nearest ring), 2.0 (br, 19 H, CH_2 and ring CH_3), 3.80 (d, 2 H, J = 7 Hz, $ArCH_2$), 3.90 (s, 6 H, CH_3O), 4.98 (br, 5 H); IR (neat) 2910 (vs), 1645 (vs), 1610 (vs), 1450 (s), 1380 (s), 1290 (s), 1265 (vs), 1205 (s), 1150 (s), 1100 (s), 740 cm^{-1} (m); mass spectrum, m/e (relative intensity) 524 (P + 2, 20), 523 (P + 1, 26), 522 (P, 33), 249 (31), 234 (76), 196 (base), 195 (38), 80 (46), 68 (91), 67 (48), 66 (48).

Anal. Calcd for $C_{34}H_{50}O_4$: C, 78.12; H, 9.64. Found: C, 78.19; H, 9.83.

(f) All-Trans Coenzyme Q_6 (13g). The stannyl reagent (**4g**, 1.2 mmol) was added to quinone **12** (182 mg, 1.0 mmol) and BF_3·OEt_2 (4.0 mmol) in 30 mL of CH_2Cl_2 at −55 °C, and the reaction temperature was maintained at −50 to −55 °C for 2 h, following the usual workup. The resulting mixture was chromatographed to afford **12** (73 mg, 40%) and all-trans coenzyme Q_6 (**13g**): 350 mg (59%); 99% Δ^2-trans; red oil (lit.[2a] mp 19–20 °C); NMR (CCl_4) δ 1.58 (s, 15 H, *trans*-CH_3), 1.65 (s, 3 H, terminal *cis*-CH_3), 1.72 (s, 3 H, *trans*-CH_3 nearest ring), 1.96 (br, 20 H, CH_2 and ring CH_3), 3.11 (d, 2 H, J = 7 Hz, $ArCH_2$), 3.93 (s, 6 H, CH_3O), 5.04 (br, 6 H); IR (neat) 2905 (vs), 1645 (vs), 1605 (vs), 1450 (vs), 1395 (s), 1290 (s), 1265 (vs), 1205 (s), 1100 (s), 740 cm^{-1} (s); mass spectrum, m/e (relative intensity) 590 (P, 17), 249 (18), 234 (47), 196 (58), 80 (22), 68 (base), 53 (36).

Anal. Calcd for $C_{39}H_{58}O_4$: C, 79.27; H, 9.89. Found: C, 79.07; H, 9.73.

(g) All-Trans Coenzyme Q_7 (13h). The stannyl reagent (**4h**, 0.85 mmol) was added to quinone **12** (182 mg, 1.0 mmol) and BF_3·OEt_2 in 30 mL of CH_2Cl_2 at −55 °C, and then the reaction temperature was maintained at −50 to −55 °C for 2 h, following the usual workup. The resulting products were chromatographed to afford **12** (100 mg, 55%) and all-trans coenzyme Q_7 (**13h**): 260 mg (40%); 99% Δ^2-trans; mp 27–28 °C (lit.[2a] mp 31–32 °C); NMR (CCl_4) δ 1.56 (s, 24 H, *trans*-CH_3), 1.63 (s, 3 H, terminal *cis*-CH_3), 1.71 (s, 3 H, CH_3 nearest ring), 1.96 (br, 27 H, CH_2 and ring CH_3), 3.08 (d, 2 H, J = 7 Hz, $ArCH_2$), 3.88 (s, 6 H, CH_3O), 4.97 (br, 7 H); IR (neat) 2920 (vs), 1650 (vs), 1610 (vs), 1445 (vs), 1390 (s), 1290 (s), 1265 (vs), 1210 (s), 1160 (s), 1105 (s), 785 cm^{-1} (s); mass spectrum, m/e (relative intensity) 658 (P, 7), 657 (P − 1, 14), 248 (15), 234 (16), 196 (base), 80 (47), 68 (98), 67 (91), 42 (65).

Anal. Calcd for $C_{44}H_{66}O_4$: C, 80,19; H, 10.10. Found: C, 80.01; H, 10.33.

(i) All-Trans Coenzyme Q_8 (13i). The stannyl reagent (**4i**, 0.52 mmol) was added to quinone **12** (78 mg, 0.43 mmol) and BF_3·OEt_2 (2.08 mmol) in 20 mL of CH_2Cl_2 at −60 °C, and then the reaction temperature was maintained at −60 to −50 °C for 2 h, following the usual workup. The resulting products were chromatographed to afford **12** (71 mg, 75%) and all-trans coenzyme Q_8 (**13i**): 79 mg (25%, based on the amount of **4i**); 98% Δ^2-trans; mp 30–33 °C (lit.[2a] mp 37–38 °C); NMR (CCl_4) δ 1.56 (s, 21 H, *trans*-CH_3), 1.65 (s, 3 H, terminal *cis*-CH_3), 1.76 (s, 3 H, CH_3 nearest ring), 1.80–2.20 (br, 28 H, CH_2 and ring CH_3), 3.15 (d, 2 H, J = 7 Hz, $ArCH_2$), 3.90 (s, 6 H, CH_3O), 4.80–5.20 (br, 8 H); IR (neat) 2930 (vs), 2850 (m), 1665 (vs), 1620 (vs), 1450 (vs), 1395 (s), 1300 (s), 1275 (vs), 1165 cm^{-1} (s); mass spectrum, m/e (relative intensity) 727 (P + 1, 0.4), 726 (P, 0.3), 437 (4.7), 409 (21), 166 (45), 138 (33), 92 (42), 80 (43), 68 (base), 58 (35).

Anal. Calcd for $C_{49}H_{74}O_4$: C, 80.94; H, 10.26. Found: C, 80.75; H, 10.43.

(j) All-Trans Coenzyme Q_9 (13j). The stannyl reagent (**4j**, 0.5 mmol) in a mixture of CH_2Cl_2 (1 mL) and hexane (1 mL) was added to quinone **12** (111 mg, 0.61 mmol) and BF_3·OEt_2 (2.6 mmol) in a mixture of CH_2Cl_2 (20 mL) and hexane (1 mL) at −50 °C, and the reaction mixture was stirred at −50 to −55 °C for 2 h. After the routine workup, the resulting products were chromatographed to afford the starting quinone (65 mg, 59%) and all-trans coenzyme Q_9 (**13j**): 210 mg (51%, based on the amount of **4j**); 100% Δ^2-trans; mp 40.5–42.5 °C (lit.[2a] mp 44–45 °C); NMR ($CDCl_3$) δ 1.60 (s, 24 H, *trans*-CH_3), 1.69 (s, 3 H, terminal *cis*-CH_3), 1.74 (s, 3 H, CH_3 nearest ring), 2.00 (br, 35 H, CH_2 and ring CH_3), 3.16 (d, 2 H, J = 7 Hz, $ArCH_2$), 3.97 (s, 6 H, CH_3O), 5.09 (br, 9 H); IR (neat) 2920 (vs), 2850 (vs), 1653 (vs), 1615 (vs), 1450 (vs), 1385 (s), 1285 (s), 1260 (vs), 1203 (s), 1153 (s), 1103 cm^{-1} (s); mass spectrum, m/e (relative intensity) 797 (P + 2, 19), 796 (P + 1, 8), 795 (P, 9), 234 (76), 196 (base), 80 (43), 69 (52).

Anal. Calcd for $C_{54}H_{82}O_4$: C, 81.54; H, 10.39. Found: C, 81.28; H, 10.22.

(k) Coenzyme Q_{10} (13k). The stannyl reagent (**4k**, 0.42 mmol) in a mixture of CH_2Cl_2 (1 mL) and isooctane (1 mL) was added to quinone **12** (111 mg, 0.61 mmol) and BF_3·OEt_2 (2.6 mmol) in a mixture of CH_2Cl_2 (25 mL) and isooctane (1 mL) at −50 °C, and the reaction mixture was maintained at −45 to −50 °C for 2 h. After a routine workup, the resulting products were chromatographed to afford the starting quinone (70 mg, 63%) and coenzyme Q_{10} (**13k**): 189 mg (51%, based on the amount of **4k**); 86% Δ^2-trans; mp 46–49 °C (lit.[2a] mp 49 °C); NMR ($CDCl_3$) δ 1.60 (s, 27 H, *trans*-CH_3), 1.68 (s, 3 H, terminal *cis*-CH_3), 1.75 (s, 3 H, *trans*-CH_3 nearest ring), 2.02 (br, 21 H, CH_2 and ring CH_3), 3.10 (d, 2 H, J = 7 Hz, $ArCH_2$), 3.98 (s, 6 H, CH_3O), 5.10 (br, 10 H); IR (neat) 2900 (vs), 2840 (s), 1640 (vs), 1605 (vs), 1445 (vs), 1380 (s), 1295 (s), 1260 (vs), 1205 (s), 1150 (s), 1100 (s); mass spectrum, m/e (relative intensity) 862 (P, 12), 234 (66), 197 (88), 80 (72), 69 (base).

Anal. Calcd for $C_{59}H_{90}O_4$: C, 82.08; H, 10.51. Found: C, 81.80; H, 10.30.

Geranyl-*p*-benzoquinone. The stannyl reagent (**4a**; 360 mg, 1.2 mmol) was added to *p*-benzoquinone (108 mg, 1.0 mmol) and BF_3·OEt_2 (3.0 mmol) in 20 mL of CH_2Cl_2 at −78 °C, following the general reaction procedure. The resulting products were chromatographed to afford geranyl-*p*-benzoquinone: 141 mg (58%); 98% Δ^2-trans; brown oil; NMR (CCl_4) δ 1.60 (s, 3 H, *trans*-CH_3), 1.66 (s, 3 H, terminal *cis*-CH_3), 1.69 (s, 3 H, *trans*-CH_3 nearest ring), 2.08 (br, 4 H, CH_2), 3.11 (d, 2 H, J = 7.5 Hz, $ArCH_2$), 5.06 (br, 1 H), 5.16 (t, 1 H, J = 7.5 Hz), 6.46 (m, 1 H, ring H), 6.68 (s, 2 H, ring H); IR (CCl_4) 2930 (s), 1665 (vs), 1602 (s), 1450 (m), 1380 (m), 1350 (m), 1298 (s), 901 cm^{-1} (s); mass spectrum, m/e (relative intensity) 244 (P, 15), 229 (12), 201 (42), 176 (26), 161 (66), 121 (33), 69 (base).

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.52; H, 8.53.

Neryl-*p*-benzoquinone. The stannyl reagent (**4b**; 360 mg, 1.2 mmol) was added to *p*-benzoquinone (108 mg, 1.0 mmol) and BF_3·OEt_2 (3.0 mmol) in 20 mL of CH_2Cl_2 at −78 °C, following the

general reaction procedure. The resulting products were chromatographed to afford neryl-*p*-benzoquinone: 181 mg (74%); 77% Δ^2-cis; brown oil; NMR (CCl_4) δ 1.56 (s, terminal *trans*-CH_3), 1.62 (s, *cis*-CH_3), 1.74 (s, *trans*-CH_3 nearest ring), 2.06 (br, CH_2), 3.06 (d, J = 7 Hz, $ArCH_2$), 5.02 (m, olefinic H), 6.42 (m, ring H), 6.65 (s, ring H); IR (neat) 2960 (vs), 2900 (vs), 1650 (vs), 1559 (vs), 1445 (s), 1375 (s), 1295 (vs), 895 cm^{-1} (s).

Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.70; H, 8.12.

Plastoquinone-2 (14). The stannyl reagent (**4a**; 300 mg, 1.0 mmol) was added to 2,3-dimethylbenzoquinone (136 mg, 1.0 mmol) and BF_3·OEt_2 (3.0 mmol) in 20 mL of CH_2Cl_2 at −58 °C, following the general reaction procedure. The resulting products were chromatographed to afford the starting quinone (16 mg, 12%) and plastoquinone-2: 63 mg (23%); 95% Δ^2-trans; yellow oil; NMR ($CDCl_3$) δ 1.61 (s, 6 H, terminal CH_3), 1.71 (s, 3 H, *trans*-CH_3 nearest ring), 2.02 (br, 10 H, CH_2 and ring CH_3), 3.12 (d, 2 H, J = 8 Hz, $ArCH_2$), 5.08 (m, 2 H, olefinic H), 6.46 (m, 1 H, ring H); IR (neat) 2920 (s), 1640 (vs), 1610 (s), 1440 (s), 1375 (s), 1315 (s), 1235 (m), 1160 (m), 1100 cm^{-1} (m).

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.33; H, 8.79.

Trimethylphytylbenzoquinone (15). The stannyl reagent (**4e**; 532 mg, 1.2 mmol) was added to trimethylbenzoquinone (150 mg, 1.0 mmol) and BF_3·OEt_2 (5.0 mmol) in 30 mL of CH_2Cl_2 at −78 °C, following the general reaction procedure. The resulting products were chromatographed to afford the starting quinone (36 mg, 24%) and **15**: 327 mg (76%); 95% Δ^2-trans; yellow oil; NMR ($CDCl_3$) δ 0.85 (d, 12 H, J = 6 Hz, CH_3CH), 1.19 (m, 19 H, CH_2 and CH), 1.72 (s, 3 H, *trans*-CH_3), 1.93 (t, 2 H, J = 6 Hz, $=C(CH_3)CH_2$), 1.99 (s, 9 H, ring CH_3), 3.18 (d, 2 H, J = 7 Hz, $ArCH_2$), 4.85 (t, 1 H, J = 7 Hz, olefinic H); IR (neat) 2920 (vs), 2860 (s), 1635 (vs), 1455 (s), 1370 (s), 1300 (s), 1255 (m), 705 cm^{-1} (m); mass spectrum, m/e (relative intensity) 428 (P, 43), 413 (3), 202 (20), 176 (17), 166 (18), 96 (63), 94 (base).

Anal. Calcd for $C_{29}H_{48}O_2$: C, 81.25; H, 11.29. Found: C, 81.50; H, 11.27.

Vitamin $K_{2(10)}$ (17a). The stannyl reagent (**4a**; 600 mg, 2.0 mmol) was added to 2-methyl-1,4-naphthoquinone (172 mg, 1.0 mmol) and BF_3·OEt_2 (3.0 mmol) in 20 mL of CH_2Cl_2 at −78 °C, following the general reaction procedure. NMR analysis of the crude mixture using *cis*-1,2-dichloroethylene as an internal standard showed it to contain the starting quinone (53%), **17a** (46%), and **18a** (trace), which was assigned by its characteristic signals of the diastereotopic ring CH_2 (δ 2.80 and 3.04, each d, J = 16 Hz). The resulting products were chromatographed to afford the starting quinone (92 mg, 53%) and **17a**: 93 mg (30%); 95% Δ^2-trans; mp 47–49 °C (lit.[8a] mp 52–53 °C); NMR ($CDCl_3$) δ 1.55 (s, 3 H, terminal *trans*-CH_3), 1.61 (s, 3 H, terminal *cis*-CH_3), 1.78 (s, 3 H, *trans*-CH_3 nearest ring), 1.99 (br, 4 H, CH_2), 2.17 (s, 3 H, ring CH_3), 3.25 (d, 2 H, J = 7 Hz, $ArCH_2$), 5.00 (m, 2 H, olefinic H), 7.63 and 8.03 (each m, 4 H, arom H); IR (neat) 2920 (vs), 1650 (vs), 1610 (m), 1590 (s), 1435 (m), 1375 (s), 1330 (s), 1290 (vs), 965 (m), 780 (s), 700 (s); mass spectrum, m/e (relative intensity) 308 (P, 69), 293 (18), 265 (34), 239 (71), 224 (base), 209 (28), 297 (89).

Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 81.96; H, 7.95.

***cis*-Vitamin $K_{2(10)}$ (17b).** The stannyl reagent (**4b**; 300 mg, 1.2 mmol) was added to 2-methyl-1,4-naphthoquinone (172 mg, 1.0 mmol) and BF_3·OEt_2 (5.0 mmol) in 20 mL of CH_2Cl_2 at −78 °C, following the general procedure. NMR analysis of the crude mixture using *cis*-1,2-dichloroethylene as an internal standard showed it to contain the starting quinone (43%), **17b** (41%), and **18b** (16%). The products were isolated by preparative LC (silica gel, 10% Et_2O–hexane). The R_f 0.48 band contained **17b**: 126 mg (41%); 76% Δ^2-cis; yellow oil; NMR ($CDCl_3$) δ 1.57 (s, terminal *trans*-CH_3), 1.67 (s, terminal *cis*-CH_3), 1.71 (s, *cis*-CH_3 nearest ring), 1.79 (s, *trans*-CH_3 nearest ring), 1.99 (br, CH_2CH_2 of trans form), 2.13 (s, ring CH_3 and CH_2CH_2 of cis form), 3.30 (d, J = 7 Hz, $ArCH_2$), 4.9–5.3 (m, olefinic H), 7.61 and 8.00 (each m, aromatic H); IR (neat) 2950 (vs), 2900 (vs), 1645 (vs), 1610 (s), 1590 (vs), 1440 (s), 1325 (vs), 1290 (vs), 1250 (s), 965 cm^{-1} (s).

The R_f 0.31 band contained the starting quinone (70 mg, 41%).

The R_f 0.26 band contained **18b**: 40 mg (13%); pale yellow oil; NMR (CCl_4) δ 1.24 (s, 3 H, ring CH_3), 1.50, 1.56, 1.66 (each s, total 9 H, side chain CH_3), 1.93 (m, 4 H, CH_2CH_2), 2.20 (dd, 1 H, J = 8, 15 Hz, diastereotopic CH_2CH=), 2.48 (dd, 1 H, J = 8, 15 Hz, diastereotopic CH_2CH=), 2.72 (d, 1 H, J = 16 Hz, diastereotopic ring H), 2.99 (d, 1 H, J = 16 Hz, diastereotopic ring H), 5.01 (br t, 2 H, J = 8 Hz, CH=C), 7.68 and 8.00 (m, 4 H, aromatic H); IR (neat) 2965 (vs), 2940 (vs), 1690 (vs), 1595 (vs), 1450 (s), 1380 (s), 1290 (vs), 1260 (vs), 1215 (s), 985 (s), 755 cm^{-1} (s).

Vitamin K_1 (17e). The stannyl reagent (**4e**; 532 mg, 1.2 mmol) was added to 2-methyl-1,4-naphthoquinone (172 mg, 1.0 mmol) and BF_3·OEt_2 (3.0 mmol) at −75 °C, following the general reaction procedure. The products were isolated by preparative LC (silica gel, 10% ether–hexane). The R_f 0.92 band contained **17e**: 216 mg (48%); 96% Δ^2-trans; yellow oil; NMR ($CDCl_3$) δ 0.84 (d, 12 H, J = 6 Hz, $CHCH_3$), 1.18 (m, 19 H, CH and CH_2), 1.78 (s, 3 H, *trans*-CH_3), 1.96 (t, 2 H, J = 6 Hz, $=C(CH_3)CH_2$), 2.16 (s, 3 H, ring CH_3), 3.33 (d, 2 H, J = 7 Hz, CH_2 nearest ring), 4.95 (t, 1 H, J = 7 Hz), 7.58 and 7.98 (each m, 4 H, arom H); IR (neat) 2940 (sh), 2920 (vs), 2850 (vs), 1650 (vs), 1610 (s), 1590 (vs), 1455 (s), 1370 (s), 1330 (s), 1290 (vs), 965 (m), 700 (s); mass spectrum, m/e (relative intensity) 450 (P, base), 435 (4), 224 (27), 197 (20), 185 (20).

Anal. Calcd for $C_{31}H_{46}O_2$: C, 82.61; H, 10.29. Found: C, 82.88; H, 10.44.

The R_f 0.65 band contained **18e**: 63 mg (14%); pale yellow oil; NMR ($CDCl_3$) δ 0.88 (d, 12 H, J = 6 Hz, $CHCH_3$), 1.23 (m, 21 H, CH and CH_2), 1.32 (s, 3 H, ring CH_3), 1.52 (s, 3 H, olefinic CH_3), 1.92 (t, 2 H, J = 7 Hz, $=C(CH_3)CH_2$), 2.27 (dd, 1 H, J = 8, 15 Hz, diastereotopic CH_2CH=), 2.50 (dd, 1 H, J = 8, 15 Hz, diastereotopic CH_2CH=), 2.83 (d, 1 H, J = 16 Hz, diastereotopic ring H), 3.09 (d, 1 H, J = 12 Hz, diastereotopic ring H), 5.04 (t, 1 H, J = 8 Hz), 7.72 and 8.03 (each m, 4 H, arom H); IR (neat) 2910 (vs), 2850 (vs), 1685 (vs), 1590 (s), 1450 (s), 1370 (s), 1280 (s), 1250 (s), 740 cm^{-1} (s); mass spectrum, m/e (relative intensity) 450 (P, 1), 278 (1), 173 (base).

Anal. Calcd for $C_{31}H_{48}O_2$: C, 82.24; H, 10.69. Found: C, 82.10; H, 10.93.

The R_f 0.45 band contained the starting quinone (65 mg, 38%).

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Registry No. **1a**, 106-24-1; **1b**, 106-25-2; **1c**, 106-28-5; **1d**, 24034-73-9; **1e**, 150-86-7; **1f**, 22488-05-7; **1g**, 68778-93-8; **1h**, 32304-16-8; **1i**, 33569-79-8; **2a**, 5389-87-7; **2b**, 20536-36-1; **2c**, 67023-84-1; **2d**, 50848-64-1; **2e**, 4444-14-8; **2f**, 74609-99-7; **2g**, 74610-00-7; **2h**, 74610-01-8; **2i**, 74610-02-9; **2j**, 52610-77-2; **2k**, 68799-83-7; **4a**, 72132-87-7; **4b**, 72132-88-8; **4c**, 72132-89-9; **4d**, 57804-27-0; **4e**, 74610-03-0; **4f**, 74610-04-1; **4g**, 74629-77-9; **4h**, 74610-05-2; **4i**, 74610-06-3; **4j**, 72247-20-2; **4k**, 72247-21-3; **5**, 63707-07-3; **6**, 52220-07-2; **7**, 68731-64-6; **8**, 74610-07-4; **9**, 74610-08-5; **10**, 74610-09-6; **11**, 74629-78-0; **12**, 605-94-7; **13a**, 606-06-4; **13b**, 38658-30-9; **13c**, 1173-76-8; **13d**, 4370-62-1; **13f**, 4370-61-0; **13g**, 1065-31-2; **13h**, 303-95-7; **13i**, 2394-68-5; **13j**, 303-97-9; **13k**, 303-98-0; **14**, 3811-24-3; **15**, 28072-25-5; **17a**, 7421-23-0; **17b**, 7421-24-1; **17c**, 84-80-0; **18b**, 74610-10-9; **18e**, 74610-11-0; lithium thiophenoxide, 2973-86-6; farnesyl benzyl ether, 56506-81-1; 12-hydroxyfarnesyl benzyl ether, 71135-48-3; (trimethylstannyl)lithium, 17946-71-3; *p*-benzoquinone, 106-51-4; geranyl-*p*-benzoquinone, 61977-06-8; neryl-*p*-benzoquinone, 74610-12-1; 2,3-dimethylbenzoquinone, 526-86-3; trimethylbenzoquinone, 935-92-2; 2-methyl-1,4-naphthoquinone, 58-27-5.