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An Expeditious Route to CoQ_n, Vitamins K_1 and K_2, and Related Allylated *para*-Quinones Utilizing Ni(0) Catalysis

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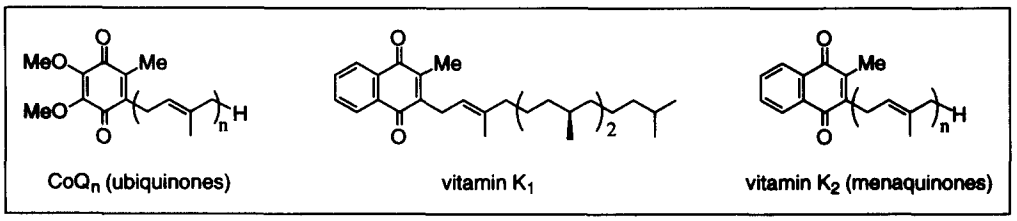
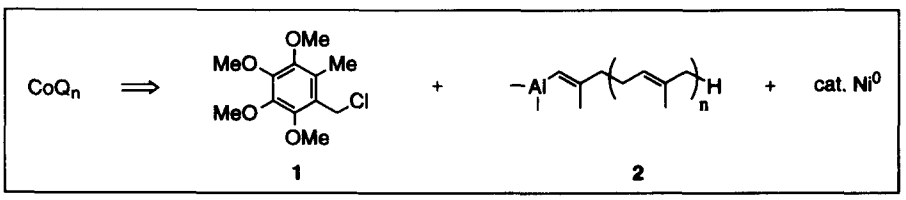
Abstract. *Coupling reactions between vinylalanes and chloromethylated para-quinones, mediated by catalytic amounts of Ni(0), lead directly to allylated products, including coenzyme Q, and vitamins K_1 and K_2.*

Quinone chemistry occupies a central role in many life processes.[1] Compounds such as coenzyme Q_n (*i.e.*, the ubiquinones), which function as mediators of electron transport in mitochondria, and vitamins K_1 (the 'clotting vitamin') and K_2 (the menaquinones), need little introduction as to their roles in many essential



CoQ_n (ubiquinones) vitamin K_1 vitamin K_2 (menaquinones)

bioprocesses. In a recent report from our laboratories[2] we disclosed a novel approach to their precursor (protected) hydroquinones which relied on a Ni(0)-induced coupling between benzylic chlorides **1**, and vinylalanes **2** prepared by standard Negishi carboalumination[3] of the corresponding terminal alkyne. Implied



1 **2**

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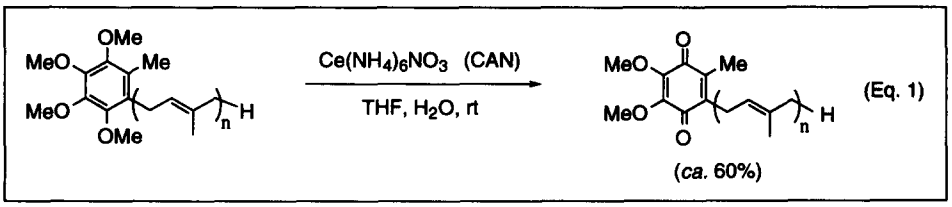
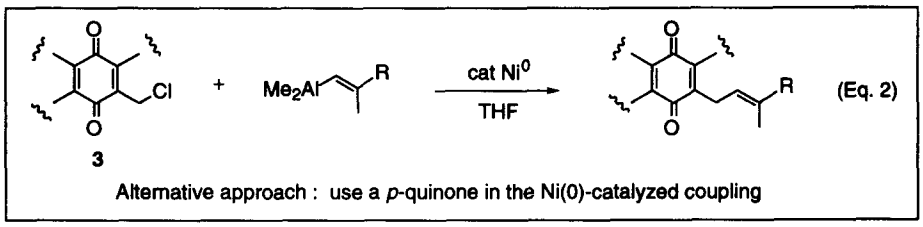
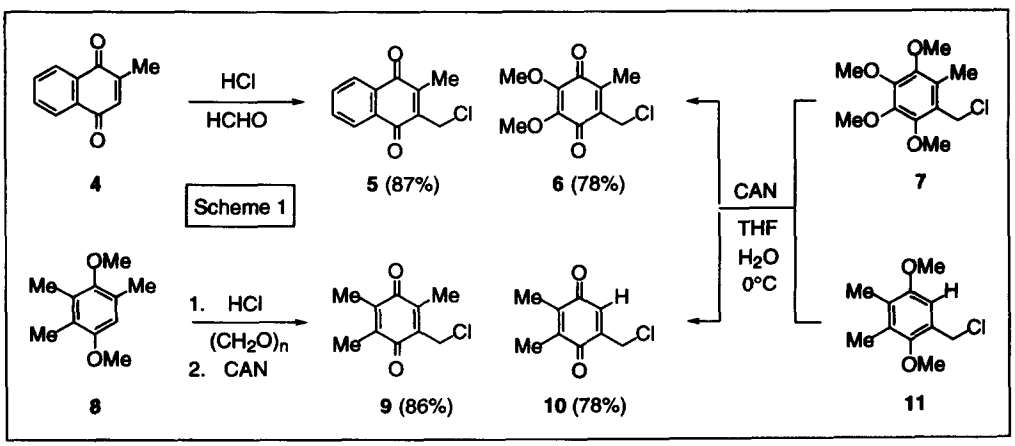
in this scheme is a final oxidation to the quinone,[4] which in our hands is only modest in efficiency using ceric ammonium nitrate (CAN; *cf.* Eq. 1). This finding was deemed unacceptable for the anticipated use of this methodology *en route* to the very expensive series of ubiquinones (*i.e.*, $CoQ_{6\text{-}9}$).[5] It was reasoned that the oxidation could be avoided at this late stage of the sequence by resorting directly to the corresponding chloro-



methylated quinones **3**,[6] which it was hoped would behave in a fashion analogous to the benzylic array (*i.e.*, **1**).[2] Such couplings of this type, to the best of our knowledge, are unprecedented. We now report that Ni(0) does in fact cleanly effect the desired C-C bond formation under very mild conditions (Eq. 2).



Substrate quinones of type **3** (**5**, **6**, **9**, and **10**) were prepared by two routes (Scheme 1). Treatment of **4** with aqueous formaldehyde and gaseous HCl at 60-65°C afforded chloromethylated product **5**, while **9** resulted from treatment of **8** with paraformaldehyde followed by CAN oxidation. Both **5** and **9** are stable yellow solids at room temperature and require no special handling. Quinones **6** and **10** were realized by CAN



oxidation of the corresponding benzylic chlorides. That **7** and **11** withstand the aqueous conditions used for their conversion to educts **6** and **10** is noteworthy. CoQ precursor **6** is obtained as an oily substance which was routinely used immediately following isolation and azeotropic drying. Chloromethylated quinone **10**, on the other hand, like **5** and **9**, is a readily stored, fairly stable solid.

A broad sampling of alkynes was studied, with results summarized in Table 1. The Ni(0) catalyst was prepared as described previously by simply mixing $NiCl_2$ with two equivalents of PPh_3 in THF, to which is added 2*n*-BuLi at room temperature (Eq. 3).[7] A stock solution of this catalyst, which has excellent shelf-life

$$NiCl_2 + 2PPh_3 \xrightarrow[THF,\ rt]{2\ n\text{-BuLi}} \text{"}(Ph_3P)_2Ni(0)\text{"} \qquad \text{(Eq. 3)}$$

at ambient temperatures when stored under argon, can be employed for ease of measuring 0.5-5.0 mol %, which is to be added to quinones **3**. Cooling of this mixture to between -60° and -78° followed by introduction of the vinylalane, with warming if necessary, leads to the coupled material. In most cases, reactions are complete in minutes at -78°, as these chloromethylated quinones behave as super-activated allylic chlorides. Particularly noteworthy are the examples involving the vitamin K_1 and CoQ / menaquinone

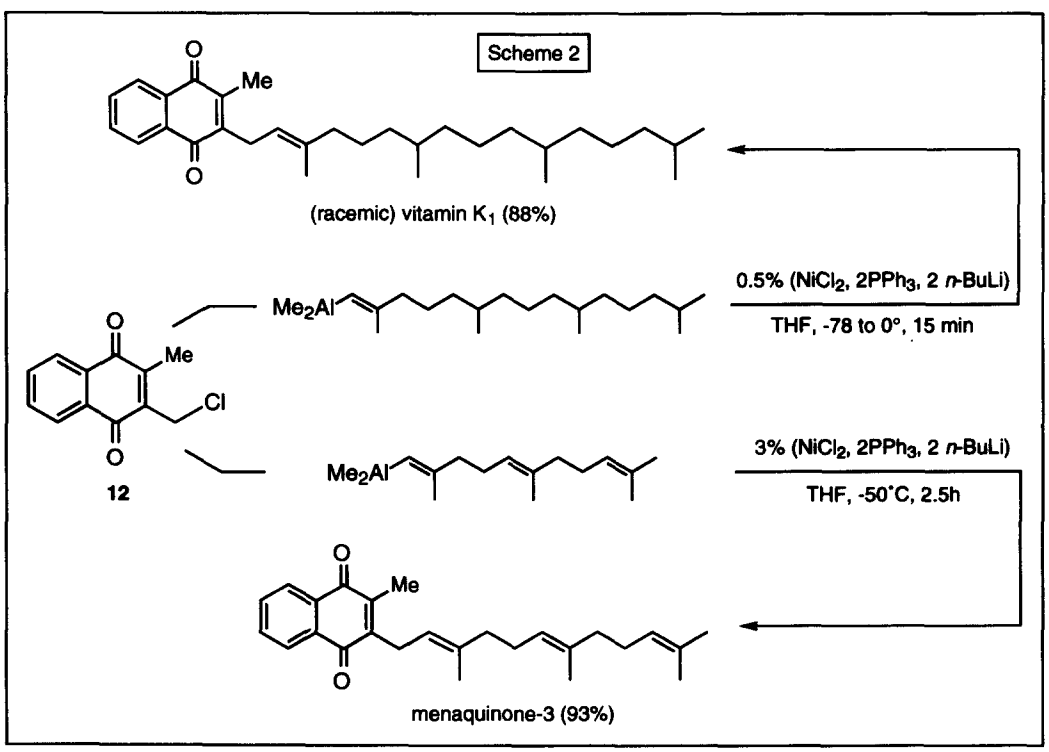
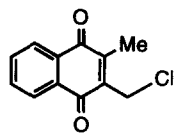
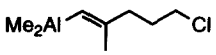
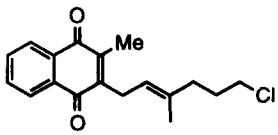
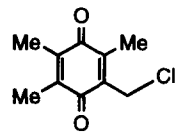
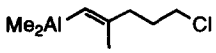
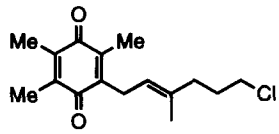
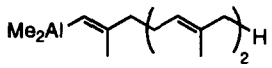
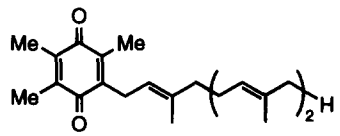
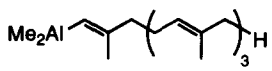
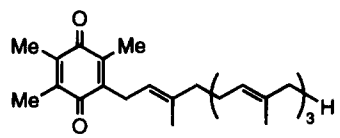
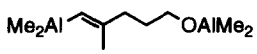
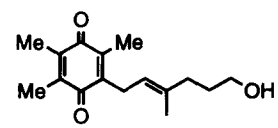
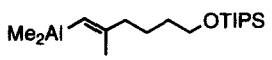
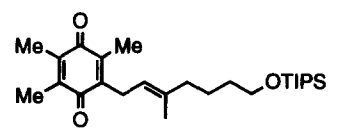
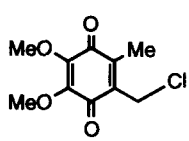
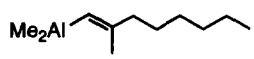
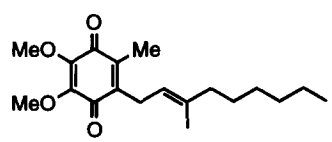
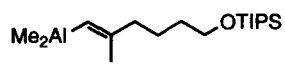
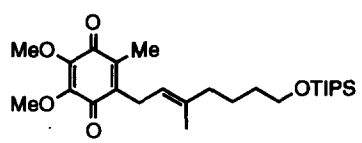
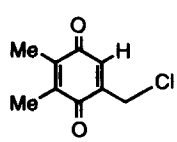
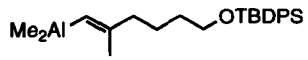
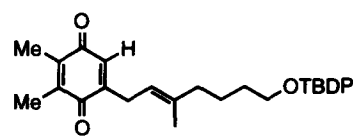
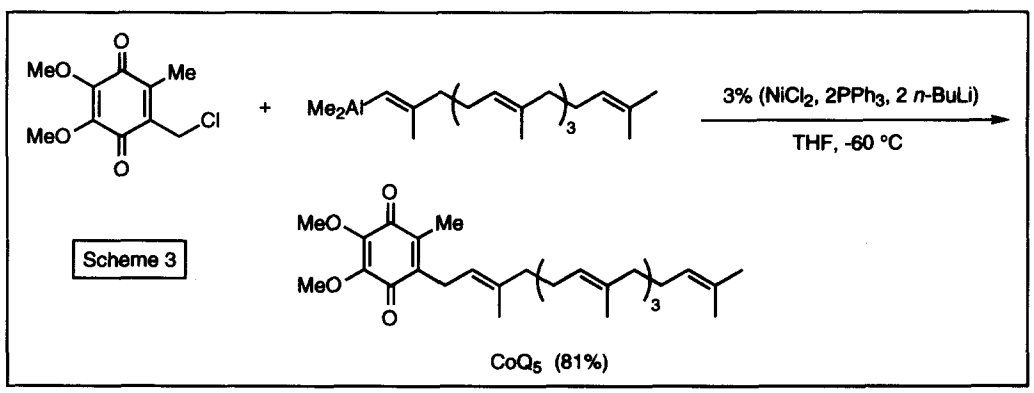


Table 1. Ni(0)-catalyzed couplings of chloromethylated quinones with vinylalanes

Quinone	Vinylalane[a]	Product[b]	Yield(%)[c]
			86
			70
			78
			83
			69
			83
			86
			67
			73

[a]Prepared *via* carboalumination of the corresponding terminal alkyne.[3] [b]Fully characterized; see Experimental Section. [c]Isolated, chromatographically purified materials.

side chains with their matching electrophilic chloromethylated *para*-benzoquinone **12** (Scheme 2). Thus, vitamin K_1[8] was obtained in 88% isolated yield using only 0.5 mol % Ni(0) as catalyst. Likewise, vitamin K_2 (menaquinone-3) was formed in 93% yield using the corresponding alkyne derived from geranyl chloride. The related coupling to arrive at CoQ_5 went smoothly at -60° (Scheme 3),[9] although prolonged exposure of the product to the reaction conditions was detrimental to the yield, and the nature of the workup employed for this particular compound proved to be critical (see Experimental Section). Although the reaction partners involved in the synthesis of CoQ_5 are individually amenable to these couplings and lead to good yields of products (*cf.* Table 1), the specific combination leading to the CoQ_n arrangement appears to have a much greater sensitivity to reaction parameters. For example, using Rochelle's salt during extraction is problematic. Chromatographic purification with base-treated adsorbent (1% Et_3N), for any of the quinones prepared in this study, led to extensive loses of material, especially in the CoQ series.



Scheme 3

In summary, a novel nickel(0)-catalyzed coupling process has been developed which allows for direct access to allylic-substituted *para*-quinones characteristic of several important biomolecules. Applications of this methodology to the synthesis of the extremely expensive higher homologs of the ubiquinones (CoQ_n, $n \geq 6$) using a new approach to polyprenoidal propyne derivatives (*i.e.*, precursors to **2** with n = 5-8) will be reported in due course.

Experimental Section

THF and hexanes were distilled from Na/benzophenone ketyl prior to use. Column chromatography was performed on ICN Biomedicals Silica, 32-63, 60 A. TLC was carried out on pre-coated silica-gel 60A F_{254} plates (EMx Science), 0.25 mm layer thickness. ^1H and ^{13}C NMR spectra were run at either 400 or 200 MHz on a Varian Unity-400 or Gemini-200 spectrometer and the chemical shifts are relative to tetramethylsilane as internal standard. All NMR samples were run in $CDCl_3$ unless noted otherwise. IR spectra were run neat, or are specified as KBr pellets, on an ATI Mattson Infinity Series FT-IR spectrometer and the data is presented in cm^{-1}. Mass spectra were run on either a VG-Autospec or an analytical VG-70-250 HF instrument. Low resolution mass spectra are presented as m/z values followed by relative intensities. All reactions were carried out under an inert atmosphere of Ar using oven dried glassware and standard syringe/septa techniques.

A general procedure for the preparation of cross-coupled products is as follows: *Carboalumination*: To a 10 mL round-bottom Schlenk flask (equipped with a medium ground glass filter frit) was added zirconocene dichloride (73 mg, 0.25 mmol). A solution of trimethylaluminum (0.75 mL, 2.0 M in hexanes, 1.5 mmol) was added at 0°C and stirred under reduced pressure until the hexanes were removed. 1,2-Dichloroethane was added (1.0 mL) and the solution was allowed to stir and warm to rt over 10 min. To this solution was added an alkyne (1.0 mmol, neat if a liquid, otherwise dissolved in a minimum of dichloroethane) and the mixture was stirred at 0°C for 30 min, after which time carboalumination was usually complete (determined by GC). The dichloroethane was pumped off *in vacuo* and freshly distilled hexanes (2 mL) were added and then also removed *in vacuo*. Additional hexanes (5 mL) were then added to the flask so as to precipitate the zirconium salts. The hexanes layer was removed by carefully decanting and filtering through the frit with great care taken to avoid contamination by the zirconiumm salts. The leftover salts were not washed. The orange hexanes solution was concentrated under reduced pressure and dissolved in THF (2.0 mL).

Nickel-catalyzed coupling: To a 5 mL round-botton flask was added nickel chloride (5.2 mg, 0.04 mmol) or *bis*(triphenylphosphine)nickel(II) chloride (26 mg, 0.04 mmol), and triphenylphosphine (21 mg, 0.08 mmol) at rt. THF (1.0 mL) was added followed by *n*-butyllithium (40 μL, 2.0M in hexanes, 0.08 mmol). The deep red solution was allowed to stir for 5 min, after which the chloromethyl quinone (0.8 mmol) was added (neat if a liquid, or dissolved in a minimum of THF if a solid) and the subsequent dark blue solution was stirred for an additional 5 min. The solution containing the nickel catalyst was then transferred *via* cannula to the vinylalane at rt, and the cross-coupling reaction followed by GC. When the reaction was complete (usually <30 min), the solution was diluted with diethyl ether (10 mL) and quenched at 0°C by carefully adding 1.0 M HCl dropwise (3 mL). The mixture was allowed to stir for an additional 5 min and then extracted with diethyl ether. The combined organic layers were dried (anhydrous $Na_2SO_4/MgSO_4$) and concentrated *in vacuo*. Silica gel column chromatography was used for purification; the products were normally clear, viscous, colored oils. Unless stated, all reactions were carried out with $NiCl_2(PPh_3)_2$ or $NiCl_2$ as the nickel source.

1,4-Dimethoxy-2,3,5-trimethylbenzene. To a solution of trimethylhydroquinone (10 g, 66 mmol) was added K_2CO_3 (45 g, 330 mmol) in methyl ethyl ketone (150 mL) at rt. After 30 min, methyl iodide (16.4 mL, 37 g, 263 mmol) was added and the mixture was stirred for 72 h at 65°C. After cooling, the solvent was removed by rotary evaporation *in vacuo* and the resulting precipitate was extracted with diethyl ether (2 x 50 mL). The organic layer was separated, and the combined organic extracts were dried over anhydrous $MgSO_4$, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (hexane/diethyl ether, 95:5) to yield 9.72 (82%) of product as a viscous clear oil; R_f = 0.26 (hexane/diethyl ether, 95:5); IR (neat or KBr) 2989, 2938, 2861, 1588, 1482, 1466, 1400, 1324, 1231, 1124, 1189, 1092, 1014, 909; ^1H NMR (200 MHz) δ 6.53 (s, 1H, ArH), 3.77 (s, 3H, 3-OCH_3), 3.65 (s, 3H, 4-OCH_3), 2.27 (s, 3H, 1-CH_3), 2.19 (s, 3H, 2-CH_3), 2.11 (s, 3H, 3-CH_3); ^{13}C NMR (50 MHz) δ 153.65, 150.68, 130.77, 127.88, 123.89, 110.43, 60.31,

55.93, 16.46, 12.81, 12.04; LREIMS 180(48), 165(100), 137(17), 122(11), 105(9), 91(19), 77(14), 65(6), 53(8); HREIMS calcd for $C_{11}H_{16}O_2$ 180.1150; found 180.1153.

1-Chloromethyl-2,5-dimethoxy-3,4,6-trimethylbenzene. To a mixture of 1,4-dimethoxy-2,3,5-trimethylbenzene (1.8 g, 10 mmol) was added formaldehyde (5.6 mL, 50 mmol, 37% w/w in H_2O) in glacial HOAc (10 mL). HCl gas was then passed through the mixture until the solution was blood red in color (~30 min). Extraction of the mixture with ether (3 x 50 mL), washing with H_2O, drying with anhydrous $MgSO_4$, and concentration *in vacuo* afforded a residue which was purified by chromatography on silica gel (hexane/diethyl ether, 9:1) to yield 1.83 g (80%) product as a bright yellow powder; R_f = 0.53 (hexane/diethyl ether, 95:5); mp 63-64°C; IR (KBr) 2990, 2945, 2852, 2824, 1460, 1401, 1244, 1087, 1066, 1004, 928, 720, 670; ^{1}H NMR (200 MHz) δ 4.86 (s, 2H, CH_2Cl), 3.92 (s, 3H, 2-OCH_3), 3.78 (s, 3H, 5-OCH_3), 2.47 (s, 3H, 6-CH_3), 2.33 (s, 3H, 3-CH_3), 2.31 (s, 3H, 4-CH_3); ^{13}C NMR (50 MHz) δ 153.34, 149.73, 132.31, 128.99, 128.64, 127.58, 61.84, 60.37, 39.44, 13.14, 12.88, 11.75; LREIMS 228(100), 213(34), 193(83), 177(29), 148(19), 133(27), 119(14), 105(18), 91(37), 77(18), 65(14), 53(21); HREIMS calcd for $C_{12}H_{17}O_2Cl$ 228.0917; found 228.0918.

2-Chloromethyl-3,5,6-trimethyl-[1,4]-benzoquinone. Oxidation of the corresponding precursor protected hydroquinone was achieved by exposure of the starting material (1.4 g, 6.14 mmol) to ceric ammonium nitrate (CAN, 6.7 g, 12.28 mmol) in CH_3CN (2 mL) and H_2O (2 mL) at 0°C for 1 h. After ether extraction (3 x 50 mL), a H_2O wash (300 mL), pooling of the organic fractions, drying (anhydrous Na_2SO_4), and concentration *in vacuo*, chromatography of the residue (hexane/diethyl ether, 9:1) afforded the title compound (1.05 g, 83%) as bright yellow crystals; R_f = 0.20 (hexane/diethyl ether, 9:1); mp 43-45°C; IR 2955, 2927, 2856, 1642, 1440, 1375, 1303, 1259, 1110, 1076, 1015, 935, 715; ^{1}H NMR (200 MHz) δ 4.45 (s, 2H, -CH_2-Cl), 2.14 (s, 3H, 3-CH_3), 2.04 (s, 6H, 5-, 6-, -CH_3); ^{13}C NMR (50 MHz) δ 187.36, 185.01, 142.88, 141.40, 140.85, 138.70, 35.82, 12.70, 12.59, 12.43; LREIMS 198(68), 172(40), 171(13), 170(100), 164(22), 163(15), 156(11), 154(29), 136(17), 135(70), 134(18), 121(22), 107(50), 105(11), 91(58), 80(11), 78(18), 77(15), 67(14), 65(11), 54(40), 53(80), 52(28), 51(44); HREIMS calcd for $C_{10}H_{11}O_2Cl$ 198.0448; found 198.0441.

2,3-Dimethoxy-5-methylbenzene-1,4-diol. To a solution of 2,3-dimethoxy-5-methyl-1,4-benzoquinone (2.1 g, 10.99 mmol) in THF (15 mL) at 0°C was added dropwise, a solution of $LiAlH_4$ (0.32 g, 8.45 mmol) in dry diethyl ether (1 mL). After 40 min, the reaction was quenched by the addition of EtOAc followed by 5% aqueous HCl. The mixture was extracted with EtOAc (3 x 50 mL) and the organic layer washed successively with water and brine, dried (anhydrous $MgSO_4$) and evaporated *in vacuo* to give 1.9 g (90%) of a clear oil.

1,2,3,4-Tetramethoxy-5-methylbenzene. To a water bath-cooled solution of 2,3-dimethoxy-5-methylbenzene-1,4-diol (0.25 g, 2.65 mmol) dissolved in EtOH (2 mL) at rt was added in six portions *simultaneously* a solution of NaOH (0.13 g, in 2 mL H_2O) and dimethyl sulfate (0.3 mL). After 45 min, 5% aqueous HCl was added and the mixture was extracted with EtOAc (3 x 50 mL). The organic layer was washed successively with water and brine, dried (anhydrous $MgSO_4$) and evaporated *in vacuo* gave 0.24 g (82%) product as an oil.

1-Chloromethyl-2,3,4,5-tetramethoxy-6-methylbenzene. A solution of 1,2,3,4-tetramethoxytoluene (0.2 g, 0.94 mmol) was dissolved in conc. HCl (15 mL) and warmed to 40°C. Paraformaldehyde (0.5 mL, 4.7 mmol, 37% w/w in H_2O) was added and HCl gas was bubbled through the mixture for 15 min. After stirring for an additional 20 min, ether was added and the organic layer was separated, washed successively with water (4 x 100 mL), brine, dried (anhydrous $MgSO_4$) and evaporated *in vacuo*. Silica gel chromatography of the residue (25% EtOAc-petroleum ether, 1 % Et_3N) afforded the benzylic chloride (0.19g, 78%) as a clear

oil; R_f = 0.72 (25% EtOAc/hexane) IR (neat) 2971, 2938, 2864, 2832, 1469, 1408, 1353, 1280, 1196, 1108, 1073, 1040, 1011, 977, 910; ^{1}H NMR (200 MHz) δ 4.69 (s, 2H, $ArCH_2$), 3.93 (s, 3H, $-CH_3$), 3.92 (s, 3H, $-CH_3$), 3.10 (s, 3H, $-CH_3$), 3.79 (s, 3H, $-CH_3$), 2.28 (s, 3H, $ArCH_3$); ^{13}C NMR (50 MHz) δ 148.69, 148.23, 147.89, 144.90, 126.86, 124.97, 61.94, 61.37, 61.28, 60.94, 38.82, 11.36; LREIMS 260(46), 245(16), 225(100), 210(33), 195(26), 167(44), 139(11), 105(8), 91(8), 81(13), 65(12), 53(25); HREIMS calcd for $C_{12}H_{17}O_4Cl$ 260.0815; found 260.0818.

2-Chloromethyl-5,6-dimethoxy-3-methyl-[1,4]-benzoquinone. Oxidation of the protected hydroquinone used in the syntheses of CoQ_5 was achieved by exposure of the starting material (0.46 g, 1.8 mmol) to CAN (2.0 g, 3.6 mmol) in CH_3CN (5 mL) and H_2O (5 mL) at 0°C for 1 h. The reaction is clean and fast (as determined by GC). After ether extraction (3 x 50 mL), a H_2O wash (300 mL), combining of the organic fractions, drying (anhydrous Na_2SO_4), and concentration *in vacuo*, chromatography of the residue (hexane/diethyl ether, 7:3) afforded the product (84%) as a yellow oil; R_f = 0.23 (hexane/diethyl ether, 7:3); IR 3004, 2952, 2845, 1655, 1611, 1451, 1380, 1343, 1279, 1210, 1155, 1108, 1011, 934; ^{1}H NMR (200 MHz) δ 4.49 (s, 2H, $-CH_2Cl$), 4.09 (s, 3H, $ArOCH_3$), 4.07 (s, 3H, $ArCH_3$), 2.20 (s, 3H, 2-CH_3); ^{13}C NMR (50 MHz) δ 184.16, 182.03, 145.05, 144.61, 142.69, 137.15, 61.52, 61.44, 35.27, 12.21; LREIMS 230(50), 194(80), 179(35), 167(55), 151(40), 131(45), 81(90), 53(100); HREIMS calcd for $C_{10}H_{11}O_4Cl$ 230.0346; found 230.0342.

2-Chloromethyl-3-methyl-[1,4]-naphthoquinone. To 2-methyl-1,4-naphthoquinone (3.0 g, 17 mmol) was added formaldehyde (10 mL, 85 mmol, 37% w/w in H_2O) in glacial HOAc (15 mL). HCl gas was then passed through the mixture until the solution was a blood red color (~30 min). Extraction of the mixture with ether (3 x 50 mL), washing with H_2O, drying over anhydrous $MgSO_4$, and concentration *in vacuo* afforded a residue which was purified by chromatography on silica gel (hexane/diethyl ether, 9:1) to yield 3.3g (86%) of product as a bright yellow powder; R_f = 0.17 (5% acetone/hexane); mp 104-105°C; IR (KBr) 3040, 2989, 2923, 1665, 1621, 1592, 1458, 1397, 1332, 1296, 1200, 974, 733; ^{1}H NMR (200 MHz) δ 8.12-7.70 (m, 4H, Ar), 4.60 (s, 2H, CH_2Cl), 2.30 (s, 3H, 3-CH_3); ^{13}C NMR (50 MHz) δ 185.04, 182.68, 146.80, 141.35, 134.11, 134.03, 132.18, 131.83, 126.80, 126.77, 35.93, 12.90; LREIMS 220(14), 192(6), 184(52), 183(14), 182(7), 184(18), 157(75), 156(6), 129(39), 128(7), 10(15), 77(20), 76(56), 53(11); HREIMS calcd for $C_{12}H_9O_2Cl$ 220.0291; found 220.0286.

2-(6-Chloro-3-methylhex-2-enyl)-3-methyl-[1,4]-naphthoquinone (Table 1, first entry). 5-Chloro-1-pentyne (106 μL, 102 mg, 1.0 mmol), $AlMe_3$ (0.75 mL, 1.5 mmol, 2.0M in hexanes), Cp_2ZrCl_2 (73 mg, 0.25 mmol), and $ClCH_2CH_2Cl$ (1 mL) were used in the carboalumination following the procedure above. $NiCl_2(PPh_3)_2$ (22 mg 0.034 mmol), PPh_3 (18 mg, 0.067 mmol), *n*-BuLi (137 μL, 0.067 mmol, 2.0M), THF (1 mL), and 2-chloromethyl-3-methyl-[1,4]naphthoquinone (147 mg, 0.067 mmol) were used in the cross-coupling reaction following the procedure above. Chromatography of the residue (5% acetone:hexane) afforded the title compound (86%) as a yellow oil; R_f = 0.50 (5% acetone:hexane); IR 3071, 2933, 2850, 1657, 1618, 1595, 1441, 1376, 1330, 1296, 1258, 1176, 1085, 949; ^{1}H NMR (200 MHz) δ 8.10-8.05 (m, 2H, Ar), 7.71-7.67 (m, 2H, Ar), 5.07 (t, J = 8.4 Hz, 1H, vinyl), 3.46 (t, J = 6.7 Hz, 2H, 6'-CH_2-), 3.37 (d, J = 6.9 Hz, 2H, 1'-CH_2-), 2.19 (s, 3H, 3-CH_3), 2.12 (t, J = 7.7 Hz, 2H, 4'-CH_2-), 1.92-1.85 (m, 2H, 5'-CH_2-) 1.80 (s, 3H, 3'-CH_3); ^{13}C NMR (50 MHz) δ 185.57, 184.70, 146.02, 143.65, 136.11, 133.56, 132.30, 126.50, 126.41, 120.52, 44.69, 36.85, 30.85, 26.22, 16.47, 12.93; LREIMS 280(32), 265(26), 217(11), 204(14), 203(83), 189(12), 188(13), 176(57), 175(100), 165(45), 164(25), 161(16), 105(15), 91(25), 81(10), 79(15), 77(17), 69(13), 67(16), 65(10), 55(16), 54(14), 53(20), 51(11); HREIMS calcd for $C_{16}H_{21}O_2Cl$ 280.1230; found 280.1229.

2-(6-Chloro-3-methylhex-2-enyl)-3, 5, 6-trimethyl-[1,4]-benzoquinone (Table 1, second entry). 5-Chloro-1-pentyne (211 μL, 205 mg, 2.0 mmol), $AlMe_3$ (1.5 mL, 3.0 mmol, 2.0M in hexanes), Cp_2ZrCl_2 (146 mg, 0.50 mmol), and $ClCH_2CH_2Cl$ (1 mL) were used in the carboalumination following the procedure above. $NiCl_2(PPh_3)_2$ (32.7 mg, 0.05 mmol), PPh_3 (26 mg, 0.10 mmol), *n*-BuLi (50 μL, 0.10 mmol, 2.0M), THF (1 mL), and chloromethyl quinone (152 mg, 1.2 mmol) were used in the cross-coupling reaction following the procedure above. Chromatography of the residue (hexane/diethyl ether, 95:5) afforded the title compound (70%) as a yellow oil; R_f = 0.10 (hexane/diethyl ether, 95:5); IR 2956, 2925, 2857, 1642, 1442, 1375, 1304, 1259, 1111, 1068, 1005, 935, 897; ^{1}H NMR (200 MHz) δ 5.04-4.97 (t, J = 5.7 Hz, 1H, vinyl), 3.47 (t, J = 6.5 Hz, 2H, 6' -CH_2-), 3.21 (d, J = 6.7 Hz, 2H, 1'-CH_2), 2.10 (t, J = 8 Hz, 2H, 4'-CH_2-), 2.02 (s, 3H, 3-CH_3), 2.01 (s, 6H, 5-, 6- CH_3), 1.92-1.81 (m, 2H, 5'-CH_2-, aliphatic), 1.75 (s, 3H, 3'-CH_3); ^{13}C NMR (50 MHz) δ 188.06, 187.17, 143.06, 140.58, 135.63, 120.93, 44.68, 36.83, 30.84, 25.79, 22.85, 16.30, 12.58, 12.41; LREIMS 280(32), 265(26), 217(11), 204(14), 203(83), 189(12), 188(13), 176(57), 175(100), 165(45), 164(25), 161(16), 105(15), 91(25), 81(10), 79(15), 77(17), 69(13), 67(16), 65(10), 55(16), 54(14), 53(20), 51(11); HREIMS calcd for $C_{16}H_{21}O_2Cl$ 280.1230; found 280.1229.

2,3,5-Trimethyl-6-(3,7,11-trimethyldodeca-2,6,10-trienyl)-[1,4]-benzoquinone (Table 1, third entry). 6,10-Dimethylundeca-5,9-dien-1-yne (176 μL, 176 mg, 1.0 mmol), $AlMe_3$ (0.75 mL, 1.5 mmol, 2.0M in hexanes), Cp_2ZrCl_2 (73 mg, 0.25 mmol), and $ClCH_2CH_2Cl$ (1 mL) were used in the carboalumination following the procedure above. $NiCl_2(PPh_3)_2$ (26 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), *n*-BuLi (40 μL, 0.08 mmol, 2.0M), THF (1 mL), and chloromethyl quinone (158 mg, 0.8 mmol) were used in the cross-coupling reaction following the procedure above. Chromatography of the residue (hexane/diethyl ether, 9/1) afforded the title compound (78%) as a yellow oil; R_f = 0.44 (hexane/diethyl ether, 9/1); IR 2695, 2922, 2855, 1642, 1441, 1375, 1303, 1258, 1109, 1066, 1007, 935, 837, 715; ^{1}H NMR (200 MHz) δ 5.07-4.94 (m, 3H, vinyl), 3.19 (d, J = 7.2 Hz, 2H, 1'-CH_2), 2.01 (s, 2H, 5-CH_3), 2.20 (s, 6H, 2-,3-CH_3), 1.99-1.86 (m, 8H, aliphatic), 1.74 (s, 3H, 3'-CH_3), 1.66 (s, 3H, 7'-CH_3), 1.57 (s, 3H, 11'-CH_3), 1.56 (s, 3H, 11'-CH_3); ^{13}C NMR (50 MHz) δ 188.09, 187.17, 143.35, 140.52, 140.44, 137.23, 135.31, 131.44, 124.52, 124.07, 119.69, 39.87, 26.93, 26.63, 25.89, 25.76, 17.85, 16.50, 16.20, 12.55, 12.35; LREIMS 354(11), 243(112), 218(14), 217(25), 206(17), 205(25), 204(25), 203(100), 202(21), 189(21), 175(20), 173(12), 165(31), 158(14), 136(11), 106(11), 91(27), 81(24), 79(12), 69(99), 67(19), 53(15); HREIMS calcd for $C_{24}H_{34}O_2$ 354.2560; found 354.2554.

2,3,5-Trimethyl-6-(3,7,11,15-tetramethylhexadeca-2,6,10,14-tetraenyl)-[1,4]-benzoquinone (Table 1, fourth entry). 6,10,14-Trimethylpentdeca-5,9,13-trien-1-yne (165 mg, 1.5 mmol), $AlMe_3$ (1.5 mL, 3.0 mmol, 2.0M in hexanes), Cp_2ZrCl_2 (219 mg, 0.75 mmol), and $ClCH_2CH_2Cl$ (1 mL) were used in the carboalumination following the procedure above. $NiCl_2(PPh_3)_2$ (78 mg, 0.12 mmol), PPh_3(63 mg, 0.24 mmol), *n*-BuLi (120 μL, 0.24 mmol, 0.42M), THF (1 mL), and chloromethyl quinone (152 mg, 1.2 mmol) were used in the cross-coupling reaction following the procedure above. Chromatography of the residue (pentane) afforded the title compound (83%) as a yellow oil; R_f = 0.70 (pentane); IR 2964, 2922, 2854, 1643, 1440, 1375, 1304, 1259, 1109, 1024, 936, 835, 715; ^{1}H NMR (200 MHz) δ 5.13-4.92 (m, 4H, vinyl), 3.21 (d, J = 6.7 Hz, 2H, 1'-CH_2), 2.04 (s, 3H, 5-CH_3), 2.02 (s, 6H, 2,3-CH_3), 2.10-2.98 (m, 12H, aliphatic), 1.75 (s, 3H, 3'-CH_3), 1.68 (s, 3H, 7'-CH_3), 1.60 (s, 3H, 11'-CH_3), 1.58 (s, 6H, 2x15'-CH_3); ^{13}C NMR (50 MHz) δ 188.04, 187.11, 143.25, 140.43, 140.37, 137.19, 135.24, 135.01, 131.36, 124.48, 124.28, 124.01, 119.55, 65.96, 39.80, 35.77, 26.85, 26.72, 26.57, 25.80, 25.68, 17.79, 16.42, 16.10, 15.37, 12.48, 12.27; LREIMS 422(8), 243(11), 217(19), 217(22), 207(31), 205(19), 204(15), 203(66), 202(18), 189(8), 175(13), 173(11), 165(46), 159(9), 137(9), 136(11), 135(8), 133(9), 105(9), 95(8), 93(8), 91(16), 81(34), 78(10), 76(13), 69(100), 66(14), 55(12), 53(13); HREIMS calcd for $C_{29}H_{42}O_2$ 422.3185; found 422.3175.

2-(6-Hydroxy-3-methylhex-2-enyl)-3,5,6-trimethyl-[1,4]-benzoquinone (Table 1, fifth entry). 4-Pentyne-1-ol (138 μL, 126 mg, 1.50 mmol), $AlMe_3$ (1.13 mL, 2.25 mmol, 2.0M in hexanes), Cp_2ZrCl_2 (11 mg, 0.375 mmol), and $ClCH_2CH_2Cl$ (1 mL) were used in the carboalumination following the procedure above. $NiCl_2(PPh_3)_2$ (65 mg, 0.10 mmol), PPh_3 (52 mg, 0.20 mmol), *n*-BuLi (100 μL, 0.20 mmol, 2.0M), THF (1 mL), and chloromethyl quinone (174 mg, 0.88 mmol) were used in the cross-coupling reaction following the procedure above. Chromatography of the residue (pentane) afforded the title compound (69%) as a yellow oil; R_f = 0.15 (20% acetone/petroleum ether); IR 3408, 2929, 2871, 1641, 1440, 1375, 1304, 1260, 1109, 1063, 1008, 935, 715; ^1H NMR (200 MHz) δ 5.00 (t, J = 1.4 Hz, 1H, vinyl), 3.60 (t, J = 6.5 Hz, 2H, 6'-CH_2OH), 3.20 (d, J = 7.0 Hz, 2H, 1'-CH_2), 2.11 (s, 3H, 3-CH_3), 2.02 (s, 6H, 5-,6-CH_3) 1.57 (s, 3H, 3'-CH_3), 1.32-1.25 (m, 2H, 5'-CH_2), 0.88 (t, J = 6.2 Hz, 2H, 4'-CH_2); LREIMS 262(12), 229(11), 207(14), 204(14), 203(100), 202(19), 188(12), 178(25), 176(24), 175(24), 174(11), 173(14), 165(19), 164(14), 163(14), 158(12), 136(20), 118(12), 105(15), 91(31), 85(58), 79(17), 77(24), 68(14), 66(18), 64(12), 55(23), 53(11), 53(28), 50(13); HREIMS calcd for $C_{16}H_{22}O_3$ 262.1567; found 262.1560.

2,3,5-Trimethyl-6-(3-methyl-7-triisopropylsilyloxyhept-2-enyl)-[1,4]-benzoquinone (Table 1, sixth entry). Hex-5-ynyloxy-triisopropylsilane (265 μL, 254 mg, 1.0 mmol), $AlMe_3$ (0.75 mL, 1.5 mmol, 2.0M in hexanes), Cp_2ZrCl_2 (73 mg, 0.25 mmol), and $ClCH_2CH_2Cl$ (1 mL) were used in the carboalumination following the procedure above. $NiCl_2(PPh_3)_2$ (16 mg, 0.025 mmol), PPh_3 (13 mg, 0.050 mmol), *n*-BuLi (25 μL, 0.05 mmol, 2.0M), THF (1 mL), and chloromethyl quinone (198 mg, 1.0 mmol) were used in the cross-coupling reaction following the procedure above. Chromatography of the residue (hexane/diethyl ether, 95:5) afforded the title compound (83%) as a yellow oil; R_f = 0.54 (hexane/diethyl ether, 95:5); IR 2939, 2865, 1644, 1462, 1377, 1301, 1257, 1107, 1070, 1007, 882, 716, 680; ^1H NMR (200 MHz) δ 4.95 (t, J = 7.1 Hz, 1H, vinyl), 3.65 (t, J = 6.2 Hz, 2H, 7'-CH_2OSi), 3.20 (d, J = 6.7 Hz, 2H, 1'-CH_2), 2.10 (s, 3H, 5-CH_3), 2.01 (s, 6H, 2,3-CH_3), 1.97 (t, J = 6.1 Hz, 2H, 4'-CH_2-), 1.73 (s, 3H, 3'-CH_3), 1.47-1.42 (m, 4H, aliphatic), 1.07-1.03 (m, 21H, TIPS); ^{13}C NMR (50 MHz) δ 188.15, 187.21, 143.38, 140.49, 137.47, 119.81, 63.46, 39.61, 32. 73, 25.75, 24.22, 18.22, 16.32, 12.58, 12.37, 12.19; LREIMS 432(21), 390(24), 389(66), 293(45), 288(16), 278(17), 263(17), 253(15), 226(34), 207(42), 204(18), 203(89), 199(26), 176(15), 175(18), 159(32), 157(14), 130(27), 120(130, 114(23), 106(19), 102(32), 101(30), 95(37), 90(30), 86(36), 76(27), 74(100), 72(29), 60(65), 59(543); HREIMS calcd for $C_{26}H_{44}O_3$ Si 432.3060; found; 432.3067.

2,3-Dimethoxy-5-methyl-6-(3-methylnon-2-enyl)-[1,4]-benzoquinone (Table 1, seventh entry). Octyne (147 μL, 110 mg, 1.0 mmol), $AlMe_3$ (0.75 mL, 1.5 mmol, 2.0M in hexanes), Cp_2ZrCl_2 (73 mg, 0.25 mmol), and $ClCH_2CH_2Cl$ (1 mL) were used in the carboalumination following the procedure above. $NiCl_2$ (2.9 mg, 0.022 mmol), PPh_3 (12 mg, 0.044 mmol), *n*-BuLi (22 μL, 0.044 mmol, 2.0M), THF(1 mL), and chloromethyl quinone (100 mg, 0.44 mmol) were used in the cross-coupling reaction following the procedure above. Chromatography of the residue (hexane/diethyl ether, 9:1) afforded the title compound (86%) as a yellow oil; R_f = 0.14 (hexane/diethyl ether, 9:1); IR 2941, 2865, 1650, 1611, 1461, 1382, 1264, 1204, 1103, 1012, 882; ^1H NMR (200 MHz) δ 4.90 (t, J = 7.2 Hz, 1H, vinyl), 3.98 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 3.16 (d, J = 6.9 Hz, 2H, 1'-CH_2), 1.99 (s, 3H, 5-CH_3), 1.92 (t, J = 7.4 Hz, 2H, 4'-CH_2-), 1.70 (s, 3H, 3'-CH_3), 1.36-1.22 (m, 8H, aliphatic), 0.84 (t, J = 6.3 Hz, 3H, 9' -CH_3); ^{13}C NMR (50 MHz) δ 184.95, 184.10, 144.53, 144.38, 141.90, 138.98, 138.14, 118.76, 61.30, 39.85, 31.86, 29.06, 27.93, 25.45, 22.78, 16.36, 14.24, 12.10; LREIMS 320(5), 305(7), 236(15), 235(100), 203(6), 197(19), 196(6), 193(6), 176(3), 153(2), 137(2), 105(2), 91(5), 79(4), 55(5), 53(3); HREIMS calcd for $C_{19}H_{28}O_4$ 320.1988; found 320.1991.

2,3-Dimethoxy-5-methyl-6-(3-methyl-7-triisopropylsilyloxyhept-2-enyl)-[1,4]-benzoquinone (Table 1, eighth entry). Hex-5-ynyloxytriisopropylsilane (265 μL, 254 mg, 1.0 mmol), $AlMe_3$ (0.75 mL, 1.5 mmol, 2.0M in hexanes), Cp_2ZrCl_2 (75 mg, 0.25 mmol), and $ClCH_2CH_2Cl$ (1 mL) were used in the carboalumination following the procedure above. $NiCl_2$ (21 mg, 0.16 mmol), PPh_3 (42 mg, 0.050 mmol), *n*-BuLi (80 μL, 0.16

mmol, 2.0M), THF (1 mL), and chloromethyl quinone (184 mg, 0.80 mmol) were used in the cross-coupling reaction following the procedure above. Chromatography of the residue (hexane/diethyl ether, 9/1) afforded the title compound (67%) as a yellow oil; R_f = 0.35 (20% acetone/petroleum ether); IR 2941, 2865, 1650, 1611, 1461, 1382, 1264, 1204, 1103, 1012, 882; ^{1}H NMR (200 MHz) δ 4.93 (t, J = 6.9 Hz, 1H, vinyl), 3.99 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 3.65 (t, J = 6.1 Hz, 2H, 7'-CH_2OSi), 3.18 (d, J = 6.7 Hz, 2H, 1'-CH_2), 2.01 (s, 3H, 5-CH_3), 1.97 (t, J = 5.7 Hz, 2H, 4'-CH_2-), 1.72 (s, 3H, 3'-CH_3), 1.47-1.43 (m, 4H, aliphatic), 1.10-1.00 (m, 21H, TIPS); ^{13}C NMR (50 MHz) δ 188.15, 187.21, 143.38, 140.49, 137.47, 119.81, 63.46, 39.61, 32.73, 25.75, 24.22, 18.22, 16.32, 12.58, 12.37, 12.19; LREIMS 464(17, M^+-2), 423(8), 389(10), 388(16), 311(20), 296(74), 295(38), 235(95), 207(16), 197(59), 181(10), 145(12), 103(27), 75(100), 61(68), 58(68), 55(36); HREIMS calcd for $C_{26}H_{44}O_5Si$ 464.2958; found 464.2967.

2,3-Dimethyl-5-(3-methyl-7-*t*-butyldiphenylsilyloxyhept-2-enyl)-[1,4]-benzoquinone (Table 1, nineth entry). Cp_2ZrCl_2 (52 mg, 0.16 mmol) was purged with argon, cooled to 0°C and 500 μL $AlMe_3$ (2M in hexanes, 1.0 mmol) added. Removal of *ca.* ~90% of solvent *in vacuo* gave a white solid residue that was dissolved in 600 μL of $ClCH_2CH_2Cl$ and allowed to warm to room temperature. After 30 minutes, the pale yellow solution was cooled to 0°C and TBDPS protected 5-hexyn-1-ol (222 mg, 0.66 mmol) was added neat. Additional $ClCH_2CH_2Cl$ (2 x 250 μL) was used to assist transfer. The cooling bath was removed and the reaction allowed to warm to room temperature. After 2.5 h the solvent was removed *in vacuo* and 1 mL of freshly distilled hexanes added and removed *in vacuo*. Another 1 mL portion of hexanes was added and removed *in vacuo*. The orange residue was dissolved in 2 mL of hexanes and carefully decanted from the zirconocene solids *via* cannula. The solids were washed with an additional 1 mL of hexanes and the liquid again carefully decanted to ensure complete alane transfer. The solution was then concentrated to an orange oil *in vacuo*, dissolved in 1 mL of THF, cooled to -78°C and wrapped in aluminum foil in preparation for catalyst and quinone addition.

$NiCl_2(PPh_3)_2$ (14.5 mg, 0.021 mmol) was thoroughly purged with argon and 1 mL of THF added. Slow addition of 80 μL *n*-BuLi (0.53M in hexanes, 0.042 mmol) gave a blood-red solution which was aged for 10 min prior to addition of 79.5 mg (0.43 mmol) of chloromethylquinone **10** in 400 μL THF. The resulting green-blue solution was cannulated into to the precooled -78°C vinyl alane solution. After 1 h at -78°, the reaction was slowly warmed to 0° over a 1.5 h period. The reaction was recooled to -78° and quenched with 10 mL chloroform and 2 g citric acid monohydrate in 10 mL H_2O. After warming to room temperature and stirring for 30 min, the layers were separated and the aqueous layer extracted with three 5 mL portions of chloroform. The combined organic layer was washed with 10 mL brine, dried over anhydrous $MgSO_4$, and concentrated *in vacuo* to a brown oil. Flash chromatography on non-base treated SiO_2 with 2.5% EtOAc / petroleum ether yielded 156 mg of a yellow oil (73%); R_f = 0.35 (5% EtOAc / petroleum ether); IR (neat) 3070, 2931, 2858, 1653, 1616, 1428, 1317, 1111, 736, 702; ^{1}H NMR (400 MHz) δ 7.64 (m, 4H), 7.37 (m, 6H), 6.44 (t, J = 3 Hz, 1H), 5.10 (t, J = 7.2 Hz, 1H), 3.64 (t, J = 6 Hz, 2H), 3.09 (s, J = 7.2 Hz, 2H), 2.0 (m, 8H), 1.57 (s, 3H), 1.51 (m, 4H), 1.02 (s, 9H); ^{13}C NMR (100 MHz) δ 187.81, 187.66, 147.99, 140.96, 140.55, 139.79, 135.55, 134.07, 131.99, 129.49, 127.56, 118.01, 77.20, 63.72, 39.31, 32.14, 27.46, 26.86, 24.00, 19.21, 15.97, 12.39, 12.05; LREIMS 500 (4), 444 (12), 443 (21), 347 (5), 331 (5), 271 (2), 200 (3), 199 (25), 190 (8), 189 (54), 183 (6), 135 (4), 91 (4), 88 (9), 86 (62), 84 (100), 77 (4), 49 (14), 47 (19); HREIMS calcd for $C_{32}H_{40}O_3Si$ 500.2747; found 500.2754.

Menaquinone-3 (vitamin K_2). Cp_2ZrCl_2 (150 mg, 0.50 mmol) was briefly heated under vacuum, cooled to rt, purged thoroughly with argon and cooled to 0°C. $AlMe_3$ in hexanes (900 uL, 1.8 mmol, 2M) was added and *ca.* 90% of the solvent removed *in vacuo* at 0°C. The residue was dissolved in 1.0 mL $ClCH_2CH_2Cl$ and removed from the 0°C bath at which time the solution turned bright yellow. After 25 min of stirring at rt, 176

mg (1.0 mmol) of alkyne were added. The reaction was allowed to slowly warm to rt and monitored by GC. After 3 h, the ratio of alkyne/alane was 7:93. The reaction was cooled to 0°C, the solvent removed *in vacuo* and the resulting orange slurry triturated with 2 mL of freshly distilled hexanes and the solvent removed *in vacuo* at 0°C. Distilled hexanes (3 mL) were again added and the solids allowed to precipitate prior to careful decantation of the solvent *via* cannula. The alane solution was cooled to 0°C and the solvent removed *in vacuo* giving an orange oil which was dissolved in 1.0 mL of THF. The flask was wrapped in aluminum foil and then cooled to -50°C.

$NiCl_2$ (13.0 mg, 0.10 mmol) and PPh_3 (52.5 mg, 0.20 mmol) were dissolved in 5.0 mL of THF in a 10 mL pear shaped flask and stirred for 5 min prior to slow addition of *n*-BuLi (383 uL 0.20 mmol, 0.522M in hexanes). The resulting red-black solution was stirred for 5 min. The quinone (157.2 mg, 0.7 mmol) was added to a separate 10 mL pear shaped flask and 1.0 mL of the Ni(0) solution added (0.02 mmol). The resulting blue solution was stirred for 1 min and then added *via* cannula to the -50°C alane/THF solution. THF (1.0 mL) was used to assist the transfer. The reaction was followed by TLC and quenched after 2.5 h at -50°C with 10 mL of Et_2O and 5 mL of 1M HCl, after which it was warmed to rt. The layers were separated and the aqueous layer extracted 3 x 5 mL Et_2O. The combined organics were washed with 10 mL of saturated aqueous NaCl, dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to a yellow-green oil. Purification by flash chromatography (SiO_2, non-base treated, 5%EtOAc/petroleum ether) yielded 249.3 mg of a vibrant yellow oil (93%); TLC: R_f = 0.29 (5% EtOAc/petroleum ether); IR: (neat) 2966, 2920, 2854, 1660, 1596, 1375, 1329, 1295, 714; ^1H NMR (400 MHz) δ 8.05 (m, 2H), 7.66 (m, 2H), 5.00 (q, 3H, J = 5.3 Hz), 3.34 (d, 2H, J = 6.8 Hz), 2.16 (s, 3H), 1.97 (m, 8H), 1.77 (s, 3H), 1.62 (s, 3H), 1.53 (s, 6H); ^{13}C NMR (100 MHz) δ 185.4, 184.5, 146.1, 143.3, 137.5, 135.1, 133.3, 133.2, 132.2, 132.1, 131.2, 126.3, 126.1, 124.3, 123.8, 119.0, 39.7, 26.7, 26.4, 25.9, 25.7, 17.6, 16.6, 16.4, 16.0, 12.7; LREIMS: 377 (M^++1, 5), 376(M^+, 19), 361(2), 307(5), 265(10), 239(23), 227(18), 226(17), 225(70), 198(13), 197(28), 196(10), 195(12), 187(18), 186(15), 181(16), 178(10), 121(12), 115(10), 105(14), 91(10), 81(22), 77(15), 69(100), 67(15), 55(11), 53(12); HREIMS calcd for $C_{26}H_{32}O_2$ 376.2402; found 376.2403.

CoQ$_5$. Cp_2ZrCl_2 (97 mg, 0.33 mmol) was purged with argon, cooled to 0°C, and $AlMe_3$ (580 μL, 2M in hexanes, 1.16 mmol) was added after which *ca.* ~90% of the solvent was removed *in vacuo*. The white residue was dissolved in 800 μL of $ClCH_2CH_2Cl$ and aged for 20 min at rt prior to addition of 250 μL of neat alkyne (209 mg, 0.66 mmol). After 3 h, a solution of Cp_2ZrCl_2 (101 mg, 0.34 mmol) in 1.2 mL of $ClCH_2CH_2Cl$ was added and allowed to stir for 10 min. The solvent was removed *in vacuo* and 2 mL of freshly distilled hexanes were added and then removed *in vacuo*. The orange residue was dissolved in 2 mL of hexanes and the liquid carefully decanted from the solid zirconocene salts. An additional 1 mL of hexanes was added and the liquid again decanted to ensure complete alane transfer. The solution was then concentrated *in vacuo*, dissolved in 500 μL of THF, and cooled to -78°C in preparation for catalyst and quinone addition.

A solution of $NiCl_2(PPh_3)_2$ (19 mg) and 2 mL of THF was stirred for 2 min prior to slow addition of 105 μL of a 0.53 M solution of *n*-BuLi in hexanes, giving a blood-red/black solution. After 10 min, 900 μL of the solution were removed. Chloromethylquinone **6** (106.4 mg, 0.46 mmol), dissolved in 200 μL of THF, was added to the remainder of the catalyst solution. Additional THF (2 x 200 μL) was used to complete the transfer. After 15 min at rt, the solution was cannulated into the precooled -78°C vinyl alane solution, with a THF wash (2 x 250 μL) being used to assist transfer. After 30 min at -78°C the solution was slowly warmed to 0°C (1.75 h) and the reaction quenched with 10 mL of chloroform and a solution of 2 g citric acid monohydrate in 10 mL H_2O. After 35 min of vigorous stirring, the layers were separated and the aqueous layer extracted with three 5 mL portions of chloroform. The combined organic layers were washed with brine

(1 x 10 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to a red oil. Flash chromatography on non-base treated SiO_2 with 10% EtOAc / petroleum ether gave 212.7 mg of a red oil (81.4%); TLC: R_f = 0.38 (15% EtOAc/petroleum ether); IR (neat) 2922, 2852, 1649, 1611, 1448, 1264, 1204, 1152, 1002, 742; ^1H NMR (400 MHz) δ 5.04 (m, 4H), 4.91 (t, 1H, J = 4.8), 3.96 (s, 3H), 3.95 (s, 3H), 3.15 (d, 2H, J = 7.2 Hz), 2.02 (m, 19H), 1.68 (s, 3H), 1.65 (s, 3H), 1.60 (s, 9H), 1.55 (s, 3H); ^{13}C NMR (100 MHz): 184.7, 183.9, 144.3, 141.6, 138.8, 137.7, 135.2, 134.8, 131.2, 124.3, 124.2, 124.1, 123.8, 118.8, 61.1, 39.7, 26.7, 26.6, 26.5, 25.7, 25.3, 17.6, 16.3, 16.0, 11.9; LREIMS 524 (M^+ + 2, 5), 522 (M^+, 5.2), 235 (40), 197 (44), 196 (15), 135 (10), 121 (9), 107 (9), 95 (11), 93 (12), 81 (39), 69 (100), 68 (11), 67 (10), 57 (14), 43 (12); HREIMS calcd for $C_{34}H_{50}O_4$ 522.3709; found 522.3725.

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