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A new synthetic route to substituted quinones by radical-mediated coupling of organotellurium compounds with quinones

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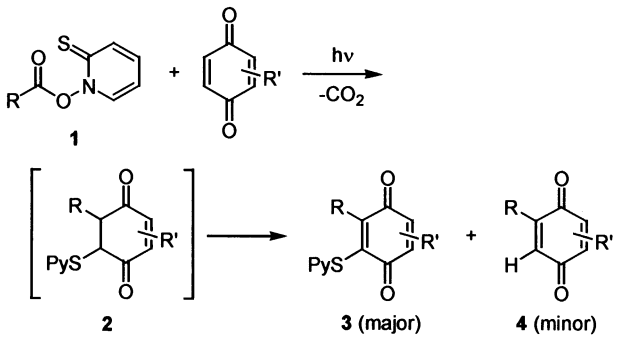
Abstract—Carbon-centered radicals generated from the corresponding organotellurium compounds react with a variety of quinones under photo-thermal conditions to give the monoaddition product in moderate to excellent yield. The reaction can be used for the synthesis of polyprenyl quinoid natural products and *C*-glycosides.

1. Introduction

A great deal of attention has been focused on the synthesis of substituted quinones because of their unique and diverse biological function as mediators for electron-transfer processes and antiviral and anticancer agents.[1] Due to the variety of available quinones, the attachment of the carbon chain to the preexistent quinone skeleton is one of the most attractive and straightforward synthetic approaches.[2] Indeed, enormous effort has been devoted to the realization of this process by organometallic-mediated reactions and cycloadditions.[3] However, while radical-mediated synthesis would seem to be a desirable alternative,[4] only a few examples have been reported so far,[5] and with limited synthetic scope. This is probably because the most conventional reaction system using alkyl halides and tin hydride for carbon-centered radical generations could not be applied owing to the high reactivity of the tin hydride toward quinones.[6] Among the radical-mediated syntheses, the use of the Barton esters **1** as radical precursors under UV irradiation seems to be the best method to date in terms of high coupling efficiency, high functional group compatibility, and availability of the radical precursors (Scheme 1).[5d] This method, however, still has drawbacks; the reaction usually gives a mixture of two quinone products, e.g. **3** and **4** from an initially formed group-transfer adduct, **2**, with moderate selectivity, and the substitution of quinone acceptors has been limited to mono and 1,2-di-substitution. Therefore, the development of a new system that would allow us to expand the synthetic efficiency of the radical-mediated route to substituted quinones is strongly needed.

We have already reported that carbon-centered radicals are reversibly generated from organotellurium compounds under thermolysis and photolysis,[7] and the resulting carbon-centered radicals could be used for various synthetic reactions.[8,9] Therefore, we envisaged that the radicals thus generated would also be useful for the functionalization of quinones. We report herein a new synthesis of substituted quinones by the radical-mediated reaction of organotellurium compounds with various quinones. Preliminary results have already been reported.[10] We now report the full details of the study to demonstrate the synthetic scope of our approach.



Scheme 1.

2. Results and discussions

2.1. Reaction with benzyl, allyl and alkyl tellurides

The reaction conditions have been examined in detail using benzyl *p*-methylphenyl telluride (**5a**)[11] and 1,4-benzoquinone (**6A**). Thus, **5a** was heated with **6A** (2.0 equiv.) in C_6H_6 at 100°C under irradiation with a 200 W high pressure Hg lamp in a Pyrex tube. After silica gel chromatography, we isolated 2-benzyl-1,4-benzoquinone (**7aA**) in 57%

Keywords: quinones; organotellurium compounds; radical precursors.

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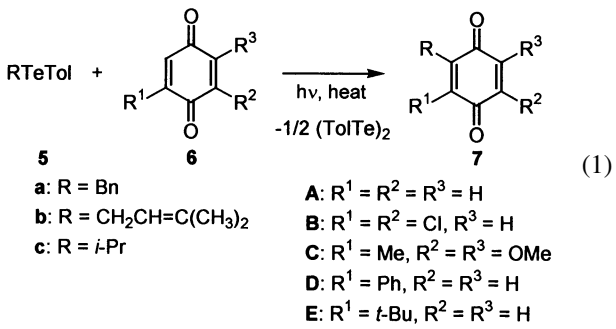


(1)

Table 1. Benzyl radical addition to 1,4-benzoquinones

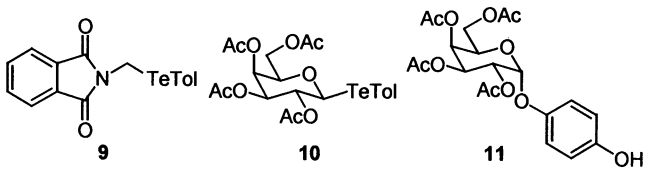
Entry	Solvent	Conditions	Yield (%)
1	C_6H_6	$h\nu$,[a] 100°C, 1 h	57
2[b]	C_6H_6	$h\nu$,[a] 100°C, 1 h	61
3	C_6H_6	100°C, 1 h (dark)	9
4[b]	C_6H_6	100°C, 7 h (dark)	58
5	EtCN	$h\nu$,[a] 100°C, 1 h	57
6	EtOH	$h\nu$,[a] 100°C, 1 h	50

[a] High pressure mercury lamp (200 W) was used.
[b] 3 equiv. of **6A** was used.

yield (Table 1, entry 1). The tellurium moiety was not incorporated into the product and was recovered quantitatively as di-*p*-methylphenyl ditellulide. We also isolated quinhydrone in about 40% yield. The reaction in the dark was slow, but eventually gave the same product after heating at 100°C (entries 3 and 4). The effect of the solvent is marginal, and the reaction in polar solvents, such as acetonitrile and ethanol, produced virtually identical results (entries 5 and 6). The lack of sensitivity to solvent is consistent with the involvement of neutral radical species rather than polar intermediates, such as radical ion species.

The synthetic scope of the current reaction was examined, and the results are summarized in Table 2. A variety of substituted quinones react with organotellurium compounds to give the monoaddition product in good to excellent yield. It is worth noting that trisubstituted quinones, e.g. 2,3-dimethoxy-5-methyl-1,4-benzoquinone (**6C**), 2-methyl-1,4-naphthoquinone (**8**) and 2-hydroxy-1,4-naphthoquinone, could be used as substrates, and that the reaction afforded tetra-substituted quinones in good to excellent yields (entries 3, 6–9 and 11). Since the reaction proceeded under neutral conditions, free hydroxyl groups were compatible with the reaction conditions (entry 7).

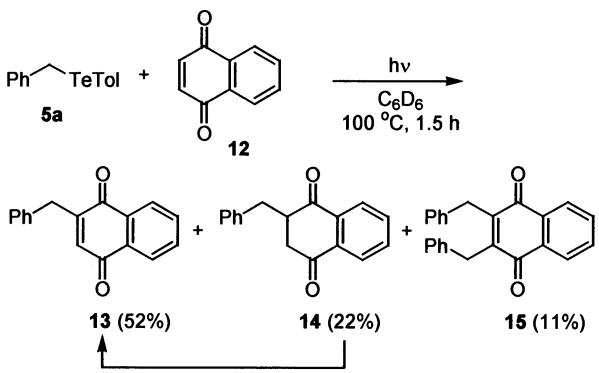
We also used a variety of organotellurium compounds as radical precursors, e.g. benzyl, prenyl isopropyl, α-amino and glycosyl radicals generated from **5**, **9** and **10**, respectively. The reaction of prenyl derivative **5b** with **6C** afforded ubiquinone **1** in good yield (entry 8). In the reaction of the glycosyl telluride **10**, we detected a considerable amount of the side product **11** (45% yield), which could have resulted from the oxidative glycosylation of **10** with 1,4-hydroquinone mediated by 1,4-benzoquinone (entry 14). Despite the side product formation, this method allows direct introduction of quinone groups onto carbohydrate molecules.



The regioselectivity of the reaction deserves comment. The reaction of the phenyl-substituted quinone **6D** occurred at the C-3 position, which is conjugated with the phenyl group, to give the 2,3-disubstituted quinone **7aD** (entry 4). In the reaction of the *t*-butyl-substituted quinone **6E**, the selectivity was controlled by steric factors, and the reaction afforded a 7:3 mixture of the 2,6- and 2,5-disubstituted quinones in a good combined yield (entry 5). In the reaction of prenyl tolyl telluride (**5b**), the prenyl moiety selectively coupled with quinones at the less hindered α-position, and the corresponding γ-coupling products could not be detected (entries 8 and 9).

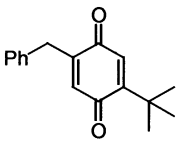
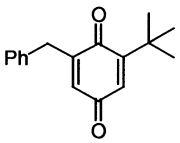
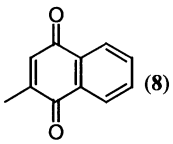
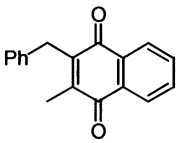
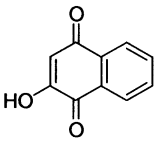
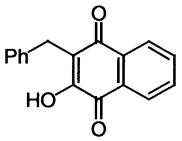
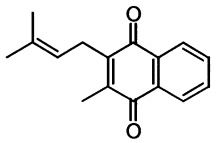
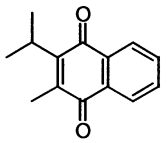
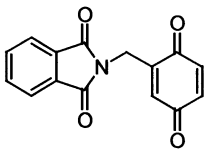
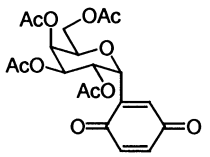
In the reaction with 1,4-naphthoquinone (**12**), the reaction mainly afforded 6-benzyl-1,4-naphthoquinone (**13**) as the major product as expected in 52% yield (Scheme 2). Analysis of the side products also revealed the formation of **14** in 22% yield together with the 5,6-dibenzyl adduct **15** in 11% yield. The formation of a 1,4-diketone adduct such as **14** was observed only in this reaction. Since triethylamine-catalyzed aromatization of **14** to the corresponding hydroquinone proceeded completely under mild thermal conditions, **14** must be formed kinetically. While the origin of the formation of **14** is unclear, it could be transformed into **13** by base-catalyzed isomerization followed by air oxidation of the resulting hydroquinone during work up. Alternatively, quinone **12** could also be used as the oxidizing agent of the hydroquinone.

The current method can be applied to the synthesis of polyprenyl quinonoids as shown in Scheme 3. Thus, geranyl tolyl telluride **16** (a 73:23 mixture of the *trans* and *cis* isomers), which was prepared by SmI_2-mediated coupling of geranyl bromide and ditolyl ditelluride,[12] was allowed to react with **6C** and **8** to give ubiquinone 2 (**17**) and Vitamin



Scheme 2. Et_3N (0.1 equiv.), C_6D_6, 50°C, 2 h, then air (87%) or Et_3N (0.1 equiv.), **12** (3 equiv.), C_6H_6, rt to 60°C, 4 h (82%).

Table 2. Radical-mediated synthesis of substituted quinones

Entry	RTeAr	Quinone	Time (h)	Product	Yield (%)
1	**5a**	**6A**	1	**7aA**	58
2		**6B**	1	**7aB**	71
3		**6C**	2	**7aC**	53
4		**6D**	2.5	**7aD**	57
5		**6E**	1		55
					23
6		 **(8)**	1		87
7			1.5		64
8	**5b**	**6C**	2	**7bC**	41
9		**8**	2		61
10	**5c**	**6A**	3	**7cA**	44
11		**8**	6		50
12	**9**	**6A**	1.5		44
14	**10**	**6A**	2		39

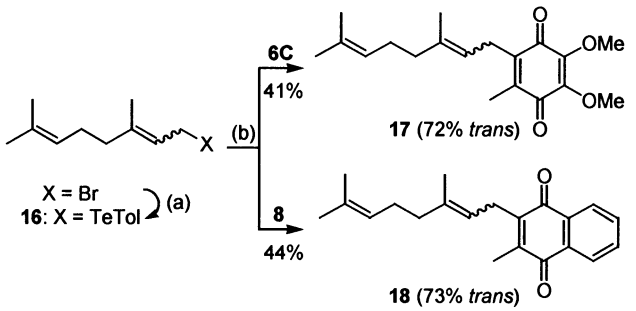
The reaction was carried out with 2 equiv. of quinone under UV irradiation (200 W high pressure Hg lamp) at 100°C.

$K_{2(10)}$ (**18**), respectively, in moderate yields. Analysis of the stereochemistry revealed that a 7:3 mixture of the *trans* and *cis* isomers was formed in both cases. Because neryl tolyl telluride, which was prepared from neryl chloride, isomerized to **16** (ca. 7:3 mixture) before the coupling reaction with the quinones took place, the observed stereoselectivity would be reflected in the stability of the geranyl and neryl radical intermediates.

2.2. Reaction mechanism

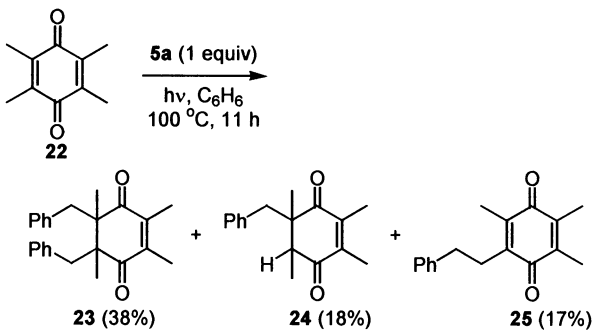
A plausible mechanism for the formation of **7** is shown in Scheme 4. As the radical-mediated carbotelluration of alkynes and alkenes is well known,[8a,e,f,9c–f] the initial step of the current reaction would also follow the same pathway to give **20**. Elimination of aryltellurol from **20** would result in the formation of **21**. The aryltellurols thus formed reduce the quinone **19** to the hydroquinone **22** with the generation of the corresponding diaryl ditelluride.[13] The key intermediate **20**, however, could not be detected by ^{1}H NMR in the experiments performed in C_6D_6 with various quinones.

To clarify the involvement of **20**, we carried out the reaction with tetra-substituted quinones, where elimination of aryl



Scheme 3. (a) SmI_2, HMPA/THF, rt, 2 h, 41% (73% *trans*), (b) *hν* (200 W Hg lamp), C_6D_6, 100°C, 1 h.

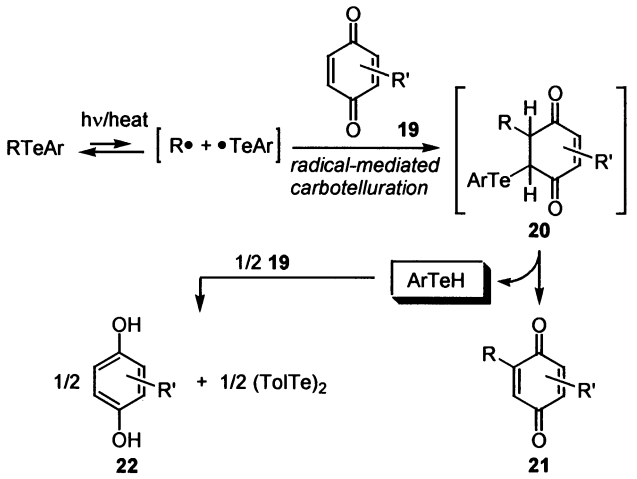
tellurol from the initial intermediate such as **20** was avoided. The reaction of **5a** with duroquinone (**22**) took place slowly and afforded a mixture of several coupling products. Although we could not observe the initial carbotellulated adduct by isolation or by ^1H NMR of the crude mixture in the experiments carried out in C_6D_6, we were able to isolate **23**, **24** and **25** in 38, 18, and 17% yields, respectively (Eq. (2)). Formation of these compounds could be explained by considering the intermediacy of the carbotellulated product **26** (Scheme 5). Thus, **26** reversibly generates radical **27** under the reaction conditions by carbon–tellurium bond homolysis.[6] The radical **27** undergoes a radical coupling reaction with the benzyl radical generated from **5a** to give **23**. It also undergoes hydrogen atom abstraction from **22** to give **24** and the conjugated radical **28**, which couples with the benzyl radical to give **25**. These results are consistent with the mechanism depicted in Scheme 4.



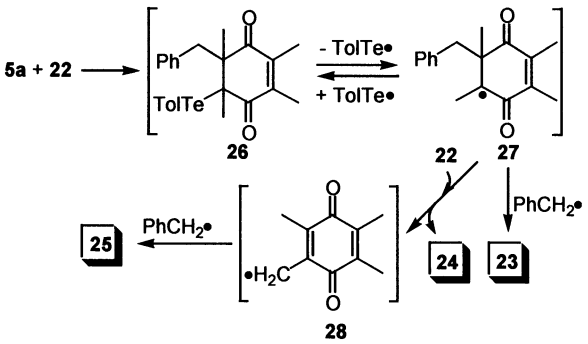
(2)

2.3. Reaction with acyl tellurides

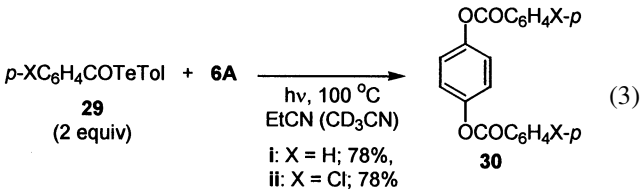
We also examined the introduction of acyl groups onto quinones via acyl radicals.[14] Thus, benzoyl tolyl telluride **29i** was heated with 1,4-benzoquinone (**6A**) in EtCN at 100°C under UV irradiation. Surprisingly, the reaction took place at the oxygen moiety of the quinones, and the bis-acylated hydroquinone **30i** was isolated as the sole product (Eq. (3)).[15] When 2 equiv. of **29i** was used, the yield was improved to 78%. The *p*-chlorobenzoyl telluride **29ii** also afforded **30ii** as the only product. The reaction could be useful for the protection of quinones under neutral conditions, and the product **30** could also serve as the starting material for the photo-Fry rearrangement for the introduction of acyl groups onto hydroquinones.[16]



Scheme 4.



Scheme 5.



(3)

3. Conclusion

We have demonstrated that a variety of organotellurium compounds undergo radical-mediated addition to the carbon–carbon double bond of quinones to give the monoaddition product in moderate to excellent yield. The reaction allows the synthesis of biologically interesting molecules, such as polyprenyl quinonoids and sugar-quinone hybrid molecules. The reaction of acyl tellurides, on the other hand, selectively takes place at the carbonyl oxygen to give the bis-acylated hydroquinones in good yields. We believe that these results clearly demonstrate the advantage of the radical-mediated synthesis of quinones using organotellurium compounds as radical precursors.

4. Experimental

4.1. General remarks

^1H and ^{13}C NMR spectra were measured for a $CDCl_3$

solution of the sample on Varian Gemini 200 or JEOL alpha 400 instruments (300/400 MHz for ^{1}H and 75/100 MHz for ^{13}C). The chemical shifts are reported in parts per million (δ). Infrared spectra were recorded on a Shimazu DR-8000; absorptions are reported in cm^{-1}. Mass spectra were recorded on JEOL IMS-300 or JEOL HX-110A spectrometers. 3-Nitrobenzyl alcohol was used as a matrix for FAB-MS unless otherwise noted. Photochemical reactions were carried out with USHIO Optical Modulex equipped with a 200 W high pressure Hg lamp. Recycling preparative HPLC was performed on a Japan Analytical Industry LC-908 machine equipped with GPC column (JAIGEL 1H and 2H) using $CHCl_3$ as eluent.

4.2. Materials

Unless otherwise noted, materials obtained from commercial suppliers were used without purification. Benzene was distilled over CaH_2, and was stored over molecular sieves. EtCN was distilled successively from P_2O_5 and K_2CO_3 and stored over molecular sieves. Organotellurium compounds were prepared according to the procedure previously reported.[8f,17]

4.2.1. *p*-Methylphenyl prenyl telluride (5b). Sodium borohydride (2.65 g, 70.0 mmol) was added to a solution of *p*-methylphenyl ditelluride (10.9 g, 25.0 mmol) and prenyl chloride (5.23 g, 50.0 mmol) in ethanol (200 mL) in several portions. After the mixture was stirred at room temperature for 2 h, polar materials were removed by passing the crude mixture through a short pad of alumina oxide (50.0 g; elution with degassed diethyl ether) under an argon atmosphere. Removal of solvents followed by distillation under reduced pressure (85°C/0.8 mm Hg) gave **5b** as an orange oil in 22% yield (3.23 g, 11.2 mmol). This compound is sensitive to oxygen, and was stored under an argon atmosphere. Due to its instability, full spectroscopic characterization could not be accomplished. ^{1}H NMR (300 MHz, $CDCl_3$) 1.39 (d, J=0.3 Hz, 3H), 1.68 (s, 3H), 2.35 (s, 3H), 3.61 (s, 3H) 5.42 (triplet of septet, J=8.7, 1.3 Hz, 1H), 7.02 (d, J=7.5 Hz, 2H), 7.65 (d, J=8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 6.71 (CH_3), 16.99 (CH_3), 21.23 (CH_3), 25.52 (CH_2), 108.28 (C), 122.12 (CH), 129.89 (CH, 2C), 134.01 (C), 137.96 (C), 140.13 (CH, 2C).

4.2.2. Reaction of organotellurium compounds with quinones. Typical experimental procedures. 2-Benzyl-1,4-benzoquinone (7aA). A solution of benzyl *p*-methylphenyl telluride (**5a**, 111 mg, 0.36 mmol) and 1,4-benzoquinone (**6A**, 78.0 mg, 0.72 mmol) in benzene (0.6 mL) in a Pyrex tube was irradiated with a 200 W high pressure mercury lamp at 100°C for 1 h. After the solvent was removed under reduced pressure, the crude mixture was purified by flush chromatography (silica gel 6.4 g; elution with 5% ethyl acetate in hexane) to give **7aA** in 57% yield (40.4 mg). IR (neat) 1655 (s), 1599 (s), 1496 (s), 1454 (m), 1352 (m), 704 (s); ^{1}H NMR (300 MHz, $CDCl_3$) 3.75 (d, J=1.2 Hz, 2H), 6.37 (m, 1H), 6.70 (dd, J=9.9, 3.2 Hz, 1H), 7.18–7.36 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) 35.14 (CH_2), 127.16 (CH), 129.00 (CH), 129.50 (CH, 2C), 133.41 (CH), 136.49 (CH, 2C), 136.79 (CH), 148.90 (C), 174.00 (C=O), 179.00 (C=O) (one sp^2 carbon could not be identified probably due to overlapping with other peaks.); LRMS (EI) *m/e* 198 $(M)^+$; HRMS (EI) Calcd for $C_{13}H_{10}O_2$ $(M)^+$, 198.0681; Found 198.0686.

4.2.3. 3-Benzyl-2,6-dichloro-1,4-benzoquione (7aB). IR (KBr) 1684 (s), 1659 (s), 1291 (m), 1213 (m), 1105 (m), 1007 (m), 893 (m), 780 (s), 768 (m), 718 (s), 696 (m); ^{1}H NMR (300 MHz, $CDCl_3$) 4.00 (s, 2H), 7.01 (s, 1H), 7.17–7.31 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) 33.35 (CH_2), 127.11 (CH), 128.76 (CH, 2C), 129.14 (CH, 2C), 133.62 (CH), 135.90 (C), 140.59 (C), 143.20 (C), 144.51 (C), 172.97 (C), 182.36 (C); LRMS (EI) *m/e* 268, 266 $(M)^+$; HRMS (EI) Calcd for $C_{13}H_8O_2Cl_2$ $(M)^+$, 266.0094; Found 265.9901; Anal. Calcd for $C_{13}H_0O_2Cl_2$: C, 58.46; H, 3.02. Found: C, 58.59; H, 2.88.

4.2.4. 2-Benzyl-5,6-dimethoxy-3-methyl-1,4-benzoquinone (7aC). IR (KBr) 1671 (s), 1642 (s), 1609 (s), 1267 (s), 1206 (m), 1156 (m); ^{1}H NMR (300 MHz, $CDCl_3$) 2.08 (s, 3H), 3.84 (s, 2H), 3.98 (s, 3H), 3.99 (s, 3H), 7.14–7.22 (m, 3H), 7.23–7.30 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 12.45 (CH_3), 31.70 (CH_2), 61.21 (CH_3, 2C), 126.60 (CH), 128.74 (CH), 128.79 (CH), 138.00 (C), 138.03 (C), 140.07 (C), 141.11 (C), 144.53 (C), 184.31 (C=O), 184.87 (C=O); LRMS (EI) *m/e* 272 $(M)^+$; HRMS (EI) Calcd for $C_{16}H_{16}O_4$ $(M)^+$, 272.1049; Found 272.1046.

4.2.5. 2-Benzyl-3-phenyl-1,4-benzoquinone (7aD). IR (KBr) 1653 (s), 1606 (m), 1588 (m), 1495 (m), 1453 (m); ^{1}H NMR (400 MHz, $CDCl_3$) 3.78 (s, 2H), 6.82 (d, J=10.1 Hz, 1H), 6.83 (d, J=10.1 Hz, 1H), 6.91–6.95 (m, 2H), 7.10–7.21 (m, 5H), 7.40–7.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 32.76 (CH_2), 126.37 (CH), 128.29 (CH, 2C), 128.43 (CH, 2C), 128.64 (CH, 2C), 128.82 (CH), 129.27 (CH, 2C), 132.45 (C), 136.28 (CH), 136.51 (CH), 138.24 (C), 143.50 (C), 144.68 (C), 187.08 (C=O), 187.65 (C=O); LRMS (EI) *m/e* 274 $(M)^+$; HRMS (EI) Calcd for $C_{17}H_{14}O_2$ $(M)^+$, 274.0994; Found 274.1003; Anal. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 83.16; H, 5.33. Regiochemistry was determined by the existence of H^4–H^5 coupling in ^{1}H NMR (10.1 Hz).

4.2.6. 2-Benzyl-3-methyl-1,4-naphthoquinone. IR (KBr) 1663 (s), 1619 (w), 1592 (m), 1333 (s), 1293 (s), 716 (s); ^{1}H NMR (300 MHz, $CDCl_3$) 2.25 (s, 3H), 4.04 (s, 2H), 7.16–7.30 (m, 5H), 7.67–7.73 (m, 2H), 8.06–8.12 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 13.22 (CH_3), 32.40 (CH_2), 126.42 (CH_3), 126.57 (CH), 126.63 (CH), 128.74 (CH, 2C), 128.80 (CH, 2C), 132.19 (C), 132.28 (C), 133.61 (CH), 133.64 (CH), 138.23 (C), 144.59 (C), 145.52 (C), 184.90 (C=O), 185.64 (C=O); LRMS (EI) *m/e* 262 $(M)^+$; HRMS (EI) Calcd for $C_{18}H_{14}O_2$ $(M)^+$, 262.0994; Found 262.0994; Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.26; H, 5.52.

4.2.7. 2-Hydroxy-3-benzyl-1,4-naphthoquinone. IR (KBr) 3345 (s, sharp), 1661 (s), 1644 (s), 1591 (m), 1371 (s), 1273 (m), 1223 (s); ^{1}H NMR (300 MHz, $CDCl_3$) 3.95 (s, 2H), 7.14–7.20 (m, 1H), 7.23–7.29 (m, 2H), 7.38–7.41 (m, 2H), 7.45 (br, s, 1H), 7.66 (dt, J=7.5, 1.5 Hz, 1H), 7.74 (dt, J=7.5, 1.5 Hz, 1H), 8.06 (dd, J=7.8, 1.5 Hz, 1H), 8.11 (dd, J=7.8, 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 28.98 (CH_2), 123.11 (C), 126.19 (CH), 126.37 (CH), 126.96 (CH), 128.51 (CH, 2C), 129.26 (CH, 2C), 129.44 (C), 132.84 (C),

133.04 (CH), 135.07 (CH), 138.97 (C), 167.95 (C), 181.81 (C═O), 184.52 (C═O); LRMS (EI) *m/e* 264 $(M)^+$; HRMS (EI) Calcd for $C_{17}H_{12}O_3$ $(M)^+$, 264.0786; Found 264.0792; Anal. Calcd for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58. Found: C, 82.26; H, 5.52.

4.2.8. 2,3-Dimethoxy-5-methyl-6-prenyl-1,4-benzoquinone (7bC). IR (neat) 1649 (s), 1611 (s), 1264 (s), 1204 (m), 1154 (m), 1032 (m); ^{1}H NMR (300 MHz, $CDCl_3$) 1.68 (d, *J*=0.9 Hz, 3H), 1.75 (s, 3H), 2.02 (s, 3H), 3.18 (br, d, *J*=7.2 Hz, 2H), 3.98 (s, 3H), 4.00 (s, 3H), 4.94 (triplet of septet, *J*=13.8, 0.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 11.84 (CH_3), 17.89 (CH_3), 25.37 (CH_3), 25.67 (CH_2), 61.15 (CH_3, 2C), 119.12 (CH), 134.15 (C), 141.75 (C), 144.39 (C), 144.55 (C), 168.05 (C), 184.18 (C═O), 185.03 (C═O); LRMS (EI) *m/e* 250 $(M)^+$; HRMS (EI) Calcd for $C_{14}H_{18}O_4$ $(M)^+$, 250.1205; Found 250.1217.

4.2.9. 2-Methyl-3-prenyl-1,4-naphthoquinone. IR (neat) 1661 (s), 1619 (m), 1597 (s), 1375 (m), 1392 (s), 1296 (s), 713 (s); ^{1}H NMR (300 MHz, $CDCl_3$) 1.69 (d, *J*=0.9 Hz, 3H), 1.80 (d, *J*=1.2 Hz, 3H), 2.19 (d, *J*=0.6 Hz, 3H), 3.36 (br, d, *J*=6.9 Hz, 2H), 5.02 (triplet of septet, *J*=7.2, 1.4 Hz, 1H) 7.65–7.71 (m, 2H), 8.03–8.10 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 12.57 (CH_3), 17.98 (CH_3), 25.69 (CH_3), 26.08 (CH_2), 119.33 (CH), 126.30 (CH), 126.40 (CH), 132.27 (C) 132.29 (C), 133.42 (CH), 133.46 (CH), 134.07 (C), 143.42 (C), 146.20 (C), 184.75 (C═O), 185.66 (C═O); LRMS (EI) *m/e* 240 $(M)^+$; HRMS (EI) Calcd for $C_{16}H_{16}O_2$ $(M)^+$, 240.1150; Found 240.1139.

4.2.10. 2-*i*-Propyl-1,4-benzoquinone (7bC)..[18] ^{1}H NMR (300 MHz, $CDCl_3$) 1.14 (d, *J*=6.9 Hz, 6H), 3.03 (doublet of sept, *J*=6.9, 1.3 Hz, 1H), 6.55 (s, 1H), 6.71 (dd, *J*=10.2, 2.1 Hz, 1H), 6.77 (d, *J*=10.2 Hz, 1H); LRMS (EI) *m/e* 150 $(M)^+$.

4.2.11. 2-Methyl-3-*i*-propyl-1,4-naphthoquinone..[5d] IR (KBr) 1465 (s), 1650 (s), 1593 (m), 1327 (m), 1296 (s), 720 (m); ^{1}H NMR (300 MHz, $CDCl_3$) 1.37 (d, *J*=7.2 Hz, 6H), 2.22 (s, 3H), 3.27 (hept, *J*=7.2 Hz, 1H), 7.62–7.73 (m, 2H), 7.95–8.15 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 12.35 (CH_3), 20.44 (CH_3, 2C), 29.31 (CH), 125.98 (CH), 126.10 (CH), 131.74 (C), 132.74 (C), 133.04 (CH), 133.32 (CH), 142.65 (C), 151.34 (C), 184.83 (C═O), 185.62 (C═O), LRMS (EI) *m/e* 414 $(M)^+$; HRMS (EI) Calcd for $C_{14}H_{14}O_2$ $(M)^+$, 214.0994; Found 214.0994.

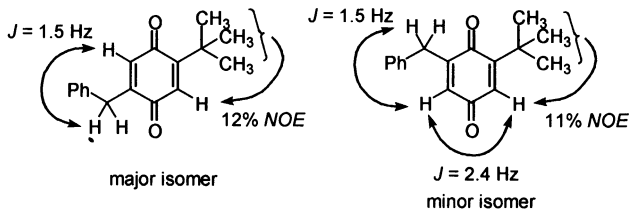
4.2.12. 2-(Methylphthalimido)-1,4-benzoquinone. IR (KBr) 1774 (s), 1711 (s), 1670 (s), 1391 (s), 1321 (m), 957 (m); ^{1}H NMR (300 MHz, $CDCl_3$) 4.72 (d, *J*=2.1 Hz, 2H), 6.38 (q, *J*=2.2 Hz, 1H), 6.76 (dd, *J*=10.1, 2.4 Hz, 1H), 6.83 (d, *J*=10.1 Hz, 1H), 7.74–7.83 (m, 2H), 7.86–7.95 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 35.77 (CH_2), 123.81 (CH, 2C), 131.32 (CH), 134.35 (C), 134.60 (CH, 2C), 136.68 (CH), 167.63 (C), 186.40 (C), 186.91 (C); LRMS (EI) *m/e* 267 $(M)^+$; HRMS (EI) Calcd for $C_{15}H_9NO_4$ $(M)^+$, 267.0532; Found 267.0529.

4.2.13. 1-(1′,4′-Benzoquinon-2′-yl)-2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranoside. IR (KBr) 1752 (s), 1661 (s), 1603 (w), 1372 (m), 1225 (s), 1046 (m); ^{1}H NMR (300 MHz, $CDCl_3$) 2.00 (s, 3H), 2.06, (s, 3H), 2.09 (s, 3H), 2.24 (s, 3H), 4.19 (dd, *J*=12.9, 2.7 Hz, 1H), 4.45 (ddd, *J*=9.6, 6.6, 2.7 Hz, 1H), 4.84 (dd, *J*=12.9, 9.6 Hz, 1H), 5.12 (dd, *J*=3.9, 1.8 Hz, 1H), 5.24 (s, 1H), 5.33 (t, *J*=3.3 Hz, 1H), 5.48 (dd, *J*=6.6, 3.3 Hz, 1H), 6.73 (d, *J*=2.1 Hz, 1H), 6.78 (dd, *J*=9.9, 2.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 20.45 (CH_3), 20.57 (CH_3), 20.62 (CH_3), 20.83 (CH_3), 59.04 (CH_2), 63.94 (CH), 65.05 (CH), 67.13 (CH), 69.50 (CH), 72.69 (CH), 132.50 (CH), 136.38 (CH), 136.79 (CH), 144.15 (C), 169.23 (C═O), 169.64 (C═O), 169.67 (C═O), 171.08 (C═O), 185.56 (C═O), 187.20 (C═O); LRMS (FAB) *m/e* 439 $(M+1)^+$; Anal. Calcd for $C_{20}H_{22}O_{11}$: C, 54.80; H, 5.28. Found: C, 54.82; H, 5.28.

4.2.14. (4-Hydroxyphenyloxy)-2,3,4,6-tetra-*O*-acetyl-D-galactopyranoside (10). IR (KBr) 3400 (s, broad), 1752 (s), 1705 (s), 1599 (w), 1512 (s), 1374 (s), 1040 (s); ^{1}H NMR (300 MHz, $CDCl_3$) 1.98 (s, 3H), 2.03 (s, 3H), 2.10 (s, 3H), 2.17 (s, 3H), 4.04–4.16 (m, 2H), 4.39 (br, t, *J*=4.8 Hz, 1H), 5.26 (dd, *J*=10.2, 3.6 Hz, 1H), 5.54 (s, 2H), 5.64 (d, *J*=3.6 Hz, 1H), 6.77 (d, *J*=9.0 Hz, 2H), 6.92 (d, *J*=9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 20.48 (CH_3), 20.49 (CH_3), 20.54 (CH_3), 20.62 (CH_3), 61.55 (CH_2), 66.90 (CH), 67.56 (CH), 67.92 (CH), 67.95 (CH), 95.83 (CH), 116.09 (CH, 2C), 118.39 (CH, 2C), 150.25 (C), 151.83 (C), 170.40 (C═O), 170.52 (C═O), 170.75 (C═O, 2C); LRMS (FAB) *m/e* 440 $(M)^+$; Anal. Calcd for $C_{20}H_{24}O_{11}$: C, 54.54; H, 5.49. Found: C, 54.29; H, 5.60.

4.2.15. 5-Benzyl-2-*t*-butyl-1,4-benzoquinone and 3-benzyl-2-*t*-butyl-1,4-benzoquinone. A solution of benzyl *p*-methylphenyl telluride (**5a**, 111 mg, 0.36 mmol) and 2-*t*-butyl-1,4-benzoquinone (118 mg, 0.72 mmol) in benzene (0.6 mL) in a Pyrex tube was irradiated with a 250 W Hg lamp at 100°C for 1 h. After the solvent was removed under reduced pressure, the crude mixture was purified by flash chromatography (silica gel 6.5 g; elution with 2% ethyl acetate in hexane) followed by preparative GPC to give the title compounds as a 71:29 inseparable mixture in 78% yield (71.7 mg). IR (neat) 1651 (s), 1599 (m), 1366 (m), 1248 (m), 698 (m); ^{1}H NMR (300 MHz, $CDCl_3$) 1.26 (s, 6.3H), 1.29 (s, 2.7H), 3.71 (d, *J*=1.5 Hz, 1.4H), 3.74 (d, *J*=1.5 Hz, 0.6H), 6.24 (dt, *J*=2.4, 1.5 Hz, 0.3H), 6.26 (t, *J*=1.5 Hz, 0.7H), 6.53 (d, *J*=2.4 Hz, 0.3H), 6.59 (s, 0.7H), 7.16–7.36 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) 29.17 (CH_3, major), 29.25 (CH_3, minor), 34.49 (CH_2, major), 35.05 (C, major), 35.36 (C, minor), 35.55 (CH_2, minor), 126.90 (CH, major), 128.80 (CH, major), 128.82 (CH, minor), 129.39 (CH, major), 131.38 (CH, minor), 131.60 (CH, major), 132.08 (CH, minor), 135.34 (CH, major), 136.72 (C, major), 136.84 (C, minor), 146.94 (C, major), 150.40 (C, minor), 155.91 (C, major), 156.20 (C, minor), 187.18 (C═O, minor), 187.89 (C═O, major), 188.26 (C═O, major), 188.41 (C═O, minor), (two sp^2 carbon could not be identified probably due to overlapping with other peaks.); LRMS (EI) *m/e* 254 $(M)^+$; HRMS (EI) Calcd for $C_{17}H_{18}O_2$ $(M)^+$, 254.1307; Found 254.1307. Regiochemistry was assigned by coupling constant analyses in ^{1}H NMR spectra and

NOE spectra as shown below.



4.2.16. 2-Benzyl-1,4-naphthoquinone (13). A solution of benzyl *p*-methylphenyl telluride (**5a**, 111 mg, 0.36 mmol) and 1,4-naphthoquinone (114 mg, 0.72 mmol) in benzene (0.6 mL) in a sealed Pyrex tube was irradiated with a 250 W Hg lamp at 100°C for 1.5 h. After the solvent was removed under reduced pressure, the crude mixture was purified by flush chromatography (silica gel 5.4 g; elution with 4% ethyl acetate in hexane) to give **13** in 54% yield (49.1 mg), 2-benzyl-2,3-dihydro-1,4-naphthoquinone (**14**) in 19% yield (17.1 mg), and, 2,3-dibenzyl-1,4-naphthoquinone (**15**) in 12% yield (15.0 mg).

13. IR (KBr) 1659 (s), 1592 (s), 1493 (m), 1330 (m), 1260 (m); ^{1}H NMR (300 MHz, $CDCl_3$) 3.90 (d, J=1.2 Hz, 2H), 6.69–6.63 (m, 1H), 7.22–7.38 (m, 5H), 7.68–7.76 (m, 2H), 8.00–8.14 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 35.62 (CH_2), 126.13 (CH), 126.70 (CH), 127.02 (CH), 128.91 (CH, 2C), 129.50 (CH, 2C), 132.14 (C), 132.22 (C), 133.76 (CH), 133.81 (CH), 135.71 (CH), 136.80 (C), 150.96 (C), 185.12 (C=O), 185.28 (C=O); LRMS (EI) *m/e* 248 $(M)^+$; HRMS (EI) Calcd for $C_{17}H_{12}O_2$ $(M)^+$, 248.0837; Found 248.0831.

14. IR (KBr) 1684 (s), 1591 (s), 1497 (w), 1459 (w), 1422 (w), 1298 (w), 1266 (m), 720 (m); ^{1}H NMR (300 MHz, $CDCl_3$) 2.74–2.88 (m, 2H), 3.02 (dd, J=16.5, 5.4 Hz, 2H), 3.28–3.42 (m, 2H), 7.18–7.36 (m, 5H), 7.70–7.80 (m, 2H), 7.98–8.14 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 36.36 (CH_2), 42.30 (CH_2), 49.04 (CH), 126.54 (CH), 126.77 (CH), 127.10 (CH), 128.72 (CH, 2C), 129.35 (CH, 2C), 134.23 (CH), 134.49 (CH), 135.15 (C), 135.24 (C), 138.11 (C), 196.05 (C=O), 197.98 (C=O); LRMS (EI) *m/e* 250 $(M)^+$; HRMS (EI) Calcd for $C_{17}H_{14}O_2$ $(M)^+$, 250.0094; Found 250.0093.

15. IR (KBr) 1659 (s), 1592 (m), 1493 (w), 1451 (w), 1293 (s), 723 (s); ^{1}H NMR (300 MHz, $CDCl_3$) 4.09 (s, 4H), 7.17–7.28 (m, 10H), 7.66–7.73 (m, 2H), 8.04–8.12 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 32.34 (CH_2, 2C), 126.55 (CH, 4C), 128.62 (CH, 2C), 128.74 (CH, 4C), 132.14 (C, 2C), 133.69 (CH, 2C), 138.05 (C, 2C), 146.30 (C=O, 2C), 185.34 (C=O, 2C); LRMS (EI) *m/e* 338 $(M)^+$; Anal. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.05; H, 5.43.

4.3. Conversion of 14 into 13

A solution of **14** (25.0 mg, 0.1 mmol) and triethylamine (3.6 mg, 0.036 mmol) in benzene-d_6 (0.6 mL) was heated at 50°C for 2 h under an argon atmosphere. After air was passed through the reaction mixture for 0.5 h, the solvent was removed. ^{1}H NMR analysis of the crude mixture in the presence of internal standard indicated the formation of **13** in 87% yield.

4.3.1. *p*-Methylphenyl geranyl telluride (16). A solution of 1,2-diiodoethane (620 mg, 2.2 mmol) in THF (22 mL) was slowly added to samarium metal (662 mg, 4.4 mmol) under a N_2 atmosphere in a glove box at room temperature, and the resulting mixture was stirred for 15 min. To this mixture was added HMPA (3 mL) followed by di-*p*-methylphenyl ditelluride (463 mg, 1.1 mmol), and the resulting solution was stirred for 1 h. Geranyl bromide (0.40 mL, 2.0 mmol) was added, and the resulting solution was stirred for 1.5 h at room temperature. Heptane (50 mL) was added, and the organic phase was washed repeatedly with saturated aqueous sodium chloride, dried over $MgSO_4$, and evaporated to give a crude oil (881 mg), which was a 60:40 mixture of **16** and di-*p*-methylphenyl ditelluride. This mixture was used in the following step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) 1.54 (s, 3H), 1.70 (s, 3H), 1.79 (s, 3H), 1.98–2.44 (m, 4H), 2.44 (s, 3H), 3.71 (d, J=8.4 Hz, 2H), 5.12–5.23 (m, 1H), 5.45–5.60 (m, 1H), 7.06–7.15 (m, 2H), 7.72–7.82 (m, 2H).

4.3.2. Ubiquinone 2 (17). A solution of crude **16** containing di-*p*-methylphenyl ditelluride (233.1 mg, **16**/ditelluride =60:40, 0.36 mmol for **16**) 2,3-dimethoxy-5-methyl-1,4-benzoquinone (131 mg, 0.72 mmol) in benzene (0.6 mL) in a sealed Pyrex tube was irradiated with a 250 W Hg lamp at 100°C for 2 h. After the solvent was removed under reduced pressure, the crude mixture was purified by flash chromatography (silica gel 8.2 g; elution with 15% ethyl acetate in hexane) to give the title compound **17** in 41% yield (48 mg) as a 72:28 mixture of *trans* and *cis* isomers. The ^{1}H NMR of the products was identical to that in the previous report.[19] ^{1}H NMR (300 MHz, $CDCl_3$) 1.58 (s, 2.1H), 1.63 (s, 0.9H), 1.65 (s, 2.1H), 1.68 (s, 0.9H), 1.70 (s, 0.9H), 1.73 (s, 2.1H), 2.02 (s, 3H), 1.92–2.23 (m, 4H), 3.18 (d, J=7.2 Hz, 2H), 3.980 (s, 0.9H), 3.985 (s, 2.1H), 3.995 (s, 0.9H), 3.998 (s, 2.1H), 4.90–4.98 (m, 1H), 5.00–5.07 (m, 0.7H), 5.11–5.19 (m, 0.3H).

4.3.3. Vitamin $K_{2(10)}$ (18). A solution of crude **16** containing di-*p*-methylphenyl ditelluride (233.1 mg, **16**/ditelluride=60:40, 0.36 mmol for **16**) 2-methyl-1,4-naphthoquinone (124 mg, 0.72 mmol) in benzene (0.6 mL) in a sealed Pyrex tube was irradiated with a 250 W Hg lamp at 100°C for 1 h. After the solvent was removed under reduced pressure, the crude mixture was purified by flash chromatography (silica gel 10.6 g; elution with 5% ethyl acetate in hexane) to give the title compound **18** in 44% yield (49 mg) as a 73:27 mixture of the *trans* and *cis* isomers. The ^{1}H NMR of the products was identical to that in the previous report.[20] ^{1}H NMR (300 MHz, $CDCl_3$) 1.49 (s, 2.1H), 1.55 (d, J=1.2 Hz, 2.1H), 1.57 (s, 0.9H), 1.62 (d, J=1.5 Hz, 0.9H), 1.63 (d, J=1.5 Hz, 0.9H), 1.71 (d, J=0.9 Hz, 2.1H), 1.82–2.21 (m, 4H), 2.11 (s, 2.1H), 2.12 (s, 0.9H), 3.29 (d, J=6.9 Hz, 2H), 4.88–4.50 (m, 1.7H), 5.05–5.14 (m, 0.3H), 7.76–7.65 (m, 2H), 7.95–8.04 (m, 2H).

4.3.4. Reaction of 5a with duroquinone. A solution of benzyl *p*-methylphenyl telluride (**5a**, 558 mg, 1.8 mmol) and duroquinone (296 mg, 1.8 mmol) in benzene (3 mL) in

a sealed Pyrex tube was irradiated with a 250 W Hg lamp at 100°C for 12 h. After the solvent was removed under reduced pressure, the crude mixture was purified by flash chromatography (silica gel 25 g; elution with 5% ethyl acetate in hexane) followed by preparative GPC to give 5,6-dibenzyl-2,3,5,6-tetramethyl-cyclohex-2-ene-1,4-dione (**23**, 237 mg), 5-benzyl-2,3,5,6-tetramethyl-cyclohex-2-ene-1,4-dione (**24**, 83 mg), and 2,3,5-trimethyl-6-phenethyl-1,4-benzoquinone (**25**, 77 mg) in 38, 18, 17% yields, respectively.

23. IR (KBr) 1674 (s), 1634 (m), 1495 (m), 1455 (m), 1374 (m), 764 (m), 702 (m); ^{1}H NMR (300 MHz, $CDCl_3$) 1.82 (s, 6H), 1.99 (s, 6H), 2.74 (d, J=13.5 Hz, 2H), 2.82 (d, J=13.5 Hz, 2H), 6.77–6.84 (m, 4H), 7.14–7.30 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) 12.99 (CH_3, 2C), 15.25 (CH_3, 2C), 44.63 (CH_2, 2C), 58.74 (C, 2C), 126.77 (CH, 2C), 127.96 (CH, 4C), 129.72 (CH, 4C), 136.31 (C, 2C), 142.90 (C, 2C), 202.29 (C=O, 2C); LRMS (EI) *m/e* 346 $(M)^+$; HRMS (EI) Calcd for $C_{24}H_{26}O_2$ $(M)^+$, 346.1933; Found 346.1922.

24. IR (KBr) 1678 (s), 1497 (m), 1374 (m), 737 (m), 702 (m); ^{1}H NMR (300 MHz, $CDCl_3$) 1.21 (s, 3H), 1.33 (d, J=6.9 Hz, 3H), 1.94 (s, 6H), 2.77 (d, J=13.5 Hz, 1H), 2.80 (q, J=6.9 Hz, 1H), 2.83 (d, J=13.5 Hz, 1H), 6.82–6.92 (m, 2H), 7.15–7.18 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) 10.03 (CH_3), 12.62 (CH_3), 13.14 (CH_3), 21.45 (CH_3), 41.11 (CH_2), 52.08 (CH), 54.16 (C), 126.68 (CH), 128.00 (CH, 2C), 129.84 (CH, 2C), 136.44 (C), 143.55 (C), 143.97 (C), 200.00 (C=O), 202.37 (C=O); LRMS (EI) *m/e* 256 $(M)^+$; HRMS (EI) Calcd for $C_{17}H_{20}O_2$ $(M)^+$, 256.1463; Found 256.1456.

25. ^{1}H NMR (300 MHz, $CDCl_3$) 1.87 (s, 3H), 2.02 (s, 6H), 2.66–2.81 (m, 4H), 7.15–7.23 (m, 3H), 7.23–7.32 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 11.89 (CH_3), 12.24 (CH_3), 12.30 (CH_3), 29.04 (CH_2), 34.78 (CH_2), 126.10 (CH), 128.38 (CH, 4C), 140.38 (C), 140.44 (C), 140.79 (C), 141.13 (C), 142.99 (C), 186.99 (C=O), 187.58 (C=O); LRMS (EI) *m/e* 254 $(M)^+$; HRMS (EI) Calcd for $C_{17}H_{18}O_2$ $(M)^+$, 254.1307; Found 254.1313.

4.3.5. Hydroquinone di-*p*-chlorobenzoate (30ii). A solution of *p*-methylphenyl *p*-chlorobenzoyl telluride (**29ii**, 215 mg, 0.60 mmol) and 1,4-benzoquinone (32.4 mg, 0.30 mmol) in acetonitrile (0.6 mL) in a Pyrex tube was irradiated with a 250 W Hg lamp at 100°C for 3 h. After the solvent was removed under reduced pressure, the crude mixture was purified by recrystallization to give **30ii** in 78% yield (91 mg).[21] ^{1}H NMR (300 MHz, $CDCl_3$) 7.29 (s, 4H), 7.51 (d, J=8.4 Hz, 4H), 8.15 (d, J=8.4 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) 122.76 (CH, 4C), 127.94 (C, 2C) 129.17 (CH, 4C), 131.72 (CH, 4C), 140.48 (C, 2C), 148.51 (C, 2C), 164.42 (C=O, 2C); LRMS (EI) *m/e* 386 $(M)^+$.

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