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Three Types of Products Obtained Unexpectedly from the Reaction of Dimedone with Chalcones

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The apparently simple Michael reaction of dimedone with chalcones afforded three types of products. The reaction of dimedone with chalcones in water at reflux, mediated by cetyltrimethylammonium bromide, gave the expected Michael adducts in good to excellent yields after purification by column chromatography. The attempted purification of the Michael adducts by recrystallization from ethanol in air unexpectedly generated hydroperoxidated and hydroxylated Michael adducts in low yields. The efficient synthesis of hydroperoxidated Michael adducts could be achieved in nearly quantitative yields by autoxidation of the Michael adducts in 1,2-dichloroethane at room temperature under aerobic conditions. The conversion of the hydroperoxidated Michael adducts to hydroxylated Michael adducts was facilitated by reduction with triphenylphosphane in excellent yields. Some of the reported Michael adducts in the literature need to be reassigned. Particular caution must be exerted to assign the Michael products generated from cyclic β-diketones, such as dimedone, because different purification processes may give different types of products.

Introduction

The Michael reaction stands as one of the most important processes for the formation of C–C bonds in organic synthesis, because the formed Michael adducts are versatile precursors for many biologically active compounds.[1] A survey of the literature indicated that, among the numerous reported Michael reactions, the addition of cyclic β-diketones to α,β-conjugated compounds has been relatively scarce,[2,3] because the reaction tends to continue to subsequent cyclization steps in most cases.[2]

On the other hand, water in place of harmful organic solvents as the environmentally friendly and benign reaction medium has gained increasing popularity in organic synthesis.[4] As a continuation of our interest in aqueous organic reactions,[2c,5] we recently investigated the Michael reaction of 5,5-dimethylcyclohexane-1,3-dione (dimedone, **1**) with 1,3-diaryl-2-propen-1-ones (chalcones, **2**) with water as the reaction medium. We unexpectedly isolated three types of products during the workup processes, which were identified as simple Michael adducts, hydroperoxidated and hydroxylated Michael adducts. Herein, we disclose these results and further manipulation of the Michael adducts for the efficient synthesis of hydroperoxidated and hydroxylated Michael adducts.

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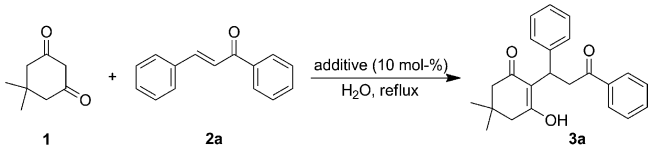
Results and Discussion

In an attempt to extend the methodology of synthesizing 1,4-dihydropyridine derivatives with water as the reaction medium,[6] we recently explored the reaction of dimedone with chalcones and ammonium acetate in refluxing water. The expected products should be 1,4-dihydropyridine derivatives formed through Michael addition followed by cyclization.[6] However, we found that ammonium acetate was not involved, and the reaction could not proceed beyond the Michael addition step. We thus focused on the aqueous Michael addition. The Michael addition of **1** to the simplest chalcone, namely, 1,3-diphenyl-2-propen-1-one (**2a**), was chosen as the model reaction for investigation. The Michael reaction is conventionally catalyzed by strong bases, such as NaOH, KOH, and NaOEt, which often lead to undesirable side reactions, such as bis(addition) and subsequent condensation. We intended to use mild conditions to avoid such side reactions. At the onset, the reaction of **1** with **2a** in water at reflux (120 °C in an oil bath) for 3 h gave Michael adduct **3a** in 28% yield (Table 1, Entry 1). Benzyl triethylammonium chloride (BTEAC) as a phase-transfer catalyst (PTC) was previously applied by us to the aqueous aminochlorination of chalcones.[5] We found that BTEAC could increase the product yield to 49% (Table 1, Entry 2), and tetrabutylammonium bromide (TBAB) further improved the product yield to 72% (Table 1, Entry 3). Cetyltrimethylammonium bromide (CTAB) was superior to

other ammonium salts and afforded **3a** in 76% yield (Table 1, Entry 4). Decreasing the temperature of the oil bath from 120 to 110 °C reduced the yield to 70% (Table 1, Entry 5). Prolonging the reaction time from 3 to 5 h enhanced the yield to 89% (Table 1, Entry 6). However, anionic surfactants, such as sodium dodecyl sulfate (SDS) and sodium dodecylbenzenesulfonate (ABS-Na), reduced the formation of **3a**, giving yields even lower than that without any additive (Table 1, Entries 7 and 8 vs. Entry 1). Therefore, equimolar amounts of **1** and **2a** with 10 mol-% of CTAB were selected as the optimal conditions for the aqueous Michael reaction of **1** and **2a**.

Table 1. Optimization of reaction conditions for the aqueous Michael reaction of **1** with chalcone **2a**.[a]

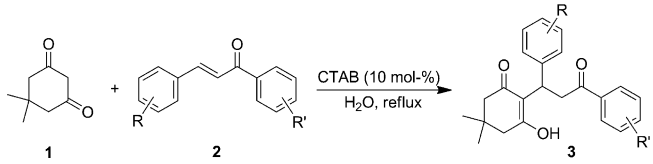


Entry	Additive	Time [h]	Temp. [°C][b]	Yield [%][c]
1	none	3	120	28
2	BTEAC	3	120	49
3	TBAB	3	120	72
4	CTAB	3	120	76
5	CTAB	3	110	70
6	CTAB	5	120	89
7	SDS	3	120	17
8	ABS-Na	3	120	24

[a] All reactions were performed with **1** (0.2 mmol), chalcone **2a** (0.2 mmol), and additive (10 mol-%) in water (2 mL). [b] Temperature of the oil bath. [c] Isolated yield after chromatographic purification.

With the optimized conditions in hands, we then extended the substrate to other chalcones. A variety of chalcones with electron-withdrawing or -donating groups on either phenyl ring performed well and afforded Michael adducts **3a**–**i** in good to excellent yields (Table 2, Entries 1–9).

Table 2. Aqueous Michael reaction of **1** with **2** mediated by CTAB.[a]



Entry	Substrate	R	R′	Time [h]	Product	Yield [%][b]
1	**2a**	H	H	5	**3a**	89
2	**2b**	4-H_3C	H	5	**3b**	84
3	**2c**	4-H_3CO	H	5	**3c**	74
4	**2d**	4-Cl	H	5	**3d**	89
5	**2e**	3,4-Cl_2	H	5	**3e**	85
6	**2f**	3-O_2N	H	7	**3f**	93
7	**2g**	4-O_2N	H	7	**3g**	87
8	**2h**	4-Cl	4-H_3CO	7	**3h**	75
9	**2i**	4-Cl	4-Cl	7	**3i**	84

[a] All reactions were performed with **1** (0.2 mmol), **2** (0.2 mmol), and CTAB (10 mol-%) in water (2 mL) at 120 °C (oil bath temperature). [b] Isolated yield after chromatographic purification.

Michael adducts **3a**–**i** were fully characterized by HRMS, as well as by ^{1}H and ^{13}C NMR and FTIR spectroscopy. The HR mass spectra of products **3a**–**i** gave the correct molecular ion masses. The ^{1}H NMR spectra in [D_6]DMSO showed the expected signals from the chalcone moiety, including two doublets and one pseudo-triplet for the newly formed –$CHCH_2$– fragment, as well as signals of the dimedone moiety. The ^{13}C NMR spectra of **3a**–**i** displayed signals for the two phenyl rings; one coincidently overlapped the signal at $\delta \approx 199$ ppm for the carbonyl groups, one signal at $\delta \approx 115$ ppm, and four signals in the range of $\delta = 28$–41 ppm for aliphatic carbon atoms. The dimedone moiety

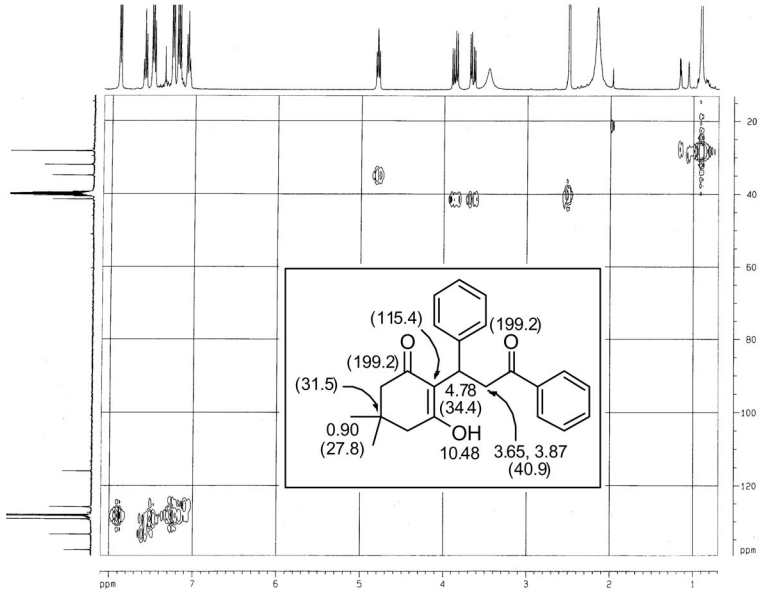
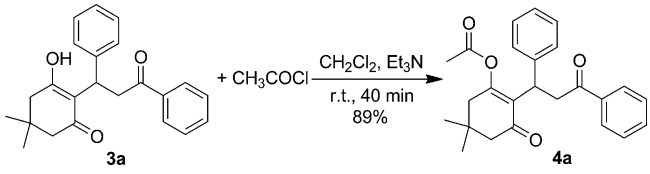


Figure 1. HMQC spectrum of **3a**. Inset: partial assignment of **3a**.

should exist in an enol form, since one broad signal at δ = 10.42–10.86 ppm due to the enolic hydroxy group and a signal at δ = 114.6–115.7 ppm for the enolic carbon atom were observed in the ^{1}H and ^{13}C NMR spectra, respectively. The dimedone moiety as an enol form was also observed previously by us in the nonreductive addition products from the manganese(III) acetate mediated reaction of 1,3-cyclohexanediones with imines.[7] Surprisingly, in the ^{13}C NMR spectra of **3**, only four signals for the seven sp^3-carbon atoms were observed. Among the four signals, one overlapped signal at δ = 27.7–27.9 ppm corresponds to two carbon atoms, leaving two of the seven sp^3-carbon atoms for which no ^{13}C NMR signals could be identified. The heteronuclear multiple quantum correlation (HMQC) spectrum of **3a** (Figure 1) was measured to help assign its molecular structure. Two protons [signals at δ = 3.65 (dd, J = 16.8, 6.8 Hz) and 3.87 (dd, J = 16.8, 8.4 Hz) ppm] are attached to the same carbon atom (signal at δ = 40.9 ppm), whereas one proton [signal at δ = 4.78 (t, J = 7.5 Hz) ppm] is bonded to the carbon atom with signal at δ = 34.4 ppm. Unexpectedly, the broad signal for the methylene protons of the dimedone moiety showed no cross-peak in the HMQC spectrum, indicating that fast ring flipping of the dimedone fragment resulted in the signal disappearance of the methylene carbon atoms in the ^{13}C NMR spectrum of **3a**. The same effect was responsible for the occurrence of only one signal at δ = 199.2 ppm for the two carbonyl carbon atoms and one signal at δ = 27.8 ppm for the two methyl carbon atoms of the dimedone moiety.

To further confirm that the integrity of the dimedone fragment was preserved in the Michael adduct, compound **3a** was treated with acetyl chloride in the presence of triethylamine at room temperature for 40 min, and acetoxylated product **4a** was obtained in 89% yield (Scheme 1).

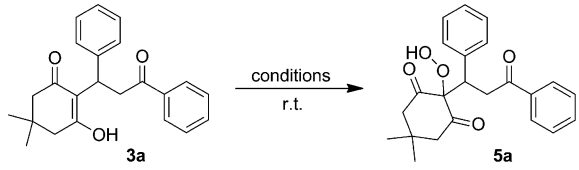


Scheme 1. Acetoxylation of Michael adduct **3a**.

The HR mass spectrum of **4a** gave a signal at m/z = 390.1829, corresponding to the molecular ion. The ^{1}H and ^{13}C NMR spectra showed all expected signals, including those at δ = 42.8, 51.8, and 167.5 ppm, which correspond to two methylene carbon atoms and one enolic carbon atom in the dimedone moiety, but were absent in the ^{13}C NMR spectrum of **3a**. The broad signals at δ = 2.02 and 2.29 ppm for the two CH_2 groups in the ^{1}H NMR spectrum of **3a** became a singlet at δ = 2.24 ppm and two doublets at δ = 2.42 and 2.53 ppm with a coupling constant of 17.7 Hz in the ^{1}H NMR spectrum of **4a**.

In initial attempts to purify Michael adducts **3**, the products were recrystallized from ethanol. Some other products, including those identified later as hydroperoxides **5** and hydroxylated Michael adducts **6**, were obtained in low yields. During the NMR spectroscopy experiments, we found that adducts **3** were stable in [D$_6$]DMSO and [D$_6$]acetone, but unstable in $CDCl_3$. We then screened different solvents with or without an additive for the efficient conversion of **3a**. We found that Michael adduct **3a** was converted to hydroperoxide **5a** in low yields at room temperature in air for 4 h when toluene, ethanol, or *N*,*N*-dimethylformamide (DMF) were employed as the solvents (Table 3, Entries 1–3). When chloroform was used, a moderate yield could be obtained (Table 3, Entry 4). The yield was significantly increased to 88% when the reaction was performed in dichloromethane (Table 3, Entry 5). Further improvement of the yield to 91% was attained if 1,2-dichloroethane (DCE) was utilized as the solvent (Table 3, Entry 6). However, when acetic acid was added, the yield decreased from 91 to 68% (Table 3, Entry 6 vs. 7). Nearly quantitative yields were achieved when the reaction in DCE was conducted under 1 atm of O_2 or prolonged from 4 to 6 h (Table 3, Entries 8 and 9), indicating that this transformation involved oxygen.

Table 3. Solvent screening for the conversion of Michael adduct **3a** into hydroperoxide **5a**.[a]



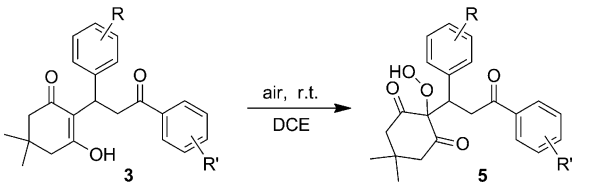
Entry	Solvent	Time [h]	Additive	Yield [%][b]
1	toluene	4	–	16
2	ethanol	4	–	12[c]
3	DMF	4	–	15
4	$CHCl_3$	4	–	44
5	CH_2Cl_2	4	–	88
6	DCE	4	–	91
7	DCE	4	AcOH[d]	68
8	DCE	4	O_2[e]	98
9	DCE	6	–	97

[a] Michael adduct **3a** (0.2 mmol), solvent (2 mL), and additive were stirred in the presence of air at room temperature for the indicated time. [b] Isolated yield after chromatographic purification. [c] Mixture of **5a** and **6a** (see below) in a ratio of 1:1. [d] AcOH (0.2 mL) as the additive. [e] Under 1 atm of O_2.

It is more convenient to operate in air than under oxygen. Therefore, the conversion of Michael adducts **3b**–**i** to hydroperoxides **5b**–**i** was performed in air at room temperature with DCE as the solvent. The results are shown in Table 4 and demonstrate that autoxidation of **3a**–**i** in DCE is very efficient and affords **5a**–**i** in 95–98% yields.

In attempts to purify products **5** by recrystallization from ethanol, a third type of products, **6**, was identified. Products **6** showed similar ^{1}H and ^{13}C NMR spectra to those of hydroperoxides **5** with the same numbers of protons and carbon atoms (see below). This puzzle was eventually solved by obtaining the single-crystal X-ray structure of **6d** (see below). The third type of products was identified as the hydroxylated Michael adducts, which were likely to be generated by the reduction of hydroperoxides **5** with ethanol. The yield from **5** to **6** by recrystallization from ethanol was

Table 4. Autoxidation of Michael adducts **3** to hydroperoxides **5**.[a]

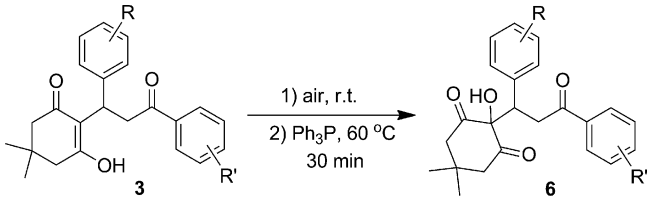


Entry	Substrate	R	R′	Time [h]	Product	Yield [%][b]
1	**3a**	H	H	6	**5a**	97
2	**3b**	4-H_3C	H	7	**5b**	96
3	**3c**	4-H_3CO	H	14	**5c**	96
4	**3d**	4-Cl	H	13	**5d**	95
5	**3e**	3,4-Cl_2	H	12	**5e**	95
6	**3f**	3-O_2N	H	18	**5f**	97
7	**3g**	4-O_2N	H	17	**5g**	96
8	**3h**	4-Cl	4-H_3CO	13	**5h**	98
9	**3i**	4-Cl	4-Cl	15	**5i**	97

[a] All reactions were performed by stirring **3** (0.2 mmol) in DCE (2 mL) in air at room temperature for the indicated time. [b] Isolated yield after chromatographic purification.

low to moderate. Therefore, triphenylphosphane was added to reduce the –OOH group to the –OH group.[8] We found that after the conversion of Michael adducts **3** into hydroperoxides **5** was complete in air at room temperature, subsequent treatment of the reaction mixture with Ph_3P (1 equiv.) gave hydroxylated products **6** in 90–95% yields (Table 5).

Table 5. One-pot conversion of Michael adducts **3** into hydroxylated products **6**.[a]



Entry	Substrate	R	R′	Time [h]	Product	Yield [%][b]
1	**3a**	H	H	6	**6a**	92
2	**3b**	4-H_3C	H	7	**6b**	94
3	**3c**	4-H_3CO	H	14	**6c**	91
4	**3d**	4-Cl	H	13	**6d**	90
5	**3e**	3,4-Cl_2	H	12	**6e**	93
6	**3f**	3-O_2N	H	18	**6f**	90
7	**3g**	4-O_2N	H	17	**6g**	93
8	**3h**	4-Cl	4-H_3CO	13	**6h**	95
9	**3i**	4-Cl	4-Cl	15	**6i**	94

[a] The reaction conditions for the first step were the same as those given in Table 4. After the completion of the first step, Ph_3P (0.2 mmol) was added to the reaction mixture, which was then stirred at 60 °C for 30 min. [b] Isolated yield after chromatographic purification.

Hydroperoxides **5a**–**i** and hydroxylated products **6a**–**i** were characterized by HRMS, as well as ^1H and ^{13}C NMR and FTIR spectroscopy. The HR mass spectra of **5** exhibited mass signals that correspond to [M–O], indicating that the hydroperoxides could easily lose an oxygen atom during mass spectrometry. While different from Michael adducts **3**, products **5** and **6** displayed similar ^1H and ^{13}C NMR spectra, and showed the expected signals for all protons and carbon atoms. The only significant differences in the NMR spectra of **5** and **6** were the signal shifts from δ = 9.38–9.46 ppm for the –OOH group to δ = 4.04–4.13 ppm for the –OH group and from δ = 99.5–100.7 to 91.2–91.9 ppm for the carbon atoms connected to the –OOH and –OH groups, respectively. The broad signal(s) for the two CH_2 groups of the dimedone moiety in the ^1H NMR spectra of **3** became two doublets and two double doublets in the ^1H NMR spectra of both **5** and **6**. In addition, the missing signals for the two CH_2 groups of the dimedone moiety in the ^{13}C NMR spectra of **3** could be observed at δ = 52.4–52.6 and 53.3–53.5 ppm for **5**, and δ = 51.6–51.7 and 51.7–51.9 ppm for **6**. Furthermore, the identity of product **6d** was unequivocally established by its single-crystal X-ray structure, which is shown in Figure 2.

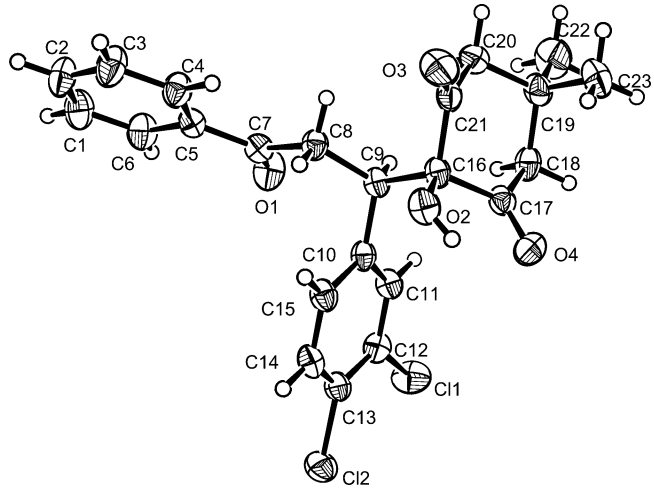


Figure 2. Single-crystal X-ray structure of **6d**. Ellipsoids are drawn at the 40% probability level.

The α-hydroxylation of β-dicarbonyl compounds by using various oxidants, such as peracids, dimethyldioxirane, or molecular oxygen, has been reported.[9] Oxidation by O_2 of compounds containing a tertiary carbon atom to give hydroperoxides is known in the literature. For example, the autoxidation of cyclic β-diketones with a tertiary α-C atom to give hydroperoxides was described over 50 years ago.[10] A large number of Michael adducts have been synthesized.[1] Nevertheless, there has been no report on the peroxidation of Michael adducts from dimedone and chalcones.[3] By comparing the spectroscopic data in ref.[3a] with ours, we found that the reported spectroscopic data of **3a**, **3d**, and **3f** in ref.[3a] match more closely with those of **6a**, **5d**, and **6f**, respectively. Therefore, the assumed Michael adducts in ref.[3a] should be corrected and reassigned. We repeated the KF/Al_2O_3-catalyzed reaction of dimedone and chalcones in DMF at 80 °C,[3a] and indeed obtained the expected Michael adducts with the same workup procedure for our aqueous Michael reaction. The hydroperoxidated

Michael adduct (**5d**) and hydroxylated Michael adducts (**6a** and **6f**) in ref.[3a] should result from further transformation of the Michael adducts during recrystallization from ethanol. This is consistent with our observation that both hydroperoxidated and hydroxylated Michael adducts could be generated by the treatment of **3** in ethanol (see above). Deduced from the reported spectroscopic data, it is likely that all of the reported Michael adducts in ref.[3a] are in fact either the corresponding hydroperoxidated or hydroxylated products after treatment with ethanol. It is taken for granted that only Michael products can be isolated from the addition of β-diketones to α,β-conjugated compounds.[3a] In our case, three types of products were obtained from the Michael reaction of dimedone with chalcones, depending on the purification processes. The present work clearly demonstrates that special caution must be exerted for the purification procedure and product assignment of Michael adducts from cyclic β-diketones, such as **1**.

Conclusions

Three types of products, that is, Michael adducts (**3**), hydroperoxidated (**5**) and hydroxylated (**6**) Michael adducts, were unexpectedly obtained from the reaction of **1** with **2** depending on different purification processes. The reaction of **1** with **2** in water at reflux mediated by CTAB gave the expected Michael adducts **3** in good to excellent yields (74–93%) after purification by column chromatography. When our Michael adducts **3** were treated in ethanol both hydroperoxidated (**5**) and hydroxylated (**6**) Michael adducts were generated in low yields. Hydroxylated Michael adducts **6** could also be formed by recrystallization of **5** from ethanol in low to moderate yields. Gratifyingly, hydroperoxidated Michael adducts **5** were easily produced in nearly quantitative yields (95–98%) by autoxidation of **3** in 1,2-dichlorethane at room temperature under aerobic conditions. The conversion of hydroperoxidated Michael adducts **5** to hydroxylated Michael adducts **6** could be facilitated by reduction with triphenylphosphane in >90% yields. Some of the reported Michael adducts in the literature may need to be revised. Particular care must be exerted to determine what type of product is generated from cyclic β-diketones, such as **1**, because purification processes have substantial effects on the type of products.

Experimental Section

General Methods: Flash chromatographic purification of products was performed on silica gel (200–300 mesh). Thin-layer chromatography was visualized with a UV light (254 and 365 nm). IR spectra were recorded with a Bruker Vector-22 spectrometer as KBr pellets and are reported in cm^{-1}. ^1H NMR spectra were recorded at 300 MHz with a Bruker Avance-300 spectrometer in $CDCl_3$ with chemical shifts (δ) given in ppm relative to TMS as an internal standard. ^{13}C NMR spectra were recorded with a Bruker Avance-300 (75.5 MHz) spectrometer with complete proton decoupling; chemical shifts are reported in ppm relative to the solvent resonance as the internal standard ($CDCl_3$: δ = 77.16 ppm). All intensities in the ^{13}C NMR spectroscopic data are 1 C, except where indicated. Single-crystal X-ray analysis was carried out with an Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire 3 CCD detector and graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å).

General Procedure A. Michael Addition of Dimedone 1 to Chalcones 2: To a mixture of dimedone (**1**; 28.0 mg, 0.2 mmol), chalcone **2a** (**2b**–**i**, 0.2 mmol), and CTAB (7.3 mg, 0.02 mmol) in a 25 mL round-bottomed flask was added H_2O (2 mL). This reaction mixture was stirred vigorously in an oil bath preheated at 120 °C for the desired time (monitored by TLC). The residue remaining after concentration was separated by column chromatography on silica gel with petroleum ether/ethyl acetate (3:1) as the eluent to give Michael product **3a** (**3b**–**i**).

3-Hydroxy-5,5-dimethyl-2-(3-oxo-1,3-diphenylpropyl)cyclohex-2-enone (3a): According to general procedure A, chalcone **2a** (41.6 mg, 0.2 mmol) was employed. Column chromatography gave **3a** as a white solid (62.0 mg, 89%). ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 0.90 (s, 6 H, CH_3), 2.02 (br. s, 2 H, CH_2), 2.29 (br. s, 2 H, CH_2), 3.65 (dd, J = 16.8, 6.8 Hz, 1 H, CH_2), 3.87 (dd, J = 16.8, 8.4 Hz, 1 H, CH_2), 4.78 (t, J = 7.5 Hz, 1 H, CH), 7.08 (t, J = 7.2 Hz, 1 H, ArH), 7.19 (t, J = 7.5 Hz, 2 H, ArH), 7.26 (d, J = 7.5 Hz, 2 H, ArH), 7.50 (t, J = 7.4 Hz, 2 H, ArH), 7.61 (t, J = 7.3 Hz, 1 H, ArH), 7.90 (d, J = 7.4 Hz, 2 H, ArH), 10.48 (br. s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 199.2 (2 C), 144.7, 137.1, 132.8, 128.6 (2 C), 127.8 (2 C), 127.7 (2 C), 127.5 (2 C), 125.2, 115.4, 40.9, 34.4, 31.5, 27.8 (2 C) ppm. FTIR (KBr): $\tilde{\nu}$ = 3426, 2957, 1685, 1599, 1493, 1449, 1378, 1253, 1210, 1151, 1076, 1008, 752, 696 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{23}H_{24}O_3$ $[M]^+$ 348.1725; found 348.1732.

3-Hydroxy-5,5-dimethyl-2-(3-oxo-3-phenyl-1-*p*-tolylpropyl)cyclohex-2-enone (3b): According to general procedure A, chalcone **2b** (44.5 mg, 0.2 mmol) was employed. Column chromatography gave **3b** as a white solid (61.0 mg, 84%). ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 0.90 (s, 6 H, CH_3), 1.99–2.35 (m, 4 H, CH_2), 2.21 (s, 3 H, CH_3), 3.62 (dd, J = 16.6, 6.9 Hz, 1 H, CH_2), 3.83 (dd, J = 16.6, 8.3 Hz, 1 H, CH_2), 4.73 (t, J = 7.5 Hz, 1 H, CH), 6.99 (d, J = 7.8 Hz, 2 H, ArH), 7.13 (d, J = 7.8 Hz, 2 H, ArH), 7.50 (t, J = 7.5 Hz, 2 H, ArH), 7.60 (t, J = 7.3 Hz, 1 H, ArH), 7.89 (d, J = 8.0 Hz, 2 H, ArH), 10.42 (br. s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 199.2 (2 C), 141.7, 137.1, 134.0, 132.8, 128.6 (2 C), 128.3 (2 C), 127.7 (2 C), 127.4 (2 C), 115.6, 40.9, 34.0, 31.5, 27.8 (2 C), 20.5 ppm. FTIR (KBr): $\tilde{\nu}$ = 3428, 2957, 2924, 1686, 1597, 1513, 1449, 1378, 1314, 1254, 1210, 1151, 1057, 1008, 814, 765, 691 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{24}H_{26}O_3$ $[M]^+$ 362.1882; found 362.1879.

3-Hydroxy-2-[1-(4-methoxyphenyl)-3-oxo-3-phenylpropyl]-5,5-dimethylcyclohex-2-enone (3c): According to general procedure A, chalcone **2c** (47.7 mg, 0.2 mmol) was employed. Column chromatography gave **3c** as a white solid (56.0 mg, 74%). ^1H NMR (300 MHz, [D$_6$]DMSO): δ = 0.90 (s, 6 H, CH_3), 2.00 (br. s, 2 H, CH_2), 2.28 (br. s, 2 H, CH_2), 3.64 (dd, J = 16.7, 6.9 Hz, 1 H, CH_2), 3.68 (s, 3 H, OCH_3), 3.84 (dd, J = 16.7, 8.4 Hz, 1 H, CH_2), 4.72 (t, J = 7.5 Hz, 1 H, CH), 6.76 (d, J = 8.6 Hz, 2 H, ArH), 7.17 (d, J = 8.6 Hz, 2 H, ArH), 7.50 (t, J = 7.3 Hz, 2 H, ArH), 7.61 (t, J = 7.3 Hz, 1 H, ArH), 7.89 (d, J = 7.3 Hz, 2 H, ArH), 10.46 (br. s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 199.3 (2 C), 157.0, 137.1, 136.7, 132.8, 128.6 (2 C), 128.4 (2 C), 127.7 (2 C), 115.7, 113.1 (2 C), 54.9, 41.2, 33.7, 31.5, 27.8 (2 C) ppm. FTIR (KBr): $\tilde{\nu}$ = 3437, 2956, 2927, 1684, 1607, 1511, 1450, 1378, 1308, 1248, 1178, 1035, 830, 765, 691 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{24}H_{26}O_4$ $[M]^+$, 378.1831; found 378.1840.

2-[1-(4-Chlorophenyl)-3-oxo-3-phenylpropyl]-3-hydroxy-5,5-dimethylcyclohex-2-enone (3d): According to general procedure A, chalcone **2d** (48.6 mg, 0.2 mmol) was employed. Column chromatography gave **3d** as a white solid (68.2 mg, 89%). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 0.90 (s, 6 H, CH$_3$), 2.03 (br. s, 2 H, CH$_2$), 2.30 (br. s, 2 H, CH$_2$), 3.68 (dd, J = 17.0, 7.1 Hz, 1 H, CH$_2$), 3.83 (dd, J = 17.0, 8.0 Hz, 1 H, CH$_2$), 4.77 (t, J = 7.5 Hz, 1 H, CH), 7.26 (s, 4 H, ArH), 7.50 (t, J = 7.5 Hz, 2 H, ArH), 7.61 (t, J = 7.2 Hz, 1 H, ArH), 7.90 (d, J = 7.6 Hz, 2 H, ArH), 10.63 (br. s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 199.0 (2 C), 143.7, 137.0, 132.9, 129.8, 129.3 (2 C), 128.6 (2 C), 127.7 (2 C), 127.6 (2 C), 115.2, 40.6, 33.8, 31.5, 27.7 (2 C) ppm. FTIR (KBr): $\tilde{\nu}$ = 3064, 2957, 1687, 1596, 1580, 1491, 1449, 1377, 1315, 1254, 1211, 1150, 1092, 1056, 1014, 825, 760, 690 cm^{-1}. HRMS (EI-TOF): calcd. for C$_{23}$H$_{23}$O$_3$^{37}Cl [M]$^+$ 384.1306; found 384.1299.

2-[1-(3,4-Dichlorophenyl)-3-oxo-3-phenylpropyl]-3-hydroxy-5,5-dimethylcyclohex-2-enone (3e): According to general procedure A, chalcone **2e** (55.4 mg, 0.2 mmol) was employed. Column chromatography gave **3e** as a white solid (70.9 mg, 85%). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 0.90 (s, 6 H, CH$_3$), 1.99–2.35 (br., 4 H, CH$_2$), 3.71 (dd, J = 17.3, 7.1 Hz, 1 H, CH$_2$), 3.85 (dd, J = 17.3, 8.0 Hz, 1 H, CH$_2$), 4.76 (t, J = 7.4 Hz, 1 H, CH), 7.23 (d, J = 8.4 Hz, 1 H, ArH), 7.46 (s, 1 H, ArH), 7.46–7.53 (m, 3 H, ArH), 7.62 (t, J = 7.3 Hz, 1 H, ArH), 7.92 (d, J = 8.2 Hz, 2 H, ArH), 10.77 (br. s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 198.7 (2 C), 146.0, 136.9, 133.0, 130.2, 129.9, 129.4, 128.7 (2 C), 128.0, 127.8 (2 C), 127.7, 114.7, 40.4, 33.7, 31.5, 27.7 (2 C) ppm. FTIR (KBr): $\tilde{\nu}$ = 3083, 2958, 1686, 1596, 1580, 1470, 1449, 1375, 1252, 1211, 1149, 1057, 1029, 818, 761, 689 cm^{-1}. HRMS (EI-TOF): calcd. for C$_{23}$H$_{22}$O$_3$^{35}Cl$_2$ [M]$^+$ 416.0946; found 416.0932.

3-Hydroxy-5,5-dimethyl-2-[1-(3-nitrophenyl)-3-oxo-3-phenylpropyl]cyclohex-2-enone (3f): According to general procedure A, chalcone **2f** (50.7 mg, 0.2 mmol) was employed. Column chromatography gave **3f** as a yellow solid (73.2 mg, 93%). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 0.91 (s, 6 H, CH$_3$), 2.07 (br. s, 2 H, CH$_2$), 2.30 (br. s, 2 H, CH$_2$), 3.81 (dd, J = 17.4, 7.4 Hz, 1 H, CH$_2$), 3.90 (dd, J = 17.4, 7.9 Hz, 1 H, CH$_2$), 4.90 (t, J = 7.4 Hz, 1 H, CH), 7.49–7.55 (m, 3 H, ArH), 7.63 (t, J = 7.3 Hz, 1 H, ArH), 7.73 (d, J = 7.7 Hz, 1 H, ArH), 7.94 (d, J = 8.2 Hz, 2 H, ArH), 7.99 (d, J = 8.1 Hz, 1 H, ArH), 8.11 (s, 1 H, ArH), 10.86 (br. s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 198.7 (2 C), 147.5, 147.0, 136.9, 134.5, 133.0, 129.2, 128.7 (2 C), 127.8 (2 C), 122.0, 120.5, 114.7, 40.4, 34.1, 31.6, 27.7 (2 C) ppm. FTIR (KBr): $\tilde{\nu}$ = 3425, 2958, 2925, 1686, 1598, 1527, 1449, 1378, 1349, 1255, 1213, 1150, 1081, 1011, 805, 748, 690 cm^{-1}. HRMS (EI-TOF): calcd. for C$_{23}$H$_{23}$NO$_5$ [M]$^+$ 393.1576; found 393.1595.

3-Hydroxy-5,5-dimethyl-2-[1-(4-nitrophenyl)-3-oxo-3-phenylpropyl]cyclohex-2-enone (3g): According to general procedure A, chalcone **2g** (50.7 mg, 0.2 mmol) was employed. Column chromatography gave **3g** as a yellow solid (68.5 mg, 87%). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 0.91 (s, 6 H, CH$_3$), 2.05 (br. s, 2 H, CH$_2$), 2.31 (br. s, 2 H, CH$_2$), 3.83 (d, J = 7.5 Hz, 2 H, CH$_2$), 4.91 (t, J = 7.5 Hz, 1 H, CH), 7.51 (d, J = 8.7 Hz, 2 H, ArH), 7.51 (t, J = 7.5 Hz, 2 H, ArH), 7.63 (t, J = 7.2 Hz, 1 H, ArH), 7.93 (d, J = 7.2 Hz, 2 H, ArH), 8.09 (d, J = 8.7 Hz, 2 H, ArH), 10.79 (br. s, 1 H, OH) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 198.6 (2 C), 153.0, 145.4, 136.8, 133.0, 128.6 (4 C), 127.8 (2 C), 122.9 (2 C), 114.6, 39.6, 34.3, 31.5, 27.7 (2 C) ppm. FTIR (KBr): $\tilde{\nu}$ = 3424, 3180, 2957, 2923, 1677, 1602, 1507, 1449, 1378, 1346, 1313, 1270, 1152, 1109, 1057, 1011, 855, 753, 698 cm^{-1}. HRMS (EI-TOF): calcd. for C$_{23}$H$_{23}$NO$_5$ [M]$^+$ 393.1576; found 393.1566.

2-[3-(4-Chlorophenyl)-1-(4-methoxyphenyl)-3-oxopropyl]-3-hydroxy-5,5-dimethylcyclohex-2-enone (3h): According to general procedure A, chalcone **2h** (54.6 mg, 0.2 mmol) was employed. Column chromatography gave **3h** as a white solid (62.0 mg, 75%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 0.88 (s, 6 H, CH$_3$), 2.15 (br. s, 4 H, CH$_2$), 3.61 (dd, J = 16.7, 7.2 Hz, 1 H, CH$_2$), 3.71 (dd, J = 16.7, 7.9 Hz, 1 H, CH$_2$), 3.81 (s, 3 H, OCH$_3$), 4.76 (t, J = 7.6 Hz, 1 H, CH), 7.00 (d, J = 8.9 Hz, 2 H, ArH), 7.22 (d, J = 9.0 Hz, 2 H, ArH), 7.25 (d, J = 9.0 Hz, 2 H, ArH), 7.87 (d, J = 8.9 Hz, 2 H, ArH), 10.85 (br. s, 1 H, OH) ppm. ^{13}C NMR (100 MHz, [D$_6$]-DMSO): δ = 197.6 (2 C), 163.1, 143.9, 130.2 (2 C), 130.0, 129.9, 129.4 (2 C), 127.7 (2 C), 115.4, 114.0 (2 C), 55.6, 40.3, 34.0, 31.6, 27.9 (2 C) ppm. FTIR (KBr): $\tilde{\nu}$ = 3079, 2957, 2928, 1676, 1600, 1575, 1509, 1491, 1376, 1313, 1256, 1169, 1091, 1056, 1014, 833 cm^{-1}. HRMS (EI-TOF): calcd. for C$_{24}$H$_{25}$O$_4$^{35}Cl [M]$^+$ 412.1441; found 412.1450.

2-[1,3-Bis(4-chlorophenyl)-3-oxopropyl]-3-hydroxy-5,5-dimethylcyclohex-2-enone (3i): According to general procedure A, chalcone **2i** (55.4 mg, 0.2 mmol) was employed. Column chromatography gave **3i** as a white solid (70.1 mg, 84%, white solid). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 0.88 (s, 6 H, CH$_3$), 2.15 (br. s, 4 H, CH$_2$), 3.65 (dd, J = 16.9, 6.9 Hz, 1 H, CH$_2$), 3.82 (dd, J = 16.9, 8.4 Hz, 1 H, CH$_2$), 4.74 (t, J = 7.6 Hz, 1 H, CH), 7.23 (d, J = 8.9 Hz, 2 H, ArH), 7.26 (d, J = 8.9 Hz, 2 H, ArH), 7.55 (d, J = 8.5 Hz, 2 H, ArH), 7.90 (d, J = 8.5 Hz, 2 H, ArH), 10.57 (br. s, 1 H, OH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 198.2 (2 C), 143.6, 138.0, 135.7, 130.0, 129.8 (2 C), 129.4 (2 C), 128.9 (2 C), 127.7 (2 C), 115.1, 40.8, 33.9, 31.6, 27.8 (2 C) ppm. FTIR (KBr): $\tilde{\nu}$ = 3087, 2958, 2928, 1687, 1589, 1490, 1377, 1314, 1254, 1092, 1150, 1011, 1055, 890, 823 cm^{-1}. HRMS (EI–TOF): calcd. for C$_{23}$H$_{22}$O$_3$^{35}Cl$_2$ [M]$^+$ 416.0946; found 416.0955.

Procedure for the Acetoxylation of Michael Adduct 3a To Give 5,5-Dimethyl-3-oxo-2-(3-oxo-1,3-diphenylpropyl)cyclohex-1-enyl Acetate (4a): Triethylamine (117 μL, 0.84 mmol) was added dropwise at room temperature to a solution of Michael adduct **3a** (104.4 mg, 0.30 mmol) in dichloromethane (3 mL). After stirring for 10 min, acetyl chloride (53.1 μL, 0.75 mmol) was added, and stirring was maintained for 40 min. The crude product obtained was separated by chromatography on silica gel with petroleum ether/acetyl acetate (4:1) as the eluent to give **4a** (104.0 mg, 89%). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.01 (s, 3 H, CH$_3$), 1.03 (s, 3 H, CH$_3$), 2.16 (s, 3 H, CH$_3$), 2.24 (s, 2 H, CH$_2$), 2.42 (d, J = 17.7 Hz, 1 H, CH$_2$), 2.53 (d, J = 17.7 Hz, 1 H, CH$_2$), 3.74 (dd, J = 17.1, 6.9 Hz, 1 H, CH$_2$), 3.82 (dd, J = 17.1, 8.1 Hz, 1 H, CH$_2$) 4.79 (t, J = 7.4 Hz, 1 H, CH), 7.12–7.18 (m, 1 H, ArH), 7.21–7.29 (m, 4 H, ArH), 7.44 (t, J = 7.5 Hz, 2 H, ArH), 7.54 (t, J = 7.4 Hz, 1 H, ArH), 7.87 (d, J = 7.5 Hz, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 198.9, 198.8, 167.5, 164.0, 142.2, 137.0, 133.1, 129.1, 128.6 (2 C), 128.3 (2 C), 128.2 (2 C), 127.6 (2 C), 126.3, 51.8, 42.8, 40.9, 35.9, 32.7, 28.0 (2 C), 21.0 ppm. FTIR (KBr): $\tilde{\nu}$ = 2960, 1768, 1684, 1598, 1494, 1450, 1358, 1272, 1183, 1142, 1078, 1015, 850, 753, 699 cm^{-1}. HRMS (EI–TOF): calcd. for C$_{25}$H$_{26}$O$_4$ [M]$^+$ 390.1831; found 390.1829.

General Procedure B. Conversion of Michael Adducts 3 to Hydroperoxides 5: Michael adduct **3a** (**3b**–**i**, 0.2 mmol) was stirred in DCE (2 mL) in air at room temperature for the indicated time (monitored by TLC). The reaction mixture was separated on a silica gel column (pretreated with AcOH) with petroleum ether/ethyl acetate (3:1) as the eluent to afford hydroperoxide **5a** (**5b**–**i**).

2-Hydroperoxy-5,5-dimethyl-2-(3-oxo-1,3-diphenylpropyl)cyclohexane-1,3-dione (5a): According to general procedure B, Michael adduct **3a** (69.7 mg, 0.2 mmol) was employed. Column chromatography gave **5a** as a white solid (73.8 mg, 97%). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 0.87 (s, 3 H, CH$_3$), 1.24 (s, 3 H, CH$_3$), 2.42 (dd, J =

14.1, 3.0 Hz, 1 H, CH_2), 2.56 (dd, J = 15.3, 3.0 Hz, 1 H, CH_2), 2.92 (d, J = 14.1 Hz, 1 H, CH_2), 3.17 (d, J = 15.3 Hz, 1 H, CH_2), 3.37 (dd, J = 18.8, 7.3 Hz, 1 H, CH_2), 3.66 (dd, J = 18.8, 4.5 Hz, 1 H, CH_2), 4.39 (dd, J = 7.3, 4.5 Hz, 1 H, CH), 7.22–7.29 (m, 3 H, ArH), 7.34 (d, J = 6.3 Hz, 2 H, ArH), 7.41 (t, J = 7.5 Hz, 2 H, ArH), 7.54 (t, J = 7.5 Hz, 1 H, ArH), 7.87 (d, J = 7.5 Hz, 2 H, ArH), 9.43 (s, 1 H, OOH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.0, 202.9, 197.2, 137.1, 136.4, 133.6, 129.3 (2 C), 128.8 (2 C), 128.7 (2 C), 128.3 (3 C), 100.5, 53.5, 52.6, 45.8, 39.1, 30.8, 30.7, 26.2 ppm. FTIR (KBr): $\tilde{\nu}$ = 3334, 3064, 2966, 2927, 1731, 1703, 1449, 1357, 1239, 1086, 1010, 748, 703, 634 cm^{-1} HRMS (EI-TOF): calcd. for $C_{23}H_{24}O_4$ $[M - O]^+$ 364.1675; found 364.1670.

2-Hydroperoxy-5,5-dimethyl-2-(3-oxo-3-phenyl-1-*p*-tolylpropyl)-cyclohexane-1,3-dione (5b): According to general procedure B, Michael adduct **3b** (72.5 mg, 0.2 mmol) was employed. Column chromatography gave **5b** as a white solid (75.7 mg, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.86 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3), 2.27 (s, 3 H, CH_3), 2.41 (dd, J = 14.0, 3.2 Hz, 1 H, CH_2), 2.55 (dd, J = 15.3, 3.2 Hz, 1 H, CH_2), 2.92 (d, J = 14.0 Hz, 1 H, CH_2), 3.16 (d, J = 15.3 Hz, 1 H, CH_2), 3.35 (dd, J = 18.7, 7.4 Hz, 1 H, CH_2), 3.62 (dd, J = 18.7, 4.4 Hz, 1 H, CH_2), 4.35 (dd, J = 7.4, 4.4 Hz, 1 H, CH), 7.06 (d, J = 8.0 Hz, 2 H, ArH), 7.21 (d, J = 8.0 Hz, 2 H, ArH), 7.41 (t, J = 7.6 Hz, 2 H, ArH), 7.52 (t, J = 7.4 Hz, 1 H, ArH), 7.87 (d, J = 7.6 Hz, 2 H, ArH), 9.38 (s, 1 H, OOH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.1, 203.0, 197.2, 137.9, 136.4, 134.0, 133.5, 129.5 (2 C), 129.1 (2 C), 128.7 (2 C), 128.2 (2 C), 100.6, 53.5, 52.6, 45.5, 39.1, 30.7, 30.6, 26.2, 21.2 ppm. FTIR (KBr): $\tilde{\nu}$ = 3420, 2955, 1736, 1705, 1449, 1360, 1240, 761, 687, 623 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{24}H_{26}O_4$ $[M - O]^+$ 378.1831; found 378.1827.

2-Hydroperoxy-2-[1-(4-methoxyphenyl)-3-oxo-3-phenylpropyl]-5,5-dimethylcyclohexane-1,3-dione (5c): According to general procedure B, Michael adduct **3c** (75.7 mg, 0.2 mmol) was employed. Column chromatography gave **5c** as a white solid (78.8 mg, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3), 2.41 (dd, J = 13.9, 3.2 Hz, 1 H, CH_2), 2.55 (dd, J = 15.3, 3.2 Hz, 1 H, CH_2), 2.90 (d, J = 13.9 Hz, 1 H, CH_2), 3.15 (d, J = 15.3 Hz, 1 H, CH_2), 3.35 (dd, J = 18.7, 7.6 Hz, 1 H, CH_2), 3.59 (dd, J = 18.7, 4.3 Hz, 1 H, CH_2), 3.74 (s, 3 H, OCH_3), 4.35 (dd, J = 7.6, 4.3 Hz, 1 H, CH), 6.78 (d, J = 8.7 Hz, 2 H, ArH), 7.25 (d, J = 8.7 Hz, 2 H, ArH), 7.41 (t, J = 7.6 Hz, 2 H, ArH), 7.53 (t, J = 7.4 Hz, 1 H, ArH), 7.87 (d, J = 7.6 Hz, 2 H, ArH), 9.45 (s, 1 H, OOH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.0, 202.9, 197.3, 159.3, 136.4, 133.6, 130.4 (2 C), 129.0, 128.7 (2 C), 128.2 (2 C), 114.2 (2 C), 100.7, 55.2, 53.5, 52.6, 45.2, 39.2, 30.7, 30.6, 26.2 ppm. FTIR (KBr): $\tilde{\nu}$ = 3400, 2957, 1737, 1704, 1686, 1611, 1514, 1449, 1371, 1298, 1249, 1181, 1072, 1033, 836, 762, 735, 690, 623 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{24}H_{26}O_5$ $[M - O]^+$ 394.1780; found 394.1791.

2-[1-(4-Chlorophenyl)-3-oxo-3-phenylpropyl]-2-hydroperoxy-5,5-dimethylcyclohexane-1,3-dione (5d): According to general procedure B, Michael adduct **3d** (76.6 mg, 0.2 mmol) was employed. Column chromatography gave **5d** as a white solid (78.9 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.87 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3), 2.43 (dd, J = 14.0, 3.3 Hz, 1 H, CH_2), 2.57 (dd, J = 15.3, 3.3 Hz, 1 H, CH_2), 2.86 (d, J = 14.0 Hz, 1 H, CH_2), 3.15 (d, J = 15.3 Hz, 1 H, CH_2), 3.33 (dd, J = 18.8, 7.6 Hz, 1 H, CH_2), 3.62 (dd, J = 18.8, 4.3 Hz, 1 H, CH_2), 4.36 (dd, J = 7.6, 4.3 Hz, 1 H, CH), 7.23 (d, J = 8.7 Hz, 2 H, ArH), 7.29 (d, J = 8.7 Hz, 2 H, ArH), 7.42 (t, J = 7.7 Hz, 2 H, ArH), 7.54 (t, J = 7.4 Hz, 1 H, ArH), 7.86 (dd, J = 8.4 Hz, 2 H, ArH), 9.46 (s, 1 H, OOH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.5, 202.5, 196.8, 136.0, 135.5, 134.1, 133.7, 130.6 (2 C), 128.9 (2 C), 128.7 (2 C), 128.1 (2 C), 100.1, 53.3, 52.4, 44.9, 38.9, 30.7, 30.5, 26.0 ppm. FTIR (KBr): $\tilde{\nu}$ = 3403, 2957, 1735, 1704, 1595, 1491, 1449, 1417, 1358, 1237, 1204, 1093, 1074, 1014, 754, 690, 618 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{23}H_{23}O_4{}^{35}Cl$ $[M - O]^+$ 398.1285; found 398.1290.

2-[1-(3,4-Dichlorophenyl)-3-oxo-3-phenylpropyl]-2-hydroperoxy-5,5-dimethylcyclohexane-1,3-dione (5e): According to general procedure B, Michael adduct **3e** (83.5 mg, 0.2 mmol) was employed. Column chromatography gave **5e** as a white solid (85.4 mg, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (s, 3 H, CH_3), 1.26 (s, 3 H, CH_3), 2.47 (dd, J = 14.0, 3.3 Hz, 1 H, CH_2), 2.58 (dd, J = 15.3, 3.3 Hz, 1 H, CH_2), 2.85 (d, J = 14.0 Hz, 1 H, CH_2), 3.14 (d, J = 15.3 Hz, 1 H, CH_2), 3.29 (dd, J = 18.9, 7.5 Hz, 1 H, CH_2), 3.63 (dd, J = 18.9, 4.2 Hz, 1 H, CH_2), 4.34 (dd, J = 7.5, 4.2 Hz, 1 H, CH), 7.22 (dd, J = 8.4, 2.1 Hz, 1 H, ArH), 7.34 (d, J = 8.3 Hz, 1 H, ArH), 7.43 (d, J = 7.5 Hz, 2 H, ArH), 7.44 (d, J = 2.1 Hz, 1 H, ArH), 7.56 (t, J = 7.4 Hz, 1 H, ArH), 7.87 (d, J = 7.5 Hz, 2 H, ArH), 9.42 (s, 1 H, OOH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.3, 202.5, 196.7, 137.4, 136.0, 133.9, 132.8, 132.6, 131.3, 130.8, 128.9 (2 C), 128.8, 128.3 (2 C), 99.9, 53.5, 52.6, 44.6, 39.0, 30.8, 30.6, 26.2 ppm. FTIR (KBr): $\tilde{\nu}$ = 3414, 2957, 1737, 1707, 1686, 1597, 1471, 1449, 1359, 1236, 1209, 1134, 1076, 1031, 1003, 758, 688, 634 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{23}H_{22}O_4{}^{35}Cl_2$ $[M - O]^+$ 432.0895; found 432.0890.

2-Hydroperoxy-5,5-dimethyl-2-[1-(3-nitrophenyl)-3-oxo-3-phenylpropyl]cyclohexane-1,3-dione (5f): According to general procedure B, Michael adduct **3f** (78.7 mg, 0.2 mmol) was employed. Column chromatography gave **5f** as a yellow solid (82.5 mg, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3), 2.47 (dd, J = 14.1, 3.3 Hz, 1 H, CH_2), 2.62 (dd, J = 15.3, 3.3 Hz, 1 H, CH_2), 2.88 (d, J = 14.1 Hz, 1 H, CH_2), 3.17 (d, J = 15.3 Hz, 1 H, CH_2), 3.37 (dd, J = 18.9, 7.5 Hz, 1 H, CH_2), 3.71 (dd, J = 18.9, 4.4 Hz, 1 H, CH_2), 4.49 (dd, J = 7.5, 4.4 Hz, 1 H, CH), 7.41–7.49 (m, 3 H, ArH), 7.56 (t, J = 7.5 Hz, 1 H, ArH), 7.73 (d, J = 7.8 Hz, 1 H, ArH), 7.88 (d, J = 7.3 Hz, 2 H, ArH), 8.11 (d, J = 7.8 Hz, 1 H, ArH), 8.23 (s, 1 H, ArH), 9.39 (s, 1 H, OOH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.4, 202.6, 196.5, 148.3, 139.2, 135.9, 135.5, 133.9, 129.7, 128.8 (2 C), 128.3 (2 C), 124.3, 123.2, 99.5, 53.4, 52.5, 44.9, 38.9, 30.8, 30.4, 26.1 ppm. FTIR (KBr): $\tilde{\nu}$ = 3413, 2956, 1739, 1710, 1682, 1597, 1525, 1447, 1352, 1257, 1208, 1074, 1004, 744, 698, 685 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{23}H_{23}NO_6$ $[M - O]^+$ 409.1525; found 409.1523.

2-Hydroperoxy-5,5-dimethyl-2-[1-(4-nitrophenyl)-3-oxo-3-phenylpropyl]cyclohexane-1,3-dione (5g): According to general procedure B, Michael adduct **3g** (78.7 mg, 0.2 mmol) was employed. Column chromatography gave **5g** as a yellow solid (81.7 mg, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.89 (s, 3 H, CH_3), 1.26 (s, 3 H, CH_3), 2.47 (dd, J = 14.1, 3.0 Hz, 1 H, CH_2), 2.62 (dd, J = 15.3, 3.0 Hz, 1 H, CH_2), 2.85 (d, J = 14.1 Hz, 1 H, CH_2), 3.16 (d, J = 15.3 Hz, 1 H, CH_2), 3.36 (dd, J = 18.9, 7.8 Hz, 1 H, CH_2), 3.68 (dd, J = 18.9, 4.2 Hz, 1 H, CH_2), 4.48 (dd, J = 7.8, 4.2 Hz, 1 H, CH), 7.43 (t, J = 7.8 Hz, 2 H, ArH), 7.53–7.58 (m, 3 H, ArH), 7.87 (d, J = 7.2 Hz, 2 H, ArH), 8.13 (d, J = 8.7 Hz, 2 H, ArH), 9.43 (s, 1 H, OOH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.3, 202.4, 196.5, 147.7, 144.4, 135.9, 134.0, 130.4 (2 C), 128.9 (2 C), 128.2 (2 C), 123.9 (2 C), 99.5, 53.4, 52.5, 45.0, 38.8, 30.8, 30.5, 26.1 ppm. FTIR (KBr): $\tilde{\nu}$ = 3405, 2955, 1735, 1707, 1680, 1598, 1515, 1450, 1349, 1236, 1211, 1111, 1074, 1003, 857, 754, 706, 690 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{23}H_{23}NO_6$ $[M - O]^+$ 409.1525; found 409.1530.

2-[3-(4-Chlorophenyl)-1-(4-methoxyphenyl)-3-oxopropyl]-2-hydroperoxy-5,5-dimethylcyclohexane-1,3-dione (5h): According to gene-

ral procedure B, Michael adduct **3h** (82.6 mg, 0.2 mmol) was employed. Column chromatography gave **5h** as a white solid (87.2 mg, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3), 2.42 (dd, J = 13.8, 3.0 Hz, 1 H, CH_2), 2.56 (dd, J = 15.3, 3.0 Hz, 1 H, CH_2), 2.86 (d, J = 13.8 Hz, 1 H, CH_2), 3.16 (d, J = 15.3 Hz, 1 H, CH_2), 3.28 (dd, J = 18.6, 7.5 Hz, 1 H, CH_2), 3.53 (dd, J = 18.6, 4.2 Hz, 1 H, CH_2), 3.85 (s, 3 H, OCH_3), 4.37 (dd, J = 7.5, 4.2 Hz, 1 H, CH), 6.88 (d, J = 8.9 Hz, 2 H, ArH), 7.23 (d, J = 8.6 Hz, 2 H, ArH), 7.28 (d, J = 8.6 Hz, 2 H, ArH), 7.85 (d, J = 8.9 Hz, 2 H, ArH), 9.40 (s, 1 H, OOH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.6, 202.7, 195.3, 164.1, 135.7, 134.1, 130.7 (2 C), 130.6 (2 C), 129.2, 129.0 (2 C), 113.9 (2 C), 100.4, 55.6, 53.4, 52.5, 45.2, 38.6, 30.8, 30.6, 26.2 ppm. FTIR (KBr): $\tilde{\nu}$ = 3417, 2959, 2925, 1733, 1704, 1688, 1603, 1574, 1510, 1492, 1420, 1358, 1241, 1170, 1093, 1031, 1014, 838, 822, 600 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{24}H_{23}O_5{}^{35}Cl$ [M – H_2O]$^+$ 426.1234; found 426.1237.

2-[1,3-Bis(4-chlorophenyl)-3-oxopropyl]-2-hydroperoxy-5,5-dimethylcyclohexane-1,3-dione (5i): According to general procedure B, Michael adduct **3i** (83.5 mg, 0.2 mmol) was employed. Column chromatography gave **5i** as a white solid (87.2 mg, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (s, 3 H, CH_3), 1.25 (s, 3 H, CH_3), 2.44 (dd, J = 13.5, 3.2 Hz, 1 H, CH_2), 2.57 (dd, J = 15.3, 3.2 Hz, 1 H, CH_2), 2.84 (d, J = 13.5 Hz, 1 H, CH_2), 3.13 (d, J = 15.3 Hz, 1 H, CH_2), 3.25 (dd, J = 18.8, 7.2 Hz, 1 H, CH_2), 3.59 (dd, J = 18.8, 4.5 Hz, 1 H, CH_2), 4.33 (dd, J = 7.2, 4.5 Hz, 1 H, CH), 7.26–7.33 (m, 4 H, ArH), 7.40 (d, J = 8.4 Hz, 2 H, ArH), 7.80 (d, J = 8.4 Hz, 2 H, ArH), 9.38 (s, 1 H, OOH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.7, 202.6, 195.8, 140.3, 135.4, 134.3, 134.1, 130.6 (2 C), 129.7 (2 C), 129.1 (2 C), 129.0 (2 C), 100.0, 53.4, 52.6, 45.0, 39.0, 30.8, 30.6, 26.1 ppm. FTIR (KBr): $\tilde{\nu}$ = 3412, 2958, 2920, 1737, 1705, 1688, 1590, 1491, 1400, 1237, 1093, 1013, 831, 778, 724 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{23}H_{22}O_4{}^{35}Cl_2$ [M – O]$^+$ 432.0895; found 432.0899.

General Procedure C. One-Pot Conversion of Michael Adducts 3 to Products 6: Michael adduct **3a** (**3b–i**, 0.2 mmol) was stirred in DCE (2 mL) in air at room temperature for the desired time until the starting Michael adduct had disappeared (monitored by TLC). Then, Ph_3P (0.2 mmol) was added to the reaction mixture, which was stirred at 60 °C for 30 min. The reaction mixture was separated on a silica gel column with petroleum ether/ethyl acetate (3:1) as the eluent to give product **6a** (**6b–i**).

2-Hydroxy-5,5-dimethyl-2-(3-oxo-1,3-diphenylpropyl)cyclohexane-1,3-dione (6a): According to general procedure C, Michael adduct **3a** (69.7 mg, 0.2 mmol) was employed. Column chromatography gave **6a** as a white solid (67.0 mg, 92%, white solid). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.77 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 2.40 (dd, J = 13.6, 2.7 Hz, 1 H, CH_2), 2.53 (dd, J = 14.5, 2.7 Hz, 1 H, CH_2), 3.09 (d, J = 13.6 Hz, 1 H, CH_2), 3.42 (dd, J = 18.7, 6.4 Hz, 1 H, CH_2), 3.46 (d, J = 14.5 Hz, 1 H, CH_2), 3.58 (dd, J = 18.7, 5.5 Hz, 1 H, CH_2), 4.06 (s, 1 H, OH), 4.39 (t, J = 5.9 Hz, 1 H, CH), 7.22–7.29 (m, 3 H, ArH), 7.37–7.44 (m, 4 H, ArH), 7.54 (t, J = 7.2 Hz, 1 H, ArH), 7.89 (d, J = 7.4 Hz, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.7, 204.6, 197.9, 138.2, 136.5, 133.6, 128.9 (2 C), 128.74 (2 C), 128.68 (2 C), 128.3 (2 C), 128.1, 91.8, 51.84, 51.80, 47.3, 40.2, 31.6, 30.9, 26.5 ppm. FTIR (KBr): $\tilde{\nu}$ = 3460, 3062, 2951, 1730, 1698, 1595, 1450, 1354, 1323, 1238, 1141, 1079, 1003, 748, 703, 686, 633, 600 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{23}H_{24}O_4$ [M]$^+$ 364.1675; found 364.1680.

2-Hydroxy-5,5-dimethyl-2-(3-oxo-3-phenyl-1-*p*-tolylpropyl)cyclohexane-1,3-dione (6b): According to general procedure C, Michael adduct **3b** (72.5 mg, 0.2 mmol) was employed. Column chromatography gave **6b** as a white solid (71.2 mg, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.77 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 2.27 (s, 3 H, CH_3), 2.40 (d, J = 13.4 Hz, 1 H, CH_2), 2.52 (d, J = 14.5 Hz, 1 H, CH_2), 3.09 (d, J = 13.4 Hz, 1 H, CH_2), 3.40 (dd, J = 18.7, 6.4 Hz, 1 H, CH_2), 3.43 (d, J = 14.5 Hz, 1 H, CH_2), 3.54 (dd, J = 18.7, 5.4 Hz, 1 H, CH_2), 4.04 (s, 1 H, OH), 4.35 (t, J = 5.8 Hz, 1 H, CH), 7.07 (d, J = 7.7 Hz, 2 H, ArH), 7.25 (d, J = 7.7 Hz, 2 H, ArH), 7.41 (t, J = 7.4 Hz, 2 H, ArH), 7.53 (t, J = 7.3 Hz, 1 H, ArH), 7.88 (d, J = 7.2 Hz, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.7, 204.7, 197.9, 137.8, 136.6, 135.1, 133.5, 129.6 (2 C), 128.7 (2 C), 128.5 (2 C), 128.2 (2 C), 91.9, 51.82, 51.79, 47.0, 40.2, 31.6, 30.8, 26.5, 21.2 ppm. FTIR (KBr): $\tilde{\nu}$ = 3491, 2957, 2924, 1734, 1694, 1515, 1450, 1365, 1238, 1142, 1079, 1000, 814, 764, 689, 529 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{24}H_{26}O_4$ [M]$^+$ 378.1831; found 378.1815.

2-Hydroxy-2-[1-(4-methoxyphenyl)-3-oxo-3-phenylpropyl]-5,5-dimethylcyclohexane-1,3-dione (6c): According to general procedure C, Michael adduct **3c** (75.7 mg, 0.2 mmol) was employed. Column chromatography gave **6c** as a white solid (71.8 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.77 (s, 3 H, CH_3), 1.30 (s, 3 H, CH_3), 2.39 (dd, J = 13.5, 2.8 Hz, 1 H, CH_2), 2.52 (dd, J = 14.4, 2.8 Hz, 1 H, CH_2), 3.07 (d, J = 13.5 Hz, 1 H, CH_2), 3.40 (dd, J = 18.6, 6.7 Hz, 1 H, CH_2), 3.42 (d, J = 14.4 Hz, 1 H, CH_2), 3.50 (dd, J = 18.6, 5.0 Hz, 1 H, CH_2), 3.74 (s, 3 H, OCH_3), 4.05 (s, 1 H, OH), 4.35 (t, J = 6.0 Hz, 1 H, CH), 6.79 (d, J = 8.7 Hz, 2 H, ArH), 7.30 (d, J = 8.7 Hz, 2 H, ArH), 7.41 (t, J = 7.7 Hz, 2 H, ArH), 7.53 (t, J = 7.4 Hz, 1 H, ArH), 7.88 (d, J = 7.2 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.7, 204.6, 198.0, 159.2, 136.5, 133.5, 130.1, 129.6 (2 C), 128.7 (2 C), 128.2 (2 C), 114.2 (2 C), 91.9, 55.2, 51.7 (2 C), 46.6, 40.2, 31.5, 30.8, 26.5 ppm. FTIR (KBr): $\tilde{\nu}$ = 3462, 2951, 2936, 1728, 1698, 1611, 1514, 1448, 1358, 1299, 1251, 1179, 1141, 1078, 1032, 820, 764, 733, 690 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{24}H_{26}O_5$ [M]$^+$ 394.1780; found 394.1775.

2-[1-(4-Chlorophenyl)-3-oxo-3-phenylpropyl]-2-hydroxy-5,5-dimethylcyclohexane-1,3-dione (6d): According to general procedure C, Michael adduct **3d** (76.6 mg, 0.2 mmol) was employed. Column chromatography gave **6d** as a white solid (71.8 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.78 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 2.41 (dd, J = 13.5, 2.6 Hz, 1 H, CH_2), 2.54 (dd, J = 14.4, 2.6 Hz, 1 H, CH_2), 3.03 (d, J = 13.5 Hz, 1 H, CH_2), 3.35–3.43 (m, 2 H, CH_2), 3.50 (dd, J = 18.6, 5.4 Hz, 1 H, CH_2), 4.07 (s, 1 H, OH), 4.36 (t, J = 5.9 Hz, 1 H, CH), 7.24 (d, J = 8.4 Hz, 2 H, ArH), 7.34 (d, J = 8.4 Hz, 2 H, ArH), 7.43 (t, J = 7.5 Hz, 2 H, ArH), 7.55 (t, J = 7.5 Hz, 1 H, ArH), 7.88 (d, J = 7.5 Hz, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.5, 204.3, 197.6, 136.7, 136.4, 134.1, 133.7, 130.0 (2 C), 129.1 (2 C), 128.8 (2 C), 128.2 (2 C), 91.6, 51.8, 51.7, 46.6, 40.0, 31.6, 30.8, 26.5 ppm. FTIR (KBr): $\tilde{\nu}$ = 3447, 2959, 2923, 1733, 1693, 1597, 1491, 1449, 1237, 1142, 1080, 1016, 822, 753, 689 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{23}H_{23}O_4Cl$ [M]$^+$ 398.1285; found 398.1286.

2-[1-(3,4-Dichlorophenyl)-3-oxo-3-phenylpropyl]-2-hydroxy-5,5-dimethylcyclohexane-1,3-dione (6e): According to general procedure C, Michael adduct **3e** (83.5 mg, 0.2 mmol) was employed. Column chromatography gave **6e** as a white solid (80.6 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.78 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 2.44 (dd, J = 13.5, 2.9 Hz, 1 H, CH_2), 2.54 (dd, J = 14.4, 2.9 Hz, 1 H, CH_2), 3.00 (d, J = 13.5 Hz, 1 H, CH_2), 3.36 (dd, J = 18.8, 6.6 Hz, 1 H, CH_2), 3.37 (d, J = 14.4 Hz, 1 H, CH_2), 3.50 (dd, J = 18.8, 5.3 Hz, 1 H, CH_2), 4.08 (s, 1 H, OH), 4.34 (t, J = 6.0 Hz, 1 H, CH), 7.27 (dd, J = 8.4, 2.0 Hz, 1 H, ArH), 7.35 (d, J = 8.4 Hz, 1 H, ArH), 7.43 (t, J = 7.7 Hz, 2 H, ArH), 7.50 (d, J = 2.0 Hz, 1 H, ArH), 7.56 (t, J = 7.5 Hz, 1 H, ArH), 7.88 (d, J = 7.2 Hz, 2 H,

ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.2, 204.2, 197.2, 138.4, 136.2, 133.8, 132.9, 132.4, 130.8, 130.6, 128.8 (2 C), 128.2 (2 C), 128.0, 91.3, 51.8, 51.6, 46.2, 39.9, 31.7, 30.8, 26.4 ppm. FTIR (KBr): $\tilde{\nu}$ = 3492, 2960, 1738, 1700, 1597, 1471, 1450, 1358, 1237, 1143, 1080, 1030, 1002, 829, 757, 688, 629 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{23}H_{22}O_4{}^{35}Cl_2$ $[M]^+$ 432.0895; found 432.0890.

2-Hydroxy-5,5-dimethyl-2-[1-(3-nitrophenyl)-3-oxo-3-phenylpropyl]cyclohexane-1,3-dione (6f): According to general procedure C, Michael adduct **3f** (78.7 mg, 0.2 mmol) was employed. Column chromatography gave **6f** as a yellow solid (73.7 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.78 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 2.44 (dd, J = 13.6, 2.8 Hz, 1 H, CH_2), 2.57 (dd, J = 14.5, 2.8 Hz, 1 H, CH_2), 3.06 (d, J = 13.6 Hz, 1 H, CH_2), 3.40 (d, J = 14.5 Hz, 1 H, CH_2), 3.45 (dd, J = 18.7, 6.9 Hz, 1 H, CH_2), 3.56 (dd, J = 18.7, 5.2 Hz, 1 H, CH_2), 4.13 (s, 1 H, OH), 4.51 (t, J = 6.0 Hz, 1 H, CH), 7.41–7.50 (m, 3 H, ArH), 7.56 (t, J = 7.4 Hz, 1 H, ArH), 7.79 (d, J = 7.7 Hz, 1 H, ArH), 7.89 (d, J = 7.3 Hz, 2 H, ArH), 8.10 (d, J = 8.1 Hz, 1 H, ArH), 8.28 (s, 1 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.1, 204.2, 197.0, 148.4, 140.2, 136.1, 134.8, 133.9, 129.8, 128.9 (2 C), 128.3 (2 C), 123.8, 123.2, 91.2, 51.9, 51.6, 46.7, 39.8, 31.7, 30.8, 26.4 ppm. FTIR (KBr): $\tilde{\nu}$ = 3481, 3431, 2957, 2917, 1738, 1692, 1529, 1348, 1234, 1143, 1079, 817, 754, 737, 693 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{23}H_{23}NO_6$ $[M]^+$ 409.1525; found 409.1518.

2-Hydroxy-5,5-dimethyl-2-[1-(4-nitrophenyl)-3-oxo-3-phenylpropyl]cyclohexane-1,3-dione (6g): According to general procedure C, Michael adduct **3g** (78.7 mg, 0.2 mmol) was employed. Column chromatography gave **6g** as a yellow solid (76.2 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.79 (s, 3 H, CH_3), 1.34 (s, 3 H, CH_3), 2.44 (dd, J = 13.6, 2.8 Hz, 1 H, CH_2), 2.58 (dd, J = 14.4, 2.8 Hz, 1 H, CH_2), 3.02 (d, J = 13.6 Hz, 1 H, CH_2), 3.39 (d, J = 14.4 Hz, 1 H, CH_2), 3.43 (dd, J = 18.8, 6.9 Hz, 1 H, CH_2), 3.54 (dd, J = 18.8, 5.2 Hz, 1 H, CH_2), 4.12 (s, 1 H, OH), 4.48 (t, J = 6.0 Hz, 1 H, CH), 7.44 (t, J = 7.6 Hz, 2 H, ArH), 7.57 (t, J = 7.8 Hz, 1 H, ArH), 7.61 (d, J = 8.8 Hz, 2 H, ArH), 7.88 (t, J = 7.8 Hz, 2 H, ArH), 8.14 (d, J = 8.8, Hz, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.1, 204.0, 197.0, 147.7, 145.5, 134.8, 134.0, 129.7 (2 C), 128.9 (2 C), 128.2 (2 C), 124.0 (2 C), 91.2, 51.9, 51.6, 46.8, 39.8, 31.7, 30.8, 26.4 ppm. FTIR (KBr): $\tilde{\nu}$ = 3490, 2952, 1732, 1693, 1596, 1515, 1449, 1353, 1237, 1143, 1080, 1002, 970, 873, 859, 752, 686 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{23}H_{23}NO_6$ $[M]^+$ 409.1525; found 409.1530.

2-[3-(4-Chlorophenyl)-1-(4-methoxyphenyl)-3-oxopropyl]-2-hydroxy-5,5-dimethylcyclohexane-1,3-dione (6h): According to general procedure C, Michael adduct **3h** (82.6 mg, 0.2 mmol) was employed. Column chromatography gave **6h** as a white solid (81.5 mg, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.77 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 2.40 (dd, J = 13.5, 2.7 Hz, 1 H, CH_2), 2.53 (dd, J = 14.4, 2.7 Hz, 1 H, CH_2), 3.03 (d, J = 13.5 Hz, 1 H, CH_2), 3.34 (dd, J = 18.3, 7.5 Hz, 1 H, CH_2), 3.40 (d, J = 14.4 Hz, 1 H, CH_2), 3.41 (dd, J = 18.3, 4.2 Hz, 1 H, CH_2), 3.85 (s, 3 H, OCH_3), 4.07 (s, 1 H, OH), 4.36 (t, J = 5.9 Hz, 1 H, CH), 6.89 (d, J = 8.6 Hz, 2 H, ArH), 7.24 (d, J = 8.7 Hz, 2 H, ArH), 7.33 (d, J = 8.6 Hz, 2 H, ArH), 7.85 (d, J = 8.7 Hz, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.5, 204.4, 195.9, 164.0, 136.8, 134.0, 130.6 (2 C), 130.0 (2 C), 129.5, 129.0 (2 C), 113.9 (2 C), 91.7, 55.6, 51.8, 51.7, 46.7, 39.6, 31.6, 30.8, 26.5 ppm. FTIR (KBr): $\tilde{\nu}$ = 3493, 2962, 2929, 1732, 1694, 1605, 1574, 1510, 1493, 1422, 1359, 1324, 1261, 1240, 1169, 1143, 1093, 1079, 1034, 996, 838, 823, 677, 604, 522 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{24}H_{25}O_5{}^{35}Cl$ $[M]^+$ 428.1391; found 428.1391.

2-[1,3-Bis(4-chlorophenyl)-3-oxopropyl]-2-hydroxy-5,5-dimethylcyclohexane-1,3-dione (6i): According to general procedure C, Michael adduct **3i** (83.5 mg, 0.2 mmol) was employed. Column chromatography gave **6i** as a white solid (81.5 mg, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.77 (s, 3 H, CH_3), 1.31 (s, 3 H, CH_3), 2.41 (dd, J = 13.5, 2.9 Hz, 1 H, CH_2), 2.53 (dd, J = 14.4, 2.9 Hz, 1 H, CH_2), 3.00 (d, J = 13.5 Hz, 1 H, CH_2), 3.32 (dd, J = 18.6, 6.6 Hz, 1 H, CH_2), 3.37 (d, J = 14.4 Hz, 1 H, CH_2), 3.49 (dd, J = 18.6, 5.4 Hz, 1 H, CH_2), 4.05 (s, 1 H, OOH), 4.33 (t, J = 6.0 Hz, 1 H, CH), 7.24 (d, J = 8.4 Hz, 2 H, ArH), 7.32 (d, J = 8.4 Hz, 2 H, ArH), 7.40 (d, J = 8.7 Hz, 2 H, ArH), 7.82 (d, J = 8.7 Hz, 2 H, ArH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.5, 204.3, 196.4, 140.3, 136.5, 134.6, 134.1, 129.9 (2 C), 129.6 (2 C), 129.1 (4C), 91.4, 51.8, 51.7, 46.5, 40.0, 31.6, 30.8, 26.5 ppm. FTIR (KBr): $\tilde{\nu}$ = 3500, 2962, 2948, 1734, 1692, 1590, 1491, 1404, 1357, 1342, 1236, 1203, 1173, 1144, 1095, 1080, 1016, 999, 970, 830, 760, 674, 621, 520 cm^{-1}. HRMS (EI-TOF): calcd. for $C_{23}H_{22}O_4{}^{35}Cl_2$ $[M]^+$ 432.0866; found 432.0890.

X-ray Crystallographic Analysis of 6d:[11–13] Compound **6d** was crystallized as white crystals from EtOAc with the diffusion of petroleum ether at 0 °C in a refrigerator for two weeks. $C_{23}H_{22}Cl_2O_4$, M_r = 433.31, T = 291(2) K, triclinic, space group $P\bar{1}$, a = 10.9377(5) Å, b = 10.9571(5) Å, c = 11.0854(6) Å, α = 67.781(5)°, β = 61.343(5)°, γ = 86.701(6)°, V = 1066.63(9) Å^3, Z = 2, $\rho_{calcd.}$ = 1.349 g cm^{-3}, crystal size: 0.50 × 0.40 × 0.40 mm, F(000) = 452, μ(Mo-K_α) = 0.331 mm^{-1}, min. transmission 0.8521, max. transmission: 0.8791, $2\theta_{max.}$ = 52.04°, 8824/4198 measured/independent reflections [R(int) = 0.0184], 3196/266 reflections used/number of parameters, refinement against |F|, GOF = 1.067, final R indices were R_1 = 0.0333 [$I > 2\sigma(I)$] and wR_2 = 0.0877 [$I > 2\sigma(I)$]. Mo-K_α radiation (λ = 0.71073). The data collection routine, unit-cell refinement, and data processing were carried out with the program CrysAlis.[11] The structure was solved by direct methods and refined by full-matrix least-squares methods with the SHELXL-97 programs.[12]

Supporting Information (see footnote on the first page of this article): Copies of ^{1}H and ^{13}C NMR spectra of compounds **3a**–**i**, **4a**, **5a**–**i**, and **6a**–**i**.

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[13] CCDC-100308 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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