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A convenient and efficient preparation of β-substituted α-haloenones from diazodicarbonyl compounds

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Abstract—Rhodium(II)-catalyzed reactions of cyclic diazodicarbonyl compounds with a variety of halides have been examined. With acid halides, β-acyloxy α-haloenones are produced in good yields. With benzyl halides, β-benzyloxy α-haloenones are obtained in good yields. Reactions with methylene halides yield β-halomethoxy α-haloenones in good yields, whereas reactions with ethyl halides and ethylene dihalides result in β-hydroxy α-haloenones in high yields. These reactions provide a useful and rapid entry to β-substituted α-haloenones. The mechanistic pathway for the formation of these products has been also described in terms of halonium ylides.

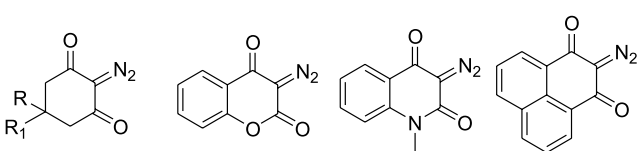
1. Introduction

The α-haloenones have been widely used as a key intermediate in the synthesis of numerous compounds[1] and biologically active natural products.[2] There are many methods available for the preparation of α-haloenones. They are typically prepared by treatment of α,β-enones with halogenating agents such as X_2,[3] NaX/oxone,[4] NaX/DMD/Amberlyst 15,[5] PhSeX,[6] pyr/HBr/Br_2,[7] $KBrO_3$/HBr/H_2O[8] followed by dehydrohalogenation under acidic or basic conditions. Although these reagents are known to be highly reactive, their synthetic exploitation has been limited due to the difficulty in controlling their regioselectivity, the strong reaction conditions, and the side reactions involving polyhalogenation.[9] The necessity for overcoming these serious problems has prompted our research for a preparation of β-substituted α-haloenones. In particular, a few methods for preparation of β-alkyl α-haloenones have been reported in the literature,[3b,4] but no facile methodology for the direct preparation of acyloxy, benzyloxy, and halomethoxy α-haloenones has yet been developed.

The rhodium(II)-catalyzed decomposition of diazodicarbonyl compounds has become a useful method in organic synthesis.[10] We have been interested in rhodium(II)-catalyzed reactions of diazodicarbonyl compounds with several substrates.[11] While continuing our work based on the rhodium(II)-catalyzed reactions, we have expanded this work to the synthesis of α-haloenones. In order to examine the breadth and mechanism of the reactions described in our preliminary communication,[12] we have studied a number of halides in reaction with metal carbenoids derived from cyclic diazodicarbonyl compounds. We report herein a facile and efficient preparation of a variety of α-haloenones as a catalytic reaction starting from diazodicarbonyl compounds.

2. Results and discussion

Diazodicarbonyl compounds **1**–**7** were prepared by diazo-transfer reaction of the corresponding 1,3-dicarbonyl compounds with MsN_3 (Fig. 1).[13] These solid compounds are fairly stable and can be stored in a refrigerator for a long time without any decomposition. We originally described reaction of diazodicarbonyl compounds with acid chlorides in the presence of $Rh_2(OAc)_4$.[12a] The influence of other metal catalysts between diazodicarbonyl compound **1** and acetyl chloride was first investigated. No products were seen with copper acetate (1 mol%) at room temperature, while both $Rh_2(OCOCF_3)_4$ (0.5 mol%) and $Rh_2(OAc)_4$ (0.5 mol%) gave product **8** in 13 and 64% yields, respectively. We found that electron-rich rhodium catalyst



1 R=R$_1$=H
2 R=H, R$_1$=Ph
3 R=H, R$_1$=2-furyl
4 R=R$_1$=Me

5 **6** **7**

Figure 1.

Keywords: rhodium(II)-catalyzed reaction; diazodicarbonyl compounds; beta-acyloxy alpha-haloenones; beta-benzyloxy alpha-haloenones; beta-halomethoxy alpha-haloenones; beta-hydroxy alpha-haloenones.

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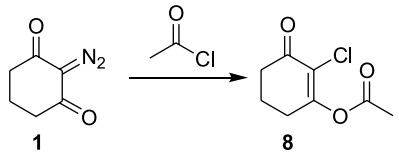
Table 1. Effect of catalyst in the reaction of diazodicarbonyl compound **1** and acetyl chloride



1 **8**

Catalyst	Condition (mol%)	Yield (%)
$Cu(OAc)_2$	1	0
$Rh_2(OCOCF_3)_4$	0.5	13
$Rh_2(OAc)_4$	0.5	64
$Rh_2(OAc)_4$	1	81

showed a much superior catalytic activity for this reaction. A higher yield of **8** (81%) was obtained when 1 mol% of $Rh_2(OAc)_4$ was used as a catalyst. The structure of **8** is easily assigned by the two IR carbonyl absorptions at 1777 and 1693 cm^{-1} associated with a vinyl ester and an enone. The ^1H NMR spectrum shows the peak of the methyl group of the vinyl acetate at δ 2.26 ppm as a singlet. Further support is obtained from its ^{13}C NMR spectrum, which shows the expected two carbonyl carbons of the enone at δ 191.31 and the vinyl ester at δ 166.15 (Table 1).

Additional reaction of diazodicarbonyl compound **1** with other acid chlorides such as propionyl chloride and butyryl chloride (20-fold excess), which serve as a reactant and a solvent, in the presence of 1 mol% of $Rh_2(OAc)_4$, afforded

Table 2. Reaction of diazodicarbonyl compounds with acid halides[a]

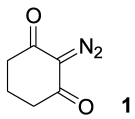
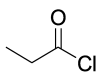
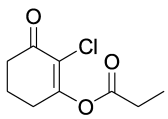
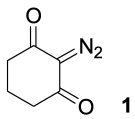
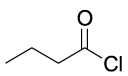
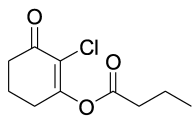
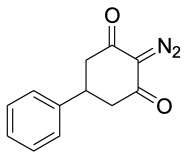
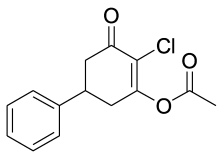
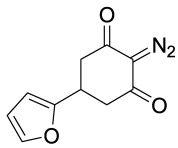
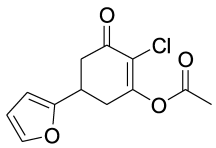
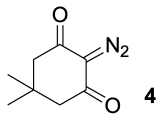
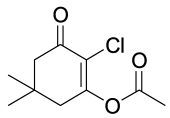
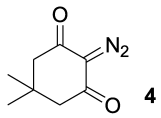
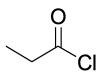
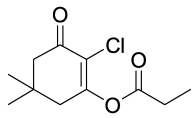
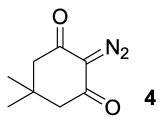
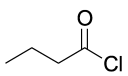
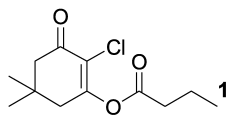
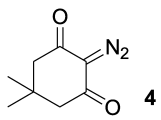
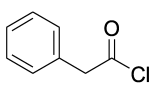
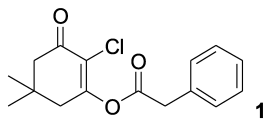
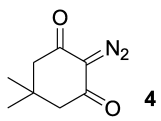
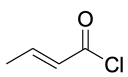
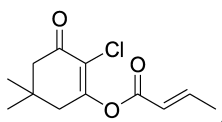
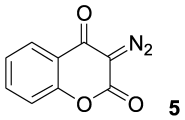
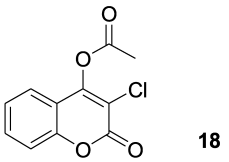
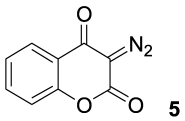
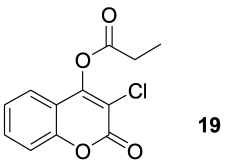
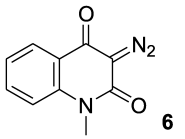
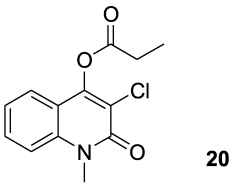
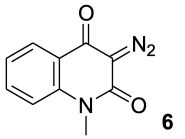
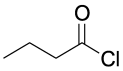
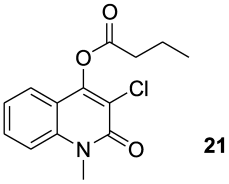
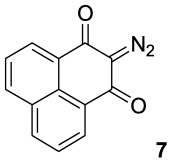
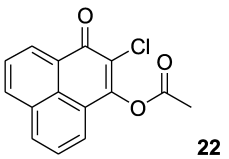
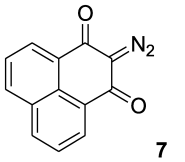
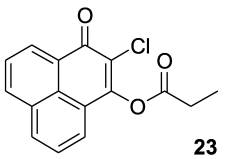
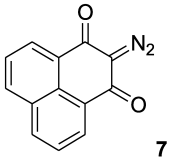
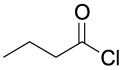
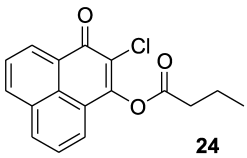
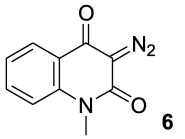
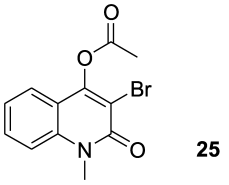
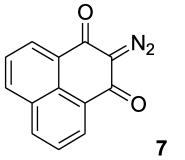
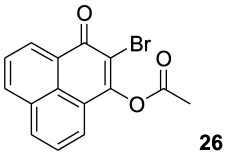
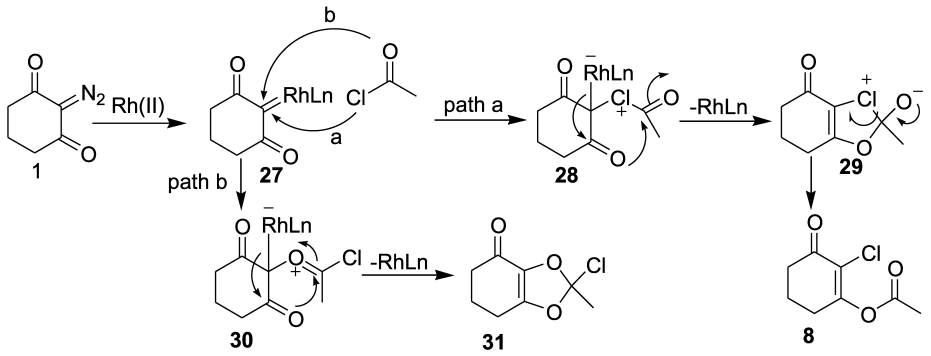
Entry	Diazodicarbonyl compound	Acid halide	Condition	Product	Yield (%)[b]
1	 **1**		rt, 12 h	 **9**	85
2	 **1**		rt, 12 h	 **10**	96
3	 **2**		50°C, 7 h	 **11**	89
4	 **3**		50°C, 7 h	 **12**	80
5	 **4**		rt, 12 h	 **13**	80
6	 **4**		rt, 12 h	 **14**	90
7	 **4**		rt, 12 h	 **15**	92
8	 **4**		rt, 12 h	 **16**	71
9	 **4**		rt, 12 h	 **17**	70

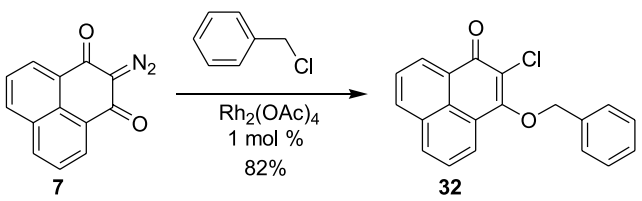
Table 2 (*continued*)

Entry	Diazodicarbonyl compound	Acid halide	Condition	Product	Yield (%)[b]
10	 **5**		50°C, 7 h	 **18**	70[c]
11	 **5**		50°C, 7 h	 **19**	75[c]
12	 **6**		50°C, 7 h	 **20**	70
13	 **6**		50°C, 7 h	 **21**	72
14	 **7**		rt, 12 h	 **22**	70
15	 **7**		rt, 12 h	 **23**	74
16	 **7**		rt, 12 h	 **24**	74
17	 **6**		50°C, 7 h	 **25**	53
18	 **7**		rt, 12 h	 **26**	46

[a] Reactions were carried out in the presence of 1 mol% of $Rh_2(OAc)_4$.
[b] Isolated yields after column chromatography.
[c] Reaction of entries 10 and 11 was carried out in the presence of 1 mol% of $Rh_2(OPiv)_4$.



Scheme 1.



Scheme 2.

compounds **9**–**10** in 85 and 96% yields, respectively (entries 1 and 2, Table 2). Reaction of diazodicarbonyl compounds **3**–**4** with a phenyl and a furyl group on the cyclic ring gave products **11**–**12** in 89 and 80% yields (entries 3 and 4), respectively. Interestingly, reaction of diazodicarbonyl compound **4** with phenylacetyl chloride and crotonyl chloride afforded products **16**–**17** in 71 and 70% yields, respectively (entries 8 and 9). In these reactions,

Table 3. Reaction of diazodicarbonyl compounds with benzyl halides[a]

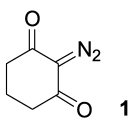
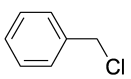
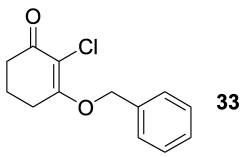
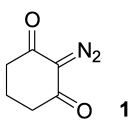
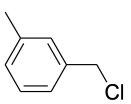
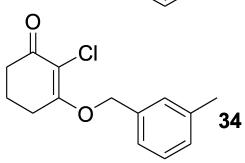
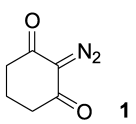
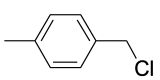
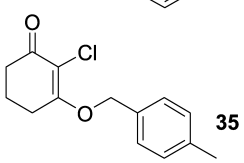
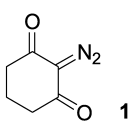
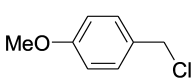
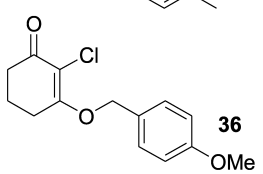
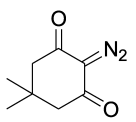
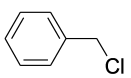
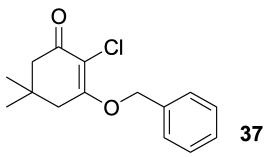
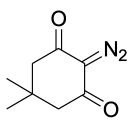
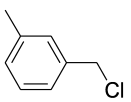
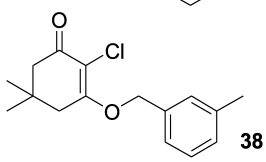
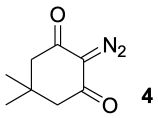
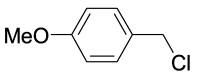
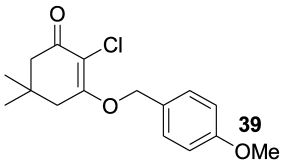
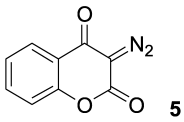
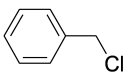
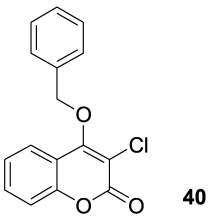
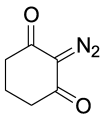
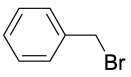
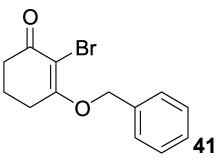
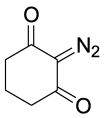
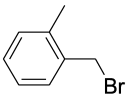
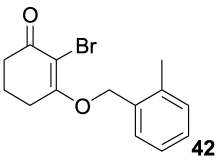
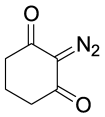
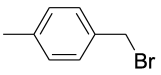
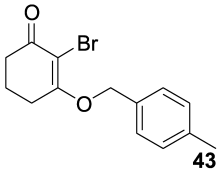
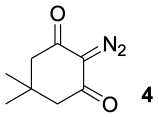
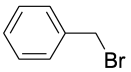
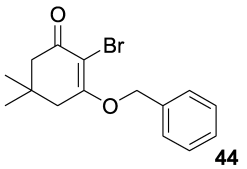
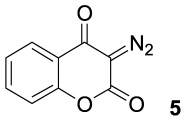
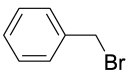
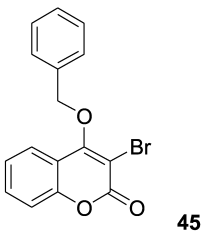
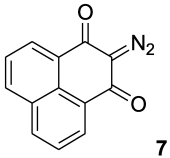
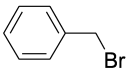
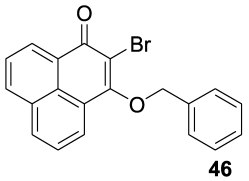
Entry	Diazodicarbonyl compound	Benzyl halide	Condition	Product	Yield (%)[b]
1	 **1**		rt, 12 h	 **33**	81
2	 **1**		rt, 12 h	 **34**	69
3	 **1**		rt, 12 h	 **35**	81
4	 **1**		rt, 9 h	 **36**	93
5	 **4**		rt, 12 h	 **37**	78
6	 **4**		rt, 12 h	 **38**	66

Table 3 (*continued*)

Entry	Diazodicarbonyl compound	Benzyl halide	Condition	Product	Yield (%)[b]
7	 **4**		rt, 9 h	 **39**	95
8	 **5**		50°C, 6 h	 **40**	55[c]
9	 **1**		rt, 10 h	 **41**	67
10	 **1**		rt, 12 h	 **42**	55
11	 **1**		rt, 10 h	 **43**	65
12	 **4**		rt, 10 h	 **44**	70
13	 **5**		50°C, 6 h	 **45**	60[c]
14	 **7**		rt, 12 h	 **46**	85

[a] Reaction were carried out in the presence of 1 mol% of $Rh_2(OAc)_4$.
[b] Isolated yields after column chromatography.
[c] Reaction of entries 8 and 13 was carried out in the presence of 1 mol% of $Rh_2(OPiv)_4$.

no addition products to the aromatic ring and C=C bond could be detected.

Reactions of more complex diazodicarbonyl compounds such as 3-diazo-2,4-chromenedione (**5**), 3-diazoquinoline-2,4-dione (**6**), and 2-diazo-1*H*-1,3-phenalenedione (**7**) were also successful. Treatment of **5** with acetyl chloride and propionyl chloride at room temperature for 12 h under 1 mol% of $Rh_2(OAc)_4$ afforded compounds **18**–**19** in 35 and 39% yields, respectively, whereas reaction at 50°C for 7 h in the presence of 1 mol% of $Rh_2(OPiv)_4$ gave **18**–**19** in high yields (70 and 75%). Similarly, reactions of **6** with propionyl chloride and butyryl chloride at 50°C for 7 h in the presence of $Rh_2(OAc)_4$ afforded products **20** and **21** in 70 and 72% yields, respectively. In these cases, only a single product was seen and no other possible regioisomers were found (entries 10–13, Table 2). Reaction of **7** with acetyl chloride, propionyl chloride, and butyryl chloride afforded products **22**–**24** in 70–74% yields (entries 14–16).

Extension of the reaction with AcBr was also successful. Reaction of **6** with AcBr at 50°C for 7 h afforded bromoenone **25** in 53% yield (entry 17). Similarly, reaction of diazodicarbonyl compound **7** with AcBr at room temperature for 12 h gave the expected product **26** in 46% yield (entry 18). The results are summarized in Table 2.

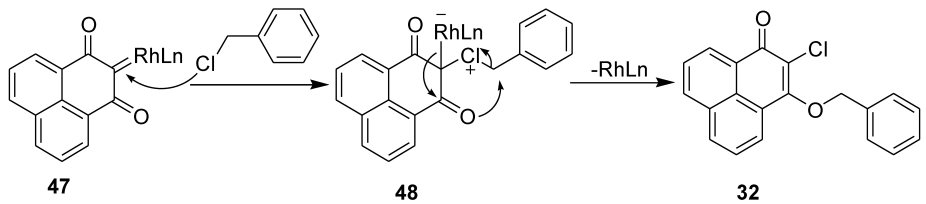
Although the exact mechanism for the formation of **8** is not clear, it is best described as shown in Scheme 1. The diazodicarbonyl compound **1** first gives a metal carbenoid **27** by displacement of nitrogen by $Rh_2(OAc)_4$. Nucleophilic attack of the chlorine or oxygen atom in the acid chloride to the electrophilic carbenoid **27** yields two possible intermediates **28** (halonium ylide)[14] and **30** (carbonyl ylide).[15] However, only compound **8** was observed experimentally, with no formation of the other possible product **31** being observed. Therefore, nucleophilic attack of the chlorine on **27** gives intermediate **28**, which undergoes fast intramolecular nucleophilic addition of oxygen to the carbonyl group followed by the cleavage of the C–Cl bond to give product **8**.

We also reported the reactions of diazodicarbonyl compounds with benzyl halides to produce β-benzyloxy α-haloenones.[12b] Reaction of **7** with benzyl chloride in the presence of 1 mol% of $Rh_2(OAc)_4$ at room temperature for 12 h afforded 3-benzyloxy-2-chlorophenalen-1-one (**32**) in an 82% yield (Scheme 2). The formation of **32** is identified by the observation of a carbonyl absorption in the IR spectrum at 1647 cm^{-1} (enone C=O) and the expected chemical shifts associated with the methylene protons of the benzyl group as a singlet at δ 5.40 ppm. Further reactions of diazodicarbonyl compounds with a range of benzyl halides were next examined under rhodium catalysis. Treatment of **1** with benzyl chloride afforded expected product **33** in 81% yield (entry 1, Table 3). In the treatment of benzyl chlorides with methyl substituents on the aromatic ring such as 3- and 4-methylbenzyl chloride, the expected products **34** and **35** were obtained in 69 and 81% yields, respectively (entries 2 and 3, Table 3). In particular, reactions with 4-methoxybenzyl chloride afforded α-chloroenones **36** (93%) and **39** (95%) in high yields, respectively (entries 4 and 7).

When benzyl bromide was used as a α-halogenating reagent, expected bromoenones were produced in good yields (entry 9–14, Table 3). Reaction of **1** with benzyl bromide in the presence of 1 mol% of $Rh_2(OAc)_4$ afforded 3-benzyloxy-2-bromocyclohex-2-enone (**41**) in 67% yield. With methyl substituted benzyl bromide, reactions were also successful. Reactions with 2-methylbenzyl bromide afforded **42** in 55% yield, whereas reaction with 4-methylbenzyl bromide gave **43** in 65% yield (entries 10 and 11). Reactions of the more complex diazodicarbonyl compounds **5** and **7** were also successful. Treatment of **5** with benzyl bromide at 50°C for 6 h in the presence 1 mol% of $Rh_2(OPiv)_4$ afforded **45** in 60% yield, whereas reaction of **7** with benzyl bromide at room temperature for 12 h gave **46** in 85% yield (entries 13 and 14). The results are summarized in Table 3.

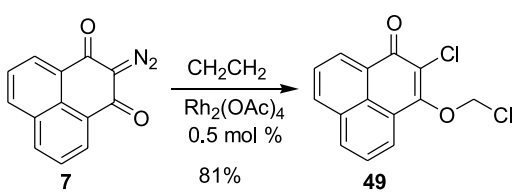
The plausible mechanism for the formation of **32** is shown in Scheme 3. The diazodicarbonyl compound **7** first gives a metal carbenoid **47**, which is attacked by the chlorine atom of benzyl chloride to give **48**. The intermediate **48** undergoes the intramolecular substitution reaction to yield product **32**.

Next, in order to obtain other types of α-halo compounds,



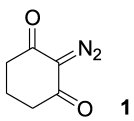
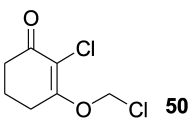
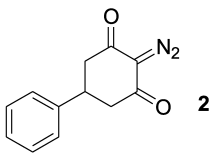
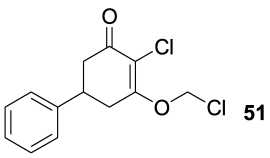
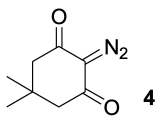
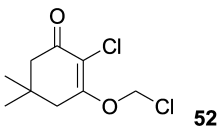
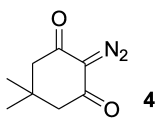
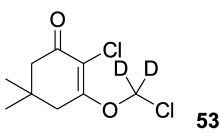
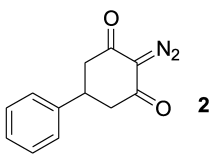
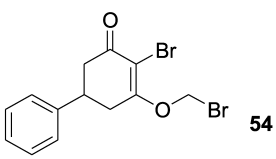
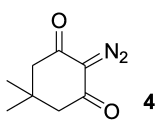
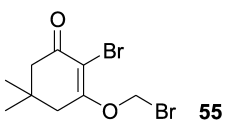
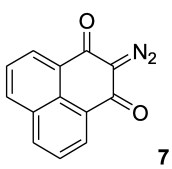
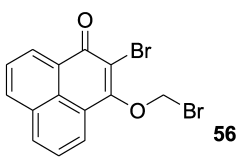
Scheme 3.

reactions of diazodicarbonyl compounds with alkyl halides such as methylene chloride or methylene bromide were attempted using a rhodium catalyst. Methylene chloride was first used as a test substrate to screen the new halogenating agents. Treatment of **7** with methylene chloride as a reactant and a solvent in the presence of 0.5 mol% of $Rh_2(OAc)_4$ at room temperature for 10 h affords the 2-chloro-3-chloromethoxyphenalen-1-one (**49**) in 81% yield (Scheme 4). Support for the structural assignment comes from its



Scheme 4.

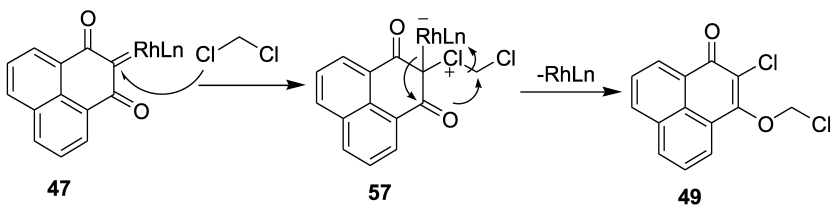
Table 4. Reaction of diazodicarbonyl compounds with methylene halides[a]

Entry	Diazodicarbonyl compound	Methyle halide	Condition	Product	Yield (%)[b]
1	 **1**	CH_2Cl_2	rt, 4 h	 **50**	79
2	 **2**	CH_2Cl_2	rt, 5 h	 **51**	90
3	 **4**	CH_2Cl_2	rt, 5 h	 **52**	81
4	 **4**	CD_2Cl_2	rt, 7 h	 **53**	75
5	 **2**	CH_2Br_2	rt, 5 h	 **54**	75
6	 **4**	CH_2Br_2	rt, 5 h	 **55**	78
7	 **7**	CH_2Br_2	50°C, 5 h	 **56**	85

[a] Reactions were carried out in the presence of 1 mol% of $Rh_2(OAc)_4$.
[b] Isolated yields after column chromatography.

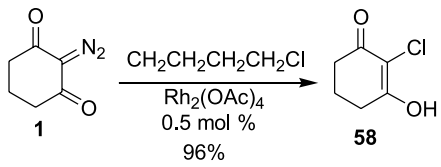
spectroscopic analysis. The formation of **49** was easily assigned by the chemical shifts associated with the methylene protons of the chloromethoxy group at δ 6.19 ppm as a singlet and by its IR carbonyl absorption of the enone at 1657 cm^{-1}. Similarly, reaction of diazodicarbonyl compound **1** with methylene chloride afforded expected compound **50** in 79% yield (entry 1, Table 4). Surprisingly, our result is in clear contrast to the rhodium (II)-catalyzed reaction of **1** with methylene chloride which gave exclusively 2-chloro-1,3-cyclohexanedione.[16]

Additional reaction of diazodicarbonyl compounds with methylene halides was also successful. Interestingly, reaction of **4** with CD_2Cl_2 afforded the product **53** in 75% yield (entry 4, Table 4). In this case, no peaks of the methylene group in the ^1H NMR spectrum could be detected, due to a change of deuterium. Treatment of **2** with methylene bromide at room temperature for 5 h in the presence of 0.5 mol% of $Rh_2(OAc)_4$ gave **54** in 75% yield. Similarly, other bromoenones **55** and **56** were produced in 78 and 85% yields, respectively



47 **57** **49**

Scheme 5.



Scheme 6.

(entries 6 and 7). The results are summarized in Table 4.

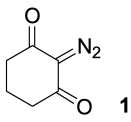
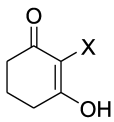
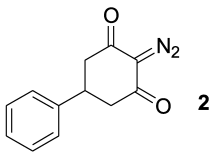
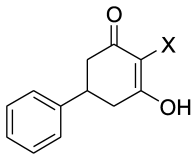
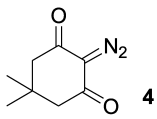
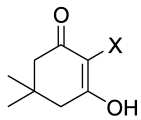
The formation of **49** can be explained in terms of a nucleophilic attack by the chlorine of methylene chloride as shown in Scheme 5. Electrophilic carbenoid **47** is attacked by chlorine to give an ylide **57**, which subsequently undergoes an intramolecular substitution reaction to give product **49**.

In order to extend the utility of this methodology, further reactions with other alkyl halides such as *n*-butyl chloride, ethyl bromide, and ethyl iodide were next examined. When diazodicarbonyl compound **1** was treated with *n*-butyl chloride as a reagent and a solvent at room temperature for 10 h in the presence of 0.5 mol% of $Rh_2(OAc)_4$, β-hydroxy α-chloroenone **58** was obtained in a high yield (96%) instead of the formation of β-substituted α-chloroenone (Scheme 6).

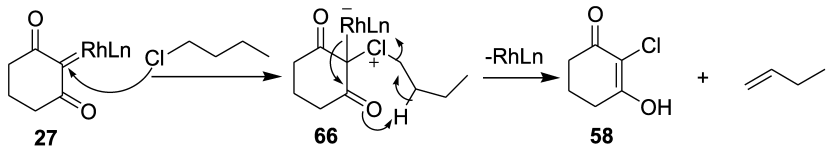
The structure of **58** was easily determined by its spectroscopic analysis. The ^1H NMR spectrum shows the peak of the enol proton at δ 6.52 ppm as a broad singlet. Interestingly, we found that the product from this reaction was very different from that with methylene halides as already shown in Scheme 4. A number of other alkyl halides were tested in the reaction (Table 5) as a new α-halogenating reagent. Reaction of **1** with ethylene dichloride also afforded product **58** in a 95% yield (entry 1, Table 5). As other α-brominating reagents, ethyl bromide, ethylene dibromide, and 1,3-dibromopropane afforded β-hydroxy α-bromoenone **59** in 95, 96, and 98% yields, respectively (entries 2–4). Although a few methods available for the synthesis of β-hydroxy α-chloro and α-bromoenone have been reported,[8] there are no known examples for the preparation of β-hydroxy α-iodoenones. Under the same conditions, reaction with ethyl iodide and propyl iodide yielded β-hydroxy α-iodoenone **60** in 94 and 96% yields, respectively (entries 5 and 6). The other similar results are collected in Table 5 (entries 7–14).

The formation of **58** could be explained as shown in Scheme 7. Unlike methylene chloride, *n*-butyl chloride has hydrogens on the β-carbon. Nucleophilic attack of chlorine of *n*-butyl chloride to the electrophilic metal carbenoid **27** gives the chloronium ylide **66**, which undergoes a hydrogen abstract and cleavage of the C–Cl bond to yield **58**. In view of our results, with alkyl halides that have no β-hydrogens such as methylene chloride and methylene bromide, β-substituted α-haloenone products are formed, while

Table 5. Reaction of diazodicarbonyl compounds with alkyl halides[a]

Entry[a]	Diazodicarbonyl compound	Alkyl halide	Product	Yield (%)[b]
				
1		$ClCH_2CH_2Cl$	**58** X=Cl	95
2		CH_3CH_2Br	**59** X=Br	95
3		$BrCH_2CH_2Br$	**59** X=Br	96
4		$BrCH_2CH_2CH_2Br$	**59** X=Br	98
5		CH_3CH_2I	**60** X=I	94
6		$CH_3CH_2CH_2I$	**60** X=I	96
				
7		$CH_3CH_2CH_2CH_2Cl$	**61** X=Cl	92
8		CH_3CH_2Br	**62** X=Br	90
				
9		$CH_3CH_2CH_2CH_2Cl$	**63** X=Cl	98
10		$ClCH_2CH_2Cl$	**63** X=Cl	98
11		CH_3CH_2Br	**64** X=Br	98
12		$BrCH_2CH_2Br$	**64** X=Br	96
13		CH_3CH_2I	**65** X=I	93
14		$ICH_2CH_2CH_2I$	**65** X=I	92

[a] Reactions run with 0.5 mol% of $Rh_2(OAc)_4$ at room temperature for 10 h.
[b] Isolated yields after column chromatography.



Scheme 7.

alkyl halides with β-hydrogens such as *n*-butyl chloride, ethyl bromide, and ethyl iodide lead to β-hydroxy α-chloroenones.

In conclusion, rhodium-catalyzed reactions of diazodicarbonyl compounds with a variety of alkyl halides are described. This reaction provides an efficient synthetic route for the preparation of α-halo enones. Further application of these products will be investigated, which is now in progress in our laboratory.

3. Experimental

All experiments were carried out under a nitrogen atmosphere. Merck precoated silica gel plates (Art. 5554) with fluorescent indicator were used for analytical TLC. Flash column chromatography was performed using silica gel 9385 (Merck). Melting points were determined with microcover glasses on a Fisher–Johns apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker Model ARX (300 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker Model ARX (75 MHz) spectrometer in $CDCl_3$ using 77.0 ppm as the solvent chemical shift. IR spectra were recorded on a JASCO FTIR 5300 spectrophotometer. Elemental analyses and HRMS mass spectra were carried out by Korea Basic Science Institute (Daegu).

3.1. General procedure for the synthesis of α-acyloxy α-haloenones (8–26)

To a solution of diazodicarbonyl compound (1.0 mmol) and acid halide (20 mmol) was added rhodium catalyst (0.01 mmol) at room temperature under a N_2 atmosphere. The reaction mixture was stirred at room temperature for 12 h or 50°C for 7 h. The halide was evaporated under reduced pressure to give the residue. The residue was purified by flash column chromatography on silica gel to give the product.

3.1.1. 3-Acetoxy-2-chlorocyclohex-2-enone (8). Reaction of **1** (138 mg, 1.0 mmol) and acetyl chloride (1.570 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **8** (153 mg, 81%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.67 (2H, t, J=6.1 Hz, CH_2), 2.59 (2H, t, J=6.1 Hz, CH_2), 2.26 (3H, s, CH_3), 2.11–2.02 (2H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.31 (C=O, enone), 166.15 (C=O, vinylic ester), 164.31, 121.97, 37.21, 29.84, 20.58, 20.13; IR (neat) 2959, 1777 (C=O, vinylic ester), 1693 (C=O, enone), 1630, 1427, 1371, 1352, 1281, 1169, 1065, 1007, 968, 912, 873, 845 cm^{-1}. Anal. calcd for $C_8H_9ClO_3$: C, 50.94; H, 4.81. Found: C, 50.82; H, 5.14.

3.1.2. 2-Chloro-3-propanoyloxycyclohex-2-enone (9). Reaction of **1** (138 mg, 1.0 mmol) and propionyl chloride (1.850 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **9** (172 mg, 85%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.64 (2H, t, J=6.1 Hz, CH_2), 2.57–2.48 (4H, m, 2×CH_2), 2.07–1.99 (2H, m, CH_2), 1.19 (3H, t, J=6.0 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.33 (C=O, enone), 169.78 (C=O, ester), 164.49, 121.85, 37.23, 29.91, 27.42, 20.15, 8.75; IR (neat) 2946, 2888, 1770 (C=O, vinylic ester), 1694 (C=O, enone), 1628, 1460, 1424, 1345, 1277, 1167, 1115, 1076, 1017, 986, 841 cm^{-1}. Anal. calcd for $C_9H_{11}ClO_3$: C, 53.35; H, 5.47. Found: C, 53.22; H, 5.54.

3.1.3. 3-Butanoyloxy-2-chlorocyclohex-2-enone (10). Reaction of **1** (138 mg, 1.0 mmol) and butyryl chloride (2.131 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **10** (208 mg, 96%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.67 (2H, t, J=6.1 Hz, CH_2), 2.59 (2H, t, J=6.3 Hz, CH_2), 2.50 (2H, t, J=7.4 Hz, CH_2), 2.11–2.02 (2H, m, CH_2), 1.80–1.64 (2H, m, CH_2), 1.00 (3H, t, J=7.4 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.54 (C=O, enone), 168.95 (C=O, ester), 164.59, 121.77, 37.14, 35.69, 29.85, 20.27, 18.05, 13.35; IR (neat) 2967, 2878, 1769 (C=O, vinylic ester), 1696 (C=O, enone), 1628, 1458, 1418, 1346, 1275, 1235, 1127, 1088, 1015, 970, 914 cm^{-1}. Anal. calcd for $C_{10}H_{13}ClO_3$: C, 55.44; H, 6.05. Found: C, 55.28; H, 5.96.

3.1.4. 3-Acetoxy-2-chloro-5-phenylcyclohex-2-enone (11). Reaction of **2** (214 mg, 1.0 mmol) and acetyl chloride (1.570 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **11** (236 mg, 89%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36–7.21 (5H, m, ArH), 3.55–3.43 (1H, m, CH), 3.07–2.75 (4H, m, 2×CH_2), 2.08 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.51 (C=O, enone), 166.25 (C=O, vinylic ester), 163.24, 141.08, 128.91, 127.47, 126.52, 122.05, 44.13, 38.49, 37.43, 20.65; IR (neat) 3032, 2928, 1777 (C=O, vinylic ester), 1694 (C=O, enone), 1632, 1427, 1372, 1244, 1169, 1044, 1019, 976, 914, 877 cm^{-1}. Anal. calcd for $C_{14}H_{13}ClO_3$: C, 63.52; H, 4.95. Found: C, 63.77; H, 5.03.

3.1.5. 3-Acetoxy-2-chloro-5-(2-furyl)-cyclohex-2-enone (12). Reaction of **3** (204 mg, 1.0 mmol) and acetyl chloride (1.570 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **12** (204 mg, 80%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (1H, d, J=1.8 Hz, CH), 6.28 (1H, dd, J=3.3, 1.8 Hz, CH), 6.07 (1H, d, J=3.3 Hz, CH), 3.62–3.52 (1H, m), 2.98–2.89 (3H, m), 2.84–2.75 (1H, m), 2.27 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.00 (C=O, enone), 166.25 (C=O, vinylic ester), 162.54, 154.11, 141.92, 122.06, 110.25, 105.43, 41.50, 34.64, 31.92, 20.66; IR (neat) 3121, 2917, 2849, 1777 (C=O, vinylic ester), 1696 (C=O, enone), 1632, 1508, 1429, 1364, 1169, 1017, 978, 943 cm^{-1}. Anal. calcd for $C_{12}H_{11}ClO_4$: C, 56.60; H, 4.35. Found: C, 56.89; H, 4.57.

3.1.6. 3-Acetoxy-2-chloro-5,5-dimethylcyclohex-2-enone (13). Reaction of **4** (166 mg, 1.0 mmol) and acetyl chloride (1.570 mg, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded

13 (173 mg, 80%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.54 (2H, s, CH_2), 2.44 (2H, s, CH_2), 2.25 (3H, s, CH_3), 1.10 (6H, s, 2×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.41 (C═O, enone), 166.39 (C═O, vinylic ester), 162.54, 121.24, 51.05, 43.53, 32.62, 28.10, 29.93, 20.69; IR (neat) 2963, 2876, 1777 (C═O, vinylic ester), 1694 (C═O, enone), 1634, 1470, 1416, 1372, 1348, 1294, 1181, 1026, 947, 920, 856 cm^{-1}; *m/z* (EI) 216 (M^+, 5%), 174 (96), 159 (68), 149 (49), 129 (19), 118 (100), 103 (120), 83 (22), 69 (6), 55 (16). Anal. calcd for $C_{10}H_{13}ClO_3$: C, 55.44; H, 6.05. Found: C, 55.43; H, 6.24.

3.1.7. 2-Chloro-5,5,-dimethyl-3-propanoyloxycyclohex-2-enone (14). Reaction of **4** (166 mg, 1.0 mmol) and propionyl chloride (1.850 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **14** (208 mg, 90%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.50 (2H, *J*=6.0 Hz, CH_2), 2.50 (2H, s, CH_2), 2.41 (2H, s, CH_2), 1.17 (3H, t, *J*=6.0 Hz, CH_3), 1.06 (6H, s, 2×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.37 (C═O, enone), 169.99 (C═O, vinylic ester), 162.73, 121.03, 50.98, 43.46, 32.55, 27.84, 27.38, 8.73; IR (neat) 2962, 2878, 1771 (C═O, vinylic ester), 1694 (C═O, enone), 1634, 1464, 1372, 1345, 1290, 1267, 1155, 1113, 1074, 1026, 947, 918, 850 cm^{-1}. Anal. calcd for $C_{11}H_{15}ClO_3$: C, 57.27; H, 6.55. Found: C, 57.54; H, 6.44.

3.1.8. 3-Butanoyloxy-2-chloro-5,5-dimethylcyclohex-2-enone (15). Reaction of **4** (166 mg, 1.0 mmol) and butyryl chloride (2.131 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **15** (224 mg, 92%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.54 (2H, s, CH_2), 2.49 (2H, t, *J*=7.4 Hz, CH_2), 2.45 (2H, s, CH_2), 1.77–1.70 (2H, m, CH_2), 1.11 (6H, s, 2×CH_3), 1.00 (3H, t, *J*=7.4 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.11 (C═O, enone), 166.20 (C═O, ester), 162.47, 121.11, 51.00, 43.44, 32.49, 27.81, 20.53; IR (neat) 2965, 2878, 1769 (C═O, vinylic ester), 1696 (C═O, enone), 1634, 1468, 1415, 1372, 1346, 1289, 1155, 1127, 1086, 1026, 947 cm^{-1}. Anal. calcd for $C_{12}H_{17}ClO_3$: C, 58.90; H, 7.00. Found: C, 58.68; H, 7.23.

3.1.9. 2-Chloro-5,5-dimethyl-3-phenylacetoxycyclohex-2-enone (16). Reaction of **4** (166 mg, 1.0 mmol) and phenylacetyl chloride (3.092 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **16** (208 mg, 71%) as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.27 (5H, m, ArH), 3.82 (2H, s, CH_2), 2.51 (2H, s, CH_2), 2.43 (2H, s, CH_2), 1.09 (6H, s, 2×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.37 (C═O, enone), 176.94 (C═O, ester), 167.25, 162.62, 132.21, 129.29, 128.61, 127.33, 51.08, 42.53, 40.87, 32.50, 27.85; IR (neat) 3065, 3032, 2963, 1769 (C═O, vinylic ester), 1694 (C═O, enone), 1634, 1497, 1454, 1412, 1372, 1345, 1290, 1221, 1101, 1024, 947, 920 cm^{-1}. Anal. calcd for $C_{16}H_{17}ClO_3$: C, 65.64; H, 5.85. Found: C, 65.83; H, 5.69.

3.1.10. 3-((*E*)-but-2-enoyloxy)-2-chloro-5,5-dimethylcyclohex-2-enone (17). Reaction of **4** (166 mg, 1.0 mmol) and crotonyl chloride (2.323 g, 20.0 mmol, 90%) under $Rh_2(OAc)_4$ (4.4 mg) afforded **17** (170 mg, 70%) as a solid; mp 59–60°C (from hexane–ethylacetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21–7.12 (1H, m, vinylic CH), 5.95 (1H, d, *J*=15.5 Hz, vinylic CH), 2.58 (2H, s, CH_2), 2.46 (2H, s, CH_2), 1.95 (3H, d, *J*=7.9 Hz, CH_3), 1.11 (6H, s, 2×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.36 (C═O, enone), 162.78 (C═O, ester), 161.59, 149.23, 120.94, 120.52, 51.00, 43.34, 32.58, 27.84, 18.29; IR (KBr) 2962, 2878, 1741 (C═O, vinylic ester), 1694 (C═O, enone), 1653, 1626, 1460, 1443, 1372, 1343, 1314, 1296, 1283, 1196, 1150, 1098, 1026, 1009, 970, 945 cm^{-1}. Anal. calcd for $C_{12}H_{15}ClO_3$: C, 59.39; H, 6.23. Found: C, 59.16; H, 6.32.

3.1.11. 4-Acetoxy-3-chlorochromen-2-one (18). Reaction of **5** (188 mg, 1.0 mmol) and acetyl chloride (1.570 g, 20.0 mmol) under $Rh_2(OPiv)_4$ (6.1 mg) afforded **18** (167 mg, 70%) as a solid; mp 167–168°C (from hexane–ethylacetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (1H, dd, *J*=8.2, 7.5 Hz, ArH), 7.49 (1H, d, *J*=7.8 Hz, ArH), 7.39 (1H, d, *J*=8.2 Hz, ArH), 7.34 (1H, dd, *J*=7.8, 7.5 Hz, ArH), 2.49 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.30 (C═O, ester), 157.75 (C═O, ester), 155.02, 151.17, 132.75, 125.00, 122.63, 116.85, 115.91, 20.34; IR (KBr) 3109, 3071, 3045, 1784 (C═O, vinylic ester), 1730 (C═O, ester), 1620, 1566, 1493, 1453, 1356, 1281, 1200, 1173, 1138, 1090, 1038, 1015, 1001, 903, 777, 734 cm^{-1}; *m/z* (EI) 238 (M^+, 17%), 196 (100), 162 (9), 121 (71), 92 (13), 63 (6). HRMS calcd for $C_{11}H_7ClO_4$ (M^+) 238.0033. Found 238.0034.

3.1.12. 3-Chloro-4-propanoyloxychromen-2-one (19). Reaction of **5** (188 mg, 1.0 mmol) and propionyl chloride (1.850 g, 20.0 mmol) under $Rh_2(OPiv)_4$ (6.1 mg) afforded **19** (189 mg, 75%) as a solid; mp 112°C (from hexane–ethylacetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (1H, dd, *J*=8.2, 7.5 Hz, ArH), 7.48 (1H, d, *J*=7.8 Hz, ArH), 7.39 (1H, d, *J*=8.2 Hz ArH), 7.33 (1H, dd, *J*=7.8, 7.5 Hz ArH), 2.79 (2H, q, *J*=7.6 Hz, CH_2), 1.37 (3H, t, *J*=7.6 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.94 (C═O, ester), 157.84 (C═O, ester), 155.17, 151.21, 132.80, 124.99, 122.63, 116.90, 116.07, 27.33, 8.95; IR (KBr) 3046, 2948, 1780 (C═O, vinylic ester), 1730 (C═O, ester), 1618, 1566, 1451, 1348, 1283, 1262, 1105, 1065, 1015, 877 cm^{-1}; *m/z* (EI) 252 (M^+, 16%), 196 (31), 167 (5.4), 121 (37), 120 (21), 92 (13), 75 (6.0), 57 (100). Anal. calcd for $C_{12}H_9ClO_4$: C, 57.05; H, 3.59. Found: C, 57.18; H, 3.69. HRMS (M^+) calcd for $C_{12}H_9ClO_4$ 252.0189. Found, 252.0186.

3.1.13. 3-Chloro-1-methyl-4-propanoyloxy-1*H*-quinolin-2-one (20). Reaction of **6** (201 mg, 1.0 mmol) and propionyl chloride (1.850 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **20** (186 mg, 70%) as a solid; mp 134–135°C (from hexane–ethylacetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64–7.57 (2H, m, ArH), 7.41 (1H, d, *J*=8.5 Hz, ArH), 7.28 (1H, d, *J*=8.0, 7.2 Hz ArH), 3.79 (3H, s, NCH_3), 2.79 (2H, q, *J*=7.5 Hz, CH_2), 1.36 (3H, t, *J*=7.5 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.86 (C═O, ester), 158.77 (C═O, amide), 151.48, 137.78, 131.56, 122.80, 118.35, 116.28, 114.47, 30.74, 27.33, 9.02; IR (KBr) 2988, 2946, 2922, 1772 (C═O, vinylic ester), 1653 (C═O, amide), 1624, 1601, 1501, 1456, 1418, 1350, 1306, 1182, 1113, 1074, 1001, 972, 882 cm^{-1}. Anal. calcd for $C_{13}H_{12}ClNO_3$: C, 58.77; H, 4.55. Found: C, 58.89; H, 4.32.

3.1.14. 4-Butanoyloxy-3-chloro-1-methyl-1*H*-quinolin-2-one (21). Reaction of **6** (201 mg, 1.0 mmol) and butyryl chloride (2.131 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg)

afforded **21**(201 mg, 72%) as a solid; mp 92°C (from hexane–ethylacetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64–7.56 (2H, m, ArH), 7.41 (1H, d, J=8.5 Hz, ArH), 7.28 (1H, d, J=8.0, 7.2 Hz, ArH), 3.78 (3H, s, NCH_3), 2.73 (2H, q, J=7.4 Hz, CH_2), 1.92–1.84 (2H, m, CH_2), 1.10 (3H, t, J=7.4 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.99 (C=O, ester), 158.77 (C=O, amide), 151.52, 137.84, 131.55, 122.83, 118.43, 116.36, 114.48, 35.70, 30.75, 18.32, 13.65; IR (KBr) 2970, 2938, 2880, 1769 (C=O, vinylic ester), 1655 (C=O, amide), 1624, 1601, 1456, 1418, 1360, 1304, 1182, 1243, 1105, 1078, 972 cm^{-1}. Anal. calcd for $C_{14}H_{14}ClNO_3$: C, 60.11; H, 5.04. Found: C, 60.34; H, 5.25.

3.1.15. 3-Acetoxy-2-chlorophenalen-1-one (22). Reaction of **7** (220 mg, 1.0 mmol) and acetyl chloride (1.570 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **22** (191 mg, 70%) as a solid; mp 195–198°C (from hexane–ethylacetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (1H, dd, J=7.4, 1.2 Hz, ArH), 8.25 (1H, dd, J=8.0, 1.1 Hz, ArH), 8.10 (1H, dd, J=8.2, 1.2 Hz, ArH), 7.89 (1H, dd, J=7.4, 1.1 Hz, ArH), 7.80 (1H, dd, J=8.0, 7.4 Hz, ArH), 7.64 (1H, dd, J=8.2, 7.4 Hz, ArH), 2.52 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.20 (C=O, enone), 167.05 (C=O, ester), 154.93, 136.37, 133.69, 132.48, 132.37, 128.61, 127.86, 127.58, 126.99, 125.63, 125.48, 124.40, 21.04; IR (KBr) 2926, 1775 (C=O, vinylic ester), 1640 (C=O, enone), 1574, 1404, 1368, 1323, 1225, 1215, 1182, 1157, 1088, 1028, 1001, 960 cm^{-1}; m/z (EI) 272 (M^+, 10%), 230 (100), 292 (15), 196 (15), 173 (22), 155 (30), 138 (34), 129 (22), 105 (9), 87 (5), 71 (6), 57 (7). Anal. calcd for $C_{15}H_9ClO_3$: C, 66.07; H, 3.33. Found: C, 65.95; H, 3.39.

3.1.16. 2-Chloro-3-propanoyloxyphenalen-1-one (23). Reaction of **7** (220 mg, 1.0 mmol) and propionyl chloride (1.850 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **23** (212 mg, 74%) as a solid; mp 146–147°C (from hexane–ethylacetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 (1H, d, J=7.5 Hz, ArH), 8.21 (1H, d, J=8.0 Hz, ArH), 8.31 (1H, d, J=8.3 Hz, ArH), 7.84 (1H, d, J=7.4 Hz, ArH), 7.76 (1H, dd, J=8.0, 7.6 Hz, ArH) 7.61 (1H, dd, J=8.3, 7.4 Hz, ArH), 2.83 (2H, q, J=7.5 Hz, CH_2), 1.38 (3H, t, J=7.5 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.71 (C=O, enone), 170.14 (C=O, ester), 154.55, 135.84, 133.16, 131.88, 128.12, 127.33, 127.06, 126.49, 124.99, 124.02, 27.48, 9.12; IR (KBr) 2963, 2932, 2874, 1765 (C=O, vinylic ester), 1647 (C=O, enone), 1577, 1404, 1377, 1323, 1300, 1211, 1182, 1148, 1122, 1063, 965, 842, 820, 777 cm^{-1}; m/z (EI) 286 (M^+, 12%), 230 (100), 196 (22), 173 (14), 155 (14), 129 (32), 112 (9), 71 (8), 57 (32). Anal. calcd for $C_{16}H_{11}ClO_3$: C, 67.03; H, 3.87. Found: C, 66.84; H, 3.69.

3.1.17. 3-Butanoyloxy-2-chlorophenalen-1-one (24). Reaction of **7** (220 mg, 1.0 mmol) and butyryl chloride (2.131 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **24** (223 mg, 74%) as a solid; mp 101°C (from hexane–ethylacetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 (1H, d, J=7.4 Hz, ArH), 8.23 (1H, d, J=8.0 Hz, ArH), 8.08 (1H, d, J=8.2 Hz, ArH), 7.85 (1H, d, J=7.4 Hz, ArH), 7.78 (1H, dd, J=8.0, 7.4 Hz, ArH) 7.62 (1H, dd, J=8.0, 7.4 Hz, ArH), 2.77 (2H, q, J=7.4 Hz, CH_2), 1.95–1.87 (2H, m, CH_2), 1.12 (3H, t, J=7.4 Hz, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.64 (C=O, enone), 169.27 (C=O, ester), 154.52, 135.79, 133.13, 131.83, 128.00, 127.26, 127.03, 126.46, 125.00, 123.94, 35.80, 18.37, 13.72; IR (KBr) 2963, 2932, 2874, 1765 (C=O, vinylic ester), 1647 (C=O, enone), 1578, 1404, 1377, 1323, 1302, 1211, 1182, 1148, 1123, 1096, 1063, 965 cm^{-1}. Anal. calcd for $C_{17}H_{13}ClO_3$: C, 67.89; H, 4.36. Found: C, 67.54; H, 4.47.

3.1.18. 4-Acetoxy-3-bromo-1-methyl-1*H*-quinolin-2-one (25). Reaction of **6** (201 mg, 1.0 mmol) and acetyl bromide (2.459 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **25** (157 mg, 53%) as a solid; mp 179°C (from hexane–ethylacetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66–7.58 (2H, m, ArH), 7.41 (1H, d, J=8.5 Hz, ArH), 7.27 (1H, d, J=8.0, 7.2 Hz, ArH), 3.80 (3H, s, NCH_3), 2.49 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.29 (C=O, ester), 158.81 (C=O, amide), 153.71, 138.38, 131.76, 122.80, 116.35, 114.51, 110.68, 30.97, 20.60; IR (KBr) 2978, 1778 (C=O, vinylic ester), 1649 (C=O, amide), 1620, 1564, 1454, 1420, 1360, 1319, 1304, 1190, 1161, 1100, 1067, 1007, 966, 889 cm^{-1}. Anal. calcd for $C_{12}H_{10}BrNO_3$: C, 48.67; H, 3.40. Found: C, 48.96; H, 3.32.

3.1.19. 3-Acetoxy-2-bromophenalen-1-one (26). Reaction of **7** (220 mg, 1.0 mmol) and acetyl chloride (1.570 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **26** (146 mg, 46%) as a solid; mp 182°C (from hexane–ethylacetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (1H, dd, J=7.4, 1.2 Hz, ArH), 8.24 (1H, d, J=8.0 Hz, ArH), 8.12 (1H, d, J=8.2 Hz, ArH), 7.88 (1H, d, J=7.4 Hz, ArH), 7.80 (1H, dd, J=8.0, 7.4 Hz, ArH), 7.63 (1H, dd, J=8.2, 7.4 Hz, ArH), 2.52 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.91 (C=O, enone), 166.63 (C=O, ester), 156.85, 135.83, 133.36, 132.30, 132.04, 128.02, 127.49, 127.24, 126.56, 125.57, 124.30, 118.81, 20.82; IR (KBr) 2930, 1779 (C=O, vinylic ester), 1645 (C=O, enone), 1580, 1404, 1374, 1323, 1227, 1181, 1146, 1088, 1026, 1005, 949, 876 cm^{-1}. Anal. calcd for $C_{15}H_9BrO_3$: C, 56.81; H, 2.86. Found: C, 57.02; H, 2.63.

3.2. General procedure for the synthesis of α-benzyloxy α-haloenones (32–46)

To a solution of diazodicarbonyl compound (1.0 mmol) and benzyl halide (20 mmol) was added rhodium catalyst (0.01 mmol) at room temperature under a N_2 atmosphere. The reaction mixture was stirred at room temperature for 9–12 h or 50°C for 6 h. The reaction mixture was purified by flash column chromatography on silica gel to give the product.

3.2.1. 3-Benzyloxy-2-chlorophenalen-1-one (32). Reaction of **7** (220 mg, 1.0 mmol) and benzyl chloride (2.52 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **32** (263 mg, 82%) as a solid; mp 95–96°C (from hexane–ethylacetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 (1H, d, J=7.3 Hz, ArH), 8.20 (1H, d, J=8.1 Hz, ArH), 8.06 (2H, dd, J=8.1, 7.3 Hz, ArH), 7.76 (1H, dd, J=7.8, 7.6 Hz, ArH), 7.60–7.52 (3H, m, ArH), 7.44–7.34 (3H, m, ArH), 5.40 (2H, s, CH_2Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.60 (C=O, enone), 162.02, 135.80, 135.25, 132.67, 131.70, 131.15, 128.61, 128.39, 127.90, 126.92, 126.44, 125.48, 125.12, 121.94, 75.99; IR (KBr) 3030, 1647 (C=O, enone), 1561, 1453, 1406, 1372, 1310, 1221, 1204, 1144, 1094,

1026, 965, 937, 903, 864, 839 cm^{-1}; *m/z* (EI) 320 (M^+, 9%), 285 (20), 284 (10), 230 (8), 201 (7), 173 (11), 164 (11), 146 (30), 129 (15), 91 (100), 71 (7), 65 (11). Anal. calcd for $C_{20}H_{13}ClO_2$: C, 74.89; H, 4.08. Found: C, 74.52; H, 4.39.

3.2.2. 3-Benzyloxy-2-chlorocyclohex-2-enone (33). Reaction of **1** (138 mg, 1.0 mmol) and benzyl chloride (2.520 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **33** (192 mg, 81%) as a solid; mp 98–99°C (from hexane–ethylacetate), ^1H NMR (300 MHz, $CDCl_3$) δ 7.41–7.33 (5H, m, ArH), 5.24 (2H, s, CH_2Ph), 2.67 (2H, dd, *J*=6.2, 6.1 Hz, CH_2), 2.48 (2H, dd, *J*=7.0, 6.2 Hz, CH_2), 2.01–1.93 (2H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.88 (C=O), 171.14, 135.86, 129.33, 128.98, 127.41, 127.13, 112.99, 71.03 (CH_2Ph), 37.09 (CH_2), 29.07 (CH_2), 20.66 (CH_2); IR (KBr) 3036, 2945, 2889, 1657 (C=O, enone), 1589, 1458, 1368, 1294, 1262, 1192, 1154, 1080, 1026, 1007, 922, 905, 817 cm^{-1}; *m/z* (EI) 236 (M^+, 10%), 146 (53), 120 (31), 118 (92), 91 (100), 89 (16), 65 (59). Anal. calcd for $C_{13}H_{13}ClO_2$: C, 65.97; H, 5.54. Found: C, 65.58, H, 5.20.

3.2.3. 2-Chloro-3-(3-methylbenzyloxy)cyclohex-2-enone (34). Reaction of **1** (138 mg, 1.0 mmol) and 3-methylbenzyl chloride (2.812 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **34** (173 mg, 69%) as a solid; mp 117–118°C (from hexane–ethylacetate), ^1H NMR (300 MHz, $CDCl_3$) δ 7.28–7.23 (1H, dd, *J*=8.0, 7.5 Hz, ArH), 7.15–7.12 (3H, m, ArH), 7.1–7.13 (3H, m, ArH), 5.20 (2H, s, CH_2Ph), 2.67 (2H, t, *J*=6.2 Hz, CH_2), 2.48 (2H, dd, *J*=7.0, 6.3 Hz, CH_2), 2.34 (3H, s, CH_3), 2.03–1.94 (2H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.34 (C=O), 170.77, 138.58, 135.32, 129.22, 128.70, 127.34, 123.74, 112.35, 70.63, 36.59, 26.96, 21.35, 20.16; IR (KBr) 2949, 1647 (C=O, enone), 1584, 1458, 1421, 1373, 1350, 1300, 1265, 1198, 1078, 1017, 920, 891 cm^{-1}. Anal. calcd for $C_{14}H_{15}ClO_2$: C, 67.07; H, 6.03. Found: C, 67.35, H, 6.20.

3.2.4. 2-Chloro-3-(4-methylbenzyloxy)cyclohex-2-enone (35). Reaction of **1** (138 mg, 1.0 mmol) and 4-methylbenzyl chloride (2.812 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **35** (203 mg, 81%) as a solid; mp 92–93°C (from hexane–ethylacetate), ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (2H, d, *J*=7.5 Hz, ArH), 7.17 (2H, d, *J*=7.5 Hz, ArH), 5.19 (2H, s, CH_2Ph), 2.67 (2H, t, *J*=6.1 Hz, CH_2), 2.47 (2H, dd, *J*=7.0, 6.3 Hz, CH_2), 2.34 (3H, s, CH_3), 1.99–1.93 (2H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.51 (C=O), 171.12, 159.66, 128.54, 127.23, 114.10, 112.15, 70.51, 55.19, 36.51, 26.99, 20.09; IR (KBr) 2949, 1657 (C=O, enone), 1591, 1516, 1454, 1420, 1368, 1329, 1294, 1273, 1190, 1150, 1082, 1038, 1007, 926, 820 cm^{-1}. Anal. calcd for $C_{14}H_{15}ClO_2$: C, 67.07; H, 6.03. Found: C, 66.95, H, 6.12.

3.2.5. 2-Chloro-3-(4-methoxybenzyloxy)cyclohex-2-enone (36). Reaction of **1** (138 mg, 1.0 mmol) and 4-methoxybenzyl chloride (3.040 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **36** (248 mg, 93%) as a solid; mp 139–140°C (from hexane–ethyl acetate); ^1H NMR (300 MHz, $CDCl_3$) δ 7.27 (2H, d, *J*=8.6 Hz, ArH), 6.91 (2H, d, *J*=8.6 Hz, ArH), 5.16 (2H, s, CH_2Ph), 3.80 (3H, s, OCH_3), 2.68 (2H, m, CH_2), 2.47 (2H, m, CH_2), 2.00 (2H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.37 (C=O), 170.92, 159.67, 128.56, 127.26, 114.12, 112.23, 70.50, 55.21, 36.56, 27.02, 20.14; IR (KBr) 2957, 1649 (C=O, enone), 1582, 1514, 1453, 1416, 1368, 1327, 1294, 1260, 1173, 1071, 1011, 897 cm^{-1}. Anal. calcd for $C_{14}H_{15}ClO_3$: C, 63.04; H, 5.67. Found: C, 62.72; H, 5.91.

3.2.6. 3-Benzyloxy-2-chloro-5,5-dimethylcyclohex-2-enone (37). Reaction of **4** (166 mg, 1.0 mmol) and benzyl chloride (2.520 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **37** (207 mg, 78%) as a solid; mp 92–93°C (from hexane–ethyl acetate); ^1H NMR (300 MHz, $CDCl_3$) δ 7.40–7.32 (5H, m, ArH), 5.23 (2H, s, CH_2Ph), 2.51 (2H, s, CH_2), 2.34 (2H, s, CH_2), 1.02 (6H, s, 2×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.02 (C=O), 168.62, 135.51, 128.79, 128.43, 126.57, 111.66, 70.43, 50.37, 46.06, 40.56, 32.05, 28.11; IR (KBr) 3038, 2963, 2934, 2880, 1649 (C=O, enone), 1586, 1460, 1400, 1358, 1302, 1252, 1171, 1152, 1053, 1011, 943, 918, 900, 842 cm^{-1}. Anal. calcd for $C_{15}H_{17}ClO_2$: C, 68.05; H, 6.47. Found: C, 67.94; H, 6.72.

3.2.7. 2-Chloro-3-(3-methylbenzyloxy)-5,5-dimethylcyclohex-2-enone (38). Reaction of **1** (138 mg, 1.0 mmol) and 3-methylbenzyl chloride (2.812 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **38** (184 mg, 66%) as a solid; mp 115–116°C (from hexane–ethylacetate), ^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (1H, dd, *J*=8.0, 7.5 Hz, ArH), 7.14–7.11 (3H, m, ArH), 5.19 (2H, s, CH_2Ph), 2.51 (2H, s, CH_2), 2.34 (5H, s, CH_2 and CH_3), 1.02 (3H, s, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.39 (C=O), 169.11, 138.52, 135.34, 129.16, 128.65, 127.22, 123.61, 111.44, 70.53, 50.24, 40.48, 32.05, 28.03, 21.30; IR (KBr) 3029, 2961, 2872, 1667 (C=O, enone), 1595, 1468, 1358, 1298, 1242, 1173, 1053, 1015, 947, 926 cm^{-1}. Anal. calcd for $C_{16}H_{19}ClO_2$: C, 68.93; H, 6.87. Found: C, 68.65, H, 6.61.

3.2.8. 2-Chloro-3-(4-methoxybenzyloxy)-5,5-dimethylcyclohex-2-enone (39). Reaction of **4** (166 mg, 1.0 mmol) and 4-methoxybenzyl chloride (3.140 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **39** (280 mg, 95%) as a solid; mp 142–143°C (from hexane–ethyl acetate); ^1H NMR (300 MHz, $CDCl_3$) δ 7.27 (2H, d, *J*=8.6 Hz, ArH), 6.89 (2H, d, *J*=8.6 Hz, ArH), 5.16 (2H, s, CH_2Ph), 3.79 (3H, s, OCH_3), 2.52 (2H, s, CH_2), 2.35 (2H, s, CH_2), 1.03 (6H, s, 2×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.02 (C=O), 168.79, 159.69, 128.49, 127.45, 114.14, 111.59, 70.44, 55.25, 50.38, 40.72, 32.07, 28.17; IR (KBr) 2957, 1649, (C=O, enone), 1586, 1514, 1462, 1304, 1246, 1175, 1032, 945 cm^{-1}. Anal. calcd for $C_{16}H_{19}ClO_3$: C, 65.19; H, 6.50. Found: C, 65.36; H, 6.82.

3.2.9. 4-Benzyloxy-3-chlorochromen-2-one (40). Reaction of **5** (188 mg, 1.0 mmol) and benzyl chloride (2.520 g, 20.0 mmol) under $Rh_2(OPiv)_4$ (6.1 mg) afforded **40** (158 mg, 55%) as a solid; mp 68°C (from hexane–ethyl acetate); ^1H NMR (300 MHz, $CDCl_3$) δ 7.71–7.24 (9H, m, ArH), 5.54 (2H, s, CH_2Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.51 (C=O, ester), 159.42, 151.08, 135.08, 132.38, 128.97, 128.74, 128.54, 128.33, 124.56, 123.53, 117.39, 116.50, 107.07, 75.81; IR (KBr) 3067, 3036, 1732 (C=O, ester), 1609, 1557, 1487, 1454, 1389, 1333, 1275, 1206, 1161, 1098, 1036, 1003, 914, 860 cm^{-1}. Anal. calcd for $C_{16}H_{11}ClO_3$: C, 67.03; H, 3.87. Found: C, 66.70; H, 3.92.

3.2.10. 3-Benzyloxy-2-bromo-cyclohex-2-enone (41). Reaction of **1** (138 mg, 1.0 mmol) and benzyl bromide

(3.420 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **41** (188 mg, 67%) as a solid; mp 104–105°C (from hexane–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.33 (5H, m, ArH), 5.25 (2H, s, CH_2Ph), 2.66 (2H, dd, J=6.3, 6.1, CH_2), 2.51 (2H, dd, J=6.8, 6.3, CH_2), 1.99 (2H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.45 (C=O), 172.75, 135.23, 128.72, 128.32, 126.81, 126.50, 70.48, 36.50, 27.27, 20.32; IR (KBr) 3063, 3036, 2949, 2887, 1655 (C=O, enone), 1585, 1499, 1458, 1368, 1287, 1260, 1192, 1154, 1080, 1026, 987, 920, 904 cm^{-1}. Anal. calcd for $C_{13}H_{13}BrO_2$: C, 55.54; H, 4.66. Found: C, 55.48; H, 4.85.

3.2.11. 2-Bromo-3-(2-methylbenzyloxy)cyclohex-2-enone (42). Reaction of **1** (138 mg, 1.0 mmol) and 2-methylbenzyl bromide (3.70 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **42** (162 mg, 55%) as a solid; mp 170–171°C (from hexane–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (1H, d, J=7.1 Hz, ArH), 7.28–7.19 (3H, m, ArH), 5.22 (2H, s, CH_2Ph), 2.71 (2H, t, J=6.2 Hz, CH_2), 2.52 (2H, dd, J=6.7, 6.2 Hz, CH_2), 2.37 (3H, s, CH_3), 2.06–1.98 (2H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.28 (C=O), 172.49, 136.30, 133.23, 130.63, 128.77, 127.77, 126.23, 103.72, 69.36, 36.65, 27.38, 20.53, 18.99; IR (KBr) 2953, 1658 (C=O, enone), 1586, 1487, 1454, 1418, 1370, 1258, 1192, 1152, 1080, 1036, 916 cm^{-1}. Anal. calcd for $C_{14}H_{15}BrO_2$: C, 56.97; H, 5.12. Found: C, 56.69; H, 5.31.

3.2.12. 2-Bromo-3-(4-methylbenzyloxy)cyclohex-2-enone (43). Reaction of **1** (138 mg, 1.0 mmol) and 4-methylbenzyl bromide (3.70 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **43** (192 mg, 65%) as a solid; mp 95°C (from hexane–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (2H, d, J=8.2 Hz, ArH), 7.18 (2H, d, J=8.2 Hz, ArH), 5.20 (2H, s, CH_2Ph), 2.651 (2H, t, J=6.2 Hz, CH_2), 2.49 (2H, dd, J=6.7, 6.2 Hz, CH_2), 2.34 (3H, s, CH_3), 2.02–1.93 (2H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.40 (C=O), 172.78, 138.33, 132.29, 129.46, 126.72, 103.78, 70.62, 36.61, 27.40, 21.13, 20.43; IR (KBr) 3027, 2951, 2920, 2876, 1657 (C=O, enone), 1584, 1516, 1366, 1289, 1273, 1229, 1188, 1148, 1080, 1036, 986 cm^{-1}. Anal. calcd for $C_{14}H_{15}BrO_2$: C, 56.97; H, 5.12. Found: C, 56.85; H, 5.27.

3.2.13. 3-Benzyloxy-2-bromo-5,5-dimethyl-cyclohex-2-enone (44). Reaction of **6** (166 mg, 1.0 mmol) and benzyl bromide (3.420 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **44** (216 mg, 70%) as a solid; mp 102–103°C (from hexane–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38–7.35 (5H, m, ArH), 5.24 (2H, s, CH_2Ph), 2.50 (2H, s, CH_2), 2.38 (2H, s, CH_2), 1.02 (6H, s, 2×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.05 (C=O), 170.50, 135.54, 128.84, 128.45, 126.53, 103.11, 70.47, 50.45, 41.06, 32.32, 28.11; IR (KBr) 3063, 2957, 2872, 1667 (C=O, enone), 1589, 1462, 1352, 1292, 1244, 1171, 1038, 1001, 910 cm^{-1}. Anal. calcd for $C_{15}H_{17}BrO_2$: C, 58.27; H, 5.54. Found: C, 58.57; H, 5.91.

3.2.14. 4-Benzyloxy-3-bromochromen-2-one (45). Reaction of **5** (188 mg, 1.0 mmol) and benzyl bromide (3.420 g, 20.0 mmol) under $Rh_2(OPiv)_4$ (4.4 mg) afforded **45** (199 mg, 60%) as a solid; mp 120°C (from hexane–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (1H, dd, J=8.0, 1.6 Hz, ArH), 7.59–7.23 (8H, m, ArH), 5.45 (2H, s, CH_2Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.40 (C=O, ester), 159.29, 151.93, 135.02, 132.63, 129.02, 128.76, 128.46, 124.58, 123.47, 117.57, 116.66, 99.06, 76.00; IR (KBr) 3079, 2890, 1725 (C=O, ester), 1605, 1553, 1451, 1321, 1273, 1215, 1190, 1152, 1094, 1032, 984, 943, 912 cm^{-1}. Anal. calcd for $C_{16}H_{11}BrO_3$: C, 58.03; H, 3.35. Found: C, 58.27; H, 3.13.

3.2.15. 3-Benzyloxy-2-bromophenalen-1-one (46). Reaction of **7** (220 mg, 1.0 mmol) and benzyl bromide (3.420 g, 20.0 mmol) under $Rh_2(OAc)_4$ (4.4 mg) afforded **46** (310 mg, 85%) as a solid; mp 116°C (from hexane–ethylacetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 (1H, dd, J=7.4, 1.1 Hz, ArH), 8.22 (1H, dd, J=8.1, 1.1 Hz, ArH), 8.07 (2H, dd, J=8.1, 7.3 Hz, ArH), 7.78 (1H, dd, J=7.8, 7.6 Hz, ArH), 7.60–7.55 (3H, m, ArH), 7.46–7.36 (3H, m, ArH), 5.34 (2H, s, CH_2Ph); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.88 (C=O, enone), 164.36, 135.79, 135.34, 132.91, 131.94, 131.63, 128.71, 128.68, 128.47, 127.98, 127.94, 127.13, 126.54, 125.77, 115.98, 76.21; IR (KBr) 3032, 2953, 2890, 1644 (C=O, enone), 1574, 1557, 1406, 1383, 1308, 1223, 1202, 1157, 1094, 1026, 957, 909 cm^{-1}. Anal. calcd for $C_{20}H_{13}BrO_2$: C, 65.77; H, 3.59. Found: C, 65.85; H, 3.81.

3.3. General procedure for the synthesis of β-halomethoxy α-haloenones (49–56)

To a solution of diazodicarbonyl compound (1.0 mmol) and methylene halide (2 mL) was added rhodium catalyst (0.005 mmol) at room temperature under a N_2 atmosphere. The reaction mixture was stirred at room temperature for 4–7 h or 50°C for 5 h. The halide was evaporated under reduced pressure to give the residue. The residue was purified by flash column chromatography on silica gel to give the product.

3.3.1. 2-Chloro-3-chloromethoxyphenalen-1-one (49). Reaction of **7** (220 mg, 1.0 mmol) and methylene chloride (2 mL) under $Rh_2(OAc)_4$ (2.2 mg) afforded **49** (226 mg, 81%) as a solid; mp 141°C (from hexane–ethylacetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72 (1H, dd, J=7.5, 1.1 Hz, ArH), 8.32–8.24 (2H, m, ArH), 8.11 (1H, dd, J=8.0, 1.1 Hz, ArH), 7.79 (1H, dd, J=8.0, 7.5 Hz, ArH), 7.69 (1H, dd, J=8.0, 7.5 Hz, ArH), 6.19 (2H, s, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.03 (C=O, enone), 159.60, 135.79, 133.22, 131.60, 129.42, 127.74, 127.08, 126.54, 125.11, 124.79, 122.62, 80.11; IR (KBr) 3065, 2926, 1657 (C=O, enone), 1626, 1578, 1562, 1454, 1404, 1377, 1343, 1314, 1206, 1146, 1098, 1030, 1003, 986, 934, 839 cm^{-1}. Anal. calcd for $C_{14}H_8Cl_2O_2$: C, 60.24; H, 2.89. Found: C, 60.03; H, 2.81. HRMS calcd for $C_{14}H_8Cl_2O_2$ (M^+) 277.9901. Found 277.9900.

3.3.2. 2-Chloro-3-chloromethoxycyclohex-2-enone (50). Reaction of **1** (138 mg, 1.0 mmol) and methylene chloride (2 mL) under $Rh_2(OAc)_4$ (2.2 mg) afforded **50** (154 mg, 79%) as a solid; mp 75°C (from hexane–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.82 (2H, s, CH_2), 2.83 (2H, t, J=6.2 Hz, CH_2), 2.55 (2H, dd, J=7.0, 6.3 Hz, CH_2), 2.14–2.05 (2H, m, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.78 (C=O), 167.79, 116.03, 74.93, 37.20, 26.18, 20.49; IR

(KBr) 3319, 3067, 3002, 2961, 1672 (C═O, enone), 1603, 1426, 1372, 1281, 1211, 1184, 1078, 1047, 1017, 992, 926 cm^{-1}. Anal. calcd for $C_7H_8Cl_2O_2$: C, 43.11; H, 4.13. Found: C, 43.42; H, 4.31.

3.3.3. 2-Chloro-3-chloromethoxy-5-phenylcyclohex-2-enone (51). Reaction of **2** (214 mg, 1.0 mmol) and methylene chloride (2 mL) under $Rh_2(OAc)_4$ (2.2 mg) afforded **51** (244 mg, 90%) as a solid; mp 92–93°C (from hexane–ethylacetate); ^1H NMR (300 MHz, $CDCl_3$) δ 7.40–7.26 (5H, m, ArH), 5.82 (2H, m, CH_2), 3.44 (1H, m, CH), 3.17–2.72 (4H, m, 2×CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.23 (C═O, enone), 165.03, 141.05, 129.00, 127.61, 126.55, 115.72, 74.43, 43.48, 38.41, 33.52; IR (KBr) 3065, 3000, 2951, 1682 (C═O), 1615, 1456, 1381, 1348, 1287, 1254, 1184, 1071, 1040, 974, 939 cm^{-1}. Anal. calcd for $C_{13}H_{12}Cl_2O_2$: C, 57.59; H, 4.46. Found: C, 57.83; H, 4.69.

3.3.4. 2-Chloro-3-chloromethoxy-5,5-dimethylcyclohex-2-enone (52). Reaction of **4** (166 mg, 1.0 mmol) and methylene chloride (2 mL) under $Rh_2(OAc)_4$ (2.2 mg) afforded **52** (181 mg, 81%) as a solid; mp 49–50°C (from hexane–ethylacetate); ^1H NMR (300 MHz, $CDCl_3$) δ 5.81 (2H, s, CH_2), 2.67 (2H, s, CH_2), 2.42 (2H, s, CH_2), 1.13 (6H, s, 2×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.12 (C═O, enone), 165.32, 114.76, 74.32, 50.32, 39.19, 32.25, 28.01; IR (KBr) 2963, 1678 (C═O), 1612, 1468, 1364, 1292, 1260, 1206, 1167, 1074, 1017, 951 cm^{-1}. Anal. calcd for $C_9H_{12}Cl_2O_2$: C, 48.45; H, 5.42. Found: C, 48.35; H, 5.19.

3.3.5. 2-Chloro-3-chloromethoxy-d_2-5,5-dimethylcyclohex-2-enone (53). Reaction of **4** (166 mg, 1.0 mmol) and CD_2Cl_2 (2 mL) under $Rh_2(OAc)_4$ (2.2 mg) afforded **53** (169 mg, 75%) as a solid; mp 53°C (from hexane–ethylacetate); ^1H NMR (300 MHz, $CDCl_3$) δ 2.66 (2H, s, CH_2), 2.41 (2H, s, CH_2), 1.13 (6H, s, 2×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.02 (C═O, enone), 165.42, 115.73, 77.20, 50.60, 39.60, 31.88, 28.13; IR (KBr) 2963, 2874, 1676 (C═O), 1613, 1470, 1296, 1236, 1103, 1055, 995 cm^{-1}. HRMS calcd for $C_9H_{10}D_2Cl_2O_2$ (M^+) 224.0338. Found, 224.0336.

3.3.6. 2-Bromo-3-bromomethoxy-5-phenylcyclohex-2-enone (54). Reaction of **2** (214 mg, 1.0 mmol) and methylene bromide (2 mL) under $Rh_2(OAc)_4$ (2.2 mg) afforded **54** (270 mg, 75%) as a solid; mp 128–129°C (from hexane–ethylacetate); ^1H NMR (300 MHz, $CDCl_3$) δ 7.40–7.22 (5H, m, ArH), 5.94 (2H, m, CH_2), 3.44 (1H, m, CH), 3.17–3.12 (1H, m), 2.96–2.74 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.95 (C═O, enone), 168.58, 141.88, 129.00, 127.50, 126.60, 107.66, 63.67, 43.43, 38.66, 33.81; IR (KBr) 3067, 1678 (C═O), 1609, 1456, 1339, 1279, 1242, 1175, 1069, 959, 959 cm^{-1}. Anal. calcd for $C_{13}H_{12}Br_2O_2$: C, 43.37; H, 3.36. Found: C, 43.66; H, 3.61.

3.3.7. 2-Bromo-3-bromomethoxy-5,5-dimethylcyclohex-2-enone (55). Reaction of **4** (166 mg, 1.0 mmol) and methylene bromide (2 mL) under $Rh_2(OAc)_4$ (2.2 mg) afforded **55** (243 mg, 78%) as a solid; mp 57–58°C (from hexane–ethylacetate); ^1H NMR (300 MHz, $CDCl_3$) δ 5.94 (2H, s, CH_2), 2.68 (2H, s, CH_2), 2.45 (2H, s, CH_2), 1.15 (6H, s, 2×CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.98 (C═O, enone), 167.11, 106.95, 63.74, 50.54, 39.55, 32.51, 28.06; IR (KBr) 2961, 1670 (C═O), 1603, 1466, 1363, 1304, 1246, 1198, 1159, 1069, 1006, 922 cm^{-1}. Anal. calcd for $C_9H_{12}Br_2O_2$: C, 34.65; H, 3.88. Found: C, 34.49; H, 3.74. HRMS calcd for $C_9H_{12}Br_2O_2$ (M^+) 309.9204. Found, 309.9201.

3.3.8. 2-Chloro-3-chloromethoxyphenalen-1-one (56). Reaction of **7** (220 mg, 1.0 mmol) and methylene bromide (2 mL) under $Rh_2(OAc)_4$ (2.2 mg) afforded **56** (313 mg, 85%) as a solid; mp 151°C (from hexane–ethylacetate); ^1H NMR (300 MHz, $CDCl_3$) δ 8.73 (1H, d, J=7.4 Hz, ArH), 8.31 (1H, d, J=7.4 Hz, ArH), 8.26 (1H, d, J=8.0 Hz, ArH), 8.14 (1H, d, J=8.0 Hz, ArH), 7.79 (1H, dd, J=8.0, 7.4 Hz, ArH), 7.69 (1H, dd, J=8.0, 7.4 Hz, ArH), 6.36 (2H, s, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.22 (C═O, enone), 162.09, 135.82, 133.46, 132.01, 131.71, 129.71, 127.57, 127.22, 126.52, 125.35, 125.09, 115.80, 70.53; IR (KBr) 3067, 1649 (C═O, enone), 1626, 1576, 1559, 1447, 1404, 1319, 1289, 1202, 1144, 1094, 1030, 993, 914 cm^{-1}. Anal. calcd for $C_{14}H_8Br_2O_2$: C, 45.69; H, 2.19. Found: C, 45.33; H, 2.36. HRMS calcd for $C_{14}H_8Br_2O_2$ (M^+) 365.8891. Found, 365.8893.

3.4. General procedure for the synthesis of β-hydroxy α-haloenones (58–65)

To a solution of diazodicarbonyl compound (1.0 mmol) and alkyl halide (2 mL) was added rhodium catalyst (0.005 mmol) at room temperature under a N_2 atmosphere. The reaction mixture was stirred at room temperature for 10 h. The halide was evaporated under reduced pressure to give the residue. The residue was purified by flash column chromatography on silica gel to give the product.

3.4.1. 2-Chloro-3-hydroxycyclohex-2-enone (58).[8] Reaction of **1** (138 mg, 1.0 mmol) and *n*-butyl chloride (2 mL) under $Rh_2(OAc)_4$ (2.2 mg) afforded **58** (140 mg, 96%) as a solid; mp 197–198°C (from hexane–ethyl acetate); ^1H NMR (300 MHz, $CDCl_3$) δ 6.52 (1H, s, OH), 2.64 (2H, t, J=6.2 Hz, CH_2), 2.53 (2H, t, J=6.6 Hz, CH_2), 2.06–1.95 (2H, m, CH_2); IR (KBr) 3043 (br OH), 1655 (C═O, enone), 1579, 1424, 1325, 1198, 1144, 1015, 972 cm^{-1}.

3.4.2. 2-Bromo-3-hydroxycyclohex-2-enone (59).[8] Reaction of **1** (138 mg, 1.0 mmol) and ethyl bromide (2 mL) under $Rh_2(OAc)_4$ (2.2 mg) afforded **59** (181 mg, 95%) as a solid; mp 177–178°C (from hexane–ethyl acetate); ^1H NMR (300 MHz, $CDCl_3$) δ 6.51 (1H, s, OH), 2.65 (2H, t, J=6.2 Hz, CH_2), 2.55 (2H, t, J=6.6 Hz, CH_2), 2.05–1.96 (2H, m, CH_2); IR (KBr) 3111 (br OH), 1655 (C═O, enone), 1591, 1422, 1318, 1194, 1144, 1067, 993, 967 cm^{-1}.

3.4.3. 2-Iodo-3-hydroxycyclohex-2-enone (60). Reaction of **1** (138 mg, 1.0 mmol) and propyl iodide (2 mL) under $Rh_2(OAc)_4$ (2.2 mg) afforded **60** (228 mg, 96%) as a solid; mp137–138°C (from hexane–ethyl acetate); ^1H NMR (300 MHz, $CDCl_3$) δ 6.33 (1H, s, OH), 2.69 (2H, t, J=6.2 Hz, CH_2), 2.57 (2H, t, J=6.6 Hz, CH_2), 2.03–1.91 (2H, m, CH_2); IR (KBr) 3099 (br OH), 1645 (C═O, enone), 1576, 1418, 1370, 1314, 1190, 1144, 1065, 981, 955 cm^{-1}; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6) δ 78.26, 32.85, 20.29. Anal. calcd for $C_6H_7IO_2$: C, 30.28; H, 2.96. Found: C, 30.54; H, 3.05.

3.4.4. 2-Chloro-3-hydroxy-5-phenylcyclohex-2-enone (61). Reaction of **2** (214 mg, 1.0 mmol) and *n*-butyl chloride (2 mL) under $Rh_2(OAc)_4$ (2.2 mg) afforded **61** (205 mg, 92%) as a solid; mp 270°C (from hexane–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.22 (5H, m, ArH), 6.52 (1H, s, OH), 3.44–3.37 (1H, m, CH), 2.89–2.66 (4H, m, 2×CH_2); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6) (141.61, 128.43, 126.78, 126.26, 107.97, 37.91, 34.13; IR (KBr) 3099 (br OH), 1645 (C═O, enone), 1576, 1418, 1370, 1314, 1190, 1144, 1065, 981, 955 cm^{-1}. Anal. calcd for $C_{12}H_{11}ClO_2$: C, 64.73; H, 4.98. Found: C, 64.99; H, 4.65.

3.4.5. 2-Bromo-3-hydroxy-5-phenylcyclohex-2-enone (62). Reaction of **2** (214 mg, 1.0 mmol) and ethyl bromide (2 mL) under $Rh_2(OAc)_4$ (2.2 mg) afforded **62** (240 mg, 90%) as a solid; mp 205°C (from hexane–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.22 (5H, m, ArH), 6.57 (1H, s, OH), 3.48–3.37 (1H, m, CH), 2.89–2.69 (4H, m, 2×CH_2); ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6) δ 141.61, 128.35, 126.70, 126.21, 99.12, 40.49, 38.11; IR (KBr) 3099 (br OH), 1645 (C═O, enone), 1576, 1418, 1370, 1314, 1190, 1144, 1065, 981, 955 cm^{-1}. Anal. calcd for $C_{12}H_{11}BrO_2$: C, 53.96; H, 4.15. Found: C, 53.84; H, 4.39.

3.4.6. 2-Chloro-3-hydroxy-5,5-dimethylcyclohex-2-enone (63).[17] Reaction of **4** (166 mg, 1.0 mmol) and ethylene dichloride (2 mL) under $Rh_2(OAc)_4$ (2.2 mg) afforded **63** (171 mg, 98%) as a solid; mp 162–163°C (from hexane–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.48 (1H, s, OH), 2.50 (2H, s, CH_2), 2.39 (2H, s, CH_2), 1.10 (6H, s, 2×CH_3); IR (KBr) 3000 (br OH), 2963, 2874, 1647 (C═O, enone), 1616, 1582, 1341, 1292, 1262, 1148, 1127, 1013, 943 cm^{-1}.

3.4.7. 2-Bromo-3-hydroxy-5,5-dimethylcyclohex-2-enone (64). Reaction of **4** (166 mg, 1.0 mmol) and ethylene dibromide (2 mL) under $Rh_2(OAc)_4$ (2.2 mg) afforded **64** (210 mg, 96%) as a solid; mp 175–176°C (from hexane–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.46 (1H, s, OH), 2.50 (2H, s, CH_2), 2.41 (2H, s, CH_2), 1.10 (6H, s, 2×CH_3); IR (KBr) 3005 (br OH), 2957, 2872, 1635 (C═O, enone), 1580, 1449, 1424, 1323, 1258, 1144, 1005, 936, 914 cm^{-1}; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d6) δ 97.55, 46.77, 31.31, 27.34. Anal. calcd for $C_8H_{11}BrO_2$: C, 43.86; H, 5.06. Found: C, 43.95; H, 4.87.

3.4.8. 3-Hydroxy-2-iodo-5,5-dimethylcyclohex-2-enone (65). Reaction of **4** (166 mg, 1.0 mmol) and ethyl iodide (2 mL) under $Rh_2(OAc)_4$ (2.2 mg) afforded **65** (247 mg, 93%) as a solid; mp 166–167°C (from hexane–ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.30 (1H, s, OH), 2.54 (2H, s, CH_2), 2.42 (2H, s, CH_2), 1.08 (6H, s, 2×CH_3); IR (KBr) 3003 (br OH), 2955, 2868, 1634 (C═O, enone), 1570, 1447, 1408, 1309, 1256, 1142, 999, 930 cm^{-1}; ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6) δ 76.04, 46.06, 31.47, 26.95. Anal. calcd for $C_8H_{11}IO_2$: C, 36.11; H, 4.17. Found: C, 36.43; H, 4.36.

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