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Ruthenium(II)-Catalyzed Protocol for Preparation of Diverse α,β- and β,β-Dihaloenones from Diazodicarbonyls

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Abstract: Efficient one-step syntheses of α,β- and β,β-dihaloenones were achieved by ruthenium(II)-catalyzed reactions between cyclic or acyclic diazodicarbonyl compounds and oxalyl chloride or oxalyl bromide in moderate to good yields. This methodology offers several significant advantages, which include ease of handling, mild reaction conditions, one-step reaction, and the use of an effective and non-toxic catalyst. The synthesized compounds were further transformed into highly functionalized novel molecules bearing aromatic rings on the enone moiety using the Suzuki reaction.

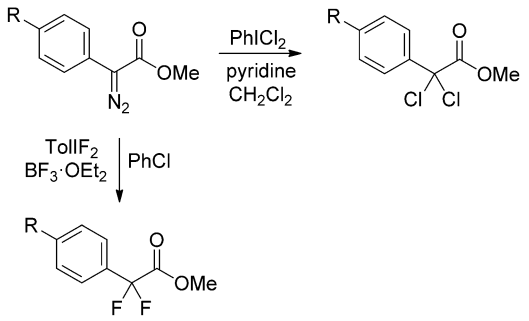
Keywords: diazodicarbonyl compounds; α,β-dihaloenones; β,β-dihaloenones; ruthenium(II)-catalyzed reaction

Introduction

Molecules bearing α- and β-haloenones are found in nature and have been shown to possess potent biological activities.[1] α-Haloenones and β-haloenones are important synthetic intermediates because various substituents can be installed at their α- and β-positions to synthesize biologically active natural products.[2,3] Because of their importance and usefulness, various synthetic methods have been developed for α-haloenones and β-haloenones.[4,5] Synthetic procedures for α-haloenones generally utilize halogenation–dehydrohalogenation,[6] an addition–elimination,[7] or halohydrin dehydration.[8] In addition, gold-catalyzed reactions of propargylic acetates to give α-haloenones have been described.[9] Recently, a number of synthetic approaches have been reported for β-haloenones, such as the Brønsted acid-promoted cyclization of 1-siloxy-1,5-diynes[10] and halogen-induced 1,2-silyl migration reaction.[11] Importantly, the 3-step synthetic route to α,β-dihaloenones from cyclohexane-1,3-dione using very toxic chlorine and phosgene has been reported.[12] On the other hand, for the synthesis of β,β-dihaloenones, reactions between alkynols, containing terminal bromine and iodine, and *N*-halosuccinimides or hydroxy(tosyloxy)iodobenzene (HITB) have been described.[13] Although a number of methods have been discussed for the synthesis of α,β-dichloroenones and β,β-bromoiodoenones, these approaches have a number of shortcomings, such as the use of toxic chlorine and phosgene, the product mixtures produced, long reaction times, and harsh reaction conditions. Thus, there is demand for general and facile synthetic methods that efficiently provide a variety of α,β- or β,β-dihaloenones under mild catalytic conditions.

The decomposition of diazocarbonyl compounds has been widely used in organic synthesis,[14] and transition metal-catalyzed reactions between diazocarbonyls and substrates have become important for the synthesis of a wide variety of heterocycles.[15] We have investigated metal(II)-catalyzed or thermal reactions between diazo compounds and different substrates.[16–18] In particular, we developed a method for preparing a variety of α-haloenones using rhodium(II)-catalyzed reactions between cyclic diazodicarbonyl compounds and acid chlorides[19] or benzyl halides.[20] In the related work, an α-halogenation reaction between acyclic diazo compounds and dihalomethanes has been reported by another group,[21] and the formation of α-haloenones from iodonium ylides has been accomplished by Moriarty's group[22] and our own.[23] Recently, a hypervalent iodine reagent-based α,α-dihalogenation of acyclic diazo compounds has been reported by Murphy's group (Scheme 1).[24]

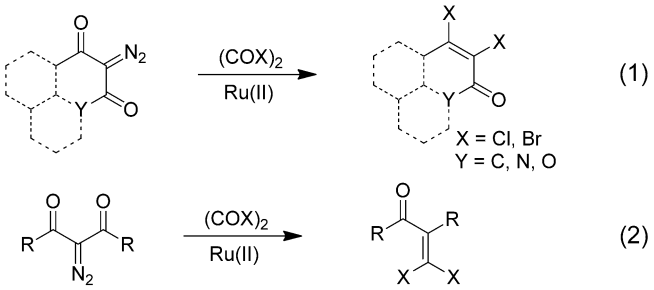
Our interest in developing a mild and efficient methodology to synthesize a variety of α,β- and β,β-dihaloenones prompted us to search for more convenient and safer catalysts. Previously, we used tris(triphenylphosphine)ruthenium(II) dichloride as a mild



Scheme 1. Recently reported α,α-chlorination and α,α-fluorination reactions starting from diazo compounds.

catalyst to synthesize multi-substituted dihydrofurans from diazodicarbonyls.[25] In our opinion, Ru(II)-phosphine complexes provide a promising basis for the syntheses of α,β- or β,β-dihaloenones, because they are readily available, generally non-toxic, and have high catalytic activities.[26]

To the best of our knowledge, no one-pot synthesis of α,β- and β,β-dihaloenones starting from diazo compounds has been published to date. Here, we first report the efficient, facile one-pot synthesis of α,β-dihaloenones [Eq. (1)] and β,β-dihaloenones [Eq. (2)] using ruthenium(II)-catalyzed reactions between cyclic diazodicarbonyls or acyclic diazodicarbonyls and oxalyl halides (Scheme 2).



Scheme 2.

Results and Discussion

Our efforts commenced with the preparation of cyclic diazodicarbonyl compounds **1a**–**1s** (65–92%) and acyclic diazodicarbonyl compounds **1t**–**1w** (85–91%) from the corresponding 1,3-dicarbonyls using a previously reported protocol (Table 1).[27]

In order to prepare α,β-dihaloenones, we first examined the reaction between the cyclic diazodicarbonyl compound **1a** with chlorinating reagents, which serve as solvent and reactant, in the presence of 0–5 mol% of $RuCl_2(PPh_3)_3$. The results are summarized in Table 2. Treatment of **1a** (1.0 mmol) with oxalyl chloride (1.5 mL) without a catalyst at room temperature for 24 h did not provide any products, whereas reaction at 50 °C for 24 h provided the product **2a** in 27% yield. In the catalyst-free conditions, formation of **2a** could be explained due to the generation of carbene *via* thermal decomposition of diazo compound **1a**. Using $RuCl_2(PPh_3)_3$ as a catalyst, we attempted further reactions by changing the chlorinating reagents, for example, diethyl chlorophosphate, thionyl chloride, sulfuryl chloride, phosphorus oxychloride, or phosphorus trichloride (entries 3–12). To our delight, with oxalyl chloride in the presence of 2 mol% of $RuCl_2(PPh_3)_3$ at 50 °C for 5 h, **2a** was produced in the best yield (88%) (entry 5). In addition, after reaction with oxalyl chloride (1.5 mmol) in PhF at 50 °C for 12 h, **2a** was isolated in 70% yield (entry 7). When the other chlorinating reagents were used, the yield of **2a** decreased (entries 8–12). Support for the structural assignment of **2a** was obtained by spectroscopic analysis. Compound **2a** was identified by its IR enone carbonyl absorptions at 1693 cm^{-1} and two methylene protons, which appeared as two singlets at $\delta = 2.69$

Table 1. Cyclic diazodicarbonyl compounds **1a**–**1s** and acyclic diazodicarbonyl compounds **1t**–**1w**.

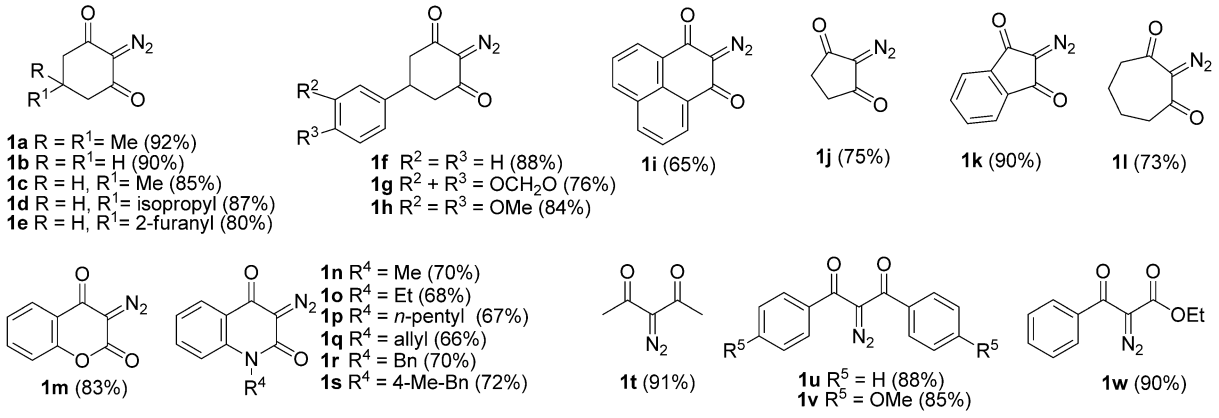
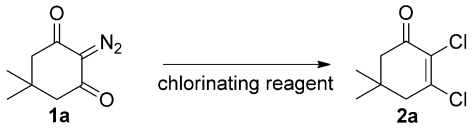


Table 2. Optimization of reaction conditions.[a]



1a 2a

Entry	Catalyst (mol%)	Chlorinating reagent	Conditions	Yield [%][b]
1	none	$(COCl)_2$	r.t., 24 h	0
2	none	$(COCl)_2$	50 °C, 24 h	27
3	$RuCl_2(PPh_3)_3$ (1.0)	$(COCl)_2$	50 °C, 8 h	56
4	$RuCl_2(PPh_3)_3$ (2.0)	$(COCl)_2$	r.t., 30 h	72
5	**$RuCl_2(PPh_3)_3$ (2.0)**	**$(COCl)_2$**	**50 °C, 5 h**	**88**
6	$RuCl_2(PPh_3)_3$ (5.0)	$(COCl)_2$	50 °C, 5 h	88
7[c]	$RuCl_2(PPh_3)_3$ (2.0)	$(COCl)_2$	PhF, 50 °C, 5 h	70
8	$RuCl_2(PPh_3)_3$ (2.0)	$(EtO)_2POCl$	50 °C, 8 h	42
9	$RuCl_2(PPh_3)_3$ (2.0)	$SOCl_2$	50 °C, 8 h	60
10	$RuCl_2(PPh_3)_3$ (2.0)	SO_2Cl_2	50 °C, 8 h	trace
11	$RuCl_2(PPh_3)_3$ (2.0)	$POCl_3$	50 °C, 8 h	53
12	$RuCl_2(PPh_3)_3$ (2.0)	PCl_3	50 °C, 8 h	10

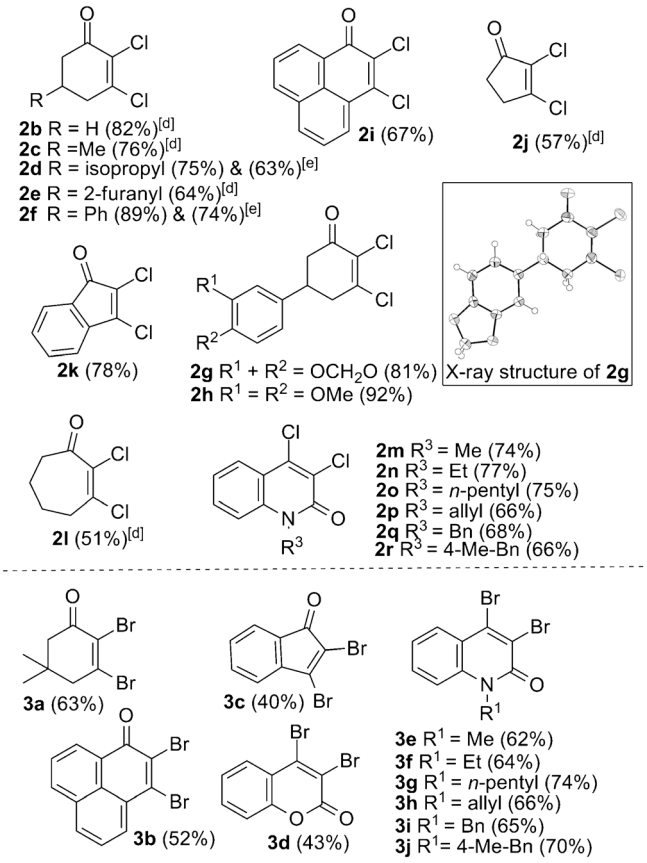
[a] *Reaction conditions:* **1a** (1.0 mmol) and chlorinating reagent (1.5 mL) under N_2.
[b] Isolated yield.
[c] Oxalyl chloride (1.5 mmol) in PhF (3.0 mL).

and 2.42 ppm, respectively, in its ^{1}H NMR spectrum. In its ^{13}C NMR spectrum, one enone carbonyl carbon was observed at $\delta = 189.2$ ppm together with two sp^2 carbons at $\delta = 151.4$ and 135.3 ppm. Furthermore, the structure determination was established by X-ray crystallographic analysis of structurally related compound **2g** (see the Supporting Information).[28]

Having optimized the reaction conditions, we further explored the generality of the reaction by using different cyclic diazodicarbonyl compounds. The results obtained are presented in Table 3. Reaction between 2-diazocyclohexane 1,3-dione (**1b**) and oxalyl chloride in the presence of 2 mol% of $RuCl_2(PPh_3)_3$ at room temperature for 10 h gave product **2b** in 82% yield. Similarly, reactions of cyclic diazodicarbonyl compounds **1c**–**1h** bearing various substituents, such as methyl, isopropyl, 2-furanyl, phenyl, and aryl groups at the 5-position on the 2-diazocyclohexane-1,3-dione ring provided the desired products **2c**–**2h** in 64–92% yields. We also tried further reactions using solvent. For example, treatment of **1d** and **1f** with oxalyl chloride (1.5 mmol) in PhF at 50 °C for 12 h afforded **2d** and **2f** in 63 and 74% yields, respectively. When 2-diazo-1*H*-phenalene-1,3(2*H*)-dione (**1i**) was used, **2i** was produced in a yield of 67%. For the diazodicarbonyls **1j**–**1l** with 5- and 7-membered rings, the desired products **2j**–**2l** were isolated in 57, 78, and 51% yields, respectively. Encouragingly, reactions between 3-diazoquinoline-2,4(1*H*,3*H*)-diones **1n-1s** and oxalyl chloride afforded the desired products **2m–2r** in 66–77% yield.

Next, we explored these reactions with oxalyl bromide to produce a number of α,β-dibromoenones

Table 3. Formation of a variety of α,β-dichloroenones **2b**–**2r** and α,β-dibromoenones **3a**–**3j** by $RuCl_2(PPh_3)_3$-catalyzed reaction of cyclic diazodicarbonyl compounds.[a–c]



[a] *Reaction conditions for α,β-dichloroenones* **2b**–**2r**: diazodicarbonyls (1.0 mmol) and oxalyl chloride (1.5 mL) in the presence of 2 mol% of $RuCl_2(PPh_3)_3$ at 50 °C for 5 h.
[b] *Reaction conditions for α,β-dibromoenones* **3a**–**3j**: diazodicarbonyls (1.0 mmol) and oxalyl bromide (1.5 mmol) in the presence of 2 mol% of $RuCl_2(PPh_3)_3$ in PhF (3.0 mL) at room temperature for 10 h.
[c] Isolated yields.
[d] Reactions were carried out at room temperature for 10 h.
[e] Oxalyl chloride (1.5 mmol) in PhF (3.0 mL) at 50 °C for 12 h.

(Table 3). Treatment of **1a** with oxalyl bromide in the presence of 2 mol% of $RuCl_2(PPh_3)_3$ in fluorobenzene at room temperature for 10 h provided **3a** in 63% yield. Importantly, in this case, a solvent was needed. In the absence of solvent, pure products were not formed and intractable mixtures were produced. Reactions between 2-diazo-1*H*-phenalene-1,3(2*H*)-dione (**1i**) or 2-diazo-1*H*-indene-1,3(2*H*)-dione (**1k**) and oxalyl bromide in fluorobenzene at room temperature for 10 h afforded the products **3b** (52%) and **3c** (40%). Similarly, reaction between 3-diazochromane-2,4-dione (**1m**) and oxalyl bromide in fluorobenzene

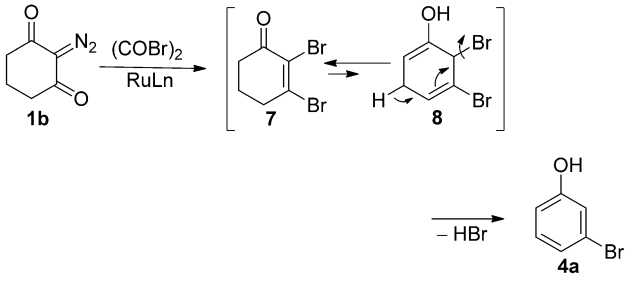
gave the desired product **3d** in 43% yield. In addition, treatment of 3-diazoquinoline-2,4(1*H*,3*H*)-diones **1n–1s** provided the desired products **3e–3j** in 62–74% yield.

A proposed mechanism for the formation of **2a** is described in Scheme 3. The diazodicarbonyl compound **1a** initially gives a metal carbenoid **4** due to the displacement of nitrogen by $RuCl_2(PPh_3)_3$. Then nucleophilic attack on the electrophilic carbenoid **4** by chlorine of oxalyl chloride yields intermediate **5**, which undergoes the intramolecular nucleophilic addition of oxygen to the carbonyl group and subsequent cleavage of the C–Cl bond to give **6**. As an evidence for intermediate **5**, a chloronium ylide intermediate was already reported by our[19,20b] and other groups.[22,29] Intramolecular nucleophilic addition of the chlorine atom to the enone in **6** gives final product **2a** through decarboxylation and decarbonylation.

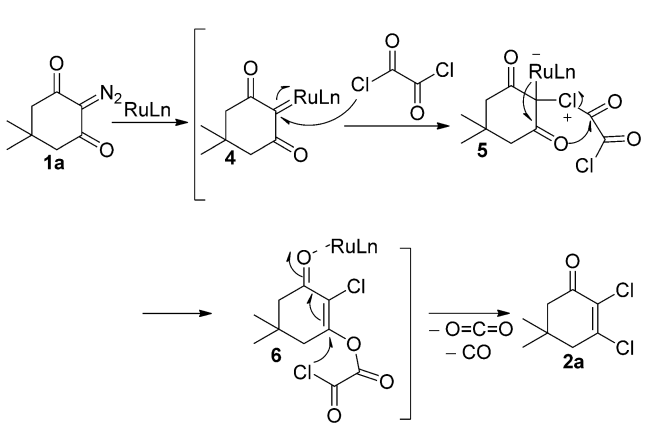
On the other hand, reactions between cyclic diazodicarbonyl compounds **1b**, **1d**, **1f**, **1g**, and **1h** bearing a mono substituent or without any substituent on the 5-position of the 2-diazocyclohexane-1,3-dione ring and oxalyl bromide did not provide the desired α,β-dibromoenones instead the aromatized products **4a–4e** were produced (Figure 1). For example, treatment of **1b** with oxalyl bromide in the presence of 2 mol% of $RuCl_2(PPh_3)_3$ in fluorobenzene at room temperature for 10 h gave aromatic compound **4a** in 68% yield. Similarly, reactions between **1d**, **1f**, **1g** or **1h** and oxalyl bromide provided the aromatic compounds **4b–4e** in 62–72% yield. The structure of **4a** was confirmed by analyzing its spectral data and by comparing them with those of a commercially available standard.

The formation of **4a** can be explained as shown in Scheme 4. The diazodicarbonyl **1b** first gives α,β-dibromoenone **7**, which then undergoes enolization followed by HBr elimination to furnish the stable aromatic **4a**. As evidence for this mechanism, the formation of intermediate **8** from **7** has been described by the Henderson's group.[30]

Next, further reactions between acyclic diazodicarbonyl compounds and oxalyl halides were attempted (Table 4). For example, treatment of the acyclic diazo-



Scheme 4.



Scheme 3.

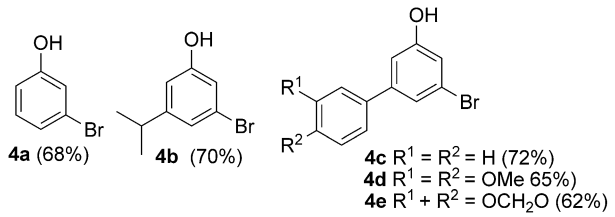
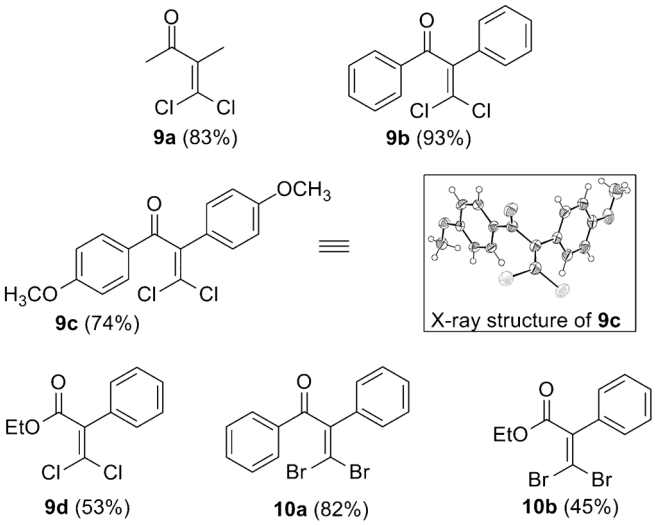


Figure 1.

Table 4. Formation of a variety of β,β-dichloroenones **9a–9d** and β,β-dibromoenones **10a**, **10b** by $RuCl_2(PPh_3)_3$-catalyzed reaction of acyclic diazodicarbonyl compounds.[a–c]



[a] *Reaction conditions:* acyclic diazodicarbonyls (1.0 mmol) and oxalyl chloride (1.5 mL) in the presence of 2 mol% of $RuCl_2(PPh_3)_3$ at room temperature for 10 h.

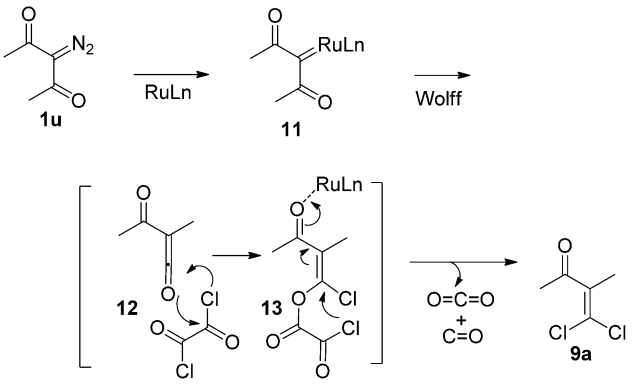
[b] *Reaction conditions:* acyclic diazodicarbonyls (1.0 mmol) and oxalyl bromide (1.5 mmol) in the presence of 2 mol% of $RuCl_2(PPh_3)_3$ in PhF (3.0 mL) at room temperature for 10 h.

[c] Isolated yields.

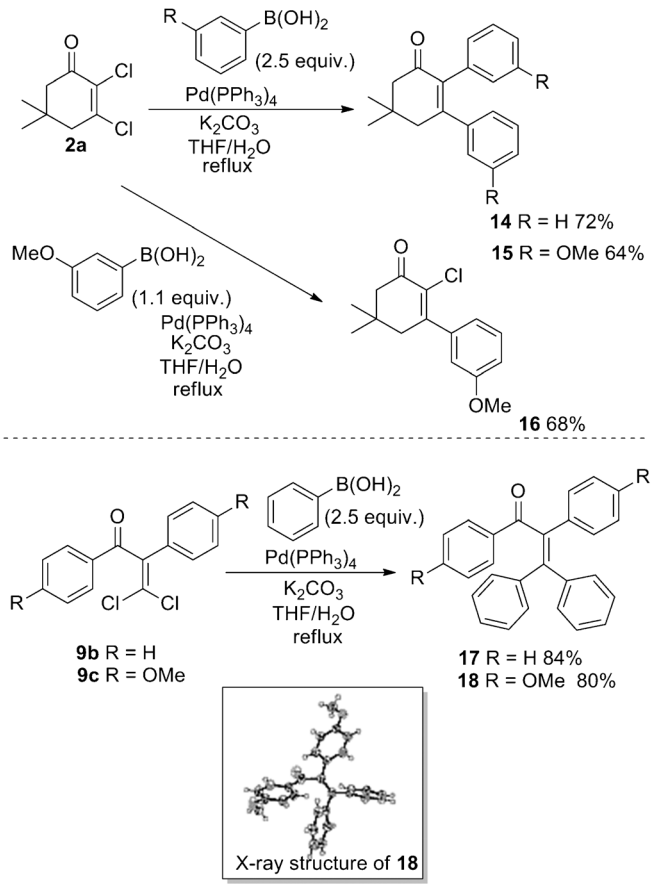
dicarbonyl **1t** with oxalyl chloride in the presence of 2 mol% of $RuCl_2(PPh_3)_3$ at room temperature for 10 h unexpectedly gave the β,β-dichloroenone **9a** in 83% yield through a Wolff rearrangement. Unlike cyclic diazodicarbonyl compounds, it was reported that acyclic diazodicarbonyl compounds can be readily converted to the corresponding ketenes through Wolff rearrangement in the presence of metal catalysts at room temperature.[31] Using the acyclic diazodicarbonyls **1u–1w**, products **9b–9d** were isolated in 93, 74, and 53% yields, respectively. Similarly, reactions between **1v** or **1w** and oxalyl bromide in the presence of 2 mol% of $RuCl_2(PPh_3)_3$ in fluorobenzene at room temperature for 10 h gave **10a** and **10b** in 82 and 45% yields, respectively. The identity of **9a** was confirmed by spectroscopic analysis. The ^{1}H NMR of **9a** shows two methyl peaks at $\delta = 2.48$ and 2.41 ppm as singlets. In the ^{13}C NMR spectrum, the carbon peak of a carbonyl group showed at $\delta = 194.0$ ppm and two sp^2 carbons at $\delta = 144.0$ and 127.4 ppm. Further confirmation of the identities of the synthesized compounds **9a–9d** and **10a**, **10b** was obtained by X-ray crystallographic analysis of compound **9c**.[32]

The formation of product **9a** is presumed to be initiated by a Ru(II)-catalyzed decomposition of **1u** to the corresponding ketene intermediate **12** *via* metal carbenoid **11** followed by Wolff rearrangement (Scheme 5).[31] Once formed, ketene **12** would undergo nucleophilic addition by a chlorine atom of the oxalyl chloride to give the final product **9a** through extrusion of CO_2 and CO from intermediate **13**. The possibility of formation of intermediate **13** could be deduced from oxalates generated by the known reaction between epoxide and oxalyl chloride.[33]

As an application of this methodology, we attempted the conversion of the synthesized compounds **2a**, **9b**, and **9c** to new small molecules using the Suzuki reactions, as shown in Scheme 6. Reaction of **2a** with 2.5 equivalents of phenylboronic acid in the presence of $Pd(PPh_3)_4$ in refluxing aqueous THF for 30 h gave **14** in 72% yield, whereas treatment with 3-methoxyphenylboronic acid formed **15** in 64% yield. Importantly, reaction of **2a** with 1.1 equivalents of 3-methoxyphenylboronic acid in refluxing aqueous THF for 30 h provided product **16** in 68% yield, with high chemoselectivity. Formation of compound **16** was confirmed by ^{1}H and ^{13}C NMR spectroscopy. Further, it was supported by the observation of a strong correlation between CH_2 at $\delta = 2.33$ of the cyclohexenone ring and a singlet proton at $\delta = 6.56$ of the aromatic ring in the 2D NOESY spectrum (see the Supporting Information). In addition, the Suzuki coupling of **9b** and **9c** with 2.5 equivalents of phenylboronic acid furnished compounds **17** and **18** in 84 and 80% yields, respectively (Scheme 6). We believe that these synthetic routes will be widely used to introduce benzene rings to cyclic and acyclic α,β-unsaturated enones. The structure of synthesized compound **18** was confirmed by analysis of spectral data and an X-ray structure determination.[34]



Scheme 5.



Scheme 6.

Conclusions

In summary, we describe here the ruthenium(II)-catalyzed reactions between diazodicarbonyls and oxalyl

chloride or oxalyl bromide. These reactions provided an efficient and facile means of synthesizing a variety of α,β-dihaloenones or β,β-dihaloenones in moderate to good yields. This protocol includes important advantages such as simple operation, a toxic and harmful chlorine- or phosgene-free route, and mild reaction catalysts over the existing methodologies. The synthesized compounds were further transformed into new small molecules using the Suzuki reaction.

Experimental Section

All experiments were carried out under a nitrogen atmosphere. Merck pre-coated silica gel plates (Art. 5554) with a fluorescent indicator were used as analytical TLC. Flash column chromatography was performed using silica gel 9385 (Merck). ^{1}H and ^{13}C NMR spectra were recorded on a Varian-VNS (300 and 75 MHz, respectively) spectrometer in $CDCl_3$ as the solvent chemical shift. IR spectra were recorded on a JASCO FTIR 5300 spectrophotometer. Melting points were measured with a Fisher–Johns melting point apparatus and uncorrected. The HR-MS were carried out at Korea Basic Science Institute (Daegu) on a Jeol JMS 700 spectrometer. Structural measurements for the complexes were performed on a Bruker SMART APEX CCD diffractometer using graphite monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) at Jeonju center of Korea Basic Science Institute.

General Procedure for the Synthesis of α,β- and β,β-Dichloroenones (2a–2r and 9a–9d)

To a solution of diazodicarbonyl compound (1.0 mmol) and oxalyl chloride (1.5 mL) was added $RuCl_2(PPh_3)_3$ (20 mg, 0.02 mmol) at room temperature. The reaction mixture was stirred at 50 °C for 5 h or at room temperature for 10 h until the completion of the reaction as indicated by TLC. The oxalyl chloride was evaporated under reduced pressure to give the residue. The residue was purified by flash column chromatography on silica gel with *n*-hexane/EtOAc (20:1) to give the product.

General Procedure for the Synthesis of α,β-Dichloroenones in Solvent (2a, 2d and 2f)

To a solution of diazodicarbonyl compound (1.0 mmol) and oxalyl chloride (190 mg, 1.5 mmol) in PhF (3.0 mL) was added $RuCl_2(PPh_3)_3$ (20 mg, 0.02 mmol) at room temperature. The reaction mixture was stirred at 50 °C for 12 h until the completion of the reaction as indicated by TLC. The oxalyl chloride was evaporated under reduced pressure to give the residue. The residue was purified by flash column chromatography on silica gel with *n*-hexane/EtOAc (20:1) to give the product.

General Procedure for the Synthesis of α,β- and β,β-Dibromoenones (3a–3j and 10a, 10b) and Aromatic Compounds (4a–4e)

To a solution of diazodicarbonyl compound (1.0 mmol) and oxalyl bromide (324 mg, 1.5 mmol) in fluorobenzene (3.0 mL) was added $RuCl_2(PPh_3)_3$ (20 mg, 0.02 mmol) at room temperature. The reaction mixture was stirred at room temperature for 10 h until the completion of the reaction as indicated by TLC. The oxalyl bromide and solvent were evaporated under reduced pressure to give the residue. The residue was purified by flash column chromatography on silica gel with *n*-hexane/EtOAc (20:1) to give the product.

General Procedure for Suzuki Coupling Reactions (14–18)

To a mixture of phenylboronic acid (2.5 mmol), dihaloenones (**2a**, **9b** and **9c**) (0.5 mmol) in 5 mL THF:2 M K_2CO_3 (8:2) was added $Pd(PPh_3)_4$ (29 mg, 0.05 mmol) under N_2 and the mixture was refluxed for 30 h. The reaction mixture was quenched with saturated NH_4Cl solution (10 mL) and extracted with ethyl acetate (3 × 10 mL). The combined layers were washed with water (10 mL), dried ($MgSO_4$), and evaporated under reduced pressure. Flash chromatography on silica gel using *n*-hexane/ethyl acetate (10:1) afforded products.

^{1}H NMR and ^{13}C NMR Data of Synthesized Compounds (2–4, 9–10 and 14–18)

2,3-Dichloro-5,5-dimethylcyclohex-2-enone (2a): Yield: 88%; solid; mp 62–64 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 2.69 (2H, s), 2.42 (2H, s), 1.06 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 189.2$, 151.4, 135.3, 50.8, 49.0, 33.3, 27.7; IR (KBr): $\nu = 2961$, 2878, 1693, 1595, 1464, 1254, 1141, 1019, 945, 854, 600 cm^{-1}; HR-MS: $m/z = 192.0107$ (M^+), calcd. for $C_8H_{10}Cl_2O$: 192.0109.

2,3-Dichlorocyclohex-2-enone (2b): Yield: 82%; yellowish solid; mp 58–60 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.83$ (2H, t, $J = 6.0$ Hz), 2.56 (2H, t, $J = 6.3$ Hz), 2.10–2.02 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 189.2$, 153.6, 130.5, 37.2, 35.4, 21.3; IR (KBr): $\nu = 2960$, 1688, 1590, 1416, 1262, 1186, 1137, 1013, 874, 790, 560 cm^{-1}; HR-MS: $m/z = 163.9797$ (M^+), calcd. for $C_6H_6Cl_2O$: 163.9796.

2,3-Dichloro-5-methylcyclohex-2-enone (2c): Yield: 76%; liquid; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.88$–2.81 (1H, m), 2.69- 2.53 (2H, m), 2.35–2.12 (2H, m), 1.08 (3H, d, $J =$ 6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 189.1$, 152.6, 130.3, 45.1, 43.1, 28.9, 20.2; IR (neat): $\nu = 2962$, 1694, 1593, 1455, 1378, 1242, 1142, 1060, 979, 824, 599 cm^{-1}; HR-MS: $m/z =$ 177.9952 (M^+), calcd. for $C_7H_8Cl_2O$: 177.9952.

2,3-Dichloro-5-isopropylcyclohex-2-enone (2d): Yield: 75%; oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.87$–2.77 (1H, m), 2.73–2.60 (2H, m), 2.32–2.19 (1H, m), 2.07–1.94 (1H, m), 1.68–1.57 (1H, m), 0.93 (6H, dd, $J = 6.6$, 1.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 189.5$, 153.0, 130.5, 41.2, 40.1, 39.3, 31.5, 19.3; IR (neat): $\nu = 2961$, 1694, 1595, 1465, 1254, 1147, 1056, 959, 862, 610 cm^{-1}; HR-MS: $m/z =$ 206.0262 (M^+), calcd. for $C_9H_{12}Cl_2O$: 206.0265.

2,3-Dichloro-5-(furan-2-yl)cyclohex-2-enone (2e): Yield: 64%; clear liquid; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.33$ (1H, br s), 6.30–6.29 (1H, m), 6.07–6.06 (1H, m), 3.62–3.53

(1H, m), 3.22–3.05 (2H, m), 3.01–2.76 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.7, 153.8, 151.5, 142.1, 130.8, 110.3, 105.5, 41.4, 39.9, 32.8; IR (neat): ν = 2988, 1763, 1693, 1593, 1424, 1376, 1243, 1054, 863, 742, 598 cm^{-1}; HR-MS: m/z = 229.9899 (M^+), calcd. for $C_{10}H_8Cl_2O_2$: 229.9901.

2,3-Dichloro-5-phenylcyclohex-2-enone (2f): Yield: 89%; solid; mp 53–55 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34–7.29 (2H, m), 7.26–7.23 (1H, m), 7.22–7.16 (2H, m), 3.50–3.39 (1H, m), 3.10–2.95 (2H, m), 2.90–2.71 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.4, 152.3, 140.7, 130.7, 128.9, 127.5, 126.4, 43.8, 42.8, 39.3; IR (KBr): ν = 2922, 1689, 1596, 1244, 1145, 1032, 967, 759, 699 cm^{-1}; HR-MS: m/z = 240.0106 (M^+), calcd. for $C_{12}H_{10}Cl_2O$: 240.0109.

5-(Benzo[*d*][1,3]dioxol-5-yl)-2,3-dichlorocyclohex-2-enone (2g): Yield: 81%; white crystalline solid; mp 118–120 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.75 (1H, d, J = 7.8 Hz), 6.68–6.63 (2H, m), 5.93 (2H, s), 3.45–3.41 (1H, m), 3.00 (2H, d, J = 8.1 Hz), 2.90–2.67 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.4, 152.3, 148.0, 146.9, 134.6, 130.7, 119.6, 108.5, 106.8, 101.2, 44.2, 43.1, 39.2; IR (KBr): ν = 2908, 1682, 1596, 1498, 1434, 1357, 1247, 1035, 976, 927, 816, 587 cm^{-1}; HR-MS: m/z = 284.0008 (M^+), calcd. for $C_{13}H_{10}Cl_2O_3$: 284.0007.

2,3-Dichloro-5-(3,4-dimethoxyphenyl)cyclohex-2-enone (2h): Yield: 92%; white solid; mp 98–100 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.70 (1H, d, J = 7.8 Hz), 6.64–6.63 (1H, m), 6.60–6.59 (1H, m), 3.73 (3H, s), 3.71 (3H, s), 3.35–3.24 (1H, m), 2.92 (2H, d, J = 7.5 Hz), 2.79–2.58 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.4, 152.2, 149.0, 148.2, 133.3, 130.5, 118.2, 111.3, 109.8, 55.8, 44.1, 43.0, 39.0; IR (KBr): ν = 2960, 1695, 1595, 1517, 1461, 1244, 1149, 1024, 977, 810 cm^{-1}; HR-MS: m/z = 300.0318 (M^+), calcd. for $C_{14}H_{14}Cl_2O_3$: 300.0320.

2,3-Dichloro-1*H*-phenalen-1-one (2i): Yield: 67%; yellow solid; mp 155–157 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.68 (1H, d, J = 7.5 Hz), 8.29 (1H, d, J = 7.5 Hz), 8.22 (1H, d, J = 8.1 Hz), 8.08 (1H, d, J = 8.1 Hz), 7.76 (1H, t, J = 7.8 Hz), 7.66 (1H, t, J = 7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 177.0, 144.5, 135.9, 133.2, 132.4, 131.8, 131.0, 130.6, 127.8, 127.3, 126.8, 126.1, 125.6; IR (KBr): ν = 2926, 1644, 1569, 1390, 1297, 1150, 994, 901, 837, 770 cm^{-1}; HR-MS: m/z = 247.9796 (M^+), calcd. for $C_{13}H_6Cl_2O$: 247.9796.

2,3-Dichlorocyclopent-2-enone (2j): Yield: 57%; liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.89 (2H, t, J = 4.8 Hz), 2.65 (2H, t, J = 4.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 196.8, 133.3, 132.6, 33.9, 31.8; IR (neat): ν = 2930, 1725, 1603, 1435, 1296, 1230, 1066, 968, 888, 818, 569 cm^{-1}; HR-MS: m/z = 149.9636 (M^+), calcd. for $C_5H_4Cl_2O$: 149.9639.

2,3-Dichloro-1*H*-inden-1-one (2k): Yield: 78%; yellow solid; mp 77–79 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (1H, d, J = 7.5 Hz), 7.70–7.63 (2H, m) 7.57 (1H, d, J = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.4, 150.2, 146.2, 134.5, 133.8, 133.7, 131.1, 123.5, 123.2; IR (KBr): ν = 2926, 1726, 1600, 1542, 1462, 1274, 1200, 1021, 911, 810, 745, 695, 593 cm^{-1}; HR-MS: m/z = 197.9635 (M^+), calcd. for $C_9H_4Cl_2O$: 197.9639.

2,3-Dichlorocyclohept-2-enone (2l): Yield: 51%; liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.94 (2H, s), 2.70 (2H, s), 1.87–1.85 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.5, 150.6, 132.6, 40.8, 37.4, 24.2, 20.7; IR (neat): ν = 2944, 1689, 1580, 1452, 1320, 1244, 1176, 1062, 966, 803, 560 cm^{-1}; HR-MS: m/z = 177.9951 (M^+), calcd. for $C_7H_8Cl_2O$: 177.9952.

3,4-Dichloro-1-methylquinolin-2(1*H*)-one (2m): Yield: 74%; white solid; mp 170–172 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (1H, dd, J = 8.1, 1.2 Hz), 7.65–7.59 (1H, m), 7.39–7.30 (2H, m), 3.77 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.4, 141.1, 137.6, 131.6, 126.4, 126.1, 123.2, 118.7, 114.4, 31.0; IR (KBr): ν = 3084, 1654, 1607, 1456, 1334, 1306, 1169, 1073, 952, 845, 748 cm^{-1}; HR-MS: m/z = 226.9903 (M^+), calcd. for $C_{10}H_7Cl_2NO$: 226.9905.

3,4-Dichloro-1-ethylquinolin-2(1*H*)-one (2n): Yield: 77%; yellow solid; mp 115–117 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (1H, dd, J = 8.4, 1.5 Hz), 7.64–7.58 (1H, m), 7.39 (1H, d, J = 8.4 Hz), 7.34–7.23 (1H, m), 4.39 (2H, q, J = 7.2 Hz), 1.36 (3H, t, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.8, 141.0, 136.7, 131.5, 126.6, 126.2, 123.0, 119.0, 114.2, 39.0, 12.5; IR (KBr): ν = 2984, 1652, 1604, 1449, 1341, 1277, 1165, 1084, 998, 841, 747 cm^{-1}; HR-MS: m/z = 241.0057 (M^+), calcd. for $C_{11}H_9Cl_2NO$: 241.0061.

3,4-Dichloro-1-pentylquinolin-2(1*H*)-one (2o): Yield: 75%; yellow solid; mp 66–68 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (1H, dd, J = 8.1, 1.2 Hz), 7.63–7.57 (1H, m), 7.37–7.27 (2H, m), 4.29 (2H, t, J = 7.8 Hz), 1.77–1.68 (2H, m), 1.46–1.31 (4H, m), 0.89 (3H, t, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.0, 141.0, 136.9, 131.5, 126.5, 126.1, 123.0, 119.0, 114.4, 44.0, 29.0, 27.0, 22.3, 13.9; IR (KBr): ν = 2947, 2861, 1645, 1603, 1453, 1310, 1161, 1084, 952, 856, 754, 660 cm^{-1}; HR-MS: m/z = 283.0532 (M^+), calcd- for $C_{14}H_{15}Cl_2NO$: 283.0531.

1-Allyl-3,4-dichloroquinolin-2(1*H*)-one (2p): Yield: 66%; white solid; mp 118–120 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 (1H, d, J = 8.1 Hz), 7.56 (1H, t, J = 7.8 Hz), 7.34–7.26 (2H, m), 5.96–5.83 (1H, m), 5.23–5.06 (2H, m), 4.96–4.94 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.9, 141.4, 136.8, 131.5, 130.7, 126.3, 125.9, 123.2, 118.7, 117.7, 115.0, 46.0; IR (KBr): ν = 3081, 1646, 1598, 1442, 1338, 1308, 1160, 1086, 929, 840, 752 cm^{-1}; HR-MS: m/z = 253.0063 (M^+), calcd. for $C_{12}H_9Cl_2NO$: 253.0061.

1-Benzyl-3,4-dichloroquinolin-2(1*H*)-one (2q): Yield: 68%; yellowish solid; mp 162–164 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (1H, d, J = 8.1 Hz), 7.43 (1H, t, J = 8.1 Hz), 7.28–7.14 (7H, m), 5.53 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.7, 142.5, 141.9, 137.1, 135.4 131.6, 128.9, 127.6, 126.6, 126.5, 123.3, 119.0, 115.3, 47.5; IR (KBr): ν = 2924, 1645, 1639, 1493, 1451, 1308, 1163, 1095, 955, 842, 739 cm^{-1}; HR-MS: m/z = 303.0215 (M^+), calcd. for $C_{16}H_{11}Cl_2NO$: 303.0218.

3,4-Dichloro-1-(4-methylbenzyl)quinolin-2(1*H*)-one (2r): Yield: 66%; white solid; mp 165–167 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (1H, d, J = 8.1 Hz), 7.41 (1H, t, J = 8.1 Hz), 7.28–7.17 (2H, m), 7.06–7.00 (4H, m), 5.47 (2H, s), 2.21 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.6, 141.6, 137.3, 137.1, 132.3, 131.6, 129.5, 126.6, 126.4, 126.0, 123.2, 118.9, 115.3, 47.2, 21.0; IR (KBr): ν = 2944, 1651, 1604, 1513, 1449, 1311, 1161, 1092, 955, 844, 757 cm^{-1}; HR-MS: m/z = 317.0371 (M^+), calcd. for $C_{17}H_{13}Cl_2NO$: 317.0374.

2,3-Dibromo-5,5-dimethylcyclohex-2-enone (3a): Yield: 63%; crystalline solid; mp 82–84 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.82 (2H, s), 2.45 (2H, s), 1.07 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 189.0, 148.2, 126.7, 52.6, 51.0, 34.7, 28.0; IR (KBr): ν = 2959, 1689, 1582, 1463, 1413, 1236, 1139, 1002, 927, 755 cm^{-1}; HR-MS: m/z = 279.9096 (M^+), calcd. for $C_8H_{10}Br_2O$: 279.9098.

2,3-Dibromo-1*H*-phenalen-1-one (3b): Yield: 52%; yellow solid; mp 164–166 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.62 (1H, d, J = 7.5 Hz), 8.28 (1H, d, J = 7.5 Hz), 8.17 (1H, d, J = 7.5 Hz), 8.04 (1H, d, J = 8.1 Hz), 7.22 (1H, t, J = 7.8 Hz), 7.59 (1H, t, J = 7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 176.7, 141.9, 135.7, 134.4, 133.3, 132.8, 132.3, 131.8, 131.2, 127.5, 127.3, 127.0, 117.3; IR (KBr): ν = 3059, 2925, 1640, 1567, 1435, 1384, 1295, 1241, 1141, 980, 832, 767, 603 cm^{-1}; HR-MS: m/z = 335.8784 (M^+), calcd. for $C_{13}H_6Br_2O$: 335.8785.

2,3-Dibromo-1*H*-inden-1-one (3c): Yield: 40%; yellow solid; mp 90–92 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.41 (2H, m), 7.30–7.25 (1H, m), 7.19–7.16 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 186.6, 146.3, 142.5, 134.4, 130.2, 129.9, 123.0, 122.4, 121.1; IR (KBr): ν = 2930, 1719, 1608, 1547, 1452, 1368, 1213, 1095, 576, 691, 499 cm^{-1}; HR-MS: m/z = 285.8626 (M^+), calcd. for $C_9H_4Br_2O$: 285.8629.

3,4-Dibromo-2*H*-chromen-2-one (3d): Yield: 43%; reddish solid; mp 78–80 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (1H, dd, J = 8.1, 1.2 Hz), 7.63–7.57 (1H, m), 7.38–7.31 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 151.1, 142.7, 133.0, 128.9, 125.5, 119.6, 117.0, 116.8, 116.6; IR (KBr): ν = 3084, 1729, 1596, 1540, 1451, 1277, 1177, 990, 753, 648 cm^{-1}; HR-MS: m/z = 301.8576 (M^+), calcd. for $C_9H_4Br_2O_2$: 301.8578.

3,4-Dibromo-1-methylquinolin-2(1*H*)-one (3e): Yield: 62%; white solid; mp 140–142 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04 (1H, dd, J = 8.1, 1.2 Hz), 7.64–7.58 (1H, m), 7.35–7.25 (2H, m), 3.76 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.2, 138.0, 137.8, 131.7, 129.8, 123.4, 122.7, 120.3, 114.4, 31.3; IR (KBr): ν = 3090, 1648, 1452, 1307, 1165, 1064, 957, 747, 657 cm^{-1}; HR-MS: m/z = 314.8897 (M^+), calcd. for $C_{10}H_7Br_2NO$: 314.8894.

3,4-Dibromo-1-ethylquinolin-2(1*H*)-one (3f): Yield: 64%; white solid; mp 100–102 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 (1H, d, J = 8.1 Hz), 7.58–7.52 (1H, m), 7.30 (1H, d, J = 8.4 Hz), 7.21 (1H, d, J = 8.1 Hz), 4.33 (2H, q, J = 7.2 Hz), 1.36 (3H, t, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.7, 137.8, 137.1, 131.6, 130.2, 123.2, 122.8, 120.6, 114.3, 39.4, 12.4; IR (KBr): ν = 2977, 1643, 1455, 1263, 1160, 1073, 990, 899, 744, 457 cm^{-1}; HR-MS: m/z = 328.9052 (M^+), calcd. for $C_{11}H_9Br_2NO$: 328.9051.

3,4-Dibromo-1-pentylquinolin-2(1*H*)-one (3g): Yield: 74%; white solid; mp 80–82 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (1H, dd, J = 8.1, 1.2 Hz), 7.59–7.53 (1H, m), 7.30–7.09 (2H, m), 4.25 (2H, q, J = 7.8 Hz), 1.73–1.63 (2H, m), 1.42–1.29 (4H, m), 0.85 (3H, t, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.0, 137.8, 137.4, 131.6, 130.2, 123.2, 122.9, 120.6, 114.5, 44.4, 29.0, 27.0, 22.3, 14.0; IR (KBr): ν = 2940, 1647, 1457, 1256, 1159, 1069, 926, 744, 457 cm^{-1}; HR-MS: m/z = 370.9519 (M^+), calcd. for $C_{14}H_{15}Br_2NO$: 370.9520.

1-Allyl-3,4-dibromoquinolin-2(1*H*)-one (3h): Yield: 66%; white solid; mp 110–112 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (1H, dd, J = 8.1, 1.2 Hz), 7.56–7.50 (1H, m), 7.32–7.19 (2H, m), 5.94–5.81 (1H, m), 5.19 (1H, d, J = 10.2 Hz), 5.08 (1H, d, J = 17.4 Hz), 4.94–4.93 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.0, 138.3, 137.5, 131.6, 130.8, 130.0, 123.4, 122.7, 120.6, 118.0, 115.1, 46.5; IR (KBr): ν = 1638, 1440, 1303, 1160, 1077, 924, 753, 657 cm^{-1}; HR-MS: m/z = 340.9047 (M^+), calcd. for $C_{12}H_9Br_2NO$: 340.9051.

1-Benzyl-3,4-dibromoquinolin-2(1*H*)-one (3i): Yield: 65%; white solid; mp 184–186 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (1H, dd, J = 8.1, 1.2 Hz), 7.45–7.39 (1H, m), 7.24–7.13 (7H, m), 5.53 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.6, 138.6, 137.6, 135.5, 131.7, 130.1, 129.0, 127.6, 126.6, 123.5, 122.7, 120.7, 115.3, 48.0; IR (KBr): ν = 1763, 1634, 1490, 1450, 1378, 1243, 1159, 1061, 930, 740 cm^{-1}; HR-MS: m/z = 390.9203 (M^+), calcd. for $C_{16}H_{11}Br_2NO$: 390.9207.

3,4-Dibromo-1-(4-methylbenzyl)quinolin-2(1*H*)-one (3j): Yield: 70%; white solid; mp 168–170 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 (1H, dd, J = 8.1, 1.2 Hz), 7.44–7.39 (1H, m), 7.26–7.15 (2H, m), 7.06–7.00 (4H, m), 5.48 (2H, s), 2.21 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 157.6, 138.5, 137.6, 137.3, 132.4, 131.6, 130.0, 129.5, 126.6, 123.4, 122.7, 120.7, 115.4, 47.7, 21.0; IR (KBr): ν = 1645, 1449, 1308, 1164, 1080, 927, 756 cm^{-1}; HR-MS: m/z = 404.9361 (M^+), calcd. for $C_{17}H_{13}Br_2NO$: 404.9364.

3-Bromophenol (4a): Yield: 68%; liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.99–6.94 (2H, m), 6.89 (1H, s), 6.66–6.62 (1H, m), 5.61 (1H, br s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.7, 130.8, 124.1, 122.7, 118.7, 114.2; IR (neat): ν = 3393, 1698, 1651, 1585, 1445, 1299, 1239, 1063, 860, 770, 676 cm^{-1}; HR-MS: m/z = 171.9522 (M^+), calcd. for C_6H_5BrO: 171.9524.

3-Bromo-5-isopropylphenol (4b): Yield: 70%; whitish solid; mp 53–55 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.00 (1H, s), 6.80 (1H, s), 6.61 (1H, s), 4.83 (1H, br s), 2.84–2.74 (1H, s), 1.20 (3H, s), 1.18 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.1, 152.5, 122.5, 122.3, 116.1, 112.4, 34.0, 23.6; IR (KBr): ν = 3399, 1703, 1596, 1441, 1268, 1177, 1096, 958, 847, 792, 692 cm^{-1}; HR-MS: m/z = 213.9994 (M^+), calcd. for $C_9H_{11}BrO$: 213.9993.

5-Bromobiphenyl-3-ol (4c): Yield: 72%; yellowish solid; mp 48–50 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.49 (2H, m), 7.44–7.35 (3H, m), 7.30–7.29 (1H, m), 6.98–6.95 (2H, m), 5.00 (1H, br s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.5, 144.3, 139.3, 128.8, 128.0, 127.0, 123.0, 122.7, 117.4, 113.1; IR (KBr): ν = 3310, 1595, 1474, 1414, 1300, 1192, 909, 849, 759, 693 cm^{-1}; HR-MS: m/z = 247.9838 (M^+), calcd. for $C_{12}H_9BrO$: 247.9837.

5-Bromo-3′,4′-dimethoxybiphenyl-3-ol (4d): Yield: 65%; whitish solid: mp 123–125 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.17 (1H, s), 7.00–6.94 (2H, m), 6.89–6.81 (3H, m), 5.70 (1H, br s), 3.83 (3H, s), 3.82 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.7, 149.0, 148.9, 144.0, 132.4, 123.0, 122.2, 119.5, 117.0, 112.8, 111.5, 110.2, 56.0; IR (KBr): ν = 3420, 1763, 1600, 1567, 1517, 1463, 1246, 1144, 1054, 851, 743, 606 cm^{-1}; HR-MS: m/z = 308.0052 (M^+), calcd. for $C_{14}H_{13}BrO_3$: 308.0048.

3-(Benzo[*d*][1,3]dioxol-5-yl)-5-bromophenol (4e): Yield: 62%; whitish solid; mp 88–90 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.21–7.20 (1H, m), 6.97–6.92 (3H, m), 6.87–6.82 (2H, m), 6.00 (2H, s), 5.17 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.3, 148.1, 147.5, 144.0, 133.5, 123.0, 122.6, 120.7, 117.1, 112.8, 108.6, 107.4, 101.2; IR (KBr): ν = 3303, 1570, 1474, 1315, 1238, 1042, 935, 857, 637 cm^{-1}; HR-MS: m/z = 291.9734 (M^+), calcd. for $C_{13}H_9BrO_3$: 291.9735.

4,4-Dichloro-3-methylbut-3-en-2-one (9a): Yield: 83%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.48 (3H, s), 2.41 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.0, 144.0, 127.4, 29.8, 25.0; IR (neat): ν = 2925, 1696, 1577, 1423, 1359, 1217, 1126, 1037, 971, 760, 583 cm^{-1}; HR-MS: m/z = 151.9793 (M^+), calcd. for $C_5H_6Cl_2O$: 151.9796.

3,3-Dichloro-1,2-diphenylprop-2-en-1-one (9b): Yield: 93%; oily liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.06–8.02 (2H, m), 7.60–7.44 (5H, m), 7.40–7.29 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.0, 139.2, 134.4, 134.2, 133.2, 129.7, 129.0, 128.9, 128.6, 128.2, 121.4; IR (neat): ν = 3044, 1681, 1585, 1446, 1251, 1050, 757, 690, 615 cm^{-1}; HR-MS: m/z = 276.0108 (M^+), calcd. for $C_{15}H_{10}Cl_2O$: 276.0109.

3,3-Dichloro-1,2-bis(4-methoxyphenyl)prop-2-en-1-one (9c): Yield: 74%; white crystalline solid; mp 114–116 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95 (2H, d, J = 9.0 Hz), 7.43 (2H, d, J = 9.0 Hz), 6.93 (2H, d, J = 9.0 Hz), 6.86 (2H, d, J = 9.0 Hz), 3.83 (3H, s), 3.76 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.0, 164.3, 160.0, 139.0, 132.2, 129.7, 127.5, 125.8, 119.8, 114.2, 114.0, 55.5, 55.2; IR (KBr): ν = 2934, 1653, 1599, 1507, 1460, 1257, 1166, 1023, 850, 555 cm^{-1}; HR-MS: m/z = 336.0317 (M^+), calcd. for $C_{17}H_{14}Cl_2O_3$: 336.0320.

Ethyl 3,3-dichloro-2-phenylacrylate (9d): Yield: 53%; liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.32 (5H, m), 3.99 (2H, q, J = 7.2 Hz), 0.92 (3H, t, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.5, 142.0, 137.0, 129.8, 128.3, 128.1, 122.5, 62.3, 13.3; IR (neat): ν = 2984, 1730, 1588, 1446, 1367, 1259, 1054, 910, 840, 760, 705, 622 cm^{-1}; HR-MS: m/z = 244.0056 (M^+), calcd. for $C_{11}H_{10}Cl_2O_2$: 244.0058

3,3-Dibromo-1,2-diphenylprop-2-en-1-one (10a): Yield: 82%; solid; mp 53–55 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.04–8.01 (2H, m), 7.61–7.55(1H, m), 7.51–7.45 (4H, m), 7.38–7.31 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.7, 146.6, 135.5, 134.2, 133.9, 129.9, 129.0, 128.8, 128.7, 128.1, 90.9; IR (KBr): ν = 3059, 1671, 1594, 1489, 1447, 1311, 1259, 1173, 1053, 903, 756, 694, 613, 554 cm^{-1}; HR-MS: m/z = 363.9096 (M^+), calcd. for $C_{15}H_{10}Br_2O$: 363.9098.

Ethyl 3,3-dibromo-2-phenylacrylate (10b): Yield: 45%; liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37(5H, m), 4.25 (2H, q, J = 7.2 Hz), 1.28 (3H, t, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.8, 141.5, 135.7, 129.6, 128.5, 128.1, 121.1, 62.2, 14.0; IR (neat): ν = 2988, 1734, 1580, 1450, 1368, 1252, 1057, 919, 839, 767, 627 cm^{-1}; HR-MS: m/z = 331.9050 (M^+), calcd. for $C_{11}H_{10}Br_2O_2$: 331.9048..

5,5-Dimethyl-2,3-diphenylcyclohex-2-enone (14): Yield: 72%; liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.50 (3H, m), 7.40–7.38 (4H, m), 7.24–7.18 (1H, m), 6.91–6.82 (2H, m), 2.64 (2H, s), 2.34 (2H, s), 1.18 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 200.4, 157.8, 156.0, 139.0, 130.0, 129.5, 128.7, 126.1, 124.3, 120.3, 115.3, 50.8, 42.3, 33.7, 28.3; IR (neat): ν = 2958, 1644, 1599, 1473, 1367, 1238, 1164, 1070, 755, 694, 508 cm^{-1}; HR-MS: m/z = 276.1512 (M^+), calcd, for $C_{20}H_{20}O$: 276.1514.

2,3-Bis(3-methoxyphenyl)-5,5-dimethylcyclohex-2-enone (15): Yield: 64%; liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.10–7.03 (2H, m), 6.69–6.63 (3H, m), 6.55–6.45 (3H, m), 3.61 (3H, s), 3.55 (3H, s), 2.70 (2H, s), 2.50 (2H, s), 1.18 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.3, 159.0, 158.9, 155.2, 142.2, 136.7, 136.5, 129.0, 128.5, 123.3, 120.1, 116.2, 113.7, 113.5, 112.7, 55.1, 55.0, 51.6, 47.0, 33.1, 28.1; IR (neat): ν = 2953, 1669, 1594, 1480, 1359, 1267, 1165, 1045, 863, 782, 700 cm^{-1}; HR-MS: m/z = 336.1728 (M^+), calcd. for $C_{22}H_{24}O_3$: 336.1725..

2-Chloro-3-(3-methoxyphenyl)-5,5-dimethylcyclo hex-2-enone (16): Yield: 68%; liquid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.26 (1H, t, J = 7.8 Hz), 6.77 (1H, dd, J = 7.8, 2.4 Hz), 6.59–6.57 (1H, m), 6.56 (1H, s), 3.79 (3H, s), 2.42 (2H, s), 2.33 (2H, s), 1.05 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.4, 166.9, 160.9, 154.1, 130.3, 112.5, 111.3, 106.5, 55.5, 50.9, 41.6, 32.4, 27.9; IR (neat): ν = 2959, 1676, 1592, 1486, 1349, 1290, 1233, 1131, 1038, 922, 778, 698 cm^{-1}; HR-MS: m/z = 264.0919 (M^+), calcd. for $C_{15}H_{17}ClO_2$: 264.0917.

1,2,3,3-Tetraphenylprop-2-en-1-one (17): Yield: 84%; solid; mp 150–152 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85–7.82 (2H, m), 7.28–7.25 (1H, m), 7.21–7.16 (2H, m), 7.09–7.06 (4H, m), 7.04–7.01 (8H, m), 6.99–6.97 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.8, 144.7, 141.6, 140.8, 139.5, 138.6, 137.6, 132.6, 131.0, 130.0, 129.8, 129.6, 128.4, 128.3, 128.2, 127.9, 127.8, 127.5, 127.2; IR (KBr): ν = 3074, 2926, 1660, 1595, 1488, 1443, 1315, 1258, 1163, 1072, 955, 754, 696, 592 cm^{-1}; HR-MS: m/z = 360.1511 (M^+), calcd. for $C_{27}H_{20}O$: 360.1514.

1,2-Bis(4-methoxyphenyl)-3,3-diphenylprop-2-en-1-one (18): Yield: 80%; yellowish crystalline solid; mp 165–167 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.91 (2H, d, J = 8.4 Hz), 7.17–7.09 (10H, m), 6.99 (2H, d, J = 8.4 Hz), 6.78 (2H, d, J = 8.4 Hz), 6.64 (2H, d, J = 8.4 Hz), 3.77 (3H, s), 3.69 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.5, 163.0, 158.5, 142.7, 142.0, 141.3, 139.2, 132.0, 131.1, 131.0, 131.0, 130.6, 129.8, 128.0, 127.8, 127.6, 127.7, 113.7, 113.5, 55.3, 55.0; IR (KBr): ν = 3034, 2930, 2837, 1658, 1598, 1509, 1444, 1256, 1172, 1028, 836, 766, 702, 554 cm^{-1}; HR-MS: m/z = 420.1726 (M^+), calcd. for $C_{29}H_{24}O_3$: 420.1725.

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[34] CCDC 980999 contains the supplementary crystallographic data for compound **18**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.