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Efficient and Facile Synthesis of α-Chloroenones Bearing β-Carbonates or β-Carbamates

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Efficient synthesis of α-chloroenones bearing β-carbonates or β-carbamates was achieved by rhodium(II)-catalyzed reaction of cyclic diazodicarbonyl compounds with a variety of chloroformates or carbamyl chlorides in good yields. These reactions provided a useful and rapid route to β-substituted α-haloenones.

Key Words : Rhodium(II)-catalyzed reaction, Diazodicarbonyl compounds, α-chloroenones

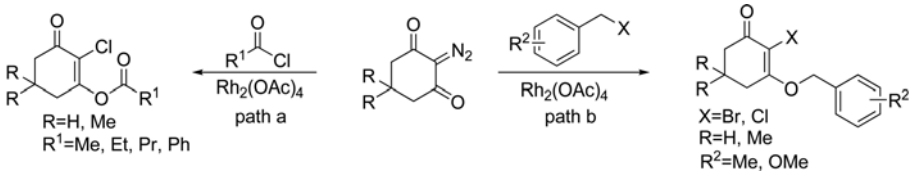
Introduction

α-Halo enones have been widely used as valuable and versatile intermediates in the synthesis of α-carbon substituted enones[1] and biologically active natural products.[2] There are many known methods for the preparation of α-haloenones. They are generally prepared by a halogenation-dehydrohalogenation reaction,[3] an addition-elimination reaction,[4] and a halohydrin-dehydration reaction.[5] Recently, the gold-catalyzed reaction of propargylic acetates to give α-haloenones has been reported.[6] Although, many methods for the preparation of these compounds have been developed, their synthetic exploitation has been limited due to difficulty in the regioselectivity, the strong acidic conditions, and the side reactions involving over-oxidation.[7] The necessity for overcoming these serious problems has prompted our research for a preparation of β-substituted α-haloenones.

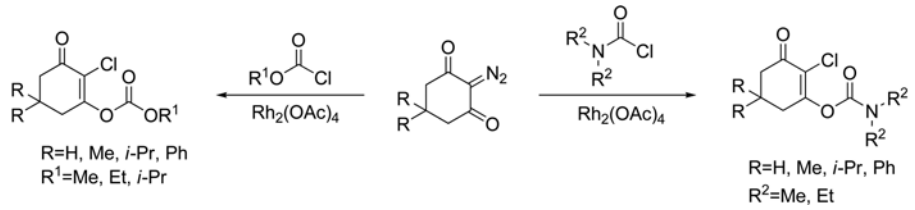
Rhodium(II)-catalyzed decomposition of diazodicarbonyl compounds has become a useful method in organic synthesis.[8] We have been interested in rhodium(II)-catalyzed reactions of diazodicarbonyl compounds with several substrates such as nitriles, isocyanates, ketones, and vinyl ethers for the formation of a number of heterocycles.[9] In particular, we developed a new and useful methodology for preparing a variety of β-substituted α-haloenones using rhodium(II)-catalyzed reactions of cyclic diazodicarbonyl compounds with acid chlorides, benzyl halides, or dihalomethanes (Scheme 1).[10] We also developed another new methodology for the preparation of β-substituted α-haloenones starting from iodonium ylides.[11] Later, a similar α-halogenation of acyclic diazo compounds with dihalomethanes has been reported by other group.[12] Importantly, our work for the formation of α-haloenones from iodonium ylides was retried by Moriarty group.[13] While continuing our study based on the rhodium(II)-catalyzed reactions, we have expanded this work to the synthesis of novel β-substituted α-chloroenones. To the best of our knowledge, no facile and efficient one-pot methodology for the synthesis of α-chloroenones bearing β-carbonates or β-carbamates has yet been developed. We report herein one-pot synthesis of α-chloroenones bearing β-carbonates or β-carbamates by rhodium(II)-catalyzed reactions of cyclic diazodicarbonyl compounds with chloroformates or carbamyl chlorides (Scheme 2).

Results and Discussion

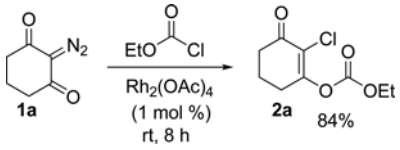
In order to give α-chloroenones bearing β-carbonates, we first examined the reaction of readily available diazodi-



Scheme 1



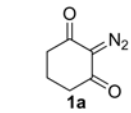
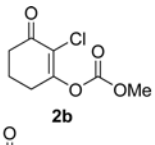
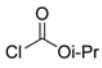
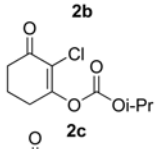
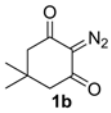
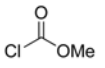
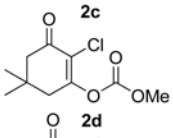
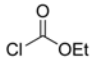
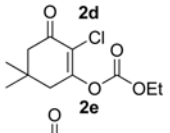
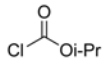
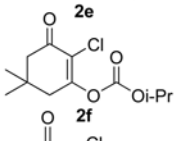
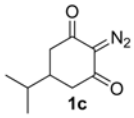
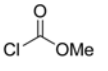
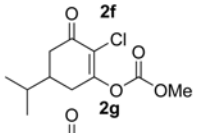
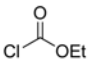
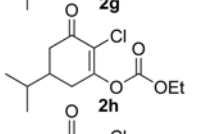
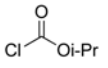
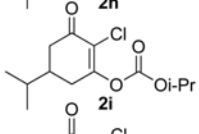
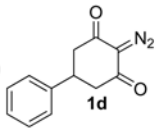
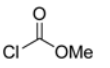
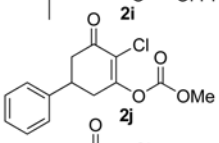
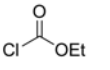
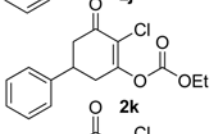
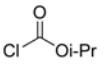
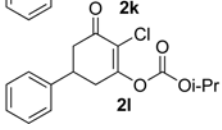
Scheme 2



Scheme 3

carbonyl compounds with several alkyl chloroformates, which serve as a solvent and a reactant, in the presence of 1 mol % of $Rh_2(OAc)_4$. For example, treatment of 2-diazo-1,3-cyclohexanedione (**1a**) with ethyl chloroformate in the presence of 1 mol % of $Rh_2(OAc)_4$ at room temperature for 8 h gave desired product **2a** in 84% yield (Scheme 3). Support for the structural assignment comes from its spectroscopic analysis. Compound **2a** is identified by its IR carbonyl absorptions of an enone at 1694 cm^{-1} and a carbonate at 1769 cm^{-1}, and its ^1H NMR peaks of the ethoxy group appeared as a quartet at δ 4.31 and a triplet at δ 1.36, respectively. Further, support for the structural assignment of **2a** is confirmed from its ^{13}C NMR spectrum, which clearly shows the expected nine carbons, including the two carbonyl carbons of the enone at δ 191.3 and the carbonate at δ 163.5.

Table 1. Additional reactions of diazodicarbonyl compounds **1a-1d** with alkyl chloroformates

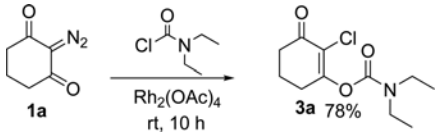
Entry	Diazodi-carbonyl	Chloro-formate	Condition	Product	Yield (%)
1			rt, 10 h		75
2			rt, 12 h		50
3			rt, 10 h		72
4			rt, 8 h		84
5			rt, 12 h		52
6			rt, 10 h		69
7			rt, 9 h		75
8			rt, 12 h		42
9			rt, 10 h		80
10			rt, 8 h		87
11			rt, 12 h		47

Additional reactions of diazodicarbonyl compounds **1a-1d** with alkyl chlorofomates in the presence of 1 mol % of $Rh_2(OAc)_4$ were next attempted. The results are summarized in Table 1. Reactions of **1a** with methyl choroformate or isopropyl chloroformate at room temperature for 10-12 h afforded the desired products **2b-2c** in 75 and 50% yield, respectively (entries 1-2, Table 1). Similarly, treatment of **1b** with methyl chlorofomate, ethyl chlorofomate, or isoprppyl chlorofomate afforded products **2d-2f** in 72, 84, and 52% yield, respectively (entries 3-5, Table 1). Reactions of diazodicarbonyl compounds **1c-1d** with substituents of isopropyl and phenyl group on the cyclohexane ring were also successful (entries 6-11, Table 1). These reactions provided desired products **2g-2l** in 42-87% yield. These reactions provided a rapid approach to the synthesis of a variety of α-chloroenones bearing β-carbonates.

In order to extend the utility of this methodology, we also examined the reactions of diazodicarbonyl compounds **1a-1d** with alkylcarbamyl chlorides to produce α-chloroenones bearing β-carbamates. Treatment of **1a** with diethylcarbamyl chloride as a solvent and reactant in the presence of 1 mol % of $Rh_2(OAc)_4$ at room temperature for 10 h afforded product **3a** in 78% yield (Scheme 4). In the IR spectrum, the structure of **3a** is confirmed by the observation of two carbonyl absorptions of an enone at 1691 cm^{-1} and a carbamate at 1729 cm^{-1}. Further support for the structural assignment is obtained from its ^{13}C NMR spectrum, which clearly shows the expected two carbonyl carbons of the enone at δ 191.8 and the carbamate at δ 165.5.

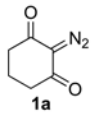
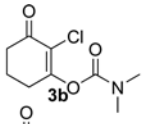
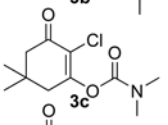
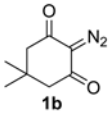
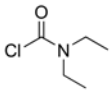
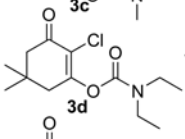
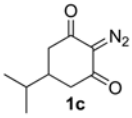
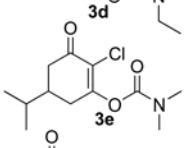
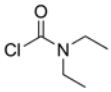
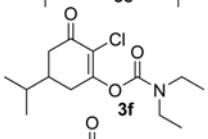
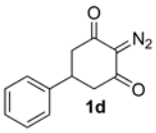
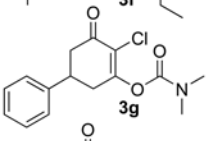
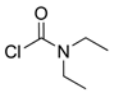
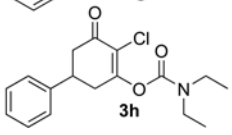
Additional reactions of diazodicarbonyl compounds **1a-1d** with dialkylcarbamyl chloride were next carried out under rhodium catalysis. Reaction of **1a** with dimethylcarbamyl chloride in the presence of 1 mol % of $Rh_2(OAc)_4$ at room temperature for 15 h afforded expected compound **3b** in 48% yield (entry 1, Table 2). Similarly, reactions of **1b-1d** with dimethylcarbamyl chloride or diethylcarbamyl chloride provided the desired products **3c-3h** in 45-80% yield (entries 2-7, Table 2). These reactions also provided a rapid synthetic route for the preparation of various α-chloroenones bearing β-carbamates.

The proposed mechanism for the formation of **2a** and **3a** is best described as shown in Scheme 5. The diazodicarbonyl



Scheme 4

Table 2. Further reactions of diazodicarbonyl compounds **1a-1d** with alkylcarbamyl chlorides

Entry	Diazodi-carbonyl	Carbamyl Chloride	Condition	Product	Yield (%)
1	 **1a**		rt, 15 h	 **3b**	48
2			rt, 15 h	 **3c**	50
3	 **1b**		rt, 10 h	 **3d**	73
4	 **1c**		rt, 15 h	 **3e**	45
5			rt, 10 h	 **3f**	80
6	 **1d**		rt, 15 h	 **3g**	49
7			rt, 10 h	 **3h**	79

compound **1a** first gives a metal carbenoid **4** by displacement of nitrogen by $Rh_2(OAc)_4$.[14] Nucleophilic attack of the chlorine atom in the acid chloride of ethyl chloroformate or diethylcarbamyl chloride to the electrophilic carbenoid **4** yields intermediate **5** or **6**,[15] which undergo fast intramolecular nucleophilic addition of oxygen to the carbonyl group followed by the cleavage of the C–Cl bond to give product **2a** or **3a** respectively.

In conclusion, rhodium-catalyzed reactions of diazodicarbonyl compounds with a variety of chloroformates and carbamyl chlorides are described. These reactions provided a simple and facile method for the synthesis of α-chloroenones bearing β-carbonates or β-carbamates in good yields.

Experimental Section

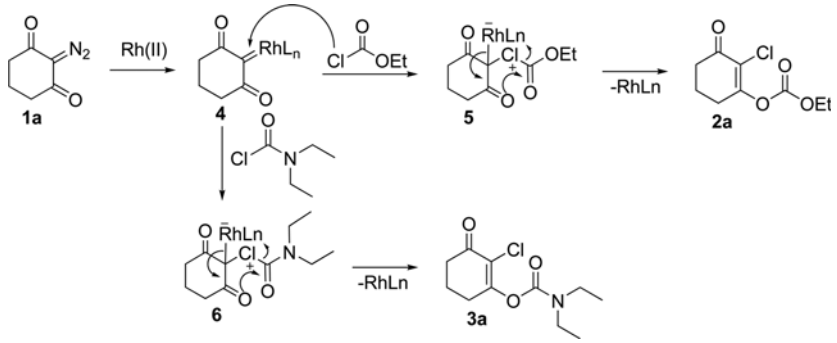
All experiments were carried out under a nitrogen atmosphere. Merck pre-coated silica gel plates (Art. 5554) with a fluorescent indicator were used as analytical TLC. Flash column chromatography was performed using silica gel 9385 (Merck). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Model ARX (300 and 75 MHz, respectively) spectrometer in $CDCl_3$ as the solvent. IR spectra were recorded on a JASCO FTIR 5300 spectrophotometer. The HRMS were carried out at Korea Basic Science Institute (Daegu) on a Jeol JMS 700 spectrometer.

General Procedure for the Synthesis of α-Chloroenones Bearing β-Carbonates (2a-2l). To a solution of diazodicarbonyl compound (1.0 mmol) and alkyl chloroformates (1 mL) was added rhodium catalyst (1 mol %) at room temperature. The reaction mixture was stirred for 8-12 h until the completion of the reaction as indicated by TLC. The halide was evaporated under reduced pressure to give the residue. The residue was purified by flash column chromatography on silica gel with *n*-hexane/EtOAc (10:1) to give the product.

2-Chloro-3-oxocyclohex-1-enyl Ethyl Carbonate (2a): Yield 84% as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.31 (2H, q, J = 7.2 Hz), 2.73 (2H, t, J = 6.3 Hz), 2.61 (2H, t, J = 6.3 Hz), 2.15-2.04 (2H, m), 1.36 (3H, t, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.3, 163.5, 150.0, 122.0, 65.8, 37.1, 29.4, 20.1, 13.9; IR (neat) 2964, 1769, 1694, 1629, 1461, 1367, 1226, 1099, 995, 882, 825, 775, 632, 555 cm^{-1}; HRMS (FAB) *m/z* $(M+H)^+$ calcd for $C_9H_{12}ClO_4$: 219.0424. Found: 219.0425.

2-Chloro-3-oxocyclohex-1-enyl Methyl Carbonate (2b): Yield 75% as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.93 (3H, s), 2.73 (2H, t, J = 6.3 Hz), 2.60 (2H, t, J = 6.3 Hz), 2.12-2.04 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.3, 163.3, 150.7, 56.1, 37.1, 32.5, 29.3, 20.1; IR (neat) 2957, 1774, 1694, 1598, 1443, 1358, 1232, 1079, 1018, 957, 920, 776, 641, 557, 481 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_8H_9ClO_4$: 204.0189. Found: 204.0190.

2-Chloro-3-oxocyclohex-1-enyl Isopropyl Carbonate (2c): Yield 50% as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.93-4.87 (1H, m), 2.71-2.65 (2H, m), 2.58-2.51 (2H, m), 2.04-2.00 (2H, m), 1.33-1.29 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.4, 163.5, 149.5, 121.9, 74.5, 37.2, 29.5, 21.5, 20.1; IR (neat) 2983, 1765, 1695, 1629, 1461, 1380, 1231,



Scheme 5

1103, 1018, 909, 625, 556 cm^{-1}; HRMS (FAB) *m/z* $(M+H)^+$ calcd for $C_{10}H_{14}ClO_4$: 233.0581. Found: 233.0582.

2-Chloro-5,5-Dimethyl-3-oxocyclohex-1-enyl Methyl Carbonate (2d): Yield 72% as a liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 3.87 (3H, s), 2.58 (2H, s), 2.44 (2H, s), 1.09 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.3, 161.5, 150.8, 121.2, 56.1, 50.9, 42.9, 32.5, 27.8; IR (neat) 2963, 1776, 1695, 1639, 1446, 1372, 1239, 1060, 1024, 944, 641, 599 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{10}H_{13}ClO_4$: 232.0502. Found: 232.0505.

2-Chloro-5,5-Dimethyl-3-oxocyclohex-1-enyl Ethyl Carbonate (2e): Yield 84% as a liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 4.31 (2H, q, J = 7.2 Hz), 2.60 (2H, s), 2.46 (2H, s), 1.37 (3H, t, J = 7.2), 1.12 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.3, 161.6, 150.2, 121.2, 65.8, 51.0, 43.0, 32.5, 29.6, 27.8, 14.0; IR (neat) 2925, 1769, 1696, 1637, 1464, 1373, 1230, 1010, 632, 599 cm^{-1}; HRMS (FAB) *m/z* $(M+H)^+$ calcd for $C_{11}H_{16}ClO_4$: 247.0737. Found: 247.0733.

2-Chloro-5,5-dimethyl-3-oxocyclohex-1-enyl Isopropyl Carbonate (2f): Yield 52% as a liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 4.98-4.90 (1H, m), 2.59 (2H, s), 2.46 (2H, s), 1.35 (6H, d, J = 6.3 Hz), 1.11 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.4, 184.0, 161.8, 149.6, 121.2, 74.5, 51.0, 46.1, 43.1, 32.5, 27.9, 21.5; IR (neat) 2962, 1764, 1699, 1464, 1374, 1234, 1102, 950, 911, 805, 623 cm^{-1}; HRMS (FAB) *m/z* $(M+H)^+$ calcd for $C_{12}H_{18}ClO_4$: 261.0894. Found: 261.0891.

2-Chloro-5-isopropyl-3-oxocyclohex-1-enyl Methyl Carbonate (2g): Yield 69% as a liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 3.89 (3H, s), 2.73-2.71 (1H, m), 2.61-2.58, (2H, m), 2.33-2.23 (1H, m), 2.06-1.94 (1H, m), 1.68-1.57 (1H, m), 0.91 (6H, d, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7, 163.2, 150.8, 121.7, 55.1, 41.1, 39.1, 33.1, 31.5, 19.4; IR (neat) 2963, 2880, 1774, 1695, 1637, 1443, 1388, 1238, 1195, 1056, 971, 776, 642, 515 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{11}H_{15}ClO_4$: 246.0659. Found: 246.0659.

2-Chloro-5-isopropyl-3-oxocyclohex-1-enyl Ethyl Carbonate (2h): Yield 75% as a liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 4.30 (2H, q, J = 7.2 Hz), 2.73-2.65 (1H, m), 2.61-2.58 (2H, m), 2.33-2.23 (1H, m), 2.06-1.93 (1H, m), 1.68-1.57 (1H, m), 1.35 (3H, t, J = 7.2 Hz), 0.91 (6H, d, J = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7, 185.1, 163.3, 150.1, 121.6, 65.8, 41.1, 39.0, 33.2, 31.4, 19.3, 14.0; IR (neat) 2965, 1770, 1695, 1636, 1467, 1387, 1232, 1003, 879, 775, 636 cm^{-1}; HRMS (FAB) *m/z* $(M+H)^+$ calcd for $C_{12}H_{18}ClO_4$: 261.0894. Found: 261.0891.

2-Chloro-5-isopropyl-3-oxocyclohex-1-enyl Isopropyl Carbonate (2i): Yield 42% as a liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 4.99-4.90 (1H, m), 2.74-2.67 (1H, m), 2.61-2.52 (2H, m), 2.33-2.24 (1H, m), 1.88-1.86 (1H, m), 1.64-1.53 (1H, m), 1.35 (6H, d, J = 6.3 Hz), 0.89 (6H, d, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.8, 185.1, 163.4, 149.6, 74.5, 41.1, 39.0, 33.3, 31.6, 29.6, 21.5, 19.4; IR (neat) 2962, 1765, 1696, 1600, 1465, 1369, 1238, 1156, 1101, 910, 637 cm^{-1}; HRMS (FAB) *m/z* $(M+H)^+$ calcd for $C_{13}H_{20}ClO_4$: 275.1050. Found: 275.1052.

2-Chloro-3-oxo-5-phenylcyclohex-1-enyl Methyl Carbonate (2j): Yield 80% as a liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.34-7.32 (2H, m), 7.24-7.22 (3H, m), 3.90 (3H, s), 3.54-3.37 (1H, m), 3.09-3.00 (1H, m), 2.94-2.87 (2H, m), 2.81-2.76 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.7, 162.5, 151.0, 141.2, 129.2, 127.8, 126.7, 122.3, 56.4, 44.3, 38.7, 37.1; IR (neat) 3030, 2959, 1773, 1694, 1598, 1445, 1367, 1232, 1039, 978, 924, 766, 702, 638, 502 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{14}H_{13}ClO_4$: 280.0502. Found: 280.0505.

2-Chloro-3-oxo-5-phenylcyclohex-1-enyl Ethyl Carbonate (2k): Yield 87% as a liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.29-7.27 (2H, m), 7.19-7.17 (3H, m), 4.25 (2H, t, J = 7.2 Hz), 3.49-3.38 (1H, m), 3.04-2.95 (1H, m), 2.90-2.80 (2H, m), 2.76-2.70 (1H, m), 1.31 (3H, t, J = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.5, 162.4, 141.0, 128.9, 127.5, 126.6, 126.5, 121.9, 65.9, 44.0, 38.4, 36.9, 14.0; IR (neat) 2984, 1768, 1695, 1634, 1454, 1370, 1225, 1004, 766, 702, 633, 578 cm^{-1}; HRMS (FAB) *m/z* $(M+H)^+$ calcd for $C_{15}H_{16}ClO_4$: 295.0737. Found: 295.0739.

2-Chloro-3-oxo-5-phenylcyclohex-1-enyl Isopropyl Carbonate (2l): Yield 47% as a liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 7.30-7.17 (5H, m), 4.94-4.86 (1H, m), 3.47-3.22 (1H, m), 2.89-2.81 (2H, m), 2.42-2.33 (2H, m), 1.30 (6H, d, J = 6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.7, 162.8, 149.8, 141.3, 129.2, 128.8, 127.7, 126.8, 74.9, 44.3, 38.8, 37.3, 21.7; IR (neat) 3031, 2982, 2924, 1761, 1697, 1635, 1497, 1458, 1375, 1230, 1194, 1102, 900, 909, 761, 701, 620 cm^{-1}; HRMS (FAB) *m/z* $(M+H)^+$ calcd for $C_{16}H_{18}ClO_4$: 309.0894. Found: 309.0891.

General Procedure for the Synthesis of α-Chloroenones Bearing β-Carbamates (3a-3h). To a solution of diazodicarbonyl compound (1.0 mmol) and carbamyl chlorides (1 mL) was added rhodium catalyst (1 mol %) at room temperature. The reaction mixture was stirred for 10 to 15 h until the completion of the reaction as indicated by TLC. The halide was evaporated under reduced pressure to give the residue. The residue was purified by flash column chromatography on silica gel with *n*-hexane/EtOAc (10:1) to give the product.

2-Chloro-3-oxocyclohex-1-enyl Diethylcarbamate (3a): Yield 78% as a liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 3.38-3.28 (4H, m), 2.76 (2H, t, J = 6.0 Hz), 2.56 (2H, t, J = 6.0 Hz), 2.08-2.00 (2H, m), 1.23-1.14 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.8, 165.5, 150.7, 121.0, 42.5, 42.3, 37.3, 30.3, 20.4, 14.0, 13.1; IR (neat) 2975, 2883, 1729, 1691, 1624, 1459, 1424, 1352, 1259, 1190, 1145, 1069, 980, 920, 826, 748, 645, 554 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{11}H_{16}ClNO_3$: 245.0819. Found: 245.0819.

2-Chloro-3-oxocyclohex-1-enyl Dimethylcarbamate (3b): Yield 48% as a liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 2.91 (3H, s), 2.84 (3H, s), 2.63 (2H, t, J = 6.0 Hz), 2.43 (2H, t, J = 6.3 Hz), 1.98-1.88 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.4, 165.2, 150.9, 120.4, 36.9, 36.3, 36.3, 29.8, 20.0; IR (neat) 2943, 1728, 1626, 1402, 1275, 1149, 1009, 827, 747, 645 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_9H_{12}ClNO_3$: 217.0506. Found: 217.0504.

2-Chloro-5,5-dimethyl-3-oxocyclohex-1-enyl Dimethylcarbamate (3c): Yield 50% as a liquid: ^1H NMR (300 MHz, $CDCl_3$) δ 3.04 (3H, s), 2.96 (3H, s), 2.64 (2H, s), 2.42

(2H, s), 1.10 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7, 163.4, 129.1, 120.2, 51.1, 43.8, 43.7, 36.7, 36.6, 32.6, 27.9; IR (neat) 2959, 1736, 1691, 1630, 1463, 1396, 1347, 1290, 1208, 1158, 1032, 949, 825, 658, 599 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{11}H_{16}ClNO_3$: 245.0819. Found: 245.0816.

2-Chloro-5,5-dimethyl-3-oxocyclohex-1-enyl Diethylcarbamate (3d): Yield 73% as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.37-3.27 (4H, m), 2.63 (2H, s), 2.42 (2H, s), 1.23-1.13 (6H, m), 1.09 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7, 163.5, 150.8, 120.1, 51.0, 43.8, 42.4, 42.2, 32.5, 27.9, 14.0, 13.1; IR (neat) 2966, 1730, 1691, 1631, 1466, 1423, 1350, 1259, 1205, 1146, 1045, 947, 785, 652, 600 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{13}H_{20}ClNO_3$: 273.1132. Found: 273.1130.

2-Chloro-5-isopropyl-3-oxocyclohex-1-enyl Dimethylcarbamate (3e): Yield 45% as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.03 (3H, s), 2.96 (3H, s), 2.70-2.55 (4H, m), 2.32-2.22 (1H, m), 1.66-1.55 (1H, m), 0.90 (6H, d, J = 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1, 165.2, 151.4, 120.6, 41.2, 39.3, 36.7, 36.6, 34.0, 31.5, 19.4; IR (neat) 2938, 1734, 1626, 1493, 1393, 1278, 1145, 1033, 822, 755, cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{12}H_{18}ClNO_3$: 259.0975. Found: 259.0973.

2-Chloro-5-isopropyl-3-oxocyclohex-1-enyl Diethylcarbamate (3f): Yield 80% as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.38-3.28 (4H, m), 2.69-2.62 (3H, m), 2.31-2.21 (1H, m), 2.03-1.91 (1H, m), 1.66-1.55 (1H, m), 1.23-1.13 (6H, m), 0.90 (6H, d, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1, 165.2, 150.7, 120.6, 42.4, 42.3, 41.1 39.2, 34.1, 31.4, 19.4, 19.9, 13.9, 13.1; IR (neat) 2967, 2879, 1731, 1691, 1629, 1466, 1424, 1374, 1200, 1194, 1144, 1042, 959, 785, 648, 595 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{14}H_{22}ClNO_3$: 287.1288. Found: 287.1285.

2-Chloro-3-oxo-5-phenylcyclohex-1-enyl Dimethylcarbamate (3g): Yield 49% as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.23 (2H, m), 7.20-7.15 (3H, m), 3.45-3.34 (1H, m), 3.07-3.01 (1H, m), 2.99 (3H, s), 2.90 (3H, s), 2.85-2.82 (1H, m), 2.80-2.77 (1H, m), 2.73-2.67 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.8, 164.2, 151.2, 141.3, 128.8, 127.3, 126.5, 120.8, 44.1, 38.6, 37.7, 36.7, 36.6; IR (neat) 2958, 1734, 1705, 1630, 1393, 1280, 1147, 1038, 820, 748 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{15}H_{16}ClNO_3$: 293.0819. Found: 293.0817.

2-Chloro-3-oxo-5-phenylcyclohex-1-enyl Diethylcarbamate (3h): Yield 79% as a liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.17 (5H, m), 3.46-3.35 (1H, m), 3.33-3.24 (4H, m), 3.11-3.00 (2H, m), 2.92-2.73 (2H, m), 1.20-1.10 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.9, 164.3, 150.6, 141.4, 128.8, 127.3, 120.9, 44.2, 42.5, 42.3, 38.8, 37.8, 14.0, 13.1; IR (neat) 2976, 2933, 1730, 1601, 1626, 1456, 1424, 1374, 1258, 1191, 1143, 1011, 978, 922, 762, 701, 640, 556 cm^{-1}; HRMS *m/z* (M^+) calcd for $C_{17}H_{20}ClNO_3$: 321.1132. Found: 321.1129.

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