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A novel synthesis of tricyclo[5.1.0.0^{3,5}]octane-2,6-dione derivatives via double Michael addition-induced cyclopropanation reactions

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Abstract—Tricyclo[5.1.0.0^{3,5}]octane-2,6-diones **1a–q** were prepared in moderate yields by the reaction of α,β-unsaturated esters **2** with dihalomethane in the presence of butyllithium, and by the reaction of dichloromethyl α,β-unsaturated ketones **3** with sodium ethoxide, respectively. This reaction was newly explained by a mechanism involving intermolecular double Michael additions of enolate anion **4** of ketones **3** and the following cyclopropanation.

1. Introduction

Michael addition is an important reaction in organic synthesis for making carbon–carbon bonds. Recently, a number of tandem reactions via Michael addition, which are useful for the construction of carbon skeletons, have been reported.[1] It is well known that Michael addition of nucleophiles to α,β-unsaturated esters and the following cyclopropanation affords cyclopropanecarboxylic esters. Michael addition of 2-methylpropenyl magnesiumbromide to α-chloroisobutylidenemalonate gave chrysanthemic acid derivate.[2] The reaction of 1,1-dipolar species with Michael acceptors can result in three-membered ring compounds. Corey et al. reported the synthesis of methyl chrysanthemate by the reaction of sulfonium ylide with methyl 2,4-hexadienoate.[3] Michael additions of phosphonium ylides or α-lithiosulfones to α,β-unsaturated esters give cyclopropanecarboxlyates.[4,5] Dimerizative cyclopropanation of methyl α-bromoacrylate by the action of nucleophiles has been reported.[6]

Tricyclo[5.1.0.0^{3,5}]octane-2,6-dione is a unique and sterically strained compound. Its synthesis via some steps is reported in the following papers. Heller et al.[7] reported the first preparation of *anti*-bishomoquinone (tricyclo-[5.1.0.0^{3,5}]octane-2,6-dione) by bromination of cyclooctane-1,5-dione and the following dehydrobromination reaction, as shown in Fig. 1.

Buchanan et al.[8] reported a convenient stereoselective synthesis of *syn*-bishomoquinone (*syn*-tricyclo[5.1.0.0^{3,5}]-octane-2,6-dione), as shown in Fig. 2.

Christopher et al.[9] reported the synthesis of tetramethylbishomoquinones with *anti*-configuration by the double additions of dichlorocarbene and dibromocarbene to tetramethylquinone, as shown in Fig. 3.

The synthesis of 1,5-dihalotricyclo[5.1.0.0^{3,5}]octane-2,6-dione **1** via intermolecular double Michael additions between the same molecules has never been reported, to the best of our knowledge. In this paper we report a novel synthesis of tricyclo[5.1.0.0.^{3,5}]octane-2,6-dione derivatives via intermolecular double Michael addition-induced cyclopropanation reactions from 1,1-dichloro-3-alken-2-ones **3** and α,β-unsaturated esters **2**.[10–12] The intermediate of the formation of **1** is also our concern.

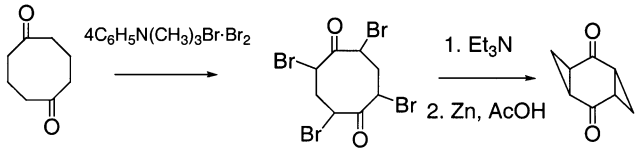

Figure 1.

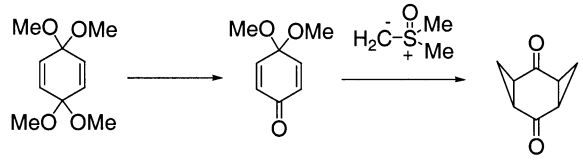

Figure 2.

Keywords: tricyclo[5.1.0.0^{3,5}]octane-2,6-dione; cyclopropanation; tandem reaction; Michael addition.

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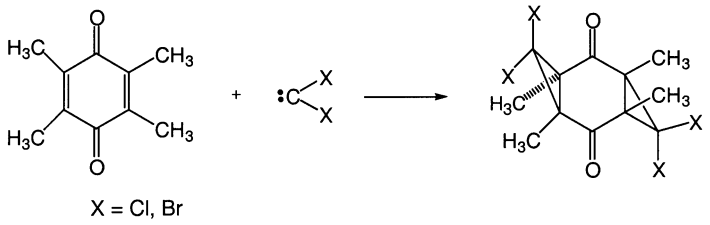


Figure 3.

2. Results and discussion

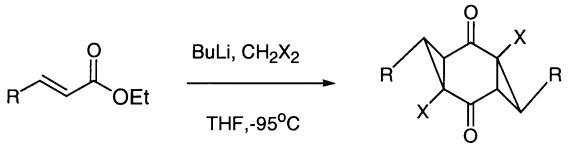
Various α,β-unsaturated esters **2** were treated with one equivalent of lithiodihalomethane ($BuLi+CH_2X_2$) in anhydrous THF at −95°C (10 min) under an atmosphere of nitrogen, and then the reaction mixture was quenched with water to give **1** as white crystals in moderate yields. The yields and physical properties of **1** are tabulated in Table 1. The yields of alkyl substituted **1** are lower than those of aryl substituted **1**. Due to the stereo-hindered effect of halogen atom, the yields of bromo-substituted **1** are lower than those of the chloro-substituted one.

Characteristic signals of the IR and NMR data were identical with those of the samples, and the stereochemistry was absolutely verified by X-ray crystallographic analysis.[13–15] Because of the deshielding effect of the aryl groups, the chemical shifts of the tricyclo-ring-proton of aryl-substituted **1** are located in lower field than those of alkyl-substituted **1**.

In a similar way, compounds **1** were also obtained by the treatment of 1,1-dichloro-3-alken-2-ones **3** with 1 equiv. of sodium ethoxide in dry diethyl ether at low temperature (−78 to −60°C for ca. 10 h, and 0°C for a few days) under an atmosphere of nitrogen and the following quenching with cold water. The reaction afforded **1** in 50–70% yields as white crystals.[15] Yields of **1** are tabulated in Table 2. In these reactions, other stereoisomers of **1** were not detected. Formation of other stereoisomers seems to be difficult due to steric hindrance. Although the reaction mixture was purified and analyzed carefully, any other compounds were not isolated except decomposed resinous materials. Compound **3** was prepared by the reaction of α,β-unsaturated aldehydes with dichloromethane in the presence of butyllithium and the following oxidation with manganese dioxide.[16] The formation of tricyclo[5.1.0.$0^{3,5}$]-octane-2,6-dione **1** from two starting materials **2** and **3** is shown in Scheme 1.

The formation of compound **1** is a process via the enolate **4** from **3**, which is also introduced from the reaction between α,β-unsaturated esters **2** with 1 equiv. of lithiodihalomethane, as shown in Scheme 3. On the other hand, Normant et al.[17] reported that the reaction of α,β-unsaturated esters with dichloromethane in the presence of butyllithium gave 1,1-dichloro-3-alken-2-one **3** predominantly without the formation of tricyclo[5.1.0.$0^{3,5}$]octane-2,6-dione **1**. We clarified this discrepancy by the following experiment. When the reaction mixture was quenched

Table 1. Preparation of **1a–q** by the reaction of various α,β-unsaturated esters with dichloromethane in the presence of butyllithium

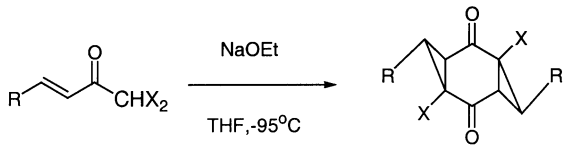


2 **1**

	R	X	Yields (%)	Mp (°C)	IR (cm^{-1})	NMR (δ, $CDCl_3$, ring H)
1a	CH_3	Cl	41	228[a]	1685	2.00, 2.21
1b	C_2H_5	Cl	41	145	1705	1.85, 2.25
1c	*n*-C_3H_7	Cl	33	109	1702	1.84, 2.24
1d	*n*-C_4H_9	Cl	31	105	1690	1.92, 2.24
1e	*n*-C_5H_{11}	Cl	32	101	1690	1.86, 2.32
1f	$(CH_3)_2CHCH_2$	Cl	32	220[a]	1700	1.87, 2.23
1g	$(CH_3)_2CH$	Cl	19	128	1700	1.60, 2.26
1h	C_6H_5	Cl	63	224[a]	1700	3.28, 3.89
1i	*p*-Cl–C_6H_4	Cl	67	225[a]	1695	3.48, 4.04[b]
1j	*p*-CH_3–C_6H_4	Cl	42	192[a]	1705	3.05, 3.29
1k	*o*-Cl–C_6H_4	Cl	24	274	1695	3.60, 3.94[b]
1l	CH_3	Br	13	192	1675	1.76, 2.28
1m	C_2H_5	Br	10.4	163	1700	1.91, 2.32
1n	*n*-C_3H_7	Br	5.3	113[a]	1685	1.91, 2.32
1o	C_6H_5	Br	60.5	224[a]	1695	3.14, 3.20
1p	*p*-Cl–C_6H_4	Br	36	183[a]	1680	3.08, 3.15
1q	*p*-CH_3–C_6H_4	Br	19	215[a]	1700	3.10, 3.16

[a] Decomposition temperature.
[b] DMSO-d_6 solvent.

Table 2. Preparation of **1** by the reaction of (*E*)-1,1-dichloro-3-alken-2-one **3** with NaOEt in THF



3 **1**

3a: R = CH_3, X = Cl

3c: R = *n*-C_3H_7, X = Cl

3r: R = CH_3CH=CH, X = Cl;

3s: R = *n*-C_6H_{13}, X = Cl

3h: R = C_6H_5, X = Cl

3t: R =  , X = Cl

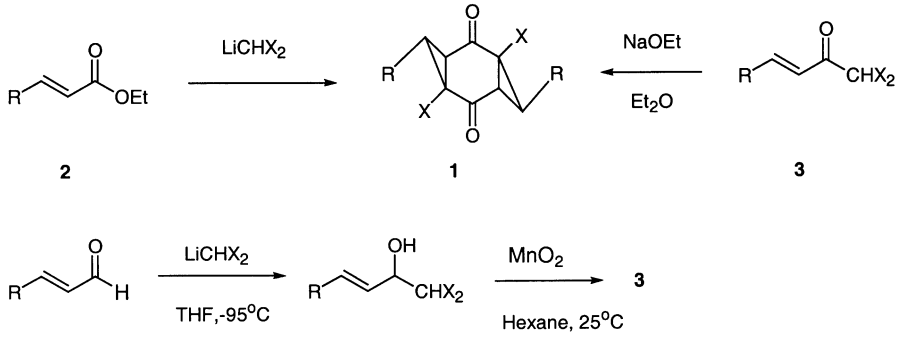
	R	X	Yield (%)
1a	CH_3	Cl	52.9
1c	*n*-C_3H_7	Cl	56.9
1r	CH_3CH=CH	Cl	48
1s	*n*-C_6H_{13}	Cl	53.4
1h	C_6H_5	Cl	70.0
1t		Cl	71.0

with water, tricyclo[5.1.0.0^{3,5}]octane-2,6-dione **1** was formed, as described above. However, the reaction of ethyl cinnamate and dichloromethane in the presence of LDA in THF at −95°C and the following quenching with 2 M HCl afforded (*E*)-1,1-dichloro-4-phenyl-3-buten-2-one (**3h**) in 41% yield, which was then treated with LiOH water solution in THF at −95°C for 10 min to give **1h** in 94% yield. These results are summarized in Scheme 2.

Namely, when an acid was added to the reaction mixture for quenching the reaction, the reaction gave **3** as a major product. However, the quenching by addition of water and the subsequent stirring of the mixture with gradually warming up to room temperature for 10–30 min afforded tricyclo-[5.1.0.0^{3,5}]octane-2,6-dione **1** as a main product. After the addition of water, the reaction proceeds under alkaline condition, giving **1** via Michael addition of enolate **4** and the cyclopropanation as shown in Scheme 3.

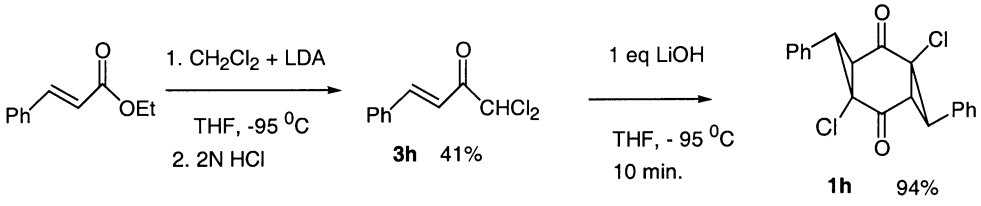
There are two possible mechanisms of the formation of tricyclo[5.1.0.0^{3,5}]octane-2,6-dione **1**. One is through the intermediate, anion **4**, and the other is through the intermediate, carbene **4′** as shown in Scheme 3. Concerning with the mechanism via **4**, two pathways (path a and path b) can be supposed. In order to determine which intermediate is more reasonable for the formation of tricyclo[5.1.0.0^{3,5}]octane-2,6-dione **1**, the calculation (AM1)[18] of the heat formation of both intermediate states **4** and **4′** was carried out and the result is illustrated in Table 3. This result shows carbene intermediate **4′** state is at a higher energy level than that of **4**. Furthermore, the carbene mechanism was rejected by a chemical reaction. When the reaction of formation of **1** was carried out in the presence of cyclohexene, no cycloaddition products of **4′** to carbon–carbon double bonds were detected. The possible intermediate state should be **4**.

When the formation of **1** as a by-product in the reaction of α,α-dichloroacetoacetate with aldehydes in the presence of alkoxides was reported in the previous paper,[13] the formation of **4** and the following double Michael addition mechanism was also postulated. In the course of this research, Mamedov et al.[19,20] reported the formation of **1** in a low yield by the reaction of some benzaldehydes with α,α-dichloroacetone or 3,3-dichloro-2,4-pentanedione. In these cases, formation of **1** can be explained by the

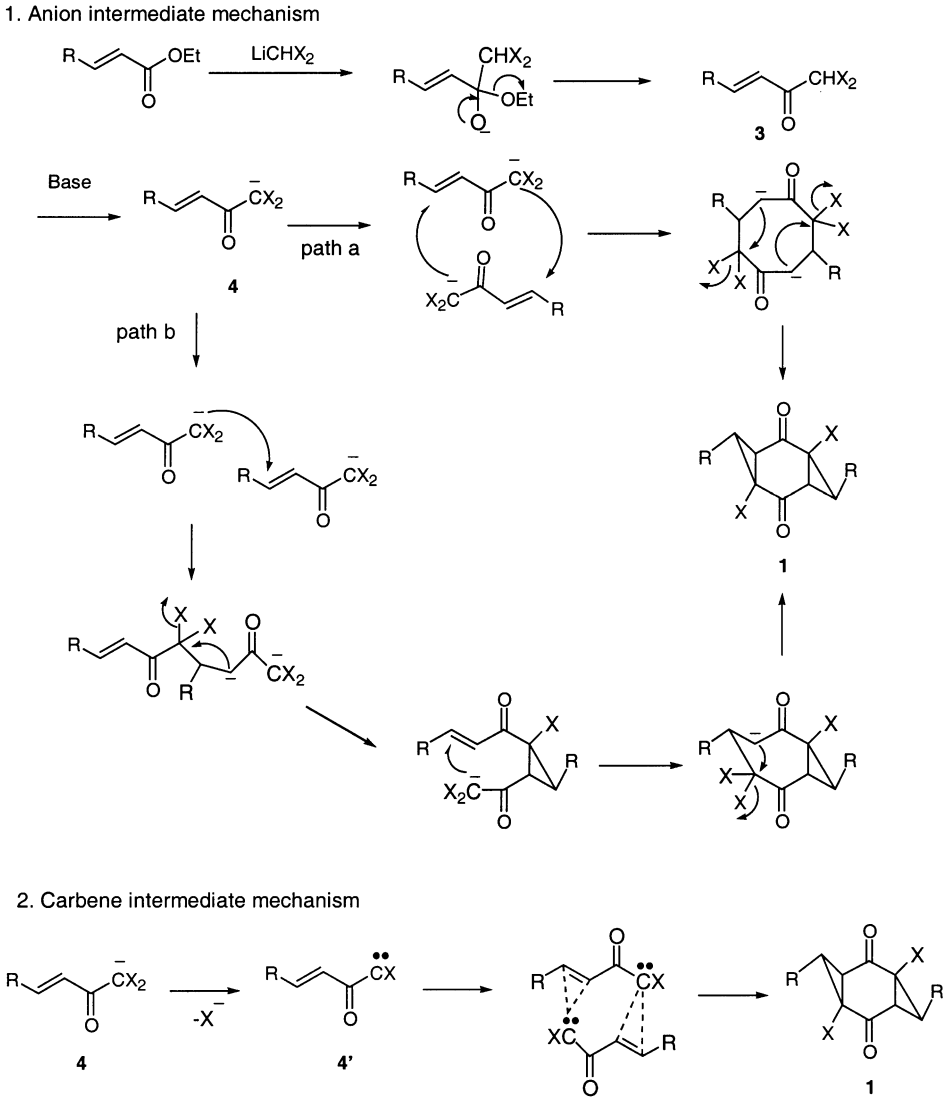


2 **1** **3**

Scheme 1. Syntheses of tricyclo[5.1.0.0^{3,5}]octane-2,6-dione **1**.



Scheme 2. Preparation of **1h** by the treatment of **3h** with LiOH.



Scheme 3. Reaction mechanism of formation of tricyclo[5.1.0.0^{3,5}]octane-2,6-dione.

Table 3. Calculations of ΔH_f with AM1 for **4** and **4′**

	R	X	**4** ΔH_f () (kcal/mol)	**4′** ΔH_f () (kcal/mol)
4a	CH_3	Cl	−45.30	−3.53
4b	C_2H_5	Cl	−48.32	−9.09
4c	n-C_3H_7	Cl	−55.85	−13.86
4d	Ph	Cl	−10.27	34.27

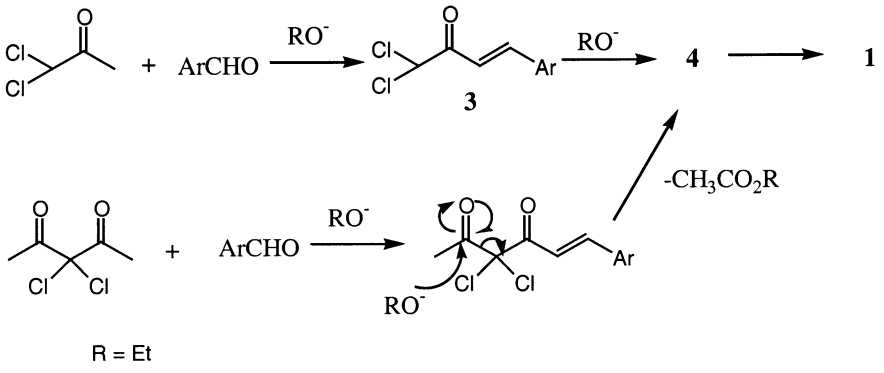
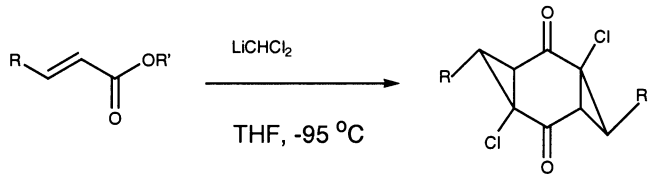


Figure 4.

Table 4. Preparation of **1a** and **1h** by the reaction of various α,β-unsaturated esters **5a–o** with $LiCHCl_2$



5a – o **1a**: R = CH_3, **1h**: R = Ph

S.T.	R	R′	**1a** Yield (%)	S.T.	R	R′	**1h** Yield (%)
5a	CH_3	C_2H_5	49	**5i**	Ph	CH_3	63
5b	CH_3	*n*-C_3H_7	49	**5j**	Ph	C_2H_5	71
5c	CH_3	n-C_4H_9	50	**5k**	Ph	*n*-C_3H_7	65
5d	CH_3	$CH(CH_3)_2$	28	**5l**	Ph	*n*-C_4H_9	72
5e	CH_3	$CH_2CH(CH_3)_2$	45	**5m**	Ph	$CH(CH_3)_2$	45
5f	CH_3	$CH(CH_3)CH_2CH_3$	23	**5n**	Ph	$CH_2CH(CH_3)_2$	43
5g	CH_3	$C(CH_3)_3$	8	**5o**	Ph	$CH(CH_3)CH_2CH_3$	36

mechanism via the aldol product **3** and the intermediate **4**, as shown in Fig. 4.

To investigate the best leaving group in various esters for synthesis of tricyclo[5.1.0.0^{3,5}]octane-2,6-dione compounds (**1a** and **1h**), various α,β-unsaturated esters **5a–o** were used to prepare **1a** and **1h**. The results are shown in Table 4. The best leaving group is the *n*-butyl group.

3. Experimental

3.1. General techniques

All reactions were carried out under a nitrogen atmosphere with dry, freshly distilled solvents under anhydrous conditions, unless otherwise noted. Tetrahydrofuran (THF), toluene, and diethyl ether were distilled from sodium benzophenone; methylene chloride (CH_2Cl_2) was freshly distilled from calcium hydride.

Reagents of the highest commercial quality were purchased and used without further purification, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as a visualizing agent and 5% ethanolic phosphomolybdic acid or *p*-anisaldehyde solution, and heat as developing agents. E. Merck silica gel (60, particle size 0.040–0.050 mm) was used for flash column chromatography.

NMR spectra were recorded on Varian Gemini 200 or Varian Gemini 500 instruments and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s=singlet, d=doublet, t=triplet, q=quartet, sept=septet, m=multiplet, b=broad, bs=broad singlet. IR spectra were recorded on a JASCO model FT-IR 5000 spectrometer. The melting points and boiling points are uncorrected. Mass spectra were measured on a Shimadzu model GC-MS QP 5000 at 70 eV. Elementary analysis was carried out on a PERKIN ELMER 2400 Series II CHNS/O Analyzer. Calculations of ΔH_f with AM1 was carried out on SPARTAN M/P Plus.

3.2. Preparation of starting materials

All α,β-unsaturated esters were synthesized by Horner–Emmons–Wardsworth reaction.[10,11]

3.3. General procedure for the preparation of tricyclo-[5.1.0.0^{3,5}]octane-2,6-diones 1

Method (a). To a solution of *n*-BuLi (1.61 M in hexane) in THF was added slowly dichloromethane at −95°C. The mixture was stirred for 30 min at the same temperature. Then α,β-unsaturated ester (1 equiv.) was added to the flask. The solution was stirred for 10 min, and then 10 mL of water was added to the flask. The cooling bath was removed. After the reaction mixture was warmed up to room temperature, 10% hydrochloric acid solution was added to acidify the solution. After the solvent was removed in vacuo, the precipitate was filtered and washed with diethyl ether to give tricyclo[5.1.0.0^{3,5}]octane-2,6-diones.

Method (b). To a solution of *n*-BuLi (1.61 M in hexane) in THF was added slowly dichloromethane at −95°C. The mixture was stirred for 30 min at the same temperature. Then α,β-unsaturated ester (1 equiv.) was added to the flask. The solution was stirred for 10 min, and then 10 mL of water was added to the flask. After the cooling bath was removed, the reaction mixture was allowed to warm up to room temperature, and then 10% hydrochloric acid solution was added to acidify the solution. The precipitate was filtered and was washed with ethyl acetate to give tricyclo[5.1.0.0^{3,5}]octane-2,6-diones.

3.3.1. 1,5-Dichloro-4,8-dimethyltricyclo[5.1.0.0^{3,5}]octane-2,6-dione (1a). Method (a) was used. *n*-BuLi (12.4 mL of 1.6 M in hexane, 20 mmol), THF (50 mL), CH_2Cl_2 (2.13 g, 25 mmol), and ethyl crotonate (3.24 g, 28 mmol) were employed to give **1a**: 0.944 g (41%) as a white solid: mp 228°C (decomposition); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.46 (d, *J*=6.0 Hz, 6H), 2.00 (dq, *J*=6.0, 6.3 Hz, 2H), 2.21 (d, *J*=6.3 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.4, 27.7, 40.6, 50.4, 192.8; IR (KBr): 3385, 3018, 2950, 2910, 2825, 1685, 1565 cm^{-1}. Anal. Calcd for $C_{10}H_{10}O_2Cl_2$: C, 51.53; H, 4.34. Found: C, 51.50; H, 4.17.

3.3.2. 1,5-Dichloro-4,8-diethyltricyclo[5.1.0.0^{3,5}]octane-2,6-dione (1b). Method (a) was used. *n*-BuLi (12.4 mL of 1.6 M in hexane, 20 mmol), THF (50 mL), CH_2Cl_2 (2.08 g, 23 mmol), and ethyl (2*E*)-pentenoate (2.42 g, 18.9 mmol) were employed to give **1b**: 1.01 g (41%) as a white solid: mp 145.5–146.5°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.10 (t, *J*=6.6 Hz, 6H), 1.62–1.91 (m, 6H), 2.25 (d, *J*=5.6 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.54, 22.38, 33.96, 39.76, 50.24, 192.7 27; IR (KBr): 3032, 2974, 2934, 2878, 1705, 1462, 1388, 1334, 1294, 1247, 1149, 1096, 1036, 784 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_2Cl_2$: C, 55.19; H, 5.40. Found: C, 55.33; H, 5.52; GC-MS 260 (M^+), 225, 197, 155, 115, 105, 91, 65(100).

3.3.3. 1,5-Dichloro-4,8-dipropyltricyclo[5.1.0.0^{3,5}]octane-2,6-dione (1c). Method (a) was used. *n*-BuLi (12.1 mL of 1.6 M in hexane, 19.3 mmol), THF (50 mL), CH_2Cl_2 (2.09 g, 24 mmol) and ethyl (2*E*)-hexenoate (2.87 g, 20 mmol) were employed to give **1c**: 0.91 g (33%) as a white solid: mp 108–109°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.96 (t, *J*=7.2 Hz, 6H), 1.15–1.60 (m, 4H), 1.67–1.77 (m, 4H), 1.84 (dt, *J*=6.2, 6.0 Hz, 2H), 2.23 (d, *J*=6.2 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.53, 21.50, 30.55, 32.53, 39.80, 50.19, 192.6; IR (KBr): 3060, 2974, 2964, 1702, 1294, 1145, 874, 681 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_2Cl_2$: C, 58.14; H, 6.27. Found: C, 57.92; H, 6.02.

3.3.4. 1,5-Dichloro-4,8-dibutyltricyclo[5.1.0.0^{3,5}]octane-2,6-dione (1d). Method (a) was used. *n*-BuLi (5 mL of 1.6 M in hexane, 7.2 mmol), THF (15 mL), CH_2Cl_2 (0.75 g, 8.9 mmol), and ethyl (2*E*)-heptenoate (1.15 g, 7.0 mmol) were employed to give **1d**: 0.338 g (31%) as a white solid: mp 105°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.91 (t, *J*=7.2 Hz, 6H), 1.30–1.53 (m, 8H), 1.68–1.90 (m, 6H), 2.22 (d, *J*=6.0 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.84, 21.18, 22.18, 28.41, 30.92, 32.74, 39.86, 50.27, 192.7; IR (KBr): 3360, 3025, 2962, 2825, 1700, 1466, 1299, 1280, 1145, 874 cm^{-1}. Anal. Calcd for $C_{16}H_{22}O_2Cl_2$: C, 60.53; H, 6.99. Found: C, 60.74; H, 7.12.

3.3.5. 1,5-Dichloro-4,8-dipentyltricyclo[5.1.0.0^{3,5}]octane-2,6-dione (1e). Method (a) was used. *n*-BuLi (7.10 mL of 1.6 M in hexane, 11 mmol), THF (20 mL), CH_2Cl_2 (1.02 g, 12 mmol), and ethyl (2*E*)-octenoate (1.70 g, 10 mmol) were employed to give **1e**: 0.545 g (32%) as a white solid: mp 101°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, *J*=5.8 Hz, 6H), 1.36–1.86 (m, 18H), 2.23 (d, *J*=6.16 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 13.89, 22.36, 27.83, 28.67, 31.18, 32.71, 39.79, 50.22, 192.7. Anal. Calcd for $C_{18}H_{26}O_2Cl_2$: C, 62.96; H, 7.63. Found: C, 61.19; H, 7.82.

3.3.6. 1,5-Dichloro-4,8-diisobutyltricyclo[5.1.0.0^{3,5}]octane-2,6-dione (1f). Method (a) was used. *n*-BuLi (2.5 mL of 1.6 M in hexane, 4.0 mmol), THF (10 mL), CH_2Cl_2 (0.418 g, 4.9 mmol), and ethyl (*E*)-5-methyl-2-hexenoate (0.703 g, 4.5 mmol) were employed to give **1f**: 0.20 g (32%) as a white solid: mp 220°C (decomposition); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97 (dd, *J*=7.0, 7.0 Hz, 12H), 1.58 (m, 4H), 1.82 (m, 2H), 1.87 (m, 2H), 2.23 (d, *J*=6.5 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.16, 22.32, 27.91, 31.57, 37.17, 39.90, 50.13, 192.58; IR (KBr): 3038, 2958, 2930, 1700, 1294, 1102, 876, 586. Anal. Calcd for $C_{16}H_{22}O_2Cl_2$: C, 60.57; H, 6.99. Found: C, 60.19; H, 7.23.

3.3.7. 1,5-Dichloro-4,8-dipropyltricyclo[5.1.0.0^{3,5}]octane-2,6-dione (1g). Method (a) was used. *n*-BuLi (1.24 mL of 1.6 M in hexane, 2.0 mmol), THF (5 mL), CH_2Cl_2 (0.213 g, 2.5 mmol), and ethyl (*E*)-4-methyl-2-pentenoate (0.342 g, 3.0 mmol) were employed to give **1g**: 0.055 g (19%) as a white solid: mp 128°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.09 (d, *J*=6.36 Hz, 6H), 1.17 (d, *J*=6.36 Hz, 6H), 1.58–1.60 (m, 2H), 1.71–1.74 (m, 2H), 2.26 (d, *J*=6.22 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.12, 21.48, 30.00, 39.27, 39.52, 50.35, 192.2; IR (KBr): 3380, 2950, 2850, 1700, 1460 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_2Cl_2$: C, 58.14; H, 6.27. Found: C, 57.92; H, 6.02.

3.3.8. 1,5-Dichloro-4,8-diphenyltricyclo[5.1.0.0^{3,5}]octane-2,6-dione (1h). Method (b) was used. *n*-BuLi (1.21 mL of 1.6 M in hexane, 2.0 mmol), THF (5 mL), CH_2Cl_2 (0.213 g, 2.5 mmol), and ethyl (*E*)-cinnamate (0.441 g, 2.5 mmol) were employed to give **1h**: 0.226 g (63%) as a white solid: mp 224°C (decomposition); ^{1}H NMR (200 MHz, DMSO): δ 3.44 (d, *J*=7.2 Hz, 2H), 3.99 (d, *J*=7.2 Hz, 2H), 7.40 (m, 10H); ^{13}C NMR (50 MHz, DMSO): δ 35.33, 37.81, 51.37, 128.39, 128.51, 129.39, 131.57, 191.99; IR (KBr): 3400, 3050, 3000, 1695, 1595, 1445 cm^{-1}. Anal. Calcd for $C_{20}H_{14}O_2Cl_2$: C, 60.32; H, 3.95. Found: C, 60.29; H, 3.88.

3.3.9. 1,5-Dichloro-4,8-di(*p*-chlorophenyl)tricyclo-[5.1.0.0^{3,5}]octane-2,6-dione (1i). Method (b) was used. *n*-BuLi (6.25 mL of 1.6 M in hexane, 10 mmol), THF (25 mL), CH_2Cl_2 (0.958 g, 11.4 mmol), and ethyl (*E*)-*p*-chlorocinnamate in 4 mL of THF (2.42 g, 11 mmol) were employed to give **1i**: 1.420 g (67%) as a white solid: mp 225°C (decomposition); ^{1}H NMR (200 MHz, DMSO-D_6) δ 3.48 (d, *J*=7.4 Hz, 2H), 4.04 (d, *J*=7.2 Hz, 2H), 7.45 (m, 8H); ^{13}C NMR (50 MHz, DMSO-D_6): δ 34.70, 37.79, 51.26, 128.53, 130.75, 131.31, 133.20, 191.66; IR (neat): 3350, 3040, 3000, 1695, 1590, 1485 cm^{-1}. Anal. Calcd for $C_{20}H_{12}O_2Cl_4$: C, 56.37; H, 2.84. Found: C, 56.46; H, 2.85.

3.3.10. 1,5-Dichloro-4,8-di(*p*-methylphenyl)tricyclo-[5.1.0.0^{3,5}]octane-2,6-dione (1j). Method (b) was used. *n*-BuLi (4.5 mL of 1.6 M in hexane, 7.2 mmol), THF (15 mL), CH_2Cl_2 (0.685 g, 8.1 mmol), and ethyl (*E*)-*p*-methylcinnamate (1.33 g, 7.0 mmol) were employed to give **1j**: 0.565 g (42%) of the product as a white solid: mp 192°C (decomposition); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.37 (s, 6H), 3.05 (d, *J*=6.8 Hz, 2H), 3.28 (d, *J*=6.9 Hz, 2H), 7.15–7.26 (m, 8H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.19, 36.05, 38.51, 50.41, 127.01, 129.10, 129.42, 138.82, 191.62; IR (KBr): 3400, 3052, 1709, 1515, 1445, 1243, 1098, 812, 517 cm^{-1}. Anal. Calcd for $C_{22}H_{18}O_2Cl_2$: C, 68.58; H, 4.71. Found: C, 68.52; H, 4.94.

3.3.11. 1,5-Dichloro-4,8-di(*o*-chlorophenyl)tricyclo-[5.1.0.0^{3,5}]octane-2,6-dione (1k). Method (b) was used. *n*-BuLi (9.3 mL of 1.6 M in hexane, 14.8 mmol), THF (25 mL), CH_2Cl_2 (1.31 g, 15.6 mmol), and ethyl (*E*)-*o*-chlorocinnamate (2.908 g, 13.8 mmol) were employed to give **1k**: 0.716 g (24.4%) as a solid: mp 247°C; ^{1}H NMR (500 MHz, DMSO-D_6) δ 3.60 (d, *J*=7.0 Hz, 2H), 3.94 (d, *J*=7.5 Hz, 2H), 7.38–7.44 (m, 4H), 7.51 (dd, *J*=1.5, 6.5 Hz, 2H), 7.55 (dd, *J*=2.0, 7.5 Hz, 2H); ^{13}C NMR (50 MHz, DMSO-D_6): δ 34.72, 37.43, 50.59, 127.50, 129.49,

130.29, 130.80, 132.04, 135.21 191.28; IR (KBr): 3400, 3050, 1695, 1595, 1445 cm^{-1}. Anal. Calcd for $C_{20}H_{12}O_2Cl_4$: C, 56.32; H, 2.84. Found: C, 56.43; H, 2.91.

3.3.12. 1,5-Dibromo-4,8-dimethyltricyclo[5.1.0.0^{3,5}]octane-2,6-dione (1l). To a solution of diisopropylamine (0.094 g, 0.93 mmol) in 3 mL of THF was added *n*-BuLi (0.67 mL of 1.61 M in hexane, 1 mmol) at 0°C. The solution was stirred at this temperature for 20 min. Then to the solution was added slowly 0.261 g (1.5 mmol) of dibromomethane at −95°C. The mixture was stirred for 30 min at this temperature. Then 0.114 g (1.0 mmol) of ethyl crotonate was added to the flask. The solution was stirred for 15 min at −95°C, and then 10 mL of water was added to the flask. The cooling bath was removed. After the reaction mixture was allowed to warm up to room temperature, 10% HCl solution was added to acidify the solution. The solvent was concentrated in vacuo. The solid was washed with diethyl ether to give the 0.02 g (13%) of **1l**: mp=192°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.49 (d, J=6.1 Hz, 6H), 1.76–3.20 (m, 2H), 2.28 (d, J=6.3 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.74, 27.39, 40.51, 41.06, 192.7; IR (KBr): 1675, 1420, 1370, 1270, 1121, 995 cm^{-1}. Anal. Calcd for $C_{10}H_{10}O_2Br_2$: C, 37.30; H, 3.13. Found: C, 37.11; H, 3.33.

3.3.13. 1,5-Dibromo-4,8-diethyltricyclo[5.1.0.0^{3,5}]octane-2,6-dione (1m). To a solution of diisopropylamine (0.094 g, 0.93 mmol) in 3 mL of THF was added *n*-BuLi (0.67 mL of 1.6 M in hexane, 1 mmol) at 0°C. The solution was stirred at this temperature for 20 min. Then to the solution was added slowly 0.261 g (1.5 mmol) of dibromomethane at −95°C. The mixture was stirred for 20 min at this temperature. Then 0.128 g (1.0 mmol) of ethyl *E*-2-pentenoate was added to the flask. The solution was stirred for 15 min. 5 mL of water was added to the reaction bottle. The cooling bath was removed. After the reaction mixture was allowed to warm up to room temperature, 10% HCl solution was added to acidify the solution. The solvent was removed in vacuo. The solid was washed with diethyl ether to give 0.017 g (10.4%)of **1m** as a solid: mp=163°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.11 (t, J=7.1 Hz, 6H), 1.58–1.91 (m, 6H), 2.32 (d, J=6.1 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 12.53, 24.63, 33.66, 39.70, 40.60, 192; IR (KBr): 1700, 1420, 1370, 1280, 1130, 1010, 870 cm^{-1}. Anal. Calcd for $C_{12}H_{14}O_2Br_2$: C, 41.17; H, 4.03. Found: C, 41.03; H, 4.27.

3.3.14. 1,5-Dibromo-4,8-dipropyltricyclo[5.1.0.0^{3,5}]octane-2,6-dione (1n). To a solution of diisopropylamine (0.094 g, 0.93 mmol) in 3 mL of THF was added *n*-BuLi (0.67 mL of 1.6 M in hexane, 1 mmol) at 0°C. The solution was stirred at the same temperature for 20 min. Then to the solution was added slowly 0.261 g (1.5 mmol) of dibromomethane at −95°C. The mixture was stirred for 20 min at the same temperature. Then 0.142 g (1.0 mmol) of ethyl (2*E*)-hexenoate was added to the flask. The solution was stirred for 15 min, and then 5 mL of water was added to the flask. The cooling bath was removed. After the mixture was warmed up to room temperature, 10% HCl solution was added to acidify the solution. The solvent was removed in vacuo. The solid was washed with diethyl ether to give 0.01 g (5.3%) of **1n** as a solid: mp=113°C (decomposition); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.98 (t, J=7.1 Hz, 6H), 1.58–1.91 (m, 10H), 2.32 (d, J=6.1 Hz, 2H); IR (KBr): 1685, 1420, 1370, 1280, 1130, 1010, 870 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_2Br_2$: C, 44.47; H, 4.80. Found: C, 44.66; H, 4.96.

3.3.15. 1,5-Dibromo-4,8-diphenyltricyclo[5.1.0.0^{3,5}]octane-2,6-dione (1o). To a solution of HMDS (0.775 g, 5.0 mmol) in 5 mL of THF was added *n*-BuLi (2.71 mL of 1.62 M in hexane, 4.4 mmol) at 0°C. The solution was stirred at the same temperature for 20 min. Then to the solution was added slowly 0.765 g (4.4 mmol) of dibromomethane at −95°C. The mixture was stirred for 20 min at the same temperature. Then 0.352 g (2.0 mmol) of ethyl (*E*)-cinnamate was added to the flask. The solution was stirred for 15 min. 5 mL of water was added to the flask. The cooling bath was removed. After the mixture was allowed to warm up to room temperature, 10% HCl solution was added to acidify the solution. The solvent was removed in vacuo. The solid was washed with diethyl ether to give 0.27 g (60.8%) of **1o** as a solid: mp=224°C (decomposition); ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.14 (d, J=7.1 Hz, 2H), 3.20 (d, J=7.0 Hz, 2H), 7.26–7.42 (m, 10H); IR (KBr): 3400, 3050, 3000, 1695, 1595, 1445 cm^{-1}. Anal. Calcd for $C_{20}H_{14}O_2Br_2$: C, 53.84; H, 3.16. Found: C, 53.77; H, 3.27.

3.3.16. 1,5-Dibromo-4,8-di(*p*-chlorophenyl)tricyclo-[5.1.0.0^{3,5}]octane-2,6-dione (1p). To a solution of diisopropylamine (0.094 g, 0.93 mmol) in 3 mL of THF was added *n*-BuLi (0.67 mL of 1.6 M in hexane, 1 mmol) at 0°C. The solution was stirred at this temperature for 20 min. Then to the solution was added slowly 0.261 g (1.5 mmol) of dibromomethane at −95°C. The mixture was stirred for 20 min at the same temperature. Then 0.210 g (1.0 mmol) of ethyl (*E*)-4-chloro cinnamate was added to the flask. The solution was stirred for 15 min, and then 5 mL of water was added to the flask. The cooling bath was removed. After the mixture was warmed up to room temperature, 10% hydrochloric acid solution was added to acidify the solution. The solvent was removed in vacuo. The solid was washed with diethyl ether to give 0.092 g (35.7%) of **1p** as a solid: mp=183°C (decomposition); ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.08(d, J=6.7 Hz, 2H), 3.15 (d, J=6.7 Hz, 2H), 7.21–7.41 (m, 8H); IR (KBr): 3050, 2950, 1680, 1480, 1470, 1300, 1270, 1240, 1200 cm^{-1}. Anal. Calcd for $C_{20}H_{12}O_2Br_2Cl_2$: C, 46.63; H, 2.34. Found: C, 44.87; H, 2.50.

3.3.17. 1,5-Dibromo-4,8-di(*p*-methylphenyl)tricyclo-[5.1.0.0^{3,5}]octane-2,6-dione (1q). To a solution of diisopropylamine (0.094 g, 0.93 mmol) in 3 mL of THF was added *n*-BuLi (0.67 mL of 1.6 M in hexane, 1 mmol) at 0°C. The solution was stirred at the same temperature for 20 min. Then to the solution was added slowly 0.261 g (1.5 mmol) of dibromomethane at −95°C. The mixture was stirred for 20 min at this temperature. Then 0.190 g (1.0 mmol) of ethyl (*E*)-4-methylcinnamate was added to the flask. The solution was stirred for 15 min and then 5 mL of water was added to the flask. The cooling bath was removed. After the mixture was allowed to warm up to room temperature, 10% hydrochloric acid solution was added to acidify the solution. The solvent was removed in vacuo. The solid was washed with diethyl ether to give 0.042 g (19%) of **1q** as a solid: mp=215°C (decomposition)

^{1}H NMR (200 MHz, $CDCl_3$) δ 2.35 (s, 6H), 3.10 (d, J=6.7 Hz, 2H), 3.16 (d, J=6.7 Hz, 2H), 7.14–7.24 (m, 8H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.22, 35.70, 38.21, 40.93, 128.3, 129.0, 129.6, 138.8, 191.6; IR (KBr) 3000, 1700, 1510, 1280, 1255, 1220, 1150, 1120, 1100 cm^{-1}. Anal. Calcd for $C_{22}H_{18}O_2Br_2$: C, 55.72; H, 3.28. Found: C, 55.66; H, 3.79.

3.3.18. Preparation of 1,5-dichloro-4,8-dimethyltricyclo[5.1.0.0^{3,5}]octane-2,6-dione (1a) with (3*E*)-1,1-dichloropenten-2-one. To a solution of 0.446 g (3 mmol) of (3*E*)-1,1-dichloropenten-2-one in 10 mL of diethyl ether was added sodium ethoxide (0.204 g, 3 mmol) at −78 to −60°C. The solution was stirred for 7 h at the same temperature. Then the mixture was warmed up to 0°C and was stirred for 37 h. The reaction mixture was quenched with ice-water, neutralized with 10% HCl, and extracted with diethyl ether (10 mL×3). The combined organic phase was washed with saturated sodium chloride, and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to give 0.185 g (53%) of **1a**.

3.3.19. Preparation of 1,5-dichloro-4,8-dipropyltricyclo[5.1.0.0^{3,5}]octane-2,6-dione (1c) with (3*E*)-1,1-dichlorohepten-2-one. To a solution of 0.412 g (2.3 mmol) of (3*E*)-1,1-dichlorohepten-2-one in 10 mL of diethyl ether was added sodium ethoxide (0.155 g, 2.3 mmol) at −78 to −60°C. The solution was stirred for 4 h at the same temperature. Then the mixture was warmed up to 0°C and was stirred for 6 h. The reaction mixture was quenched with ice-water, neutralized with 10% HCl, and extracted with diethyl ether (10 mL×3). The combined organic phase was washed with saturated sodium chloride, and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to give 0.188 g (57%) of **1c**.

3.3.20. Preparation of 1,5-dichloro-4,8-di(1′-propenyl)-tricyclo[5.1.0.0^{3,5}]octane-2,6-dione (1r) with (3*E*, 5*E*)-1,1-dichloroheptadien-2-one. To a solution of 0.539 g (3 mmol) of (3*E*, 5*E*)-1,1-dichloroheptadien-2-one in 10 mL of diethyl ether was added sodium ethoxide (0.222 g, 3 mmol) at −78 to −60°C. The solution was stirred for 7 h at the same temperature. Then the mixture was warmed up to 0°C and was stirred for 88 h. The reaction mixture was quenched with ice-water, neutralized with 10% HCl, and extracted with diethyl ether (10 mL×3). The combined organic phase was washed with saturated sodium chloride, and dried over anhydrous magnesium sulfate to give 0.204 g (48%) of **1r** as a solid: mp=153°C (decomposition); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.74–1.79 (dd, J=1.85, 6.62 Hz, 6H), 2.47–2.60 (m, 4H), 5.20–5.33 (dq, J=7.74, 1.68 Hz, 2H), 5.83–5.97 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.22, 34.65, 39.93, 49.71 122.21, 134.59, 190.84; IR (KBr): 3050, 1700, 1290, 1235, 1155, 1045, 970, 860, 795, 665 cm^{-1}. Anal. Calcd for $C_{14}H_{14}Cl_2O_2$: C, 58.97; H, 4.95. Found: C, 58.74; H, 4.98.

3.3.21. Preparation of 1,5-dichloro-4,8-dihexyltricyclo-[5.1.0.0^{3,5}]octane-2,6-dione (1s) with (*E*)-1,1-dichloro-3-decen-2-one. To a solution of 0.52 g (2.33 mmol) of (*E*)-1,1-dichloro-3-decen-2-one in 15 mL of diethyl ether was added sodium ethoxide (0.16 g, 2.3 mmol) at −78 to −60°C. The solution was stirred for 11 h at the same temperature. Then the mixture was warmed up to 0°C and was stirred for 16 h. The reaction mixture was quenched with ice-water, neutralized with 10% HCl, and extracted with diethyl ether (10 mL×3). The combined organic phase was washed with saturated sodium chloride, and dried over anhydrous magnesium sulfate to give 0.232 g (53%) of **1s** as a solid: mp=105°C (decomposition); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.88 (t, J=6.84 Hz, 6H), 1.28–1.79 (m, 20H), 1.84 (q, J=6.87 Hz, 2H), 2.23 (d, J=6.06 Hz, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.99, 22.46, 28.13, 28.72, 31.49, 32.75, 39.84, 50.25, 192.67; IR (KBr): 3400, 2940, 1695, 1295, 1100, 940, 870, 680, 970, 860 cm^{-1}. Anal. Calcd for $C_{20}H_{30}Cl_2O_2$: C, 64.34; H, 8.10. Found: C, 64.67; H, 7.85.

3.3.22. Preparation of 1,5-dichloro-4,8-diphenyltricyclo[5.1.0.0^{3,5}]octane-2,6-dione (1h) with (*E*)-1,1-dichloro-4-phenyl-3-butene-2-one in the presence of sodium ethoxide. To a solution of 0.444 g (2.03 mmol) of (3*E*)-1,1-dichloro-4-phenylbutene-2-one in 15 mL of diethyl ether was added sodium ethoxide (0.139 g, 2.03 mmol) at −78 to −60°C. The solution was stirred for 10 h at the same temperature. Then the mixture was warmed up to 0°C and was stirred for 13 h. The reaction mixture was quenched with ice-water, neutralized with 10% HCl. The residue was washed with ethyl acetate to give 0.182 g (70%) of **1h**.

3.3.23. Preparation of 1,5-dichloro-4,8-diphenyltricyclo[5.1.0.0^{3,5}]octane-2,6-dione (1h) with (*E*)-1,1-dichloro-4-phenyl-3-buten-2-one in the presence of lithium hydroxide. To a solution of 0.197 g (0.92 mmol) of (*E*)-1,1-dichloro-4-phenyl-3-buten-2-one in 1 mL of THF was added a solution of 0.022 g (0.92 mmol) of lithium hydroxide in 0.7 mL of water at −95°C. The solution was stirred for 14 min, and 2 mL of water was added to the reaction bottle at −95°C. The cooling bath was removed. After the reaction mixture was warmed up room temperature, and 2 M hydrochloric acid solution was added to acidify the solution. The solvent was removed in vacuo and the precipitate was filtered and washed with ether to give 0.110 g (94%) of **1h**.

3.3.24. Preparation of 1,5-dichloro-4,8-di(3,4-methylenedioxa)phenyltricyclo[5.1.0.0^{3,5}]octane-2,6-dione (1t) with (3*E*)-1,1-dichloro-4-(3,4-methylenedioxa)phenylbuten-2-one. To a solution of 0.154 g (0.6 mmol) of (3*E*)-1,1-dichloro-4-(3,4-methylenedioxa)phenylbuten-2-one in 5 mL of diethyl ether was added sodium ethoxide (0.041 g, 0.6 mmol) at −78 to −60°C. The solution was stirred for 8 h at the same temperature. Then the mixture was warmed up to 0°C and was stirred for 16 h. The reaction mixture was quenched with ice-water, neutralized with 10% HCl, and extracted with diethyl ether (10 mL×3). The combined organic phase was washed with saturated sodium chloride, and dried over anhydrous magnesium sulfate to give 0.081 g (71%) of **1t** as a solid: mp: 171°C (decomposition); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.97 (d, J=6.84 Hz, 2H), 3.22 (d, J=6.84 Hz, 2H), 6.00 (s, 4H), 6.74–6.83 (m, 3H); IR (KBr): 2900, 1695, 1490, 1445, 1350, 1295, 845, 800, 710, 670 cm^{-1}. Anal. Calcd for $C_{22}H_{14}Cl_2O_2$: C, 59.35; H, 3.17. Found: C, 59.30; H, 3.13.

3.3.25. (*E*)-1,1-Dichloro-3-penten-2-one (3a). *Step 1:* To a solution of 2.40 g (30 mmol) of dried dichloromethane in 40 mL of THF was added 18 mL (30 mmol) BuLi (1.6 M in hexane) at −95°C in 30 min, and then 2.10 g (30 mmol) of (2*E*)-butenal was added. The mixture was stirred for 2.5 h at the same temperature. The reaction was quenched with ice-water, neutralized with 10% HCl, extracted with ethyl acetate (20 mL×3). The organic phases were combined, washed with saturated NaCl solution, and dried over anhydrous magnesium sulfate. The solvent was removed and the crude product was purified on silica gel chromatography (hexane/ethyl acetate 30:1) to give 4.05 g (87%) of (*E*)-1,1-dichloro-3-penten-2-ol. *Step 2:* To a solution of 30.7 g (350 mmol) of manganese dioxide in 35 mL of dried hexane was added 2.72 g (17.5 mmol) of (*E*)-1,1-dichloro-3-penten-2-ol, and stirred for 20 h at room temperature. The excess of MnO_2 was filtrated out and the solvent was removed in vacuo and the residue was purified on silica gel chromatography to give 1.89 g (71%) of **3a**: ^{1}H NMR (60 MHz, CCl_4) δ 2.01 (d, J=6.0 Hz, 3H), 5.72 (s, 1H), 6.22–7.14 (m, 2H); IR (neat): 2950, 1700, 1625, 1440, 1290, 765, 710 cm^{-1}.

3.3.26. (*E*)-1,1-Dichloro-3-hepten-2-one (3c). *Step 1:* To a solution of 2.40 g (30 mmol) of dried dichloromethane in 30 mL of THF was added 18 mL (30 mmol) BuLi (1.6 M in hexane) at −95°C in 30 min, and then 2.99 g (30 mmol) of (2*E*)-hexenal was added. The mixture was stirred for 2.5 h at the same temperature. The reaction was quenched with ice-water, neutralized with 10% HCl, extracted with ethyl acetate (20 mL×3). The organic phases were combined, washed with saturated NaCl solution, and dried over anhydrous magnesium sulfate. The solvent was removed and the crude product was purified on silica gel chromatography (hexane/ethyl acetate 30:1) to give 3.92 g (21 mmol, 71%) of 1,1-dichloro-3-hepten-2-ol. *Step 2:* To a solution of 7.80 g (89.3 mmol) of manganese dioxide in 30 mL of dried hexane was added 0.817 g (4.46 mmol) of (*E*)-1,1-dichloro-3-hepten-2-ol, and stirred for 23 h at room temperature. The excess of MnO_2 was filtrated out and the solvent was removed in vacuo and the residue was purified on silica gel chromatography to give 0.409 g (51%) of **3c**: ^{1}H NMR (60 MHz, CCl_4) δ 0.96 (t, J=6.2 Hz, 3H), 1.25–1.72 (m, 2H), 2.06–2.35 (m, 2H), 5.76 (s, 1H), 6.22–7.32 (m, 2H); IR (neat): 2980, 1700, 1620, 1460, 1380, 1300, 1160, 980 cm^{-1}.

3.3.27. (*E*)-1,1-Dichloro-4-phenyl-3-buten-2-one (3h). To a solution of 1.59 g (9.0 mmol) of ethyl (*E*)-cinnamate and 1.01 g (12 mmol) of dichloromethane in 10 mL of THF was added 8.7 mmol of LDA at −95°C for 15 min. The solution was stirred for 30 min at the same temperature. Then the reaction mixture was quenched with 10% HCl at −95°C, and extracted with diethyl ether (10 mL×3). The combined organic phase was washed with saturated sodium chloride, and dried over anhydrous magnesium sulfate. The crude product was purified on a silica gel chromatography (hexane/ethyl acetate 100:1) to give 0.767 g (41%) of **3h**. ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.99 (s, 1H), 7.20 (d, J=16 Hz, 1H), 7.42–7.46 (m, 3H), 7.62–7.67 (m, 2H), 7.90 (d, J=16 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 69.80, 117.54, 128.87, 129.06, 131.50, 133.80, 147.98, 185.73.

3.3.28. (3*E*, 5*E*)-1,1-Dichloroheptadien-2-one (3r). *Step 1:* To a solution of 0.8 g (10 mmol) of dried dichloromethane in 30 mL of THF was added 6.2 mL of BuLi (1.6 M in hexane, 10 mmol) at −95°C in 30 min, and then 0.96 g (10 mmol) of (2*E*, 4*E*)-1,1-dichloro-hexadienal was added. The mixture was stirred for 2.5 h at the same temperature. The reaction was quenched with ice-water, neutralized with 10% HCl, extracted with ethyl acetate (20 mL×3). The organic phases were combined, washed with saturated NaCl solution, and dried over anhydrous magnesium sulfate. The solvent was removed and the crude product was purified on silica gel chromatography (hexane/ethyl acetate 30:1) to give 1.27 g (71%) of (3*E*, 5*E*)-1,1-dichloroheptadien-2-ol. Step 2: To a solution of 13.2 g (160 mmol) of manganese dioxide in 30 mL of dried hexane was added 1.32 g (7.9 mmol) of (3*E*, 5*E*)-1,1-dichloro-heptadien-2-ol, and stirred for 42 h at room temperature. The excess of MnO_2 was filtrated out and the solvent was removed in vacuo and the residue was purified on silica gel chromatography (hexane/ethyl acetate 30:1) to give 0.838 g (59.7%) of **3r**: ^{1}H NMR (60 MHz, CCl_4) δ 2.60 (d, J=5.0 Hz, 3H), 5.75 (s, 1H), 6.15–7.51 (m, 4H); IR (neat): 2980, 1690, 1630, 1590, 1440, 1375, 1330, 1240, 1130, 1060, 1000, 810, 760 cm^{-1}. Anal. Calcd for $C_7H_8Cl_2O_2$: C, 46.96; H, 4.50. Found: C, 47.02; H, 4.47.

3.3.29. (3*E*)-1,1-Dichlorodecen-2-one (3s). *Step 1:* To a solution of 1.7 g (20 mmol) of dried dichloromethane in 10 mL of THF was added 12.8 mL (20 mmol) BuLi (1.6 M in hexane) at −95°C in 30 min, and then 0.82 g (5.82 mmol) of (2*E*)-1,1-dichlorononenal was added. The mixture was stirred for 2.5 h at the same temperature. The reaction was quenched with ice-water, neutralized with 10% HCl, extracted with ethyl acetate (20 mL×3). The organic phases were combined, washed with saturated NaCl solution, and dried over anhydrous magnesium sulfate. The solvent was removed to give 1.25 g of the crude product of (3*E*)-1,1-dichloro-nonen-2-ol. *Step 2:* To a solution of 10.2 g (117 mmol) of manganese dioxide in 20 mL of dried hexane was added 1.25 g of the crude product of (3*E*)-1,1-dichloro-nonen-2-ol, and was stirred for 4.8 days at room temperature. The excess of MnO_2 was filtrated out and the solvent was removed in vacuo. The residue was purified on silica gel chromatography (hexane/ethyl acetate 30:1) to give 0.29 g (in two steps yield 44.5%) of **3s**: IR (neat): 2925, 1690, 1620, 1460, 1460, 1210, 1150, 960, 790.

3.3.30. (3*E*)-1,1-Dichloro-4(3′,4′-methylenedioxyphenyl)-buten-2-one (3t). *Step 1:* To a solution of 0.252 g (3 mmol) of dried dichloromethane in 10 mL of THF was added 1.78 mL (3 mmol) BuLi (1.6 M in hexane) at −95°C in 30 min, and then 0.50 g (2.8 mmol) of (3*E*)-1,1-dichloro-4-(3′,4′-methylenedioxyphenyl)butenal was added. The mixture was stirred for 2.5 h at the same temperature. The reaction was quenched with ice-water, neutralized with 10% HCl, extracted with ethyl acetate (20 mL×3). The organic phases were combined, washed with saturated NaCl solution, and dried over anhydrous magnesium sulfate. The solvent was removed to give 0.799 g of the crude product of (3*E*)-1,1-dichloro-4(3′,4′-methylene-dioxyphenyl)buten-2-ol. *Step 2:* To a solution of 5.22 g (60 mmol) of manganese dioxide in 20 mL of dried hexane was added 0.799 g of

the crude product of (3*E*)-1,1-dichloro-4-(3′,4′-methylenedioxyphenyl)buten-2-ol, and stirred for 67 h at room temperature. The excess of MnO_2 was filtrated out and the solvent was removed in vacuo and the residue was purified on silica gel chromatography (hexane/ethyl acetate 30:1) to give 0.141 g (in two steps yield 19.8%) of **3t**: ^{1}H NMR (60 MHz, CCl_4) δ 5.76 (s, 1H), 5.94 (s, 2H), 6.76 (m, 2H), 7.01 (m, 3H).

3.3.31. Preparation of 1a and 1h with various α,β-unsaturated esters 5a–o. To a solution of *n*-BuLi (1.61 M in hexane) in THF was added slowly dichloromethane at −95°C. The mixture was stirred for 30 min at the same temperature. Then α,β-unsaturated ester (1 equiv.) was added to the flask. The solution was stirred for 10 min, and then 10 mL of water was added to the flask. The cooling bath was removed. After the reaction mixture was warmed up to room temperature, 10% hydrochloric acid solution was added to acidify the solution. The solvent was removed in vacuo and the residue was washed with ether to give tricyclo[5.1.0.0^{3,5}]octane-2,6-diones **1a** and **1h**. Starting material **5** and product **1** are as follows: **5a**: 0.114 g (1.0 mmol), **1a**: 57 mg (49%); **5b**: 0.128 g (1.0 mmol) **1a**: 57 mg (49%); **5c**: 0.142 g (1 mmol), **1a**: 58 mg (49.8%); **5d**: 0.142 g (1 mmol), **1a**: 33 mg (28%); **5e**: 156 mg (1 mmol), **1a**: 52 mg (44.6%); **5f**: 156 mg (1 mmol), **1a**: 27 mg (23.2%); **5g**: 156 mg (1 mmol), **1a**: 9 mg (7.6%); **5i**: 162 mg (1 mmol), **1h**: 112 mg (63%); **5j**: 176 mg (1 mmol), **1h**: 127 mg (71%); **5k**: 190 mg (1 mmol), **1h**: 115 mg (65.2%); **5l**: 204 mg (1 mmol), **1h**: 129 mg (72.8%); **5m**: 190 mg (1 mmol), **1h**: 81 mg (45.4%); **5n**: 204 mg (1 mmol), **1h**: 76 mg (43.4%); **5o**: 204 mg (1 mmol), **1h** 64 mg (36.4%).

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