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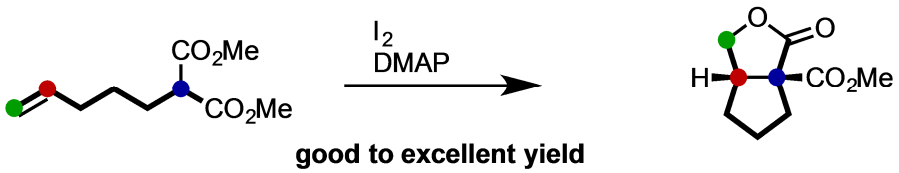
Gifu Pharmaceutical University



good to excellent yield

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Synthesis of bicyclic lactones *via* I_2-mediated intramolecular tandem C–C/C–O bond formation

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ABSTRACT

The iodine/DMAP-mediated intramolecular tandem C–C/C–O bond forming reaction of malonate bearing alkene moiety proceeded to give bicyclic lactones with good diastereoselectivity in good yield. The mechanistic investigation was also discussed on the basis of various control experimental results.

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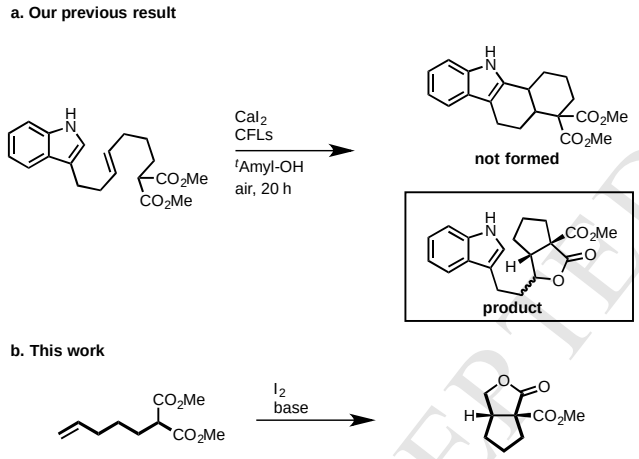
1. Introduction

The high abundance of naturally occurring polycyclic lactones and their unique biological activities make the stereoselective construction of these species a matter of great importance for the fields of pharmaceuticals, agrichemicals, and organic synthesis.[1–3] Consequently, a range of corresponding synthetic methods have been developed, e.g., Pd-catalyzed intramolecular cyclization,[4] Lewis or Bronsted acid–mediated cyclization,[5] Os-catalyzed oxidative carboesterification of olefins,[6] ferrocenium ion–mediated oxidative cyclization,[7] and Mn-mediated intramolecular radical cyclization,[8] although the search for more environmentally friendly methodologies is still ongoing. By way of an example, polycyclic lactones can be obtained by iodine-mediated electrophilic cyclization performed utilizing a combination of molecular iodine with strong Lewis acids or bases.[9,10]

Recently, we have developed iodine-mediated (catalyzed) intra- and intermolecular transformations affording polyfunctionalized heterocyclic compounds.[11] In the course of our work on iodine-mediated transformation of carbonyl compounds with non-activated C=C π-bonds, we unexpectedly found that carbocyclization furnished bicyclic lactones,[11b] which indicated that the intramolecular formation of a C–C bond between the olefin and the carbon α to the carbonyl group occurred in a *5-exo-trig* manner (Scheme 1a). Therefore, we proposed that intramolecular C–C/C–O bond formation could be realized for olefin moiety-bearing malonates under similar reaction conditions (Scheme 1b).



Scheme 1. (a) Previously reported iodine-mediated bicyclic lactone formation and (b) the reaction investigated in this work.

Herein, we report that intramolecular C–C/C–O bond formation in alkene group-containing malonates is efficiently promoted by molecular iodine/base combinations to afford bicyclic lactones.

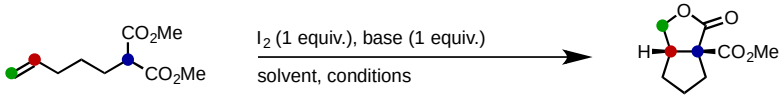
2. Result and discussion

Initially, we focused on the lactonization of **1a** to afford **2a** in the presence of various iodine/base mixtures under irradiation with visible light emitted by a compact fluorescent lamps (CFLs) (Table 1). When the above reaction was conducted using methanolic K_2CO_3 as the base, only traces of **2a** were obtained (entry 1), while other carbonate bases (Na_2CO_3, $CaCO_3$, $SrCO_3$, and $BaCO_3$) were equally ineffective (entries 2–5). Although the use of $Ca(OH)_2$ and $Sr(OH)_2$ as stronger bases did not result in product formation, **2a** was obtained in 19% yield in the presence of $Ba(OH)_2$ (entries 6–8). Encouraged by this result, several key parameters including solvent, temperature, and reaction time were screened for the second step using $Ba(OH)_2$ as the base. As a result, we found that bicyclic lactonization could be achieved by heating **1a** in the presence of molecular iodine and $Ba(OH)_2$ instead of utilizing visible light irradiation (entries 8 vs. 9 and 10).

Subsequently, various organic bases were screened under heating conditions. Aliphatic amines such as trimethylamine, diisopropylamine, and pyrrolidine were inferior to $Ba(OH)_2$ in terms of reaction yield (entries 10 vs. 11–13), with pyridine and lutidine, known to induce electrophilic iodine activation, being equally ineffective (entries 14 and 15).[12] When *N*,*N*-dimethylaminopyridine (DMAP) was employed as a base, the target product was obtained in 63% yield (entry 16). Finally, the best yield of 88% was obtained using 1.5 equivalents of molecular iodine and DMAP even under the air condition (entry 18).

With the optimized reaction conditions in hand, the reaction scope was explored by varying substituents on the side chain of malonates **1** (Table 2). Similarly to the non-functionalized dimethylmalonate derivative **1a**, malonate **1b** (dimethyl substituted at the allylic position) also gave the corresponding bicyclic lactone **2b** in good yield (77%) in the presence of iodine and DMAP (entry 2). In the case of 3-phenyl-4-pentenylmalonate **1c**, product **2c** was obtained in moderate yield with almost complete diastereoselectivity (entry 3). The iodine/DMAP–mediated lactonization could also be applied to 2-substituted 4-pentenylmalonate derivatives **1d**, **1e**, and **1f**, affording the corresponding products in moderate to good yields with good diastereoselectivities (entries 4–6). Furthermore, 1-methyl derivative **1g** afforded the desired bicyclic lactone **2g** in good yield without any diastereoselectivity decrease (entry 7).

Table 1. Optimization of reaction conditions[a]



1a **2a**

Entry	Base	Solvent	Conditions[b]	Yield (%)[c]
1	K_2CO_3	MeOH (1 mL)	CFLs, Ar, 20 h	trace
2	Na_2CO_3	MeOH (1 mL)	CFLs, Ar, 20 h	trace
3	$CaCO_3$	MeOH (1 mL)	CFLs, Ar, 20 h	trace
4	$SrCO_3$	MeOH (1 mL)	CFLs, Ar, 20 h	trace

5	$BaCO_3$	MeOH (1 mL)	CFLs, Ar, 20 h	trace
6	$Ca(OH)_2$	MeOH (1 mL)	CFLs, Ar, 20 h	trace
7	$Sr(OH)_2$	MeOH (1 mL)	CFLs, Ar, 20 h	trace
8	$Ba(OH)_2$	MeOH (1 mL)	CFLs, Ar, 20 h	(19)[e]
9	$Ba(OH)_2$	MeOH (1 mL)	40 °C, Ar, 20 h	39
10	$Ba(OH)_2$	MeOH (1 mL)	70 °C, Ar, 20 h	51
11	Et_3N	MeOH (1 mL)	70 °C, Ar, 20 h	trace
12	HN^iPr_2	MeOH (1 mL)	70 °C, Ar, 20 h	35
13	pyrrolidine	MeOH (1 mL)	70 °C, Ar, 20 h	28
14	pyridine	MeOH (1 mL)	70 °°C, Ar, 20 h	n.r.
15	lutidine	MeOH (1 mL)	70 °C, Ar, 20 h	6
16	DMAP	MeOH (1 mL)	70 °C, Ar, 20 h	63
17	DMAP	MeOH (2 mL)	70 °C, Ar, 20 h	67
18[d]	DMAP	MeOH (2 mL)	70 °C, Air, 20 h	90 (88)[e]

[a] Reaction conditions: **1a** (0.3 mmol), I_2 (1.0 equiv.) and base (1.0 equiv.) in solvent were stirred under the condition above.

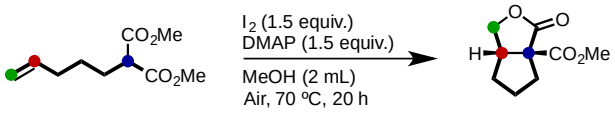
[b] CFLs represents Compact Fluorescent Lamps

[c] Yield was determined by the NMR analysis of the crude reaction mixture using 1,1,2,2-tetrachloroethane as an internal standard.

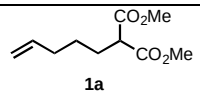
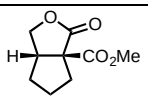
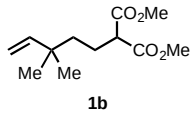
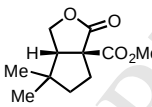
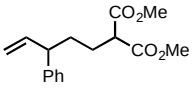
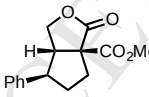
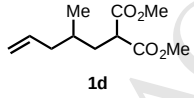
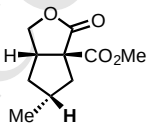
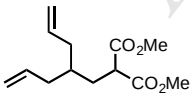
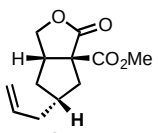
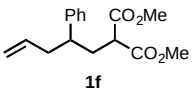
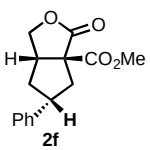
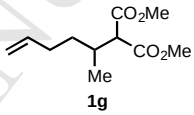
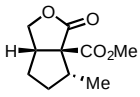
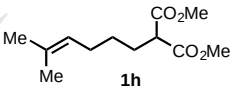
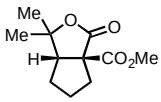
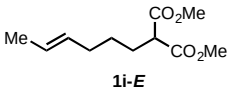
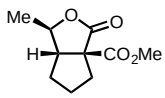
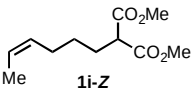
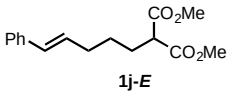
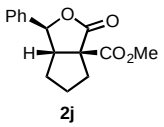
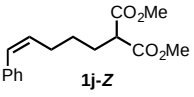
[d] The reaction performed using I_2 (1.5 equiv.) and DMAP (1.5 equiv.).

[e] Isolated yield.

Table 2. Scope of the developed bicyclic lactone formation reaction[a, b]



1 **2**

Entry	1	2	Yield (%)
1	 **1a**	 **2a**	88
2	 **1b**	 **2b**	77
3	 **1c**	 **2c**	50 *dr* > 95:5
4	 **1d**	 **2d**	66 *dr* = 85:15
5	 **1e**	 **2e**	94 *dr* = 77:23
6	 **1f**	 **2f**	53 *dr* = 88:12
7	 **1g**	 **2g**	68 *dr* = 88:12
8	 **1h**	 **2h**	78
9	 **1i-*E***	 **2i**	68 *dr* = 67:33
10	 **1i-*Z***	**2i**	71 *dr* = 67:33
11	 **1j-*E***	 **2j**	62 *dr* = 88:12
12	 **1j-*Z***	**2j**	31 *dr* = 84:16

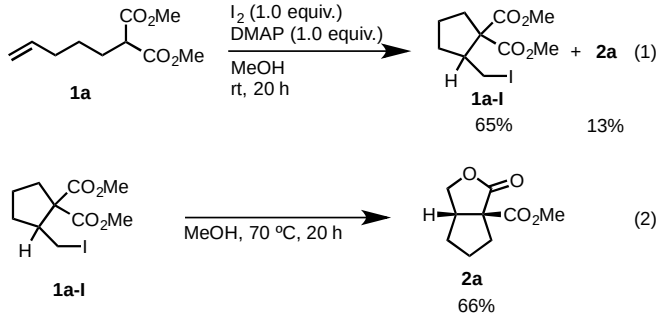
[a] Isolated yield.

[b] Diastereomeric ratio (*dr*) was determined by ^{1}H NMR analysis of crude reaction mixture.

The developed reaction was applicable to 5,5-dimethylsubstituted derivative **1h**, furnishing the desired product in 78% yield (entry 8). Moreover, the cyclization of **1i-*E*** and **1i-*Z*** gave bicyclic lactone **2i** in yields of 68 and 71% with identical diastereoselectivity, respectively (entries 9 and 10). The assignments were based on a comparison of the obtained ^{1}H NMR and ^{13}C NMR spectra with those reported by Taguchi.[9a] Therefore, the developed lactonization was concluded to be markedly different from the titanium alkoxide/iodine–mediated S_N2-type cyclization of **1i-*E*** and **1i-*Z***, which was reported to

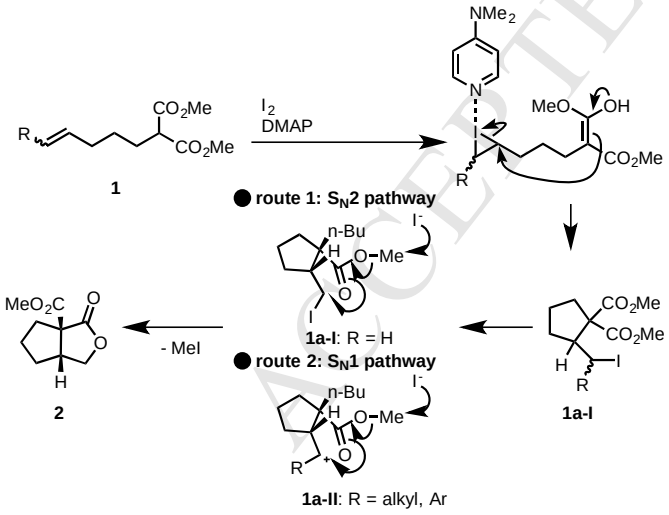
almost exclusively afford a single *syn* diastereomer of bicyclic lactone **2i** in the case of **1i-*E*** and *trans* bicyclic lactone **2i** in the case of **1i-*Z*** (entries 9 and 10).[9a] This tendency was also observed when **1j-*E*** and **1j-*Z*** were used as substrates (entries 11 and 12), which indicated that the cyclization step proceed *via* an S_N1-type mechanism and gave the thermodynamically most stable diastereomer.[9d]

To elucidate the reaction mechanism, control experiments were carried out (Scheme 2). The reaction of **1a** with iodine/DMAP at room temperature afforded the desired product in only 13% yield, mainly furnishing cyclopentyl ring–containing **1a-I** (65% yield), which was tentatively identified as a possible reaction intermediate (Scheme 2, eq. 1). Heating of **1a-I** at 70 °C in methanol in the absence of base resulted in the formation of the desired product in 66% yield (Scheme 2, eq. 2). Thus, it was concluded that the first carbocyclization proceeded smoothly under optimal conditions even at room temperature to afford intermediate **1a-I**, whereas the second rate-determining step corresponded to lactone formation.



Scheme 2. Control experiments for evaluation of the reaction mechanism

Based on the previously reported iodine-mediated bicyclic lactone formation reactions and the results of our control experiments, the following mechanism was suggested (Scheme 3).[9]



Scheme 3. Plausible reaction mechanism

The reaction is thought to be initiated by the coordination of the iodonium-DMAP adduct to the olefin moiety of **1**, with the subsequent cyclization at the α-position of the carbonyl affording the five-membered intermediate **1a-I**. If the rate of this cyclization is slow, the iodonium intermediate can be attacked by iodide instead of the carbon nucleophile to form a diiodide species. It is assumed that mechanism for lactonization step is different depend on the structure **1a-I**. First, the lactonization of primary alkyl iodide could be occurred through S_N2-type reaction (route 1).[13] Second mechanism is through carbocation intermediate. The heterolytic cleavage of the C–I bond of **1a-I** under thermal conditions is believed to furnish the stable carbocation intermediate **1a-II**, which undergoes iodide-mediated cyclization to give the desired bicyclic lactone **2** (route 2).

3. Conclusion

In summary, we have developed a robust synthetic method for the formation of functionalized and bicyclic lactones containing all-carbon quaternary stereocenters from simple linear precursors and are currently investigating the above transformation in the context of natural product synthesis.

4. Experimental section

4.1. General Information

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. Malonate **1a-1j**[8i] were prepared according to the procedure reported. Malonates **1a**,[14] **1d**,[9d] **1e**,[9e] **1i**[9a] are known and their analytical data are in full agreement with those reported in cited references.

Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Merck silica gel 60 F_{254}). Flash column chromatography was performed with Kanto silica gel 60N (Spherical, Neutral, 40–50 μm). Visualization of the developed chromatogram was performed by UV lamp (254 nm) and *p*-anisaldehyde or basic potassium permanganate stain. NMR spectra were recorded on a JEOL ECA 500 spectrometer (500 MHz for ^{1}H NMR, 125MHz for ^{13}C NMR), and are internally referenced to residual protic solvent signals or TMS (note: $CDCl_3$ referenced at δ 7.26 and 77.0 ppm respectively, TMS referenced at δ 0 and 0 ppm respectively). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets), coupling constant (Hz), integration, and assignment. Data for ^{13}C NMR are reported in terms of chemical shifts (δ ppm). IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer and are reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-T100TD and are reported as m/z.

4.2. General procedure for the preparation of 4-pentenyl malonate derivatives **1**

Triethylamine (1.5 equiv.) was added to a stirred solution of alcohol (1.0 equiv.) in dry DCM (0.2 M) and cooled to 0 °C after which MsCl (1.2 equiv.) was added. The solution was allowed to warm to room temperature and stirred for 1.5 h after which time aqueous 0.5 M HCl solution (4.5 mL/mmol alcohol) was added. The layers were separated and the aqueous layer was extracted with DCM (3×4.5 mL/mmol). The combined organic extracts were dried ($MgSO_4$), filtered, and the solvent removed *in vacuo* to give the mesylate. Sodium hydride (60 % in mineral oil, 2.5 equiv.) was suspended in dry DMF (0.2 M) and cooled to 0 °C, after which dimethyl malonate (2.5 equiv.) was added dropwise and the mixture was stirred for 20 minutes. A solution of the mesylate (1.0 equiv.) in dry THF (0.2 M) was added followed by potassium iodide (1.0 equiv.) and the solution was stirred at 80 °C overnight. After cooling to RT, the solution was poured onto saturated NH_4Cl solution (7 mL/mmol mesylate) and extracted with EtOAc (3×7 mL/mmol mesylate). The combined organic

extracts were washed with water, dried ($MgSO_4$), filtered, and the solvent removed in vacuo to give the crude product.

*4.2.1. Dimethyl (3,3-dimethyl-4-pentenyl)propanediate (**1b**)*

The product was obtained in 57% yield (2.6 g, 11.4 mmol) after column chromatography on silica gel (*n*-hexane : EtOAc = 10 : 1) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.42 (ddd, *J* = 17.2, 10.9, 2.9 Hz, 1H), 4.96-4.91 (m, 2H), 3.74 (s, 6H), 3.29 (t, *J* = 7.5 Hz, 1H), 1.86-1.80 (m, 2H). 1.30-1.26 (m, 2H), 1.00 (s, 6H).; ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.8, 147.4, 111.0, 52.4, 52.1, 39.9, 36.4, 26.5, 24.3.; FTIR (neat): 2958, 1754, 1736, 1640, 1457, 1435, 1345, 1273, 1253, 1225, 1203, 1144, 1004, 913, 689 cm^{-1}.; HMRS *m/z* (DART) $[M+H]^+$: calcd for $C_{12}H_{21}O_4$: 229.1434; found: 229.1439.

*4.2.2. Dimethyl (3-phenyl-4-pentenyl)propanediate (**1c**)*

The product was obtained in 52% yield (284 mg, 2.0 mmol) after column chromatography on silica gel (*n*-hexane : EtOAc = 10 : 1) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.16 (m, 5H), 5.91 (ddd, *J* = 17.2, 9.2, 7.5 Hz, 1H), 5.06-5.03 (m, 2H), 3.72 (s, 3H), 3.71 (s, 3H), 3.35 (t, *J* = 7.5 Hz, 1H), 3.25 (q, *J* = 7.5 Hz, 1H), 1.98-1.61 (m, 4H).; ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.7, 143.6, 141.4, 128.5, 127.4, 126.4, 114.6, 52.5, 51.5, 49.6, 32.8, 26.9.; FTIR (neat): 3066, 3028, 3001, 2954, 1752, 1733, 1637, 1601, 1493, 1453, 1435, 1346, 1243, 1222, 1197, 1152, 1002, 917, 751, 702 cm^{-1}.; HMRS *m/z* (DART) $[M+H]^+$: calcd for $C_{16}H_{21}O_4$: 277.1434; found: 277.1432.

*4.2.3. Dimethyl (2-phenyl-4-pentenyl)propanediate (**1f**)*

The product was obtained in 16% yield (193 mg, 0.7 mmol) after column chromatography on silica gel (*n*-hexane : EtOAc = 10 : 1) as a coloress oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.12 (m, 5H), 5.62 (ddd, *J* = 17.2, 10.3, 6.9 Hz, 1H), 5.01-4.93 (m, 2H), 3.74 (s, 3H), 3.60 (s, 3H), 3.16 (dd, *J* = 9.7, 4.6 Hz, 1H), 2.65-2.60 (m, 1H), 2.41-2.35 (m, 3H), 2.11 (ddd, *J* = 16.0, 10.3, 4.6 Hz, 1H).; ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.8, 142.9, 136.1, 128.5, 127.7, 126.7, 116.5, 52.4, 49.7, 43.6, 41.4, 34.7.; FTIR (neat): 3064, 3026, 2998, 2954, 1750, 1732, 1641, 1603, 1494, 1435, 1340, 1259, 1231, 1200, 1149, 1027, 999, 914, 845, 765, 701 cm^{-1}.; HMRS *m/z* (DART) $[M+H]^+$: calcd for $C_{16}H_{21}O_4$: 277.1434; found: 277.1436.

*4.2.4. Dimethyl (1-methyl-4-pentenyl)propanediate (**1g**)*

The product was obtained in 77% yield (1.1 g, 5.1 mmol) after column chromatography on silica gel (*n*-hexane : EtOAc = 10 : 1) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.79 (ddd, *J* = 16.6, 10.3, 6.6 Hz, 1H), 5.04-4.95 (m, 2H), 3.73 (s, 6H), 3.30 (d, *J* = 8.0 Hz, 1H), 2.31-2.25 (m, 1H), 2.17-2.11 (m, 1H), 2.07-1.99 (m, 1H), 1.55-1.48 (m, 1H), 1.33-1.26 (m, 1H), 1.00 (d, *J* = 6.9 Hz, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.2, 138.0, 114.8, 57.3, 52.2, 33.4, 32.9, 31.0, 16.7.; FTIR (neat): 2954, 1755, 1735, 1641, 1455, 1435, 1346, 1286, 1239, 1223, 1194, 1152, 1018, 1000, 912 cm^{-1}.; HMRS *m/z* (DART) $[M+H]^+$: calcd for $C_{11}H_{19}O_4$: 215.1278; found: 215.1286.

*4.2.5. Dimethyl (5-methyl-4-hexynyl)propanediate (**1h**)*

The product was obtained in 75% yield (1.3 g, 5.9 mmol) after column chromatography on silica gel (*n*-hexane : EtOAc = 10 : 1) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.10-5.06 (m, 1H), 3.74 (s, 3H), 3.37 (t, *J* = 7.5 Hz, 1H), 2.01 (q, *J* = 7.5 Hz, 2H), 1.93-1.88 (m, 2H), 1.68 (s, 3H), 1.59 (s, 3H), 1.38-1.31 (m, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 132.0, 123.6, 52.3, 51.5, 28.4, 27.5, 25.6, 17.6.; FTIR (neat): 2955, 1752, 1735, 1435, 1379, 1346, 1288, 1271, 1225, 1201, 1147, 1112, 1063, 1008, 838 cm^{-1}.; HMRS *m/z* (DART) $[M+H]^+$: calcd for $C_{12}H_{21}O_4$: 229.1434; found: 229.1437.

*4.2.6. (E)-Dimethyl (5-phenyl-4-pentenyl)propanediate (**1j-E**)*

The product was obtained in 64% yield (3.5 g, 12.8 mmol) after column chromatography on silica gel (*n*-hexane : EtOAc = 10 : 1) as a coloress oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.45-5.34 (m, 2H), 3.74 (s, 6H), 3.36 (t, *J* = 7.5 Hz, 1H), 2.02 (q, *J* = 7.5 Hz, 2H), 1.92-1.87 (m, 2H), 1.64 (d, *J* = 6.3 Hz, 3H), 140-1.31 (m, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.9, 130.3, 125.5, 52.4, 51.5, 32.0, 28.3, 27.2, 17.8.; FTIR (neat): 3026, 2998, 2955, 2859, 1752, 1735, 1435, 1345, 1282, 1265, 1236, 1215, 1197, 1152, 1054, 1011, 967, 920 cm^{-1}.; HMRS *m/z* (DART) $[M+H]^+$: calcd for $C_{16}H_{21}O_4$: 277.1434; found: 277.1433.

*4.2.7. (Z)-Dimethyl (5-phenyl-4-pentenyl)propanediate (**1j-Z**)*

The product was obtained in 67% yield (8.6 g, 31 mmol) after column chromatography on silica gel (*n*-hexane : EtOAc = 10 : 1) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.49-5.34 (m, 2H), 3.74 (s, 6H), 3.37 (t, *J* = 7.5 Hz, 1H), 2.07 (q, *J* = 7.5 Hz, 2H), 1.94-1.89 (m, 2H), 1.60 (d, *J* = 6.3 Hz, 3H), 140-1.35 (m, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.8, 129.5, 124.5, 52.4, 51.5, 28.4, 27.1, 26.3.; FTIR (neat): 3014, 2955, 2938, 2862, 1753, 1735, 1435, 1341, 1270, 1238, 1215, 1199, 1152, 1119, 1046, 1005, 832, 704 cm^{-1}.; HMRS *m/z* (DART) $[M+H]^+$: calcd for $C_{16}H_{21}O_4$: 277.1434; found: 277.1437.

*4.3. General procedure for the preparation of bicyclic lactones **2***

A Pyrex® test tube (16.5 cm × 1.5 cm) containing a mixture of **2** (0.3 mmol), I_2 (114 mg, 1.5 epuiv., 0.3 mmol) and DMAP (54.9 mg, 1.5 epuiv., 0.3 mmol) in methanol (2.0 mL) was stirred at 70 ºC under air for 20 h. After cooling to room temperature, the solvent was removed under reduced pressure. The resulting mixture was purified by flash column chromatography on silica gel (*n*-hexane : EtOAc) to give **2**.

*4.3.1. (3aRS,6aSR)-Methyl 3-oxohexahydro-1H-cyclopenta-[c]-furan-3a-carboxylate (**2a**)*

The product was obtained in 88% yield (48.5 mg, 0.26 mmol) after column chromatography on silica gel (*n*-hexane : EtOAc = 4 : 1) as a colorless oil.; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.56 (dd, *J* = 9.2, 8.5 Hz, 1H), 4.08 (dd, *J* = 9.2, 2.3 Hz, 1H), 3.78 (s, 3H), 3.13-3.09 (m, 1H), 2.41-2.35 (m, 1H), 2.29-2.25 (m, 1H), 2.11-2.05 (m, 1H), 1.85-1.81 (m, 1H), 1.71-1.62 (m, 2H).; ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.4, 170.4, 73.0, 61.5, 53.1, 45.5, 34.6, 34.0, 25.6.; FTIR (neat): 2957, 2874, 1767, 1738, 1449, 1435, 1379, 1320, 1251, 1203, 1168, 1142, 1114, 1053, 1010, 976, 920, 863, 841, 792, 757, 726, 684 cm^{-1}.; HMRS *m/z* (DART) $[M+H]^+$: calcd for $C_9H_{13}O_4$: 185.0808; found: 185.0805. Data was consisted with the literature. [8f]

*4.3.2. (3aRS,6aSR)-Methyl-6,6-dimethyl-3-oxohexahydro-1H-cyclopenta[c]-furan-3a-carboxylate (**2b**)*

The product was obtained in 77% yield (49 mg, 0.23 mmol) after column chromatography on silica gel (*n*-hexane : EtOAc = 4 : 1) as a colorless oil.; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.42 (dd, *J* = 9.7, 7.5 Hz, 1H), 4.28 (dd, *J* = 9.7, 2.3 Hz, 1H), 3.78 (s, 3H), 2.70 (dd, (s, *J* = 7.5, 2.3 HZ, 1H), 2.59 (ddd, *J* = 13.8, 8.0, 5.7 Hz, 1H), 2.22 (ddd, *J* = 13.8, 7.5, 5.2 Hz, 1H), 1.65 (ddd, *J* = 13.2, 7.5, 5.7 Hz, 1H), 1.55 (dd, *J* = 13.2, 8.0, 5.2 Hz, 1H), 1.06 (s, 3H), 1.01 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.8, 170.7, 68.0, 61.5, 56.0, 55.1, 42.4, 40.5, 31.7, 28.8, 23.0.; FTIR (neat): 2959, 2871, 1769, 1738, 1459, 1435, 1370, 1311, 1255, 1206, 1171, 1125, 1059, 1043, 996, 978, 930, 881, 797, 730, 685 cm^{-1}.; HMRS *m/z* (DART) $[M+H]^+$: calcd for $C_{11}H_{17}O_4$: 213.1121; found: 213.1111.

*4.3.3. (3aRS,6aSR)-Methyl-3-oxo-6-phenyltetrahydro-1H-cyclopenta[c]-furan-3a-carboxylate (**2c**)*

The product was obtained in 50% yield (39.2 mg, 0.15 mmol) after column chromatography on silica gel (*n*-hexane : EtOAc = 4 : 1) as a colorless oil.; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.22 (m, 5H), 4.46 (dd, *J* = 9.2, 6.3 Hz, 1H), 4.22 (dd, *J* = 9.2, 1.2 Hz, 1H), 3.81 (s, 3H), 3.08 (dd, *J* = 9.7, 6.3 Hz, 1H), 2.95-2.91 (m, 1H), 2.83-2.76 (m, 1H), 2.27-2.17 (m, 2H), 2.05-1.98 (m, 1H).; ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.5, 170.3, 140.5, 128.9, 127.3, 127.2, 70.2, 61.0, 54.5, 53.3, 52.4, 35.4, 32.7.; FTIR (neat): 2956, 1771, 17371603, 1496, 1453, 1435, 1375, 1265, 1242, 1190, 1149, 1088, 1070, 1057, 1026, 991, 963, 922, 820, 792, 753, 701 cm^{-1}.; HMRS *m/z* (DART) $[M+H]^+$: calcd for $C_{15}H_{17}O_4$: 261.1121; found: 261.1133.

*4.3.4. (3aRS,5RS,6aSR)-Methyl-3-oxo-5-methyltetrahydro-1H-cyclopenta[c]-furan-3a-carboxylate (**2d**)*

The product was obtained in 66% yield (39 mg, 0.2 mmol) after column chromatography on silica gel (*n*-hexane : EtOAc = 4 : 1) as a colorless oil.; ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.50 (dd, *J* = 9.2, 6.9 Hz, 1H), 4.16 (dd, *J* = 9.3, 1.2 Hz, 1H), 3.77 (s, 6H), 3.06-3.03 (m, 1H), 2.77-2.72 (m, 1H), 2.24-2.13 (m, 2H), 1.68-1.64 (m, 1H), 1.24-1.17 (m, 1H), 1.05 (d, *J* = 6.3 Hz, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.7, 170.6, 71.5, 61.1, 53.1, 47.5, 41.9, 41.4, 36.4, 18.6.; FTIR (neat): 2957, 2873, 1768, 1739, 1458, 1435, 1377, 1300, 1260, 1246, 1204, 1145, 1109, 1084, 1067, 1050, 1015, 985, 950, 844, 788, 722, 669 cm^{-1}.; HMRS *m/z* (DART) $[M+H]^+$: calcd for $C_{10}H_{15}O_4$: 199.0965; found: 199.0957.

*4.3.5. (3aRS,5RS,6aSR)-Methyl-3-oxo-5-allyltetrahydro-1H-cyclopenta[c]-furan-3a-carboxylate (**2e**)*

The product was obtained in 94% yield (63.1 mg 0.28 mmol) after column chromatography on silica gel (*n*-hexane : EtOAc = 4 : 1) as a colorless oil.; ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.74 (tdd, *J* = 17.0, 10.0, 6.8 Hz, 1H), 5.05-4.99 (m, 2H), 4.50 (dd, *J* = 9.2, 6.3 Hz, 1H), 4.16 (dd, *J* = 9.2, 1.7 Hz, 1H), 3.77 (s, 3H), 3.07-3.02 (m, 1H), 2.76-2.72 (m, 1H), 2.26-2.09 (m, 4H), 1.73 (dd, *J* = 14.3, 9.7 Hz, 1H), 1.27-1.20 (m, 1H).; ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.6, 170.5, 136.3, 116.2, 71.4, 60.7, 53.2, 47.1, 41.3, 39.4, 39.2, 38.3.; FTIR (neat): 2956, 2915, 1768, 1739, 1641, 1479, 1435, 1377, 1301, 1255, 1233, 1209, 1151, 1053, 986, 917, 846, 790, 728, 668 cm^{-1}.; HMRS *m/z* (DART) $[M+H]^+$: calcd for $C_{12}H_{17}O_4$: 225.1121; found: 225.1116. Data was consisted with the literature.[9e]

*4.3.6. (3aRS,5RS,6aSR)-Methyl-3-oxo-5-phenyltetrahydro-1H-cyclopenta[c]-furan-3a-carboxylate (**2f**)*

The product was obtained in 53% yield (41.7 mg, 0.16 mmol) after column chromatography on silica gel (*n*-hexane : EtOAc = 4 : 1) as a colorless oil.; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.21 (m, 5H), 4.58 (dd, *J* = 9.2, 6.3 Hz, 1H), 4.26 (dd, *J* = 9.2, 1.2 Hz, 1H), 3.82 (s, 3H), 3.34-3.26 (m, 1H), 3.21-3.16 (m, 1H), 3.06 (ddd, *J* = 13.8, 8.0, 1.7 Hz, 1H), 2.52-2.46 (m, 1H), 2.17 (dd, *J* = 13.8, 11.5 Hz, 1H), 1.78-1.70 (m, 1H).; ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.3, 170.4, 141.3, 128.6, 126.8, 128.8, 71.1, 60.5, 53.3, 47.3, 46.5, 40.8, 40.6.; FTIR (neat): 2956, 2349, 2326, 1769, 1239, 1711, 1603, 1496, 1435, 1378, 1256, 1238, 1222, 1204, 1148, 1116, 1100, 1060, 1030, 985, 935, 848, 755, 699, 672, 663 cm^{-1}.; HMRS *m/z* (DART) $[M+H]^+$: calcd for $C_{15}H_{17}O_4$: 261.1121; found: 261.1129.

*4.3.7. (3aRS,6aSR)-Methyl-4-methyl-3-oxotetrahydro-1H-cyclopenta[c]-furan-3a-carboxylate (**2g**)*

The product was obtained in 68% yield (40.4 mg, 0.2 mmol) after column chromatography on silica gel (*n*-hexane : EtOAc = 4 : 1) as a colorless oil.; ^{1}H NMR (500 MHz, $CDCl_3$): ***Major isomer*** δ 4.44 (dd, *J* = 9.2, 6.8 Hz, 1H), 4.12 (d, *J* = 9.2 Hz, 1H), 3.80 (s, 3H), 3.39-3.35 (m, 1H), 2.80-2.75 (m, 1H), 2.32-2.24 (m, 1H), 1.89-1.82 (m, 1H), 1.63-1.54 (m, 2H), 1.02 (d, *J* = 7.5 Hz, 3H). ***Minor isomer*** δ 4.56 (dd, *J* = 9.2, 7.5 Hz, 1H), 3.97 (dd, *J* = 9.2, 4.0 HZ, 1H), 3.80 (s, 3H), 3.26-3.23 (m, 1H), 2.75-2.71 (m, 1H), 2.02-1.93 (m, 2H), 1.71-1.69 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$): δ ***Major isomer*** 175.4, 168.4, 73.1, 65.9, 52.9, 42.9, 42.5, 33.8, 31.3, 16.1. δ ***Minor isomer*** 173.7, 170.7, 63.0, 53.0, 46.0, 42.3, 35.5, 32.3, 14.6 (one carbon atom was overlapped.).; FTIR (neat): 2957, 2877, 1770, 1726, 1454, 1435, 1378, 1243, 1167, 1145, 1053, 1004, 972, 955, 930, 797, 715, 667 cm^{-1}.; HMRS *m/z* (DART) $[M+H]^+$: calcd for $C_{10}H_{15}O_4$: 199.0965; found: 199.0957.

*4.3.8. (3aRS,6aSR)-Methyl-1,1-dimethyl-3-oxotetrahydro-1H-cyclopenta[c]-furan-3a-carboxylate (**2h**)*

The product was obtained in 78% yield (50 mg, 0.23 mmol) after column chromatography on silica gel (*n*-hexane : EtOAc = 4 : 1) as a colorless oil.; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.80 (s, 3H), 2.91-2.88 (m, 1H), 2.35-2.25 (m, 2H), 1.90-1.77 (m, 2H), 1.61-1.52 (m, 1H), 1.47 (s, 3H), 1.41 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.3, 171.8, 84.9, 63.8, 54.5, 53.1, 36.8, 30.3, 30.0, 26.6, 24.2.; FTIR (neat): 2956, 2873, 1761, 1729, 1649, 1435, 1389, 1374, 1328, 1256, 1222, 1179, 1160, 1104, 1058, 1037, 1000, 980, 960, 932, 922, 909, 876, 804, 786, 731 cm^{-1}.; HMRS *m/z* (DART) $[M+H]^+$: calcd for $C_{11}H_{17}O_4$: 213.1121; found: 213.1115.

*4.3.9. (1RS,3aRS,6aSR)-Methyl-1-phenyl-3-oxotetrahydro-1H-cyclopenta[c]-furan-3a-carboxylate (**2i**)*

The product was obtained in 71% yield (42.3 mg, 0.21 mmol) for the *E isomer* and 68% yield (40.1 mg, 0.2 mmol) for the *Z isomer* after column chromatography on silica gel (*n*-hexane : EtOAc = 4 : 1) as a colorless oil.; ^{1}H NMR (500 MHz, $CDCl_3$): ***Major isomer*** δ 4.27 (dq, *J* = 6.3, 4.0 Hz, 1H), 3.79 (s, 3H), 2.79-2.77 (m, 1H), 2.37-2.32 (m, 1H), 2.29-2.23 (m, 1H), 2.00-1.94 (m, 1H), 1.88-1.56 (m, 2H), 1.47 (d, *J* = 6.3 Hz, 3H). ***Minor isomer*** δ 4.89 (quin, *J* = 6.3 Hz, 1H), 3.78 (s, 3H), 2.95 (dd, *J* = 7.5, 6.3 Hz, 1H), 2.43-2.38 (m, 1H), 2.29-2.23 (m, 1H), 1.89-1.56 (m, 4H), 1.40 (d, *J* = 6.3 Hz, 1H).; ^{13}C NMR (125 MHz, $CDCl_3$): δ ***Major isomer*** 175.9, 171.1, 82.4, 62.6, 53.1, 52.2, 35.4, 33.9, 25.7, 22.0. ***Minor isomer*** δ 176.0, 170.6, 63.8, 53.0, 50.7, 34.3, 27.1, 26.4, 16.1 (one carbon atom was overlapped.).; FTIR (neat): 2956, 2873, 1765, 1737, 1450, 1435, 1384, 1352, 1253, 1207, 1162, 1128, 1108, 1059, 1039, 992, 976, 936, 913, 803, 733, 660 cm^{-1}.; HMRS *m/z* (DART) $[M+H]^+$: calcd for $C_{10}H_{15}O_4$: 199.0965; found: 199.0963. Data was consisted with the literature.[8i]

*4.3.10. (1RS,3aRS,6aSR)-Methyl-1-methyl-3-oxotetrahydro-1H-cyclopenta[c]-furan-3a-carboxylate (**2j**)*

The product was obtained in 31% yield (24.3 mg, 0.093 mmol) for the *E isomer* and 62% yield (48.5 mg, 0.19 mmol) for the *Z isomer* after column chromatography on silica gel (*n*-hexane : EtOAc = 4 : 1) as a colorless oil.; ^{1}H NMR (500 MHz, $CDCl_3$): ***Major isomer*** δ 7.41-7.27 (m, 5H), 5.05 (d, *J* = 4.6 Hz, 1H), 3.72 (s, 3H), 3.15 (ddd, *J* = 7.0, 4.6, 1.9 Hz, 1H), 2.47-2.32 (m, 2H), 2.05-1.90 (m, 3H). ***Minor isomer*** δ 7.41-7.27 (m, 5H), 5.88 (d, *J* = 6.9 Hz, 1H), 3.84 (s, 3H), 3.33-3.29 (ddd, *J* = 8.8, 6.9. 5.6 Hz, 1H), 2.48-2.35 (m, 2H), 1.70-1.50 (m, 3H), 1.30-1.24 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): ***Major isomer*** δ 175.9, 1708, 139.7, 128.7, 128.5, 125.4, 86.0, 54.3, 53.1, 35.2, 33.6, 25.5. ***Minor isomer*** δ 175.9, 170.8, 136.4, 128.6, 128.0, 124.9, 81.4, 63.6, 53.2, 34.7, 28.5, 25.9.; FTIR (neat): 2955, 2872, 1769, 1738,

1497, 1451, 1435, 1340, 1254, 1235, 1212, 1195, 1148, 1097, 1055, 1007, 924, 842, 766, 735, 718, 698 cm^{-1}.; HMRS *m/z* (DART) $[M+H]^+$: calcd for $C_{15}H_{17}O_4$: 261.1121; found: 261.1127. Data was consisted with the literature.[9a]

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Supplementary Material

Supplementary data associated with this article can be found in the online version at doi: