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A flexible approach to hexahydronaphthalene-1-carboxylates

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Dedicated with respect and admiration to Professor Gilbert Stork on the occasion of his 90th birthday

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ABSTRACT

A flexible approach to hexahydronaphthalene-1-carboxylates based on the Favorskii rearrangement of 1,1-dichloro bicyclo[5.4.0]undec-5-en-2-ones has been devised. 1,1-Dichloro bicyclo[5.4.0]undec-5-en-2-ones can be prepared from readily available cyclohexanones by a short sequence.

1. Introduction

Hexahydronaphthalenecarboxylates (Fig. 1) have proved to be versatile building blocks in natural product synthesis,[1] but, to date, only few reports have described their synthesis.[1,2] The most popular approach to these scaffolds uses the Diels–Alder reaction as the key step.[3] However, the intra-molecular Diels–Alder reaction only affords hexahydronaphthalene-1-carboxylates of general structure **III**,[1,2b,d] while the intermolecular cycloaddition is complicated by regioselectivity problems and leads to mixtures of isomeric hexahydronaphthalenecarboxylates **I** and **II**.[2a,c]

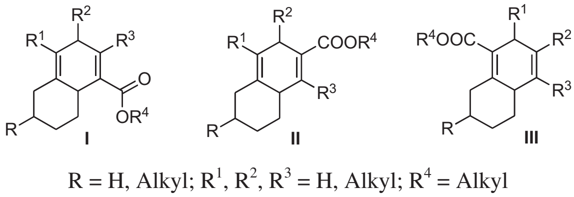
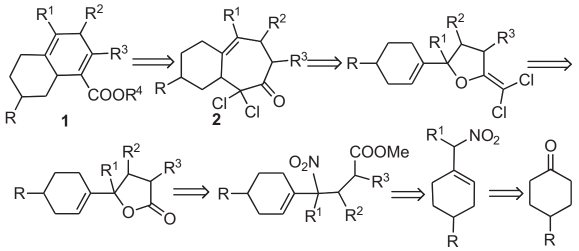


Fig. 1. Hexahydronaphthalenecarboxylates **I**, **II**, and **III**.

2. Results/discussion

In the present article, we describe a completely different strategy for the construction of hexahydronaphthalenecarboxylates. Our conception, outlined in Scheme 1, hinges on the sole obtention of hexahydronaphthalene-1-carboxylate **I** via the Favorskii rearrangement of 1,1-dichloro bicyclo[5.4.0]undec-5-en-2-ones **2**.[4] Precusors **2** could in principle be prepared from readily available cyclohexanones by exploiting the rich chemistry of allylic nitro intermediates, as shown by the sequence in Scheme 1.



Scheme 1. Synthetic route to structures **I**.

We therefore began our work by preparing the requisite allylic nitro starting compounds **3**.[5] As shown in Scheme 2, these nitro compounds **3** can be obtained in good yield by condensation of the corresponding cyclohexanones with nitromethane or nitroethane

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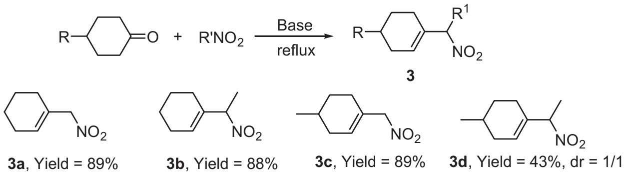
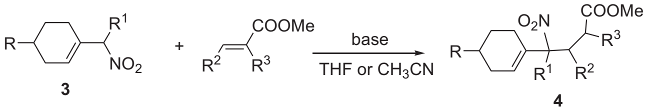
in the presence of ethylenediamine (for synthesis of **3a** and **3c**) or *N*,*N*-dimethylethylenediamine (for synthesis of **3b** and **3d**) as base. We had previously demonstrated that ethylenediamine and some of its congeners were particularly effective catalysts for this transformation.[5a,b]

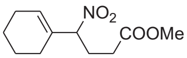
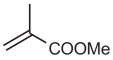
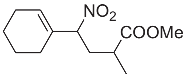
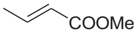
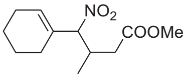
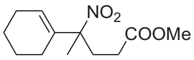
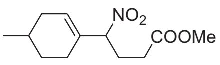
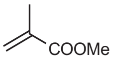
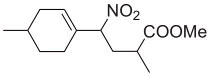
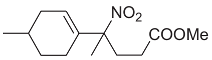


Scheme 2. Synthesis of nitro compounds **3**.

With nitro compounds **3** in hand, we set out to assemble γ-nitro esters **4** by the Michael addition of **3** with various α,β-unsaturated esters in the presence of base.[5d,f,6] Triethylamine was used for the synthesis of **4a** (Table 1, entry 1), DBU for the synthesis of **4b**, **4c**, **4d**, **4f**, and **4g** (Table 1, entries 2, 3, 4, 6, and 7), and KF for the synthesis of **4e** (Table 1, entry 5). The γ-nitro esters **4** were obtained in moderate to good yield and the diastereomeric ratios for **4b**, **4c**, **4e**, **4g**, and **4f** were 3:2, 3:2, 1:1, 1:1, and 3:3:2:2, respectively (Table 1, entries 2, 3, 5, 7, and 6). The choice of the base was empirical. We found that the use of the stronger base DBU was advantageous when either the nitroalkene or the unsaturated ester was substituted near the reacting centers and therefore somewhat less reactive.

Table 1
Synthesis of γ-nitro esters **4**

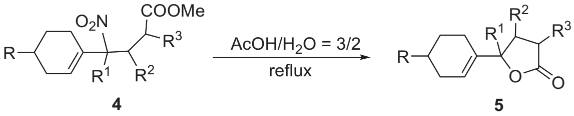


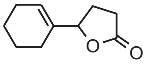
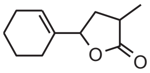
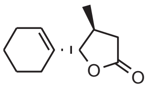
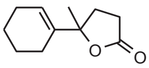
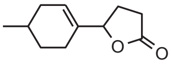
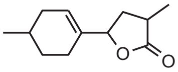
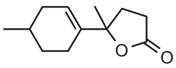
Entry	Substrate **3**	Michael acceptor	γ-Nitro esters **4**	Yield[a] [%]
1	**3a**		 **4a**	74[f]
2	**3a**		 **4b**	59[b,e,g]
3	**3a**		 **4c**	37[b,e,g]
4	**3b**		 **4d**	87[g]
5	**3c**		 **4e**	78[c,e,h]
6	**3c**		 **4f**	57[d,e,g]
7	**3d**		 **4g**	96[c,e,g]

[a] Isolated yield.
[b] dr=3:2.
[c] dr=1:1.
[d] dr=3:3:2:2.
[e] Diastereomeric ratio were determined by the ^{1}H NMR of the crude product.
[f] Et_3N as base.
[g] DBU as base.
[h] KF as base.

Upon refluxing in a mixture of $AcOH/H_2O$ (v/v=3:2) overnight, the γ-nitro esters **4** were converted into lactones **5** smoothly and in good yield (Table 2).[7] The diastereomeric ratios of **5b**, **5e**, and **5g** were 3:2, 1:1, and 1:1, respectively (Table 2, entries 2, 5,and 7). γ-Nitro ester **4f** was converted into **5f** and **5f′** in 2:3 ratio with 62% total yield (Table 2, entry 6). Compounds **5f** and **5f′** can be separated by flash column chromatography and the ^{1}H NMR of **5f** and **5f′** indicated that both of **5f** and **5f′** were diastereoisomers with 1:1 diastereomeric ratio.

Table 2
Synthesis of lactones **5**



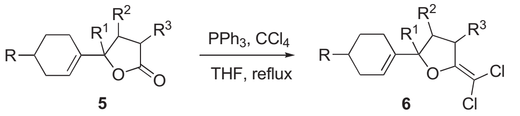
Entry	Esters **4**	Lactones **5**	Yield[a] [%]
1	**4a**	 **5a**	76
2	**4b**	 **5b**	71[b,e]
3	**4c**	 **5c**	61
4	**4d**	 **5d**	59
5	**4e**	 **5e**	78[c,e]
6	**4f**	 **5f/5f’**	62[d,e]
7	**4g**	 **5g**	50[c,e]

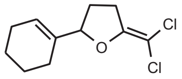
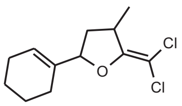
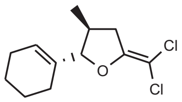
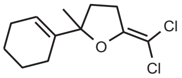
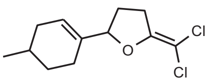
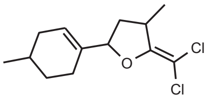
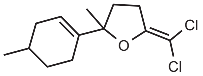
[a] Isolated yield.
[b] dr=3:2.
[c] dr=1:1.
[d] Total yield of **5f** and **5f′**. **5f**/**5f′**=2:3. Compound **5f** (R_f=0.5, petroleum/EtOAc=10:1), Compound **5f′** (R_f=0.4, petroleum/EtOAc=10:1). Both of **5f** and **5f′** are diastereoisomers with 1:1 diastereomeric ratio.
[e] Diastereomeric ratio was determined by the ^{1}H NMR of the crude product.

The formation of unsaturated lactones **5** by solvolysis of the allylic nitro group is a key transformation in the sequence. It was discovered serendipitously two decades ago[7a] and opens up numerous possibilities for synthesis since it simplifies considerably the access to unsaturated lactones. Such compounds are not trivial to prepare by more traditional approaches.

Our next task was to prepare dichlorovinyl compounds **6** from lactones **5** by a Wittig type condensation. The desired dichloromethylenation was smoothly accomplished using PPh_3 and CCl_4 in THF.[8] As shown by the results collected in Table 3, the yields were variable and ranged from moderate to good. The diastereomeric ratios of **6b**, **6e**, **6f**, and **6g** were 4:1, 1:1, 1:1, and 1:1, respectively (Table 3, entries 2, 5, 6, and 7). Compounds **6b** and **6d** could be obtained in 80% and 62% yields, respectively, based on recovered starting material (Table 3, entries 2 and 4).

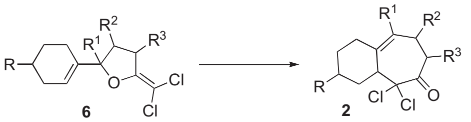
Table 3
Synthesis of dichlorovinyl enol ethers **6**

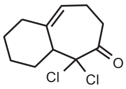
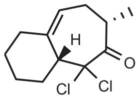
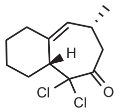
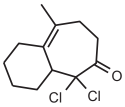
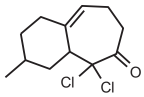
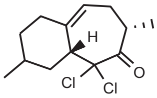
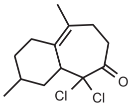


Entry	Lactones **5**	Products **6**	Yield[a] [%]
1	**5a**	 **6a**	51
2	**5b**	 **6b**	51[b,e] (80)[c]
3	**5c**	 **6c**	76
4	**5d**	 **6d**	38 (62)[c]
5	**5e**	 **6e**	59[d,e]
6	**5f**	 **6f**	82[d,e]
7	**5g**	 **6g**	55[d,e]

[a] Isolated yield.
[b] dr=4:1.
[c] Yield based on recovered starting material.
[d] dr=1:1.
[e] Diastereomeric ratio was determined by the ^{1}H NMR of the crude product.

Table 4
Claisen rearrangement of intermediates **6**



Entry	Compounds **6**	Products **2**	Yield[a] [%]
1	**6a**	 **2a**	43[e]
2	**6b**	 **2b**	38 (50)[b,e]
3	**6c**	 **2c**	40[g]
4	**6d**	 **2d**	62 (73)[b,f]
5	**6e**	 **2e**	58[c,d,g]
6	**6f**	 **2f**	59[c,d,g]
7	**6g**	 **2g**	56[c,d,f] (72)[b]

[a] Isolated yield.
[b] Yield based on recovered starting material.
[c] dr=1:1.
[d] Diastereomeric ratio was determined by the ^{1}H NMR of the crude product.
[e] The solvent is chlorobenzene.
[f] The solvent is toluene.
[g] The solvent is mesitylene.

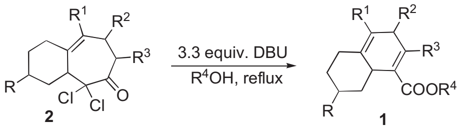
We were now in a position to access the 1,1-dichloro bicyclo[5.4.0]undec-5-en-2-ones **2** from precursors **6** via the Claisen rearrangement.[9] Indeed, the desired sigmatropic rearrangement proceeded reasonably cleanly upon prolonged (12–17 h) heating to reflux a solution of dichlorovinyl ethers **6** in chlorobenzene in the case of **2a** and **2b** (Table 4, entries 1 and 2), in toluene in the case of **2d** and **2g** (Table 4, entries 4 and 7), or in mesitylene in the case of **2c**, **2e**, and **2f** (Table 4, entries 3, 5, and 6). The various 1,1-dichloro bicyclo[5.4.0]undec-5-en-2-ones **2** were obtained in useful yields as summarized in Table 4. The diastereomeric ratios of **2e**, **2f**, and **2g** were 1:1 (Table 4, entries 5, 6, and 7). Dichloroketones **2b**, **2d**, and **2g** could be obtained in 50%, 73%, and 72% yields, respectively, based on recovered starting material (Table 4, entries 2, 4, and 7).

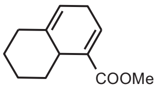
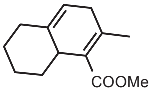
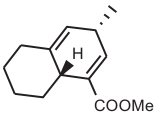
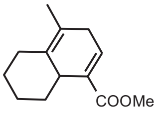
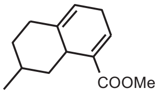
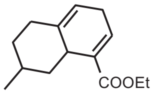
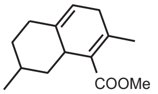
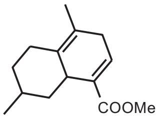
Finally, for synthesis of the 3,5,6,7,8,8a-hexahydronaphthalene-1-carboxylates **1**, the Favorskii rearrangement[4] of the 1,1-dichloro bicyclo[5.4.0]undec-5-en-2-ones, **2**, was attempted. Dichloroketones **2** and DBU were dissolved in MeOH (Table 5, entries 1–5 and entries 7, 8) or EtOH (Table 5, entry 6) and the solutions were heated to reflux under N_2 atmosphere for 30 min. The anticipated Favorskii rearrangement took place smoothly and afforded the desired 3,5,6,7,8,8a-hexahydronaphthalene-1-carboxylates **1** in good yield (Table 5). The hexahydronaphthalene-1-carboxylates **1** could be methyl esters (Table 5, entries 1–5 and entries 7, 8) or ethyl esters (Table 5, entry 6). Methyl groups could be appended in the 2-position (Table 5, entries 2 and 7), in the 3-position (Table 5, entry 3), in the 4-position (Table 5, entries 4 and 8), and in the 7-position (Table 5, entries 5–8). The diastereomeric ratios of **1e**, **1g**, **1f**, and **1h** were 1:1, 1:1, 4:7, and 2:3, respectively (Table 5, entries 5, 7, 6, and 8). It is interesting to note that no alkene migration to give conjugated dienes was observed under the reaction conditions.

3. Conclusion

In summary, we have established a flexible approach to 3,5,6,7,8,8a-hexahydronaphthalene-1-carboxylates **1**. It highlights the utility of the unsaturated lactone formation from allylic nitro compounds and features an uncommon variant of the Favorskii rearrangement involving an α,α-dichloroketone (normally monohaloketones are used). This furnishes in the present case 1,4-cyclohexadienes with a substitution pattern that is not readily accessible through a Birch reduction of a substituted benzene ring or by an inter-or intra-molecular Diels–Alder reaction. There is also a broad scope for introducing substituents, as these may be placed

Table 5
Favorskii rearrangement of substances **2**



Entry	Substrates **2**	Products **1**	Yield[a] [%]
1	**2a**	 **1a**	58[f]
2	**2b**	 **1b**	58[f]
3	**2c**	 **1c**	65[f]
4	**2d**	 **1d**	77[f]
5	**2e**	 **1e**	68[b,e,f]
6	**2e**	 **1f**	57[c,e,g]
7	**2f**	 **1g**	77[b,e,f]
8	**2g**	 **1h**	84[d,e,f]

[a] Isolated yield.
[b] dr=1:1.
[c] dr=4:7.
[d] dr=2:3.
[e] Diastereomeric ratio was determined by the ^{1}H NMR of the crude product.
[f] The solvent is MeOH.
[g] The solvent is EtOH.

on the starting ketone and on the acrylate partner. Finally, it is worth pointing out that the [5.4.0]undecane intermediates **2** are interesting in their own right, as they correspond to core structures found in numerous terpenes.

4. Experimental section

4.1. General

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on Bruker (400 MHz) spectrometer. Chemical shifts were reported in parts per m relative to $(CH_3)_4Si$ (0 ppm, ^{1}H) or $CDCl_3$ (77.0 ppm, ^{13}C). IR spectra were recorded on PERKIN ELMER 2000 FT-IR spectrometer. Mass spectra were recorded on JOEL GCmateIImass spectrometer (EI).

Reactions were conducted under nitrogen atmosphere unless otherwise noted. Thin layer chromatography (TLC) was performed on Silica Gel 60 F_{254} plates and visualized with UV light, $KMnO_4$ stain or vanillin stain. THF was distilled from sodium benzophenone ketyl radical prior to use.

4.2. Synthesis of nitro compounds 3

*4.2.1. Nitro compound **3a**.* A solution of cyclohexanone (1.0 equiv, 0.102 mol, 10 g) and ethylenediamine (0.05 equiv 5.1 mmol, 0.34 mL) in 70 mL nitromethane was heated to reflux under nitrogen atmosphere for 7 h. After cooling to room temperature, the solvent was removed under vacuum and the residue was purified by flash chromatography (SiO_2, petroleum ether/ethyl acetate=10:1) to afford the nitro compound **3a** (12.9 g, 89% yield) as a yellow oil. IR (neat): 2941, 2863, 2839, 1555, 1436, 1427, 1369, 1302 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.90 (s, 1H), 4.77 (s, 2H), 2.08–2.04 (m, 4H), 1.68–1.62 (m, 2H), 1.59–1.54 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 133.0, 128.4, 82.6, 26.4, 25.2, 22.0, 21.3. HRMS (EI): m/z calcd for $[C_7H_{11}NO_2-NO_2]^+$: 95.0860. Found: 95.0861.

*4.2.2. Nitro compound **3b**.* A solution of cyclohexanone (1.0 equiv, 0.051 mol, 5 g) and *N*,*N*-dimethyl ethane-1,2-diamine (0.25 equiv, 12.7 mmol, 1.4 mL) in 55 mL nitroethane was heated to reflux under nitrogen atmosphere while removing the water through a Dean–Stark apparatus. After 24 h, the resulting mixture was allowed to cool to room temperature and the solvent was removed under vacuum. The residue was purified by flash chromatography (SiO_2, petroleum ether/ethyl acetate=10:1) to afford the nitro compound **3b** (6.9 g, 88% yield) as a yellow oil. IR (neat): 1540 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.92 (s, 1H), 4.97 (q, J=6.9 Hz, 1H), 2.10–1.98 (m, 4H), 1.67–1.62 (m, 4H), 1.61 (d, J=6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 132.9, 129.6, 88.3, 25.1, 24.1, 22.2, 21.7, 16.8. HRMS (EI): m/z calcd for $[C_8H_{13}NO_2]$: 155.0946. Found: 155.0945. The ^{1}H NMR and the ^{13}C NMR spectral data are consistent with the literature.[5c]

*4.2.3. Nitro compound **3c**.* A solution of 4-methyl cyclohexanone (1.0 equiv, 0.1 mol, 11 g) and ethylene diamine (0.05 equiv 5.1 mmol, 0.34 mL) in 65 mL nitromethane was heated to reflux under nitrogen atmosphere for 7 h. After cooling to room temperature, the solvent was removed under vacuum and the residue was purified by flash chromatography (SiO_2, petroleum ether/ethyl acetate=10:1) to afford the nitro compound **3c** (13.8 g, 89% yield) as a yellow oil. IR (neat): 2955, 2927, 2913, 2878, 1555, 1456, 1427, 1371 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.85 (s, 1H), 4.76 (s, 2H), 2.17–2.13 (m, 1H), 2.07–2.06 (m, 2H), 1.73–1.58 (m, 3H), 1.28–1.18 (m, 1H), 0.92 (d, J=6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 132.5, 128.0, 82.2, 33.6, 30.1, 27.4, 26.3, 21.1. HRMS (EI): m/z calcd for $[C_8H_{13}NO_2]$: 155.0946. Found: 155.0940.

*4.2.4. Nitro compound **3d**.* A solution of 4-methyl cyclohexanone (1.0 equiv, 0.1 mol, 11 g) and *N*,*N*-dimethyl ethane-1,2-diamine (0.25 equiv, 25 mmol, 2.8 mL) in 70 mL nitroethane was heated to reflux under nitrogen atmosphere while removing the water through a Dean–Stark. After 7 h, the resulting mixture was allowed to cool to room temperature and the solvent was removed under vacuum. The residue was purified by flash chromatography (SiO_2, petroleum ether/ethyl acetate=10:1) to afford the nitro compound **3d** (7.2 g, 43% yield, dr=1:1) as a yellow oil. IR (neat): 2954, 2927, 2878, 1551, 1456, 1383, 1355, 1274 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.87–5.84 (m, 1H), 4.96 (q, J=6.8 Hz, 1H), 2.18–2.10 (m, 1H), 2.07–1.92 (m, 2H), 1.76–1.61 (m, 3H), 1.60–1.57 (m, 3H), 1.26–1.15 (m, 1H), 0.94–0.92 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 132.6, 132.5, 129.4, 128.9, 88.1, 87.9, 33.6, 33.4, 30.3, 30.2, 27.8, 27.6, 24.3, 23.9, 21.4, 21.1, 17.0, 16.7. HRMS (EI): m/z calcd for $[C_9H_{15}NO_2-NO_2]^+$: 123.1174. Found: 123.1176.

4.3. Synthesis of γ-nitro esters 4

*4.3.1. γ-Nitro ester **4a**.* A solution of **3a** (1.0 equiv, 21.3 mmol, 3 g), methyl acrylate (3.0 equiv, 63.8 mmol, 5.75 mL), and triethylamine (0.25 equiv, 5.3 mmol, 0.74 mL) in 17 mL acetonitrile was heated to reflux under nitrogen atmosphere for 20 h. After cooling to room temperature, the solvent was removed under vacuum. The residue was purified by flash chromatography (SiO_2, petroleum ether/Et_2O=9:1) to afford the ester **4a** (3.6 g, 74% yield) as a yellow oil. IR (neat): 2938, 2861, 1743, 1546, 1437, 1365, 1202 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.96–5.94 (m, 1H), 4.92 (t, J=7.2 Hz, 1H), 3.70 (s, 3H), 2.52–2.43 (m, 1H), 2.36–2.32 (m, 2H), 2.25–2.16 (m, 1H), 2.12–2.09 (m, 2H), 2.02–2.01 (m, 2H), 1.68–1.54 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 172.4, 131.5, 92.3, 51.8, 30.0, 25.7, 25.2, 23.9, 22.1, 21.6. HRMS (EI): m/z calcd for $[C_{11}H_{17}NO_4]$: 227.1158. Found: 227.1154.

*4.3.2. γ-Nitro ester **4b**.* A solution of **3a** (1.0 equiv, 7.1 mmol, 1 g), methyl methacrylate (3.0 equiv, 21.3 mmol, 2.28 mL), and DBU (0.5 equiv, 3.5 mmol, 0.53 mL) in 10 mL acetonitrile was stirred at room temperature for 6 h. After removal of the solvent under vacuum, the residue was purified by flash chromatography (SiO_2, petroleum ether/Et_2O=9:1) to afford the ester **4b** (1 g, 59% yield, dr=3:2) as a yellow oil. IR (neat): 1741, 1549, 1213 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.91–5.90 (m, 1H), 4.93–4.85 (m, 1H), 3.68 (s, 1.8H), 3.66 (s, 1.2H), 2.55–2.48 (m, 0.5H), 2.43–2.32 (m, 1H), 2.23–2.18 (m, 1H), 2.07–2.06 (m, 2H), 2.02–1.95 (m, 2.5H), 1.63–1.51 (m, 4H), 1.22–1.18 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 175.6, 175.3, 131.9, 131.6, 130.8, 91.8, 91.0, 51.8, 36.3, 36.0, 34.4, 33.8, 25.2, 24.0, 23.9, 22.1, 21.6, 17.6, 17.2. HRMS (EI): m/z calcd for $[C_{12}H_{19}NO_4]$: 241.1314. Found: 241.1309.

*4.3.3. γ-Nitro ester **4c**.* A solution of **3a** (1.0 equiv, 7.1 mmol, 1 g), methyl crotonate (3.0 equiv, 21.3 mmol, 2.28 mL), and DBU (0.5 equiv, 3.5 mmol, 0.53 mL) in 10 mL acetonitrile was stirred at room temperature for 12 h. After removal of the solvent under vacuum, the residue was purified by flash chromatography (SiO_2, petroleum ether/Et_2O=9:1) to afford the ester **4c** (0.628 g, 37% yield, dr=3:2) as a yellow oil. IR (neat): 2940, 2840, 1743, 1551, 1437, 1362 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.96–5.95 (m, 1H), 4.72–4.68 (m, 1H), 3.67 (s, 1.8H), 3.66 (s, 1.2H), 2.87–2.77 (m, 1H), 2.39–2.29 (m, 1H), 2.21–2.06 (m, 4H), 1.63–1.54 (m, 5H), 1.01 (d, J=6.4 Hz, 1.8H), 0.91 (d, J=6.4 Hz, 1.2H). ^{13}C NMR ($CDCl_3$): δ 171.7, 133.3, 132.7, 131.0, 130.9, 99.0, 98.3, 51.7, 51.6, 37.5, 36.8, 30.7, 25.4, 23.7, 22.2, 21.7, 21.6, 16.7, 15.6. HRMS (EI): m/z calcd for $[C_{12}H_{19}NO_4]$: 241.1314. Found: 241.1316.

*4.3.4. γ-Nitro ester **4d**.* A solution of **3b** (1.0 equiv, 6.5 mmol, 1 g), methyl acrylate (3.0 equiv, 19.4 mmol, 1.74 mL), and DBU (0.25 equiv, 5.3 mmol, 0.24 mL) in 10 mL acetonitrile was heated to reflux under nitrogen atmosphere for 30 min. After cooling to room temperature, the solvent was removed under vacuum. The residue was purified by flash chromatography (SiO_2, petroleum ether/Et_2O=9:1) to afford the ester **4d** (1.4 g, 87% yield) as a yellow oil. IR (neat): 1756, 1546 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.89–5.85 (m, 1H), 3.69 (s, 3H), 2.48–2.34 (m, 2H), 2.29–2.22 (m, 2H), 2.15–2.10 (m, 2H), 1.87–1.85 (m, 2H), 1.64 (s, 3H), 1.61–1.55 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 172.8, 134.8, 126.8, 94.0, 51.9, 31.8, 29.9, 25.7, 24.6, 22.9, 22.7, 22.0. HRMS (EI): m/z calcd for $[C_{12}H_{19}NO_4]$: 241.1314. Found: 241.1317.

*4.3.5. γ-Nitro ester **4e**.* To a solution of **3c** (1.0 equiv, 20 mmol, 3.1 g) and methyl acrylate (22.0 equiv, 440 mmol, 32 mL) in 100 mL MeOH was added KF (2.6 equiv, 51 mmol, 3 g). The mixture was heated to reflux under nitrogen atmosphere for 4 h. The solvent was removed under vacuum and 30 mL of water was added to the residue. After extraction with Et_2O (3×10 mL), the combined organic layer was dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under vacuum and the residue was purified by flash chromatography (SiO_2, petroleum ether/EtOAc=10:1) to afford the ester **4e** (3.76 g, 78% yield, dr=1:1) as a yellow oil. IR (neat): 2954, 2928, 1743, 1552, 1437, 1239, 1176 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.89–5.87 (m, 1H), 4.89 (t, J=7.6 Hz, 1H), 3.65 (s, 3H), 2.45–2.38 (m, 1H), 2.31–2.27 (m, 2H), 2.20–2.10 (m, 2H), 2.03–1.92 (m, 2H), 1.73–1.55 (m, 3H), 1.24–1.14 (m, 1H), 0.92 (d, J=2.4 Hz, 1.5H), 0.90 (d, J=2.4 Hz, 1.5H). ^{13}C NMR ($CDCl_3$): δ 172.3, 172.2, 131.1, 131.0, 130.7, 92.0, 91.9, 51.7, 33.6, 33.5, 30.2, 30.1, 29.9, 27.8, 27.5, 25.9, 25.5, 24.0, 23.6, 21.3, 21.1. HRMS (EI): m/z calcd for $[C_{12}H_{19}NO_4]$: 241.1314. Found: 241.1318.

*4.3.6. γ-Nitro ester **4f**.* A solution of **3c** (1.0 equiv, 20 mmol, 3.1 g), methyl methacrylate (3.0 equiv, 60 mmol, 6.4 mL), and DBU (0.5 equiv, 10 mmol, 1.6 mL) in 15 mL acetonitrile was stirred at room temperature for 12 h. After removal of the solvent under vacuum, the residue was purified by flash chromatography (SiO_2, petroleum ether/EtOAc=10:1) to afford the ester **4f** (2.9 g, 57% yield, dr=3:3:2:2) as a yellow oil. IR (neat): 2954, 1739, 1552, 1457, 1435, 1359, 1173 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.87–5.85 (m, 1H), 4.94–4.85 (m, 1H), 3.66–3.65 (m, 3H), 2.40–2.31 (m, 1H), 2.25–1.89 (m, 5H), 1.73–1.52 (m, 3H), 1.21–1.17 (m, 4H), 0.93–0.91 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 175.5, 175.3, 131.5, 131.4, 131.3, 131.2, 131.1, 131.0, 130.6, 130.2, 91.5, 90.7, 51.7, 36.3, 35.9, 34.6, 34.2, 34.1, 33.7, 33.6, 30.3, 30.2, 27.8, 27.5, 24.1, 24.0, 23.8, 23.6, 21.3, 21.2, 21.1, 17.5, 17.1. HRMS (EI): m/z calcd for $[C_{13}H_{21}NO_4]$: 255.1471. Found: 255.1477.

*4.3.7. γ-Nitro ester **4g**.* A solution of **3d** (1.0 equiv, 6.5 mmol, 1.1 g), methyl acrylate (3.0 equiv, 19.4 mmol, 1.74 mL), and DBU (0.5 equiv, 3.3 mmol, 0.33 mL) in 15 mL THF was heated to reflux for 5 h. After cooling to room temperature, the solvent was removed under vacuum and the residue was purified by flash chromatography (SiO_2, petroleum ether/EtOAc=20:1) to afford the ester **4g** (1.6 g, 96% yield, dr=1:1) as a yellow oil. IR (neat): 2955, 1743, 1543, 1437, 1343, 1239, 1198 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.80 (s, 1H), 3.64 (m, 3H), 2.46–2.30 (m, 2H), 2.22–2.16 (m, 3H), 1.94–1.81 (m, 2H), 1.70–1.64 (m, 2H), 1.60–1.59 (m, 4H), 1.21–1.11 (m, 1H), 0.91–0.89 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 172.6, 134.5, 134.3, 126.5, 126.2, 93.8, 93.7, 51.7, 33.7, 33.6, 31.6, 31.2, 30.5, 30.4, 29.3, 27.7, 27.4, 24.3, 23.9, 22.2, 22.1, 21.3, 21.2. HRMS (EI): m/z calcd for $[C_{13}H_{21}NO_4]$: 255.1471. Found: 255.1473.

4.4. General procedure for synthesis of lactones 5

The appropriate ester **4** was dissolved in a mixture of $AcOH/H_2O$ (v/v=3:2) and the resultant solution was heated to reflux overnight. After cooling to room temperature, the mixture was added slowly to a saturated Na_2CO_3 solution. The resultant mixture was extracted with Et_2O and the combined organic layer was back-extracted with water. The organic layer was dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under vacuum and the residue was purified by flash chromatography (SiO_2, petroleum ether/EtOAc=10:1) to afford the lactones **5**.

*4.4.1. Lactone **5a**.* A solution of **4a** (1.0 equiv, 15.9 mmol, 3.6 g) in 107 mL of $AcOH/H_2O$ (v/v=3:2) was subjected to the general procedure (SiO_2, petroleum ether/Et_2O=3:2), affording the lactone **5a** (2.0 g, 76% yield) as a yellow oil. IR (neat): 2934, 2860, 1782, 1713, 1436, 1320, 1291, 1188, 1138 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.72 (s, 1H), 4.78 (t, J=7.5 Hz, 1H), 2.51–2.46 (m, 2H), 2.27–1.91 (m, 6H), 1.61–1.52 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 177.3, 134.5, 125.0, 83.8, 28.7, 26.3, 24.6, 23.0, 22.0. HRMS (EI): m/z calcd for $[C_{10}H_{14}O_2]$: 166.0994. Found: 166.0997.

*4.4.2. Lactone **5b**.* A solution of **4b** (1.0 equiv, 4.1 mmol, 0.985 g) in 30 mL of $AcOH/H_2O$ (v/v=3:2) was subjected to the general procedure (SiO_2, petroleum ether/EtOAc=10:1), affording the lactone

5b (0.522 g, 71% yield, dr=3:2) as a yellow oil. IR (neat): 2934, 1780, 1437, 1201, 1158, 1118 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.80 (s, 0.6H), 5.74 (s, 0.4H), 4.83–4.80 (m, 0.4H), 4.68 (dd, *J*=7.6, 14.4 Hz, 0.6H), 2.73–2.63 (m, 1H), 2.45–2.38 (m, 0.6H), 2.33–2.26 (m, 0.4H), 2.04 (br s, 2H), 2.00–1.94 (m, 2H), 1.78–1.69 (m, 1H), 1.67–1.52 (m, 4H), 1.29–1.26 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 179.3, 134.5, 125.5, 124.1, 81.6, 80.8, 35.9, 35.6, 34.2, 33.9, 24.8, 24.7, 23.8, 23.2, 22.2, 15.7, 14.9. HRMS (EI): *m/z* calcd for [$C_{11}H_{16}O_2$]: 180.1150. Found: 180.1145.

4.4.3. Lactone ***5c****.* A solution of **4c** (1.0 equiv, 1.3 mmol, 300 mg) in 9 mL of AcOH/H_2O (v/v=3:2) was subjected to the general procedure (SiO_2, petroleum ether/EtOAc=10:1), affording the lactone **5c** (143 mg, 61% yield) as a yellow oil. IR (neat): 2932, 2861, 1787, 1456, 1437, 1280, 1209 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.76 (s, 1H), 4.29 (d, *J*=8.0 Hz, 1H), 2.69–2.63 (m, 1H), 2.44–2.36 (m, 1H), 2.21–2.14 (m, 1H), 2.05–2.01 (m, 3H), 1.92–1.87 (m, 1H), 1.67–1.52 (m, 4H), 1.09 (d, *J*=6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 176.3, 133.4, 127.1, 91.2, 37.0, 34.0, 24.9, 23.0, 22.2, 17.1. HRMS (EI): *m/z* calcd for [$C_{11}H_{16}O_2$]: 180.1150. Found: 180.1147.

4.4.4. Lactone ***5d****.* A solution of **4d** (1.0 equiv, 5.4 mmol, 1.3 g) in 40 mL of AcOH/H_2O (v/v=3:2) was subjected to the general procedure (SiO_2, petroleum ether/Et_2O=7:3), affording the lactone **5d** (573 mg, 59% yield) as a yellow oil. IR (neat): 1779 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.74 (s, 1H), 2.55–2.51 (m, 2H), 2.31–2.23 (m, 1H), 2.03–1.98 (m, 5H), 1.60–1.56 (m, 4H), 1.48 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 176.8, 138.2, 120.9, 87.8, 32.5, 28.8, 25.7, 24.6, 24.1, 22.5, 21.9. HRMS (EI): *m/z* calcd for [$C_{11}H_{16}O_2$]: 180.1150. Found: 180.1152.

4.4.5. Lactone ***5e****.* A solution of **4e** (1.0 equiv, 5 mmol, 1.2 g) in 30 mL of AcOH/H_2O (v/v=3:2) was subjected to the general procedure (SiO_2, petroleum ether/EtOAc=10:1), affording the lactone **5e** (700 mg, 78% yield, dr=1:1) as a yellow oil. IR (neat): 2954, 2927, 1784, 1715, 1457, 1423, 1289, 1187, 1140 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.73–5.70 (m, 1H), 4.82 (t, *J*=7.6 Hz, 1H), 2.53–2.49 (m, 2H), 2.32–2.22 (m, 1H), 2.12–1.97 (m, 4H), 1.75–1.70 (m, 1H), 1.68–1.56 (m, 2H), 1.26–1.12 (m, 1H), 0.93 (d, *J*=2.4 Hz, 1.5H), 0.92 (d, *J*=2.4 Hz, 1.5H). ^{13}C NMR ($CDCl_3$): δ 177.2, 134.3, 125.3, 124.0, 83.7, 83.4, 33.3, 33.1, 30.3, 30.2, 28.9, 28.6, 28.2, 28.0, 26.6, 26.5, 23.3, 23.1, 21.5, 21.4. HRMS (EI): *m/z* calcd for [$C_{11}H_{16}O_2$]: 180.1150. Found: 180.1155.

4.4.6. Lactone ***5f/5f′****.* A solution of **4f** (1.0 equiv, 8.0 mmol, 2.04 g) in 60 mL of AcOH/H_2O (v/v=3:2) was subjected to the general procedure (SiO_2, petroleum ether/EtOAc=10:1), affording the lactone **5f** (396 mg, 25% yield, dr=1:1, R_f=0.5) and lactone **5f′** (568 mg, 37% yield, dr=1:1, R_f=0.4).

Compound **5f**: IR (neat): 2953, 2927, 2878, 1780, 1456, 1192, 1165, 1077 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.68(s, 1H), 4.84–4.80 (m, 1H), 2.70–2.60 (m, 1H), 2.31–2.24 (m, 1H), 2.12–2.09 (m, 1H), 2.02–1.93 (m, 3H), 1.75–1.71 (m, 1H), 1.67–1.61 (m, 2H), 1.27 (d, *J*=1.6 Hz, 1.5H), 1.25 (d, *J*=1.6 Hz, 1.5H), 1.23–1.15 (m, 1H), 0.93 (d, *J*=5.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 180.1, 180.0, 134.6, 134.4, 124.2, 123.2, 80.8, 80.5, 34.3, 34.2, 34.0, 33.7, 33.3, 33.2, 30.3, 28.2, 28.1, 23.9, 23.7, 21.5, 21.4, 15.7, 15.6. HRMS (EI): *m/z* calcd for [$C_{12}H_{18}O_2$]: 194.1307. Found: 194.1301.

Compound **5f′**: IR (neat): 2953, 2927, 2912, 2878, 1781, 1456, 1335, 1194, 1156 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.76–5.73 (m, 1H), 4.68 (dd, *J*=5.6 Hz, *J*=10.4 Hz, 1H), 2.70–2.62 (m, 1H), 2.45–2.36 (m, 1H), 2.13–2.09 (m, 1H), 2.02–1.99 (m, 2H), 1.77–1.59 (m, 4H), 1.25 (d, *J*=7.2 Hz, 3H), 1.22–1.19 (m, 1H), 0.95 (d, *J*=2.8 Hz, 1.5H), 0.93 (d, *J*=2.8 Hz, 1.5H). ^{13}C NMR ($CDCl_3$): δ 179.3, 134.1, 125.7, 124.2, 81.6, 81.2, 35.9, 35.8, 35.5, 33.5, 33.2, 30.4, 30.3, 28.3, 28.1, 23.2, 21.5, 21.4, 14.9. HRMS (EI): *m/z* calcd for [$C_{12}H_{18}O_2$]: 194.1307. Found: 194.1302.

4.4.7. Lactone ***5g****.* A solution of **4g** (1.0 equiv, 4.26 mmol, 1.088 g) in 30 mL of AcOH/H_2O (v/v=3:2) was subjected to the general procedure (SiO_2, petroleum ether/EtOAc=20:1), affording the lactone **5g** (410 mg, 50% yield, dr=1:1) as a yellow oil. IR (neat): 2955, 2927, 2874, 1782, 1456, 1376, 1241, 1211, 1125 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.68–5.64 (m, 1H), 2.50–2.45 (m, 2H), 2.30–2.17 (m, 1H), 2.13–2.08 (m, 1H), 2.00–1.90 (m, 3H), 1.74–1.67 (m, 1H), 1.65–1.52 (m, 2H), 1.43 (d, *J*=4.8 Hz, 3H), 1.23–1.10 (m, 1H), 0.91 (d, *J*=6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 176.7, 176.6, 138.0, 121.0, 120.5, 87.8, 87.7, 33.2, 32.8, 32.4, 30.8, 30.6, 28.9, 28.8, 28.0, 27.8, 25.9, 25.6, 24.3, 24.0, 21.4, 21.3. HRMS (EI): *m/z* calcd for [$C_{12}H_{18}O_2$]: 194.1307. Found: 194.1310.

4.5. Synthesis of compounds 6

4.5.1. Compound ***6a****.* A solution of **5a** (1.0 equiv, 1.8 mmol, 300 mg) and PPh_3 (4.0 equiv, 7.2 mmol, 1.9 g) in 18 mL of THF was heated to reflux under nitrogen atmosphere. To the solution, 8.3 mL of CCl_4 (48.0 equiv, 86.7 mmol) was added dropwise. The resultant mixture was refluxed for 5 h. After cooling to room temperature, the mixture was filtered and the filtrate was washed with saturated $NaHCO_3$ solution. The aqueous layer was extracted with Et_2O and the combined organic layer was dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under vacuum and the residue was purified by flash chromatography (SiO_2, petroleum ether/CH_2Cl_2=9:1), affording **6a** (213 mg, 51% yield) as a colorless oil. IR (neat): 2927, 2862, 1681, 1492, 1202 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.75 (s, 1H), 4.77 (t, *J*=7.2 Hz, 1H), 2.81–2.63 (m, 2H), 2.18–1.94 (m, 6H), 1.69–1.52 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 153.9, 135.2, 124.8, 93.1, 88.4, 29.7, 28.9, 24.9, 23.4, 22.3. HRMS (EI): *m/z* calcd for [$C_{11}H_{14}Cl_2O$]: 232.0422. Found: 232.0426.

4.5.2. Compound ***6b****.* A solution of **5b** (1.0 equiv, 0.5 mmol, 90 mg) and PPh_3 (10.0 equiv, 5 mmol, 1.35 g) in 4 mL THF was heated to reflux under nitrogen atmosphere. To the mixture a solution of CCl_4 (5.0 equiv, 2.5 mmol, 0.24 mL) in 4 mL THF was added dropwise. After refluxed for 6 h, the resultant mixture was allowed to cool to room temperature and filtered through a bed of silica gel. The filtrate was collected and the solvent was removed under vacuum. The residue was purified by flash chromatography (SiO_2, petroleum ether/CH_2Cl_2=30:1), affording **6b** (63 mg, 51% yield, dr=4:1). IR (neat): 2934, 2861, 1656, 1458, 1438, 1377, 1322, 1199, 1033 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.77–5.74 (m, 1H), 4.85 (dd, *J*=5.6, 10.6 Hz, 0.2H), 4.63 (t, *J*=7.2 Hz, 0.8H), 3.17–3.01 (m, 1H), 2.44–2.36 (m, 0.8H), 2.17–2.10 (m, 0.2H), 2.03 (br s, 2H), 1.96–1.89 (m, 2H), 1.82–1.68 (m, 1H), 1.67–1.55 (m, 4H), 1.31 (d, *J*=7.2 Hz, 2H), 1.25 (d, *J*=7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 158.1, 157.7, 135.6, 135.0, 125.4, 123.8, 94.9, 86.7, 85.8, 37.5, 37.2, 37.1, 36.5, 24.9, 24.8, 23.9, 23.0, 22.4, 22.3, 18.6, 17.2. HRMS (EI): *m/z* calcd for [$C_{12}H_{16}Cl_2O$]: 246.0578. Found: 246.0579.

4.5.3. Compound ***6c****.* A solution of **5c** (1.0 equiv, 0.44 mmol, 80 mg) and PPh_3 (10.0 equiv, 4.5 mmol, 1.22 g) in 4 mL THF was heated to reflux under nitrogen atmosphere. To the mixture a solution of CCl_4 (5.0 equiv, 2.2 mmol, 0.22 mL) in 4 mL THF was added dropwise. After refluxed for 6 h, the resultant mixture was allowed to cool to room temperature and filtered through a bed of silica gel. The filtrate was collected and the solvent was removed under vacuum. The residue was purified by flash chromatography (SiO_2, petroleum ether), affording **6c** (82 mg, 76% yield). IR (neat): 2932, 2840, 1742, 1667, 1456, 1437, 1373, 1282, 1239, 1223 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.74 (s, 1H), 4.20 (d, *J*=7.6 Hz, 1H), 2.96–2.82 (m, 1H), 2.33–2.26 (m, 2H), 2.05–2.04 (m, 3H), 1.90–1.85 (m, 1H), 1.67–1.51 (m, 4H), 1.04 (d, *J*=6.0 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 153.2, 134.0, 127.1, 127.0, 123.7, 95.2, 37.9, 35.9, 25.0, 22.9, 22.3, 16.3. HRMS (EI): *m/z* calcd for [$C_{12}H_{16}Cl_2O$]: 246.0578. Found: 246.0580.

4.5.4. Compound ***6d****.* A solution of **5d** (1.0 equiv, 1.5 mmol, 273 mg) and PPh_3 (6.0 equiv, 9.1 mmol, 2.4 g) in 15 mL of THF was heated to reflux under nitrogen atmosphere. To the solution 14 mL of CCl_4 (96.0 equiv, 146 mmol) was added dropwise. The resultant mixture was refluxed for 12 h. After cooling to room temperature, the mixture was filtered and the filtrate was washed with saturated $NaHCO_3$ solution. The aqueous layer was extracted with Et_2O and the combined organic layer was dried over anhydrous Na_2SO_4. After filtration, the solvent was removed under vacuum and the residue was purified by flash chromatography (SiO_2, petroleum ether/CH_2Cl_2=4:1), affording **6d** (141 mg, 38% yield) as a yellow oil. IR (neat): 2932, 2858, 1665, 1448, 1373, 1260, 998 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.69–5.67 (m, 1H), 2.75–2.58 (m, 2H), 2.19–2.12 (m, 1H), 2.06–2.01 (m, 2H), 1.96–1.94 (m, 2H), 1.88–1.81 (m, 1H), 1.67–1.51 (m, 4H), 1.44 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 153.5, 138.6, 120.7, 92.9, 92.2, 34.7, 29.4, 25.4, 24.9, 24.6, 22.8, 22.2. HRMS (EI): *m*/*z* calcd for [$C_{12}H_{16}Cl_2O$]: 246.0578. Found: 246.0573.

*4.5.5. Compound **6e**.* A solution of **5e** (1.0 equiv, 1.0 mmol, 180 mg) and PPh_3 (10.0 equiv, 10.0 mmol, 2.7 g) in 8 mL THF was heated to reflux under nitrogen atmosphere. To the mixture a solution of CCl_4 (5.0 equiv, 5 mmol, 0.48 mL) in 8 mL THF was added dropwise. After refluxed for 6 h, the resultant mixture was allowed to cool to room temperature and filtered through a bed of silica gel. The filtrate was collected and the solvent was removed under vacuum. The residue was purified by flash chromatography (SiO_2, petroleum ether/CH_2Cl_2=30:1), affording **6e** (145 mg, 59% yield, dr=1:1). IR (neat): 2956, 2926, 1742, 1667, 1456, 1289, 1222, 1006 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.72–5.69 (m, 1H), 4.77 (t, *J*=7.6 Hz, 1H), 2.80–2.62 (m, 2H), 2.21–2.11 (m, 2H), 2.03–1.91 (m, 3H), 1.76–1.58 (m, 3H), 1.27–1.23 (m, 1H), 0.95 (d, *J*=3.2 Hz, 1.5H), 0.94 (d, *J*=3.2 Hz, 1.5H). ^{13}C NMR ($CDCl_3$): δ 153.8, 134.9, 134.8, 124.8, 123.6, 93.1, 93.0, 88.3, 88.0, 33.5, 33.2, 30.5, 30.4, 29.7, 29.5, 29.1, 29.0, 28.4, 28.1, 23.5, 23.4, 21.7, 21.5. HRMS (EI): *m*/*z* calcd for [$C_{12}H_{16}Cl_2O$]: 246.0578. Found: 246.0574.

*4.5.6. Compound **6f**.* A solution of **5f** (1.0 equiv, 0.5 mmol, 97 mg) and PPh_3 (10.0 equiv, 5.0 mmol, 1.35 g) in 4 mL THF was heated to reflux under nitrogen atmosphere. To the mixture a solution of CCl_4 (5.0 equiv, 2.5 mmol, 0.24 mL) in 4 mL THF was added dropwise. After refluxed for 6 h, the resultant mixture was allowed to cool to room temperature and filtered through a bed of silica gel. The filtrate was collected and the solvent was removed under vacuum. The residue was purified by flash chromatography (SiO_2, petroleum ether/CH_2Cl_2=30:1), affording **6f** (107 mg, 82% yield, dr=1:1). IR (neat): 2955, 2927, 1661, 1457, 1377, 1219, 1195, 1008 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.76–5.72 (m, 1H), 4.89–4.84 (m, 1H), 3.18–3.10 (m, 1H), 2.19–1.99 (m, 4H), 1.84–1.56 (m, 4H), 1.26–1.17 (m, 4H), 0.95 (d, *J*=4.4 Hz, 1.5H), 0.94 (d, *J*=4.4 Hz, 1.5H). ^{13}C NMR ($CDCl_3$): δ 158.0, 134.8, 125.4, 123.9, 86.5, 86.2, 37.6, 37.1, 37.0, 33.6, 33.3, 30.6, 30.4, 28.5, 28.1, 23.2, 23.1, 21.4, 17.2, 17.1. HRMS (EI): *m*/*z* calcd for [$C_{13}H_{18}Cl_2O$]: 260.0735. Found: 260.0738.

*4.5.7. Compound **6g**.* A solution of **5g** (1.0 equiv, 0.5 mmol, 97 mg) and PPh_3 (10.0 equiv, 5.0 mmol, 1.35 g) in 4 mL THF was heated to reflux under nitrogen atmosphere. To the mixture a solution of CCl_4 (5.0 equiv, 2.5 mmol, 0.24 mL) in 4 mL THF was added dropwise. After refluxed for 6 h, the resultant mixture was allowed to cool to room temperature and filtered through a bed of silica gel. The filtrate was collected and the solvent was removed under vacuum. The residue was purified by flash chromatography (SiO_2, petroleum ether/CH_2Cl_2=30:1), affording **6g** (71 mg, 55% yield, dr=1:1). IR (neat): 2956, 2926, 2873, 1742, 1667, 1456, 1435, 1373, 1262, 1241 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.66–5.63 (m, 1H), 2.75–2.57 (m, 2H), 2.20–2.11 (m, 2H), 2.03–1.99 (m, 2H), 1.90–1.80 (m, 1H), 1.76–1.57 (m, 3H), 1.43 (s, 1.5H), 1.42 (s, 1.5H), 1.27–1.13 (m, 1H), 0.94 (d, *J*=6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 153.5, 153.4, 138.4, 138.2, 120.6, 120.2, 92.1, 92.0, 35.0, 34.6, 33.5, 33.4, 31.1, 30.9, 29.5, 29.4, 28.2, 28.0, 25.5, 25.3, 24.8, 24.3, 21.6, 21.4. HRMS (EI): *m*/*z* calcd for [$C_{13}H_{18}Cl_2O$]: 260.0735. Found: 260.0739.

4.6. Synthesis of 1,1-dichloro bicyclo[5.4.0]undec-5-en-2-ones 2

*4.6.1. 1,1-Dichloro bicyclo[5.4.0]undec-5-en-2-one **2a**.* A solution of **6a** (1.0 equiv, 0.862 mmol, 200 mg) in 2.5 mL of chlorobenzene was heated to reflux under nitrogen atmosphere for 12 h. After cooling to room temperature, the solvent was removed under vacuum and the residue was purified by flash chromatography (SiO_2, petroleum ether/Et_2O=9:1), affording **2a** (86 mg, 43% yield). IR (neat): 2935, 2861, 1735, 1436, 1263 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.55–5.52 (m, 1H), 3.33–3.29 (m, 1H), 3.27–3.19 (m, 1H), 2.74–2.67 (m, 1H), 2.62–2.57 (m, 1H), 2.53–2.43 (m, 1H), 2.35–2.27 (m, 1H), 2.18–2.12 (m, 1H), 2.07–2.01 (m, 1H), 1.95–1.79 (m, 2H), 1.66–1.57 (m, 2H), 1.52–1.42 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 196.2, 139.4, 122.9, 94.1, 51.5, 37.1, 34.8, 26.1, 25.2, 24.2, 22.9. HRMS (EI): *m*/*z* calcd for [$C_{11}H_{14}Cl_2O$]: 232.0422. Found: 232.0420.

*4.6.2. 1,1-Dichloro bicyclo[5.4.0]undec-5-en-2-one **2b**.* A solution of **6b** (1.0 equiv, 0.813 mmol, 200 mg) in 2.5 mL chlorobenzene was heated to reflux under nitrogen atmosphere for 22 h. After cooling to room temperature, the solvent was removed under vacuum and the residue was purified by flash chromatography (SiO_2, petroleum ether/Et_2O=20:1), affording **2b** (76 mg, 38% yield). IR (neat): 2935, 2871, 1748, 1460, 1378, 1136, 1046, 1004 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.42–5.40 (m, 1H), 3.75–3.60 (m, 2H), 2.68–2.59 (m, 1H), 2.34–2.25 (m, 1H), 2.16–2.10 (m, 1H), 2.07–1.99 (m, 3H), 1.91–1.84 (m, 1H), 1.76–1.70 (m, 1H), 1.52–1.38 (m, 2H), 1.22 (d, *J*=6.4 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 198.2, 138.0, 124.7, 94.9, 48.0, 38.3, 35.7, 31.7, 22.6, 22.5, 20.7, 17.4. HRMS (EI): *m*/*z* calcd for [$C_{12}H_{16}Cl_2O$]: 246.0578. Found: 246.0572.

*4.6.3. 1,1-Dichloro bicyclo[5.4.0]undec-5-en-2-one **2c**.* A solution of **6c** (1.0 equiv, 0.16 mmol, 40 mg) in 1.0 mL mesitylene was heated to reflux under nitrogen atmosphere for 17 h. After cooling to room temperature, the mixture was purified by flash chromatography (SiO_2, petroleum ether/CH_2Cl_2=5:1), affording **2c** (16 mg, 40% yield). IR (neat): 2959, 2933, 2872, 1742, 1460, 1373, 1240, 1047 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.34 (s, 1H), 3.36–3.30 (m, 2H), 2.97–2.92 (m, 1H), 2.40 (dd, *J*=6.0 Hz, *J*=14.0 Hz, 1H), 2.35–2.28 (m, 1H), 2.13–2.02 (m, 2H), 1.92–1.80 (m, 2H), 1.68–1.58 (m, 2H), 1.51–1.40 (m, 1H), 1.13 (d, *J*=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 194.6, 138.2, 131.0, 94.1, 50.8, 44.4, 34.0, 29.9, 25.8, 24.8, 23.5, 22.5. HRMS (EI): *m*/*z* calcd for [$C_{12}H_{16}Cl_2O$]: 246.0578. Found: 246.0575.

*4.6.4. 1,1-Dichloro bicyclo[5.4.0]undec-5-en-2-one **2d**.* A solution of **6d** (1.0 equiv, 0.813 mmol, 200 mg) in 2.5 mL toluene was heated to reflux under nitrogen atmosphere for 14 h. After cooling to room temperature, the solvent was removed under vacuum and the residue was purified by flash chromatography (SiO_2, petroleum ether/Et_2O=9:1), affording **2d** (124 mg, 62% yield). IR (neat): 2938, 2864, 1744, 1458, 1449, 1079 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.42–3.39 (m, 1H), 3.27–3.19 (m, 1H), 2.70–2.62 (m, 1H), 2.58–2.51 (m, 1H), 2.33–2.27 (m, 1H), 2.24–2.16 (m, 1H), 2.09–1.97 (m, 2H), 1.88–1.77 (m, 2H), 1.65–1.62 (m, 1H), 1.57 (s, 3H), 1.33–1.27 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 195.7, 131.7, 94.4, 48.9, 35.1, 30.8, 25.9, 23.7, 23.2, 20.0. HRMS (EI): *m*/*z* calcd for [$C_{12}H_{16}Cl_2O$]: 246.0578. Found: 246.0579.

*4.6.5. 1,1-Dichloro bicyclo[5.4.0]undec-5-en-2-one **2e**.* A solution of **6e** (1.0 equiv, 0.16 mmol, 40 mg) in 1.0 mL mesitylene was heated to reflux under nitrogen atmosphere for 10 h. After cooling to room temperature, the mixture was purified by flash chromatography (SiO_2, petroleum ether/CH_2Cl_2=5:1), affording **2e** (23 mg, 58% yield, dr=1:1). IR (neat): 2954, 2928, 2871, 2852, 1745, 1456, 1436, 1379 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.55–5.53 (m, 1H), 3.65–3.63 (m, 0.5H), 3.41–3.34 (m, 0.5H), 3.21–3.08 (m, 1H), 2.78–2.71 (m, 0.5H), 2.65–2.38 (m, 3H), 2.33–2.26 (m, 1H), 2.21–2.16 (m, 1H), 2.12–1.98 (m, 1H), 1.83–1.78 (m, 0.5H), 1.74–1.60 (m, 1H), 1.51–1.44 (m, 0.5H), 1.18–1.08 (m, 1H), 1.00–0.96 (m, 3.5H). ^{13}C NMR ($CDCl_3$): δ 196.4, 195.6, 139.4, 138.7, 125.0, 121.9, 95.0, 93.6, 53.1, 46.1, 38.3, 35.9, 35.5, 34.7, 33.1, 32.2, 30.8, 27.7, 23.9, 23.6, 22.2. HRMS (EI): *m/z* calcd for [$C_{12}H_{16}Cl_2O$]: 246.0578. Found: 246.0574.

4.6.6. 1,1-Dichloro bicyclo[5.4.0]undec-5-en-2-one ***2f***. A solution of **6f** (1.0 equiv, 0.13 mmol, 34 mg) in 1.0 mL mesitylene was heated to reflux under nitrogen atmosphere for 14 h. After cooling to room temperature, the mixture was purified by flash chromatography (SiO_2, petroleum ether/CH_2Cl_2=5:1), affording **2f** (20 mg, 59% yield, dr=1:1). IR (neat): 2955, 2930, 2872, 1747, 1457, 1375, 1240, 1048 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.46–5.40 (m, 1H), 3.80–3.57 (m, 2H), 2.75–2.56 (m, 1H), 2.46–2.18 (m, 2H), 2.14–1.94 (m, 3H), 1.80–1.57 (m, 2.5H), 1.47–1.39 (m, 0.5H), 1.23–1.19 (m, 3H), 1.04 (d, *J*=6.4 Hz, 1.5H), 0.97 (d, *J*=6.4 Hz, 1.5H). ^{13}C NMR ($CDCl_3$): δ 198.5, 197.9, 137.8, 137.4, 125.7, 123.9, 95.9, 94.4, 49.1, 44.9, 38.9, 37.7, 35.9, 35.0, 33.1, 32.8, 31.7, 31.5, 31.3, 31.1, 27.9, 27.7, 22.7, 22.6, 17.5. HRMS (EI): *m/z* calcd for [$C_{13}H_{18}Cl_2O$]: 260.0735. Found: 260.0732.

4.6.7. 1,1-Dichloro bicyclo[5.4.0]undec-5-en-2-one ***2g***. A solution of **6g** (1.0 equiv, 0.123 mmol, 32 mg) in 1.0 mL toluene was heated to reflux under nitrogen atmosphere for 14 h. After cooling to room temperature, the solvent was removed under vacuum and the residue was purified by flash chromatography (SiO_2, petroleum ether/CH_2Cl_2=5:1), affording **2g** (18 mg, 56% yield, dr=1:1). IR (neat): 2955, 2927, 2870, 1743, 1457, 1377, 1217, 1093 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.62 (d, *J*=8.0 Hz, 0.5H), 3.50 (dd, *J*=5.6 Hz, *J*=10.8 Hz, 0.5H), 3.37–3.27 (m, 1H), 2.88–2.79 (m, 0.5H), 2.73–2.60 (m, 1.5H), 2.56–2.45 (m, 1H), 2.39–2.31 (m, 0.5H), 2.29–2.15 (m, 2H), 2.07–2.01 (m, 1H), 1.80–1.74 (m, 1H), 1.70 (s, 1.5H), 1.65 (s, 1.5H), 1.54–1.32 (m, 1.5H), 1.25 (s, 1H), 1.01 (d, *J*=6.4 Hz, 1.5H), 0.94 (d, *J*=6.4 Hz, 1.5H). ^{13}C NMR ($CDCl_3$): δ 195.8, 195.0, 132.9, 131.6, 131.3, 130.4, 95.1, 93.7, 50.6, 47.4, 35.6, 34.5, 33.1, 32.6, 32.2, 31.7, 31.5, 29.7, 28.0, 27.5, 27.0, 26.0, 22.7, 22.5, 21.1, 20.9. HRMS (EI): *m/z* calcd for [$C_{13}H_{18}Cl_2O$]: 260.0735. Found: 260.0738.

4.7. General procedure for synthesis of 3,5,6,7,8,8a-hexahydronaphthalene-1-carboxylates 1

A solution of the appropriate **2** (1.0 equiv) and DBU (3.3 equiv) in MeOH or EtOH was heated to reflux under nitrogen atmosphere for 30 min. After cooling to room temperature, the solvent was removed under vacuum and the residue was purified by flash chromatography (SiO_2, petroleum ether/EtOAc=30:1), affording **1**.

4.7.1. Hexahydronaphthalene-1-carboxylate ***1a***. A solution of **2a** (1.0 equiv, 0.858 mmol, 200 mg) and DBU (3.0 equiv, 2.6 mmol, 0.38 mL) in 1.7 mL MeOH was subjected to the general procedure (SiO_2, petroleum ether/Et_2O=9:1), affording **1a** (96 mg, 58% yield). IR (neat): 2930, 2855, 1720, 1689, 1436, 1255 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.91–6.88 (m, 1H), 5.30 (d, *J*=1.2 Hz, 1H), 3.74 (s, 3H), 2.97–2.92 (m, 1H), 2.85–2.83 (m, 2H), 2.28–1.77 (m, 4H), 1.59–0.98 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 167.6, 139.9, 136.2, 131.8, 113.2, 51.4, 38.0, 35.9, 34.9, 28.9, 27.6, 26.9. HRMS (EI): *m/z* calcd for [$C_{12}H_{16}O_2$]: 192.1150. Found: 192.1153.

4.7.2. Hexahydronaphthalene-1-carboxylate ***1b***. A solution of **2b** (1.0 equiv, 0.061 mmol, 15 mg) and DBU (3.2 equiv, 0.19 mmol, 29 mg) in 1.0 mL MeOH was subjected to the general procedure (SiO_2, petroleum ether/EtOAc=30:1), affording **1b** (7 mg, 58% yield). IR (neat): 2958, 2930, 2873, 1720, 1554, 1457, 1377, 1268, 1242 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.29–5.27 (m, 1H), 3.74 (s, 3H), 2.98–2.94 (m, 1H), 2.82–2.75 (m, 1H), 2.70–2.62 (m, 1H), 2.26–2.21 (m, 1H), 2.01–1.93 (m, 1H), 1.88 (s, 3H), 1.83–1.75 (m, 3H), 1.53–1.41 (m, 1H), 1.33–1.24 (m, 1H), 1.11–1.01 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 169.7, 138.8, 127.2, 113.8, 51.0, 39.9, 35.5, 34.7, 34.3, 28.5, 26.7, 20.7. HRMS (EI): *m/z* calcd for [$C_{13}H_{18}O_2$]: 206.1307. Found: 206.1305.

4.7.3. Hexahydronaphthalene-1-carboxylate ***1c***. A solution of **2c** (1.0 equiv, 0.045 mmol, 11 mg) and DBU (3.2 equiv, 0.143 mmol, 22 mg) in 1.0 mL MeOH was subjected to the general procedure (SiO_2, petroleum ether/EtOAc=30:1), affording **1c** (6 mg, 65% yield). IR (neat): 2959, 2929, 2872, 1719, 1457, 1436, 1252 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.81 (dd, *J*=1.6 Hz, *J*=3.2 Hz, 1H), 5.25 (d, *J*=1.6 Hz, 1H), 3.74 (s, 3H), 2.94–2.86 (m, 2H), 2.30–2.24 (m, 1H), 2.22–2.21 (m, 1H), 2.04–1.95 (m, 2H), 1.86–1.71 (m, 4H), 1.12 (d, *J*=7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 167.7, 141.4, 138.9, 131.1, 119.9, 51.3, 38.4, 35.9, 35.8, 32.1, 29.0, 26.9, 22.0. HRMS (EI): *m/z* calcd for [$C_{13}H_{18}O_2$]: 206.1307. Found: 206.1303.

4.7.4. Hexahydronaphthalene-1-carboxylate ***1d***. A solution of **2d** (1.0 equiv, 0.81 mmol, 200 mg) and DBU (3.0 equiv, 2.4 mmol, 0.36 mL) in 1.6 mL MeOH was subjected to the general procedure (SiO_2, petroleum ether/Et_2O=4:1), affording **1d** (129 mg, 77% yield). IR (neat): 2927, 2854, 1718, 1691, 1436, 1258, 1222 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.86–6.85 (m, 1H), 3.74 (s, 3H), 2.93–2.91 (m, 1H), 2.80–2.69 (m, 2H), 2.17–1.67 (m, 4H), 1.65 (s, 3H), 1.59–0.96 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 167.6, 135.9, 132.2, 132.1, 118.1, 51.4, 39.4, 35.4, 33.9, 30.1, 28.4, 26.9, 17.7. HRMS (EI): *m/z* calcd for [$C_{13}H_{18}O_2$]: 206.1307. Found: 206.1310.

4.7.5. Hexahydronaphthalene-1-carboxylate ***1e***. A solution of **2e** (1.0 equiv, 0.08 mmol, 20 mg) and DBU (3.0 equiv, 0.27 mmol, 41 mg) in 2.0 mL MeOH was subjected to the general procedure (SiO_2, petroleum ether/EtOAc=30:1), affording **1e** (11 mg, 68% yield, dr=1:1). IR (neat): 2952, 2927, 2852, 1719, 1645, 1456, 1436, 1252 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.89–6.87 (m, 1H), 5.31–5.29 (m, 1H), 3.74 (s, 1.5H), 3.73 (s, 1.5H), 3.25–3.17 (m, 0.5H), 3.03–2.96 (m, 0.5H), 2.86–2.81 (m, 2H), 2.27–2.22 (m, 1H), 2.15–1.95 (m, 3H), 1.82–1.67 (m, 1H), 1.62–1.58 (m, 1H), 1.33–1.25 (m, 1H), 1.15 (d, *J*=7.2 Hz, 1.5H), 0.87 (d, *J*=7.2 Hz, 1.5H). ^{13}C NMR ($CDCl_3$): δ 167.5, 140.4, 139.5, 136.2, 136.0, 131.9, 131.7, 113.2, 112.8, 51.3, 42.9, 40.4, 37.3, 37.2, 35.4, 34.1, 33.1, 32.2, 30.5, 28.3, 27.7, 27.5, 22.0, 17.5. HRMS (EI): *m/z* calcd for [$C_{13}H_{18}O_2$]: 206.1307. Found: 206.1311.

4.7.6. Hexahydronaphthalene-1-carboxylate ***1f***. A solution of **2e** (1.0 equiv, 0.048 mmol, 12 mg) and DBU (3.2 equiv, 0.15 mmol, 24 mg) in 1.0 mL EtOH was subjected to the general procedure (SiO_2, petroleum ether/EtOAc=30:1), affording **1f** (6 mg, 57% yield, dr=4:7). IR (neat): 2955, 2927, 2853, 1716, 1689, 1456, 1250, 1179, 1069 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.90–6.86 (m, 1H), 5.31–5.29 (m, 1H), 4.23–4.16 (m, 2H), 3.26–3.18 (m, 0.5H), 3.04–2.95 (m, 0.5H), 2.86–2.82 (m, 2H), 2.27–2.22 (m, 1H), 2.17–2.12 (m, 1H), 2.08–1.96 (m, 2H), 1.82–1.67 (m, 2H), 1.62–1.58 (m, 1H), 1.31–1.28 (m, 3H), 1.15 (d, *J*=7.2 Hz, 1.1H), 0.88 (d, *J*=7.2 Hz, 1.9H). ^{13}C NMR ($CDCl_3$): δ 167.1, 140.4, 139.5, 135.9, 135.6, 132.0, 113.3, 112.8, 60.1, 42.9, 40.4, 37.4, 37.2, 35.4, 34.1, 33.1, 32.3, 30.6, 28.3, 27.7, 27.5, 22.1, 17.4, 14.2. HRMS (EI): *m/z* calcd for [$C_{14}H_{20}O_2$]: 220.1463. Found: 220.1467.

4.7.7. Hexahydronaphthalene-1-carboxylate ***1g***. A solution of **2f** (1.0 equiv, 0.061 mmol, 16 mg) and DBU (3.2 equiv, 0.20 mmol, 30 mg) in 1.0 mL MeOH was subjected to the general procedure (SiO_2, petroleum ether/EtOAc=30:1), affording **1g** (10 mg, 77% yield, dr=1:1). IR (neat): 2957, 2928, 2872, 1741, 1435, 1373, 1240, 1138, 1048 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.28–5.26 (m, 1H), 3.75 (s, 1.5H), 3.74 (s, 1.5H), 3.23–3.20 (m, 0.5H), 3.01–2.97 (m, 0.5H), 2.82–2.62 (m, 2H), 2.25–2.20 (m, 1H), 2.04–1.99 (m, 1H), 1.88 (s, 1.5H), 1.87 (s, 1.5H), 1.81–1.72 (m, 2H), 1.65–1.59 (m, 1H), 1.36–1.23 (m, 2H), 1.10 (d, J=7.2 Hz, 1.5H), 0.87 (d, J=6.8 Hz, 1.5H). ^{13}C NMR (CDCl$_3$): δ 169.8, 169.5, 139.3, 139.2, 138.5, 138.3, 127.2, 113.9, 113.4, 51.1, 51.0, 42.9, 40.3, 39.2, 36.8, 35.0, 34.4, 34.3, 34.1, 33.7, 32.9, 30.1, 28.1, 22.0, 20.8, 20.7, 17.4. HRMS (EI): m/z calcd for [$C_{14}H_{20}O_2$]: 220.1463. Found: 220.1460.

4.7.8. Hexahydronaphthalene-1-carboxylate ***1h***. A solution of **2g** (1.0 equiv, 0.061 mmol, 16 mg) and DBU (3.2 equiv, 0.21 mmol, 33 mg) in 1.0 mL MeOH was subjected to the general procedure (SiO$_2$, petroleum ether/EtOAc=30:1), affording **1h** (11 mg, 84% yield, dr=2:3). IR (neat): 2952, 2927, 1722, 1456, 1435, 1283, 1263, 1245, 1192, 1134 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 6.87–6.84 (m, 1H), 3.74 (s, 1.2H), 3.73 (s, 1.8H), 3.21–3.15 (m, 0.6H), 2.98–2.94 (m, 0.4H), 2.86–2.47 (m, 3.5H), 2.12–1.99 (m, 1H), 1.94–1.89 (m, 1H), 1.83–1.77 (m, 0.5H), 1.75–1.67 (m, 1H), 1.64 (s, 3H), 1.30–1.21 (m, 2H), 1.15 (d, J=7.2 Hz, 1.8H), 0.87 (d, J=6.8 Hz, 1.2H). ^{13}C NMR (CDCl$_3$): δ 167.4, 136.0, 135.8, 132.5, 132.2, 132.0, 131.7, 118.1, 117.8, 51.3, 43.4, 40.8, 38.7, 36.6, 33.9, 33.8, 33.5, 33.4, 33.1, 29.6, 28.0, 24.7, 22.0, 17.8, 17.6, 17.5. HRMS (EI): m/z calcd for [$C_{14}H_{20}O_2$]: 220.1463. Found: 220.1464.

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Supplementary data

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