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A conceptually novel approach is described for the synthesis of larger-ring cyclic carbonates derived from carbon dioxide. The approach utilizes homoallylic precursors that are converted into five-membered cyclic carbonates having a beta-positioned alcohol group in one of the ring substituents. The activation of the pendent alcohol group through an N-heterocyclic base allows for equilibration towards a thermodynamically disfavored six-membered carbonate analogue that can be conveniently trapped by an acylation agent. Various control experiments and computational analysis of this manifold are in line with a process that is primarily dictated by a kinetically controlled acylation step. This cascade process delivers an ample diversity of novel six-membered cyclic carbonates in excellent yields and chemoselectivities under remarkably mild reaction conditions. This newly developed protocol helps to expand the repertoire of CO₂-based heterocycles that are otherwise difficult to generate by conventional approaches.

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Organocatalytic Trapping of Elusive Carbon Dioxide based Heterocycles through a Kinetically Controlled Cascade Process

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Dedicated to the memory of Prof. Kilian Muñiz

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Abstract

A conceptually novel approach is described for the synthesis of larger-ring cyclic carbonates derived from carbon dioxide. The approach utilizes homoallylic precursors that are converted into five-membered cyclic carbonates having a β -positioned alcohol group in one of the ring substituents. The activation of the pendent alcohol group through an N-heterocyclic base allows for equilibration towards a thermodynamically disfavored six-membered carbonate analogue that can be conveniently trapped by an acylation agent. Various control experiments and computational analysis of this manifold are in line with a process that is primarily dictated by a kinetically controlled acylation step. This cascade process delivers an ample diversity of novel six-membered cyclic carbonates in excellent yields and chemoselectivities under remarkably mild reaction conditions. This newly developed protocol helps to expand the repertoire of CO₂-based heterocycles that are otherwise difficult to generate by conventional approaches.

Introduction

The last decade has witnessed a spectacular development of a plethora of new catalytic processes that focus on the valorization of carbon dioxide (CO₂)^[1] affording organic molecules of use as precursors in fine chemical,^[2] pharmaceutical^[3] and polymer chemistry.^[4] One of the most widely applied valorization routes is undoubtedly the non-reductive transformation of CO₂. Catalyst engineering in this area has been mainly focusing on using both metal-^[5] and organo-catalysts^[6] for the activation of the requisite co-reactant (often cyclic ethers such as epoxides) to produce a nucleophilic intermediate species that activates CO₂ followed by the formation of the desired product. The preparation of heterocyclic targets such as cyclic carbonates,^[7] carbamates^[8] and ureas^[9] has greatly advanced as testified by the growing complexity of these CO₂-based products.

Larger-ring, typically difficult to prepare CO₂ based heterocycles remain challenging targets (Scheme 1, top). In the area of organic carbonate synthesis, methods to generate six-membered heterocycles are scarce and often rely on stoichiometric approaches.^[10] An exception is presented by the coupling reaction between oxetanes and CO₂, although to date very few catalysts have been shown to be effective for these substrates,^[11] and oxetanes are much less ubiquitous than epoxides. Therefore, new concepts are required to empower the potential of such novel, functionalized heterocyclic scaffolds and widen their prospective as synthetic intermediates^[12] and polymerizable monomers.^[13] With this challenge in mind, we set out to design a new conceptual route towards the synthesis of six-membered cyclic carbonates from simple and accessible building blocks (Scheme 1). Homoallylic

alcohols of type **A** are ubiquitous precursors and play a significant role in organic synthesis.^[14] Their epoxidation directly affords substrates of type **B** that should be easily converted into intermediate 5-membered cyclic carbonate products **1**. Inspired by our previous work on substrate-controlled synthesis of organic carbonates,^[15] we envisioned that the presence of a suitable organocatalyst (base) should be able to induce isomerization between carbonates **1** and **1'** with the latter being thermodynamically less stable. Selective acylation of the primary alcohol in **1'** offers then a tangible route to isolate the more elusive cyclic carbonate product **2**. Herein, we illustrate this successful, new and generally high-yielding route towards highly substituted six-membered carbonates of type **2** creating a superior diversity of such valuable heterocycles.

Scheme 1. Top: larger-ring, naturally occurring cyclic organic carbonates. Bottom: new conceptual approach towards six-membered cyclic carbonates. B stands for a base.

Results & Discussion

We first prepared a series of 5-membered cyclic carbonates of type **1** by employing various homoallylic alcohols (**A1–A17**) as precursors that are conveniently prepared from readily available ketones and allyl magnesium bromide. Epoxidation of these homoallylic compounds using *m*-CPBA at room temperature (rt) afforded the oxiranes **B1–B17** with a β-hydroxy group (see the Supporting Information, SI, for details). The oxiranes **B1–B17** (Scheme 2) were then used as reagents to furnish the cyclic carbonates **1a–1q** typically in good yields (with some exceptions) in the presence of CO₂ and suitable binary catalysts derived from Al-aminotriphenolate complexes **Al^{Cl}** and **Al^{Me}**.^[16] In some cases, significant byproduct formation occurred, and these products were identified as substituted tetrahydrofuran derivatives (see the SI for analysis details). The observed *dr* values for some of the 5-membered cyclic carbonates are similar to the ones of their respective precursors **B**, and hence supports the view that the formation of these five-membered carbonates is diastereospecific.

Scheme 2. Preparation of 5-membered carbonates **1a–1q** from precursors **B1–B17** that are prepared from homoallylic alkenes **A1–A17** using either Al^{Cl} or Al^{Me} .

For the screening studies focusing on the preparation of six-membered cyclic carbonate **2a** (Table 1), we chose carbonate **1a** as a benchmark substrate. Various *N*-heterocyclic and standard bases were examined and acetyl imidazole (AcIm) was used as acylation reagent.^[15c] The nature of the base had a significant effect on both the yield of **2a** and the overall chemo-selectivity. Among the eight bases tested, the *N*-heterocyclic ones (Table 1, entries 1, 2 and 4–6) gave the best results, with TBD (entry 1, 64%) providing comparatively the best yield of **2a**. By further variation of the solvent and the amount of TBD (entries 9–17), the best considered conditions (entry 15; 30 mol% TBD) offered an easy access to **2a** in high yield. In the absence of AcIm and by using a high loading of TBD, only tetrahydrofuran derivative **3a** could be identified (entry 17). In the absence of TBD (entry 18), no conversion of **1a** could be observed. This rt catalytic conversion of a 5- into a 6-membered cyclic carbonate is rather unique as the latter type of product is typically difficult to prepare under such mild conditions.

We then investigated the scope of this novel approach towards the formation of a wider diversity of 6-membered cyclic carbonate products (Scheme 3) by varying the R^1 and R^2 substituents. The presence of substituted aryl groups in the carbonate substrates **1a–1e** was well tolerated and provided smooth access to six-membered cyclic carbonates **2a–2e** in good to excellent yields (65–91%; gram-scale synthesis of **2a**: 1.24 g). The introduction of alkyl groups such as those present in the carbonate products **2f–2i** also did not pose any significant issue. Apart from the combination of two equal groups, carbonate substrates with distinct R^1 and R^2 substituents (**1j–1n**) were also probed. Whereas six-membered cyclic carbonates **2j**, **2k**, **2m** and **2n** were synthesized in good yields, the presence of a strongly electron-withdrawing CF_3 group (cf., attempted preparation of **2l**) changed the chemo-

selectivity in favour of the decarboxylated, *O*-acetyl protected tetrahydrofuran product **3I-Ac** which was isolated in 89% (see SI for analysis details). Finally, the *spiro*-derivative **2p** (95%) and biphenyl-based carbonate **2q** (80%) were prepared in good yields, and the identity of **2p** was further substantiated by X-ray analysis (see the inset in Scheme 3).^[17]

Next, a series of control experiments were conducted to investigate the proposed role of the pendent alcohol group in substrate **1a** and the relative stability of the free alcohol carbonates (Scheme 4). In the presence of TBD only, there is no observable conversion of the 5-membered carbonate **1a** into a

Table 1. Screening conditions for the conversion of cyclic carbonate **1a** into its 6-membered congener **2a** under various conditions.^[a]

1a $\xrightarrow[\text{solvent, rt, 2 h, Ar or N}_2]{\text{Base, AcIm (1.2 equiv)}}$ **2a**

Entry	Base [mol%]	Solvent	Conv. of 1a [%] ^[b]	Yield of 2a [%] ^[c]
1	TBD (20)	CH ₃ CN	64	64
2	DBU (20)	CH ₃ CN	49	49
3	KOH (20)	CH ₃ CN	100	0 ^[d]
4	DMAP (20)	CH ₃ CN	8	2
5	DBN (20)	CH ₃ CN	43	18
6	DABCO (20)	CH ₃ CN	6	0
7	TEA (20)	CH ₃ CN	6	0
8	K ₂ CO ₃ (20)	CH ₃ CN	16	0
9	TBD (20)	THF	31	31
10	TBD (20)	Et ₂ O	84	22
11	TBD (20)	Toluene	63	59
12	TBD (20)	DMF	15	15
13	TBD (20)	EtOH	21	3
14	TBD (20)	DCM	53	53
15	TBD (30)	CH ₃ CN	94	93 (91) ^[f]
16	TBD (50)	CH ₃ CN	97	97 (96) ^[f]
17 ^[e]	TBD (100)	CH ₃ CN	>99	14 ^[g]
18	—	CH ₃ CN	<1	0

[a] Reaction conditions: substrate **1a** (0.10 mmol), solvent (0.20 mL), 2 h, under Ar or N₂. [b] Conversions measured by ¹H NMR (CDCl₃). [c] Determined by ¹H NMR using mesitylene as internal standard. [d] An unidentified byproduct was formed. [e] In the absence of acetyl imidazole. [f] In brackets the isolated yield of **2a**. [g] Note that 5,5-diphenyl-tetrahydrofuran-3-ol (**3a**) was isolated in 14% yield, see the SI for analysis details. Abbreviations: TBD = triazabicyclodecene, DBU = 1,8-diazabicyclo[5.4.0]-undec-7-ene, DBN = 1,5-diazabicyclo[4.3.0]non-5-ene, DABCO = 1,4-diazabicyclo[2.2.2]octane, TEA = triethyl amine.

6-membered one suggesting indeed that **1a** is thermodynamically significantly more stable (Scheme 4a). We separately prepared acylated **1h**-Ac and subjected this compound to the conditions that are present at the end of the cascade process (Scheme 4b). No conversion was observed pointing at the crucial role of a free alcohol group in carbonate **1h** prior to equilibration of the 5- to a 6-membered cyclic carbonate.

Whereas 6-membered cyclic carbonate **2h** is stable at lower temperatures, at elevated ones deprotection of the O-Ac group occurs giving the free alcohol, 5-membered cyclic carbonate **1h** as the sole carbonate product in 40% isolated yield.^[18] Deprotection of **2h** therefore leads to equilibration to

Scheme 3. Scope of six-membered cyclic carbonates **2a-2q** using **1a-1q** as precursors and the reaction conditions of entry 15 in Table 1. [a] Gram-scale synthesis of **2a** using 5 mmol **1a**: yield 1.24 g, 76%. [b] The acetyl-protected tetrahydrofuran product **3l**-Ac was isolated in 89% yield, see SI for analysis data.

5-membered cyclic carbonate **1h** reinforcing the view that the free alcohol cyclic carbonate equilibrium is under thermodynamic control.

To further probe the role of the alcohol group, 5-membered cyclic carbonate **1o** comprising a secondary (instead of tertiary) OH was examined. By following the optimized conditions (Table 1, entry 15), acetylated **1o**-Ac (50%) was isolated as the major carbonate product and only a trace amount of the 6-membered carbonate was noted. This result can be anticipated as secondary alcohols should be much more susceptible towards protection largely precluding competitive carbonate equilibration to the unprotected 6-membered carbonate (cf., Scheme 1: **1** → **1'**) and subsequent acylation.

Scheme 4. Various control experiments.

To further shed light on the mechanism, density functional theory (DFT) calculations were carried out (Figure 1).^[19] DFT calculations were performed using ω B97X-D functional and the 6-311G** basis set. All structures in this study were calculated with the Gaussian16 program. To obtain results as close as possible to reality, all calculations were performed at 298 K (room temperature) and an acetonitrile solvent model SMD was used. Further details are provided in the supporting information. The conversion of **1a** into **2a** was examined as a representative case.

The overall cascade process (Figure 1) can be best described as two consecutive reactions. The first one is the conversion of the five-membered carbonate **5MCC-OH** (**1a**) into the six-membered one named **6MCC-OH**, while the second step involves the protection of the alcohol of **6MCC-OH** using acetyl imidazole (AcIm) leading to the final product **2a**. The first part of the mechanism only involves **1a** and TBD with AcIm as spectator.

First, the tertiary alcohol in **5MCC-OH** is deprotonated by TBD through **TS1** obtaining **5MCC-O** and TBD-H⁺. The alkoxide group in **5MCC-O** subsequently approaches the carbonate carbon center and generates intermediate **5MCC-Int**. From here, an isomerisation of **5MCC-Int** to **6MCC-Int1** takes place via **TS2**. This second step needs the presence of TBD-H⁺ as to induce a closer interaction between the

Figure 1. Relative Gibbs free energy profile in kcal·mol⁻¹ for the formation of acylated six-membered cyclic carbonate **2a** from five-membered **1a** using TBD as catalyst and acetyl imidazole as acylating agent.

alkoxide and the carbonyl in **5MCC-Int** thus enabling the opening of the five-membered ring generating six-membered **6MCC-Int1**. This transformation has an energetic span of 17.6 kcal·mol⁻¹ and supports the feasibility of all steps at room temperature. Then, the latter intermediate is converted into **6MCC-OH** through proton transfer from TBD-H⁺ (**TS3**) and produces the six-membered carbonate which contains a primary alcohol. This is an important step since the conformational change while forming **TS3** positions the alkoxide group away from the carbonate carbon avoiding (to some extent) a back-reaction to **5MCC-Int1**. Importantly, **6MCC-OH** is computed to be thermodynamically significantly less stable than **5MCC-OH** (nearly 3 kcal·mol⁻¹, $K_{eq} = 7.5 \times 10^{-3}$) and corroborates with the observation that an NMR mixture of **2a** and TBD (*cf.*, Scheme 4a+c) did not show any sign of **6MCC-OH**. In order to be able to isolate the six-membered carbonate, O-protection by AcIm is thus crucial.

The second part of the cascade process describes the acylation of the primary alcohol in **6MCC-OH** (Figure 1). This O-protection using AcIm is catalyzed by TBD affording **6MCC-OAc (2a)** as a thermodynamically and kinetically stable product. The acylation process occurs in three steps. The first one is the deprotonation of the primary alcohol in **6MCC-OH** by TBD (via **TS4**) generating intermediate **6MCC-O-1** and TBD-H⁺. Notably, **6MCC-Int1** is different from **6MCC-O-1** in that the alkoxide group is located nearer the carbonate carbon center of **6MCC-Int1**. This larger separation present in ternary intermediate **6MCC-O-2** and facilitated by TBD-H⁺ allows the nucleophilic alkoxide to attack the carbonyl fragment in AcIm through **TS5** and furnishes intermediate **6MCC-Int2**. As a consequence, the carbonyl carbon of AcIm undergoes a change from sp² to sp³ hybridization. Finally, TBD-H⁺ transfers a proton to the outer nitrogen atom of the imidazole group (**TS6**) thus provoking an electronic rearrangement that allows for the generation of the final product **6MCC-OAc (2a)** and Im-H as by-product while regenerating TBD. The highest barrier (**TS6**) of the acylation process is located at 14.6 kcal·mol⁻¹ and is substantially lower than the energetic requirement for the isomerization of **5MCC-OH** to **6MCC-OH**. This isomerization appears to be rate-limiting, and the final product **6MCC-OAc (2a)** is thermodynamically more stable than **1a** by 10.2 kcal·mol⁻¹.

Since all intermediates are in dynamic equilibrium, O-protection seems to make the overall cascade process irreversible at ambient temperature. To substantiate that hypothesis, we also computed the acylation of the starting carbonate **5MCC-OH (1a)** through the same pathway that leads to **6MCC-OAc (2a)**. Interestingly, the acetylated carbonate **5MCC-OAc** has a substantially higher free energy than

6MCC-OAc (1.8 and $-10.2 \text{ kcal}\cdot\text{mol}^{-1}$, respectively) but the difference in activation barrier ($\Delta\Delta G^\ddagger$) of both acylation processes is markedly different (see Figure S1). At rt, the O-protection in **5MCC-OH** (having a tertiary alcohol) is energetically not competitive with the 5-to-6 carbonate isomerization/acylation cascade with a $\Delta\Delta G^\ddagger$ of $7.2 \text{ kcal}\cdot\text{mol}^{-1}$. Therefore, key to formation of the protected product **6MCC-OAc** is a kinetic differentiation between both alcohol protection pathways allowing to selectively trap the acylated six-membered carbonate **2a** in high isolated yield.

Conclusion

In summary, we here present a unique organocatalytic manifold for the formation of elusive 6-membered heterocycles at room temperature. The six-membered cyclic carbonates that are attained this way are highly versatile and allow for the presence of several alkyl and aryl ring substituents. Computational analysis complemented by control experiments emphasize the importance of kinetic differentiation in pendent alcohol protection as a way to isolate otherwise difficult to prepare CO₂ based heterocycles through a unique cascade process.

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- [19] For fast scans in the potential energy surface the xTB program developed by Grimme was used, see ref. 20. This program allows the scanning of one or more distances, angles and dihedral angles at the same time or sequentially, giving a general idea of each structure. Furthermore, it performs meta-dynamics simulations using the root-mean-square deviation (RMSD) in Cartesian space as

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Supporting Information For:

Organocatalytic Trapping of Elusive Carbon Dioxide based Heterocycles through a Kinetically Controlled Cascade Process

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S2: General comments

All reagents were used as received from commercial suppliers (Aldrich, Acros or TCI) unless stated otherwise. Carbon dioxide was purchased from PRAXAIR and used without further purification. Solvents were dried using an Innovative Technology PURE SOLV solvent purification system. NMR spectra were recorded on Bruker AV-300, AV-400 or AV-500 spectrometers. The residual solvent signals were used as references for ^1H and ^{13}C NMR spectra (CDCl_3 : $\delta_{\text{H}} = 7.26$ ppm, $\delta_{\text{C}} = 77.16$ ppm, CD_3CN : $\delta_{\text{H}} = 1.94$ ppm, $\delta_{\text{C}} = 1.32$ ppm). ^{19}F NMR spectra were not calibrated by an internal reference. FT-IR measurements were carried out on a Bruker Optics FTIR-ATR TR0 spectrometer. Exact mass analyses and X-ray diffraction studies were performed by the Research Support Area (RSA) at ICIQ.

S3: Experimental procedures for the synthesis of the homoallylic epoxides

Method A

The starting ketone or aldehyde (10 mmol) was added in a 50 mL oven-dried Schleck flask under nitrogen, and then 10 mL of dry THF was added via a syringe. Allylmagnesium bromide (12 mL, 1.2 equiv, 1.0 M Et₂O solution) was added dropwise at 0 °C using an ice bath. The reaction was stirred at room temperature for 16 h, then quenched with saturated NH₄Cl (aq) and extracted with Et₂O (3 × 30 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and then concentrated to obtain the corresponding homoallylic alcohol.

The homoallylic alcohols were used without further purification unless stated otherwise. The latter were dissolved in DCM (50 mL) at 0 °C and *m*-CPBA (1.1 eq., 11 mmol, 2.5 g) was added. The mixture was allowed to warm to room temperature and was stirred for 16 h. The reaction mixture was washed with NaHCO₃ (4 × 30 mL) and dried over Na₂SO₄. The solvent was removed *in vacuo* and the crude product was purified by flash chromatography employing 5 % - 25% EA in hexane as eluent. **Note:** EA stands for ethyl acetate.

Method B

To a stirred suspension of cyclohexanone (0.98 g, 10 mmol, 1.0 equiv), zinc powder (976 mg, 15 mmol, 1.5 equiv), and ammonium acetate (1.156 g, 15 mmol, 1.5 equiv) in THF (40.0 mL, 0.25 M) at 0 °C was added allyl bromide (1.3 mL, 15 mmol, 1.5 equiv) dropwise over 1 min.^[1] After stirring for 10 min, the reaction mixture was quenched at 0 °C by addition of 20 mL of saturated aqueous NaHCO₃ and allowed to warm to room temperature over 20 min. The mixture was then transferred to a separation funnel together with Et₂O (30 mL) and H₂O (30 mL). After separation of the organic layer, the aqueous one was extracted with Et₂O (3 × 20 mL). The organic layers were combined, dried over Na₂SO₄ and evaporated under reduced pressure to yield homoallylic alcohol **A8** as a colorless oil.

The homoallylic alcohol **A8** was used without further purification. The following epoxidation process was similar to the one described in **Method A**. The product, **B8**, was isolated as a light yellow oil using as eluent 10 % - 25% EA in hexane. Yield: 86%.

Method C

To a suspension of zinc powder (1.3 g, 20 mmol, 2 equiv) in dry THF (40.0 mL) at rt under nitrogen was added allyl bromide (2.42 g, 20 mmol, 2 equiv).^[2] The reaction mixture was refluxed for 2 min, and then cooled to rt. The ketone (1.34 g, 10 mmol, 1 equiv) was added dropwise to the mixture via a syringe. The mixture was stirred for 16 h, quenched with saturated NH_4Cl (aq) and extracted with Et_2O (3×30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered, concentrated and then purified by flash chromatography employing 3 % - 10% EA in hexane as eluent to obtain homoallylic alcohol **A10**.

The following epoxidation process was similar to the one described in **Method A**. The product **B10** was isolated as a light yellow oil using as eluent 5 % - 10% EA in hexane. Yield: 89%.

S6: Experimental procedures for the synthesis of the 5-membered carbonates 1a-1q

The non-commercial cyclic carbonates^[3,4] and Al(III) aminotriphenolate complexes Al^{Cl} and Al^{Me} ^[5] were prepared according to literature procedures.

Condition A

In a 30 mL stainless steel reactor, the epoxide (1 mmol) was dissolved in MEK (3 mL) and Al^{Cl} (0.02 mmol, 2 mol%, 12.8 mg) and TBAB (0.05 mmol 5 mol%, 16.0 mg) were added. Three cycles of pressurization and depressurization of the reactor with 10 bar of CO_2 were carried out before finally stabilizing at 10 bar. The mixture was stirred at 45 °C for 18 h, then cooled in an ice bath and carefully depressurized. The solvent was removed *in vacuo* and the resulting product was purified by flash chromatography. Unless stated otherwise, the eluent was 10 % - 25% EA in hexane.

Condition B

In a stainless-steel HEL-multireactor, the epoxide (0.5 mmol) was dissolved in MEK (400 μL) and Al^{Me} (0.01 mmol 2 mol%, 5.1 mg) and TBAB (0.05 mmol 10 mol%, 8.0 mg) were added. The reactor was purged twice with CO_2 (10 bar) and then charged with CO_2 (10 bar). The mixture was stirred at 50 °C for 18 h, then cooled in an ice bath and carefully depressurized. The solvent was removed *in vacuo* and the resulting product was purified by flash chromatography employing 10 % - 25% EA in hexane as eluent.

S7: Experimental procedure for the synthesis of 6-membered carbonates 2a-2q

The respective 5-membered cyclic carbonate (0.1 mmol), TBD (0.3 equiv, 0.03 mmol, 4.2 mg) and 1-acetylimidazole (AcIm, 1.2 equiv, 0.12 mmol, 13.2 mg) were added in an oven-dried glassware glass vial under argon, and then 0.2 mL of CH₃CN was added via a syringe. The reaction mixture was stirred at room temperature. After 2 h, the mixture was transferred to a round-bottom flask, concentrated and purified by flash column chromatography with 10-25 % EA in hexane as eluent. In some cases, TLC plates were used to purify the product mixtures.

S8: Experimental procedure for the synthesis of 1h-Ac

Cf., Scheme 4b in the main text:

Cyclohexanone (10 mmol) was added to a 50 mL oven-dried Schleck flask under nitrogen, and then 10 mL of dry THF was added via a syringe. Allylmagnesium bromide (12 mL, 1.2 equiv, 1.0 M Et₂O solution) was added dropwise at 0 °C using an ice bath. The reaction mixture was stirred at room temperature for 16 h, quenched with Ac₂O (1.2 equiv, 12 mmol, 1.23 g). The mixture was stirred for another 2 h, and then extracted with Et₂O (3 × 30 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, concentrated and purified by flash column chromatography using 1-5 % EA in hexane as eluent. The first product **A18** (the acetyl-protected homo-allylic alcohols) was isolated as a yellow liquid. Yield: 50% (0.91 g).

The following epoxidation and cycloaddition reactions were similar to the procedures described under **Method A** (page S3) and **Condition A** (page S6). The epoxide intermediate **B18** (scale: 5 mmol) was isolated as a light yellow oil. Yield: 13%, 130.2 mg.

The final product **1h-Ac** (scale: 0.5 mmol) was isolated as an orange oil. Yield: 77%, 92.8 mg.

S9: Qualitative reactions between Al^{Cl} and epoxy alcohol B1

Entry ^[a]	Cat.	DBU	CO ₂	AcIm	Conv.	1a/3a
1	✓	✓	✓	✓	High	1a+3a
2	✓	×	✓	✓	High	1a
3	×	✓	✓	✓	Low	1a+3a
4	✓	✓	×	✓	0	–
5 ^[b]	×	✓	×	×	Low	3a

^[a] Reaction conditions: substrate (0.25 mmol), butanone (3 mL), 45 °C, 18 h.

^[b] Using **1a** as starting material.

S10: Characterization data for all new and relevant compounds

Homoallylic alcohols:

Note: See reference ^[6]. The product was isolated as colorless oil, eluent: 1%-2% EA in hexane. Yield: 27%, 95:5 *dr*.

¹H NMR (400 MHz, CDCl₃) δ 7.58 (dd, *J* = 7.3, 1.9 Hz, 2H), 7.47 – 7.34 (m, 3H), 5.63 – 5.49 (m, 1H), 5.32 – 5.17 (m, 2H), 2.99 (dd, *J* = 14.3, 6.7 Hz, 1H), 2.85 (dd, *J* = 14.2, 8.1 Hz, 1H), 2.61 (s, 1H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 136.98, 130.53, 129.70, 128.69, 128.49, 128.37, 126.87, 126.59, 126.58, 124.03, 122.16, 76.06, 75.78, 75.50, 40.46 ppm; **¹⁹F NMR (376 MHz, CDCl₃)** δ -78.91, -79.16 ppm.

Note: See reference ^[7]. The product was isolated as a light yellow solid, eluent: 2 % - 3% EA in hexane, yield: 37%.

¹H NMR (500 MHz, CDCl₃) δ 7.24 – 7.13 (m, 4H), 6.13 – 5.89 (m, 1H), 5.26 – 5.16 (m, 2H), 3.57 (s, 1H), 3.09 (d, *J* = 16.2 Hz, 2H), 2.96 (d, *J* = 16.2 Hz, 2H), 2.52 (dt, *J* = 7.3, 1.2 Hz, 2H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 141.30, 134.10, 126.76, 125.12, 119.18, 81.61, 46.64, 45.16 ppm.

The product was isolated as light yellow oil, eluent: 2%-3% EA in hexane. Yield: 50%.

¹H NMR (400 MHz, CDCl₃) δ 5.85 – 5.66 (m, 1H), 5.11 – 4.93 (m, 2H), 2.64 (dt, *J* = 7.4, 1.2 Hz, 2H), 2.25 – 2.11 (m, 2H), 2.00 (s, 3H), 1.66 – 1.30 (m, 8H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 170.52, 133.25, 118.15, 83.45, 42.07, 34.60, 25.63, 22.38, 21.94 ppm; **HRMS (ESI⁺; MeOH):** *m/z* calcd. (C₁₁H₁₈O₂) 123.1168 (M–CH₃COO)⁺: found: 123.1169.

Expoxy alcohols B1-B18:

The product was isolated as a white solid, yield: 98%.

¹H NMR (400 MHz, CDCl₃) δ 7.50 – 7.42 (m, 4H), 7.36 – 7.22 (m, 6H), 3.21 (s, 1H), 2.98 (dtd, *J* = 7.0, 4.2, 2.7 Hz, 1H), 2.78 – 2.64 (m, 2H), 2.47 (dd, *J* = 4.9, 2.8 Hz, 1H), 2.35 (dd, *J* = 14.4, 7.2 Hz, 1H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 146.91, 146.27, 128.43, 128.42, 127.31, 127.14, 126.16, 125.95, 78.24, 49.80, 47.18, 44.27 ppm; **HRMS (ESI⁺; MeOH):** *m/z* calcd. (C₁₆H₁₆NaO₂) 236.1043 (M+Na)⁺: found: 263.1046.

The product was isolated as an orange oil, yield: 56%.

¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.29 (m, 4H), 6.89 – 6.81 (m, 4H), 3.80 (s, 3H), 3.78 (s, 3H), 3.08 (s, 1H), 2.97 (dtd, *J* = 7.1, 4.3, 2.8 Hz, 1H), 2.68 (dd, *J* = 4.9, 4.0 Hz, 1H), 2.61 (dd, *J* = 14.3, 4.4 Hz, 1H), 2.45 (dd, *J* = 4.9, 2.8 Hz, 1H), 2.34 (dd, *J* = 14.3, 7.0 Hz, 1H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 158.68, 158.58, 139.46, 138.73, 127.37, 127.23, 113.65, 113.63, 77.68, 55.37, 49.85, 47.23, 44.59 ppm; **HRMS (ESI⁺; MeOH):** *m/z* calcd. (C₁₈H₂₀NaO₄) 323.1254; (M+Na)⁺: found: 323.1246.

The product was isolated as a pale-colored oil, eluent: 5%-10% EA in hexane, yield: 73%.

¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.29 (m, 4H), 7.18 – 7.10 (m, 4H), 3.11 (s, 1H), 2.98 (dtd, *J* = 7.0, 4.2, 2.7 Hz, 1H), 2.70 – 2.62 (m, 2H), 2.45 (dd, *J* = 4.9, 2.8 Hz, 1H), 2.40 – 2.30 (m, 7H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 144.18, 143.58, 136.78,

136.61, 129.04, 129.02, 126.02, 125.83, 77.91, 49.82, 47.19, 44.36, 21.09; **HRMS**
(ESI+; MeOH): *m/z* calcd. (C₁₈H₂₀NaO₂) 291.1356 (M+Na)⁺: found: 291.1358.

The product was isolated as a white solid, yield: 83%.

¹H NMR (400 MHz, CDCl₃) δ 7.44 – 7.38 (m, 2H), 7.36 – 7.26 (m, 6H), 3.47 (s, 1H), 2.94 (dtd, *J* = 7.8, 3.9, 2.7 Hz, 1H), 2.77 – 2.69 (m, 2H), 2.49 (dd, *J* = 4.8, 2.8 Hz, 1H), 2.20 (dd, *J* = 14.5, 7.7 Hz, 1H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 145.06, 144.36, 133.38, 133.27, 128.69, 128.61, 127.59, 127.32, 77.67, 49.58, 47.08, 43.87 ppm; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₆H₁₄Cl₂NaO₂) 331.0263 (M+Na)⁺: found: 331.0258.

The product was isolated as a white solid, yield: 79%.

¹H NMR (500 MHz, CDCl₃) δ 7.46 – 7.41 (m, 2H), 7.39 – 7.34 (m, 2H), 7.07 – 6.94 (m, 4H), 3.43 (s, 1H), 2.95 (dtd, *J* = 7.8, 4.0, 2.7 Hz, 1H), 2.74 – 2.66 (m, 2H), 2.48 (dd, *J* = 4.8, 2.8 Hz, 1H), 2.25 (dd, *J* = 14.4, 7.5 Hz, 1H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 162.98, 162.93, 161.02, 160.97, 142.66, 142.63, 141.87, 141.85, 127.91, 127.85, 127.72, 127.66, 115.36, 115.28, 115.19, 115.11, 77.64, 49.65, 47.09, 44.32 ppm; **¹⁹F NMR (376 MHz, CDCl₃)** δ -115.55, -115.82 ppm; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₆H₁₃F₂O) 259.0929 (M – OH)⁺: found: 259.0929.

The product was isolated as a light yellow oil, yield: 76%.

¹H NMR (500 MHz, CDCl₃) δ 3.10 (dtd, *J* = 7.0, 4.1, 2.7 Hz, 1H), 2.78 (dd, *J* = 5.1, 4.0 Hz, 1H), 2.47 (dd, *J* = 5.0, 2.7 Hz, 1H), 1.79 (dd, *J* = 14.5, 4.2 Hz, 2H), 1.59 – 1.46 (m, 5H), 1.40 – 1.26 (m, 4H), 0.93 (td, *J* = 7.3, 2.6 Hz, 6H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 74.63, 49.24, 46.99, 42.15, 42.11, 42.03, 17.05, 16.94, 14.80, 14.77 ppm; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₀H₁₉O) 155.1430 (M–OH)⁺: found: 155.1428.

The product was isolated as a colorless oil, yield: 83%.

¹H NMR (500 MHz, CDCl₃) δ 3.04 (dtd, *J* = 7.0, 4.2, 2.7 Hz, 1H), 2.80 (dd, *J* = 5.1, 4.0 Hz, 1H), 2.49 (dd, *J* = 5.0, 2.8 Hz, 1H), 1.89 – 1.72 (m, 10H), 1.64 – 1.52 (m, 4H), 1.33 – 0.95 (m, 10H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 77.37, 49.61, 48.10, 45.29, 44.91, 37.15, 27.58, 27.39, 27.32, 27.22, 27.18, 27.16, 27.12, 27.09, 26.81 ppm; **HRMS (ESI⁺; MeOH):** *m/z* calcd. (C₁₆H₂₇O) 235.2056 (M–OH)⁺: found: 235.2057.

The product was isolated as a light yellow oil, yield: 86%.^[1]

¹H NMR (400 MHz, CDCl₃) δ 3.15 (dtd, *J* = 7.1, 4.2, 2.8 Hz, 1H), 2.79 (dd, *J* = 5.0, 4.0 Hz, 1H), 2.47 (dd, *J* = 5.0, 2.7 Hz, 1H), 1.80 (dd, *J* = 14.4, 4.3 Hz, 2H), 1.70 – 1.41 (m, 11H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 71.70, 49.05, 46.93, 44.67, 38.13, 37.84, 25.78, 22.30, 22.21 ppm.

The product was isolated as a colorless oil, yield: 59%.

¹H NMR (400 MHz, CDCl₃) δ 3.21 – 3.11 (m, 1H), 2.80 (t, *J* = 4.5 Hz, 1H), 2.48 (dd, *J* = 5.1, 2.8 Hz, 1H), 1.95 – 1.77 (m, 4H), 1.71 – 1.37 (m, 14H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 75.22, 49.25, 47.03, 44.04, 36.79, 36.68, 28.35, 28.28, 25.06, 22.34, 22.30 ppm. **HRMS (ESI⁺; MeOH):** *m/z* calcd. (C₁₁H₂₀NaO₂) 207.1356 (M+Na)⁺: found: 207.1357.

The product was isolated as a light yellow oil, yield: 89%, 63:37 *dr*.

¹H NMR (500 MHz, CDCl₃) δ 7.43 – 7.34 (m, 5.57H), 7.22 – 7.11 (m, 5.51H), 3.00 – 2.95 (m, 1H), 2.87 (dtd, *J* = 8.1, 3.8, 2.8 Hz, 1.73H), 2.77 (s, 1.29H), 2.72 (dd, *J* = 5.0, 4.0 Hz, 1.09H), 2.66 (dd, *J* = 4.9, 4.1 Hz, 1.76H), 2.44 (dd, *J* = 5.0, 2.7 Hz, 1.09H), 2.41 (dd, *J* = 4.9, 2.7 Hz, 1.99H), 2.35 (s, 8.26H), 2.29 (dd, *J* = 14.5, 3.5 Hz, 1.82H), 2.07 (dd, *J* = 14.3, 4.8 Hz, 1.09H), 1.98 (dd, *J* = 14.3, 6.7 Hz, 1.09H), 1.75 (dd, *J* = 14.5, 8.3 Hz, 1.99H), 1.66 (s, 3.43H), 1.59 (s, 5.74H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 144.77, 144.56, 136.64, 136.43, 129.13, 129.11, 124.77, 124.71, 74.81, 74.17, 49.72, 49.51, 47.07, 46.65, 46.42, 46.18, 31.02, 29.87, 21.09, 21.07 ppm; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₂H₁₆NaO₂) 215.1043 (M+Na)⁺: found: 215.1047.

The product was isolated as a colorless oil, yield: 85%, 69:31 *dr*.

¹H NMR (400 MHz, CDCl₃) δ 7.44 (ddt, *J* = 8.4, 6.3, 1.2 Hz, 2.87H), 7.36 (td, *J* = 7.7, 1.6 Hz, 2.86H), 7.28 – 7.22 (m, 1.69H), 2.97 (tdd, *J* = 5.8, 4.0, 2.7 Hz, 0.45H), 2.87 (s, 0.93H), 2.81 (dddd, *J* = 8.5, 4.1, 3.4, 2.8 Hz, 1H), 2.71 (dd, *J* = 5.0, 4.0 Hz, 0.46H), 2.63 (dd, *J* = 4.9, 4.1 Hz, 1.01H), 2.45 (dd, *J* = 5.0, 2.8 Hz, 0.46H), 2.40 (dd, *J* = 4.9, 2.8 Hz, 1.01H), 2.34 (d, *J* = 3.3 Hz, 0.91 H), 2.30 (d, *J* = 3.4 Hz, 0.53H), 2.06 (d, *J* = 5.7 Hz, 0.86H), 1.97 (qd, *J* = 7.4, 1.1 Hz, 0.86H), 1.87 (qd, *J* = 7.4, 2.4 Hz, 1.95H), 1.76 (dd, *J* = 14.5, 8.4 Hz, 0.98H), 0.78 (td, *J* = 7.4, 1.8 Hz, 4.47H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 145.67, 128.35, 126.84, 126.69, 125.49, 125.33, 76.76, 49.71, 49.37, 47.27, 46.73, 44.98, 44.72, 36.20, 34.94, 7.79, 7.65 ppm; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₂H₁₅O) 175.1117 (M–OH)⁺: found: 175.1115.

Scale: 1.85 mmol. The product was isolated as white solid, eluent: 3%-10% EA in hexane. Yield: 42%, 97:3 *dr*.

¹H NMR (500 MHz, CDCl₃) δ 7.71 – 7.63 (m, 2H), 7.49 – 7.34 (m, 3H), 3.78 (s, 1H), 2.87 – 2.77 (m, 2H), 2.70 (dd, *J* = 4.7, 3.9 Hz, 1H), 2.51 (dd, *J* = 4.6, 2.6 Hz, 1H), 1.92 (dd, *J* = 15.3, 9.4 Hz, 1H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 136.55, 128.87, 128.65, 128.56, 126.80, 126.18, 123.91, 121.64, 48.56, 46.40, 37.77 ppm; **¹⁹F NMR (376 MHz, CDCl₃)** δ -78.45, -80.95; **HRMS (ESI⁺; MeOH):** *m/z* calcd. (C₁₁H₁₁F₃NaO₂) 255.0603 (M+Na)⁺: found: 255.0605.

The product was isolated as a yellow oil. Yield: 63%, 57:43 *dr*.

¹H NMR (400 MHz, CDCl₃) δ 7.48 (d, *J* = 8.0 Hz, 0.43H), 7.41 – 7.32 (m, 0.57H), 7.04 – 6.92 (m, 2H), 3.01 – 2.85 (m, 0.99H), 2.77 – 2.67 (m, 1.46H), 2.56 – 2.50 (m, 3.50), 2.45 (td, *J* = 4.8, 2.8 Hz, 1.04H), 2.30 – 2.28 (m, 3.59H), 2.21 (dd, *J* = 14.4, 4.7 Hz, 0.62H), 2.08 (dd, *J* = 14.4, 6.7 Hz, 0.56H), 1.80 – 1.72 (m, 2.20H), 1.66 (s, 1.28H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 141.80, 141.56, 136.90, 136.74, 135.41, 134.52, 133.72, 133.58, 126.76, 126.52, 126.22, 126.04, 75.80, 75.39, 49.91, 49.66, 47.00, 46.71, 44.40, 29.78, 29.67, 22.47, 22.38, 20.80 ppm; **HRMS (ESI⁺; MeOH):** *m/z* calcd. (C₁₃H₁₇O) 189.1274 (M–OH)⁺: found: 189.1279.

The product was isolated as a brown oil. Yield: 42%, 74:26 *dr*.

¹H NMR (400 MHz, CDCl₃) δ 8.08 – 7.79 (m, 6.35H), 7.64 – 7.43 (m, 4.94H), 3.10 (s, 0.95H), 3.00 (dddd, *J* = 6.7, 4.9, 3.1, 2.0 Hz, 1H), 2.87 (dddd, *J* = 8.3, 4.1, 3.5, 2.8 Hz,

0.35H), 2.72 (dd, $J = 4.9, 4.0$ Hz, 0.62H), 2.64 (dd, $J = 4.9, 4.1$ Hz, 1.15H), 2.45 – 2.39 (m, 2.16H), 2.18 (dd, $J = 14.4, 4.9$ Hz, 0.36H), 2.09 (dd, $J = 14.3, 6.7$ Hz, 0.38H), 1.84 (dd, $J = 14.5, 8.3$ Hz, 1.1H), 1.77 (s, 1.08H), 1.69 (s, 3.11H) ppm; **^{13}C NMR (101 MHz, CDCl_3)** δ 145.03, 144.79, 133.40, 133.31, 132.52, 132.44, 128.43, 128.34, 128.20, 128.18, 127.63, 127.61, 126.46, 126.30, 126.00, 125.94, 123.51, 123.49, 123.47, 123.23, 75.17, 74.47, 49.73, 49.52, 47.11, 46.63, 46.16, 45.94, 31.08, 29.85 ppm; **HRMS (ESI+; MeOH):** m/z calcd. ($\text{C}_{15}\text{H}_{15}\text{O}$) 211.1117 ($\text{M}-\text{OH}$) $^+$: found: 211.1119.

The product was isolated as colorless oil, eluent: 3%-10% EA in hexane. Yield: 47%, 58:42 *dr*.

^1H NMR (400 MHz, CDCl_3) δ 3.64 (ddd, $J = 9.4, 5.6, 2.8$ Hz, 1H), 3.58 (ddd, $J = 9.7, 5.7, 2.7$ Hz, 0.71H), 3.19 – 3.13 (m, 0.73H), 3.10 (dtd, $J = 7.1, 4.2, 2.7$ Hz, 0.91H), 2.82 (dd, $J = 4.9, 4.0$ Hz, 0.75H), 2.78 (dd, $J = 4.9, 4.0$ Hz, 0.98H), 2.61 (dd, $J = 4.9, 2.8$ Hz, 0.7H), 2.49 (dd, $J = 4.9, 2.7$ Hz, 1.01H), 2.14 (s, 1.39H), 1.92 – 0.95 (m, 25.75H) ppm; **^{13}C NMR (101 MHz, CDCl_3)** δ 74.98, 73.48, 51.32, 50.74, 47.23, 46.70, 43.91, 43.81, 36.72, 36.10, 29.13, 28.99, 28.04, 28.03, 26.61, 26.59, 26.35, 26.23, 26.21 ppm; **HRMS (ESI+; MeOH):** m/z calcd. ($\text{C}_{10}\text{H}_{19}\text{O}_2$) 171.1380 ($\text{M}+\text{H}$) $^+$: found: 171.1379.

Scale: 3.6 mmol. The product was isolated as a light yellow solid, eluent: 2 % - 3% EA in hexane. Yield: 64%.

^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.15 (m, 4H), 3.24 (dtd, $J = 6.8, 4.1, 2.7$ Hz, 1H), 3.16 (d, $J = 16.2$ Hz, 2H), 3.06 (d, $J = 16.2$ Hz, 2H), 2.84 (dd, $J = 5.0, 4.1$ Hz, 1H), 2.55 (dd, $J = 5.0, 2.7$ Hz, 1H), 2.14 (dd, $J = 14.3, 4.1$ Hz, 1H), 1.81 (dd, $J = 14.3, 7.5$ Hz, 1H) ppm; **^{13}C NMR (126 MHz, CDCl_3)** δ 141.17, 140.94, 126.90, 126.85, 125.24, 125.17, 81.90, 49.69, 47.14, 47.13, 46.93, 42.76 ppm; **HRMS (ESI+; MeOH):** m/z calcd. ($\text{C}_{12}\text{H}_{13}\text{O}$) 173.0961 ($\text{M}-\text{OH}$) $^+$: found: 173.0962.

The product was isolated as a light yellow oil. Yield: 66%, 67:33 *dr*.

¹H NMR (400 MHz, CDCl₃) δ 7.67 – 7.51 (m, 18H), 7.50 – 7.41 (m, 6H), 7.38 – 7.31 (m, 3H), 3.04 (dddd, *J* = 6.8, 4.8, 4.0, 2.7 Hz, 1H), 2.97 – 2.88 (m, 2H), 2.76 (dd, *J* = 5.0, 4.0 Hz, 1H), 2.70 (dd, *J* = 4.9, 4.1 Hz, 2H), 2.49 (dd, *J* = 5.0, 2.7 Hz, 1H), 2.45 (dd, *J* = 4.9, 2.8 Hz, 2H), 2.37 (dd, *J* = 14.5, 3.4 Hz, 2H), 2.15 (dd, *J* = 14.4, 4.8 Hz, 1H), 2.02 (dd, *J* = 14.4, 6.8 Hz, 1H), 1.79 (dd, *J* = 14.5, 8.4 Hz, 2H), 1.72 (s, 3H), 1.65 (s, 6H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 146.76, 146.55, 140.88, 140.85, 139.95, 139.78, 128.93, 128.90, 127.40, 127.38, 127.18, 127.15, 125.36, 125.29, 74.94, 74.26, 49.74, 49.51, 47.12, 46.69, 46.34, 46.10, 31.06, 29.82 ppm; **HRMS (ESI⁺; MeOH):** *m/z* calcd. (C₁₇H₁₇O) 237.1274 (M–OH)⁺: found: 237.1281.

Scale: 5 mmol. The product was isolated as light yellow oil, eluent: 5% EA in hexane. Yield: 13%. [See page S8 for details.](#)

¹H NMR (400 MHz, CDCl₃) δ 2.97 (dtd, *J* = 7.0, 4.1, 2.7 Hz, 1H), 2.73 (dd, *J* = 5.1, 4.0 Hz, 1H), 2.42 (dd, *J* = 5.1, 2.7 Hz, 1H), 2.34 – 2.24 (m, 3H), 2.04 (s, 3H), 1.91 (dd, *J* = 14.7, 7.3 Hz, 1H), 1.60 – 1.39 (m, 7H), 1.33 – 1.20 (m, 1H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 170.74, 83.09, 48.51, 46.34, 40.58, 35.14, 34.98, 25.52, 22.40, 21.89, 21.79 ppm; **HRMS (ESI⁺; MeOH):** *m/z* calcd. (C₁₁H₁₈NaO₃) 221.1148 (M+Na)⁺: found: 221.1142.

5-Membered Cyclic Carbonates 1a-1q:

Condition A. The product was isolated as a white solid. Yield: 85%.

¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.27 (m, 10H), 4.68 (dddd, J = 9.3, 8.5, 7.6, 3.6 Hz, 1H), 4.30 (dd, J = 9.0, 7.6 Hz, 1H), 4.05 (t, J = 8.8 Hz, 1H), 2.99 (dd, J = 13.7, 3.6 Hz, 1H), 2.73 (dd, J = 13.7, 9.3 Hz, 1H), 2.34 (s, 1H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 155.00, 145.99, 145.10, 128.78, 128.70, 127.93, 127.72, 125.80, 125.79, 76.83, 75.34, 71.01, 45.49 ppm. **IR (neat):** ν = 1777 cm⁻¹; **HRMS (ESI⁺; MeOH):** m/z calcd. (C₁₇H₁₆NaO₄) 307.0941 (M+Na)⁺: found: 307.0941.

Condition A. The product was isolated as a light yellow solid. Yield: 99%.

¹H NMR (500 MHz, CDCl₃) δ 7.24 (dd, J = 13.1, 8.8 Hz, 4H), 6.84 (dd, J = 12.4, 8.6 Hz, 4H), 4.64 (qd, J = 8.4, 3.3 Hz, 1H), 4.24 (t, J = 8.1 Hz, 1H), 4.00 (t, J = 8.7 Hz, 1H), 3.77 (d, J = 6.3 Hz, 6H), 2.88 (dd, J = 13.6, 3.4 Hz, 1H), 2.73 (s, 1H), 2.63 (dd, J = 13.6, 9.4 Hz, 1H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 159.22, 159.07, 154.97, 138.35, 137.47, 131.13, 129.42, 127.18, 127.12, 114.06, 114.01, 76.45, 75.41, 71.07, 55.45, 45.90 ppm; **IR (neat):** ν = 1769 cm⁻¹; **HRMS (ESI⁺; MeOH):** m/z calcd. (C₁₉H₂₀NaO₆) 367.1152 (M+Na)⁺: found: 367.1146.

Condition A. The product was isolated as a white solid. Yield: 95%.

¹H NMR (500 MHz, CDCl₃) δ 7.23 – 7.18 (m, 4H), 7.12 (dd, *J* = 11.0, 8.1 Hz, 4H), 4.64 (dddd, *J* = 9.5, 8.6, 7.6, 3.4 Hz, 1H), 4.25 (dd, *J* = 9.1, 7.6 Hz, 1H), 4.02 (t, *J* = 8.8 Hz, 1H), 2.92 (dd, *J* = 13.6, 3.4 Hz, 1H), 2.65 (dd, *J* = 13.7, 9.5 Hz, 1H), 2.37 (s, 1H), 2.31 (d, *J* = 6.6 Hz, 6H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 155.02, 143.28, 142.33, 137.73, 137.44, 129.44, 129.38, 125.71, 76.71, 75.44, 71.09, 45.60, 21.10 ppm; **IR (neat):** ν = 1786 cm⁻¹; **HRMS (ESI⁺; MeOH):** *m/z* calcd. (C₁₉H₂₀NaO₄) 335.1254 (M+Na)⁺: found: 335.1265.

Condition A. The product was isolated as a white solid. Yield: 87%.

¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.26 (m, 8H), 4.62 (tdd, *J* = 8.5, 7.6, 4.1 Hz, 1H), 4.34 (dd, *J* = 9.0, 7.6 Hz, 1H), 4.07 (t, *J* = 8.7 Hz, 1H), 2.90 (dd, *J* = 13.9, 4.1 Hz, 1H), 2.79 (s, 1H), 2.66 (dd, *J* = 13.9, 8.6 Hz, 1H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 154.83, 144.06, 143.27, 134.12, 133.91, 129.04, 128.97, 127.29, 127.22, 76.26, 74.94, 70.87, 45.36 ppm; **IR (neat):** ν = 1776 cm⁻¹; **HRMS (ESI⁺; MeOH):** *m/z* calcd. (C₁₇H₁₄Cl₂NaO₄) 375.0161 (M+Na)⁺: found: 375.0160.

Condition A. The product was isolated as a white solid. Yield: 85%.

¹H NMR (500 MHz, CDCl₃) δ 7.33 (tdd, *J* = 9.1, 5.2, 2.1 Hz, 4H), 7.04 (td, *J* = 8.7, 7.5 Hz, 4H), 4.64 (tdd, *J* = 8.5, 7.6, 4.0 Hz, 1H), 4.34 (dd, *J* = 9.0, 7.6 Hz, 1H), 4.07 (t, *J* = 8.7 Hz, 1H), 2.92 (dd, *J* = 13.8, 4.0 Hz, 1H), 2.69 (dd, *J* = 13.8, 8.7 Hz, 1H), 2.54 (s, 1H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 163.31, 163.22, 161.34, 161.25, 154.79, 141.63, 141.60, 140.79, 140.77, 127.76, 127.70, 127.66, 127.60, 115.87, 115.77, 115.70, 115.61, 77.41, 74.98, 70.88, 45.81 ppm; **¹⁹F NMR (376 MHz, CDCl₃)** δ -113.76, -114.32 ppm; **IR (neat):** *ν* = 1772 cm⁻¹; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₇H₁₄F₂NaO₄) 343.0752 (M+Na)⁺: found: 343.0756.

Condition A. The product was isolated as a light yellow oil. Yield: 82%.

¹H NMR (500 MHz, CDCl₃) δ 4.97 – 4.92 (m, 1H), 4.58 (dd, *J* = 8.8, 7.7 Hz, 1H), 4.14 (t, *J* = 8.6 Hz, 1H), 2.05 (dd, *J* = 14.5, 6.1 Hz, 1H), 1.79 (dd, *J* = 14.5, 6.7 Hz, 1H), 1.54 – 1.24 (m, 10H), 0.93 (td, *J* = 7.2, 5.1 Hz, 6H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 155.20, 74.78, 73.62, 71.07, 43.06, 42.98, 41.26, 17.24, 16.72, 14.63, 14.61 ppm; **IR (neat):** *ν* = 1775 cm⁻¹; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₁H₂₀NaO₄) 239.1254 (M+Na)⁺: found: 239.1252.

Condition A. The product was isolated as a white solid. Yield: 67%.

¹H NMR (400 MHz, CDCl₃) δ 4.93 (qd, *J* = 8.0, 4.7 Hz, 1H), 4.53 (t, *J* = 8.3 Hz, 1H), 4.13 (t, *J* = 8.4 Hz, 1H), 2.06 – 1.89 (m, 2H), 1.87 – 1.59 (m, 11H), 1.44 (qt, *J* = 11.7, 2.9 Hz, 2H), 1.23 – 0.90 (m, 10H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 155.28, 76.06, 76.00, 71.43, 46.35, 45.31, 37.21, 27.22, 27.05, 26.79, 26.72, 26.62, 26.52, 26.48 ppm; **IR (neat):** ν = 1789 cm⁻¹; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₇H₂₈NaO₄) 319.1880 (M+Na)⁺: found: 319.1864.

Condition A. The product was isolated as a light yellow solid. Yield: 87%.

¹H NMR (500 MHz, CDCl₃) δ 4.99 (tt, *J* = 8.1, 6.4 Hz, 1H), 4.58 (dd, *J* = 8.8, 7.7 Hz, 1H), 4.14 (t, *J* = 8.6 Hz, 1H), 2.10 (dd, *J* = 14.5, 6.3 Hz, 1H), 1.80 – 1.74 (m, 2H), 1.64 – 1.28 (m, 10H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 155.30, 74.60, 71.01, 70.52, 45.49, 39.37, 36.96, 25.45, 22.14, 22.07 ppm; **IR (neat):** ν = 1787 cm⁻¹; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₀H₁₆NaO₄) 223.0941 (M+Na)⁺: found: 223.0941.

Condition A. The product was isolated as a white solid. Yield: 93%.

¹H NMR (400 MHz, CDCl₃) δ 5.02 – 4.95 (m, 1H), 4.59 (dd, *J* = 8.8, 7.7 Hz, 1H), 4.15 (t, *J* = 8.6 Hz, 1H), 2.15 (dd, *J* = 14.5, 6.2 Hz, 1H), 1.85 – 1.40 (m, 16H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 155.34, 74.89, 73.93, 71.05, 44.56, 38.49, 34.99, 28.16, 27.91, 24.96, 22.24, 22.05 ppm; **IR (neat):** ν = 1776 cm⁻¹; **HRMS (ESI⁺; MeOH):** *m/z* calcd. (C₁₂H₂₀NaO₄) 251.1254 (M+Na)⁺: found: 251.1258.

Condition A. The product was isolated as a white solid. Yield: 79%, 73:27 *dr*.

¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.26 (m, 2.78H), 7.20 – 7.15 (m, 2.72H), 4.87 (tt, *J* = 8.1, 6.4 Hz, 1H), 4.47 (dd, *J* = 8.7, 7.5 Hz, 0.38H), 4.38 (dddd, *J* = 9.3, 8.4, 7.5, 4.0 Hz, 0.37H), 4.25 (t, *J* = 8.5 Hz, 0.38H), 4.21 (dd, *J* = 8.8, 7.8 Hz, 1H), 3.79 (t, *J* = 8.6 Hz, 1H), 2.49 – 2.33 (m, 5.75H), 2.22 – 2.10 (m, 1.44H), 1.64 (s, 4.34H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 155.13, 154.95, 143.80, 142.70, 137.25, 137.23, 129.47, 124.42, 124.32, 75.19, 74.81, 73.63, 73.17, 71.16, 70.35, 47.83, 47.29, 32.15, 30.72, 21.06 ppm; **IR (neat):** ν = 1783 cm⁻¹; **HRMS (ESI⁺; MeOH):** *m/z* calcd. (C₁₃H₁₆NaO₄) 259.0941 (M+Na)⁺: found: 259.0952.

Condition B. The product was isolated as a pale yellow oil. Yield: 73%, 7:3 *dr*.

¹H NMR (500 MHz, CDCl₃) δ 7.39 – 7.32 (m, 5.68H), 7.29 – 7.25 (m, 1.42H), 4.82 (dddd, *J* = 8.3, 7.7, 6.8, 5.8 Hz, 1H), 4.48 (dd, *J* = 8.5, 7.2 Hz, 0.42H), 4.36 (dddd, *J* = 9.5, 8.4, 7.1, 3.4 Hz, 0.42H), 4.30 (t, *J* = 8.5 Hz, 0.42H), 4.03 (dd, *J* = 8.8, 7.7 Hz, 1H), 3.67 (t, *J* = 8.6 Hz, 1H), 2.50 – 2.40 (m, 1.42H), 2.37 – 2.10 (m, 2.46H), 2.01 – 1.82 (m, 2.94H), 0.74 (td, *J* = 7.4, 1.5 Hz, 4.40H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 155.24, 154.96, 144.38, 143.83, 128.71, 128.69, 127.32, 127.28, 125.02, 124.95, 76.16, 75.67, 75.28, 74.84, 71.34, 70.26, 46.77, 45.95, 36.47, 35.60, 7.46, 7.24 ppm; **IR (neat):** ν = 1776 cm⁻¹; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₃H₁₆NaO₄) 259.0941 (M+Na)⁺: found: 259.0948.

Condition B. Scale: 0.5 mmol. The product was isolated as white solid, eluent: 10%-20% EA in hexane. Yield: 78%, 9:1 *dr*.

¹H NMR (400 MHz, CDCl₃) δ 7.57 – 7.48 (m, 2H), 7.42 – 7.33 (m, 3H), 4.73 (qd, *J* = 7.5, 4.7 Hz, 1H), 3.97 (ddd, *J* = 8.8, 7.7, 1.0 Hz, 1H), 3.72 (td, *J* = 8.7, 1.0 Hz, 1H), 3.03 (s, 3H), 2.70 (ddd, *J* = 14.6, 5.2, 1.0 Hz, 1H), 2.42 (dd, *J* = 14.6, 7.3 Hz, 1H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 154.23, 135.57, 129.53, 129.12, 128.50, 126.15, 126.10, 123.87, 121.60, 76.35, 76.12, 73.35, 69.75, 39.95 ppm; **¹⁹F NMR (376 MHz, CDCl₃)** δ -79.29, -80.21 ppm; **IR (neat):** ν = 1786 cm⁻¹; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₂H₁₃F₃NaO₄) 299.0502 (M+Na)⁺: found: 299.0491.

Condition A. The product was isolated as a colorless oil. Yield: 46%, 74:26 *dr*.

¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.34 (m, 1.35H), 7.06 – 6.90 (m, 2.75H), 4.93 (tt, *J* = 8.1, 6.1 Hz, 1H), 4.46 – 4.35 (m, 0.72H), 4.31 (dd, *J* = 8.8, 7.7 Hz, 1H), 4.23 – 4.18 (m, 0.35H), 3.91 (t, *J* = 8.7 Hz, 1.01H), 2.68 (dd, *J* = 14.1, 3.8 Hz, 0.35H), 2.52 – 2.46 (m, 4.22H), 2.41 – 2.32 (m, 2.02H), 2.30 (s, 4.17H), 2.25 – 2.12 (m, 1.14H), 1.72 – 1.70 (m, 4.26H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 155.14, 155.03, 141.25, 139.80, 137.42, 137.41, 134.28, 134.26, 133.98, 133.86, 127.00, 126.92, 125.77, 125.54, 75.45, 75.07, 74.36, 74.04, 71.17, 70.52, 45.49, 45.12, 31.10, 29.67, 22.39, 22.34, 20.75 ppm; **IR (neat):** ν = 1778 cm⁻¹; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₄H₁₈NaO₄) 273.1097 (M+Na)⁺: found: 273.1094.

Condition A. The product was isolated as a pink solid employing 10 % - 70% Et₂O in hexane as eluent. Yield: 58%, 9:1 *dr*.

¹H NMR (500 MHz, CDCl₃) δ 7.94 – 7.92 (m, 0.99H), 7.86 – 7.83 (m, 3.37H), 7.54 – 7.43 (m, 3.79H), 4.88 (tt, *J* = 8.1, 6.3 Hz, 1H), 4.48 (dd, *J* = 8.7, 7.4 Hz, 0.10H), 4.42 – 4.33 (m, 0.08H), 4.28 (t, *J* = 8.5 Hz, 0.07H), 4.19 (dd, *J* = 8.8, 7.8 Hz, 0.97H), 3.79 (t, *J* = 8.5 Hz, 1H), 2.68 – 2.55 (m, 0.14H), 2.44 (dd, *J* = 14.5, 6.4 Hz, 1.04H), 2.24 (dd, *J* = 14.5, 6.2 Hz, 0.99H), 1.74 (s, 3.43H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 155.05, 154.86, 144.01, 143.00, 133.28, 133.22, 132.61, 132.58, 128.79, 128.68, 128.30, 128.24, 127.72, 127.69, 126.70, 126.40, 126.25, 123.16, 123.06, 122.88, 122.84, 76.90, 75.08, 74.73, 73.88, 73.49, 71.11, 70.28, 47.57, 47.05, 32.10, 30.68 ppm; **IR (neat):** ν = 1782 cm⁻¹; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₆H₁₆NaO₄) 295.0941 (M+Na)⁺: found: 295.1043.

Condition A. The product was isolated as light yellow solid, eluent: 10%-25% EA in hexane. Yield: 27%, 58:42 *dr*.

¹H NMR (400 MHz, CDCl₃) δ 4.99 – 4.91 (m, 1H), 4.61 – 4.54 (m, 1.02H), 4.25 – 4.21 (m, 0.42H), 4.15 (dd, *J* = 8.7, 7.7 Hz, 0.58H), 3.63 – 3.59 (m, 0.58H), 3.52 – 3.48 (m, 0.42H), 2.06 – 1.63 (m, 8.64H), 1.40 – 0.93 (m, 6.46H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 155.26, 75.93, 75.66, 72.57, 72.43, 70.61, 69.67, 44.29, 43.82, 38.29, 37.21, 28.93, 28.88, 27.99, 27.87, 26.42, 26.40, 26.16, 26.13, 26.04, 26.01 ppm; **IR (neat):** *ν* = 1791 cm⁻¹; **HRMS (ESI⁺; MeOH):** *m/z* calcd. (C₁₁H₁₈NaO₄) 237.1079 (M+Na)⁺: found: 237.1089.

The product was isolated as light yellow solid, eluent: 5%-15% EA in hexane. Yield: 50%, 69:31 *dr*.

¹H NMR (400 MHz, CDCl₃) δ 4.94 – 4.89 (ddd, *J* = 9.7, 5.5, 3.0 Hz, 0.31H), 4.78 – 4.66 (m, 1.69H), 4.58 – 4.48 (m, 1.02H), 4.13 – 4.06 (m, 1.02H), 2.21 – 2.10 (m, 0.98H), 2.08 – 2.07 (m, 3.12H), 1.93 – 1.84 (m, 1.15H), 1.78 – 1.66 (m, 5.32H), 1.57 – 1.48 (m, 1.14H), 1.27 – 1.10 (m, 3.80H), 1.05 – 0.93 (m, 2.24H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 171.27, 170.62, 154.85, 154.65, 74.85, 74.82, 74.35, 73.65, 69.69, 69.58, 41.80, 41.58, 36.03, 35.87, 28.97, 28.62, 28.26, 28.11, 26.35, 26.28, 26.05, 25.96, 25.90, 21.18, 21.12 ppm; **IR (neat):** *ν* = 1729, 1798 cm⁻¹; **HRMS (ESI⁺; MeOH):** *m/z* calcd. (C₁₃H₂₀NaO₅) 279.1210 (M+Na)⁺: found: 279.1203.

Condition B. The product was isolated as a colorless oil. Yield: 58%.

¹H NMR (500 MHz, CDCl₃) δ 7.25 – 7.17 (m, 4H), 5.06 (tt, J = 8.0, 6.4 Hz, 1H), 4.61 (dd, J = 8.8, 7.8 Hz, 1H), 4.20 (t, J = 8.5 Hz, 1H), 3.21 – 2.93 (m, 4H), 2.28 – 2.18 (m, 3H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 155.19, 140.65, 140.05, 127.16, 127.12, 125.43, 125.27, 80.54, 75.08, 70.68, 48.34, 46.67, 43.66 ppm; **IR (neat):** ν = 1779 cm⁻¹; **HRMS (ESI⁺; MeOH):** m/z calcd. (C₁₃H₁₄NaO₄) 257.0784 (M+Na)⁺: found: 257.0792.

Condition A. The product was isolated as a white solid. Yield: 41%, 83:17 *dr*.

¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.57 (m, 4.06H), 7.51 – 7.43 (m, 4.11H), 7.40 – 7.34 (m, 1.07H), 4.92 (tt, J = 8.0, 6.3 Hz, 0.83H), 4.54 – 4.41 (m, 0.37H), 4.31 – 4.24 (m, 1H), 3.85 (t, J = 8.6 Hz, 0.84H), 2.58 – 2.28 (m, 1.93H), 2.27 – 2.13 (m, 1.23H), 1.68 (s, 3.12H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 155.18, 155.02, 145.85, 144.72, 140.41, 140.29, 128.95, 128.90, 127.60, 127.57, 127.39, 127.36, 127.12, 127.10, 125.03, 124.93, 75.19, 74.81, 73.51, 73.13, 71.18, 70.36, 47.66, 47.23, 32.00, 30.50 ppm; **IR (neat):** ν = 1768 cm⁻¹; **HRMS (ESI⁺; MeOH):** m/z calcd. (C₁₈H₁₈NaO₄) 321.1097 (M+Na)⁺: found: 321.1102.

Note: this carbonate was separately prepared for the control experiment reported in Scheme 4b (see the main text and page S8 for details):

Condition A. Scale: 0.5 mmol. The product was isolated as orange oil, eluent: 10%-25% EA in hexane. Yield: 77%.

¹H NMR (400 MHz, CDCl₃) δ 4.84 (tdd, *J* = 8.5, 7.8, 3.5 Hz, 1H), 4.52 (dd, *J* = 8.5, 7.8 Hz, 1H), 4.00 (t, *J* = 8.4 Hz, 1H), 2.46 – 2.21 (m, 4H), 2.05 (s, 3H), 1.64 – 1.26 (m, 8H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 170.96, 154.90, 81.91, 73.74, 70.02, 41.87, 35.12, 34.95, 25.28, 22.37, 21.84, 21.61 ppm; **IR (neat):** ν = 1725, 1794 cm⁻¹; **HRMS (ESI⁺; MeOH):** *m/z* calcd. (C₁₂H₁₈NaO₅) 265.1046 (M+Na)⁺: found: 265.1045.

Note: the following tetrahydrofuran derivative **3o** was isolated in the synthesis of cyclic carbonate **1o**:

Condition A. The product was isolated as colorless oil, eluent: 10%-25% EA in hexane. Yield: 48%.

¹H NMR (400 MHz, CDCl₃) δ 4.46 – 4.38 (m, 1H), 3.92 (dd, *J* = 9.8, 4.3 Hz, 0.52H), 3.86 – 3.74 (m, 1H), 3.70 – 3.58 (m, 1H), 3.46 (q, *J* = 7.7 Hz, 0.5H), 2.29 – 2.20 (m, 1.44H), 1.98 – 1.87 (m, 1.62H), 1.81 – 0.87 (m, 12.09H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 83.77, 82.66, 75.41, 75.24, 72.56, 72.28, 43.14, 42.98, 39.33, 39.29, 29.92, 29.85, 29.22, 28.97, 26.58, 26.11, 26.06, 25.94, 25.88 ppm; **HRMS (ESI⁺; MeOH):** *m/z* calcd. (C₁₀H₁₉O₂) 171.1380 (M+H)⁺: found: 171.1380.

6-Membered Cyclic Carbonates 2a-2q:

The product was isolated as a white solid. Yield: 91%.

¹H NMR (500 MHz, CDCl₃) δ 7.42 – 7.38 (m, 7H), 7.37 – 7.25 (m, 4H), 4.51 – 4.43 (m, 1H), 4.28 (dd, J = 12.3, 3.3 Hz, 1H), 4.24 – 4.16 (m, 1H), 2.93 (dd, J = 14.3, 3.2 Hz, 1H), 2.58 (dd, J = 14.4, 12.2 Hz, 1H), 2.08 (s, 3H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 170.58, 148.12, 142.42, 141.07, 129.37, 128.76, 128.56, 128.55, 125.37, 125.20, 86.31, 74.10, 64.68, 34.21, 20.74 ppm; **IR (neat):** ν = 1737 cm⁻¹; **HRMS (ESI+; MeOH):** m/z calcd. (C₁₉H₁₈NaO₅) 349.1046 (M+Na)⁺: found: 349.1039.

The product was isolated as a colorless oil. Yield: 83%.

¹H NMR (500 MHz, CD₃CN) δ 7.33 – 7.26 (m, 4H), 7.00 – 6.95 (m, 2H), 6.93 – 6.87 (m, 2H), 4.42 (ddt, J = 12.0, 5.4, 3.2 Hz, 1H), 4.26 (dd, J = 12.4, 3.0 Hz, 1H), 4.16 (dd, J = 12.4, 5.6 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 2.99 (dd, J = 14.5, 3.4 Hz, 1H), 2.58 (dd, J = 14.5, 12.1 Hz, 1H), 2.03 (s, 3H) ppm; **¹³C NMR (126 MHz, CD₃CN)** δ 171.38, 160.51, 160.45, 149.07, 136.42, 134.66, 127.88, 127.54, 115.33, 114.77, 87.02, 75.89, 65.50, 56.06, 56.00, 34.03, 20.87 ppm; **IR (neat):** ν = 1742 cm⁻¹; **HRMS (ESI+; MeOH):** m/z calcd. (C₂₁H₂₃O₇) 387.1423 (M+H)⁺: found: 387.1438.

The product was isolated as a colorless oil. Yield: 82%.

¹H NMR (400 MHz, CDCl₃) δ 7.26 (dd, *J* = 8.5, 0.8 Hz, 4H), 7.23 – 7.17 (m, 2H), 7.16 – 7.12 (m, 2H), 4.52 – 4.43 (m, 1H), 4.28 (dd, *J* = 12.3, 3.3 Hz, 1H), 4.20 (dd, *J* = 12.3, 5.0 Hz, 1H), 2.86 (dd, *J* = 14.3, 3.2 Hz, 1H), 2.54 (dd, *J* = 14.3, 12.2 Hz, 1H), 2.33 (d, *J* = 10.8 Hz, 6H), 2.09 (s, 3H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 170.66, 148.33, 139.83, 138.45, 138.40, 138.33, 130.01, 129.40, 125.37, 125.14, 86.39, 77.48, 77.16, 76.84, 74.13, 64.80, 34.36, 21.13, 21.11, 20.80 ppm; **IR (neat):** ν = 1741 cm⁻¹; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₂₁H₂₂NaO₅) 377.1359 (M+Na)⁺: found: 377.1370.

The product was isolated as a colorless oil. Yield: 65%.

¹H NMR (500 MHz, CDCl₃) δ 7.43 – 7.38 (m, 2H), 7.36 – 7.28 (m, 6H), 4.46 (ddt, *J* = 12.2, 4.9, 3.3 Hz, 1H), 4.29 (dd, *J* = 12.4, 3.4 Hz, 1H), 4.22 (dd, *J* = 12.4, 4.9 Hz, 1H), 2.86 (dd, *J* = 14.4, 3.2 Hz, 1H), 2.54 (dd, *J* = 14.4, 12.2 Hz, 1H), 2.10 (s, 3H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 170.60, 147.54, 140.60, 139.25, 135.08, 134.96, 129.80, 129.15, 126.80, 126.69, 85.46, 74.04, 64.56, 34.21, 20.80 ppm; **IR (neat):** ν = 1738 cm⁻¹;
HRMS (ESI+; MeOH): *m/z* calcd. (C₁₉H₁₆Cl₂NaO₅) 417.0267 (M+Na)⁺: found: 417.0270.

The product was isolated as a white solid. Yield: 84%.

¹H NMR (500 MHz, CDCl₃) δ 7.39 – 7.31 (m, 4H), 7.15 – 7.09 (m, 2H), 7.07 – 7.01 (m, 2H), 4.47 (ddt, *J* = 12.2, 4.9, 3.3 Hz, 1H), 4.30 (dd, *J* = 12.3, 3.4 Hz, 1H), 4.22 (dd, *J* = 12.4, 4.9 Hz, 1H), 2.85 (dd, *J* = 14.4, 3.1 Hz, 1H), 2.56 (dd, *J* = 14.4, 12.2 Hz, 1H), 2.10 (s, 3H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 170.62, 163.68, 163.67, 161.70, 161.69, 147.74, 138.31, 138.28, 136.77, 136.75, 127.48, 127.41, 127.28, 127.21, 116.66, 116.49, 115.94, 115.77, 85.63, 74.07, 64.63, 34.56, 20.80 ppm; **¹⁹F NMR (376 MHz, CDCl₃)** δ -112.70, -112.85 ppm; **IR (neat):** ν = 1741 cm⁻¹; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₉H₁₆F₂NaO₅) 385.0858 (M+Na)⁺: found: 385.0855.

The product was isolated as a white solid. Yield: 79%.

¹H NMR (400 MHz, CDCl₃) δ 4.72 – 4.62 (m, 1H), 4.26 (dd, *J* = 12.1, 3.5 Hz, 1H), 4.16 (dd, *J* = 12.2, 5.5 Hz, 1H), 2.11 (s, 3H), 1.96 – 1.74 (m, 3H), 1.70 – 1.56 (m, 4H), 1.48 – 1.28 (m, 4H), 0.95 (td, *J* = 7.3, 4.1 Hz, 6H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 170.73, 149.11, 85.26, 73.12, 65.09, 41.49, 39.36, 31.64, 20.83, 16.97, 16.31, 14.43, 14.28 ppm; **IR (neat):** ν = 1737 cm⁻¹; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₃H₂₂NaO₅) 281.1359 (M+Na)⁺: found: 281.1362.

The product was isolated as a colorless oil. Yield: 82%.

¹H NMR (400 MHz, CDCl₃) δ 4.48 (ddt, *J* = 12.2, 6.1, 3.6 Hz, 1H), 4.25 (dd, *J* = 12.2, 3.3 Hz, 1H), 4.15 (dd, *J* = 12.1, 6.1 Hz, 1H), 2.11 (s, 3H), 2.01 – 1.68 (m, 15H), 1.27 – 1.08 (m, 10H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 170.77, 151.16, 89.96, 73.86, 64.82, 45.47, 45.00, 27.51, 26.96, 26.87, 26.84, 26.66, 26.57, 26.53, 26.29, 26.28, 26.04, 20.87 ppm; **IR (neat):** *ν* = 1744 cm⁻¹; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₉H₃₀NaO₅) 361.1985 (M+Na)⁺: found: 361.1981.

The product was isolated as a white solid. Yield: 85%.

¹H NMR (400 MHz, CDCl₃) δ 4.71 (ddt, *J* = 12.4, 5.5, 3.5 Hz, 1H), 4.27 (dd, *J* = 12.2, 3.5 Hz, 1H), 4.16 (dd, *J* = 12.2, 5.4 Hz, 1H), 2.10– 2.09 (m, 3H), 2.02 – 1.94 (m, 2H), 1.84 – 1.72 (m, 4H), 1.62 – 1.49 (m, 5H), 1.51 – 1.32 (m, 1H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 170.74, 148.85, 82.03, 72.91, 65.06, 38.72, 35.04, 33.74, 25.14, 21.78, 21.45, 20.83 ppm; **IR (neat):** *ν* = 1736 cm⁻¹; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₂H₁₈NaO₅) 256.1046 (M+Na)⁺: found: 256.1052.

The product was isolated as a brown oil. Yield: 94%.

¹H NMR (500 MHz, CDCl₃) δ 4.68 (ddt, *J* = 12.4, 5.4, 3.5 Hz, 1H), 4.26 (dd, *J* = 12.1, 3.4 Hz, 1H), 4.16 (dd, *J* = 12.1, 5.5 Hz, 1H), 2.19 – 1.99 (m, 6H), 1.80 – 1.32 (m, 13H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 170.73, 148.81, 86.10, 73.20, 65.09, 37.98, 33.17, 32.78, 28.10, 27.69, 24.95, 21.88, 21.42, 20.83 ppm; **IR (neat):** ν = 1738 cm⁻¹; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₄H₂₂NaO₅) 293.1359 (M+Na)⁺: found: 293.1362.

The product was isolated as a colorless oil. Yield: 96%, 63:37 *dr*.

¹H NMR (400 MHz, CDCl₃) δ 7.34 – 7.27 (m, 0.8H), 7.24 – 7.15 (m, 3.17H), 4.86 (ddt, *J* = 11.9, 5.4, 3.5 Hz, 0.37H), 4.32 – 4.08 (m, 2.63H), 2.47 – 2.28 (m, 4.09H), 2.23 – 2.12 (m, 1.02H), 2.09– 2.08 (m, 2.83H), 1.78 (s, 1.08H), 1.71 (s, 1.86H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 170.68, 170.65, 148.59, 148.53, 140.96, 139.07, 138.26, 138.11, 129.99, 129.54, 124.00, 123.76, 84.08, 83.14, 74.06, 73.75, 64.86, 64.69, 35.73, 35.50, 31.26, 27.66, 21.11, 21.07, 20.80, 20.78 ppm; **IR (neat):** ν = 1743 cm⁻¹; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₅H₁₈NaO₅) 301.1046 (M+Na)⁺: found: 301.1050.

The product was isolated as a colorless oil. Yield: 90%, 7:3 *dr*.

¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.31 (m, 3.53H), 7.30 – 7.24 (m, 1.51H), 4.84 (ddt, *J* = 11.7, 5.5, 3.6 Hz, 1H), 4.30 – 4.08 (m, 2.7H), 2.49 – 2.35 (m, 0.99H), 2.26 – 2.13 (m, 1.34H), 2.10 – 2.04 (m, 2.54H), 2.03 – 1.95 (m, 1.73H), 0.84 (t, *J* = 7.4 Hz, 2.10H), 0.79 (t, *J* = 7.4 Hz, 0.9H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 170.64, 170.60, 148.68, 148.47, 141.82, 140.50, 129.25, 128.80, 128.32, 128.07, 124.74, 124.42, 86.60, 85.88, 73.87, 73.53, 64.84, 64.74, 36.32, 34.46, 33.87, 33.47, 20.78, 20.76, 7.76, 7.33 ppm; **IR (neat):** ν = 1735 cm⁻¹; **HRMS (ESI⁺; MeOH):** *m/z* calcd. (C₁₅H₁₈NaO₅) 301.1046 (M+Na)⁺: found: 301.1045.

The product was isolated as a colorless oil. Yield: 83%, 72:28 *dr*.

¹H NMR (500 MHz, CDCl₃) δ 7.30 (d, *J* = 8.6 Hz, 0.29H), 7.19 – 7.14 (m, 0.71H), 7.05 – 7.01 (m, 2H), 4.84 (ddt, *J* = 12.1, 5.3, 3.5 Hz, 0.28H), 4.35 – 4.29 (m, 1.03H), 4.24 – 4.19 (m, 1.04H), 4.14 (dd, *J* = 12.2, 5.0 Hz, 0.72H), 2.76 (dd, *J* = 14.6, 3.2 Hz, 0.71H), 2.53 – 2.36 (m, 3.63H), 2.34 – 2.26 (m, 3.45H), 2.17 – 2.06 (m, 3.81H), 1.86 (s, 0.89H), 1.77 (s, 2.16H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 170.68, 170.65, 148.60, 148.49, 138.40, 138.29, 138.25, 136.12, 134.50, 134.08, 133.84, 127.50, 127.00, 125.31, 124.77, 85.11, 84.51, 74.14, 73.47, 64.85, 64.82, 34.75, 34.49, 29.43, 26.89, 22.11, 22.04, 20.82, 20.79 ppm; **IR (neat):** ν = 1736 cm⁻¹; **HRMS (ESI⁺; MeOH):** *m/z* calcd. (C₁₆H₂₀NaO₅) 315.1197 (M+Na)⁺: found: 315.1203.

The product was isolated preparative TLC, white solid, eluent: 25% EA in hexane. Yield: 76%, 91:9 *dr*.

¹H NMR (500 MHz, CDCl₃) δ 7.91 – 7.81 (m, 3.85H), 7.56 – 7.50 (m, 1.99H), 7.33 (dd, *J* = 8.6, 2.1 Hz, 0.90H), 4.92 (ddt, *J* = 12.2, 5.3, 3.5 Hz, 0.09H), 4.33 (dd, *J* = 12.2, 3.6 Hz, 0.08H), 4.26 – 4.10 (m, 2.83H), 2.58 (dd, *J* = 14.4, 3.0 Hz, 0.90H), 2.27 (dd, *J* = 14.3, 12.1 Hz, 0.97H), 2.09 – 2.04 (m, 2.86H), 1.89 (s, 0.24H), 1.82 (s, 2.7H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 170.57, 148.54, 141.00, 139.16, 133.20, 133.11, 132.86, 132.84, 129.53, 128.92, 128.44, 128.41, 127.70, 127.12, 126.96, 126.85, 126.75, 123.53, 122.69, 121.80, 121.53, 84.20, 83.25, 74.10, 73.76, 64.81, 64.61, 35.63, 35.41, 31.04, 27.63, 20.78, 20.74 ppm; **IR (neat):** ν = 1735 cm⁻¹; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₈H₁₈NaO₅) 337.1046 (M+Na)⁺: found: 337.1055.

The product was isolated as a white solid. Yield: 95%.

¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.18 (m, 4H), 4.83 (dtd, *J* = 10.8, 5.0, 3.6 Hz, 1H), 4.33 (dd, *J* = 12.2, 3.6 Hz, 1H), 4.23 (dd, *J* = 12.2, 5.3 Hz, 1H), 3.39 (dd, *J* = 19.3, 16.6 Hz, 2H), 3.19 (dd, *J* = 16.5, 2.9 Hz, 2H), 2.26 – 2.08 (m, 5H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 170.69, 148.27, 138.84, 138.42, 127.63, 127.47, 124.88, 124.82, 89.72, 74.38, 64.88, 46.39, 44.53, 32.83, 20.83 ppm; **IR (neat):** ν = 1734 cm⁻¹; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₅H₁₆NaO₅) 299.0890 (M+Na)⁺: found: 299.0882.

The product was isolated by preparative TLC, light yellow oil, eluent: 25% EA in hexane. Yield: 80%, 94:6 *dr*.

¹H NMR (500 MHz, CDCl₃) δ 7.66 – 7.61 (m, 1.97H), 7.61 – 7.55 (m, 1.97H), 7.48 – 7.43 (m, 1.97H), 7.41 – 7.34 (m, 2.79H), 4.92 – 4.87 (m, 0.06H), 4.37 – 4.13 (m, 2.94H), 2.50 (dd, *J* = 14.3, 3.1 Hz, 0.93H), 2.24 (dd, *J* = 14.3, 12.3 Hz, 0.99H), 2.09 (s, 2.43H), 1.78 (s, 2.76H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 170.64, 148.47, 141.43, 140.94, 140.10, 129.05, 128.05, 127.89, 127.20, 124.63, 84.00, 74.09, 64.68, 35.52, 31.26, 20.80 ppm; **IR (neat):** ν = 1736 cm⁻¹; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₂₀H₂₀NaO₅) 363.1203 (M+Na)⁺: found: 363.1201.

Note: product **3a** was isolated when using the conditions of Table 1, entry 17: ^[8]

The product was isolated as white solid, eluent: 10%-25% EA in hexane. Yield: 15%.

¹H NMR (400 MHz, CDCl₃) δ 7.54 – 7.48 (m, 2H), 7.44 – 7.39 (m, 2H), 7.35 – 7.27 (m, 4H), 7.25 – 7.17 (m, 2H), 4.55 (s, 1H), 4.16 (dd, *J* = 9.9, 5.2 Hz, 1H), 3.96 (ddd, *J* = 9.9, 2.6, 0.9 Hz, 1H), 2.87 (dd, *J* = 13.5, 6.3 Hz, 1H), 2.78 (ddd, *J* = 13.5, 3.0, 0.9 Hz, 1H), 1.53 (s, 1H) ppm; **¹³C NMR (101 MHz, CDCl₃)** δ 146.22, 146.18, 128.57, 128.43, 127.18, 127.06, 125.87, 125.75, 87.89, 75.29, 73.40, 48.49 ppm.

Note: this tetrahydrofuran product (**3l-Ac**) was the only product isolated while attempting the synthesis of cyclic carbonate **2l**:

The product was isolated as white solid, eluent: 2%-5% EA in hexane. Yield: 89%, 97:3 *dr*.

¹H NMR (500 MHz, CDCl₃) δ 7.55 – 7.50 (m, 2H), 7.41 – 7.32 (m, 3H), 5.38 (ddt, *J* = 6.8, 4.4, 2.3 Hz, 1H), 4.34 (dd, *J* = 10.2, 4.6 Hz, 1H), 4.13 (ddq, *J* = 10.2, 2.3, 1.1 Hz, 1H), 2.97 (dd, *J* = 14.4, 6.3 Hz, 1H), 2.58 (ddt, *J* = 14.4, 2.5, 1.1 Hz, 1H), 1.77 (s, 3H) ppm; **¹³C NMR (126 MHz, CDCl₃)** δ 170.63, 137.82, 128.93, 128.60, 128.23, 126.66, 126.57, 126.56, 124.39, 122.13, 85.85, 85.62, 85.38, 85.15, 74.46, 74.30, 40.44, 20.75 ppm; **¹⁹F NMR (471 MHz, CDCl₃)** δ -78.80, -79.10 ppm; **HRMS (ESI+; MeOH):** *m/z* calcd. (C₁₃H₁₃F₃NaO₃) 297.0709 (M+Na)⁺: found: 297.0719.

S37: References:

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S38: IR, ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra

Note: for all compounds in this section the order of the presented spectra is: ^1H , ^{13}C , ^{19}F (where applicable) and IR

NMR spectra for the homoallylic alcohols:

Spectra for epoxy alcohol products B1-B18:

Spectra for 5-membered cyclic carbonate products 1a-1q:

S95

S120

Spectra for 6-membered cyclic carbonate products 2a-2q:

S143

Spectra for tetrahydrofuran derivative **3a**:

Spectra for tetrahydrofuran derivative **3I-Ac**:

Spectra for tetrahydrofuran derivative **3o**:

S151: X-ray molecular structure of 2p

For more details see [CCDC-1997736](#)

S152: Computational acylation of 5MCC-OH (1a)

The acylation of the **5MCC-OH (1a)** having a tertiary OH group was calculated using the same acylation method/steps as reported in Figure 1 (main text) for **6MCC-OH**. These additional studies were performed to elucidate why under the optimized experimental conditions for the preparation of **6MCC-OAc (2a)**, no acylated 5-membered carbonate could be detected (see **Figure S1** below).

Figure S1: Relative Gibbs free energy profile in kcal·mol⁻¹ for the acylation of **5MCC-OH (1a)**. Note that the acylation pathway for 6MCC-OH is provided in the main text.

The $\Delta\Delta G^\ddagger$ between the two pathways leading to either **5MCC-OAc** and **6MCC-OAc (2a)** were compared. Both pathways begin with the same reactant **5MCC-OH (1a)**.

Note that the acylation of 6MCC-OH involves *first* the isomerization of **5MCC-OH (1a)** to **6MCC-OH**:

Figure S1: $\Delta G^\ddagger = 24.8$ kcal·mol⁻¹

Figure 1: $\Delta G^\ddagger = 17.6$ kcal·mol⁻¹

Thus, the acylation of **6MCC-OH** (starting from **5MCC-OH**) is **7.2 kcal·mol⁻¹** more favored, and provides a rationale for the exclusive observation and formation of **6MCC-OAc** at rt.

S153: Relative Gibbs free energy and potential energy profiles

Figure S2 : Relative Gibbs free energy (black) and potential energy (purple) profiles in $\text{kcal}\cdot\text{mol}^{-1}$. This is the entire mechanism that involves both the isomerization of **1a** and acylation towards the formation of **2a**.

Figure S3: Relative Gibbs free energy (black) and potential energy (purple) profiles in $\text{kcal}\cdot\text{mol}^{-1}$. This is the acylation mechanism for **5MCC-OH (1a)**.

S154: Visual description of the mechanism leading to 6MCC-OAc

Full access to the computational data can be achieved through the following link:

<http://dx.doi.org/10.19061/iochem-bd-1-171>

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