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Copper porphyrin-catalyzed cross dehydrogenative coupling of alkanes with carboxylic acids: Esterification and decarboxylation dual pathway

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ABSTRACT

A dual-functional copper porphyrin-catalyzed cross dehydrogenative coupling (CDC) of carboxylic acids with alkanes was reported firstly. The reaction gives allylic esters or alkylalkenes depending on the carboxylic acid substrates. Copper porphyrin catalyzed CDC method has the superiority of short reaction time, good functional group tolerance, base and solvent free, producing target products in an atom-economic manner.

1. Introduction

Direct functionalization of inert C(sp [3])-H bond is of considerable challenge, owing to the high C–H bond dissociation energy and low polarity of alkanes [1]. To date, remarkable advances have been made on the formation of C-X (X = C, N, O, S) bonds via cross dehydrogenative coupling (CDC) involving C–H activation [2]. The active investigation and application of CDC reaction are mainly initiated from C–C bond formation [3]. In recent years, C–H functionalization towards C–O bond construction of esters via CDC method has attracted much attentions [4], due to the typical uses of bioactive esters in nature [5]. The CDC reactions of α-C(sp [3])-H bond adjoining to heteroatoms or unsaturated bonds with carboxylic acid [6] or its precursors [7] (benzyl alcohols, aldehydes, alkylbenzenes and alkenes) have been achieved successfully, either using copper, iron and MOFs catalyst or under metal-free conditions. However, using alkanes as starting materials in CDC reaction for the preparation of esters is scarce. In 2014, Pan's group developed a $Cu(OAc)_2$-catalyzed CDC reaction of cycloalkanes with aromatic aldehydes, which involved four C–H bond activations and gave cycloallyl esters directly [8]. Afterwards, the synthesis of allylic esters via the oxidative dehydrogenative carboxylation of cyclohexane using copper catalysts has been quickly developed [9].

Metalloporphyrins [10], as a class of bioinspired multifunctional catalysts [11], have been successfully applied in many reactions such as cyclopropanation [12], olefination [13], cycloaddition [14], oxidation [15], carbene [16] and nitrene [17] C–H insertion reactions. Whereas the application of metalloporphyrin catalysts in CDC reaction is a less explored topic. In 2013, Che reported the first use of palladium porphyrin in CDC reaction between tertiary amines and dimethyl malonate or diethyl phosphite under illumination [18]. In 2016, Guo applied copper porphyrin catalyst to the homocoupling reaction of terminal alkynes [19]. Recently, we have found copper [20] or iron-porphyrin [21] may be used in CDC reaction of carboxylic acids and cyclic ethers, which provided esters in high yields (Scheme 1, a). The CDC esterification of cyclohexene and carboxylic acids could also be achieved with high TON by using

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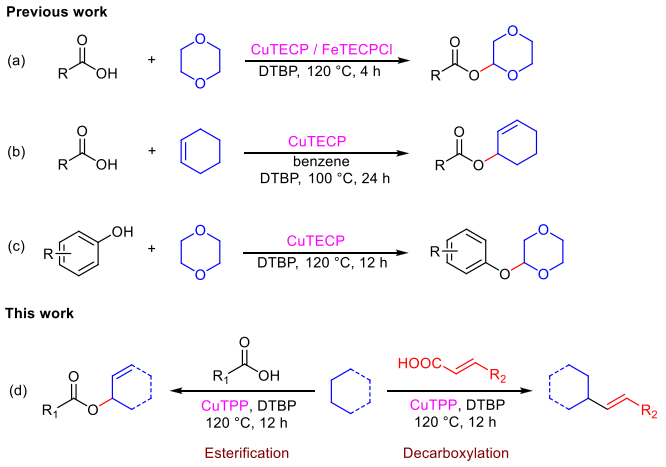
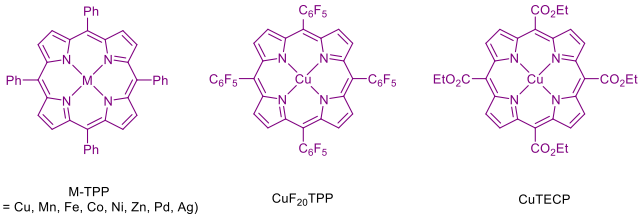


Scheme 1. Direct functionalization of C(sp [3])-H bonds.

copper-porphyrin catalyst [22] (Scheme 1, b). While acetals could be obtained from copper-porphyrin catalyzed CDC reaction of phenol derivatives and cyclic ethers [23] (Scheme 1, c). In all these reactions, the C(sp [3])-H bonds of substrates are adjacent to the ethereal oxygen atom or allyl group. We herein would like to report the extension of C(sp [3])-H substrate to alkanes (Scheme 1, d). Surprisingly, except for the normal ester products, alkylalkenes could also be obtained when using cinnamic acid as substrates.

2. Results and discussion

We commenced our investigation via examining the reaction of benzoic acid (**1a**) with cyclohexane (**2a**) utilizing DTBP as the oxidant to determine the optimal reaction conditions (Table 1). Initially, copper porphyrin catalysts substituted by different push- or pull-electron groups (Scheme 2) were tested and

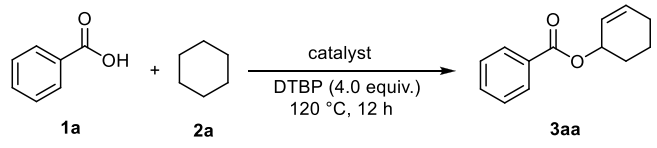


Scheme 2. Molecular structure of metal porphyrin complexes.

tetrakis(phenyl)porphyrinato-copper(II) (CuTPP) showed the supreme catalysis reactivity, offering the allylic ester in 80 % yield (Table 1, entry 1). Meanwhile, tetrakis(perfluorophenyl) porphyrinato-copper(II) ($CuF_{20}TPP$) provided higher yield than tetrakis(ethoxycarbonyl)porphyrinato-copper(II) (CuTECP) (Table 1, entries 2 and 3). It turns out that electron-donating groups on the porphyrin rings are more favorable for this reaction. Contrary to our expectation, the other tested tetrakis(phenyl)porphyrinato-metal complexes (M-TPP) (M = Mn, Fe, Co, Ni, Zn, Pd, Ag) were not active (Table 1, entries 4–10), why these metal porphyrins did not work for current reaction is unclear. The reaction could not yield the target product without catalyst (Table 1, entry 11). Furthermore, no significant improvements in the yield of cyclohex-2-en-1-yl benzoate (**3aa**) when decreasing or increasing the loading amounts of catalyst (Table 1, entries 12 and 13).

The influence of oxidant on this reaction was next investigated as shown in Table 2, when oxidant DTBP was replaced by other oxidants such as $PhI(OAc)_2$, *m*-CPBA, DDQ, H_2O_2, Oxone and $K_2S_2O_8$, the coupling reaction of benzoic acid and cyclohexane could not happen (Table 2, entries 1–6). A remarkable drop in yield of **3aa** was given by TBHP (Table 2, entry 7), perhaps owing to the strong oxidation power of hydroxyl radical from TBHP is unfavorable for the regeneration of CuTPP in the catalytic cycle. Significantly, the yield of desired product was up to 93 % using 5.0 equivalent DTBP,

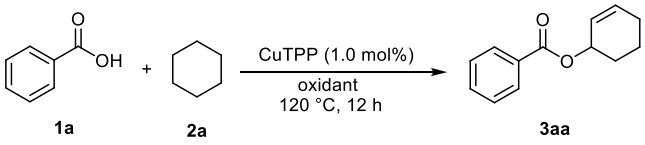
Table 1
Catalyst optimization[a].



Entry	Catalyst	Yield[b](%)
1	CuTPP	80
2	$CuF_{20}TPP$	75
3	CuTECP	70
4	MnTPPCl	N.D.
5	FeTPPCl	trace
6	CoTPP	trace
7	NiTPP	N.D.
8	ZnTPP	trace
9	PdTPP	N.D.
10	AgTPP	N.D.
11	–	N.D.
12	CuTPP	66[c]
13	CuTPP	78[d]

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mL), catalyst (1.0 mol%), DTBP (4.0 equiv.) at 120 °C for 12 h.
[b] Yields were determined by ^{1}H NMR spectra using trimethylphenylsilane as an internal standard.
[c] 0.5 mol% of catalyst was used.
[d] 3.0 mol% of catalyst was used. N.D. = not detected.

Table 2
Oxidant optimization[a].



Entry	Oxidant	Yield[b](%)
1	$PhI(OAc)_2$	N.D.
2	*m*-CPBA	N.D.
3	DDQ	N.D.
4	H_2O_2	N.D.
5	Oxone	N.D.
6	$K_2S_2O_8$	N.D.
7	TBHP	22
8	DTBP	47[c]
9	DTBP	93[d]
10	DTBP	69[e]
11	–	N.D.

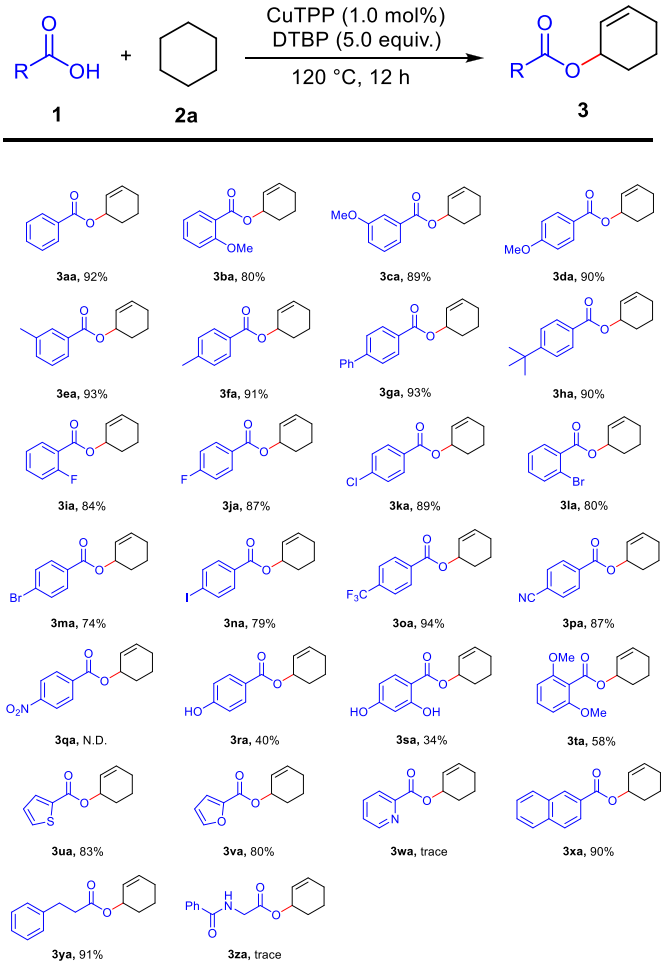
[a] Reaction conditions: benzoic acid (0.5 mmol), cyclohexane (1.0 mL), CuTPP (1.0 mol%), oxidant (4.0 equiv.) at 120 °C for 12 h.
[b] Yields were determined by ^{1}H NMR spectra using trimethylphenylsilane as an internal standard.
[c] 3.0 equiv. of DTBP was used.
[d] 5.0 equiv. of DTBP was used.
[e] 6.0 equiv. of DTBP was used. DTBP = di-*tert*-butyl peroxide. *m*-CPBA = 3-chloroperbenzoic acid. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. H_2O_2 (30 % in water). Oxone = potassium peroxymonosulfate. TBHP = *tert*-butyl hydroperoxide (5–6 M, in decane). N.D. = not detected.

but it would decrease with higher or lower amounts of DTBP (Table 2, entries 8–10). Besides, no product was detected entirely in the absence of oxidant (Table 2, entry 11). Other elements such as reaction time and temperature were studied to complete the reaction optimization (Table S2).

With the optimum reaction conditions in hand (Table 2, entry 8), the oxidative esterification of a vast array of structurally variable carboxylic acids and cyclohexane (**2a**) was explored. As illustrated in Table 3, benzoic acids with miscellaneous mono-substituted groups were all applicable in the developed strategy, corresponding coupled products were obtained in good to excellent yields. Benzoic acids bearing electron-donating groups gave corresponding products in 80%–93 % yields (**3ba-3ha**), regardless of the substituent (methoxy or methyl) positions (**3ba-3fa**). Otherwise, carboxylic acids bearing various electron-withdrawing substituents such as fluoro, chloro, bromo, iodo, trifluoromethoxy and cyano group were perfectly tolerated (**3ia-3pa**). Nevertheless, the reaction failed to form target product when *p*-nitrobenzoic acid was used as substrate, which possibly due to the capture of radical by nitro group [24] (**3qa**). 4-hydroxybenzoic acid and 2,4-dihydroxybenzoic acid were also tested but both gave slightly low yields (**3ra-3sa**). In the case of two methoxy groups on aromatic moiety, providing moderated yield may be attributed to the substituents steric hindrance (**3ta**). Gratifyingly, this protocol was compatible well with heteroaryl carboxylic acids and 1-naphthoic acid (**3ua-3va, 3xa**). Besides, aliphatic carboxylic acids such as 3-phenylpropionic acid could also furnish excellent yield of **3ya**. Possibly owing to the strong axial coordination between pyridyl or amide group and CuTPP, the esterification reaction could not proceed smoothly (**3wa**, **3za**).

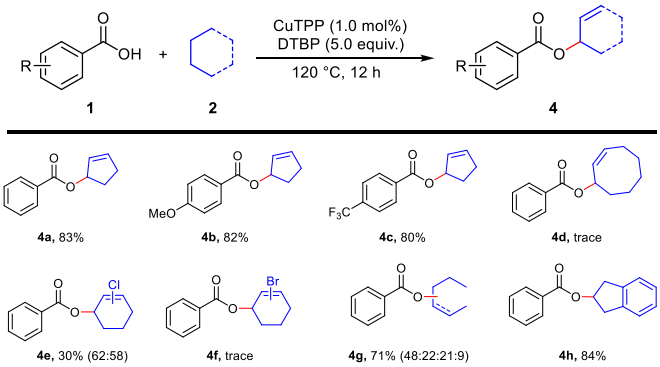
Subsequently, the substrate scope of alkanes was also explored and the results were summarized in Table 4. Under the optimum reaction parameters, cyclopentane possessing bigger tension could react with carboxylic acid and its derivatives smoothly, which gained corresponding products in excellent yields (**4a-4c**). By contrast, using cyclooctane as coupling partner, only a trace quantity of the product was given (**4d**). Other cyclohexane derivatives such as chlorocyclohexane and bromocyclohexane provided isomer mixture products in poor and trace yields, perhaps due to the electron-withdrawing effect of chlorine and bromine (**4e-4f**). Moreover, acyclic alkane was suitable to present transformation as well. When *n*-hexane as the substrate was tested, we found that the ratio of four regioselective isomers analyzed by GC-MS was 48:22:21:8, respectively (**4g**). To our surprise, when indan

Table 3
Substrate scope of carboxylic acids[a].



[a]Reaction conditions: **1** (0.5 mmol), **2a** (1.0 mL), CuTPP (1.0 mol%), DTBP (5.0 equiv.) at 120 °C for 12 h. Isolated yield is based on the initial amount of benzoic acid. N.D. = not detected.

Table 4
Substrate scope of alkanes[a].



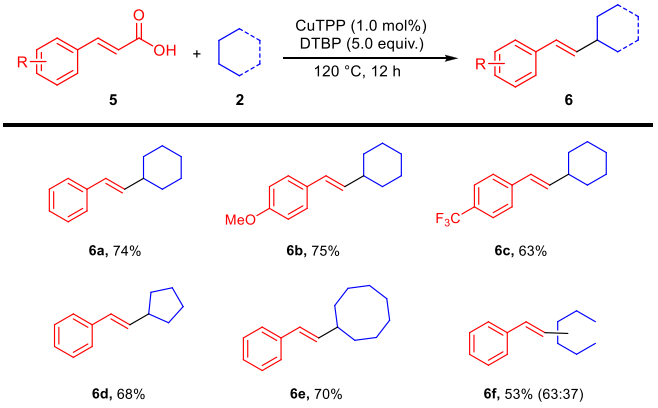
[a]Reaction conditions: **1** (0.5 mmol), **2** (1.0 mL), CuTPP (1.0 mol%), DTBP (5.0 equiv.) at 120 °C for 12 h. Isolated yield is based on the initial amount of benzoic acid. The regioselectivity ratio is determined by GC-MS in the parenthesis.

was employed to couple with benzoic acid, a direct functionalization on indan C(sp [3])-H bond delivered ester **4h**, rather than produce allylic ester by the oxidative CDC protocol. This result suggests that the methodology has a great prospect in alkylation of more complicated alkanes.

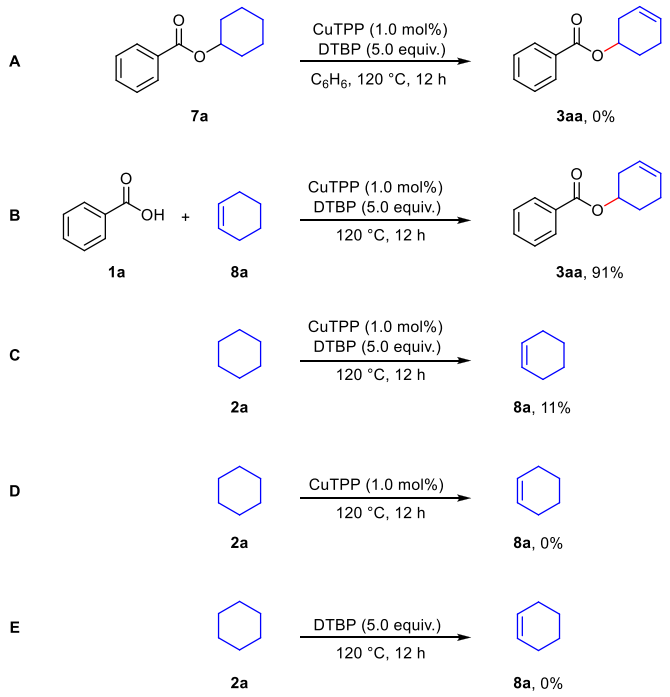
In order to prove feasibility of this CDC strategy further, the reactivity patterns of cinnamic acid derivatives and alkanes were investigated under typical conditions (Table 5). Strikingly, the reaction could not generate anticipated allylic esters, but the decarboxylative coupling alkenylation products (*E*-alkenes) in good to moderate yields. Hence, several representative cinnamic acid substrates were selected to react with cyclohexane, and all provided good yields regardless electron-rich or electron-poor cinnamic acids (**6a-6c**). Furthermore, diverse alkanes including cycloalkanes and linear alkanes were studied likewise. Good yields were obtained by coupling cinnamic acid with cyclopentane and cyclooctane respectively **(6d-6e)**. In terms of *n*-hexane, a mixture of two regioselective alkyl olefin products in a ratio of 63:37 was provided (**6f**).

Concerning to the reaction sequence of bond formation for oxidative dehydrogenative carboxylation of alkanes to generate allylic esters, two possible reaction pathways are involved: (i) initial the C(sp [3])-O bond formation between alkanes and carboxylic acids, followed by dehydrogenation in the *situ* of cyclohexyl benzoate; (ii) initial conversion of alkanes to olefins, followed by the formation of allylic C–O bond. Consequently, a series of control experiments were performed to verify the sequence of bond formation in Scheme 3. Target product cyclohex-2-en-1-yl benzoate (**3aa**) was not detected when cyclohexyl benzoate (**7a**) as the substrate, suggesting that **7a** is not the key intermediate in current reaction (Scheme 3, A). Under the identical reaction conditions, the CDC reaction of cyclohexene (**8a**) with benzoic acid could furnish a high ^{1}H NMR yield (91 %) of the expected product **3aa** (Scheme 3, B). Meanwhile, cyclohexane was also successfully converted to cyclohexene (Scheme 3, C). This shows that cyclohexene may be generated in process of the reaction between benzoic acid and cyclohexane. Besides, the dehydrogenation of cyclohexane to cyclohexene could not proceed without catalyst CuTPP or oxidant

Table 5
Decarboxylative coupling of cinnamic acids with alkanes[a].



[a]Reaction conditions: **5** (0.5 mmol), **2** (1.0 mL), CuTPP (1.0 mol%), DTBP (5.0 equiv.) at 120 °C for 12 h. Isolated yield is based on the initial amount of cinnamic acid. The regioselectivity ratio is determined by GC-MS in the parenthesis.

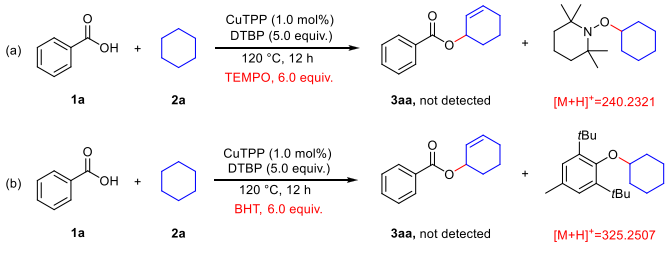


Scheme 3. Control experiments to check the sequence of bond formation.

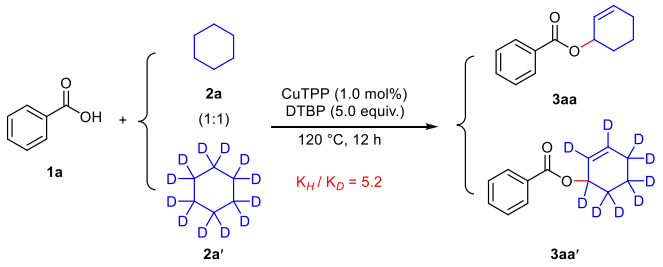
DTBP, indicating catalyst and oxidant are crucial for this transformation (Scheme 3, D and E). According to these experimental results, we can infer that during the CDC reaction of alkanes and carboxylic acids, dehydrogenative olefination precedes ester C—O bond formation, which is in consistent with literature results recorded previously [9a].

In addition, radical trapping and kinetic isotope effect (KIE) experiments were performed to elucidate the reaction mechanism in detailed. The reaction was absolutely inhibited when adding radical scavenger 2,2,6,6-tetramethylpiperidinooxy (TEMPO) or butylated hydroxytoluene (BHT) to the reaction system. Besides, TEMPO-cyclohexane or BHT-cyclohexane adduct could be detected by ESI-MS respectively, manifesting the cyclohexane radical intermediate is involved in this reaction (Scheme 4). In order to check the possible rate-limiting step, an intermolecular competitive KIE experiments were conducted (Scheme 5). A significant K_H/K_D value was estimated 5.25, indicating that the cleavage of cyclohexane C(sp [3])-H bond probably constitutes a rate-determing step among the whole catalytic system.

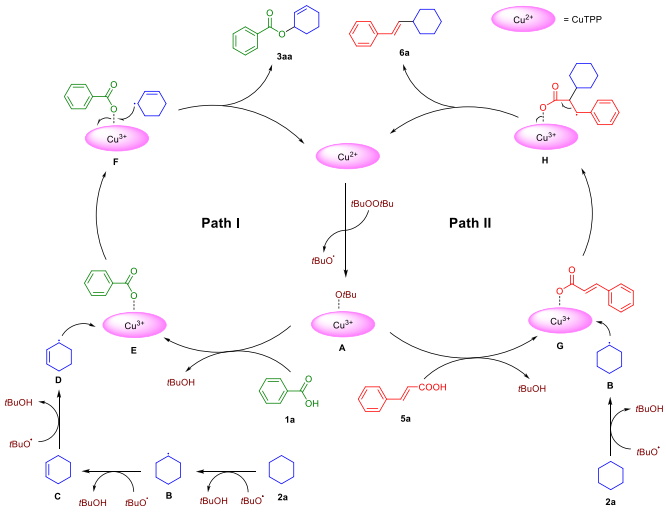
On the basis of above-obtained experimental results and documented literature [9a,20], a plausible reaction mechanism for esterification and decarboxylation of alkanes with carboxylic acids is depicted in Scheme 6. The catalysis is initiated by the homolysis of DTBP with the assistance of TPPCu(II), generating a *tert*-butoxy radical and [TPPCu(III)-*t*BuO] (**A**) complex [25], which quickly



Scheme 4. Radical trapping experiments with TEMPO or BHT.



Scheme 5. Study on kinetic isotope effect experiments.



Scheme 6. Plausible reaction mechanism.

reacts with benzoic acid (**1a**) to form a key intermediate [TPPCu(III)—O_2CPh] (**E**) and deliver *tert*-butanol concurrently. Next, the generated *tert*-butoxy radical abstracts a hydrogen atom from cyclohexane (**2a**) to furnish a relatively instantaneous cyclohexyl radical (**B**), followed by oxidative dehydrogenation to cyclohexene (**C**) via hydrogen atom transfer (HAT) process. A third C—H abstraction by a *tert*-butoxy radical occurs on the resulting cyclohexene (**C**) to afford a cyclohexenyl radical species (**D**), which is trapped by the TPPCu(III)-benzoate (**E**) immediately. The desired esterification product allylic ester (**3aa**) is obtained by the classical Kharasch-Sosnovsky reaction route [26] (Scheme 6, path I). On the other hand, substrate cinnamic acid (**5a**) can also react with complex **A** to produce intermediate **G**. Subsequently, addition of cyclohexyl (**B**) to the α-position of the double bond in **G** gives intermediate **H**. The radical intermediate **H** undergoes oxidative decarboxylation to afford product alkylalkene (**6a**) and releases carbon dioxide (Scheme 6, path II). Finally, two paths regenerate the efficient catalyst TPPCu(II) to finish the catalytic cycle.

3. Conclusion

In conclusion, we have developed an efficient and facile copper porphyrin-catalyzed CDC esterification and decarboxylation dual pathway for the coupling of carboxylic acids with alkanes. Various carboxylic acid derivatives and alkanes were excellent substrates for this transformation, delivering allylic ester or alkylalkene products in high yields. The preliminary mechanistic experiments revealed the key intermediate for two class products might be the TPPCu(III)-benzoate or TPPCu(III)-cinnamate intermediate. The mechanistic details of current reaction are still needed to be further explored.

4. Experimental section

4.1. General information

All the reagents and chemicals employing in the experiments were purchased from commercial suppliers and used without purification unless mentioned specially. The free-base tetraphenylporphyrin (TPP) [27] and all metallporphyrins [20] were synthesized from a modified method based on the literature. Reactions were monitored by Thin-layer chromatography (TLC) on silica gel 60 F254 (0.25 mm) using UV light as visualizing agent. Silica gel (300–400 mesh) was used for flash column chromatography at atmospheric pressure and room temperature and the eluent was a mixture of hexane and ethyl acetate. ^{1}H, ^{13}C or ^{19}F NMR spectra of all products were recorded in $CDCl_3$ on Bruker AscendTM 500 (^{1}H: 500 MHz and ^{13}C: 126 MHz) or Bruker Advance 400 M NMR (^{1}H: 400 MHz, ^{13}C: 101 MHz ^{19}F: 471 MHz) spectrometers. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.0 ppm) or solvent peak (CDCl3 at 7.26 ppm for ^{1}H NMR and $CDCl_3$ at 77.16 ppm for ^{13}C NMR) as the internal standard. The following abbreviations were used: (s = single; d = double (d); t = triple; q = quartet; dd = doublet of doublets; dt = triplet of doublets; td = doublet of triplets; dq = quartet of doublets; qd = doublet of quartets; m = multiplet; High resolution mass (HR-MS) spectra were obtained using an Agilent 6210 ESI mass spectrometer.

4.2. General procedures for the synthesis of allylic esters via oxidative esterification of carboxylic acids and alkanes: preparation of ***3aa*** as a representative example

To a 25 mL Schlenk tube was charged with a magnetic stir bar, CuTPP (3.4 mg, 0.005 mmol, 1.0 mol %), benzoic acid (**1a**, 61 mg, 0.5 mmol, 1.0 equiv.), cyclohexane (**2a**, 1.0 mL) and DTBP (2.5 mmol, 475 μL, 5.0 equiv.) were added, and then the tube was sealed with Teflon screw cap tightly. This resulting mixture was stirred at 120 °C for 12 h in air atmosphere. After accomplishment, the reaction was cooled to room temperature. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel with hexane/ethyl acetate as the eluent (10/1) to afford the pure allylic ester **3aa**.

4.3. General procedures for the synthesis of alkylalkenes via decarboxylative alkenylation of cinnamic acids with alkanes: preparation of ***6a*** as a representative example

To a 25 mL Schlenk tube was charged with a magnetic stir bar, CuTPP (3.4 mg, 0.005 mmol, 1.0 mol %), *trans*-cinnamic acid (**5a**, 74 mg, 0.5 mmol, 1.0 equiv.), cyclohexane (**2a**, 1.0 mL) and DTBP (2.5 mmol, 475 μL, 5.0 equiv.) were added, and then the tube was sealed with Teflon screw cap tightly. This resulting mixture was stirred at 120 °C for 12 h in air atmosphere. After accomplishment, the reaction was cooled to room temperature. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel with hexane/ethyl acetate as the eluent (10/1) to afford the pure (*E*)-alkene **6a**.

4.4. Procedure for control experiments

4.4.1. To check the sequence of bond formation

(i) To a 25 mL Schlenk tube was charged with a magnetic stir bar, CuTPP (3.4 mg, 0.005 mmol, 1.0 mol %), cyclohexyl benzoate (**7a**, 102 mg, 0.5 mmol, 1.0 equiv.), benzene (1.0 mL) and DTBP (2.5 mmol, 475 μL, 5.0 equiv.) were added, and then the tube was sealed with Teflon screw cap tightly. This resulting mixture was stirred at 120 °C for 12 h in air atmosphere. After accomplishment, the reaction was cooled to room temperature. No expected product allylic ester **3aa** was detected by TLC.

(ii) To a 25 mL Schlenk tube was charged with a magnetic stir bar, CuTPP (3.4 mg, 0.005 mmol, 1.0 mol %), benzoic acid (**1a**, 61 mg, 0.5 mmol, 1.0 equiv.), cyclohexene (**8a**, 1.0 mL) and DTBP (2.5 mmol, 475 μL, 5.0 equiv.) were added, and then the tube was sealed with Teflon screw cap tightly. This resulting mixture was stirred at 120 °C for 12 h in air atmosphere. After accomplishment, the reaction was cooled to room temperature. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel with hexane/ethyl acetate as the eluent (10/1) to afford the pure allylic ester **3aa.**

(iii) To a 25 mL Schlenk tube was charged with a magnetic stir bar, CuTPP (3.4 mg, 0.005 mmol, 1.0 mol %), cyclohexane (**2a**, 1.0 mL) and DTBP (2.5 mmol, 475 μL, 5.0 equiv.) were added, and then the tube was sealed with Teflon screw cap tightly. This resulting mixture was stirred at 120 °C for 12 h in air atmosphere. After accomplishment, the reaction was cooled to room temperature. No expected product allylic ester **3aa** was detected by TLC.

4.4.2. Free radical capture experiments

To a 25 mL Schlenk tube was charged with a magnetic stir bar, CuTPP (3.4 mg, 0.005 mmol, 1.0 mol %), benzoic acid (**1a**, 61 mg, 0.5 mmol, 1.0 equiv.), cyclohexane (**2a**, 1.0 mL), DTBP (2.5 mmol, 475 μL, 5.0 equiv.) and 2,2,6,6-tetramethylpiperidinooxy (TEMPO, 469 mg, 6.0 equiv.) or butylated hydroxytoluene (BHT, 661 mg, 6.0 equiv.) were added, and then the tube was sealed with Teflon screw cap tightly. This resulting mixture was stirred at 120 °C for 12 h in air atmosphere. After accomplishment, the reaction was cooled to room temperature. No expected product allylic ester **3aa** was detected by TLC.

4.4.3. Intermolecular competitive kinetic isotopic effect experiments

To a 25 mL Schlenk tube was charged with a magnetic stir bar, CuTPP (3.4 mg, 0.005 mmol, 1.0 mol %), benzoic acid (**1a**, 61 mg, 0.5 mmol, 1.0 equiv.), cyclohexane (**2a**, 0.5 mL), cyclohexane-d_{12} (**2a′**, 0.5 mL) and DTBP (2.5 mmol, 475 μL, 5.0 equiv.) were added, and then the tube was sealed with Teflon screw cap tightly. This resulting mixture was stirred at 120 °C for 12 h in air atmosphere. After accomplishment, the reaction was cooled to room temperature. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel with hexane/ethyl acetate as the eluent (10/1) to afford the pure allylic ester.

4.5. Characterization data of all compounds

4.5.1. Cyclohex-2-en-1-yl benzoate (***3aa***) [9d]

Colorless oil (93 mg, 92 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, J = 8.4, 1.4 Hz, 2H), 7.58–7.49 (m, 1H), 7.48–7.37 (m, 2H), 6.06–5.94 (m, 1H), 5.84 (ddt, J = 10.0, 3.8, 2.0 Hz, 1H), 5.52 (dtq, J = 5.3, 3.6, 1.7 Hz, 1H), 2.14 (dttd, J = 13.1, 5.6, 3.8, 1.9 Hz, 1H), 2.09–1.93 (m, 2H), 1.93–1.79 (m, 2H), 1.70 (dqt, J = 13.8, 5.9, 3.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 132.9, 132.8, 130.9, 129.7, 128.3, 125.8, 77.5, 77.2, 76.8, 68.7, 28.5, 25.0, 19.0.

4.5.2. Cyclohex-2-en-1-yl 2-methoxybenzoate (***3ba***) [9d]

Colorless oil (93 mg, 80 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 7.9, 1.8 Hz, 1H),

7.46–7.38 (m, 1H), 7.00–6.89 (m, 2H), 6.03–5.90 (m, 1H), 5.83 (ddt, J = 10.0, 3.8, 2.0 Hz, 1H), 5.57–5.40 (m, 1H), 3.87 (s, 3H), 2.16–2.05 (m, 1H), 2.05–1.90 (m, 2H), 1.83 (ddtt, J = 20.3, 10.1, 5.6, 2.7 Hz, 2H), 1.67 (dddt, J = 13.5, 8.1, 5.6, 3.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 159.2, 133.3, 132.7, 131.5, 125.9, 120.8, 120.1, 112.1, 77.5, 77.2, 76.8, 68.4, 56.0, 56.0, 28.4, 25.0, 19.0.

*4.5.3. Cyclohex-2-en-1-yl 3-methoxybenzoate (**3ca**) [22]*

Colorless oil (103 mg, 89 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 7.6 Hz, 1H), 7.56 (s, 1H), 7.31 (t, J = 7.9 Hz, 1H), 7.07 (dd, J = 8.2, 2.7 Hz, 1H), 5.99 (dt, J = 10.0, 3.8 Hz, 1H), 5.89–5.76 (m, 1H), 5.55–5.43 (m, 1H), 3.83 (s, 3H), 2.18–2.07 (m, 1H), 2.07–1.91 (m, 2H), 1.85 (dddd, J = 24.9, 15.9, 10.3, 6.2 Hz, 2H), 1.69 (tt, J = 10.3, 5.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 159.6, 132.9, 132.2, 129.3, 125.8, 122.0, 119.2, 114.2, 77.5, 77.2, 76.8, 68.8, 55.4, 28.4, 25.0, 19.0.

*4.5.4. Cyclohex-2-en-1-yl 4-methoxybenzoate (**3da**) [9d]*

Colorless oil (105 mg, 90 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.8 Hz, 2H), 6.05–5.90 (m, 1H), 5.82 (ddt, J = 10.1, 4.0, 2.1 Hz, 1H), 5.56–5.39 (m, 1H), 3.83 (s, 3H), 2.18–2.07 (m, 1H), 2.07–1.91 (m, 2H), 1.84 (ttd, J = 17.8, 9.7, 9.0, 3.1 Hz, 2H), 1.73–1.65 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.0, 163.3, 132.7, 131.7, 126.1, 123.3, 113.6, 77.5, 77.2, 76.8, 68.3, 55.5, 28.6, 25.1, 19.1.

*4.5.5. Cyclohex-2-en-1-yl 3-methylbenzoate (**3ea**) [9d]*

Colorless oil (101 mg, 93 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.3 Hz, 2H), 7.38–7.27 (m, 2H), 6.07–5.92 (m, 1H), 5.84 (ddt, J = 10.0, 4.0, 2.1 Hz, 1H), 5.51 (qd, J = 4.3, 2.6 Hz, 1H), 2.39 (s, 3H), 2.18–2.09 (m, 1H), 2.08–1.94 (m, 2H), 1.86 (dddd, J = 25.3, 12.8, 7.7, 3.1 Hz, 2H), 1.70 (tdt, J = 13.9, 5.9, 3.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 138.1, 133.5, 132.8, 130.8, 130.1, 128.2, 126.8, 125.9, 77.5, 77.2, 76.8, 68.6, 28.5, 25.0, 21.3, 19.1.

*4.5.6. Cyclohex-2-en-1-yl 4-methylbenzoate (**3fa**) [9d]*

Colorless oil (99 mg, 91 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 5.99 (dt, J = 8.9, 3.2 Hz, 1H), 5.83 (ddd, J = 12.4, 3.9, 2.1 Hz, 1H), 5.58–5.42 (m, 1H), 2.39 (s, 3H), 2.13 (ddd, J = 16.5, 3.9, 1.9 Hz, 1H), 2.08–1.93 (m, 2H), 1.85 (ddtt, J = 19.2, 9.7, 6.7, 2.8 Hz, 2H), 1.69 (tdt, J = 13.9, 5.9, 3.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 143.4, 132.7, 129.7, 129.0, 128.1, 126.0, 77.5, 77.2, 76.8, 68.4, 28.5, 25.0, 21.7, 21.6, 19.0.

*4.5.7. Cyclohex-2-en-1-yl [1,1′-biphenyl]-4-carboxylate (**3ga**) [22]*

Colorless oil (130 mg, 93 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22–8.09 (m, 2H), 7.65 (dd, J = 13.9, 7.8 Hz, 4H), 7.47 (t, J = 7.4 Hz, 2H), 7.40 (t, J = 7.2 Hz, 1H), 6.10–5.97 (m, 1H), 5.96–5.83 (m, 1H), 5.65–5.50 (m, 1H), 2.24–2.13 (m, 1H), 2.12–1.98 (m, 2H), 1.91 (tdd, J = 13.7, 7.1, 4.2 Hz, 2H), 1.74 (ddt, J = 13.5, 8.1, 2.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 145.5, 140.1, 132.9, 130.2, 129.6, 128.9, 128.1, 127.3, 127.0, 125.9, 77.5, 77.2, 76.8, 68.7, 28.5, 25.0, 19.1.

*4.5.8. Cyclohex-2-en-1-yl 4-(tert-butyl) benzoate (**3ha**) [9d]*

Colorless oil (116 mg, 90 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 5.99 (dt, J = 6.7, 3.7 Hz, 1H), 5.92–5.75 (m, 1H), 5.61–5.41 (m, 1H), 2.20–2.08 (m, 1H), 2.08–1.93 (m, 2H), 1.86 (tdt, J = 15.2, 9.6, 7.4 Hz, 2H), 1.70 (dddt, J = 13.7, 8.7, 5.9, 3.3 Hz, 1H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 156.3, 132.6, 129.5, 128.1, 126.0, 125.2, 77.5, 77.2, 76.8, 68.3, 35.0, 31.2, 28.5, 25.0, 19.0.

*4.5.9. Cyclohex-2-en-1-yl 2-fluorobenzoate (**3ia**) [22]*

Colorless oil (93 mg, 84 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (td, J = 7.6, 1.9 Hz, 1H), 7.54–7.41 (m, 1H), 7.22–7.03 (m, 2H), 6.08–5.92 (m, 1H), 5.90–5.76 (m, 1H), 5.58–5.44 (m, 1H), 2.18–2.07 (m, 1H), 2.07–1.88 (m, 3H), 1.82 (dddt, J = 13.1, 9.5, 5.6, 3.1 Hz, 1H), 1.68 (ttd, J = 11.4, 5.7, 3.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1, 164.1, 163.4, 160.8, 134.3, 134.2, 133.2, 132.1, 125.5, 123.9, 123.9, 119.6, 119.5, 117.1, 116.9, 77.5, 77.2, 76.8, 69.1, 28.5, 25.0, 18.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ −109.62.

*4.5.10. Cyclohex-2-en-1-yl 4-fluorobenzoate (**3ja**) [22]*

Colorless oil (96 mg, 87 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 8.6, 5.6 Hz, 2H), 7.07 (t, J = 8.6 Hz, 2H), 6.07–5.90 (m, 1H), 5.89–5.74 (m, 1H), 5.56–5.39 (m, 1H), 2.17–2.07 (m, 1H), 2.06–1.92 (m, 2H), 1.90–1.76 (m, 2H), 1.68 (dtd, J = 13.6, 8.8, 5.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 165.2, 164.4, 132.9, 132.1, 132.0, 127.1, 127.0, 125.6, 115.5, 115.2, 77.4, 77.1, 76.8, 68.8, 28.4, 24.9, 18.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ −106.08.

*4.5.11. Cyclohex-2-en-1-yl 4-chlorobenzoate (**3ka**) [9d]*

Colorless oil (105 mg, 89 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–7.91 (m, 2H), 7.38 (d, J = 8.5 Hz, 2H), 5.99 (dt, J = 8.9, 3.2 Hz, 1H), 5.81 (ddd, J = 8.0, 3.4, 1.7 Hz, 1H), 5.56–5.40 (m, 1H), 2.18–2.08 (m, 1H), 2.07–1.92 (m, 2H), 1.90–1.76 (m, 2H), 1.69 (tdt, J = 13.7, 5.8, 3.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 139.2, 133.1, 131.1, 129.4, 128.7, 125.6, 77.5, 77.2, 76.8, 69.0, 69.0, 28.5, 25.0, 19.0.

*4.5.12. Cyclohex-2-en-1-yl 2-bromobenzoate (**3la**) [9d]*

Colorless oil (112 mg, 80 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 7.6, 1.8 Hz, 1H), 7.72–7.59 (m, 1H), 7.35 (dtd, J = 20.2, 7.4, 1.4 Hz, 2H), 6.04 (dt, J = 10.7, 3.6 Hz, 1H), 5.96–5.81 (m, 1H), 5.55 (dd, J = 3.6, 1.7 Hz, 1H), 2.21–2.11 (m, 1H), 2.11–1.94 (m, 3H), 1.91–1.81 (m, 1H), 1.77–1.67 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 134.3, 133.3, 133.0, 132.3, 131.2, 127.2, 125.3, 121.5, 77.5, 77.2, 76.8, 69.6, 28.3, 25.0, 18.9.

*4.5.13. Cyclohex-2-en-1-yl 4-bromobenzoate (**3ma**) [9d]*

Colorless oil (104 mg, 74 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.83 (m, 2H), 7.62–7.46 (m, 2H), 5.99 (dt, J = 9.8, 3.6 Hz, 1H), 5.90–5.70 (m, 1H), 5.59–5.37 (m, 1H), 2.12 (dtdd, J = 15.4, 5.8, 3.9, 1.9 Hz, 1H), 2.07–1.91 (m, 2H), 1.83 (dtdd, J = 23.7, 10.0, 5.6, 3.1 Hz, 2H), 1.69 (tdt, J = 13.7, 5.9, 3.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 133.1, 131.7, 131.2, 129.8, 127.9, 125.6, 77.5, 77.2, 76.8, 69.0, 28.5, 25.0, 19.0.

*4.5.14. Cyclohex-2-en-1-yl 4-iodobenzoate (**3na**) [9b]*

Colorless oil (129 mg, 79 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.58 (m, 4H), 6.09–5.88 (m, 1H), 5.80 (dt, J = 10.1, 2.0 Hz, 1H), 5.55–5.39 (m, 1H), 2.12 (dd, J = 16.4, 4.1 Hz, 1H), 2.06–1.91 (m, 2H), 1.90–1.75 (m, 2H), 1.69 (td, J = 8.8, 4.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 137.7, 133.1, 131.1, 130.3, 125.6, 100.6, 77.5, 77.2, 76.8, 69.0, 28.4, 25.0, 19.0.

*4.5.15. Cyclohex-2-en-1-yl 4-(trifluoromethyl)benzoate (**3oa**) [22]*

Colorless oil (127 mg, 94 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.2 Hz, 2H), 6.13–5.92 (m, 1H), 5.83 (ddd, J = 8.0, 3.5, 1.7 Hz, 1H), 5.60–5.45 (m, 1H), 2.19–2.10 (m, 1H), 2.09–1.94 (m, 2H), 1.86 (dtdd, J = 20.2, 13.0, 5.5, 3.2 Hz, 2H), 1.71 (dddt, J = 13.6, 8.2, 5.6, 3.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 134.5, 134.2, 134.2, 134.2, 133.4, 130.1, 125.5, 125.4, 125.4, 125.3, 125.2, 122.5, 77.5, 77.2, 76.8, 69.4, 28.5, 25.0, 19.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ −63.11.

*4.5.16. Cyclohex-2-en-1-yl 4-cyanobenzoate (**3pa**) [22]*

Colorless oil (99 mg, 87 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). 1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 6.01 (d, J = 9.9 Hz, 1H), 5.80 (d, J = 8.7 Hz, 1H), 5.50 (s, 1H), 2.22–2.08 (m, 1H), 2.08–1.92 (m, 2H), 1.91–1.76 (m, 2H), 1.69 (dp, J = 13.5, 4.3, 3.3 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 134.7, 133.6, 132.2, 130.2, 125.1, 118.1, 116.2, 77.5, 77.2, 76.8, 69.7, 28.3, 25.0, 18.9.

*4.5.17. Cyclohex-2-en-1-yl 4-hydroxybenzoate (**3ra**)*

Colorless oil (44 mg, 40 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.2 Hz, 2H), 6.87 (d, J = 8.3 Hz, 2H), 6.08–5.91 (m, 1H), 5.90–5.74 (m, 1H), 5.47 (d, J = 1.8 Hz, 1H), 2.18–2.08 (m, 1H), 2.08–1.98 (m, 1H), 1.97–1.91 (m, 1H), 1.90–1.79 (m, 2H), 1.71 (dd, J = 8.0, 3.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 166.6, 160.4, 160.4, 132.9, 132.1, 125.9, 123.0, 115.3, 77.5, 77.2, 76.8, 68.6, 28.6, 25.5, 25.1, 24.2, 19.1. HR-MS (ESI) calcd for $C_{14}H_{14}NaO_3$ $[M+Na]^+$ 241.0835, found: 241.0830.

*4.5.18. Cyclohex-2-en-1-yl 2,4-dihydroxybenzoate (**3sa**)*

Colorless oil (39 mg, 34 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.11 (s, 1H), 7.74 (d, J = 8.7 Hz, 1H), 6.46–6.29 (m, 2H), 6.09–5.95 (m, 1H), 5.87–5.73 (m, 1H), 5.59–5.39 (m, 1H), 2.14 (ddd, J = 18.2, 4.9, 1.9 Hz, 1H), 2.09–2.03 (m, 1H), 1.97–1.87 (m, 2H), 1.86–1.77 (m, 1H), 1.71 (dd, J = 7.6, 3.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 163.8, 162.3, 133.5, 132.1, 125.4, 107.9, 106.4, 103.2, 77.5, 77.2, 76.8, 69.1, 28.5, 25.0, 18.9. HR-MS (ESI) calcd for $C_{13}H_{15}O_4$ $[M+H]^+$ 235.0965, found: 235.0960.

*4.5.19. Cyclohex-2-en-1-yl 2,6-dimethoxybenzoate (**3ta**) [22]*

Colorless oil (76 mg, 58 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.27 (m, 1H), 6.57 (d, J = 8.4 Hz, 2H), 6.08–5.94 (m, 1H), 5.93–5.79 (m, 1H), 5.59 (qd, J = 5.3, 3.6 Hz, 1H), 3.83 (s, 6H), 2.18–2.03 (m, 2H), 2.03–1.90 (m, 2H), 1.83 (tdt, J = 12.9, 5.7, 3.4 Hz, 1H), 1.74–1.63 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 157.5, 132.8, 130.9, 125.9, 113.8, 104.2, 77.5, 77.2, 76.8, 69.1, 56.1, 28.4, 25.0, 19.0.

*4.5.20. Cyclohex-2-en-1-yl thiophene-2-carboxylate (**3ua**) [9d]*

Colorless oil (87 mg, 83 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 2.8 Hz, 1H), 7.51 (d, J = 4.8 Hz, 1H), 7.05 (t, J = 4.2 Hz, 1H), 6.02–5.92 (m, 1H), 5.80 (dd, J = 10.0, 3.2 Hz, 1H), 5.44 (d, J = 5.0 Hz, 1H), 2.10 (dd, J = 17.9, 5.0 Hz, 1H), 2.05–1.98 (m, 1H), 1.93 (ddt, J = 13.7, 8.9, 4.1 Hz, 1H), 1.88–1.75 (m, 2H), 1.66 (dddd, J = 16.9, 13.7, 7.4, 4.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.1, 134.6, 133.3, 133.1, 132.3, 127.8, 125.6, 77.5, 77.2, 76.8, 69.1, 28.5, 25.0, 19.0.

*4.5.21. Cyclohex-2-en-1-yl furan-2-carboxylate (**3va**) [9d]*

Colorless oil (77 mg, 80 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.13 (d, J = 3.5 Hz, 1H), 6.50–6.41 (m, 1H), 6.06–5.87 (m, 1H), 5.76 (d, J = 9.2 Hz, 1H), 5.45 (d, J = 4.9 Hz, 1H), 2.09 (dd, J = 18.5, 4.7 Hz, 1H), 2.03–1.88 (m, 2H), 1.80 (tdd, J = 16.2, 7.3, 3.9 Hz, 2H), 1.69–1.59 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 146.1, 145.0, 133.2, 125.4, 117.7, 111.7, 77.4, 77.1, 76.8, 68.8, 28.3, 24.9, 18.9.

*4.5.22. Cyclohex-2-en-1-yl 2-naphthoate (**3xa**) [9d]*

Colorless oil (113 mg, 90 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, J = 8.6 Hz, 1H), 8.21 (d, J = 7.2 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.63 (t, J = 7.7 Hz, 1H), 7.52 (dt, J = 15.8, 7.6 Hz, 2H), 6.06 (d, J = 10.1 Hz, 1H), 5.97 (d, J = 11.2 Hz, 1H), 5.67 (s, 1H), 2.23–2.13 (m, 1H), 2.04 (ddq, J = 21.2, 13.1, 5.2, 4.5 Hz, 3H), 1.89 (ddd, J = 16.4, 13.1, 9.6 Hz, 1H), 1.80–1.71 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 133.9, 133.2, 133.0, 131.4, 130.1, 128.6, 127.9, 127.7, 126.2, 125.9, 125.8, 124.5, 77.5, 77.2, 76.8, 68.8, 28.5, 25.0, 19.1.

*4.5.23. Cyclohex-2-en-1-yl 3-phenylpropanoate (**3ya**) [22]*

Colorless oil (105 mg, 91 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (q, J = 7.4 Hz, 2H), 7.11 (d, J = 7.4 Hz, 3H), 5.84 (dd, J = 8.6, 4.8 Hz, 1H), 5.66–5.50 (m, 1H), 5.27–5.08 (m, 1H), 2.86 (t, J = 7.8 Hz, 2H), 2.53 (t, J = 7.8 Hz, 2H), 2.04–1.82 (m, 2H), 1.75 (td, J = 13.2, 12.2, 4.6 Hz, 1H), 1.66–1.48 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 140.6, 132.7, 128.5, 128.4, 126.2, 125.7, 77.5, 77.2, 76.8, 68.1, 36.2, 31.1, 28.3, 24.9, 18.9.

*4.5.24. Cyclopent-2-en-1-yl benzoate (**4a**) [9a]*

Colorless oil (78 mg, 83 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.6 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 6.15 (d, J = 4.4 Hz, 1H), 5.95 (d, J = 4.2 Hz, 2H), 2.59 (td, J = 15.0, 13.2, 6.8 Hz, 1H), 2.40 (tt, J = 12.1, 6.3 Hz, 2H), 1.96 (ddt, J = 13.6, 11.2, 3.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 137.8, 132.8, 130.8, 129.6, 129.4, 128.3, 81.2, 77.5, 77.2, 76.8, 31.3, 30.0.

*4.5.25. Cyclopent-2-en-1-yl 4-methoxybenzoate (**4b**) [9b]*

Colorless oil (90 mg, 82 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 8.5 Hz, 2H), 6.88 (d, J = 8.5 Hz, 2H), 6.12 (d, J = 5.4 Hz, 1H), 6.02–5.81 (m, 2H), 3.83 (s, 3H), 2.56 (dd, J = 12.4, 8.0 Hz, 1H), 2.44–2.29 (m, 2H), 1.95 (dq, J = 13.0, 5.3, 4.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 163.3, 137.5, 131.6, 129.6, 123.2, 113.5, 80.8, 77.4, 77.2, 76.9, 55.4, 31.2, 30.0.

*4.5.26. Cyclopent-2-en-1-yl 4-(trifluoromethyl)benzoate (**4c**)*

Colorless oil (103 mg, 80 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, J = 8.1 Hz, 2H), 7.67 (d, J = 8.1 Hz, 2H), 6.18 (d, J = 5.6 Hz, 1H), 5.95 (t, J = 7.9 Hz, 2H), 2.67–2.52 (m, 1H), 2.50–2.30 (m, 2H), 1.98 (ddt, J = 10.6, 8.0, 4.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4, 138.3, 134.5, 134.2, 134.0, 130.1, 129.1, 125.5, 125.4, 125.4, 125.4, 124.9, 122.7, 82.0, 77.4, 77.2, 76.9, 31.3, 29.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ −63.10. HR-MS (ESI) calcd for $C_{13}H_{11}F_3NaO_2$ $[M+Na]^+$ 279.0603, found: 279.0599.

*4.5.27. Benzoic acid indan-2-yl ester (**4h**) [28]*

Colorless oil (100 mg, 84 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.01 (m, 2H), 7.58 (t, J = 6.5 Hz, 2H), 7.51–7.42 (m, 2H), 7.37 (d, J = 3.5 Hz, 2H), 7.31 (dq, J = 8.2, 4.1 Hz, 1H), 6.53 (dt, J = 7.3, 4.3 Hz, 1H), 3.31–3.18 (m, 1H), 3.06–2.94 (m, 1H), 2.77–2.62 (m, 1H), 2.39–2.21 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 144.4, 141.2, 132.9, 130.5, 129.7, 129.0, 128.3, 126.8, 125.7, 124.9, 79.0, 77.5, 77.2, 76.8, 32.5, 30.3.

*4.5.28. (E)-(2-cyclohexylvinyl)benzene (**6a**) [9b]*

Colorless oil (69 mg, 74 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.3 Hz, 2H), 7.30 (t, J = 7.7 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 6.37 (d, J = 16.0 Hz, 1H), 6.20 (dd, J = 16.0, 6.9 Hz, 1H), 2.15 (dtt, J = 10.9, 7.1, 3.5 Hz, 1H), 1.85 (d, J = 3.3 Hz, 1H), 1.81 (s, 2H), 1.78 (t, J = 3.4 Hz, 1H), 1.73–1.68 (m, 1H), 1.37–1.33 (m, 1H), 1.32–1.28 (m, 1H), 1.24 (dt, J = 10.9, 3.9 Hz, 2H), 1.19 (d, J = 3.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 137.0, 128.6, 127.4, 126.9, 126.1, 77.5, 77.2, 76.8, 41.3, 33.1, 26.3, 26.2.

*4.5.29. (E)-1-(2-cyclohexylvinyl) 4-methoxybenzene (**6b**) [29]*

Colorless oil (81 mg, 75 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.3 Hz, 2H), 6.88 (d, J = 8.3 Hz, 2H), 6.34 (d, J = 16.0 Hz, 1H), 6.08 (dd, J = 15.9, 7.0 Hz, 1H), 3.83 (s, 3H), 2.20–2.09 (m, 1H), 1.88–1.78 (m, 4H), 1.75–1.69 (m, 1H), 1.39–1.31 (m, 2H), 1.23 (t, J = 11.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 134.9, 131.0, 127.1, 126.7, 114.0, 77.5, 77.2,

76.8, 55.4, 41.3, 33.2, 26.3, 26.2.

*4.5.30. (E)-1-(2-cyclohexylvinyl) 4-(trifluoromethyl)benzene (**6c**) [29]*

Colorless oil (80 mg, 63 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 6.38 (d, J = 16.0 Hz, 1H), 6.28 (dd, J = 16.0, 6.6 Hz, 1H), 2.16 (dtd, J = 10.9, 7.3, 3.3 Hz, 1H), 1.87–1.74 (m, 4H), 1.73–1.67 (m, 1H), 1.36–1.31 (m, 1H), 1.31–1.20 (m, 3H), 1.17 (dd, J = 13.1, 3.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 139.7, 128.5, 126.3, 126.2, 125.6, 125.5, 77.5, 77.2, 76.8, 41.4, 32.9, 26.3, 26.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ −62.34.

*4.5.31. (E)-(2-cyclopentylvinyl)benzene (**6d**) [9b]*

Colorless oil (58 mg, 68 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 7.7 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.20 (t, J = 7.3 Hz, 1H), 6.39 (d, J = 15.8 Hz, 1H), 6.23 (dd, J = 15.8, 7.7 Hz, 1H), 2.62 (h, J = 8.0 Hz, 1H), 1.88 (dq, J = 11.3, 6.3 Hz, 2H), 1.73 (dq, J = 7.0, 4.1 Hz, 2H), 1.63 (td, J = 7.8, 4.5 Hz, 2H), 1.42 (dq, J = 15.1, 8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.1, 135.8, 128.6, 128.0, 126.8, 126.1, 77.5, 77.2, 76.8, 44.0, 33.4, 25.4.

*4.5.32. (E)-styrylcyclooctane (**6e**) [9b]*

Colorless oil (75 mg, 70 %). Hex/EA as the eluent (Hex/EA = 10:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 7.8 Hz, 2H), 7.31 (t, J = 7.4 Hz, 2H), 7.22 (d, J = 7.4 Hz, 1H), 6.36 (d, J = 15.9 Hz, 1H), 6.25 (dd, J = 15.8, 7.3 Hz, 1H), 2.42 (d, J = 8.4 Hz, 1H), 1.80 (q, J = 11.1, 10.2 Hz, 4H), 1.63–1.55 (m, 11H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 137.9, 128.6, 127.0, 126.8, 126.1, 77.5, 77.2, 76.8, 41.5, 32.0, 27.6, 26.1, 25.2.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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