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ORIGINAL PAPER

Iodine-catalyzed synthesis of β-uramino crotonic esters as well as oxidative esterification of carboxylic acids in choline chloride/urea: a desirable alternative to organic solvents

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Abstract
Iodine-mediated selective synthesis of β-uramino crotonic esters was achieved via the reaction of β-dicarbonyls and urea at room temperature. Choline chloride/urea mixture, as an eco-friendly, cheap, non-toxic, and recyclable deep eutectic solvent (DES), was employed as sustainable media as well as reagent at the same time in these transformations. Some derivatives of β-uramino crotonic esters were synthesized with good to high yields without a tedious work-up. The process could be done to synthesize the above-mentioned compounds in gram scale. Moreover, oxidative cross-esterification of carboxylic acids with alkyl benzenes was carried out in the above-mentioned DES by the employment of tetrabutylammonium iodide (TBAI) as the catalyst and *tert*-butyl hydroperoxide (TBHP) as the oxidant at 80 °C. DES/TBAI system was reused up to five consecutive times.

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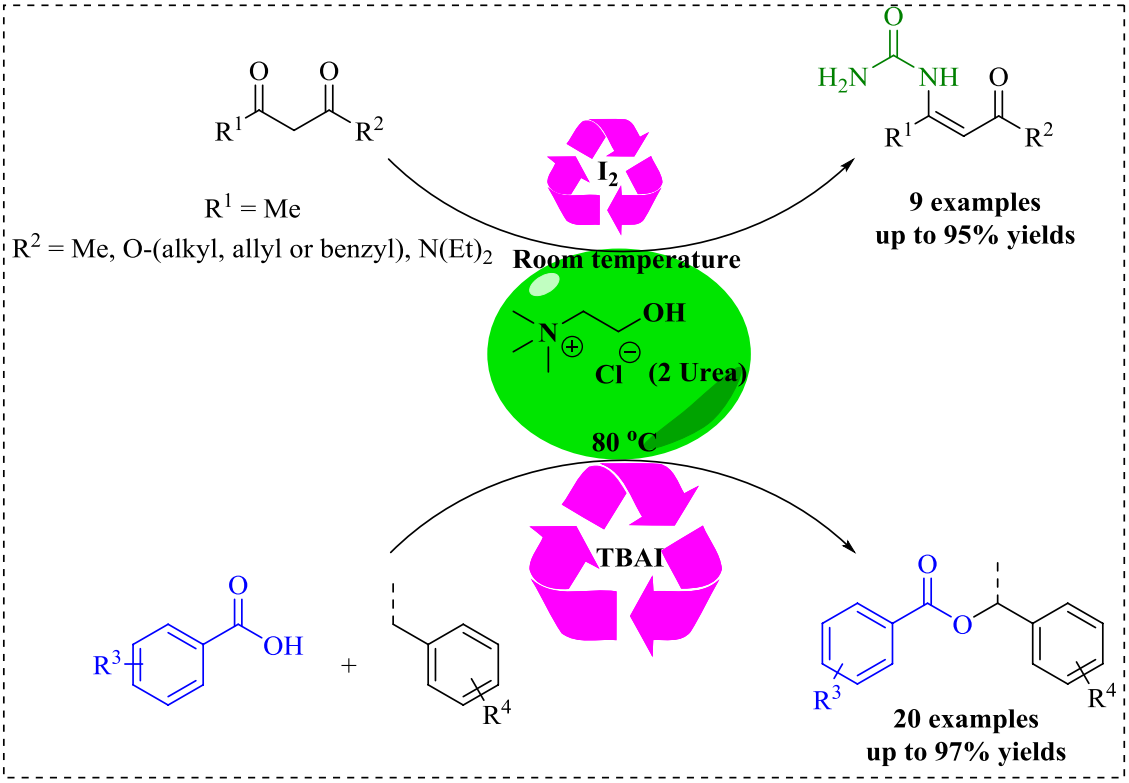
Graphic abstract

Iodine-catalyzed C–N and C–O bond formation in choline chloride/urea as a green solvent under the mild reaction conditions. Providing the clean procedure toward synthesis of *β*-uramino crotonic esters and benzylic esters.



Keywords Homogeneous catalysis · Deep eutectic solvent · Crotonic esters · Choline chloride · Esterification

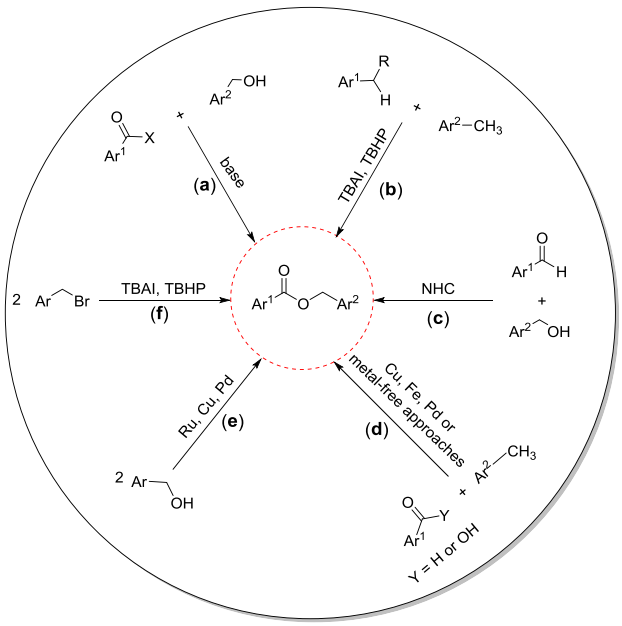
Introduction

Since their occurrence in 2003 [1], deep eutectic solvents (DESs) have been shown to be a good substitute for organic solvents in chemical reactions. They are structurally similar to conventional ionic liquids [2–10] with the same good properties (nonvolatile, low flammability, and biodegradable). Also, they have two other important attributes with superiority over ILs: their easy preparation and lower toxicity [11–17]. Despite the variety of raw materials used to form a DES, the most widely used precursors are choline chloride and urea, which are very cheap and non-toxic. This eutectic mixture has been used in many organic reactions as solvent and catalyst [18–26]. In some cases, it and its congeners have been employed as a reagent with a dual or triple role at the same time. For example, in 2011, Shankarling et al. reported the halogenation reactions in ChCl/urea as a dual catalyst and green reaction medium [27]. As another example, eco-efficiency and scalable synthesis of bisamides in ChCl/urea DES as a triple role of being a solvent, a catalyst and a reagent was reported by Azizi et al. in 2015 [28].

In this study, we are going to report a simple, green, and eco-friendly procedure for the synthesis of two different families of esters called *β*-uramino crotonic esters and benzyl benzoates. The former are important intermediates for the synthesis of 6-methyl-2,4-(1*H*,3*H*)pyrimidinediones which are biologically active compounds serving a variety of purposes [29]. The latter are the most important functional groups, found in many natural products and pharmaceuticals. Moreover, they serve as significant protecting groups in amino acids as well as outstanding building blocks in organic reactions [30–33]. There are few articles in the literature for the synthesis of *β*-uramino crotonic esters, mainly by the use of an acid as a catalyst or in microwave conditions [29, 34–36]. Employment of ChCl/urea as both solvent and reagent under the acid-free conditions at room temperature and easy work-up without any extra operation for product purification are salient features of this protocol.

Various methods for the synthesis of benzyl benzoates have been reported, including activated carboxylic acid derivatives (or their equivalents) with alcohols in the presence of a base [37–39], cross-dehydrogenative coupling (CDC) of alkyl benzenes [40], CDC reaction of aromatic aldehydes with benzyl alcohols [41], CDC reaction of aromatic aldehydes or benzoic acids with alkyl benzenes [42–47], oxidative self-coupling of benzyl alcohols [48–50], and oxidative self-coupling of benzyl bromides [51] (Scheme 1, equations a–f, respectively). Among them, the most popular and simplest route is the direct esterification of benzyl alcohols, aromatic aldehydes or carboxylic acids with alkyl benzenes, catalyzed by a transition metal such as Pd [44], Cu [42], Pt [52], and Fe [43]. Nevertheless, the use of metals as a catalyst, which is often toxic and expensive, limits the scope of these methods for large-scale or industrial applications. In 2012, an elegant metal-free approach was reported by Zhang et al. for oxidative esterification of benzyl C–H bonds by employing Bu_4NI as the catalyst [47]. Various derivatives of carboxylic acids reacted smoothly with benzylic substrates toward the synthesis of benzyl esters with good to excellent yields. In the same year, Wang and co-authors reported the Bu_4NI-catalyzed benzylic carboxylation of alkyl arenes with aromatic aldehydes toward the synthesis of carboxylic acid esters [46]. Subsequently, the elegant metal-free approaches had been developed in recent years for oxidative cross-esterification of benzylic substrates [40, 45, 53].

In the above-mentioned metal-free approaches, alkyl benzenes act as both coupling partner and solvent. Given the importance of metal-free oxidative esterification reactions in the synthesis of benzyl benzoates, the development of the greener and more environmentally benign procedures is still required for these reactions. Here, we report the synthesis of benzyl benzoates via the oxidative esterification of carboxylic acids with alkyl benzenes in ChCl/urea as a green reaction media. By employment of only two equivalent of alkyl benzenes per one mmol of carboxylic acids, various derivatives of benzyl benzoates were synthesized in good to high yields.



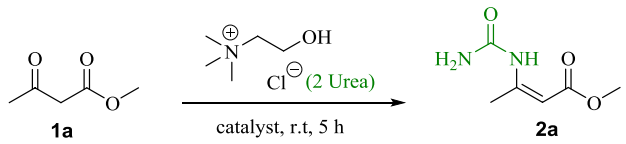
Scheme 1 Various methods for synthesis of benzyl benzoates

Results and discussion

Initially, the synthesis of *β*-uramino crotonic esters is discussed. Synthesis of product **2a,** result of the reaction between methyl acetoacetate **1a** and urea, was put into the agenda to achieve optimal conditions. It was initially found that without the presence of a catalyst, there is no reaction at all between **1a** and urea (Table 1, entry 1). It was thought that the presence of a base would help to carry out the reaction, but in the presence of bases such as KOH and DABCO no results were obtained (Table 1, entries 2 and 3). Surprisingly, when the $K_2S_2O_8$ was used as a stoichiometric reagent, product efficiency increased by 95%, even though, in the presence of the sub-stoichiometric amount of it, the yield was reduced to 10% (Table 1, entries 4 and 5). The best result was obtained in the presence of iodine (10 mol%), and the product was achieved with 95% yield (Table 1, entry 6). In the presence of the salts such as KI, TBAI, CuI, $FeCl_2$, and $ZnCl_2$, the product was isolated with low to moderate efficiency (Table 1, entries 7–11). 5 mol% of iodine resulted in a 90% product efficiency (Table 1, entry 12). Then, the solvent effect on the reaction performance was studied. When the reaction was carried out in the solvents such as H_2O, THF, toluene, EtOAc, CH_3CN, DMF, and DMSO, the efficiency was lower than that of ChCl/urea. In toluene, no product was formed at all (Table 1, entries 13–19). By increasing the temperature to 60 °C, the yield of the product remained unchanged (Table 1, entry 20). Worthy of note is that, for unknown reasons, in the presence of $K_2S_2O_8$ at 60 °C, the reaction was fully stopped (Table 1, entry 21). Therefore, we employed the optimized conditions as follows: *β*-dicarbonyl (1 mmol), DES (0.5 mL, containing 4.6 mmol urea), I_2 (10 mol%), at room temperature, for the synthesis of other derivatives of *β*-uramino crotonic esters (Scheme 2).

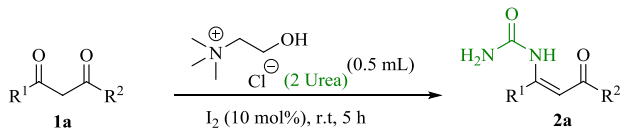
With optimal conditions in hand, we investigated the generality and limitation of this transformation for the several *β*-dicarbonyls (Table 2). Alkyl (methyl, ethyl, isobutyl, isopropyl, and *tert*-butyl) acetoacetates smoothly reacted with urea, and the corresponding crotonic esters were easily extracted with good to high yields (**2a**–**2e**). Also, allyl and benzyl acetoacetate were well coupled with urea and

Table 1 Screening the reaction conditions[a]



Entry	Solvent	Catalyst	Yield (%)
1	ChCl/urea	–	–
2	ChCl/urea	KOH (1 mmol)	–
3	ChCl/urea	DABCO (1 mmol)	–
4	ChCl/urea	$K_2S_2O_8$ (1 mmol)	95
5	ChCl/urea	$K_2S_2O_8$ (10 mol%)	10
6	ChCl/urea	I_2 (10 mol%)	95
7	ChCl/urea	KI (10 mol%)	5
8	ChCl/urea	TBAI (10 mol%)	10
9	ChCl/urea	CuI (10 mol%)	20
10	ChCl/urea	$FeCl_2$ (10 mol%)	60
11	ChCl/urea	$ZnCl_2$ (10 mol%)	30
12	ChCl/urea	I_2 (5 mol%)	90
13[b]	H_2O	I_2 (10 mol%)	20
14	THF	I_2 (10 mol%)	10
15	Toluene	I_2 (10 mol%)	–
16	EtOAc	I_2 (10 mol%)	20
17	CH_3CN	I_2 (10 mol%)	20
18	DMF	I_2 (10 mol%)	40
19	DMSO	I_2 (10 mol%)	60
20[c]	ChCl/urea	I_2 (10 mol%)	95
21	ChCl/urea	$K_2S_2O_8$ (10 mol%)	–

[a]*Reaction conditions*: **1a** (1 mmol), ChCl/urea (0.5 mL). [b]For entries 13–19, solvent (1 mL) and urea (2 mmol) were used. [c]Performing the reaction at 60 °C



Scheme 2 I_2-mediated synthesis of β-uramino crotonic esters in DES

products **2f** and **2 g** were obtained in 92% and 88% yields, respectively. Acetylacetone was also subjected to the reaction conditions, and the corresponding product, (*Z*)-1-(4-oxopent-2-en-2-yl)urea (**2h**), was successfully formed and purified with a high yield of 95%. Cyclic 1,3-diketone compounds such as cyclohexane-1,3-dione and dimedone failed to form the corresponding products and quantitatively recovered. Subsequently, *N*,*N*-diethylacetoacetamide **1i** was converted to the corresponding product **2i** with good efficiency of 80%. Unfortunately, the reaction was not successful with *tert*-butyl, and CF_3 groups as the R^1 substituent, probably due to electronic property and steric hindrance. Moreover, diethyl malonate did not also succeed in forming related products under the optimized reaction conditions.

To confirm the practicality of this method, the synthesis of compound **2a** was investigated on a gram scale. For this purpose, methyl acetoacetate (10 mmol, 1.16 gr) was subjected to the reaction conditions and **2a** was isolated in 90% yield (1.42 gr). This shows the efficiency of this method for the synthesis of crotonic esters in high levels.

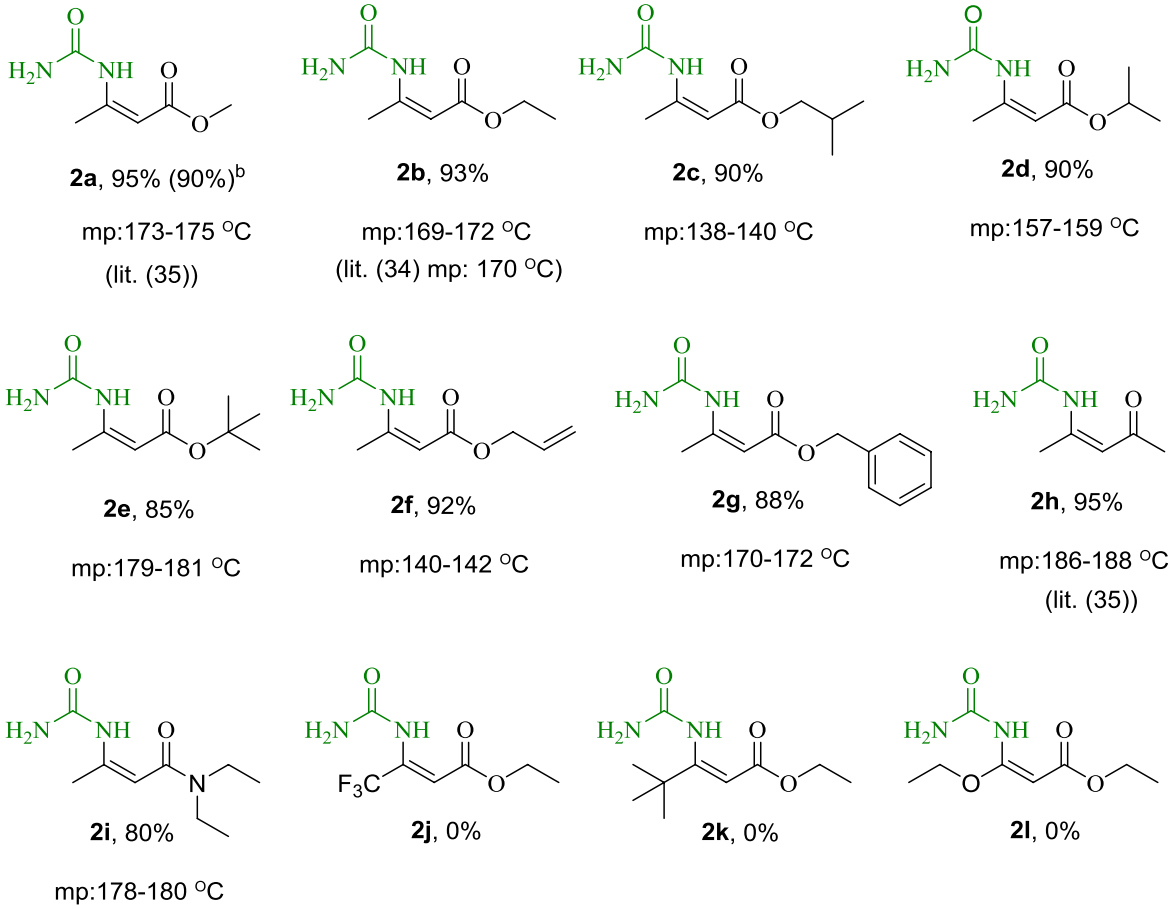
To gain more insights into the mechanism and whether the reaction is going through a radical path, the radical inhibition study was performed under the standard reaction conditions with TEMPO, and the formation of the corresponding compound **2a** in 95% yields showed that a radical mechanism could be ruled out (Scheme 3).

However, the following pathway, shown in Scheme 4, is proposed as the reaction mechanism. Urea attacks the activated carbonyl group by iodine in intermediate **A**, resulting in the formation of intermediate **B** along with releasing of HI. This intermediate then loses HOI and is converted to the **C** which is the tautomer of the final product **2**. Iodine is recycled and returns to the catalytic cycle via the reaction of HOI and HI compounds.

Recyclability of ChCl/urea as solvent was studied in the synthesis of product **2a**. After completion in the first run, the water (10 mL) was added to the reaction mixture, and the organic compounds were extracted with ethyl acetate (2 × 10 mL). The aqueous phase including DES was concentrated, and the fresh reagent (methyl acetoacetate and iodine) was added to it. After stirring for 5 h at room temperature, the conversion was 60% (based on GC) and the product **2a** isolated in 55% yield. Since the DES plays both the reagent and the solvent and some of the urea is lost in the first run, this reduction in efficiency was somewhat predictable. In another attempt, after the first run, urea (1 mmol) was also added to the reaction mixture, and fortunately the isolated yield increased to 92%. This procedure was repeated for four consecutive steps with only a negligible decrease in efficiency (Table 3).

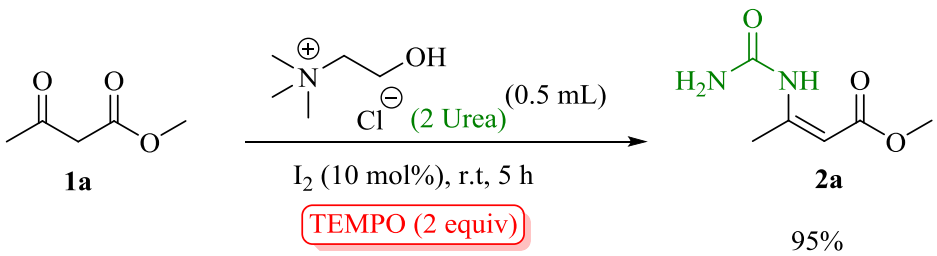
In addition, oxidative cross-esterification of carboxylic acids with alkyl benzenes in ChCl/urea as a green solvent was investigated. Benzoic acid and toluene were selected as the model substrates for optimization of the reaction conditions. The results are shown in Table 4. At first and under the following conditions, benzoic acid (1 mmol), toluene (2 mmol), ChCl/urea (0.5 mL), TBAI (20 mol%) as the catalyst and TBHP (2 equiv.) as the oxidant at 80 °C, the product **5a** was obtained in 80% yield (Table 4, entry 1). The importance of TBAI as the catalyst for this reaction was identified when no product was formed in the presence of $PhI(OAc)_2$ as the catalyst or under catalyst-free

Table 2 Scope and limitation of the reaction[a]



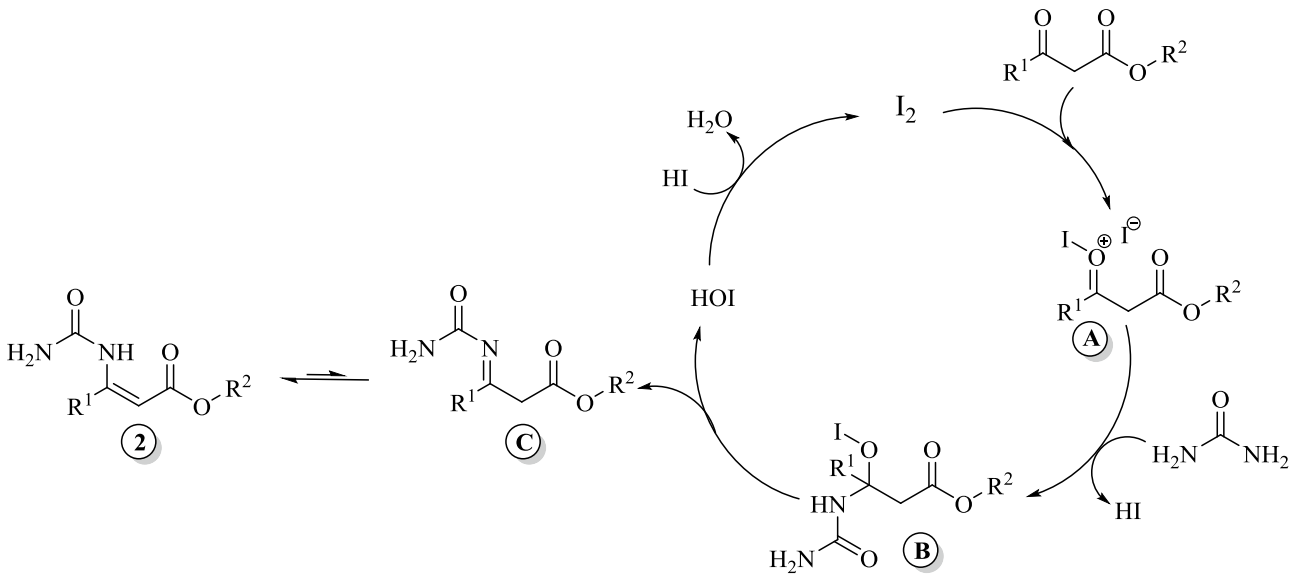
[a] Reaction conditions: 1,3-diketone (1 mmol), ChCl/urea (0.5 mL, contain 4.6 mmol urea), I_2 (10 mol%), room temperature, 5 h; [b]Gram scale reaction; The yields refers to the isolated pure products.

Scheme 3 Radical scavenger study to prove the radical pathway of the reaction



conditions as well as the decrease in yield in the presence of KI or I_2 (Table 4, entries 2–5). Among the oxidants used, TBHP was superior to NaOCl, *m*CPBA, DTBP, and H_2O_2 (Table 4, entries 6–9). Reducing the amount of the catalyst as well as the oxidant to 50% resulted in a significant reduction in efficiency. However, their increase had no effect on the product yield (Table 4, entries 10–13). Temperature also had a similar effect. Increasing it to 100 °C was ineffective on the yield of the product, but the yield drastically decreased at 40 °C (Table 4, entries 14 and 15). Performing the reaction in water or ethyl acetate as the solvent, instead of ChCl/urea, hurts the efficiency (Table 4, entries 16 and 17). When one mmol of toluene was used, the yield reduced to 55% (Table 4, entry 18).

Eventually, the scope of this transformation was further studied between carboxylic acids and alkyl benzenes in the presence of TBAI (20 mol%) as the catalyst, TBHP



Scheme 4 Plausible reaction mechanism

Table 3 Recycling of DES for the formation of product **2a**

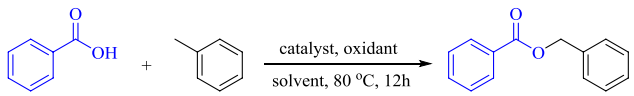
Entry	Cycle	% Yield
[a]1.	Fresh	95
[b]2.	1st recycle	55
[c]3.	2nd recycle	92
4.	3rd recycle	92
5.	4th recycle	90
6.	5th recycle	88

[a]*Reaction conditions*: same to the optimized conditions of the model reaction; [b]The recovered DES was charged with the fresh reagents (methyl acetoacetate (1 mmol) and I_2 (10 mol%)); [c]For entries 3–6, the fresh reagents (methyl acetoacetate (1 mmol), I_2 (10 mol%) and urea (1 mmol)) were added to the recovered DES

(2 equiv) as the oxidant, and ChCl/urea as the solvent at 80 °C under air atmosphere.

Table 5 shows the structures of the synthesized benzyl benzoates. Various conventional benzoic acids as well as cinnamic acid and 2-naphtanoic acid were converted to the corresponding esters in the reaction with toluene in acceptable yields (products **5a–j**). Generally speaking, the acids including electron-donating groups on the aromatic ring had a better performance than those of electron-withdrawing or halogen groups. Moreover, the reaction was not sensitive to the position of the substituents on the aromatic ring. Ethylbenzene was also subjected to the reaction conditions and coupled with benzoic acid toward the synthesis of product

Table 4 Results of screening conditions for the synthesis of compound **5a**[a]

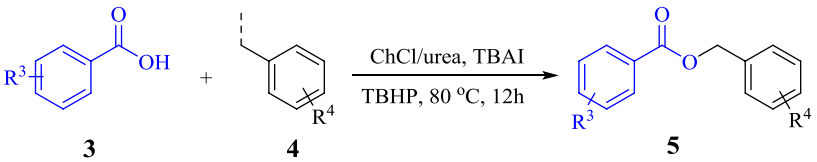


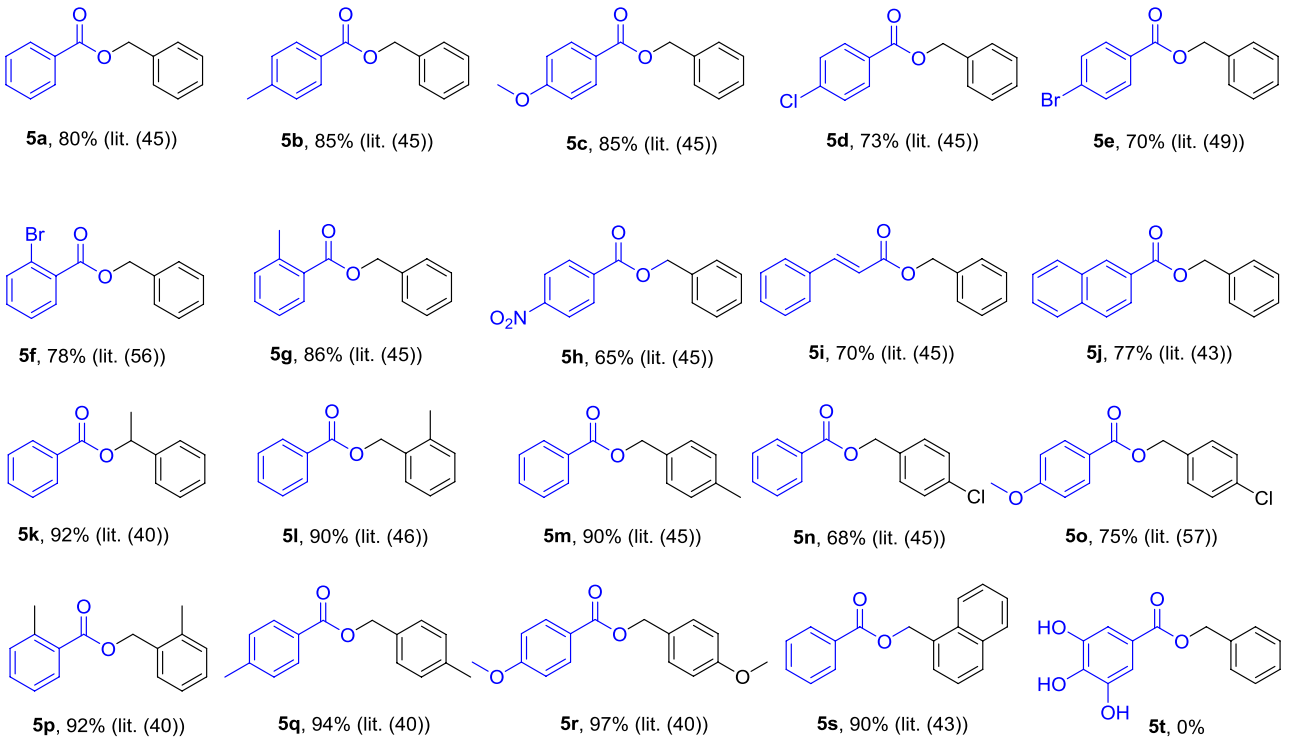
3a **4a** **5a**

Entry	Solvent	Catalyst (mol%)	Oxidant (equiv.)	Yield (%)[b]
1	ChCl/urea	TBAI (20)	TBHP (2)	80
2	ChCl/urea	I_2 (20)	TBHP (2)	trace
3	ChCl/urea	KI (20)	TBHP (2)	30
4	ChCl/urea	$PhI(OAc)_2$ (20)	TBHP (2)	N.R.
5	ChCl/urea	–	TBHP (2)	N.R.
6	ChCl/urea	TBAI (20)	NaOCl (2)	N.R.
7	ChCl/urea	TBAI (20)	*m*CPBA (2)	N.R.
8	ChCl/urea	TBAI (20)	DTBP (2)	N.R.
9	ChCl/urea	TBAI (20)	H_2O_2 (2)	N.R.
10	ChCl/urea	TBAI (10)	TBHP (2)	60
11	ChCl/urea	TBAI (30)	TBHP ((2)	82
12	ChCl/urea	TBAI (20)	TBHP (1)	40
13	ChCl/urea	TBAI (20)	TBHP (3)	80
14[c]	ChCl/urea	TBAI (20)	TBHP (2)	trace
15[d]	ChCl/urea	TBAI (20)	TBHP (2)	80
16	H_2O	TBAI (20)	TBHP (2)	40
17	EtOAc	TBAI (20)	TBHP (2)	50
18[e]	ChCl/urea	TBAI (20)	TBHP (2)	55

[a]*Reaction conditions*: **3a** (1 mmol), **4a** (2 mmol), ChCl/urea (0.5 mL), 12 h, 80 °C, TBAI (20 mol%), TBHP (2 equiv.), under air atmosphere; [b]Isolated yields; [c,d]At 40 °C and 100 °C, respectively; [e]1 mmol of **4a** was used

Table 5 The structures of the synthesized benzyl benzoates[a]





[a]Reaction conditions: carboxylic acid (1 mmol), alkyl benzene (2 mmol), ChCl/urea (0.5 mL), TBAI (20 mol%), TBHP (2 equiv.), 12 h, 80 °C, under air atmosphere; The yields refers to the isolated pure products.

5k in high yield. Subsequently, some derivatives of toluene were checked for this esterification with carboxylic acid moiety. As shown in Table 5, the presence of electron-donating groups such as methyl or methoxy on the aromatic ring of alkyl benzene improved the reaction efficiency (products **5l**–**r**). 1-Methylnaphthalene was well reacted with benzoic acid and product **5s** was obtained in 90% yield. Worthy of note is that only one methyl group of both *o*-xylene and *p*-xylene participated in the esterification reaction, and no mixture of products was detected. Unfortunately, gallic acid was failed to the reaction with toluene and quantitatively recovered.

Recycling test of the TBAI and ChCl/urea was examined for this transformation, and the results shown in Table 6 were obtained. The recycling process was carried out for the synthesis of product **5a**. After first run, the water (10 mL) was added to the reaction mixture and then the organic compounds were extracted with ethyl acetate (2 × 10 mL). The aqueous phase including DES and TBAI was concentrated, charged with fresh reagents, and subjected to the next run.

Table 6 Recycling of deep eutectic solvent and TBAI for the formation of product **5a**[a]

Entry	Cycle	% Yield
1.	Fresh	80
2.	1st recycle	80
3.	2nd recycle	78
4.	3rd recycle	77
5.	4th recycle	75
6.	5th recycle	65
[b]7.	6th recycle	78

[a]*Reaction conditions*: same to the optimized conditions of the model reaction; [b]TBAI (10 mol%) was added to the reaction mixture

The process was repeated for four successive cycles, and in the fifth run a tangible decrease in the product efficiency was observed. Fortunately, by adding 10 mol% of TBAI with the fresh reagents in the sixth run, the efficiency increased again by 78%.

Finally, the mechanism of the reaction pathway was studied. Based on the similar previously reported procedure [48–52], this reaction performs through the radical pathway. To check this hypothesis, when 2,6-di-tert-butyl-4-methylphenol (BHT), a well-known radical scavenger, was added to the model reaction, the formation of the desired product **5a** suppressed. This result reinforced the hypothesis that the reaction path is radical. However, a plausible mechanism, shown in Scheme 5, is proposed for this reaction. Initially, TBAI is oxidized by TBHP to hypoiodite **6a** which further oxidized to a key intermediate iodite **6b** with one more equivalent of TBHP [54, 55]. Then, the allylic radical **7** is obtained via the homolysis of allylic C–H bond with **6**. Subsequently, **7** is oxidized by active iodine species to give the allylic cation **8**. Eventually, the nucleophilic attack of benzoate anion **9** to the allylic cation **8** furnishes the desired product **5a**. According to the previous report by Liu et al. [45], it is also possible to combine **7** with benzoic acid to form the corresponding benzyl ester radical anion **10**, which is converted to product **5a** by the loss of an electron.

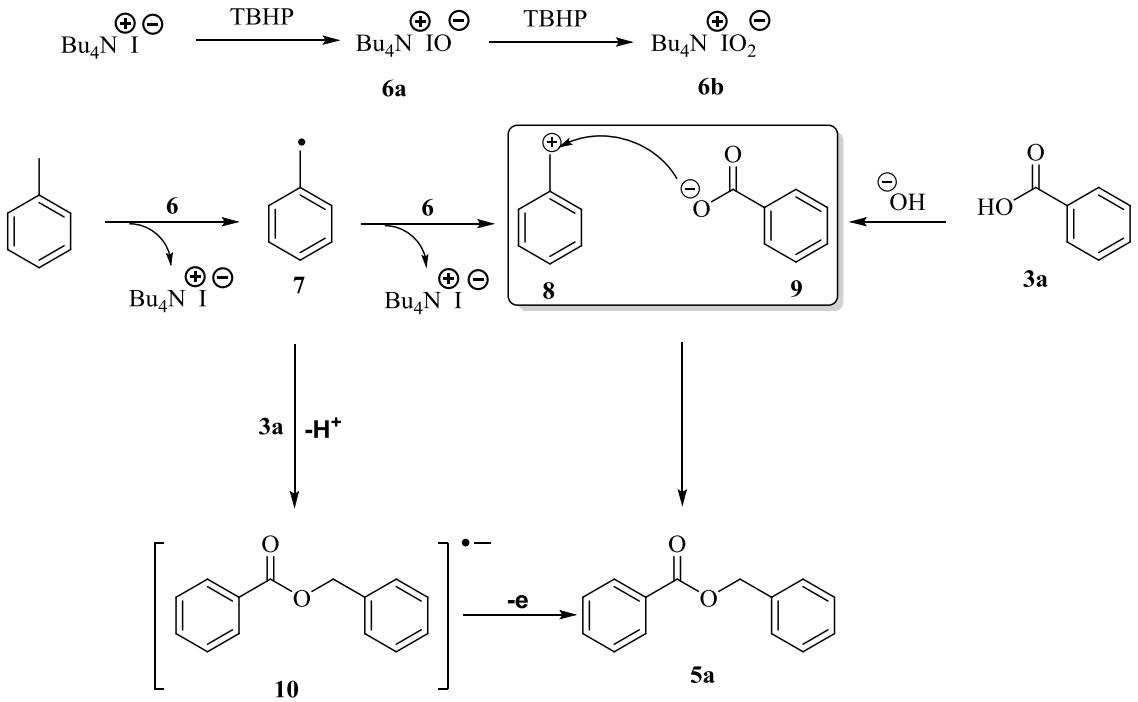
Conclusions

In summary, we developed the usage of ChCl/urea deep eutectic solvent as a recyclable and green reaction media in the synthesis of organic compounds. A green and efficient method was reported for the construction of β-uramino crotonic esters through the reaction of 1,3-dicarbonyl compounds with urea in the presence of iodine as the catalyst and ChCl/urea as a dual-role reagent both as solvent and as urea at room temperature. Moreover, ChCl/urea was employed as the solvent for oxidative esterification of carboxylic acids with alkyl benzenes in the presence of TBAI as the catalyst and TBHP as the oxidant.

Experimental section

General information

All reagents were purchased from commercial suppliers and used without further purification. All experiments were carried out air atmosphere. Analytical TLC was performed with Merck silica gel 60 F_{254} plates, and the products were visualized by ^{1}H NMR and ^{13}C NMR (300 or 400 MHz and 75 or 100 MHz, respectively) spectra recorded in $CDCl_3$ or DMSO-d6. Chemical shifts (δ) are reported in ppm using TMS as internal standard, and spin–spin coupling constants (J) are given in Hz. IR spectra were recorded on a PerkinElmer FT/IR 1760 as KBr pellets. Melting points were determined in open-end capillary tubes on a Büchi B-540 melting point apparatus and are uncorrected.



Scheme 5 Proposed mechanism of the metal-free oxidative esterification

General procedure for the synthesis of β-uramino crotonic esters

1,3-dicarbonyl compound 1 (1.0 mmol), I_2 (10.0 mol%), and ChCl/urea (0.5 mL, containing 4.6 mmol urea) were added to a 10-mL Schlenk tube, and the mixture was stirred at room temperature. After completion (5 h), the water (10 mL) was added to the reaction mixture, and the organic compound was extracted with ethyl acetate (2 × 10 mL). The solvent was evaporated under reduced pressure to give the crude mixture, which was purified by recrystallization (*n*-hexane/CH_2Cl_2) to afford the desired products **2**.

General procedure for the synthesis of benzyl benzoates

A mixture of carboxylic acid (1 mmol), alkyl benzene (2 mmol), and TBAI (73 mg, 20 mol%), in ChCl/urea (0.5 mL), was placed in the two-necked round-bottomed flask fitted with a condenser under an air atmosphere at room temperature. Then, TBHP (70% aqueous solution, two equiv.) was added to the reaction vessel and the mixture was placed in an oil bath with magnetic stirring at 80 °C. After completion (12 h), the reaction mixture was cooled to room temperature and quenched by addition of a saturated solution of sodium thiosulfate and then the organic compound was extracted with ethyl acetate (2 × 10 mL). The combined ethyl acetate layers were dried with anhydrous Na_2SO_4 and filtered. The solvent was evaporated under reduced pressure to give the crude mixture, which was purified by column chromatography on silica gel (*n*-hexane/ethyl acetate, 20:1 v/v) to afford the desired product 5.

Recycling test of ChCl/urea for the synthesis of the products 2a and 5a

Recyclability of ChCl/urea as solvent was studied in the synthesis of product **2a**. After completion in the first run, the water (10 mL) was added to the reaction mixture and the organic compounds were extracted with ethyl acetate (2 × 10 mL). The aqueous phase including DES was concentrated, and the fresh reagent (methyl acetoacetate and iodine) was added to it. After stirring for 5 h at room temperature, the conversion was 60% (based on GC) and the product **2a** was isolated in 55% yield. Since the DES plays both the reagent and the solvent and some of the urea is lost in the first run, this reduction in efficiency was somewhat predictable. In another attempt, after the first run, urea (1 mmol) was also added to the reaction mixture and fortunately the isolated yields increased to 92%. This procedure was repeated for four consecutive steps with only a negligible decrease in efficiency.

The recycling process was also carried out for the synthesis of the product **5a**. After the first run, the water (10 mL) was added to the reaction mixture and the organic compounds extracted with ethyl acetate (2 × 10 mL). The aqueous phase including DES and TBAI was concentrated, charged with fresh reagents, and subjected to the next run. The process was repeated for four successive cycles, and in the fifth run a tangible decrease in the product efficiency was observed. Fortunately, by adding 10 mol% of TBAI with the fresh reagents in the sixth run, the efficiency increased again by 78%.

Analytical data of some selected compounds

Methyl (Z)-3-ureidobut-2-enoate (**2a**). Following the general procedure, the product **2a** was obtained in 95% yield as white solid with m.p. = 173–175 °C after recrystallization process. ^{1}H-NMR (DMSO, 500 MHz): δ 2.26 (s, 3H), 3.60 (s, 3H), 4.78 (s, 1H), 6.81 (brs, 2H), 10.12 (s, 1H); ^{13}C-NMR (DMSO, 125 MHz): δ 22.1, 50.8, 91.8, 154.6, 157.3, 169.0; Anal. Calcd for $C_6H_{10}N_2O_3$ (158.16): C, 45.57; H, 6.37; N, 17.71. Found: C, 45.48; H, 6.30; N, 17.60.

Ethyl(Z)-3-ureidobut-2-enoate (**2b**). Following the general procedure, the product **2b** was obtained in 93% yield as white solid with m.p. = 169–174 °C after recrystallization process. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 1.28 (t, J = 7.1 Hz, 3H), 2.37 (s, 3H), 4.14 (q, J = 7.1 Hz, 2H), 4.85 (s, 1H), 4.98 (s, 2H), 10.69 (s, 1H); ^{13}C-NMR (DMSO, 125 MHz): δ 14.3, 21.6, 59.6, 93.8, 154.2, 156.7, 169.7; Anal. Calcd for $C_7H_{12}N_2O_3$ (172.18): C, 48.83; H, 7.03; N, 16.27. Found: C, 48.88; H, 7.20; N, 16.19.

Isopropyl(Z)-3-ureidobut-2-enoate (**2c**). Following the general procedure, the product **2c** was obtained in 90% yield as white solid with m.p. = 157–160 °C after recrystallization process. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ 1.26 (d, J = 6.3 Hz, 6H), 2.37 (s, 3H), 4.82 (s, 1H), 4.94 (brs, 2H), 5.00 (septet, J = 6.3 Hz, 1H), 10.73 (s, 1H); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 21.5, 21.9, 66.9, 94.3, 154.2, 156.4, 169.3; Anal Calcd for $C_8H_{14}N_2O_3$ (186.21): C, 51.60; H, 7.58; N, 15.04. Found: C, 51.68; H, 7.43; N, 15.33.

Isobutyl(Z)-3-ureidobut-2-enoate (**2d**). Following the general procedure, the product **2d** was obtained in 90% yield as white solid with m.p. = 138–143 °C after recrystallization process. ^{1}H-NMR ($CDCl_3$, 500 MHz,): δ 0.94 (d, J = 6.7 Hz, 6H), 1.90-1.98 (m, 1H), 2.37 (s, 3H), 3.85 (d, J = 6.6 Hz, 2H), 4.87 (s, 1H), 5.12 (s, 2H), 10.67 (s, 1H); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 19.1, 21.6, 27.8, 69.8, 93.8, 154.4, 156.7, 169.8. Anal. Calcd for $C_9H_{16}N_2O_3$ (200.24): C, 53.99; H, 8.05; N, 13.99. Found: C, 53.80; H, 8.11; N, 13.89.

tert-Butyl(Z)-3-ureidobut-2-enoate (**2e**). Following the general procedure, the product **2e** was obtained in 85% yield

as white solid with m.p. = 179–186 °C after recrystallization process. ^{1}H-NMR ($CDCl_3$, 500 MHz,): δ 1.48 (s, 9H), 2.34 (s, 3H), 4.77 (s, 1H), 4.97 (s, 2H), 10.71 (s, 1H); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 21.5, 28.3, 79.9, 95.5, 154.4, 155.7, 169.6; Anal. Calcd for $C_9H_{16}N_2O_3$ (200.24): C, 53.99; H, 8.05; N, 13.99. Found: C, 53.78; H, 8.09; N, 13.73.

Allyl(Z)-3-ureidobut-2-enoate (**2f**). Following the general procedure, the product **2f** was obtained in 88% yield as white solid with m.p. = 140–142 °C after recrystallization process. ^{1}H-NMR (DMSO, 300 MHz): δ 2.28 (d, J = 0.5 Hz, 3H), 4.57 (dt, J_1 = 5.4 Hz, J_2 = 1.4 Hz, 2H), 4.83 (d, J = 0.7 Hz, 1H), 5.22 (dq, J_1 = 10.4 Hz, J_2 = 1.3 Hz, 1H), 5.29 (dq, J_1 = 17.2 Hz, J_2 = 1.6 Hz, 1H), 5.88-6.01 (m, 1H), 6.83 (brs, 2H), 10.13 (s, 1H); ^{13}C-NMR (DMSO, 75 MHz): δ 22.1, 63.8, 91.8, 117.9, 133.6, 154.6, 157.8, 168.3; Anal. Calcd for $C_8H_{12}N_2O_3$ (184.20): C, 52.17; H, 6.57; N, 15.21. Found: C, 52.07; H, 6.46; N, 15.17.

Benzyl(Z)-3-ureidobut-2-enoate (**2g**). Following the general procedure, the product **2g** was obtained in 88% yield as white solid with m.p. = 170–172 °C after recrystallization process. ^{1}H-NMR (DMSO, 500 MHz): δ 2.27 (s, 3H), 4.85 (s, 1H), 5.12 (s, 2H), 6.84 (brs, 2H), 7.32-7.39 (m, 5H), 10.13 (s, 1H); ^{13}C-NMR (DMSO, 125 MHz): δ 22.1, 64.8, 91.8, 128.2, 128.9, 137.1, 154.5, 157.9, 168.4; Anal. Calcd for $C_{12}H_{14}N_2O_3$ (234.26): C, 61.53; H, 6.02; N, 11.96. Found: C, 61.48; H, 6.09; N, 11.83.

(Z)-1-(4-oxopent-2-en-2-yl)urea (**2h**). Following the general procedure, the product **2h** was obtained in 95% yield as white solid with m.p. = 186–191 °C after recrystallization process. ^{1}H-NMR (DMSO, 500 MHz): δ 2.02 (s, 3H), 2.26 (s, 3H), 5.28 (s, 1H), 6.88 (brs, 2H), 11.51 (s, 1H); ^{13}C-NMR (DMSO, 125 MHz): δ 21.8, 30.27, 102.6, 154.7, 157.1, 197.9; Anal. Calcd for $C_6H_{10}N_2O_2$ (142.16): C, 50.69; H, 7.09; N, 19.71. Found: C, 50.63; H, 7.15; N, 19.66.

(Z)-N,N-diethyl-3-ureidobut-2-enamide (**2i**). Following the general procedure, the product **2i** was obtained in 80% yield as white solid with m.p. = 178–182 °C after recrystallization process. ^{1}H-NMR (DMSO, 300 MHz,): δ 1.05-1.11 (m, 6H), 2.26 (s, 3H), 3.31-3.33 (m, 4H), 5.03 (d, J = 0.8 Hz, 1H), 6.53 (s, 2H), 11.53 (s, 1H); ^{13}C-NMR (DMSO, 75 MHz): δ 13.8, 15.0, 22.4, 42.0, 92.0, 153.4, 155.2, 168.0; Anal. Calcd for $C_9H_{17}N_3O_2$ (199.25): C, 54.25; H, 8.60; N, 21.09. Found: C, 54.18; H, 8.68; N, 21.17.

Benzyl benzoate (**5a**). Following the general procedure, the product **5a** was obtained in 80% yield as a yellow oil after column chromatography. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.43 (s, 2H), 7.40–7.53 (m, 7H), 7.61 (tt, J_1 = 7.3 Hz, J_2 = 1. 3 Hz, 1H), 8.13 (d, J = 1.4 Hz, 1H), 8.16 (d, J = 1.3 Hz, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 66.7, 128.2, 128,3, 128.4, 128.6, 129.7, 130.2, 133.0, 136.1, 166.4.

Benzyl-4-methoxybenzoate (**5c**). Following the general procedure, the product **5c** was obtained in 85% yield as a yellow oil after column chromatography. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.89 (s, 3H), 5.39 (s, 2H), 6.96 (d, J = 9.0 Hz, 2H), 7.38-7.51 (m, 5H), 8.08 (d, J = 9.0 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 55.4, 66.4, 113.6, 122.6, 128.1, 128.2, 128.6, 131.8, 136.3, 163.4, 166.2.

Benzyl-2-bromobenzoate (**5f**). Following the general procedure, the product **5f** was obtained in 78% yield as a yellow oil after column chromatography. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.43 (s, 2H), 7.35-7.54 (m, 7H), 7.68-7.71 (m, 1H), 7.85-7.88(m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 67.4, 121.8, 127.2, 128.4, 128.5, 128.6, 131.5, 132.0, 132.7, 134.4, 135.5, 165.9.

Benzyl-2-naphthoate (**5j**). Following the general procedure, the product **5j** was obtained in 77% yield as a yellow oil after column chromatography. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 5.49 (s, 2H), 7.41-7.66 (m, 7H), 7.92 (d, J = 8.6 Hz, 2H), 7.99 (d, J = 7.9 Hz, 1H), 8.16 (dd, J_1 = 8.6 Hz, J_2 = 1.6 Hz 1H), 8.70 (s, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 66.9, 125.3, 126.7, 127.4, 127.8, 128.2, 128.30, 128.4, 128.6, 129.4, 131.2, 132.5, 135.6, 136.1, 166.6.

Naphthalen-1-ylmethyl benzoate (**5s**). Following the general procedure, the product **5s** was obtained in 90% yield as a yellow oil after column chromatography. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.88 (s, 2H), 7.43-7.76 (m, 7H), 7.91-8.32 (m, 5H); ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 65.1, 123.6, 125.3, 126.0, 126.6, 127.5, 128.4, 128.7, 129.3, 129.7, 130.1, 131.5, 131.8, 133.0, 133.8, 166.5.

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