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Generation of bis-Acyl Ketals from Esters and Benzyl Amines Under Oxidative Conditions

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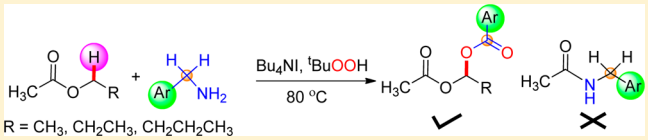
Supporting Information

ABSTRACT: Treatment of benzylamines with esters at an elevated temperature are expected to give amides. However, in the presence of TBAI/TBHP, esters possessing a methylene carbon α-to oxygen with benzylamines provide bis-esters rather than the expected amides. Benzylamines under oxidative conditions generate less nucleophilic carboxylates, which couples at the sp^3 C−H bonds of esters and cyclic ethers to give bis-acyl ketals and α-acyloxy ethers, respectively.



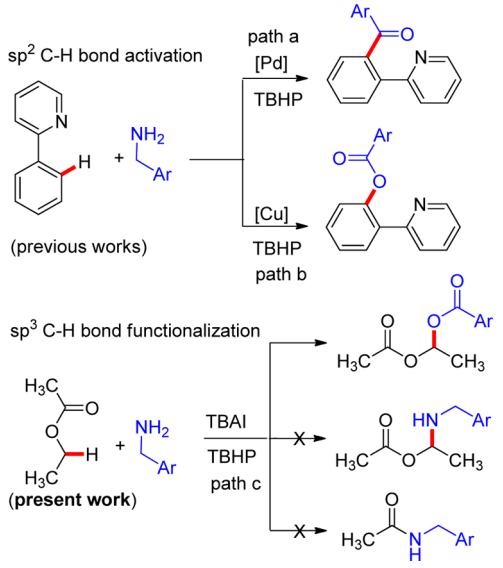
INTRODUCTION

In the modern era of organic chemistry, the atom and step economical synthesis of complex target molecules from simple precursors via direct C(sp^3)−H bond functionalization is of paramount interest to both academia and industrial research.[1] Thus, synthetic chemists continue to strive toward the development of "ideal synthetic procedures" to directly transform C−H bonds into other functional groups, which could eventually be applied to the synthesis of natural products.[2] In this perspective, cross dehydrogenative coupling (CDC) has played a vital role in the construction of a diverse array of C−C and C−heteroatom bonds, by functionalizing C−H bonds of all types.[3] One of the extensively studied approaches in this forum is the CDC strategy involving simple solvents (i.e., alkylbenzenes, cyclic ethers, and cycloalkanes with various coupling partners), most of which have ultimately lead to the synthesis of esters via C(sp^3)−H functionalization.[4]

Barring one example from our group, functionalization of α sp^3 C−H bond in ethyl acetate (ester) has been virtually unexplored.[5] Ethyl acetate is predominantly used as a solvent and diluents because it is inexpensive and less toxic. Due to its reactive nature toward various nucleophiles and its susceptibility to hydrolysis, selective functionalization of esters in general and ethyl acetate in particular is a challenging task. Pertinent to this "solvent chemistry" in CDC reactions, recently our group has developed a protocol for the synthesis of esters via oxidative esterification of α sp^3 C−H bond in ethyl acetate with terminal alkenes and alkynes under metal-free conditions, where alkenes and alkynes served as ArCOO- surrogates.[5] It would be exciting if one can explore the selective α sp^3 C−H functionalization of ethyl acetate as uncharted so far.

Benzylamines are latent sources to aroyl (ArCO−) and aryl carboxy (ArCOO−) groups.[6,7] The Wu group has reported a Pd catalyzed ortho-acylation of 2-phenylpyridine using benzylamines, where it serve as ArCO- surrogates (path a, Scheme 1).[6a] Very recently our group has developed a copper-catalyzed protocol for the *o*-benzoxylation of 2-phenylpyridines using benzylamines as the arylcarboxy (ArCOO−) equivalents (path b, Scheme 1).[7] Recently, alkenes and alkynes are also found to be the surrogates of the ArCOO- group and have been utilized for the bis-esterification of ethyl acetate.[5] Further, when Pd is used as the catalyst, benzylamine act as an aroyl (ArCO−) source, while the use of Cu installs an aryl carboxy (ArCOO−) group into ortho-directing substrates. Of late, metal free combinations, viz., tetrabutylammonium iodide (TBAI)/TBHP, are an efficient substitute to transition metals/oxidant combinations. Thus, the reaction of benzylamine and ethyl acetate under a metal-free oxidative condition is expected to yield an amide or a bis-ester of ethyl acetate.[5,8]

Scheme 1. Selectivity Achieved with Various Catalysts in the Reactions of Benzylamine



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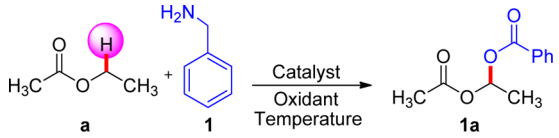
To seek an answer to the above possibilities, an initial reaction was performed by reacting ethyl acetate (2 mL) and benzylamine (1 mmol) in the presence of TBAI (20 mol %) and oxidant TBHP (5−6 M in decane) (6 equiv) at 80 °C (Table 1, entry 1). The outcome of this reaction was not

Table 1. Screening of Reaction Conditions[a]



a 1 1a

entry	catalyst (mol %)	oxidant (equiv)	temp (°C)	yield (%)[b]
1	Bu_4NI (20)	TBHP (dec.) (6)	80	32
2	Bu_4NI (20)	aq TBHP (6)	80	69
3	Bu_4NI (20)	aq TBHP (5)	80	62
4	Bu_4NI (10)	aq TBHP (6)	80	58
5	Bu_4NI (30)	aq TBHP (6)	80	68
6	Bu_4NI (20)	aq TBHP (7)	80	65
7	Bu_4NI (20)	aq TBHP (6)	100	64
8	Bu_4NI (20)	aq H_2O_2 (6)	80	nd
9	Bu_4NI (20)	DTBP (6)	80	nd
10	Bu_4NI (20)	PhCOOCOPh (6)	80	nd
11	Bu_4NI (20)	Oxone (6)	80	nd
12	Bu_4NI (20)	$K_2S_2O_8$ (6)	80	nd
13	Bu_4NI (20)	DDQ (6)	80	nd
14	Bu_4NBr (20)	aq TBHP (6)	80	nd
15	I_2 (20)	aq TBHP (6)	80	nd
16	KI (20)	aq TBHP (6)	80	nd
17	–	aq TBHP (6)	80	nd
18	Bu_4NI (20)	–	80	nd

[a]Reaction condition: ethyl acetate (2 mL), benzylamine (1 mmol), time 8 h. [b]Isolated yield. nd = not detected.

amidation, rather it was further esterification of ethyl acetate obtained (**1a**) in 32% yield (path c, Scheme 1). This observation suggests incorporation of the ArCOO- group into an ester where benzylamine serves as a source to the aryl carboxy (ArCOO−) group. It may be mentioned here that Wang et al. have reported a direct amidation of benzylamine with *N*-substituted formamide via oxidative coupling in the presence of I_2/TBHP, where benzylamine is the aroyl (ArCO−) equivalent.[6b] It has been observed earlier that the same precursor may operate either as an aryl carboxy (ArCOO−) or an aroyl (ArCO−) equivalent, depending upon the nature of the metal catalyst used. For example, benzylamine and alkylbenzene are both surrogates to ArCOO- and ArCO- groups.[6,7,9] Thus, generation of ArCOO- from $ArCH_2NH_2$ and its subsequent incorporation into an ester under a metal-free condition (TBAI) shows identical reactivity to that of the Cu catalyst.[7] Therefore, the present protocol for the formation of a double ester via the α sp^3 C−H bond functionalization of ethyl acetate without affecting the existing ester functionality is unexplored.

RESULTS AND DISCUSSION

Encouraged by this unique esterification of ester, further optimization reactions were performed by varying reaction parameters to attain the best yield of the product. Gratifyingly, when the above reaction was performed using an aqueous TBHP (70% in water) (6 equiv) in lieu of a decane solution of the TBHP (5−6 M) product yield improved up to 69% (Table 1, entry 2). Keeping all other parameters constant but decreasing the quantity of TBHP from 6 to 5 equiv. or the Bu_4NI quantity from 20 to 10 mol %, a reduction in the product yields (62% and 58%, respectively) (Table 1, entries 3−4) were found. No further improvement in the yield was observed by either increasing the catalyst Bu_4NI (30 mol %), oxidant TBHP (7 equiv), or reaction temperature (100 °C) (Table 1, entries 5−7). Other oxidants such as aq H_2O_2, di-*tert* butyl peroxide (DTBP), benzoylperoxide, oxone, $K_2S_2O_8$, and DDQ were completely unproductive (Table 1, entries 8−13). Surprisingly, no desired product could be obtained when other halogen species such as Bu_4NBr, I_2, and KI (Table 1, entries 14−16) were used instead of Bu_4NI. Control experiments performed in the absence of either oxidant (TBHP) or catalyst (Bu_4NI) failed to achieve the desired transformation (Table 1, entries 17−18). The byproducts formed in these reactions (entries 8, 10−12, and 14−17) are benzaldehyde and benzoic acid only. However, using oxidants such as DTBP (Table 1, entry 9), DDQ (Table 1, entry 13) and in the absence of any oxidant (Table 1, entry 18), benzylamine remained intact. Benzaldehyde is generated in situ from benzylamine under oxidative condition via the intermediacy of phenylmethanimine and benzoic acid by the oxidation of performed benzaldehyde. Therefore, the use of benzylamine (1 mmol), ethyl acetate (2 mL), Bu_4NI (20 mol %), and aqueous TBHP (70% in water) (6 equiv) at a temperature of 80 °C gave the best conversion after 8 h (entry 2).

The above optimized condition was then implemented for the oxidative esterification of ethyl acetate (**a**) using various substituted benzylamines. The electron neutral −H (**1**) and electron-donating substituents, *viz.*, *p*-Me (**2**), *p*-OMe (**3**), 2,4-di-OMe (**4**), as well as electron-withdrawing substituents, *viz.*, *p*-F (**5**), *p*-Cl (**6**), *p*-Br (**7**), *o*-Cl (**8**), *o*-Br (**9**), *m*-Cl (**10**), and *m*-CF_3 (**11**) present in the phenyl ring of benzylamines were all found to serve as ArCOO- surrogates providing the desired double esters (i.e., unsymmetrical *gem*-diacylates (**1a**−**11a**) in good to moderate yields as shown in Scheme 2). It was observed that substituted benzylamines possessing electron-withdrawing groups provided the corresponding products in lower yields than those bearing electron-donating groups. These results imply that the electronic effect of substituents on the phenyl ring of benzylamines played a role in controlling the product yields. This trend in reactivity is similar to our recent *o*-benzoxylation of 2-phenylpyridine using benzylamines as ArCOO- sources.[7]

The synthetic utility of this double esterification strategy was further examined with another ester, *n*-propyl acetate (**b**), having a methylene carbon α- to oxygen. When various benzylamines (**1**), (**3**), and (**6**) were reacted with *n*-propyl acetate (**b**) under identical reaction conditions, the desired double esters (**1b**), (**3b**), and (**6b**) were obtained in similar yields to that using ethyl acetate (**a**) (Scheme 2). Yet another analogous ester *n*-butyl acetate (**c**) upon treatment with a set of benzylamines (**1**), (**3**), and (**6**) produced their respective desired double esters (**1c**), (**3c**), and (**6c**) in modest yields (Scheme 2). Here again, the trends in the reactivity of substituted benzylamines were found to be identical to those observed for ethyl acetate (**a**). The use of allylamine in lieu of benzylamine was not successful. Neither amidation nor ester formation was observed when allyl amine was subjected under the present reaction conditions with ethyl acetate as the allyl amine remain intact. Interestingly, when α-methyl benzylamine (**12**) was treated with ethyl acetate (**a**) under the present

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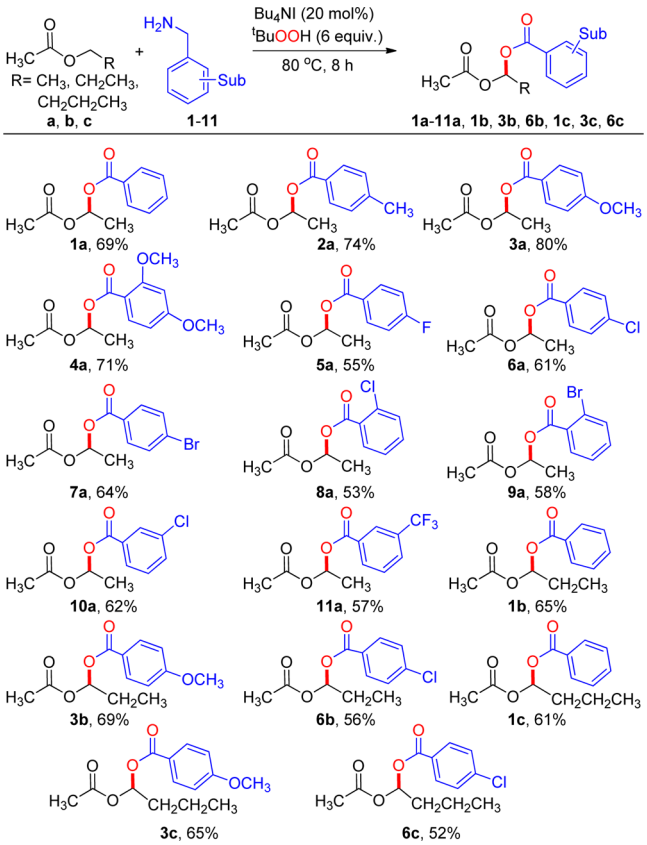
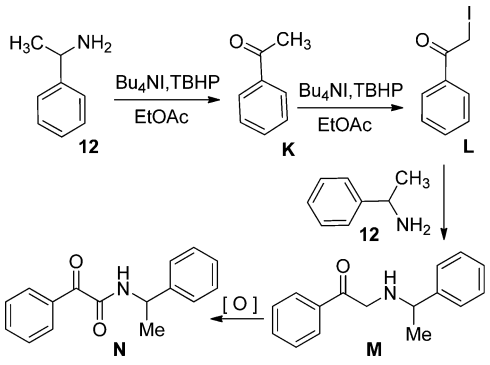
Scheme 2. Substrate Scope for Esterification of Esters[a,b]



[a]Reaction conditions: benzylamine (1 mmol), ester (2 mL), TBAI (0.2 mmol), and TBHP (6 mmol) at 80 °C. [b]Isolated yields.

reaction condition, no amidation was observed. The reaction gave a complex mixture from which two major products, viz., acetophenone (**K**) (15%) and 2-oxo-2-phenyl-*N*-(1-phenylethyl)acetamide (**N**) (40%), could be isolated (Scheme 3). Under the reaction conditions, α-methyl benzylamine (**12**)

Scheme 3. Fate of α-Methyl Benzylamine



is converted to acetophenone (**K**). Further reaction of acetophenone with the in situ generated iodine gave α-iodoacetophenone (**L**). Reaction of α-iodoacetophenone (**L**) with α-methyl benzylamine (**12**) provided intermediate product (**M**), which is rapidly oxidized to 2-oxo-2-phenyl-*N*-(1-phenylethyl)acetamide (**N**) as shown in Scheme 3.

The successful oxidative esterifications of sp^3 C−H bonds α- to an oxygen atom in esters with benzylamines led us to scrutinize the feasibility of this protocol with cyclic ether (i.e., 1,4-dioxane (**d**) having sp^3 C−H bonds α- to an oxygen atom). To demonstrate the practical utility of the above-mentioned concept, benzylamine (**1**) was treated with 1,4-dioxane (**d**) under the above optimized conditions. To our delight, the product was found to be α-acyloxyether (**1d**) obtained in good yield (74%). For the synthesis of α-acyloxyethers, in addition to the traditional methods such as (i) addition of carboxylic acids to alkenyl ethers,[10] (ii) α-halo substitution of ethers with carboxylic acids,[11] (iii) esterification of hemiacetals with acids or its derivatives,[12] and (iv) complex routes comprising of a two-step synthesis,[13] several elegant CDC protocols have been developed lately.[14] Recently, our group has also developed two CDC protocols, one involving a Cu-mediated solvent−solvent coupling between alkylbenzenes and cyclic ethers,[9a] and the other a metal free oxidative esterification of α sp^3 C−H bonds in cyclic ethers with terminal alkenes and alkynes.[5] Proceeding further toward the substrate exploration, 1,4-dioxane (**d**) was reacted with a set of benzylamines having electron-donating substituents such as *p*-Me (**2**), *p*-OMe (**3**), 2,4-di-OMe (**4**), and electron-withdrawing substituents such as *p*-F (**5**), *p*-Cl (**6**), *p*-Br (**7**), *o*-Cl (**8**), *o*-Br (**9**), and *m*-CF_3 (**11**), all of which provided the desired α-acyloxyethers (**2d**−**9d** and **11d**) in good-to-moderate yields (Scheme 4).

This approach was subsequently applied to other cyclic ethers possessing a single oxygen [i.e., tetrahydropyran (**e**) and tetrahydrofuran (**f**)]. Unlike in 1,4-dioxane (**d**), the oxidative esterification of tetrahydropyran (**e**) and tetrahydrofuran (**f**) with benzylamines (**1**), (**2**), and (**6**) were not so effective in terms of yields, and they afforded α-acyloxy ethers (**1e**), (**2e**), (**6e**), (**1f**), (**2f**), and (**6f**) in lower yields as shown in Scheme 3. Due to the presence of eight equivalent sp^3 C−H's in 1,4-dioxane (**d**), it gave better yields of product compared to four such sp^3 C−H's containing substrates, tetrahydropyran (**e**) and tetrahydrofuran (**f**), which may be possibly due to the statistical reason. The oxidative esterification of 1,3-dioxolane with benzylamines (**1**), (**3**), and (**6**) provided single regioisomer (**1g**), (**3g**), and (**6g**), respectively, in good yields when the reaction was performed at 120 °C (Scheme 4). Here the esterification is taking place at the less acidic sp^3 C−H bond rather than at the more acidic sp^3 C−H, which is possibly due to the instability of the radical formed at the bridged head methylene carbon.

To elucidate a plausible mechanism for this coupling reaction, several control experiments were carried out. Analysis of the reaction mixture between 1,4-dioxane (**d**) and benzylamine (**1**), along with the formation of the desired product, revealed the presence of benzaldehyde and benzoic acid in the medium, suggesting their intermediacy (Scheme 5). Formation of benzaldehyde from benzylamine is expected to go via the hydrolysis of the in situ generated imine, which, in turn, is obtained by the oxidation of benzylamine.[6b] The benzaldehyde so generated gets converted to benzoic acid under oxidative conditions, which could be the possible source of the ArCOO-group in these reactions.[4a] Product (**1a**) was obtained in 90% yield when benzoic acid was reacted with ethyl acetate (**a**) under the present reaction conditions, implying the coupling partners are carboxylic acid and ethyl acetate.[14a] The presence of a radical scavenger 2,2,6,6-tetramethylpyridine *N*-oxide (TEMPO) considerably quenches the coupling reaction between benzylamine (**1**) and ethyl acetate (**a**) giving <4% yield of the expected product, indicating the radical nature of

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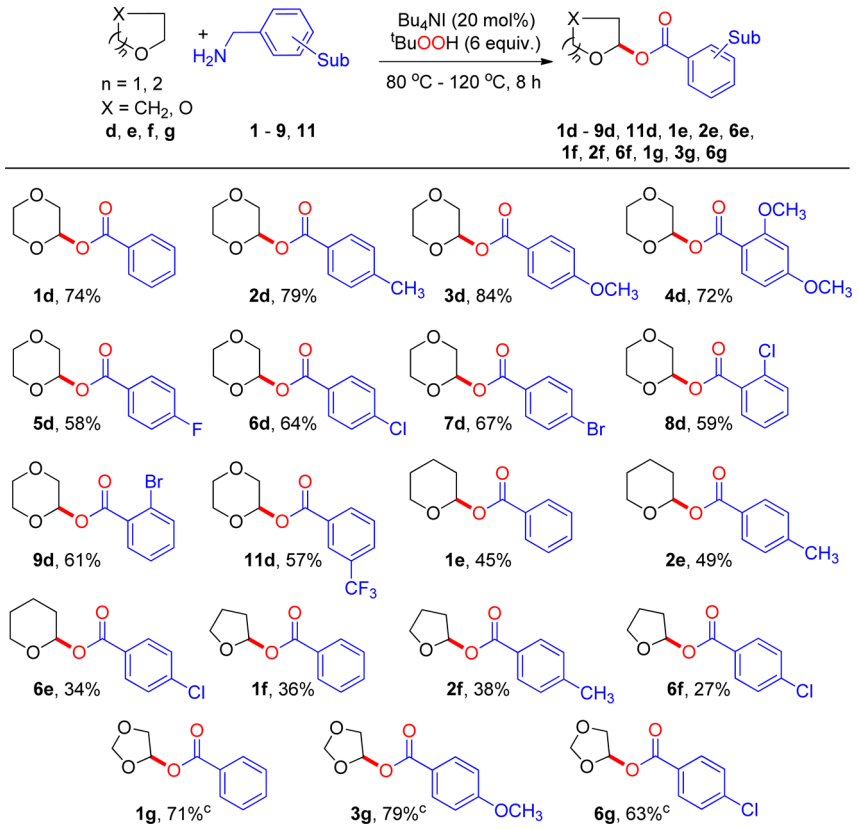
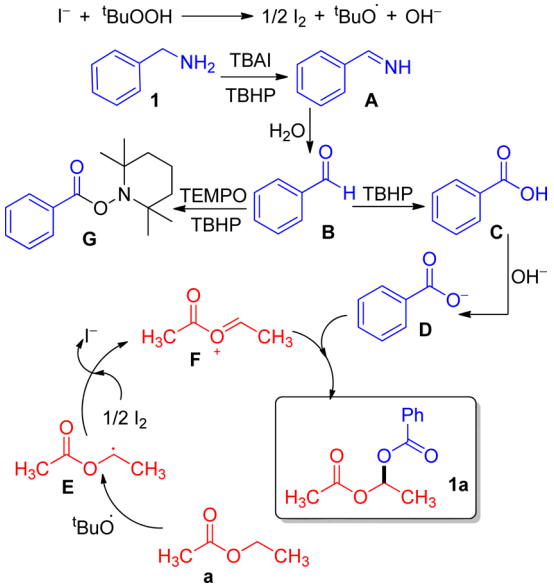
Scheme 4. Substrate Scope for α-Acyloxyether[a,b]



[a]Reaction conditions: benzylamine (1 mmol), cyclic ethers (1 mL), TBAI (0.2 mmol), TBHP (6 mmol) at 80 °C. [b]Isolated yields. [c]Reaction performed at 120 °C.

Scheme 5. Proposed Mechanism for Oxidative Esterification



the mechanism. The trapped TEMPO-ester (**G**) has been isolated and characterized (see the Supporting Information).

Taking cues from the control experiments that were carried out and from the literature reports,[7,14a] a possible mechanism as shown in Scheme 5 has been proposed. Initially, benzylamine (**1**) in the presence of TBAI/TBHP is converted to benzoic acid (**C**) via the intermediacy of phenylmethanimine (**A**) and benzaldehyde (**B**) (Scheme 5). Benzamide from possible oxidation of the aminal formed between aldehyde (**B**) and amine was not isolated from the reaction mixture. Furthermore, subjection of the benzamide to the reaction conditions with ethyl acetate gave rise to no coupling, ruling out the intervention of a benzamide intermediate. Though benzaldehyde is generated in the reaction mixture, formation of benzylschiff base adduct under these conditions was not detected. If at all formed, it can possibly be hydrolyzed rapidly back to corresponding aldehyde and amine. Subsequently, less nucleophilic benzoate (**D**) is generated by the deprotonation of benzoic acid (**C**). On the other hand, radical abstraction of α sp^3 C−H bond in ethyl acetate gives the radical intermediate (**E**), which then undergoes a further single electron transformation (SET) with iodine to give an oxonium species (**F**) (Scheme 5). Finally, nucleophilic attack of benzoate ion (**D**) on the α carbon of oxonium species (**F**) provided the double ester (**1a**) (Scheme 5). A similar mechanism can be proposed involving 1,4-dioxane instead of ester.

CONCLUSION

In conclusion, treatment of benzylamines with esters possessing α- sp^3 C−H bond in the presence of TBAI/TBHP provided bis-acyl ketals rather than amides. Symmetrical cyclic ethers afforded a monoester; however, unsymmetrical cyclic ether provided a single regioisomeric ester via sp^3 C−H bond functionalization. Benzylamine under oxidative condition provided aryl carboxylic ion which is one of the coupling partners in this solvent chemistry. A plausible reaction

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mechanism involving radical pathways has been suggested for this CDC coupling.

EXPERIMENTAL SECTION

General Information. All the reagents were commercial grade and used without purification. Organic extracts were dried over anhydrous sodium sulfate. Solvents were removed in a rotary evaporator under reduced pressure. Silica gel (60−120 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 F_{254} (0.25 mm). NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard for ^1H NMR (400 and 600 MHz) and $CDCl_3$ solvent as the internal standard for ^{13}C NMR (100 and 150 MHz). ^{19}F NMR spectra were recorded in $CDCl_3$ with CF_3COOH as the internal standard (564.7 MHz). HRMS spectra were recorded using the ESI mode (Q-TOF MS Analyzer). IR spectra were recorded in KBr or neat.

*General Procedure for the Synthesis of 1-Acetoxyethyl Benzoate (**1a**).* A mixture of Bu_4NI (73.8 mg, 20 mol %), benzylamine (**1**) (107 mg, 1 mmol), and ethyl acetate (**a**) (2 mL) were taken in an oven-dried round-bottom flask fitted with a refluxed condenser. To this mixture, an aqueous solution of TBHP (70% in H_2O) (857 μL, 6 equiv) was added, and the reaction mixture was heated at 80 °C for 8 h. The reaction mixture was cooled to room temperature and admixed with ethyl acetate (20 mL). The ethyl acetate layer was washed successively with a 5% solution of sodium bicarbonate (2 × 5 mL) and a 5% solution of sodium thiosulfate (2 × 5 mL). The ethyl acetate layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was purified over a column of silica gel and eluted with 97:3 hexane:ethyl acetate to afford 1-acetoxyethyl benzoate (**1a**) (143.5 mg, 69% yield).

*General Procedure for the Synthesis of 1,4-Dioxan-2-yl Benzoate (**1d**).* A mixture of Bu_4NI (73.8 mg, 20 mol %), benzylamine (**1**) (107 mg, 1 mmol), and 1,4-dioxane (**d**) (1 mL) were taken in an oven-dried round-bottom flask fitted with a refluxed condenser. To this mixture, an aqueous solution of TBHP (70% in H_2O) (857 μL, 6 equiv) was added and the reaction mixture was heated at 80 °C for 8 h. The reaction mixture was cooled to room temperature and admixed with ethyl acetate (20 mL). The ethyl acetate layer was washed successively with a 5% solution of sodium bicarbonate (2 × 5 mL) and a 5% solution of sodium thiosulfate (2 × 5 mL). The ethyl acetate layer was dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure. The crude product was purified over a column of silica gel and eluted with (96:4, hexane/ethyl acetate) to afford 1,4-dioxan-2-yl benzoate (**1d**) (154 mg, 74% yield).

*1-Acetoxyethyl Benzoate (**1a**).* ^1H NMR (400 MHz, $CDCl_3$): δ 1.61 (d, 3H, *J* = 5.2 Hz), 2.09 (s, 3H), 7.12 (q, 1H, *J* = 5.2 Hz), 7.44 (t, 2H, *J* = 7.6 Hz), 7.58 (t, 1H, *J* = 7.6 Hz), 8.05 (d, 2H, *J* = 6.8 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 19.9, 21.1, 89.2, 128.6, 129.5, 130.1, 133.6, 164.8, 169.2; IR (KBr): 2929, 2851, 1768, 1731, 1602, 1446, 1375, 1278, 1228, 1064, 1011, 945, 713 cm^{-1}. HRMS (ESI): calcd for $C_{11}H_{12}O_4$ $(M + Na)^+$, 231.0634; found, 231.0640.

*1-Acetoxyethyl 4-Methylbenzoate (**2a**).* ^1H NMR (400 MHz, $CDCl_3$): δ 1.60 (d, 3H, *J* = 5.6 Hz), 2.09 (s, 3H), 2.41 (s, 3H), 7.10 (q, 1H, *J* = 5.6 Hz), 7.25 (d, 2H, *J* = 3.6 Hz), 7.93 (d, 2H, *J* = 8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.8, 21.1, 21.9, 89.1, 129.3, 130.1, 130.1, 144.4, 164.7, 169.1. IR (KBr): 2926, 2856, 1758, 1729, 1613, 1446, 1371, 1276, 1228, 1183, 1065, 1012, 945, 752, 699 cm^{-1}. HRMS (ESI): calcd for $C_{12}H_{14}O_4$ $(M + Na)^+$, 245.0790; found, 245.0783.

*1-Acetoxyethyl 4-Methoxybenzoate (**3a**).* ^1H NMR (400 MHz, $CDCl_3$): δ 1.57 (d, 3H, *J* = 5.2 Hz), 2.06 (s, 3H), 3.83 (s, 3H), 6.89 (d, 2H, *J* = 8.8 Hz), 7.07 (q, 1H, *J* = 5.2 Hz), 7.97 (d, 2H, *J* = 8.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.9, 21.1, 55.7, 89.1, 113.9, 121.9, 132.2, 164.0, 164.5, 169.2. IR (KBr): 2931, 2845, 1759, 1725, 1607, 1512, 1460, 1421, 1375, 1260, 1169, 945, 848, 769 cm^{-1}. HRMS (ESI): calcd for $C_{12}H_{14}O_5$ $(M + Na)^+$, 261.0739; found, 261.0731.

*1-Acetoxyethyl 2,4-Dimethoxybenzoate (**4a**).* ^1H NMR (400 MHz, $CDCl_3$): δ 1.58 (d, 3H, *J* = 5.6 Hz), 2.08 (s, 3H), 3.85 (s, 3H), 3.89 (s, 3H), 6.48−6.50 (m, 2H), 7.06 (q, 1H, *J* = 5.6 Hz), 7.88 (d, 1H, *J* = 8.0 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 19.9, 21.1, 55.7, 56.2, 88.9, 99.1, 104.9, 111.2, 134.3, 162.4, 163.2, 165.0, 169.2. IR (KBr): 2943, 2843, 1744, 1723, 1609, 1577, 1506, 1421, 1253, 1031, 945, 836, 770 cm^{-1}. HRMS (ESI): calcd for $C_{13}H_{16}O_6$ $(M + Na)^+$, 291.0845; found, 291.0840.

*1-Acetoxyethyl 4-Fluorobenzoate (**5a**).* ^1H NMR (400 MHz, $CDCl_3$): δ 1.61 (d, 3H, *J* = 5.6 Hz), 2.10 (s, 3H), 7.08−7.16 (m, 3H), 8.05−8.09 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 19.9, 21.1, 89.3, 115.8 (d, *J* = 22.1 Hz), 125.8, 132.6, 132.7 (d, *J* = 9.0 Hz), 163.8, 166.3 (d, *J* = 252 Hz), 169.1. ^{19}F NMR (564.7 MHz, $CDCl_3$) δ −105.5. IR (KBr): 2994, 2941, 1759, 1732, 1605, 1508, 1414, 1376, 1279, 1231, 1064, 1011, 946, 854, 767 cm^{-1}. HRMS (ESI): calcd for $C_{11}H_{11}FO_4$ $(M + Na)^+$, 249.0539; found, 249.0546.

*1-Acetoxyethyl 4-Chlorobenzoate (**6a**).* ^1H NMR (400 MHz, $CDCl_3$): δ 1.60 (d, 3H, *J* = 5.6 Hz), 2.09 (s, 3H), 7.09 (q, 1H, *J* = 5.6 Hz), 7.41 (d, 2H, *J* = 8.8 Hz), 7.97 (d, 2H, *J* = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.8, 21.0, 89.2, 127.9, 128.9, 131.4, 140.1, 163.8, 169.1. IR (KBr): 2924, 2854, 1759, 1732, 1595, 1488, 1376, 1275, 1227, 1067, 1012, 945, 759 cm^{-1}. HRMS (ESI): calcd for $C_{11}H_{11}ClO_4$ $(M + Na)^+$, 265.0244; found, 265.0250.

*1-Acetoxyethyl 4-Bromobenzoate (**7a**).* ^1H NMR (600 MHz, $CDCl_3$): δ 1.60 (d, 3H, *J* = 4.8 Hz), 2.09 (s, 3H), 7.09 (q, 1H, *J* = 5.4 Hz), 7.58 (d, 2H, *J* = 7.8 Hz), 7.89 (d, 2H, *J* = 8.4 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 19.8, 21.0, 89.3, 128.4, 128.8, 131.5, 132.0, 164.0, 169.0. IR (KBr): 2996, 2935, 1759, 1732, 1590, 1484, 1397, 1374, 1275, 1226, 1068, 1009, 945, 847, 756 cm^{-1}. HRMS (ESI): calcd for $C_{11}H_{11}BrO_4$ $(M + Na)^+$, 308.9739; found, 308.9748.

*1-Acetoxyethyl 2-Chlorobenzoate (**8a**).* ^1H NMR (600 MHz, $CDCl_3$): δ 1.61 (d, 3H, *J* = 6.0 Hz), 2.10 (s, 3H), 7.09 (q, 1H, *J* = 5.4 Hz), 7.31 (t, 1H, *J* = 7.2 Hz), 7.41−7.46 (m, 2H), 7.83 (d, 1H, *J* = 7.8 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 19.7, 21.0, 89.6, 126.8, 129.3, 131.4, 131.8, 133.2, 134.3, 163.7, 169.1; IR (KBr): 2927, 1760, 1635, 1599, 1438, 1374, 1294, 1253, 1224, 1077, 1041, 1010, 945, 867, 749 cm^{-1}. HRMS (ESI): calcd for $C_{11}H_{11}ClO_4$ $(M+Na)^+$, 265.0244; found, 265.0240.

*1-Acetoxyethyl 2-Bromobenzoate (**9a**).* ^1H NMR (400 MHz, $CDCl_3$): δ 1.63 (d, 3H, *J* = 5.2 Hz), 2.12 (s, 3H), 7.09 (q, 1H, *J* = 5.2 Hz), 7.33−7.39 (m, 2H), 7.67 (d, 1H, *J* = 7.2 Hz), 7.81 (d, 1H, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.7, 21.0, 89.7, 122.2, 127.4, 131.4, 131.8, 133.2, 134.7, 164.1, 169.1. IR (KBr): 2922, 1760, 1638, 1433, 1374, 1293, 1223, 1073, 1010, 945, 746, 699 cm^{-1}. HRMS (ESI): calcd for $C_{11}H_{11}BrO_4$ $(M + Na)^+$, 308.9739; found, 308.9743.

*1-Acetoxyethyl 3-Chlorobenzoate (**10a**).* ^1H NMR (400 MHz, $CDCl_3$): δ 1.59 (d, 3H, *J* = 5.6 Hz), 2.08 (s, 3H), 7.07 (q, 1H, *J* = 5.6 Hz), 7.35−7.40 (m, 1H), 7.51−7.55 (m, 1H), 7.91 (d, 1H, *J* = 8.0 Hz), 8.05 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.8, 21.0, 89.4, 128.2, 130.1, 130.2, 131.3, 133.7, 134.8, 163.6, 169.1. IR (KBr): 2923, 2081, 1760, 1735, 1635, 1426, 1374, 1290, 1259, 1223, 1068, 1010, 947, 746 cm^{-1}. HRMS (ESI): calcd for $C_{11}H_{11}ClO_4$ $(M + Na)^+$, 265.0244; found, 265.0238.

*1-Acetoxyethyl 3-(Trifluoromethyl)benzoate (**11a**).* ^1H NMR (400 MHz, $CDCl_3$): δ 1.64 (d, 3H, *J* = 5.2 Hz), 2.12 (s, 3H), 7.14 (q, 1H, *J* = 5.2 Hz), 7.61 (t, 1H, *J* = 7.6 Hz), 7.84 (d, 1H, *J* = 7.6 Hz), 8.24 (d, 1H, *J* = 7.6 Hz), 8.30 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 19.8, 21.1, 89.6, 122.9, 124.7, 127.0 (t, *J* = 5.3 Hz), 129.4, 130.2 (t, *J* = 5.3 Hz), 130.5, 131.4 (q, *J* = 33.0 Hz), 133.3, 163.5, 169.1. ^{19}F NMR (564.7 MHz, $CDCl_3$): δ −63.6; IR (KBr): 2926, 1762, 1620, 1445, 1375, 1335, 1260, 1223, 1171, 1130, 1071, 1011, 946, 756, 695 cm^{-1}. HRMS (ESI): calcd for $C_{12}H_{11}F_3O_4$ $(M + Na)^+$, 299.0507; found, 299.0512.

*1-Acetoxypropyl Benzoate (**1b**).* ^1H NMR (400 MHz, $CDCl_3$): δ 1.04 (t, 3H, *J* = 7.6 Hz), 1.91−1.98 (m, 2H), 2.10 (s, 3H), 7.01 (t, 1H, *J* = 8.4 Hz), 7.43−7.48 (m, 2H), 7.56−7.60 (m, 1H); 8.05 (d, 2H, *J* = 8.8 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 7.9, 21.1, 26.8, 91.9, 128.7, 129.6, 130.1, 133.6, 164.9, 169.3. IR (KBr): 2978, 2939, 1760, 1732, 1602, 1452, 1373, 1276, 1222, 1117, 1018, 961, 711 cm^{-1}. HRMS (ESI): calcd for $C_{12}H_{14}O_4$ $(M + Na)^+$, 245.0790; found, 245.0783.

*1-Acetoxypropyl 4-Methoxybenzoate (**3b**).* ^1H NMR (600 MHz, $CDCl_3$): δ 1.03 (t, 3H, *J* = 7.2 Hz), 1.91−1.93 (m, 2H), 2.09 (s, 3H), 3.86 (s, 3H), 6.92 (d, 2H, *J* = 9.0 Hz), 6.98 (t, 1H, *J* = 5.4 Hz), 8.00 (d, 2H, *J* = 8.4 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 7.9, 21.1, 26.9, 55.7,

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91.7, 113.9, 121.9, 132.2, 164.0, 164.6, 169.3. IR (KBr): 2976, 2939, 2843, 1759, 1726, 1607, 1512, 1422, 1318, 1224, 1168, 1021, 961, 848, 769 cm^{-1}. HRMS (ESI): calcd for $C_{13}H_{16}O_5$ $(M + Na)^+$, 275.0896; found, 275.0902.

*1-Acetoxypropyl 4-Chlorobenzoate (**6b**).* ^1H NMR (600 MHz, $CDCl_3$): δ 1.03 (t, 3H, J = 7.2 Hz), 1.92−1.94 (m, 2H), 2.10 (s, 3H), 6.98 (t, 1H, J = 4.8 Hz), 7.42 (d, 2H, J = 6.6 Hz), 7.98 (d, 2H, J = 6.6 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 7.9, 21.0, 26.8, 92.0, 128.1, 129.0, 131.5, 140.2, 164.0, 169.3. IR (KBr): 2978, 2939, 1760, 1733, 1595, 1489, 1372, 1274, 1221, 1092, 1013, 850, 758 cm^{-1}. HRMS (ESI): calcd for $C_{12}H_{13}ClO_4$ $(M + Na)^+$, 279.0400; found, 279.0409.

*1-Acetoxybutyl Benzoate (**1c**).* ^1H NMR (600 MHz, $CDCl_3$): δ 0.97 (t, 3H, J = 7.2 Hz), 1.46−1.51 (m, 2H), 1.86−1.90 (m, 2H), 2.07 (s, 3H), 7.04 (t, 1H, J = 5.4 Hz), 7.41−7.45 (m, 2H), 7.56 (t, 1H, J = 7.2 Hz), 8.03 (d, 2H, J = 7.8 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.0, 17.1, 21.1, 35.6, 91.1, 128.7, 129.6, 130.1, 133.6, 164.9, 169.3. IR (KBr): 2963, 2933, 2876, 1761, 1732, 1602, 1453, 1374, 1272, 1219, 1117, 1015, 802, 712 cm^{-1}. HRMS (ESI): calcd for $C_{13}H_{16}O_4$ $(M + Na)^+$, 259.0947; found, 259.0941.

*1-Acetoxybutyl 4-Methoxybenzoate (**3c**).* ^1H NMR (600 MHz, $CDCl_3$): δ 0.99 (t, 3H, J = 7.2 Hz), 1.47−1.51 (m, 2H), 1.87−1.89 (m, 2H), 2.09 (s, 3H), 3.86 (s, 3H), 6.91−6.94 (m, 2H), 7.04 (t, 1H, J = 5.4 Hz), 8.00 (d, 2H, J = 7.2 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 14.0, 17.1, 21.1, 35.6, 55.7, 90.9, 113.9, 122.0, 132.2, 164.0, 164.6, 169.3. IR (KBr): 2962, 2934, 2875, 1759, 1725, 1607, 1512, 1464, 1373, 1260, 1168, 1028, 847, 769 cm^{-1}. HRMS (ESI): calcd for $C_{14}H_{18}O_5$ $(M + Na)^+$, 289.1052; found, 289.1045.

*1-Acetoxybutyl 4-Chlorobenzoate (**6c**).* ^1H NMR (600 MHz, $CDCl_3$): δ 0.99 (t, 3H, J = 7.2 Hz), 1.46−1.51 (m, 2H), 1.88−1.89 (m, 2H), 2.09 (s, 3H), 7.03 (t, 1H, J = 5.4 Hz), 7.41−7.44 (m, 2H), 7.96 (d, 2H, J = 7.2 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 13.9, 17.1, 21.0, 35.5, 91.2, 128.1, 129.0, 131.5, 140.2, 164.0, 169.2. IR (KBr): 2963, 2933, 2876, 1760, 1732, 1595, 1488, 1372, 1219, 1173, 1013, 849, 685 cm^{-1}. HRMS (ESI): calcd for $C_{13}H_{15}ClO_4$ $(M + Na)^+$, 293.0557; found, 293.0549.

*1,4-Dioxan-2-yl Benzoate (**1d**).*[14e] ^1H NMR (400 MHz, $CDCl_3$): δ 3.64−3.68 (m, 1H), 3.80−3.82 (m, 2H), 3.83−3.88 (m, 2H), 4.18−4.24 (m, 1H), 6.08 (s, 1H), 7.44 (t, 2H, J = 7.6 Hz), 7.57 (t, 1H, J = 7.2 Hz), 8.11 (d, 2H, J = 7.2 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 61.8, 66.1, 67.8, 89.8, 128.5, 129.8, 129.9, 133.4, 165.2. IR (KBr): 2971, 2925, 2856, 1726, 1602, 1452, 1258, 1155, 1065, 1018, 912, 880, 713 cm^{-1}.

*1,4-Dioxan-2-yl 4-Methylbenzoate (**2d**).*[14f] ^1H NMR (600 MHz, $CDCl_3$): δ 2.42 (s, 3H), 3.66−3.69 (m, 1H), 3.82−3.83 (m, 2H), 3.88−3.89 (m, 2H), 4.20−4.24 (m, 1H), 6.08 (s, 1H), 7.26 (d, 2H, J = 10.2 Hz), 8.02 (d, 2H, J = 8.4 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 21.7, 61.8, 66.1, 67.9, 89.7, 127.0 129.2, 130.0, 144.2, 165.2. IR (KBr): 2974, 2926, 2857, 1726, 1612, 1453, 1355, 1156, 1016, 912, 882, 755, 691, 577 cm^{-1}.

*1,4-Dioxan-2-yl 4-Methoxybenzoate (**3d**).*[14f] ^1H NMR (400 MHz, $CDCl_3$): δ 3.63−3.66 (m, 1H), 3.78−3.80 (m, 2H), 3.84−3.89 (m, 5H), 4.15−4.21 (m, 1H), 6.04 (s, 1H), 6.91 (d, 2H, J = 7.6 Hz), 8.05 (d, 2H, J = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 62.0, 66.3, 68.1, 89.7, 113.9, 122.2, 132.2, 164.0, 165.1. IR (KBr): 2971, 2929, 2855, 1723, 1607, 1511, 1458, 1421, 1257, 1168, 1087, 1021, 912, 881, 852, 771 cm^{-1}.

*1,4-Dioxan-2-yl 2,4-Dimethoxybenzoate (**4d**).*[14e] ^1H NMR (400 MHz, $CDCl_3$): δ 3.62−3.65 (m, 2H), 3.76−3.78 (m, 2H), 3.82 (s, 3H), 3.86 (s, 3H), 4.16−4.22 (m, 2H), 6.02 (s, 1H), 6.45−6.48 (m, 2H), 7.93 (d, 1H, J = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.7, 56.1, 62.0, 66.3, 68.1, 89.4, 99.1, 104.8, 111.7, 134.3, 162.1, 164.0, 164.9. IR (KBr): 2971, 2937, 2853, 1725, 1609, 1576, 1505, 1459, 1213, 1163, 1019, 911, 882, 770 cm^{-1}.

*1,4-Dioxan-2-yl 4-Fluorobenzoate (**5d**).*[14a] ^1H NMR (600 MHz, $CDCl_3$): δ 3.67−3.69 (m, 1H), 3.82−3.83 (m, 2H), 3.88−3.89 (m, 2H), 4.19−4.23 (m, 1H), 6.09 (s, 1H), 7.12−7.15 (m, 2H), 8.13−8.15 (m, 2H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 61.8, 66.1, 67.8, 90.0, 115.7 (d, J = 21.8 Hz), 126.1, 132.5 (d, J = 9.3 Hz), 164.7 (d, J = 144 Hz), 166.9. ^{19}F NMR (564.7 MHz, $CDCl_3$): δ −105.5. IR (KBr): 2977, 2951, 2870, 1725, 1606, 1509, 1453, 1362, 1284, 1148, 1092, 1067, 912, 884 cm^{-1}.

*1,4-Dioxan-2-yl 4-Chlorobenzoate (**6d**).*[14a] ^1H NMR (400 MHz, $CDCl_3$): δ 3.67−3.71 (m, 1H), 3.83−3.85 (m, 2H), 3.89−3.90 (m, 2H), 4.18−4.24 (m, 1H), 6.09 (t, 1H, J = 1.6 Hz), 7.44 (d, 2H, J = 8.4 Hz), 8.07 (d, 2H, J = 8.4 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 62.0, 66.3, 68.0, 90.2, 128.4, 129.0, 131.5, 140.1, 164.6. IR (KBr): 2924, 2855, 1726, 1594, 1260, 1155, 1090, 1012, 912, 881, 756 cm^{-1}.

*1,4-Dioxan-2-yl 4-Bromobenzoate (**7d**).*[14a] ^1H NMR (400 MHz, $CDCl_3$): δ 3.63−3.67 (m, 1H), 3.79−3.81 (m, 2H), 3.86 (d, 2H, J = 1.6 Hz), 4.14−4.20 (m, 1H), 6.06 (s, 1H), 7.57 (d, 2H, J = 8.4 Hz), 7.95 (d, 2H, J = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 62.0, 66.3, 67.9, 90.3, 128.9, 131.6, 132.1, 164.8. IR (KBr): 2972, 2929, 2856, 1729, 1589, 1397, 1274, 1259, 1155, 1090, 1067, 1009, 911, 881, 757 cm^{-1}.

*1,4-Dioxan-2-yl 2-Chlorobenzoate (**8d**).*[14c] ^1H NMR (400 MHz, $CDCl_3$): δ 3.61−3.64 (m, 1H), 3.76−3.77 (m, 2H), 3.83−3.84 (m, 2H), 4.16−4.22 (m, 1H), 6.06 (s, 1H), 7.26−7.30 (m, 1H), 7.37−7.42 (m, 2H), 7.88 (d, 1H, J = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 61.9, 66.1, 67.7, 90.5, 126.7, 129.5, 131.3, 131.9, 133.1, 134.1, 164.4. IR (KBr): 2975, 2857, 2717, 1731, 1633, 1593, 1438, 1353, 1292, 1159, 1108, 1066, 1044, 1012, 911, 880 cm^{-1}.

*1,4-Dioxan-2-yl 2-Bromobenzoate (**9d**).*[9a] ^1H NMR (600 MHz, $CDCl_3$): δ 3.63−3.66 (m, 1H), 3.77−3.79 (m, 2H), 3.83−3.88 (m, 2H), 4.19−4.23 (m, 1H), 6.06 (t, 1H, J = 1.8 Hz), 7.29−7.35 (m, 2H), 7.63−7.64 (m, 1H), 7.85−7.87 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 61.9, 66.2, 67.8, 90.7, 122.1, 127.4, 131.6, 131.9, 133.1, 134.6, 164.9. IR (KBr): 2971, 2924, 2852, 1734, 1581, 1387, 1276, 1255, 1159, 1093, 1069, 921, 871, 752 cm^{-1}.

*1,4-Dioxan-2-yl 3-(Trifluoromethyl)benzoate (**11d**).* ^1H NMR (400 MHz, $CDCl_3$): δ 3.67−3.70 (m, 1H), 3.82−3.84 (m, 2H), 3.89−3.90 (m, 2H), 4.17−4.24 (m, 1H), 6.10 (s, 1H), 7.60 (t, 1H, J = 8.0 Hz), 7.83 (d, 1H, J = 8.0 Hz), 8.29 (d, 1H, J = 8.4 Hz), 8.34 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 62.1, 66.3, 67.9, 90.7, 122.9, 124.7, 127.0 (t, J = 4.2 Hz), 129.4, 130.2 (d, J = 6.0 Hz), 130.9, 131.4 (q, J = 32.7 Hz), 133.3, 164.2. ^{19}F NMR (564.7 MHz, $CDCl_3$): δ −63.4. IR (KBr): 2924, 1730, 1636, 1449, 1333, 1251, 1166, 1128, 1071, 1016, 914, 879, 695 cm^{-1}. HRMS (ESI): calcd for $C_{12}H_{11}F_3O_4$ $(M + Na)^+$, 299.0507; found, 299.0501.

*Tetrahydro-2H-pyran-2-yl Benzoate (**1e**).*[14a] ^1H NMR (400 MHz, $CDCl_3$): δ 1.58−1.77 (m, 3H), 1.81−1.99 (m, 3H), 3.72−3.75 (m, 1H), 3.94−4.01 (m, 1H), 6.23 (t, 1H, J = 3.2 Hz), 7.42 (t, 2H, J = 7.2 Hz), 7.54 (t, 1H, J = 7.2 Hz), 8.07 (d, 2H, J = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.6, 25.0, 29.3, 63.2, 93.1, 128.4, 129.8, 130.3, 133.1, 165.2. IR (KBr): 2924, 2853, 1723, 1607, 1456, 1289, 1121, 709 cm^{-1}.

*Tetrahydro-2H-pyran-2-yl 4-Methylbenzoate (**2e**).*[14f] ^1H NMR (600 MHz, $CDCl_3$): δ 1.60−1.62 (m, 1H), 1.67−1.71 (m, 2H), 1.80−1.95 (m, 3H), 2.39 (s, 3H), 3.71−3.74 (m, 1H), 3.94−3.98 (m, 1H), 6.21 (t, 1H, J = 2.0 Hz), 7.22 (d, 2H, J = 8.4 Hz), 7.95 (d, 2H, J = 8.4 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 18.8, 21.8, 25.2, 29.5, 63.4, 93.1, 127.7, 129.3, 129.9, 143.9, 165.4. IR (KBr): 2945, 2873, 1722, 1611, 1274, 1177, 1206, 1088, 1036, 943, 900, 871, 753 cm^{-1}.

*Tetrahydro-2H-pyran-2-yl 4-Chlorobenzoate (**6e**).*[9a] ^1H NMR (400 MHz, $CDCl_3$): δ 1.59−1.67 (m, 1H), 1.72−1.77 (m, 2H), 1.83−1.91 (m, 3H), 3.72−3.75 (m, 1H), 3.92−3.98 (m, 1H), 6.21 (s, 1H), 7.40 (d, 2H, J = 8.4 Hz), 8.00 (d, 2H, J = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.8, 25.2, 29.4, 63.5, 93.6, 128.92, 128.97, 131.3, 139.8, 164.6. IR (KBr): 2944, 2871, 1725, 1593, 1272, 1206, 1089, 1016, 940, 898, 868, 758 cm^{-1}.

*Tetrahydrofuran-2-yl Benzoate (**1f**).*[14a] ^1H NMR (400 MHz, $CDCl_3$): δ 2.05−2.12 (m, 2H), 2.45−2.54 (m, 2H), 4.10−4.22 (m, 2H), 5.52 (s, 1H), 7.39−7.43 (m, 2H), 7.52−7.56 (m, 1H), 7.98−8.04 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.7, 29.7, 67.1, 100.7, 128.6, 129.88, 129.93, 133.5, 166.2. IR (KBr): 2901, 1720, 1637, 1489, 1450, 1349, 1317, 1277, 1117, 1069, 1028, 958, 909, 713 cm^{-1}.

*Tetrahydrofuran-2-yl 4-Methylbenzoate (**2f**).*[14f] ^1H NMR (400 MHz, $CDCl_3$): δ 2.03−2.09 (m, 2H), 2.36 (s, 3H), 2.43−2.52 (m, 2H), 4.08−4.21 (m, 2H), 5.51 (s, 1H), 7.18 (d, 2H, J = 8.4 Hz), 7.87 (d, 2H, J = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.8, 28.6, 29.7, 67.0, 100.6, 127.1, 129.2, 129.9, 144.1, 166.3. IR (KBr): 2901, 2127,

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1717, 1613, 1445, 1349, 1278, 1179, 1112, 1029, 958, 909, 842, 755, 691 cm^{-1}.

*Tetrahydrofuran-2-yl 4-Chlorobenzoate (**6f**).* ^1H NMR (400 MHz, $CDCl_3$): δ 1.99−2.10 (m, 2H), 2.45−2.54 (m, 2H), 4.09−4.23 (m, 2H), 5.51 (s, 1H), 7.36 (d, 2H, J = 8.0 Hz), 7.91 (d, 2H, J = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.5, 29.6, 67.0, 100.6, 128.3, 128.9, 131.2, 140.0, 165.3. IR (KBr): 2943, 2906, 1718, 1593, 1486, 1402, 1344, 1276, 1107, 1032, 943, 889, 760 cm^{-1}. HRMS (ESI): calcd for $C_{11}H_{11}ClO_3$ $(M + Na)^+$, 249.0295; found, 249.0300.

*1,3-Dioxolan-4-yl Benzoate (**1g**).* ^1H NMR (600 MHz, $CDCl_3$): δ 4.12−4.19 (m, 2H), 5.16 (s, 1H), 5.21 (s, 1H), 6.59−6.60 (m, 1H), 7.45 (t, 2H, J = 7.8 Hz), 7.59 (t, 1H, J = 7.2 Hz), 8.05 (d, 2H, J = 7.8 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 71.0, 94.9, 96.2, 128.7, 129.7, 130.0, 133.7, 166.1. IR (KBr): 2926, 2881, 1729, 1602, 1452, 1316, 1269, 1167, 1069, 1024, 990, 870, 711 cm^{-1}. HRMS (ESI): calcd for $C_{10}H_{10}O_4$ $(M + Na)^+$, 217.0477; found, 217.0470.

*1,3-Dioxolan-4-yl 4-Methoxybenzoate (**3g**).*[14e] ^1H NMR (600 MHz, $CDCl_3$): δ 3.83 (s, 3H), 4.07−4.14 (m, 2H), 5.12 (s, 1H), 5.16 (s, 1H), 6.53−6.54 (m, 1H), 6.89 (d, 2H, J = 9.0 Hz), 7.97 (d, 2H, J = 8.4 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 55.5, 70.8, 94.5, 95.9, 113.8, 121.9, 132.0, 163.9, 165.6. IR (KBr): 2970, 2882, 1719, 1607, 1512, 1422, 1318, 1260, 1169, 1028, 1087, 922, 769 cm^{-1}.

*1,3-Dioxolan-4-yl 4-Chlorobenzoate (**6g**).* ^1H NMR (600 MHz, $CDCl_3$): δ 4.10−4.17 (m, 2H), 5.14 (s, 1H), 5.19 (s, 1H), 6.56−6.57 (m, 1H), 7.41 (d, 2H, J = 6.6 Hz), 7.97 (d, 2H, J = 7.8 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ 70.9, 95.0, 96.2, 128.1, 129.0, 131.3, 140.2, 165.1. IR (KBr): 2975, 2881, 2782, 1731, 1594, 1488, 1402, 1269, 1169, 1038, 1014, 921, 851, 759 cm^{-1}. HRMS (ESI): calcd for $C_{10}H_9ClO_4$ $(M+Na)^+$, 251.0087; found, 251.0095.

*2,2,6,6-Tetramethylpiperidin-1-yl Benzoate (**G**).* ^1H NMR (400 MHz, $CDCl_3$): δ 1.16 (s, 6H), 1.31 (s, 6H), 1.48−1.52 (broad singlet, 1H), 1.61−1.64 (broad singlet, 2H), 1.71 (m, 3H), 7.50 (t, 2H, J = 7.6 Hz), 7.61 (t, 1H, J = 6.8 Hz), 8.11 (d, 2H, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.1, 21.0, 32.1, 39.2, 60.5, 128.6, 129.7, 133.0, 166.5. IR (KBr): 2974, 2934, 1749, 1540, 1378, 1255, 1176, 1081 cm^{-1}. HRMS (ESI): calcd for $C_{16}H_{23}NO_2$ (MH^+), 262.1807; found, 262.1812.

*2-Oxo-2-phenyl-N-(1-phenylethyl)acetamide (**N**).* ^1H NMR (400 MHz, $CDCl_3$): δ 1.58 (d, 3H, J = 6.8 Hz), 5.13−5.20 (m, 1H), 7.35−7.36 (m, 5H), 7.45 (t, 2H, J = 8.4 Hz), 7.60 (t, 1H, J = 7.6 Hz), 8.32 (d, 2H, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.9, 49.3, 126.4, 127.9, 128.7, 129.0, 131.5, 133.5, 134.6, 142.4, 160.9, 187.8. IR (KBr): 3451, 2962, 2925, 2851, 1662, 1596, 1449, 1218, 1178, 1021, 744, 698 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{15}NO_2$ (MH^+), 254.1176; found, 254.1185.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectral data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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