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Base-Promoted Amidation and Esterification of Imidazolium Salts *via* Acyl C-C bond Cleavage: An Access to Aromatic Amides and Esters

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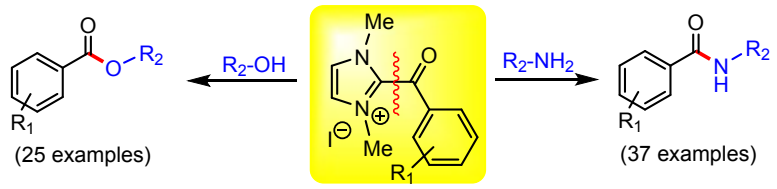
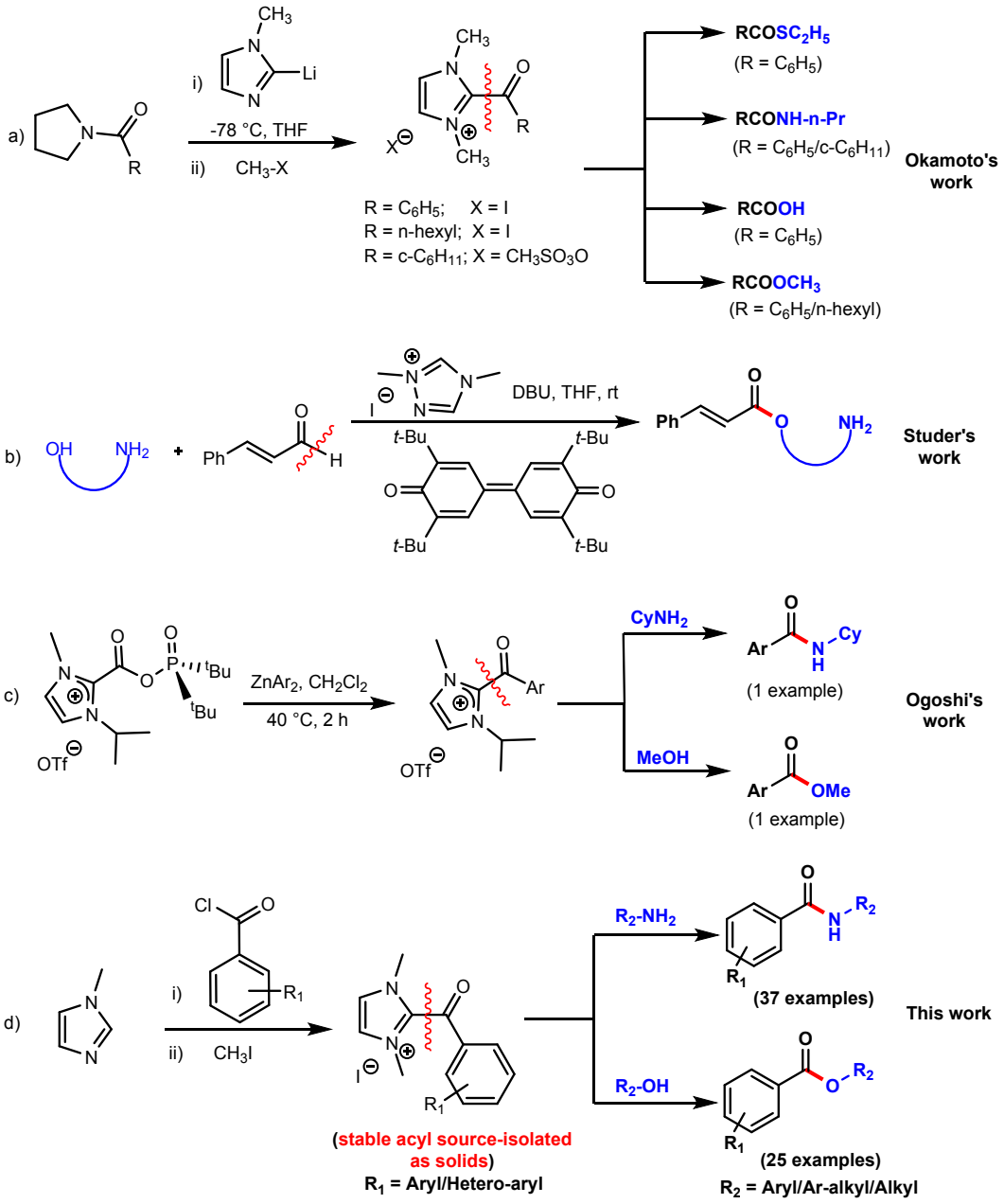


Abstract. Imidazolium salts are effectively employed as a suitable acyl transfer agent in amidation and esterification in organic synthesis. The weak acyl C(O)-C imidazolium bond was exploited to generate acyl electrophiles which on further reacts with amines and alcohols to afford amides and esters. The broad substrate scope of anilines and benzylic amines, and base-promoted conditions are the benefits of this route. Interestingly, phenol, benzylic alcohols, and biologically active alcohol can also be subjected to esterification under the optimized conditions.

Introduction. Amides are common and highly notable linkage prevalent in nature as a backbone of proteins.[1] The high stability of amides favors them as a key constituent in biological compounds, active pharmaceutical agents, and agrochemicals.[2] Their profound resistance to hydrolysis makes them ubiquitous in polymers[3] and functional materials.[4] Conventionally, amides are accessible by direct condensation of carboxylic acids and amines. Alternatively, there are numerous non-classical methods in generating amides by utilizing stoichiometric coupling reagents,[5] carboxylic acid surrogates,[6] amine surrogates,[7] alkenes or alkynes aminocarbonylation,[8] cross-dehydrogenating coupling of aldehydes with amines by visible light photoredox catalysis[9] and NHC catalyzed direct oxidative amidation of aldehydes.[10] The split and union of the C-C bond are fundamental steps witnessed and manipulated by the chemists with great fervor, due to its potential applicability both in academics and industry.[11] Widely, the C-C bond cleavages

Scheme 1 a) Synthesis of Esters and Amides **a-c** (previous work) b) Imidazolium Salts as a Stable Acyl Transfer Agent in Amidation and Esterification **d** (this work).



were achieved in strained and unstrained ring systems by employing transition metal catalysts.[12] In the myriad of C-C bond cleavage, acyl C(O)-C bond cleavage attract great attention in organic synthesis owing to its simple and convenient transformation towards useful derivatives.[13] Recently, the acyl group revealed to be a promising electrophile which reacts efficiently with amines catalyzed by acid, base, oxidizing agent and transition metals to afford amides.[14] Strategically, functional groups are converted into their salts and employed as a suitable transfer agent for various organic transformations. This methodology found to be very

attractive owing to their facile leaving ability, air, and thermal stability. In this context, ammonium salts especially benzylic were successfully utilized in Buchwald-Hartwig, Kumada, Negishi, and Suzuki coupling reactions.[15] Similarly, diazonium,[16] iodonium,[17] phosphonium,[18] pyridinium,[19] silanolate[20] and sulphonium[21] salts play a vital role in offering necessary electrophiles. From the acylation viewpoint, azoles such as pyrrole,[22] pyrazole,[23] triazole,[24] and imidazoles[25] have been explored both in metal and metal-free conditions *via* a C(O)-N cleavage. Very recently, Beutner and co-workers elegantly utilized *in situ* generated *N*-acyl imidazolium salts for challenging amide bond formations *via* C(O)-N cleavage.[26] However, the precedence of using *C*-acyl imidazolium salts as a bench stable acylating agent *via* C(O)-C cleavage is scarce.

Okamoto research group revealed the synthesis of *C*-acyl imidazolium salts by the reaction of (1-methyl-1*H*-imidazol-2-yl)lithium with amide to yield *C*-acyl imidazoles followed by quaternization with methyl iodide or dimethyl sulphate (Scheme 1a).[27] Studer and co-workers have disclosed the oxidation of aldehydes to esters from *in situ* generated acyl triazolium and imidazolium salts (Scheme 1b).[28] The same group has reported the utilization of α,β-unsaturated acyl azolium salts in the synthesis of pyranones and pyridinones.[29] In related research, Ogoshi group has effectively utilized the imidazolium carbene to generate carboxylic phosphinic mixed anhydride from CO_2, which further effected to amide and ester *via* acyl imidazolium intermediate (Scheme 1c).[30] Unfortunately, all the reported methods suffer from certain shortcomings. Thus, we envisioned a straightforward, mild base-promoted, amidation and esterification of stable acyl imidazolium salts *via* C(O)-C bond cleavage (Scheme 1d). The synthesis of C-acyl imidazoles was accomplished by following Bildstein[31] and Meggers[32] literatures and it avoids the usage of organolithium reagents.[29] The novelty of this methodology resides on;

i) Evading air and moisture sensitive carbenes as a catalyst,[33] and non-green, expensive oxidants[34] and organometallic reagents for the coupling reaction.[27,35]

ii) Precluding multistep process.[36]

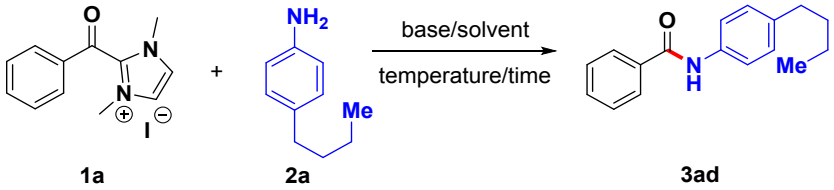
iii) Acyl imidazolium salts are inexpensive, and they can be prepared easily.

iv) The wide range of substrate scope especially aromatic, benzylic amines and aromatic, benzylic alcohols can be studied.

Results and Discussion

We commenced our exploration with 2-benzoyl-1,3-dimethyl-1*H*-imidazol-3-ium iodide **1** (1.5 equiv) as an electrophilic acyl source, 4-butylaniline **2** (1.0 equiv) as a coupling partner, K_2CO_3 (1.5 equiv) as a base in CH_3CN (1 mL) at room temperature for 18 h (Table 1). This resulted in the formation of *N*-(4-butylphenyl)benzamide **3ad** in 20% yield (entry 1). Replacement of TBAB and DMF in place of K_2CO_3 and CH_3CN respectively resulted in 15 and 25% yield of **3ad** (entries 2 and 3). The elevation of temperature from rt to 80 °C (14 h) improves the yield of **3ad** (65%) (entry 4). Screening of bases NaOH, Cs_2CO_3 and Et_3N were not promising (entries 5-7), and K_2CO_3 was found to be the best.

Table 1. Optimization of the Reaction with Acylimidazolium Salt[a]



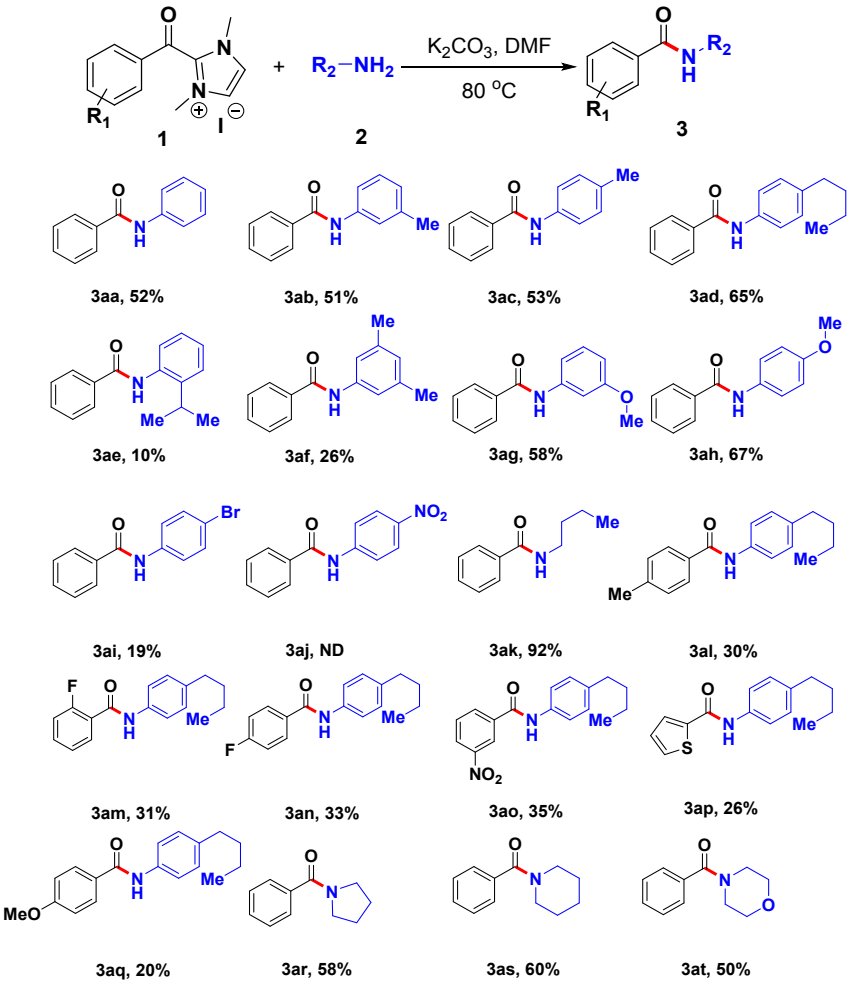
1a **2a** **3ad**

Entry	Base/additive	Solvent	Temp (°C)	Yield[b] (%)
1	K_2CO_3	CH_3CN	rt	20[c]
2	TBAB	CH_3CN	rt	15[c]
3	K_2CO_3	DMF	rt	25[c]
4	***K_2CO_3***	***DMF***	***80***	***65***
5	NaOH	DMF	80	5
6	Cs_2CO_3	DMF	80	50
7	Et_3N	DMF	80	31
8	K_2CO_3	DMF	100	67[d]
9	-	DMF	80	33
10	K_2CO_3	ethanol	80	8
11	K_2CO_3	toluene	80	-
12	K_2CO_3	DMF	80	34[e]

Reaction conditions: [a]**1a** (1.5 equiv), **2a** (1.0 equiv), K_2CO_3 (1.5 equiv), DMF (1 mL), 80 °C, 14 h (entries 4-7). [b]isolated yields. [c]rt 18 h, [d]100 °C, 18 h, [e]with **1a** (1.0 equiv). TBAB: Tetrabutylammonium bromide; DMF: *N*, *N*-Dimethylformamide.

Furthermore, the increase in reaction temperature and time to 100 °C and 18 h respectively shown a slight improvement in the yield of **3ad** (entry 8). Notably, the absence of base reduces the yield of **3ad** to 33% (entry 9). Replacing the solvent DMF with ethanol and toluene hamper the reaction (entries 10 and 11). With **1a** (1 equiv) the yield of **3ad** drops to 34%. Thus, the optimized reaction condition for base promoted amidation of acyl imidazolium salt is **1** 1.5 equiv, **2** 1 equiv, K_2CO_3 1.5 equiv, in DMF (1 mL) at 80 °C for 14 h. Encouraged by the optimized conditions, we explored the substrate scope of amidation reaction with various amines (Table 2). Aniline possessing alkyl substituents at *meta* **3ab** and *para* **3ac** sites afforded better yields of amidation product as compared with unsubstituted **3aa**. Predictably, sterically hindered **3ae** and multi-substituted aniline **3af** results in poor yield. Methoxy group positioned at *meta* **3ag** and *para* **3ah** showed an improved yield of 58% and 67% respectively.

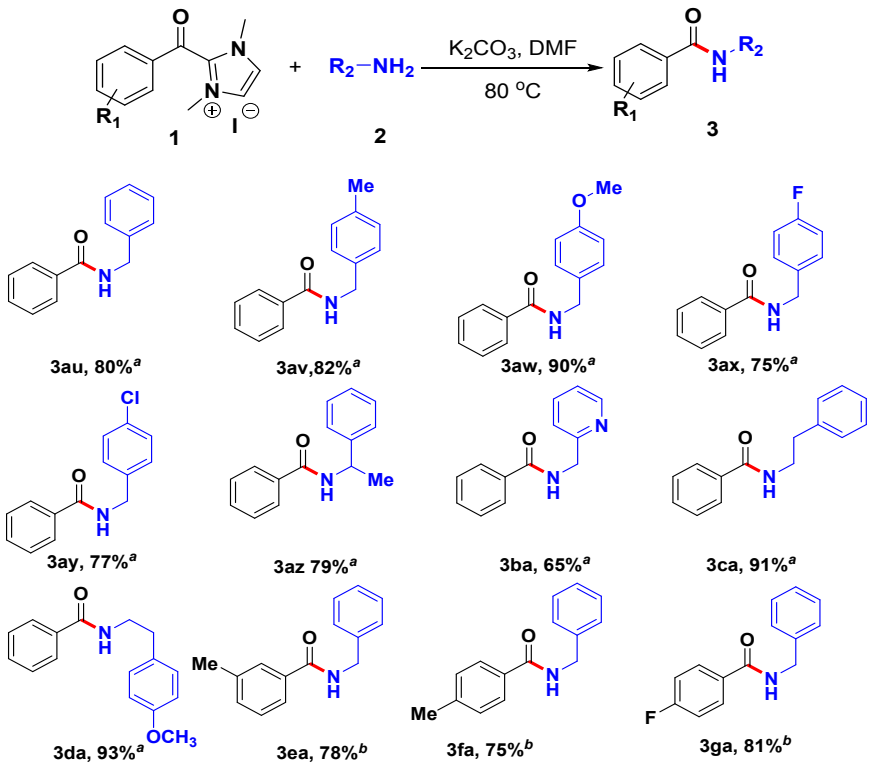
Table 2. Substrate Scope of Aromatic and Aliphatic Amines[a,b]



Reaction conditions: [a]**1** (1.5 equiv), **2** (1.0 equiv), K_2CO_3 (1.5 equiv), DMF (1 mL), 80 °C, 14 h. [b]Isolated yields.

Electron-withdrawing 4-Br **3ai** exhibited reduced yield (19%) whereas 4-NO_2 **3aj** derivate was not detected. Strikingly, aliphatic amines afforded the maximum yield of **3ak** (92%). Next, we turned our attention to various substituted acyl imidazolium salts. On the contrary to the above observation, methyl substrate **3al** displayed lower in yield (30%) and electron-withdrawing substrates **3am-3ao** resulted in slightly improved yield (31%-35%). Heterocyclic thiophenyl substrate moderate the yield of **3ap** (26%). Electron rich -OCH_3 group at para position of acyl imidazolium salts further decreases the yield of **3aq** to 20%. Notably, cyclic secondary amines such as pyrrolidine **3ar** (58%), piperidine **3as** (60%) and morpholine **3at** (50%) reacts efficiently to afford the amides. Then, we examined the reactivity of ar-alkyl amines in the amidation reaction (Table 3). Benzylamine **3au** and its electron-donating congeners **3av** & **3aw** offers maximum yields (80%-90%). Halogen substituents 4-F **3ax** and 4-Cl **3ay** on the phenylic group reduce the yields (75%-77%). α-Methylbenzyl amine and 2-picolylamine reacted smoothly to offer **3az** and **3ba** in 79% and 65% yields respectively. The reaction proceeded cleanly with phenethyl amine derivatives **3ca** (91%) and **3da** (93%). Substituted acyl imidazolium salts such as 3-Me, 4-Me and 4-F tolerate the reaction conditions to offer amidation product **3ea**, **3fa**, and **3ga** in 78%, 75%, and 81% yield respectively.

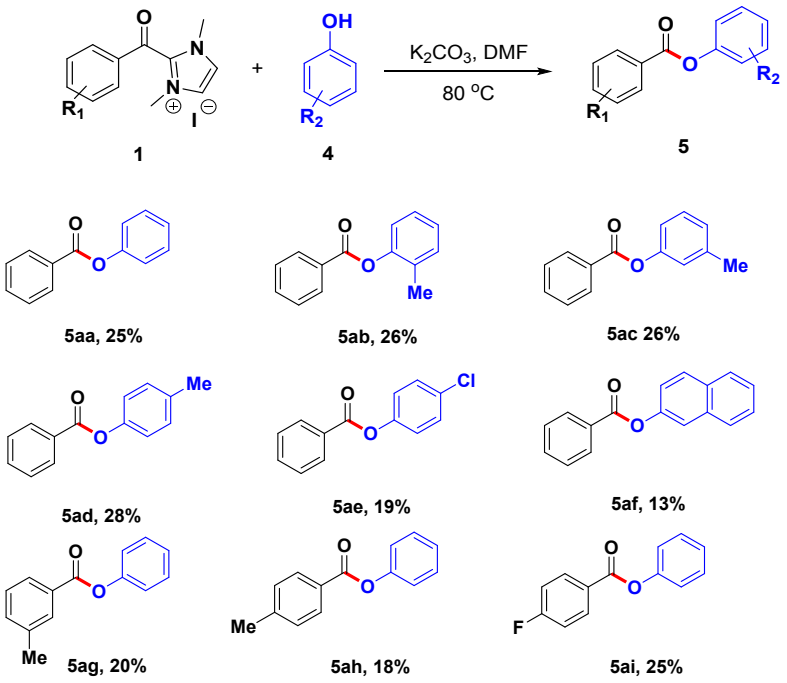
Table 3. Substrate Scope of Benzylic amines



[a]The reactions were executed at 80 °C for 1 h. [b]The reactions were executed at 80 °C for 3 h.

Esters constitutes major subunits prevalent in natural products, pharmaceuticals, polymers and functional materials.[37] The well-established synthetic routes to prepare ester involve acid chlorides,[38] acids[39] and acid anhydrides[40] with alcohols. Besides, esters were accessible from amides,[41] methyl ketones,[42] nitriles,[43] allylic group,[44] ethers[45] and amino acids.[46] The synthesis of esters *via* acyl transfer from stable imidazolium salts is in its infancy. Usually, this approach avoids consumption of concentrated acids, ionic liquids, harmful and expensive metal salts. We applied our optimized reaction conditions in synthesizing the esters using acyl imidazolium salts **1a** with alcohol **4a** in the presence of K_2CO_3 as a base at 80 °C, for 14 h (Table 4). To our delight, phenols undergo esterification smoothly to afford **5aa** in 25% of yield. Phenols with *ortho*, *meta*, and *para*-methyl substituents gave the corresponding esters **5ab**-**5ad** in 26%-28% yields. 4-Chlorophenol and 2-naphthol diminish the yield of **5ae** and **5af** to 19% and 13% respectively. Conversely, functionalized acyl imidazolium salts possessing 3-Me, 4-Me and 4-F were all compatible, give **5ag, 5ah**, and **5ai** in similar yield (18%-25%).

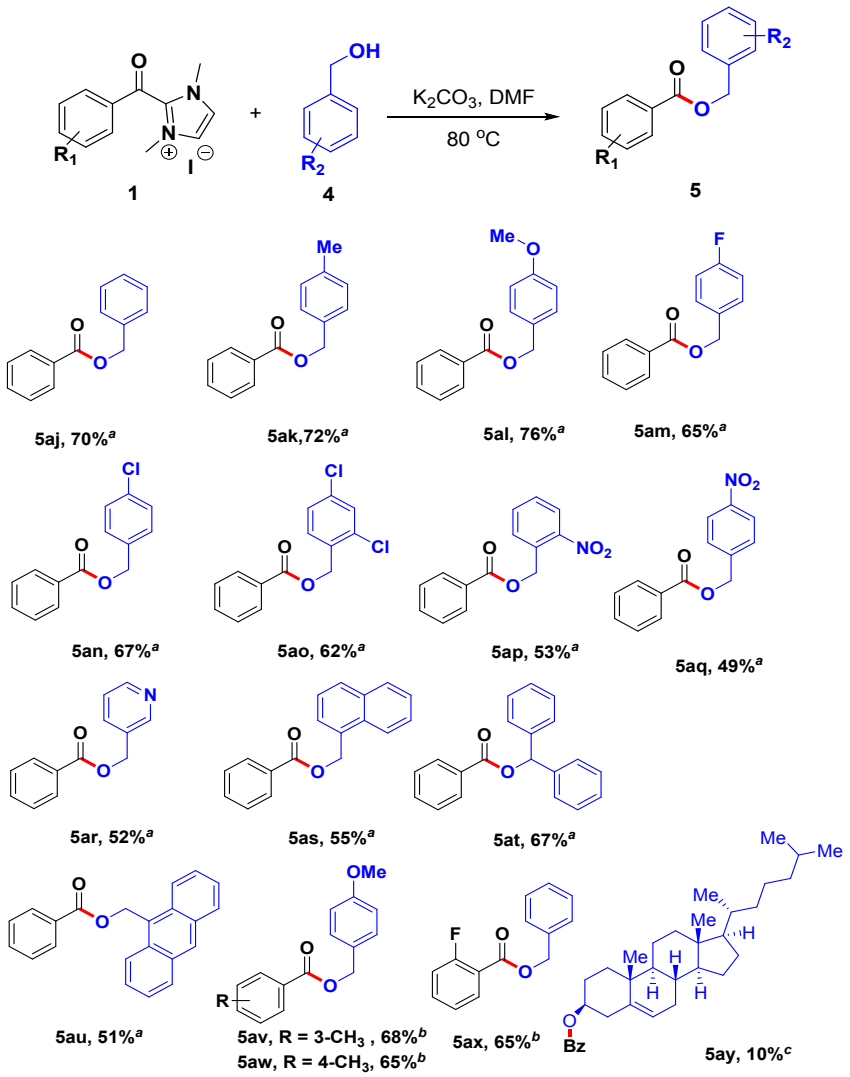
Table 4. Substrate Scope of Phenols[a,b]



Reaction conditions: [a]**1** (1.5 equiv), **4** (1.0 equiv), K_2CO_3 (1.5 equiv), DMF, (1 mL), 80 °C, 14 h. [b]Isolated yields.

Furthermore, the applicability of this protocol was realized for benzylic alcohol substrates (Table 5). Notably, simple benzylic alcohol **5aj**, 4-Me **5ak**, and 4-MeO **5al** confer the esters in improved yields of 70%-76%. Benzylic alcohols having halogen substituents such as 4-F, 4-Cl, 2,4-dichloro gave the desired products **5am**, **5an**, and **5ao** respectively in good yields (62%-65%). Evidently, highly electron-withdrawing -NO_2 substituent at *ortho* and *para* position deteriorates the yield of **5ap** and **5aq** in 53% and 49% respectively. Pertinently, 3-pyridine **5ar**, naphthyl **5as**, diphenyl **5at** and anthracenyl derivatives **5au** result in low yield of product (51%-67%). Acyl imidazolium derivative possessing 3-Me, 4-Me and 2-F react amicably to yield **5av**, **5aw**, and **5ax** (68%-65%). Biologically active cholesterol ester **5ay** can be synthesized in 10% of isolated yield by using this strategy.

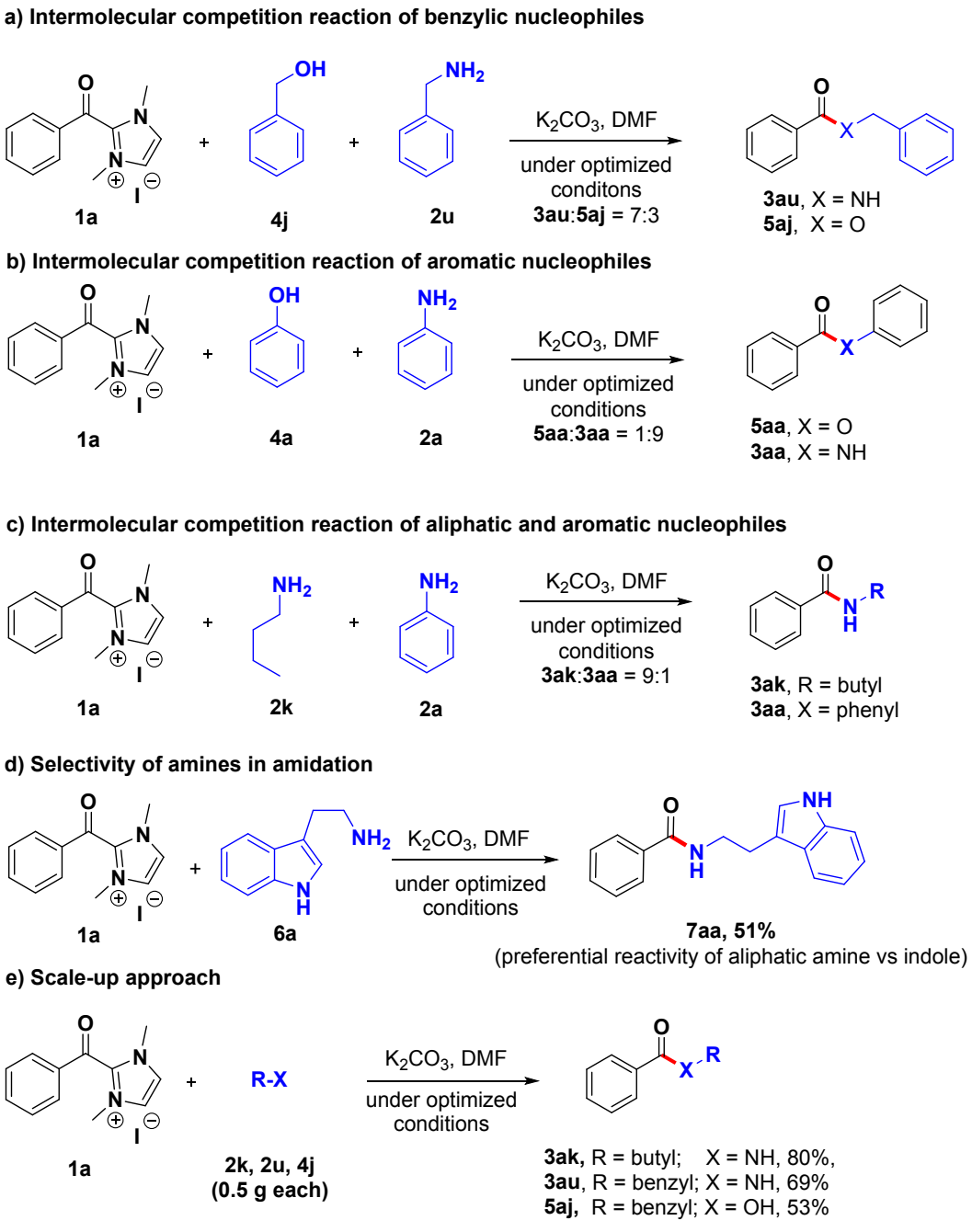
Table 5. Substrate Scope of Benzyl Alcohols and Cholesterol



[a]The reactions were executed at 80 °C, 1 h. [b]80 °C for 3 h. [c]80 °C for 14 h.

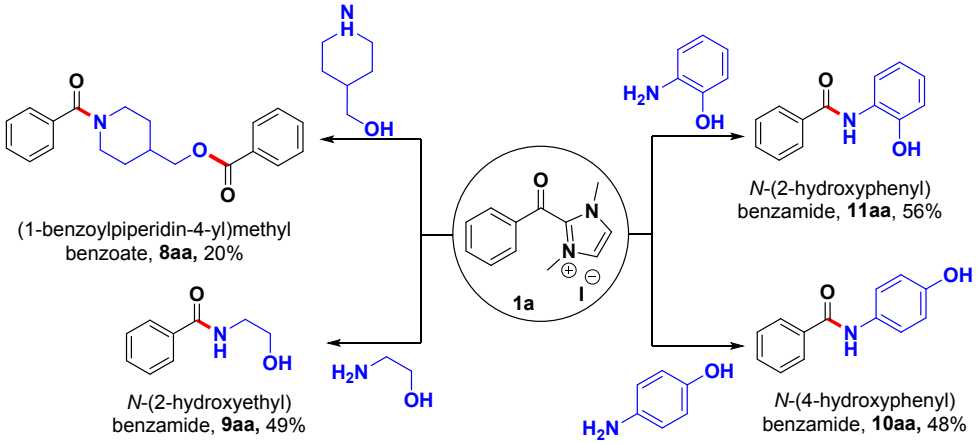
To get further insights into the reaction pathway selectivity studies were executed. Intermolecular competition reaction between benzyl alcohol **4j** and benzyl amine **2u** with *C*-benzoyl imidazolium iodide **1a** was studied. It was found that **2u** are more reactive as compared to its alcoholic counterpart **4j** to substantiate nucleophilic addition across acyl C-C bond (Scheme 2a); The intermolecular competitive reaction between phenol **4a** and aniline **2a** with **1a** also revealed its innate nucleophilicity (Scheme 2b); The higher reactivity of aliphatic amine **2k** than aromatic amine **2a** is elucidated by their intermolecular competition reaction with **1a** (Scheme 2c);

Scheme 2. Control Experiments (**a-d**) and Scale-up (**e**) Studies



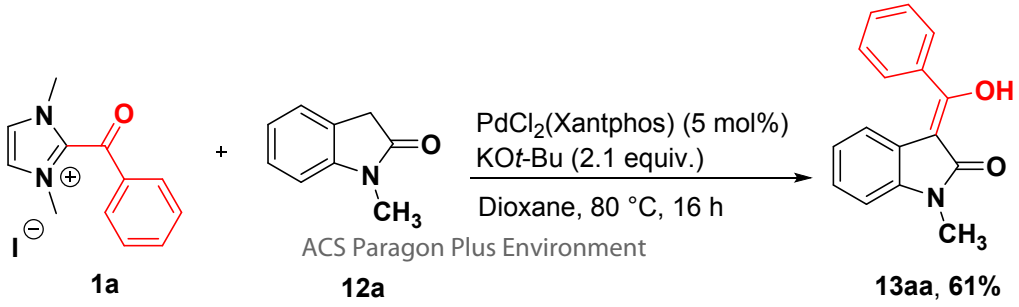
The compound possessing two different amine functionalities have been chosen such as 2-(1*H*-indol-3-yl)ethan-1-amine **6a** (scheme 2d) where selectively primary amidated product **7aa** was observed (51% yield). This is owing to the easy availability and high reactivity of aliphatic primary amine group –($CH_2CH_2NH_2$) to couple with acyl electrophiles. But, in case of indole-*NH*, the secondary amine is involved in extended conjugation with benzene ring to lowers its reactivity with **1a**. From these competition experiments, it is proved that these substrates (*C*-acyl imidazolium salts) can be efficiently used in the synthetically advantageous level of selectivity towards amines and alcohols. Besides, this optimized condition can be scaled-up (Scheme 2e). Additionally, the **1a** was used as an acylating agent for the substrate having binucleophilic centers (ex: -NH_2 and OH) to yield **8aa-11aa** in 20%-56% (Scheme 3).

Scheme 3. Acylation of Binucleophilic Centers



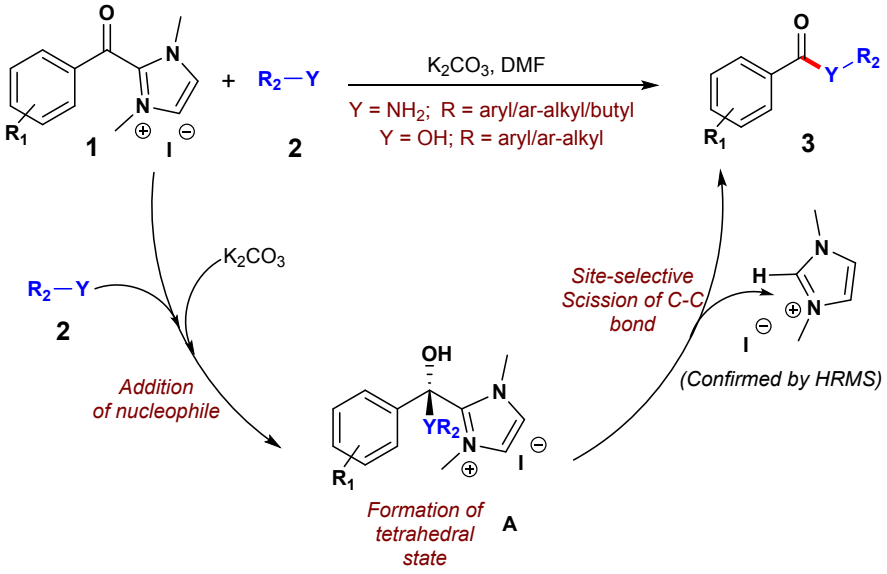
Intriguingly, these acyl imidazolium salt **1a** can be efficiently used as an acyl source for the reaction with carbon nucleophiles such as 1-methylindolin-2-one **12a** to furnish (Z)-3-(hydroxy(phenyl)methylene)-1-methylindolin-2-one **13aa** in 61% of yields (Scheme 4). This method offers a direct and straightforward way to acylate carbon nucleophiles. Further, optimization of reaction conditions and substrate scope studies are in progress in our research group.

Scheme 4. Acylation with Carbon Nucleophiles



Recently, Szostak[47] and Zeng[48] group proposed a base-promoted pathway for transamidation of amides *via* formation of tetrahedral transition state. Based on this observation a possible reaction pathway is proposed for amidation and esterification of imidazolium salts (Scheme 5). Initially, nucleophilic addition of amines or alcohols to the regio selectively activated acyl imidazolium salts **1** in the presence of K_2CO_3 furnishes tetrahedral transitions state **A**. Further, site-selective fissure of C(O)-C bond delivers amidation and esterification outputs. This pathway is promoted thermodynamically by easy leaving ability and poor nucleophilic nature of imidazolium unit as compared with participating amines or phenols.

Scheme 5. Proposed Mechanism for Acyl C-C bond Cleavage of Imidazolium Salts with Nucleophiles



Conclusions

In conclusion, the feeble nature of C(O)-C bond of acyl imidazolium salts has been exploited for the augmentation of a highly regioselective amidation and esterification of aryl, ar-alkyl and alkyl amine and alcohols under base promoted conditions. This protocol reveals the

benefits such as low-cost, simple in operation, wide range of substrate scopes of anilines, benzylic amines, and butylamine. Fascinatingly, this procedure can be extended into esterification of substituted phenols, benzylic alcohols. Selectivity studies deal with a preferential attack of aliphatic amines and competition experiments discuss the high nucleophilicity of nitrogen donor than oxygen.

Experimental Section

General Experimental Information

Unless otherwise mentioned all the reactions were carried out in screw capped reaction tubes (8 mL) under an inert atmosphere of nitrogen. Anhydrous solvents (THF, $CHCl_3$) purchased from commercial sources and used without further purification. Chemicals were purchased from Sigma-Aldrich, Alfa Aesar, AVRA. Thin layer chromatography was done by using market available TLC plates with eluents hexanes-ethyl acetate and chloroform wherever required with monitoring the reaction under UV radiation. ^{1}H NMR spectra were recorded on Bruker spectrometer (400 MHz) and are reported in units ppm (parts per million) relative to the signals for residual chloroform (7.26 ppm) and DMSO (2.54 ppm) in the deuterated solvent. ^{13}C NMR spectra were recorded on Bruker spectrometer (100 MHz) and are reported in ppm relative to deuterated chloroform (77.23 ppm) and DMSO (39.52 ppm) with tetramethyl silane as an internal standard. Coupling constants (*J*) are reported in Hz; splitting patterns are assigned *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *br* = broad signal. High-resolution mass spectra (HRMS) were performed as EI analyzer mode.

General procedure for the synthesis of acyl imidazolium salts (1a-1g) with characterization data

A 100 mL round bottom flask equipped with a stir bar was charged with 1-methylimidazole **A** (500 mg, 1.0 equiv), DMAP (4 mg, 1 mol %), placed under a positive pressure of nitrogen. Chloroform (10 mL) was added with stirring followed by addition of Et_3N (1230 mg, 2 equiv) at 0 °C was done. Benzoyl chloride (939 mg, 1.1 equiv) was added dropwise at 0 °C and the reaction mixture was stirred for 12 h at room temperature. After the indicated time, the reaction mixture was diluted with water (100 mL), extracted with chloroform (15 mL X 2) and concentrated. The crude material was purified by column chromatography on silica gel with chloroform or hexanes-ethyl acetate (70:30 v/v) as eluent, to yield (1-methyl-1*H*-imidazol-2-yl)(phenyl)methanone (**B**) as pale-yellow oil. Then, **B** (0.5 g, 1 equiv) was taken in 2 mL of Dioxane in a screw capped reaction tube of 15 mL capacity and CH_3I (20 equiv) was added

and the reaction mixture was heated at 70 °C, for 16 h. The precipitated solid was filtered and washed with dioxane (3 mL), followed by hexanes (25 mL) to give the imidazolium benzoyl derivatives **1a-1g.**

2-Benzoyl-1,3-dimethyl-1*H*-imidazol-3-ium iodide, 1a.[27] Pale yellow solid, 0.77 mg, 88% of yield, m.p. 192-194 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (s, 2H), 7.95 (d, J = 8.0 Hz, 2H), 7.87 (t, J = 7.6 Hz, 1H), 7.69 (t, J = 7.6 Hz, 2H), 3.80 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 180.9, 138.9, 136.5, 135.1, 130.8, 130.0, 125.9, 37.9.

1,3-Dimethyl-2-(4-methylbenzoyl)-1*H*-imidazol-3-ium iodide, 1b. Pale brown solid, 0.675g, 79% of yield, m.p. 186-188 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (s, 2H), 7.86 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 3.79 (s, 6H), 2.46 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 180.4, 147.9, 139.1, 132.6, 131.0, 130.7, 125.7, 37.7, 22.0. HRMS (ESI-QTOF) m/z: $[M - I]^+$ Calcd for $C_{13}H_{15}N_2O$ 215.1179; found 215.1171.

2-(2-Fluorobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium iodide, 1c. Grey solid, 0.414 g, 49% of yield, m.p. 150-152 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06 (s, 2H), 7.95-7.91 (m, 2H), 7.54-7.49 (m, 2H), 3.85 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 176.7, 161.1 (d, $^{1}J_{C-F}$ = 255.9 Hz), 138.6 (d, $^{3}J_{C-F}$ = 9.3 Hz), 132.5, 126.2 (d, $^{4}J_{C-F}$ = 3.2 Hz), 126.1, 124.0 (d, $^{3}J_{C-F}$ = 9.4 Hz), 117.7 (d, $^{2}J_{C-F}$ = 20.6 Hz), 37.8. ^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6) δ -113.9. HRMS (ESI-QTOF) m/z: $[M - I]^+$ Calcd for $C_{12}H_{12}FN_2O$ 219.0928; found 219.0923.

2-(4-Fluorobenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium iodide, 1d. Brown solid, 0.43 g, 51% of yield, m.p. 195-197 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06-8.05 (m, 2H), 8.03 (s, 2H), 7.55-7.51 (m, 2H), 3.81 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 179.5, 166.9 (d, $^{1}J_{C-F}$ = 255.0 Hz), 138.6, 134.3 (d, $^{3}J_{C-F}$ = 10.1 Hz), 131.9 (d, $^{4}J_{C-F}$ = 2.7 Hz), 125.9, 117.3 (d, $^{2}J_{C-F}$ = 22.5 Hz), 37.9. ^{19}F{^{1}H} NMR (376 MHz, DMSO-d_6) δ -100.8. HRMS (ESI-QTOF) m/z: $[M - I]^+$ Calcd for $C_{12}H_{12}FN_2O$ 219.0928; found 219.0922.

1,3-Dimethyl-2-(3-nitrobenzoyl)-1*H*-imidazol-3-ium iodide, 1e. Bright yellow solid, 0.523g, 65% of yield, m.p. 200-202 °C. (synthesis imidazolium salt was carried out in acetonitrile instead of dioxane). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.06-8.05 (m, 2H), 8.35 (d, J = 7.6 Hz, 1H), 8.08 (s, 2H), 7.96 (t, J = 8.0 Hz, 1H), 3.83 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 179.4, 148.5, 137.9, 136.7, 131.6, 129.8, 126.5, 124.9, 38.4. HRMS (ESI-QTOF) m/z: $[M - I]^+$ Calcd for $C_{12}H_{12}N_3O_3$ 246.0873; found 246.0864.

1,3-Dimethyl-2-(thiophene-2-carbonyl)-1*H*-imidazol-3-ium iodide, 1f. Pale yellow solid, 0.39 g, 46% of yield, m.p. 170-172 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.50 (d, J = 4.4 Hz, 1H), 8.11-8.01 (m, 3H), 7.43 (t, J = 4.0 Hz, 1H), 3.86 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 172.0, 142.3, 140.8, 138.9, 130.6, 125.6, 37.5. HRMS (ESI-QTOF) m/z: [M - I]$^+$ Calcd for $C_{10}H_{11}N_2OS$ 207.0587; found 207.0580.

2-(4-Methoxybenzoyl)-1,3-dimethyl-1*H*-imidazol-3-ium iodide, 1g.[30] Brown solid, 0.55g, 66% of yield, m.p. 180-182 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99 (s, 2H), 7.94 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 3.93 (s, 3H), 3.79 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 178.8, 166.2, 139.5, 133.7, 127.7, 125.4, 115.6, 56.6, 37.4.

General Procedure for Amidation from Imidazolium Salts *via* C-C bond Cleavage with Characterization Data

An oven-dried 8 mL vial equipped with a stir bar was charged with **2a** (50 mg, 1 equiv), **1a** (264 mg, 1.5 equiv), potassium carbonate (111 mg, 1.5 equiv) in DMF (1 mL). The reaction mixture was placed in a preheated oil bath at 80 °C and stirred for 14 h. After the indicated time, the solvent was evaporated, and the crude material was purified by column chromatography on silica gel with n-hexane-ethyl acetate or hexanes–diethyl ether as eluent, to yield the title compound.

***N*-phenylbenzamide, 3aa.**[49] Pale yellow solid, 54 mg, 52% of yield (hexanes/diethyl ether, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.2 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 7.6 Hz, 1H), 7.39 (t, J = 6.8 Hz, 2H), 7.28 (t, J = 8.0 Hz, 2H), 7.08 (t, J = 7.6 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.8, 137.9, 135.0, 131.8, 129.1, 128.8, 127.0, 124.6, 120.3.

***N*-(*m*-tolyl)benzamide, 3ab.**[50] Pale brown solid, 49 mg, 51% of yield (hexanes/diethyl ether, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.42-7.30 (m, 5H), 7.11 (t, J = 7.6 Hz, 1H), 6.86 (d, J = 7.6 Hz, 1H), 2.22 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.9, 137.9, 136.9, 133.9, 130.7, 127.8, 127.6, 126.0, 124.3, 120.0, 116.4, 20.4.

***N*-(*p*-tolyl)benzamide, 3ac**.[49] Grey solid, 56 mg, 53% of yield (hexanes/diethyl ether, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.2 Hz, 2H), 7.73 (s, 1H), 7.47-7.38 (m, 5H), 7.10 (d, J = 8.0 Hz, 2H), 2.27 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.7, 135.3, 135.1, 134.3, 131.8, 129.6, 128.8, 127.0, 120.3, 20.9.

***N*-(4-butylphenyl)benzamide, 3ad**.[49] Off-white solid, 54 mg, 65% of yield (hexanes/diethyl ether, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.6 Hz, 2H), 7.74 (s, 1H), 7.47-7.38 (m, 5H), 7.10 (d, J = 8.0 Hz, 2H), 2.52 (t, J = 7.6 Hz, 2H), 1.54-1.48 (m, 2H), 1.32-1.23 (m, 2H), 0.85 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.7, 139.4, 135.5, 135.1, 131.8, 128.9, 128.8, 127.0, 120.3, 35.1, 33.7, 22.3, 13.9.

***N*-(2-isopropylphenyl)benzamide, 3ae**.[51] Grey solid, 9 mg, 10% of yield (hexanes/diethyl ether, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.2 Hz, 2H), 7.84 (d, J = 7.2 Hz, 1H), 7.80 (s, 1H), 7.61-7.50 (m, 3H), 7.37-7.23 (m, 3H), 3.17-3.10 (m, 1H), 1.31 (d, J = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.0, 140.6, 135.0, 134.2, 131.8, 128.9, 127.1, 126.5, 126.2, 125.7, 124.8, 28.2, 23.0.

***N*-(3,5-dimethylphenyl)benzamide, 3af**.[52] Grey solid, 24 mg, 26% of yield (hexanes/diethyl ether, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.2 Hz, 2H), 7.56-7.45 (m, 3H), 7.30 (s, 2H), 6.81 (s, 1H), 2.32 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.8, 138.8, 137.8, 135.1, 131.7, 128.7, 128.4, 127.0, 126.3, 118.1, 21.4.

***N*-(3-methoxyphenyl)benzamide, 3ag.**[49] Pale brown solid, 53 mg, 58% of yield (hexanes/diethyl ether, 85:15 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.87 (d, J = 7.2 Hz, 2H), 7.57-7.45 (m, 4H), 7.26 (d, J = 8.0 Hz, 1H), 7.13 (d, J = 8.0 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 3.83 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.1, 160.2, 139.3, 134.9, 131.8, 129.7, 128.7, 127.1, 112.5, 110.5, 105.9, 55.3.

***N*-(4-methoxyphenyl)benzamide, 3ah.**[49] Grey solid, 61 mg, 67% of yield (hexanes/diethyl ether, 85:15 v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.14 (s, 1H), 7.96 (d, J = 7.6 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.59-7.50 (m, 3H), 6.93 (d, J = 8.8 Hz, 2H), 3.71 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 170.3, 160.7, 140.3, 137.4, 136.6, 133.6, 132.8, 127.2, 118.9, 60.4.

***N*-(4-bromophenyl)benzamide, 3ai.**[53] Grey solid, 15 mg, 19% of yield (hexanes/diethyl ether, 90:10 v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.37 (s, 1H), 7.95 (d, J = 6.8 Hz, 2H), 7.77 (d, J = 8.8 Hz, 2H), 7.60-7.52 (m, 5H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 166.1, 139.0, 135.1, 132.1, 131.9, 128.8, 128.1, 122.7, 115.8.

***N*-butyl benzamide, 3ak.**[49] Colorless oil, 111 mg, 92% of yield. (0.5 g batch yielded 0.96 g) (hexanes/diethyl ether, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.2 Hz, 2H), 7.40 (t, J = 7.2 Hz, 1H), 7.33 (t, J = 7.6 Hz, 2H), 6.22 (s, 1H), 3.39-3.34 (m, 2H), 1.55-1.48 (m,

2H), 1.37-1.28 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) 167.6, 134.8, 131.2, 128.5, 126.8, 39.8, 31.7, 20.2, 13.8.

***N*-(4-butylphenyl)-4-methylbenzamide, 3al.**[54] Pale brown solid, 26 mg, 30% of yield (hexanes/diethyl ether, 90:10 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0 Hz, 2H), 7.66 (s, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 2.52 (t, J = 7.6 Hz, 2H), 2.35 (s, 3H), 1.54-1.48 (m, 2H), 1.31-1.25 (m, 2H), 0.85 (t, J = 7.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.7, 142.3, 139.2, 135.6, 132.2, 129.4, 128.9, 126.9, 120.2, 35.1, 33.7, 22.3, 21.5, 13.9.

***N*-(4-butylphenyl)-2-fluorobenzamide, 3am.**[55] Grey solid, 28 mg, 31% of yield (hexanes/diethyl ether, 90:10 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 8.35-8.27 (m, 1H), 8.10 (t, J = 8.0 Hz, 1H), 7.49-7.43 (m, 3H), 7.24 (t, J = 7.2 Hz, 1H), 7.11 (d, J = 8.4 Hz, 2H), 2.53 (t, J = 7.6 Hz, 2H), 1.54-1.50 (m, 2H), 1.29-1.25 (m, 2H), 0.85 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.6, 159.9 (d, $^1J_{C\text{-}F}$ = 258.1 Hz), 139.6, 135.3, 133.6 (d, $^3J_{C\text{-}F}$ = 9.3 Hz), 132.3, 128.9, 125.1 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 120.6, 116.2 (d, $^2J_{C\text{-}F}$ = 24.9 Hz), 35.1, 33.7, 22.3, 13.9. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -113.3.

***N*-(4-butylphenyl)-4-fluorobenzamide, 3an.**[55] Grey solid, 29 mg, 33% of yield (hexanes/diethyl ether, 90:10 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.80-7.77 (m, 2H), 7.77 (s, 1H), 7.43 (d, J = 8.4 Hz, 2H), 7.10-7.03 (m, 4H), 2.52 (t, J = 7.6 Hz, 2H), 1.55-1.47 (m, 2H), 1.30-1.24 (m, 2H), 0.85 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.8 (d, $^1J_{C\text{-}F}$ = 250.1 Hz), 164.7, 139.5, 135.3, 131.2 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 131.4 (d, $^3J_{C\text{-}F}$ = 8.9 Hz), 128.9, 120.4, 115.8 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 35.1, 33.6, 22.3, 13.9. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -107.6.

***N*-(4-butylphenyl)-3-nitrobenzamide, 3ao.**[55] Brown solid, 35 mg, 35% of yield (hexanes/diethyl ether, 80:20 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.30 (d, J = 7.2 Hz, 1H), 8.17 (d, J = 7.2 Hz, 1H), 8.03 (s, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.11 (d, J = 8.0 Hz, 2H), 2.52 (t, J = 7.6 Hz, 2H), 1.55-1.47 (m, 2H), 1.30-1.24 (m, 2H), 0.85 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.3, 148.2, 140.1, 136.7, 134.8, 133.4, 130.0, 129.1, 126.2, 121.9, 120.6, 35.1, 33.6, 22.3, 13.9.

***N*-(4-butylphenyl)thiophene-2-carboxamide, 3ap.**[56] Brown solid, 22 mg, 26% of yield (hexanes/diethyl ether, 90:10 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.54 (d, J = 3.2 Hz, 1H), 7.46-7.41 (m, 3H), 7.10-7.02 (m, 3H), 2.52 (t, J = 7.6 Hz, 2H), 1.55-1.47 (m, 2H), 1.30-1.24 (m, 2H), 0.85 (t, J = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.9, 139.4, 135.1, 130.6, 128.9, 128.4, 127.8, 120.3, 35.1, 33.6, 22.3, 13.9.

***N*-(4-butylphenyl)-4-methoxybenzamide, 3aq.**[57] Off-white solid, 18 mg, 20% of yield (hexanes/diethyl ether, 80:20 v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.0 (s, 1H), 7.95 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 3.83 (s, 3H), 2.54 (t, J = 7.6 Hz, 2H), 1.58-1.50 (m, 2H), 1.33-1.27 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.1, 162.3, 137.8, 137.4, 129.9, 128.7, 127.5, 120.8, 114.0, 55.9, 34.7, 33.7, 22.2, 14.3.

Phenyl(pyrrolidine-1-yl)methanone, 3ar.[58] Pale yellow oil, 70 mg, 58% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2H), 7.45-7.42 (m, 3H), 3.46 (t, J = 6.8 Hz, 2H), 3.35 (t, J = 6.8 Hz, 2H), 1.89-1.82 (m, 2H), 1.81-1.76 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.6, 137.7, 130.1, 128.6, 127.4, 49.3, 46.3, 26.4, 24.3.

Phenyl(piperidin-1-yl)methanone, 3as.[59] Pale yellow oil, 65 mg, 60% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 5H), 3.63 (s, 2H), 3.26 (s, 2H), 1.60 (s, 4H), 1.44 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.4, 136.5, 129.4, 128.4, 126.8, 48.8, 43.1, 29.7, 26.5, 25.6.

Morpholino(phenyl)methanone, 3at.[58] colorless liquid, 53 mg, 50% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 5H), 3.69-3.38 (m, 8H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.5, 135.3, 129.9, 128.6, 127.1, 66.9, 48.2, 42.6.

***N*-benzyl benzamide, 3au.**[47] Off-white solid, 78 mg, 80% of yield (hexanes/ethyl acetate, 80:20 v/v). (0.5 g batch yielded 0.680 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.0 Hz, 2H), 7.41 (t, J = 6.4 Hz, 1H), 7.33 (t, J = 7.6 Hz, 2H), 7.27-7.21 (m, 5H), 6.49 (s, 1H), 4.54 (d, J = 2.8 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.4, 138.2, 134.4, 131.6, 128.8, 128.6, 127.9, 127.6, 126.9, 44.1.

***N*-(4-methylbenzyl)benzamide, 3av.**[60] Off- white solid, 75 mg, 82% of yield (hexanes/ethyl acetate, 80:20 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.6 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.32 (t, J = 7.6 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.07 (d, J = 7.6 Hz, 2H), 6.41 (s, 1H), 4.50 (d, J = 5.6 Hz, 2H), 2.26 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.3, 137.3, 135.2, 134.5, 131.5, 129.4, 128.6, 127.9, 126.9, 43.9, 21.1.

***N*-(4-methoxybenzyl)benzamide, 3aw.**[61] Off-white solid, 79 mg, 90% of yield (hexanes/ethyl acetate, 80:20 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.6 Hz, 2H), 7.52-7.40 (m, 3H), 7.28 (d, J = 7.6 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 6.60 (s, 1H), 4.57 (d, J = 5.6 Hz, 2H), 3.80

(s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.4, 159.1, 134.4, 131.5, 129.3, 128.6, 126.9, 114.5, 55.3, 43.6.

***N*-(4-fluorobenzyl)benzamide, 3ax.**[62] Grey solid, 68 mg, 75% of yield (hexanes/ethyl acetate, 80:20 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 6.4 Hz, 1H), 7.33 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 6.4 Hz, 2H), 6.93 (t, J = 8.0 Hz, 2H), 6.58 (s, 1H), 4.50 (d, J = 5.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.4, 162.2 (d, $^1J_{C\text{-}F}$ = 244.1 Hz), 134.2, 134.1 (d, $^4J_{C\text{-}F}$ = 2.9 Hz), 131.7, 129.5 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 128.6, 126.9, 115.6 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 43.3. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -114.9.

***N*-(4-chlorobenzyl)benzamide, 3ay.**[63] Off-white solid, 66 mg, 77% of yield (hexanes/ethyl acetate, 80:20 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 7.6 Hz, 2H), 7.41 (t, J = 7.2 Hz, 1H), 7.33 (t, J = 7.6 Hz, 2H), 7.23-7.20 (m, 2H), 6.93 (t, J = 8.4 Hz,2H), 6.58 (s, 1H), 4.50 (d, J = 5.6Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.4, 163.4, 161.0, 134.2, 131.6, 129.5, 128.6, 126.9, 115.7, 115.5, 43.3.

***N*-(1-phenylethyl)benzamide, 3az.**[64] Off white-solid, 73 mg, 79% of yield (hexanes/ethyl acetate, 80:20 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 6.8 Hz, 1H), 7.33-7.24 (m, 6H), 7.18 (t, J = 7.2 Hz, 1H), 6.43 (s, 1H), 5.27-5.20 (m, 1H), 1.50 (d, J = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.6, 143.2, 134.6, 131.5, 128.7, 128.5, 127.4, 126.9, 126.3, 49.2, 21.7.

***N*-(pyridin-2-ylmethyl)benzamide, 3ba.**[62] Off-white solid, 63 mg, 65% of yield (hexanes/ethyl acetate, 80:20 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, J = 4.0 Hz, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.71 (s, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.42-7.29 (m, 4H), 7.15 (t, J = 7.2 Hz, 1H), 4.69 (d, J = 5.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.4, 156.3, 148.7, 137.2, 134.3, 131.5, 128.5, 127.1, 122.3, 122.6, 44.7.

***N*-phenethyl benzamide, 3ca.**[65] Off-white solid, 84 mg, 91% of yield (hexanes/ethyl acetate, 80:20 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.2 Hz, 2H), 7.50 (t, J = 7.2 Hz, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.27 (t, J = 7.2 Hz, 3H), 6.30 (s, 1H), 3.76-3.71 (m, 2H), 2.95 (t, J = 6.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.5, 138.9, 134.7, 131.4, 128.8, 128.7, 128.6, 126.8, 126.6, 41.2, 35.7.

***N*-(4-methoxyphenethyl)benzamide, 3da.**[66] Off-white solid, 78 mg, 93% of yield (hexanes/ethyl acetate, 70:30 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.2 Hz, 2H), 7.49 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.8 Hz,

2H), 6.28 (s, 1H), 3.81 (s, 3H) 3.72-3.67 (m, 2H), 2.89 (t, J = 6.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.5, 158.3, 134.7, 131.4, 130.9, 129.8, 128.6, 126.8, 114.1, 55.3, 41.3, 34.8.

***N*-benzyl-3-methylbenzamide, 3ea.**[67] Pale brown solid, 82 mg, 78% of yield (hexanes/ethyl acetate, 80:20 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.48 (t, J = 4.8 Hz, 1H), 7.28-7.21 (m, 7H), 6.39 (s, 1H), 4.56 (d, J = 5.6 Hz, 2H), 2.30 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.6, 138.5, 138.3, 134.4, 132.3, 128.8, 127.9, 127.6, 123.9, 44.1, 21.4.

***N*-benzyl-4-methylbenzamide, 3fa.**[68] Off-white solid, 78 mg, 75% of yield (hexanes/ethyl acetate, 80:20 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 2H), 7.28-7.20 (m, 5H), 7.15 (d, J = 8.0 Hz, 2H), 6.32 (s, 1H), 4.57 (d, J = 5.6 Hz, 2H), 2.31 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 167.3, 142.0, 138.3, 131.5, 129.3, 128.8, 127.9, 127.6, 126.9, 44.1, 21.4.

***N*-benzyl-4-fluorobenzamide, 3ga.**[69] Grey-solid, 87 mg, 81% of yield (hexanes/ethyl acetate, 80:20 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74-7.70 (m, 2H), 7.28-7.22 (m, 5H), 7.02 (t, J = 8.4 Hz, 2H), 6.36 (s, 1H), 4.55 (d, J = 5.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.3, 164.7(d, $^1J_{C\text{-}F}$ = 244.1 Hz), 138.03, 130.5 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 129.3 (d, $^3J_{C\text{-}F}$ = 8.9 Hz), 128.8, 127.9, 127.7, 115.7 (d, $^2J_{C\text{-}F}$ = 21.7 Hz), 44.2. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -108.0.

General Procedure for Esterification from Imidazolium Salts *via* C-C bond Cleavage with Characterization Data

An oven-dried 8 mL vial equipped with a stir bar was charged with **4a** (1 equiv), **1a** (1.5 equiv), potassium carbonate (1.5 equiv) in DMF (1 mL). The reaction mixture was placed in a preheated oil bath at 80 °C and stirred for 14 h. After the indicated time, the solvent was evaporated, and the crude material was purified by column chromatography on silica gel with n-hexane-ethyl acetate or hexanes–diethyl ether as eluent, to yield the title compound.

Phenyl benzoate, 5aa.[40] Off-white solid, 31 mg, 25% of yield (hexanes/ethyl acetate, 90:10 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 8.0 Hz, 2H), 7.21 (d, J = 7.2 Hz, 1H), 7.14 (d, J = 7.2 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.2, 150.9, 133.6, 130.2, 129.5, 128.6, 125.9, 121.7.

***o*-Tolyl benzoate, 5ab.**[70] Colorless oil, 25 mg, 26% of yield (hexanes/ethyl acetate, 90:10 v/v). ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.22-7.17 (m, 2H), 7.13-7.02 (m, 2H), 2.17 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 164.8, 149.5, 133.6, 131.2, 130.2, 128.6, 127.0, 126.1, 122.0, 16.3.

***m*-Tolyl benzoate, 5ac.**[71] Colorless oil, 25 mg, 26% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.02-6.93 (m, 3H), 2.31 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.3, 150.9, 139.7, 133.5, 130.2, 129.2, 128.6, 126.7, 122.3, 118.6, 21.3.

***p*-Tolyl benzoate, 5ad.**[70] Off white solid, 27 mg, 28% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.2 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 2.31 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.4, 148.7, 135.5, 133.5, 130.2, 130.0, 128.5, 121.4, 20.9.

4-Chlorophenyl benzoate, 5ae.[72] Yellow oil, 17 mg, 19% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.9, 149.4, 133.8, 131.3, 130.2, 129.6, 128.6, 123.1.

Naphthalen-2-yl benzoate, 5af.[72] Off-white solid, 11 mg, 13% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.6 Hz, 2H), 7.85-7.75 (m, 3H), 7.63-7.57 (m, 2H), 7.49-7.41 (m, 4H), 7.30-7.28 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.0, 151.1, 133.8, 133.7, 131.5, 130.2, 129.6, 129.5, 128.6, 127.8, 127.7, 126.6, 125.7, 121.3, 118.7.

Phenyl-3-methylbenzoate, 5ag.[73] Colorless oil, 22 mg, 20% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.92 (m, 2H), 7.37-7.30 (m, 4H), 7.21-7.12 (m, 3H) 2.37 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.4, 151.0, 138.4, 134.4, 130.7, 129.5, 128.5, 127.3, 125.9, 121.8, 21.3.

Phenyl-4-methylbenzoate, 5ah.[74] Colorless oil, 20 mg, 18% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.35-7.23 (m, 5H), 2.48 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.3, 151.0, 144.4, 130.2, 129.5, 129.3, 126.8, 125.8, 121.8, 21.8.

Phenyl-4-fluorobenzoate, 5ai.[74] Off-white solid, 28 mg, 25% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27-8.24 (m, 2H), 7.46 (t, *J* = 5.6 Hz, 2H), 7.33-7.19 (m, 5H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.1 (d, $^{1}J_{C\text{-}F}$ = 253.4 Hz), 164.2, 150.9, 132.9 (d, $^{3}J_{C\text{-}F}$ = 9.4 Hz), 129.5, 126.02, 125.8 (d, $^{4}J_{C\text{-}F}$ = 2.9 Hz), 121.6, 115.9 (d, $^{2}J_{C\text{-}F}$ = 21.9 Hz). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -104.4.

Benzyl benzoate, 5aj.[75] Colorless oil, 68 mg, 70% of yield. (0.5 g batch yielded 0.520 g) (hexanes/ethyl acetate, 95:05 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.50- 7.37 (m, 7H), 5.41 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.5, 136.1, 133.1, 130.2, 129.7, 128.6, 128.4, 128.3, 128.2, 66.7.

4-Methylbenzyl benzoate, 5ak.[75] Colorless oil, 80 mg, 72% of yield (hexanes/ethyl acetate, 95:05 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.0 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.33-7.23 (m, 4H), 7.09 (d, *J* = 8.0 Hz, 2H), 5.22 (s, 2H), 2.25 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.5, 138.2, 133.1, 133.0, 130.3, 129.7, 129.3, 128.4, 128.4, 66.7, 21.3.

4-Methoxybenzyl benzoate, 5al.[75] Off-white solid, 66 mg, 76% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.36-7.30 (m, 4H), 7.09 (d, *J* = 7.8 Hz, 2H), 5.22 (s, 2H), 3.75 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.5, 159.7, 132.9, 130.3, 130.1, 129.7, 128.3, 128.2, 113.9, 66.6, 55.3.

4-Fluorobenzyl benzoate, 5am.[75] Colorless oil, 59 mg, 65% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.33-7.30 (m, 4H), 6.95 (t, *J* = 8.2 Hz, 2H), 5.21 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.1 (d, $^{1}J_{C\text{-}F}$ = 246.1 Hz), 161.4, 133.1, 131.9 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 130.2 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 130.0, 129.7, 128.4, 115.6 (d, $^{2}J_{C\text{-}F}$ = 21.6 Hz), 66.0. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -113.6.

4-Chlorobenzyl benzoate, 5an.[76] Yellow oil, 57 mg, 67% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.33-7.23 (m, 6H), 5.21 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.3, 134.6, 134.2, 133.2, 129.9, 129.7, 129.6, 128.8, 128.5, 65.9.

2,4-Dichlorobenzyl benzoate, 5ao.[77] Grey solid, 49 mg, 62% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.38-7.34 (m, 4H), 7.19-7.16 (m, 1H), 5.33 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.1, 133.7, 133.4, 132.2, 131.4, 129.6, 128.7, 128.4, 127.4, 126.2, 62.4.

2-Nitrobenzyl benzoate, 5ap.[78] Pale yellow solid, 44 mg, 53% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-8.01 (m, 3H), 7.62-7.50 (m, 3H), 7.45-7.38 (m, 3H), 5.71 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.9. 147.6, 133.8, 133.4, 132.4, 129.8, 129.6, 128.9, 128.8, 128.6, 125.1, 63.4.

4-Nitrobenzyl benzoate, 5aq.[77] Yellow solid, 40 mg, 49% of yield (hexanes/ethyl acetate, 85:15 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.2 Hz, 2H), 8.01 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 8.2 Hz, 3H), 7.40 (t, *J* = 8.2 Hz, 2H), 5.39 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.1. 147.7, 143.4, 133.5, 129.7, 129.5, 128.6, 128.3, 123.9, 65.2.

Pyridin-3-ylmethyl benzoate, 5ar.[79] Pale brown liquid, 50 mg, 52% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 1.6 Hz, 1H), 8.59 (d, *J* = 4.8 Hz, 1H), 8.06 (d, *J* = 7.2 Hz, 2H), 8.79 (d, *J* = 7.6 Hz, 1H), 7.58-7.31 (m, 4H), 5.38 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.2, 149.6, 136.0, 133.3, 131.7, 129.7, 128.5, 123.5, 64.1.

Naphthalen-1-ylmethyl benzoate, 5as.[76] Off-white solid, 45 mg, 55% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.95-7.90 (m, 2H), 7.68-7.42 (m, 7H), 5.86 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.5, 133.8, 133.0, 131.8, 131.5, 130.1, 129.8, 129.4, 128.8, 128.4, 127.5, 126.7, 126.0, 125.3, 123.7, 65.2.

Benzhydryl benzoate, 5at.[80] Colorless oil, 52 mg, 67% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.39-7.16 (m, 12H), 7.04 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 165.6, 140.3, 133.2, 130.2, 129.8, 128.6, 128.5, 127.9, 127.2, 77.4.

Anthracen-9-ylmethyl benzoate, 5au.[81] Pale yellow solid, 38 mg, 51% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.34 (d, *J* = 9.2 Hz, 2H), 7.95-7.89 (m, 4H), 7.51-7.23 (m, 7H), 6.29 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.8, 133.0, 131.4, 131.2, 129.8, 129.3, 129.1, 128.3, 126.7, 126.3, 125.2, 124.0, 59.4.

4-Methoxybenzyl-3-methylbenzoate, 5av.[82] Colorless oil, 63 mg, 68% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.87 (m, 2H), 7.42-7.28 (m, 4H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.31 (s, 2H), 3.84 (s, 3H), 2.41 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.7, 159.6, 138.1, 133.7, 130.2, 130.1, 128.2, 126.8, 113.9, 66.5, 55.3, 21.3.

4-Methoxybenzyl-4-methylbenzoate, 5aw.[83] Colorless oil, 59 mg, 65% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.31 (s, 2H), 3.84

(s, 3H), 2.42 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.6, 159.6, 143.6, 130.0, 129.7, 129.0, 128.3, 127.5, 113.9, 66.4, 55.3, 21.7.

Benzyl-2-fluorobenzoate, 5ax.[84] Colorless oil, 65% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (t, J = 7.2 Hz, 1H), 7.43-7.35 (m, 3H), 7.30-7.22 (m, 3H), 7.10-7.01 (m, 2H), 5.29 (s, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 164.2 (d, $^{4}J_{C\text{-}F}$ = 3.6 Hz), 162.0 (d, $^{1}J_{C\text{-}F}$ = 258.5 Hz), 135.8, 134.6 (d, $^{3}J_{C\text{-}F}$ = 9.0 Hz), 132.2, 128.6, 128.3, 128.1, 124.0 (d, $^{4}J_{C\text{-}F}$ = 4.0 Hz), 118.7 (d, $^{3}J_{C\text{-}F}$ = 9.7 Hz), 117.1 (d, $^{2}J_{C\text{-}F}$ = 22.3 Hz), 66.9.

(3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[*a*]phenanthren-3-yl benzoate, **5ay.**[85] Colorless solid, 6 mg, 10% of yield (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 6.8 Hz, 2H), 7.47 (t, J = 8.4 Hz, 1H), 7.35 (t, J = 8.0 Hz, 2H), 5.34 (d, J = 3.6 Hz, 1H), 4.82-4.76 (m, 1H), 2.39 (d, J = 7.6 Hz, 2H), 1.48 (m, 26H), 0.93 (s, 3H), 0.85 (d, J = 6.4 Hz, 3H), 0.79 (dd, J = 6.8, 2.0 Hz, 6H), 0.61 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 164.9, 138.6, 131.7 129.8, 128.5, 127.2, 121.8, 73.6, 55.7, 55.1, 49.0, 41.3, 38.7, 38.5, 37.2, 36.0, 35.6, 34.8, 30.9, 28.7, 28.3, 27.2, 26.8, 23.3, 22.8, 21.8, 21.5, 20.0, 18.3, 10.8.

***N*-(2-(1*H*-indol-3-yl) ethyl) benzamide, 7aa**.[86] Off-white solid 42 mg, 51% of yield (hexanes/ethyl acetate, 75:25 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.82 (s, 1H), 8.64 (t, J = 6.8 Hz, 1H). 7.87 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.52-7.45 (m,3H), 7.36 (d, J = 8.0 Hz, 1H), 7.19 (s,1H), 7.08 (t, J = 8.0 Hz, 1H), 6.99 (t, J = 8.0 Hz, 1H), 3.58-3.53 (m,2H), 2.96 (t, J = 8.0 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 166.6, 136.7, 135.2, 131.5, 128.7, 127.7, 127.6, 123.1, 121.4, 118.8, 118.7, 112.4, 111.8, 40.7, 25.6.

(1-benzoylpiperidin-4-yl)methyl benzoate, 8aa,[87] Off-white solid, 28 mg, 20% (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98 (d, J = 7.2 Hz, 2H), 7.67 (t, J = 7.6 Hz, 1H), 7.54 (t, J = 7.6 Hz, 2H), 7.45-7.43 (m, 3H), 7.39-7.36 (m, 2H), 4.52 (bs, 1H), 4.18 (d, J = 6.4 Hz, 2H), 3.60 (bs, 1H), 3.06 (bs, 1H), 2.80 (bs, 1H), 2.09-1.71 (m, 4H), 1.29-1.26 (m, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 169.4, 166.1, 136.8, 133.8, 130.2, 129.8, 129.6, 129.3, 128.8, 127.1, 68.8, 47.3, 35.6, 29.3, 28.6.

***N*-(2-hydroxyethyl)benzamide, 9aa,**[88] Brown liquid, 66 mg, 49 % (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.44 (s, 1H), 7.86 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 3.52 (t, J = 6.4 Hz, 2H), 3.41(bs, 1H), 3.35 (t, J = 6.4 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 166.8, 134.9, 131.5, 128.6, 127.6, 60.2, 42.6.

***N*-(4-hydroxyphenyl)benzamide, 10aa,**[89] Brown flakes, 46 mg, 48% (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.02 (s, 1H), 9.25 (s, 1H), 7.93 (d, J = 7.2 Hz, 2H), 7.58-7.49 (m, 5H), 6.74 (d, J = 8.2 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.4, 154.2, 135.6, 131.7, 131.1, 128.7, 127.9, 122.7, 116.1, 115.4.

***N*-(2-hydroxyphenyl)benzamide, 11aa,**[90] Brown solid, 54 mg, 56% (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.76 (s, 1H), 9.53 (s, 1H), 7.98 (d, J = 7.6 Hz, 2H), 7.69 (d, J = 7.6 Hz, 1H), 7.62-7.52 (m, 3H), 7.05 (t, J = 8.0 Hz, 1H), 6.93 (d, J = 8.0 Hz, 1H), 6.84 (t, J = 7.8 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 165.7, 149.8, 134.8, 132.1, 128.9, 127.9, 126.1, 124.6, 119.5, 116.4.

(*Z*)-3-(hydroxy(phenyl)methylene)-1-methylindolin-2-one, 13aa.[91] pale yellow solid, 52 mg, 61% (hexanes/ethyl acetate, 90:10 v/v). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 6.4 Hz, 2H), 7.49-7.44 (m, 3H), 7.11 (t, J = 7.6 Hz, 2H), 6.87-6.80 (m, 2H), 3.32 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.0, 170.9, 139.1, 134.1, 131.3, 128.6, 128.4, 125.9, 121.8, 121.5, 119.7, 108.3, 101.4, 25.8.

ASSOCIATED CONTENT

Supporting Information

Isolated *C*-acyl imidazolium salts and the ^{1}H, ^{13}C and ^{19} F NMR spectra. This material is available free of charge *via* the Internet at http:// pubs.acs.org.

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