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Photocatalytic acyl azolium-promoted alkoxycarbonylation of trifluoroborates

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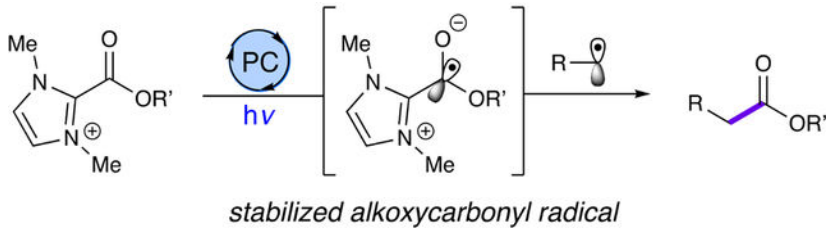
Abstract

Despite recent advancements in the selective generation and coupling of organic radical species, the alkoxycarbonyl radical remains underexplored relative to other carbon-containing radical species. Drawing inspiration from new strategies for generating acyl radical equivalents utilizing dual *N*-heterocyclic carbene catalysis and photocatalysis, we have prepared dimethylimidazolium esters that can function as an alkoxycarbonyl radical surrogate under photocatalytic conditions. We demonstrate the synthetic utility of these azolium-based partners through the preparation of esters arising from the coupling of this radical surrogate with an oxidatively generated alkyl radical.

Graphical Abstract



Keywords

Photocatalysis; *N*-Heterocyclic Carbene; Alkoxycarbonyl radical; Esterification; Radical-radical coupling

1. Introduction

During the past few decades, organic synthetic methodology has seen a resurgence of interest in radical reactivity. Out of the various carbon-containing radical species that have

Supplementary Material

Supporting Information contains complete structures of all compounds as well as relevant characterization data for new compounds.

Declaration of interests

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

recently shown novel applications, acyl radicals have attracted special interest due to their potential synthetic utility.[1] A subset of acyl radicals, alkoxycarbonyl radicals, are difficult to generate and extremely short-lived due to their tendency to decarboxylate and decarbonylate, generating undesired species *in situ* that can then participate in competing reactions.[2] Nevertheless, they have been historically employed in intramolecular reactions to construct complex lactones from acylic esters. One representative example is from Corey and coworkers' 1987 synthesis of atractyligenin, wherein a phenylselenocarbonate, in the presence of tributyltinhydride and azobisisobutyronitrile (AIBN), fragments to form an alkoxycarbonyl radical (Fig. 1A). This alkoxycarbonyl radical is trapped by an adjacent alkene to form a bridging lactone.[3] Trost and coworkers employed a similar strategy to construct the key lactone component of (−)-pseudolaric acid B.[4]

Recent advancements in radical chemistry have enabled the selective generation of a much broader variety of useful carbon-containing radicals, but the alkoxycarbonyl radical remains comparatively unexplored due to its relative instability. In 2010, Taniguchi and coworkers demonstrated the catalytic generation of alkoxycarbonyl radicals from carbazates (Fig. 1A).[5] Using an iron (II) catalyst and a superstoichiometric quantity of alkoxycarbonyl radical precursor, their group was able to difunctionalize alkenes using the alkoxycarbonyl radical. In contrast, a recent report from the groups of Hou and Li details the generation of alkoxycarbonyl radicals through hydrogen atom abstraction from formate esters by a reductively generated isopropoxy radical.[6] Notably, the reaction was performed using the formate ester as the solvent which limited the scope of compatible ester substrates (Fig.1A).[7]

To further expand the reactivity accessible by single-electron transformations, our group has developed photochemical *N*-heterocyclic carbene (NHC) catalysis.[8] Work from the Ohmiya group in this field demonstrated that thiazolium-derived Breslow intermediates can be spontaneously oxidized to generate a stabilized acyl radical that engages in radical-radical coupling.[9] Subsequently, our group identified that acyl azoliums, both isolated[8a] and generated in-situ[8b], can undergo single-electron reduction to generate stabilized acyl radical equivalents for coupling, providing ketones in high yield under mild conditions (Fig.1B). Studer and others have since harnessed the reaction of single-electron NHC operators to forge key C–C and C–X bonds.[10]

Drawing inspiration from the NHC-derived stabilization demonstrated earlier by our group and others, we sought to develop a modular alkoxycarbonyl radical surrogate for the formation of C–C bonds. An azolium ester, following single-electron transfer, could act as a stabilized alkoxycarbonyl radical to couple with an oxidatively generated alkyl radical (Fig. 1C). If successful, this reaction would be, to the best of our knowledge of the literature, the first intermolecular radical-radical coupling employing an alkoxycarbonyl radical.

2. Results and Discussion

2.1. Initial Screening and Optimization

Our initial investigation of the radical-radical coupling of stabilized alkoxycarbonyl radicals began with the selection of coupling partners. Since we planned on developing an azolium-tethered species that would be reduced by the photocatalyst, an oxidative radical precursor

would be needed to turn over the photocatalyst. From a variety of oxidative alkyl radical precursors, we selected potassium benzyltrifluoroborate which was prepared on multigram scale without chromatography. Potassium alkyltrifluoroborates have multiple attractive features including bench stability, substrate diversity, and higher atom economy[11] compared to other oxidative alkyl radical precursors.[12]

To proceed with the optimization and substrate scope, we required a streamlined route to **1a** and other imidazolium esters. Fortunately, the precursor monomethylated imidazole ester **5a** could be prepared on decagram scale according to a known procedure (Scheme 1A).[13] To synthesize a variety of imidazolium esters, we needed a common precursor that could react directly with a variety of alcohols to yield various precursor esters. This precursor came in the form of 2-trichloroacetyl-N-methylimidazole **6**, which could be prepared on 50 gram scale without chromatography.[14] Furthermore, reacting **6** with a slight excess of partner alcohol and 4-dimethylaminopyridine (DMAP) gave precursor esters **5** in moderate to high yields (Scheme 1B). With this general route secured, we prepared imidazolium esters **1** in high yields without column chromatography by simple addition of methyl triflate, in up to a 3 gram scale (Scheme 1C).

Previous work from our group demonstrated that isolated acyl imidazoliums and acyl benzimidazoliums were both effective reductive precursors to acyl radical equivalents.[8a] After preparing both the ethyl imidazolium and benzimidazolium esters, screening the two with a variety of solvent systems and photocatalysts provided a number of hits, with the highest-performing utilizing the imidazolium ester in dichloromethane with heteroleptic iridium photocatalyst **PC1**. Contrary to our group's previously reported results that determined acyl benzimidazoliums outperform other scaffolds in terms of effiency,[8a] the benzimidazolium ester precursor provided lower yields than the imidazolium ester (Table 1, entries 1–2), so we decided to pursue optimization using the imidazolium scaffold.

With ready access to imidazolium esters, we pursued optimization of the radical-radical coupling (Table 1). A solvent screen indicated that the reaction performed better in dichloromethane compared to other more polar solvents (entries 3–5). Further, we discovered that increasing the equivalents of trifluoroborate did not lead to an increase in yield (entry 6). Given the relative insolubility of the trifluoroborate salt in dichloromethane, it was unsurprising that lower reaction concentrations, which would allow for more trifluoroborate in solution, performed better (entries 7–9). The organophotocatalyst **PC2**, which has similar oxidation and reduction potentials to **PC1**,[15] did not improve the yield (entry 10). Finally, a screen of light sources led to an increase in yield to 50% under 427 nm LED irradiation (entries 11–12). We examined Lewis and Brønsted basic additives commonly employed in reactions using potassium trifluoroborate salts[16] but neither approach improved the yields in our system (entries 13–14).

2.2. Trifluoroborate Substrate Scope

We initially investigated the scope of this radical-radical coupling, initially examining substitution on the alkyl portion of the trifluoroborate salt. A variety of functional groups were tolerated on the aryl ring of the benzyl trifluoroborate in low to moderate yields (**4a**-**4g**). The reaction also accommodated a secondary benzylic alkyl group (**4h**) and a

naphthylic group (**4i**) in moderate yields. Disubstitution was also tolerated on the aryl ring, again in low to moderate yields (**4j-k**). More interestingly, the radical-radical coupling was accomplished with alkyltrifluoroborates derived from conjugate acceptors (**4l-n**). These products represent a formal umpolung addition of an ester group to a conjugate acceptor, which remains a challenging transformation currently inaccessible by two-electron NHC chemistry.

Additionally, the chromone-derived trifluoroborate product **4n** is generated from a heteroatom-stabilized alkyl radical, rather than a benzylic stabilized alkyl radical, suggesting the reaction could be optimized for other heteroatom-stabilized radicals to produce glycolic and α-amino esters. This product also demonstrates a new way to access 2-carboxychromanone products such as **4n**, which form the core of a large number of natural products.[17] Secondary alkyl radical precursors (cyclohexyl and 2-indanyl) were also tested under the standard conditions, but provided no desired product.

2.3. Imidazolium Ester Substrate Scope

The scope with regard to imidazolium esters was investigated using the ester-containing alkyl trifluoroborate **3f** (Table 3). We obtained moderate to good yields with primary and secondary alcohol-derived esters including one containing a sensitive thiophene ring (**4f,4o-4u**). Substrates containing carbamates proceeded in low to moderate yields, potentially due to competing hydrogen atom transfer from the substrate to the benzylic radical to generate α-amino stabilized radicals (**4v,4w**). Tertiary alcohol-derived esters provided products in low yields, likely due to competing β-scission of the reduced imidazolium ester resulting in a stabilized tertiary radical (**4x,4y**). Inclusion of a trimethylsilyl propargyl ester resulted in low yields as well (**4z**). Finally, esters of more complex alcohols such as epi-androsterone proceeded in low to moderate yields (**4aa,4ab**). It is worth noting that when starting with enantiopure imidazolium esters, the products were obtained with complete retention of stereochemistry (**4w,4aa,4ab**). Despite the mixed performance of the coupling, this demonstrates a readily accessible and modular method to prepare these unique di- and triesters.

2.4. Mechanistic Studies and Proposed Pathway

To probe the mechanism of this coupling, several control experiments were performed (Scheme 2). Both light and photocatalyst proved necessary for formation of product (Table 1, entries 15–16). Substituting ethyl chloroformate or diethyl carbonate for **1a** also yielded no product, suggesting that the imidazolium ester is necessary to turn over the photocatalyst (Scheme 2A). Addition of one equivalent of the radical trapping agent (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) resulted in dramatically reduced yields, suggesting the involvement of open-shell species (Scheme 2B). In 1994, the Smith group reported the formation of asymmetric carbonates through the addition of alcohols to dimethylimidazolium esters similar to **1a**.[18] To ensure that the products **4** formed in this reaction were not generated from a nucleophilic addition to the imidazolium ester with elimination of the NHC, we performed a crossover experiment, combining cyclohexyl imidazolium ester **1h** with an equimolar amount of diethyl carbonate or ethyl chloroformate and subjecting the mixture to the standard reaction conditions with trifluoroborate **3a**

(Scheme 2C). For both reactions, the cyclohexyl ester was the major product, with only trace quantities of the ethyl ester detected by gas chromatography mass spectrometry (GC-MS), indicating that the reaction likely proceeds through a direct radical-radical coupling rather than in-situ generation of an anionic carbon nucleophile.

Given the oxidation and reduction potentials of the substrates and **PC1**,[19] we propose the photocatalyst proceeds through a reductive quenching cycle (Fig. 2). The reduction potential of **1a** at −1.5 V vs SCE (Fig. 2) is outside the excited state reduction potential of **PC1** ($E_{1/2}$ Ir^{III*}/Ir^{IV} = −0.89 V), but more in line with the reduced state reduction potential of **PC1** ($E_{1/2}$ Ir^{III}/Ir^{II} = −1.37 V). Moreover, the oxidation potential of **3a**, +1.1 V vs SCE,[20] is within the excited state oxidation potential of **PC1**, ($E_{1/2}$ Ir^{III*}/Ir^{II} = +1.21 V). In accordance with cyclic voltammetry data and mechanistic studies, we propose that the mechanism begins with the initial oxidation of the trifluoroborate salt **3** by excited state **PC1**. Subsequent reduction of **1a** by reduced **PC1** generates the stabilized alkoxycarbonyl radical. Fragmentation of the oxidized trifluoroborate to the alkyl radical, followed by radical-radical coupling and elimination of the free carbene affords the product ester **4**.

3. Conclusion

We have demonstrated a new reductive alkoxycarbonyl radical surrogate easily accessed from inexpensive commercial chemicals *via* two different routes. Inspired by recent developments in single-electron NHC chemistry, we demonstrate the unique potential of the dimethylimidazolium moiety to enable single-electron reduction and stabilize the highly transient alkoxycarbonyl radical. Additionally, we have developed a new radical-radical cross-coupling reaction combining diakylimidazolium esters and potassium alkyltrifluoroborates to prepare esters bearing a variety of functional groups. Current studies are underway to leverage the unique stabilizing properties of *N*-heterocyclic carbenes to further the scope of NHC-radical surrogates beyond acyl and alkoxycarbonyl radicals.

4. Experimental

4.1. General Information

All reactions were carried out under an argon or nitrogen atmosphere in oven-dried glassware with magnetic stirring. All solvents were purified by passing through a bed of activated alumina, dried over 3Å molecular sieves, and then degassed using the freeze-pump-thaw method (3–4 cycles). Reagents were purified prior to use unless otherwise stated following the guidelines of Perrin and Armarego. Purification of reaction products was carried out by flash chromatography on Biotage Isolera 4 systems with Ultra-grade silica cartridges. Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light. 1H NMR spectra were recorded on a Bruker AVANCE III 500 MHz with direct cryoprobe (500 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl3 at 7.26 ppm). Data are reported as (ap = apparent, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, b = broad; coupling constant(s) in Hz; integration.) Proton-decoupled 13C NMR spectra were recorded on a Bruker AVANCE III 500 MHz with direct cryoprobe (125 MHz) spectrometer and are reported in ppm using solvent as an internal standard (CDCl3 at 77.16

ppm). 19F and 11B NMR spectra were acquired on a 500 MHz Bruker AVANCE III HD spectrometer equipped with a TXO prodigy probe. Reactions were monitored by LCMS or GCMS using a WATERS Acquity-H UPLC-MS with a single quad detector (ESI) or an Agilent 7890 gas chromatograph equipped with a 5975C single quadrupole EI-MS, respectively. High-resolution mass spectrometry (HRMS) was obtained using an Agilent 6201 MSLC-TOF (ESI). FTIR data were collected at room temperature on a Bruker Tensor 37 FTIR Spectrometer equipped with a Mid IR detector and KBr beam splitter. The spectrum was collected in attenuated total reflectance (ATR) mode in the range of 4000 to 600 cm^{-1}. The data were averaged over 16 scans. The OPUS software was used for the data acquisition. Optical rotation data was obtained with an AUTOPOL VI polarimeter using the 589 nm sodium D line. All photocatalytic reactions were irradiated using a SynLED Parallel Photoreactor (465–470 nm) purchased from Sigma-Aldrich or four PR160L Kessil Lamps of the corresponding wavelength (390 or 427 nm).

See Supporting Information for complete structures of all compounds as well as relevant characterization data for new compounds.

4.2. Preparation of Trifluoroborate Salts

Trifluoroborate salts **3a**,[21] **3b**,[13] **3c**,[13] **3d**,[22] **3e**,[13] **3f**,[22] **3g**,[23] **3h**,[24] **3i**,[22] **3j**,[25] **3l**,[24] **3m**,[26] and **3n**[27] were prepared according to known procedures and ^{1}H and ^{11}B NMR were consistent with the literature.

4.2.1. Potassium (2,6-difluorobenzyl)trifluoroborate 3k—

Potassium (2,6-difluorobenzyl)trifluoroborate **3k** was prepared according to a modified literature procedure.[22] To an oven-dried 20 mL vial equipped with a stir bar was added 2,6-difluorobenzyl bromide (5 mmol), triphenylphosphine (0.65 mmol), and bis(pinacolato)diboron (7.5 mmol). The vial was taken into the glovebox and copper (I) iodide (0.5 mmol) and lithium methoxide (10 mmol) were added. DMF (10 mL) was added, and the reaction was sealed. The mixture was stirred vigorously for 24 hours, after which the slurry was diluted with EtOAc (10 mL) and filtered through a plug of silica, washing with additional EtOAc (50 mL). The unpurified boronic ester was concentrated to ~25 mL and diluted with methanol (25 mL), then cooled to 0 °C. Saturated aq. KHF_2 (7 mL, 6 equiv.) was added dropwise, and the mixture was allowed to come to room temperature. After stirring an additional 1 hr, the solution was concentrated, and residual pinacol/water was removed by azeotropic evaporation with toluene (3×50 mL). The solid was dried under high vacuum overnight, then triturated with acetone (5×50 mL). The solution was concentrated, dissolved in a minimum volume of acetone, and diethyl ether (approx. 3x volume of acetone) was added to give a white precipitate. The solid was filtered, washed with diethyl ether and hexanes, and dried to afford **3k** as a white powder (300 mg, 26%). ^{1}H NMR (500 MHz, acetone-d_6) □ 6.90 (m, 1H), 6.71 (m, 2H), 1.65 (bs, 2H). ^{13}C NMR (126 MHz, acetone-d_6) δ 162.6 (d, J = 10.9 Hz), 160.6 (d, J = 11.2 Hz), 122.8 (t, J = 10.2 Hz), 109.8 (dd, J = 19.5, 7.3 Hz). ^{19}F NMR (470 MHz, acetone-d_6) δ −115.87, −140.49 (dd, J = 112.0, 51.9 Hz). 11B NMR (160 MHz, acetone-d_6) δ 3.86 (q, J = 58.1 Hz). FTIR (ATR) cm^{-1}: 3229, 1589, 1465, 1261, 1065, 1011, 957, 776. HRMS (ESI/TOF) m/z: $[M-K]^-$ Calcd. for $C_7H_5BF_5$ 195.0410; Found 195.0410.

4.3. Preparation of Imidazole Esters

Imidazole ester 5a was prepared according to a known procedure, and **^{1}H** NMR was consistent with the literature.[28]

General procedure for the preparation of N-methyl imidazole esters **5**: To an oven-dried 20 mL vial equipped with a stir bar was added 2-trichloroacetyl-N-methylimidazole (5.0 mmol), DMAP (0.5 mmol), and the corresponding alcohol (10.0 mmol). The mixture was dissolved in THF (10 mL), then stirred overnight at room temperature. The unpurified reaction was concentrated and purified by column chromatography (ethyl acetate/hexanes) to afford imidazole ester **5**.

4.3.1. cyclopropylmethyl 1-methyl-1H-imidazole-2-carboxylate 5b—Prepared according to the general imidazole ester synthesis using cyclopropylmethanol. Isolated as a white solid (771 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (s, 1H), 6.95 (s, 1H), 4.08 (d, J = 7.4 Hz, 2H), 3.92 (s, 3H), 1.32 – 1.12 (m, 1H), 0.62 – 0.46 (m, 2H), 0.37 – 0.25 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 136.5, 129.2, 126.0, 70.0, 35.6, 9.7, 3.4. FTIR (ATR) cm^{-1}: 3103, 3008, 1709, 1427, 1394, 1261, 1137, 959, 789, 662. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_9H_{13}N_2O_2$ 181.0972; Found 181.0975.

4.3.2. cyclohexylmethyl 1-methyl-1H-imidazole-2-carboxylate 5c—Prepared according to the general imidazole ester synthesis using cyclohexylmethanol. Isolated as a white solid (937 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (s, 1H), 6.95 (s, 1H), 4.07 (d, J = 6.4 Hz, 2H), 3.93 (s, 3H), 1.82 – 1.71 (m, 3H), 1.70 – 1.63 (m, 2H), 1.62 – 1.56 (m, 1H), 1.26 – 1.05 (m, 3H), 1.02 – 0.89 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 136.6, 129.2, 126.0, 70.1, 36.8, 35.6, 29.5, 26.1, 25.4. FTIR (ATR) cm^{-1}: 3123, 2921, 2852, 1701, 1426, 1257, 1132, 787, 664. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{12}H_{19}N_2O_2$ 223.1441; Found 223.1441.

4.3.3. dodecyl 1-methyl-1H-imidazole-2-carboxylate 5d—Prepared according to the general imidazole ester synthesis using 1-dodecanol. Isolated as a white solid (1.38 g, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (s, 1H), 7.01 (s, 1H), 4.32 (t, J = 6.9 Hz, 2H), 4.00 (s, 3H), 1.78 (p, J = 7.1 Hz, 2H), 1.44 – 1.36 (m, 2H), 1.36 – 1.18 (m, 16H), 0.86 (t, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 136.7, 129.3, 126.1, 65.5, 35.8, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 28.6, 25.9, 22.6, 14.1. FTIR (ATR) cm^{-1}: 3096, 2951, 2920, 2850, 1721, 1466, 1421, 1253, 1135, 799, 663. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{31}N_2O_2$ 295.2380; Found 295.2378.

4.3.4. 2-(thiophen-2-yl)ethyl 1-methyl-1H-imidazole-2-carboxylate 5e—Prepared according to the general imidazole ester synthesis using 2-thiopheneethanol. Isolated as a white solid (1.02 g, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 – 7.11 (m, 2H), 7.00 (s, 1H), 6.93 – 6.86 (m, 2H), 4.53 (t, J = 7.3 Hz, 2H), 3.94 (s, 3H), 3.30 (td, J = 7.3, 0.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 139.1, 136.3, 129.4, 126.9, 126.3, 125.6, 123.9, 65.2, 35.7, 29.1. FTIR (ATR) cm^{-1}: 3092, 2953, 1715, 1411, 1258, 1129, 801, 699, 660. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{11}H_{13}N_2O_2S$ 237.0692; Found 237.0694;

4.3.5. 4-methoxyphenethyl 1-methyl-1H-imidazole-2-carboxylate 5f—Prepared according to the general imidazole ester synthesis using 4-methoxyphenethyl alcohol. Isolated as a clear oil (1.05 g, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.4 Hz, 2H), 7.14 (s, 1H), 7.01 (s, 1H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.48 (t, *J* = 7.7 Hz, 2H), 3.96 (s, 3H), 3.77 (s, 3H), 3.05 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 158.3, 136.6, 129.9, 129.4, 129.2, 126.2, 113.9, 65.9, 55.2, 35.8, 34.2. FTIR (ATR) cm^{-1}: 2955, 2835, 2361, 1706, 1512, 1415, 1243, 1123, 1030, 779, 663. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{17}N_2O_3$ 261.1234; Found 261.1235.

4.3.6. (tetrahydro-2H-pyran-4-yl)methyl 1-methyl-1H-imidazole-2-carboxylate 5g—Prepared according to the general imidazole ester synthesis using (tetrahydro-2H-pyran-4-yl)methanol. Isolated as a clear oil (896 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.18 (s, 1H), 4.31 (d, *J* = 6.9 Hz, 2H), 4.13 (s, 3H), 4.10 (dd, *J* = 11.5, 4.1 Hz, 2H), 3.52 (t, *J* = 11.1 Hz, 2H), 2.24 (ttt, *J* = 11.1, 7.1, 3.8 Hz, 1H), 1.86 (d, *J* = 12.7 Hz, 2H), 1.54 (qd, *J* = 12.3, 4.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 136.2, 129.2, 126.1, 69.0, 67.0, 35.5, 34.2, 29.3. FTIR (ATR) cm^{-1}: 2948, 2843, 1707, 1418, 1257, 1123, 1088, 988, 780, 664. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{11}H_{17}N_2O_3$ 225.1234; Found 225.1238.

4.3.7. cyclohexyl 1-methyl-1H-imidazole-2-carboxylate 5h—Prepared according to the general imidazole ester synthesis using cyclohexanol. Isolated as a clear oil (1.03 g, 99%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (s, 1H), 7.00 (s, 1H), 4.97 (tt, *J* = 9.9, 4.1 Hz, 1H), 3.99 (s, 3H), 2.08 – 1.95 (m, 2H), 1.88 – 1.78 (m, 2H), 1.68 – 1.54 (m, 3H), 1.47 – 1.32 (m, 2H), 1.32 – 1.18 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 137.0, 129.3, 126.0, 74.3, 35.9, 31.6, 25.2, 24.1. FTIR (ATR) cm^{-1}: 2934, 2858, 1702, 1412, 1256, 1127, 1011, 920, 781, 664. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{11}H_{17}N_2O_2$ 209.1285; Found 209.1286.

4.3.8. tert-butyl 4-((1-methyl-1H-imidazole-2-carbonyl)oxy)piperidine-1-carboxylate 5i—Prepared according to the general imidazole ester synthesis using 1-Boc-4-hydroxypiperidine. Isolated as an amorphous white solid (1.37 g, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (s, 1H), 7.03 (s, 1H), 5.14 (tt, *J* = 8.6, 4.0 Hz, 1H), 4.00 (s, 3H), 3.90 (bs, 2H), 3.16 (ddd, *J* = 13.4, 9.6, 3.4 Hz, 2H), 2.05 – 1.90 (m, 2H), 1.80 (dtd, *J* = 13.2, 9.2, 4.1 Hz, 2H), 1.46 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 154.8, 136.6, 129.5, 126.4, 79.7, 71.5, 41.6, 35.9, 30.6, 28.4. FTIR (ATR) cm^{-1}: 2967, 2932, 2867, 1716, 1683, 1423, 1233, 1171, 1125, 1025, 795. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{24}N_3O_4$ 310.1761; Found 310.1759.

4.3.9. (S)-2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl 1-methyl-1H-imidazole-2-carboxylate 5j—Prepared according to the general imidazole ester synthesis using N-Boc-L-serine methyl ester. Isolated as a thick clear oil (574 mg, 35%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (s, 1H), 6.99 (s, 1H), 5.93 (d, *J* = 8.7 Hz, 1H), 4.71 (dd, *J* = 11.2, 3.9 Hz, 1H), 4.65 (dd, *J* = 8.4, 4.0 Hz, 1H), 4.46 (dd, *J* = 11.2, 3.6 Hz, 1H), 3.92 (s, 3H), 3.71 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 158.3, 155.3, 135.7, 129.3, 126.5, 80.0, 64.8, 52.7, 52.6, 35.7, 28.1. FTIR (ATR) cm^{-1}: 2978, 1710,

1510, 1417, 1249, 1157, 1125, 1065, 916, 779, 729, 663. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{22}N_3O_6$ 328.1503; Found 328.1500.

4.3.10. tert-butyl 1-methyl-1H-imidazole-2-carboxylate 5k—To a 25 mL round-bottom flask equipped with a stir bar and reflux condenser was added 2-trichloroacetyl-N-methylimidazole (5 mmol), followed by sodium *tert*-butoxide (10 mmol). The mixture was suspended in *tert*-butanol (15 mL) and refluxed for 24 hours, after which it was cooled and diluted with dichloromethane (15 mL). Water (30 mL) was added and the layers separated. The aqueous layer was extracted with dichloromethane (3×15 mL), and the organic layers were combined, dried with sodium sulfate, and concentrated *in vacuo*. The unpurified residue was purified by silica gel chromatography (ethyl acetate/hexanes) to afford **5j** as a tan solid (341 mg, 37%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (s, 1H), 6.96 (s, 1H), 3.96 (s, 3H), 1.60 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 137.7, 129.0, 125.8, 82.5, 69.1, 35.9, 28.2, 21.8. FTIR (ATR) cm^{-1}: 3110, 2983, 1698, 1410, 1273, 1129, 922, 845, 782, 665. HRMS (ESI/TOF) m/z: $[M+Na]^+$ Calcd. for $C_9H_{14}N_2NaO_2$ 205.0947; Found 205.0951.

4.3.11. adamantan-1-yl 1-methyl-1H-imidazole-2-carboxylate 5l—To a 25 mL round-bottom flask equipped with a stir bar and reflux condenser was added sodium hydride (12 mmol), which was suspended in THF (15 mL). 1-adamantanol (10 mmol) was added in portions, and the mixture was stirred for 2 hours. 2-trichloroacetyl-N-methylimidazole (5 mmol) was added in portions, and the mixture was refluxed for 24 hours. The unpurified mixture was cooled to room temperature, then diluted with dichloromethane (15 mL) and water (15 mL). The layers were separataed, and the aqueous layer further extracted with dichloromethane (3×15 mL). The organic layers were combined, dried with sodium sulfate, and concentrated *in vacuo*. The unpurified residue was purified by silica gel chromatography (ethyl acetate/hexanes) to afford **5k** as a white solid (120 mg, 9%). 1H NMR (500 MHz, CDCl3) δ 7.11 (s, 1H), 6.97 (s, 1H), 3.97 (s, 3H), 2.30 (s, 6H), 2.22 (s, 3H), 1.70 (q, J = 12.3 Hz, 6H), 1.64 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 137.8, 129.0, 125.9, 82.8, 41.4, 36.2, 36.0, 31.0. FTIR (ATR) cm^{-1}: 3085, 2911, 2852, 2361, 2338, 1700, 1405, 1258, 1134, 1051, 799, 664. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{21}N_2O_2$ 261.1598; Found 261.1600.

4.3.12. 3-(trimethylsilyl)prop-2-yn-1-yl 1-methyl-1H-imidazole-2-carboxylate 5m—Prepared according to the general imidazole ester synthesis using 3-(trimethylsilyl)propargyl alcohol. Isolated as a clear oil (1.00 g, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (s, 1H), 7.04 (s, 1H), 4.91 (s, 2H), 4.00 (s, 3H), 0.15 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 136.0, 129.7, 126.5, 98.4, 92.5, 53.2, 35.8, −0.4. FTIR (ATR) cm^{-1}: 2959, 2184, 1716, 1410, 1248, 1114, 1049, 1028, 839, 759, 644. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{11}H_{17}N_2O_2Si$ 237.1054; Found 237.1054.

4.3.13. (3S,8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a] phenanthren-3-yl 1-methyl-1H-imidazole-2-carboxylate 5n—Prepared according to the general imidazole ester synthesis using epi-androsterone. Isolated as a white solid (1.02 g, 51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (s, 1H), 6.99 (s, 1H),

4.92 (tt, J = 11.2, 5.0 Hz, 1H), 3.97 (s, 3H), 2.39 (ddd, J = 19.2, 8.9, 1.1 Hz, 1H), 2.02 (dt, J = 19.2, 9.1 Hz, 1H), 1.95 – 1.85 (m, 2H), 1.82 – 1.68 (m, 5H), 1.61 (t, J = 11.8 Hz, 2H), 1.58 – 1.40 (m, 2H), 1.37 – 1.15 (m, 6H), 1.11 – 1.02 (m, 1H), 0.96 (qd, J = 12.2, 5.1 Hz, 1H), 0.84 (s, 3H), 0.82 (s, 3H), 0.70 (ddd, J = 12.2, 10.5, 4.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 136.8, 129.2, 126.1, 74.7, 54.2, 51.3, 47.7, 44.7, 36.7, 35.8, 35.7, 35.6, 34.9, 33.8, 31.4, 30.7, 28.2, 27.2, 21.7, 20.4, 13.7, 12.1. FTIR (ATR) cm^{-1}: 2949, 2852, 1732, 1705, 1421, 1256, 1131, 1009, 919, 792, 665. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{24}H_{35}N_2O_3$ 399.2642; Found 399.2644.

4.3.14. (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 1-methyl-1H-imidazole-2-carboxylate 5o—

Prepared according to the general imidazole ester synthesis using (−)-menthol. Isolated as a white solid (976 mg, 74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (s, 1H), 6.92 (s, 1H), 4.85 (td, J = 10.9, 4.4 Hz, 1H), 3.90 (s, 3H), 2.01 – 1.88 (m, 2H), 1.67 – 1.51 (m, 3H), 1.43 (ddtd, J = 15.1, 12.0, 6.6, 3.2 Hz, 1H), 1.12 (td, J = 12.1, 10.9 Hz, 1H), 0.99 (qd, J = 13.3, 12.7, 12.7, 3.6 Hz, 1H), 0.86 – 0.76 (m, 7H), 0.68 (d, J = 7.0 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 136.6, 129.0, 125.9, 75.0, 46.3, 40.5, 35.6, 33.9, 31.3, 25.7, 23.0, 21.7, 20.5, 15.8. FTIR (ATR) cm^{-1}: 2925, 2870, 1702, 1410, 1257, 1126, 955, 783, 665. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{15}H_{25}N_2O_2$ 265.1911; Found 265.1905.

4.4. Preparation of dimethylimidazolium esters

General procedure for the preparation of dimethylimidazolium esters **1**: To an oven-dried 20 mL scintillation vial equipped with a stir bar was added the corresponding imidazole ester **5**. The ester was dissolved in diethyl ether (0.1 M), and methyl triflate (1.1 equiv.) was added dropwise with vigorous stirring. The product immediately began precipitating and the mixture was stirred an additional 30 minutes. The mixture was filtered and rinsed with diethyl ether (5 mL). The unpurified solid was then dissolved in a minimum amount of dichloromethane, and then diethyl ether was added dropwise until the product precipitated. The mixture was filtered again, and rinsed with additional diethyl ether (5 mL) and hexanes (5 mL). The product was dried under high vacuum overnight to afford dimethylimidazolium **1**.

4.4.1. 2-(ethoxycarbonyl)-1,3-dimethyl-1H-imidazol-3-ium trifluoromethanesulfonate 1a—

Prepared according to the general dimethylimidazolium ester synthesis using **5a** (20.0 mmol). Isolated as a white powder (5.23 g, 82%). ^{1}H NMR was consistent with literature data.[18]

4.4.2. 2-((cyclopropylmethoxy)carbonyl)-1,3-dimethyl-1H-imidazol-3-ium trifluoromethanesulfonate 1b—

Prepared according to the general dimethylimidazolium ester synthesis using **5b** (1.0 mmol). Isolated as a white powder (286 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 2H), 4.35 (d, J = 7.7 Hz, 2H), 4.23 (s, 6H), 1.31 (pt, J = 7.9, 4.7 Hz, 1H), 0.77 – 0.67 (m, 2H), 0.43 (dt, J = 6.2, 4.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.7, 126.7, 73.7, 39.6, 9.4, 3.8. FTIR (ATR) cm^{-1}: 3132, 2361, 2339, 1735, 1448, 1248, 1222, 1153, 1026, 944, 795, 637. HRMS (ESI/TOF) m/z: $[M-CF_3O_3S]^+$ Calcd. for $C_{10}H_{15}N_2O_2$ 195.1128; Found 195.1128.

4.4.3. 2-((cyclohexylmethoxy)carbonyl)-1,3-dimethyl-1H-imidazol-3-ium trifluoromethanesulfonate 1c—Prepared according to the general dimethylimidazolium ester synthesis using **5c** (1.0 mmol). Isolated as a white powder (335 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 2H), 4.27 (d, *J* = 5.9 Hz, 2H), 4.15 (s, 6H), 1.85 – 1.63 (m, 6H), 1.32 – 1.20 (m, 2H), 1.15 (qt, *J* = 12.7, 3.1 Hz, 1H), 1.02 (qd, *J* = 13.1, 12.1, 3.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.8, 132.2, 126.7, 120.6 (q, *J* = 320.2 Hz), 73.3, 39.4, 36.7, 29.6, 26.0, 25.4. FTIR (ATR) cm^{-1}: 3126, 2935, 2860, 2360, 1737, 1448, 1261, 1149, 1029, 637. HRMS (ESI/TOF) m/z: $[M\text{-}CF_3O_3S]^+$ Calcd. for $C_{13}H_{21}N_2O_2$ 237.1598; Found 237.1602.

4.4.4. 2-((dodecyloxy)carbonyl)-1,3-dimethyl-1H-imidazol-3-ium trifluoromethanesulfonate 1d—Prepared according to the general dimethylimidazolium ester synthesis using **5d** (1.0 mmol). Isolated as a white powder (377 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 2H), 4.48 (t, *J* = 6.9 Hz, 2H), 4.18 (s, 6H), 1.82 (p, *J* = 7.1 Hz, 2H), 1.51 – 1.20 (m, 18H), 0.87 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.8, 132.3, 126.8, 120.6 (q, *J* = 320.5 Hz), 68.6, 39.4, 31.9, 29.6, 29.6, 29.4, 29.3, 29.1, 28.2, 25.8, 22.7, 14.1. FTIR (ATR) cm^{-1}: 3130, 2915, 2851, 2361, 2338, 1735, 1456, 1274, 1248, 1153, 1030, 640. HRMS (ESI/TOF) m/z: $[M\text{-}CF_3O_3S]^+$ Calcd. for $C_{18}H_{33}N_2O_2$ 309.2537; Found 309.2532.

4.4.5. 1,3-dimethyl-2-((2-(thiophen-2-yl)ethoxy)carbonyl)-1H-imidazol-3-ium trifluoromethanesulfonate 1e—Prepared according to the general dimethylimidazolium ester synthesis using **5e** (1.0 mmol). Isolated as a white foam (272 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 2H), 7.19 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.96 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.92 (dd, *J* = 3.4, 1.1 Hz, 1H), 4.75 (t, *J* = 6.5 Hz, 2H), 4.07 (s, 7H), 3.37 (t, *J* = 6.5, 0.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.5, 138.7, 132.1, 127.3, 126.8, 126.2, 124.5, 121.9, 119.3, 68.3, 39.4, 28.8. FTIR (ATR) cm^{-1}: 3123, 1743, 1530, 1434, 1255, 1226, 1154, 1027, 817, 705, 629. HRMS (ESI/TOF) m/z: $[M\text{-}CF_3O_3S]^+$ Calcd. for $C_{12}H_{15}N_2O_2S$ 251.0849; Found 251.0841.

4.4.6. 2-((4-methoxyphenethoxy)carbonyl)-1,3-dimethyl-1H-imidazol-3-ium trifluoromethanesulfonate 1f—Prepared according to the general dimethylimidazolium ester synthesis using **5f** (1.0 mmol). Isolated as an amorphous white solid (375 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.70 (t, *J* = 6.9 Hz, 2H), 4.03 (s, 6H), 3.78 (s, 3H), 3.07 (t, *J* = 6.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 153.6, 132.2, 129.7, 128.4, 126.7, 119.4 (q, *J* =319.7 Hz), 114.3, 68.7, 55.3, 39.3, 33.5. FTIR (ATR) cm^{-1}: 3126, 2954, 1742, 1439, 1245, 1158, 1024, 631. HRMS (ESI/TOF) m/z: $[M\text{-}CF_3O_3S]^+$ Calcd. for $C_{15}H_{19}N_2O_3$ 275.1390; Found 275.1387.

4.4.7. 1,3-dimethyl-2-(((tetrahydro-2H-pyran-4-yl)methoxy)carbonyl)-1H-imidazol-3-ium trifluoromethanesulfonate 1g—Prepared according to the general dimethylimidazolium ester synthesis using **5g** (1.0 mmol). Isolated as an amorphous white solid (264 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 2H), 4.35 (d, *J* = 6.6 Hz, 2H), 4.17 (s, 6H), 3.99 (dd, *J* = 11.7, 4.9 Hz, 2H), 3.42 (t, *J* = 11.8 Hz, 2H), 2.12 (dddd, *J* = 18.5,

14.4, 7.1, 3.7 Hz, 1H), 1.70 (d, *J* = 12.9 Hz, 2H), 1.43 (qd, *J* = 12.4, 4.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.8, 132.3, 126.7, 120.6 (q, *J* = 320.3 Hz), 72.3, 67.2, 39.4, 34.1, 29.4. FTIR (ATR) cm^{-1}: 3124, 2962, 2858, 1742, 1446, 1259, 1144, 1031, 804, 639. HRMS (ESI/TOF) m/z: $[M\text{-}CF_3O_3S]^+$ Calcd. for $C_{12}H_{19}N_2O_3$ 239.1390; Found 239.1390.

4.4.8. 2-((cyclohexyloxy)carbonyl)-1,3-dimethyl-1H-imidazol-3-ium trifluoromethanesulfonate 1h—

Prepared according to the general dimethylimidazolium ester synthesis using **5h** (1.0 mmol). Isolated as a pale yellow powder (303 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 2H), 5.18 (tdd, *J* = 9.5, 3.8, 1.6 Hz, 1H), 4.18 (s, 6H), 2.02 (dd, *J* = 12.7, 5.3 Hz, 2H), 1.81 – 1.72 (m, 2H), 1.70 – 1.54 (m, 3H), 1.46 (dt, *J* = 13.6, 10.0 Hz, 2H), 1.40 – 1.30 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.1, 132.3, 126.7, 120.6 (q, *J* = 320.2 Hz), 78.3, 39.4, 31.2, 24.9, 23.5. FTIR (ATR) cm^{-1}: 3128, 2930, 2860, 1740, 1530, 1446, 1253, 1151, 1030, 635. HRMS (ESI/TOF) m/z: $[M\text{-}CF_3O_3S]^+$ Calcd. for $C_{12}H_{19}N_2O_2$ 223.1441; Found 223.1438.

4.4.9. 2-(((1-(tert-butoxycarbonyl)piperidin-4-yl)oxy)carbonyl)-1,3-dimethyl-1H-imidazol-3-ium trifluoromethanesulfonate 1i—

Prepared according to the general dimethylimidazolium ester synthesis using **5i** (1.0 mmol). Isolated as a white powder (369 mg, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 2H), 5.35 (tt, *J* = 8.2, 4.0 Hz, 1H), 4.19 (s, 6H), 3.77 (dt, *J* = 14.3, 5.0 Hz, 2H), 3.30 (ddd, *J* = 13.3, 8.5, 3.6 Hz, 2H), 2.06 (ddt, *J* = 10.0, 7.0, 3.9 Hz, 2H), 1.82 (dtd, *J* = 12.8, 8.4, 3.9 Hz, 2H), 1.47 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.6, 153.1, 132.4, 126.6, 121.8, 119.3, 80.1, 75.5, 41.0, 39.6, 30.3, 28.4. FTIR (ATR) cm^{-1}: 3128, 2976, 1739, 1680, 1443, 1425, 1248, 1153, 1027, 878, 636. HRMS (ESI/TOF) m/z: $[M\text{-}CF_3O_3S]^+$ Calcd. for $C_{16}H_{26}N_3O_4$ 324.1918; Found 324.1916.

4.4.10. (S)-2-((2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropoxy)carbonyl)-1,3-dimethyl-1H-imidazol-3-ium trifluoromethanesulfonate 1j—

Prepared according to a modified version of the general dimethylimidazolium ester synthesis using **5j** (1.0 mmol). Instead of filtering and recrystallizing, the reaction mixture was concentrated, then triturated with diethyl ether (3×5 mL) and hexanes (3×5 mL). Isolated as a thick clear oil (187 mg, 38%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 2H), 6.01 (d, *J* = 7.0 Hz, 1H), 4.92 (d, *J* = 9.4 Hz, 1H), 4.72 – 4.63 (m, 2H), 4.12 (s, 6H), 3.79 (s, 3H), 1.41 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.6, 153.4, 132.1, 126.7, 120.5 (q, *J* = 320.2 Hz), 80.4, 67.4, 53.0, 52.5, 39.4, 28.2. FTIR (ATR) cm^{-1}: 3333, 3132, 2980, 1746, 1707, 1531, 1442, 1256, 1156, 1031, 638. HRMS (ESI/TOF) m/z: $[M\text{-}CF_3O_3S]^+$ Calcd. for $C_{15}H_{24}N_3O_6$ 342.1660; Found 342.1657.

4.4.11. 2-(tert-butoxycarbonyl)-1,3-dimethyl-1H-imidazol-3-ium trifluoromethanesulfonate 1k—

Prepared according to the general dimethylimidazolium ester synthesis using **5k** (1.0 mmol). Isolated as a tan powder (346 mg, 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 2H), 4.16 (s, 6H), 1.66 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.5, 132.9, 126.4, 121.9, 119.4, 88.8, 39.5, 28.0. FTIR (ATR) cm^{-1}: 3129, 1737, 1442, 1253, 1146, 1028, 800, 635. HRMS (ESI/TOF) m/z: $[M\text{-}CF_3O_3S]^+$ Calcd. for $C_{10}H_{17}N_2O_2$ 197.1285; Found 197.1289.

4.4.12. 2-((((1s,3s)-adamantan-1-yl)oxy)carbonyl)-1,3-dimethyl-1H-imidazol-3-ium trifluoromethanesulfonate 1l—Prepared according to the general dimethylimidazolium ester synthesis using **5l** (0.4 mmol). Isolated as a white powder (158 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 2H), 4.16 (s, 6H), 2.28 (s, 9H), 1.72 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.0, 132.7, 126.5, 122.0, 119.4, 89.2, 41.4, 39.5, 35.8, 31.1. FTIR (ATR) cm^{-1}: 2915, 2860, 2361, 2339, 1726, 1272, 1255, 1168, 1027, 636. HRMS (ESI/TOF) m/z: $[M\text{-}CF_3O_3S]^+$ Calcd. for $C_{16}H_{23}N_2O_2$ 275.1754; Found 275.1752.

4.4.13. 1,3-dimethyl-2-(((3-(trimethylsilyl)prop-2-yn-1-yl)oxy)carbonyl)-1H-imidazol-3-ium trifluoromethanesulfonate 1m—Prepared according to the general dimethylimidazolium ester synthesis using **5m** (1.0 mmol). Isolated as a white powder (294 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 2H), 5.08 (s, 2H), 4.21 (s, 6H), 0.19 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.9, 131.7, 127.1, 120.6 (q, J = 321.0 Hz), 96.1, 95.2, 55.9, 39.5, −0.5. FTIR (ATR) cm^{-1}: 3128, 2965, 2361, 2338, 1741, 1436, 1254, 1152, 1030, 941, 810, 758, 637. HRMS (ESI/TOF) m/z: $[M\text{-}CF_3O_3S]^+$ Calcd. for $C_{12}H_{19}N_2O_2Si$ 251.1210; Found 251.1208.

4.4.14. 2-((((3S,8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a] phenanthren-3-yl)oxy)carbonyl)-1,3-dimethyl-1H-imidazol-3-ium trifluoromethanesulfonate 1n—Prepared according to the general dimethylimidazolium ester synthesis using **5n** (1.0 mmol). Isolated as an amorphous white solid (365 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 2H), 5.10 (tt, J = 11.0, 4.9 Hz, 1H), 4.19 (s, 6H), 2.45 (dd, J = 19.3, 8.9 Hz, 1H), 2.13 – 2.03 (m, 2H), 1.94 (ddd, J = 12.4, 8.8, 5.9 Hz, 1H), 1.83 (tt, J = 12.6, 3.8 Hz, 4H), 1.76 – 1.46 (m, 5H), 1.45 – 1.19 (m, 6H), 1.12 (td, J = 13.8, 3.4 Hz, 1H), 1.01 (qd, J = 12.4, 4.8 Hz, 1H), 0.90 (s, 3H), 0.87 (s, 3H), 0.75 (td, J = 11.2, 4.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.1, 132.3, 126.7, 79.2, 54.2, 51.3, 47.7, 44.7, 39.5, 36.5, 35.8, 35.6, 35.0, 33.6, 31.5, 30.7, 28.1, 27.3, 21.7, 20.5, 13.8, 12.3. FTIR (ATR) cm^{-1}: 2931, 2854, 1733, 1444, 1260, 1153, 1031. HRMS (ESI/TOF) m/z: $[M\text{-}CF_3O_3S]^+$ Calcd. for $C_{25}H_{37}N_2O_3$ 413.2799; Found 413.2787.

4.4.15. 2-((((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)-1,3-dimethyl-1H-imidazol-3-ium trifluoromethanesulfonate 1o—Prepared according to the general dimethylimidazolium ester synthesis using **5o** (1.0 mmol). Isolated as an amorphous white solid (365 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 2H), 5.12 (td, J = 11.0, 4.5 Hz, 1H), 4.19 (s, 6H), 2.17 (dtd, J = 12.0, 4.4, 4.0, 1.8 Hz, 1H), 1.87 (pd, J = 6.9, 2.6 Hz, 1H), 1.81 – 1.71 (m, 2H), 1.62 – 1.50 (m, 2H), 1.20 (q, J = 12.1, 12.0, 11.4 Hz, 1H), 1.17 – 1.07 (m, 1H), 0.99 – 0.89 (m, 7H), 0.80 (d, J = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.3, 132.0, 127.0, 120.6 (q, J = 320.2 Hz), 79.9, 47.1, 40.6, 39.5, 33.7, 31.6, 26.29, 23.0, 21.8, 20.8, 15.8. FTIR (ATR) cm^{-1}: 3127, 2957, 2924, 2867, 1736, 1442, 1254, 1145, 1030, 948, 910, 804, 635. HRMS (ESI/TOF) m/z: $[M\text{-}CF_3O_3S]^+$ Calcd. for $C_{16}H_{27}N_2O_2$ 279.2067; Found 279.2066.

4.4.16. 2-(ethoxycarbonyl)-1,3-dimethyl-1H-benzo[d] imidazol-3-ium trifluoromethanesulfonate 2a—Prepared according to the general dimethylimidazolium ester synthesis using ethyl 1-methyl-1H-benzo[d]imidazole-2-carboxylate (1.0 mmol).

Isolated as a white powder (347 mg, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (dt, *J* = 7.2, 3.6 Hz, 2H), 7.75 (dt, *J* = 6.5, 3.6 Hz, 2H), 4.68 (q, *J* = 7.2 Hz, 2H), 4.37 (s, 6H), 1.53 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 137.3, 132.1, 129.1, 121.8, 119.2, 113.6, 65.4, 35.0, 13.8. FTIR (ATR) cm^{-1}: 3003, 2979, 2362, 1742, 1522, 1256, 1224, 1140, 1006, 750, 637. HRMS (ESI/TOF) m/z: $[M\text{-}CF_3O_3S]^+$ Calcd. for $C_{12}H_{15}N_2O_2$ 219.1128; Found 219.1123.

4.5. General procedure for the esterification of potassium trifluoroborate salts

To an oven-dried 2-dram vial equipped with a stir bar was added the corresponding trifluoroborate salt **3** (0.3 mmol) and the corresponding dimethylimidazolium ester **1** (0.2 mmol). The vial was cycled into the glovebox, and **PC1** (0.2 μmol) was added. Dichloromethane (6 mL) was added, and the vial was sealed. Parafilm was wrapped around the cap, and the mixture was irradiated with stirring using four 427 nm Kessil PR160L lamps (~5 cm away). After 18 hours, the irradiation was stopped and the reaction mixture was diluted with water (10 mL). The layers were separated and the aqueous layer was extracted with dichloromethane (2×10 mL). The organic layers were combined, dried with sodium sulfate, and concentrated. The unpurified residue was purified using silica gel chromatography (ethyl acetate/hexanes) to afford ester **4**.

4.5.1. ethyl 2-phenylacetate 4a—Prepared according to the general esterification procedure with trifluoroborate **3a** and ester **1a**, except yield (16 mg, 50%) was determined by GC-MS without workup. Retention time and fragmentation matched a commercial analytical standard from Sigma Aldrich.

4.5.2. ethyl 2-(4-chlorophenyl)acetate 4b—Prepared according to the general esterification procedure with trifluoroborate **3b** and ester **1a**. Isolated as a clear oil (8 mg, 20%). ^{1}H NMR was consistent with literature data.[29]

4.5.3. ethyl 2-(p-tolyl)acetate 4c—Prepared according to the general esterification procedure with trifluoroborate **3c** and ester **1a**. Isolated as a clear oil (16 mg, 45%). ^{1}H NMR was consistent with literature data.[29]

4.5.4. ethyl 2-(4-methoxyphenyl)acetate 4d—Prepared according to the general esterification procedure with trifluoroborate **3d** and ester **1a**. Isolated as a clear oil (7 mg, 19%). ^{1}H NMR was consistent with literature data.[29]

4.5.5. ethyl 2-([1,1′-biphenyl] −4-yl)acetate 4e—Prepared according to the general esterification procedure with trifluoroborate **3e** and ester **1a**. Isolated as a clear oil (19 mg, 40%). ^{1}H NMR was consistent with literature data.[29]

4.5.6. methyl 4-(2-ethoxy-2-oxoethyl)benzoate 4f—Prepared according to the general esterification procedure with trifluoroborate **3f** and ester **1a**. Isolated as a clear oil (26 mg, 59%). ^{1}H NMR was consistent with literature data.[30]

4.5.7. ethyl 2-(4-bromophenyl)acetate 4g—Prepared according to the general esterification procedure with trifluoroborate **3g** and ester **1a**. Isolated as a clear oil (9 mg, 20%). ^{1}H NMR was consistent with literature data.[29]

4.5.8. ethyl 2-phenylpropanoate 4h—Prepared according to the general esterification procedure with trifluoroborate **3h** and ester **1a**. Isolated as a clear oil (17 mg, 48%). ^{1}H NMR was consistent with literature data.[29]

4.5.9. ethyl 2-(naphthalen-2-yl)acetate 4i—Prepared according to the general esterification procedure with trifluoroborate **3i** and ester **1a**. Isolated as a clear oil (14 mg, 33%). ^{1}H NMR was consistent with literature data.[29]

4.5.10. ethyl 2-(3,5-dimethylphenyl)acetate 4j—Prepared according to the general esterification procedure with trifluoroborate **3j** and ester **1a**. Isolated as a clear oil (8 mg, 21%). ^{1}H NMR was consistent with literature data.[29]

4.5.11. ethyl 2-(2,6-difluorophenyl)acetate 4k—Prepared according to the general esterification procedure with trifluoroborate **3k** and ester **1a**. Isolated as a clear oil (20 mg, 50%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (tt, J = 8.4, 6.6 Hz, 1H), 6.94 – 6.85 (m, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.70 (s, 2H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.7, 162.5 (d, J = 8.0 Hz), 160.5 (d, J = 8.0 Hz), 128.9 (t, J = 10.3 Hz), 111.1 (dd, J = 20.4, 5.7 Hz), 110.7 (t, J = 20.0 Hz), 61.2, 28.0 (t, J = 3.2 Hz), 14.1. ^{19}F NMR (470 MHz, $CDCl_3$) δ −114.6. FTIR (ATR) cm^{-1}: 2983, 2934, 1741, 1471, 1272, 1216, 1171, 1019, 785. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{10}H_{11}F_2O_2$ 201.0722; Found 201.0722.

4.5.12. diethyl 2-phenylsuccinate 4l—Prepared according to the general esterification procedure with trifluoroborate **3l** and ester **1a**. Isolated as a clear oil (19 mg, 38%). ^{1}H NMR was consistent with literature data.[30]

4.5.13. ethyl 4-oxo-2,4-diphenylbutanoate 4m—Prepared according to the general esterification procedure with trifluoroborate **3m** and ester **1a**. Isolated as a white solid (24 mg, 43%). ^{1}H NMR was consistent with literature data.[31]

4.5.14. ethyl 4-oxochromane-2-carboxylate 4n—Prepared according to the general esterification procedure with trifluoroborate **3n** and ester **1a**. Isolated as a clear oil (12 mg, 27%). ^{1}H NMR was consistent with literature data.[32]

4.5.15. methyl 4-(2-(cyclopropylmethoxy)-2-oxoethyl)benzoate 4o—Prepared according to the general esterification procedure with trifluoroborate **3f** and ester **1b**. Isolated a clear oil (30 mg, 61%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.3 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 3.93 (d, J = 7.3 Hz, 2H), 3.90 (s, 3H), 3.69 (s, 2H), 1.17 – 1.05 (m, 1H), 0.57 – 0.52 (m, 2H), 0.28 – 0.23 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 166.8, 139.3, 129.8, 129.3, 129.0, 69.8, 52.0, 41.3, 9.7, 3.2. FTIR (ATR) cm^{-1}: 3006, 2952, 1718, 1613, 1435, 1276, 1155, 1106, 1022, 984, 765, 721. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{14}H_{17}O_4$ 249.1121; Found 249.1125.

4.5.16. methyl 4-(2-(cyclohexylmethoxy)-2-oxoethyl)benzoate 4p—Prepared according to the general esterification procedure with trifluoroborate **3f** and ester **1c**. Isolated as a clear oil (34 mg, 58%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 3.91 (s, 3H), 3.91 (d, *J* = 6.5 Hz, 2H), 3.67 (s, 2H), 1.74 – 1.59 (m, 6H), 1.27 – 1.08 (m, 3H), 0.97 – 0.86 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 166.9, 139.3, 129.8, 129.3, 129.0, 70.2, 52.1, 41.4, 37.0, 29.6, 26.3, 25.6. FTIR (ATR) cm^{-1}: 2924, 2852, 1720, 1435, 1275, 1149, 1106, 999, 741. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{17}H_{23}O_4$ 291.1591; Found 291.1586.

4.5.17. methyl 4-(2-(dodecyloxy)-2-oxoethyl)benzoate 4q—Prepared according to the general esterification procedure with trifluoroborate **3f** and ester **1d**. Isolated as a white waxy solid (37 mg, 51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.08 (t, *J* = 6.7 Hz, 2H), 3.90 (s, 3H), 3.66 (s, 2H), 1.60 (p, *J* = 6.8 Hz, 2H), 1.33 – 1.21 (m, 18H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 166.8, 139.3, 129.8, 129.3, 129.0, 65.2, 52.0, 41.4, 31.9, 29.6, 29.6, 29.5, 29.5, 29.3, 29.1, 28.5, 25.8, 22.7, 14.1. FTIR (ATR) cm^{-1}: 2952, 2918, 2850, 1725, 1275, 1223, 1178, 1108, 721. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{22}H_{35}O_4$ 363.2530; Found 262.2528.

4.5.18. methyl 4-(2-oxo-2-(2-(thiophen-2-yl)ethoxy)ethyl)benzoate 4r—Prepared according to the general esterification procedure with trifluoroborate **3f** and ester **1e**. Isolated as a clear oil (40 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 6.9 Hz, 2H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.15 (d, *J* = 5.1 Hz, 1H), 6.92 (ddd, *J* = 4.9, 3.5, 1.1 Hz, 1H), 6.78 (d, *J* = 3.4 Hz, 1H), 4.33 (t, *J* = 6.7 Hz, 2H), 3.91 (s, 3H), 3.69 (s, 3H), 3.14 (t, *J* = 6.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 166.8, 139.6, 138.9, 129.8, 129.3, 129.0, 126.8, 125.6, 124.0, 65.2, 52.1, 41.3, 29.1. FTIR (ATR) cm^{-1}: 2952, 1717, 1434, 1276, 1152, 1106, 1020, 698. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{17}O_4S$ 305.0842; Found 305.0846.

4.5.19. methyl 4-(2-(4-methoxyphenethoxy)-2-oxoethyl)benzoate 4s—Prepared according to the general esterification procedure with trifluoroborate **3f** and ester **1f**. Isolated as a clear oil (24 mg, 37%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 4.28 (t, *J* = 6.9 Hz, 2H), 3.92 (s, 3H), 3.79 (s, 3H), 3.65 (s, 3H), 2.85 (t, *J* = 6.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 166.8, 158.3, 139.1, 129.8, 129.5, 129.3, 129.0, 113.9, 65.7, 55.2, 52.1, 41.4, 34.1. FTIR (ATR) cm^{-1}: 2953, 2837, 1720, 1613, 1584, 1513, 1435, 1278, 1246, 1179, 1157, 1108, 1034, 831. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{21}O_5$ 329.1384; Found 329.1384.

4.5.20. methyl 4-(2-oxo-2-((tetrahydro-2H-pyran-4-yl)methoxy)ethyl)benzoate 4t—Prepared according to the general esterification procedure with trifluoroborate **3f** and ester **1g**. Isolated as a clear oil (25 mg, 43%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 3.97 – 3.92 (m, 4H), 3.90 (s, 3H), 3.67 (s, 2H), 3.35 (td, *J* = 11.8, 2.2 Hz, 2H), 1.92 – 1.82 (m, 1H), 1.54 (ddq, *J* = 13.0, 4.0, 2.0 Hz, 2H), 1.32 (dtd, *J* = 13.4, 11.9, 4.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.7, 166.8, 139.1, 129.8, 129.3, 129.0, 69.2, 67.3, 52.1, 41.3, 34.4, 29.4. FTIR (ATR) cm^{-1}: 2950, 2844, 1718, 1613, 1435,

1419, 1276, 1147, 1107, 1017, 853. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{21}O_5$ 293.1384; Found 293.1387.

4.5.21. methyl 4-(2-(cyclohexyloxy)-2-oxoethyl)benzoate 4u—Prepared according to the general esterification procedure with trifluoroborate **3f** and ester **1h**. Isolated as a clear oil (33 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 4.78 (tt, *J* = 8.8, 3.9 Hz, 1H), 3.91 (s, 3H), 3.65 (s, 2H), 1.88 – 1.76 (m, 2H), 1.74 – 1.62 (m, 2H), 1.54 – 1.48 (m, 1H), 1.45 – 1.29 (m, 4H), 1.29 – 1.20 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 166.9, 139.6, 129.8, 129.3, 128.9, 73.4, 52.1, 41.8, 31.5, 25.3, 23.6. FTIR (ATR) cm^{-1}: 2937, 2859, 1721, 1435, 1278, 1165, 1107, 1017, 742. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{21}O_4$ 277.1434; Found 277.1440.

4.5.22. tert-butyl 4-(2-(4-(methoxycarbonyl)phenyl)acetoxy)piperidine-1-carboxylate 4v—Prepared according to the general esterification procedure with trifluoroborate **3f** and ester **1i**. Isolated as an amorphous white solid (17 mg, 23%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 2H), 4.94 (tt, *J* = 7.8, 3.8 Hz, 1H), 3.91 (s, 3H), 3.67 (s, 2H), 3.64 – 3.55 (m, 2H), 3.22 (ddd, *J* = 13.6, 8.3, 3.7 Hz, 2H), 1.85 – 1.77 (m, 2H), 1.62 – 1.52 (m, 2H), 1.44 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 166.8, 154.6, 139.1, 129.9, 129.2, 129.1, 79.7, 70.4, 52.1, 41.6, 40.8, 30.4, 28.4. FTIR (ATR) cm^{-1}: 2976, 2949, 2926, 1721, 1680, 1416, 1358, 1271, 1180, 1163, 1107, 1019, 767, 726. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{28}NO_6$ 378.1911; Found 378.1913.

4.5.23. methyl (S)-4-(2-(2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropoxy)-2-oxoethyl)benzoate 4w—Prepared according to the general esterification procedure with trifluoroborate **3f** and ester **1j**. Isolated as a clear oil (24 mg, 30%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 5.20 (d, *J* = 8.2 Hz, 1H), 4.55 (dd, *J* = 8.3, 4.0 Hz, 1H), 4.46 – 4.35 (m, 2H), 3.90 (s, 3H), 3.68 (s, 3H), 3.67 (s, 2H), 1.44 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 170.1, 166.8, 155.1, 138.6, 129.9, 129.4, 80.4, 64.8, 52.8, 52.7, 52.1, 49.2, 41.0, 28.3. FTIR (ATR) cm^{-1}: 3362, 2977, 2955, 1743, 1715, 1508, 1436, 1278, 1158, 1108, 1020, 768. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{19}H_{26}NO_8$ 396.1653; Found 396.1649. Optical data: $[\alpha]^{23}$(D) −25.0 (*c*, 0.90, MeOH).

4.5.24. methyl 4-(2-(tert-butoxy)-2-oxoethyl)benzoate 4x—Prepared according to the general esterification procedure with trifluoroborate **3f** and ester **1k**. Isolated as a clear oil (5 mg, 10%). ^{1}H NMR was consistent with literature data.[33]

4.5.25. methyl 4-(2-(((3s,5s,7s)-adamantan-1-yl)oxy)-2-oxoethyl)benzoate 4y —Prepared according to the general esterification procedure with trifluoroborate **3f** and ester **1l**. Isolated as a clear oil (18 mg, 27%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 3.91 (s, 3H), 3.57 (s, 2H), 2.14 (bs, 3H), 2.07 (d, *J* = 3.0 Hz, 6H), 1.64 (bs, *J* = 3.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.8, 167.0, 140.0, 129.7, 129.3, 128.8, 81.3, 52.0, 42.8, 41.2, 36.1, 30.8. FTIR (ATR) cm^{-1}: 2911, 2853, 1724, 1279, 1254, 1107, 1055, 970. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{25}O_4$ 329.1747; Found 329.1753

4.5.26. methyl 4-(2-oxo-2-((3-(trimethylsilyl)prop-2-yn-1-yl)oxy)ethyl)benzoate 4z—Prepared according to the general esterification procedure with trifluoroborate **3f** and ester **1m**. Isolated as a clear oil (6 mg, 10%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 4.71 (s, 2H), 3.91 (s, 3H), 3.73 (s, 2H), 0.18 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 166.8, 138.6, 129.9, 129.3, 129.2, 98.6, 92.5, 53.3, 52.1, 40.9, −0.4. FTIR (ATR) cm^{-1}: 2956, 1745, 1724, 1436, 1280, 1251, 1147, 1108, 845, 762. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{16}H_{21}O_4Si$ 305.1204; Found 305.1201.

4.5.27. methyl 4-(2-(((3S,8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1H-cyclopenta[a] phenanthren-3-yl)oxy)-2-oxoethyl)benzoate 4aa—Prepared according to the general esterification procedure with trifluoroborate **3f** and ester **1n**. Isolated as an amorphous white solid (27 mg, 29%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 4.70 (tt, *J* = 11.4, 4.9 Hz, 1H), 3.90 (s, 3H), 3.63 (s, 2H), 2.42 (ddd, *J* = 19.3, 8.9, 1.1 Hz, 1H), 2.05 (dt, *J* = 19.2, 9.1 Hz, 1H), 1.95 – 1.88 (m, 1H), 1.82 – 1.75 (m, 3H), 1.72 (dt, *J* = 13.4, 3.7 Hz, 1H), 1.65 – 1.55 (m, 2H), 1.55 – 1.42 (m, 3H), 1.40 – 1.13 (m, 7H), 1.06 – 0.93 (m, 2H), 0.84 (s, 3H), 0.83, (s, 3H), 0.69 (ddd, *J* = 12.0, 10.4, 4.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 166.9, 139.5, 129.8, 129.2, 128.9, 74.2, 54.2, 52.0, 51.3, 47.7, 44.6, 41.7, 36.6, 35.8, 35.6, 35.0, 33.8, 31.5, 30.7, 28.2, 27.3, 21.7, 20.4, 13.8, 12.2. FTIR (ATR) cm^{-1}: 2932, 2851, 1734, 1710, 1276, 1167, 1106, 1012, 727. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{29}H_{39}O_5$ 467.2792; Found 467.2786. Optical data: $[\alpha]^{23}$(D) −72.7 (*c*, 0.42, MeOH).

4.5.28. methyl 4-(2-(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)-2-oxoethyl)benzoate 4ab—Prepared according to the general esterification procedure with trifluoroborate **3f** and ester **1o**. Isolated as an amorphous white solid (27 mg, 41%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 4.56 (td, *J* = 10.9, 4.4 Hz, 1H), 3.79 (s, 3H), 3.53 (s, 2H), 1.89 – 1.78 (m, 1H), 1.65 – 1.58 (m, 1H), 1.58 – 1.50 (m, 2H), 1.34 (ddtd, *J* = 15.1, 12.0, 6.6, 3.1 Hz, 1H), 1.22 (ddt, *J* = 12.3, 10.8, 3.2 Hz, 1H), 0.91 (qd, *J* = 13.4, 12.8, 3.8 Hz, 1H), 0.82 (td, *J* = 12.1, 10.9 Hz, 1H), 0.74 (m, 7H), 0.56 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 166.9, 139.5, 129.7, 129.2, 128.9, 75.0, 52.0, 47.0, 41.8, 40.7, 34.2, 31.3, 26.2, 23.4, 21.9, 20.6, 16.2. FTIR (ATR) cm^{-1}: 2953, 2927, 2869, 1721, 1435, 1275, 1148, 1106, 985, 967, 724. HRMS (ESI/TOF) m/z: $[M+H]^+$ Calcd. for $C_{20}H_{29}O_4$ 333.2060; Found 333.2054. Optical data: $[\alpha]^{23}$(D) −59.2 (*c*, 1.22, MeOH).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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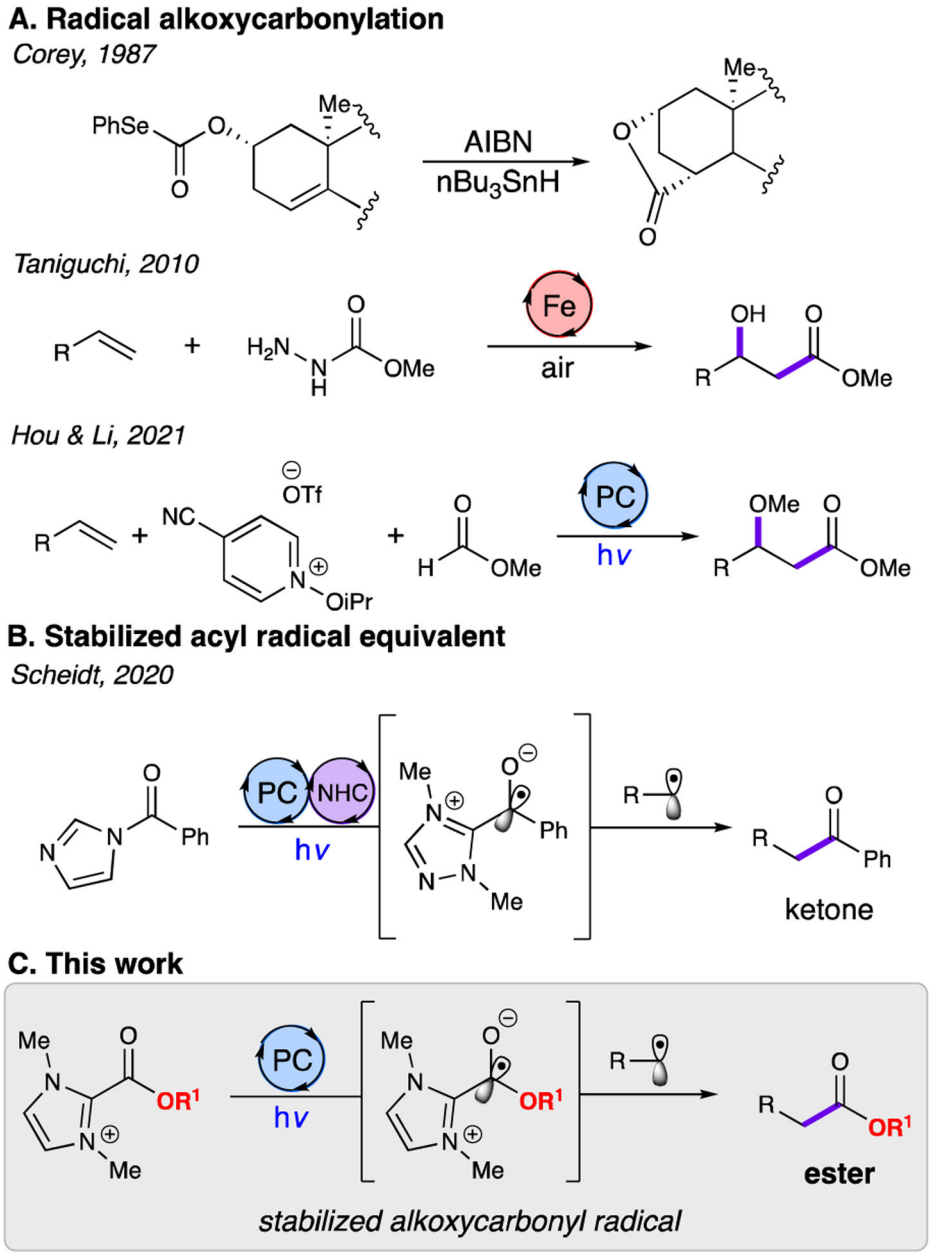


Figure 1:

Synthetic applications of alkoxycarbonyl radicals, development of NHC-stabilized acyl radicals, and design of a stabilized alkoxycarbonyl radical

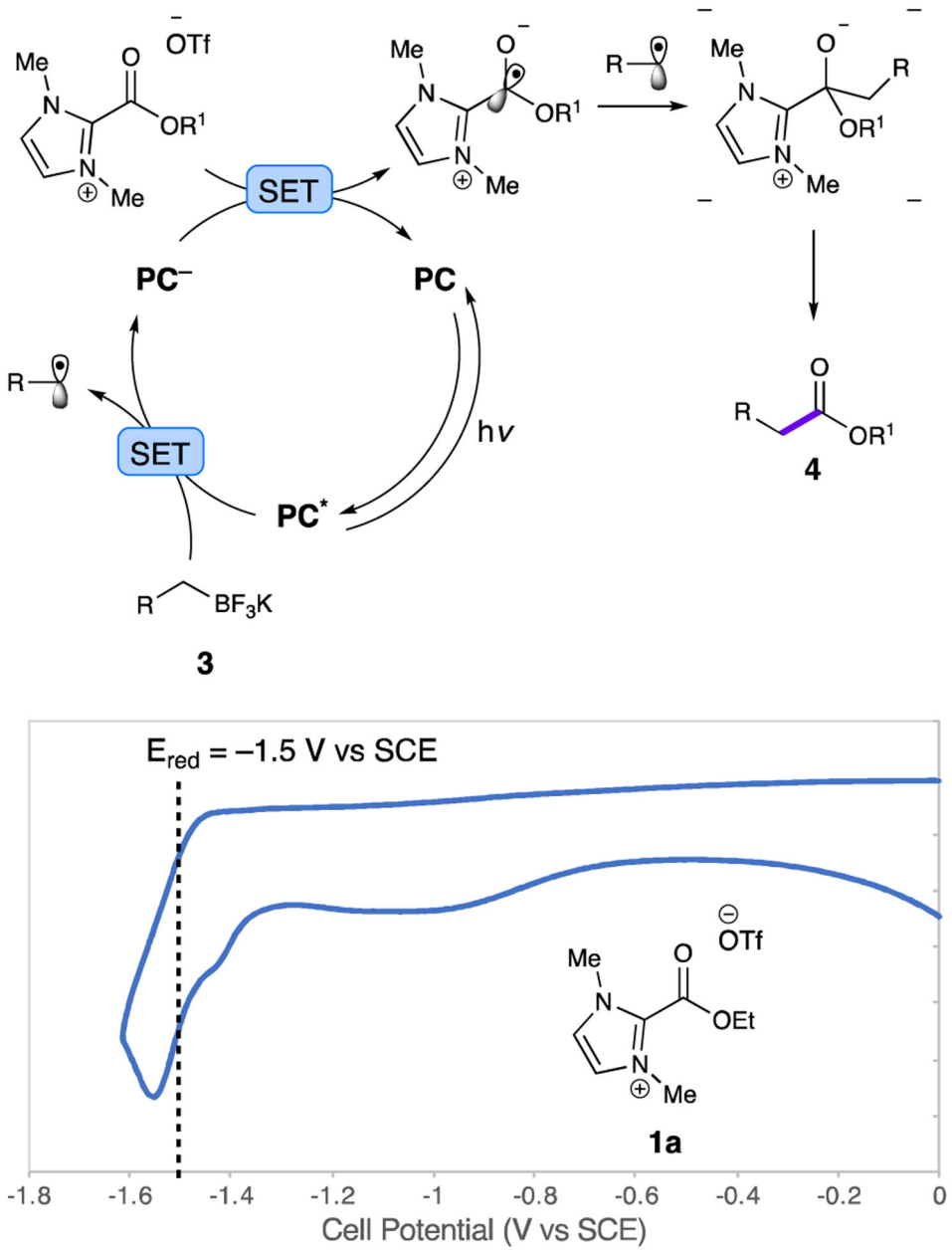
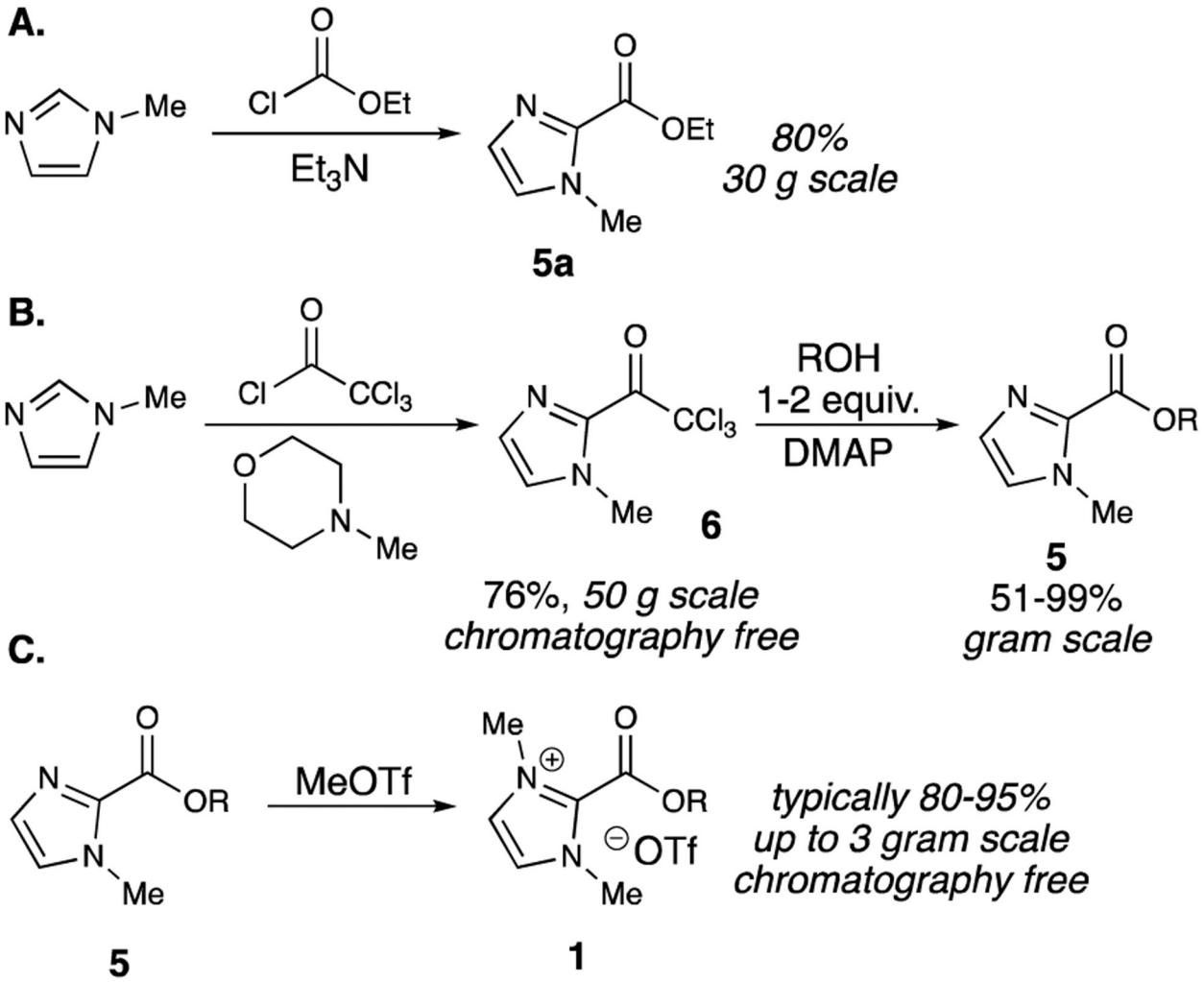
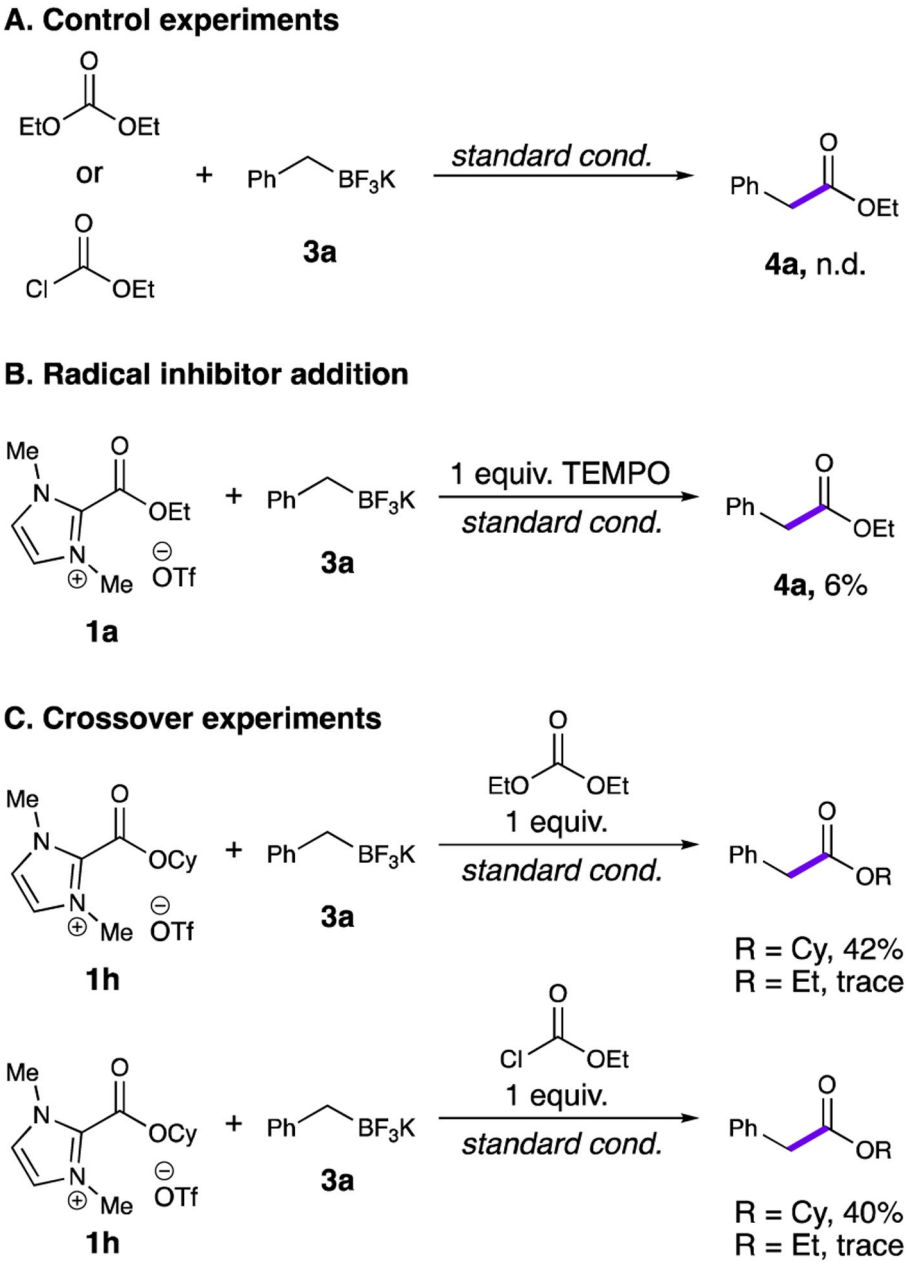


Figure 2:

Proposed mechanism/pathway for alkoxycarbonyl radical-radical coupling and cyclic voltammogram of **1a**



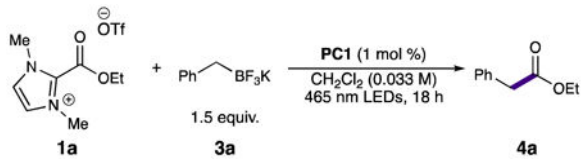
Scheme 1:
Synthetic routes to imidazolium esters



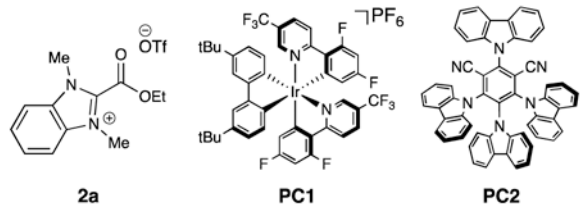
Scheme 2:
Mechanistic studies

Table 1:

Optimization for radical-radical coupling



entry	deviation from standard	GC yield of 4a (%)[a]
1	none	39
2	**2a** instead of **1a**	21
3	CH_3CN instead of CH_2CI_2	31
4	DMF instead of CH_2CI_2	16
5	1,4-dioxane instead of CH_2CI_2	17
6	2 equiv. **3a**	39
7	0.1 M	32
8	0.05 M	38
g	0.025 M	38
10	3 mol % **PC2** instead of **PC1**	25
11	390 nm LEDs	36
12	427 nm LEDs	50
13	1.0 equiv lutidine	24
14	1.0 equiv Cs_2CO_3	30
15	no light	n.d.
16	no photocatalyst	n.d.



[a]Gas chromatography (GC) yield is based on a calibration curve using 1,3,5-trimethoxybenzene as the internal standard. n.d. = not detected

Table 2:

Scope with regards to alkyl trifluoroborate

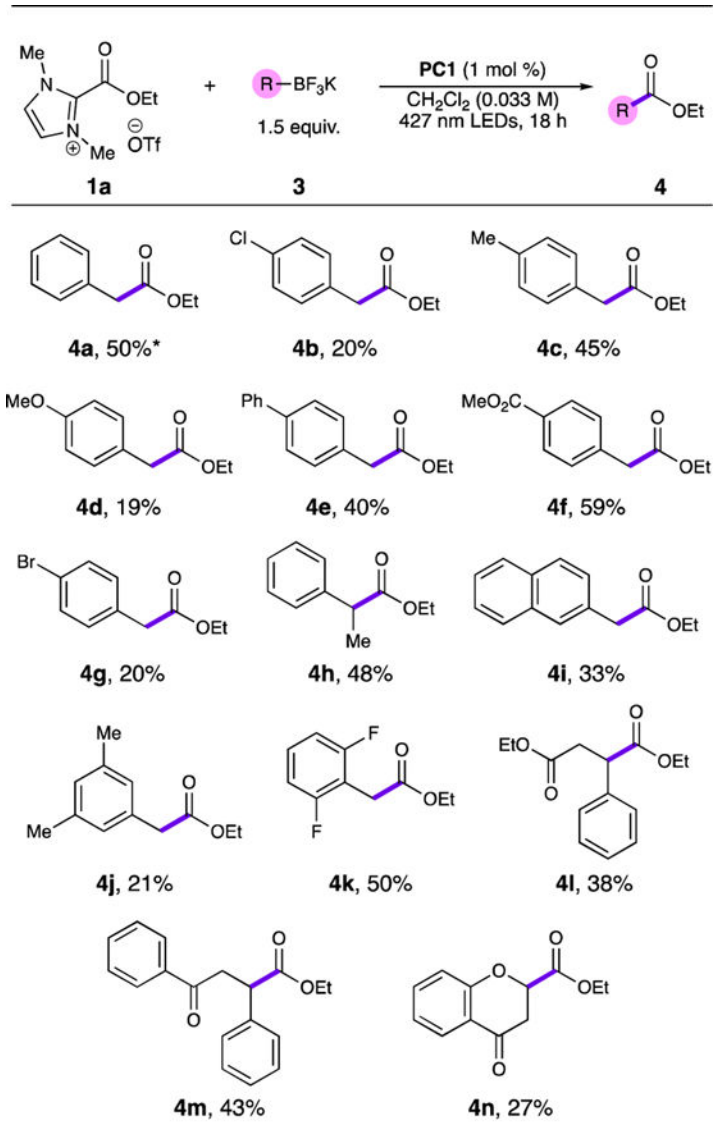


Table 3:

Scope with regards to imidazolium ester