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TEMPO-Mediated Synthesis of *N*-(Fluoroalkyl)imidazolones via Reaction of Imidazoles with Iodofluoroacetate

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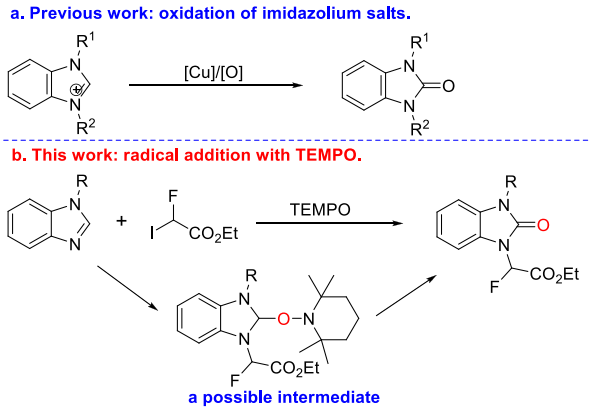
Abstract. We report a TEMPO-mediated oxidative copper-catalyzed synthesis of *N*-(fluoroalkyl)imidazolones via the radical addition of imidazoles with iodofluoroacetate. A possible key intermediate involving TEMPO was observed by ESI-MS. We also found that aerobic oxidation conditions were effective for the transformation in the presence of a copper catalyst, enabling access to a number of *N*-(fluoroalkyl)imidazolones in moderate to good yields.

Keywords: Imidazolone; Copper; TEMPO; Aerobic oxidation; Radical reaction

Introduction

Imidazolones are found frequently in medicines.[1-5] Several natural products possess 2-imidazolones as their core structure.[1] Such skeletons are common in pharmaceutically interesting compounds such as human dopamine D_4 receptor antagonists,[2] MurB enzyme inhibitors,[3] potential antitumor agents,[4] and antioxidants.[5] Due to the medicinal importance of imidazolones, much effort has been devoted to their synthesis.[6-12] In recent years, the oxidation of imidazolium salts using strong oxidants has proven to be an effective pathway to imidazolones (Scheme 1a).[6-9] Ollevier and colleagues recently demonstrated that imidazolidinone, imidazolone, and benzimidazolone derivatives could be synthesized efficiently via the oxidation of imidazolium salts using a copper catalyst and air as an oxidant at room temperature.[9b] However, this route requires the initial synthesis of imidazolium salts. In 2013, Guo and coworkers developed a copper/DTBP (Di-tert-butyl peroxide)-catalyzed oxidation of imidazolium salts, formed *in situ* via the nucleophilic substitution of alkyl halides with imidazoles.[10] Very recently, we developed an efficient and practical sulfite-promoted synthesis of *N*-(fluoroalkyl) or *N*-(difluoromethyl)imidazothiones through the fluoroalkylation and sulfurization of imidazoles with elemental sulfur and ethyl 2-bromo-2-fluoroacetate (or ethyl 2-bromo-2,2-difluoroacetate).[13] This work aimed at incorporating a fluoroalkyl group into heterocycles for use as novel medicines and agrochemicals.[14] We therefore attempted to synthesize *N*-(fluoroalkyl)imidazolones for the development of pesticides. However, we found that the sulfite-promoted methods were not suitable for the synthesis of *N*-(fluoroalkyl)imidazolones. The development of new synthetic strategies for such transformations is needed. Herein, we report a TEMPO-mediated oxidative synthesis of *N*-(fluoroalkyl)imidazolones by the radical addition of imidazoles with fluoroalkyl radicals generated from iodofluoroacetate (Scheme 1b).

Scheme 1. Synthetic methods for the preparation of *N*-(fluoroalkyl)imidazolones.



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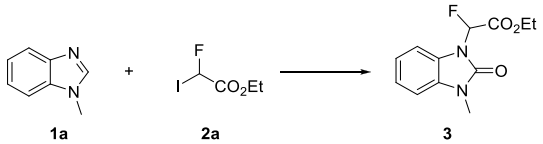
Results and Discussion

Our study began with the reaction of 1-methyl-benzimidazole **1a** with ethyl 2-fluoro-2-iodoacetate **2a** in the presence of $CuBr_2$ and TEMPO in different solvents (Table 1, Entries 1-6). Solvents such as toluene, dioxane, CH_3CN, and DMF are effective for this reaction and offer the target product **3** in moderate yields (Table 1, Entries 1-4). However, the reaction did not proceed in DMSO (Table 1, Entry 5). An excellent yield (96%) was obtained when the reaction was conducted in DCE (Table 1, Entry 6). Carrying out the reaction at 60 °C furnished the product in lower yield (69%), a result of the low conversion of compound **1a** (Table 1, entry 7). Reaction at 100 °C produced some unknown byproducts, leading to a decrease in yield (67%) (Table 1, Entry 8). To further investigate the effect of copper catalysts, $CuCl_2$, $Cu(OAc)_2$, CuO, and CuBr were examined with good yields (82%-87%, Table 1, Entries 9–12). Interestingly, carrying out the reaction with TEMPO still furnished the target product in 62% yield in the absence of copper catalyst (Table 1, Entry 13). Further studies showed that the reaction still proceeded smoothly under an N_2 atmosphere and the desired product was afforded in a similar yield to that obtained when the reaction was carried out in air (Table 1, Entry 14 *vs* Entry 6, Entry 15 *vs* Entry 13). These results indicate that TEMPO plays a key role in the transformation. To compare these results with the effect of traditional oxidants, $K_2S_2O_8$, Oxone and TBHP were employed in the reaction, but use of these oxidants resulted in much lower yields of the desired product (12%, 8%, and 54%, respectively; Table 1, Entries 16-18). Air can be used as a green oxidant,[15] and so the reaction was conducted in the presence of $CuBr_2$ and air to provide the target product **3** in 36% yield (Table 1, Entry 19). The yield was greatly increased to 83% under an O_2 atmosphere (Table 1, Entry 20). A gram-scale reaction proved the good scalability of this reaction; product **3** was obtained in 81% yield with 8 mmol of compound **1a** (Table 1, entry 6).

The reaction scope was studied with these optimized conditions in hand. In the presence of $CuBr_2$ and TEMPO, a variety of significant functional groups such as chloro, bromo, fluoro, methoxy, ester, and nitro substituents were well tolerated and furnished their corresponding products **3**-**12** in moderate to good yields (Table 2). We note that a range of modifications can be made on these functional groups. Starting materials bearing an electron-withdrawing group were not completely converted, leading to moderate yields (products **6**-**12**). The scope of different *N*-substituents on the benzimidazoles was also investigated (products **13**-**22**). Numerous functional groups, such as ether, nitrile, alkene and aryl functionalities were also amenable to the reaction conditions and afforded their corresponding products **13**-**22** in yields of 58% to 93%. Imidazopyridine also furnished its corresponding product **23** in 56% yield. Importantly, *N*-aryl-substituted imidazoles were also compatible with the

Table 1. Screening of optimal conditions [a].



1a 2a 3

Entry	[Cu]	Oxidant	Solvent	Yield (%)
1	$CuBr_2$	TEMPO	Toluene	75
2	$CuBr_2$	TEMPO	Dioxane	67
3	$CuBr_2$	TEMPO	CH_3CN	69
4	$CuBr_2$	TEMPO	DMF	47
5	$CuBr_2$	TEMPO	DMSO	0
6	$CuBr_2$	TEMPO	DCE	96 (81)[e]
7 [b]	$CuBr_2$	TEMPO	DCE	69
8 [c]	$CuBr_2$	TEMPO	DCE	67
9	$CuCl_2$	TEMPO	DCE	87
10	$Cu(OAc)_2$	TEMPO	DCE	82
11	CuO	TEMPO	DCE	82
12	CuBr	TEMPO	DCE	83
13	—	TEMPO	DCE	62
14 [d]	$CuBr_2$	TEMPO	DCE	95
15 [d]	—	TEMPO	DCE	64
16	$CuBr_2$	$K_2S_2O_8$	DCE	12
17	$CuBr_2$	Oxone	DCE	8
18	$CuBr_2$	TBHP	DCE	54
19	$CuBr_2$	Air	DCE	36
20	$CuBr_2$	O_2	DCE	83

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol, 2 equiv.), [Cu] (10 mol%), oxidant (0.4 mmol, 2 equiv.), solvent (2 mL), at 80 °C, reaction for 24 h. [b] at 60 °C. [c] at 100 °C. [d] under N_2. [e] gram-scale reaction: **1a** (8 mmol), **2a** (16 mmol, 2 equiv.), [Cu] (10 mol%), TEMPO (16 mmol, 2 equiv.), DCE (50 mL), at 80 °C, reaction for 24 h.

optimized reaction condition to yield products **24** and **25** in 68% and 41% yields, respectively. Such compounds are structurally related to a number of herbicides.[16] Generally, imidazoles are less reactive than benzimidazoles, hence the conjugation effect between the benzene ring and imidazole ring may facilitate transformation. The reaction still proceeded for substrates lacking a fluoro group but with the corresponding products being obtained in lower yields. For example, reaction of **2a** provided the corresponding products **26**-**29** in yields of 31-68%. This indicates that the fluoro group in **2a** can enhance the reactivity via formation of an alkyl free radical. The low yields mostly result from the decomposition of iodoalkanes and the formation of unknown byproducts. ICF_2CO_2Et was also subjected to the reaction conditions, but the corresponding product was not obtained. Neither benzothiazole nor benzoxazole were suitable for this reaction. Since a good yield was obtained under aerobic conditions (Table 1, Entry 20), these reactions were also conducted in the presence of

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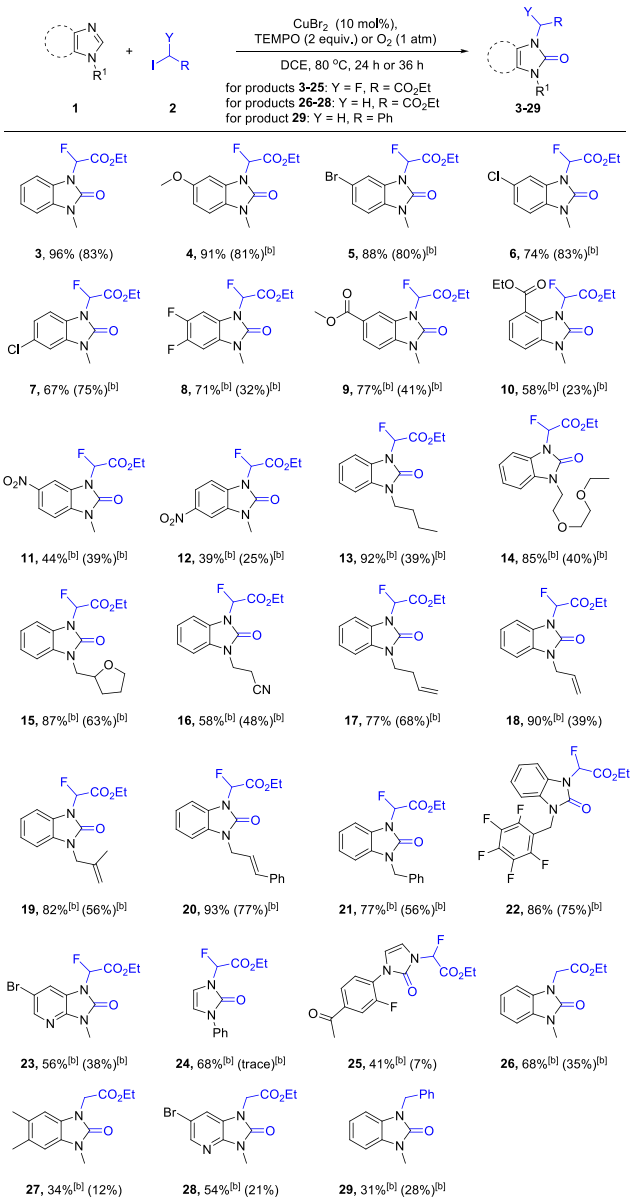
$CuBr_2$ and O_2 (Table 2); the desired products were obtained in moderate to good yields. Generally, O_2 is less effective than TEMPO in such transformations. For products **6** and **7**, using O_2 proved more efficient than TEMPO. However, $CuBr_2/O_2$ is not suitable for the formation of product **24**.

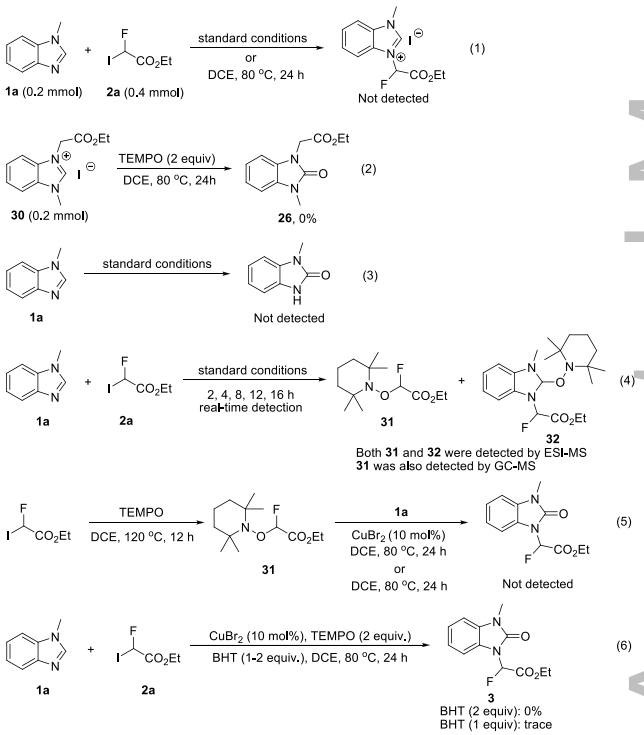
Table 2. Reaction scope of imidazoles [a].



[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol, 2 equiv.), $CuBr_2$ (10 mol%), TEMPO (0.4 mmol, 2 equiv.), solvent (2 mL), at 80 °C, reaction for 24 h. [b] reaction for 36 h. Reaction conditions for the yield of parentheses: TEMPO was replaced with O_2 (1 atm).

Next, we focused on understanding the mechanism of this TEMPO mediated reaction. Several control experiments were conducted to understand the role of TEMPO (Scheme 2). No benzimidazolium species was detected by ESI-MS analysis via the reaction of **1a** with **2a** in the absence of TEMPO (Scheme 2, eq. 1). When the benzimidazolium salt **30** was treated with TEMPO in the absence of copper catalyst, none of the target product **26** was observed (Scheme 2, eq. 2 *vs* Table 1, entry 13). These results suggest that this reaction pathway differs from previous methods involving an imidazolium salt.[6-9] The *N*-methyl benzimidazole **1a** did not furnish the required benzimidazolone in the absence of alkyl halide under standard conditions (Scheme 2, eq. 3). ESI-MS real-time analysis showed the presence of compounds **31** and **32** in the reaction mixture (Scheme 2, eq. 4; see the SI). Further studies showed that compound **31** can be quantitatively prepared from the reaction of TEMPO with iodofluoroacetate at 120 °C without any additives (see the SI); however, its reaction with **1a** did not afford the target product **3** (Scheme 2, eq. 5). Intermediate **32** disappears as the reaction progresses. These results clearly indicate that compound **31** is not an intermediate but a byproduct, and that compound **32** is a reaction intermediate. In the presence of the radical trapping reagent BHT (2,6-di-*tert*-butyl-4-methylphenol), the reaction was completely suppressed, and no target product was observed suggesting that the reaction may undergo a free radical process (Scheme 2, eq. 5).

Scheme 2. Control experiments.



Based on the results of the control experiments and previous work,[13,15] a plausible reaction mechanism is depicted in scheme 3. $CuBr_2$ may act as a redox agent for the oxidation of **1a** to species **A.** The resulting Cu(I) species could be reoxidized to Cu(II) via conversion of TEMPO to 2,2,6,6-tetramethylpiperidin-1-olate **B**. Under heating conditions, iodofluoroacetate **2a** may undergo mesolytic cleavage of the C-I bond to afford a radical

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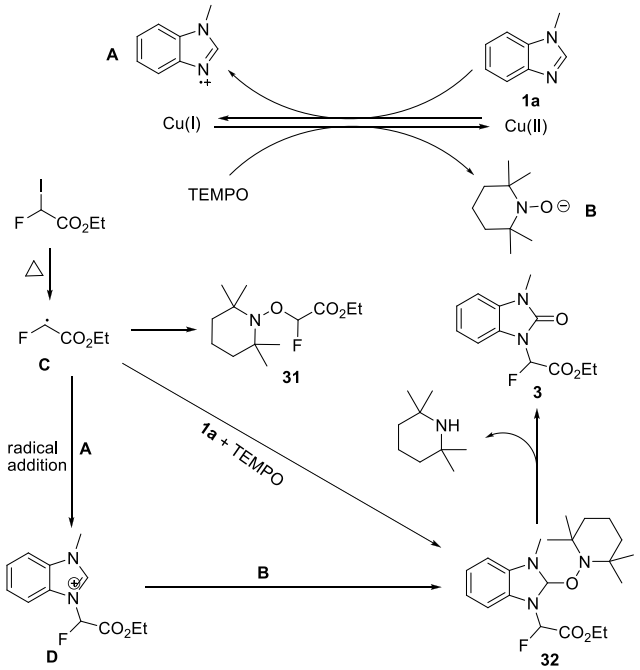
C,[17] which then undergoes radical addition with **1a** and TEMPO to form intermediate **32**.[18] Radical **C** may couple with intermediate **A** to produce intermediate **D**, which upon addition with intermediate **B** gives **32**. Finally, intermediate **32** undergoes a β-elimination to afford 2,2,6,6-tetramethylpiperidine and target product **3**.

Scheme 3. A plausible reaction pathway.



Conclusion

In summary, we have developed a novel and convenient strategy for the transformation of imidazoles into *N*-(fluoroalkyl)imidazolones via a radical addition of imidazoles with iodofluoroacetate and TEMPO. This new chemistry facilitates the formation of a number of products in moderate to excellent yields. It is worth noting that *N*-(fluoroalkyl) imidazolones could also be synthesized under aerobic oxidation conditions. Good functional group tolerance allows for the preparation of a number of diverse products which are of great interest in drug and pesticide development.

Experimental Section

General Methods

^{1}H and ^{13}C NMR spectra were measured on a Bruker Avance-Ⅲ 600 instrument (600MHz for ^{1}H, 151 MHz for ^{13}C NMR spectroscopy) using $CDCl_3$ as the solvent. Chemical shifts for ^{1}H and ^{13}C NMR were referred to internal Me_4Si (0 ppm) as the standard. The following abbreviations (or combinations thereof) were used to explain chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, and coupling constants (*J*) in hertz (Hz). GC-MS (EI) analysis was measured on an Agilent GC-MS-5975C Plus spectrometer. LC-MS (ESI) analysis was measured on an AB Sciex API3200. IR spectra was measured on a Nicolet IS10. HRMS (ESI) analysis was measured on a Thermo Scientific LTQ Orbitrap XL.

General procedure for the synthesis of *N*-(Fluoroalkyl)imidazolones 3-29: A 15 mL sealed tube (with a Teflon cap) equipped with a magnetic stir bar was charged with imidazole (0.20 mmol), $CuBr_2$ (10 mol%) and TEMPO (0.40 mmol, 2 equiv). DCE (1.0 mL) was added to the mixture, followed by alkyl halide (0.4 mmol, 2 equiv) and, finally, another portion of DCE (1.0 mL). The tube was then capped and submerged into an oil bath pre-heated to 80 °C. The reaction was stirred for 24 h or 36 h and cooled to room temperature. An excess of anhydrous $Na_2S_2O_3$ was added to the reaction mixture, diluted with ethyl acetate (5 mL) and filtered through a short pad of celite washing with an additional 20 mL ethyl acetate. The filtrate was concentrated in vacuo, and the resulting residue was purified by flash column chromatography using n-hexane or petroleum ether and ethyl acetate as the eluent.

Experimental procedure for the preparation of compound 30: A 50 mL round bottom flask, equipped with a magnetic stirrer bar was charged with 1-methyl-benzimidazole (4.0 mmol), ethyl iodoacetate (1.2 equiv.) and ethyl acetate (20 mL). The reaction mixture was stirred at room temperature overnight. After the completion of the reaction, ethyl acetate was removed in vacuo, and the residue was washed with diethyl ether. The benzimidazolium salt **30** was obtained as a white solid.

Experimental procedure for the *in situ* preparation of compound 31: A 15 mL sealed tube (with a Teflon cap) equipped with a magnetic stirrer bar was charged with TEMPO (0.40 mmol, 2 equiv), DCE (1.0 mL), 2-fluoro-2-iodoacetate **2a** (0.4 mmol, 2 equiv) and, finally, another portion of DCE (1.0 mL). The tube was then capped and submerged into an oil bath pre-heated to 120 °C. The reaction was stirred for 12 h and then cooled to room temperature. The reaction mixture was directly used for control experiments (see Scheme 2, eq. 5).

Ethyl 2-fluoro-2-(3-methyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)acetate (3). CAS number: 1516303-22-2. Yellow solid. M.P.: 83.1 – 84.6 °C. 96% Yield (48 mg, Eluent: EtOAc/petroleum = 1:5). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 – 7.13 (m, 1H), 7.07 (q, *J* = 7.8 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.65 (d, *J* = 48.0 Hz, 1H), 4.36 – 4.24 (m, 2H), 3.39 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.65 (d, J_{C-F} = 35.9 Hz, 1C), 153.11, 130.21, 126.16 (d, J_{C-F} = 2.9 Hz, 1C), 123.12, 122.07, 109.32, 108.12, 85.05 (d, J_{C-F} = 212.2 Hz, 1C), 62.99, 27.30, 13.97. IR (KBr, cm^{-1}): 2924, 2853, 1765, 1724, 1620, 1497, 1434, 1393, 1373, 1056, 1023, 753.

Ethyl 2-fluoro-2-(6-methoxy-3-methyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)acetate (4). Yellow solid. M.P.: 103.3 – 104.1 °C. 91% Yield (51 mg, Eluent: EtOAc/petroleum = 1:4). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.87 (d, *J* = 8.3 Hz, 1H), 6.75 – 6.68 (m, 2H), 6.63 (d, *J* = 47.9 Hz, 1H), 4.38 – 4.25 (m, 2H), 3.77 (s, 3H), 3.37 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.63 (d, J_{C-F} = 36.1 Hz, 1C), 155.88, 153.28, 126.92 (d, J_{C-F} = 3.0 Hz, 1C), 124.15, 108.55, 108.43, 96.74, 85.06 (d, J_{C-F} = 212.2 Hz, 1C), 62.98, 55.94, 27.32, 14.00. IR (KBr, cm^{-1}): 2952, 2907, 2835, 1764, 1721, 1631, 1613, 1503, 1430, 1396, 1289, 1211, 1160, 1050, 1023, 745, 692. HRMS (ESI) for $C_{13}H_{16}FN_2O_4^+$ $(M+H)^+$: calcd 283.10886, found 283.10907.

Ethyl 2-(6-bromo-3-methyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)-2-fluoroacetate (5). Yellow solid. M.P.: 124.3 – 125.4 °C. 88% Yield (58 mg, Eluent: EtOAc/petroleum = 1:4). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.3 Hz, 1H), 7.24 (s, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.61 (d, *J* = 47.6 Hz, 1H), 4.42 – 4.26 (m, 2H), 3.39 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$)

δ 164.22 (d, J_{C-F} = 35.5 Hz, 1C), 152.78, 129.36, 127.22 (d, J_{C-F} = 2.9 Hz, 1C), 125.99, 114.60, 112.73, 109.26, 85.06 (d, J_{C-F} = 213.6 Hz, 1C), 63.20, 27.42, 13.98. IR (KBr, cm^{-1}): 2956, 2924, 2852, 1730, 1619, 1604, 1494, 1429, 1391, 1223, 1047, 1016, 799, 747, 696. HRMS (ESI) for $C_{12}H_{13}BrFN_2O_3^+$ $(M+H)^+$: calcd 331.00881, found 331.00928.

Ethyl 2-(6-chloro-3-methyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)-2-fluoroacetate (6). Light yellow solid. M.P.: 93.0 – 93.7 °C. 74% Yield (42 mg, Eluent: EtOAc/petroleum = 1:4). ^1H NMR (600 MHz, $CDCl_3$) δ 7.06 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.04 – 6.99 (m, 2H), 6.63 (d, *J* = 47.6 Hz, 1H), 4.38 – 4.25 (m, 2H), 3.41 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.36 (d, J_{C-F} = 35.8 Hz, 1C), 153.06, 131.23, 128.88, 124.72 (d, J_{C-F} = 2.9 Hz, 1C), 121.98, 110.28, 108.67, 85.04 (d, J_{C-F} = 212.89 Hz, 1C), 63.13, 27.48, 13.99. IR (KBr, cm^{-1}): 3079, 2982, 2930, 2855, 1732, 1623, 1607, 1499, 1430, 1392, 1373, 1226, 1048, 1017, 802, 750. HRMS (ESI) for $C_{12}H_{13}FClN_2O_3^+$ $(M+H)^+$: calcd 287.05932, found 287.05984.

Ethyl 2-(5-chloro-3-methyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)-2-fluoroacetate (7). Light yellow solid. M.P.: 90.5 – 91.5 °C. 67% Yield (38 mg, Eluent: EtOAc/petroleum = 1:4). ^1H NMR (600 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.12 (d, *J* = 1.8 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.62 (d, *J* = 47.5 Hz, 1H), 4.42 – 4.29 (m, 2H), 3.41 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.26 (d, J_{C-F} = 35.5 Hz, 1C), 152.95, 128.89, 127.70, 126.90 (d, J_{C-F} = 2.9 Hz, 1C), 123.16, 110.10, 108.78, 85.04 (d, J_{C-F} = 213.5 Hz, 1C), 63.21, 27.46, 13.99. IR (KBr, cm^{-1}): 3078, 2981, 2925, 2852, 1732, 1622, 1607, 1497, 1431, 1394, 1224, 1051, 1018, 801, 749, 703. HRMS (ESI) for $C_{12}H_{13}FClN_2O_3^+$ $(M+H)^+$: calcd 287.05932, found 287.05984.

Ethyl 2-(5,6-difluoro-3-methyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)-2-fluoroacetate (8). Light yellow solid. M.P.: 84.2 – 84.8 °C. 71% Yield (41 mg, Eluent: EtOAc/petroleum = 1:3). ^1H NMR (600 MHz, $CDCl_3$) δ 7.05 – 6.98 (m, 1H), 6.89 – 6.82 (m, 1H), 6.62 (d, *J* = 47.2 Hz, 1H), 4.40 – 4.28 (m, 2H), 3.40 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.18 (d, J_{C-F} = 35.7 Hz, 1C), 153.31, 147.72 (dd, J_{C-F} = 243.5, 14.0 Hz, 1C), 146.11 (dd, J_{C-F} = 242.7, 14.1 Hz, 1C), 126.04 (d, J_{C-F} = 10.2 Hz, 1C), 121.37 (d, J_{C-F} = 10.2 Hz, 1C), 100.00 (d, J_{C-F} = 24.8 Hz, 1C), 98.01 (d, J_{C-F} = 23.9 Hz, 1C), 85.13 (d, J_{C-F} = 213.4 Hz, 1C), 63.25, 27.60, 13.98. IR (KBr, cm^{-1}): 3065, 2984, 2926, 2854, 1736, 1634, 1510, 1449, 1395, 1223, 1165, 1053, 1019, 851, 790, 747. HRMS (ESI) for $C_{12}H_{12}F_3N_2O_3^+$ $(M+H)^+$: calcd 289.07945, found 289.07977.

Methyl 3-(2-ethoxy-1-fluoro-2-oxoethyl)-1-methyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazole-5-carboxylate (9). White solid. M.P.: 118.5 – 119.4 °C. 77% Yield (48 mg, Eluent: EtOAc/petroleum = 1:4). ^1H NMR (600 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.77 (d, *J* = 1.2 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.65 (d, *J* = 47.9 Hz, 1H), 4.44 – 4.28 (m, 2H), 3.90 (s, 3H), 3.45 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.47, 164.25 (d, J_{C-F} = 34.7 Hz, 1C), 153.26, 133.94, 126.02 (d, J_{C-F} = 2.8 Hz, 1C), 125.70, 124.28, 110.52, 107.57, 85.08 (d, J_{C-F} = 214.6 Hz, 1C), 63.23, 52.19, 27.56, 13.96. IR (KBr, cm^{-1}): 3076, 2954, 2851, 1739, 1716, 1625, 1508, 1468, 1434, 1394, 1377, 1270, 1246, 1103, 1050, 1019, 764. HRMS (ESI) for $C_{14}H_{16}FN_2O_5^+$ $(M+H)^+$: calcd 311.10378, found 311.10394.

Ethyl 3-(2-ethoxy-1-fluoro-2-oxoethyl)-1-methyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazole-4-carboxylate (10). Light yellow solid. M.P.: 111.2 – 112.0 °C. 58% Yield (38 mg, Eluent: EtOAc/petroleum = 1:3). ^1H NMR (600 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.42 (d, *J* = 48.4 Hz, 1H), 7.22 (t, *J* = 7.9 Hz, 1H), 7.16 (dd, *J* = 7.8, 1.1 Hz, 1H), 4.41 – 4.35 (m, 4H), 3.42 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.34 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.83, 165.15 (d, J_{C-F} = 30.5 Hz, 1C), 153.44, 132.03, 127.09 (d, J_{C-F} = 3.1 Hz, 1C), 124.62, 122.35, 115.68, 111.88, 87.19 (d, J_{C-F} = 217.1 Hz, 1C), 62.57, 61.87, 27.38, 14.13, 14.01. IR (KBr, cm^{-1}): 2956, 2924, 2853, 1770, 1736, 1650, 1615, 1468, 1392, 1371, 1260, 1223, 1053, 1018, 756. HRMS (ESI) for $C_{15}H_{18}FN_2O_5^+$ $(M+H)^+$: calcd 325.11943, found 325.11969.

Ethyl 2-fluoro-2-(3-methyl-6-nitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)acetate (11). Yellow solid. M.P.: 105.3 – 106.3 °C. 44% Yield (26 mg, Eluent: EtOAc/petroleum = 1:3). ^1H NMR (600 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.92 (d, *J* = 2.1 Hz, 1H), 7.21 (d, *J* = 8.7 Hz, 1H), 6.68 (d, *J* = 46.9 Hz, 1H), 4.41 – 4.29 (m, 2H), 3.52 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.90 (d, J_{C-F} = 34.9 Hz, 1C), 153.08, 144.08, 131.04 (d, J_{C-F} = 2.7 Hz, 1C), 130.58, 118.78, 109.19, 103.93, 85.03 (d, J_{C-F} = 214.5 Hz, 1C), 63.47, 27.81, 14.00. IR (KBr, cm^{-1}): 2954, 2924, 2853, 1736, 1618, 1523, 1500, 1430, 1392, 1337, 1225, 1041, 1015, 752. HRMS (ESI) for $C_{12}H_{13}FN_3O_5^+$ $(M+H)^+$: calcd 298.08338, found 298.08365.

Ethyl 2-fluoro-2-(3-methyl-5-nitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)acetate (12). Yellow solid. M.P.: 125.9 – 127.0 °C. 39% Yield (23 mg, Eluent: EtOAc/petroleum = 1:3). ^1H NMR (600 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 8.7, 2.0 Hz, 1H), 8.03 (d, *J* = 2.0 Hz, 1H), 7.09 (d, *J* = 8.7 Hz, 1H), 6.67 (d, *J* = 47.3 Hz, 1H), 4.48 – 4.32 (m, 2H), 3.51 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.84 (d, J_{C-F} = 34.2 Hz, 1C), 153.21, 143.11, 135.23, 126.10 (d, J_{C-F} = 2.8 Hz, 1C), 120.10, 107.46, 105.64, 85.15 (d, J_{C-F} = 216.0 Hz, 1C), 63.58, 27.84, 14.01. IR (KBr, cm^{-1}): 2955, 2924, 2853, 1742, 1623, 1523, 1504, 1434, 1393, 1338, 1285, 1044, 1018, 750. HRMS (ESI) for $C_{12}H_{13}FN_3O_5^+$ $(M+H)^+$: calcd 298.08338, found 298.08365.

Ethyl 2-(3-butyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)-2-fluoroacetate (13). Yellow oil. 92% Yield (54 mg, Eluent: EtOAc/petroleum = 1:6). ^1H NMR (600 MHz, $CDCl_3$) δ 7.15 (td, *J* = 7.7, 1.3 Hz, 1H) 7.11 – 7.06 (m, 2H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.65 (d, *J* = 47.9 Hz, 1H), 4.38 – 4.26 (m, 2H), 3.88 (td, *J* = 7.1, 2.0 Hz, 2H), 1.77 – 1.72 (m, 2H), 1.43 – 1.37 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.67 (d, J_{C-F} = 36.0 Hz, 1C), 152.97, 129.72, 126.34 (d, J_{C-F} = 3.0 Hz, 1C), 122.98, 121.84, 109.47, 108.31, 85.13 (d, J_{C-F} = 212.2 Hz, 1C), 62.93, 41.24, 30.15, 20.01, 13.96, 13.64. IR (KBr, cm^{-1}): 3066, 2959, 2929, 2873, 1766, 1723, 1612, 1492, 1398, 1373, 1223, 1171, 1049, 754. HRMS (ESI) for $C_{15}H_{20}FN_2O_3^+$ $(M+H)^+$: calcd 295.14525, found 295.14545.

Ethyl 2-(3-(2-(2-ethoxyethoxy)ethyl)-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)-2-fluoroacetate (14). Yellow oil. 85% Yield (60 mg, Eluent: EtOAc/petroleum = 1:3). ^1H NMR (600 MHz, $CDCl_3$) δ 7.20 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.3 Hz, 1H), 7.10 – 7.05 (m, 2H), 6.65 (d, *J* = 48.0 Hz, 1H), 4.39 – 4.25 (m, 2H), 4.13 – 4.03 (m, 2H), 3.84 – 3.75 (m, 2H), 3.59 (t, *J* = 3.9 Hz, 2H), 3.50 (t, *J* = 3.6 Hz, 2H), 3.45 (q, *J* = 7.0 Hz, 2H), 1.26 (t, *J* = 7.3 Hz, 3H), 1.15 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.66 (d, J_{C-F} = 35.8 Hz, 1C), 153.05, 130.15, 126.18 (d, J_{C-F} = 2.8 Hz, 1C), 123.00, 121.95, 109.42, 109.25, 85.07 (d, J_{C-F} = 212.5 Hz, 1C), 70.73, 69.78, 69.01, 66.63, 62.97, 41.68, 15.09, 13.98. IR (KBr, cm^{-1}): 3065, 2971, 2960, 2924, 2856, 1765, 1722, 1618, 1492, 1397, 1375, 1220, 1110, 1059, 1024, 754. HRMS (ESI) for $C_{17}H_{24}FN_2O_5^+$ $(M+H)^+$: calcd 355.16638, found 355.16678.

Ethyl 2-fluoro-2-(2-oxo-3-((tetrahydrofuran-2-yl)methyl)-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)acetate (15). Yellow solid. M.P.: 71.4 – 72.5 °C. 87% Yield (56 mg, Eluent: EtOAc/petroleum = 1:4). ^1H NMR (600 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 7.8, 3.2 Hz, 1H), 7.16 – 7.14 (m, 1H), 7.11 – 7.05 (m, 2H), 6.65 (d, *J* = 47.9 Hz, 1H), 4.38 – 4.23 (m, 3H), 4.02 (dd, *J* = 14.6, 4.1 Hz, 1H), 3.91

(dq, J = 14.4, 3.0 Hz, 1H), 3.85 – 3.81 (m, 1H), 3.76 – 3.68 (m, 1H), 2.07 – 2.01 (m, 1H), 1.92 – 1.82 (m, 2H), 1.76 – 1.71 (m, 1H), 1.26 (t, 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.65 (d, J_{C-F} = 35.8 Hz, 1C), 153.36, 130.22, 126.23 (d, J_{C-F} = 2.9 Hz, 1C), 123.11, 122.03, 109.61, 109.24, 85.10 (d, J_{C-F} = 212.2 Hz, 1C), 68.28, 62.97, 45.69, 28.95, 28.89, 25.65, 13.98. IR (KBr, cm^{-1}): 3066, 2957, 2927, 2871, 2857, 1767, 1724, 1618, 1493, 1401, 1376, 1227, 1059, 1013, 756. HRMS (ESI) for $C_{16}H_{20}FN_2O_4^+$ $(M+H)^+$: calcd 323.14016, found 323.14078.

Ethyl 2-(3-(2-cyanoethyl)-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)-2-fluoroacetate (16). Yellow solid. M.P.: 101.2 – 102.9 °C. 58% Yield (34 mg, Eluent: EtOAc/petroleum = 1:2). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 1H), 7.16 – 7.10 (m, 3H), 6.63 (d, J = 47.7 Hz, 1H), 4.39 – 4.27 (m, 2H), 4.19 (t, J = 6.9 Hz, 2H), 2.85 (td, J = 6.9, 1.7 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.30 (d, J_{C-F} = 35.4 Hz, 1C), 152.61, 128.62, 126.31 (d, J_{C-F} = 2.8 Hz, 1C), 123.52, 122.81, 116.93, 109.94, 108.15, 85.01 (d, J_{C-F} = 213.3 Hz, 1C), 63.15, 37.48, 17.06, 13.96. IR (KBr, cm^{-1}): 3068, 2982, 2967, 2941, 2252, 1766, 1728, 1615, 1493, 1401, 1376, 1229, 1057, 1024, 755. HRMS (ESI) for $C_{14}H_{15}FN_3O_3^+$ $(M+H)^+$: calcd 292.10920, found 292.10956.

Ethyl 2-(3-(but-3-enyl)-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)-2-fluoroacetate (17). Yellow oil. 77% Yield (45 mg, Eluent: EtOAc/petroleum = 1:6). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (t, J = 7.5 Hz, 1H), 7.11 – 7.07 (m, 2H), 7.03 (d, J = 7.8 Hz, 1H), 6.65 (d, J = 47.9 Hz, 1H), 5.86 – 5.77 (m, 1H), 5.11 – 5.01 (m, 2H), 4.39 – 4.24 (m, 2H), 3.95 (t, J = 7.3 Hz, 2H), 2.52 (q, J = 7.0 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.65 (d, J_{C-F} = 36.0 Hz, 1C), 152.92, 133.98, 129.56, 126.31 (d, J_{C-F} = 3.0 Hz, 1C), 123.03, 121.95, 117.84, 109.51, 108.38, 85.09 (d, J_{C-F} = 212.2 Hz, 1C), 62.95, 40.88, 32.36, 13.97. IR (KBr, cm^{-1}): 3069, 2979, 2958, 2925, 2853, 1767, 1723, 1641, 1618, 1493, 1400, 1375, 1225, 1055, 1023, 754. HRMS (ESI) for $C_{15}H_{18}FN_2O_3^+$ $(M+H)^+$: calcd 293.12960, found 293.12988.

Ethyl 2-(3-allyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)-2-fluoroacetate (18). Yellow oil. 90% Yield (50 mg, Eluent: EtOAc/petroleum = 1:6). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 – 7.09 (m, 2H), 7.09 – 7.04 (m, 1H), 6.99 (d, J = 7.7 Hz, 1H), 6.66 (d, J = 47.9 Hz, 1H), 5.91 – 5.85 (m, 1H), 5.24 – 5.20 (m, 2H), 4.49 (d, J = 5.2 Hz, 2H), 4.37 – 4.24 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.58 (d, J_{C-F} = 35.8 Hz, 1C), 152.72, 131.25, 129.46, 126.28 (d, J_{C-F} = 2.9 Hz, 1C), 123.09, 122.07, 117.94, 109.37, 108.92, 85.14 (d, J_{C-F} = 212.3 Hz, 1C), 62.97, 43.64, 13.94. IR (KBr, cm^{-1}): 3068, 2983, 2925, 2854, 1765, 1724, 1646, 1618, 1491, 1396, 1375, 1224, 1048, 1016, 754. HRMS (ESI) for $C_{14}H_{16}FN_2O_3^+$ $(M+H)^+$: calcd 279.11395, found 279.11411.

Ethyl 2-fluoro-2-(3-(2-methylallyl)-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)acetate (19). Yellow oil. 82% Yield (48 mg, Eluent: EtOAc/petroleum = 1:5). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 – 7.07 (m, 3H), 7.00 (d, J = 7.7 Hz, 1H), 6.67 (d, J = 47.8 Hz, 1H), 4.96 (s, 1H), 4.86 (s, 1H), 4.44 (s, 2H), 4.37 – 4.26 (m, 2H), 1.74 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.61 (d, J_{C-F} = 36.0 Hz, 1C), 153.04, 138.96, 129.65, 126.27 (d, J_{C-F} = 3.0 Hz, 1C), 123.09, 122.10, 113.10, 109.42, 109.06, 85.24 (d, J_{C-F} = 212.2 Hz, 1C), 62.96, 47.23, 19.74, 13.96. IR (KBr, cm^{-1}): 3068, 2980, 2924, 2854, 1766, 1722, 1660, 1615, 1492, 1396, 1376, 1225, 1051, 1023, 753. HRMS (ESI) for $C_{15}H_{18}FN_2O_3^+$ $(M+H)^+$: calcd 293.12960, found 293.12982.

(E)-ethyl 2-fluoro-2-(2-oxo-3-(3-phenylallyl)-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)acetate (20). Yellow oil. 93% Yield (66 mg, Eluent: EtOAc/petroleum = 1:6). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, J = 7.8 Hz, 2H), 7.30 (t, J = 7.3 Hz, 2H), 7.25 (t, J = 7.3 Hz, 1H), 7.15 (t, J = 6.8 Hz, 2H), 7.12 – 7.08 (m, 2H), 6.72 (d, J = 47.9 Hz, 1H), 6.65 (d, J = 15.9 Hz, 1H), 6.27 (dt, J = 15.8, 6.0 Hz, 1H), 4.69 (d, J = 5.4 Hz, 2H), 4.42 – 4.29 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.66 (d, J_{C-F} = 35.9 Hz, 1C), 152.83, 136.00, 133.54, 129.55, 128.63, 128.09, 126.56, 126.38 (d, J_{C-F} = 2.7 Hz, 1C), 123.20, 122.67, 122.17, 109.54, 108.97, 85.20 (d, J_{C-F} = 212.6 Hz, 1C), 63.04, 43.47, 14.03. IR (KBr, cm^{-1}): 3062, 3027, 2982, 2926, 1766, 1725, 1617, 1492, 1399, 1375, 1227, 1050, 1014, 755, 692. HRMS (ESI) for $C_{20}H_{20}FN_2O_3^+$ $(M+H)^+$: calcd 355.14525, found 355.14560.

Ethyl 2-(3-benzyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)-2-fluoroacetate (21). Yellow solid. M.P.: 72.6 – 73.9 °C. 77% Yield (51 mg, Eluent: EtOAc/petroleum = 1:6). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, J = 4.4 Hz, 4H), 7.28 (dd, J = 8.8, 4.4 Hz, 1H), 7.14 – 7.10 (m, 1H), 7.10 – 7.04 (m, 2H), 6.93 – 6.88 (m, 1H), 6.72 (d, J = 47.8 Hz, 1H), 5.10 (d, J = 15.7 Hz, 1H), 5.06 (d, J = 15.8 Hz, 1H), 4.40 – 4.29 (m, 2H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.63 (d, J_{C-F} = 35.9 Hz, 1C), 153.24, 135.49, 129.46, 128.88, 127.96, 127.45, 126.40 (d, J_{C-F} = 2.9 Hz, 1C), 123.16, 122.21, 109.54, 109.00, 85.27 (d, J_{C-F} = 212.5 Hz, 1C), 63.03, 45.16, 14.00. IR (KBr, cm^{-1}): 3064, 3031, 2956, 2923, 2853, 1764, 1716, 1613, 1490, 1455, 1397, 1375, 1225, 1044, 1011, 751, 695. HRMS (ESI) for $C_{18}H_{18}FN_2O_3^+$ $(M+H)^+$: calcd 329.12960, found 329.12985.

Ethyl 2-fluoro-2-(2-oxo-3-((perfluorophenyl)methyl)-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)acetate (22). Yellow oil. 86% Yield (72 mg, Eluent: EtOAc/petroleum = 1:6). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 – 7.07 (m, 3H), 7.01 (d, J = 7.7 Hz, 1H), 6.64 (d, J = 47.6 Hz, 1H), 5.18 (s, 2H), 4.38 – 4.26 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.37 (d, J_{C-F} = 35.7 Hz, 1C), 152.47, 145.69 (dm, J_{C-F} = 249.3 Hz; 146.52 – 146.32, 144.86 – 144.63, 1C), 141.62 (dm, J_{C-F} = 246.5 Hz; 142.44 – 142.21, 140.80 – 140.52, 1C), 137.81 (dm, J_{C-F} = 256.8 Hz; 138.66 – 138.35, 136.96 – 136.66, 1C), 128.54, 126.38 (d, J_{C-F} = 2.7 Hz, 1C), 123.39, 122.68, 109.79, 108.79 (td, J_{C-F} = 18.0, 2.5 Hz, 1C), 108.14, 85.12 (d, J_{C-F} = 212.9 Hz, 1C), 63.09, 33.10, 13.88. IR (KBr, cm^{-1}): 3068, 2986, 2968, 2946, 1766, 1735, 1657, 1616, 1523, 1508, 1493, 1401, 1367, 1230, 1127, 1050, 1022, 754, 689. HRMS (ESI) for $C_{18}H_{13}F_6N_2O_3^+$ $(M+H)^+$: calcd 419.08249, found 419.08292.

Ethyl 2-(6-bromo-3-methyl-2-oxo-2,3-dihydro-1*H*-imidazo[4,5-*b*]pyridin-1-yl)-2-fluoroacetate (23). White solid. M.P.: 135.4 – 136.2 °C. 56% Yield (37 mg, Eluent: EtOAc/petroleum = 1:5). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, J = 1.7 Hz, 1H), 7.49 (d, J = 1.8 Hz, 1H), 6.66 (d, J = 47.1 Hz, 1H), 4.48 – 4.20 (m, 2H), 3.48 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.86 (d, J_{C-F} = 35.4 Hz, 1C), 152.30, 143.08, 142.72, 121.44 (d, J_{C-F} = 2.8 Hz, 1C), 118.99, 112.89, 84.73 (d, J_{C-F} = 214.1 Hz, 1C), 63.43, 26.36, 14.00. IR (KBr, cm^{-1}): 2978, 2923, 2854, 1748, 1613, 1594, 1489, 1415, 1393, 1259, 1220, 1059, 1016, 875, 746, 584. HRMS (ESI) for $C_{11}H_{12}FBrN_3O_3^+$ $(M+H)^+$: calcd 332.00406, found 332.00461.

Ethyl 2-fluoro-2-(2-oxo-3-phenyl-2,3-dihydro-1*H*-imidazol-1-yl)acetate (24). Brown oil. 68% Yield (36 mg, Eluent: EtOAc/petroleum = 1:4). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, J = 8.2 Hz, 2H), 7.43 (t, J = 7.6 Hz, 2H) 7.27 (t, J = 7.2 Hz, 1H), 6.66 (d, J = 1.9 Hz, 1H), 6.59 (d, J = 2.9 Hz, 1H), 6.47 (d, J = 49.2 Hz, 1H), 4.40 – 4.31 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.45 (d, J_{C-F} = 35.1 Hz, 1C), 151.11, 136.43, 129.31, 126.46, 121.79, 112.40, 108.62, 85.49 (d, J_{C-F} = 212.1 Hz, 1C), 62.95, 13.98. IR (KBr, cm^{-1}): 3065, 2981, 2926, 2854, 1738, 1694, 1598, 1502, 1458, 1409, 1206, 1096, 1024, 758, 694. HRMS (ESI) for $C_{13}H_{14}FN_2O_3^+$ $(M+H)^+$: calcd 265.09830, found 265.09854.

Ethyl 2-(3-(4-acetyl-2-fluorophenyl)-2-oxo-2,3-dihydro-1*H*-imidazol-1-yl)-2-fluoroacetate (25). Yellow solid. M.P.: 39.9 – 41.4 °C. 41% Yield (27 mg, Eluent: EtOAc/petroleum = 1:3). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 1H), 7.80 – 7.60 (m, 2H), 6.67 (t, J = 2.8 Hz,

1H), 6.61 (d, J = 3.3 Hz, 1H), 6.43 (d, J = 49.0 Hz, 1H), 4.40 – 4.30 (m, 2H), 2.59 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.62, 164.19 (d, J_{C-F} = 34.7 Hz, 1C), 155.19 (d, J_{C-F} = 252.8 Hz, 1C), 151.04, 137.11 (d, J_{C-F} = 5.8 Hz, 1C), 127.92 (d, J_{C-F} = 11.0 Hz, 1C), 126.45, 124.84 (d, J_{C-F} = 3.3 Hz, 1C), 116.42 (d, J_{C-F} = 21.1 Hz, 1C), 113.51 (d, J_{C-F} = 5.4 Hz, 1C), 108.89, 85.47 (d, J_{C-F} = 212.9 Hz, 1C), 63.08, 26.54, 13.98. IR (KBr, cm^{-1}): 3072, 2985, 2925, 1763, 1716, 1687, 1614, 1577, 1425, 1369, 1271, 1233, 1198, 743, 658. HRMS (ESI) for $C_{15}H_{15}F_2N_2O_4^+$ $(M+H)^+$: calcd 325.09944, found 325.09982.

Ethyl 2-(3-methyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)acetate (26). CAS number: 1153349-40-6. White solid. M.P.: 105.6 – 107.1 °C. 68% Yield (32 mg, Eluent: EtOAc/petroleum = 1:4). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 – 7.06 (m, 2H), 6.99 (d, J = 8.0 Hz, 1H), 6.88 (d, J = 7.3 Hz, 1H), 4.62 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.43 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.84, 154.28, 130.14, 129.07, 121.75, 121.46, 107.68, 107.55, 61.74, 42.35, 27.25, 14.13. IR (KBr, cm^{-1}): 3062, 2924, 2853, 1709, 1621, 1500, 1439, 1401, 1376, 1206, 1052, 1011, 754.

Ethyl 2-(3,5,6-trimethyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-1-yl)acetate (27). CAS number: 2114881-86-4. White solid. M.P.: 145.6 – 146.2 °C. 34% Yield (19 mg, Eluent: EtOAc/petroleum = 1:5). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.76 (s, 1H), 6.66 (s, 1H), 4.57 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.38 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.03, 154.39, 129.85, 129.53, 128.24, 127.17, 108.92, 108.74, 61.63, 42.36, 27.19, 19.91, 14.13. IR (KBr, cm^{-1}): 2961, 2918, 2852, 1744, 1713, 1696, 1508, 1446, 1417, 1374, 1216, 1023, 885, 745, 650.

Ethyl 2-(6-bromo-3-methyl-2-oxo-2,3-dihydro-1*H*-imidazo[4,5-*b*]pyridin-1-yl)acetate (28).[19] White solid. M.P.: 154.1 – 156.0 °C. 54% Yield (34 mg, Eluent: EtOAc/petroleum = 1:5). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, J = 1.6 Hz, 1H), 7.21 (d, J = 1.7 Hz, 1H), 4.57 (s, 2H), 4.22 (q, J = 7.1 Hz, 2H), 3.45 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.08, 153.51, 142.66, 141.49, 124.52, 116.49, 112.36, 62.13, 42.02, 26.19, 14.09. IR (KBr, cm^{-1}): 3062, 2981, 2924, 2852, 1705, 1614, 1590, 1493, 1436, 1396, 1375, 1256, 1220, 1160, 885, 754, 636.

1-benzyl-3-methyl-1*H*-benzo[*d*]imidazol-2(3*H*)-one (29).[9a] Yellow solid. M.P.: 87.0 – 89.0 °C. 31% Yield (15 mg, Eluent: EtOAc/petroleum = 1:4). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 4H), 7.27 – 7.25 (m, 1H), 7.08 (td, J = 7.7, 1.0 Hz, 1H), 7.02 – 7.98 (m, 2H), 6.88 (d, J = 7.7 Hz, 1H), 5.08 (s, 2H), 3.47 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.60, 136.38, 130.13, 129.20, 128.72, 127.65, 127.48, 121.32, 121.25, 108.20, 107.43, 44.91, 27.24. IR (KBr, cm^{-1}): 3060, 3031, 2955, 2924, 2854, 1703, 1620, 1610, 1497, 1456, 1439, 1400, 1389, 1357, 1249, 1173, 748, 698.

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UPDATE

TEMPO-Mediated Synthesis of *N*-(Fluoroalkyl) imidazolones via the Reaction of Imidazoles with Iodofluoroacetate

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