Synthesis V. V. Rao et al. Paper

Highly Selective Approach to α-Iodoketones from Aminoalkynols with Iodine Monochloride

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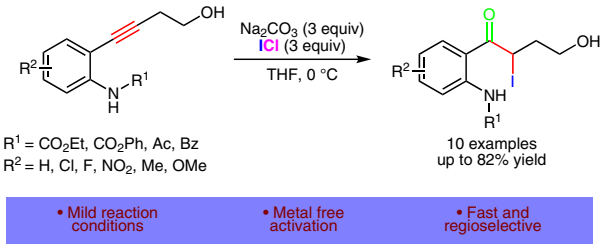

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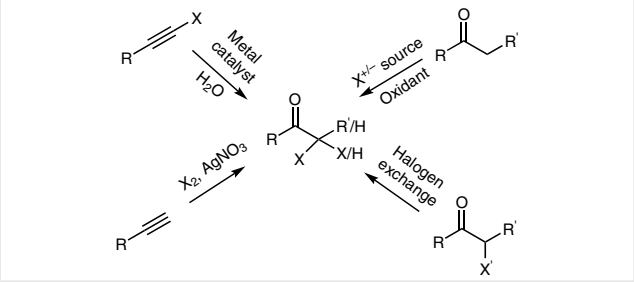
Abstract A protocol has been developed to achieve selective and direct synthesis of α-iodoketones under mild condition, from the reaction of aminoalkynols with iodine monochloride. The scope of the reaction was investigated using various aminoalkynols with iodine monochloride and the corresponding α-iodoketones were obtained selectively without forming iodocyclized and/or addition products.

Key words iodine monochloride, regioselective, iodonium activation, α-iodoketones, iodocyclization

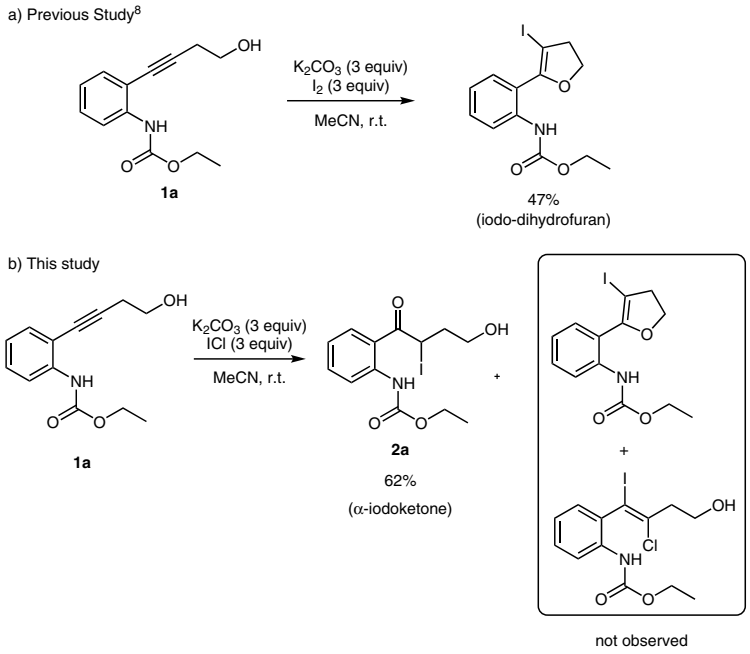
α-Haloketones are often found in natural products and biologically active molecules[1] and are one of the versatile synthetic intermediates, finding wide applications in organic synthesis owing to their various reactive sites.[2] Conventionally, they are synthesized by halogenation of the ketones in the presence of oxidants[3] or by converting one α-haloketone into the other by halogen exchange reaction.[4] Olefins are converted into α-haloketones by oxidative halogenation using reagents like, Ag_2CrO_4-I_2, IBX, NBS, NIS, and even by photoirradiation.[5] There have been comparatively less reports for the conversion of alkynes into α-haloketones. The reaction of terminal alkynes with molecular iodine in the presence of silver nitrate gives α,α-diiodoketones along with few other side products like di-iodoalkenes and iodoalkynes.[2] Haloalkynes have also been used to generate α-haloketones, aided by metal catalysts such as gold and silver.[6] Though there exists a plethora of reactions to make α-haloketones (Scheme 1), they sometimes suffer from undesirable multiple halogenation on the α-carbon, and the need for expensive catalysts when alkynes are used as substrates. Moreover, there is a lack of reports to synthesize them directly from internal alkynes.

In our previous study, we have reported the selective formation of pyrrole nucleus over indole in the electrophilic cyclization of alkynes[7] and the synthesis of iodo-dihydrofuran by electrophilic cyclization of amino alkynols mediated by molecular iodine.[8] While optimizing the reaction conditions for the synthesis of iodo-substituted dihydrofurans from aminoalkynols, various electrophilic I^+ sources were examined to enhance the product yield. Surprisingly, when iodine monochloride was tested in place of molecular iodine, the reaction failed to give the desired iodo-substituted dihydrofuran product, instead a different product was observed within 30 minutes (Scheme 2). The isolated product **2a** was characterized by ^1H and ^{13}C NMR spectroscopy, HRMS, and X-ray diffraction (Figure 1), and surprisingly proved to be α-iodoketone rather than an iodocyclized product.

Contrary to previous observations, this finding on the formation of α-iodoketone from iodine monochloride and aminoalkynols, is first to be reported. As far as our knowledge is concerned such conversion has never been observed with iodine monochloride, which usually gives the cyclized product or addition of iodine and chlorine across the triple bond.[10]



Scheme 1 Established procedures for the formation of α-haloketones



Scheme 2 Synthesis of α-iodoketones from aminoalkynols mediated by ICl

Having discovered this unique reaction with respect to iodine monochloride, we aimed to optimize the reaction conditions to enhance the yield of the reaction by varying solvent, base and temperature. The results are summarized in Table 1.

The initial reaction of alkynol **1a** was performed with K_2CO_3 (3 equiv) and ICl (3 equiv) in MeCN at room temperature and the yield of α-iodoketone obtained was about 62% (Table 1, entry 1). There was a slight increase in the yield when Na_2CO_3 was used as a base (entry 2) and further increase when THF was used as the solvent (entry 3). In the presence of $NaHCO_3$, the desired product was formed along with the by-products, which were inseparable from the crude mixture of products (entry 4). When the reaction was carried out in the presence of Na_2CO_3 at 0 °C, the yield increased to 76% (entry 5). Similarly, when the reaction was performed at low temperature (0 °C) using $NaHCO_3$, again inseparable mixture of products were obtained (entry 6).

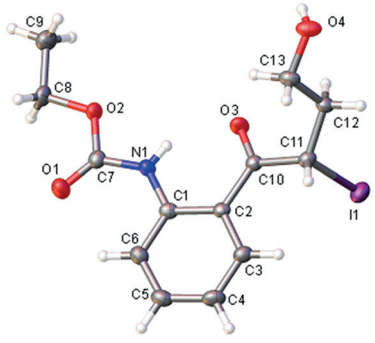
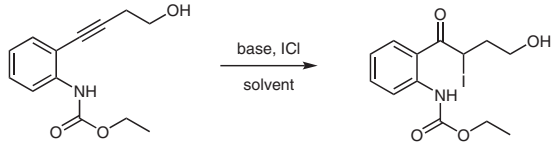


Figure 1 X-ray crystal structure of **2a** ($C_{13}H_{16}INO_4$).[9] Pale yellow needles obtained from EtOAc/pentane. Ellipsoids show 50% probability levels. The hydrogen atoms bonded to N1 and O4 were located in the difference Fourier map but refined to unusually short distances. In this case, bond length and displacement restraints were used to achieve a stable refinement.

Table 1 Optimization for the Reaction of Aminoalkynol with ICl[a]



Entry	Reactant	Solvent	Temp (°C)	Base	Yield of **2a** (%)[b]
1	**1a**	MeCN	r.t.	K_2CO_3	62
2	**1a**	MeCN	r.t.	Na_2CO_3	65
3	**1a**	THF	r.t.	Na_2CO_3	71
4	**1a**	THF	r.t.	$NaHCO_3$	–[c]
5	**1a**	THF	0	Na_2CO_3	76
6	**1a**	CH_2Cl_2	0	$NaHCO_3$	–[c]

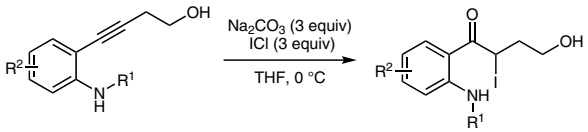
[a] Reaction conditions: Alkynol **1a** (0.08 mmol), base (3 equiv), ICl (3 equiv), solvent (2 mL) at the mentioned temperature for 30 min under N_2.
[b] Isolated yield.
[c] Inseparable mixture of products.

Thus, the optimal conditions used in entry 5 were extended further to examine the scope of the reaction.

Various aminoalkynols with different amine protective groups and substituents on the aromatic ring were prepared using previously reported methods.[8] These substrates were subjected to optimized reaction conditions and tested for the synthesis of α-iodoketones. The results are summarized in Table 2.

The presence of amine protective groups such as ethyl formate, benzyl formate, acetyl, and benzoyl were investigated; they all led to good yields (**2a–c**, Table 2, entries 3–5) except the benzoyl group, for which no desired product was observed (**2d**, entry 6). The effect of various substituents on the aromatic ring was also examined. Presence of fluoro, chloro, and nitro groups on the aromatic ring decreased the yield of reaction (**2e–h**, entries 7–10), the lowest yield was observed for the nitro substituent (**2h**, entry 10). The electronically rich substituents like methyl (**2i**) and methoxy groups (**2j**) afforded a high yield of α-iodoketones (entries 11 and 12). Overall, the reaction seemed to tolerate both electron-withdrawing and electron-donating groups and amine protecting groups as mentioned above.

Table 2 Scope of the Reaction Using Various Aminoalkynols with ICl[a]



1a–j **2a–j**

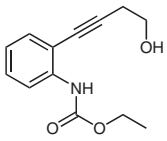
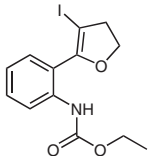
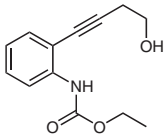
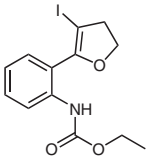
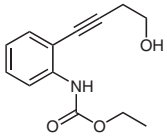
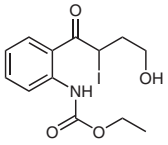
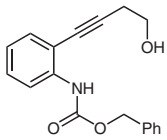
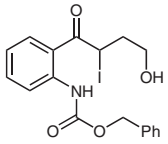
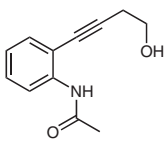
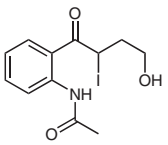
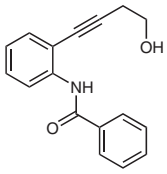
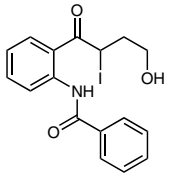
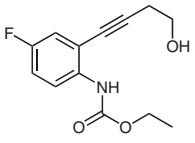
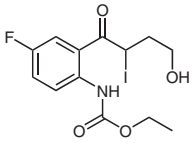
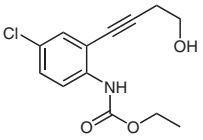
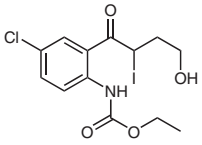
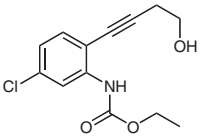
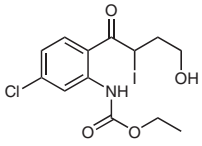
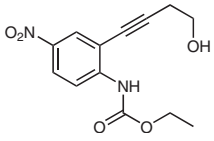
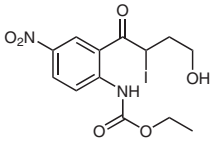
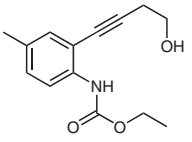
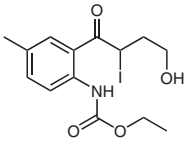
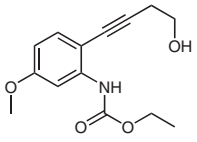
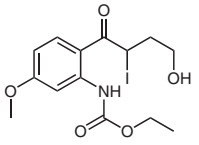
Entry	Reactant	I⁺ Source	Conditions	Product	Yield (%)[b]
1	**1a** 	I_2	K_2CO_3, MeCN, r.t.		47
2	**1a** 	I_2	KO*t*-Bu, MeCN, r.t.		78
3	**1a** 	ICl	Na_2CO_3, THF, 0 °C	**2a** 	76 (69)[c]
4	**1b** 	ICl	Na_2CO_3, THF, 0 °C	**2b** 	71
5	**1c** 	ICl	Na_2CO_3, THF, 0 °C	**2c** 	63

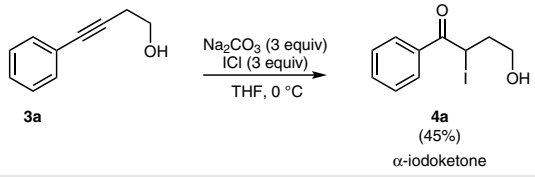
Table 2 (continued)

Entry	Reactant	I⁺ Source	Conditions	Product	Yield (%)[b]
	1d			**2d**	
6		ICl	Na_2CO_3, THF, 0 °C		–[d]
	1e			**2e**	
7		ICl	Na_2CO_3, THF, 0 °C		64 (54)[c]
	1f			**2f**	
8		ICl	Na_2CO_3, THF, 0 °C		55
	1g			**2g**	
9		ICl	Na_2CO_3, THF, 0 °C		60[e]
	1h			**2h**	
10		ICl	Na_2CO_3, THF, 0 °C		53[e]
	1i			**2i**	
11		ICl	Na_2CO_3, THF, 0 °C		75
	1j			**2j**	
12		ICl	Na_2CO_3, THF, 0 °C		82

[a] Reaction conditions: alkynol (0.2 mmol), base (3 equiv), I⁺ source (3 equiv), solvent (5 mL) for 30–60 min under N_2.
[b] Isolated yield.
[c] Isolated yield for gram scale (5 mmol) synthesis in parentheses.
[d] No desired product observed.
[e] Iodo-dihydrofuran product was also observed in 5–10% yield.

The scalability of the reaction was demonstrated by testing the two substrates **1a** and **1e** in 5 mmol scale. The scale-up reaction proceeded well in both cases though with a slight decrease in the reaction yield (entry 3 and 7).

The same reaction conditions optimized for α-iodoketone synthesis were applied to 4-phenylbut-3-yn-1-ol (**3a**; 0.2 mmol) and the α-iodoketone product **4a** was obtained in 45% yield (Scheme 3). But when homopropargyl amine-substituted aniline **5a** was tested for the formation of α-iodoketone, surprisingly only iodocyclized product was observed in 68% yield (Scheme 4). The product **6a** was the same as reported in our previous iodocyclization study with molecular iodine[7] and no α-iodoketone product was observed.

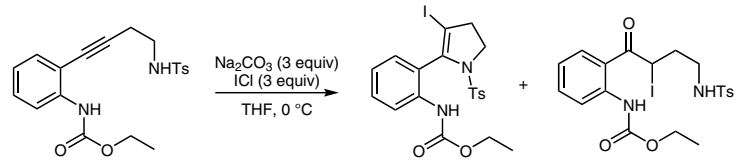


3a **4a** (45%) α-iodoketone

Scheme 3 ICl-mediated conversion of 4-phenylbut-3-yn-1-ol into α-iodoketone

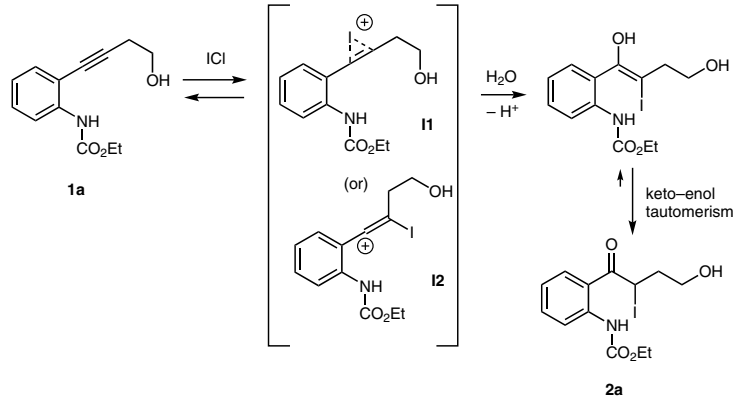
Though there are few reports of alkynes being converted into α-iodoketones due to the hydration of the activated alkyne-iodonium ion intermediate, they are often encountered as a minor product, usually below 10% yield as observed in the Berliner's and Rossi's study.[11] All the previous reports employ molecular iodine as the electrophilic reagent and there have been no reports of such reaction with respect to iodine monochloride. The attack of hydroxyl nucleophile generating from the residual water in the solvent, on the activated intermediate over other favorably placed intramolecular nucleophiles (forming iodocyclized product) or chloride ion, is seldom observed. Even in cases where water is used as a solvent for iodocyclization, such reactions are not observed.[12] We believe that the mechanism of the reaction involves alkyne activation by coordination of I^+ to the C–C triple bond. This activated intermediate can either exist in symmetrical iodonium form **I1** or vinyl cation form **I2**. In the next step, the addition of the hydroxyl group from the water molecule gives iodo-enol, which tautomerises, giving the α-iodoketone **2a** (Scheme 5).

To summarize, we were successfully able to discover and identify an unusual reactivity of the aminoalkynol substrate with iodine monochloride, which is a surprising deviation from our previously reported study. The newly developed reaction conditions were applied to synthesize various α-iodoketone derivatives from aminoalkynols. The reaction is regioselective and can accommodate a wide range of substituted amino alkynols both on the aromatic ring and on the amine group. We were also able to successfully apply the optimized reactions condition for 4-phenylbut-3-yn-1-ol and synthesize the respective α-iodoketone.



5a **6a** (68%) Iodo-pyrrole (not observed)

Scheme 4 ICl-mediated iodocyclization of homopropargyl amine-substituted aniline giving iodopyrrole



1a **2a**

Scheme 5 Plausible mechanism for the formation of α-iodoketone from aminoalkynol

The chemistry and drastic change in the reactivity of the same substrates toward two similar yet different electrophilic source is interesting to observe, especially the selectivity towards hydration rather than iodocyclization by the internal potential nucleophiles. More investigations into such conversions will be done in the future.

All reactions were performed using oven dried glassware under N_2 atmosphere. Chemicals were purchased from Sigma Aldrich and used as received, unless otherwise mentioned. The products were purified by column chromatography on silica gel 60–120 mesh. Technical grade solvents were used for chromatography and distilled prior to use. NMR spectra were recorded in Fourier transform mode. The ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a 300 MHz, 400 MHz, and 500 MHz spectrophotometer using $CDCl_3$ and TMS as the internal standard. Standard abbreviations were used to describe the multiplicities in the ^{1}H NMR spectra; coupling constants are reported in Hz. Low- and high-resolution mass spectra were recorded by an ion-trap method and mass/charge (*m*/*z*) ratios are reported as values in atomic mass units. All melting points are uncorrected.

α-Iodoketones 2a–j and 4a from Aminoalkynols 1a–j and Alkynol 3a; General Procedure

Aminoalkynol **1a–j** or alkynol **3a** (0.2 mmol) and Na_2CO_3 (64 mg, 0.6 mmol, 3 equiv) were added to THF maintained at 0 °C under N_2. To the above stirred solution, a 1 M solution of ICl in CH_2Cl_2 (97.5 mg, 0.6 mL, 0.6 mmol, 3 equiv) was slowly added dropwise and the reaction was allowed to proceed till the starting material was consumed (30–60 min). Once the reaction was complete, EtOAc was added to the reaction mixture and the organic phase was washed with sat. aq $Na_2S_2O_3$ and then washed with H_2O. The organic layer was separated and dried (anhyd Na_2SO_4). The solvent was evaporated under vacuum and the crude product was purified by silica gel column chromatography using PE/EtOAc (7:3) mixture as eluent.

Ethyl [2-(4-Hydroxy-2-iodobutanoyl)phenyl]carbamate (2a)

Yield: 57.3 mg (76%, 0.152 mmol); gram-scale yield: 1.30 g (69%, 3.45 mmol); yellow solid; mp 82–84 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 10.90 (s, 1 H), 8.52 (dd, *J* = 8.6, 0.9 Hz, 1 H), 7.92 (dd, *J* = 8.1, 1.4 Hz, 1 H), 7.59–7.54 (m, 1 H), 7.08–7.03 (m, 1 H), 5.74 (t, *J* = 7.1 Hz, 1 H), 4.23 (q, *J* = 7.1 Hz, 2 H), 3.87–3.75 (m, 2 H), 2.38–2.32 (m, 2 H), 1.33 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 198.21, 153.82, 142.62, 135.60, 130.32, 121.37, 119.71, 118.45, 61.48, 61.37, 37.46, 23.44, 14.51.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{16}INO_4Na^+$: 400.0016; found: 400.0056.

Benzyl [2-(4-Hydroxy-2-iodobutanoyl)phenyl]carbamate (2b)

Yield: 62.4 mg (71%, 0.142 mmol); yellow solid; mp 78–80 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 11.00 (s, 1 H), 8.53 (d, *J* = 8.5 Hz, 1 H), 7.91 (dd, *J* = 8.1, 1.2 Hz, 1 H), 7.59–7.54 (m, 1 H), 7.45–7.30 (m, 5 H), 7.09–7.04 (m, 1 H), 5.73 (t, *J* = 7.1 Hz, 1 H), 5.22 (s, 2 H), 3.84–3.73 (m, 2 H), 2.36–2.30 (m, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 198.20, 153.58, 142.41, 136.00, 135.60, 130.35, 128.60, 128.33, 121.57, 119.78, 118.56, 67.08, 61.47, 37.43, 23.39.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{18}INO_4Na^+$: 462.0173; found: 462.0194.

N-[2-(4-Hydroxy-2-iodobutanoyl)phenyl]acetamide (2c)

Yield: 43.7 mg (63%, 0.126 mmol); yellow solid; mp 124–126 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.41 (s, 1 H), 8.76 (d, *J* = 8.5 Hz, 1 H), 7.93 (dd, *J* = 8.1, 1.3 Hz, 1 H), 7.62–7.54 (m, 1 H), 7.15–7.08 (m, 1 H), 5.76 (t, *J* = 7.1 Hz, 1 H), 3.88–3.74 (m, 2 H), 2.39–2.31 (m, 2 H), 2.25 (s, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 198.75, 169.50, 142.07, 135.70, 130.21, 122.43, 121.29, 118.89, 61.42, 37.43, 25.65, 23.48.

HRMS (ESI): *m*/*z* [M + H – H_2O]$^+$ calcd for $C_{12}H_{13}INO_2^+$: 329.9985; found: 329.9997.

Ethyl [4-Fluoro-2-(4-hydroxy-2-iodobutanoyl)phenyl]carbamate (2e)

Yield: 50.6 mg (64%, 0.128 mmol); gram-scale yield: 1.077 g (54%, 2.7 mmol); yellow solid; mp 98–100 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.64 (s, 1 H), 8.54–8.46 (m, 1 H), 7.57 (dd, *J* = 9.4, 2.9 Hz, 1 H), 7.33–7.27 (m, 1 H), 5.63 (t, *J* = 7.1 Hz, 1 H), 4.23 (q, *J* = 7.1 Hz, 2 H), 3.87–3.72 (m, 2 H), 2.39–2.30 (m, 2 H), 1.33 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.22 (s), 156.48 (d, *J* = 242.8 Hz), 153.88 (s), 138.74 (s), 122.70 (d, *J* = 22.1 Hz), 121.63 (d, *J* = 7.0 Hz), 119.48 (d, *J* = 5.6 Hz), 115.99 (d, *J* = 23.6 Hz), 61.50 (s), 61.35 (s), 37.32 (s), 23.16 (s), 14.49 (s).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –120.12.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{15}INO_4Na^+$: 417.9922; found: 417.9952.

Ethyl [4-Chloro-2-(4-hydroxy-2-iodobutanoyl)phenyl]carbamate (2f)

Yield: 45.3 mg (55%, 0.11 mmol); yellow solid; mp 92–95 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.74 (s, 1 H), 8.51 (d, *J* = 9.1 Hz, 1 H), 7.84 (d, *J* = 2.3 Hz, 1 H), 7.51 (dd, *J* = 9.1, 2.3 Hz, 1 H), 5.65 (t, *J* = 7.1 Hz, 1 H), 4.23 (q, *J* = 7.1 Hz, 2 H), 3.89–3.73 (m, 2 H), 2.40–2.31 (m, 2 H), 1.33 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.23, 153.67, 141.07, 135.27, 129.60, 126.45, 121.23, 119.67, 61.59, 61.39, 37.30, 23.13, 14.48.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{15}ClINO_4Na^+$: 433.9626; found: 433.9716.

Ethyl [5-Chloro-2-(4-hydroxy-2-iodobutanoyl)phenyl]carbamate (2g)

Yield: 49.4 mg (60%, 0.12 mmol); yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.99 (s, 1 H), 8.62 (d, *J* = 2.1 Hz, 1 H), 7.84 (d, *J* = 8.7 Hz, 1 H), 7.02 (dd, *J* = 8.7, 2.1 Hz, 1 H), 5.67 (t, *J* = 7.1 Hz, 1 H), 4.24 (q, *J* = 7.1 Hz, 2 H), 3.87–3.72 (m, 2 H), 2.38–2.30 (m, 2 H), 1.34 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.41, 153.55, 143.69, 142.01, 131.46, 121.64, 119.59, 116.55, 61.66, 61.39, 37.33, 23.25, 14.46.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{15}ClINO_4Na^+$: 433.9626; found: 433.9653.

Ethyl [2-(4-Hydroxy-2-iodobutanoyl)-4-nitrophenyl]carbamate (2h)

Yield: 44.8 mg (53%, 0.106 mmol); yellow solid; mp 116–118 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.19 (s, 1 H), 8.82 (d, *J* = 2.5 Hz, 1 H), 8.75 (d, *J* = 9.5 Hz, 1 H), 8.41–8.35 (m, 1 H), 5.79 (t, *J* = 7.0 Hz, 1 H), 4.29 (q, *J* = 7.1 Hz, 2 H), 3.91–3.77 (m, 2 H), 2.44–2.35 (m, 2 H), 1.36 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 197.22, 153.22, 147.77, 140.75, 129.86, 126.21, 119.78, 117.62, 62.25, 61.25, 37.21, 22.82, 14.39.

HRMS (ESI): *m*/*z* [M + H – H_2O]$^+$ calcd for $C_{13}H_{14}IN_2O_5^+$: 404.9942; found: 404.9917.

Ethyl [2-(4-Hydroxy-2-iodobutanoyl)-4-methylphenyl]carbamate (2i)

Yield: 58.7 mg (75%, 0.15 mmol); yellow solid; mp 100–103 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.75 (s, 1 H), 8.39 (dd, *J* = 8.7, 1.6 Hz, 1 H), 7.68 (s, 1 H), 7.38 (d, *J* = 8.7 Hz, 1 H), 5.73 (t, *J* = 7.1 Hz, 1 H), 4.22 (q, *J* = 7.1 Hz, 2 H), 3.88–3.74 (m, 2 H), 2.39–2.31 (m, 5 H), 1.32 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 198.14, 153.87, 140.23, 136.50, 130.78, 130.19, 119.73, 118.49, 61.56, 61.23, 37.46, 23.51, 20.77, 14.50.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{18}INO_4Na^+$: 414.0173; found: 414.0045.

Ethyl [2-(4-Hydroxy-2-iodobutanoyl)-5-methoxyphenyl]carbamate (2j)

Yield: 66.8 mg (82%, 0.164 mmol); yellow solid; mp 107–110 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.39 (s, 1 H), 8.16 (d, *J* = 2.6 Hz, 1 H), 7.85 (d, *J* = 9.1 Hz, 1 H), 6.58 (dd, *J* = 9.1, 2.6 Hz, 1 H), 5.68 (t, *J* = 7.1 Hz, 1 H), 4.23 (q, *J* = 7.1 Hz, 2 H), 3.90 (s, 3 H), 3.85–3.72 (m, 2 H), 2.38–2.29 (m, 2 H), 1.33 (t, *J* = 7.1 Hz, 3 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 196.63, 165.39, 153.92, 145.70, 132.55, 111.37, 109.13, 102.73, 61.59, 61.36, 55.66, 37.62, 23.44, 14.50.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{18}INO_5Na^+$: 430.0122; found: 430.0105.

4-Hydroxy-2-iodo-1-phenylbutan-1-one (4a)

Yield: 26.1 mg (45%, 0.09 mmol); light yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 7.2 Hz, 2 H), 7.62–7.54 (m, 1 H), 7.52–7.43 (m, 2 H), 5.68 (t, *J* = 7.1 Hz, 1 H), 3.89–3.74 (m, 2 H), 2.42–2.32 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.75, 133.93, 133.64, 128.78, 128.74, 61.67, 37.17, 22.71.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{12}IO_2^+$: 290.9876; found: 290.9869.

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Supporting Information

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