

Supporting Information

I₂-Mediated [3 + 2] cycloaddition of methyl-azaarenes with alkyl 2-isocyanoacetates or amino acid ester hydrochlorides: selective synthesis of iodine-functionalized and non-iodine-functionalized fused imidazoles

Yong-Ji Hu,^{a+} Yu Zhou,^{a+} Jing-Jing Gao,^{a+} Han Zhang,^{a+} Kai-Rui Yang,^a Jia-Jun Li,^a Xiao-Xin Yan,^a Yuan-Lin Li,^a Yan-Ping Zhu^{*,a}

^a School of Pharmacy, Key Laboratory of Molecular Pharmacology and Drug Evaluation, Ministry of Education, Collaborative Innovation Center of Advanced Drug Delivery System and Biotech Drugs in Universities of Shandong, Yantai University, Shandong, Yantai, 264005, P. R. China.

E-mail: chemzyp@foxmail.com; chemzyp@ytu.edu.cn

+ These authors contributed equally to this work

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1. General information

Materials and General Experimental: Methyl-azaheteroarenes, isocyanoacetates and alkyl glycinates were purchased from Shanghai Shaoyuan Co. Ltd. Cholesterol, palladium acetate, phenylacetylene and diphenyl diselenide were purchased from Energy Chemical. Bis(triphenylphosphine)palladium chloride was purchased from Laajoo. Ethyl acrylate was purchased from Aladdin. Cuprous iodide was purchased from Innochem. Unless stated otherwise, all solvents and commercially available reagents were obtained from commercial suppliers and used without further purification. In addition, petroleum ether (b.p. 60-90 °C), which was used for column chromatography, was distilled prior to use. Non-commercial starting materials were prepared as described below or according to literature procedures. Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel HF254 glass plates. Column chromatography was performed using silica gel (200-300 mesh).

Instrumentation: Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance 400 MHz spectrometer at ambient temperature using the non or partly deuterated solvent as internal standard (^1H : δ 7.26 ppm and $^{13}\text{C}\{1\text{H}\}$: δ 77.0 ppm for CDCl_3). Chemical shifts (δ) are reported in ppm, relative to the internal standard of tetramethylsilane (TMS). The coupling constants (J) are quoted in hertz (Hz). Resonances are described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) or combinations thereof. High resolution mass spectra were obtained on Thermo Scientific Q-Exactive (ESI mode). Melting points were determined using SGW X-4 apparatus and not corrected. IR spectra were obtained on a Thermo Fisher Scientific Nicolet iS10 FTIR infrared spectrometer as KBr pellets and was reported in terms of frequency of transmittance (cm^{-1}).

2. Experimental Procedures

2.1 General procedure

2.1.1 General procedure for synthesis of 3 (3a as an example)

A 25 mL pressure vial was charged with 2-methylquinoline (**1a**) (0.2 mmol, 1.0 equiv.), I_2 (0.32 mmol, 1.6 equiv.) and TFA (0.3 mmol, 1.5 equiv.) in DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 120 °C for 4-6 h under an air atmosphere, after disappearance of the reactant (monitored by TLC), then ethyl 2-isocyanoacetate (**2a**) (0.4 mmol, 2.0 equiv.) and TBAI (0.1 mmol, 0.5 equiv.) were added at 120 °C for another 6 h. After the reaction completed, and added 50 mL water to the mixture, then extracted with EtOAc 3 times (3×50 mL). The extract was washed with 10% $\text{Na}_2\text{S}_2\text{O}_3$ solution (w/w), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the corresponding product **3a**.

2.1.2 General procedure for synthesis of 4 (4a as an example)

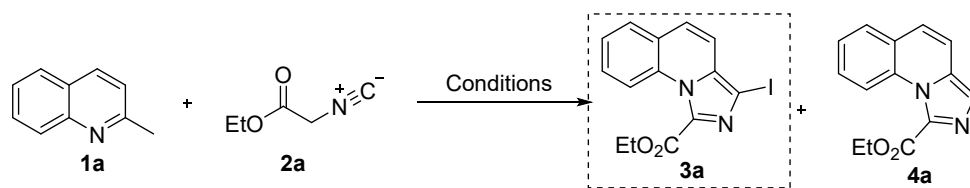
A 25 mL pressure vial was charged with 2-methylquinoline (**1a**) (0.2 mmol, 1.0

equiv.), I₂ (0.32 mmol, 1.6 equiv.) and TFA (0.3 mmol, 1.5 equiv.) in DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 120 °C for 4-6 h under an air atmosphere, after disappearance of the reactant (monitored by TLC), then ethyl 2-isocyanoacetate (**2a**) (0.4 mmol, 2.0 equiv.) was added at 80 °C for another 6 h. After the reaction completed, and added 50 mL water to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% Na₂S₂O₃ solution (w/w), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the corresponding product **4a**.

2.2 Reaction Optimization

We optimized the reaction conditions using 2-methylquinoline (**1a**) (0.2 mmol, 1.0 equiv.) and ethyl 2-isocyanoacetate (**2a**) (0.4 mmol, 2.0 equiv.) as model substrates. Initially, the reaction was carried out with various acid (0.3 mmol, 1.5 equiv.) by using I₂ (0.4 mmol, 2.0 equiv.), such as HCl, TsOH, HOAc, TfOH and TFA (Table S1, entries 1-5). The results show that TFA is the best choice giving the product **3a** and **4a** in 55% and 30% yield (Table S1, entry 5). Next, the amount of I₂ was examined and the results showed that 1.6 equivalents of the I₂ provided **3a** in 60% yield (Table S1, entries 5-7). Surprisingly, when **1a**, I₂ and TFA were heated in DMSO at 120 °C for 4-6 h, followed by **2a** for another 6 h, the yield of **3a** increasing to 66% (Table S1, entry 8). When additives were added, such as NH₄I, KI, NaI, NIS, TBAI, the yield of **3a** was increased to 78% by using TBAI (Table S1, entries 9-14).

Table S1 Optimization of the product 3a^a



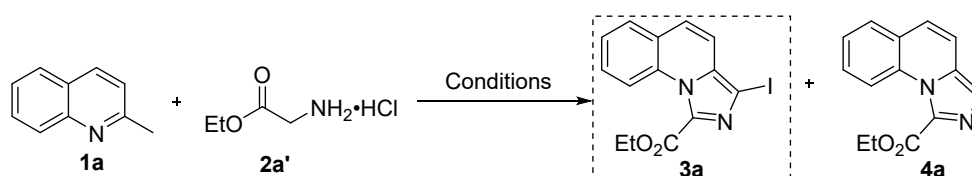
Entry	Oxidant (eq.)	Acid (eq.)	Additive (eq.)	Solvent	T (°C)	Yield (%) ^c	
						3a	4a
1	I ₂ (2.0)	HCl (1.5)		DMSO	120	20	15
2	I ₂ (2.0)	TsOH (1.5)		DMSO	120	35	20
3	I ₂ (2.0)	HOAc (1.5)		DMSO	120	40	25
4	I ₂ (2.0)	TfOH (1.5)		DMSO	120	45	35
5	I ₂ (2.0)	TFA (1.5)		DMSO	120	55	30
6	I ₂ (1.8)	TFA (1.5)		DMSO	120	58	30
7	I ₂ (1.6)	TFA (1.5)		DMSO	120	60	20
8 ^b	I ₂ (1.6)	TFA (1.5)		DMSO	120	66	15
9 ^b	I ₂ (1.6)	TFA (1.5)	NH ₄ I (1.0)	DMSO	120	68	22
10 ^b	I ₂ (1.6)	TFA (1.5)	KI (1.0)	DMSO	120	55	20
11 ^b	I ₂ (1.6)	TFA (1.5)	NaI (1.0)	DMSO	120	70	25
12 ^b	I ₂ (1.6)	TFA (1.5)	NIS (1.0)	DMSO	120	72	15
13 ^b	I ₂ (1.6)	TFA (1.5)	TBAI (1.0)	DMSO	120	75	5

14^b I₂ (1.6) TFA (1.5) TBAI (0.5) DMSO 120 78 5

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), oxidant and acid in solvent (2.0 mL), at different temperatures for 12 h under air atmosphere. ^b **1a** (0.2 mmol), I₂ (1.6 equiv.) and TFA (1.5 equiv.) were heated in DMSO (2 mL) at 120 °C for 4-6 h, followed by **2a** (0.4 mmol) and additive were added for another 6 h. ^c Isolated yield.

We optimized the reaction conditions using 2-methylquinoline (**1a**) (0.2 mmol, 1.0 equiv.) and glycine ethyl ester hydrochloride (**2a'**) (0.4 mmol, 2.0 equiv.) as model substrates. Initially, the reaction was carried out with different equivalents of I₂ by using TFA (0.3 mmol, 1.5 equiv.) and TBAI (0.5 equiv.) in DMSO (2 mL) at 120 °C (Table S2, entries 1-3). The results show that 2.0 equivalents of I₂ is the best choice giving the major product **3a** in 72% yield. Next, a series of acid were examined and the results showed that TFA is the best choice (Table S2, entries 3-6). Finally, **1a** (0.2 mmol), **2a'** (0.4 mmol), I₂ (2.0 equiv.), TFA (1.5 equiv.) and TBAI (0.5 equiv.) were heated in DMSO (2 mL) at 120 °C for 12 h in one pot giving the product **3a** and **4a** in 40% and 30% yields (Table S2, entry 7).

Table S2 Optimization of the product **3a (Glycine ethyl ester hydrochloride as substrate) ^a**



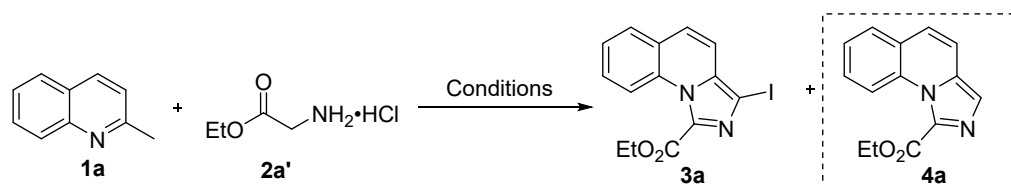
Entry	Oxidant (eq.)	Acid (eq.)	Additive (eq.)	Solvent	T (°C)	Yield (%) ^c	
						3a	4a
1	I ₂ (1.6)	TFA (1.5)	TBAI (0.5)	DMSO	120	55	25
2	I ₂ (1.8)	TFA (1.5)	TBAI (0.5)	DMSO	120	60	18
3	I₂ (2.0)	TFA (1.5)	TBAI (0.5)	DMSO	120	70	trace
4	I ₂ (2.0)	TfOH (1.5)	TBAI (0.5)	DMSO	120	62	15
5	I ₂ (2.0)	HOAc (1.5)	TBAI (0.5)	DMSO	120	52	22
6	I ₂ (2.0)	TsOH (1.5)	TBAI (0.5)	DMSO	120	42	25
7 ^b	I ₂ (2.0)	TFA (1.5)	TBAI (0.5)	DMSO	120	40	30

^a Reaction conditions: **1a** (0.2 mmol), I₂ and acid (1.5 equiv.) were heated in DMSO (2 mL) at 120 °C for 4-6 h, followed by **2a'** (0.4 mmol) and additive were added for another 6 h. ^b **1a** (0.2 mmol), **2a'** (0.4 mmol), I₂ (2.0 equiv.), TFA (1.5 equiv.) and TBAI (0.5 equiv.) were heated in DMSO (2 mL) at 120 °C for 12 h ^c Isolated yield.

We optimized the reaction conditions using 2-methylquinoline (**1a**) (0.2 mmol, 1.0 equiv.) and glycine ethyl ester hydrochloride (**2a'**) (0.4 mmol, 2.0 equiv.) as model substrates. Firstly, the reaction of 2-methylquinoline (**1a**) (0.2 mmol, 1.0 equiv.) and glycine ethyl ester hydrochloride (**2a'**) (0.4 mmol, 2.0 equiv.) was carried out under standard condition C, giving the major product **4a** in 40% yield (Table S3, entry 1).

Surprisingly, when 2 equivalents of K_2CO_3 were added to the reaction system, the yield of **4a** increased to 50%. Next, a series of base were examined, such as Na_2CO_3 , TEA, K_3PO_4 and Cs_2CO_3 (Table S3, entries 3-7). The results show that 2.0 equivalents of K_2CO_3 is the best choice giving the product **4a** in 83% yield (Table S3, entry 3). Finally, **1a** (0.2 mmol), **2a'** (0.4 mmol), I_2 (1.6 equiv.), and K_2CO_3 (2.0 equiv.) were heated in DMSO (2 mL) at 80 °C for 12 h in one pot, giving the product **4a** in 63% (Table S3, entry 8).

Table S3 Optimization of the product 4a (Glycine ethyl ester hydrochloride as substrate) ^a

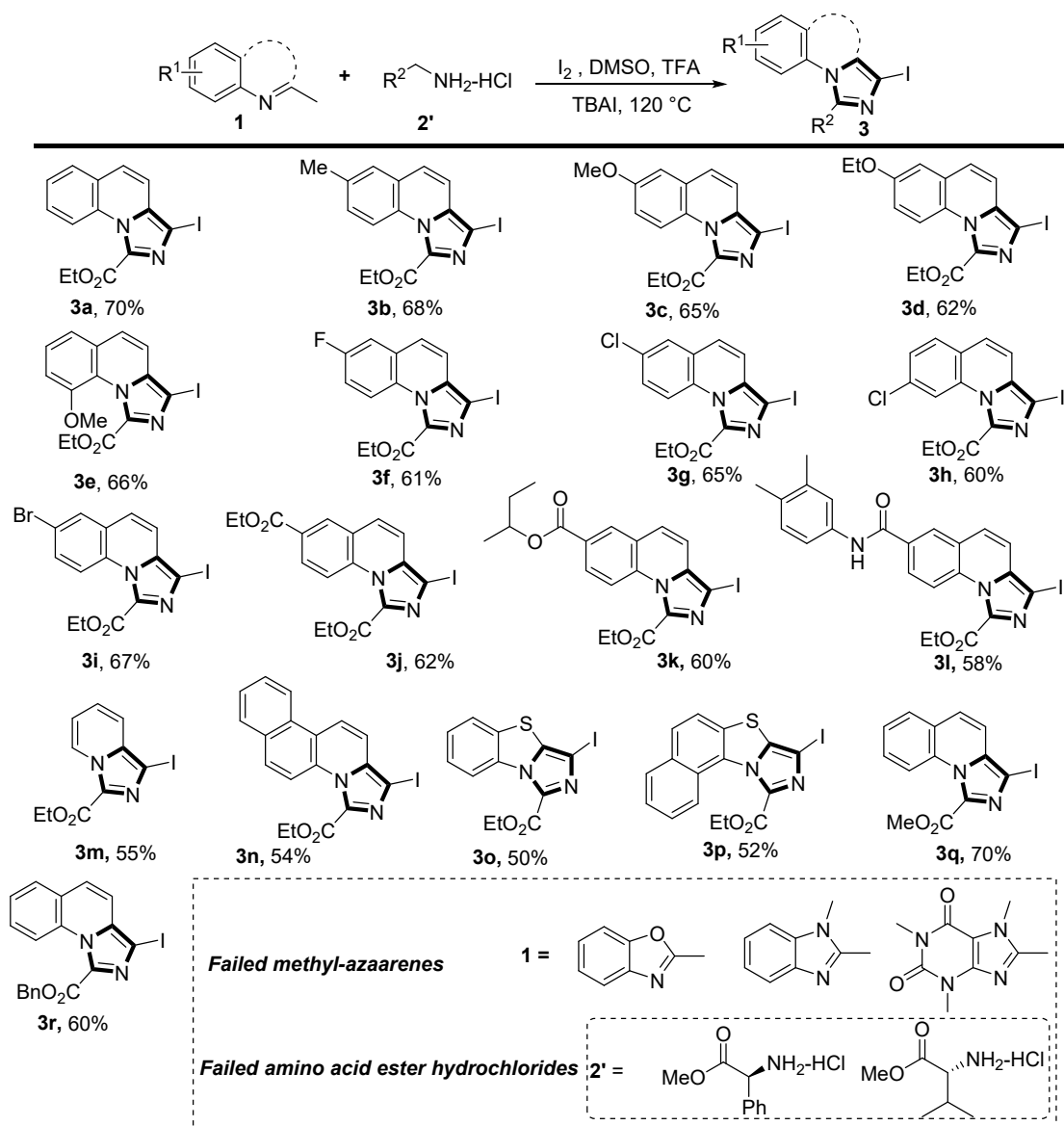


Entry	Oxidant (eq.)	Acid (eq.)	Additive (eq.)	Solvent	T (°C)	Yield (%) ^c	
						3a	4a
1	I_2 (1.6)	TFA (1.5)		DMSO	80	20	40
2	I_2 (1.6)	TFA (1.5)	K_2CO_3 (2.0)	DMSO	80	15	50
3	I_2 (1.6)		K_2CO_3 (2.0)	DMSO	80	trace	83
4	I_2 (1.6)		Na_2CO_3 (2.0)	DMSO	80	10	56
5	I_2 (1.6)		TEA (2.0)	DMSO	80	trace	30
6	I_2 (1.6)		K_3PO_4 (2.0)	DMSO	80	15	54
7	I_2 (1.6)		Cs_2CO_3 (2.0)	DMSO	80	trace	70
8 ^b	I_2 (1.6)		K_2CO_3 (2.0)	DMSO	80	trace	63

^a Reaction conditions: **1a** (0.2 mmol), I_2 (1.6 equiv.) and acid (1.5 equiv.) were heated in DMSO (2 mL) at 120 °C for 4-6 h, followed by **2a'** (0.4 mmol) and additive (2.0 equiv.) were added for another 6 h at 80 °C. ^b **1a** (0.2 mmol), **2a'** (0.4 mmol), I_2 (1.6 equiv.), and K_2CO_3 (2.0 equiv.) were heated in DMSO (2 mL) at 80 °C for 12 h ^c Isolated yield.

2.3 The scope of substrates

Table S4 Substrate scope of iodine-functionalized products. (Amino acid ester hydrochloride as substrate) ^{a,b}



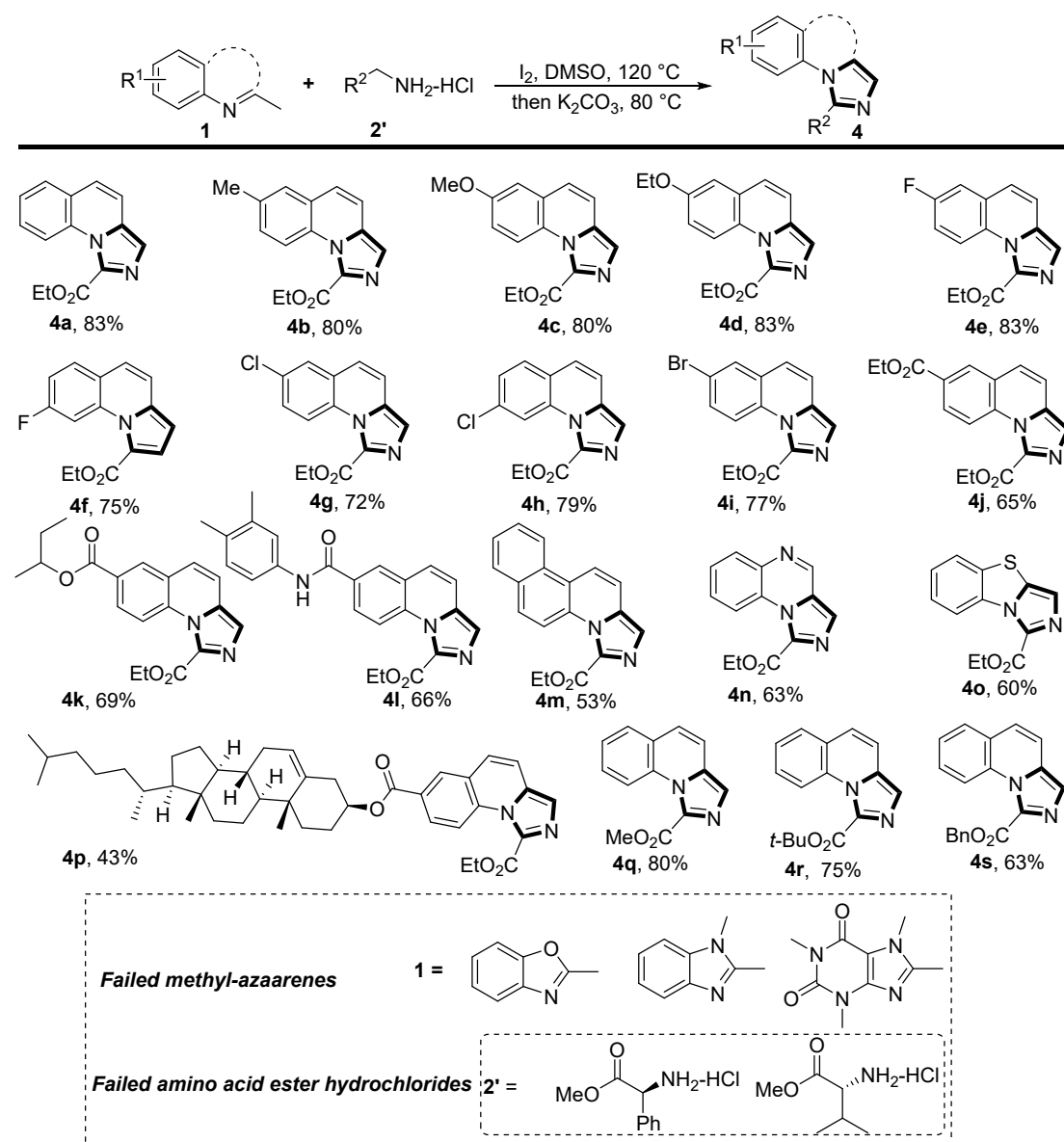
^a Reaction conditions: **1a** (0.2 mmol), I₂ (2.0 equiv.) and TFA (1.5 equiv.) were heated in DMSO (2 mL) at 120 °C for 4-6 h, followed by **2a'** (0.4 mmol) and TBAI (0.5 equiv.) were added for another 6 h. ^b Isolated yield.

With the optimized conditions established, the scope of the iodine-functionalized products was tested using various substituted 2-methylquinolines and other methyl azaheterocycles with amino acid ester hydrochlorides as shown in Table S4. At first, we investigated a series of 2-methylquinolines bearing electron-rich substituents on the aryl ring (e.g., 6-Me, 6-OMe, 6-OEt, 8-OMe). To our delight, the reactions could afford the desired products **3b-3e** in 62%-68% yields. And the 2-methylquinolines attached with halogen atoms (e.g., 6-F, 6-Cl, 7-Cl, 6-Br) were also tolerated in the reaction, giving the corresponding products **3f-3i** in 61%-67% yields. In addition, esterified and amidated 2-methylquinoline carboxylic acids could proceed well in the reaction, affording the desired products **3j-3l** in 58%-62% yields. Various methyl azaarenes, such as 2-methylpyridine, 3-methylbenzo[*f*]quinoline, 2-

methylbenzo[*d*]thiazole and 2-methylnaphtho[1,2-*d*]thiazole, were all well tolerated in the protocol and giving the corresponding products **3m-3p** in moderate yields. When glycine ethyl ester hydrochloride was replaced by glycine methyl ester hydrochloride and benzyl glycinate hydrochloride, generating the desired products **3q** and **3u** in good yields. However, 2-methylbenzo[*d*]oxazole, 1,2-dimethyl-1*H*-benzo[*d*]imidazole and 1,3,7,8-tetramethyl-3,7-dihydro-1*H*-purine-2,6-dione were not suitable for this reaction to generate the iodine-functionalized products.

Table S5 Substrate scope of non-iodine-functionalized products.

(Amino acid ester hydrochloride as substrate) ^{a,b}

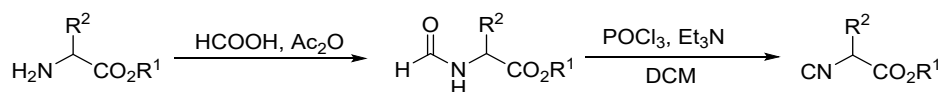


^a Reaction conditions: **1a** (0.2 mmol), I_2 (1.6 equiv.) were heated in DMSO (2 mL) at 120 °C for 4-6 h, followed by **2a'** (0.4 mmol) and K_2CO_3 (2.0 equiv.) were added for another 6 h at 80 °C. ^b Isolated yield.

We next examined the scope of this reaction for non-iodine-functionalized products

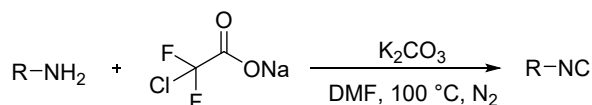
(Table S5). Firstly, we studied the 2-methylquinolines in which the phenyl ring had electron-rich substituents (e.g., 6-Me, 6-OMe 6-OEt) the annulation reactions proceeded smoothly to deliver products **4b-4d** in good yields. When the phenyl ring of 2-methylquinolines bearing halogen groups (e.g., 6-F, 7-F, 6-Cl, 7-Cl, 6-Br), the reactions could also perform smoothly to afford the desired products **4e-4i** in 72%-83% yields. Esterified and amidated 2-methylquinoline carboxylic acids could also proceed well in this reaction, affording the desired products **4j-4l** in moderate yields. In addition, other methyl azaarenes, such as 3-methylbenzo[*f*]quinoline, 2-methylquinoxaline, and 2-methylbenzo[*d*]thiazole, were all well tolerated in the strategy and giving the corresponding products **4m-4o** in moderate yields. In addition, 2-methylquinoline carboxylic acid modified by natural product (cholesterol) was also suitable for this reaction giving the desired product **4p** in 43% yield. When glycine ethyl ester hydrochloride was replaced by glycine methyl ester hydrochloride, glycine *tert*-butyl ester hydrochloride and benzyl glycinate hydrochloride to generate the desired products **4q-4s** in moderate to good yields. However, 2-methylbenzo[*d*]oxazole, 1,2-dimethyl-1*H*-benzo[*d*]imidazole and 1,3,7,8-tetramethyl-3,7-dihydro-1*H*-purine-2,6-dione were still not suitable for this reaction to generate the desired products.

2.4 Synthesis of starting materials



Scheme S1 Synthesis of α -isocyanoacetates

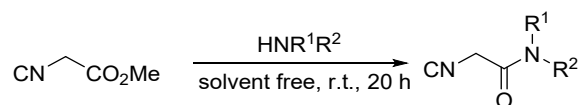
General procedure A: Followed the procedure in the literature.¹ Acetic anhydride (22.0 mL, 242.1 mmol, 8.0 equiv.) was added dropwise to a solution of methyl phenylalaninate (25.0 mmol, 1.0 equiv.) in HCOOH (50.0 mL) at 0 °C. After the addition was complete, the reaction mixture was stirred at room temperature for an additional 1 h. Ice-water (20.0 mL) was added and then the solvent was evaporated at reduced pressure to give the *N*-formamide as a colorless oil. A stirred solution of amide (18.5 mmol, 1.0 equiv.) and Et₃N (12.8 mL, 92.0 mmol, 5.0 equiv.) in CH₂Cl₂ (90.0 mL) was cooled to -30 °C. Phosphorus oxychloride (2.6 mL, 27.5 mmol, 1.5 equiv.) was added dropwise and the reaction mixture was stirred for 3h at -30 °C. A saturated aqueous solution of Na₂CO₃ was added dropwise and the temperature of the mixture was maintained at -30 °C. The mixture was stirred at -30 °C for 0.5 h and then raised to room temperature. The aqueous layer was separated and extracted with CH₂Cl₂. The organic extracts were combined, washed with brine, dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to provide the isocyanide.



Scheme S2 Synthesis of isocyanides

General procedure B: Followed the procedure in the literature.² In an oven-dried 25

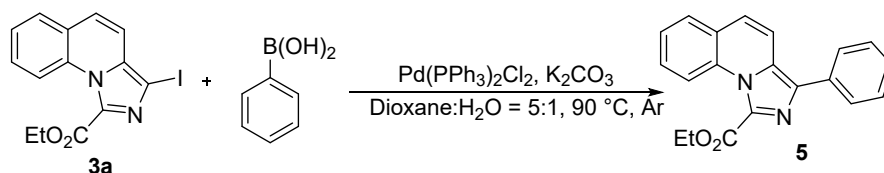
mL Schlenk tube equipped with a magnetic stir bar were added a primary amine R-NH₂ (0.4 mmol), sodium chlorodifluoroacetate (0.8 mmol) and K₂CO₃ (0.8 mmol). The Schlenk tube was evacuated and refilled with dry nitrogen. Dry DMF (5 mL) was then added by syringe. The contents in the tube were vigorously stirred for 12 hours at 100 °C (heated in an oil bath). The reaction mixture was then allowed to cool to room temperature. The resulting mixture was extracted by dichloromethane. The combined organic layers were washed with a large amount of water for 4 times, with brine for once and then dried over magnesium sulfate. The solvent was removed under vacuum and the residuals were purified by column chromatography on silica using a mixture of petroleum ether (PE) and ethyl acetate (EA) as the eluent to give purified isocyanide.



Scheme S3 Synthesis of α -isocyanoacetamides

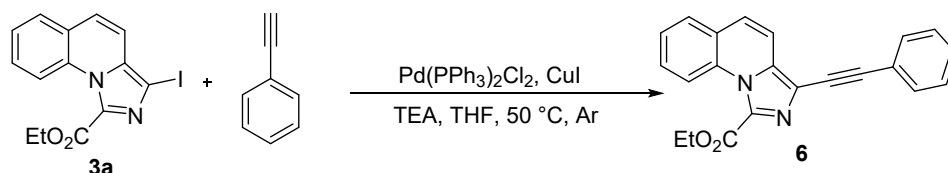
General procedure C: Followed the procedure in the literature.³ To 30 mmol of amine was added 30 mmol of methyl 2-isocyanoacetate and the mixture was stirred overnight at room temperature. If the product precipitated during the reaction, it was filtered off, washed three times with cold diethyl ether, and dried under vacuum overnight. If no precipitation was observed, cold diethylether was added to the reaction mixture, and the product was allowed to crystallize in the freezer at -20 °C. In the rare cases, the product was formed as an oil or no crystallization occurred, the product was purified by preparative chromatography with silica gel and ethyl acetate as eluent.

2.5 The further application of iodinated products



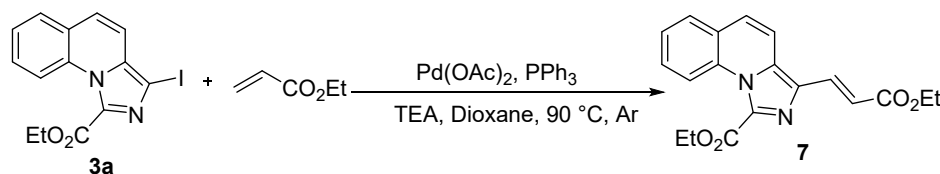
Scheme S4 Arylation of iodinated product

Adapting a literature procedure,⁴ potassium carbonate (0.4 mmol, 2.0 equiv.), phenylboronic acid (0.26 mmol, 1.3 equiv.) and Pd(PPh₃)₂Cl₂ (5 mol%) were added to a solution of **3a** (0.2 mmol, 1.0 equiv.) in a 5:1 solvent mixture of dioxane and water. The reaction mixture was heated to 90 °C and stirred at this temperature until complete consumption of **3a** was observed (monitored by TLC). After cooling to room temperature, the mixture was diluted with a mixture of EA and water and the aqueous layer was extracted with EtOAc (3 × 50 mL). dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired **5** in 76% yield.



Scheme S5 Alkynylation of iodinated product

Adapting a literature procedure,⁵ **3a** (0.2 mmol, 1 equiv.), Pd(PPh₃)₂Cl₂ (5 mol%), CuI (10 mol%) and phenylacetylene (0.24 mmol, 1.2 equiv.) were added to a 25 mL Schlenk flask with a stir bar under an Ar atmosphere. Then tetrahydrofuran (2 mL) and triethylamine (1 mL) were added sequentially. The reaction mixture was then stirred at 50 °C. Afterwards 15 mL of water were added and the reaction mixture was extracted with EtOAc (3 × 50 mL). The combined organic fractions were washed with brine and dried over anhydrous Na₂SO₄. After filtration, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether and ethyl acetate as the eluent to afford the desired **6** in 78% yield.



Scheme S6 Alkenylation of iodinated product

Adapting a literature procedure,⁶ **3a** (0.2 mmol, 1 equiv.), Pd(OAc)₂ (10 mol%), PPh₃ (20 mol%) and ethyl acrylate (0.3 mmol, 1.5 equiv.) were added to a 25 mL Schlenk flask with a stir bar under an Ar atmosphere. Then dioxane (2 mL) and triethylamine (1 mL) were added sequentially. The reaction mixture was then stirred at 90 °C. Afterwards 50 mL of water were added and the reaction mixture was extracted with EtOAc (3 × 50 mL). The combined organic fractions were washed with brine and dried over anhydrous Na₂SO₄. After filtration, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography using petroleum ether and ethyl acetate as the eluent to afford the desired **7** in 85% yield.



Scheme S7 Selenization of iodinated product

Adapting a literature procedure,⁷ a 25 mL pressure vial was charged with **3a** (0.2 mmol, 1.0 equiv.), diphenyl diselenide (0.12 mmol, 0.6 equiv.) in DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 110 °C for 24 h under an air atmosphere. After the reaction completed, and added 50 mL water to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with brine, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the desired **8** in

70% yield.

3. Molecular structure and crystallographic data

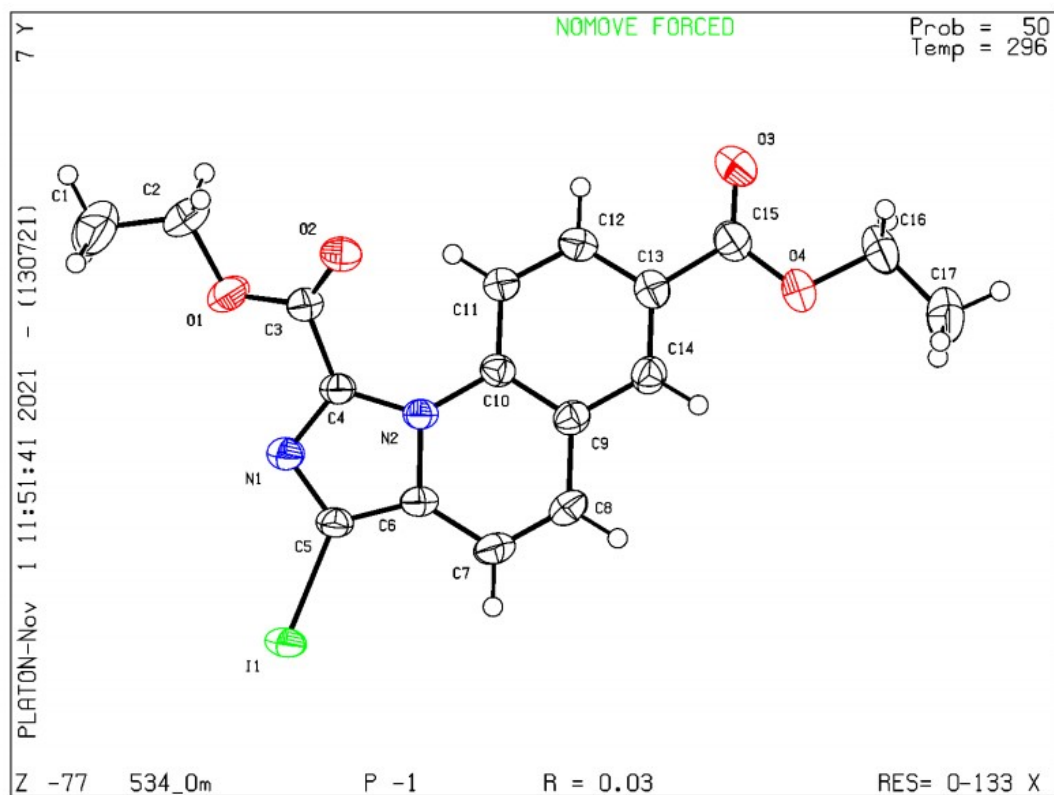


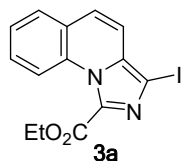
Figure S1 X-ray crystal structure of compound 3j

Table S6. Crystal data and structure refinement for compound 3j

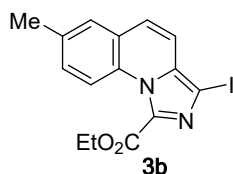
Identification code	CCDC: 2120040
Empirical formula	C ₁₇ H ₁₅ IN ₂ O ₄
Formula weight	438.21
Temperature/K	296(2)
Space group	P -1
Hall group	-P 1
a/Å	9.3683(16)
b/Å	9.4908(16)
c/Å	10.5784(18)
α /°	87.911(2)

$\beta/^\circ$	71.723(2)
$\gamma/^\circ$	70.747(2)
Volume/ \AA^3	840.8(2)
Z	2
Dx,g /cm ³	1.731
Mu /mm ⁻¹	1.928
F(000)	432.0
h,k,lmax	12,12,13
Nref	3909
Tmin,Tmax	0.715,0.750
Tmin'	0.701
Data completeness	0.966
Theta(max)	27.612
R(reflections)	0.0314(3403)

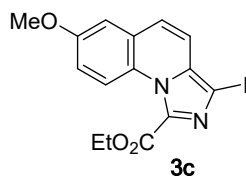
4. Characterization of Products



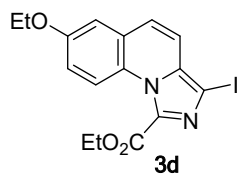
Ethyl 3-iodoimidazo[1,5-*a*]quinoline-1-carboxylate (3a), 57 mg, 78%, yellow solid, m.p. 101-102 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.71-8.59 (m, 1H), 7.80-7.70 (m, 1H), 7.64-7.57 (m, 1H), 7.52 (ddd, *J* = 7.8, 7.3, 1.1 Hz, 1H), 7.35 (d, *J* = 4.7 Hz, 2H), 4.58 (q, *J* = 7.1 Hz, 2H), 1.52 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.2, 135.3, 135.0, 131.9, 128.9, 128.6, 126.8, 126.3, 125.8, 119.5, 116.4, 79.6, 62.5, 14.3. IR (KBr, cm⁻¹): 2831, 1706, 1597, 1364, 1191, 776. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₄H₁₂IN₂O₂: 366.9865, found: 366.9866.



Ethyl 3-iodo-7-methylimidazo[1,5-*a*]quinoline-1-carboxylate (3b), 60 mg, 78%, yellow solid, m.p. 140-142 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.56 (d, *J* = 8.8 Hz, 1H), 7.53-7.49 (m, 1H), 7.40 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.29 (s, 2H), 4.56 (q, *J* = 7.1 Hz, 2H), 2.49 (s, 3H), 1.51 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.1, 136.7, 135.2, 134.7, 129.9, 129.8, 128.5, 126.1, 125.7, 119.3, 116.2, 79.4, 62.4, 20.9, 14.3. IR (KBr, cm⁻¹): 2832, 1690, 1597, 1364, 1195, 776. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₅H₁₄IN₂O₂: 381.0022, found: 381.0023.

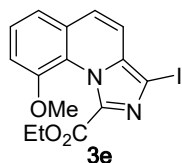


Ethyl 3-iodo-7-methoxyimidazo[1,5-*a*]quinoline-1-carboxylate (3c), 55 mg, 70%, yellow solid, m.p. 148-150 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.66 (d, *J* = 9.4 Hz, 1H), 7.30-7.24 (m, 2H), 7.15 (ddd, *J* = 9.4, 2.9, 1.0 Hz, 1H), 7.10 (d, *J* = 2.9 Hz, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 157.6, 134.9, 134.4, 127.2, 126.2, 126.0, 121.0, 116.7, 116.6, 110.0, 79.6, 62.4, 55.6, 14.3. IR (KBr, cm⁻¹): 2832, 1687, 1597, 1364, 1200, 1065, 776. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₅H₁₄IN₂O₃: 396.9971, found: 396.9974.

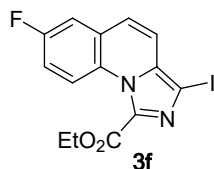


Ethyl 7-ethoxy-3-iodoimidazo[1,5-*a*]quinoline-1-carboxylate (3d), 59 mg, 72%, yellow solid, m.p. 152-153 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.67 (dd, *J* = 9.4, 1.8

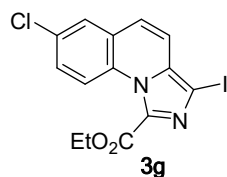
Hz, 1H), 7.33-7.26 (m, 2H), 7.17 (ddd, $J = 9.4, 2.8, 1.9$ Hz, 1H), 7.12 (t, $J = 2.7$ Hz, 1H), 4.56 (q, $J = 7.1$ Hz, 2H), 4.14 (qd, $J = 7.0, 1.2$ Hz, 2H), 1.53-1.49 (m, 3H), 1.49-1.44 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.1, 157.1, 135.0, 134.5, 127.3, 126.2, 126.1, 121.1, 117.2, 116.6, 110.8, 79.6, 63.9, 62.3, 14.7, 14.3. IR (KBr, cm^{-1}): 2832, 1699, 1597, 1364, 1196, 1065, 776. HR-MS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_3$: 411.0127, found: 411.0128.



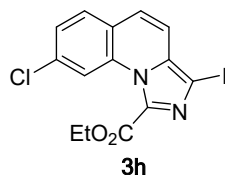
Ethyl 3-iodo-9-methoxyimidazo[1,5-*a*]quinoline-1-carboxylate (3e), 52 mg, 66%, yellow oil, ^1H NMR (400 MHz, CDCl_3) δ 7.39 (t, $J = 8.0$ Hz, 1H), 7.27 (dd, $J = 7.7, 0.9$ Hz, 1H), 7.22-7.14 (m, 2H), 7.04 (dd, $J = 8.1, 1.2$ Hz, 1H), 4.41 (q, $J = 7.2$ Hz, 2H), 3.87 (s, 3H), 1.37 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.2, 149.5, 139.4, 133.9, 127.6, 126.8, 124.5, 122.4, 120.1, 116.7, 110.4, 61.7, 55.3, 14.2. IR (KBr, cm^{-1}): 2832, 1654, 1597, 1364, 776. HR-MS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_3$: 396.9971, found: 396.9973.



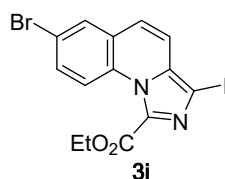
Ethyl 7-fluoro-3-iodoimidazo[1,5-*a*]quinoline-1-carboxylate (3f), 54 mg, 71%, yellow solid, m.p. 175-176 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.79 (dd, $J = 9.4, 4.7$ Hz, 1H), 7.42-7.34 (m, 2H), 7.34-7.26 (m, 2H), 4.56 (q, $J = 7.1$ Hz, 2H), 1.51 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.5, 160.0, 159.0, 135.0 (d, $J = 12.0$ Hz), 128.4 (d, $J = 3.0$ Hz), 127.6 (d, $J = 9.0$ Hz), 125.4 (d, $J = 4.0$ Hz), 121.9 (d, $J = 8.0$ Hz), 117.63, 116.3 (d, $J = 23.0$ Hz), 113.6 (d, $J = 23.0$ Hz), 80.2, 62.6, 14.3. IR (KBr, cm^{-1}): 2832, 1711, 1698, 1478, 1234, 1192, 776. HR-MS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{11}\text{FIN}_2\text{O}_2$: 384.9771, found: 384.9773.



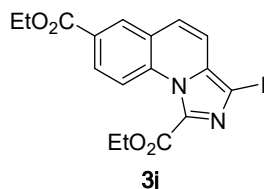
Ethyl 7-chloro-3-iodoimidazo[1,5-*a*]quinoline-1-carboxylate (3g), 60 mg, 75%, yellow solid, m.p. 192-193 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.85 (d, $J = 1.9$ Hz, 1H), 7.65 (d, $J = 8.4$ Hz, 1H), 7.48 (dd, $J = 8.4, 1.9$ Hz, 1H), 7.30 (d, $J = 2.8$ Hz, 2H), 4.59 (q, $J = 7.1$ Hz, 2H), 1.52 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.8, 135.2, 135.0, 134.2, 132.2, 129.7, 127.3, 125.4, 124.1, 119.8, 116.5, 80.0, 62.7, 14.2. IR (KBr, cm^{-1}): 2832, 1695, 1597, 1363, 1192, 776. HR-MS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{11}\text{ClIN}_2\text{O}_2$: 400.9475, found: 400.9477.



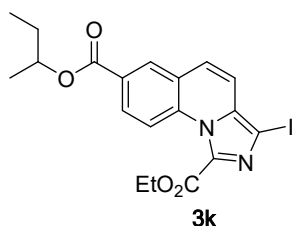
Ethyl 8-chloro-3-iodoimidazo[1,5-*a*]quinoline-1-carboxylate (3h), 64 mg, 80%, yellow solid, m.p. 161-162 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.71 (d, *J* = 9.2 Hz, 1H), 7.70 (d, *J* = 2.4 Hz, 1H), 7.52 (dd, *J* = 9.2, 2.5 Hz, 1H), 7.35 (d, *J* = 9.4 Hz, 1H), 7.24 (s, 1H), 4.57 (q, *J* = 7.1 Hz, 2H), 1.51 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.9, 135.1, 132.4, 130.3, 128.5, 127.8, 127.1, 125.1, 121.2, 117.6, 80.3, 62.6, 14.3. IR (KBr, cm⁻¹): 2832, 1710, 1601, 1437, 1364, 1190, 1066, 829, 776. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₄H₁₁ClIN₂O₂: 400.9475, found: 400.9476.



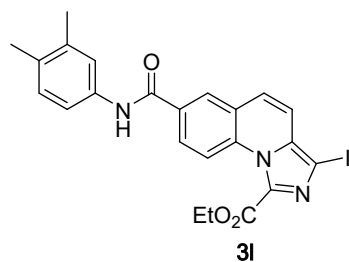
Ethyl 7-bromo-3-iodoimidazo[1,5-*a*]quinoline-1-carboxylate (3i), 65 mg, 74%, yellow solid, m.p. 182-183 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.61 (d, *J* = 9.4 Hz, 1H), 7.83 (d, *J* = 2.3 Hz, 1H), 7.64 (dd, *J* = 9.2, 2.3 Hz, 1H), 7.32 (d, *J* = 9.4 Hz, 1H), 7.21 (d, *J* = 9.3 Hz, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 1.51 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 159.9, 135.1, 135.0, 131.3, 130.9, 130.6, 127.4, 124.9, 121.3, 120.2, 117.59, 80.3, 62.6, 14.3. IR (KBr, cm⁻¹): 2832, 1693, 1597, 1363, 1190, 776. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₄H₁₁BrIN₂O₂: 444.8970, found: 444.8974.



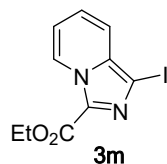
Diethyl 3-iodoimidazo[1,5-*a*]quinoline-1,7-dicarboxylate (3j), 61 mg, 70%, yellow solid, m.p. 193-194 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.73 (d, *J* = 9.0 Hz, 1H), 8.45 (d, *J* = 2.0 Hz, 1H), 8.23 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.48-7.33 (m, 2H), 4.58 (q, *J* = 7.1 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.52 (t, *J* = 7.1 Hz, 3H), 1.45 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.3, 160.0, 135.5, 134.3, 130.6, 129.1, 128.7, 126.1, 125.6, 119.7, 117.3, 80.1, 62.8, 61.5, 14.3. IR (KBr, cm⁻¹): 2979, 2832, 1711, 1693, 1600, 1428, 1364, 1287, 1186, 1059, 776. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₇H₁₆IN₂O₄: 439.0076, found: 439.0078.



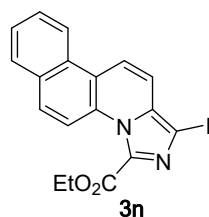
7-(*sec*-butyl) 1-Ethyl 3-iodoimidazo[1,5-*a*]quinoline-1,7-dicarboxylate (3k), 68 mg, 73%, yellow solid, m.p. 130-131 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.71 (d, *J* = 9.0 Hz, 1H), 8.43 (d, *J* = 2.0 Hz, 1H), 8.23 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.40 (q, *J* = 9.4 Hz, 2H), 5.15 (dt, *J* = 12.6, 6.2 Hz, 1H), 4.58 (q, *J* = 7.1 Hz, 2H), 1.81-1.69 (m, 2H), 1.51 (t, *J* = 7.1 Hz, 3H), 1.38 (d, *J* = 6.3 Hz, 3H), 1.00 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.9, 159.9, 135.4, 134.2, 130.5, 129.1, 126.1, 125.5, 119.6, 117.2, 80.0, 73.6, 62.7, 28.9, 19.5, 14.3, 9.7. IR (KBr, cm⁻¹): 2970, 2831, 1579, 1362, 1328, 1282, 1191, 793, 763. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₉H₂₀IN₂O₄: 467.0390, found: 467.0392.



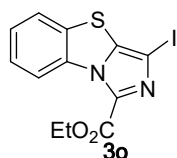
Ethyl 7-((3,4-dimethylphenyl)carbamoyl)-3-iodoimidazo[1,5-*a*]quinoline-1-carboxylate (3l), 68 mg, 67%, yellow solid, m.p. 230-231 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.59 (d, *J* = 9.0 Hz, 1H), 8.35 (s, 1H), 8.08 (d, *J* = 1.7 Hz, 1H), 7.86 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.52 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.24-7.15 (m, 2H), 7.13 (d, *J* = 8.1 Hz, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 2.25 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.5, 159.9, 137.3, 135.6, 135.2, 133.6, 133.2, 132.9, 130.1, 127.9, 126.6, 125.8, 125.4, 121.6, 119.7, 117.8, 117.1, 80.2, 62.8, 19.9, 19.2, 14.3. IR (KBr, cm⁻¹): 2832, 1712, 1583, 1504, 1362, 1248, 1184, 1051, 867. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₂₃H₂₁IN₃O₃: 514.0549, found: 514.0551.



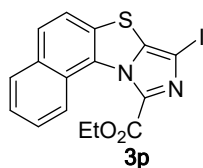
Ethyl 1-iodoimidazo[1,5-*a*]pyridine-3-carboxylate (3m), 38 mg, 60%, yellow solid, m.p. 110-111 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.39-9.23 (m, 1H), 7.53 (dt, *J* = 9.1, 1.2 Hz, 1H), 7.15 (ddd, *J* = 9.1, 6.6, 0.9 Hz, 1H), 6.97 (td, *J* = 7.1, 1.2 Hz, 1H), 4.50 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 158.7, 136.2, 129.5, 125.9, 123.8, 118.7, 116.3, 61.5, 14.5. IR (KBr, cm⁻¹): 2917, 2832, 1593, 1363, 1215, 776. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₀H₁₀IN₂O₂: 316.9781, found: 316.9781.



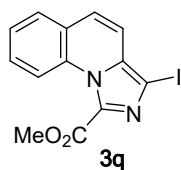
Ethyl 1-iodobenzo[*f*]imidazo[1,5-*a*]quinoline-3-carboxylate (3n), 57 mg, 68%, yellow solid, m.p. 188-189 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.51-8.30 (m, 2H), 8.10 (d, *J* = 9.5 Hz, 1H), 7.90 (d, *J* = 8.7 Hz, 2H), 7.62 (dq, *J* = 14.7, 7.1 Hz, 2H), 7.42 (d, *J* = 9.5 Hz, 1H), 4.60 (q, *J* = 7.0 Hz, 2H), 1.54 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.1, 135.3, 134.2, 131.2, 129.9, 129.2, 129.1, 128.6, 127.7, 126.9, 123.0, 121.3, 120.6, 118.0, 116.2, 78.6, 62.4, 14.3. IR (KBr, cm⁻¹): 2832, 1659, 1592, 1363, 775. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₈H₁₄IN₂O₂: 417.0022, found: 417.0024.



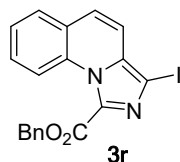
Ethyl 3-iodobenzo[*d*]imidazo[5,1-*b*]thiazole-1-carboxylate (3o), 51 mg, 68%, white solid, m.p. 176-177 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.15 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.66 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.51-7.46 (m, 1H), 7.43 (td, *J* = 7.6, 1.4 Hz, 1H), 4.52 (q, *J* = 7.1 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 157.8, 140.2, 134.1, 133.8, 132.3, 126.8, 126.4, 123.9, 119.2, 70.6, 62.1, 14.4. IR (KBr, cm⁻¹): 2831, 1705, 1597, 1363, 1171, 775. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₂H₁₀IN₂O₂S: 372.9429, found: 372.9430.



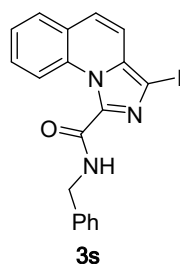
Ethyl 8-iodoimidazo[5,1-*b*]naphtho[1,2-*d*]thiazole-10-carboxylate (3p), 54 mg, 64%, yellow solid, m.p. 183-184 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.03-7.98 (m, 1H), 7.95 (d, *J* = 8.7 Hz, 1H), 7.80-7.74 (m, 1H), 7.71 (d, *J* = 8.7 Hz, 1H), 7.65-7.58 (m, 2H), 4.51 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 158.4, 139.9, 135.5, 132.4, 130.7, 128.7, 128.5, 128.5, 126.4, 126.1, 123.5, 122.1, 120.5, 69.9, 62.4, 14.2. IR (KBr, cm⁻¹): 2831, 1711, 1597, 1363, 775. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₆H₁₂IN₂O₂S: 422.9586, found: 422.9588.



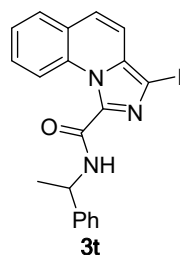
Ethyl 3-iodoimidazo[1,5-*a*]quinoline-1-carboxylate (3q), 55 mg, 79%, yellow solid, m.p. 192-193 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.76 (d, *J* = 8.7 Hz, 1H), 7.75 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.61 (ddd, *J* = 8.8, 7.2, 1.7 Hz, 1H), 7.56-7.50 (m, 1H), 7.36 (q, *J* = 9.3 Hz, 2H), 4.09 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.4, 135.6, 134.6, 131.9, 128.9, 128.7, 126.9, 126.5, 125.8, 119.6, 116.3, 79.7, 53.2. IR (KBr, cm⁻¹): 2831, 1710, 1593, 1363, 1188, 775. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₃H₁₀IN₂O₂: 352.9709, found: 352.9710.



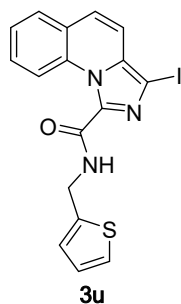
Benzyl 3-iodoimidazo[1,5-*a*]quinoline-1-carboxylate (3r), 56 mg, 65%, yellow solid, m.p. 135–136 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.60 – 8.46 (m, 1H), 7.74 – 7.68 (m, 1H), 7.57 – 7.54 (m, 2H), 7.52 – 7.47 (m, 2H), 7.40 (ddd, *J* = 7.3, 6.1, 1.6 Hz, 2H), 7.38 – 7.34 (m, 1H), 7.34 – 7.28 (m, 2H), 5.55 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 159.9, 135.4, 135.3, 134.7, 131.7, 128.8, 128.6, 128.6, 128.5, 126.8, 126.30, 125.7, 119.4, 79.7, 67.8. IR (KBr, cm⁻¹): 2831, 1705, 1597, 1366, 1176, 774. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₉H₁₄IN₂O₂: 428.0022, found: 428.0024.



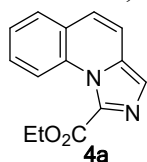
***N*-benzyl-3-iodoimidazo[1,5-*a*]quinoline-1-carboxamide (3s)**, 47 mg, 55%, yellow solid, m.p. 146–147 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.50 – 9.42 (m, 1H), 7.90 (s, 1H), 7.72 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.63 (ddd, *J* = 8.8, 7.2, 1.7 Hz, 1H), 7.51 (td, *J* = 7.5, 1.1 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.40 – 7.35 (m, 2H), 7.34 – 7.29 (m, 3H), 4.72 (d, *J* = 6.1 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 159.1, 138.5, 137.9, 135.2, 128.8, 128.7, 128.5, 127.9, 127.6, 126.7, 125.8, 125.7, 121.1, 116.2, 43.9. IR (KBr, cm⁻¹): 2831, 1597, 1537, 1363, 774. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₉H₁₅IN₃O: 428.0182, found: 428.0184.



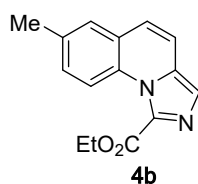
3-Iodo-*N*-(1-phenylethyl)imidazo[1,5-*a*]quinoline-1-carboxamide (3t), 44 mg, 50%, yellow solid, m.p. 156–157 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.45 – 9.35 (m, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.70 – 7.67 (m, 1H), 7.58 (ddd, *J* = 8.8, 7.2, 1.7 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.40 – 7.35 (m, 2H), 7.29 (s, 2H), 7.27 (s, 1H), 5.34 (p, *J* = 7.1 Hz, 1H), 1.68 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 158.3, 143.1, 138.6, 135.2, 132.4, 128.7, 128.6, 128.4, 127.4, 126.7, 126.2, 125.7, 125.7, 121.2, 116.2, 49.6, 22.2. IR (KBr, cm⁻¹): 2917, 2831, 1601, 1531, 1363, 791, 774, 756, 700. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₂₀H₁₇IN₃O: 442.0338, found: 442.0342.



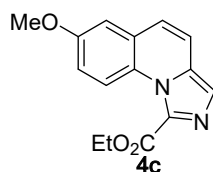
3-Iodo-*N*-(thiophen-2-ylmethyl)imidazo[1,5-*a*]quinoline-1-carboxamide (3u), 39 mg, 45%, yellow solid, m.p. 164–165 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.63 – 9.31 (m, 1H), 7.93 (s, 1H), 7.71 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.64 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.51 (td, *J* = 7.8, 1.0 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.26 – 7.24 (m, 1H), 7.10 (dd, *J* = 3.5, 1.0 Hz, 1H), 6.99 (dd, *J* = 5.1, 3.5 Hz, 1H), 4.96 – 4.75 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 158.8, 140.5, 138.2, 135.3, 132.3, 128.8, 128.5, 126.9, 126.8, 126.3, 125.9, 125.7, 125.4, 121.1, 116.2, 38.6. IR (KBr, cm⁻¹): 2917, 2831, 1601, 1509, 1363, 790, 774, 753, 702. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₇H₁₃IN₃OS: 433.9746, found: 433.9750.



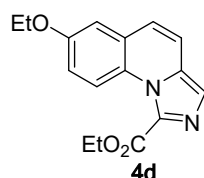
Ethyl imidazo[1,5-*a*]quinoline-1-carboxylate (4a), 38 mg, 80%, yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 8.76 (d, *J* = 8.7 Hz, 1H), 7.70 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.61-7.54 (m, 2H), 7.50-7.45 (m, 1H), 7.38 (d, *J* = 9.3 Hz, 1H), 7.26 (d, *J* = 9.3 Hz, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 1.52 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.8, 133.5, 131.8, 128.5, 128.2, 126.2, 125.5, 124.9, 123.7, 119.7, 116.0, 62.1, 14.2. IR (KBr, cm⁻¹): 2831, 1708, 1605, 1365, 1192, 1158, 774. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₄H₁₃N₂O₂: 240.0899, found: 240.0890.



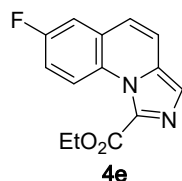
Ethyl 7-methylimidazo[1,5-*a*]quinoline-1-carboxylate (4b), 39 mg, 76%, yellow solid, m.p. 79-80 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.61 (d, *J* = 8.8 Hz, 1H), 7.52 (s, 1H), 7.43-7.40 (m, 1H), 7.33 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.30 (d, *J* = 9.3 Hz, 1H), 7.14 (d, *J* = 9.2 Hz, 1H), 4.53 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.8, 136.1, 133.5, 132.9, 129.9, 129.4, 128.3, 125.6, 124.9, 123.6, 119.6, 115.9, 61.9, 20.9, 14.3. IR (KBr, cm⁻¹): 2831, 1601, 1364, 774. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₅H₁₅N₂O₂: 254.1055, found: 254.1057.



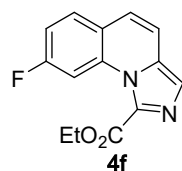
Ethyl 7-methoxyimidazo[1,5-*a*]quinoline-1-carboxylate (4c), 45 mg, 84%, yellow solid, m.p. 107-108 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.81 (d, *J* = 9.4 Hz, 1H), 7.58 (s, 1H), 7.40 (d, *J* = 9.3 Hz, 1H), 7.24 (d, *J* = 9.3 Hz, 1H), 7.19 (dd, *J* = 9.4, 3.0 Hz, 1H), 7.12 (d, *J* = 2.9 Hz, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 1.52 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.9, 157.4, 133.3, 132.8, 127.1, 126.5, 124.8, 123.9, 121.5, 116.5, 116.4, 110.1, 62.0, 55.6, 14.4. IR (KBr, cm⁻¹): 2831, 1596, 1487, 1363, 1245, 774. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₅H₁₅N₂O₃: 271.1004, found: 271.1005.



Ethyl 7-ethoxyimidazo[1,5-*a*]quinoline-1-carboxylate (4d), 47 mg, 82%, yellow solid, m.p. 96-97 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.76 (d, *J* = 9.4 Hz, 1H), 7.54 (s, 1H), 7.33 (d, *J* = 9.3 Hz, 1H), 7.20 – 7.10 (m, 2H), 7.05 (d, *J* = 2.8 Hz, 1H), 4.53 (q, *J* = 7.1 Hz, 2H), 4.10 (q, *J* = 7.0 Hz, 2H), 1.50 (t, *J* = 7.1 Hz, 3H), 1.44 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.8, 156.6, 133.3, 132.6, 127.0, 126.3, 124.8, 123.8, 121.3, 116.6, 116.3, 110.7, 63.8, 61.9, 14.7, 14.3. IR (KBr, cm⁻¹): 2980, 2832, 1579, 1371, 776. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₆H₁₇N₂O₃: 285.1161, found: 285.1163.

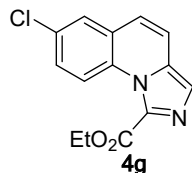


Ethyl 7-fluoroimidazo[1,5-*a*]quinoline-1-carboxylate (4e), 37 mg, 72%, yellow solid, m.p. 86-87 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.88 (dd, *J* = 9.5, 4.8 Hz, 1H), 7.61 (s, 1H), 7.42 (d, *J* = 9.3 Hz, 1H), 7.35 (dd, *J* = 8.5, 3.0 Hz, 1H), 7.28 (ddd, *J* = 9.4, 7.7, 3.0 Hz, 1H), 7.20 (d, *J* = 9.3 Hz, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 1.51 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.8, 160.0 (d, *J* = 247.0 Hz), 133.3 (d, *J* = 9.0 Hz), 128.5 (d, *J* = 3.0 Hz), 127.4 (d, *J* = 9.0 Hz), 124.2 (d, *J* = 3.0 Hz), 122.1 (d, *J* = 9.0 Hz), 117.3, 115.9 (d, *J* = 77.0 Hz), 113.3 (d, *J* = 22.0 Hz), 62.2, 14.3. IR (KBr, cm⁻¹): 2832, 1706, 1593, 1483, 1366, 1190, 777. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₄H₁₂FN₂O₂: 259.0805, found: 259.0807.

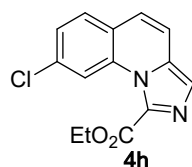


Ethyl 8-fluoroimidazo[1,5-*a*]quinoline-1-carboxylate (4f), 36 mg, 70%, yellow solid, m.p. 97-98 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.77 (dd, *J* = 11.7, 2.4 Hz, 1H), 7.70 (dd, *J* = 8.7, 6.3 Hz, 1H), 7.60 (s, 1H), 7.37 (d, *J* = 9.3 Hz, 1H), 7.29-7.24 (m, 2H), 4.57 (q, *J* = 7.1 Hz, 2H), 1.52 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ

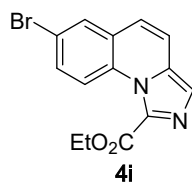
161.5 (d, $J = 247.0$ Hz), 160.6, 133.4 (d, $J = 40.0$ Hz), 132.9 (d, $J = 11.0$ Hz), 130.2 (d, $J = 10.0$ Hz), 124.4 (d, $J = 1.0$ Hz), 123.8 (d, $J = 1.0$ Hz), 122.2 (d, $J = 2.0$ Hz), 115.3 (d, $J = 3.0$ Hz), 114.7 (d, $J = 23.0$ Hz), 107.3 (d, $J = 29.0$ Hz), 62.3, 14.3. IR (KBr, cm^{-1}): 2832, 1709, 1593, 1486, 1363, 1187, 776. HR-MS (ESI): m/z $[M+H]^+$ calcd for $\text{C}_{14}\text{H}_{12}\text{FN}_2\text{O}_2$: 259.0805, found: 259.0806.



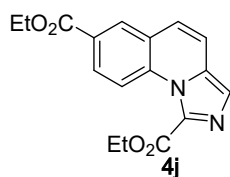
Ethyl 7-chloroimidazo[1,5-*a*]quinoline-1-carboxylate (4g), 43 mg, 79%, yellow solid, m.p. 153-154 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.68 (d, $J = 9.2$ Hz, 1H), 7.67 (d, $J = 2.3$ Hz, 1H), 7.50 (dd, $J = 9.2, 2.4$ Hz, 1H), 7.32 (d, $J = 9.4$ Hz, 1H), 7.21 (d, $J = 9.4$ Hz, 1H), 4.56 (q, $J = 7.1$ Hz, 2H), 1.51 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.9, 135.1, 135.1, 132.4, 130.2, 128.5, 127.8, 127.1, 125.0, 121.1, 117.6, 80.3, 62.6, 14.3. IR (KBr, cm^{-1}): 2831, 1712, 1697, 1598, 1470, 1363, 1318, 1193, 775. HR-MS (ESI): m/z $[M+H]^+$ calcd for $\text{C}_{14}\text{H}_{12}\text{ClN}_2\text{O}_2$: 275.0509; found: 275.0511.



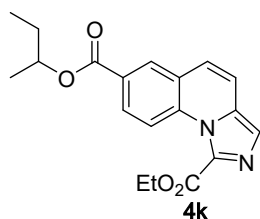
Ethyl 8-chloroimidazo[1,5-*a*]quinoline-1-carboxylate (4h), 41 mg, 75%, yellow solid, m.p. 97-98 °C. ^1H NMR (400 MHz, CDCl_3) δ 9.00 (s, 1H), 7.64 (dd, $J = 8.4, 2.7$ Hz, 1H), 7.60 (d, $J = 2.2$ Hz, 1H), 7.49-7.43 (m, 1H), 7.40 (dd, $J = 9.3, 2.7$ Hz, 1H), 7.28-7.23 (m, 1H), 4.58 (q, $J = 7.1$ Hz, 2H), 1.53 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.6, 133.9, 133.5, 133.4, 132.5, 129.5, 126.8, 124.2, 124.1, 124.0, 120.20, 116.4, 62.4, 14.3. IR (KBr, cm^{-1}): 2831, 1704, 1606, 1419, 1366, 1185, 836, 775. HR-MS (ESI): m/z $[M+H]^+$ calcd for $\text{C}_{14}\text{H}_{12}\text{ClN}_2\text{O}_2$: 275.0509, found: 275.0510.



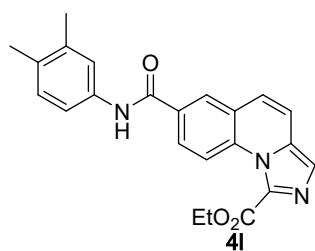
Ethyl 7-bromoimidazo[1,5-*a*]quinoline-1-carboxylate (4i), 48 mg, 75%, yellow solid, m.p. 99-100 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.75 (d, $J = 9.2$ Hz, 1H), 7.83 (d, $J = 2.3$ Hz, 1H), 7.65 (dd, $J = 9.2, 2.3$ Hz, 1H), 7.60 (s, 1H), 7.42 (d, $J = 9.3$ Hz, 1H), 7.17 (d, $J = 9.3$ Hz, 1H), 4.55 (q, $J = 7.1$ Hz, 2H), 1.51 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.7, 133.3, 131.0, 130.9, 130.6, 127.3, 124.3, 123.7, 121.7, 119.6, 117.3, 62.3, 14.3. IR (KBr, cm^{-1}): 2831, 1703, 1596, 1442, 1365, 1293, 1212, 864, 802, 665. HR-MS (ESI): m/z $[M+H]^+$ calcd for $\text{C}_{14}\text{H}_{12}\text{BrN}_2\text{O}_2$: 319.0004, found: 319.0005.



Diethyl imidazo[1,5-*a*]quinoline-1,7-dicarboxylate (4j), 44 mg, 70%, yellow solid, m.p. 137-138 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.83 (d, *J* = 9.0 Hz, 1H), 8.41 (d, *J* = 2.0 Hz, 1H), 8.22 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.62 (s, 1H), 7.45 (d, *J* = 9.3 Hz, 1H), 7.34 (d, *J* = 9.3 Hz, 1H), 4.57 (q, *J* = 7.1 Hz, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.52 (t, *J* = 7.1 Hz, 3H), 1.44 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.5, 160.8, 134.5, 133.8, 133.6, 130.4, 128.9, 128.2, 125.4, 124.8, 124.1, 119.9, 116.9, 62.4, 61.4, 14.3. IR (KBr, cm⁻¹): 2831, 1723, 1698, 1596, 1363, 1280, 1196, 775, 765. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₇H₁₇N₂O₄: 313.1110, found: 313.1112.

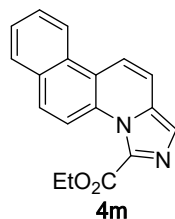


7-(*sec*-butyl) 1-Ethyl imidazo[1,5-*a*]quinoline-1,7-dicarboxylate (4k), 49 mg, 73%, yellow solid, m.p. 106-107 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.81 (d, *J* = 9.0 Hz, 1H), 8.40 (d, *J* = 2.0 Hz, 1H), 8.22 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.61 (s, 1H), 7.45 (d, *J* = 9.3 Hz, 1H), 7.34 (d, *J* = 9.3 Hz, 1H), 5.14 (dt, *J* = 12.6, 6.3 Hz, 1H), 4.57 (q, *J* = 7.1 Hz, 2H), 1.79-1.70 (m, 2H), 1.52 (t, *J* = 7.1 Hz, 3H), 1.37 (d, *J* = 6.3 Hz, 3H), 1.00 (t, *J* = 7.5 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.1, 160.8, 134.4, 133.6, 130.3, 128.8, 128.6, 125.3, 124.9, 124.1, 119.9, 116.9, 73.5, 62.3, 28.9, 19.5, 14.3, 9.7. IR (KBr, cm⁻¹): 2975, 2831, 1713, 1596, 1363, 1191, 831, 775, 764, 734. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₉H₂₁N₂O₄: 341.1423, found: 341.1424.

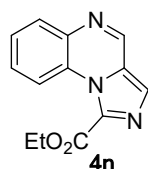


Ethyl 7-((3,4-dimethylphenyl)carbamoyl)imidazo[1,5-*a*]quinoline-1-carboxylate (4l), 53 mg, 69%, yellow solid, m.p. 154–155 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.74 (d, *J* = 9.0 Hz, 1H), 8.24 (s, 1H), 8.15 (d, *J* = 2.1 Hz, 1H), 7.91 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.58 (s, 1H), 7.49 (s, 1H), 7.42 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.36 (d, *J* = 9.3 Hz, 1H), 7.19 (d, *J* = 9.3 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 2.26 (d, *J* = 8.4 Hz, 6H), 1.52 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.5, 160.8, 137.4, 135.5, 133.6, 133.5, 133.4, 133.2, 132.8, 130.1, 127.9, 126.1, 125.5, 124.7, 124.1, 121.6, 120.1, 117.8, 117.1, 62.4, 19.9, 19.2, 14.3. IR (KBr, cm⁻¹): 2832, 1702,

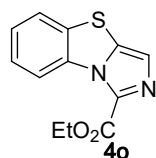
1597, 1541, 1407, 1363, 1329, 1188, 776. HR-MS (ESI): m/z $[M+H]^+$ calcd for $C_{23}H_{22}N_3O_3$: 388.1583, found: 388.1584.



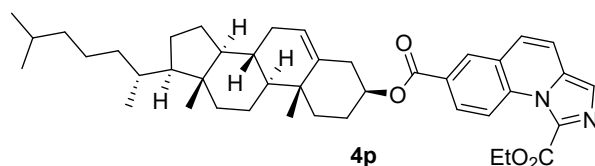
Ethyl benzo[f]imidazo[1,5-a]quinoline-3-carboxylate (4m), 35 mg, 65%, yellow solid, m.p. 140-141 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, $J = 9.4$ Hz, 1H), 8.55 (d, $J = 8.4$ Hz, 1H), 8.23 (d, $J = 9.6$ Hz, 1H), 8.04-7.95 (m, 2H), 7.74 – 7.60 (m, 4H), 4.60 (q, $J = 7.1$ Hz, 2H), 1.55 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 133.8, 132.6, 131.3, 130.1, 129.6, 128.9, 128.7, 127.6, 126.7, 123.4, 123.2, 121.2, 119.7, 118.8, 116.3, 62.1, 14.4. IR (KBr, cm^{-1}): 2832, 1592, 1363, 775. HR-MS (ESI): m/z $[M+H]^+$ calcd for $C_{18}H_{15}N_2O_2$: 291.1055, found: 291.1057.



Ethyl imidazo[1,5-a]quinoxaline-1-carboxylate (4n), 29 mg, 60%, yellow solid, m.p. 101-102 °C. 1H NMR (400 MHz, $CDCl_3$) δ 9.08-8.73 (m, 2H), 8.08-8.00 (m, 1H), 7.95-7.87 (m, 1H), 7.68-7.53 (m, 2H), 4.58 (q, $J = 7.1$ Hz, 2H), 1.57-1.46 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 144.4, 137.6, 134.4, 130.4, 128.6, 127.9, 127.6, 127.3, 126.3, 119.3, 62.8, 14.2. IR (KBr, cm^{-1}): 2977, 2831, 1719, 1592, 1459, 1365, 1256, 1203, 1147, 1053, 879, 776, 749. HR-MS (ESI): m/z $[M+H]^+$ calcd for $C_{13}H_{12}N_3O_2$: 242.0851, found: 242.0852.

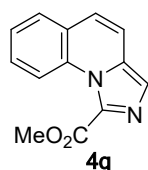


Ethyl benzo[d]imidazo[5,1-b]thiazole-1-carboxylate (4o), 33 mg, 68%, white solid, m.p. 107-108 °C. 1H NMR (400 MHz, $CDCl_3$) δ 9.27-9.21 (m, 1H), 7.67-7.62 (m, 1H), 7.48 (ddd, $J = 8.5, 7.4, 1.4$ Hz, 1H), 7.45-7.39 (m, 1H), 7.33 (s, 1H), 4.52 (q, $J = 7.1$ Hz, 2H), 1.50 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 133.1, 126.4, 126.2, 123.7, 120.0, 118.9, 61.8, 14.4. IR (KBr, cm^{-1}): 2957, 2832, 1582, 1414, 1359, 777. HR-MS (ESI): m/z $[M+H]^+$ calcd for $C_{12}H_{11}N_2O_2S$: 247.0463, found: 247.0464.

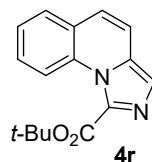


7-((3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-

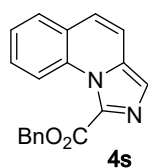
cyclopenta[*a*]phenanthren-3-yl) 1-ethyl imidazo[1,5-*a*]quinoline-1,7-dicarboxylate (**4p**), 65 mg, 50%, yellow solid, m.p. 139-141 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.83 (d, *J* = 9.0 Hz, 1H), 8.42 (d, *J* = 1.8 Hz, 1H), 8.23 (dd, *J* = 9.0, 1.9 Hz, 1H), 7.63 (s, 1H), 7.46 (d, *J* = 9.3 Hz, 1H), 7.35 (d, *J* = 9.4 Hz, 1H), 5.48-5.40 (m, 1H), 4.91 (ddt, *J* = 12.9, 8.5, 4.2 Hz, 1H), 4.57 (q, *J* = 7.1 Hz, 2H), 2.51 (d, *J* = 7.7 Hz, 2H), 2.08-1.96 (m, 4H), 1.52 (d, *J* = 7.1 Hz, 7H), 1.39-1.22 (m, 7H), 1.10 (d, *J* = 12.1 Hz, 7H), 1.05-0.96 (m, 4H), 0.92 (d, *J* = 6.5 Hz, 4H), 0.87 (dd, *J* = 6.6, 1.7 Hz, 8H), 0.70 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.9, 160.8, 139.5, 134.5, 133.6, 130.4, 128.9, 128.6, 125.4, 124.9, 124.1, 122.9, 119.9, 116.9, 62.4, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.7, 36.2, 35.8, 31.9, 31.9, 28.2, 28.0, 27.9, 24.3, 23.8, 22.8, 22.6, 21.1, 19.4, 18.7, 14.3, 11.9. IR (KBr, cm⁻¹): 2950, 2832, 1715, 1581, 1467, 1366, 1330, 1281, 1191, 776. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₄₂H₅₇N₂O₄: 653.4240, found: 653.4242.



Methyl imidazo[1,5-*a*]quinoline-1-carboxylate (**4q**), 36 mg, 79%, yellow solid, m.p. 143-144 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.79 (d, *J* = 8.7 Hz, 1H), 7.68 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.46 (ddd, *J* = 7.8, 7.3, 1.1 Hz, 1H), 7.36 (d, *J* = 9.3 Hz, 1H), 7.24 (s, 1H), 4.07 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 161.1, 133.7, 132.8, 131.9, 128.5, 128.3, 126.3, 125.5, 125.1, 123.8, 119.8, 115.9, 52.9. IR (KBr, cm⁻¹): 2832, 1704, 1581, 1448, 1362, 1205, 1114, 777, 759. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₃H₁₁N₂O₂: 227.0742, found: 227.0744.

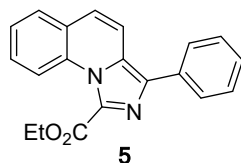


tert-Butyl imidazo[1,5-*a*]quinoline-1-carboxylate (**4r**), 38 mg, 70%, yellow solid, m.p. 95-96 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.54 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.47 (td, *J* = 7.5, 1.0 Hz, 1H), 7.37 (d, *J* = 9.3 Hz, 1H), 7.27 – 7.21 (m, 1H), 1.73 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 160.6, 134.5, 132.8, 131.8, 128.6, 128.1, 126.1, 125.5, 124.4, 123.3, 119.4, 116.2, 83.3, 28.2. IR (KBr, cm⁻¹): 2976, 2832, 1704, 1595, 1428, 1363, 1322, 1171, 1148, 1109, 775, 758. HR-MS (ESI): *m/z* [M+H]⁺ calcd for C₁₆H₁₇N₂O₂: 269.1212, found: 269.1215.

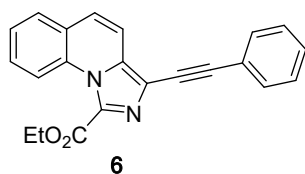


Benzyl imidazo[1,5-*a*]quinoline-1-carboxylate (**4s**), 36 mg, 60%, yellow solid, m.p. 111-112 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.74 – 8.63 (m, 1H), 7.69 (d, *J* = 7.7 Hz,

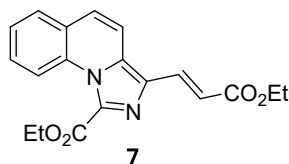
1H), 7.60 (s, 1H), 7.56 (dt, $J = 7.7, 1.9$ Hz, 2H), 7.52 (dd, $J = 8.6, 1.6$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 1H), 7.43 – 7.38 (m, 2H), 7.39 – 7.32 (m, 2H), 7.29 – 7.24 (m, 1H), 5.55 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.7, 135.5, 133.6, 132.9, 131.9, 128.6, 128.6, 128.5, 128.3, 128.3, 126.3, 125.6, 125.0, 123.9, 119.8, 116.0, 67.5. IR (KBr, cm^{-1}): 2831, 1580, 1358, 1182, 1153, 1105, 775, 753, 739. HR-MS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{15}\text{N}_2\text{O}_2$: 303.1055, found: 303.1058.



Ethyl 3-phenylimidazo[1,5-*a*]quinoline-1-carboxylate (5), 48 mg, 76%, yellow solid, m.p. 78-79 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.55 (d, $J = 8.6$ Hz, 1H), 7.89-7.84 (m, 2H), 7.75-7.70 (m, 2H), 7.60 (ddd, $J = 8.7, 7.2, 1.6$ Hz, 1H), 7.53-7.46 (m, 3H), 7.40-7.35 (m, 1H), 7.32 (d, $J = 9.4$ Hz, 1H), 4.62 (q, $J = 7.1$ Hz, 2H), 1.54 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.4, 135.1, 133.6, 132.7, 131.9, 129.4, 128.7, 128.5, 128.4, 127.9, 127.6, 126.3, 125.7, 125.1, 119.5, 116.5, 62.3, 14.4. IR (KBr, cm^{-1}): 2831, 1597, 1363, 775, 698. HR-MS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_2$: 317.1212, found: 317.1214.

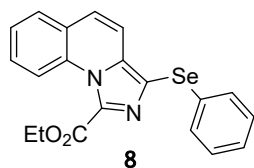


Ethyl 3-(phenylethynyl)imidazo[1,5-*a*]quinoline-1-carboxylate (6), 53 mg, 78%, yellow solid, m.p. 93-94 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.70 (d, $J = 6.6$ Hz, 1H), 7.76 (dd, $J = 7.7, 1.5$ Hz, 1H), 7.69-7.57 (m, 4H), 7.58-7.47 (m, 1H), 7.45-7.32 (m, 4H), 4.59 (q, $J = 7.1$ Hz, 2H), 1.54 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.6, 135.5, 132.8, 131.8, 131.5, 128.8, 128.7, 128.3, 126.7, 126.2, 125.8, 122.9, 119.6, 118.2, 115.8, 93.0, 81.3, 62.5, 14.3. IR (KBr, cm^{-1}): 2831, 2193, 1597, 1499, 1363, 1186, 1068, 775. HR-MS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{22}\text{H}_{17}\text{N}_2\text{O}_2$: 341.1212, found: 341.1214.



Ethyl (*E*)-3-(3-ethoxy-3-oxoprop-1-en-1-yl)imidazo[1,5-*a*]quinoline-1-carboxylate (7), 57 mg, 85%, yellow solid, m.p. 158-159 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.47 (d, $J = 8.7$ Hz, 1H), 7.91 (d, $J = 15.6$ Hz, 1H), 7.75 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.64-7.58 (m, 2H), 7.52 (td, $J = 7.6, 1.0$ Hz, 1H), 7.41 (d, $J = 9.3$ Hz, 1H), 6.87 (d, $J = 15.6$ Hz, 1H), 4.60 (q, $J = 7.1$ Hz, 2H), 4.28 (q, $J = 7.1$ Hz, 2H), 1.53 (t, $J = 7.1$ Hz, 3H), 1.34 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 167.4, 161.1, 134.0, 132.8, 131.7, 129.9, 128.9, 128.9, 126.7, 126.6, 125.5, 119.2, 117.8, 114.7, 62.7, 60.4, 14.3.

IR (KBr, cm^{-1}): 2831, 1717, 1693, 1607, 1366, 1294, 1270, 1163, 775. HR-MS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}_4$: 339.1267, found: 339.1268.



Ethyl 3-(phenylselanyl)imidazo[1,5-*a*]quinoline-1-carboxylate (8), 55 mg, 70%, yellow oil, ^1H NMR (400 MHz, CDCl_3) δ 8.62 (d, $J = 8.7$ Hz, 1H), 7.72 (dd, $J = 7.8$, 1.6 Hz, 1H), 7.60 (ddd, $J = 8.7$, 7.2, 1.6 Hz, 1H), 7.55-7.46 (m, 2H), 7.35-7.29 (m, 3H), 7.19-7.11 (m, 3H), 4.59 (q, $J = 7.1$ Hz, 2H), 1.52 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.9, 136.9, 134.1, 132.0, 131.8, 130.1, 129.1, 128.8, 128.6, 126.6, 126.5, 126.3, 125.6, 120.8, 119.4, 116.4, 62.5, 14.3. IR (KBr, cm^{-1}): 2831, 1713, 1600, 1365, 1181, 1159, 1071, 803, 775, 738, 687. HR-MS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{17}\text{N}_2\text{O}_2\text{Se}$: 397.0377, found: 397.0379.

5. References

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6. Copy of ^1H and ^{13}C NMR Spectra of Products

