Supporting Information

Aerobic C(sp³)-H Oxidation and Oxygenation of Quaternized Quinolines and Pyridines by Visible-Light-Induced

Photocatalysis

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1. General information

The reactions via general procedure were carried out under an atmosphere of oxygen unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh) or thin layer chromatography was performed using silica gel (GF254). ¹H NMR and ¹³C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument using CD₃OD, D₂O, acetone- d_6 or dimethyl sulfoxide- d_6 as solvent. High-resolution mass spectra (ESI) were obtained with the Thermo Scientific LTQ Orbitrap XL mass spectrometer. Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected. Quaternized N-heterocycles were prepared from the corresponding N-heterocycles and alkylhalides (I or Br) that were obtained from commercial suppliers without further purification. Other reagents inculding photocatalysts and solvents were obtained from commercial suppliers without further purification. Cyclic voltammograms were recorded with a CHI830B potentiostat at room temperature in CH₃CN. *n*-Bu₄NBF₄ (0.1 M) was used as the supporting electrolyte, and a glass carbon electrode was used as the working electrode. The auxiliary electrode was a platinum wire electrode. All potentials are referenced against the Ag/AgCl redox couple. The scan rate was 100 mV·s⁻¹.

2. Optimization of reaction conditions

		or N I- CH	PC (2 mol%) base (1 equiv) O ₂ (balloon) H ₃ CN/H ₂ O, 25 °C, 60 h 12 W blue LED	CO_2^{-} CO_2^{-} or N_1^{+}	
	1a	1ab		2a 2ab	
Entry	1	Catalyst	Addtive	Solvent	Product,
					Yield[%] ^b
1	1 a	[Ru]	K ₂ HPO ₄	CH ₃ OH	2a , 11
2	1 a	[Ru]	K ₂ HPO ₄	CH_2Cl_2	2a, trace
3	1 a	[Ru]	K ₂ HPO ₄	THF	2a, trace
4	1 a	[Ru]	K ₂ HPO ₄	CH ₃ CN	2a , 37
5	1a	[Ru]	K ₂ HPO ₄	CH ₃ CN:H ₂ O (1:1)	2a , 77
6	1a	[Ru]	K ₂ HPO ₄	CH ₃ CN:H ₂ O (1.5:0.5)	2a , 62
7	1a	[Ru]	K ₂ HPO ₄	CH ₃ CN:H ₂ O (1.0:0.5)	2a , 57
8	1a	[Ru]	K ₂ HPO ₄	H ₂ O	2a , 14
9	1a	[Ir]	K ₂ HPO ₄	CH ₃ CN:H ₂ O (1:1)	2a , 33
10	1a	Rose Bengal	K ₂ HPO ₄	CH ₃ CN:H ₂ O (1:1)	2a , 52
11	1a	$Ru(bpy)_3(BF_6)_2$	K ₂ HPO ₄	CH ₃ CN:H ₂ O (1:1)	2a , 47
12	1 a	Eosin Y	K ₂ HPO ₄	CH ₃ CN:H ₂ O (1:1)	2a , 46
13	1a	[Ru]	KH ₂ PO ₄	CH ₃ CN:H ₂ O (1:1)	2a , 17
14	1a	[Ru]	Cs ₂ CO3	CH ₃ CN:H ₂ O (1:1)	2a , 21
15	1a	[Ru]	NaO ^t Bu	CH ₃ CN:H ₂ O (1:1)	2a , 15
16	1a	[Ru]	K ₃ PO ₄	CH ₃ CN:H ₂ O (1:1)	2a , 25
17	1a	[Ru]	DBU	CH ₃ CN:H ₂ O (1:1)	2a , 12
18	1a	[Ru]	КОН	CH ₃ CN:H ₂ O (1:1)	2a , 10
19	1a	[Ru]	0.5 eq K ₂ HPO ₄	CH ₃ CN:H ₂ O (1:1)	2a , 49
20	1a	[Ru]	2.0 eq K ₂ HPO ₄	CH ₃ CN:H ₂ O (1:1)	2a , 63
21	1a	[Ru]	3.0 eq K ₂ HPO ₄	CH ₃ CN:H ₂ O (1:1)	2a , 60

Table S1 Optimization of Reaction conditions^a

22	1a	none	K ₂ HPO ₄	CH ₃ CN:H ₂ O (1:1)	2a , ND
23	1a	[Ru]	none	CH ₃ CN:H ₂ O (1:1)	2a , ND
24 ^{<i>c</i>}	1a	[Ru]	K ₂ HPO ₄	CH ₃ CN:H ₂ O (1:1)	2a , 76
25^d	1a	[Ru]	K ₂ HPO ₄	CH ₃ CN:H ₂ O (1:1)	2a , ND
26 ^e	1a	[Ru]	K ₂ HPO ₄	CH ₃ CN:H ₂ O (1:1)	2a , 23
27 ^f	1a	[Ru]	K ₂ HPO ₄	CH ₃ CN:H ₂ O (1:1)	2a, trace
28^g	1a	[Ru]	K ₂ HPO ₄	CH ₃ CN:H ₂ O (1:1)	2a , 87
29 ^{<i>g</i>}	1ab	[Ru]	K ₂ HPO ₄	CH ₃ CN:H ₂ O (1:1)	2ab, ND
30 ^{<i>g</i>}	1ab	[Ru]	Cs ₂ CO ₃	CH ₃ CN:H ₂ O (1:1)	2ab , 54
31 ^{<i>g</i>}	1ab	[Ru]	NaO ^t Bu	CH ₃ CN:H ₂ O (1:1)	2ab , 79
32 ^{<i>g</i>}	1ab	[Ru]	KO ^t Bu	CH ₃ CN:H ₂ O (1:1)	2ab , 70
33 ^g	1ab	[Ru]	K ₃ PO ₄	CH ₃ CN:H ₂ O (1:1)	2ab , 45

^{*a*} reaction conditions: **1a** (0.2 mmol), base (1 equiv), catalyst (2 mol%), O₂ balloon, solvent (2 mL), 12 W blue LED, 25 °C, 60 h. [Ru] = Ru(bpy)₃Cl₂·6H₂O [Ir] = [Ir(dF(CF₃)ppy)₂(dtbbpy)](PF₆) ^{*b*} Isolated yields were given and product in trace amount was determined by TLC. ND refers to not detected. ^{*c*} O₂ (sealed tube). ^{*d*} No light. ^{*e*} 40 W CFL instead of LED. ^{*f*} Under N₂ atmosphere. ^{*g*} Using 2*12 W blue LEDs.

3. General procedures for the photoredox oxygenation

General procedure A: Quinolinium salt or pyridinium salt (**1** or **3**) (0.2 mmol), K_2HPO_4 (1.0 equiv.), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (2 mol%), H_2O (1.0 mL), and acetonitrile (1.0 mL) were added into a 15 mL tube successively. The tube was attached to an oxygen balloon. The reaction mixture was stirred at 25 °C under the irradiation by two 12 W blue LED for 60 h. After completion, purification by flash column chromatography (CH₃OH) gave the pure product **2**. Or otherwise the resulting mixture was concentrated under reduced pressure and washed by CH₃OH to yield the crude product, which was purified by recrystallization from acetone/ethyl acetate to afford the product **4**.

General procedure B: Pyridinium salt **1** (0.2 mmol), NaO^{*t*}Bu (1.0 equiv.), Ru(bpy)₃Cl₂·6H₂O (2 mol%), H₂O (1.0 mL), and acetonitrile (1.0 mL) were added into a 15 mL tube successively. The reaction mixture was stirred at 25 °C under the irradiation by two 12 W blue LED with an oxygen balloon for 60 h. After completion, purification by flash column chromatography (CH₃OH) gave the pure product.

4. Mechanistic investigations

4.1. The correspondence between time and yield at different reaction temperature

1a (0.2 mmol), K_2HPO_4 (1.0 equiv.) and $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (2 mol%), and H_2O (1.0 mL), acetonitrile (1.0 mL) were added into a 15 mL tube successively. The reaction mixture was stirred at 25 °C, 35 °C and 45 °C under the irradiation by two 12 W blue LED with an oxygen balloon for different time. After completion, yield of **2a** were determined from the crude ¹H NMR spectra using CH_2Br_2 as an internal standard. The studies on the correspondence between time and yield at different reaction temperature revealed that elevated reaction temperature (35 °C and 45 °C) indeed accelerated the initial reaction rate of the desired aerobic oxidation. However, milder conditions (25 °C) afforded the best final yield within prolonged reaction time to 60 h.



Then, the yield of **4a** at 25 °C within different reaction time was determined according to the same way.

time (h)	0	4	8	12	24	48	60
yield at 25 °C (%)	0	4	41	67	78	88	88



4.2. Control experiments

(a) The following reaction was carried out under **General procedure A**: **1a** (0.2 mmol), K₂HPO₄ (1.0 equiv.) and Ru(bpy)₃Cl₂·6H₂O (2 mol%), and H₂¹⁸O (1.0 mL), and acetonitrile (1.0 mL) were added into a 15 mL tube successively. The reaction mixture was stirred at 25 °C under the irradiation by two 12 W blue LED for 60 h under O₂ balloon. After completion, purification by flash column chromatography (CH₃OH) gave the pure product. High resolution positive ion electrospray mass spectra (HRMS-ESI) for the final products were shown.



(b) The following reaction was carried out under **General procedure A**: **1a** (0.2 mmol), K₂HPO₄ (1.0 equiv.) and Ru(bpy)₃Cl₂·6H₂O (2 mol%), H₂O (1.0 mL), and acetonitrile (1.0 mL) were added into a 15 mL tube successively. The reaction mixture was stirred at 25 °C under the irradiation by two 12 W blue LED for 60 h under ¹⁸O₂ balloon. After completion, purification by flash column chromatography (CH₃OH) gave the pure product. High resolution positive ion electrospray mass spectra (HRMS-ESI) for the final products were shown.



(c) The following reaction was carried out under **General procedure A**: **3a** (0.2 mmol), K₂HPO₄ (1.0 equiv.) and Ru(bpy)₃Cl₂·6H₂O (2 mol%), and H₂¹⁸O (1.0 mL), acetonitrile (1.0 mL) were added into a 15 mL tube successively. The reaction mixture was stirred at 25 °C under the irradiation by two 12 W blue LED with an oxygen balloon for 60 h. After completion, purification by flash column chromatography (CH₃OH) gave the pure product. High resolution positive ion electrospray mass spectra (HRMS-ESI) for the final products were shown.



(d) The following reaction was carried out under **General procedure A**, **1a** (0.2 mmol), K₂HPO₄ (1.0 equiv.) and Ru(bpy)₃Cl₂·6H₂O (2 mol%), and CH₃CN/H₂O (200:1) or (20:1) or (1:1) were added into a 15 mL tube successively. The reaction mixture was stirred at 25 °C under the irradiation by two 12 W blue LED with an oxygen balloon for 60 h. After completion, purification by flash column chromatography (CH₃OH) gave the pure product. The 4-quinolone **5a** was competitively formed when the amount of water was dramatically reduced, which indicated that a dioxetane intermediate was probably involved in the formation of carboxylate products.



(e) The following reaction was carried out under **General procedure A**: **1a** (0.2 mmol), K_2HPO_4 (1.0 equiv.) and $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (2 mol%), and H_2O (1.0 mL), acetonitrile (1.0 mL), and radical inhibitor TEMPO or DPE or BHT (2.0 equiv.) were added into a 15 mL tube successively. The reaction mixture was stirred at 25 °C under the irradiation by two 12 W blue LED with an

oxygen balloon for 60 h. After completion, yield of 2a were determined from the crude ¹H NMR spectra using CH₂Br₂ as an internal standard. The addition of TEMPO and BHT afforded the product in moderate yield, DPE completely quenched the formation of 2a and instead benzophenone was generated.



(f) The following reaction was carried out under **General procedure A**: **1a** (0.2 mmol), K₂HPO₄ (1.0 equiv.) and Ru(bpy)₃Cl₂·6H₂O (2 mol%), and CH₃CN:H₂O or CD₃CN:D₂O (1:1) (2 mL) were added into a 15 mL tube successively. The reaction mixture was stirred at 25 °C under the irradiation by two 12 W blue LED with an oxygen balloon for 60 h. After completion, yield of **2a** were determined from the crude ¹H NMR spectra using CH₂Br₂ as an internal standard, and the result indicates higher yield was obtained when deuterated solvent was used and the formation of photoexcited singlet oxygen in this reaction system because of longer lifetime of singlet oxygen in deuterated solvents.



(g) The following reaction was carried out under **General procedure A**: **1a** (0.2 mmol), **3a** (0.2 mmol), $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (2 mol%), H_2O (1.0 mL), and acetonitrile (1.0 mL) were added into a 15 mL tube successively. The reaction mixture was stirred at 25 °C under the irradiation by two 12 W blue LED with an oxygen balloon for 24 h. After completion, crude 1H NMR analysis of the reaction mixture revealed the yield of **2a** and **4a** to be 24% and 3%, respectively.



(h) The following reaction was carried out under **General procedure B**: **6a** or **6b** (0.2 mmol), NaO^tBu (1.0 equiv.) and Ru(bpy)₃Cl₂·6H₂O (2 mol%), and H₂O (1.0 mL), acetonitrile (1.0 mL) were added into a 15 mL tube successively. The reaction mixture was stirred at 25 °C under the irradiation by two 12 W blue LED with an oxygen balloon for 60 h. After completion, yield of **2ae** were determined from the crude ¹H NMR spectra using CH₂Br₂ as an internal standard. The direct subjection of hydroxy methylpyridinium (**6a**) afforded carboxylate **2ae** in a moderate yield (42%). Moreover, only trace amounts of the target product were detected when dihydroxy methylpyridinium (**6b**) was used.



(i) The following reaction was carried out under **General procedure A**: **1q** (0.2 mmol), K₂HPO₄ (1.0 equiv.) and Ru(bpy)₃Cl₂·6H₂O (2 mol%), and CH₃CN : H₂O (200:1) (2 mL) were added into a 15 mL tube successively. The reaction mixture was stirred at 25 °C under the irradiation by two 12 W blue LED with an oxygen balloon for 60 h. After completion, purification by flash column chromatography (CH₃OH) gave the **7a**, (White solid, 45%).



4.3. Stern-Volmer fluorescence quenching experiments

Formulation solution: 1,4-dimethylquinolin-1-ium iodide (715 mg) was dissolved in $CH_3CN/H_2O = (1/1)$ in a 25 mL volumetric flask to set the concentration to be 0.1 M.

Photocatalyst Ru(bpy)₃Cl₂·6H₂O (1.9 mg) was dissolved in CH₃CN/H₂O = (1/1) (25.0 mL) to set the concentration to be 0.1 mM.

Experimental procedure: The resulting 0.1 mM solution (25 μ L) was added to cuvette to obtain different concentrations of catalyst solution. This solution was then diluted to a volume of 2.0 mL by adding CH₃CN/H₂O = (1/1) to prepare a 1.25 μ M solution. 10.0 μ L of a 1,4-dimethylquinolin-1-ium iodide solution was successively added and uniformly stirred, and the resulting mixture was bubbled with nitrogen for 3 minutes and irradiated at 493 nm. Fluorescence emission spectra of 0 μ L, 10.0 μ L, 20.0 μ L, 30.0 μ L, 40.0 μ L, 50.0 μ L, 60.0 μ L fluorescence intensity. Follow this method and make changes to the amount to obtain the Stern–Volmer relationship in turn.

Subsequently, we performed another Stern–Volmer fluorescence quenching experiment to investigate the influence of oxygen. In a typical experiment, 2.0 mL of solution of $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (1.25 µM) in $CH_3CN/H_2O = (1/1)$ was bubbled a stream of oxygen for several seconds. The solution was excited at $\lambda = 493$ nm.

(a) Stern-Volmer quenching of 1a to [Ru] photocatalyst.



(b) Stern-Volmer quenching of O₂ to [Ru] photocatalyst.



4.4. Cyclic Voltammetry experiments

Cyclic voltammetry experiments were performed using a CHI830B potentiostat, a glassy carbon working electrode, a platinum mesh counter electrode, and a Ag/AgCl (0.01M) reference electrode. Samples were prepared with a substrate concentration of 0.1 M in a 0.1 M tetraethylammonium hexafluorophosphate in acetonitrile electrolyte solution. From the result, E $_{1/2ox}$ (**6a**) = -0.092 V vs SCE in CH₃CN, E $_{1/2ox}$ (**6b**) = -0.390 V vs SCE in CH₃CN, E $_{1/2ox}$ (**4a**) = -0.251 V vs SCE in CH₃CN.



Figure S5. Cyclic voltammetry experiments. Experiment conditions: Init E = 2.0 V, High E = 2.0 V, Low E = -2.0 V, Init P/N = N, Scan Rate = 0.1 V/s, Sample Interval = 0.001 V, Quiet Time = 2 s, Sensitivity = 2e-4 A/V.

5. Characterization data of products



1-methylquinolin-1-ium-4-carboxylate (2a)

According to General procedure A, 2a was obtained as white solid in 87% yield (32.5 mg), using CH₃OH ($R_f = 0.2$) as eluent. mp: 161 – 164 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 9.25 (d, J = 6.0 Hz, 1H), 8.60 (d, J = 8.5 Hz, 1H), 8.44 (d, J = 9.0 Hz, 1H), 8.23 (ddd, J = 8.8, 7.0, 1.4 Hz, 1H), 8.00 (t, J = 7.7 Hz, 1H), 7.88 (d, J = 5.9 Hz, 1H), 4.64 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 170.8, 159.3, 151.1, 140.9, 136.7, 131.0, 130.3, 127.3, 119.7, 119.1, 46.0. HRMS (ESI) m/z calcd for C₁₁H₁₀NO₂⁺ (M+H)⁺ 188.0706, found 188.0707.



1,6-dimethylquinolin-1-ium-4-carboxylate (2b)

According to General procedure A, 2b was obtained as white solid in 71% yield (28.6 mg) using CH₃OH ($R_f = 0.2$) as eluent. mp: 175 – 177 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.16 (d, *J* = 6.0 Hz, 1H), 8.32 (s, 1H), 8.27 (d, *J* = 9.0 Hz, 1H), 8.01 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.69 (d, *J* = 5.9 Hz, 1H), 4.49 (s, 3H), 2.57 (s, 3H); ¹³C NMR (100 MHz, Deuterium Oxide) δ 171.6, 154.9, 148.3, 141.7, 137.6, 126.5, 125.3, 118.0, 117.3, 45.2, 20.7. HRMS (ESI) m/z calcd for $C_{12}H_{12}NO_2^+$ (M+H)⁺ 202.0863, found 202.0862.



6-ethyl-1-methylquinolin-1-ium-4-carboxylate (2c)

According to General procedure A, 2c was obtained as white solid in 76% yield (32.7 mg) using CH₃OH ($R_f = 0.2$) as eluent. mp: 187 – 188 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 9.17 (d, J = 5.9 Hz, 1H), 8.38 (s, 1H), 8.36 (d, J = 7.2 Hz, 1H), 8.12 (d, J = 9.2 Hz, 1H), 7.83 (d, J = 5.9 Hz, 1H), 4.62 (s, 3H), 2.96 (q, J = 7.6 Hz, 2H), 1.37 (t, J = 7.6 Hz, 3H); 13C NMR (100 MHz, Methanol- d_4) δ 148.7, 136.4, 126.3, 118.2, 117.6, 48.3, 48.0, 47.8, 47.6, 47.41, 47.2, 47.0, 44.5, 28.3, 13.9. HRMS (ESI) m/z calcd for C₁₃H₁₄NO₂⁺ (M+H)⁺ 216.1019, found 216.1019.



6-methoxy-1-methylquinolin-1-ium-4-carboxylate (2d)

According to General procedure A, 2d was obtained as white solid in 81% yield (35.2 mg) using CH₃OH ($R_f = 0.2$) as eluent. mp: 213 – 215 °C.

¹H NMR (400 MHz, Methanol-*d*₄) δ 9.05 (d, *J* = 5.9 Hz, 1H), 8.35 (d, *J* = 9.7 Hz, 1H), 7.93 (d, *J* = 2.6 Hz, 1H), 7.85 (d, *J* = 5.9 Hz, 1H), 7.81 (dd, *J* = 9.6, 2.7 Hz, 1H), 4.61 (s, 3H), 4.01 (s, 3H); ¹³C NMR (100 MHz, Methanol-*d*₄) δ 169.5, 159.9, 155.5, 146.5, 135.3, 128.0, 127.7, 119.9, 118.5, 106.0, 55.4, 44.7. HRMS (ESI) m/z calcd for $C_{12}H_{12}NO_3^+$ (M+H)⁺ 218.0812, found 218.0811.



6-ethoxy-1-methylquinolin-1-ium-4-carboxylate (2e)

According to General procedure A, 2e was obtained as white solid in 89% yield (41.1 mg) using CH₃OH ($R_f = 0.2$) as eluent. mp: 161 – 162 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.06 (d, *J* = 5.9 Hz, 1H), 8.29 (d, *J* = 9.6 Hz, 1H), 8.04 (d, *J* = 2.9 Hz, 1H), 7.78 (dd, *J* = 9.6, 2.8 Hz, 1H), 7.73 (d, *J* = 5.9 Hz, 1H), 4.48 (s, 3H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 6.9 Hz, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 166.4, 158.4, 158.2, 147.4, 135.1, 128.1, 127.0, 120.9, 118.7, 108.2, 64.6, 45.3, 14.8. HRMS (ESI) m/z calcd for C₁₃H₁₄NO₃⁺ (M+H)⁺ 232.0968, found 232.0966.



6-fluoro-1-methylquinolin-1-ium-4-carboxylate (2f)

According to **General procedure A**, **2f** was obtained as white solid in 79% yield (32.4 mg) using $CH_3OH (R_f = 0.2)$ as eluent. mp: 217 – 218 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 9.28 (d, J = 5.9 Hz, 1H), 8.56 (dd, J = 9.7, 4.6 Hz, 1H), 8.36 (dd, J = 9.3, 2.9 Hz, 1H), 8.14 – 8.00 (m, 1H), 7.97 (d, J = 5.9 Hz, 1H), 4.68 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 169.9, 163.0 (d, J = 251.3 Hz), 158.0 (d, J = 5.5 Hz), 150.9, 138.1, 129.2 (d, J = 10.9 Hz), 126.2 (d, J = 26.6 Hz), 123.8 (d, J = 9.6 Hz), 120.3, 113.8 (d, J = 24.3 Hz), 46.5. HRMS (ESI) m/z calcd for C₁₁H₉FNO₂⁺ (M+H)⁺ 206.0612, found 206.0612.



6-chloro-1-methylquinolin-1-ium-4-carboxylate (2g, CCDC NO. 1973939)

According to General procedure A, 2g was obtained as white solid in 61% yield (27.0 mg) using CH₃OH ($R_f = 0.2$) as eluent. mp: 230 – 231 °C.

¹H NMR (400 MHz, Deuterium Oxide) δ 9.17 (d, J = 5.7 Hz, 1H), 8.34 (s, 1H), 8.32 (d, J = 8.8 Hz, 1H), 8.10 (d, J = 9.4 Hz, 1H), 7.89 (d, J = 5.8 Hz, 1H), 4.59 (s, 3H); ¹³C NMR (100 MHz, Deuterium Oxide) δ 170.6, 154.7, 150.0, 138.0, 136.2, 136.0, 126.7, 126.2, 120.4, 118.9, 45.6. HRMS (ESI) m/z calcd for C₁₁H₉ClNO₂⁺ (M+H)⁺ 222.0316, found 222.0315.



6-bromo-1-methylquinolin-1-ium-4-carboxylate (2h)

According to **General procedure A**, **2h** was obtained as white solid in 62% yield (33.4 mg) using $CH_3OH (R_f = 0.2)$ as eluent. mp: 215 – 217 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 9.30 (d, J = 5.9 Hz, 1H), 8.82 (d, J = 2.1 Hz, 1H), 8.39 (d, J = 9.4 Hz, 1H), 8.30 (dd, J = 9.4, 2.2 Hz, 1H), 7.95 (d, J = 5.9 Hz, 1H), 4.65 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 169.8, 157.7, 151.7, 139.7, 139.4, 132.2, 128.5, 125.1, 121.9, 120.8, 46.3. HRMS (ESI) m/z calcd for C₁₁H₉BrNO₂⁺ (M+H)⁺ 265.9811, found 265.9813.



1-methyl-6-(trifluoromethyl)quinolin-1-ium-4-carboxylate (2i)

According to **General procedure A**, **2i** was obtained as white solid in 73% yield (37.2 mg) using $CH_3OH (R_f = 0.2)$ as eluent. mp: 161 - 164 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 9.45 (d, J = 5.9 Hz, 1H), 9.08 (s, 1H), 8.69 (d, J = 9.3 Hz, 1H), 8.45 (d, J = 9.2 Hz, 1H), 8.10 (d, J = 5.9 Hz, 1H), 4.71 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 169.6, 159.6, 153.5, 142.2, 132.2 (q, J = 33.5 Hz), 131.7 (q, J = 3.1 Hz), 128.2 (q, J = 4.7 Hz), 127.1, 124.6 (q, J = 270.5 Hz) 122.0, 121.3, 46.4. HRMS (ESI) m/z calcd for $C_{12}H_9F_3NO_2^+$ (M+H)⁺ 256.0580, found 256.0582.



1-methyl-6-(trifluoromethoxy)quinolin-1-ium-4-carboxylate (2j)

According to **General procedure A**, **2j** was obtained as white solid in 46% yield (25.0 mg) using $CH_3OH (R_f = 0.2)$ as eluent. mp: 225 – 226 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 9.35 (d, J = 5.8 Hz, 1H), 8.64 (s, 1H), 8.62 (d, J = 9.6 Hz, 1H), 8.15 (d, J = 9.3 Hz, 1H), 8.05 (d, J = 5.8 Hz, 1H), 4.69 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 169.7, 158.3, 151.9, 150.1 (q, J = 1.8 Hz), 139.3, 129.7, 128.6, 123.1, 121.8 (q, J = 256.8 Hz), 121.2, 119.8, 46.5. HRMS (ESI) m/z calcd for C₁₂H₉F₃NO₃⁺ (M+H)⁺ 272.0529, found 272.0531.



1-methyl-6-phenoxyquinolin-1-ium-4-carboxylate (2k)

According to General procedure A, 2k was obtained as white solid in 41% yield (22.9 mg) using CH₃OH ($R_f = 0.2$) as eluent. mp: 141 – 143 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 9.13 (d, J = 5.8 Hz, 1H), 8.47 (d, J = 9.3 Hz, 1H), 7.96 (d, J = 8.8 Hz, 1H), 7.94 (s, 1H), 7.84 (d, J = 5.8 Hz, 1H), 7.48 (t, J = 7.3 Hz, 2H), 7.29 (t, J = 7.4 Hz, 1H), 7.19 (d, J = 7.9 Hz, 2H), 4.63 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 170.5, 160.0, 157.5, 156.1, 149.2, 137.2, 131.6, 129.1, 129.1, 126.7, 122.1, 121.5, 119.9, 113.2, 46.2. HRMS (ESI) m/z calcd for C₁₇H₁₄NO₃⁺ (M+H)⁺ 280.0968, found 280.0971.



6-(tert-butyl)-1-methylquinolin-1-ium-4-carboxylate (2l)

According to **General procedure A**, **2I** was obtained as white solid in 91% yield (44.1 mg) using $CH_3OH (R_f = 0.2)$ as eluent. mp: 253 – 256 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 9.18 (d, J = 5.9 Hz, 1H), 8.57 (s, 1H), 8.39 – 8.38 (m, 2H), 7.86 (d, J = 5.9 Hz, 1H), 4.63 (s, 3H), 1.47 (s, 9H); ¹³C NMR (100 MHz, Methanol- d_4) δ 171.1, 159.0, 154.6, 150.1, 139.4, 135.8, 127.3, 125.3, 119.4, 119.1, 45.8, 36.4, 31.1. HRMS (ESI) m/z calcd for C₁₅H₁₈NO₂⁺ (M+H)⁺ 244.1332, found 244.1333.



8-methoxy-1-methylquinolin-1-ium-4-carboxylate (2m)

According to General procedure A, 2m was obtained as white solid in 53% yield (23.0 mg) using CH₃OH ($R_f = 0.2$) as eluent. mp: 243 – 245 °C.

¹1H NMR (400 MHz, Methanol- d_4) δ 9.06 (d, J = 5.9 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H), 7.86 (t, J = 8.2 Hz, 1H), 7.77 (d, J = 5.9 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 4.83 (s, 3H), 4.13 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 171.2, 159.2, 153.1, 152.7, 133.1, 131.4, 129.5, 121.6, 118.9, 117.0, 57.6, 53.0. HRMS (ESI) m/z calcd for C₁₂H₁₂NO₃⁺ (M+H)⁺ 218.0812, found 218.0811.



6,7-dimethoxy-1-methylquinolin-1-ium-4-carboxylate (2n)

According to **General procedure A**, **2n** was obtained as white solid in 61% yield (30.1 mg) using $CH_3OH (R_f = 0.15)$ as eluent. mp: 260 – 263 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.89 (d, J = 6.1 Hz, 1H), 7.93 (s, 1H), 7.72 (d, J = 6.1 Hz, 1H), 7.54 (s, 1H), 4.54 (s, 3H), 4.18 (s, 3H), 4.04 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 171.4, 158.8, 155.2, 153.2, 146.3, 139.2, 123.8, 117.9, 107.0, 98.9, 57.6, 56.9, 45.8. HRMS (ESI) m/z calcd for C₁₃H₁₄NO₄⁺ (M+H)⁺ 248.0917, found 248.0918.



5,6,7-trimethoxy-1-methylquinolin-1-ium-4-carboxylate (20)

According to **General procedure A**, **20** was obtained as white solid in 67% yield (37.1 mg) using $CH_3OH (R_f = 0.15)$ as eluent. mp: 177 – 179 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.93 (d, *J* = 6.2 Hz, 1H), 7.33 (s, 1H), 7.26 (d, *J* = 6.1 Hz, 1H), 4.38 (s, 3H), 4.12 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 167.4, 159.6, 158.5, 150.0, 147.3, 142.1, 137.6, 116.5, 115.1, 94.8, 62.2, 60.8, 57.1, 44.6. HRMS (ESI) m/z calcd for C₁₅H₁₈NO₅⁺ (M+H)⁺ 292.1180, found 292.1184.



1,6,8-trimethylquinolin-1-ium-4-carboxylate (2p)

According to General procedure A, 2p was obtained as white solid in 67% yield (28.8 mg) using CH₃OH ($R_f = 0.25$) as eluent. mp: 245 – 246 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 9.09 (d, J = 6.1 Hz, 1H), 8.09 (s, 1H), 7.69 (s, 1H), 7.62 (d, J = 6.0 Hz, 1H), 4.56 (s, 3H), 2.96 (s, 3H), 2.68 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 174.1, 159.2, 149.5, 148.7, 142.5, 140.4, 135.3, 123.8, 118.5, 117.0, 46.5, 22.4, 20.9. HRMS (ESI) m/z calcd for C₁₃H₁₄NO₂⁺ (M+H)⁺ 216.1019, found 216.1019.



1-methylquinolin-1-ium-2-carboxylate (2q)

According to General procedure A, 2q was obtained as white solid in 75% yield (29.6 mg) using CH₃OH ($R_f = 0.25$) as eluent. mp: 161 – 163 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 9.07 (d, J = 8.5 Hz, 1H), 8.48 (d, J = 9.0 Hz, 1H), 8.38 – 8.30 (m, 1H), 8.27– 8.23 (m, 1H), 8.00 (t, J = 7.2 Hz, 1H), 7.95 (d, J = 8.5 Hz, 1H), 4.60 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 166.2, 159.3, 148.6, 139.5, 137.0, 131.7, 130.8, 129.9, 121.6, 120.0, 42.1. HRMS (ESI) m/z calcd for C₁₁H₁₀NO₂⁺ (M+H)⁺ 188.0706, found 188.0707.



1,6-dimethylquinolin-1-ium-2-carboxylate (2r)

According to **General procedure A**, **2r** was obtained as white solid in 86% yield (34.6 mg) using $CH_3OH (R_f = 0.25)$ as eluent. mp: 175 – 177 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.95 (d, J = 8.5 Hz, 1H), 8.35 (d, J = 9.6 Hz, 1H), 8.22 – 7.99 (m, 2H), 7.89 (d, J = 8.5 Hz, 1H), 4.57 (s, 3H), 2.65 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 166.3, 158.4, 147.8, 142.0, 138.9, 137.9, 130.3, 130.0, 121.5, 119.7, 42.0, 21.2. HRMS (ESI) m/z calcd for C₁₂H₁₂NO₂⁺ (M+H)⁺ 202.0863, found 202.0863.



6-ethoxy-1-methylquinolin-1-ium-2-carboxylate (2s)

According to General procedure A, 2s was obtained as white solid in 87% yield (40.1 mg) using CH₃OH ($R_f = 0.2$) as eluent. mp: 163 – 164 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.90 (d, J = 8.6 Hz, 1H), 8.36 (d, J = 9.7 Hz, 1H), 7.86 (d, J = 8.6 Hz, 1H), 7.80 (dd, J = 9.7, 2.8 Hz, 1H), 7.66 (d, J = 2.8 Hz, 1H), 4.56 (s, 3H), 4.28 (q, J = 7.0 Hz, 2H), 1.51 (t, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 166.4, 160.5, 156.5, 146.7, 134.8, 131.9, 129.2, 121.9, 121.5, 109.6, 66.0, 42.1, 14.8. HRMS (ESI) m/z calcd for C₁₃H₁₄NO₃⁺ (M+H)⁺ 232.0968, found 232.0969.



6-fluoro-1-methylquinolin-1-ium-2-carboxylate (2t)

According to **General procedure A**, **2t** was obtained as white solid in 71% yield (29.1 mg) using CH₃OH ($R_f = 0.25$) as eluent. mp: 182 – 183 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 9.04 (d, J = 8.6 Hz, 1H), 8.63 – 8.55 (m, 1H), 8.14 – 8.03 (m, 2H), 7.99 (d, J = 8.6 Hz, 1H), 4.62 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 165.9, 163.0 (d, J = 251.5 Hz), 159.0, 147.9 (d, J = 4.9 Hz), 136.6, 131.4 (d, J = 10.3 Hz), 126.2 (d, J = 26.3 Hz), 123.4 (d, J = 9.3Hz), 122.8, 115.0 (d, J = 23.0 Hz), 42.5. HRMS (ESI) m/z calcd for C₁₁H₉FNO₂⁺ (M+H)⁺ 206.0612, found 206.0612.



6-cyclopropyl-1-methylquinolin-1-ium-2-carboxylate (2u)

According to General procedure A, 2u was obtained as white solid in 43% yield (19.5 mg) using CH₃OH ($R_f = 0.3$) as eluent. mp: 113 – 114 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.94 (d, J = 8.5 Hz, 1H), 8.35 (d, J = 9.1 Hz, 1H), 8.08 – 7.92 (m, 2H), 7.88 (d, J = 8.5 Hz, 1H), 4.56 (s, 3H), 2.28 – 2.22 (m, 1H), 1.25 – 1.20 (m, 2H), 0.99 –

0.95 (m, 2H); ¹³C NMR (100 MHz, Methanol- d_4) δ 166.3, 158.1, 148.5, 147.6, 137.9, 135.4, 130.17, 126.6, 121.6, 119.8, 42.0, 16.1, 11.2. HRMS (ESI) m/z calcd for C₁₄H₁₄NO₂⁺ (M+H)⁺ 228.1019, found 228.1023.



8-butoxy-1-methylquinolin-1-ium-2-carboxylate (2v)

According to General procedure A, 2v was obtained as white solid in 41% yield (21.2 mg) using CH₃OH ($R_f = 0.3$) as eluent. mp: 160 – 161 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.97 (d, J = 8.5 Hz, 1H), 7.95 – 7.78 (m, 3H), 7.72 (dd, J = 7.6, 1.6 Hz, 1H), 4.78 (s, 3H), 4.31 (t, J = 6.4 Hz, 2H), 2.00 – 1.93 (m, 2H), 1.64 – 1.55 (m, 2H), 1.04 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 166.6, 160.7, 152.7, 148.6, 132.4, 132.4, 131.5, 131.3, 123.3, 121.6, 118.5, 71.9, 48.3, 32.1, 20.6, 14.1. HRMS (ESI) m/z calcd for C₁₅H₁₈NO₃⁺ (M+H)⁺ 260.1281, found 260.1286.



8-(heptyloxy)-1-methylquinolin-1-ium-2-carboxylate (2w)

According to **General procedure A**, **2w** was obtained as white solid in 39% yield (23.5 mg) using CH₃OH ($R_f = 0.4$) as eluent. mp: 107 – 108 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 9.00 (d, J = 8.5 Hz, 1H), 7.96 – 7.80 (m, 3H), 7.74 (dd, J = 7.6, 1.5 Hz, 1H), 4.80 (s, 3H), 4.32 (t, J = 6.5 Hz, 2H), 2.04 – 1.97 (m, 2H), 1.61 – 1.54(m, 2H), 1.47 – 1.36 (m, 6H), 0.93 (t, J = 6.9 Hz, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 166.7, 160.5, 152.7, 148.7, 132.4, 131.5, 131.3, 123.2, 121.6, 118.5, 72.2, 48.3, 32.9, 30.1, 30.0, 27.3, 23.6, 14.4. HRMS (ESI) m/z calcd for C₁₈H₂₄NO₃⁺ (M+H)⁺ 302.1751, found 302.1757.



1-methyl-8-(prop-2-yn-1-yloxy)quinolin-1-ium-2-carboxylate (2x)

According to **General procedure A**, **2x** was obtained as white solid in 31% yield (14.9 mg) using CH₃OH ($R_f = 0.3$) as eluent. mp: 151 – 153 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.99 (d, J = 8.5 Hz, 1H), 8.02 – 7.77 (m, 4H), 5.14 (s, 2H), 4.78 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 166.3, 161.2, 151.0, 148.6, 132.3, 131.7, 131.2, 124.5, 121.8, 120.2, 78.9, 78.1, 59.1, 48.2. HRMS (ESI) m/z calcd for C₁₄H₁₂NO₃⁺ (M+H)⁺ 242.0812, found 242.0815.



7-chloro-1-methylquinolin-1-ium-2-carboxylate (2y)

According to **General procedure A**, **2y** was obtained as white solid in 63% yield (27.9 mg) using $CH_3OH (R_f = 0.3)$ as eluent. mp: 147 – 149 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 9.08 (d, J = 8.5 Hz, 1H), 8.62 (s, 1H), 8.34 (d, J = 8.8 Hz, 1H), 8.00 (dd, J = 8.8, 1.7 Hz, 1H), 7.95 (d, J = 8.5 Hz, 1H), 4.57 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 165.8, 160.0, 148.4, 143.3, 140.1, 133.2, 131.7, 128.5, 121.9, 120.0, 42.3. HRMS (ESI) m/z calcd for C₁₁H₉CINO₂⁺ (M+H)⁺ 222.0316, found 222.0315.



4-methylbenzo[f]quinolin-4-ium-3-carboxylate (2z)

According to General procedure A, 2z was obtained as white solid in 43% yield (20.3 mg) using CH₃OH ($R_f = 0.2$) as eluent. mp: 162 – 164 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 9.89 (d, J = 8.7 Hz, 1H), 8.94 (d, J = 8.2 Hz, 1H), 8.58 (d, J = 9.6 Hz, 1H), 8.35 (d, J = 9.6 Hz, 1H), 8.21 (d, J = 7.8 Hz, 1H), 8.10 (d, J = 8.7 Hz, 1H), 7.98 (t, J = 7.1 Hz, 1H), 7.92 (t, J = 7.4 Hz, 1H), 4.68 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 166.5, 157.3, 142.4, 140.6, 139.3, 132.7, 131.3, 131.0, 130.6, 129.8, 128.3, 124.8, 122.0, 116.9, 42.9. HRMS (ESI) m/z calcd for C₁₅H₁₂NO₂⁺ (M+H)⁺ 238.0863, found 238.0864.



2-methylisoquinolin-2-ium-1-carboxylate (2aa)

According to General procedure A, 2aa was obtained as white solid in 51% yield (19.1 mg) using CH₃OH ($R_f = 0.25$) as eluent. mp: 171 – 172 °C.

¹H NMR (400 MHz, Methanol-*d*₄) δ 8.42 (d, *J* = 6.9 Hz, 1H), 8.38 (d, *J* = 7.9 Hz, 1H), 8.31 – 8.21 (m, 2H), 8.21 – 8.14 (m, 1H), 8.03 – 8.00 (m, 1H), 4.42 (s, 3H); ¹³C NMR (100 MHz, Methanol-*d*₄) δ 164.6, 160.1, 139.2, 137.7, 135.9, 132.4, 130.9, 128.7, 125.2, 125.0, 46.4. HRMS (ESI) m/z calcd for $C_{11}H_{10}NO_2^+$ (M+H)⁺ 188.0706, found 188.0707.



1-methylpyridin-1-ium-4-carboxylate (2ab)

According to **General procedure B**, **2ab** was obtained as white solid in 79% yield (21.6 mg) using CH₃OH ($R_f = 0.3$) as eluent. mp: 251 – 252 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.90 (d, J = 6.5 Hz, 2H), 8.31 (d, J = 6.4 Hz, 2H), 4.41 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 167.8, 155.2, 147.0, 128.0, 48.5. HRMS (ESI) m/z calcd for C₇H₈NO₂⁺ (M+H)⁺ 138.0550, found 138.0549.



1-methyl-2-phenylpyridin-1-ium-4-carboxylate (2ac)

According to **General procedure B**, **2ac** was obtained as white solid in 52% yield (22.2 mg) using CH₃OH ($R_f = 0.35$) as eluent. mp: 201 – 204 °C.

¹H NMR (400 MHz, DMSO-*d*₆) δ 9.01 (d, *J* = 6.3 Hz, 1H), 8.18 (dd, *J* = 6.2, 1.6 Hz, 1H), 7.98 (d, *J* = 1.5 Hz, 1H), 7.69 – 761 (m, 5H), 4.06 (s, 3H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 163.0, 156.6, 154.7, 146.5, 132.3, 130. 9, 129.1, 128.0, 125.0, 46.4. HRMS (ESI) m/z calcd for C₁₃H₁₂NO₂⁺ (M+H)⁺ 214.0863, found 214.0864.



1,3-dimethylpyridin-1-ium-4-carboxylate (2ad)

According to **General procedure B**, **2ad** was obtained as white solid in 47% yield (14.2 mg) using CH₃OH ($R_f = 0.3$) as eluent. mp: 233 – 234 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.73 (s, 1H), 8.66 (d, J = 6.1 Hz, 1H), 7.83 (d, J = 6.1 Hz, 1H), 4.33 (s, 3H), 2.54 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 171.1, 157.7, 147.2, 144.2, 136.0, 125.2, 48.1, 17.1. HRMS (ESI) m/z calcd for C₈H₁₀NO₂⁺ (M+H)⁺ 152.0706, found 152.0708.



1-methylpyridin-1-ium-2-carboxylate (2ae)

According to General procedure B, 2ae was obtained as white solid in 71% yield (19.5 mg) using CH₃OH ($R_f = 0.3$) as eluent. mp: 171 – 173 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.78 (d, J = 6.2 Hz, 1H), 8.61 – 8.42 (m, 1H), 8.08 (d, J = 7.2 Hz, 1H), 8.00 – 7.87 (m, 1H), 4.43 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 165.2, 155.5, 147.00 146.5, 127.5, 47.4. HRMS (ESI) m/z calcd for C₇H₈NO₂⁺ (M+H)⁺ 138.0550, found 138.0550.



1-benzylquinolin-1-ium-4-carboxylate (2af)

According to General procedure A, 2af was obtained as white solid in 43% yield (22.6 mg) using CH₃OH ($R_f = 0.5$) as eluent. mp: 161 – 164 °C.

¹H NMR (400 MHz, DMSO- d_6) δ 9.58 (d, J = 6.0 Hz, 1H), 8.57 (d, J = 8.4 Hz, 1H), 8.38 (d, J = 9.0 Hz, 1H), 8.08 (t, J = 7.9 Hz, 1H), 7.90 – 7.86 (m, 2H), 7.42 – 7.32 (m, 5H), 7.33 (s, 1H), 6.29 (s, 2H); ¹³C NMR (100 MHz, Methanol- d_4) δ 170.7, 159.9, 151.1, 140.1, 136.8, 134.6, 131.0, 130.5, 130.2, 128.3, 127.8, 120.3, 119.3, 61.9. HRMS (ESI) m/z calcd for C₁₇H₁₄NO₂⁺ (M+H)⁺ 264.1019, found 264.1022.



8-hydroxy-1-methyl-5,6,7,8-tetrahydroquinolin-1-ium iodide (4a)

According to **General procedure A**, **4a** was obtained as white solid in 88% yield (51.2 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 141 – 143 °C.

¹H NMR (400 MHz, Methanol-*d₄*) δ 8.83 (d, *J* = 6.0 Hz, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 7.90 (dd, *J* = 8.0, 6.0 Hz, 1H), 5.18 (t, *J* = 2.7 Hz, 1H), 4.52 (s, 3H), 3.15 – 3.10 (m, 1H), 3.00 – 2.92 (m, 1H), 2.25 – 2.21 (m, 1H), 2.06 – 1.98 (m, 2H), 1.95 – 1.88 (m, 1H); ¹³C NMR (100 MHz, Methanol-*d₄*) δ 153.7, 148.1, 146.7, 141.2, 127.1, 63.2, 46.0, 32.1, 29.6, 16.6. HRMS (ESI) m/z calcd for $C_{10}H_{14}NO^{+}$ (M)⁺ 164.1070, found 164.1066.



7-hydroxy-1-methyl-6,7-dihydro-5H-cyclopenta[b]pyridin-1-ium iodide (4b)

According to **General procedure A**, **4b** was obtained as pale yellow solid in 83% yield (45.9 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 121 - 123 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.71 (d, J = 6.0 Hz, 1H), 8.43 (d, J = 7.8 Hz, 1H), 8.02 – 7.84 (m, 1H), 5.60 (dd, J = 7.7, 4.2 Hz, 1H), 4.44 (s, 3H), 3.41 – 3.32 (m, 1H), 3.14 – 3.06 (m, 1H),

2.74 - 2.64 (m, 1H), 2.23 - 2.15 (m, 1H); ¹³C NMR (100 MHz, DMSO- d_6) δ 158.8, 144.2, 143.8, 142.3, 126.9, 71.7, 44.3, 32.6, 28.0. HRMS (ESI) m/z calcd for C₉H₁₂NO⁺ (M)⁺ 150.0913, found 150.0910.

2-(1-hydroxyethyl)-1-methylpyridin-1-ium iodide (4c)

According to **General procedure A**, **4c** was obtained as pale yellow solid in 86% yield (45.6 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 109 – 111 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.87 (d, J = 6.2 Hz, 1H), 8.58 (t, J = 7.9 Hz, 1H), 8.28 (d, J = 8.1 Hz, 1H), 7.96 (t, J = 6.9 Hz, 1H), 5.37 (q, J = 6.5 Hz, 1H), 4.42 (s, 3H), 1.61 (d, J = 6.5 Hz, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 163.0, 147.2, 127.4, 126.8, 65.7, 46.3, 22.3. HRMS (ESI) m/z calcd for C₈H₁₂NO⁺ (M)⁺ 138.0913, found 138.0918.



2-(1-hydroxypentyl)-1-methylpyridin-1-ium iodide (4d)

According to **General procedure A**, **4d** was obtained as pale yellow solid in 90% yield (55.3 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 87 - 89 °C.

¹H NMR (400 MHz, Methanol-*d*₄) δ 8.85 (d, *J* = 6.2 Hz, 1H), 8.56 (t, *J* = 7.9 Hz, 1H), 8.25 (d, *J* = 8.1 Hz, 1H), 7.95 (t, *J* = 6.9 Hz, 1H), 5.17 (dd, *J* = 8.9, 3.4 Hz, 1H), 4.40 (s, 3H), 1.94 – 1.85 (m, 1H), 1.80 – 1.71 (m, 1H), 1.61 – 1.38 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, Methanol-*d*₄) δ 162.7, 147.8, 147.0, 127.4, 127.3, 69.6, 46.4, 36.7, 28.8, 23.4, 14.3. HRMS (ESI) m/z calcd for C₁₁H₁₈NO⁺ (M)⁺ 180.1383, found 180.1380.



2-(1-hydroxy-3-phenylpropyl)-1-methylpyridin-1-ium iodide (4e)

According to **General procedure A**, **4e** was obtained as pale yellow solid in 73% yield (51.9 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 111 - 113 °C.

¹H NMR (400 MHz, Methanol-*d*₄) δ 8.80 (d, *J* = 6.1 Hz, 1H), 8.53 (t, *J* = 8.2 Hz, 1H), 8.27 (d, *J* = 8.1 Hz, 1H), 7.95 – 7.84 (m, 1H), 7.31 – 7.25 (m, 4H), 7.22 – 7.17 (m, 1H), 5.10 (dd, *J* = 9.3, 2.9 Hz, 1H), 4.18 (s, 3H), 2.99 – 2.85 (m, 2H), 2.19 – 2.11 (m, 1H), 2.08 – 1.99 (m, 1H); ¹³C NMR (100 MHz, Methanol-*d*₄) δ 162.7, 147.8, 147.0, 142.1, 129.7, 129.6, 127.4, 127.3, 127.3, 68.5, 46.1, 38.8, 32.5. HRMS (ESI) m/z calcd for C₁₅H₁₈NO⁺ (M+H)⁺ 228.1383, found 228.1382.



2-(3-(benzyloxy)-1-hydroxypropyl)-1-methylpyridin-1-ium iodide (4f)

According to **General procedure A**, **4f** was obtained as pale yellow solid in 83% yield (64.1 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 97 - 99 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.74 (d, J = 6.1 Hz, 1H), 8.50 (t, J = 7.9 Hz, 1H), 8.27 (d, J = 8.1 Hz, 1H), 7.92 – 7.76 (m, 1H), 7.38 – 7.21 (m, 5H), 5.40 (dd, J = 8.0, 4.0 Hz, 1H), 4.50 – 4.41 (m, 2H), 4.35 (s, 3H), 3.83 – 3.78 (m, 1H), 3.70 – 3.65 (m, 1H), 2.27 – 2.19 (m, 1H), 2.12 – 2.04 (m, 1H); ¹³C NMR (100 MHz, Methanol- d_4) δ 163.0, 147.4, 146.7, 139.4, 129.5, 128.9, 128.8, 127.5, 127.2, 74.1, 67.2, 66.9, 46.3, 37.6. HRMS (ESI) m/z calcd for C₁₆H₂₀NO₂⁺ (M)⁺ 258.1489, found 258.1489.



2-(3-acetoxy-1-hydroxypropyl)-1-methylpyridin-1-ium iodide (4g)

According to **General procedure A**, **4g** was obtained as pale yellow solid in 66% yield (44.5 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 86 - 87 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.87 (d, J = 6.1 Hz, 1H), 8.57 (t, J = 8.0 Hz, 1H), 8.29 (d, J = 7.9 Hz, 1H), 7.96 (t, J = 6.7 Hz, 1H), 5.32 (dd, J = 9.2, 2.9 Hz, 1H), 4.40 (s, 3H), 4.36 – 4.27 (m, 2H), 2.30 – 2.21 (m, 1H), 2.10 – 2.03 (m, 1H), 2.01 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 172.7, 162.1, 148.0, 147.2, 127.6, 127.4, 66.7, 61.6, 46.2, 35.8, 20.8. HRMS (ESI) m/z calcd for C₁₁H₁₆NO₃⁺ (M)⁺ 210.1125, found 210.1120.



2-(2-((tert-butoxycarbonyl)amino)-1-hydroxyethyl)-1-methylpyridin-1-ium iodide (4h)

According to **General procedure A**, **4h** was obtained as pale yellow solid in 74% yield (56.2 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 77 - 79 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.91 (d, J = 6.1 Hz, 1H), 8.56 (t, J = 7.9 Hz, 1H), 8.28 (d, J = 8.0 Hz, 1H), 7.97 (t, J = 6.8 Hz, 1H), 5.38 (t, J = 4.6 Hz, 1H), 4.50 (s, 3H), 3.50 (t, J = 4.6 Hz, 2H), 1.31 (s, 9H); ¹³C NMR (100 MHz, Methanol- d_4) δ 160.6, 158.4, 147.7, 146.5, 128.4, 127.5, 80.5, 69.4, 46.5, 45.9, 28.6. HRMS (ESI) m/z calcd for C₁₃H₂₁N₂O₃⁺ (M)⁺ 253.1547, found 253.1545.



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2-(2-(benzyloxy)-1-hydroxyethyl)-1-methylpyridin-1-ium iodide (4i, CCDC NO. 1973937)

According to **General procedure A**, **4i** was obtained as pale yellow solid in 73% yield (51.2 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 104 - 105 °C.

¹H NMR (400 MHz, Methanol-*d*₄) δ 8.87 (d, *J* = 6.1 Hz, 1H), 8.55 (t, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 8.0 Hz, 1H), 7.97 (t, *J* = 6.9 Hz, 1H), 7.32-7.27 (m, 3H), 7.24 – 7.15 (m, 2H), 5.45 (t, *J* = 12.4 Hz, 1H), 4.54 (q, *J* = 12.0 Hz, 2H), 4.42 (s, 3H), 3.98 (dd, *J* = 9.7, 5.4 Hz, 1H), 3.74 (dd, *J* = 9.7, 6.9 Hz, 1H); ¹³C NMR (100 MHz, Methanol-*d*₄) δ 160.9, 147.6, 146.77, 138.8, 129.5, 129.0, 128.2, 128.2, 127.7, 74.5, 73.7, 68.4, 47.1. HRMS (ESI) m/z calcd for C₁₅H₁₈NO₂⁺ (M)⁺ 244.1332, found 244.1328.



2-(2-((4-fluorobenzyl)oxy)-1-hydroxyethyl)-1-methylpyridin-1-ium iodide (4j)

According to **General procedure A**, **4j** was obtained as pale yellow solid in 69% yield (53.7 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 125 - 127 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.89 (d, J = 6.1 Hz, 1H), 8.57 (t, J = 7.9 Hz, 1H), 8.27 (d, J = 9.2 Hz, 1H), 7.98 (t, J = 7.7 Hz, 1H), 7.32 – 7.19 (m, 2H), 7.11 – 6.97 (m, 2H), 5.51 (t, J = 6.0 Hz 1H), 4.52 (q, J = 11.6 Hz, 2H), 4.45 (s, 3H), 3.98 (dd, J = 9.8, 5.5 Hz, 1H), 3.76 (dd, J = 9.8, 6.7 Hz, 1H); ¹³C NMR (100 MHz, Methanol- d_4) δ 165.0, 161.6 (d, J = 243.2 Hz), 147.7, 146.8, 134.9 (d, J = 3.1 Hz), 131.0 (d, J = 8.3 Hz), 128.2, 127.7, 116.1 (d, J = 21.5 Hz), 73.7, 73.7, 68.4, 47.2. HRMS (ESI) m/z calcd for C₁₅H₁₇FNO₂⁺ (M)⁺ 262.1238, found 262.1235.



2-(2-((4-chlorobenzyl)oxy)-1-hydroxyethyl)-1-methylpyridin-1-ium iodide (4k)

According to **General procedure A**, **4k** was obtained as pale yellow solid in 65% yield (52.5 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 103 - 105 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.89 (d, J = 6.0 Hz, 1H), 8.57 (t, J = 7.5 Hz, 1H), 8.28 (d, J = 8.1 Hz, 1H), 7.98 (t, J = 7.6 Hz, 1H), 7.40 – 7.27 (m, 2H), 7.24 – 7.22 (m, 2H), 5.52 (t, J = 5.8 Hz, 1H), 4.53 (q, J = 12.0 Hz, 2H), 4.45 (s, 3H), 3.99 (dd, J = 9.8, 5.5 Hz, 1H), 3.77 (dd, J = 9.8, 6.7 Hz, 1H); ¹³C NMR (100 MHz, Methanol- d_4) δ 160.7, 147.7, 146.8, 137.7, 134.6, 130.5, 129.6, 128.2, 127.7, 73.9, 73.6, 68.5, 47.2. HRMS (ESI) m/z calcd for C₁₅H₁₇ClNO₂⁺ (M)⁺ 278.0942, found 278.0942.



2-(2-((4-bromobenzyl)oxy)-1-hydroxyethyl)-1-methylpyridin-1-ium iodide (4l)

According to **General procedure A**, **4I** was obtained as pale yellow solid in 64% yield (57.5 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 140 - 141 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.85 (d, J = 6.1 Hz, 1H), 8.26 (s, 1H), 7.97 (t, J = 7.5 Hz, 1H), 7.46 (d, J = 8.3 Hz, 2H), 7.15 (d, J = 8.3 Hz, 2H), 5.48 (t, J = 6.5 Hz, 1H), 4.50 (q, J = 12.1 Hz, 2H), 4.42 (s, 3H), 3.98 (dd, J = 9.7, 5.4 Hz, 1H), 3.74 (dd, J = 9.7, 6.8 Hz, 1H); ¹³C NMR (100 MHz, Methanol- d_4) δ 160.8, 147.7, 146.8, 138.2, 132.6, 130.8, 128.2, 127.7, 122.7, 74.0, 73.7, 68.5, 47.1. HRMS (ESI) m/z calcd for C₁₅H₁₇BrNO₂⁺ (M)⁺ 322.0437, found 322.0434.



2-(2-((4-cyanobenzyl)oxy)-1-hydroxyethyl)-1-methylpyridin-1-ium iodide (4m)

According to **General procedure A**, **4m** was obtained as pale yellow solid in 68% yield (53.9 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 151 - 154 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.89 (d, J = 5.9 Hz, 1H), 8.58 (t, J = 7.6 Hz, 1H), 8.31 (d, J =8.0 Hz, 1H), 7.99 (t, J = 7.5 Hz, 1H), 7.69 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 5.53 (t, J = 3.2 Hz, 2H), 5.53 (t, J = 3.= 5.9 Hz, 1H), 4.68 - 4.59 (m, 2H), 4.46 (s, 3H), 4.01 (dd, J = 9.8, 5.5 Hz, 1H), 3.82 (dd, J = 9.8, 3.8 (dd, J = 9.8, 3.8 6.4 Hz, 1H); ¹³C NMR (100 MHz, Methanol- d_4) δ 160.6, 147.8, 146.9, 144.8, 133.4, 129.3, 128.3, 127.8, 119.6, 112.5, 74.2, 73.5, 68.5, 467.0. HRMS (ESI) m/z calcd for $C_{16}H_{17}N_2O_2^+$ (M)⁺ 269.1285, found 269.1284.



2-(1-hydroxy-2-((4-(trifluoromethyl)benzyl)oxy)ethyl)-1-methylpyridin-1-ium iodide (4n)

According to General procedure A, 4n was obtained as pale yellow solid in 65% yield (57.1 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 167-169 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.89 (d, J = 6.1 Hz, 1H), 8.57 (t, J = 7.9 Hz, 1H), 8.30 (d, J =8.1 Hz, 1H), 7.99 (t, J = 6.9 Hz, 1H), 7.62 (d, J = 8.1 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 5.53 (t, J = 6.0 Hz, 1H), 4.76 - 4.56 (m, 2H), 4.46 (s, 3H), 4.03 (dd, J = 9.8, 5.5 Hz, 1H), 3.82 (dd, J = 9.8, 6.5 Hz, 1H); 13 C NMR (100 MHz, Methanol- d_4) δ 160.8, 147.9, 146.9, 143.6, 131.0, 129.2, 128.4, 127.9, 126.5, (q, J = 3.9 Hz), 125.7 (q, J = 269.9 Hz), 74.3, 73.7, 68.6, 47.2. HRMS (ESI) m/z calcd for $C_{16}H_{17}F_3NO_2^+$ (M)⁺ 312.1206, found 312.1203.



2-(2-((4-(*tert*-butyl)benzyl)oxy)-1-hydroxyethyl)-1-methylpyridin-1-ium iodide (40)

According to General procedure A, 40 was obtained as pale yellow solid in 63% yield (53.8 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 117-119 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.86 (d, J = 6.0 Hz, 1H), 8.53 (t, J = 7.9 Hz, 1H), 8.24 (d, J = 6.0 Hz, 1H), 8.53 (t, J = 7.9 Hz, 1H), 8.24 (d, J = 6.0 Hz, 1H), 8.53 (t, J = 7.9 Hz, 1H), 8.24 (d, J = 6.0 Hz, 1H), 8.53 (t, J = 7.9 Hz, 1H), 8.24 (d, J = 6.0 Hz, 1H), 8.53 (t, J = 7.9 Hz, 1H), 8.54 (t, J = 6.0 Hz, 1H), 8.53 (t, J = 7.9 Hz, 1H), 8.54 (t, J = 6.0 Hz, 1H), 8.53 (t, J = 7.9 Hz, 1H), 8.54 (t, J = 6.0 Hz, 1H), 8.53 (t, J = 7.9 Hz, 1H), 8.54 (t, J = 6.0 Hz, 1H), 8.54 (t, J = 6.0S35

9.0 Hz, 1H), 7.96 (t, J = 6.9 Hz, 1H), 7.33 (d, J = 8.3 Hz, 2H), 7.12 (d, J = 8.3 Hz, 2H), 5.47 (dd, J = 6.8, 5.6 Hz, 1H), 4.54 – 4.43 (m, 2H), 4.40 (s, 3H), 3.96 (dd, J = 9.7, 5.4 Hz, 1H), 3.71 (dd, J = 9.7, 7.0 Hz, 1H), 1.29 (s, 9H); ¹³C NMR (100 MHz, Methanol- d_4) δ 161.0, 152.1, 147.6, 146.7, 135.7, 128.9, 128.2, 127.7, 126.4, 74.3, 73.7, 68.4, 47.0, 35.4, 31.8. HRMS (ESI) m/z calcd for C₁₉H₂₆NO₂⁺ (M)⁺ 300.1958, found 300.1954.



1-methyl-2-(1-((4-vinylbenzyl)oxy)propan-2-yl)pyridin-1-ium iodide (4p)

According to **General procedure A**, **4p** was obtained as pale yellow solid in 61% yield (48.2 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 131 – 133 °C.

¹H NMR (400 MHz, Methanol-*d4*) δ 8.85 (d, J = 6.0 Hz, 1H), 8.54 (t, J = 7.9 Hz, 1H), 8.26 (d, J = 8.1 Hz, 1H), 7.97 (t, J = 6.9 Hz, 1H), 7.37 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.72 (dd, J = 17.6, 10.9 Hz, 1H), 5.77 (d, J = 17.6 Hz, 1H), 5.51 – 5.45 (m, 1H), 5.23 (d, J = 10.9 Hz, 1H), 4.56 – 4.46 (m, 2H), 4.41 (s, 3H), 3.98 (dd, J = 9.7, 5.4 Hz, 1H), 3.73 (dd, J = 9.7, 7.0 Hz, 1H); ¹³C NMR (100 MHz, Methanol-*d4*) δ 159.5, 146.1, 145.3, 137.3, 136.8, 136.2, 127.8, 126.7, 126.2, 125.8, 112.9, 72.7, 72.3, 67.0, 45.4. HRMS (ESI) m/z calcd for C₁₇H₂₀NO₂⁺ (M)⁺ 270.1489, found 270.1485.



2-(1-hydroxy-2-((4-methylbenzyl)oxy)ethyl)-1-methylpyridin-1-ium iodide (4q)

According to **General procedure A**, **4q** was obtained as pale yellow solid in 67% yield (51.7 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 122 - 123 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.86 (d, J = 6.1 Hz, 1H), 8.54 (t, J = 7.8 Hz, 1H), 8.24 (d, J = 8.1 Hz, 1H), 7.97 (t, J = 7.6 Hz, 1H), 7.12 – 1.06 (m, 4H), 5.47 (t, J = 5.6 Hz 1H), 4.471 (q, J = 11.6 Hz 2H), 4.41 (s, 3H), 3.96 (dd, J = 9.8, 5.4 Hz, 1H), 3.72 (dd, J = 9.7, 7.0 Hz, 1H); ¹³C NMR
(100 MHz, Methanol- d_4) δ 161.0, 147.6, 146.7, 138.9, 135.7, 130.1, 129.2, 128.2, 127.7, 74.3, 73.58, 68.4, 47.1, 21.2. HRMS (ESI) m/z calcd for C₁₆H₂₀NO₂⁺ (M)⁺ 258.1489, found 258.1485.



2-(1-hydroxy-2-((3-methylbenzyl)oxy)ethyl)-1-methylpyridin-1-ium iodide (4r)

According to **General procedure A**, **4r** was obtained as pale yellow solid in 73% yield (56.4 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 117 – 119 °C.

¹H NMR (400 MHz, Methanol-*d*₄) δ 8.88 (d, *J* = 6.1 Hz, 1H), 8.55 (t, *J* = 7.8 Hz, 1H), 8.24 (d, *J* = 9.2 Hz, 1H), 7.97 (t, *J* = 7.7 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.01 (s, 1H), 6.69 (d, *J* = 12.0 Hz, 1H), 5.49 (t, *J* = 6.4 Hz, 1H), 4.55 – 4.45 (m, 2H), 4.42 (s, 3H), 3.97 (dd, *J* = 9.8, 5.5 Hz, 1H), 3.73 (dd, *J* = 9.8, 6.9 Hz, 1H) 2.29 (s, 3H); ¹³C NMR (100 MHz, Methanol-*d*₄) δ 160.9, 147. 6, 146.7, 139.2, 138.6, 129.7, 129.4, 128.2, 127.7, 126.1, 74.5, 73.6, 68.4, 47.1, 21.4. HRMS (ESI) m/z calcd for C₁₆H₂₀NO₂⁺ (M)⁺ 258.1489, found 258.1485.



2-(1-hydroxy-2-((2-methylbenzyl)oxy)ethyl)-1-methylpyridin-1-ium iodide (4s)

According to **General procedure A**, **4s** was obtained as pale yellow solid in 74% yield (57.1 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 130 - 132 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.87 (d, J = 6.1 Hz, 1H), 8.55 (t, J = 8.1 Hz, 1H), 8.26 (d, J = 8.1 Hz, 1H), 7.97 (t, J = 7.6 Hz, 1H), 7.26 – 7.15 (m, 2H), 7.13 – 7.10 (m, 2H), 5.57 – 5.44 (m, 1H), 4.61 – 4.52 (m, 2H), 4.40 (s, 3H), 4.00 (dd, J = 9.8, 5.5 Hz, 1H), 3.77 (dd, J = 9.8, 6.8 Hz, 1H), 2.16 (s, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 160.9, 147.6, 146.8, 138.1, 136.5, 131.3,

130.1, 129.3, 128.2, 127.7, 126.8, 73.7, 72.9, 68.5, 47.1, 18.8. HRMS (ESI) m/z calcd for $C_{16}H_{20}NO_2^+(M)^+$ 258.1489, found 258.1485.



2-(2-((3,4-dimethylbenzyl)oxy)-1-hydroxyethyl)-1-methylpyridin-1-ium iodide (4t)

According to **General procedure A**, **4t** was obtained as pale yellow solid in 71% yield (56.8 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 125 - 127 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.84 (d, J = 6.1 Hz, 1H), 8.52 (t, J = 7.9 Hz, 1H), 8.21 (d, J = 7.7 Hz, 1H), 7.95 (t, J = 7.5 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.92 (s, 1H), 6.89 (d, J = 7.6 Hz, 1H), 5.54 – 5.42 (m, 1H), 4.49 – 4.36 (m, 5H), 3.94 (dd, J = 9.8, 5.4 Hz, 1H), 3.69 (dd, J = 9.7, 7.0 Hz, 1H), 2.20 (d, J = 6.0 Hz, 6H); ¹³C NMR (100 MHz, Methanol- d_4) δ 161.0, 147.5, 146.7, 137.7, 137.4, 136.0, 130.6, 130.4, 128.2, 127.7, 126.8, 74.4, 73.5, 68.5, 47.1, 19.8, 19.5. HRMS (ESI) m/z calcd for C₁₇H₂₂NO₂⁺ (M)⁺ 272.1645, found 272.1647.



2-(2-((2,6-dichlorobenzyl)oxy)-1-hydroxyethyl)-1-methylpyridin-1-ium iodide (4u)

According to **General procedure A**, **4u** was obtained as pale yellow solid in 53% yield (46.5 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 123 – 125 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.84 (d, J = 6.1 Hz, 1H), 8.51 (t, J = 7.9 Hz, 1H), 8.22 (d, J = 9.1 Hz, 1H), 8.00 – 7.88 (m, 1H), 7.42 – 7.30 (m, 3H), 7.30 – 7.26 (m, 1H), 5.47 (dd, J = 7.8, 5.3 Hz, 1H), 4.83 – 4.72 (m, 2H), 4.13 (dd, J = 9.3, 5.3 Hz, 1H), 3.73 (dd, J = 9.3, 7.9 Hz, 1H); ¹³C NMR (100 MHz, Methanol- d_4) δ 161.3, 147.5, 146.8, 137.7, 133.6, 131.9, 129.8, 128.0, 127.7, 74.7, 68.6, 68.1, 47.0. HRMS (ESI) m/z calcd for C₁₅H₁₆Cl₂NO₂⁺ (M)⁺ 312.0553, found 312.0552. S38



2-(1-hydroxy-2-((2,4,6-trimethylbenzyl)oxy)ethyl)-1-methylpyridin-1-ium iodide (4v)

According to **General procedure A**, **4v** was obtained as pale yellow solid in 70% yield (57.8 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 191 – 193 °C.

¹H NMR (400 MHz, Acetonitrile-*d*₃) δ 8.57 (d, *J* = 6.1 Hz, 1H), 8.42 (t, *J* = 7.9 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.85 (t, *J* = 6.6 Hz, 1H), 6.80 (s, 2H), 5.42 (t, *J* = 5.9 Hz, 1H), 4.93 (s, 1H), 4.50 (q, *J* = 10.9 Hz, 2H), 4.25 (s, 3H), 3.92 (dd, *J* = 9.7, 5.5 Hz, 1H), 3.71 (dd, *J* = 9.7, 6.6 Hz, 1H), 2.21 (s, 3H), 2.16 (s, 6H); ¹³C NMR (100 MHz, Acetonitrile-*d*₃) δ 160.5, 146.9, 146.3, 138.8, 138.7, 131.7, 129.6, 128.2, 127.3, 73.0, 68.1, 68.0, 47.3, 21.0, 19.5. HRMS (ESI) m/z calcd for $C_{18}H_{24}NO_2^+$ (M)⁺ 286.1802, found 286.1799.



2-(1-hydroxy-2-(naphthalen-1-ylmethoxy)ethyl)-1-methylpyridin-1-ium iodide (4w)

According to **General procedure A**, **4w** was obtained as pale yellow solid in 66% yield (55.6 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 99 - 102 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.50 (d, J = 6.2 Hz, 1H), 8.24 (t, J = 7.9 Hz, 1H), 7.99 (d, J = 8.7 Hz, 1H), 7.86 – 7.78 (m, 3H), 7.71 – 7.64 (m, 1H), 7.50 – 7.46 (m, 1H), 7.43 – 7.39 (m, 3H), 5.41 (dd, J = 7.8, 5.3 Hz, 1H), 5.06 (d, J = 12.0 Hz, 1H), 4.81 (d, J = 12.0 Hz, 1H), 4.24 (s, 3H), 4.09 (dd, J = 9.5, 5.2 Hz, 1H), 3.70 (dd, J = 9.5, 7.9 Hz, 1H); ¹³C NMR (100 MHz, Methanol- d_4) δ 161.0, 147.0, 146.1, 135.3, 133.8, 132.9, 130.2, 129.7, 128.7, 127.7, 127.5, 127.3, 127.0, 126.2, 124.8, 73.6, 72.7, 68.2, 47.0. HRMS (ESI) m/z calcd for C₁₉H₂₀NO₂⁺ (M)⁺ 294.1489, found 294.1486.



1-ethyl-8-hydroxy-5,6,7,8-tetrahydroquinolin-1-ium iodide (4x)

According to **General procedure A**, **4x** was obtained as pale yellow solid in 60% yield (36.6 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 191 - 192 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.94 (d, J = 6.1 Hz, 1H), 8.37 (d, J = 8.0 Hz, 1H), 7.95 (t, J = 7.1 Hz, 1H), 5.20 (t, J = 3.2 Hz, 1H), 4.99 – 4.90 (m, 1H), 4.83 – 4.74 (m, 1H), 3.14 – 3.10 (m, 1H), 3.01 – 2.92 (m, 1H), 2.25 – 2.18 (m, 1H), 2.10 – 2.88 (m, 3H), 1.68 (t, J = 7.3 Hz, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 153.2, 148.0, 141.4, 127.6, 62.9, 53.9, 32.2, 29.9, 17.4, 16.6. HRMS (ESI) m/z calcd for C₁₁H₁₆NO⁺ (M)⁺ 178.1226, found 178.1224.



1-ethyl-2-(1-hydroxyethyl)pyridin-1-ium iodide (4y)

According to **General procedure A**, **4y** was obtained as pale yellow solid in 81% yield (45.2 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 151 – 153 °C.

¹H NMR (400 MHz, Methanol-*d*₄) δ 9.00 (d, *J* = 6.2 Hz, 1H), 8.60 (t, *J* = 8.4 Hz, 1H), 8.30 (d, *J* = 7.9 Hz, 1H), 8.02 (t, *J* = 7.4 Hz, 1H), 5.42 (q, *J* = 6.5 Hz, 1H), 4.77 (q, *J* = 7.3 Hz, 2H), 1.69 – 1.61 (m, 6H); ¹³C NMR (100 MHz, Methanol-*d*₄) δ 162.6, 147.2, 146.4, 128.0, 127.4, 65.5, 54.4, 23.4, 17.0. HRMS (ESI) m/z calcd for C₉H₁₄NO⁺ (M)⁺ 152.1070, found 152.1066.



1-benzyl-2-(1-hydroxyethyl)pyridin-1-ium iodide (4z)

According to **General procedure A**, **4z** was obtained as pale yellow solid in 80% yield (54.5 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 86 - 87 °C.

¹H NMR (400 MHz, DMSO- d_6) δ 9.12 (d, J = 5.8 Hz, 1H), 8.69 (t, J = 7.8 Hz, 1H), 8.31 (d, J = 8.1 Hz, 1H), 8.18 – 8.04 (m, 1H), 7.50 – 7.33 (m, 3H), 7.29 – 7.18 (m, 2H), 6.37 (brs, 1H), 6.03 (q, J = 15.5 Hz, 2H), 5.30 (q, J = 6.3 Hz, 1H), 1.31 (d, J = 6.4 Hz, 3H); ¹³C NMR (100 MHz, DMSO- d_6) δ 161.9, 146.8, 146.1, 134.1, 129.3, 128.9, 127.5, 126.8, 126.6, 63.8, 59.6, 23.1. HRMS (ESI) m/z calcd for C₁₄H₁₆NO⁺ (M)⁺ 214.1226, found 214.1221.



2-(2-(benzyloxy)-1-hydroxyethyl)-5-ethyl-1-methylpyridin-1-ium iodide (4aa)

According to **General procedure A**, **4aa** was obtained as pale yellow solid in 67% yield (53.5 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 143 – 145 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 8.78 (s, 1H), 8.41 (d, J = 8.3 Hz, 1H), 8.12 (d, J = 8.3 Hz, 1H), 7.32 – 7.23 (m, 3H), 7.22 – 7.15 (m, 2H), 5.50 – 5.28 (m, 1H), 4.59 – 4.46 (m, 2H), 4.38 (s, 3H), 3.96 (dd, J = 9.8, 5.4 Hz, 1H), 3.73 (dd, J = 9.8, 6.9 Hz, 1H), 2.87 (q, J = 7.6 Hz, 2H), 1.34 (t, J = 7.6 Hz, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 158.0, 146.6, 146.3, 144.8, 138.8, 129.5, 129.0, 129.0, 127.7, 74.5, 73.8, 68.2, 46.9, 26.4, 14.8. HRMS (ESI) m/z calcd for C₁₇H₂₂NO₂⁺ (M)⁺ 272.1645, found 272.1643.



4-(1-hydroxybutyl)-1-methylquinolin-1-ium iodide (4ab)

According to **General procedure A**, **4ab** was obtained as pale yellow solid in 67% yield (46.0 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 91 - 93 °C.

¹H NMR (400 MHz, Methanol-*d*₄) δ 9.37 (d, *J* = 6.2 Hz, 1H), 8.63 – 8.49 (m, 2H), 8.29 – 8.26 (m, 1H), 8.21 (d, *J* = 6.4 Hz, 1H), 8.13 – 8.00 (m, 1H), 5.72 (dd, *J* = 8.4, 3.6 Hz, 1H), 4.69 (s, 3H), 1.93 – 1.84 (m, 1H), 1.81 – 1.72 (m, 1H), 1.67 – 1.55 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (100 MHz, Methanol-*d*₄) δ 166.6, 150.5, 139.8, 136.4, 131.1, 127.9, 127.0, 120.6, 119.7, 70.1, 46.6, 42.1, 20.1, 14.2. HRMS (ESI) m/z calcd for C₁₄H₁₈NO⁺ (M)⁺ 216.1383, found 216.1378.



4-(1-hydroxy-2-methylpropyl)-1-methylquinolin-1-ium iodide (4ac)

According to **General procedure A**, **4ac** was obtained as pale yellow solid in 74% yield (50.7 mg), purified by recrystalization from (acetone/ethyl acetate). mp: 87 – 89 °C.

¹H NMR (400 MHz, Methanol- d_4) δ 9.35 (d, J = 6.2 Hz, 1H), 8.61 (d, J = 8.6 Hz, 1H), 8.51 (d, J = 8.9 Hz, 1H), 8.28 – 8.24 (m, 1H), 8.18 (d, J = 6.1 Hz, 1H), 8.09 – 7.99 (m, 1H), 5.53 (d, J = 4.4 Hz, 1H), 4.68 (s, 3H), 2.21 – 2.13 (m, 1H), 1.11 (d, J = 6.8 Hz, 3H), 0.87 (d, J = 6.7 Hz, 3H); ¹³C NMR (100 MHz, Methanol- d_4) δ 165.8, 150.0, 139.8, 136.4, 130.9, 128.3, 127.4, 120.7, 120.5, 74.4, 46.6, 36.6, 20.5, 16.5. HRMS (ESI) m/z calcd for C₁₄H₁₈NO⁺ (M)⁺ 216.1383, found 216.1382.



¹H and ¹³C NMR spectra of **2a**



 1 H and 13 C NMR spectra of **2b**



 ^1H and ^{13}C NMR spectra of 2c



 1 H and 13 C NMR spectra of **2d**





¹H and ¹³C NMR spectra of **2f**



 1 H and 13 C NMR spectra of **2g**



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 ^1H and ^{13}C NMR spectra of 2h





200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)

¹H and ¹³C NMR spectra of **2j**



 1 H and 13 C NMR spectra of **2k**





Ċ 90 80 f1 (ppm)

¹H and ¹³C NMR spectra of **2m**









90 80 f1 (ppm)

 1 H and 13 C NMR spectra of **2**q



 1 H and 13 C NMR spectra of **2r**



¹H and ¹³C NMR spectra of **2s**



 1 H and 13 C NMR spectra of **2t**







 1 H and 13 C NMR spectra of **2w**





 $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra of 2y



 1 H and 13 C NMR spectra of 2z



¹H and ¹³C NMR spectra of 2aa





-1 90 80 f1 (ppm) 170 160 Ó 110 100



¹H and ¹³C NMR spectra of **2ad**



90 80 f1 (ppm)
¹H and ¹³C NMR spectra of **2ae**



-1 90 80 f1 (ppm) 170 160 110 100

¹H and ¹³C NMR spectra of **2af**



¹H and ¹³C NMR spectra of **4a**



f1 (ppm)



 1 H and 13 C NMR spectra of **4**c



f1 (ppm)



 1 H and 13 C NMR spectra of **4e**



f1 (ppm) -1









f1 (ppm) . 70 -1

$\begin{array}{c} 8.802\\ 8.887\\ 8.887\\ 8.887\\ 8.8561\\ 8.8561\\ 8.8564\\ 8.8564\\ 8.2651\\ 7.2655\\ 7.7265\\ 7.2655\\ 7.2655\\ 7.056\\$







¹H and ¹³C NMR spectra of **4m**



f1 (ppm)



4 F.O





S90

 1 H and 13 C NMR spectra of 4q







S93



f1 (ppm) -1

 1 H and 13 C NMR spectra of **4u**



f1 (ppm)





 1 H and 13 C NMR spectra of 4x



 1 H and 13 C NMR spectra of **4**y





f1 (ppm) -1(



f1 (ppm) ¹H and ¹³C NMR spectra of **4ab**



¹H and ¹³C NMR spectra of **4ac**

