An environmentally benign cascade reaction of chromone-3-carboxaldehydes with ethyl 2-(pyridine-2-yl)acetate derivatives for highly site-selective synthesis of quinolizines and quinolizinium salts in water

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General Information

All compounds were fully characterised by spectroscopic data. The NMR spectra were recorded on a Bruker DRX600. Chemical shifts (δ) are expressed in ppm, J values are given in Hz, and deuterated DMSO-d6 were used as solvent. IR spectra were recorded on a FT-IR Thermo Nicolet Avatar 360 using a KBr pellet. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF254. The melting points were determined on a XT-4A melting point apparatus and are uncorrected. HRMs were performed on an Agilent LC/Msd TOF instrument. Materials used were purchased from Adamas-beta Corporation Limited.

The materials were purchased from Adamas-beta Corporation Limited. All chemicals and solvents were used as received without further purification unless otherwise stated. Column chromatography was performed on silica gel (200–300 mesh). The chromone-3-carboxaldehydes 1 and ethyl 2-(pyridine-2-yl)acetates 2 were commercially available reagents.

General Procedure for the Preparation of 3 and 4

First, chromone-3-carboxaldehydes 1 (1.0 ml) was charged into a round-bottom flask. Then, water (5 ml) and ethyl 2-(pyridine-2-yl)acetate derivatives 2 (1.1 mmol) were added to the mixture. The mixture was stirred at reflux for approximately 3 hours and monitored by TLC until the intermediate was completely consumed. The reaction mixture was cooled to room temperature and then was filtered by a suction funnel and washing with a few drops of water or recrystallized by EtOH or acetone. Finally, the obtained red solid was dried using an infrared lamp. As a result, we obtained the target compounds 3 with good to excellent yields (85–96%).
hours and monitored by TLC until the intermediate was completely consumed, and then was filtered by a suction funnel and washing with a few drops of water or recrystallized by EtOH or acetone. We can obtain the target compounds 3. Then compounds 3 and H$_2$O were charged in a round-bottom flask. Then, the mixture was added a few drops of perchloric acid and make the value of pH of the mixture is up to 1–2 at room temperature under the magneton agitation. Then, the mixture was filtered by suction funnel and washed by small of water. We obtained the target compounds 4 (yellow solid) with good to excellent yields. It should be noted that compounds 4 are in equilibrium with compounds 3 in the solution. The cascade reaction produces compounds 4 at strong acidic conditions (pH < 3) and obtains compounds 3 at neutral or basic conditions.

**Spectroscopic Data of 3-4**

**Ethyl 2-fluoro-13-oxo-5a,13-dihydrochromeno[2,3-b]quinolizine-6-carboxylate (3a)**

Red solid; Mp: 266.3-267.1 °C; IR (KBr): 2928, 1671, 1648, 1597, 1528, 1492, 1478, 1385, 1366, 1196, 823, 801, 777, 765 cm$^{-1}$; $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ = 1.28 (t, $J$ = 7.0 Hz, 3H, CH$_3$), 4.18 (d, $J$ = 7.0 Hz, 2H, CH$_2$), 7.17 (s, 2H, ArH), 7.47 (s, 1H, ArH), 7.51 (d, $J$ = 7.5 Hz, 2H, ArH), 7.85 (t, $J$ = 7.7 Hz, 1H, ArH), 7.94 (s, 1H, ArH), 8.38 (d, $J$ = 5.5 Hz, 1H, ArH), 8.82 (d, $J$ = 8.5 Hz, 1H, ArH); $^{13}$C NMR (150 MHz, DMSO-$d_6$): $\delta$ = 15.0, 59.7, 89.1, 91.2, 106.3, 112.0, 112.2, 116.6, 120.7, 122.0, 123.3 (d, $J_2$ = 24.0 Hz), 125.1, 133.6, 139.4, 140.0, 148.0, 151.0, 165.2, 177.3. HRMS (TOF ES$^+$): $m/z$ calcd for C$_{19}$H$_{14}$FNO$_4$ [(M+H)$^+$], 340.0980; found, 340.0979.

**Ethyl-9-ethyl-2-fluoro-13-oxo-5a,13-dihydrochromeno[2,3-b]quinolizine-6-carboxylate (3b)**

Red solid; Mp: 234.4-235.1 °C; IR (KBr): 2962, 2927, 1655, 1616, 1574, 1492, 1355, 1275, 1247, 1201, 1171, 1137, 837, 785, 758 cm$^{-1}$; $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ = 1.22 (t, $J$ =
7.6 Hz, 3H, CH$_3$), 1.27 (t, $J$ = 7.1 Hz, 3H, CH$_3$), 2.61-2.65 (m, 2H, CH$_2$), 4.15-4.19 (m, 2H, CH$_2$), 7.21 (s, 2H, ArH), 7.43 (s, 1H, ArH), 7.50 (s, 1H, ArH), 7.51 (s, 1H, ArH), 7.85 (d, $J$ = 9.2 Hz, 1H, ArH), 7.93 (s, 1H, ArH), 8.25 (s, 1H, ArH), 8.81 (d, $J$ = 9.0 Hz, 1H, ArH); $^{13}$C NMR (150 MHz, DMSO-$d_6$): $\delta$ = 14.7, 14.9, 24.8, 59.6, 89.3, 90.9, 105.8, 112.0 (d, $J_2$ = 24.0 Hz), 120.9, 122.0, 123.1 (d, $J_2$ = 25.5 Hz), 125.3, 132.2, 133.6, 136.4, 141.2, 146.7, 151.0, 158.8, 165.2, 177.2. HRMS (TOF ES$^+$): $m/z$ calcd for C$_{21}$H$_{19}$FNO$_4$ [(M+H)$^+$], 368.1293; found, 368.1289.

**Methyl 2-fluoro-13-oxo-5a,13-dihydrochromeno[2,3-b]quinolizine-6-carboxylate (3c)**

Red solid; Mp: 283.0-283.6 °C; IR (KBr): 2950, 1686, 1644, 1593, 1533, 1491, 1459, 1390, 1367, 1220, 1173, 878, 832, 777, 761 cm$^{-1}$; $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ = 3.71 (s, 3H, CH$_3$), 7.18 (d, $J$ = 5.5 Hz, 2H, ArH), 7.48-7.52 (m, 3H, ArH), 7.87 (t, $J$ = 7.9 Hz, 1H, ArH), 7.94 (s, 1H, ArH), 8.39 (d, $J$ = 6.3 Hz, 1H, ArH), 8.82 (d, $J$ = 8.9 Hz, 1H, ArH); $^{13}$C NMR (150 MHz, DMSO-$d_6$): $\delta$ = 51.4, 89.1, 91.0, 106.5, 112.1 (d, $J_2$ = 22.5 Hz), 116.6, 120.8, 122.0, 123.3 (d, $J_2$ = 24.0 Hz), 125.2, 133.5, 139.5, 140.1, 148.0, 151.0, 158.0 (d, $J_1$ = 241.5 Hz), 165.6, 177.4. HRMS (TOF ES$^+$): $m/z$ calcd for C$_{19}$H$_{12}$FNO$_4$ [(M+H)$^+$], 326.0823; found, 326.0821.

**2-Fluoro-13-oxo-5a,13-dihydrochromeno[2,3-b]quinolizine-6-carbonitrile (3d)**

Red solid; Mp: 256.3-257.1 °C; IR (KBr): 2201, 1647, 1619, 1533, 1481, 1396, 1368, 1288, 1208, 1181, 875, 782, 766 cm$^{-1}$; $^1$H NMR (600 MHz, DMSO-$d_6$): $\delta$ = 7.14-7.19 (m, 2H, ArH), 7.40 (t, $J$ = 5.9 Hz, 2H, ArH), 7.50-7.54 (m, 3H, ArH), 7.86 (t, $J$ = 7.6 Hz, 1H, ArH), 8.38 (d, $J$ = 6.7 Hz, 1H, ArH); $^{13}$C NMR (150 MHz, DMSO-$d_6$): $\delta$ = 79.7, 89.0, 112.1 (d, $J_2$ = 22.5 Hz), 116.9, 119.4, 120.9 (d, $J_3$ = 7.5 Hz), 121.3, 123.5, 123.7, 125.0 (d, $J_3$ = 6.0 Hz), 132.7, 139.6, 140.7, 148.4, 150.9, 158.9, 176.7. HRMS (TOF ES$^+$): $m/z$ calcd for C$_{17}$H$_9$ FN$_2$O$_2$ [(M+H)$^+$], 293.0721; found, 293.0720.

**6-Acetyl-2-fluorochromeno[2,3-b]quinoliniz-13(5aH)-one (3e)**
Red solid; Mp: 269.5-270.3 °C; IR (KBr): 2925, 1642, 1561, 1519, 1484, 1437, 1360, 1316, 1276, 1211, 1172, 1114, 780 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆): δ = 2.37 (s, 3H, CH₃), 7.19 (d, J = 4.7 Hz, 1H, ArH), 7.28 (t, J = 6.3 Hz, 1H, ArH), 7.45 (s, 1H, ArH), 7.52 (t, J = 7.3 Hz, 2H, ArH), 7.89 (s, 1H, ArH), 7.94 (t, J = 7.5 Hz, 1H, ArH), 8.49 (d, J = 6.2 Hz, 1H, ArH), 9.19 (d, J = 8.8 Hz, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆): δ = 28.6, 88.8, 101.2, 105.6, 112.1 (d, J₂ = 21.0 Hz), 117.9, 120.7, 123.0, 123.2 (d, J₂ = 24.0 Hz), 125.1, 134.9, 139.5, 141.1, 147.4, 151.0, 158.0 (d, J₁ = 244.5 Hz), 177.0, 192.4. HRMS (TOF ES⁻): m/z calcd for C₁₈H₁₂FNO₃ [(M+H)⁺], 310.0874; found, 310.0873.

6-Acetyl-2-chlorochromeno[2,3-b]quinolizin-13(5aH)-one (3f)

Red solid; Mp: 269.3-269.9 °C; IR (KBr): 2923, 1647, 1604, 1567, 1474, 1453, 1359, 1269, 1217, 1205, 1186, 1150, 1006, 817, 779, 733 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆): δ = 2.38 (s, 3H, CH₃), 7.18 (d, J = 8.6 Hz, 1H, ArH), 7.30 (s, 1H, ArH), 7.48 (s, 1H, ArH), 7.67 (t, J = 1.8 Hz, 1H, ArH), 7.76 (s, 1H, ArH), 7.90 (s, 1H, ArH), 7.95 (s, 1H, ArH), 8.49 (d, J = 6.2 Hz, 1H, ArH), 9.19 (d, J = 8.9 Hz, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆): δ = 28.6, 88.9, 101.3, 105.4, 118.0, 120.9, 123.0, 125.4, 126.0, 127.5, 135.0, 135.6, 139.5, 141.2, 147.4, 153.5, 176.8, 192.5. HRMS (TOF ES⁺): m/z calcd for C₁₈H₁₃ClNO₃ [(M+H)⁺], 326.0578; found, 326.0576.

6-Acetyl-2-bromochromeno[2,3-b]quinolizin-13(5aH)-one (3g)

Red solid; Mp: 234.6-235.5 °C; IR (KBr): 2925, 1644, 1597, 1566, 1514, 1478, 1358, 1331, 1269, 1218, 1183, 814, 779, 713 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆): δ = 2.37 (s, 3H, CH₃), 7.11 (d, J = 8.6 Hz, 1H, ArH), 7.29 (t, J = 7.2 Hz, 1H, ArH), 7.48 (s, 1H, ArH), 7.77-7.78 (m, 1H, ArH), 7.89 (d, J = 6.4 Hz, 2H, ArH), 7.95 (t, J = 7.2 Hz, 1H, ArH), 8.49 (d, J = 6.1 Hz, 1H, ArH), 9.19 (d, J = 8.9 Hz, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆): δ = 28.6, 88.9, 101.3, 105.3, 115.1, 118.0, 121.2, 123.0, 125.8, 129.0, 135.0, 138.3, 139.5, 141.2, 147.4, 153.9, 176.6, 192.5. HRMS (TOF ES⁻): m/z calcd for C₁₈H₁₃BrNO₃ [(M+H)⁺], 370.0073; found, 370.0071.

Ethyl 13-oxo-5a,13-dihydrochromeno[2,3-b]quinolizine-6-carboxylate (3h)
Red solid; Mp: 231.5-232.3 °C; IR (KBr): 2928, 1674, 1641, 1593, 1526, 1489, 1384, 1338, 1222, 1192, 1043, 773 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆): δ = 1.21 (t, J = 7.0 Hz, 3H, CH₃), 4.16-4.19 (m, 2H, CH₂), 7.11-7.15 (m, 2H, ArH), 7.19 (t, J = 7.4 Hz, 1H, ArH), 7.48 (s, 1H, ArH), 7.63 (t, J = 7.4 Hz, 1H, ArH), 7.82-7.84 (m, 2H, ArH), 7.92 (s, 1H, ArH), 8.35 (d, J = 6.5 Hz, 1H, ArH), 8.83 (d, J = 9.1 Hz, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆): δ = 14.9, 59.6, 89.0, 90.7, 107.3, 116.3, 118.6, 122.0, 123.2, 124.2, 127.1, 133.0, 136.2, 139.4, 139.7, 148.0, 154.8, 165.3, 178.5. HRMS (TOF ES⁺): m/z calcd for C₁₀H₁₆NO₄ [(M+H)+], 322.1074; found, 322.1071.

6-Acetyl-2-methylchromeno[2,3-b]quinolin-13(5aH)-one (3i)

Red solid; Mp: 280.0-280.9 °C; IR (KBr): 2923, 1652, 1611, 1569, 1527, 1491, 1473, 1400, 1328, 1283, 1203, 1179, 1020, 813, 767, 703 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆): δ = 2.33 (s, 3H, CH₃), 2.37 (s, 3H, CH₃), 7.03 (d, J = 7.2 Hz, 1H, ArH), 7.25 (s, 1H, ArH), 7.40 (s, 1H, ArH), 7.44 (d, J = 6.8 Hz, 1H, ArH), 7.64 (s, 1H, ArH), 7.86 (s, 1H, ArH), 7.91 (s, 1H, ArH), 8.44 (d, J = 4.2 Hz, 1H, ArH), 9.19 (d, J = 8.5 Hz, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆): δ = 20.6, 28.6, 88.5, 100.7, 106.7, 117.6, 118.3, 122.9, 123.8, 126.7, 132.4, 134.1, 136.9, 139.4, 140.8, 147.4, 152.9, 178.3, 192.3. HRMS (TOF ES⁺): m/z calcd for C₁₉H₁₈NO₅ [(M+H)+], 306.1125; found, 306.1122.

1-(Ethoxycarbonyl)-3-(5-fluoro-2-hydroxybenzoyl) quinolin-5-ium (4a)

Yellow solid; Mp: 278.2-283.9 °C; IR (KBr): 3445, 2925, 1731, 1652, 1625, 1482, 1367, 1343, 1257, 1206, 1121, 1107, 1079, 792, 624 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆+HClO₄): δ = 1.37 (t, J = 7.1 Hz, 3H, CH₃), 4.46-4.50 (m, 2H, CH₂), 7.04-7.07 (m, 1H, ArH), 7.38-7.44 (m, 2H, ArH), 8.23 (t, J = 6.8 Hz, 1H, ArH), 8.60 (t, J = 8.0 Hz, 1H, ArH), 8.89 (s, 1H, ArH), 9.24 (d, J = 8.9 Hz, 1H, ArH), 9.58 (d, J = 1H, ArH), 9.86 (s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆+HClO₄): δ = 14.3, 63.6, 117.1, 117.2, 119.4 (d, J = 7.5 Hz), 122.8 (d, J = 22.5 Hz), 123.3 (d, J = 7.5 Hz), 125.3, 127.2, 131.5, 138.1, 140.1, 141.4, 142.3, 142.7, 154.4, 155.6 (d, J = 235.5 Hz), 163.2, 190.1. HRMS (ESI-TOF, [M-CI0₄]⁺): calcd for C₁₉H₁₃FNO₄⁺, 340.0980; found, 340.0979.
1-(Ethoxycarbonyl)-7-ethyl-3-(5-fluoro-2-hydroxybenzoyl)quinolizin-5-ium (4b)

Yellow solid; Mp: 171.3-172.1 °C; IR (KBr): 3438, 2938, 1730, 1652, 1631, 1482, 1348, 1258, 1158, 1098, 1032, 855, 793, 678, 623 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆+HClO₄): δ = 1.35 (t, J = 7.5 Hz, 3H, CH₃), 1.42 (t, J = 7.1 Hz, 3H, CH₃), 2.95-2.99 (m, 2H, CH₂), 4.50-4.54 (m, 2H, CH₂), 7.09-7.11 (m, 1H, ArH), 7.43-7.49 (m, 2H, ArH), 8.63 (d, J = 9.6 Hz, 1H, ArH), 8.88 (s, 1H, ArH), 9.19 (d, J = 9.2 Hz, 1H, ArH), 9.58 (s, 1H, ArH), 9.81(s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆+HClO₄): δ = 14.0, 14.4, 25.6, 63.5, 117.1 (d, J₂ = 24.0 Hz), 119.4 (d, J₂ = 7.5 Hz), 122.6 (d, J₂ = 22.5 Hz), 123.6 (d, J₃ = 7.5 Hz), 124.9, 127.1, 131.5, 137.2, 137.7, 140.8, 142.4, 142.6, 154.3, 155.6 (d, J₄ = 234.0 Hz), 163.3, 190.1. HRMS (ESI-TOF, [M-ClO₄]⁺): calcd for C₂₁H₁₉FNO₄⁺, 368.1293; found, 368.1289.

3-(5-Fluoro-2-hydroxybenzoyl)-1-(methoxycarbonyl)quinolizin-5-ium (4c)

Yellow solid; Mp: 165.8-166.4 °C; IR (KBr): 3439, 2961, 2023, 1733, 1630, 1486, 1425, 1346, 1247, 1210, 1120, 1109, 801, 712, 624 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆+HClO₄): δ = 4.05 (s, 3H, CH₃), 7.08-7.11 (m, 1H, ArH), 7.44-7.46 (m, 1H, ArH), 7.48 (d, J = 3.0 Hz, 1H, ArH), 8.31 (t, J = 7.0 Hz, 1H, ArH), 8.67 (t, J = 8.2 Hz, 1H, ArH), 8.93 (s, 1H, ArH), 9.27 (d, J = 9.0 Hz, 1H, ArH), 9.66 (d, J = 6.7 Hz, 1H, ArH), 9.95 (s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆+HClO₄): δ = 54.3, 117.2 (d, J₂ = 24.0 Hz), 119.4, 122.8 (d, J₂ = 22.5 Hz), 123.4, 125.4, 125.5, 126.9, 131.6, 138.2, 140.3, 141.5, 142.2, 142.8, 154.4, 155.7 (d, J₄ = 234.0 Hz), 163.7, 190.1. HRMS (ESI-TOF, [M-ClO₄]⁺): calcd for C₁₈H₁₅FNO₄⁺, 326.0823; found, 326.0820.

1-Acetyl-3-(5-fluoro-2-hydroxybenzoyl)quinolizin-5-ium (4d)

Yellow solid; Mp: > 300 °C; IR (KBr): 3439, 2927, 2021, 1694, 1630, 1581, 1486, 1363, 1347, 1279, 1218, 1121, 1108, 784, 683, 623 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆+HClO₄): δ = 2.86 (s, 3H, CH₃), 7.09-7.11 (m, 1H, ArH), 7.48 (t, J = 9.0 Hz, 2H, ArH), 8.29 (t, J = 6.8 Hz, 1H, ArH), 8.63 (t, J = 8.0 Hz, 1H, ArH), 8.97 (d, J = 8.9 Hz, 1H, ArH), 9.00 (s, 1H, ArH), 9.66 (d, J = 6.6 Hz, 1H, ArH), 9.87 (s, 1H, ArH); ¹³C NMR (150 MHz,
DMSO-d$_6$+HClO$_4$): $\delta$ = 30.6, 117.2 (d, $J_2$ = 24.0 Hz), 119.5 (d, $J_3$ = 7.5 Hz), 122.9 (d, $J_2$ = 24.0 Hz), 123.4 (d, $J_3$ = 7.5 Hz), 125.3, 125.7, 131.8, 134.1, 136.4, 140.0, 141.3, 141.4, 141.8, 154.6, 155.7 (d, $J_1$ = 235.5 Hz), 190.3, 198.5. HRMS (ESI-TOF, [M-C10H4ClO$_4$]$^+$): caled for C$_{10}$H$_{13}$FNO$_3$+, 310.0874; found, 310.0871.

1-Acetyl-3-(5-fluoro-2-hydroxybenzoyl)-7-methylquinoliniz-5-iium (4e)

![Chemical structure](image)

Yellow solid; Mp: > 300 °C; IR (KBr): 3439, 2933, 1701, 1650, 1624, 1487, 1365, 1346, 1284, 1211, 1108, 836, 789, 684, 624 cm$^{-1}$; $^1$H NMR (600 MHz, DMSO-d$_6$+HClO$_4$): $\delta$ = 2.61 (s, 3H, CH$_3$), 2.86 (s, 3H, CH$_3$), 7.09-7.11 (m, 1H, ArH), 7.45-7.50 (m, 2H, ArH), 8.52 (d, $J$ = 9.2 Hz, 1H, ArH), 8.90 (d, $J = 9.1$ Hz, 1H, ArH), 8.95 (s, 1H, ArH), 9.52 (s, 1H, ArH), 9.69 (s, 1H, ArH); $^{13}$C NMR (150 MHz, DMSO-d$_6$+HClO$_4$): $\delta$ = 18.4, 30.5, 117.1 (d, $J_3$ = 22.5 Hz), 119.5 (d, $J_1$ = 7.5 Hz), 122.7 (d, $J_2$ = 24.0 Hz), 123.5 (d, $J_3$ = 6.0 Hz), 125.0, 131.8, 134.0, 135.5, 136.1, 139.7, 141.2, 143.3, 154.4, 155.7 (d, $J_1$ = 234.0 Hz), 190.3, 198.5. HRMS (ESI-TOF, [M-C10H4ClO$_4$]$^+$): caled for C$_{10}$H$_{13}$FNO$_3$+, 324.1030; found, 324.1031.

1-Cyano-3-(5-fluoro-2-hydroxybenzoyl)quinoliniz-5-iium (4f)

![Chemical structure](image)

Yellow solid; Mp: 276.2-277.1 °C; IR (KBr): 3439, 2023, 1693, 1636, 1482, 1437, 1345, 1283, 1249, 1213, 1121, 1108, 1001, 784, 681, 624 cm$^{-1}$; $^1$H NMR (600 MHz, DMSO-d$_6$+HClO$_4$): $\delta$ = 7.05-7.08 (m, 1H, ArH), 7.38-7.39 (m, 1H, ArH), 7.43-7.45 (m, 1H, ArH), 8.34-8.35 (m, 1H, ArH), 8.72 (t, $J = 2.8$ Hz, 2H, ArH), 9.24 (d, $J = 1.2$ Hz, 1H, ArH), 9.66 (d, $J = 6.8$ Hz, 1H, ArH), 9.97 (s, 1H, ArH); $^{13}$C NMR (150 MHz, DMSO-d$_6$+HClO$_4$): $\delta$ = 110.7, 113.8, 117.1 (d, $J_2$ = 24.0 Hz), 119.6, 123.0 (d, $J_3$ = 22.5 Hz), 123.2, 125.2, 126.3, 132.0, 140.4, 142.6, 142.8, 142.9, 143.0, 154.5, 154.9, 189.2. HRMS (ESI-TOF, [M-C10H4ClO$_4$]$^+$): caled for C$_{17}$H$_{16}$F$_3$O$_5$+, 293.0721; found, 293.0720.

3-(5-Chloro-2-hydroxybenzoyl)-1-(ethoxycarbonyl)quinoliniz-5-iium (4g)

![Chemical structure](image)

Yellow solid; Mp: 169.2-170.6 °C; IR (KBr): 3439, 2924, 2024, 1726, 1632, 1467, 1438, 1405, 1343, 1261, 1225, 1096, 785, 622 cm$^{-1}$; $^1$H NMR (600 MHz, DMSO-d$_6$+HClO$_4$): $\delta$ = 1.39 (t, $J = 7.1$ Hz, 3H, CH$_3$), 4.47-4.51 (m, 2H, CH$_2$), 7.07 (d, $J = 9.1$ Hz, 1H, ArH), 7.59 (t, $J = 2.6$ Hz, 2H, ArH), 8.27 (t, $J = 6.9$ Hz, 1H, ArH), 8.63 (t, $J = 7.9$ Hz, 1H, ArH), 8.90 (s,
1H, ArH), 9.24 (d, J = 9.0 Hz, 1H, ArH), 9.61 (d, J = 6.7 Hz, 1H, ArH), 9.90 (s, 1H, ArH); 13C NMR (150 MHz, DMSO-d6+HClO4): δ = 14.3, 63.6, 119.7, 123.8, 124.6, 125.3, 125.5, 127.2, 130.6, 131.4, 135.1, 138.0, 140.2, 141.4, 142.3, 142.9, 156.6, 163.2, 190.0. HRMS (ESI-TOF, [M-CIO4]+): calcd for C19H15ClNO4+, 356.0684; found, 356.0686.

3-(5-Chloro-2-hydroxybenzoyl)-1-(ethoxycarbonyl)-7-ethylquinolizin-5-ium (4h)

Yellow solid; Mp: 150.3-151.1 °C; IR (KBr): 3433, 2924, 1726, 1631, 1465, 1356, 1267, 1188, 1082, 776, 695, 623 cm⁻¹; 1H NMR (600 MHz, DMSO-d6+HClO4): δ = 1.35 (t, J = 7.5 Hz, 3H, CH₃), 1.42 (t, J = 7.1 Hz, 3H, CH₃), 2.95-2.99 (m, 2H, CH₂), 4.50-4.54 (m, 2H, CH₂), 7.10 (d, J = 8.6 Hz, 1H, ArH), 7.61 (d, J = 2.6 Hz, 1H, ArH), 7.63 (d, J = 2.5 Hz, 1H, ArH), 8.62 (d, J = 9.2 Hz, 1H, ArH), 8.88 (s, 1H, ArH), 9.19 (d, J = 9.2 Hz, 1H, ArH), 9.57 (s, 1H, ArH), 9.81 (s, 1H, ArH); 13C NMR (150 MHz, DMSO-d6+HClO4): δ = 14.0, 14.3, 25.6, 63.5, 119.7, 123.7, 124.8, 124.9, 127.1, 130.5, 131.4, 135.0, 137.1, 137.6, 140.8, 141.4, 142.4, 142.6, 156.5, 163.3, 190.0. HRMS (ESI-TOF, [M-CIO4]+): calcd for C21H19ClNO4+, 384.0997; found, 384.0996.

3-(5-Chloro-2-hydroxybenzoyl)-1-(methoxycarbonyl)quinolizin-5-ium (4i)

Yellow solid; Mp: > 300 °C; IR (KBr): 3439, 2926, 2025, 1735, 1654, 1637, 1470, 1426, 1341, 1280, 1266, 1102, 1002, 798, 780, 625 cm⁻¹; 1H NMR (600 MHz, DMSO-d6+HClO4): δ = 4.02 (s, 3H, CH₃), 7.08 (d, J = 9.4 Hz, 1H, ArH), 7.59 (s, 1H, ArH), 7.60 (s, 1H, ArH), 8.28 (t, J = 6.8 Hz, 1H, ArH), 8.64 (t, J = 7.9 Hz, 1H, ArH), 8.90 (s, 1H, ArH), 9.25 (d, J = 8.9 Hz, 1H, ArH), 9.63 (d, J = 6.6 Hz, 1H, ArH), 9.92 (s, 1H, ArH); 13C NMR (150 MHz, DMSO-d6+HClO4): δ = 54.3, 119.7, 123.8, 124.6, 125.4, 125.5, 126.9, 130.6, 131.5, 135.1, 138.1, 140.2, 141.5, 142.3, 142.8, 156.6, 163.7, 189.9. HRMS (ESI-TOF, [M-CIO4]+): calcd for C18H13ClNO4+, 342.0528; found, 342.0529.

1-Acetyl-3-(5-chloro-2-hydroxybenzoyl)quinolizin-5-ium (4j)

Yellow solid; Mp: 138.8–139.4 °C; IR (KBr): 3433, 2923, 2022, 1694, 1632, 1510, 1472, 1359, 1343, 1284, 1208, 1176, 1097, 784, 697, 622 cm⁻¹; 1H NMR (600 MHz,
DMSO-d$_6$+HClO$_4$: $\delta = 2.82$ (s, 3H, CH$_3$), 7.08 (d, $J = 8.5$ Hz, 1H, ArH), 7.59 (d, $J = 7.9$ Hz, 1H, ArH), 7.60 (s, 1H, ArH), 8.24 (t, $J = 6.9$ Hz, 1H, ArH), 8.59 (t, $J = 7.8$ Hz, 1H, ArH), 8.94 (s, 1H, ArH), 8.95 (s, 1H, ArH), 9.59 (d, $J = 6.7$ Hz, 1H, ArH), 9.82 (s, 1H, ArH); $^{13}$C NMR (150 MHz, DMSO-d$_6$+HClO$_4$): $\delta = 30.5, 119.9, 123.8, 124.6, 125.3, 125.7, 130.7, 131.7, 134.1, 135.2, 136.3, 139.9, 141.3, 141.4, 141.8, 156.8, 190.1, 198.5. HRMS (ESI-TOF, [M-ClO$_4$]$^+$): cycled for C$_{18}$H$_{13}$ClNO$_3$+, 326.0578; found, 326.0576.

**1-Acetyl-3-(5-chloro-2-hydroxybenzoyl)-7-methylquinolinizin-5-ium (4k)**

Yellow solid; Mp: 236.1-237.2 °C; IR (KBr): 3430, 2925, 1695, 1631, 1420, 1352, 1320, 1280, 1237, 1194, 1121, 1076, 824, 777, 621 cm$^{-1}$; $^1$H NMR (600 MHz, DMSO-d$_6$+HClO$_4$): $\delta = 2.60$ (s, 3H, CH$_3$), 2.85 (s, 3H, CH$_3$), 7.10 (t, $J = 4.7$ Hz, 1H, ArH), 7.62 (d, $J = 2.3$ Hz, 2H, ArH), 8.51 (d, $J = 9.0$ Hz, 1H, ArH), 8.51 (d, $J = 9.1$ Hz, 1H, ArH), 8.93 (s, 1H, ArH), 9.51 (s, 1H, ArH), 9.68 (s, 1H, ArH); $^{13}$C NMR (150 MHz, DMSO-d$_6$+HClO$_4$): $\delta = 18.4, 30.5, 119.8, 123.8, 124.8, 125.0, 130.6, 131.7, 134.0, 135.1, 135.4, 136.1, 138.0, 139.8, 141.3, 143.3, 156.7, 190.1, 198.5. HRMS (ESI-TOF, [M-ClO$_4$]$^+$): cycled for C$_{18}$H$_{13}$ClNO$_3$+, 340.0735; found, 340.0732.

**3-(5-Chloro-2-hydroxybenzoyl)-1-cyanoquinolinizin-5-ium (4l)**

Yellow solid; Mp: > 300 °C; IR (KBr): 3440, 2199, 1637, 1472, 1438, 1402, 1351, 1289, 1213, 1121, 1097, 848, 787, 702, 625 cm$^{-1}$; $^1$H NMR (600 MHz, DMSO-d$_6$+HClO$_4$): $\delta = 7.10$ (d, $J = 8.8$ Hz, 1H, ArH), 7.60-7.63 (m, 1H, ArH), 7.64 (d, $J = 2.6$ Hz, 1H, ArH), 8.39-8.41 (m, 1H, ArH), 8.76 (t, $J = 2.6$ Hz, 2H, ArH), 9.30 (s, 1H, ArH), 9.70 (d, $J = 6.7$ Hz, 1H, ArH), 10.03 (s, 1H, ArH); $^{13}$C NMR (150 MHz, DMSO-d$_6$+HClO$_4$): $\delta = 110.6, 113.9, 119.9, 123.8, 124.4, 125.3, 126.3, 130.6, 132.0, 135.3, 140.5, 142.7, 142.8, 142.9, 143.0, 156.8, 189.1. HRMS (ESI-TOF, [M-ClO$_4$]$^+$): cycled for C$_{17}$H$_{16}$Cl$_2$O$_2$+, 309.0425; found, 309.0421.

**3-(5-Bromo-2-hydroxybenzoyl)-1-(ethoxycarbonyl) quinolinizin-5-ium (4m)**

Yellow solid; Mp: 164.0-164.9 °C; IR (KBr): 3439, 2923, 1729, 1663, 1630, 1594, 1416, 1389, 1278, 1259, 1094, 982, 781, 662, 624 cm$^{-1}$; $^1$H NMR (600 MHz, DMSO-d$_6$+HClO$_4$): $\delta$
= 1.40 (t, J = 7.1 Hz, 3H, CH₃), 4.49-4.53 (m, 2H, CH₂), 7.04 (d, J = 8.9 Hz, 1H, ArH), 7.71 (s, 1H, ArH), 7.73 (d, J = 2.4 Hz, 1H, ArH), 8.29 (t, J = 7.0 Hz, 1H, ArH), 8.65 (t, J = 8.2 Hz, 1H, ArH), 8.91 (s, 1H, ArH), 9.25 (d, J = 9.0 Hz, 1H, ArH), 9.64 (d, J = 6.7 Hz, 1H, ArH), 9.92 (s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆+HClO₄): δ = 14.3, 63.6, 111.1, 120.2, 125.2, 125.4, 125.5, 127.2, 131.5, 133.5, 137.9, 138.0, 140.2, 141.5, 142.3, 142.8, 157.0, 163.2, 189.9. HRMS (ESI-TOF, [M-CIO₄]⁺): calcd for C₁₅H₁₃BrNO₄⁺, 400.0179; found, 400.0177.

3-(5-Bromo-2-hydroxybenzoyl)-1-(ethoxycarbonyl)-7-ethylquinolizin-5-ium (4n)

Yellow solid; Mp: 110.1–110.8 °C; IR (KBr): 3433, 2920, 1710, 1630, 1611, 1587, 1515, 1427, 1330, 1311, 1246, 1221, 1093, 989, 847, 772, 624 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆+HClO₄): δ = 1.35 (t, J = 7.5 Hz, 3H, CH₃), 1.41 (t, J = 7.1 Hz, 3H, CH₃), 2.96 (t, J = 7.5 Hz, 2H, CH₂), 4.51 (t, J = 7.1 Hz, 2H, CH₂), 7.05 (d, J = 8.8 Hz, 1H, ArH), 7.71 (d, J = 2.2 Hz, 1H, ArH), 7.72-7.74 (m, 1H, ArH), 8.61 (d, J = 9.2 Hz, 1H, ArH), 8.87 (s, 1H, ArH), 9.19 (d, J = 9.2 Hz, 1H, ArH), 9.56 (s, 1H, ArH), 9.80 (s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆+HClO₄): δ = 13.9, 14.3, 25.6, 63.5, 111.1, 120.1, 124.9, 125.3, 127.0, 131.4, 133.3, 137.1, 137.6, 137.8, 140.8, 141.5, 142.4, 142.6, 156.8, 163.2, 189.9. HRMS (ESI-TOF, [M-CIO₄]⁺): calcd for C₂₁H₁₀BrNO₄⁺, 428.0492; found, 428.0490.

3-(5-Bromo-2-hydroxybenzoyl)-1-(methoxycarbonyl)quinolizin-5-ium (4o)

Yellow solid; Mp: 172.7–173.8 °C; IR (KBr): 3439, 2959, 1734, 1655, 1621, 1470, 1339, 1280, 1265, 1225, 1101, 1026, 798, 687, 624 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆+HClO₄): δ = 4.05 (s, 3H, CH₃), 7.06 (t, J = 1.6 Hz, 1H, ArH), 7.73 (s, 1H, ArH), 7.74 (d, J = 2.5 Hz, 1H, ArH), 8.31-8.33 (m, 1H, ArH), 8.68 (t, J = 8.5 Hz, 1H, ArH), 8.92 (d, J = 1.3 Hz, 1H, ArH), 9.26 (d, J = 9.0 Hz, 1H, ArH), 9.67 (d, J = 6.7 Hz, 1H, ArH), 9.95 (s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆+HClO₄): δ = 54.3, 111.2, 120.2, 125.3, 125.4, 125.5, 127.0, 131.5, 133.5, 137.9, 138.2, 140.3, 141.5, 142.3, 142.8, 157.0, 163.7, 189.8. HRMS (ESI-TOF, [M-CIO₄]⁺): calcd for C₁₇H₁₀BrNO₄⁺, 386.0022; found, 386.0020.

1-Acetyl-3-(5-bromo-2-hydroxybenzoyl)quinolizin-5-ium (4p)
Yellow solid; Mp: >300 °C; IR (KBr): 3440, 2924, 1698, 1625, 1599, 1469, 1439, 1352, 1291, 1210, 1121, 1107, 1092, 790, 699, 636, 624 cm⁻¹; ¹H NMR (600 MHz, DMSO-δ6+HClO₄): δ = 2.86 (s, 3H, CH₃), 7.06 (d, J = 8.4 Hz, 1H, ArH), 7.75 (s, 1H, ArH), 7.76 (s, 1H, ArH), 8.30 (t, J = 6.8 Hz, 1H, ArH), 8.64 (t, J = 7.9 Hz, 1H, ArH), 8.97 (d, J = 8.9 Hz, 1H, ArH), 9.01 (s, 1H, ArH), 9.63 (d, J = 6.6 Hz, 1H, ArH), 9.88 (s, 1H, ArH), 10.97 (s, 1H, ArOH); ¹³C NMR (150 MHz, DMSO-δ6+HClO₄): δ = 30.7, 111.2, 120.3, 125.3, 125.4, 125.7, 131.8, 133.5, 134.1, 136.3, 138.0, 140.0, 141.3, 141.4, 141.9, 157.2, 190.0, 198.6. HRMS (ESI-TOF, [M-CIOT₄]⁺): calcd for C₁₈H₁₃BrNO₃⁺, 370.0073; found, 370.0073.

3-(5-Bromo-2-hydroxybenzoyl)-1-cyanoquinolinizin-5-ium (4q)

Yellow solid; Mp: >300 °C; IR (KBr): 3443, 2201, 1637, 1605, 1498, 1469, 1351, 1289, 1199, 1121, 1095, 809, 698, 625 cm⁻¹; ¹H NMR (600 MHz, DMSO-δ6+HClO₄): δ = 6.95 (s, 1H, ArH), 7.61 (d, J = 6.5 Hz, 1H, ArH), 7.63 (d, J = 6.7 Hz, 1H, ArH), 8.28 (s, 1H, ArH), 8.65 (s, 2H, ArH), 9.18 (s, 1H, ArH), 9.59 (s, 1H, ArH), 9.91 (s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-δ6+HClO₄): δ = 110.6, 111.2, 113.9, 120.3, 125.0, 125.3, 126.3, 132.0, 133.4, 138.1, 140.4, 142.6, 142.8, 142.9, 143.1, 157.2, 189.0. HRMS (ESI-TOF, [M-CIOT₄]⁺): calcd for C₁₇H₁₀BrN₂O₂⁺, 352.9920; found, 352.9917.

1-(Ethoxycarbonyl)-3-(2-hydroxy-5-nitrobenzoyl)quinolinizin-5-ium (4r)

Yellow solid; Mp: 118.5–119.3 °C; IR (KBr): 3440, 2923, 1729, 1676, 1636, 1496, 1338, 1252, 1115, 1035, 984, 802, 736, 634 cm⁻¹; ¹H NMR (600 MHz, DMSO-δ6+HClO₄): δ = 1.40 (t, J = 9.1 Hz, 3H, CH₃), 4.49-4.52 (m, 2H, CH₂), 7.24 (d, J = 8.8 Hz, 1H, ArH), 8.29 (t, J = 6.9 Hz, 1H, ArH), 8.42 (d, J = 2.6 Hz, 1H, ArH), 8.68 (s, 1H, ArH), 8.66 (t, J = 8.0 Hz, 1H, ArH), 8.94 (s, 1H, ArH), 9.25 (d, J = 8.9 Hz, 1H, ArH), 9.60 (d, J = 6.7 Hz, 1H, ArH), 9.94 (s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-δ6+HClO₄): δ = 14.3, 63.6, 118.5, 123.8, 125.4, 125.6, 127.3, 127.8, 130.2, 131.1, 137.6, 140.2, 140.3, 141.7, 142.4, 143.3, 163.0, 163.2, 189.2. HRMS (ESI-TOF, [M-CIOT₄]⁺): calcd for C₁₅H₁₀N₂O₆⁺, 367.0925; found, 367.0922.

1-(Ethoxycarbonyl)-7-ethyl-3-(2-hydroxy-5-nitrobenzoyl)quinolinizin-5-ium (4s)
Yellow solid; Mp: 169.3–170.2 °C; IR (KBr): 3439, 2925, 1732, 1664, 1632, 1613, 1591, 1523, 1433, 1338, 1315, 1247, 1228, 1097, 1083, 989, 852, 777, 624 cm⁻¹; ¹H NMR (600 MHz, DMSO-dma+HClO₄): δ = 1.34 (t, J = 7.5 Hz, 3H, CH₃), 1.42 (t, J = 7.1 Hz, 3H, CH₃), 2.96 (d, J = 7.5 Hz, 2H, CH₂), 4.52 (t, J = 7.1 Hz, 2H, CH₂), 7.26 (d, J = 9.7 Hz, 1H, ArH), 8.44 (d, J = 2.5 Hz, 1H, ArH), 8.45 (s, 1H, ArH), 8.63 (d, J = 9.2 Hz, 1H, ArH), 8.91 (s, 1H, ArH), 9.19 (d, J = 9.2 Hz, 1H, ArH), 9.52 (s, 1H, ArH), 9.82 (s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-dma+HClO₄): δ = 140.0, 143.3, 25.6, 63.6, 118.5, 123.9, 125.0, 127.2, 127.7, 130.1, 131.1, 136.7, 137.7, 140.2, 140.9, 141.5, 142.8, 142.8, 162.9, 163.2, 189.3. HRMS (ESI-TOF, [M+ClO₄]⁺): calcd for C₂₁H₁₉N₂O₆⁺, 395.1238; found, 395.1235.

3-(2-Hydroxy-5-nitrobenzoyl)-1-(methoxycarbonyl)quinolizin-5-ium (4t)

Yellow solid; Mp: 122.8–123.6 °C; IR (KBr): 3439, 2923, 1729, 1658, 1634, 1621, 1515, 1437, 1357, 1336, 1292, 1263, 1147, 1121, 1102, 1027, 998, 805, 685, 624 cm⁻¹; ¹H NMR (600 MHz, DMSO-dma+HClO₄): δ = 4.05 (s, 3H, CH₃), 7.26 (d, J = 9.1 Hz, 1H, ArH), 8.33 (t, J = 6.9 Hz, 1H, ArH), 8.44-8.47 (m, 2H, ArH), 8.70 (t, J = 8.0 Hz, 1H, ArH), 8.96 (s, 1H, ArH), 9.26 (d, J = 8.9 Hz, 1H, ArH), 9.63 (d, J = 6.7 Hz, 1H, ArH), 9.98 (s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-dma+HClO₄): δ = 54.4, 118.5, 123.9, 125.5, 125.6, 127.1, 127.9, 130.2, 131.2, 137.8, 140.2, 140.4, 141.7, 142.4, 143.3, 163.0, 163.7, 189.2. HRMS (ESI-TOF, [M+ClO₄]⁺): calcd for C₁₉H₁₃N₂O₆⁺, 353.0768; found, 353.0767.

1-Acetyl-3-(2-hydroxy-5-nitrobenzoyl)quinolizin-5-ium (4u)

Yellow solid; Mp: 242.8-243.6 °C; IR (KBr): 3439, 2924, 1703, 1654, 1630, 1475, 1344, 1289, 1247, 1206, 1121, 1094, 906, 782, 747, 624 cm⁻¹; ¹H NMR (600 MHz, DMSO-dma+HClO₄): δ = 2.84 (s, 3H, CH₃), 7.24 (d, J = 9.0 Hz, 1H, ArH), 8.27 (t, J = 6.9 Hz, 1H, ArH), 8.42 (d, J = 2.8 Hz, 1H, ArH), 8.43-8.45 (m, 1H, ArH), 8.62 (t, J = 8.0 Hz, 1H, ArH), 8.95 (d, J = 8.9 Hz, 1H, ArH), 9.0 (s, 1H, ArH), 9.57 (d, J = 6.7 Hz, 1H, ArH), 9.87 (s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-dma+HClO₄): δ = 30.6, 118.6, 123.9, 125.4, 125.8, 127.8, 130.2, 131.3, 134.3, 134.3, 135.9, 140.0, 140.2, 141.5, 142.3, 163.1, 189.4, 198.6. HRMS (ESI-TOF, [M+ClO₄]⁺): calcd for C₁₉H₁₃N₂O₆⁺, 337.0819; found, 337.0818.
1-Cyano-3-(2-hydroxy-5-nitrobenzoyl)quinolinizin-5-ium (4v)

Yellow solid; Mp: >300 °C; IR (KBr): 3432, 2245, 1683, 1634, 1525, 1498, 1438, 1339, 1296, 1261, 1121, 1102, 898, 837, 627 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆+HClO₄): δ = 7.25-7.26 (m, 1H, ArH), 8.40-8.43 (m, 2H, ArH), 8.45-8.46 (m, 1H, ArH), 8.76 (s, 1H, ArH), 8.78 (d, J = 3.4 Hz, 1H, ArH), 9.37 (d, J = 1.1 Hz, 1H, ArH), 9.69 (d, J = 6.7 Hz, 1H, ArH), 10.07 (s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆+HClO₄): δ = 110.6, 113.9, 118.7, 123.6, 125.3, 126.4, 127.9, 130.3, 131.6, 140.3, 140.5, 142.6, 143.2, 163.2, 188.6. HRMS (ESI-TOF, [M-CI₂O₄⁺]): calc'd for C₁₇H₁₁N₃O₄⁺, 320.0666; found, 320.0660.

1-(Ethoxycarbonyl)-3-(2-hydroxybenzoyl) quinolinizin-5-ium (4w)

Yellow solid; Mp: 170.3–171.1 °C; IR (KBr): 3439, 2925, 1730, 1647, 1635, 1620, 1487, 1342, 1258, 1222, 1156, 1104, 1078, 769, 665, 624 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆+HClO₄): δ = 1.42 (t, J = 7.1 Hz, 3H, CH₃), 4.51-4.54 (m, 2H, CH₂), 7.05-7.10 (m, 2H, ArH), 7.60-7.66 (m, 2H, ArH), 8.31 (t, J = 7.0 Hz, 1H, ArH), 8.66-8.68 (m, 1H, ArH), 8.93 (s, 1H, ArH), 9.27 (d, J = 8.9 Hz, 1H, ArH), 9.66 (d, J = 6.5 Hz, 1H, ArH), 9.93 (s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆+HClO₄): δ = 14.4, 63.5, 117.9, 120.3, 122.9, 125.3, 125.5, 127.1, 132.0, 132.0, 136.2, 138.3, 140.2, 141.3, 142.2, 142.5, 158.4, 163.3, 191.4. HRMS (ESI-TOF, [M-CI₂O₄⁺]): calc'd for C₁₉H₁₆NO₄⁺, 322.1074; found, 322.1071.

1-Cyano-3-(2-hydroxybenzoyl)quinolinizin-5-ium (4x)

Yellow solid; Mp: >300 °C; IR (KBr): 3439, 2197, 1637, 1611, 1485, 1436, 1351, 1319, 1287, 1242, 1174, 1121, 1096, 810, 705, 625 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆+HClO₄): δ = 7.06 (d, J = 7.1 Hz, 1H, ArH), 7.09 (d, J = 8.3 Hz, 1H, ArH), 7.61 (d, J = 7.4 Hz, 1H, ArH), 7.64 (d, J = 8.0 Hz, 1H, ArH), 8.39 (s, 1H, ArH), 8.76 (s, 2H, ArH), 9.28 (s, 1H, ArH), 9.70 (d, J = 6.1 Hz, 1H, ArH), 10.01 (s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆+HClO₄): δ = 110.6, 113.9, 118.0, 120.3, 122.7, 125.2, 126.3, 132.1, 132.6, 136.4, 140.4, 142.5, 142.8, 142.9, 158.5, 190.5. HRMS (ESI-TOF, [M-CI₂O₄⁺]): calc'd for C₁₇H₁₁N₂O₄⁺, 275.0815; found, 275.0814.
1-Cyano-3-(2-hydroxy-5-methylbenzoyl)quinolin-5-ium (4y)

Yellow solid; Mp: >300 °C; IR (KBr): 3438, 2925, 2022, 1637, 1489, 1435, 1353, 1289, 1248, 1196, 1173, 1094, 919, 790, 678, 625 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆+HClO₄): δ = 2.26 (s, 3H, CH₃), 6.96 (d, J = 9.0 Hz, 1H, ArH), 7.41 (d, J = 7.0 Hz, 2H, ArH), 8.33–8.36 (m, 1H, ArH), 8.70 (s, 1H, ArH), 8.72 (d, J = 6.4 Hz, 1H, ArH), 9.22 (s, 1H, ArH), 9.66 (d, J = 6.7 Hz, 1H, ArH), 9.96 (s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆+HClO₄): δ = 20.2, 110.6, 113.9, 117.9, 122.2, 125.2, 126.2, 129.2, 131.8, 132.6, 137.3, 140.3, 142.4, 142.6, 142.7, 142.9, 156.4, 190.6. HRMS (ESI-TOF, [M-Clo₄⁺]⁺): calcd for C₁₁H₁₂N₂O₅⁺, 289.0972; found, 289.0970.

1-Acetyl-3-(2-hydroxy-5-methylbenzoyl)quinolin-5-ium (4z)

Yellow solid; Mp: 206.5–207.3 °C; IR (KBr): 3432, 2925, 1702, 1634, 1488, 1460, 1438, 1356, 1294, 1251, 1177, 1121, 1094, 785, 677, 624 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆+HClO₄): δ = 2.34 (s, 3H, CH₃), 2.89 (s, 3H, CH₃), 7.04 (d, J = 8.4 Hz, 1H, ArH), 7.47–7.49 (m, 1H, ArH), 7.52 (s, 1H, ArH), 8.31 (t, J = 6.5 Hz, 1H, ArH), 8.64–8.66 (m, 1H, ArH), 9.02 (s, 1H, ArH), 9.04 (s, 1H, ArH), 9.65 (d, J = 6.7 Hz, 1H, ArH), 9.87(s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆+HClO₄): δ = 20.2, 30.5, 117.9, 122.3, 125.2, 125.6, 129.2, 131.9, 132.4, 134.0, 136.7, 137.2, 139.9, 141.1, 141.3, 141.3, 156.6, 191.7, 198.5. HRMS (ESI-TOF, [M-Clo₄⁺]⁺): calcd for C₁₀H₁₆NO₃⁺, 306.1125; found, 306.1122.

1-Cyano-3-(2-hydroxy-4,6-dimethylbenzoyl)quinolin-5-ium (4a')

Yellow solid; Mp: 283.5–284.5 °C; IR (KBr): 3437, 2198, 1643, 1563, 1468, 1399, 1305, 1256, 1222, 1109, 837, 788, 624 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆+HClO₄): δ = 2.19 (s, 3H, CH₃), 2.31 (s, 3H, CH₃), 6.68 (s, 1H, ArH), 6.73 (s, 1H, ArH), 8.34–8.37 (m, 1H, ArH), 8.74 (d, J = 4.1 Hz, 2H, ArH), 9.18 (d, J = 1.3 Hz, 1H, ArH), 9.77 (d, J = 6.8 Hz, 1H, ArH), 9.90(s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆+HClO₄): δ = 19.6, 21.6, 111.2, 113.8, 114.8, 121.3, 123.5, 125.2, 126.2, 132.2, 138.6, 140.6, 141.8, 142.9, 143.2, 143.2, 143.2, 156.4, 192.0. HRMS (ESI-TOF, [M-Clo₄⁺]⁺): calcd for C₁₀H₁₃N₂O₄⁺, 303.1128; found,
1-Acetyl-3-(2-hydroxy-4,6-dimethylbenzoyl)quinolizin-5-ium (4b′)

Yellow solid; Mp: 226.5–227.5 °C; IR (KBr): 3430, 1701, 1635, 1553, 1473, 1400, 1375, 1256, 1163, 1120, 1008, 804, 665, 625 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆+HClO₄): δ = 2.21 (s, 3H, CH₃), 2.31 (s, 3H, CH₃), 2.86 (s, 3H, CH₃), 6.68 (s, 1H, ArH), 6.73 (s, 1H, ArH), 8.23-8.25 (m, 1H, ArH), 8.59-8.62 (m, 1H, ArH), 8.94-8.97 (m, 2H, ArH), 9.69 (d, J = 6.8 Hz, 1H, ArH), 9.71 (s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆+HClO₄): δ = 19.6, 21.6, 30.5, 114.8, 121.6, 123.4, 125.3, 125.7, 131.9, 134.6, 135.4, 138.4, 140.2, 141.4, 141.6, 142.0, 142.9, 156.3, 198.5. HRMS (ESI-TOF, [M-ClO₄]⁺): calcd for C₂₀H₁₈NO₅⁺, 320.1281; found, 320.1273.

3-(5-Chloro-2-hydroxy-4-methylbenzoyl)-1-cyanoquinolizin-5-ium (4c′)

Yellow solid; Mp: >300 °C; IR (KBr): 3439, 2194, 1637, 1561, 1483, 1401, 1325, 1246, 1210, 1122, 1108, 824, 785, 625 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆+HClO₄): δ = 2.37 (s, 3H, CH₃), 7.04 (s, 1H, ArH), 7.60 (s, 1H, ArH), 8.36-8.39 (m, 1H, ArH), 8.72-8.75 (m, 2H, ArH), 9.26 (d, J = 1.1 Hz, 1H, ArH), 9.66 (d, J = 6.7 Hz, 1H, ArH), 9.99 (s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆+HClO₄): δ = 20.6, 110.6, 113.9, 120.4, 122.1, 124.5, 125.2, 126.3, 131.3, 132.3, 140.3, 142.6, 142.7, 142.8, 143.0, 144.2, 157.0, 188.9. HRMS (ESI-TOF, [M-ClO₄]⁺): calcd for C₁₈H₁₂ClN₂O₂⁺, 323.0582; found, 323.0573.

3-(3,5-Dichloro-2-hydroxybenzoyl)-1-(ethoxycarbonyl)quinolizin-5-ium (4d′)

Yellow solid; Mp: >300 °C; IR (KBr): 3432, 3065, 1709, 1656, 1640, 1462, 1394, 1318, 1278, 1237, 1088, 1035, 919, 872, 797, 624 cm⁻¹; ¹H NMR (600 MHz, DMSO-d₆+HClO₄): δ = 1.41 (t, J = 7.1 Hz, 3H, CH₃), 4.49-4.53 (m, 2H, CH₂), 7.61 (d, 1H, J = 2.6 Hz, ArH), 7.92 (d, J = 2.5 Hz, 1H, ArH), 8.28-8.31 (m, 1H, ArH), 8.65-8.68 (m, 1H, ArH), 8.93 (d, J = 1.5 Hz, 1H, ArH), 9.27 (d, J = 8.9 Hz, 1H, ArH), 9.58 (d, J = 6.7 Hz, 1H, ArH), 9.88 (s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-d₆+HClO₄): δ = 14.3, 63.6, 124.3, 125.5, 125.5, 126.4, 127.5, 129.8, 129.8, 130.9, 134.4, 137.6, 140.3, 141.7, 142.3, 143.2, 152.5, 163.1, 190.0.

1-Cyano-3-(3,5-dichloro-2-hydroxybenzoyl)quinolizin-5-ium (4e')

Yellow solid; Mp: >300 °C; IR (KBr): 3440, 2197, 1637, 1600, 1560, 1483, 1401, 1325, 1217, 1189, 1103, 875, 848, 767, 700 cm⁻¹; ¹H NMR (600 MHz, DMSO-⁶+HClO₄): δ = 7.53 (d, J = 2.5 Hz, 1H, ArH), 7.87 (d, J = 2.5 Hz, 1H, ArH), 8.34-8.36 (m, 1H, ArH), 8.73 (d, J = 4.2 Hz, 2H, ArH), 9.22 (d, J = 1.0 Hz, 1H, ArH), 9.62 (d, J = 6.6 Hz, 1H, ArH), 9.95 (s, 1H, ArH); ¹³C NMR (150 MHz, DMSO-⁶+HClO₄): δ = 111.0, 113.7, 124.5, 125.2, 126.2, 126.4, 129.7, 129.7, 131.3, 134.5, 140.5, 142.1, 143.0, 143.1, 152.5, 189.2. HRMS (ESI-TOF, [M-ClO₄]⁺): calcd for C₁₉H₉Cl₂N₂O₂⁺, 343.0036; found, 343.0031.
**X-ray Structure and Data** of 4a.

**Figure S1.** X-Ray crystal structure of 4a

**Table S1.** Crystal data and structure refinement for 4a

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Table S2. Bond lengths [Å] and angles [deg] for 4a

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Figure S2. $^1$H NMR (600 MHz, DMSO-$d_6$) spectra of compound 3a
Figure S3. $^{13}$C NMR (150 MHz, DMSO-$d_6$) spectra of compound 3a
Figure S4. $^{19}$F NMR (564 MHz, DMSO-$d_6$) spectra of compound 3a
Figure S5. $^1$H NMR (600 MHz, DMSO-$d_6$) spectra of compound 3b
Figure S6. $^{13}$C NMR (150 MHz, DMSO-$d_6$) spectra of compound 3b
Figure S7. $^{19}$F NMR (564 MHz, DMSO-$d_6$) spectra of compound 3b
Figure S8. $^1$H NMR (600 MHz, DMSO-$d_6$) spectra of compound 3c
Figure S9. $^{13}$C NMR (150 MHz, DMSO-$d_6$) spectra of compound 3c
Figure S10. $^{19}$F NMR (564 MHz, DMSO-$d_6$) spectra of compound 3c
Figure S11. $^1$H NMR (600 MHz, DMSO-$d_6$) spectra of compound 3d
Figure S12. $^{13}$C NMR (150 MHz, DMSO-$d_6$) spectra of compound 3d
Figure S13. $^{19}$F NMR (564 MHz, DMSO-$d_6$) spectra of compound 3d


Figure S14. $^1$H NMR (600 MHz, DMSO-$d_6$) spectra of compound 3e
Figure S15. $^{13}$C NMR (150 MHz, DMSO-$d_6$) spectra of compound 3e
Figure S16. $^{19}$F NMR (564 MHz, DMSO-$d_6$) spectra of compound 3e
Figure S17. $^1$H NMR (600 MHz, DMSO-$d_6$) spectra of compound 3f
Figure S18. $^{13}$C NMR (150 MHz, DMSO-$d_6$) spectra of compound 3f
Figure S19. $^1$H NMR (600 MHz, DMSO-$d_6$) spectra of compound 3g
Figure S20. $^{13}$C NMR (150 MHz, DMSO-$d_6$) spectra of compound 3g
Figure S21. $^1$H NMR (600 MHz, DMSO-$d_6$) spectra of compound 3h
Figure S2. $^{13}$C NMR (150 MHz, DMSO-$d_6$) spectra of compound 3h
Figure S23. $^1$H NMR (600 MHz, DMSO-$d_6$) spectra of compound 3i
Figure S24. $^{13}$C NMR (150 MHz, DMSO-$d_6$) spectra of compound 3i
Figure S25. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4a
Figure S26. $^{13}$C NMR (150 MHz, DMSO-$d_6+$HClO$_4$) spectra of compound 4a
Figure S27. $^{19}$F NMR (564 MHz, DMSO-$d_6$+HClO4) spectra of compound 4a
Figure S28. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4b
Figure S29. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4b
Figure S30. $^{19}$F NMR (564 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4b
Figure S31. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4c
Figure S32. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4c
Figure S33. $^{19}$F NMR (564 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4c
Figure S34. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4d
Figure S35. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4d
Figure S36. $^{19}$F NMR (564 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4d.
Figure S37. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4e
Figure S38. $^{13}$C NMR (150 MHz, DMSO-${d_6}+\text{HClO}_4$) spectra of compound 4e
Figure S39. $^{19}$F NMR (564 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4e
Figure S40. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4f
Figure S41. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4f
Figure S42. $^{19}$F NMR (564 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4f
Figure S43. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4g
Figure S44. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4g
Figure S45. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4h
Figure S46. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4h
Figure S47. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4i
Figure S48. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4i
Figure S49. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4j
**Figure S50.** $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4j.
Figure S51. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4k
Figure S52. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4k
**Figure S53.** $^1$H NMR (600 MHz, DMSO-d$_6$+HClO$_4$) spectra of compound 4l
Figure S54. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4l
Figure S55. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4m
Figure S56. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4m
Figure S57. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4n
Figure S58. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4n
Figure S59. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4o
Figure S60. $^{13}$C NMR (150 MHz, DMSO-$d_6+$HClO$_4$) spectra of compound 4o
Figure S61. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4p
Figure S62. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4p
Figure S63. $^1$H NMR (600 MHz, DMSO-$_d_6$+HClO$_4$) spectra of compound 4q
Figure S6. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4q
Figure S65. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4r
Figure S66. $^{13}$C NMR (150 MHz, DMSO-d$_6$+HClO$_4$) spectra of compound 4r
Figure S67. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4s
Figure S68. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4s
Figure S69. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4t
Figure S70. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4t
**Figure S71.** $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4u
Figure S72. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4u
**Figure S73.** $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4v
Figure S74. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4v
Figure S75. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4w
Figure S76. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4w
Figure S77. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4x
Figure S78. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4x
Figure S79. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4y
Figure S80. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4y
Figure S81. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4z
**Figure S82.** $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4z
Figure S83. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4a'}
Figure S84. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4a'}
Figure S85. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4b'
Figure S86. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound $4b'$
Figure S8. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4c'
Figure S8. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4c'
Figure S89. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4d'}
Figure S90. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4d'
Figure S91. $^1$H NMR (600 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4e'
Figure S92. $^{13}$C NMR (150 MHz, DMSO-$d_6$+HClO$_4$) spectra of compound 4e'
Figure S93. HPLC of the reaction mixture
Figure S94. HRMS of substrate 2a
Figure S95. HRMS of intermediate 5a
Figure S96. HRMS of intermediate 6a/7a/8a
Figure S97. HRMS of intermediate 6a/7a/8a
2 79 RT: 1.38  AV: 1  NL: 6.17E5
T: FTMS + c ESI Full ms [100.00-400.00]

358.1082
C$_{19}$H$_{17}$O$_{5}$N F = 358.1085

357.2954
C$_{18}$H$_{23}$O$_{3}$N$_{2}$F Na = 357.1585

Figure S98. HRMS of intermediate 6a/7a/8a
Figure S99. HRMS of compound 3a
Figure S100. HPLC of the reaction mixture
Figure S101. HRMS of compound 4a/9a
Figure S102. HRMS of compound 4a/9a