Supporting Information available

Sustainable Byproduct Catalyzed Domino Strategy: Facile Synthesis of \( \alpha \)-formyloxy and Acetoxy Ketones via Iodination/Nucleophilic Substitution/Hydrolyzation/Oxidation Sequences

Yan-Ping Zhu, Qing-He Gao, Mi Lian, Jing-Jing Yuan, Mei-Cai Liu, Qin Zhao, Yan Yang, An-Xin Wu*

Key Laboratory of Pesticide & Chemical Biology, Ministry of Education, Central China Normal University, Wuhan 430079, P. R. China

E-mail: chwuax@mail.ccnu.edu.cn

Table of Contents

1. General..........................................................S2
2. Synthesis of \( \text{3a-3m, 5a-5f} \)..................................................S2
3. Evidence in support of the hypothetic mechanism..................S2-S5
4. Crystallographic data and molecular structure..........................S5-S6
5. Spectral data of compound \( \text{3a-3m, 5a-5f} \)..............................S6-S12
6. Appendix: spectral copies of \(^1\)H NMR, and \(^{13}\)C NMR ..........S12-S48
1. General

All aryl methyl ketones (1a-1n), and other reagents were obtained from commercial suppliers and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200-300 mesh). IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption in cm⁻¹. ¹H NMR spectra were recorded on a Varian Mercury 400 or 600 MHz spectrometer. Chemical shifts are reported in ppm, relative to the internal standard of tetramethylsilane (TMS). HRMS were obtained on a Bruker 7-tesla FT-ICR MS equipped with an electrospray source. The X-ray crystal-structure determinations of 2e and 3d were obtained on a Bruker SMART APEX CCD system. Melting points were determined using XT-4 apparatus and not corrected.

2. Synthesis of 2a-2x, 3a-3m

2.1. General procedure for preparation of 2 and 3 (2b as an example)

A mixture of benzalacetone 1b (120 mg, 1 mmol), iodine (254 mg, 1.0 mmol), and CuO (80 mg, 1.0 mmol) in common DMF (3.0 mL) was heated at 110 °C for 1 h, after disappearance of the reactant (monitored by TLC), and added 50 mL water to the residue, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% Na₂S₂O₃, dried over anhydrous Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography on silica gel using petroleum ether/EtOAc as the eluent to give the expected products 2b in 96% yield.

3. In order to support the hypothetic mechanism following experiments were carried out.

(a) The reaction process of Acetophenone 1a, iodine and CuO in DMF at 110 °C:

The reaction process of acetophenone 1a (120 mg, 1.0 mmol), iodine (254 mg, 1.0 mmol) and CuO (80 mg, 1.0 mmol) in DMF (6 mL) at 110°C was monitored by ¹H NMR (400 MHz, CDCl₃, 298 K) over time.

\[
\text{PhCO} + \text{I}_2 + \text{CuO} \xrightarrow{\text{DMF, 110°C}} \text{PhCOOH}
\]

1a 2a
(b) A mixture of phenacyl iodine (246 mg, 1.0 mmol), I₂ (253.81 mg, 1.0 mmol), and CuO (80 mg, 1.0 mmol) in DMF (3-4 mL) was stirred at 110°C for 2 h. After the reaction completed, the reaction mixture was filtered, diluted with water and extracted with EtOAc (3×20 mL). The extract was washed with Na₂S₂O₃ (5% w/w, aq.), and brine successively. After drying over Na₂SO₄ and evaporation, the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the product 2a (>95% yield) as a yellow oil.

\[
\text{PhCOI} + \text{I}_2 + \text{CuO} \xrightarrow{\text{DMF, 110°C}} \text{PhCOO}_2\text{H}
\]

>95% yield

(c) The isotope labeling experiment

1. A mixture of 1-(4-methoxyphenyl)ethanone (150.17 mg, 1.0 mmol), I₂ (253.81 mg, 1.0 mmol), and CuO (80 mg, 1.0 mmol) in DMF (3-4 mL) was stirred at 110°C for 2 h. After the reaction completed, the reaction mixture was filtered, diluted with water and extracted with EtOAc (3×20 mL). The extract was washed with Na₂S₂O₃ (5% w/w, aq.), and brine successively. After drying over Na₂SO₄ and evaporation, the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the product 2a (>95% yield).
2. A mixture of 1-(4-methoxyphenyl)ethanone (150.17 mg, 1.0 mmol), I₂ (253.81 mg, 1.0 mmol), CuO (80 mg, 1.0 mmol) and 0.15 mL H₂O (O¹⁸>90%) in anhydrous DMF (3-4 mL) under the Ar atmosphere was stirred at 110°C for 4 h. After the reaction completed, the reaction mixture was filtered, diluted with water and extracted with EtOAc (3×20 mL). The extract was washed with Na₂S₂O₃ (5% w/w, aq.), and brine successively. After drying over Na₂SO₄ and evaporation, the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the product 3c' (92% yield)
3. A mixture of 4-methoxyphenacyl iodine (246 mg, 1.0 mmol), CuI (190 mg, 1.0 mmol) and 0.15mL H$_2$O (O$^{18}$$>$90%) in anhydrous DMF (3-4 mL) under the Ar atmosphere was stirred at 110°C for 4 h. After the reaction completed, the reaction mixture was filtered, diluted with water and extracted with EtOAc (3×20 mL). The extract was washed with Na$_2$S$_2$O$_3$ (5% w/w, aq.), and brine successively. After drying over Na$_2$SO$_4$ and evaporation, the crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the product 3c'' (>95% yield).

![Chemical structure and reaction scheme]

4. Crystallographic data and molecular structure
Crystal structure data for macrocycle 2e: CCDC 844753.
C₉H₇NO₅, chemical formula weight: 209.16, Orthorhombic space group P2(1)/c, \( a = 9.6790(1) \), \( b = 15.1737(15) \), \( c = 6.3703(6) \) Å; \( \alpha = 90.00^\circ \), \( \beta = 92.00^\circ \), \( \gamma = 90.00^\circ \), \( U = 927.02(16) \) Å³, \( T = 298(2) \) K, \( Z = 4 \), DC = 1.499 Mg/M³, \( \mu = 0.125 \) mm⁻¹, \( \lambda = 0.71073 \) Å, F(000) 432, crystal size 0.20 × 0.10× 0.10 mm³, 2289 independent reflections\([R(int) = 0.1244]\), reflections collected 11219, refinement method: full-matrix least-squares on F²: goodness-of-fit on F² 1.049, final R indices \([I > 2\sigma(I)]\), R1 = 0.1007, wR2 = 0.2348, largest diff. peak and hole 0.688Å⁻³ and −0.438eÅ⁻³.

Crystal Structure of 2e

![Figure 1 The X-Ray crystal structure of compound 2e](image)

Crystal structure data for macrocycle 3d: CCDC 844754.
C₁₀H₉NO₅, chemical formula weight: 227.69, Orthorhombic space group P2(1)/c, \( a = 9.077(5) \), \( b = 12.606(7) \), \( c = 9.405(5) \) Å; \( \alpha = 90.00^\circ \), \( \beta = 102.097(9)\)°, \( \gamma = 90.00^\circ \), \( U = 1052.3(10) \) Å³, \( T = 298(2) \) K, \( Z = 4 \), DC = 1.437 Mg/M³, \( \mu = 0.118 \) mm⁻¹, \( \lambda = 0.71073 \) Å, F(000) 474, crystal size 0.20 × 0.20 × 0.20 mm³, 1954 independent reflections\([R(int) = 0.0300]\), reflections collected 10229, refinement method: full-matrix least-squares on F²: goodness-of-fit on F² 1.074, final R indices \([I > 2\sigma(I)]\), R1 = 0.0561, wR2 = 0.1588, largest diff. peak and hole 0.318Å⁻³ and −0.133eÅ⁻³.

Crystal Structure of 3d

![Figure 1 The X-Ray crystal structure of compound 3d](image)

5. Spectral data of compound 3a-3m, 5a-5f

2-oxo-2-phenylethyl formate (2a)

IR (KBr): 3425, 3064, 2933, 1731, 1598, 1540, 1288, 1234, 1171, 1103 cm⁻¹; \(^1\)H NMR (600 MHz, CDCl₃); δ = 8.26 (s, 1H), 7.93 (d, J = 7.8 Hz, 2H), 7.61-7.64 (t, J = 7.2 Hz, 1H), 7.49-7.52 (t, J = 7.8 Hz, 2H), 5.44 (s, 2H); \(^13\)C NMR (150 MHz, CDCl₃); δ = 191.1, 160.0, 134.1, 133.9, 128.9, 127.8, 65.3;


2-oxo-2-(p-tolyl)ethyl formate (2b)

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2011
IR (KBr): 3437, 3046, 2951, 1726, 1692, 1606, 1420, 1371, 1281, 1239, 1170, 1012 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 8.25 (s, 1H), 7.82 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 5.41 (s, 2H), 2.42 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 190.6, 160.0, 145.0, 131.1, 129.5, 127.8, 65.2, 21.7; HRMS (ESI): m/z [M + H]⁺ calcd for C₁₀H₁₀O₃: 179.0703; found: 179.0711.

2-((4-methoxyphenyl)-2-oxoethyl formate (2c)

IR (KBr): 3413, 2944, 2847, 1731, 1682, 1601, 1572, 1512, 1464, 1424, 1372, 1316, 1267, 1111, 1014 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 8.25 (s, 1H), 7.89 (d, J = 7.8 Hz, 2H), 6.95 (d, J = 7.8 Hz, 2H), 5.40 (s, 2H), 3.87 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 189.5, 164.0, 160.1, 130.0, 129.9, 114.0, 65.0, 55.4; HRMS (ESI): m/z [M + H]⁺ calcd for C₁₀H₁₀O₄: 195.0652; found: 195.0143.

2-(2,4-dimethoxyphenyl)-2-oxoethyl formate (2d)

IR (KBr): 3411, 3314, 3097, 2953, 2844, 1729, 1665, 1605, 1478, 1421, 1370, 1336, 1289, 1219, 114.0, 1111, 1017 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 8.25 (s, 1H), 8.00 (d, J = 8.4 Hz, 1H), 6.58 (d, J = 8.4 Hz, 1H), 6.46 (s, 1H), 3.93 (s, 3H), 3.87 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 190.0, 165.6, 161.4, 160.4, 133.2, 117.3, 105.9, 97.9, 69.2, 55.6; HRMS (ESI): m/z [M + H]⁺ calcd for C₁₁H₁₂O₅: 225.0757; found: 225.0753.

2-(4-nitrophenyl)-2-oxoethyl formate (2e)

IR (KBr): 3444, 3109, 2949, 1727, 1702, 1605, 1585, 1427, 1399, 1283, 1210, 1070, 1003 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 8.36 (d, J = 8.4 Hz, 2H), 8.26 (s, 1H), 8.11 (d, J = 8.4 Hz, 2H), 5.47 (s, 2H); ¹³C NMR (150 MHz, CDCl₃): δ = 190.0, 159.8, 150.7, 138.2, 128.9, 124.1, 65.3; HRMS (ESI): m/z [M + H]⁺ calcd for C₉H₇NO₅: 210.0216; found: 210.0404.

2-(4-bromophenyl)-2-oxoethyl formate (2f)

IR (KBr): 3427, 3094, 2945, 1719, 1690, 1585, 1427, 1399, 1283, 1210, 1070, 1003 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 8.25 (s, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 5.40 (s, 2H); ¹³C NMR (150 MHz, CDCl₃): δ = 190.2, 159.9, 132.5, 132.3, 129.3, 129.2, 65.1; HRMS (ESI): m/z [M + H]⁺ calcd for C₉H₇BrO₃: 290.9627; found: 290.9872.

2-(3,4-dichlorophenyl)-2-oxoethyl formate (2g)

IR (KBr): 3449, 3090, 3011, 2942, 1731, 1696, 1582, 1429, 1398, 1287, 1264, 1223, 1172, 1042 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 8.24 (s, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 5.40 (s, 2H); ¹³C NMR (150 MHz, CDCl₃): δ = 190.2, 159.9, 132.5, 132.3, 129.3, 129.2, 65.1; HRMS (ESI): m/z [M + H]⁺ calcd for C₉H₆Cl₂O₃: 234.9767; found: 234.9773.

2-(naphthalen-2-yl)-2-oxoethyl formate (2h)

IR (KBr): 3444, 3109, 2949, 1727, 1702, 1605, 1529, 1372, 1348, 1321, 1284, 1226, 1156, 1006 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 8.25 (s, 1H), 7.82 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 5.41 (s, 2H), 2.42 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 190.6, 160.0, 145.0, 131.1, 129.5, 127.8, 65.2, 21.7; HRMS (ESI): m/z [M + H]⁺ calcd for C₁₃H₁₀O₃: 237.0522; found: 237.0520.

2-[(1,1'-biphenyl)-4-yl]-2-oxoethyl formate (2i)
IR (KBr): 3419, 3036, 2943, 1728, 1697, 1604, 1447, 1422, 1373, 1286, 1237, 1167, 1005 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ =8.27 (s, 1H), 7.99 (d, J = 1.8 Hz, 2H), 7.62 (d, J = 1.8 Hz, 2H), 7.46-7.49 (t, J = 7.8 Hz, 1H), 5.46 (s, 2H); ¹³C NMR (150 MHz, CDCl₃): δ = 191.6, 160.0, 146.7, 139.4, 132.5, 129.0, 128.4, 127.5, 127.2, 65.3; HRMS (ESI): m/z [M + H]⁺ calcd for C₁₅H₁₂O₃: 263.0679; found: 263.0677.

2-(furan-2-yl)-2-oxoethyl acetate (2j)
IR (KBr): 3422, 3131, 2929, 2856, 1730, 1688, 1570, 1468, 1399, 1276, 1161, 1021 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 8.23 (s, 1H), 7.65 (d, J = 1.2 Hz, 1H), 7.31 (d, J = 3.6 Hz, 1H), 6.60-6.61 (q, J = 1.8 Hz, 1H), 5.29 (s, 2H); ¹³C NMR (150 MHz, CDCl₃): δ = 180.5, 159.9, 150.1, 146.9, 117.9, 112.5, 64.4; HRMS (ESI): m/z [M + H]⁺ calcd for C₇H₆O₄: 192.9930; found: 192.9979.

2-oxo-2-(thiophen-2-yl)ethyl acetate (2k)
IR (KBr): 3429, 3096, 3001, 2942, 1724, 1671, 1520, 1413, 1387, 1274, 1252, 1194, 1059 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 8.24 (s, 1H), 7.77 (d, J = 4.2 Hz, 1H), 7.74 (d, J = 4.2 Hz, 1H), 7.18-7.19 (q, J = 4.2 Hz, 1H), 5.34 (s, 1H); ¹³C NMR (150 MHz, CDCl₃): δ = 180.5, 159.9, 150.1, 146.9, 117.9, 112.5, 64.4; HRMS (ESI): m/z [M + H]⁺ calcd for C₇H₇SO₃: 171.00996; found: 171.01104.

2-(benzofuran-2-yl)-2-oxoethyl formate (2l)
IR (KBr): 3414, 2926, 1723, 1695, 1609, 1157, 1138 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 8.26 (s, 1H), 7.72 (d, J = 1.8 Hz, 1H), 7.61 (d, J = 1.8 Hz, 1H), 7.57 (d, J = 1.8 Hz, 1H), 7.50-7.52 (t, J = 1.8 Hz, 1H), 7.32-7.36 (q, J = 1.8 Hz, 1H), 5.43 (s, 2H); ¹³C NMR (150 MHz, CDCl₃): δ = 182.6, 159.9, 155.5, 150.0, 128.8, 126.5, 124.2, 123.5, 113.6, 112.4, 65.0; HRMS (ESI): m/z [M + H]⁺ calcd for C₁₁H₉O₄: 205.04858; found: 205.04954.

2-(1H-indol-3-yl)-2-oxoethyl formate (2m)
IR (KBr): 3237, 2931, 1729, 1649, 1579, 1520, 1415, 1313, 1238, 1195, 1156 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 8.76 (s, 1H), 8.33 (s, 1H), 8.29 (s, 1H), 7.94 (s, 1H), 7.45 (s, 1H), 7.33 (s, 1H), 5.31 (s, 2H); ¹³C NMR (150 MHz, d6-DMSO): δ = 187.1, 161.9, 136.3, 133.8, 125.3, 123.3, 122.2, 112.8, 112.4, 65.5; HRMS (ESI): m/z [M + H]⁺ calcd for C₁₁H₉NO₃: 204.0655; found: 204.0653.

2-(4-hydroxyphenyl)-2-oxoethyl formate (2n)
IR (KBr): 3349, 3029, 1727, 1677, 1604, 1577, 1515, 1432, 1370, 1352, 1289, 1250, 1217, 1192, 1168, 1034, 951, 847 cm⁻¹; ¹H NMR (600 MHz, DMSO): δ = 10.58 (s, 1H), 8.40 (s, 1H), 7.86 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 9.0 Hz, 2H), 5.49 (s, 2H); ¹³C NMR (150 MHz, d6-DMSO): δ = 190.3, 162.6, 161.7, 130.5, 125.4, 115.6, 115.5, 65.6; HRMS (ESI): m/z [M + H]⁺ calcd for C₉H₈O₄: 181.0495; found: 181.0501.

(E)-2-oxo-4-phenylbut-3-en-1-yl formate (2o)
IR (KBr): 3435, 3060, 2934, 1730, 1685, 1613, 1576, 1495, 1450, 1376, 1332, 1268, 1170, 1091, 1055 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 8.21 (s, 1H), 7.67 (d, J = 16.2 Hz, 1H), 7.55 (d, J = 9.0 Hz, 2H), 7.38-7.41 (m, 3H), 6.79 (d, J = 16.2 Hz, 1H), 5.03 (s, 2H), 2.39 (s, 2H); ¹³C NMR (150 MHz, CDCl₃): δ = 191.3, 160.0, 144.5, 133.8, 131.1, 129.0, 128.5, 121.1, 66.5; HRMS (ESI): m/z [M + H]⁺ calcd for C₁₂H₁₄O₃: 191.0703; found: 191.0865.
(E)-2-oxo-4-(p-tolyl)but-3-en-1-yl formate (2p)

IR (KBr): 3440, 2942, 1728, 1690, 1599, 1511, 1415, 1372, 1270, 1167, 1087, 1037 cm\(^{-1}\); \(^1^H\) NMR (600 MHz, CDCl\(_3\)): \(\delta = 8.23\) (s, 1H), 7.65-7.68 (q, J = 16.2 Hz, 1H), 7.46 (d, J = 7.8 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 6.75-6.78 (q, J = 16.2 Hz, 1H), 5.03 (s, 2H), 2.39 (s, 3H); \(^1^C\) NMR (150 MHz, CDCl\(_3\)): \(\delta = 191.3, 160.0, 144.6, 141.8, 131.1, 129.8, 128.5, 120.1, 66.5, 21.5\); HRMS (ESI): m/z [M + Na]\(^+\) calcd for C\(_{12}\)H\(_{12}\)O\(_3\): 227.0679; found: 227.5765.

(E)-4-(4-methoxyphenyl)-2-oxobut-3-en-1-yl formate (2q)

IR (KBr): 3445, 2934, 2837, 1671, 1594, 1511, 1421, 1209, 1145, 1095, 1025 cm\(^{-1}\); \(^1^H\) NMR (600 MHz, CDCl\(_3\)): \(\delta = 8.15\) (s, 1H), 7.58 (d, J = 15.6 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.08 (s, 1H), 6.61 (d, J = 16.4 Hz, 1H), 4.96 (d, J = 8.4 Hz, 2H), 3.79 (s, 3H); \(^1^C\) NMR (100 MHz, CDCl\(_3\)): \(\delta = 191.2, 162.1, 160.0, 144.3, 130.4, 126.5, 118.8, 114.5, 66.6, 55.4\); HRMS (ESI): m/z [M + H]\(^+\) calcd for C\(_{12}\)H\(_{12}\)O\(_4\): 224.0628; found: 224.0651.

(E)-4-(3,4-dimethoxyphenyl)-2-oxobut-3-en-1-yl formate (2r)

IR (KBr): 3417, 2937, 2841, 1716, 1680, 1620, 1594, 1443, 1423, 1268, 1234, 1166, 1139, 1084, 1022 cm\(^{-1}\); \(^1^H\) NMR (600 MHz, CDCl\(_3\)): \(\delta = 8.24\) (s, 1H), 7.65 (d, J = 16.2 Hz, 1H), 7.17 (d, J = 7.8 Hz, 1H), 7.08 (s, 1H), 6.90 (d, J = 8.4 Hz, 1H), 6.69 (d, J = 16.2 Hz, 1H), 5.05 (s, 2H), 3.94 (s, 6H); \(^1^C\) NMR (150 MHz, CDCl\(_3\)): \(\delta = 191.2, 160.0, 151.8, 149.2, 144.6, 126.7, 123.7, 118.9, 111.0, 110.0, 66.5, 55.8\); HRMS (ESI): m/z [M + H]\(^+\) calcd for C\(_{13}\)H\(_{15}\)O\(_5\): 251.09061; found: 251.09140.

(E)-4-(4-(benzyloxy)-3-methoxyphenyl)-2-oxobut-3-en-1-yl formate (2s)

IR (KBr): 3442, 2943, 1724, 1676, 1619, 1593, 1515, 1469, 1425, 1384, 1271, 1235, 1141, 1087, 1034 cm\(^{-1}\); \(^1^H\) NMR (600 MHz, CDCl\(_3\)): \(\delta = 8.21\) (s, 1H), 7.61 (d, J = 16.2 Hz, 1H), 7.38-7.36 (t, J = 7.2 Hz, 2H), 7.32 (d, J = 7.2 Hz, 1H), 7.08 (s, 2H), 6.88 (d, J = 8.4 Hz, 1H), 6.66 (d, J = 16.2 Hz, 1H), 5.19 (s, 2H), 5.01 (s, 2H), 3.92 (s, 3H); \(^1^C\) NMR (150 MHz, CDCl\(_3\)): \(\delta = 191.1, 159.9, 151.0, 149.7, 144.5, 136.3, 128.6, 128.0, 127.1, 123.3, 119.1, 113.3, 110.4, 70.7, 66.5, 56.0\); HRMS (ESI): m/z [M + H]\(^+\) calcd for C\(_{19}\)H\(_{18}\)O\(_5\): 349.1046; found: 349.1040.

(E)-4-(4-(dimethylamino)phenyl)-2-oxobut-3-en-1-yl formate (2t)

IR (KBr): 3437, 2925, 1725, 1688, 1666, 1580, 1528, 1436, 1370, 1268, 1227, 1173, 1144, 1083 cm\(^{-1}\); \(^1^H\) NMR (600 MHz, CDCl\(_3\)): \(\delta = 8.23\) (s, 1H), 7.64 (d, J = 16.2 Hz, 1H), 7.38-7.36 (t, J = 7.2 Hz, 2H), 7.32 (d, J = 7.2 Hz, 1H), 7.08 (s, 2H), 6.88 (d, J = 8.4 Hz, 1H), 6.66 (d, J = 16.2 Hz, 1H), 5.19 (s, 2H), 5.01 (s, 2H), 3.92 (s, 3H); \(^1^C\) NMR (150 MHz, CDCl\(_3\)): \(\delta = 191.1, 159.9, 151.0, 149.7, 144.5, 136.3, 128.6, 128.0, 127.1, 123.3, 119.1, 113.3, 110.4, 70.7, 66.5, 56.0\); HRMS (ESI): m/z [M + H]\(^+\) calcd for C\(_{13}\)H\(_{13}\)NO\(_3\): 256.0944; found: 256.0940.

(E)-4-(3-nitrophenyl)-2-oxobut-3-en-1-yl formate (2u)

IR (KBr): 3436, 3071, 2929, 1727, 0718, 1680, 1629, 1526, 1430, 1354, 1206, 1171, 1099 cm\(^{-1}\); \(^1^H\) NMR (600 MHz, CDCl\(_3\)): \(\delta = 8.40\) (s, 1H), 8.23 (d, J = 7.8 Hz, 1H), 8.21 (s, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.70 (d, J = 16.2 Hz, 1H), 7.60-7.69 (t, J = 7.8 Hz, 1H), 6.93 (d, J = 16.8 Hz, 1H), 5.04 (s, 2H); \(^1^C\) NMR (150 MHz, CDCl\(_3\)): \(\delta = 191.0, 159.9, 159.8, 148.6, 141.4, 135.6, 134.2, 130.1, 125.1, 123.4, 122.6, 122.5, 66.8\); HRMS (ESI): m/z [M + H]\(^+\) calcd for C\(_{13}\)H\(_{13}\)NO\(_2\): 236.0544; found: 236.0553.
IR (KBr): 3421, 3112, 3065, 2931, 1718, 1681, 1593, 1513, 1343, 1178, 1106 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 8.28 (d, J = 8.4 Hz, 2H), 8.24 (s, 1H), 7.74 (d, J = 8.4 Hz, 3H), 6.94 (d, J = 15.6 Hz, 1H), 5.06 (s, 2H); ¹³C NMR (150 MHz, CDCl₃): δ = 191.0, 159.8, 148.8, 141.4, 140.0, 129.1, 124.4, 124.3, 66.8; HRMS (ESI): m/z [M + H]⁺ calecd for C₁₁H₉NO₅: 236.0553; found: 236.0558.

(E)-4-(4-hydroxyphenyl)-2-oxobut-3-en-1-yl formate (2w)

IR (KBr): 3380, 2925, 2855, 1729, 1682, 1584, 1515, 1453, 1379, 1286, 1171, 1024 cm⁻¹; ¹H NMR (600 MHz, DMSO): δ = 10.21 (s, 1H), 8.39 (s, 1H), 7.65 (d, J = 16.8 Hz, 1H), 7.61 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 7.8 Hz, 2H), 6.79 (d, J = 16.8 Hz, 1H), 5.15 (s, 2H); ¹³C NMR (150 MHz, CDCl₃): δ = 192.0, 160.3, 143.9, 130.9, 125.2, 119.0, 116.0, 66.8; HRMS (ESI): m/z [M + H]+= calcd for C₁₁H₁₀O₄: 229.0471; found: 229.0782.

(E)-4-(4-bromophenyl)-2-oxobut-3-en-1-yl formate (2x)

IR (KBr): 3433, 2998, 2934, 2926, 1725, 1666, 1584, 1428, 1391, 1285, 1261, 1190, 1164, 1072, 1008 cm⁻¹; ¹H NMR (600 MHz, DMSO): δ = 8.22 (s, 1H), 7.62 (d, J = 16.2 Hz, 1H), 7.54 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 16.2 Hz, 1H), 5.02 (s, 2H); ¹³C NMR (150 MHz, CDCl₃): δ = 191.2, 159.9, 143.1, 132.7, 132.3, 129.8, 125.5, 121.5, 66.6; HRMS (ESI): m/z [M + H]+= calcd for C₁₁H₉BrO₃: 290.99627; found: 290.9631.

2-oxo-2-phenylethyl acetate (3a)

IR (KBr): 3472, 3064, 2937, 1750, 1703, 1597, 1448, 1422, 1375, 1221, 1085, 998 cm⁻¹; ¹H NMR (600 MHz, CDCl₃): δ = 7.92 (d, J = 8.4 Hz, 2H), 7.59-7.63 (t, J = 7.2 Hz, 1H), 7.47-7.51 (t, J = 7.2 Hz), 5.35 (s, 2H), 2.23 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 192.1, 170.4, 134.0, 133.8, 128.8, 127.7, 66.0, 20.5; HRMS (ESI): m/z [M + H]+= calcd for C₁₀H₁₁O₃: 179.07027; found: 179.06977.

2-oxo-2-(p-tolyl)ethyl acetate (3b)

IR (KBr): 3465, 2954, 2926, 1749, 1699, 1605, 1420, 1372, 1289, 1226, 1180, 1085, 1051 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.74 (d, J = 8.0 Hz, 2H), 5.25 (s, 2H), 5.35 (s, 3H), 2.16 (s, 3H),; ¹³C NMR (100 MHz, CDCl₃): δ = 191.7, 144.8, 131.6, 129.5, 129.4, 128.7, 127.8, 65.9, 21.7, 20.6; HRMS (ESI): m/z [M + H]+= calcd for C₁₁H₁₂O₃: 215.0679; found: 215.0680.

2-(4-methoxyphenyl)-2-oxoethyl acetate (3c)

IR (KBr): 3465, 3040, 2954, 1926, 1749, 1696, 1605, 1571, 1420, 1372, 1289, 1226, 1180, 1085, 1051 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.74 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 5.25 (s, 2H), 5.35 (s, 3H), 2.16 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ = 190.6, 170.5, 164.0, 130.0, 127.1, 65.7, 55.5, 20.6; HRMS (ESI): m/z [M + H]+= calcd for C₁₁H₁₃O₄: 209.07980; found: 209.08084.

2-(4-nitrophenyl)-2-oxoethyl acetate (3d)

IR (KBr): 3478, 3119, 2926, 2855, 1748, 1703, 1603, 1524, 1416, 1373, 1348, 1319, 1284, 1248, 1218, 1107, 1081 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 8.35 (d, J = 8.0 Hz, 2H), 8.09 (d, J = 8.0 Hz, 2H), 5.34 (s, 2H), 2.24 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 191.0, 170.3, 150.7, 138.6, 128.9, 124.1, 66.0, 29.7, 20.5; HRMS (ESI): m/z [M + H]+= calcd for C₁₁H₁₀NO₅: 224.05463; found: 224.05535.

2-(4-bromophenyl)-2-oxoethyl acetate (3e)
IR (KBr): 3487, 3376, 2990, 2950, 1746, 1694, 1585, 1430, 1398, 1378, 1292, 1225, 1069 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.77-7.80 (m, 2H), 7.63-7.65 (m, 2H), 5.30 (s, 2H), 2.23 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 191.3, 170.3, 132.8, 132.2, 129.2, 129.1, 65.8, 20.5; HRMS (ESI): m/z [M + H]$^+$ calcd for C$_{10}$H$_9$BrO$_3$: 278.9627; found: 278.9631.

2-(furan-2-yl)-2-oxoethyl acetate (3f)
IR (KBr): 3484, 3135, 2942, 1751, 1693, 1572, 1469, 1421, 1400, 1374, 1229, 1162, 1080, 1029 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.62 (d, $J = 2.4$ Hz, 1H), 7.29 (d, $J = 4.0$ Hz, 1H), 6.58-6.59 (q, $J = 2$ Hz, 1H), 5.19 (s, 2H), 2.22 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 181.7, 170.3, 150.5, 146.7, 117.7, 112.5, 65.3, 20.5; HRMS (ESI): m/z [M + H]$^+$ calcd for C$_8$H$_8$O$_4$: 191.0315; found: 191.0312.

2-oxo-2-(thiophen-2-yl)ethyl acetate (3g)
IR (KBr): 3484, 3135, 2942, 1751, 1693, 1572, 1469, 1421, 1400, 1374, 1229, 1162, 1080, 1029 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.76 (d, $J = 2.4$ Hz, 1H), 7.71 (d, $J = 4.8$ Hz, 1H), 7.16-7.18 (t, $J = 4.4$ Hz, 1H), 5.23 (s, 2H), 2.23 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 185.4, 170.3, 134.3, 131.9, 128.2, 65.7, 20.5; HRMS (ESI): m/z [M + H]$^+$ calcd for C$_8$H$_8$O$_3$S: 207.0086; found: 207.0082.

2-(naphthalen-2-yl)-2-oxoethyl acetate (3h)
IR (KBr): 3466, 3062, 2943, 1750, 1696, 1624, 1592, 1575, 1572, 1469, 1421, 1400, 1374, 1229, 1162, 1080, 1029 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.41 (s, 1H), 7.951-7.976 (q, $J = 8.4$ Hz, 2H), 7.891-7.938 (t, $J = 8.4$ Hz, 1H), 7.56-7.62 (m, 2H), 5.47 (s, 2H), 2.25 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 192.1, 170.5, 135.9, 132.3, 131.5, 129.5, 128.8, 127.0, 123.2, 66.1, 20.6; HRMS (ESI): m/z [M + H]$^+$ calcd for C$_{14}$H$_{12}$O$_3$: 251.0679; found: 251.0885.

(E)-2-oxo-4-phenylbut-3-en-1-yl acetate (3o)
IR (KBr): 3457, 2932, 1751, 1696, 1624, 1592, 1467, 1417, 1375, 1235, 1176, 1081, 1026, 1008 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.67 (d, $J = 16.4$ Hz, 1H), 7.55-7.58 (q, $J = 6.8$ Hz, 2H), 6.79 (s, $J = 16.0$ Hz, 1H), 4.95 (s, 3H), 2.22 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 192.41, 170.3, 144.2, 134.0, 131.0, 129.0, 128.5, 121.5, 67.4, 20.6; HRMS (ESI): m/z [M + H]$^+$ calcd for C$_{12}$H$_{12}$O$_3$: 227.0679; found: 227.0895.

(E)-4-(4-(benzyloxy)-3-methoxyphenyl)-2-oxobut-3-en-1-yl acetate (3r)
IR (KBr): 3452, 3016, 2923, 1724, 1680, 1620, 1513, 1454, 1424, 1384, 1367, 1326, 1271, 1226, 1200, 1168, 1137, 1066, 1025 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.67 (d, $J = 16.4$ Hz, 1H), 7.55-7.58 (q, $J = 6.8$ Hz, 2H), 6.79 (s, $J = 16.0$ Hz, 1H), 4.95 (s, 3H), 2.22 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 192.1, 170.4, 150.9, 149.7, 144.1, 136.3, 128.7, 128.1, 127.2, 123.2, 119.5, 113.3, 110.3, 70.8, 67.2, 56.0, 20.6; HRMS (ESI): m/z [M + H]$^+$ calcd for C$_{20}$H$_{20}$O$_5$: 341.1384; found: 341.1387.

(E)-4-(3,4-dimethoxyphenyl)-2-oxobut-3-en-1-yl acetate (3s)
IR (KBr): 3487, 3376, 2990, 2950, 1746, 1694, 1585, 1430, 1398, 1378, 1292, 1225, 1069 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.77-7.80 (m, 2H), 7.63-7.65 (m, 2H), 5.30 (s, 2H), 2.23 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 191.3, 170.3, 132.8, 132.2, 129.2, 129.1, 65.8, 20.5; HRMS (ESI): m/z [M + H]$^+$ calcd for C$_{10}$H$_9$BrO$_3$: 278.9627; found: 278.9631.
113.3, 110.3, 70.8, 67.2, 56.0, 20.6; HRMS (ESI): m/z [M + H]^+ calcd for C_{14}H_{16}O_5: 287.0890; found: 287.0888.

**(E)-4-(3-nitrophenyl)-2-oxobut-3-en-1-yl acetate (3v)**

IR (KBr): 3460, 3067, 2927, 2855, 1740, 1667, 1630, 1439, 1384, 1351, 1250, 1199, 1068 cm⁻¹; \(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 8.42\) (s, 1H), 8.26 (d, J = 7.2 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 16.04 Hz, 1H), 7.612-7.685 (t, J = 8.4 Hz, 1H), 6.91 (d, J = 16.4 Hz, 2H), 4.95 (s, 1H), 2.23 (s, 3H); \(^1\)C NMR (100 MHz, CDCl₃): \(\delta = 192.0, 141.1, 134.2, 130.1, 125.1, 123.7, 122.6, 67.6, 20.5\); HRMS (ESI): m/z [M + H]^+ calcd for C_{12}H_{12}NO_{5}: 250.07035; found: 250.07100.

**(E)-4-(4-nitrophenyl)-2-oxobut-3-en-1-yl acetate (3w)**

IR (KBr): 3443, 2927, 1740, 1702, 1621, 1594, 1513, 1415, 1349, 1265, 1235, 1115, 1058, 1002 cm⁻¹; \(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 8.27\) (d, J = 7.6 Hz, 2H), 7.72 (d, J = 7.2 Hz, 2H), 7.68 (s, 1H), 6.90 (d, J = 16.4 Hz, 1H), 2.23 (s, 3H); \(^1\)C NMR (100 MHz, CDCl₃): \(\delta = 191.9, 170.2, 148.8, 141.0, 140.1, 129.0, 124.8, 124.2, 67.6, 20.5\); HRMS (ESI): m/z [M + H]^+ calcd for C_{12}H_{12}NO_{5}: 250.07035; found: 250.07100.

7. **Appendix:** spectral Copies of \(^1\)H NMR and \(^13\)C NMR of compounds obtained in this Study