Supporting Materials

Heterogeneous Cu/OMS-2 as an efficient catalysts for the synthesis of tetrasubstituted 1,4-enediones and 4H-pyrido[1,2-a]-pyrimidin-4-ones

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Experimental
All reagents were purchased from commercial suppliers and used without further purification. Metal salts and catalyst supports were commercially available and were used directly. All experiments were carried out under air. Flash chromatography was carried out with Merck silica gel 60 (200-300 mesh). Analytical TLC was performed with Merck silica gel 60 F254 plates, and the products were visualized by UV detection. $^1$H NMR and $^{13}$C NMR (400 and 100 MHz respectively) spectra were recorded in CDCl$_3$. Chemical shifts (δ) are reported in ppm using TMS as internal standard, and spin-spin coupling constants (J) are given in Hz. All heterogeneous catalysts are synthesized by wet impregnation in deionized water and Cu(OH)$_x$/OMS-2 is made by deposition-precipitation in water.

**Preparation of OMS-2**[1]

5.89 g of KMnO$_4$ in 100 mL of deionized water was added to a solution of 8.8 g of MnSO$_4$ · H$_2$O in 30 mL of deionized water and 3 mL concentrated HNO$_3$. The solution was refluxed at 100 °C for 24 hours, and the product was filtered, washed, and dried at 120 °C for 8 hours. Finally, the dry OMS-2 was calcined in a muffle furnace at 350 °C for 2 hours. Then, the black powder OMS-2 was obtained.

**Preparation of Cu/OMS-2**[2]

Support OMS-2 (2 g) was added to a 50 mL round-bottom flask. A
solution of Cu(NO\textsubscript{3})\textsubscript{2} \cdot 3\textsubscript{H}\textsubscript{2}O (0.15 g) in deionized water (10 mL) was added to OMS-2, and additional deionized water (10 mL) was added to wash down the sides of the flask. Then the flask was submerged into an ultrasound bath for 3 hours at room temperature and stirred for further 20 hours at room temperature. After that, the water was distilled under reduced pressure on a rotary evaporator at 80 °C for more than 2 hours. Finally, the black powder was dried into an oven at 110 °C for 4 hours followed by calcination at 350 °C for 2 hours. The Inductive Coupled Plasma Optical Emission Spectrum (ICP-OES) showed Cu content is 1.3 wt%.

**General procedure for Cu/OMS-2-catalyzed synthesis of tetrasubstituted 1,4-enediones 3**

Cu/OMS-2 (30 mg, 2 mol%), 1,4-enediones 1 (0.3 mmol), N-substituted nucleophiles 2 (0.6 mmol), DMSO (1.8 mL) were added to a flask with a bar. The flask was stirred at 80 °C for 12 hours under air. After cooling to room temperature, the mixture was diluted with ethyl acetate and filtered. The filtrate was removed under reduced pressure to get the crude product, which was further purified by silica gel chromatography (petroleum/ethyl acetate = 4/1 as eluent) to yield corresponding product. The identity and purity of the products was confirmed by \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopic analysis.
General procedure for Cu/OMS-2-catalyzed synthesis of 4H-pyrido[1,2-a]-pyrimidin-4-ones 5

Cu/OMS-2 (30 mg, 2 mol%), 1,4-enediones 1 (0.3 mmol), 2-aminopyridines 4 (0.6 mmol), DMSO (1.8 mL) were added to a flask with a bar. The flask was stirred at 80 °C for 12 hours under air. After cooling to room temperature, the mixture was diluted with ethyl acetate and filtered. The filtrate was removed under reduced pressure to get the crude product, which was further purified by silica gel chromatography (petroleum/ethyl acetate = 2/1 as eluent) to yield corresponding product. The identity and purity of the products was confirmed by ¹H and ¹³C NMR spectroscopic analysis.

Hot filtration experiment

Cu/OMS-2 (30 mg, 2 mol%), 1,4-enedione 1g (0.3 mmol), pyrazole 2a (0.6 mmol), DMSO (1.8 mL) were added to a flask with a stirring bar. The mixture was stirred at 80 °C for 3 hours under air. Then, Cu/OMS-2 was removed by hot filtration. The filtrate was kept at 80 °C under stirring again for 9 hours. ICP-AES was used to analyze the filtrate.

Characterization of Cu/OMS-2

The BET surface areas and porosities of OMS-2 and Cu/OMS-2 were determined by N₂ adsorption-desorption at 77 K and the results were
listed in Table S1. Transmission electron microscopy (TEM) was employed to characterize the retrieved Cu/OMS-2 (Figure S1). In addition, X-ray photoelectron spectroscopy (XPS) was also used to characterize Cu/OMS-2 (Figure S2).

**Table S1.** BET surface area, pore volume, pore size and Cu content of catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (Å)</th>
<th>Cu content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMS-2</td>
<td>158</td>
<td>0.52</td>
<td>127.0</td>
<td>_</td>
</tr>
<tr>
<td>Cu/OMS-2</td>
<td>127</td>
<td>0.48</td>
<td>137.2</td>
<td>1.3</td>
</tr>
</tbody>
</table>

**Figure S1.** TEM images of Cu/OMS-2 after the first use
Figure S2. XPS profiles of (a) Mn 2p and (b) Cu 2p
Spectrum data of the products

2-Benzoyl-1,4-diphenyl-3-(1H-pyrazol-1-yl)but-2-ene-1,4-dione (3aa)\textsuperscript{[3]}

\[
\text{White solid, isolated yield 72\%, 87 mg. } \text{\(^1\)H NMR (400 MHz, CDCl}_3\text{) } \delta = 8.00 (d, 2H, } J = 8 \text{ Hz), 7.81-7.78 (m, 4H), 7.54-7.48 (m, 2H), 7.44-7.35 (m, 7H), 7.27 (t, 2H, } J = 8 \text{ Hz), 6.17 (t, 1H, } J = 4 \text{ Hz); } \\
\text{\(^{13}\)C NMR (100 MHz, CDCl}_3\text{) } \delta = 191.9, 191.7, 189.2, 143.3, 142.9, 136.6, 136.2, 135.3, 134.1, 133.6, 133.4, 130.6, 129.4, 129.1, 129.0, 128.8, 128.7, 128.4, 109.4.
\]

2-Benzoyl-1-phenyl-3-(1H-pyrazol-1-yl)-4-(p-tolyl)but-2-ene-1,4-dione (3ba)\textsuperscript{[3]}

\[
\text{White solid, isolated yield 57\%, 72 mg. } \text{\(^1\)H NMR (400 MHz, CDCl}_3\text{) } \delta = 8.00 (d, 2H, } J = 8 \text{ Hz), 7.80 (d, 2H, } J = 8 \text{ Hz), 7.71 (d, 2H, } J = 8 \text{ Hz), 7.52 (t, 1H, } J = 8 \text{ Hz), 7.45-7.36 (m, 5H), 7.31 (t, 2H, } J = 8 \text{ Hz), 6.19-6.17 (m, 1H), 2.37 (s, 3H); } \\
\text{\(^{13}\)C NMR (100 MHz, CDCl}_3\text{) } \delta = 192.0, 191.7, 188.8, 145.5, 143.5, 142.8, 136.6, 136.3, 133.6, 133.3, 132.9, 130.6, 129.6, 129.4, 129.3, 129.0, 128.7, 128.4, 109.3, 21.8.
\]

2-Benzoyl-4-(4-methoxyphenyl)-1-phenyl-3-(1H-pyrazol-1-yl)-but-2-ene-1,4-dione (3ca)\textsuperscript{[3]}

\[
\text{Light yellow solid, isolated yield 68\%, 87 mg. } \text{\(^1\)H NMR (400 MHz, CDCl}_3\text{) } \delta = 7.99 (d, 2H, } J = 4 \text{ Hz), 7.83 (d, 2H, } J = 8 \text{ Hz), 7.77 (d, 2H, } J = 8 \text{ Hz), 7.5 (t, 1H, } J = 8 \text{ Hz), 7.44 – 7.37 (m, 5H), 7.29 (t, 2H, } J = 8 \text{ Hz), 6.86 (d, 2H, } J = 8 \text{ Hz), 6.19-6.18 (m, 1H), 3.83 (s, 1H); } \\
\text{\(^{13}\)C NMR (100 MHz, CDCl}_3\text{) } \delta = 192.0, 191.8, 187.6, 164.5, 143.3, 142.8, 136.7, 136.4, 133.5, 133.4, 133.3, 132.5, 131.8, 130.5, 130.3, 129.5, 129.0, 128.7, 128.4, 128.4, 114.2, 109.3, 55.5.
\]

2-Benzoyl-4-(4-chlorophenyl)-1-phenyl-3-(1H-pyrazol-1-yl)-but-2-ene-1,4-dione (3da)\textsuperscript{[3]}

\[
\text{White solid, isolated yield 56\%, 75 mg. } \text{\(^1\)H NMR (400 MHz, CDCl}_3\text{) } \delta = 7.99 (d, 2H, } J = 8 \text{ Hz), 7.80}
\]
(d, 2H, J = 4 Hz), 7.74 (d, 2H, J = 8 Hz), 7.52 (t, 1H, J = 8 Hz), 7.48-7.36 (m, 7H), 7.30 (t, 2H, J = 8 Hz), 6.21-6.19 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 191.8, 191.6, 188.0, 143.3, 143.1, 140.7, 136.5, 136.0, 133.9, 133.7, 133.6, 130.5, 130.4, 129.4, 129.3, 129.0, 128.8, 128.5, 109.6.

2-Benzyol-4-(4-bromophenyl)-1-phenyl-3-(1H-pyrazol-1-yl)but-2-ene-1,4-dione (3ea)\[3\]

White solid, isolated yield 59%, 87 mg. $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.98 (d, 2H, J = 8 Hz), 7.80 (d, 2H, J = 4 Hz), 7.66 (d, 2H, J = 8 Hz), 7.55-7.50 (m, 3H), 7.30 (t, 2H, J = 8 Hz), 6.20-6.19 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 191.8, 191.6, 188.2, 143.3, 143.1, 136.4, 136.0, 134.1, 133.9, 133.6, 132.2, 132.2, 132.0, 130.5, 130.4, 130.0, 129.9, 129.6, 129.4, 129.0, 128.8, 128.5, 109.6.

2-Benzyol-4-(4-fluorophenyl)-1-phenyl-3-(1H-pyrazol-1-yl)but-2-ene-1,4-dione (3fa)\[3\]

White solid, isolated yield 75%, 96 mg. $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.99 (d, 2H, J = 8 Hz), 7.84-7.79 (m, 4H), 7.52 (t, 1H, J = 8 Hz), 7.46-7.38 (m, 5H), 7.30 (t, 2H, J = 8 Hz), 6.20-6.19 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 191.8, 191.7, 187.6, 167.5, 164.9, 143.3, 143.0, 136.5, 136.1, 133.8, 133.7, 133.6, 132.0, 131.9, 131.7, 130.5, 130.4, 129.9, 129.6, 129.4, 129.0, 128.8, 128.6, 128.5, 116.3, 116.1, 109.6.

Ethyl 2-benzoyl-4-oxo-4-phenyl-3-(1H-pyrazol-1-yl)but-2-enoate (3ga)\[3\]

White solid, isolated yield 80% (E:Z=66:34), 90 mg. $^1$H NMR (400 MHz, CDCl$_3$) δ = 8.07 (d, 2H, J = 4 Hz), 8.03 (d, 2H, J = 8 Hz), 7.63 (t, 1H, J = 8 Hz), 7.56-7.52 (m, 3H), 7.46 (t, 3H, J = 8 Hz), 7.38-7.36 (m, 2H), 4.04 (q, 2H, J = 8 Hz), 0.96 (t, 3H, J = 8 Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 191.1, 190.5, 189.1, 189.0, 164.6, 163.9, 144.6, 143.5, 143.1, 136.8, 135.3, 135.1, 134.4, 134.1, 133.4, 133.3, 130.7, 130.3, 129.1, 129.1, 129.0, 128.8, 128.7, 128.6, 128.5, 119.0, 109.6, 109.4, 62.0, 13.7, 13.5.

Ethyl 2-benzoyl-4-oxo-4-(p-tolyl)-3-(1H-pyrazol-1-yl)but-2-enoate (3ha)
Yellow solid, isolated yield 78% \((E:Z=77:23)\), 90 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.07\) (d, 2H, \(J = 4\) Hz), 8.03 (d, 2H, \(J = 8\) Hz), 7.63 (t, 1H, \(J = 8\) Hz), 7.56-7.52 (m, 3H), 7.46 (t, 3H, \(J = 8\) Hz), 7.38-7.36 (m, 2H), 4.04 (q, 2H, \(J = 8\) Hz), 0.96 (t, 3H, \(J = 8\) Hz); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 191.2, 188.7, 163.9, 145.7, 144.8, 143.4, 143.0, 136.8, 133.4, 133.3, 132.7, 130.7, 130.2, 129.9, 129.5, 129.3, 129.1, 128.8, 128.6, 128.4, 118.7, 109.5, 61.9, 21.8, 13.5.

**Ethyl 2-benzoyl-4-(4-methoxyphenyl)-3-(1H-pyrazol-1-yl)-4-oxobut-2-enoate (3ia)**

![Chemical Structure](image)

White solid, isolated yield 87% \((E:Z=67:33)\), 105 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.02\) (t, 4H, \(J = 8\) Hz), 7.46-7.38 (m, 5H), 6.99 (d, 2H, \(J = 8\) Hz), 6.22-6.21 (m, 1H), 4.05 (q, 2H, \(J = 8\) Hz), 3.87 (s, 3H), 0.97 (t, 3H, \(J = 8\) Hz); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 191.2, 190.5, 187.6, 187.5, 164.7, 164.6, 164.4, 163.8, 144.8, 144.6, 143.3, 142.9, 136.9, 136.8, 133.4, 133.2, 131.7, 131.5, 130.7, 130.3, 128.8, 128.7, 128.6, 128.2, 126.5, 118.7, 114.5, 114.2, 109.4, 109.2, 62.0, 61.8, 55.6, 55.5, 13.7, 13.5.

**Ethyl 2-benzoyl-4-(4-nitrophenyl)-3-(1H-pyrazol-1-yl)-4-oxobut-2-enoate (3ja)**

![Chemical Structure](image)

Yellow solid, isolated yield 67\% \((E:Z=87:13)\), 84 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.37\) (d, 2H, \(J = 8\) Hz), 8.21 (d, 2H, \(J = 8\) Hz), 8.03 (d, 2H, \(J = 8\) Hz), 7.60 (t, 1H, \(J = 8\) Hz), 7.51-7.47 (m, 3H), 7.43 (d, 1H, \(J = 4\) Hz), 6.29-6.28 (m, 1H), 4.06 (q, 2H, \(J = 8\) Hz), 1.00 (t, 3H, \(J = 8\) Hz); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 190.8, 187.3, 163.9, 150.7, 144.0, 143.9, 139.7, 136.2, 134.0, 130.2, 129.7, 128.9, 128.7, 124.3, 119.3, 110.1, 62.4, 13.6.

**Ethyl 2-benzoyl-4-oxo-4-(4-(trifluoromethyl)phenyl)-3-(1H-pyrazol-1-yl)but-2-enoate (3ka)**

![Chemical Structure](image)

Yellow solid, isolated yield 88\% \((E:Z=90:10)\), 117 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.17\) (d, 2H, \(J = 8\) Hz), 8.03 (d, 2H, \(J = 8\) Hz), 7.79 (d, 2H, \(J = 8\) Hz), 7.58 (t, 1H, \(J = 8\) Hz), 7.50-7.46 (m, 3H), 7.40 (d, 1H, \(J = 4\) Hz), 6.27-6.26 (m, 1H), 4.06 (q, 2H, \(J = 8\) Hz), 0.99 (t, 3H, \(J = 8\) Hz); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 190.9, 188.0, 163.9, 144.2, 143.8, 137.8, 136.4, 135.4, 134.5, 129.0, 128.9, 128.8, 126.2, 125.7, 124.2, 120.0, 119.2, 109.9, 62.2, 13.6.

**Ethyl 2-benzoyl-4-(naphthalen-2-yl)-3-(1H-pyrazol-1-yl)-4-oxobut-2-enoate (3la)**

![Chemical Structure](image)
Yellow solid, isolated yield 90% (E:Z = 81:19), 114 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.54\) (s, 1H), 8.18 (d, 1H, \(J = 8\) Hz), 8.08 (d, 2H, \(J = 8\) Hz), 7.98 (t, 2H, \(J = 8\) Hz), 7.90 (d, 1H, \(J = 8\) Hz), 7.87 (t, 1H, \(J = 8\) Hz), 7.59-7.55 (m, 2H), 7.48 (d, 3H, \(J = 4\) Hz), 7.43 (d, 1H, \(J = 4\) Hz), 4.03 (q, 2H, \(J = 8\) Hz), 0.95 (t, 3H, \(J = 8\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 191.2, 189.1, 163.9\), 144.7, 143.5, 136.8, 136.2, 133.3, 132.6, 132.5, 131.5, 130.8, 130.3, 129.9, 129.2, 129.1, 128.8, 128.7, 128.6, 128.4, 127.9, 127.7, 127.1, 126.9, 123.57, 118.9, 109.6, 109.4, 61.9, 13.5.

Ethyl 2-benzoyl-4-(4-chlorophenyl)-3-(1H-pyrazol-1-yl)-4-oxobut-2-enoate (3ma)

Yellow solid, isolated yield 84% (E:Z = 88:12), 105 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.01-7.98\) (m, 4H), 7.56 (t, 1H, \(J = 4\) Hz), 7.50-7.44 (m, 5H), 7.38 (d, 1H, \(J = 4\) Hz), 6.25-6.24 (m, 1H), 4.06 (q, 2H, \(J = 8\) Hz), 0.99 (t, 3H, \(J = 8\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 191.0, 187.9, 163.9, 144.3, 143.6, 141.0, 136.6, 133.6, 133.5, 130.2, 130.2, 129.5, 128.8, 128.7, 119.1, 109.8, 62.1, 13.6.

Ethyl 2-benzoyl-4-(4-bromophenyl)-3-(1H-pyrazol-1-yl)-4-oxobut-2-enoate (3na)

White solid, isolated yield 87% (E:Z = 89:11), 120 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.01\) (d, 2H, \(J = 8\) Hz), 7.92 (d, 2H, \(J = 8\) Hz), 7.67 (d, 2H, \(J = 8\) Hz), 7.56 (t, 1H, \(J = 4\) Hz), 7.48-7.44 (m, 3H), 7.38 (d, 1H, \(J = 4\) Hz), 6.26-6.24 (m, 1H), 4.06 (q, 2H, \(J = 8\) Hz), 0.99 (t, 3H, \(J = 8\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 191.0, 188.1, 163.8, 144.2, 143.6, 141.0, 136.6, 133.6, 133.5, 130.2, 130.2, 129.5, 128.8, 128.7, 119.1, 109.7, 62.1, 13.6.

Ethyl 2-benzoyl-4-(4-fluorophenyl)-3-(1H-pyrazol-1-yl)-4-oxobut-2-enoate (3oa)

White solid, isolated yield 81% (E:Z = 88:12), 96 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.10-8.06\) (m, 2H), 8.01 (d, 2H, \(J = 8\) Hz), 7.56 (t, 1H, \(J = 8\) Hz), 7.48-7.44 (m, 3H), 7.38 (d, 1H, \(J = 4\) Hz), 7.19 (t, 2H, \(J = 8\) Hz), 6.26-6.24 (m, 1H), 4.05 (q, 2H, \(J = 8\) Hz), 0.98 (t, 3H, \(J = 8\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 191.0, 187.5, 167.7, 165.1, 163.8, 144.4, 143.6, 136.6, 133.5, 131.7, 131.6, 130.2, 128.8, 128.7, 119.0, 116.6, 116.4, 109.7, 62.0, 13.5.

Ethyl 2-(4-methoxybenzoyl)-4-oxo-4-phenyl-3-(1H-pyrazol-1-yl)but-2-enoate (3pa)
Yellow solid, isolated yield 78% \((E:Z=63:37)\), 96 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.05\) (d, 2H, \(J = 8\) Hz), 8.01 (d, 2H, \(J = 8\) Hz), 7.61 (t, 1H, \(J = 8\) Hz), 7.50-7.48 (m, 2H), 7.44 (d, 1H, \(J = 4\) Hz), 7.36 (t, 1H, \(J = 8\) Hz), 6.94 (d, 2H, \(J = 8\) Hz), 6.23-6.22 (m, 1H), 4.04 (q, 2H, \(J = 8\) Hz), 3.86 (s, 3H), 0.98 (t, 3H, \(J = 8\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 189.9, 189.2, 189.1, 188.7, 164.6, 164.0, 163.9, 144.5, 143.6, 143.5, 142.8, 135.3, 135.2, 134.2, 134.1, 131.5, 131.3, 130.6, 130.4, 129.7, 129.6, 129.1, 129.1, 128.9, 128.7, 127.5, 119.3, 114.0, 113.8, 109.4, 109.1, 62.1, 61.9, 55.5, 13.8, 13.5.

Ethyl 2-(4-fluorobenzoyl)-4-oxo-4-phenyl-3-(1H-pyrazol-1-yl)but-2-enoate (3qa)

White solid, isolated yield 86% \((E:Z=86:14)\), 102 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.06-8.01\) (m, 4H), 7.64 (t, 1H, \(J = 8\) Hz), 7.52 (t, 2H, \(J = 8\) Hz), 7.47 (d, 1H, \(J = 4\) Hz), 7.37 (d, 1H, \(J = 4\) Hz), 7.12 (t, 2H, \(J = 8\) Hz), 6.25-6.24 (m, 1H), 4.04 (q, 2H, \(J = 8\) Hz), 0.97 (t, 3H, \(J = 8\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 189.5, 189.0, 167.1, 164.5, 163.8, 144.6, 143.6, 143.1, 135.0, 134.5, 134.2, 133.3, 133.3, 131.6, 131.5, 131.4, 131.3, 130.7, 130.3, 129.2, 129.0, 128.8, 118.5, 115.9, 115.7, 109.7, 62.0, 13.5.

Methyl 2-(4-methoxybenzoyl)-4-oxo-4-phenyl-3-(1H-pyrazol-1-yl)but-2-enoate (3ra)

Yellow solid, isolated yield 91% \((E:Z=74:26)\), 108 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.04-7.99\) (m, 4H), 7.62 (t, 1H, \(J = 8\) Hz), 7.50-7.48 (m, 3H), 7.43 (d, 1H, \(J = 4\) Hz), 6.94 (d, 2H, \(J = 8\) Hz), 6.24-6.23 (m, 1H), 3.85 (s, 3H), 3.57 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 189.8, 189.1, 188.4, 165.2, 164.5, 164.0, 144.9, 143.5, 143.0, 135.3, 135.0, 134.3, 134.1, 131.5, 131.3, 130.6, 130.4, 129.6, 129.5, 129.1, 129.0, 128.9, 128.7, 126.8, 118.5, 114.0, 113.8, 109.5, 109.2, 55.4, 52.8.

Methyl 2-(4-chlorobenzoyl)-4-oxo-4-phenyl-3-(1H-pyrazol-1-yl)but-2-enoate (3sa)

Yellow solid, isolated yield 83% \((E:Z=92:8)\), 99 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.06\) (d, 2H, \(J = 8\) Hz), 7.96 (d, 2H, \(J = 8\) Hz), 7.65 (t, 1H, \(J = 8\) Hz), 7.53 (t, 2H, \(J = 8\) Hz), 7.47-7.41 (m, 3H), 7.36 (d, 1H, \(J = 4\) Hz), 6.26-6.25 (m, 1H), 3.58 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 189.7, 189.0, 164.3, 145.1, 143.7, 139.7, 135.2, 134.9, 134.6, 130.3, 130.1, 129.2, 129.1, 128.9, 117.5, 109.8, 52.9.

Ethyl 2-benzoyl-4-oxo-4-phenyl-3-(phenylamino)but-2-enoate (3gb)
Brown solid, isolated yield 76% \((E:Z=56:44)\), 90 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 13.16\) (s, 1H), 7.90 (d, 2H, \(J = 8\) Hz), 7.60 (d, 2H, \(J = 8\) Hz), 7.52 (t, 1H, \(J = 8\) Hz), 7.44-7.36 (m, 6H), 7.18-7.14 (m, 2H), 7.06 (d, 2H, \(J = 8\) Hz), 3.72 (q, 2H, \(J = 8\) Hz), 0.65 (t, 3H, \(J = 8\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 196.6, 193.8, 191.2, 190.0, 169.3, 167.3, 164.1, 163.5, 142.1, 140.9, 137.0, 136.6, 135.5, 135.3, 133.9, 133.6, 131.3, 129.1, 129.0, 128.8, 128.6, 128.5, 128.4, 128.3, 127.8, 127.6, 127.1, 127.0, 126.6, 125.1, 124.4, 102.4, 101.8, 60.3, 60.1, 13.5, 13.1.

**Ethyl 2-benzoyl-4-oxo-4-phenyl-3-(p-tolylamino)but-2-enoate (3gc)**

Brown solid, isolated yield 53% \((E:Z=57:43)\), 66 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 13.13\) (s, 1H), 7.91 (d, 2H, \(J = 8\) Hz), 7.59 (d, 2H, \(J = 8\) Hz), 7.53 (t, 1H, \(J = 8\) Hz), 7.45-7.39 (m, 6H), 6.94 (s, 3H), 3.71 (q, 2H, \(J = 8\) Hz), 2.21 (s, 3H), 0.64 (t, 3H, \(J = 8\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 196.5, 193.8, 191.2, 190.0, 169.4, 167.4, 164.4, 164.0, 142.2, 141.1, 137.2, 136.6, 135.6, 135.3, 134.4, 133.9, 133.9, 133.6, 131.3, 129.7, 129.6, 128.8, 128.7, 128.6, 128.5, 128.3, 127.8, 127.6, 127.1, 125.0, 124.4, 101.8, 101.4, 60.3, 60.0, 20.9, 20.8, 13.5, 13.1.

**Ethyl 2-benzoyl-4-oxo-4-phenyl-3-(4-methoxyphenyl)amino)but-2-enoate (3gd)**

Brown solid, isolated yield 62% \((E:Z=60:40)\), 81 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 13.03\) (s, 1H), 7.88 (d, 2H, \(J = 8\) Hz), 7.59 (d, 2H, \(J = 8\) Hz), 7.52 (t, 1H, \(J = 8\) Hz), 7.45-7.39 (m, 5H), 6.99 (d, 2H, \(J = 8\) Hz), 6.67 (d, 2H, \(J = 8\) Hz), 3.73-3.69 (m, 5H), 0.64 (t, 3H, \(J = 8\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 196.6, 190.1, 169.5, 167.4, 165.0, 158.5, 158.2, 142.3, 141.2, 135.6, 135.3, 133.9, 133.5, 131.2, 130.4, 129.7, 129.2, 128.8, 128.5, 128.2, 127.8, 127.6, 127.1, 127.0, 126.6, 114.2, 114.1, 101.4, 101.2, 60.4, 60.3, 60.0, 55.3, 14.2, 13.5, 13.1.

**Ethyl 2-benzoyl-4-oxo-4-phenyl-3-(4-nitrophenyl)amino)but-2-enoate (3ge)**
Yellow solid, isolated yield 70% (E:Z=60:40), 93 mg. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 11.62$ (s, 1H), 8.03 (d, 2H, $J = 8$ Hz), 7.90 (d, 2H, $J = 8$ Hz), 7.73 (d, 2H, $J = 8$ Hz), 7.59 (t, 2H, $J = 8$ Hz), 7.43-7.35 (m, 4H), 7.11 (d, 2H, $J = 8$ Hz), 4.10 (q, 2H, $J = 8$ Hz), 0.91 (t, 3H, $J = 8$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 196.8, 193.3, 191.2, 189.8, 168.8, 166.7, 161.2, 159.3, 144.5, 143.4, 142.8, 141.2, 139.8, 135.0, 134.7, 134.5, 132.2, 131.3, 129.3, 129.0, 128.8, 128.6, 128.0, 127.9, 127.2, 125.1, 125.0, 123.7, 122.0, 106.3, 104.5, 60.8, 13.5, 13.1.

**Ethyl 2-benzoyl-4-oxo-4-phenyl-3-((4-chlorophenyl)amino)but-2-enoate (3gf)**

Yellow solid, isolated yield 71% (E:Z=52:48), 93 mg. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 13.06$ (s, 1H), 7.89 (d, 2H, $J = 8$ Hz), 7.58-7.52 (m, 3H), 7.46-7.39 (m, 5H), 7.14 (d, 2H, $J = 8$ Hz), 7.00 (d, 2H, $J = 8$ Hz), 3.71 (q, 2H, $J = 8$ Hz), 0.67 (t, 3H, $J = 8$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 196.7, 193.7, 191.1, 189.9, 169.3, 167.1, 163.8, 163.0, 141.8, 140.7, 135.7, 135.3, 135.2, 135.1, 134.2, 133.9, 132.9, 132.2, 131.5, 130.7, 129.3, 129.2, 129.0, 128.7, 128.6, 128.3, 127.9, 127.7, 127.1, 126.4, 125.5, 102.9, 102.2, 60.5, 60.3, 13.5, 13.1.

**Ethyl 2-benzoyl-4-oxo-4-phenyl-3-((2-chlorophenyl)amino)but-2-enoate (3gg)**

Light yellow solid, isolated yield 57% (E:Z = 47:53), 75 mg. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 13.02$ (s, 1H), 7.90 (d, 2H, $J = 8$ Hz), 7.64 (d, 2H, $J = 8$ Hz), 7.51 (t, 1H, $J = 8$ Hz), 7.47-7.40 (m, 5H), 7.25-7.22 (m, 2H), 7.06-7.02 (m, 2H), 3.75 (q, 2H, $J = 8$ Hz), 0.67 (t, 3H, $J = 8$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta = 196.6, 193.9, 191.2, 189.8, 168.9, 167.1, 163.2, 161.9, 141.7, 140.5, 135.1, 134.8, 134.6, 134.2, 134.1, 133.8, 131.6, 130.8, 129.8, 129.7, 129.3, 129.1, 128.8, 128.6, 128.4, 128.2, 128.1, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 126.0, 118.9, 115.8, 104.0, 102.8, 60.5, 60.3, 13.5, 13.1.

**Ethyl 2-benzoyl-4-oxo-4-phenyl-3-(methyl(phenyl)amino)but-2-enoate (3gh)**
Brown solid, isolated yield 31% (E:Z=91:9), 39 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.95\) (d, 2H, \(J = 8\) Hz), 7.86 (d, 2H, \(J = 8\) Hz), 7.53-7.48 (m, 2H), 7.44-7.39 (m, 4H), 7.07-6.99 (m, 5H), 3.78 (q, 2H, \(J = 8\) Hz), 3.14 (s, 3H), 0.74 (t, 3H, \(J = 8\) Hz);

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 192.4, 192.1, 167.3, 160.9, 144.4, 139.3, 136.3, 133.3, 132.3, 129.0, 128.8, 128.6, 128.5, 128.2, 127.7, 127.2, 126.9, 106.5, 60.4, 45.0, 13.4.

**Ethyl 2-benzoyl-4-oxo-4-phenyl-3-((6-chloropyridin-2-yl)amino)but-2-enoate (3gi)**

Yellow solid, isolated yield 64% (E:Z=65:35), 84 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 11.62\) (s, 1H), 7.95 (d, 2H, \(J = 8\) Hz), 7.76 (d, 2H, \(J = 8\) Hz), 7.40-7.33 (m, 7H), 6.77 (q, 2H, \(J = 4\) Hz), 4.10 (q, 2H, \(J = 8\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 196.6, 193.3, 189.8, 189.2, 168.6, 166.7, 156.1, 149.8, 149.0, 141.2, 140.6, 140.5, 139.5, 136.9, 136.8, 132.8, 132.3, 131.3, 129.9, 128.8, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.1, 119.7, 118.6, 111.2, 110.1, 107.3, 60.8, 60.7, 13.5, 13.0.

**Ethyl 2-benzoyl-4-oxo-4-phenyl-3-morpholinobut-2-enoate (3gj)**

Brown solid, isolated yield 53% (E:Z>99:1), 63 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 11.62\) (s, 1H), 7.95 (d, 2H, \(J = 8\) Hz), 7.76 (d, 2H, \(J = 8\) Hz), 7.40-7.33 (m, 7H), 6.77 (q, 2H, \(J = 4\) Hz), 4.10 (q, 2H, \(J = 8\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 196.6, 193.3, 189.8, 189.2, 168.6, 166.7, 156.1, 149.8, 149.0, 141.2, 140.6, 140.5, 139.5, 136.9, 136.8, 132.8, 132.3, 131.3, 129.9, 128.8, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.1, 119.7, 118.6, 111.2, 110.1, 107.3, 60.8, 60.7, 13.5, 13.0.

**Ethyl 2-benzoyl-4-oxo-4-phenyl-3-(pyrrolidin-1-yl)but-2-enoate (3gk)**

Yellow solid, isolated yield 36% (E:Z>99:1), 42 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.07\) (d, 2H, \(J = 8\) Hz), 7.93 (d, 2H, \(J = 8\) Hz), 7.61-7.57 (m, 1H), 7.52-7.40 (m, 5H), 3.74-3.66 (m, 2H), 3.44-2.97 (m, 4H), 1.96-1.68 (m, 4H), 0.65 (t, 3H, \(J = 8\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 193.1, 191.4, 167.2, 159.3, 140.5, 135.3, 134.6, 133.7, 131.9, 129.9, 129.1, 129.0, 128.9, 128.6, 128.0, 101.0, 59.7,
46.6, 45.2, 25.2, 24.0, 13.4.

(4-Oxo-4H-pyrido[1,2-a]pyrimidine-2,3-diyl)bis(phenylmethanone) (5ga)\(^4\)

Yellow solid, isolated yield 89%, 93 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 9.20\) (d, 1H, \(J = 8\) Hz), 7.99-7.95 (m, 3H), 7.86-7.83 (m, 3H), 7.59-7.53 (m, 2H), 7.48-7.41 (m, 4H), 7.37 (t, 1H, \(J = 8\) Hz); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 193.1, 192.9, 163.5, 156.1, 151.4, 139.0, 137.5, 134.8, 133.8, 133.2, 130.3, 129.2, 128.5, 128.3, 128.2, 127.1, 117.7, 114.4.

3-Benzoyl-2-(4-methylbenzoyl)-4H-pyrido[1,2-a]pyrimidin-4-one (5ha)\(^4\)

Yellow solid, isolated yield 87%, 96 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 9.20\) (d, 1H, \(J = 8\) Hz), 7.99-7.94 (m, 1H), 7.89-7.83 (m, 5H), 7.54 (t, 1H, \(J = 8\) Hz), 7.54-7.40 (m, 2H), 7.36 (t, 1H, \(J = 8\) Hz), 7.26-7.24 (m, 2H), 2.41 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 193.1, 192.5, 163.6, 156.2, 151.3, 146.9, 144.9, 138.8, 138.2, 137.5, 133.1, 132.3, 130.4, 129.3, 129.2, 128.3, 128.2, 127.1, 117.6, 114.4, 113.7, 109.0, 21.8.

3-Benzoyl-2-(4-methoxybenzoyl)-4H-pyrido[1,2-a]pyrimidin-4-one (5ia)\(^4\)

Yellow solid, isolated yield 86%, 99 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 9.20\) (d, 1H, \(J = 8\) Hz), 7.99-7.95 (m, 3H), 7.87-7.84 (m, 3H), 7.55 (t, 1H, \(J = 8\) Hz), 7.44-7.41 (m, 2H), 7.36 (t, 1H, \(J = 8\) Hz), 6.94 (d, 2H, \(J = 8\) Hz), 3.86 (s, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 193.1, 191.4, 164.2, 163.5, 156.2, 151.3, 138.7, 137.5, 133.1, 132.3, 130.4, 129.3, 128.3, 128.2, 127.9, 127.1, 117.5, 114.6, 113.8, 55.5.

3-Benzoyl-2-(4-(trifluoromethyl)phenyl)-4H-pyrido[1,2-a]pyrimidin-4-one (5ka)

Yellow solid, isolated yield 83%, 105 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 9.24\) (d, 1H, \(J = 8\) Hz), 8.11 (d, 2H, \(J = 8\) Hz), 8.04-8.00 (m, 1H), 7.86-7.84 (m, 3H), 7.75 (d, 2H, \(J = 8\) Hz), 7.57 (t, 1H, \(J = 8\) Hz).
Hz), 7.47-7.40 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 193.1, 192.0, 163.0, 156.1, 151.5, 139.3, 137.6, 137.4, 134.9, 134.6, 133.4, 130.5, 129.8, 129.2, 128.4, 128.3, 128.2, 127.2, 125.5, 125.4, 117.9, 114.5.

2-(2-Naphthoyl)-3-benzoyl-4H-pyrido[1,2-a]pyrimidin-4-one (5la)$^{[4]}$

Yellow solid, isolated yield 93%, 114 mg. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 9.24 (d, 1H, $J$ = 8 Hz), 8.48 (s, 1H), 8.06 (d, 1H, $J$ = 8 Hz), 8.01-7.96 (m, 1H), 7.91-7.85 (m, 6H), 7.62-7.49 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 193.1, 192.9, 163.6, 156.2, 151.5, 139.0, 137.5, 136.0, 133.2, 132.3, 132.2, 129.3, 128.9, 128.5, 128.4, 128.3, 127.8, 127.2, 126.7, 124.8, 117.7, 114.5.

3-Benzoyl-2-(4-chlorobenzoyl)-4H-pyrido[1,2-a]pyrimidin-4-one (5ma)$^{[4]}$

Yellow solid, isolated yield 81%, 93 mg. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 9.20 (d, 1H, $J$ = 8 Hz), 7.99-7.91 (m, 3H), 7.85-7.82 (m, 3H), 7.56 (t, 1H, $J$ = 8 Hz), 7.46-7.36 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 193.1, 191.7, 163.0, 156.1, 151.4, 140.4, 139.1, 137.4, 133.3, 133.2, 131.7, 129.2, 128.9, 128.4, 128.3, 127.1, 117.8, 114.5.

2-Benzoyl-3-(4-methoxybenzoyl)-4H-pyrido[1,2-a]pyrimidin-4-one (5pa)$^{[4]}$

Yellow solid, isolated yield 91%, 105 mg. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 9.22 (d, 1H, $J$ = 8 Hz), 7.98-7.94 (m, 3H), 7.87-7.82 (m, 3H), 7.58 (t, 1H, $J$ = 8 Hz), 7.45 (t, 2H, $J$ = 8 Hz), 7.37 (t, 1H, $J$ = 8 Hz), 6.92 (d, 2H, $J$ = 8 Hz), 3.85 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ = 193.0, 191.3, 163.8, 163.0, 156.1, 151.2, 138.6, 134.8, 133.8, 131.9, 130.4, 128.4, 128.2, 127.1, 117.5, 115.0, 113.6, 55.4.

2-Benzoyl-3-(4-fluorobenzoyl)-4H-pyrido[1,2-a]pyrimidin-4-one (5qa)$^{[4]}$
Yellow solid, isolated yield 77%, 87 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 9.22\) (d, 1H, \(J = 8\) Hz), 8.02-7.97 (m, 3H), 7.91-7.84 (m, 3H), 7.60 (t, 1H, \(J = 8\) Hz), 7.47 (t, 2H, \(J = 8\) Hz), 7.40 (t, 1H, \(J = 8\) Hz), 7.10 (t, 2H, \(J = 8\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 192.9, 191.5, 167.1, 164.6, 163.5, 156.1, 151.4, 139.0, 134.7, 133.9, 133.8, 133.7, 132.1, 132.0, 130.3, 128.5, 128.2, 127.2, 117.8, 115.6, 115.4, 114.3.

\[(9\text{-Methyl-4-oxo-4H-pyrido[1,2-a]pyrimidine-2,3-diyl)bis(phenylmethanone)} (5gb)]^4\]

Yellow solid, isolated yield 74%, 81 mg. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 9.10\) (d, 1H, \(J = 8\) Hz), 8.04-8.01 (m, 2H), 7.87-7.82 (m, 3H), 7.61-7.52 (m, 2H), 7.48-7.40 (m, 4H), 7.29 (d, 1H), 2.60 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta = 193.3, 192.9, 161.9, 156.7, 150.7, 137.7, 137.6, 136.4, 135.1, 133.6, 133.1, 130.4, 129.2, 128.6, 128.3, 128.2, 126.2, 117.1, 114.3, 18.0.

References


Copies of \(^1\)H and \(^{13}\)C NMR spectra
3ha

3ha
3na