Supporting Information

for

DBU-promoted carboxylative cyclization of o-hydroxyand o-acetamidoacetophenone

Wen-Zhen Zhang*, Si Liu and Xiao-Bing Lu

Address: State Key Laboratory of Fine Chemicals, Dalian University of Technology, Dalian, 116024, P. R. China

Email: Wen-Zhen Zhang - zhangwz@dlut.edu.cn;

* Corresponding author

Experimental procedures, spectroscopic and analytical data, and copies of NMR spectra of the products

Table of contents

| 1. | General methods | .S2 |
|----|--|-----|
| 2. | General procedure for reaction of <i>o</i> -hydroxyacetophenone with CO ₂ | .S2 |
| 3. | General procedure for reaction of <i>o</i> -acetamidoacetophenone with CO ₂ | .S6 |
| 4. | ¹ H NMR and ¹³ C NMR spectra of the products | .S8 |

1. General methods

Unless otherwise stated, all manipulations were performed using standard Schlenk techniques under a dry nitrogen or carbon dioxide atmosphere. DMF, DMAc and DMSO were distilled from CaH₂ at 60 °C under reduced pressure and stored over 4 Å molecular sieves. Column chromatography was performed on silica gel (200–300 mesh). Thin layer chromatography was performed on 0.20 mm GF254 plates. Visualization was accomplished with UV light (254 nm), cerium ammonium molybdate, or potassium permanganate.

NMR spectra were recorded on a Bruker Avance II 400M type (¹H NMR, 400 MHz; ¹³C NMR, 100 MHz) spectrometer in CDCl₃ at ambient temperature and chemical shifts are expressed in parts per million (δ , ppm). Proton chemical shifts are referenced to 7.26 ppm (CHCl₃) and carbon chemical shifts are referenced to 77.0 ppm (CDCl₃). Data reporting uses the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; hept, heptet, and *J*, coupling constant in Hz. High resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometry (Micromass, Wythenshawe, UK) equipped with Z-spray ionization source. Infrared spectra (IR) were measured using a Nicolet NEXUS FTIR spectrophotometer.

Unless otherwise indicated, commercially available starting materials were purchased from Energy Chemical.

2. General procedure for reaction of *o*-hydroxyacetophenone with CO₂



Similarly as described in our previous paper (*Catal. Sci. Technol.* **2014**, *4*, 1570), a 20 mL oven-dried autoclave containing a stirring bar was charged with *o*-hydroxyacetophenone (**1**) (0.5 mmol), DBU (1.0 mmol), and 2 mL dry DMSO. After purging the autoclave with CO_2 three times, the sealed autoclave was pressurized to the appropriate pressure with CO_2 . The reaction mixture was stirred at 80 °C for 24 h, then the autoclave was cooled to room temperature and the remaining CO_2 was vented slowly. Then *n*-BuI (1.0 mmol) was added into the autoclave and the reaction mixture was stirred at 80 °C for 4 h. The reaction mixture was then diluted with water (30 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with water and brine, dried over Na₂SO₄ and filtered. The solvent was removed under vacuum. The product was isolated by column chromatography on silica gel (hexane/ethyl acetate 2:1).

 $\int_{0}^{1} \int_{0}^{1} \frac{1}{4} \frac{1}{8} \frac{1}{8}$

for C₁₄H₁₇O₃ [M+H]⁺: 233.1178, found: 233.1169.

OⁿBu

OⁿBu

OⁿBu

Me

^{MeO} **4-Butoxy-3-methyl-7-methoxy-2H-chromen-2-one** (**2b**). 79% yield. ¹**H NMR** (400 MHz, CDCl₃) δ 7.59 (d, J = 8.7 Hz, 1H), 6.87-6.82 (m, 2H), 4.10 (t, J = 6.5 Hz, 2H), 3.87 (s, 3H), 2.13 (s, 3H), 1.87-1.81 (m, 2H), 1.58-1.52 (m, 2H), 1.01 (t, J = 7.4 Hz, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 164.86, 163.49, 162.23, 153.95, 124.05, 112.14, 111.10, 109.13, 100.48, 74.03, 55.70, 32.36, 19.15, 13.83, 10.69. **IR** (neat, cm⁻¹) v 2958, 2928, 2873, 1711, 1614, 1508, 1443, 1378, 1357, 1336, 1248, 1160, 1104, 1064, 1028, 969, 835, 758, 737. **HRMS** (EI, *m/z*) calcd for C₁₅H₁₈O₄ [M]⁺: 262.1205, found: 262.1208.

4-Butoxy-6-methyl-2*H***-chromen-2-one** (2c). 56% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.59 (s, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 5.65 (s, 1H), 4.13 (t, *J* = 6.4 Hz, 2H), 2.42 (s, 3H), 1.93-1.88 (m, 2H), 1.61-1.53 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.79, 163.32, 151.54, 133.55, 133.32, 122.65, 116.56, 115.50, 90.33, 69.08, 30.53, 20.93, 19.23, 13.75. **IR** (neat, cm⁻¹) v 3077, 2953, 1732, 1633, 1608, 1577, 1444, 1370, 1209, 1189, 1106, 935, 856, 827. **HRMS** (ESI, *m/z*) calcd for C₁₄H₁₇O₃ [M+H]⁺: 233.1178, found: 233.1172.

MeO 4-Butoxy-7-methoxy-2*H*-chromen-2-one (2d). 45% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, J = 8.8 Hz, 1H), 6.86-6.80 (m, 2H), 4.09 (t, J = 6.6 Hz, 2H),

3.86 (s, 3H), 2.13 (s, 3H), 1.88-1.81 (m, 2H), 1.60-1.50 (m, 2H), 1.01 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.39, 163.78, 163.39, 155.39, 124.31, 112.36, 109.32, 100.63, 88.12, 69.21, 55.96, 30.77, 19.45, 13.99. **IR** (neat, cm⁻¹) v 3055, 2957, 2927, 1707, 1620, 1456, 1422, 1381, 1153, 1030, 970, 908, 882. **HRMS** (ESI, *m/z*) calcd for C₁₄H₁₇O₄ [M+H]⁺: 249.1127, found: 249.1128.

F **4-Butoxy-7-fluoro-2***H***-chromen-2-one (2e)**. 49% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (dd, J = 8.7, 6.1 Hz, 1H), 7.02-6.98 (m, 2H), 5.63 (s, 1H), 4.14 (t, J = 6.4 Hz, 2H), 1.91-1.86 (m, 2H), 1.58-1.52 (m, 2H), 1.02 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.38, 164.93, 162.74, 154.57, 124.92, 111.96, 104.19, 89.42, 69.27, 53.43, 30.47, 19.19, 13.72. **IR** (neat, cm⁻¹) v 3079, 2962, 2934, 1734, 1632, 1508, 1457, 1422, 1382, 1262, 1140, 1113, 994, 965, 843, 818, 741. **HRMS** (ESI, *m/z*) calcd for C₁₃H₁₃FO₃Na [M+Na]⁺: 259.0746, found: 259.0741.

4-Butoxy-6-bromo-2*H***-chromen-2-one (2f)**. 36% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.92 (s, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 5.69 (s, 1H), 4.14 (t, *J* = 6.4 Hz, 2H), 1.94-1.87 (m, 2H), 1.58-1.51 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.52, 162.27, 152.21, 135.14, 125.68, 118.56, 117.43, 116.68, 91.07, 69.48, 30.43, 19.18, 13.71. **IR** (neat, cm⁻¹) v 2965, 2920, 1736, 1624, 1602, 1467, 1430, 1359, 1265, 1243, 1191, 1112, 1022, 925, 826, 796, 749, 730, 702. **HRMS** (ESI, *m/z*) calcd for C₁₃H₁₄BrO₃ [M+H]⁺: 297.0126, found: 297.0132.



OⁿBu

OⁿBu

Br

^tBu **4-Butoxy-7-(4-***tert*-**butylphenylethynyl)**-2*H*-chromen-2-one (2g). 65% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, J = 8.2 Hz, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.44-7.39 (m, 4H), 5.67 (s, 1H), 4.14 (t, J = 6.4 Hz, 2H), 1.92-1.86 (m, 2H), 1.59-1.53 (m, 2H), 1.34 (s, 10H), 1.03 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.30, 161.77, 152.10, 151.36, 130.54, 126.76, 126.04, 124.47, 121.94, 118.35, 114.38, 91.97, 89.56, 86.47, 68.22, 33.87, 30.13, 29.48, 28.68, 18.18, 12.71. **IR** (neat, cm⁻¹) v 2961, 2925, 2855, 2213, 1727, 1617, 1499, 1462, 1416, 1376, 1261, 1094, 1021, 870, 800. **HRMS** (ESI, *m/z*) calcd for $C_{25}H_{27}O_3$ [M+H]⁺: 375.1960, found: 375.1955.

O"Bu

4-Butoxy-3*H***-benzo[***f***]chromen-3-one (2h). 42% yield. ¹H NMR (400 MHz, CDCl₃) δ 9.10 (d, J = 8.7 Hz, 1H), 7.93 (d, J = 9.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.63-7.50 (m, 2H), 7.39 (d, J = 7.3 Hz, 1H), 5.78 (s, 1H), 4.21 (t, J = 6.4 Hz, 2H), 2.06-1.99 (m, 2H), 1.68-1.58 (m, 2H), 1.05 (t, J = 7.4 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 169.64, 162.70, 154.66, 134.18, 130.89, 129.09, 128.34, 126.24, 125.67, 117.39, 109.10, 90.79, 69.96, 30.67, 19.50, 13.89. IR** (neat, cm⁻¹) v 2954, 2919, 2850, 1737, 1587, 1564, 1461, 1428, 1380, 1322, 1263, 1242, 1209, 1192, 1145, 1070, 940, 923, 815, 741. **HRMS** (ESI, *m/z*) calcd for C₁₇H₁₇O₃ [M+H]⁺: 269.1178, found: 269.1179.

3. General procedure for reaction of o-acetamidoacetophenone with CO₂



Similarly as described in our previous paper (*Catal. Sci. Technol.* **2014**, *4*, 1570), a 20 mL oven-dried autoclave containing a stirring bar was charged with *o*-acetamidoacetophenone (**3**, 0.5 mmol), DBU (2.0 mmol), and 2 mL dry DMSO. After purging the autoclave with CO₂ three times, the sealed autoclave was pressurized to the appropriate pressure with CO₂. The reaction mixture was stirred at 80 °C for 24 h, then the autoclave was cooled to room temperature and the remaining CO₂ was vented slowly. Then CH₃I (2.0 mmol) was added into the autoclave and the reaction mixture was stirred at 30 °C for 4 h. The reaction mixture was diluted with water (30 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with water and brine, dried over Na₂SO₄ and filtered. The solvent was removed under vacuum. The product was isolated by column chromatography on silica gel (hexane/ethyl acetate 2:1).



^{Me} **3-Acetyl-4-methoxy-1-methyl-2**(1*H*)-quinolinone (4a). 42% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (dd, J = 8.1, 1.1 Hz, 1H), 7.64-7.60 (m, 1H), 7.38 (d, J = 8.5 Hz, 1H), 7.30 (d, J = 7.4 Hz, 1H), 3.97 (s, 3H), 3.72 (s, 3H), 2.47 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 167.21, 159.11, 143.74, 139.45, 131.50, 126.49, 125.92, 122.46, 120.39, 114.53, 52.64, 29.46, 16.35. **IR** (neat, cm⁻¹) v 2953, 2917, 2250, 1737, 1643, 1596, 1461, 1319, 1286, 1248, 1162, 1086, 910, 754, 729. **HRMS** (ESI, *m/z*) calcd for C₁₃H₁₄NO₃ [M+H]⁺: 232.0974, found: 232.0974.



^{Me} **3-Acetyl-4,7-dimethoxy-1-methyl-2(1***H***)-quinolinone (4b)**. 38% yield. ¹**H NMR** (400 MHz, CDCl₃) δ 7.69 (d, *J* = 8.9 Hz, 1H), 6.87 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.78 (d, *J* = 2.3 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 3.68 (s, 3H), 2.43 (s, 3H). ¹³**C NMR** (100 MHz, CDCl₃) δ 166.45, 161.31, 158.55, 142.93, 140.25, 126.47, 122.56, 113.37, 108.90, 97.77, 54.59, 51.51, 28.46, 15.29. **IR** (neat, cm⁻¹) v 2957, 2905, 2245, 1736, 1639, 1598, 1445, 1306, 1224, 1079, 1049, 906, 828, 726. **HRMS** (ESI, m/z) calcd for C₁₄H₁₆NO₄ [M+H]⁺: 262.1079, found: 262.1052.

^{Me} **3-Acetyl-6-bromo-4-methoxy-1-methyl-2(1***H***)-quinolinone (4c). 32% yield. ¹H NMR (400 MHz, CDCl₃) \delta 7.87 (d, J = 1.9 Hz, 1H), 7.69 (dd, J = 9.0, 1.9 Hz, 1H), 7.25 (s, 1H), 3.97 (s, 3H), 3.69 (s, 3H), 2.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) \delta 165.67, 157.71, 141.56, 137.37, 133.16, 127.38, 126.46, 120.97, 115.20, 114.54, 51.71, 28.58, 15.29. IR** (neat, cm⁻¹) v 2950, 2927, 2252, 1729, 1647, 1587, 1557, 1493, 1243, 1168, 1108, 1052, 874, 807, 728. **HRMS** (ESI, *m/z*) calcd for C₁₃H₁₃BrNO₃ [M+H]⁺: 310.0079, found: 310.0070.













































