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# A METAL-FREE OXIDATION OF BENZO[*C*]CHROMEN TO BENZO[*C*]CHROMEN-6-ONES BY *t*-BUTYL HYDROPEROXIDE IN THE PRESENCE OF POTASSIUM IODIDE

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**Abstract** – An effective and eco-friendly oxidation method for the synthesis of benzo[*c*]chromen-6-ones is described. The condition constitutes 6 molar ratio TBHP, catalytic KI and pyridine in acetonitrile as the solvent. Altogether, 16 structurally diverse substituted benzo[*c*]chromen-6-ones were prepared through this protocol from corresponding benzo[*c*]chromenes in excellent yields.

Selective oxidation of C–H bonds to give oxygen-containing compounds is an extremely important reaction in synthetic chemistry. In this field, benzylic oxidation is one of the most valuable transformations in not only manufacture of pharmaceuticals and agrochemicals, but also in synthesis of natural products.[1] However, the traditional oxidation methods based heavy mental have provoked environmental issue in recent years.[2] Therefore the use of eco-friendly oxidants to replace metals is highly desirable in terms of sustainable chemical production.[3]

Benzo[*c*]chromen-6-one is a privileged scaffold in a number of pharmacologically relevant natural products such as graphislactones,[4] autumnariol,[5] autumnariniol,[6] alternariol[7] and altenuisol.[8] It has also been demonstrated that benzo[*c*]chromen-6-one can be used as synthetic intermediates in the synthesis of several pharmaceutically interesting compounds including progesterone, glucocorticoids modulators,[9] and endothelial cell proliferation inhibitors.[10] Furthermore, benzo[*c*]chromen-6-ones occur naturally in many food sources including citrus fruits, herbs and vegetables.[11]

The most popular synthesis route for benzo[*c*]chromen-6-one is Suzuki-Miyaura cross-coupling followed by intramolecular cyclization process (Figure 1, eq 1). Indeed, a plethora of papers have been published on modifications of this protocol.[12] Despite these advancements, this methodology suffers from some drawbacks from a practical point of view, such as expensive organoborane compounds and catalyst. Other

synthetic approaches involving Diels-Alder cycloaddition to construct benzene ring,[13] Pd-catalyzed decarboxylative cross-coupling and lactonization[14] can also be found in the literature. More recently, an $H_2O_2$ oxidation of benzo[*c*]chromenes under microwave irradiation was reported.[15] However, the practicality of these methodologies are confined, owing to toxic residues, more steps, additional apparatus, low practicability and poor yields to some extent.

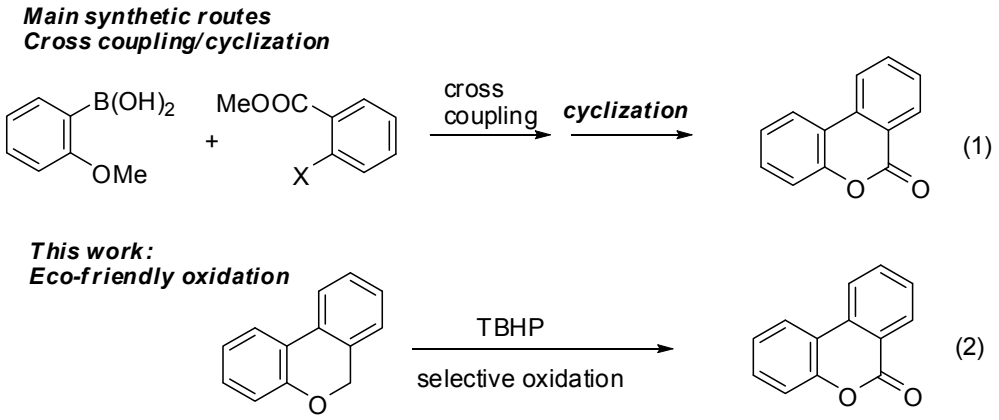


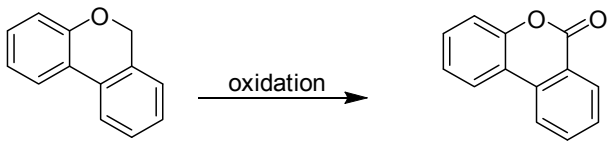

**Figure 1**

Our research group is searching for new heterocyclic structures to serve as potential bioactive compounds in agriculture.[16] Recently, we have reported the efficient and convenient palladium-catalyzed formation of 6*H*-benzo[*c*]chromen from inexpensive diazonium salts.[17] We envisaged an eco-friendly oxidation of benzo[*c*]chromen without any heavy metal in order to obtain benzo[*c*]chromenes. Herein, we would like to report an efficient synthesis of benzo[*c*]chromen-6-one from benzo[*c*]chromen by homogeneous TBHP oxidation with acetonitrile as the solvent in excellent yields.

Initially, the oxidation of simple 6*H*-benzo[*c*]chromene was set as a model reaction and we were strongly interested in a general oxidizer such as potassium persulfate. Regarding potassium persulfate, the oxidation reaction did not occur, and those conditions proved to be inappropriate in a non-polar solvent (Table 1, entries 1, 2). Then, sodium bromide was added as a co-oxidizer, but the oxidation reaction did not occur in nitromethane, either (Table 1, entry 3). Our studies subsequently showed that the nature of the reaction solvent was very important for this reaction. When acetonitrile was chosen as the solvent, benzo[*c*]chromen-6-ones together with an unknown byproduct could be obtained in 55% yield. Then, the oxidizer *t*-butyl hydroperoxide (TBHP) (in aqueous solution) was tested in acetonitrile without any additive. The transformation was sluggish, and a 50% yield of the product as obtained at 80 °C after 48 h (Table 1, entry 5). Then, a simple 10% molar ratio of KI (48 h) or a combination of a 10% molar ratio of KI and a 10% molar ratio *N*-methylmophine were used as additives; 60% yields (48 h) were obtained, but the reaction is still sluggish (Table 1, entries 5-7). After the combination of a 10% molar ratio of KI and a 10% molar ratio pyridine as the additive was employed, the reaction was markedly more effective (Table

1, entry 8). Then, the use of TBHP was investigated for the model reaction. When 3 equiv. of TBHP was used, 90% yield was obtained and when 6 equiv. TBHP was used, 95% yield was obtained (Table 1, entries 8-9). Indeed, a large excess of TBHP was found to be needless because of the inconvenience in the work-up (Table 1, entry 10). So, the optimum conditions included 3 equiv. 70% aqueous TBHP as the oxidizer, acetonitrile as the solvent, a 10% molar ratio of KI[21] and a 10% molar ratio pyridine as additives and the temperature as 80 °C.

**Table 1.** Screening conditions of oxidation

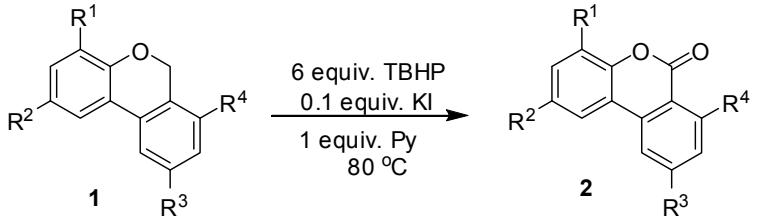



**1a** **2a**

| entry | oxidizer | solvent | additive | temperature | yield[a] |
|---|---|---|---|---|---|
| 1 | $K_2S_2O_8$ (3 eq) | $CH_2Cl_2$ | - | 40 °C | 0 |
| 2 | $K_2S_2O_8$ (3 eq) | $CH_2Cl_2/H_2O$(1:1) | - | 40 °C | 0 |
| 3 | $K_2S_2O_8$ (3 eq) | $MeNO_2/H_2O$(10:1) | NaBr(0.5 eq) | 80 °C | 0 |
| 4 | $K_2S_2O_8$ (3 eq) | MeCN/$H_2O$(10:1) | NaBr(0.5 eq) | 40 °C | 55%[b] |
| 5 | TBHP (3 eq) | MeCN | - | 80 °C | 50%[c] |
| 6 | TBHP (3 eq) | MeCN | KI (10%) | 80 °C | 60%[c] |
| 7 | TBHP (3 eq) | MeCN | KI(10%)/ NMO (10%) | 80 °C | 60%[c] |
| 8 | TBHP (3 eq) | MeCN | KI (10%) Pyr (10%) | 80 °C | 90% |
| 9 | TBHP (6 eq) | MeCN | KI (10%), Pyr (10%) | 80 °C | 95% |
| 10 | TBHP (8 eq) | MeCN | KI (10%), Pyr (10%) | 80 °C | 95% |

With the optimized reaction conditions, we next examined the scope of TBHP selective oxidation for the synthesis of substituted benzo[*c*]chromen-6-ones. The results are summarized in Table 2. A wide range of structurally diverse benzo[*c*]chromens (Table 2), including chloro (Table 2, entries 9-12), bromo (Table 2, entries 13-16), fluoro (Table 2, entry 8), and ester (entry 3) groups were subjected to this protocol to provide the corresponding benzo[*c*]chromen-6-ones in excellent yields. As for the variations of $R_2$, electron-neutral (Table 2, entries 3-6) and electron-deficient (Table 2, entry 7) groups were good substrates for this reaction. It was found that $R_3$ did not show a great influence (Table 2, entries 9-16) to this protocol. The bromo moieties could be easily functionalized to boric acid substituents, which make it possible to obtain more complicated substituted benzo[*c*]chromen-6-ones by the subsequent coupling reaction.

**Table 2.** TBHP Oxidation of benzo[*c*]chromens to benzo[*c*]chromen-6-ones




| Entry | Compound **1** | Product **2** | Yield (%)[a] |
|---|---|---|---|
| 1 | $R^1$=$R^2$=$R^3$=$R^4$=H | **2a** | 95 |
| 2 | $R^1$=$R^2$=$R^4$=H, $R^3$=Me | **2b** | 88 |
| 3 | $R^1$=$R^3$=$R^4$=H, $R^2$=Me, | **2c** | 86 |
| 4 | $R^1$=$R^3$=H, $R^2$=*t*-Bu | **2d** | 95 |
| 5 | $R^1$=$R^4$=H, $R^2$=*t*-Bu, $R^3$=Me | **2e** | 92 |
| 6 | $R^1$=$R^4$=H, $R^2$=$R^3$=Me | **2f** | 86 |
| 7 | $R^1$=$R^3$=$R^4$=H, $R^2$=COOEt | **2g** | 98 |
| 8 | $R^1$=$R^2$=$R^4$=H, $R^3$=F | **2h** | 96 |
| 9 | $R^1$=$R^2$=$R^4$=H, $R^3$=Cl | **2i** | 96 |
| 10 | $R^1$=$R^2$=$R^3$=H, $R^4$=Cl | **2j** | 95 |
| 11 | $R^1$=$R^4$=H, $R^2$=Me, $R^3$=Cl | **2k** | 90 |
| 12 | $R^1$=$R^4$=H, $R^2$=*t*-Bu, $R^3$=Cl | **2l** | 92 |
| 13 | $R^1$=$R^4$=H, $R^2$=Me, $R^3$=Br | **2m** | 86 |
| 14 | $R^1$=$R^2$=$R^4$=H, $R^3$=Br | **2n** | 95 |
| 15 | $R^1$=$R^4$=H, $R^2$=*t*-Bu, $R^3$=Br | **2o** | 95 |
| 16 | $R^1$=$R^3$=$R^4$=H, $R^2$=Br | **2p** | 92 |

In conclusion, an efficient and convenient oxidation method was developed for the formation of benzo[*c*]chromen-6-ones from benzo[*c*]chromens in the presence of 70% aqueous TBHP, a catalytic amount of KI and pyridine. This method is bestowed with several unique merits, such as high conversions and yields, simplicity in operation, cost-effectiveness and functional group tolerance. Thus, we believe that this novel methodology will be a practical alternative to the existing procedures and cater to the need of academia as well as industry.

## EXPERIMENTAL

To a solution of the 6*H*-benzo[*c*]chromene (0.5 mmol) in MeCN (3 mL), *tert*-butylhydroperoxide (TBHP) (70% aqueous solution, 6 eq.), KI (0.1 eq.) and pyridine (0.1 eq.) were added in turn at room temperature. The solution was stirred at 80 °C for 48 h. The reaction mixture was concentrated under reduced pressure. The mixture was dissolved in EtOAc and then washed by saturated aqueous $CuSO_4$ solution and saturated aqueous $Na_2SO_3$ solution. The organic phase was concentrated under reduced pressure. The product was isolated by column chromatography on silica gel (Table 2). The $^1$H-NMR and $^{13}$C-NMR data were recorded in deuterated chloroform solution with Bruker-NMR spectrometers (DRX 500, AM 400) if not noted otherwise.

**6*H*-Benzo[*c*]chromen-6-one (2a)**

Mp 91-92 °C (lit.,[12h] 91-92 °C). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 8.39 (d, 1H, $J$ = 7.5 Hz), 8.10 (d, 1H, $J$ = 8.0 Hz), 8.04 (d, 1H, $J$ = 8.0 Hz), 7.82 (t, 1H, $J$ = 7.5 Hz), 7.57 (t, 1H, $J$ = 8.0 Hz), 7.47 (t, 1H, $J$ = 7.5 Hz), 7.36-7.31 (m, 2H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 161.1, 151.3, 134.8, 134.7, 130.6, 130.4, 130.5, 128.9, 124.5, 122.8, 121.7, 121.3, 118.0, 117.8 ppm. IR ($cm^{-1}$): 1730, 1605, 1236, 1077.

**9-Methyl-6*H*-benzo[*c*]chromen-6-one (2b)**

Mp 100-102 °C (lit.,[18] 102.5-103 °C). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 8.26 (d, 1H, $J$ = 8.0 Hz), 8.02 (d, 1H, $J$ = 8.0 Hz), 7.87 (s, 1H), 7.46 (d, 1H, $J$ = 7.5 Hz), 7.38-7.30 (m, 3H), 2.55 (s, 3H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 161.2, 151.5, 145.9, 134.7, 130.5, 130.3, 130.2, 124.4, 122.7, 121.8, 118.8, 118.1,117.7, 22.3 ppm. IR ($cm^{-1}$): 1723, 1615, 1302, 1268, 1101.

**2-Methyl-6*H*-benzo[*c*]chromen-6-one (2c)**

Mp 126-128 °C (lit.,[19] 127-129 °C). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.22 (d, 1H, $J$ = 8.1 Hz), 7.98 (d, 1H, $J$ = 7.6 Hz), 7.82 (s, 1H), 7.44 (t, 1H, $J$ = 7.3 Hz), 7.35-7.27 (m, 3H), 2.53 (s, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 161.2, 151.4, 145.9, 134.6, 130.5, 130.2, 130.1, 124.4, 122.7, 121.8, 118.7, 118.0, 117.7, 22.3 ppm. IR ($cm^{-1}$): 1715, 1604, 1296, 1234, 1096.

**2-*tert*-Butyl-6*H*-benzo[*c*]chromen-6-one (2d)**

Mp 100-102 °C (lit.,[20] 106.9-107.4 °C). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.40 (dd, 1H, $J$ = 0.8, 8.0 Hz), 8.17 (d, 1H, $J$ = 8.1 Hz), 8.05 (d, 1H, $J$ = 2.3 Hz), 7.82 (td, 1H, $J$ = 1.2, 10.3 Hz), 7.59-7.52 (m, 2H), 7.30 (d, 1H, $J$ = 8.7 Hz), 1.41 (s, 9H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 156.7, 144.5, 142.8, 130.4, 130.0, 125.9, 123.9, 123.3, 116.8, 116.5, 114.2, 112.6, 112.4, 30.0, 26.7 ppm. IR ($cm^{-1}$): 1729, 1609, 1363, 1296, 1072.

**2-*tert*-Butyl-9-methyl-6*H*-benzo[*c*]chromene (2e)**

Mp 117-119 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, 1H, $J$ = 8.1 Hz), 8.03 (d, 1H, $J$ = 2.2 Hz), 7.92 (td, 1H, $J$ = 2.1, 10.3 Hz), 7.52 (dd, 1H, $J$ = 2.2, 8.7 Hz), 7.37 (d, 1H, $J$ = 7.6 Hz), 7.29 (d, 1H, $J$ = 8.7 Hz), 2.58 (s, 3H), 1.42 (s, 9H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 161.6, 149.4, 147.3, 145.8, 137.9, 135.1, 130.6, 130.0, 127.9, 121.6, 118.9, 117.3, 117.2, 34.8, 31.5, 22.3 ppm. IR ($cm^{-1}$): 1728, 1616, 1273, 1072.

**2,9-Dimethyl-6*H*-benzo[*c*]chromen-6-one (2f)**

Mp 180-182 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 8.25 (d, 1H, $J$ = 8.0 Hz), 7.85 (s, 1H), 7.79 (s, 1H), 7.35 (d, 1H, $J$ = 8.0 Hz), 7.24-7.21 (m, 2H), 2.54 (s, 3H), 2.45 (s, 3H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 161.4, 149.6, 145.7, 134.8, 133.9, 131.2, 130.5, 130.0, 122.7, 121.7, 118.9, 117.7, 117.4, 22.2, 21.1 ppm. IR ($cm^{-1}$): 1722, 1616, 1275, 1219, 1072, 1043.

**Ethyl 6-oxo-6*H*-benzo[*c*]chromene-2-carboxylate (2g)**

Mp 145-146 °C. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.75 (d, 1H, $J$ = 1.9 Hz), 8.39 (dd, 1H, $J$ = 0.9, 8.0 Hz), 8.21 (d, 1H, $J$ = 8.0 Hz), 8.13 (dd, 1H, $J$ = 1.9, 8.6 Hz), 7.87 (td, 1H, $J$ = 1.3, 7.9 Hz), 7.63 (td, 1H, $J$ =

0.8, 7.7 Hz), 7.39 (d, 1H, *J* = 8.6 Hz), 4.45 (q, 2H, *J* = 7.2 Hz), 1.45 (t, 3H, *J* = 7.2 Hz) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 165.6, 160.5, 154.1,135.2, 134.1, 131.4, 129.5, 126.9, 125.0, 122.0, 121.1, 118.0, 117.9, 61.46, 14.4 ppm. IR ($cm^{-1}$): 1755, 1720, 1612, 1317, 1263, 1108, 1093, 1070, 1033.

**9-Fluoro-6*H*-benzo[*c*]chromen-6-one (2h)**

Mp 157-159 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 8.41(d, 1H, *J* = 8.0 Hz), 8.03 (d, 1H, *J* = 8.0 Hz), 7.85 (t, 1H, *J* = 7.5 Hz), 7.71 (dd, 1H, *J* = 2.6, 9.0 Hz), 7.63 (t, 1H, *J* = 7.6 Hz), 7.35 (m, 1H), 7.20 (td, 1H, *J* = 2.6, 8.6 Hz) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 160.5 (d, 1C, *J* = 63.8 Hz), 158.3, 147.4, 135.0, 130.7, 129.6, 121.9, 121.3, 119.4,119.3, 117.7 (d, 1C, *J* = 23.8 Hz), 108.8 (d, 1C, *J* = 25.0 Hz) ppm. IR ($cm^{-1}$): 1721, 1487, 1299, 1273, 1165, 1076.

**9-Chloro-6*H*-benzo[*c*]chromen-6-one (2i)**

Mp 182-184 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 8.33 (d, 1H, *J* = 8.5 Hz), 8.07 (s, 1H), 7.98 (d, 1H, *J* = 8.0 Hz), 7.52 (t, 2H, *J* = 9.0 Hz), 7.38-7.34 (m, 2H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 160.4, 151.7, 141.9, 136.3, 132.2, 131.2, 129.3, 124.8, 122.9, 121.8, 119.6, 117.9, 117.0 ppm. IR ($cm^{-1}$): 1738, 1603, 1265, 1232, 1097, 747.

**7-Chloro-6*H*-benzo[*c*]chromen-6-one (2j)**

Mp 187-189 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 8.40 (d, 1H, *J* = 7.8 Hz), 8.10 (d, 1H, *J* = 8.0 Hz), 7.96 (d, 1H, *J* = 8.0 Hz), 7.85 (t, 1H, *J* = 7.6 Hz), 7.62 (t, 1H, *J* = 7.6 Hz), 7.53 (d, 1H, *J* = 7. 8 Hz), 7.26 (t, 1H, *J* = 8.2 Hz) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 160.0, 147.1, 135.1, 134.2, 130.9, 130.7, 129.5, 124.5, 122.7, 122.0, 121.2, 121.1, 119.6 ppm. IR ($cm^{-1}$): 1745, 1604, 1272, 1224, 1038, 748.

**9-Chloro-2-methyl-6*H*-benzo[*c*]chromen-6-one (2k)**

Mp 188-190 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 8.28 (s, 1H), 7.98 (s, 1H), 7.69 (s, 1H), 7.49 (s, 1H), 7.27 (s, 1H), 7.21 (s, 1H), 2.44 (s, 3H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 160.5, 149.6, 141.7, 136.3, 134.4, 132.2, 132.1, 129.1, 122.8, 121.7, 119.6, 117.6, 21.1 ppm. IR ($cm^{-1}$): 1724, 1603, 1412, 1186, 1068, 809, 774.

**2-*tert*-Butyl-9-chloro-6*H*-benzo[*c*]chromen-6-one (2l)**

Mp 149-150 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 8.33 (d, 1H, *J* = 8.5 Hz), 8.10 (s, 1H), 7.96 (s, 1H), 7.57 (dd, 1H, *J* = 1.0, 8.5 Hz), 7.52 (d, 1H, *J* = 8.5 Hz), 7.31 (d, 1H, *J* = 8.5 Hz), 1.42 (s, 9H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$160.7, 149.6, 147.8, 141.7, 136.7, 132.3, 129.1, 128.9, 121.6, 119.6, 119.0, 117.5, 116.2, 34.8, 31.4 ppm. IR ($cm^{-1}$): 1730, 1604, 1258, 1213, 1096, 1038, 680.

**9-Bromo-2-methyl-6*H*-benzo[*c*]chromen-6-one (2m)**

Mp 180-183 °C. $^1$H NMR (500 Hz, $CDCl_3$): $\delta$ 8.23 (d, 2H, *J* = 8.0 Hz), 7.55 (s, 1H), 7.67 (d, 1H, *J* = 8.5 Hz), 7.31 (d, 1H, *J* = 8.5 Hz), 7.25 (d, 1H, *J* = 8.5 Hz), 2.46 (s, 3H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 160.7, 149.7, 136.4, 134.4, 132.2, 132.1, 132.0, 130.5, 124.8, 122.8, 120.0, 117.6, 116.5, 21.1 ppm. IR ($cm^{-1}$): 1725, 1599, 1294, 1214, 1086, 1066, 774, 676.

**9-Bromo-6*H*-benzo[*c*]chromen-6-one (2n)**

Mp 181-183 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 8.24-8.23 (m, 2H), 7.98 (d, 1H, $J$ = 7.8 Hz), 7.69 (dd, 1H, $J$ = 1.2, 8.5 Hz), 7.52 (t, 1H, $J$ = 7.2 Hz), 7.37-7.35 (m, 2H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 160.5, 151.6, 136.3, 132.2, 132.19, 131.2, 130.6, 124.9, 124.8, 122.9, 120.0, 118.0, 116.9 ppm. IR ($cm^{-1}$): 1738, 1597, 1261, 1231, 1090, 1014, 817.

**9-Bromo-2-*tert*-butyl-6*H*-benzo[*c*]chromen-6-one (2o)**

Mp 156-157 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 8.35 (d, 1H, $J$ = 9.0 Hz), 8.12 (s, 1H),7.98 (d, 1H, $J$ = 2.0 Hz), 7.59 (dd, 1H, $J$ = 2.0, 8.6 Hz), 7.54 (dd, 1H, $J$ = 1.2, 8.4 Hz), 7.33 (d, 1H, $J$ = 8.6 Hz), 1.45 (s, 9H) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 160.6, 149.6, 147.8,141.7, 136.7, 132.3, 129.0, 128.9, 121.6, 119.6, 119.0, 117.5, 116.1, 34.8, 31.5 ppm. IR ($cm^{-1}$): 1730, 1604, 1364, 1258, 1096, 1038, 821, 776, 680.

**2-Bromo-6*H*-benzo[*c*]chromen-6-one (2p)**

Mp 183-185 °C. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 8.41(d, 1H, $J$ = 8.0 Hz), 8.12 (d, 1H, $J$ = 2.0 Hz), 8.06 (d, 1H, $J$ = 8.0 Hz), 7.85 (td, 1H, $J$ = 0.5, 8.0 Hz), 7.63 (t, 1H, $J$ = 7.5 Hz), 7.57 (dd, 1H, $J$ = 2.5, 8.5 Hz), 7.26 (d, 1H, $J$ = 8.5 Hz) ppm. $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 160.5, 150.2, 135.1, 133.5, 133.2, 130.8, 129.6, 125.7, 121.8, 121.3, 119.9, 119.5, 117.5 ppm. IR ($cm^{-1}$): 1739, 1602, 1263.5, 1213.7, 1035, 1018, 810.

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## REFERENCES (AND NOTES)

1. R. A. Sheldon and J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981.
2. M. Hudlicky, *Oxidations in Organic Chemistry*, American Chemical Society, Washington DC, 1990, ACS Monography, No. 186.
3. (a) W. Wang, T. Li, and G. Attardo, *J. Org. Chem.*, 1997, **62**, 6598; (b) K. Moriyama, M. Takemura, and H. Togo, *Org. Lett.*, 2012, **14**, 2414; (c) A. Dhakshinamoorthy, M. Alvaro, and H. Garcia, *ACS Catalysis*, 2011, **1**, 48.
4. H. Abe, K. Nishioka, S. Takeda, M. Arai, Y. Takeuchi, and T. Harayama, *Tetrahedron Lett.*, 2005, **46**, 3197.
5. H. Raistrick, C. E. Stickings, and R. Thomas, *Biochem. J.*, 1953, **55**, 421.
6. W. T. L. Sidwell, H. Fritz, and C. Tamm, *Helv. Chim. Acta*, 1971, **54**, 207.
7. C. Tamm, *Arzneim.-Forsch.,* 1972, **22**, 1776.

8. R. W. Pero, D. Harvan, and M. C. Blois, *Tetrahedron Lett.*, 1973, **14**, 945.
9. (a) M. J. Coghlan, P. R. Kym, S. W. Elmore, A. X. Wang, J. R. Luly, D. Wilcox, M. Stashko, C.-W. Lin, J. Miner, C. Tyree, M. Nakane, P. Jacobson, and B. C. Lane, *J. Med. Chem.*, 2001, **44**, 2879; (b) J. P. Edwards, S. J. West, K. B. Marschke, D. E. Mais, M. M. Gottardis, and T. K. Jones, *J. Med. Chem.*, 1998, **41**, 303; (c) L. G. Hamann, R. I. Higuchi, L. Zhi, J. P. Edwards, X.-N. Wang, K. B. Marschke, J. W. Kong, L. J. Farmer, and T. K. Jones, *J. Med. Chem.*, 1998, **41**, 623.
10. J. M. Schmidt, G. B. Tremblay, M. Pagé, J. Mercure, M. Feher, R. Dunn-Dufault, M. G. Peter, and P. R. Redden, *J. Med. Chem.*, 2003, **46**, 1289.
11. R. Myrray, J. Mendez, and S. Brown, *The Natural Coumarins: Occurrence, Chemistry and Biochemistry*, John Wiley & Sons, New York, 1982, p. 97.
12. (a) K. Vishnumurthy and A. Makriyannis, *J. Comb. Chem.*, 2010, **12**, 664; (b) G. J. Kemperman, B. Ter Horst, D. Van de Goor, T. Roeters, J. Bergwerff, R. Van der Eem, and J. Basten, *Eur. J. Org. Chem.*, 2006, 3169; (c) N. Thasana, R. Worayuthakarn, P. Kradanrat, E. Hohn, L. Young, and S. Ruchirawat, *J. Org. Chem.*, 2007, **72**, 9379; (d) B. I. Alo, A. Kandil, P. A. Patil, M. J. Sharp, M. A. Siddiqui, V. Snieckus, and P. D. Josephy, *J. Org. Chem*., 1991, **56**, 3763; (e) R. Singha, S. Roy, S. Nandi, P. Ray, and J. K. Ray, *Tetrahedron Lett.*, 2013, **54**, 657; (f) P. R. Kym, M. E. Kort, M. J. Coghlan, J. L. Moore, R. Tang, J. D. Ratajczyk, D. P. Larson, S. W. Elmore, J. K. Pratt, M. A. Stashko, H. D. Falls, C. W. Lin, M. Nakane, L. Miller, C. M. Tyree, J. N. Miner, P. B. Jacobson, D. M. Wilcox, P. Nguyen, and B. C. Lane, *J. Med. Chem*., 2003, **46**, 1016; (g) I. Hussain, V. T. H. Nguyen, M. A. Yawer, T. T. Dang, C. Fischer, H. Reinke, and P. Langer, *J. Org. Chem.*, 2007, **72**, 6255; (h) S. Furuyama and H. Togo, *Synlett*, 2010, 2325.
13. (a) M. E. Jung and D. A. Allen, *Org. Lett.*, 2009, **11**, 757; (b) I. R. Pottie, P. R. Nandaluru, W. L. Benoit, D. O. Miller, L. N. Dawe, and G. J. Bodwell, *J. Org. Chem*., 2011, **76**, 9015.
14. J. Luo, Y. Lu, S. Liu, J. Liu, and G.-J. Deng, *Adv. Syn. Catal.*, 2011, **353**, 2604.
15. Y. He, X. Zhang, L. Cui, J. Wang, and X. Fan, *Green Chem.*, 2012, **14**, 3429.
16. (a) T. Zhang, L.-Z. Huang, J. Wu, D. Lu, B.-L. Ma, and Z.-T. Du, *Heterocycles*, 2013, **87**, 1545; (b) Z. T. Du, J. Zhou, C. M. Si, and W. L. Ma, *Synlett*, 2011, 3023; (c) Z. T. Du, C. M. Si, Y. Q. Li, Y. Wang, and J. Lu, *Int. J. Mol. Sci.*, 2012, **13**, 4696.
17. J. Zhou, L. Z. Huang, Y. Q. Li, and Z. T. Du, *Tetrahedron Lett.*, 2012, **53**, 7036.
18. C. Koelsch and H. D. Embree, *J. Org. Chem.*, 1958, **23**, 1606.
19. R. S. S. Pal and M. M. Bokadia, *J. Indian Chem. Soc*., 1975, **52**, 983.
20. R. B. Bedford, R. L. Webster, and C. J. Mitchell, *Org. Biomol. Chem*., 2009, **7**, 4853.
21. TBAI and NaI showed same catalytic effect when they were used as replacement of KI in this protocol.
22. The first two authors contributed equally to this work.