Supporting Information

AlBr₃·6H₂O Catalyzed Oxidation of Alcohols

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General information

AlBr₃·6H₂O was obtained from commercial sources. All solvents used were analytical grade and were used as received. All of the alcohols used in the reaction were obtained from ABCR GmbH & Co. KG and used as received without further treatment. H₂¹⁸O was obtained from Huayi Isotope Co. and used as received. All NMR spectra are recorded on MERCURY (400 MHz for ¹H NMR, 100 MHz for ¹³C NMR) spectrometers; chemical shifts are expressed in ppm (δ units) relative to TMS signal as internal reference in CDCl₃. Gas chromatography (GC) analysis was performed on a Shimadzu GC-2010 equipped with a 15 m × 0.53 mm × 1.5 μm RTX-1 capillary column and a oxyhydrogen flame detector. GC/MS analysis were carried out on a trace HP GC6890/MS5973 equipped with a 25 m × 0.25 mm SE-54 column and a Shimadzu GC-16A gas chromatograph with a 3 m × 3 mm OV-17 column.

General procedure for the oxidation of alcohols with AlBr₃·6H₂O

To a 10 mL round flask were added 0.10 mmol alcohol substrate, 2 mL of 1, 4-dioxane, and 0.03 mmol AlBr₃·6H₂O (0.011 g). Then the flask was immersed in a preheated 70 °C oil bath for the desired reaction time. Percentage conversion and reaction selectivity were determined by GC analysis. The yield was calculated on the basis of 1.0 mmol of substrate. Isolated product is obtained by column chromatograph. (Petroleum ether / ethyl acetate = 1 ~ 10:1)

Preparation of ¹⁸O enriched benzyl alcohol

0.05 g Na was added to 0.75 mL ¹⁸O enriched water (98 % H₂¹⁸O, Huayi Isotope Co.) in a flask, and then 0.5 mL 1-chloromethylbenzene was added into the flask. The mixture was heated to 368 K and refluxed for 48 h with continuous stirring. The product was purified by column chromatography and 0.2 g C₆H₅CH₂¹⁸OH was obtained. The ¹⁸O enriched benzyl alcohol was examined by GC-MS, and the abundance of C₆H₅CH₂¹⁸OH was 98 %.
The Data for Products 2b, 3b, 8b, 9b, 9c,10b, 11b

4-Chlorobenzaldehyde (2b)

\[ \text{\(^1\)H NMR (CDCl}_3\text{, 400 MHz): } \delta = 10.00 \text{ (s, 1H, CHO), 7.85 - 7.83 (d, } J = 8 \text{ Hz, 2H, Ar-H), 7.54 - 7.52 (d, } J = 8 \text{ Hz, 2H, Ar-H);} \]
\[ \text{\(^{13}\)C NMR (100 MHz): } \delta = 190.84, 140.92, 134.67, 130.88, 129.42. \]

4-Nitrobenzaldehyde (3b)

\[ \text{\(^1\)H NMR (CDCl}_3\text{, 400 MHz): } \delta = 10.17 \text{ (s, 1H, CHO), 8.42 – 8.40 (d, } J = 8 \text{ Hz, 2H, Ar–H), 8.10 – 8.08 (d, } J = 8 \text{ Hz, 2H, Ar–H);} \]
\[ \text{\(^{13}\)C NMR (100 MHz): } \delta = 190.27, 151.10, 140.01, 130.48, 124.31. \]

Benzil (8b)

\[ \text{\(^1\)H NMR (CDCl}_3\text{, 400 MHz): } \delta = 7.99 - 7.96 (m, 4H, Ar-H), 7.68 - 7.64 (m, 2H, Ar-H), 7.54 - 7.50 (m, 4H, Ar-H); \]
\[ \text{\(^{13}\)C NMR (100 MHz): } \delta = 194.56, 134.88, 132.96, 129.89, 129.01. \]

Benzophenone (9b)

\[ \text{\(^1\)H NMR (CDCl}_3\text{, 400 MHz): } \delta = 7.82 - 7.79 (m, 4H, Ar-H), 7.60-7.58 (m, 2H, Ar-H), 7.49 - 7.45 (m, 4H, Ar-H); \]
\[ \text{\(^{13}\)C NMR (100 MHz): } \delta = 196.67, 137.49, 132.35, 129.98, 128.20. \]

Bromodiphenylmethane (9c)

\[ \text{\(^1\)H NMR (CDCl}_3\text{, 400 MHz): } \delta = 7.37 - 7.23 (m, 10H, Ar-H), 5.39 (s, 1H, CH); \]
\[ \text{\(^{13}\)C NMR (100 MHz): } \delta = 142.19, 128.36, 127.41, 127.24, 79.96. \]

4-Methylbenzophenone (10b)

\[ \text{\(^1\)H NMR(CDCl}_3\text{, 400 MHz): } \delta = 7.79 - 7.77 (d, } J = 8 \text{ Hz, 2H, Ar-H), 7.73 - 7.71 (d, } J = 8 \text{ Hz, 2H, Ar-H), 7.59 - 7.55 (t, } J = 8 \text{ Hz, 1H, Ar-H), 7.49 - 7.45 (t, } J = 8 \text{ Hz, 2H, Ar-H), 7.29 - 7.27 (t, } J = 8 \text{ Hz, 2H, Ar-H), 2.44 (s, 3H, CH}_3\text{);} \]
\[ \text{\(^{13}\)C NMR (100 MHz, CDCl}_3\text{): } \delta = 196.43, 143.19, 137.93, 134.87, 132.11, 130.26, 129.88, 128.94, 128.16, 21.63. \]

4-Chlorobenzophenone (11b)

\[ \text{\(^1\)H NMR (CDCl}_3\text{, 400 MHz): } \delta = 7.79 - 7.75 (m, 4H, Ar-H), 7.62 - 7.58 (m, 1H, Ar-H), 7.51 - 7.46 (m, 4H, Ar-H); \]
\[ \text{\(^{13}\)C NMR (100 MHz): } \delta = 195.51, 138.88, 137.21, 135.83, 132.63, 131.45, 129.92, 128.62, 128.39. \]
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