Supplementary Material

Selective and efficient Oxidation of benzylic alcohols to benzaldehydes and methyl benzoates by Dibromo-5, 5-dimethylhydantoin

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General Methods

All required chemicals were used directly without purification unless mentioned. ^1H (500 Mz) and ^{13}C (125 Mz) NMR spectra were recorded on a Varian INOVA spectrometer with CDCl_3 as the solvent and TMS as the internal standard. Capillary GC was performed with Agilent 6890, RTx-50 column. Analytical thin-layer chromatography (TLC) was carried out on precoated plates (silica gel 60 F254), and spots were visualized with ultraviolet (UV) light. Flash column chromatography was carried out with silica gel (300-350 mesh).

The gas-phase products were analyzed with Shimadzu GC-2014 gas chromatograph (GC) equipped with $30\text{ m} \times 0.32\text{ mm}$ Rtx-50 capillary column and FID detector. A volume of $2.0\text{ }\mu\text{l}$ was injected in splitless mode for each sample. The column was initially held at $60\text{ }^\circ\text{C}$. The temperature was ramped to $250\text{ }^\circ\text{C}$ at $15\text{ }^\circ\text{C}\cdot\text{min}^{-1}$

Representative Procedure for the Oxidation of Benzyl alcohols to Methyl enzoates (2b)^[1] with DBDMH:

DBDMH (20 mmol) was added in portion wise to a mixture of **1b** (5 mmol) and methanol (30 ml). The reaction was kept at room temperature. After the mixture was stirred for 12h, the methanol was vacuum evaporated. The residue was dissolved by MTBE (30 ml), washed with water ($3 \times 30\text{ ml}$). The organic extracts was dried by anhydrous MgSO_4 , filtered, and concentrated under reduce pressure. The residue was purified by column chromatography (silica gel: petroleum ether/ethyl acetate, 30:1) to afford the product as light yellow solid (92% yield). m.p. $42\text{--}44\text{ }^\circ\text{C}$ (lit. $43\text{ }^\circ\text{C}$), ^1H NMR (500 MHz, CDCl_3): δ 3.93(s, 3H), 7.39(d, 2H, $J=8.0\text{ Hz}$), 7.95(d, 2H, $J=8.0\text{ Hz}$); ^{13}C NMR (125 MHz, CDCl_3): δ 52.2, 128.5, 128.6, 130.9, 139.3, 166.1.

Representative procedure for the Oxidation of Benzyl alcohols to Benzaldehyde (3b)^[2] with DBDMH:

DBDMH (1 mmol) was added to a mixture of **1b** (1 mmol) and dichloromethane (20 ml). The reaction was kept at room temperature. After the mixture was stirred for 0.5h, the mixture was washed with water ($3 \times 30\text{ ml}$), dried with anhydrous MgSO_4 , filtered, and vacuum evaporated. The residue was purified by column chromatography

(silica gel: petroleum ether/ethyl acetate, 30:1) to afford the product as light yellow solid (93% yield). m.p.47 -48°C (lit. 48-50°C), ^1H NMR (500 MHz, CDCl_3): δ 7.22 (d, 2H, $J=8.0$ Hz), 7.92(d, 2H, $J=8.0$ Hz), 9.97(s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 129.4, 131.0, 134.9, 141.1, 190.7.

Representative procedure for the Oxidation of Benzaldehyde (3a) to Methyl benzoate (2a) ^[1] with DBDMH:

DBDMH (2 mmol) was added to a mixture of 3a (1 mmol) and methanol (15 ml). The reaction was kept at room temperature. After the mixture was stirred for 12h, the methanol was vacuum evaporated. The residue was dissolved by MTBE (15 ml), washed with water (3 x 10 ml). The organic extracts was dried by anhydrous MgSO_4 , filtered, and concentrated under reduce pressure. The residue was purified by column chromatography (silica gel: petroleum ether/ethyl acetate, 30:1) to afford the product as colorless liquid (93% yield). ^1H NMR (500 MHz, CDCl_3): δ 3.90(s, 3H), 7.41(d, 2H, $J=8.0$ Hz), 7.51~7.55(m, 1H), 8.02~8.04(m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ 52.4, 128.1, 129.3, 130.3, 132.6, 166.4.

Preparation of 5-Bromo-piperonyl aldehyde (5) ^[3]:

DBDMH (2.5 mmol) was added to a mixture of compound **4** (5 mmol) and dichloromethane (20 ml). The reaction was kept at room temperature. After the mixture was stirred for 12h, the mixture was washed with water (3 x 30ml), dried with anhydrous MgSO_4 , filtered, and vacuum evaporated. The residue was purified by column chromatography (silica gel: petroleum ether/ethyl acetate, 30:1) to afford the product as white solid (89% yield). m.p.123 -125°C (lit. 124-124.5°C), ^1H NMR (500 MHz, CDCl_3): δ 6.16(s, 2H), 7.26(s, 1H), 7.54(s, 1H), 9.76(s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 101.3, 103.1, 106.7, 131.4, 133.3, 149.4, 151.7, 189.5.

Preparation of 6-Bromo-piperonyl aldehyde (3n) ^[4] from Piperonyl alcohol (1n):

DBDMH (1 mmol) was added to a mixture of 1n (1 mmol) and dichloromethane (20 ml). The reaction was kept at room temperature. After the mixture was stirred for

0.5h, the mixture was washed with water (3 x 30 ml), dried with anhydrous MgSO_4 , filtered, and vacuum evaporated. The residue was purified by column chromatography (silica gel: petroleum ether/ethyl acetate, 30:1) to afford the product as white solid (75% yield). m.p. 128 -130°C (lit. 129-130°C), ^1H NMR (500 MHz, CDCl_3): δ 6.11(s, 2H), 7.05(s, 1H), 7.36(s, 1H), 10.20(s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 102.9, 108.1, 113.3, 121.7, 128.0, 148.2, 153.4, 190.4.

Spectral Data of Products:

Methyl 4-bromo-1-benzoate (2c) ^[1]:

White solid, m.p. 77-79°C (lit. 77-79°C), ^1H NMR (500 MHz, CDCl_3): δ 3.90(s, 3H), 7.57(d, 2H, $J=8.0$ Hz), 7.88(d, 2H, $J=8.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 52.2, 128.0, 129.0, 131.1, 131.7, 166.3.

Methyl 4-methyl-1-benzoate (2d) ^[1]:

White solid, m.p. 32-34(33-34°C), ^1H NMR (500 MHz, CDCl_3): δ 2.41(s, 3H), 3.90(s, 3H), 7.24(d, 2H, $J=8.0$ Hz), 7.93(d, 2H, $J=8.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 21.5, 51.8, 127.4, 129.0, 129.5, 143.4, 167.0.

Methyl 3-Bromo-4-methoxy-1-benzoate (2e) ^[5]:

White solid, m.p.96-98°C(lit. 96-97°C), ^1H NMR (500 MHz, CDCl_3): δ 3.90(s, 3H), 3.96(s, 3H), 6.92(d, 1H, $J=9.0$ Hz), 7.99(d, 1H, $J=9.0$ Hz), 8.23(s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 52.1, 56.4, 111.0, 111.4, 123.8, 130.6, 134.8, 159.5, 165.7.

Methyl 4-(trifluoromethyl)-1- benzoate (2f) ^[1]:

Light yellow liquid, ^1H NMR (500 MHz, CDCl_3): δ 3.90(s, 3H), 7.63 (d, 2H, $J=8.0$ Hz), 8.08(d, 2H, $J=8.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 52.4, 123.6 (q, $J_{\text{C-F}}=270.7$ Hz), 125.3 (d, $J_{\text{C-F}}=3.6$ Hz), 129.9, 133.3, 134.3 (q, $J_{\text{C-F}}=32.4$ Hz), 165.8.

Methyl 4-nitro-1-benzoate (2g) ^[6]:

White solid, m.p.92-94°C(lit. 93-95°C), ^1H NMR (500 MHz, CDCl_3): δ 3.99(s, 3H), 8.22(d, 2H, $J=9.0$ Hz), 8.30(d, 2H, $J=9.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 52.7, 123.5, 135.5, 150.5, 165.1.

Methyl-6-chloronicotinate (2h) ^[7]:

White solid, m.p.86-88°C(lit.86-87°C), ^1H NMR (500 MHz, CDCl_3): δ 3.90(s, 3H), 7.36(d, 1H, $J=8.0$ Hz), 8.17~8.20(m, 1H), 8.92(s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 52.5, 120.9, 123.2, 138.9, 147.4, 154.2, 165.0.

Methyl 3-nitro-1-benzoate (2i) ^[8]:

White solid, m.p.77-79°C (lit.77-79°C), ¹H NMR (500 MHz, CDCl₃): δ 3.98(s, 3H), 7.36(t, 1H, *J*=8.0 Hz), 8.41~8.52(m, 2H), 8.86(s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 52.9, 124.8, 127.5, 129.8, 132.0, 135.4, 148.4, 165.1.

Methyl 2-chloro-1-benzoate (2j) ^[9]:

Yellow oil, ¹H NMR (500 MHz, CDCl₃): δ 3.93(s, 3H), 7.31(t, 1H, *J*=8.0 Hz), 7.39~7.46(m, 2H), 7.82(d, 1H, *J*=8.0 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 52.3, 126.5, 130.0, 131.0, 131.3, 132.5, 133.6, 166.1.

Methyl 2-bromo-1-benzoate (2k) ^[4]:

colorless liquid, ¹H NMR (500 MHz, CDCl₃): δ 3.90(s, 3H), 7.30~7.36(m, 2H), 7.61(d, 1H, *J*=8.0 Hz), 7.76(d, 1H, *J*=8.0 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 52.4, 126.5, 130.0, 131.0, 131.3, 132.5, 133.6, 166.1.

Methyl 2-methyl-1-benzoate (2l) ^[1]:

colorless oil, ^1H NMR (500 MHz, CDCl_3): δ 2.61(s, 3H), 3.95(s, 3H), 7.26~7.43(m, 2H), 7.47(d, 1H, $J=8.0$ Hz), 8.07(d, 1H, $J=8.0$ Hz); ^{13}C NMR (125 MHz, CDCl_3): δ 21.6, 51.7, 125.6, 129.5, 130.5, 131.6, 131.9, 140.1, 168.0.

Methyl 5-bromo-2-methoxy-1-benzoate (2m)^[10]:

White solid, m.p.115-117°C (lit.115-118°C), ^1H NMR (500 MHz, CDCl_3): δ 3.83(s, 3H), 3.92(s, 3H), 6.86(d, 1H, $J=9.0$ Hz), 7.56(d, 1H, $J=9.0$ Hz), 8.03(s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 52.1, 56.1, 112.1, 113.8, 121.6, 134.1, 135.9, 158.1, 165.1.

Benzaldehyde (3a):

colorless liquid, ^1H NMR (500 MHz, CDCl_3): δ 7.30~7.43(m, 2H), 7.50~7.54(m, 1H), 7.86(d, 2H, $J=8.0$ Hz), 10.00(s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 129.6, 129.8, 135.2, 137.1, 191.1.

4-Bromobenzaldehyde (3c)^[11]:

Light yellow solid, m.p.57-59 °C (lit.56-57 °C), ^1H NMR (500 MHz, CDCl_3): δ 7.61~7.77(m, 4H), 9.98(s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 129.7, 130.8, 132.3, 135.2, 191.2.

4-methylbenzaldehyde (3d)^[12]:

colorless liquid, ^1H NMR (500 MHz, CDCl_3): δ 2.44(s, 3H), 7.33(d, 2H, $J=8.0$ Hz), 7.77(d, 2H, $J=8.0$ Hz), 9.96(s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 21.8, 129.7, 129.8, 134.0, 145.4, 192.0.

3-Bromo-4-methoxybenzaldehyde (3e)^[13]:

colorless solid, m.p.43-45 °C (lit.43-44 °C) ^1H NMR (500 MHz, CDCl_3): δ 3.87(s, 3H), 6.85(d, 1H, $J=9.0$ Hz), 7.64(d, 1H, $J=9.0$ Hz), 7.87(s, 1H), 9.87(s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 56.6, 111.6, 112.7, 130.8, 131.1, 134.6, 160.7, 189.5.

4-(trifluoromethyl)benzaldehyde (3f)^[14]:

colorless liquid (lit. colorless oil), ^1H NMR (500 MHz, CDCl_3): δ 7.97(d, 2H, $J=8.0$ Hz), 8.17(d, 2H, $J=8.0$ Hz), 10.16(s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 123.5(q, $J_{\text{C-F}}=271.0$ Hz), 126.1, 129.9, 135.6(q, $J_{\text{C-F}}=32.0$ Hz), 138.7, 191.1.

4-Nitrobenzaldehyde (3g)^[2]:

Yellow solid, m.p.104-106°C(lit.104-106°C), ¹H NMR (500 MHz, CDCl₃): δ 8.09(d, 2H, *J*=9.0 Hz), 8.41(d, 2H, *J*=9.0 Hz), 10.17(s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 124.3, 130.5, 140.1, 151.5, 190.3.

6-Chloro-pyridine-3-carboxyaldehyde (3h)^[15]:

White solid, m.p.78-80°C(lit.79-80°C), ¹H NMR (500 MHz, CDCl₃): δ 7.49(d, 1H, *J*=8.0 Hz), 8.12(d, 1H, *J*=8.0 Hz), 8.84(s, 1H), 10.07(s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 125.2, 130.4, 138.0, 152.4, 157.0, 189.3.

3-Nitrobenzaldehyde (3i)^[16]:

Yellow solid, m.p.56-58°C(lit.56-57°C), ¹H NMR (500 MHz, CDCl₃): δ 7.77(t, 1H, *J*=8.0 Hz), 8.23(d, 1H, *J*=8.0 Hz), 8.49(dd, 1H, *J*=2.0 Hz, *J*=8.0 Hz), 8.72(s, 1H), 10.12(s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 124.4, 128.6, 130.5, 134.8, 137.4, 148.8, 189.9.

2-Chlorobenzaldehyde (3j):

Light yellow liquid (commercial, colorless liquid), ^1H NMR (500 MHz, CDCl_3): δ 7.39(t, $J=8.0$ Hz, 1H), 7.45(d, 1H, $J=8.0$ Hz), 7.51~7.54(m, 1H), 7.92(d, 1H, $J=8.0$ Hz), 10.49(s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 127.3, 129.5, 130.3, 132.2, 135.2, 137.7, 189.8.

2-bromobenzaldehyde (3k)^[11]:

colorless liquid, ^1H NMR (500 MHz, CDCl_3): δ 7.37~7.42(m, 4H), 10.32(s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 126.8, 127.9, 130.2, 133.2, 133.6, 135.3, 191.3.

2-Methylbenzaldehyde (3l)^[17]:

colorless liquid, ^1H NMR (500 MHz, CDCl_3): δ 2.67(s, 3H), 7.26~7.28(m, 1H), 7.37(t, 1H, $J=8.0$ Hz), 7.43~7.49(m, 1H), 7.80(d, 1H, $J=8$ Hz), 10.27(s, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ 20.1, 126.2, 131.6, 131.9, 133.5, 133.9, 140.3, 192.8.

5-Bromo-2-methoxybenzaldehyde (3m)^[18]:

Yellow solid, m. p. 116-118°C (lit. 117-118°C) ^1H NMR (500 MHz, CDCl_3): δ 3.92(s, 3H), 6.77(d, 1H, $J=9.0$ Hz), 7.40(d, 1H, $J=9.0$ Hz), 7.64(s, 1H), 10.38(s, 1H); ^{13}C

NMR (125 MHz, CDCl₃): δ 56.1, 113.6, 113.9, 125.2, 131.1, 138.4, 160.9, 188.5.

6-Bromobenzo[d][1,3]dioxole-5-carbaldehyde (3n)^[4]:

white solid, m.p. 128–130 °C (lit. 129–130 °C), ¹H NMR (500 MHz, CDCl₃): δ 6.11(s, 2H), 7.05(s, 1H), 7.36(s, 1H), 10.20(s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 102.9, 108.1, 113.3, 121.7, 128.0, 148.2, 153.4, 190.4.

Acetophenone (3o):

Light yellow oil (commercial, light yellow oil), ¹H NMR (500 MHz, CDCl₃): δ 2.62(s, 3H), 7.47(t, 2H, *J*=7.5 Hz), 7.58(t, 1H, *J*=7.5 Hz), 7.97(t, 2H, *J*=5.0 Hz); ¹³C NMR (125 MHz, CDCl₃): δ 26.5, 128.2, 128.5, 133.0, 137.1, 198.1.

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