Supporting Information
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Supporting Information for:

**Diphenyl diselenide-catalyzed oxidative degradation of benzoin to benzoic acid**

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Experimental general

All chemicals and solvents were purchased and directly used without any purification. The organoselenium catalysts could be prepared through known methods or purchased from reagent merchant. The reactions were carried out in open air without inert gas protection. All reactions were monitored by TLC. Melting point was measured using a WRS-2A digital instrument. Infrared spectrum was measured using Bruker Tensor 27 IR instrument. \(^{1}\)H and \(^{13}\)C NMR spectra were recorded on an Agilent Technologies 400/54 Annual Refill (400 MHz for \(^{1}\)H and 100 MHz for \(^{13}\)C NMR spectroscopy) instrument using CDCl\(_3\) as the solvent and Me\(_4\)Si as the internal standard. Chemical shifts for \(^{1}\)H and \(^{13}\)C NMR were referred to internal Me\(_4\)Si (0 ppm) and \(J\)-values were shown in Hz.

Procedure for scale magnified preparation of benzoic acid and the catalyst recycle and reuse.

To a 500 mL round bottom flask, 100 mmol of benzoin 1a (21.2 g), 5 mmol (PhSe)\(_2\) (1.56 g) and a magnetic bar were added. The mixture was then stirred and a solution of 240 mmol 30\% H\(_2\)O\(_2\) (27.2 g) in 200 mL MeCN was slowly dropped. After stirring at rt for 24 h, 0.5 g of MnO\(_2\) was added to decompose the excess H\(_2\)O\(_2\) (CAUTION, very important detail), which could be monitored by starch-KI test paper. MnO\(_2\) could be removed by filtration and the solvent MeCN was removed by the atmospheric distillation. Further distillation under reduced pressure (95-100 °C/0.6 mmHg) afforded the benzoic acid 2 in 88\% yield. The residue, containing organoselenium compounds as the major component, could be reused as catalyst in the next turn of reaction directly without any purification.

Characterization of the products

**Benzoic acid 2a:** White solid, m.p. 122.0-122.4 °C (lit. 122 °C); IR (KBr): 3717, 3067, 2835, 2673, 2557, 1688, 1419, 1286, 1179, 930, 705, 541 cm\(^{-1}\); \(^{1}\)H NMR (400 MHz, CDCl\(_3\), TMS): \(\delta\) 8.13 (d, \(J = 8.9\) Hz, 2H), 7.62 (t, \(J = 7.4\) Hz, 1H), 7.49 (t, \(J = 7.8\) Hz, 2H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 171.6, 133.7, 130.2, 129.2, 128.5; Known compound.\(^1\)

**4-Methylbenzoic acid 2b:** White solid, m.p. 178.6-179.3 °C (lit. 179.6 °C); IR (KBr): 2974, 2653, 1677, 1414, 1283, 955, 751, 536, 466 cm\(^{-1}\); \(^{1}\)H NMR (400 MHz, CDCl\(_3\), TMS): \(\delta\) 12.52 (s, 1H),
8.01 (d, $J = 7.2$ Hz, 2H), 7.27 (d, $J = 7.5$ Hz, 2H), 2.43 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 172.61, 144.67, 130.25, 129.20, 126.56, 21.78; Known compound.$^1$

4-Methoxybenzoic acid 2c: White solid, m.p. 184.4-185.0 °C ($lit.$ 185 °C); IR (KBr): 3691, 2984, 2838, 2665, 2549, 1684, 1599, 1424, 1256, 1165, 1020, 927, 842, 770, 612, 545 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$ 8.08 (d, $J = 8.4$ Hz, 2H), 6.96 (d, $J = 7.6$ Hz, 2H), 3.89 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 171.52, 164.01, 132.34, 121.56, 113.72, 55.48. Known compound.$^1$

4-Fluorobenzoic acid 2d: White solid, m.p. 184.1-184.6 °C ($lit.$ 184 °C); IR (KBr): 3080, 2844, 2673, 2559, 1684, 1426, 1297, 848, 608 cm$^{-1}$; $^1$H NMR (400 MHz, $d_6$-DMSO, TMS): $\delta$ 13.02 (s, 1H), 7.97 (t, $J = 5.3$ Hz, 2H), 7.26 (t, $J = 8.6$ Hz, 2H); $^{13}$C NMR (100 MHz, $d_6$-DMSO): $\delta$ 166.56, 164.07, 132.55, 127.76, 116.10. Known compound.$^1$

4-Chlorobenzoic acid 2e: White solid, m.p. 242.9-243.5 °C ($lit.$ 243 °C); IR (KBr): 2986, 2668, 2554, 1688, 1420, 1313, 1083, 928, 755, 543; $^1$H NMR (400 MHz, $d_6$-DMSO, TMS): $\delta$ 13.16 (s, 1H), 7.90 (d, $J = 8.0$ Hz, 2H), 7.50 (d, $J = 7.9$ Hz, 2H); $^{13}$C NMR (100 MHz, $d_6$-DMSO): $\delta$ 166.88, 138.21, 131.54, 130.03, 129.11. Known compound.$^1$

4-Bromobenzoic acid 2f: White solid, m.p. 254.1-254.6 °C ($lit.$ 254 °C); IR (KBr): 2981, 2672, 2557, 1685, 1422, 1315, 926, 750, 545; $^1$H NMR (400 MHz, $d_6$-DMSO, TMS): $\delta$ 13.18 (s, 1H), 7.83 (d, $J = 8.2$ Hz, 2H), 7.67 (d, $J = 8.1$ Hz, 2H); $^{13}$C NMR (100 MHz, $d_6$-DMSO): $\delta$ 167.03, 132.12, 131.71, 130.41, 127.31. Known compound.$^1$

2-Phenylacetic acid 2g: White solid, m.p. 76.6-77.0 °C ($lit.$ 76 °C); IR (KBr): 3034, 1701, 1409, 1240, 909, 697 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$, TMS): $\delta$ 11.77 (s, 1H), 7.53–7.15 (m, 5H), 3.67 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 178.41, 133.22, 129.40, 128.67, 127.39, 41.11. Known compound.$^1$

References

1 Spectral Database for Organic Compounds, SDBS:

http://sdb.sdb.db.aist.go.jp/sdb/cgi-bin/direct_frame_top.cgi
Spectra of the products

2a, $^1$H NMR, CDCl$_3$, 400 MHz

2a, $^{13}$C NMR, CDCl$_3$, 100 MHz
2a, IR, KBr

2b, $^1$H NMR, CDCl$_3$, 400 MHz
2b, $^{13}$C NMR, CDCl$_3$, 100 MHz

Chemical shifts (ppm): 21.78, 76.70, 77.02, 77.34, 126.56, 129.20, 130.25, 144.67, 172.61

2b, IR, KBr

Wavenumber cm$^{-1}$: 3174.01, 2962.89, 2858.46, 1777.39, 1413.82, 1283.87, 944.69, 750.88, 696.63, 535.68, 456.63
2c, $^1$H NMR, CDCl$_3$, 400 MHz

2c, $^{13}$C NMR, CDCl$_3$, 100 MHz
2c, IR, KBr

\[
\begin{align*}
\text{Wavenumber cm}^{-1} & \\
4000 & \quad 3000 & \quad 2000 & \quad 1000 \\
& \quad 3910.07 & \quad 3897.00 & \quad 3855.12 & \quad 2950.73 & \quad 1984.40 & \quad 1359.22 & \quad 1023.08 & \quad 1226.19 & \quad 1564.06 & \quad 1623.30 & \quad 2653.50 & \quad 942.71 & \quad 964.04 & \quad 811.97 & \quad 564.73
\end{align*}
\]

2d, \( ^1H \) NMR, \( d_6 \)-DMSO, 400 MHz

\[
\begin{align*}
& \quad 2.00 & \quad 1.97 & \quad 1.00 & \quad 1.97 & \quad 2.00 & \quad 2.00 & \quad 2.00 \\
& \quad 13.02 & \quad 7.88 & \quad 7.88 & \quad 7.29 & \quad 7.24 & \quad 7.24 & \quad 3.47 \\
\end{align*}
\]
2d, $^{13}$C NMR, $d_6$-DMSO, 100 MHz

2d. IR, KBr
2e, $^1$H NMR, $d_6$-DMSO, 400 MHz

2e, $^{13}$C NMR, $d_6$-DMSO, 100 MHz
2e, IR, KBr

2f, $^1$H NMR, $d_6$-DMSO, 400 MHz
2f, $^{13}$C NMR, $d_6$-DMSO, 100 MHz

2f, IR, KBr
2g, $^1$H NMR, CDCl$_3$, 400 MHz

2g, $^{13}$C NMR, CDCl$_3$, 100 MHz
2g, IR, KBr