Supporting Information

Redox-Neutral Iron-Sulfur Promoted Transformation of 2,6-Disubstituted \( p \)-Cresols and 2-Nitrophenols into 2-Arylbenzoxazoles

Masahiko Saibara,*\(^a\) Kazuhito Ashida,\(^a\) Kouji Satomi,\(^a\) Toshiyuki Iwai,\(^b\) Takeo Nakai,\(^b\)
Masatoshi Mihara,\(^b\) Takatoshi Ito,\(^b\) and Takumi Mizuno*\(^b\)

\(^a\) Research Center, Honshu Chemical Industry Co., Ltd., 2-5-115, Kozaika, Wakayama 641-0007, Japan
\(^b\) Organic Materials Research Division, Osaka Municipal Technical Research Institute, 1-6-50, Morinomiya, Joto-ku, Osaka 536-8553, Japan

Fax: +81(6)69638030; E-mail: tmizuno@omtri.or.jp

List of Contents

1. General S2
2. Typical procedure for the synthesis of 2-arylbenzoxazoles 3 S2
3. Analytical data of 3 S2-S6
4. Analytical data of 4a, 4b, 5a, 5b S6-S7
5. Reference S7
6. \(^1\)H NMR and \(^{13}\)C NMR spectra of 3 S8-S17
7. \(^1\)H NMR spectra of 4a, 4b, 5a S17-S18
**General.** Melting points were determined on a Yanaco MP-J3 instrument and were uncorrected. FT-IR spectra were recorded on a JASCO FT/IR-4100 instrument. $^1$H NMR, $^{13}$C NMR, and $^{19}$F NMR spectra were obtained on a JEOL JNM-AL300 (300 MHz, 75 MHz, and 280 MHz) instrument. Chemical shifts were reported in ppm relative to tetramethylsilane or solvent peak (δ-units). Mass spectra were measured on a Shimadzu MALDI-TOFMS AXIMA or JEOL JMS-600 spectrometer. 2-Nitrophenols 1, cresols 2, elemental sulfur, iron catalysts, and solvents were used as purchased. 1h was prepared by nitration of bisphenol.

**Typical procedure for the synthesis of 2-arylbenzoxazoles 3.** 2-Nitrophenols 1 (3.0 mmol), cresols 2 (6.0 mmol), iron (16.8 mg, 0.3 mmol), sulfur (96.2 mg, 3.0 mmol), and o-dichlorobenzene (8.0 mL) were placed in a test tube charged with a magnetic stirring bar under argon atmosphere. The reaction mixture was heated to 180 °C and vigorously stirred for 24 h. The solution was cooled to room temperature, and the solvent was removed under vacuum. The residue was purified by column chromatography to give the corresponding product, unless otherwise noted.

**2-(3,5-Di-tert-butyl-4-hydroxyphenyl)benzoxazole (3aa).** Compound 3aa was isolated in 58% yield (559.5 mg); $^1$H NMR (300 MHz, CDCl$_3$): δ 8.09 (s, 2H), 7.75-7.72 (m, 1H), 7.57-7.54 (m, 1H), 7.33-7.29 (m, 2H), 5.64 (s, 1H), 1.53 (s, 18H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ164.1, 157.1, 150.7, 142.4, 136.6, 125.0, 124.3, 124.2, 119.5, 118.4, 110.3, 34.5, 30.2; MS (EI) m/z 324 [M+H]$^+$; IR (KBr) ν 3625 cm$^{-1}$; mp 169-170 °C (169-170 °C).1
**2-(3,5-Di-tert-butyl-4-hydroxyphenyl)-4-methylbenzoxazole (3ba).** Compound 3ba was isolated in 84% yield (847.0 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.09 (s, 2H), 7.37 (br d, $J = 7.9$ Hz, 1H), 7.18 (t, $J = 7.7$ Hz, 1H), 7.10 (br d, $J = 7.3$ Hz, 1H), 5.60 (s, 1H), 2.67 (s, 3H), 1.53 (s, 18H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 163.4, 156.9, 150.4, 141.7, 136.4, 130.0, 125.0, 124.8, 123.9, 118.7, 107.6, 34.5, 30.2, 16.6; HRMS (EI) Calcd for C$_{22}$H$_{27}$NO$_2$, 337.2042 [M$^+$], found 337.2017; IR (KBr) v 3630 cm$^{-1}$; mp 138-139 °C.

**2-(3,5-Di-tert-butyl-4-hydroxyphenyl)-5-methylbenzoxazole (3ca).** Compound 3ca was isolated in 72% yield (725.4 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.08 (s, 2H), 7.52 (br s, 1H), 7.42 (d, $J = 8.2$ Hz, 1H), 7.10 (dd, $J = 8.3$, 1.1 Hz, 1H), 5.63 (s, 1H), 2.47 (s, 3H), 1.52 (s, 18H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 164.2, 157.0, 148.9, 142.6, 136.5, 134.0, 125.4, 124.9, 119.5, 118.6, 109.6, 34.5, 30.2, 21.5; HRMS (EI) Calcd for C$_{22}$H$_{27}$NO$_2$, 337.2042 [M$^+$], found 337.2063; IR (KBr) v 3626 cm$^{-1}$; mp 163-164 °C (168-169 °C).$^1$

**2-(3,5-Di-tert-butyl-4-hydroxyphenyl)-6-methylbenzoxazole (3da).** Compound 3da was isolated in 62% yield (628.5 mg); $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 8.07 (s, 2H), 7.60 (d, $J = 8.1$ Hz, 1H), 7.37 (br s, 1H), 7.13 (br d, $J = 8.1$ Hz, 1H), 5.62 (s, 1H), 2.50 (s, 3H), 1.52 (s, 18H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 163.7, 156.9, 151.0, 140.2, 136.5, 134.7, 125.4, 124.8, 118.8, 118.6, 110.6, 34.5, 30.2, 21.8; HRMS (EI) Calcd for C$_{22}$H$_{27}$NO$_2$, 337.2042 [M$^+$], found 337.2044; IR (KBr) v 3623 cm$^{-1}$; mp 187-188 °C (187-188 °C).$^1$

**2-(3,5-Di-tert-butyl-4-hydroxyphenyl)-5-methoxybenzoxazole (3ea).** Compound
3ea was isolated in 76% yield (803.2 mg); $^1$H NMR (300 MHz, CDCl$_3$): δ 8.07 (s, 2H), 7.43 (d, $J = 8.8$ Hz, 1H), 7.25 (d, $J = 2.6$ Hz, 1H), 6.90 (dd, $J = 8.8$, 2.5 Hz, 1H), 5.64 (s, 1H), 3.86 (s, 3H), 1.52 (s, 18H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 164.9, 157.2, 157.0, 145.3, 143.2, 136.5, 124.9, 118.5, 112.7, 110.4, 102.7, 55.9, 34.5, 30.2; HRMS (EI) Calcd for C$_{22}$H$_{27}$NO$_3$, 353.1991 [M$^+$], found 353.1984; IR (KBr) ν 3585 cm$^{-1}$; mp 170-171 °C (177-178 °C).$^1$

2-(3,5-Di-tert-butyl-4-hydroxyphenyl)-5-trifluoromethylbenzoxazole (3fa). Compound 3fa was isolated in 43% yield (501.5 mg); $^1$H NMR (300 MHz, CDCl$_3$): δ 8.10 (s, 2H), 8.01 (br s, 1H), 7.64 (d, $J = 8.6$ Hz, 1H), 7.57 (dd, $J = 8.7$, 1.4 Hz, 1H), 5.72 (s, 1H), 1.53 (s, 18H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 165.8, 157.7, 152.4, 142.6, 136.7, 127.1 (q, $J = 32.4$ Hz), 125.3, 124.3 (q, $J = 272.2$ Hz), 121.5 (q, $J = 3.4$ Hz), 117.7, 117.1 (q, $J = 3.7$ Hz), 110.6, 34.5, 30.2; $^{19}$F NMR (280 MHz, CDCl$_3$): δ -60.0; HRMS (EI) Calcd for C$_{22}$H$_{24}$F$_3$NO$_2$, 391.1759 [M$^+$], found 391.1735; IR (KBr) ν 3596 cm$^{-1}$; mp 137-138 °C.

2-(3,5-Di-tert-butyl-4-hydroxyphenyl)benzimidazole (3ga). Compound 3ga was isolated in 5% yield (52.2 mg); $^1$H NMR (300 MHz, DMSO-d$_6$): δ 12.7 (s, 1H), 7.94 (s, 2H), 7.60 (br d, $J = 7.0$ Hz, 1H), 7.47 (br d, $J = 6.4$ Hz, 1H), 7.38 (s, 1H), 7.15-7.13 (m, 2H), 1.45 (s, 18H); MS (EI) m/z 323 [M+H$^+$]; IR (KBr) ν 3626 cm$^{-1}$; mp >300 °C (300 °C).$^1$

2-(3,5-Dimethoxy-4-hydroxyphenyl)benzoxazole (3ab). Compound 3ab was isolated in 21% yield (168.7 mg); $^1$H NMR (300 MHz, CDCl$_3$): δ 7.76-7.73 (m, 1H),
7.58-7.55 (m, 1H), 7.52 (s, 2H), 7.37-7.30 (m, 2H), 6.00 (s, 1H), 4.02 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 163.2, 150.7, 147.3, 142.1, 138.1, 124.7, 124.5, 119.6, 118.2, 110.3, 104.6, 56.5; HRMS (EI) Calcd for C$_{15}$H$_{13}$NO$_4$, 271.0845 [M$^+$], found 271.0854; IR (KBr) ν 3256 cm$^{-1}$; mp 191-192 °C.

2-(3-tert-Butyl-4-hydroxyphenyl)benzoxazole (3ac). Compound 3ac was isolated in 5% yield (44.0 mg); $^1$H NMR (300 MHz, CDCl$_3$): δ 8.20 (d, $J = 2.2$ Hz, 1H), 7.97 (dd, $J = 8.3$ Hz, 1H), 7.75-7.72 (m, 1H), 7.58-7.55 (m, 1H), 7.36-7.29 (m, 2H), 6.81 (d, $J = 8.3$ Hz, 1H), 5.98 (br, 1H), 1.49 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$): δ 163.8, 158.0, 150.6, 142.0, 137.0, 127.2, 127.1, 124.5, 124.4, 119.4, 119.0, 117.1, 110.4, 34.8, 29.4; HRMS (EI) Calcd for C$_{17}$H$_{17}$NO$_2$, 267.1259 [M$^+$], found 267.1274; IR (KBr) ν 3059 cm$^{-1}$; mp 241-245 °C.

1,1-Bis[2-(3,5-di-tert-butyl-4-hydroxyphenyl)benzoxazolyl]-3,3,5-trimethylcyclohexane (3ha). A mixture of 1h (601 mg, 1.5 mmol), 2a (1.322 g, 6.0 mmol), iron (16.8 mg, 0.3 mmol), sulfur (96.2 mg, 3.0 mmol) in o-dichlorobenzene (8.0 ml) was stirred under argon at 180 °C for 48 h. After the reaction was complete, the reaction mixture was purified by short-column chromatography to obtain compound 3ha. Compound 3ha was isolated in 50% yield (571.5 mg); $^1$H NMR (300 MHz, CDCl$_3$): δ 8.06 (s, 2H), 8.03 (s, 2H), 7.87 (d, $J = 1.1$ Hz, 1H), 7.74 (d, $J = 1.7$ Hz, 1H), 7.40 (d, $J = 8.7$ Hz, 1H), 7.33 (d, $J = 8.8$ Hz, 1H), 7.25 (dd, $J = 8.5$, 1.6 Hz, 1H), 7.15 (dd, $J = 8.6$, 1.8 Hz, 1H), 5.63 (s, 1H), 5.61 (s, 1H), 2.87 (br d, $J = 13.9$ Hz, 1H), 2.62 (br d, $J = 13.0$ Hz, 1H), 2.23-2.13 (br s, 1H), 2.13 (d, $J = 13.6$ Hz, 1H), 1.52 (s, 18H), 1.50 (s, 18H), 1.48-1.38 (m, 1H), 1.33-1.23 (m, 1H), 1.01 (s, 3H), 1.01 (d, $J = 6.2$ Hz, 3H), 0.92 (br t, $J = 12.6$ Hz, 3H).
6,6′-Thiobis(2-(tert-butyl)-4-methylphenol) (4a). ¹H NMR (300 MHz, CDCl₃): δ 7.03 (d, J = 2.0 Hz, 2H), 6.99-6.98 (m, 2H), 6.55 (s, 2H), 2.19 (s, 6H), 1.40 (s, 18H); MS (EI) m/z 358 (M⁺).

6,6′-Thiobis(2-(tert-butyl)-4-methylphenol) (4a) was identified by comparison of MS spectrum with that from Spectral Database for Organic Compounds (SDBS) in National Institute of Advanced Industrial Science and Technology (AIST), Japan.

4,4′-Thiobis(2-(tert-butyl)-6-methylphenol) (4b). ¹H NMR (300 MHz, CDCl₃): δ 7.16 (d, J = 2.2 Hz, 2H), 6.99 (d, J = 2.2 Hz, 2H), 4.75 (s, 2H), 2.19 (s, 6H), 1.37 (s, 18H); MS (EI) m/z 358 (M⁺).

4,4′-Thiobis(2-(tert-butyl)-6-methylphenol) (4b) was identified by comparison of ¹H NMR and MS spectra with those from SDBS.

3,5-Di-tert-butyl-4-hydroxybenzaldehyde (5a). ¹H NMR (300 MHz, CDCl₃): δ 9.85 (s, 1H), 7.73 (s, 2H), 5.85 (s, 1H), 1.48 (s, 18H); MS (EI) m/z 235 [M+H]⁺.

3,5-Di-tert-butyl-4-hydroxybenzaldehyde (5a) was identified by comparison of MS spectrum with that from SDBS.

2,6-Di-tert-butyl-4-(2,3-dihydrobenzo[d]oxazol-2-yl)phenol (5b) or 2,6-di-tert-
butyl-4-(((2-hydroxyphenyl)imino)methyl)phenol (5b’). MS (EI) m/z 325 (M⁺).

Isolation of 5b (or 5b’) is difficult by instability under reaction conditions. Analysis of 5b (or 5b’) in reaction solution was performed by GC-MS. Identification of 5b (or 5b’) was carried out by comparison with that of authentic sample, which prepared 5a with o-aminophenol.

Reference