Electronic Supplementary Information for

Fluorescence enhancement by hydroperoxides based on the change in intramolecular charge transfer character of benzofurazan

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General. Melting points (Mp), determined on a Yanako melting point apparatus, are uncorrected. ^{1}H-NMR spectra were determined on a JEOL LA-500 spectrometer (500 MHz) or a JEOL JNM-ECP600 spectrometer (600 MHz). ^{13}C-NMR spectra were determined on a JEOL JNM-ECP600 spectrometer (150 MHz). Chemical shifts for ^{1}H-NMR were reported in parts per million (ppm) downfield from tetramethylsilane as the internal standard and coupling constants (*J*) are in Hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet, and br = broad. Chemical shifts for ^{13}C-NMR were reported in ppm relative to the central line of a triplet at 77.0 ppm for deuteriochloroform and coupling constants (*J*) are in Hertz (Hz). Infrared (IR) spectra were recorded on a JASCO FT/IR-8000 Fourier Transform Infrared Spectrophotometer and are reported in wavenumbers (cm^{-1}). High resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX 102A. UV-vis absorption spectra were obtained on a Shimadzu UV-260 spectrophotometer. Fluorescence spectra were obtained on a Shimadzu RF-5000 fluorescence spectrophotometer. Analytical thin layer chromatography (TLC) was performed on HPTLC aluminium sheets, silica gel 60 F_{254} (Merck). Open column chromatography was performed on Merck silica gel 60 (70-230 mesh). Preparative TLC (PTLC) was performed on 6.7 × 20 cm Merck precoated analytical plates, 0.50 mm thick, silica gel 60 F_{254}. Reagents and solvents were commercial grades and were used as supplied. THF and DMF were purchased anhydrous. Chlorodiethylphosphine was purchased from Acros Organics.

Design of the fluorescent reagents. Figure 1, obtained in our previous research [1], shows the relationship between the fluorescence intensities of 4,7-disubstituted benzofurazan compounds and the Hammett substituent constants (σ_p) at the 4- and 7-positions. In this figure, the abscissa (*x* axis) and the ordinate (*y* axis) are the sum of the σ_p values at the 4- and 7-positions ($x = \sigma_p(4) + \sigma_p(7)$) and the difference in the σ_p values between the 4- and 7-positions ($y = |\sigma_p(4) - \sigma_p(7)|$), respectively. Seventy 4,7-disubstituted benzofurazan compounds were plotted in the figure and classified into three groups according to their relative fluorescence intensity (RFI; fluorescence intensity of 4-amino-7-*N*,*N*-dimethyl-aminosulfonyl-2,1,3-benzoxadiazole is arbitrarily taken as 1.0. RFI = 0-1, having no or weak fluorescence (○); RFI = 1-5, having moderate fluorescence (▲); RFI > 5, having strong fluorescence (■)). The fluorescent compounds, represented as closed squares and closed triangles, were concentrated in two areas (A and B), in contrast, the non-fluorescent compounds scattered out of these two areas. Using this relationship, the compounds in the area A or B were predicted to be fluorescent, whereas the compounds out of these areas were predicted to be non-fluorescent.

At first, the diphenylphosphino (PPh_2; $\sigma_p = 0.19$ [2]) and diethylphosphino (PEt_2; $\sigma_p = 0.13$ [2]) groups were selected as the reaction group at the 4-position. The compounds having the PPh_2 group at the 4-position were plotted on the line ① (line ① in Figure 1a; $y = |x - 0.38|$, only $y = -x + 0.38$ ($x < 0.38$) was drawn because $y = x - 0.38$ ($x > 0.38$) was unnecessary for this discussion). Similarly, the compounds having the PEt_2 group were plotted on the line ② (line ② in Figure 1b; $y = |x - 0.26|$, only $y = -x + 0.26$ ($x < 0.26$) was drawn). After the reaction with hydroperoxides, the PPh_2 and PEt_2 groups at the 4-position would be converted into the diphenylphosphoryl ($POPh_2$; $\sigma_p = 0.53$ [2]) and diethylphosphoryl ($POEt_2$; $\sigma_p = 0.47$ [2]) groups, respectively. The compounds having the $POPh_2$ at the 4-position were plotted on the line ③ (line ③ in Figure 1a; $y = |x - 1.06|$, only $y = -x + 1.06$ ($x < 1.06$) was drawn) and the compounds having the $POEt_2$ at the 4-position were plotted on the line ④ (line ④ in Figure 1b; $y = |x - 0.94|$, only $y = -x + 0.94$ ($x < 0.94$) was drawn), respectively. These data suggested that the compounds on the lines ① and ② would be oxidized by hydroperoxides and converted into the compounds on the lines ③ and ④, respectively.

Next, the selection of the substituent groups at the 7-position was carried out. In Figure 1, the point of intersection of two lines represents the 4,7-disubstituted benzofurazan compound having the substituent groups corresponding to the two lines. The appropriate lines, with which the points of intersection of line ① or ② were out of the fluorescent area (A and B) and the points of intersection of line ③ or ④ were in the fluorescent area (A or B), were searched to determine the substituted group at the 7-position. As the lines in the ranges of ⑤ and ⑥ (from $y = x + 0.54$ to $y = x - 0.06$) were suited for the above conditions, the substituent groups with σ_p values from –0.27 to 0.03 were appropriate at the 7-position. Among the substituent

groups having σ_p values in these ranges, acetylamino (NHAc; σ_p = 0.00 [2]) and methylthio (SMe; σ_p = 0.00 [2]) groups were selected. In this manner, compounds **1**-**3** were designed as fluorescent reagents for hydroperoxides.

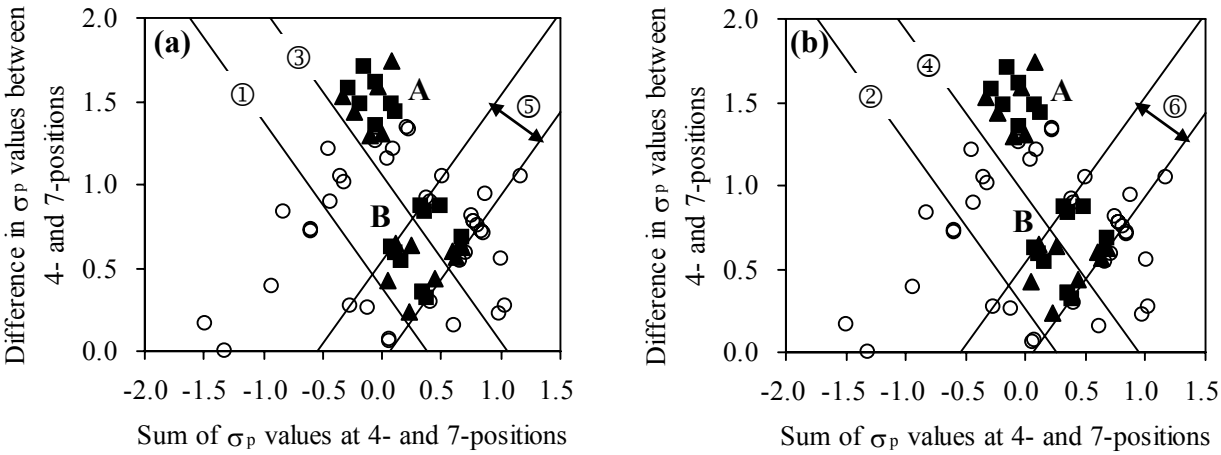

Figure 1: Design of the fluorescent reagents for hydroperoxides using the relationship between the fluorescence intensities of 4,7-disubstituted benzofurazan compounds and the Hammett substituent constants (σ_p) at the 4- and 7-positions.

Synthesis. 4-Bromo-7-nitro-2,1,3-benzoxadiazole (**a**) [3] and 4-bromo-2,1,3-benzoxadiazole (**d**) [4] were synthesized as previously described.

4-Amino-7-bromo-2,1,3-benzoxadiazole (b). To a solution of **a** (400 mg, 1.64 mmol) in a mixture of dichloromethane (15 mL), methanol (12 mL) and conc. hydrochloric acid (3 mL) at room temperature was slowly added iron powder (400 mg), and the mixture was vigorously stirred at room temperature for 25 min. The reaction mixture was poured into 1M aqueous NaOH (100 mL), and extracted with dichloromethane (50 mL × 3). The organic layer was dried over Na_2SO_4, and concentrated under reduced pressure, and the residue was chromatographed on silica gel (*n*-hexane–dichloromethane, 1:2) to afford **b** (254 mg, 1.19 mol, 72%) as orange powder. Mp: 179-180 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.62 (br, 2H), 6.25 (d, 1H, *J* = 7.6 Hz), 7.36 (d, 1H, *J* = 7.6 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 93.6, 107.2, 134.7, 135.7, 144.8, 149.7; IR (KBr) 3451, 3360, 3241, 1645, 1564, 1520, 1420, 1377, 1015, 932, 872, 812 cm^{-1}; Anal. Calcd for $C_6H_4BrN_3O$: C, 33.67; H, 1.88; N, 19.63. Found: C, 33.71; H, 2.08; N, 19.65.

4-Acetylamino-7-bromo-2,1,3-benzoxadiazole (c). To a solution of **b** (200 mg, 0.934 mmol) in pyridine (1 mL) at room temperature was added acetic anhydride (2 mL). After stirring at 50 °C for 4 h, 0.5 M aqueous HCl (50 mL) was added to the reaction mixture and

extracted with dichloromethane (50 mL × 2). The organic layer was washed with saturated aqueous Na_2CO_3 (80 mL), and dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by PTLC (dichloromethane) to afford **c** (163 mg, 0.637 mmol, 68%) as pale yellow powder. Mp: 141 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.30 (s, 3H), 7.57 (d, 1H, *J* = 8.0 Hz), 8.04 (br, 1H), 8.17 (d, 1H, *J* = 8.0 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 24.7, 101.1, 117.0, 125.6, 135.6, 144.5, 149.3, 168.9; IR (KBr) 3260, 3206, 3152, 3048, 1672, 1559, 1524, 1433, 1372, 1269, 1020, 889, 847 cm^{-1}; Anal. Calcd for $C_8H_6BrN_3O_2$: C, 37.53; H, 2.36; N, 16.41. Found: C, 37.79; H, 2.61; N, 16.23.

4-Acetylamino-7-diphenylphosphino-2,1,3-benzoxadiazole (1). (In the 'Design of the fluorescent reagents' section, we described the substituent groups at the 4- and 7-positions as the phosphino and the acetylamino groups, respectively, in order to simplify explanations. The 4- and 7-positions are equivalent in the benzofurazan skeleton.) To a stirred mixture of lithium (42.0 mg, 6.05 mmol) and THF (1.75 mL) at 0 °C under nitrogen was slowly added chlorodiphenylphosphine (270 μL, 1.51 mmol) over 30 min. After addition was completed, the red reaction mixture was stirred at room temperature for additional 3 h, and THF solution of lithium diphenylphosphide was obtained. To a solution of **c** (30.0 mg, 0.117 mmol) in THF (0.4 mL) at –10 °C under nitrogen was added THF solution of lithium diphenylphosphide (0.4 mL), and the mixture was stirred at –10 °C for 10 min. The untreated reaction mixture was purified by PTLC (dichloromethane) to afford **1** (8.9 mg, 0.0246 mmol, 21%) as yellow powder. Mp: 225-227 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.28 (s, 3H), 6.96 (dd, 1H, *J* = 7.3, 5.2 Hz), 7.32-7.38 (m, 10H), 8.03 (br, 1H), 8.14 (d, 1H, *J* = 7.3 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 24.7, 116.4, 121.9 (d, *J* = 21.8 Hz), 126.3, 128.8 (d, *J* = 8.0 Hz), 129.5, 134.0 (d, *J* = 20.6 Hz), 134.1, 138.3 (d, *J* = 6.9 Hz), 144.4 (d, *J* = 2.3 Hz), 150.6 (d, *J* = 16.0 Hz), 168.8; IR (KBr) 3254, 3056, 2963, 1672, 1557, 1420, 1262, 1092, 1028 cm^{-1}; HRMS (EI$^+$) m/z: Calcd for $C_{20}H_{16}N_3O_2P$ (M^+) 361.0980, found 361.0975.

4,7-Dibromo-2,1,3-benzoxadiazole (e). To a solution of **d** (660 mg, 3.32 mmol) in dichloromethane (2 mL) at room temperature were sequentially added iron powder (20 mg), and bromine (1 mL). After stirring at 100 °C for 1 h, the reaction mixture was concentrated under reduced pressure and the residue was chromatographed on silica gel (*n*-hexane–ethyl acetate, 10:1) to afford **e** (660 mg, 2.37 mmol, 72%) as white needle. Mp: 114-115 °C, lit. [5] mp: 112-112.5 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.51 (s, 2H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 108.7, 134.2, 149.4; IR (KBr) 1518, 1377, 1348, 1204, 1028, 959, 880, 845 cm^{-1}; Anal. Calcd for $C_6H_2Br_2N_2O$: C, 25.93; H, 0.73; N, 10.08. Found: C, 25.85; H, 0.89; N, 9.92.

4-Bromo-7-methylthio-2,1,3-benzoxadiazole (f). To a solution of **e** (150 mg, 0.540 mmol) in a mixture of acetonitrile (2 mL) and saturated aqueous $NaHCO_3$ (2 mL) at room temperature was added 15% methyl mercaptan sodium salt (2 mL) in acetonitrile (5 mL). After stirring at room temperature for 1.5 h, 0.5 M aqueous HCl (50 mL) was added to the

reaction mixture and extracted with dichloromethane (50 mL × 3). The organic layer was dried over Na_2SO_4, and concentrated under reduced pressure, and the residue was chromatographed on silica gel (*n*-hexane–ethyl acetate, 4:1) to afford **f** (118 mg, 0.481 mmol, 89%) as yellow powder. Mp: 113-114 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.65 (s, 3H), 6.89 (d, 1H, *J* = 7.6 Hz), 7.51 (d, 1H, *J* = 7.6 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 14.8, 104.0, 124.4, 129.5, 134.0, 148.6, 149.3; IR (KBr) 1522, 1420, 1211, 1032, 978, 880, 833 cm^{-1}; Anal. Calcd for $C_7H_5BrN_2OS$: C, 34.30; H, 2.06; N, 11.43. Found: C, 34.42; H, 2.20; N, 11.33.

4-Diphenylphosphino-7-methylthio-2,1,3-benzoxadiazole (2). To a stirred mixture of lithium (100 mg, 14.4 mmol) and THF (2.5 mL) at 0 °C under nitrogen was slowly added chlorodiphenylphosphine (720 μL, 4.01 mmol) over 30 min. After addition was completed, the red reaction mixture was stirred at room temperature for additional 3 h. Then the red solution thus obtained was transferred to the other flask by cannulation to remove excess lithium. To the red solution were sequentially added THF (1 mL) and trimethylsilyl chloride (610 μL, 4.81 mmol) at 0 °C under nitrogen. After stirring at 0 °C for 30 min, THF solution of (trimethylsilyl)diphenylphosphine was obtained. To a DMF (1 mL) solution of **f** (100 mg, 0.408 mmol), palladium acetate (10.3 mg, 0.0459 mmol), and tris(2-methylphenyl)phosphine (48.8 mg, 0.160 mmol) was slowly added THF solution of (trimethylsilyl)diphenylphosphine (1.5 mL), and the resulting mixture was stirred at 90 °C for 4 h under nitrogen. The reaction mixture was cooled to room temperature and diluted with chloroform (3 mL), and the organic layer was sequentially washed with saturated aqueous $NaHCO_3$ (3 mL) and saturated aqueous NaCl (3 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was chromatographed on silica gel (*n*-hexane–dichloromethane, 3:2) to afford **2** (46.0 mg, 0.131 mmol, 32%) as yellow powder. Mp: 152-153 °C; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.63 (s, 3H), 6.86 (d, 1H, *J* = 5.1, 7.1 Hz), 6.92 (d, 1H, *J* = 7.1 Hz), 7.35-7.41 (m, 10H); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 14.5, 123.4 (d, *J* = 21.8 Hz), 123.8, 128.8 (d, *J* = 8.0 Hz), 129.5, 130.2, 134.1 (d, *J* = 20.6 Hz), 134.1, 136.2 (d, *J* = 5.7 Hz), 148.4, 150.4 (d, *J* = 16.0 Hz); IR (KBr) 1516, 1433, 1090, 1030, 841 cm^{-1}; HRMS (EI$^+$) m/z: Calcd for $C_{19}H_{15}N_2OPS$ (M^+) 350.0643, found 350.0638.

4-Diethylphosphino-7-methylthio-2,1,3-benzoxadiazole (3). To a stirred mixture of lithium (111 mg, 16.0 mmol) and THF (2.5 mL) at 0 °C under nitrogen was slowly added chlorodiethylphosphine (500 μL, 4.11 mmol) over 15 min. After addition was completed, the reaction mixture was stirred at 65 °C for additional 14 h. The yellow solution thus obtained was transferred to the other flask by cannulation to remove excess lithium. To the yellow solution were sequentially added THF (1 mL), and trimethylsilyl chloride (520 μL, 4.10 mmol) at 0 °C under nitrogen. After stirring at 0 °C for 30 min, THF solution of (trimethylsilyl)diethylphosphine was obtained. To a DMF (1 mL) solution of **f** (60 mg, 0.245 mmol), palladium acetate (6.0 mg, 0.0267 mmol), and tris(2-methylphenyl)phosphine

(31.2 mg, 0.103 mmol) was slowly added THF solution of (trimethylsilyl)diethylphosphine (3 mL). The mixture was then stirred at 90 °C for 4 h under nitrogen. The reaction mixture was cooled to room temperature and diluted with chloroform (4 mL), and the organic layer was sequentially washed with saturated aqueous $NaHCO_3$ (3 mL) and saturated aqueous NaCl (3 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was chromatographed on silica gel (*n*-hexane–dichloromethane, 3:2) to afford **3** (21.8 mg, 0.0857 mmol, 35%) as yellow powder. Mp: 46-48 °C; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 0.99-1.04 (m, 6H), 1.89-2.13 (m, 4H), 2.65 (s, 3H), 6.98 (d, 1H, *J* = 6.8 Hz), 7.48 (dd, 1H, *J* = 6.8, 8.1 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 9.8 (d, *J* = 12.6 Hz), 14.6, 17.8, 123.5 (d, *J* = 8.0 Hz), 125.9, 130.6, 137.7 (d, *J* = 24.0 Hz), 148.7, 149.7; IR (KBr) 2965, 1520, 1420, 1262, 1092, 1026 cm^{-1}; HRMS (EI$^+$) m/z: Calcd for $C_{11}H_{15}N_2OPS$ (M^+) 254.0643, found 254.0647.

4-Acetylamino-7-diphenylphosphoryl-2,1,3-benzoxadiazole (1'). To a solution of **1** (7.0 mg, 0.0194 mmol) in chloroform (2 mL) at room temperature was added *tert*-butyl hydroperoxide (30 μL). After stirring at room temperature for 20 min, the reaction mixture was concentrated under reduced pressure and the residue was chromatographed on silica gel (dichloromethane–methanol, 20:1) to afford **1'** (6.1 mg, 0.0162 mmol, 83%) as pale yellow powder. Mp: 279-280 °C; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 2.34 (s, 3H), 7.45-7.58 (m, 6H), 7.79-7.83 (m, 4H), 8.16 (dd, 1H, *J* = 7.6, 13.7 Hz), 8.29 (br, 1H), 8.38 (d, 1H, *J* = 7.6 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 24.8, 115.1 (d, *J* = 11.4 Hz), 115.5 (d, *J* = 104.2 Hz), 128.6 (d, *J* = 12.6 Hz), 129.9 (d, *J* = 2.3 Hz), 131.0 (d, *J* = 108.7 Hz), 132.1 (d, *J* = 10.3 Hz), 132.5 (d, *J* = 2.3 Hz), 142.6 (d, *J* = 6.9 Hz), 144.3 (d, *J* = 6.9 Hz), 148.3 (d, *J* = 8.0 Hz), 169.2; IR (KBr) 3254, 3181, 3123, 3009, 1707, 1553, 1422, 1310, 1242, 1177, 1117, 970 cm^{-1}; HRMS (EI$^+$) m/z: Calcd for $C_{20}H_{16}N_3O_3P$ (M^+) 377.0929, found 377.0929.

4-Diphenylphosphoryl-7-methylthio-2,1,3-benzoxadiazole (2'). To a solution of **2** (17.2 mg, 0.0491 mmol) in chloroform (2 mL) at room temperature was added *tert*-butyl hydroperoxide (10 μL). After stirring at room temperature for 20 min, the reaction mixture was concentrated under reduced pressure and the residue was purified by PTLC (dichloromethane–methanol, 20:1) to afford **2'** (14.7 mg, 0.0401 mmol, 82%) as yellow powder. Mp: 226-227 °C; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 2.68 (s, 3H), 7.13 (d, 1H, *J* = 7.1 Hz), 7.45-7.48 (m, 4H), 7.55-7.58 (m, 2H), 7.81-7.85 (m, 4H), 8.21 (dd, 1H, *J* = 7.1, 13.7 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 14.2, 116.5 (d, *J* = 103.0 Hz), 122.0 (d, *J* = 11.4 Hz), 128.6 (d, *J* = 12.6 Hz), 131.1 (d, *J* = 107.6 Hz), 132.1 (d, *J* = 10.3 Hz), 132.5 (d, *J* = 2.3 Hz), 136.1 (d, *J* = 2.3 Hz), 139.9 (d, *J* = 5.7 Hz), 147.8 (d, *J* = 8.0 Hz), 148.3 (d, *J* = 6.9 Hz); IR (KBr) 1510, 1437, 1414, 1190, 1121, 941 cm^{-1}; HRMS (EI$^+$) m/z: Calcd for $C_{19}H_{15}N_2O_2PS$ (M^+) 366.0592, found 366.0621.

4-Diethylphosphoryl-7-methylthio-2,1,3-benzoxadiazole (3'). To a solution of **3** (12.1 mg, 0.0476 mmol) in chloroform (2 mL) at room temperature was added *tert*-butyl hydroperoxide

(10 μL). After stirring at room temperature for 20 min, the reaction mixture was concentrated under reduced pressure and the residue was purified by PTLC (dichloromethane–methanol, 20:1) to afford **3'** (11.0 mg, 0.0407 mmol, 86%) as pale yellow powder. Mp: 168-169 °C; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 1.08-1.13 (m, 6H), 2.10-2.25 (m, 4H), 2.70 (s, 3H), 7.13 (d, 1H, J = 6.9 Hz), 8.06 (dd, 1H, J = 6.9, 12.5 Hz); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 5.4 (d, J = 5.7 Hz), 14.4, 22.4 (d, J = 71.0 Hz), 115.4 (d, J = 89.3 Hz), 122.2 (d, J = 10.3 Hz), 135.2 (d, J = 2.3 Hz), 140.3 (d, J = 3.4 Hz), 147.4 (d, J = 9.2 Hz), 148.2 (d, J = 6.9 Hz); IR (KBr) 2963, 2934, 2876, 1514, 1420, 1246, 1179, 1017, 936 cm^{-1}; HRMS (EI$^+$) m/z: Calcd for $C_{11}H_{15}N_2O_2PS$ (M^+) 270.0592, found 270.0590.

Reaction of compound (f) with lithium diphenylphosphide. THF solution of lithium diphenylphosphide was prepared as described above. To a solution of **f** (20 mg, 0.0816 mmol) in THF (0.4 mL) at –10 °C under nitrogen was added THF solution of lithium diphenylphosphide (0.3 mL), and the mixture was stirred at –10 °C for 10 min. To the cooled reaction mixture chloroform (3 mL) was added, and the organic layer was sequentially washed with saturated aqueous $NaHCO_3$ (3 mL) and saturated aqueous NaCl (3 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by PTLC (*n*-hexane–ethyl acetate, 4:1) to afford 4,7-bis(diphenylphosphino)-2,1,3-benzoxadiazole (**g**) (14.7 mg). ^{1}H-NMR (600 MHz, $CDCl_3$) δ 6.75 (t, 2H), 7.29-7.45 (m, 20H); HRMS (EI$^+$) m/z: Calcd for $C_{30}H_{22}N_2OP_2$ (M^+) 488.1207, found 488.1189.

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