Supporting Information for

Zinc-Catalyzed Regioselective C–P Couplings of p-Quinol Ethers with Secondary Phosphine Oxides to Afford 2-Phosphinylphenols

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1. General Information

Unless otherwise specified, all reactions were performed under dry N₂ atmosphere. Anhydrous solvents were distilled prior to use: THF and toluene were distilled from sodium using benzophenone as the indicator; DCM, DMF, MeCN and DMSO were distilled from CaH₂. p-Quinol ethers were prepared following known procedures by oxidation of the corresponding phenols with Phl(OAc)₂ in MeOH. Secondary phosphine oxides were prepared via a known procedure. Thin layer chromatography was performed on precoated glass-backed plates and visualized with UV light at 254 nm. Flash chromatography was performed on silica gel using petroleum ether and EtOAc as eluent. ¹H NMR spectra were recorded on a Bruker Ascend™ 400 spectrometer at 400 MHz. ¹³C NMR spectra were recorded on a Bruker Ascend™ 400 spectrometer at 100 MHz. ³¹P NMR spectra were recorded on a Bruker Ascend™ 400 spectrometer at 160 MHz. Spectra were obtained in CDCl₃. Chemical shifts are expressed in ppm and J values are given in Hz. Proton chemical shifts are reported relative to internal tetramethylsilane (TMS, δ 0.0 ppm), or with the solvent reference relative to TMS employed as the internal standard (CDCl₃, δ 7.26 ppm). Carbon chemical shifts were reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard (CDCl₃, δ 77.0 ppm). Phosphorus chemical shifts were recorded using 85% phosphoric acid as the external standard. HRMS analysis was performed at the analytical center of State Key Laboratory of Materials-Oriented Chemical Engineering at NanJing Tech University. The X-Ray crystallographic analysis were performed on a Bruker SMART APEX II CCD diffractometer using a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation.

2. Experimental procedures and the characterization data of the products

General procedure for the Zn(OTf)₂-catalyzed preparation of 2-phosphinyl phenols 3: An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with Zn(OTf)₂ (7.2 mg, 10 mol %). The Schlenk tube was sealed and then evacuated and backfilled with N₂ (3 cycles). Then 1 (0.2 mmol) and 2 (0.6 mmol) dissolved in 2 mL of DCE was injected. The Schlenk tube was sealed and immersed in an oil bath which was heated to 100 °C. After the reaction was complete (monitored by TLC, 6-48 h), removal of the solvent under vacuum left a slurry residue, which was purified by flash chromatography on silica (petroleum ether/ethyl acetate 3/1) to afford the product 3.

(2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3aa): white solid, mp. 219.3–220.6 °C, 52.5 mg (yield 85%). ¹H NMR (CDCl₃, 400 MHz): δ = 10.96 (s, 1H), 7.72–7.67 (m, 4H), 7.61–7.57 (m, 2H), 7.52–7.48 (m, 4H), 7.22 (d, J = 8.0 Hz, 1H), 6.89 (dd, J₁ = 8.4 Hz, J₂ = 5.2 Hz, 1H), 6.75 (dd, J₁ = 13.2 Hz, J₂ = 1.6 Hz, 1H), 2.19 (3H). ³¹P NMR (CDCl₃, 162 MHz): δ = 39.5. This is a known compound.

(5-ethyl-2-hydroxyphenyl)diphenylphosphine oxide (3ba): White solid, mp. 199.3–201.2 °C, 49.0 mg (yield 76%). ¹H NMR (CDCl₃, 400 MHz): δ = 10.96 (s, 1H), 7.72–7.67 (m, 4H), 7.61–7.57 (m, 2H), 7.52–7.47 (m, 4H), 7.25 (d, J = 7.6 Hz, 1H), 6.92 (dd, J₁ = 8.8 Hz, J₂ = 4.8 Hz, 1H), 6.77 (dd, J₁ = 13.6 Hz, J₂ = 2.0 Hz, 1H), 2.48 (q, J = 7.6 Hz).

(4-hydroxy-[1,1'-biphenyl]-3-yl)diphenylphosphine oxide (3ca): White solid, mp. 178.8–180.2 °C, 40.7 mg (yield 55%). \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 11.26\) (s, 1H), 7.77–7.71 (m, 4H), 7.66–7.59 (m, 3H), 7.54–7.49 (m, 4H), 7.39–7.36 (m, 4H), 7.31–7.26 (m, 1H), 7.18 (dd, \(J_1 = 14.0\) Hz, \(J_2 = 2.4\) Hz, 1H), 7.07 (dd, \(J_1 = 8.8\) Hz, \(J_2 = 4.8\) Hz, 1H). \(^{31}\)P NMR (CDCl\(_3\), 162 MHz): \(\delta = 39.8\). This is a known compound. [4]

(2-hydroxy-3,5-dimethylphenyl)diphenylphosphine oxide (3da): White solid, mp. 161.3–163.1 °C, 48.6 mg (yield 75%). \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 11.08\) (s, 1H), 7.71–7.66 (m, 4H), 7.59–7.55 (m, 2H), 7.50–7.46 (m, 4H), 7.09 (s, 1H), 6.59 (dd, \(J_1 = 14.0\) Hz, 1H), 2.23 (s, 3H), 2.15 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 159.9\) (d, \(J_{PC} = 2.4\) Hz), 136.3 (d, \(J_{PC} = 2.9\) Hz), 132.3 (d, \(J_{PC} = 13.3\) Hz), 132.0 (d, \(J_{PC} = 10.5\) Hz), 131.9 (d, \(J_{PC} = 103.0\) Hz), 128.9 (d, \(J_{PC} = 10.1\) Hz), 128.6 (d, \(J_{PC} = 12.2\) Hz), 127.5 (d, \(J_{PC} = 13.3\) Hz), 127.4 (d, \(J_{PC} = 8.3\) Hz), 109.5 (d, \(J_{PC} = 103.4\) Hz), 20.5, 15.9 (d, \(J_{PC} = 1.0\) Hz). \(^{31}\)P NMR (CDCl\(_3\), 162 MHz): \(\delta = 39.9\). This is a known compound. [6]

(3-(tert-butyl)-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3ea): 16.8 mg (yield 23%). \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 11.19\) (s, 1H), 7.71–7.66 (m, 4H), 7.60–7.56 (m, 2H), 7.51–7.46 (m, 4H), 7.22 (d, \(J = 1.6\) Hz, 1H), 6.59 (dd, \(J_1 = 13.6\) Hz, \(J_2 = 1.6\) Hz, 1H), 2.17 (s, 3H), 1.41 (s, 9H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 161.0\), 138.6 (d, \(J_{PC} = 7.0\) Hz), 132.6, 132.4, 132.1 (d, \(J_{PC} = 10.2\) Hz), 131.6, 129.4 (d, \(J_{PC} = 10.3\) Hz), 128.6 (d, \(J_{PC} = 12.4\) Hz), 127.1 (d, \(J_{PC} = 15.5\) Hz), 110.1 (d, \(J_{PC} = 102.6\) Hz), 35.1, 29.4, 20.9. \(^{31}\)P NMR (CDCl\(_3\), 162 MHz): \(\delta = 41.0\). HRMS (ESI-TOF): \(m/z = 365.1672\), calcld for C\(_{36}\)H\(_{36}\)O\(_3\)P [MH\(^+\)] 365.1670

(3-bromo-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3fa): 69.6 mg (yield 90%). \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 11.77\) (s, 1H), 7.71–7.66 (m, 4H), 7.63–7.59 (m, 2H), 7.53–7.49 (m, 5H), 6.73 (dd, \(J_1 = 13.2\) Hz, \(J_2 = 1.2\) Hz, 1H), 2.18 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 157.7\) (d, \(J_{PC} = 4.0\) Hz), 138.3 (d, \(J_{PC} = 2.3\) Hz), 132.7 (d, \(J_{PC} = 2.0\) Hz), 132.0 (d, \(J_{PC} = 9.7\) Hz), 131.0 (d, \(J_{PC} = 104.9\) Hz), 130.9 (d, \(J_{PC} = 9.0\) Hz), 129.4 (d, \(J_{PC} = 12.9\) Hz), 128.8 (d, \(J_{PC} = 12.3\) Hz), 112.2 (d, \(J_{PC} = 11.1\) Hz), 112.1 (d, \(J_{PC} = 100.6\) Hz), 20.2. \(^{31}\)P NMR (CDCl\(_3\), 162 MHz): \(\delta = 39.5\). HRMS (ESI-TOF): \(m/z = 387.0152\), calcld for C\(_{36}\)H\(_{35}\)BrO\(_3\)PBr [MH\(^+\)] 387.0150.

(2-hydroxy-3-iodo-5-methylphenyl)diphenylphosphine oxide (3ga): 69.6 mg (yield 82%). \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 11.98\) (s, 1H), 7.74–7.65 (m, 5H), 7.62–7.58 (m, 2H), 7.52–7.48 (m, 4H), 6.76 (dd, \(J_1 = 13.2\) Hz, \(J_2 = 0.8\) Hz, 1H), 2.16 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 159.9\) (d, \(J_{PC} = 3.7\) Hz), 144.5 (d, [4] S. Shuvaev, O. Kotova, V. Utochinkova, A. Vaschenko, L. Punctus, V. Baulin, N. Kuzmina, A. Tzivadze, Inorg. Chem. Comm. 2012, 20, 73.

[53]
$J_{P.C} = 2.5 \text{ Hz}$), 132.8 (d, $J_{P.C} = 2.4 \text{ Hz}$), 132.0 (d, $J_{P.C} = 11.0 \text{ Hz}$), 131.9 (d, $J_{P.C} = 9.0 \text{ Hz}$), 130.9 (d, $J_{P.C} = 104.7 \text{ Hz}$), 130.1 (d, $J_{P.C} = 13.6 \text{ Hz}$), 128.8 (d, $J_{P.C} = 12.3 \text{ Hz}$), 111.0 (d, $J_{P.C} = 100.8 \text{ Hz}$), 87.2 (d, $J_{P.C} = 9.9 \text{ Hz}$), 20.0. $^{31}P$ NMR (CDCl$_3$, 162 MHz): $\delta = 39.4$. HRMS (ESI-TOF): $m/z = 435.0015$, calc'd for C$_{18}$H$_{18}$O$_2$P [MH$^+$] 435.0011.

(2-hydroxy-4,5-dimethylphenyl)diphenylphosphine oxide (3ha): white solid, mp. 210.7–212.2 °C, 37.3 mg (yield 58%). $^1H$ NMR (CDCl$_3$, 400 MHz): $\delta = 10.88$ (s, 1H), 7.72–7.67 (m, 4H), 7.60–7.56 (m, 2H), 7.51–7.46 (m, 4H), 6.79 (d, $J = 4.8 \text{ Hz}$, 1H), 6.69 (d, $J = 13.2 \text{ Hz}$, 1H), 2.23 (s, 3H), 2.09 (s, 3H). $^{31}P$ NMR (CDCl$_3$, 162 MHz): $\delta = 39.4$. This is a known compound. [7]

(6-hydroxy-2,3-dimethylphenyl)diphenylphosphine oxide (3ha): white solid, mp. 205.3–206.1 °C, 22.4 mg (yield 35%). $^1H$ NMR (CDCl$_3$, 400 MHz): $\delta = 12.41$ (s, 1H), 7.78–7.73 (m, 4H), 7.61–7.57 (m, 2H), 7.53–7.49 (m, 4H), 7.25 (d, $J = 7.2 \text{ Hz}$, 1H), 6.82 (dd, $J_1 = 8.4 \text{ Hz}$, $J_2 = 4.8 \text{ Hz}$, 1H), 2.10 (s, 3H), 1.73 (s, 3H). $^{13}C$ NMR (CDCl$_3$, 100 MHz): $\delta = 164.5$ (d, $J_{C.P} = 4.4 \text{ Hz}$), 138.4 (d, $J_{C.P} = 8.8 \text{ Hz}$), 136.5 (d, $J_{C.P} = 2.4 \text{ Hz}$), 132.4 (d, $J_{C.P} = 2.7 \text{ Hz}$), 132.3 (d, $J_{C.P} = 103.9 \text{ Hz}$), 132.0 (d, $J_{C.P} = 11.2 \text{ Hz}$), 128.8 (d, $J_{C.P} = 12.3 \text{ Hz}$), 127.8 (d, $J_{C.P} = 10.2 \text{ Hz}$), 116.8 (d, $J_{C.P} = 8.3 \text{ Hz}$), 108.0 (d, $J_{C.P} = 101.4 \text{ Hz}$), 20.6 (d, $J_{C.P} = 6.4 \text{ Hz}$), 19.6 (d, $J_{C.P} = 1.9 \text{ Hz}$). $^{31}P$ NMR (CDCl$_3$, 162 MHz): $\delta = 44.0$. HRMS (ESI-TOF): $m/z = 323.1206$, calc'd for C$_{20}$H$_{19}$O$_2$P [MH$^+$] 323.1201

(2-hydroxy-5-methylphenyl)di-p-tolyphosphine oxide (3ab): white solid, mp. 190.0–190.8 °C, 54.3 mg (yield 81%). $^1H$ NMR (CDCl$_3$, 400 MHz): $\delta = 11.03$ (s, 1H), 7.59–7.54 (m, 4H), 7.30–7.28 (m, 4H), 7.19 (d, $J = 8.4 \text{ Hz}$, 1H), 6.87 (dd, $J_1 = 8.4 \text{ Hz}$, $J_2 = 4.8 \text{ Hz}$, 1H), 6.73 (dd, $J_1 = 13.2 \text{ Hz}$, $J_2 = 1.6 \text{ Hz}$, 1H), 2.42 (s, 6H), 2.18 (s, 3H). $^{13}C$ NMR (CDCl$_3$, 100 MHz): $\delta = 161.7$, 143.1, 135.1, 132.1 (d, $J_{C.P} = 10.7 \text{ Hz}$), 131.5 (d, $J_{C.P} = 10.1 \text{ Hz}$), 129.4 (d, $J_{C.P} = 12.8 \text{ Hz}$), 128.8 (d, $J_{C.P} = 106.6 \text{ Hz}$), 128.0 (d, $J_{C.P} = 14.5 \text{ Hz}$), 118.4 (d, $J_{C.P} = 8.1 \text{ Hz}$), 111.0 (d, $J_{C.P} = 103.1 \text{ Hz}$), 21.7, 20.5. $^{31}P$ NMR (CDCl$_3$, 162 MHz): $\delta = 39.7$. HRMS (ESI-TOF): $m/z = 337.1356$, calc'd for C$_{21}$H$_{22}$O$_2$P [MH$^+$] 337.1357

(2-hydroxy-5-methylphenyl)bis(4-methoxyphenyl) phosphine oxide (3ac): white solid, mp. 181.1–181.8 °C, 62.0 mg (yield 84%). $^1H$ NMR (CDCl$_3$, 400 MHz): $\delta = 11.05$ (s, 1H), 7.63–7.58 (m, 4H), 7.19 (d, $J = 8.0 \text{ Hz}$, 1H), 7.00–6.97 (m, 4H), 6.87 (dd, $J_1 = 8.4 \text{ Hz}$, $J_2 = 4.8 \text{ Hz}$, 1H), 6.72 (dd, $J_1 = 13.6 \text{ Hz}$, $J_2 = 2.0 \text{ Hz}$, 1H), 3.85 (s, 6H), 2.18 (s, 3H). $^{13}C$ NMR (CDCl$_3$, 100 MHz): $\delta = 162.8$ (d, $J_{C.P} = 3.2 \text{ Hz}$), 161.5 (d, $J_{C.P} = 3.4 \text{ Hz}$), 135.1 (d, $J_{C.P} = 2.0 \text{ Hz}$), 134.0 (d, $J_{C.P} = 11.8 \text{ Hz}$), 131.6 (d, $J_{C.P} = 9.5 \text{ Hz}$), 128.1 (d, $J_{C.P} = 12.7 \text{ Hz}$), 123.1 (d, $J_{C.P} = 110.6 \text{ Hz}$), 118.3 (d, $J_{C.P} = 8.0 \text{ Hz}$), 114.2 (d, $J_{C.P} = 13.6 \text{ Hz}$), 111.5 (d, $J_{C.P} = 103.9 \text{ Hz}$), 55.4, 20.5. $^{31}P$ NMR (CDCl$_3$, 162 MHz): $\delta = 39.2$. HRMS (ESI-TOF): $m/z = 369.1266$, calc'd for C$_{23}$H$_{24}$O$_3$P [MH$^+$] 369.1256.

bis(4-fluorophenyl)(2-hydroxy-5-methylphenyl)phosphine oxide (3ad): white solid, mp. 185.8–
186.5 °C, 54.9 mg (yield 80%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 10.77$ (s, 1H), 7.72–7.65 (m, 4H), 7.25–7.18 (m, 5H), 6.90 (dd, $J_1 = 8.4$ Hz, $J_2=4.8$Hz, 1H), 6.68 (dd, $J_1 = 13.6$ Hz, $J_2=1.6$ Hz, 1H), 2.20 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 165.4$ (dd, $J_{PC} = 252.9$ Hz, $J_{PC} = 3.2$ Hz), 161.7 (d, $J_{PC} = 2.8$ Hz), 135.7 (d, $J_{PC} = 2.2$ Hz), 134.5 (dd, $J_{PC} = 11.7$ Hz, $J_{PC} = 9.0$ Hz), 131.2 (d, $J_{PC} = 9.8$ Hz), 128.5 (d, $J = 12.4$ Hz), 127.7 (dd, $J_{PC} = 108.0$ Hz, $J_{PC} = 3.5$ Hz), 118.7 (d, $J_{PC} = 8.8$ Hz), 116.3 (dd, $J_{PC} = 21.6$ Hz, $J_{PC} = 13.2$ Hz), 110.2 (d, $J_{PC} = 105.5$ Hz), 20.6. $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 37.9$. HRMS (ESI-TOF): $m/z = 345.0856$, calcd for C$_9$H$_6$O$_2$PF$_2$ [MH$^+$] 345.0856.

(2-hydroxy-5-methylphenyl)bis(4-trifluoromethyl)phenylphosphine oxide (3ae): 63.1 mg (yield 71%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 10.51$ (s, 1H), 7.86–7.76 (m, 8H), 7.27 (d, $J = 8.4$ Hz, 1H), 6.93 (dd, $J_1 = 8.4$ Hz, $J_2=5.2$Hz, 1H), 6.75 (dd, $J_1 = 13.6$ Hz, $J_2=1.2$ Hz, 1H), 2.22 (s, 3H). Due to the coupling of F-C and P-C, the $^{13}$C NMR spectra show complex peaks not easily interpreted. A full list of the $^{13}$C NMR data: $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 161.80$, 161.78, 163.31, 136.29, 136.1, 135.1, 134.76, 134.73, 134.44, 134.40, 134.08, 132.5, 132.4, 131.1, 130.9, 128.98, 128.86, 127.4, 125.90, 125.86, 125.82, 125.79, 125.74, 125.70, 125.66, 124.7, 122.0, 119.3, 119.03, 118.95, 109.4, 108.3, 20.5. $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 36.7$. HRMS (ESI-TOF): $m/z = 445.0796$, calcd for C$_{21}$H$_{16}$F$_6$O$_5$P [MH$^+$] 445.0792.

(2-hydroxy-5-methylphenyl)(4-methoxyphenyl)(phenyl) phosphine oxide (3af): 66.9 mg (yield 94%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 11.03$ (s, 1H), 7.72–7.67 (m, 2H), 7.63–7.56 (m, 3H), 7.51–7.47 (m, 2H), 7.20 (d, $J = 8.0$ Hz, 1H), 7.34 (dd, $J_1 = 8.8$ Hz, $J_2=2.0$ Hz, 2H), 6.88 (dd, $J_1 = 8.4$ Hz, $J_2=4.8$ Hz, 1H), 6.73 (dd, $J_1 = 13.6$ Hz, $J_2=1.6$ Hz, 1H), 3.86 (s, 3H) , 2.18 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 162.9$ (d, $J_{PC} = 3.2$ Hz), 161.7 (d, $J_{PC} = 2.1$ Hz), 135.2 (d, $J_{PC} = 2.3$ Hz), 134.0 (d, $J_{PC} = 11.8$ Hz), 132.4 (d, $J_{PC} = 3.2$ Hz), 132.2 (d, $J = 104.2$ Hz), 132.0 (d, $J_{PC} = 10.0$ Hz), 131.7 (d, $J_{PC} = 10.9$ Hz), 128.7 (d, $J_{PC} = 11.6$ Hz), 128.1 (d, $J_{PC} = 12.7$ Hz), 122.9 (d, $J_{PC} = 11.0$ Hz), 118.4 (d, $J_{PC} = 7.9$ Hz), 114.3 (d, $J_{PC} = 12.8$ Hz), 111.0 (d, $J_{PC} = 103.6$ Hz), 55.4, 20.6. $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 39.3$. HRMS (ESI-TOF): $m/z = 339.1155$, calcd for C$_{20}$H$_{18}$O$_5$P [MH$^+$] 339.1150.

(4-fluorophenyl)(2-hydroxy-5-methylphenyl)(phenyl) phosphine oxide (3ag): 58.0 mg (yield 89%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 10.85$ (s, 1H), 7.73–7.66 (m, 4H), 7.63–7.59 (m, 1H), 7.53–7.49 (m, 2H), 7.24–7.17 (m, 3H), 6.90 (dd, $J_1 = 9.2$ Hz, $J_2=5.2$Hz, 1H), 6.71 (dd, $J_1 = 13.6$ Hz, $J_2=1.6$ Hz, 1H), 2.19 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 165.8$ (dd, $J_{PC} = 253.1$ Hz, $J_{PC} = 2.9$ Hz), 161.7 (d, $J_{PC} = 2.7$ Hz), 135.5 (d, $J_{PC} = 2.2$ Hz), 134.6 (dd, $J_{PC} = 21.6$ Hz, $J_{PC} = 9.1$ Hz), 132.6 (d, $J_{PC} = 3.2$ Hz), 131.9 (d, $J_{PC} = 9.8$ Hz), 131.5 (d, $J = 105.8$ Hz), 131.3 (d, $J_{PC} = 9.8$ Hz), 128.8 (d, $J_{PC} = 12.3$ Hz), 128.3 (d, $J_{PC} = 12.4$ Hz), 127.8 (d, $J_{PC} = 103.7$ Hz), 118.6 (d, $J_{PC} = 8.3$ Hz), 116.1 (dd, $J_{PC} = 21.6$ Hz, $J_{PC} = 13.2$ Hz), 111.2 (d, $J_{PC} = 104.8$ Hz), 20.5. $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 38.7$. HRMS (ESI-TOF): $m/z = 327.0956$, calcd for C$_{19}$H$_{15}$O$_2$PF$_2$ [MH$^+$] 327.0950.
bis(3-chlorophenyl)(2-hydroxy-5-methylphenyl) phosphine oxide (3ah): 58.0 mg (yield 77%). ¹H NMR (CDCl₃, 400 MHz): δ = 10.62 (s, 1H), 7.68–7.64 (m, 2H), 7.60–7.52 (m, 4H), 7.49–7.44 (m, 2H), 7.26 (d, J = 4.8 Hz, 1H), 6.92 (dd, J₁ = 8.4 Hz, J₂ = 5.2 Hz, 1H), 6.72 (d, J = 13.6 Hz, 1H), 2.22 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 161.8 (d, J₁P₂C = 2.5 Hz), 136.1 (d, J₁P₂C = 2.2 Hz), 135.4 (d, J₁P₂C = 16.4 Hz), 133.6 (d, J₁P₂C = 103.0 Hz), 133.0 (d, J = 3.4 Hz), 131.7 (d, J₁P₂C = 10.3 Hz), 131.1 (d, J₁P₂C = 10.2 Hz), 130.3 (d, J₁P₂C = 13.6 Hz), 130.0 (d, J₁P₂C = 10.7 Hz), 128.7 (d, J₁P₂C = 12.8 Hz), 118.9 (d, J₁P₂C = 8.8 Hz), 109.1 (d, J₁P₂C = 104.7 Hz), 20.6. ³¹P NMR (CDCl₃, 162 MHz): δ = 37.2. HRMS (ESI-TOF): m/z = 377.0265, calc for C₁₉H₁₆O₂PCl₂ [MH⁺] 377.0265.

bis(3-chlorophenyl)(2-hydroxy-3,5-dimethylphenyl)phosphine oxide (3dh): 54.8 mg (yield 70%). ¹H NMR (CDCl₃, 400 MHz): δ = 10.76 (s, 1H), 7.68–7.64 (m, 2H), 7.58–7.51 (m, 4H), 7.49–7.43 (m, 2H), 7.14 (s, 1H), 6.55 (d, J = 13.2 Hz, 1H), 2.23 (s, 3H), 2.18 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 160.1 (d, J₁P₂C = 3.1 Hz), 137.0 (d, J₁P₂C = 3.2 Hz), 135.4 (d, J₁P₂C = 16.2 Hz), 133.9 (d, J₁P₂C = 103.1 Hz), 132.9 (d, J₁P₂C = 2.9 Hz), 131.7 (d, J₁P₂C = 11.8 Hz), 130.3 (d, J₁P₂C = 13.3 Hz), 130.0 (d, J₁P₂C = 10.5 Hz), 128.5 (d, J₁P₂C = 10.2Hz), 128.1 (d, J₁P₂C = 13.3 Hz), 127.9 (d, J₁P₂C = 9.3 Hz), 108.1 (d, J₁P₂C = 105.7 Hz), 20.6, 16.0 (d, J₁P₂C = 1.4 Hz). ³¹P NMR (CDCl₃, 162 MHz): δ = 37.7. HRMS (ESI-TOF): m/z = 391.0426, calc for C₂₀H₁₆O₂PCl₂ [MH⁺] 391.0421.

(2-hydroxy-5-methylphenyl)dio-tolylyphosphine oxide (3ai): white solid, mp. 198.2–199.0 °C, 42.5 mg (yield 63%). ¹H NMR (CDCl₃, 400 MHz): δ = 11.10 (s, 1H), 7.49–7.45 (m, 2H), 7.36–7.33 (m, 2H), 7.25–7.16 (m, 3H), 7.13–7.07 (m, 2H), 6.92 (dd, J₁ = 8.4 Hz, J₂ = 4.8Hz, 1H), 6.43 (dd, J₁ = 13.6 Hz, J₂ = 1.6 Hz, 1H), 2.57 (s, 6H), 2.15 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 162.2 (d, J₁P₂C = 2.8 Hz), 143.4 (d, J₁P₂C = 8.4 Hz), 135.4 (d, J₁P₂C = 2.3 Hz), 132.6 (d, J₁P₂C = 8.5 Hz), 132.5 (d, J₁P₂C = 2.7 Hz), 132.3 (d, J₁P₂C = 10.6 Hz), 131.7 (d, J₁P₂C = 9.8 Hz), 129.8 (d, J₁P₂C = 102.7 Hz), 128.0 (d, J₁P₂C = 12.6 Hz), 125.6 (d, J₁P₂C = 13.2 Hz), 118.5 (d, J₁P₂C = 7.8 Hz), 110.3 (d, J₁P₂C = 101.8 Hz), 21.7 (d, J₁P₂C = 4.8 Hz), 20.6. ³¹P NMR (CDCl₃, 162 MHz): δ = 46.6. HRMS (ESI-TOF): m/z = 337.1356, calc for C₂₁H₂₆O₂P [MH⁺] 337.1357.

(2-hydroxy-5-methylphenyl)(di(thiophen-2-yl)phosphine oxide (3aj): white solid, mp. 188.4–189.8 °C. 41.6 mg (yield 65%). ¹H NMR (CDCl₃, 400 MHz): δ = 10.76 (s, 1H), 7.79 (t, J = 4.2 Hz, 2H), 7.61–7.58 (m, 2H), 7.24–7.20 (m, 3H), 6.95–6.88 (m, 2H), 2.21 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 160.9 (d, J₁P₂C = 3.5 Hz), 137.4 (d, J₁P₂C = 11.3 Hz), 135.8 (d, J₁P₂C = 2.0 Hz), 134.8 (d, J₁P₂C = 6.2 Hz), 133.5 (d, J₁P₂C = 120.3 Hz), 131.1 (d, J₁P₂C = 10.5 Hz), 128.4 (d, J₁P₂C = 14.2 Hz), 128.3 (d, J₁P₂C = 13.1 Hz), 118.3 (d, J₁P₂C = 8.2 Hz), 111.4 (d, J₁P₂C = 115.5 Hz), 20.4. ³¹P NMR (CDCl₃, 162 MHz): δ = 23.7. HRMS (ESI-TOF): m/z = 321.0172, calc for C₁₅H₁₄O₃S₂P [MH⁺] 321.0173.

(2-hydroxy-5-methylphenyl)(methyl)(phenyl)phosphine oxide (3ak): 40.8 mg (yield 83%). ¹H NMR
(CDCl$_3$, 400 MHz): $\delta = 10.92$ (s, 1H), 7.79–7.74 (m, 2H), 7.58–7.48 (m, 3H), 7.19 (d, $J = 8.0$ Hz, 1H), 6.87–6.81 (m, 2H), 2.22 (s, 3H), 2.09 (d, $J = 13.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 161.1$ (d, $J_{PC} = 2.8$ Hz), 135.2 (d, $J_{PC} = 2.2$ Hz), 133.7 (d, $J_{PC} = 102.0$ Hz), 132.3 (d, $J_{PC} = 3.0$ Hz), 131.1 (d, $J_{PC} = 10.1$ Hz), 130.0 (d, $J_{PC} = 9.8$ Hz), 128.5 (d, $J_{PC} = 11.7$ Hz), 118.4 (d, $J_{PC} = 7.8$ Hz), 112.2 (d, $J_{PC} = 101.3$ Hz), 20.5, 17.0 (d, $J_{PC} = 73.0$ Hz). $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 42.4$. HRMS (ESI-TOF): $m/z = 247.0885$, calc'd for C$_9$H$_{12}$O$_2$P [M$^+$$] 247.0888$.

butyl(2-hydroxy-5-methylphenyl)(phenyl)phosphine oxide (3al): 49.5 mg (yield 86%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 11.06$ (s, 1H), 7.81–7.76 (m, 2H), 7.56–7.49 (m, 3H), 7.17 (d, $J = 8.4$ Hz, 1H), 6.86–6.81 (m, 2H), 2.33–2.25 (m, 2H), 2.23 (s, 3H), 1.74–1.56 (m, 2H), 1.50–1.41 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 161.5$, 135.0 (d, $J_{PC} = 2.3$ Hz), 132.9 (d, $J_{PC} = 97.9$ Hz), 132.1 (d, $J_{PC} = 3.1$ Hz), 130.3 (d, $J_{PC} = 9.5$ Hz), 129.8 (d, $J_{PC} = 10.4$ Hz), 128.7 (d, $J_{PC} = 11.6$ Hz), 128.3 (d, $J_{PC} = 11.2$ Hz), 118.2 (d, $J_{PC} = 8.3$ Hz), 111.2 (d, $J_{PC} = 97.4$ Hz), 29.7 (d, $J_{PC} = 71.0$ Hz), 23.9 (d, $J_{PC} = 14.5$ Hz), 23.0 (d, $J_{PC} = 3.7$ Hz), 20.5, 13.6. $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 44.9$. HRMS (ESI-TOF): $m/z = 289.1361$, calc'd for C$_{13}$H$_{22}$O$_2$P [M$^+$$] 289.1357$.

(3-bromo-2-hydroxy-5-methylphenyl)(cyclohexyl)(phenyl)phosphine oxide (3fm): 63.2 mg (yield 80%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 1.98$ (s, 1H), 7.84–7.79 (m, 2H), 7.56–7.49 (m, 3H), 7.44 (d, $J = 2.0$ Hz, 1H), 6.87 (dd, $J_1 = 12.0$ Hz, $J_2 = 1.6$ Hz, 1H), 2.32–2.25 (m, 1H), 2.23 (s, 3H), 1.84–1.64 (m, 6H), 1.35–1.23 (m, 4H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 157.8$ (d, $J_{PC} = 3.2$ Hz), 137.8 (d, $J_{PC} = 2.0$ Hz), 132.2 (d, $J_{PC} = 2.8$ Hz), 130.7 (d, $J_{PC} = 8.6$ Hz), 130.5 (d, $J_{PC} = 94.7$ Hz), 129.5 (d, $J_{PC} = 13.2$ Hz), 128.95 (d, $J_{PC} = 9.4$ Hz), 128.89 (d, $J_{PC} = 11.4$ Hz), 112.0 (d, $J_{PC} = 91.2$ Hz), 111.9 (d, $J_{PC} = 10.0$ Hz), 37.1 (d, $J_{PC} = 72.6$ Hz), 26.1 (d, $J_{PC} = 4.2$ Hz), 26.0 (d, $J_{PC} = 5.2$ Hz), 25.5 (d, $J_{PC} = 1.4$ Hz), 24.2 (d, $J_{PC} = 3.1$ Hz), 23.7 (d, $J_{PC} = 3.1$ Hz), 20.2. $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 47.4$. HRMS (ESI-TOF): $m/z = 393.0612$, calc'd for C$_{16}$H$_{22}$O$_2$PBr [M$^+$$] 393.0619$.

dibutyl(2-hydroxy-5-methylphenyl)phosphine oxide (3an): 33.6 mg (yield 63%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 11.08$ (s, 1H), 7.19 (d, $J = 8.4$ Hz, 1H), 6.82 (dd, $J_1 = 8.8$ Hz, $J_2 = 4.4$ Hz, 1H), 6.75 (dd, $J_2 = 12.4$ Hz, $J_2 = 1.6$ Hz, 1H), 2.27 (s, 3H), 2.01–1.84 (m, 4H), 1.72–1.63 (m, 4H), 1.43–1.38 (m, 4H), 0.90 (t, $J = 7.2$ Hz, 6H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 162.0$ (d, $J_{PC} = 2.0$ Hz), 134.9 (d, $J_{PC} = 2.1$ Hz), 128.7 (d, $J_{PC} = 10.0$ Hz), 128.3 (d, $J_{PC} = 11.8$ Hz), 118.1 (d, $J_{PC} = 7.2$ Hz), 110.5 (d, $J_{PC} = 92.0$ Hz), 30.3 (d, $J_{PC} = 67.4$ Hz), 23.9 (d, $J_{PC} = 14.9$ Hz), 23.1 (d, $J_{PC} = 4.1$ Hz), 20.5, 13.6. $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 56.0$. HRMS (ESI-TOF): $m/z = 269.1671$, calc'd for C$_{15}$H$_{25}$O$_2$P [M$^+$$] 269.1670$.

dicyclohexyl(2-hydroxy-5-methylphenyl)phosphine oxide (3ao): 38.2 mg (yield 60%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 11.33$ (s, 1H), 7.19 (d, $J = 8.4$ Hz, 1H), 6.81 (dd, $J_1 = 8.4$ Hz, $J_2 = 4.0$ Hz, 1H), 6.73 (dd, $J_1 = 10.8$ Hz, $J_2 = 1.2$ Hz, 1H), 2.28 (s, 3H), 2.06–2.01 (m, 4H), 1.87–1.69 (m, 8H), 1.42–1.20 (m, 10H). $^{13}$C NMR
(CDCl$_3$, 100 MHz): $\delta = 163.1, 134.7$ (d, $J_{P,C} = 1.9$ Hz), 129.2 (d, $J_{P,C} = 10.0$ Hz), 127.6 (d, $J_{P,C} = 10.9$ Hz), 111.3 (d, $J_{P,C} = 2.9$ Hz), 107.9 (d, $J_{P,C} = 5.9$ Hz), 35.7 (d, $J_{P,C} = 6.5$ Hz), 26.3 (d, $J_{P,C} = 14.9$ Hz), 26.1 (d, $J_{P,C} = 11.8$ Hz), 25.7, 25.2 (d, $J_{P,C} = 2.9$ Hz), 24.0 (d, $J_{P,C} = 3.1$ Hz), 20.6. $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 60.5$. HRMS (ESI-TOF): $m/z = 321.1986$, calcld for C$_{30}$H$_{30}$O$_3$P [MH$^+$] 321.1983.

General procedure for the Zn(OTf)$_2$-catalyzed preparation of 2-phosphinyl phenols 6: An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with Zn(OTf)$_2$ (7.2 mg, 10 mol %). The Schlenk tube was sealed and then evacuated and backfilled with N$_2$ (3 cycles). Then 5 (0.2 mmol) and 2 (0.6 mmol) dissolved in 2 mL of toluene was injected. The Schlenk tube was sealed and immersed in an oil bath which was heated to 100 °C. After the reaction was complete (monitored by TLC), removal of the solvent under vacuum left a slurry residue, which was purified by flash chromatography on silica (petroleum ether/ethyl acetate 10/1 to 4/1) to afford the product 6.

(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)diphenylphosphine oxide (6a): white solid, mp 201.5–202.4 °C, 69.7 mg (yield 84%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 11.47$ (s, 1H), 7.73–7.68 (3H, 7.61–7.55 (4H), 7.52–7.48 (3H, 7.45 (s, 1H), 7.34–7.32 (2H, 6.78 (d, $J = 12.0$ Hz, 1H), 2.19 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 161.9$ (d, $J_{P,C} = 2.8$ Hz), 138.2 (d, $J_{P,C} = 2.5$ Hz), 132.6 (d, $J_{P,C} = 3.1$ Hz), 132.0 (d, $J_{P,C} = 10.1$ Hz), 131.9 (d, $J_{P,C} = 9.6$ Hz), 131.7, 130.9, 128.7 (d, $J_{P,C} = 12.4$ Hz), 128.23, 128.21, 128.1 (d, $J_{P,C} = 12.6$ Hz), 123.2, 113.2 (d, $J_{P,C} = 9.5$ Hz), 111.3 (d, $J_{P,C} = 103.1$ Hz), 94.4, 84.6 (d, $J_{P,C} = 2.5$ Hz), 20.3. $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 39.1$. HRMS (ESI-TOF): $m/z = 409.1350$, calcld for C$_{32}$H$_{22}$O$_3$P [MH$^+$] 409.1357. The structure of this compound was further confirmed by an X-ray crystallographic analysis.

(2-hydroxy-5-methyl-3-(m-tolylethynyl)phenyl)diphenylphosphine oxide (6b): 59.2 mg (yield 70%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 11.43$ (s, 1H), 7.73–7.67 (m, 4H), 7.61–7.57 (m, 2H), 7.51–7.47 (m, 4H), 7.44–7.35 (m, 3H), 7.21 (t, $J = 7.6$ Hz, 1H), 7.12 (d, $J = 7.6$ Hz, 1H), 6.78 (dd, $J_1 = 13.6$ Hz, $J_2 = 1.6$ Hz, 1H), 2.33 (s, 3H), 2.19 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 161.8$ (d, $J_{P,C} = 3.7$ Hz), 138.2 (d, $J_{P,C} = 2.5$ Hz), 137.8, 132.6 (d, $J_{P,C} = 3.4$ Hz), 132.2, 132.0 (d, $J_{P,C} = 9.9$ Hz), 131.3 (d, $J_{P,C} = 96.5$ Hz), 129.1, 128.68, 128.66 (d, $J_{P,C} = 12.4$ Hz), 128.1, 128.0, 123.0, 113.3 (d, $J_{P,C} = 9.4$ Hz), 111.3 (d, $J_{P,C} = 102.2$ Hz), 94.6, 84.2 (d, $J_{P,C} = 2.7$ Hz), 21.1, 20.3. $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 39.0$. HRMS (ESI-TOF): $m/z = 423.1516$, calcld for C$_{32}$H$_{20}$O$_3$P [MH$^+$] 423.1514.

(2-hydroxy-5-methyl-3-(p-tolylethynyl)phenyl)diphenylphosphine oxide (6c): white solid, mp 181.4–182.8 °C, 57.0 mg (yield 68%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 11.40$ (s, 1H), 7.73–7.67 (m, 4H), 7.61–7.57 (m, 2H), 7.51–7.44 (m, 7H), 7.13 (d, $J = 8.0$ Hz, 2H), 6.77 (dd, $J_1 = 13.6$ Hz, $J_2 = 1.6$ Hz, 1H), 2.34 (s, 3H), 2.18 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 161.8$ (d, $J_{P,C} = 2.9$ Hz), 138.4, 138.2 (d, $J_{P,C} = 3.0$ Hz), 132.6 (d, $J_{P,C} = 3.5$ Hz), 132.0 (d, $J_{P,C} = 10.6$ Hz), 131.8 (d, $J_{P,C} = 9.4$ Hz), 131.5, 130.9, 129.0, 128.7 (d, $J_{P,C} = 12.4$ Hz), 128.0 (d, $J_{P,C} = 12.4$ Hz), 120.1, 113.4 (d, $J_{P,C} = 9.5$ Hz), 111.3 (d, $J_{P,C} = 102.5$ Hz), 94.6, 83.9 (d, $J_{P,C} = 1.8$ Hz), 21.5, 20.3. $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 39.0$. HRMS
(2-hydroxy-5-methyl-3-((4-propylyphenyl)ethynyl)phenyl) diphenylphosphine oxide (6d): white solid, mp 154.6–155.5 °C, 58.6 mg (yield 65%). 

\[ \text{H NMR (CDCl}_3, 400 MHz): \delta = 11.37 \text{ (s, 1H), 7.73–7.68 (m, 4H), 7.61–7.57 (m, 2H), 7.52–7.44 (m, 7H), 7.14 (d, } J = 8.4 \text{ Hz, 2H), 6.77 (dd, } J_1 = 13.2 \text{ Hz, } J_2 = 1.2 \text{ Hz, 1H), 2.58 (t, } J = 7.4 \text{ Hz, 2H), 2.19 (s, 3H), 1.68–1.58 (m, 2H), 0.93 (t, } J = 7.4 \text{ Hz, 3H).} \]

\[ \text{C NMR (CDCl}_3, 100 MHz): \delta = 161.7 \text{ (d, } J_{PC} = 3.2 \text{ Hz), 143.1, 138.2 (d, } J_{PC} = 1.9 \text{ Hz), 132.5 (d, } J_{PC} = 2.3 \text{ Hz), 132.0 (d, } J_{PC} = 9.7 \text{ Hz), 131.8 (d, } J_{PC} = 9.6 \text{ Hz), 131.7, 131.3 (d, } J_{PC} = 95.7 \text{ Hz), 128.7 (d, } J_{PC} = 12.4 \text{ Hz), 128.4, 128.0 (d, } J_{PC} = 12.5 \text{ Hz), 120.3, 113.4 (d, } J_{PC} = 9.5 \text{ Hz), 111.2 (d, } J_{PC} = 101.6 \text{ Hz), 94.7, 83.9 (d, } J_{PC} = 1.8 \text{ Hz), 37.9, 24.3, 20.3, 13.7.} \]

\[ \text{P NMR (CDCl}_3, 162 MHz): \delta = 38.9. \]

HRMS (ESI-TOF): \( m/z = 423.1514 \), calcd for \( C_{24}H_{24}O_2P \, [MH^+]^+ 423.1514 \).

(3-((3-fluorophenyl)ethynyl)-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (6e): 64.5 mg (yield 76%). 

\[ \text{H NMR (CDCl}_3, 400 MHz): \delta = 11.58 \text{ (s, 1H), 7.73–7.68 (m, 4H), 7.62–7.58 (m, 2H), 7.53–7.48 (m, 4H), 7.44 (s, 1H), 7.35–7.24 (m, 3H), 7.04–6.99 (m, 1H), 6.79 (dd, } J_1 = 13.6 \text{ Hz, } J_2 = 1.6 \text{ Hz, 1H), 2.20 (s, 3H). Due to the coupling of F-C and P-C, the } ^{13}C \text{ NMR spectra show complex peaks not easily interpreted. Typical signals belong to the alkyne unit: } \delta = 92.98 \text{ (d, } J_{PC} = 3.7 \text{ Hz), 85.66 (d, } J_{PC} = 2.4 \text{ Hz). Signals belong to the methyl group: } \delta = 20.3. A full list of the } ^{13}C \text{ NMR data: } ^{13}C \text{ NMR (CDCl}_3, 100 MHz): \delta = 163.5, 162.2, 162.1, 161.1, 138.33, 138.31, 132.67, 132.65, 132.3, 132.2, 132.1, 132.0, 131.9, 130.8, 129.8, 129.7, 128.8, 128.7, 128.2, 128.0, 127.60, 127.58, 125.1, 125.0, 118.5, 118.3, 115.7, 115.4, 112.9, 112.8, 111.9, 110.8, 92.99, 92.96, 85.67, 85.65, 20.3. ^{31}P \text{ NMR (CDCl}_3, 162 MHz): } \delta = 39.3. \]

HRMS (ESI-TOF): \( m/z = 427.1261 \), calcd for \( C_{21}H_{23}O_2PF \, [MH^+]^+ 427.1263 \).

(5-ethyl-2-hydroxy-3-(phenylethynyl)phenyl)diphenylphosphine oxide (6f): white solid, mp 238.0–239.0 °C, 53.6 mg (yield 63%). 

\[ \text{H NMR (CDCl}_3, 400 MHz): \delta = 11.43 \text{ (s, 1H), 7.73–7.68 (m, 4H), 7.61–7.48 (m, 9H), 7.34–7.31 (m, 3H), 6.81 (dd, } J_1 = 13.2 \text{ Hz, } J_2 = 2.0 \text{ Hz, 1H), 2.49 (q, } J = 7.6 \text{ Hz, 2H), 1.13 (t, } J = 7.6, 3 \text{H). C NMR (CDCl}_3, 100 MHz): } \delta = 162.0 \text{ (d, } J_{PC} = 3.0 \text{ Hz), 137.0 (d, } J_{PC} = 3.1 \text{ Hz), 134.5 (d, } J_{PC} = 12.2 \text{ Hz), 132.6 (d, } J_{PC} = 2.8 \text{ Hz), 131.9 (d, } J_{PC} = 11.0 \text{ Hz), 131.6, 131.3 (d, } J_{PC} = 104.6 \text{ Hz), 131.0 (d, } J_{PC} = 10.2 \text{ Hz), 128.7 (d, } J_{PC} = 12.4 \text{ Hz), 128.23, 128.19, 123.12, 113.2 (d, } J_{PC} = 9.5 \text{ Hz), 111.3 (d, } J_{PC} = 102.1 \text{ Hz), 94.3, 84.7 (d, } J_{PC} = 2.4 \text{ Hz), 27.6, 15.5. ^{31}P \text{ NMR (CDCl}_3, 162 MHz): } \delta = 39.1. \]

HRMS (ESI-TOF): \( m/z = 423.1516 \), calcd for \( C_{25}H_{25}O_2P \, [MH^+]^+ 423.1514 \).

bis(4-fluorophenyl)(2-hydroxy-5-methyl-3-(phenyl ethynyl) phenyl)phosphine oxide (6g): white solid, mp 199.3–200.5 °C, 61.8 mg (yield 70%). 

\[ \text{H NMR (CDCl}_3, 400 MHz): \delta = 11.07 \text{ (s, 1H), 7.73–7.67 (m, 4H), 7.56–7.54 (m, 2H), 7.47 (s, 1H), 7.34–7.32 (m, 3H), 7.23–7.18 (m, 4H), 6.77 (dd, } J_1 = 13.6 \text{ Hz, } J_2 = 1.6 \text{ Hz, 1H), 2.21 (s, 3H). Due to the coupling of F-C and P-C, the } ^{13}C \text{ NMR spectra show complex peaks not easily interpreted. Typical signals belong to the alkyne unit: } \delta = 94.75, 84.27 \]
(d, $J_{PC} = 3.0$ Hz). Signals belong to the methyl group: $\delta = 20.3$. A full list of the $^{13}$C NMR data: $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 166.70$, 166.68, 161.49, 161.45, 138.46, 138.43, 134.65, 134.56, 134.53, 134.44, 131.79, 131.70, 131.65, 128.47, 128.36, 128.23, 127.81, 127.79, 126.73, 126.70, 123.00, 116.42, 116.28, 116.21, 116.07, 113.45, 113.36, 111.74, 110.70, 94.7, 84.28, 84.25, 20.3. $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 36.9$. HRMS (ESI-TOF): $m/z = 445.1171$, calcd for C$_{27}$H$_{20}$O$_2$PF$_2$ [MH$^+$] 445.1169.

(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)di-p-tolylphosphine oxide (6h): white solid, mp 211.1–212.3 °C, 69.8 mg (yield 80%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 11.65$ (s, 1H), 7.60–7.54 (m, 6H), 7.42 (d, $J = 2.0$ Hz, 1H), 7.33–7.25 (m, 7H), 6.76 (dd, $J_1 = 13.2$ Hz, $J_2 = 1.6$ Hz, 1H), 2.41 (s, 6H), 2.17 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 161.9$ (d, $J_{PC} = 2.7$ Hz), 143.1 (d, $J_{PC} = 2.5$ Hz), 138.0 (d, $J_{PC} = 2.7$ Hz), 132.0 (d, $J_{PC} = 10.6$ Hz), 131.9 (d, $J_{PC} = 9.5$ Hz), 131.6, 129.4 (d, $J_{PC} = 13.8$ Hz), 128.3 (d, $J_{PC} = 107.2$ Hz), 128.1, 127.8 (d, $J_{PC} = 12.6$ Hz), 123.2, 113.0 (d, $J_{PC} = 9.4$ Hz), 111.8 (d, $J_{PC} = 102.7$ Hz), 94.2, 84.8 (d, $J_{PC} = 2.5$ Hz), 21.6, 20.3. $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 39.4$. HRMS (ESI-TOF): $m/z = 437.1675$, calcd for C$_{29}$H$_{26}$O$_2$P [MH$^+$] 437.1670.

(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)bis(4-methoxypHENyl)phosphine oxide (6i): 47.9 mg (yield 51%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 11.69$ (s, 1H), 7.64–7.54 (m, 6H), 7.42 (d, $J = 1.6$ Hz, 1H), 7.35–7.31 (m, 3H), 7.00–6.97 (m, 4H), 6.74 (dd, $J_1 = 13.6$ Hz, $J_2 = 1.6$ Hz, 1H), 3.85 (s, 6H), 2.18 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 162.9$ (d, $J_{PC} = 3.1$ Hz), 161.9 (d, $J_{PC} = 2.7$ Hz), 137.9 (d, $J_{PC} = 1.8$ Hz), 133.9 (d, $J_{PC} = 11.6$ Hz), 132.0 (d, $J_{PC} = 9.6$ Hz), 131.6, 128.2, 127.8 (d, $J_{PC} = 12.5$ Hz), 122.2, 114.2 (d, $J_{PC} = 12.8$ Hz), 113.0 (d, $J_{PC} = 9.6$ Hz), 112.2 (d, $J_{PC} = 103.0$ Hz), 94.1, 84.9 (d, $J_{PC} = 2.9$ Hz), 55.3, 20.3. $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 39.0$. HRMS (ESI-TOF): $m/z = 469.1566$, calcd for C$_{29}$H$_{26}$O$_2$P [MH$^+$] 469.1569.

bis(3-chlorophenyl)(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6j): 63.5 mg (yield 67%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 10.68$ (s, 1H), 7.70–7.66 (m, 2H), 7.59–7.54 (m, 6H), 7.49–7.43 (m, 3H), 7.34–7.32 (m, 3H), 6.84 (dd, $J_1 = 13.6$ Hz, $J_2 = 1.6$ Hz, 1H), 2.23 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 161.1$ (d, $J_{PC} = 4.2$ Hz), 138.7 (d, $J_{PC} = 2.8$ Hz), 135.3 (d, $J_{PC} = 16.4$ Hz), 133.2 (d, $J_{PC} = 103.8$ Hz), 133.0 (d, $J_{PC} = 1.9$ Hz), 131.8 (d, $J_{PC} = 9.7$ Hz), 131.62, 131.60 (d, $J_{PC} = 11.0$ Hz), 131.6, 130.2 (d, $J_{PC} = 13.2$ Hz), 129.9 (d, $J_{PC} = 10.5$ Hz), 128.7 (d, $J_{PC} = 13.3$ Hz), 128.4, 128.2, 122.8, 113.4 (d, $J_{PC} = 9.7$ Hz), 110.5 (d, $J_{PC} = 104.2$ Hz), 95.0, 84.0 (d, $J_{PC} = 2.7$ Hz), 20.3. $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 35.7$. HRMS (ESI-TOF): $m/z = 477.0571$, calcd for C$_{27}$H$_{26}$Cl$_2$O$_2$P [MH$^+$] 477.0578.
(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)di-o-tolylphosphine oxide (6k): 21.0 mg (yield 24%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 8.32$–8.27 (m, 2H), 7.43–7.31 (m, 9H), 7.28–7.23 (m, 2H), 7.15 (t, $J = 6.4$ Hz, 2H), 6.94 (dd, $J_1 = 8.4$ Hz, $J_2 = 2.0$ Hz, 1H), 2.39 (s, 6H), 2.24 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 149.7$ (d, $J_{PC} = 8.0$ Hz), 141.8 (d, $J_{PC} = 11.1$ Hz), 133.9 (d, $J_{PC} = 10.0$ Hz), 133.5, 133.3, 132.5 (d, $J_{PC} = 2.8$ Hz), 131.5 (d, $J_{PC} = 13.2$ Hz), 130.2, 129.7 (d, $J_{PC} = 132.7$ Hz), 128.3, 125.6 (d, $J_{PC} = 12.9$ Hz), 123.2, 119.2 (d, $J_{PC} = 5.1$ Hz), 114.8 (d, $J_{PC} = 6.8$ Hz), 93.6, 85.6, 21.2 (d, $J_{PC} = 4.3$ Hz), 20.4. $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 30.0$. HRMS (ESI-TOF): $m/z = 437.1676$, calcd for C$_{25}$H$_{32}$O$_2$P [MH$^+$] 437.1670.

dibutyl(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl) phosphine oxide (6l): 53.8 mg (yield 73%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 11.33$ (s, 1H), 7.58–7.55 (m, 2H), 7.43 (s, 1H), 7.34–7.32 (m, 3H), 6.83 (dd, $J_1 = 12.4$ Hz, $J_2 = 1.6$ Hz, 1H), 2.28 (s, 3H), 2.04–1.85 (m, 4H), 1.73–1.63 (m, 2H), 1.52–1.36 (m, 6H), 0.89 (t, $J = 7.2$ Hz, 6H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 161.7$ (d, $J_{PC} = 2.4$ Hz), 137.8 (d, $J_{PC} = 2.7$ Hz), 131.7, 129.7 (d, $J_{PC} = 9.8$ Hz), 128.31, 128.27, 128.22, 123.1, 112.6 (d, $J_{PC} = 8.5$ Hz), 111.4 (d, $J_{PC} = 90.5$ Hz), 94.4, 84.6 (d, $J_{PC} = 1.2$ Hz), 30.1 (d, $J_{PC} = 67.9$ Hz), 23.9 (d, $J_{PC} = 13.8$ Hz), 23.1 (d, $J_{PC} = 4.3$ Hz), 20.3, 13.6. $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 55.3$. HRMS (ESI-TOF): $m/z = 369.1987$, calcd for C$_{25}$H$_{32}$O$_2$P [MH$^+$] 369.1983.

dicyclohexyl(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl) phosphine oxide (6m): 48.1 mg (yield 57%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 12.03$ (s, 1H), 7.57–7.55 (m, 2H), 7.43 (s, 1H), 7.34–7.31 (m, 3H), 6.74 (dd, $J_1 = 10.8$ Hz, $J_2 = 1.6$ Hz, 1H), 2.29 (s, 3H), 2.07–2.02 (m, 4H), 1.87–1.69 (m, 8H), 1.43–1.20 (m, 10H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 163.4, 137.8$ (d, $J_{PC} = 2.2$ Hz), 131.7, 129.6 (d, $J_{PC} = 8.8$ Hz), 128.14, 128.12, 127.4 (d, $J_{PC} = 10.5$ Hz), 123.3, 112.9 (d, $J_{PC} = 9.0$ Hz), 108.4 (d, $J_{PC} = 84.0$ Hz), 94.1, 85.0 (d, $J_{PC} = 2.2$ Hz), 35.6 (d, $J_{PC} = 65.8$ Hz), 26.16 (d, $J_{PC} = 3.3$ Hz), 26.15 (d, $J_{PC} = 28.3$ Hz), 25.6, 25.1 (d, $J_{PC} = 2.9$ Hz), 24.0 (d, $J_{PC} = 3.4$ Hz), 20.3. $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta = 60.9$. HRMS (ESI-TOF): $m/z = 421.2291$, calcd for C$_{25}$H$_{32}$O$_2$P [MH$^+$] 421.2296.

3. Experimental procedure for gram-scale synthesis of 3ab

An oven-dried 50 mL Schlenk tube containing a Teflon-coated stir bar was charged with Zn(OTf)$_2$ (26.3 mg, 10 mol %) and di-p-tolylphosphine oxide 2b (5.002 g, 21.75 mmol). The Schlenk tube was
sealed and then evacuated and backfilled with N₂ (3 cycles). 15 mL DCE was injected. Then 1a (1.000 g, 7.25 mmol) was introduced with 5 mL of DCE. The Schlenk tube was sealed and immersed in an oil bath which was heated to 100 °C for 6 h. The reaction mixture was cooled to room temperature, and EtOAc (20 mL) and water (20 mL) were added. The organic layer was separated, and the aqueous phase was extracted with EtOAc (20 mL × 3). The combined organic layers were washed with brine and dried over anhydrous MgSO₄. The solvent was removed under vacuum, and the product 3ab (1.960 g, 80%) was obtained after purification by flash chromatography on silica (petroleum ether/ethyl acetate 3/1).

4. Experimental procedure for the synthesis of 2-phosphanylphenol 4

![Reaction scheme](image)

To a solution of 3ab (1.233 g, 4.0 mmol) and triethylamine (2.8 mL, 20 mmol) in toluene (20 mL) was added trichlorosilane (1.9 mL, 20 mmol) dropwise at 0 °C. The mixture was then stirred at 100 °C for 48 h. After the mixture was cooled to 0 °C, 1 N NaOH (aq) (20 mL) was slowly added, and the mixture was warmed to room temperature, and then stirred at 60 °C for 30 min. The mixture was cooled to room temperature, and filtered through a pad of celite eluted with ethyl acetate. The organic layer was separated, dried over MgSO₄, filtered, and concentrated on a rotary evaporator. The residue was subjected to flash column chromatography on silica gel (petroleum ether/ethyl acetate 30/1–10/1) to give 4 (0.846 g, 66%). ¹H NMR (CDCl₃, 400 MHz): δ = 7.25–7.15 (m, 8H), 7.08 (dd, J₁ = 8.4 Hz, J₂ = 1.6 Hz, 1H), 6.82–6.79 (m, 2H), 5.99 (s, 1H), 2.35 (s, 6H), 2.17 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 156.9 (d, Jₚ-C = 16.8 Hz), 139.0, 134.7 (d, Jₚ-C = 5.9 Hz), 133.4 (d, Jₚ-C = 19.2 Hz), 132.2, 131.6 (d, Jₚ-C = 3.8 Hz), 130.1 (d, Jₚ-C = 2.4 Hz), 129.5 (d, Jₚ-C = 7.2 Hz), 120.9 (d, Jₚ-C = 6.0 Hz), 115.4 (d, Jₚ-C = 1.6 Hz), 21.4, 20.6. ³¹P NMR (CDCl₃, 162 MHz): δ = -29.6. HRMS (ESI-TOF): m/z = 321.1416, calcld for C₂₁H₂₂OP [MH⁺] 321.1408.

5. Experimental procedure for the synthesis of 7-phosphiny1benzofuran 7

![Reaction scheme](image)

An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with 6a (81.7 mg, 0.2 mmol) NaHCO₃ (50.4, 0.6 mmol) and MeCN (2 mL). After stirring at rt for 30 min, I₂ (151.8 mg, 0.6 mmol) was added. After the reaction was complete (monitored by TLC, 2 h), the reaction was quenched with aq. Na₂S₂O₃. The mixture was extracted with EtOAc. The combined organic layers were dried over MgSO₄, filtered and concentrated. The residue was purified with silica gel column chromatography (PE/EtOAc 3/1 to 1/1) to afford compound 7 (93.6 mg, 88%). White solid, mp. 240.4–
241.0 °C. $^1$H NMR (CDCl$_3$, 400 MHz): 7.87–7.77 (m, 5H), 7.68–7.64 (m, 2H), 7.58–7.53 (m, 2H), 7.48–7.44 (m, 5H), 7.37–7.33 (m, 3H), 2.53 (s, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ = 153.5, 151.5 (d, $J_{P-C}$ = 3.0 Hz), 133.4 (d, $J_{P-C}$ = 100.1 Hz), 133.8, 133.0, 132.0 (d, $J_{P-C}$ = 3.3 Hz), 131.9 (d, $J_{P-C}$ = 10.2 Hz), 131.6 (d, $J_{P-C}$ = 4.6 Hz), 129.3, 128.6, 128.4 (d, $J_{P-C}$ = 7.3 Hz), 127.2, 126.3 (d, $J_{P-C}$ = 2.3 Hz), 115.6 (d, $J_{P-C}$ = 101.4 Hz), 60.6, 21.2. $^{31}$P NMR (CDCl$_3$, 162 MHz): $\delta$ = 23.3; HRMS (ESI-TOF): $m/z$ = 535.0327, calcd for C$_{27}$H$_{21}$O$_2$PI [MH$^+$] 535.0324.

6. Crystal structure determination

The well-shaped single crystals were selected for X-ray diffraction study. The unit cell parameters and intensity data were collected at 296(2) K on a Bruker SMART APEX II CCD diffractometer using a graphite-monochromated Mo K$_\alpha$ ($\lambda = 0.71073$ Å) radiation. The structure was solved by direct methods and refined on $F^2$ by full-matrix least squares procedures using SHELXTL software. All non-hydrogen atoms were refined anisotropically. All H atoms were located from a difference map and refined isotropically. CCDC 1874221 and CCDC 1874220 contains the crystallographic data of compounds 3ao and 6a for this article. ORTEP representations (30% probability level) of the molecular structures are presented in Table S1. Crystallographic data are listed in Table S2. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk.

**Table S1** Molecular structures of 3an and 6a

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Table S2 Crystal data and structure refinements for the products

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7. Copies of $^1$H, $^{13}$C and $^{31}$P NMR spectra

$^1$H NMR of (2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3aa)
$^{13}$C NMR of (2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3aa)
$^{31}$P NMR of (2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3aa)
$^1$H NMR of (5-ethyl-2-hydroxyphenyl)diphenylphosphine oxide (3ba)
$^{13}$C NMR of (5-ethyl-2-hydroxyphenyl)diphenylphosphine oxide (3ba)
$^{31}$P NMR of (5-ethyl-2-hydroxyphenyl)diphenylphosphine oxide (3ba)
$^1$H NMR of (4-hydroxy-[1,1'-biphenyl]-3-yl)diphenylphosphine oxide (3ca)
$^{31}$P NMR of (4-hydroxy-[1,1'-biphenyl]-3-yl)diphenylphosphine oxide (3ca)
$^1$H NMR of (2-hydroxy-3,5-dimethylphenyl)diphenylphosphine oxide (3da)
$^{13}$C NMR of (2-hydroxy-3,5-dimethylphenyl)diphenylphosphine oxide (3da)
$^{31}$P NMR of (2-hydroxy-3,5-dimethylphenyl)diphenylphosphine oxide (3da)
\(^1\text{H NMR of (3-(tert-butyl)-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3ea)}\)
$^{13}$C NMR of (3-(tert-butyl)-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3ea)
$^{31}$P NMR of (3-(tert-butyl)-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3ea)
$^{1}$H NMR of (3-bromo-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3fa)
$^{13}$C NMR of (3-bromo-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3fa)
$^{31}$P NMR of (3-bromo-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (3fa)
\(^1\)H NMR of (2-hydroxy-3-iodo-5-methylphenyl)diphenylphosphine oxide (3ga)

![NMR Spectrogram](image-url)
$^{13}$C NMR of (2-hydroxy-3-iodo-5-methylphenyl)diphenylphosphine oxide (3ga)
$^{31}$P NMR of (2-hydroxy-3-iodo-5-methylphenyl)diphenylphosphine oxide (3ga)
$^1$H NMR of (2-hydroxy-4,5-dimethylphenyl)diphenylphosphine oxide (3ha)
$^{31}$P NMR of (2-hydroxy-4,5-dimethylphenyl)diphenylphosphine oxide (3ha)
$^1$H NMR of (6-hydroxy-2,3-dimethylphenyl)diphenylphosphine oxide (3ha')
$^{13}$C NMR of (6-hydroxy-2,3-dimethylphenyl)diphenylphosphine oxide (3ha')
$^{31}$P NMR of (6-hydroxy-2,3-dimethylphenyl)diphenylphosphine oxide (3ha')
$^1$H NMR of (2-hydroxy-5-methylphenyl)di-p-tolylphosphine oxide (3ab)
$^{13}$C NMR of (2-hydroxy-5-methylphenyl)di-p-tolylphosphine oxide (3ab)
$^{31}$P NMR of (2-hydroxy-5-methylphenyl)di-p-tolylphosphine oxide (3ab)
$^1$H NMR of (2-hydroxy-5-methylphenyl)bis(4-methoxyphenyl)phosphine oxide (3ac)
\[^{13}\text{C} \text{NMR of (2-hydroxy-5-methylphenyl)bis(4-methoxyphenyl)phosphine oxide (3ac)}\]
$^{31}$P NMR of (2-hydroxy-5-methylphenyl)bis(4-methoxyphenyl)phosphine oxide (3ac)
$^1$H NMR of bis(4-fluorophenyl)(2-hydroxy-5-methylphenyl)phosphine oxide (3ad)
\(^{13}\)C NMR of bis(4-fluorophenyl)(2-hydroxy-5-methylphenyl)phosphine oxide (3ad)
$^{31}$P NMR of bis(4-fluorophenyl)(2-hydroxy-5-methylphenyl)phosphine oxide (3ad)
$^1$H NMR of (2-hydroxy-5-methylphenyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3ae)
$^{13}$C NMR of (2-hydroxy-5-methylphenyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3ae)
$^{31}$P NMR of (2-hydroxy-5-methylphenyl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3ae)
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$^{13}\text{C}$ NMR of (2-hydroxy-5-methylphenyl)(4-methoxyphenyl)(phenyl)phosphine oxide (3af)
$^{31}$P NMR of (2-hydroxy-5-methylphenyl)(4-methoxyphenyl)(phenyl)phosphine oxide (3af)
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$^{13}$C NMR of (4-fluorophenyl)(2-hydroxy-5-methylphenyl)(phenyl)phosphine oxide (3ag)
$^{31}$P NMR of (4-fluorophenyl)(2-hydroxy-5-methylphenyl)(phenyl)phosphine oxide (3ag)
$^1$H NMR of bis(3-chlorophenyl)(2-hydroxy-5 methylphenyl)phosphine oxide (3ah)
$^{13}$C NMR of bis(3-chlorophenyl)(2-hydroxy-5 methylphenyl)phosphine oxide (3ah)
$^{31}$P NMR of bis(3-chlorophenyl)(2-hydroxy-5 methylphenyl)phosphine oxide (3ah)
$^1$H NMR of bis(3-chlorophenyl)(2-hydroxy-3,5-dimethylphenyl)phosphine oxide (3dh)
$^{13}$C NMR of bis(3-chlorophenyl)(2-hydroxy-3,5-dimethylphenyl)phosphine oxide (3dh)
$^{31}$P NMR of bis(3-chlorophenyl)(2-hydroxy-3,5-dimethylphenyl)phosphine oxide (3dh)
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13C NMR of (2-hydroxy-5-methylphenyl)di-o-tolylphosphine oxide (3ai)
$^{31}$P NMR of (2-hydroxy-5-methylphenyl)di-o-tolylphosphine oxide (3ai)
$^1$H NMR of (2-hydroxy-5-methylphenyl)di(thiophen-2-yl)phosphine oxide (3aj)
$^{13}$C NMR of (2-hydroxy-5-methylphenyl)di(thiophen-2-yl)phosphine oxide (3aj)
$^{31}$P NMR of (2-hydroxy-5-methylphenyl)di(thiophen-2-yl)phosphine oxide (3aj)
$^1$H NMR of (2-hydroxy-5-methylphenyl)(methyl)(phenyl)phosphine oxide (3a)
$^{13}$C NMR of (2-hydroxy-5-methylphenyl)(methyl)(phenyl)phosphine oxide (3ak)
\[^{31}P\text{ NMR of (2-hydroxy-5-methylphenyl)(methyl)(phenyl)phosphine oxide (3ak)}\]
$^1$H NMR of butyl(2-hydroxy-5-methylphenyl)(phenyl)phosphine oxide (3al)
$^{13}$C NMR of butyl(2-hydroxy-5-methylphenyl)(phenyl)phosphine oxide (3a-l)
$^{31}$P NMR of butyl(2-hydroxy-5-methylphenyl)(phenyl)phosphine oxide (3a)
$^1$H NMR of (3-bromo-2-hydroxy-5-methylphenyl)(cyclohexyl)(phenyl)phosphine oxide (3fm)
$^{13}$C NMR of (3-bromo-2-hydroxy-5-methylphenyl)(cyclohexyl)(phenyl)phosphine oxide (3fm)
$^{31}$P NMR of (3-bromo-2-hydroxy-5-methylphenyl)(cyclohexyl)(phenyl)phosphine oxide (3f)
$^1$H NMR of dibutyl(2-hydroxy-5-methylphenyl)phosphine oxide (3an)
$^{13}$C NMR of dibutyl(2-hydroxy-5-methylphenyl)phosphine oxide (3an)
$^{31}$P NMR of dibutyl(2-hydroxy-5-methylphenyl)phosphine oxide (3an)
$^1$H NMR of dicyclohexyl(2-hydroxy-5-methylphenyl)phosphine oxide (3ao)
$^{13}$C NMR of dicyclohexyl(2-hydroxy-5-methylphenyl)phosphine oxide (3ao)
$^{31}$P NMR of dicyclohexyl(2-hydroxy-5-methylphenyl)phosphine oxide (3ao)
$^1$H NMR of 2-(di-p-tolylphosphanyl)-4-methylphenol (4)
$^{13}$C NMR of 2-(di-p-tolylphosphanyl)-4-methylphenol (4)
$^{31}$P NMR of 2-(di-p-tolylphosphanyl)-4-methylphenol (4)
$^1$H NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)diphenylphosphine oxide (6a)
$^{13}$C NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)diphenylphosphine oxide (6a)
$^{31}$P NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)diphenylphosphine oxide (6a)
$^1$H NMR of (2-hydroxy-5-methyl-3-(m-tolylethynyl)phenyl)diphenylphosphine oxide (6b)
$^{13}$C NMR of (2-hydroxy-5-methyl-3-(m-tolylethynyl)phenyl)diphenylphosphine oxide (6b)
$^{31}$P NMR of (2-hydroxy-5-methyl-3-(m-tolylethynyl)phenyl)diphenylphosphine oxide (6b)
$\text{H NMR of (2-hydroxy-5-methyl-3-(p-tolylethynyl)phenyl)diphenylphosphine oxide (6c)}$

![NMR Spectral Image](image-url)
$^{13}$C NMR of (2-hydroxy-5-methyl-3-(p-tolylethynyl)phenyl)diphenylphosphine oxide (6c)
$^{31}$P NMR of (2-hydroxy-5-methyl-3-(p-tolylethynyl)phenyl)diphenylphosphine oxide (6c)
$^1$H NMR of (2-hydroxy-5-methyl-3-((4-propylphenyl)ethynyl)phenyl)diphenylphosphine oxide (6d)
$^{13}$C NMR of (2-hydroxy-5-methyl-3-((4-propylphenyl)ethynyl)phenyl)diphenylphosphine oxide (6d)
$^{31}$P NMR of (2-hydroxy-5-methyl-3-((4-propylphenyl)ethynyl)phenyl)diphenylphosphine oxide (6d)
$^1$H NMR of (3-((3-fluorophenyl)ethynyl)-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (6e)
$^{13}$C NMR of (3-((3-fluorophenyl)ethynyl)-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (6e)
$^{31}$P NMR of (3-((3-fluorophenyl)ethynyl)-2-hydroxy-5-methylphenyl)diphenylphosphine oxide (6e)
$^1$H NMR of (5-ethyl-2-hydroxy-3-(phenylethynyl)phenyl)diphenylphosphine oxide (6f)
$^{13}$C NMR of (5-ethyl-2-hydroxy-3-(phenylethynyl)phenyl)diphenylphosphine oxide (6f)
$^{31}$P NMR of (5-ethyl-2-hydroxy-3-(phenylethynyl)phenyl)diphenylphosphine oxide (6f)
$^{1}$H NMR of bis(4-fluorophenyl)(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6g)
$^{13}$C NMR of bis(4-fluorophenyl)(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6g)
$^{31}P$ NMR of bis(4-fluorophenyl)(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6g)
$\textsuperscript{1}H$ NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)di-p-tolylphosphine oxide (6h)
$^{13}$C NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)di-p-tolylphosphine oxide (6h)
$^{31}$P NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)di-p-tolylphosphine oxide (6h)
$^1$H NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)bis(4-methoxyphenyl)phosphine oxide (6i)
$^{13}$C NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)bis(4-methoxyphenyl)phosphine oxide (6i)
$^{31}$P NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)bis(4-methoxyphenyl)phosphine oxide (6i)
$^1$H NMR of bis(3-chlorophenyl)(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6j)
$^{13}$C NMR of bis(3-chlorophenyl)(2-hydroxy-5-methyl-3-phenylethynyl)phenylphosphine oxide (6j)
$^{31}$P NMR of bis(3-chlorophenyl)(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6j)
$^1$H NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)di-o-tolylphosphine oxide (6k)
$^{13}$C NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)di-o-tolylphosphine oxide (6k)
$^{31}$P NMR of (2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)di-o-tolylphosphine oxide (6k)
$^1$H NMR of dibutyl(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6l)
$^{13}$C NMR of dibutyl(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6l)
$^{31}$P NMR of dibutyl(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6l)
$^1$H NMR of dicyclohexyl(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6m)
$^{13}$C NMR of dicyclohexyl(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6m)
$^{31}$P NMR of dicyclohexyl(2-hydroxy-5-methyl-3-(phenylethynyl)phenyl)phosphine oxide (6m)
\(^1\)H NMR of (3-iodo-5-methyl-2-phenylbenzofuran-7-yl)diphenylphosphine oxide (7)
$^{13}$C NMR of (3-iodo-5-methyl-2-phenylbenzofuran-7-yl)diphenylphosphine oxide (7)
$^{31}$P NMR of (3-iodo-5-methyl-2-phenylbenzofuran-7-yl)diphenylphosphine oxide (7)