SYNTHESIS OF 2-ARYL-BENZO[*b*]FURANS VIA COPPER(I) CATALYZED COUPLING REACTION OF O-IODOPHENOLS AND ARYL ACETYLENES

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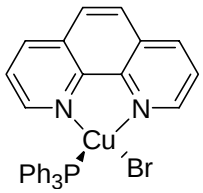
SUPPORTING INFORMATION

General. All of the reactions reported herein were conducted under an inert atmosphere of argon in oven-dried glassware. All reagents and solvents were obtained from Acros, Alfa Aesar or from Aldrich and were used without further purification. Cesium Carbonate (Aldrich, 99%) was stored in an argon filled glove box. Purification was performed by flash chromatography using ICN Flash Silica Gel, 230-400 mesh. The yields given refer to isolated yields of the characterized compounds, deemed pure by elemental analyses, ^{1}H NMR and ^{13}C NMR. NMR spectra were recorded on a Bruker AVANCE 300 MHz spectrometer. Chemical shifts were reported in parts per million (δ). The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; dd, doublet of doublets; dt, doublet of triplets; and m, multiplet. The coupling constants, *J*, are reported in Hertz (Hz). TMS was used as the internal reference. Elemental analyses were performed at the Microanalysis Laboratory, University of Massachusetts - Amherst by Dr. Greg Dabkowski. The reported melting points were corrected using benzoic acid as a standard. X-ray data were collected using a Nonius kappa-CCD diffractometer with MoKα (λ=0.71073 Å) as the incident radiation. Diffraction data were collected at ambient temperature. The raw data were integrated, refined, scaled and corrected for Lorentz polarization and absorption effects, if necessary, using the programs DENZO and SCALEPAK, supplied by Nonius. Structures solutions and refinements were done (on F_o^2) using SIR92 and SHELXL 97 within the Nonius' MAXUS module. All structures were checked for any missing symmetry using MISSYM of PLATON. The Gas Chromatograph was a Hewlett Packard 6850 GC series with a 30-meter HP-1 100% dimethylpolysiloxane capillary column

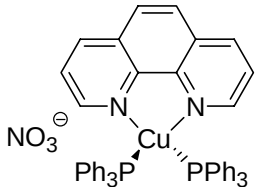
SYNTHESIS OF COPPER(I) COMPLEXES

Nitratobis(triphenylphosphine)copper(I): In an Erlenmeyer flask equipped with a Teflon-coated stir bar, methanol (100 mL) was heated to boiling and triphenylphosphine (Alfa Aesar, 24.22 g, 92.34 mmol) was slowly added to the stirring methanol. After the complete dissolution of triphenylphosphine, $Cu(NO_3)_2 \cdot 2.5\ H_2O$ (Fisher Scientific, 7.16 g, 30.78 mmol) was added in small portions. No special precautions were taken for the exclusion of air. Upon addition of the copper(II) nitrate, a white precipitate formed. After the completion of the addition, the contents were stirred for 30 minutes and the flask was allowed to cool to ambient temperature. The reaction mixture was then filtered through a Buchner funnel and the white residue was washed repeatedly with ethanol and then with diethyl ether. The resultant white solid was dried under dynamic vacuum to give $Cu(PPh_3)_2NO_3$ (12.378 g, 62% yield). m.p. : 238-240 ^oC. The cell constants, contents and the space group are identical to that of the already reported structure of $Cu(PPh_3)_2NO_3$ (Cambridge Structural Database Refcode-NITPPC01).

Tris(triphenylphosphine)copper(I) bromide: In an Erlenmeyer flask equipped with a Teflon-coated stir bar, methanol (100 mL) was heated to boiling and triphenylphosphine (Alfa Aesar, 24.22 g, 92.34 mmol) was slowly added to the stirring methanol. After the complete dissolution of triphenylphosphine, $CuBr_2$ (Acros, 5.15 g, 23.09 mmol) was added in small portions. No special precautions were taken for the exclusion of air. Upon addition of the copper(II) bromide, a white precipitate formed. After the completion of the addition, the contents were stirred for 30 minutes and the flask was allowed to cool to ambient temperature. The reaction mixture was then filtered through a Buchner funnel and the white residue was washed repeatedly with ethanol and then with diethyl ether. The resultant white solid was dried under dynamic vacuum to give $Cu(PPh_3)_3Br$ (20.03 g, 93% yield). m.p.: 164-166 ^oC. The cell constants, contents and the space group are identical to that of the already reported structure of $Cu(PPh_3)_3Br$ (Cambridge Structural Database Refcode-FEYVAG).



[Cu(phen)(PPh$_3$)Br]: In an Erlenmeyer flask equipped with a Teflon-coated magnetic stir bar, tris(triphenylphosphine)copper(I) bromide (1.40 g, 1.50 mmol) was added to chloroform (50 mL). After complete dissolution, 1,10-phenanthroline (856 mg, 1.50 mmol) was then added. The colorless solution immediately turned orange. The contents of the flask were allowed to stir for 30 minutes at room temperature. Afterwards the solvent was removed *in vacuo* to afford an orange solid. Recrystallization was achieved by layering 40 mL of diethyl ether onto a solution of the solid dissolved in 20 mL of dichloromethane (931 mg, 75% yield). m.p.: 252-253 ^{o}C. The cell constants, contents and the space group are identical to that of the already reported structure of Cu(phen)(PPh$_3$)Br (Cambridge Structural Database Refcode-BEQLAK).



[Cu(phen)(PPh$_3$)$_2$]NO$_3$: In an Erlenmeyer flask equipped with a Teflon-coated magnetic stir bar, Nitratobis(triphenylphosphine)copper(I) (977 mg, 1.50 mmol) was added to chloroform (20 mL). After complete dissolution, triphenylphosphine (393 mg, 1.50 mmol), followed by 1,10-phenanthroline (270 mg, 1.50 mmol) was then added. The colorless solution immediately turned yellow. The contents of the flask were allowed to stir for 30 minutes at room temperature. Afterwards the solvent was removed *in vacuo* to afford a yellow solid. Recrystallization was achieved by vapor diffusion of diethyl ether into a solution of the solid dissolved in 30 mL of dichloromethane (931 mg, 75% yield). m.p.: 202-204 ^{o}C.

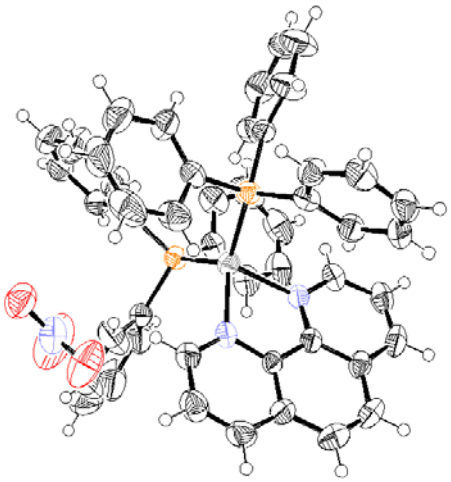


Figure S1: ORTEP figure of $[Cu(Phen)(PPh_3)_2]NO_3$ (**1**)

CRYSTAL DATA FOR 1

$C_{48}H_{38}CuN_3O_3P_2$
$C_{48}H_{38}CuN_3O_3P_2$
M_r = 830.338
Monoclinic
$P2_1$
a = 10.0266 (2)Å
b = 19.7098 (5)Å
c = 10.6355 (3)Å
α = 90.00°
β = 103.2034 (9)°
γ = 90.00°
V = 2046.25 (9)Å^3
Z = 2

D_x = 1.348 Mg m^{-3}
Density measured by: not measured
fine-focus sealed tube
Mo $K\alpha$ radiation
λ = 0.71073
Cell parameters from 1928
θ = 4.076—19.980 °
μ = 0.658 mm^{-1}
T = 298 K
Cube
Yellow
Crystal source: local laboratory

DATA COLLECTION

KappaCCD
Absorption correction: none
3530 measured reflections
3523 independent reflections
3435 observed reflections

Criterion: >2σ (I)
θ_{max} = 19.99 °
h = -9 →9
k = -18 →18
l = -10 →10

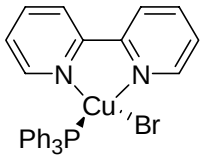
REFINEMENT

Refinement on F^2
fullmatrix least squares refinement
R(all) = 0.0241

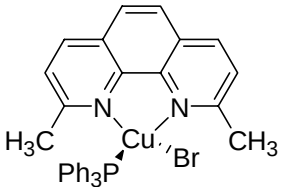
R(gt) = 0.0228
wR(ref) = 0.0593
wR(gt)= 0.0581
S(ref) = 1.014

3523 reflections
514 parameters
1 restraints
H-atom parameters not refined
Calculated weights calc
$\Delta/\sigma_{max} = 0.005$
$\Delta\rho_{max} = 0.115 e Å^3$
$\Delta\rho_{min} = -0.128 e Å^3$

Extinction correction: none
Atomic scattering factors from International Tables Vol C Tables 4.2.6.8 and 6.1.1.4
Flack parameter = -0.014 (10)
Flack H D (1983), *Acta Cryst*. A39, 876-881



[Cu(bipy)(PPh$_3$)Br]: In an Erlenmeyer flask equipped with a Teflon-coated magnetic stir bar, tris(triphenylphosphine)copper(I) bromide (7.45 g, 8.00 mmol) was added to chloroform (100 mL). After complete dissolution, 2,2'-bipyridine (1.27 g, 8.00 mmol) was then added. The colorless solution immediately turned orange. The contents of the flask were allowed to stir for 30 minutes at room temperature. Afterwards the solvent was removed *in vacuo* to afford an orange solid. Recrystallization was achieved by layering 80 mL of diethyl ether onto a solution of the solid dissolved in 40 mL of dichloromethane (3.06 g, 68% yield). m.p.: 215-217 ^oC. The cell constants, contents and the space group are identical to that of the already reported structure of Cu(bipy)(PPh$_3$)Br (Cambridge Structural Database Refcode-COYNOT).



[Cu(neocup)(PPh$_3$)Br]: In an Erlenmeyer flask equipped with a Teflon-coated magnetic stir bar, tris(triphenylphosphine)copper(I) bromide (2.61 g, 2.73 mmol) was added to chloroform (50 mL). After complete dissolution, neocuproine (2,9-dimethyl-1,10-phenanthroline (575 mg, 2.76 mmol) was then added. The colorless solution immediately turned yellow-orange. The contents of the flask were allowed to stir for 30

minutes at room temperature. Afterwards the solvent was removed *in vacuo* to afford a yellow solid. Recrystallization was achieved by layering 80 mL of diethyl ether onto a solution of the solid dissolved in 40 mL of dichloromethane (1.02 g, 61% yield). m.p.: 286-288 ^{o}C. The cell constants, contents and the space group are identical to that of the already reported structure of Cu(neocup)(PPh_3)Br.[1]

SYNTHESIS OF 4-SUBSTITUTED-2-IODOPHENOLS: GENERAL PROCEDURE

4-methyl-2-Iodophenol:[2] 4-Methylphenol (2.69 g, 24.86 mmol) was dissolved in 50 mL of methanol, and then sodium iodide (3.84 g, 25.60 mmol) and sodium hydroxide (1.16 g, 29.00 mmol) were added. Under nitrogen atmosphere, the solution was cooled down to 0 ^{o}C. One equivalent of sodium hypochlorite (5.0 % NaOCl, 40.0 mL) was added drop wise adjusting the drip rate to maintain a reaction temperature of 0-3 ^{o}C. A red color appeared and faded instantly when sodium hypochlorite hit the solution. After complete addition, the mixture was stirred for 1 hr at 0-3 ^{o}C. Then, 10% aqueous sodium thiosulfate solution (28.0 mL) was added and the pH was adjusted to 3-4 using 5% hydrochloric acid or until a white suspension came out. The reaction mixture was extracted with diethyl ether 3 x 50 mL. The combined organic layers were washed with brine, dried over sodium sulfate, filtered and the solvent was removed *in vacuo* to afforded light yellow oil, which solidified upon standing. The crude solid was purified by column chromatography (hexane : dichloromethane, 1:3 as the eluent) to afford a white solid (4.54 g, 77.9 % yield). ^{1}H NMR δ 2.24 (s, 3H), 5.16 (s, 1H), 6.85 (d, *J*=8.3, 1H), 7.01 (dd, *J*=8.3, and 2.1, 1 H), 7.46 (dd, *J*=1.5, 1H). m.p.: 34.5-35.5 ^{o}C.

Synthesis of 2-Iodo-4-cyanophenol: Following the same procedure above for the synthesis of 4-methyl-2-iodophenol, iodine monochloride in methanol (1.0 equivalent) was used as iodinating reagent instead of sodium iodide and sodium hypochlorite. This afforded a solid which was purified by column chromatography (dichloromethane as the eluent). 2-Iodo-4-cyanophenol was obtained as a white solid (40 % yield); ^{1}H NMR δ 5.96 (s, 1H), 7.02 (d, *J*=8.5, 1H), 7.53 (dd, *J*=8.5, and 2.1, 1H), 7.96 (d, *J*=2.1, 1H). m.p.: 144 - 146 ^{o}C.

GENERAL SYNTHESIS OF ARYL ACETYLENES:

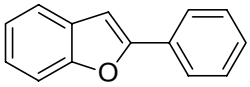
In an argon-filled glove box, $Pd_3(dba)_5$ (0.8 mol%), copper iodide (2.0 mol%), and triphenylphosphine (10.0 mol%) were added to a thick-walled glass tube (similar to Chemglass AF-0523) equipped with Teflon-coated stirred bar and Teflon stopper. The sealed tube was taken out of the box and under a flow of argon, triethylamine (75 mL), the bromoarene (25 mmol), and 35 mmol of trimethylsilylacetylene were added. The tube was sealed under argon and the contents were stirred at 75-80 ^{o}C for 24 h. After reaction was complete (by GC), the reaction mixture was filtered through a Buchner funnel and the residue was washed with dichloromethane until the filtrate was clear. The combined filtrate was concentrated by dynamic vacuum. The resultant yellow oil was purified by column chromatography to afford a yellow oil or light yellow solid.

Deprotection of the silyl group was accomplished by adding a small amount of potassium carbonate into solution of the protected acetylene, dissolved in a dichloromethane / methanol (30/50 mL) solution, under an argon atmosphere. The reaction mixture was stirred at room temperature for 2-3 h or until deprotection was complete (monitored by TLC). Then the reaction mixture was filtered through a Buchner funnel and the residue was washed with dichloromethane until the filtrate was clear. The solvent removed under dynamic vacuum, to afford a yellow oil or solid, which was then purified by column chromatography or filtered through a plug of silica gel. Product was analyzed (using a Direct Reading Echelle ICP) for trace amounts of Pd and none was found.

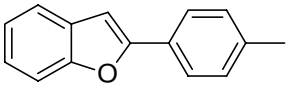
CU-CATALYZED SYNTHESIS OF 2-ARYL-BENZO[*B*]FURANS

General Procedure: In an argon-filled glove box, a Pyrex glass tube (2.5 cm in diameter) equipped with a Teflon-coated stir bar, was charged with cesium carbonate (Aldrich, 1.31g, 4.0 mmol), $[Cu(phen)(PPh_3)_2]NO_3$ (10 mol% with respect to the iodophenol), and 2.0 mmol of the appropriate 2-iodophenol. The tube was then sealed with a rubber septum, taken out of the glove box and toluene (5.0 mL) and 2.00 mmol of the appropriate phenylacetylene were injected into the tube through the septum. The contents were then stirred at 110 °C for the time indicated in Table 2 and 3. The reaction

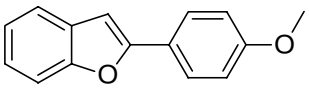
mixture was then cooled to room temperature and filtered to remove any insoluble residues. The filtrate was concentrated *in vacuo*; the residue was purified by flash column chromatography on silica gel to obtain the analytically pure product.



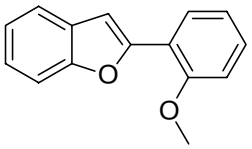
2-phenyl-benzo[*b*]furan (entry 1, Table 2): The general procedure was used to convert phenylacetylene and 2-iodophenol to the title product. Purification by flash chromatography (hexanes as the eluent) gave the analytically pure product as a white solid (358 mg, 93% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86-7.83 (dd, *J*= 6.97, 2H) 7.56-7.49 (m, 2H), 7.41-7.39 (m, 2H), 7.34-7.18 (m, 3H), 6.97 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.88, 154.86, 130.44, 129.20, 128.75, 128.51, 124.89, 124.24, 122.91, 120.89, 111.16, 101.28. Anal. Calcd. for $C_{14}H_{10}O$: C, 86.57; H, 5.19; Found C, 86.41; H, 5.34. m.p.: 120 ^{o}C (lit.,[3] 118-120 ^{o}C).



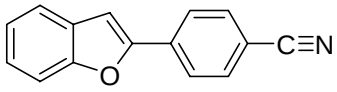
2-*p*-Tolyl-benzo[*b*]furan (entry 2, Table 2): The general procedure was used to convert 4-ethynyl-toluene and 2-iodophenol to the title product. Purification by flash chromatography (10% CH_2Cl_2 in hexanes as the eluent) gave the analytically pure product as a white solid (268 mg, 64% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J*= 8.29, 2H), 7.56-7.48 (m, 2H), 7.28-7.17 (m, 4H), 6.93 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.16, 154.75, 138.56, 132.85, 129.47, 127.73, 124.86, 123.97, 122.84, 120.72, 111.07, 100.54, 21.36. Anal. Calcd. for $C_{15}H_{12}O$: C, 86.51; H, 5.81; Found C, 86.34; H, 5.98. m.p.: 124-125 ^{o}C. (lit.,[3] 126-128 ^{o}C)



2-(4-Methoxy-phenyl)-benzo[*b*]furan (entry 3, Table 2): The general procedure was used to convert 4-ethynyl-anisole and 2-iodophenol to the title product. Purification by flash chromatography (20% ethyl acetate in hexanes as the eluent) gave the analytically pure product as a white solid (277 mg, 62% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J*= 8.48, 2H), 7.54-7.47 (m, 2H), 7.34-7.20 (m, 2H), 6.95 (d, 2H), 6.85 (s, 1H), 3.82 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.95, 156.03, 154.68, 129.49, 126.39, 123.72, 123.31, 122.81, 120.55, 114.22, 110.97, 99.65, 55.31. Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39; Found C, 80.34; H, 5.40. m.p.: 149-150 ^{o}C. (lit.,[3] 146-147 ^{o}C)

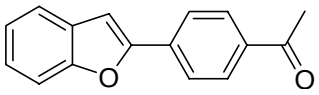


2-(2-Methoxy-phenyl)-benzo[*b*]furan (entry 4, Table 2): The general procedure was used to convert 2-ethynyl-anisole and 2-iodophenol to the title product. Purification by flash chromatography (10% ethyl acetate in hexanes as the eluent) gave the analytically pure product as a white solid (348 mg, 77% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, *J*= 7.73, 1H), 7.58 (d, *J*= 6.41, 1H), 7.48 (d, *J*= 8.10, 1H), 7.34 (s, 1H), 7.26-7.18 (m, 3H), 7.03 (t, 1H), 6.89 (d, *J*= 8.29, 1H), 3.86 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.42, 153.83, 152.15, 129.77, 129.20, 126.95, 124.08, 122.62, 121.01, 120.69, 119.25, 110.93, 110.78, 106.31, 55.87. Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39; Found C, 80.60; H, 5.65. m.p.: 76 ^{o}C.

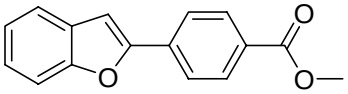


4-Benzo[*b*]furan-2-yl-benzonitrile (entry 5, Table 2): The general procedure was used to convert 4-Ethynyl-benzonitrile and 2-iodophenol to the title product. Purification by flash chromatography (20% ethyl acetate in hexanes as the eluent) gave the analytically pure product as a white solid (337 mg, 77% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J*= 8.85, 2H), 7.71 (d, *J*= 8.67, 2H), 7.62 (d, *J*= 7.54, 1H), 7.53 (d, *J*=8.10, 1H), 7.38-7.24 (m, 2H), 7.16 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.08, 153.37, 134.25, 132.45, 128.52, 125.45, 124.93, 123.34, 121.40, 118.66, 111.33, 111.28, 104.23. Anal. Calcd.

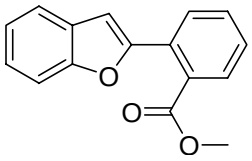
for $C_{15}H_9NO$: C, 82.18; H, 4.14; N, 6.39; Found C, 81.98; H, 4.09; N, 6.15. m.p.: 149 ^oC. (lit.,[4] 145-146 ^oC).



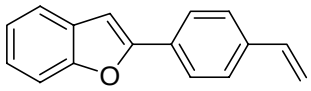
2-(4-Acetylphenyl)benzo[*b*]furan (entry 6, Table 2): The general procedure was used to convert 1-(4-Ethynyl-phenyl)-ethanone and 2-iodophenol to the title product. Purification by flash chromatography (10% ethyl acetate in hexanes as the eluent) gave the analytically pure product as a white solid (326 mg, 69% yield). ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J*= 8.67, 2H), 7.92 (d, *J*= 8.67, 2H), 7.60 (d, *J*= 7.72, 1H), 7.52 (d, *J*= 7.35, 1H), 7.35-7.22 (m, 2H), 7.14 (s, 1H), 2.62 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 197.33, 155.18, 154.50, 136.48, 134.55, 128.91, 128.87, 125.14, 124.75, 123.24, 121.32, 111.35, 103.65, 26.62. HRMS EI calcd for $C_{16}H_{12}O_2$ – 236.0837, Found – 236.0835. mp. – 168-170 ^oC (lit.,[3] 168-170 ^oC).



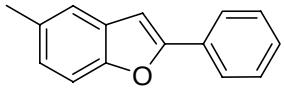
2-(4-(Methoxycarbonyl)phenyl)benzo[*b*]furan (entry 7, Table 2): The general procedure was used to convert 4-Ethynyl-benzoic acid methyl ester and 2-iodophenol to the title product. Purification by flash chromatography (10% ethyl acetate in hexanes) gave the analytically pure product as a white solid (300 mg, 67% yield). ^1H NMR δ 8.09 (dd, *J*= 8.70, 2H), 7.90 (d, *J*= 8.70, 2H), 7.52-7.62 (dd, *J*= 8.10, 2H), 7.24-7.33 (m, 2H), 7.13 (s, 1H), 3.93 (s, 3H). ^{13}C NMR δ 167.00, 155.50, 155.00, 134.80, 130.50, 130.00, 129.30, 125.40, 125.0, 123.60, 121.60, 111.70, 103.80, 52.60. Anal. Calcd. for $C_{16}H_{12}O_3$: C 76.18, H 4.79. Found C 75.97, H 4.75. m.p. 176-178 ^oC (lit.,[5] 176-177 ^oC).



2-(2-(Methoxycarbonyl)phenyl)benzo[*b*]furan (entry 8, Table 2): The general procedure was used to convert 2-Ethynyl-benzoic acid methyl ester and 2-iodophenol to the title product. Purification by flash chromatography (10% ethyl acetate in hexanes) gave the analytically pure product as an oil (458 mg, 67% yield). ^{1}H NMR δ 7.75-7.70 (m, 2H), 7.61-7.40 (m, 4H), 7.31-7.22 (m, 2H), 6.92 (s, 1H), 3.81 (s, 3H). ^{13}C NMR δ 169.35, 155.10, 154.67, 131.09, 130.94, 129.61, 129.36, 128.99, 128.88, 128.64, 124.54, 122.94, 121.21, 111.09, 104.38, 52.48. Anal. Calcd. for $C_{16}H_{12}O_3$: C 76.18, H 4.79. Found C 75.95, H 4.75.

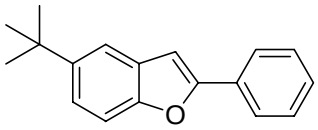


2-(4-Vinyl-phenyl)-benzo[*b*]furan (entry 9, Table 2): The general procedure was used to convert 1-Ethynyl-4-vinyl-benzene and 2-iodophenol to the title product. Purification by flash chromatography (hexanes as the eluent) gave the analytically pure product as a white solid (300 mg, 68% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J*= 8.45, 2H), 7.56-7.44 (m, 4H), 7.29-7.19 (m, 2H), 6.98 (s, 1H), 6.74 (dd, *J*=10.93 and *J*=6.59, 1H), 5.78 (d, *J*= 17.71, 1H), 5.28 (d, *J*= 10.93, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.66, 154.87, 137.69, 136.26, 129.75, 129.22, 126.61, 125.02, 124.28, 122.94, 120.87, 114.40, 111.13, 101.37. Anal. Calcd. for $C_{16}H_{12}O$: C, 87.25; H, 5.49; Found C, 87.54; H, 5.62. m.p.: 164-165 ^{o}C.

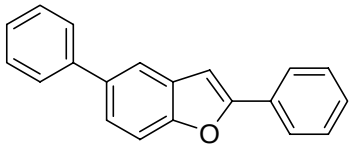


5-Methyl-2-phenyl-benzo[*b*]furan (entry 1, Table 3): The general procedure was used to convert phenylacetylene and 4-methyl-2-iodophenol to the title product. Purification by flash chromatography (hexanes as the eluent) gave the analytically pure product as a white solid (353 mg, 85% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J*=7.16, 2H), 7.41-7.30 (m, 5H), 7.06 (d, *J*= 7.35, 1H), 6.88 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.92, 153.29, 132.2, 130.57, 129.27, 128.70, 128.35, 125.49, 124.79, 120.70,

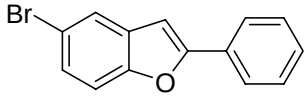
110.61, 101.06, 21.30. Anal. Calcd. for $C_{15}H_{12}O$: C, 86.51; H, 5.81; Found C, 86.28; H, 5.90. m.p.: 131 ^{o}C. (lit.,[6] 131-133 ^{o}C).



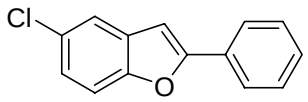
5-*tert*-Butyl-2-phenyl-benzo[*b*]furan (entry 2, Table 3): The general procedure was used to convert phenylacetylene and 4-*tert*-Butyl-2-iodophenol to the title product. Purification by flash chromatography (10% ethyl acetate in hexanes as the eluent) gave the analytically pure product as a white solid (398 mg, 80% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (dd, *J*=7.16, 2H), 7.57-7.56 (m, 1H), 7.44-7.38 (m, 3H), 7.34-7.30 (m, 2H), 6.96 (s, 1H), 1.38 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.99, 153.12, 145.92, 130.65, 128.88, 128.72, 128.33, 124.82, 122.23, 117.06, 110.42, 101.48, 34.68, 31.83. Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25; Found C, 86.34; H, 7.13. m.p.: 103-104 ^{o}C. (lit.,[7] 102-103 ^{o}C).



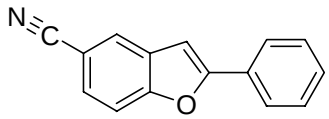
2,5-Diphenyl-benzo[*b*]furan (entry 3, Table 3): The general procedure was used to convert phenylacetylene and 4-phenyl-2-iodophenol to the title product. Purification by flash chromatography (10% CH_2Cl_2 in hexanes as the eluent) gave the analytically pure product as a white solid (427 mg, 79% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J*= 7.53, 2H), 7.78-7.75 (m, 1H), 7.67-7.33 (m, 10H), 7.07 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.56, 154.49, 141.63, 136.61, 130.37, 129.74, 128.79, 128.73, 128.62, 127.41, 126.86, 124.93, 123.98, 119.36, 111.25, 101.45. Anal. Calcd. For $C_{20}H_{14}O$: C, 88.86; H, 5.22; Found C, 88.99; H, 5.28. m.p.: 166-167 ^{o}C. (lit.,[8] 166-168 ^{o}C).



5-Bromo-2-phenyl-benzo[*b*]furan (entry 4, Table 3): The general procedure was used to convert phenylacetylene and 4-bromo-2-iodophenol to the title product. Purification by flash chromatography (20% CH_2Cl_2 in hexanes as the eluent) gave the analytically pure product as a white solid (468 mg, 86% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J*= 6.97, 2H), 7.69-7.67 (m, 1H), 7.46-7.35 (m, 5H), 6.91 (s, 1H).^{13}C NMR (75 MHz, $CDCl_3$) δ 157.18, 153.56, 131.17, 129.85, 128.97, 128.82, 127.04, 125.02, 123.43, 115.95, 112.56, 100.58. Anal. Calcd. for $C_{14}H_9BrO$: C, 61.57; H, 3.32; Br, 29.26; Found C, 61.46; H, 3.26; Br, 29.50. m.p.: 157 ^{o}C. (lit.,[9], 158-159 ^{o}C).



5-Chloro-2-phenyl-benzo[*b*]furan (entry 5, Table 3): The general procedure was used to convert phenylacetylene and 4-chloro-2-iodophenol to the title product. Purification by flash chromatography (10% CH_2Cl_2 in hexanes as the eluent) gave the analytically pure product as a white solid (411 mg, 90% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, *J*= 6.97, 2H), 7.52 (d, *J*= 2.26, 1H), 7.46-7.35 (m, 4H), 7.21 (dd, *J*= 6.59, 1H), 6.93 (s, 1H).^{13}C NMR (75 MHz, $CDCl_3$) δ 157.36, 153.22, 130.56, 129.93, 128.98, 128.84, 128.46, 125.03, 124.37, 120.40, 112.10, 100.78. Anal. Calcd. for $C_{14}H_9ClO$: C, 73.53; H, 3.97; Cl, 15.50; Found C, 73.31; H, 3.99; Cl, 15.68. m.p.: 155.5-157 ^{o}C. (lit.,[10] 156 ^{o}C).



5-Cyano-2-phenyl-benzo[*b*]furan (entry 6, Table 3): The general procedure was used to convert phenylacetylene and 4-cyano-2-iodophenol to the title product. Purification by flash chromatography (15% ethyl acetate in hexanes as the eluent) gave the analytically pure product as a white solid (421 mg, 96% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88-7.82 (m, 3H), 7.58-7.40 (m, 5H), 7.01 (s, 1H).^{13}C NMR (75 MHz, $CDCl_3$) δ 158.30, 156.41, 129.85, 129.55, 129.23, 128.98, 127.84, 125.72, 125.22, 119.49, 112.25, 106.85, 100.72. Anal. Calcd. for $C_{15}H_9NO$: C, 82.18; H, 4.14; N, 6.39; Found C, 82.04; H, 4.21; N, 6.21. m.p.: 143-145 ^{o}C.

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