Ni-NHC-catalyzed Cross-coupling of 2-Methylsulfanylbenzofurans with Alkyl Grignard Reagents

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1. General Remarks

1H and 13C NMR spectra were recorded on a JEOL delta-600 spectrometer, and chemical shifts are reported as the δ scale in ppm relative to an internal standard (CHCl3: δ = 7.26 ppm for 1H, CDCl3: 77.16 ppm for 13C). Spectroscopic grade solvents were used for all spectroscopic studies without further purification. The terms m, s, d, t, q, quint., sex., dd and td represent multiplet, singlet, doublet, triplet, quartet, quintet, sextet, doublet of doublets and triplet of doublets respectively. Coupling constants (J) are given in hertz (Hz). Otherwise noted, NMR spectra were recorded in CDCl3 at 300 K.

ESI-TOF-MS spectra were recorded on a Bruker Daltonics micrOTOF II LC instrument using a positive-ion mode. Melting points were measured with a Stanford Research System MPA100 instrument.

IR spectra were recorded with a Thermo Fischer Scientific, Nicolet iS5 model instrument. IR was reported as characteristic bands (cm⁻¹).

Thin layer chromatography (TLC) was performed on silica gel Merck 60F 254. Preparative separations were performed by silica gel chromatography (Wako gel C-300).

Materials obtained from commercial suppliers were used without further purification. NiCl2(IPr)(PPh3) (CAS = 903592-98-3) was purchased from TCI.

Toluene was distilled over CaH2 and kept in a Schlenck tube on molecular sieves (4Å). THF (Kanto Chemicals Co. Inc.) was purified on Glass Counter Ultra Solvent Purifier.

All reactions were carried out under argon atmosphere.

2. Synthesis and Characterization of KDMs.

KDMs were synthesized according to the procedure 1.

**Methyl[(E)-1-(methylsulfinyl)-2-phenylvinyl]sulfane (Method A):**

\[
\begin{align*}
\text{H-NMR (600 MHz, CDCl}_3) \delta (ppm) & \quad 7.89 (d, 2H, J = 7.8 \text{ Hz}), 7.63 (s, 1H), 7.22 (t, 2H, J = 7.2 \text{ Hz}), 7.37 (t, 1H, J = 7.2 \text{ Hz}), 2.77 (s, 3H), 2.31 (s, 3H).
\end{align*}
\]

**Methyl[1-(methylsulfinyl)vinyl]sulfane² (Method C):**

\[
\begin{align*}
\text{H-NMR (600 MHz, CDCl}_3) \delta (ppm) & \quad 6.21 (s, 1H), 5.67 (s, 1H), 2.72 (s, 3H), 2.41 (s, 3H).
\end{align*}
\]

**[(E)-2-(4’-methoxy-1,1’-biphenyl-4-yl)-1-(methylsulfinyl)vinyl]methylsulfane (3) (Method A):**

\[
\begin{align*}
\text{C-NMR (151 MHz, CDCl}_3) \delta (ppm) & \quad 159.73, 142.06, 139.94, 135.92, 132.74, 132.00, 130.61, 128.22, 126.82, 114.49, 55.49, 40.45, 18.38.
\end{align*}
\]

FTIR (cm⁻¹) ν 1062, 1034, 814, 577.

HRMS (ESI) calcld for C17H18O2S2H ([M+H]+): 319.0821; found 319.0808.

mp = 139-141°C. Pale yellow solid, n-Hex./AcOEt (1/0.75), 56% (15 mmol scale).

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In a flame-dried Schlenk tube equipped with a magnetic stir bar were introduced phenol derivative (1 equiv.), KDM (1.2 equiv.) and DCM (1 mL/1 mmol of phenol). The mixture was then stirred at 0 °C for 10 min. TFAA (1 equiv.) was added dropwise at 0 °C. After the addition of TFAA, the mixture was stirred for 1 h at room temperature. The resulting mixture was filtered through a pad of alumina and the filtrate was concentrated under vacuum. The desired benzofuran was obtained after purification by flash chromatography.

\[
\text{2-(methylsulfanyl)-3-phenylbenzofuran (1a):}
\]

\[
\begin{align*}
\text{\(\delta\) (ppm) 7.64 (m, 3H), 7.52 (m, 3H), 7.41 (d, 1H, } J = 7.8 \text{ Hz), 7.33 (t, 1H, } J = 7.2 \text{ Hz), 7.27 (t, 1H, } J = 7.2 \text{ Hz), 2.55 (s, 3H).} \\
\text{\(\delta\) (ppm) 75.68, 147.65, 131.98, 129.25, 128.72, 128.50, 127.66, 124.64, 123.17, 122.74, 119.91, 111.06, 17.13.} \\
\text{FTIR (cm\(^{-1}\)) } \nu = 1444, 1120, 1090, 963, 768, 697, 564. \\
\text{HRMS (ESI) calcd for C\(_{15}\)H\(_{12}\)OS ([M]+): 240.0609; found 240.0620.}
\end{align*}
\]

\[
\text{Colorless oil, n-Hex./DCM (5/1), } 80\% \text{ (6 mmol scale).}
\]

\[
\text{5-methoxy-2-(methylsulfanyl)-3-phenylbenzofuran}\(^3\) (1b):
\]

\[
\begin{align*}
\text{\(\delta\) (ppm) 7.60 (d, 2H, } J = 8.4 \text{ Hz), 7.51 (t, 2H, } J = 7.8 \text{ Hz), 7.41-7.37 (m, 2H), 7.05 (d, 1H, } J = 3.0 \text{ Hz), 6.92 (dd, 1H, } J = 9.0 \text{ Hz, } J = 3.0 \text{ Hz), 3.83 (s, 3H).} \\
\text{\(\delta\) (ppm) 156.41, 150.69, 148.37, 132.08, 129.16, 129.02, 128.78, 127.63, 122.78, 113.27, 113.27, 111.53, 102.39, 56.12, 17.09.} \\
\text{Colorless oil, n-Hex./DCM (5/1), } 60\% \text{ (10 mmol scale).}
\end{align*}
\]

\[
\text{2-(methylsulfanyl)-3-phenyl-5-(trifluoromethyl)benzofuran}\(^3\) (1c):
\]

\[
\begin{align*}
\text{\(\delta\) (ppm) 7.89 (s, 1H), 7.60-7.57 (m, 4H), 7.54 (t, 2H, } J = 7.8 \text{ Hz), 7.43 (t, 1H, } J = 7.2 \text{ Hz), 2.57 (s, 3H).} \\
\text{\(\delta\) (ppm) 156.93, 150.06, 131.03, 129.13, 129.00, 128.79, 128.12, 125.99 (q, } J = 31.6 \text{ Hz), 124.72 (q, } J = 270.0 \text{ Hz), 122.32, 121.62, 117.45, 111.40, 16.73.} \\
\text{Colorless oil, n-Hex./DCM (5/1), } 64\% \text{ (6 mmol scale).}
\end{align*}
\]

\[
\text{2-(methylsulfanyl)benzofuran}\(^4\) (1i):
\]

\[
\begin{align*}
\text{\(\delta\) (ppm) 7.49 (d, 1H, } J = 7.8 \text{ Hz), 7.44 (d, 1H, } J = 7.8 \text{ Hz), 7.25 (t, 1H, } J = 7.2 \text{ Hz), 7.21 (t, 1H, } J = 7.2 \text{ Hz), 6.69 (s, 1H), 2.55 (s, 3H).} \\
\text{\(\delta\) (ppm) 156.21, 152.40, 128.86, 124.08, 122.99, 120.22, 110.88, 107.96, 17.17.} \\
\text{Light yellow oil, n-Hex., } 25\% \text{ (6 mmol scale).}
\end{align*}
\]


3-(4'-methoxy-1,1'-biphenyl-4-yl)-2-(methylsulfanyl)benzofuran\(^5\) (4):

\(^{1}\)H-NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.70-7.66 (m, 5H), 7.61-7.60 (d, 2H, \(J = 7.2\) Hz), 7.50 (d, 1H, \(J = 7.8\) Hz), 7.32 (t, 1H, \(J = 7.2\) Hz), 7.01 (d, 2H, \(J = 9.0\) Hz), 3.87 (s, 3H), 2.87 (s, 3H).

\(^{13}\)C-NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm) 159.44, 155.74, 147.64, 140.10, 133.41, 130.31, 129.56, 128.51, 128.25, 126.00, 124.67, 123.21, 122.43, 119.99, 114.45, 111.10, 55.50, 17.18.

FTIR (cm\(^{-1}\)) \(\nu\) 1594, 1446, 1256, 1037, 819, 807, 735.

HRMS (ESI) calc for C\(_{22}\)H\(_{18}\)O\(_2\)SH ([M+H\(^+\)]): 347.1100; found 347.1084.

mp = 155-157°C. White solid, n-Hex./DCM (5/2), 61% (2 mmol scale).

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**General procedure for cross-coupling reactions:**

Reactions were carried in THF at room temperature unless stated.

In a flame-dried Schlenk tube equipped with a magnetic stir bar and a rubber septum were introduced NiCl\(_2\)(IPr)(PPh\(_3\)) (11.7 mg, 0.015 mmol, 3 mol%) and a solution of the desired benzofuran (0.5 mmol, 1 equiv. in 5 mL distilled THF). To the mixture was then added dropwise \(n\-)butylmagnesium bromide (0.6 mmol, 1.2 equiv., 0.6 M in THF). The reaction mixture was stired at room temperature until completion of the reaction (checked by TLC). The crude mixture was then filtered through a pad of silica gel (DCM). The desired benzofuran was obtained after purification by flash chromatography.

### 2-butyl-3-phenylbenzofuran (2a):

\(^{1}\)H-NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.60 (d, 1H, \(J = 7.8\) Hz), 7.54-7.50 (m, 5H), 7.40 (t, 1H, \(J = 6.6\) Hz), 7.30 (t, 1H, \(J = 6.6\) Hz), 2.90 (t, 2H, \(J = 7.8\) Hz), 1.81 (quint., 2H, \(J = 7.2\) Hz), 1.44 (sex., 2H, \(J = 7.2\) Hz), 0.95 (t, 3H, \(J = 7.2\) Hz).

\(^{13}\)C-NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm) 155.46, 154.18, 133.07, 129.25, 129.06, 128.86, 127.12, 123.66, 122.68, 119.57, 116.93, 110.97, 30.68, 26.66, 22.61, 13.95.

FTIR (cm\(^{-1}\)) \(\nu\) 2956, 2928, 2871, 1610, 1496, 1454, 1255, 1219, 1174, 1012, 969, 769, 700.

HRMS (ESI) calc for C\(_{18}\)H\(_{18}\)O\(_2\)H ([M+H\(^+\)]): 251.1430; found 251.1427.

Colorless oil, \(n\-)Hex., 97% (0.5 mmol scale).

### 2-butyl-5-methoxy-3-phenylbenzofuran (2b):

\(^{1}\)H-NMR (600 MHz, CDCl\(_3\)) \(\delta\) (ppm) 7.51-7.47 (m, 4H), 7.39-7.35 (m, 2H), 7.01 (d, 1H, \(J = 3.0\) Hz), 6.87 (dd, 1H, \(J = 8.4\) Hz, \(J = 2.4\) Hz), 3.82 (s, 3H), 2.84 (t, 2H, \(J = 7.8\) Hz), 1.76 (quint., 2H, \(J = 7.2\) Hz), 1.39 (sex., 2H, \(J = 7.2\) Hz), 0.91 (t, 3H, \(J = 7.2\) Hz).

\(^{13}\)C-NMR (150 MHz, CDCl\(_3\)) \(\delta\) (ppm) 156.41, 154.18, 133.07, 129.25, 129.06, 128.86, 127.12, 123.66, 122.68, 119.57, 116.93, 110.97, 30.68, 26.66, 22.61, 13.95.

FTIR (cm\(^{-1}\)) \(\nu\) 2956, 2929, 2871, 1610, 1496, 1454, 1255, 1219, 1174, 1012, 969, 769, 700.

HRMS (ESI) calc for C\(_{19}\)H\(_{20}\)O\(_2\)H ([M+H\(^+\)]): 281.1536; found 281.1538.

Colorless oil, \(n\-)Hex./DCM (15/1), 97% (0.5 mmol scale).

---

2-butyl-3-phenyl-5-(trifluoromethyl)benzofuran (2c):

$^1$H-NMR (600 MHz, CDCl$_3$) $\delta$ (ppm) 7.82 (s, 1H), 7.54-7.47 (m, 6H), 7.42 (td, 1H, $J = 7.8$ Hz, $J = 1.8$ Hz), 2.89 (t, 2H, $J = 7.2$ Hz), 1.78 (quint., 2H, $J = 7.8$ Hz), 1.41 (sex., 2H, $J = 7.8$ Hz), 0.93 (t, 3H, $J = 7.2$ Hz).

$^{13}$C-NMR (150 MHz, CDCl$_3$) $\delta$ (ppm) 157.44, 155.59, 132.01, 129.29, 129.21, 129.11, 127.66, 125.47 (q., $J = 31.6$ Hz), 124.94 (q., $J = 270$ Hz), 120.86, 117.26, 111.30, 30.50, 26.64, 22.57, 13.89.

FTIR (cm$^{-1}$) $\nu$ 2959, 2931, 1453, 1596, 1441, 1531, 1316, 1270, 1161, 1118, 1054, 815, 753, 700, 643.

HRMS (ESI) calcd for C$_{19}$H$_{17}$F$_3$OH ([M+H]$^+$): 319.1304; found 319.1296.

Colorless oil, n-Hex, 93% (0.5 mmol scale).

2-methyl-3-phenylbenzofuran (2d):

$^1$H-NMR (600 MHz, CDCl$_3$) $\delta$ (ppm) 7.58 (d, 1H, $J = 7.2$ Hz), 7.52-7.45 (m, 5H), 7.37 (t, 1H, $J = 8.4$ Hz), 7.26 (t, 1H, $J = 7.2$ Hz), 7.22 (t, 1H, $J = 7.8$ Hz), 2.55 (s, 3H).

$^{13}$C-NMR (150 MHz, CDCl$_3$) $\delta$ (ppm) 154.18, 151.44, 133.01, 129.08, 128.89 (2C merged), 127.09, 123.69, 122.76, 119.48, 117.06, 110.90, 12.96. Colorless oil, n-Hex, 100% (0.5 mmol scale).

2-benzyl-3-phenylbenzofuran (2e):

Reaction carried out at 50 °C in Toluene for 4 h with 5 equiv. of Grignard reagent.

$^1$H-NMR (600 MHz, CDCl$_3$) $\delta$ (ppm) 7.63 (d, 1H, $J = 6.6$ Hz), 7.56 (d, 2H, $J = 8.4$ Hz), 7.52-7.49 (m, 3H), 7.41 (t, 1H, $J = 7.2$ Hz), 7.35-7.25 (m, 7H), 4.25 (s, 2H).

$^{13}$C-NMR (150 MHz, CDCl$_3$) $\delta$ (ppm) 154.50, 152.69, 138.05, 132.63, 129.21, 128.98, 128.81, 128.76, 128.63, 127.45, 126.72, 124.11, 122.85, 119.88, 118.42, 111.27, 33.01.

FTIR (cm$^{-1}$) $\nu$ 3029, 1602, 1494, 1453, 1258, 1223, 1174, 1012, 977, 771, 698.

HRMS (ESI) calcd for C$_{21}$H$_{16}$O ([M]+): 284.1201; found 284.1203.

Pale yellow oil, n-Hex/AcOEt (100/1), 95% (0.5 mmol scale).

3-phenyl-2-(undec-10-en-1-yl)benzofuran (2f):

$^1$H-NMR (600 MHz, CDCl$_3$) $\delta$ (ppm) 7.57 (d, 1H, $J = 7.8$ Hz), 7.50-7.47 (m, 5H), 7.39-7.37 (m, 1H), 7.26 (t, 1H, $J = 6.6$ Hz), 5.83 (m, 1H), 4.99 (d, 1H, $J = 17.4$ Hz), 4.93 (d, 1H, $J = 10.2$ Hz), 2.85 (t, 2H, $J = 8.4$ Hz), 2.05 (q, 2H, $J = 6.6$ Hz), 1.79 (quint., 2H, $J = 7.8$ Hz), 1.33-1.24 (m, 8H).

$^{13}$C-NMR (150 MHz, CDCl$_3$) $\delta$ (ppm) 155.48, 154.17, 139.38, 133.07, 129.24, 129.05, 128.86, 127.12, 123.66, 122.67, 119.58, 116.93, 114.26, 110.97, 33.95, 29.58 (2C merged), 29.43 (2C merged), 29.25, 29.07, 28.52, 26.90.

FTIR (cm$^{-1}$) $\nu$ 2923, 2852, 1497, 1454, 1175, 1012, 969, 908, 769, 745, 699.

HRMS (ESI) calcd for C$_{25}$H$_{30}$O ([M]+): 346.2297; found 346.2294.

Colorless oil, n-Hex, 93% (0.5 mmol scale).

Trimethyl[(3-phenylbenzofuran-2-yl)methyl]silane (2g):

Reaction carried out at 50 °C in toluene for 24 h with 5 equiv. of Grignard reagent.

$^1$H-NMR (600 MHz, CDCl$_3$) $\delta$ (ppm) 7.52-7.42 (m, 5H), 7.43 (m, 1H), 7.34-7.37 (m, 1H), 7.26 (t, 1H, $J = 8.4$ Hz), 7.21 (t, 1H, $J = 6.6$ Hz), 5.83 (m, 1H), 4.99 (d, 1H, $J = 17.4$ Hz), 4.93 (d, 1H, $J = 10.2$ Hz), 2.85 (t, 2H, $J = 8.4$ Hz), 2.05 (q, 2H, $J = 6.6$ Hz), 1.79 (quint., 2H, $J = 7.8$ Hz), 1.33-1.24 (m, 8H).

$^{13}$C-NMR (150 MHz, CDCl$_3$) $\delta$ (ppm) 155.48, 154.17, 139.38, 133.07, 129.24, 129.05, 128.86, 127.12, 123.66, 122.67, 119.58, 116.93, 114.26, 110.97, 33.95, 29.58 (2C merged), 29.43 (2C merged), 29.25, 29.07, 28.52, 26.90.

FTIR (cm$^{-1}$) $\nu$ 2954, 1607, 1593, 1455, 1365, 1249, 1216, 1180, 1012, 968, 772, 747, 701.

HRMS (ESI) calcd for C$_{18}$H$_{20}$O$_2$SiH ([M+H]$^+$): 281.1356; found 281.1360.

Colorless oil, n-Hex, 65% (0.5 mmol scale).

---

3-phenyl-2-(11-((tetrahydro-2H-pyran-2-yl)oxy)undecyl)benzofuran (2h):

\[
\text{\textsuperscript{1}H-NMR (600 MHz, CDCl}_3\text{)} \delta (ppm) 7.55 (d, 1H, J = 7.8 Hz), 7.49-7.46 (m, 5H), 7.38-7.35 (m, 1H), 7.27-7.25 (m, 1H), 7.21 (t, 1H, J = 7.8 Hz), 4.58 (t, 1H, J = 2.4 Hz), 3.89-3.85 (m, 1H), 3.75-3.71 (m, 1H), 3.52-3.50 (m, 1H), 3.40-3.36 (m, 1H), 2.85 (t, 2H, J = 7.8 Hz), 1.84-1.69 (m, 4H), 1.60-1.51 (m, 7H), 1.35-1.24 (m, 13H).
\]

\[
\text{\textsuperscript{13}C-NMR (150 MHz, CDCl}_3\text{)} \delta (ppm) 155.48, 154.15, 133.05, 129.23, 129.03, 128.85, 127.11, 123.64, 122.65, 119.56, 116.90, 110.96, 98.99, 67.84, 62.48, 30.94, 29.91, 29.69 (2C merge), 29.62 (2C merge), 29.44 (2C merge), 28.52, 26.90, 26.39, 25.66, 19.85.
\]

\[
\text{FTIR (cm}^{-1}\text{)} \nu 2923, 2852, 1455, 1200, 1175, 1135, 1119, 1076, 1032, 969, 770, 700.
\]

\[
\text{HRMS (ESI) calcd for C}_{30}\text{H}_{40}\text{O}_3 ([M] \cdot) : 448.2977; found 448.2996.}
\]

Colorless oil, n-Hex /AcOEt (50/1), 94% (0.5 mmol scale).

2-butylbenzofuran\(^7\) (2i):

\[
\text{\textsuperscript{1}H-NMR (600 MHz, CDCl}_3\text{)} \delta (ppm) 7.50 (d, 1H, J = 7.8 Hz), 7.44 (d, 1H, J = 7.8 Hz), 7.23-7.18 (m, 2H), 6.39 (s, 1H), 2.79 (t, 2H, J = 7.2 Hz), 1.76 (quint., 2H, J = 7.8 Hz), 1.46 (sex., 2H, J = 7.2 Hz), 0.99 (t, 3H, J = 7.8 Hz).
\]

\[
\text{\textsuperscript{13}C-NMR (150 MHz, CDCl}_3\text{)} \delta (ppm) 159.88, 154.77, 129.18, 123.14, 122.49, 120.28, 110.83, 101.87, 29.94, 28.28, 22.42, 13.93.
\]

Colorless oil, n-Hex, 94% (0.5 mmol scale).

2-cyclohexyl-3-benzofuran (2j):

\[
\text{6 mol\% catalyst loading, 1 equiv. of Grignard reagent added at t = 0 min, 30 min, 2h, 4h and reaction was stirred for two more hours after last addition.}
\]

\[
\text{\textsuperscript{1}H-NMR (600 MHz, CDCl}_3\text{)} \delta (ppm) 7.53 (d, 1H, J = 7.8 Hz), 7.50-7.46 (m, 4H), 7.39-7.36 (t, 1H, J = 7.2 Hz), 7.26 (t, 2H, J = 7.2 Hz), 7.20 (t, 1H, J = 7.8 Hz), 2.93 (td, 1H, J = 11.4 Hz, J = 3.0 Hz), 1.89-1.73 (m, 7H), 1.37-1.29 (m, 3H).
\]

\[
\text{\textsuperscript{13}C-NMR (150 MHz, CDCl}_3\text{)} \delta (ppm) 159.21, 154.00, 133.16, 129.38, 129.12, 128.87, 127.10, 123.59, 122.60, 119.61, 115.42, 111.02, 34.43, 31.84, 26.40, 26.00.
\]

\[
\text{FTIR (cm}^{-1}\text{)} \nu 2927, 2852, 1454, 1257, 1234, 1191, 1178, 1011, 967, 771, 745, 699.
\]

\[
\text{HRMS (ESI) calcd for C}_{20}\text{H}_{20}\text{O ([M] \cdot) : 276.1509; found 276.1517.}
\]

Colorless oil, n-Hex, 65% (0.5 mmol scale).

2-butyl-3-(4'-methoxy-1,1'-biphenyl-4-yl)benzofuran\(^4\) (5a):

\[
\text{\textsuperscript{1}H-NMR (600 MHz, CDCl}_3\text{)} \delta (ppm) 7.68 (d, 2H, J = 7.8 Hz), 7.62-7.60 (m, 3H), 7.55 (d, 2H, J = 7.2 Hz), 7.48 (d, 1H, J = 8.4 Hz), 7.28 (t, 1H, J = 7.8 Hz), 7.24 (t, 1H, J = 7.8 Hz), 7.02 (d, 2H, J = 8.4 Hz), 3.88 (s, 3H), 2.91 (t, 2H, J = 7.8 Hz), 1.80 (quint., 2H, J = 7.8 Hz), 1.43 (sex., 2H, J = 7.2 Hz), 0.94 (t, 3H, J = 7.2 Hz).
\]

\[
\text{\textsuperscript{13}C-NMR (150 MHz, CDCl}_3\text{)} \delta (ppm) 159.38, 155.50, 154.21, 139.52, 133.42, 131.39, 129.52, 129.03, 128.16, 127.08, 123.67, 122.69, 119.62, 116.57, 114.43, 110.97, 55.44, 30.68, 26.76, 22.64, 13.96.
\]

\[
\text{mp = 89-91°C. White solid, n-Hex./DCM (5/2), 95% (0.5 mmol scale).}
\]

2-benzyl-3-(4’-methoxy-1,1’-biphenyl-4-yl)benzofuran\(^4\) (5b):

Reaction carried out at 50 °C in toluene for 4 h with 5 equiv. of Grignard reagent.

\( ^1\text{H-NMR (600 MHz, CDCl}_3 \) δ (ppm) 7.68 (d, 2H, \( J = 7.8 \) Hz), 7.65 (d, 1H, \( J = 7.8 \)Hz), 7.61-7.58 (m, 4H), 7.48 (d, 1H, \( J = 7.8 \) Hz), 7.34-7.23 (m, 7H), 7.02 (d, 2H, \( J = 9.0 \) Hz), 4.26 (s, 2H), 3.88 (s, 3H).

\( ^1^\text{C-NMR (150 MHz, CDCl}_3 \) δ (ppm) 159.43, 154.54, 152.73, 139.88, 138.08, 133.38, 130.97, 129.52, 128.80 (2C merged), 128.65, 128.21, 127.22, 126.74, 124.13, 122.88, 119.94, 118.12, 114.46, 111.30, 55.51, 33.12.

\textit{mp} = 120-122°C. White solid, n-Hex./DCM (5/2), \textit{99}\% (0.5 mmol scale).
5. $^1$H-NMR and $^{13}$C-NMR.

5.a. KDMs
5.b. Benzofurans (Starting material).
5.c. Cross coupling products
<table>
<thead>
<tr>
<th>X</th>
<th>Parts per Million</th>
<th>1H</th>
<th>13C</th>
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**Graph 1:**
- X-axis: Parts per Million
- Y-axis: Abundance

**Graph 2:**
- X-axis: Parts per Million
- Y-axis: Abundance

**Chemical Structure 2d:**
- Molecular formula: C22H18O2
- Functional groups: Furan, Benzene
- Important peaks:
  - 7.90 ppm (1H)
  - 7.54 ppm (1H)
  - 7.51 ppm (1H)
  - 7.49 ppm (1H)

**Chemical Structure 2d:**
- Molecular formula: C22H18O2
- Functional groups: Furan, Benzene
- Important peaks:
  - 5.81 ppm (1H)
  - 3.67 ppm (1H)
  - 2.97 ppm (1H)
  - 1.10 ppm (1H)