Supporting Information

**General information.** All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. THF was dried over alumina under N₂ using a Grubbs-type solvent purification system. All arylmagnesium bromides were prepared from the corresponding aryl bromides and magnesium (turnings) using diisobutylaluminum hydride for activation.¹ All aryl tosylates² and aryl chlorides³ were prepared according to the literature procedures. Yields refer to chromatographically and spectroscopically (1H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by Agilent GC Series 6890N and GCMS 7890A. Merck silica gel plates (60F-254) using UV light as visualizing agent. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. NMR spectra were recorded on Bruker DRX-400 calibrated using residual deuterated solvent (CDCl₃: δH = 7.26 ppm, δC = 77.10 ppm) as an internal reference. The following abbreviations were used to designate the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, br = broad. Infrared (IR) spectra were recorded on a Perkin–Elmer Spectrum 100 FT-IR spectrometer. High resolution mass spectra (HRMS) were recorded on an Agilent 6210 Series 1969A ESI-TOF (time of flight) mass spectrometer using EI (electron ionization) or ESI (electrospray ionization).

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Procedure for the reduction of iron salts with 2a:

In a glovebox, a mixture of Fe(OTf)$_2$ (0.1 mmol), SIPr (0.1 mmol) and dodecane (0.1 mmol) in THF was stirred at rt for 5min. $p$-tolylmagnesium bromide 2a (1.0 mmol) was added and the mixture was heated at 60 °C for the specified time. The yield of 3a’ was determined by GC analysis.

Synthesis and Characterization of Fe-catalyzed Biaryl Cross-coupling Reaction

General Procedure A1 (GPA1) for Iron-catalyzed Biaryl Cross-coupling Reaction of Aryl Chlorides:

In a glovebox, Fe(OTf)$_2$ (5.3 mg, 0.015 mmol, 3 mol%), SIPr$\cdot$HCl (6.4 mg, 0.015 mmol, 3 mol%) and NaO$\cdot$Bu (1.4 mg, 0.015 mmol, 3 mol%) in THF (0.5 mL) were charged to a dried reaction tube. The mixture was allowed to stir at rt for 1 h before a solution of aryl chloride (0.5 mmol, 1.0 eq) and Grignard reagent (0.6 mmol, 1.2 eq) was added. The tube was sealed, taken out of the glovebox and stirred at 60 °C for 16h. The reaction progress was monitored by GC using dodecane as the internal standard. Once completed, the reaction mixture was quenched with saturated NH$_4$Cl and extracted with CH$_2$Cl$_2$ several times. The combined organic layers were dried over anhydrous MgSO$_4$, concentrated in vacuo and the resulting crude mixture was purified by silica gel column chromatography.

General Procedure A2 (GPA2) for Iron-catalyzed Biaryl Cross-coupling Reaction of Aryl Chlorides:

Procedure is similar to GPA1 except for Fe(OTf)$_2$ (5.3 mg, 0.015 mmol, 3 mol%), SIPr$\cdot$HCl (19 mg, 0.045 mmol, 9 mol%) and NaO$\cdot$Bu (4.3 mg, 0.045 mmol, 9 mol%) were used.

General Procedure B (GPB) for Iron-catalyzed Biaryl Cross-coupling Reaction of Aryl Chlorides:
In a glovebox, Fe(OTf)$_2$ (5.3 mg, 0.015 mmol, 0.5 mol%) and NaOH$_2$Bu (4.3 mg, 0.045 mmol, 1.5 mol%) in THF (0.5 mL) were charge to a dried reaction tube. The mixture was allowed to stir at rt for 1 h before a solution of aryl chloride (3.0 mmol, 1.0 eq) and Grignard reagent (3.6 mmol, 1.2 eq) was added. The tube was sealed, taken out of the glovebox and stirred at 60 °C for 16h. The reaction progress was monitored by GC using dodecane as the internal standard. Once completed, the reaction mixture was quenched with saturated NH$_4$Cl and extracted with CH$_2$Cl$_2$ several times. The combined organic layers were dried over anhydrous MgSO$_4$, concentrated in vacuo and the resulting crude mixture was purified by silica gel column chromatography.

**General Procedure C (GPC) for Iron-catalyzed Biaryl Cross-coupling Reaction of Aryl Chlorides:**

In a glovebox, Fe(OTf)$_2$ (5.3 mg, 0.015 mmol, 3 mol%) and SPr (5.9 mg, 0.015 mmol, 3 mol% ) in THF (0.5 mL) were charge to a dried reaction tube. The mixture was allowed to stir at rt for 30 mins before a solution of aryl chloride (0.5 mmol, 1.0 eq) and Grignard reagent (0.6 mmol, 1.2 eq) was added. The tube was sealed, taken out of the glovebox and stirred at 60 °C for 16h. The reaction progress was monitored by GC using dodecane as the internal standard. Once completed, the reaction mixture was quenched with saturated NH$_4$Cl and extracted with CH$_2$Cl$_2$ several times. The combined organic layers were dried over anhydrous MgSO$_4$, concentrated in vacuo and the resulting crude mixture was purified by silica gel column chromatography.

**General Procedure D1 (GPD1) for Iron-catalyzed Biaryl Cross-coupling Reaction of Aryl Tosylates:**

In a glovebox, Fe(OTf)$_2$ (5.3 mg, 0.015 mmol, 3 mol%), IPr•HCl (19 mg, 0.045 mmol, 9 mol% ) and NaO'Bu (4.3 mg, 0.045 mmol, 9 mol%) in THF (0.5 mL) were charged to a dried reaction tube. The mixture was allowed to stir at rt for 1 h before it was diluted with THF (6.5 mL). A solution of aryl chloride (0.5 mmol, 1.0 eq) and Grignard reagent (0.6 mmol, 1.2 eq) was added subsequently. The tube was sealed, taken out of the glovebox and stirred at 60 °C for 16h. The reaction progress was monitored by GC using dodecane as the internal standard. Once completed, the reaction mixture was quenched with saturated NH$_4$Cl and extracted with CH$_2$Cl$_2$ several
times. The combined organic layers were dried over anhydrous MgSO₄, concentrated in vacuo and the resulting crude mixture was purified by silica gel column chromatography.

**General Procedure D2 (GPD2) for Iron-catalyzed Biaryl Cross-coupling Reaction of Aryl Tosylates:**
Procedure is similar to GPD1 except for, Fe(OTf)₂ (8.8 mg, 0.025 mmol, 5 mol%), IPr•HCl (32 mg, 0.075 mmol, 15 mol%) and NaO'Bu (7.2 mg, 0.075 mmol, 15 mol%) were used.

**Competitive reaction between p-chlorotoluene (1 equiv) and phenyl tosylate (1 equiv) with p-anisylmagnesium bromide (1 equiv):**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>% conv. 1e</th>
<th>% conv. 4a</th>
<th>% yield 3e</th>
<th>% yield 3l</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 mol% Fe(OTf)₂, 3 mol% SiPr•HCl, 3 mol% NaO'Bu</td>
<td>74</td>
<td>32</td>
<td>45</td>
<td>12</td>
</tr>
<tr>
<td>3 mol% Fe(OTf)₂, 9 mol% SiPr•HCl, 9 mol% NaO'Bu</td>
<td>63</td>
<td>45</td>
<td>26</td>
<td>15</td>
</tr>
</tbody>
</table>
4-Methyl-1,1'-biphenyl (3a)

\[
\begin{align*}
\text{GPA1 and GPC:} & \quad \text{prepared from chlorobenzene (56.3 mg, 0.5 mmol) and } p\text{-tolylmagnesium bromide (0.79 mL, 0.6 mmol, 0.76 M in THF). The crude mixture was purified by flash column chromatography (pentane) to afford the desired product as white solid (83.4 mg, 99%, >96% pure on GC analysis).} \\
\text{GPB:} & \quad \text{prepared from chlorobenzene (0.338 g, 3.0 mmol) and } p\text{-tolylmagnesium bromide (4.7 mL, 0.6 mmol, 0.76 M in THF, 1.2 eq). The crude mixture was purified by flash column chromatography (pentane) to afford the desired product as white solid (0.479 g, 95%, >95% pure on GC analysis).}
\end{align*}
\]

\(\text{^1H NMR (400 MHz, Chloroform-d)} \delta 7.72 \text{–} 7.65 (m, 2H), 7.64 \text{–} 7.55 (m, 2H), 7.54\text{–}7.50 (m, 2H), 7.47 \text{–} 7.37 (m, 1H), 7.35 (d, } J = 7.9 \text{ Hz, 2H), } 2.50 \text{ (s, 3H).} \text{^13C NMR (101 MHz, Chloroform-d) } \delta 141.3, 138.5, 137.0, 129.5, 128.8, 127.1, 127.0, 126.9, 21.1.\]

4-Methoxy-4'-methyl-1,1'-biphenyl (3b)

\[
\begin{align*}
\text{GPA1:} & \quad \text{prepared from 1-chloro-4-methoxybenzene (71.3 mg, 0.5 mmol) and } p\text{-tolylmagnesium bromide (0.79 mL, 0.6 mmol, 0.76 M in THF). The crude mixture was purified by flash column chromatography (5% Et}_2\text{O/petroleum ether) to afford the desired product as a white solid (90.1 mg, 91%).} \\
\text{GPC:} & \quad \text{prepared from 1-chloro-4-methoxybenzene (71.3 mg, 0.5 mmol) and } p\text{-tolylmagnesium bromide (0.65 mL, 0.6 mmol, 0.92 M in THF). The crude mixture was purified by flash column}
\end{align*}
\]

5
chromatography (5% Et₂O/petroleum ether) to afford the desired product as a white solid (92.9 mg, 95%).

^1^H NMR (400 MHz, Chloroform-\(d\)) δ 7.41 (d, \(J = 8.8\) Hz, 2H), 7.35 (d, \(J = 8.1\) Hz, 2H), 7.13 (d, \(J = 7.9\) Hz, 2H), 6.87 (d, \(J = 8.8\) Hz, 2H), 3.74 (s, 3H), 2.29 (s, 3H).

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) δ 159.1, 138.1, 136.4, 133.9, 129.5, 128.0, 126.7, 114.3, 55.4, 21.1.

4-Fluoro-4'-methyl-1,1'-biphenyl\(^3\) (3c)

\[\text{4-Fluoro-4’-methyl-1,1’-biphenyl}\]

**GPA1 and GPC**: prepared from 1-chloro-4-fluorobenzene (65.3 mg, 0.5 mmol) and \(p\)-tolylmagnesium bromide (0.79 mL, 0.6 mmol, 0.76 M in THF). The crude mixture was purified by flash column chromatography (pentane) to afford the desired product as white solid (92.3 mg, 99%, >97% pure on GC analysis).

**GPD1**: prepared from 4-fluorophenyl 4-methylbenzenesulfonate (0.133 g, 0.5 mmol) and \(p\)-tolylmagnesium bromide (0.65 mL, 0.6 mmol, 0.92 M in THF). The crude mixture was purified by flash column chromatography (pentane) to afford the desired product as white solid (65.9 mg, 71%, >97% pure on GC analysis).

^1^H NMR (400 MHz, Chloroform-\(d\)) δ 7.58 – 7.50 (m, 2H), 7.46 (d, \(J = 8.1\) Hz, 2H), 7.26 (d, \(J = 7.9\) Hz, 2H), 7.16 – 7.09 (m, 2H), 2.41 (s, 3H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) δ 162.4 (d, \(J = 245.9\) Hz), 137.5, 137.4 (d, \(J = 3.2\) Hz), 137.1, 129.6, 128.5 (d, \(J = 7.9\) Hz), 126.9, 115.6 (d, \(J = 21.3\) Hz), 21.1.

4-Fluoro-1,1'-biphenyl\(^3\) (3d)

\[\text{4-Fluoro-1,1’-biphenyl}\]
**GPA1:** prepared from chlorobenzene (56.3 mg, 0.5 mmol) and (4-fluorophenyl)magnesium bromide (0.72 mL, 0.6 mmol, 0.83 M in THF). The crude mixture was purified by flash column chromatography (pentane) to afford the desired product as a white solid (69.8 mg, 81%, >99% pure on GC).

**GPC:** prepared from chlorobenzene (56.3 mg, 0.5 mmol) and (4-fluorophenyl)magnesium bromide (0.74 mL, 0.6 mmol, 0.81 M in THF). The crude mixture was purified by flash column chromatography (pentane) to afford the desired product as a white solid (70.1 mg, 82%, >99% pure on GC).

**GPD1:** prepared from phenyl 4-methylbenzenesulfonate (0.124 g, 0.5 mmol) and (4-fluorophenyl)magnesium bromide (0.74 mL, 0.6 mmol, 0.81 M in THF). The crude mixture was purified by flash column chromatography (pentane) to afford the desired product as a white solid (71.3 mg, 83%, >99% pure on GC).

\[ ^1H \text{ NMR (400 MHz, Chloroform-}d\text{)} \delta 7.62 – 7.54 (m, 4H), 7.48-7.44 (m, 2H), 7.39-7.37 (m, 1H), 7.18-7.13 (m, 2H). \]
\[ ^{13}C \text{ NMR (101 MHz, Chloroform-}d\text{)} \delta 162.6 (d, J = 246.2 Hz), 140.4, 137.5 (d, J = 3.2 Hz), 128.9, 128.8 (d, J = 8.1 Hz), 127.3, 127.1, 115.7 (d, J = 21.3 Hz). \]

**4-Methoxy-4'-methyl-1,1'-biphenyl** (3e)

![Structure of 4-Methoxy-4'-methyl-1,1'-biphenyl](image)

**GPC:** prepared from 1-chloro-4-methylbenzene (63.3 mg, 0.5 mmol) and (4-methoxyphenyl)magnesium bromide (0.83 mL, 0.6 mmol, 0.72 M in THF). The crude mixture was purified by flash column chromatography (20% CH₂Cl₂/petroleum ether) to afford the desired product as white solid (84.1 mg, 85%).

\[ ^1H \text{ NMR (400 MHz, Chloroform-}d\text{)} \delta 7.59 – 7.52 (m, 2H), 7.51 – 7.47 (m, 2H), 7.26 (d, J = 7.9 Hz, 2H), 7.10 – 6.83 (m, 2H), 3.87 (s, 3H), 2.42 (s, 3H). \]
\[ ^{13}C \text{ NMR (101 MHz, Chloroform-}d\text{)} \delta 159.0, 138.1, 136.4, 133.9, 129.5, 128.0, 126.7, 114.3, 55.4, 21.1. \]

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4-Methyl-4'-vinyl-1,1'-biphenyl\(^3\) (3f)

\[
\begin{array}{c}
\text{Me} \\
\end{array}
\]

**GPA1:** prepared from 1-chloro-4-vinylbenzene (69.3 mg, 0.5 mmol), \(p\)-tolylmagnesium bromide (0.79 mL, 0.6 mmol, 0.76 M in THF) and THF (5.7 mL). The crude mixture was purified by flash column chromatography (pentane) to afford the desired product as white solid (89.2 mg, 92\%, >96\% pure on GC analysis).

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.52 – 7.33 (m, 6H), 7.16 (d, \(J = 6.9\) Hz, 2H), 6.67 (dd, \(J = 17.6, 10.9\) Hz, 1H), 5.69 (d, \(J = 17.6\) Hz, 1H), 5.17 (d, \(J = 10.9\) Hz, 1H), 2.31 (s, 3H).

\(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 140.6, 138.0, 137.2, 136.6, 136.4, 129.6, 127.1, 126.9, 126.7, 113.8, 21.2.

\(N\)-Benzyl-\(N,4'\)-dimethyl-[1,1'-biphenyl]-3-amine\(^3\) (3g)

\[
\begin{array}{c}
\text{Me} \\
\end{array}
\]

**GPA1:** prepared from \(N\)-benzyl-3-chloro-\(N\)-methylaniline (0.116 g, 0.5 mmol) and \(p\)-tolylmagnesium bromide (0.79 mL, 0.6 mmol, 0.76 M in THF). The crude mixture was purified by flash column chromatography (0-10\% Et\(_2\)O/petroleum ether) to afford the desired product as a yellow oil (0.117 g, 82\%).

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.47 (d, \(J = 8.1\) Hz, 2H), 7.36 – 7.18 (m, 8H), 7.00 – 6.92 (m, 2H), 6.75 (dd, \(J = 8.3, 2.2\) Hz, 1H), 4.58 (s, 2H), 3.07 (s, 3H), 2.39 (s, 3H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 150.2, 142.3, 139.4, 139.1, 136.8, 129.5, 129.4, 128.6, 127.2, 127.0, 126.9, 115.8, 111.4, 111.3, 56.9, 38.7, 21.2.
**tert-Butyldimethyl((4'-methyl-[1,1'-biphenyl]-3-yl)oxy)silane** (3h)

![Chemical Structure](image)

**GPA1**: prepared from *tert*-butyl(3-chlorophenoxy)dimethylsilane (0.121 g, 0.5 mmol) and *p*-tolylmagnesium bromide (0.79 mL, 0.6 mmol, 0.76 M in THF). The crude mixture was purified by flash column chromatography (petroleum ether) to afford the desired product as a colourless oil (0.128 g, 86%, >95% pure on GC analysis).

\[ ^1H \text{NMR} (400 \text{ MHz, Chloroform-}d) \delta 7.50 - 7.44 (m, 2H), 7.32 - 7.21 (m, 3H), 7.17 (dt, J = 7.7, 1.6 Hz, 1H), 7.07 - 7.04 (m, 1H), 6.81 (ddd, J = 8.0, 2.4, 1.1 Hz, 1H), 2.40 (s, 3H), 1.01 (s, 9H), 0.24 (s, 6H). ~ ^13C \text{NMR} (101 \text{ MHz, Chloroform-}d) \delta 156.1, 142.7, 138.3, 137.2, 129.7, 129.5, 127.0, 120.1, 118.8, 118.7, 25.8, 21.2, 18.3, -4.2. ~

**5-Methoxy-1-methyl-3-(p-tolyl)-1H-indole** (3i)

![Chemical Structure](image)

**GPA2**: prepared from 3-chloro-5-methoxy-1-methyl-1H-indole (97.8 mg, 0.5 mmol) and *p*-tolylmagnesium bromide (0.79 mL, 0.6 mmol, 0.76 M in THF). The crude mixture was purified by flash column chromatography (20% CH\textsubscript{2}Cl\textsubscript{2}/petroleum ether) to afford the desired product as an off-white solid (0.105 g, 84%).

\[ ^1H \text{NMR} (400 \text{ MHz, Chloroform-}d) \delta 7.59 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 2.4 Hz, 1H), 7.36-7.26 (m, 3H), 7.18 (s, 1H), 7.00 (dd, J = 8.9, 2.4 Hz, 1H), 3.92 (s, 3H), 3.78 (s, 3H), 2.46 (s, 3H). ~ ^13C \text{NMR} (101 \text{ MHz, Chloroform-}d) \delta 154.6, 135.2, 132.9, 129.5, 127.2, 127.0, 126.6, 116.3, 112.2, 110.3, 101.9, 56.1, 32.9, 21.2. ~
2-(p-Tolyl)pyridine\(^3\) (3j)

GPA1: prepared from 2-chloropyridine (56.8 mg, 0.5 mmol) and p-tolylmagnesium bromide (0.79 mL, 0.6 mmol, 0.76 M in THF). The crude mixture was purified by flash column chromatography (0-10% Et\(_2\)O/petroleum ether) to afford the desired product as a colorless oil (52 mg, 61%).

GPB: prepared from 2-chloropyridine (0.341 g, 3.0 mmol) and p-tolylmagnesium bromide (3.9 mL, 3.6 mmol, 0.92 M in THF). The crude mixture was purified by flash column chromatography (0-10% Et\(_2\)O/petroleum ether) to afford the desired product as a colorless oil (0.37 g, 73%).

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 8.69-8.67 (m, 1H), 7.90 (d, \(J = 8.2\) Hz, 2H), 7.75-7.70 (m, 2H), 7.28 (d, \(J = 7.9\) Hz, 2H), 7.21-7.18 (m, 1H), 2.41 (s, 3H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 157.6, 149.7, 139.0, 136.7, 129.5, 126.7, 121.8, 120.3, 21.3.

3-(Trifluoromethyl)-1,1'-biphenyl\(^5\) (3k)

GPA2: prepared from chlorobenzene (56.3 mg, 0.5 mmol) and (3-(Trifluoromethyl)phenyl)magnesium bromide (0.80 mL, 0.6 mmol, 0.75 M in THF). The crude mixture was purified by flash column chromatography (pentane) to afford the desired product as colourless oil (88.1 mg, 79%, >97% pure on GC).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.87 (s, 1H), 7.78 (d, $J = 7.5$ Hz, 1H), 7.55-7.70 (m, 4H), 7.49 (t, $J = 7.4$ Hz, 2H), 7.42 (t, $J = 7.3$ Hz, 1H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 142.2, 139.9, 131.3 (q, $J = 32.2$ Hz), 130.5, 129.6, 129.3, 129.1, 128.1, 127.3, 124.3 (q, $J = 270.6$ Hz), 124.0 (q, $J = 3.7$ Hz).

4-Methoxy-1,1'-biphenyl$^3$ (3l)

![4-Methoxy-1,1'-biphenyl](image)

**GPA1:** prepared from chlorobenzene (56.3 mg, 0.5 mmol) and (4-methoxyphenyl)magnesium bromide (0.74 mL, 0.6 mmol, 0.81 M in THF). The crude mixture was purified by flash column chromatography (20% CH$_2$Cl$_2$/petroleum ether) to afford the desired product as white solid (92.8 mg, 99%).

**GPB:** prepared from chlorobenzene (0.338 g, 3.0 mmol) and (4-methoxyphenyl)magnesium bromide (4.4 mL, 3.6 mmol, 0.82 M in THF). The crude mixture was purified by flash column chromatography (20% CH$_2$Cl$_2$/petroleum ether) to afford the desired product as white solid (0.535 g, 97%).

**GPD1:** prepared from phenyl 4-methylbenzenesulfonate (0.124 g, 0.5 mmol) and (4-methoxyphenyl)magnesium bromide (0.83 mL, 0.6 mmol, 0.72 M in THF). The crude mixture was purified by flash column chromatography (20% CH$_2$Cl$_2$/petroleum ether) to afford the desired product as white solid (87.4 mg, 95%).

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.60 – 7.52 (m, 4H), 7.47 – 7.40 (m, 2H), 7.35 – 7.29 (m, 1H), 7.03 – 6.97 (m, 2H), 3.87 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-$d$) $\delta$ 159.3, 140.9, 133.9, 128.8, 128.2, 126.8, 126.7, 114.3, 55.4.

4-Methoxy-4'-(trifluoromethyl)-1,1'-biphenyl$^6$ (3m)

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**GPA2:** prepared from 1-chloro-4-(trifluoromethyl)benzene (90.3 mg, 0.5 mmol) and (4-methoxyphenyl)magnesium bromide (0.83 mL, 0.6 mmol, 0.72 M in THF). The crude mixture was purified by flash column chromatography (20% CH₂Cl₂/petroleum ether) to afford the desired product as white solid (99.5 mg, 79%).

$^1$H NMR (400 MHz, Chloroform-\(d\)) $\delta$ 7.73 – 7.63 (m, 4H), 7.60 – 7.53 (m, 2H), 7.06 – 7.00 (m, 2H), 3.88 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-\(d\)) $\delta$ 160.0, 144.4, 132.2, 128.9 (q, $J = 32.2$ Hz), 128.4, 126.9, 125.7 (q, $J = 3.8$ Hz), 124.5 (q, $J = 270.1$ Hz), 114.5, 55.4.

**N,N,2',6-Tetramethyl-[1,1'-biphenyl]-3-amine**\(^7\) (3n)

**GPA1:** prepared from 1-chloro-2-methylbenzene (63.3 mg, 0.5 mmol) and (5-(dimethylamino)-2-methylphenyl)magnesium bromide (0.83 mL, 0.6 mmol, 0.72 M in THF). The crude mixture was purified by flash column chromatography (0-40% CH₂Cl₂/petroleum ether) to afford the desired product as off-white solid (85.6 mg, 76%).

$^1$H NMR (400 MHz, Chloroform-\(d\)) $\delta$ 7.28 – 7.17 (m, 3H), 7.16 – 7.09 (m, 2H), 6.69 (dd, $J = 8.4$, 2.8 Hz, 1H), 6.53 (d, $J = 2.8$ Hz, 1H), 2.90 (s, 6H), 2.10 (s, 3H), 1.95 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-\(d\)) $\delta$ 148.8, 142.5, 142.2, 135.9, 130.4, 129.8, 129.3, 127.0, 125.5, 124.0, 114.2, 112.0, 41.0, 19.9, 18.6.

**2-Methoxy-2'-methyl-1,1'-biphenyl**\(^8\) (3o)

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GPA1: prepared from 1-chloro-2-methoxybenzene (71.3 mg, 0.5 mmol) and o-tolylmagnesium bromide (0.67 mL, 0.6 mmol, 0.90 M in THF). The crude mixture was purified by flash column chromatography (5% Et₂O/petroleum ether) to afford the desired product as colourless oil (98.3 mg, 99%).

\[^{1}\text{H} \text{NMR (400 MHz, Chloroform-}d\text{)} \delta 7.38 - 7.31 \text{ (m, 1H), 7.29} - 7.18 \text{ (m, 4H), 7.16 (dd, } J = 7.4, 1.8 \text{ Hz, 1H), 7.02 (td, } J = 7.4, 1.1 \text{ Hz, 1H), 6.98} - 6.94 \text{ (m, 1H), 3.75 (s, 3H), 2.16 (s, 3H). \[^{13}\text{C} \text{NMR (101 MHz, Chloroform-}d\text{)} \delta 156.7, 138.7, 136.8, 131.1, 131.0, 130.1, 129.6, 128.6, 127.3, 125.5, 120.5, 110.8, 55.4, 20.0.}\]

4-Fluoro-4'-methoxy-1,1'-biphenyl\(^{4}\) (3p)

GPD1: prepared from 4-fluorophenyl 4-methylbenzenesulphonate (0.133 g, 0.5 mmol) and (4-methoxyphenyl)magnesium bromide (0.83 mL, 0.6 mmol, 0.72 M in THF). The crude mixture was purified by flash column chromatography (20% CH₂Cl₂/petroleum ether) to afford the desired product as white solid (82.3 mg, 81%).

\[^{1}\text{H} \text{NMR (400 MHz, Chloroform-}d\text{)} \delta 7.54 - 7.47 \text{ (m, 4H), 7.17} - 7.07 \text{ (m, 2H), 7.03} - 6.96 \text{ (m, 2H), 3.86 (s, 3H). \[^{13}\text{C} \text{NMR (101 MHz, Chloroform-}d\text{)} \delta 162.2 (d, } J = 245.5 \text{ Hz), 159.2, 137.1 (d, } J = 3.2 \text{ Hz), 132.9, 128.3 (d, } J = 8.0 \text{ Hz), 128.1, 115.6 (d, } J = 21.4 \text{ Hz), 114.4, 55.4.}\]

4'-Fluoro-N,N-dimethyl-[1,1'-biphenyl]-4-amine\(^{9}\) (3q)

GPD2: prepared from 4-(dimethylamino)phenyl 4-methylbenzenesulfonate (0.139 g, 0.5 mmol), (4-fluorophenyl)magnesium bromide (0.74 mL, 0.6 mmol, 0.81 M in THF). The crude mixture was purified by flash column chromatography (5% Et₂O/petroleum ether) to afford the desired product as white solid (62.6 mg, 60%).

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.58 – 7.44 (m, 4H), 7.16 – 7.07 (m, 2H), 6.87 – 6.79 (m, 2H), 3.02 (s, 6H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 161.8 (d, \(J = 244.7\) Hz), 150.0, 137.5 (d, \(J = 3.2\) Hz), 128.4, 127.8 (d, \(J = 7.9\) Hz), 127.6, 115.5 (d, \(J = 21.3\) Hz), 112.9, 40.6.

4'-Methoxy-3-(trifluoromethyl)-1,1'-biphenyl\(^{10}\) (3r)

GPD1: prepared from 3-(trifluoromethyl)phenyl 4-methylbenzenesulfonate (0.158 g, 0.5 mmol), (4-methoxyphenyl)magnesium bromide (0.83 mL, 0.6 mmol, 0.72 M in THF). The crude material was purified by flash column chromatography (20% CH₂Cl₂/petroleum ether) to afford the desired product as colourless oil (61.5 mg, 49%).

\(^1\)H NMR (400 MHz, Chloroform-\(d\)) \(\delta\) 7.82 (s, 1H), 7.73 (d, \(J = 7.5\) Hz, 1H), 7.65 – 7.47 (m, 4H), 7.09 – 6.96 (m, 2H), 3.87 (s, 3H). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta\) 159.8, 141.7, 132.3, 131.2 (q, \(J = 32.1\) Hz), 130.0, 129.2, 128.3, 124.4 (q, \(J = 270.6\) Hz), 123.5 (q, \(J = 3.8\) Hz), 123.4 (q, \(J = 3.8\) Hz), 114.5, 55.4.

4'-Methoxy-2-methyl-1,1'-biphenyl\(^{11}\) (3s)

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**GPD1:** prepared from *o*-tolyl 4-methylbenzenesulfonate (0.131 g, 0.5 mmol), (4-methoxyphenyl)magnesium bromide (0.83 mL, 0.6 mmol, 0.72 M in THF). The crude mixture was purified by flash column chromatography (20% CH$_2$Cl$_2$/petroleum ether) to afford the desired product as colourless oil (88.4 mg, 89%).

$^1$H NMR (400 MHz, Chloroform-*$d$) $\delta$ 7.14-7.09 (m, 6H), 6.86 – 6.79 (m, 2H), 3.71 (s, 3H), 2.16 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*$d$) $\delta$ 158.6, 141.6, 135.5, 134.5, 130.3, 130.3, 129.9, 127.0, 125.8, 113.6, 55.3, 20.6.

**1-(4-Methoxyphenyl)naphthalene**$^{11}$ (3t)

**GPD1:** prepared from naphthalen-1-yl 4-methylbenzenesulfonate (0.149 g, 0.5 mmol), (4-methoxyphenyl)magnesium bromide (0.83 mL, 0.6 mmol, 0.72 M in THF). The crude mixture was purified by flash column chromatography (20% CH$_2$Cl$_2$/petroleum ether) to afford the desired product as white solid (48.2 mg, 41%).

$^1$H NMR (400 MHz, Chloroform-*$d$) $\delta$ 8.00 – 7.90 (m, 2H), 7.86 (d, $J = 8.2$ Hz, 1H), 7.57 – 7.48 (m, 2H), 7.48 – 7.41 (m, 4H), 7.09 – 7.04 (m, 2H), 3.92 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*$d$) $\delta$ 159.1, 140.0, 134.0, 133.3, 132.0, 131.2, 128.3, 127.4, 127.0, 126.2, 126.0, 125.8, 125.5, 113.8, 55.4.
4'-Fluoro-2-methyl-1,1'-biphenyl\textsuperscript{12} (3u)

\[
\begin{array}{c}
\text{Me} \\
\text{F}
\end{array}
\]

GPD\textsuperscript{2}: prepared from o-tolyl 4-methylbenzenesulfonate (0.131 g, 0.5 mmol), (4-fluorophenyl)magnesium bromide (0.74 mL, 0.6 mmol, 0.81 M in THF). The crude material was purified by flash column chromatography (pentane) to afford the desired product as colourless oil (83.7 mg, 90\%, >97\% pure on GC analysis).

\(^1\)H NMR (400 MHz, Chloroform-\textit{d}) \(\delta 7.44 - 7.23 \text{ (m, 6H)}, 7.20 - 7.14 \text{ (m, 2H)}, 2.33 \text{ (s, 3H)}\). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta 162.0 \text{ (d, } J = 245.5 \text{ Hz)}, 141.0, 138.0 \text{ (d, } J = 3.4 \text{ Hz)}, 135.4, 130.8 \text{ (d, } J = 7.9 \text{ Hz)}, 130.4, 129.9, 127.5, 125.9, 115.0 \text{ (d, } J = 21.3 \text{ Hz)}, 20.5.\)

4'-Fluoro-2-methoxy-1,1'-biphenyl\textsuperscript{12} (3v)

\[
\begin{array}{c}
\text{Me} \\
\text{F}
\end{array}
\]

GPD\textsuperscript{2}: prepared from 2-methoxyphenyl 4-methylbenzenesulfonate (0.139 g, 0.5 mmol), (4-fluorophenyl)magnesium bromide (0.74 mL, 0.6 mmol, 0.81 M in THF). The crude material was purified by flash column chromatography (5\% Et\(_2\)O/ petroleum ether) to afford the desired product as colourless oil (76.7 mg, 76\%).

\(^1\)H NMR (400 MHz, Chloroform-\textit{d}) \(\delta 7.62 - 7.57 \text{ (m, 2H)}, 7.44 - 7.34 \text{ (m, 2H)}, 7.23 - 7.14 \text{ (m, 2H)}, 7.12 \text{ (td, } J = 7.5, 0.9 \text{ Hz, 1H)}, 7.07 \text{ (d, } J = 8.3 \text{ Hz, 1H)}, 3.88 \text{ (s, 3H)}\). \(^{13}\)C NMR (101 MHz, Chloroform-\(d\)) \(\delta 162.1 \text{ (d, } J = 245.8 \text{ Hz)}, 156.5, 134.5 \text{ (d, } J = 3.4 \text{ Hz)}, 131.2 \text{ (d, } J = 8.0 \text{ Hz)}, 130.8, 129.8, 128.8, 120.9, 114.9 \text{ (d, } J = 21.3 \text{ Hz)}, 111.4, 55.5.\)

NMR Spectra

3a