Supporting Information

Directed ortho Metalation Methodology. The $N,N$-Dialkyl Aryl O-Sulfamate as a New Directed Metalation Group and Cross Coupling Partner for Grignard Reagents

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General Methods

Melting points are uncorrected. Infrared spectra were recorded as neat or KBr discs using a BOMEM MB-100 FTIR spectrophotometer. $^1$H NMR spectra were recorded using an Avance 300 MHz or Bruker 400 MHz spectrometer. When peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; qn, quintet; sx, sextet; dd, doublet of doublet; td, triplet of doublet; m, multiplet; bs, broad singlet. GC-MS analyses were performed with an Agilent 6890N GC coupled with an Agilent 5973 inert MS under EI conditions. THF and Et$_2$O were freshly distilled from sodium benzophenone ketyl under argon and $N,N$-diethylcarbamoyl chloride was distilled from CaH$_2$ and stored over 4 Å molecular sieves prior to use. $n$- and sec-Butyllithium were purchased from Aldrich as solutions in hexanes, stored in a resealable container, and titrated periodically against $N$-benzylbenzamide. LDA was freshly prepared before reactions by stirring a 1:1 mixture of diisopropylamine and $n$-BuLi at 0 °C in THF (1 M) for 10 min. $N,N,N^\prime,N^\prime$-tetramethylethlenediamine (TMEDA) was stored over solid KOH prior to use. All reactions involving alkyllithiums were carried out in oven or flame-dried glassware cooled under argon using syring-septum cap techniques. The -93, -78, -10, and 0 °C temperatures designated are approximate as achieved by a liquid nitrogen-hexanes, dry ice-acetone, ice-acetone, and ice-salt bath, respectively. When internal temperature readings were essential, a Barnant Dual J stainless steel-sheathed thermocouple thermometer was employed. $N,N$-diethylsulfamoyl chloride and NiClCpIMes were prepared from literature procedures.$^{1,2}$ Pd(PPh$_3$)$_4$ was freshly prepared according to a literature procedure$^3$ and solutions were pre-degassed using sonication.
associated with argon bubbling. Furan was freshly distilled from KOH prior to use. Reaction monitoring was done by TLC and GC where appropriate. Flash column chromatography was carried out using Merck silica gel 60 (particle size: 32-63).

**A. Preparation of N,N-Diethyl Aryl O-Sulfamates**

To a suspension of NaH (80% in mineral oil, 3.35 g, 112 mmol) in DMF (300 mL) under an argon atmosphere was added via canula a solution of phenol (10 g, 106 mmol) in DMF (50 mL) at -10 °C. The resulting sodium aryloxide was stirred for 30 min at rt before recooling to -10 °C and treated with N,N-diethylsulfamoyl chloride (15.75 mL, 112 mmol). The solution was allowed to warm to rt, quenched with satd aq NH₄Cl solution (20 mL), diluted with water (1.5 L), extracted with hexanes (3 x 100 mL), dried (Na₂SO₄), and concentrated in vacuo to give the crude product which was subjected to high vacuum distillation to afford the pure product.

**B. Lithiation of N,N-Diethyl Benzene O-Sulfamate 3**

A solution of 3 (229 mg, 1 mmol) and TMEDA (0.17 mL, 1.1 mmol) in THF (5 mL) cooled to -93 °C under argon atmosphere was treated with a solution of s-BuLi (1.1 mmol, 1.1 equiv) The resulting yellow solution was stirred (45 min), treated dropwise via a syringe with an electrophile (1.2 mmol, 1.2 equiv), and the whole was allowed to warm to rt over 15 min. Standard workup afforded the crude product.

**C. Suzuki-Miyaura Cross-coupling Reactions of 2-Bromo, 2-Iodo, and 2-Pinacolboronate Phenyl O-Sulfamate 4h, i, k**

A round-bottom flask fitted with a reflux condenser under Ar atmosphere containing a degassed solvent/base mixture (DME / Na₂CO₃ 2 M) was charged with the appropriate aryl O-sulfamate and aryl boronic acid or aryl bromide in eqimolar amounts. Pd(PPh₃)₄ (5 mol %), dispensed in a glovebag, was quickly added, and the stirred reaction mixture was purged with argon for an additional 10 min, refluxed (90 °C) until consumption of starting material (TLC monitoring) and then allowed to cool to ambient temperature. DME was removed in vacuo and the remaining aqueous solution was extracted with EtOAc (3 x 10 mL). The combined extract was washed with brine, dried (Na₂SO₄),
subjected to filtration through a short pad of silica, and concentrated in \textit{vacuo} to afford a residue, which was purified by flash column chromatography (silica gel, hexanes / EtOAc).

**D. Cross-coupling of Aryl O-Sulfamates 4e, l-q**

To a solution of \(N,N\)-diethyl benzene O-sulfamate 3 (1 mmol) in anhydrous Et\(_2\)O (2.5 mL) under an Ar atmosphere was added NiClCpIMes (0.01 mmol) followed by \(p\)-tolylphenylmagnesium bromide (1.5 mmol) \textit{via} syringe. The brown mixture was stirred at rt until consumption of starting material (TLC monitoring) and then quenched carefully with saturated NH\(_4\)Cl solution. The magnesium salts were dissolved by the addition of H\(_2\)O, the whole was diluted with EtOAc and the layers were separated. The aqueous layer was further extracted with EtOAc (x2). The combined extracts were washed with brine, dried (Na\(_2\)SO\(_4\)), and concentrated \textit{in vacuo}. The crude biaryl was purified \textit{via} flash column chromatography (silica gel, hexanes / EtOAc).

**E. Naphthols 7a, b via Benzyne Trapping of 2-Bromo Phenyl O-Sulfamate 4h**

A solution of 4h (307 mg, 1 mmol) and furan (0.73 ml, 10 mmol) in Et\(_2\)O (2 mL) cooled to \(-10\) °C under argon atmosphere was treated with a solution of \(n\)-BuLi (1.1 mmol, 1.1 equiv). The resulting solution was allowed to warm to rt over 15 min. Standard workup afforded the crude product which was dissolved in absolute EtOH (5 mL), added 2 drops of concentrated HCl (12 M), and refluxed for 12 h. Workup afforded the crude product.

**\(N, N\)-Diethyl phenyl O-sulfamate 3**

This compound was prepared by \textbf{Method A} using the following materials: NaH (80% in mineral oil, 3.35 g, 112 mmol), phenol (10 g, 106 mol), \(N, N\)-diethylsulfamoyl chloride (15.75 mL, 112 mmol) in DMF (350 mL). Work-up and high vacuum distillation afforded pure 3 (22 g, 92%) as a colourless oil, bp 120 °C/3.5 mm Hg, [lit\(^d\) 118 °C/4 mm Hg]; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(d\) 7.43-7.37 (m, 2H), 7.31-7.28 (m, 3H), 3.39 (q, 4H, \(J = 7.2\) Hz), 1.24 (t, 6H, \(J = 7.2\) Hz); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(d\) 130.3 (2C), 127.2, 122.6 (2C), 44.1 (2C), 14.2 (2C).
**N,N-Diethyl 2-formylphenyl O-sulfamate 4a**

This compound was prepared by **Method B** using the following materials: 3 (0.315 g, 1.38 mmol), TMEDA (0.229 mL, 1.52 mmol), s-BuLi (1.17 mL, 1.3 M in cyclohexane, 1.52 mmol), THF (5 mL), DMF (0.128 mL, 1.66 mmol). Standard workup and flash chromatography (8:2 hexanes / EtOAc) afforded 4a (0.222 g, 63%) as a yellow oil; IR (neat) \( \delta_{\text{max}} \) 2991, 2889, 1700, 1611, 1470, 1208, 1157 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 10.39 (s 1H), 7.93 (dd, 1H, \( J = 7.7, 1.2 \) Hz), 7.63 (td 1H, \( J = 1.4, 8.5 \) Hz), 7.48 (d, 1H, \( J = 8.2 \) Hz), 7.39 (t, 1H, \( J = 7.6 \) Hz), 3.47 (q, 4H, \( J = 7.1 \) Hz), 1.27 (t, 6H, \( J = 7.2 \) Hz); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 188.9, 152.8, 136.1, 129.7, 129.5, 127.6, 123.9, 44.2 (2C), 14.2 (2C); LRMS (EI) \( m/z \) (rel. intensity) 258(M\(^+\) + 1, 37), 256(M\(^+\) - 1, 36), 242(100); HRMS (EI) calcd for C\(_{11}\)H\(_{15}\)NO\(_4\)S 258.0801: found 258.0800.

**N,N-Diethyl 2-diethylcarbamoylphenyl O-sulfamate 4b**

This compound was prepared by **Method B** using the following materials: 3 (0.315 g, 1.38 mmol), TMEDA (0.229 mL, 1.52 mmol), s-BuLi (1.17 mL, 1.3 M in cyclohexane, 1.52 mmol), THF (5 mL), N,N-diethylcarbamoyl chloride (0.210 mL, 1.66 mmol). Standard workup and flash chromatography (8:2 hexanes / EtOAc) afforded 4b (0.320 g, 70%) as a yellow oil; IR (neat) \( \delta_{\text{max}} \) 2985, 2944, 1649, 1445, 1374, 1214, 1163 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta \) 7.50 (d, 1H, \( J = 8.2 \) Hz), 7.36 (m, 1H), 7.24 (m, 1H), 3.62 (m, 1H), 3.34 (q, 5H, \( J = 7.2 \) Hz), 3.15 (m, 2H), 1.21 (t, 3H, \( J = 7.1 \) Hz), 1.17 (t, 6H, \( J = 7.2 \) Hz), 1.04 (t, 3H, \( J = 7.1 \) Hz); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 167.6, 147.0, 131.3, 130.7, 128.3, 126.9, 122.9, 44.2 (2C), 43.8, 39.6, 14.5, 14.2 (2C), 13.4; LRMS (EI) \( m/z \) (rel. intensity) 330(M\(^+\) + 3, 20), 329(M\(^+\) + 2, 100); HRMS (EI) calcd for C\(_{16}\)H\(_{25}\)NO\(_4\)S 327.1534: found 329.1535.

**N,N-Diethyl 2-(hydroxy-phenyl-methyl)phenyl O-sulfamate 4c**

This compound was prepared by **Method B** using the following materials: 3 (0.300 g, 1.32 mmol), TMEDA (0.219 mL, 1.45 mmol), s-BuLi (1.32 mL, 1.1 M in cyclohexane, 1.45 mmol), THF (5 mL),
benzaldehyde (0.160 mL, 1.58 mmol). Standard workup and flash chromatography (8:2 hexanes / EtOAc) afforded 4c (0.375 g, 85%) as a colourless oil; IR (neat) \( \nu_{\text{max}} \) 3528, 2971, 2940, 1604, 1374, 1208, 1157 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) d 7.44-7.32 (m, 9H), 6.30 (d, 1H, J = 3.2 Hz), 3.44 (q, 4H, 7.2 Hz), 3.17 (d, 1H, J = 1.5 Hz), 1.27 (t, 6H, J = 7.2 Hz); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) d 148.3, 143.1, 137.7, 130.1, 129.6, 129.0 (2C), 128.0, 127.8, 127.1 (2C), 122.9, 70.1, 44.1 (2C), 14.2 (2C); LRMS (EI) \( m/z \) (rel. intensity) M\(^+\) not found, 318(M\(^+\) - H\(_2\)O, 100); HRMS (EI) calcd for C\(_{17}\)H\(_{21}\)NO\(_4\)S 335.1198: found 335.1191.

**N,N-Diethyl 2-thiomethylphenyl O-sulfamate 4d**

This compound was prepared by **Method B** using the following materials: 3 (0.300 g, 1.32 mmol), TMEDA (0.219 mL, 1.45 mmol), s-BuLi (1.21 mL, 1.2 M in cyclohexane, 1.45 mmol), THF (5 mL), methyl disulfide (0.142 mL, 1.58 mmol). Standard workup and flash chromatography (9:1 hexanes / EtOAc) afforded 3d (1.50 g, 88%) as a colourless oil; IR (neat) \( \nu_{\text{max}} \) 2978, 2936, 1578, 1470, 1389, 1208, 1157 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) d 7.46 (dd, 1H, J = 1.2, 7.4 Hz), 7.23-7.14 (m, 3H), 3.49 (q, 4H, 7.2 Hz), 2.46 (s, 3H), 1.28 (t, 6H, J = 7.2 Hz); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) d 147.7, 132.3, 127.1, 126.6, 121.9, 43.8 (2C), 15.1, 13.9 (2C); LRMS (EI) \( m/z \) (rel. intensity) 276(M\(^+\) + 1, 29), 275(M\(^+\), 100); HRMS (EI) calcd for C\(_{11}\)H\(_{17}\)NO\(_3\)S 275.0653: found 275.0650.

**N,N-Diethyl 2-trimethylsilylphenyl O-sulfamate 4e**

This compound was prepared by **Method B** using the following materials: 3 (0.50 g, 2.18 mmol), TMEDA (0.36 mL, 2.40 mmol), s-BuLi (1.73 mL, 1.39 M in cyclohexane, 2.40 mmol), THF (10 mL), chlorotrimethylsilane (0.33 mL, 2.62 mmol). Standard workup and flash chromatography (9:1 hexanes / EtOAc) afforded 4e (0.63 g, 96%) as a colourless oil; IR (neat) \( \nu_{\text{max}} \) 2967, 2908, 1591, 1470, 1380, 1253, 1144, 831 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) d 7.55 (d, 1H, J = 7.8 Hz), 7.49 (dd, 1H, J = 1.5, 7.1 Hz), 7.40 (td, 1H, J = 7.3, 1.8 Hz), 7.22 (td, 1H, J = 7.3, 1.0 Hz), 3.50 (q, 4H, 7.2 Hz), 1.30 (t, 6H, J = 7.2 Hz), 0.48 (s, 9H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) d 157.0, 136.3, 131.5, 131.4, 125.9, 119.6, 44.1 (2C), 14.5 (2C), 0.2
Diethyl 1-(2-diethylphenyl O-sulfamate)-1,2,hydrazinedicarboxylate 4f

This compound was prepared by Method B using the following materials: 3 (300 mg, 1.3 mmol), TMEDA (0.22 mL, 1.5 mmol), s-BuLi (1.32 mL, 1.1 M in cyclohexane, 1.5 mmol), THF (5 mL), diethyl diazodicarboxylate (0.25 mL, 1.6 mmol). Standard workup and flash chromatography (7:3 hexanes / EtOAc) afforded 4f (280 mg, 53%) as a colourless oil; IR (neat) $\nu_{\text{max}}$ 3388, 2991, 2940, 1726, 1496, 1374, 1234, 1157 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.73 (bs, 1H), 7.47-7.28 (m, 4H), 4.21 (m, 4H), 3.43 (q, 4H, 7.0 Hz), 1.27 (t, 6H, $J = 7.0$ Hz), 1.26 (t, 6H, $J = 7.0$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 156.5, 155.4, 145.6, 1 35.6, 129.8 (2C), 128.0, 123.8, 63.1 (2C), 43.7 (2C), 14.7 (2C), 13.6 (2C); LRMS (EI) $m/z$ (rel. intensity) 404($M^+ + 1$, 25), 331(40), 223(100); HRMS (EI) calcd for C$_{16}$H$_{25}$N$_3$O$_7$S 403.1485: found 404.1492.

$N,N$-Diethyl 2-chlorophenyl O-sulfamate 4g

This compound was prepared by Method B using the following materials: 3 (1.00 g 4.37 mmol), TMEDA (0.72 mL, 4.81 mmol), s-BuLi (3.36 mL, 1.43 M in cyclohexane, 4.81 mmol), THF (10 mL), 1,1,1,2,2,2-hexachloroethane (1.24 g, 5.24 mmol) in THF (3 mL). Standard workup and flash chromatography (9:1 hexanes / EtOAc) afforded 4g (0.52 g, 45%) as a colourless oil; IR (neat) $\nu_{\text{max}}$ 2985, 2941, 1579, 1470, 1368, 1214, 1163 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.55 (d, 1H, $J = 8.1$ Hz), 7.44 (d, 1H, $J = 7.9$ Hz), 7.30 (t, 1H, $J = 6.4$ Hz), 7.20 (t, 1H, $J = 6.2$ Hz), 3.49 (q, 4H, 7.2 Hz), 1.28 (t, 6H, $J = 7.2$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 147.1, 131.3, 128.5, 127.8, 127.4, 124.1, 44.2 (2C), 14.2 (2C); LRMS (EI) $m/z$ (rel. intensity) 265($M^+ + 2$, 34), 263($M^+$, 100); HRMS (EI) calcd for C$_{10}$H$_{14}$ClNO$_3$S 263.0381: found 263.0383.

$N,N$-Diethyl 2-bromophenyl O-sulfamate 4h
This compound was prepared by Method B using the following materials: 3 (2.00 g, 8.73 mmol), TMEDA (1.2 mL, 9.60 mmol), s-BuLi (6.72 mL, 1.43 M in cyclohexane, 9.60 mmol), THF (20 mL), 1,1,2,2-tetrabromoethane (1.22 mL, 10.48 mmol). Standard workup and flash chromatography (9:1 hexanes / EtOAc) afforded 3h (1.50 g, 56%) as a colourless oil; IR (neat) $\nu_{\text{max}}$ 2978, 2946, 1585, 1470, 1374, 1208, 1163 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.62 (d, 1H, $J = 7.9$ Hz), 7.56 (d, 1H, $J = 8.2$ Hz), 7.35 (t, 1H, $J = 7.7$ Hz), 7.13 (t, 1H, $J = 7.6$ Hz), 3.51 (q, 4H, $J = 7.2$ Hz), 1.28 (t, 6H, $J = 7.2$ Hz); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 147.7, 133.8, 128.6, 127.4, 123.1, 115.7, 43.6 (2C), 13.5 (2C); LRMS (EI) $m/z$ (rel. intensity) 309(M$^+$ + 2, 53), 307(M$^+$, 51), 294(22), 292(21), 136(100); HRMS (EI) calcd for C$_{10}$H$_{14}$BrNO$_3$S 306.9876: found 306.9878.

$N,N$-Diethyl 2-iodophenyl O-sulfamate 4i

This compound was prepared by Method B using the following materials: 3 (5.00 g, 21.8 mmol), TMEDA (3.6 mL, 24.0 mmol), s-BuLi (21.8 mL, 1.1 M in cyclohexane, 24.0 mmol), THF (50 mL), iodine (6.64 g, 26.2 mmol) in THF (20 mL). Standard workup and high vacuum distillation afforded 4i (6.0 g, 78%) as yellow solid, mp 42-44 °C; IR (neat) $\nu_{\text{max}}$ 2978, 2935, 1572, 1464, 1388, 1208, 1170 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 7.84 (dd, 1H, $J = 1.3$, 7.9 Hz), 7.54 (dd, 1H, $J = 1.2$, 8.2 Hz), 7.35 (td, 1H, $J = 1.3$, 7.3 Hz), 6.98 (t, 1H, $J = 7.6$ Hz), 3.56 (q, 4H, 7.1 Hz), 1.31 (t, 6H, $J = 7.2$ Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 150.8, 140.2, 129.9, 128.0, 122.2, 89.6, 43.9 (2C), 13.9 (2C); LRMS (EI) $m/z$ (rel. intensity) 355(M$^+$, 100); HRMS (EI) calcd for C$_{10}$H$_{14}$INO$_3$S 354.9738: found 354.9739.

$N,N$-Diethyl 2-tri-$n$-butylstannanylphenyl O-sulfamate 4j

This compound was prepared by Method B using the following materials: 3 (0.300 g, 1.32 mmol), TMEDA (0.219 mL, 1.45 mmol), s-BuLi (1.21 mL, 1.2 M in cyclohexane, 1.45 mmol), THF (5 mL), tributyltin chloride (0.430 mL, 1.58 mmol). Standard workup and flash chromatography (9:1 hexanes / EtOAc) afforded 4j (0.625 g, 91%) as a colourless oil; IR (neat) $\nu_{\text{max}}$ 2959,
2921, 1566, 1457, 1374, 1208, 1150 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.47-7.41 (m, 2H), 7.34 (td, 1H, J = 1.1, 7.0 Hz), 7.22 (t, 1H, J = 7.1 Hz), 3.44 (q, 4H, 7.2 Hz), 1.55 (m, 6H), 1.36 (m, 6H), 1.28 (t, 6H, J = 7.2 Hz), 1.18 (m, 6H), 0.92 (t, 9H, J = 7.3 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 157.1, 138.4, 134.7, 130.3, 126.5, 120.3, 44.2 (2C), 29.7 (3C), 28.0 (3C), 14.6 (2C), 14.3 (3C), 11.1 (3C); LRMS (EI) m/z (rel. intensity) M⁺ not found, 462(M⁺ - Bu, 100); HRMS (EI) calcd for C_{22}H_{41}NO_{3}SSn 518.1749: found 518.1751.

**N,N-Diethyl 2-pinacolboronatephenyl O-sulfamate 4k**

This compound was prepared by Method B using the following materials: 3 (1.00 g, 4.39 mmol), TMEDA (0.73 mL, 4.83 mmol), s-BuLi (4.00 mL, 1.2 M in cyclohexane, 4.83 mmol), THF (10 mL), triisopropyl borate (1.22 mL, 5.27 mmol). Standard workup afforded the crude boronic acid that was dissolved in MeOH (20 mL) containing pinacol (0.57 g, 4.83 mmol), concentrated in vacuo, and diluted with brine (20 mL). Standard workup and flash chromatography (9:1 hexanes / EtOAc) afforded 4k (1.35 g, 87%) as a colourless oil; IR (neat) ν_max 2978, 2940, 1610, 1496, 1444, 1361, 1272, 1157 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.79 (dd, 1H, J = 1.8, 7.2 Hz), 7.45 (td, 1H, J = 1.9, 7.1 Hz), 7.37 (dd, 1H, J = 0.9, 7.4 Hz), 7.25 (td, 1H, J = 1.1, 7.0 Hz), 3.45 (q, 4H, 7.2 Hz), 1.36 (s, 12H), 1.26 (td, 6H, J = 1.3, 7.1 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 154.7, 137.1, 132.5, 126.2, 122.1, 84.2 (2C), 43.7 (2C), 25.2 (4C), 14.0 (2C); LRMS (EI) m/z (rel. intensity) 356(M⁺ + 1, 4), 163(100); HRMS (EI) calcd for C_{16}H_{26}BNO_{5}S 355.1622: found 355.1625.

**N,N-Diethyl 2-bromo-6-trimethylsilylphenyl O-sulfamate 4l**

This compound was prepared by Method B using the following materials: 4h (1.0 g, 3.3 mmol), TMEDA (0.54 mL, 3.6 mmol), LDA (3.60 mL, 1 M in THF, 3.6 mmol), THF (10 mL), chlorotrimethylsilane (0.50 mL, 3.90 mmol). Standard workup and flash chromatography (9:1 hexanes / EtOAc) afforded 4l (1.00 g, 81%) as a colourless solid, mp 67-68 °C (hexanes); IR (KBr) ν_max 2966, 1470, 1368, 1253, 1195, 844 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.60 (dd, 1H, J = 1.6, 7.8 Hz), 7.49 (dd, 1H, J = 1.7, 7.4 Hz),
7.14 (t, 1H, J = 7.6 Hz), 3.55 (q, 4H, J = 7.2 Hz), 1.29 (t, 6H, J = 7.2 Hz), 0.41 (s, 9H);
$^{13}$C NMR (101 MHz, CDCl$_3$) δ 151.0, 138.0, 135.6, 134.7, 127.5, 117.7, 44.0 (2C), 14.1 (2C), 0.5 (3C); LRMS (EI) m/z (rel. intensity) 366(M$^+$ + 2 - Me, 100), 364(M$^+$ - Me, 95);
HRMS (ESI) calcd for C$_{13}$H$_{22}$BrNO$_3$SSi 380.0346: found 380.0346.

$N,N$-Diethyl 2-bromo-6-methoxyphenyl O-sulfamate 4m

This compound was prepared by Method B using the following materials: 4h (1.75 g, 5.7 mmol), TMEDA (0.94 mL, 6.3 mmol), LDA (6.25 mL, 1 M in THF, 6.3 mmol), THF (20 mL), triisopropyl borate (1.57 mL, 6.8 mmol). The reaction mixture was warmed to 0°C, H$_2$O$_2$ (5.5 mL of 35 % w/w solution, 57 mmol) was added and the reaction mixture was warmed to rt over 12 h. The reaction was quenched with H$_2$O and the pH adjusted to 7 with 1 M HCl solution. Standard workup afforded a residue which was taken up in MeCN (20 mL), anhydrous K$_2$CO$_3$ (3.9 g, 28.4 mmol) and MeI (1.8 mL, 28.4 mmol) were added and the reaction mixture was heated at reflux 12 h. Standard workup including washing the EtOAc extracts with NaOH (10 % w/v) solution and flash chromatography (9:1 hexanes / EtOAc) afforded 4m (1.1 g, 57%) as a colourless solid, mp 83-85 °C (hexanes); IR (KBr) $\tilde{\nu}$max 2985, 1585, 1476, 1387, 1253, 1195 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.18 (dd, 1H, J = 1.4, 8.2 Hz), 7.07 (t, 1H, J = 8.2 Hz), 6.93 (dd, 1H, J = 1.4, 8.3 Hz), 3.89 (s, 3H), 3.49 (q, 4H, J = 7.2 Hz), 1.29 (t, 6H, J = 7.2 Hz); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 153.8, 138.4, 127.6, 125.2, 118.0, 112.1, 56.4, 44.0 (3C), 14.0 (3C); LRMS (EI) m/z (rel. intensity) 339(M$^+$ + 2, 90), 337(M$^+$, 100), 203(44), 201(51), 194(70), 166(76), 136(27), 72(25); HRMS (ESI) calcd for C$_{11}$H$_{16}$BrNO$_4$S 338.0051: found 338.0062.

$N,N$-Diethyl 4-methoxyphenyl O-sulfamate 4n

This compound was prepared by Method A using the following materials: NaH (80% in mineral oil, 0.73 g, 24.2 mmol), phenol (3.00 g, 24.2 mmol), $N,N$-diethylsulfamoyl chloride (3.4 mL, 24.2 mmol) in DMF (100 mL). Standard workup and high vacuum distillation afforded pure 4n (5.4 g, 86 %) as a colourless oil; IR (neat) $\tilde{\nu}$max 2985, 2926, 2844, 1591, 1502,
$^{1^*}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.11 (d, 2H, $J$ = 9.2 Hz), 6.79 (d, 2H, $J$ = 9.2 Hz), 3.70 (s, 3H), 3.26 (q, 4H, $J$ = 7.2 Hz), 1.11 (t, 6H, $J$ = 7.1 Hz); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 158.0, 143.7, 123.0 (2C), 114.6 (2C), 55.6, 43.5 (2C), 13.6 (2C); LRMS (EI) $m/z$ (rel. intensity) 259(M$^+$, 92), 123(100); HRMS (ESI) calcd for C$_{11}$H$_{17}$NO$_4$S 260.0947: found 260.0957.

$N,N$-$\text{Diethyl}$ 4-(2,5-$\text{dimethyl-pyrrol-1-yl}$)phenyl O-$\text{sulfamate}$ 4o

$N,N$-$\text{Diethyl}$ 4-(2,5-$\text{dimethyl-pyrrol-1-yl}$)phenyl O-$\text{sulfamate}$ 4o was prepared by Method A using the following materials: NaH (80% in mineral oil, 0.88 g, 29.4 mmol), 4-(2,5-$\text{dimethyl-pyrrol-1-yl}$)-phenol$^5$ (5.00 g, 26.7 mmol), $N,N$-$\text{diethylsulfamoyl}$ chloride (4.53 mL, 32.0 mmol) in DMF (100 mL). Work-up and high vacuum distillation afforded pure 4o (8.00 g, 93%) as a pale-yellow solid, mp 73-74 $^\circ$C (hexanes); IR (KBr) $\nu_{\text{max}}$ 2991, 2945, 1502, 1366, 1157 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37 (d, 2H, $J$ = 8.7 Hz), 7.22 (d, 2H, $J$ = 8.7 Hz), 5.90 (s, 2H), 3.42 (q, 4H, $J$ = 7.2 Hz), 2.02 (s, 6H), 1.23 (t, 6H, $J$ = 7.2 Hz); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 149.5, 137.2, 129.5 (2C), 128.8 (2C), 122.5 (2C), 106.0 (2C), 43.5 (2C), 13.4 (2C), 13.0 (2C); LRMS (EI) $m/z$ (rel. intensity) 323(M$^+$ + 1, 100), 322(M$^+$, 32); HRMS (ESI) calcd for C$_{16}$H$_{22}$N$_2$O$_3$S 323.1430: found 323.1424.

$N,N$-$\text{Diethyl}$ naphthalene-1-yl O-$\text{sulfamate}$ 4p

$N,N$-$\text{Diethyl}$ naphthalene-1-yl O-$\text{sulfamate}$ 4p was prepared by Method A using the following materials: NaH (80% in mineral oil, 1.1 g, 36 mmol), 1-napthol (5.00 g, 34.7 mmol), $N,N$-$\text{diethylsulfamoyl}$ chloride (5.38 mL, 38.2 mmol) in DMF (120 mL). Work-up and high vacuum distillation afforded pure 4p (8.2 g, 85%) as a grey-green solid, mp 51-52 $^\circ$C (hexanes); IR (KBr) $\nu_{\text{max}}$ 2987, 2943, 1606, 1472, 1371, 1218, 1180 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.19 (dd, 1H, $J$ = 1.3, 8.3 Hz), 7.88 (d, 1H, $J$ = 1.3, 7.4 Hz), 7.77 (d, 1H, $J$ = 8.2 Hz), 7.57 (m, 3H), 7.47 (t, 1H, $J$ = 8.0 Hz), 3.50 (q, 4H, $J$ = 7.1 Hz), 1.27 (t, 6H, $J$ = 7.0 Hz); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 146.4, 134.8, 127.9, 127.2 (2C), 126.7, 126.5, 125.4, 121.7, 117.7,
N,N-Diethyl naphthalene-2-yl O-sulfamate 4q

This compound was prepared by Method A using the following materials: NaH (80% in mineral oil, 1.1 g, 36 mmol), 1-napthol (5.00 g, 34.7 mmol), N,N-diethylsulfamoyl chloride (5.38 mL, 38.2 mmol) in DMF (120 mL). Work-up and high vacuum distillation afforded pure 4q (8.6 g, 89%) as a yellow oil; IR (neat) $\nu_{\text{max}}$ 2969, 2940, 1598, 1508, 1464, 1374, 1208, 1170, 1144 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85-7.79 (m, 3H), 7.73 (d, 1H, $J = 2.6$ Hz), 7.57 (m, 2H), 7.40 (dd, 1H, $J = 2.4$, 8.9 Hz), 3.39 (q, 4H, $J = 7.1$ Hz), 1.20 (t, 6H, $J = 7.1$ Hz); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.9, 133.7, 131.8, 129.8, 127.8 (2C), 126.9, 126.2, 121.1, 119.1, 43.6 (2C), 13.6 (2C); LRMS (EI) $m/z$ (rel. intensity) 279(M$^+$, 100); HRMS (EI) calcd for C$_{14}$H$_{17}$NO$_3$S 279.0932: found 279.0931.

N,N-Diethyl pyridin-3-yl O-sulfamate 4r

To a slurry of 3-hydroxypyridine (4.6 g, 48.8 mmol) in PhMe (100 mL) at rt was sequentially added Et$_3$N (8.0 mL, 58.5 mmol), N,N-diethylsulfamoyl chloride (8.25 mL, 58.5 mmol) via syringe. A condenser was then attached, and the mixture brought to reflux. After 12 h, the mixture was cooled and concentrated in vacuo. The residue was dissolved in EtOAc, poured in water and the layers were separated. Standard work-up and high vacuum distillation afforded pure 4r (9.5 g, 85%) as light yellow oil; IR (neat) 2985, 2967, 1579, 1483, 1419, 1391, 1208, 1157 $\nu_{\text{max}}$ cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.53 (d, 1H, $J = 2.7$ Hz), 8.51 (d, 1H, $J = 4.7$ Hz), 7.66 (m, 1H), 7.37 (dd, 1H, $J = 4.7$, 8.4 Hz), 3.40 (q, 4H, $J = 7.2$ Hz), 1.22 (t, 6H, $J = 7.1$ Hz) ppm; $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 147.9, 147.2, 143.7, 129.4, 124.2, 43.5, 13.5 ppm; LRMS (EI) $m/z$ (rel. intensity) 231(M$^+$ + 1, 100); HRMS (ESI) calcd for C$_9$H$_{14}$N$_2$O$_3$S 231.0792: found 231.0798.

N,N-Diethyl pyridin-2-yl O-sulfamate 4s
To a slurry of 2-hydroxypyridine (4.6 g, 48.8 mmol) in PhMe (100 mL) at rt was sequentially added Et₃N (8.0 mL, 58.5 mmol), N,N-diethylsulfamoyl chloride (8.25 mL, 58.5 mmol) via syringe. A condenser was then attached, and the mixture brought to reflux. After 12 h, the reaction mixture was cooled and concentrated in vacuo. The residue was dissolved in EtOAc, poured in water and the layers were separated. Standard work-up and high vacuum distillation afforded pure 4s (9.5 g, 85 %) as light yellow oil; IR (neat) \( \nu_{\text{max}} \) 2978, 1598, 1470, 1432, 1380, 1221, 1157 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.31 (dd, 1H, J = 1.8, 4.8 Hz), 7.75 (ddd, 1H, J = 2.0, 7.6 Hz), 7.19 (dd, 1H, J = 4.9, 7.3 Hz), 7.16 (d, 1H, J = 8.2 Hz), 3.41 (q, 4H, J = 7.3 Hz), 1.19 (t, 6H, J = 7.3 Hz) ppm; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 157.6, 148.2, 140.0, 122.1, 115.2, 43.6 (2C), 13.5 (2C) ppm; LRMS (EI) \( m/z \) (rel. intensity) 231(M\(^+\) + 1, 100); HRMS (ESI) calcd for C\(_9\)H\(_{14}\)N\(_2\)O\(_3\)S 231.0804: found 231.0803.

**N,N-Diethyl 4-diethylcarbamoylphenyl O-sulfamate 4t**

This compound was prepared by Method B using the following materials: N,N-Diethyl 4-brom phenyl O-sulfamate (2.00 g, 6.49 mmol), n-BuLi (2.75 mL, 2.5 M in hexanes, 6.82 mmol), THF (20 mL), N,N-diethylcarbamoyl chloride (0.91 mL, 7.14 mmol). Standard work-up and high vacuum distillation afforded pure 4t (2.00 g, 94 %) as a colourless solid; mp 91-92 °C (hexanes); IR (neat) \( \nu_{\text{max}} \) 2978, 1630, 1464, 1374, 1202, 1150, 863 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.41 (d, 2H, J = 8.6 Hz), 7.31 (d, 2H, J = 8.6 Hz), 3.40 (q, 8H, J = 7.2 Hz), 1.23 (t, 12H, J = 7.2 Hz); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 170.2, 150.8, 135.5, 128.0 (2C), 121.9 (2C), 43.6 (2C), 13.5 (2C) ppm; LRMS (EI) \( m/z \) (rel. intensity) 329(M\(^+\) + 1, 84), 256(100); HRMS (EI) calcd for C\(_{15}\)H\(_{24}\)N\(_2\)O\(_4\)S 327.1381: found 327.1379.

**N,N-Diethyl 2',3'-dimethylbiphenyl-2-yl O-sulfamate 6a**

This compound was prepared by Method C using the following materials: 4i (0.300 g, 0.845 mmol), 2,3-dimethylphenylboronic acid (0.127 g, 0.845 mmol), Na\(_2\)CO\(_3\) (2M, 2 mL), Pd(PPh\(_3\))\(_4\) (48 mg, 5 mol
%, in DME (4 mL), and the reaction mixture was refluxed for 24 h. Standard workup and flash chromatography (19:1 hexanes / EtOAc) afforded 6a (0.267 g, 85%) as a colourless solid, mp 68-70 °C (hexanes); IR (KBr) \( \nu_{\text{max}} \) 2998, 2940, 1585, 1470, 1366, 1214, 1157 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.58 (dd, 1H, \( J = 0.7, 8.2 \) Hz), 7.41 (td, 1H, \( J = 2.1, 8.2 \) Hz), 7.34-7.27 (m, 2H), 7.18 (dd, 1H, \( J = 1.2, 7.2 \) Hz), 7.15 (t, 1H, \( J = 7.4 \) Hz), 7.11 (d, 1H, \( J = 7.2 \) Hz), 2.90 (q, 4H, \( J = 7.2 \) Hz), 2.34 (s, 3H), 2.06 (s, 3H), 0.97 (t, 6H, \( J = 7.2 \) Hz); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 148.1, 137.5, 136.9, 135.8, 135.7, 131.7, 129.5, 128.9, 128.5, 126.5, 125.3, 121.9, 42.8 (2C), 20.8, 17.1, 13.4 (2C); LRMS (EI) \( m/z \) (rel. intensity) 333(M\(^+\), 100); HRMS (EI) calcd for C\(_{18}\)H\(_{23}\)NO\(_3\)S 333.1401: found 333.1399.

\textit{N,N-Diethyl 2',4',6'-trimethylbiphenyl-2-yl O-sulfamate 6b}

This compound was prepared by Method C using the following materials: \textit{4i} (0.300 g, 0.845 mmol), 2,4,6-trimethylphenylboronic acid (0.139 g, 0.845 mmol), Na\(_2\)CO\(_3\) (2M, 2 mL), Pd(PPh\(_3\))\(_4\) (48 mg, 5 mol %), in DME (4 mL), and the reaction mixture was refluxed for 24 h. Additional 2,4,6-trimethylphenylboronic acid (0.139 g, 0.845 mmol) and Pd(PPh\(_3\))\(_4\) (48 mg, 5 mol %) was added and the reaction mixture was refluxed for an additional 24 h. Standard workup and flash chromatography (19:1 hexanes / EtOAc) afforded 6b (0.165 g, 56%) as a colourless solid, mp 61-64 °C (hexanes); IR (KBr) \( \nu_{\text{max}} \) 2978, 2940, 1617, 1444, 1361, 1202, 1182, 1163 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.59 (d, 1H, \( J = 8.1 \) Hz), 7.41 (t, 1H, \( J = 7.8 \) Hz), 7.32 (t, 1H, \( J = 7.6 \) Hz), 7.21 (d, 1H, \( J = 7.5 \) Hz), 7.11 (d, 1H, \( J = 7.2 \) Hz), 2.90 (q, 4H, \( J = 7.2 \) Hz), 2.34 (s, 3H), 2.03 (s, 6H), 0.98 (t, 6H, \( J = 7.2 \) Hz); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 147.9, 137.0, 136.9, 135.8, 135.7, 131.7, 129.5, 128.9, 128.5, 126.5, 125.3, 121.9, 42.8 (2C), 20.8, 17.1, 13.4 (2C); LRMS (EI) \( m/z \) (rel. intensity) 347(M\(^+\), 100); HRMS (EI) calcd for C\(_{19}\)H\(_{25}\)NO\(_3\)S 347.1562: found 347.1556.

\textit{N,N-Diethyl 3'-t-butoxymethyl-biphenyl-2-yl O-sulfamate 6c}

This compound was prepared by Method C using the following materials: \textit{4i} (0.300 g, 0.845 mmol), 3-\textit{t}-butoxymethylphenylboronic acid (0.176 g, 0.845 mmol), Na\(_2\)CO\(_3\)
(2M, 2 mL), Pd(PPh₃)₄ (48 mg, 5 mol %), in DME (4 mL), and the reaction mixture was refluxed for 24 h. Standard workup and flash chromatography (9:1 hexanes / EtOAc) afforded 6c (0.326 g, 99%) as a colourless oil; IR (neat) \( \nu_{\text{max}} \) 3062, 2978, 2940, 2883, 1610, 1470, 1380, 1208, 1163, 1112, 1074 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 7.61 (d, 1H, J = 8.0 Hz), 7.34 (d, 1H, J = 7.3 Hz), 7.49 (s, 1H), 7.42-7.37 (m, 5H), 4.51 (s, 2H), 2.93 (q, 4H, J = 7.2 Hz), 1.33 (s, 9H), 1.02 (t, 6H, J = 7.1 Hz); \(^{13}\)C NMR (101 MHz, CDCl₃) \( \delta \) 147.5, 139.9, 137.2, 135.2, 131.2, 128.9, 128.6, 128.5, 128.1, 126.7, 126.5, 122.5, 73.5, 64.1, 43.0 (2C), 27.7 (3C), 13.5 (2C); LRMS (EI) \( m/z \) (rel. intensity) M⁺ not found, 334(M⁺ - tBu, 45), 318(100); HRMS (EI) calcd for C₂₁H₂₉NO₄S 391.1816: found 391.1817.

\textbf{\( N,N\)-Diethyl 4’-cyanobiphenyl-2-yl O-sulfamate 6d }  

This compound was prepared by \textbf{Method C} using the following materials: 4i (0.300 g, 0.845 mmol), 4-cyanophenylboronic acid (0.147 g, 0.845 mmol), Na₂CO₃ (2M, 2 mL), Pd(PPh₃)₄ (48 mg, 5 mol %), in DME (4 mL), and the reaction mixture was refluxed for 24 h. Standard workup and flash chromatography (8:2 hexanes / EtOAc) afforded 6d (0.260 g, 93%) as a colourless oil; IR (neat) \( \nu_{\text{max}} \) 2972, 2838, 1598, 1163 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 7.74 (d, 2H, J = 8.1 Hz), 7.62 (d, 2H, J = 8.5 Hz), 7.47-7.43 (m, 1H), 7.39 - 7.36 (m, 2H), 3.05 (q, 4H, J = 7.2 Hz), 1.05 (t, 6H, J = 7.2 Hz); \(^{13}\)C NMR (101 MHz, CDCl₃) \( \delta \) 147.2, 142.3, 133.4, 131.9 (2C), 130.9, 130.5 (2C), 129.9, 126.9, 122.7, 118.8, 111.3, 43.0 (2C), 13.4 (2C); LRMS (EI) \( m/z \) (rel. intensity) 330(M⁺, 100); HRMS (EI) calcd for C₁₇H₁₈N₂O₃S 330.1040: found 330.1038.

\textbf{\( N,N\)-Diethyl 2’-methoxybiphenyl-2-yl O-sulfamate 6e }  

This compound was prepared by \textbf{Method C} using the following materials: 4i (0.300 g, 0.845 mmol), 3-methoxyphenylboronic acid (0.129 g, 0.845 mmol), Na₂CO₃ (2M, 2 mL), Pd(PPh₃)₄ (48 mg, 5 mol %), in DME (4 mL), and the reaction mixture was refluxed for 24 h. Standard workup and flash chromatography (9:1 hexanes / EtOAc) afforded 6e (0.240 g, 85%) as a colourless solid, mp 69-70 °C (hexanes); IR (KBr) \( \nu_{\text{max}} \) 2972, 2838, 1598,
1483, 1368, 1253, 1208, 1157 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) d 7.57 (d, 1H, J = 8.1 Hz), 7.41-7.34 (m, 4H), 7.31 (t, 1H, J = 7.6 Hz), 7.03 (t, 1H, 7.5 Hz), 6.97 (d, 1H, 8.3 Hz), 3.78 (s, 1H), 2.91 (q, 4H, 7.2 Hz), 1.00 (t, 1H, J = 7.2 Hz); $^{13}$C NMR (101 MHz, CDCl$_3$) d 157.4, 148.4, 132.2, 132.1, 132.0, 129.5, 129.0, 126.8, 126.4, 122.0, 120.6, 111.0, 55.9, 43.0 (2C), 13.6 (3C); LRMS (EI) $m/z$ (rel. intensity) 335(M$^+$, 100); HRMS (EI) calcd for C$_{17}$H$_{21}$NO$_4$S 335.1200: found 335.1191.

**N,N-Diethyl 3'-methoxybiphenyl-2-yl O-sulfamate 6f**

This compound was prepared by **Method C** using the following materials: 4i (0.300 g, 0.845 mmol), 3-methoxyphenylboronic acid (0.129 g, 0.845 mmol), Na$_2$CO$_3$ (2M, 2 mL), Pd(PPh$_3$)$_4$ (48 mg, 5 mol %), in DME (4 mL), and the reaction mixture was refluxed for 24 h. Standard workup and flash chromatography (9:1 hexanes / EtOAc) afforded 6f (0.260 g, 92%) as a colourless oil; IR (neat) $\nu_{\text{max}}$ 2985, 2946, 2838, 1598, 1476, 1374, 1208, 1157 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) d 7.59 (dd, 1H, J = 1.0, 8.1 Hz), 7.42-7.31 (m, 4H), 7.09-7.06 (m, 2H), 6.92 (dd, 1H, J = 1.8, 8.3 Hz), 3.83 (s, 1H), 2.97 (q, 4H, J = 7.2 Hz), 1.01 (t, 6H, J = 7.2 Hz); $^{13}$C NMR (101 MHz, CDCl$_3$) d 159.7, 147.7, 139.0, 135.3, 131.4, 129.4, 129.1, 126.9, 122.8, 122.5, 115.6, 113.5, 55.7, 43.3 (2C), 13.8 (2C); LRMS (EI) $m/z$ (rel. intensity) 335(M$^+$, 100); HRMS (EI) calcd for C$_{17}$H$_{21}$NO$_4$S 335.1190: found 335.1191.

**N,N-Diethyl 4'-methoxybiphenyl-2-yl O-sulfamate 6g**

From 4h compound 6g was prepared by **Method C** using the following materials: 4h (0.308 g, 1.00 mmol), 4-methoxyphenylboronic acid (0.151 g, 1.00 mmol), Na$_2$CO$_3$ (2M, 5 mL), Pd(PPh$_3$)$_4$ (57 mg, 5 mol %), in DME (5 mL), and the reaction mixture was refluxed for 24 h. Standard workup and flash chromatography (9:1 hexanes / EtOAc) afforded 6g (0.282 g, 85%) as a colourless oil.

From 4k compound 6g was also prepared by **Method C** using the following materials: 4k (0.355 g, 1.00 mmol), 4-bromoanisole (0.126 mL, 1.00 mmol), Na$_2$CO$_3$ (2M, 5 mL), Pd(PPh$_3$)$_4$ (56 mg, 5 mol %), in DME (5 mL), and the reaction mixture was
refluxed for 24 h. Standard workup and flash chromatography (9:1 hexanes / EtOAc) afforded 6g (0.312 g, 93%) as a colourless oil; IR (neat) $\nu_{\text{max}}$ 2985, 2934, 2838, 1611, 1515, 1483, 1368, 1246, 1208, 1150 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) d 7.59 (dd, 1H, $J = 2.0, 8.8$ Hz), 7.45 (dd, 2H, $J = 2.0, 6.8$ Hz), 7.39-7.28 (m, 3H), 6.88 (dd, 2H, $J = 2.0, 8.8$ Hz), 3.38 (s, 3H), 2.96 (q, 4H, $J = 7.1$ Hz), 1.02 (t, 6H, 7.2 Hz); $^{13}$C NMR (75 MHz, CDCl$_3$) d 159.8, 146.3, 135.5, 131.8, 131.5, 130.4, 128.9, 127.2, 123.2, 114.3, 56.0, 43.7, 14.2; LRMS (EI) $m/z$ (rel. intensity) 335(M$^+$, 66), 199(100), 184(25), 128(12); HRMS (EI) calcd for C$_{17}$H$_{21}$NO$_4$S 335.1195; found 335.1191.

$N,N$-Diethyl 3',5'-dichlorobiphenyl-2-yl O-sulfamate 6h

This compound was prepared by Method C using the following materials: 4i (0.300 g, 0.845 mmol), 3,5-dichlorophenylboronic acid (0.162 g, 0.845 mmol), Na$_2$CO$_3$ (2M, 2 mL), Pd(PPh$_3$)$_4$ (48 mg, 5 mol %), in DME (4 mL), and the reaction mixture was refluxed for 24 h. Standard workup and flash chromatography (19:1 hexanes / EtOAc) afforded 6h (0.255 g, 91%) as a colourless oil; IR (neat) $\nu_{\text{max}}$ 2978, 2940, 1591, 1489, 1451, 1368, 1208, 1157 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) d 7.61 (dd, 1H, $J = 0.7, 8.2$ Hz), 7.44-7.31 (m, 6H), 3.19 (q, 4H, 7.2 Hz), 1.13 (t, 6H, $J = 7.2$ Hz); $^{13}$C NMR (101 MHz, CDCl$_3$) d 147.6, 140.6, 134.9 (2C), 132.6, 131.1, 130.1, 128.5 (2C), 127.7, 127.0, 122.8, 43.3 (2C), 13.6 (2C); LRMS (EI) $m/z$ (rel. intensity) 375(M$^+$ + 2, 60), 373(M$^+$, 100); HRMS (EI) calcd for C$_{16}$H$_{17}$Cl$_2$NO$_3$S 373.0306; found 373.0306.

$N,N$-Diethyl 2-furan-2-ylphenyl O-sulfamate 6i

This compound was prepared by Method C using the following materials: 4i (0.300 g, 0.845 mmol), furan-2-boronic acid (0.112 g, 0.845 mmol), Na$_2$CO$_3$ (2M, 2 mL), Pd(PPh$_3$)$_4$ (96 mg, 10 mol %), in DME (4 mL), and the reaction mixture was refluxed for 24 h. Additional furan-2-boronic acid (0.112 g, 0.845 mmol) and Pd(PPh$_3$)$_4$ (48 mg, 5 mol %) was added and the reaction mixture was stirred at reflux for an additional 24 h. Standard workup and flash chromatography (9:1 hexanes / EtOAc) afforded 6i (0.190 g, 76%) as a colourless oil; IR (neat) $\nu_{\text{max}}$ 2985, 2940, 1483, 1374, 1202, 1157 cm$^{-1}$; $^1$H NMR (400
Benzyne Trapping Experiments on 4h, i, l, m. 1-Naphthol 7a

This compound was prepared by Method E using the following materials: 4h (500 mg, 1.62 mmol), n-BuLi (0.7 mL, 2.44 M in hexanes, 1.7 mmol), furan (1.2 mL, 16.2 mmol), Et₂O (3.5 mL), followed by standard workup and flash chromatography (9:1 hexanes / EtOAc) afforded a residue that was taken up in absolute EtOH (5 mL), concentrated HCl was added (2 drops), and the whole was refluxed for 12 h. The mixture was diluted with H₂O, extracted with Et₂O (x3), dried (Na₂SO₄), and concentrated affording a solid that was recrystallized (MeOH) yielding 7a (50 mg, 21 %) as colourless crystals.

This compound was also prepared by Method E using the following materials: 4l (500 mg, 1.32 mmol), n-BuLi (0.61 mL, 2.4 M in hexanes, 1.45 mmol), furan (1.0 mL, 13.2 mmol), Et₂O (3 mL), followed by standard workup afforded a residue that was taken up in absolute EtOH (5 mL), concentrated HCl was added (2 drops), and the whole was refluxed for 12 h. The mixture was diluted with H₂O (10 mL), extracted with CH₂Cl₂ (x3), extracted with aqueous NaOH (x 2, 4 M), acidified with HCl (concentrated), extracted with CH₂Cl₂ (x3), dried (Na₂SO₄), and concentrated affording a solid that was recrystallized (MeOH) yielding 7a (94 mg, 50 %) as colourless crystals.

This compound was also prepared by a modified procedure₆ using the following materials: 4i (500 mg, 1.4 mmol), iPrMgCl (0.77 mL, 2.0 M in Et₂O, 1.54 mmol), furan (1.0 mL, 14 mmol), Et₂O (20 mL), followed by standard workup afforded a residue that was taken up in MeOH (5 mL), concentrated HCl was added (3 drops), and the whole was refluxed for 3 h. The mixture was diluted with H₂O (10 mL), extracted with CH₂Cl₂ (x3), dried (Na₂SO₄), concentrated, and flash chromatographed (9:1 hexanes / EtOAc) affording 7a (140 mg, 70 %) as colourless crystals, mp 91-92 °C (MeOH) [lit⁷ mp 89-90 °C] whose spectral data was consistent with that reported for the authentic material.
5-Methoxynaphthol 7b

This compound was prepared by **Method E** using the following materials: 4m (500 mg, 1.48 mmol), n-BuLi (0.67 mL, 2.44 M in hexanes, 1.63 mmol), furan (1.1 mL, 14.8 mmol), Et$_2$O (3 mL), followed by standard workup and flash chromatography (9:1 hexanes / EtOAc) afforded a residue that was taken up in MeOH (10 mL), concentrated HCl was added (2 drops), and the whole was refluxed for 12 h. The mixture was concentrated, diluted with H$_2$O (10 mL) extracted with CH$_2$Cl$_2$ (x3), extracted with aqueous NaOH (x2, 4 M), acidified with conc HCl, extracted with CH$_2$Cl$_2$ (x3), dried (Na$_2$SO$_4$), and concentrated affording a solid that was recrystallized (MeOH) yielding 7b (80 mg, 31 %) as brown crystals, mp 137-138 °C (MeOH) [lit$^8$ mp 137-139 °C] $^1$H NMR (400 MHz, CDCl$_3$) d 7.89 (d, 1H, J = 8.5 Hz), 7.77 (d, 1H, J = 8.5 Hz), 7.43 (t, 1H, J = 7.8 Hz), 7.33 (t, 1H, J = 7.6 Hz), 6.89-6.86 (m, 2H), 5.23 (bs, 1H), 4.03 (s, 3H) ppm; $^{13}$C NMR (101 MHz, CDCl$_3$) d 155.4, 151.2, 127.0, 125.3, 125.2, 114.8, 113.6, 109.5, 104.5, 55.6 ppm; (EI) $m$/z (rel. intensity) 174 (M$^+$, 100).

(3’-Methoxy-biphenyl-2-yl)-trimethyl-silane 9a

This compound was prepared by **Method D** using the following materials: 4e (322 mg, 1.0 mmol), NiClCpIMes (12 mg, 0.025 mmol), Et$_2$O (2.5 mL), 3-methoxyphenylmagnesium bromide (2.5 mL, 1.0 M (THF), 2.5 mmol), was stirred at reflux for 12 h. Standard workup and flash chromatography (99:1 hexanes / EtOAc) afforded 9a (195 mg, 76 %) as a colourless oil; IR (neat) $\nu_{\text{max}}$ 2953, 2896, 2838, 1611, 1592, 1259, 844 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) d 7.59-7.57 (m, 1H), 7.36-7.28 (m, 2H), 7.26-7.16 (m, 2H), 6.85-6.88 (m, 2H), 6.82-6.81 (m, 1H), 3.79 (s, 3H), 0.00 (s, 9H) ppm; $^{13}$C NMR (101 MHz, CDCl$_3$) d 158.4, 148.5, 145.3, 137.3, 134.0, 128.7, 128.1, 127.9, 125.8, 121.4, 114.4, 112.2, 54.6, 0.0 (3C) ppm; LRMS (EI) $m$/z (rel. intensity) 234 (M$^+$, 3), 241 (M$^+$ - Me, 100); HRMS (EI) calcd for C$_{16}$H$_{20}$OSi 256.1283: found 256.1294.
3-Methoxy-2''',3''''-dimethyl-[1,1';2',1'']tertphenyl 9b

This compound was prepared by Method D using the following materials: 6a (200 mg, 0.6 mmol), NiClCpIMes (6 mg, 0.02 mmol), Et₂O (2 mL), 3-methoxyphenylmagnesium bromide (1.5 mL, 1.0 M (THF), 1.5 mmol), was stirred at reflux for 24 h. Standard workup and flash chromatography (19:1 hexanes / EtOAc) afforded 9b (111 mg, 64 %) as a colourless oil; IR (neat) \( \nu_{\text{max}} \) 2940, 1608, 1565, 1482, 1432, 1186, cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.46 (t, 1H, \( J = 7.1 \) Hz), 7.40 (qn, 2H, \( J = 6.1 \) Hz), 7.33 (d, 1H, \( J = 7.4 \) Hz), 7.13 (t, 1H, \( J = 8.0 \) Hz), 7.08-7.03 (m, 3H), 6.80 (d, 1H, \( J = 7.6 \) Hz), 6.73 (d, 1H, \( J = 8.3 \) Hz), 6.61 (s, 1H), 3.57 (s, 3H), 2.21 (s, 3H), 1.83 (s, 3H) ppm; \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 158.7, 142.8, 141.5, 140.9 (2C), 136.6, 134.5, 130.8, 129.7, 128.7, 128.5, 128.3, 127.4, 127.1, 124.9, 121.8, 114.5, 112.9, 55.0, 20.5, 16.7 ppm; LRMS (EI) \( m/z \) (rel. intensity) 288 (M\(^+\), 100); HRMS (EI) calcd for C\(_{21}\)H\(_{20}\)O 288.1513: found 288.1514.

4-Methoxybiphenyl 9c

This compound was prepared by Method D using the following materials: 4l (259 mg, 1.0 mmol), NiClCpIMes (4.6 mg, 0.01 mmol), Et₂O (5 mL), phenylmagnesium bromide (0.87 mL, 2.88 M (Et₂O), 2.5 mmol), was stirred at reflux for 19 h. Standard workup and flash chromatography (99:1 hexanes / EtOAc) afforded 9c (86 mg, 47 %) as a colourless solid, mp 82-83 °C (hexanes) [lit\(^9\) mp 83.5-85.5 °C] whose spectral data was consistent with that reported for the authentic material.

\( N \)-Acetyl-4-aminobiphenyl 9d

This compound was prepared by Method D using the following materials: 4m (322 mg, 1.0 mmol), NiClCpIMes (12 mg, 0.025 mmol), Et₂O (5 mL), phenylmagnesium bromide (0.60 mL, 2.88 M (Et₂O), 1.7 mmol), was stirred at rt for 1 h. Standard workup afforded a brown oil that was dissolved in EtOH/H₂O (2:1, 6 mL) and hydroxylamine hydrochloride (690 mg, 10 mmol) and triethylamine (0.28 mL, 2 mmol) were added. The
mixture was stirred at 90°C for 24 h, 1 M HCl (6 mL) was added, and the solution was washed with Et₂O (x2), adjusted to pH 10 (4 M NaOH), and extracted with Et₂O (x2). The organic extract was dried (Na₂SO₄) and concentrated *in vacuo* to afford a colourless oil that was dissolved in anhyd CH₂Cl₂ (5 mL) and treated with acetic anhydride (0.1 mL, 1.2 mmol) and triethylamine (0.28 mL, 2 mmol) under an Ar atmosphere. The mixture was stirred at rt for 1 h before treatment with satd aq NH₄Cl solution (5 mL). Standard workup and flash chromatography (1:1 hexanes / EtOAc) yielded 9d (105 mg, 50%) as a colourless solid, mp 171-172°C [lit¹⁰ mp 150-153°C] whose spectral data was consistent with that reported for the authentic material.

**N-(4-(3-Methoxyphenyl)phenyl)acetamide 9e**

This compound was prepared by Method D using the following materials: 4m (322 mg, 1.0 mmol), NiClCpIMes (12 mg, 0.025 mmol), Et₂O (5 mL), 3-methoxyphenylmagnesium bromide (2 mL, 1.0 M (THF), 2 mmol), was stirred at rt for 3 h. Standard workup afforded a brown oil that was dissolved in EtOH/H₂O (2:1, 6 mL) and hydroxylamine hydrochloride (690 mg, 10 mmol) and triethylamine (0.28 mL, 2 mmol) were added. The mixture was stirred at 90°C for 24 h, 1 M HCl (6 mL) was added, and the solution was washed with Et₂O (x2), brought to pH 10 (4 M NaOH), extracted with Et₂O (x2). The organic extract was dried (Na₂SO₄) and concentrated *in vacuo* to afford a colourless oil that was dissolved in anhyd CH₂Cl₂ (5 mL) and added acetic anhydride (0.1 mL, 1.2 mmol) and triethylamine (0.28 mL, 2 mmol) under an Ar atmosphere. The mixture was stirred at rt for 1 h before treatment with satd aq NH₄Cl solution (5 mL). Standard workup and flash chromatography (1:1 hexanes / EtOAc) yielded 9e (110 mg, 46%) as a pale oil; IR (neat) \( \nu_{\text{max}} \) 3344, 3311, 1675, 1598, 1534, 1393, 1214 cm\(^{-1}\); \(^1\)H NMR (400 MHz, acetone-\(d_6\)) \( d \) 9.37 (s, 1H), 7.78 (d, 2H, \( J = 8.4 \) Hz), 7.61 (d, 2H, \( J = 8.5 \) Hz), 7.34 (t, 1H, \( J = 7.8 \) Hz), 7.19 (m, 2H), 6.89 (d, 1H, \( J = 7.1 \) Hz), 3.86 (s, 3H), 3.12 (s, 1H), 2.14 (s, 3H) ppm; \(^13\)C NMR (101 MHz, acetone-\(d_6\)) \( d \) 168.3, 160.0, 142.0, 137.6, 137.0, 129.9, 127.6 (3C), 120.5, 119.4, 112.6, 112.5, 55.3, 24.5 ppm; LRMS (EI) \( m/z \) (rel. intensity) 241 (M⁺, 70), 199(100); HRMS (EI) calcd for C\(_{15}\)H\(_{15}\)NO\(_2\) 241.1103: found 241.1103.
1-Phenylnapthalene 9f

This compound was prepared by Method D using the following materials: 4n (279 mg, 1.0 mmol), NiClCpIMes (4.6 mg, 0.01 mmol), Et₂O (5 mL), phenylmagnesium bromide (0.42 mL, 2.88 M (Et₂O), 1.2 mmol), was stirred at 0°C for 10 min. Standard workup and flash chromatography (99:1 hexanes / EtOAc) afforded 9f (171 mg, 84 %) as an oil whose spectral data was consistent with that reported for the authentic material.\(^8\)

1-(3-Methoxy-phenyl)-naphthalene 9g

This compound was prepared by Method D using the following materials: 4n (279 mg, 1.0 mmol), NiClCpIMes (4.6 mg, 0.01 mmol), Et₂O (3.0 mL), 3-methoxyphenylmagnesium bromide (2.0 mL, 1.0 M (THF), 2.0 mmol), was stirred at rt for 1 h. Standard workup and flash chromatography (44:1 hexanes / EtOAc) afforded 9g (185 mg, 79 %) as a waxy oil whose spectral data was consistent with that reported for the authentic material.\(^11\)

2-(2,4,6-Trimethyl-phenyl)-naphthalene 9h

This compound was prepared by Method D using the following materials: 4o (279 mg, 1.0 mmol), NiClCpIMes (12 mg, 0.025 mmol), Et₂O (2.5 mL), 3-mesitylmagnesium bromide (2.5 mL, 1.0 M (Et₂O), 2.5 mmol), was stirred at reflux for 18 h. Standard workup and flash chromatography (99:1 hexanes / EtOAc) afforded 9h (170 mg, 69 %) as a waxy oil\(^12\); \(^1\)H NMR (400 MHz, CDCl₃) d 8.08-8.00 (m, 3H), 7.81 (s, 1H), 7.68-7.64 (m, 2H), 7.48 (dd, 1H, \(J = 1.4, 8.4\) Hz), 7.18 (s, 2H), 2.56 (s, 3H), 2.23 (s, 6H) ppm; \(^13\)C NMR (101 MHz, CDCl₃) d 140.0, 138.9, 136.9, 136.3, 132.5, 128.3 (4C), 128.2, 128.1 (3C), 127.9, 126.2, 125.9, 21.3, 21.0 (2C) ppm; LRMS (El) \(m/z\) (rel. intensity) 246 (M⁺, 100).

2-(3-Methoxy-phenyl)-naphthalene 9i
This compound was prepared by **Method D** using the following materials: **4o** (279 mg, 1.0 mmol), NiClCpIMes (12 mg, 0.025 mmol), Et₂O (2.5 mL), 3-methoxyphenylmagnesium bromide (2.5 mL, 1.0 M (THF), 2.5 mmol), was stirred at rt for 1 h. Standard workup and flash chromatography (44:1 hexanes / EtOAc) afforded **9i** (200 mg, 86%) as a colourless solid, mp 68-70 °C [lit.\(^{13}\) mp 90 °C]; \(^1\)H NMR (400 MHz, CDCl₃) δ 8.11 (d, 1H, J = 7.8 Hz), 8.03 (d, 1H, J = 7.8 Hz), 7.99 (d, 1H, J = 7.8 Hz), 7.67-7.51 (m, 5H), 7.25-7.21 (m, 2H), 7.13-7.11 (m, 1H), 3.97 (s, 3H) ppm; \(^{13}\)C NMR (101 MHz, CDCl₃) δ 159.7, 142.4, 140.3, 134.0, 131.8, 129.4, 128.4, 127.4, 127.0, 126.2, 125.9 (2C), 125.5, 122.7, 115.8, 113.0, 55.4 ppm.

**3-p-Tolyl-pyridine 9j**

This compound was prepared by **Method D** using the following materials: **4p** (690 mg, 3.0 mmol), NiClCpIMes (28 mg, 0.02 mmol), Et₂O (5 mL), tolylmagnesium bromide (4 mL, 1.0 M (Et₂O), 2.0 mmol), was stirred at rt for 8 h. Standard workup and flash chromatography (19:1 hexanes / EtOAc) afforded **9j** (395 mg, 78 %) as an off-white solid, mp 38-39 °C whose spectral data was consistent with that reported for the authentic material.\(^{14}\)

**3-(3-Methoxy-phenyl)-pyridine 9k**

This compound was prepared by **Method D** using the following materials: **4p** (460 mg, 2.0 mmol), NiClCpIMes (24 mg, 0.025 mmol), Et₂O (5 mL), 3-methoxyphenylmagnesium bromide (4.0 mL, 1.0 M (THF), 4.0 mmol), was stirred at rt for 4 h. Standard workup and flash chromatography (65:35 hexanes / EtOAc) afforded **9k** (160 mg, 85 %) as a colourless oil\(^{15}\); \(^1\)H NMR (400 MHz, CDCl₃) δ 8.87 (bs, 1H), 8.61 (bs, 1H), 7.89 (d, 1H, J = 7.6 Hz), 7.41 (t, 1H, J = 7.9 Hz), 7.39 (bs, 1H), 7.18 (dd, 1H, J = 1.4, 7.6 Hz), 7.13-7.12 (m, 1H), 6.99-6.96 (m, 1H), 3.89 (s, 3H) ppm; \(^{13}\)C NMR (101 MHz, CDCl₃) δ 160.2, 148.5, 139.0, 136.6, 134.5, 130.2, 129.4, 123.6, 113.5, 113.0, 55.4 ppm; LRMS (EI) m/z (rel. intensity) 185(M⁺, 100).
2-p-Tolyl-pyridine 9l

This compound was prepared by Method D using the following materials: 4q (690 mg, 3.0 mmol), NiClCpIMes (28 mg, 0.02 mmol), Et₂O (5 mL), tolylmagnesium bromide (6 mL, 1.0 M (Et₂O), 6.0 mmol), was stirred at rt for 8 h. Standard workup and flash chromatography (9:1 hexanes / EtOAc) afforded 9l (415 mg, 82 %) as a colourless oil whose spectral data was consistent with that reported for the authentic material.¹⁶

2-(3-Methoxy-phenyl)-pyridine 9m

This compound was prepared by Method D using the following materials: 4q (460 mg, 2.0 mmol), NiClCpIMes (24 mg, 0.05 mmol), Et₂O (5 mL), 3-methoxyphenylmagnesium bromide (4.0 mL, 1.0 M (THF), 4.0 mmol), was stirred at rt for 4 h. Standard workup and flash chromatography (7:3 hexanes / EtOAc) afforded 9m (173 mg, 73 %) as a colourless oil whose spectral data was consistent with that reported for the authentic material.¹⁷
Copies of $^1$H or $^{13}$C NMR Spectral Data
$^{13}$C NMR spectrum of compound $4b$ in CDCl$_3$.

$^{1}H$ NMR spectrum of compound $4c$ in CDCl$_3$. 

Chemical shifts are indicated in ppm.