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. ^1H 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_2O 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',N'*-tetramethylethylenediamine (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 syringe-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} $\text{Pd}(\text{PPh}_3)_4$ was freshly prepared according to a literature procedure³ 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 equimolar 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 *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 Et₂O (2.5 mL) under an Ar atmosphere was added NiClCpIMes (0.01 mmol) followed by *p*-tolylphenylmagnesium bromide (1.5 mmol) *via* syringe. The brown mixture was stirred at rt until consumption of starting material (TLC monitoring) and then quenched carefully with saturated NH₄Cl solution. The magnesium salts were dissolved by the addition of H₂O, 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 (Na₂SO₄), and concentrated *in vacuo*. The crude biaryl was purified *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 Et₂O (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 **Method A** using the following materials: NaH (80% in mineral oil, 3.35 g, 112 mmol), phenol (10 g, 106 mmol), *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, [lit⁴ 118 °C/4 mm Hg]; ¹H NMR (300 MHz, CDCl₃) δ 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); ¹³C NMR (75 MHz, CDCl₃) δ 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) ν_{max} 2991, 2889, 1700, 1611, 1470, 1381, 1208, 1157 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 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, 7.1 Hz), 1.27 (t, 6H, $J = 7.2$ Hz); ^{13}C NMR (75 MHz, CDCl_3) δ 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($\text{M}^+ + 1$, 37), 256($\text{M}^+ - 1$, 36), 242(100); HRMS (EI) calcd for $\text{C}_{11}\text{H}_{15}\text{NO}_4\text{S}$ 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) ν_{max} 2985, 2944, 1649, 1445, 1374, 1214, 1163 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 7.50 (d, 1H, $J = 8.2$ Hz), 7.36 (m, 1H), 7.24 (m, 1H), 3.62 (m, 1H), 3.34 (q, 5H, 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) δ 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($\text{M}^+ + 3$, 20), 329($\text{M}^+ + 2$, 100); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{25}\text{NO}_4\text{S}$ 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) $\nu_{\max}$ 3528, 2971, 2940, 1604, 1451, 1374, 1208, 1157 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 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) δ 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_2O , 100); HRMS (EI) calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_4\text{S}$ 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) $\nu_{\max}$ 2978, 2936, 1578, 1470, 1389, 1208, 1157 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 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) δ 147.7, 132.3, 127.1, 126.6, 126.0, 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 $\text{C}_{11}\text{H}_{17}\text{NO}_3\text{S}_2$ 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) $\nu_{\max}$ 2967, 2908, 1591, 1470, 1380, 1253, 1144, 831 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 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) δ 157.0, 136.3, 131.5, 131.4, 125.9, 119.6, 44.1 (2C), 14.5 (2C), 0.2

(3C); LRMS (EI) m/z (rel. intensity) 302($M^+ + 1$, 1), 286(100); HRMS (EI) calcd for $C_{13}H_{17}NO_3SSi$ 301.1171; found 301.1168.

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) $\nu_{\max}$ 3388, 2991, 2940, 1726, 1496, 1374, 1234, 1157 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 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) δ 156.5, 155.4, 145.6, 135.6, 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 $C_{16}H_{25}N_3O_7S$ 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) $\nu_{\max}$ 2985, 2941, 1579, 1470, 1368, 1214, 1163 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 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) δ 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 $C_{10}H_{14}ClNO_3S$ 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) $\nu_{\max}$ 2978, 2946, 1585, 1470, 1374, 1208, 1163 cm^{-1} ; ^1H 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, 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($\text{M}^+ + 2$, 53), 307(M^+ , 51), 294(22), 292(21), 136(100); HRMS (EI) calcd for $\text{C}_{10}\text{H}_{14}\text{BrNO}_3\text{S}$ 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 $^{\circ}\text{C}$; IR (neat) $\nu_{\max}$ 2978, 2935, 1572, 1464, 1388, 1208, 1170 cm^{-1} ; ^1H 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 $\text{C}_{10}\text{H}_{14}\text{INO}_3\text{S}$ 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) $\nu_{\max}$ 2959,

2921, 1566, 1457, 1374, 1208, 1150 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) 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); ^{13}C NMR (75 MHz, CDCl_3) 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($\text{M}^+ - \text{Bu}$, 100); HRMS (EI) calcd for $\text{C}_{22}\text{H}_{41}\text{NO}_3\text{SSn}$ 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, CDCl_3) 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); ^{13}C NMR (100 MHz, CDCl_3) 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($\text{M}^+ + 1$, 4), 163(100); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{26}\text{BNO}_5\text{S}$ 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 $^{\circ}\text{C}$ (hexanes); IR (KBr) ν_{max} 2966, 1470, 1368, 1253, 1195, 844 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) 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($\text{M}^+ + 2 - \text{Me}$, 100), 364($\text{M}^+ - \text{Me}$, 95); HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{22}\text{BrNO}_3\text{SSi}$ 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_2O_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_2O 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_2CO_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) ν_{max} 2985, 1585, 1476, 1387, 1253, 1195 cm^{-1} ; ^1H 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($\text{M}^+ + 2$, 90), 337(M^+ , 100), 203(44), 201(51), 194(70), 166(76), 136(27), 72(25); HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{16}\text{BrNO}_4\text{S}$ 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) ν_{max} 2985, 2926, 2844, 1591, 1502,

1368, 1253, 1202, 1157 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 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) δ 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 $\text{C}_{11}\text{H}_{17}\text{NO}_4\text{S}$ 260.0947; found 260.0957.

N,N-Diethyl 4-(2,5-dimethyl-pyrrol-1-yl)phenyl O-sulfamate **4o**

This compound was prepared by **Method A** using the following materials: NaH (80% in mineral oil, 0.88 g, 29.4 mmol), 4-(2,5-dimethyl-pyrrol-1-yl)-phenol⁵ (5.00 g, 26.7 mmol), *N,N*-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 °C (hexanes); IR (KBr) ν_{max} 2991, 2945, 1502, 1366, 1157 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 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) δ 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($\text{M}^+ + 1$, 100), 322(M^+ , 32); HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{22}\text{N}_2\text{O}_3\text{S}$ 323.1430; found 323.1424.

N,N-Diethyl naphthalene-1-yl O-sulfamate **4p**

This compound was prepared by **Method A** using the following materials: NaH (80 % in mineral oil, 1.1 g, 36 mmol), 1-naphthol (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 **4p** (8.2 g, 85 %) as a grey-green solid, mp 51-52 °C (hexanes); IR (KBr) ν_{max} 2987, 2943, 1606, 1472, 1371, 1218, 1180 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 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) δ 146.4, 134.8, 127.9, 127.2 (2C), 126.7, 126.5, 125.4, 121.7, 117.7,

43.5 (2C), 13.7 (2C); LRMS (EI) m/z (rel. intensity) 279(M^+ , 100); HRMS (EI) calcd for $C_{14}H_{17}NO_3S$ 279.0929; found 279.0931.

***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-naphthol (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) $\nu_{\max}$ 2969, 2940, 1598, 1508, 1464, 1374, 1208, 1170, 1144 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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 $C_{14}H_{17}NO_3S$ 279.0932; found 279.0929.

***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_3N (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 $\nu_{\max}$ cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 147.6, 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 $C_9H_{14}N_2O_3S$ 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*-diethylsulfonyl 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) $\nu_{\max}$ 2978, 1598, 1470, 1432, 1380, 1221, 1157 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 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; ¹³C NMR (101 MHz, CDCl₃) δ 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 C₉H₁₄N₂O₃S 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-bromophenyl 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) $\nu_{\max}$ 2978, 1630, 1464, 1374, 1202, 1150, 863 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 170.2, 150.8, 135.5, 128.0 (2C), 121.9 (2C), 43.6 (2C), 13.5 (2C); LRMS (EI) *m/z* (rel. intensity) 329(M⁺ + 1, 84), 256(100); HRMS (EI) calcd for C₁₅H₂₄N₂O₄S 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), 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 (19:1 hexanes / EtOAc) afforded **6a** (0.267 g, 85%) as a colourless solid, mp 68-70 °C (hexanes); IR (KBr) $\nu_{\max}$ 2998, 2940, 1585, 1470, 1366, 1214, 1157 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 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) δ 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 $\text{C}_{18}\text{H}_{23}\text{NO}_3\text{S}$ 333.1401: found 333.1399.

N,N*-Diethyl 2',4',6'-trimethylbiphenyl-2-yl O-sulfamate **6b*

This compound was prepared by **Method C** using the following materials: **4i** (0.300 g, 0.845 mmol), 2,4,6-trimethylphenylboronic acid (0.139 g, 0.845 mmol), Na_2CO_3 (2M, 2 mL), $\text{Pd}(\text{PPh}_3)_4$ (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 $\text{Pd}(\text{PPh}_3)_4$ (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) $\nu_{\max}$ 2978, 2940, 1617, 1444, 1361, 1202, 1182, 1163 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, 1H, $J = 8.1$ Hz), 7.41 (t, 1H, $J = 7.8$), 7.32 (t, 1H, $J = 7.6$ Hz), 7.21 (d, 1H, $J = 7.5$ Hz), 6.94 (s, 2H), 2.94 (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) δ 147.9, 137.0, 136.9, 133.7, 131.5, 128.6, 127.8 (4C), 126.3, 121.5, 42.3 (2C), 21.0, 20.4 (2C), 12.7 (2C); LRMS (EI) m/z (rel. intensity) 347(M^+ , 100); HRMS (EI) calcd for $\text{C}_{19}\text{H}_{25}\text{NO}_3\text{S}$ 347.1562: found 347.1556.

N,N*-Diethyl 3'-*t*-butoxymethyl-biphenyl-2-yl O-sulfamate **6c*

This compound was prepared by **Method C** using the following materials: **4i** (0.300 g, 0.845 mmol), 3-*t*-butoxymethylphenylboronic acid (0.176 g, 0.845 mmol), Na_2CO_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) ν_{max} 3062, 2978, 2940, 2883, 1610, 1470, 1380, 1208, 1163, 1112, 1074 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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⁺ - *t*Bu, 45), 318(100); HRMS (EI) calcd for C₂₁H₂₉NO₄S 391.1816: found 391.1817.

N,N*-Diethyl 4'-cyanobiphenyl-2-yl O-sulfamate **6d*

This compound was prepared by **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) ν_{max} 2972, 2947, 2231, 1617, 1489, 1374, 1221, 1163 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 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); ¹³C NMR (101 MHz, CDCl₃) δ 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.

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

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), 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) ν_{max} 2972, 2838, 1598,

1483, 1368, 1253, 1208, 1157 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 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) δ 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 $\text{C}_{17}\text{H}_{21}\text{NO}_4\text{S}$ 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_2CO_3 (2M, 2 mL), $\text{Pd}(\text{PPh}_3)_4$ (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) ν_{max} 2985, 2946, 2838, 1598, 1476, 1374, 1208, 1157 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 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) δ 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 $\text{C}_{17}\text{H}_{21}\text{NO}_4\text{S}$ 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_2CO_3 (2M, 5 mL), $\text{Pd}(\text{PPh}_3)_4$ (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_2CO_3 (2M, 5 mL), $\text{Pd}(\text{PPh}_3)_4$ (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) ν_{max} 2985, 2934, 2838, 1611, 1515, 1483, 1368, 1246, 1208, 1150 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 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) δ 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 $\text{C}_{17}\text{H}_{21}\text{NO}_4\text{S}$ 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_2CO_3 (2M, 2 mL), $\text{Pd}(\text{PPh}_3)_4$ (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) ν_{max} 2978, 2940, 1591, 1489, 1451, 1368, 1208, 1157 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 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) δ 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($\text{M}^+ + 2$, 60), 373(M^+ , 100); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{17}\text{Cl}_2\text{NO}_3\text{S}$ 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_2CO_3 (2M, 2 mL), $\text{Pd}(\text{PPh}_3)_4$ (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 $\text{Pd}(\text{PPh}_3)_4$ (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) ν_{max} 2985, 2940, 1483, 1374, 1202, 1157 cm^{-1} ; ^1H NMR (400

MHz, CDCl₃) δ 7.84-7.82 (m, 1H), 7.62-7.60 (m, 1H), 7.41 (t, 1H, J = 7.9 Hz), 7.33-7.29 (m, 2H), 6.94 (d, 1H, J = 3.3 Hz), 6.54 (t, 1H, J = 1.7 Hz), 3.29 (q, 4H, 7.2 Hz), 1.12 (t, 6H, 7.1 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 149.0, 146.2, 142.2, 128.2, 127.3, 126.5, 124.0, 122.0, 111.8, 110.6, 43.4 (2C), 13.6 (2C); LRMS (EI) *m/z* (rel. intensity) 295(M⁺, 61), 131(100); HRMS (EI) calcd for C₁₄H₁₇NO₄S 295.0879; found 295.0878.

Benzynes 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), *i*PrMgCl (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), Et₂O (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 H₂O (10 mL) extracted with CH₂Cl₂ (x3), extracted with aqueous NaOH (x2, 4 M), acidified with conc HCl, extracted with CH₂Cl₂ (x3), dried (Na₂SO₄), and concentrated affording a solid that was recrystallized (MeOH) yielding **7b** (80 mg, 31 %) as brown crystals, mp 137-138 °C (MeOH) [lit⁸ mp 137-139 °C] ¹H NMR (400 MHz, CDCl₃) δ 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; ¹³C NMR (101 MHz, CDCl₃) δ 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), Et₂O (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) ν_{max} 2953, 2896, 2838, 1611, 1592, 1259, 844 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 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; ¹³C NMR (101 MHz, CDCl₃) δ 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 C₁₆H₂₀OSi 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) ν_{max} 2940, 1608, 1565, 1482, 1432, 1186, cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 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; ¹³C NMR (101 MHz, CDCl₃) δ 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 C₂₁H₂₀O 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) [lit⁹ 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) ν_{max} 3344, 3311, 1675, 1598, 1534, 1393, 1214 cm⁻¹; ¹H NMR (400 MHz, acetone-*d*₆) δ 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; ¹³C NMR (101 MHz, acetone-*d*₆) δ 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 C₁₅H₁₅NO₂ 241.1103; found 241.1103.

1-Phenylnaphthalene **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 oil¹²; ¹H NMR (400 MHz, CDCl₃) δ 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; ¹³C NMR (101 MHz, CDCl₃) δ 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 (EI) *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 [lit¹³ mp 90 °C]; ¹H 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; ¹³C 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 oil¹⁵; ¹H 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; ¹³C 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 ^1H or ^{13}C NMR Spectral Data