Supporting information
for
DoM-linked Corriu-Kumada, Negishi and Suzuki-Miyaura Cross-Coupling Protocols: A Comparative Study

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General Methods
Flash chromatography was carried out using “fine” Merck silica gel 60 (0.04-0.06 mm) purchased from VWR Scientific of Canada Ltd. with hexane:EtOAc as eluent unless otherwise specified. Chromatotron refers to a centrifugally accelerated, radial chromatography apparatus purchased from Harrison Research, Palo Alto, California, USA. Melting points were determined using a Buchi model SMP-20 instrument and are uncorrected. IR spectra were recorded on either a Perkin-Elmer 983 or Bomem FTIR infrared spectrophotometer in neat, nujol or KBr plate form. 1H NMR and 13C NMR spectra were recorded on AC-200 or AM-250 spectrometers in CDCl3 solution using tetramethylsilane as internal standard unless otherwise specified. 1H spectra listed are tabulated in the order: chemical shifts, multiplicity, coupling constants in Hertz, number of protons and assignment of protons. 13C spectra listed are tabulated in the order: chemical shift, type of carbon ('o' designates an odd number of attached protons (i.e. CH3, CH), 'e' designates an even number (i.e. CH2, C), as determined by the JMOD pulse sequence), multiplicity and coupling constants in Hertz where applicable and assignment of carbons. Mass spectra and HRMS were determined by Dr. R. Smith, McMaster University, Hamilton, Ontario, Canada, using VG 7070F or Varian spectrometers, Dr. H. S. McKinnon, Guelph Centre for Mass Spectrometry, University of Guelph, Guelph,

Ontario, Canada using KRATOS MS 890 spectrometers, or Dr. F. Hileman, Monsanto Co., St. Louis, Missouri. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee and MHW Laboratories, Phoenix, Arizona.

All dry solvents used were purified according to Perrin. All tetrahydrofuran, dimethoxyethane and diethyl ether were distilled from benzophenone ketyl under nitrogen immediately prior to use. MeLi, s-BuLi and t-BuLi were purchased from Aldrich Chemical Co. as solutions in Et2O, cyclohexane and pentane, respectively. n-BuLi was kindly supplied by FMC, Lithco Division, as a solution in hexane. The alkyl lithium reagents were stored in resealable containers and titrated periodically against 1,10-phenanthroline / n-BuOH. N,N,N'N'-Tetramethylethylenediamine (TMEDA) was dried and distilled over CaH2 before use. ZnCl2 was purchased from Aldrich Chemical Co. as a 1.0 M solution in Et2O. Solutions of MeMgBr, EtMgBr, i-PrMgCl and TMSCH2MgCl were purchased from Aldrich Chemical Co. as solutions in Et2O and PhMgBr as a solution in THF. MgBr2•2Et2 solution prepared according to the procedure of Seebach. All the commercial materials were purchased from Aldrich Chemical Co. or Lancaster Synthesis Ltd. Pd(PPh3)45 and the nickel catalysts6 (NiCl2(PPh3)2, NiCl2(Pn-Bu3)2, NiCl2(PEt3)2, NiCl2(dppe), NiCl2(dppp) and NiCl2(dppf)) were prepared by following the literature methods.

All the reactions were carried out under inert atmosphere (Ar, N2) unless otherwise specified. The transfer via canula employed additional solvent for quantitative transfer, designated by (amount of solvent + additional amount of solvent). The -78 °C temperature designated is approximate as achieved by a dry ice-acetone bath. Allowing a reaction to proceed overnight implies a period of 10-12 h. The phrase “normal workup” means the addition of saturated aqueous NH4Cl solution to the reaction mixture followed by CH2Cl2 or Et2O extraction, drying over Na2SO4, filtration, and evaporation of the filtrate in vacuo to afford the crude product.

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Standard Methods

Procedure A. Preparation of aryl trifluoromethanesulfonates

Prepared following an adaptation of the published procedure.\(^7\) To a cooled (0 °C), stirred solution of the phenol (10 mmol) and pyridine (20 mmol) in CH\(\text{2Cl}_2\) (50 mL) under Ar or N\(_2\) was added via syringe trifluoromethanesulfonic anhydride (13 mmol). After stirring for 1-3 h, the reaction mixture was treated with aq sat NH\(_4\)Cl. The CH\(\text{2Cl}_2\) phase was washed sequentially with aqueous copper sulfate (2x) and H\(_2\)O and dried over MgSO\(_4\). Filtration, concentration \textit{in vacuo} and purification afforded the product.

Procedure B. Preparation of Aryl Grignard and Zinc reagents

Method A: To a cold (-78 °C), stirred solution of aryl bromide (2 mmol) in THF (10 mL) under Ar or N\(_2\) was added a solution of either \(n\)-BuLi (2.2 mmol) or \(t\)-BuLi (4.2 mmol). After 15 minutes, the reaction mixture was allowed to warm to rt. This solution was then used in subsequent reactions.

Method B (Directed ortho Metalation Method): To a cold (-78 °C), stirred solution of the aryl DMG compound (2 mmol) in THF (10 mL) under Ar or N\(_2\) was added a solution of \(t\)-BuLi (2.4 mmol). After 1 h, ZnCl\(_2\) (3 mmol) was added and the solution allowed to warm to rt. This solution was then subsequently used.

Procedure C. Nickel catalyzed coupling of Grignard reagents with organo triflates

A flask charged with triflate (1 mmol) and nickel catalyst (0.05 mmol) in either Et\(_2\)O or THF (5 mL) under Ar or N\(_2\) at 0 °C was treated with a Grignard reagent (2 mmol). After immediate black coloration, the reaction flask was removed from the ice bath and stirring was continued until TLC indicated lack of starting material (~ 2 h). The reaction mixture was treated with aq satd NH\(_4\)Cl and extracted with Et\(_2\)O. The combined organics were dried (MgSO\(_4\)). Filtration, concentration \textit{in vacuo} and purification by flash chromatography on silica gel yielded the coupled product.

Procedure D. Nickel catalyzed coupling of organozinc reagents with organotriflates


To a stirred solution at rt of nickel catalyst (0.05 mmol) in THF (3 mL) under Ar or N₂ was added sequentially either DIBAH or MeMgBr (0.1 mmol), a freshly prepared aryl organozinc solution (2 mmol) via canula and an organotriflate (1 mmol) in THF (2 mL) with an additional amount of THF (1 mL) for quantitative transfer. Once all additions were complete, the reaction mixture was stirred until TLC indicated disappearance of starting material, typically 12-18 h. At this time, the reaction was treated with aq satd NH₄Cl and extracted with Et₂O. The combined extracts were dried (MgSO₄), subjected to filtration, and the filtrate concentrated in vacuo to give a residue which was subjected to flash chromatography on silica gel to afford the diaryl product.

**Procedure E. Palladium catalyzed coupling of aryl boronic acids with aryl bromides and triflates**

A mixture of Pd(PPh₃)₄ (0.04 mmol) and aryl halide or aryl triflate (1 mmol) in DME (3 mL) was stirred at rt for 10 min. A 2 M aqueous Na₂CO₃ solution (3 mL) was added, followed by a solution of aryl boronic acid (1.4 mmol) in DME (3 mL), and EtOH (3 mL) if required for solubility. The resulting mixture was heated at reflux overnight, cooled to rt to end always with a black color. The crude mixture was treated with aq satd NH₄Cl, extracted with Et₂O, the extract was dried (MgSO₄), subjected to filtration and the filtrate concentrated in vacuo and purified by flash chromatography to afford the diaryl product.

**Preparation of Aryl Triflates**

*N,N-Diethyl 2-trifluoromethanesulfonyloxybenzamide (Table 2, Entry 1)*

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\text{TFO} \quad \text{CONET₂}
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According to General Procedure A, a solution of *N,N*-diethyl 2-hydroxybenzamide (1.95 g, 10.1 mmol) and pyridine (1.4 mL, 17.3 mmol) in CH₂Cl₂ (50 mL) was treated with Tf₂O (2.2 mL, 13.1 mmol). After 1.5 h, normal workup followed by bulb to bulb distillation afforded the product (2.52 g, 77%) as a colourless oil: bp 95-6 °C / 0.01 mm Hg; IR (neat) ν (max) 1642, 1429, 1215 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 1.11 (t, J = 7.1 Hz, 3H, NCH₂CH₃), 1.26 (t, J = 7.1 Hz, 3H, NCH₂CH₃), 3.20 (q, J = 7.1 Hz, 2H, NCH₂CH₃), 3.56 (bs, 2H, NCH₂CH₃), 7.33-7.50 (m, 4H); ¹³C NMR (62.9 MHz, CDCl₃)
δ 12.1 (o, NCH₂CH₃), 13.6 (o, NCH₂CH₃), 38.9 (e, NCH₂CH₃), 42.8 (e, NCH₂CH₃), 118.3 (e, q, J = 320.3, CF₃), 121.6 (o), 128.2 (o), 128.3 (o), 130.6 (o), 130.9 (e), 145.0 (e), 165.1 (e); MS (EI (70 eV)) m/z (rel intensity) 325 (M⁺, 25), 296 (11), 253 (100), 176 (14), 120 (55), 92 (22), 72 (69); HRMS calcd for C₁₂H₁₅NO₄F₃S: 325.0596. Found: 325.0601.

_N,N-Diethyl 3-trifluoromethanesulfonyloxybenzamide (Table 2, Entry 2)_

According to General Procedure A, a solution of _N,N-diethyl 3-hydroxybenzamide_ (1.02 g, 5.28 mmol) and pyridine (1.0 mL, 12.4 mmol) in CH₂Cl₂ (50 mL) was treated with Tf₂O (1.3 mL, 7.73 mmol). After 2 h, normal workup followed by bulb to bulb distillation afforded the product (1.15 g, 67%) as a colourless oil: bp 91-3 °C / 0.01 mm Hg; IR (neat) ν (max) 1633, 1436, 1223, 1139 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 1.15 (m, 6H, NCH₂CH₃), 3.20 (bs, 2H, NCH₂CH₃), 3.55 (bm, 2H, NCH₂CH₃), 7.56-7.31 (m, 4H); MS (EI (70 eV)) m/z (rel intensity) 325 (M⁺, 3), 253 (100), 192 (48), 164 (20), 120 (26), 92 (18); HRMS calcd for C₁₂H₁₅NO₄F₃S: 326.0674. Found: 326.0678.

_N,N-Diethyl 4-trifluoromethanesulfonyloxybenzamide (Table 2, Entry 3)_

According to General Procedure A, a solution of _N,N-diethyl 4-hydroxybenzamide_ (1.51 g, 7.79 mmol) and pyridine (1.3 mL, 16.1 mmol) in CH₂Cl₂ (35 mL) was treated with Tf₂O (2.0 mL, 11.9 mmol). After 4 h, normal workup followed by bulb to bulb distillation afforded the product (2.53 g, 68%) as a colourless oil that solidified to a colourless solid, mp 39.5-40.5 °C (pentane); bp 107-108°C / 0.03 mm Hg; IR (neat) ν (max) 1626, 1436, 1223, 1140 cm⁻¹; ¹H (200 MHz, CDCl₃) δ 1.18 (bs, 6H, NCH₂CH₃), 3.26 (bs, 2H, NCH₂CH₃), 3.54 (bs 2H, NCH₂CH₃), 7.33 (d, J = 8.7, Hz, 2H), 7.49 (d, J = 8.7 Hz, 2H); ¹³C (50 MHz, CDCl₃) δ 12.6 (o, NCH₂CH₃), 13.9 (o, NCH₂CH₃), 39.2 (e, NCH₂CH₃), 43.2 (e, NCH₂CH₃), 118.5 (e, q, J = 320.1 Hz, CF₃), 121.3 (o), 128.3 (o), 137.4 (e), 149.5 (e), 169.1 (e); MS (EI (70 eV)) m/z (rel intensity) 325 (M⁺, 20), 324 (41), 253 (M-NEt₂,
According to General Procedure A, a solution of methyl salicylate (2.21 g, 14.5 mmol) and pyridine (2.3 mL, 28.4 mmol) in CH$_2$Cl$_2$ (50 mL) was treated with Tf$_2$O (3.6 mL, 21.4 mmol). After 2 h, normal workup followed by bulb to bulb distillation afforded the product (3.93 g, 95%) as a colourless oil: bp 88-90 °C / 0.5 mm Hg; IR (neat) \( \nu \) (max) 1732, 1429, 1207 cm$^{-1}$; $^1$H NMR (200 MHz, CDCl$_3$) \( \delta \) 3.95 (s, 3H, OCH$_3$), 7.31 (d, \( J = 8.2 \) Hz, 1H), 7.46 (td, \( J = 7.7, 1.2 \) Hz, 1H), 7.62 (td, \( J = 8.2, 1.9 \) Hz, 1H), 8.08 (dd, \( J = 7.7, 1.9 \) Hz, 1H); $^{13}$C NMR (50 MHz, CDCl$_3$) \( \delta \) 52.4 (o, OCH$_3$), 118.7 (e, q, \( J = 323.4 \) Hz, CF$_3$), 122.6 (o), 124.2 (e), 128.3 (o), 132.6 (o), 134.2 (o), 148.2 (e), 164.0 (e); MS (EI (70 eV)) \text{m/z} \text{(rel intensity)} 284 (M$^+$, 86), 253 (57), 189 (100), 135 (14), 120 (37), 95 (40), 69 (31); HRMS calcd for C$_9$H$_7$O$_5$F$_3$S: 283.9983.

Ethyl 3-trifluoromethanesulfonyloxybenzoate (Table 2, Entry 5)

According to General Procedure A, a solution of ethyl 3-hydroxybenzoate (3.0 g, 18.1 mmol) and pyridine (4.2 mL, 51.9 mmol) in CH$_2$Cl$_2$ (50 mL) was treated with Tf$_2$O (5.6 mL, 33.3 mmol). After 2 h, normal workup followed by bulb to bulb distillation afforded the product (5.04 g, 94%) as a colourless oil: bp 70-2 °C / 0.1 mm Hg; IR (neat) \( \nu \) (max) 1726, 1427, 1225 cm$^{-1}$; $^1$H NMR (200 MHz, CDCl$_3$) \( \delta \) 1.41 (t, \( J = 7.1 \) Hz, 3H, OCH$_2$C$_2$H$_5$), 4.42 (q, \( J = 7.1 \) Hz, 2H, OCH$_2$CH$_3$), 7.47 (m, 1H), 7.55 (t, \( J = 7.3 \) Hz, 1H), 7.95 (m, 1H), 8.09 (dt, \( J = 7.3, 1.5 \) Hz, 1H); $^{13}$C NMR (50 MHz, CDCl$_3$) \( \delta \) 14.1 (o, OCH$_2$CH$_3$), 61.7 (e, OCH$_2$CH$_3$), 118.7 (e, q, \( J = 320.9 \) Hz, CF$_3$), 122.4 (o), 125.5 (o), 129.4 (o), 130.3 (o), 133.1 (e), 149.4 (e), 164.6 (e); MS (EI (70 eV)) \text{m/z} \text{(rel intensity)} 298 (M$^+$, 40), 270 (54), 253 (100), 206 (14), 189 (57).
Ethyl 4-trifluoromethanesulfonyloxybenzoate (Table 2, Entry 6)

According to General Procedure A, a solution of ethyl 4-hydroxybenzoate (2.04 g, 12.3 mmol) and pyridine (2.0 mL, 24.7 mmol) in CH₂Cl₂ (50 mL) was treated with Tf₂O (3.1 mL, 18.4 mmol). After 3 h, normal workup followed by bulb to bulb distillation afforded the product (3.46 g, 94%) as a colourless oil: bp 75-8 °C / 0.2 mm Hg; IR (neat) ν (max) 1726, 1280, 1218 cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 1.40 (t, J = 7.1 Hz, 3H, OCH₂CH₃), 4.40 (q, J = 7.1 Hz, 2H, OCH₂CH₃), 7.35 (d, J = 8.7 Hz, 2H), 8.15 (d, J = 8.7 Hz, 2H); ¹³C NMR (62.9 MHz, CDCl₃) δ 118.6 (q, J = 320.5 Hz, CF₃), 121.2, 130.6, 131.6, 152.3, 164.6; MS (EI (70 eV)) m/z (rel intensity) 298 (M⁺, 24), 270 (M-Et, 48), 253 (100), 189 (49), 165 (8), 109 (20); HRMS calcd for C₁₀H₉F₃O₅S: 298.0123. Found: 298.0096.

N-tert-Butoxycarbonyl-2-trifluoromethanesulfonyloxyaniline (Table 2, Entry 7)

According to General Procedure A, a solution of N-tert-butoxycarbonyl-2-hydroxyaniline (2.07 g, 9.89 mmol) and pyridine (1.7 mL, 21.0 mmol) in CH₂Cl₂ (50 mL) was treated with Tf₂O (2.4 mL, 14.3 mmol). After 3 h, normal workup followed by bulb to bulb distillation afforded the product (3.02 g, 89%) as a pale yellow oil: bp 90-3 °C / 0.2 mm Hg; IR (neat) ν (max) 3378, 1723, 1520, 1430, 1196 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 1.52 (s, 9H, OC(CH₃)₃), 6.73 (bs, 1H, NH), 7.07 (m, 1H), 7.24-7.35 (m, 2H), 8.04 (d, J = 8.22 Hz, 1H); MS (EI (70 eV)) m/z (rel intensity) 341 (M⁺, 5), 285 (6), 241 (5), 152 (5), 108 (29), 69 (21), 57 (100).

N-tert-Butoxycarbonyl-3-trifluoromethanesulfonyloxyaniline (Table 2, Entry 8)

According to General Procedure A, a solution of N-tert-butoxycarbonyl-3-hydroxyaniline (2.08 g, 9.94 mmol) and pyridine (1.7 mL, 21.0 mmol) in CH₂Cl₂ (50 mL) was treated with Tf₂O (2.4 mL, 14.3 mmol). After 1 h, normal workup afforded a solid that was
recrystallized from hexane to afford the product (2.40 g, 71%) as a colourless solid, mp 75-6 °C (hexane); IR (KBr) ν (max) 3330, 1699, 1541, 1440, 1419, 1290, 1246, 1217, 1146 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 1.52 (s, 9H, OC(CH₃)₃), 6.86 (bs, 1H, NH), 6.92 (m, 1H), 7.20-7.36 (m, 2H), 7.55 (m, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 28.2 (o, OC(CH₃)₃), 81.4 (e, OC(CH₃)₃), 111.3 (o), 115.2 (o), 117.8 (o), 118.7 (e, q, J = 320.4 Hz, CF₃), 130.3 (o), 140.4 (e), 149.9 (e), 152.3 (e); MS (EI (70 eV)) m/z (rel intensity) 341 (M⁺, 5), 185 (16), 241 (29), 57 (100).

**N-tert-Butoxycarbonyl-4-trifluoromethanesulfonyloxyaniline (Table 2, Entry 9)**

According to General Procedure A, a solution of N-tert-butoxycarbonyl-4-hydroxyaniline (2.01 g, 9.61 mmol) and pyridine (1.7 mL, 21.0 mmol) in CH₂Cl₂ (50 mL) was treated with Tf₂O (2.4 mL, 14.3 mmol). After 2 h, normal workup afforded a solid that was recrystallized from hexane to afford the product (2.44 g, 74%) as a colourless solid, mp 96.5-97.5 °C (hexane); IR (KBr) ν (max) 3381, 1700, 1523, 1422, 1208, 1139 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 1.52 (s, 9H, OC(CH₃)₃), 6.69 (bs, 1H, NH), 7.18 (d, J = 9.1 Hz, 2H), 7.44 (d, J = 9.1 Hz, 2H); MS (EI (70 eV)) m/z (rel intensity) 341 (M⁺, 5), 285 (14), 152 (12), 108 (15), 57 (100).

**N,N-Diethyl 2-trifluoromethanesulfonyloxyphenyl-O-carbamate (Table 2, Entry 10)**

According to General Procedure A, a solution of N,N-diethyl 2-hydroxyphenyl-O-carbamate (1.86 g, 8.89 mmol) and pyridine (1.4 mL, 17.3 mmol) in CH₂Cl₂ (50 mL) was treated with Tf₂O (2.2 mL, 13.1 mmol). After 1.5 h, normal workup followed by bulb to bulb distillation afforded the product (2.96 g, 97%) as a colourless oil: bp 90-1 °C / 0.03 mm Hg; IR (neat) ν (max) 1724, 1437, 1236 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 1.20 (t, J = 7.1 Hz, 3H, NCH₂CH₃), 1.26 (t, J = 7.1 Hz, 3H, NCH₂CH₃), 3.38 (q, J = 7.1 Hz, 2H, NCH₂CH₃), 3.49 (q, J = 7.1 Hz, 2H, NCH₂CH₃), 7.18-7.37 (m, 4H); ¹³C NMR

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(50 MHz, CDCl₃) δ 12.8 (o, NCH₂CH₃), 13.8 (o, NCH₂CH₃), 41.8 (e, NCH₂CH₃), 42.3 (e, NCH₂CH₃), 118.5 (e, q, J = 320.4 Hz, CF₃), 122.1 (o), 124.8 (o), 126.1 (o), 128.8 (o), 141.2 (e), 143.3 (e), 152.3 (e); MS (EI (70 eV)) m/z (rel intensity) 341 (M⁺, 2), 326 (1), 100 (100), 72 (38); HRMS Calcd for C₁₂H₁₄NO₅SF₃: 341.0545. Found: 341.0548.

**N,N-Diethyl 3-trifluoromethanesulfonyloxyphenyl-O-carbamate (Table 2, Entry 11)**

According to General Procedure A, a solution of N,N-diethyl 3-hydroxyphenyl-O-carbamate (1.71 g, 8.17 mmol) and pyridine (1.3 mL, 16.1 mmol) in CH₂Cl₂ (50 mL) was treated with Tf₂O (1.6 mL, 9.51 mmol). After 2 h, normal workup followed by bulb to bulb distillation afforded the product (2.57 g, 92%) as a colourless oil: bp 95-6 °C / 0.3 mm Hg; IR (neat) ν (max) 1727, 1421, 1216 cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 1.23 (m, 6H, NCH₂CH₃), 3.41 (m, 4H, NCH₂CH₃), 7.16 (m, 3H), 7.42 (t, J = 8.1 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 12.4, 13.3, 41.4, 41.8, 114.9, 117.0, 118.3 (q, J = 320.47 Hz, CF₃), 121.3, 129.6, 148.9, 152.2, 152.4; MS (EI (70 eV)) m/z (rel intensity) 341 (M⁺, 1), 100 (100), 72 (38); HRMS Calcd for C₁₂H₁₄NO₅SF₃: 341.0545. Found: 341.0536.

**N,N-Diethyl 4-trifluoromethanesulfonyloxyphenyl-O-carbamate (Table 2, Entry 12)**

According to General Procedure A, a solution of N,N-diethyl 4-hydroxyphenyl-O-carbamate (2.02g 9.65 mmol) and pyridine (1.6 mL, 19.8 mmol) in CH₂Cl₂ (50 mL) was treated with Tf₂O (2.4 mL, 14.3 mmol). After 3 h, normal workup followed by bulb to bulb distillation afforded the product (2.98 g, 91%) as a colourless oil: bp 103-7 °C / 0.2 mm Hg; IR (neat) ν (max) 1722, 1421, 1213, 1138 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 1.23 (m, 6H), 3.45 (m, 4H), 7.25 (m, 4H); ¹³C NMR (62.9 MHz, CDCl₃) δ 12.8 (o, NCH₂CH₃), 13.8 (o, NCH₂CH₃), 41.7 (e, NCH₂CH₃), 42.1 (e, NCH₂CH₃), 118.5 (e, q, J = 320.4 Hz, CF₃), 121.8 (o), 123.2 (o), 145.9 (e), 150.9 (e), 153.2 (e); MS (EI (70 eV)) m/z (rel intensity) 341 (M⁺, 2), 326 (0.5), 100 (100), 72 (40). HRMS Calcd for C₁₂H₁₄NO₅SF₃: 341.0545. Found: 341.0531.
2-Fluorophenyl trifluoromethanesulfonate (Table 2, Entry 13)

According to General Procedure A, a solution of 2-fluorophenol (2.01 g, 17.9 mmol) and pyridine (2.9 mL, 35.9 mmol) in CH₂Cl₂ (50 mL) was treated with Tf₂O (4.5 mL, 26.7 mmol). After 7 h, normal workup followed by bulb to bulb distillation afforded the product (3.70 g, 85%) as a colourless oil: bp 45-50 °C / 0.2 mm Hg; IR (neat) ν (max) 1608, 1427, 1234, 1148, 896 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.14-7.39 (m); ¹³C NMR (50 MHz, CDCl₃) δ 117.6 (o, d, J = 18.2 Hz), 118.8 (e, q, J = 320.4 Hz, CF₃), 123.5 (o), 125.1 (o, d, J = 3.84 Hz), 129.7 (o, d, J = 7.5 Hz), 136.9 (e, d, J = 13.7 Hz), 153.8 (e, d, J = 253.2 Hz, C₆H₂-F); MS (CI (CH₄)) m/z (rel intensity) 245 (M⁺, 100).

3-Fluorophenyl trifluoromethanesulfonate (Table 2, Entry 14)

According to General Procedure A, a solution of 3-fluorophenol (1.01g, 9.01 mmol) and pyridine (1.5 mL, 18.5 mmol) in CH₂Cl₂ (50 mL) was treated with Tf₂O (2.3 mL, 13.7 mmol). After 6 h, normal workup followed by bulb to bulb distillation afforded the product (1.74 g, 79%) as a colourless oil: bp 45-50 °C / 0.1 mm Hg (lit. ⁹ bp 46-7 °C / 3.6 mm Hg).

4-Fluorophenyl trifluoromethanesulfonate (Table 2, Entry 15)

According to General Procedure A, a solution of 4-fluorophenol (4.37 g, 39.0 mmol) and pyridine (6.3 mL, 77.9 mmol) in CH₂Cl₂ (50 mL) was treated with Tf₂O (7.8 mL, 46.4 mmol). After 3 h, normal workup followed by bulb to bulb distillation afforded the product (6.57 g, 90%) as a colourless oil: bp 45-50 °C / 0.1 mm Hg; IR (neat) ν (max) 3088, 1422, 1189 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.10 (dd, J = 9.4, 7.7 Hz, 2H), 7.26 (dd, J = 9.4, 4.3 Hz, 2H); ¹³C NMR (50 MHz, CDCl₃) δ 117.0 (o, d, J = 24.3), 118.8 (e, q, J = 320.5 Hz, CF₃), 123.1 (o, d, J = 9.0 Hz), 145.4 (e, d, J = 2.9 Hz), 161.7 (e, d, J = 248.7 Hz, C₆H₂-F); MS (EI (70 eV))

m/z (rel intensity) 244 (M+, 33), 180 (8), 149 (5), 111 (100), 83 (59); HRMS Calcd for C7H4O3SF4: 243.9817. Found: 243.9798.

3-Trifluoromethanesulfonyloxyapyridine (Table 2, Entry 16)

To a cold (-78 °C), stirred solution of 3-hydroxypyridine (6.18 g, 65.0 mmol) and Et3N (18.0 mL, 129.0 mmol) in CH2Cl2 (60 mL) under Ar was added Tf2O (14.0 mL, 83.2 mmol). After stirring at -78 °C for 3 h, an aqueous, saturated NH4Cl was added. The organic phase was washed with H2O and dried (MgSO4). Filtration, concentration in vacuo and purified by bulb to bulb distillation to afford the product (7.25 g, 49%) as a colourles s oil: bp 44-45 °C / 0.5 mm Hg.

4-Nitrophenyl trifluoromethanesulfonate Table 2, Entry 17)

According to General Procedure A, a solution of 4-nitrophenol (2.10 g, 15.1 mmol) and pyridine (2.4 mL, 29.7 mmol) in CH2Cl2 (50 mL) was treated with Tf2O (3.8 mL, 22.6 mmol). After 4 h, normal workup afforded a solid that was recrystallized from CH2Cl2/hexane to afford the product (3.56 g, 87%) as colourless platelets, mp 53-4 °C (CH2Cl2/hexane) (lit. 9 mp 54-5°C (EtOH/water)).

N-tert-Butoxycarbonyl-2-(4′-trifluoromethanesulfonyloxyphenyl)ethylamine (Table 2, Entry 18)

According to General Procedure A, a solution of N-tert-butoxycarbonyltyramine11 (1.74 g, 7.33 mmol) and pyridine (1.2 mL, 14.8 mmol) in CH2Cl2 (50 mL) was treated with Tf2O (1.6 mL, 9.51 mmol). After 2.5 h, normal workup followed by flash chromatography (4:1 hexane:EtOAc) gave the product (968 mg, 40%) as a colourless oil which solidified, mp 48-9 °C; 1H NMR (250 MHz, CDCl3) δ 1.53 (s, 9H, OC(CH3)3),

2.82 (t, $J = 7.0$ Hz, 2H, ArCH$_2$CH$_2$N), 3.36 (t, $J = 7.0$ Hz, 2H, ArCH$_2$CH$_2$N), 4.70 (bs, 1H, NH), 7.11-7.29 (m, 4H); $^{13}$C NMR (62.9 MHz, CDCl$_3$) $\delta$ 28.2 (o, OC(C$_3$H$_3$)$_3$), 35.6 (e, ArCH$_2$CH$_2$N), 41.5 (e, ArCH$_2$CH$_2$N), 79.3 (e, OC(C$_3$H$_3$)$_3$), 118.7 (e, q, $J = 320.9$ Hz, CF$_3$), 121.2 (o), 130.5 (o), 139.7 (e), 148.1 (e), 155.8 (e); MS (EI (70 eV)) $m/z$ (rel intensity) 369 (M$^+$, 3), 313 (11), 251 (13), 239 (12), 149 (11), 120 (24), 107 (63), 77 (12), 57 (100).

$N$-Benzyl-4-trifluoromethanesulfonyloxyquinol-2-one (Table 2, Entry 19)

According to General Procedure A, a solution of $N$-benzyl-4-hydroxyquinol-2-one$^{12}$ (0.675 g, 2.71 mmol) and pyridine (0.50 mL, 6.18 mmol) in CH$_2$Cl$_2$ (50 mL) was treated with Tf$_2$O (0.6 mL, 3.57 mmol). After 1.5 h, normal workup followed by flash chromatography on silica gel (2:1 hexane:EtOAc) afforded the product (921 mg, 89%) as a colourless solid, m.p. 114-115 °C (hexane); IR (KBr) $\nu$ (max) 1655, 1433, 1217 cm$^{-1}$; $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 5.50 (s, 2H, PhCH$_2$), 6.85 (s, 1H), 7.4-7.2 (m, 7H), 7.49 (t, $J = 7.2$ Hz, 1H), 7.78 (d, $J = 7.2$ Hz, 1H); $^{13}$C NMR (62.9 MHz, CDCl$_3$) $\delta$ 46.0 (e, PhCH$_2$), 111.3 (o), 114.9 (e), 115.3 (o), 118.3 (e, q, $J = 320.7$ Hz, CF$_3$), 122.5 (o), 122.9 (o), 126.3 (o), 127.3 (o), 128.6 (o), 132.5 (o), 135.3 (e), 139.4 (e), 153.8 (e), 161.2 (e); MS (EI(70 eV)) $m/z$ (rel intensity) 383 (M$^+$, 25), 250 (M-Tf, 100), 232 (21), 208 (14), 91 (94). Anal. Calcd for C$_{17}$H$_{12}$F$_3$NO$_4$S: C, 53.27; H, 3.16. Found: C, 53.62; H, 3.39.

4-Methoxy-3-trifluoromethanesulfonyloxybenzaldehyde (Table 2, Entry 20)

According to General Procedure A, a solution of isovanillin (5.38 g, 35.3 mmol) and pyridine (6.0 mL, 74.2 mmol) in CH$_2$Cl$_2$ (50 mL) was treated with Tf$_2$O (0.6 mL, 44.6 mmol). After 1.5 h, normal workup followed by flash chromatography on silica gel (1:1 hexane:EtOAc) afforded the product (7.55 g, 75%) as a colourless oil: bp 78-80 °C / 0.1 mm Hg; $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 3.99 (s, 3H, OCH$_3$), 7.42 (d, $J = 8.2$ Hz, 1H), 7.52 (dd, $J = 8.2, 1.8$ Hz, 1H), 7.57 (d, $J = 1.8$ Hz, 1H), 9.97 (s, 1H, CHO); $^{13}$C NMR
(62.9 MHz, CDCl₃) δ 56.2 (OCH₃), 111.8, 118.5 (q, J = 320.1 Hz, CF₃), 123.0, 123.6, 136.7, 142.4, 152.0, 190.1 (CHO); HRMS calcd for C₉H₆O₅F₃S: 285.0045. Found: 285.0042.

1-Trifluoromethanesulfonyloxyfluorenone (Table 2, Entry 21)

According to General Procedure A, a solution of 1-hydroxyfluorenone (1.13 g, 5.76 mmol) and pyridine (0.90 mL, 11.1 mmol) in CH₂Cl₂ (40 mL) was treated with Tf₂O (1.3 mL, 7.73 mmol). After 3 h, normal workup gave a solid residue that was recrystallized from CH₂Cl₂/hexane to afford the product (1.62 g, 86%) as yellow needles, mp 137-8 °C (CH₂Cl₂/hexane); ¹H (200 MHz, CDCl₃) δ 7.09-7.64 (m).

Table 2 Products:

N,N-Diethyl 2-(3',4'-methylenedioxyphenyl)benzamide (Table 2, Entry 1)

Procedure 1: According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (431 mg, 2.15 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (3.8 mL, 1.24 M, 4.71 mmol) and ZnCl₂ (3.0 mL, 1.0 M, 3.00 mmol) and the reaction mixture was warmed to rt. According to General Procedure D, to a second flask containing Ni(acac)₂ (20 mg, 0.077 mmol) and PPh₃ (88 mg, 0.33 mmol) in THF (3 mL) was added sequentially a solution of MeMgBr (0.10 mL, 3.0 M, 0.30 mmol), a freshly prepared organozinc solution via canula and a solution of N,N-diethyl 2-trifluoromethanesulfonyloxybenzamide (339 mg, 1.04 mmol) in THF (2+1 mL). After 18 h, normal workup followed by flash chromatography (1:1 hexane:EtOAc) gave the product (262 mg, 85%) as a colourless oil: IR (neat) ν (max) 1611 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 0.78 (t, J = 7.1 Hz, 3H, NCH₂CH₃), 0.97 (t, J = 7.1 Hz, 3H, NCH₂CH₃), 2.72 (m, 1H, NCH₂CH₃), 2.89-3.07 (m, 2H, NCH₂CH₃), 3.77 (m, 1H, NCH₂CH₃), 5.94 (s, 2H, OCH₂O), 6.81 (d, J = 7.8 Hz, 1H), 6.92-6.98 (m, 2H, OCH₂O).

¹² Snieckus, V., unpublished results.
Procedure 2: According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (403 mg, 2.01 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (2.7 mL, 1.65 M, 4.46 mmol) and MgBr₂•OEt₂ (1.0 mL, 2.62 N, 2.62 mmol) and whole was warmed to rt. According to General Procedure C, to a second flask containing N,N-diethyl 2-(trifluoromethanesulfonyloxy)benzamide (322 mg, 0.99 mmol) and NiCl₂(dppe) (36 mg, 0.067 mmol) in THF (5 mL) was added the freshly prepared Grignard reagent via canula. After 5 h, normal workup followed by flash chromatography (1:1 hexane:EtOAc) gave the product (195 mg, 66%) shown to be identical to that prepared in Procedure 1.

Procedure 3: According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (416 mg, 2.07 mmol) in THF (10 mL) was sequentially treated with a solution of t-BuLi (3.0 mL, 1.52 M, 4.56 mmol) and MgBr₂•OEt₂ (1.2 mL, 2.62 N, 3.14 mmol) and the whole was warmed to rt. According to General Procedure C, to a second flask containing N,N-diethyl 2-trifluoromethanesulfonyloxybenzamide (329 mg, 1.01 mmol) and Ni(acac)₂ (16 mg, 0.063 mmol) in THF (5 mL) was added the freshly prepared Grignard reagent via canula. After 2.5 h, normal workup followed by flash chromatography (1:1 hexane:EtOAc) gave the product (235 mg, 78%) shown to be identical to that prepared in Procedure 1.

Procedure 4: According to General Procedure E, N,N-diethyl 2-trifluoromethanesulfonyloxybenzamide (316 mg, 0.97 mmol) in DME (3 mL) was treated with 3,4-methylenedioxyphenyl boronic acid (224 mg, 1.35 mmol) in DME (3 mL) and EtOH (3 mL) in the presence of Pd(PPh₃)₄ (37 mg, 0.032 mmol) and the reaction mixture was refluxed at ? for 16 h and cooled to rt. Normal workup followed by
flash chromatography (1:1 hexane:EtOAc) afforded the product (190 mg, 66%) shown to be identical to that prepared in Procedure 1.

_N,N-Diethyl 3-(3',4'-methylenedioxyphenyl)benzamide (Table 2, Entry 2)_

**Procedure 1:** According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (400 mg, 1.99 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (2.6 mL, 1.66 M, 4.32 mmol) and ZnCl2 (3.0 mL, 1.0 M, 3.00 mmol) and the whole was warmed to rt. According to General Procedure D, to a second flask containing Ni(acac)2 (20 mg, 0.077 mmol) and PPh3 (82 mg, 0.31 mmol) in THF (3 mL) was added sequentially a solution of MeMgBr (0.10 mL, 3.0 M, 0.30 mmol), the freshly prepared organozinc solution via canula and a solution of _N,N_ -diethyl 3-trifluoromethanesulfonyloxybenzamide (326 mg, 1.00 mmol) in THF (2+1 mL). After 20 h, normal workup followed by flash chromatography (1:1 hexane:EtOAc) gave the product (284 mg, 95%) as a colourless solid, mp 78-9 °C (Et2O/hexane); IR (KBr) ν (max) 1618 cm⁻¹; 1H NMR (200 MHz, CDCl3) δ 1.13-1.24 (bm, 6H, NCH2C3H3), 3.29-3.54 (bm, 4H, NCH2CH3), 5.97 (s, 2H, OCH2O), 6.86 (d, J = 8.5 Hz, 1H), 7.03-7.06 (m, 2H), 7.25-7.55 (m, 4H); 13C NMR (50 MHz, CDCl3) δ 12.7 (o, NCH2CH3), 14.0 (o, NCH2CH3), 39.1 (e, NCH2CH3), 43.1 (e, NCH2CH3), 101.0 (e, OCH2O), 107.3 (o), 108.4 (o), 120.5 (o), 124.5 (o), 127.3 (o), 128.6 (o), 134.5 (e), 137.6 (e), 140.9 (e), 147.2 (e), 148.0 (e), 170.9 (e); MS (EI (60 eV)) m/z (rel intensity) 297 (M⁺, 100), 268 (2), 225 (53), 197 (6), 167 (3), 139 (23). Anal. Calcd for C18H19NO3: C, 72.71; H, 6.44. Found: C, 72.64; H, 6.40.

**Procedure 2:** According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (401 mg, 1.99 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (2.7 mL, 1.65 M, 4.46 mmol) and MgBr2•OEt2 (1.0 mL, 2.62 N, 2.62 mmol) and warmed to rt. According to General Procedure C, to a second flask containing _N,N_ -diethyl 3-(trifluoromethanesulfonyloxy)benzamide (325 mg, 1.00 mmol) and NiCl2(dppe) (37 mg, 0.071 mmol) in THF (5 mL) was added the freshly prepared
Grignard reagent via canula. After reaction for 5 h, normal workup followed by flash chromatography (1:1 hexane:EtOAc) gave the product (188 mg, 63%) shown to be identical to that prepared in Procedure 1.

Procedure 3: According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (413 mg, 2.06 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (3.0 mL, 1.52 M, 4.56 mmol) and MgBr₂·OEt₂ (1.2 mL, 2.62 N, 3.14 mmol) and the whole was warmed to rt. According to General Procedure C, to a second flask containing N,N-diethyl 3-trifluoromethanesulfonyloxybenzamide (329 mg, 1.01 mmol) and Ni(acac)₂ (18 mg, 0.070 mmol) in THF (5 mL) was added a solution of freshly prepared Grignard reagent via canula. After reaction for 2.5 h, normal workup followed by flash chromatography (1:1 hexane:EtOAc) gave the product (203 mg, 67%) shown to be identical to that prepared in Procedure 1.

Procedure 4: According to General Procedure E, a solution of N,N-diethyl 3-trifluoromethanesulfonyloxybenzamide (323 mg, 0.99 mmol) in DME (3 mL) was treated with a solution of 3,4-methylenedioxyphenyl boronic acid (220 mg, 1.33 mmol) in DME (3 mL) and EtOH (3 mL) in the presence of Pd(PPh₃)₄ (49 mg, 0.043 mmol). After 25 h, the reaction mixture was cooled to rt. Normal workup followed by flash chromatography (1:1 hexane:EtOAc) afforded the product (237 mg, 80%) shown to be identical to that prepared in Procedure 1.

N,N-Diethyl 4-(3',4'-methylenedioxyphenyl)benzamide (Table 2, Entry 3)

\[
\begin{align*}
\text{Procedure 1:} & \quad \text{According to General Procedure B, Method A, a solution of} \\
& \quad 4\text{-bromo-1,2-methylenedioxybenzene (409 mg, 2.03 mmol) in THF (10 mL) was sequentially treated} \\
& \quad \text{with solutions of} \quad t\text{-BuLi (2.7 mL, 1.66 M, 4.48 mmol) and ZnCl}_2 (3.0 \text{mL, 1.0 M, 3.0 mmol) and the reaction mixture was warmed to rt. According to General Procedure} \\
& \quad \text{D, to a second flask containing Ni(acac)_2 (18 mg, 0.071 mmol) and PPh}_3 (82 mg,}
\end{align*}
\]
0.31 mmol) in THF (3 mL) was added sequentially a solution of MeMgBr (0.10 mL, 3.0 M, 0.30 mmol), a freshly prepared solution of the above organozinc reagent via canula and a solution of N,N-diethyl 4-trifluoromethanesulfonyloxybenzamide (325 mg, 1.00 mmol) in THF (2+1 mL). After 20 h, normal workup followed by flash chromatography (1:1 hexane:EtOAc) afforded the product (256 mg, 86%) as a colourless solid, mp 76-7 °C (Et₂O/hexane); \( ^1H \) NMR (200 MHz, CDCl₃) \( \delta \) 1.20 (bs, 6H, NCH₂CH₃), 3.45 (bs, 4H, NCH₂CH₃), 5.99 (s, 2H, OCH₂O), 6.87 (d, \( J = 8.5 \) Hz, 1H), 7.03-7.08 (m, 2H), 7.41 (d, \( J = 8.2 \) Hz, 2H), 7.53 (d, \( J = 8.2 \) Hz, 2H); \( ^13C \) NMR (200 MHz, CDCl₃) \( \delta \) 101.1 (e, OCH₂O), 107.4 (o), 108.5 (o), 120.6 (o), 126.7 (o), 126.8 (o), 134.6 (e), 135.6 (e), 141.6 (e), 147.3 (e), 148.1 (e), 170.9 (e); MS (EI (70 eV)) \( m/z \) (rel intensity) 297 (M⁺, 53), 225 (100), 139 (34), 112 (14). Anal. Calcd for C₁₈H₁₉NO₃: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.80; H, 6.40; N, 4.81.

Procedure 2: According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (404 mg, 2.01 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (2.9 mL, 1.55 M, 4.50 mmol) and MgBr₂•OEt₂ (1.0 mL, 2.62 N, 2.62 mmol) and the whole was warmed to rt. According to General Procedure C, to a second flask containing N,N-diethyl 4-(trifluoromethanesulfonyloxy)benzamide (326 mg, 1.00 mmol) and NiCl₂(dppe) (31 mg, 0.059 mmol) in THF (5 mL) was added the freshly prepared solution of the above Grignard reagent via canula. After 3 h, normal workup followed by flash chromatography (1:1 hexane:EtOAc) gave the product (232 mg, 78%) shown to be identical to that prepared in Procedure 1.

Procedure 3: According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (411 mg, 2.04 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (3.0 mL, 1.52 M, 4.56 mmol) and MgBr₂•OEt₂ (1.2 mL, 2.62 N, 3.14 mmol) and the whole was warmed to rt. According to General Procedure C, to a second flask containing N,N-diethyl 4-trifluoromethanesulfonyloxybenzamide (329 mg, 1.01 mmol) and Ni(acac)₂ (20 mg, 0.079 mmol) in THF (5 mL) was added the above freshly prepared Grignard reagent via canula. After 3 h, normal workup followed by flash chromatography (1:1
hexane:EtOAc) gave the product (197 mg, 65%) shown to be identical to that prepared in Procedure 1.

Procedure 4: According to General Procedure E, a solution of N,N-diethyl 4-trifluoromethanesulfonyloxybenzamide (331 mg, 1.02 mmol) in DME (3 mL) was treated with a solution of 3,4-methylenedioxyphenyl boronic acid (200 mg, 1.21 mmol) DME (3 mL) and EtOH (3 mL) in the presence of Pd(PPh₃)₄ (49 mg, 0.043 mmol). After 6 h, the reaction was cooled to rt. Normal workup followed by flash chromatography (1:1 hexane:EtOAc) afforded the product (203 mg, 67%) shown to be identical to that prepared in Procedure 1.

Methyl 2-(3′,4′-methylenedioxyphenyl)benzoate (Table 2, Entry 4)

Procedure 1: According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (413 mg, 2.05 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (2.6 mL, 1.74 M, 4.52 mmol) and ZnCl₂ (3.0 mL, 1.0 M, 3.00 mmol) and the whole was warmed to rt. According to General Procedure D, to a second flask containing Ni(acac)₂ (21 mg, 0.081 mmol) and PPh₃ (97 mg, 0.37 mmol) in THF (3 mL) was added sequentially solutions of MeMgBr (0.10 mL, 3.0 M, 0.30 mmol), the as above freshly prepared organozinc solution via canula and a solution of methyl 2-trifluoromethanesulfonyloxybenzoate (296 mg, 1.04 mmol) in THF (2+1 mL). After stirring the reaction mixture for 24 h, normal workup followed by flash chromatography (1:1 hexane:CH₂Cl₂) gave the product (257 mg, 96%) as a colourless oil: IR (neat) ν (max) 1724 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 3.68 (s, 3H, OCH₃), 5.97 (s, 2H, OCH₂O), 6.72-6.85 (m, 3H), 7.24-7.52 (m, 3H), 7.76 (m, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 51.9 (o, OCH₃), 101.6 (e, OCH₂O), 107.9 (o), 108.9 (o), 121.7 (o), 126.9 (o), 129.6 (o), 130.6 (o), 130.9 (e), 131.1 (o), 135.1 (e), 141.9 (e), 146.9 (e), 147.4 (e), 169.0 (e); MS (EI (70 eV)) m/z (rel intensity) 256 (M⁺, 100), 225 (10), 195 (28), 167 (16), 139 (21); HRMS calcld for C₁₅H₁₂O₄: 256.0736.
Procedure 2: To a solution of methyl 2-trifluoromethanesulfonfylxybenzoate (293 mg, 1.03 mmol) and 3,4-methylenedioxyphenyl boronic acid (236 mg, 1.42 mmol) in DME (5 mL) was added Pd(PPh₃)₄ (45 mg, 0.039 mmol) and Cs₂CO₃ (1.02 g, 3.12 mmol) and the reaction mixture was stirred at rt. After 25 h, normal workup followed by flash chromatography (1:1 hexane:EtOAc) gave the product (106 mg, 40%) shown to be identical to that prepared in Procedure 1.

Ethyl 3-(3′,4′-methylenedioxyphenyl)benzoate (Table 2, Entry 5)

Procedure 1: According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (418 mg, 2.08 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (3.7 mL, 1.24 M, 4.59 mmol) and ZnCl₂ (3.0 mL, 1.0 M, 3.00 mmol) and the whole was warmed to rt. According to General Procedure D, to a second flask containing Ni(acac)₂ (18 mg, 0.069 mmol) and PPh₃ (103 mg, 0.39 mmol) in THF (3 mL) was added sequentially solutions of MeMgBr (0.10 mL, 3.0 M, 0.30 mmol), the as above freshly prepared organozinc solution via canula and a solution of ethyl 3-fluoromethanesulfonylbenzoate (339 mg, 1.14 mmol) in THF (2+1 mL). After stirring the reaction mixture for 20 h, normal workup followed by flash chromatography (9:1 hexane:Et₂O) gave the product (185 mg, 60%) as a colourless oil: IR (neat) ν (max) 1717 cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 1.40 (t, J = 7.1 Hz, 3H, OCH₂CH₃), 4.39 (q, J = 7.1 Hz, 2H, OCH₂CH₃), 5.96 (s, 2H, OCH₂O), 6.86 (d, J = 8.5 Hz, 1H), 7.04-7.06 (m, 2H), 7.43 (t, J = 7.7 Hz, 1H), 7.65 (d, J = 7.9 Hz, 1H), 7.97 (d, J = 7.7 Hz, 1H), 8.18 (s, 1H); ¹³C NMR (62.9 MHz, CDCl₃) δ 14.2 (o, OCH₂CH₃), 60.9 (e, OCH₂CH₃), 101.1 (e, OCH₂O), 107.5 (o), 108.5 (o), 120.6 (o), 127.7 (o), 127.8 (o), 128.6 (o), 131.0 (o), 134.4 (o), 141.0 (e), 147.3 (e), 148.2 (e), 166.4 (e); MS (EI (60 eV)) m/z (rel intensity) 270 (M⁺, 67), 242 (12), 197 (2), 167 (2), 139 (12), 84 (67), 49 (100); HRMS calcd for C₁₆H₁₅O₄: 271.0970. Found: 271.0970.

Procedure 2: According to General Procedure E, a solution of ethyl 3-fluoromethanesulfonylbenzoate (307 mg, 1.03 mmol) in DME (3 mL) was treated with
a solution of 3,4-methylenedioxyphenyl boronic acid (224 mg, 1.37 mmol) in DME (3 mL) and EtOH (3 mL) in the presence of Pd(PPh₃)₄ (48 mg, 0.042 mmol). After stirring for 30 h, the reaction mixture was cooled to rt. Normal workup followed by flash chromatography (9:1 hexane:Et₂O) afforded the product (22 mg, 8%) shown to be identical to that prepared in Procedure 1.

**Procedure 3:** To a flask charged with a solution of ethyl 3-fluoromethanesulfonylbenzoate (305 mg, 1.02 mmol) and 3,4-methylenedioxyphenyl boronic acid (234 mg, 1.41 mmol) in toluene (6 mL), EtOH (1.5 mL) and 2N Na₂CO₃ (3 mL) was added Pd(PPh₃)₄ (56 mg, 0.048 mmol). The reaction vessel was fitted with a reflux condenser and the contents heated to reflux. After 23 h, the reaction was cooled to rt. Normal workup followed by flash chromatography (4:1 hexane:Et₂O) afforded the product (216 mg, 78%) shown to be identical to that prepared in Procedure 1.

**Ethyl 4-(3',4'-methylenedioxyphenyl)benzoate (Table 2, Entry 6)**

**Procedure 1:** According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (426 mg, 2.12 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (3.7 mL, 1.24 M, 4.59 mmol) and ZnCl₂ (3.0 mL, 1.0 M, 3.00 mmol) and the whole was warmed to rt. According to General Procedure D, to a second flask containing Ni(acac)₂ (25 mg, 0.095 mmol) and PPh₃ (111 mg, 0.42 mmol) in THF (3 mL) was added sequentially MeMgBr (0.10 mL, 3.0 M, 0.30 mmol), the as above freshly prepared organozinc solution via canula and a solution of ethyl 4-trifluoromethanesulfonloybenzoate (345 mg, 1.16 mmol) in THF (2+1 mL). After stirring the reaction mixture for 20 h, normal workup followed by flash chromatography (8:1 hexane:EtOAc) gave the product (204 mg, 65%) as a colourless solid, mp 92-92.5 °C (Et₂O/hexane); IR (KBr) ν (max) 1710 cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 1.39 (t, J = 7.1 Hz, 3H, OCH₂CH₃), 4.38 (q, J = 7.1 Hz, 2H, OCH₂O), 5.96 (s, 2H, OCH₂O), 6.84 (d, J = 8.5 Hz, 1H), 7.04-7.07 (m, 2H), 7.52 (d, J = 8.3 Hz, 2H), 8.05 (d, J = 8.3 Hz, 2H); ¹³C NMR (62.9 MHz, CDCl₃) δ 14.2 (OCH₂CH₃), 60.7 (OCH₂CH₃), 101.2 (OCH₂O), 107.4, 108.5, 120.8,
Procedure 2: According to General Procedure E, a solution of ethyl 4-trifluoromethanesulfonyloxybenzoate (306 mg, 1.03 mmol) in DME (3 mL) was treated with a solution of 3,4-methylenedioxyphenyl boronic acid (240 mg, 1.45 mmol) in DME (3 mL) and EtOH (3 mL) in the presence of Pd(PPh₃)₄ (44 mg, 0.038 mmol). After stirring for 30 h, the reaction mixture was cooled to rt. Normal workup followed by flash chromatography (8:1 hexane:EtOAc) afforded the product (43 mg, 16%) shown to be identical to that prepared in Procedure 1.

Procedure 3: To a flask charged with a solution of ethyl 4-trifluoromethanesulfonyloxybenzoate (318 mg, 1.07 mmol) and 3,4 methylenedioxyphenyl boronic acid (239 mg, 1.44 mmol) in toluene (6 mL), EtOH (1.5 mL) and 2N Na₂CO₃ (3 mL) was added Pd(PPh₃)₄ (53 mg, 0.046 mmol). The reaction vessel was fitted with a reflux condenser and the contents heated to reflux. After 23 h, the reaction mixture was cooled to rt. Normal workup followed by flash chromatography (9:1 hexane:EtOAc) afforded the product (230 mg, 80%) shown to be identical to that prepared in Procedure 1.

Procedure 4: According to General Procedure E, a solution of ethyl 4-trifluoromethanesulfonyloxybenzoate (313 mg, 1.05 mmol) in DME (3 mL) was treated with a solution of 3,4-methylenedioxyphenyl boronic acid (201 mg, 1.21 mmol) in DME (3 mL) and EtOH (3 mL) in the presence of Pd(PPh₃)₄ (46 mg, 0.040 mmol). After 18 h, the reaction mixture was cooled to rt, acidified with 10% HCl and extracted with Et₂O. The combined extracts were concentrated in vacuo. The residue was dissolved in EtOH (50 mL), concentrated H₂SO₄ (1 mL) added and a reflux condenser fitted and the reaction was refluxed for 18 h, cooled to rt and the solvent removed in vacuo. The residue was dissolved in Et₂O, the organic layer was washed with H₂O and dried (MgSO₄). Filtration, concentration and purification by flash chromatography (9:1 hexane:EtOAc)
afforded the product (224 mg, 79%) shown to be identical to that prepared in Procedure 1.

**N-tert-Butoxycarbonyl-2-(3’,4’-methylenedioxyphenyl)aniline (Table 2, Entry 7)**

![Structure of N-tert-Butoxycarbonyl-2-(3’,4’-methylenedioxyphenyl)aniline](image)

According to General Procedure E, a solution of *N*-tert-butoxycarbonyl-2-trifluoromethanesulfonyloxyaniline (336 mg, 0.98 mmol) in DME (3 mL) was treated with a solution of 3,4-methylenedioxyphenyl boronic acid (216 mg, 1.30 mmol) in DME (3 mL) and EtOH (3 mL) in the presence of Pd(PPh₃)₄ (47 mg, 0.041 mmol). After 24 h, the reaction mixture was cooled to rt. Normal workup followed by flash chromatography (9:1 hexane:EtOAc) afforded the product (242 mg, 79%) as a colorless solid, mp 136-7 °C (hexane); IR (KBr) ν (max) 3426, 1728 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 1.47 (s, 9H, OC(CH₃)₃), 6.00 (s, 2H, OCH₂O), 6.54 (b, 1H, NH), 6.77-6.92 (m, 3H), 7.01-7.17 (m, 2H), 7.30 (td, J = 8.6, 1.8 Hz, 1H), 8.10 (d, J = 8.2 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 28.3 (o, OC(CH₃)₃), 80.4 (e, OC(CH₃)₃), 101.2 (e, OCH₂O), 108.7 (o), 109.8 (o), 119.6 (o), 122.6 (o), 122.8 (o), 128.2 (o), 130.1 (o), 130.9 (e), 131.9 (e), 135.4 (e), 147.2 (e), 148.1 (e), 152.8 (e); MS (EI (70 eV)) m/z (rel intensity) 313 (M⁺, 48), 257 (100), 240 (11), 213 (69), 182 (8), 154 (16), 57 (89). Anal. Calcd for C₁₈H₁₉NO₄: C, 69.00; H, 6.11; N, 4.47. Found: C, 69.20; H, 6.21; N, 4.67.

**N-tert-Butoxycarbonyl-3-(3’,4’-methylenedioxyphenyl)aniline (Table 2, Entry 8)**

![Structure of N-tert-Butoxycarbonyl-3-(3’,4’-methylenedioxyphenyl)aniline](image)

According to General Procedure E, a solution of *N*-tert-butoxycarbonyl-trifluoromethanesulfonyloxyaniline (322 mg, 0.94 mmol) in DME (3 mL) was treated with a solution of 3,4-methylenedioxyphenyl boronic acid (268 mg, 1.62 mmol) in DME (3 mL) and EtOH (3 mL) in the presence of Pd(PPh₃)₄ (39 mg, 0.034 mmol). After 19 h, the reaction mixture was cooled to rt. Normal workup followed by flash chromatography (6:1 hexane:EtOAc) afforded the product (255 mg, 86%) as a colorless solid, mp 94.5-95 °C (hexane); IR (KBr) ν (max) 3378, 1731 cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 1.51 (s, 9H, OC(CH₃)₃), 5.93 (s, 2H, OCH₂O), 6.76 (bs,
1H, NH), 6.81 (d, $J = 8.7$ Hz, 1H), 6.99-7.03 (m, 2H), 7.14 (m, 1H), 7.25-7.27 (m, 2H), 7.55 (bs, 1H); MS (EI (70 eV)) m/z (rel intensity) 313 ($M^+$, 39), 257 (80), 240 (6), 213 (65), 185 (6), 154 (6), 127 (6), 57 (100). Anal. Calcd for C$_{18}$H$_{19}$NO$_4$: C, 69.00; H, 6.11; N, 4.47. Found: C, 68.74; H, 6.13; N, 4.46.

$\text{N-tert-Butoxycarbonyl-4-}(\text{3',4'-methylenedioxyphenyl})\text{aniline (Table 2, Entry 9)}$

According to General Procedure E, a solution of $\text{N-tert-butoxycarbonyl-4-}$trifluoromethanesulfonyloxyaniline (361 mg, 1.06 mmol) in DME (3 mL) was treated with a solution of 3,4-methylenedioxyphenyl boronic acid (246 mg, 1.48 mmol) in DME (3 mL) and EtOH (3 mL) in the presence of Pd(PPh$_3$)$_4$ (48 mg, 0.041 mmol). After 17 h, the reaction mixture was cooled to rt. Normal workup followed by flash chromatography (4:1 hexane:EtOAc) afforded the product (289 mg, 87%) as a colorless solid, mp 161-2 °C (hexane); IR (KBr) $\nu$ (max) 3357, 1699 cm$^{-1}$; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 1.53 (s, 9H, OC(C$_3$H$_3$)$_3$), 5.98 (s, 2H, OC($\text{CH}_2$)$_2$O), 6.49 (bs, 1H), 6.86 (d, $J = 8.6$ Hz, 1H), 6.99-7.04 (m, 2H), 7.36-7.47 (m, 4H); $^{13}$C NMR (62.9 MHz, CDCl$_3$) $\delta$ 28.3 (o, OC(CH$_3$)$_3$), 80.6 (e, OC(CH$_3$)$_3$), 101.0 (e, OCH$_2$O), 107.3 (o), 108.5 (o), 118.9 (o), 120.1 (o), 127.2 (o), 135.0 (e), 135.7 (e), 137.3 (e), 146.7 (e), 148.0 (e), 152.8 (e); MS (EI (70 eV)) m/z (rel intensity) 313 ($M^+$, 24), 257 (100), 213 (36), 154 (7), 127 (7), 57 (52). Anal. Calcd for C$_{18}$H$_{19}$NO$_4$: C, 69.00; H, 6.11; N, 4.47. Found: C, 68.74; H, 5.87; N, 4.48.

$\text{N,N-Diethyl 2-}(\text{3',4'-methylenedioxyphenyl})\text{-O-phenyl carbamate (Table 2, Entry 10)}$

According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (425 mg, 2.12 mmol) in THF (10 mL) was sequentially treated with solutions of $t$-BuLi (3.8 mL, 1.24 M, 4.71 mmol) and ZnCl$_2$ (3.0 mL, 1.0 M, 3.00 mmol) and the reaction mixture was warmed to rt. According to General Procedure D, to a second flask containing a solution of Ni(acac)$_2$ (19 mg,
0.073 mmol) and PPh$_3$ (76 mg, 0.29 mmol) in THF (3 mL) was added sequentially solutions of MeMgBr (0.10 mL, 3.0 M, 0.30 mmol), the the above freshly prepared organozinc solution via canula and a solution of $N,N$-diethyl 2-trifluoromethanesulfonyleoxyphenyl-$O$-carbamate (344 mg, 1.01 mmol) in THF (21 mL). After 17 h, normal workup followed by flash chromatography (3:1 hexane:EtOAc) gave the product (291 mg, 92%) as a colourless oil: IR (neat) $\nu$ (max) 2975, 1714 cm$^{-1}$; $^1$H NMR (200 MHz, CDCl$_3$) $\delta$ 1.06 (t, $J = 7.1$ Hz, 6H, NCH$_2$CH$_3$), 3.27 (q, $J = 7.1$ Hz, 4H, NCH$_2$CH$_3$), 5.93 (s, 2H, OCH$_2$O), 6.8-6.9 (m, 3H), 7.1-7.4 (m, 4H); $^{13}$C NMR (62.9 MHz, CDCl$_3$) $\delta$ 13.0 (o, NCH$_2$CH$_3$), 13.8 (o, NCH$_2$CH$_3$), 41.5 (e, NCH$_2$CH$_3$), 41.9 (e, NCH$_2$CH$_3$), 100.9 (e, OCH$_2$O), 107.9 (o), 109.6 (o), 122.5 (o), 123.2 (o), 125.4 (o), 128.0 (o), 130.5 (o), 131.8 (e), 134 (6, e), 146.7 (e), 147 (2, e), 148.4 (e), 153.9 (e); MS (EI (60 eV)) m/z (rel intensity) 313 (M$^+$, 100), 183 (15), 155 (12), 127 (9), 100 (94), 87 (31), 72 (31); HRMS calcd for C$_{18}$H$_{20}$NO$_4$: 314.1392. Found: 314.1392.

**Procedure 2:** According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (399 mg, 1.99 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (2.4 mL, 1.84 M, 4.42 mmol) and MgBr$_2$$\cdot$OEt$_2$ (0.9 mL, 2.62 N, 2.36 mmol) and warmed to rt. According to General Procedure C, to a second flask containing a solution of $N,N$-diethyl 2-trifluoromethanesulfonyleoxyphenyl-$O$-carbamate (340 mg, 1.00 mmol) and NiCl$_2$(dppe) (33 mg, 0.063 mmol) in THF (5 mL) was added the above freshly prepared Grignard reagent via canula. After 4.5 h, normal workup followed by flash chromatography (3:1 hexane:EtOAc) gave the product (77 mg, 23%) shown to be identical to that prepared in **Procedure 1**.

**Procedure 3:** According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (407 mg, 2.02 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (2.4 mL, 1.84 M, 4.42 mmol) and MgBr$_2$$\cdot$OEt$_2$ (1.0 mL, 2.62 N, 2.62 mmol) and the whole was warmed to rt. According to General Procedure C, to a second flask containing a solution of $N,N$-diethyl 2-trifluoromethanesulfonyleoxyphenyl-$O$-carbamate (341 mg, 1.00 mmol) and Ni(acac)$_2$ (15 mg, 0.058 mmol) in THF (5 mL) was added the above freshly prepared Grignard
reagent via canula. After 4 h, normal workup followed by flash chromatography (3:1 hexane:EtOAc) gave the product (42 mg, 13%) shown to be identical to that prepared in Procedure 1.

**Procedure 4:** According to General Procedure E, \(N,N\)-diethyl 2-trifluoromethanesulfonyloxyphenyl-O-carbamate (347 mg, 1.02 mmol) in DME (3 mL) was coupled with 3,4-methylenedioxyphenyl boronic acid (238 mg, 1.43 mmol) in DME (3 mL) in the presence of Pd(PPh\(_3\))\(_4\) (39 mg, 0.034 mmol). After 20 h, the reaction was cooled to rt. Normal workup followed by flash chromatography (3:1 hexane:EtOAc) afforded the product (310 mg, 97%) shown to be identical to that prepared in Procedure 1.

**N,N-Diethyl 3-(3',4'-methylenedioxyphenyl)-O-phenyl carbamate (Table 2, Entry 11)**

![Chemical structure](image)

**Procedure 1:** According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (442 mg, 2.20 mmol) in THF (10 mL) was sequentially treated with solutions of \(t\)-BuLi (3.3 mL, 1.45 M, 4.79 mmol) and ZnCl\(_2\) (3.0 mL, 1.0 M, 3.00 mmol) and the whole was warmed to rt. According to General Procedure D, to a second flask containing a solution of Ni(acac)\(_2\) (18 mg, 0.072 mmol) and PPh\(_3\) (89 mg, 0.34 mmol) in THF (3 mL) was added sequentially MeMgBr (0.10 mL, 3.0 M, 0.30 mmol), the freshly above prepared organozinc solution via canula and a solution of \(N,N\)-diethyl 3-trifluoromethanesulfonyloxyphenyl-O-carbamate (379 mg, 1.11 mmol) in THF (2+1 mL). After 26 h reaction, normal workup followed by flash chromatography (3:1 hexane:EtOAc) gave the product (309 mg, 89%) as a colourless oil: IR (neat) \(\nu\) (max) 1713 cm\(^{-1}\); \(^1\)H NMR (200 MHz, CDCl\(_3\)) \(\delta\) 1.18-1.22 (m, 6H, NCH\(_2\)C\(_3\)H), 3.36 (bs, 4H, NCH\(_2\)CH\(_3\)), 5.90 (s, 2H, OCH\(_2\)O), 6.81 (d, \(J = 8.7\) Hz, 1H), 7.00-7.09 (m, 3H), 7.25-7.4 (m, 3H); \(^{13}\)C NMR (50 MHz, CDCl\(_3\)) \(\delta\) 13.3 (o, NCH\(_2\)CH\(_3\)), 14.2 (o, NCH\(_2\)CH\(_3\)), 41.9 (e, NCH\(_2\)CH\(_3\)), 42.2 (e, NCH\(_2\)CH\(_3\)), 101.1 (e, OCH\(_2\)O), 107.6 (o), 108.4 (o), 120.2 (o), 120.7 (o), 123.5 (o), 129.3 (o), 134.7 (e), 142.2 (e), 147.2 (e), 148.0 (e), 151.8 (e), 154.2 (e).
(e); MS (EI (60 eV)) m/z (rel intensity) 313 (M+, 100), 185 (7), 100 (30), 72 (7); HRMS calcd for C18H20NO4: 314.1392. Found: 314.1392.

**Procedure 2:** According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (405 mg, 2.02 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (2.4 mL, 1.84 M, 4.42 mmol) and MgBr2•OEt2 (0.9 mL, 2.62 N, 2.36 mmol) and the whole was warmed to rt. According to General Procedure C, to a second flask containing a solution of N,N-diethyl 3-trifluoromethanesulfonyloxyphenyl-O-carbamate (341 mg, 1.00 mmol) and NiCl2(dppe) (33 mg, 0.062 mmol) in THF (5 mL) was added the above freshly prepared Grignard reagent via canula. After 4.5 h reaction, normal workup followed by flash chromatography (3:1 hexane:EtOAc) gave the product (134 mg, 41%) shown to be identical to that prepared in Procedure 1.

**Procedure 3:** According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (398 mg, 1.98 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (2.9 mL, 1.52 M, 4.41 mmol) and MgBr2•OEt2 (1.3 mL, 2.62 N, 3.41 mmol) and the whole was warmed to rt. According to General Procedure C, to a second flask containing a solution of N,N-diethyl 3-trifluoromethanesulfonyloxyphenyl-O-carbamate (349 mg, 1.02 mmol) and Ni(acac)2 (22 mg, 0.087 mmol) in THF (5 mL) was added the above freshly prepared Grignard reagent via canula. After 2 h reaction, normal workup followed by flash chromatography (3:1 hexane:EtOAc) gave the product (174 mg, 54%) shown to be identical to that prepared in Procedure 1.

**Procedure 4:** According to General Procedure E, a solution of N,N-diethyl 3-trifluoromethanesulfonyloxyphenyl-O-carbamate (342 mg, 1.00 mmol) in DME (3 mL) was treated with a solution of 3,4-methylenedioxyphenyl boronic acid (219 mg, 1.32 mmol) in DME (3 mL) and EtOH (3 mL) in the presence of Pd(PPh3)4 (41 mg, 0.036 mmol). After 24 h, the reaction mixture was cooled to rt. Normal workup followed by flash chromatography (3:1 hexane:EtOAc) afforded the product (307 mg, 98%) shown to be identical to that prepared in Procedure 1.
\[ N,N-\text{Diethyl 4-(3',4'-methylenedioxyphenyl)-O-phenyl carbamate (Table 2, Entry 12)} \]

**Procedure 1:** According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (407 mg, 2.03 mmol) in THF (10 mL) was sequentially treated with solutions of \( t\)-BuLi (3.6 mL, 1.24 M, 4.46 mmol) and \( \text{ZnCl}_2 \) (3.0 mL, 1.0 M, 3.00 mmol) and the whole was warmed to rt. According to General Procedure D, to a second flask containing a solution of \( \text{Ni(acac)}_2 \) (18 mg, 0.071 mmol) and \( \text{PPh}_3 \) (87 mg, 0.33 mmol) in THF (3 mL) was added sequentially solutions of MeMgBr (0.10 mL, 3.0 M, 0.30 mmol), the above freshly prepared organozinc solution via canula and a solution of \( N,N\)-diethyl 4-trifluoromethanesulfonyloxyphenyl-O-carbamate (356 mg, 1.04 mmol) in THF (2+1 mL). After 30 h reaction, normal workup followed by flash chromatography (4:1 hexane:EtOAc) gave the product (277 mg, 85%) as a colourless solid, mp 66.5–67.5 °C (Et\(_2\)O/hexane); IR (KBr) \( \nu \) (max) 1703 cm\(^{-1}\); \(^1\)H NMR (250 MHz, CDCl\(_3\)) \( \delta \) 1.23 (bs, 6H, NCH\(_2\)C\(_3\)H\(_3\)), 3.41 (bs, 4H, NC\(_2\)H\(_2\)CH\(_3\)), 5.96 (s, 2H, OCH\(_2\)O), 6.85 (d, \( J = 8.68 \) Hz, 1H), 6.99-7.02 (m, 2H), 7.15 (d, \( J = 8.6 \) Hz, 2H), 7.50 (d, \( J = 8.6 \) Hz, 2H); \(^1^{3}\)C NMR (50 MHz, CDCl\(_3\)) \( \delta \) 13.3 (o, NCH\(_2\)C\(_3\)H\(_3\)), 14.1 (o, NCH\(_2\)CH\(_3\)), 41.8 (e, NCH\(_2\)CH\(_3\)), 42.1 (e, NCH\(_2\)CH\(_3\)), 101.0 (e, OCH\(_2\)O), 107.5 (o), 108.4 (o), 120.4 (o), 121.9 (o), 127.6 (o), 134.9 (e), 137.8 (e), 146.9 (e), 148.0 (e), 150.6 (e), 154.1 (e); MS (EI (60 eV)) \( m/z \) (rel intensity) 313 (M\(^+\), 100), 213 (11), 185 (7), 155 (2), 127 (5), 100 (46), 72 (16). Anal. Calcd for C\(_{18}\)H\(_{19}\)NO\(_4\): C, 69.00; H, 6.11. Found: C, 68.95; H, 6.13.

**Procedure 2:** According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (399 mg, 1.98 mmol) in THF (10 mL) was sequentially treated with \( t\)-BuLi (2.4 mL, 1.84 M, 4.42 mmol) and MgBr\(_2\)•OEt\(_2\) (1.0 mL, 2.62 N, 2.62 mmol) and warmed to rt. According to General Procedure C, to a second flask containing \( N,N\)-diethyl 4-trifluoromethanesulfonyloxyphenyl-O-carbamate (341 mg, 1.00 mmol) and NiCl\(_2\)(dppe) (34 mg, 0.064 mmol) in THF (5 mL) was added the freshly prepared Grignard reagent via canula. After 4 h, normal workup followed by
flash chromatography (4:1 hexane:EtOAc) gave the product (151 mg, 46%) shown to be identical to that prepared in Procedure 1.

**Procedure 3:** According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (417 mg, 2.07 mmol) in THF (10 mL) was sequentially treated with t-BuLi (3.0 mL, 1.52 M, 4.56 mmol) and MgBr₂·OEt₂ (1.4 mL, 2.62 N, 3.67 mmol) and warmed to rt. According to General Procedure C, to a second flask containing N,N-diethyl 4-trifluoromethanesulfonyloxyphenyl-O-carbamate (341 mg, 1.00 mmol) and Ni(acac)₂ (20 mg, 0.078 mmol) in THF (5 mL) was added the freshly prepared Grignard reagent via canula. After 3 h, normal workup followed by flash chromatography (3:1 hexane:EtOAc) gave the product (157 mg, 50%) shown to be identical to that prepared in Procedure 1.

**Procedure 4:** According to General Procedure E, N,N-diethyl 4-trifluoromethanesulfonyloxyphenyl-O-carbamate (338 mg, 0.99 mmol) in DME (3 mL) was coupled with 3,4-methylenedioxyphenyl boronic acid (221 mg, 1.33 mmol) in DME (3 mL) and EtOH (3 mL) in the presence of Pd(PPh₃)₄ (40 mg, 0.035 mmol). After 24 h, the reaction was cooled to rt. Normal workup followed by flash chromatography (3:1 hexane:EtOAc) afforded the product (276 mg, 89%) shown to be identical to that prepared in Procedure 1.

**2-Fluoro-3′,4′-methylenedioxybiphenyl (Table 2, Entry 13)**

![2-Fluoro-3′,4′-methylenedioxybiphenyl](image)

**Procedure 1:** According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (396 mg, 1.97 mmol) in THF (10 mL) was sequentially treated with t-BuLi (2.8 mL, 1.58 M, 4.42 mmol) and ZnCl₂ (3.0 mL, 1.0 M, 3.00 mmol) and warmed to rt. According to General Procedure D, to a second flask containing Ni(acac)₂ (27 mg, 0.10 mmol) and PPh₃ (119 mg, 0.45 mmol) in THF (3 mL) was added sequentially MeMgBr (0.10 mL, 3.0 M, 0.30 mmol), the freshly prepared organozinc solution via canula and a solution of 2-fluorophenyl trifluoromethanesulfonate (189 mg, 0.77 mmol) in THF (2+1 mL). After 24 h, normal
workup followed by flash chromatography (9:1 → 4:1 hexane:CH₂Cl₂) gave the product (159 mg, 95%) as a colourless oil: IR (neat) ν (max) 2895, 1470, 1231, 1040, 757 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.93 (s, 2H, OCH₂O), 6.85 (d, J = 7.9 Hz, 1H), 6.95-7.39 (m, 6H); ¹³C NMR (50 MHz, CDCl₃) δ 101.1 (e, OCH₂O), 108.3 (o), 109.5 (o, d, J = 3.6 Hz), 116.0 (o, d, J = 22.9 Hz), 122.6 (o, d, J = 2.5 Hz), 124.2 (o, d, J = 3.1 Hz), 128.6 (o, J = 7.9 Hz), 129.6 (e), 130.5 (o, d, J = 3.1 Hz), 147.2 (e), 147.7 (e), 159.6 (e, d, J = 247.2 Hz, CAr-F); MS (EI (60 eV)) m/z (rel intensity) 216 (M⁺, 100), 198 (13), 157 (19), 139 (3); HRMS calcd for C₁₃H₁₀FO₂: 217.0665. Found: 217.0665.

**Procedure 2:** According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (394 mg, 1.96 mmol) in THF (10 mL) was sequentially treated with t-BuLi (2.4 mL, 1.84 M, 4.42 mmol) and MgBr₂•OEt₂ (1.0 mL, 2.62 N, 2.62 mmol) and warmed to rt. According to General Procedure C, to a second flask containing 2-fluorophenyl trifluoromethanesulfonate (229 mg, 1.02 mmol) and NiCl₂(dppe) (35 mg, 0.067 mmol) in THF (5 mL) was added the freshly prepared Grignard reagent via canula. After 1.5 h, normal workup followed by flash chromatography (9:1 hexane:CH₂Cl₂) gave the product (82 mg, 37%) shown to be identical to that prepared in Procedure 1.

**Procedure 3:** According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (415 mg, 2.06 mmol) in THF (10 mL) was sequentially treated with t-BuLi (3.0 mL, 1.52 M, 4.56 mmol) and MgBr₂•OEt₂ (1.3 mL, 2.62 N, 3.41 mmol) and warmed to rt. According to General Procedure C, to a second flask containing 2-fluorophenyl trifluoromethanesulfonate (245 mg, 1.00 mmol) and Ni(acac)₂ (18 mg, 0.071 mmol) in THF (5 mL) was added the freshly prepared Grignard reagent via canula. After 3 h, normal workup followed by flash chromatography (4:1 hexane:CH₂Cl₂) gave the product (104 mg, 48%) shown to be identical to that prepared in Procedure 1.

**Procedure 4:** According to General Procedure E, 2-fluorophenyl trifluoromethanesulfonate (253 mg, 1.13 mmol) in DME (3 mL) was coupled with 3,4-methylenedioxyphenyl boronic acid (244 mg, 1.47 mmol) DME (3 mL) and EtOH
(3 mL) in the presence of Pd(PPh₃)₄ (43 mg, 0.037 mmol). After 19 h, the reaction was cooled to rt. Normal workup followed by flash chromatography (9:1 hexane:CH₂Cl₂) afforded the product (194 mg, 80%) shown to be identical to that prepared in Procedure 1.

3-Fluoro-3',4'-methylenedioxybiphenyl (Table 2, Entry 14)

**Procedure 1:** According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (402 mg, 2.00 mmol) in THF (10 mL) was sequentially treated with t-BuLi (2.8 mL, 1.58 M, 4.42 mmol) and ZnCl₂ (3.0 mL, 1.0 M, 3.00 mmol) and warmed to rt. According to General Procedure D, to a second flask containing Ni(acac)₂ (22 mg, 0.084 mmol) and PPh₃ (89 mg, 0.34 mmol) in THF (3 mL) was added sequentially solutions MeMgBr (0.10 mL, 3.0 M, 0.30 mmol), the above freshly prepared organozinc solution via canula and a solution of 3-fluorophenyl trifluoromethanesulfonate (188 mg, 1.00 mmol) in THF (2+1 mL). After 19 h reaction, normal workup followed by flash chromatography (4:1 hexane:CH₂Cl₂) gave the product (161 mg, 74%) as a colourless solid, mp 59-60 °C (pentane); IR (KBr) ν (max) 2908, 1478, 1233, 1033, 780 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 5.96 (s, 2H, OCH₂O), 6.84 (d, J = 8.5 Hz, 1H), 6.92-7.03 (m, 3H), 7.15-7.34 (m, 3H); ¹³C NMR (50 MHz, CDCl₃) δ 101.2 (e, OCH₂O), 107.5 (o), 108.6 (o), 113.6 (o, d, J = 21.1 Hz), 113.7 (o, d, J = 21.7 Hz), 120.6 (o), 122.4 (o, d, J = 2.6 Hz), 130.1 (o, d, J = 8.9 Hz), 134.2 (e), 143.1 (e, d, J = 7.6 Hz), 147.5 (e), 148.2 (e), 163.1 (e, d, J = 245.6 Hz, CAr-F); MS (EI (60 eV)) m/z (rel intensity) 216 (M⁺, 100), 157 (13). Anal. Calcd for C₁₃H₉FO₂: C, 72.22; H, 4.20. Found: C, 72.04; H, 4.42.

**Procedure 2:** According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (396 mg, 1.97 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (2.4 mL, 1.84 M, 4.42 mmol) and MgBr₂•OEt₂ (1.0 mL, 2.62 N, 2.62 mmol) and the whole was warmed to rt. According to General Procedure C, to a second flask containing a solution of 3-fluorophenyl trifluoromethanesulfonate (231 mg, 1.03 mmol) and NiCl₂(dppe) (34 mg, 0.064 mmol) in
THF (5 mL) was added the above freshly prepared Grignard reagent via canula. After 1.5 h, normal workup followed by flash chromatography (9:1 hexane:CH₂Cl₂) gave the product (105 mg, 47%) shown to be identical to that prepared in Procedure 1.

Procedure 3: According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (409 mg, 2.03 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (3.0 mL, 1.52 M, 4.56 mmol) and MgBr₂•OEt₂ (1.3 mL, 2.62 N, 3.41 mmol) and the whole was warmed to rt. According to General Procedure C, to a second flask containing a solution of 3-fluorophenyl trifluoromethanesulfonate (249 mg, 1.02 mmol) and Ni(acac)₂ (20 mg, 0.078 mmol) in THF (5 mL) was added the above freshly prepared Grignard reagent via canula. After 4 h reaction, normal workup followed by flash chromatography (9:1 hexane:CH₂Cl₂) gave the product (97 mg, 44%) shown to be identical to that prepared in Procedure 1.

Procedure 4: According to General Procedure E, a solution of 3-fluorophenyl trifluoromethanesulfonate (256 mg, 1.05 mmol) in DME (3 mL) was treated with a solution of 3,4-methylenedioxyphenyl boronic acid (251 mg, 1.51 mmol) in DME (3 mL) and EtOH (3 mL) in the presence of Pd(PPh₃)₄ (45 mg, 0.039 mmol). After 17 h, the reaction mixture was cooled to rt. Normal workup followed by flash chromatography (9:1 hexane:CH₂Cl₂) afforded the product (194 mg, 86%) shown to be identical to that prepared in Procedure 1.

4-Fluoro-3',4'-methylenedioxybiphenyl (Table 2, Entry 15)

Procedure 1: According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (408 mg, 2.03 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (2.8 mL, 1.58 M, 4.42 mmol) and ZnCl₂ (3.0 mL, 1.0 M, 3.00 mmol) and the whole was warmed to rt. According to General Procedure D, to a second flask containing a solution of Ni(acac)₂ (16 mg, 0.061 mmol) and PPh₃ (74 mg, 0.28 mmol) in THF (3 mL) was added sequentially solutions of MeMgBr (0.09 mL, 3.0 M, 0.30 mmol), the above freshly prepared organozinc solution
via canula and a solution of 4-fluorophenyl trifluoromethanesulfonate (193 mg, 0.79 mmol) in THF (2+1 mL). After 24 h reaction, normal workup followed by flash chromatography (9:1 → 4:1 hexane:CH₂Cl₂) gave the product (124 mg, 73%) as a colourless solid, mp 56-7 °C (pentane); IR (KBr) \( \nu \) (max) 1487, 1221, 810 cm\(^{-1}\); \(^1\)H NMR (250 MHz, CDCl₃) \( \delta \) 6.00 (s, 2H, OC\( \text{H}_2\text{O} \)), 6.88 (dd, \( J = 7.5, 0.9 \) Hz, 1H), 6.99-7.05 (m, 2H), 7.11 (t, \( J = 8.8 \) Hz, 2H), 7.36 (m, 1H), 7.47 (dd, \( J = 8.8, 5.3 \) Hz, 2H); \(^{13}\)C NMR (50 MHz, CDCl₃) \( \delta \) 101.1 (e, O\( \text{C}_\text{H}_2\text{O} \)), 108.0 (o, d, \( J = 50.4 \) Hz), 115.4 (o, d, \( J = 21.4 \) Hz), 120.4 (o), 128.2 (o), 128.4 (o), 134.5 (e), 137.0 (e), 147.0 (e), 148.1 (e), 162.1 (e, d, \( J = 245.7 \) Hz, C\( \text{Ar}-\text{F} \)); MS (EI (70 eV)) \( m/z \) (rel intensity) 219 (M⁺, 100), 157 (30), 107 (11). Anal. Calcd for C\(_{13}\)H\(_9\)FO\(_2\): C, 72.22; H, 4.20. Found: C, 72.46; H, 4.45.

**Procedure 2:** According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (402 mg, 2.00 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (2.4 mL, 1.84 M, 4.42 mmol) and MgBr\(_2\)•OEt\(_2\) (1.0 mL, 2.62 N, 2.62 mmol) and the whole was warmed to rt. According to General Procedure C, to a second flask containing a solution of 4-fluorophenyl trifluoromethanesulfonate (239 mg, 1.07 mmol) and NiCl\(_2\)(dppe) (33 mg, 0.062 mmol) in THF (5 mL) was added the above freshly prepared Grignard reagent via canula. After 1 h reaction, normal workup followed by flash chromatography (9:1 hexane:CH₂Cl₂) gave the product (87 mg, 38%) shown to be identical to that prepared in **Procedure 1**.

**Procedure 3:** According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (407 mg, 2.02 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (2.9 mL, 1.55 M, 4.50 mmol) and MgBr\(_2\)•OEt\(_2\) (1.0 mL, 2.62 N, 2.62 mmol) and the whole was warmed to rt. According to General Procedure C, to a second flask containing a solution of 4-fluorophenyl trifluoromethanesulfonate (223 mg, 1.00 mmol) and NiCl\(_2\)(dppe) (32 mg, 0.060 mmol) in THF (5 mL) was added the above freshly prepared Grignard reagent via canula. After 2 h reaction, normal workup followed by flash chromatography (9:1 hexane:CH₂Cl₂) gave the product (93 mg, 43%) shown to be identical to that prepared in **Procedure 1**.
Procedure 4: According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (407 mg, 2.02 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (3.0 mL, 1.52 M, 4.56 mmol) and MgBr$_2$•OEt$_2$ (1.3 mL, 2.62 N, 3.41 mmol) and the whole was warmed to rt. According to General Procedure C, to a second flask containing a solution of 4-fluorophenyl trifluoromethanesulfonate (258 mg, 1.15 mmol) and Ni(acac)$_2$ (20 mg, 0.079 mmol) in THF (5 mL) was added the above freshly prepared Grignard reagent via canula. After 4 h reaction, normal workup followed by flash chromatography (9:1 hexane:CH$_2$Cl$_2$) gave the product (106 mg, 43%) shown to be identical to that prepared in Procedure 1.

Procedure 5: According to General Procedure E, a solution of 4-fluorophenyl trifluoromethanesulfonate (250 mg, 1.13 mmol) in DME (3 mL) was treated with a solution of 3,4-methylenedioxyphenyl boronic acid (236 mg, 1.42 mmol) DME (3 mL) and EtOH (3 mL) in the presence of Pd(PPh$_3$)$_4$ (45 mg, 0.039 mmol). After 18 h reaction, the reaction mixture was cooled to rt. Normal workup followed by flash chromatography (9:1 hexane:CH$_2$Cl$_2$) afforded the product (198 mg, 89%) shown to be identical to that prepared in Procedure 1.

1,2-Methylenedioxy-4-(3-pyridyl)benzene (Table 2, Entry 16)

Procedure 1: According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (400 mg, 1.99 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (2.6 mL, 1.66 M, 4.32 mmol) and ZnCl$_2$ (3.0 mL, 1.0 M, 3.00 mmol) and the whole was warmed to rt. According to General Procedure D, to a second flask containing a solution of Ni(acac)$_2$ (18 mg, 0.069 mmol) and PPh$_3$ (71 mg, 0.27 mmol) in THF (3 mL) was added sequentially solutions of MeMgBr (0.090 mL, 3.0 M, 0.27 mmol), the above freshly prepared organozinc solution via canula and a solution of 3-pyridyl trifluoromethanesulfonate (239 mg, 1.05 mmol) in THF (2+1 mL). After 18 h reaction, normal workup followed by flash chromatography (2:1 EtOAc:hexane) gave the product (182 mg, 87%) as a colourless solid, mp 91-91.5 °C (hexane); IR (KBr) ν (max) 2905, 1512, 1477, 1418, 1235, 1033 cm$^{-1}$; $^1$H NMR (200
MHz, CDCl₃) δ 6.00 (s, 2H, OCH₂O), 6.90 (d, J = 8.4 Hz, 1H), 7.01-7.06 (m, 2H), 7.31 (dd, J = 7.9, 4.8 Hz, 1H), 7.78 (dd, J = 7.9, 2.3 Hz, 1H), 8.54 (d, J = 4.8 Hz, 1H), 8.78 (d, J = 2.3 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃) δ 101.3 (e, OCH₂O), 107.4 (o), 108.8 (o), 120.7 (o), 123.4 (o), 131.9 (e), 133.9 (o), 136.3 (e), 147.7 (e), 148.0 (o), 148.4 (e); MS (EI (70 eV)) m/z (rel intensity) 199 (M⁺, 100), 140 (11), 114 (11), 99 (9). Anal. Calcd for C₁₂H₉NO₂: C, 72.35; H, 4.55; N, 7.03. Found: C, 72.45; H, 4.63; N, 7.14.

Procedure 2: According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (410 mg, 2.04 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (2.7 mL, 1.65 M, 4.46 mmol) and MgBr₂•OEt₂ (1.0 mL, 2.62 N, 2.62 mmol) and the whole was warmed to rt. According to General Procedure C, to a second flask containing a solution of 3-pyridyl trifluoromethanesulfonate (249 mg, 1.09 mmol) and NiCl₂(dppe) (37 mg, 0.069 mmol) in THF (5 mL) was added the above freshly prepared Grignard reagent via canula. After 4.5 h reaction, normal workup followed by flash chromatography (1:2 hexane:EtOAc) gave the product (171 mg, 78%) shown to be identical to that prepared in Procedure 1.

Procedure 3: According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (405 mg, 2.01 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (2.9 mL, 1.52 M, 4.41 mmol) and MgBr₂•OEt₂ (1.2 mL, 2.62 N, 3.14 mmol) and the whole was warmed to rt. According to General Procedure C, to a second flask containing a solution of 3-pyridyl trifluoromethanesulfonate (235 mg, 1.03 mmol) and Ni(acac)₂ (19 mg, 0.074 mmol) in THF (5 mL) was added the above freshly prepared Grignard reagent via canula. After 2.5 h reaction, normal workup followed by flash chromatography (2:1 EtOAc:hexane) gave the product (100 mg, 49%) shown to be identical to that prepared in Procedure 1.

Procedure 4: According to General Procedure E, a solution of 3-pyridyl trifluoromethanesulfonate (241 mg, 1.06 mmol) in DME (3 mL) was treated with a solution of 3,4-methylenedioxyphenyl boronic acid (234 mg, 1.41 mmol) in DME (3 mL) and EtOH (3 mL) in the presence of Pd(PPh₃)₄ (41 mg, 0.035 mmol). After 18 h, the reaction mixture was cooled to rt. Normal workup followed by flash chromatography
(3:2 EtOAc:hexane) afforded the product (171 mg, 81%) shown to be identical to that prepared in Procedure 1.

4-(3',4'-Methylenedioxyphenyl)nitrobenzene (Table 2, Entry 17)

Procedure 1: According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (412 mg, 2.05 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (2.7 mL, 1.66 M, 4.48 mmol) and ZnCl₂ (3.0 mL, 1.0 M, 3.00 mmol) and the whole was warmed to rt. According to General Procedure D, to a second flask containing Pd(PPh₃)₄ (63 mg, 0.054 mmol) in THF (3 mL) was added sequentially the above freshly prepared organozinc solution via canula and a solution of 4-nitrophenyl trifluoromethanesulfonate (290 mg, 1.07 mmol) in THF (2+1 mL). The reaction vessel was then equipped with a reflux condenser and the contents subsequently heated to reflux. After 21 h, the reaction mixture was cooled to rt. Normal workup followed by flash chromatography (9:1 hexane:EtOAc) gave the product (91 mg, 35%) as a yellow solid: mp 155-60 °C (subl); IR (KBr) ν (max) 2912, 1594, 1509, 1335, 1231, 1032 cm⁻¹; ¹H NMR (250 MHz, CDCl₃) δ 6.04 (s, 2H, OC₆H₄O), 6.92 (d, J = 7.9 Hz, 1H), 7.09-7.13 (m, 2H), 7.64 (d, J = 8.9 Hz, 2H), 8.25 (d, J = 8.9 Hz, 2H); MS (EI (70 eV)) m/z (rel intensity) 243 (M⁺, 100), 197 (7), 167 (6), 139 (40). Anal. Calcd for C₁₃H₉NO₄: C, 64.20; H, 3.73; N, 5.76. Found: C, 64.40; H, 4.00; N, 5.85.

Procedure 2: According to General Procedure E, a solution of 4-nitrophenyl trifluoromethanesulfonate (269 mg, 0.99 mmol) in DME (3 mL) was treated with a solution of 3,4-methylenedioxyphenyl boronic acid (215 mg, 1.29 mmol) in DME (3 mL) and EtOH (3 mL) in the presence of Pd(PPh₃)₄ (50 mg, 0.043 mmol). After 15 h, the reaction mixture was cooled to rt. Normal workup followed by flash chromatography (9:1 hexane:EtOAc) afforded the product (147 mg, 61%) shown to be identical to that prepared in Procedure 1.
**N-tert-Butoxycarbonyl 2-(4-biphenyl)ethylamine (Table 2, Entry 18)**

**Procedure 1:** To a flask charged with a solution of ZnCl₂ (1.5 mL, 1.0 M, 1.5 mmol) in THF (4 mL) was added at rt a solution of PhLi (1.0 mL, 1.51 M, 1.51 mmol). According to General Procedure D, to a second flask containing a solution of Ni(acac)₂ (15 mg, 0.059 mmol) in THF (4 mL) was added sequentially solutions of i-PrMgCl (0.10 mL, 2.0 M, 0.20 mmol), the above freshly prepared organozinc solution via canula and a solution of N-tert-butoxycarbonyltyramine trifluoromethanesulfonate (119 mg, 0.32 mmol) in THF (2+1 mL) via canula. After 4.5 h reaction, normal workup followed by flash chromatography (6:1 hexane:EtOAc) gave the product (35 mg, 37%) as a colourless solid, mp 87.5-8.5 °C (hexane), ¹H NMR (250 MHz, CDCl₃) δ 1.45 (s, 9H, OC(CH₃)₃), 2.82 (t, J = 6.9 Hz, 2H, ArCH₂CH₂N), 3.4 (b, 2H, ArCH₂N), 4.63 (bs, 1H, NH), 6.83-6.92 (m, 2H), 7.18-7.59 (m, 7H); MS (EI (70 eV)) m/z (rel intensity) 297 (M⁺, 9), 241 (61), 180 (100), 105 (26), 57 (22). Anal. Calcd for C₁₉H₂₃NO₂: C, 76.74; H, 7.80; N, 4.71. Found C, 76.61; H, 7.62; N, 4.78.

**Procedure 2:** According to General Procedure C, to a flask containing a solution of N-tert-butoxycarbonyltyramine trifluoromethanesulfonate (342 mg, 1.03 mmol) and NiCl₂(dppe) (27 mg, 0.052 mmol) in THF (10 mL) was added a solution of PhMgCl (1.5 mL, 2.0 M, 3.00 mmol). After 4 h reaction time, normal workup followed by flash chromatography (4:1 hexane:EtOAc) gave the product (178 mg, 58%) shown to be identical to that prepared in Procedure 1.

**Procedure 3:** According to General Procedure E, a solution of N-tert-butoxycarbonyltyramine trifluoromethanesulfonate (337 mg, 1.01 mmol) in DME (3 mL) was treated with a solution of phenyl boronic acid (179 mg, 1.47 mmol) in DME (3 mL) in the presence of Pd(PPh₃)₄ (39 mg, 0.034 mmol). After 16 h, the reaction mixture was cooled to rt. Normal workup followed by flash chromatography (4:1 hexane:EtOAc) afforded the product (246 mg, 82%) shown to be identical to that prepared in Procedure 1.
**N-Benzyl-4-phenyl-2-quinolone (Table 2, Entry 19)**

**Procedure 1:** To a flask charged with a solution of ZnBr$_2$ (285 mg, 1.26 mmol) in THF (3 mL) was added at rt a solution of PhLi (0.56 mL, 1.82 M, 1.02 mmol). According to General Procedure D, to a second flask containing N-benzyl-4-trifluoromethanesulfonyl-2-one (191 mg, 0.50 mmol), Ni(acac)$_2$ (10 mg, 0.039 mmol) and PPh$_3$ (39 mg, 0.15 mmol) in THF (3 mL) was added sequentially solutions of DIBAH (0.03 mL, 1.5 M, 0.045 mmol) and the above freshly prepared organozinc solution via canula. After 4.5 h reaction, normal workup followed by flash chromatography (2:1 hexane:EtOAc) gave the product (104 mg, 67%) as a colourless solid, mp 116-7 °C (CH$_2$Cl$_2$/hexane); $^1$H NMR (250 MHz, CDCl$_3$) δ 6.10 (s, 2H, PhCH$_2$), 7.53-8.06 (m, 15H); $^{13}$C NMR (50 MHz, CDCl$_3$) δ 45.9 (e), 115.2 (o), 120.6 (e), 121.0 (o), 121.9 (o), 126.6 (o), 127.2 (o), 127.6 (o), 127.8 (o), 128.7 (o), 130.5 (o), 136.3 (e), 137.0 (e), 139.6 (e), 151.4 (e), 162.0 (e).

**Procedure 2:** According to General Procedure C, to a flask containing a solution of N-benzyl-4-trifluoromethanesulfonyl-2-one (187 mg, 0.49 mmol) and Ni(acac)$_2$ (13 mg, 0.051 mmol) in Et$_2$O (5 mL) was added a solution of PhMgBr (0.40 mL, 2.0 M, 0.80 mmol). After 5 h of reaction time, normal workup followed by flash chromatography (2:1 hexane:EtOAc) gave the product (187 mg, 52%) shown to be identical to that prepared in Procedure 1.

**Procedure 3:** According to General Procedure E, a solution of N-benzyl-4-trifluoromethanesulfonyl-2-one (89 mg, 0.23 mmol) in DME (2 mL) was treated with a solution of phenyl boronic acid (99 mg, 0.82 mmol) in DME (2 mL) in the presence of Pd(PPh$_3$)$_4$ (16 mg, 0.014 mmol) and 2N Na$_2$CO$_3$ (1.0 mL). After 17 h, the reaction mixture was cooled to rt. Normal workup followed by flash chromatography (2:1 hexane:EtOAc) afforded the product (51 mg, 71%) shown to be identical to that prepared in Procedure 1.
4-Methoxy-3-(2'-tolyl)benzaldehyde (Table 2, Entry 20)

**Procedure 1:** According to General Procedure B, Method A, a solution of 2-bromotoluene (340 mg, 1.99 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (2.6 mL, 1.66 M, 4.32 mmol) and ZnCl$_2$ (3.0 mL, 1.0 M, 3.00 mmol) and the whole was warmed to rt. According to General Procedure D, to a second flask containing a solution of Ni(acac)$_2$ (16 mg, 0.063 mmol) and PPh$_3$ (70 mg, 0.027 mmol) in THF (3 mL) was added sequentially solutions of MeMgBr (0.090 mL, 3.0 M, 0.27 mmol), the above freshly prepared organozinc solution via canula and a solution of 4-methoxy-3-trifluoromethanesulfonyloxy benzaldehyde (307 mg, 1.08 mmol) in THF (2+1 mL). After 2 h of reaction time, normal workup followed by flash chromatography (4:1 hexane:EtOAc) gave the product (182 mg, 74%) as a colourless oil: IR (neat) $\nu$ (max) 2729, 1689 cm$^{-1}$; $^1$H NMR (250 MHz, CDCl$_3$) $\delta$ 2.11 (s, 3H, ArC$_3$H$_3$), 3.82 (s, 3H, OCH$_3$), 7.06 (d, $J = 8.5$ Hz, 1H), 7.1-7.3 (m, 4H), 7.68 (d, $J = 2.2$ Hz, 1H), 7.88 (dd, $J = 8.5, 2.2$ Hz, 1H), 9.89 (s, 1H, CHO); $^{13}$C NMR (62.9 MHz, CDCl$_3$) $\delta$ 19.7 (o, ArCH$_3$), 55.7 (o, OCH$_3$), 110.6 (o), 125.5 (o), 127.7 (o), 129.6 (o), 129.8 (o), 131.3 (o), 131.6 (e), 132.5 (o), 136.5 (e), 137.1 (e), 161.6 (e), 190.7 (o, CHO); MS (EI (60 eV)) m/z (rel intensity) 226 (M$^+$, 100), 211 (5), 197 (7), 182 (9), 165 (17), 152 (10); HRMS calcd for C$_{15}$H$_{15}$O$_2$: 227.1072. Found: 227.1072.

**Procedure 2:** According to General Procedure E, a solution of 4-methoxy-3-trifluoromethanesulfonyloxybenzaldehyde (296 mg, 1.04 mmol) in DME (3 mL) was treated with a solution of 2-tolyl boronic acid (200 mg, 1.47 mmol) in DME (3 mL) and EtOH (3 mL) in the presence of Pd(PPh$_3$)$_4$ (39 mg, 0.034 mmol). After 14 h, the reaction mixture was cooled to rt. Normal workup followed by flash chromatography (4:1 hexane:EtOAc) afforded the product (225 mg, 95%) shown to be identical to that prepared in Procedure 1.
1-(3',4'-Methylenedioxyphenyl)fluorenone (Table 2, Entry 21)

**Procedure 1:** According to General Procedure B, Method A, a solution of 4-bromo-1,2-methylenedioxybenzene (400 mg, 1.99 mmol) in THF (10 mL) was sequentially treated with solutions of t-BuLi (2.5 mL, 1.73 M, 4.33 mmol) and ZnCl₂ (3.0 mL, 1.0 M, 3.0 mmol) and the whole was warmed to rt. According to General Procedure D, to a second flask containing Ni(acac)₂ (16 mg, 0.062 mmol) and PPh₃ (63 mg, 0.24 mmol) in THF (3 mL) was added sequentially solutions of MeMgBr (0.08 mL, 3.0 M, 0.24 mmol), the above freshly prepared organozinc solution via canula and a solution of 9-trifluoromethanesulfonyloxyfluorenone (336 mg, 0.98 mmol) in THF (4+1 mL) via canula. After 2 h of reaction time, normal workup followed by flash chromatography (4:1 hexane:EtOAc) gave the product (169 mg, 58%) as a yellow solid, mp 132-132.5 °C (Et₂O/hexane); IR (KBr) ν (max) 1702, 1227, 1034 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 6.00 (s, 2H, OC₆H₂O), 6.86 (m, 1H), 6.97-7.01 (m, 2H), 7.16 (m, 1H), 7.26 (m, 1H), 7.41-7.59 (m, 5H); ¹³C NMR (50 MHz, CDCl₃) δ 101.1 (e, OCH₂O), 107.9 (o), 109.8 (o), 118.9 (o), 119.9 (o), 122.9 (o), 124.0 (o), 129.1 (o), 129.5 (o), 131.2 (e), 131.5 (o), 134.1 (o), 134.2 (e), 134.4 (o), 141.9 (e), 143.4 (e), 145.5 (e), 147.2 (e), 147.7 (e), 192.9 (e); MS (EI (60 eV)) m/z (rel intensity) 300 (M⁺, 100), 271 (3), 242 (8), 213 (24), 187 (6), 163 (2), 121 (5). Anal. Calcd for C₂₀H₁₂O₃: C, 79.99; H, 4.03. Found: C, 79.76; H, 4.23.

**Procedure 2:** According to General Procedure E, a solution of 9-trifluoromethanesulfonyloxyfluorenone (333 mg, 1.02 mmol) in DME (3 mL) was treated with a solution of 3,4-methylenedioxyphenyl boronic acid (216 mg, 1.30 mmol) in DME (3 mL) and EtOH (3 mL) in the presence of Pd(PPh₃)₄ (42 mg, 0.036 mmol). After 30 h, the reaction mixture was cooled to rt. Normal workup followed by flash chromatography (4:1 hexane:EtOAc) afforded the product (286 mg, 94%) shown to be identical to that prepared in **Procedure 1**.