Supporting Information

Selective and General Exhaustive Cross-Coupling of Di-Chloroarenes With a Deficit of Nucleophile Mediated by a Pd-NHC Complex

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Table of Contents

General Experimental Section

General Procedures

Experimental Data

Scheme 2

Figure 1

Synthesis of Starting Materials

$^1$H and $^{13}$C NMR Spectra

References
General Experimental

Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. Anhydrous solvents were obtained by passing the solvent through an activated alumina column on an MBRAUN MB SPS-800 solvent purification system. 2,7-Dichlorofluorenone,\textsuperscript{1} 4a-e,\textsuperscript{2,3,4} were prepared according to reported procedures. All reactions were carried out under an atmosphere of N\textsubscript{2} unless otherwise stated. Microwave vials were supplied by CEM. Flash column chromatography was carried out using a Varian Inteliflash or Biotage Isolera with Biotage Snap cartridges. THF stands for tetrahydrofuran, NMP stands for N-methylpyrrolidone and DMI stands for 1,3-dimethyl-2-imidazolidinone, dba stands for dibenzylideneacetone and Binap stands for 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl. Petrol refers to the fraction of petroleum ether boiling in the range 40 – 60 °C. Solutions of organometallic reagents were titrated prior to use according to literature procedures.\textsuperscript{5}

\textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded on a Bruker AV600, AV 400 or AVIII 400 instrument. Chemical shifts are reported in parts per million and referenced to residual solvent. Coupling constants (\textit{J}) are reported in Hz. Standard abbreviations indicating multiplicity were used as follows: m = multiplet, quint. = quintet, q = quartet, t = triplet, d = doublet, s = singlet. Low resolution GC-MS samples were recorded at Queen Mary University of London analytical services on Varian combined 450-GC and 220-MS (ESI) or Agilent combined 6890N-GC and 5973N-MS (ESI) systems. High resolution mass spectrometry was carried out by the EPSRC National Mass Spectrometry Centre in Swansea. Melting points were determined using a Sanyo Gallenkamp apparatus and are uncorrected.
General Procedures

Titration of Organometallics: A CEM microwave vial was charged with I$_2$ (0.127 g, 0.50 mmol), sealed, purged with N$_2$ and anhydrous LiBr (0.5 M in THF, 4.0 mL, 2.0 mmol) was added. The resulting brown solution was cooled to 0 °C. A solution of the organometallic compound of interest was added dropwise until the solution became colourless which indicated consumption of one equivalent (0.50 mmol) of the organometallic.

Preparation of ZnCl$_2$ (1M in THF): A flask equipped with a Young’s tap was charged with ZnCl$_2$ (35.2 g, 251 mmol) and the solid dried under high vacuum at 160 °C for 16 h. The flask was cooled to rt and filled with N$_2$. THF (251 mL) was added and the mixture stirred for 24 h at rt until all solid had fully dissolved.

General procedure for Kumada couplings: A CEM microwave vial was charged with PEPPSI-IPent (4.0 mg, 5.0 µmol), and, if solid at rt, the organohalide (0.25 mmol). The vial was sealed, flushed with N$_2$, THF (0.88 mL) was added and the solution was stirred at 50 °C. If the organohalide was a liquid at rt, it was added immediately after the addition of THF. PhMgBr (1.0 M in THF, 0.25 mL, 0.25 mmol) was added and the resultant solution was stirred for 3 h at 50 °C. Mesitylene was added as an internal standard (0.50 M in CDCl$_3$, 0.50 mL, 0.25 mmol), and the crude reaction mixture was analysed by GC-MS and $^1$H NMR. To facilitate the analysis of the outcome of cross coupling reactions the major product was isolated to confirm its identity and to verify the peaks of interest in the crude reaction mixture. All novel compounds were fully characterized.

General procedure for Suzuki couplings: A CEM microwave vial was charged with PEPPSI-IPent (4.0 mg, 5.0 µmol), K$_2$CO$_3$ (105 mg, 0.75 mmol), PhB(OH)$_2$ (30 mg, 0.25 mmol) and, if solid at rt, the organohalide (0.25 mmol). The vial was sealed, flushed with N$_2$, 1,4-dioxane (1.0 mL) was added and the resultant mixture was stirred at 60 °C for 12 h. If the organohalide was a liquid at rt, it was added immediately after the addition of 1,4-dioxane. Mesitylene was added as an internal standard (0.50 M in CDCl$_3$, 0.50 mL, 0.25 mmol), and the crude reaction mixture was analysed by GC-MS and $^1$H NMR. To facilitate the analysis of the outcome of cross coupling reactions the major product was
isolated to confirm its identity and to verify the peaks of interest in the crude reaction mixture. All novel compounds were fully characterized.

**General procedure for Negishi couplings:**\(^7\) ZnCl\(_2\) (1.0 M in THF, 2.0 mL, 2.0 mmol) and PhMgBr (1.0 M in THF, 2.0 mL, 2.0 mmol) were stirred vigorously under N\(_2\) at rt for 30 min. NMP (4.0 mL) was added to the mixture and the resulting PhZnCl (1.0 mL, 0.25 mmol) was added by syringe to a CEM vial charged with PEPPSI-IPent (4.0 mg, 5.0 µmol), and the organohalide (0.25 mmol) in NMP (0.50 mL). The reaction mixture was stirred at 30 °C for 2 h. Mesitylene was added as an internal standard (0.50 M in CDCl\(_3\), 0.50 mL, 0.25 mmol), and the crude reaction mixture was analysed by GC-MS and \(^1\)H NMR. To facilitate the analysis of the outcome of cross coupling reactions the major product was isolated to confirm its identity and to verify the peaks of interest in the crude reaction mixture. All novel compounds were fully characterized.

The characterization data for 2a, 3a, 3b, 3c, 3f, 3h, 3j, 3k, 3n, 3o, 3p, 3q, 3r, 2s, 3u, 3v, 3w matched those previously reported.

**Experimental Data**

**Scheme 1, Entry 1:**

Using the general procedure for Kumada couplings employing PEPPSI-IMes (3.0 mg, 5.0 µmol) in place of PEPPSI-IPent a product mixture of 2a and 3a is obtained in a >99 : <1 ratio by GC-MS analysis. \(^1\)H NMR analysis using mesitylene as internal standard indicates a 16% yield of 2a+3a based on PhMgBr. The remaining reaction mixture was diluted in CH\(_2\)Cl\(_2\), filtered through a silica plug and reduced in vacuo. Automated flash chromatography (petrol raising to 1 : 9 CH\(_2\)Cl\(_2\) : petrol) gave an analytical sample of major product 2a as a white solid: m.p. 78 - 79 °C (lit.\(^25\) 77-78); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.59 – 7.49 (m, 4H), 7.48 – 7.39 (m, 4H), 7.39 – 7.33 (m, 1H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 140.2, 139.8, 133.5 129.1, 129.0, 128.5, 127.7, 127.1.
**Scheme 1, Entry 2:**

Using the general procedure for Kumada couplings, employing PEPPSI-I\text{Et} (3.1 mg, 5.0 µmol) in place of PEPPSI-I\text{Pent}, a product mixture of 2\text{a} and 3\text{a} is obtained in a 70 : 30 ratio by GC-MS analysis. \textsuperscript{1}H NMR analysis using mesitylene as internal standard indicates a 50% yield of 2\text{a}+3\text{a} based on PhMgBr.

**Scheme 1, Entry 3:**

Using the general procedure for Kumada couplings, employing PEPPSI-I\text{Pr} (3.4 mg, 5.0 µmol) in place of PEPPSI-I\text{Pent}, a product mixture of 2\text{a} and 3\text{a} is obtained in a 45 : 55 ratio by GC-MS. \textsuperscript{1}H NMR analysis using mesitylene as internal standard indicates an 83% yield of 2\text{a}+3\text{a} based on PhMgBr. The remaining reaction mixture was diluted in CH\textsubscript{2}Cl\textsubscript{2}, filtered through a silica plug and reduced in vacuo. Automated flash chromatography (petrol raising to 1 : 9 CH\textsubscript{2}Cl\textsubscript{2} : petrol) gave an analytical sample of major product 3\text{a} as a white solid: m.p. 207 – 208 °C (lit.\textsuperscript{26} 210 – 211 °C); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 7.69 (s, 4H), 7.65 (d, J = 7.3, 4H), 7.47 (t, J = 7.6, 4H), 7.37 (t, J = 7.4, 2H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ 140.9, 140.3, 129.0, 127.7, 127.5, 127.2.

**Scheme 1, Entry 4:**
Using the general procedure for Kumada couplings a product mixture of 2a and 3a is obtained in a 6 : 94 ratio by GC-MS analysis. $^1$H NMR analysis using mesitylene as internal standard indicates a 96% yield of 2a+3a based on PhMgBr.

**Figure 1, 3b:**

Using the general procedure for Kumada couplings a product mixture of 2b and 3b is obtained in a 13 : 87 ratio by GC-MS analysis. $^1$H NMR analysis using mesitylene as internal standard indicates an 80% yield of 2b+3b based on PhMgBr. The remaining reaction mixture was diluted in CH$_2$Cl$_2$, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 1 : 9 CH$_2$Cl$_2$ : petrol) gave an analytical sample of major product 3b as a white solid: m.p. 86 - 88 °C (lit. 27 84 - 85); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.82 (q, $J = 1.5$, 1H), 7.65 (dq, $J = 2.5, 1.7$, 4H), 7.61 - 7.56 (m, 2H), 7.55 – 7.43 (m, 5H), 7.41 – 7.34 (m, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 142.0, 141.4, 129.3, 129.0, 127.6, 127.4, 126.3, 126.3.

**Figure 1, 3c:**

Using the general procedure for Kumada couplings a product mixture of 2c and 3c is obtained in a 84 : 16 ratio by GC-MS analysis. $^1$H NMR analysis using mesitylene as internal standard indicates a 66% yield of 2c+3c based on PhMgBr. The remaining reaction mixture was diluted in CH$_2$Cl$_2$, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 1 : 9 CH$_2$Cl$_2$ : petrol) gave an analytical sample of major product 3c as a white solid: m.p. 55 – 58 °C.
Using the general procedure for Kumada couplings a product mixture of 2d and 3d is obtained in a 3 : 97 ratio by GC-MS analysis. $^1$H NMR analysis using mesitylene as internal standard indicates a 91% yield of 2d+3d based on PhMgBr. The remaining reaction mixture was diluted in CH$_2$Cl$_2$, filtered through a silica plug and reduced in vacuo. Automated flash chromatography (petrol raising to 1 : 9 CH$_2$Cl$_2$ : petrol) gave an analytical sample of major product 3d as a white solid: m.p. 70 – 71 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.67 – 7.57 (m, 5H), 7.48 (dd, $J = 10.2, 4.7, 4H), 7.43 – 7.37 (m, 2H), 7.28 (dd, $J = 9.7, 1.5, 2H); $^1$C NMR (101 MHz, CDCl$_3$) δ 164.9, 162.4, 144.0, 143.9, 129.1, 128.1, 127.3, 121.9, 113.1, 112.8; LRMS (ESI) 248.6 [M]$^+$; IR (cm$^{-1}$) 3064, 3037, 2925, 1594, 1575, 1408, 1336, 1165, 866, 756, 695, 689.

Using the general procedure for Kumada couplings a product mixture of 2e and 3e is obtained in a 5 : 95 ratio by GC-MS analysis. $^1$H NMR analysis using mesitylene as internal standard indicates a 94% yield of 2e+3e based on PhMgBr. The remaining reaction mixture was diluted in CH$_2$Cl$_2$, filtered through a silica plug and reduced in vacuo. Automated flash chromatography (petrol) gave an analytical sample of major product 3e as a white solid: m.p. 75 - 76 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 – 7.40 (m, 4H), 7.25 – 7.12 (m, 10H); $^1$C NMR (101 MHz, CDCl$_3$) δ 141.7, 140.7, 130.7, 130.0, 128.0, 127.6, 126.6.
δ 8.02 – 7.98 (m, 1H), 7.85 (dd, J = 1.6, 0.7, 2H), 7.72 - 7.66 (m, 4H), 7.56 – 7.50 (m, 4H), 7.49 - 7.43 (m, 2H); 13C NMR (101 MHz, CDCl₃) δ 142.8, 134.0, 129.4, 129.2, 128.3, 127.4, 122.9, 122.9; LRMS (ESI) 298.2 [M⁺]; HRMS (EI) 298.0965 [M⁺] (calc. for C₁₉H₁₃F₃ 298.0964 [M⁺]); IR (cm⁻¹) 3036, 1363, 1264, 1167, 1110, 758, 694.

**Figure 1, 3f:**

Using the general procedure for Kumada couplings a product mixture of 2f and 3f is obtained in a 2 : 98 ratio by GC-MS analysis. ¹H NMR analysis using mesitylene as internal standard indicates a 84% yield of 2h+3h based on PhMgBr. The remaining reaction mixture was diluted in CH₂Cl₂, filtered through a silica plug and reduced in vacuo. Automated flash chromatography (petrol raising to 1 : 9 CH₂Cl₂ : petrol) gave an analytical sample of major product 3f as a white solid: m.p. 137 - 140 °C (lit.28 135 – 138 °C); ¹H NMR (400 MHz, CDCl₃) δ 7.67 (m, 5H), 7.48 (t, J = 7.6, 4H), 7.43 (d, J = 0.7, 2H), 7.41 – 7.36 (m, 2H), 2.52 (s, 3H); 13C NMR (101 MHz, CDCl₃) δ 142.0, 141.5, 138.9, 128.9, 127.5, 127.4, 127.1, 123.6, 21.8.

**Figure 1, 3g:**

Using the general procedure for Kumada couplings a product mixture of 2g and 3g is obtained in a >1 : 99 ratio by GC-MS analysis. ¹H NMR analysis using mesitylene as internal standard indicates a 71% yield of 2g+3g based on PhMgBr. The remaining reaction mixture was diluted in CH₂Cl₂, filtered through a silica plug and reduced in vacuo. Automated flash chromatography (1 : 9 petrol : CH₂Cl₂ raising to CH₂Cl₂) gave an analytical sample of major product 3g as a white solid:
Using the general procedure for Kumada couplings a product mixture of 2h and 3h is obtained in a <1: >99 ratio by GC-MS analysis. 1H NMR analysis using mesitylene as internal standard indicates an 82% yield of 2h+3h based on PhMgBr. The remaining reaction mixture was diluted in CH2Cl2, filtered through a silica plug and reduced in vacuo. Automated flash chromatography (petrol raising to 3 : 7 CH2Cl2 : petrol) gave an analytical sample of major product 3h as a white solid: m.p. 91 - 93 °C (lit.29 91 – 92 °C); 1H NMR (400 MHz, CDCl3) δ 7.66 (dd, J = 5.2, 3.3 , 4H), 7.47 (dd, J = 10.3, 4.7 , 4H), 7.43 – 7.35 (m, 3H), 7.13 (d, J = 1.5 , 2H), 3.93 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 160.5, 143.3, 141.3, 128.9, 127.7, 127.4, 119.1, 111.9, 55.6.

Using the general procedure for Kumada couplings a product mixture of 2i and 3i is obtained in a 8 : 92 ratio by GC-MS analysis. 1H NMR analysis using mesitylene as internal standard indicates an 85% yield of 2i+3i based on PhMgBr. The remaining reaction mixture was diluted in CH2Cl2, filtered...
through a silica plug and reduced in vacuo. Automated flash chromatography (petrol raising to 3 : 7 CH₂Cl₂ : petrol) gave an analytical sample of major product 3i as a colourless oil: \(^1\text{H NMR (400 MHz, CDCl}_3\) δ 7.65 – 7.60 (m, 4H), 7.48 – 7.41 (m, 4H), 7.40 – 7.33 (m, 4H), 7.25 (dd, \(J = 8.2, 6.9, 1\text{H})\), 3.18 (s, 3H); \(^{13}\text{C NMR (101 MHz, CDCl}_3\) δ 155.1, 138.9, 135.9, 130.5, 129.5, 128.3, 127.3, 124.4, 60.6; LRMS (ESI) 260.2 [M\(^+\)]; HRMS (EI) 260.1198 [M\(^+\)] (calc. for C₁₉H₁₆O 260.1196 [M\(^+\)]; IR (cm\(^{-1}\)) 3060, 3025, 2929, 1462, 1407, 1226, 1005, 749, 697.

**Figure 1, 3j:**

Using the general procedure for Kumada couplings a product mixture of 2j or 2j’ and 3j is obtained in a 12 : 0 : 88 ratio by GC-MS analysis. \(^1\text{H NMR analysis using mesitylene as internal standard indicates an 81\% yield of 2j+3j based on PhMgBr. The remaining reaction mixture was diluted in CH₂Cl₂, filtered through a silica plug and reduced in vacuo. Automated flash chromatography (petrol raising to 3 : 7 CH₂Cl₂ : petrol) gave an analytical sample of major product 3j as a white solid: m.p. 116-117 °C (lit.\(^{30}\) 113 – 115 °C); \(^1\text{H NMR (400 MHz, CDCl}_3\) δ 7.39 – 7.34 (m, 1H), 7.26 – 7.13 (m, 8H), 7.13 – 7.08 (m, 2H), 7.00 – 6.96 (m, 2H), 3.89 (s, 3H); \(^{13}\text{C NMR (101 MHz, CDCl}_3\) δ 158.9, 141.8, 141.5, 141.2, 133.3, 131.7, 130.0, 129.8, 127.9, 127.8, 126.6, 126.1, 115.9, 113.1, 55.4.

**Figure 1, 3k:**

Using the general procedure for Kumada couplings a product mixture of 2k, 2k’ and 3k is obtained in a 29 : 1 : 70 ratio by GC-MS analysis. \(^1\text{H NMR analysis using mesitylene as internal standard...
indicates a 94% yield of $2k + 2k' + 3k$ based on PhMgBr. The remaining reaction mixture was diluted in CH$_2$Cl$_2$, filtered through a silica plug and reduced in vacuo. Automated flash chromatography (petrol raising to 3 : 7 CH$_2$Cl$_2$ : petrol) gave an analytical sample of major product $3k$ as a white solid: m.p. 99 - 100 °C (lit.$^{31}$ 93 – 94 °C); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 – 7.54 (m, 6H), 7.43 (ddd, $J$ = 7.9, 5.9, 2.9, 4H), 7.38 – 7.29 (m, 2H), 7.07 (d, $J$ = 8.5, 1H), 3.86 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.2, 140.9, 138.6, 134.1, 131.2, 129.9, 129.7, 128.9, 128.2, 127.2, 127.2, 126.9, 126.9, 111.7, 55.9.

**Figure 1, 3l:**

Using the general procedure for Kumada couplings a product mixture of $2l$, $2l'$ and $3l$ is obtained in a 21 : 0 : 79 ratio by GC-MS analysis. $^1$H NMR analysis using mesitylene as internal standard indicates a 99% yield of $2l + 3l$ based on PhMgBr. The remaining reaction mixture was diluted in CH$_2$Cl$_2$, filtered through a silica plug and reduced in vacuo. Automated flash chromatography (petrol raising to 3 : 7 CH$_2$Cl$_2$ : petrol) gave an analytical sample of major product $3l$ as a white solid: m.p. 96 - 100 °C; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.70 – 7.64 (m, 2H), 7.63 – 7.58 (m, 2H), 7.52 – 7.33 (m, 7H), 7.31 – 7.27 (m, 1H), 7.22 (d, $J$ = 1.5, 1H), 3.90 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 156.9, 142.1, 141.2, 138.4, 131.3, 129.9, 129.7, 128.9, 128.2, 127.6, 127.3, 127.1, 119.9, 110.4, 55.8.; LRMS (ESI) 260.2 [M]$^+$; HRMS (EI) 260.1200 [M]$^+$ (calc. for C$_{19}$H$_{16}$O 260.1196 [M]$^+$); IR (cm$^{-1}$) 3033, 2956, 2932, 1215, 753, 694.

**Figure 1, 3m:**
Using the general procedure for Kumada couplings a product mixture of 2m, 2m′ and 3m is obtained in a 70 : 0 : 30 ratio by GC-MS analysis. 1H NMR analysis using mesitylene as internal standard indicates an 85% yield of 2m+3m based on PhMgBr. The remaining reaction mixture was diluted in CH₂Cl₂, filtered through a silica plug and reduced in vacuo. Automated flash chromatography (petrol raising to 3 : 7 CH₂Cl₂ : petrol) gave analytical samples of 2m, 2m′ (colourless oil):

1H NMR (600 MHz, CDCl₃) δ 7.45 – 7.42 (m, 4H), 7.41 – 7.36 (m, 1H), 7.30 – 7.26 (m, 1H), 6.97 – 6.94 (m, 2H), 3.96 (s, 3H); 13C NMR (101 MHz, CDCl₃) δ 155.6, 142.4, 139.6, 129.6, 128.1, 127.7, 127.1, 123.4, 121.3, 110.9, 56.5; LRMS (ESI) 218.3 [M]+; HRMS (APCI) 219.0571 [M+H]+ (calc. for C₁₃H₁₂O₃5Cl 219.0571 [M+H]+); IR (cm⁻¹) 3060, 2939, 2839, 1568, 1465, 1422, 1262, 1218, 757, 698.

3m (white solid): m.p. 108 – 109 °C 1H NMR (400 MHz, CDCl₃) δ 7.39 (t, J = 8.0 Hz, 1H), 7.24 – 7.03 (m, 11H), 7.01 (dd, J = 8.3, 0.8 Hz, 1H), 3.79 (s, 3H); 13C NMR (101 MHz, CDCl₃) δ 157.1, 143.0, 141.6, 137.0, 131.4, 130.0, 129.9, 128.4, 127.7, 127.5, 126.5, 126.4, 122.9, 110.2, 56.1.

Using the general procedure for Kumada couplings a product mixture of 2n, 2n′ and 3n is obtained in a 2 : 5 : 93 ratio by GC-MS. 1H NMR analysis using mesitylene as internal standard indicates an 75% yield of 2n+2n′+3n based on PhMgBr. The remaining reaction mixture was diluted in CH₂Cl₂, filtered through a silica plug and reduced in vacuo. Automated flash chromatography (petrol raising to 4 : 6 CH₂Cl₂ : petrol) gave an analytical sample of major product 3n as a white solid: m.p. 172 °C (lit. 32173 – 174 °C); 1H NMR (400 MHz, CDCl₃) δ 7.79 (s, 3H), 7.71 (dq, J = 2.5, 1.7 , 6H), 7.52 – 7.45 (m, 6H), 7.43 – 7.36 (m, 3H); 13C NMR (101 MHz, CDCl₃) δ 142.5, 141.3, 129.0, 127.7, 127.5, 125.3.

Figure 1, 3n:

Figure 1, 3o:
Using the general procedure for Kumada couplings a product mixture of mono, di and tri-coupled products and 3o is obtained in a 19 : 1 : 2 : 78 ratio by GC-MS analysis. \textsuperscript{1}H NMR analysis using mesitylene as internal standard indicates a combined 49% yield based on PhMgBr. The remaining reaction mixture was diluted in CH\textsubscript{2}Cl\textsubscript{2}, filtered through a silica plug and reduced \textit{in vacuo}. Automated flash chromatography (petrol raising to 6 : 4 CH\textsubscript{2}Cl\textsubscript{2} : petrol) gave an analytical sample of major product 3o as a white solid: m.p. >250 °C (lit.\textsuperscript{33} 274 – 275 °C); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.53 (s, 2H), 7.25 – 7.21 (m, 20H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 141.1, 139.8, 133.1, 130.1, 128.1.

\textbf{Figure 1, 3p:}

Using the general procedure for Kumada couplings a product mixture of 2p and 3p is obtained in a 11 : 89 ratio by GC-MS analysis. \textsuperscript{1}H NMR analysis using mesitylene as internal standard indicates a 92% yield of 2p+3p based on 4-MePhMgBr. The remaining reaction mixture was diluted in CH\textsubscript{2}Cl\textsubscript{2}, filtered through a silica plug and reduced \textit{in vacuo}. Automated flash chromatography (petrol raising to 2 : 8 CH\textsubscript{2}Cl\textsubscript{2} : petrol) gave an analytical sample of major product 3p as a white solid: m.p. >250 °C (lit.\textsuperscript{34} 249 – 250 °C); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.57 (s, 4H), 7.49 – 7.44 (m, 4H), 7.22 – 7.17 (m, 4H), 2.33 (s, 6H); \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 139.9, 138.1, 137.2, 129.7, 127.4, 127.0, 21.3.

\textbf{Figure 1, 3q:}
Using the general procedure for Kumada couplings a product mixture of 2q and 3q is obtained in a 10 : 90 ratio by GC-MS analysis. ¹H NMR analysis using mesitylene as internal standard indicates a 72% yield of 2q + 3q based on 4-MeOPhMgBr. The remaining reaction mixture was diluted in CH₂Cl₂, filtered through a silica plug and reduced in vacuo. Automated flash chromatography (petrol raising to 7 : 3 CH₂Cl₂ : petrol) gave an analytical sample of major product 3q as a white solid: m.p. >250 °C (lit. 35270 – 271 °C); ¹H NMR (400 MHz, CDCl₃) δ 7.61 (s, 4H), 7.60 – 7.55 (m, 4H), 7.02 – 6.97 (m, 4H), 3.86 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 159.3, 139.3, 133.5, 128.2, 127.2, 114.4, 55.5.

**Figure 1, 3r:**

Using the general procedure for Kumada couplings a product mixture of 2r and 3r is obtained in a 4 : 96 ratio by GC-MS analysis. ¹H NMR analysis using mesitylene as internal standard indicates a 93% yield of 2r + 3r based on 4-FPhMgBr. The remaining reaction mixture was diluted in CH₂Cl₂, filtered through a silica plug and reduced in vacuo. Automated flash chromatography (petrol raising to 4 : 6 CH₂Cl₂ : petrol) gave an analytical sample of major product 3r as a white solid: m.p. 224 - 226 °C (lit. 36219 – 222 °C); ¹H NMR (400 MHz, CDCl₃) δ 7.63 – 7.56 (m, 8H), 7.19 – 7.11 (m, 4H); ¹³C NMR (101 MHz, CDCl₃) δ 163.9, 161.5, 139.3, 136.9, 128.8, 128.7, 127.6, 116.0, 115.8.

**Figure 1, 3s:**
Using the general procedure for Kumada couplings a product mixture of 2s and 3s is obtained in a 81 : 19 ratio by GC-MS analysis. $^1$H NMR analysis using mesitylene as internal standard indicates a 92% yield of 2s+3s based on 2-thienylMgBr. The remaining reaction mixture was diluted in CH$_2$Cl$_2$, filtered through a silica plug and reduced in vacuo. Automated flash chromatography (petrol) gave an analytical sample of major product 2s as a white solid: m.p. 71 – 72 °C (lit. 71 - 73 °C); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.57 – 7.50 (m, 2H), 7.38 – 7.31 (m, 2H), 7.31 – 7.27 (m, 2H), 7.08 (dd, $J$ = 4.9, 3.8 , 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.3, 133.4, 133.1, 129.2, 128.3, 127.3, 125.3, 123.6.

**Figure 1, 3t:**

Using the general procedure for Kumada couplings a product mixture of 2t and 3t is obtained in a 2 : 98 ratio by GC-MS analysis. $^1$H NMR analysis using mesitylene as internal standard indicates a 77% yield of 2t+3t based on 2-thienylMgBr. The remaining reaction mixture was diluted in CH$_2$Cl$_2$, filtered through a silica plug and reduced in vacuo. Automated flash chromatography (petrol raising to 1 : 1 CH$_2$Cl$_2$ : petrol) gave an analytical sample of major product 3t as a pale blue oil: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.46 (t, $J$ = 1.4, 1H), 7.36 (dd, $J$ = 3.6, 1.0, 2H), 7.31 (dd, $J$ = 5.1, 1.0, 2H), 7.13 - 7.06 (m, 4H), 3.90 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 160.5, 144.0, 136.4, 128.1, 125.3, 116.7, 110.9, 55.6; LRMS (ESI) 272.2 [M]$^+$; HRMS (APCI) 273.0403 [M+H]$^+$ (calc. for C$_{15}$H$_{13}$OS$_2$ 273.0402 [M+H]$^+$); IR (cm$^{-1}$) 1587, 1222, 1170, 821, 694.

**Figure 1, 3a (Negishi coupling)**
Using the general procedure for Negishi couplings a product mixture of 2a and 3a is obtained in a 11 : 89 ratio by GC-MS analysis. $^1$H NMR analysis using mesitylene as internal standard indicates an 83% yield of 2a+3a based on PhZnCl.

**Figure 1, 3a (Suzuki coupling):**

Using the general procedure for Negishi couplings a product mixture of 2a and 3a is obtained in a 3 : 97 ratio by GC-MS analysis. $^1$H NMR analysis using mesitylene as internal standard indicates a 56% yield of 2a+3a based on PhB(OH)$_2$.

**Figure 1, 3u (Kumada coupling):**

Using the general procedure for Kumada couplings a product mixture of 2u and 3u is obtained in a 3 : 97 ratio by GC-MS analysis. $^1$H NMR analysis using mesitylene as internal standard indicates a 90% yield of 2u+3u based on PhMgBr. The remaining reaction mixture was diluted in CH$_2$Cl$_2$, filtered through a silica plug and reduced *in vacuo*. The residue was recrystallised from EtOH to give an analytical sample of major product 3u as a white solid: m.p. 146 - 148 °C (lit. $^{38}$ 149 – 150 °C); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62 – 7.57 (m, 4H), 7.48 – 7.41 (m, 4H), 7.39 – 7.32 (m, 2H), 6.98 (s, $J = 4.6$, 2H), 3.79 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.8, 138.5, 130.6, 129.6, 128.3, 127.3, 114.9, 56.6.

**Figure 1, 3u (Negishi coupling):**
Using the general procedure for Negishi couplings a product mixture of 2u and 3u is obtained in a 14 : 86 ratio by GC-MS analysis. ³H NMR analysis using mesitylene as internal standard indicates a 67% yield of 2u+3u based on PhZnCl.

**Figure 1, 3u (Suzuki coupling):**

Using the general procedure for Negishi couplings a product mixture of 2u and 3u is obtained in a 15 : 85 ratio by GC-MS analysis. ³H NMR analysis using mesitylene as internal standard indicates a 71% yield of 2u+3u based on PhB(OH)₂.

**Figure 1, 3v:**

Using the general procedure for Kumada couplings a product mixture of 2v and 3v is obtained in a 10 : 90 ratio by GC-MS analysis. ³H NMR analysis using mesitylene as internal standard indicates a 83% yield of 2v+3v based on 2-thienylMgBr. The remaining reaction mixture was diluted in CH₂Cl₂, filtered through a silica plug and reduced in vacuo. The residue was recrystallized from EtOH to give an analytical sample of major product 3v as a white solid: m.p. 134 - 136 °C (lit. 135 – 136 °C); ³H NMR (400 MHz, CDCl₃) δ 7.54 (dd, J = 3.7, 1.2 , 2H), 7.35 (dd, J = 5.1, 1.1 , 2H), 7.26 (s, 2H),
7.11 (dd, J = 5.1, 3.7, 2H), 3.95 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 150.1, 139.2, 127.1, 125.9, 125.6, 123.2, 112.5, 56.6.

**Figure 1, 3w (Kumada coupling):**

Using the general procedure for Kumada couplings a product mixture of 2w and 3w is obtained in a 8 : 92 ratio by GC-MS analysis. $^1$H NMR analysis using mesitylene as internal standard indicates a 68% yield of 2w+3w based on PhMgBr. The remaining reaction mixture was diluted in CH$_2$Cl$_2$, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 1 : 1 CH$_2$Cl$_2$ : petrol) gave an analytical sample of major product 3a as a white solid: m.p. >250 °C (lit. 269 – 270 °C); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.87 (d, J = 7.9, 2H), 7.80 (s, J = 0.7, 2H), 7.70 – 7.62 (m, 6H), 7.50 – 7.43 (m, 4H), 7.39 – 7.33 (m, 2H), 4.03 (s, 2H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 144.3, 141.6, 140.8, 140.1, 128.9, 127.3, 127.3, 126.3, 124.0, 120.4, 37.2.

**Figure 1, 3w (Negishi coupling):**

Using the general procedure for Negishi couplings a product mixture of 2w and 3w is obtained in a 11 : 89 ratio by GC-MS analysis. $^1$H NMR analysis using mesitylene as internal standard indicates an 87% yield of 2w+3w based on PhZnCl.

**Figure 1, 3w (Suzuki coupling):**

Using the general procedure for Suzuki couplings a product mixture of 2w and 3w is obtained in a 85 : 15 ratio by GC-MS analysis. $^1$H NMR analysis using mesitylene as internal standard indicates an 84% yield of 2w+3w based on PhB(OH)$_2$. 

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S19
Using the general procedure for Suzuki couplings a product mixture of 2w and 3w is obtained in a 10 : 90 ratio by GC-MS analysis. 1H NMR analysis using mesitylene as internal standard indicates a 58% yield of 2w+3w based on PhB(OH)2.

**Figure 1, 3x (Kumada coupling):**

Using the general procedure for Kumada couplings a product mixture of 2x and 3x is obtained in a 11 : 89 ratio by GC-MS analysis. 1H NMR analysis using mesitylene as internal standard indicates a 78% yield of 2x+3x based on PhMgBr. The remaining reaction mixture was diluted in CH2Cl2, filtered through a silica plug and reduced in vacuo. Automated flash chromatography (petrol raising to 1 : 1 CH2Cl2 : petrol) gave an analytical sample of major product 3x as a white solid: m.p. 150-152 °C; 1H NMR (400 MHz, CDCl3) δ 7.79 (d, J = 7.8, 2H), 7.74 – 7.68 (m, 4H), 7.64 – 7.57 (m, 4H), 7.49 (t, J = 7.7, 4H), 7.38 (t, J = 7.4, 2H), 2.06 (dt, J = 26.7, 11.4, 4H), 1.18 – 1.05 (m, 4H), 0.79 – 0.66 (m, 10H); 13C NMR (101 MHz, CDCl3) δ 151.8, 141.8, 140.2, 128.9, 127.3, 127.3, 126.2, 121.7, 120.1, 55.3, 40.4, 26.2, 23.2, 14.0; LRMS (ESI) 430 [M]+; HRMS (ACPI) 431.2731 [M+H]⁺ (calc. for C33H35 431.2733 [M+H]+); IR (cm⁻¹) 2955, 2926, 2856, 2464, 822, 755, 695.

**Figure 1, 3x (Negishi coupling):**

Using the general procedure for sp² Negishi couplings a product mixture of 2x and 3x is obtained in a 9 : 91 ratio by GC-MS analysis. 1H NMR analysis using mesitylene as internal standard indicates a 79% yield of 2x+3x based on PhZnCl.
Using the general procedure for Suzuki couplings a product mixture of 2x and 3x is obtained in a 22 : 78 ratio by GC-MS analysis. ¹H NMR analysis using mesitylene as internal standard indicates a 44% yield of 2x+3x based on PhB(OH)₂.

Using the general procedure for Kumada couplings a product mixture of 2y and 3y is obtained in a 15 : 85 ratio by GC-MS analysis. ¹H NMR analysis using mesitylene as internal standard indicates an 86% yield of 2y+3y based on PhMgBr. The remaining reaction mixture was diluted in CH₂Cl₂, filtered through a silica plug and reduced in vacuo. Automated flash chromatography (petrol raising to 1 : 1 CH₂Cl₂ : petrol) gave an analytical sample of major product 3y as a white solid: m.p. 157 - 158 ⁰C; ¹H NMR (600 MHz, CDCl₃) δ 8.36 (d, J = 1.4, 2H), 7.75 – 7.70 (m, 6H), 7.51 – 7.45 (m, 6H), 7.37 – 7.32 (m, 2H), 4.36 (t, J = 7.2, 2H), 1.95 – 1.88 (m, 2H), 1.49 – 1.41 (m, 2H), 0.98 (t, J = 7.4, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 142.3, 140.6, 132.6, 128.9, 127.4, 126.6, 125.5, 123.7, 119.1, 109.2, 43.3, 31.4, 20.8, 14.1; LRMS (ESI) 375 [M]⁺; HRMS (APCI) 376.2060 [M+H]⁺ (calc. for C₂₈H₂₆N 376.2060 [M+H]⁺); IR (cm⁻¹) 2956, 2927, 2871, 1600, 1475, 759, 696.

Using the general procedure for Kumada couplings a product mixture of 2x and 3x is obtained in a 22 : 78 ratio by GC-MS analysis. ¹H NMR analysis using mesitylene as internal standard indicates a 44% yield of 2x+3x based on PhB(OH)₂.
Using the general procedure for Negishi couplings a product mixture of \(2y\) and \(3y\) is obtained in a 17 : 83 ratio by GC-MS analysis. \(^1\)H NMR analysis using mesitylene as internal standard indicates a 51\% yield of \(2y+3y\) based on PhZnCl.

**Figure 1, 3z (Negishi coupling):**

Using the general procedure for \(sp^2\) Negishi couplings a product mixture of \(2z\) and \(3z\) is obtained in a 57 : 43 ratio by GC-MS analysis. \(^1\)H NMR analysis using mesitylene as internal standard indicates a 54\% yield of \(2z+3z\) based on PhZnCl. The remaining reaction mixture was diluted in CH\(_2\)Cl\(_2\), filtered through a silica plug and reduced \textit{in vacuo}. Automated flash chromatography (petrol raising to CH\(_2\)Cl\(_2\)) gave an analytical sample of \(2z\) and further recrystallization from EtOH gave an analytical sample of \(3z\).

\(2z\) (orange solid): m.p. 206 – 210 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.91 (d, \(J = 1.3\), 1H), 7.74 (dd, \(J = 7.8\), 1.8, 1H), 7.66 – 7.55 (m, 4H), 7.52 – 7.44 (m, 4H), 7.42 – 7.36 (m, 1H); \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 192.6, 142.7, 142.6, 142.6, 139.8, 136.1, 135.2, 134.9, 134.5, 133.7, 129.1, 128.2, 127.0, 124.9, 123.4, 121.6, 121.0; LRMS (ESI) 290.3 [M]'; HRMS (APCI) 291.0574 [M+H]'; IR (cm\(^{-1}\)) 1708, 1599, 1451, 1184, 823, 763.

\(3z\) (orange solid): m.p. 214 - 216 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.93 (d, \(J = 1.3\), 2H), 7.75 (dd, \(J = 7.7\), 1.7, 2H), 7.67 – 7.58 (m, 6H), 7.51 – 7.43 (m, 4H), 7.43 – 7.36 (m, 2H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 193.9, 143.2, 142.4, 140.0, 135.4, 133.5, 129.1, 128.1, 127.0, 123.2, 120.9; LRMS (ESI) 332 [M]'; HRMS (APCI) 333.1274 [M+H]'; IR (cm\(^{-1}\)) 3029, 1713, 1607, 1444, 840, 758, 736, 696.
Figure 1, 3z (Suzuki coupling):

Using the general procedure for Suzuki couplings a product mixture of 2z and 3z is obtained in a 51:49 ratio by GC-MS analysis. $^1$H NMR analysis using mesitylene as internal standard indicates a 46% yield of 2z+3z based on PhB(OH)$_2$.

Figure 1, 3aa (Kumada coupling):

Using the general procedure for Kumada couplings a product mixture of 2aa and 3aa is obtained in a 85:15 ratio by GC-MS analysis. $^1$H NMR analysis using mesitylene as internal standard indicates a 62% yield of 2aa+3aa based on PhMgBr. The remaining reaction mixture was diluted in CH$_2$Cl$_2$, filtered through a silica plug and reduced in vacuo. The residue was recrystallised from EtOH to give an analytical sample of major product 2aa as a white solid: m.p. 64 - 66 °C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.53 – 7.48 (m, 2H), 7.41 – 7.34 (m, 2H), 7.33 – 7.27 (m, 1H), 7.07 (d, $J = 3.9$, 1H), 6.89 (d, $J = 3.9$, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.1, 134.0, 129.3, 129.2, 128.0, 127.2, 125.7, 122.4; LRMS (ESI) 194.3 [M]$^+$; HRMS (APCI) 195.0029 [M+H]$^+$ (calc. for C$_{10}$H$_8$ClS 195.0030 [M+H]$^+$); IR (cm$^{-1}$) 2952, 2918, 2847, 1448, 794, 147, 684.

Figure 1, 3aa (Negishi coupling):
Using the general procedure for sp² Negishi couplings a product mixture of 2aa and 3aa is obtained in a 97 : 3 ratio by GC-MS analysis. ¹H NMR analysis using mesitylene as internal standard indicates a 60% yield of 2aa+3aa based on PhZnCl.

**Figure 1, 3ab:**

Using the general procedure for Kumada couplings a product mixture of 2ab and 3ab is obtained in an 81 : 19 ratio by GC-MS analysis. ¹H NMR analysis using mesitylene as internal standard indicates an 86% yield of 2ab+3ab based on PhMgBr.
Synthesis of Starting Materials

3,5-dichlorotoluene (1f): All manipulations were carried out under air. 2,4-Dichloro-6-methylaniline (880 mg, 5.0 mmol) was dissolved in EtOH (20 mL) and the solution cooled to 0 °C. Concentrated H₂SO₄ (1.8 mL) was added drop-wise and the mixture allowed to warm to rt. NaNO₂ (1.06 g, 12.5 mmol) was added portion-wise and the reaction mixture heated at 75 °C for 3 h. The reaction mixture was cooled to rt and poured onto ice (20 mL). The precipitate was collected by suction filtration, washed with H₂O (10 mL), dissolved in CH₂Cl₂, dried over MgSO₄, and concentrated in vacuo. The residue was dissolved in petrol, filtered through a SiO₂ plug and concentrated in vacuo to give 1f as a low melting colourless solid (679 mg, 84%): m.p. 26 °C (lit. 24.5 ºC); ¹H NMR (400 MHz, CDCl₃) δ 7.20 – 7.12 (m, 1H), 7.09 – 7.02 (m, 2H) 2.32 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 141.3, 134.7, 127.7, 125.8, 21.2.

4-(3,5-dichlorophenyl)morpholine (1g): A CEM vial was charged with Pd₂dba₃ (46 mg, 100 µmol), Binap (93 mg, 150 µmol), NaO'Bu (231 mg, 2.4 mmol) and 1-bromo-3,5-dichlorobenzene (452 mg, 2.0 mmol). The vial was sealed and purged with N₂ before the addition of PhMe (5.0 mL) and morpholine (173 µL, 2.0 mmol). The mixture was stirred at 80 °C for 16 h. The reaction mixture was diluted with Et₂O (10 mL), filtered through a pad of Celite and concentrated in vacuo. Chromatography (CH₂Cl₂) gave 1g as a white solid (334 mg, 72%): m.p. 67 - 69 ºC (lit. 86 ºC);
1H NMR (400 MHz, CDCl$_3$) $\delta$ 6.83 (t, $J = 1.7$, 1H) 6.73 (d, $J = 1.7$, 2H), 3.85 – 3.79 (m, 4H), 3.18 - 3.11 (m, 4H); 13C NMR (101 MHz, CDCl$_3$) $\delta$ 152.8, 135.7, 119.4, 113.7, 66.7, 48.5.

**2,7-Dichloro-9,9-dibutylfluorene (1x):** A CEM vial was charged with 2,7-dichlorofluorene (235 mg, 2.0 mmol), $^n$Bu$_3$NI (73 mg, 200 µmol) and flushed with N$_2$. NaOH (50% w/w, degassed, 20 mL) was added and the mixture stirred for 5 minutes at rt. $^n$BuBr (1.51 mL, 14.0 mmol) was added and the reaction mixture heated at 70 °C for 12 h. The reaction mixture was cooled to rt and extracted with CHCl$_3$ (100 mL). The organic phase was washed with H$_2$O (100 mL), dried over MgSO$_4$, and concentrated in vacuo. Chromatography (9 : 1 petrol-CHCl$_3$) gave 1x as a white solid (336 mg, 97%): m.p. 110 - 111 °C; 1H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (dd, $J = 7.8$, 0.6, 2H), 7.33 – 7.27 (m, 4H), 1.97 – 1.87 (m, 4H), 1.15 – 1.03 (m, 4H), 0.69 (t, $J = 7.4$, 6H), 0.63 – 0.52 (m, 4H); 13C NMR (101 MHz, CDCl$_3$) $\delta$ 152.5, 138.8, 133.3, 127.5, 123.4, 120.9, 55.7, 40.2, 26.0, 23.1, 13.9; LRMS (ESI) 346.3 [M]$^+$; HRMS (EI) 346.1256 [M]$^+$ (calc. for C$_{21}$H$_{24}$Cl$_2$ 346.1250 [M]$^+$); IR (cm$^{-1}$) 2952, 2927, 2857, 1451, 1421, 1069, 807.

**3,6-Dichloro-9-butylcarbazole (1z):** To a mixture of 3,6-dichlorocarbazole (472 mg, 2.0 mmol), KO'Bu (270 mg, 2.4 mmol) and THF (10 mL) was added $^n$BuBr (260 µL, 2.0 mmol) and the resulting mixture was stirred at 60 °C for 4 h. H$_2$O (50 mL) was added and the mixture extracted with CH$_2$Cl$_2$ (50 mL). The organic phase was dried over MgSO$_4$, and concentrated in vacuo. Chromatography (petrol $\rightarrow$ 3 : 1 petrol-CH$_2$Cl$_2$) gave 1z as a white solid (519 mg, 89%): m.p. 68 – 70 °C; 1H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 (d, $J = 2.0$, 2H), 7.45 (dd, $J = 8.7$, 2.0, 2H), 7.34 (d, $J = 8.7$, 2H), 4.28 (t,
\[ J = 7.2, \ 2H \), 1.89 – 1.79 (m, 2H), 1.45 – 1.33 (m, 2H), 0.97 (t, \ J = 7.4, \ 3H); \ ^{13}\text{C NMR} (101 \text{ MHz, } \text{CDCl}_3) \ \delta 139.3, 126.5, 124.7, 123.1, 120.3, 110.1, 43.3, 31.2, 20.6, 14.0; \ \text{LRMS} \ (\text{ESI}) 291.1; \ \text{HRMS (EI)} \ 291.0573 \ [\text{M}]^+ \ (\text{calc. for } \text{C}_{16}\text{H}_{15}\text{Cl}_3\text{N} \ 291.0576 \ [\text{M}]^+); \ \text{IR (cm}^{-1}) \ 2959, 2935, 2876, 2857, 1473, 1439, 1076, 857, 794, 680.

\[ \text{SO} \text{O} \text{Cl} \text{C} \text{S} \text{T} \text{H} \text{F} \]

2,5-Dichloro-3,4-ethylenedioxythiophene, 1ab: 3,4-Ethylenedioxythiophene (1.41 g, 10 mmol) was dissolved in THF (50 mL) and cooled to 0 °C. N-Chlorosuccinimide (2.94 g, 22 mmol) was added and the resultant mixture was stirred at rt for 48 h. Na$_2$SO$_3$ (1.0 g, 7.9 mmol) was added, the suspension filtered and the filtrate concentrated in vacuo. The residue was dissolved in CH$_2$Cl$_2$, filtered through a short plug of SiO$_2$ to remove the dark blue colour and concentrated in vacuo. Chromatography (petrol \( \rightarrow \) 4:1 petrol-CH$_2$Cl$_2$) gave 1ab as a white solid (1.21 g, 57%) which was stored under N$_2$ at – 18 °C: m.p. 59 – 60 °C (lit.\(^{43} \) 60 – 62 °C); \(^1\text{H NMR} \ (400 \text{ MHz, } \text{CDCl}_3) \ \delta 4.26 \ (s, \ 4H); \ ^{13}\text{C NMR} (101 \text{ MHz, } \text{CDCl}_3) \ \delta 137.4, 100.6, 65.1.
Graphical NMR Data for all novel compounds

$^1$H NMR (400 MHz, CDCl$_3$, 300K) of compound 3d

$^{13}$C NMR (101 MHz, CDCl$_3$, 300K) of compound 3d
$^1$H NMR (400 MHz, CDCl$_3$, 300K) of compound 3e

$^{13}$C NMR (100 MHz, CDCl$_3$, 300K) of compound 3e
$^1$H NMR (400 MHz, CDCl$_3$, 300K) of compound 3g

$^{13}$C NMR (100 MHz, CDCl$_3$, 300K) of compound 3g
$^1$H NMR (400 MHz, CDCl$_3$, 300K) of compound 3i

$^{13}$C NMR (100 MHz, CDCl$_3$, 300K) of compound 3i
\[^1\text{H NMR (400 MHz, CDCl}_3, 300\text{K)}\] of compound 3l

\[^{13}\text{C NMR (100 MHz, CDCl}_3, 300\text{K)}\] of compound 3l
$^1$H NMR (400 MHz, CDCl$_3$, 300K) of compound 2m

$^{13}$C NMR (100 MHz, CDCl$_3$, 300K) of compound 2m
$^1$H NMR (400 MHz, CDCl$_3$, 300K) of compound 3t

$^{13}$C NMR (100 MHz, CDCl$_3$, 300K) of compound 3t
$^1$H NMR (400 MHz, CDCl$_3$, 300K) of compound 1x

$^{13}$C NMR (100 MHz, CDCl$_3$, 300K) of compound 1x
$^1$H NMR (400 MHz, CDCl$_3$, 300K) of compound 3x

$^{13}$C NMR (100 MHz, CDCl$_3$, 300K) of compound 3x
$^1$H NMR (400 MHz, CDCl$_3$, 300K) of compound 1y

$^{13}$C NMR (100 MHz, CDCl$_3$, 300K) of compound 1y
$^1$H NMR (400 MHz, CDCl$_3$, 300K) of compound 3y

$^{13}$C NMR (100 MHz, CDCl$_3$, 300K) of compound 3y
\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, 300K) of compound 2z

\[ \text{S39} \]

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}, 300K) of compound 2z
$^1$H NMR (400 MHz, CDCl$_3$, 300K) of compound 3z

$^{13}$C NMR (100 MHz, CDCl$_3$, 300K) of compound 3z
$^1$H NMR (400 MHz, CDCl$_3$, 300K) of compound 3aa

$^{13}$C NMR (100 MHz, CDCl$_3$, 300K) of compound 3aa
References