Supporting Information

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

Benjamin J. Groombridge,[a] Stephen M. Goldup[b*] and Igor Larrosa[c*]

[a]*School of Biological and Chemical Sciences, Queen Mary University of London, Mile End Road, London, E1 4NS, UK.*

[b]*Department of Chemistry, University of Southampton, Highfield, Southampton, Hampshire, SO17 1BJ, UK. Email: s.goldup@soton.ac.uk*

[c]*School of Chemistry, The University of Manchester, Oxford Road, Manchester, M13 9PL, UK. Email: igor.larrosa@manchester.ac.uk*

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,[1] **4a-e**,[2,3,4] were prepared according to reported procedures. All reactions were carried out under an atmosphere of N_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.[5]

^{1}H and ^{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 (*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:[3] 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:[6] 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:[2] A CEM microwave vial was charged with PEPPSI-IPent (4.0 mg, 5.0 μmol), K_2CO_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

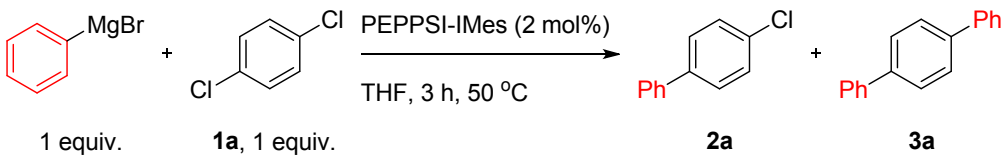
isolated to confirm its identity and to verify the peaks of interest in the crude reaction mixture. All novel compounds were fully characterized.

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**,[8] **3a**,[9] **3b**,[10] **3c**,[11] **3f**,[12] **3h**,[13] **3j**,[14] **3k**,[15] **3n**,[16] **3o**,[17] **3p**,[18] **3q**,[19] **3r**,[20] **2s**,[21] **3u**,[22] **3v**,[23] and **3w**[24] matched those previously reported.

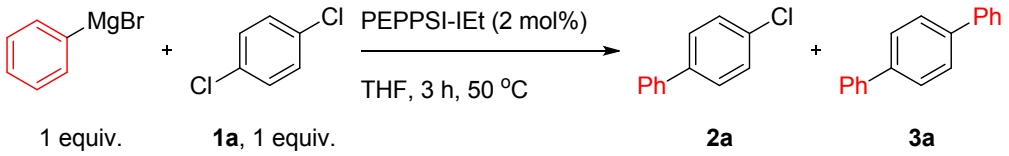
Experimental Data

Scheme 1, Entry 1:



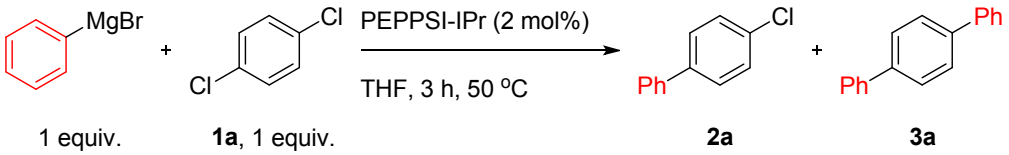
Using the general procedure for Kumada couplings employing PEPPSI-IMes (3.0 mg, 5.0 µmol) in place of PEPPSI-IPent a product mixture of **2a** and **3a** is obtained in a >99 : <1 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 16% yield of **2a**+**3a** based on PhMgBr. The remaining reaction mixture was diluted in CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 1 : 9 CH_2Cl_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, $CDCl_3$) δ 7.59 – 7.49 (m, 4H), 7.48 – 7.39 (m, 4H), 7.39 – 7.33 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 139.8, 133.5 129.1, 129.0, 128.5, 127.7, 127.1.

Scheme 1, Entry 2:



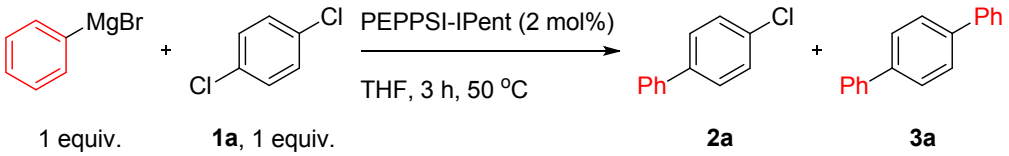
Using the general procedure for Kumada couplings, employing PEPPSI-IEt (3.1 mg, 5.0 µmol) in place of PEPPSI-IPent, a product mixture of **2a** and **3a** is obtained in a 70 : 30 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 50% yield of **2a**+**3a**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

Scheme 1, Entry 3:



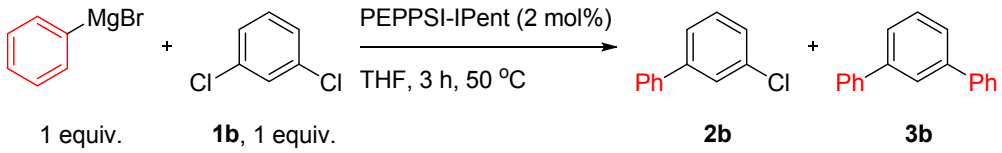
Using the general procedure for Kumada couplings, employing PEPPSI-IPr (3.4 mg, 5.0 µmol) in place of PEPPSI-IPent, a product mixture of **2a** and **3a** is obtained in a 45 : 55 ratio by GC-MS. ^{1}H NMR analysis using mesitylene as internal standard indicates an 83% yield of **2a**+**3a** based on PhMgBr. The remaining reaction mixture was diluted in CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 1 : 9 CH_2Cl_2 : petrol) gave an analytical sample of major product **3a** as a white solid: m.p. 207 – 208 °C (lit.[26] 210 – 211 °C); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 140.3, 129.0, 127.7, 127.5, 127.2.

Scheme 1, Entry 4:



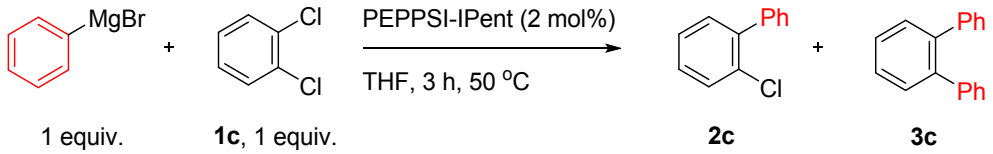
Using the general procedure for Kumada couplings a product mixture of **2a** and **3a** is obtained in a 6 : 94 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 96% yield of **2a**+**3a** based on PhMgBr.

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_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 1 : 9 CH_2Cl_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, $CDCl_3$) δ 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, $CDCl_3$) δ 142.0, 141.4, 129.3, 129.0, 127.6, 127.4, 126.3, 126.3.

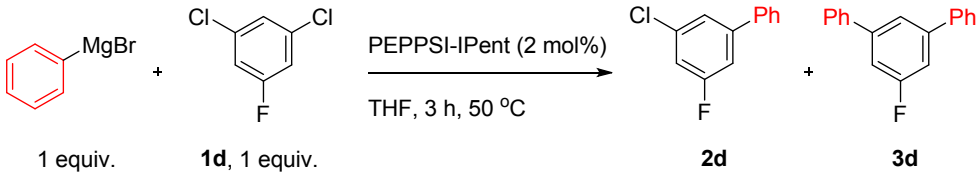
Figure 1, 3c:



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_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 1 : 9 CH_2Cl_2 : petrol) gave an analytical sample of major product **3c** as a white solid: m.p. 55 – 58 °C

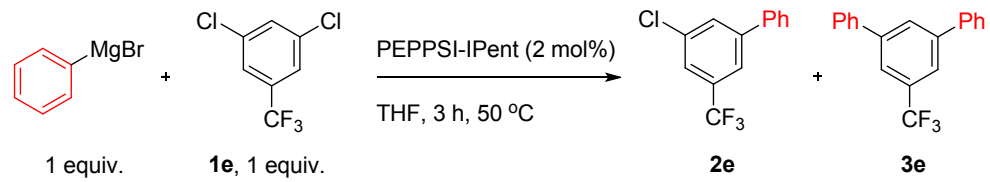
(lit.[24] 56 – 57 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 4H), 7.25 – 7.12 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.7, 140.7, 130.7, 130.0, 128.0, 127.6, 126.6.

Figure 1, 3d:



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_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 1 : 9 CH_2Cl_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); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.9, 162.4, 144.0, 143.9, 129.1, 128.1, 127.3, 121.9, 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.

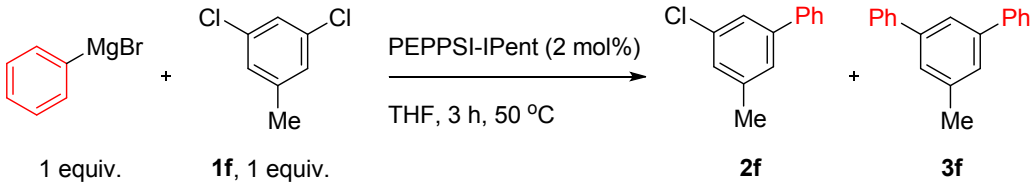
Figure 1, 3e:



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_2Cl_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, CDCl3)

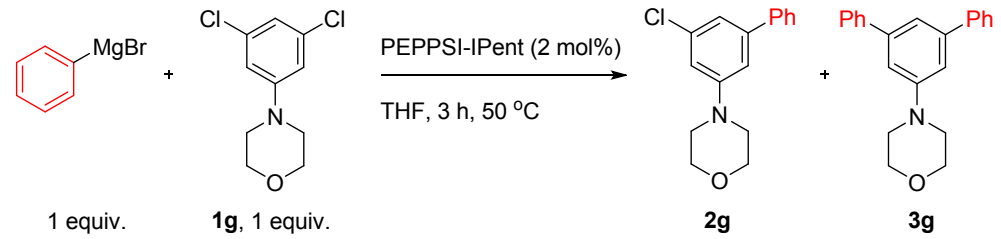
δ 8.02 – 7.98 (m, 1H), 7.85 (dd, J = 1.6, 0.7, 2H), 7.72 - 7.66 (m, 4H), 7.56 – 7.50 (m, 4H), 7.49 - 7.43 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 134.0, 129.4, 129.2, 128.3, 127.4, 122.9, 122.9; LRMS (ESI) 298.2 [M^+]; HRMS (EI) 298.0965 [M]$^+$ (calc. for $C_{19}H_{13}F_3$ 298.0964 [M]$^+$); 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. ^{1}H NMR analysis using mesitylene as internal standard indicates a 84% yield of **2h**+**3h** based on PhMgBr. The remaining reaction mixture was diluted in CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 1 : 9 CH_2Cl_2 : petrol) gave an analytical sample of major product **3f** as a white solid: m.p. 137 - 140 °C (lit.[28] 135 – 138 °C); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 141.5, 138.9, 128.9, 127.5, 127.4, 127.1, 123.6, 21.8.

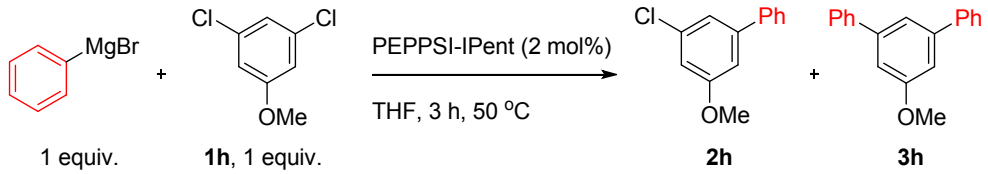
Figure 1, 3g:



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. ^{1}H NMR analysis using mesitylene as internal standard indicates a 71% yield of **2g**+**3g** based on PhMgBr. The remaining reaction mixture was diluted in CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (1 : 9 petrol : CH_2Cl_2 raising to CH_2Cl_2) gave an analytical sample of major product **3g** as a white solid:

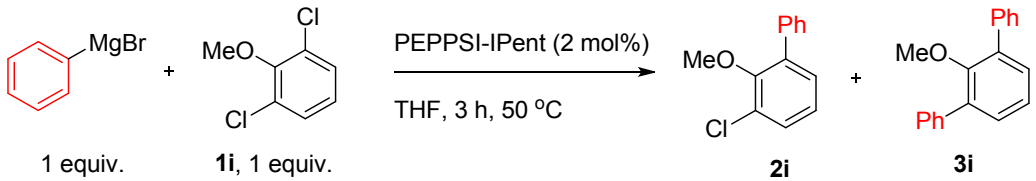
m.p. 100 - 102 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dq, J = 2.6, 1.7, 4H), 7.48 – 7.42 (m, 4H), 7.40 – 7.34 (m, 2H), 7.32 (t, J = 1.5, 1H), 7.11 (d, J = 1.5, 2H), 3.94 – 3.88 (m, 4H), 3.33 – 3.27 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 141.9, 128.9, 127.6, 127.5, 118.7, 114.0, 67.1, 49.8; LRMS (ESI) 315.3 $[M]^+$; HRMS (EI) 315.1617 $[M]^+$ (calc. for $C_{22}H_{21}ON$ 315.1618 $[M]^+$); IR (cm^{-1}) 2967, 2849, 1592, 1419, 1448, 118, 955, 753, 695.

Figure 1, 3h:



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. ^{1}H NMR analysis using mesitylene as internal standard indicates a 82% yield of **2h**+**3h** based on PhMgBr. The remaining reaction mixture was diluted in CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 3 : 7 CH_2Cl_2 : petrol) gave an analytical sample of major product **3h** as a white solid: m.p. 91 - 93 °C (lit.[29] 91 – 92 °C); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 143.3, 141.3, 128.9, 127.7, 127.4, 119.1, 111.9, 55.6.

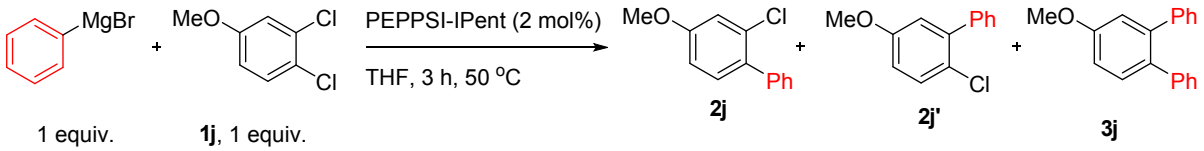
Figure 1, 3i:



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. ^{1}H NMR analysis using mesitylene as internal standard indicates a 85% yield of **2i**+**3i** based on PhMgBr. The remaining reaction mixture was diluted in CH_2Cl_2, filtered

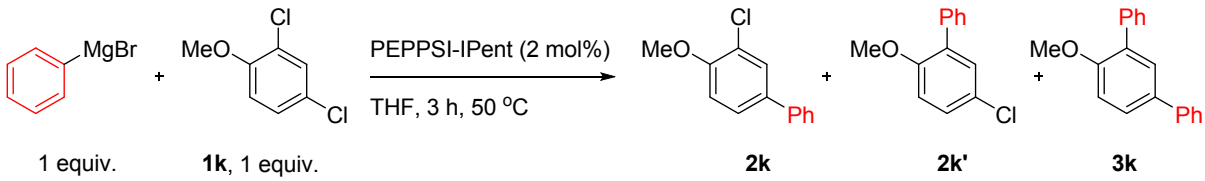
through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 3 : 7 CH_2Cl_2 : petrol) gave an analytical sample of major product **3i** as a colourless oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 4H), 7.48 – 7.41 (m, 4H), 7.40 – 7.33 (m, 4H), 7.25 (dd, J = 8.2, 6.9, 1H), 3.18 (s, 3H); ^{13}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 $C_{19}H_{16}O$ 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}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 CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 3 : 7 CH_2Cl_2 : petrol) gave an analytical sample of major product **3j** as a white solid: m.p. 116-117 °C (lit.[30] 113 – 115 °C); ^{1}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}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.

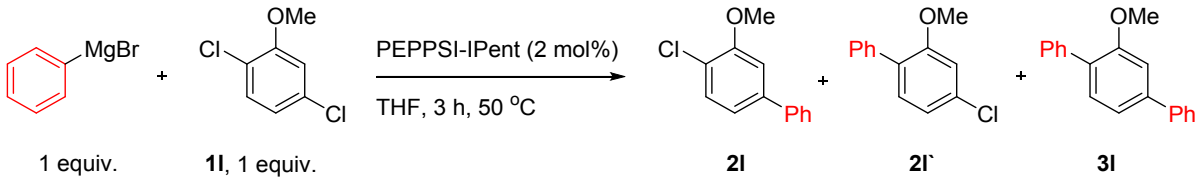
Figure 1, 3k:



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}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_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 3 : 7 CH_2Cl_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, $CDCl_3$) δ 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, $CDCl_3$) δ 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:

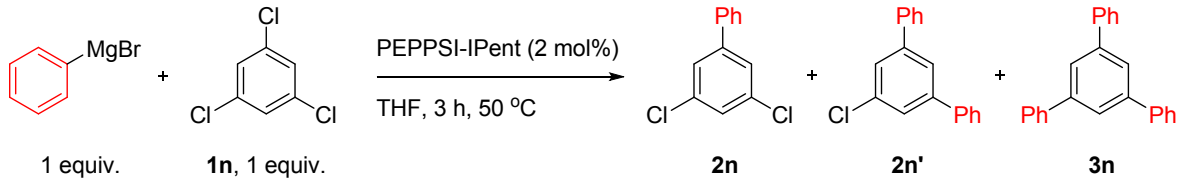


Using the general procedure for Kumada couplings a product mixture of **2l, 2l'** and **3l** is obtained in a 21 : 0 : 79 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 99% yield of **2l**+**3l** based on PhMgBr. The remaining reaction mixture was diluted in CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 3 : 7 CH_2Cl_2 : petrol) gave an analytical sample of major product **3l** as a white solid: m.p. 96 - 100 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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:

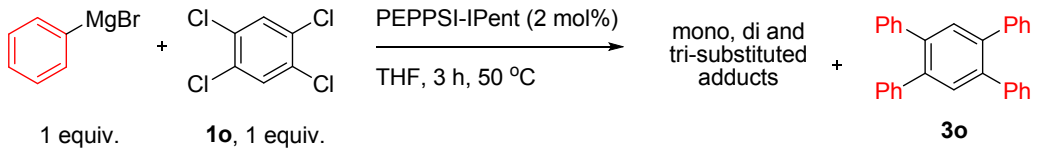
Using the general procedure for Kumada couplings a product mixture of **2m, 2m`** and **3m** is obtained in a 70 : 0 : 30 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates an 85% yield of **2m**+**3m** based on PhMgBr. The remaining reaction mixture was diluted in CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 3 : 7 CH_2Cl_2 : petrol) gave analytical samples of **2m**. **2m** (colourless oil): ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{13}H_{12}O^{35}Cl$ 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 ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (101 MHz, $CDCl_3$) 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.

Figure 1, 3n:



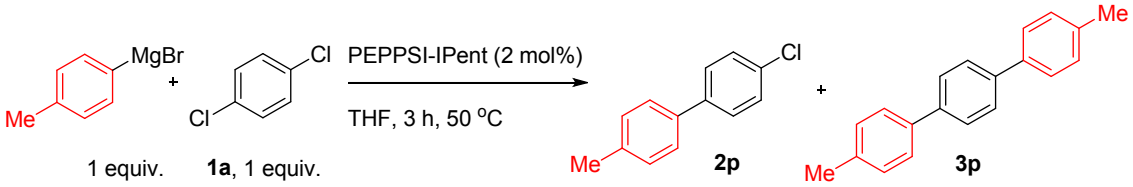
Using the general procedure for Kumada couplings a product mixture of **2n**, **2n`** and **3n** is obtained in a 2 : 5 : 93 ratio by GC-MS. $^{1}$H NMR analysis using mesitylene as internal standard indicates an 75% yield of **2n**+**2n`**+**3n** based on PhMgBr. The remaining reaction mixture was diluted in CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 4 : 6 CH_2Cl_2 : petrol) gave an analytical sample of major product **3n** as a white solid: m.p. 172 °C (lit.[32] 173 – 174 °C); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 141.3, 129.0, 127.7, 127.5, 125.3.

Figure 1, 3o:



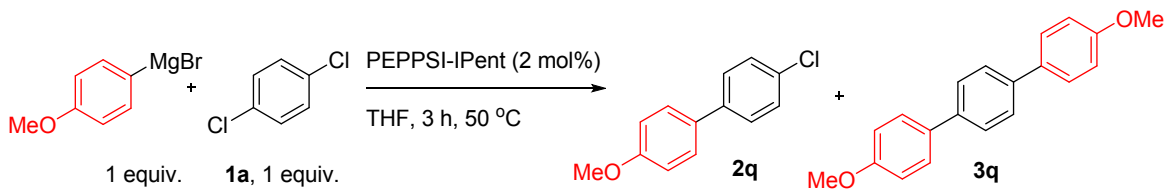
Using the general procedure for Kumada couplings a product mixture of mono, di and tri-coupled products and **3o** is obtained in a 19 : 1 : 2 : 78 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a combined 49% yield based on PhMgBr. The remaining reaction mixture was diluted in CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 6 : 4 CH_2Cl_2 : petrol) gave an analytical sample of major product **3o** as a white solid: m.p. >250 °C (lit.[33] 274 – 275 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 2H), 7.25 – 7.21 (m, 20H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 139.8, 133.1, 130.1, 128.1, 126.8.

Figure 1, 3p:



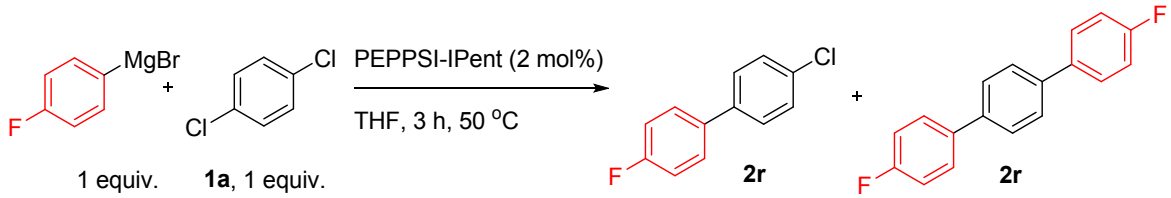
Using the general procedure for Kumada couplings a product mixture of **2p** and **3p** is obtained in a 11 : 89 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 92% yield of **2p**+**3p** based on 4-MePhMgBr. The remaining reaction mixture was diluted in CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 2 : 8 CH_2Cl_2 : petrol) gave an analytical sample of major product **3p** as a white solid: m.p. >250 °C (lit.[34] 249 – 250 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 4H), 7.49 – 7.44 (m, 4H), 7.22 – 7.17 (m, 4H), 2.33 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 138.1, 137.2, 129.7, 127.4, 127.0, 21.3.

Figure 1, 3q:



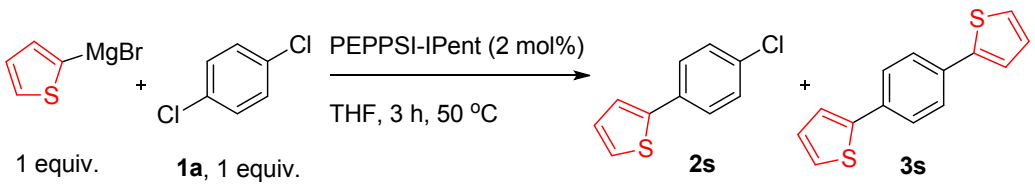
Using the general procedure for Kumada couplings a product mixture of **2q** and **3q** is obtained in a 10 : 90 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 72% yield of **2q**+**3q** based on 4-MeOPhMgBr. The remaining reaction mixture was diluted in CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 7 : 3 CH_2Cl_2 : petrol) gave an analytical sample of major product **3q** as a white solid: m.p. >250 °C (lit.[35] 270 – 271 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 4H), 7.60 – 7.55 (m, 4H), 7.02 – 6.97 (m, 4H), 3.86 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 139.3, 133.5, 128.2, 127.2, 114.4, 55.5.

Figure 1, 3r:



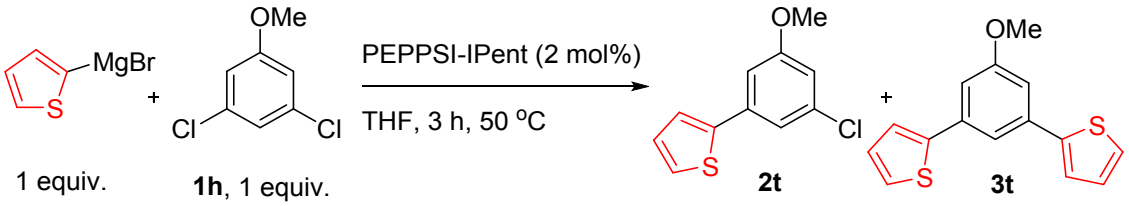
Using the general procedure for Kumada couplings a product mixture of **2r** and **3r** is obtained in a 4 : 96 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 93% yield of **2r**+**3r** based on 4-FPhMgBr. The remaining reaction mixture was diluted in CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 4 : 6 CH_2Cl_2 : petrol) gave an analytical sample of major product **3r** as a white solid: m.p. 224 - 226 °C (lit.[36] 219 – 222 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 8H), 7.19 – 7.11 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 161.5, 139.3, 136.9, 136.9, 128.8, 128.7, 127.6, 116.0, 115.8.

Figure 1, 3s:



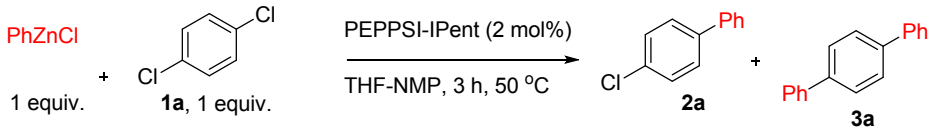
Using the general procedure for Kumada couplings a product mixture of **2s** and **3s** is obtained in a 81 : 19 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 92% yield of **2s**+**3s** based on 2-thienylMgBr. The remaining reaction mixture was diluted in CH_2Cl_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.[37] 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:



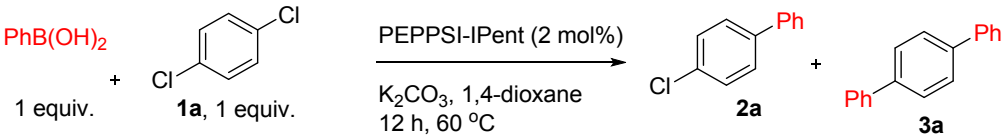
Using the general procedure for Kumada couplings a product mixture of **2t** and **3t** is obtained in a 2 : 98 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 77% yield of **2t**+**3t** based on 2-thienylMgBr. The remaining reaction mixture was diluted in CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 1 : 1 CH_2Cl_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, 123.8, 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)



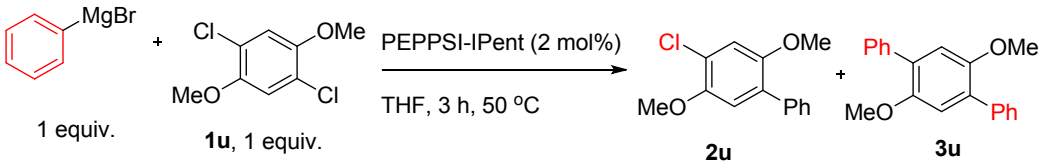
Using the general procedure for Negishi couplings a product mixture of **2a** and **3a** is obtained in a 11 : 89 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates an 83% yield of **2a**+**3a** based on PhZnCl.

Figure 1, 3a (Suzuki coupling)



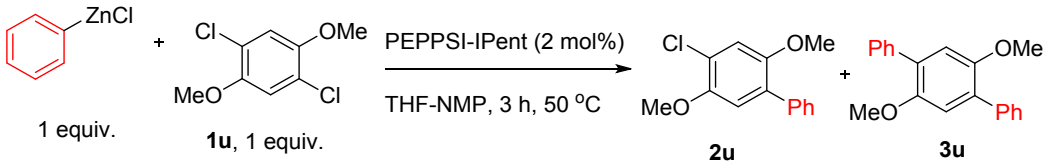
Using the general procedure for Negishi couplings a product mixture of **2a** and **3a** is obtained in a 3 : 97 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 56% yield of **2a**+**3a** based on $PhB(OH)_2$.

Figure 1, 3u (Kumada coupling):



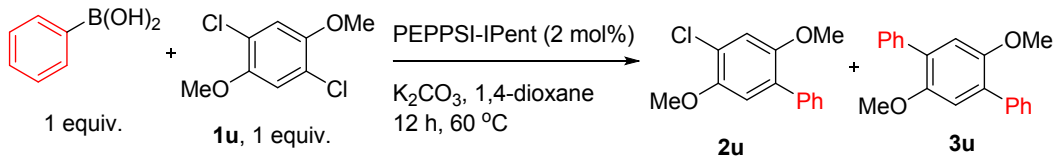
Using the general procedure for Kumada couplings a product mixture of **2u** and **3u** is obtained in a 3 : 97 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 90% yield of **2u**+**3u** based on PhMgBr. The remaining reaction mixture was diluted in CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. The residue was recrystalised 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, $CDCl_3$) δ 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, $CDCl_3$) δ 150.8, 138.5, 130.6, 129.6, 128.3, 127.3, 114.9, 56.6.

Figure 1, 3u (Negishi coupling):



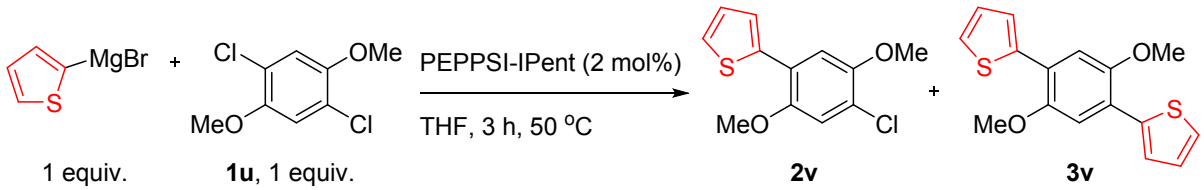
Using the general procedure for Negishi couplings a product mixture of **2u** and **3u** is obtained in a 14 : 86 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 67% yield of **2u**+**3u** based on PhZnCl.

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. ^{1}H NMR analysis using mesitylene as internal standard indicates a 71% yield of **2u**+**3u** based on PhB(OH)$_2$.

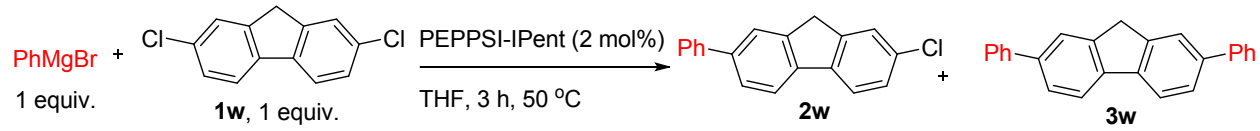
Figure 1, 3v:



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. ^{1}H 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 CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. The residue was recrystalized from EtOH to give an analytical sample of major product **3v** as a white solid: m.p. 134 - 136 °C (lit.[39] 135 – 136 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 3.7, 1.2 , 2H), 7.35 (dd, *J* = 5.1, 1.1 , 2H), 7.26 (s, 2H),

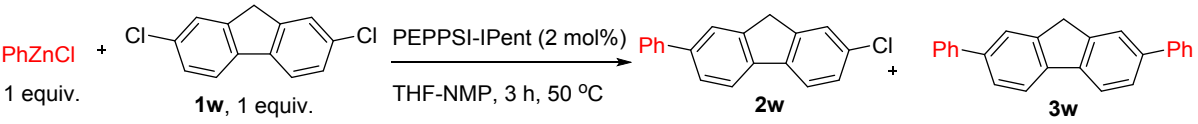
7.11 (dd, J = 5.1, 3.7 , 2H), 3.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 139.2, 127.1, 125.9, 125.6, 123.2, 112.5, 56.6.

Figure 1, 3w (Kumada coupling):



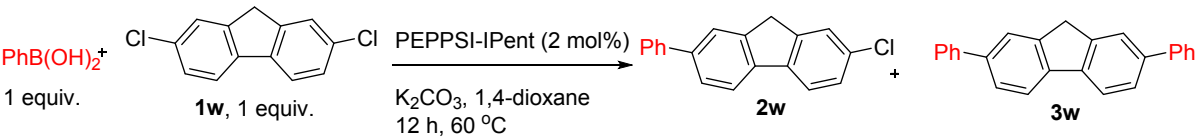
Using the general procedure for Kumada couplings a product mixture of **2w** and **3w** is obtained in a 8 : 92 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 68% yield of **2w**+**3w** based on PhMgBr. The remaining reaction mixture was diluted in CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 1 : 1 CH_2Cl_2 : petrol) gave an analytical sample of major product **3a** as a white solid: m.p. >250 °C (lit.[40] 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):



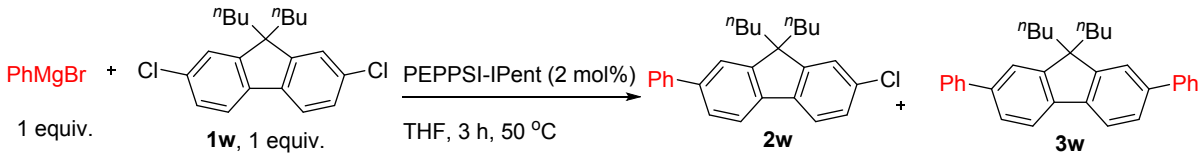
Using the general procedure for Negishi couplings a product mixture of **2w** and **3w** is obtained in a 11 : 89 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates an 87% yield of **2w**+**3w** based on PhZnCl.

Figure 1, 3w (Suzuki coupling):



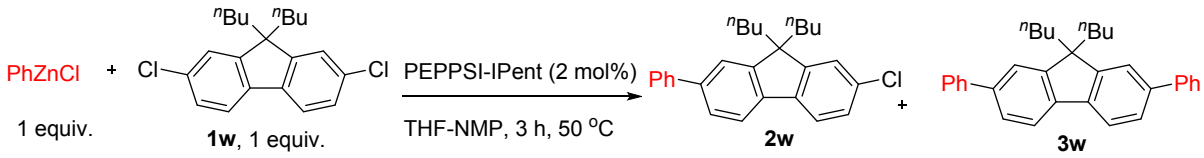
Using the general procedure for Suzuki couplings a product mixture of **2w** and **3w** is obtained in a 10 : 90 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 58% yield of **2w**+**3w** based on $PhB(OH)_2$.

Figure 1, 3x (Kumada coupling):



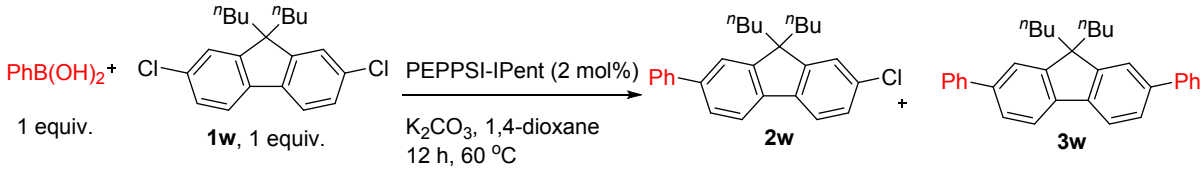
Using the general procedure for Kumada couplings a product mixture of **2x** and **3x** is obtained in a 11 : 89 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 78% yield of **2x**+**3x** based on PhMgBr. The remaining reaction mixture was diluted in CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 1 : 1 CH_2Cl_2 : petrol) gave an analytical sample of major product **3x** as a white solid: m.p. 150-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{33}H_{35}$ 431.2733 $[M+H]^+$); IR (cm^{-1}) 2955, 2926, 2856, 2464, 822, 755, 695.

Figure 1, 3x (Negishi coupling):



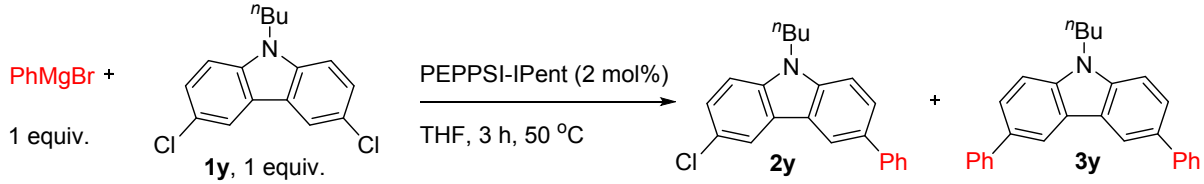
Using the general procedure for sp^2 Negishi couplings a product mixture of **2x** and **3x** is obtained in a 9 : 91 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 79% yield of **2x**+**3x** based on PhZnCl.

Figure 1, 3x (Suzuki coupling):



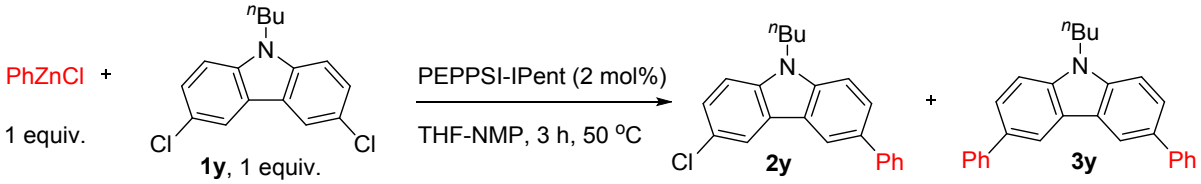
Using the general procedure for Suzuki couplings a product mixture of **2x** and **3x** is obtained in a 22 : 78 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 44% yield of **2x**+**3x** based on $PhB(OH)_2$.

Figure 1, 3y (Kumada coupling):



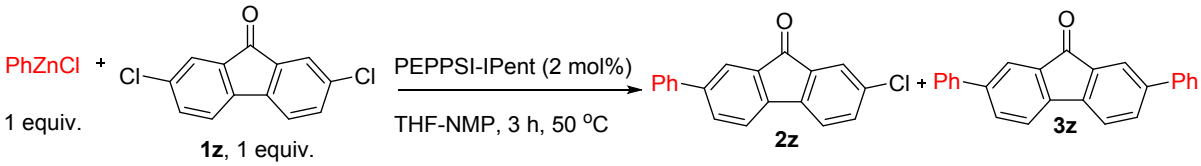
Using the general procedure for Kumada couplings a product mixture of **2y** and **3y** is obtained in a 15 : 85 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates an 86% yield of **2y**+**3y** based on PhMgBr. The remaining reaction mixture was diluted in CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to 1 : 1 CH_2Cl_2 : petrol) gave an analytical sample of major product **3y** as a white solid: m.p. 157 - 158 °C; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (151 MHz, $CDCl_3$) 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 $C_{28}H_{26}N$ 376.2060 $[M+H]^+$); IR (cm^{-1}) 2956, 2927, 2871, 1600, 1475, 759, 696.

Figure 1, 3y (Nehishi coupling):



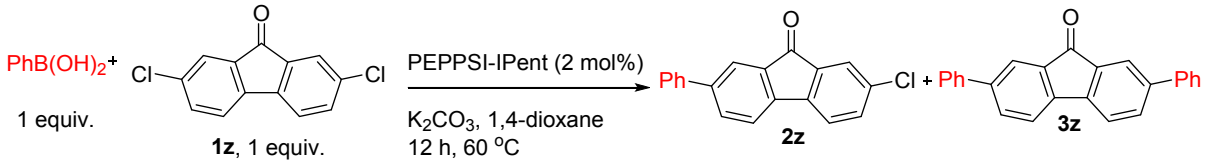
Using the general procedure for Negishi couplings a product mixture of **2y** and **3y** is obtained in a 17 : 83 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 51% yield of **2y**+**3y** based on PhZnCl.

Figure 1, 3z (Negishi coupling):



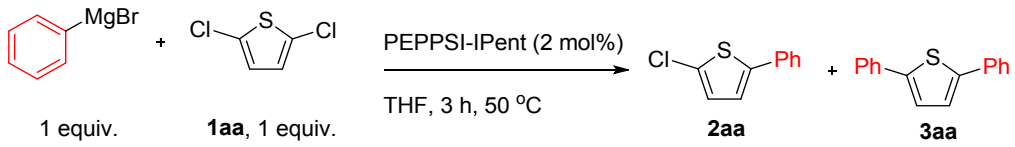
Using the general procedure for sp^2 Negishi couplings a product mixture of **2z** and **3z** is obtained in a 57 : 43 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 54% yield of **2z**+**3z** based on PhZnCl. The remaining reaction mixture was diluted in CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. Automated flash chromatography (petrol raising to CH_2Cl_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, $CDCl_3$) δ 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, $CDCl_3$) δ 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 $[M+H]^+$ (calc. for $C_{19}H_{12}O^{35}Cl$ 291.0571 $[M+H]^+$); IR (cm^{-1}) 1708, 1599, 1451, 1184, 823, 763. **3z (orange solid)**: m.p. 214 - 216 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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 $[M+H]^+$ (calc. for $C_{25}H_{17}O$ 333.1274 $[M+H]^+$); IR (cm^{-1}) 3029, 1713, 1607, 1444, 840, 758, 736, 696.

Figure 1, 3z (Suzuki coupling):



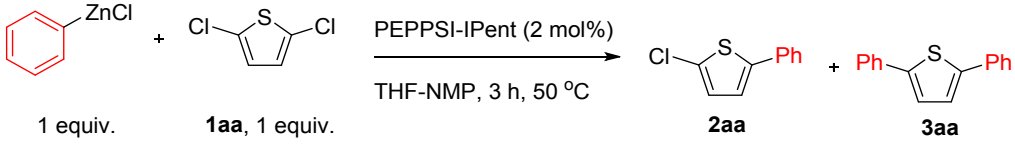
Using the general procedure for Suzuki couplings a product mixture of **2z** and **3z** is obtained in a 51 : 49 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 46% yield of **2z**+**3z** based on $PhB(OH)_2$.

Figure 1, 3aa (Kumada coupling):



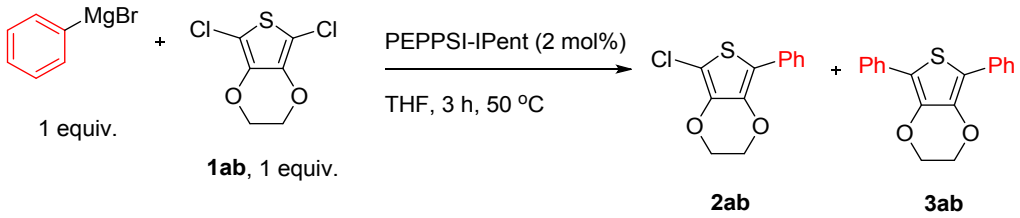
Using the general procedure for Kumada couplings a product mixture of **2aa** and **3aa** is obtained in a 85 : 15 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 62% yield of **2aa**+**3aa** based on PhMgBr. The remaining reaction mixture was diluted in CH_2Cl_2, filtered through a silica plug and reduced *in vacuo*. The residue was recrystalised 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 $C_{10}H_8{}^{35}ClS$ 195.0030 $[M+H]^+$); IR (cm^{-1}) 2952, 2918, 2847, 1448, 794, 147, 684.

Figure 1, 3aa (Negishi coupling):



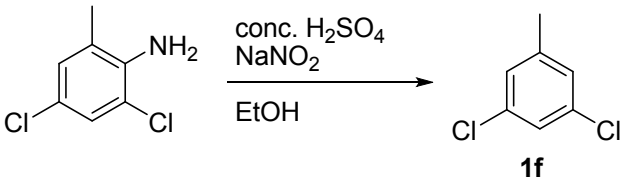
Using the general procedure for sp^2 Negishi couplings a product mixture of **2aa** and **3aa** is obtained in a 97 : 3 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates a 60% yield of **2aa**+**3aa** based on PhZnCl.

Figure 1, 3ab:



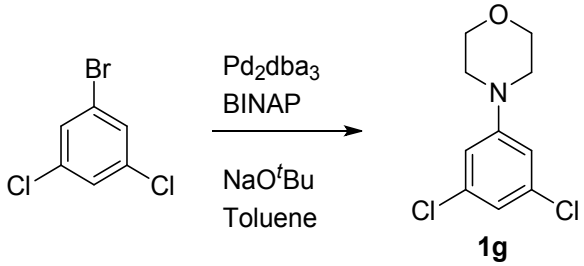
Using the general procedure for Kumada couplings a product mixture of **2ab** and **3ab** is obtained in an 81 : 19 ratio by GC-MS analysis. ^{1}H NMR analysis using mesitylene as internal standard indicates an 86% yield of **2ab**+**3ab** based on PhMgBr.

Synthesis of Starting Materials



1f

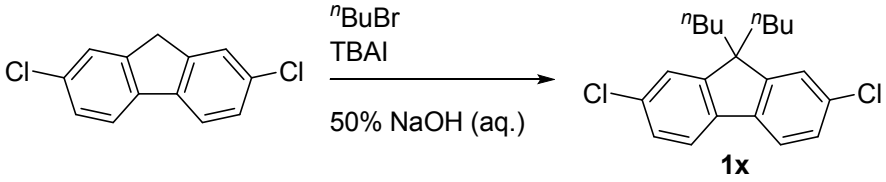
3,5-dichlorotoluene (1f): All manipulations were carried out under air. 2,4-Dichloro-6-methylaniline (880 mg, 5.0 mmol) was dissolved in EtOH (20 mL) and the solution cooled to 0 °C. Concentrated H_2SO_4 (1.8 mL) was added drop-wise and the mixture allowed to warm to rt. $NaNO_2$ (1.06 g, 12.5 mmol) 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 H_2O (10 mL), dissolved in CH_2Cl_2, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was dissolved in petrol, filtered through a SiO_2 plug and concentrated *in vacuo* to give **1f** as a low melting colourless solid (679 mg, 84%): m.p. 26 °C (lit.[41] 24.5 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.12 (m, 1H), 7.09 – 7.02 (m, 2H) 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 134.7, 127.7, 125.8, 21.2.



1g

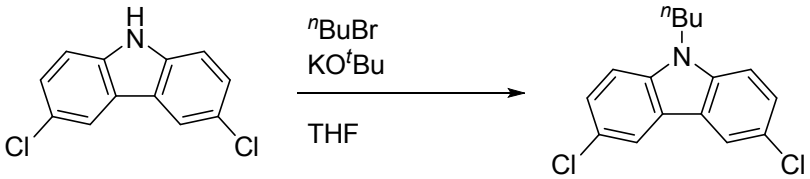
4-(3,5-dichlorophenyl)morpholine (1g): A CEM vial was charged with Pd_2dba_3 (46 mg, 100 µmol), Binap (93 mg, 150 µmol), NaO^{t}Bu (231 mg, 2.4 mmol) and 1-bromo-3,5-dichlorobenzene (452 mg, 2.0 mmol). The vial was sealed and purged with N_2 before the addition of PhMe (5.0 mL) and morpholine (173 µL, 2.0 mmol). The mixture was stirred at 80 °C for 16 h. The reaction mixture was diluted with Et_2O (10 mL), filtered through a pad of Celite and concentrated *in vacuo*. Chromatography (CH_2Cl_2) gave **1g** as a white solid (334 mg, 72%): m.p. 67 - 69 °C (lit.[42] 86 ºC);

^{1}H NMR (400 MHz, $CDCl_3$) δ 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); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.8, 135.7, 119.4, 113.7, 66.7, 48.5.



1x

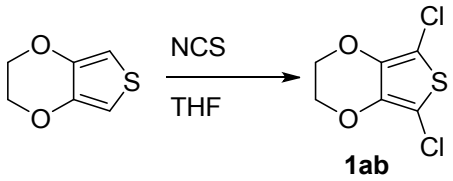
2,7-Dichloro-9,9-dibutylfluorene (1x): A CEM vial was charged with 2,7-dichlorofluorene (235 mg, 2.0 mmol), $^{n}Bu_4NI$ (73 mg, 200 µmol) and flushed with N_2. NaOH (50% w/w, degassed, 20 mL) was added and the mixture stirred for 5 minutes at rt. ^{n}BuBr (1.51 mL, 14.0 mmol) was added and the reaction 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_2O (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; ^{1}H NMR (400 MHz, CDCl3) δ 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); ^{13}C NMR (101 MHz, $CDCl_3$) δ 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 $C_{21}H_{24}{}^{35}Cl_2$ 346.1250 $[M]^+$); IR (cm^{-1}) 2952, 2927, 2857, 1451, 1421, 1069, 807.



1z

3,6-Dichloro-9-butylcarbazole (1z): To a mixture of 3,6-dichlorocarbazole (472 mg, 2.0 mmol), KO^{t}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_2O (50 mL) was added and the mixture extracted with CH_2Cl_2 (50 mL). The organic phase was dried over $MgSO_4$, and concentrated *in vacuo*. Chromatography (petrol → 3 : 1 petrol-CH_2Cl_2) gave **1z** as a white solid (519 mg, 89%): m.p. 68 – 70 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 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}C NMR (101 MHz, $CDCl_3$) δ 139.3, 126.5, 124.7, 123.1, 120.3, 110.1, 43.3, 31.2, 20.6, 14.0; LRMS (ESI) 291.1; HRMS (EI) 291.0573 $[M]^+$ (calc. for $C_{16}H_{15}{}^{35}Cl_2N$ 291.0576 $[M]^+$); IR (cm^{-1}) 2959, 2935, 2917, 2876, 2857, 1473, 1439, 1076, 857, 794, 680.

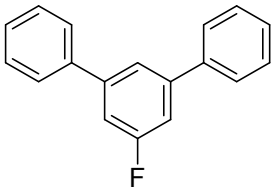


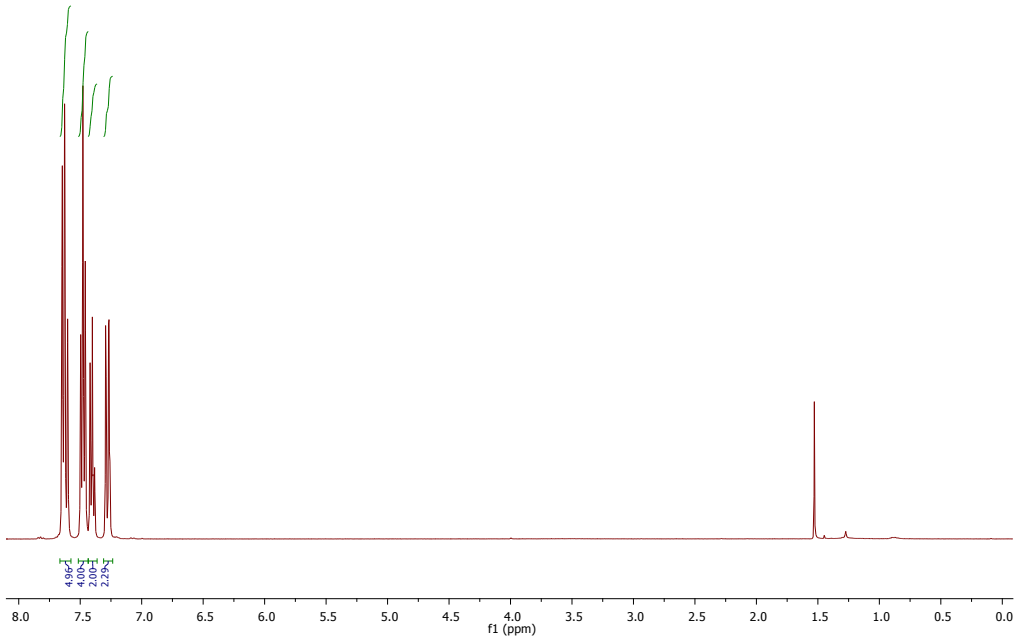
1ab

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_2SO_3 (1.0 g, 7.9 mmol) was added, the suspension filtered and the filtrate concentrated *in vacuo*. The residue was dissolved in CH_2Cl_2, filtered through a short plug of SiO_2 to remove the dark blue colour and concentrated *in vacuo*. Chromatography (petrol → 4:1 petrol-CH_2Cl_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 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.26 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 100.6, 65.1.

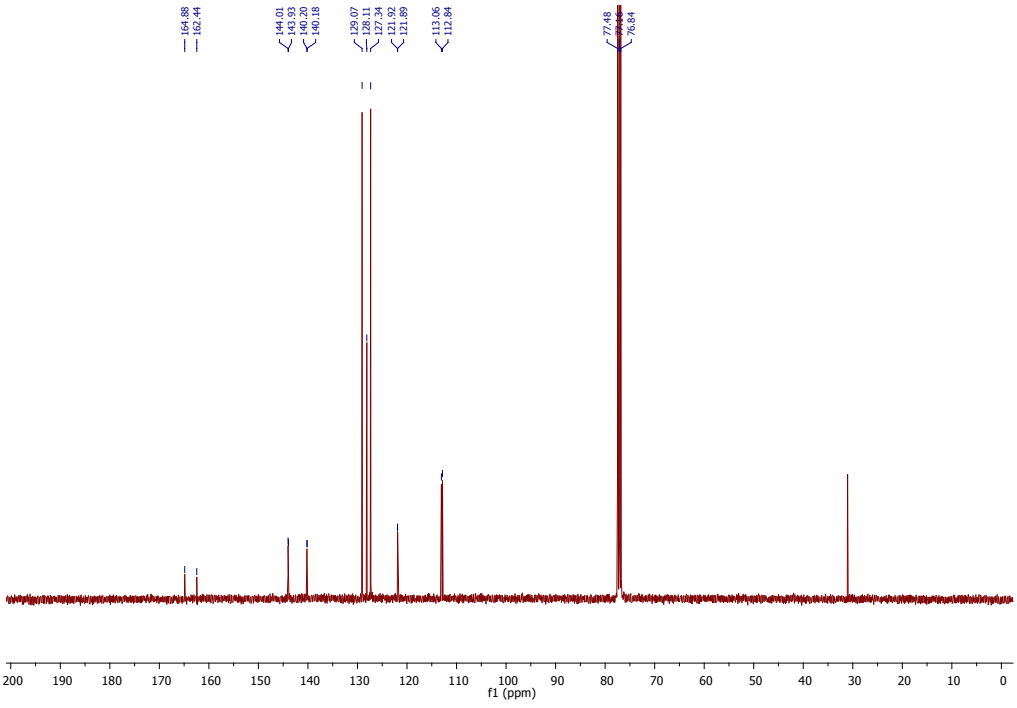
Graphical NMR Data for all novel compounds

^{1}H NMR (400 MHz, $CDCl_3$, 300K) of compound 3d

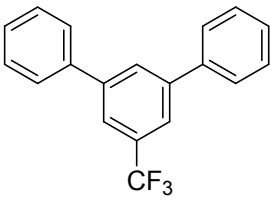


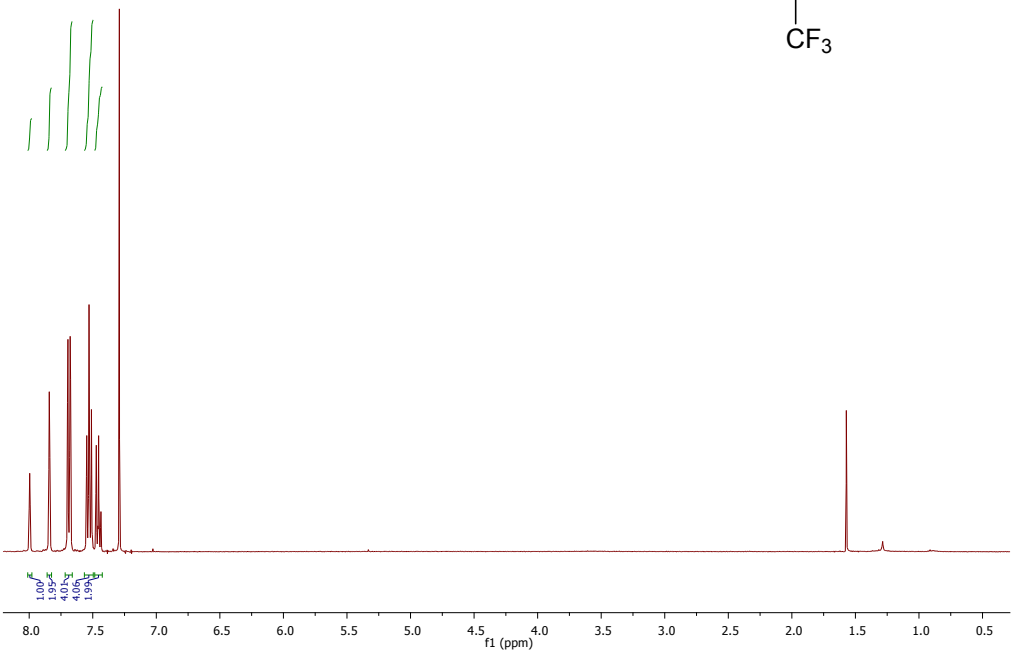


^{13}C NMR (101 MHz, $CDCl_3$, 300K) of compound 3d

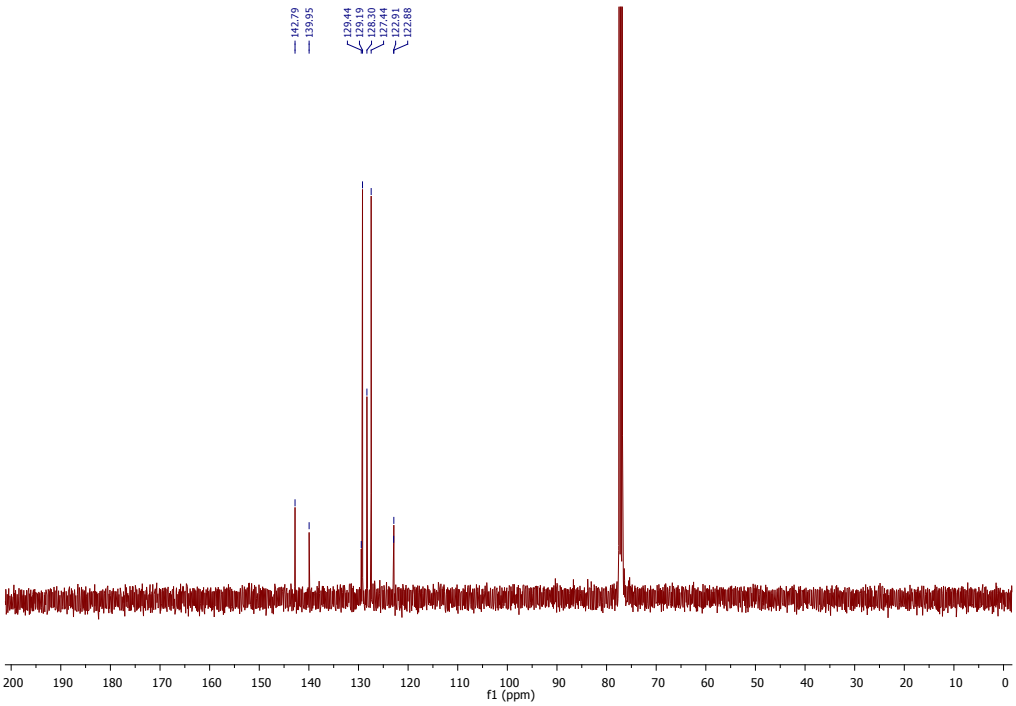


^{1}H NMR (400 MHz, $CDCl_3$, 300K) of compound 3e

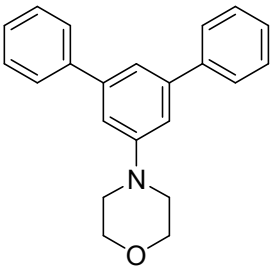


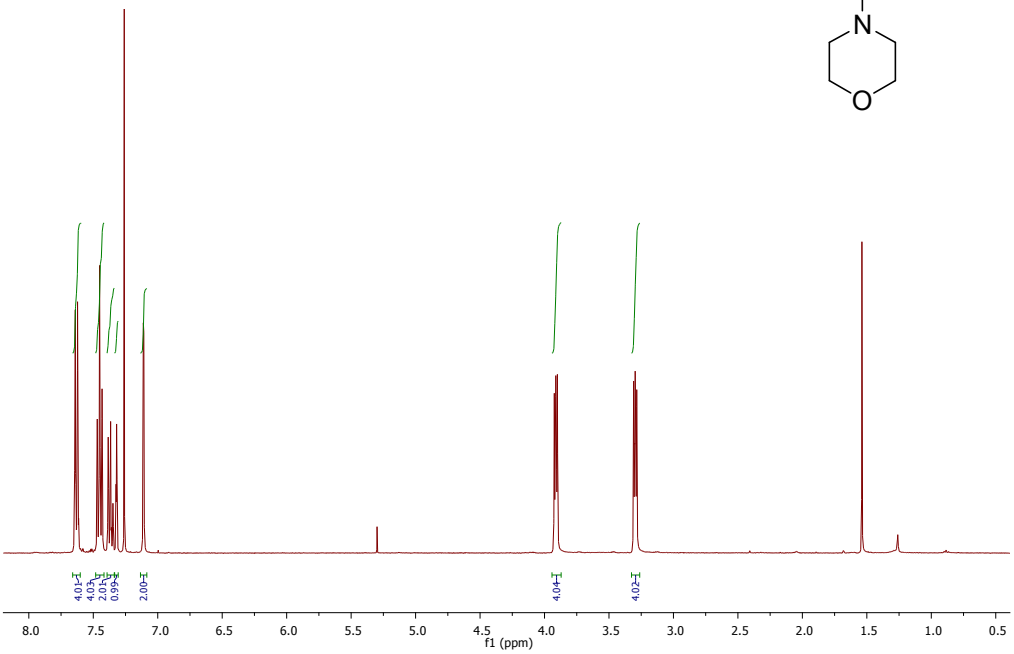


^{13}C NMR (100 MHz, $CDCl_3$, 300K) of compound 3e

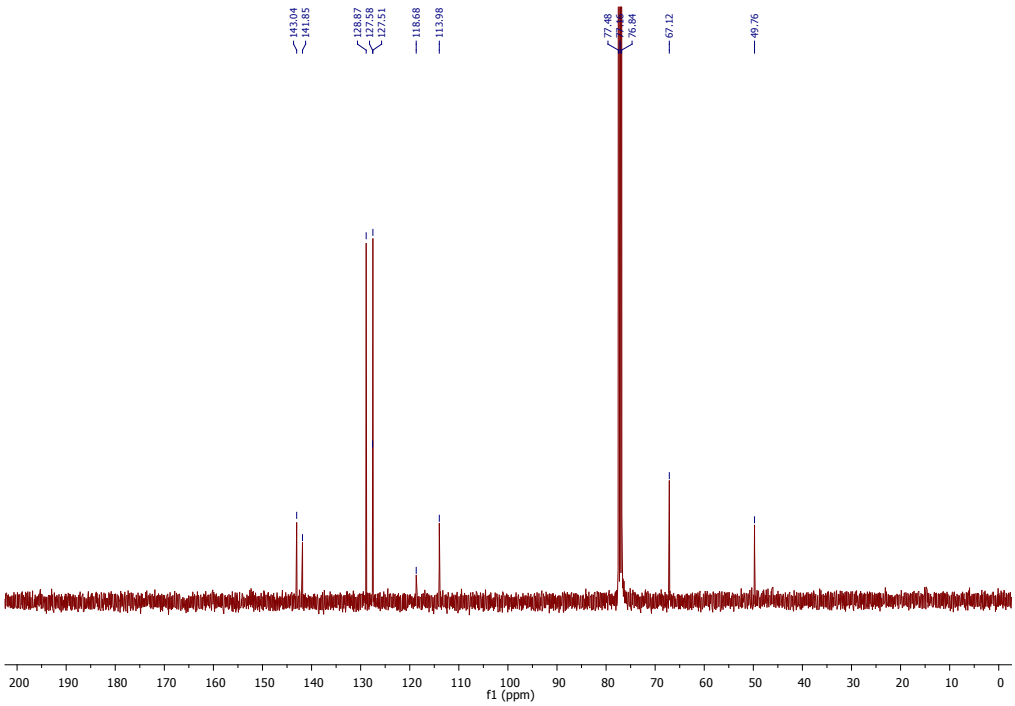


^{1}H NMR (400 MHz, $CDCl_3$, 300K) of compound 3g

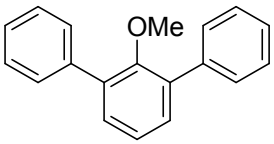


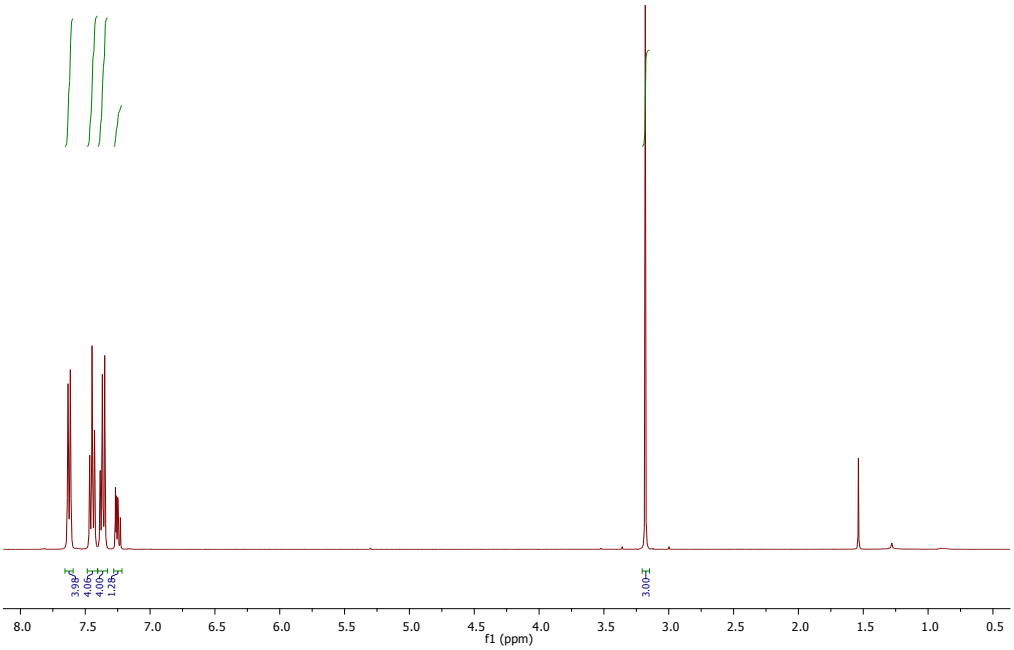


^{13}C NMR (100 MHz, $CDCl_3$, 300K) of compound 3g

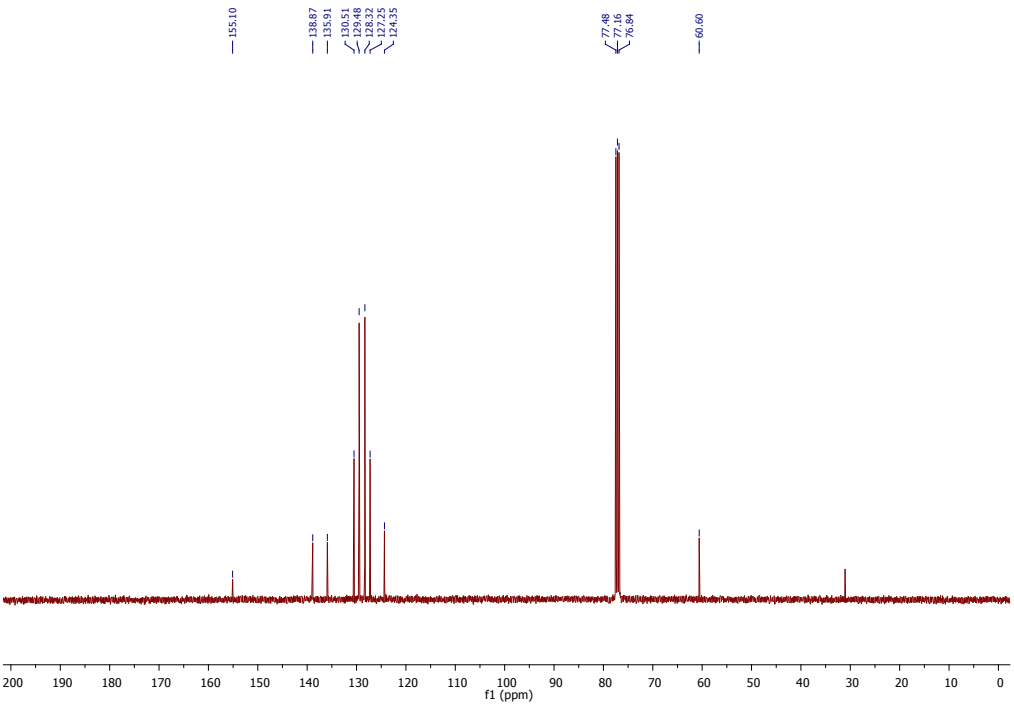


^{1}H NMR (400 MHz, $CDCl_3$, 300K) of compound 3i

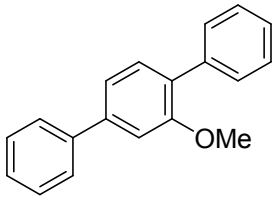


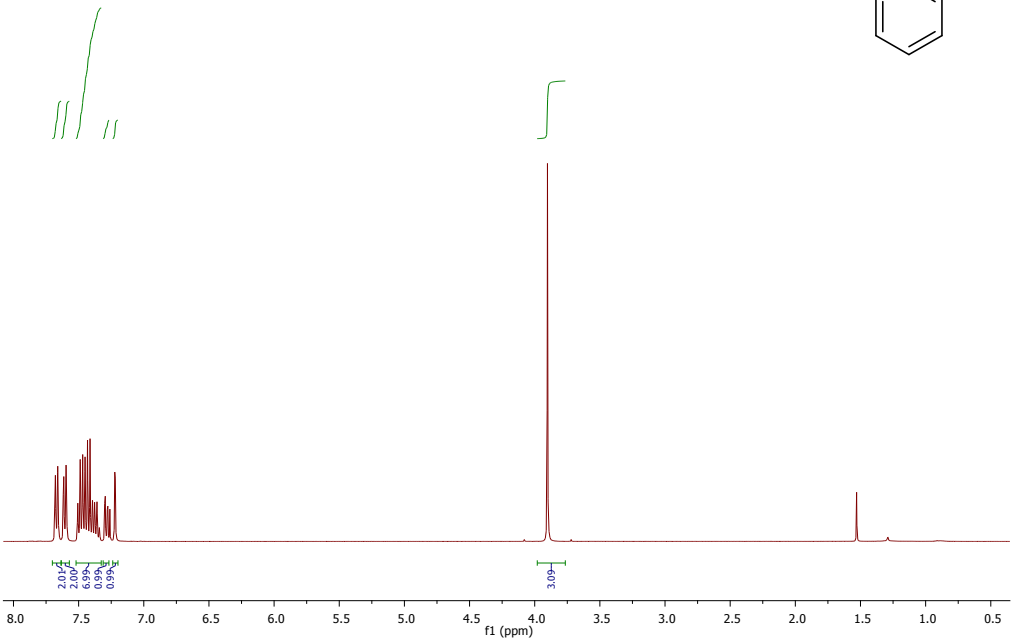


^{13}C NMR (100 MHz, $CDCl_3$, 300K) of compound 3i

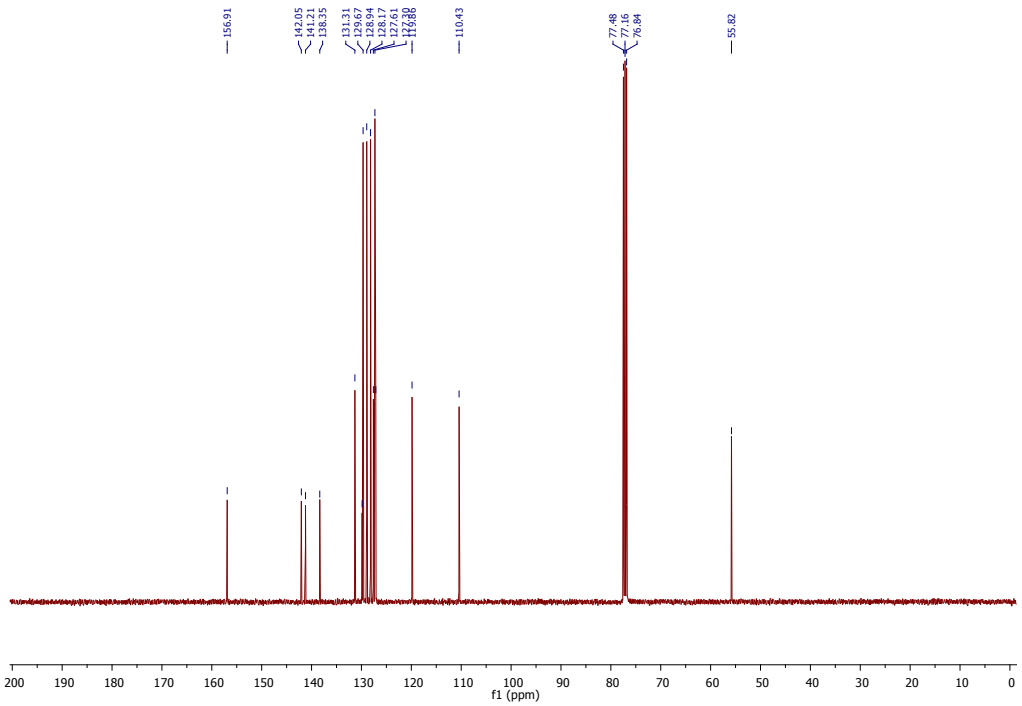


^{1}H NMR (400 MHz, $CDCl_3$, 300K) of compound 3l

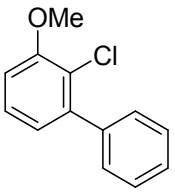


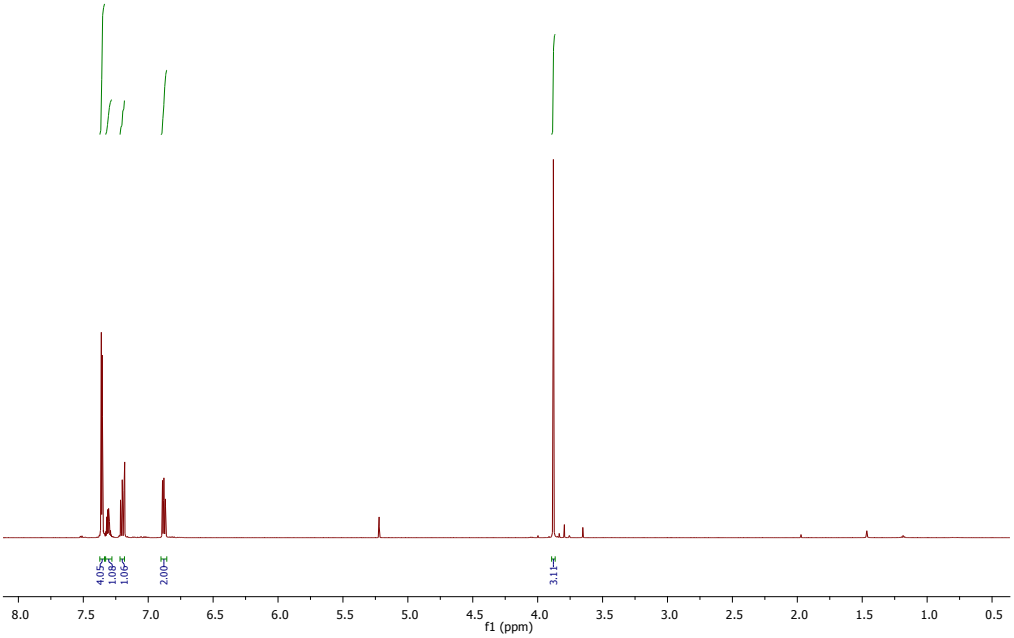


^{13}C NMR (100 MHz, $CDCl_3$, 300K) of compound 3l

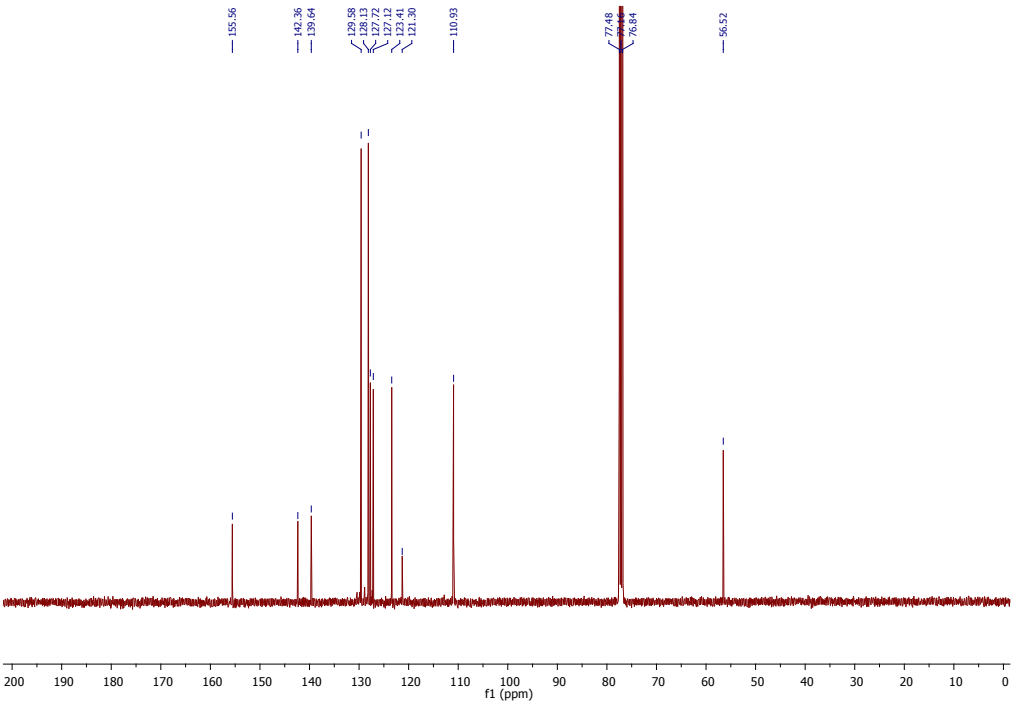


^{1}H NMR (400 MHz, $CDCl_3$, 300K) of compound 2m

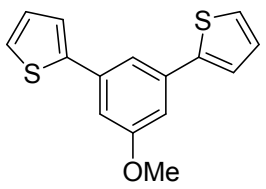


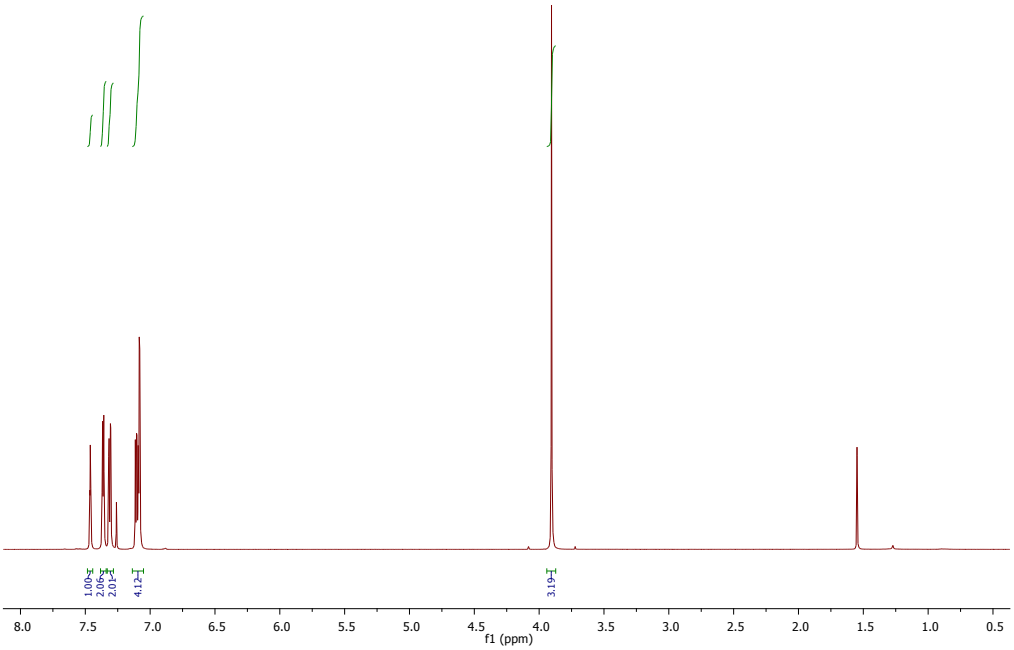


^{13}C NMR (100 MHz, $CDCl_3$, 300K) of compound 2m

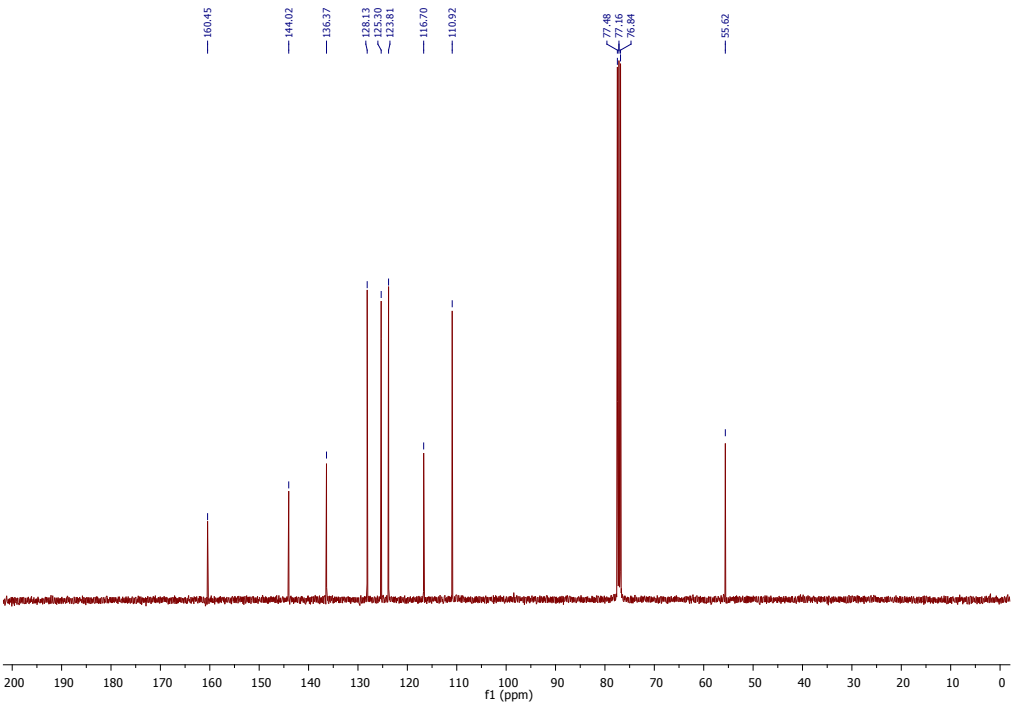


^{1}H NMR (400 MHz, $CDCl_3$, 300K) of compound 3t

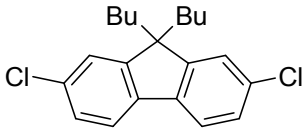


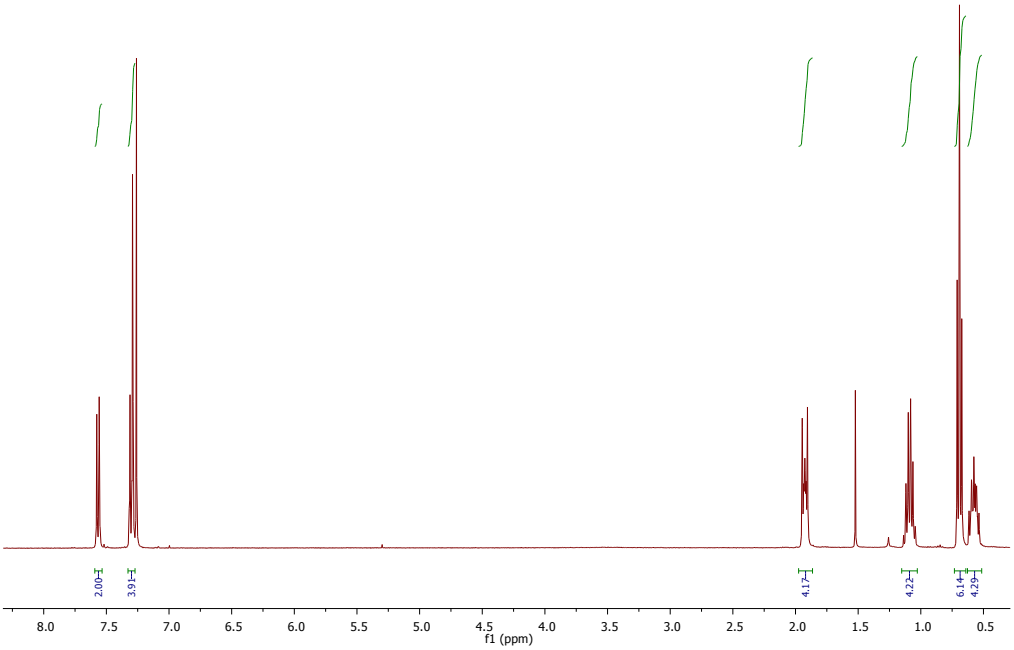


^{13}C NMR (100 MHz, $CDCl_3$, 300K) of compound 3t

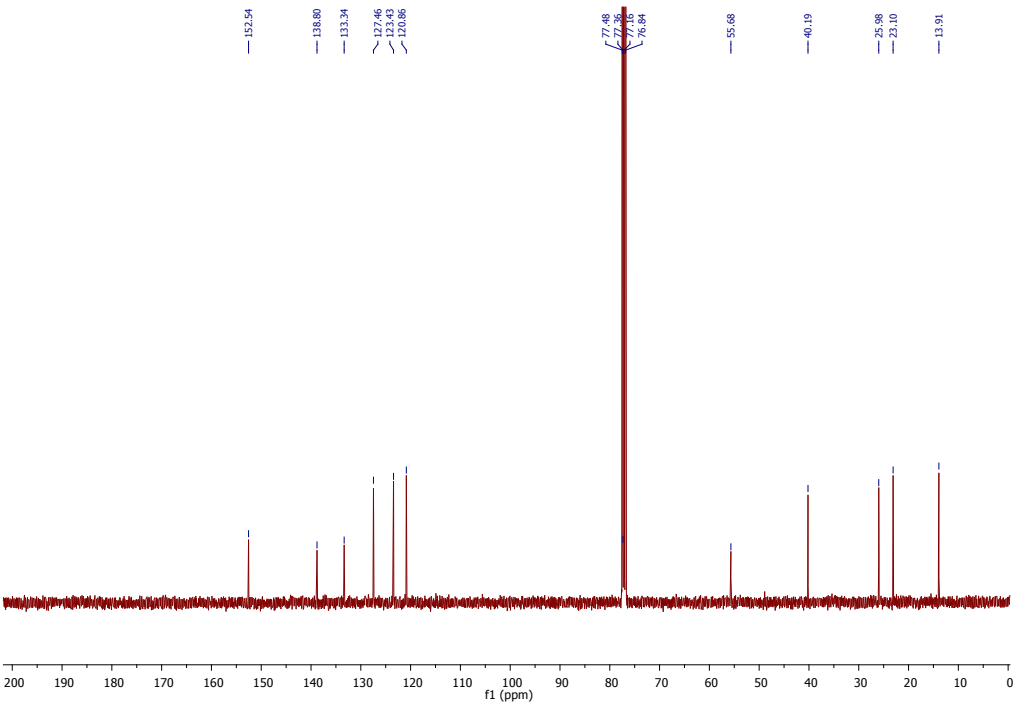


^{1}H NMR (400 MHz, $CDCl_3$, 300K) of compound 1x

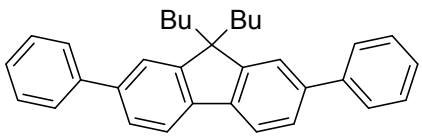


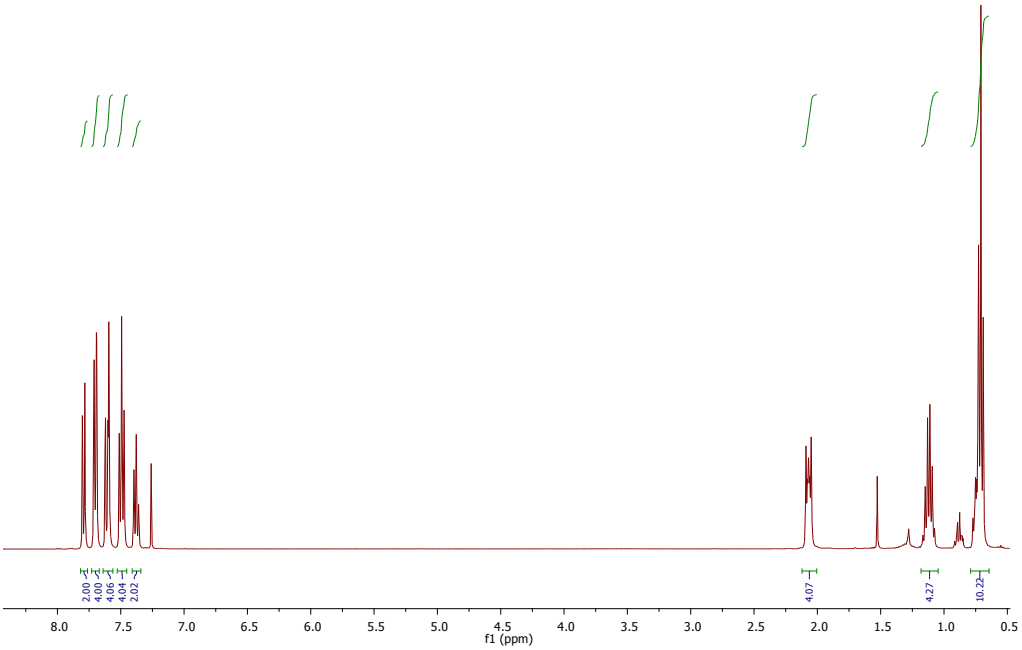


^{13}C NMR (100 MHz, $CDCl_3$, 300K) of compound 1x

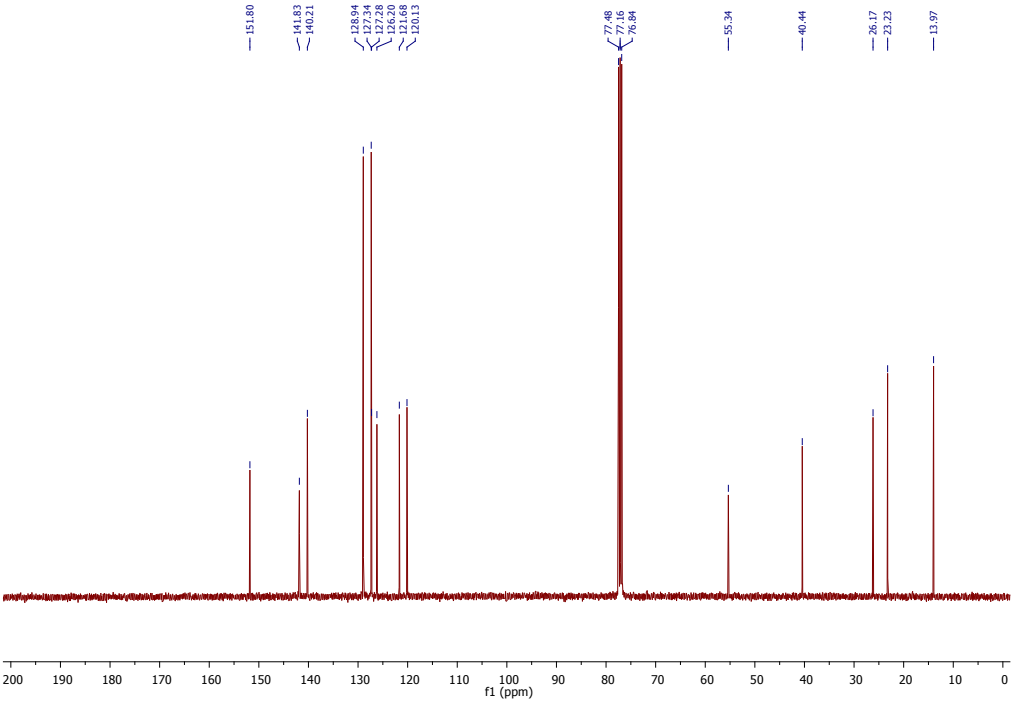


^{1}H NMR (400 MHz, $CDCl_3$, 300K) of compound 3x

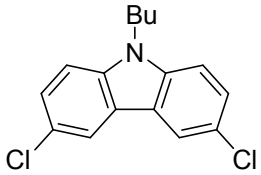


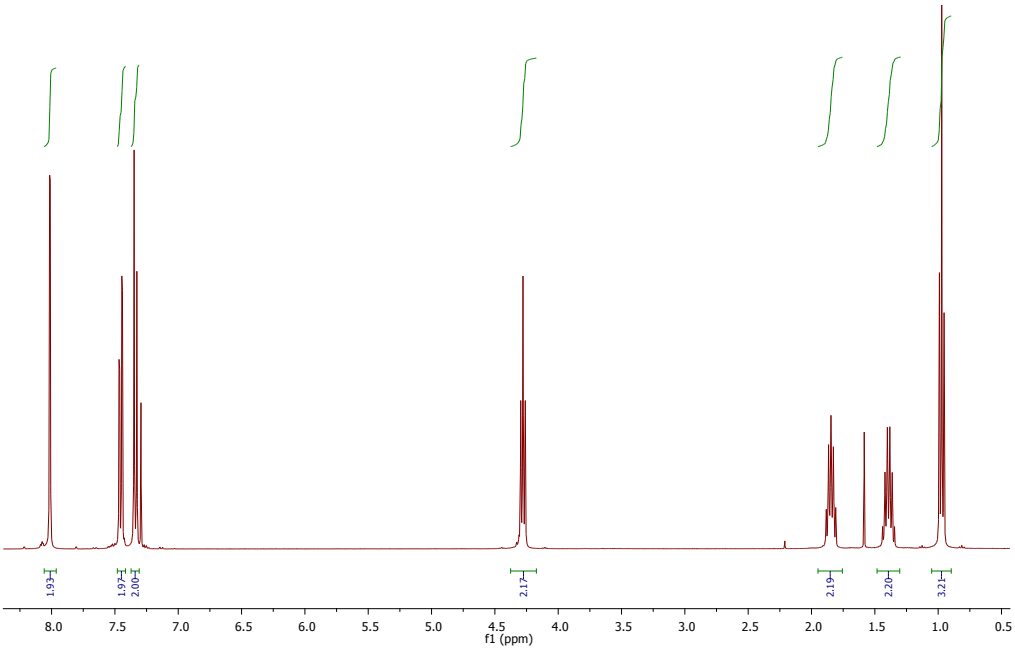


^{13}C NMR (100 MHz, $CDCl_3$, 300K) of compound 3x

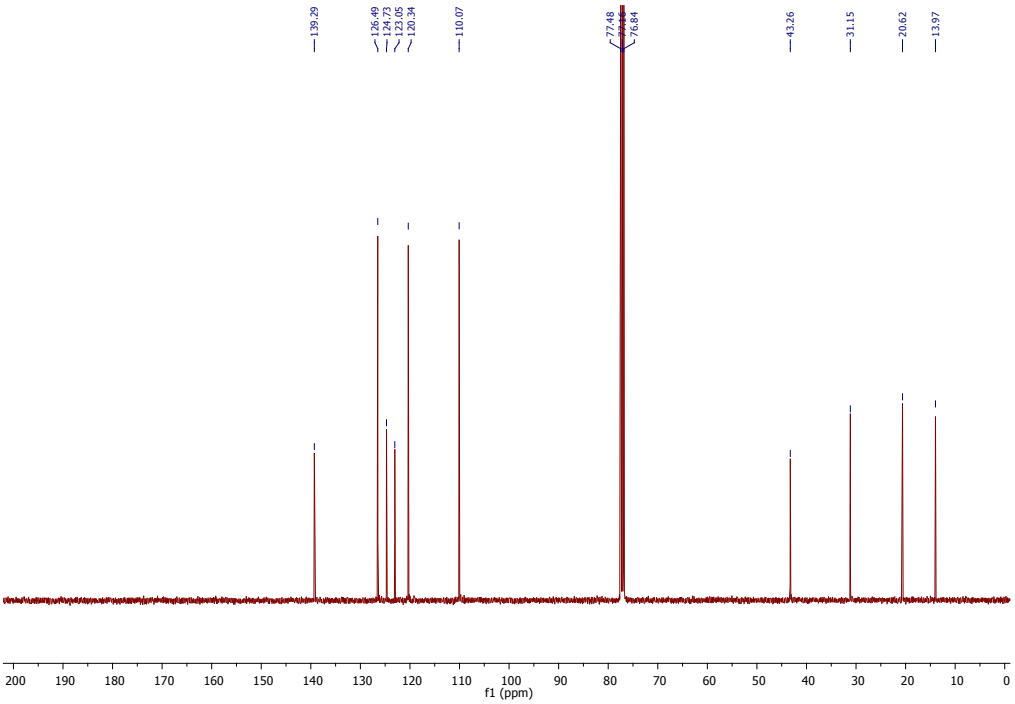


^{1}H NMR (400 MHz, $CDCl_3$, 300K) of compound 1y





^{13}C NMR (100 MHz, $CDCl_3$, 300K) of compound 1y



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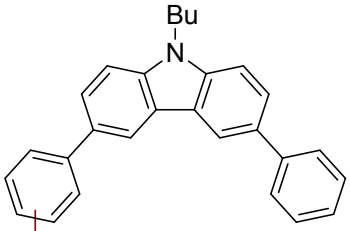
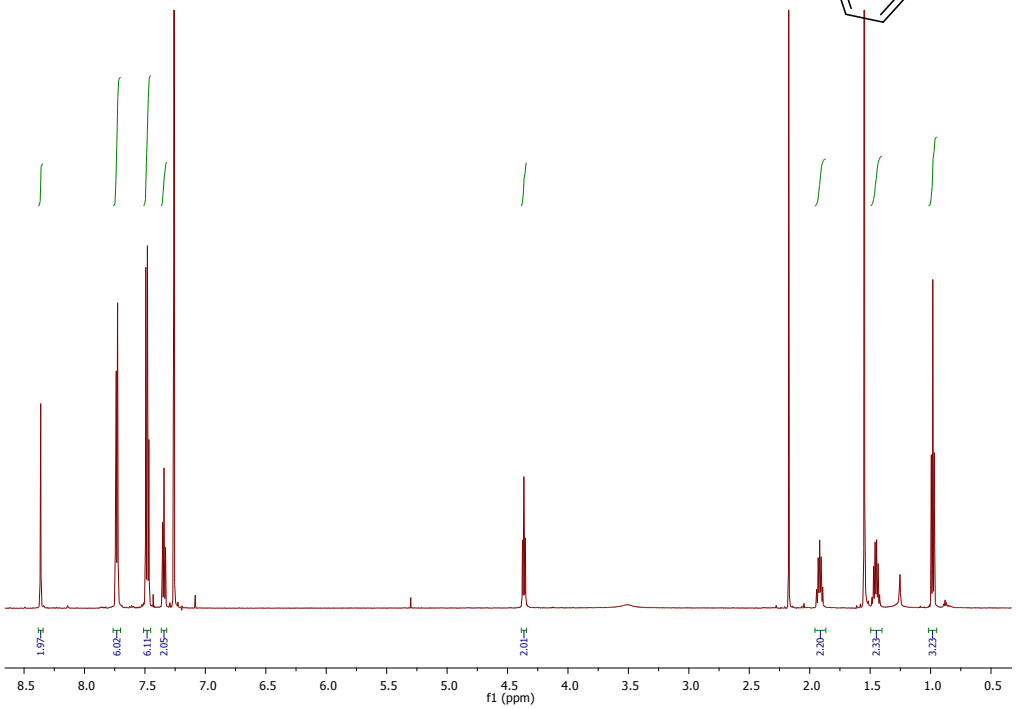
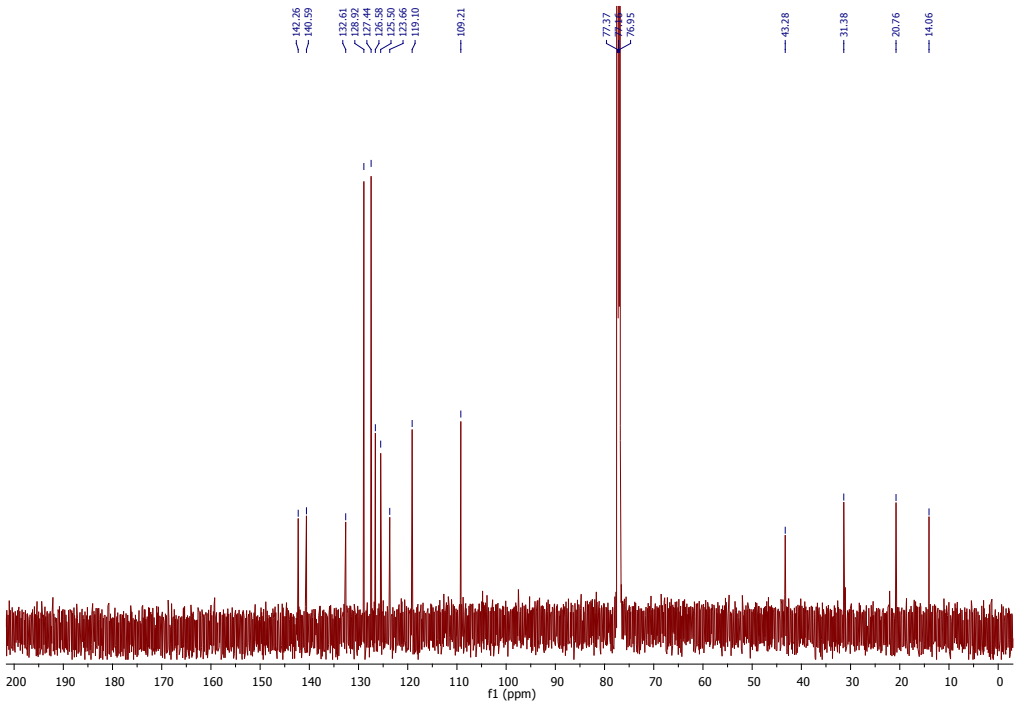




^{13}C NMR (100 MHz, $CDCl_3$, 300K) of compound 3y



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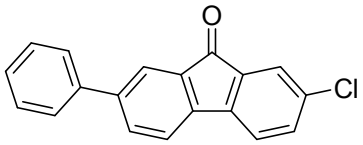

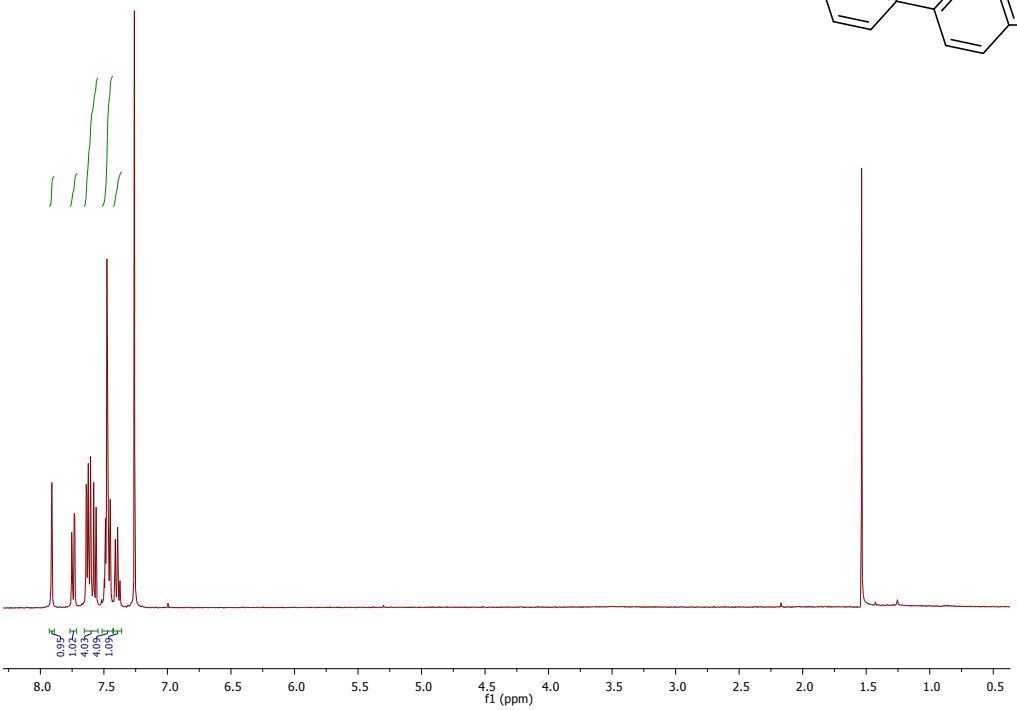

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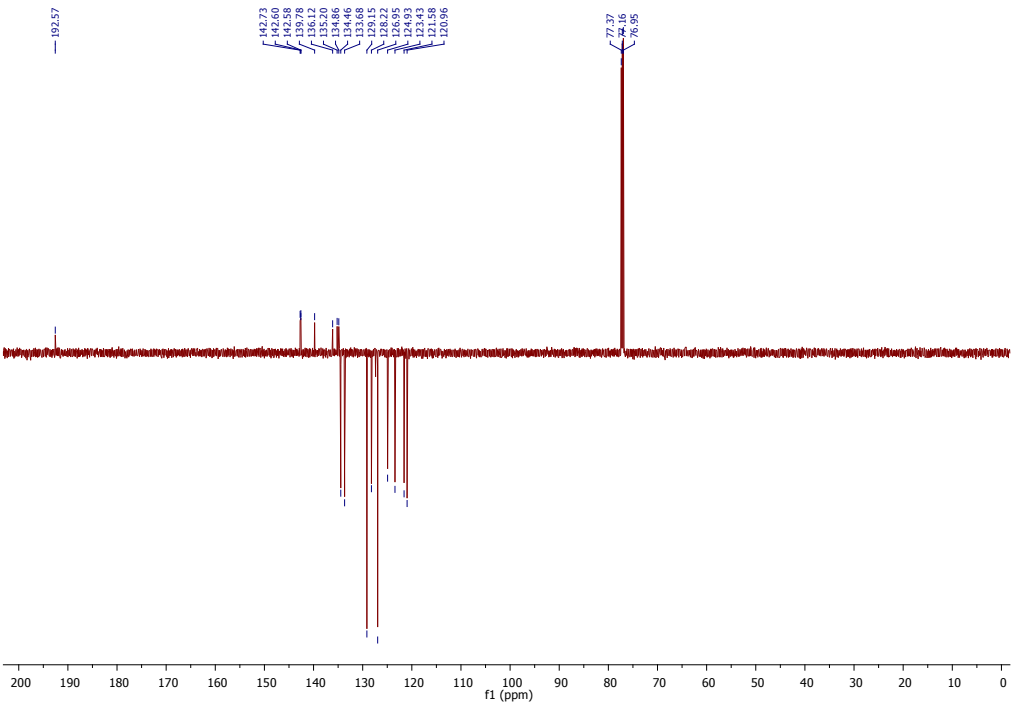

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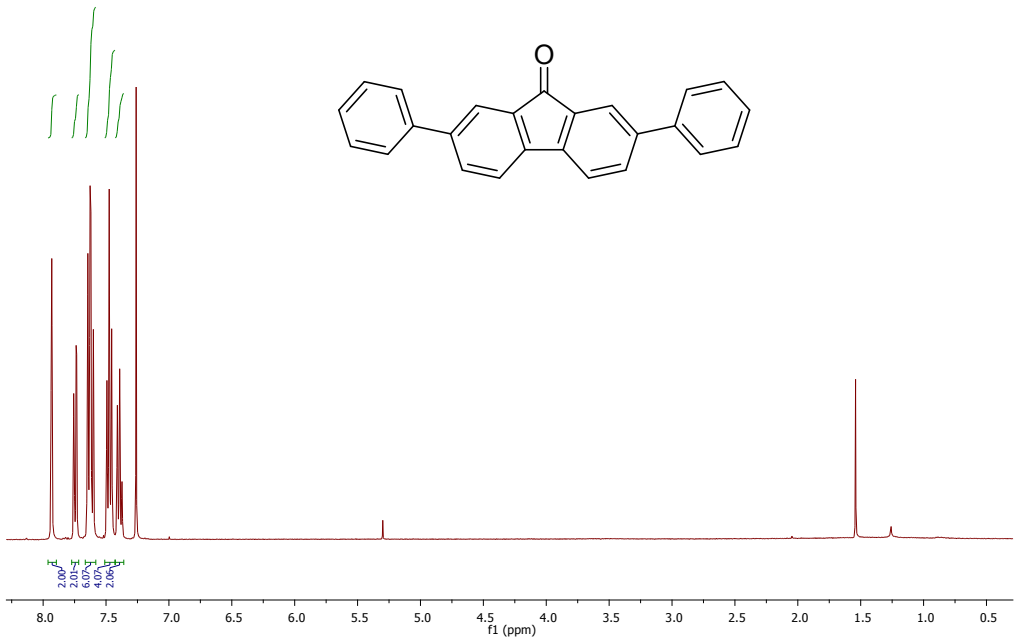

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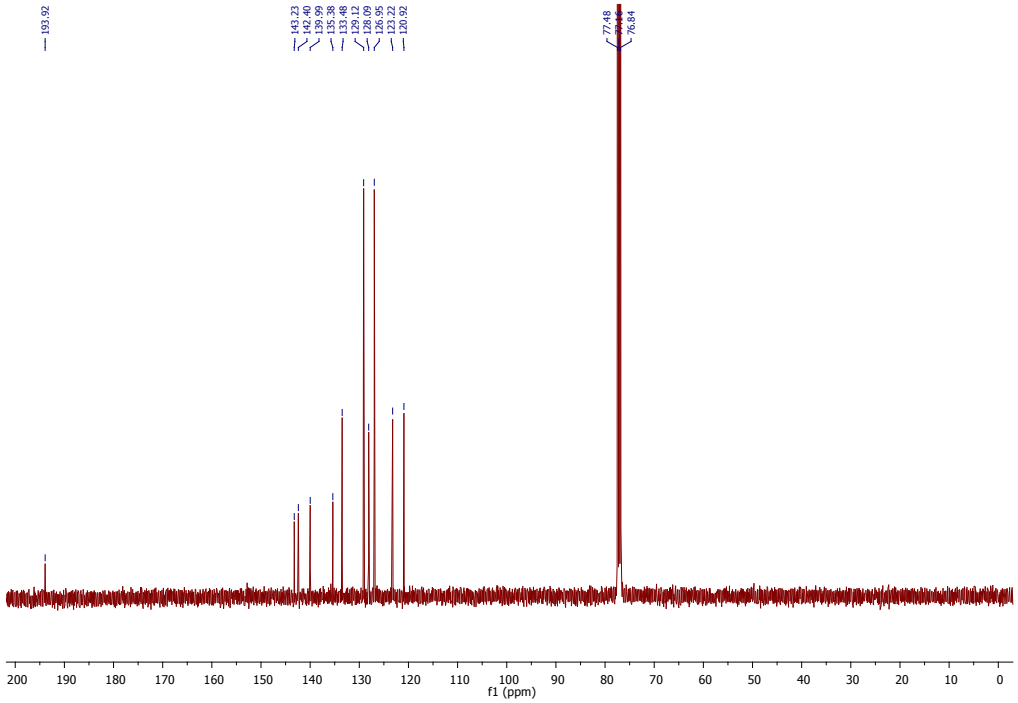
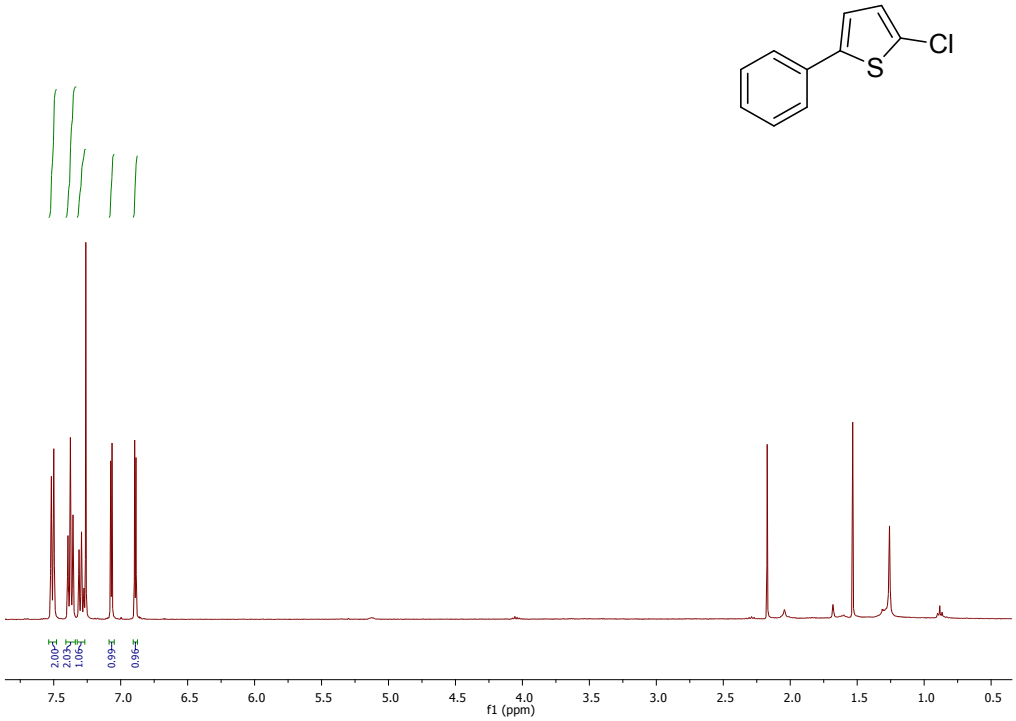


^{1}H NMR (400 MHz, $CDCl_3$, 300K) of compound 3aa



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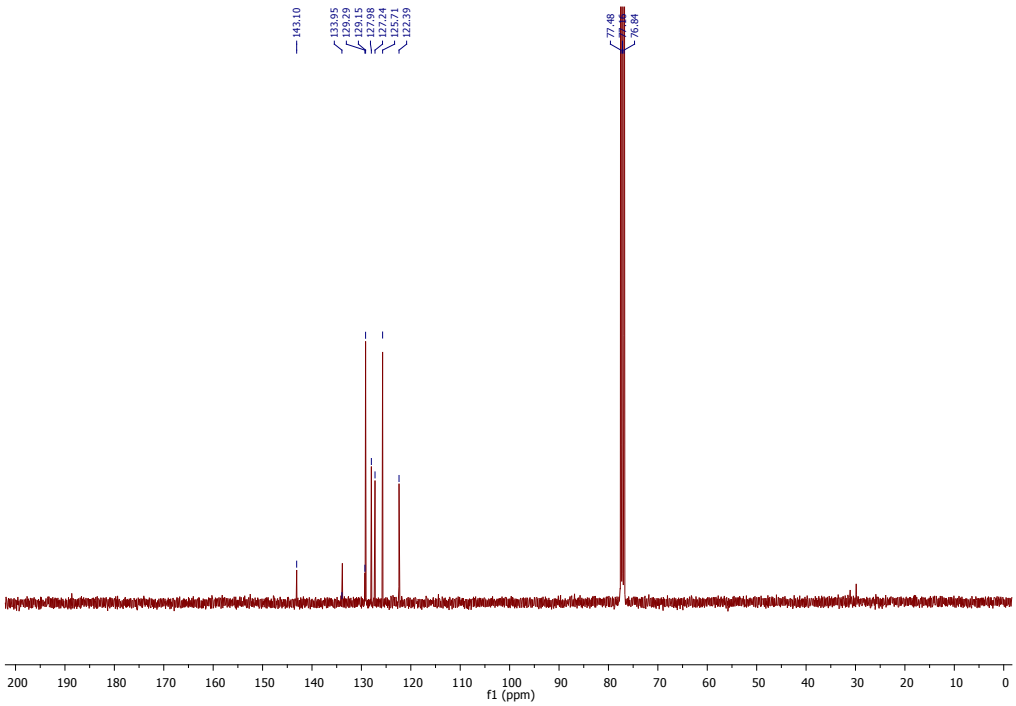

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