Suzuki–Miyaura reaction of chloroarenes using $Pd(PPh_3)_4$ as catalyst

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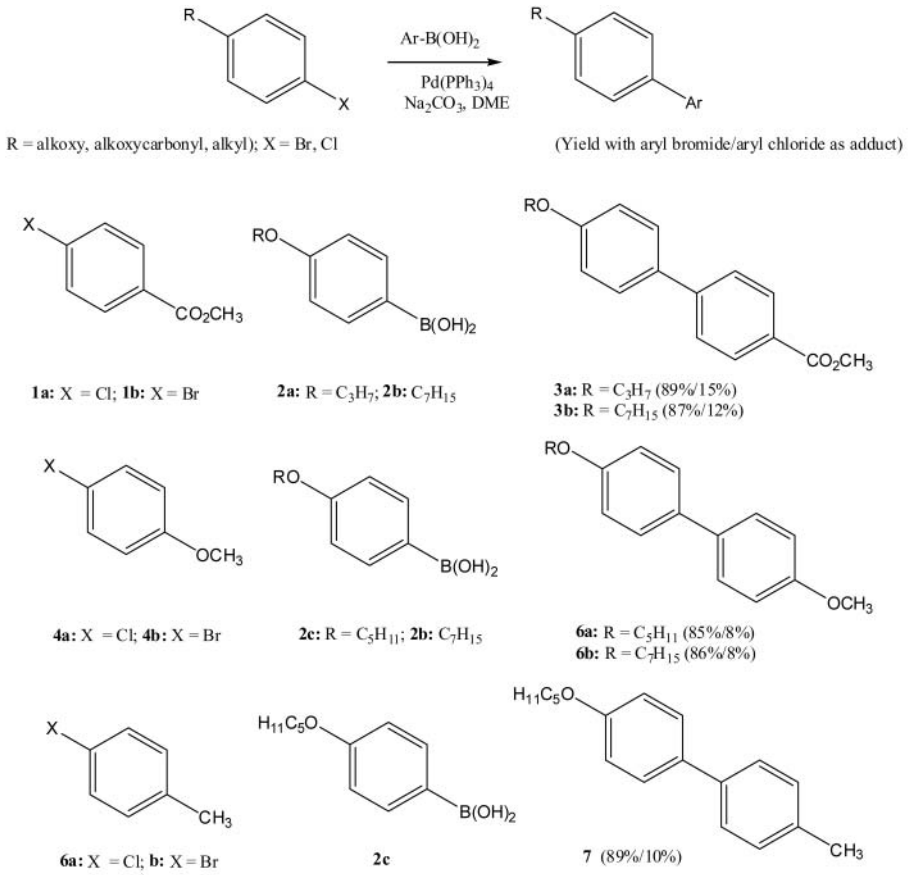
The reactivity of a number of chloroarenes was investigated and chloro–nitroarenes were found to undergo facile arylation with $Pd(PPh_3)_4$ / $[Pd(PPh_3)_2Cl_2/n{\cdot}PPh_3]$ as catalyst. Furthermore, 4–chlorobenzaldehyde underwent arylation under the conditions, albeit with a higher catalyst loading.

Keywords: nitrochlorobenzenes, Suzuki–Miyaura cross–coupling, tetrakis(triphenylphosphino)palladium(0)

The Suzuki–Miyaura cross–coupling reaction of aryl– and alkylboronic acids with bromo– and iodoarenes has become a powerful tool in organic synthesis.[1] For economic reasons, the use of chloroarenes in this reaction has become of great interest,[2] and the development of new catalysts and reaction protocols for such transformations has been found to be important. Commencing in the late 1990s, a number of new Pd–, Pt– and Ni–catalysts have been proposed[1—11] with a variety of exchangeable ligands. Furthermore, in the area of ligandless catalysts for Suzuki–Miyaura reactions, a number of highly reactive nanopalladium catalysts[12] have been developed as effective catalysts for the coupling of chloroarenes. It was also found that ligandless palladium catalysts could be used with aryl tetrafluoroborates in coupling reactions with aryl halides.[13] Our interest in the application of the Suzuki–Miyaura coupling to chloroarenes stems from our work on the synthesis of arylated anthraquinones, where we were surprised to find that chloroanthraquinones undergo C–C coupling reactions with arylboronic acids under $Pd(PPh_3)_4$ catalysis with great ease.[14] We now report the effectiveness of $Pd(PPh_3)_4$ as a catalyst for the coupling of chloroarenes other than chloroanthraquinones.

Thus, a number of electron donor and electron acceptor substituted aryl chlorides were reacted with arylboronic acids under $Pd(PPh_3)_4$ catalysis. For comparison, the corresponding aryl bromides were reacted under the same conditions (biphasic aq. Na_2CO_3, DME, 65 °C). Generally, the Suzuki coupling reaction of alkyl–, alkoxy–, and alkoxycarbonyl substituted aryl chlorides such as 1–chloro–4–methylbenzene (**1a**) gave poor results under $Pd(PPh_3)_4$ catalysis, and a large difference in reactivity between the chloroarenes and the bromoarenes was observed.



Scheme 1

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Results and discussion

Chloroaryl carbaldehydes such as 4–chlorobenzaldehyde (**8b**) and 4,4′–chlorobiphenylcarbaldehyde (**10**) were found to undergo Suzuki–cross coupling catalysed by $Pd(PPh_3)_4$. However, a relatively high catalyst loading was necessary for an adequate reaction turnover to take place.

Nitroaryl chlorides were found to react well, especially with electron donor substituted, very stable arylboronic acids such as with alkoxyarylboronic acids. Nitroaryl halides are often used as test substrates for testing the reactivity of new palladium catalysts and it is interesting that they will in fact react easily with most palladium catalysts, and thus they may not be a good benchmark for the efficacy of a catalyst.

In conclusion, we have shown that certain aryl chlorides, especially the electron poor nitroaryl halides undergo Suzuki–Miyaura coupling with the commercially available tet rakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] and with the combination of $Pd(PPh_3)_2Cl_2$ and triphenylphosphine. The ease with which these compounds undergo the reaction should also indicate that they should not be used as substrates to demonstrate the reactivity of catalysts in the Suzuki cross coupling of aryl halides.

Experimental

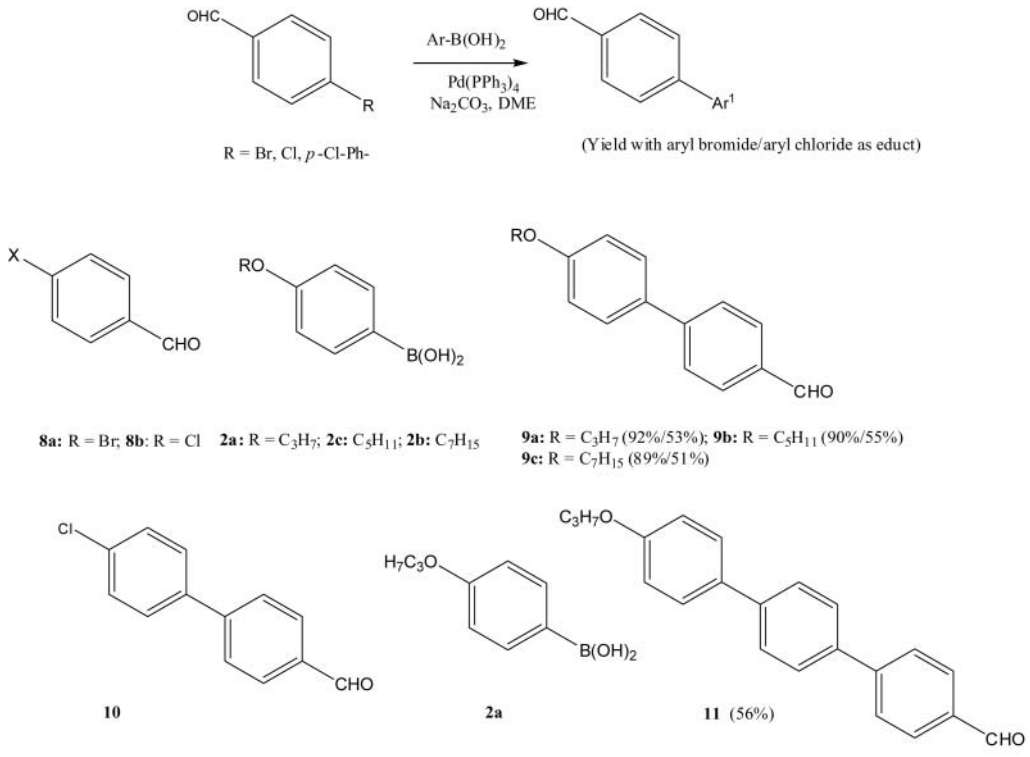
IR spectra were measured with JASCO IR–700, JASCO FTIR–6300 and Nippon Denshi JIR–AQ2OM machines. ^1H and ^{13}C NMR spectra were recorded with a JEOL EX–270 spectrometer (^1H at 270 MHz and ^{13}C at 67.8 MHz). The chemical shifts are relative to TMS (solvent $CDCl_3$, unless otherwise noted). Mass spectra were measured with a JMS–01–SG–2 spectrometer [electron impact mode (EI), 70 eV or fast atom bombardment (FAB)]. Column chromatography was carried out on Wakogel C–300.

Phenylboronic acid (**2d**) (TCI), *p*–vinylphenylboronic acid (**2f**), and 2–thienylboronic acid (**2g**) were acquired commercially. *p*–Alkoxyphenylboronic acids **2a–2c**, **2e**, **2h**, and **2i** were prepared from the corresponding *p*–alkoxy–bromobenzenes (a. *n*–BuLi, $B(OR)_3$, THF; b. HCl).[15]

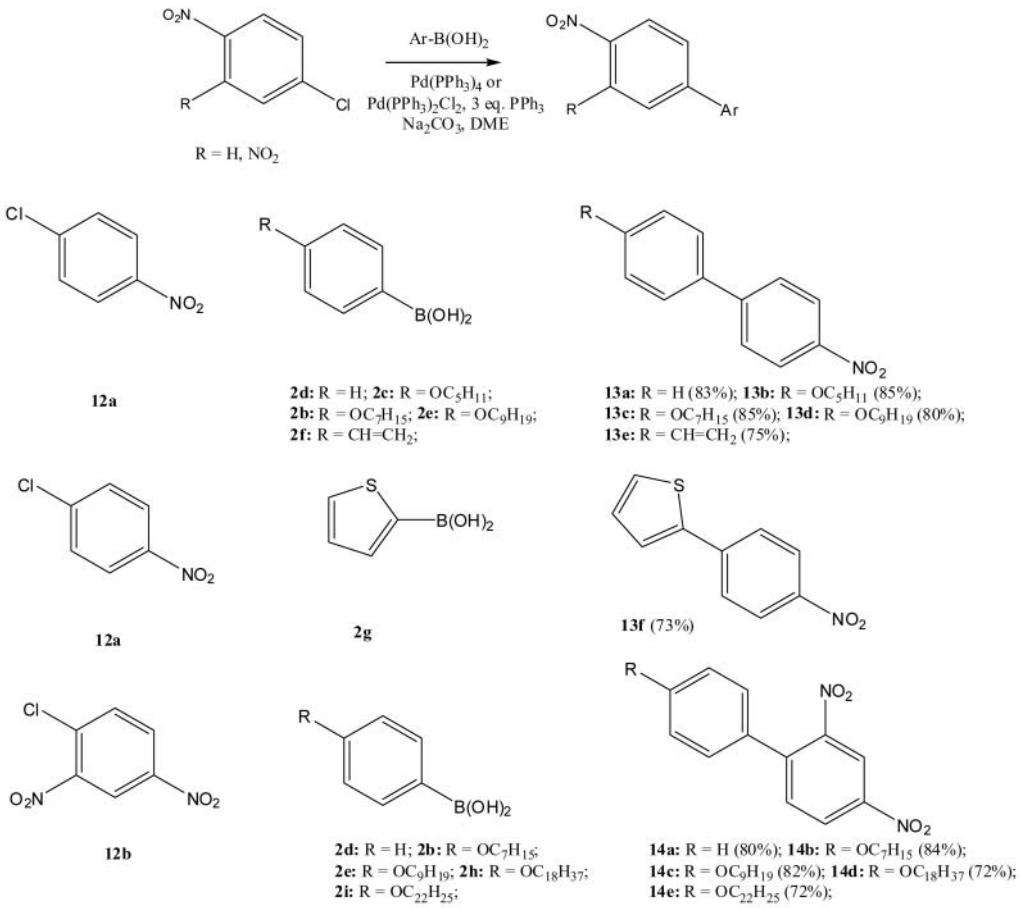
Methyl 4′–propoxybiphenyl–4–carboxylate (**3a**);[16] *general procedure A*: A solution of methyl 4–chlorobenzoate (**1a**, 170 mg, 1.0 mmol) or methyl 4–bromobenzoate (**1b**, 215 mg, 1.0 mmol), 4–propoxyphenylboronic acid (225 mg, 1.25 mmol) and $Pd(PPh_3)_4$ (45 mg, 4×10^{-5} mol) in a mixture of DME (15 mL) and aq. Na_2CO_3 (2.32 g Na_2CO_3 in 15 mL H_2O, 9 mL) was kept at 70 °C for 18h under an inert atmosphere. The cooled solution was then poured into water (25 mL) and extracted with chloroform (3 × 15 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and was concentrated *in vacuo*. Column chromatography of the residue on silica gel (hexane/$CHCl_3$/ether 3:1:1) gave **3a** (40 mg, [15%], 240 mg [89%], respectively) as a colourless solid; m.p. 165 °C; (Found: M^+, 270.1255. $C_{17}H_{18}O_3$ requires M^+, 270.1256). δ_H (270 MHz, $CDCl_3$) 1.06 (3H, t, ^3J = 7.4 Hz, CH_3), 1.83 (tt, 2H, ^3J = 7.4 Hz, ^3J = 6.5 Hz), 3.93 (3H, s, $CO_2C\underline{H}_3$), 3.97 (2H, t, ^3J = 6.5 Hz, OCH_2), 6.98 (2H, d, ^3J = 8.9 Hz), 7.56 (2H, d, ^3J = 8.9 Hz), 7.61 (2H, d, ^3J = 8.6 Hz), 8.07 (2H, d, ^3J = 8.6 Hz); δ_C (67.8 MHz, $CDCl_3$) 10.5 (CH_3), 22.6 (CH_2), 50.05 (OCH_3), 69.6 (OCH_2), 114.9 (2C, CH), 126.4 (2C, CH), 128.1 (C_{quat}), 128.3 (2C, CH), 130.1 (2C, CH), 132.1 (C_{quat}), 145.3 (C_{quat}), 159.4 (C_{quat}), 167.1 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) = 270 (M^+) (61), 228 (100), 197 (83).

Methyl 4′–heptoxybiphenyl–4–carboxylate (**3b**);[16] *general procedure A*: Shiny flakes; m.p. 134 °C; (Found: M^+, 326.1883. $C_{21}H_{26}O_3$ requires M^+, 326.1882). δ_H (270 MHz, $CDCl_3$) 0.88 (3H, t, ^3J = 7.0 Hz, CH_3), 1.22–1.43 (8H, m), 1.76–1.86 (2H, m), 3.92 (3H, s, $CO_2C\underline{H}_3$), 3.95 (2H, t, ^3J = 6.7 Hz, OCH_2), 7.00 (2H, d, ^3J = 8.9 Hz), 7.58 (2H, d, ^3J = 8.9 Hz), 7.62 (2H, d, ^3J = 8.6 Hz), 8.08 (2H, d, ^3J = 8.6 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.1 (CH_3), 22.6 (CH_2), 26.0 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 31.8 (CH_2), 52.1 (OCH_3), 68.1 (OCH_2), 114.9 (2C, CH), 126.4 (2C, CH), 128.1 (C_{quat}), 128.3 (2C, CH), 130.1 (2C, CH), 132.1 (C_{quat}), 145.3 (C_{quat}), 159.4 (C_{quat}), 167.1 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) = 326 (M^+) (57), 228 (100), 197 (38). Calcd for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03. Found: C, 77.13; H, 8.03%.

4–Methoxy–4′pentoxybiphenyl (**6a**); *general procedure A*: Colourless solid; m.p. 131 °C; (Found: 270.1624. $C_{18}H_{22}O_2$ requires M^+, 270.1620). δ_H (270 MHz, $CDCl_3$) 0.94 (3H, t, ^3J = 7.0 Hz, CH_3), 1.38–1.44 (4H, m), 1.78–1.81 (2H, m), 3.84 (3H, s, OCH_3), 3.98 (2H, t, ^3J = 6.7 Hz, OCH_2), 6.94 (2H, d, ^3J = 8.9 Hz), 6.95 (2H, d, ^3J = 8.9 Hz), 7.46 (2H, d, ^3J = 8.9 Hz), 7.48 (2H, d, ^3J = 8.9 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.0 (CH_3), 22.5 (CH_2), 28.2 (CH_2), 29.0 (CH_2), 55.3



Scheme 2



Scheme 3

(OCH_3), 68.1 (OCH_2), 114.1 (2C, CH), 114.7 (2C, CH), 127.7 (4C, CH), 133.2 (C_{quat}), 133.6 (C_{quat}), 158.2 (C_{quat}), 158.6 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 270 (M^+) (95), 200 (M^+–C_5H_{10}) (100), 185 (M^+–CH_3–C_5H_{10}). Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.97; H, 8.21%.

4–Methoxy–4′–heptoxybiphenyl (**6b**); *general procedure A*: Colourless solid; m.p. 123 °C; (Found: M^+, 298.1931. $C_{20}H_{26}O_2$ requires M^+, 298.1933). δ_H (270 MHz, $CDCl_3$) 0.88 (3H, t, ^3J = 7.0 Hz, CH_3), 1.21–1.46 (8H, m), 1.74–1.82 (2H, m), 3.83 (3H, s, OCH_3), 3.98 (2H, t, ^3J = 6.7 Hz, OCH_2), 6.94 (2H, d, ^3J = 8.9 Hz), 6.95 (2H, d, ^3J = 8.9 Hz), 7.46 (2H, d, ^3J = 8.9 Hz), 7.48 (2H, d, ^3J = 8.9 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.1 (CH_3), 22.6 (CH_2), 28.2 (CH_2), 26.0 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 55.3 (OCH_3), 68.1 (OCH_2), 114.1 (2C, CH), 114.7 (2C, CH), 127.7 (4C, CH), 133.2 (C_{quat}), 133.5 (C_{quat}), 158.2 (C_{quat}), 158.6 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 298 (M^+) (100), 200 (95), 185 (26). Calcd for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78. Found: C, 80.24; H, 8.76%.

4–Methyl–4′–pentoxybiphenyl (**7**);[17] *general procedure A*: Colourless solid; m.p. 87 °C; (Found: M^+, 254.1668. $C_{18}H_{22}O$ requires M^+, 254.1671). δ_H (270 MHz, $CDCl_3$) 0.94 (3H, t, ^3J = 7.0 Hz, CH_3), 1.38–1.44 (4H, m), 1.78–1.83 (2H, m), 2.38 (3H, s, CH_3), 3.99 (2H, t, ^3J = 6.7 Hz, OCH_2), 6.95 (2H, d, ^3J = 8.9 Hz), 7.22 (2H, d, ^3J = 7.8 Hz), 7.44 (2H, d, ^3J = 7.8 Hz), 7.49 (2H, d, ^3J = 8.9 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.0 (CH_3), 21.0 (CH_3), 22.5 (CH_2), 28.2 (CH_2), 29.0 (CH_2), 68.1 (OCH_2), 114.7 (2C, CH), 126.5 (2C, CH), 127.9 (2C, CH), 129.4 (2C, CH), 133.5 (C_{quat}), 136.3 (C_{quat}), 138.0 (C_{quat}), 158.5 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 254 (M^+) (50), 184 (100). Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.77; H, 8.80%.

4′–Propoxy–biphenyl–4–carbaldehyde (**9a**); *general procedure B*: A solution of 4–bromobenzaldehyde (**8a**, 185 mg, 1.0 mmol) or 4–chlorobenzaldehyde (**8b**, 140 mg, 1.0 mmol), 4–propoxyphenylboronic acid (**2a**, 225 mg, 1.25 mmol) and $Pd(PPh_3)_4$ (60 mg, 5.2×10^{-5} mol) [or $Pd(PPh_3)_2Cl_2$ (40 mg, $5.2 \cdot 10^{-5}$ mol) and triphenylphosphine (37 mg, 0.14 mmol)] was reacted and worked up according to procedure A to give **9a** (220 mg [92%], 127 mg [53%], respectively) as a colourless solid; m.p. 94 °C; (Found: M^+, 240.1149. $C_{16}H_{16}O_2$ requires M^+, 240.1150). δ_H (270 MHz, $CDCl_3$) 1.06 (3H, t, ^3J = 7.6 Hz, CH_3), 1.83 (2H, tt, ^3J = 7.6 Hz, ^3J = 6.7 Hz), 3.98 (2H, t, ^3J = 6.7 Hz, OCH_2), 7.01 (2H, d, ^3J = 8.9 Hz), 7.58 (2H, d, ^3J = 8.9 Hz), 7.71 (2H, d, ^3J = 8.4 Hz), 7.92 (2H, d, ^3J = 8.4 Hz), 10.0 (1H, s, CHO); δ_C (67.8 MHz, $CDCl_3$) 10.5 (CH_3), 22.6 (CH_2), 69.6 (OCH_2), 115.0 (2C, CH), 127.0 (2C, CH), 128.5 (2C, CH), 130.3 (2C, CH), 131.8 (C_{quat}), 134.6 (C_{quat}), 146.9 (C_{quat}), 159.7 (C_{quat}), 191.9 (CHO); MS (EI, 70 eV) *m/z* (%) 240 (M^+) (61), 198 (100), 141 (26). Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.72; H, 6.71%.

4′–Pentoxy–biphenyl–4–carbaldehyde (**9b**); *general procedure B*: Colourless solid, m.p. 71 °C; (Found: M^+, 268.1462. $C_{18}H_{20}O_2$ requires M^+, 268.1463). δ_H (270 MHz, $CDCl_3$) 0.95 (3H, t, ^3J = 7.0 Hz, CH_3), 1.43 (4H, m), 1.82 (2H, m), 4.01 (2H, t, ^3J = 6.7 Hz, OCH_2), 7.00 (2H, d, ^3J = 8.9 Hz), 7.58 (2H, d, ^3J = 8.9 Hz), 7.71 (2H, d, ^3J = 8.1 Hz), 7.92 (2H, d, ^3J = 8.1 Hz), 10.0 (1H, s, CHO); δ_C (67.8 MHz, $CDCl_3$) 14.0 (CH_3), 22.4 (CH_2), 28.2 (CH_2), 28.9 (CH_2), 68.1 (OCH_2), 115.0 (2C, CH), 127.0 (2C, CH), 128.4 (2C, CH), 130.3 (2C, CH), 131.8 (C_{quat}), 134.6 (C_{quat}), 146.9 (C_{quat}), 159.7 (C_{quat}), 191.9 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 268 (M^+), 198 (100). Calcd for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.32; H, 7.47%.

4′–Heptoxy–biphenyl–4–carbaldehyde (**9c**);[18] *general procedure B*: Colourless solid, m.p. 80 °C; (Found: M^+, 296.1774. $C_{20}H_{24}O_2$ requires M^+, 296.1776). δ_H (270 MHz, $CDCl_3$) 0.88 (3H, t, ^3J = 7.0 Hz, CH_3), 1.19–1.43 (8H, m), 1.76–1.84 (2H, m), 3.96 (2H, t, ^3J = 6.7 Hz, OCH_2), 7.00 (2H, d, ^3J = 8.9 Hz), 7.60 (2H, d, ^3J = 8.9 Hz), 7.71 (2H, d, ^3J = 8.1 Hz), 7.92 (2H, d, ^3J = 8.1 Hz), 10.0 (1H, s, CHO); δ_C (67.8 MHz, $CDCl_3$) 14.1 (CH_3), 22.6 (CH_2), 26.0 (CH_2), 29.0 (CH_2), 29.2 (CH_2), 31.8 (CH_2), 68.1 (OCH_2), 115.0 (2C, CH), 127.0 (2C, CH), 128.4 (2C, CH), 130.3 (2C, CH), 131.7 (C_{quat}), 134.6 (C_{quat}), 146.8 (C_{quat}), 159.7 (C_{quat}), 191.9 (C_{quat}, CO); MS (EI, 70 eV) *m/z* (%) 296 (M^+) (56), 198 (100). Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 81.11; H, 8.17%.

4′–Propoxyterphenyl–4–carbaldehyde (**11**); *general procedure B*: Colourless solid, m.p. 254 °C; (Found: M+, 316.1466. $C_{22}H_{20}O_2$ requires M+, 316.1463). δ_H (270 MHz, $CDCl_3$) 1.03 (3H, t, ^3J = 7.6 Hz, CH_3), 1.81 (2H, tt, ^3J = 7.6 Hz, ^3J = 6.7 Hz), 3.96 (2H, t, ^3J = 6.7 Hz, OCH_2), 6.98 (2H, d, ^3J = 8.9 Hz), 7.63 (2H, d, ^3J = 8.9 Hz), 7.65 (2H, d, ^3J = 8.1 Hz), 7.70 (2H, d, ^3J = 8.4 Hz), 7.72 (2H, d, ^3J = 8.4 Hz), 7.92 (2H, d, ^3J = 8.1 Hz), 9.98 (1H, s, CHO); MS (EI, 70 eV) *m/z* (%) = 316 (M^+) (5.0).

4–Nitrobiphenyl (**13a**); *general procedure C*: A solution of *p*–chloronitrobenzene (**12a**, 315 mg, 2.0 mmol), phenylboronic acid (366 mg, 3.0 mmol) and $Pd(PPh_3)_4$ (32 mg, $2.8\cdot10^{-5}$ mol) [or $Pd(PPh_3)_2Cl_2$ (20 mg, $2.8\cdot10^{-5}$ mol) and PPh_3 (22 mg, $8.6\cdot10^{-5}$ mol)] in a biphasic mixture of DME (10 mL) and aq. Na_2CO_3 (2.32 g Na_2CO_3 in 15 mL H_2O, 6 mL) was kept at 70 °C for 10h. Work–up according to procedure B gave **13a** (330 mg, 83%) as a pale yellow solid, m.p. 114 °C; (Found: 199.0633. Calcd for $C_{12}H_9O_2N$: 199.0633). (KBr/cm^{-1}) ν_{max} 1592, 1508, 1420, 1336, 1183, 1106, 1027, 848, 836, 750, 728; δ_H (270 MHz, $CDCl_3$) 7.42–7.54 (3H, m), 7.62–7.69 (2H, m), 7.74 (2H, d, ^3J = 8.9 Hz), 8.31 (2H, d, ^3J = 8.9 Hz); δ_C (67.8 MHz, $CDCl_3$) 124.1 (2C, CH), 127.4 (2C, CH), 127.8 (2C, CH), 128.9 (CH), 129.1 (2C, CH), 138.7 (C_{quat}), 147.0 (C_{quat}), 147.6 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 199 (M^+) (100), 169 (29), 152 (63).

4–Nitro–4′–pentoxybiphenyl (**13b**);[19]*general procedure C*: Colourless solid; m.p. 63 °C (Found: M+, 285.1366. $C_{17}H_{19}O_3N$ requires M+, 285.1365). ν_{max} (KBr/cm^{-1}) 3105, 2920, 2855, 1610, 1539, 1470, 1355, 1255, 1180, 835, 750; δ_H (270 MHz, $CDCl_3$) 0.95 (3H, t, ^3J = 6.5 Hz), 1.39–1.49 (4H, m), 1.79–1.85 (2H, m), 4.01 (2H, t, ^3J = 6.7 Hz), 7.00 (2H, d, ^3J = 8.9 Hz), 7.57 (2H, d, ^3J = 8.9 Hz), 7.69 (2H, d, ^3J = 8.9 Hz), 8.27 (2H, d, ^3J = 8.9 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.0 (CH_3), 22.4 (CH_2), 28.2 (CH_2), 28.9 (CH_2), 68.2 (OCH_2), 115.1 (2C, CH), 124.1 (2C, CH), 127.0 (2C, CH), 128.5 (2C, CH), 130.7 (C_{quat}), 146.4 (C_{quat}), 147.2 (C_{quat}), 160.0 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 285 (M^+), 215 ($M^+–C_5H_{10}$) (100).

4–Nitro–4′–heptoxybiphenyl (**13c**); *general procedure C*: Pale yellow oil; (Found: M+, 313.1677. $C_{19}H_{23}O_3N$ requires M+, 313.1678). ν_{max} (KBr/cm^{-1}) 3100, 2920, 2850, 1605, 1535, 1470, 1360, 1260, 1180, 840, 750; δ_H (270 MHz, $CDCl_3$) 0.90 (3H, t, ^3J = 6.5 Hz), 1.27–1.46 (8H, m), 1.79–1.82 (2H, m), 4.02 (2H, t, ^3J = 6.7 Hz), 7.00 (2H, d, ^3J = 8.9 Hz), 7.57 (2H, d, ^3J = 8.9 Hz), 7.69 (2H, d, ^3J = 8.9 Hz), 8.27 (2H, d, ^3J = 8.9 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.1 (CH_3), 22.6 (CH_2), 26.0 (CH_2), 28.2 (CH_2), 29.0 (CH_2), 31.8 (CH_2), 68.2 (OCH_2), 115.1 (2C, CH), 124.1 (2C, CH), 127.0 (2C, CH), 128.5 (2C, CH), 130.7 (C_{quat}), 146.4 (C_{quat}), 147.2 (C_{quat}), 160.0 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 313 (M^+) (43), 283 (12), 215 (100), 185 (22).

4–Nitro–4′–nonyloxybiphenyl (**13d**); *general procedure C*: Pale yellow solid; m.p. 60 °C; (Found: M+, 341.1987. $C_{21}H_{27}O_3N$ requires M+, 341.1991). ν_{max} (KBr/cm^{-1}) 3100, 2920, 2850, 1610, 1540, 1470, 1357, 1255, 1180, 836, 747; δ_H (270 MHz, $CDCl_3$) 0.89 (3H, t, ^3J = 7.0 Hz), 1.28–1.48 (12H, m), 1.76–1.84 (2H, m), 4.01 (2H, t, ^3J = 6.7 Hz), 7.00 (2H, d, ^3J = 8.9 Hz), 7.57 (2H, d, ^3J = 8.9 Hz), 7.68 (2H, d, ^3J = 8.9 Hz), 8.27 (2H, d, ^3J = 8.9 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.1 (CH_3), 22.7 (CH_2), 26.0 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 31.9 (CH_2), 68.2 (OCH_2), 115.1 (2C, CH), 124.1 (2C, CH), 127.0 (2C, CH), 128.5 (2C, CH), 130.8 (C_{quat}), 146.4 (C_{quat}), 147.3 (C_{quat}), 160.0 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 341 (M^+) (68), 215 (100). Calcd for $C_{21}H_{27}NO_3$: C, 73.87; H, 7.97; N, 4.10. Found: C, 73.89; H, 7.95, N, 4.09%.

4–Nitro–4′–vinylbiphenyl (**13e**); *general procedure* C: Colourless solid, m.p. 123 °C; (Found: 225.0789. $C_{14}H_{11}O_2N$ requires M+, 225.0790). (KBr/cm^{-1}) ν_{max} 1629, 1512, 1341, 1106, 1031, 930, 855; δ_H (270 MHz, $CDCl_3$) 5.35 (1H, d, *J* = 10.8 Hz), 5.85 (1H, d, *J* = 17.5 Hz), 6.77 (1H, dd, *J* = 17.5 Hz, *J* = 10.8 Hz), 7.54 (2H, d, ^3J = 8.1 Hz), 7.61 (2H, d, ^3J = 8.1 Hz), 7.75 (2H, d, ^3J = 8.6 Hz), 8.30 (2H, d, ^3J = 8.6 Hz); δ_C (67.8 MHz, $CDCl_3$) 115.1, 124.1 (2C,), 126.9 (2C), 127.5 (4C), 135.9 (C_{quat}), 137.9 (C_{quat}), 138.2 (C_{quat}), 147.1 (C_{quat}); MS (EI, 70 eV) *m/z* (%) 225 (M^+) (100), 195 (18), 178 (39), 152 (21). Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22. Found: C, 74.59; H, 5.00, N, 6.29%.

1–Nitro–4–(thien–2–yl)benzene (**13f**); *general procedure C*: Solid; m.p. 197 °C; (Found: M+, 205.0198. $C_{10}H_7O_2NS$ requires M+, 205.0198). δ_H (270 MHz, $CDCl_3$) 7.16 (1H, dd, *J* = 5.1 Hz, *J* = 3.8 Hz), 7.44 (1H, dd, *J* = 5.1 Hz, *J* = 1.1 Hz), 7.48 (1H, dd, *J* = 3.8 Hz, *J* = 1.1 Hz), 7.74 (2H, d, ^3J = 8.9 Hz), 8.24 (2H, d, ^3J = 8.9 Hz); δ_C (67.8 MHz, $CDCl_3$) 124.4 (2C, CH), 125.7 (CH), 126.0 (2C, CH), 127.7 (CH), 128.7 (CH), 140.5 (C_{quat}), 141.6 (C_{quat}), 146.5 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 205 (M^+) (100), 175 (39), 115 (58). Calcd for $C_{10}H_7NO_2S$: C, 58.52; H, 3.44; N, 6.82. Found: C, 58.53; H, 3.55, N, 6.88%.

2,4–Dinitrobiphenyl (**14a**); *general procedure C*: Pale yellow solid; m.p. 110 °C; (Found: M+, 244.0480. $C_{12}H_8O_4N_2$ requires M+, 244.0484). ν_{max} (KBr/cm^{-1}) 3100, 2920, 2850, 1605, 1540, 1470, 1360. δ_H (270 MHz, $CDCl_3$) 7.33–7.36 (2H, m), 7.47–7.52 (3H, m), 7.69 (1H, d, ^3J = 8.4 Hz), 8.48 (1H, dd, ^3J = 8.4 Hz, ^4J = 2.4 Hz), 8.85 (1H, d, ^4J = 2.4 Hz); δ_C (67.8 MHz, $CDCl_3$) 119.7 (CH), 126.5 (CH), 127.7 (2C, CH), 129.1 (2C, CH), 129.6 (CH), 130.7 (C_{quat}), 133.2 (CH), 135.2 (C_{quat}), 142.3 (C_{quat}), 146.8 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 244 (M^+) (45), 227 (38), 216 (100), 168 (36), 139 (81).

2,4–Dinitro–4′–heptoxybiphenyl (**14b**); *general procedure C:* Colourless solid, m.p. 45 °C; ν_{max} (KBr/cm^{-1}) 3102, 2922, 2853, 1606, 1537, 1472, 1357, 1257, 1180, 836, 747; δ_H (270 MHz, $CDCl_3$) 0.88 (3H, t, ^3J = 5.8 Hz, CH_3), 1.27–1.44 (8H, m), 1.76–1.84 (2H, m), 4.00 (2H, t, ^3J = 6.5 Hz, OCH_2), 6.98 (2H, d, ^3J = 8.6 Hz), 7.28 (2H, d, ^3J = 8.6 Hz), 7.66 (1H, d, ^3J = 8.4 Hz), 8.43 (1H, dd, ^3J = 8.4 Hz, ^4J = 2.2 Hz), 8.65 (1H, d, ^4J = 2.2 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.1 (CH_3), 22.6 (CH_2), 26.0 (CH_2), 29.0 (CH_2), 29.1 (CH_2), 31.7 (CH_2), 68.2 (OCH_2), 115.1 (2C, CH), 119.7 (CH), 126.3 (CH), 126.8 (C_{quat}), 129.1 (2C, CH), 132.9 (CH), 141.9 (C_{quat}), 146.4 (C_{quat}), 149.0 (C_{quat}), 160.4 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 358 (M^+) (64), 328 (16), 260 (100).

2,4–Dinitro–4′–nonyloxybiphenyl (**14c**); *general procedure C*: Pale yellow solid; m.p. 39 °C; (Found: M+, 386.1844. $C_{21}H_{26}O_5N_2$ requires M+, 386.1842). ν_{max} (KBr/cm^{-1}) 3099, 2920, 1606, 1539, 1471, 1358, 1255, 1185, 840, 749; δ_H (270 MHz, $CDCl_3$) 0.88 (3H, t, ^3J = 5.8 Hz, CH_3), 1.30–1.47 (12H, m), 1.78–1.84 (2H, m), 4.00 (2H, t, ^3J = 6.5 Hz, OCH_2), 6.98 (2H, d, ^3J = 8.6 Hz), 7.28 (2H, d, ^3J = 8.6 Hz), 7.66 (1H, d, ^3J = 8.6 Hz), 8.43 (1H, dd, ^3J = 8.6 Hz, ^4J = 2.2 Hz), 8.65 (1H, d, ^4J = 2.2 Hz); δ_C (67.8 MHz, $CDCl_3$) 14.1 (CH_3), 22.7 (CH_2), 26.0 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 31.9 (CH_2), 68.2 (OCH_2), 115.2 (2C, CH), 119.8 (CH), 126.4 (CH), 126.8 (C_{quat}), 129.1 (2C, CH), 132.9 (CH), 141.9 (C_{quat}), 146.3 (C_{quat}), 148.9 (C_{quat}), 160.4 (C_{quat}); MS (EI, 70 eV) *m/z* (%) = 386 (M^+) (68), 356 (19), 260 (100).

2,4–Dinitro–4′–octadecanyloxybiphenyl (**14d**); *general procedure C*: At 80 °C for 15h. Final work–up consisted of flash chromatography on silica gel (ethyl acetate/PE 80–100); yellow solid; m.p. 75 °C; (Found: M+, 512.3254. $C_{30}H_{44}O_5N_2$ requires M+, 512.3250). IR (KBr/cm^{-1}) 3101, 2916, 2851, 1604, 1575, 1521, 1471; δ_H ($CDCl_3$, 200 MHz) 0.80–2.00 (32H, m), 4.03 (2H, t, *J* 5.8 Hz), 7.01 (2H, m, *J* 8.0 Hz), 7.29 (2H, m, *J* = 8.0 Hz), 7.68 (1H, *J* = 8.2 Hz, 1H), 8.45 (1H, d, *J* = 8.6 Hz), 8.67 (1H, m); δ_C ($CDCl_3$, 50 MHz) 14.4, 22.9, 26.2, 29.3–29.9 (overlapping peaks), 32.1, 68.2, 115.0, 119.6, 126.1, 126.6, 128.9, 132.7, 141.6, 146.1, 148.7, 160.1; MS (FAB, 3–nitrobenzyl alcohol) *m/z* (%) = 512 (M^+) (13).

4–Docosanyloxy–2,′4′–dinitrobiphenyl (**14e**); *general procedure C*: Analogous to the preparation of **14d**: yellow solid; m.p. 82 °C; (Found: M+, 568.3871. $C_{34}H_{52}O_5N_2$ requires M+, 568.3876). IR (KBr/cm^{-1}) 3101, 2950, 2850, 1604, 1575, 1525, 1471; δ_H ($CDCl_3$, 200 MHz) 0.85–0.91 (6H, m), 1.15–1.57 (38H, m), 1.72–1.88 (2H, m), 3.98 (2H, t, *J* = 6.6 Hz), 6.96 (2H, m, *J* = 8.6, 2.0 Hz), 7.25 (2H, m, *J* = 8.6, 2.0 Hz), 7.63 (1H, m, *J* = 8.6, 1.4 Hz), 8.68 (1H, m, *J* = 8.2, 2.4 Hz, 1H), 8.62 (1H, m, *J* = 2.4Hz); δ_C ($CDCl_3$, 50 MHz) 14.3, 22.9, 26.2, 29.3–29.9 (overlapping peaks), 32.1, 68.2, 115.0, 119.6, 126.1, 126.6, 128.9, 132.7, 141.7, 146.0, 148.7, 160.1; MS (FAB, 3–nitrobenzyl alcohol) *m/z* (%) = 568 (M^+) (8.8), 481 (6.2), 437 (12), 393 (20), 349 (25), 305 (26).

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