Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information

A Chemical Method for the Convenient Surface Functionalisation of Polymers

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Synthesis and Characterisation Details

General Method A for the formation of benzophenone hydrazones

The required benzophenone was refluxed in ethanol and hydrazine hydrate overnight. The solvent was removed *in vacuo* and the residue dissolved in DCM, washed with water, dried and concentrated under vacuum. The hydrazones, which were obtained as inseparable mixtures of the *syn* - and *anti*- isomers, were then used without further purification.

General Method B for the formation of diphenyl diazomethanes

The required benzophenone hydrazone was dissolved in Et_2O and stirred vigorously with yellow mercuric oxide (1.2 eq), sodium sulphate and saturated KOH in ethanol. Stirring was continued overnight and the mixture was filtered through Celite®. Excess solvent was removed under vacuum and the product was used without further purification.

4-Bromomethylbenzophenone 1b

A stirred mixture of 4-methylbenzophenone (15.02 g, 76.6 mmol) and *N*-bromosuccinimide (14.2 g, 79.8 mmol) in $CHCl_3$ (100 cm^3) was heated under gentle reflux for 18h with a 100W bulb shining 2 cm from the flask. The reaction mixture was washed with water, dried ($MgSO_4$) and solvent was removed *in vacuo*. The resulting solid was then washed with Et_2O to remove any starting material to leave the product **1b** as a white solid (15.07 g, 71.5%), **mp** 110-112˚C(lit.[1]110-111˚ C); δ_H (200 MHz; $CDCl_3$) 4.55 (2 H, s, C<u>H</u>$_2$Br), 7.46-7.70 (5 H, m, Ar<u>H</u>), 7.80-7.90 (4 H, m, Ar<u>H</u> *o*- to C=O); **m/z** 277 ([M^{81}Br + H]$^+$, 25%) and 275 ([M^{79}Br + H]$^+$, 25%), 197 (100%).

4-([3,4-Dimethoxyphenyl]oxymethyl)benzophenone 1c

To 3,4-dimethoxyphenol (1.69 g, 11 mmol) in THF was added NaH (60% dispersion in oil, 1.2 eq., 0.53 g) and stirring continued for 1 hour. 4-Bromomethyl benzophenone **1b** (3.01 g, 11 mmol) was then added to the solution and stirring continued for a further 24 hours. The solution was concentrated *in vacuo* diluted with DCM, washed with citric acid (10% aq.), NaOH (1N) dried and solvent removed under vacuum. The residue was then purified by column chromatography, eluting with petrol (bp 40-

60ºC):EtOAc 9:1 yielding the product **1c** as a white solid (2.58 g, 68%) (Found: C, 75.73; H, 5.96. $C_{22}H_{20}O_4$ requires C, 75.84; H, 5.79%), **mp** 74-75˚C; $\mathbf{R_f}$ = 0.23 (Petrol:EtOAc 4:1); δ_H (250 MHz, $CDCl_3$) 3.82 (3 H, s, $OC\underline{H}_3$), 3.86 (3 H, s, $OC\underline{H}_3$), 5.10 (2 H, s, $C\underline{H}_2$), 6.47 (1 H, dd, *J* 9, 1, Ar<u>H</u> *p*- to OMe), 6.65 (1 H, d, *J* 1, Ar<u>H</u> *o*- to 2 OR), 6.80 (1 H, d, *J* 9, Ar<u>H</u> *m*- to 2 OR), 7.47-7.75 (5 H, m, Ar<u>H</u>), 7.80-7.91 (4 H, m, Ar<u>H</u> *o*- to C=O); δ_C (50.3 MHz, $CDCl_3$) 55.8 ($O\underline{C}H_3$), 56.4 ($O\underline{C}H_3$), 69.9 ($\underline{C}H_2O$), 101.2 and 104.0 (Ar<u>C</u>H *o*- to OCH_2Ar), 111.7 (Ar<u>C</u>H *m*- to OCH_2Ar), 127.0, 128.3, 130.0 and 130.3 (Ar<u>C</u>H *o*- and *m*- to C=O), 132.5 (Ar<u>C</u>H *p*- to C=O), 137.0 and 137.5 (4˚ Ar<u>C</u>C=O), 141.9 (4˚ Ar<u>C</u>CH_2O), 143.8 (4˚ Ar<u>C</u>OCH_2), 149.9 (4˚ Ar<u>C</u>OMe *p*- to OCH_2Ar), 153.0 (4˚ Ar<u>C</u>OMe *m*- to OCH_2Ar), 196.3 (<u>C</u>=O); **m/z** ($APCI^+$) 349 ($[M+H]^+$, 100%).

4-([3-*N,N*-Diethylaminophenyl]oxymethyl)benzophenone 1d

3-*N,N*-Diethylaminophenol (3.03 g, 18.4 mmol, 1.2 eq) in THF (20 cm^3) was treated with NaH (60% dispersion in oil, 524 mg, 13.1 mmol, 1.4 eq) and stirred at 20˚C for 1 hour. 4-Bromomethylbenzophenone **1b** (4.21 g, 15.3 mmol) was then added and stirring continued for 72 hours. Excess solvent was removed *in vacuo* and the residue diluted with DCM, washed with water and $NaHCO_3$ solution (sat.), dried ($MgSO_4$) and solvent removed under vacuum. The resulting oil was purified by flash chromatography, eluting with petrol (bp 40-60˚C):EtOAc (9:1), to give the desired product **1d** as a yellow oil (4.29 g, 65%), $\mathbf{R_f}$ = 0.51 (4:1, petrol:EtOAc) (Found: C, 79.99; H, 7.13; N, 5.23. $C_{24}H_{25}NO_2$ requires C, 80.19; H, 7.01; N, 3.90%); ν_{max} (film)/cm^{-1} 1657 (s), 1610 (s); δ_H (500 MHz; $CDCl_3$) 1.17 (6 H, t, *J* 7, $C\underline{H}_3$), 3.35 (4 H, q, *J* 7, $C\underline{H}_2CH_3$), 5.16 (2 H, s, Ar$C\underline{H}_2O$), 6.27-6.40 (3 H, m, Ar<u>H</u> *o*- and *p*- to NEt_2), 7.15 (1 H, dd, *J* 7, 7, Ar<u>H</u> *m*- to NEt_2), 7.45-7.66 (5 H, m, Ar<u>H</u>), 7.80-7.89 (4 H, m, Ar<u>H</u> *o*- to C=O); δ_C (125.8 MHz; $CDCl_3$) 12.6 ($\underline{C}H_3$), 44.4 ($N\underline{C}H_2CH_3$), 69.2 (Ar<u>C</u>H_2O), 99.1, 100.8 and 105.4 (Ar<u>C</u>H *o*- and *p*- to NEt_2), 127.0, 128.3, 130.0 and 130.4 (Ar<u>C</u>H), 132.4 (Ar<u>C</u>H *p*- to C=O), 136.9 and 137.6 (4˚ Ar<u>C</u>C=O), 142.3 (4˚ Ar<u>C</u>CH_2O), 149.2 (4˚ Ar<u>C</u>NEt_2), 159.9 (4˚ Ar<u>C</u>OCH_2), 196.4 (<u>C</u>=O); **m/z** ($APCI^+$) 360 ($[M + H]^+$, 100%).

4-([3,4-Dimethoxyphenyl]oxymethyl)benzophenone hydrazone

The benzophenone **1c** (1.52 g, 4.36 mmol) was reacted with hydrazine hydrate according to General Method **A** yielding the hydrazone as a yellow oil (1.50 g, 95%), δ_H (200 MHz, $CDCl_3$) 3.76, 3.77, 3.79 and 3.81 (6 H, 4 x s, $OC\underline{H}_3$), 4.91 and 5.03 (2 H, 2 x s, $C\underline{H}_2$), 5.47 (2 H, br s, $N\underline{H}_2$), 6.40 and 6.46 (1 H, 2 x dd, *J* 9, 1, Ar<u>H</u> *p*- to OMe), 6.55 and 6.60 (1 H, 2 x d, *J* 1, Ar<u>H</u> *o*- to 2 OR), 6.68 and 6.73 (1 H, 2 x d, *J* 9, Ar<u>H</u> *m*- to 2 OR), 7.20-7.60 (9 H, m, Ar<u>H</u>); δ_C (50.3 MHz, $CDCl_3$) 55.7 ($O\underline{C}H_3$), 56.3 ($O\underline{C}H_3$), 70.0 ($\underline{C}H_2O$), 101.2 and 104.0 (Ar<u>C</u>H *o*- to OCH_2Ar), 111.8 (Ar<u>C</u>H *m*- to OCH_2Ar), 126.4, 126.5, 127.3, 128.0, 128.1, 128.5, 128.8, 128.9, 129.1 and 129.4 (Ar<u>C</u>H *o*- and *m*- to C=N), 132.5 and 132.9 (Ar<u>C</u>H *p*- to C=N), 136.9, 137.9, 138.2 and 138.4 (4˚ Ar<u>C</u>C=N), 143.6 and 143.8 (4˚ Ar<u>C</u>CH_2O), 148.1 (4˚ Ar<u>C</u>OCH_2), 149.8 and 149.9 (4˚ Ar<u>C</u>OMe *p*- to OCH_2Ar), 153.2 (Ar<u>C</u>OMe *m*- to OCH_2Ar); **m/z** ($APCI^+$) 363 ($[M+H]^+$, 100%).

4-([3,4-Dimethoxyphenyl]oxymethyl)phenyl phenyl diazomethane 2b

The above benzophenone hydrazone (1.50 g, 4.14 mmol) was reacted with mercuric oxide and sodium sulphate according to General Method **B** yielding the diazomethane as a purple oil (1.35 g, 91%) (Found: C, 73.83; H, 5.33; N, 7.31. $C_{22}H_{20}N_2O_3$ requires C, 73.32; H, 5.59; N, 7.77%), ν_{max} (film)/cm^{-1} 2038 (s), 1595 (m), 1511 (s); δ_H (500 MHz, $CDCl_3$) 3.85 (3 H, s, OC$\underline{H}_3$), 3.87 (3 H, s, OC$\underline{H}_3$), 5.02 (2 H, s, C$\underline{H}_2$), 6.49 (1 H, dd, *J* 9, 1, Ar$\underline{H}$ *p*- to OMe), 6.62 (1 H, d, *J* 1, Ar$\underline{H}$ *o*- to 2 OR), 6.80 (1 H, d, *J* 9, Ar$\underline{H}$ *m*- to 2 OR), 7.16-7.49 (9 H, m, Ar$\underline{H}$); δ_C (125.8 MHz, $CDCl_3$) 55.8 (O$\underline{C}H_3$), 56.4 (O$\underline{C}H_3$), 70.2 ($\underline{C}H_2O$), 101.2 and 104.0 (Ar$\underline{C}$H *o*- to OCH_2Ar), 111.6 (Ar$\underline{C}$H *m*- to OCH_2Ar), 125.1, 125.2, 128.5 and 129.1 (Ar$\underline{C}$H *o*- and *m*- to C=N), 125.7 (Ar$\underline{C}$H *p*- to C=N), 129.3 and 129.4 (4˚ Ar$\underline{C}$C=N), 134.4 (4˚ Ar$\underline{C}CH_2O$), 143.6 (4˚ Ar$\underline{C}OCH_2$), 149.8 (4˚ Ar$\underline{C}$OMe *p*- to OCH_2Ar), 153.3 (4˚ Ar$\underline{C}$OMe *m*- to OCH_2Ar).

4-([3-*N*,*N*-Diethylaminophenyl]oxymethyl)benzophenone hydrazone

The benzophenone **1d** (1.76 g, 1.95 mmol) was reacted with hydrazine hydrate according to General Method **A** yielding the hydrazone as a colourless oil (1.31g, 72%), (Found: C, 76.26; H, 7.30; N, 12.47. $C_{24}H_{27}N_3O$ requires C, 77.18; H, 7.29; N, 11.25%); ν_{max} (film)/cm^{-1} 1605 (m); δ_H (200 MHz; $CDCl_3$) 1.24-1.34 (6 H, m, C$\underline{H}_3$), 3.39-3.54 (4 H, m, NC$\underline{H}_2CH_3$), 5.16 and 5.24(2 H, 2 x s, ArC$\underline{H}_2$O), 5.61 (2 H, br s, NN$\underline{H}_2$), 6.45-6.52 (3 H, m, Ar$\underline{H}$ *o*- and *p*- to NEt_2), 7.25-7.77 (10 H, m, Ar$\underline{H}$); δ_C (50.3 MHz; $CDCl_3$) 12.7 ($\underline{C}H_3$), 44.5 (N$\underline{C}H_2CH_3$), 69.6 and 69.7 (Ar$\underline{C}H_2O$), 99.4 and 99.5, 101.1 and 101.2, 105.6 and 105.7 (Ar$\underline{C}$H *o*- and *p*- to NEt_2), 126.8, 127.0, 127.7, 128.1, 128.4, 128.5, 128.9, 129.2, 129.5, 129.8, 130.3, 130.4, 132.8, 133.3, 137.7, 138.5, 138.7 and 138.9 (Ar$\underline{C}$H, 4˚ Ar$\underline{C}$C=N and 4˚ Ar$\underline{C}CH_2O$), 148.8 ($\underline{C}$=NNH_2), 149.5 (4˚ Ar$\underline{C}NEt_2$), 160.6 (4˚ Ar$\underline{C}OCH_2$); **m/z** (APCI$^+$) 374 ([M + H]$^+$, 15%), 209 (100), 195 (50), 178 (75).

4-([3-*N*,*N*-Diethylaminophenyl]oxymethyl)phenyl phenyl diazomethane 2c

The above benzophenone hydrazone (1.30 g, 3.49 mmol) was stirred vigorously with yellow mercuric oxide (1.40 g, 6.5 mmol), anhydrous sodium sulphate (2.00 g, 14.1 mmol) in diethyl ether (33 cm^3)and saturated KOH in ethanol (1 cm^3) for 18 hours. The solution was filtered through Celite® and solvent removed *in vacuo* yielding the product **2c** as a red oil (1.22 g, 94%), ν_{max} (film)/cm^{-1} 2037 (s), 1612 (m); δ_H (200 MHz; $CDCl_3$) 1.27 (6 H, m, C$\underline{H}_3$), 3.44 (4 H, m, NC$\underline{H}_2CH_3$), 5.15 (2 H, s, ArC$\underline{H}_2$O), 6.42-6.50 (3 H, m Ar$\underline{H}$ *o*- and *p*- to NEt_2), 7.21-7.55 (10 H, m Ar$\underline{H}$); δ_C (50.3 MHz; $CDCl_3$) 12.8 ($\underline{C}H_3$), 44.5 (N$\underline{C}H_2CH_3$), 69.6 (Ar$\underline{C}H_2O$), 99.3, 101.0 and 105.5 (Ar$\underline{C}$H *o*- and *p*- to NEt_2), 128.2, 128.6, 128.7, 129.2 and 129.3 (Ar$\underline{C}$H *o*- and *m*- to C=N and Ar$\underline{C}$H *m*- to NEt_2), 130.0 (Ar$\underline{C}$H *p*- to C=N), 132.5 and 133.0 (4˚ Ar$\underline{C}$C=N), 135.0 (4˚ Ar$\underline{C}CH_2O$), 149.2 (4˚ Ar$\underline{C}NEt_2$), 160.3 (4˚ Ar$\underline{C}OCH_2$).

4-([*N*-Ethyl-*N*-phenyl-2-aminoethyl]oxymethyl) benzophenone 1e

2-(*N*-Ethylanilino)ethanol (3.03 g, 18.4 mmol, 1.2 eq) in THF (20 cm^3) was treated with NaH (60% dispersion in oil, 524 mg, 13.1 mmol, 1.4 eq) and stirred at 20˚C for 1 hour. 4-Bromomethylbenzophenone **1b** (4.21 g, 15.3 mmol) was then added and stirring continued for 72 hours. Excess solvent was removed *in vacuo* and the residue diluted with DCM, washed with water and $NaHCO_3$ solution (sat.), dried ($MgSO_4$) and solvent removed under vacuum. The resulting oil was

purified by flash chromatography, eluting with petroleum (bp 40-60˚C):EtOAc (9:1), to give the desired product **1e** as a yellow oil (4.36 g, 80%), $\mathbf{R_f}$ = 0.54 (4:1, petrol:EtOAc) (Found: C, 78.34; H, 6.86; N, 5.29. $C_{24}H_{25}NO_2$ requires C, 80.19; H, 7.01; N, 3.90%); $\boldsymbol{\nu_{max}}$ (film)/cm^{-1} 1658 (s), 1598 (s), 1506 (s); $\boldsymbol{\delta_H}$ (200 MHz; $CDCl_3$) 1.22 (3 H, t, *J* 7, C$\underline{H}_3$), 3.49 (2 H, q, *J* 7, C$\underline{H}_2$CH$_3$), 3.58-3.79 (4 H, m, OC$\underline{H}_2$C$\underline{H}_2$N), 4.66 (2 H, s, ArC$\underline{H}_2$O), 6.69-6.79 (3 H, m, Ar$\underline{H}$ *o*- and *p*- to NR_2), 7.28 (2 H, dd, *J* 7, 7, Ar$\underline{H}$ *m*- to NR_2), 7.46-7.68 (5 H, m, Ar$\underline{H}$), 7.80-7.88 (4 H, m, Ar$\underline{H}$ *o*- to C=O); $\boldsymbol{\delta_C}$ (50.3 MHz; $CDCl_3$) 12.2 (C$\underline{H}_3$), 45.5 (NC$\underline{H}_2$CH$_3$), 50.1 (NC$\underline{H}_2$CH$_2$O), 68.5 (NCH$_2$C$\underline{H}_2$O), 72.2 (ArC$\underline{H}_2$O), 111.8 (ArC$\underline{H}$ *o*- to NR_2), 115.8 (ArC$\underline{H}$ *p*- to NR_2), 127.0, 128.3, 129.3, 130.0 and 130.3 (ArC$\underline{H}$ *o*- and *m*- to C=O and ArC$\underline{H}$ *m*- to NR_2), 132.4 (ArC$\underline{H}$ *p*- to C=O), 136.8 and 137.7 (4˚ ArC$\underline{C}$=O), 143.2 (4˚ ArC$\underline{C}$H$_2$O), 147.7 (4˚ ArC$\underline{N}R_2$), 196.4 (C$\underline{=}$O); **m/z** (APCI$^+$) 360 ([M + H]$^+$, 30%); HRMS $C_{24}H_{26}O_2N$ requires 360.1963; found 360.1963.

4-([*N*-Ethyl-*N*-phenyl-2-aminoethyl]oxymethyl) benzophenone hydrazone

The benzophenone **1e** (701 mg, 1.95 mmol) was reacted with hydrazine hydrate according to General Method **A** yielding the hydrazone as a colourless oil (710 mg, 97%), $\boldsymbol{\nu_{max}}$ (film)/cm^{-1} 1598 (s), 1506 (s); $\boldsymbol{\delta_H}$ (500 MHz; $CDCl_3$) 1.27 and 1.31 (3 H, 2 x t, *J* 7, C$\underline{H}_3$), 3.52 and 3.57 (2 H, 2 x q, *J* 7, C$\underline{H}_2$CH$_3$), 3.60-3.87 (4 H, m, NC$\underline{H}_2$C$\underline{H}_2$O), 4.63 and 4.71 (2 H, 2 x s, ArC$\underline{H}_2$O), 5.57 (2 H, br s, NN$\underline{H}_2$), 6.76-6.87 (3 H, m, Ar$\underline{H}$ *o*- and *p*- to NR_2), 7.30-7.42 (7 H, m, Ar$\underline{H}$), 7.53-7.64 (4 H, m, Ar$\underline{H}$ *o*- to C=N); $\boldsymbol{\delta_C}$ (125.8 MHz; $CDCl_3$) 12.0 (C$\underline{H}_3$), 45.1 and 45.2 (NC$\underline{H}_2$CH$_3$), 49.8 (NC$\underline{H}_2$CH$_2$O), 67.8 and 68.1 (OC$\underline{H}_2$CH$_2$N), 72.6 and 72.7 (ArC$\underline{H}_2$O), 111.5 and 111.6 (ArC$\underline{H}$ *o*- to NR_2), 115.5 and 115.6 (ArC$\underline{H}$ *p*- to NR_2), 126.2, 127.1, 127.7, 127.8, 128.1, 128.5, 128.6, 128.9, 129.0 and 129.1 (ArC$\underline{H}$), 131.9 and 132.8 (4˚ ArC$\underline{C}$H$_2$O), 137.7, 137.8, 138.3 and 138.9 (4˚ ArC$\underline{C}$=N), 147.5 (4˚ ArC$\underline{N}R_2$), 148.1 (C$\underline{=}$NNH$_2$); **m/z** (APCI$^+$) 374 ([M + H]$^+$, 5%), 357 (5), 209 (100).

4-([*N*-Ethyl-*N*-phenyl-2-aminoethyl]oxymethyl)phenyl phenyl diazomethane 2d

The above benzophenone hydrazone (701 mg, 1.88 mmol) was reacted with mercuric oxide and sodium sulphate according to General Method **B** yielding the diazomethane **2d** as a purple oil (690 mg, 99%) (Found: C, 78.06; H, 6.89; N, 12.36. $C_{24}H_{25}N_3O$ requires C, 77.60; H, 6.78; N, 11.31%); $\boldsymbol{\nu_{max}}$ (film)/cm^{-1} 2037 (s), 1599 (m); $\boldsymbol{\delta_H}$ (500 MHz; $CDCl_3$) 1.26-1.32 (3 H, m, C$\underline{H}_3$), 3.50-3.80 (6 H, m, NC$\underline{H}_2$CH$_3$ and NC$\underline{H}_2$C$\underline{H}_2$O), 4.65 (2 H, s, ArC$\underline{H}_2$O), 6.78-6.86 (3 H, m Ar$\underline{H}$ *o*- and *p*- to NR_2), 7.28-7.65 (11 H, m Ar$\underline{H}$); $\boldsymbol{\delta_C}$ (125.8 MHz; $CDCl_3$) 12.1 (C$\underline{H}_3$), 45.3 (NC$\underline{H}_2$CH$_3$), 50.0 (NC$\underline{H}_2$CH$_2$O), 67.9 (OC$\underline{H}_2$CH$_2$N), 72.8 (ArC$\underline{H}_2$O), 111.7 (ArC$\underline{H}$ *o*- to NR_2), 115.6 (ArC$\underline{H}$ *p*- to NR_2), 125.0, 125.5, 126.3, 128.3, 128.4, 128.7, 129.0, 129.1 and 129.2 (4˚ ArC and ArC$\underline{H}$), 135.7 (4˚ ArC$\underline{C}$H$_2$O), 147.7 (4˚ ArC$\underline{N}R_2$); **m/z** (APCI$^+$) 344 ([M - N_2]$^+$, 20%), 209 (100).

2-Sulphonyl-4-nitrobenzene diazonium chloride (0.1M aq.) 5

To a suspension of 2-amino-5-nitrobenzene sulphonic acid, sodium salt (2.40 g, 10 mmol) in iced water (50 cm^3) and HCl (10M, 5 cm^3), $NaNO_2$ (1 M, 11 cm^3) was slowly added and stirred vigorously for 5 minutes whilst maintaining the temperature at 0˚C. The solution was made to pH 4 with sodium acetate

and diluted to 100 cm^3, the diazonium ion was then used without further purification at 0˚C within one hour of formation.

Fast Blue RR salt **6** and Disperse Yellow **7** were obtained from Sigma-Aldrich.

Commercial Suppliers of Polymers

Mercerised woven cotton was supplied by ICI Specialities (Blackley, Manchester), Nylon membrane (Hybond M, ex Amersham International, Cat. No. RPN203N), polystyrene (Aldrich, Amberlite XAD-4 non-ionic polymeric adsorbent beads), and silica (Sorbsil™ $C_{60}H$ (40-60 μm) silica gel).

Functionalisation of Polymers

The solvent ether, and solutions of the appropriate benzophenone **1e** in ether, or diaryldiazomethane **2d** in ether were applied to three portions of the appropriate polymer. The solvent was then allowed to evaporate and a small sample of the polymer was retained (Samples # 1, 2 and 3 in Tables 2-8 below). The remainder of the polymer was then heated, in foil or conical flasks, with a heat gun for the time required to decolourise the polymer which had been treated with the diazocompound. Another sample from each batch of treated polymer was kept aside at this point (Samples # 4, 5 and 6 in Tables 2-8 below). The remaining polymer was then moistened with ethanol (2 cm^3) and a suspension of the diazonium salt (50 cm^3, 0.1 M) prepared as described above was added and the mixture stirred overnight. The polymer was then removed, washed with water, hot water and soap, acetone, HCl (1N), NaOH (1N), water and acetone until no further colour leached out of the polymer into the liquid. The polymer was allowed to dry to obtain the final sample (Samples # 6, 7 and 8 in Tables 2-8 below). The sample numbering is given in Table 1, and these samples were scanned using a Hewlett-Packard ScanJet 6100C/T with HP DeskScanII software.

Table 1 : Control experiments – Sample numbers

Sample	Polymer Treatment		
	Ether	Benzophenone **1e** in ether	Diphenyldiazomethane **2d** in ether
Initial Compound adsorption	1	4	7
After Heating	2	5	8
After Diazotization with **5** and washing	3	6	9

The results of this experiment for the dyeing of cotton are given in Tables 2 and 3, nylon in Tables 4 and 5, polystyrene in Tables 6 and 7, CPG in Table 8 and silica in Table 9.

Table 2 – Control experiments for the dyeing of cotton with diazonium salt **5**

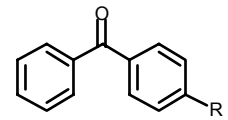
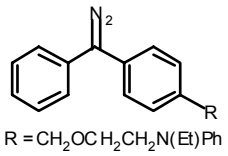
Cotton	After Application	After Heating	After Diazonium coupling with **5** and Washing
	1	2	3
No Compound			
Benzophenone  **1e**	4	5	6
			
Diazomethane  **2d**	7	8	9
			

Table 3 - Soxhlet extraction of cotton dyed with diazo compound **2d** and diazonium salt **5**

Before Soxhlet extraction	After Soxhlet extraction
	

Table 4 – Control experiments for the dyeing of nylon with diazonium salt **5**

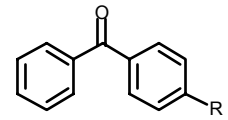
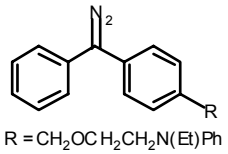
Nylon	After Application	After Heating	After Diazonium coupling with **5** and Washing
	1	2	3
No Compound			
Benzophenone  **1e**	4	5	6
			
Diazomethane  **2d**	7	8	9
			

Table 5 - Soxhlet extraction of nylon dyed with diazo compound **2d** and diazonium salt **5**

Before Soxhlet extraction	After Soxhlet extraction
9	10
	

Supplementary Material (ESI) for Chemical Communications

Table 6 – Control experiments for the dyeing of polystyrene with diazo compound **2d** and diazonium salt **5**

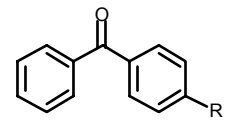
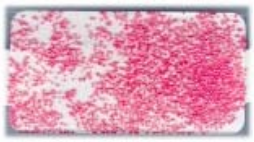
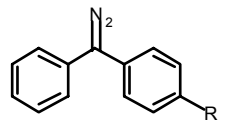
Polystyrene	After Application	After Heating	After Diazonium coupling with **5** and Washing
	1	2	3
No Compound			
Benzophenone  R =$CH_2OCH_2CH_2N(Et)Ph$ **1b**	4	5	6
			
Diazomethane  R = $CH_2OCH_2CH_2N(Et)Ph$ **2d**	7	8	9
			

Table 7 - Soxhlet extraction of polystyrene dyed with diazo compound **2d** and diazonium salt **5**

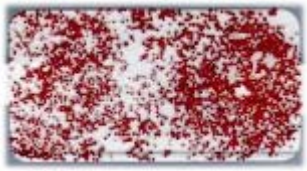
Before Soxhlet extraction	After Soxhlet extraction
9	10
	

Table 8 – Control experiments for the dyeing of CPG with diazo compound **2d** and diazonium salt **5**

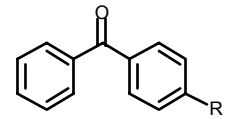
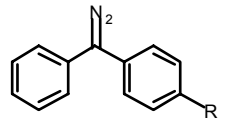
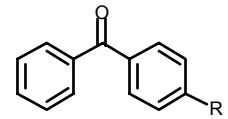
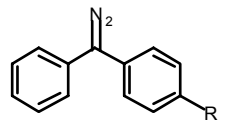
CPG	After Application	After Heating	After Diazonium coupling with **5** and Washing
No Compound	1 	2 	3 
Benzophenone  **1e**	4 	5 	6 
Diazomethane  **2d**	7 	8 	9 

Table 9 – Control experiments for the dyeing of silica with diazo compound **2d** and diazonium salt **5**

Silica	After Application	After Heating	After Diazonium coupling with **5** and Washing
	1	2	3
No Compound		-	
Benzophenone  **1e**	4	5	6
		-	
Diazomethane  **2d**	7	8	9
		-	

References

[1] D. D. Tanner, J. A. Plambeck, D. W. Reed, and T. W. Mojelski, *J.Org.Chem.*, 1980, **45**, 5177.