Supporting Information

Study of the Structure-Properties Relationship of Phenolic Molecular Glass Resists for Next Generation Photolithography

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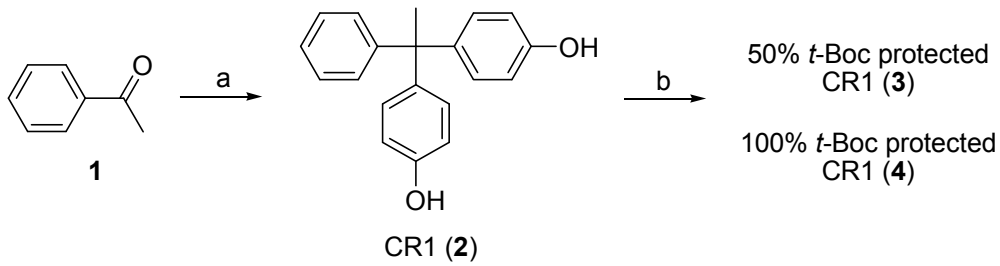
Synthesis and characterization of *t*-BOC protected CR1-CR10



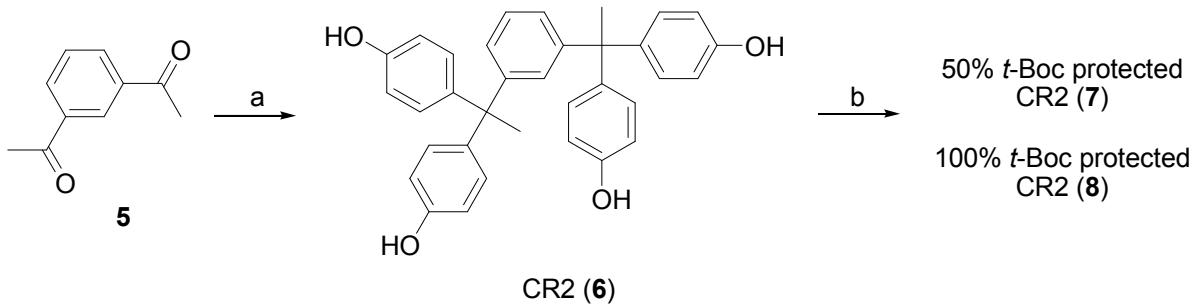
Scheme 1. Preparation of *t*-Boc protected CR1.

50% *t*-Boc-protected CR1 (**3**)

T_g (DSC) 42 °C; T_d (TGA) 121°C; Weight loss cacld for 50% *t*-BOC protection 26%, found 25%; IR (film) ν_{max} 3430, 1759 cm^{-1}; ^1H NMR (300 MHz, acetone-d6):δ = 1.52 [s, 9 H, $(CH_3)_3C$], 2.08-2.20 (m, 3 H, CH_3), 6.72-7.34 (m, 13 H, Ar-*H*), 8.20-8.27 ppm (broad, m, 1H, Ar-O*H*).

100% *t*-Boc protected CR1 (**4**)

T_g (DSC) 42 °C;T_d (TGA) 165 ºC; Weight loss cacld for 100% *t*-BOC protection 41%, found 41%; IR (film) ν_{max} 1760 cm^{-1}; ^1H NMR (300 MHz, acetone-d6):δ = 1.52 [s, 18H, 2x $(CH_3)_3C$], 2.20 (s, 3 H, CH_3), 7.07-7.34 ppm (m, 13 H, Ar-*H*).



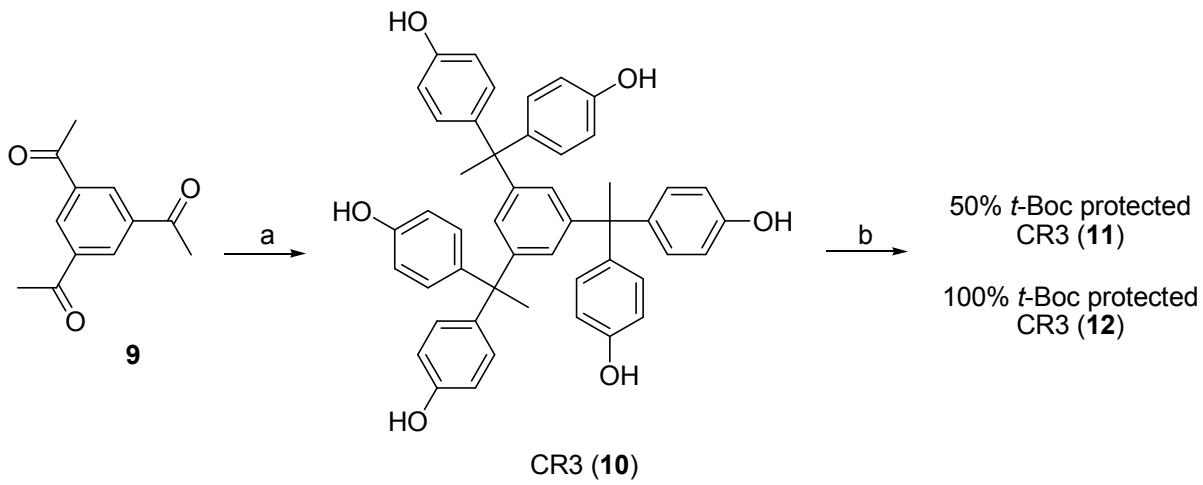
Scheme 2. Preparation of *t*-Boc protected CR2.

50% *t*-Boc protected CR2 (**7**)

T_g (DSC) 80 °C; T_d (TGA) 126 °C; Weight loss cacld for 50% *t*-BOC protection 27%, found 24%; IR (film) ν_{max}: 3441, 1759; ^1H NMR (300 MHz, DMSO-d6):δ = 1.47 [s, 18H, 2x $(CH_3)_3C$], 1.85-2.1 (m, 6 H, 2x CH_3), 6.51-7.18 (m, 20 H, Ar-*H*), 8.20-9.40 ppm (broad, m, 2H, 2 x Ar-O*H*).

100% *t*-Boc protected CR2 (**8**)

T_g (DSC) 74 °C; T_d (TGA) 160 ºC; Weight loss cacld for 100% *t*-BOC protection 44%, found 44%; IR (film) ν_{max}: 1759 cm^{-1}; ^1H NMR (300 MHz, DMSO-d6):δ = 1.46 [s, 36H, 4x (CH_3)$_3$C], 2.02 (s, 6 H, 2x CH_3), 6.91-7.28 ppm (m, 20 H, Ar-*H*)



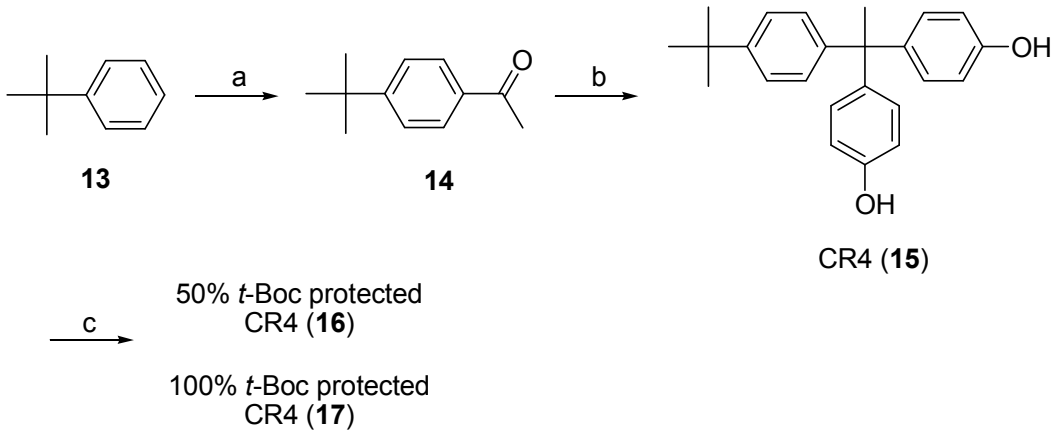
***Scheme 3*.** Preparation of *t*-Boc protected CR3.

50% *t*-Boc-protected CR3 (**11**)

T_g (DSC) 94 °C; T_d (TGA) 120 °C; Weight loss cacld for 50% *t*-BOC protection 30%, found 28%; IR (film) ν_{max} 3445, 1759 cm^{-1}; ^1H NMR 300 MHz, DMSO-d6):δ = 1.47 [s, 27H, 3x (CH_3)$_3$C], 1.71-2.01 (m, 9 H, 3x CH_3), 6.43-7.10 (m, 27H, Ar-*H*), 9.12-9.34ppm (broad, m, 3H, 3x Ar-O*H*).

100% *t*-Boc-protected CR3 (**12**)

T_g (DSC) 83 °C; T_d (TGA) 163 °C; Weight loss cacld for 100% *t*-BOC protection 46%, found 44%; IR (film) ν_{max} 1760 cm^{-1}; ^1H NMR (300 MHz, DMSO-d6):δ = 1.53 [s, 54H, 6x (CH_3)$_3$C], 2.02 (s, 9 H, 3x CH_3), 6.86 (s, 3 H, Ar-*H*), 7.04 ppm (s, 24H, Ar-*H*)



Scheme 4. Preparation of *t*-Boc protected CR4.

1-(4-*tert*-butylphenyl)ethanone (**14**)

To magnetically stirred acetyl chloride (25 cm^3) was added $AlCl_3$ (12.4 g, 93.1 mmol) at -78 °C. The mixture was stirred for 10 min, to which *tert*-butylbenzene **13** (5.00 g, 37.3 mmol) was added at the same temperature. The resulting solution was then allowed to warm up to room temperature and stirred for 1 h. It was poured into crushed ice-water mixture (300 cm^3) to quench the reaction. The crude product was extracted with CH_2Cl_2 (100 cm^3). The organic layer was washed with saturated $NaHCO_3$ aqueous solution (150 cm^3) and water (100 cm^3), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting yellow liquid was purified by vacuum distillation to give the acetophenone **14** as a pale-yellow liquid (5.80 g, 88%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36 [s, 9 H, $(CH_3)_3C$], 2.63 (s, 3 H, CH_3), 7.50 (d, *J* = 8.5 Hz, 2 H, Ar-*H*), 7.92 (d, *J* = 8.5 Hz, 2 H, Ar-*H*). The ^{1}H NMR data are in agreement with literature values.

CR4 (**15**)

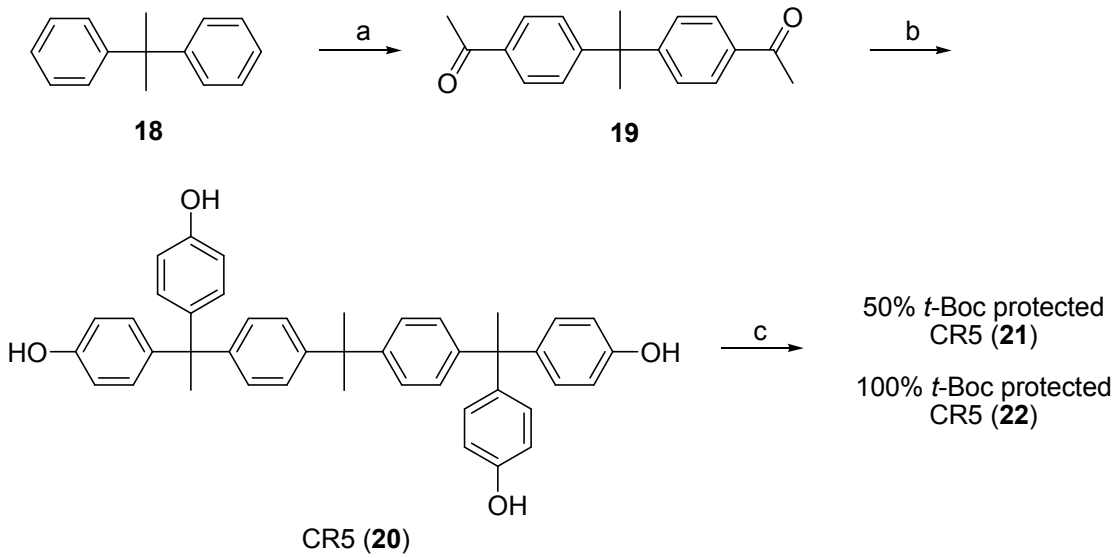
50% *t*-Boc-protected CR4 (**16**)

T_g (DSC) 51 °C; T_d (TGA) 123 °C; IR (film) ν_{max} 3430, 1759 cm^{-1}; Weight loss cacld for 50% *t*-BOC protection 22%, found 23%; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 [s, 9 H, $(CH_3)_3C$], 1.58 [s, 9.3 H, $(CH_3)_3C$], 2.11-2.16 (m, 3 H, CH_3), 6.72-7.28 ppm (m, 12 H, Ar-*H*).

100% *t*-Boc protected CR4 (**17**)

No Tg observed; T_d (TGA) 165 ºC; Weight loss cacld for 100% *t*-BOC protection 37%, found 37%; IR (film) ν_{max} 1760 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.32 [s, 9 H, $(CH_3)_3C$], 1.58 [s, 18 H, 2 x $(CH_3)_3C$], 2.15 (s, 3 H, CH_3), 7.02 (d, *J* = 8.5 Hz, 2 H, Ar-*H*), 7.07 (d, *J* = 9

Hz, 4 H, Ar-*H*), 7.11 (d, *J* = 9 Hz, 4 H, Ar-*H*), 7.28 ppm (d, *J* = 8.5 Hz, 2 H, Ar-*H*).



Scheme 5. Preparation of *t*-Boc protected CR5.

2,2-Bis(4-acetylphenyl)propane (**19**)

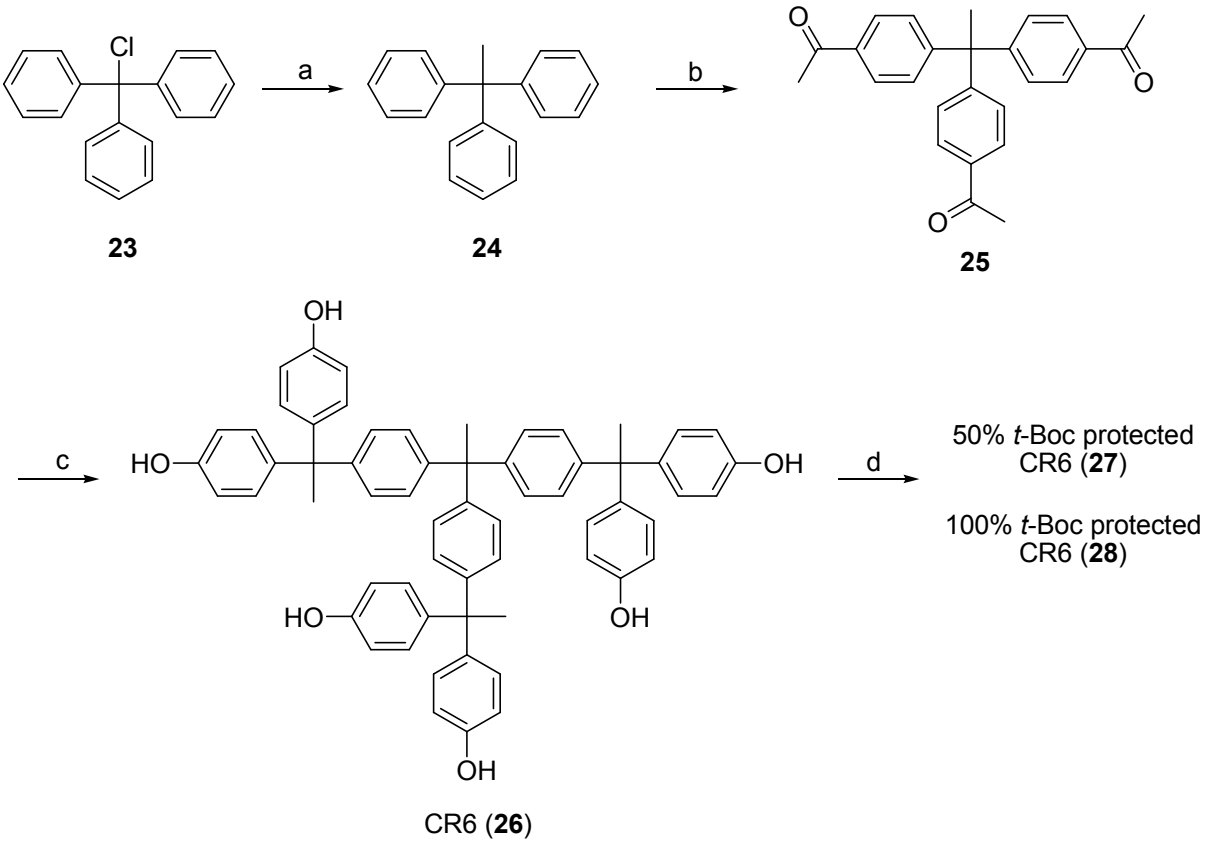
To magnetically stirred acetyl chloride (27 cm^3) was added $AlCl_3$ (15.3 g, 115 mmol) at -78 °C. The mixture was stirred for 10 min, to which 2,2-diphenylpropane **18** (5.00 g, 25.5 mmol) was added. The resulting solution was then allowed to warm up to room temperature and stirred for 1 h. It was then poured into crushed ice-water mixture (400 cm^3). The product was extracted with EtOAc twice (100 cm^3 and 50 cm^3). The organic layer was washed with saturated $NaHCO_3$ aqueous solution (100 cm^3) and brine (100 cm^3), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, EtOAc:hexane 1:3) to give the diacetophenone **19** as an off-white solid (6.09 g, 85%); mp 62-63 °C [Lit.,[1] 66-68 °C (from methylcyclohexane)]; IR (film) ν_{max}: 1680 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.74 (s, 6 H, 2 x C*H*$_3$), 2.59 [s, 6 H, 2 x C*H*$_3$C(O)], 7.32 (d, *J* = 8.5 Hz, 4 H, Ar-*H*), 7.89 ppm (d, *J* = 8.5 Hz, 4 H, Ar-*H*).

50% *t*-Boc protected CR5 (**21**)

T_g (DSC) 80 °C; T_d (TGA) 123 °C; Weight loss cacld for 50% *t*-BOC protection 24%, found 25%; IR (film) ν_{max}: 3441, 1759; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.58 [s, 19 H, (C*H*$_3$)$_3$C], 1.66 (s, 6 H, 2 x C*H*$_3$), 2.09-2.15 (m, 6 H, 2 x C*H*$_3$), 6.65-7.15 ppm (m, 24 H, Ar-*H*).

100% *t*-Boc protected CR5 (**22**)

No Tg observed; T_d (TGA) 165 ºC; Weight loss cacld for 100% *t*-BOC protection 39%, found 39%; IR (film) ν_{max}: 1759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.58 [s, 36 H, 4 x (CH_3)$_3$C], 1.66 (s, 6 H, 2 x CH_3), 2.15 (s, 6 H, 2 x CH_3), 6.96-7.00 (m, 4 H, Ar-*H*), 7.05-7.15 ppm (m, 20 H, Ar-*H*).



Scheme 6. Preparation of *t*-Boc protected CR6.

1,1,1-Triphenylethane (**24**)

To a magnetically stirred solution of chlorotriphenylmethane **23** (10.0 g, 35.9 mmol) in Et_2O (120 cm^3), which was immersed in water bath, was added methylmagnesium chloride solution (3 M solution in THF, 17.9 cm^3, 53.8 mmol) slowly under a N_2 atmosphere. The mixture was then stirred overnight and quenched with 10% w/w citric acid aqueous solution (100 cm^3). The organic layer was recovered and washed with water (100 cm^3) and brine (100 cm^3), dried over anhydrous $MgSO_4$ and then concentrated under reduced pressure. The resulting crude product crystallized from EtOH (70 cm^3) to give 1,1,1-triphenylethane **24** as

yellow crystals (6.55 g, 71%); mp 91-93 ºC (Lit.,[1] 94.5-95.5 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.22 (3 H, s, C*H*$_3$), 7.11-7.13 (6 H, m, Ar-*H*), 7.21-7.23 (3 H, m, Ar-*H*), 7.27-7.31 ppm (6 H, m, Ar-*H*). The ^{1}H NMR data are in agreement with literature values.

1,1,1-Tris(4-acetylphenyl)ethane (**25**)

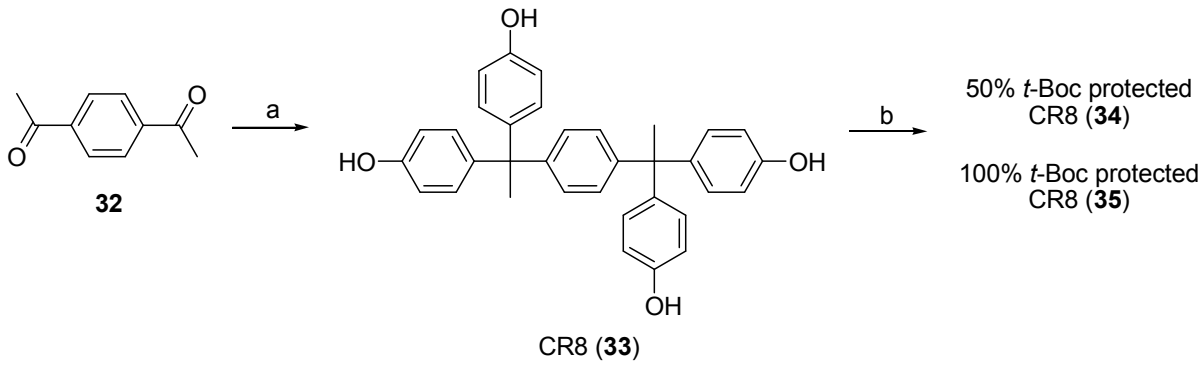
To magnetically stirred acetyl chloride (16 cm^3) was added $AlCl_3$ (7.02 g, 52.6 mmol) at -78 °C. The mixture was stirred for 10 min, to which **24** (2.00 g, 7.74 mmol) was added. The resulting solution was allowed to warm up to room temperature and stirred for 1 h. It was poured into crushed ice-water mixture (300 cm^3). The viscous material deposited on the bottom was recovered and dissolved in EtOAc (50 cm^3). The organic solution was then washed with water (50 cm^3) and brine (50 cm^3), dried over anhydrous $MgSO_4$ and then concentrated under reduced pressure. The crude product was purified by flash column chromatography (EtOAc:hexane 1:1) to give the trisacetophenone **25** as a pale-yellow viscous liquid (2.64 g, 89%); R_f = 0.48 (silica gel, EtOAc:hexane 1:1); IR (film) ν_{max} 1683, 1604 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.24-2.26 (3 H, C*H*$_3$), 2.60 (s, 9 H, 3 x acetyl-C*H*$_3$), 7.20 (d, *J* = 8.5 Hz, 6 H, Ar-*H*), 7.90 ppm (d, *J* = 8.5 Hz, 6 H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.6, 30.0, 53.1, 128.2, 128.7, 135.3, 152.7, 197.6 ppm. The ^{1}H NMR data are in agreement with literature values.

50% *t*-Boc-protected CR6 (**27**)

T_g (DSC) 129 °C; T_d (TGA) 141 °C; Weight loss cacld for 50% *t*-BOC protection 25%, found 29%; IR (film) ν_{max} 3445, 1759 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.58 [s, 35 H, (C*H*$_3$)$_3$C], 2.13 (s, 12 H, 4 x C*H*$_3$), 6.60-7.15 ppm (m, 36 H, Ar-*H*).

100% *t*-Boc-protected CR6 (**28**)

T_g (DSC) 129 °C; T_d (TGA) 167 °C; Weight loss cacld for 100% *t*-BOC protection 40%, found 40% IR (film) ν_{max} 1760 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.57 [s, 54 H, 6 x (C*H*$_3$)$_3$C], 2.13 (s, 3 H, C*H*$_3$), 2.15 (s, 9 H, 3 x C*H*$_3$), 6.96 (s, 12 H, Ar-*H*), 7.09 ppm (q, *J* = 9.0 Hz, 24 H, Ar-*H*).



Scheme 7.Preparation of *t*-Boc protected CR8.

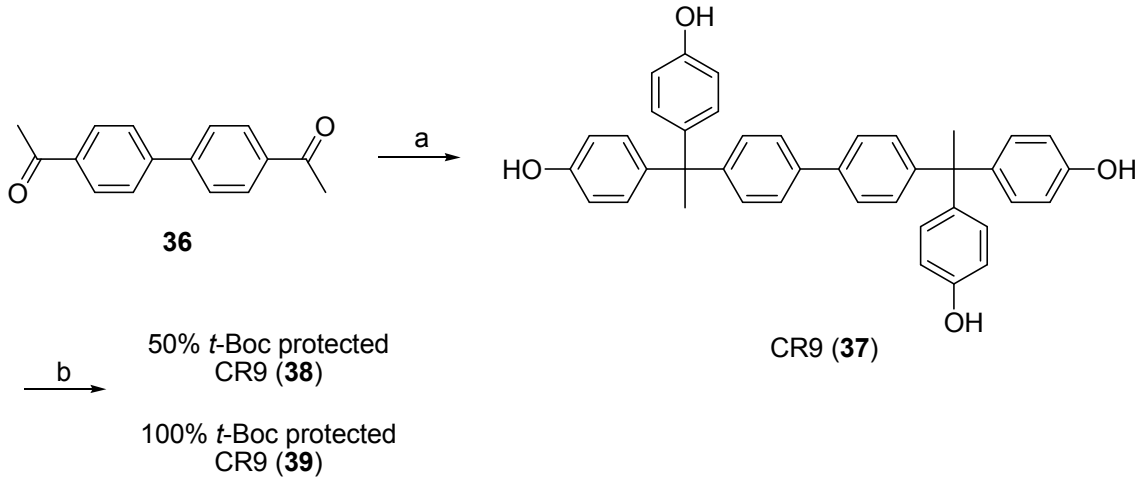
CR8 (**33**)

50% *t*-Boc protected CR8 (**34**)

No Tg observed; T_d (TGA) 115 ºC; Weight loss cacld for 50% *t*-BOC protection 27%, found 28%; IR (film) ν_{max}: 3441, 1759; ^{1}H NMR (300 MHz, DMSO-d6):δ = 1.46 [s, 18H, 2x (CH_3)$_3$C], 1.92-2.12 (m, 6 H, 2x CH_3), 6.58-7.18 (m, 20 H, Ar-*H*), 9.20-9.33 ppm (broad, m, 2H, 2 x Ar-O*H*).

100% *t*-Boc protected CR8 (**35**)

No Tg observed; T_d (TGA) 180 ºC; Weight loss cacld for 100% *t*-BOC protection 44%, found 44%; IR (film) ν_{max}: 1759 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d6):δ = 1.54 [s, 36H, 4x (CH_3)$_3$C], 2.15 (s, 6 H, 2x CH_3), 7.01-7.17 ppm (m, 20 H, Ar-*H*)



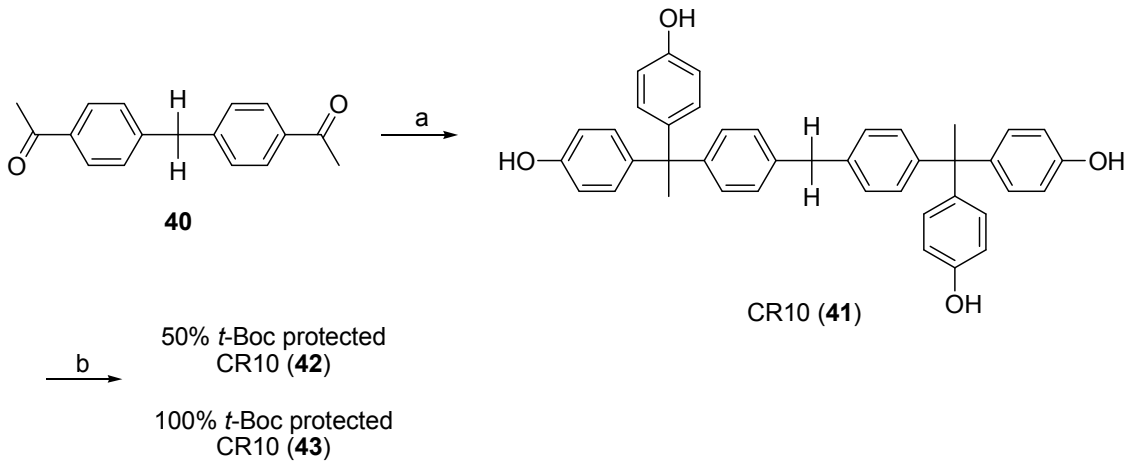
Scheme 8. Preparation of *t*-Boc protected CR9.

50% *t*-Boc protected CR9 (**38**)

T_g (DSC) 83 °C; T_d (TGA) 122 °C; Weight loss cacld for 50% *t*-BOC protection 26%, found 29%; IR (film) ν_{max}: 3441, 1759; ^{1}H NMR (300 MHz, acetone-d6):δ = 1.49 [s, 18H, 2x (CH_3)$_3$C], 1.96 (s, 6 H, 2x CH_3), 6.78-7.89 (m, 24 H, Ar-*H*), 8.40-8.59 ppm (broad, m, 2H, 2 x Ar-O*H*).

100% *t*-Boc protected CR9 (**39**)

T_g (DSC) 98 °C; T_d (TGA)164 ºC; Weight loss cacld for 100% *t*-BOC protection 41%, found 38%; IR (film) ν_{max}: 1759 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d6):δ = 1.47 [s, 36H, 4x (CH_3)$_3$C], 2.14 (s, 6 H, 2x CH_3), 7.04-7.66 ppm (m, 24 H, Ar-*H*).



Scheme 9. Preparation of *t*-Boc protected CR10.

50% *t*-Boc protected CR10 (**42**)

T_g (DSC) 81 °C; T_d (TGA) 133 °C; Weight loss cacld for 50% *t*-BOC protection 25%, found 27%; IR (film) ν_{max}: 3441, 1759; ^{1}H NMR (300 MHz, DMSO-d6):δ = 1.45 [s, 18H, 2x (CH_3)$_3$C], 1.90-2.10 (m, 6 H, 2x CH_3), 3.84 (s, 2H, 1 x C*H*2) 6.51-7.22 (m, 24 H, Ar-*H*), 9.15-9.32 ppm (broad, m, 2H, 2 x Ar-O*H*).

100% *t*-Boc protected CR10 (**43**)

T_g (DSC) 73 °C; T_d (TGA) 171 ºC Weight loss cacld for 100% *t*-BOC protection 40%, found 40%; IR (film) ν_{max}: 1759 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d6):δ = 1.46 [s, 36H, 4x (CH_3)$_3$C], 2.08 (m, 6 H, 2x CH_3), 3.87 (s, 2H, 1 x C*H*2) 6.90-7.23 ppm (m, 24 H, Ar-*H*)

Table1. Characterization of the Additional Molecular Glasses

MG Compound	% of tBOC protection	Phenolic function	Mw (g/mol)	Tg (°C)	C/O ratio
CR7-0	0	3	424.5	94	7.25
CR8-0	0	4	502.6	119	6.38
CR9-0	0	4	578.7	129	7.51
CR10-0	0	4	592.7	117	7.69
CR7-66	66	2	624.8	65	4.18
CR8-50	50	2	702.9	No Tg	4.13
CR9-50	50	2	778.9	83	4.69
CR10-50	50	2	792.9	81	4.79
CR7-100	100	0	724.9	53	3.67
CR8-100	100	0	903.1	No Tg	3.38
CR9-100	100	0	979.2	98	3.75
CR10-100	100	0	993.2	73	3.82

DSC Data for MG Series 1

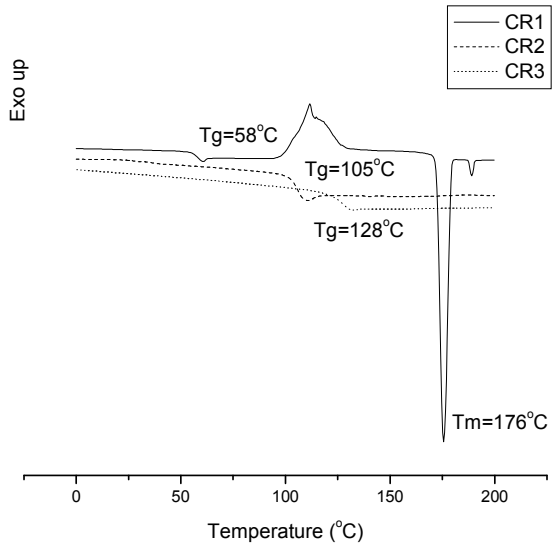


Figure 1: DSC curves for MG series 1 (unprotected)

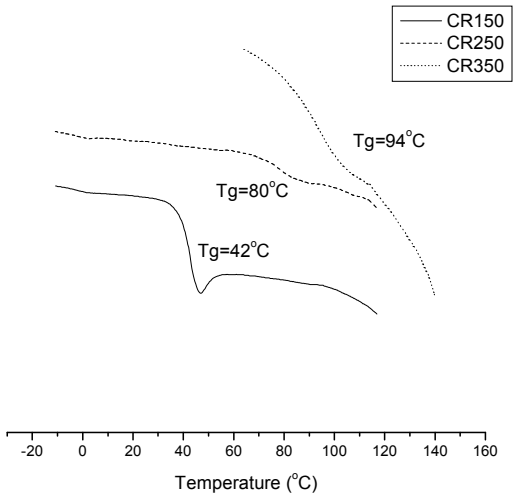


Figure 2: DSC curves for partially protected MG series 1

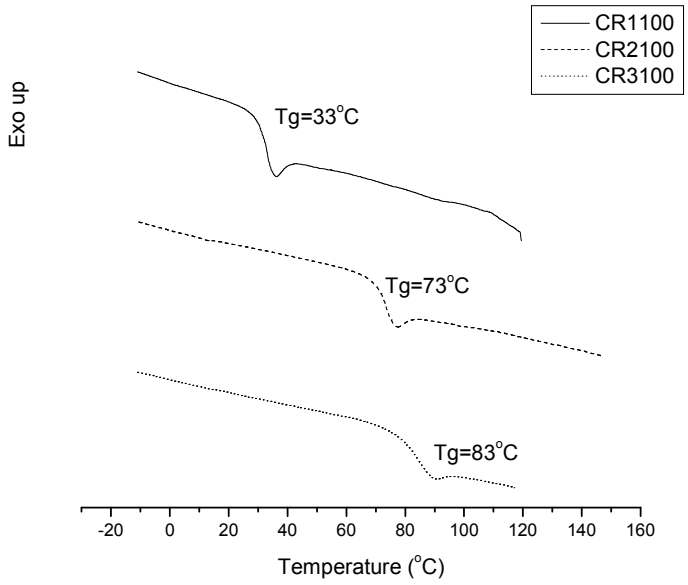


Figure 3: DSC curves for fully protected MG series 1

DSC Data for MG Series 2

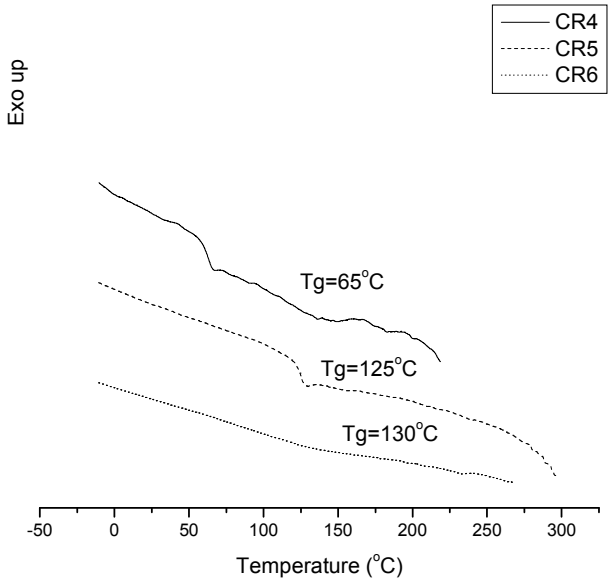


Figure 4: DSC curves for MG series 2 (unprotected)

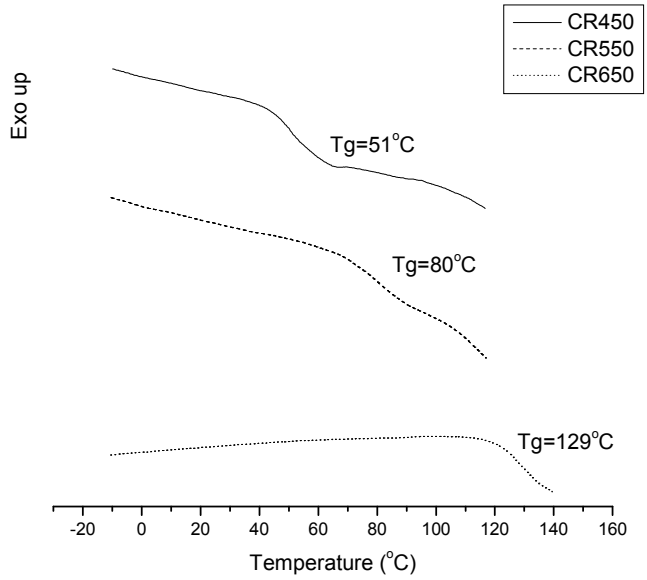


Figure 5: DSC curves for partially protected MG series 2

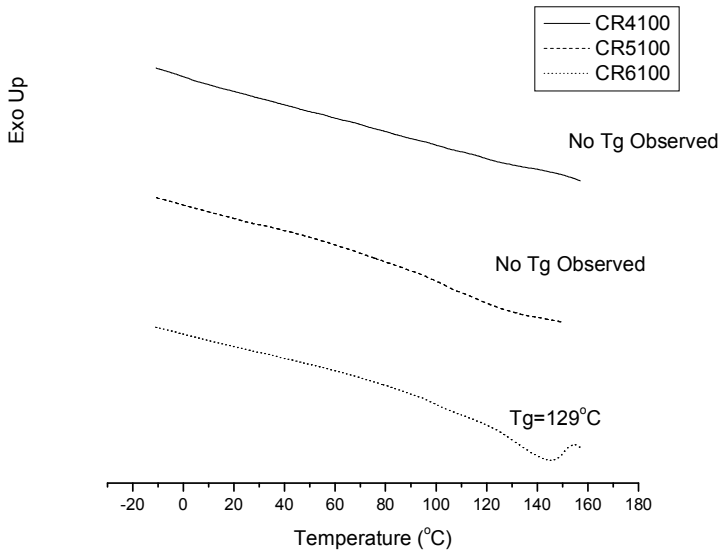


Figure 6: DSC curves for fully protected MG series 2

XRD Data for MG series 1

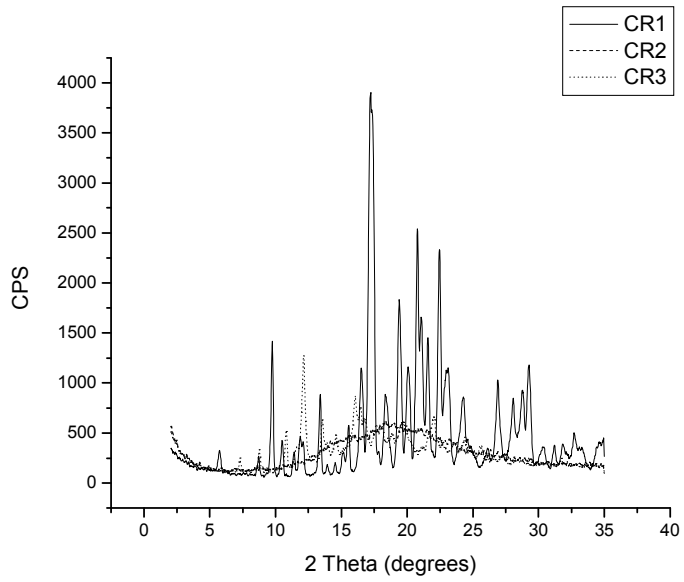


Figure 7: XRD graphs for MG series 1 (unprotected)

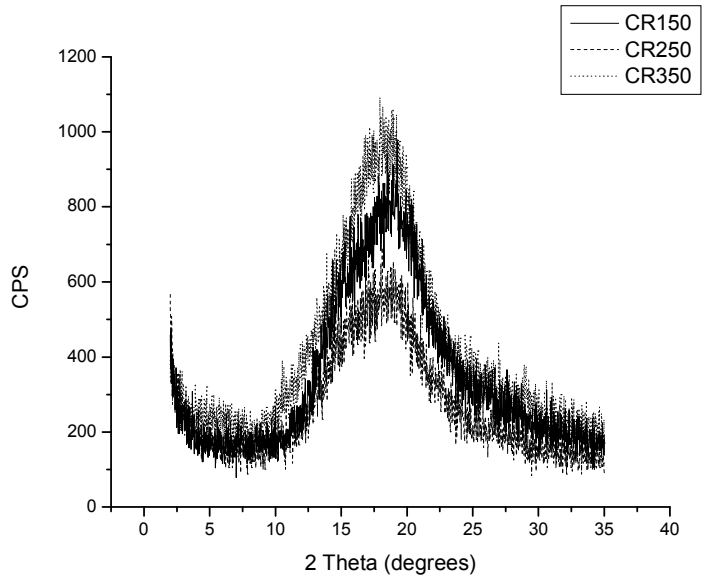


Figure 8: XRD graphs for partially protected MG series 1

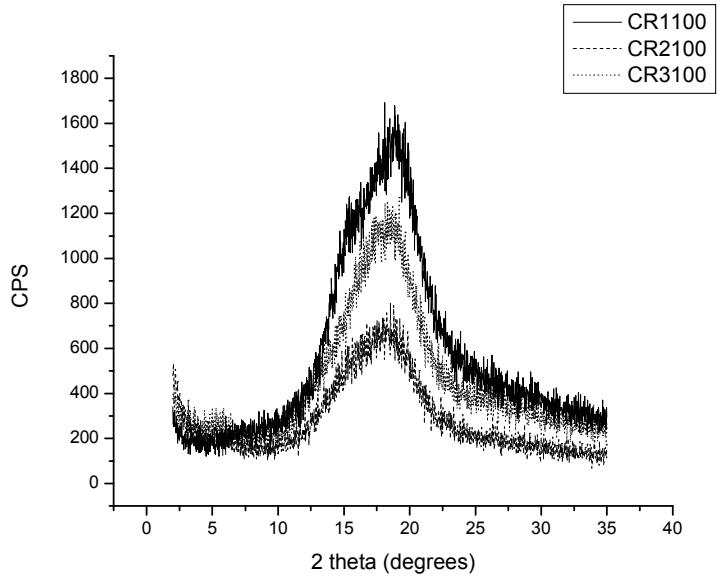


Figure 9: XRD garphs for fully protected MG series 1

XRD Data for MG series 2

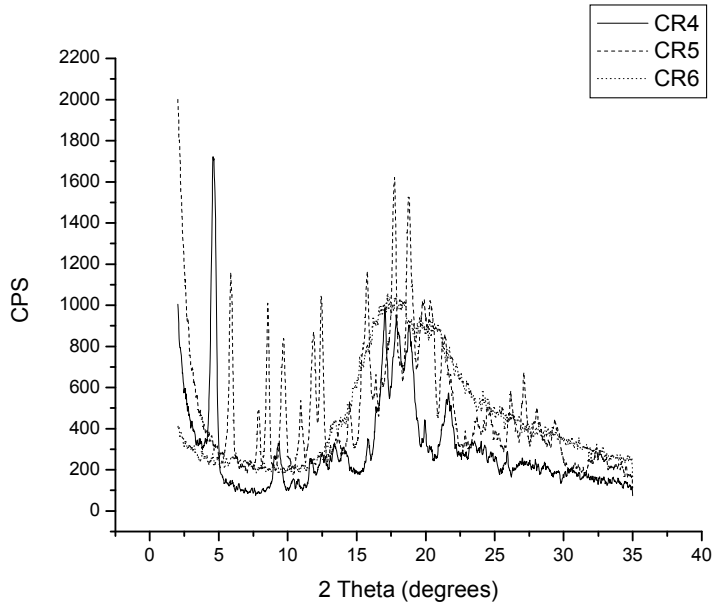


Figure 10: XRD graphs for MG series 2 (unprotected)

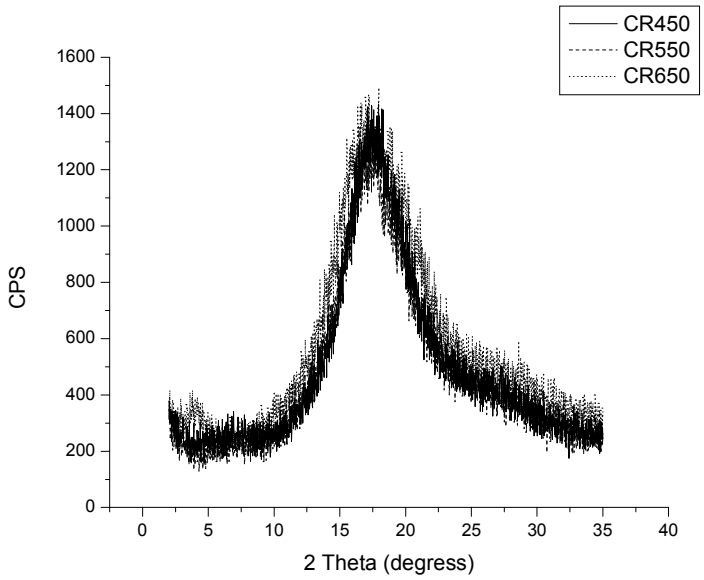


Figure 11: XRD graphs for partially protected MG series 2

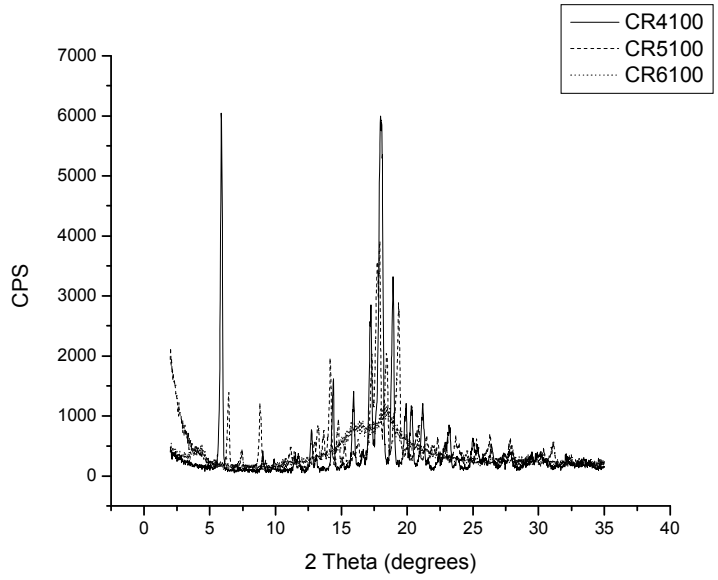


Figure 12: XRD graphs for fully protected MG series 2