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Use of triazole-ring formation to attach a Ru/TsDPEN complex for asymmetric transfer hydrogenation to a soluble polymer.

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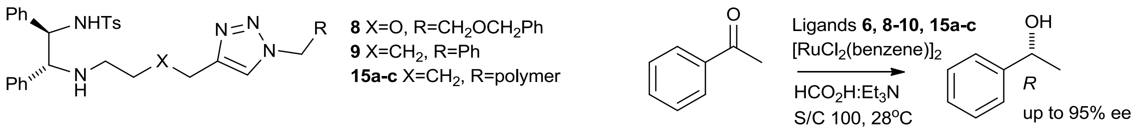

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Use of triazole-ring formation to attach a Ru/TsDPEN complex for asymmetric transfer hydrogenation to a soluble polymer.

Charlotte M. Zammit and Martin Wills*

Department of Chemistry, Warwick University, Coventry, CV4 7AL, UK

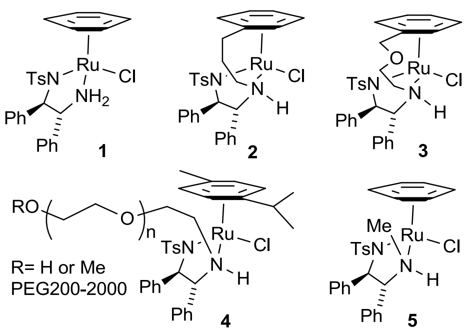
Abstract—The cycloaddition of a chiral ligand containing a terminal alkyne to a soluble polymer containing an azide provides a convenient means for the attachment of an asymmetric transfer hydrogenation catalyst to a soluble polymer support. Using these ligands in complexes with Ru(II), good results were obtained in terms of conversion and enantioselectivity (up to 95% ee) in ketone reduction reactions.

1. Introduction

A series of asymmetric transfer hydrogenation (ATH) catalysts based on the 'Ru(II)/TsDPEN' system have been reported and successfully applied to the enantioselective reduction of ketones to alcohols.[1] The first of this series was the complex **1**, reported in 1995 by Noyori and co-workers.[2] Since then, many applications have been reported[1-3] and a number of related derivatives have been developed, including the tethered complexes **2** and **3**.[4]

Significant efforts have been made towards the development of 'supported' versions of the Ru(II)/TsDPEN catalyst system. Popular methods include immobilisation via a covalent attachment to a support, or entrapment within a support (e.g.silica or polystyrene).[5] In other cases the catalyst is converted into a form which permits its ready removal from a reaction mixture e.g. as a surfactant[6] or as a derivative containing polyethylene glycol (PEG) chains.[7] In the majority of examples the linkage (to silica or polymer) is made to the sulfonyl group, the η^6-arene ring or a side chain of the diamine unit, thereby leaving a primary amine group to co-ordiante to the metal. Complex **4** represents an unusual example where a soluble PEG chain is attached via the basic nitrogen atom, without significent reduction to the catalyst activity.[7a] This mirrors our own findings with *N*-alkylated TsDPEN derivatives **5**, in which a linear alkyl chain is tolerated by the catalyst.[8]

In earlier studies, we employed copolymers of methyl methacrylate (MMA) and hydroxyethylmethacrylate (HEMA) as the basis of soluble catalysts.[9] In this paper, we describe a method for attachment of an ATH catalyst to a soluble methacrylate polymer using a cycloaddition reaction.



2. Results and Discussion

To attach a Ru(II)/TsDPEN catalyst to a soluble polymer, we used the well-established cycloaddition of an azide with an alkyne (a 'click' reaction),[10] which has been used to attach biologically-active groups to polymers.[11] As it has been demonstrated that a proximal triazole ring can itself become involved in co-ordination to the ruthenium atom, and participate in catalysis,[12] we investigated systems where this was distant from the TsDPEN unit. We first prepared derivative **6** containing a terminal alkyne (Scheme 1). This was then reacted in a copper-catalysed [3+2] cycloaddition reaction with azide **7** (prepared from 2-benzyloxyethanol in two steps) to furnish the triazole product **8**, a model for the supported compound.

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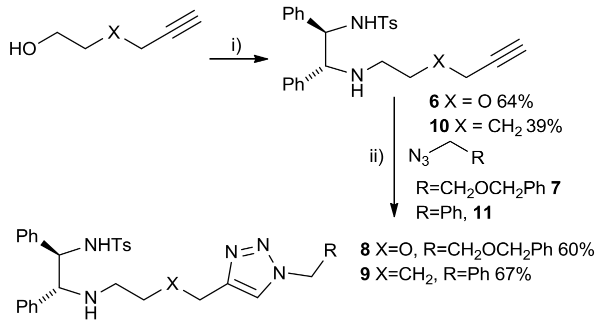
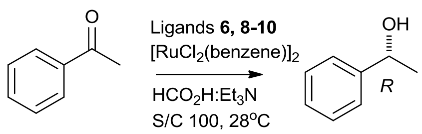


Reagents and conditions: (i) 2,6-lutidine, $(CF_3SO_2)_2O$, CH_2Cl_2, 0 °C to 22 °C, then Et_3N, (*R*,*R*)-TsDPEN, CH_2Cl_2, 0 °C to rt, o/n, 64 % (X=O), 39% (X=CH_2); (ii) for **8:** $CuSO_4.5H_2O$, sodium ascorbate, tBuOH:H_20, 30 °C, 5 h, 60%. (iii) for **9**: $C_6H_5CH_2Br$, NaN_3, $CuSO_4.5H_2O$, sodium ascorbate, tBuOH:H_2O, 60 °C, 3 h, 67 %.

Scheme 1. Preparation of triazole-functionalised TsDPEN derivatives.

The same procedure was adopted for the synthesis of 1,4-disubstituted 1,2,3-triazole **9** by reacting **10** with benzyl azide **11** (formed in situ),[13] 5 mol % copper(II) sulfate pentahydrate and 10 mol % sodium ascorbate. The catalytic activity of each ligand was investigated in the ATH of acetophenone (Table 1) by preparing catalysts in situ from the Ru(II)-pre-catalyst $[RuCl_2(benzene)]_2$. Using formic acid/triethylamine (FA/TEA) as the hydrogen donor, at 28 °C each derivative demonstrated good catalytic activity (92 – 99 %) and enantioselectivity (93 – 95 % ee).

Table 1: Evaluation of (*R*,*R*)-TsDPEN and ligands **6, 8** – **10** in the ATH of acetophenone.



Entry	Ligand	t / h[a]	Conv./ %[b]	Ee /%[b]
1	(*R*,*R*)-TsDPEN	6	>99	95
2	(*R*,*R*)-**6**	53	92	93
3	(*R*,*R*)-**8**	136	99	95
4	(*R*,*R*)-**9**	71	97	95
5	(*R*,*R*)-**10**	45	97	95

a. Number of hours necessary to observe a levelling-off in conversion. b. Conversion and ee determined by GC analysis.

The ligands exhibited lower activities but similar enantioselectivities compared to (*R*,*R*)-TsDPEN and other *N*'-alkylated TsDPEN ligands.[2-4] Using the (*R*,*R*)-configuration ligands in each case, the alcohol of *R*-configuration was always formed. The nitrogen of the triazole moiety in **8** and **9** might be coordinating to ruthenium in a reversible manner,[12] reducing the catalytic activity.

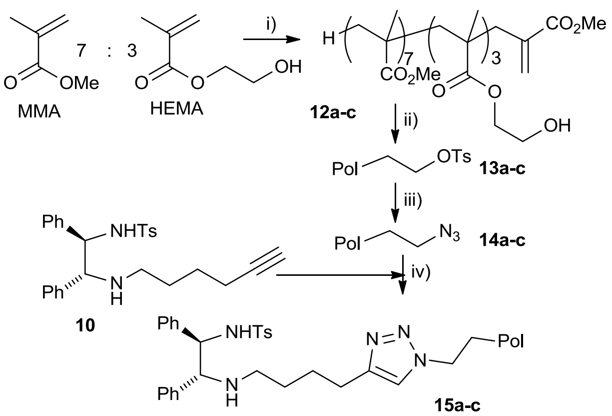
Investigations into the immobilisation of the chiral ligand onto a polymer support were undertaken.[14] The synthesis of copolymers **12** was achieved by catalytic chain transfer polymerisation (CCTP) using methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) in a 70:30 mixture, in combination with 4,4'-azobis(4-cyanovaleric acid) and $(CH_3OH)_2Co\text{-}(dmgBF_2)_2$ (CoBF) as the initiator and chain-transfer catalyst respectively (Scheme 2).[14] The first sample (**12a**) was prepared without active CoBF, and this was found to have a high molecular weight, as expected. We prepared a sample of CoBF,[15] and the FTIR spectrum of this sample matched that of a standard.[16] Similar molecular weights were obtained and the dispersity (PDI) was approximately 2 for copolymer sample **12b** (Table 2) prepared with the fresh CoBF and the standard.[16] A higher molecular weight HEMA/MMA copolymer (**12c**) was prepared using half the amount of CoBF (Table 2). All the polymers prepared exhibited monomodal distributions, and the M_n values calculated by ^{1}H NMR for the low molecular weight polymer **12b** correlated well with those calculated by GPC.

Table 2: Molecular weight (M_n) determination by ^{1}H NMR and GPC analysis for the HEMA/MMA copolymers prepared using different samples of CoBF.

En-Try	Poly-mer	Ratio[a]	^{1}H NMR g/mol M_n	GPC g/mol M_n	GPC g/mol M_w	GPC g/mol PDI[b]
1	**12a**	A[c]	n/a[d]	146K	337K	2.30
2	**12b**	A[16]	1,570	970	1,790	1.84
3	**12b**	A	2,430	1,080	2,710	2.50
4	**12c**	B	n/a[d]	2,710	9,210	3.40

a. [HEMA]:[MMA]:[CoBF] ratios: **A** = [0.42]:[1.0]:[4.27 x 10^{-5}] and **B** = [0.42]:[1.0]:[2.14 x 10^{-5}]. b. PDI (polydispersity index) = M_n/M_w. c. inactive CoBF. d. polymer too large for M_n to be calculated accurately by ^{1}H NMR.

The HEMA:MMA copolymer ratio of 3:7 was calculated using the integration of the methylene signals of the HEMA unit (OCH_2CH_2OH) at 4.12 and 3.85 ppm and the methoxy signal of the MMA unit (OCH_3) at 3.61 ppm. This ratio was utilised to calculate the hydroxyl group functionalisation value ($f_{hydroxyl}$) as 2.77 mmol/g. The molecular weight (M_n) of the copolymer was calculated from the ^{1}H NMR spectrum by integrating the vinyl protons of the end group with respect to the methylene protons of the HEMA repeating unit and the methyl protons of the MMA repeat unit (Scheme 2). Tosylation of copolymer **12a-c** using a known procedure[9] furnished **13a-c**. The O-tosyl group was subsequently substituted for an azide upon reaction of **13a-c** with 3 equivalents of sodium azide to afford copolymer **14a-c**. The conversion of the HEMA/MMA copolymer **12a-c** to the tosylated polymer **13a-c** was confirmed by ^{1}H NMR spectroscopy through the appearance of the aromatic signals at 7.8 ppm and 7.4 ppm together with the methyl signal at 2.5 ppm of the O-tosyl (OTs) group. A change in chemical shift to higher frequency was observed for the methylene group adjacent to the OTs functionality (3.8 ppm to 4.1 ppm) of the HEMA repeating unit, and indicated quantitative conversion. Subsequent disappearance of the characteristic signals belonging to the OTs group, in combination with a chemical shift for the methylene group to a lower frequency value of 3.5 ppm, gave strong evidence for the complete formation of the azido derivatised copolymer **14a-c**. The FTIR spectrum of the azido derivatised copolymer **14a-c** showed a strong absorption signal at 2104 cm^{-1} that is characteristic of the azide group, and this was used as a diagnostic tool to monitor the subsequent click reaction.



Reagents and conditions: (i) dioctylsulfosuccinate sodium salt, 4,4'-azobis(4-cyanovaleric acid), CoBF, 80^{o}C, 4h, see Table 2; (ii) TsCl, DMAP, Et_3N, DCM, rt, 2d; (iii) NaN_3, DMF, 80 ^{o}C, 2.75 h then rt, 48 h; (iv) Et_3N, CuBr, TBTA, DMSO, 20 ^{o}C, 24 h, 41% (polymer b), Et_3N, CuBr, TBTA, DMSO, 25 ^{o}C, 24 h, then 50 ^{o}C, 72h, 66% (polymer c), $CuSO_4.5H_2O$, sodium ascorbate, tBuOH:H_2O, 80 ^{o}C, 3 d, 98% (polymer a).

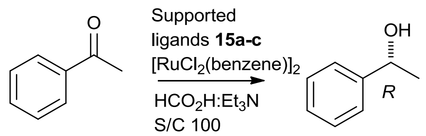
Scheme 2. Preparation of triazole-functionalised TsDPEN derivatives on soluble polymer support.

Copolymers **14a-c** were reacted with ligand **10** to afford **15a-c** as indicated by the disappearance of the azide signal, and were isolated by filtration in moderate to high yield (41 % - 98 %). The high molecular weight polymer, **15a** was too insoluble to be analysed by solution phase techniques. The chemical modification of the hydroxyl repeating unit in copolymers **12b** and **12c** required slightly different work-up procedures due to their distinct solubility behaviour. In addition, the click protocol was modified with the direct use of Cu(I) in combination with tris-[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA).[17] Recent ligand screening experiments[11] have revealed the superior behaviour of this ligand in the Cu(I)-catalysed alkyne-azide cycloaddition reaction for the formation of glycopolymers.

Owing to the complexity of the ^{1}H NMR spectra obtained for polymer-immobilised ligands **15b** and **15c**, the vinyl end group protons were not visible. A recent report by Haddleton and co-workers[11] revealed experimental evidence for the retention of the vinyl end group during the CuAAc reaction between poly(propargyl methacrylate) and cellobiose azide; and this was assumed to be the case for the copolymer-supported 1,2-diamine ligands.

The supported catalysts were tested by pre-mixing 0.5 mol % of Ru(II) pre-catalyst, $[RuCl_2(benzene)]_2$ and 1 mol % of (*R*,*R*)-**15a-c** in FA/TEA at 28 ^{o}C for 1 h, followed by the addition of acetophenone (1.6 M). Ligand (*R*,*R*)-**15a** yielded (*R*)-phenylethanol with 98 % conversion and 94 % ee (Table 3).

Table 3: Evaluation of the HEMA/MMA copolymer-supported ligands (**15a**-**c**) in the ATH of acetophenone.

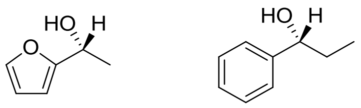


Entry	Cat[a] (run)	T /^{o}C	t/h[b]	Conv./%[c]	Ee/%[c]
1	**15a (1)**	28	120	98	94 (*R*)
2	**15a (1)**	40	24	98	94 (*R*)
3	**15a (2)**	40	28	33	91 (*R*)
4	**15a (2)[d]**	40	46	73	90 (*R*)
5	**15c (1)**	28	136	100	95 (*R*)
6	**15c(2)**	40	48	20	94 (*R*)
7	**15b (1)**	28	144	90	95 (*R*)

a. **Entry 1**: 6.6 x 10^{-3} mmol $[RuCl_2(benzene)]_2$, 1.3 x 10^{-2} mmol ligand in HCO_2H:Et_3N; **Entries 2**: 3.3 x 10^{-3} mmol $[RuCl_2(benzene)]_2$, 3.2 x 10^{-2} mmol ligand in HCO_2H:Et_3N; **Entries 3 and 4**: reuse in HCO_2H:Et_3N as in entry 1, [acetophenone] = 1.6 M. **Entries 5 and 7**: 4.6 x 10^{-3} mmol $[RuCl_2(benzene)]_2$, 9.2 x 10^{-3} mmol ligand in HCO_2H:Et_3N; **Entry 6**: reuse from entry 5. b. Number of hours necessary to observe a levelling-off in conversion. c. Conversion and ee determined by GC analysis. d. After addition of 0.5 mol% $[RuCl_2(benzene)]_2$.

The acetophenone reduction was repeated at 40 ^{o}C to furnish alcohol in 98 % conversion and 94 % ee (*R*) in 24 h (Table 3: entry 2). Upon completion of the reduction, the Ru(II)-**15a** catalyst was recovered by filtration, washed with a 50:50 (v/v) mixture of EtOAc/petroleum ether and neat DCM, and dried under vacuum. The activity of the recovered Ru(II)-**15a** catalyst was assessed by adding fresh portions of FA/TEA and ketone. In this case the ketone was reduced to the alcohol in only 33% conversion although only a slight erosion in ee was observed. Another portion of $[RuCl_2(benzene)]_2$, was added to the reaction mixture and conversion rose to 43 % after 1 h and to 73 % after 46 h. Using 0.5 mol % $[RuCl_2(benzene)]_2$ and 4.8 mol % (*R*,*R*)-

15a ligand at 40 ºC in FA/TEA, acetylfuran was reduced to the *R* enriched alcohol **16** in 99 % conversion and 98 % ee in 24 h and propiophenone to alcohol **17** in 70 % conversion and 92 % ee (*R*) after 24 h.



16 98% ee **17** 92% ee

The high molecular weight ligand (*R*,*R*)-**15a** displayed almost no activity (1 % conversion) in isopropanol/KOH after 24 h at 28 ºC. (*R*,*R*)-**15a** was also evaluated in aqueous phase ATH but gave alcohol in just 3 % conversion and 59 % ee. Treatment of 1 mol % ligand (*R*,*R*)-**15b** with 0.5 mol % $[RuCl_2(benzene)]_2$ in FA/TEA at 28 ºC afforded (*R*)-phenylethanol in high selectivity (95 % ee) and 90 % conversion achieved in 6 days (Table 3: entry 7). The use of 1 mol % of (*R*,*R*)-**15c** in combination with 0.5 mol % $[RuCl_2(benzene)]_2$ in FA/TEA at 28 ºC resulted in acetophenone reduction in 100 % conversion and 95 % ee in 136 h (Table 3, entry 5).

The addition of water, in an attempt to recover the catalyst, precipitated the Ru(II)-**15c** complex. The FA/TEA mixture was then carefully removed, following which the red solid catalyst was washed with fresh portions of FA/TEA. The hydrogen donor and ketone substrate were then recharged for the next cycle. Disappointingly, the recovered polymer-bound catalyst exhibited poor reactivity with 15 % conversion in 24 h and only 20 % conversion after 48 h (Table 3: entry 6). Sodium formate/water was also unsuccessful with alcohol being produced in only 7 % conversion after a 24 h reaction at 40 ºC.

3. Conclusion

In conclusion, a series of TsDPEN ligands containing a triazole unit have been prepared and tested in the ATH of ketones. The triazole represents a convenient method for attachment of the ligand to a soluble polymer support. The resulting supported ligand is effective in the ATH of ketones.

4. Experimental

4.1. General

Unless otherwise stated, all reactions were performed in flame or oven-dried glassware under an atmosphere of nitrogen. Room temperature refers to 20 – 22 ºC, and -78 ºC refers to a dry ice-acetone bath. Commercially available reagents were used without purification unless otherwise stated. Anhydrous solvents were used as supplied. ^{1}H and ^{13}C NMR analysis were obtained on Bruker DPX-300 (300 MHz), DPX-400 (400 MHz) and DPX-700 (700 MHz) spectrometers. All NMR chemical shift (δ) values are reported in parts per million (ppm) downfield from TMS (Me_4Si) and all coupling constants (*J*) are in Hertz (Hz). GPC measurements were performed in *N*,*N*-dimethylformamide (0.03 % w/v LiBr) at 50 ºC and dichloromethane at 30 ºC as appropriate; using Agilent (Polymer Labs) 390-LC systems equipped with a PL-AT autosampler, a PL gel 5μm bead-size guard column, two PL gel 5μm Mixed D columns (300 x 7.5 mm) and a refractive index detector; and the data was analysed using Cirrus (V3.0) software. Polymethyl methacrylate standards (200 – 467,400 g mol^{-1}) were used to calibrate the GPC. Low resolution mass spectrometry was run on a Bruker Esquire 2000 electrospray mass spectrometer and high resolution mass spectrometry was run on a Bruker MicrOTOF. Melting points were obtained using a Stuart Scientific Melting Point SMP1 and are uncorrected. Infrared spectra were recorded on a PerkinElmer Spectrum 100 FTIR and a Nicolet Model Avatar 320 FTIR. Optical rotations were measured using an Optical Activity Ltd. AA-1000 Polarimeter and are recorded in 10^{-1} deg cm^2 g^{-1}. GC analysis was obtained using a Perkin Elmer 8500 chromatograph linked to a PC running DataApex Clarity Software. HPLC measurements were obtained using a Hewlett Packard 1050 HPLC system and the data was analysed using DataApex Clarity Software. The following compounds were prepared following literature methods; bis(methanol)bis((difluoroboryl)dimethylglyoximato)cobalt (II) (CoBF)[15]), benzyl azide.[13] tris-[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA).[17]

4.2. Synthesis of 2-(2-propynyloxy)ethanol.[18]

To a stirred solution of ethylene glycol (16.70 g, 269.1 mmol) under nitrogen was slowly added, portionwise, sodium hydride (2.69 g, 67.3 mmol, 60 % in mineral oil). Once effervescence stopped, propargyl bromide (10.0 g, 67.3 mmol, 80 % (w/w) in toluene) was added to the white suspension, heated to 45 ºC and stirred at this temperature for 7.5 h. after cooling to rt, water (10 cm^3) was added and the mixture was extracted with chloroform (3 x 10 cm^3). The organic layers were combined, dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography using gradient elution from 30/70 v/v diethyl ether/petroleum ether to 100 % diethyl ether to give the product (2.91 g, 29.1 mmol, 43.2 %) as a pale yellow oil; (found (EI): M^+ + Na, 123.0416. $C_5H_8NaO_2$ requires M 123.0417); υ_{max}/cm^{-1} (thin film) 3398 (OH), 3281 (≡CH), 2934 and 2870 (CH_2), 2116 (C≡C), 1354, 1104 (C-O-C), 1065, 1027, 888; δ_H (300 MHz, $CDCl_3$) 4.22 (2 H, d, *J* 2.4, ≡CCH_2), 3.80-3.75 (2 H, m, C*H*$_2$O), 3.67-3.65 (2 H, m, C*H*$_2$O), 2.48 (1 H, t, *J* 2.4, ≡CH), 2.33 (1 H, t, *J* 6.0, OH); δ_C (100 MHz, $CDCl_3$) 79.42 (≡CH), 74.67 (*C*≡CH), 71.16 (CH_2), 61.63 (CH_2), 58.36 (CH_2); ESI-MS *m/z* (CI) 123 (M^+ + Na).

4.3. Synthesis of 2-(benzyloxy)ethanol.[19] To a stirred solution of ethylene glycol (11.13 g, 179.3 mmol) in a *N*,*N*-

dimethylformamide:methanol solution (1:1 v/v, 10 cm^3) was added sodium hydride (1.04 g, 26.0 mmol, 60 % in mineral oil) portion wise over a period of 20 – 25 minutes. The resulting solution was stirred at 20 – 22 ºC for 17 h, followed by the dropwise addition of benzyl bromide (3.07 g, 18.0 mmol). The reaction mixture was stirred at 20 – 22 ºC for 24 h, quenched with 10 % (v/v) HCl solution (11 cm^3) and extracted with ethyl acetate (3 x 20 cm^3). The organic layers were combined, washed with saturated NaCl solution (60 cm^3), dried (Na_2SO_4), filtered, and concentrated under reduced pressure to give the product (1.09 g, 7.16 mmol, 39.9 %) as a colourless oil. This was used directly without further purification in the next step; (found (EI): M^+ + Na 175.0732. $C_9H_{12}NaO_2$ requires M 175.0730); υ_{max}/cm^{-1} (thin film) 3394 (OH), 2927 and 2865 (CH_2), 1719, 1453, 1115 (C-O-C), 1068, 1028, 892, 739 and 698 (Ph); δ_H (400 MHz, $CDCl_3$) 7.38-7.27 (5 H, m, ArH), 4.56 (2 H, s, OC*H2*Ph), 3.75 (2 H, t, *J* 4.5, C*H2*O), 3.59 (2 H, t, *J* 4.5, C*H2*OH), 2.25 (1H, br s, OH); δ_C (100 MHz, $CDCl_3$) 137.90 (C), 128.42 (2 x CH), 127.76 (overlapping CH and 2 x CH), 73.25 (CH_2), 71.34 (CH_2), 61.83 (CH_2); ESI-MS *m/z* (CI) 175 (M^+ + Na). The spectroscopic data was in agreement with the literature values.

4.4. Synthesis of 2-(phenylmethoxy)ethanol-1-(4-4.4 methylbenzenesulfonate).[20] To a stirred solution of 2-(benzyloxy)ethanol (0.92 g, 6.0 mmol) in pyridine (9 cm^3) at 0 ºC was added *p*-toluenesulfonyl chloride (1.15 g, 6.05 mmol). The reaction mixture was stirred overnight at room temperature, diluted with water (20 cm^3) and extracted with diethyl ether (3 x 7 cm^3). The organic layers were combined, washed with saturated $NaHCO_3$ solution (10 cm^3) and saturated NaCl solution (10 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was then purified by flash column chromatography using gradient elution from 10/90 to 12/88 v/v EtOAc/petroleum ether to give the product (0.32 g, 1.04 mmol, 17.4 %) as a colourless oil; (found (EI): M^+ + Na 329.0816. $C_{16}H_{18}NaO_4S$ requires M 329.0818); υ_{max}/cm^{-1} (thin film) 2864 (CH_2), 1353 and 1174 (SO_2O), 1095 (C-O-C), 814 (*p*-substituted Ph), 722 and 698 (Ph); δ_H (300 MHz, $CDCl_3$) 7.79 (2 H, d, *J* 8.4, ArH), 7.36-7.24 (7 H, m, ArH), 4.48 (2 H, s, OC*H2*Ph), 4.21-4.18 (2 H, m, C*H2*OTs), 3.67-3.64 (2 H, m, C*H2*OCH2Ph), 2.43 (3 H, s, CH_3 of OTs); δ_C (75 MHz, $CDCl_3$) 144.74 (C), 137.50 (C), 132.95 (C), 129.77 (2 x CH), 128.38 (2 x CH), 127.94 (2 x CH), 127.77 (CH), 127.62 (2 x CH), 73.19 (CH_2), 69.24 (CH_2), 67.45 (CH_2), 21.61 (CH_3); ESI-MS *m/z* (CI) 329 (M^+ + Na).

4.5, Synthesis of [(2-azidoethoxy)methyl]benzene 7.[21] To a stirred solution of 2-(phenylmethoxy)ethanol-1-(4-methylbenzenesulfonate) (0.10 g, 0.33 mmol) in *N,N*-dimethylformamide (3 cm^3) was added sodium azide (0.032 g, 0.49 mmol); and the reaction mixture was heated to 85 – 90 ºC, and stirred at this temperature for 3.5 h. After cooling rt, water (3 cm^3) was added to the pale yellow solution and extracted with diethyl ether (3 x 3 cm^3). The organic layers were combined, washed with water (10 cm^3) and saturated NaCl (10 cm^3) successively, dried (Na_2SO_4), filtered and concentrated under reduced pressure to give **7** (0.042 g, 0.24 mmol, 72.7 %) as a pale yellow oil; (found (EI): M^+ + Na, 200.0799. $C_9H_{11}N_3NaO$ requires M 200.0794); υ_{max}/cm^{-1} (thin film) 2923 and 2861 (CH_2), 2092 (N_3), 1107 (C-O-C), 1092, 697 (Ph); δ_H (400 MHz, $CDCl_3$) 7.38-7.27 (5 H, m, ArH), 4.58 (2 H, s, OC*H2*Ph), 3.66 (2 H, t, *J* 5.0, C*H2*CH2N3), 3.41 (2 H, t, *J* 5.0, CH2C*H2*N3); δ_C (100 MHz, $CDCl_3$) 137.69 (C), 128.41 (2 x CH), 127.73 (CH), 127.58 (2 x CH), 73.23 (CH_2), 68.81 (CH_2), 50.77 (CH_2); ESI-MS *m/z* (CI) 200 (M^+ + Na).

4.6, Synthesis of *N*-[(*R*,*R*)-2-(prop-2-ynyloxyethylamino)-1,2-diphenylethyl]-4-methyl benzenesulfonamide 6. To a stirred solution of 2-(2-propynyloxy)ethanol (0.25 g, 2.5 mmol) and 2,6-lutidine (0.35 g, 3.3 mmol) in dichloromethane (5 cm^3) was added dropwise trifluoromethanesulfonic anhydride (0.70 g, 2.5 mmol) at 0 – 5 ºC. The solution was then stirred at 5 – 10 ºC for 45 minutes, heated to 22 ºC and stirred at this temperature for 1.5 h. In a separate round-bottomed flask, triethylamine (0.37 g, 3.7 mmol) was added to a solution of (*R*,*R*)-TsDPEN (0.57 g, 1.6 mmol) in dichloromethane (3 cm^3) at 5 ºC. The triflate solution was then added dropwise to this TsDPEN solution whilst maintaining the temperature between 0 – 5 ºC. The reaction mixture was warmed to rt and left to stir overnight. The solution was then diluted with saturated $NaHCO_3$ (20 cm^3) and extracted with dichloromethane (10 cm^3). The organic layer was further washed with saturated $NaHCO_3$ (2 x 20 cm^3), water (20 cm^3), saturated NaCl (20 cm^3), dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash column chromatography (20/80 v/v EtOAc/petroleum ether) to give **6** (0.45 g, 1.0 mmol, yield 64.3 %) as a colourless oil; (found (EI): M^+ + H, 449.1896. $C_{26}H_{29}N_2O_3S$ requires M, 449.1893); $[\alpha]_D^{30}$ +5.6 (*c* 0.22, $CHCl_3$); υ_{max}/cm^{-1} (thin film) 3273 (≡CH), 2919 and 2856 (CH_2), 2100 (C≡C), 1598, 1323 and 1154 (SO_2), 1090 (C-O-C), 812 (Ph), 762 and 698 (Ph), 665; δ_H (400 MHz, $CDCl_3$) 7.38 (2 H, d, *J* 8.4, ArH), 7.13-6.89 (12 H, m, ArH), 6.31 (1H, br s, NHTs), 4.23 (1 H, d, *J* 8.0, PhC*H*NHTs), 4.06 (2 H, t, *J* 1.8, C*H2*C≡CH), 3.65 (2 H, d, *J* 8.0, PhC*H*NHCH2), 3.60-3.55 (1 H, m, NHCH_aH$_b$), 3.52-3.47 (1 H, m, NHCH$_a$$H_b$), 2.67-2.61 (1 H, m, CH2CH_aH$_b$O), 2.51-2.46 (1 H, m, CH2CH$_a$CH_bO), 2.44 (1 H, t, *J* 2.4, ≡CH), 2.34 (3 H, s, CH_3 of NTs), 1.72 (1 H, br s, NH); δ_C (100 MHz, $CDCl_3$) 142.68 (C), 139.10 (C), 138.27 (C), 137.08 (C), 129.10 (2 x CH), 128.32 (2 x CH), 127.89 (2 x CH), 127.63 (2 x CH), 127.50 (CH), 127.45 (2 x CH), 127.26 (CH), 127.17 (2 x CH), 79.64 (≡CH), 74.62 (*C*≡CH), 69.18 (CH_2), 67.78 (CH), 63.13 (CH), 58.17 (CH_2), 46.46 (CH_2), 21.45 (CH_3); ESI-MS *m/z* (CI) 449 (M^+ + H), 471 (M^+ + Na).

5.7. Synthesis of *N*-[(*R*,*R*)-2-(hex-5-ynylamino)-1,2-diphenylethyl]-4-methyl benzenesulfonamide 10. To a stirred solution of hexyn-1-ol (1.04 g, 10.6 mmol) and 2,6-lutidine (2.38 g, 22.2 mmol) in dichloromethane (21 cm^3) was added dropwise trifluoromethanesulfonic anhydride (4.78 g, 16.95 mmol) at 0 – 5 ºC. The solution was then stirred at 5 – 10 ºC for 1 h, heated to 22 ºC and stirred at this temperature for 1.5 h. In a separate round-bottomed flask, triethylamine (1.61 g, 15.9 mmol) was added to a solution of (*R*,*R*)-TsDPEN (2.32 g, 6.33 mmol) in dichloromethane (10 cm^3) at 5 ºC. The triflate solution was then added dropwise to this TsDPEN solution whilst maintaining the temperature between 0 – 5 ºC. The reaction mixture was warmed to rt and left to stir overnight. The solution was then diluted with saturated $NaHCO_3$ (50 cm^3) and extracted with dichloromethane (24 cm^3). The organic layer was washed further with saturated $NaHCO_3$ (3 x 20 cm^3), water (2 x 50 cm^3), saturated NaCl (50 cm^3), dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash column chromatography (16/84 v/v EtOAc/petroleum ether) to give **10** (1.11 g, 2.49 mmol, 39.3 %) as a white solid; Mp 95 – 97 ºC; (found (EI): M^+ + H, 447.2105. $C_{27}H_{31}N_2O_2S$ requires M 447.2101); $[\alpha]_D^{24}$ -26.6 (*c* 0.38, $CHCl_3$); υ_{max}/cm^{-1} (solid) 3281 (≡CH), 2932 and 2859 (CH_2), 2324 (C≡C), 1601, 1326 and 1159 (SO_2), 1086 (C-O-C), 816 (Ph), 762 and 699 (Ph), 669; δ_H (400 MHz, $CDCl_3$) 7.38 (2 H, d, *J* 8.4, ArH), 7.14-6.89 (12 H, m, ArH), 6.25 (1 H, br s, NHTs), 4.25 (1 H, d, *J* 8.0, PhC*H*NHTs), 3.61 (2 H, d, *J* 8.0, PhC*H*NHCH$_2$), 2.44-2.37 (1 H, m, NHCH_aH_bCH$_2$), 2.33 (3 H, s, CH_3 of NTs), 2.33-2.26 (1 H, m, NHCH$_a$$H_bCH_2$), 2.15-2.12 (2 H, m, C$H_2$C≡CH), 1.93 (1 H, t, *J* 2.6, ≡CH), 1.56-1.41 (4H, m, NHCH$_2$CH_2CH_2), 1.23 (1 H, br s, NH); δ_C (100 MHz, $CDCl_3$) 142.63 (C), 139.19 (C), 138.25 (C), 136.97 (C), 129.01 (2 x CH), 128.21 (2 x CH), 127.81 (2 x CH), 127.48 (2 x CH), 127.37 (CH), 127.32 (2 x CH), 127.16 (CH), 127.04 (2 x CH), 84.12 (≡CH), 68.47 (*C*≡CH), 67.74 (CH), 63.01 (CH), 46.49 (CH_2), 28.95 (CH_2), 25.87 (CH_2), 21.35 (CH_3), 18.14 (CH_2). ESI-MS *m/z* (CI) 447 (M^+ + H), 469 (M^+ + Na).

4.8. Synthesis of *N*-[(*R*,*R*)-2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)butylamino)-1,2-diphenylethyl]-4-methylbenzene-sulfonamide 9. To a stirred solution of benzyl bromide (0.083 g, 0.48 mmol) in *tert*-butanol:water (1:1 v/v, 1.2 cm^3) was added *N*-[(*R*,*R*)-2-(hex-5-ynylamino)-1,2-diphenylethyl]-4-methylbenzene-sulfonamide **10** (0.22 g, 0.49 mmol) and sodium azide (0.033 g, 0.51 mmol). Sodium ascorbate (9.6 x 10^{-3} g, 0.048 mmol) and copper(II) sulfate pentahydrate (6.0 x 10^{-3} g, 0.024 mmol) were then added sequentially to this solution and the reaction mixture was stirred at 60 ºC for 3 h (whilst monitoring by TLC and mass spectrometry). The resultant brown solution was quenched with cold water (1.8 cm^3) and 10 % aqueous ammonia solution (0.4 cm^3); and the mixture was stirred for 15 minutes. The mixture was concentrated under reduced pressure to remove *tert*-butanol and the residue was dissolved in a solution of water (5 cm^3) and EtOAc (6 cm^3). The water layer was re-extracted with ethyl acetate (5 cm^3) and the organic layers combined, washed with water (10 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash column chromatography using gradient elution from 70/30 to 80/20 v/v EtOAc/petroleum ether (silica column pre-treated with 1 % triethylamine) to give **9** (0.19 g, 0.33 mmol, 66.6 %) as a colourless oil; $[\alpha]_D^{30}$ +4.7 (*c* 0.315, $CHCl_3$); (found (EI): M^+ + H, 580.2758. $C_{34}H_{38}N_5O_2S$ requires M 580.2741); υ_{max}/cm^{-1} (thin film) 3254 (NH), 2926 and 2858 (CH_2), 1600, 1454, 1320 and 1153 (SO_2), 811 (*p*-substituted Ph), 760 and 698 (Ph), 666; δ_H (700 MHz, $CDCl_3$) 7.38-7.33 (5 H, m, ArH), 7.28-7.26 (2 H, m, ArH), 7.21 (1 H, s, CH of triazole), 7.11-7.10 (3 H, m, ArH), 7.04-6.98 (5 H, m, ArH), 6.91-6.87 (4 H, m, ArH), 6.35 (1 H, br s, NH), 5.50 (2 H, s, CH_2Ph), 4.23 (1 H, d, *J* 9.1, PhC*H*NHTs), 3.59 (1 H, d, *J* 9.1, PhC*H*NHCH$_2$), 2.64 (2 H, t, *J* 8.8, CH_2C(C)N), 2.43-2.39 (1 H, m, NHCH_aH_bCH$_2$), 2.32 (3 H, s, CH_3 of NHTs), 2.32-2.27 (1 H, m, NHCH$_a$$H_bCH_2$), 1.66-1.55 (2 H, m, NHCH$_2$CH$_2$CH_2), 1.48-1.37 (2H, m, NHCH$_2$CH_2CH$_2$); δ_C (176 MHz, $CDCl_3$) 148.33 (C), 142.65 (C), 139.17 (C), 138.18 (C), 136.97 (C), 134.95 (C), 129.02 (4 x CH), 128.56 (CH), 128.23 (2 x CH), 127.98 (2 x CH), 127.80 (2 x CH), 127.54 (2 x CH), 127.40 (CH), 127.36 (2 x CH), 127.16 (CH), 127.06 (2 x CH), 120.65 (CH of triazole), 67.69 (CH), 63.04 (CH), 53.96 (CH_2), 46.64 (CH_2), 29.30 (CH_2), 26.78 (CH_2), 25.36 (CH_2), 21.38 (CH_3). ESI-MS *m/z* (CI) 580 (M^+ + H), 602 (M^+ + Na).

4.9. Synthesis of *N*-[(*R*,*R*)-2-(1-phenoxymethyl-1*H*-1,2,3-triazol-4-yl)methoxy ethylamino)-1,2-diphenylethyl]-4-methylbenzenesulfonamide 8. To a stirred solution of [(2-azidoethoxy)methyl]benzene **7** (0.030 g, 0.17 mmol) in *tert*-butanol:water (8:2 v/v, 1.3 cm^3) was added *N*-[(*R*,*R*)-2-(prop-2-ynyloxyethylamino)-1,2-diphenylethyl]-4-methylbenzene sulfonamide **6** (0.076 g, 0.17 mmol). Sodium ascorbate (3.3 x 10^{-3} g, 0.017 mmol) and copper(II) sulfate pentahydrate (0.021 g, 0.08 mmol) were added sequentially and the reaction mixture was stirred at 30 ºC for 5 h whilst monitoring by TLC (R_f product = 0.48, R_f starting alkyne = 0.85; eluent: EtOAc = 100 %; potassium permanganate stain). The pale blue solution was concentrated under reduced pressure and the oily residue was dissolved in a mixture of water (2.5 cm^3) and ethyl acetate (3 cm^3). The water layer was re-extracted with EtOAc (3 cm^3) and the organic layers combined, washed with 6 % (w/v) NaCl solution, dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash column chromatography using gradient elution from 70/30 to 75/25 v/v EtOAc/petroleum ether to give **8** (0.064 g, 0.10 mmol, 60.5 %) as a colourless oil; $[\alpha]_D^{32}$ +6.7 (*c* 0.115, $CHCl_3$); (found (EI): M^+ + H, 626.2801. $C_{35}H_{40}N_5O_4S$ requires M, 626.2796); υ_{max}/cm^{-1}

(thin film) 3272 (NH), 2919 and 2866 (CH_2), 1720, 1600, 1453, 1319 and 1154 (SO_2), 1093, 932, 813 (*p*-substituted Ph), 768 and 699 (Ph), 667; δ_H (400 MHz, $CDCl_3$) 7.71 (1 H, s, CH of triazole), 7.37-7.25 (7 H, m, ArH), 7.10-7.09 (3 H, m, ArH), 7.01-6.95 (5 H, m, ArH), 6.92-6.86 (4 H, m, ArH), 4.59 (overlapping 2 H, s, C*H₂*C(C)N and 2 H, t, *J* 5.2, $PhCH_2OCH_2$), 4.52 (2 H, s, $PhCH_2OCH_2$), 4.25 (1 H, d, *J* 8.2, PhC*H*NHTs), 3.87 (2 H, t, *J* 5.2, $PhCH_2OCH_2CH_2$), 3.67 (1 H, d, *J* 8.2, PhC*H*NHCH₂), 3.61-3.56 (1 H, qd, $NHCH_2CH_aH_bO$), 3.51-3.47 (1 H, m, $NHCH_2CH_aH_bO$), 2.68-2.63 (1 H, m, $NHCH_aH_bCH_2O$), 2.52-2.46 (1 H, m, $NHCH_aH_bCH_2O$), 2.31 (3 H, s, CH_3 of NHTs); δ_C (100 MHz, $CDCl_3$) 144.88 (C), 142.58 (C), 139.18 (C), 138.21 (C), 137.12 (C), 129.01 (2 x CH), 128.49 (2 x CH), 128.21 (2 x CH), 127.91 (CH), 127.78 (2 x CH), 127.68 (2 x CH), 127.54 (overlapping CH and 2 x CH), 127.53 (2 x CH), 127.40 (CH), 127.08 (2 x CH), 123.71 (CH of triazole), 73.25 (CH_2), 69.29 (CH_2), 68.28 (CH_2), 67.55 (CH), 64.32 (CH_2), 63.28 (CH), 50.33 (CH_2), 46.44 (CH_2), 21.38 (CH_3); ESI-MS *m/z* (CI) 626 (M^+ + H), 648 (M^+ + Na).

4.10. Synthesis of HEMA/MMA copolymers 12a-c. The synthesis of polymer **12b** is provided as a representative procedure for the polymerisation of HEMA and MMA with 4,4'-azobis(4-cyanovaleric acid) as the initiator and CoBF as the catalyst. MMA and HEMA were purified by passing through basic alumina to remove inhibitors and acidic impurities; and degassed by bubbling nitrogen gas for 30 minutes. The water was also degassed by bubbling nitrogen gas for 30 minutes prior to use. All three polymers were prepared using a [HEMA]:[MMA] molar ratio of [30]:[70]. The [HEMA]/[MMA]/[CoBF] ratios for **12a/b** and **12c** were [0.42]/[1.0]/[4.27 x 10^{-5}] and [0.42]/[1.0]/[2.14 x 10^{-5}] respectively. Functionalisation of hydroxyl groups $f_{hydroxyl}$ = 2.77 mmol/g, calculated from ^{1}H NMR analysis. The spectroscopic data was in agreement with the literature values.[9]

4.11. Synthesis of HEMA/MMA copolymer 12b.
Dioctylsulfosuccinate sodium salt (0.29 g, 0.67 mmol) was added to deoxygenated water (65 cm^3) in a 150 mL 3-necked round-bottomed flask under nitrogen. The aqueous mixture was further degassed by two freeze-pump-thaw cycles before being heated to 80 ºC. The monomer/catalyst feed was then prepared in a Schlenk tube, whereby deoxygenated and inhibitor-free MMA (18.72 g, 187.0 mmol) and HEMA (10.34 g, 79.46 mmol) were added; and the tube was pump-filled with nitrogen three times. The catalytic chain transfer agent, CoBF (3.6 x 10^{-3} g, 8.0 x 10^{-3} mmol) was then added, and the mixture was left to stir for 10 minutes until all the CoBF dissolved to give an orange solution. Immediately prior to the transfer of the monomer/catalyst feed, 4,4'-azobis(4-cyanovaleric acid) (0.29 g, 1.0 mmol) was added to the aqueous solution at 80 ºC. The monomer/catalyst feed was then transferred to the aqueous solution *via* syringe at a rate of 3 mL min^{-1} during which the aqueous solution turned opaque. Once addition was complete the mixture was left to stir at 80 ºC for 4 h. The water was then removed from the polymer by concentrating the mixture at 90 ºC under reduced pressure to give the HEMA/MMA copolymer as a pale yellow paste. This was triturated with petroleum ether, filtered, dried under reduced pressure and ground using a pestle and mortar to give the HEMA/MMA (3:7 ratio) copolymer **12b** (28.4 g, 98.1 % based on mass) as a white solid; υ_{max}/cm^{-1} (solid) 3502 (OH), 2992 and 2952, 1721 (C=O), 1480, 1448, 1387, 1240, 1147, 1075, 987, 965; δ_H (300 MHz, $CDCl_3$) 6.26-6.20 (m, CH), 5.62-5.48 (m, CH), 4.12 (2 H of HEMA, br s, CH_2CH_2OH), 3.84 (2 H of HEMA, br s, CH_2CH_2OH), 3.61 (3 H of MMA, br s, OCH_3), 2.18-1.83 (2 H of polymer, br m, CH_2), 1.27-0.84 (3 H of polymer, br m, CCH_3); δ_C (100 MHz, $CDCl_3$) 178.01 (C=O), 176.73 (C=O), 66.67 (CH_2CH_2OH), 60.27 (CH_2CH_2OH), 54.27 (CH_2), 52.89 (C), 51.71 (OCH_3), 44.84 (CH_2), 44.43 (CH_2), 18.64 (CH_3), 16.85 (CH_3); GPC *m/z* M_n = 973, M_w = 1789, PDI = 1.84; ESI-MS *m/z* (CI); M_n was also determined to be 1570 g/mol by the integration of the multiplets at 6.2 ppm (0.11 H) and 5.6 ppm (0.11 H); the two CH_2 signals at 4.1 ppm (0.95 H) and 3.8 ppm (0.95 H); and the CH_3 signal at 3.6 ppm (3 H) in the ^{1}H NMR spectrum.

4.12. Synthesis of Tosylated HEMA/MMA Copolymers 13a-c. The synthesis of tosylated HEMA/MMA copolymer **13b** is a representative procedure for the functionalisation of copolymers **12a-c**. Functionalisation of tosyl groups f_{tosyl} = 1.93 mmol/g, calculated from ^{1}H NMR analysis. This compound has been reported and fully characterised; and the spectroscopic data was in agreement with the literature values.[9]

4.13. Synthesis of tosylated HEMA/MMA copolymer 13b.
HEMA/MMA copolymer **12b** (5.00 g, 13.9 mmol HEMA units), dichloromethane (35 cm^3), *p*-toluenesulfonyl chloride (4.90 g, 25.7 mmol), DMAP (0.25 g, 2.1 mmol) and triethylamine (2.46 g, 24.3 mmol) were reacted according to the general procedure to give the crude product as a red gum. This was triturated using petroleum ether and the pale red solid was filtered and washed with petroleum ether (400 cm^3). The polymer was then ground using a pestle and mortar and dried under reduced pressure to give the tosylated HEMA/MMA copolymer **13b** (4.70 g, 9.07 mmol HEMA units, 65.5 %) as a pale yellow oil; υ_{max}/cm^{-1} (thin film) 2991 and 2951, 1724 (C=O), 1481, 1448, 1360 (SO_2), 1242, 1173 (SO_2), 1147, 920, 815, 749 (Ph); δ_H (300 MHz, $CDCl_3$) 7.81 (2 H, br s, CH *o* to SO_2 on OTs), 7.38 (2 H, br s, CH *o* to CH_3 on OTs), 6.21-6.17 (m, CH), 5.55-5.48 (m, CH), 4.22 (2 H of HEMA, br s, CH_2CH_2OTs), 4.14 (2 H of HEMA, br s, CH_2CH_2OTs), 3.60 (3 H of MMA, br s, OCH_3), 2.5 (3 H of HEMA, br s, CH_3 of OTs), 2.07-1.82 (2 H of polymer, br m, CH_2), 1.10-

0.83 (3 H of polymer, br m, CCH_3); δ_C (75 MHz, $CDCl_3$) 177.63 (C=O), 176.64 (C=O), 144.95 (C *o* to SO_2 on OTs), 132.46 (C *o* to CH_3 on OTs), 129.85 (CH *o* to SO_2 on OTs), 127.72 (CH *o* to CH_3 on OTs), 67.19 (CH_2CH_2OTs), 61.92 (CH_2CH_2OTs), 54.16 (CH_2), 52.67 (C), 51.60 (OCH_3), 44.63 (CH_2), 44.27 (CH_2), 21.47 (CH_3 of OTs), 18.51 (CH_3), 16.23 (CH_3); *m/z* (GPC) M_n = 1773, M_w = 2817, PDI = 1.59; M_n was also determined to be 1617 g/mol by the integration of the multiplets at 6.2 ppm (0.11 H) and 5.5 ppm (0.10 H); the two CH_2 signals at 4.2 ppm and 4.1 ppm (1.82 H combined); and the CH_3 signal at 3.6 ppm (3 H) in the ^{1}H NMR spectrum.

4.14. Synthesis of Azido Derivatised HEMA/MMA Copolymers 14a-c. The synthesis of azido derivatised HEMA/MMA copolymer **14b** is a representative procedure for the functionalisation of tosylated HEMA/MMA copolymers **13a-c**. Functionalisation of azido groups f_{azido} = 2.58 mmol/g, calculated from ^{1}H NMR analysis. This compound is novel.

4.15. Synthesis of azido derivatised HEMA/MMA copolymer 14b. The tosylated HEMA/MMA copolymer **13b** (2.43 g, 4.69 mmol), sodium azide (0.93 g, 14.3 mmol) and anhydrous *N,N*-dimethylformamide (61 cm^3) were reacted according to the general procedure for 2 days. Dichloromethane (200 cm^3) and water (100 cm^3) were then added to the reaction mixture and the organic layer separated, re-extracted with water (4 x 100 cm^3) and saturated NaCl solution (100 cm^3), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was triturated with petroleum ether, and the resultant solid was filtered and washed with water (100 cm^3) and petroleum ether (100 cm^3). The polymer was then dried under reduced pressure at 90 ºC and ground using a pestle and mortar to give **14b** (0.45 g, 1.2 mmol, 25.6 %) as a pale yellow solid; υ_{max}/cm $^{-1}$ (solid) 2993 and 2951, 2104 (N_3), 1722 (C=O), 1479, 1446, 1388, 1270, 1239, 1143, 989, 965, 842; δ_H (400 MHz, $CDCl_3$) 6.30-6.20 (m, CH), 5.60-5.47 (m, CH), 4.12 (2 H of HEMA, br s $CH_2CH_2N_3$), 3.60 (3 H of MMA, br s, OCH_3), 3.50 (2 H of HEMA, br s, $CH_2CH_2N_3$), 2.07-1.82 (2 H of polymer, br m, CH_2), 1.26-0.84 (3 H of polymer, br m, CCH_3); δ_C (100 MHz, $CDCl_3$) 178.33 (C=O), 177.06 (C=O), 63.74 ($CH_2CH_2N_3$), 54.33 (CH_2), 52.87 (C), 51.78 (OCH_3), 49.47 ($CH_2CH_2N_3$), 44.86 (CH_2), 44.49 (CH_2), 18.72 (CH_3), 16.44 (CH_3); *m/z* (GPC) M_n = 2451, M_w = 7110, PDI = 2.90; M_n was also determined to be 2878 g/mol by the integration of the multiplets at 6.3 ppm (0.05 H) and 5.5 ppm (0.06 H); the two CH_2 signals at 4.1 ppm (0.81 H) and 3.5 ppm (0.81 H); and the CH_3 signal at 3.6 ppm (3 H) in the ^{1}H NMR spectrum.

4.16. Synthesis of *N*-[(*R*,2*R*)-2-(1-ethoxy-1*H*-1,2,3-triazol-4-yl)butylamino)-1,2-diphenylethyl]-4-methylbenzenesulfonamide derivatised HEMA/MMA Copolymers 15a-c. The monotosylated 1,2-diamine derivatised HEMA/MMA copolymer **15a** was synthesised from the azido derivatised HEMA/MMA copolymer **14a** using a Cu(II)/sodium ascorbate mixture. Polymers **15b-c** were synthesised using the Cu(I)/TBTA system. Functionalisation of monotosylated 1,2-diamine $f_{diamine}$ = 1.20 mmol/g, calculated from the HEMA:MMA (3:7) ratio of the previous polymers (**12** – **14**). This compound is novel.

4.17. Synthesis of *N*-[(*R*,2*R*)-2-(1-ethoxy-1*H*-1,2,3-triazol-4-yl)butylamino)-1,2-diphenylethyl]-4-methylbenzenesulfonamide derivatised HEMA/MMA copolymer 15a. To a stirred mixture of azido derivatised HEMA/MMA copolymer **14a** (0.24 g, 0.62 mmol) and *N*-[(*R*,*R*)-2-(hex-5-ynylamino)-1,2-diphenylethyl]-4-methyl benzenesulfonamide **10** (0.20 g, 0.44 mmol) in *tert*-butanol:water (1:1 v/v, 17 cm^3) were added sequentially sodium ascorbate (0.0009 g, 4 x 10^{-6} mmol) and copper(II) sulfate (0.0055 g, 2.2 x 10^{-5} mmol). The suspension was heated to 80 ºC and stirred at this temperature for 3 days, following which the solid was filtered and washed with dichloromethane. The filtered polymer was suspended in dichloromethane (100 cm^3) and stirred at 40 ºC for 30 minutes, cooled to room temperature, filtered, washed with dichloromethane and dried under vacuum to give **15a** (0.36 g, 0.43 mmol, 97.7 %) as a blue solid; υ_{max}/cm $^{-1}$ (solid) 2991 and 2949, 1725 (C=O), 1599, 1452, 1387, 1266, 1241, 1146, 985, 966, 914, 812, 757 and 699 (Ph), 665. Spectroscopic and GPC data could not be obtained due to the insolubility of the functionalised polymer in a range of solvents, namely acetone, chloroform, dichloromethane, *N,N*-dimethylformamide, dimethylsulfoxide, methanol, tetrahydrofuran, 1,2-dichloroethane, benzene, pyridine, acetonitrile and water. Attempts at dissolving the polymer at higher temperatures were not successful.

4.18. Synthesis of *N*-[(*R*,*R*)-2-(1-ethoxy-1*H*-1,2,3-triazol-4-yl)butylamino)-1,2-di phenylethyl]-4-methylbenzene-sulfonamide derivatised HEMA/MMA copolymer 15b. To a stirred solution of azido derivatised HEMA/MMA copolymer **14b** (0.024 g, 0.062 mmol), triethylamine (2 µl, 1.45 mg, 1.40 x 10^{-2} mmol) and DMSO-d_6 (1.0 cm^3) was added *N*-[(*R*,*R*)-2-(hex-5-ynylamino)-1,2-diphenylethyl]-4-methylbenzene sulfonamide **10** (0.022 g, 0.049 mmol); and the mixture was degassed by two freeze-pump-thaw cycles before being placed under nitrogen. TBTA (0.008 g, 0.015 mmol) and copper(I) bromide (0.002 g, 0.014 mmol) were then added to the solution, and the reaction was quickly placed under vacuum and then nitrogen. The reaction mixture was stirred at 20 ºC for 24 h, following which the solution was analysed by ^{1}H NMR to determine the extent of reaction. Once the presence of the azido derivatised HEMA/MMA copolymer could not be detected; water (20 cm^3) was added to the solution and the precipitated solid was filtered, washed with water (50 cm^3) and petroleum ether (50 cm^3), and dried under reduced pressure to give

15b (0.017 g, 0.02 mmol, 40.8 %) as a blue solid; υ_{max}/cm^{-1} (solid) 2989 and 2949, 1726 (C=O), 1600, 1455, 1267, 1137, 966, 911, 812, 758 and 670 (Ph), 665; δ_H (400 MHz, $CDCl_3$) 7.70 (1 H, s, CH of triazole), 7.35-6.85 (14 H of diamine, m, ArH), 5.45 (2 H of HEMA, s, CH_2), 4.65 (2 H of HEMA, br s, CH_2), 4.35 (2 H of polymer, br s, CH_2), 3.70 (1 H of diamine, s, CH-1,2-diamine), 3.55 (br s, overlapping 3 H, OCH_3 and CH_2-1,2-diamine), 2.48 (3 H of diamine, br s, CH_3 of NTs), 2.10-1.40 (2 H of polymer, br m, CH_2), 1.67-1.47 (2 H of diamine, br m, CH_2-1,2-diamine), 1.25-0.78 (3 H of polymer, br m, CCH_3).

4.19. Representative Procedures for ketone reductions

Method A: A solution of ruthenium dimer (0.008 mmol) and diamine ligand (0.016 mmol) in the formic acid/triethylamine (5:2) azeotropic mixture (1.0 cm^3) was stirred at 28 ºC for 1 h, after which the substrate (1.6 mmol) was added. The reaction mixture was then stirred at 28 ºC for the amount of time recorded. At intervals, a small aliquot of the reaction mixture was passed through a short column of silica gel in a Pasteur pipette and eluted with ethyl acetate. This solution was analysed by chiral GC to determine the conversion and enantiomeric excess. Once the specified conversion was achieved, the solution was passed through a column of silica gel, eluted with ethyl acetate, concentrated under reduced pressure and purified by flash column chromatography to afford the alcohol product.

Method B: A solution of ruthenium dimer (0.008 mmol) and diamine ligand (0.016 mmol) in anhydrous isopropanol (0.32 cm^3) was stirred at 80 ºC for 25 minutes. After cooling to 28 ºC, a 0.1 M potassium hydroxide solution (0.284 cm^3, 0.04 mmol) was added followed by a solution of substrate (1.6 mmol) in isopropanol (13 cm^3); and the reaction mixture was stirred at 28 ºC for the amount of time recorded. At intervals, a small aliquot of the reaction mixture was passed through a short column of silica gel packed in a Pasteur pipette and eluted with ethyl acetate. The solution was analysed by chiral GC to determine the conversion and enantiomeric excess.

Method C: A solution of ruthenium dimer (6.6 x 10^{-3} mmol) and diamine ligand (13.2 x 10^{-3} mmol) in water (3 cm^3) was stirred at 60 ºC for 1 h. Sodium formate (6.6 mmol) was added to the solution followed by the substrate (0.6 mmol); and the reaction mixture was stirred at 60 ºC for the amount of time recorded. At intervals, a small aliquot of the reaction mixture was cooled to room temperature and the product extracted with ethyl acetate. The ethyl acetate layer was passed through a short column of silica gel in a Pasteur pipette and analysed by chiral GC to determine the conversion and enantiomeric excess.

4.20. Procedure for ketone reductions using the polymer-supported diamine ligand: Ruthenium dimer (6.6 x 10^{-3} mmol), polymer-supported diamine ligand (0.013 mmol or 0.063 mmol: equivalent to 1 mol % and 4.8 mol % respectively), substrate (1.3 mmol) and formic acid/triethylamine (5:2) azeotrope (0.8 cm^3) were reacted according to method A. After completion of the reaction, the polymeric ligand was removed from the mixture by filtration for the recycle experiment; washed with an appropriate solvent; and dried under reduced pressure. The ligand was then added to a clean Schlenk tube and subjected to fresh portions of formic acid/triethylamine (5:2) azeotrope (0.8 cm^3) and substrate (1.3 mmol); and reduction monitored by GC analysis.

4.21. NMR Monitoring Experiments.

In a NMR tube equipped with a magnetic stirrer was added ruthenium dimer (0.005 mmol), diamine ligand (0.01 mmol) and d^6-benzene (0.05 cm^3) in the formic acid/triethylamine (5:2) azeotropic mixture (0.7 cm^3). The NMR tube was shaken gently and a NMR cap with holes was then fitted. The catalytic mixture was stirred at 28 ºC for 1 h, following which acetophenone (1.1 mmol) was added using a syringe. The NMR tube was again shaken gently using a cap without holes and then left to stir at 28 ºC for the amount of time recorded. The reduction was monitored in two ways: (1) NMR tube was placed in the NMR spectrometer, and the reaction monitored using a pre-set program which records chromatograms at regular intervals at 28 ºC; and (2) at intervals the NMR sample was removed from the oil bath set at 28 ºC and analysed using the NMR spectrometer. Data analysis was performed using the MestreC software. The conversion of acetophenone to 1-phenylethanol was calculated by comparing the integration of the proton C***H***OH in the product alcohol (4.9 ppm) with the integration of the 3 protons C$\boldsymbol{H_3}$ in acetophenone (2.5 ppm).

4.22. 1-Phenylethanol.[4] $[\alpha]_D^{28}$ +52.2 (c 1.0 $CHCl_3$) 95 % ee (*R*) (lit.[4] $[\alpha]_D^{22}$ +49.0 (c 1.0, $CHCl_3$) 98 % ee (*R*)); δ_H (400 MHz; $CDCl_3$) 7.38-7.24 (5 H, m, ArH), 4.88 (1 H, q, *J* 6.4, PhC*H*(OH)), 1.98 (1 H, br s, OH), 1.49 (3 H, d, *J* 6.4, CH_3); δ_C (75 MHz; $CDCl_3$) 145.8 (C), 128.5 (2 x CH), 127.4 (CH), 125.4 (2 x CH), 70.4 (CH), 25.1 (CH_3); Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-*β*-236M-19 50m, T = 115 ºC, P = 15 psi, gas H_2, ketone 10.0 min, *R* isomer 15.4 min, *S* isomer 16.7 min). The spectroscopic data was in agreement with the literature values. The product configuration was determined by comparing the result to an authentic, commercially bought reference sample.

4.23. 2-Furylethanol 16. δ_H (400 MHz; $CDCl_3$) 7.28 (1 H, d, *J* 2.0, ArH α to O), 6.24 (1 H, dd, *J* 3.4 and 2.0, ArH *β* to O and *β* to CH(OH)CH_3), 6.14 (1 H, d, *J* 3.4, ArH α to CH(OH)CH_3), 4.78 (1 H, q, *J* 6.4, C*H*OH), 2.32 (1 H, br s, OH), 1.44 (3 H, d, *J* 6.4, CH_3); δ_C (100 MHz; $CDCl_3$) 157.58 (C), 141.78 (CH), 110.03 (CH), 105.00 (CH), 63.48

(CH), 21.17 (CH_3); Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-*β*-236M-19 50m, T = 85 °C, P = 15 psi, gas H_2, ketone 11.2 min, *R* isomer 17.2 min, *S* isomer 18.3 min). The spectroscopic data was in agreement with the literature values.[22]

4.24. 1-Phenylpropan-1-ol 17. δ_H (300 MHz; $CDCl_3$) 7.38-7.24 (5 H, m, ArH), 4.59 (1 H, td, *J* 6.6 and 3.3, PhC*H*(OH)), 1.90-1.68 (overlapping 1 H, d, *J* 3.3, OH and 2 H, m, CH_2), 0.92 (3 H, t, *J* 7.5, CH_3); δ_C (75 MHz; $CDCl_3$) 144.56 (C), 128.38 (2 x CH), 127.48 (CH), 125.94 (2 x CH), 76.01 (CH), 31.86 (CH_2), 10.13 (CH_3); Enantiomeric excess and conversion determined by GC analysis (Chrompac cyclodextrin-*β*-236M-19 50m, T = 115 °C, P = 15 psi, gas H_2, ketone 13.6 min, *R* isomer 20.8 min, *S* isomer 21.9 min). The spectroscopic data was in agreement with the literature values.[23]

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Supplementary Material

Contains details of polymer synthesis and functionalization,and 1H NMR spectra.