Supplementary Material for Organic & Biomolecular Chemistry

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Instrumentation

NMR spectra were recorded on a Bruker AC 400 spectrometer at 400 MHz for ^{1}H and 100 MHz for ^{13}C measurements. The internal reference used in all spectra was tetramethylsilane. Chemical shifts δ are reported in parts per million (ppm) and coupling constants J are in Hz (rounded to the nearest whole number, unless at x.5 Hz). Couplings with J values $\leq$2.5 Hz are not reported. Mass spectra were obtained on a Micromass Quattro II low-resolution triple-quadrupole mass spectrometer using electron impact (EI), chemical ionisation (CI) or electrospray (ES) ionisation. Accurate mass data were obtained on a MAT900 XLT high-resolution double focussing mass spectrometer by manual peak matching. The fast atom bombardment (FAB) and accurate mass LSIMS analyses were performed on a Micromass Autospec high-resolution double focussing mass spectrometer. IR spectra were recorded on a Perkin Elmer FT-IR 1725x spectrometer. An ALPHA2-atomic absorption spectrophotometer (BAIRD) fitted with a Mn lamp was used to determine Mn content. An air–acetylene flame was used under the manufacturer's recommended conditions for the Mn 279.5 nm line with a Mn hollow cathode lamp. GC analyses were performed on a Hewlett-Packard Series II 5890 instrument using an RTX-1 dimethylpolysiloxane capillary column (30 m) and a FID detector. Melting points (mp) were measured on a Griffin capillary melting point apparatus and are uncorrected. Microanalyses were performed with a Carlo-Erba 1106 analyser by the microanalysis laboratory at the University of Wales Cardiff.

Materials

All chemicals were obtained from Aldrich Chemical Company or Lancaster Synthesis Ltd. Merrifield's peptide resin (*ca*. 2.0 mmol g^{-1} Cl, 1% cross-linked, 200-400 mesh) was obtained from Aldrich and hydroxymethyl polystyrene (*ca*. 1.7 mmol g^{-1} OH, 1% cross-linked, 100-300 mesh) was obtained from Fluka. Glassware was usually dried in an oven at 150 ^{o}C and cooled to room temperature under a flow of nitrogen. Purification of diethyl ether or tetrahydrofuran was achieved by passing the solvent through a short column of activated alumina, distillation from calcium hydride, and drying over sodium benzophenone. Other solvents were purified by standard procedures.[34] 2,2'-Dihydroxy-1,1'-binaphthyl[35] and its separated enantiomers,[36] 6,6'-dibromobinaphthol,[37] and benzyl iodide[38] were all prepared by literature methods. Columns for flash chromatography were packed with Fisher Chemicals Matrex Silica 60 (35-70 mesh) or Aldrich aluminium oxide (activated, neutral, Brockmann STD Grade 1, *ca*. 150 mesh). TLC was carried out on Whatman aluminium silica gel or polygram® Alox N/UV 254 plates and visualised under ultraviolet light.

Synthesis of (*R*)-2-hydroxy-2'-trifluoromethanesulfonyloxy-1,1'-binaphthyl (9)[21]

To a mixture of (*R*)-2,2'-dihydroxyl-1,1'-binaphthyl (**8**) (12.81 g, 44.75 mmol), 4-dimethylaminopyridine (0.66 g, 5.4 mmol) and *N*-phenylbis(trifluoromethanesulfonimide) (15.99 g, 44.75 mmol) under nitrogen was added 2,4,6-collidine (5.42 g, 5.9 ml, 44.75 mmol) and anhydrous dichloromethane (180 ml). The reaction mixture was refluxed for 18 h and concentrated *in vacuo*. Purification by column chromatography (SiO_2, toluene) gave a cream viscous product (15.91 g, 85% yield); $[\alpha]_D^{20}$ +11.2 (*c* 2.01, $CHCl_3$); lit.[21] $[\alpha]_D^{25}$ +12.59 (*c* 4.01, $CHCl_3$). The ^{1}H NMR spectrum was consistent with that described in the literature.[21] $\delta_F(CDCl_3)$ -74.89 (s); $\delta_C(CDCl_3)$ 112.0, 117.9, 119.8,

123.8, 124.2, 125.2, 126.5, 127.1, 127.6, 128.2, 128.3, 128.5, 129.1, 131.4, 131.6, 132.9, 133.2, 133.3, 146.2 and 151.8 (the CF_3 signal was not observed); *m/z* (EI) 418 (M^+, 1%), 225 (50) and 92 (100); *m/z* (CI) 436 ($M^+ + NH_4$, 100%) and 214 (20).

Synthesis of (*R*)-2-hydroxy-2'-phenyl-1,1'-binaphthyl (10)[21]

To a mixture of **9** (14.88 g, 35.60 mmol) and $NiCl_2$(dppe) (0.38 g, 0.72 mmol) in dry diethyl ether (300 ml) under nitrogen was slowly added an ethereal phenylmagnesium bromide solution (3.0 M, 59 ml, 178 mmol). The reaction mixture was refluxed for 3 h and then quenched with aqueous NH_4Cl (300 ml), and extracted with ether (600 ml). The extract was washed with aqueous $NaHCO_3$ (100 ml) and brine (2 x 300 ml), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by column chromatography (SiO_2, toluene) gave a cream solid (9.85 g, 80% yield); $[\alpha]_D^{20}$ +25.3 (*c* 0.35, $CHCl_3$), mp 174-175 ^oC; lit.,[21] $[\alpha]_D^{24}$ +27.2 (*c* 1.00, $CHCl_3$), mp 174 ^oC). The ^1H NMR spectrum was consistent with that described in the literature.[21] $\delta_C(CDCl_3)$ 117.2, 117.7, 123.2, 125.1, 126.3, 126.4, 126.6, 127.0, 127.2, 2 x 127.7, 128.0, 128.2, 3 x 128.6, 128.7, 129.0, 129.4, 129.8, 133.1, 133.2, 134.2, 140.8, 141.6 and 151.0; *m/z* (EI) 346 (M^+, 100%); *m/z* (CI) 364 ($M^+ + NH_4$, 100%).

Synthesis of (*R*)-2-(methoxymethoxy)-2'-phenyl-1,1'-binaphthyl (17)[21]

To a solution of **10** (730 mg, 2.11 mmol) in dichloromethane (8 ml) under nitrogen was added *i*-Pr_2NEt (1.1 ml, 6.0 mmol) and $ClCH_2OMe$ (0.46 ml, 6.0 mmol) at room temperature. The mixture was stirred for 24 h and then quenched with water (20 ml) and extracted with dichloromethane (30 ml). The extract was washed with water (2 x 10 ml), dried over Na_2SO_4 and concentrated *in vacuo* to give the crude product (720 mg, 87%

yield). Purification by column chromatography (SiO_2, hexane–ether 19 : 1) gave a cream-coloured product (0.45 g); $[\alpha]_D^{20}$ +60.7 (*c* 0.69, $CHCl_3$), mp 88-90 °C; lit.,[21] $[\alpha]_D^{20}$ +59.6 (*c* 0.55, $CHCl_3$), mp 86-88 C. The ^{1}H NMR spectrum was consistent with that described in the literature.[21]

$\delta_C(CDCl_3)$ 55.7, 95.0, 116.3, 122.9, 123.8, 125.6, 125.8, 126.2, 126.4, 126.5, 126.8, 2 x 127.3, 127.8, 127.9, 128.0, 128.2, 2 x 128.8, 129.3, 129.5, 131.8, 132.8, 133.1, 134.4, 140.0, 142.0 and 152.8; *m/z* (EI) 390 (M^+, 20%) and 45 (100); *m/z* (CI) 408 ($M + NH_4^+$, 100%) and 60 (85).

Synthesis of (*R*)-3-formyl-2-(methoxymethoxy)-2'-phenyl-1,1'-binaphthyl (18)[21]

To a solution of **17** (450 mg, 1.15 mmol) in THF (10 ml) at -78 °C under nitrogen was added a solution of *tert*-butyllithium (1.5 M in pentane, 1.7 ml, 2.55 mmol) by syringe and the mixture was stirred for 3 h at the same temperature. *N*,*N*-Dimethylformamide (0.8 ml, 5.75 mmol) was added and the mixture was allowed to warm to room temperature and was stirred for 1 h. The reaction mixture was quenched with aqueous NH_4Cl (20 ml) and extracted with ethyl acetate (30 ml). The extract was washed with aqueous $NaHCO_3$ (20 ml) and brine (2 x 10 ml), dried over Na_2SO_4 and concentrated *in vacuo* to give an oil (450 mg, 93% yield). Purification by column chromatography (SiO_2, hexane–ether 5 : 4) gave a cream-coloured solid (400 mg, 83% yield); $[\alpha]_D^{20}$ -19.4 (*c* 0.18, $CHCl_3$), mp 52-54 °C; lit.,[21] (as an oil) $[\alpha]_D^{20}$ -12.6 (*c* 0.17, $CHCl_3$). The ^{1}H NMR spectrum was consistent with that described in the literature.[21]

$\delta_C(CDCl_3)$ 56.9, 99.7, 2 x 125.8, 125.9, 126.5, 126.6, 126.7, 126.8, 2 x 127.5, 128.2, 128.5, 2 x 128.6, 2 x 128.7, 129.3, 129.4, 129.5, 130.3, 131.4, 132.7, 133.7, 137.7, 140.8, 141.5, 153.5 and 191.0; *m/z* (EI) 418 (M^+, 90%), 327 (70), 326 (80), 316 (90), 315 (100),

313 (80), 302 (50), 239 (50), 77 (70) and 45 (100); *m/z* (CI) 436 ($M + NH_4^+$, 15%), 419 (25), 387 (30) and 78 (100).

Synthesis of (*R*)-3-formyl-2-hydroxy-2'-phenyl-1,1'-binaphthyl (3)[21]

To a solution of **18** (0.43 g, 1.03 mmol) in dichloromethane (10 ml) containing 4 Å molecular sieves under nitrogen was added bromotrimethylsilane (1.0 ml, 1.16 g, 7.58 mmol). The mixture was stirred for 1 h, quenched with aqueous $NaHCO_3$ (20 ml) and extracted with dichloromethane (30 ml). The extract was washed with water (2 x 20 ml), dried over $MgSO_4$, and concentrated *in vacuo* to give a yellow solid (0.34 g, 88% yield). Purification by column chromatography (SiO_2, hexane–toluene 3 : 7) gave a yellow solid product (308 mg, 80% yield); $[\alpha]_D^{20}$ -56 (*c* 0.10, $CHCl_3$), mp 190-192 °C; lit.,[21] $[\alpha]_D^{20}$ -50.7 (*c* 1.00, $CHCl_3$), mp 205 °C. The ^1H NMR spectrum was consistent with that described in the literature.[21]

$\delta_C(CDCl_3)$ 121.3, 121.5, 124.2, 125.4, 125.8, 126.0, 126.5, 126.6, 127.4, 2 x 127.7, 128.2, 128.3, 128.5, 2 x 128.7, 129.6, 129.8, 130.3, 132.6, 132.9, 137.8, 137.9, 140.7, 141.8, 153.5 and 196.8; *m/z* (EI) 374 (M^+, 100%), 327 (70), 326 (60) and 77 (20); *m/z* (CI) 392 ($M^+ + NH_4$, 85%) and 375 (100).

Synthesis of formylpolystyrene (23)[28]

A mixture of chloromethylated polystyrene (5.0 g, 2.0 mmol g^{-1} Cl, 200–400 mesh, 1% cross-linked) and sodium bicarbonate (10.4 g, 124 mmol) in dimethyl sulfoxide (100 ml) was heated to 155 °C for 6 h. The polymer-bound aldehyde resin was filtered, washed with dimethyl sulfoxide (50 ml), hot water (50 ml), and a 2 : 1 mixture of dioxane and water (100 ml), then with dioxane (20 ml), acetone (50 ml), ethanol (50 ml),

dichloromethane (50 ml), benzene (50 ml) and finally ethanol (50 ml). It was then dried in a vacuum oven (100 ^{o}C/2.0 mmHg) for 24 h to give cream-coloured formylpolystyrene, 4.70 g.

ν_{max}/cm^{-1} (KBr) 2720 (CHO) and 1700 (C=O).

Synthesis of carboxypolystyrene (24)[29]

To a mixture of formylpolystyrene (4.17 g) in 1,2-dimethoxyethane (70 ml) was added *m*-chloroperbenzoic acid (2.93 g, 17.0 mmol) and the mixture was heated to 55 ^{o}C and stirred for 19 h. The polymer-bound carboxylic acid resin was filtered, washed with water (100 ml), ether (100 ml), a 1 : 1 mixture of ether and water (100 ml), methanol (100 ml), ether (100 ml) water (100 ml), and finally methanol (100 ml). It was then dried in a vacuum oven (100 ^{o}C, 2.0 mmHg) for 24 h to give white carboxypolystyrene (4.055 g). Treatment with excess standard sodium hydroxide solution and back-titration of the excess base against standard HCl solution,[30] showed that the resin contained *ca*. 1.4 mmol g^{-1} carboxyl groups.

ν_{max}/cm^{-1} (KBr) 3457 (OH), 1730 (C=O free) and 1700 (C=O H-bonded).

Synthesis of polystyrenecarbonyl chloride (22)[31]

To a suspension of carboxypolystyrene (3.02 g) in dry benzene (80 ml) was added freshly distilled thionyl chloride (50 ml) under argon and the mixture was refluxed overnight. The mixture was filtered, washed with dry benzene (2 x 50 ml) and dry ether (2 x 50 ml), and immediately dried under vacuum overnight to remove any excess thionyl chloride, leaving the polymer-bound carbonyl chloride (2.92 g).

ν_{max}/cm^{-1} (KBr) 1700–1780 (COCl).

A sample of the polystyrenecarbonyl chloride was swollen in dioxane (10 ml) for 10 min, water (10 ml) was added and the mixture was heated to reflux for 24 h. The resulting polymer was filtered off and washed with water (30 ml). The combined aqueous solution was back-titrated against 0.1 M NaOH, which showed that the polystyrenecarbonyl chloride resin contained 1.17 mmol g^{-1} of displaceable chloride.

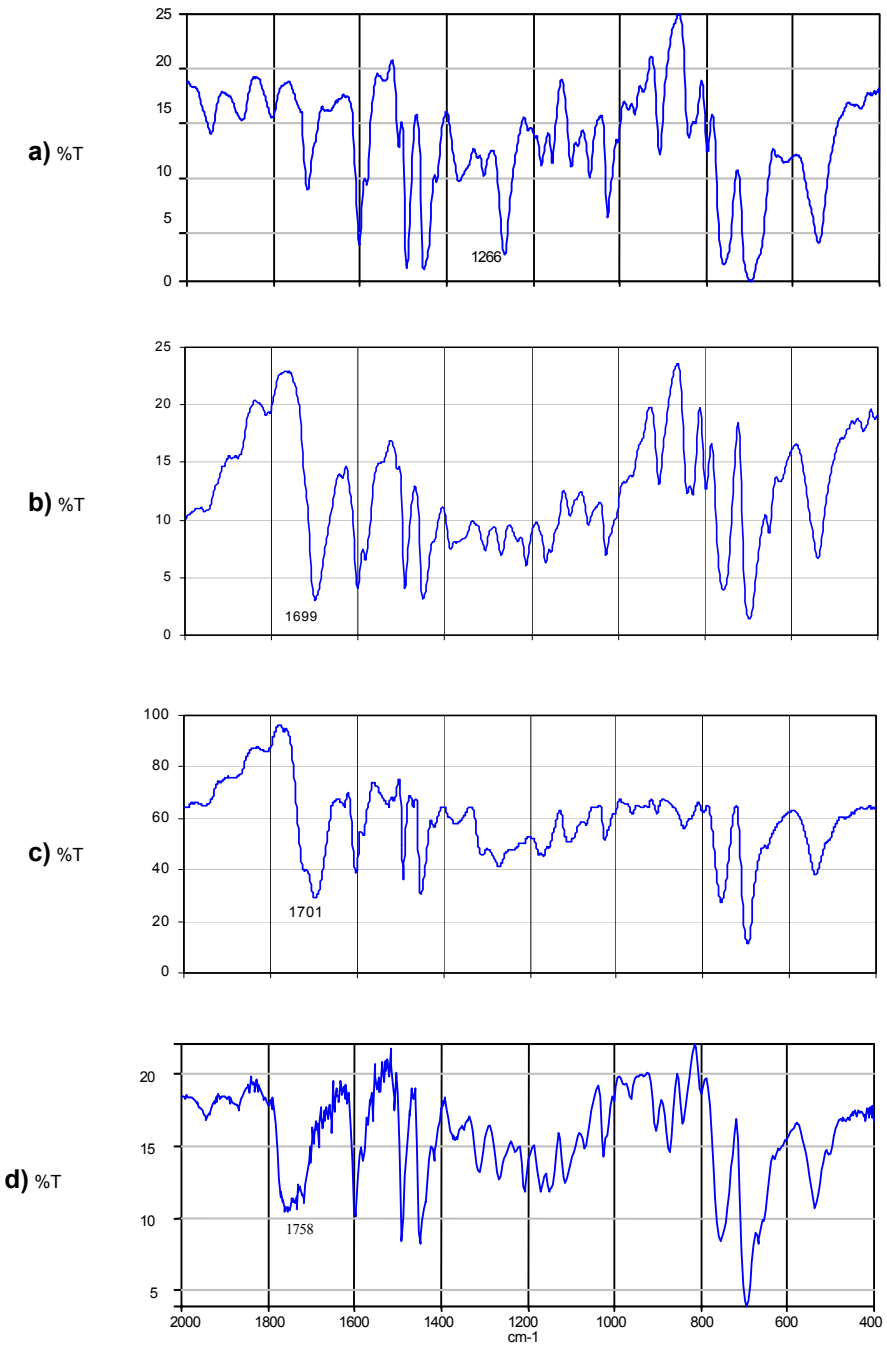

Fig. 1 IR spectra of (**a**) chloromethylated polystyrene; (**b**) formylpolystyrene; (**c**) carboxypolystyrene; and (**d**) polystyrenecarbonyl chloride.

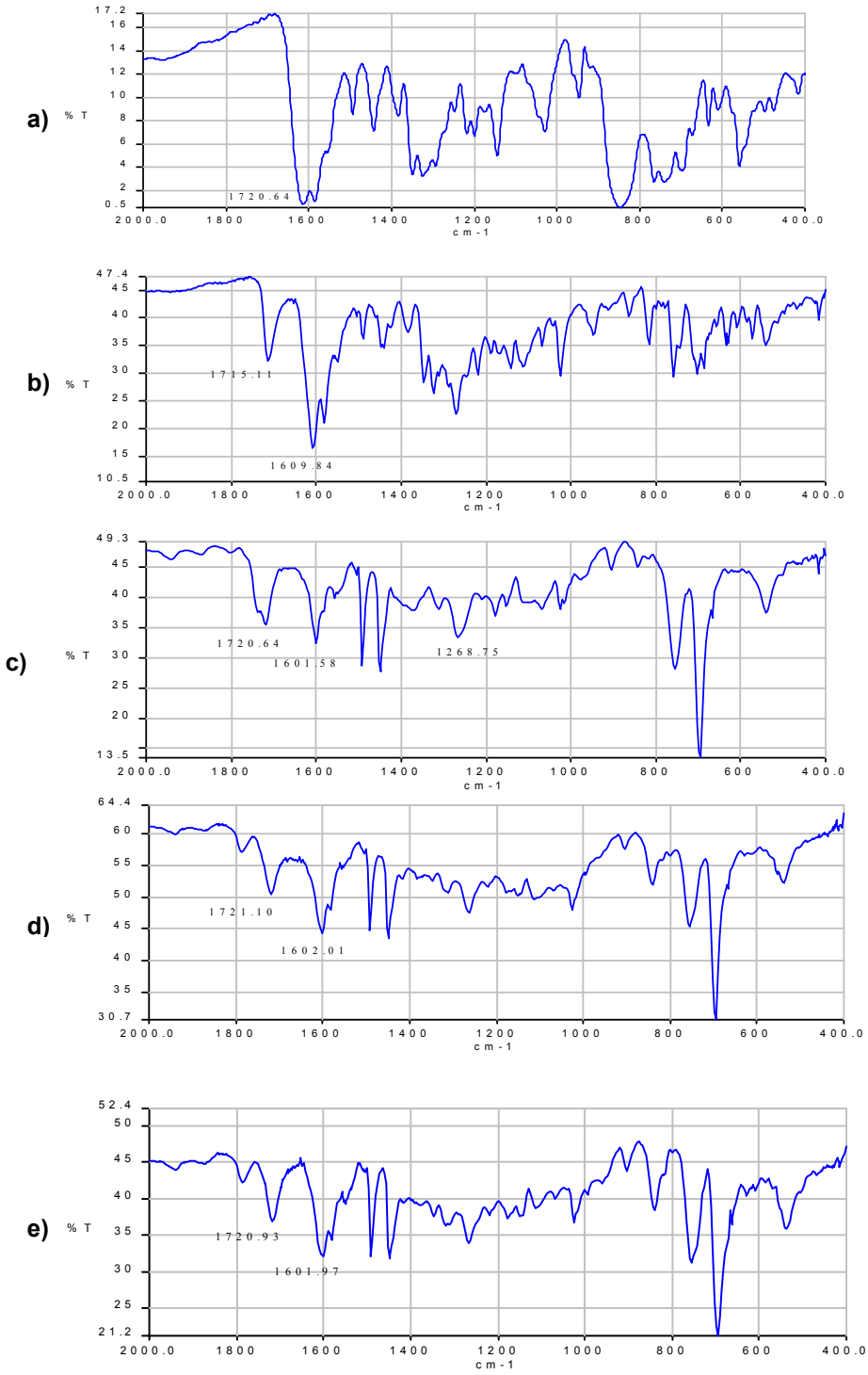

Fig. 2 IR spectra of **(a)** unsymmetrical chiral (salen)Mn complex **1b**; **(b)** the benzoyl derivative of complex **1c**, *i.e.* **21**; **(c) polymer A**; **(d) polymer B**; **(e) polymer C**.

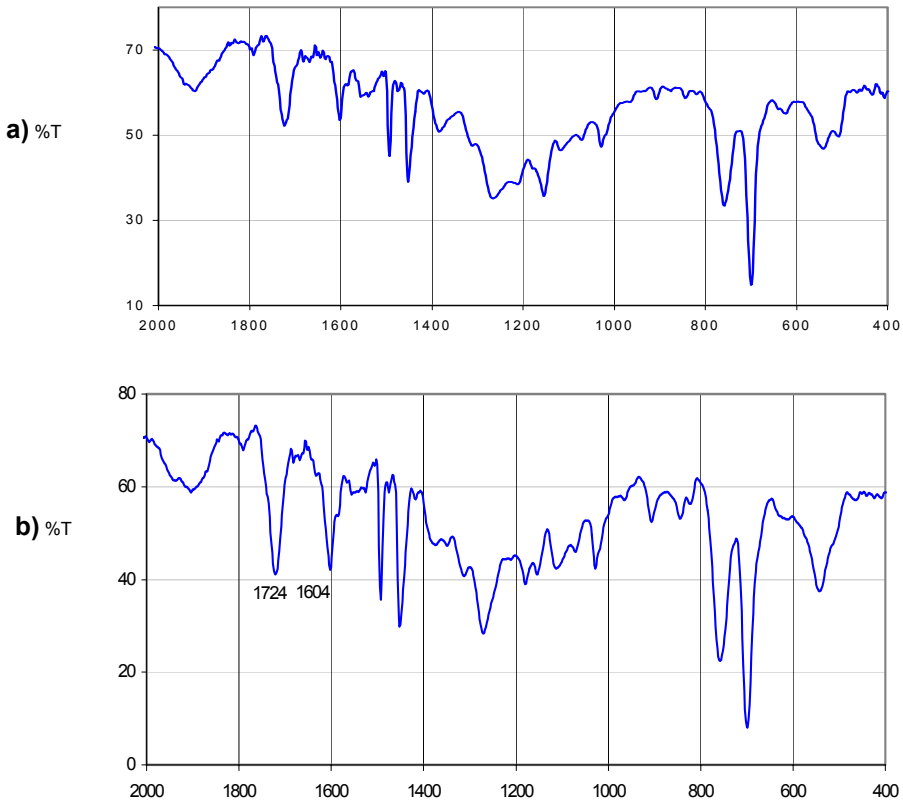

Fig. 3 IR spectra of **(a) polymer B** after 4 uses; **(b) polymer C** after 6 uses.

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