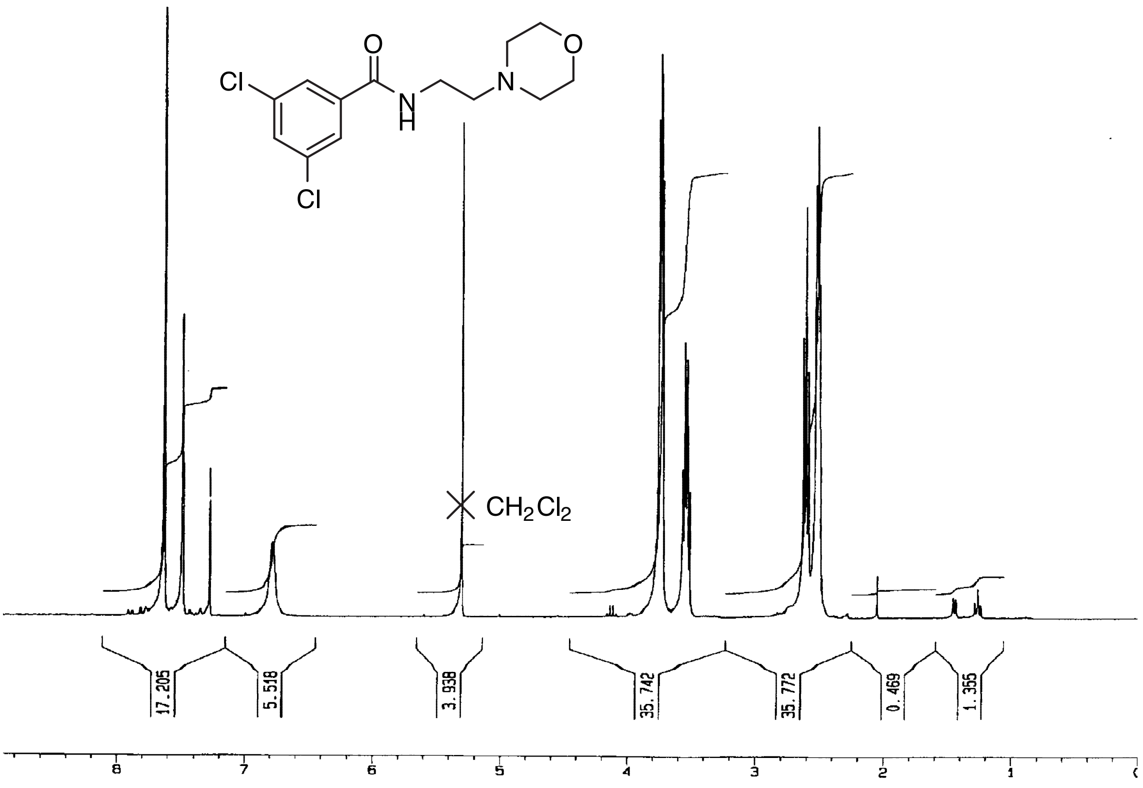
Supplementary Material

General procedure for the synthesis of ROMPGELs 3. A typical procedure is as follows: Benzylidenebis(tricyclohexylphosphine)dichlororuthenium **4** (4 mg, 4.8 μmol, 1.5 mol%) in CH_2Cl_2 (0.25 mL) was slowly added to a stirred solution of monomer **2a** (88 mg, 0.32 mmol) and norbornadiene (1.5 mg, 16 μmol, 5 mol%) in CH_2Cl_2 (0.36 mL). The purple solution was stirred at room temperature overnight. Ethyl vinyl ether (1.5 mL) was added followed by addition of a large excess of EtOAc to precipitate the ROMPGEL **3a**. The polymer was collected by filtration and dried in a stream on nitrogen to give ROMPGEL **3a** (90 mg, 100% yield) as a brown solid.

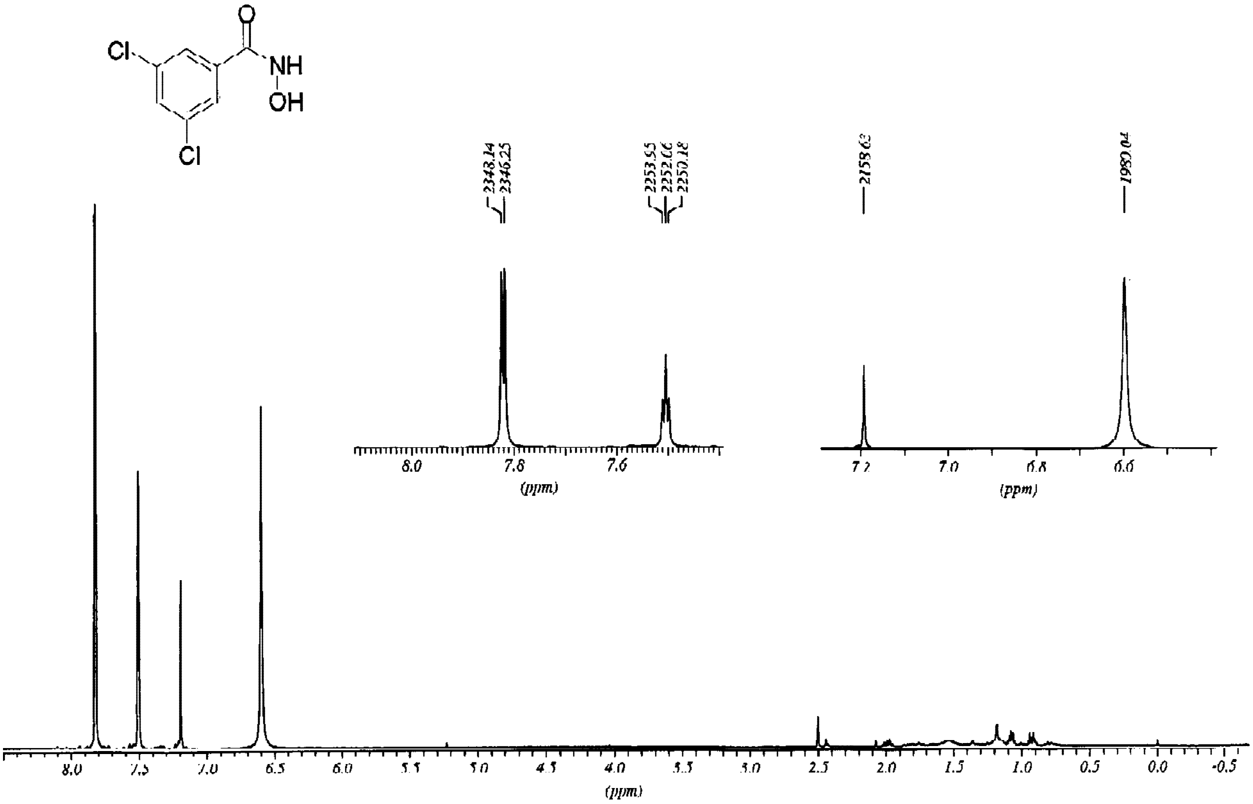
General procedure for the acylation of amines using ROMPGELs 3. A representative procedure is as follows: 4-(2-aminoethyl)morpholine **6C** (21μL, 0.15 mmol) was added to ROMPGEL **3c** (70 mg, 0.19 mmol) suspended in EtOAc (3 mL) and the mixture was stirred at room temperature for 16 h. The resulting mixture was filtered through a plug of cotton wool. The solvent was removed under a stream of nitrogen to give the amide **7cC** (46.9 mg, 98%): ^1H NMR ($CDCl_3$) δ 2.52 (t, J = 4.6 Hz, 4H), 2.62 (t, J = 5.9 Hz, 2H), 3.55 (app q, J = 6.0 Hz, 2H), 3.84 (t, J = 4.6 Hz, 4H), 6.79 (bs, 1H), 7.49 (t, J = 2Hz, 1H), 7.64 (d, J = 2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 38.3, 53.3, 56.7, 66.9, 125.6, 131.2, 135.4, 137.5, 164.9; HRMS (ES+) calcd for $C_{13}H_{17}N_2O_2{}^{35}Cl_2 + H^+$: 303.0667. Found: 303.0678.



Crude ^1H NMR ($CDCl_3$) of amide 7cC

General procedure for the acylation of amine hydrochlorides using ROMPGELs 3. A representative procedure is as follows: isoleucine methyl ester hydrochloride **6F** (37 mg, 0.20 mmol) and triethylamine (70 μL, 0.50mmol) were added to a stirred suspension of ROMPGEL **3a** (70 mg, 0.25 mmol) and polymer-supported 1,5,7-triazabicyclo[4.4.0]dec-5-ene (100 mg) in EtOAc (3 mL). The mixture was stirred at room temperature for 16 h and then filtered through a plug of cotton wool. Evaporation of the solvent under a stream of nitrogen gave the amide **7aF** (46.7 mg, 96%): ^{1}H NMR (CDCl$_3$) δ 0.97 (m, 6H) 1.24 (m, 1H), 1.45 (m, 1H), 2.03 (m, 1H), 3.78 (s, 3H), 4.77 (m, 1H), 6.52 (s, 1H), 6.84 (bd, J = 4 Hz, 1H), 7.14 (s, 1H), 7.48 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 11.5, 15.5, 25.2, 38.2, 52.1, 56.0, 112.2, 114.1, 147.6, 149.2, 157.9, 172.3; HRMS (ES+) calcd for $C_{12}H_{17}NO_4 + H^+$: 240.1236. Found: 240.1233.

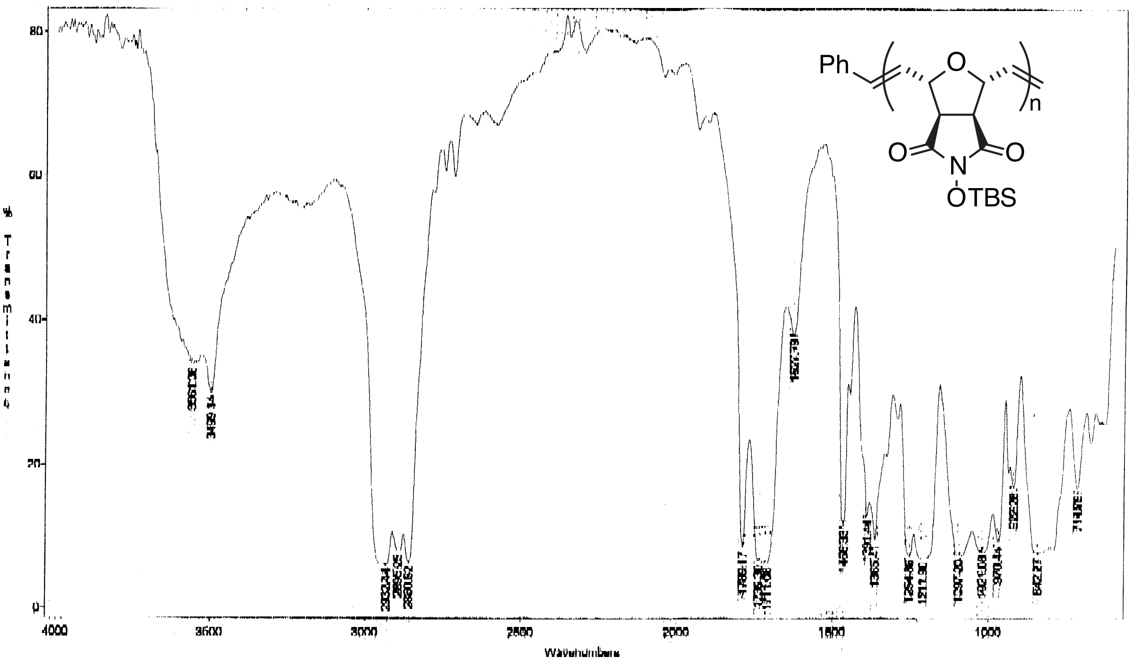
General procedure for the synthesis of hydroxamic acids using ROMPGELs 3. A typical procedure is as follows: hydroxylamine hydrochloride **6E** (11 mg, 0.16 mmol) was added to a stirred suspension of ROMPGEL **3c** (70 mg, 0.20 mmol) and powdered potassium hydroxide (9 mg, 0.16 mmol) in CH_2Cl_2 (3 mL). The mixture was stirred at room temperature for 16 hours and then filtered through a plug of cotton wool. Evaporation of the solvent under a stream of nitrogen gave the hydroxamic acid **7cE** (31.2 mg, 96%): ^{1}H NMR (CDCl$_3$) δ 6.60 (bs, 2H), 7.51 (t, J = 2 Hz, 1H), 7.82 (d, J = 2 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 125.9, 128.8, 134.4, 133.7, 166.3.



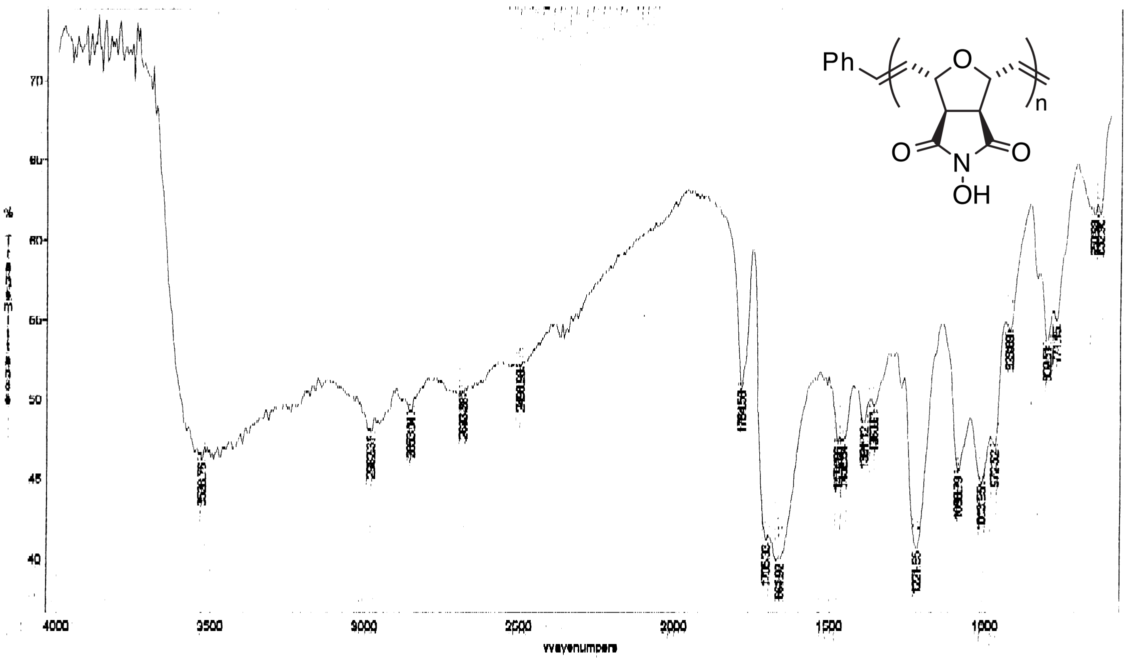
Crude ^{1}H NMR (CDCl$_3$) of hydroxamic acid 7cE

Synthesis of *N*-hydroxysuccinimide ROMPGEL 8. *tert*-Butyldimethylsilyl chloride (1.24 g, 8.28 mmol) was added portionwise to *exo*-*N*-hydroxy monomer **1** (1.0 g, 5.5 mmol) and imidazole (1.12g, 16.5 mmol) in CH_2Cl_2 (15 mL), forming a white precipitate. The mixture was stirred at room temperature overnight. Water (100 mL) and CH_2Cl_2 (100 mL) were added, the aqueous layer was extracted with CH_2Cl_2 (100 mL) and the combined organics were dried over $MgSO_4$. Removal of the solvents *in vacuo* and flash chromatography (SiO_2, hexane-EtOAc gradient, 90:10 increasing to 50:50) gave the protected monomer (1.59 g, 98%): ^1H NMR ($CDCl_3$) δ 0.22 (s, 6H), 1.03 (s, 9H), 2.75 (s, 2H), 5.26 (s, 2H), 6.52 (s, 2H); ^{13}C NMR ($CDCl_3$) δ –5.1, 18.3, 25.5, 43.8, 80.3, 136.1, 171.0; HRMS (ES+) calcd for $C_{14}H_{21}NO_4Si + H^+$: 296.1318. Found: 296.1324.

The monomer was polymerized according to the general procedure (see above). Triethylamine trihydrofluoride (0.79 g, 4.9 mmol) was added dropwise to a portion of the polymer (2.5 g, 9.8 mmol) in CH_2Cl_2 (25 mL), precipitating the polymer upon addition, and the mixture was stirred for 1 h. Methoxytrimethylsilane (2 mL, 14.8 mmol) was added slowly and the suspension was stirred for 1 h at room temperature. ROMPGEL **8** was collected by filtration, washed successively with THF, CH_2Cl_2 and Et_2O and dried in a stream of nitrogen.



FT-IR spectrum (transmittance) of TBS-protected polymer



FT-IR spectrum (transmittance) of ROMPGEL 8

General procedure for recycling ROMPGELs 3. Methanolic ammonia (obtained by bubbling NH_3 through MeOH for 2h) (25 mL) was added to a suspension of spent ROMPGEL **3** (0.7 g) suspended in THF (25 mL), and the mixture was stirred at room temperature overnight. The polymer was collected by filtration, was washed successively with water, THF, CH_2Cl_2 and Et_2O and finally dried under reduced pressure to give ROMPGEL **8**, ready for re-use.