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Reactions of Nitroalkenes with Nitroalkanes or Sulfur Ylides Catalyzed by Amine-Thiourea Bifunctional Polymeric Organocatalysts

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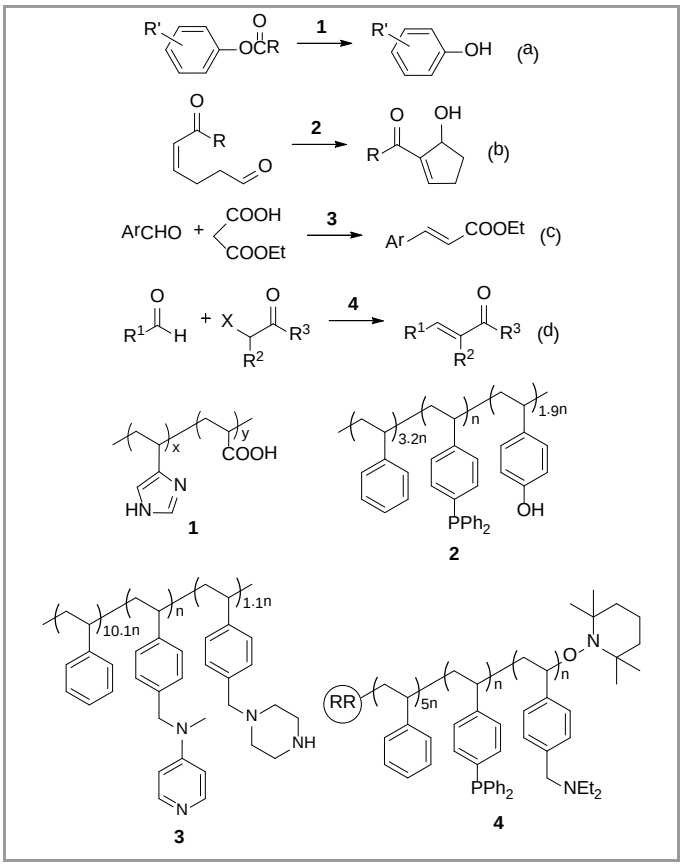
Abstract: Non-cross-linked and cross-linked bifunctional polystyrenes bearing both amine and thiourea groups have been synthesized, and used as organocatalysts in reactions between nitroalkenes and nitroalkanes or sulfur ylides. Control experiments using monofunctional polymers with only either amine or thiourea groups attached indicated that both functional groups were essential for efficient catalysis of the reactions studied. The non-cross-linked polystyrene was soluble in typical organic solvents and was used as a homogeneous catalyst, while the cross-linked polystyrene was used as a heterogeneous catalyst.

Key words: polymer-supported organocatalyst, polystyrene, Jandajel, nitroalkanes, nitroalkenes, sulfur ylides

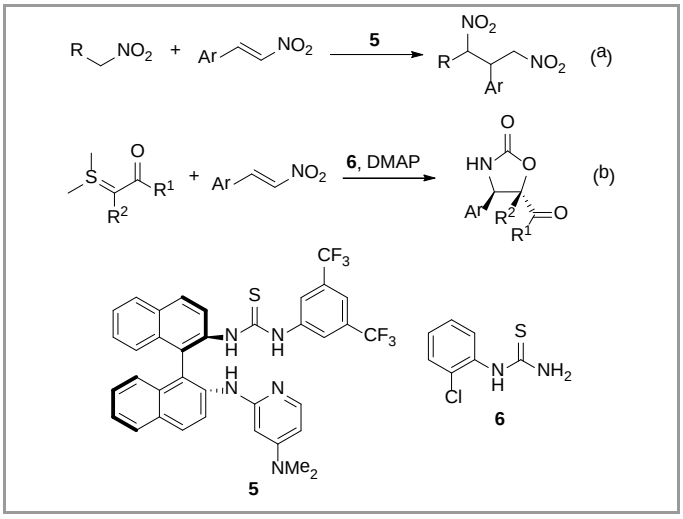
In tandem with the recent explosion of interest in organocatalysis, the use of polymeric supports to immobilize organic molecules has also garnered much attention. While many examples of organic polymer-supported organocatalysts have been reported,[1] virtually all of the reports in the literature describe polymers functionalized with only a single catalytic group. This is in stark contrast to small molecule organocatalysts, which often times are polyfunctional, and require cooperation between the various functional groups for efficient catalysis.[2,3]

A notable exception to this is the early work reported by Overberger et al. regarding the use polymers functionalized with both acidic and imidazole groups, such as **1**, that were used to catalyze ester hydrolysis reactions (Scheme 1a).[4,5] Additionally, we have studied the use of numerous organic polymers as platforms for organic chemistry,[6] especially in the context of polymer-supported phosphine reagents and catalysts,[7-9] and have more recently reported bifunctional phenol-phosphine polystyrene **2** as a catalyst for Morita-Baylis-Hillman[10] and alkyne isomerization reactions (Scheme 1b).[11,12] Furthermore, we have studied numerous polymer-supported amines,[13] and have reported polystyrene bearing DMAP and piperidine groups **3** that proved to be an excellent catalyst for decarboxylative Doebner-Knoevenagel reactions (Scheme 1c).[14] Finally, we have also extended the concept of bifunctional polymers to supported reagents, and developed heterogeneous amine-phosphine rasta resin **4** that was used as the sole reagent in one-pot Wittig reactions (Scheme 1d).[15]

During the course of this latter work, we were inspired by the recent report of using bifunctional amine-thiourea organocatalyst **5** in reactions involving the addition of nitroalkanes to nitroalkenes (Scheme 2a),[16] and the work of Xiao et al. regarding the use of a combination of thiourea **6** and DMAP to catalyze cycloaddition reactions between sulfur ylides and nitroalkenes (Scheme 2b).[17] Thus, we wanted to see if we could extend the concept of bifunctional polymeric organocatalyst and develop an amine-thiourea polymeric organocatalyst for these reactions.[18] Herein we report the realization of this objective, and describe both homogeneous and heterogeneous bifunctional polymeric organocatalysts.

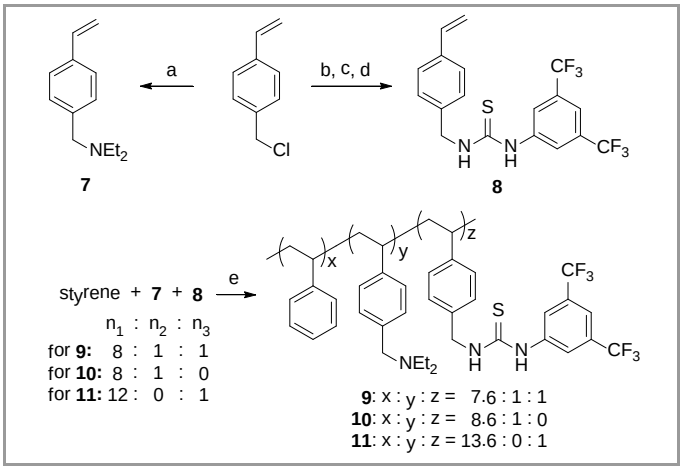


Scheme 1 Bifunctional polymeric organocatalysts and reagents



Scheme 2 Reactions of nitroalkenes

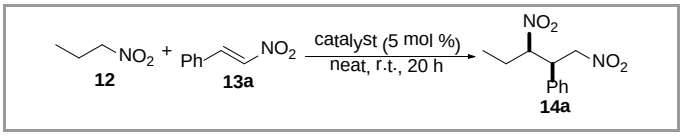
For synthesis of our envisioned homogeneous bifunctional amine-thiourea polymer, we planned to co-polymerize a pair of functionalized monomers together with styrene, as we did previously for the synthesis of **2** and **3**. Thus, trialkylamine monomer **7**, and thiourea monomer **8** were chosen to incorporate the desired functionality into non-cross-linked polystyrene **9** (Scheme 3). Monomers **7** and **8** were both prepared from commercially available 4-vinylbenzyl chloride. The former was synthesized according to the literature procedure using diethylamine,[19] and the latter by a 3-step route involving reaction with sodium azide, followed by reduction to the corresponding amine, and finally reaction of this with 3,5-bis(trifluoromethyl)phenyl isocyanate.[20] Once **7** and **8** were in hand, they were co-polymerized with styrene in a 8:1:1 (styrene:**7**:**8**) ratio using AIBN as the initiator in chlorobenzene to afford **9**. The monomer ratio used was chosen because we felt that it would be important to impart flexibility in **9** by using a relatively high percentage of styrene. ^{1}H NMR analysis was used to determine the monomer incorporation ratio of **9** to be 7.6:1:1, and thus its loading level of 0.72 mmol g^{-1}. For control reactions, we also synthesized monofunctional polymers **10** (0.90 mmol g^{-1}) and **11** (0.55 mmol g^{-1}), possessing only amine or thiourea groups by the omission of **8** or **7**, respectively, from the polymerization reaction. In all three cases, the monomer incorporation ratio in the product was similar to the polymerization reaction input ratio.



Scheme 3 *Reagents and conditions*: (a) $HNEt_2$, MeOH, reflux, 2 h; (b) NaN_3, DMSO, r.t, 18 h; (c) $LiAlH_4$, Et_2O, 0 °C-r.t., 4 h; (d) 3,5-$(CF_3)_2$-C_6H_3NCS, CH_2Cl_2, r.t., overnight; (e) AIBN, toluene, 80-85 °C, 24 h.

With the synthesis of polymers **9**-**11** completed, we then studied their utility as catalysts for the addition of nitropropane (**12**) to *trans*-β-nitrostyrene (**13a**) to form product **14a** (Table 1). As can be seen in entry 1, when monofunctional polymer **10**, with only tertiary amine groups, was used to catalyze the reaction, only low yield of the desired product **14a** could be obtained, and using thiourea functionalized polymer **11** did not lead to any desired reaction (entry 2). Interestingly, when an equal molar mixture of both **10** and **11** was used, excellent yield of **14a** was obtained with high stereoselectivity (entry 3), and gratifyingly, when **9** was used as the sole catalyst, very similar results were obtained (entry 4). Thus, from these results it appears that both amine and thiourea groups are required for efficient catalysis in such nitroalkane addition to nitroalkene reactions, and that **9** can indeed function as a homogeneous bifunctional polymeric organocatalyst in such processes.

Table 1



Entry	Catalyst(s)	Yield of **14a** (%)[a]	*syn*:*anti*[b]
1	**10**	18	n.d.[c]
2	**11**	no reaction	n.d [c]
3	**10** + **11**	86	87:13
4	**9**	92	85:15

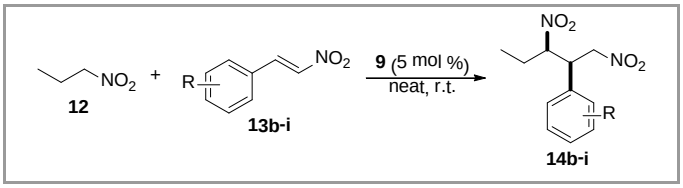
[a] Total isolated yield of products from reactions after column chromatography using **12** (30.0 mmol), **13a** (1.0 mmol) and catalyst (0.05 mmol) at r.t. for 20 h.

[b] Determined by ^{1}H NMR analysis.

[c] Not determined.

Having achieved our initial goal, we then tested the general utility of polymeric catalyst **9** in a series of related reactions using **12** and substituted β-nitrostyrenes **13b-i**[21] (Table 2).[22] As can be seen in entries 1-8, excellent yield of the desired product (**14b-i**) could be obtained in all cases, regardless of the location or electronic nature of the substituent(s). Furthermore, the stereoselectivity of all of the reactions was also very high.

Table 2



Entry	**13**	Product	Yield (%)[a]	*syn*:*anti*[b]
1	**13b**: R = 2,3-$(MeO)_2$	**14b**	97	84:16
2	**13c**: R = 4-MeO	**14c**	95	86:14
3	**13d**: R = 4-Me	**14d**	94	87:13
4	**13e**: R = 4-Br	**14e**	88	83:17
5	**13f**: R = 2-Br	**14f**	93	87:13
6	**13g**: R = 4-Cl	**14g**	95	90:10
7	**13h**: R = 2,4-Cl_2	**14h**	92	82:18
8	**13i**: R = 4-F	**14i**	96	86:14

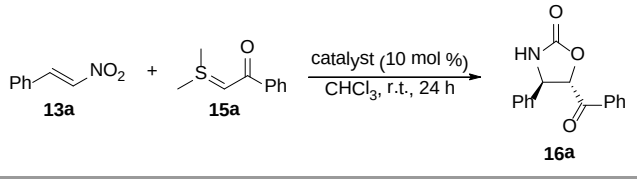
[a] Total isolated yield of products after column chromatography from reactions using **12** (15.0 mmol), **13** (0.5 mmol) and **9** (0.025 mmol) at r.t. for 20 h.

[b] Determined by ^{1}H NMR analysis.

Next polymers **9**-**11** were examined as catalysts in the cycloaddition reactions represented in Scheme 2b. For these reactions, **13a** and ylide **15a** were chosen as test substrates to form **16a** (Table 3). As before, we first examined catalysis of this reaction using monofunctional polymers **10** and **11**. With

the former, low yield of **16a** was formed with excellent stereoselectivity (entry 1), and with the latter, moderate yield of product was obtained (entry 2). Therefore it appears that thiourea groups alone are moderately efficient at catalyzing such reactions, but amine groups are not. However, when a mixture of **10** and **11** was used as the catalyst, higher yield of **16a** was obtained with similar stereoselectivity (entry 3). Similarly, high yield of **16a** was also obtained using bifunctional polymer **9**. Thus, once again it appears that **9** is an efficient homogeneous bifunctional polymeric organocatalyst.

Table 3



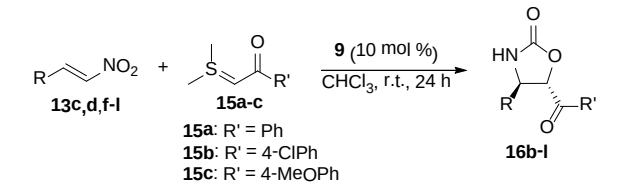
Entry	Catalyst(s)	Yield of **16a** (%)[a]	*anti*:*syn*[b]
1	**10**	37	99:1
2	**11**	60	92:8
3	**10** + **11**	77	96:4
4	**9**	81	96:4

[a] Isolated yield of reaction using **13a** (0.5 mmol), **15a** (0.625 mmol), and catalyst (0.05 mmol) at r.t. in $CHCl_3$ (1 mL) for 24 h.

[b] Determined by ^{1}H NMR analysis.

The use of **9** to catalyze a series of similar reactions was then undertaken with combinations of nitroalkenes **13c**,**d**,**f-l** and ylides **15a-c** as the reaction partners to form products **16b-l** (Table 4).[23] Not only were substituted *trans*-β-nitrostyrenes generally good substrates in these reactions (entries 1-7), but alkyl substituted nitroalkenes were useful as well (entries 8 and 9). Furthermore, the phenyl group of the ylide reaction partner could also be substituted with either an electron-withdrawing or -donating group to good effect (entries 10 and 11). In all cases, excellent stereoselectivity was observed, as in the model reaction

Table 4

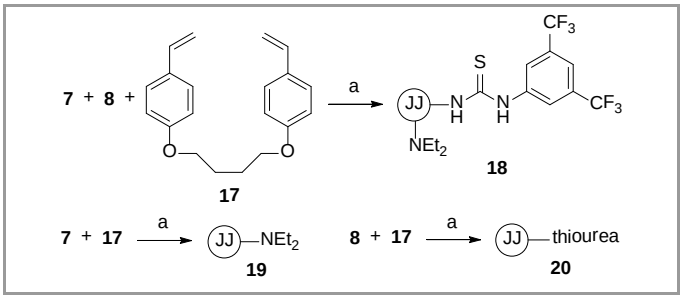


Entry	**13**	**15**	Product	Yield (%)[a]	*anti*:*syn*[b]
1	**13c**: R = 4-MeOPh	**15a**	**16b**	52	95:5
2	**13d**: R = 4-MePh	**15a**	**16c**	67	98:2
3	**13f**: R = 2-BrPh	**15a**	**16d**	78	98:2
4	**13g**: R = 4-ClPh	**15a**	**16e**	78	98:2
5	**13h**: R = 2,4-Cl_2Ph	**15a**	**16f**	72	96:4
6	**13i**: R = 4-FPh	**15a**	**16g**	75	97:3
7	**13j**: R = 1-naphthyl	**15a**	**16h**	74	98:2
8	**13k**: R = *i*Bu	**15a**	**16i**	44	94:6
9	**13l**: R = C_7H_{15}	**15a**	**16j**	60	94:6
10	**13a**: R = Ph	**15b**	**16k**	73	95:5
11	**13a**: R = Ph	**15c**	**16l**	77	98:2

[a] Isolated yield of reaction using **13** (0.5 mmol), **15** (0.625 mmol), and **9** (0.05 mmol) at r.t. in $CHCl_3$ (1 mL) for 24 h.

[b] Determined by ^{1}H NMR analysis.

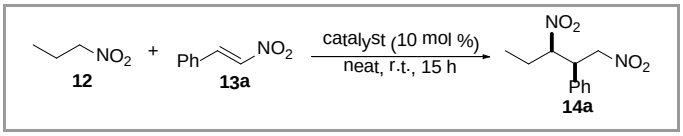
Having demonstrated the general catalytic utility of linear and soluble **9** in a pair of different reactions, we were interested to see if a cross-linked and insoluble version of it would also be a useful catalyst in such reactions, since such a polymer would be more easily separated from reaction mixtures. Thus, suspension co-polymerization of styrene, **7**, **8** and Jandajel cross-linker **17**[24] afforded heterogeneous bifunctional polymer **18** (Scheme 4). Monofunctional polymers **19** and **20** for control experiments were synthesized similarly. Elemental analysis was used to determine the loading level of **18** (0.73 mmol g^{-1} for thiourea and 0.82 mmol g^{-1} for amine), **19** (0.90 mmol g^{-1}) and **20** (0.81 mmol g^{-1}).



Scheme 4 *Reagents and conditions*: (a) styrene, PhCl, acacia solution, AIBN, 85 °C, 24 h.

With the synthesis of heterogeneous polymers **18**-**20** complete, we examined their catalytic activity as we did previously with homogeneous polymers **9**-**11** in the reaction between **12** and **13a** to form **14a** (Table 5). As before, using either monofunctional polymer **19** or **20**, little or no product was formed (entries 1 and 2). However, the use of a mixture of heterogeneous monofunctional polymers did not afford high yield in this case (entry 3), in contrast to what we observed with the homogeneous polymers **10** and **11** (Table 1, entry 3). This observation seems to highlight the cooperative nature of catalysis in such reactions, since the heterogeneous nature of **19** and **20** precludes the immobilized amine and thiourea groups from interacting in close proximity with each other. Satisfyingly, bifunctional **18**, in which the amine and thiourea groups are co-located in the resin interior was an excellent catalyst for this reaction (entry 4), and provided results similar to what were obtained using homogeneous **9** (Table 1, entry 4).

Table 5



Entry	Catalyst(s)	Yield of **14a** (%)[a]	*syn*:*anti*[b]

1	**19**	20	n.d.[c]
2	**20**	no reaction	n.d.[c]
3	**19 + 20**	18	n.d.[c]
4	**18**	96	85:15

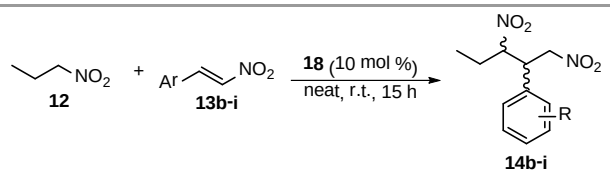
[a] Total isolated yield of products from reactions using **12** (30.0 mmol), **13a** (1.0 mmol) and catalyst (0.1 mmol) at r.t. for 15 h.

[b] Determined by ^{1}H NMR analysis.

[c] Not determined.

Polymer **18** was then used to catalyze the same reactions shown in Table 2, and the results of these experiments are summarized in Table 6.[25] As is readily evident from comparing Tables 2 and 6, **9** and **18** both function well as the catalyst for these reactions. However, a larger amount of **18** (10 mol % vs. 5 mol %) was required for efficient reaction completion, but the heterogeneous nature of **18** meant that it could be removed from the reaction mixture simply by filtration.

Table 6



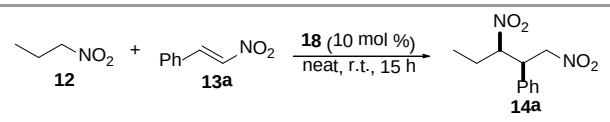
Entry	**13**	Product	Yield (%)[a]	*syn*:*anti*[b]
1	**13b**: R = 2,3-$(OMe)_2$	**14b**	96	85:15
2	**13c**: R = 4-OMe	**14c**	96	81:19
3	**13d**: R = 4-Me	**14d**	99	85:15
4	**13e**: R = 4-Br	**14e**	96	84:16
5	**13f**: R = 2-Br	**14f**	98	86:14
6	**13g**: R =-4-Cl	**14g**	98	83:16
7	**13h**: R = 2,4-Cl_2	**14h**	99	86:14
8	**13i**: R = 4-F	**14i**	98	86:14

[a] Reactions using **12** (15.0 mmol), **13b-i** (0.5 mmol) and **18** (0.05 mmol) at r.t. for 15 h. Yield is based on the mass of the residue after removal of polymer and excess nitropropane.

[b] Determined by ^{1}H NMR analysis.

Finally, we examined the reusability of **18** after it was recovered at the end of reactions, and the results of these experiments are summarized in Table 7.[26] As can be clearly seen, using **18** in 6 reaction cycles (5 reuses) with **12** and **13a** as substrates was possible without any observable decrease in catalytic efficiency. Thus, it seems that heterogeneous **18** has the advantage over homogeneous **9** of being readily recovered and reused.

Table 7



Cycle	1	2	3	4	5	6
Yield (%)[a]	97	98	98	98	97	98

[a] Reactions using **12** (15.0 mmol), **13a** (0.5 mmol) and **18** (0.05 mmol) at r.t. for 15 h. Yield is based on the mass of the residue after removal of polymer and excess nitropropane.

In conclusion, we have extended the concept of bifunctional polymeric organocatalysts to the synthesis homogeneous (non-cross-linked) and heterogeneous (cross-linked) polymers functionalized with both amine and thiourea catalytic groups. These polymers were used effectively as catalysts for reactions involving the addition of nitroalkanes to nitroalkenes and cycloaddition reactions between nitroalkenes and sulfur ylides. For both of these reaction types, good substrate variability and high stereoselectivity were observed. While soluble polymer **9** was generally more efficient and could be used at lower loading than insoluble polymer **18**, the latter was removable by filtration and readily reused. We are currently examining other applications of **9** and **18** in the context of complex organic molecule synthesis and will report our findings shortly.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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(22) **General Procedure for Michael Addition Reactions of Nitroalkanes to Nitrostyrenes Catalyzed by Polymer 9:** Nitrostyrene **13a-i** (1 mmol) and catalyst **9** (0.05 mmol) were dissolved in **12** (2.6 mL, 30 mmol). The mixture was stirred at r.t. for 20 h, and then the reaction mixture was purified directly by column chromatography to afford the desired product**14a-i** as a mixture of stereoisomers. The *syn*:*anti* ratio was determined by ^{1}H NMR analysis of the crude product mixture.

(23) **General Procedure for Cycloaddition Reactions Catalyzed by Polymer 9:** Nitrostyrene **13a,c,d,f-l** (0.5 mmol) and **9** (0.05 mmol) were dissolved in $CHCl_3$ (1 mL). Sulfur ylide **15a-c** (0.6 mmol) in $CHCl_3$ (1 mL) was then added dropwisely to the mixture. After stirring at r.t. for 24 h, the reaction mixture was purified directly by column chromatography to afford the desired products **16a-l**. The *anti*:*syn* ratio was determined by ^{1}H NMR analysis of the crude product mixture.

(24) For the Jandajel concept, see: (a) Toy, P. H.; Janda, K. D. *Tetrahedron Lett.* **1999**, *40*, 6329. (b) Toy, P. H.; Reger, T. S.; Janda, K. D. *Aldrichimica Acta.* **2000**, *33*, 87. (c) Toy, P. H.; Reger, T. S.; Garibay, P.; Garno, J. C.; Malikayil, J. A.; Liu, G.-Y.; Janda, K. D. *J. Comb. Chem.* **2001**, *3*, 117. (d) Choi, M. K. W.; Toy, P. H. *Tetrahedron* **2004**, *60*, 2903.

(25) **General Procedure for Michael Addition Reactions of Nitroalkanes to Nitrostyrenes Catalyzed by Polymer 18:** To nitrostyrene **13a-i** (1 mmol) in **12** (2.6 mL, 30 mmol) was added catalyst **18** (0.1 mmol). The mixture was stirred at r.t. for 15 h. The polymer was then removed by filtration, washed with THF and the filtrate was concentrated in vacuo to remove the excess nitropropane. The *syn:anti* ratio was determined by ^{1}H NMR analysis.

(26) **General Procedure for the Reuse of Polymer 18:** To nitrostyrene **13a** (3.0 mmol) in **12** (90 mmol) was added catalyst **18** (0.3 mmol). Cycles 3-5 were performed on a 1.5 mmol scale and cycle 6 was performed on a 1.2 mmol scale. The mixture was stirred at r. t. for 15 h, and then the polymer was then removed by filtration, washed with THF and dried. The filtrate was concentrated in vacuo to remove the excess nitropropane. The *syn*:*anti* ratio was determined by ^{1}H NMR analysis to be 85:15 in all cycles.

Graphical abstract