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Polymer-Supported Hantzsch 1,4-Dihydropyridine Ester: An Efficient Biomimetic Hydrogen Source

Rongjun He,[a] Patrick H. Toy,[b,*] and Yulin Lam[a,*]

[a] Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543
Fax: (+65)-6779-1691; e-mail: chmlamyl@nus.edu.sg
[b] Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, People's Republic of China
Fax: (+852)-2857-1586; e-mail: phtoy@hku.hk

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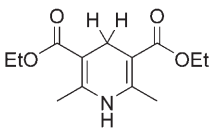
Abstract: An efficient synthesis of a polymer-supported Hantzsch 1,4-dihydropyridine ester has been developed and its use in a variety of reduction reactions was studied using α,β-unsaturated aldehydes, imines and an activated benzoquinone as substrates. Reductive amination using the polymer-supported Hantzsch 1,4-dihydropyridine ester and a catalytic amount of 1.5 M HCl was found to proceed rapidly and with good yields.

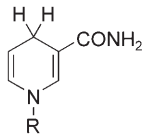
Keywords: biomimetic hydrogen source; 1,4-dihydropyridine; Hantzsch ester; polymer-supported reducing agent; reduction; reductive amination

Advances in the use of polymers in organic synthesis[1] have led to the development of improved technologies for the preparation of chemical libraries. In particular, the use of polymer-supported reagents[2] in what is commonly referred to as polymer-assisted organic synthesis is an attractive technique that combines the advantages of solid-phase chemistry with those of solution-phase synthesis. In this technique, a polymer-bound reagent is added to a substrate in solution to effect a chemical transformation. In addition to the reagent, undesired reagent by-products formed are bound to the polymeric-support, thus allowing the product to be purified by simple filtration. Furthermore, since both the substrate and product are in solution during the reaction, conventional solution-phase analytical techniques, such as thin-layer chromatography, can be employed for reaction monitoring. The versatility of this methodology facilitates the process of library synthesis and has been the main stimulus for the recent growth of interest in polymer-supported reagents and catalysts.

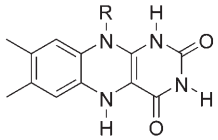
Hydrogenations of double-bond containing compounds such as carbonyls, alkenes and imines are important transformations both in biological organisms and industrial processes. Whilst chemical hydrogenation reactions have generally relied on metal catalysts[3] or metal hydrides, recent studies have shown that metal-free transfer hydrogenation reactions can be accomplished in what can be considered a biomimetic strategy using the combination of an organocatalyst and a dihydropyridine (Hantzsch) ester.[4,5] In



Hantzsch ester



NADH



$FADH_2$

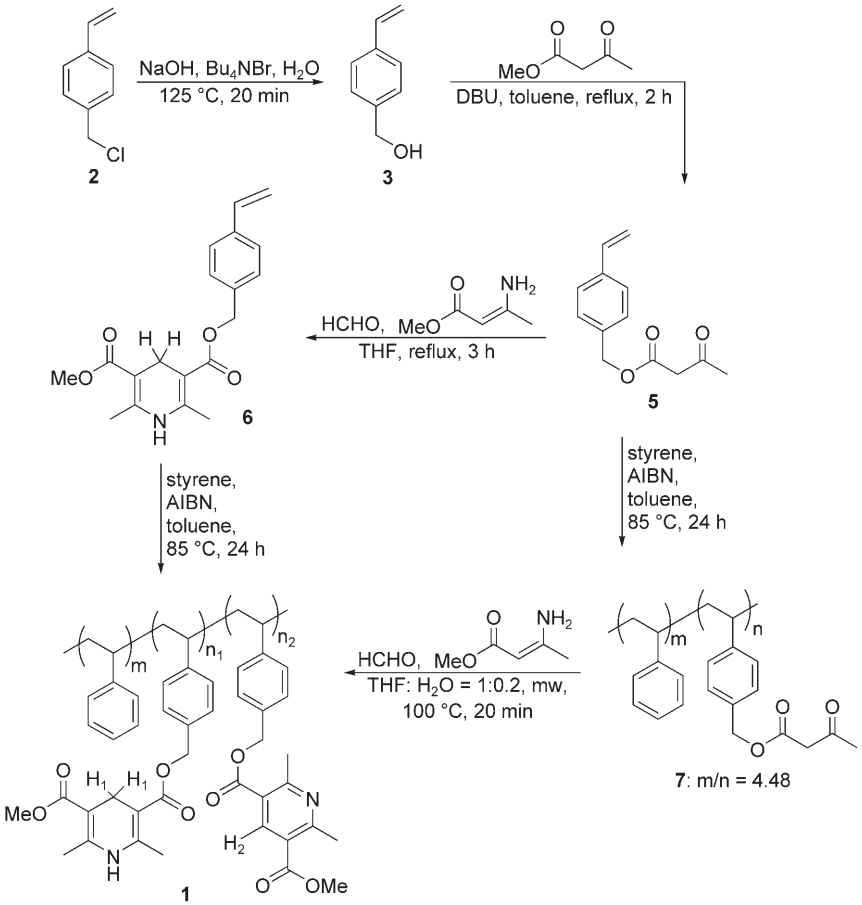
such metal-free reactions, the Hantzsch ester can serve as a surrogate for NADH or $FADH_2$ and the reactions are attractive compared to metal-based reductions because complete removal of metal impurities from reaction products is often difficult but necessary, especially in the production of pharmaceutical intermediates due to toxicity issues.[6]

In order to facilitate reduction processes, several polymer-supported reducing agents have been developed, many of which are immobilized on an insoluble polymeric matrix.[7] The primary advantage of using such polymer supports in this context lies in the insolubility of such supported reagents, which simplifies separation of the product from the spent reagent. However, the heterogeneous nature of such reactions also imposes various limitations,[8] and in recent years soluble polymer supports[8,9] have been increasing exploited in an effort to combine the useful features of both heterogeneous and homogeneous reaction systems. To date various soluble polymer-supported reagents including phosphines,[10] Swern oxidants,[11] a borane complex,[7a,12] and nitroxyl radicals,[13] among

others, have been developed. However to our knowledge, no report of any type of polymer-supported Hantzsch ester has appeared in the literature. To address the need for a metal- and purification-free (mix, filter and evaporate) reduction process, we herein present the synthesis of soluble polymer-supported Hanztsch 1,4-dihydropyridine ester **1** (Scheme 1) and its use in the reduction of various substrate types.

The synthesis of **1** began with the conversion of 4-vinylbenzyl chloride (**2**) into 4-vinylbenzyl alcohol (**3**). Previously this has been accomplished by reaction of **2** with acetate ion followed by saponification.[14] However, in this project we sought a new and direct procedure for the conversion of **2** into **3**, and examined various hydrolysis reaction conditions. Unlike the hydrolysis of benzyl chloride, which proceeded very efficiently under basic conditions, the hydrolysis of **2** was more complicated and readily afforded the by-product di(4-vinylbenzyl) ether (**4**). Hence, various reaction conditions were studied (Table 1) and it was found that **3** could be obtained in 98% yield when **2** was treated with NaOH (0.1 equiv.) in H_2O and Bu_4NBr (1 equiv.) as phase-transfer catalyst (Table 1, entry 8). Alcohol **3** was then reacted with methyl acetoacetate in the presence of DBU for 2 h to afford key intermediate **5** in 52% yield. It is worth noting that prolonged reaction heating resulted in lower yield of **5** due to the formation of by-products.

With compound **5** in hand, we carried out a condensation of it with formaldehyde and methyl 3-amino-2-butenoate which afforded **6** in 63% yield. Subsequent polymerization of **6** with styrene using standard AIBN-initiated radical polymerization methods afforded polymer **1**. However, analysis of **1** produced by this method using ^{1}H NMR showed that 40% of the dihydropyridine groups had been converted to pyridine moieties [n_1:n_2 was derived by either comparing the integration ratio of the CH_3 in CO_2CH_3 of dihydropyridine ($\delta = 3.65$ ppm) with the CH_3 in CO_2CH_3 of pyridine ($\delta = 3.87$ ppm) or by comparing the integration ratios of H_1 ($\delta = 3.35$ ppm) and H_2 ($\delta = 8.80$ ppm) (Scheme 1], which do not have reducing ability. Since the dihydropyridine unit of **6** appeared to be heat-sensitive and a long reaction time at elevated temperature is generally required for radical polymerization, we decided to copolymerize **5** with styrene to obtain polymer-supported keto ester **7**. Polymer **7** was amenable to KBr FTIR (i.e., the appearance of C=O signals at 1744 cm^{-1} and 1719 cm^{-1}) and ^{1}H NMR analysis. Using such techniques, the sty-



Scheme 1. Synthesis of polymeric reagent **1**.

Table 1. Synthesis of **3**.

Entry	Reagents and Solvent	Reaction Conditions	Result[a]
1	NaOH (1 equiv.), Bu_4NBr (1 equiv.), H_2O	r.t., 3 h	**3**: trace amount
2	NaOH (1 equiv.), Bu_4NBr (1 equiv.), H_2O	95 °C, 110 °C or 130 °C, 10 min to 1 h	**3**: 24-40 %; **4**: major product
3	NaOH (2 equivs.), Bu_4NI (1 equiv.), KI (0.1 equiv.), H_2O	r.t., 2 h	**3**: trace amount
4	NaOH (2 equivs.), Bu_4NI (1 equiv.), KI (0.1 equiv.), H_2O	65 °C, 5 h	**3**: trace amount; **4**: major product
5	NaOH (2 equivs.), H_2O, EtOH	r.t., 24 h	**3**: 19 %, **4**: 81 %
6	H_2O	reflux under N_2, 3 h	**3**: 70 %
7	NaOH (0.1 equiv.), Bu_4NBr (1 equiv.), H_2O	125 °C, 10 min	**3**: 58 %; **4**: trace amount
8	NaOH (0.1 equiv.), Bu_4NBr (1 equiv.), H_2O	125 °C, 20 min	**3**: 98 %; **4**: trace amount

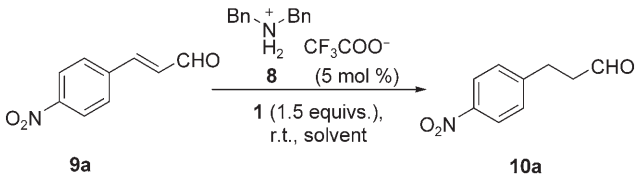
[a] Yield of purified product.

rene/**5** (m/n) ratio of **7** was determined to be approximately 5:1, which corresponds to a loading level of approximately 1.6 mmol g^{-1}. Attempts to synthesize polymer **1** by refluxing **7** with formaldehyde and methyl 3-amino-2-butenoate resulted again in predominantly the pyridine formation. We considered the mechanism proposed for the reduction of dihydropyridines[15] and figured that the presence of water might possibly prevent pyridine formation. Furthermore, in order to shorten the reaction time, we turned to microwave irradiation. To our delight, after much experimentation (Table 2), we found that condensation with 20 % H_2O in THF as the solvent afforded significantly better results with the amount of pyridine by-product formed was dramatically reduced (Entry 5, Table 2). Further addition of H_2O resulted in the precipitation of polymer **7** from the reaction mixture and the reaction ceased under such conditions.

Table 2. Synthesis of polymer **1**.

Entry	Solvent	Condition	Result
1	THF	mw, 100 °C, 20 min	$n_1/(n_1+n_2)=62\,\%$
2	THF/H_2O (1 drop)	mw, 100 °C, 20 min	$n_1/(n_1+n_2)=63\,\%$
3	THF:H_2O = 1:0.05	mw, 100 °C, 20 min	$n_1/(n_1+n_2)=62\,\%$
4	THF:H_2O = 1:0.1	mw, 100 °C, 20 min	$n_1/(n_1+n_2)=67\,\%$
5	THF:H_2O = 1:0.2	mw, 100 °C, 20 min	$n_1/(n_1+n_2)=89\,\%$
6	THF:H_2O = 1:0.2	mw, 100 °C, 10 min	$n_1/(n_1+n_2)=85\,\%$, traces of **7**
7	THF:H_2O = 1:0.2	mw, 120 °C, 5 min	$n_1/(n_1+n_2)=82\,\%$, traces of **7**
8	THF:H_2O = 1:0.25	mw, 100 °C, 20 min	No reaction. Precipitation of **7**

Reduction of α,β-unsaturated aldehydes: List and co-workers[5a] recently reported the reduction of α,β-unsaturated aldehydes using a Hantzsch ester with dibenzylammonium trifluoroacetate (**8**) as a catalyst. Therefore, with polymer **1** in hand, we proceeded to examine it in such reactions using *trans*-4-nitrocinnamaldehyde (**9a**) in THF (Scheme 2). Using GC to monitor the reaction, it was found that the conversion to 3-(4-nitrophenyl)propionaldehyde (**10a**) (90 %) was comparable to the reported yield obtained *via* solution-phase reduction (94 %),[5a] but with **1** allowed for much easier product isolation. However it should be noted that with **1**, the reaction required 24 h to reach completion versus 5–6 h for the solution-phase reduction. Thus, in order to optimize the reaction using **1**, we screened various solvents and found it to be dependent on both solvent and concentration (Table 3). Amongst the solvents screened, CH_2Cl_2 was the best solvent as the reaction was completed within 12 h. Furthermore, when the concentration of **1** was increased to 0.2 M (Entry 8, Table 3), the reaction was completed within 4 h.



Scheme 2. Reduction of *trans*-4-nitrocinnamaldehyde (**9a**) with polymer **1**.

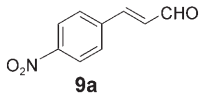
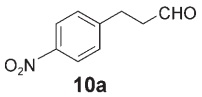
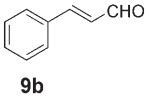
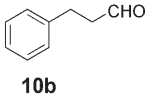
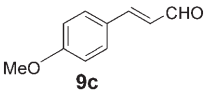
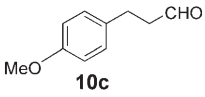
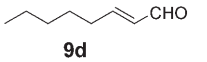
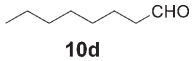
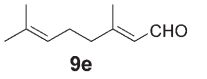
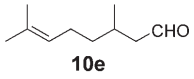
We next explored the use of **1** in the reduction of a variety of α,β-unsaturated aldehydes (Table 4). Five substrates were tested and the results obtained showed that, in general, both aromatic and aliphatic substrates could be reduced to the corresponding saturated products in good yields. These results together

Table 3. Solvent screening for reduction of α,β-unsaturated aldehydes.

Entry	Solvent	Concentration of polymer **1**[a]	Time	% Conversion[b]
1	THF	0.05 M	24 h	90 %
2	THF	0.05 M	12 h	52 %
3	CH_2Cl_2	0.05 M	12 h	100 %
4	$CHCl_3$	0.05 M	12 h	81 %
5	DMF	0.05 M	12 h	14 %
6	Toluene	0.05 M	12 h	82 %
7	CH_2Cl_2	0.1 M	7 h	100 %
8	CH_2Cl_2	0.2 M	4 h	100 %

[a] Ratio of *trans*-4-nitrocinnamaldehyde to polymer **1** is 1:1.5.
[b] Determined by GC (Agilent 6890 series GC system).

Table 4. Reduction of α,β-unsaturated aldehydes using **1**.

Entry	Substrate	Product	Yield[a]
1	 **9a**	 **10a**	90 %
2	 **9b**	 **10b**	87 %
3	 **9c**	 **10c**	85 %
4	 **9d**	 **10d**	82 % (24 h)[b]
5	 **9e**	 **10e**	63 % (4 h); 93 % (20 h)

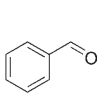
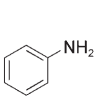
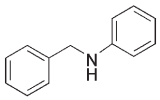
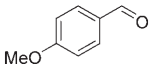
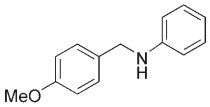
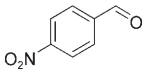
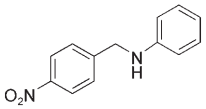
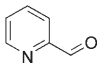
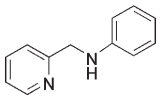
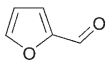
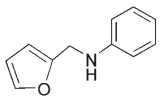
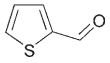
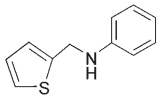
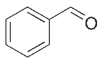
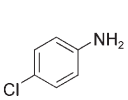
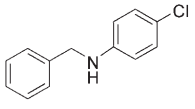
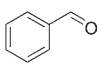
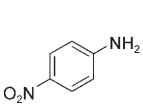
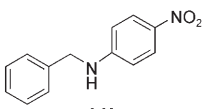
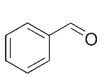
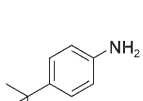
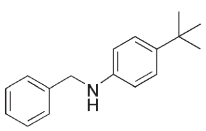
[a] Yield of purified product.
[b] Yield determined by GC (Shimadzu GC-14A gas chromatograph) because of difficulty of product isolation. Decane was used as the internal standard.

with the product purification by filtration work-up makes polymer **1** an attractive reagent for the reduction of α,β-unsaturated aldehydes.

Reductive amination of aldehydes: Reductive amination reactions with Hantzsch esters has been previously studied[15] and various catalyst, such as Bronsted acids,[16a–b] Lewis acids [Mg^{2+},[16c] SiO_2,[16d] Al_2O_3,[16d] $Sc(OTf)_3$[16e–f]], and thiourea[16g] have been used in this reaction. Generally, in the presence of a catalyst, these reactions require a few hours to a few days to go to completion. To examine the utility of **1** in reductive amination reactions, we treated benzaldehyde and aniline with **1** (1.5 equivs.) and catalyst **8** (5 mol %) at room temperature for 3 h and obtained benzylphenylamine (**11a**) in 27 % yield. Since this yield was lower than what was obtained using other reported catalysts,[17] we decided to search for a more efficient procedure for this reaction. Incidentally, we discovered that reductive amination of benzaldehyde with aniline in the presence of a catalytic amount of 1.5 M HCl and **1** (1.5 equivs.) was complete within 5 min and **11a** was obtained in 90 % yield. Encouraged by this result, we examined reductive amination of various combinations of aryl aldehydes and anilines using the same reaction conditions and obtained excellent yield in all cases (Table 5).

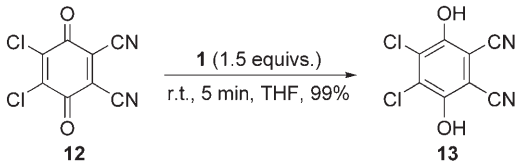
Benzoquinone aromatization: In order to identify additional applications of **1**, we examined its use in

Table 5. Reductive amination of aldehydes.

Entry	Aldehyde	Amine	Product	Yield[a]
1			 **11a**	99 %
2			 **11b**	87 %
3			 **11c**	90 %
4			 **11d**	91 %
5			 **11e**	99 %
6			 **11f**	97 %
7			 **11g**	99 %
8			 **11h**	96 %
9			 **11i**	88 %

[a] Yield of purified product.

the aromatization of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, **12**).[18] Gratifyingly we found that the reaction was complete within 5 min at room temperature. No catalyst was required and product **13** was obtained in essentially quantitative yield [Eq. (1)].



(1)

In conclusion, we have developed a new and direct synthesis of alcohol **3** and used it to prepare the first polymer-supported Hanztsch 1,4-dihydropyridine ester, **1**. The utility of **1** was demonstrated by its effectiveness in the reduction of α,β-unsaturated aldehydes, imines and an activated-benzoquinone, with high yields and simple work-up. Efforts are currently underway to prepare analogous reagents that contain catalytic moities in addition to the 1,4-dihydropyridine ester groups.

Experimental Section

All chemical reagents were obtained from Aldrich, Merck, Lancaster or Fluka and used without further purification. Analytical TLC was carried out on pre-coated plates (Merck silica gel 60, F254) and visualized with UV light or stained with ninhydrin. Column chromatography was performed with silica (Merck, 70–230 mesh). ^{1}H NMR and ^{13}C NMR spectra were measured at 298 K on a Bruker DPX 300 or DPX 500 Fourier Transform spectrometer. Chemical shifts were reported in δ (ppm), relative to the internal standard of TMS. The signals observed were described as: s, d, t, q, m. The number of protons (n) for a given resonance was indicated as nH. All IR spectra were recorded on a Bio-Rad FTS 165 spectrometer. Mass spectra were performed on VG Micromass 7035 spectrometer under EI, Finnigan/MAT LCQ under ESI (Normal), and Finnigan/MAT 95XL-T under ESI (accurate). GC analysis were performed on Agilent 6890 series GC system using a DB-1 column (30 m × 250 μm × 0.25 μm) (oven: 50 °C, injector: 230 °C, detector: 250 °C) or Shimadzu GC-14 A gas chromatograph using a PEG-HT column (25 m × 250 μm × 0.15 μm) (oven: 50 °C, injector: 100 °C, detector: 120 °C).

Synthesis of 4-Vinylbenzyl Alcohol (3)

To NaOH (0.04 g, 1 mmol) and Bu_4NBr (3.224 g, 10 mmol) in H_2O (50 mL) was added 4-vinylbenzyl chloride (1.409 mL, 10 mmol). The mixture was heated at 125 °C for 20 min and subsequently cooled in an ice/water bath. Upon cooling, the mixture was extracted with EtOAc (50 mL × 3) and the combined organic layer was dried with $MgSO_4$, filtered, concentrated and purified by column chromatography (EtOAc:hexane = 1:5) to give **3** as a colorless oil; yield: 1.310 g (98 %). ^{1}H NMR ($CDCl_3$): δ = 7.28–7.15 (m, *ArH*, 4H), 6.65–6.56 (m, *CH*=CH_2, 1H), 5.67–5.61 (d, J = 17.4 Hz, CH=*CH*$_2$, 1H), 5.16–5.12 (d, J = 10.8 Hz, CH=*CH*$_2$, 1H), 4.48 (s, *CH*$_2$, 2H), 2.47 (s, *OH*, 1H); ^{13}C NMR ($CDCl_3$): δ = 140.4, 136.8, 136.4, 127.1, 126.2, 113.7, 64.7; MS (EI): m/z = 133.9 (M^+); exact mass: calcd. for $C_9H_{10}O$: m/z = 134.0732; found: 134.0732.

Synthesis of 4-Vinylbenzyl Acetoacetate (5)

To methyl acetoacetate (1.1 mL, 10.188 mmol) and DBU (0.385 mL, 2.547 mmol) in toluene (30 mL) was added **3** (1.1393 g, 8.49 mmol) and the mixture was refluxed at 125 °C for 1 h. Thereafter another portion of methyl acetoacetate (1.1 mL, 10.188 mmol) was added, and the mixture was further refluxed for 1 h and then concentrated and purified by column chromatography (EtOAc:hexane = 1:5) to give **5** as a colorless oil; yield: 0.963 g (52 %). ^{1}H NMR ($CDCl_3$): δ = 7.42–7.30 (m, *ArH*, 4H), 6.75–6.66 (m, *CH*=CH_2, 1H), 5.79–5.73 (d, J = 17.4 Hz, CH=*CH*$_2$, 1H), 5.28–5.25 (d, J = 10.8 Hz, CH=*CH*$_2$, 1H), 5.16 (s, Ar*CH*$_2$, 2H), 3.49 (s, CO*CH*$_2$CO, 2H), 2.24 (s, *CH*$_3$, 3H); ^{13}C NMR ($CDCl_3$): δ = 200.2, 166.8, 137.8, 136.2, 134.7, 128.6, 126.4, 114.4, 66.8, 50.0, 30.0; MS (EI): m/z = 218.0 (M^+); exact mass: calcd. for $C_{13}H_{14}O_3$: m/z = 218.0943; found: 218.0946.

Synthesis of Monomer 6

To compound **5** (0.8548 g, 3.917 mmol) in THF (20 mL) was added methyl 3-aminocrotonate (0.4548 g, 3.917 mmol) and HCHO (37 % solution, 0.108 mL, 3.917 mmol). The mixture was refluxed for 3 h then concentrated and purified by column chromatography (EtOAc:hexane = 1:3) to give **6** as a yellow solid; yield: 0.807 g (63 %). ^{1}H NMR ($CDCl_3$): δ = 7.40–7.30 (m, *ArH*, 4H), 6.74–6.65 (m, *CH*=CH_2, 1H), 5.76–5.70 (d, J = 17.8 Hz, CH=*CH*$_2$, 1H), 5.25–5.21 (d, J = 10.8 Hz, CH=*CH*$_2$, 1H), 5.14 (s, Ar*CH*$_2$, 2H), 3.68 (s, CO_2CH_3, 3H), 3.30 (s, *CH*$_2$, 2H), 2.17 (s, *CH*$_3$, 6H); ^{13}C NMR ($CDCl_3$): δ = 168.4, 167.6, 145.7, 145.2, 141.0, 137.1, 136.4, 128.0, 126.2, 113.9, 99.2, 98.9, 65.1, 50.9, 24.8, 19.1, 18.9; MS (EI): m/z = 327.3 (M^+); exact mass: calcd. for $C_{19}H_{21}NO_4$: m/z = 327.1471; found: 327.1470.

Synthesis of Polymer 7

To monomer **5** (0.3337 g, 1.53 mmol) and styrene (1.05 mL, 9.13 mmol) in toluene (8.7 mL) was added AIBN (0.0175 g, 0.1066 mmol). The mixture was purged with N_2 at room temperature for 0.5 h and then heated at 85 °C for 24 h under N_2. Thereafter the solution was concentrated and the resulting residue was dissolved in THF (5 mL) and added slowly into vigorously stirred cold MeOH (0 °C, 50 mL). The resulting suspension was filtered by suction filtration to afford polymer **7**; yield: 62 %. Loading calculated by ^{1}H NMR: 1.562 mmol g^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.05–6.48 (m, *ArH*, 26H), 5.09 (s, Ar*CH*$_2$, 2H), 3.47 (s, CO*CH*$_2$CO, 2H), 2.21 (s, *CH*$_3$, 3H), 1.96–0.89 (m, 18H): IR (KBr): ν = 3448.8, 3059.7, 3026.0, 2923.5, 2849.8, 1744.2, 1719.7, 1601.4, 1493.2, 1452.7, 1150.1, 1028.8, 759.2, 699.6, 540.5 cm^{-1}.

Synthesis of Polymer 1

*From monomer **6***: To monomer **6** (0.5 g, 1.53 mmol) and styrene (1.05 mL, 9.13 mmol) in toluene (8.7 mL) was added AIBN (0.0175 g, 0.1066 mmol). The homogeneous mixture was purged with N_2 at room temperature for 0.5 h and then heated at 85 °C for 24 h under N_2. Thereafter the solution was concentrated and the crude polymer product which precipitated was dissolved in THF (5 mL). The polymer product was purified by adding the THF solution slowly to vigorously stirred cold MeOH (0 °C, 50 mL). The resulting suspension was filtered by suction filtration to afford polymer **1**; yield: 0.80 g (55 %). Loading calculated by ^{1}H NMR: 0.780 mmol g^{-1}.

*From polymer **7***: To polymer **7** (1.042 g, 1.6272 mmol) in THF (20 mL) and H_2O (4 mL) were added methyl 3-aminocrotonate (0.1873 g, 1.6272 mmol) and formaldehyde (37 % solution, 0.122 mL, 1.6272 mmol). The homogeneous mixture was heated under microwave irradiation at 100 °C for 20 min and then the product polymer was precipitated by adding the solution slowly to vigorously stirred cold MeOH (0 °C, 200 mL). The resulting suspension was filtered to afford polymer **1** as a white powder; yield: 1.17 g (96 %). Loading calculated by ^{1}H NMR only: 0.925 mmol g^{-1}, loading calculated based on a combination of % N content (obtained *via* elemental analysis) and ^{1}H NMR: 0.908 mmol g^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 8.80$ [s, *CH* (pyridine), 1 H], 7.07–6.49 (m, *ArH*, 420 H), 5.27 [s, Ar*CH*$_2$ (pyridine], 9 H), 5.10 [s, Ar*CH*$_2$ (dihydropyridine), 25 H], 3.87 [s, CO_2CH_3 (pyridine], 4 H), 3.65 (s, CO_2CH_3 (dihydropyridine), 29 H), 3.35 [s, *CH*$_2$ (dihydropyridine), 15 H], 2.94 [s, *CH*$_3$ (pyridine), 7 H], 2.19 [s, *CH*$_3$ (dihydropyridine), 69 H], 1.82–0.94 (m, 318 H). IR (KBr): $\nu = 3468.9$, 3409.6, 3082.3, 3059.2, 3025.5, 2922.8, 2849.6, 1736.02, 1716.55, 1601.8, 1493.2, 1452.4, 1271.2, 1184.2, 1114.0, 759.9, 699.3, 540.4 cm^{-1}.

General Procedure for the Reduction of α,β-Unsaturated Aldehydes

To the respective α,β-unsaturated aldehyde **9** (0.2 mmol) in CH_2Cl_2 (1.5 mL) was added polymer **1** (0.324 g, 0.3 mmol) and catalyst **8** (5 mol %). This mixture was allowed to stir at room temperature for 4 h. After which, the mixture was filtered through silica gel and the latter was washed with a small volume of EtOAc:hexane (1:3) mixture. The combined filtrate and washing was then concentrated to afford **10**.

General Procedure for Reductive Amination

To the respective aldehyde (0.2 mmol), amine (0.2 mmol) and polymer **1** (0.324 g, 0.3 mmol) in THF (3 mL) was added one drop of 1.5 M HCl. The mixture was allowed to stir at room temperature for 5 min. After which, the mixture was filtered through silica gel and the latter was washed with a small volume of EtOAc:hexane (1:5) mixture. The combined filtrate and washing was then concentrated to afford **11**.

Procedure for the Aromatization of 12

To 2,3-dichloro-5,6-dicyano-1,4-benzoquinone **12** (0.0454 g, 0.2 mmol) in THF (2 mL) was added polymer **1** (0.324 g, 0.3 mmol). The mixture was allowed to stir at room temperature for 5 min. Thereafter the mixture was poured into cold MeOH (20 mL), filtered and concentrated to afford **13** as a yellow solid; yield: 0.0455 g (99 %). ^{13}C NMR ($CDCl_3$): $\delta =$ 150.8, 129.2, 113.7, 101.7; MS (EI): $m/z = 227.8$ (M^+); exact mass: calcd. for $C_8H_2Cl_2N_2O_2$: $m/z = 227.9493$; found 227.9491.

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