Polymer-Supported Lewis Bases for the Baylis – Hillman Reaction

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Supporting Information for this article is available on the WWW under http://asc.wiley-vch.de or from the author.

Abstract: The use of polymer-supported Lewis bases such as PEG_{4600}-$(PPh_2)_2$ and poly(DMAP) in the Baylis–Hillman reactions of *N*-tosylimines (ArCH=NTs) **1** or the corresponding arenecarbaldehydes with α,β-unsaturated ketones has been investigated. The corresponding Baylis–Hillman adducts are obtained in good yields. The polymer-supported Lewis bases can be easily recovered by filtration and the Lewis base PEG_{4600}-$(PPh_2)_2$ can be reproduced by reduction with $LiAlH_4$ and $CeCl_3$.

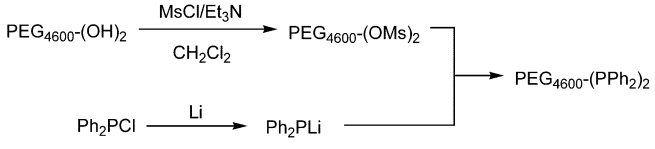
Keywords: acrylic esters; arenecarbaldehydes; Baylis–Hillman reaction; Lewis bases; methyl vinyl ketone (MVK); PEG_{4600}-$(PPh_2)_2$; polyDMAP; *N*-tosylimines (ArCH=NTs)

Since Baylis and Hillman first reported the reactions of acetaldehyde with ethyl acrylate and acrylonitrile in the presence of catalytic amounts of a strong Lewis base such as 1,4-diazabicyclo[2.2.2]octane (DABCO) in 1972,[1] the Baylis–Hillman reaction has made great progress,[2] including development of a catalytic, asymmetric version[3] and aza-Baylis–Hillman reactions.[4] However, so far in this very simple and useful reaction, only small molecules of Lewis bases such as DABCO, DMAP, DBU, PPh_3, PBu_3 or PPh_2Me have, in general, been used as the promoters which are difficult to recover from the reaction solution. Nowadays, serious environmental problems necessitate our rethinking of strategies towards organic synthesis. The design or synthesis of recyclable catalyst has become the key factor for a chemical reaction to be an economical, safe, environmentally benign, resource- and energy-saving process. For the Baylis–Hillman reaction, it is very clear that if we can design and synthesize a recyclable Lewis base as a promoter, this reaction would be accomplished in a perfect atom-economic way. Herein, we wish to report the unprecedented poly(ethylene glycol)s (PEGs)-supported phosphine Lewis base PEG_{4600}-$(PPh_2)_2$ and dimethylaminopyridine, a polymer-bound nitrogen Lewis base, polyDMAP-catalyzed Baylis–Hillman reactions of *N*-tosylimines **1** or arenecarbaldehydes with α,β-unsaturated ketones.

Poly(ethylene glycol)s (PEGs) have recently emerged as very convenient supports for the synthesis of a variety of small molecules.[5] PEGs are inexpensive and commercially available polymers[6] that can readily be functionalized with different spacers and linkers.[7] PEGs are soluble in many polar solvents and insoluble in non-polar solvents. Therefore, based on these previous results, we decided to pursue a PEGs-supported Lewis base-promoted Baylis–Hillman reaction. We expected that the PEGs-supported Lewis base can be very easily recovered or reproduced from the reaction solution and can be reused for the next batch of the Baylis–Hillman reaction.

The promoters for the aza-Baylis–Hillman reaction of *N*-tosylimines **1** with MVK have already been systematically examined.[4] The phosphine Lewis bases are very effective promoters for this reaction. Thus, we first prepared a polymer-supported phosphine Lewis base PEG-$(PPh_2)_2$ as shown in Scheme 1 for this reaction. Dimesylation of PEG (4600) in dichloromethane by MsCl gave PEG_{4600}-$(OMs)_2$ in the presence of triethylamine (Et_3N)[8] which further reacted with PPh_2Li freshly prepared from Ph_2PCl and Li in THF to afford PEG_{4600}-$(PPh_2)_2$ as a colorless solid.[9] The structure of PEG_{4600}-$(PPh_2)_2$ was established by ^1H NMR and ^{31}P NMR spectroscopic data. Their spectral charts are elucidated in Figures 1 – 3, respectively (see supporting information).

In order to develop the optimal reaction conditions, the aza-Baylis–Hillman reaction of **1** with methyl vinyl



Scheme 1.

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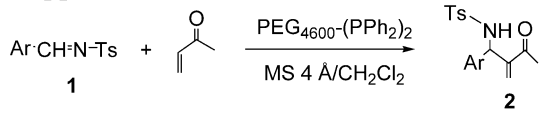
Table 1. The aza-Baylis–Hillman reactions of *N*-sulfonated imines (1.0 equiv.) with MVK in the presence of PEG_{4600}-$(PPh_2)_2$ (10 mol %).

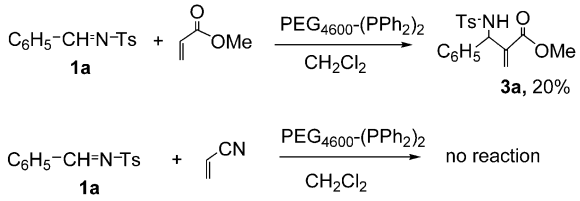


Entry	1/2	Ar	Time [h]	Yield [%][a] 2
1	**a**	C_6H_5	36	57
2	**a**	C_6H_5	36	47[b]
3	**b**	*p*-MeC_6H_4	36	41
4	**b**	*p*-MeC_6H_4	72	48
5	**c**	*p*-$MeOC_6H_4$	72	25
6	**d**	*p*-FC_6H_4	36	64
7	**e**	*p*-ClC_6H_4	36	58
8	**f**	*m*-ClC_6H_4	36	47
9	**g**	*p*-BrC_6H_4	36	61
10	**h**	*p*-$NO_2C_6H_4$	36	79
11	**i**	*m*-$NO_2C_6H_4$	20	45
12	**i**	*m*-$NO_2C_6H_4$	36	77

[a] Isolated yields.
[b] In the absence of MS 4 Å.

ketone (MVK) in the presence of PEG_{4600}-$(PPh_2)_2$ was carried out in various polar solvents at room temperature. We found that in DMF or methanol, the starting material **1** decomposed rapidly and the corresponding aza-Baylis–Hillman adduct was produced in low yield. PEG_{4600}-$(PPh_2)_2$ is insoluble in THF. Dichloromethane is the most suitable solvent for this polymer-supported phosphine Lewis base-catalyzed aza-Baylis–Hillman reaction. However, since PEG_{4600}-$(PPh_2)_2$ is a very hygroscopic compound, in some cases, the starting materials **1** still partially decomposed during reaction even in dichloromethane. We found that this problem can be solved by addition of molecular sieve 4 Å.

For the aza-Baylis–Hillman reactions of **1** with MVK using PEG_{4600}-$(PPh_2)_2$ as a Lewis base under the optimized reaction conditions, the Baylis–Hillman adducts **2** were obtained in moderate to good yields. The results are summarized in Table 1. In the presence of molecular sieve 4 Å, the yield of **2** was improved (Table 1, entries 1–2). For *N*-tosylimines **1** having an electron-donating group on the benzene ring, the corresponding Baylis–Hillman adducts **2b** and **2c** were obtained in moderate yields in CH_2Cl_2 (Table 1, entries 3–5). The prolonged reaction time can slightly improve the yield of **2b** (Table 1, entry 4). For *N*-tosylimines **1** having an electron-withdrawing group on the benzene ring, the Baylis–Hillman adducts **2d**–**i** were produced in good yields (Table 1, entries 6–12). Especially, using *p*-nitrobenzylidene-4-methylbenzenesulfonamide **1 h** as the substrate, the corresponding aza-Baylis–Hillman adduct **2 h** can be obtained in 79% yield (Table 1, entry 10).



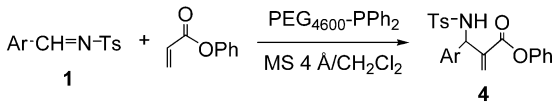
Scheme 2.

We also examined the aza-Baylis–Hillman reactions of **1** with methyl acrylate and acrylonitrile in the presence of PEG_{4600}-$(PPh_2)_2$ (Scheme 2). But, we found that when using methyl acrylate as the Michael acceptor the corresponding Baylis–Hillman adduct **3** was obtained in low yield under the same conditions. While using acrylonitrile as the Michael acceptor, no reaction occurred.

After several experiments, we were pleased to find that when using phenyl acrylate as the Michael acceptor in dichloromethane, the corresponding Baylis–Hillman adducts **4** were obtained in good yields under the same conditions. The results are listed in Table 2. It should be noted that using a poly(ethylene glycol)s (PEGs)-supported phosphine Lewis base, PEG_{4600}-$(PPh_2)_2$, the Lewis base can be easily recovered from the reaction mixture after reaction because on addition of Et_2O, the Lewis base PEG_{4600}-$(PPh_2)_2$ precipitates from the reaction solution. After filtration, the precipitates were washed with Et_2O and the filtrates combined with Et_2O solutions were further purified by column chromatography (SiO_2) to give the corresponding Baylis–Hillman adduct. The recovered Lewis base PEG_{4600}-$(PPh_2)_2$ can be used for the next reaction. We show the results in the aza-Baylis–Hillman reaction of *N*-(*m*-chlorobenzylidene)-4-methylbenzenesulfonamide with MVK using recovered Lewis base PEG_{4600}-$(PPh_2)_2$ in Table 3. As can be seen from Table 3, in a short reaction time, the recovered phosphane Lewis base gave very similar results (Table 3, entries 1–4). However, we found that the polymer-supported phosphine Lewis base is gradually oxidized during the reaction and work-up (Please see the ^{31}P NMR spectroscopic charts in Figures 4 and 5 in the supporting information). As the result, the aza-Baylis–Hillman reaction became sluggish if the Lewis base PEG_{4600}-$(PPh_2)_2$ was used twice. Therefore, the treatment of the oxidized phosphine Lewis base with $LiAlH_4$ and $CeCl_3$ is required to reproduce the desired Lewis base, which can be employed to the next bath of Baylis–Hillman reaction (Scheme 3, see also Figure 6 in supporting information).[10]

Due to the fact that the phosphine Lewis base is oxidized during the reaction and a reduction process is

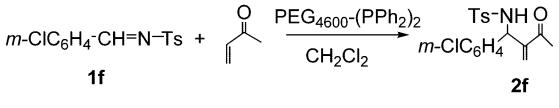
Table 2. The aza-Baylis–Hillman reactions of *N*-sulfonated imine (1.0 equiv.) with phenyl acrylate in the presence of PEG_{4600}-PPh_2 (10 mol %).



Entry	1/4	Ar	Time [h]	Yield [%][a] 4
1	**a**	C_6H_5	36	85
2	**b**	*p*-MeC_6H_4	36	87
3	**c**	*p*-$MeOC_6H_4$	36	76
4	**d**	*p*-FC_6H_4	36	68
5	**e**	*p*-ClC_6H_4	36	63
6	**f**	*m*-ClC_6H_4	36	56
7	**g**	*p*-BrC_6H_4	36	66
8	**h**	*p*-$NO_2C_6H_4$	36	81
9	**i**	*m*-$NO_2C_6H_4$	36	50

[a] Isolated yields.

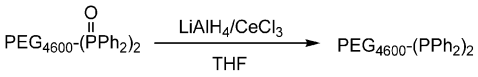
Table 3. The aza-Baylis–Hillman reaction of *N*-(*m*-chlorobenzylidene)-4-methylbenzenesulfonamide (**1f**, 1.0 equiv.) with MVK in the presence of recovered PEG_{4600}-$(PPh_2)_2$ (10 mol %).



Entry	Time	Yield [%][a] 2f
1	30 min	24
2[b]	35 min	42
3[b]	45 min	32
4[b]	45 min	28

[a] Isolated yields.

[b] Recovered PEG-(PPh_2) was used.

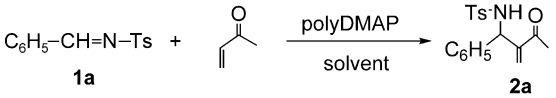


Scheme 3.

required to reproduce the catalyst, it is necessary to find out a more efficient polymer-supported nitrogen Lewis base in the Baylis–Hillman reaction. As we previously reported,[4] DMAP also can effectively catalyze the Baylis–Hillman reaction of *N*-tosylimines **1** or arene-carbaldehydeswith MVK. Therefore, we decided to utilize a polymer-supported DMAP (polyDMAP) as a recyclable nitrogen Lewis base for the Baylis–Hillman reaction. In the aza-Baylis–Hillman reaction of *N*-tosylimines with MVK, the solvent effects were first examined. We found that in dichloromethane, the corresponding aza-Baylis–Hillman adduct was obtained in good yield (Table 4, entries 1 – 6). Polymer-supported Lewis base polyDMAP was easily recovered from reaction mixture just by filtration and can be reused for the same reaction (Table 4, entries 7 – 9). The effectiveness of polyDMAP in the aza-Baylis–Hillman reaction of other *N*-tosylimines has also been examined. In general, the aza-Baylis–Hillman adducts were formed in moderate yields (Table 5, entries 1 – 4).

We found that polyDMAP is more effective in the Baylis–Hillman reaction of aryl aldehydes with MVK. In Table 6, we elucidated the solvent effects for this recyclable nitrogen Lewis base in the Baylis–Hillman reaction of *p*-bromobenzaldehyde with MVK (Table 6, entries 1 – 5). In methanol, the corresponding Baylis–Hillman adduct **5a** was obtained in good yield (53%) for 3 days, but along with by-product **6a** derived from the Michael addition of methanol to **5a** (Table 6, entry 6). The prolonged reaction time increased the yield of **6a** (Table 6, entry 7). Using the sterically bulky *tert*-amyl alcohol as the solvent, the Baylis–Hillman adduct **5a** was

Table 4. The aza-Baylis–Hillman reactions of *N*-sulfonated imines (1.0 equiv.) with MVK (1.5 equiv.) in the presence of polyDMAP (20 mol %).



Entry	Solvent	Time [day]	Yield [%][a] 2a
1	CH_2Cl_2	3	58
2	CH_3CN	3	21
3	THF	3	46
4	DMF	3	13
5	toluene	3	21
6	MeOH	3	trace
7[b]	CH_2Cl_2	3	54
8[b]	CH_2Cl_2	3	42
9[b]	CH_2Cl_2	3	41

[a] Isolated yields.

[b] In the absence of MS 4 Å.

polyDMAP: dimethylaminopyridine, polymer-bound Lewis base:

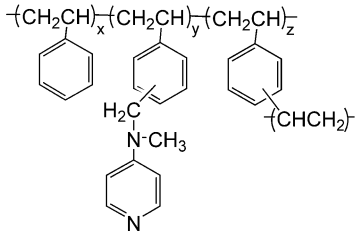
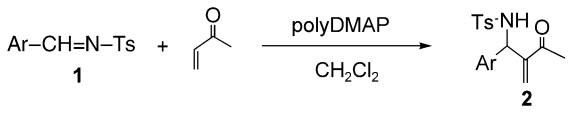


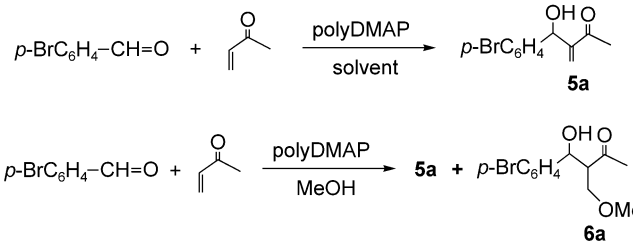
Table 5. The aza-Baylis–Hillman reactions of *N*-sulfonated imines (1.0 equiv.) with MVK (1.5 equiv.) in the presence of polyDMAP (20 mol %).



Entry	1/2	Ar	Time [h]	Yield [%][a] 2
1	**f**	*m*-ClC_6H_4	36	47
2	**g**	*p*-BrC_6H_4	72	48
3	**i**	*m*-$NO_2C_6H_4$	72	25
4	**j**	*m*-FC_6H_4	36	57

[a] Isolated yields.

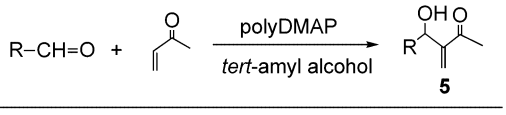
Table 6. The Baylis–Hillman reactions of *p*-bromobenzaldehyde (1.0 equiv.) with MVK (1.5 equiv.) in the presence of polyDMAP (20 mol %).



Entry	Solvent	Time [day]	Yield [%][a] 5a
1	CH_2Cl_2	3	47
2	CH_3CN	3	5
3	THF	3	8
4	DMF	3	7
5	toluene	3	12
6	MeOH	3	53 (6)[b]
7	MeOH	7	46 (32)[b]
8	*tert*-amyl alcohol	7	73

[a] Isolated yields.
[b] The yield of **6a**.

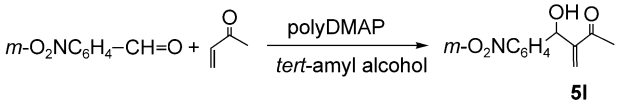
Table 7. The Baylis-Hillman reactions of aryl aldehydes (1.0 equiv.) with MVK (1.5 equiv.) in the presence of polyDMAP (20 mol %).



Entry	5	R	Time [day]	Yield [%][a] 5
1	**b**	*p*-MeC_6H_4	7	41
2	**c**	*p*-$MeOC_6H_4$	7	15
3	**d**	C_6H_5	7	66
4	**e**	*m*-FC_6H_4	7	84
5	**f**	*p*-ClC_6H_4	7	83
6	**g**	*o,p*-$Cl_2C_6H_3$	3	64
7	**h**	3-pyridyl	0.5	75
8	**i**	*p*-$NO_2C_6H_4$	0.5	63
9	**j**	*o*-$NO_2C_6H_4$	0.5	80
10	**k**	n-C_4H_9	7	33

[a] Isolated yields.

Table 8. The Baylis–Hillman reactions of *m*-nitrobenzaldehyde (1.0 equiv.) with MVK (1.5 equiv.) in the presence of recovered polyDMAP (20 mol %).



Run	Time [day]	Yield [%][a] 5l
1[b]	1.0	91
2[b]	1.0	86
3[b]	1.0	92
4[b]	1.0	95
5[b]	1.0	91

[a] Isolated yields.
[b] The recovered polyDMAP was used a Lewis base.

produced as the sole product in 73% after 7 days (Table 6, entry 8). For other aryl aldehydes, the reactions proceeded very well in *tert*-amyl alcohol (Table 7). In the Baylis–Hillman reaction of arenecarbaldehydes having strongly electron-withdrawing groups on the benzene ring such as 3-pyridinecarboxaldehyde and nitrobenzaldehydes with MVK, the corresponding Baylis–Hillman adducts were obtained in high yields after 0.5 day (Table 7, entries 7–9). For other arenecarbaldehydes and the aliphatic aldehyde pentanal, the Baylis–Hillman adducts were obtained in moderate to good yields after 3 or 7 days (Table 7, entries 1–6 and 10). In all these cases, the Lewis base polyDMAP can be recovered from the reaction mixture just by filtration and no further treatment is required. In Table 8, we show that using *m*-nitrobenzaldehyde as the substrate, the recovered polyDMAP effectively catalyzed the Baylis–Hillman reaction in ~90% after 1 day (Table 8, runs 1–5).

In conclusion, we have disclosed a new poly(ethylene glycol)s (PEGs)-supported phosphine Lewis base

PEG_{4600}-$(PPh_2)_2$ in the aza-Baylis–Hillman reaction of *N*-arylidene-4-methylbenzenesulfonamides (ArCH=NTs) **1** with MVK and phenyl acrylate. This polymer-supported Lewis base can be easily recovered from the reaction solution and reproduced by treatment with $LiAlH_4$ and $CeCl_3$. Using polyDMAP as a recyclable nitrogen Lewis base in the Baylis–Hillman reaction of arenecarbaldehydes with MVK, the corresponding adducts were obtained in good to high yields in *tert*-amyl alcohol. Efforts are underway to elucidate mechanistic details of this polymer-supported, Lewis base-catalyzed reaction and the key factors required for the polymer-supported Lewis base to the different substrates of the Baylis-Hillman reactions. Work along these lines is currently in progress.

Experimental Section

General Remarks

Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were measured on Perkin-Elmer-983. Elemental analyses were measured on Italian Carlo-Erba 110. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer as a solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; *J* values are in Hz. Mass spectra were recorded with an HP-5989 instrument. *N*-Tosylimines were prepared according to the literature.[10] All of the solid compounds reported in this paper gave satisfactory CHN microanalyses. Commercially obtained reagents were used without further purification. TLC monitoring all reactions was with Huanghai GF_{254} silica gel-coated plates. Flash column chromatography was carried out using 200–300 mesh silica gel at increased pressure. PEG_{4600} and dimethylaminopyridine, polymer-bound (typical loading 5.5–6.0 mmol N/g) were purchased from Aldrich. Co.

Preparation of the Polymer-Supported Lewis Base

PEG_{4600}-$(OMs)_2$: PEG_{4600} (10.5 g, 2.28 mmol) and Et_3N (11.5 mL, 41.0 mmol) were dissolved in CH_2Cl_2 (200 mL) and cooled to 0 °C. Methanesulfonyl chloride (2.5 mL, 13.7 mmol) was then added dropwise. After the reaction mixture had been stirred at room temperature for 24 hours, it was concentrated to volume of 200 mL and was added dropwise with vigorous stirring to diethyl ether (1.5 L). The resulting precipitates were collected by filtration and washed with diethyl ether (3 × 100 mL). The precipitates were then dried under vacuum to give the desired product as a white solid; yield: 11.0 g (100% based on the recovered polymer). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 4.37–4.41 (m, 4H, PEG-α-ethylenes), 3.75–3.90 (m, 4H, PEG-β-ethylenes), 3.50–3.66 (brm, PEG-ethylenes), 3.09 (s, 6H, SO_2CH_3).

PEG_{4600}-$(PPh_2)_2$: PEG dimesylate (5.0 g, 1.05 mmol) was added to the freshly prepared Ph_2PLi (12 mmol) solution in anhydrous THF at 0 °C, the resulting suspension was stirred at room temperature for 24 hours and concentrated under vacuum. The crude product was then dissolved in CH_2Cl_2 (50 mL) and added dropwise with vigorous stirring to diethyl ether (500 mL), the resulting precipitates were isolated by filtration and washed with isopropyl alcohol (50 mL) and diethyl ether (3 × 100 mL) to give the desired polymeric phosphine as a white solid; yield: 5.20 g (95%). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.41 (t, *J* = 7.8, 4H, PEG-β-ethylenes), 3.39–3.89 (brm, PEG-methylenes), 7.30–7.45 (m, 20H, ArH); ^{31}P NMR ($CDCl_3$, 85% H_3PO_4, 121 MHz): δ = –21.39.

Regeneration of the Polymer-Supported Lewis Base

Powdery anhydrous $CeCl_3$ (92 mg, 0.375 mmol) was suspended in dry THF (10 mL). After stirring for 1 h under Ar atmosphere, the oxidized phosphine Lewis base (320 mg, 0.06 mmol) and $LiAlH_4$ (20 mg, 0.5 mmol) were added. The mixture was heated at reflux for 12 hours, then cooled to room temperature and quenched with MeOH. The crude mixture was filtered through a short pad of silica and the clear filtrate was then dried in vacuum to give the desired phosphine Lewis base; yield: 314 mg (99%). ^{31}P NMR ($CDCl_3$, 85% H_3PO_4, 121 MHz): δ = –21.25.

Typical Procedure for the Baylis–Hillman reaction of 1e with Methyl Vinyl Ketone (MVK)

To a Schlenk tube charged with 1e (147 mg, 0.5 mmol) and poly(ethylene glycol)s (PEGs)-supported phosphine Lewis base PEG_{4600}-$(PPh_2)_2$ (280 mg, 0.05 mmol) in CH_2Cl_2 (5.0 mL) was added methyl vinyl ketone (MVK) (53 mg, 62 μL, 0.75 mmol) under an argon atmosphere and the reaction mixture was stirred for 36 h at room temperature (20 °C). The reaction mixture was precipitated by addition of Et_2O (20 mL) and then filtered. The filtrate (ether solution) was concentrated under reduced pressure and the residue purified by silica gel column chromatography (eluent: EtOAc/petroleum, 1/4) to give 2e as a colorless solid; yield: 105 mg (58%). The precipitates were collected for the next Baylis-Hillman reaction.

***N*-[1-(4-Chlorophenyl)-2-methylene-3-oxobutyl]-4-methylbenzenesulfonamide (2e):** colorless solid; mp 108–110 °C; IR ($CHCl_3$): ν = 1674 cm^1 (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.11 (3H, s, Me), 2.38 (3H, s, Me), 5.24 (1H, d, *J* = 9.1 Hz, NH), 5.99 (1H, d, *J* = 9.1 Hz, CH), 6.03 (1H, s), 6.06 (1H, s, CH), 7.01 (2H, d, *J* = 8.6 Hz, ArH), 7.12 (2H, d, *J* = 8.6 Hz, ArH), 7.19 (2H, d, *J* = 8.1 Hz, ArH), 7.59 (2H, d, *J* = 8.1 Hz, ArH); MS (EI): *m/e* = 294 (M^+ – 69, 2.36), 208 (M^+ – 155, 100), 91 ($PhMe^+$, 39.81); anal. calcd. for $C_{18}H_{18}ClNO_3S$: C 59.42%, H 4.99%, N 3.85%; found: C 59.43%, H 4.94%, N 3.78%.

2-[(4-Chlorophenyl)-(toluene-4-sulfonylamino)-methyl]-acrylic acid phenyl ester (4e): colorless solid, yield: 146 mg (63%); mp 98–100 °C; IR (KCl): ν = 3296 (N-H), 1720.8 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.44 (3H, s, Me), 5.38 (1H, d, *J* = 9.0 Hz, NH), 5.64 (1H, d, *J* = 9.0 Hz, CH), 6.05 (1H, s, C=CH_2), 6.50 (1H, s, C=CH_2), 6.87–6.90 (2H, m, ArH), 7.12–7.16 (2H, m, ArH), 7.20–7.28 (5H, m, ArH), 7.33–7.38 (2H, m, ArH), 7.69–7.71 (2H,m, ArH); MS (EI): *m/e* = 348 (M^+ – 93, 30.24), 294 (M^+ – 93–54, 19.66), 177 (M^+ – 93–171, 65.22). 155 (M^+ – 286, 81.92), 115 (M^+ – 93–170–28–

35, 33.60), 91 (M^+ – 350, 100), 65 (M^+ – 350 – 26, 50.99); anal. calcd. for $C_{23}H_{20}ClNO_4S$: C 62.51%, H 4.56%, N 3.17%; found: C 62.48%, H 4.56%, N 3.12%.

Typical Procedure for the Baylis–Hillman Reaction of *p*-Bromobenzaldehyde with MVK in the Presence of PolyDMAP

To a Schlenk tube charged with *p*-bromobenzaldehyde (95 mg, 0.5 mmol) and a polymer-supported nitrogen Lewis base polyDMAP (18 mg, ~0.1 mmol) in *tert*-amyl alcohol (1.0 mL) was added methyl vinyl ketone (MVK) (53 mg, 62 μL, 0.75 mmol) and the reaction mixture was stirred for 3 days at room temperature (20 °C). The mixture remains heterogeneous throughout the reaction time. After filtration, the precipitates were washed with CH_2Cl_2 (10 mL). The filtrate combined with the CH_2Cl_2 layer was concentrated under reduced pressure and the residue was purified by a silica gel column chromatography (eluent: EtOAc/petroleum, 1/4) to give **5a** as a colorless oil; yield: 78 mg (60%). IR (KBr): $\nu = 3423$ (O-H), 2963, 1676 (C=O), 1487, 822 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS): $\delta = 2.33$ (3H, s, Me), 3.20 (1H, d, $J = 4.8$ Hz, OH), 5.58 (1H, d, $J = 4.8$ Hz, CH), 5.99 (1H, s, C=CH_2), 6.22 (1H, s, C=CH_2), 7.25 (2H, d, $J = 8.4$ Hz, ArH), 7.48 (2H, d, $J = 8.4$ Hz, ArH); MS (EI): $m/e = 255$ (M^+, 38.5), 239 (M^+ – 17, 10.3), 175 (M^+ – 80, 100), 157 (M^+ – 98, 45.1), 77 (M^+ – 178, 42.6), 43 (M^+ – 212, 54.7); HRMS (EI): found $m/z = 253.9946$ (M^+); $C_{11}H_{11}O_2Br$ requires: 253.9942.

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