JOC Article

Highly Efficient aza-Baylis−Hillman Reaction of *N*-Tosylated Imines with MVK, Acrolein, and Phenyl Acrylate or α-Naphthyl Acrylate: Lewis Base Effects and A Convenient Method to Synthesize α,*β*-Unsaturated *β*-Amino Carbonyl Compounds

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Received July 29, 2003

This paper describes several highly efficient aza-Baylis−Hillman reactions of *N*-tosylated imines with MVK, acrolein, and phenyl acrylate or α-naphthyl acrylate in the presence of a Lewis base. In most cases, the reaction can be completed within 1 h using the appropriate Lewis base catalyst. An efficient method to synthesize *β*-amino ketones, aldehydes and esters in high yields and short reaction time has been developed.

Introduction

The Baylis−Hillman reaction, notorious for its poor reaction rate, is an important carbon−carbon bond-forming process that affords densely functionalized products. This reaction is generally catalyzed by Lewis bases such as tertiary amines or phosphines [DABCO (1,4-diazabicyclic[2,2,2]octane) or triphenylphosphine (PPh_3)].[1] A plausible mechanism for this reaction was previously proposed in which the addition of ammonium or phosphonium enolate to an electrophile is believed to be the rate-determining step.[2] Efforts to accelerate the reaction rate have been explored, including chemical methods[3] and physical techniques.[4] During our own investigations on this very simple and useful reaction,[5] we found that in the reaction of arylaldehydes, especially having the electron-donating groups such as Et or MeO on the benzene ring, with some Michael acceptors such as methyl vinyl ketone (MVK) or methyl acrylate, either the reactions were sluggish or no reactions occurred under the traditional Baylis−Hillman reaction conditions. However, our previous investigations disclosed that, using *N*-tosylated imines to replace arylaldehydes, the aza-Baylis−Hillman reaction can be accelerated to some extent to provide *β*-amino carbonyl compounds in higher yields compared with their arylaldehydes in the presence of nitrogen or phosphine Lewis base catalyst (Scheme 1).[6,7]

According to the generally accepted mechanism of the Baylis−Hillman reaction,[1,2] we attempted to vary the structures of the Michael acceptors and nucleophilic Lewis base catalysts in order to allow the ammonium or phosphonium enolates to be formed more easily. By this protocol, the zwitterionic ammonium or phosphonium

(1) (a) Baylis, A. B.; Hillman, M. E. D. *Ger. Offen*. **1972**, *2*,155,113; *Chem. Abstr*. **1972**, *77*, 34174q; Hillman, M. E. D.; Baylis, A. B. U.S. Patent, **1973**, 3, 743, 669. (b) Morita, K.; Suzuki, Z.; Hirose, H. *Bull. Chem. Soc. Jpn*. **1968**, *41*, 2815−2819. For reviews, see: (c) Basavaiah, D.; Rao, P. D.; Hyma, R. S. *Tetrahedron* **1996**, *52*, 8001−8062. (d) Drewes, S. E.; Roo, G. H. P. *Tetrahedron* **1988**, *44*, 4653−4670. (e) Ciganek, E. *Org. React*. **1997**, *51*, 201−350. (f) Langer, P. *Angew. Chem., Int. Ed*. **2000**, *39*, 3049−3052. (g) Basavaiah, D.; Rao, A. J.; Satyanarayana, T. *Chem. Rev*. **2003**, *103*, 811−892.

(2) Hill, J. S.; Issacs, N. S. *J. Phys. Org. Chem*. **1990**, *44*, 285−292.

(3) (a) Rafel, S.; Leahy, J. W. *J. Org. Chem*. **1997**, *62*, 1521−1522. (b) Aggarwal, V. K.; Tarver, G. J.; McCague, R. *Chem. Commun*. **1996**, 2713−2714. (c) Aggarwal, V. K.; Mereu, A.; Tarver, G. J.; McCague, R. *J. Org. Chem*. **1998**, *63*, 7183−7189. (d) Aggarwal, V. K.; Dean, D. K.; Mereu, A.; Williams, R. *J. Org. Chem*. **2002**, *67*, 510−514. (e) Aggarwal, V. K.; Mereu, A. *Chem. Commun*. **1999**, 2311−2312. (f) Hayase, T.; Shibata, T.; Soai, K.; Wakatsuki, Y. *Chem. Commun*. **1998**, 1271−1272. (g) Barrett, A. G. M.; Cook, A. S.; Kamimura, A. *Chem. Commun*. **1998**, 2533−2534. (h) Kawamura, M.; Kobayashi, S. *Tetrahedron Lett*. **1999**, *40*, 1539−1542. (i) Basavaiah, D.; Kumaragurubaran, N. *Tetrahedron Lett*. **2001**, *42*, 477−479. (j) Lee, W. D.; Yang, K. S.; Chen, K. *Chem. Commun*. **2001**, 1612−1613. (k) Yu, C. Z.; Liu, B.; Hu, L. Q. *J. Org. Chem*. **2001**, *66*, 5413−5418. (l) Li, G.-G.; Wei, H.-X.; Gao, J.-J.; Caputo, T. D. *Tetrahedron Lett*. **2000**, *41*, 1−3. (m) Li, G.-G.; Gao, J.-J.; Wei, H.-X.; Enright, M. *Org. Lett*. **2000**, *2*, 617−619 and references therein. (n) Iwamura, T.; Fujita, M.; Kawakita, T.; Kinoshita, S.; Watanabe, S.-I.; Kataoka, T. *Tetrahedron* **2001**, *57*, 8455−8461 and references therein.

(4) (a) Jenner, G. *High-Pressure Res*. **1999**, *16*, 243−252. (b) Kun, M. K.; Mukherjee, S. B.; Balu, N.; Padmakumar, R.; Bhat, S. V. *Synlett* **1994**, 444−446. (c) Roos, G. H. P.; Padmakumar, R. *Synth. Commun*. **1993**, *23*, 1261−1266. (d) Isaacs, N. S. *Tetrahedron* **1991**, *47*, 8463−8497.

(5) (a) Shi, M.; Jiang, J.-K.; Feng, Y.-S. *Org. Lett*. **2000**, *2*, 2397−2400. (b) Shi, M.; Feng, Y.-S. *J. Org. Chem*. **2001**, *66*, 406−411. (c) Shi, M.; Li, C.-Q.; Jiang, J.-K. *Chem. Commun*. **2001**, 833−834.

(6) (a) Shi, M.; Xu, Y.-M. *Chem. Commun*. **2001**, 1876−1877. (b) Shi, M.; Xu, Y.-M. *Eur. J. Org. Chem*. **2002**, 696−701. (c) Shi, M.; Xu, Y.-M.; Zhao, G.-L.; Wu, X.-F. *Eur. J. Org. Chem*. **2002**, 3666−3679. (d) Shi, M.; Zhao, G.-L. *Tetrahedron Lett*. **2002**, *43*, 4499−4502. (e) Shi, M.; Xu, Y.-M. *J. Org. Chem*. **2003**, *68*, 4784−4790. (f) Shi, M.; Xu, Y. M. *Angew. Chem., Int. Ed*. **2002**, *41*, 4507−4510. (g) Shi, M.; Chen, L. H. *Chem. Commun*. **2003**, 1310−1311.

(7) The following reports relate to the aza-Baylis−Hillman reaction of methyl acrylate with sulfonated imines. Please see: (a) Perlmutter, P.; Teo, C. C. *Tetrahedron Lett*. **1984**, *25*, 5951−5952. (b) Takagi, M.; Yamamoto, K. *Tetrahedron* **1991**, *47*, 8869−8871. (c) Campi, E. M.; Holmes, A.; Perlmutter, P.; Teo, C. C. *Aust. J. Chem*. **1995**, *48*, 1535−1540. The following reports relate to the aza-Baylis−Hillman reaction of MVK with imine generated in situ. Please see: (c) Bertenshow, S.; Kahn, M. *Tetrahedron Lett*. **1989**, *30*, 2731−2734. (d) Balan, D.; Adolfsson, H. *J. Org. Chem*. **2002**, *67*, 2329−2334 and references therein.

10.1021/jo035103p CCC: $27.50
Published on Web 12/16/2003

SCHEME 1

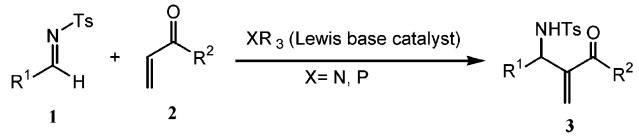
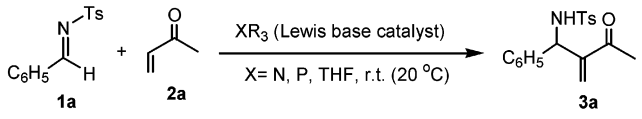


TABLE 1. aza-Baylis−Hillman Reaction of *N*-Benzylidene-4-methylbenzenesulfonamide 1a (0.5 equiv) with MVK 2a (1.0 equiv) in the Presence of Various Lewis Bases



entry	catalyst (10 mol %)	time (h)	yield (%) of **3a**[a]
1	DMAP	22	30
2	DABCO	22	45
3	PPh_3	24	72
4	PBu_3	2	*b*
5	Ph_2PMe	0.75	80
6	$PhPMe_2$	2	*b*
7	dppe	9	65
8	PBu^t_3	48	*c*
9	P(*o*-Tol)$_3$	48	*c*

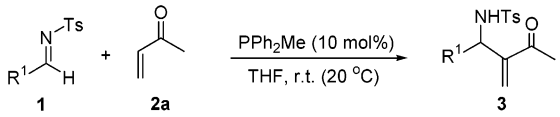
[a] Yields of isolated product. [b] Other products were obtained.[6b] [c] No reaction occurred.

enolate species, generated from the Michael addition of a nucleophilic Lewis base to an α,*β*-unsaturated enone, can be maintained in higher concentration in the reaction solution, which may shift the equilibrium forward to accomplish the nucleophilic attack of the formed enolate species to the electrophile, giving the Baylis−Hillman adduct. As a result, the reaction rate can be accelerated. Herein we wish to report several highly efficient aza-Baylis−Hillman reactions of *N*-tosylated imines **1** with α,*β*-unsaturated aldehydes, ketones, and esters **2** in the presence of appropriate Lewis base catalysts to give *β*′-amino-α,*β*-unsaturated carbonyl compounds in good yields. Most of these aza-Baylis−Hillman reactions can be accomplished within 1 h.

Results and Discussion

During our careful investigations, we found that this type of aza-Baylis−Hillman reaction is extremely sensitive to temperatures, solvents, and Lewis base catalysts. First, we examined the reaction of *N*-benzylidene-4-methylbenzenesulfonamide **1a** (R^1 = Ph) (0.5 equiv) with methyl vinyl ketone (MVK) **2a** (R^2 = Me) (1.0 equiv) under various reaction conditions. A variety of Lewis base catalysts (10 mol %) were examined, and the results are summarized in Table 1. The use of tertiary amines such as 4-*N*,*N*-(dimethylamino)pyridine (DMAP) or DABCO as a Lewis base gave the corresponding aza-Baylis−Hillman adduct **3a** in 30% or 45% yield, respectively, after 22 h at room temperature (20 °C) (entries 1 and 2 in Table 1). Tertiary phosphines can more efficiently catalyze this reaction. For example, Lewis base Ph_3P gave the normal aza-Baylis−Hillman adduct **3a** in 72% yield after 24 h (entry 3 in Table 1). The use of 1,2-bis(diphenylphosphino)ethane (dppe) as a Lewis base afforded a similar result (entry 7 in Table 1). A significant rate acceleration was observed when PPh_2Me was employed as a Lewis base in THF.[8] For example, treatment of *N*-benzylidene-4-methylbenzenesulfonamide **1a** with MVK in the presence of PPh_2Me (10 mol %) provided the desired product **3a** in 80% yield within 45 min under the same conditions (entry 5 in Table 1). At higher reaction temperature (>30 °C), the polymerization of MVK was observed and the aza-Baylis−Hillman adduct **3a** was formed in lower yield. The use of stronger Lewis bases such as PBu_3 or $PhPMe_2$ gave the pyrrolidine derivatives without the formation of the corresponding normal aza-Baylis−Hillman adduct **3** (entries 4 and 6 in Table 1).[6b] Using P^{t}Bu$_3$ or P(*o*-Tol)$_3$ as a Lewis base, no reaction occurred under the same conditions because the sterically bulky *tert*-butyl or *o*-tolyl group around the phosphine atom diminished the nucleophilicity of the tertiary phosphine and therefore reduced its catalytic ability as a Lewis base to initiate the aza-Baylis−Hillman reaction (entries 8 and 9 in Table 1). Thus, PPh_2Me is the best Lewis base for this version of aza-Baylis−Hillman reaction.

TABLE 2. aza-Baylis−Hillman Reaction of *N*-Tosylated Imines 1 (0.5 equiv) with Methyl Vinyl Ketone 2a (1.0 equiv)



entry	R^1	time (min)	product	yield (%) of **3**[a]
1	*p*-ClC_6H_4 (**1b**)	30	**3b**	77
2	*m*-FC_6H_4 (**1c**)	30	**3c**	78
3	*p*-MeC_6H_4 (**1d**)	45	**3d**	88
4	*p*-$NO_2C_6H_4$ (**1e**)	30	**3e**	67
5	*p*-$CH_3OC_6H_4$ (**1f**)	50	**3f**	87
6	2,3-$Cl_2C_6H_3$ (**1g**)	35	**3g**	63

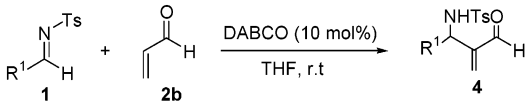
[a] Yield of isolated product.

We then examined the aza-Baylis−Hillman reaction of other *N*-tosylated aromatic imines (0.5 equiv) with MVK **2a** (1.0 equiv) under the optimized conditions. The results are summarized in Table 2. As can be seen from Table 2, similar results were observed, and the aza-Baylis−Hillman adducts **3** were obtained in very high yields. The substituents on the benzene ring of *N*-tosylated aromatic imines have little effect on the reaction rate. Specifically, when *N*-(4-methoxybenzylidene)-4-methylbenzenesulfonamide **1f** was used as the substrate, this version of the aza-Baylis−Hillman reaction can be finished within 50 min in 87% yield as well (entry 5 in Table 2).

This result stimulated us to seek out other versions of fast aza-Baylis−Hillman reactions using other Michael acceptors. Therefore, we selected the more active Michael acceptor acrolein **2b** (R^2 = H) as the substrate. After screening of various Lewis base catalysts as the procedures shown in Table 1, we found that the aza-Baylis−Hillman reactions of *N*-benzylidene-4-methylbenzenesulfonamide **1a** (0.5 equiv) with acrolein **2b** (1.0 equiv) in THF in the presence of DABCO (10 mol %) at room temperature gave the corresponding aza-Baylis−Hillman adduct **4a** in 80% yield within 50 min. To further determine the feasibility of this catalytic system, various

(8) The solvent effect has been examined throughout this report. THF is the best choice of solvent for various Lewis base catalysts.

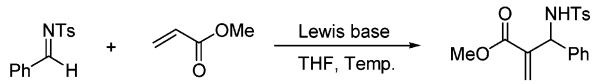
TABLE 3. aza-Baylis−Hillman Reaction of *N*-Tosylated Imines 1 (0.5 equiv) with Acrolein 2b (10 equiv)



entry	R^1	time (min)	product	yield (%) of **4**[b]
1	C_6H_5 (**1a**)	50	**4a**	80
2	*p*-ClC_6H_4 (**1b**)	25	**4b**	83
3	*p*-$CH_3C_6H_4$ (**1d**)	120	**4c**	82
4	*p*-$NO_2C_6H_4$ (**1e**)	30	**4d**	43
5	*p*-CH_3OC_6H4 (**1f**)	180	**4e**	77
6	*m*-ClC_6H_4 (**1h**)	20	**4f**	82
7	*p*-BrC_6H_4 (**1i**)	25	**4g**	88
8	*p*-FC_6H_4 (**1j**)	30	**4h**	89
9	*p*-EtC_6H_4 (**1k**)	90	**4i**	91

[a] All reactions were conducted using 2:1 molar ratio of acrolein and *N*-tosylimine in THF at room temperature. [b] Isolated yields based on the imine.

TABLE 4. aza-Baylis−Hillman Reaction of *N*-Benzylidene-4-methylbenzenesulfonamide 1a (0.5 equiv) with Methyl Acrylate 2c (1.0 equiv)



entry	catalyst	temp (°C)	time (h)	yield (%)[a]
1	Ph_3P	rt	24	
2	Ph_3P[b]	40	40	
3	Ph_3P	40	48	
4	DABCO	rt	24	63
5	PBu_3	rt	10	
6	PPh_2Me	rt	6	62
7	$PPhMe_2$	rt	4	43
8[c]	DABCO	rt	15	73

[a] Isolated yields. [b] The reaction was carried out in ^{i}PrOH. [c] *N*-(4-Chlorobenzylidene)-4-methylbenzenesulfonamide **1b** was used, and the product was **5b**.

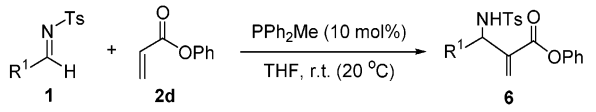
N-tosylated imines **1** were also examined under the optimal conditions. Most of the *N*-tosylated imines **1** gave the desired adducts in good to excellent yields within a short reaction time, although the substituents on the benzene ring of **1** have some effects on the reaction rate. This is because, as can be seen from Table 3, when the benzene ring of the *N*-tosylated imines **1** has electron-withdrawing groups, the reactions can be finished within 30 min (entries 2, 4, 6−8 in Table 3). On the other hand, the reaction time has to be prolonged to 2 or 3 h if the electron-donating substituents are present on the benzene ring of **1** (entries 1, 3, 5, 9 in Table 3). In the aza-Baylis−Hillman reaction of **1e**, which has the strongest electron-withdrawing nitro group on the benzene ring, with **2b**, we found that **1e** decomposed rapidly and the corresponding aza-Baylis−Hillman adduct **4d** was obtained in 43% yield along with many unidentified products under the same conditions (Table 1, entry 4). In addition, it should be emphasized here that in this type of aza-Baylis−Hillman reaction, the reaction furnished complicated products and none of the corresponding normal aza-Baylis−Hillman adduct **4** was formed if using PPh_3, PBu_3, or PPh_2Me as a Lewis base promoter.

Furthermore, we also attempted the aza-Baylis−Hillman reaction of *N*-benzylidene-4-methylbenzenesulfonamide **1a** with various acrylates. This was done because we also want to find a version of an efficient aza-Baylis−Hillman reaction to prepare *β*-amino esters. First, we used methyl acrylate **2c** (R^2= OMe) (1.0 equiv) as the Michael acceptor to react with *N*-benzylidene-4-methylbenzenesulfonamide **1a** (0.5 equiv) in the presence of various Lewis base catalysts (10 mol %). The results are presented in Table 4. In the aza-Baylis−Hillman reaction of *N*-benzylidene-4-methylbenzenesulfonamide **1a** with methyl acrylate **2c**, the tertiary phosphine Lewis base catalyst PPh_3 did not give the corresponding aza-Baylis−Hillman adduct **5a**, although the solvent was changed and the reaction temperature was raised (entries 1−3 in Table 4). Tributylphosphine also showed no catalytic activity for this aza-Baylis−Hillman reaction (entry 5 in Table 4). Using tertiary nitrogen Lewis base DABCO as a catalyst, the corresponding aza-Baylis−Hillman adduct **5a** was obtained in 63% yield after 24 h (entry 4 in Table 4). Introducing an electron-withdrawing group such as Cl on the benzene ring of *N*-tosylated imine **1** slightly improved the reaction rate in the presence of DABCO but did not significantly affect the outcome of this aza-Baylis−Hillman reaction (Table 4, entry 8). Using PPh_2-Me or $PhPMe_2$ as the catalyst, the reaction was somewhat accelerated to give **5a** in 62% yield after 6 h or in 43% after 4 h, respectively (entries 6 and 7 in Table 4). However, the achieved yields and reaction rates are still not satisfactory enough.

Previously, Chen and co-workers reported that, using phenyl acrylate **2d** (R^2 = OPh) or α-naphthyl acrylate **2e** [R^2 = O(α-Nap)] as a Michael acceptor, the Baylis−Hillman reaction with aldehydes can be significantly accelerated in the presence of DABCO (30 mol %).[3j] Encouraged by this result, we exchanged methyl acrylate with more reactive phenyl acrylate **2d** as a Michael acceptor (1.0 equiv) for the above aza-Baylis−Hillman reaction with **1a** (0.5 equiv). We delightfully found that in the presence of PPh_2Me (10 mol %) or DABCO (30 mol %) the desired aza-Baylis−Hillman adduct **6a** was obtained in 94% yield in THF after 30 min or in 81% yield in MeCN after 40 min, respectively (entries 1 and 2 in Table 5). The phosphine Lewis base PPh_2Me is also more effective than DABCO in the aza-Baylis−Hillman reaction of *N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide **1b** (0.5 equiv) or *N*-(4-methoxybenzylidene)-4-methylbenzenesulfonamide **1f** (0.5 equiv) with phenyl acrylate **2d** (1.0 equiv) (entries 3, 4 and 8, 9 in Table 5). The results are summarized in Table 5. Similar results were obtained for other *N*-tosylated imines **1** using PPh_2-Me (10 mol %) as a catalyst under the optimal reaction conditions. Using α-naphthyl acrylate **2e** as a Michael acceptor under the same conditions, the corresponding aza-Baylis−Hillman adducts **6k**−**m** were also obtained in good yields within 30 min (Scheme 2). The aza-Baylis−Hillman reaction was accelerated dramatically using phenyl acrylate **2d** or α-naphthyl acrylate **2e** as a Michael acceptor, and most of the corresponding aza-Baylis−Hillman adducts **6** were obtained in good to excellent yields within 1 h (Table 5 and Scheme 2).

The effect of Lewis bases in the aza-Baylis−Hillman reaction has been throughout studied in this Article. If the catalytic activities of the employed Lewis base catalysts and the reactivities of Michael acceptors match, the Baylis−Hillman reaction can proceed very well to

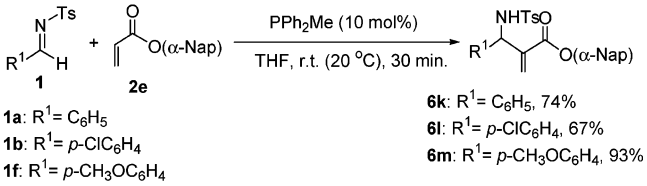
TABLE 5. aza-Baylis−Hillman Reaction of *N*-Tosylated Imines 1 (0.5 equiv) with Phenyl Acrylate 2d (1.0 equiv)



entry	R^1	time (min)	product	yield (%) of **6**[a]
1	C_6H_5 (**1a**)	30	**6a**	94
2	C_6H_5 (**1a**)	40	**6a**	81[b]
3	*p*-ClC_6H_4 (**1b**)	25	**6b**	90
4	*p*-ClC_6H_4 (**1b**)	25	**6b**	84[b]
5	*m*-FC_6H_4 (**1c**)	40	**6c**	90
6	*p*-MeC_6H_4 (**1d**)	45	**6d**	88
7	*p*-$NO_2C_6H_4$ (**1e**)	15	**6e**	71
8	*p*-$CH_3OC_6H_4$ (**1f**)	30	**6f**	96
9	*p*-$CH_3OC_6H_4$ (**1f**)	100	**6f**	57[b]
10	2,3-$Cl_2C_6H_3$ (**1g**)	30	**6g**	74
11	*p*-EtC_6H_4 (**1k**)	35	**6h**	92
12	*m*-$CH_3C_6H_4$ (**1l**)	25	**6i**	90
13	*2*-furyl (**1m**)	60	**6j**	84

[a] Isolated yield. [b] Using DABCO (30 mol %) as a catalyst in CH_3CN.

SCHEME 2

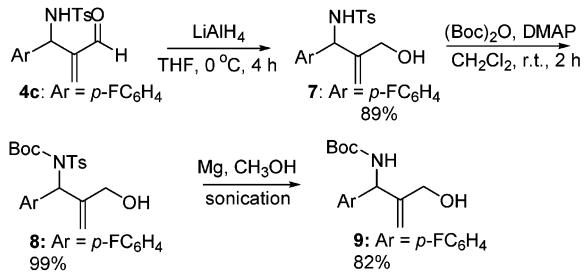


give the corresponding aza-Baylis−Hillman adducts in high yields and with a short reaction time (30−60 min). Moreover, the results obtained in the aza-Baylis−Hillman reaction of methyl vinyl ketone, acrolein, phenyl acrylate, and α-naphthyl acrylate with *N*-tosylated imines **1** suggest that when the Michael acceptor is more reactive (e.g., acrolein), less nucleophilic Lewis base should be selected as a catalyst (e.g., DABCO). For the less reactive Michael acceptor such as MVK, phenyl acrylate, or α-naphthyl acrylate, the aza-Baylis−Hillman adducts can also be obtained in higher yields within a short reaction time if a stronger nucleophilic Lewis base (e.g., PPh_2Me) is employed as a catalyst. In general, PPh_2-Me accelerates the reaction rate more efficiently than DABCO in the aza-Baylis−Hillman reaction (Table 1, Table 4, entries 1, 2 and 3, 4 and 8, 9 in Table 5).

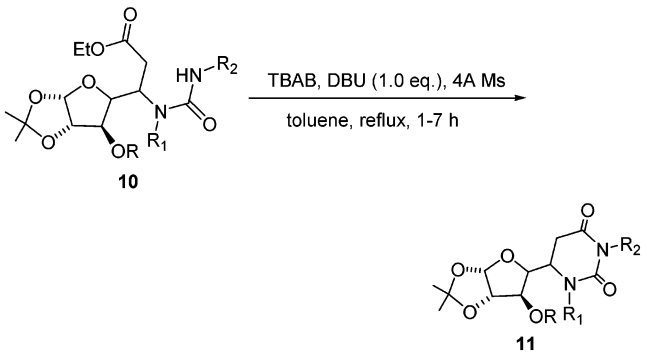
On the other hand, in the aza-Baylis−Hillman reaction of aliphatic *N*-tosylated imines with MVK, acrolein, or phenyl acrylate, under similar reaction conditions, none of the corresponding normal aza-Baylis−Hillman adduct was formed and the reaction usually gave complicated products.

If the *N*-tosyl group of these aza-Baylis−Hillman adducts (*β*′-amino-α,*β*-unsaturated aldehydes, ketones, and esters) could be easily removed, the synthetic utility of these amino adducts could be expanded. However, the *N*-tosyl group is usually very difficult to be removed. In Scheme 3, we presented the further potential synthetic application of this adduct by a preparation of *γ*-amino alcohol via reduction of the aza-Baylis−Hillman adduct and removal of the *N*-tosyl group. The aza-Baylis−Hillman adduct **4c** derived from the aza-Baylis−Hillman reaction of *N*-tosylated imine with acrolein was first

SCHEME 3



SCHEME 4



reduced by $LiAlH_4$ to give the corresponding *γ*-amino alcohol **7** in 89% yield. The amino alcohol **7** was transformed to the Boc-protected amino alcohol **8** by reaction with di-*tert*-butyl dicarbonate [$(Boc)_2O$] and DMAP in dichloromethane in 99% yield. Treatment of the obtained amino alcohol **8** with Mg/MeOH resulted in the selective removal of the *N*-tosyl substituent,[9] and the Boc-protected amino alcohol **9** was isolated in 82% yield. Thus, the *N*-tosyl group has been changed to the synthetically more useful Boc group because the Boc protecting group can be easily removed by various methods (Scheme 3).

In 2002, Tewari and co-workers reported a convenient synthesis of C-nucleoside **11** analogues by cyclic amidation of **10** catalyzed by DBU, *tert*-butylammonium bromide (TBAB), and 4 Å molecular sieves (Scheme 4).[10] We intended to convert, under similar conditions, the aza-Baylis−Hillman adducts **5** and **6** derived by reaction of *N*-tosylated imines with acrylates to *β*-lactams, which are more important synthetic intermediates in organic chemistry. However, under the reported reaction conditions, we found that the aza-Baylis−Hillman adducts **5b** and **6a** were stereoselectively transformed to the corresponding methyl (2*E*)-3-(4-chlorophenyl)-2-[(toluene-4-sulfonylamino)methyl]acrylate **12** and phenyl (2*E*)-3-phenyl-2-[(toluene-4-sulfonylamino)methyl]acrylate **13** in good yields.[11] The structure of **12** was determined by X-ray diffraction (Figure 1).[12] On the basis of further investiga-

(9) Juhl, K.; Gathergood. N.; J*ϕ*rgenson, A. K. *Angew. Chem., Int. Ed.* **2001**, *40*, 2995−2997.

(10) Tewari, N.; Mishra, R. C.; Tiwari, V. K.; Tripathi, R. P. *Synlett* **2002**, *11*, 1779−1782.

(11) The reaction of the Baylis−Hillman acetate with amines of *N*-sulfonated amines in the presence of K_2CO_3 has been previously reported. See: (a) Kim, J. N.; Kim, H. S.; Gong, J. H.; Chung, Y. M. *Tetrahedron Lett.* **2001**, *42*, 8341−8344. (b) Chung, Y. M.; Lee, H. J.; Hwang, S. S.; Kim, J. N. *Bull. Korean Chem. Soc.* **2001**, *22*, 799−805. (c) Kim, J. N.; Chung, Y. M.; Im, Y. J. *Tetrahedron Lett.* **2002**, *43*, 6209−6212.

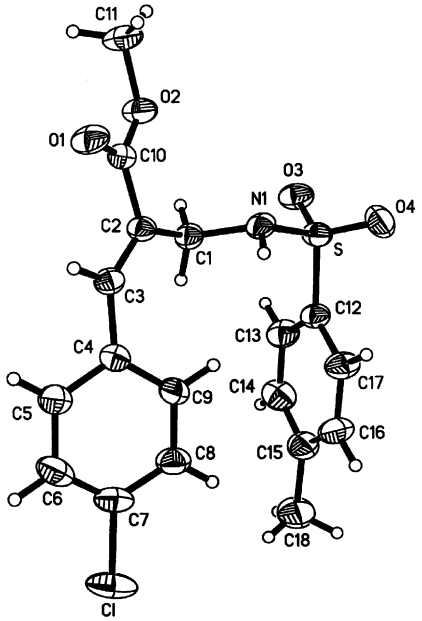


FIGURE 1. ORTEP drawing of **12**.

tions, we found that this reaction can also be carried out by only using a catalytic amount of DBU (0.3 equiv) (Scheme 5). This transformation can provide a convenient method to the preparation of quinoline derivatives.[11]

Conclusion

Usually the Baylis−Hillman reaction, which possesses the two most important requirements, atom economy and generation of functional groups, is a slow reaction requiring a few days to a few weeks for completion depending upon the reactivities of both activated alkene and electrophile.[1] In this paper, we have found several highly efficient aza-Baylis−Hillman reactions by the appropriate combination of Michael acceptors and Lewis base promoters. Most of these aza-Baylis−Hillman reactions of *N*-tosylated imines with α,*β*-unsaturated enones reported can be accomplished within 1 h. These presented, to the best our knowledge, are the best rate acceleration systems in the aza-Baylis−Hillman reactions under mild reaction conditions. Moreover, several transformations of these aza-Baylis−Hillman adducts have been disclosed in this paper. Therefore, a highly efficient synthetic method to prepare α-methylene-*β*-amino carbonyl compounds in good to excellent yields has been established. We believe that the pronounced acceleration of the rate in these reactions further extends the aza-Baylis−Hillman reaction into a viable transformation and allows the Baylis−Hillman reaction to be qualified as one of the efficient synthetic reactions. Further studies on applications of these aza-Baylis−Hillman reaction products are underway.

Experimental Section

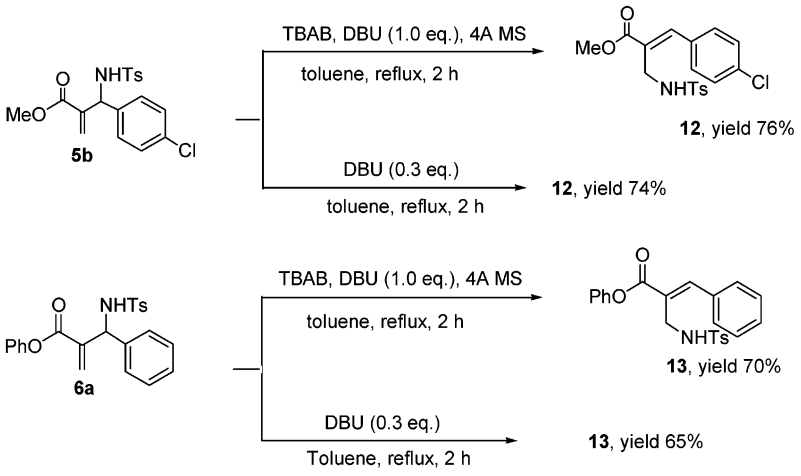
All of the *N*-tosylated imines were prepared according to the literature.[13] The spectroscopic data for compounds **3a**−**g** shown in Tables 1 and 2 have been reported in our previous paper.[6b]

Typical Reaction Procedure for PPh_2Me (Methyldiphenylphosphine)-Catalyzed aza-Baylis−Hillman Reaction of Methyl Vinyl Ketone with *N*-Benzylidene-4-methylbenzenesulfonamide. To a solution of *N*-benzylidene-4-methylbenzsulfonamide **1a** (129 mg, 0.5 mmol) and PPh_2Me (9 *μ*L, 0.05 mmol) in THF (1.0 mL) at room temperature was added methyl vinyl ketone **2a** (70 *μ*L, 1.0 mmol), and the reaction mixture was further stirred at room temperature. The reaction was monitored by a TLC plate. When the *N*-tosylated imine disappeared, the solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:5) to yield **3a** (132 mg, 80%) as a colorless solid.

Typical Reaction Procedure for DABCO-Catalyzed aza-Baylis−Hillman Reaction of Acrolein with *N*-Benzylidene-4-methylbenzenesulfonamide. To a solution of *N*-benzylidene-4-methylbenzsulfonamide **1a** (129 mg, 0.5 mmol) and DABCO (6 mg, 0.05 mmol) in THF (1.0 mL) at room temperature was added acrolein **2b** (67 *μ*L, 1.0 mmol), and the reaction mixture was further stirred at room temperature. The reaction was monitored by a TLC plate. When the *N*-tosylated imine disappeared, the solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:5) to yield **4a** (126 mg, 80%) as a colorless solid.

***N*-(2-Formyl-1-phenylallyl)-4-methyl Benzenesulfonamide (4a).** A colorless solid: mp 107−108 °C; IR ($CHCl_3$) *ν* 1690 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) *δ* 2.46 (3H, s, Me), 5.26 (1H, d, *J* = 8.1 Hz), 5.49 (1H, d, *J* = 8.1 Hz), 6.12 (1H, s), 6.54 (1H, s), 7.06−7.09 (2H, m, Ar), 7.19−7.22 (3H, m, Ar), 7.25 (2H, d, *J* = 8.7 Hz, Ar), 7.66 (2H, d, *J* = 8.7

SCHEME 5. Transformation of aza-Baylis−Hillman Adducts 5 and 6



Hz, Ar), 9.39 (1H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.5, 56.7, 126.7, 127.2, 127.9, 128.6, 129.5, 135.9, 137.1, 138.0, 143.5, 148.0, 192.8; MS (EI) *m/e* 314 ($M^+ - 1$, 4.05), 91 ($PhMe^+$, 100). Anal. Calcd for $C_{17}H_{17}NO_3S$ requires C, 64.76; H, 5.39; N, 4.44. Found: C, 64.77; H, 5.53; N, 4.33.

***N*-[2-Formyl-1-(4-chlorophenyl)allyl]-4-methyl Benzenesulfonamide (4b).** A colorless solid (144 mg, 83%): mp 101−102 °C; IR ($CHCl_3$) ν 1691 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.46 (3H, s, Me), 5.26 (1H, d, J = 8.6 Hz), 5.62 (1H, d, J = 8.6 Hz), 6.12 (1H, s), 6.52 (1H, s), 7.04 (2H, d, J = 8.4 Hz, Ar), 7.19 (2H, d, J = 8.4 Hz, Ar), 7.25 (2H, d, J = 8.6 Hz, Ar), 7.64 (2H, d, J = 8.6 Hz, Ar), 9.38 (1H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.4, 56.2, 127.1, 128.1, 128.7, 129.5, 133.8, 136.0, 136.5, 137.0, 143.7, 147.6, 192.7; MS (EI) *m/e* 294 ($M^+ - 55$, 15.60), 194 ($M^+ - 155$, 100). Anal. Calcd for $C_{17}H_{16}ClNO_3S$ requires C, 58.37; H, 4.61; N, 4.01. Found: C, 58.57; H, 4.84; N, 3.90.

***N*-[2-Formyl-1-(4-methylphenyl)allyl]-4-methyl Benzenesulfonamide (4c).** A colorless solid (135 mg, 82%): mp 108−109 °C; IR ($CHCl_3$) ν 1691 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.26 (3H, s, Me), 2.41 (3H, s, Me), 5.22 (1H, d, J = 8.0 Hz), 5.45 (1H, d, J = 8.0 Hz), 6.10 (1H, s), 6.53 (1H, s), 6.93 (2H, d, J = 8.2 Hz, Ar), 7.01 (2H, d, J = 8.2 Hz, Ar), 7.23 (2H, d, J = 8.4 Hz, Ar), 7.64 (2H, d, J = 8.4 Hz, Ar), 9.41 (1H, s). ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.0, 21.5, 56.6, 126.6, 127.3, 129.3, 129.5, 135.1, 135.8, 137.1, 137.8, 143.5, 148.2, 192.9; MS (EI) *m/e* 274 ($M^+ - 55$, 7.41), 174 ($M^+ - 155$, 100). Anal. Calcd for $C_{18}H_{19}NO_3S$ requires C, 65.65; H, 5.78; N, 4.26. Found: C, 65.80; H, 5.50; N, 4.09.

***N*-[2-Formyl-1-(4-nitrophenyl)allyl]-4-methyl Benzenesulfonamide (4d).** A colorless solid (77 mg, 43%): mp 144−145 °C; IR ($CHCl_3$) ν 1692 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.40 (3H, s, Me), 5.39 (1H, d, J = 8.7 Hz), 6.14 (1H, s), 6.19 (1H, d, J = 8.7 Hz), 6.52 (1H, s), 7.21 (2H, d, J = 7.8 Hz, Ar), 7.31 (2H, d, J = 8.4 Hz, Ar), 7.63 (2H, d, J = 8.4 Hz, Ar), 8.02 (2H, d, J = 7.8 Hz, Ar), 9.35 (1H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.5, 56.1, 123.6, 127.0, 127.7, 129.6, 136.8, 136.9, 144.0, 145.3, 146.8, 147.2, 192.5; MS (EI) *m/e* 205 ($M^+ - 155$, 4.62), 130 ($M^+ - 230$, 20.82), 91 ($M^+ - 269$, 100). Anal. Calcd for $C_{17}H_{16}N_2O_5S$ requires C, 56.66; H, 4.47; N, 7.77. Found: C, 56.60; H, 4.39; N, 7.72.

***N*-[2-Formyl-1-(4-methoxyphenyl)allyl]-4-methyl Benzenesulfonamide (4e).** A colorless solid (132 mg, 77%): mp 120−122 °C; IR ($CHCl_3$) ν 1689 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.44 (3H, s, Me), 3.76 (3H, s, Me), 5.22 (1H, d, J = 7.8 Hz), 5.37 (1H, d, J = 7.8 Hz), 6.12 (1H, s), 6.57 (1H, s), 6.75 (2H, d, J = 8.8 Hz, Ar), 6.98 (2H, d, J = 8.8 Hz, Ar), 7.27 (2H, d, J = 8.5 Hz, Ar), 7.66 (2H, d, J = 8.5 Hz, Ar), 9.41 (1H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.5, 55.2, 56.3, 114.0, 127.3, 128.0, 129.5, 130.1, 135.7, 137.1, 143.5, 148.2, 159.2, 193.0; MS (EI) *m/e* 290 ($M^+ - 55$, 7.64), 190 ($M^+ - 155$, 100). Anal. Calcd for $C_{18}H_{19}NO_4S$ requires C, 62.59; H, 5.54; N, 4.06. Found: C, 62.80; H, 5.71; N, 3.97.

***N*-[2-Formyl-1-(3-chlorophenyl)allyl]-4-methyl Benzenesulfonamide (4f).** A colorless solid (142 mg, 82%): mp 112−114 °C; IR ($CHCl_3$) ν 1691 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.49 (3H, s, Me), 5.32 (1H, d, J = 8.1 Hz), 5.65 (1H, d, J = 8.1 Hz), 6.20 (1H, s), 6.57 (1H, s), 7.06−7.09 (2H, m, Ar), 7.22−7.25 (2H, m, Ar), 7.32 (2H, d, J = 8.7 Hz, Ar), 7.70 (2H, d, J = 8.7 Hz, Ar), 9.45 (1H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.5, 56.5, 124.8, 126.9, 127.2, 128.1, 129.6, 129.9, 134.5, 136.3, 137.0, 140.0, 143.8, 147.4, 192.7; MS (EI) *m/e* 294 ($M^+ - 56$, 4.34), 194 ($M^+ - 156$, 100). Anal. Calcd for $C_{17}H_{16}ClNO_3S$ requires C, 58.37; H, 4.61; N, 4.00. Found: C, 58.45; H, 4.51; N, 4.13.

***N*-[2-Formyl-1-(4-bromophenyl)allyl]-4-methyl Benzenesulfonamide (4g).** A colorless solid (172 mg, 88%): mp 106−107 °C; IR ($CHCl_3$) ν 1690 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.45 (3H, s, Me), 5.25 (1H, d, J = 8.3 Hz), 5.56 (1H, d, J = 8.3 Hz), 6.14 (1H, s), 6.53 (1H, s), 7.00 (2H, d, J = 8.4 Hz, Ar), 7.27 (2H, d, J = 8.5 Hz, Ar), 7.36 (2H, d, J = 8.4 Hz, Ar), 7.65 (2H, d, J = 8.5 Hz, Ar), 9.40 (1H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.5, 56.0, 121.9, 127.1, 128.5, 129.6, 131.6, 136.1, 136.9, 137.1, 143.7, 147.6, 192.7; MS (EI) *m/e* 339 ($M^+ - 55$, 3.39), 337 ($M^+ - 57$, 3.15). Anal. Calcd for $C_{17}H_{16}BrNO_3S$ requires C, 51.79; H, 4.09; N, 3.55. Found: C, 51.90; H, 4.27; N, 3.48.

***N*-[2-Formyl-1-(4-fluorophenyl)allyl]-4-methyl Benzenesulfonamide (4h).** A colorless solid (148 mg, 89%): mp 135−136 °C; IR ($CHCl_3$) ν 1690 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.42 (3H, s, Me), 5.26 (1H, d, J = 7.8 Hz), 5.61 (1H, d, J = 7.8 Hz), 6.12 (1H, s), 6.52 (1H, s), 6.90 (2H, dd, J = 8.4, 8.3 Hz, Ar), 7.07 (2H, dd, J = 8.3, 5.8 Hz, Ar), 7.25 (2H, d, J = 8.4 Hz, Ar), 7.64 (2H, d, J = 8.4 Hz, Ar), 9.38 (1H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.4, 55.6, 115.3 (d, J_{C-F} = 21.2 Hz), 127.0, 128.4, 128.5, 129.4, 133.8 (d, J_{C-F} = 2.5 Hz), 136.3 (d, J_{C-F} = 79.5 Hz), 143.6, 147.8, 162.0 (d, J_{C-F} = 242.5 Hz), 192.7; MS (EI) *m/e* 278 ($M^+ - 55$, 4.51), 178 ($M^+ - 155$, 82.25). Anal. Calcd for $C_{17}H_{16}FNO_3S$ requires C, 61.25; H, 4.84; N, 4.20. Found: C, 61.36; H, 5.05; N, 4.12.

***N*-[2-Formyl-1-(4-ethylphenyl)allyl]-4-methyl Benzenesulfonamide (4i).** A colorless solid (156 mg, 91%): mp 90−92 °C; IR ($CHCl_3$) ν 1689 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.18 (3H, t, J = 7.6 Hz, Me), 2.42 (3H, s, Me), 2.56 (2H, q, J = 7.6 Hz, CH_2), 5.25 (1H, d, J = 8.3 Hz), 5.51 (1H, d, J = 8.3 Hz), 6.11 (1H, s), 6.56 (1H, s), 6.97 (2H, d, J = 8.2 Hz, Ar), 7.01 (2H, d, J = 8.2 Hz, Ar), 7.24 (2H, d, J = 8.4 Hz, Ar), 7.65 (2H, d, J = 8.4 Hz, Ar), 9.40 (1H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 15.4, 21.5, 28.3, 56.6, 126.6, 127.2, 128.1, 129.5, 135.2, 135.8, 135.8, 137.0, 143.5, 144.1, 148.0, 193.0; MS (EI) *m/e* 288 ($M^+ - 55$, 8.23), 188 ($M^+ - 155$, 100). Anal. Calcd for $C_{19}H_{21}BNO_3S$ requires C, 66.45; H, 6.16; N, 4.08. Found: C, 66.54; H, 6.34; N, 3.89.

Typical Reaction Procedure for PPh_2Me (Methyldiphenylphosphine)-Catalyzed aza-Baylis−Hillman Reaction of Methyl Acrylate with *N*-Benzylidene-4-methylbenzene Sulfonamide. To a solution of *N*-benzylidene-4-methylbenzenesulfonamide **1a** (129 mg, 0.5 mmol) and methyldiphenylphosphine (9 μL, 0.05 mmol) in THF (1.0 mL) at room temperature was added methyl acrylate (89 mg, 0.60 mmol), and the reaction mixture was further stirred at room temperature. The reaction was monitored by TLC plate. When the *N*-tosylated imine disappeared, the solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:5) to yield **5a** (108 mg, 63%) as a colorless solid.

Methyl 2-[Phenyl-(toluene-4-sulfonylamino)methyl]-acrylate (5a). This is an known compound:[7c] a colorless oil, IR ($CHCl_3$) ν 1708 cm^{-1} (C=O), 1633 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.40 (3H, s, Me), 3.60 (3H, s, Me), 5.29 (1H, d, J = 9.2 Hz, NH), 5.65 (1H, d, J = 9.2 Hz), 5.83 (1H, s), 6.22 (1H, s), 7.13 (2H, m, Ar), 7.21 (3H, m, Ar), 7.67 (2H, d, J = 8.6 Hz, Ar); MS (EI) *m/e* 314 ($M^+ - 31$, 1.94), 190 ($M^+ - 155$, 100.00), 155 (SO_2PhMe^+, 67.94); HRMS calcd for $C_{17}H_{16}NO_3S$ requires 314.0859 ($M^+ - OCH_3$), found 314.0890.

Methyl 2-[(4-Chlorophenyl)−(toluene-4-sulfonylamino)methyl]acrylate (5b). This is an known compound:[7c] a colorless solid, mp 105−106 °C; IR ($CHCl_3$) ν 1713 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.42 (3H, s, Me), 3.62 (3H, s, Me), 5.27 (1H, d, J = 9.2 Hz, NH), 5.76 (1H, d, J = 9.2 Hz, CH), 5.80 (1H, s), 6.21 (1H, s), 7.09 (2H, d, J = 8.6 Hz, Ar), 7.19 (2H, d, J = 8.6 Hz, Ar), 7.23 (2H, d, J = 8.6 Hz, Ar), 7.65 (2H, d, J = 8.6 Hz, Ar); MS (EI) *m/e* 348 ($M^+ - 31$, 2.52), 225 ($M^+ - 155$, 100), 91 ($PhMe^+$, 13.95). Anal. Calcd for

(12) The X-ray data of **12** has been deposited in CCDC with number 215232. Empirical formula: $C_{18}H_{18}NO_4SCl$. Formula weight: 379.84. Crystal color, habit: colorless, prismatic. Crystal dimensions: 0.456 × 0.226 × 0.203 mm^3. Crystal system: triclinic. Lattice type: primitive. Lattice parameters: a = 7.679(4) Å, b = 8.422(5) Å, c = 14.216(8) Å, α = 97.700(10)°, β = 91.157(10)°, γ = 90.604(9)°, V = 910.8(8) Å^3. Space group: P-1. Z value = 2; D_{calc} = 1.385 g/cm^3; F_{000} = 396; μ(Mo Kα) = 1.98 cm^{-1}. Diffractometer: Rigaku AFC7R. Residuals: R, Rw: 0.0942, 0.2726.

(13) Love, B. E.; Raje, P. S. *Synlett* **1994**, 493.

$C_{18}H_{18}ClNO_4S$ requires C, 56.99; H, 4.78; N, 3.69%; Found C, 57.21; H, 4.62; N, 3.60.

Typical Reaction Procedure for PPh_2Me (Methyldiphenylphosphine)-Catalyzed aza-Baylis−Hillman Reaction of Phenyl Acrylate with *N*-Benzylidene-4-methylbenzene Sulfonamide. To a solution of *N*-benzylidene-4-methylbenzenesulfonamide **1a** (129 mg, 0.5 mmol) and methyldiphenylphosphine (9 μL, 0.05 mmol) in THF (1.0 mL) at room temperature was added phenyl acrylate (89 mg, 0.60 mmol), and the reaction mixture was further stirred at room temperature. The reaction was monitored by TLC plate. When the *N*-tosylated imine disappeared, the solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:5) to yield **6a** (192 mg, 94%) as a colorless solid.

Phenyl 2-[Phenyl-(toluene-4-sulfonylamino)methyl]-acrylate (6a). A colorless solid: mp 107−108 °C; IR ($CHCl_3$) ν 1650 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.40 (3H, s, Me), 5.46 (1H, d, J = 8.4 Hz), 5.76 (1H, s), 5.91 (1H, d, J = 8.4 Hz), 6.13 (1H, s), 7.19−7.25 (7H, m, Ar), 7.36−7.42 (2H, m, Ar), 7.50−7.56 (3H, m, Ar), 7.72 (2H, d, J = 8.7 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.5, 58.8, 121.3, 126.0, 126.6, 127.2, 127.9, 128.6, 129.1, 129.3, 129.5, 137.5, 138.4, 138.6, 143.4, 150.1, 163.8; MS (EI) *m/e* 276 (M^+ − 131, 5.94), 252 (M^+ − 155 100). Anal. Calcd for $C_{23}H_{21}NO_4S$ requires C, 67.81; H, 5.16; N, 3.44. Found: C, 67.83; H, 5.37; N, 3.48.

Phenyl 2-[(4-Chlorophenyl)-(toluene-4-sulfonylamino)-methyl]acrylate (6b). A colorless solid (199 mg, 90%): mp 108−110 °C; IR ($CHCl_3$) ν 1729 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.42 (3H, s, Me), 5.38 (1H, d, J = 9.1 Hz), 5.71 (1H, d, J = 9.1 Hz), 6.04 (1H, s), 6.49 (1H, s), 6.88 (2H, d, J = 8.8 Hz, Ar), 7.12 (2H, d, J = 8.8 Hz, Ar), 7.20−7.36 (7H, m, Ar), 7.68 (2H, d, J = 8.5 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.5, 58.3, 121.2, 126.1, 127.1, 128.0, 128.7, 129.4, 129.5, 129.6, 133.7, 137.0, 137.3, 138.2, 143.6, 150.0, 163.7; MS (EI) *m/e* 441 (M^+ − 1, 3.55), 155 ($TolSO_2^+$ − 1, 100). Anal. Calcd for $C_{23}H_{20}ClNO_4S$ requires C, 62.66; H, 4.54; N, 3.17. Found: C, 62.66; H, 4.61; N, 3.04.

Phenyl 2-[(3-Fluorophenyl)-(toluene-4-sulfonylamino)-methyl]acrylate (6c). A colorless solid (192 mg, 90%): mp 107−109 °C; IR ($CHCl_3$) ν 1733 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.39 (3H, s, Me), 5.39 (1H, d, J = 8.7 Hz), 5.71 (1H, d, J = 8.7 Hz), 6.04 (1H, s), 6.50 (1H, s), 6.89−7.00 (5H, m, Ar), 7.19−7.36 (6H, m, Ar), 7.70 (2H, d, J = 8.2 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.5, 58.4, 113.7 (d, J_{C-F} = 0.3 Hz), 114.8 (d, J_{C-F} = 0.3 Hz), 121.2, 122.1 (d, J_{C-F} = 0.04 Hz), 126.1, 127.1, 129.5 (d, J_{C-F} = 0.2 Hz), 129.7, 130.2 (d, J_{C-F} = 0.1 Hz), 137.3, 138.0, 140.9, 141.0, 143.7, 150.0, 162.7 (d, J_{C-F} = 3.3 Hz), 163.6; MS (EI) *m/e* 332 (M^+ − 93, 42.44), 155 ($TolSO_2^+$ − 1, 83.82). Anal. Calcd for $C_{23}H_{20}FNO_4S$ requires C, 64.94; H, 4.71; N, 3.29. Found: C, 64.96; H, 5.10; N, 3.24.

Phenyl 2-[(4-Methylphenyl)-(toluene-4-sulfonylamino)-methyl]acrylate (6d). A colorless solid (186 mg, 88%): mp 93−94 °C; IR ($CHCl_3$) ν 1730 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.32 (3H, s, Me), 2.44 (3H, s, Me), 5.38 (1H, d, J = 8.7 Hz), 5.54 (1H, d, J = 8.7 Hz), 6.11 (1H, s), 6.52 (1H, s), 6.89 (2H, d, J = 7.5 Hz, Ar), 7.04−7.07 (4H, m, Ar), 7.22−7.37 (5H, m, Ar), 7.73 (2H, d, J = 8.4 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.3, 21.8, 58.7, 121.6, 126.2, 126.9, 127.5, 129.1, 129.6, 129.6, 129.8, 135.8, 137.8, 137.9, 139.1, 143.7, 150.5, 164.2; MS (EI) *m/e* 328 (M^+ − 94, 34.25), 157 ($TolSO_2^+$ + 2, 100). Anal. Calcd for $C_{24}H_{23}NO_4S$ requires C, 68.39; H, 5.50; N, 3.32. Found: C, 68.41; H, 5.58; N, 3.10.

Phenyl 2-[(4-Nitrophenyl)-(toluene-4-sulfonylamino)-methyl]acrylate (6e). A colorless solid (148 mg, 71%): mp 122−124 °C; IR (KCl) ν 1730.4 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.42 (3H, s, Me), 5.48 (1H, d, J = 9.1 Hz), 5.87 (1H, d, J = 9.1 Hz), 6.06 (1H, s), 6.53 (1H, s), 6.87−6.90 (2H, m, Ar), 7.23−7.37 (5H, m, Ar), 7.43 (2H, d, J = 8.7 Hz, Ar), 7.70 (2H, d, J = 8.7 Hz, Ar), 8.12 (2H, dd, J = 8.7, 2.0 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.3, 58.2, 121.0, 123.5, 126.1, 127.0, 129.3, 129.6, 130.3, 137.0, 137.4, 143.8, 145.6, 147.1, 149.8, 163.3; MS (EI): *m/e* 359 (M^+ − 93, 9.48), 155 (M^+ − 297, 38.73). Anal. Calcd for $C_{23}H_{20}N_2O_6S$ requires C, 61.05; H, 4.45; N, 6.19%, Found: C, 61.06; H, 4.51; N, 6.05.

Phenyl 2-[(4-Methoxyphenyl)-(toluene-4-sulfonylamino)methyl]acrylate (6f). A colorless solid (209 mg, 96%): mp 95−96 °C; IR ($CHCl_3$) ν 1731 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.42 (3H, s, Me), 3.88 (3H, s, Me), 5.35 (1H, d, J = 8.8 Hz), 5.46 (1H, d, J = 8.8 Hz), 6.08 (1H, s), 6.49 (1H, s), 6.76 (2H, d, J = 8.8 Hz, Ar), 6.87 (2H, d, J = 7.3 Hz. Ar), 7.07 (2H, d, J = 8.8 Hz, Ar), 7.18−7.35 (5H, m, Ar), 7.71 (2H, d, J = 7.3 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.5, 55.2, 58.4, 114.0, 121.3, 126.0, 127.2, 127.8, 128.8, 129.3, 129.5, 130.4, 137.4, 138.6, 143.5, 150.1, 159.2, 163.9; MS (EI) *m/e* 345 (M^+ − 92, 11.07), 281 (M^+ − 156, 4.18). Anal. Calcd for $C_{24}H_{23}NO_5S$ requires C, 65.90; H, 5.26; N, 3.20. Found: C, 65.80; H, 5.36; N, 3.22.

Phenyl 2-[(2,3-Dichlorophenyl)-(toluene-4-sulfonylamino)methyl]acrylate (6g). A viscous liquid (176 mg, 74%): IR ($CHCl_3$) ν 1735 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.36 (3H, s, Me), 5.72 (1H, d, J = 8.7 Hz), 5.88 (1H, d, J = 8.7 Hz), 6.13 (1H, s), 6.59 (1H, s), 6.94 (2H, d, J = 7.8 Hz, Ar), 7.08 (1H, dd, J = 8.2, 7.8 Hz, Ar), 7.16−7.38 (7H, m, Ar), 7.65 (2H, d, J = 8.2 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.3, 55.6, 121.2, 125.9, 127.0, 127.2, 129.2, 129.3, 129.7, 130.3, 131.2, 133.2, 136.7, 137.5, 137.5, 138.1, 143.5, 150.0, 163.6; MS (EI) *m/e* 382 (M^+ − 94, 35.43), 155 ($TolSO_2^+$, 90.16); HRMS Calcd for $C_{23}H_{19}Cl_2NO_4S$ requires 475.0412. Found: 475.0405.

Phenyl 2-[(4-Ethylphenyl)-(toluene-4-sulfonylamino)-methyl]acrylate (6h). A colorless solid (200 mg, 92%): mp 77−79 °C; IR ($CHCl_3$) ν 1732 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.18 (3H, t, J = 7.7 Hz, CH_3), 2.42 (3H, s, Me), 2.58 (2H, q, J = 7.8 Hz, CH_2), 5.37 (1H, d, J = 8.7 Hz), 5.49 (1H, d, J = 8.7 Hz), 6.08 (1H, s), 6.50 (1H, s), 6.87 (2H, d, J = 8.7 Hz, Ar), 7.03−7.13 (4H, m, Ar), 7.19−7.34 (5H, m, Ar), 7.70 (2H, d, J = 8.2 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 15.8, 21.8, 28.7, 58.9, 121.6, 126.3, 126.9, 127.5, 128.4, 129.2, 129.6, 129.8, 135.9, 137.7, 139.0, 143.7, 144.3, 150.4, 164.2; MS (EI) *m/e* 343 (M^+ − 92, 45.03), 155 ($TolSO_2^+$, 34.93). Anal. Calcd for $C_{25}H_{25}NO_4S$ requires C, 68.97; H, 5.75; N, 3.22. Found: C, 68.97; H, 5.94; N, 3.20.

Phenyl 2-[(3-Methylphenyl)-(toluene-4-sulfonylamino)-methyl]acrylate (6i). A colorless solid (190 mg, 90%): mp 82−84 °C; IR ($CHCl_3$) ν 1732 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.25 (3H, s, Me), 2.43 (3H, s, Me), 5.37 (1H, d, J = 9.0 Hz), 5.49 (1H, d, J = 9.0 Hz), 6.10 (1H, s), 6.51 (1H, s), 6.85−6.90 (3H, m, Ar), 6.94 (1H, d, J = 6.5 Hz, Ar), 7.04 (1H, d, J = 6.5 Hz, Ar), 7.12−7.36 (6H, m, Ar), 7.71 (2H, d, J = 8.1 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.6, 21.8, 59.0, 121.6, 123.9, 126.3, 127.5, 127.7, 128.8, 128.9, 129.0, 129.2, 129.6, 129.8, 137.7, 138.6, 139.2, 143.7, 150.4, 164.2; MS (EI) *m/e* 328 (M^+ − 94, 72.34), 157 ($TolSO_2^+$ + 2, 100). Anal. Calcd for $C_{24}H_{23}NO_4S$ requires C, 68.39; H, 5.50; N, 3.32. Found: C, 68.15; H, 5.68; N, 3.42.

Phenyl 2-[Furan-2-yl-(toluene-4-sulfonylamino)methyl]-acrylate (6j). A colorless solid (166 mg, 84%): mp 120−122 °C; IR ($CHCl_3$) ν 1732 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.41 (3H, s, Me), 5.50 (1H, d, J = 9.1 Hz), 5.65 (1H, d, J = 9.1 Hz), 6.05 (1H, s), 6.10−6.16 (2H, m, Ar), 6.50 (1H, s), 6.95 (2H, d, J = 8.2 Hz, Ar), 7.18−7.39 (6H, m, Ar), 7.72 (2H, d, J = 8.2 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.8, 53.5, 107.9, 110.9, 121.6, 126.3, 127.4, 129.7, 129.8, 130.1, 137.0, 137.6, 142.6, 143.8, 150.4, 151.1, 163.9; MS (EI) *m/e* 304 (M^+ − 93, 61.06), 242 (M^+ − 155, 74.69). Anal. Calcd for $C_{21}H_{19}NO_5S$ requires C, 63.48; H, 4.79; N, 3.53. Found: C, 63.28; H, 4.88; N, 3.45.

α-Naphthyl2-[Phenyl-(toluene-4-sulfonylamino)methyl]-acrylate (6k). A colorless solid: mp 152−154 °C; IR ($CHCl_3$) ν 1735 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.43 (3H, s, Me), 5.52 (1H, d, J = 8.8 Hz), 5.54 (1H, d, J = 8.8 Hz), 6.18 (1H, s), 6.66 (1H, s), 7.03 (1H, d, J = 7.6 Hz, Ar), 7.19−7.46 (9H, m, Ar), 7.71 (2H, d, J = 9.1 Hz, Ar), 7.75 (2H, d, J

= 8.5 Hz, Ar), 7.82 (1H, J = 8.5 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.5, 59.0, 117.9, 120.8, 125.2, 126.3, 126.4, 126.5, 126.6, 127.2, 127.8, 127.9, 128.0, 128.8, 129.4, 129.6, 134.5, 137.4, 138.3, 138.4, 143.6, 146.0, 164.0; MS (EI) *m/e* 457 (M^+, 4.91), 314 ($M^+ - 143$, 7.80). Anal. Calcd for $C_{27}H_{23}NO_4S$ requires C, 70.88; H, 5.07; N, 3.06. Found: C, 71.14; H, 5.41; N, 3.04.

α-Naphthyl 2-[(4-Chlorophenyl)-(toluene-4-sulfonylamino)methyl]acrylate (6l). A colorless solid: mp 180−181 °C; IR ($CHCl_3$) ν 1731 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.44 (3H, s, Me), 5.47 (1H, d, J = 8.8 Hz), 5.66 (1H, d, J = 8.8 Hz), 6.14 (1H, s), 6.66 (1H, s), 7.05 (1H, d, J = 8.5 Hz, Ar), 7.19 (2H, d, J = 8.5 Hz, Ar), 7.24−7.51 (9H, m, Ar), 7.73 (2H, d, J = 8.5 Hz, Ar), 7.85 (1H, J = 8.5 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.6, 58.6, 117.9, 120.6, 125.2, 126.3, 126.4, 126.5, 126.6, 127.2, 128.0, 128.9, 129.6, 129.7, 134.0, 134.6, 137.0, 137.4, 138.1, 143.7, 143.8, 145.9, 163.9; MS (EI) *m/e* 491 (M^+, 1.52), 348 ($M^+ - 143$, 2.84). Anal. Calcd for $C_{27}H_{22}ClNO_4S$ requires C, 65.91; H, 4.51; N, 2.85. Found: C, 65.83; H, 4.74; N, 2.59.

α-Naphthyl 2-[(4-Methoxyphenyl)-(toluene-4-sulfonylamino)methyl]acrylate (6m). A colorless solid: mp 152−154 °C; IR ($CHCl_3$) ν 1735 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.43 (3H, s, Me), 3.78 (3H, s, Me), 5.44 (2H, s), 6.18 (1H, s), 6.65 (1H, s), 6.81 (2H, d, J = 8.8 Hz, Ar), 7.04 (1H, d, J = 8.5 Hz, Ar), 7.13 (2H, d, J = 8.8 Hz, Ar), 7.21−7.49 (6H, m, Ar), 7.71 (1H, d, J = 8.5 Hz, Ar), 7.74 (2H, d, J = 8.2 Hz, Ar), 7.83 (1H, J = 8.5 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.6, 55.3, 58.5, 114.2, 117.9, 120.9, 125.2, 126.3, 126.4, 126.5, 126.6, 127.3, 128.0, 128.9, 129.6, 130.5, 134.5, 137.5, 138.7, 143.5, 143.6, 146.0, 159.4, 164.1; MS (EI) *m/e* 487 (M^+, 0.39), 344 ($M^+ - 143$, 4.68). Anal. Calcd for $C_{28}H_{25}NO_5S$ requires C, 68.98; H, 5.17; N, 2.87. Found: C, 68.92; H, 5.36; N, 2.72.

Reduction of Compound 4c with $LiAlH_4$. Compound **4c** (166 mg, 0.5 mmol) was placed in a flask under argon atmosphere. THF (3.0 mL) was added into the solution, and then $LiAlH_4$ (38 mg, 1.0 mmol) was added into the reaction mixture at 0 °C. The reaction mixture was further stirred at room temperature. The reaction was monitored by TLC plate. After 4 h, compound **4c** was consumed completely, and the reaction was quenched by addition of saturated NH_4Cl aqueous solution at 0 °C. The reaction mixture was extracted with CH_2Cl_2 three times. The organic phases were combined and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was subject to a flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:2) to give the compound **7** (148 mg, 89%) as a colorless solid.

***N*-[1-(4-Fluorophenyl)-2-hydroxymethyl-allyl]-4-methylbenzenesulfonamide (7).** A colorless solid: mp 78−80 °C; IR ($CHCl_3$) ν 3278 cm^{-1} (OH), 1603 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.41 (3H, s, Me), 2.02−2.07 (1H, br, OH), 3.95 (1H, dd, J = 9.9, 5.7 Hz), 4.08 (1H, dd, J = 9.9, 5.7 Hz), 4.97 (1H, s), 5.07 (1H, d, J = 7.8 Hz), 5.15 (1H, s), 5.78 (1H, d, J = 7.8 Hz), 6.91 (2H, dd, J = 8.7, 8.1 Hz, Ar), 7.11 (2H, dd, J = 8.7, 5.4 Hz, Ar), 7.23 (2H, d, J = 8.4 Hz, Ar), 7.64 (2H, d, J = 8.4 Hz, Ar), 9.38 (1H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.7, 59.7, 64.1, 115.4, 115.5 (1C, J_{C-F} = 21.4 Hz), 127.4, 129.0 (1C, J_{C-F} = 8.4 Hz), 129.7, 134.6 (1C, J_{C-F} = 3.6 Hz), 137.4, 143.7, 146.8, 162.7 (1C, J_{C-F} = 246.8 Hz); MS (EI) *m/e* 317 ($M^+ - 18$, 0.75), 278 ($M^+ - 157$, 30.61). Anal. Calcd for $C_{17}H_{18}FNO_3S$ requires C, 60.88; H, 5.41; N, 4.18. Found: C, 61.21; H, 5.54; N, 4.07.

Boc-Protection of Compound 7. Compound **7** (68 mg, 0.20 mmol) was placed in a flask under argon atmosphere. Solvent CH_2Cl_2 (2.0 mL) was added into the reaction vessel, and then DMAP (4.5 mg, 0.04 mmol, 0.2 equiv) and di-*tert*-butyl dicarbonate (87 mg, 0.4 mmol, 2 equiv) were added into the reaction mixture at room temperature. The reaction mixture was further stirred at room temperature. The reaction was monitored by TLC plate. After 2 h, the substrate was consumed completely. The solvent was removed under reduced pressure, and the residue was subject to a flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:10) to give the compound **8** (85 mg, 99%) as a viscous liquid.

***tert*-Butyl [1-(4-Fluorophenyl)-2-(hydroxymethyl)allyl-(toluene-4-sulfonil)]carbamate (8).** A viscous liquid: IR ($CHCl_3$) ν 2892, 2934 cm^{-1}, 1740 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.28 (9H, s, Me), 1.53 (1H, s, br, OH), 2.45 (3H, s, Me), 4.63 (2H, s), 5.15 (1H, d, J = 1.8 Hz), 5.52 (1H, d, J = 1.8 Hz), 6.31 (1H, s), 7.06 (2H, dd, J = 9.0, 8.7 Hz, Ar), 7.29 (2H, d, J = 8.7 Hz, Ar), 7.41 (2H, dd, J = 8.7, 5.4 Hz, Ar), 7.70 (2H, d, J = 8.7 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.5, 27.7, 61.7, 67.5, 82.3, 84.8, 115.1 (d, J_{C-F} = 21.5 Hz), 118.0, 128.6 (d, J_{C-F} = 62.6 Hz), 130.6 (d, J_{C-F} = 8.1 Hz), 133.1, 136.7, 140.9, 144.2, 150.5, 153.1, 162.1 (d, J_{C-F} = 247.2 Hz); MS (EI) *m/e* 423 ($M^+ - 15$, 16.14), 224 ($M^+ - 213$, 100.00). Anal. Calcd for $C_{22}H_{28}FNO_5S$ requires C, 60.39; H, 6.45; N, 3.20. Found: C, 60.38; H, 6.60; N, 3.20.

Detosylation of *tert*-Butyl [1-(4-Fluorophenyl)-2-(hydroxymethyl)allyl(toluene-4-sulfonil)]carbamate (8). Compound **8** (85 mg, 0.194 mmol) was transferred to an oven-dried flask under argon atmosphere. Then, this reaction vessel was charged with 1.5 mL of dry MeOH, followed by the addition of Mg (24 mg, 5 equiv). The reaction mixture was sonicated for 45 min and then was poured into 1.0 M HCl. The organic compound was extracted with ether (3 × 15 mL). The organic phase was washed with saturated $NaHCO_3$ and brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was subject to a flash column chromatography (SiO_2, EtOAc/petroleum ether = 1:6) to give compound **9** (48 mg, 82%) as a colorless solid.

***tert*-Butyl [1-(4-Fluorophenyl)-2-hydroxymethylallyl]-carbamate (9).** A colorless solid: mp 98−99 °C; IR ($CHCl_3$) ν 3447 cm^{-1} (OH), 1738, 1712 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.47 (9H, s), 4.48 (2H, s), 5.08−5.16 (1H, br, s), 5.25 (1H, s), 5.32−5.41 (1H, br, s), 5.37 (1H, s), 7.04 (2H, dd, J = 8.7, 9.0 Hz, Ar), 7.26−7.30 (2H, m, Ar); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 27.7 (3C), 28.3, 67.1, 82.3, 115.5, 115.5 (d, J_{C-F} = 21.4 Hz), 128.7 (d, J_{C-F} = 8.2 Hz), 135.4, 153.1, 154.8, 162.2 (d, J_{C-F} = 246.1 Hz); MS (EI) *m/e* 224 ($M^+ - 57$, 28.16), 207 ($M^+ - 74$, 74.22); HRMS calcd for $C_{11}H_{11}FNO_3$ requires 224.0723, found 224.0706.

Typical Reaction Procedure of the Synthesis of Compound 12. A mixture of compound **5b** (114 mg, 0.3 mmol) and DBU (16 μL, 0.1 mmol) in anhydrous toluene (5 mL) was refluxed for 2 h. The solvent was evaporated under reduced pressure, and the residue was chromatographed over a SiO_2 flash column using a gradient of petroleum/ethyl acetate (5:1) as eluent to give the compound **12** (84 mg, 74%). The compound **13** was similarly synthesized from the compound **6a**.

Methyl (2*E*)-3-(4-Chlorophenyl)-2-[(toluene-4-sulfonylamino)methyl]acrylate (12). A colorless solid: mp 118−119 °C; IR ($CHCl_3$) ν 1706 cm^{-1} (C=O), 1633 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.44 (3H, s, Me), 3.77 (3H, s, Me), 3.89 (2H, d, J = 6.0 Hz), 5.16 (1H, t, J = 6.0 Hz), 7.29 (2H, d, J = 8.4 Hz, Ar), 7.33 (2H, d, J = 8.7 Hz, Ar), 7.36 (1H, s, =CH), 7.39 (2H, d, J = 8.7 Hz, Ar), 7.68 (2H, d, J = 8.4 Hz, Ar); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.5, 40.4, 52.4, 126.9, 127.2, 129.0, 129.6, 130.8, 132.2, 135.5, 136.2, 142.1, 143.6, 167.4; MS (EI) *m/e* 379 ($M^+ - 1$, 0.24), 224 ($M^+ - 155$, 100.00). Anal. Calcd for $C_{18}H_{18}ClNO_4S$ requires C, 56.91; H, 4.78; N, 3.69. Found: C, 56.90; H, 4.75; N, 3.63.

Phenyl (2*E*)-3-Phenyl-2-[(toluene-4-sulfonylamino)-methyl]acrylate (13). A colorless solid (79 mg, 65%): mp 95−96 °C; IR ($CHCl_3$) ν 1713 cm^{-1} (C=O), 1633 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.42 (3H, s, Me), 4.06 (2H, d, J = 6.9 Hz), 5.23 (1H, t, J = 6.9 Hz), 7.06 (2H, d, J = 7.2 Hz), 7.26 (2H, d, J = 8.4 Hz, Ar), 7.25−7.31 (1H, m, Ar), 7.40−7.52 (7H, m, Ar), 7.68 (2H, d, J = 8.4 Hz, Ar), 8.03 (1H, s); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 21.5, 40.7, 121.4, 125.8, 126.1, 127.2, 128.8, 129.5, 129.7, 129.7, 129.9, 133.6, 136.2, 143.5, 145.1, 150.4, 166.0; MS (EI) *m/e* 408 ($M^+ + 1$, 1.57), 143 ($M^+ - 264$,

100.00). Anal. Calcd for $C_{23}H_{21}NO_4S$ requires C, 67.81; H, 5.16; N, 3.44. Found: C, 68.02; H, 5.03; N, 3.31.

Acknowledgment. We thank the State Key Project of Basic Research (Project 973) (no. G2000048007), Shanghai Municipal Committee of Science and Technology, and the National Natural Science Foundation of China for financial support (20025206, 203900502, and 20272069).

Supporting Information Available: X-ray diffraction data of **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO035103P