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An Unexpected Highly Stereoselective Double Aza-Baylis−Hillman Reaction of Sulfonated Imines with Phenyl Vinyl Ketone

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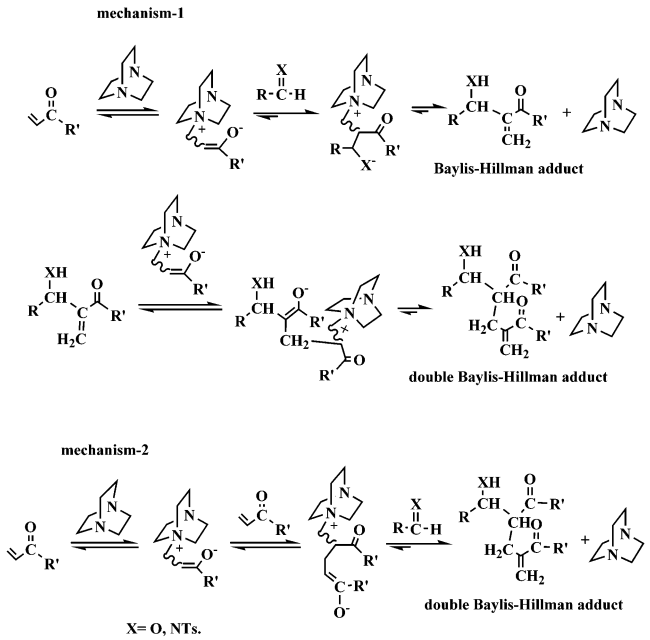
The aza-Baylis−Hillman reaction of *N*-sulfonated imine with phenyl vinyl ketone gave the double aza-Baylis−Hillman adduct in good yields with excellent stereoselectivities in the presence of Lewis base 1,4-diazabicyclo[2.2.2]octane.

Great progress has been made in the execution of the Baylis−Hillman reaction,[1] for which a catalytic asymmetric version has been published,[2] since Baylis and Hillman first reported in 1972 the reaction of acetaldehyde with ethyl acrylate and acrylonitrile in the presence of a catalytic amount of 1,4-diazabicyclo[2.2.2]octane (DABCO).[3] However, during our own investigation of this simple and useful reaction,[4] we found that in the reaction of arylaldehydes with methyl vinyl ketone (MVK) catalyzed by DABCO, the reaction products are not simple as those reported before. For example, using *p*-nitrobenzaldehyde (1.0 equiv) and MVK (2.0 equiv) as substrates in the presence of catalytic amounts of DABCO (0.1 equiv) in DMF or DMSO, we found that besides the normal Baylis−Hillman product a double Baylis−Hillman reaction product was also formed at the same time as a 2:3 mixture of *syn*- and *anti*-isomers.[5] The substituent effects on the benzene ring of arylaldehydes have also been extensively examined.

SCHEME 1



Two plausible mechanisms for the formation of the double Baylis−Hillman adduct can be speculated which have been elucidated in Scheme 1. The first mechanism is the Michael addition of enolate derived from DABCO and MVK to the Baylis−Hillman adduct, and the second is the aldol condensation reaction of enolate derived from DABCO and MVK (a MVK dimer type enolate) with the substrate.

This interesting result stimulated us to further examine the Baylis−Hillman reaction of the other substrates with α,*β*-unsaturated ketone because we attempt to find a new version of the Baylis−Hillman reaction in which the double Baylis−Hillman reaction product can be exclusively formed with high stereoselectivity. Herein we report an unprecedented highly stereoselective double aza-Baylis−Hillman reaction of *N*-sulfonated imine with phenyl vinyl ketone (PVK).

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(1) (a) Ciganek, E. *Org. React*. **1997**, *51*, 201. (b) Basavaiah, D.; Rao, P. D.; Hyma, R. S. *Tetrahedron* **1996**, *52*, 8001. (c) Drewes, S. E.; Roos, G. H. P. *Tetrahedron* **1988**, *44*, 4653. (d) Brzezinski, L. J.; Rafel, S.; Leahy, J. M. *J. Am. Chem. Soc*. **1997**, *119*, 4317. (e) Miyakoshi, T.; Saito, S. *Nippon Kagaku Kaishi* **1983**, 1623; *Chem. Abstr*. **1984**, *100*, 156191g. (f) Marko, I. E.; Giles, P. R.; Hindley, N. J. *Tetrahedron* **1997**, *53*, 1015. (g) Richter, H.; Jung, G. *Tetrahedron Lett*. **1998**, *39*, 2729. (h) Barrett, A. G. M.; Cook, A. S.; Kamimura, A. *Chem. Commun*. **1999**, 2533. (i) Kunidig, E. P.; Xu, L. H.; Romanens, P.; Bernardinelli, G. *Tetrahedron Lett*. **1993**, *34*, 7049. (j) Aggarwal, V. K.; Mereu, A.; Tarver, G. J.; McMague, R. *J. Org. Chem*. **1998**, *63*, 7183. (k) Kawamura, M.; Kobayashi, S. *Tetrahedron Lett*. **1999**, *40*, 1539. (l) Li, G.-G.; Wei, H.-X.; Gao, J.-J.; Caputo, T. D. *Tetrahedron Lett*. **2000**, *41*, 1. (m) Li, G.-G.; Gao, J.-J.; Wei, H.-X.; Enright, M. *Org. Lett*. **2000**, *2*, 617 and references therein. (o) Iwamura, T.; Fujita, M.; Kawakita, T.; Kinoshita, S.; Watanabe, S.-I.; Kataoka, T. *Tetrahedron* **2001**, *57*, 8455 and references therein.

(2) (a) Iwabuchi, Y.; Nakatani, M.; Yokoyama, N.; Hatakeyama, S. *J. Am. Chem. Soc*. **1999**, *121*, 10219. (b) Langer, P. *Angew. Chem., Int. Ed*. **2000**, *39*, 3049.

(3) (a) Baylis, A. B.; Hillman, M. E. D. Ger. Offen. 2,155,113, 1972; *Chem. Abstr*. **1972**, *77*, 34174q. Hillman, M. E. D.; Baylis, A. B. U.S. Patent 3,743,669, 1973. (b) Morita, K.; Suzuki, Z.; Hirose, H. *Bull. Chem. Soc. Jpn*. **1968**, *41*, 2815.

(4) (a) Shi, M.; Jiang, J.-K.; Feng, Y.-S. *Org. Lett*. **2000**, *2*, 2397. (b) Shi, M.; Feng, Y.-S. *J. Org. Chem*. **2001**, *66*, 406 and references therein.

(5) (a) Shi, M.; Li, C.-Q.; Jiang, J.-K. *Chem. Commun*. **2001**, 833. (b) Shi, M.; Li, C.-Q.; Jiang, J.-K. *Tetrahedron* **2003**, *59*, 1183.

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SCHEME 2

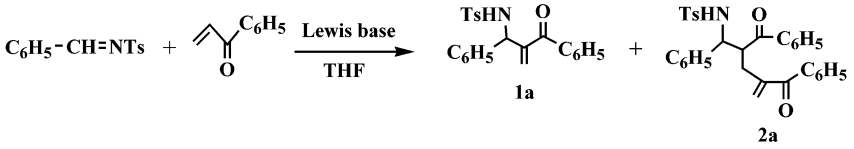


TABLE 1. Lewis Base Effect in the Aza-Baylis−Hillman Reaction of Sulfonated Imine with PVK

entry	Lewis base	time (h)	yield[a] (%) 1a	yield[a] (%) 2a
1	PPh_3[b]	1.0	92	
2	Ph_2PMe[b]	0.2	20	50
3	$PhPMe_2$[b]	0.1		30
4	DABCO[b]	5.5		65
5	DABCO[c]	5.5		50

[a] Isolated yields. [b] The molar ratio of sulfonated imine with PVK is 0.5:0.75. [c] The molar ratio of sulfonated imine with PVK is 0.5:0.5.

Results and Discussion

During our examination of aza-Baylis−Hillman reactions using *N*-sulfonated imine as the substrate,[6,7] we found that a Lewis base catalyst played a very important role in the aza-Baylis−Hillman reaction of *N*-sulfonated imine (0.5 mmol) with PVK (0.75 mmol) (Scheme 2, Table 1). Using triphenylphosphine (10 mol %) as a Lewis base, the corresponding normal aza-Baylis−Hillman adduct **1a** was obtained as a sole product in good yield (Table 1, entry 1). Lewis base Ph_2PMe (10 mol %) gave **1a** and the double aza-Baylis−Hillman adduct **2a** at the same time in 20% and 50% yields, respectively (Table 1, entry 2). In addition, the stronger Lewis base $PhPMe_2$ gave the aza-Baylis−Hillman adduct exclusively in low yield along with many unidentified products (Table 1, entry 3). While using DABCO (10 mol %) as a Lewis base, we delightfully found that the double aza-Baylis−Hillman adduct **2a** was formed exclusively in good yield (Table 1, entry 4). The molar ratio of *N*-sulfonated imine with PVK does not affect the reaction product because, in the presence of *N*-sulfonated imine (0.5 mmol) and PVK (0.5 mmol) (*N*-sulfonated imine:PVK = 1:1), the double aza-Baylis−Hillman adduct was also exclusively obtained in 50% yield under the same conditions (Table 1, entry 5). Moreover, on the basis of the ^1H and ^{13}C NMR spectroscopic data and X-ray analysis, we are pleased to find that, in this aza-Baylis−Hillman reaction, the double aza-Baylis−Hillman reaction product **2a** was formed stereoselectively in the *anti*-configuration (Figure 1).[8]

In Tables 2 and 3, we summarize the results of the aza-Baylis−Hillman reaction of *N*-sulfonated imines with PVK in the presence of Lewis base PPh_3 and DABCO, respectively.

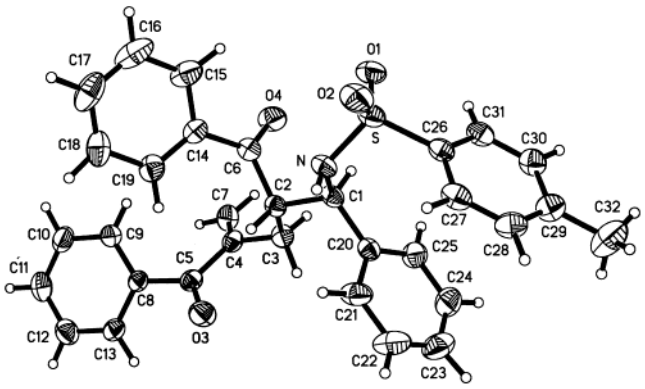
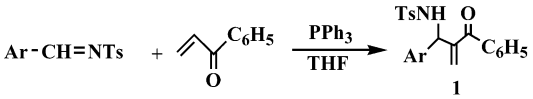


FIGURE 1. ORTEP drawing of **2a**.

TABLE 2. Aza-Baylis−Hillman Reaction of Sulfonated Imine with PVK in THF in the Presence of Lewis Base PPh_3



entry	Ar[b]	time (h)	yield of 1[a] (%)
1	*p*-$MeOC_6H_4$	10	**1b**, 75
2	*p*-FC_6H_4	0.5	**1c**, 93
3	*p*-ClC_6H_4	1.0	**1d**, 89
4	*p*-BrC_6H_4	1.0	**1e**, 84
5	2,3-$Cl_2C_6H_3$	0.5	**1f**, 87
6	*p*-MeC_6H_4	2.5	**1g**, 84
7	*m*-MeC_6H_4	3	**1h**, 99
8	*p*-EtC_6H_4	6.5	**1i**, 68

[a] Isolated yields. [b] The molar ratio of sulfonated imine with PVK is 0.5:0.75.

As can be seen from Table 2, the other *N*-sulfonated imines (0.5 mmol) can react with PVK (0.75 mmol) smoothly in the presence of Lewis base PPh_3 to give the corresponding normal aza-Baylis−Hillman adducts **1b**−**h** in high yields (Table 2). For substrates having an electron-withdrawing group on the benzene ring, the reaction proceeded very well to give **1** in high yields within shorter reaction time (Table 2, entries 3−6).

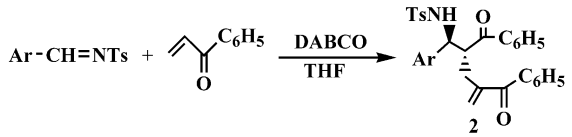
On the other hand, if using DABCO as a Lewis base, in all cases the corresponding double aza-Baylis−Hillman adducts **2** were obtained exclusively as a sole product with the *anti*-configuration (Table 3). To obtain **2** in higher yields, 3 equiv of PVK was employed in all cases

(6) (a) Shi, M.; Xu, Y.-M. *Chem. Commun*. **2001**, 1876. (b) Shi, M.; Xu, Y.-M. *Eur. J. Org. Chem*. **2002**, 696. (c) Shi, M.; Xu, Y.-M.; Zhao, G.-L.; Wu, X.-F. *Eur. J. Org. Chem*. **2002**, 3666. (d) Shi, M.; Zhao, G.-L. *Tetrahedron Lett.* **2002**, *43*, 4499.

(7) For previous reports related 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. (b) Takagi, M.; Yamamoto, K. *Tetrahedron* **1991**, *47*, 8869. For previous reports related 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. (d) Balan, D.; Adolfsson, H. *J. Org. Chem*. **2002**, *67*, 2329 and references therein. The aza-Baylis−Hillman reaction of sulfonated imines with PVK has not been examined before.

(8) The X-ray data of **2a** have been deposited with Cambridge Crystallographic Data Centre with the number 194351: empirical formula, $C_{32}H_{29}O_4NS$; formula weight, 523.62; crystal color (habit), colorless (prismatic); crystal dimensions, 0.20 × 0.20 × 0.30 mm; crystal system, monoclinic; lattice type, primitive; lattice parameters, a = 12.3996(8) Å, b = 18.3652(5) Å, c = 12.3047(8) Å, α = 90°, β = 90.9440(10)°, γ = 90°, V = 2801.7(3) Å^3; space group, $P2(1)/c$; Z value, 4; D_{calcd} = 1.241 g/cm^3; F_{000} = 1104; μ(Mo Kα) = 1.98 cm^{-1}; residuals, R = 0.0566, R_w = 0.0930.

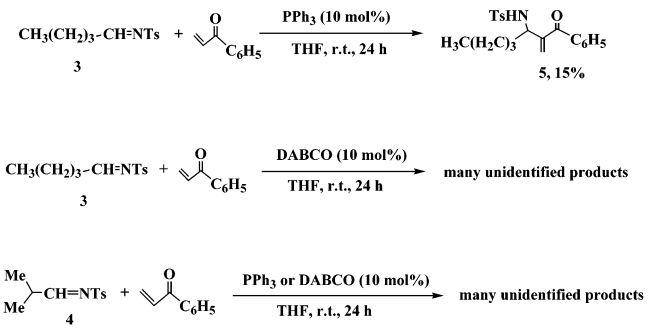
TABLE 3. Aza-Baylis−Hillman Reaction of Sulfonated Imine with PVK in THF in the Presence of Lewis Base DABCO



entry	Ar[b]	time (h)	yield of **2**[a] (%) (*anti*:*syn*)
1	C_6H_5	5.5	**2a**, 65 (100:0)
2	*m*-MeC_6H_4	5.5	**2b**, 75 (100:0)
3	p-MeC_6H_4	6.5	**2c**, 71 (100:0)
4	*p*-$MeOC_6H_4$	12	**2d**, 85 (100:0)
5	*p*-FC_6H_4	5.5	**2e**, 74 (100:0)
6	*p*-ClC_6H_4	5.5	**2f**, 70 (100:0)
7	*m*-ClC_6H_4	3.5	**2g**, 57 (100:0)
8	*m*-FC_6H_4	5	**2h**, 61 (100:0)
9	1-naphthyl	12	**2i**, 54 (100:0)

[a] Isolated yields. [b] The molar ratio of sulfonated imine with PVK is 0.5:1.5.

SCHEME 3



(Table 3). The substituents on the benzene ring do not significantly affect the reaction rate (Table 3).

It should be emphasized here that for other Michael acceptors such as MVK, methyl acrylate, and acrylonitrile no such double aza-Baylis−Hillman reaction product can be observed at all. To expand the scope and explore the limitations of this interesting aza-Baylis−Hillman reaction, we tried to synthesize aliphatic *N*-sulfonated imines as starting materials. However, we found that many of these are very labile, even stored in a refrigerator under −20 °C. So far we prepared two aliphatic *N*-tosylated imines, **3** and **4**, according to the literature[9] which must be used immediately for the reaction. Aliphatic *N*-tosylated imine **4** is more stable than aliphatic *N*-tosylated imine **3**. In the aza-Baylis−Hillman reaction of **3** with PVK in the presence of PPh_3 under the same conditions as those described above, the corresponding normal aza-Baylis−Hillman adduct **5** was formed in 15% yield along with some unidentified products (Scheme 3). Using DABCO as a Lewis base for this reaction, none of the corresponding aza-Baylis−Hillman adduct was formed, but many unidentified products were formed. In the case of aliphatic *N*-tosylated imine **4**, the reaction gave many unidentified products using either PPh_3 or DABCO as a promoter (Scheme 3).

(9) The aliphatic *N*-sulfonated imines **3** and **4** were prepared according to the literature: Chemla, F.; Hebbe, V.; Normant, J. F. *Synthesis* **2000**, *1*, 75.

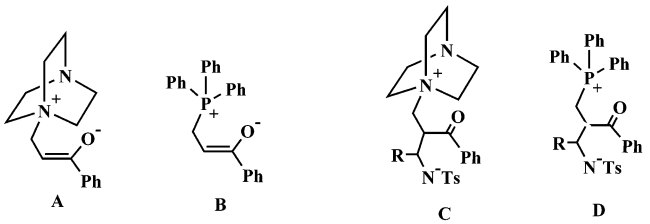
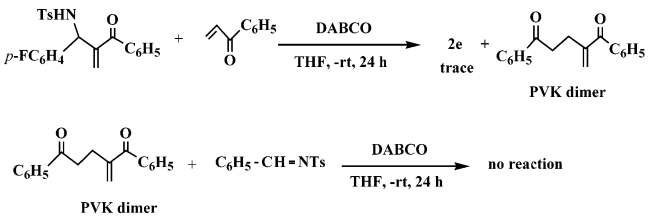


FIGURE 2. Zwitterion species in the Baylis−Hillman reaction.

SCHEME 4

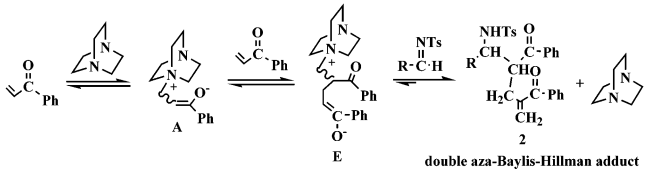


To confirm the reaction mechanism of the formation of the double aza-Baylis−Hillman product **2**, we conducted the reaction of PVK with the normal aza-Baylis−Hillman adduct **1e** under the same conditions (Scheme 4). To our surprise, only trace **2e** and the dimer of PVK were formed.[10] We also confirmed that the PVK dimer does not react with *N*-sulfonated imine in the presence of DABCO (Scheme 4). This is simply due to the fact that the PVK dimer type enolate (shown in mechanism 2 of Scheme 1) cannot be formed from DABCO with the PVK dimer. These results suggest that the double aza-Baylis−Hillman products **2** are not derived from the first mechanism as shown in Scheme 1, and this unexpected highly stereoselective double aza-Baylis−Hillman reaction can only proceed via the second mechanism. Namely, a PVK dimer type enolate was formed *during the reaction* which further react with *N*-sulfonated imine to give exclusively the double aza-Baylis−Hillman adduct.

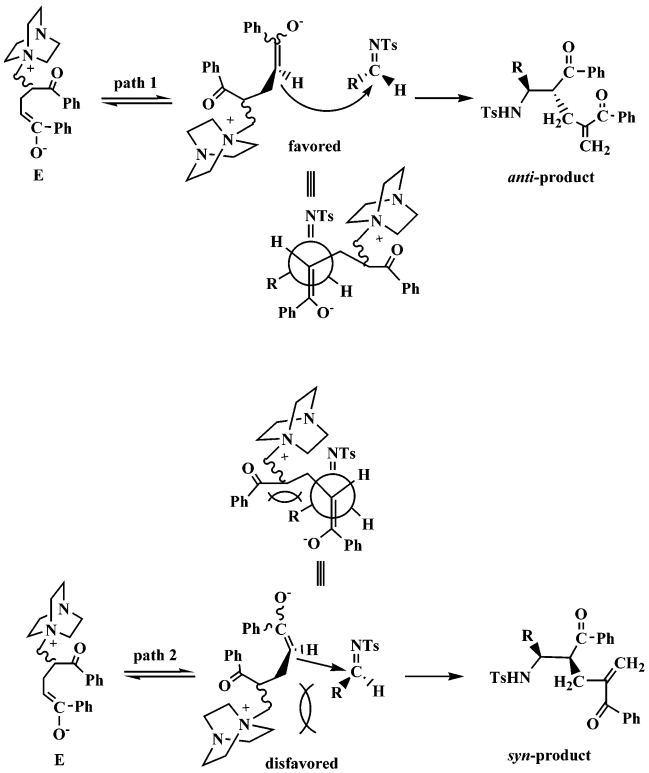
According to the generally accepted reaction mechanism for the Baylis−Hillman reaction, addition of the catalyst to the activated olefin furnishes a zwitterion species (Figure 2, **A** or **B**), which reacts with the electrophiles such as *N*-sulfonated imine to give another zwitterion species (Figure 2, **C** or **D**).[1a] Namely, it carries the Lewis base molecule in the next reactions such as the aldol condensation or Michael addition reaction. Moreover, the subsequent elimination (E2 or E1cB) from the betain intermediate (nitrogen and phosphane betain) should also have some differences (Figure 2, **C** and **D**). Thus, we believe that triphenylphosphine and DABCO are different Lewis bases which have certainly different properties such as nucleophilicity. Thus, different results could be obtained in the aza-Baylis−Hillman reaction of *N*-sulfonated imines with PVK. But it is very difficult to strictly clarify the differences between phosphine Lewis bases and nitrogen Lewis bases. On the basis of these

(10) In our previous report, we confirmed that, in the Baylis−Hillman reaction of arylaldehyde (1.0 equiv) with MVK (2.0 equiv) in the presence of catalytic amounts of DABCO (0.1 equiv) in DMF or DMSO, the double Baylis−Hillman reaction product was formed via the first reaction mechanism as shown in Scheme 1 (please see ref 5). But the stereoselectivities of the corresponding double Baylis−Hillman reaction adducts are low (∼2:3) along with the normal Baylis−Hillman reaction product.

SCHEME 5



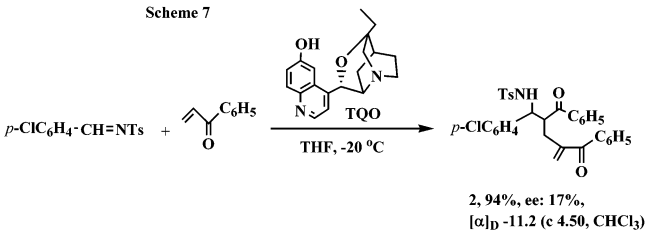
SCHEME 6



results, at the present stage we can only speculate that the PVK enolate **B** derived from triphenylphosphine and PVK could be easily formed under the same conditions with higher nucleophilicity and then immediately react with *N*-sulfonated imine (1,2-addition) to give the normal aza-Baylis−Hillman adducts **1** in high yields. For nitrogen Lewis base DABCO, the PVK enolate **A** derived from DABCO and PVK would have lower nucleophilicity, react more easily with another PVK to give the enolate **E** of the PVK dimer (PVK dimer type enolate) through Michael addition (1,4-addition) with higher nucleophilicity, and subsequently react with *N*-sulfonated imine (1,2-addition) to exclusively give the corresponding double aza-Baylis−Hillman adducts **2** in high yields (Scheme 5).

In Scheme 6, we elucidated the open, extended transition state for the stereoselective formation of **2** on the basis of the previous investigations.[11] This reaction proceeded in a stepwise manner. It involves (i) a staggered arrangement of bonds around the interacting $sp^{2-}sp^2$ centers, (ii) an *anti* relationship of the PVK enolate and imino group (C═N) to maximize the distance between the oxygen atom and nitrogen atom, which, in the transition state, will both have partial negative charge, and (iii) arrangement of the other substituents on the PVK enolate and *N*-sulfonated imine to minimize steric interactions overall. As can be seen from the Newman projection, path 1 is the favored way for the formation of **2** to give the *anti*-product and path 2 is disfavored because it suffers from severe steric interaction between R and the enolate of the PVK dimer (Scheme 6).

SCHEME 7



Furthermore, we also tried to use 4-(3-ethyl-4-oxa-1-azatricyclo[4.4.0.0^{3,8}]dec-5-yl)quinolin-6-ol (TQO) reported by Hatakeyama as a chiral Lewis base for this reaction because it is very easily prepared from (+)-quinidine[2a] and high enantiomeric excesses have been achieved in the reactions of 1,1,1,3,3,3-hexafluoroisopropyl acrylate with arylaldehydes (Scheme 7).[2] We found that the double aza-Baylis−Hillman adduct was also obtained in very high yield as a sole product with the *anti*-configuration and 17% ee (column, Chiralcel OD; eluent, 95:5 hexane−2-propanol mixture; flow rate, 1.0 mL min^{-1}; detection, 254 nm light). Now we are exploring some novel chiral Lewis bases to get high ee in this interesting double aza-Baylis−Hillman reaction.

Conclusion

We found that, in the aza-Baylis−Hillman reaction of sulfonated imines with PVK using DABCO as a Lewis base, double aza-Baylis−Hillman adduct **2** (diadduct) was exclusively formed in the *anti*-configuration, which was confirmed to be derived from the Baylis−Hillman reaction of the enolate of the PVK dimer induced by DABCO and PVK with *N*-tosylated imine. Efforts are under way to elucidate the mechanistic details of this reaction and to disclose the scope and limitations of this reaction. Work along this line is currently in progress.

Experimental Section

General Remarks. Unless otherwise stated, all reactions were carried out under an argon atmosphere. Phenyl vinyl ketone[12] and all *N*-tosylated imines[13] were prepared according to the literature. Infrared spectra were measured on a spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Mass spectra were recorded by the EI method. All solid compounds reported in this paper gave satisfactory CHN microanalyses. Melting points are uncorrected.

Typical Reaction Procedure for the Triphenylphosphine-Catalyzed Aza-Baylis−Hillman Reaction of Phenyl Vinyl Ketone with *N*-Benzylidene-4-methylbenzenesulfonamide.

(11) (a) Nelson, S. G. *Tetrahedron*: *Asymmetry* **1998**, *9*, 357. (b) Atkinson, R. S., Ed. *Stereoselective Synthesis*; John Wiley & Sons: New York, pp 218−242.

(12) Burckhalter, J. H.; Fuson, R. C. *J. Am. Chem. Soc.* **1948**, *70*, 4184.

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

To a solution of *N*-benzylidene-4-methylbenzenesulfonamide (129 mg, 0.5 mmol) and triphenylphosphine (13 mg, 0.05 mmol) in THF (1.0 mL) at room temperature was added phenyl vinyl ketone (99 mg, 0.75 mmol). The reaction was monitored by TLC; when the imine disappeared, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography [SiO_2, EtOAc−petroleum ether (1:5)] to yield **1a** (180 mg, 92%) as a colorless solid.

Data for *N*-(2-benzoyl-1-phenylallyl)-4-methylbenzenesulfonamide (1a): colorless solid; mp 141−143 °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 ($CDCl_3$, TMS, 75.44 MHz) δ 21.48, 59.72, 126.54, 127.23, 127.77, 128.23, 128.66, 128.87, 129.41, 129.54, 132.69, 137.05, 137.52, 138.67, 143.35, 145.23, 196.90; MS (EI) *m/e* 260 (M^+ − 131, 5.94), 236 (M^+ − 155, 100). Anal. Calcd for $C_{23}H_{21}NO_3S$: C, 70.56; H, 5.41; N, 3.58. Found: C, 70.41; H, 5.58; N, 3.49.

Data for *N*-[2-benzoyl-1-(4-methoxyphenyl)allyl]-4-methylbenzenesulfonamide (1b): colorless solid (158 mg, 75%); mp 91−92 °C; IR ($CHCl_3$) ν 1655 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.39 (3H, s, Me), 3.73 (3H, s, OMe), 5.40 (1H, d, J = 8.2 Hz), 5.72 (1H, s), 5.81 (1H, d, J = 8.2 Hz), 6.11 (1H, s), 6.74 (2H, d, J = 8.4 Hz), 7.10 (2H, d, J = 8.4 Hz, Ar), 7.22 (2H, d, J = 7.9 Hz, Ar), 7.35−7.42 (2H, m, Ar), 7.50−7.58 (3H, m, Ar), 7.70 (2H, d, J = 7.9 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz) δ 21.43, 55.15, 58.92, 113.97, 127.20, 127.88, 128.01, 128.17, 129.39, 129.46, 130.75, 132.59, 137.06, 137.50, 143.23, 145.66, 159.02, 196.81; MS (EI) *m/e* 290 (M^+ − 131, 5.42), 266 (M^+ − 155, 100). Anal. Calcd for $C_{24}H_{23}NO_4S$: C, 68.39; H, 5.50; N, 3.32. Found: C, 68.44; H, 5.63; N, 3.09.

Data for *N*-[2-benzoyl-1-(4-fluorophenyl)allyl]-4-methylbenzenesulfonamide (1c): colorless solid (189 mg, 93%); mp 138−140 °C; IR ($CHCl_3$) ν 1654 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.39 (3H, s, Me), 5.43 (1H, d, J = 8.5 Hz), 5.74 (1H, s), 6.01 (1H, d, J = 8.5 Hz), 6.08 (1H, s), 6.89−6.95 (2H, dd, J = 8.6 Hz, 8.6 Hz), 7.18−7.22 (2H, m, Ar), 7.24 (2H, d, J = 8.2 Hz, Ar), 7.37−7.42 (2H, m, Ar), 7.52−7.56 (3H, m, Ar), 7.70 (2H, d, J = 8.2 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz) δ 21.41, 58.81, 115.40 (d, J_{C-F} = 21.35 Hz), 115.55, 127.12, 128.22, 128.33, 128.44, 128.63, 129.43 (d, J_{C-F} = 10.94 Hz), 132.76, 134.53 (d, J_{C-F} = 3.47 Hz), 136.82, 137.41, 143.40, 145.20, 167.07 (d, J_{C-F} = 246.46 Hz), 196.67; MS (EI) *m/e* 278 (M^+ − 132, 4.68), 254 (M^+ − 155, 100). Anal. Calcd. for $C_{23}H_{20}FNO_3S$: C, 67.46; H, 4.92; N, 3.42. Found: C, 67.75; H, 5.16; N, 3.32.

Data for *N*-[2-benzoyl-1-(4-chlorophenyl)allyl]-4-methylbenzenesulfonamide (1d): colorless solid (190 mg, 89.2%); mp 119−121 °C; IR ($CHCl_3$) ν 1654 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.39 (3H, s, Me), 5.41 (1H, d, J = 8.5 Hz), 5.74 (1H, s), 6.03 (1H, d, J = 8.5 Hz), 6.07 (1H, s), 7.14−7.20 (5H, m, Ar), 7.21 (2H, d, J = 8.1 Hz, Ar), 7.35−7.40 (2H, m, Ar), 7.50−7.55 (3H, m, Ar), 7.68 (2H, d, J = 8.1 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz) δ 21.51, 59.29, 127.19, 128.00, 128.33, 128.77, 129.25, 129.42, 129.60, 132.90, 133.65, 136.84, 137.31, 137.49, 143.53, 144.85, 196.79; MS (EI) *m/e* 294 (M^+ − 132, 3.72), 270 (M^+ − 155, 100). Anal. Calcd for $C_{23}H_{20}ClNO_3S$: C, 70.56; H, 5.41; N, 3.58. Found: C, 70.41; H, 5.58; N, 3.49.

Data for *N*-[2-benzoyl-1-(4-bromophenyl)allyl]-4-methylbenzenesulfonamide (1e): colorless solid (197 mg, 84%); mp 114−115 °C; IR ($CHCl_3$) ν 1654 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.39 (3H, s, Me), 5.39 (1H, d, J = 8.6 Hz), 5.74 (1H, s), 6.03 (1H, d, J = 8.6 Hz), 6.07 (1H, s), 7.10 (2H, d, J = 8.6 Hz, Ar), 7.21 (2H, d, J = 8.3 Hz, Ar), 7.34 (2H, d, J = 8.6 Hz, Ar), 7.39 (2H, d, J = 7.1 Hz, Ar), 7.50−7.55 (3H, m, Ar), 7.68 (2H, d, J = 8.3 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz) δ 21.41, 59.10, 121.68, 127.08, 128.22, 128.30, 128.32, 129.02, 129.32, 129.49, 131.60, 132.78, 136.74, 137.76, 143.42, 144.81, 196.58; MS (EI) *m/e* 470 (M^+, 0.62), 472 (M^+ + 2, 0.59), 316 (M^+ − 156, 100), 316 (M^+ − 154, 97.39). Anal. Calcd for $4C_{23}H_{20}BrNO_3S{\cdot}C_6H_6$: C, 59.82; H, 4.82; N, 2.85. Found: C, 59.75; H, 4.86; N, 2.77.

Data for *N*-[2-benzoyl-1-(2,3-dichlorophenyl)allyl]-4-methylbenzenesulfonamide (1f): colorless solid (199 mg, 87%); mp 165−166 °C; IR ($CHCl_3$) ν 1655 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.37 (3H, s, Me), 5.75 (1H, s), 5.80 (1H, d, J = 8.8 Hz), 6.04 (1H, s), 6.31 (1H, d, J = 8.8 Hz), 7.08 (1H, dd, J = 8.2, 7.8 Hz, Ar), 7.19 (2H, d, J = 8.1 Hz, Ar), 7.31−7.32 (1H, m, Ar), 7.36−7.41 (3H, m, Ar), 7.51−7.60 (3H, m, Ar), 7.68 (2H, d, J = 8.1 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz) δ 20.83, 56.91, 105.52, 126.52, 126.54, 126.72, 127.04, 127.71, 128.79, 128.92, 129.12, 130.25, 132.41, 132.71, 136.09, 137.48, 142.85, 142.99, 196.04; MS (EI) *m/e* 328 (M^+ − 132, 5.16), 304 (M^+ − 156, 100). Anal. Calcd for $C_{23}H_{19}Cl_2NO_3S$: C, 60.00; H, 4.16; N, 3.04. Found: C, 60.22; H, 4.01; N, 3.03.

Data for *N*-[2-benzoyl-1-(4-methylphenyl)allyl]-4-methylbenzenesulfonamide (1g): colorless solid (171 mg, 84%); mp 111−112 °C; IR ($CHCl_3$) ν 1654 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.26 (3H, s, Me), 2.39 (3H, s, Me), 5.41 (1H, d, J = 8.1 Hz), 5.74 (1H, s), 5.81 (1H, d, J = 8.6 Hz), 6.13 (1H, s), 7.02 (2H, d, J = 8.1 Hz, Ar), 7.08 (2H, d, J = 8.1 Hz), 7.22 (2H, d, J = 8.4 Hz, Ar), 7.35−7.40 (2H, m), 7.49−7.56 (3H, m, Ar), 7.71 (2H, d, J = 8.4 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz) δ 21.24, 21.75, 59.45, 126.79, 127.49, 128.42, 128.45, 128.71, 129.57, 129.69, 129.75, 132.88, 135.94, 137.32, 137.73, 143.53, 145.76, 197.07; MS (EI) *m/e* 274 (M^+ − 132, 5.90), 250 (M^+ − 156, 100.00). Anal. Calcd for $C_{24}H_{23}NO_3S$: C, 71.08; H, 5.72; N, 3.45. Found: C, 71.12; H, 5.56; N, 3.32.

Data for *N*-[2-benzoyl-1-(3-methylphenyl)allyl]-4-methylbenzenesulfonamide (1h): colorless solid (202 mg, 99.5%); mp 144−146 °C; IR ($CHCl_3$) ν 1653 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.29 (3H, s, Me), 2.46 (3H, s, Me), 5.49 (1H, d, J = 8.4 Hz), 5.81 (1H, s), 5.91 (1H, d, J = 8.4 Hz), 6.20 (1H, s), 7.05 (2H, d, J = 7.5 Hz, Ar), 7.06 (1H, s), 7.29 (2H, d, J = 8.7 Hz, Ar), 7.42−7.47 (2H, m, Ar), 7.50−7.55 (3H, m, Ar), 7.77 (2H, d, J = 8.7 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz) δ 21.57, 21.73, 59.55, 123.83, 127.51, 127.79, 128.47, 128.73, 129.70, 129.73, 132.91, 137.33, 137.77, 138.51, 138.78, 143.53, 145.77, 197.02; MS (EI) *m/e* 274 (M^+ − 132, 4.42), 250 (M^+ − 156, 100). Anal. Calcd for $C_{24}H_{23}NO_3S$: C, 71.08; H, 5.72; N, 3.45. Found: C, 71.22; H, 5.57; N, 3.28.

Data for *N*-[2-benzoyl-1-(4-ethylphenyl)allyl]-4-methylbenzenesulfonamide (1i): colorless solid (143 mg, 68%); mp 102−104 °C; IR ($CHCl_3$) ν 1654 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.17 (3H, t, J = 7.8 Hz, Me), 2.40 (3H, s, Me), 2.56 (2H, q, J = 7.8 Hz, CH_2), 5.44 (1H, d, J = 8.2 Hz), 5.76 (1H, s), 5.84 (1H, d, J = 8.2 Hz), 6.14 (1H, s), 7.05 (2H, d, J = 7.8 Hz, Ar), 7.11 (2H, d, J = 8.8 Hz, Ar), 7.23 (2H, d, J = 8.2 Hz, Ar), 7.36−7.41 (2H, m, Ar), 7.50−7.57 (3H, m, Ar), 7.71 (2H, d, J = 8.2 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz) δ 15.36, 21.46, 28.33, 59.24, 126.59, 127.22, 128.09, 128.16, 128.48, 129.42, 129.45, 132.58, 135.86, 137.09, 137.49, 143.19, 143.76, 145.51, 196.80; MS (EI) *m/e* 288 (M^+ − 132, 5.97), 264 (M^+ − 156, 100). Anal. Calcd for $C_{25}H_{25}NO_3S$: C, 71.57; H, 6.01; N, 3.34. Found: C, 71.87; H, 6.17; N, 3.21.

Typical Reaction Procedure for the DABCO-Catalyzed aza-Baylis−Hillman Reaction of Phenyl Vinyl Ketone with *N*-Benzylidene-4-methylbenzenesulfonamide.

To a solution of *N*-benzylidene-4-methylbenzenesulfonamide (65 mg, 0.25 mmol) and DABCO (3 mg, 0.025 mmol) in THF (0.5 mL) at room temperature was added phenyl vinyl ketone (99 mg, 0.75 mmol). After the resulting solution was stirred for 5.5 h at room temperature, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography [SiO_2, EtOAc−petroleum ether (1:5)] to yield **2a** (85 mg, 65%) as a colorless solid.

Data for *N*-(2,4-dibenzoyl-1-phenylpent-4-enyl)-4-methylbenzenesulfonamide (2a): colorless solid; mp 112−113 °C; IR ($CHCl_3$) ν 1651 cm^{-1} (C═O), 1666 cm^{-1} (C═O); ^1H NMR

($CDCl_3$, TMS, 300 MHz) δ 2.29 (3H, s, Me), 2.94 (1H, dd, J = 13.2, 9.0 Hz), 3.02 (1H, dd, J = 13.2, 6.6 Hz), 4.24 (1H, ddd, J = 9.0, 6.6, 4.2 Hz), 4.86 (1H, dd, J = 9.6, 4.2 Hz), 5.87 (1H, s), 6.24 (1H, s), 6.85−6.95 (6H, m), 7.00 (2H, d, J = 8.3 Hz), 7.32 (2H, d, J = 7.5 Hz), 7.41−7.49 (5H, m, Ar), 7.53−7.59 (1H, m), 7.66 (2H, d, J = 7.9 Hz, Ar), 7.73 (2H, d, J = 8.1 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 21.28, 34.43, 49.02, 58.48, 126.44, 126.75, 126.92, 128.04, 128.28, 128.32, 128.38, 128.56, 128.97, 129.34, 132.33, 132.68, 133.59, 136.59, 137.53, 138.15, 138.77, 142.58, 198.04, 204.18; MS (EI) *m/e* 368 (M^+ − 154, 29.15), 105 ($PhCO^+$, 100.00). Anal. Calcd for $C_{32}H_{29}NO_4S$: C, 73.40; H, 5.58; N, 2.67. Found: C, 73.54; H, 5.65; N, 2.51.

Data for *N*-[2,4-dibenzoyl-1-(3-methylphenyl)pent-4-enyl]-4-methylbenzenesulfonamide (2b): colorless solid (101 mg, 75%); mp 130−132 °C; IR ($CHCl_3$) ν 1651 cm^{-1} (C═O), 1667 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.98 (3H,s), 2.30 (3H, s, Me), 2.95 (1H, dd, J = 13.2, 8.7 Hz), 3.03 (1H, dd, J = 13.2, 6.3 Hz), 4.24 (1H, ddd, J = 8.7, 6.3, 3.9 Hz), 4.83 (1H, dd, J = 9.3, 3.9 Hz), 5.88 (1H, s), 6.27 (1H, s), 6.55 (1H, s), 6.67−6.87 (4H, m), 7.02 (2H, d, J = 8.7 Hz), 7.27−7.34 (2H, m), 7.42−7.49 (5H, m, Ar), 7.54−7.60 (1H, m), 7.68 (2H, d, J = 7.2 Hz, Ar), 7.75 (2H, d, J = 7.2 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 20.91, 21.22, 48.94, 58.42, 123.63, 126.68, 127.12, 127.59, 127.93, 128.23, 128.34, 128.49, 128.81, 129.30, 132.28, 132.70, 133.51, 136.58, 137.46, 137.50, 138.13, 138.35, 142.42, 142.54, 198.01, 204.14; MS (EI) *m/e* 382 (M^+ − 155, 41.88), 105 ($PhCO^+$, 100.00). Anal. Calcd for $C_{33}H_{31}NO_4S$: C, 73.72; H, 5.81; N, 2.61. Found: C, 73.78; H, 5.73; N, 2.35.

Data for *N*-[2,4-dibenzoyl-1-(4-methylphenyl)pent-4-enyl]-4-methylbenzenesulfonamide (2c): colorless solid (95 mg, 71%); mp 118−119 °C; IR ($CHCl_3$) ν 1652 cm^{-1} (C═O), 1669 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.12 (3H, s), 2.29 (3H, s, Me), 2.95 (1H, dd, J = 13.5, 9.0 Hz), 3.03 (1H, dd, J = 13.5, 6.6 Hz), 4.23 (1H, ddd, J = 9.0, 6.6, 3.6 Hz), 4.81 (1H, dd, J = 9.3, 3.6 Hz), 5.84 (1H, s), 6.21 (1H, s), 6.73 (5H, s), 6.78 (2H, d, J = 9.3 Hz, NH), 6.99 (2H, d, J = 8.1 Hz), 7.28−7.33 (2H, m), 7.39−7.47 (5H, m, Ar), 7.52−7.57 (1H, m), 7.63 (2H, d, J = 7.0 Hz, Ar), 7.74 (2H, d, J = 8.2 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 20.82, 21.34, 34.41, 49.07, 58.39, 126.44, 126.83, 128.31, 128.47, 128.61, 128.71, 128.83, 128.96, 129.37, 132.34, 132.66, 133.59, 135.77, 136.61, 137.57, 138.21, 142.53, 142.70, 198.05, 204.13; MS (EI) *m/e* 382 (M^+ − 155, 24.79), 105 ($PhCO^+$, 91.37). Anal. Calcd for $C_{33}H_{31}NO_4S$: C, 73.72; H, 5.81; N, 2.61. Found: C, 73.79; H, 5.73; N, 2.43.

Data for *N*-[2,4-Dibenzoyl-1-(4-methoxyphenyl)pent-4-enyl]-4-methylbenzenesulfonamide (2d): colorless solid (117 mg, 85%); mp 127−128 °C; IR ($CHCl_3$) ν 1651 cm^{-1} (C═O), 1664 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.31 (3H, s, Me), 2.95 (1H, dd, J = 13.2, 8.5 Hz), 3.03 (1H, dd, J = 13.2, 6.5 Hz), 3.64 (3H, s, Me), 4.23 (1H, ddd, J = 8.5, 6.5, 3.8 Hz), 4.82 (1H, dd, J = 8.9, 3.8 Hz), 5.86 (1H, s), 6.23 (1H, s), 6.47 (1H, d, J = 8.8 Hz), 6.78 (2H, d, J = 8.9 Hz), 7.03 (2H, d, J = 8.4 Hz), 7.30−7.35 (2H, m), 7.41−7.50 (5H, m, Ar), 7.54−7.59 (1H, m), 7.65 (2H, d, J = 6.9 Hz, Ar), 7.76 (2H, d, J = 6.6 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 21.25, 34.36, 49.07, 54.99, 58.05, 113.35, 126.74, 127.62, 128.21, 128.35, 128.54, 128.90, 129.27, 130.87, 132.26, 132.48, 133.54, 136.58, 137.46, 138.17, 142.40, 142.60, 158.38, 197.94, 204.24; MS (EI) *m/e* 399 (M^+ − 155, 3.79), 105 ($PhCO^+$, 91.37). Anal. Calcd for $C_{33}H_{31}NO_5S$: C, 71.59; H, 5.64; N, 2.53. Found: C, 71.51; H, 5.72; N, 2.59.

Data for *N*-[2,4-dibenzoyl-1-(4-fluorophenyl)pent-4-enyl]-4-methylbenzenesulfonamide (2e): colorless solid (100 mg, 74%); mp 141−142 °C; IR ($CHCl_3$) ν 1650 cm^{-1} (C═O), 1666 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.33 (3H, s, Me), 2.94 (1H, dd, J = 12.6, 9.0 Hz), 3.03 (1H, dd, J = 12.6, 6.6 Hz), 4.25 (1H, ddd, J = 9.0, 6.6, 3.9 Hz), 4.85 (1H, dd, J = 9.6, 3.9 Hz), 5.89 (1H, s), 6.26 (1H, s), 6.59−6.65 (2H, m), 6.82−6.90 (3H, m), 7.04 (2H, d, J = 8.1 Hz), 7.31−7.36 (2H, m), 7.43−7.51 (5H, m, Ar), 7.55−7.60 (1H, m), 7.66 (2H, d, J = 6.9 Hz, Ar), 7.76 (2H, d, J = 8.1 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 21.31, 34.46, 48.98, 57.76, 114.89 (d, J_{C-F} = 21.75 Hz), 126.74, 128.16 (d, J_{C-F} = 4.16 Hz), 128.33, 128.39, 128.67, 129.04, 129.35, 132.42, 132.91, 133.81, 134.67 (d, J_{C-F} = 2.4 Hz), 136.35, 137.48, 138.12, 142.33, 142.87, 161.58 (d, J_{C-F} = 246.09 Hz), 198.09, 204.11; MS (EI) *m/e* 386 (M^+ − 155, 30.12), 105 ($PhCO^+$, 100.00). Anal. Calcd for $C_{32}H_{28}FNO_4S$: C, 70.96; H, 5.21; N, 2.59. Found: C, 70.98; H, 5.26; N, 2.67.

Data for *N*-[2,4-dibenzoyl-1-(4-chlorophenyl)pent-4-enyl]-4-methylbenzenesulfonamide (2f): colorless solid (98 mg, 70%); mp 137−138 °C; IR ($CHCl_3$) ν 1650 cm^{-1} (C═O), 1666 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.35 (3H, s, Me), 2.94 (1H, dd, J = 13.5, 9.0 Hz), 3.03 (1H, dd, J = 13.5, 6.0 Hz), 4.25 (1H, ddd, J = 9.0, 6.0, 3.9 Hz), 4.84 (1H, dd, J = 9.3, 3.9 Hz), 5.91 (1H, s), 6.27 (1H, s), 6.81 (2H, d, J = 8.4 Hz), 6.90 (2H, d, J = 9.3 Hz), 7.05 (2H, d, J = 7.8 Hz), 7.33−7.38 (2H, m), 7.44−7.52 (5H, m, Ar), 7.56−7.62 (1H, m), 7.69 (2H, d, J = 6.9 Hz, Ar), 7.79 (2H, d, J = 7.2 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 21.34, 34.47, 48.84, 57.91, 126.78, 128.05, 128.18, 128.35, 128.45, 128.73, 129.11, 129.38, 132.46, 132.83, 132.94, 133.88, 136.33, 137.38, 137.47, 138.01, 142.32, 143.01, 198.08, 203.86; MS (EI) *m/e* 402 (M^+ − 156, 19.18), 105 ($PhCO^+$, 100.00). Anal. Calcd for $C_{32}H_{28}ClNO_4S$: C, 68.87; H, 5.06; N, 2.51. Found: C, 69.04; H, 5.07; N, 2.35.

Data for *N*-[2,4-dibenzoyl-1-(3-chlorophenyl)pent-4-enyl]-4-methylbenzenesulfonamide (2g): colorless solid (80 mg, 57%); mp 165−167 °C; IR ($CHCl_3$) ν 1650 cm^{-1} (C═O), 1668 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.30 (3H, s, Me), 2.93 (1H, dd, J = 13.5, 9.0 Hz), 3.04 (1H, dd, J = 13.5, 6.0 Hz), 4.24 (1H, ddd, J = 9.0, 6.0, 3.9 Hz), 4.81 (1H, dd, J = 9.6, 3.9 Hz), 5.91 (1H, s), 6.30 (1H, s), 6.70−6.78 (2H, m), 6.85−6.89 (3H, m), 7.02 (2H, d, J = 8.4 Hz), 7.31−7.36 (2H, m), 7.43−7.50 (5H, m, Ar), 7.55−7.60 (1H, m), 7.68 (2H, d, J = 7.8 Hz, Ar), 7.78 (2H, d, J = 7.2 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 21.14, 34.22, 48.66, 57.73, 124.66, 126.45, 126.63, 126.93, 128.16, 128.27, 128.49, 128.94, 129.18, 129.22, 132.26, 132.86, 133.64, 133.78, 136.08, 137.27, 137.65, 140.48, 142.04, 142.82, 197.89, 203.51; MS (EI) *m/e* 402 (M^+ − 156, 45.04), 105 ($PhCO^+$, 100.00). Anal. Calcd for $C_{32}H_{28}ClNO_4S$: C, 68.87; H, 5.06; N, 2.51. Found: C, 68.84; H, 4.96; N, 2.28.

Data for *N*-[2,4-dibenzoyl-1-(3-fluorophenyl)pent-4-enyl]-4-methylbenzenesulfonamide (2h): colorless solid (83 mg, 61%); mp 109−110 °C; IR ($CHCl_3$) ν 1654 cm^{-1} (C═O), 1680 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.33 (3H, s, Me), 2.96 (1H, dd, J = 13.5, 9.0 Hz), 3.06 (1H, dd, J = 13.5, 6.3 Hz), 4.28 (1H, ddd, J = 9.0, 6.3, 3.6 Hz), 4.87 (1H, dd, J = 9.6, 3.6 Hz), 5.93 (1H, s), 6.30 (1H, s), 6.53 (2H, d, J = 9.6 Hz), 6.3−6.71 (2H, m), 6.92−6.98 (2H, m), 7.06 (2H, d, J = 7.8 Hz), 7.33−7.38 (2H, m), 7.46−7.53 (5H, m, Ar), 7.58−7.63 (1H, m), 7.71 (2H, d, J = 6.9 Hz, Ar), 7.80 (2H, d, J = 7.2 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 21.29, 34.41, 48.78, 57.88, 113.60 (d, J_{C-F} = 21.83 Hz), 113.89 (d, J_{C-F} = 20.70 Hz), 122.23 (d, J_{C-F} = 2.93 Hz), 126.69, 128.38 (d, J_{C-F} = 6.23 Hz), 128.67, 129.07, 129.36, 129.60, 129.71, 132.44, 133.03, 133.82, 136.27, 137.46, 138.01, 141.47 (d, J_{C-F} = 6.15 Hz), 142.24, 142.91, 162.29 (d, J_{C-F} = 245.70 Hz), 198.09, 203.86; MS (EI) *m/e* 386 (M^+ − 155, 42.45), 105 ($PhCO^+$, 100.00). Anal. Calcd for $C_{32}H_{28}FNO_4S$: C, 70.96; H, 5.21; N, 2.59. Found: C, 70.95; H, 5.17; N, 2.39.

Data for *N*-(2,4-dibenzoyl-1-naphthalen-1-ylpent-4-enyl)-4-methylbenzenesulfonamide (2i): colorless solid (78 mg, 54%); mp 164−165 °C; IR ($CHCl_3$) ν 1651 cm^{-1} (C═O), 1667 cm^{-1} (C═O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.22 (3H, s, Me), 3.11 (2H, d, J = 7.2 Hz), 4.47 (1H, dt, J = 7.2, 3.3 Hz), 5.76 (1H, dd, J = 9.3, 3.3 Hz), 6.01 (1H, s), 6.41 (1H, s), 6.82−6.91 (4H, m), 7.06 (1H, d, J = 9.3 Hz), 7.13−7.18 (2H, m), 7.32−7.56 (11H, m, Ar), 7.69−7.75 (3H, m), 7.82 (2H, d, J = 8.4 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 21.20, 34.53, 46.93, 53.91, 121.50, 124.59, 124.65, 125.36, 126.46, 126.58, 127.33, 128.16, 128.31, 128.39, 128.59, 128.81, 128.90, 129.36,

129.71, 132.30, 133.34, 133.46, 133.51, 136.44, 137.42, 138.01, 142.41, 142.52, 197.76, 204.31; MS (EI) *m/e* 418 ($M^+ - 156$, 16.95), 105 ($PhCO^+$, 100.00). Anal. Calcd for $C_{36}H_{31}NO_4S$: C, 75.37; H, 5.45; N, 2.44. Found: C, 75.39; H, 5.21; N, 2.19.

Data for *N*-[1-(1-benzoylvinyl)pentyl]-4-methylbenzenesulfonamide (5): viscous liquid; IR ($CHCl_3$) ν 1685 cm^{-1} (C═O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.84 (3H, J = 7.5 Hz, Me), 1.20−1.35 (4H, m, CH_2CH_2), 1.58−1.75 (2H, m, CH_2), 2.38 (3H, s, Me), 4.13 (1H, dt, J = 9.3, 7.8 Hz, CH), 5.52 (1H, s, ═CH), 5.62 (1H, d, J = 9.3 Hz, NH), 5.81 (1H, s, ═CH), 7.22 (2H, d, J = 8.1 Hz, Ar), 7.37−7.43 (2H, m, Ar), 7.49−7.58 (3H, m, Ar), 7.71 (2H, d, J = 8.1 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 13.87, 21.44, 22.05, 28.31, 35.15, 57.67, 127.15, 128.16, 129.09, 129.37, 129.45, 132.57, 137.30, 138.03, 143.06, 145.39, 197.63; MS (EI) *m/e* 372 ($M^+ + 1$, 6.70), 314 ($M^+ - 57$, 40.38), 216 ($M^+ - 155$, 32.68); HRMS *m/e* calcd for $C_{17}H_{16}NO_3S$ 314.08509, found 314.08501.

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Supporting Information Available: X-ray crystal data of **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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