Aza-Baylis–Hillman Reaction of β-Substituted Activated Olefins with *N*-Tosyl Imines

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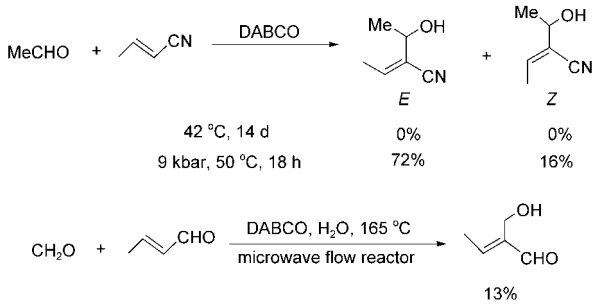
Abstract: Aza-Baylis–Hillman reactions of β-substituted activated olefins such as crotonaldehyde, (*E*)-propenyl phenyl ketone, hex-2-enal or pent-3-en-2-one with *N*-tosyl imines can be carried out for the first time in the presence of tertiary phosphine Lewis bases such as PPh_2Me or $PPhMe_2$ to give the corresponding Baylis–Hillman adducts in moderate to good yields under mild reaction conditions.

Keywords: aza-Baylis–Hillman reaction; enones; Lewis base catalyst; organic catalysis; phosphanes; *N*-tosyl imines

Introduction

The Baylis–Hillman reaction, an exquisite reaction as simple starting materials are converted into densely functionalized products in a catalytic process without generating waste or by-products, has made great progress[1,2] since Baylis and Hillman first reported the reaction of acetaldehyde with ethyl acrylate or acrylonitrile in the presence of catalytic amounts of a strong nitrogen Lewis base such as 1,4-diazabicyclo[2.2.2]octane (DABCO) in 1972.[3] However, the reaction has traditionally suffered from low reaction rates and limited substrate scopes. For example, the Baylis–Hillman reaction of aldehydes with β-substituted electron-deficient olefins is extremely sluggish. According to the literature reported to date, the successful examples of the Baylis–Hillman reaction of aldehydes with β-substituted activated olefins such as crotononitrile or crotonaldehyde were only achieved under high pressure or by microwave irradiation (Scheme 1).[4] This is because the zwitterionic ammonium species, generated from the Michael addition of the nitrogen nucleophilic Lewis base (DABCO) to the α,β-unsaturated enone according to the generally accepted mechanism of the Baylis–Hillman reaction,[1] is difficult to be formed in high concentration in the reaction solution due to the steric bulkiness of β-substituted activated olefins.

In order to extend the scope and limitations of this atom-economic reaction, we decided to explore a catalytic method for the Baylis–Hillman reaction using β-substituted activated olefins as the Michael acceptor under mild conditions. During our investigations on this



Scheme 1. The Baylis–Hillman reaction of aldehyde with β-substituted active olefins.

very simple and useful reaction,[5] we found that in the reaction of aryl aldehydes, especially those having 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*-tosyl imines **1** to replace aryl aldehydes, the aza-Baylis–Hillman reaction can be accelerated to some extent to provide β-amino carbonyl compounds in higher yields compared with their aryl aldehydes in the presence of a nitrogen or phosphine Lewis base catalyst.[6] Hence, in our continuous studies on the development of Baylis–Hillman reaction, we attempted to use *N*-tosyl imines **1** (Ar-CH=NTs) instead of aldehydes in the traditional Baylis–Hillman reaction with β-substituted electron-deficient olefins under mild conditions because we expect

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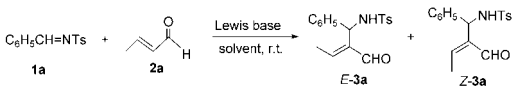
Table 1. The aza-Baylis–Hillman reaction of crotonaldehyde (**2a**; 2.0 equivs.) with *N*-benzylidene-4-methylbenzenesulfonamide (**1a**; 1.0 equiv.) in the presence of 20 mol % of Lewis base.



Entry	Lewis base	Solvent	Time [h]	Yield of **3a** [%][a] (*E*:*Z*)
1	DABCO	THF	24	NR[b]
2	PMe_3	THF	20	–[c]
3	PPh_3	THF	24	NR[b]
4	PPh_2Me	THF	28	33 (>99:1)
5	PPh_2Me	THF	60	51 (>99:1)
6	$PPhMe_2$	THF	5	–[c]
7	PBu_3	THF	0.4	–[c]
8	PPh_2Me	CH_3OH	60	16 (>99:1)
9	PPh_2Me	CH_2Cl_2	60	44 (>99:1)
10	PPh_2Me	CH_3CN	60	35 (>99:1)

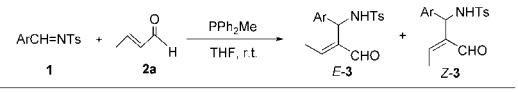
[a] Yields of isolated products.
[b] No reaction occurred.
[c] Complex reaction from which no products could be identified.

that the *N*-tosyl imino group will have a high reactivity toward nucleophilic attack even when the nueclophiles are formed in low concentration. Herein, we report on several aza-Baylis–Hillman reactions of *N*-tosyl imines **1** with β-substituted activated olefins under mild conditions.

Results and Discussion

The aza-Baylis–Hillman reaction of crotonaldehyde (**2a**), which has a methyl group on the β-position, with *N*-tosyl imines **1** was first examined. Using *N*-benzylidene-4-methylbenzenesulfonamide (**1a**) as the substrate, the reaction was carried out in the presence of different Lewis base catalysts in various solvents at room temperature and under ambient pressure to develop the optimal reaction conditions. The results are summarized in Table 1. As can be seen from Table 1, using DABCO or PPh_3 as a Lewis base in THF, no reaction occurred (Table 1, entries 1 and 3). Using PPh_2Me as the Lewis base catalyst, we found that the reaction proceeded slowly to give the corresponding normal aza-Baylis–Hillman adduct **3a** in 33% yield after 28 hours with the *E*-configuration ($E:Z>99:1$) in THF (Table 1, entry 4). The yield of **3a** can be raised to 51% after a prolonged the reaction time (60 hours) (Table 1, entry 5). The more nucleophilic phosphine Lewis base catalysts such as $PhPMe_2$, PMe_3, and PBu_3 resulted in complex reactions from which no products could be identified rather than the corresponding normal aza-Baylis–Hillman adduct, although the staring material *N*-tosyl imine **1a** disappeared more quickly during the reaction (Table 1, entries 2, 6 and 7). The solvent effect was also examined

Table 2. The aza-Baylis–Hillman reaction of crotonaldehyde (**2a**; 2.0 equivs.) with other *N*-tosyl imines **1** (1.0 equiv.) in the presence of 20 mol % PPh_2Me.



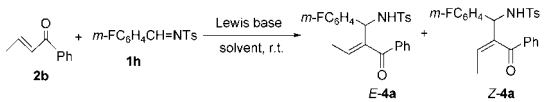
Entry	Ar	Time [h]	Yield of **3** (%)[a] (*E*:*Z*)
1	*p*-ClC_6H_4 **1b**	23	**3b**, 65 (>99:1)
2	*p*-MeC_6H_4 **1c**	72	**3c**, 40 (>99:1)
3	*m*-MeC_6H_4 **1d**	72	**3d**, 42 (>99:1)
4	*p*-$NO_2C_6H_4$ **1e**	22	**3e**, 65 (>99:1)
5	*m*-$NO_2C_6H_4$ **1f**	22	**3f**, 80 (>99:1)
6	*p*-FC_6H_4 **1g**	48	**3g**, 70 (>99:1)
7	*m*-FC_6H_4 **1h**	23	**3h**, 66 (>99:1)
8	*p*-BrC_6H_4 **1i**	24	**3i**, 60 (>99:1)
9	2,3-$Cl_2C_6H_3$ **1j**	15	**3j**, 64 (>99:1)

[a] Yields of isolated products.

in the presence of Lewis base PPh_2Me (Table 1, entries 8–10). THF is the solvent of choice. The best reaction conditions are using PPh_2Me as a Lewis base promoter in THF at room temperature. Under the optimized reaction conditions, we next carried out the aza-Baylis–Hillman reaction of **2a** with a number of other aromatic *N*-tosyl imines **1**. The results are summarized in Table 2. As can be seen from Table 2, the substituents on the benzene ring of **1** affected the reaction rates. For *N*-tosyl imines **1b**, **1e**–**j** having electron-withdrawing groups on the benzene ring, the reactions were complete within 2 days to give the addition product **3** in moderate to good yields (Table 2, entries 1, 4–9). But, for *N*-tosyl imine **1c** or **1d** having an electron-donating group on the benzene ring, a prolonged reaction time (3 days) is required for this aza-Baylis–Hillman reaction to give the corresponding products in moderate yields under the same conditions (Table 2, entries 2 and 3). In all these cases, the addition products *E*-**3** were obtained as the major products ($E:Z>99:1$). The *E*/*Z* ratios of **3** were determined by ^1H NMR spectroscopic data and the configuration of *E*-isomer was confirmed by its NOESY spectrum (see Supporting Information).

In order to extend the scope and limitations, we next used the (*E*)-propenyl phenyl ketone (**2b**) as the Michael acceptor for this aza-Baylis–Hillman reaction. The Lewis base and solvent effects were first examined using *N*-tosyl imine **1 h** as the electrophile. The results are summarized in Table 3. Nitrogen Lewis bases such as DABCO or DBU again have no catalytic activity for this reaction (Table 3, entries 1–3). The tertiary phosphine Lewis base PPh_2Me can promote this reaction to give the corresponding aza-Baylis–Hillman adduct **4a** in moderate to good yields in various solvents (THF, MeCN, CH_2Cl_2, PhMe, and Et_2O) as an *E*- and *Z*-isomeric mixture ($E:Z=40:60\sim70:30$) (Table 3, entries 6–10). The stronger Lewis base $PPhMe_2$ also can catalyze this reaction to give **4a** in 55% yield in THF and in 23% yield in toluene (Table 3, entries 4 and 5).

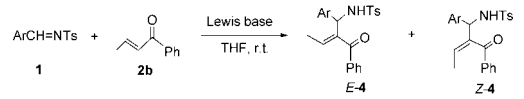
Table 3. The aza-Baylis–Hillman reaction of (*E*)-propenyl phenyl ketone (**2b**; 2.0 equivs.) with *N*-(3-fluorobenzylidene)-4-methylbenzenesulfonamide (**1 h**; 1.0 equiv.) in the presence of 20 mol % Lewis base.



Entry	Lewis base	Solvent	Time [h]	Yield of **4a** (%)[a] (*E*:*Z*)
1	DABCO	THF	48	NR[b]
2	DBU	THF	18	–[c]
3	DBU	CH_3OH	18	–[d]
4	$PPhMe_2$	THF	3	55 (86:14)
5	$PPhMe_2$	PhMe	16	23 (87:13)
6	PPh_2Me	THF	32	77 (67:33)
7	PPh_2Me	MeCN	36	52 (40:60)
8	PPh_2Me	CH_2Cl_2	16	47 (61:39)
9	PPh_2Me	PhMe	30	65 (60:40)
10	PPh_2Me	Et_2O	16	59 (70:30)

[a] Isolated yields.
[b] No reaction occurred.
[c] The Michael addition adduct of $TsNH_2$ to **2b** was obtained.
[d] Complex reaction from which no products could be identified.

Table 4. The aza-Baylis–Hillman reaction of (*E*)-propenyl phenyl ketone (**2b**; 2.0 equivs.) with other *N*-tosyl imines **1** (1.0 equiv.) in the presence of 20 mol % Lewis base.



Entry	Ar	Lewis base	Time [h]	Yield of **4** (%)[a] (*E*:*Z*)
1	C_6H_5 **1a**	PPh_2Me	48	**4b**, 86 (74:26)
2	C_6H_5 **1a**	$PPhMe_2$	3	**4b**, 66 (80:20)
3	*p*-ClC_6H_4 **1b**	PPh_2Me	48	**4c**, 66 (58:42)
4	*p*-ClC_6H_4 **1b**	$PPhMe_2$	3	**4c**, 63 (84:16)
5	*m*-MeC_6H_4 **1d**	PPh_2Me	72	**4d**, 45 (81:19)
6	*m*-MeC_6H_4 **1d**	$PPhMe_2$	9	**4d**, 68 (81:19)
7	*p*-$NO_2C_6H_4$ **1e**	PPh_2Me	36	**4e**, 56 (44:56)
8	α-naphthyl **1k**	PPh_2Me	60	**4f**, 47[b]
9	α-naphthyl **1k**	$PPhMe_2$	9	**4f**, trace

[a] Yields of isolated products.
[b] Only the *E*-isomer was formed.

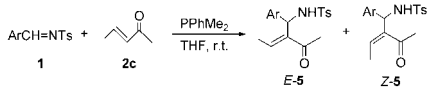
THF is the best solvent for this tertiary phosphine Lewis base catalyzed aza-Baylis–Hillman reaction.

Using PPh_2Me and $PPhMe_2$ as the Lewis base catalysts, we next examined the aza-Baylis–Hillman reaction of several *N*-tosyl imines **1** with **2b** in THF at room temperature. The results are summarized in Table 4. As can be seen from Table 4, the similar substituent effect of **1** as described above is observed for this aza-Baylis–Hillman reaction. $PPhMe_2$ is more effective than PPh_2Me as a Lewis base promoter for various *N*-tosyl imines **1** because a shorter reaction time is required under the same conditions. But in some cases the isolated yields of **4** are much lower than those with PPh_2Me (Table 4, entries 1, 2 and 8, 9). The *E*/*Z* ratios of **4** were determined by ^1H NMR spectroscopic data and the configuration of *E*-isomer was confirmed by its NOESY spectrum (see Supporting Information).

It should be emphasized here that the aromatic substituent in (*E*)-propenyl phenyl ketone (**2b**) seems to be essential for this type of aza-Baylis–Hillman reaction because when we used pent-3-en-2-one (**2c**) as the β-substituted activated olefin, PPh_2Me has no catalytic activity under the same conditions. Therefore, we again examined the different Lewis bases in this reaction using *N*-tosyl imine **1a** as the substrate. The results are summarized in Table S1 in the Supporting Information. Among the Lewis base catalysts examined, only $PPhMe_2$ can effectively promote this reaction to give the corresponding aza-Baylis–Hillman adduct **5a** in 26% yield as an *E*- and *Z*-isomeric mixture (Table S1 in the Supporting Information, entries 1–7). Carrying out the reaction at a lower temperature (0 °C) did not give a higher yield of **5a**, while a longer reaction time was required (Table S1 in the Supporting Information, entry 8). The optimized conditions for this aza-Baylis–Hillman reaction are using $PPhMe_2$ as the catalyst in THF at room temperature. Next we adopted several other *N*-tosyl imines **1** as the substrates to examine the generality of these optimized conditions. The results are shown in Table 5. As can be seen from the Table 5, for *N*-tosyl imines **1b**, **1c** and **1i**, the corresponding adducts **5b**, **5c** and **5 g** were obtained in moderate yields (Table 5, entries 1, 2, and 7). However, the achieved yields are lower than those from (*E*)-propenyl phenyl ketone (**2b**) under the same conditions. For *N*-tosyl imines **1e** and **1f** which have a strongly electron-withdrawing nitro group on the benzene ring, the starting materials **1e** and **1f** decomposed rapidly to the corresponding aldehyde and tosylamide in the presence of $PPhMe_2$ to give the adducts **5** in 12% yield and trace (Table 5, entries 3 and 4). For *N*-tosyl imines **1 g** and **1 h** which have an electron-withdrawing fluoro group on the benzene ring, the corresponding adducts **5e** and **5f** were formed in 24% and 12% yields, respectively for the same reason (Table 5, entries 5 and 6). The *E*/*Z* ratios of **5** were determined by ^1H NMR spectroscopic data and the configuration of *E*-isomer was confirmed by its NOESY spectrum (see Supporting Information).

Since the above three types of activated olefins all have a methyl group at the β-position, we want to know whether or not an activated olefin that has a longer substituent at the β-position can react with *N*-tosyl imines **1** in the presence of a Lewis base. Therefore, we selected hex-2-enal (**2d**) as the activated olefin to examine the feasibility of its aza-Baylis–Hillman reaction. The Lewis base and solvent effects were first examined using *N*-tosyl imine **1b** as the electrophile. The results are summarized in Table S2 in the Supporting Information. Nitrogen Lewis bases such as DABCO, DMAP and

Table 5. The aza-Baylis-Hillman reaction of (*E*)-pent-3-en-2-one (**2c**; 1.25 equivs.) with other *N*-tosyl imines **1** (1.0 equiv.) in the presence of 25 mol % of $PPhMe_2$.

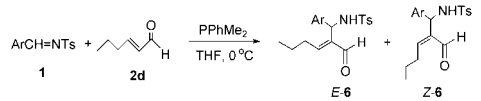


1 2c

Entry	Ar	Time [h]	Yield of **5** (%)[a] (*E*:*Z*)
1	*p*-ClC_6H_4 **1b**	2	**5b**, 36 (81:19)
2	*p*-MeC_6H_4 **1c**	7	**5c**, 40[b]
3	*p*-$NO_2C_6H_4$ **1e**	0.6	**5d**, 12 (86:14)
4	*m*-$NO_2C_6H_4$ **1f**	0.7	–[c]
5	*p*-FC_6H_4 **1g**	3	**5e**, 24[b]
6	*m*-FC_6H_4 **1h**	2	**5f**, 12 (86:14)
7	*p*-BrC_6H_4 **1i**	2	**5g**, 34 (91:9)

[a] Yields of isolated products.
[b] Only the *E*-isomer was obtained.
[c] Complex reaction from which no products could be identified.

Table 6. The aza-Baylis–Hillman reaction of (*E*)-hex-2-enal (**2d**; 2.0 equivs.) with other *N*-tosyl imines **1** (1.0 equiv.) in the presence of 25 mol % $PPhMe_2$.

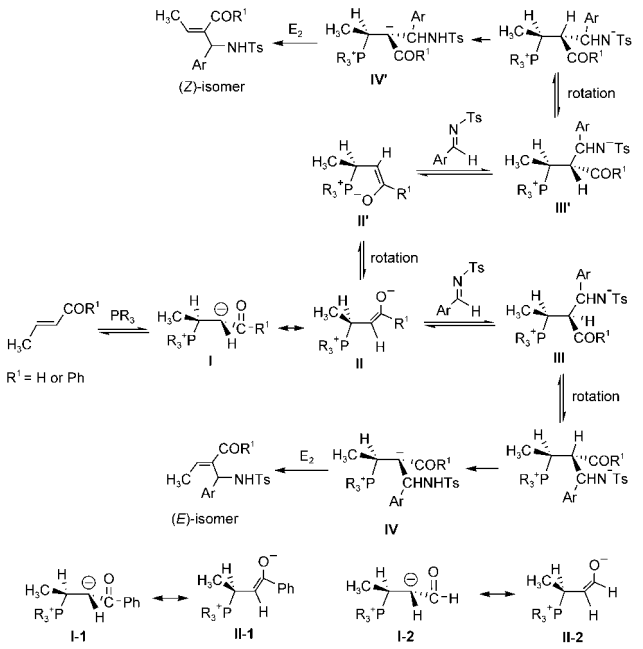


1 2d

Entry	Ar	Time [h]	Yield of **6** (%)[a] (*E*:*Z*)
1	C_6H_5 **1a**	9	**6a**, 35 (87:13)
2	*p*-MeC_6H_4 **1c**	12	**6c**, 32 (90:10)
4	*p*-$NO_2C_6H_4$ **1e**	2	**6d**, 31 (93:7)
5	*m*-$NO_2C_6H_4$ **1f**	2	**6e**, 30 (91:9)
6	*p*-FC_6H_4 **1g**	3	**6f**, 38 (88:12)
7	*m*-FC_6H_4 **1h**	3	**6g**, 32 (89:11)
8	*p*-BrC_6H_4 **1i**	3	**6h**, 53 (92:8)

[a] Yields of isolated products.

DBU again have no catalytic activity for this reaction (Table S2 in the Supporting Information, entries 1–3). Many tertiary phosphine Lewis bases have no catalytic activity for this reaction as well (Table S2 in the Supporting Information, entries 4, 6–8). Only tertiary phosphine $PPhMe_2$ can promote this reaction to give the corresponding aza-Baylis–Hillman adduct **6b** in 10–20% yields as an *E*- and *Z*-isomeric mixture in various solvents at room temperature (Table S2 in the Supporting Information, entries 5, 9–11). Among the solvents examined, THF is the best solvent for this reaction. Some other conditions were examined in order to get higher yields of **6b**. Using molecular sieves 4 Å as the additives to prevent the decomposition of *N*-tosyl imine **1b** due to ambient moisture did not improve the yield of **6b** (Table S2 in the Supporting Information, entry 12). On the other hand, using hydroquinone as the radical scavenger resulted in a complex reaction without the formation of **6b** (Table S2 in the Supporting Information, entry 13). Finally, we found that if carrying out this reaction at lower temperature (0 °C or −20 °C), the corresponding adduct **6b** could be isolated in higher yields (Table S2 in the Supporting Information, entries 14 and 15). Thus, we established the optimized reaction conditions for this aza-Baylis–Hillman reaction using $PPhMe_2$ as the catalyst in THF at 0 °C.



Scheme 2. The plausible reaction mechanism of aza-Baylis–Hillman reaction of *N*-tosyl imines with β-substituted active olefins.

Under the optimized conditions, we next examined the aza-Baylis–Hillman reaction of several *N*-tosyl imines **1** with **2d**. The results are summarized in Table 6. As can be seen from Table 6, the corresponding aza-Baylis–Hillman adducts **6** were obtained in 30–53% as an *E*- and *Z*-isomeric mixture. The similar substituent effect of **1** as described above (Table 2) was observed for this aza-Baylis–Hillman reaction. The *E*/*Z* ratios of **6** were determined by ^1H NMR spectroscopic data and the configuration of *E*-isomer was confirmed by its NOESY spectrum (see Supporting Information).

In order to clarify the novelty of the aza-Baylis–Hillman reactions mentioned above, we used benzaldehyde as the electrophile to react with crotonaldehyde, the most reactive substrate of the above four electron-deficient olefins, under the same conditions in the presence of various Lewis bases such as DABCO, DMAP, DBU, PPh_3, PPh_2Me, $PPhMe_2$, PMe_3 or PBu_3 (25 mol %). However, we found that no reaction occurred. Even using the more electron-poor aldehyde, 4-nitrobenzaldehyde, as the electrophile to react with crotonaldehyde, we found that the corresponding Baylis–Hillman adduct **7** was isolated in 25% yield as an *E*- and *Z*-isomeric mix-

ture after 21 hours only under the catalysis of $PPhMe_2$ (25 mol %). The *E*/*Z* ratio of **7** (7:1) was determined by ^{1}H NMR spectroscopic data and the configuration of the *E*-isomer was confirmed by its NOESY spectrum (see Supporting Information and Scheme S1 in Supporting Information). Thus, *N*-tosyl imines **1** are crucial as electrophiles for the Baylis–Hillman reactions with β-substituted activated olefins under mild conditions.

Concerning the mechanism on the formation of *Z*- and *E*-isomeric mixtures in this aza-Baylis–Hillman reaction, we proposed a mechanistic explanation in Scheme 2 on the basis of the generally accepted mechanism of Baylis–Hillman reaction.[1,3] The phosphonium enolate **I** or **II** generated from the tertiary phosphine with the β-substituted activated olefins **2a–d** can produce another phosphonium enolate **II′** due to the rotation around the C–C bond. The phosphonium enolate **II** reacts with *N*-tosyl imine **1** to give zwitterionic species **III** which furnishes zwitterionic species **IV** *via* the rotation around the C–C bond and the subsequent proton transformation. The *anti*-E_2 elimination of the catalyst affords the *E*-isomer. In the same way, the *Z*-isomer can be produced *via* phosphonium enolate **II′**. Therefore, an *E*- and *Z*-isomeric mixture should be produced in the Baylis–Hillman reaction using β-substituted activated olefins as the Michael acceptors. If R^1 is a phenyl group, the enolate **II-1** (or **I-1**) is more stabilized than enolate **II-2** (or **I-2**) (R^1 = H) owing to the conjugation effect of the phenyl group. The equilibrium can lean to enolate **II′** to some extent. This is why for the Michael acceptor (*E*)-propenyl phenyl ketone, the *Z*-isomers are formed in higher ratios than those of crotonaldehyde.

Conclusion

We found that the aza-Baylis–Hillman reaction of *N*-tosyl imines **1** with β-substituted activated olefins proceeded to give the corresponding adducts in reasonable yields as an *E*- and *Z*-isomeric mixture (major isomer having *E*-configuration) in the presence of tertiary phosphine Lewis bases such as PPh_2Me or $PPhMe_2$ under mild conditions. In some cases, the corresponding adducts can be obtained in good yields with high stereoselectivities. This is because *N*-tosyl imines **1** have higher reactivity toward the nucleophilic attack of the enolate generated from the nucleophilic promoter with β-substituted activated olefins than aldehydes under the same conditions. We believe that these findings further extend the aza-Baylis-Hillman reaction into a viable transformation and allow 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

General Remarks

Unless otherwise stated, all reactions were carried out under an argon atmosphere. All solvents were purified by distillation. Tributylphosphine were obtained from Tokyo Chemical Industry (Tokyo Kasei Co. Ltd.) and used without purification. $PPhMe_2$, PPh_2Me, hex-2-enal and pent-3-en-2-one were obtained from Aldrich Chem. Co. and used without purification. All *N*-tosyl imines[7] and (*E*)-propenyl phenyl ketone[8] were prepared according to the literature. Infrared spectra were measured on a Perkin-Elmer 983 spectrometer. ^{1}H NMR spectra were recorded on a 300 MHz spectrometer in $CDCl_3$ using tetramethylsilane as the internal standard. Mass spectra were recorded with an HP-5989 instrument and HRMS was measured by a Finnigan MA + mass spectrometer or an Ion Spec 4.7 Tesla FTMS mass spectrometer. Satisfactory CHN microanalyses were obtained with a Carlo-Erba 1106 analyzer. Melting points were obtained by means of a micromelting point apparatus and are uncorrected.

Typical Procedure for PPh_2Me-Catalyzed Aza-Baylis–Hillman Reaction of Crotonaldehyde with 4-Methyl-*N*-(4-nitrobenzylidene)benzenesulfonamide

To a solution of 4-methyl-*N*-(4-nitrobenzylidene)benzenesulfonamide (152 mg, 0.5 mmol) and PPh_2Me (18 μL, 0.1 mmol) in THF (1.0 mL) at room temperature was added crotonaldehyde (**2a**; 67 μL, 1.0 mmol) and the reaction mixture was further stirred at room temperature. The reaction was monitored on a TLC plate. When the *N*-tosyl imine disappeared, the solvent was removed under reduced pressure and the residue was purified by a flash chromatography (SiO_2, EtOAc:petroleum ether = 1:5) to afford **3e** as a colorless solid; yield: 122 mg (65%). The pure *E*-isomer of **3e** can be isolated by flash chromatography, but the pure *Z*-isomer of **3e** is very difficult to be isolated. The ratio of the two isomers is obtained based on ^{1}H NMR spectroscopic data. The configuration of *E*-isomer of **3e** is confirmed by its 2D NOESY spectrum (see Supporting Information).

***(E)-N-(2-Formyl-1-phenylbut-2-enyl)-4-methylbenzenesulfonamide* (3a):** an orange viscous liquid: IR ($CHCl_3$): ν = 1676 (C=O), 1450, 1333, 1162, 1090 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.01 (3H, d, *J* = 6.9 Hz), 2.39 (3H, s, Me), 5.53 (1H, d, *J* = 10.2 Hz), 6.38 (1H, d, *J* = 10.2 Hz), 6.55 (1H, q, *J* = 6.9 Hz), 7.19–7.27 (7H, m, Ar), 7.63 (2H, d, *J* = 8.7 Hz, Ar), 9.09 (1H, d, *J* = 2.1 Hz); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 15.43, 21.75, 53.54, 126.35, 126.39, 127.21, 127.80, 128.78, 129.62, 138.06, 138.45, 143.62, 153.01, 194.93; MS (EI): *m/e* = 260 ($M^+ - 69$, 3.29), 174 ($M^+ - 155$, 100); HRMS: calcd. for $C_{14}H_{14}NO_2S^+$ ($M^+ - 69$): 260.0740; found: 260.0747.

***(E)-N-[1-(4-Chlorophenyl)-2-formylbut-2-enyl]-4-methylbenzenesulfonamide* (3b):** a pale yellowish solid; yield: 118 mg (65%); mp 104–105 °C; IR ($CHCl_3$): ν = 1677 (C=O), 1492, 1336, 1162, 1092 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.02 (3H, d, *J* = 7.2 Hz), 2.42 (3H, s, Me), 5.49 (1H, d, *J* = 10.2 Hz), 6.38 (1H, d, *J* = 10.2 Hz), 6.59 (1H, q, *J* = 7.2 Hz), 7.14–7.23 (6H, m, Ar), 7.63 (2H, d, *J* = 8.7 Hz, Ar), 9.10 (1H, d, *J* = 1.2 Hz); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz):

δ = 15.45, 21.75, 52.94, 127.16, 127.83, 128.84, 129.69, 133.61, 137.15, 137.87, 141.25, 143.82, 153.38, 194.83; MS (EI): *m/e* = 294 ($M^+ - 70$, 2.16), 208 ($M^+ - 156$, 100); anal. calcd. for $C_{18}H_{18}ClNO_3S$: C 59.34, H 4.95, N 3.85%; found: C 59.46, H 5.07, N 3.60%.

***(E)-N-[1-(4-Methylphenyl)-2-formylbut-2-enyl]-4-methylbenzenesulfonamide* (3c):** a pale yellowish solid; yield: 68 mg (40%); mp 123–125 °C; IR ($CHCl_3$): ν = 1678 (C=O), 1424, 1337, 1161, 1093 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.01 (3H, d, *J* = 7.2 Hz, Me), 2.28 (3H, s, Me), 2.40 (3H, s, Me), 5.49 (1H, d, *J* = 10.5 Hz), 6.36 (1H, d, *J* = 10.5 Hz), 6.53 (1H, q, *J* = 7.2 Hz), 7.05 (2H, d, *J* = 8.7 Hz, Ar), 7.10 (2H, d, *J* = 8.7 Hz, Ar), 7.21 (2H, d, *J* = 8.4 Hz, Ar), 7.63 (2H, d, *J* = 8.4 Hz, Ar), 9.08 (1H, d, *J* = 2.1 Hz); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 15.04, 20.85, 21.39, 53.05, 125.94, 126.87, 129.08, 129.23, 135.13, 137.21, 137.75, 141.40, 143.19, 152.48, 194.63; MS (EI): *m/e* = 274 ($M^+ - 69$, 98.18), 188 ($M^+ - 155$, 100); anal. calcd. for $C_{19}H_{21}NO_3S$: C 66.45, H 6.16, N 4.08%; found: C 66.10, H 6.27, N 3.82%.

***(E)-N-[1-(3-Methylphenyl)-2-formylbut-2-enyl]-4-methylbenzenesulfonamide* (3d):** a white solid; yield: 72 mg (42%); mp 97–98 °C; IR ($CHCl_3$): ν = 1677 (C=O), 1642, 1337, 1162, 1093 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.02 (3H, d, *J* = 7.2 Hz, Me), 2.27 (3H, s, Me), 2.41 (3H, s, Me), 5.50 (1H, d, *J* = 10.2 Hz), 6.37 (1H, d, *J* = 10.2 Hz), 6.55 (1H, q, *J* = 7.2 Hz), 6.96–7.03 (3H, m, Ar), 7.11–7.14 (1H, m, Ar), 7.21 (2H, d, *J* = 8.4 Hz, Ar), 7.63 (2H, d, *J* = 8.4 Hz, Ar), 9.10 (1H, d, *J* = 1.8 Hz); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 15.06, 21.27, 21.36, 53.21, 123.01, 126.73, 126.84, 128.19, 128.27, 129.20, 137.76, 137.96, 138.10, 141.32, 143.16, 152.53, 194.60; MS (EI): *m/e* = 274 ($M^+ - 69$, 3.59), 188 ($M^+ - 155$, 100); anal. calcd. for $C_{19}H_{21}NO_3S$: C 66.45, H 6.16, N 4.08%; found: C 66.30, H 6.16, N 3.92%.

***(E)-N-[1-(4-Nitrophenyl)-2-formylbut-2-enyl]-4-methylbenzenesulfonamide* (3e):** a pale yellowish solid; yield: 122 mg (65%); mp 150–152 °C; IR ($CHCl_3$): ν = 1678 (C=O), 1523, 1348, 1163, 1090 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.06 (3H, d, *J* = 7.2 Hz, Me), 2.43 (3H, s, Me), 5.61 (1H, d, *J* = 10.2 Hz), 6.38 (1H, d, *J* = 10.2 Hz), 6.69 (1H, q, *J* = 7.2 Hz), 7.26 (2H, d, *J* = 8.4 Hz, Ar), 7.42 (2H, d, *J* = 8.7 Hz, Ar), 7.66 (2H, d, *J* = 8.4 Hz, Ar), 8.12 (2H, d, *J* = 8.7 Hz, Ar), 9.13 (1H, d, *J* = 1.5 Hz); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 15.60, 21.75, 52.82, 123.89, 126.52, 127.14, 127.34, 129.82, 137.67, 140.87, 144.12, 146.03, 147.37, 194.54; MS (EI): *m/e* = 305 ($M^+ - 69$, 1.06), 219 ($M^+ - 155$, 100); anal. calcd. for $C_{18}H_{18}N_2O_5S$: C 57.74, H 4.85, N 7.48%; found: C 57.66, H 4.74, N 7.41%.

***(E)-N-[1-(3-Nitrophenyl)-2-formylbut-2-enyl]-4-methylbenzenesulfonamide* (3f):** a white solid; yield: 150 mg (80%); mp 124–125 °C; IR ($CHCl_3$): ν = 1680 (C=O), 1531, 1350, 1161, 1091 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.08 (3H, d, *J* = 6.9 Hz, Me), 2.42 (3H, s, Me), 5.61 (1H, d, *J* = 10.2 Hz), 6.40 (1H, d, *J* = 10.2 Hz), 6.71 (1H, q, *J* = 6.9 Hz), 7.25 (2H, d, *J* = 8.1 Hz, Ar), 7.46–7.51 (1H, m, Ar), 7.65–7.71 (3H, m, Ar), 7.94 (1H, s, Ar), 8.08–8.11 (1H, m, Ar), 9.14 (1H, d, *J* = 1.5 Hz); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 15.59, 21.73, 52.67, 121.27, 122.78, 127.14, 129.83, 129.84, 132.66, 137.65, 140.71, 140.96, 144.08, 148.42, 154.13, 194.66; MS (EI): *m/e* = 305 ($M^+ - 69$, 4.10), 219 ($M^+ - 155$, 100); anal. calcd. for $C_{18}H_{18}N_2O_5S$: C 57.74, H 4.85, N 7.48%; found: C 57.64, H 4.91, N 7.46%.

***(E)-N-[1-(4-Fluorophenyl)-2-formylbut-2-enyl]-4-methylbenzenesulfonamide* (3g):** a white solid; yield: 121 mg (70%); mp 110–111 °C; IR ($CHCl_3$): ν = 1677 (C=O), 1509, 1426, 1336, 1162, 1097 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.02 (3H, d, *J* = 7.2 Hz), 2.42 (3H, s, Me), 5.49 (1H, d, *J* = 10.2 Hz), 6.38 (1H, d, *J* = 10.2 Hz), 6.59 (1H, q, *J* = 7.2 Hz), 7.14–7.23 (6H, m, Ar), 7.63 (2H, d, *J* = 8.7 Hz, Ar), 9.10 (1H, d, *J* = 1.2 Hz); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 15.38, 21.73, 52.99, 115.58 (1C, d, $J_{C\text{-}F}$ = 21.35 Hz), 127.18, 128.19 (1C, d, $J_{C\text{-}F}$ = 8.2 Hz), 129.65, 134.32 (1C, d, $J_{C\text{-}F}$ = 2.9 Hz), 137.95, 141.45, 143.74, 153.14, 162.30 (1C, d, *J* = 246.8 Hz), 194.90; MS (EI): *m/e* = 278 ($M^+ - 69$, 3.43), 192 ($M^+ - 155$, 100); anal. calcd. for $C_{18}H_{18}FNO_3S$: C 62.23, H 5.22, N 4.03%; found: C 62.23, H 5.20, N 3.86%.

***(E)-N-[1-(3-Fluorophenyl)-2-formylbut-2-enyl]-4-methylbenzenesulfonamide* (3h):** a white solid; yield: 114 mg (66%); mp 81–82 °C; IR ($CHCl_3$): ν = 1677 (C=O), 1593, 1444, 1336, 1162, 1090 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.02 (3H, d, *J* = 7.2 Hz), 2.42 (3H, s, Me), 5.49 (1H, d, *J* = 10.2 Hz), 6.38 (1H, d, *J* = 10.2 Hz), 6.59 (1H, q, *J* = 7.2 Hz), 7.14–7.23 (6H, m, Ar), 7.63 (2H, d, *J* = 8.7 Hz, Ar), 9.10 (1H, d, *J* = 1.2 Hz); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 15.41, 21.73, 53.02, 113.55 (1C, d, *J* = 23.2 Hz), 114.62 (1C, d, *J* = 21.6 Hz), 121.93 (1C, d, *J* = 2.9 Hz), 127.17, 129.68, 130.31 (1C, d, *J* = 8.1 Hz), 137.92, 141.16 (1C, d, *J* = 6.9 Hz), 141.27, 143.80, 153.27, 163.09 (1C, d, *J* = 246.2 Hz), 194.74; MS (EI): *m/e* = 278 ($M^+ - 69$, 2.74), 192 ($M^+ - 155$, 100); anal. calcd. for $C_{18}H_{18}FNO_3S$: C 62.23, H 5.22, N 4.03%; found: C 62.33, H 5.27, N 3.90%.

***(E)-N-[1-(4-Bromophenyl)-2-formylbut-2-enyl]-4-methylbenzenesulfonamide* (3i):** a white solid; yield: 121 mg (60%); mp 93–95 °C; IR ($CHCl_3$): ν = 1678 (C=O), 1488, 1338, 1162, 1075 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.02 (3H, d, *J* = 7.2 Hz), 2.42 (3H, s, Me), 5.49 (1H, d, *J* = 10.2 Hz), 6.38 (1H, d, *J* = 10.2 Hz), 6.59 (1H, q, *J* = 7.2 Hz), 7.14–7.23 (6H, m, Ar), 7.63 (2H, d, *J* = 8.7 Hz, Ar), 9.10 (1H, d, *J* = 1.2 Hz); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 15.24, 21.54, 52.81, 121.56, 126.94, 127.95, 129.47, 131.58, 137.43, 137.68, 141.01, 143.58,153.09, 194.82; MS (EI): *m/e* = 340 ($M^+ - 67$, 2.60), 338 ($M^+ - 69$, 2.56), 252 ($M^+ - 155$, 100), 254 ($M^+ - 153$, 96.62); anal. calcd. for $C_{18}H_{18}BrNO_3S$: C 53.07, H 4.42, N 3.44%; found: C 52.90, H 4.30, N 3.41%.

***(E)-N-[1-(2,3-Dichlorophenyl)-2-formylbut-2-enyl]-4-methylbenzenesulfonamide* (3j):** a white solid; yield: 128 mg (64%): IR ($CHCl_3$): ν = 1680 (C=O), 1644, 1424, 1337, 1162, 1083 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.12 (3H, d, *J* = 7.2 Hz), 2.39 (3H, s, Me), 5.89 (1H, d, *J* = 10.5 Hz), 6.35 (1H, d, *J* = 10.5 Hz), 6.64 (1H, q, *J* = 7.2 Hz), 7.05–7.11 (1H, m, Ar), 7.20 (2H, d, *J* = 8.1 Hz, Ar), 7.24–7.47 (2H, m, Ar), 7.64 (2H, d, *J* = 8.1 Hz, Ar), 9.15 (1H, d, *J* = 1.5 Hz); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 16.03, 21.37, 51.34, 126.92, 127.05, 127.75, 129.27, 129.37, 130.45, 132.87, 137.17, 138.02, 139.79, 143.40, 154.31,194.69; MS (EI): *m/e* = 328 ($M^+ - 69$, 2.64), 242 ($M^+ - 155$, 85.60); anal. calcd. for $C_{18}H_{17}Cl_2NO_3S$: C 54.28, H 4.30, N 3.52%.; found: C 54.10, H 4.25, N 3.25%.

Typical Procedure for PPh_2Me-Catalyzed Aza-Baylis–Hillman Reaction of (*E*)-Propenyl Phenyl Ketone with *N*-(3-Fluorobenzylidene)-4-methylbenzenesulfonamide

To a solution of *N*-(3-fluorobenzylidene)-4-methylbenzsulfonamide (70 mg, 0.25 mmol) and PPh_2Me (9 μL, 0.05 mmol) in THF (0.5 mL) at room temperature was added (*E*)-propenyl phenyl ketone (**2b**; 73 mg, 0.5 mmol) and the reaction mixture was further stirred at room temperature. The reaction was monitored by TLC plate. When the *N*-tosyl imine had disappeared, the solvent was removed under reduced pressure and the residue was purified by a flash chromatography (SiO_2, EtOAc:petroleum ether = 1:5) to afford **4a**; yield: 83 mg (77%). The pure *E*-isomer of **4a** can be isolated by flash chromatography, but the pure *Z*-isomer of **4a** is very difficult to isolate and is obtained along with small amount of the *E*-isomer. The ratio of the two isomers is obtained based on ^{1}H NMR spectroscopic data. The configuration of the *E*-isomer of **4a** is confirmed by its 2D NOESY spectrum (see Supporting Information).

(E)*-N-*[2-Benzoyl-1-(3-fluorophenyl)-but-2-enyl]-4-methylbenzenesulfonamide **(4a):** a colorless solid; mp 164–165 °C; IR ($CHCl_3$): ν = 1627 (C=O), 1595, 1443, 1332, 1161, 1093 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.91 (3H, d, *J* = 7.2 Hz, Me), 2.39 (3H, s, Me), 5.69 (1H, d, *J* = 10.2 Hz), 6.48 (1H, q, *J* = 7.2 Hz, =CH), 6.64 (1H, d, *J* = 10.2 Hz), 6.91 (1H, dd, *J* = 8.4, 8.4 Hz, Ar), 6.99–7.03 (1H, m, Ar), 7.10 (1H, dd, *J* = 8.4, 0.9 Hz, Ar), 7.20–7.52 (8H, m, Ar), 7.71 (2H, d, *J* = 8.4 Hz, Ar)M; ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 14.73, 21.46, 53.86, 113.28 (d, $J_{C\text{-}F}$ = 22.78 Hz), 114.26 (d, $J_{C\text{-}F}$ = 21.1 Hz), 121.65 (d, $J_{C\text{-}F}$ = 2.9 Hz), 126.86, 128.08, 129.14, 129.51, 129.97 (d, $J_{C\text{-}F}$ = 8.5 Hz), 132.16, 137.53, 138.18, 138.48, 141.78 (d, $J_{C\text{-}F}$ = 6.9 Hz), 143.28, 145.25, 162.85 (d, $J_{C\text{-}F}$ = 246.1 Hz), 198.17; MS (EI): *m/e* = 278 ($M^+ - 145$, 11.39), 268 ($M^+ - 155$, 100); anal. calcd. for $C_{24}H_{22}FNO_3S$: C 68.07, H 5.24, N 3.31%; found: C 68.24, H 5.22, N 3.35%.

(Z)-N-*[2-Benzoyl-1-(3-fluorophenyl)-but-2-enyl]-4-methylbenzenesulfonamide **(4a):** ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.30 (3H, d, *J* = 7.2 Hz, Me), 2.36 (3H, s, Me), 5.18 (1H, d, *J* = 8.1 Hz), 5.87 (1H, q, *J* = 7.2 Hz, =CH), 6.18 (1H, d, *J* = 8.1 Hz), 6.81 (1H, dd, *J* = 8.4, 8.4 Hz, Ar), 6.96–7.00 (1H, m, Ar), 7.09–7.14 (1H, m, Ar), 7.17–7.58 (8H, m, Ar), 7.65 (2H, d, *J* = 8.1 Hz, Ar).

(E)*-N-*[2-Benzoyl-1-phenylbut-2-enyl]-4-methylbenzenesulfonamide **(4b):** a colorless solid; mp 152–154 °C; IR ($CHCl_3$): ν = 1636 (C=O), 1448, 1334, 1289, 1160, 1091 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.91 (3H, d, *J* = 7.5 Hz, Me), 2.38 (3H, s, Me), 5.73 (1H, d, *J* = 10.2 Hz), 6.45 (1H, q, *J* = 7.5 Hz, =CH), 6.70 (1H, d, *J* = 10.2 Hz), 7.19–7.36 (11H, m, Ar), 7.45–7.50 (1H, m, Ar), 7.71 (2H, d, *J* = 8.4 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 14.58, 21.35, 54.23, 125.99, 126.82, 127.20, 127.92, 128.37, 129.06, 129.33, 131.90, 137.71, 138.27, 138.80, 138.92, 142.97, 144.62, 198.31; MS (EI): *m/e* = 388 ($M^+ - 18$, 2.41), 338 ($M^+ - 68$, 100); anal. calcd. for $C_{24}H_{23}NO_3S$: C 71.08, H 5.72, N 3.45%; found: C 71.08, H 5.70, N 3.34%.

(Z)*-N-*[2-Benzoyl-1-phenylbut-2-enyl]-4-methylbenzenesulfonamide **(4b):** ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.31 (3H, d, *J* = 7.5 Hz, Me), 2.37 (3H, s, Me), 5.22 (1H, d, *J* = 7.8 Hz), 5.88 (1H, q, *J* = 7.5 Hz, =CH), 6.08 (1H, d, *J* = 7.8 Hz), 7.19–7.36 (11H, m, Ar), 7.45–7.50 (1H, m, Ar), 7.71 (2H, d, *J* = 8.4 Hz, Ar).

(E)*-N-*[2-Benzoyl-1-(4-chlorophenyl)-but-2-enyl]-4-methylbenzenesulfonamide **(4c):** a colorless solid; mp 148–149 °C; IR ($CHCl_3$): ν = 1636 (C=O), 1491, 1336, 1160, 1092 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.91 (3H, d, *J* = 7.2 Hz, Me), 2.40 (3H, s, Me), 5.68 (1H, d, *J* = 9.9 Hz), 6.45 (1H, q, *J* = 7.2 Hz, =CH), 6.65 (1H, d, *J* = 9.9 Hz), 7.13–7.38 (10H, m, Ar), 7.46–7.53 (1H, m, Ar), 7.69 (2H, d, *J* = 8.1 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 14.67, 21.43, 53.85, 126.84, 127.56, 128.07, 128.56, 129.13, 129.47, 132.15, 133.16, 137.53, 137.64, 138.20, 138.60, 143.22, 144.90, 198.19; MS (EI): *m/e* = 294 ($M^+ - 146$, 3.36), 284 ($M^+ - 156$, 100); anal. calcd. for $C_{24}H_{22}ClNO_3S \cdot 1/3\ C_6H_{14}$: C 66.82, H 5.82, N 2.96%; found: C 66.69, H 5.92, N 2.71% (Compound **4c** was recrystallized from acetone and *n*-hexane. The crystals including C_6H_{14} were used for elemental analysis with the ratio of compound **4c** to *n*-hexane of 3:1 which has also been indicated by ^{1}H NMR spectroscopic data).

(Z)*-N-*[2-Benzoyl-1-(4-chlorophenyl)-but-2-enyl]-4-methylbenzenesulfonamide **(4c):** ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.31 (3H, d, *J* = 6.6 Hz, Me), 2.38 (3H, s, Me), 5.18 (1H, d, *J* = 7.8 Hz), 5.88 (1H, q, *J* = 6.6 Hz, =CH), 5.99 (1H, d, *J* = 7.8 Hz), 7.07–7.38 (8H, m, Ar), 7.46–7.53 (1H, m, Ar), 7.58 (2H, d, *J* = 7.5 Hz, Ar), 7.64 (2H, d, *J* = 8.4 Hz, Ar).

(E)*-N-*[2-Benzoyl-1-(3-methylphenyl)-but-2-enyl]-4-methylbenzenesulfonamide **(4d):** a colorless solid; mp 158–160 °C; IR ($CHCl_3$): ν = 1638 (C=O), 1412, 1335, 1288, 1160, 1093 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.91 (3H, d, *J* = 7.5 Hz, Me), 2.27 (3H, s, Me), 2.39 (3H, s, Me), 5.69 (1H, d, *J* = 10.2 Hz), 6.45 (1H, q, *J* = 7.5 Hz, =CH), 6.68 (1H, d, *J* = 10.2 Hz), 6.99–7.38 (8H, m, Ar), 7.21 (2H, d, *J* = 8.4 Hz, Ar), 7.45–7.52 (1H, m, Ar), 7.72 (2H, d, *J* = 8.4 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 14.69, 14.71, 21.44, 54.32, 123.07, 126.89, 126.93, 128.02, 128.07, 128.31, 129.18, 129.40, 131.98, 137.89, 138.13, 138.43, 138.89, 138.99, 143.02, 144.66, 198.44; MS (EI): *m/e* = 274 ($M^+ - 146$, 5.57), 264 ($M^+ - 156$, 100); anal. calcd. for $C_{25}H_{25}NO_3S$: C 71.57, H 6.01, N 3.34%; found: C 71.59, H 6.15, N 3.15%.

(Z)*-N-*[2-Benzoyl-1-(3-methylphenyl)-but-2-enyl]-4-methylbenzenesulfonamide **(4d):** ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.26 (3H, d, *J* = 7.2 Hz, Me), 2.13 (3H, s, Me), 2.31 (3H, s, Me), 5.18 (1H, d, *J* = 8.1 Hz), 5.88 (1H, q, *J* = 7.2 Hz, =CH), 5.99 (1H, d, *J* = 8.1 Hz), 6.91–7.09 (4H, m, Ar), 7.18 (2H, d, *J* = 8.1 Hz, Ar), 7.31–7.37 (2H, m, Ar), 7.46–7.52 (1H, m, Ar), 7.61 (2H, d, *J* = 8.7 Hz, Ar), 7.66 (2H, d, *J* = 8.1 Hz, Ar).

(E)*-N-*[2-Benzoyl-1-(4-nitrophenyl)-but-2-enyl]-4-methylbenzenesulfonamide **(4e):** a colorless solid; mp 173–175 °C; IR ($CHCl_3$): ν = 1636 (C=O), 1597, 1522, 1348, 1162, 1092 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.95 (3H, d, *J* = 7.5 Hz, Me), 2.41 (3H, s, Me), 5.78 (1H, d, *J* = 10.2 Hz), 6.56 (1H, q, *J* = 7.5 Hz, =CH), 6.65 (1H, d, *J* = 10.2 Hz), 7.23 (2H, d, *J* = 7.5 Hz, Ar), 7.25–7.30 (2H, m, Ar), 7.33–7.39 (2H, m, Ar), 7.49 (2H, d, *J* = 7.5 Hz, Ar), 7.47–7.56 (1H, m, Ar), 7.71 (2H, d, *J* = 8.7 Hz, Ar), 8.12 (2H, d, *J* = 8.7 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 14.60, 21.20, 53.76, 123.43, 126.58, 126.75, 127.93, 128.52, 128.85, 129.35, 132.17, 136.91, 137.78, 137.97, 143.30, 145.46, 146.37, 196.64; MS (EI): *m/e* = 305 ($M^+ - 145$, 1.36), 295 ($M^+ - 155$, 100); anal. calcd. for $C_{24}H_{22}N_2O_5S$: C 63.98, H 4.92, N 6.22%; found: C 63.90, H 5.15, N 6.04%.

(Z)*-N-*[2-Benzoyl-1-(4-nitrophenyl)-but-2-enyl]-4-methylbenzenesulfonamide **(4e):** ^{1}H NMR ($CDCl_3$, TMS,

300 MHz): δ = 1.33 (3H, d, *J* = 7.5 Hz, Me), 2.37 (3H, s, Me), 5.28 (1H, d, *J* = 8.1 Hz), 5.90 (1H, q, *J* = 7.5 Hz, =CH), 6.35 (1H, d, *J* = 8.1 Hz), 7.19 (2H, d, *J* = 8.7 Hz, Ar), 7.22–7.28 (2H, m, Ar), 7.32–7.52 (5H, m, Ar), 7.65 (2H, d, *J* = 8.1 Hz, Ar), 8.03 (2H, d, *J* = 8.1 Hz, Ar).

***(E)-N-[2-Benzoyl-1-naphthyl-but-2-enyl]-4-methylbenzenesulfonamide* (4f):** a colorless solid; mp 171–173 °C; IR ($CHCl_3$): ν = 1652 (C=O), 1449, 1333, 1159, 1091 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.32 (3H, d, *J* = 7.5 Hz, Me), 2.34 (3H, s, Me), 5.89 (1H, q, *J* = 7.5 Hz, =CH), 5.98 (1H, d, *J* = 7.8 Hz), 6.03 (1H, d, *J* = 7.8 Hz), 7.09 (2H, d, *J* = 8.1 Hz, Ar), 7.21 (2H, d, *J* = 7.5 Hz, Ar), 7.28 (2H, d, *J* = 7.8 Hz, Ar), 7.39–7.52 (5H, m, Ar), 7.61 (2H, d, *J* = 7.8 Hz, Ar), 7.65 (1H, d, *J* = 8.1 Hz, Ar), 7.79 (1H, d, *J* = 8.4 Hz, Ar), 7.98 (1H, d, *J* = 8.4 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 15.86, 21.43, 58.01, 122.83, 125.13, 125.41, 125.57, 126.38, 127.17, 128.45, 128.47, 128.91, 129.23, 130.16, 131.70, 133.41, 133.59, 133.70, 137.02, 137.30, 138.07, 143.03, 144.80, 198.93; MS (EI): *m/e* = 455 (M^+, 0.31), 300 ($M^+ - 155$, 100); anal. calcd. for $C_{28}H_{25}NO_3S$: C 73.82, H 5.53, N 3.07%; found: C 73.59, H 5.33, N 2.83%.

Typical Procedure for $PPhMe_2$-Catalyzed Aza-Baylis–Hillman Reaction of Pent-3-en-2-one with *N*-(4-Bromobenzylidene)-4-methylbenzenesulfonamide

To a solution of *N*-(4-bromobenzylidene)-4-methylbenzenesulfonamide (136 mg, 0.40 mmol) and $PPhMe_2$ (15 μL, 0.10 mmol) in THF (1.6 mL) at room temperature was added (*E*)-pent-3-en-2-one (**2c**; 75 μL, 0.50 mmol) and the reaction mixture was further stirred at room temperature. The reaction was monitored by TLC plate. When the *N*-tosyl imine had disappeared, the solvent was removed under reduced pressure and the residue was purified by a flash chromatography (SiO_2, EtOAc:petroleum ether = 1:5) to afford **5g**; yield: 58 mg (34%). The pure *E*-isomer of **5g** can be isolated by flash chromatography, but the pure *Z*-isomer of **5g** is very difficult to be isolated and is obtained along with small amount of the *E*-isomer. The ratio of the two isomers is obtained based on ^1H NMR spectroscopic data. The configuration of the *E*-isomer of **5g** is confirmed by its 2D NOESY spectrum (see Supporting Information).

***(E)-N-(2-Acetyl-1-phenyl-but-2-enyl)-4-methylbenzenesulfonamide* (5a):** a yellow solid; mp 129–131 °C; IR ($CHCl_3$): ν = 1658 (C=O), 1494, 1415, 1334, 1161, 1091, 1066 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.91 (3H, d, *J* = 7.2 Hz, Me), 2.01 (3H, s, Me), 2.39 (3H, s, Me), 5.53 (1H, d, *J* = 10.5 Hz), 6.46 (1H, d, *J* = 10.5 Hz), 6.73 (1H, q, *J* = 7.2 Hz), 7.18–7.24 (7H, m, Ar), 7.80 (2H, d, *J* = 8.1 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 14.74, 21.43, 25.93, 53.70, 125.76, 126.91, 127.12, 128.31, 129.27, 138.17, 138.94, 140.01, 142.61, 143.06, 199.69; MS (EI): *m/e* = 260 ($M^+ - 83$, 4.59), 188 ($M^+ - 155$, 100); anal. calcd. for $C_{19}H_{21}NO_3S$: C 66.45, H 6.16, N 4.08%; found: C 66.69, H 6.14, N 3.94%.

***(E)-N-[2-Acetyl-1-(4-chlorophenyl)-but-2-enyl]-4-methylbenzenesulfonamide* (5b):** a colorless solid; mp 156–158 °C; IR ($CHCl_3$): ν = 1659 (C=O), 1492, 1419, 1335, 1162, 1092, 1074 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.91 (3H, d, *J* = 7.2 Hz, Me), 2.02 (3H, s, Me), 2.40 (3H, s, Me), 5.47 (1H, d, *J* = 10.5 Hz), 6.43 (1H, d, *J* = 10.5 Hz), 6.74 (1H, q, *J* = 7.5 Hz), 7.12–7.23 (6H, m, Ar), 7.62 (2H, d, *J* = 8.4 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 14.76, 21.43, 25.89, 53.22, 121.86, 127.23, 128.40, 129.32, 132.94, 137.60, 138.00, 139.72, 142.92, 143.24, 199.63; MS (EI): *m/e* = 294 ($M^+ - 83$, 2.17), 222 ($M^+ - 155$, 100); anal. calcd. for $C_{19}H_{20}ClNO_3S$: C 60.39, H 5.33, N 3.71%; found: C 60.47, H 5.34, N 3.70%.

***(Z)-N-[2-Acetyl-1-(4-chlorophenyl)-but-2-enyl]-4-methylbenzenesulfonamide* (5b):** ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.76 (3H, d, *J* = 7.5 Hz, Me), 2.11 (3H, s, Me), 2.40 (3H, s, Me), 5.09 (1H, d, *J* = 9.0 Hz), 5.88 (1H, d, *J* = 9.0 Hz), 5.95 (1H, q, *J* = 7.5 Hz), 7.12–7.23 (6H, m, Ar), 7.62 (2H, d, *J* = 8.7 Hz, Ar).

***(E)-N-[2-Acetyl-1-(4-methylphenyl)-but-2-enyl]-4-methylbenzenesulfonamide* (5c):** a yellow solid; mp 144–146 °C; IR ($CHCl_3$): ν = 1659 (C=O), 1513, 1420, 1334, 1161, 1093, 1078 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.89 (3H, d, *J* = 7.2 Hz, Me), 2.00 (3H, s, Me), 2.27 (3H, s, Me), 2.38 (3H, s, Me), 5.48 (1H, d, *J* = 10.5 Hz), 6.45 (1H, d, *J* = 10.5 Hz), 6.71 (1H, q, *J* = 7.2 Hz), 6.99–7.10 (4H, m, Ar), 7.20 (2H, d, *J* = 8.1 Hz, Ar), 7.63 (2H, d, *J* = 8.1 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 14.66, 20.84, 21.38, 25.90, 53.52, 125.66, 126.87, 128.96, 129.20, 135.93, 136.73, 138.14, 139.95, 142.50, 142.99, 199.72; MS (EI): *m/e* = 274 ($M^+ - 83$, 2.79), 202 ($M^+ - 155$, 100); anal. calcd. for $C_{23}H_{23}NO_3S$: C 67.20, H 6.49, N 3.92%; found: C 67.30, H 6.46, N 3.87%.

***(E)-N-[2-Acetyl-1-(4-nitrophenyl)-but-2-enyl]-4-methylbenzenesulfonamide* (5d):** a yellow solid; mp 147–149 °C; IR ($CHCl_3$): ν = 1659 (C=O), 1599, 1522, 1348, 1162, 1093 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.98 (3H, d, *J* = 7.2 Hz, Me), 2.06 (3H, s, Me), 2.42 (3H, s, Me), 5.58 (1H, d, *J* = 10.2 Hz), 6.35 (1H, d, *J* = 10.2 Hz), 6.84 (1H, q, *J* = 7.2 Hz), 7.25 (2H, d, *J* = 8.4 Hz Ar), 7.37 (2H, d, *J* = 8.7 Hz, Ar), 7.65 (2H, d, *J* = 8.4 Hz, Ar), 8.10 (2H, d, *J* = 8.7 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 15.02, 21.53, 25.87, 53.34, 123.62, 126.69, 126.92, 129.52, 137.95, 139.69, 143.54, 143.60, 146.65, 147.04, 199.43; MS (EI): *m/e* = 233 ($M^+ - 155$, 6.76), 91 ($M^+ - 297$, 100); anal. calcd. for $C_{19}H_{20}N_2O_5S$: C 58.75, H 5.19, N 7.21%; found: C 58.43, H 5.13, N 7.00%.

***(E)-N-[2-Acetyl-1-(4-fluorophenyl)-but-2-enyl]-4-methylbenzenesulfonamide* (5e):** a colorless solid; mp 127–128 °C; IR ($CHCl_3$): ν = 1660 (C=O), 1509, 1421, 1335, 1161, 1094, 1077 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.90 (3H, d, *J* = 7.2 Hz, Me), 2.02 (3H, s, Me), 2.40 (3H, s, Me), 5.48 (1H, d, *J* = 10.2 Hz), 6.45 (1H, d, *J* = 10.2 Hz), 6.73 (1H, q, *J* = 7.2 Hz), 6.91 (2H, t, *J* = 8.7 Hz, Ar), 7.15–7.23 (4H, m, Ar), 7.63 (2H, d, *J* = 8.4 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 14.72, 21.42, 25.92, 53.22, 115.10 (1C, d, $J_{C\text{-}F}$ = 21.2 Hz), 126.88, 127.53 (1C, d, $J_{C\text{-}F}$ = 8.2 Hz), 129.30, 134.74 (1C, d, $J_{C\text{-}F}$ = 3.2 Hz), 138.03, 139.82, 142.80, 143.19, 161.81 (1C, d, $J_{C\text{-}F}$ = 245.6 Hz), 199.72; MS (EI): *m/e* = 278 ($M^+ - 83$, 3.44), 206 ($M^+ - 155$, 100); anal. calcd. for $C_{19}H_{20}FNO_3S$: C 63.14, H 5.58, N 3.88%; found: C 62.99, H 5.57, N 3.85%.

***(Z)-N-[2-Acetyl-1-(4-fluorophenyl)-but-2-enyl]-4-methylbenzenesulfonamide* (5e):** ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.75 (3H, d, *J* = 7.5 Hz, Me), 2.01 (3H, s, Me), 2.41 (3H, s, Me), 5.10 (1H, d, *J* = 8.7 Hz), 5.80 (1H, d, *J* = 8.7 Hz), 5.94 (1H, q, *J* = 7.5 Hz), 6.90 (2H, t, *J* = 8.7 Hz, Ar), 7.09–7.13 (2H, m, Ar), 7.23 (2H, d, *J* = 7.8 Hz, Ar), 7.72 (2H, d, *J* = 7.8 Hz, Ar).

***(E)-N-[2-Acetyl-1-(3-fluorophenyl)-but-2-enyl]-4-methylbenzenesulfonamide* (5f):** a colorless solid; mp 97–98 °C; IR ($CHCl_3$): ν = 1662 (C=O), 1593, 1488, 1336, 1162, 1091,

1066 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.93 (3H, d, J = 7.2 Hz, Me), 2.04 (3H, s, Me), 2.41 (3H, s, Me), 5.50 (1H, d, J = 10.5 Hz), 6.40 (1H, d, J = 10.5 Hz), 6.76 (1H, q, J = 7.2 Hz), 6.85–6.91 (2H, m, Ar), 6.99 (1H, d, J = 7.5 Hz, Ar), 7.16–7.24 (3H, m, Ar), 7.64 (2H, d, J = 8.1 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 14.79, 21.46, 25.90, 53.29 (1C, d, $J_{C\text{-}F}$ = 2.1 Hz), 112.97 (1C, d, $J_{C\text{-}F}$ = 23.1 Hz), 114.08 (1C, d, $J_{C\text{-}F}$ = 21.5 Hz), 121.33 (1C, d, $J_{C\text{-}F}$ = 2.9 Hz), 126.90, 129.36, 129.85 (1C, d, $J_{C\text{-}F}$ = 15.5 Hz), 138.06, 139.78, 141.75 (1C, d, $J_{C\text{-}F}$ = 6.8 Hz), 142.99, 143.27, 162.81 (1C, d, $J_{C\text{-}F}$ = 245.8 Hz), 199.57; MS (EI): m/e = 278 (M^+ − 83, 2.97), 206 (M^+ − 155, 100); anal. calcd. for $C_{19}H_{20}FNO_3S$: C 63.14, H 5.58, N 3.88%; found: C 63.04, H 5.56, N 3.80%.

***(Z)*-N-*[2-Acetyl-1-(3-fluorophenyl)-but-2-enyl]*-4-methylbenzenesulfonamide (5f):** ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.77 (3H, d, J = 7.5 Hz, Me), 2.11 (3H, s, Me), 2.41 (3H, s, Me), 5.09 (1H, d, J = 9.3 Hz), 5.84 (1H, d, J = 9.3 Hz), 5.98 (1H, q, J = 7.5 Hz), 6.82–6.88 (3H, m, Ar), 7.16–7.25 (3H, m, Ar), 7.64 (2H, d, J = 8.4 Hz, Ar).

***(E)*-N-*[2-Acetyl-1-(4-bromophenyl)-but-2-enyl]*-4-methylbenzenesulfonamide (5g):** a colorless solid; mp 144–146 °C; IR ($CHCl_3$): ν = 1659 (C=O), 1487, 1417, 1336, 1161, 1092, 1076 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.91 (3H, d, J = 7.2 Hz, Me), 2.01 (3H, s, Me), 2.40 (3H, s, Me), 5.45 (1H, d, J = 10.2 Hz), 6.43 (1H, d, J = 10.2 Hz), 6.74 (1H, q, J = 7.2 Hz), 7.08 (2H, d, J = 8.4 Hz, Ar), 7.21 (2H, d, J = 8.4 Hz, Ar), 7.34 (2H, d, J = 8.4 Hz, Ar), 7.62 (2H, d, J = 8.4 Hz, Ar); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 14.77, 21.43, 25.87, 53.25, 121.06, 126.84, 127.58, 129.32, 131.33, 137.96, 138.15, 139.64, 142.98, 143.25, 199.61; MS (EI): m/e = 338 (M^+ − 83, 1.64), 91 (M^+ − 330, 100); anal. calcd. for $C_{19}H_{20}BrNO_3S$: C 54.03, H 4.77, N 3.32%; found: C 53.99, H 4.79, N 3.37%.

***(Z)*-N-*[2-Acetyl-1-(4-bromophenyl)-but-2-enyl]*-4-methylbenzenesulfonamide (5g):** ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.76 (3H, d, J = 7.5 Hz, Me), 2.11 (3H, s, Me), 2.41 (3H, s, Me), 5.06 (1H, d, J = 9.3 Hz), 5.83 (1H, d, J = 9.3 Hz), 5.96 (1H, q, J = 7.5 Hz), 7.02 (2H, d, J = 8.1 Hz, Ar), 7.22 (2H, d, J = 8.1 Hz, Ar), 7.32–7.35 (2H, m, Ar), 7.62 (2H, d, J = 8.1 Hz, Ar).

Typical Procedure for $PPhMe_2$-Catalyzed Aza-Baylis-Hillman Reaction of Hex-2-enal with *N*-(4-Chlorobenzylidene)-4-methylbenzenesulfonamide

To a solution of *N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide (75 mg, 0.25 mmol) and $PPhMe_2$ (9 μL, 0.06 mmol) in THF (0.5 mL) at 0 °C was added (*E*)-hex-2-enal (**2d**; 58 μL, 0.5 mmol) and the reaction mixture was further stirred at 0 °C. The reaction was monitored on TLC plates. When the *N*-tosyl imine had disappeared, the solvent was removed under reduced pressure and the residue was purified by a flash chromatography (SiO_2, EtOAc:petroleum ether = 1:6) to afford **6b**; yield: 49 mg (50%). The pure *E*-isomer of **6b** can be isolated by flash chromatography, but the pure *Z*-isomer of **6b** is very difficult to isolate and is obtained along with small amount of the *E*-isomer. The ratio of the two isomers is obtained based on ^1H NMR spectroscopic data. The configuration of the *E*-isomer of **6b** is confirmed by its 2D NOESY spectrum (see Supporting Information.)

***(E)*-N-*[2-Formyl-1-phenylhex-2-enyl]*-4-methylbenzenesulfonamide (6a):** a colorless viscous liquid; IR ($CHCl_3$): ν = 1678 (C=O), 1495, 1337, 1161, 1092 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 0.95 (3H, t, J = 7.5 Hz, Me), 1.47 (2H, tq, J = 7.5, 7.5 Hz, CH_2), 2.32 (2H, q, J = 7.5 Hz, CH_2), 2.38 (3H, s, Me), 5.50 (1H, d, J = 10.2 Hz), 6.39 (1H, d, J = 10.2 Hz), 6.45 (1H, t, J = 7.5 Hz), 7.18–7.24 (7H, m, Ar), 7.62 (2H, d, J = 8.4 Hz, Ar), 9.10 (1H, d, J = 1.8 Hz); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 13.85, 21.42, 21.51, 31.08, 53.69, 126.14, 126.93, 127.49, 128.45, 129.29, 137.83, 138.31, 140.24, 143.20, 157.87, 194.81; MS (EI): m/e = 358 (M^+ + 1, 6.96), 202 (M^+ − 155, 100); HRMS: calcd. for $C_{20}H_{23}NO_3SNa^+$: 380.1291; found: 380.1324.

***(Z)*-N-*[2-Formyl-1-phenylhex-2-enyl]*-4-methylbenzenesulfonamide (6a):** ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 0.92 (3H, t, J = 7.5 Hz, Me), 1.47 (2H, tq, J = 7.5, 7.5 Hz, CH_2), 2.32 (2H, q, J = 7.5 Hz, CH_2), 2.40 (3H, s, Me), 5.13 (1H, d, J = 9.0 Hz), 5.72 (1H, d, J = 9.0 Hz), 6.66 (1H, t, J = 7.5 Hz), 7.14–7.24 (7H, m, Ar), 7.64 (2H, d, J = 8.4 Hz, Ar), 9.84 (1H, s).

***(E)*-N-*[1-(4-Chlorophenyl)-2-formylhex-2-enyl]*-4-methylbenzenesulfonamide (6b):** a white solid; mp 101–103 °C; IR ($CHCl_3$): ν = 1677 (C=O), 1491, 1338, 1162, 1093 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 0.95 (3H, t, J = 7.5 Hz, Me), 1.47 (2H, tq, J = 7.5, 7.5 Hz, CH_2), 2.31 (2H, q, J = 7.5 Hz, CH_2), 2.39 (3H, s, Me), 5.46 (1H, d, J = 10.5 Hz), 6.39 (1H, d, J = 10.5 Hz), 6.47 (1H, t, J = 7.5 Hz), 7.12–7.21 (6H, m, Ar), 7.60 (2H, d, J = 8.4 Hz, Ar), 9.10 (1H, d, J = 2.1 Hz); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 13.86, 21.44, 21.53, 31.10, 53.20, 126.92, 127.64, 128.58, 129.37, 133.43, 136.95, 137.73, 139.95, 143.40, 158.08, 194.71; MS (EI): m/e = 294 (M^+ + 1, 3.11), 208 (M^+ − 155, 100); anal. calcd. for $C_{20}H_{22}ClNO_3S$: C 61.29, H 5.66, N 3.57%; found: C 61.37, H 5.80, N 3.42%.

***(Z)*-N-*[1-(4-Chlorophenyl)-2-formylhex-2-enyl]*-4-methylbenzenesulfonamide (6b):** ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 0.91 (3H, t, J = 7.5 Hz, Me), 1.47 (2H, tq, J = 7.5, 7.5 Hz, CH_2), 2.31 (2H, q, J = 7.5 Hz, CH_2), 2.40 (3H, s, Me), 5.09 (1H, d, J = 9.0 Hz), 5.79 (1H, d, J = 9.0 Hz), 6.63 (1H, t, J = 7.5 Hz), 7.12–7.21 (6H, m, Ar), 7.60 (2H, d, J = 8.4 Hz, Ar), 9.82 (1H, s).

***(E)*-N-*[1-(4-Methylphenyl)-2-formylhex-2-enyl]*-4-methylbenzenesulfonamide (6c):** a pale yellowish solid; mp 86–89 °C; IR ($CHCl_3$): ν = 1678 (C=O), 1422, 1338, 1161, 1094 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 0.95 (3H, t, J = 7.5 Hz, Me), 1.47 (2H, tq, J = 7.5, 7.5 Hz, CH_2), 2.28 (3H, s, CH_3), 2.31 (2H, q, J = 7.5 Hz, CH_2), 2.38 (3H, s, Me), 5.46 (1H, d, J = 10.5 Hz), 6.38 (1H, d, J = 10.5 Hz), 6.43 (1H, t, J = 7.5 Hz), 7.02–7.10 (4H, m, Ar), 7.19 (2H, d, J = 8.1 Hz, Ar), 7.61 (2H, d, J = 8.1 Hz, Ar), 9.10 (1H, d, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 13.86, 20.92, 21.43, 21.55, 31.06, 53.59, 126.12, 126.99, 129.15, 129.28, 135.38, 137.28, 137.94, 140.42, 143.15, 157.70, 194.85; MS (EI): m/e = 372 (M^+ + 1, 1.67), 216 (M^+ − 155, 100); HRMS: calcd. for $C_{21}H_{25}NO_3SNa^+$: 394.1447; found: 394.1456.

***(Z)*-N-*[1-(4-Methylphenyl)-2-formyl-hex-2-enyl]*-4-methylbenzenesulfonamide (6c):** ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 0.92 (3H, t, J = 7.5 Hz, Me), 1.47 (2H, tq, J = 7.5, 7.5 Hz, CH_2), 2.28 (3H, s, CH_3), 2.31 (2H, q, J = 7.5 Hz, CH_2), 2.40 (3H, s, Me), 5.09 (1H, d, J = 8.4 Hz), 5.65 (1H, d, J = 8.4 Hz), 6.66 (1H, t, J = 7.5 Hz), 7.02–7.10 (4H, m, Ar), 7.19 (2H, d, J = 8.4 Hz, Ar), 7.64 (2H, d, J = 8.4 Hz, Ar), 9.84 (1H, s).

***(E)*-N-*[1-(4-Nitrophenyl)-2-formylhex-2-enyl]*-4-methylbenzenesulfonamide (6d):** a yellow solid; mp 125–127 °C; IR

($CHCl_3$): ν = 1678 (C=O), 1521, 1347, 1162, 1093 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 0.96 (3H, t, *J* = 7.5 Hz, Me), 1.49 (2H, tq, *J* = 7.5, 7.5 Hz, CH_2), 2.34 (2H, q, *J* = 7.5 Hz, CH_2), 2.39 (3H, s, Me), 5.56 (1H, d, *J* = 10.2 Hz), 6.45 (1H, d, *J* = 10.2 Hz), 6.58 (1H, t, *J* = 7.5 Hz), 7.22 (2H, d, *J* = 8.1 Hz, Ar), 7.40 (2H, d, *J* = 8.7 Hz, Ar), 7.63 (2H, d, *J* = 8.1 Hz, Ar), 8.08 (2H, d, *J* = 8.7 Hz, Ar), 9.13 (1H, d, *J* = 1.5 Hz); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 13.82, 21.40, 21.50, 31.20, 53.01, 123.59, 126.85, 127.11, 129.48, 137.51, 139.49, 143.71, 145.81, 147.13, 158.58, 194.39; MS (EI): *m/e* = 305 ($M^+ - 97$, 2.06), 247 ($M^+ - 155$, 100); anal. calcd. for $C_{20}H_{22}N_2O_5S$: C 59.69, H 5.51, N 6.96%; found: C 59.84, H 5.51, N 6.76%.

***(Z)-N-[1-(4-Nitrophenyl)-2-formylhex-2-enyl]-4-methylbenzenesulfonamide* (6d):** ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 0.93 (3H, t, *J* = 7.5 Hz, Me), 1.49 (2H, tq, *J* = 7.5, 7.5 Hz, CH_2), 2.34 (2H, q, *J* = 7.5 Hz, CH_2), 2.44 (3H, s, Me), 5.17 (1H, d, *J* = 9.6 Hz), 5.89 (1H, d, *J* = 9.6 Hz), 6.66 (1H, t, *J* = 7.5 Hz), 7.20–7.24 (2H, m, Ar), 7.30–7.41 (2H, m, Ar), 7.64 (2H, d, *J* = 8.1 Hz, Ar), 8.09 (2H, d, *J* = 8.7 Hz, Ar), 9.81 (1H, s).

***(E)-N-[1-(3-Nitrophenyl)-2-formylhex-2-enyl]-4-methylbenzenesulfonamide* (6e):** a yellow solid; mp 91–93 °C; IR ($CHCl_3$): ν = 1677 (C=O), 1531, 1350, 1162, 1092 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 0.98 (3H, t, *J* = 7.5 Hz, Me), 1.51 (2H, tq, *J* = 7.5, 7.5 Hz, CH_2), 2.36 (2H, q, *J* = 7.5 Hz, CH_2), 2.39 (3H, s, Me), 5.57 (1H, d, *J* = 9.9 Hz), 6.48 (1H, d, *J* = 9.9 Hz), 6.60 (1H, t, *J* = 7.5 Hz), 7.22 (2H, d, *J* = 7.8 Hz, Ar), 7.44 (1H, t, *J* = 7.8 Hz, Ar), 7.63–7.67 (3H, m, Ar), 7.96 (1H, s, Ar), 8.05 (1H, d, *J* = 7.8 Hz, Ar), 9.15 (1H, d, *J* = 1.5 Hz); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 13.82, 21.38, 21.50, 31.20, 52.88, 121.05, 122.49, 126.86, 129.48, 129.51, 132.39, 137.49, 139.40, 140.74, 143.66, 148.14, 158.70, 194.47; MS (EI): *m/e* = 305 ($M^+ - 97$, 2.55), 247 ($M^+ - 155$, 100); anal. calcd. for $C_{20}H_{22}N_2O_5S$: C 59.69, H 5.51, N 6.96%; found: C 59.56, H 5.27, N 6.82%.

***(Z)-N-[1-(3-Nitrophenyl)-2-formylhex-2-enyl]-4-methylbenzenesulfonamide* (6e):** ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 0.94 (3H, t, *J* = 7.5 Hz, Me), 1.51 (2H, tq, *J* = 7.5, 7.5 Hz, CH_2), 2.36 (2H, q, *J* = 7.5 Hz, CH_2), 2.40 (3H, s, Me), 5.17 (1H, d, *J* = 9.6 Hz), 5.70 (1H, d, *J* = 9.6 Hz), 6.69 (1H, t, *J* = 7.5 Hz), 7.23 (2H, d, *J* = 8.7 Hz, Ar), 7.46 (1H, t, *J* = 7.8 Hz, Ar), 7.67–7.70 (3H, m, Ar), 7.92 (1H, s, Ar), 8.07 (1H, d, *J* = 7.8 Hz, Ar), 9.83 (1H, s).

***(E)-N-[1-(4-Fluorophenyl)-2-formylhex-2-enyl]-4-methylbenzenesulfonamide* (6f):** a yellow viscous liquid; IR ($CHCl_3$): ν = 1678 (C=O), 1509, 1339, 1161, 1094 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 0.95 (3H, t, *J* = 7.5 Hz, Me), 1.47 (2H, tq, *J* = 7.5, 7.5 Hz, CH_2), 2.31 (2H, q, *J* = 7.5 Hz, CH_2), 2.39 (3H, s, Me), 5.47 (1H, d, *J* = 10.2 Hz), 6.39 (1H, d, *J* = 10.2 Hz), 6.46 (1H, t, *J* = 7.5 Hz), 6.91 (2H, t, *J* = 8.7 Hz, Ar), 7.15–7.22 (4H, m, Ar), 7.61 (2H, d, *J* = 8.4 Hz, Ar), 9.11 (1H, d, *J* = 1.5 Hz); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 13.87, 21.45, 21.53, 31.08, 53.20, 115.32 (1C, d, $J_{C\text{-}F}$ = 21.6 Hz), 126.94, 127.98 (1C, d, $J_{C\text{-}F}$ = 8.5 Hz), 129.36, 134.17 (1C, d, $J_{C\text{-}F}$ = 3.2 Hz), 137.78, 140.11, 143.35, 158.01, 162.06 (1C, d, $J_{C\text{-}F}$ = 246.6 Hz), 194.81; MS (EI): *m/e* = 376 ($M^+ + 1$, 5.07), 220 ($M^+ - 155$, 100); HRMS: calcd. for $C_{20}H_{22}NO_3SNaF^+$: 398.1197; found: 398.1229.

***(Z)-N-[1-(4-Fluorophenyl)-2-formylhex-2-enyl]-4-methylbenzenesulfonamide* (6f):** ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 0.92 (3H, t, *J* = 7.5 Hz, Me), 1.47 (2H, tq, *J* = 7.5, 7.5 Hz, CH_2), 2.31 (2H, q, *J* = 7.5 Hz, CH_2), 2.40 (3H, s, Me), 5.10 (1H, d, *J* = 9.0 Hz), 5.74 (1H, d, *J* = 9.0 Hz), 6.64 (1H, t, *J* = 7.5 Hz), 6.91 (2H, t, *J* = 8.7 Hz, Ar), 7.09–7.25 (4H, m, Ar), 7.59–7.64 (2H, m, Ar), 9.83 (1H, s).

***(E)-N-[1-(3-Fluorophenyl)-2-formylhex-2-enyl]-4-methylbenzenesulfonamide* (6g):** a colorless viscous liquid; IR ($CHCl_3$): ν = 1679 (C=O), 1593, 1488, 1339, 1162, 1092 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 0.97 (3H, t, *J* = 7.5 Hz, Me), 1.49 (2H, tq, *J* = 7.5, 7.5 Hz, CH_2), 2.33 (2H, q, *J* = 7.5 Hz, CH_2), 2.39 (3H, s, Me), 5.48 (1H, d, *J* = 10.5 Hz), 6.38 (1H, d, *J* = 10.5 Hz), 6.49 (1H, t, *J* = 7.5 Hz), 6.87–6.89 (2H, m, Ar), 6.92–6.93 (1H, m, Ar), 7.17–7.24 (3H, m, Ar), 7.62 (2H, d, *J* = 8.4 Hz), 9.12 (1H, d, *J* = 1.5 Hz); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 13.87, 21.45, 21.56, 31.13, 53.25(1C, d, $J_{C\text{-}F}$ = 2.0 Hz), 113.41 (1C, d, $J_{C\text{-}F}$ = 23.2 Hz), 114.49 (1C, d, $J_{C\text{-}F}$ = 21.1 Hz), 121.78 (1C, d, $J_{C\text{-}F}$ = 2.6 Hz), 126.95, 129.40, 130.12 (1C, d, $J_{C\text{-}F}$ = 8.4 Hz), 137.80, 139.99, 141.03 (1C, d, $J_{C\text{-}F}$ = 6.9 Hz), 143.41, 158.06, 162.81 (1C, d, $J_{C\text{-}F}$ = 246.4 Hz), 194.63; MS (EI): *m/e* = 376 ($M^+ + 1$, 6.09), 220 ($M^+ - 155$, 100); HRMS: calcd. for $C_{20}H_{22}NO_3SNaF^+$: 398.1197; found: 398.1214.

***(Z)-N-[1-(3-Fluorophenyl)-2-formylhex-2-enyl]-4-methylbenzenesulfonamide* (6g):** ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 0.90 (3H, t, *J* = 7.5 Hz, Me), 1.43 (2H, tq, *J* = 7.5, 7.5 Hz, CH_2), 2.33 (2H, q, *J* = 7.5 Hz, CH_2), 2.40 (3H, s, Me), 5.10 (1H, d, *J* = 9.3 Hz), 5.81 (1H, d, *J* = 9.3 Hz), 6.63 (1H, t, *J* = 7.5 Hz), 6.84–6.86 (2H, m, Ar), 6.96–7.00 (1H, m, Ar), 7.15–7.25 (3H, m, Ar), 7.63–7.67 (2H, m, Ar), 9.83 (1H, s).

***(E)-N-[1-(4-Bromophenyl)-2-formylhex-2-enyl]-4-methylbenzenesulfonamide* (6h):** a white solid; mp 114–116 °C; IR ($CHCl_3$): ν = 1678 (C=O), 1488, 1422, 1338, 1162, 1075 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 0.95 (3H, t, *J* = 7.5 Hz, Me), 1.47 (2H, tq, *J* = 7.5, 7.5 Hz, CH_2), 2.31 (2H, q, *J* = 7.5 Hz, CH_2), 2.39 (3H, s, Me), 5.44 (1H, d, *J* = 9.9 Hz), 6.40 (1H, d, *J* = 9.9 Hz), 6.47 (1H, t, *J* = 7.5 Hz), 7.07 (2H, d, *J* = 8.1 Hz, Ar), 7.19 (2H, d, *J* = 8.1 Hz, Ar), 7.33–7.36 (2H, m, Ar), 7.60 (2H, d, *J* = 8.1 Hz, Ar), 9.10 (1H, d, *J* = 1.5 Hz); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 13.87, 21.46, 21.53, 31.13, 53.28, 121.58, 126.94, 128.02, 129.39, 131.56, 137.53, 139.94, 143.43, 158.11, 194.70; MS (EI): *m/e* = 338 ($M^+ - 97$, 2.85), 280 ($M^+ - 155$, 100); anal. calcd. for $C_{20}H_{22}BrNO_3S$: C 55.05, H 5.08, N 3.21%; found: C 54.99, H 5.09, N 3.06%.

***(Z)-N-[1-(4-Bromophenyl)-2-formylhex-2-enyl]-4-methylbenzenesulfonamide* (6h):** ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 0.90 (3H, t, *J* = 7.5 Hz, Me), 1.47 (2H, tq, *J* = 7.5, 7.5 Hz, CH_2), 2.31 (2H, q, *J* = 7.5 Hz, CH_2), 2.40 (3H, s, Me), 5.06 (1H, d, *J* = 9.3 Hz), 5.78 (1H, d, *J* = 9.3 Hz), 6.63 (1H, t, *J* = 7.5 Hz), 7.00–7.37 (6H, m, Ar), 7.62 (2H, d, *J* = 8.1 Hz, Ar), 9.82 (1H, s).

Procedure for $PPhMe_2$-Catalyzed Aza-Baylis–Hillman Reaction of Crotonaldehyde with 4-Nitrobenzaldehyde

To a solution of 4-nitrobenzaldehyde (152 mg, 1.0 mmol) and $PPhMe_2$ (36 μL, 0.25 mmol) in THF (4.0 mL) at room temperature was added crotonaldehyde (**2a**; 134 μL, 2.0 mmol) and the reaction mixture was further stirred at room temperature. The reaction was monitored on TLC plates. When 4-nitrobenzaldehyde had disappeared after 21 hours, the solvent was removed under reduced pressure and the residue was purified

by a flash chromatography (SiO_2, EtOAc:petroleum ether = 1:10) to afford **7** as a colorless solid; yield: 55 mg (25%). The pure *E*-isomer of **7** can be isolated by flash chromatography, but the pure *Z*-isomer of **7** is very difficult to isolate and is obtained along with a small amount of the *E*-isomer. The ratio of the two isomers is obtained based on ^{1}H NMR spectroscopic data. The configuration of the *E*-isomer of **7** is confirmed by its 2D NOESY spectrum (see Supporting Information).

***(E)-2-[Hydroxy-(4-nitrophenyl)methyl]-but-2-enal* (7):** a yellow viscous liquid; IR ($CHCl_3$): ν = 3454, 1678, 1643, 1605, 1518, 1345 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.14 (3H, d, J = 7.2 Hz, Me), 3.96 (1H, d, J = 10.2 Hz), 5.80 (1H, d, J = 10.2 Hz), 6.88 (1H, q, J = 7.2 Hz), 7.51–7.54 (2H, m, Ar), 8.18–8.21 (2H, m, Ar), 9.41 (1H, d, J = 1.2 Hz); ^{13}C NMR ($CDCl_3$, TMS, 75.44 MHz): δ = 15.35, 68.14, 123.42, 126.07, 143.12, 149.55, 153.63, 195.29; MS (EI): *m/e* = 220 ($M^+ - 1$, 6.04), 204 ($M^+ - 17$, 100); HRMS: calcd. for $C_{11}H_{10}NO_3^+$ ($M^+ - 17$): 204.0655; found: 204.0640.

***(Z)-2-[Hydroxy-(4-nitrophenyl)methyl]-but-2-enal* (7):** ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.21 (3H, d, J = 7.2, Me), 3.15 (1H, d, J = 5.4 Hz), 5.64 (1H, d, J = 5.4 Hz), 6.80 (1H, q, J = 7.2 Hz), 7.51–7.56 (2H, m, Ar), 8.17–8.20 (2H, m, Ar), 10.16 (1H, s).

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