Lewis Base Effects in the Baylis−Hillman Reaction of Arenecarbaldehydes and *N*-Arylidene-4-methylbenzenesulfonamides with α,β-Unsaturated Cyclic Ketones

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Keywords: Aldehydes / Amides / Baylis−Hillman reaction / Ketones / Lewis bases

In investigations into the Baylis–Hillman reaction between arenecarbaldehydes and 2-cyclohexen-1-one or 2-cyclopenten-1-one, we found that the reaction is very complicated, because the Lewis bases, solvents, the substrates, and the ring-size of the α,β-unsaturated cyclic ketone can all significantly affect the Baylis–Hillman reaction rate and even the reaction product. In particular, the abnormal adducts **3** were formed along with the normal Baylis–Hillman adducts **2** on treatment of arenecarbaldehydes and 2-cyclopenten-1-one under Baylis–Hillman reaction conditions in the presence of PBu_3 as a Lewis base. On the other hand, in Baylis–Hillman reactions between *N*-benzylidene-4-methylbenzenesulfonamides and 2-cyclohexen-1-one or 2-cyclopenten-1-one, we found that the reaction could be greatly accelerated in the presence of catalytic amounts of DMAP to give the normal Baylis–Hillman adducts **4** or **6** in good or excellent yields. Moreover, application of Baylis–Hillman reaction conditions to *N*-arylidene-4-methylbenzenesulfonamide and 2-cyclopenten-1-one in the presence of PBu_3 as a Lewis base provided the normal Baylis–Hillman adducts **6** in very high yields within 5 h. In the presence of PBu_3 or DBU as a Lewis base for reactions between *N*-arylidene-4-methylbenzenesulfonamides and 2-cyclohexen-1-one, however, the abnormal Baylis–Hillman adducts 3-aryl-2-(4-tolylsulfonyl)-2-azabicyclo[2.2.2]octan-5-ones **5** were formed at the same time. In addition, in reactions between *N*-arylidene-4-methylbenzenesulfonamides and 2-cyclohepten-1-one or 2-cycloocten-1-one, the reactions were very sluggish in the presence of a range of Lewis bases, and the abnormal Baylis–Hillman adducts **7** or **9** – derived from aldol condensations – were obtained in moderate yields together with the normal Baylis–Hillman adduct **4**. When Baylis–Hillman reaction conditions were applied to *N*-arylidene-4-methylbenzenesulfonamides and 2-cycloocten-1-one in methanol, products **10** – derived from Michael additions of methanol to **9** – were formed as the major products, along with traces of **9**. In general, the ring-size of the α,β-unsaturated cyclic ketone can significantly affect the reaction products and rates, the Baylis–Hillman reaction and the aldol condensation reaction taking place at the same time for 2-cyclohexen-1-one or 2-cyclohepten-1-one. For large-sized α,β-unsaturated cyclic ketones such as 2-cycloocten-1-one, only aldol condensation reactions occurred. The substituent effects in all α,β-unsaturated cyclic ketone substrates were also examined.

Introduction

The Baylis−Hillman reaction has recently made great progress,[1] and now includes a catalytic asymmetric version,[2] since Baylis and Hillman first reported the reaction between acetaldehyde and ethyl acrylate or acrylonitrile in the presence of catalytic amounts of strong Lewis bases such as 1,4-diazabicyclo[2.2.2]octane (DABCO) in 1972.[3] During our own investigations into this very simple and useful reaction, we found that Baylis−Hillman reactions between many arenecarbaldehydes and α,β-unsaturated cyclic ketones were very sluggish under the traditional Baylis−Hillman reaction conditions, or even in the presence of $TiCl_4$ (1.4 equiv. as a Lewis acid) and catalytic amounts of amine, SMe_2, or phosphane (0.2 equiv.) as Lewis bases at −37 °C.[4] Additionally, as we have previously reported in a short communication, if the arenecarbaldehyde components are replaced with *N*-arylidene-4-methylbenzenesulfonamides (imines), Baylis−Hillman reactions between these species and 2-cyclohexen-1-one or 2-cyclopenten-1-one can be greatly accelerated in the presence of catalytic amounts of the Lewis bases DMAP or PBu_3.[4f] In the presence in particular of PBu_3 or DBU as Lewis bases, however, unexpected abnormal Baylis−Hillman adducts **5** were also formed on treatment of *N*-arylidene-4-methylbenzenesulfonamides (imines) and 2-cyclohexen-1-one under the same Baylis−Hillman reaction conditions.[4f] Therefore, in order to understand Baylis−Hillman reaction behavior between arenecarbaldehydes or *N*-arylidene-4-methylbenzenesulfonamides (imines) and α,β-unsaturated cyclic ketones comprehensively,[5] we intensely studied the Baylis−Hillman reaction behavior of arenecarbaldehydes and imines with α,β-unsaturated cyclic ketones and found many unusual results. Since Baylis−Hillman reactions between imines and α,β-unsaturated cyclic ketones have not so far been systematically investigated, except in our short communication, we wish here to report full details of the

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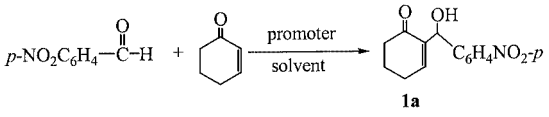
reaction behavior between arenecarbaldehydes or imines and α,β-unsaturated cyclic ketones under Baylis−Hillman conditions. In this full paper, we have significantly expanded the scope and defined the limitations of the Baylis−Hillman reaction with α,β-unsaturated cyclic ketones as Michael acceptors. Moreover, we also disclose in this full paper that the ring-sizes of α,β-unsaturated cyclic ketones can drastically affect the reaction products and reaction rates.

Results and Discussion

1) Application of Baylis−Hillman Reaction Conditions to Arenecarbaldehydes and 2-Cyclohexen-1-one or 2-Cyclopenten-1-one

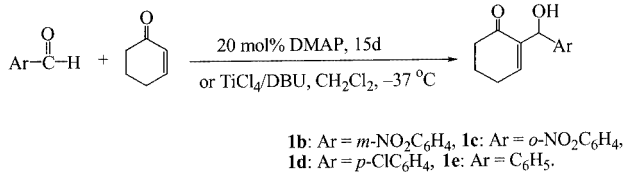
As shown in Scheme 1 and Table 1, we first systematically investigated various conditions for the Baylis−Hillman reaction between *p*-nitrobenzaldehyde and 2-cyclohexen-1-one. The best reaction conditions are: (1) with 4-dimethylaminopyridine (DMAP) or 4-pyrrolidinopyridine as a Lewis base in dichloromethane, the Baylis−Hillman adduct **1a** being obtained in 75% yield after 15 d at room temperature (Table 1, Entries 20 and 21), and (2) with $TiCl_4$ (1.4 equiv.) as a Lewis acid in dichloromethane at −37 °C, **1a** being obtained in 78% yield within 1 d (Table 1, Entry 25). The combination of $TiCl_4$ (1.4 equiv.) with Lewis base (0.2 equiv.) did not significantly improve the yield of **1a** (Table 1, Entries 26 and 27). However, as can be seen from Scheme 2 and Table 2, we elucidated that the two best reaction systems can only promote Baylis−Hillman reactions between arenecarbaldehydes with strongly electron-withdrawing groups (such as nitrobenzaldehyde) and 2-cyclohexen-1-one (Table 2, Entries 1, 2, 5, and 6). For other arenecarbaldehydes, no reaction occurred (Table 2, Entries 3, 4, 7, and 8).

We also examined the application of Baylis−Hillman conditions to reactions between *p*-nitrobenzaldehyde and 2-cyclopenten-1-one, either under the traditional Baylis−Hillman conditions or in the presence of $TiCl_4$ (1.4 equiv.) as a Lewis acid and catalytic amounts of amine, SMe_2, or phosphane (0.2 equiv.) as a Lewis base. Treatment



1a

Scheme 1



1b: Ar = *m*-$NO_2C_6H_4$, **1c**: Ar = *o*-$NO_2C_6H_4$, **1d**: Ar = *p*-ClC_6H_4, **1e**: Ar = C_6H_5.

Scheme 2

Table 1. The reactions between arenecarbaldehyde and 2-cyclohexene-1-one under various reaction conditions

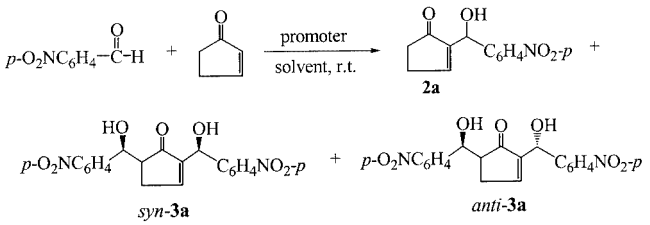
Entry	Promoter[a]	Solvent	Time [d]	Temp. [°C]	Yields (%)[b]
1	DBU	CH_2Cl_2	0.5	15	8
2	DBU	DMF	0.5	15	many products
3	DBU	MeOH	0.17	15	26
4	DABCO	CH_2Cl_2	10	15	trace
5	DABCO	DMF	7	15	15
6	DABCO	MeOH	6	15	10
7	DABCO/L-proline	$ClCH_2CH_2Cl$	5	70	many products
8	DABCO/morpholine	$ClCH_2CH_2Cl$	5	70	no reaction
9	DMAP/L-proline	CH_2Cl_2	3	15	trace
10	DMAP/Yb(OTf)$_3$	CH_2Cl_2	3	15	trace
11	DMAP/L-proline	DMF	2	15	10
12	DMAP	THF	2	15	5
13	DMAP	$ClCH_2CH_2Cl$	5	70	trace
14	DMAP/Binol	THF	5	15	36
15	DMAP/MS4A	CH_2Cl_2	2	15	15
16	DMAP/MgO	CH_2Cl_2	5	15	30
17	DMAPLiCl	CH_2Cl_2	5	15	42
18	DMAP	DMF	5	50	trace
19	DMAP	CH_2Cl_2	4	15	41
20	DMAP	CH_2Cl_2	15	15	75
21	4-pyrrolidinophyridine	CH_2Cl_2	15	15	75
22	PBu_3	THF	4	15	5
23	PBu_3/Binol	THF	4	15	15
24	PBu_3/MS4A	CH_2Cl_2	7	15	trace
25	$TiCl_4$[c]	CH_2Cl_2	1	−37	78
26	$TiCl_4$/DBU[d]	CH_2Cl_2	1	−37	58
27	BBr_3/Me_2S[e]	CH_2Cl_2	0.2	−37	65

[a] 10 mol % of Lewis base. [b] Isolated yields. [c] 1.4 equiv. of $TiCl_4$. [d] 1.4 equiv. of $TiCl_4$ and 0.2 equiv. of DBU. [e] 1.4 equiv. of BBr_3 and 0.2 equiv. of Me_2S.

Table 2. Reactions between arenecarbaldehydes and 2-cyclohexene-1-one under various reaction conditions

Entry	Ar	Promoter	Yields (%)[a]
1	*m*-$NO_2C_6H_4$	DMAP	70
2	*o*-$NO_2C_6H_4$	DMAP	70
3	*p*-ClC_6H_4	DMAP	no reaction
4	C_6H_5	DMAP	no reaction
5	*m*-$NO_2C_6H_4$	$TiCl_4$/DBU (−37 °C)	55
6	*o*-$NO_2C_6H_4$	$TiCl_4$/DBU (−37 °C)	49
7	*p*-ClC_6H_4	$TiCl_4$/DBU (−37 °C)	no reaction
8	C_6H_5	$TiCl_4$/DBU (−37 °C)	no reaction

[a] Isolated yields.



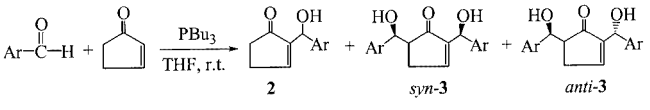
Scheme 3

of *p*-nitrobenzaldehyde and 2-cyclopenten-1-one in the presence of DMAP as a Lewis base resulted in only traces of the corresponding Baylis−Hillman adduct **2a** (Scheme 3, Entry 2). In the presence of PBu_3 as a Lewis base, **2a** could be obtained in 53% yield in THF, but only together with the formation of another, abnormal, Baylis−Hillman reaction product **3a** (*syn* and *anti* mixture) (Table 3, Entry 1). The $TiCl_4$ and Lewis base reaction system gave **2a** in 40% yield (Table 3, Entry 3). We also examined Baylis−Hillman reactions between other arenecarbaldehydes and 2-cyclopenten-1-one under the same conditions but in the presence of PBu_3 as a Lewis base (Scheme 4). The substituents on the phenyl ring of arenecarbaldehydes do not impair this reaction; treatment of *p*-ethylbenzaldehyde or *p*-methoxybenzaldehyde and 2-cyclopenten-1-one under Baylis−Hillman reaction conditions produced the normal Baylis−Hillman adducts **2e** or **2f** as the sole products (Table 4, Entries 4 and 5). The crystal structure of the major isomer of *syn*-**3b** was determined by X-ray analysis (Figure 1). The *syn*/*anti* ratios obtained are based on the ^1H NMR spectroscopic data. We believe that compounds **3** are derived from aldol condensation reactions between the Baylis−Hillman adducts **2** and the arenecarbaldehydes in the presence of the Lewis base PBu_3.

Table 3. Reactions between arenecarbaldehydes and 2-cyclopenten-1-ene under various reaction conditions

Entry	Promoter	Solvent	Time [h]	Yield (%)[a] **2**	**3** (*syn*/*anti*)
1	PBu_3	THF	15	53	26 (60:40)
2	DMAP	CH_2Cl_2	24	trace	
3	$TiCl_4$/DBU (−37 °C)	CH_2Cl_2	36	40	

[a] Isolated yields.



b: R = C_6H_5, **c**: R = *p*-BrC_6H_4, **d**: R = *p*-ClC_6H_4, **e**: R = *p*-EtC_6H_4, **f**: R = *p*-$MeOC_6H_4$.

Scheme 4

Table 4. Reactions between arenecarbaldehydes and 2-cyclopentene-1-one in the presence of PBu_3

Entry	Ar	Time [h]	Yield (%)[a] **2**	**3** (*syn*/*anti*)
1	C_6H_5	24	59	24 (65:35)
2	*p*-ClC_6H_4	5	69	13 (68:32)
3	*p*-ClC_6H_4	7	79	11 (70:30)
4	*p*-EtC_6H_4	24	84	0
5	*p*-$MeOC_6H_4$	8	75	0

[a] Isolated yields.

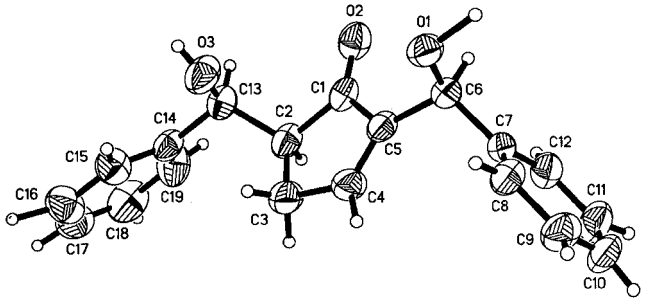


Figure 1. The crystal structure of *syn*-**3b**

These results clearly showed that Baylis−Hillman reaction behavior of arenecarbaldehydes and α,β-unsaturated cyclic ketones is very complicated, since the Lewis bases, the solvents, the substrates, and the ring-sizes of the α,β-unsaturated cyclic ketones can all significantly affect the Baylis−Hillman reaction rates and even the reaction products.

2) Application of Baylis−Hillman Reaction Conditions to *N*-Benzylidene-4-methylbenzenesulfonamides and 2-Cyclohexen-1-one or 2-Cyclopenten-1-one

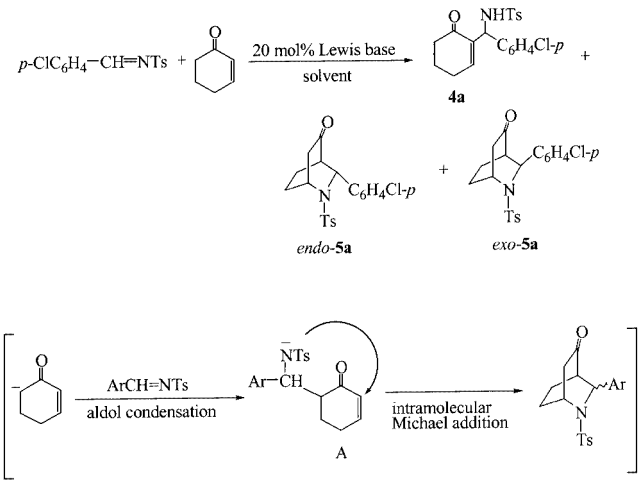
The substituents on the phenyl ring can significantly affect the reaction products and rates of Baylis−Hillman reactions between arenecarbaldehydes and α,β-unsaturated cyclic ketones. We therefore attempted to use *N*-arylidene-4-methylbenzenesulfonamides in place of arenecarbaldehydes, as the very strongly electron-withdrawing sulfonyl groups (−SO_2Ar) should reduce the influence of the substituents on the phenyl ring on the Baylis−Hillman reaction rates. At first, promoters for the reaction between *N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide[6] and 2-cyclohexen-1-one were examined systematically (Scheme 5, Table 5). We found that the solvents, the reaction temper-

atures, and the Lewis bases played very important roles for this reaction. In the presence of 20 mol % of DMAP as a Lewis base, for example, the reaction proceeded very well in methanol at 40 °C to give the normal Baylis–Hillman adduct **4** in good yield (Table 5, Entry 9), although this Lewis base was unable to promote the same reaction in DMF (Table 5, Entry 5). With 20 mol % of PPh_3 or dppe as Lewis bases, no reactions occurred (Table 5, Entries 1–3). However, in the presence of PBu_3 or DBU as a Lewis base in MeOH at 40 °C, an unexpected adduct **5** (*endo*/*exo* mixture; abnormal Baylis–Hillman adduct) was obtained along with **4** (Scheme 5, Table 5, Entries 8 and 11–12). Similar results were obtained for other *N*-arylidene-4-methylbenzenesulfonamides under the optimized reaction conditions in MeOH in the presence of PBu_3, $PhPMe_2$, Ph_2PMe, or DBU as Lewis bases (Scheme 6); the results are summarized in Table 6. The substituents on the phenyl ring of the *N*-arylidene-4-methylbenzenesulfonamide indeed do not significantly affect the reaction products and rates. We believe that **5** is produced stepwise through an aldol condensation reaction of the enolate derived from 2-cyclohexen-1-one in the presence of Lewis base to the imine and an intramolecular conjugated addition (Michael addition) of the anion formed to the α,β-unsaturated cyclic ketone moiety. The structures of **4** and **5** were determined by spectroscopic data, and the crystal structure of isomer *exo*-**5d** was established by X-ray analysis (Figure 2).

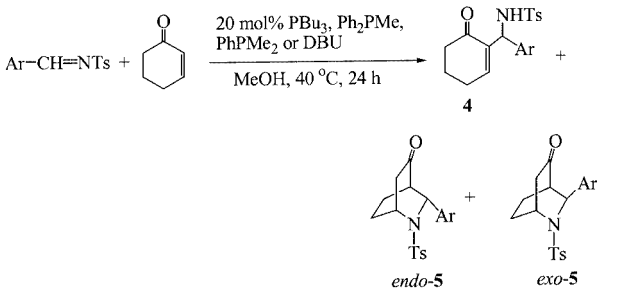
Table 5. Baylis–Hillman reactions between *N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide (1.0 equiv.) and 2-cyclohexen-1-one (1.0 equiv.) in the presence of Lewis base (20 mol %)

Entry	Lewis base	Solvent	Time [h]	Temp. [°C]	Yields (%)[a] **4a**	*endo*-**5a**	*exo*-**5a**
1	PPh_3	MeOH	24	20	0	0	0
2	PPh_3/BINOL	THF	48	40	0	0	0
3	dppe/BINOL	THF	72	20	0	0	0
4	PBu_3	DMF	48	40	trace	0	0
5	DMAP	DMF	36	20	0	0	0
6	DBU	DMF	24	20	0	0	0
7	DABCO	MeOH	36	20	30	0	0
8	PBu_3	MeOH	24	40	20	15	22
9	DMAP	MeOH	24	40	65	0	0
10	DMAP	MeOH	24	20	41	0	0
11	DBU	CH_2Cl_2	24	40	32	10	18
12	DBU	MeOH	24		40	10	20

[a] Isolated yields.



Scheme 5



b: Ar = C_6H_5, **c**: Ar = *p*-EtC_6H_4, **d**: Ar = *p*-$MeOC_6H_4$, **e**: Ar = *p*-FC_6H_4, **f**: Ar = *p*-$NO_2C_6H_4$.

Scheme 6

Table 6. Baylis–Hillman reactions between *N*-(benzylidene)-4-methylbenzenesulfonamide (1.0 equiv.) and 2-cyclohexen-1-one in the presence of Lewis base (20 mol %)

Entry	Ar	Lewis base	Time [h]	Yields (%)[a] **4a**	*endo*-**5**	*exo*-**5**
1	C_6H_5	DBU	3	40	12	20
2	C_6H_5	PBu_3	24	16	16	22
3	C_6H_5	$PhPMe_2$	5	14	18	29
4	C_6H_5	Ph_2PMe	24	9	20	33
5	*p*-EtC_6H_4	DBU	3	32	10	18
6	*p*-$MeOC_6H_4$	PBu_3	24	25	25	23
7	*p*-FC_6H_4	PBu_3	26	20	19	22
8	*p*-$NO_2C_6H_4$	PBu_3	24	15	10	25

[a] Isolated yields.

Meanwhile, we also examined reactions between other *N*-arylidene-4-methylbenzenesulfonamides and 2-cyclohexen-1-one in the presence of DMAP as a Lewis base (Scheme 7).

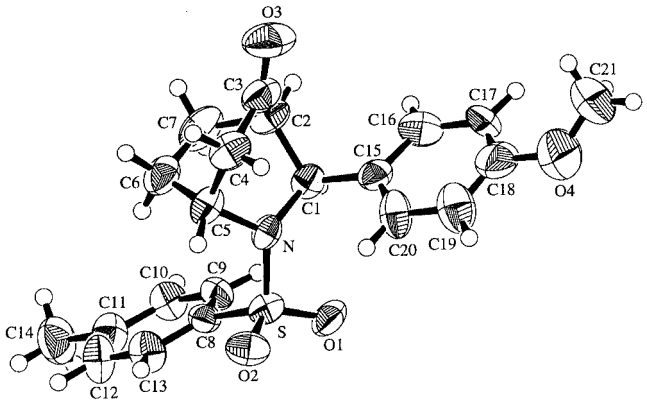
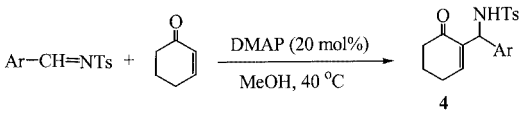


Figure 2. The crystal structure of *exo*-**5d**



b: Ar = C_6H_5, **c**: Ar = *p*-EtC_6H_4, **d**: Ar = *p*-$MeOC_6H_4$, **e**: Ar = *p*-FC_6H_4, **f**: Ar = *p*-$NO_2C_6H_4$.

Scheme 7

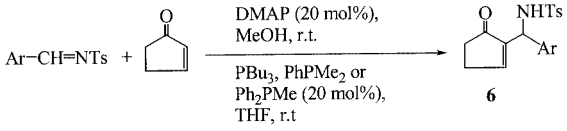
Table 7. Baylis−Hillman reactions between *N*-(benzylidene)-4-methylbenzenesulfonamide (1.0 equiv.) and 2-cyclohexen-1-one in the presence of the Lewis base DMAP (20 mol %)

Entry	Ar	Time [h]	Yield (%)[a] **4**
1	C_6H_5	24	50
2	*p*-EtC_6H_4	24	40
3	*p*-$MeOC_6H_4$	36	30
4	*p*-FC_6H_4	24	60
5	*p*-$NO_2C_6H_4$	24	52

[a] Isolated yields.

Only the normal Baylis−Hillman products **4** were formed, in moderate yields. The results are elucidated in Table 7.

For reactions between *N*-arylidene-4-methylbenzenesulfonamides and 2-cyclopenten-1-one, on the other hand, we were delighted to find that the normal Baylis−Hillman products **6** could be exclusively obtained in the presence of DMAP, $PhPMe_2$, Ph_2PMe, or PBu_3 as Lewis bases under the same reaction conditions, although PPh_3 or DABCO had no activity for this reaction (Scheme 8, Table 8). No abnormal adducts were formed, and the Baylis−Hillman adducts **6** were obtained in very high yields. This may be due to the aldol condensation reaction being difficult for small cyclic ketones in the presence of Lewis bases. The reaction rates are much faster than those for 2-cyclohexen-1-one under similar conditions. Especially with $PhPMe_2$ or PBu_3 as a Lewis base, yields of products **6** can reach 90% within 5 h at room temperature, the reactions in some cases proceeding quantitatively. This result also suggests that the ring-size of α,β-unsaturated cyclic ketones can significantly affect the reaction products and rates. Meanwhile, the substituents on the phenyl ring also do not affect the reaction products and rates.



a: Ar = C_6H_5, b: Ar = *p*-EtC_6H_4, **c**: Ar = *p*-$MeOC_6H_4$, **d**: Ar = *p*-$Me_2NC_6H_4$, **e**: Ar = *p*-ClC_6H_4, **f**: Ar = *p*-BrC_6H_4, **g**: Ar = *p*-$NO_2C_6H_4$.

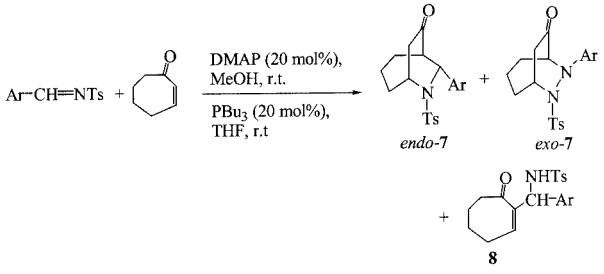
Scheme 8

We found that reactions between imines and 2-cyclohepten-1-one[7] are in general sluggish under various conditions. The abnormal Baylis−Hillman adducts **7** were formed along with the normal Baylis−Hillman adducts **8** (Scheme 9), the results for several imines substrates being summarized in Table 9. The crystal structure of the major

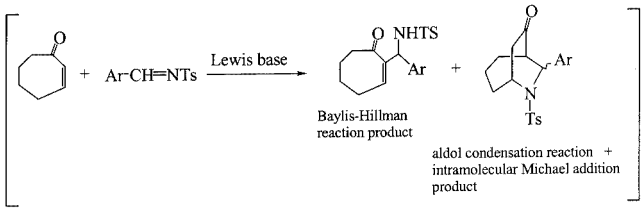
Table 8. Baylis−Hillman reactions between *N*-(benzylidene)-4-methylbenzenesulfonamide (1.0 equiv.) and 2-cyclopenten-1-one (1.0 equiv.) in the presence of the Lewis bases DMAP or PBu_3 (20 mol %)

Entry	R	Lewis base	Time [h]	Yields (%)[a] **6**
1	C_6H_5	DMAP	24	75
2	C_6H_5	PBu_3	5	70
3	C_6H_5	Ph_2PMe	27	67
4	*p*-EtC_6H_4	DMAP	24	82
5	*p*-EtC_6H_4	PBu_3	6	85
6	*p*-$MeOC_6H_4$	PBu_3	6	87
7	*p*-$MeOC_6H_4$	$PhPMe_2$	4	99
8	*p*-$Me_2NC_6H_4$	PBu_3	6	90
9	*p*-ClC_6H_4	PBu_3	5	99
10	*p*-ClC_6H_4	DMAP	24	54
11	*p*-BrC_6H_4	PBu_3	5	83
12	*p*-$NO_2C_6H_4$	DMAP	24	80
13	*p*-$NO_2C_6H_4$	PBu_3	5	90

[a] Isolated yields.



a: Ar= C_6H_5, **b**: Ar= *p*-ClC_6H_4, **c**: Ar= *p*-$MeOC_6H_4$



Scheme 9

Table 9. Baylis−Hillman reactions between *N*-(benzylidene)-4-methylbenzenesulfonamide (1.0 equiv.) and 2-cyclohepten-1-one (1.0 equiv.) in the presence of the Lewis bases DMAP or PBu_3 (20 mol %)

Entry	R	Lewis base	Solvent	Time [h]	Yields (%)[a] **7** (*endo*/*exo*)	**8**
1	C_6H_5	DMAP	MeOH	48	14 (41:59)	27
2	C_6H_5	PBu_3	THF	5	−	−
3	*p*-ClC_6H_4	PBu_3	THF	5	−	−
4	*p*-ClC_6H_4	DBU	MeOH	48	22 (22:78)	9
5	*p*-$MeOC_6H_4$	DBU	MeOH	48	21 (35:65)	trace
6	*p*-$MeOC_6H_4$	PBu_3	THF	6	−	−

[a] Isolated yields.

isomer *exo*-**7a** was determined by X-ray analysis (Figure 3). The *endo*/*exo* ratios obtained are based on the ^{1}H NMR spectroscopic data. It is very clear that the abnormal Baylis–Hillman adducts **7** derive from aldol condensation reactions, followed by intramolecular Michael addition, as in the case of the formation of **5** shown in Scheme 5.

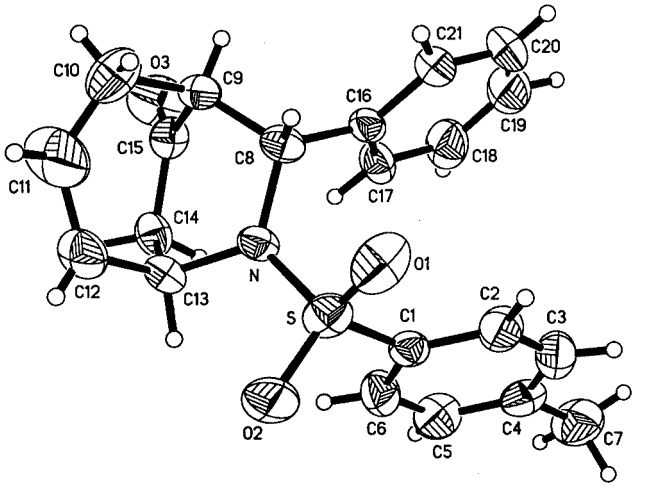
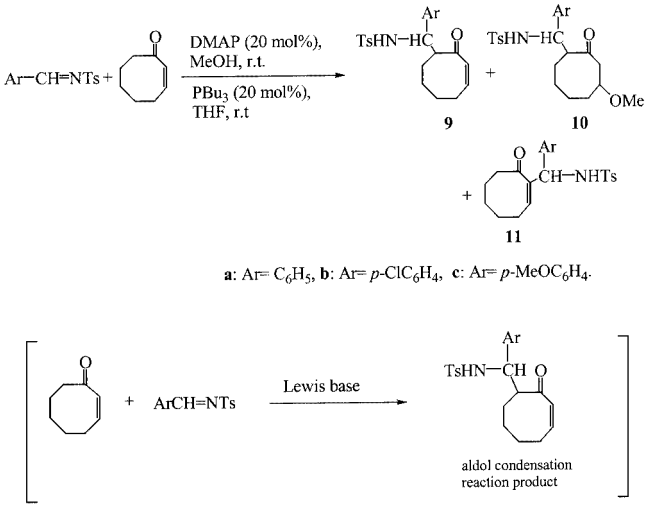


Figure 3. The crystal structure of *exo*-**7a**

For reactions between imines and 2-cycloocten-1-one,[8] however, we surprisingly found that, although none of the Baylis–Hillman adducts **11** were formed at all and the reactions were sluggish, the abnormal Baylis–Hillman adducts **9** (*syn* and *anti* mixtures) were formed exclusively in THF in the presence of DMAP or PBu_3 as Lewis bases (Scheme 10). Obviously, compounds **9** are derived from aldol reactions between imines and 2-cycloocten-1-one in the presence of a Lewis base. In addition, when the reactions were carried out in methanol, the products **10**, derived from Michael addition of methanol to **9**, became the major products along with traces of **9** (Scheme 10). The results for several imine substrates are summarized in Table 10. The structures of **9** and **10** were established by spectroscopic data and microanalysis, while the X-ray crystal structures of the major isomers of **9** and **10** are shown in Figures 4 and 5. The *syn*/*anti* ratios obtained are based on ^{1}H NMR spectroscopic data.

These results suggest that, for medium-sized α,β-unsaturated cyclic ketones such as 2-cyclohexen-1-one or 2-cyclohepten-1-one, the aldol condensation reaction in general takes place along with the Baylis–Hillman reaction. For the larger 2-cycloocten-1-one, however, the aldol condensation reaction occurred exclusively, rather than the Baylis–Hillman reaction. This is because the Lewis bases used for Baylis–Hillman reactions, such as DMAP, DABCO, PBu_3, or DBU, are also organic bases used for aldol condensation reactions in organic chemistry. Thus, both the Baylis–Hillman reaction and aldol condensation can take place at the same time for the α,β-unsaturated cyclic ketone. For 2-cyclopenten-1-one (a small α,β-unsaturated cyclic ketone), abstraction of the α-H by the organic base is difficult. The organic base thus plays a role only as



Scheme 10

Table 10. Baylis–Hillman reactions between *N*-(benzylidene)-4-methylbenzenesulfonamide (1.0 equiv.) and 2-cycloocten-1-one (1.0 equiv.) in the presence of the Lewis bases DMAP or PBu_3 (20 mol %)

Entry	R	Lewis base	Time [h]	Yields (%)[a] **9** (*syn*/*anti*)	**10**
1	C_6H_5	DMAP	48	–	45
2	C_6H_5	PBu_3	48	42 (35:65)	–
3	*p*-ClC_6H_4	PBu_3	48	30 (40:60)	–
4	*p*-ClC_6H_4	DMAP	48	–	51
5	*p*-$MeOC_6H_4$	DMAP	48	–	44
6	*p*-$MeOC_6H_4$	PBu_3	48	49 (41:59)	–

[a] Isolated yields.

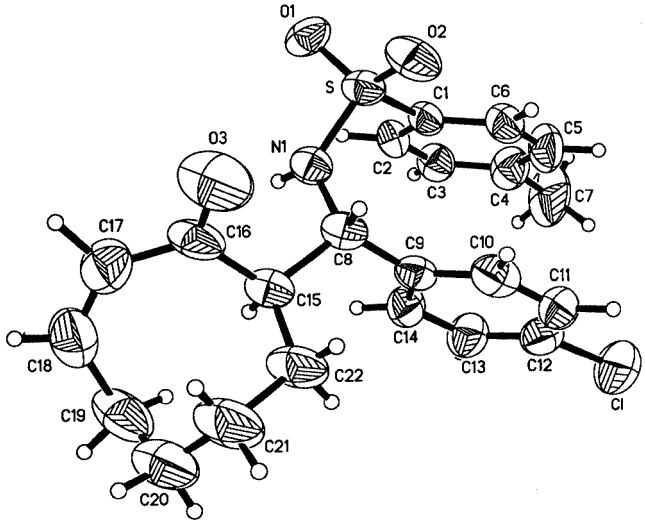


Figure 4. The crystal structure of **9b**

Lewis base, and so the Baylis–Hillman reaction takes place exclusively. For medium-sized α,β-unsaturated cyclic ketones such as 2-cyclohexen-1-one or 2-cyclohepten-1-one, both the Baylis–Hillman reaction and aldol condensation occur at the same time.

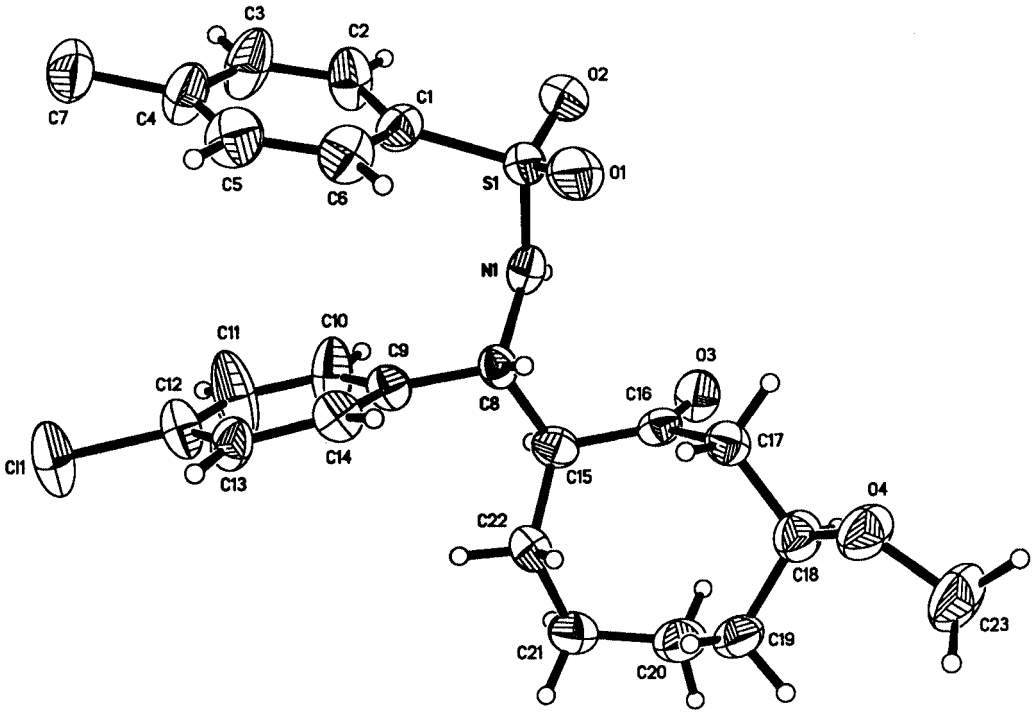
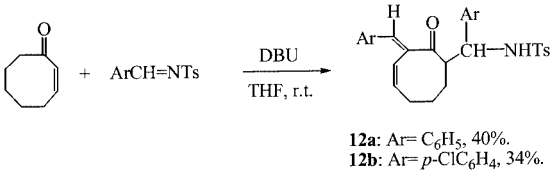


Figure 5. The crystal structure of **10c**

Additionally, we also found a very interesting result in the application of Baylis–Hillman reaction conditions to imines and 2-cycloocten-1-one in the presence of DBU as a Lewis base. The abnormal Baylis–Hillman reaction products **12** were formed in moderate yields, each as a single (*anti*) stereoisomer (Scheme 11). The structures of **12** were established by spectroscopic data and X-ray analysis (Figure 6). We believe that products **12** derive from aldol reactions between **9** and the imines, followed by the elimination of $TsNH^-$. Scheme 12 elucidates a plausible reaction mechanism for the formation of **12** (Scheme 12). Attack of the allyl enolate anion to tosylimine gives the adduct **A**, in which the α-carbonyl hydrogen atom, particularly acidic because of double activation (carbonyl + double bond), can be selectively abstracted by DBU. This results in the elimination of $TsNH^-$, a good leaving group because of the stabilization of the negative charge by the sulfonyl group, giving product **12**.



Scheme 11

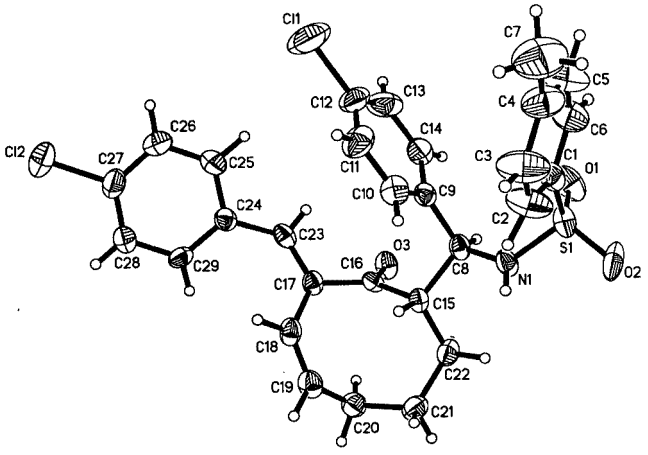
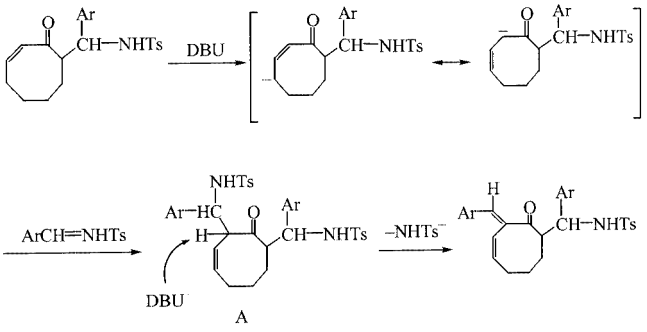


Figure 6. The crystal structure of **12b**



Scheme 12

Conclusion

In this full paper, we have clearly elucidated that the application of Baylis–Hillman reaction conditions to arenecarbaldehydes or tosylimines and α,β-unsaturated cyclic ketones is very complicated, since the Lewis bases, the solvents, the substrates, and the ring-sizes of α,β-unsaturated

cyclic ketones can all significantly affect the Baylis−Hillman reaction rates and even products. However, it is clear that aldol condensation reactions can take place along with the Baylis−Hillman reactions, to give abnormal Baylis−Hillman adducts such as **3**, **5**, **7** and **9**, **10** and **12** in each case. Efforts are currently underway both to obtain mechanistic insights regarding the Lewis bases used in these Baylis−Hillman reactions of arenecarbaldehydes or *N*-arylidene-4-methylbenzenesulfonamides (imines) with α,β-unsaturated cyclic ketones and to determine the scope and limitations of this type of Baylis−Hillman reaction.

Experimental Section

General Remarks: Unless otherwise stated, all reactions were carried out under argon. All solvents were purified by distillation. Tributylphosphane were obtained from Tokyo Chemical Industries (Tokyo Kasei Co. Ltd.) and used without purification. All *N*-tosylimines were prepared according to the literature. Infrared spectra were measured with a Perkin−Elmer 983 spectrometer. ^{1}H NMR spectra were recorded with a 300 MHz spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard. Mass spectra were recorded with an HP-5989 instrument and HRMS was performed with a Finnigan MA+ mass spectrometer. Satisfactory CHN microanalyses were obtained with a Carlo−Erba 1106 analyzer for solid products. For oily products, HRMS was used to analyze the elemental composition since we do not have a diffusion pump (high pressure) suitable to distill oily products. Melting points were obtained by means of a micro melting point apparatus and are uncorrected.

Typical Reaction Procedure for the DMAP-Catalyzed Baylis−Hillman Reaction between 2-Cyclohexen-1-one and 4-Nitrobenzenaldehyde: 2-Cyclohexen-1-one (48 μL, 0.5 mmol) was added at room temperature to a solution of *p*-nitrobenzenaldehyde (76 mg, 0.5 mmol) and DMAP (6 mg, 0.05 mmol) in CH_2Cl_2 (0.5 mL). After the mixture had been stirred for 15 d, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (SiO_2; EtOAc/petroleum ether, 1:2) to yield **1a** (93 mg, 75%) as a yellow solid, which was recrystallized from acetone/*n*-hexane (1:4).

2-[Hydroxy(4-nitrophenyl)methyl]cyclohex-2-enone (1a): Yellow solid; 93 mg, 75%; m.p. 88−89 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 1666 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.97−2.05 (m, 2 H, CH_2), 2.41−2.48 (m, 4 H, CH_2), 3.57 (d, *J* = 6.0 Hz, 1 H, OH), 5.60 (d, *J* = 6.0 Hz, 1 H, CH), 6.82 (t, *J* = 4.1 Hz, 1 H, =CH), 7.55 (d, *J* = 8.7 Hz, 2 H, Ar), 8.20 (d, *J* = 8.7 Hz, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 247 (3.39) [M$^+$], 230 (100) [M$^+$ − 17]. $C_{13}H_{13}NO_4$: calcd. C 63.15, H 5.30, N 5.67; found C 63.23, H 5.36, N 5.65.

2-[Hydroxy(2-nitrophenyl)methyl]cyclohex-2-enone (1b): Yellow solid; 86 mg, 70%; m.p. 124−125 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 1658 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.96−2.04 (m, 2 H, CH_2), 2.35−2.40 (m, 2 H, CH_2), 2.46−2.50 (m, 2 H, CH_2), 3.67 (d, *J* = 4.9 Hz, 1 H, OH), 6.18 (d, *J* = 4.9 Hz, 1 H, CH), 6.62 (t, *J* = 4.1 Hz, 1 H, =CH), 7.45 (dd, *J* = 7.5, 7.9 Hz, 1 H, Ar), 7.66 (dd, *J* = 7.5, 8.1 Hz, 1 H, Ar), 7.82 (d, *J* = 7.9 Hz, 1 H, Ar), 7.94 (d, *J* = 8.1 Hz, 1 H, Ar) ppm. MS (EI): *m*/*z* (%) = 248 (3.23) [M$^+$], 230 (31.18) [M$^+$ − 18]. $C_{13}H_{13}NO_4$: calcd. C 63.15, H 5.30, N 5.67; found C 62.97, H 5.10, N 5.41.

2-[Hydroxy(3-nitrophenyl)methyl]cyclohex-2-enone (1c): Colorless oil; 87 mg, 70%. IR ($CHCl_3$): $\tilde{\nu}$ = 1666 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.01−2.05 (m, 2 H, CH_2), 2.43−2.47 (m, 4 H, CH_2), 3.75 (d, *J* = 5.9 Hz, 1 H, OH), 5.60 (d, *J* = 5.9 Hz, 1 H, CH), 6.90 (t, *J* = 4.2 Hz, 1 H, =CH), 7.51 (t, *J* = 7.9 Hz, 1 H, Ar), 7.75 (d, *J* = 8.2 Hz, 1 H, Ar), 8.10 (d, *J* = 8.2 Hz, 1 H, Ar), 8.22 (s, 1 H, Ar) ppm. MS (EI): *m*/*z* (%) = 248 (8.15) [M$^+$], 230 (100) [M$^+$ − 18]. $C_{13}H_{13}NO_4$: calcd. C 63.15, H 5.30, N 5.67; found C 63.05, H 5.24, N 5.67.

Typical Reaction Procedure for the Tributylphosphane-Catalyzed Baylis−Hillman Reaction between 2-Cyclopenten-1-one and 4-Nitrobenzaldehyde: 2-Cyclopenten-1-one (42 μL, 0.5 mmol) was added at room temperature to a solution of 4-nitrobenzaldehyde (113 mg, 0.75 mmol) and tributylphosphane (24 μL, 0.1 mmol) in THF (1.0 mL). After the mixture had been stirred for 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, 1:2) to yield **2a** (62 mg, 53%) and **3a** (50 mg, 26%) as yellow solids which were recrystallized from acetone/*n*-hexane (1:6).

2-[Hydroxy(4-nitrophenyl)methyl]cyclopent-2-enone (2a): Pale yellow solid; m.p. 135−137 °C; 62 mg, 53%. IR ($CHCl_3$): $\tilde{\nu}$ = 1692 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.36−2.39 (m, 2 H, CH_2), 2.50−2.54 (m, 2 H, CH_2), 3.63 (d, *J* = 4.3 Hz, 1 H, OH), 5.68 (s, 1 H, CH), 7.31 (t, *J* = 1.1 Hz, 1 H, =CH), 7.47 (d, *J* = 8.6 Hz, 2 H, Ar), 8.10 (d, *J* = 8.6 Hz, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 233 (100) [M$^+$], 216 (73.62) [M$^+$ − 17]. $C_{12}H_{11}NO_4$: calcd. C 61.80, H 4.72, N 6.00; found C 61.92, H 4.74, N 6.22.

***syn*-2,5-Bis[hydroxy(4-nitrophenyl)methyl]cyclopent-2-enone (3a):** Pale yellow solid; m.p. 82−83 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 1696 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.34−2.36 (m, 1 H,), 2.46−2.48 (m, 1 H,), 2.67−2.68 (m, 1 H), 2.80−2.82 (m, 1 H), 3.32−3.34 (m, 1 H), 5.53−5.55 (m, 1 H, CH), 5.71−5.72 (m, 1 H, CH), 7.44 (t, *J* = 1.4 Hz, 1 H, =CH), 7.56 (d, *J* = 8.7 Hz, 2 H, Ar), 7.60 (d, *J* = 8.7 Hz, 2 H, Ar), 8.22 (d, *J* = 8.7 Hz, 2 H, Ar), 8.25 (d, *J* = 8.7 Hz, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 233 (100) [M$^+$ − 151], 216 (43.83) [M$^+$ − 168].$C_{19}H_{116}N_2O_7{\cdot}H_2O$: calcd. C 56.43, H 4.99, N 6.99; found C 57.05, H 4.74, N 7.11.

***anti*-2,5-Bis[hydroxy(4-nitrophenyl)methyl]cyclopent-2-enone (3a):** Pale yellow solid; m.p. 82−83 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 1696 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.41−2.44 (m, 1 H,), 2.45−2.47 (m, 1 H,), 2.74−2.75 (m, 1 H), 2.81−2.84 (m, 1 H), 3.35−3.37 (m, 1 H), 5.55−5.56 (m, 1 H, CH), 5.68−5.70 (m, 1 H, CH), 7.38 (t, *J* = 1.4 Hz, 1 H, =CH), 7.57 (d, *J* = 8.7 Hz, 2 H, Ar), 7.62 (d, *J* = 8.7 Hz, 2 H, Ar), 8.23 (d, *J* = 8.7 Hz, 2 H, Ar), 8.26 (d, *J* = 8.7 Hz, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 233 (100) [M$^+$ − 151], 216 (43.83) [M$^+$ − 168]. $C_{19}H_{116}N_2O_7{\cdot}H_2O$: calcd. C 56.43, H 4.99, N 6.99; found C 57.05, H 4.74, N 7.11.

The total yield of *syn*-**3a** and *anti*-**3a** was 50 mg, 26%.

2-[Hydroxy(phenyl)methyl]cyclopent-2-enone (2b): Colorless liquid; 56 mg, 59%. IR ($CHCl_3$): $\tilde{\nu}$ = 1692 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.42−2.45 (m, 2 H, CH_2), 2.56−2.58 (m, 2 H, CH_2), 3.52 (s, 1 H, br, OH), 5.54 (s, 1 H, CH), 7.26(t, *J* = 1.1 Hz, 1 H, =CH), 7.27−7.56 (m, 5 H) ppm. MS (EI): *m*/*z* (%) = 188 (87.72) [M], 269 (2.66) [M$^+$ + 2], 170 (8.25) [M$^+$ − 18], 128 (100) [M$^+$ − 60]. HRMS: calcd. for $C_{12}H_{12}O_2$ 188.0837; found 188.0830.

***syn*-2,5-Bis[hydroxy(phenyl)methyl]cyclopent-2-enone (3b):** Pale yellow solid; m.p. 138−139 °C. IR ($CHCl_3$): $\tilde{\nu}$ = 1680 cm^{-1} (C=

O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.40−2.42(m, 1 H,), 2.66−2.67 (m, 1 H, CH), 2.68 (s, 1 H, br, OH), 2.78−2.79 (m, 1 H), 3.49 (s, 1 H, br, OH), 5.40−5.41 (m, 1 H, CH), 5.58−5.59 (m, 1 H, CH), 7.34 (t, *J* = 1.4 Hz, 1 H, =CH), 7.34−7.42 (m, 10 H, Ar) ppm. MS (EI): *m*/*z* (%) = 276 (32.24) [M^+ − 18], 259 (100) [M^+ − 35]. $C_{19}H_{18}O_3$: calcd. C 77.55, H 6.12; found C 77.58, H 6.08.

***anti*-2,5-Bis[hydroxy(phenyl)methyl]cyclopent-2-enone (3b):** Pale yellow solid; m.p. 138−139 °C. IR ($CHCl_3$): ṽ = 1680 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.34−2.36 (m, 1 H, CH), 2.70 (s, 1 H, br, OH), 2.76−2.77 (m, 1 H, CH), 2.79−2.80 (m, 1 H), 3.38 (s, 1 H, br, OH), 5.41−5.42 (m, 1 H, CH), 5.59−5.60 (m, 1 H, CH), 7.32 (t, *J* = 1.4 Hz, 1 H, =CH), 7.27−7.36 (m, 10 H, Ar) ppm. MS (EI): *m*/*z* (%) = 276 (32.24) [M^+ − 18], 259 (100) [M^+ − 35]. $C_{19}H_{18}O_3$: calcd. C 77.55, H 6.12; found C 77.58, H 6.08.

The total yield of *syn*-**3b** and *anti*-**3b** was 35 mg, 24%.

2-[(4-Bromophenyl)(hydroxy)methyl]cyclopent-2-enone (2c): Colorless liquid; 92 mg, 69%. IR ($CHCl_3$): ṽ = 1688 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.40−2.45 (m, 2 H, CH_2), 2.57−2.58 (m, 2 H, CH_2), 3.78 (s, 1 H, br, OH), 5.47 (s, 1 H, CH), 7.23−7.27 (m, 2 H), 7.28 (t, *J* = 1.1 Hz, 1 H, =CH), 7.43 (d, *J* = 8.5 Hz, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 267 (2.57) [M], 269 (2.66) [M^+ + 2], 249 (100) [M^+ − 18], 251 (96.13) [M^+ − 16]. $C_{12}H_{11}BrO_2$: calcd. C 53.96, H 4.15; found C 54.27, H 4.58.

***syn*-2,5-Bis[(4-bromophenyl)(hydroxy)methyl]cyclopent-2-enone (3c):** Pale yellow solid; m.p. 150−152 °C. IR ($CHCl_3$): ṽ = 1687 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.37−2.40 (m, 1 H), 2.58 −2.61 (m, 1 H), 2.71−2.74 (m, 1 H), 3.28 (s, 1 H, br, OH), 3.76 (s, 1 H, br, OH), 5.34 (d, *J* = 2.4 Hz, 1 H, CH), 5.49−5.50 (m, 1 H, CH), 7.17−7.24 (m, 4 H, Ar), 7.34 (t, *J* = 1.4 Hz, 1 H, = CH), 7.42−7.48 (m, 4 H, Ar) ppm. MS (EI): *m*/*z* (%) = 452 (0.43) [M], 266 (30.72) [M^+ − 186]. $C_{19}H_{16}Br_2O_3$: calcd. C 50.47, H 3.57; found C 50.62, H 3.41.

***anti*-2,5-Bis[(4-bromophenyl)(hydroxy)methyl]cyclopent-2-enone (3c):** Pale yellow solid; m.p. 150−152 °C. IR ($CHCl_3$): ṽ = 1687 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.27−2.33 (m, 1 H), 2.65−2.67 (m, 1 H), 2.75−2.78 (m, 1 H), 2.91 (s, 1 H, br, OH), 3.52 (s, 1 H, br, OH), 5.29 (d, *J* = 2.4 Hz, 1 H, CH), 5.50−5.51 (m, 1 H, CH), 7.19−7.26 (m, 4 H, Ar), 7.31 (t, *J* = 1.4 Hz, 1 H, =CH), 7.44−7.49 (m, 4 H, Ar) ppm. MS (EI): *m*/*z* (%) = 452 (0.43) [M^+], 266 (30.72) [M^+ − 186]. $C_{19}H_{16}Br_2O_3$: calcd. C 50.47, H 3.57; found C 50.62, H 3.41.

The total yield of *syn*-**3c** and *anti*-**3c** was 30 mg, 13%.

2-[(4-Chlorophenyl)(hydroxy)methyl]cyclopent-2-enone (2d): Colorless liquid; 88 mg, 79%. IR ($CHCl_3$): ṽ = 1690 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.45−2.49 (m, 2 H, CH_2), 2.58−2.63 (m, 2 H, CH_2), 3.50 (d, *J* = 4.3 Hz, 1 H, OH), 5.55 (d, *J* = 4.3 Hz, 1 H, CH), 7.25 (t, *J* = 1.1 Hz, 1 H, =CH), 7.31−7.40 (m, 4 H, Ar) ppm. MS (EI): *m*/*z* (%) = 222 (40.11) [M^+], 205 (75.61) [M^+ − 17]. $C_{12}H_{11}ClO_2$: calcd. C 64.72, H 4.94; found C 64.55, H 5.18.

***syn*-2,5-Bis[(4-chlorophenyl)(hydroxy)methyl]cyclopent-2-enone (3d):** Colorless, viscous liquid. IR ($CHCl_3$): ṽ = 1688 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.40−2.41 (m, 1 H), 2.59−2.60 (m, 1 H, CH), 2.61−2.63 (m, 1 H, CH), 2.73−2.75 (m, 1 H, CH), 3.37−3.39 (m, 1 H, CH), 5.36−5.38 (m, 1 H, CH), 5.52−5.54 (m, 1 H, CH), 7.35 (t, *J* = 1.4 Hz, 1 H, =CH), 7.28−7.33 (m, 8 H, Ar) ppm. MS (EI): *m*/*z* (%) = 345 (5.51) [M^+ − 18], 205 (44.07) [M^+ − 158, . HRMS: calcd. for $C_{19}H_{15}Cl_2O_2$ [M^+ + 1 − H_2O) 345.0449; found 345.0446.

***anti*-2,5-Bis[(4-chlorophenyl)(hydroxy)methyl]cyclopent-2-enone (3d):** Colorless, viscous liquid. IR ($CHCl_3$): ṽ = 1688 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.39−2.40 (m, 1 H, CH), 2.48−2.51 (m, 1 H, CH), 2.66−2.70 (m, 1 H, CH), 2.76−2.79 (m, 1 H, CH), 3.27−3.28 (m, 1 H, CH), 5.31−5.34 (m, 1 H, CH), 5.51−5.53 (m, 1 H, CH), 7.35 (t, *J* = 1.4 Hz, 1 H, =CH), 7.30−7.38 (m, 8 H, Ar) ppm. MS (EI): *m*/*z* (%) = 345 (5.51) [M^+ − 18], 205 (44.07) [M^+ − 158]. HRMS: calcd. for $C_{19}H_{15}Cl_2O_2$ [M^+ + 1 − H_2O) 345.0449; found 345.0446.

The total yield of *syn*-**3d** and *anti*-**3d** was 19 mg, 11%.

2-[(4-Ethylphenyl)(hydroxy)methyl]cyclopent-2-enone (2e): Colorless liquid; 81 mg, 75%. IR ($CHCl_3$): ṽ = 1690 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.21 (t, *J* = 7.6 Hz, 3 H, CH_3), 2.41−2.44 (m, 2 H, CH_2), 2.55−2.58 (m, 2 H, CH_2), 2.61 (q, *J* = 7.6 Hz, 2 H, CH_2), 3.30−3.70 (s, 1 H, br, OH), 5.51 (s, 1 H, CH), 7.16 (d, *J* = 8.0 Hz, 2 H, Ar), 7.26−7.30 (m, 2 H), 7.31 (t, *J* = 1.1 Hz, 1 H, =CH) ppm. MS (EI): *m*/*z* = 216 (5.50) [M^+], 199 (100)[M^+ − 17]. $C_{14}H_{16}O_2$: calcd. C 77.75, H 7.46; found C 77.49, H 7.34.

2-[Hydroxy(4-methoxyphenyl)methyl]cyclopent-2-enone (2f): Colorless liquid; 92 mg, 84%. IR ($CHCl_3$): ṽ = 1689 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.38−2.42 (m, 2 H, CH_2), 2.53−2.56 (m, 2 H, CH_2), 3.70 (s, 1 H, br, OH), 3.79 (s, 3 H, CH_3), 5.45 (s, 1 H, CH), 6.84 (d, *J* = 8.7 Hz, 2 H, Ar), 7.24−7.31 (m, 2 H), 7.32 (t, *J* = 1.1 Hz, 1 H, =CH) ppm. MS (EI): *m*/*z* (%) = 218 (34.89) [M^+], 201 (100) [M^+ − 17]. HRMS: calcd. for $C_{13}H_{14}O_3$: calcd. 218.0943; found 218.0933.

Typical Reaction Procedure for the Tributylphosphane-Catalyzed Baylis−Hillman Reaction between 2-Cyclohexen-1-one and *N*-(4-Ethylbenzylidene)-4-methylbenzenesulfonylamide: 2-Cyclohexen-1-one (48 μL, 0.5 mmol) was added at 40 °C to a solution of *N*-(4-ethylbenzylidene)-4-methylbenzenesulfonylamide (144 mg, 0.5 mmol) and tributylphosphane (25 μL, 0.1 mmol) in CH_3OH (0.5 mL). After the mixture had been stirred for 24 h, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (SiO_2; EtOAc/petroleum ether, 1:5) to yield **4c** (58 mg, 31.3%), *endo*-**5c** (11 mg, 5.74%), and *exo*-**5c** (33 mg, 17.2%) as colorless solids, which were recrystallized from acetone/*n*-hexane (1:3).

***N*-[(4-Chlorophenyl)(6-oxocyclohex-1-enyl)methyl]-4-methylbenzenesulfonamide (4a):** Colorless solid; m.p. 135−136 °C; 39 mg, 20%. IR ($CHCl_3$): ṽ = 1667 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.62−2.32 (m, 6 H, CH_2), 2.39 (s, 3 H, Me), 5.09 (d, *J* = 9.6 Hz, 1 H, NH), 6.18 (d, *J* = 9.6 Hz, 1 H, CH), 6.80 (t, *J* = 4.1 Hz, 1 H, =CH), 7.10 (d, *J* = 8.7 Hz, 2 H, Ar), 7.15 (2 H, *J* = 8.7 Hz, Ar), 7.21 (d, *J* = 8.2 Hz, 2 H, Ar), 7.60 (d, *J* = 8.2 Hz, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 294 (1.59) [M^+ − 96], 234 (100) [M^+ − 156]. $C_{20}H_{20}ClNO_3S$: calcd. C 61.61, H 5.17, N 3.59; found C 61.54, H 5.18, N 3.71.

***endo*-3-(4-Chlorophenyl)-2-(4-tolylsulfonyl)-2-azabicyclo[2.2.2]-octan-5-one (5a):** Colorless solid; m.p. 158−159 °C; 29 mg, 15%. IR ($CHCl_3$): ṽ = 1727 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.23−2.48 (m, 7 H, CH_2), 2.43 (s, 3 H, Me), 4.46 (d, *J* = 2.4 Hz, 1 H, CH), 5.06 (d, *J* = 2.0 Hz, 1 H, CH), 7.30 (m, 6 H, Ar), 7.62 (2 H, *J* = 8.3 Hz, Ar) ppm. MS (EI): *m*/*z* (%) = 389(16.15) [M^+ − 1], 234 (100) [M^+ − 156]. $C_{20}H_{20}ClNO_3S$: calcd. C 61.61, H 5.17, N 3.59; found C 61.74, H 5.20, N 3.38.

***exo*-3-(4-Chlorophenyl)-2-(4-toluylsulfonyl)-2-azabicyclo[2.2.2]-octan5-one (5a):** Colorless solid; m.p. 201−202 °C; 43 mg, 22%. IR ($CHCl_3$): $\tilde{\nu}$ = 1728 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.55−2.75 (m, 7 H, CH_2), 2.42 (s, 3 H, Me), 4.53 (s, 1 H, CH), 4.97 (d, *J* = 2.5 Hz, 1 H, CH), 7.05 (d, *J* = 8.5 Hz, 2 H, Ar), 7.18 (d, *J* = 8.5 Hz, 2 H, Ar), 7.22 (d, *J* = 8.2 Hz, 2 H, Ar), 7.61 (2 H, *J* = 8.2 Hz, Ar) ppm. MS (EI): *m/z* (%) = 389 (16.15) [M^+ − 1], 234 (100) [M^+ − 156]. $C_{20}H_{20}ClNO_3S$: calcd. C 61.61, H 5.17, N 3.59; found C 61.45, H 5.23, N 3.58.

4-Methyl-*N*-[(6-oxocyclohex-1-enyl)(phenyl)methyl]benzenesulfonamide (4b): Colorless solid; m.p. 148−149 °C; 29 mg, 16%. IR ($CHCl_3$): $\tilde{\nu}$ = 1670 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.67−2.31 (m, 6 H, CH_2), 2.41 (s, 3 H, Me), 5.10 (d, *J* = 9.5 Hz, 1 H, NH), 5.93 (d, *J* = 9.5 Hz, 1 H, CH), 6.82 (t, *J* = 4.1 Hz, 1 H, =CH), 7.20 (m, 7 H, Ar), 7.64 (d, *J* = 8.2 Hz, 2 H, Ar) ppm. MS (EI): *m/z* (%) = 278 (1.84) [M^+ − 77], 200 (100) [M^+ − 155]. $C_{20}H_{21}NO_3S$: calcd. C 67.58, H 5.95, N 3.94; found C 67.02, H 5.83, N 3.80.

***endo*-3-Phenyl-2-(4-toluylsulfonyl)-2-azabicyclo[2.2.2]octan-5-one (5b):** Colorless solid; m.p. 182−183 °C; 29 mg, 16%. IR ($CHCl_3$): $\tilde{\nu}$ = 1726 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.56−2.53 (m, 7 H, CH_2), 2.42 (s, 3 H, Me), 4.47 (s, 1 H, CH), 5.11 (d, *J* = 1.8 Hz, 1 H, CH), 7.25−7.36 (m, 7 H, Ar), 7.63 (d, *J* = 8.2 Hz, 2 H, Ar) ppm. MS (EI): *m/z* (%) = 355 (10.61) [M] 200 (100) [M^+ − 155]. $C_{20}H_{21}NO_3S$: calcd. C 67.58, H 5.95, N 3.94; found C 67.63, H 5.93, N 3.89.

***exo*-3-Phenyl-2-(4-toluylsulfonyl)-2-azabicyclo[2.2.2]octan-5-one (5b):** Colorless solid; m.p. 188−189 °C; 39 mg, 22%. IR ($CHCl_3$): $\tilde{\nu}$ = 1734 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.56−2.80 (m, 7 H, CH_2), 2.42 (s, 3 H, Me), 4.54 (s, 1 H, CH), 5.01 (d, *J* = 2.5 Hz, 1 H, CH), 7.09−7.26 (m, 7 H, Ar), 7.61 (d, *J* = 8.2 Hz, 2 H, Ar) ppm. MS (EI): *m/z* = 355 (2.15) [M^+], 200 (100) [M^+ − 155]. $C_{20}H_{21}NO_3S$: calcd. C 67.58, H 5.95, N 3.94; found C 67.41, H 5.88, N 3.84.

***N*-[(4-Ethylphenyl)(6-oxocyclohex-1-enyl)methyl]-4-methylbenzenesulfonamide (4c):** Colorless solid; m.p. 111−112 °C; 61 mg, 32%. IR ($CHCl_3$): $\tilde{\nu}$ = 1730 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.17 (t, *J* = 7.6 Hz, 3 H, Me), 1.79−2.30 (m, 6 H, CH_2), 2.40 (s, 3 H, Me), 2.55 (q, *J* = 7.6 Hz, 2 H, CH_2), 5.09 (d, *J* = 9.3 Hz, 1 H, NH), 6.01 (d, *J* = 9.3 Hz, 1 H, CH), 6.81 (t, *J* = 4.1 Hz, 1 H, =CH), 7.04 (d, *J* = 8.2 Hz, 2 H, Ar), 7.09 (2 H, *J* = 8.2 Hz, Ar), 7.22 (d, *J* = 8.2 Hz, 2 H, Ar), 7.63 (d, *J* = 8.2 Hz, 2 H, Ar) ppm. MS (EI): *m/z* (%) = 383 (1.00) [M^+ − 1], 228 (100) [M^+ − 155]. $C_{22}H_{25}NO_3S$: calcd. C 68.90, H 6.57, N 3.65; found C 68.89, H 6.50, N 3.66.

***endo*-3-(4-Ethylphenyl)-2-(4-toluylsulfonyl)-2-azabicyclo[2.2.2]octan-5-one (5c):** Colorless solid; m.p. 140−142 °C; 19 mg, 10%. IR ($CHCl_3$): $\tilde{\nu}$ = 1723 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.24 (t, *J* = 7.6 Hz, 3 H, Me), 1.44−2.50 (m, 7 H, CH_2), 2.42 (s, 3 H, Me), 2.63 (q, *J* = 7.6 Hz, 2 H, CH_2), 4.47 (s, 1 H, CH), 5.07 (s, 1 H, CH), 7.16 (d, *J* = 8.2 Hz, 2 H, Ar), 7.24 (2 H, *J* = 8.2 Hz, Ar), 7.27 (d, *J* = 8.3 Hz, 2 H, Ar), 7.63 (d, *J* = 8.3 Hz, 2 H, Ar) ppm. MS (EI): *m/z* (%) = 383 (4.15) [M^+ − 1], 228 (100) [M^+ − 155]. $C_{22}H_{25}NO_3S$: calcd. C 68.90, H 6.57, N 3.65; found C 68.82, H 6.60, N 3.45.

***exo*-3-(4-Ethylphenyl)-2-(4-toluylsulfonyl)-2-azabicyclo[2.2.2]octan-5-one (5c):** Colorless solid; m.p. 171−172 °C; 34 mg, 18%. IR ($CHCl_3$): $\tilde{\nu}$ = 1730 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.18 (1 H, *J* = 7.6 Hz, Me), 1.43−2.79 (m, 7 H, CH_2), 2.39 (s, 3 H, Me), 2.56 (q, *J* = 7.6 Hz, 2 H, CH_2), 4.53 (d, *J* = 2.5 Hz, 1 H, CH), 4.98 (d, *J* = 2.5 Hz, 1 H, CH), 7.03 (d, *J* = 8.3 Hz, 2 H, Ar), 7.09 (2 H, *J* = 8.2 Hz, Ar), 7.20 (d, *J* = 8.3 Hz, 2 H, Ar), 7.60 (d, *J* = 8.2 Hz, 2 H, Ar) ppm. MS (EI): *m/z* (%) = 383 (1.26) [M^+ − 1], 228 (100) [M^+ − 155]. $C_{22}H_{25}NO_3S$: calcd. C 68.90 H, 6.57 N, 3.65; found C 69.15 H, 6.64 N, 3.60.

***N*-[(4-Methoxyphenyl)(6-oxocyclohex-1-enyl)methyl]-4-methylbenzenesulfonamide (4d):** Colorless solid; m.p. 113−115 °C; 48 mg, 25%. IR ($CHCl_3$): $\tilde{\nu}$ = 1666 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.65−2.35 (m, 6 H, CH_2), 2.41 (s, 3 H, Me), 3.73 (s, 3 H, Me), 5.05 (d, *J* = 9.2 Hz, 1 H, NH), 5.86 (d, *J* = 9.2 Hz, 1 H, CH), 6.76 (d, *J* = 8.7 Hz, 2 H, Ar), 6.81 (t, *J* = 4.1 Hz, 1 H, =CH), 7.09 (d, *J* = 8.7 Hz, 2 H, Ar), 7.25 (d, *J* = 8.2 Hz, 2 H, Ar), 7.63 (d, *J* = 8.2 Hz, 2 H, Ar) ppm. MS (EI): *m/z* (%) = 278 (1.84) [M^+ − 107], 230 (100) [M^+ − 155]. $C_{21}H_{23}NO_4S$: calcd. C 65.43, H 6.01, N 3.63; found C 65.31, H 6.09, N 3.52.

***endo*-3-(4-Methoxyphenyl)-2-(4-toluylsulfonyl)-2-azabicyclo[2.2.2]-octan-5-one (5d):** Colorless solid; m.p. 174−175 °C; 48 mg, 25%. IR ($CHCl_3$): $\tilde{\nu}$ = 1724 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.22−2.46 (m, 7 H, CH_2), 2.44 (s, 3 H, Me), 3.73 (s, 3 H, Me), 4.44 (d, *J* = 2.2 Hz, 1 H, CH), 5.05 (d, *J* = 1.8 Hz, 1 H, CH), 6.85 (d, *J* = 8.5 Hz, 2 H, Ar), 7.21 (d, *J* = 8.5 Hz, 2 H, Ar), 7.24 (d, *J* = 8.2 Hz, 2 H, Ar), 7.62 (d, *J* = 8.2 Hz, 2 H, Ar) ppm. MS (EI): *m/z* = 385 (25.63) [M^+], 230 (88.03) [M^+ − 155]. $C_{21}H_{23}NO_4S$: calcd. C 65.43, H 6.01, N 3.63; found C 64.92, H 6.18, N 3.49.

***exo*-3-(4-Methoxyphenyl)-2-(4-tolylsulfonyl)-2-azabicyclo[2.2.2]-octan-5-one (5d):** Colorless solid: m.p. 197−198 °C; 44 mg, 23%. IR ($CHCl_3$): $\tilde{\nu}$ = 1731 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.48−2.75 (m, 7 H, CH_2), 2.38 (s, 3 H, Me), 3.73 (s, 3 H, Me), 4.50 (s, 1 H, CH), 4.94 (d, *J* = 2.4 Hz, 1 H, CH), 6.72 (d, *J* = 8.7 Hz, 2 H, Ar), 7.00 (d, *J* = 8.7 Hz, 2 H, Ar), 7.20 (d, *J* = 8.2 Hz, 2 H, Ar), 7.58 (d, *J* = 8.2 Hz, 2 H, Ar) ppm. MS (EI): *m/z* (%) = 385 (26.36) [M^+], 230 (78.47) [M^+ − 155]. $C_{21}H_{23}NO_4S$: calcd. C 65.43, H 6.01, N 3.63; found C 64.73, H 5.93, N 3.53.

***N*-[(4-Fluorophenyl)(6-oxocyclohex-1-enyl)methyl]-4-methylbenzenesulfonamide (4e):** Colorless solid; m.p. 132−133 °C; 37 mg, 20%. IR ($CHCl_3$): $\tilde{\nu}$ = 1652 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.67−2.36 (m, 6 H, CH_2), 2.43 (s, 3 H, Me), 5.07 (d, *J* = 9.5 Hz, 1 H, NH), 5.95 (d, *J* = 9.5 Hz, 1 H, CH), 6.81 (t, *J* = 4.1 Hz, 1 H, =CH), 6.92 (d, *J* = 8.6 Hz, 2 H, Ar), 7.17 (d, *J* = 8.6 Hz, 2 H, Ar), 7.27 (d, *J* = 8.2 Hz, 2 H, Ar), 7.64 (d, *J* = 8.2 Hz, 2 H, Ar) ppm. MS (EI): *m/z* (%) = 278 (1.59) [M^+ − 95], 218 (100) [M^+ − 155. $C_{20}H_{20}FNO_3S$: calcd. C 64.32, H 5.40, N 3.75; found C 64.42, H 5.37, N 3.59.

***endo*-3-(4-Fluorophenyl)-2-(4-tolylsulfonyl)-2-azabicyclo[2.2.2]octan-5-one (5e):** Colorless solid; m.p. 163−164 °C; 35 mg, 19%. IR ($CHCl_3$): $\tilde{\nu}$ = 1728 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.42−2.47 (m, 7 H, CH_2), 2.44 (s, 3 H, Me), 4.46 (s, 1 H, CH), 5.07 (s, 1 H, CH), 7.04 (d, *J* = 8.6 Hz, 2 H, Ar), 7.25 (d, *J* = 8.2 Hz, 2 H, Ar), 7.32 (d, *J* = 8.6 Hz, 2 H, Ar), 7.62 (d, *J* = 8.2 Hz, 2 H, Ar) ppm. MS (EI): *m/z* (%) = 373 (5.98) [M^+], 218 (100) [M^+ − 155]. $C_{20}H_{20}FNO_3S$: calcd. C 64.32, H 5.40, N 3.75; found C 64.55, H 5.21, N 3.57.

***exo*-3-(4-Fluorophenyl)-2-(4-tolylsulfonyl)-2-azabicyclo[2.2.2]octan-5-one (5e):** Colorless solid; m.p. 186−187 °C; 41 mg, 22%. IR ($CHCl_3$): $\tilde{\nu}$ = 1726 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.40−2.75 (m, 7 H, CH_2), 2.40 (s, 3 H, Me), 4.51 (d, *J* = 2.4 Hz, 1 H, CH), 4.97 (1 H,d, *J* = 2.4 Hz, CH), 6.92 (d, *J* = 8.6 Hz, 2 H, Ar), 7.08 (d, *J* = 8.6 Hz, 2 H, Ar), 7.22 (d, *J* =

8.2 Hz, 2 H, Ar), 7.60 (d, J = 8.2 Hz, 2 H, Ar) ppm. MS (EI): m/z (%) = 373 (1.27) [M^+], 218 (100) [$M^+ - 155$]. $C_{20}H_{20}FNO_3S$: calcd. C 64.32, H 5.40, N 3.75; found C 64.15, H 5.53, N 3.64.

4-Methyl-*N*-[(4-nitrophenyl)(6-oxocyclohex-1-enyl)methyl]benzenesulfonamide (4f): Colorless solid; m.p. 183−185 °C; 30 mg, 15%. IR ($CHCl_3$): $\tilde{\nu}$ = 1647 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.69−2.35 (m, 6 H, CH_2), 2.43 (s, 3 H, Me), 5.16 (d, J = 9.8 Hz, 1 H, NH), 6.10 (d, J = 9.8 Hz, 1 H, CH), 6.86 (t, J = 4.1 Hz, 1 H, =CH), 7.27 (d, J = 7.4 Hz, 2 H, Ar), 7.42 (2 H, J = 8.6 Hz, Ar), 7.64 (d, J = 7.4 Hz, 2 H, Ar), 8.10 (d, J = 8.6 Hz, 2 H, Ar) ppm. MS (EI): m/z (%) = 278 (1.59) [$M^+ - 122$], 245 (100) [$M^+ - 155$]. $C_{20}H_{20}N_2O_5S$: calcd. C 59.99, H 5.03, N 7.00; found C 59.99, H 4.96, N 6.76.

***endo*-3-(4-Nitrophenyl)-2-(4-tolylsulfonyl)-2-azabicyclo[2.2.2]octan-5-one (5f):** Colorless solid; m.p. 191−193 °C; 20 mg, 10%. IR ($CHCl_3$): $\tilde{\nu}$ = 1728 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.48−2.54 (m, 7 H, CH_2), 2.45 (s, 3 H, Me), 4.48 (d, J = 2.4 Hz, 1 H, CH), 5.14 (d, J = 2.0 Hz, 1 H, CH), 7.28 (d, J = 8.2 Hz, 2 H, Ar), 7.55 (d, J = 8.7 Hz, 2 H, Ar), 7.64 (2 H, J = 8.2 Hz, Ar), 8.24 (d, J = 8.7 Hz, 2 H, Ar) ppm. MS (EI): m/z (%) = 400 (5.13) [M^+], 245 (100) [$M^+ - 155$]. $C_{20}H_{20}N_2O_5S$: calcd. C 59.99, H 5.03, N 7.00; found C 59.97, H 4.96, N 7.04.

***exo*-3-(4-Nitrophenyl)-2-(4-tolylsulfonyl)-2-azabicyclo[2.2.2]octan-5-one (5f):** Colorless solid; m.p. 221−222 °C; 50 mg, 25%. IR ($CHCl_3$): $\tilde{\nu}$ = 1730 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.23−2.48 (m, 7 H, CH_2), 2.43 (s, 3 H, Me), 4.46 (d, J = 2.4 Hz, 1 H, CH), 5.06 (d, J = 2.0 Hz, 1 H, CH) 7.26 (d, J = 8.2 Hz, 2 H, Ar), 7.32 (d, J = 8.7 Hz, 2 H, Ar), 7.63 (2 H, J = 8.2 Hz, Ar), 8.11 (d, J = 8.7 Hz, 2 H, Ar) ppm. MS (EI): m/z (%) = 400 (3.09) [M^+], 245 (100) [$M^+ - 155$]. $C_{20}H_{20}N_2O_5S$: calcd. C 59.99, H 5.03, N 7.00; found C 59.95, H 5.13, N 7.11.

Typical Reaction Procedure for the Tributylphosphane-Catalyzed Baylis−Hillman Reaction between 2-Cyclopenten-1-one and *N*-(4-Ethylphenylsulfonyl)benzaldimine: 2-Cyclopenten-1-one (42 μL, 0.5 mmol) was added at room temperature to a solution of *N*-(4-ethylphenylsulfonyl)benzaldimine (144 mg, 0.5 mmol) and tributylphosphane (24 μL, 0.1 mmol) in THF (1.0 mL). After the mixture had been stirred for 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, 1:2) to yield **6b** (157 mg, 85%) as a colorless solid, which was recrystallized from acetone/*n*-hexane (1:5).

4-Methyl-*N*-[(5-oxo-cyclopent-1-enyl)(phenyl)methyl]benzenesulfonamide (6a): Colorless solid; m.p. 124−125 °C; 19 mg, 70%. IR ($CHCl_3$): $\tilde{\nu}$ = 1689 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.09−2.49 (m, 4 H, CH_2), 2.35 (s, 3 H, Me), 5.27 (d, J = 8.5 Hz, 1 H, NH), 6.02 (d, J = 8.5 Hz, 1 H, CH), 7.15-7.26 (m, 7 H, Ar), 7.35 (t, J = 2.6 Hz, 1 H, =CH), 7.62 (2 H, J = 8.2 Hz, Ar) ppm. MS (EI): m/z (%) = 341 (0.03) [M^+], 186 (100) [$M^+ - 155$] $C_{19}H_{19}NO_3S$: calcd. C 66.84, H 5.61, N 4.10; found C 66.51, H 5.69, N 3.86.

***N*-[(4-Ethylphenyl)(5-oxocyclopent-1-enyl)methyl]-4-methylbenzenesulfonamide (6b):** Colorless solid; m.p. 110−111 °C; 157 mg, 85%. IR ($CHCl_3$): $\tilde{\nu}$ = 1676 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.17 (t, J = 7.6 Hz, 3 H, Me), 2.15−2.47 (m, 4 H, CH_2), 2.35 (s, 3 H, Me), 2.57 (q, J = 7.6 Hz, 2 H, CH_2), 5.24 (d, J = 8.5 Hz, 1 H, NH), 6.01 (d, J = 8.5 Hz, 1 H, CH), 7.04 (m, 4 H, Ar), 7.19 (2 H, J = 8.2 Hz, Ar), 7.35 (t, J = 2.6 Hz, 1 H, = CH), 7.59 (d, J = 8.2 Hz, 2 H, Ar) ppm. MS (EI): m/z (%) = 288 (0.82) [$M^+ - 81$], 214 (100) [$M^+ - 155$]. $C_{21}H_{23}NO_3S$: calcd. C 68.27, H 6.27, N 3.79; found C 67.82, H 6.21, N 3.71.

***N*-[(4-Methoxyphenyl)(5-oxocyclopent-1-enyl)methyl]-4-methylbenzenesulfonamide (6c):** Colorless solid; m.p. 118−120 °C; 162 mg, 87%. IR ($CHCl_3$): $\tilde{\nu}$ = 1684 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.13−2.45 (m, 4 H, CH_2), 2.35 (s, 3 H, Me), 3.73 (s, 3 H, CH_3), 5.20 (d, J = 8.4 Hz, 1 H, NH), 5.92 (d, J = 8.4 Hz, 1 H, CH), 6.72 (d, J = 8.6 Hz, 2 H, Ar), 7.05 (d, J = 8.6 Hz, 2 H, Ar), 7.19 (2 H, J = 8.2 Hz, Ar), 7.35 (t, J = 2.6 Hz, 1 H, =CH), 7.59 (d, J = 8.2 Hz, 2 H, Ar) ppm. MS (EI): m/z (%) = 371 (0.39) [M^+], 216 (100) [$M^+ - 155$]. $C_{20}H_{22}NO_4S$: calcd. C 64.67, H 5.70, N 3.77; found C 64.60, H 5.60, N 3.53.

***N*-{[4-(Dimethylamino)phenyl](5-oxocyclopent-1-enyl)methyl}-4-methylbenzenesulfonamide (6d):** Yellow solid; m.p. 175−176 °C; 173 mg, 90%. IR ($CHCl_3$): $\tilde{\nu}$ = 1676 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.12−2.46 (m, 4 H, CH_2), 2.36 (s, 3 H, Me), 2.88 (s, 6 H, CH_3), 5.14 (d, J = 8.1 Hz, 1 H, NH), 5.79 (d, J = 8.1 Hz, 1 H, CH), 6.53 (d, J = 8.8 Hz, 2 H, Ar), 6.97 (d, J = 8.8 Hz, 2 H, Ar), 7.19 (2 H, J = 8.2 Hz, Ar), 7.33 (t, J = 2.6 Hz, 1 H, =CH), 7.59 (d, J = 8.2 Hz, 2 H, Ar) ppm. MS (EI): m/z (%) = 384 (33.88) [M^+], 229 (100) [$M^+ - 155$]. $C_{21}H_{24}N_2O_3S$: calcd. C 65.60, H 6.29, N 7.29; found C 65.51, H 6.24, N 7.14.

***N*-[(4-Chlorophenyl)(5-oxocyclopent-1-enyl)methyl]-4-methylbenzenesulfonamide (6e):** Colorless solid; m.p. 190−192 °C; 186 mg, 99%. IR ($CHCl_3$): $\tilde{\nu}$ = 1675 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.14−2.53 (m, 4 H, CH_2), 2.36 (s, 3 H, Me), 5.28 (d, J = 8.6 Hz, 1 H, NH), 6.08 (d, J = 8.6 Hz, 1 H, CH), 7.14 (d, J = 8.6 Hz, 2 H, Ar), 7.21 (d, J = 8.3 Hz, 2 H, Ar), 7.22 (2 H, J = 8.6 Hz, Ar), 7.37 (t, J = 2.6 Hz, 1 H, =CH), 7.61 (d, J = 8.3 Hz, 2 H, Ar) ppm. MS (EI): m/z (%) = 294 (0.60) [$M^+ - 81$], 220 (100) [$M^+ - 155$]. $C_{19}H_{18}ClNO_3S$: calcd. C 60.71, H 4.83, N 3.73; found C 60.54, H 4.84, N 3.42.

***N*-[(4-Bromophenyl)(5-oxocyclopent-1-enyl)methyl]-4-methylbenzenesulfonamide (6f):** Colorless solid; m.p. 198−201 °C; 174 mg, 83%. IR ($CHCl_3$): $\tilde{\nu}$ = 1676 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.12−2.48 (m, 4 H, CH_2), 2.36 (s, 3 H, Me), 5.21 (d, J = 8.6 Hz, 1 H, NH), 6.04 (d, J = 8.6 Hz, 1 H, CH), 7.02 (d, J = 8.4 Hz, 2 H, Ar), 7.18 (d, J = 8.3 Hz, 2 H, Ar), 7.30 (2 H, J = 8.4 Hz, Ar), 7.31 (t, J = 2.6 Hz, 1 H, =CH), 7.57 (d, J = 8.3 Hz, 2 H, Ar) ppm. MS (EI): m/z (%) = 266 (93.12) [$M^+ - 153$], 264 (100) [$M^+ - 155$]. $C_{19}H_{18}BrNO_3S$: calcd. C 54.29, H 4.32, N 3.33; found C 54.18, H 4.38, N 3.08.

4-Methyl-*N*-[(4-nitrophenyl)(5-oxocyclopent-1-enyl)methyl]benzenesulfonamide (6g): Pale yellow solid; m.p. 187−188 °C; 174 mg, 90%. IR ($CHCl_3$): $\tilde{\nu}$ = 1676 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 2.17−2.56 (m, 4 H, CH_2), 2.43 (s, 3 H, Me), 5.42 (d, J = 8.8 Hz, 1 H, NH), 6.27 (d, J = 8.8 Hz, 1 H, CH), 7.25 (d, J = 8.2 Hz, 2 H, Ar), 7.40 (d, J = 6.8 Hz, 2 H, Ar), 7.43 (t, J = 2.6 Hz, 1 H, =CH), 7.64 (2 H, J = 8.2 Hz, Ar), 8.10 (d, J = 6.8 Hz, 2 H, Ar) ppm. MS (EI): m/z (%) = 305 (0.73) [$M^+ - 81$], 231 (100) [$M^+ - 155$]. $C_{19}H_{18}N_2O_5S$: calcd. C 59.06, H 4.70, N 7.25; found C 59.30, H 4.85, N 7.25.

Typical Reaction Procedure for the Tributylphosphane-Catalyzed Baylis−Hillman Reaction between 2-Cyclohepten-1-one and *N*-(4-Methylphenylsulfonyl)araldimine: The reaction was carried out in the same manner as those described above, but the scale was: imine (1.0 mmol), 2-cyclohepten-1-one (1.0 mmol), PBu_3 (0.2 mmol).

***exo*-7-Phenyl-6-(4-tolylsulfonyl)-6-azabicyclo[3,2,2]nonan-8-one (7a):** White solid; m.p. 65−66 °C; 30 mg, 8%. IR (neat): $\tilde{\nu}$ = 1723

(C=O), 1157 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.34−2.14 (m, 6 H, CH_2), 2.51 (s, 3 H, CH_3), 2.51−2.56 (m, 1 H), 2.71−2.83 (m, 2 H), 4.61 (m, 1 H), 4.97 (1H m), 7.37−7.42 (m, 2 H, Ar), 7.46−7.48 (m, 5 H, Ar), 7.67−7.70 (m, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 327 (16.25) [M^+ − 42], 250 (52.67) [M^+ − 119], 91 (100) [$PhMe^+$]. $C_{21}H_{23}NO_3S$: calcd. C 68.26, H 6.27, N 3.79; found C 67.71, H 6.30, N 3.64.

***endo*-7-Phenyl-6-(4-tolylsulfonyl)-6-azabicyclo[3,2,2]nonan-8-one (7a):** White solid; m.p. 65−66 °C; 22 mg, 6%. IR (neat): $\tilde{\nu}$ = 1723 (C=O), 1157 cm^{-1}. ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.77−2.32 (m, 6 H), 2.32 (s, 3 H, CH_3), 2.43−2.51 (m, 1 H), 2.76−2.82 (m, 2 H), 4.70 (d, *J* = 4.3 Hz, 1 H, CH), 5.26 (d, *J* = 1.8 Hz, 1 H, CH), 6.94−6.97 (m, 2 H, Ar), 7.07−7.13 (m, 5 H, Ar), 7.39−7.41 (m, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 327 (16.25) [M^+ − 42], 250 (52.67) [M^+ − 119], 91 (100) [$PhMe^+$]. $C_{21}H_{23}NO_3S$: calcd. C 68.26, H 6.27, N 3.79; found C 67.71, H 6.30, N 3.64.

***exo*-7-(4-Chlorophenyl)-6-(4-tolylsulfonyl)-6-azabicyclo[3.2.2]nonan-8-one (7b):** White solid; m.p. 162−166 °C; 70 mg, 17%. IR (neat): $\tilde{\nu}$ = 1723 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.26−2.15 (m, 6 H, CH_2), 2.39 (s, 3 H, CH_3), 2.45−2.53 (m, 1 H), 2.72−2.81 (m, 2 H, CH_2), 4.56 (m, 1 H, CH), 4.93 (d, *J* = 4.4 Hz, 1 H), 7.23−7.27 (m, 2 H, Ar), 7.31−7.42 (m, 4 H, Ar), 7.67−7.69 (m, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 403 (1.42) [M^+], 250 (100) [M^+ − 153], 91 (61.99) [$PhMe^+$]. $C_{21}H_{22}ClNO_3S$: calcd. C 62.44, H 5.49, N 3.47; found C 62.40, H 5.86, N 3.29.

***endo*-7-(4-Chlorophenyl)-6-(4-tolylsulfonyl)-6-azabicyclo[3.2.2]-nonan-8-one (7b):** White solid; m.p. 162−166 °C; 20 mg, 5%. IR (neat): $\tilde{\nu}$ = 1723 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.78−2.15 (m, 6 H, CH_2), 2.39 (s, 3 H, CH_3), 2.45−2.53 (m, 1 H), 2.73−2.80 (m, 2 H, CH_2), 4.72−4.73 (m, 1 H, CH), 5.23 (d, *J* = 1.3 Hz, 1 H), 6.90−6.93 (m, 2 H, Ar), 7.07−7.15 (m, 4 H, Ar), 7.42−7.45 (m, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 403 (1.42) [M^+], 250 (100) [M^+ − 153], 91 (61.99) [$PhMe^+$]. $C_{21}H_{22}ClNO_3S$: calcd. C 62.44, H 5.49, N 3.47; found C 62.40, H 5.86, N 3.29.

***exo*-7-(4-Methoxyphenyl)-6-(4-tolylsulfonyl)-6-azabicyclo[3.2.2]-nonan-8-one (7c):** Light yellow solid: m.p. 173−174 °C; 54 mg, 13%. IR (neat): $\tilde{\nu}$ = 1723 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.26−1.99 (m, 6 H, CH_2), 2.44 (s, 3 H, CH_3), 2.50−2.51 (m, 1 H), 2.68−2.76 (m, 2 H, CH_2), 3.82 (s, 3 H, OCH_3), 4.59−4.61 (m, 1 H, CH), 4.92 (d, *J* = 4.2 Hz, 1 H), 7.09−7.12 (m, 2 H, Ar), 7.26−7.35 (m, 4 H, Ar), 7.66−7.69 (m, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 399 (19.20) [M^+], 244 (86.24) [M^+ − 155], 91 (100) [$PhMe^+$]. $C_{22}H_{25}NO_4S{\cdot}1/10CH_2Cl_2$: calcd. C 65.13, H 6.24, N 3.44; found C 65.17, H 6.53, N 3.25.

***endo*-7-(4-Methoxyphenyl)-6-(4-tolylsulfonyl)-6-azabicyclo[3.2.2]-nonan-8-one (7c):** Light yellow solid: m.p. 173−174 °C; 30 mg, 7%. IR (neat): $\tilde{\nu}$ = 1723 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.79−2.14 (m, 6 H, CH_2), 2.36 (s, 3 H, CH_3), 2.50−2.53 (m, 1 H), 2.74−2.82 (m, 2 H, CH_2), 3.74 (s, 3 H, OCH_3), 4.68−4.69 (m, 1 H,CH), 5.22 (d, *J* = 1.3 Hz, 1 H), 6.62−6.66 (m, 2 H, Ar), 6.87−6.94 (m, 4 H, Ar), 7.39−7.41 (m, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 399 (19.20) [M^+], 244 (86.24) [M^+ − 155, 91 (100) [$PhMe^+$]. $C_{22}H_{25}NO_4S{\cdot}1/10CH_2Cl_2$: calcd. C 65.13, H 6.24, N 3.44; found C 65.17, H 6.53, N 3.25.

4-Methyl-*N*-[(7-oxocyclohept-1-enyl)(phenyl)methyl]benzenesulfonamide (8a): White solid; m.p. 109−110 °C; 100 mg, 27%. IR (neat): $\tilde{\nu}$ = 1660 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.26−2.04 (m, 6 H, CH_2), 2.11−2.31 (m, 2 H, CH_2), 2.33 (s, 3 H, CH_3), 2.95−3.17 (m, 1 H, CH_2), 5.06 (d, *J* = 9.4 Hz, 1 H, NH), 6.06 (d, *J* = 9.7 Hz, 1 H, CH), 6.48 (t, *J* = 7.6 Hz, 1 H, =CH), 6.91−7.01 (m, 2 H, Ar), 7.05−7.18 (m, 5 H, Ar), 7.39−7.42 (m, 1 H, Ar), 7.59−7.61 (m, 1 H, Ar) ppm. MS (EI): *m*/*z* (%) = 369 (79.71) [M^+ − 155], 91 (100) [$PhMe^+$]. $C_{21}H_{23}NO_3S$: calcd. C 68.26, H 6.27, N 3.79; found C 67.75, H 6.33, N 3.66.

***anti*-4-Methyl-*N*-[(2-oxocyclooct-3-enyl)(phenyl)methyl]benzenesulfonamide (9a):** White solid; m.p. 175−178 °C; 105 mg, 27%. IR (neat): $\tilde{\nu}$ = 1662 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.23−1.88 (m, 6 H, CH_2), 1.90−2.05 (m, 1 H), 2.30 (s, 3 H, CH_3), 2.59−2.67 (m, 1 H), 3.34−3.41 (m, 1 H, CH), 4.53−4.58 (m, 1 H, CH), 5.89 (d, *J* = 12.2 Hz, 1 H, NH), 6.27−6.36 (1H, m, = CH), 6.44 (d, *J* = 8.6 Hz, 1 H, =CH), 6.90−6.94 (m, 2 H, Ar), 6.95−7.08 (m, 5 H, Ar), 7.43−7.49 (m, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 260 (30.26) [M^+ − 155], 91 (100) [$PhMe^+$]. $C_{22}H_{25}NO_3S$: calcd. C 68.90, H 6.53, N 3.66; found C 68.69, H 6.81, N 3.56.

***syn*-4-Methyl-*N*-[(2-oxocyclooct-3-enyl)(phenyl)methyl]benzenesulfonamide (9a):** White solid; m.p. 175−178 °C; 56 mg, 15%. IR (neat): $\tilde{\nu}$ = 1662 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.23−1.90 (m, 6 H, CH_2), 1.90−2.07 (m, 1 H), 2.33 (s, 3 H, CH_3), 2.67−2.75 (m, 1 H), 3.30−3.34 (m, 1 H, CH), 4.46−4.53 (m, 1 H, CH), 5.36 (d, *J* = 7.9 Hz, 1 H, NH), 5.64 (d, *J* = 12.8 Hz, 1 H, =CH), 6.16−6.21 (m, 1 H, =CH), 7.02−7.08 (m, 2 H, Ar), 7.30−7.32 (m, 5 H, Ar), 7.81−7.84 (m, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 260 (30.26) [M^+ − 155], 91 (100) [$PhMe^+$]. $C_{22}H_{25}NO_3S$: calcd. C 68.90, H 6.53, N 3.66; found C 68.69, H 6.81, N 3.56.

***anti*-*N*-[(4-Chlorophenyl)(2-oxocyclooct-3-enyl)methyl]-4-methylbenzenesulfonamide (9b):** White solid; m.p. 150−153 °C; 75 mg, 18%. IR (neat): $\tilde{\nu}$ = 1659 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.23−1.72 (m, 6 H, CH_2), 1.87−2.05 (m, 1 H), 2.34 (s, 3 H, CH_3), 2.64−2.73 (m, 1 H), 3.51−3.54 (m, 1 H, CH), 4.34−4.39 (m, 1 H, CH), 5.91 (d, *J* = 12.2 Hz, 1 H, =CH), 6.31−6.40 (1H, m, =CH), 6.56 (d, *J* = 8.6 Hz, 1 H, NH), 6.84−6.99 (m, 2 H, Ar), 7.01−7.13 (m, 4 H, Ar), 7.44−7.48 (m, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 418 (1.14) [M^+], 294 (100) [M^+ − 124], 91 (42.82) [$PhMe^+$]. $C_{22}H_{24}ClNO_3S$: calcd. C 63.22, H 5.79, N 3.35; found C 63.24, H 5.93, N 3.12.

***syn*-*N*-[(4-Chlorophenyl)(2-oxocyclooct-3-enyl)methyl]-4-methylbenzenesulfonamide (9b):** White solid; m.p. 150−153 °C; 50 mg, 12%. IR (neat): $\tilde{\nu}$ = 1659 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.23−1.72 (m, 6 H, CH_2), 1.87−2.05 (m, 1 H), 2.36 (s, 3 H, CH_3), 2.64−2.73 (m, 1 H), 3.34−3.41 (m, 1 H, CH), 4.43−4.47 (m, 1 H, CH), 5.95 (d, *J* = 12.2 Hz, 1 H, =CH), 6.50−6.53 (1 H, m, =CH), 6.56 (d, *J* = 8.6 Hz, 1 H, NH), 6.84−6.99 (m, 2 H, Ar), 7.01−7.13 (m, 4 H, Ar), 7.44−7.48 (m, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 418 (1.14) [M^+], 294 (100) [M^+ − 124], 91 (42.82) [$PhMe^+$]. $C_{22}H_{24}ClNO_3S$: calcd. C 63.22, H 5.79, N 3.35; found C 63.24, H 5.93, N 3.12.

***anti*-*N*-[(4-Methoxyphenyl)(2-oxocyclooct-3-enyl)methyl]-4-methylbenzenesulfonamide (9c):** White solid: m.p. 135−138 °C; 120 mg, 29%. IR (neat): $\tilde{\nu}$ = 1656 cm^{-1} (C=O). ^1H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.41−1.64 (m, 6 H, CH_2), 1.89−1.98 (m, 1 H), 2.34 (s, 3 H, CH_3), 2.64−2.67 (m, 1 H), 3.34−3.38 (m, 1 H, CH), 3.72 (s, 3 H, OCH_3), 4.39−4.43 (m, 1 H, CH), 5.90 (d, *J* = 12.8 Hz, 1 H, =CH), 6.27−6.37 (1H, m, =CH), 6.27−6.37 (m, 1 H, NH), 6.58−6.60 (m, 2 H, Ar), 6.87−6.91 (m, 2 H, Ar), 6.91−7.05 (m, 2 H, Ar), 7.43−7.46 (m, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 376 (8.09) [M^+ − 37], 290 (100) [M^+ − 123], 91 (95.10) [$PhMe^+$]. $C_{23}H_{27}NO_4S$: calcd. C 66.80, H 6.58, N 3.39; found C 65.33, H 6.72, N 3.44.

Table 11. Crystal data of syn-3b, exo-5d, exo-7a, 9b, 10c and 12b ((AUTHOR: If 9b is orthorhombic, β is by definition 90° [not 90(2)°]; please check! Is 12b really monoclinic or is it orthorhombic; how significant is the β value? Please check!))

	syn-**3b**	*exo*-**5d**	*exo*-**7a**	**9b**	**10c**	12b
Empirical formula	$C_{19}H_{18}O_3$	$C_{21}H_{23}O_4NS$	$C_{21}H_{21}O_3NS$	$C_{22}H_{24}ClO_3NS$	$C_{23}H_{28}ClO_4NS$	$C_{29}H_{27}Cl_2O_3NS$
Formula mass	294.13	385.48	367.45	417.93	449.98	540.48
Temperature [K]	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	triclinic	orthorhombic	monoclinic	orthorhombic	triclinic	monoclinic
Lattice type	primitive	primitive	primitive	primitive	primitive	primitive
Unit cell dimensions						
a [Å]	12.0362(9)	7.935(3)	11.8564811)	7.7059(10)	11.8173(19)	12.642(2)
b [Å]	12.4221(8)	10.593(3)	6.4710(6)	11.4103(14)	12.932(2)	6.7653(10)
c [Å]	14.2841(10)	22.562(2)	12.2722(11)	24.388(3)	15.095(3)	31.543(5)
α [°]	65.6880	90	90	90	85.122(3)	90
β [°]	89.3970	90	94.886(2)	90	89.983	90
γ [°]	65.9370	90	90	90	89.923	90
V [Å^3]	1745.1(2)	1896(1)	938.14(15)	2144.3(5)	2298.6(6)	2697.8(7)
Space group	$P\bar{1}$	$Pna2_1$	*Pna*2(1)	*Pna*2(1)	$P\bar{1}$	$P2_1/c$
*Z*e	3	4	2	4	2	4
$D_{calcd.}$ [g/cm^3]	1.273	1.350	1.301	1.295	1.300	1.221
F(000)	704.00	816.00	388.00	880.00	952	1128.00

***syn*-*N*-[(4-Methoxyphenyl)(2-oxocyclooct-3-enyl)methyl]-4-methylbenzenesulfonamide (9c):** White solid: m.p. 135−138 °C; 82 mg, 20%. IR (neat): $\tilde{\nu}$ = 1656 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.41−1.75 (m, 6 H, CH_2), 1.89−1.98 (m, 1 H), 2.29 (s, 3 H, CH_3), 2.54−2.69 (m, 1 H), 3.31−3.40 (m, 1 H, CH), 3.66 (s, 3 H, OCH_3), 4.47−4.53 (m, 1 H, CH), 5.68 (d, *J* = 12.8 Hz, 1 H, =CH), 6.19−6.27 (m, 1 H, =CH), 6.27−6.37 (m, 1 H, NH), 6.83−6.87 (m, 2 H, Ar), 7.05−7.10 (m, 2 H, Ar), 7.30−7.33 (m, 2 H, Ar), 7.81−7.84 (m, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 376 (8.09) [M$^+$ − 37], 290 (100) [M$^+$ − 123], 91 (95.10) [PhMe$^+$]. $C_{23}H_{27}NO_4S$: calcd. C 66.80, H 6.58, N 3.39; found C 65.33, H 6.72, N 3.44.

***N*-[(4-Methoxy-2-oxocyclooctyl)(phenyl)methyl]-4-methylbenzenesulfonamide (10a):** Colorless, oily compound; 22 mg, 6%; 187 mg, 45%. IR (neat): $\tilde{\nu}$ = 1698 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.27−1.94 (m, 8 H, CH_2), 2.34−2.51 (m, 2 H, CH_2), 2.36 (s, 3 H, CH_3), 2.79−2.80(m, 1 H, CH), 3.29 (s, 3 H, OCH_3), 3.55−3.56 (m, 1 H, CH), 4.39−4.44 (m, 1 H, CH), 6.18 (d, *J* = 8.6 Hz, 1 H, NH), 7.01−7.16 (m, 7 H, Ar), 7.46−7.49 (m, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 260 (100) [M$^+$ − 155], 155 (43.69) [M$^+$ − 260], 91 (53.18) [PhMe$^+$]. HRMS: calcd. for $C_{16}H_{21}NO_2$ [M$^+$ − 156] 259.1572; found 259.1603.

***N*-[(4-Chlorophenyl)(4-methoxy-2-oxocyclooctyl)methyl]-4-methylbenzenesulfonamide (10b):** Colorless solid; m.p. 136−140 °C; 230 mg, 51%. IR (neat): $\tilde{\nu}$ = 1698 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.33−1.93 (m, 8 H, CH_2), 2.20−2.46 (m, 2 H), 2.35 (s, 3 H, CH_3), 2.68−2.76 (m, 1 H, CH), 3.28 (s, 3 H, OCH_3), 3.49−3.57 (m, 1 H, CH), 4.34−4.39 (m, 1 H, CH), 5.96 (d, *J* = 7.9 Hz, 1 H, NH), 6.92−6.95 (m, 2 H, Ar), 7.08−7.12 (m, 4 H, Ar), 7.43−7.46 (m, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 433 (0.21) [M$^+$ − 15], 294 (35.86) [M$^+$ − 155], 91 (100) [PhMe$^+$]. $C_{23}H_{28}ClNO_4S$: calcd. C 61.39, H 6.27, N 3.11; found C 61.06, H 6.42, N 3.26.

***N*-[(4-Methoxy-2-oxocyclooctyl)(4-methoxyphenyl)methyl]-4-methylbenzenesulfonamide (10c):** Light yellow solid; m.p. 65−67 °C; 196 mg, 44%. IR (neat): $\tilde{\nu}$ = 1702 cm^{-1} (C=O). ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.24−1.83 (m, 8 H, CH_2), 2.02−2.32 (m, 2 H), 2.36 (s, 3 H, CH_3), 2.68 (m, 1 H, CH), 3.26 (s, 3 H, OCH_3), 3.39−3.42 (m, 1 H, CH), 3.73 (s, 3 H, OCH_3) 4.36−4.42 (m, 1 H, CH), 5.32 (d, *J* = 8.4 Hz, 1 H, NH), 6.58−6.64 (m, 2 H, Ar), 6.76−6.91 (m, 2 H, Ar), 7.04−7.10 (m, 2 H, Ar), 7.44−7.49 (m, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 290 (100) [M$^+$ − 155], 91 (75.76) [PhMe$^+$]. $C_{24}H_{31}NO_5S$: calcd. C 64.69, H 7.01, N 3.14; found C 64.72, H 7.04, N 3.05.

***N*-[(3-Benzylidene-2-oxocyclooct-4-enyl)(phenyl)methyl]-4-methylbenzenesulfonamide (12a):** m.p. 208−210 °C; 188 mg, 40%. IR (KBr): $\tilde{\nu}$ = 1674 (C=O), 1584, 1215 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ = 1.30−1.45 (m, 1 H, CH_2), 1.80−2.0 (m, 3 H, CH_2), 2.12−2.42 (m, 2 H, CH_2), 2.33 (s, 3 H, CH_3), 3.42 (t, *J* = 11.4 Hz, 1 H, CH), 4.37 (t, *J* = 9.1 Hz, 1 H, CH), 5.05 (d, *J* = 9.1 Hz, 1 H, CH), 5.85−6.0 (m, 1 H, =CH), 6.07 (s, 1 H, =CH), 6.10 (d, *J* = 9.1 Hz, 1 H, NH), 6.79 (d, *J* = 8.6 Hz, 2 H, Ar), 6.98−7.12 (m, 6 H, Ar), 7.20−7.30 (m, 4 H, Ar), 7.48 (d, *J* = 8.6 Hz, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 454 [M$^+$ − 17]. $C_{29}H_{29}NO_3S$: calcd. C 73.86, H 6.20, N 2.97; found C 73.72, H 6.24, N 2.88.

***N*-[(3-Chlorobenzylidene-2-oxocyclooct-4-enyl](4-chlorophenyl)-methyl]-4-methylbenzenesulfonamide (12b):** M.p. 204−206 °C; 184 mg, 34%. IR (KBr): $\tilde{\nu}$ = 1674 (C=O), 1496, 1216 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz, TMS): δ = 1.30−1.45 (m, 1 H, CH_2), 1.72−2.0 (m, 3 H, CH_2), 2.12−2.42 (m, 2 H, CH_2), 2.37 (s, 3 H, CH_3), 3.41 (t, *J* = 11.4 Hz, 1 H, CH), 4.37 (t, *J* = 9.1 Hz, 1 H, CH), 5.29 (d, *J* = 9.1 Hz, 1 H, CH), 5.85−6.0 (m, 1 H, =CH), 6.02 (s, 1 H, =CH), 6.10 (d, *J* = 9.1 Hz, 1 H, NH), 6.79 (d, *J* = 8.6 Hz, 2 H, Ar), 6.98−7.12 (m, 6 H, Ar), 7.20−7.30 (m, 4 H, Ar), 7.48 (d, *J* = 8.6 Hz, 2 H, Ar) ppm. MS (EI): *m*/*z* (%) = 384 [M$^+$ − 156]. $C_{29}H_{27}Cl_2NO_3S$: calcd. C 64.44, H 5.04, N 2.59; found C 64.42, H 4.99, N 2.52.

X-ray Crystal Data: Diffractometer: Rigaku AFC7R. *syn*-**3b**: *R*, *Rw*: 0.0762, 0.2311; CCDC-176795. *exo*-**5d**: *R*, *Rw*: 0.062, 0.063; CCDC-165558. *exo*-**7a**: *R*, *Rw*: 0.0459, 0.0763; CCDC-175594. **9b**: *R*, *Rw*: 0.0561, 0.1263; CCDC-175595. **10c**: *R*, *Rw*: 0.0467, 0.0566; CCDC-193516. **12b**: *R*, *Rw*: 0.0442, 0.0516; CCDC-175596. The CCDC numbers refer to the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cam-

bridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We thank the State Key Project of Basic Research (Project 973) (no. G2000048007) and the National Natural Science Foundation of China for financial support (20025206). We also thank the Inoue Photochirogenesis Project (ERATO, JST) for chemical reagents.

[1] [1a] E. Ciganek, *Org. React*. **1997**, *51*, 201−350. [1b] D. Basavaiah, P. D. Rao, R. S. Hyma, *Tetrahedron* **1996**, *52*, 8001−8062. [1c] S. E. Drewes, G. H. P. Roos, *Tetrahedron* **1988**, *44*, 4653−4670. [1d] L. J. Brzezinski, S. Rafel, J. M. Leahy, *J. Am. Chem. Soc.* **1997**, *119*, 4317. [1e] T. Miyakoshi, S. Saito, *Nippon Kagaku Kaishi,* **1983**, 1623−1628; *Chem. Abstr.* **1984**, *100*, 156191g. [1f] I. E. Marko, P. G. Giles, N. J. Hindley, *Tetrahedron* **1997**, *53*, 1015. [1g] H. Richter, G. Jung, *Tetrahedron Lett.* **1998**, *39*, 2729−2730. [1h] A. G. M. Barrett, A. S. Cook, A. Kamimura, *Chem. Commun.* **1999**, 2533−2534. [1i] E. P. Kunidig, L. H. Xu, P. Romanens, G. Bernardinelli, *Tetrahedron Lett.* **1993**, *34*, 7049−7052. [1j] V. K. Aggarwal, A. Mereu, G. J. Tarver, R. MaCague, *J. Org. Chem.* **1998**, *63*, 7183−7189. [1k] M. Kawamura, S. Kobayashi, *Tetrahedron Lett.* **1999**, *40*, 1539−1542. [1l] M. Ono, K. Nishimura, Y. Nagaoka, K. Tomioka, *Tetrahedron Lett.* **1999**, *40*, 1509−1512.

[2] [2a] Y. Iwabuchi, M. Nakatani, N. Yokoyama, S. Hatakeyama, *J. Am. Chem. Soc.* **1999**, *121*, 10219. [2b] A. G. M. Barrett, A. S. Cook, A. Kamimura, *Chem. Commun.* **1998**, 2533−2534. [2c] P. Langer, *Angew. Chem. Int. Ed*. **2000**, *39*, 3049−3052.

[3] [3a] A. B. Baylis, M. E. D. Hillman, *Ger. Offen*. **1972**, 2,155,113; *Chem. Abstr*. **1972**, *77*, 34174q; M. E. D. Hillman, A. B. Baylis, *U. S. Patent* **1973**, 3,743,669. [3b] K. Morita, Z. Suzuki, H. Hirose, *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2815−2816.

[4] [4a] M. Shi, J.-K. Jiang, Y.-S. Feng, *Org. Lett.* **2000**, *2*, 2397−2400. [4b] M. Shi, Y.-S. Feng, *J. Org. Chem.* **2001**, *66*, 406−411. [4c] M. Shi, J.-K. Jiang, S.-C. Cui, Y.-S. Feng, *J. Chem. Soc., Perkin Trans. 1* **2001**, 390−393. [4d] M. Shi, J.-K. Jiang, *Tetrahedron* **2000**, *56*, 4793−4797. [4e] M. Shi, C.-Q. Li, J.-K. Jiang, *Chem. Commun.* **2001**, 833−834. [4f] M. Shi, Y.-M. Xu, *Chem. Commun.* **2001**, 1876−1877.

[5] The Baylis−Hillman reaction between 2-cyclopenten-1-one and aldehydes has been reported before; see: Y. M. A. Yamada, S. Ikegami, *Tetrahedron Lett.* **2000**, *41*, 2165−2168. However, the formation of the abnormal Baylis−Hillman adduct **3** is first reported in this paper. For previous reports related to the Baylis−Hillman reactions between methyl acrylate and imines; see: [5a] P. Perlmutter, C. C. Teo, *Tetrahedron Lett.* **1984**, *25*, 5951−5952. [5b] M. Takagi, K. Yamamoto, *Tetrahedron* **1991**, *47*, 8869−8882. For a previous report related to Baylis−Hillman reactions between methyl vinyl ketone and imines generated in situ; see: [5c] S. Bertenshow, M. Kahn, *Tetrahedron Lett.* **1989**, *30*, 2731−2732.

[6] B. E. Love, P. S. Raje, T. C. Williams, *Synlett* **1994**, 493−494.

[7] Y. Ito, S. Fuji, M. Nakatsuka, F. Kawamoto, T. Saegusa, *J. Org. Chem.* **1976**, *41*, 2073−2074.

[8] [8a] E. Cope, *J. Am. Chem. Soc.* **1950**, *72*, 1128−1131. [8b] V. Heap, G. H. Whitham, *J. Chem. Soc. B* **1966**, 164−170. [8c] E. Cope, *J. Am. Chem. Soc.* **1957**, *79*, 3905−3907.

Received April 19, 2002
[O02216]