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Baylis–Hillman reactions of *N*-tosyl aldimines and aryl aldehydes with 3-methylpenta-3,4-dien-2-one†

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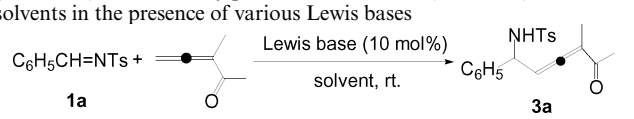
The attempted Baylis–Hillman reactions of *N*-tosyl aldimines and aryl aldehydes with 3-methylpenta-3,4-dien-2-one gave the corresponding Baylis–Hillman adducts **3** and **6** in moderate to good yields in the presence of DMAP in DMSO, respectively. In the case of the aza-Baylis–Hillman reactions of *N*-tosyl aldimines with 3-methylpenta-3,4-dien-2-one catalyzed by PBu_3, the corresponding aza-Baylis–Hillman derivatives **4** and **5** were formed at the same time.

Investigation of the Baylis–Hillman reaction has made great progress,[1] including development of a catalytic, asymmetric version,[2] since Baylis and Hillman first reported the reaction of acetaldehyde with ethyl acrylate and acrylonitrile in the presence of catalytic amounts of a strong Lewis base such as 1,4-diazabicyclo[2,2,2]octane (DABCO) in 1972.[3] However, the reaction has traditionally suffered from low reaction rates and limited substrate scope. Therefore, a number of methods have been developed to accelerate this reaction.[4] In addition, aldimines have also been employed as electrophiles in place of aldehydes in this reaction providing a very useful and rapid entry to the corresponding β-amino products.[5] During our ongoing investigation on the aza-Baylis–Hillman reactions of *N*-tosyl aldimines with α,β-unsaturated carbonyl compounds,[6] we found that the aza-Baylis–Hillman reaction of *N*-tosyl aldimines with ethyl 2,3-butadienoate or penta-3,4-dien-2-one gave azetidine derivatives in the presence of DABCO and in the case of the aza-Baylis–Hillman reaction of *N*-tosyl aldimines with ethyl 2,3-butadienoate catalyzed by 4-(*N*,*N*-dimethylamino)pyridine (DMAP), novel dihydropyridine derivatives were formed.[7] These interesting results stimulate us to further investigate such unprecedented Baylis–Hillman reactions. In this paper, we wish to report the Baylis–Hillman reaction of *N*-tosyl aldimines **1** and aryl aldehydes **2** with 3-methylpenta-3,4-dien-2-one catalyzed by nitrogen and phosphine Lewis bases.[8,9,10] The corresponding interesting Baylis–Hillman adducts are derived from the methyl group in 3-methylpenta-3,4-dien-2-one to block the normal Baylis–Hillman reaction site.

In the aza-Baylis–Hillman reaction of *N*-tosyl aldimine **1a** with 3-methylpenta-3,4-dien-2-one catalyzed by nitrogen Lewis bases such as DABCO, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or DMAP, we found that the corresponding aza-Baylis–Hillman adduct **3a** was exclusively produced in the presence of DMAP or DBU. The results are summarized in Table 1. In THF, toluene or Et_2O, **3a** was obtained in low yields at room temperature (Table 1, entries 2–5). In polar solvents such as DMF, MeCN or DMSO, **3a** was obtained in higher yields within a shorter reaction time (Table 1, entries 6–10). In the presence of 4 Å molecular sieves to get rid of the ambient moisture in THF and MeCN, the reactions were accelerated and **3a** could be obtained in higher yields (Table 1, entries 3 and 8). In DMSO, **3a** was formed in 81% within 10 minutes (Table 1, entry 9). In addition, **3a** was obtained in a similar yield in the presence of 4 Å molecular sieves (Table 1, entry 10). DABCO showed no catalytic ability for this reaction (Table 1, entries 1 and 14). DBU also can promote this reaction under similar conditions, but it is not as effective as DMAP (Table 1, entries 11–13). In all these cases, **3a** was obtained as a pair of diastereoisomeric mixtures in a 1 : 1 ratio on the basis of ^{1}H NMR spectroscopic data.

Table 1 Aza-Baylis–Hillman reactions of *N*-tosyl aldimine **1a** (0.5 mmol) with 3-methylpenta-3,4-dien-2-one (1.0 mmol) in various solvents in the presence of various Lewis bases



1a 3a

Entry	Lewis base	Solvent	Time/h[b]	Yield (%)[a] **3a**[c]
1	DABCO	THF	36	NR
2	DMAP	THF	12	17
3	DMAP	THF[d]	2	32
4	DMAP	PhMe	24	Trace
5	DMAP	Et_2O	1	19
6	DMAP	DMF	1/6	71
7	DMAP	MeCN	1/6	49
8	DMAP	MeCN[d]	1/12	53
9	DMAP	DMSO	1/6	81
10	DMAP	DMSO[d]	1/6	80
11	DBU	DMF	1/6	51
12	DBU	THF	4	33
13	DBU	DMSO	1/6	60
14	DABCO	DMSO	24	Trace

[a] Isolated yields. [b] The reaction time is determined by TLC on the basis of consuming the starting materials **1a**. [c] Mixtures of the diastereoisomers with 1 : 1 ratio were obtained on the basis of ^{1}H NMR spectroscopy. [d] 4 Å MS (100 mg) was added.

Next, we examined the aza-Baylis–Hillman reactions of other *N*-tosyl aldimines with 3-methylpenta-3,4-dien-2-one under these optimized conditions. The results are shown in Table 2. The corresponding adducts **3** were obtained in moderate to good yields within 10 minutes as a pair of diastereoisomeric mixtures for a variety of *N*-tosyl aldimines at room temperature (Table 2, entries 1–11).

On the other hand, using tertiary phosphine as a Lewis base promoter in this type of aza-Baylis–Hillman reaction, we found that the corresponding aza-Baylis–Hillman adducts **4a** and **5a** were formed at the same time. The results on the screen of the reaction conditions are summarized in Table 3. The best reaction conditions were found to carry out the

† Electronic supplementary information (ESI) available: ^{1}H NMR and ^{13}C spectroscopic and analytic data for compounds **3–6** and the ORTEP drawing for **3k** and detailed description of experimental procedures. See http://dx.doi.org/10.1039/b510572b

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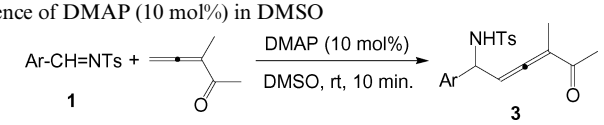
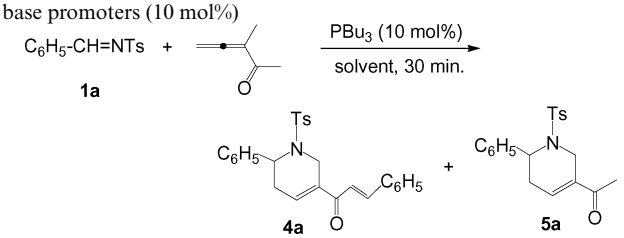
Table 2 Aza-Baylis–Hillman reactions of the other *N*-tosyl aldimines (0.5 mmol) with 3-methylpenta-3,4-dien-2-one (1.0 mmol) in the presence of DMAP (10 mol%) in DMSO



Entry	Ar	Yield (%)[a] **3**[b]
1	*p*-MeC_6H_4	**3b**, 74
2	*p*-EtC_6H_4	**3c**, 76
3	*p*-$MeOC_6H_4$	**3d**, 70
4	*p*-$Me_2NC_6H_4$	**3e**, 62
5	*p*-FC_6H_4	**3f**, 66
6	*p*-ClC_6H_4	**3g**, 76
7	*p*-BrC_6H_4	**3h**,74
8	*p*-$NO_2C_6H_4$	**3i**, 40
9	*m*-$NO_2C_6H_4$	**3j**, 64
10	*o*,*m*-$Cl_2C_6H_3$	**3k**, 60
11	1-Naphthyl	**3l**, 81

[a] Isolated yields. [b] Mixtures of the diastereoisomers with 1 : 1 ratio were obtained on the basis of ^{1}H NMR spectroscopy.

Table 3 Reactions of *N*-tosyl aldimines with 3-methylpenta-3,4-dien-2-one in various solvents in the presence of a variety of phosphine Lewis base promoters (10 mol%)



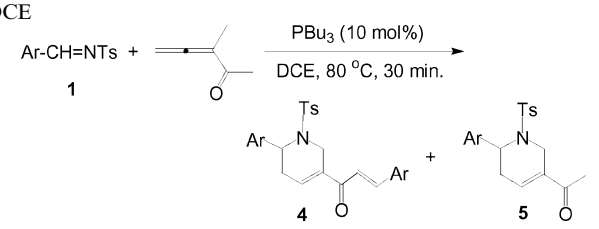
Entry	Lewis base	Solvent	Temp./°C	Yield (%)[a] **4a**	**5a**
1	Ph_3P	THF	20	Trace	0
2	Ph_2PMe	THF	20	22	0
3	Ph_2PMe	CH_2Cl_2	20	32	0
4	$PhPMe_2$	THF	20	Trace	0
5	PMe_3	THF	20	16	16
6	PBu_3	THF	20	18	22
7	PBu_3	DMF	20	44	0
8	PBu_3	CH_3CN	20	Trace	0
9	PBu_3	DMSO	20	36	0
10	PBu_3	CH_2Cl_2	20	51	0
11	PBu_3	DCE	40	45	0
12	PBu_3	DCE	60	47	16
13	PBu_3	DCE	80	65	29
14	PBu_3	DMSO	80	47	15
15	PBu_3	DMSO	120	Trace	0

[a] Isolated yields.

reaction in 1,2-dichloroethane (DCE) at 80 °C with PBu_3 as a promoter. Under these optimized conditions, we examined a variety of *N*-tosyl aldimines with 3-methylpenta-3,4-dien-2-one. The corresponding adducts **4** were formed as the major products in moderate yields with *E*-configuration along with the formation of adducts **5** in some cases (Table 4, entries 1–8). Similar adducts to compounds **5** were also observed in the reaction of 2-methyl-2,3-butadienoate with *N*-tosyl aldimines catalyzed by tributylphosphine.[9]

The traditional Baylis–Hillman reactions[10] of aryl aldehydes with 3-methylpenta-3,4-dien-2-one was also examined in various solvents by a variety of Lewis base promoters. We found that this reaction also gave the corresponding Baylis–Hillman adducts. The best reaction conditions were found to carry out the reaction in DMSO at 80 °C in the presence of DMAP (20 mol%). Under these optimized conditions, a variety of

Table 4 Reactions of *N*-tosyl aldimines **1** (0.5 mmol) with 3-methylpenta-3,4-dien-2-one (1.0 mmol) in the presence of PBu_3 (10 mol%) in DCE



Entry	Ar	Yield (%)[a] **4**	**5**
1	C_6H_5	**4a**,65	**5a**, 29
2	*p*-MeC_6H_4	**4b**, 57	**5b**, 14
3	*p*-EtC_6H_4	**4c**, 60	**5c**, 20
4	*p*-$MeOC_6H_4$	**4d**, 42	Trace
5	*p*-FC_6H_4	**4e**, 57	Trace
6	*p*-ClC_6H_4	**4f**, 49	**5f**, 20
7	p-BrC_6H_4	**4g**, 67	**5g**, 15
8	1-Naphthyl	**4h**, 52	Trace

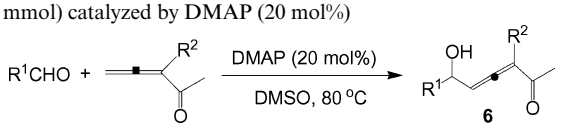
[a] Isolated yields.

aryl aldehydes were examined and the corresponding Baylis–Hillman adducts **6** were obtained in moderate to good yields as a pair of diastereoisomeric mixtures within one hour in most cases (Table 5, entries 2–8). The Baylis–Hillman reaction of *p*-chlorobenzaldehyde with 3-benzylpenta-3,4-dien-2-one could also proceed smoothly under the same conditions to give the corresponding Baylis–Hillman adduct **6i** in 64% yield (Table 5, entry 9).

Their structures were determined by spectroscopic data, HRMS and microanalyses and X-ray diffraction. The ORTEP drawing of **3k** is shown in Fig. 1 and crystal data are summarized in the Supporting Information.[11]

The mechanisms of these unprecedented Baylis–Hillman reactions have not been unequivocally established, but plausible explanations are proposed in Schemes 1 and 2 based on previous investigations.[7–10] The nitrogen Lewis base DMAP acts as a nucleophilic trigger and produces the intermediate **A-1**, which exists as a resonance-stabilized zwitterionic intermediate **A-1** (enolate) or zwitterionic intermediate **C-1** (allylic carbanion) represented by a common delocalized structure **B-1**. Due to the steric hindrance (methyl group), intermediate **A-1** (enolate) is difficult to react with an electrophile to give the aldol reaction intermediate. Therefore, the allylic carbanion **C-1** adds to the *N*-tosyl aldimine or aldehyde to give the intermediate **D-1**

Table 5 Baylis–Hillman Reactions of Aryl Aldehydes (0.5 mmol) with 3-methylpenta-3,4-dien-2-one and 3-benzylpenta-3,4-dien-2-one (2.0 mmol) catalyzed by DMAP (20 mol%)



Entry	R^1	R^2	Time/h	Yield (%)[a] **6**[b]
1	C_6H_5	Me	5	**6a**, 50
2	*p*-FC_6H_4	Me	1/2	**6b**, 75
3	*p*-ClC_6H_4	Me	1/2	**6c**, 61
4	*o*-ClC_6H_4	Me	1/2	**6d**, 71
5	*p*-BrC_6H_4	Me	1/2	**6e**, 70
6	*p*-$NO_2C_6H_4$	Me	1/6	**6f**, 45
7	*m*-$NO_2C_6H_4$	Me	1/6	**6g**, 64
8	*o*,*m*-$Cl_2C_6H_3$	Me	1/2	**6h**, 70
9	*p*-ClC_6H_4	Bn	12	**6i**, 64

[a] Isolated yields. [b] Mixtures of the diastereoisomers with 1 : 1 ratio were formed on the basis of ^{1}H NMR spectroscopy. [c] 4 Å MS was added.

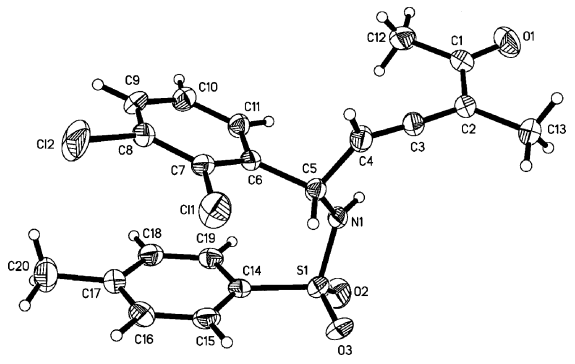
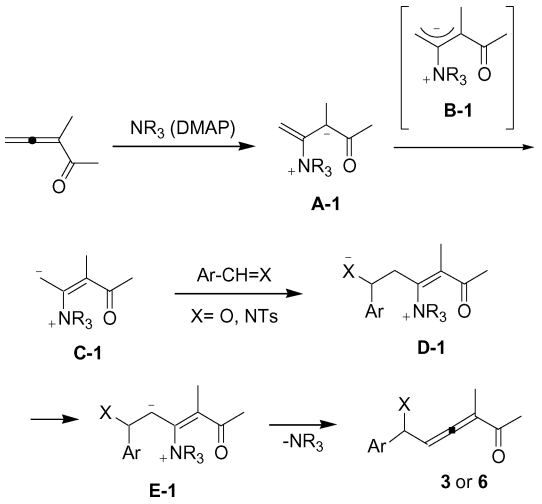


Fig. 1 ORTEP drawing of **3k**.

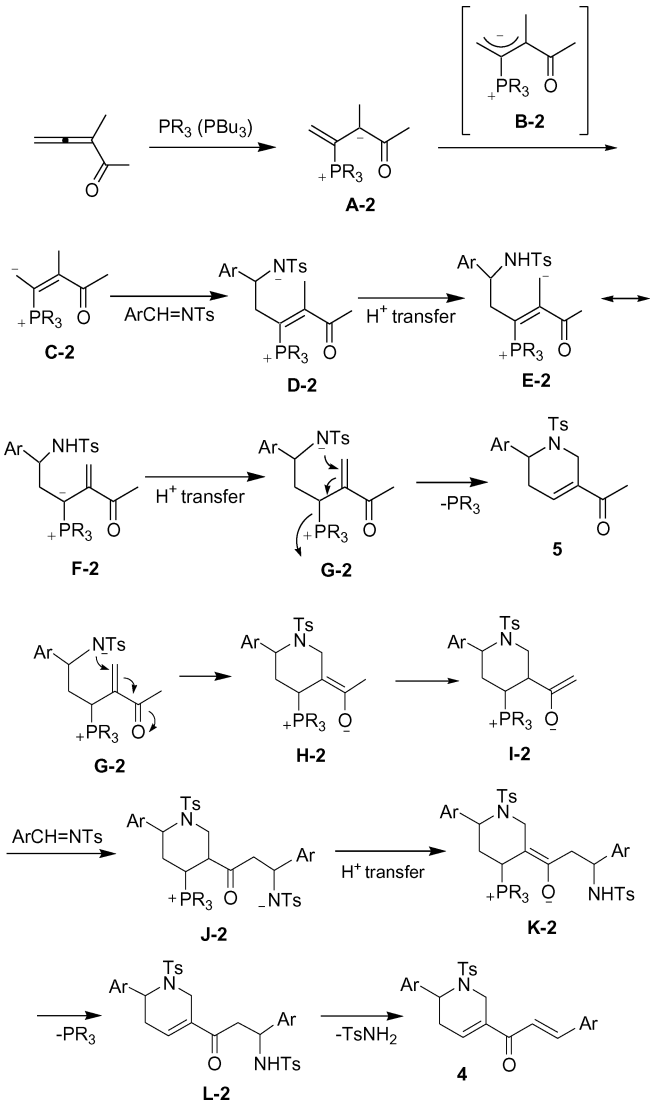
which undergoes a proton transfer to give another zwitterionic intermediate **E-1**. The elimination of NR_3 from **E-1** affords product **3** or **6** and regenerates DMAP. However, in the case of PBu_3, the corresponding zwitterionic intermediate **C-2** (allylic carbanion) adds to the *N*-tosyl aldimine to afford the intermediate **D-2**, which undergoes intramolecular proton transfer to give the intermediate **E-2**. The intermediate **E-2** exists as a resonance-stabilized zwitterionic intermediate **F-2**. The proton transfer produces the intermediate **G-2** and the subsequent intramolecular Michael addition gives the product **5**. This mechanism, as proposed by others,[9] benefits from the ability of phosphorus to stabilize the ylide structure **F-2**. In contrast, the amine-catalyzed pathway does not benefit from the similar stabilization.[12,13] Therefore, the reaction proceeds *via* two different pathways with the catalysis of nitrogen or phosphine Lewis base (Scheme 2).



Scheme 1 A plausible mechanism for the aza-Baylis–Hillman reaction catalyzed by DMAP.

From the intermediate **G-2**, the zwitterionic intermediate **H-2** can be formed *via* a Michael addition, which produces the zwitterionic intermediate **I-2** (enolate). The nucleophilic addition of **I-2** to another molecule of *N*-tosyl aldimines gives another zwitterionic intermediate **J-2**. After proton transfer, regeneration of catalyst, and *trans*-elimination of tosylamine ($TsNH_2$), product **4** is produced. The control experiment has indicated that in the presence of PBu_3, the isolated aza-Baylis–Hillman adduct **5** did not react with the second *N*-tosyl aldimine to produce compound **4**. This result suggests that the compounds **4** are indeed derived from the consequence as shown in Scheme 2. The acidity of the allylic protons in the intermediates **D-1** (Scheme 1) and **D-2** (Scheme 2) plays a key role for phosphine and nitrogen Lewis bases to give different results.

In this paper, we disclose the unprecedented Baylis–Hillman reactions of *N*-tosyl aldimines and aryl aldehydes with 3-



Scheme 2 A plausible mechanism for the aza-Baylis–Hillman reaction catalyzed by PBu_3.

methylpenta-3,4-dien-2-one by means of DMAP and PBu_3 under mild conditions. Most of these interesting Baylis–Hillman reactions completed at 20 °C or 80 °C within 10 min–several hours to give the corresponding Baylis–Hillman adducts **3**, **4**, **5** or **6** in moderate to good yields. Efforts are under way to elucidate the mechanistic details and Lewis base effects of these Baylis–Hillman or aza-Baylis–Hillman reactions.

Experimental

General remarks

Mps were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer for solutions in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; *J*-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. Satisfactory CHN microanalyses were obtained with a Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at medium pressure. The starting materials such as *N*-tosyl aldimines,[14] 3-methylpenta-3,4-dien-2-one,[15] were prepared according to the literatures.

The aza-Baylis–Hillman reaction of *N*-tosyl aldimines with 3-methylpenta-3,4-dien-2-one catalyzed by DMAP. Typical reaction procedure of *N*-tosyl aldimines with 3-methylpenta-3,4-dien-2-one at room temperature catalyzed by DMAP

To a Schlenk tube with *N*-(*p*-methylbenzenesulfonyl)benzaldimine (130 mg, 0.5 mmol) and DMAP (6 mg, 0.05 mmol) in DMSO (1 mL) was added 3-methylpenta-3,4-dien-2-one (96 mg, 1 mmol) and the reaction mixture was stirred for 10 min at room temperature (20 °C). The reaction mixture was washed with water (10 mL) and extracted with dichloromethane (20 mL). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: EtOAc–petroleum = 1 : 3) to give adduct **3a** (144 mg, yield 81%) as a white solid.

In all cases, **3** was obtained as a pair of diastereoisomeric mixtures in a 1 : 1 ratio on the basis of ^{1}H NMR spectroscopic data and could not be separated by silica gel column chromatography. ^{13}C NMR spectroscopic data also indicated a pair of diastereoisomeric mixtures in a 1 : 1 ratio.

4-Methyl-*N*-(4-methyl-5-oxo-1-phenylhexa-2,3-dienyl)benzenesulfonamide 3a. Mp 91–95 °C; IR (CH_2Cl_2) ν 3273, 1680 (C=O), 1598, 1330, 1160, 1093 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**3a** and (1*S*,3*S*)-**3a**: 1.65 (3H, d, J = 2.4 Hz, CH_3), 2.08 (3H, s, CH_3), 2.39 (3H, s, CH_3), 5.05–5.11 (2H, m, CH, NH), 5.76–5.77 (1H, m, =CH), 7.10–7.15 (2H, m, ArH), 7.19–7.27 (5H, m, ArH), 7.62–7.67 (2H, m, ArH); (1*S*,3*R*)-**3a** and (1*R*,3*S*)-**3a**: 1.72 (3H, d, J = 2.4 Hz, CH_3), 2.14 (3H, s, CH_3), 2.40 (3H, s, CH_3), 5.05–5.11 (2H, m, CH, NH), 5.70–5.71 (1H, m, =CH), 7.10–7.15 (2H, m, ArH), 7.19–7.27 (5H, m, ArH), 7.62–7.67 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.92, 13.02, 21.37 (2C), 26.71, 26.76, 56.24, 56.30, 96.83, 96.92, 107.41, 107.65, 126.45, 126.50, 126.88, 126.95, 127.97 (2C), 128.51, 128.59, 129.44, 129.47, 137.31 (2C), 138.94, 139.00, 143.34, 143.40, 198.44, 198.51, 211.72, 211.82; MS (EI) *m*/*e* 356 (M^+ + 1, 2.51), 355 (M^+, 0.44), 260 (M^+ − 95, 100), 185 (M^+ − 170, 23.07), 155 (M^+ − 200, 51.31), 91 (M^+ − 264, 68.34) [Found: C, 67.45; H, 6.13; N, 3.83%. $C_{20}H_{21}O_3NS$ requires C, 67.58; H, 5.95; N, 3.94%].

4-Methyl-*N*-(4-methyl-5-oxo-1-*p*-tolylhexa-2,3-dienyl)benzenesulfonamide 3b. Mp 107–110 °C; IR (CH_2Cl_2) ν 3271, 1952, 1681 (C=O), 1598, 1435, 1331, 1160, 1094 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**3b** and (1*S*,3*S*)-**3b**:1.63 (3H, d, J = 2.4 Hz, CH_3), 2.07 (3H, s, CH_3), 2.28 (3H, s, CH_3), 2.39 (3H, s, CH_3), 5.00–5.07 (1H, m, CH), 5.52–5.56 (1H, m, NH), 5.72–5.75 (1H, m, =CH), 7.01 (4H, d, J = 6.6 Hz, ArH), 7.17–7.22 (2H, m, ArH), 7.62–7.67 (2H, m, ArH); (1*S*,3*R*)-**3b** and (1*R*,3*S*)-**3b**: 1.68 (3H, d, J = 2.4 Hz, CH_3), 2.12 (3H, s, CH_3), 2.29 (3H, s, CH_3), 2.40 (3H, s, CH_3), 5.00–5.07 (1H, m, CH), 5.52–5.56 (1H, m, NH), 5.66–5.69 (1H, m, =CH), 7.01 (4H, d, J = 6.6 Hz, ArH), 7.17–7.22 (2H, m, ArH), 7.62–7.67 (2H, m, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.93, 13.05, 20.94 (2C), 21.36 (2C), 26.72, 26.78, 56.04, 56.09, 96.89, 97.01, 107.29, 107.54, 126.37, 126.41, 126.89, 126.96, 129.14, 129.22, 129.40, 129.42, 135.98, 136.05, 137.36 (2C), 137.74 (2C), 143.24, 143.31, 198.52, 198.58, 211.68, 211.75; MS (EI) *m*/*e* 370 (M^+ + 1, 2.29), 274 (M^+ − 95, 100), 199 (M^+ − 170, 65.72), 155 (M^+ − 214, 43.38), 91 (M^+ − 278, 71.76) [Found: C, 68.15; H, 6.28; N, 3.63%. $C_{21}H_{23}O_3NS$ requires C, 68.27; H, 6.27; N, 3.79%].

***N*-[1-(4-Ethylphenyl)-4-methyl-5-oxohexa-2,3-dienyl]-4-methylbenzenesulfonamide 3c.** Mp 78–81 °C; IR (CH_2Cl_2) ν 3271, 1952, 1681 (C=O), 1435, 1330, 1160, 1094 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**3c** and (1*S*,3*S*)-**3c**: 1.16 (3H, t, J = 7.8 Hz, CH_3), 1.61 (3H, d, J = 3.0 Hz, CH_3), 2.06 (3H, s, CH_3), 2.36 (3H, s, CH_3), 2.56 (2H, d, J = 7.8 Hz, CH_2), 5.06 (1H, dd, J = 14.1, 7.5 Hz, CH), 5.71–5.74 (1H, m, =CH), 6.00–6.02 (1H, m, NH), 6.99–7.03 (4H, m, ArH), 7.13–7.18 (2H, m, ArH), 7.60–7.65 (2H, m, ArH); (1*S*,3*R*)-**3c** and (1*R*,3*S*)-**3c**: 1.16 (3H, t, J = 7.8 Hz, CH_3), 1.65 (3H, d, J = 3.0 Hz, CH_3), 2.10 (3H, s, CH_3), 2.37 (3H, s, CH_3), 2.56 (2H, d, J = 7.8 Hz, CH_2), 5.06 (1H, dd, J = 14.1, 7.5 Hz, CH), 5.66–5.69 (1H, m, =CH), 6.00–6.02 (1H, m, NH), 6.99–7.03 (4H, m, ArH), 7.13–7.18 (2H, m, ArH), 7.60–7.65 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.92, 13.03, 15.42 (2C), 21.33 (2C), 26.70, 26.75, 28.30 (2C), 56.06, 56.11, 96.88, 96.98, 107.29, 107.53, 126.43, 126.49, 126.87, 126.93, 127.90, 127.98, 129.34, 129.37, 136.14, 136.21, 137.37 (2C), 143.11, 143.19, 144.03, 144.05, 198.53, 198.59, 211.66, 211.72; MS (EI) *m*/*e* 288 (M^+ − 95, 100), 272 (M^+ − 111, 8.59), 155 (M^+ − 228, 55.17), 91 (M^+ − 292, 50.20); MS (MALDI) *m*/*e* 406 (M^+ + Na, 100); HRMS (MALDI) calcd. for $C_{22}H_{26}NO_3S^{+1}$: 384.1628, Found: 384.1640.

***N*-[1-(4-Methoxyphenyl)-4-methyl-5-oxohexa-2,3-dienyl]-4-methylbenzenesulfonamide 3d.** Mp 94–98 °C; IR (CH_2Cl_2) ν 3272, 1680 (C=O), 1513, 1327, 1160, 1094 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**3d** and (1*S*,3*S*)-**3d**: 1.62 (3H, d, J = 2.4 Hz, CH_3), 2.06 (3H, s, CH_3), 2.38 (3H, s, CH_3), 2.74 (3H, s, CH_3), 4.99–5.07 (1H, m, CH), 5.71–5.74 (1H, m, =CH), 5.90 (1H, dd, J = 7.5, 1.5 Hz, NH), 6.69–6.74 (2H, m, ArH), 7.02–7.07 (2H, m, ArH), 7.17–7.21 (2H, m, ArH), 7.61–7.66 (2H, m, ArH); (1*S*,3*R*)-**3d** and (1*R*,3*S*)-**3d**: 1.66 (3H, d, J = 2.4 Hz, CH_3), 2.11 (3H, s, CH_3), 2.39 (3H, s, CH_3), 2.74 (3H, s, CH_3), 4.99–5.07 (1H, m, CH), 5.65–5.68 (1H, m, =CH), 5.90 (1H, dd, J = 7.5, 1.5 Hz, NH), 6.69–6.74 (2H, m, ArH), 7.02–7.07 (2H, m, ArH), 7.17–7.21 (2H, m, ArH), 7.61–7.66 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.95, 13.08, 20.94, 21.36, 26.72, 26.79, 55.13 (2C), 55.75, 55.80, 96.96, 97.10, 107.33, 107.57, 113.80, 113.88, 126.89, 126.96, 127.73, 127.79, 129.42, 129.44, 131.07, 131.15, 137.39 (2C), 143.25, 143.32, 159.17 (2C), 198.48, 198.55, 211.66, 211.75; MS (EI) *m*/*e* 290 (M^+ − 95, 100), 231 (M^+ − 154, 6.56), 155 (M^+ − 230, 38.52), 91 (M^+ − 294, 53.26) [Found: C, 65.65; H, 6.13; N, 3.51%. $C_{21}H_{23}O_4NS$ requires C, 65.43; H, 6.01; N, 3.63%].

***N*-{1-[4-(Dimethylamino)phenyl]-4-methyl-5-oxohexa-2,3-dienyl}-4-methylbenzenesulfonamide 3e.** Mp 103–106 °C; IR (CH_2Cl_2) ν 3265, 2924, 1678 (C=O), 1524, 1327, 1160, 1088 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**3e** and (1*S*,3*S*)-**3e**: 1.65 (3H, d, J = 2.7 Hz, CH_3), 2.17 (3H, s, CH_3), 2.38 (3H, s, CH_3), 2.89 (6H, s, $2CH_3$), 4.93–4.98 (1H, m, CH), 5.47–5.49 (1H, m, NH), 5.73–5.76 (1H, m, =CH), 6.51–6.56 (2H, m, ArH), 6.94–6.99 (2H, m, ArH), 7.18–7.22 (2H, m, ArH), 7.63–7.67 (2H, m, ArH); (1*S*,3*R*)-**3e** and (1*R*,3*S*)-**3e**: 1.71 (3H, d, J = 2.7 Hz, CH_3), 2.10 (3H, s, CH_3), 2.39 (3H, s, CH_3), 2.90 (6H, s, $2CH_3$), 4.96–5.01 (1H, m, CH), 5.49–5.52 (1H, m, NH), 5.67–5.70 (1H, m, =CH), 6.51–6.56 (2H, m, ArH), 6.94–6.99 (2H, m, ArH), 7.18–7.22 (2H, m, ArH), 7.63–7.67 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.03, 13.20, 21.40 (2C), 26.80, 26.90, 40.32 (2C), 55.93, 56.00, 97.15, 97.33, 107.16, 107.45, 112.18, 112.24, 126.39, 126.46, 126.96, 127.03, 127.38, 127.43, 129.42 (2C), 137.50 (2C), 143.08, 143.15, 150.12, 150.14, 198.72, 198.76, 211.65, 211.70; MS (EI) *m*/*e* 398 (M^+, 5.27), 303 (M^+ − 95, 77.14), 243 (M^+ − 155, 15.55), 148 (M^+ − 250, 100), 91 (M^+ − 307, 53.80) [Found: C, 66.36; H, 6.67; N, 6.99%. $C_{22}H_{26}O_3N_2S$ requires C, 66.30; H, 6.58; N, 7.03%].

***N*-[1-(4-Fluorophenyl)-4-methyl-5-oxohexa-2,3-dienyl]-4-methylbenzenesulfonamide 3f.** Mp 98–101 °C; IR (CH_2Cl_2) ν 3270, 1680 (C=O), 1510, 1333, 1159, 1094 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**3f** and (1*S*,3*S*)-**3f**: 1.62 (3H, d, J = 3.0 Hz, CH_3), 2.06 (3H, s, CH_3), 2.41 (3H, s, CH_3), 5.09 (1H, dd, J = 13.8, 7.8 Hz, CH), 5.70–5.73 (1H, m, =CH), 5.89–5.90 (1H, m, NH), 6.86–6.93 (2H, m, ArH), 7.08–7.15 (2H, m, ArH), 7.18–7.28 (2H, m, ArH), 7.60–7.65 (2H, m, ArH); (1*S*,3*R*)-**3f** and (1*R*,3*S*)–**3f**: 1.66 (3H, d, J = 3.0 Hz, CH_3), 2.09 (3H, s, CH_3), 2.41 (3H, s, CH_3), 5.09 (1H, dd, J = 13.8, 7.8 Hz, CH), 5.65–5.68 (1H, m, =CH), 5.86–5.87 (1H, m, NH), 6.86–6.93 (2H, m, ArH), 7.08–7.15 (2H, m, ArH),

7.18–7.28 (2H, m, ArH), 7.60–7.65 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.89, 12.98, 21.32 (2C), 26.66, 26.70, 55.55, 55.59, 96.63, 96.74, 107.51, 107.70, 115.28 (d, J = 21.8 Hz), 115.35 (d, J = 20.9 Hz), 126.80, 126.86, 128.27 (d, J = 8.6 Hz), 128.32 (d, J = 8.3 Hz), 129.43, 129.46, 134.85 (d, J = 3.5 Hz), 134.92 (d, J = 3.4 Hz), 137.19 (2C), 143.48, 143.53, 162.07 (2C, d, J = 245.4 Hz), 198.26, 198.34, 211.66, 211.75; MS (EI) m/e 373 (M^+, 0.56), 278 (M^+ − 95, 90.01), 203 (M^+ − 170, 25.32), 160 (M^+ − 213, 39.72), 155 (M^+ − 218, 76.45), 91 (M^+ − 282, 100) [Found: C, 64.62; H, 5.35; N, 3.96%. $C_{20}H_{20}O_3NSF$ requires C, 64.33; H, 5.40; N, 3.75%].

***N*-[1-(4-Chlorophenyl)-4-methyl-5-oxohexa-2,3-dienyl]-4-methylbenzenesulfonamide 3g.** Mp 135–140 °C; IR (CH_2Cl_2) ν 3270, 1680 (C=O), 1510, 1333, 1159, 1094 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**3g** and (1*S*,3*S*)-**3g**: 1.61 (3H, d, J = 3.0, CH_3), 2.04 (3H, s, CH_3), 2.39 (3H, s, CH_3), 5.06 (1H, dd, J = 14.1, 7.5 Hz, CH), 5.68–5.71 (1H, m, =CH), 6.00 (1H, d, J = 7.5 Hz, NH), 7.03–7.08 (2H, m, ArH), 7.13–7.20 (4H, m, ArH), 7.57–7.62 (2H, m, ArH); (1*S*,3*R*)-**3g** and (1*R*,3*S*)-**3g**: 1.64 (3H, d, J = 2.4, CH_3), 2.08 (3H, s, CH_3), 2.40 (3H, s, CH_3), 5.06 (1H, dd, J = 14.1, 7.5 Hz, CH), 5.62–5.65 (1H, m, =CH), 6.00 (1H, d, J = 7.5 Hz, NH), 7.03–7.08 (2H, m, ArH), 7.13–7.20 (4H, m, ArH), 7.57–7.62 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.98, 13.07, 21.40 (2C), 26.76, 26.78, 55.65, 55.68, 96.34, 96.44, 107.68, 107.87, 126.86, 126.91, 127.96, 128.01, 128.62, 128.69, 129.50, 129.54, 133.80 (2C), 137.14 (2C), 137.48, 137.54, 143.64, 143.69, 198.13, 198.21, 211.64, 211.71; MS (EI) m/e 390 (M^+ + 1, 1.35), 294 (M^+ − 95, 72.41), 219 (M^+ − 170, 17.08), 176 (M^+ − 213, 25.67), 155 (M^+ − 234, 83.85), 91 (M^+ − 198, 100) [Found: C, 61.52; H, 5.12; N, 3.55%. $C_{20}H_{20}O_3NSCl$ requires C, 61.61; H, 5.17; N, 3.59%].

***N*-[1-(4-Bromophenyl)-4-methyl-5-oxohexa-2,3-dienyl]-4-methylbenzenesulfonamide 3h.** Mp 132–136 °C; IR (CH_2Cl_2) ν 3268, 1681 (C=O), 1435, 1333, 1160, 1093 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**3h** and (1*S*,3*S*)-**3h**: 1.62 (3H, dd, J = 3.0, 1.5 Hz, CH_3), 2.05 (3H, d, J = 1.5 Hz, CH_3), 2.41 (3H, s, CH_3), 5.05 (1H, dd, J = 14.4, 6.3 Hz, CH), 5.68–5.70 (1H, m, =CH), 5.95–6.01 (1H, m, NH), 6.97–7.02 (2H, m, ArH), 7.17–7.20 (2H, m, ArH), 7.27–7.33 (2H, m, ArH), 7.56–7.62 (2H, m, ArH); (1*S*,3*R*)-**3h** and (1*R*,3*S*)-**3h**: 1.65 (3H, dd, J = 3.0, 1.5 Hz, CH_3), 2.08 (3H, d, J = 1.5 Hz, CH_3), 2.41 (3H, s, CH_3), 5.05 (1H, dd, J = 14.4, 6.3 Hz, CH), 5.62–5.65 (1H, m, =CH), 5.95–6.01 (1H, m, NH), 6.97–7.02 (2H, m, ArH), 7.17–7.20 (2H, m, ArH), 7.27–7.33 (2H, m, ArH), 7.56–7.62 (2H, m, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.97, 13.07, 21.42 (2C), 26.76, 26.78, 55.70, 55.73, 96.23, 96.33, 107.70, 107.88, 121.93 (2C), 126.85, 126.90, 128.28, 128.33, 129.51, 129.54, 131.57, 131.63, 137.10 (2C), 137.96, 138.02, 143.66, 143.70, 198.18, 198.36, 211.62, 211.68; MS (EI) m/e 340 (M^+ − 93, 38.74), 338 (M^+ − 95, 38.26), 294 (M^+ − 139, 14.62), 155 (M^+ − 278, 91.82), 91 (M^+ − 342, 100) [Found: C, 55.30; H, 4.68; N, 3.04%. $C_{20}H_{20}O_3NSBr$ requires C, 55.30; H, 4.64; N, 3.22%].

4-Methyl-*N*-[4-methyl-1-(4-nitrophenyl)-5-oxohexa-2,3-dienyl]-benzenesulfonamide 3i. Mp 134–140 °C; IR (CH_2Cl_2) ν 3270, 1681 (C=O), 1522, 1347, 1160, 1093 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**3i** and (1*S*,3*S*)-**3i**: 1.65 (3H, d, J = 2.7 Hz, CH_3), 2.09 (3H, s, CH_3), 2.40 (3H, s, CH_3), 5.19–5.23 (1H, m, CH), 5.48–5.20 (1H, m, NH), 5.72–5.73 (1H, m, =CH), 7.20–7.23 (2H, m, ArH), 7.33–7.37 (2H, m, ArH), 7.60–7.65 (2H, m, ArH), 8.07–8.12 (2H, m, ArH); (1*S*,3*R*)-**3i** and (1*R*,3*S*)-**3i**: 1.69 (3H, d, J = 2.7 Hz, CH_3), 2.07 (3H, s, CH_3), 2.40 (3H, s, CH_3), 5.19–5.23 (1H, m, CH), 5.48–5.20 (1H, m, NH), 5.66–5.69 (1H, m, =CH), 7.20–7.23 (2H, m, ArH), 7.33–7.37 (2H, m, ArH), 7.60–7.65 (2H, m, ArH), 8.07–8.12 (2H, m, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.12, 13.18, 21.47 (2C), 26.85, 26.87, 55.58 (2C), 95.69, 95.73, 108.31 (2C), 123.80, 123.87, 126.37 (2C), 126.93, 126.96, 127.62, 127.64, 129.71, 129.74, 136.92 (2C), 144.21 (2C), 146.15 (2C), 197.59 (2C), 211.55 (2C); MS (EI) m/e 305 (M^+ − 95, 33.27), 229 (M^+ − 171, 9.05), 187 (M^+ − 213, 14.82), 155 (M^+ − 245, 73.22), 91 (M^+ − 309, 100) [Found: C, 59.89; H, 5.12; N, 6.90%. $C_{20}H_{20}O_5N_2S$ requires C, 59.99; H, 5.03; N, 7.00%].

4-Methyl-*N*-[4-methyl-1-(3-nitrophenyl)-5-oxohexa-2,3-dienyl]-benzenesulfonamide 3j. Pale yellow oil; IR (CH_2Cl_2) ν 3267, 1953, 1681 (C=O), 1531, 1351, 1160, 1092 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**3j** and (1*S*,3*S*)-**3j**: 1.62 (3H, s, CH_3), 2.09 (3H, s, CH_3), 2.36 (3H, s, CH_3), 5.21–5.27 (1H, m, CH), 5.74–5.77 (1H, m, =CH), 6.21 (1H, br s, NH), 7.15–7.20 (2H, m, ArH), 7.40–7.47 (1H, m, ArH), 7.55–7.64 (3H, m, ArH), 7.94–7.95 (1H, m, ArH), 8.03–8.07 (1H, m, ArH); (1*S*,3*R*)-**3j** and (1*R*,3*S*)-**3j**: 1.63 (3H, s, CH_3), 2.08 (3H, s, CH_3), 2.37 (3H, s, CH_3), 5.21–5.27 (1H, m, CH), 5.69–5.72 (1H, m, =CH), 6.21 (1H, br s, NH), 7.15–7.20 (2H, m, ArH), 7.40–7.47 (1H, m, ArH), 7.55–7.64 (3H, m, ArH), 7.94–7.95 (1H, m, ArH), 8.03–8.07 (1H, m, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.00, 13.06, 21.34, 21.35, 26.77, 26.78, 55.51, 55.54, 95.82, 95.85, 108.13, 108.26, 121.67, 121.74, 122.85, 122.86, 126.84, 126.88, 129.60, 129.62, 129.66 (2C), 132.83, 132.88, 136.89, 136.92, 141.05, 141.10, 143.92, 143.99, 148.00 (2C), 197.83, 197.89, 211.75 (2C); MS (EI) m/e 400 (M^+, 7.77), 383 (M^+ − 17, 36.66), 245 (M^+ − 155, 66.33), 244 (M^+ − 156, 100), 229 (M^+ − 171, 34.59), 201 (M^+ − 199, 26.85), 184 (M^+ − 216, 24.94); HRMS (EI) calcd. for $C_{20}H_{20}N_2O_5S$: 400.1093, Found: 400.1096.

***N*-[1-(2,3-Dichlorophenyl)-4-methyl-5-oxohexa-2,3-dienyl]-4-methylbenzenesulfonamide 3k.** Mp 118–122 °C; IR (CH_2Cl_2) ν 3271, 1683 (C=O), 1435, 1337, 1161, 1092 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**3k** and (1*S*,3*S*)-**3k**: 1.59 (3H, d, J = 2.7 Hz, CH_3), 2.04 (3H, s, CH_3), 2.37 (3H, s, CH_3), 5.52–5.59 (1H, m, CH), 5.72–5.74 (1H, m, =CH), 5.97–5.99 (1H, m, NH), 7.07–7.12 (1H, m, ArH), 7.16 (3H, d, J = 8.4 Hz, ArH), 7.27–7.31 (1H, m, ArH), 7.63 (2H, d, J = 8.4 Hz, ArH); (1*S*,3*R*)-**3k** and (1*R*,3*S*)-**3k**: 1.62 (3H, d, J = 2.4 Hz, CH_3), 2.05 (3H, s, CH_3), 2.37 (3H, s, CH_3), 5.52–5.59 (1H, m, CH), 5.65–5.68 (1H, m, =CH), 6.14–6.21 (1H, m, NH), 7.02–7.10 (1H, m, ArH), 7.05–7.22 (3H, m, ArH), 7.27–7.31 (1H, m, ArH), 7.61–7.65 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.74, 12.94, 21.37 (2C), 26.65, 26.75, 55.81 (2C), 95.23, 95.26, 107.98, 108.07, 126.32, 126.35, 126.84 (2C), 127.36, 127.46, 129.40, 129.42, 129.61, 129.63, 130.21, 130.34, 133.10, 133.16, 136.39, 136.44, 138.71, 138.73, 143.73, 143.77, 198.10, 198.14, 211.71, 211.05; MS (EI) m/e 424 (M^+ + 1, 1.26), 423 (M^+, 0.84), 330 (M^+ − 93, 72.94), 328 (M^+ − 95, 100), 155 (M^+ − 268, 19.77), 91 (M^+ − 332, 32.90); HRMS (MALDI) calcd. for $C_{20}H_{20}NO_3SCl_2^{+1}$: 424.0536, Found: 424.0551.

4-Methyl-*N*-[4-methyl-1-(naphthalen-1-yl)-5-oxohexa-2,3-dienyl]benzenesulfonamide 3l. Mp 136–141 °C; IR (CH_2Cl_2) ν 3272, 1680 (C=O), 1433, 1337, 1159, 1091 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**3l** and (1*S*,3*S*)-**3l**: 1.52 (3H, d, J = 2.7 Hz, CH_3), 1.98 (3H, s, CH_3), 2.33 (3H, s, CH_3), 5.42–5.44 (1H, m, NH), 5.81–5.88 (1H, m, CH), 5.92–5.95 (1H, m, =CH), 7.06–7.11 (2H, m, ArH), 7.29–7.39 (2H, m, ArH), 7.43–7.50 (2H, m, ArH), 7.55–7.62 (2H, m, ArH), 7.70–7.74 (1H, m, ArH), 7.79–7.91 (2H, m, ArH); (1*S*,3*R*)-**3l** and (1*R*,3*S*)-**3l**: 1.57 (3H, d, J = 2.7 Hz, CH_3), 1.96 (3H, s, CH_3), 2.34 (3H, s, CH_3), 5.42–5.44 (1H, m, NH), 5.81–5.88 (2H, m, CH, =CH), 7.06–7.11 (2H, m, ArH), 7.29–7.39 (2H, m, ArH), 7.43–7.50 (2H, m, ArH), 7.55–7.62 (2H, m, ArH), 7.70–7.74 (1H, m, ArH), 7.79–7.91 (2H, m, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.52, 12.79, 21.22, 21.24, 26.61, 26.63, 53.10 (2C), 96.68, 96.83, 107.30, 107.44, 122.55, 122.69, 124.37, 124.54, 124.93 (2C), 125.58, 125.60, 126.22, 126.24, 126.68, 126.76, 128.48, 128.53, 128.65, 128.72, 129.13, 129.19, 129.61, 129.74, 133.48, 133.50, 134.35, 134.37, 136.90, 136.97,

143.11, 143.20, 198.41, 198.48, 211.96, 211.99; MS (EI) *m/e* 310 ($M^+ - 95$, 100), 191 ($M^+ - 214$, 29.63), 155 ($M^+ - 250$, 50.60), 91 ($M^+ - 314$, 75.73) [Found: C, 70.85; H, 5.71; N, 3.33%. $C_{24}H_{23}O_3NS$ requires C, 71.08; H, 5.72; N, 3.45%].

The aza-Baylis–Hillman reaction of *N*-tosylated aldimines with 3-methylpenta-3,4-dien-2-one catalyzed by PBu_3. Typical reaction procedure of *N*-tosylated aldimines with 3-methylpenta-3,4-dien-2-one at 80 °C catalyzed by PBu_3

To a Schlenk tube with *N*-(*p*-methylbenzenesulfonyl)-benzaldimine (130 mg, 0.5 mmol) in DMSO (1 mL) under argon atmosphere was added 3-methylpenta-3,4-dien-2-one (96 mg, 1 mmol) and PBu_3 (12.5 mg, 0.05 mmol). The reaction mixture was stirred for 30 min at 80 °C. The reaction mixture was washed with water (10 mL) and extracted with dichloromethane (20 mL). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography to afford **4a** (eluent: EtOAc–petroleum = 1 : 3) 72 mg (yield 65%) as a major product and **5a** (eluent: EtOAc–petroleum = 1 : 2) 52 mg (yield 29%) as a minor product.

(*E*)-3-Phenyl-1-(6-phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)prop-2-en-1-one 4a. Mp 170–174 °C IR (CH_2Cl_2) *v* 3030, 1653 (C=O), 1596, 1339, 1154, 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.39 (3H, s, CH_3), 2.74–2.75 (2H, m, CH_2), 3.54 (1H, dm, J = 18.3 Hz, CH_2), 4.60 (1H, dm, J = 18.3 Hz, CH_2), 5.43–5.45 (1H, m, CH), 7.06–7.07 (1H, m, =CH), 7.18 (1H, d, J = 15.6 Hz, =CH), 7.22–7.26 (7H, m, ArH), 7.39–7.41 (3H, m, Ar), 7.54–7.57 (2H, m, Ar), 7.61 (1H, d, J = 15.6 Hz, =CH), 7.69 (2H, d, J = 8.1 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.44, 27.40, 39.36, 52.20, 119.78, 126.96, 127.04, 127.75, 128.22, 128.53, 128.85, 129.58, 130.45, 134.55, 135.90, 136.69, 137.12, 138.15, 143.31, 143.72, 187.78; MS (EI) *m/e* 443 (M^+, 28.85), 288 ($M^+ - 155$, 37.70), 193 ($M^+ - 250$, 100), 131 ($M^+ - 312$, 39.37), 91 ($M^+ - 352$, 46.69); HRMS (MALDI) calcd. for $C_{27}H_{25}NO_3SNa^{+1}$: 466.1447, Found: 466.1455.

(*E*)-3-*p*-Tosyl-1-(6-*p*-tolyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)prop-2-en-1-one 4b. Mp 155–159 °C; IR (CH_2Cl_2) *v* 2922, 1653 (C=O), 1595, 1324, 1159, 1096 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.29 (3H, s, CH_3), 2.37 (3H, s, CH_3), 2.39 (3H, s, CH_3), 2.70 (2H, m, CH_2), 3.52 (1H, dd, J = 15.6, 2.4 Hz, CH_2), 4.56 (1H, dm, J = 15.6 Hz, CH_2), 5.38–5.40 (1H, m, CH), 7.02 (1H, m, =CH), 7.05–7.26 (9H, m, =CH, ArH), 7.45 (2H, d, J = 8.4 Hz, ArH), 7.58 (1H, d, J = 15.3 Hz, =CH), 7.69 (2H, d, J = 8.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 20.96, 21.48 (2C), 27.48, 39.37, 52.00, 118.87, 127.03, 127.04, 128.28, 129.21, 129.60, 129.63, 131.89, 135.17, 135.65, 136.81, 137.32, 137.52, 141.01, 143.25, 143.82, 187.95; MS (EI) *m/e* 472 ($M^+ + 1$, 11.66), 471 (M^+, 34.58), 316 ($M^+ - 155$, 36.16), 221 ($M^+ - 250$, 100), 198 ($M^+ - 273$, 26.65), 145 ($M^+ - 326$, 35.68), 91 ($M^+ - 380$, 37.87); HRMS (MALDI) calcd. for $C_{29}H_{29}NO_3SNa^{+1}$: 494.1760, Found: 494.1782.

(*E*)-3-(4-Ethylphenyl)-1-[6-(4-ethylphenyl)-1-tosyl-1,2,5,6-dropyridin-3-yl]prop-2-en-1-one 4c. Colorless oil; IR (CH_2Cl_2) *v* 2965, 1651 (C=O), 1596, 1341, 1160, 1096 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 0.81–0.88 (6H, m, CH_3), 2.38 (3H, s, CH_3), 2.56–2.73 (6H, m, CH_2), 3.56 (1H, dd, J = 15.6, 2.4 Hz, CH_2), 4.58 (1H, d, J = 15.6 Hz, CH_2), 5.39–5.41 (1H, m, CH), 7.03 (1H, m, =CH), 7.05–7.24 (9H, m, =CH, ArH), 7.48 (2H, d, J = 8.4 Hz, ArH), 7.60 (1H, d, J = 15.9 Hz, =CH), 7.69 (2H, d, J = 8.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 15.29, 15.49, 21.48, 27.63, 28.37, 28.79, 39.42, 52.07, 118.93, 127.08, 127.11, 127.95, 128.03, 128.39, 128.46, 129.57, 132.14, 135.43, 135.67, 136.82, 137.25, 143.22, 143.87, 147.30, 188.00; MS (EI) *m/e* 499 (M^+, 17.32), 344 ($M^+ - 155$, 33.11), 249 ($M^+ - 250$, 100), 194 ($M^+ - 305$, 37.68), 91 ($M^+ - 408$, 63.22); HRMS (MALDI) calcd. for $C_{31}H_{33}NO_3SNa^{+1}$: 522.2073, Found: 522.2073.

(*E*)-3-(4-Methoxyphenyl)-1-[6-(4-methoxyphenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl]prop-2-en-1-one 4d. Colorless oil; IR (CH_2Cl_2) *v* 2930, 1651 (C=O), 1590, 1512, 1254, 1159, 1096 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.40 (3H, s, CH_3), 2.69–2.70 (2H, m, CH_2), 3.51 (1H, dd, J = 18.3, 2.4 Hz, CH_2), 3.77 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 4.57 (1H, dm, J = 18.3 Hz, CH_2), 5.37–5.39 (1H, m, CH), 6.77–6.82 (2H, m, ArH), 6.89–6.93 (2H, m, ArH), 7.00–7.02 (1H, m, =CH), 7.05 (1H, d, J = 15.6 Hz, =CH), 7.16–7.24 (4H, m, ArH), 7.51–7.53 (2H, m, Ar), 7.59 (1H, d, J = 15.6 Hz, =CH), 7.67–7.71 (2H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.49, 27.64, 39.34, 51.77, 55.26, 55.37, 113.83, 114.33, 117.52, 127.01, 127.03, 127.34, 128.38, 129.59, 130.03, 130.23, 135.26, 136.84, 143.22, 143.60, 159.01, 161.56, 187.86; MS (EI) *m/e* 503 (M^+, 15.93), 348 ($M^+ - 155$, 42.34), 253 ($M^+ - 250$, 69.93), 214 ($M^+ - 289$, 42.19), 161 ($M^+ - 342$, 100), 91 ($M^+ - 412$, 66.27); HRMS (MALDI) calcd. for $C_{29}H_{29}NO_5SNa^{+1}$: 526.1659, Found: 526.1685.

(*E*)-3-(4-Fluorophenyl)-1-[6-(4-fluorophenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl]prop-2-en-1-one 4e. Mp 84–88 °C; IR (CH_2Cl_2) *v* 1711, 1654 (C=O), 1509, 1340, 1160, 1096 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.40 (3H, s, CH_3), 2.71–2.72 (2H, m, CH_2), 3.51 (1H, dd, J = 18.6, 2.1 Hz, CH_2), 4.59 (1H, dm, J = 18.6 Hz, CH_2), 5.39–5.42 (1H, m, CH), 6.92–6.98 (2H, m, ArH), 7.05–7.13 (4H, m, =CH, ArH, =CH), 7.20–7.27 (4H, m, ArH), 7.53–7.61 (3H, m, ArH, =CH), 7.68 (2H, d, J = 8.7 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.49, 27.67, 39.30, 51.61, 115.45 (d, J = 21.2 Hz), 116.09 (d, J = 21.8 Hz), 119.42, 127.02, 128.88 (d, J = 8.0 Hz), 129.68, 130.20 (d, J = 8.6 Hz), 130.84 (d, J = 2.9 Hz), 133.98 (d, J = 3.4 Hz), 135.56, 136.82, 137.05, 142.66, 143.50, 162.16 (d, J = 245.6 Hz), 163.99 (d, J = 250.8 Hz), 187.51; MS (EI) *m/e* 480 ($M^+ + 1$, 11.12), 479 (M^+, 35.99), 324 ($M^+ - 155$, 41.34), 229 ($M^+ - 250$, 100), 202 ($M^+ - 277$, 30.23), 149 ($M^+ - 330$, 52.71), 91 ($M^+ - 388$, 44.69); HRMS (MALDI) calcd. for $C_{27}H_{23}NO_3F_2SNa^{+1}$: 502.1259, Found: 502.1281.

(*E*)-3-(4-Chlorophenyl)-1-[6-(4-chlorophenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl]prop-2-en-1-one 4f. Mp 163–166 °C; IR (CH_2Cl_2) *v* 2923, 1655 (C=O), 1600, 1567, 1491, 1319, 1159, 1094 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.40 (3H, s, CH_3), 2.71–2.72 (2H, m, CH_2), 3.51 (1H, dd, J = 18.9, 2.1 Hz, CH_2), 4.58 (1H, dm, J = 18.9 Hz, CH_2), 5.39–5.41 (1H, m, CH), 7.03–7.04 (1H, m, =CH), 7.14 (1H, d, J = 15.0 Hz, =CH), 7.16–7.19 (2H, m, ArH), 7.23–7.26 (4H, m, ArH), 7.35–7.38 (2H, m, ArH), 7.49 (2H, d, J = 8.4 Hz, ArH), 7.56 (1H, d, J = 15.0 Hz, =CH), 7.68 (2H, d, J = 8.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.47, 27.43, 39.33, 51.64, 120.06, 126.96, 128.48, 128.71, 129.15, 129.41, 129.69, 133.03, 133.67, 135.65, 136.37, 136.66, 136.73, 136.95, 142.46, 143.56, 187.37; MS (EI) *m/e* 513 ($M^+ + 2$, 23.12), 511 (M^+, 31.86), 358 ($M^+ - 153$, 30.14), 356 ($M^+ - 155$, 46.88), 263 ($M^+ - 248$, 66.26), 261 ($M^+ - 250$, 100), 165 ($M^+ - 346$, 94.06), 155 ($M^+ - 356$, 37.42), 91 ($M^+ - 420$, 98.65); HRMS (MALDI) calcd. for $C_{27}H_{23}NO_3Cl_2SNa^{+1}$: 534.0668, Found: 534.0662.

(*E*)-3-(4-Bromophenyl)-1-[6-(4-bromophenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl]prop-2-en-1-one 4g. Mp 168–170 °C; IR (CH_2Cl_2) *v* 3054, 2923, 1655 (C=O), 1600, 1488, 1320, 1159, 1096 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.40 (3H, s, CH_3), 2.70–2.71 (2H, m, CH_2), 3.51 (1H, dd, J = 18.6, 2.4 Hz, CH_2), 4.58 (1H, dm, J = 18.6 Hz, CH_2), 5.36–5.38 (1H, m, CH), 7.03–7.04 (1H, m, =CH), 7.10–7.13 (2H, m, ArH), 7.20 (1H, d, J = 15.0 Hz, =CH), 7.25–7.27 (2H, m, ArH), 7.37–7.42 (4H, m, ArH), 7.50–7.53 (2H, m, ArH), 7.54 (1H, d, J = 15.0 Hz, =CH), 7.67 (2H, d, J = 8.1 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.51, 27.44, 39.37, 51.69, 120.14, 121.85, 124.79, 126.98, 128.82, 129.62, 129.70, 131.70, 132.14,

133.46, 135.60, 136.78, 136.93, 137.20, 142.56, 143.58, 187.35; MS (EI) *m/e* 603 ($M^+ + 5$, 1.29), 601 ($M^+ + 3$, 2.28), 446 ($M^+ - 152$, 6.52), 351 ($M^+ - 247$, 13.54), 211 ($M^+ - 387$, 32.34), 209 ($M^+ - 389$, 33.37), 155 ($M^+ - 433$, 33.19), 102 ($M^+ - 496$, 51.73), 91 ($M^+ - 507$, 100); HRMS (MALDI) calcd. for $C_{27}H_{23}NO_3Br_2SNa^{+1}$: 621.9658, Found: 621.9651.

(*E*)-3-(Naphthalene-1-yl)-1-[6-(naphthalen-1-yl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl]prop-2-en-1-one 4h. Mp 208–212 °C; IR (CH_2Cl_2) *v* 3051, 1650 (C=O), 1597, 1341, 1158, 1092 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.34 (3H, s, CH_3), 2.80–2.88 (1H, m, CH_2), 3.03–3.11 (1H, m, CH_2), 3.35–3.43 (1H, m, CH_2), 4.46 (1H, dm, $J = 18.6$ Hz, CH_2), 6.30 (1H, d, $J = 7.2$ Hz, CH), 7.17–7.34 (6H, m, =CH, ArH, =CH), 7.48–7.66 (5H, m, ArH), 7.74–7.94 (7H, m, ArH), 8.20 (1H, d, $J = 8.1$ Hz, ArH), 8.47 (1H, d, $J = 15.6$ Hz, =CH), 8.63 (1H, d, $J = 8.1$ Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.45, 28.04, 39.46, 49.16, 122.58, 123.34, 124.02, 124.14, 124.59, 124.85, 125.35, 126.01, 126.31, 126.85, 126.96, 127.64, 128.71, 128.75, 129.30, 129.53, 130.76, 131.37, 131.63, 132.17, 133.45, 133.67, 134.08, 136.44, 136.85, 136.91, 140.75, 143.67, 187.98; MS (EI) *m/e* 543 (M^+, 6.78), 388 ($M^+ - 155$, 11.30), 293 ($M^+ - 250$, 7.69), 206 ($M^+ - 337$, 24.35), 181 ($M^+ - 362$, 82.16), 152 ($M^+ - 391$, 100), 91 ($M^+ - 452$, 86.59); HRMS (MALDI) calcd. for $C_{35}H_{29}NO_3SNa^{+1}$: 566.1760, Found: 566.1788.

1-(6-Phenyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)ethanone 5a. IR (CH_2Cl_2) *v* 2925, 1667 (C=O), 1598, 1338, 1159, 1097 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.24 (3H, s, CH_3), 2.40 (3H, s, CH_3), 2.70–2.71 (2H, m, CH_2), 3.38 (1H, dm, $J = 18.6$ Hz, CH_2), 4.46 (1H, br d, $J = 18.6$ Hz, CH_2), 5.39–5.41 (1H, m, CH), 6.93–6.94 (1H, m, =CH), 7.18–7.29 (7H, m, ArH), 7.66 (2H, d, $J = 8.4$ Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.46, 24.95, 27.57, 38.90, 52.08, 126.99, 127.00, 127.75, 128.54, 129.55, 136.20, 137.04, 137.06, 138.14, 143.33, 196.52; MS (EI) *m/e* 355 (M^+, 19.99), 200 ($M^+ - 155$, 100), 156 ($M^+ - 199$, 22.01), 155 ($M^+ - 200$, 31.14), 91 ($M^+ - 264$, 68.21); HRMS (EI) calcd. for $C_{20}H_{21}NO_3S$: 355.1242, Found: 355.1250.

1-(6-*p*-Tolyl-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl)ethanone 5b. IR (CH_2Cl_2) *v* 2923, 1699, 1667 (C=O), 1598, 1338, 1160, 1096 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.24 (3H, s, CH_3), 2.30 (3H, s, CH_3), 2.41 (3H, s, CH_3), 2.69–2.70 (2H, m, CH_2), 3.37 (1H, dm, $J = 18.6$ Hz, CH_2), 4.44 (1H, br d, $J = 18.6$ Hz, CH_2), 5.36–5.38 (1H, m, CH), 6.91–6.92 (1H, m, =CH), 7.07 (4H, s, ArH), 7.23 (2H, d, $J = 8.4$ Hz, ArH), 7.66 (2H, d, $J = 8.4$ Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 20.96, 21.49, 24.97, 27.65, 38.85, 51.87, 126.94, 127.06, 128.26, 129.22, 129.57, 135.10, 136.27, 137.16, 137.54, 143.30, 196.56; MS (EI) *m/e* 369 (M^+, 36.26), 214 ($M^+ - 155$, 91.46), 184 ($M^+ - 185$, 40.87), 155 ($M^+ - 214$, 78.23), 91 ($M^+ - 278$, 100), 84 ($M^+ - 285$, 96.58); HRMS (MALDI) calcd. for $C_{21}H_{23}NO_3SNa^{+1}$: 392.1291, Found: 392.1303.

1-[6-(4-Ethylphenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl]ethanone 5c. IR (CH_2Cl_2) *v* 2927, 1698, 1667 (C=O), 1597, 1337, 1160, 1095 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.19 (3H, t, $J = 7.5$ Hz, CH_3), 2.25 (3H, s, CH_3), 2.40 (3H, s, CH_3), 2.60 (2H, q, $J = 7.5$ Hz, CH_2), 2.69–2.71 (2H, m, CH_2), 3.38 (1H, dm, $J = 18.6$ Hz, CH_2), 4.45 (1H, dm, $J = 18.6$ Hz, CH_2), 5.37 (1H, t, $J = 3.9$ Hz, CH), 6.92–6.95 (1H, m, =CH), 7.09 (4H, s, ArH), 7.22 (2H, d, $J = 8.4$ Hz, ArH), 7.66 (2H, d, $J = 8.4$ Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 15.50, 21.48, 24.96, 27.75, 28.35, 38.90, 51.93, 127.02, 127.07, 128.01, 129.53, 135.34, 136.25, 137.14, 137.20, 143.25, 143.88, 196.60; MS (EI) *m/e* 384 ($M^+ + 1$, 12.68), 228 ($M^+ - 155$, 100), 184 ($M^+ - 199$, 22.42), 155 ($M^+ - 228$, 32.53), 91 ($M^+ - 292$, 75.24); HRMS (MALDI) calcd. for $C_{22}H_{25}NO_3SNa^{+1}$: 406.1447, Found: 406.1456.

1-[6-(4-Chlorophenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl]ethanone 5f. IR (CH_2Cl_2) *v* 3261, 1708, 1658, 1598, 1509, 1335, 1304, 1160, 1094 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.24 (3H, s, CH_3), 2.43 (3H, s, CH_3), 2.68–2.70 (2H, m, CH_2), 3.37 (1H, dm, $J = 18.6$ Hz, CH_2), 4.46 (1H, br d, $J = 18.6$ Hz, CH_2), 5.36–5.39 (1H, m, CH), 6.89–6.91 (1H, m, =CH), 7.13 (2H, d, $J = 8.1$ Hz, ArH), 7.22–7.26 (4H, m, ArH), 7.65 (2H, d, $J = 8.1$ Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.48, 24.95, 27.52, 38.91, 51.54, 126.99, 128.44, 128.71, 129.66, 133.67, 136.24, 136.57, 136.69, 136.90, 143.56, 196.46; MS (EI) *m/e* 391 ($M^+ + 2$, 10.55), 389 (M^+, 23.81), 236 ($M^+ - 153$, 32.85), 234 ($M^+ - 155$, 100), 190 ($M^+ - 199$, 16.03), 155 ($M^+ - 234$, 31.46), 91 ($M^+ - 298$, 60.30); HRMS (MALDI) calcd. for $C_{20}H_{20}NO_3SClNa^{+1}$: 412.0745, Found: 412.0762.

1-[6-(4-Bromophenyl)-1-tosyl-1,2,5,6-tetrahydropyridin-3-yl]ethanone 5g. IR (CH_2Cl_2) *v* 3271, 2924, 1713, 1667, 1597, 1488, 1338, 1260, 1160, 1096 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ 2.24 (3H, s, CH_3), 2.43 (3H, s, CH_3), 2.67–2.69 (2H, m, CH_2), 3.37 (1H, dm, $J = 18.3$ Hz, CH_2), 4.46 (1H, br d, $J = 18.6$ Hz, CH_2), 5.34–5.37 (1H, m, CH), 6.89–6.90 (1H, m, =CH), 7.08 (2H, d, $J = 8.4$ Hz, ArH), 7.23–7.26 (2H, m, ArH), 7.39 (2H, d, $J = 8.4$ Hz, ArH), 7.65 (2H, d, $J = 8.4$ Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 21.51, 24.98, 27.50, 38.94, 51.61, 126.41, 127.01, 128.79, 129.67, 131.70, 136.28, 136.50, 136.90, 137.24, 143.58, 196.42; MS (EI) *m/e* 435 ($M^+ + 2$, 31.42), 433 (M^+, 31.00), 280 ($M^+ - 153$, 90.55), 278 ($M^+ - 155$, 100), 236 ($M^+ - 197$, 17.91), 234 ($M^+ - 199$, 16.31), 155 ($M^+ - 278$, 58.61), 91 ($M^+ - 342$, 67.75); HRMS (MALDI) calcd. for $C_{20}H_{20}NO_3SBrNa^{+1}$: 456.0240, Found: 456.0253.

The aza-Baylis–Hillman reactions of aldehydes with 3-methylpenta-3,4-dien-2-one catalyzed by DMAP. Typical reaction procedure of benzaldehyde with 3-methylpenta-3,4-dien-2-one at 80 °C catalyzed by DMAP

To a Schlenk tube with benzaldehyde (53 mg, 0.5 mmol) and DMAP (6 mg, 0.05 mmol) in DMSO (1 mL) was added 3-methylpenta-3,4-dien-2-one (192 mg, 2 mmol) and the reaction mixture was stirred for 30 min at 80 °C. The reaction mixture was washed with water (10 mL) and extracted with dichloromethane (20 mL). The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (eluent: EtOAc–petroleum = 1 : 3) to give adduct **6a** (75 mg, yield 61%) as a colorless oil.

In all cases, **6** was obtained as a pair of diastereoisomeric mixtures in 1 : 1 ratio on the basis of ^1H NMR spectroscopic data and could not be separated by silica gel column chromatography. ^{13}C NMR spectroscopic data also indicated a pair of diastereoisomeric mixtures in 1 : 1 ratio.

6-Hydroxy-3-methyl-6-phenylhexa-3,4-dien-2-one 6a. Colorless oil; IR (CH_2Cl_2) *v* 3410, 2925, 1948, 1674, 1667, 1491, 1356, 1356, 1016 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**6a** and (1*S*,3*S*)-**6a**: 1.75 (3H, d, $J = 2.7$ Hz, CH_3), 2.14 (3H, s, CH_3), 2.91 (1H, br s, OH), 5.40 (1H, d, $J = 6.3$ Hz, CH), 5.80–5.84 (1H, m, =CH), 7.27–7.42 (5H, m, ArH); (1*S*,3*R*)-**6a** and (1*R*,3*S*)-**6a**: 1.77 (3H, d, $J = 2.7$ Hz, CH_3), 2.23 (3H, s, CH_3), 2.91 (1H, br s, OH), 5.40 (1H, d, $J = 6.3$ Hz, CH), 5.80–5.84 (1H, m, =CH), 7.27–7.42 (5H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.19, 13.27, 26.67, 26.76, 71.88, 71.96, 98.84, 98.92, 106.73, 106.90, 125.77, 125.82, 128.07, 128.09, 128.55, 128.58, 142.23, 142.26, 198.90, 198.93, 211.66, 211.72; MS (EI) *m/e* 202 (M^+, 0.43), 185 ($M^+ - 17$, 28.27), 141 ($M^+ - 61$, 36.52), 107 ($M^+ - 95$, 34.98), 96 ($M^+ - 106$, 50.80), 79 ($M^+ - 123$, 55.33), 43 ($M^+ - 159$, 100); HRMS (EI) calcd. for $C_{13}H_{12}O$ ($M-H_2O$): 184.0888, Found: 184.0899.

6-(4-Fluorophenyl)-6-hydroxy-3-methylhexa-3,4-dien-2-one 6b. Pale yellow oil; IR (CH_2Cl_2) *v* 3424, 1950, 1678, 1603, 1509, 1360, 1157, 1098 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, TMS)

δ (1*R*,3*R*)-**6b** and (1*S*,3*S*)-**6b**: 1.77 (3H, d, J = 2.7 Hz, CH_3), 2.17 (3H, s, CH_3), 2.36 (1H, br s, OH), 5.42 (1H, d, J = 6.0 Hz, CH), 5.79–5.83 (1H, m, =CH), 7.04–7.10 (2H, m, ArH), 7.36–7.41 (2H, m, ArH); (1*S*,3*R*)-**6b** and (1*R*,3*S*)-**6b**: 1.80 (3H, d, J = 2.7 Hz, CH_3), 2.26 (3H, s, CH_3), 2.36 (1H, br s, OH), 5.42 (1H, d, J = 6.0 Hz, CH), 5.79–5.83 (1H, m, =CH), 7.04–7.10 (2H, m, ArH), 7.36–7.41 (2H, m, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.17, 13.23, 26.63, 26.71, 71.15, 71.21, 98.83, 98.91, 106.78, 106.88, 115.35 (d, J = 21.2 Hz), 115.38 (d, J = 21.8 Hz), 127.52 (d, J = 8.6 Hz), 127.57 (d, J = 8.0 Hz), 138.07 (d, J = 3.4 Hz), 138.09 (d, J = 2.9 Hz), 162.28 (2C, d, J = 245.0 Hz), 198.96 (2C), 211.66, 211.71; MS (EI) *m/e* 220 (M^+, 1.95), 159 ($M^+ - 61$, 82.68), 125 ($M^+ - 95$, 96.11), 96 ($M^+ - 124$, 98.49), 84 ($M^+ - 136$, 97.60), 43 ($M^+ - 177$, 100); HRMS (EI) calcd. for $C_{13}H_{13}O_2F$: 220.0919, Found: 220.0938.

6-(4-Chlorophenyl)-6-hydroxy-3-methylhexa-3,4-dien-2-one 6c. Mp 84–86 °C; IR (CH_2Cl_2) ν 3417, 1950, 1678, 1665, 1491, 1360, 1264, 1014 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**6c** and (1*S*,3*S*)-**6c**: 1.75 (3H, d, J = 2.7 Hz, CH_3), 2.15 (3H, s, CH_3), 2.46 (1H, br s, OH), 5.38 (1H, d, J = 6.0 Hz, CH), 5.78–5.80 (1H, m, =CH), 7.34 (4H, m, ArH); (1*S*,3*R*)-**6c** and (1*R*,3*S*)-**6c**: 1.77 (3H, d, J = 2.7 Hz, CH_3), 2.24 (3H, s, CH_3), 2.46 (1H, br s, OH), 5.38 (1H, d, J = 6.0 Hz, CH), 5.78–5.80 (1H, m, =CH), 7.34 (4H, m, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.20, 13.25, 26.67, 26.74, 71.15, 71.21, 98.60, 98.70, 106.83, 106.95, 127.16, 127.20, 128.64, 128.66, 133.67, 133.69, 140.72 (2C), 198.97 (2C), 211.64, 211.73; MS (EI) *m/e* 237 ($M^+ + 1$, 1.24), 219 ($M^+ - 17$, 76.60), 176 ($M^+ - 60$, 10.92), 141 ($M^+ - 95$, 69.17), 96 ($M^+ - 140$, 75.81), 43 ($M^+ - 193$, 100) [Found: C, 65.85; H, 5.63%. $C_{13}H_{13}O_2Cl$ requires C, 65.97; H, 5.54%]

6-(2-Chlorophenyl)-6-hydroxy-3-methylhexa-3,4-dien-2-one 6d. Colorless oil; IR (CH_2Cl_2) ν 3419, 2925, 1951, 1680, 1441, 1360, 1264, 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**6d** and (1*S*,3*S*)-**6d**: 1.71 (3H, d, J = 1.8 Hz, CH_3), 2.13 (3H, s, CH_3), 3.47 (1H, br s, OH), 5.80–5.84 (2H, m, CH, =CH), 7.21–7.35 (3H, m, ArH), 7.60–7.63 (1H, m, ArH); (1*S*,3*R*)-**6d** and (1*R*,3*S*)-**6d**: 1.72 (3H, d, J = 1.5 Hz, CH_3), 2.20 (3H, s, CH_3), 3.47 (1H, br s, OH), 5.80–5.84 (2H, m, CH, =CH), 7.21–7.35 (3H, m, ArH), 7.60–7.63 (1H, m, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.99, 13.13, 26.67, 26.69, 68.28, 68.30, 97.52, 97.54, 106.95, 107.01, 126.94, 127.07, 127.13, 127.14, 128.94, 128.96, 129.30, 129.33, 131.51, 131.62, 139.62 (2C), 199.19 (2C), 211.99, 212.17; MS (EI) *m/e* 236 (M^+, 0.15), 219 ($M^+ - 17$, 15.96), 141 ($M^+ - 95$, 39.20), 96 ($M^+ - 140$, 38.72), 77 ($M^+ - 159$, 26.51), 43 ($M^+ - 193$, 100); HRMS (EI) calcd. for $C_{13}H_{13}O_2Cl$: 236.0604, Found: 236.0608.

6-(4-Bromophenyl)-6-hydroxy-3-methylhexa-3,4-dien-2-one 6e. Mp 65–68 °C; IR (CH_2Cl_2) ν 3423, 1950, 1678, 1591, 1487, 1359, 1261, 1071 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**6e** and (1*S*,3*S*)-**6e**: 1.76 (3H, d, J = 2.7 Hz, CH_3), 2.16 (3H, s, CH_3), 2.68 (1H, br s, OH), 5.38 (1H, d, J = 6.3 Hz, CH), 5.77–5.80 (1H, m, =CH), 7.28 (2H, d, J = 8.4 Hz, ArH), 7.50 (2H, d, J = 8.4 Hz, ArH); (1*S*,3*R*)-**6e** and (1*R*,3*S*)-**6e**: 1.79 (3H, d, J = 2.7 Hz, CH_3), 2.25 (3H, s, CH_3), 2.68 (1H, br s, OH), 5.38 (1H, d, J = 6.3 Hz, CH), 5.77–5.80 (1H, m, =CH), 7.28 (2H, d, J = 8.4 Hz, ArH), 7.50 (2H, d, J = 8.4 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.20, 13.25, 26.69, 26.75, 71.17, 71.25, 98.52, 98.62, 106.81, 106.94, 121.81 (2C), 127.48, 127.52, 131.57, 131.60, 141.28 (2C), 198.84 (2C), 211.60, 211.71; MS (EI) *m/e* 283 ($M^+ + 3$, 3.30), 281 ($M^+ + 1$, 2.93), 193 ($M^+ - 87$, 19.65), 185 ($M^+ - 95$, 10.97), 183 ($M^+ - 97$, 10.02), 149 ($M^+ - 131$, 16.99), 84 ($M^+ - 196$, 29.52), 43 ($M^+ - 237$, 100); HRMS (EI) calcd. for $C_{13}H_{13}O_2BrNa^{+1}$: 302.9991, Found: 303.0003.

6-Hydroxy-3-methyl-6-(4-nitrophenyl)hexa-3,4-dien-2-one 6f. Mp 118–121 °C; IR (CH_2Cl_2) ν 3322, 1946, 1655, 1597, 1514, 1344, 1268, 1058 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**6f** and (1*S*,3*S*)-**6f**: 1.79 (3H, d, J = 1.2 Hz, CH_3), 2.19 (3H, s, CH_3), 2.67 (1H, br s, OH), 5.55 (1H, d, J = 6.6 Hz, CH), 5.80–5.84 (1H, m, =CH), 7.61 (2H, d, J = 8.1 Hz, ArH), 8.25 (2H, d, J = 8.1 Hz, ArH); (1*S*,3*R*)-**6f** and (1*R*,3*S*)-**6f**: 1.80 (3H, d, J = 0.9 Hz, CH_3), 2.26 (3H, s, CH_3), 2.67 (1H, br s, OH), 5.55 (1H, d, J = 6.6 Hz, CH), 5.80–5.84 (1H, m, =CH), 7.61 (2H, d, J = 8.1 Hz, ArH), 8.25 (2H, d, J = 8.1 Hz, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.25, 13.28, 26.77, 26.83, 70.97, 71.02, 98.11, 98.21, 107.22, 107.27, 123.79, 123.81, 126.62, 126.67, 147.41 (2C), 149.30, 149.36, 198.44, 198.51, 211.65, 211.83; MS (EI) *m/e* 247 (M^+, 2.55), 229 ($M^+ - 18$, 3.70), 187 ($M^+ - 60$, 31.18), 176 ($M^+ - 81$, 43.53), 152 ($M^+ - 95$, 11.19), 43 ($M^+ - 204$, 100); HRMS (EI) calcd. for $C_{13}H_{13}O_4N$: 247.0845, Found: 247.0828.

6-Hydroxy-3-methyl-6-(3-nitrophenyl)hexa-3,4-dien-2-one 6g. Pale yellow oil; IR (CH_2Cl_2) ν 3419, 1951, 1678, 1609, 1526, 1350, 1263, 1099 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**6g** and (1*S*,3*S*)-**6g**: 1.70 (3H, d, J = 2.4 Hz, CH_3), 2.16 (3H, s, CH_3), 3.19 (1H, br s, OH), 5.95–5.97 (1H, m, =CH), 6.08 (1H, J = 5.4 Hz, CH), 7.46–7.51 (1H, m, ArH), 7.67–7.72 (1H, m, ArH), 7.88 (1H, d, J = 8.1 Hz, ArH), 7.99 (1H, d, J = 8.1 Hz, ArH); (1*S*,3*R*)-**6g** and (1*R*,3*S*)-**6g**: 1.73 (3H, d, J = 2.4 Hz, CH_3), 2.17 (3H, s, CH_3), 3.19 (1H, br s, OH), 5.95–5.97 (1H, m, =CH), 6.03 (1H, J = 5.4 Hz, CH), 7.46–7.51 (1H, m, ArH), 7.67–7.72 (1H, m, ArH), 7.88 (1H, d, J = 8.1 Hz, ArH), 7.99 (1H, d, J = 8.1 Hz, ArH);^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 12.99, 13.15, 26.61, 26.64, 67.05, 67.09, 97.84, 97.88, 107.38 (2C), 124.49 (2C), 128.12, 128.14, 128.66 (2C), 133.74, 133.78, 137.71, 137.76, 147.21 (2C), 199.06, 199.08, 211.98, 211.10; MS (EI) *m/e* 247 (M^+, 0.28), 229 ($M^+ - 18$, 3.40), 176 ($M^+ - 71$, 15.74), 130 ($M^+ - 117$, 27.30), 104 ($M^+ - 143$, 26.30), 43 ($M^+ - 204$, 100); HRMS (EI) calcd. for $C_{13}H_{13}NO_4$: 247.0845, Found: 247.0849.

6-(2,3-Dichlorophenyl)-6-hydroxy-3-methylhexa-3,4-dien-2-one 6h. Mp 88–92 °C; IR (CH_2Cl_2) ν 3424, 1951, 1679, 1450, 1420, 1359, 1262, 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**6h** and (1*S*,3*S*)-**6h**: 1.74 (3H, d, J = 2.4 Hz, CH_3), 2.17 (3H, s, CH_3), 2.57–2.65 (1H, br s, OH), 5.82–5.86 (2H, m, CH, =CH), 7.25–7.30 (1H, m, ArH), 7.42–7.44 (1H, m, ArH), 7.55–7.58 (1H, m, ArH); (1*S*,3*R*)-**6h** and (1*R*,3*S*)-**6h**: 1.76 (3H, d, J = 2.4 Hz, CH_3), 2.21 (3H, s, CH_3), 2.57–2.65 (1H, br s, OH), 5.82–5.86 (2H, m, CH, =CH), 7.25–7.30 (1H, m, ArH), 7.42–7.44 (1H, m, ArH), 7.55–7.58 (1H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 13.03, 13.25, 26.77, 26.79, 68.79, 68.82, 97.07, 97.14, 107.31 (2C), 124.99 (2C), 125.17 (2C), 129.69, 129.73, 129.91 (2C), 133.03, 133.05, 141.98 (2C), 198.85 (2C), 211.99, 212.16; MS (EI) *m/e* 253 ($M^+ - 17$, 1.12), 210 ($M^+ - 60$, 3.51), 175 ($M^+ - 95$, 26.56), 96 ($M^+ - 174$, 47.01), 43 ($M^+ - 227$, 100); HRMS (MALDI) calcd. for $C_{13}H_{13}O_2Cl_2^{+1}$: 271.0287, Found: 271.0275.

3-Benzyl-6-(4-chlorophenyl)-6-hydroxyhexa-3,4-dien-2-one 6i. Mp 75–79 °C; IR (CH_2Cl_2) ν 3427, 1947, 1676, 1493, 1453, 1359, 1244, 1090 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ (1*R*,3*R*)-**6i** and (1*S*,3*S*)-**6i**: 2.23 (3H, s, CH_3), 2.47 (1H, br s, OH), 3.39–3.47 (1H, dm, J = 15.3 Hz, CH_2), 3.57 (1H, dm, J = 15.3 Hz, CH_2), 5.15 (1H, dd, J = 7.2, 7.2 Hz, CH), 5.73–5.75 (1H, m, =CH), 7.02–7.33 (9H, m, ArH); (1*S*,3*R*)-**6i** and (1*R*,3*S*)-**6i**: 2.26 (3H, s, CH_3), 2.47 (1H, br s, OH), 3.39–3.47 (1H, dm, J = 15.3 Hz, CH_2), 3.57 (1H, dm, J = 15.3 Hz, CH_2), 5.15 (1H, dd, J = 7.2, 7.2 Hz, CH), 5.66–5.68 (1H, m, =CH), 7.00–7.32 (9H, m, ArH); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 27.11 (2C), 33.04, 33.16, 70.92, 71.05, 100.56, 100.78, 112.23, 112.78, 126.31, 126.36, 127.04, 127.33, 128.29, 128.34, 128.47, 128.58, 128.94, 129.10, 133.43, 133.67, 138.81, 139.03, 140.05, 140.27, 197.66, 197.70, 211.12, 211.30; MS (EI) *m/e* 312 (M^+, 0.72), 295 ($M^+ - 17$, 2.43), 251 ($M^+ - 61$, 17.72), 217 ($M^+ - 95$, 10.10), 172 ($M^+ - 140$, 14.14), 77 ($M^+ - 235$, 29.70), 43 ($M^+ - 269$, 100); HRMS (EI) calcd. for $C_{19}H_{17}O_2Cl$: 312.0917, Found: 312.0907.

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