One-pot synthesis of new type *aza*- Baylis–Hillman adducts from chlorovinyl aldehydes under solvent-free condition

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A series of new type *aza*- Baylis–Hillman adducts were prepared in moderate yields by one-pot treatment of chlorovinyl aldehydes, benzenesulfonamides and activated olefins under solvent-free condition. The chlorovinyl aldehydes were obtained via chloroformylation of ketones using bis(trichloromethyl)carbonate(BTC)/DMF system.

Keywords: *aza*- Baylis–Hillman reaction, chlorovinyl aldehydes, chloroformylation, benzenesulfonamides

The Baylis–Hillman reaction has become an important tool in organic synthesis because of the formation of carbon–carbon bonds under mild conditions.[1–3] The *aza* version provides a convenient method for the synthesis of α-methylene-β-amino carbonyl compounds. The *aza*- Baylis–Hillman adducts and their rearranged derivatives are used extensively for the synthesis of many heterocyclic compounds which are key skeletons in many biologically important compounds.[2,4–9] To improve the *aza*- Baylis–Hillman reaction, various methods including Lewis acids catalysis,[10–12] ultrasound[13,14] or microwaves irradiation,[15] using ionic liquids[16,17] or supercritical carbon dioxide[18] as solvents, under high pressure[19,20] have proved advantageous in some cases.

In continuation of our research on Baylis–Hillman reaction and its adducts,[21–23] recently we have developed an efficient synthesis of new type Baylis–Hillman adducts from the chlorovinyl aldehydes which were prepared by treatment of ketones with the Vilsmeier reagent derived from *bis*(trichloromethyl) carbonate(BTC)/DMF system instead of the traditional $POCl_3$/DMF system[24] (Scheme 1). Then, we suspected that new type *aza*- Baylis–Hillman adducts might be synthesised in one pot from the chlorovinyl aldehydes.

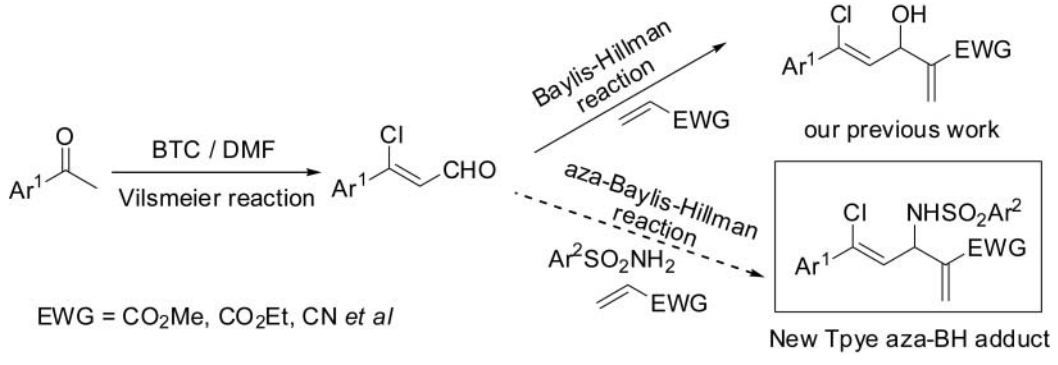
Initially, (*Z*)-3-chloro-3-phenylacrylaldehyde **1a** was mixed with toluenesulfonamide **2a** and methyl acrylate **3a** at room temperature in DMF catalysed by DABCO (Table 1, entry 1), however, no desired new *aza*- Baylis–Hillman adduct **4a** was detected but a new Baylis–Hillman adduct **5a** was isolated with 86%. When the Lewis acid $AlCl_3$ was added to the above reaction, 30% of **4a**, accompanied with 8% of **5a** and 23% of chlorovinyl aldehyde **1a** was isolated (Table 1, entry 2). Other solvents such as toluene and THF gave also unsatisfactory results. When this reaction was carried out under solvent-free conditions at room temperature for 3 hours, the desired product **4a** was isolated with a yield of 58% (Table 1, entry 5). Attempts to elevate or decrease reaction temperature and prolong the reaction time under solvent-free conditions failed to improve the product yield, but some of the starting material **1a** was recovered (Table 1, entries 6–8). Compared to DABCO, the base DMAP and DBU provided only traces of **4a** and worse results were observed using $ZnCl_2$ or CF_3CO_2H as additives instead of $AlCl_3$.

On the other hand, to improve the reaction yield, we tried to prepare **4a** *via* formation of benzenesufonimide derivative **6a**. Firstly treatment of (*Z*)-3-chloro-3-phenylacrylaldehyde **1a** with toluenesulfonamide **2a** catalysed by $AlCl_3$ generated a benzenesufonimide derivative **6a** *in situ*, which was directly used for Baylis–Hillman reaction by mixture with methyl acrylate **3a** in the presence of DABCO at room temperature for 48 h. To our disappointment, TLC showed that no reaction took place and a mixture of the starting material **1a** and the intermediate **6a** was isolated after column chromatography on silica gel (Scheme 2). So, the optimal condition for the preparation of **4** was to mix **1**, **2** with **3** at room temperature under solvent-free conditions catalysed by DABCO and $AlCl_3$ system.

In order to extend the scope of this strategy, various chlorovinyl aldehydes **1**, benzenesulfonamides **2** and activated olefins **3** were used for *aza*- Baylis–Hillman reaction under similar conditions and the full results are summarised in Table 2. It was found that most of the substrates **1** gave the corresponding *aza*- Baylis–Hillman adducts **4a–o** in low to moderate yields (30–60%).

According to Table 2, the electron-withdrawing groups on the aromatic ring were found to benefit the formation of *aza*- Baylis–Hillman adducts. Compared to methyl acrylate, ethyl acrylate provided the corresponding products **4** with lower yield over prolonged reaction times. To our surprise, when but-3-en-2-one was used instead of methyl acrylate, only Baylis–Hillman adducts **5n–o** were formed quickly in high yields (Table 2, entries 14–15), which is very different from the previously reported results.[25]

In addition, other special substrates were also investigated under the optimal condition. The substrate **1p** could be provided the desired product **4p** and the side product **5p** in



Scheme 1

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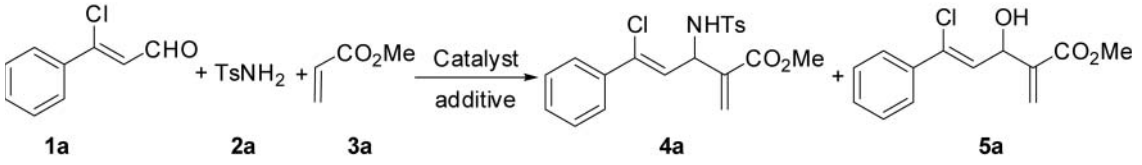
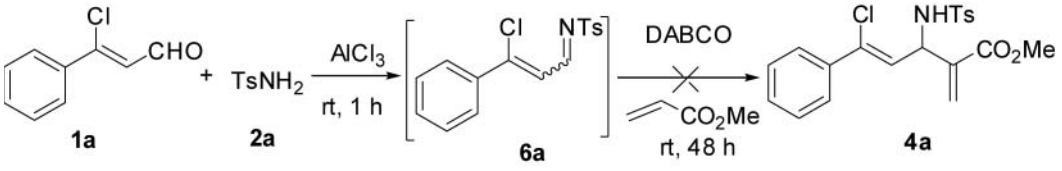
Table 1 The *aza*- Baylis–Hillman reactions of **1a** under different conditions[a]



1a **2a** **3a** **4a** **5a**

Entry	Catalyst	Additives	Solvents	Temp./°C	Time/h	Yield/%[b]	
						4a	**5a**
1	DABCO	–	DMF	rt	14	–	86
2	DABCO	$AlCl_3$	DMF	rt	14	30[c]	8
3	DABCO	$AlCl_3$	Toluene	rt	14	35[c]	10
4	DABCO	$AlCl_3$	THF	rt	14	32[c]	11
5	DABCO	$AlCl_3$	Solvent-free	rt	3	58	20
6	DABCO	$AlCl_3$	Solvent-free	rt	14	56	18
7	DABCO	$AlCl_3$	Solvent-free	0	14	48	15
8	DABCO	$AlCl_3$	Solvent-free	50	3	50	12
9	DMAP	$AlCl_3$	Solvent-free	rt	48	Trace[c]	9
10	DBU	$AlCl_3$	Solvent-free	rt	48	Trace[c]	12
11	K_2CO_3	$AlCl_3$	Solvent-free	rt	48	Trace[c]	14
12	DABCO	$ZnCl_2$	Solvent-free	rt	8	49	18
13	DABCO	CF_3CO_2H	Solvent-free	rt	36	34[c]	13

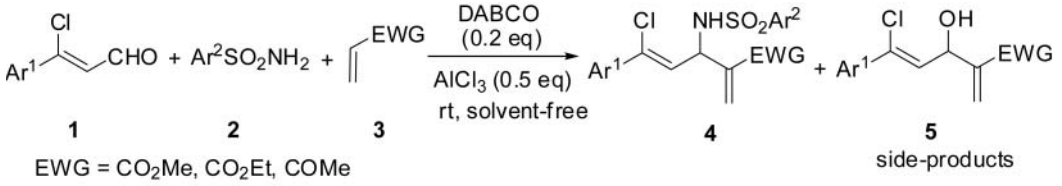
[a]Conditions: **1a** (3.0 mmol), **2a** (3.0 mmol), **3a** (9.0 mmol), additives (1.5 mmol), bases (0.6 mmol), solvents (10 mL) were used.
[b]Isolated yields based on **1a**.
[c]Some chlorovinyl aldehyde **1a** was recovered.



1a **2a** **6a** **4a**

Scheme 2

Table 2 The synthesis of new type *aza*- Baylis–Hillman adducts[a]



1 **2** **3** **4** **5**

EWG = CO_2Me, CO_2Et, COMe

side-products

Entry	Ar^1	Ar^2	EWG	Time/h	Product (Yield/%)[b]	
					4	**5**
1	C_6H_5	4-MeC_6H_4	CO_2Me	10	**4a** (58)	**5a** (20)
2	C_6H_5	Ph	CO_2Me	24	**4b** (48)	**5a** (18)
3	C_6H_5	2-ClC_6H_4	CO_2Me	72	**4c** (28[c])	**5a** (10)
4	C_6H_5	4-MeC_6H_4	CO_2Et	72	**4d** (36)	**5d** (15)
5	*p*-MeC_6H_4	4-MeC_6H_4	CO_2Me	1	**4e** (47)	**5e**(17)
6	*p*-MeC_6H_4	4-MeC_6H_4	CO_2Et	72	**4f** (33[c])	**5f** (11)
7	*p*-MeC_6H_4	Ph	CO_2Me	24	**4g** (45)	**5e**(16)
8	*p*-FC_6H_4	4-MeC_6H_4	CO_2Me	1	**4h** (42)	**5h** (15)
9	*p*-ClC_6H_4	4-MeC_6H_4	CO_2Me	2	**4i**(55)	**5i** (15)
10	*m*-ClC_6H_4	4-MeC_6H_4	CO_2Me	10	**4j** (40[c])	**5j** (12)
11	*m*-ClC_6H_4	Ph	CO_2Me	12	**4k** (30[c])	**5j** (10)
12	*p*-$MeOC_6H_4$	4-MeC_6H_4	CO_2Me	2	**4l** (53)	**5l** (15)
13	*p*-$NO_2C_6H_4$	4-MeC_6H_4	CO_2Me	1	**4m** (60)	**5m** (16)
14	C_6H_5	4-MeC_6H_4	COMe	0.5	**4n** (ND[d])	**5n** (68)
15	*p*-FC_6H_4	4-MeC_6H_4	COMe	0.5	**4o** (ND[d])	**5o** (70)

[a]Conditions: **1** (3.0 mmol), **2** (3.0 mmol), **3** (9.0 mmol), $AlCl_3$ (1.5 mmol), DABCO (0.6 mmol) were used.
[b]Isolated yields based on **1**.
[c]The reaction was carried out under ultrasound and solvent-free conditions.
[d]No desired products were detected.

50% and 15%, respectively (Scheme 3). When (*Z*)-3-chloro-2-methyl-3-phenylacrylaldehyde **1q** derived from propiophenone was tested under similar conditions, 30% of the *aza*- Baylis–Hillman adduct **4q**, accompanied with the unexpected 4-chloro-3-methyl-1-tosyl-1,2-dihydroquinoline **7** (50%) was obtained (Scheme 3). Further study showed that the unique product **7** was formed in 85% when using just $AlCl_3$ as catalyst. A plausible mechanism of this process includes Friedel-Crafts acylation and ring enlargement as shown in Scheme 4.

In summary, we have developed a one-pot synthesis of new *aza*- Baylis–Hillman adducts from chlorovinyl aldehydes with low to moderate yields. Further studies on their application are now in progress in our laboratory.

Experimental

Melting points were determined on a Büchi B-540 capillary melting point apparatus and uncorrected. IR spectra were recorded on a Thermo Nicolet Avatar 370 spectropho-tometer. ^1H and ^{13}C spectra were recorded in $CDCl_3$ with tetramethylsilane (TMS, $\delta = 0$) as an internal standard at ambient temperature on a Varian-400 MHz spectrometer at 400 and 100 MHz. Chemical shifts (δ) are expressed in ppm and coupling constants *J* are given in Hz. Mass spectra were obtained on a Trace DSQ mass spectrometer. Elemental analyses were carried out on a Vario EL III instrument. The chlorovinyl aldehydes were prepared by treatment of ketones with *bis*(trichloromethyl)carbonate (BTC)/DMF system.[24]

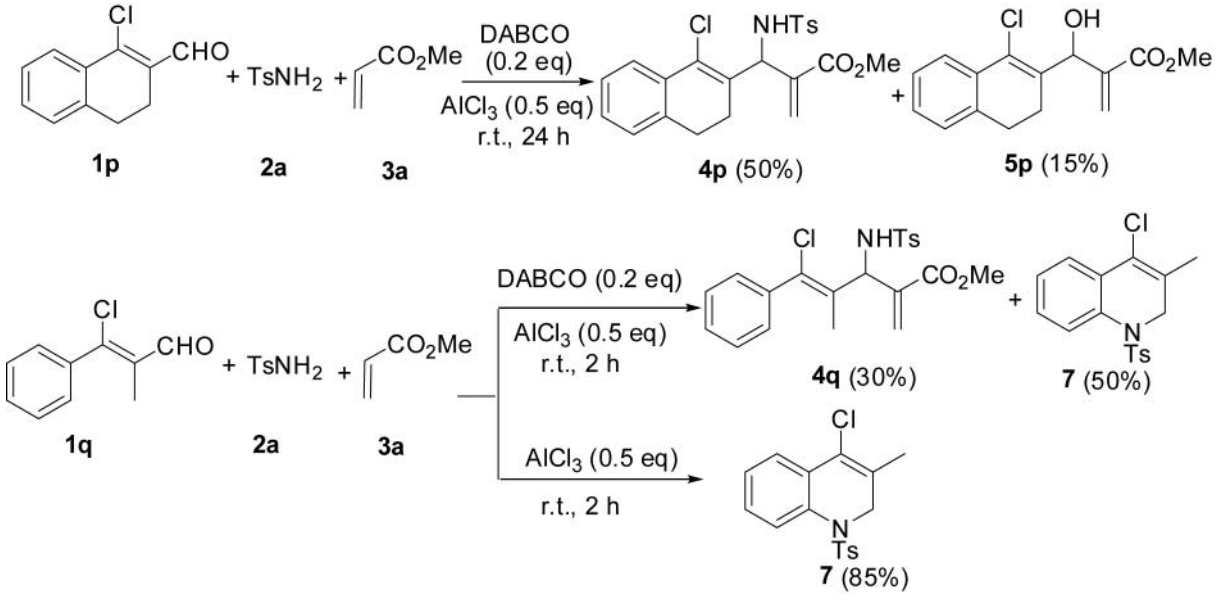
*Typical procedure for (Z)-methyl 5-chloro-2-methylene-3-(tolylsulfonamido)-5-phenylpent-4-enoate (**4a**) and (Z)-methyl 5-chloro-3-hydroxy-2-methylene-5-phenylpent-4-enoate* **(5a)**

To a mixture of (*Z*)-3-chloro-3-phenylacrylaldehyde **1a** (3.0 mmol), toluenesulfonamide **2a** (3.0 mmol) and methyl acrylate **3a** (9.0 mmol), were added $AlCl_3$ (1.5 mmol) and DABCO (0.6 mmol). The mixture was stirred at room temperature for a given time (Table 2). Then the reaction was quenched with water and extracted with dichloromethane (30 mL×3). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum and the obtained residue was further purified by flash column chromatography on silica gel (petroleum ether:ethyl acetate = 8:1) to give the desired product **4a** and the side product **5a**.

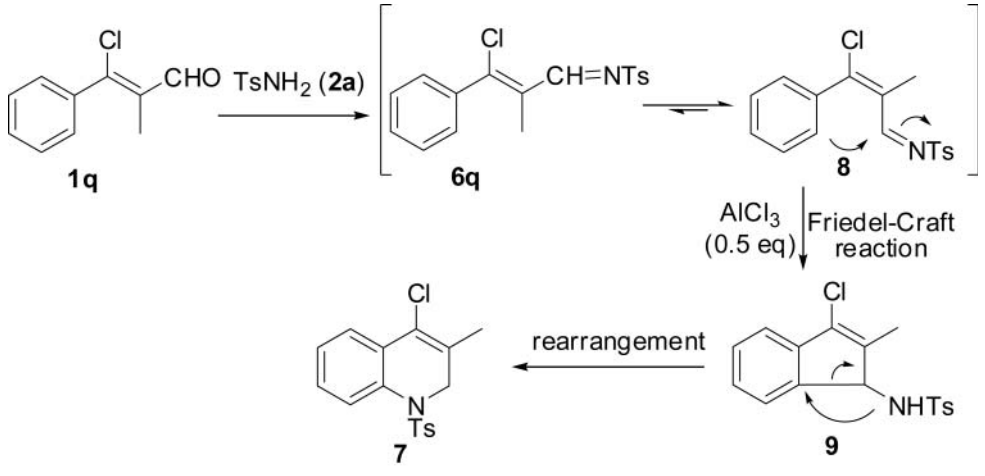
The products **4b–q** and **5d–f, 5h–j, 5l–p** could also be prepared under the similar conditions.

Typical procedure for 4-chloro-3-methyl-1-tosyl-1,2-dihydroquinoline **(7)**

To a mixture of (*Z*)-3-chloro-2-methyl-3-phenylacrylaldehyde **1q** (3.0 mmol), toluenesulfonamide **2a** (3.0 mmol) were added $AlCl_3$ (1.5 mmol). The mixture was stirred at room temperature for 2h. Then the reaction was quenched with water and extracted with



Scheme 3



Scheme 4 Plausible mechanism for the formation of **7**.

dichloromethane (30 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated under vacuum and the obtained residue was further purified by flash column chromatography on silica gel (petroleum ether:ethyl acetate = 8:1) to give the product **7**.

(Z)-Methyl 5-chloro-2-methylene-3-(tolylsulfonamido)-5-phenylpent-4-enoate (**4a**): Yellow solid; m.p. 112–114 °C. ^{1}H NMR($CDCl_3$, 400MHz): δ 2.29 (3H, s, C*H*$_3$), 3.71 (3H, s, C*H*$_3$O), 5.24 (1H, t, *J* = 8.8 Hz, C*H*), 5.83 (1H, d, *J* = 10.0 Hz, C=C*H*), 5.93 (1H, s, $MeCO_2C$=C*H*), 6.00 (1H, d, *J* = 8.4 Hz, N*H*), 6.17 (1H, s, $MeCO_2C$=C*H*), 7.18–7.74 (7H, m, Ar*H*), 7.75 (2H, d, *J* = 8.0 Hz, Ar*H*); ^{13}C NMR($CDCl_3$, 100M Hz): δ 21.4, 52.2, 56.3, 124.8, 126.4, 127.2, 128.1(2C), 128.4(2C), 129.1(2C), 129.5(2C), 134.9, 136.5, 136.6, 137.8, 143.5, 166.0; IR (KBr): 3252, 1709, 1634, 1589, 1164 cm^{-1}; MS (ESI) 428[M+Na]$^+$; Anal. Calcd for $C_{20}H_{20}ClNO_4S$: C, 59.18; H, 4.97; N, 3.45. Found: C, 59.29; H, 5.13; N, 3.51%.

(Z)-Methyl 5-chloro-2-methylene-5-phenyl-3-(phenylsulfonamido) pent-4-enoate (**4b**): Yellow oil. ^{1}H NMR($CDCl_3$, 400MHz): δ 3.71 (3H, s, C*H*$_3$O), 5.27 (1H, m, C*H*), 5.83 (1H, d, *J* = 10.0 Hz, C=C*H*), 5.93 (1H, s, $MeCO_2C$=C*H*), 6.05 (1H, d, *J* = 8.8 Hz, N*H*), 6.15 (1H, s, $MeCO_2C$=C*H*), 7.27–7.49 (7H, m, Ar*H*), 7.87 (2H, m, Ar*H*); ^{13}C NMR($CDCl_3$, 100MHz): δ 52.2, 56.3, 124.6, 126.5, 127.1, 128.2(2C), 128.5(2C), 128.9(2C),129.2(2C), 132.6, 135.1, 136.5, 136.7, 140.8, 165.9; IR (neat): 3280, 1715, 1578, 1446, 1164 cm^{-1}; MS (ESI) 390[M-1]$^-$; Anal. Calcd for $C_{19}H_{18}ClNO_4S$: C, 58.23; H, 4.63; N, 3.57. Found: C, 58.34; H, 4.53; N, 3.31%.

(Z)-Methyl 5-chloro-3-(2-chlorophenylsulfonamido)-2-methylene-5-phenylpent-4-enoate (**4c**): Yellow oil. ^{1}H NMR($CDCl_3$, 400MHz): δ 3.76 (3H, s, C*H*$_3$O), 5.25 (1H, m, C*H*), 5.86 (1H, s, $MeCO_2C$=C*H*), 6.14 (1H, s, $MeCO_2C$=C*H*), 6.18 (1H, d, *J* = 8.8 Hz, C=C*H*), 6.42 (1H, d, *J* = 10.0 Hz, N*H*), 7.24–7.43 (8H, m, Ar*H*), 7.75 (1H, m, Ar*H*); ^{13}C NMR($CDCl_3$, 100MHz): δ 52.3, 56.6, 123.6, 126.4, 127.2, 128.2, 128.4, 129.2(2C), 130.1(2C), 131.2, 133.6(2C), 135.1, 136.3, 136.5, 138.1, 165.9; IR (neat): 3321, 1712, 1586, 1444, 1166 cm^{-1}; MS (ESI) 460[M+Cl]$^-$; Anal. Calcd for $C_{19}H_{17}Cl_2NO_4S$: C, 53.53; H, 4.02; N, 3.29. Found: C, 53.43; H, 4.11; N, 3.37%.

(Z)-Ethyl 5-chloro-2-methylene-3-(tolylsulfonamido)-5-phenylpent-4-enoate (**4d**): Light yellow solid; m.p. 113–115 °C. ^{1}H NMR($CDCl_3$, 400MHz): δ 1.27 (3H, t, *J* = 9.2 Hz, C*H*$_3$), 2.29 (3H, s, C*H*$_3$), 4.17 (1H, d, *J* = 9.2 Hz, C*H*$_2$O), 4.17 (1H, d, *J* = 9.2 Hz, C*H*$_2$O), 5.23 (1H, t, *J* = 9.2 Hz, C*H*), 5.78 (1H, d, *J* = 10.0 Hz, C=C*H*), 5.93 (1H, s, $MeCO_2C$=C*H*), 6.00 (1H, d, *J* = 8.4 Hz, N*H*), 6.16 (1H, s, $MeCO_2C$=C*H*), 7.19–7.30 (7H, m, Ar*H*), 7.74 (2H, d, *J* = 8.0 Hz, Ar*H*); ^{13}C NMR($CDCl_3$, 100MHz): δ 14.3, 21.7, 30.0, 56.7, 61.6, 125.2, 126.7, 127.5(2C), 128.5(2C), 129.4(2C), 129.8(2C), 135.2, 137.0, 137.1, 138.2, 143.7, 165.9; IR (neat): 3411, 1715, 1634, 1441, 1160 cm^{-1}; MS (ESI) 418[M-1]$^-$; Anal. Calcd for $C_{21}H_{22}ClNO_4S$: C, 60.06; H, 5.28; N, 3.34. Found: C, 59.93; H, 5.21; N, 3.45%.

(Z)-Methyl 5-chloro-2-methylene-3-(tolylsulfonamido)-5-tolylpent-4-enoate (**4e**): Yellow solid; m.p. 105–106 °C. ^{1}H NMR($CDCl_3$, 400MHz): δ 2.31 (6H, t, C*H*$_3$), 3.71 (3H, s, C*H*$_3$O), 5.23 (1H, t, *J* = 8.8 Hz, C*H*), 5.77 (1H, d, *J* = 9.6 Hz, C=C*H*), 5.92 (1H, s, $MeCO_2C$=C*H*), 5.94 (1H, d, *J* = 8.2 Hz, N*H*), 6.15 (1H, s, $MeCO_2C$=C*H*), 7.07 (2H, d, Ar*H*), 7.13 (2H, d, *J* = 8.4 Hz, Ar*H*), 7.20 (2H, d, *J* = 8.0 Hz, Ar*H*), 7.73 (2H, d, *J* = 8.0 Hz, Ar*H*); ^{13}C NMR($CDCl_3$, 100MHz): δ 21.2, 21.4, 52.1, 56.3, 123.8, 126.4, 127.2(2C), 128.3(2C), 128.8(2C), 129.5(2C), 133.9, 135.1, 136.7, 137.9, 139.2, 143.4, 166.0; IR (KBr): 3256, 1691, 1630, 1335, 1164 cm^{-1}; MS (ESI) 418[M-1]$^-$; Anal. Calcd for $C_{21}H_{22}ClNO_4S$: C, 60.06; H, 5.28; N, 3.34. Found: C, 60.19; H, 5.45; N, 3.42%.

(Z)-Ethyl 5-chloro-2-methylene-3-(tolylsulfonamido)-5-tolylpent-4-enoate (**4f**): Yellow oil. ^{1}H NMR($CDCl_3$, 400MHz): δ 1.25–1.29 (3H, m, C*H*$_3$), 2.31 (6H, d, *J* = 8.8 Hz, C*H*$_3$), 4.11–4.20 (2H, m, C*H*$_2$O), 5.22 (1H, t, *J* = 9.2 Hz, C*H*), 5.77 (1H, s, C=C*H*), 5.91 (1H, s, $MeCO_2C$=C*H*), 5.95 (1H, d, *J* = 8.4 Hz, N*H*), 6.15 (1H, s, $MeCO_2C$=C*H*), 7.07 (2H, d, *J* = 8.4 Hz, Ar*H*), 7.13 (2H, d, *J* = 4.4 Hz, Ar*H*), 7.19 (2H, d, *J* = 8.0 Hz, Ar*H*), 7.73 (2H, d, *J* = 8.0 Hz, Ar*H*); ^{13}C NMR($CDCl_3$, 100MHz): δ 14.0, 21.1, 21.4, 56.4, 61.2, 123.9, 126.3(2C), 127.2(2C), 128.0, 128.8(2C), 129.5(2C), 134.0, 135.0, 137.0, 138.0, 139.2, 143.3, 165.6; IR (neat): 3260, 1690, 1625, 1439, 1161 cm^{-1}; MS (ESI) 456[M+Na]$^+$; Anal. Calcd for $C_{22}H_{24}ClNO_4S$: C, 60.89; H, 5.57; N, 3.23. Found: C, 60.96; H, 5.49; N, 3.19%.

(Z)-Methyl 5-chloro-2-methylene-3-(phenylsulfonamido)-5-tolylpent-4-enoate (**4g**): Yellow oil. ^{1}H NMR($CDCl_3$, 400MHz): δ 2.33 (3H, s, C*H*$_3$), 3.71 (3H, s, C*H*$_3$O), 5.25 (1H, t, *J* = 9.6 Hz, C*H*), 5.80 (1H, d, *J* = 9.6 Hz, C=C*H*), 5.91 (1H, s, $MeCO_2C$=C*H*), 6.00 (1H, d, *J* = 8.4 Hz, N*H*), 6.14 (1H, s, $MeCO_2C$=C*H*), 7.07 (2H, d, *J* = 8.4 Hz, Ar*H*), 7.16 (2H, d, *J* = 8.4 Hz, Ar*H*), 7.40–7.47 (3H, m, Ar*H*), 7.85–7.87 (2H, m, Ar*H*); ^{13}C NMR($CDCl_3$, 100MHz): δ 21.1, 29.7, 52.2, 56.4, 123.7, 126.4(2C), 127.1(2C), 128.3(2C), 128.9(2C), 132.6, 133.9, 135.2, 136.6, 139.4, 140.9, 166.0; IR (neat): 3273, 1716, 1633, 1446, 1163 cm^{-1}; MS (ESI) 440[M+Cl]$^-$; Anal. Calcd for $C_{20}H_{20}ClNO_4S$: C, 59.18; H, 4.97; N, 3.45. Found: C, 59.25; H, 4.91; N, 3.29%.

(Z)-Methyl 5-chloro-5-(4-fluorophenyl)-2-methylene-3-(tolylsulfonamido)pent-4-enoate (**4h**): Yellow solid; m.p. 118–120 °C. ^{1}H NMR($CDCl_3$, 400MHz): δ 2.30 (3H, s, C*H*$_3$), 3.71 (3H, s, C*H*$_3$O), 5.22 (1H, t, *J* = 9.6 Hz, C*H*), 5.90 (2H, m, C=C*H* and $MeCO_2C$=C*H*), 5.98 (1H, d, *J* = 9.6 Hz, N*H*), 6.16 (1H, s, $MeCO_2C$=C*H*), 6.93–6.97 (2H, m, Ar*H*), 7.18–7.74 (4H, m, Ar*H*), 7.75 (2H, d, *J* = 8.0 Hz, Ar*H*); ^{13}C NMR($CDCl_3$, 100MHz): δ 21.3, 52.1, 56.2, 114.7, 115.0, 124.8, 128.3 (2C), 128.4(2C), 129.4(2C), 132.9(2C), 133.8, 136.6, 137.9, 143.4, 163.1 (d, J_{CF} 250.1 Hz), 165.9; IR (neat): 3255, 1708, 1633, 1597, 1164 cm^{-1}; MS (ESI) 446[M+Na]$^+$; Anal. Calcd for $C_{20}H_{19}ClFNO_4S$: C, 56.67; H, 4.52; N, 3.30. Found: C, 56.58; H, 4.40; N, 3.42%.

(Z)-Methyl 5-chloro-5-(4-chlorophenyl)-2-methylene-3-(tolylsulfonamido)pent-4-enoate (**4i**): White solid; m.p. 108–110 °C. ^{1}H NMR($CDCl_3$, 400MHz): δ 2.31 (3H, s, C*H*$_3$), 3.72 (3H, s, C*H*$_3$O), 5.21 (1H, t, *J* = 8.8 Hz, C*H*), 5.77 (1H, d, *J* = 10.0 Hz, C=C*H*), 5.93 (1H, s, $MeCO_2C$=C*H*), 6.00 (1H, d, *J* = 8.4 Hz, N*H*), 6.17 (1H, s, $MeCO_2C$=C*H*), 7.18 (2H, d, *J* = 8.6 Hz, Ar*H*), 7.22 (2H, d, *J* = 9.6 Hz, Ar*H*), 7.26 (2H, d, *J* = 2.4 Hz, Ar*H*), 7.73 (2H, d, *J* = 8.0 Hz, Ar*H*); ^{13}C NMR($CDCl_3$, 100MHz): δ 21.4, 52.2, 56.4, 125.4, 127.2, 127.7(2C), 128.3(2C), 128.6(2C), 129.5(2C), 133.8, 135.1, 135.1, 136.4, 137.9, 143.5, 166.0; IR (KBr): 3259, 1708, 1634, 1486, 1162 cm^{-1}; MS (ESI) 474[M+Cl]$^-$; Anal. Calcd for $C_{20}H_{19}Cl_2NO_4S$: C, 54.55; H, 4.35; N, 3.18. Found: C, 54.59; H, 4.45, N, 3.29%.

(Z)-Methyl 5-chloro-5-(3-chlorophenyl)-2-methylene-3-(tolylsulfonamido)pent-4-enoate (**4j**): Yellow oil. ^{1}H NMR($CDCl_3$, 400MHz): δ 2.32 (3H, s, C*H*$_3$), 3.74 (3H, s, C*H*$_3$O), 5.21 (1H, t, *J* = 8.4 Hz, C*H*), 5.76 (1H, d, *J* = 10.0 Hz, C=C*H*), 5.96 (1H, s, $MeCO_2C$=C*H*), 5.98 (1H, d, *J* = 8.4 Hz, N*H*), 6.19 (1H, s, $MeCO_2C$=C*H*), 7.12 (2H, d, *J* = 7.2 Hz, Ar*H*), 7.18 (2H, d, *J* = 16.8 Hz, Ar*H*), 7.22 (2H, d, *J* = 8.0 Hz, Ar*H*), 7.74 (2H, d, *J* = 8.4 Hz, Ar*H*); ^{13}C NMR($CDCl_3$, 100MHz): δ 21.4, 52.3, 56.4, 124.7, 126.1, 126.5, 127.2, 128.7(2C), 129.1(2C), 129.4, 129.6, 130.5, 133.4, 136.3, 138.5, 139.7, 143.7, 166.0; IR (neat): 3280, 1707, 1593, 1503, 1160 cm^{-1}; MS (ESI) 474[M+Cl]$^-$; Anal. Calcd for $C_{20}H_{19}Cl_2NO_4S$: C, 54.55; H, 4.35; N, 3.18. Found: C, 54.65; H, 4.21; N, 3.32%.

(Z)-Methyl 5-chloro-5-(3-chlorophenyl)-2-methylene-3-(phenylsulfonamido)pent-4-enoate (**4k**): Yellow oil. ^{1}H NMR($CDCl_3$, 400MHz): δ 3.73 (3H, s, C*H*$_3$O), 5.24 (1H, t, *J* = 9.6 Hz, C*H*), 5.85 (1H, d, *J* = 9.6 Hz, C=C*H*), 5.94 (1H, s, $MeCO_2C$=C*H*), 6.04 (1H, d, *J* = 8.4 Hz, N*H*), 6.17 (1H, s, $MeCO_2C$=C*H*), 7.15–7.29 (4H, m, Ar*H*), 7.43–7.51 (3H, m, Ar*H*), 7.87 (2H, d, *J* = 6.8 Hz, Ar*H*); ^{13}C NMR($CDCl_3$, 100MHz): δ 52.3, 56.3, 124.7, 125.9, 126.6, 127.1, 128.8, 129.0(2C), 129.2, 129.5(2C), 132.7, 133.6, 134.2, 136.2, 138.3, 140.8, 165.7; IR (neat): 3256, 1711, 1629, 1425, 1164 cm^{-1}; MS (ESI) 460[M+Cl]$^-$; Anal. Calcd for $C_{19}H_{17}Cl_2NO_4S$: C, 53.53; H, 4.02; N, 3.29. Found: C, 53.45; H, 3.94; N, 3.37%.

(Z)-Methyl 5-chloro-5-(4-methoxyphenyl)-2-methylene-3-(tolylsulfonamido)pent-4-enoate (**4l**): White solid; m.p. 101–103 °C. ^{1}H NMR($CDCl_3$, 400MHz): δ 2.31 (3H, s, C*H*$_3$), 3.71 (3H, s, C*H*$_3$O), 3.80 (3H, s, C*H*$_3$O), 5.22 (1H, t, *J* = 9.2 Hz, C*H*), 5.77 (1H, d, *J* = 9.6 Hz, C=C*H*), 5.87 (1H, s, $MeCO_2C$=C*H*), 5.91 (1H, d, *J* = 10.0 Hz, N*H*), 6.15 (1H, s, $MeCO_2C$=C*H*), 6.78 (2H, d, *J* = 8.8 Hz, Ar*H*), 7.16–7.27 (4H, m, Ar*H*), 7.74 (2H, d, *J* = 8.4 Hz, Ar*H*); ^{13}C NMR($CDCl_3$, 100MHz): δ 21.4, 29.7, 52.1, 55.3, 56.4, 113.4, 122.9, 127.2(2C), 127.8(2C), 128.2(2C), 129.5(2C), 134.7, 136.7, 137.9, 143.4, 160.2, 166.0; IR (KBr): 3250, 1708, 1633, 1508, 1164 cm^{-1}; MS (ESI) 470[M+Cl]$^-$; Anal. Calcd for $C_{21}H_{22}ClNO_5S$: C, 57.86; H, 5.09; N, 3.21. Found: C, 57.99; H, 5.19; N, 3.29%.

(Z)-Methyl 5-chloro-2-methylene-3-(tolylsulfonamido)-5-(4-nitrophenyl)pent-4-enoate (**4m**): Yellow solid; m.p. 106–108 °C. ^{1}H NMR($CDCl_3$, 400MHz): δ 2.42 (3H, s, C*H*$_3$), 3.71 (3H, s, C*H*$_3$O), 4.61 (1H, t, *J* = 9.6 Hz, C*H*), 5.42 (1H, s, $MeCO_2C$=C*H*), 5.65 (1H, d, *J* = 9.2 Hz, C=C*H*), 6.03 (1H, s, $MeCO_2C$=C*H*), 6.16 (1H, d, *J* = 10.4 Hz, N*H*), 7.21–7.26 (2H, m, Ar*H*), 7.45 (2H, d, *J* = 9.2 Hz, Ar*H*), 7.48–7.58 (2H, m, Ar*H*), 8.22–8.24 (2H, m, Ar*H*); ^{13}C NMR($CDCl_3$, 100MHz): δ 21.5, 29.3, 56.4, 120.2, 123.5, 123.8(2C), 127.2(2C), 128.6(2C), 129.5(2C), 132.8, 137.1, 137.5, 142.0, 143.7, 148.1, 165.4;

IR (KBr): 3253, 1709, 1629, 1593, 1164 cm^{-1}; MS (ESI) 449[M-1]$^-$; Anal. Calcd for $C_{20}H_{19}ClN_2O_6S$: C, 53.28; H, 4.25; N, 6.21. Found: C, 53.43; H, 4.13; N, 6.29%.

Methyl 2-((1-chloro-3,4-dihydronaphthalen-2-yl)(tolylsulfonamido)methyl)acrylate **(4p)**: Yellow solid; m.p. 130–133 °C.^{1}H NMR($CDCl_3$, 400MHz): δ 2.21 (2H, t, *J* = 8.0 Hz, CH_2), 2.29 (3H, s, CH_3), 2.44–2.59 (2H, m, CH_2), 3.67 (3H, s, CH_3O), 5.64 (1H, d, *J* = 8.8 Hz, C*H*), 5.93 (1H, s, MeCO$_2$C=C*H*), 6.10 (1H, s, N*H*), 6.26 (1H, s, MeCO$_2$C=C*H*), 7.02 (1H, d, *J* = 7.2 Hz, Ar*H*), 7.14–7.26 (4H, m, Ar*H*), 7.53 (1H, d, *J* = 7.6 Hz, Ar*H*), 7.77 (2H, t, *J* = 6.8 Hz, Ar*H*); ^{13}C NMR($CDCl_3$, 100MHz): δ 21.4, 24.8, 27.3, 52.1, 56.4, 124.7, 126.5, 126.7, 127.2, 128.1(2C), 128.3, 128.8, 129.4(2C), 132.4, 132.4, 135.9, 136.8, 137.0, 143.5, 166.1; IR (KBr): 3264, 1727, 1629, 1589, 1154 cm^{-1}; MS (ESI) 454[M+Na]$^+$; Anal. Calcd for $C_{22}H_{22}ClNO_4S$: C, 61.18; H, 5.13; N, 3.24. Found: C, 61.22; H, 5.19; N, 3.29%.

(Z)-Methyl 5-chloro-4-methyl-2-methylene-3-(tolylsulfonamido)-5-phenylpent-4-enoate **(4q)**: Yellow solid; m.p. 122–124 °C.^{1}H NMR($CDCl_3$, 400MHz): δ 1.85 (3H, s, CH_3), 2.40 (3H, s, CH_3), 3.61 (3H, s, CH_3O), 5.03 (1H, d, *J* = 8.4 Hz, MeCO$_2$C=C*H*), 5.29 (1H, d, *J* = 8.4 Hz, MeCO$_2$C=C*H*), 5.58–5.70 (1H, m, N*H*), 6.06 (1H, s, C*H*), 7.19–7.34 (7H, m, Ar*H* and MeCO$_2$C=C*H*), 7.55 (2H, d, *J* = 8.4 Hz, Ar*H*); ^{13}C NMR($CDCl_3$, 100MHz): δ 15.9, 21.5, 52.1, 56.6, 127.2, 128.2, 128.5, 128.7(2C), 128.8(2C), 129.4(2C), 131.1(2C), 132.1, 137.2, 137.5, 137.9, 143.4, 166.1; IR (neat): 3215, 1708, 1580, 1437, 1163 cm^{-1}; MS (ESI) 418[M-1]$^-$; Anal. Calcd for $C_{21}H_{22}ClNO_4S$: C, 60.06; H, 5.28; N, 3.34. Found: C, 60.17; H, 5.42; N, 3.44%.

(Z)-Methyl 5-chloro-3-hydroxy-2-methylene-5-phenylpent-4-enoate **(5a)**: Yellow oil[24]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.44 (1H, br s, O*H*), 3.79 (3H, s, CO$_2$CH_3), 5.48 (1H, d, *J* = 7.6 Hz, C*H*OH), 5.94 (1H, s, C = CH_2-*b*), 6.29 (1H, s, C = CH_2-*a*), 6.35 (1H, d, *J* = 7.6 Hz, ClC = C*H*), 7.33–7.37 (3H, m, Ar*H*), δ 7.57–7.60 (2H, m, Ar*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 52.070.2, 120.1, 126.5(2C), 127.2, 128.3(2C), 129.0, 134.7, 137.1,139.5, 166.7; IR (neat): 3466, 2954, 1724, 1507, 1238, 1161 cm^{-1}; MS (EI) *m/z* 252 (M$^+$, 3), 217 (81), 185(100); Anal. Calcd for $C_{13}H_{13}ClO_3$: C, 61.79; H, 5.19. Found: C, 61.67; H, 5.12%.

(Z)-Ethyl 5-chloro-3-hydroxy-2-methylene-5-phenylpent-4-enoate **(5d)***:* Yellow oil[24]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.33 (3H, t, *J* = 7.2 Hz, CO$_2$CH$_2$CH_3), 3.34 (1H, br s, O*H*), 4.26 (2H, q, *J* = 7.2 Hz, CO$_2$CH_2CH$_3$), 5.47 (1H, d, *J* = 7.6 Hz, C*H*OH),5.93 (1H, s, C = CH_2-*b*),6.30 (1H, s, C = CH_2-*a*),6.35 (1H, d, *J* = 7.6 Hz, ClC = C*H*), 7.33–7.39 (3H, m, Ar*H*),δ 7.59–7.61 (2H, m, Ar*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.1, 61.1, 70.5, 126.3, 126.6 (2C), 127.3, 128.3 (2C), 129.1, 134.8, 137.2, 139.7, 166.4 ; IR (neat): 3500, 2983, 1720, 1328, 1266 cm^{-1}; MS (EI) *m/z* 266(M$^+$, 4), 231(65), 185(100); Anal. Calcd for $C_{14}H_{15}ClO_3$: C, 63.04; H, 5.67. Found: C, 63.11; H, 5.62%.

(Z)-Methyl 5-chloro-3-hydroxy-2-methylene-5-p-tolylpent-4-enoate **(5e)**: Yellow oil[24]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.35 (3H, s, CH_3), 3.36 (1H, br s, O*H*), 3.80 (3H, s, CO$_2$CH_3), 5.47 (1H, d, *J* = 8.0 Hz, C*H*OH), 5.94 (1H, s, C = CH_2-*b*), 6.29 (1H, s, C = CH_2-*a*), 6.31 (1H, d, *J* = 8.0 Hz, ClC = C*H*), 7.15 (2H, d, *J* = 8.4 Hz, Ar*H*), 7.49 (2H, d, *J* = 8.4 Hz, Ar*H*); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.1, 52.1, 70.4, 126.2, 126.5(2C), 126.6, 129.0(2C), 134.4, 135.0, 139.2, 139.5,166.9; IR (neat): 3478, 2982, 1716, 1260, 1177 cm^{-1}; MS (EI) *m/z* 266(M$^+$, 1), 231(51), 199(100); Anal. Calcd for $C_{14}H_{15}ClO_3$: C, 63.04; H, 5.67. Found: C, 62.98; H, 5.59%.

(Z)-Ethyl 5-chloro-3-hydroxy-2-methylene-5-p-tolylpent-4-enoate **(5f):** Yellow oil[24]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.32 (3H, t, *J* = 7.2 Hz, CO$_2$CH$_2$CH_3), 2.35 (3H, s, CH_3), 3.39 (1H, br s, O*H*) δ, 4.25 (2H, q, *J* = 7.2 Hz, CO$_2$CH_2CH$_3$), 5.47 (1H, d, *J* = 7.6 Hz, C*H*OH), 5.92 (1H, s, C = CH_2-*b*), 6.29 (1H, s, C = CH_2-*a*), 6.30 (1H, d, *J* = 8.0 Hz, ClC = C*H*), 7.15 (2H, d, *J* = 8.0 Hz, Ar*H*), 7.48 (2H, d, *J* = 8.0 Hz, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 21.4, 61.4, 70.6, 126.5, 126.6 126.7 (2C), 129.3 (2C), 134.7, 135.1, 139.4, 140.2, 166.7; IR (neat): 3501, 3127, 1703, 1400, 1300, 1188 cm^{-1}; MS (EI) *m/z* 280(M$^+$, 2), 245(63), 199(100); Anal. Calcd for $C_{15}H_{17}ClO_3$: C, 64.17; H, 6.10. Found: C, 64.08; H, 6.19.

(Z)-Methyl 5-chloro-5-(4-fluorophenyl)-3-hydroxy-2-methylene-pent-4-enoate **(5h):** Yellow oil[24]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.38 (1H, br s, O*H*), 3.81 (3H, s, CO$_2$CH_3), 5.45 (1H, d, *J* = 7.6 Hz, C*H*OH), 5.95 (1H, s, C = CH_2-*b*), 6.30 (1H, s, C = CH_2-*a*), 6.31 (1H, d, *J* = 8.0 Hz, ClC = C*H*), 7.02–7.06 (2H, m, Ar*H*), 7.55–7.59 (2H, m, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.1, 70.4, 115.2, 115.4, 126.7, 127.2, 128.4, 128.5, 133.3, 133.7, 139.5 163.1 (d, J_{CF} = 247.9 Hz), 166.8; IR (neat): 3466, 2954, 1724, 1507, 1238 cm^{-1}; MS (EI) *m/z* 270(M$^+$, 3), 203(100); Anal. Calcd for $C_{13}H_{12}ClFO_3$: C, 57.68; H, 4.47. Found: C, 57.77; H, 4.39%.

(Z)-Methyl 5-chloro-5-(4-chlorophenyl)-3-hydroxy-2-methylene-pent-4-enoate **(5i):** Yellow oil[24]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.37 (1H, br s, O*H*), 3.81 (3H, s, CO$_2$CH_3), 5.45 (1H, d, *J* = 7.6 Hz, C*H*OH), 5.94 (1H, s, C = CH_2-*b*), 6.30 (1H, s, C = CH_2-*a*), 6.35 (1H, d, *J* = 7.6 Hz, ClC = C*H*) 7.31–7.33 (2H, m, Ar*H*), 7.51–7.53 (2H, m, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.1, 70.4, 126.8, 127.7, 127.8 (2C), 128.5 (2C), 133.6, 135.1, 135.6, 139.3, 166.7; IR (neat): 3463, 2953, 1723, 1507, 1237 cm^{-1}; MS (EI) *m/z* 286(M$^+$, 1), 219(100); Anal. Calcd for $C_{13}H_{12}Cl_2O_3$: C, 54.38; H, 4.21. Found: C, 54.45; H, 4.31%.

(Z)-Methyl 5-chloro-5-(3-chlorophenyl)-3-hydroxy-2-methylene-pent-4-enoate **(5j):** Yellow oil[24]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.82 (3H, s, CO$_2$CH_3), 5.44 (1H, d, *J* = 7.6 Hz, C*H*OH), 5.95 (1H, s, C = CH_2-*b*), 6.31 (1H, s, C = CH_2-*a*), 6.38 (1H, d, *J* = 7.6 Hz, ClC = C*H*), 7.29–7.31 (2H, m, Ar*H*), 7.46–7.49 (1H, m, Ar*H*), 7.58 (1H, s, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.1, 70.4, 124.7, 126.7, 126.9, 128.4, 129.1, 129.6, 133.3, 134.4, 138.8, 139.2, 166.7; IR (neat): 3435, 2952, 1720, 1440, 1335, 1156 cm^{-1}; MS (EI) *m/z* 286(M$^+$, 3), 251(100); Anal. Calcd for $C_{13}H_{12}Cl_2O_3$: C, 54.38; H, 4.21. Found: C, 54.47; H, 4.18%.

(Z)-Methyl 5-chloro-3-hydroxy-5-(4-methoxyphenyl)-2-methylene-pent-4-enoate **(5l):** Yellow oil[24]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.45 (1H, br s, O*H*), 3.80 (6H, s, CO$_2$CH_3 and OCH_3), 5.47 (1H, d, *J* = 8.0 Hz, C*H*OH), 5.94 (1H, s, C = CH_2-*b*), 6.24 (1H, d, *J* = 8.0 Hz, ClC = C*H*), 6.28 (1H, s, C = CH_2-*a*), 6.86 (2H, d, *J* = 8.8 Hz, Ar*H*), 7.52 (2H, d, *J* = 8.4 Hz, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.0, 55.2, 70.2, 113.6 (2C), 125.2, 126.4, 127.9 (2C), 129.6, 134.5, 139.7, 160.2, 166.8; IR(neat): 3479, 2953, 1715, 1509, 1255, 1178 cm^{-1}; MS (EI) *m/z* 282(M$^+$, 9), 215(100); Anal. Calcd for $C_{14}H_{15}ClO_4$: C, 59.48; H, 5.35. Found: C, 59.33; H, 5.26%.

(Z)-Methyl 5-chloro-3-hydroxy-2-methylene-5-(4-nitrophenyl)pent-4-enoate **(5m):** Yellow oil[24]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.46 (1H, br s, O*H*), 3.83 (3H, s, CO$_2$CH_3), 5.47 (1H, d, *J* = 8.0 Hz, C*H*OH), 5.99 (1H, s, C = CH_2-*b*), 6.34 (1H, s, C = CH_2-*a*), 6.56 (1H, d, *J* = 8.0 Hz, ClC = C*H*), 7.77 (2H, d, *J* = 8.8 Hz, Ar*H*), 8.21 (2H, d, *J* = 9.2 Hz, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.5, 70.8, 123.9 (2C), 127.5, 127.6 (2C), 131.5, 132.6, 139.3, 143.2, 148.2, 166.9; IR (neat): 3480, 3106, 1703, 1518 cm^{-1}; MS (EI) *m/z* 297(M$^+$, 12), 1667(100); Anal. Calcd for $C_{13}H_{12}ClNO_5$: C, 52.45; H, 4.06; N, 4.71. Found: C, 52.53; H, 3.96; N, 4.72%.

(Z)-6-Chloro-4-hydroxy-3-methylene-6-phenylhex-5-en-2-one **(5n)**: Yellow oil[24]. ^{1}H NMR($CDCl_3$, 400MHz): δ 2.40 (3H, s, CH_3), 5.44 (1H, d, *J* = 7.6 Hz, C*H*), 6.14(1H, s, MeCO$_2$C=C*H*), 6.17(1H, s, C=C*H*), 6.37(1H, d, *J* = 7.6 Hz, MeCO$_2$C=C*H*), 7.26–7.38(3H, m, Ar*H*), 7.58–7.61 (2H, m, Ar*H*); ^{13}C NMR($CDCl_3$, 100MHz): δ 26.4, 71.0, 126.5(2C), 127.5, 127.6, 128.3(2C), 129.1, 134.4, 137.0, 147.0, 201.3; IR (neat): 3434, 1714, 1667, 1608 cm^{-1}; MS (ESI) 271[M+Cl]$^-$; Anal. Calcd for $C_{13}H_{13}ClO_2$: C, 65.97; H, 5.54. Found: C, 66.02; H, 5.43%.

(Z)-6-Chloro-6-(4-fluorophenyl)-4-hydroxy-3-methylenehex-5-en-2-one **(5o)**: Yellow oil[24]. ^{1}H NMR($CDCl_3$, 400MHz): δ 2.40 (3H, s, CH_3), 5.41 (1H, d, *J* = 8.0 Hz, C*H*), 6.13 (1H, s, MeCO$_2$C=C*H*), 6.18 (1H, s, C=C*H*), 6.30 (1H, d, *J* = 7.6 Hz, MeCO$_2$C=C*H*), 7.02–7.06 (2H, m, Ar*H*), 7.55–7.58 (2H, m, Ar*H*); ^{13}C NMR($CDCl_3$, 100MHz): δ 26.4, 71.0, 115.2, 115.4(2C), 127.5, 127.6(2C), 128.5, 133.3, 147.0, 163.1 (d, J_{CF} = 240.2 Hz), 201.2; IR (neat): 3280, 1704, 1589, 1505 cm^{-1}; MS (ESI) 289[M+Cl]$^-$; Anal. Calcd for $C_{13}H_{12}ClFO_2$: C, 61.31; H, 4.75. Found: C, 61.39; H, 4.65%.

Methyl 2-((1-chloro-3,4-dihydronaphthalen-2-yl)(hydroxy)methyl) acrylate **(5p):** Yellow oil[24]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.27–2.33 (1H, m, CH_2-*b*), 2.51–2.59 (1H, m, CH_2-*a*), 2.77–2.82 (2H, m, CH_2), 2.93 (1H, br s, O*H*), 3.76 (3H, s, CO$_2$CH_3), 5.89 (1H, s, C*H*OH), 5.94 (1H, s, C = CH_2-*b*), 6.35 (1H, s, C = CH_2-*a*), 7.12 (1H, d, *J* = 6.8 Hz, Ar*H*), 7.18–7.25 (2H, m, Ar*H*), 7.64 (1H, d, *J* = 7.6 Hz, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.5, 27.8, 52.0, 70.2, 124.7, 126.3, 126.6, 127.0, 128.0, 128.2, 132.7, 135.0, 136.3, 139.0, 166.8; IR (neat): 3478, 2952, 1727, 1438, 1270, 1146 cm^{-1};MS (EI) *m/z* 278(M$^+$, 4), 165(100); Anal. Calcd for $C_{15}H_{15}ClO_3$: C, 64.64; H, 5.42. Found: C, 64.71; H, 5.36%.

4-Chloro-3-methyl-1-tosyl-1,2-dihydroquinoline **(7)**: Yellow solid; m.p. 192–195 °C. ^{1}H NMR($CDCl_3$, 400MHz): δ 1.89 (3H, s, CH_3), 2.48 (3H, s, CH_3), 4.61 (1H, d, *J* = 9.6 Hz, CH_2), 5.78 (1H, d,

J = 10.0 Hz, CH_2), 6.81 (1H, d, J = 7.2 Hz, ArH), 7.04–7.08 (1H, m, ArH), 7.20–7.29 (2H, m, ArH), 7.37 (2H, d, J = 8.0 Hz, ArH), 7.86 (2H, d, J = 8.4 Hz, ArH); ^{13}C NMR($CDCl_3$, 100MHz): δ 11.2, 21.5, 61.0, 118.6, 123.2, 126.4, 127.2, 128.7(2C), 129.3, 129.9(2C), 138.3, 138.4, 140.7, 141.2, 143.8; IR(KBr): 3444, 1625, 1405, 1327, 1164 cm^{-1}; MS(ESI) 368[M+Cl]$^-$; Anal. Calcd for $C_{17}H_{16}ClNO_2S$: C, 61.16; H, 4.83; N, 4.20. Found: C, 61.27; H, 4.75; N, 4.17%.

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