

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 dioxide¹⁸ 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 POCl₃/DMF system²⁴ (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 AlCl₃ 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

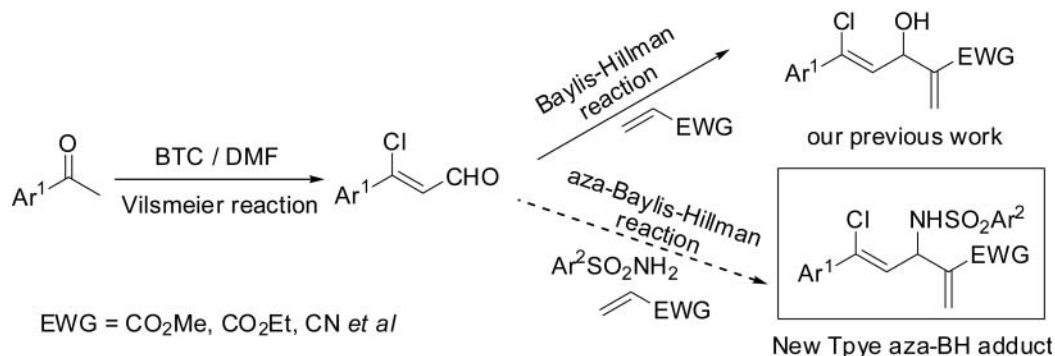
1a was recovered (Table 1, entries 6–8). Compared to DABCO, the base DMAP and DBU provided only traces of **4a** and worse results were observed using ZnCl₂ or CF₃CO₂H as additives instead of AlCl₃.

On the other hand, to improve the reaction yield, we tried to prepare **4a** via formation of benzenesulfonimide derivative **6a**. Firstly treatment of (Z)-3-chloro-3-phenylacrylaldehyde **1a** with toluenesulfonamide **2a** catalysed by AlCl₃ generated a benzenesulfonimide 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 AlCl₃ 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

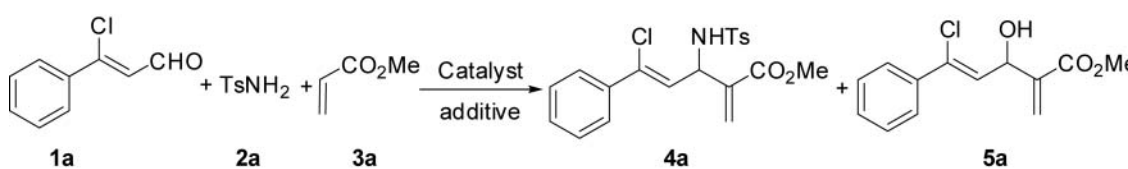
In addition, other special substrates were also investigated under the optimal condition. The substrate **1p** could be provided the desired product **4p** and the side product **5p** in

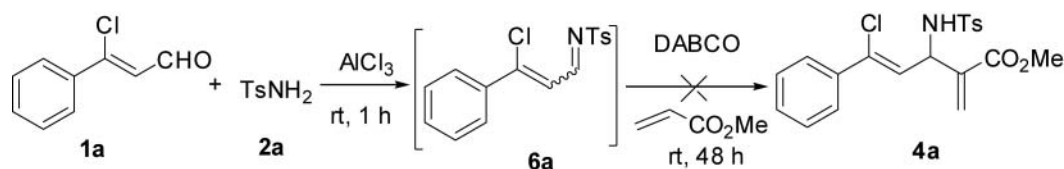


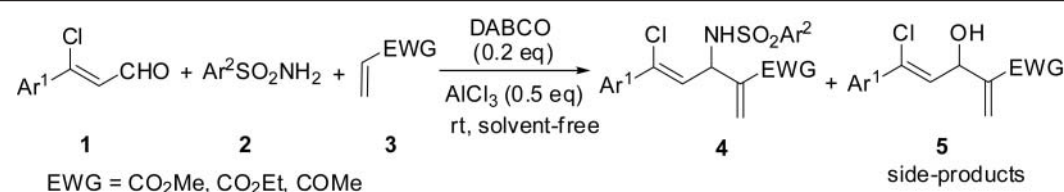
Scheme 1

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

							
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 ₂ CO ₃	AlCl ₃	Solvent-free	rt	48	Trace ^c	14
12	DABCO	ZnCl ₂	Solvent-free	rt	8	49	18
13	DABCO	CF ₃ CO ₂ H	Solvent-free	rt	36	34 ^c	13

^aConditions: **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.^bIsolated yields based on **1a**.^cSome chlorovinyl aldehyde **1a** was recovered.**Scheme 2****Table 2** The synthesis of new type *aza*- Baylis–Hillman adducts^a

						
Entry	Ar ¹	Ar ²	EWG	Time/h	Product (Yield/%) ^b	
					4	5
1	C ₆ H ₅	4-MeC ₆ H ₄	CO ₂ Me	10	4a (58)	5a (20)
2	C ₆ H ₅	Ph	CO ₂ Me	24	4b (48)	5a (18)
3	C ₆ H ₅	2-ClC ₆ H ₄	CO ₂ Me	72	4c (28 ^c)	5a (10)
4	C ₆ H ₅	4-MeC ₆ H ₄	CO ₂ Et	72	4d (36)	5d (15)
5	<i>p</i> -MeC ₆ H ₄	4-MeC ₆ H ₄	CO ₂ Me	1	4e (47)	5e (17)
6	<i>p</i> -MeC ₆ H ₄	4-MeC ₆ H ₄	CO ₂ Et	72	4f (33 ^c)	5f (11)
7	<i>p</i> -MeC ₆ H ₄	Ph	CO ₂ Me	24	4g (45)	5e (16)
8	<i>p</i> -FC ₆ H ₄	4-MeC ₆ H ₄	CO ₂ Me	1	4h (42)	5h (15)
9	<i>p</i> -ClC ₆ H ₄	4-MeC ₆ H ₄	CO ₂ Me	2	4i (55)	5i (15)
10	<i>m</i> -ClC ₆ H ₄	4-MeC ₆ H ₄	CO ₂ Me	10	4j (40 ^c)	5j (12)
11	<i>m</i> -ClC ₆ H ₄	Ph	CO ₂ Me	12	4k (30 ^c)	5j (10)
12	<i>p</i> -MeOC ₆ H ₄	4-MeC ₆ H ₄	CO ₂ Me	2	4l (53)	5l (15)
13	<i>p</i> -NO ₂ C ₆ H ₄	4-MeC ₆ H ₄	CO ₂ Me	1	4m (60)	5m (16)
14	C ₆ H ₅	4-MeC ₆ H ₄	COMe	0.5	4n (ND ^d)	5n (68)
15	<i>p</i> -FC ₆ H ₄	4-MeC ₆ H ₄	COMe	0.5	4o (ND ^d)	5o (70)

^aConditions: **1** (3.0 mmol), **2** (3.0 mmol), **3** (9.0 mmol), AlCl₃ (1.5 mmol), DABCO (0.6 mmol) were used.^bIsolated yields based on **1**.^cThe reaction was carried out under ultrasound and solvent-free conditions.^dNo 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 spectrophotometer. ^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

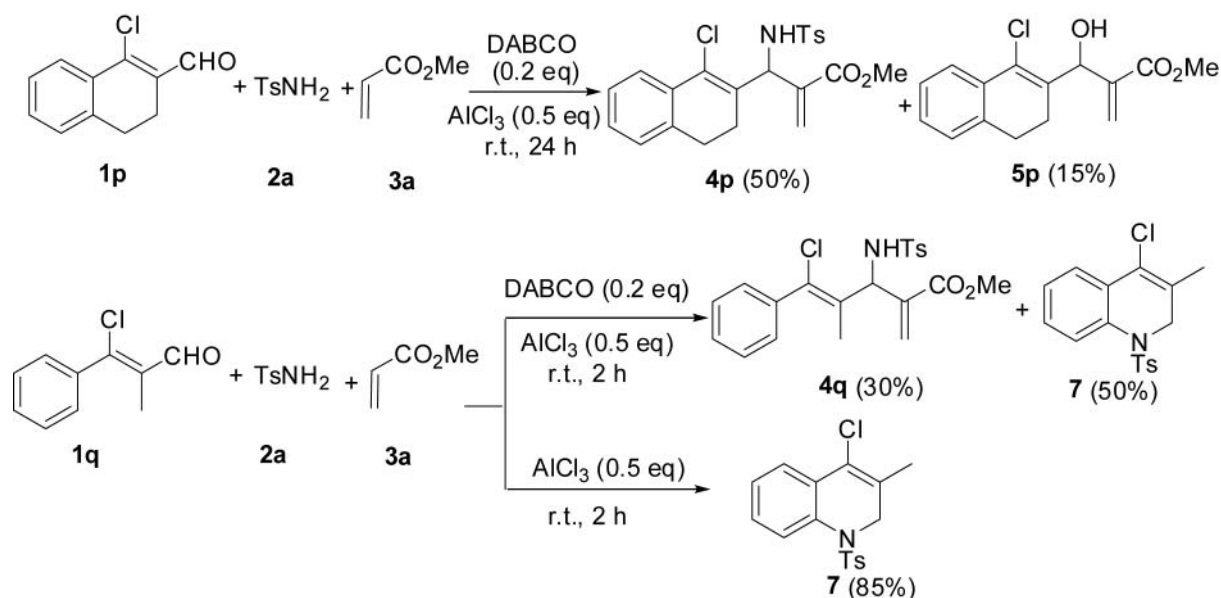
Typical procedure for (Z)-methyl 5-chloro-2-methylene-3-(toluenesulfonamido)-5-phenylpent-4-enoate (4a) and (Z)-methyl 5-chloro-3-hydroxy-2-methylene-5-phenylpent-4-enoate (5a)

To a mixture of (Z)-3-chloro-2-methyl-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 $\times$ 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**.

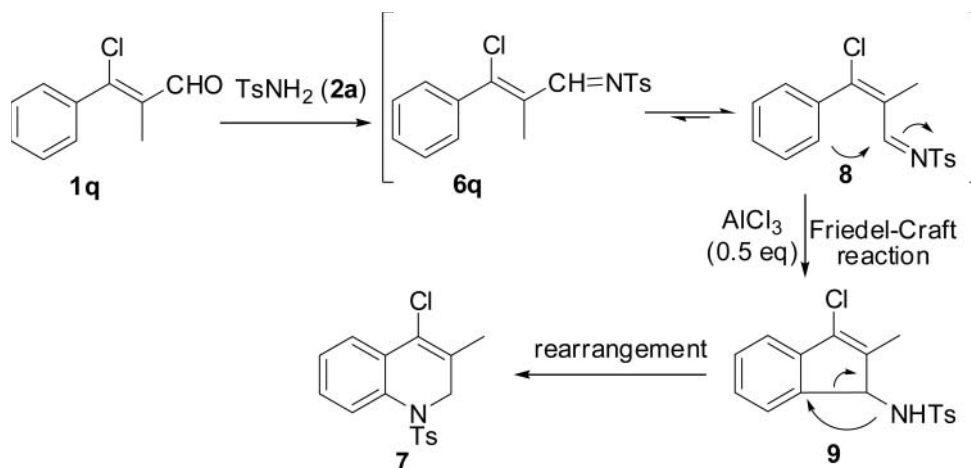
The products **4b–q** and **5d–f**, **5h–j**, **5l–p** could also be prepared under the similar conditions.

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 2 h. Then the reaction was quenched with water and extracted with



Scheme 3



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

dichloromethane (30 mL $\times$ 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. ^1H NMR(CDCl_3 , 400MHz): δ 2.29 (3H, s, CH_3), 3.71 (3H, s, CH_3O), 5.24 (1H, t, J = 8.8 Hz, CH), 5.83 (1H, d, J = 10.0 Hz, C=CH), 5.93 (1H, s, $\text{MeCO}_2\text{C=CH}$), 6.00 (1H, d, J = 8.4 Hz, NH), 6.17 (1H, s, $\text{MeCO}_2\text{C=CH}$), 7.18–7.74 (7H, m, ArH), 7.75 (2H, d, J = 8.0 Hz, ArH); ^{13}C NMR(CDCl_3 , 100MHz): 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 $\text{C}_{20}\text{H}_{20}\text{ClNO}_4\text{S}$: 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. ^1H NMR(CDCl_3 , 400MHz): δ 3.71 (3H, s, CH_3O), 5.27 (1H, m, CH), 5.83 (1H, d, J = 10.0 Hz, C=CH), 5.93 (1H, s, $\text{MeCO}_2\text{C=CH}$), 6.05 (1H, d, J = 8.8 Hz, NH), 6.15 (1H, s, $\text{MeCO}_2\text{C=CH}$), 7.27–7.49 (7H, m, ArH), 7.87 (2H, m, ArH); ^{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 $\text{C}_{19}\text{H}_{18}\text{ClNO}_4\text{S}$: 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. ^1H NMR(CDCl_3 , 400MHz): δ 3.76 (3H, s, CH_3O), 5.25 (1H, m, CH), 5.86 (1H, s, $\text{MeCO}_2\text{C=CH}$), 6.14 (1H, s, $\text{MeCO}_2\text{C=CH}$), 6.18 (1H, d, J = 8.8 Hz, C=CH), 6.42 (1H, d, J = 10.0 Hz, NH), 7.24–7.43 (8H, m, ArH), 7.75 (1H, m, ArH); ^{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 $\text{C}_{19}\text{H}_{17}\text{Cl}_2\text{NO}_4\text{S}$: 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. ^1H NMR(CDCl_3 , 400MHz): δ 1.27 (3H, t, J = 9.2 Hz, CH_3), 2.29 (3H, s, CH_3), 4.17 (1H, d, J = 9.2 Hz, CH), 4.17 (1H, d, J = 9.2 Hz, CH_2O), 5.23 (1H, t, J = 9.2 Hz, CH), 5.78 (1H, d, J = 10.0 Hz, C=CH), 5.93 (1H, s, $\text{MeCO}_2\text{C=CH}$), 6.00 (1H, d, J = 8.4 Hz, NH), 6.16 (1H, s, $\text{MeCO}_2\text{C=CH}$), 7.19–7.30 (7H, m, ArH), 7.74 (2H, d, J = 8.0 Hz, ArH); ^{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), 132.2, 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 $\text{C}_{21}\text{H}_{22}\text{ClNO}_4\text{S}$: 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. ^1H NMR(CDCl_3 , 400MHz): δ 2.31 (6H, t, CH_3), 3.71 (3H, s, CH_3O), 5.23 (1H, t, J = 8.8 Hz, CH), 5.77 (1H, d, J = 9.6 Hz, C=CH), 5.92 (1H, s, $\text{MeCO}_2\text{C=CH}$), 5.94 (1H, d, J = 8.2 Hz, NH), 6.15 (1H, s, $\text{MeCO}_2\text{C=CH}$), 7.07 (2H, d, ArH), 7.13 (2H, d, J = 8.4 Hz, ArH), 7.20 (2H, d, J = 8.0 Hz, ArH), 7.73 (2H, d, J = 8.0 Hz, ArH); ^{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 $\text{C}_{21}\text{H}_{22}\text{ClNO}_4\text{S}$: 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. ^1H NMR(CDCl_3 , 400MHz): δ 1.25–1.29 (3H, m, CH_3), 2.31 (6H, d, J = 8.8 Hz, CH_3), 4.11–4.20 (2H, m, CH_2O), 5.22 (1H, t, J = 9.2 Hz, CH), 5.77 (1H, s, C=CH), 5.91 (1H, s, $\text{MeCO}_2\text{C=CH}$), 5.95 (1H, d, J = 8.4 Hz, NH), 6.15 (1H, s, $\text{MeCO}_2\text{C=CH}$), 7.07 (2H, d, J = 8.4 Hz, ArH), 7.13 (2H, d, J = 4.4 Hz, ArH), 7.19 (2H, d, J = 8.0 Hz, ArH), 7.73 (2H, d, J = 8.0 Hz, ArH); ^{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 $\text{C}_{22}\text{H}_{24}\text{ClNO}_4\text{S}$: 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. ^1H NMR(CDCl_3 , 400MHz): δ 2.33 (3H, s, CH_3), 3.71 (3H, s, CH_3O), 5.25 (1H, t, J = 9.6 Hz, CH), 5.80 (1H, d, J = 9.6 Hz, C=CH), 5.91 (1H, s, $\text{MeCO}_2\text{C=CH}$), 6.00 (1H, d,

J = 8.4 Hz, NH), 6.14 (1H, s, $\text{MeCO}_2\text{C=CH}$), 7.07 (2H, d, J = 8.4 Hz, ArH), 7.16 (2H, d, J = 8.4 Hz, ArH), 7.40–7.47 (3H, m, ArH), 7.85–7.87 (2H, m, ArH); ^{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 $\text{C}_{20}\text{H}_{20}\text{ClNO}_4\text{S}$: 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. ^1H NMR(CDCl_3 , 400MHz): δ 2.30 (3H, s, CH_3), 3.71 (3H, s, CH_3O), 5.22 (1H, t, J = 9.6 Hz, CH), 5.90 (2H, m, C=CH and $\text{MeCO}_2\text{C=CH}$), 5.98 (1H, d, J = 9.6 Hz, NH), 6.16 (1H, s, $\text{MeCO}_2\text{C=CH}$), 6.93–6.97 (2H, m, ArH), 7.18–7.74 (4H, m, ArH), 7.75 (2H, d, J = 8.0 Hz, ArH); ^{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 $\text{C}_{20}\text{H}_{19}\text{ClFNO}_4\text{S}$: 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. ^1H NMR(CDCl_3 , 400MHz): δ 2.31 (3H, s, CH_3), 3.72 (3H, s, CH_3O), 5.21 (1H, t, J = 8.8 Hz, CH), 5.77 (1H, d, J = 10.0 Hz, C=CH), 5.93 (1H, s, $\text{MeCO}_2\text{C=CH}$), 6.00 (1H, d, J = 8.4 Hz, NH), 6.17 (1H, s, $\text{MeCO}_2\text{C=CH}$), 7.18 (2H, d, J = 8.6 Hz, ArH), 7.22 (2H, d, J = 9.6 Hz, ArH), 7.26 (2H, d, J = 2.4 Hz, ArH), 7.73 (2H, d, J = 8.0 Hz, ArH); ^{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 $\text{C}_{20}\text{H}_{19}\text{Cl}_2\text{NO}_4\text{S}$: 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. ^1H NMR(CDCl_3 , 400MHz): δ 2.32 (3H, s, CH_3), 3.74 (3H, s, CH_3O), 5.21 (1H, t, J = 8.4 Hz, CH), 5.76 (1H, d, J = 10.0 Hz, C=CH), 5.96 (1H, s, $\text{MeCO}_2\text{C=CH}$), 5.98 (1H, d, J = 8.4 Hz, NH), 6.19 (1H, s, $\text{MeCO}_2\text{C=CH}$), 7.12 (2H, d, J = 7.2 Hz, ArH), 7.18 (2H, d, J = 16.8 Hz, ArH), 7.22 (2H, d, J = 8.0 Hz, ArH), 7.74 (2H, d, J = 8.4 Hz, ArH); ^{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 $\text{C}_{20}\text{H}_{19}\text{Cl}_2\text{NO}_4\text{S}$: 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. ^1H NMR(CDCl_3 , 400MHz): δ 3.73 (3H, s, CH_3O), 5.24 (1H, t, J = 9.6 Hz, CH), 5.85 (1H, d, J = 9.6 Hz, C=CH), 5.94 (1H, s, $\text{MeCO}_2\text{C=CH}$), 6.04 (1H, d, J = 8.4 Hz, NH), 6.17 (1H, s, $\text{MeCO}_2\text{C=CH}$), 7.15–7.29 (4H, m, ArH), 7.43–7.51 (3H, m, ArH), 7.87 (2H, d, J = 6.8 Hz, ArH); ^{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 $\text{C}_{19}\text{H}_{17}\text{Cl}_2\text{NO}_4\text{S}$: 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. ^1H NMR(CDCl_3 , 400MHz): δ 2.31 (3H, s, CH_3), 3.71 (3H, s, CH_3O), 3.80 (3H, s, CH_3O), 5.22 (1H, t, J = 9.2 Hz, CH), 5.77 (1H, d, J = 9.6 Hz, C=CH), 5.87 (1H, s, $\text{MeCO}_2\text{C=CH}$), 5.91 (1H, d, J = 10.0 Hz, NH), 6.15 (1H, s, $\text{MeCO}_2\text{C=CH}$), 6.78 (2H, d, J = 8.8 Hz, ArH), 7.16–7.27 (4H, m, ArH), 7.74 (2H, d, J = 8.4 Hz, ArH); ^{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 $\text{C}_{21}\text{H}_{22}\text{ClNO}_5\text{S}$: 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. ^1H NMR(CDCl_3 , 400MHz): δ 2.42 (3H, s, CH_3), 3.71 (3H, s, CH_3O), 4.61 (1H, t, J = 9.6 Hz, CH), 5.42 (1H, s, $\text{MeCO}_2\text{C=CH}$), 5.65 (1H, d, J = 9.2 Hz, C=CH), 6.03 (1H, s, $\text{MeCO}_2\text{C=CH}$), 6.16 (1H, d, J = 10.4 Hz, NH), 7.21–7.26 (2H, m, ArH), 7.45 (2H, d, J = 9.2 Hz, ArH), 7.48–7.58 (2H, m, ArH), 8.22–8.24 (2H, m, ArH); ^{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 $\text{C}_{20}\text{H}_{19}\text{ClN}_2\text{O}_6\text{S}$: 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. ¹H 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, CH), 5.93 (1H, s, $\text{MeCO}_2\text{C}=\text{CH}$), 6.10 (1H, s, NH), 6.26 (1H, s, $\text{MeCO}_2\text{C}=\text{CH}$), 7.02 (1H, d, J = 7.2 Hz, ArH), 7.14–7.26 (4H, m, ArH), 7.53 (1H, d, J = 7.6 Hz, ArH), 7.77 (2H, t, J = 6.8 Hz, ArH); ¹³C 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 $\text{C}_{22}\text{H}_{22}\text{ClNO}_4\text{S}$: 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. ¹H 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, $\text{MeCO}_2\text{C}=\text{CH}$), 5.29 (1H, d, J = 8.4 Hz, $\text{MeCO}_2\text{C}=\text{CH}$), 5.58–5.70 (1H, m, NH), 6.06 (1H, s, CH), 7.19–7.34 (7H, m, ArH and $\text{MeCO}_2\text{C}=\text{CH}$), 7.55 (2H, d, J = 8.4 Hz, ArH); ¹³C 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 $\text{C}_{21}\text{H}_{22}\text{ClNO}_4\text{S}$: 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 oil²⁴. ¹H NMR (CDCl_3 , 400 MHz): δ 3.44 (1H, br s, OH), 3.79 (3H, s, CO_2CH_3), 5.48 (1H, d, J = 7.6 Hz, CHOH), 5.94 (1H, s, $\text{C}=\text{CH}_2$ -b), 6.29 (1H, s, $\text{C}=\text{CH}_2$ -a), 6.35 (1H, d, J = 7.6 Hz, $\text{CIC}=\text{CH}$), 7.33–7.37 (3H, m, ArH), δ 7.57–7.60 (2H, m, ArH); ¹³C 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 $\text{C}_{13}\text{H}_{13}\text{ClO}_3$: 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 oil²⁴. ¹H NMR (CDCl_3 , 400 MHz): δ 1.33 (3H, t, J = 7.2 Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 3.34 (1H, br s, OH), 4.26 (2H, q, J = 7.2 Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 5.47 (1H, d, J = 7.6 Hz, CHOH), 5.93 (1H, s, $\text{C}=\text{CH}_2$ -b), 6.30 (1H, s, $\text{C}=\text{CH}_2$ -a), 6.35 (1H, d, J = 7.6 Hz, $\text{CIC}=\text{CH}$), 7.33–7.39 (3H, m, ArH), δ 7.59–7.61 (2H, m, ArH); ¹³C 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 $\text{C}_{14}\text{H}_{15}\text{ClO}_3$: 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 oil²⁴. ¹H NMR (CDCl_3 , 400 MHz): δ 2.35 (3H, s, CH_3), 3.36 (1H, br s, OH), 3.80 (3H, s, CO_2CH_3), 5.47 (1H, d, J = 8.0 Hz, CHOH), 5.94 (1H, s, $\text{C}=\text{CH}_2$ -b), 6.29 (1H, s, $\text{C}=\text{CH}_2$ -a), 6.31 (1H, d, J = 8.0 Hz, $\text{CIC}=\text{CH}$), 7.15 (2H, d, J = 8.4 Hz, ArH), 7.49 (2H, d, J = 8.4 Hz, ArH); ¹³C 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 $\text{C}_{14}\text{H}_{15}\text{ClO}_3$: 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 oil²⁴. ¹H NMR (400 MHz, CDCl_3): δ 1.32 (3H, t, J = 7.2 Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 2.35 (3H, s, CH_3), 3.39 (1H, br s, OH), δ 4.25 (2H, q, J = 7.2 Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 5.47 (1H, d, J = 7.6 Hz, CHOH), 5.92 (1H, s, $\text{C}=\text{CH}_2$ -b), 6.29 (1H, s, $\text{C}=\text{CH}_2$ -a), 6.30 (1H, d, J = 8.0 Hz, $\text{CIC}=\text{CH}$), 7.15 (2H, d, J = 8.0 Hz, ArH), 7.48 (2H, d, J = 8.0 Hz, ArH); ¹³C 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 $\text{C}_{15}\text{H}_{17}\text{ClO}_3$: 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 oil²⁴. ¹H NMR (400 MHz, CDCl_3): δ 3.38 (1H, br s, OH), 3.81 (3H, s, CO_2CH_3), 5.45 (1H, d, J = 7.6 Hz, CHOH), 5.95 (1H, s, $\text{C}=\text{CH}_2$ -b), 6.30 (1H, s, $\text{C}=\text{CH}_2$ -a), 6.31 (1H, d, J = 8.0 Hz, $\text{CIC}=\text{CH}$), 7.02–7.06 (2H, m, ArH), 7.55–7.59 (2H, m, ArH); ¹³C 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 $\text{C}_{13}\text{H}_{12}\text{ClFO}_3$: 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 oil²⁴. ¹H NMR (400 MHz, CDCl_3): δ 3.37 (1H, br s, OH), 3.81 (3H, s, CO_2CH_3), 5.45 (1H, d, J = 7.6 Hz, CHOH), 5.94 (1H, s, $\text{C}=\text{CH}_2$ -b), 6.30 (1H, s, $\text{C}=\text{CH}_2$ -a), 6.35 (1H, d, J = 7.6 Hz, $\text{CIC}=\text{CH}$), 7.31–7.33 (2H, m, ArH), 7.51–7.53 (2H, m, ArH); ¹³C 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 $\text{C}_{13}\text{H}_{12}\text{Cl}_2\text{O}_3$: 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 oil²⁴. ¹H NMR (400 MHz, CDCl_3): δ 3.82 (3H, s, CO_2CH_3), 5.44 (1H, d, J = 7.6 Hz, CHOH), 5.95 (1H, s, $\text{C}=\text{CH}_2$ -b), 6.31 (1H, s, $\text{C}=\text{CH}_2$ -a), 6.38 (1H, d, J = 7.6 Hz, $\text{CIC}=\text{CH}$), 7.29–7.31 (2H, m, ArH), 7.46–7.49 (1H, m, ArH), 7.58 (1H, s, ArH); ¹³C 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 $\text{C}_{13}\text{H}_{12}\text{Cl}_2\text{O}_3$: 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 oil²⁴. ¹H NMR (400 MHz, CDCl_3): δ 3.45 (1H, br s, OH), 3.80 (6H, s, CO_2CH_3 and OCH_3), 5.47 (1H, d, J = 8.0 Hz, CHOH), 5.94 (1H, s, $\text{C}=\text{CH}_2$ -b), 6.24 (1H, d, J = 8.0 Hz, $\text{CIC}=\text{CH}$), 6.28 (1H, s, $\text{C}=\text{CH}_2$ -a), 6.86 (2H, d, J = 8.8 Hz, ArH), 7.52 (2H, d, J = 8.4 Hz, ArH); ¹³C 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 $\text{C}_{14}\text{H}_{15}\text{ClO}_4$: 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 oil²⁴. ¹H NMR (400 MHz, CDCl_3): δ 3.46 (1H, br s, OH), 3.83 (3H, s, CO_2CH_3), 5.47 (1H, d, J = 8.0 Hz, CHOH), 5.99 (1H, s, $\text{C}=\text{CH}_2$ -b), 6.34 (1H, s, $\text{C}=\text{CH}_2$ -a), 6.56 (1H, d, J = 8.0 Hz, $\text{CIC}=\text{CH}$), 7.77 (2H, d, J = 8.8 Hz, ArH), 8.21 (2H, d, J = 9.2 Hz, ArH); ¹³C 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 $\text{C}_{15}\text{H}_{15}\text{ClNO}_5$: 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 oil²⁴. ¹H NMR(CDCl_3 , 400MHz): δ 2.40 (3H, s, CH_3), 5.44 (1H, d, J = 7.6 Hz, CH), 6.14(1H, s, $\text{MeCO}_2\text{C}=\text{CH}$), 6.17(1H, s, $\text{C}=\text{CH}$), 6.37(1H, d, J = 7.6 Hz, $\text{MeCO}_2\text{C}=\text{CH}$), 7.26–7.38(3H, m, ArH), 7.58–7.61 (2H, m, ArH); ¹³C 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 $\text{C}_{13}\text{H}_{13}\text{ClO}_2$: 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 oil²⁴. ¹H NMR(CDCl_3 , 400MHz): δ 2.40 (3H, s, CH_3), 5.41 (1H, d, J = 8.0 Hz, CH), 6.13 (1H, s, $\text{MeCO}_2\text{C}=\text{CH}$), 6.18 (1H, s, $\text{C}=\text{CH}$), 6.30 (1H, d, J = 7.6 Hz, $\text{MeCO}_2\text{C}=\text{CH}$), 7.02–7.06 (2H, m, ArH), 7.55–7.58 (2H, m, ArH); ¹³C 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 $\text{C}_{13}\text{H}_{12}\text{ClFO}_2$: 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 oil²⁴. ¹H 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, OH), 3.76 (3H, s, CO_2CH_3), 5.89 (1H, s, CHOH), 5.94 (1H, s, $\text{C}=\text{CH}_2$ -b), 6.35 (1H, s, $\text{C}=\text{CH}_2$ -a), 7.12 (1H, d, J = 6.8 Hz, ArH), 7.18–7.25 (2H, m, ArH), 7.64 (1H, d, J = 7.6 Hz, ArH); ¹³C 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 $\text{C}_{15}\text{H}_{15}\text{ClO}_3$: 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. ¹H 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 $[\text{M}+\text{Cl}]^-$; Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{ClNO}_2\text{S}$: C, 61.16; H, 4.83; N, 4.20. Found: C, 61.27; H, 4.75; N, 4.17%.

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