# Stereoselective Chlorination of New Type Baylis-Hillman Adducts by bis(Trichloromethyl)carbonate with the Aid of Catalytic Amount of Triphenylphosphine Oxide

Weihui Zhong\*, Lingjuan Hong and Yemin Zheng

Key Laboratory of Pharmaceutical Engineering (Ministry of Education), College of Pharmaceutical Sciences, Zhejiang University of Technology, Hangzhou 310014, P.R. China

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**Abstract:** The chlorination of the new type Baylis-Hillman adducts by bis(trichloromethyl)carbonate (BTC) with the aid of catalytic amount of triphenylphosphine oxide (Ph<sub>3</sub>PO) was achieved with high yields and high stereoselectivities. A plausible mechanism is presented.

**Keywords:** New type Baylis-Hillman adducts, chlorination, triphenylphosphine oxide, *bis*(trichloromethyl)carbonate, stereoselectivity.

# INTRODUCTION

Baylis-Hillman adducts have been successfully utilized as valuable intermediates for stereoselective synthesis of different multifunctional molecules [1,2]. In particular, the halogenation of Baylis-Hillman adducts has attracted much attention in recent years [3,4], since they can be employed for the synthesis of various natural bioactive products and their analogues, such as micanecic acid, kizanolide, rennin inhibitor A-72517,  $\beta$ -lactams,  $\alpha$ -methylene- $\gamma$ -butyrolactones and flavonoids [5]. To date, various reagents have been used to promote the conversion to corresponding chlorides, such as strong acids (HCl/H<sub>2</sub>SO<sub>4</sub>) [6], organic acid halides (MsCl, oxalyl chloride [7]), complex systems (Cl<sub>3</sub>CCONH<sub>2</sub>-Ph<sub>3</sub>P, HCA-PPh<sub>3</sub> complex, NCS/Me<sub>2</sub>S, POCl<sub>3</sub>/DMF, PPh<sub>3</sub>/CCl<sub>4</sub>, TCT/DMF) [8], Lewis acid (iron(III) or indium(III) chloride, AlCl<sub>3</sub>, TiCl<sub>4</sub>) [9], [bmim][HSO<sub>4</sub>] [10] and Silica chloride [11]. However, most of reported methods suffered from certain limitations, including the use of concentrated acids [6], the need to use O-acetyl derivatives of Baylis-Hillman adducts [12] as well as requirement for complex experimental procedures.

Recently we successfully prepared a new type Baylis-Hillman adducts *via* Vilsmeier reaction of ketones with *bis*(trichloromethyl)carbonate (BTC)/DMF system to construct chlorovinyl aldehydes, followed by sonochemical Baylis-Hillman reaction under solvent-free condition [3]. In continuation of our research on the application of Baylis-Hillman adducts for construction of heterocylces [13], we herein described a high stereroselective chlorization of the new type Baylis-Hillman adducts to the corresponding allyl chlorides by using BTC with the aid of catalytic amount of triphenylphosphine oxide (Ph<sub>3</sub>PO).

#### **RESULT AND DISCUSSION**

Initially, the Baylis-Hillman adduct [3] (Z)-methyl-5-chloro-5-(4-fluorophenyl)-3-hydroxy-2-methylenepent-4enoate **1a** was subjected to chlorination with the Vilsmeier reagent derived from BTC/DMF system instead of traditional POCl<sub>3</sub>/DMF system (Scheme **1**). Unfortunately, almost no stereoselectivity was observed. The products (2Z,4Z)-methyl-5-chloro-2-(chloromethyl)-5-(4-fluorophenyl) penta-2,4-dienoate **2a** and its isomer (2*E*,4*Z*)-**3a** were isolated with 46% and 44%, respectively.

Stimulated by our previous finding that dichlorotriphenylphosphine (PPh<sub>3</sub>Cl<sub>2</sub>) can be formed from Ph<sub>3</sub>PO and BTC [14], we examined the activity of PPh<sub>3</sub>Cl<sub>2</sub> as chlorination reagent for the conversion of **1a** into the corresponding allyl chlorides [15] (Scheme **2**). Surprisingly, treatment of the new type Baylis-Hillman adduct **1a** with PPh<sub>3</sub>Cl<sub>2</sub> generated *in situ* could afford **2a** in higher yield and stereoselectivity.

One drawback of this reaction was related to the fact that  $Ph_3PCl_2$  is quite sensitive to water and difficult to detect. Considering that BTC is an efficient chlorination reagent in organic synthesis [16], we reasoned that a reaction cycle could be established between  $Ph_3PO$  and  $PPh_3Cl_2$  in the above reaction. To our delight, when the protocol was applied, **2** were successfully obtained (Fig. 1), indicating that the reaction cycle could proceed smoothly.

Subsequently, we found that an experiment carried out with a catalytic amount (10%) of  $Ph_3PO$  did not affect the yield (Table 1, entry 6). However, the reaction did not take place with 5 mmol% of  $Ph_3PO$  (Table 1, entry 7).

A plausible reaction mechanism [2,14] is shown in Scheme **3**. Firstly, the reaction of BTC with PPh<sub>3</sub>O catalyzed by  $Et_3N$  gives intermediate **A**, which then reacts with the Baylis-Hillman adduct to give the alkoxyphosphonium salt **B**. Chloride nucleophilic attack leads to the trisubstituted allyl chloride with regeneration of Ph<sub>3</sub>PO.

<sup>\*</sup>Address correspondence to this author at the Key Laboratory of Pharmaceutical Engineering (Ministry of Education), College of Pharmaceutical Sciences, Zhejiang University of Technology, Hangzhou 310014, P.R. China; Fax: (0086)57188320752;

E-mail: pharmlab@zjut.edu.cn



Scheme 1.



Scheme 2.

Cl EWG R Ph<sub>3</sub>PO BTC  $R_2$ Cl 2 OH Cl EWG  $CO_2$ Ph<sub>3</sub>PCl<sub>2</sub>  $R_1$  $R_2$ 1  $\begin{array}{l} R_1 = aryl, \, alkyl, \, R_2 = H, \, CH_3 \ or \ (CH_2)_2 \\ EWG = CO_2 Me, \, CO_2 Et, \, CN \ et \ al \end{array}$ 

Fig. (1).

# Table 1. Chlorination of Compound 1a Under Various Conditions<sup>a</sup>

Entry	Ph <sub>3</sub> PO (mmol%)	Temp. (°C)	Time	Yield of 2a (%) <sup>b</sup>
1	100	0	40 min	89
2	50	r.t.	2 h	54°
3	50	r.t.	5 h	89
4	30	r.t.	8 h	88
5	20	r.t.	10 h	88
6	10	r.t.	10 h	89
7	5	r.t.	2 days	Trace <sup>c</sup>

<sup>a</sup>Reaction conditions: 1a (1 mmol), Et<sub>3</sub>N (3 drops), BTC (0.67 mmol), solvents (3 mL) were used. <sup>b</sup>Isolated yields based on 1a. <sup>c</sup>1a was recovered.



#### Scheme 3.

With the optimized conditions in hand, we then expanded the scope of the reaction and verified the compatibility with functional groups and structural features. According to Table **2**, the substrates with ester moiety could provide the desired (Z,Z)-isomers with high stereoselectivities in good yields. In the case of nitrile moiety, (E,Z)-isomer **3n** was isolated (Table **2**, entry 14). Among substrates bearing aryl groups, the yields of those containing electron-donating (Table **2**, entry 10) were slightly higher than electron-withdrawing groups (Table **2**, entry 3), but there was not much difference respecting reaction time and stereoselectivities. Further, we investigated the chlorination of methyl 2-((2chloro-6-methylquinolin-3-yl)(hydroxy)methyl)acrylate **10** by BTC with the aid of 10 mmol%  $Ph_3PO$  (Scheme **4**). Gratifyingly, the desired product (*Z*)-**20** was successfully isolated in good yield (87%) with high stereoselectivity.

The stereochemistry of the conversion has been confirmed by <sup>1</sup>H NMR, and NOE effect. <sup>1</sup>H NMR spectra of **2a** showed typical chemical shifts of  $H_a$  (7.90 ppm) and  $H_b$  (7.04 ppm), while 7.49 ppm of  $H_a$  and 7.99 ppm of  $H_b$  were revealed in compound **3a**. It was found that large NOE existed between  $H_b$  and  $H_c$  of **2a**, while in the case of **3a**,

Entry	R <sub>1</sub>	$\mathbf{R}_2$	EWG	Time (h)	Product	Yield (%) <sup>b</sup>
1	<b>1a</b> : <i>p</i> -FC <sub>6</sub> H <sub>4</sub>	Н	CO <sub>2</sub> Me	10	2a	89
2	<b>1b</b> : <i>p</i> -ClC <sub>6</sub> H <sub>4</sub>	Н	CO <sub>2</sub> Me	10	2b	89
3	<b>1c</b> : <i>m</i> -ClC <sub>6</sub> H <sub>4</sub>	Н	CO <sub>2</sub> Me	10	2c	90
4	<b>1d</b> : <i>m</i> -ClC <sub>6</sub> H <sub>4</sub>	Н	CO <sub>2</sub> Et	10	2d	88
5	<b>1e</b> : <i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Н	CO <sub>2</sub> Me	11	2e	86
6	<b>1f</b> : C <sub>6</sub> H <sub>5</sub>	Н	CO <sub>2</sub> Me	10	2f	90
7	<b>1g</b> : C <sub>6</sub> H <sub>5</sub>	Н	CO <sub>2</sub> Et	10	2g	89
8	<b>1h</b> : <i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	Н	CO <sub>2</sub> Me	9	2h	91
9	<b>1i</b> : <i>p</i> -MeC <sub>6</sub> H <sub>4</sub>	Н	CO <sub>2</sub> Et	9	2i	90
10	<b>1j</b> : <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	Н	CO <sub>2</sub> Me	8	2j	93
11	1k:		CO <sub>2</sub> Me	10	2k	89
12		Н	CO <sub>2</sub> Me	15	21	80
13	<b>1m</b> : C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	CO <sub>2</sub> Me	10	2m	85
14	<b>1n</b> : C <sub>6</sub> H <sub>5</sub>	Н	CN	10	3n°	88

#### Table 2. The Chlorination of New Type Baylis-Hillman Adducts<sup>a</sup>

<sup>a</sup>Reaction conditions: 1 (1 mmol), Et<sub>3</sub>N (3 drops), BTC (0.67 mmol), CH<sub>2</sub>Cl<sub>2</sub> (3 mL) were used. <sup>b</sup>Isolated yields based on 1. <sup>c</sup>The conformation of 3n is (*E*,*Z*)-style.



Scheme 4.

#### Fig. (2).

evident NOE was observed between  $H_a$  and  $H_c$  (Fig. 2). Integrated with the hydrogen NOE effect in benzene ring, it could be readily identified that compound 2a should be (Z,Z)-isomer while compound 3a should be (E,Z)-isomer as the major configuration in this case.

#### CONCLUSION

In summary, we have successfully developed a new method for the synthesis of allyl chlorides by using  $Ph_3PO/BTC$  system. The mild cycle reaction condition, convenient operational procedure, high stereoselectivity and good yield were the notable advantages. The application of the new type Baylis-Hillman adducts and chlorides have been developing in our lab.

#### EXPERIMENTAL

#### General

Melting points were determined with a Büchi B-540 capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Thermo Nicolet Avatar-370 instrument, using samples as KBr plates. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were measured in CDCl<sub>3</sub> with tetramethylsilane (TMS,  $\delta = 0$ ) as an internal standard on a Varian-400 MHz spectrometer at 400 and 100 MHz or Bruker Avance DRX 500 spectrometer at 500 and 125 MHz. Chemical shifts ( $\delta$ ) were expressed in ppm and coupling constants *J* given in Hz. Mass spectra were obtained with a Trace DSQ mass spectrometer. High resolution mass spectra were recorded using an Agilent 6210 TOF mass spectrometer.

#### (2Z,4Z)-Methyl-5-chloro-2-(chloromethyl)-5-(4-fluorophenyl)penta-2,4-dienoate (2a); typical procedure

To a mixture of (Z)-methyl 5-chloro-5-(4-fluorophenyl)-3-hydroxy-2-methylenepent- 4-enoate 1a (270.7 mg, 1 mmol), Ph<sub>3</sub>PO (27.8 mg, 0.1 mmol) and Et<sub>3</sub>N (10.1 mg, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL), was added dropwise a solution of BTC (199.0 mg, 0.67 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) at 0 °C. The mixture was stirred at room temperature for 10 h. Then reaction was quenched with water (5 mL) and extracted with  $CH_2Cl_2$  (3 ×20 mL). The combined organic layer was successively washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuum to obtain a crude product. which was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 20:1 as eluent) to give the desired product 2a (257.2 mg, yield: 89%). Light yellow solid, mp: 87.0-88.5 °C. IR (KBr) v<sub>max</sub>: 3132, 1670, 1507, 1152, 833 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 3.87 (s, 3 H), 4.51 (s, 2 H), 7.04 (d, J = 11.2 Hz,1 H), 7.12 (t, J = 8.8 Hz, 2 H), 7.71-7.74 (m, 2 H), 7.90 (d, J = 11.2 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 37.1, 52.1, 115.5(2C), 119.1, 128.8(2C), 129.1, 132.9, 137.3, 141.7, 163.6 (d,  $J_{CF} = 250.6$  Hz), 165.9. MS (EI) m/z 290 (M+2, 2), 288 (M<sup>+</sup>, 7), 255 (30), 253 (M-Cl, 100). HRMS (EI) m/z calcd for C<sub>13</sub>H<sub>11</sub>Cl<sub>2</sub>FO<sub>2</sub>: 288.0120; found: 288.0131.

### (2Z,4Z)-Methyl-5-chloro-2-(chloromethyl)-5-(4-chlorophenyl)penta-2,4-dienoate (2b)

Light yellow solid, mp: 108.3-109.9 °C. IR (KBr)  $v_{max}$ : 3132, 1712, 1435, 1180, 833 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 3.87 (s, 3 H), 4.51 (s, 2 H), 7.08 (d, J = 11.6Hz, 1 H), 7.40 (d, J = 8.8Hz, 2 H), 7.67 (d, J = 8.8Hz, 2 H), 7.89 (d, J = 11.6Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 37.7, 52.8, 120.1, 128.6(2C), 129.2(2C), 130.1, 135.7, 136.8, 137.7, 142.2, 166.5. MS (EI) m/z 304 (M<sup>+</sup>, 2), 271 (66), 269 (M-Cl, 100), 209 (28). HRMS (EI) m/z calcd for  $C_{13}H_{11}Cl_{3}O_{2}$ : 303.9825; found: 303.9808.

# (2Z,4Z)-Methyl-5-chloro-2-(chloromethyl)-5-(3-chlorophenyl)penta-2,4-dienoate (2c)

Light yellow solid, mp: 99.2-100.9 °C. IR (KBr)  $v_{max}$ : 3132, 1693, 1435, 1176, 784 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 3.88 (s, 3 H), 4.51 (s, 2 H), 7.10 (d, J = 11.2 Hz, 1 H), 7.35-7.42 (m, 2 H), 7.61 (d, J = 7.6 Hz, 1 H), 7.71 (s, 1 H), 7.89 (d, J = 11.2 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 37.6, 52.8, 120.8, 125.5, 127.5, 130.2, 130.6(2C), 135.2, 137.5, 139.1, 141.8, 166.5. MS (EI) m/z 304 (M<sup>+</sup>, 2), 271 (66), 269 (M-Cl, 100), 209 (24). HRMS (EI) m/z calcd for C<sub>13</sub>H<sub>11</sub>Cl<sub>3</sub>O<sub>2</sub>: 303.9825; found: 303.9840.

### (2Z,4Z)-Ethyl-5-chloro-2-(chloromethyl)-5-(3-chlorophenyl)penta-2,4-dienoate (2d)

Yellow solid, mp: 75.5-77.4 °C. IR (KBr)  $v_{max}$ : 3132, 1699, 1626, 1400, 1185, 788 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.37 (t, *J* = 7.2 Hz, 3 H), 4.33 (dd, *J* = 14.4 Hz, 2 H), 4.51 (s, 2 H), 7.10 (d, *J* = 11.2 Hz, 1 H), 7.34-7.41 (m, 2 H), 7.60 (d, *J* = 7.6 Hz, 1 H), 7.70 (s, 1 H), 7.88 (d, *J* = 11.2 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 14.2, 37.3, 61.5, 120.5, 125.1, 127.1, 129.8, 130.2, 130.6, 134.8, 136.8, 138.7, 141.1, 165.6. MS (EI) *m*/*z* 320 (M<sup>+</sup>, 5), 285 (M-Cl, 60), 283 (94), 221 (33), 219 (100). HRMS (EI) m/z calcd for C<sub>14</sub>H<sub>13</sub>Cl<sub>3</sub>O<sub>2</sub>: 317.9981; found: 318.0002.

#### (2Z,4Z)-Methyl-5-chloro-2-(chloromethyl)-5-(4-nitrophenyl)penta-2,4-dienoate (2e)

Yellow solid, mp: 116.7-119.0 °C. IR (KBr)  $v_{max}$ : 3133, 1713, 1401, 1349, 1268, 845 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 3.89 (s, 3 H), 4.53 (s, 2 H), 7.24 (d, *J* = 11.2 Hz, 1 H), 7.90 (q, *J* = 5.6 Hz, 3 H), 8.29 (d, *J* = 8.8Hz, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 37.1, 52.7, 122.6, 123.9(2C), 127.9(2C), 131.6, 136.6, 140.1, 142.6, 148.4, 165.9. MS (CI) *m*/z 316 (M+1, 5), 282 (25), 280 (M-Cl, 75), 250 (34), 248 (100). HRMS (CI) m/z calcd for C<sub>13</sub>H<sub>11</sub>Cl<sub>2</sub>NO<sub>4</sub>: 315.0065; found: 315.0043.

#### (2Z,4Z)-Methyl-2-(chloromethyl)-5-chloro-5-phenylpenta-2,4-dienoate (2f)

Light yellow solid, mp: 58.7-60.2 °C. IR (KBr)  $v_{max}$ : 3133, 1712, 1612, 1176, 762 cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ : 3.87 (s, 3 H), 4.51 (s, 2 H), 7.11 (d, *J* = 11.0 Hz, 1 H), 7.43-7.45 (m, 3 H), 7.73-7.74 (m, 2 H), 7.93 (d, *J* = 11.0 Hz, 1 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 37.5, 52.5, 119.5, 127.1(2C), 128.7(2C), 129.3, 130.5, 137.0, 137.8, 143.4, 166.3. MS (EI) *m*/*z* 270 (M<sup>+</sup>, 4), 237 (33), 235 (M-Cl, 100), 203 (23), 175 (64). HRMS (EI) m/*z* calcd for C<sub>13</sub>H<sub>12</sub>Cl<sub>2</sub>O<sub>2</sub>: 270.0214; found: 270.0205.

## (2Z,4Z)-Ethyl-5-chloro-2-(chloromethyl)-5-phenylpenta-2,4-dienoate (2g)

Light yellow solid, mp: 57.7-59.2 °C. IR (KBr)  $v_{max}$ : 3132, 1700, 1605, 1400, 1264 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.36 (t, J = 7.2 Hz, 3 H), 4.31 (dd, J = 14.8 Hz, 2 H), 4.51 (s, 2 H), 7.11 (d, J = 11.6 Hz, 1 H), 7.41-7.43 (m, 3 H), 7.71-7.73 (m, 2 H), 7.92 (d, J = 11.6 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 14.2, 37.4, 61.4, 119.5, 128.4,

128.6(2C), 129.6(2C), 130.3, 136.9, 137.4, 143.1, 165.7. MS (EI) m/z 286 (M+2, 5), 284 (M<sup>+</sup>, 9), 251 (M-Cl, 40), 249 (75), 185 (100). HRMS (EI) m/z calcd for  $C_{14}H_{14}Cl_2O_2$ : 284.0371; found: 284.0360.

# (2Z,4Z)-Methyl-5-chloro-2-(chloromethyl)-5-p-tolylpenta-2,4-dienoate (2h)

Yellow solid, mp: 72.4-74.2 °C. IR (KBr)  $v_{max}$ : 3129, 1720, 1603, 1430, 1169, 819 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.40 (s, 3 H), 3.86 (s, 3 H), 4.51 (s, 2 H), 7.08 (d, J = 11.6 Hz, 1 H), 7.24 (t, J = 8.4 Hz, 2 H), 7.63 (d, J = 8.4 Hz, 2 H), 7.93 (d, J = 11.6 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 21.3, 37.5, 52.4, 118.6, 128.8 (2C), 129.2, 129.4(2C), 134.2, 138.0, 140.9, 143.6, 166.3. MS (EI) m/z 284 (M<sup>+</sup>, 2), 251 (30), 249 (M-Cl, 100), 189 (57). HRMS (EI) m/z calcd for C<sub>14</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>2</sub>: 284.0393; found: 284.0381.

# (2Z,4Z)-Ethyl-5-chloro-2-(chloromethyl)-5-p-tolylpenta-2,4-dienoate (2i)

Yellow solid, mp: 79.0-81.0 °C. IR (KBr)  $v_{max}$ : 3134, 1699, 1599, 1182, 814 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 1.37 (t, *J* = 6.8 Hz, 3 H), 2.40 (s, 3 H), 4.32 (dd, *J* = 14.4 Hz, 2 H), 4.51 (s, 2 H), 7.08 (d, *J* = 11.2 Hz, 1 H), 7.24 (t, *J* = 8.4 Hz, 2 H), 7.63 (d, *J* = 8.0 Hz, 2 H), 7.92 (d, *J* = 11.2 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 14.2, 21.3, 37.6, 61.3, 118.6, 127.0(2C), 129.0, 129.3(2C), 134.1, 137.7, 140.9, 143.3, 165.8. MS (EI) *m*/*z* 298 (M<sup>+</sup>, 4), 265 (32), 263 (M-Cl, 100), 199 (91), 189 (31). HRMS (EI) m/z calcd for C<sub>15</sub>H<sub>16</sub>Cl<sub>2</sub>O<sub>2</sub>: 298.0527; found: 298.0512.

#### (2Z,4Z)-Methyl-5-chloro-2-(chloromethyl)-5-(4-methoxyphenyl)penta-2,4-dienoate (2j)

Yellow solid, mp: 97.5-99.3 °C. IR (KBr)  $v_{max}$ : 3132, 1700, 1594, 1178, 1084, 828 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 3.86 (s, 6 H), 4.51 (s, 2 H), 6.94 (d, *J* = 8.8 Hz, 2 H), 7.02 (d, *J* = 11.2 Hz, 1 H), 7.69 (d, *J* = 8.8 Hz, 2 H), 7.92 (d, *J* = 11.2 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 38.0, 52.7, 55.8, 114.3(2C), 117.9, 128.5, 129.0(2C), 129.7, 138.5, 143.6, 161.8, 166.7. MS (EI) *m*/*z* 300 (M<sup>+</sup>, 8), 267 (38), 265 (M-Cl, 100), 233 (24), 231 (90). HRMS (EI) m/z calcd for C<sub>14</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>3</sub>: 300.0320; found: 300.0339.

# (Z)-Methyl-3-(1-chloro-3,4-dihydronaphthalen-2-yl)-2-(chloromethyl)acrylate (2k)

Yellow solid, mp: 70.3-71.8 °C. IR (KBr)  $v_{max}$ : 3132, 1713, 1432, 1287, 1153 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.83-2.92 (m, 4 H), 3.87 (s, 3 H), 4.40 (s, 2 H), 7.17-7.19 (m, 1 H), 7.26-7.70 (m, 2 H), 7.68-7.70 (m, 1 H), 7.90 (s, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 27.8, 28.4, 38.8, 52.5, 125.7, 127.0, 128.6, 129.5, 130.2, 132.3, 134.8, 136.7, 141.3, 166.6. MS (CI) *m*/z 297 (M+1, 6), 263 (31), 261 (M-Cl, 100). HRMS (CI) m/z calcd for C<sub>15</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>2</sub>:296.0371; found: 296.0388.

#### (2Z,4Z,6E)-Methyl-5-chloro-2-(chloromethyl)-7-phenylhepta-2,4,6-trienoate (2l)

Light yellow solid, mp: 50.1-51.7 °C. IR (KBr) v<sub>max</sub>: 3383, 1711, 1636, 1405, 686 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 3.85 (s, 3 H), 4.49 (s, 2 H), 6.76 (d, J = 12.0 Hz, 1 H), 6.99 (d, J = 14.8 Hz, 1 H), 7.23-7.27 (m, 1 H), 7.31-7.40 (m, 3 H), 7.49-7.50 (m, 2 H), 7.91 (d, J = 12.0 Hz, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 37.1, 52.1, 123.0, 125.3,

127.2(2C), 128.3, 128.6(2C), 129.0, 135.2, 136.4, 137.0, 141.6, 165.9. MS (EI) m/z 296 (M<sup>+</sup>, 2), 263 (21), 261 (M-Cl, 51), 247 (24), 201 (76), 165 (100). HRMS (EI) m/z calcd for  $C_{15}H_{14}Cl_2O_2$ : 296.0371; found: 296.0385.

# (2Z,4Z)-Methyl-5-chloro-2-(chloromethyl)-4-methyl-5-phenylpenta-2,4-dienoate (2m)

Light yellow solid, mp: 65.1-67.0 °C. IR (KBr)  $v_{max}$ : 3129, 1700, 1634, 1500, 1185 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.32 (s, 3 H), 3.72 (s, 3 H), 4.32 (s, 2 H), 7.32-7.33 (m, 6 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 20.0, 38.4, 52.2, 127.9, 128.1(2C), 128.3, 128.8, 129.2(2C), 137.6, 137.7, 142.9, 166.3. MS (EI) *m*/*z* 285 (M<sup>+</sup>, 6), 251 (34), 249 (M-Cl, 100), 234 (21), 199 (47). HRMS (EI) m/z calcd for C<sub>14</sub>H<sub>14</sub>Cl<sub>2</sub>O<sub>2</sub>: 284.0371; found: 284.0349.

#### (2E,4Z)-5-Chloro-2-(chloromethyl)-5-phenylpenta-2,4-dienenitrile (3n)

Yellow solid, mp: 73.1-74.9 °C. IR (KBr)  $v_{max}$ : 3143, 2213, 1605, 1400, 1212 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 4.28 (s, 2 H), 7.17 (d, *J* =11.2 Hz, 1 H), 7.42-7.50 (m, 4 H), 7.72-7.74 (m, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 44.1, 112.0, 116.0, 120.4, 127.1(2C), 128.8(2C), 130.8, 136.1, 142.1, 143.5. MS (EI) *m*/*z* 239 (M+2, 28), 237 (M<sup>+</sup>, 43), 204 (31), 202 (M-Cl, 100), 166 (94). HRMS (EI) m/z calcd for C<sub>12</sub>H<sub>9</sub>Cl<sub>2</sub>N: 237.0112; found: 237.0137.

# (Z)-Methyl-2-(chloromethyl)-3-(6-methylquinolin-3-yl) acrylate (20)

Yellow solid, mp: 102.9-104.7 °C. IR (KBr)  $v_{max}$ : 3131, 1719, 1435, 1285, 1054 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ : 2.57 (s, 3 H), 3.94 (s, 3 H), 4.40 (s, 2 H), 7.62-7.68 (m, 2 H), 7.95 (d, *J* =8.8 Hz, 1 H), 8.04 (s, 1 H), 8.43 (s, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 21.6, 38.7, 52.7, 126.7, 127.2, 128.1, 131.3, 134.0, 138.0, 138.2, 138.9, 146.2, 148.7, 165.8. MS (EI) *m*/z 309 (M<sup>+</sup>, 4), 276 (35), 274 (M-Cl, 100). HRMS (EI) m/z calcd for C<sub>15</sub>H<sub>14</sub>ClNO<sub>2</sub>: 275.0713; found: 275.0732.

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