Toward a Novel Approach to Bis-β-Lactam Synthesis Using Vilsmeier Reagent as an Efficient Entity *via* Staudinger Cycloaddition Reaction

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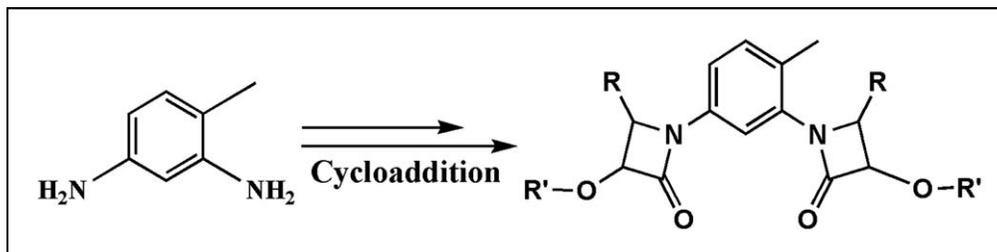
A facile synthesis of bis-β-lactams has been executed using chloromethylenedimethylammonium chloride (Vilsmeier reagent), prepared easily from *N,N*-dimethylformamide and phosphorus oxychloride. It works out as a versatile acid activator reagent for the direct [2 + 2] ketene–imine cycloaddition of substituted acetic acid and bis-imines in one-pot synthesis under mild conditions. Thus, this method has been proved as a high yielding, efficient, and cheap protocol for bis-β-lactam synthesis.

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INTRODUCTION

The β-lactam skeleton is the key structural unit of the most widely employed β-lactam antibiotics [1]. The constant need for new drugs displaying broader antibacterial activity and the necessity for new β-lactam antibiotics to combat the microorganisms that have built up resistance against the most traditional drugs [2] have maintained the interest of organic chemists in β-lactams for decades. In addition to its use in the synthesis of variety of β-lactam antibiotics, the β-lactam skeleton has been recognized as a useful building block by exploiting its strain energy associated with four member ring [3]. Efforts have been made in exploring such new aspects of β-lactam chemistry using pure β-lactams as versatile intermediates for organic syntheses [4]. Ojima *et al.* [5] have shown the utility of bis-β-lactams for the synthesis of peptides. The synthesis of bis-β-lactams, in general, has been reported by a step-wise construction of β-lactam rings [6]. In continuation of our work on synthesis of bis-β-lactams [7], we were interested in building bis-β-lactams from bis-imines using the Staudinger cycloaddition reaction.

Among the various methods available for the synthesis of β-lactams, the Staudinger cycloaddition reaction (ketene–imine cycloaddition reaction) is the most widely used [8] mainly because of the simplicity in reaction procedures. This method has been used for the synthesis of a large number of monocyclic, bicyclic, tricyclic, and spirocyclic β-lactams [9]. The ketenes are commonly generated *in situ* from acyl halides in the presence of tertiary amines [10]. In addition to the utilization of acyl halides, a variety of other methods have been described to activate carboxylic acids [11]. These methods are conventionally useful when the acid halides are not commercially available, difficult to prepare or when they are unstable. Some acid activating agents include 1,1-carbonyldi-imidazole [12], triphosgene [13], ethyl chloroformate [14], trifluoroacetic anhydride [15], p-toluenesulfonyl chloride [16], phosphorus-derived reagents [17], cyanuric chloride [18], the Mukaiyama reagent [19], and acetic anhydride [20].

Herein this communication, we report the synthesis of bis-β-lactams using Vilsmeier reagent. Chloromethylenedimethylammonium chloride (Vilsmeier reagent) has been known as a formylating agent [21]. It has also emerged as an efficient synthetic auxiliary for the synthesis of some important class of organic compounds. This white solid is easily synthesized by reaction of *N,N*-dimethylformamide (DMF) and chlorinating agents such as $POCl_3$ or $SOCl_2$ [22]. But in our methodology, we have generated this reagent *in situ* using DMF and $POCl_3$ in dichloromethane as reported [23]. This reagent was reported for the synthesis of monobactams by Jarrahpour and Zarei [24]. We have extended its applicability in the synthesis of bis β-lactams by generating it *in situ*. In this article, we wish to describe the versatility and utility of the Vilsmeier reagent for the activation of carboxylic acids in bis-β-lactam synthesis under simple

Scheme 1. Synthesis of bis-imines **2a–h**.

2a,3a R=C$_6$H$_5$, 2e,3e R=3-NO$_2$C$_6$H$_4$,
2b,3b R=2-OHC$_6$H$_4$, 2f,3f R=4-N,N-C$_6$H$_3$(CH$_3$)$_2$
2c,3c R=4-OHC$_6$H$_4$, 2g,3g R=2-ClC$_6$H$_4$
2d,3d R=2-NO$_2$C$_6$H$_4$, 2h,3h R=4-ClC$_6$H$_4$
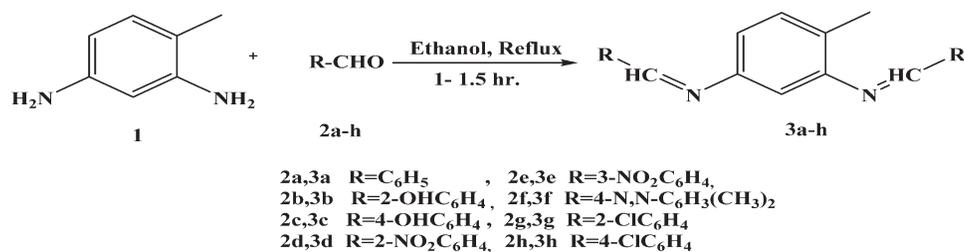
and mild conditions. It has proved to be a high yielding protocol for the synthesis.

RESULTS AND DISCUSSION

We selected toluene-2,4-diamine for the preparation of various bis-imines from different aldehydes and this imine were used for the construction of bis-β-lactams. The bis-imines **3a–h** were prepared by refluxing toluene-2,4-diamine with 2 mol equivalent of aldehydes (benzaldehyde, 2-hydroxybenzaldehyde, 4-hydroxybenzaldehyde, 2-nitrobenzaldehyde, 3-nitrobenzaldehyde, 4-methoxybenzaldehyde, 2-chlorobenzaldehyde, 4-chlorobenzaldehyde, and 4-methoxy-benzaldehyde in ethanol for about 1 to 1.5 h as shown in Scheme 1 according to known method [23]. Crude bis-imines were recrystallized with hot methanol.

Chloromethylenedimethylammonium chloride **4** was prepared from DMF and phosphorus oxychloride in dry CH$_2$Cl$_2$. We have successfully employed the Vilsmeier reagent for the one-step cycloaddition reaction of various imines **3a–h** and substituted phenoxyacetic acid to obtain bis-β-lactams **5a–h** (Scheme 2). Solution of Chloromethylenedimethylammonium chloride **4** was

added to a solution of mixture of acid, imines, and triethylamine in CH$_2$Cl$_2$ between 0 and −5°C, and the reaction mixture was stirred at room temperature for 10 h. The usual work-up and then crystallization from hot methanol gave pure bis-β-lactams **5a–h** in high yields. We found that this method was very efficient, simple, and clean. The DMF and triethylammonium salt are two by-products, which were removed by simple aqueous work-up. In all cases the cycloaddition afforded only *cis, cis* bis-β-lactams **5a–h**.

The *cis* steriochemistry for bis-β-lactam **5a–h** was assigned on the basis of ^{1}H NMR spectral analysis. The ^{1}H NMR spectra showed two doublets between 5.24 and 5.56 ppm for cis-β-lactam ring protons (J = 4.6 to 4.8 Hz for *cis* β-lactam protons). The absence of —CH=N protons in **5a–h** show the azetidinone ring formation. The IR spectra of the bis-imines **3a–h** were compared with those of the bis-β-lactams to draw conclusion on cycloaddition. There were some guide peaks in the spectrum of the bis-imines and bis-lactams, which were helpful in achieving this goal. The position and the intensities of these peaks are expected to change upon cycloaddition. In the spectrum of bis-imines, the characteristic absorption around 1618–1650 cm^{-1} can be assigned to (—C=N) azomethine linkage, which

Scheme 2. General synthesis of bis-β-lactam products **5a–h**.

3a,5a R=C$_6$H$_5$, 3e, 5e R=3-NO$_2$C$_6$H$_4$,
3b,5b R=2-OHC$_6$H$_4$, 3f, 5f R=4-OMe
3c,5c R=4-OHC$_6$H$_4$, 3g, 5g R=2-ClC$_6$H$_4$
3d,5d R=2-NO$_2$C$_6$H$_4$, 3h, 5h R=4-ClC$_6$H$_4$
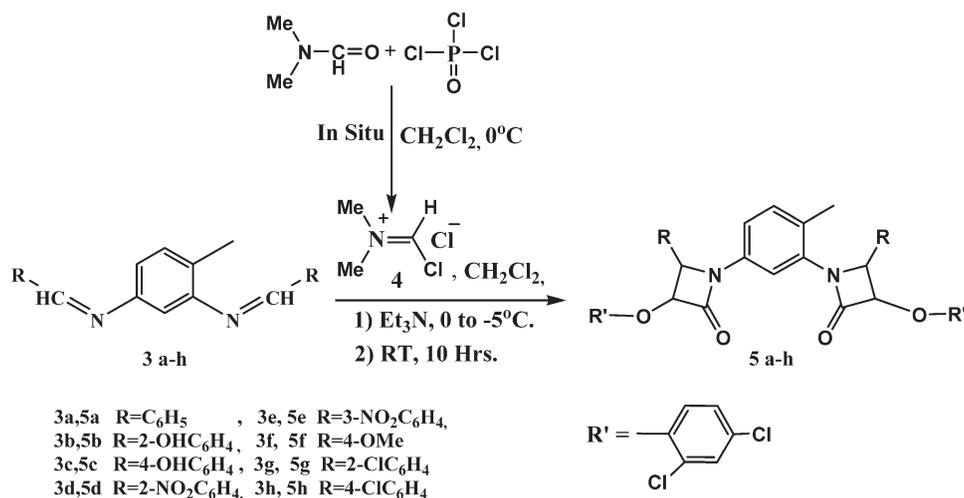
Scheme 3. Approaches in the formation of *cis, cis* bis-β-lactam.

I st Approach

Ketene Generated Insitu

II nd Approach
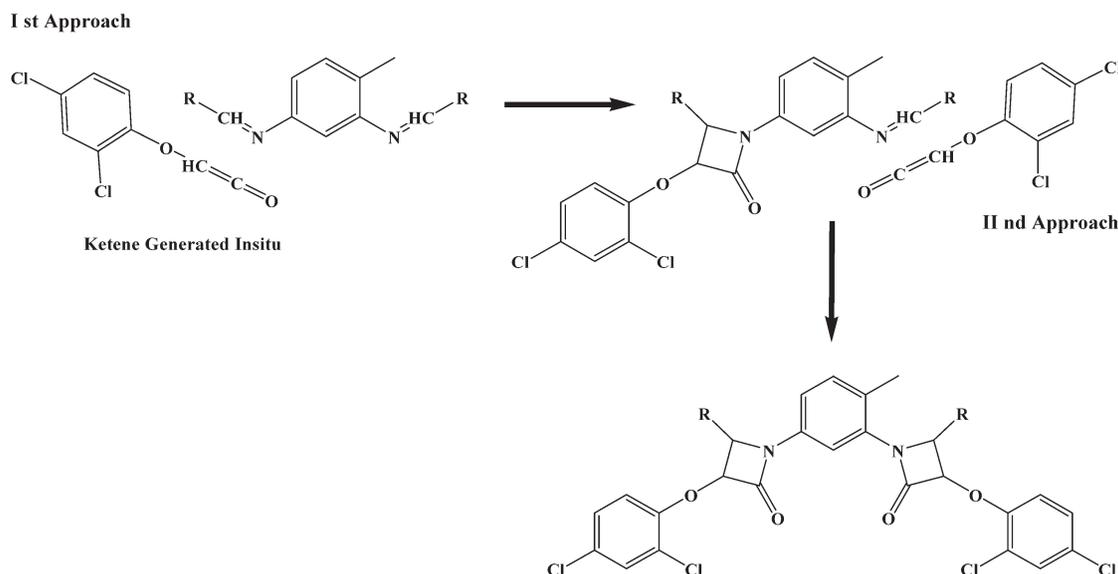
disappears in the spectrum of the bis-β-lactams confirming the cycloaddition. In the spectrum of bis-lactams, the characteristic absorption around 1750–1700 cm^{-1} can be assigned to (—C=O) linkage. The mass spectra of these compounds displayed a molecular ion peak at their respective *m/z* values, which are corresponding well with the respective molecular mass. All the compounds have given the satisfactory elemental analysis.

We believe that mono-β-lactam is initially formed by the reaction of the most stable bis-imine (I approach) with ketene. The approach of the ketene in the Staudinger cycloaddition reaction is such that the steric interaction between the aryl group of the imine and phenoxy group of the ketene is minimum in the transition state (Scheme 3) resulting in the formation of *cis*-β-lactam. However, the formation of trans-β-lactam is unfavorable due to severe steric interaction between the aryl group of imine and phenoxy group of ketene in the transition state. The mono β-lactam further undergoes cycloaddition reaction with the second molecule of ketene to give bis-β-lactam (Scheme 3). The approach of the second ketene towards the imine is from the opposite site of the preformed azetidinone ring to give bis-β-lactam **5a**. In this approach, the ketenes are generated directly from the carboxylic acid using Vilsmeier reagent instead of acid chloride. Thus, the Staudinger reaction of imines with carboxylic acids using Vilsmeier reagent **4** as an activator proceeded smoothly under milder reaction conditions. As acid chlorides are usually unstable, this approach is quite practical as starting carboxylic acid can be easily handled and stored as compared to respected acid chloride.

EXPERIMENTAL

The solvents and reagents used in the synthetic work were of analytical grade obtained from Qualigens India and were purified by distillation or crystallization, where necessary and their boiling or melting points were compared with the available literature values. Melting points were determined in open capillaries and are uncorrected. ^{1}H NMR spectra were recorded on a Perkin Elmer FT NMR Cryo-magnet Spectrometer 400 MHz (Bruker) instrument using tetramethylsilane (TMS) as an internal standard and DMSO-d_6 as a solvent. Chemical shifts are given in parts per million (ppm). Infrared spectra were recorded on Schimadzu-IR Prestige 21. Mass spectra were recorded on a Waters Micromass Q-T of Micro spectrometer. The reactions were monitored, and the purity of products was checked out on pre-coated TLC plates (Silica gel 60 F254, Merck), visualizing the spots under ultraviolet light and iodine chamber.

General procedure for the preparation of bis-imines 3a–h. A mixture of freshly distilled benzaldehyde (2.78 g, 26.3 mmol) and toluene-2,4-diamine (2.20 g, 17.5 mmol) in ethanol (30 mL) was refluxed for 1–1.5 h. The completion of the reaction was monitored by thin layer chromatography. After disappearance of the starting materials, the reaction mixture was allowed to attain the room temperature during which solid precipitated out. It was filtered out and recrystallized from hot methanol to afford **3a** as yellow crystalline solid. Following this procedure, bis-imines **3b–h** were prepared in excellent yield. All the bis-imines are well known in the refs. 25–27 and identified by comparison of their physical and spectral data.

A typical procedure for the preparation of bis-β-lactams 5a–h. In a 100 mL Round Bottom Flask, (1.0 g, 3.35 mmol) bis-imine **3a** was charged followed by (10 mL) dichloromethane. To it (1.48 g, 6.70 mmol), 2,4-dichlorophenoxyacetic acid followed by (1.35 g, 13.40 mmol) triethylamine was charged. It was chilled to −5°C. To a separate 50 mL Round Bottom Flask, (1.2 g, 8.04 mmol), POCl$_3$ in (10 mL) dichloromethane was charged. The solution was cooled to 10°C and a

solution of DMF (0.50 g, 6.7 mmol) in 5 mL dichloromethane was added over 10 min maintaining the temperature between 10 and 15°C. When the addition was complete, the mixture was allowed to stir at room temperature for 30 min. This Vilsmeier solution was then added gradually to the above prepared bis-imine solution over 15 min, maintaining the temperature between 0 and −5°C. After the addition was complete, the reaction mixture was allowed to warm up to room temperature and stirred for 10 h. The reaction mixture was then washed with water (2 × 20 mL), saturated sodium bicarbonate solution (20 mL) and saturated brine solution (20 mL). The organic layer was then dried over anhydrous Na_2SO_4 and concentrated to give the crude bis-β-lactams. It was recrystallized from hot methanol to give pure bis-β-lactams. Following this procedure other β-lactams **5b–h** were prepared.

3-(2,4-Dichlorophenoxy)-1-(3-(3-(2,4-dichlorophenoxy)-2-oxo-4-phenylazetidin-1-yl)-4-methyl phenyl)-4-phenylazetidin-2-one 5(a). This compound was obtained as white solid, 81%, m.p. 193–194°C, IR (KBr): 3120, 2965, 2970, 1755, 1365 cm^{-1}. ^{1}H NMR (DMSO-d_6): 2.34 (s, 3H, —CH$_3$), 6.80–7.62 (m, 19H, Ar), 5.25 (d, 1H, J = 4.7 Hz), 5.51 (d, 1H, J = 4.7 Hz), 5.26 (d, 1H, J = 4.6 Hz), 5.56 (d, 1H, J = 4.6 Hz). MS: m/z: 704 (M$^+$, 100%), 702 (71%), 706 (52%). Anal. Calc. for $C_{37}H_{26}Cl_4N_2O_4$: C, 63.09; H, 3.72; Cl, 20.13; N, 3.98; O, 9.09. Found: C, 63.12; H, 3.75; Cl, 20.10; N, 3.96; O, 9.12.

3-(2,4-Dichlorophenoxy)-1-(3-(3-(2,4-dichlorophenoxy)-2-oxo-4-(2-hydroxyphenyl)azetidin-1-yl)-4-methyl phenyl)-4-(2-hydroxyphenyl)azetidin-2-one 5(b). This compound was obtained as light yellow solid, 79%, m.p. 201–203°C, IR (KBr): 3300, 3122, 2960, 2965, 1760, 1368 cm^{-1}. ^{1}H NMR (DMSO-d_6): 2.33 (s, 3H, —CH$_3$), 5.25 (d, 1H, J = 4.7 Hz), 5.51 (d, 1H, J = 4.7 Hz), 5.26 (d, 1H, J = 4.6 Hz), 5.56 (d, 1H, J = 4.6 Hz), 6.85–7.72 (m, 17H, Ar), 12.10–12.20 (s, 2H, —OH). MS: m/z: 736 (M$^+$, 100), 737 (68%), 738 (30%). Anal. Calc. for $C_{37}H_{26}Cl_4N_2O_6$: C, 60.35; H, 3.56; Cl, 19.26; N, 3.80; O, 13.0. Found: C, 60.38; H, 3.53; Cl, 19.29; N, 3.83; O, 13.10.

3-(2,4-Dichlorophenoxy)-1-(3-(3-(2,4-dichlorophenoxy)-2-oxo-4-(4-hydroxyphenyl)azetidin-1-yl)-4-methyl phenyl)-4-(4-hydroxyphenyl)azetidin-2-one 5(c). This compound was obtained as light yellow solid, 82%, m.p. 185–186°C, IR (KBr): 3300, 3120, 2962, 2964, 1758, 1366 cm^{-1}. ^{1}H NMR (DMSO-d_6): 2.33 (s, 3H, —CH$_3$), 5.24 (d, 1H, J = 4.7 Hz), 5.54 (d, 1H, J = 4.7 Hz), 5.26 (d, 1H, J = 4.6 Hz), 5.60 (d, 1H, J = 4.6 Hz), 6.83–7.74 (m, 17H, Ar), 12.12 (s, 1H, —OH). MS: m/z: 736 (M$^+$, 100), 737 (73%), 738 (42%). Anal. Calc. for $C_{37}H_{26}Cl_4N_2O_6$: C, 60.35; H, 3.56; Cl, 19.26; N, 3.80; O, 13.0. Found: C, 60.38; H, 3.53; Cl, 19.29; N, 3.83; O, 13.10.

3-(2,4-Dichlorophenoxy)-1-(3-(3-(2,4-dichlorophenoxy)-2-oxo-4-(2-nitrophenyl)azetidin-1-yl)-4-methyl phenyl)-4-(2-nitrophenyl)azetidin-2-one 5(d). This compound was obtained as yellow solid, 75%, m.p. 190–191°C, IR (KBr): 3122, 2975, 2970, 1756, 1366 cm^{-1}. ^{1}H NMR (DMSO-d_6): 2.12 (s, 3H, —CH$_3$), 6.79–8.03 (m, 17H, Ar), 5.26 (d, 1H, J = 4.7 Hz), 5.51 (d, 1H, J = 4.7 Hz), 5.26 (d, 1H, J = 4.6 Hz), 5.55 (d, 1H, J = 4.6 Hz). MS: m/z: 794 (M$^+$, 100%), 795 (62%), 796 (26%). Anal. Calc. for $C_{37}H_{24}Cl_4N_4O_8$: C, 55.94; H, 3.05; Cl, 17.85; N, 7.05; O, 16.11. Found: C, 55.92; H, 3.10; Cl, 17.83; N, 7.08; O, 16.13.

3-(2,4-Dichlorophenoxy)-1-(3-(3-(2,4-dichlorophenoxy)-2-oxo-4-(3-nitrophenyl)azetidin-1-yl)-4-methyl phenyl)-4-(3-nitrophenyl)azetidin-2-one 5(e). This compound was obtained as yellow solid, 72%, m.p. 214–215°C, IR (KBr): 3118, 2971, 2969,
1765, 1365 cm^{-1}. ^{1}H NMR (DMSO-d_6): 2.13 (s, 3H, —CH$_3$), 6.75–8.10 (m, 17H, Ar), 5.26 (d, 1H, J = 4.7 Hz), 5.51 (d, 1H, J = 4.7 Hz), 5.26 (d, 1H, J = 4.6 Hz), 5.55 (d, 1H, J = 4.6 Hz). MS: m/z: 794 (M$^+$, 100%), 795 (65%), 796 (32%). Anal. Calc. for $C_{37}H_{24}Cl_4N_4O_8$: C, 55.94; H, 3.05; Cl, 17.85; N, 7.05; O, 16.11. Found: C, 55.90; H, 3.11; Cl, 17.83; N, 7.09; O, 16.16.

3-(2,4-Dichlorophenoxy)-1-(3-(3-(2,4-dichlorophenoxy)-2-oxo-4-(4-methoxyphenyl)azetidin-1-yl)-4-methyl phenyl)-4-(4-methoxyphenyl)azetidin-2-one 5(f). This compound was obtained as brown solid, 69%, m.p. 206–208°C, IR (KBr): 3120, 2965, 2970, 1755, 1365, 1040 cm^{-1}. ^{1}H NMR (DMSO-d_6): 2.25 (s, 3H, —CH$_3$), 3.85 (s, 3H, —OCH$_3$), 6.93–7.60 (m, 17H, Ar), 5.45 (d, 1H, J = 4.7), 5.50 (d, 1H, J = 4.7 Hz), 5.28 (d, 1H, J = 4.6 Hz), 5.66 (d, 1H, J = 4.6 Hz). MS: m/z: 764 (M$^+$, 100%), 765 (61%), 766 (23%). Anal. Calc. for $C_{39}H_{30}Cl_4N_2O_6$: C, 61.27; H, 3.96; Cl, 18.55; N, 3.66; O, 12.56. Found: C, 61.25; H, 3.86; Cl, 18.40; N, 3.90; O, 12.60.

3-(2,4-Dichlorophenoxy)-1-(3-(3-(2,4-dichlorophenoxy)-2-oxo-4-(2-chlorophenyl)azetidin-1-yl)-4-methyl phenyl)-4-(2-chlorophenyl)azetidin-2-one 5(g). This compound was obtained as white solid, 71%, m.p. 189–190°C, IR (KBr): 3122, 2965, 2970, 1765 cm^{-1}. ^{1}H NMR (DMSO-d_6): 2.20 (s, 3H, —CH$_3$), 6.78–7.60 (m, 17H, Ar), 5.25 (d, 1H, J = 4.7), 5.50 (d, 1H, J = 4.7 Hz), 5.27 (d, 1H, J = 4.6 Hz), 5.56 (d, 1H, J = 4.6 Hz). MS: m/z: 773 (M$^+$, 100%), 774 (73%), 776 (30%). Anal. Calc. for $C_{37}H_{24}Cl_6N_2O_4$: C, 57.43; H, 3.13; Cl, 27.51; N, 3.52; O, 28.09. Found: C, 57.45; H, 3.15; Cl, 27.52; N, 3.50; O, 28.10.

3-(2,4-Dichlorophenoxy)-1-(3-(3-(2,4-dichlorophenoxy)-2-oxo-4-(4-chlorophenyl)azetidin-1-yl)-4-methyl phenyl)-4-(4-chlorophenyl)azetidin-2-one 5(h). This compound was obtained as white solid, 76%, m.p. 211–212°C, IR (KBr): 3130, 2971, 2975, 1768 cm^{-1}. ^{1}H NMR (DMSO-d_6): 2.22 (s, 3H, —CH$_3$), 6.78–8.10 (m, 17H, Ar), 5.24 (d, 1H, J = 4.7 Hz), 5.54 (d, 1H, J = 4.7 Hz), 5.30 (d, 1H, J = 4.6 Hz), 5.58 (d, 1H, J = 4.6 Hz). MS: m/z: 773 (M$^+$, 100%), 774 (76%), 776 (34%). Anal. Calc. for $C_{37}H_{24}Cl_6N_2O_4$: C, 57.43; H, 3.13; Cl, 27.51; N, 3.52; O, 28.09. Found: C, 57.50; H, 3.21; Cl, 27.55; N, 3.61; O, 28.15.

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