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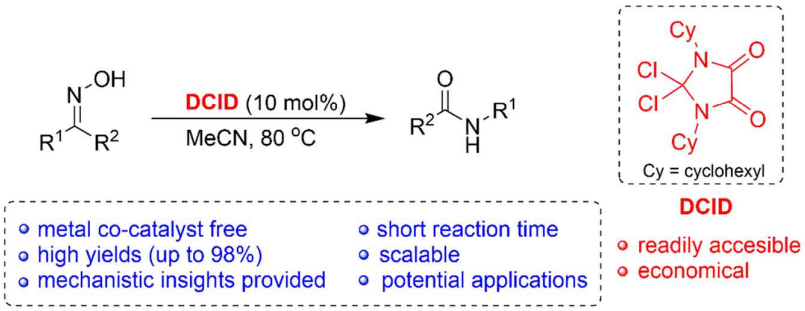
ABSTRACT



A novel protocol for the activation of Beckmann rearrangement utilizing the readily available and economical geminal dichloroimidazolidinediones (DCIDs) on a substoichiometric scale (10 mol%) has been developed. A unique self-propagating mechanism for substoichiometric dichloroimidazolidinedione-activated transformation was proposed and validated. The substrate scope of the developed protocol has been demonstrated by 23 examples with good to excellent yields (mostly 90–98%) in a short time (mostly 10–30 min), including a substrate for synthesizing monomer of nylon-12 and a complicated steroidal substrate on a preparative scale. This research not only unveils for the first time the synthetic potential of substoichiometric amounts of dichloroimidazolidinediones in promoting chemical transformation, but also offers yet another important illustration of the self-propagating cycle in the context of the Beckmann rearrangement activated by a structurally novel organic promoter.

INTRODUCTION

Geminal dihalides are privileged building blocks in modern synthetic organic chemistry in that the two halogens on the same carbon nucleus could function as good leaving groups.[1-3]

2,2-Dichloroimidazolidine-4,5-diones (DCIDs) (**1**), as a category of cyclic geminal dihalides, were initially prepared by Stachel[4] in 1959 through the condensation of carbodiimides with oxalyl chloride and subsequently investigated by others[5-10] (Figure 1). The connection of four electron-withdrawing groups on DCIDs (**1**) makes the quaternary carbon nucleus at 2-position electron-deficient and thus highly electrophilic (Figure 1). Moreover, the two chlorines on the 2-position quaternary carbon nucleus could serve as good leaving groups (Figure 1). Besides, the *N*-substituents on DCIDs (**1**) can be easily modified, offering opportunities to tune their electronic and physical properties (Figure 1). However, despite possessing these intriguing and valuable characteristics, DCIDs have rarely been applied in practical synthetic chemistry.[11-13] Bielawski and co-workers leveraged dihaloimidazolidinediones as halodehydrating agents to generate alkyl halides from their corresponding alcohols in the stoichiometric version recently.[13] To the best of our knowledge, DCIDs have never been employed in substoichiometric amounts for promoting chemical transformations.

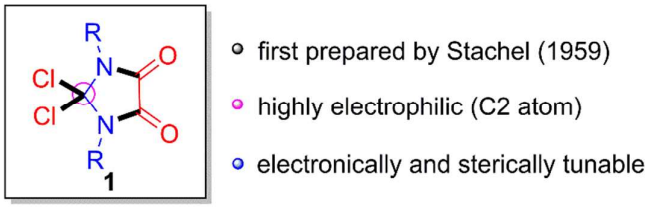
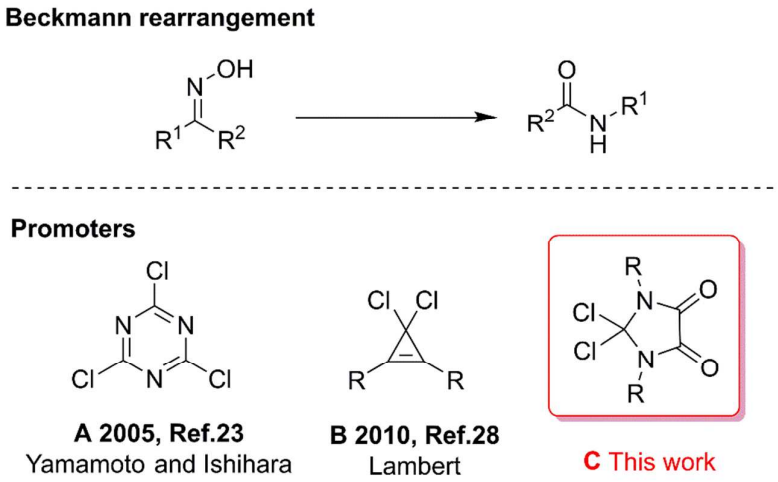


Figure 1. Dichloroimidazolidinediones (DCIDs).

The Beckmann rearrangement,[14-20] discovered in 1886, is undoubtedly a powerful and atom economic tool to construct amides and lactams from their corresponding oximes. A very important application of this reaction lies in manufacturing monomers for polymerization of polyamides nylon-6 and nylon-12 on a large scale in industrial chemistry.[21,22] Traditionally, this reaction involves harsh conditions such as strongly acidic media and high reaction temperature, which generates considerable amounts of byproducts and precludes its compatibility with acid sensitive substrates. Accordingly, to overcome these deficiencies, several organocatalytic methods via the activation of the oxime hydroxyl group have been developed in recent years.[23-30] Yamamoto and Ishihara reported cyanuric chloride as the first highly efficient organocatalyst for Beckmann rearrangement in 2005 (Scheme 1A).[23] Most notably, Lambert and co-workers reported elegant studies in which they used chlorocyclopropenium to activate Beckmann rearrangement with satisfying outcomes (Scheme 1B).[28] What's more, they made a mechanistic distinction between authentic catalysis and self-propagation. Their experimental results gave evidence to support the latter self-propagation

mode, casting doubt on the mechanisms of other reported "organocatalytic" Beckmann rearrangements.[28]

Scheme 1. Organic Promoters for Beckmann Rearrangement

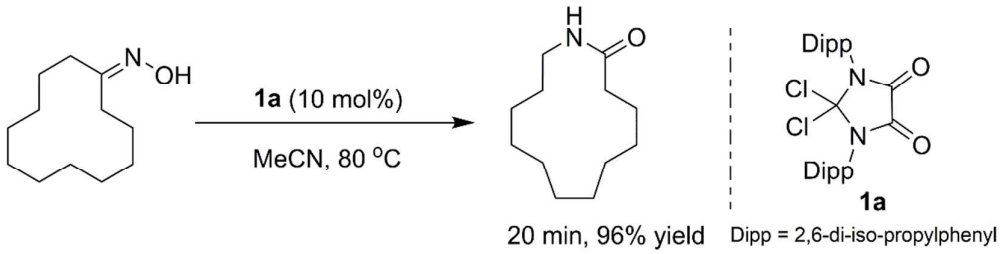


In this context, we have become interested in developing a novel activation method for Beckmann rearrangement by employing geminal dichloroimidazolidinediones and revisiting this intriguing mechanistic controversy. On the basis of the intrinsic characteristic of DCIDs, we envisioned that under the suitable conditions, DCIDs might serve as a well suited electrophilic activator of the oxime hydroxyl group for the efficient transformation of ketoximes to amides and lactams. In fact, we have successfully demonstrated for the first time that DCIDs can be utilized in substoichiometric amounts for promoting the Beckmann rearrangement with extremely high reactivity in a unique self-propagating mode. Herein, we would like to elaborate the development of such a new DCID-activated Beckmann rearrangement method (Scheme 1C).

RESUITS AND DISCUSSION

At the onset, we chose cyclododecanone oxime as an oxime substrate to investigate the feasibility of DCID-activated Beckmannn rearrangement. To our amazement, treatment of the oxime with 10 mol% of 2,2-dichloro-1,3-bis(2,6-diisopropylphenyl)imidazolidine-4,5-dione (**1a**) in acetonitrile (MeCN) at 80 ^{o}C for 20 min led to the corresponding ω-laurolactam, a monomer for the manufacture of nylon-12 polymer, in 96% isolated yield (Scheme 2). Noticeably, this favorable preliminary result demonstrates DCIDs can actually serve as a potent reagent to activate the Beckmannn rearrangement.

Scheme 2. Demonstration of DCID-Activated Beckmannn Rearrangement



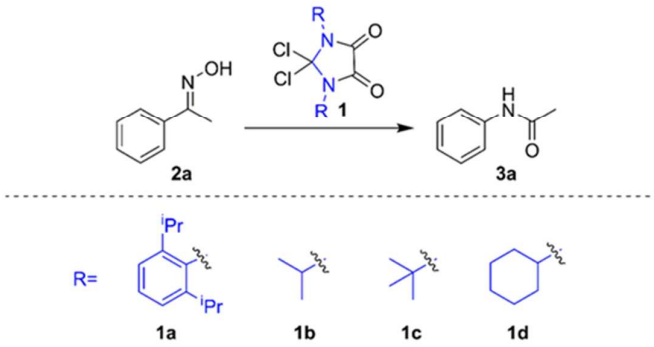
To screen for the optimal conditions, acetophenone oxime (**2a**) was selected as a model substrate to run a series of trial reactions under various conditions as compiled in Table 1. Given that a potential equivalent of acid HCl was produced *in situ* by reaction of ketoxime (**2a**) with DCIDs (**1**) at room temperature, our initial trial commenced with the addition of an equivalent of HCl at room temperature. The result ruled out the possibility that the rearrangement was due to a background reaction (Table 1, entry 1). When the reaction was conducted in MeCN at room temperature, among the four different *N*-substituted DCIDs tested, which were readily prepared through the condensation of commercially available carbodiimides (RN=C=NR, R = Dipp, ^{i}Pr, ^{t}Bu, Cy) with oxalyl chloride, DCID **1a** was found to give the rearranged product *N*-phenylacetamide **3a** in 91% yield (via GC analysis) after 3 h (Table 1, entry 2). DCIDs **1b** and **1d** gave similar results with shorter times and comparatively higher yields than DCID **1a**. Compared with the other three DCIDs, DCID **1c** showed slightly poor reactivity presumably due to the steric hindrance of the *tert*-butyl group (Table 1, entries 2–5). In terms of the lower cost of *N,N'*-dicyclohexylcarbodiimide (DCC) than *N,N'*-diisopropylcarbodiimide (DIC), which are the raw materials of synthesizing the DCIDs, 2,2-dichloro-1,3-dicyclohexylimidazolidine-4,5-dione (**1d**) was chosen as the optimal reagent.

Satisfied with the superior reactivity of stoichiometric DCIDs at room temperature, we next examined the performance of a substoichiometric amount of DCID at slightly elevated temperatures. It was found that raising the reaction temperature from 25 to 50 °C could induce rearrangement in 98% yield within 40 min by using 10 mol% of DCID **1d** (Table 1, entry 7), whereas at room temperature only 31% of the title compound **3a** in 3 h was observed in the presence of 10 mol% of DCID **1d** (Table 1, entry 6). Moreover, further heating the reaction to 80 °C gave rise to rearrangement in quantitative yield within shorter time (20 min, entry 10). Once again, to exclude the possibility that a potential acid HCl catalyzed rearrangement under heating conditions, we performed control experiments as shown in Table 1, entries 8–9. As expected, neither heat nor HCl

promoted the reaction. Afterward, lowering the amount of DCID **1d** to 5 mol% resulted in a similar yield of **3a**, yet three times of the duration of reaction was needed (Table 1, entry 11). In continuing to decrease the loading to 3 mol%, it was observed that the yield of amide **3a** was lowered to 77% as well as the reaction time was prolonged to 2 h (Table 1, entry 12).

To investigate the solvent effect on this transformation, several aprotic solvents including 1,4-dioxane, *N,N*-dimethylformamide (DMF), 1,2-dichloroethane (DCE), toluene, nitromethane ($MeNO_2$) and tetrahydrofuran (THF) were utilized (Table 1, entry 10 *vs*. entries 13–18). It turned out that the reaction efficiency was strongly dependent on the solvent. For example, the reaction in DCE was nearly as efficient as in MeCN and delivered **3a** in 95% yield within 20 min at 80 ^{o}C, whereas in other solvents it proved to be far less effective than in MeCN and DCE at 80 ^{o}C, especially in 1,4-dioxane and THF, where the reaction process was almost entirely suppressed (Table 1, entries 13 and 18). In terms of safety, among MeCN and DCE, we preferred to select MeCN rather than DCE as the optimal reaction solvent.

Table 1. Optimization of the Reaction Conditions[a]



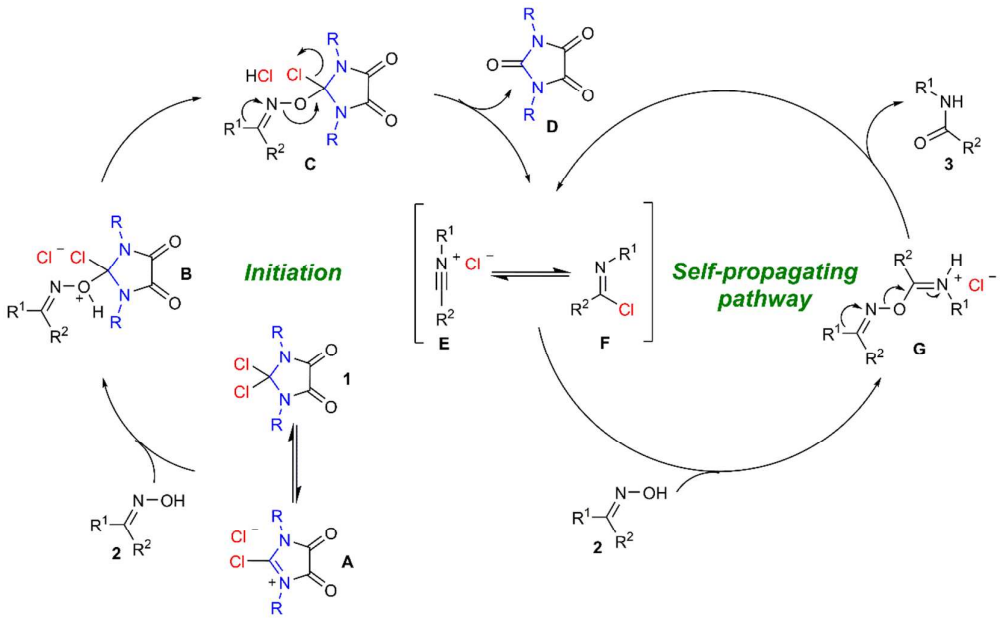
Entry	Reagent (mol %)	Solvent	T (°C)	time (min)	yield (%)[b]
1[c]	-	MeCN	25	10 h	7
2	1a (100)	MeCN	25	3 h	91
3	1b (100)	MeCN	25	60	94
4	1c (100)	MeCN	25	2 h	87
5	1d (100)	MeCN	25	60	98
6	1d (10)	MeCN	25	3 h	31
7	1d (10)	MeCN	50	40	98
8	-	MeCN	80	12 h	0
9[d]	-	MeCN	80	2 h	5
10	1d (10)	MeCN	80	20	99
11	1d (5)	MeCN	80	60	96
12	1d (3)	MeCN	80	2 h	77
13	1d (10)	1,4-dioxane	80	60	2
14	1d (10)	DMF	80	20	36
15	1d (10)	DCE	80	20	95
16	1d (10)	toluene	80	60	24
17	1d (10)	$MeNO_2$	80	2 h	23
18	1d (10)	THF	68	60	3

[a] The rearrangement of acetophenone oxime (0.5 mmol) was carried out in MeCN (2 mL). [b] Yield (%) of *N*-phenylacetamide determined by GC analysis using standard working curve method. [c] HCl (36–38 wt%, 1.0 equiv., 0.5 mmol) was added. [d] HCl (36–38 wt%, 10 mol%) was added.

The striking high reactivity of substoichiometric DCIDs intrigued us to contemplate the mechanism in this protocol setting. On the basis of the above experimental facts and literature reports,[28,31-33] a putative mechanism for substoichiometric DCID-mediated Beckmann rearrangement is proposed in Scheme 3. Initially, the heterolysis of the C–Cl bond in DCID **1** occurs with the aid of the election donating of two amide nitrogen atoms adjacent to the quaternary carbon nucleus, affording 2-chloro-4,5-dioxo-imidazolinium chloride salt **A**. Subsequently, attack of the oxime substrate **2** by the electrophile **A** forms the activated protonated species **B**. Then, the

corresponding intermediate **C** is formed after deprotonation of **B**. Next, the arrangement of the oxime moiety in the intermediate **C** happens along with the loss of the second chlorine atom, producing the urea **D** as well as nitrilium ion **E** (or the imidoyl chloride **F**). The reaction then proceeds through a self-propagating pathway. Another molecule of the oxime substrate **2** might be directly alkylated by the imidoyl chloride **F**/nitrilium ion **E**, affording a dimer-like cation intermediate **G**, which then yields the amide product **3** via Beckmann rearrangement and retrieves **F**/**E** so that this self-propagating pathway could continue. It is worth mentioning that this mode would represent a special case of autocatalytic reaction, which requires the intermediate formed rather than the final product in the rate-limiting step to accelerate the reaction rate.

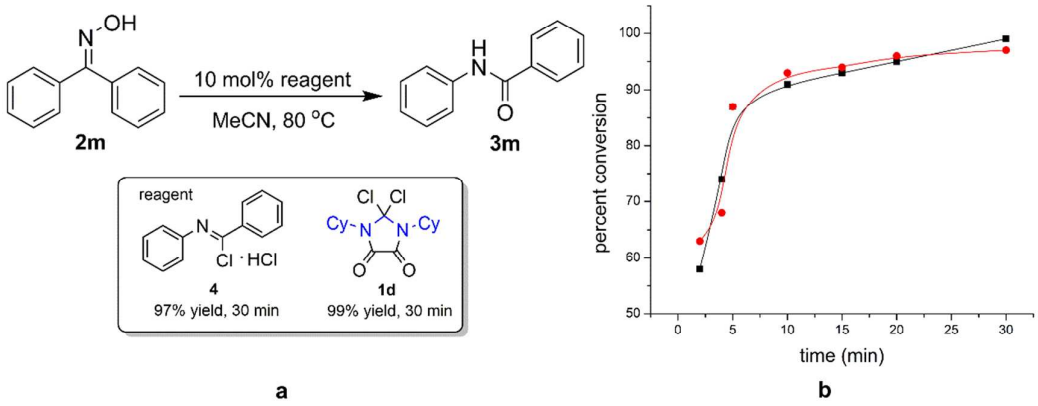
Scheme 3. Putative Mechanism for Substoichiometric DCID-Activated Beckmann Rearrangement



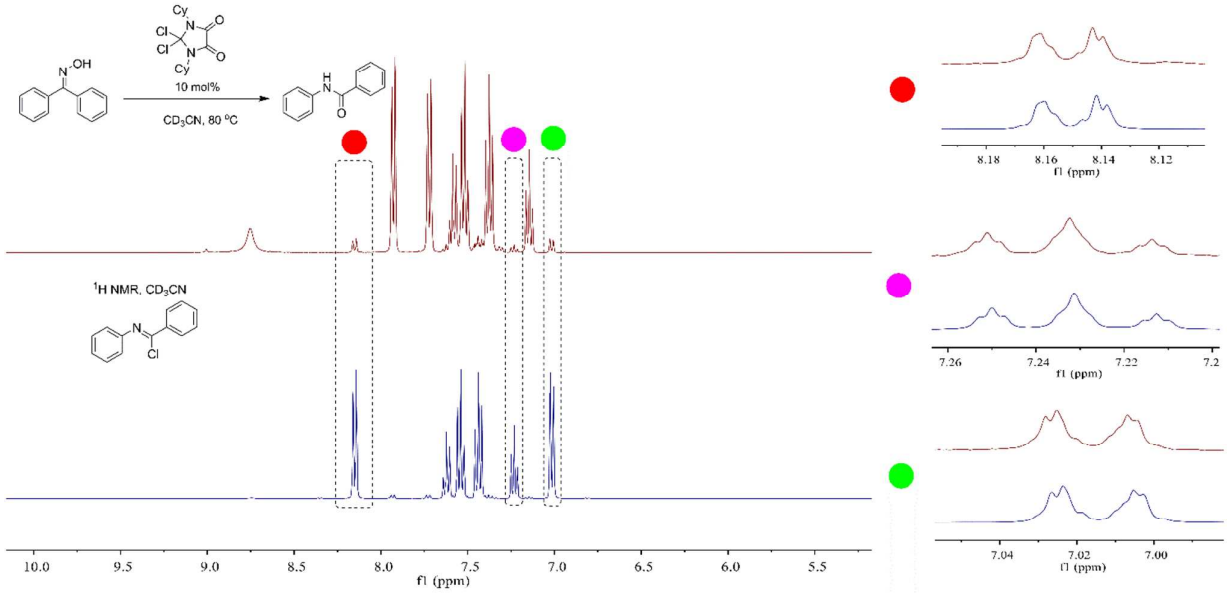
To confirm the catalytic role of **E**/**F** in our protocol, the *N*-phenylbenzimidoyl chloride **4** was synthesized and 10 mol% loading of **4** in the presence of HCl was utilized to mimic **F** to promote the rearrangement of benzophenone oxime **2m** at 80 ^{o}C in MeCN. It turned out that this reagent (**4**+**HCl**; 10 mol %:10 mol %) promoted the Beckmann rearrangement of **2m** at 80 °C with excellent yields (via GC analysis) in only 30 min (Scheme 4a). Furthermore, we ran a rate comparison experiment between DCID **1d** and *N*-phenylbenzimidoyl chloride **4** by comparing the rate of conversion of the oxime **2m** to the amide product **3m** and found that imidoyl chloride activated Beckmann rearrangement at almost the same rate as did DCID **1d** (Scheme 4b). [34] Additionally, it is noteworthy that species **D** was detected via HRMS analysis in the course of rate comparison experiment (see

page S2 in the Supporting Information) and the presence of imidoyl chloride intermediate **4** was detected by ^{1}H NMR in the duration of the reaction promoted by DCID **1d** in deuterated acetonitrile at 80 °C (Scheme 5, see page S3 in the Supporting Information for full extended version).[35] These experimental results certainly suggest that under our protocol conditions DCID **1d** may merely serve as an initiator and imidoyl chloride may in fact be responsible for catalysis.

Scheme 4. (a) Rate comparison of imidoyl chloride **4** *versus* DCID **1d**. (b) Percent conversions of benzophenone oxime in MeCN at 80 °C, with 10 mol% activator loading, were determined by GC analysis, comparing DCID **1d** (black squares) *versus N*-phenylbenimidoyl chloride and HCl (red circles).



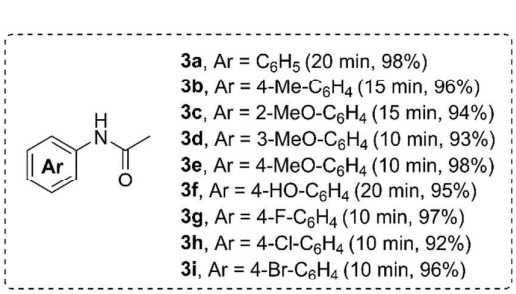
Scheme 5. Demonstration of the Presence of Imidoyl Chloride Intermediate by ^{1}H NMR via Monitoring the Reaction Promoted by DCID **1d**

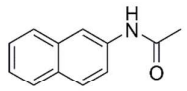


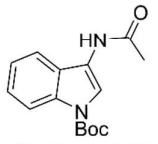
With the optimized conditions being established and the tentative mechanism being proposed and investigated, the scope and generality of this DCID-activation protocol was then probed (Table 2). Pleasantly, a broad range of aromatic and aliphatic oximes were found to be rearranged smoothly under this protocol to afford the corresponding amides/lactams in good to excellent yields and a functional group-tolerant fashion. The acetophenone oximes with electron-donating or -withdrawing groups on the phenyl ring, such as methyl (**2b**), methoxy (**2c–2e**), hydroxyl (**2f**) or halides (**2g–2i**), all delivered the corresponding acetanilides in high yields within very short time (10–20 min). It is noteworthy that product **3f**, namely Paracetamol, possesses antipyretic-analgesic effect. Moreover, 2-acetonaphthone oxime **2j** and the ketoxime with N-Boc indole ring **2k** featuring an aromatic fused ring and a heterocyclic aromatic ring respectively were amenable to the protocol condition, which furnished their rearranged products **3j** and **3k** in 91% and 72% yields, respectively. In addition to methyl, other variations in the R^2 moiety of the ketoxime **2**, such as phenyl (**2m**), ethyl (**2p**), cyclopropyl (**2o**) and an extended aliphatic chain ($R^2 = MeO_2C(CH_2)_2–$, **2r**) were studied and also found to be successfully and efficiently engaged in the Beckmann rearrangement. Besides, the symmetrical ketoxime **2n** and **2q** can be rapidly converted into the corresponding amides **3n** and **3q** with high yields as well. When alkyl oximes including cyclohexyl, cyclododecyl and nonanone oximes were subjected to this reaction, the results turned out to be different from each other to a great extent. *N*-heptylacetamide **3t** could be obtained in 87% yield, albeit with extended reaction time. However, cyclohexyl oxime **2s** was failed to give the desired ε-caprolactam **3s** in acceptable yield at 80 ^{o}C using 10 mol% **1d**. Gratifyingly, yield improvement was reached by switching to employing one equivalent of **1d** at room temperature. Remarkably, cyclododecyl oxime **2u** was one exception. ω-Laurolactam **3u**, a monomer of nylon-12 polymer, was obtained with near quantitative yield in 10 min, with 6-fold decrease in reaction time compared to the reported[23] organocatalytic method. Furthermore, a 1.5 : 1 (*E* : *Z*) isomeric mixture of the unsymmetrical oxime (4-hydroxyphenyl)(phenyl)methanone oxime was selected to examine the selectivity of the migrating group. As speculated, the rearrangement of this oxime proceeded with exclusive *trans* migration, giving access to an isomeric mixture of the amide products **3v** and **3w** in the ratio of 1.5 : 1 in an overall yield of 91%, which suggests that no oxime isomerization happens under this protocol. Additionally, it is worth mentioning that this protocol also exhibited compatibility with acid labile functional groups such as a Boc group and a sily ether to furnish the desired amides in

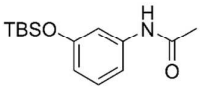
satisfactory yields (**3k** and **3l**). Finally, we leveraged our DCID activation strategy to examine its validity in the context of a complex molecule. The oxime of pregnenolone acetate **2x** was prepared and subjected to our protocol conditions. Gratifyingly, after 1 h, the steroidal amide **3x** could be isolated in 90% yield.

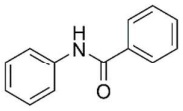
Table 2. The Substrate Generality of the Beckmann Rearrangement Activated by DCID[a,b]

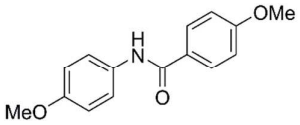


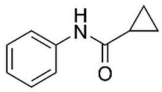

3j, 20 min, 91%

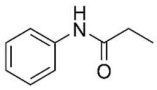

3k, 20 min, 72%

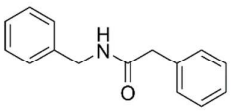

3l, 40 min, 83%

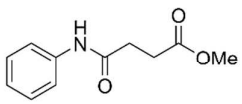

3m, 20 min, 96%

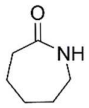

3n, 10 min, 94%

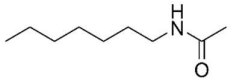

3o, 10 min, 89%

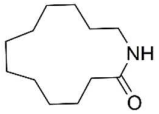

3p, 15 min, 97%

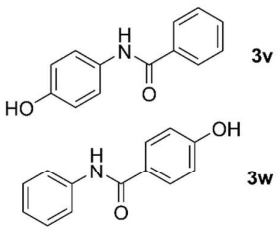

3q, 20 min, 93%

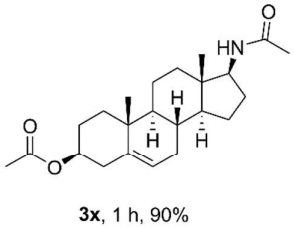

3r, 15 min, 96%


3s, 3 h, 80%[c]


3t, 5 h, 87%


3u, 10 min, 98%


3v
3w
3v:**3w** = 1.5:1, 15 min, 91%

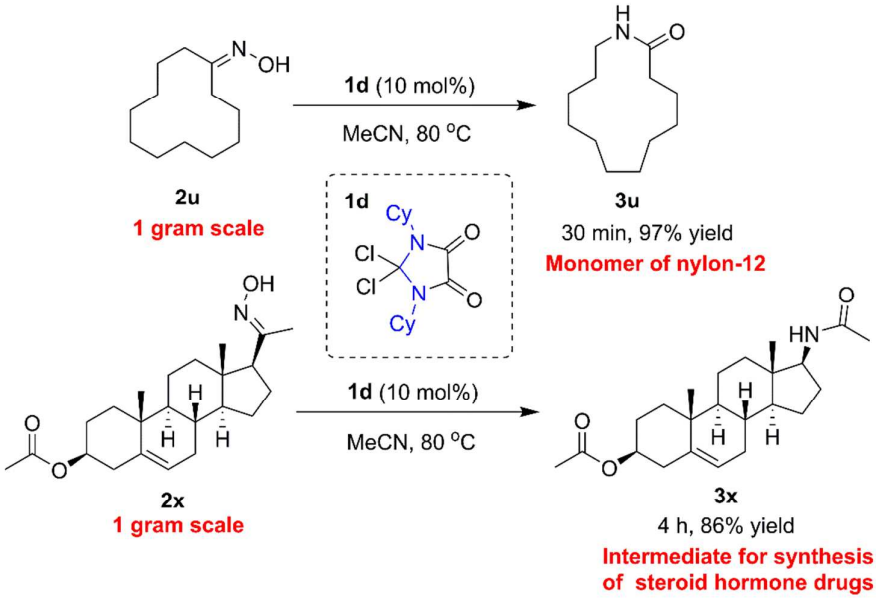

3x, 1 h, 90%

[a] Reaction conditions: ketoxime substrate **2** (1 mmol), **1d** (10 mol%), 5.0 mL of anhydrous MeCN as

solvent, 80 °C. [b] Isolated yields based on **2**. [c] Performed using 1.0 equiv. of **1d** at room temperature.

The favorable results found in mmol-scale substrate scope studies prompted us to further examine the scalability of this protocol. As evidently illustrated in Scheme 6, the arrangement of cyclododecyl oxime **2u** and 3β-acetoxypregnenone oxime **2x** were conducted on one gram scale, furnishing the amide products **3u** in 97% yield on a 0.97 gram scale and **3x** in 86% yield on a 0.86 gram scale, respectively.

Scheme 6. The 1-Gram Scale Beckmannn Rearrangement of the Oxime **2u** and **2x**



CONCLUSION

In conclusion, this work has demonstrated for the first time the synthetic potential of substoichiometric amounts of dichloroimidazolidinediones in promoting Beckmann rearrangement. The new promoter can be easily prepared from commercially available and economical starting materials in a one step process. This novel method of activation features rapid access to amides and lactams of chemical, industrial and medicinal importance in good to excellent yields, exhibits good functional group tolerance, and could be amenable to scale-up. The mechanistic study offers yet another important illustration of the self-propagating cycle in the context of a structurally novel organic promoter, as profound and complementary to Lambert's pioneering mechanistic insights into Beckmann rearrangement[28]. Ongoing research including the potential synthetic applications of dichloroimidazolidinediones in the catalytic version is underway in our laboratory.

EXPERIMENTAL SECTION

General Information. Reactions, unless otherwise stated, were carried out with magnetic stirring under argon atmosphere in oven-dried glassware. Reagents were used as received without further purification, unless otherwise noted. All reaction solvents prior to use were distilled according to standard laboratory methods. Analytical thin layer chromatograph (TLC) was performed on 0.2 mm coated silica gel plates (HSGF 254) and visualized using a UV light (254 nm or 365 nm). Flash column chromatography was performed employing silica gel (200 – 300 mesh) at increased pressure.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 & 100 MHz NMR spectrometer in $CDCl_3$ or as stated deuterated solvents. Chemical shifts δ are reported in part per million (ppm) relative to residual undeuterated solvent as an internal reference (^{1}H: δ 7.26 for $CDCl_3$, δ 2.50 for DMSO-d_6, δ 1.94 for CD_3CN; ^{13}C: δ 77.16 for $CDCl_3$, δ 39.52 for DMSO-d_6). The following abbreviations were used to explain NMR peak multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad signal. High resolution mass spectra (HRMS) were performed on Agilent Acrrurate-Mass Q-TOF LC/MS 6520 mass spectrometer with electron spray ionization (ESI) mode. Gas chromatograms were obtained using an Agilent 7890A gas chromatograph equipped with a G4513A injector and an Agilent DB-WAXETR column (30 m × 0.320 mm × 0.25 µm). Melting points were recorded in degrees Celsius (°C) using a Shanghai Precision & Scientific capillary melting point apparatus and are reported uncorrected. Infrared spectra were obtained on a Thermo Nicolet iS10 FT-IR spectrometer using KBr salt plates. Optical rotations were measured on a Rudolph Research Analytical Autopol II automatic polarimeter.

Representative Procedure for the Synthesis of 2,2-Dichloro-imidazolidine-4,5-dione 1. Example for synthesis of 1a: In a 100 mL Schlenk flask, *N,N'*-bis(2,6-diisopropylphenyl)carbodiimide (1 g, 2.76 mmol, 1.0 equiv.) was dissolved in 15 mL dry DCM. The resultant solution was cooled to 0 ^{o}C. Oxalyl chloride (0.35 mL, 0.53 g, 4.14 mmol, 1.5 equiv.) was added dropwise at 0 ^{o}C. Then the reaction was allowed to stir at room temperature for 4 h. Solvent and excess oxalyl chloride were removed under reduced pressure. The residue was washed by dry hexane (×3) and dried under reduced pressure, affording *2,2-dichloro-1,3-bis(2,6-diisopropylphenyl)imidazolidine-4,5-dione (1a)*.[36] A colorless solid; 1.28 g, 95% yield; mp 201.3−202.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (t, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 4H), 3.09 – 3.06 (m, 4H), 1.38 (d, *J* = 6.4 Hz, 12H), 1.18 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 149.2, 131.5, 125.6, 125.1, 104.9, 30.6, 26.3, 22.7.

2,2-dichloro-1,3-diisopropylimidazolidine-4,5-dione (1b).[4,11] Prepared according to the

representative procedure with the following exception: *N,N'*-diisopropylmethanediimine (1 mL, 815 mg, 6.46 mmol, 1.0 equiv.), Oxalyl chloride (0.66 mL, 984 mg, 7.75 mmol, 1.2 equiv.). A colorless solid; 1.47 g, 90% yield; mp 172.5−175.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 – 4.12 (m, 2H), 1.57 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 103.0, 49.5, 19.2.

1,3-di-tert-butyl-2,2-dichloroimidazolidine-4,5-dione (1c).[37] Prepared according to the representative procedure with the following exception: *N,N'*-di-*tert*-butylmethanediimine (800 mg, 5.19 mmol, 1.0 equiv.), Oxalyl chloride (0.50 mL, 0.53 g, 5.70 mmol, 1.1 equiv.). A colorless solid; 1.34 g, 92% yield; mp 129.1−130.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.78 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 102.0, 62.5, 28.3.

2,2-dichloro-1,3-dicyclohexylimidazolidine-4,5-dione (1d).[13] Prepared according to the representative procedure with the following exception: *N,N'*-dicyclohexylmethanediimine (2 g, 9.69 mmol, 1.0 equiv.), Oxalyl chloride (0.90 mL, 1.29 g, 10.18 mmol, 1.1 equiv.), 25 mL DCM and a reaction time of 1 h. A colorless solid; 3.07 g, 95% yield; mp 176.0−178.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (tt, *J* = 12.0, 3.6 Hz, 2H), 2.30 – 2.20 (m, 4H), 1.94 – 1.89 (m, 8H), 1.71 – 1.68 (m, 2H), 1.42 – 1.26 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 103.2, 57.0, 28.6, 25.9, 24.8.

Note：Compounds **1a** – **1d** were found to be moisture sensitive, especially **1b**. We failed to obtain spectra of pure **1b** in that it is high sensitive to moisture and inevitably partially forms 1,3-diisopropylimidazolidine-2,4,5-trione (**1'b**) upon exposure to even trace water. When **1b** was open to the ambient atmosphere for one day, it completely converted into **1'b**. Thus, it is recommended that **1a** – **1d** be stored under an inert atmosphere.

General Procedure for the Preparation of Oxime Substrates 2. In a 50 mL round-bottom flask equipped with a condenser, aromatic or aliphatic ketones (10 mmol, 1.0 equiv.) were dissolved in the mixture of EtOH/H_2O (v/v = 4:1, 25 mL). Then, hydroxylamine hydrochloride (16 mmol, 1.6 equiv.) and AcONa (20 mmol, 2.0 equiv.) was added in one portion. The reaction mixture was stirred at 80 ^{o}C until the consumption of the starting material was observed by TLC. After that, the reaction was cooled to room temperature, diluted with water (55 mL), extracted with ethyl acetate (80 mL × 3), dried with anhydrous Na_2SO_4 and concentrated. The residue was purified by recrystallization or flash column chromatograph on silica gel to afford the desired products **2a** – **2x**.

(E)-1-phenylethan-1-one oxime (2a).[28] A colorless solid after purification by flash column chromatography (petroleum ether (PE)/ethyl acetate (EA) = 30/1); 1.22 g, 90% yield; R_f = 0.42

(hexane/EtOAc, 5/1); mp 56.9–58.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.89 (brs, 1H), 7.67 – 7.65 (m, 2H), 7.42 – 7.41 (m, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 136.6, 129.4, 128.7, 126.2, 12.5.

(E)-1-(p-tolyl)ethan-1-one oxime (2b).[28] A colorless solid after purification by flash column chromatography (PE/EA = 30/1); 1.28 g, 86% yield; R_f = 0.40 (hexane/EtOAc, 5/1); mp 85.2–86.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.80 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 139.4, 133.8, 129.4, 126.1, 21.4, 12.5.

(E)-1-(2-methoxyphenyl)ethan-1-one oxime (2c).[23] A colorless crystal after recrystallization from EA/PE; 1.01 g, 61% yield; mp 85.8–86.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.00 (s, 1H), 7.36 – 7.32 (m, 1H), 7.21 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 1H), 6.95 – 6.91 (m, 1H), 3.78 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.1, 154.2, 129.9, 129.2, 127.4, 120.2, 111.5, 55.4, 15.4.

(E)-1-(3-methoxyphenyl)ethan-1-one oxime (2d).[28] A colorless oil after purification by flash column chromatography (PE/EA = 10/1); 1.55 g, 94% yield; R_f = 0.38 (hexane/EtOAc, 2/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.18 (brs, 1H), 7.24 – 7.15 (m, 3H), 6.88 – 6.86 (m, 1H), 3.72 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.2, 152.8, 138.5, 129.5, 118.1, 114.3, 110.8, 55.0, 11.6.

(E)-1-(4-methoxyphenyl)ethan-1-one oxime (2e).[30] A colorless solid after purification by flash column chromatography (PE/EA = 8/1); 1.52 g, 92% yield; R_f = 0.57 (hexane/EtOAc, 2/1); mp 86.2–87.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.00 (s, 1H), 7.60 – 7.58 (m, 2H), 6.94 – 6.92 (m, 2H), 3.76 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.7, 152.4, 129.5, 126.9, 113.8, 55.1, 11.5.

(E)-1-(4-hydroxyphenyl)ethan-1-one oxime (2f).[38,39] A colorless solid after purification by flash column chromatography (PE/EA = 10/1); 1.28 g, 85% yield; R_f = 0.45 (hexane/EtOAc, 5/1); mp 146.2–147.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.86 (s, 1H), 9.62 (s, 1H), 7.49 – 7.46 (m, 2H), 6.77 – 6.75(m, 2H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.0, 152.6, 127.9, 126.9, 115.1, 11.5.

(E)-1-(4-fluorophenyl)ethan-1-one oxime (2g).[30] A colorless solid after purification by flash column chromatography (5% EA/PE to 10% EA/PE); 1.41 g, 92% yield; R_f = 0.50 (hexane/EtOAc, 5/1); mp 75.6–76.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (brs, 1H), 7.63 – 7.59 (m, 2H), 7.10 – 7.05 (m, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6 (d, $^1J_{CF}$ = 247.6 Hz), 155.3, 132.7 (d, $^4J_{CF}$ = 3.3 Hz), 128.0 (d, $^3J_{CF}$ = 8.2 Hz), 115.6 (d, $^2J_{CF}$ = 21.6 Hz), 12.6.

(E)-1-(4-chlorophenyl)ethan-1-one oxime (2h).[38,40] A colorless solid after purification by flash

column chromatography (5% EA/PE to 10% EA/PE); 1.58 g, 93% yield; R_f = 0.48 (hexane/EtOAc, 5/1); mp 97.2−98.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.33 (s, 1H), 7.67 – 7.65 (m, 2H), 7.44 – 7.42 (m, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.0, 135.8, 133.3, 128.4, 127.3, 11.4.

(E)-1-(4-bromophenyl)ethan-1-one oxime (2i).[28] A colorless solid after purification by flash column chromatography (PE/EA = 10/1); 1.99 g, 93% yield; R_f = 0.51 (hexane/EtOAc, 5/1); mp 128.0−129.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (brs, 1H), 7.53 – 7.48 (m, 4H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 135.4, 131.8, 127.7, 123.7, 12.3.

(E)-1-(naphthalen-2-yl)ethan-1-one oxime (2j).[41] A colorless solid after purification by flash column chromatography (PE/EA = 10/1); 1.67 g, 90% yield; R_f = 0.52 (hexane/EtOAc, 3/1); mp 143.4−144.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (brs, 1H), 8.05 (s, 1H), 7.89 – 7.85 (m, 4H), 7.54 – 7.52 (m, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 133.9, 133.8, 133.2, 128.6, 128.4, 127.8, 126.8, 126.6, 126.1, 123.4, 12.3.

tert-butyl (E)-3-(1-(hydroxyimino)ethyl)-1H-indole-1-carboxylate (2k). A colorless solid after purification by flash column chromatography (5% EA/PE to 10% EA/PE); 1.48 g, 54% yield; R_f = 0.41 (hexane/EtOAc, 6/1); mp 121.5−123.2 °C; IR (KBr) ν_{max} 3275, 3004, 2984, 1739, 1560, 1453, 1370, 1281, 1243, 1151, 1062 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.09 (s, 1H), 8.24 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.91 (s, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.28 (t, J = 7.6 Hz, 1H), 2.20 (s, 3H), 1.65 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.0, 148.9, 135.3, 127.1, 125.6, 124.9, 123.4, 123.2, 118.3, 114.6, 84.3, 27.7, 12.0; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}N_2O_3H$ 275.1390; Found 275.1381.

(E)-1-(3-((tert-butyldimethylsilyl)oxy)phenyl)ethan-1-one oxime (2l). A viscous light yellow liquid after purification by flash column chromatography (PE/EA = 15/1); 2.26 g, 85% yield; R_f = 0.45 (hexane/EtOAc, 10/1); IR (KBr) ν_{max} 3251, 2930, 2858, 1598, 1579, 1391, 1365, 1313, 1228, 1164, 1094, 1005, 910, 783, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (brs, 1H), 7.18 – 7.14 (m, 2H), 7.03 – 7.02 (m, 1H), 6.80 – 6.77 (m, 1H), 2.20 (s, 3H), 0.92 (s, 9H), 0.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.91, 155.90, 138.0, 129.6, 121.2, 119.3, 117.8, 25.8, 18.4, 12.5, −4.3; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{23}NO_2SiH$ 266.1571; Found 266.1578.

diphenylmethanone oxime (2m).[30] A colorless solid after purification by flash column chromatography (PE/EA = 10/1); 1.85 g, 94% yield; R_f = 0.59 (hexane/EtOAc, 5/1); mp 140.4−141.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.37 (s, 1H), 7.46 – 7.34 (m, 8H), 7.30 – 7.28 (m,

2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.2, 136.8, 133.6, 128.92, 128.86, 128.40, 128.36, 128.2, 127.0.

bis(4-methoxyphenyl)methanone oxime (2n).[30] A colorless crystal after recrystallization from EA/PE; 2.08 g, 81% yield; mp 54.9−56.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.51 (brs, 1H), 7.42 (dd, *J* = 8.8, 6.8 Hz, 4H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 160.1, 157.2, 131.2, 129.6, 129.3, 125.1, 113.8, 113.6, 55.42, 55.39.

cyclopropyl(phenyl)methanone oxime (2o).[28] A colorless solid after recrystallization from EA/PE as a mixture of (*E*) and (*Z*)-isomers; 1.32 g, 82% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.01 (s, 0.76H), 10.52 (s, 0.19H), 7.44 – 7.33 (m, 5H), 2.19 – 2.14 (m, 0.79H), 1.74 – 1.67(m, 0.20H), 0.89 – 0.84 (m, 1.64H), 0.75 – 0.72 (m, 0.42H), 0.69 – 0.67 (m, 0.41H), 0.52 – 0.45 (m, 1.58H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.4, 155.7, 135.1, 134.4, 128.2, 128.0, 127.93, 127.88, 15.2, 8.8, 5.5, 5.2; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{11}NOH$ 162.0913; Found 162.0928.

(E)-1-phenylpropan-1-one oxime (2p).[41] A colorless solid after purification by flash column chromatography (PE/EA = 5/1); 1.37 g, 92% yield; R_f = 0.50 (hexane/EtOAc, 6/1); mp 50.3−51.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 7.64 – 7.62 (m, 2H), 7.43 – 7.40 (m, 3H), 2.84 (q, *J* = 7.6 Hz, 2H), 1.19 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 135.6, 129.3, 128.7, 126.4, 19.9, 11.0.

1,3-diphenylpropan-2-one oxime (2q).[28] A colorless solid after purification by flash column chromatography (PE/EA = 15/1); 2.03 g, 90% yield; R_f = 0.55 (hexane/EtOAc, 3/1); mp 121.4−122.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (brs, 1H), 7.25 – 7.09 (m, 10H), 3.58 (s, 2H), 3.37 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 136.7, 136.5, 129.4, 129.3, 128.7, 126.9, 126.6, 39.7, 32.7; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{15}NONa$ 248.1046; Found 248.1056.

methyl (E)-4-(hydroxyimino)-4-phenylbutanoate (2r).[23] A colorless oil after purification by flash column chromatography (PE/EA = 15/1 – 6/1); 1.20 g, 58% yield; R_f = 0.52 (hexane/EtOAc, 2/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (brs, 1H), 7.62 – 7.59 (m, 2H), 7.40 – 7.38 (m, 3H), 3.66 (s, 3H), 3.15 – 3.11 (m, 2H), 2.67 – 2.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 158.0, 135.1, 129.6, 128.8, 126.4, 51.9, 30.5, 22.2; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{13}NO_3Na$ 230.0788; Found 230.0785.

cyclohexanone oxime (2s).[28] An off-white solid after purification by flash column chromatography (PE/EA = 20/1); 0.84 g, 74% yield; R_f = 0.54 (hexane/EtOAc, 5/1); mp 89.1−90.5 °C;

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.43 (brs, 1H), 2.51 (t, *J* = 5.7 Hz, 2H), 2.22 (t, *J* = 5.7 Hz, 2H), 1.69 – 1.61 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.8, 32.2, 27.0, 25.9, 25.7, 24.6.

nonan-2-one oxime (2t).[42] A clear colorless oil after purification by flash column chromatography (PE/EA = 5/1) as a 2.7:1 mixture of (*E*) and (*Z*)-isomers; 1.46 g, 93% yield; R_f = 0.50 (hexane/EtOAc, 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (brs, 1H), 2.36 (t, *J* = 7.6 Hz, 0.53H), 2.17 (t, *J* = 7.6 Hz, 1.49H), 1.87 (s, 2.14H), 1.85 (s, 0.78H), 1.51 – 1.47 (m, 2H), 1.31 – 1.27 (m, 8H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (C), 158.8 (C), 35.9 (CH_2), 31.9 (CH_2), 29.8 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.2 (CH_2), 28.8 (CH_2), 26.4 (CH_2), 25.6 (CH_2), 22.8 (CH_2), 20.0 (CH_3), 14.2 (CH_3), 13.5 (CH_3); HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_9H_{19}NONa$ 180.1359; Found 180.1348.

cyclododecanone oxime (2u).[28] A colorless solid after purification by flash column chromatography (PE/EA = 20/1); 1.76 g, 89% yield; R_f = 0.55 (hexane/EtOAc, 6/1); mp 131.9−132.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (brs, 1H), 2.42 (t, *J* = 6.8 Hz, 2H), 2.27 (t, *J* = 6.4 Hz, 2H), 1.66 – 1.57 (m, 4H), 1.38 – 1.32 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 30.4, 26.3, 25.6, 25.2, 24.9, 24.1, 23.6, 23.4, 23.32, 23.28, 22.8.

(4-hydroxyphenyl)(phenyl)methanone oxime (2v). A colorless solid after purification by flash column chromatography (10% EA/PE to 50% EA/PE) as a 1.5:1 mixture of (*E*) and (*Z*)-isomers; 1.83 g, 86% yield; R_f = 0.52 (hexane/EtOAc, 2/1); IR (KBr) ν_{max} 3412, 3201, 3052, 2922, 1608, 1514, 1326, 1271, 1195, 1160, 995, 914, 838 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.21 (brs, 0.39H), 10.98 (brs, 0.57H), 9.88 (brs, 1H), 7.43 – 7.35 (m, 4H), 7.24 – 7.13 (m, 3H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.3, 157.6, 155.1, 155.0, 137.6, 134.0, 130.9, 128.9, 128.7, 128.4, 128.24, 128.17, 128.1, 127.6, 127.4, 123.7, 115.2, 114.8; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{11}NO_2Na$ 236.0682; Found 236.0681.

*3*β*-Acetoxypregn-5-en-20-one Oxime (2x)*.[28] A colorless solid after purification by flash column chromatography (PE/EA = 10/1); 3.18 g, 85% yield; R_f = 0.48 (hexane/EtOAc, 5/1); mp 183.2−185.5 °C; $[\alpha]_D^{20}$ = −45 (*c* 0.2, C_2H_5OH); IR (KBr) ν_{max} 3271, 2937, 2854, 1731, 1654, 1440, 1368, 1250, 1040, 900 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (brs, 1H), 5.40 (d, *J* = 4.8 Hz, 1H), 4.67 – 4.59 (m, 1H), 2.36 – 2.34 (m, 2H), 2.28 – 2.24 (m, 1H), 2.16 – 2.11 (m, 1H), 2.06 (s, 3H), 1.95 – 1.88 (m, 6H), 1.75 – 1.20 (m, 12H), 1.05 (s, 3H), 1.03 – 1.00 (m, 1H), 0.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 158.8, 139.8, 122.5, 74.0, 56.9, 56.2, 50.2, 43.9, 38.7, 38.2, 37.1, 36.7, 32.1, 31.8, 27.8, 24.3, 23.2, 21.6, 21.1, 19.4, 15.3, 13.2; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{35}NO_3Na$ 396.2509;

Found 396.2530.

Synthesis of *N*-Phenylbenzimidoyl chloride. Prepared according to the procedure reported in the literature.[43] A mixture of $SOCl_2$ (1.4 mL) and *N*-phenyl benzamide (220 mg, 1.12 mmol) was heated to 65 °C for 2 h. After cooling to room temperature, the reaction mixture was concentrated under reduced pressure. The residue was then stirred in n-hexane (2.0 mL) at 50 °C for 1 h, filtered, and concentrated to afford the title compound as an off-white solid (241.6 mg, 90% yield). Mp 38.9−40.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.17 (m, 2H), 7.58 – 7.40 (m, 5H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.04 – 7.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 143.4, 135.6, 132.2, 129.6, 129.0, 128.6, 125.2, 120.5.

General Procedure for the Synthesis of Amides/Lactams 3. In a 10 mL dry Schlenk tube, DCID **1d** (33.33 mg, 0.1 mmol, 0.1 equiv.), the oxime substrates **2a** – **2x** (1 mmol, 1.0 equiv.) and dry MeCN (5.0 mL) were sequentially added under argon atmosphere. Then the reaction was heated to 80 ^{o}C and stirred until the completion of the reaction as indicated by TLC. The organic solvent was removed *in vacuum*, and the crude material was purified by silica gel column to afford the desired products **3a** – **3x**.

N-phenylacetamide (3a).[44] Prepared from the oxime **2a** (135 mg, 1 mmol) following the general procedure. Reaction time: 20 min. Purification by flash column chromatography (PE/EA = 5/1 – 1/1) furnished **3a** (132.3 mg, 98% yield) as a colorless solid. R_f = 0.38 (hexane/EtOAc, 1/1); mp 113.2−114.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (brs, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 2H), 6.99 (t, *J* = 7.2 Hz, 1H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 138.1, 128.9, 124.3, 120.3, 24.4.

N-(p-tolyl)acetamide (3b).[44] Prepared from the oxime **2b** (149.2 mg, 1 mmol) following the general procedure. Reaction time: 15 min. Purification by flash column chromatography (PE/EA = 8/1 – 2/1) furnished **3b** (143.2 mg, 96% yield) as a colorless solid. R_f = 0.35 (hexane/EtOAc, 1/1); mp 150.5−152.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (brs, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 2.30 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 135.5, 134.0, 129.5, 120.3, 24.5, 21.0.

N-(2-methoxyphenyl)acetamide (3c).[23] Prepared from the oxime **2c** (165.2 mg, 1 mmol) following the general procedure. Reaction time: 15 min. Purification by flash column chromatography (PE/EA = 10/1 – 2/1) furnished **3c** (155.3 mg, 94% yield) as a colorless solid. R_f =

0.47 (hexane/EtOAc, 1/1); mp 86.6−88.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.0 Hz, 1H), 7.76 (brs, 1H), 7.04 (t, *J* = 8.0 Hz, 1H), 6.96 (t, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 3.88 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 147.7, 127.8, 123.7, 121.1, 119.8, 109.9, 55.7, 25.0.

N-(3-methoxyphenyl)acetamide (3d).[28] Prepared from the oxime **2d** (165.2 mg, 1 mmol) following the general procedure. Reaction time: 10 min. Purification by flash column chromatography (PE/EA = 8/1 – 1/1) furnished **3d** (153.6 mg, 93% yield) as a yellow solid. R_f = 0.38 (hexane/EtOAc, 1/1); mp 102.5−103.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.90 (brs, 1H), 7.27 (t, *J* = 2.0 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.60 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.71 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.4, 159.5, 140.5, 129.5, 111.3, 108.3, 104.9, 54.9, 24.1.

N-(4-methoxyphenyl)acetamide (3e).[44] Prepared from the oxime **2e** (165.2 mg, 1 mmol) following the general procedure. Reaction time: 10 min. Purification by flash column chromatography (PE/EA = 10/1 – 1/1) furnished **3e** (161.9 mg, 98% yield) as a colorless solid. R_f = 0.30 (hexane/EtOAc, 1/1); mp 129.7−131.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (brs, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 3.76 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 156.4, 131.2, 122.2, 114.1, 55.5, 24.2.

N-(4-hydroxyphenyl)acetamide (3f).[44] Prepared from the oxime **2f** (151.2 mg, 1 mmol) following the general procedure. Reaction time: 20 min. Purification by flash column chromatography (PE/EA = 10/1 – 1/1) furnished **3f** (143.6 mg, 95% yield) as a colorless solid. R_f = 0.44 (hexane/EtOAc, 1/4); mp 170.2−170.6 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.65 (brs, 1H), 9.14 (s, 1H), 7.34 (d, *J* = 9.2 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.6, 153.2, 131.1, 120.9, 115.1, 23.8.

N-(4-fluorophenyl)acetamide (3g).[44] Prepared from the oxime **2g** (153.2 mg, 1 mmol) following the general procedure. Reaction time: 10 min. Purification by flash column chromatography (PE/EA = 8/1 – 1/1) furnished **3g** (148.6 mg, 97% yield) as a light yellow solid. R_f = 0.42 (hexane/EtOAc, 1/1.5); mp 154.0−154.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.98 (brs, 1H), 7.59 (dd, *J* = 9.2, 5.2 Hz, 2H), 7.12 (t, *J* = 8.8 Hz, 2H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.2, 157.8 (d, $^{1}J_{CF}$ = 237.9 Hz), 135.8 (d, $^{4}J_{CF}$ = 2.0 Hz), 120.7 (d, $^{3}J_{CF}$ = 8.0 Hz), 115.2 (d, $^{2}J_{CF}$ = 22.0 Hz), 23.9.

N-(4-chlorophenyl)acetamide (3h).[44] Prepared from the oxime **2h** (169.6 mg, 1 mmol) following the general procedure. Reaction time: 10 min. Purification by flash column chromatography (PE/EA

= 8/1 – 1/1) furnished **3h** (156.0 mg, 92% yield) as a light yellow solid. R_f = 0.49 (hexane/EtOAc, 1/1.5); mp 177.4−179.1 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.06 (s, 1H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.4, 138.3, 128.6, 126.5, 120.5, 24.0.

N-(4-bromophenyl)acetamide (3i).[44] Prepared from the oxime **2i** (214.1 mg, 1 mmol) following the general procedure. Reaction time: 10 min. Purification by flash column chromatography (PE/EA = 10/1 – 1/1) furnished **3i** (205.5 mg, 96% yield) as a light yellow solid. R_f = 0.46 (hexane/EtOAc, 1/1.5); mp 166.2−167.6 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.06 (brs, 1H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.5, 138.7, 131.5, 120.9, 114.5, 24.0.

N-(naphthalen-2-yl)acetamide (3j).[27] Prepared from the oxime **2j** (185.2 mg, 1 mmol) following the general procedure. Reaction time: 20 min. Purification by flash column chromatography (PE/EA = 10/1 – 2/1) furnished **3j** (168.5 mg, 91% yield) as a colorless solid. R_f = 0.37 (hexane/EtOAc, 1/1); mp 132.6−133.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.97 (brs, 1H), 7.77 – 7.72 (m, 3H), 7.48 – 7.39 (m, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 135.5, 133.9, 130.7, 128.8, 127.7, 127.6, 126.6, 125.1, 120.1, 116.9, 24.7.

tert-butyl 3-acetamido-1H-indole-1-carboxylate (3k). Prepared from the oxime **2k** (274.3 mg, 1 mmol) following the general procedure. Reaction time: 20 min. Purification by flash column chromatography (PE/EA = 10/1 – 1/1) furnished **3k** (197.5 mg, 72% yield) as a light yellow solid. R_f = 0.46 (hexane/EtOAc, 1/1); mp 164.0−165.7 °C; IR (KBr) ν_{max} 3269, 3078, 2979, 1724, 1658, 1581, 1556, 1454, 1377, 1284, 1160, 1097, 864, 748, 536 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.11 (brs, 1H), 8.07 – 8.06 (m, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 2.15 (s, 3H), 1.62 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.0, 149.2, 132.5, 125.0, 124.0, 122.3, 119.7, 118.6, 114.7, 113.3, 83.4, 27.7, 23.1; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{18}N_2O_3Na$ 297.1210; Found 297.1210.

N-(3-((tert-butyldimethylsilyl)oxy)phenyl)acetamide (3l). Prepared from the oxime **2l** (265.4 mg, 1 mmol) following the general procedure. Reaction time: 40 min. Purification by flash column chromatography (PE/EA = 10/1 – 1/1) furnished **3l** (220.3 mg, 83% yield) as a colorless solid. R_f = 0.58 (hexane/EtOAc, 1/1); mp 49.0−50.6 °C; IR (KBr) ν_{max} 3283, 3208, 3086, 1668, 1589, 1563, 1471, 1396, 1282, 858, 816, 747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (brs, 1H), 7.17 – 7.12 (m, 2H), 7.00

(d, *J* = 8.0 Hz, 1H), 6.60 – 6.56 (m, 1H), 2.16 (s, 3H), 0.97 (s, 9H), 0.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 156.3, 139.1, 129.7, 116.1, 112.8, 111.9, 25.8, 24.8, 18.3, −4.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{23}NO_2SiNa$ 288.1390; Found 288.1388.

N-phenylbenzamide (3m).[44] Prepared from the oxime **2m** (197.2 mg, 1 mmol) following the general procedure. Reaction time: 20 min. Purification by flash column chromatography (PE/EA = 5/1) furnished **3m** (189.3 mg, 96% yield) as a colorless solid. R_f = 0.52 (hexane/EtOAc, 3/1); mp 161.2−163.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (brs, 1H), 7.87 – 7.85 (m, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.56 – 7.52 (m, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 138.1, 135.1, 132.0, 129.2, 128.9, 127.2, 124.7, 120.4.

4-methoxy-N-(4-methoxyphenyl)benzamide (3n).[28] Prepared from the oxime **2n** (257.3 mg, 1 mmol) following the general procedure. Reaction time: 10 min. Purification by flash column chromatography (PE/EA = 5/1) furnished **3n** (241.9 mg, 94% yield) as a colorless solid. R_f = 0.59 (hexane/EtOAc, 1/1); mp 201.3−202.8 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.98 (brs, 1H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 9.2 Hz, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 164.5, 161.8, 155.4, 132.4, 129.5, 127.1, 122.0, 113.7, 113.6, 55.4, 55.2.

N-phenylcyclopropanecarboxamide (3o).[28] Prepared from the oxime **2o** (161.2 mg, 1 mmol) following the general procedure. Reaction time: 10 min. Purification by flash column chromatography (PE/EA = 10/1 – 5/1) furnished **3o** (143.5 mg, 89% yield) as a colorless solid. R_f = 0.38 (hexane/EtOAc, 3/1); mp 107.8−109.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.17 (brs, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.9 Hz, 2H), 7.01 (t, *J* = 7.2 Hz, 1H), 1.79 – 1.74 (m, 1H), 0.80 – 0.77 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.0, 139.8, 129.1, 123.3, 119.4, 15.0, 7.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{10}H_{11}NONa$ 184.0733; Found 184.0729.

N-phenylpropionamide (3p).[27] Prepared from the oxime **2p** (149.2 mg, 1 mmol) following the general procedure. Reaction time: 15 min. Purification by flash column chromatography (PE/EA = 10/1 – 3/1) furnished **3p** (144.7 mg, 97% yield) as a yellow solid. R_f = 0.60 (hexane/EtOAc, 1/1); mp 102.8−104.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (brs, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 7.2 Hz, 1H), 2.38 (q, *J* = 7.2 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 138.2, 129.0, 124.2, 120.0, 30.8, 9.8.

N-benzyl-2-phenylacetamide (3q).[28,45] Prepared from the oxime **2q** (225.3 mg, 1 mmol)

following the general procedure. Reaction time: 20 min. Purification by flash column chromatography (PE/EA = 10/1 – 3/1) furnished **3q** (209.5 mg, 93% yield) as a colorless solid. R_f = 0.53 (hexane/EtOAc, 1/1); mp 121.5−122.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.15 (m, 8H), 7.09 – 7.08 (m, 2H), 5.82 (brs, 1H), 4.30 (d, *J* = 6.0 Hz, 2H), 3.51 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 138.2, 134.9, 129.5, 129.1, 128.7, 127.6, 127.5, 127.4, 43.8, 43.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{15}NONa$ 248.1046; Found 248.1047.

methyl 4-oxo-4-(phenylamino)butanoate (3r).[23] Prepared from the oxime **2r** (207.2 mg, 1 mmol) following the general procedure. Reaction time: 15 min. Purification by flash column chromatography (PE/EA = 10/1 – 1/1) furnished **3r** (198.9 mg, 96% yield) as a colorless solid. R_f = 0.48 (hexane/EtOAc, 1/1); mp 94.5−95.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (brs, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 3.71 (s, 3H), 2.76 (t, *J* = 6.4 Hz, 2H), 2.67 (t, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 169.9, 138.0, 129.0, 124.3, 119.9, 52.1, 32.0, 29.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{11}H_{13}NO_3Na$ 230.0788; Found 230.0787.

ε-caprolactam (3s).[44] Prepared from the oxime **2s** (113.2 mg, 1 mmol) following the general procedure with the following exception: the reaction performed using 1.0 equiv. of **1d** at room temperature. Reaction time: 3 h. Purification by flash column chromatography (PE/EA = 10/1 – 1/1) furnished **3s** (90.56 mg, 80% yield) as an off-white solid. R_f = 0.30 (hexane/EtOAc, 3/1); mp 68.1−69.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (brs, 1H), 3.23 – 3.19 (m, 2H), 2.47 – 2.45 (m, 2H), 1.79 – 1.62(m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 42.7, 36.8, 30.6, 29.7, 23.2.

N-heptylacetamide (3t).[46] Prepared from the oxime **2t** (157.3 mg, 1 mmol) following the general procedure. Reaction time: 5 h. Purification by flash column chromatography (PE/EA = 3/1 – 2/3) furnished **3t** (136.9 mg, 87% yield) as a yellow oil. R_f = 0.41 (hexane/EtOAc, 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (brs, 1H), 3.16 (q, *J* = 7.2 Hz, 2H), 1.92 (s, 3H), 1.46 – 1.42 (m, 2H), 1.27 – 1.22 (m, 8H), 0.82 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 39.7, 31.8, 29.6, 29.0, 26.9, 23.3, 22.6, 14.1; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_9H_{19}NONa$ 180.1359; Found 180.1348.

ω-Laurolactam (3u).[28] Prepared from the oxime **2u** (197.3 mg, 1 mmol) following the general procedure. Reaction time: 10 min. Purification by flash column chromatography (PE/EA = 8/1 – 1/1) furnished **3u** (193.4 mg, 98% yield) as a colorless solid. R_f = 0.43 (hexane/EtOAc, 1/2); mp 150.7−153.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (brs, 1H), 3.27 (q, *J* = 5.6 Hz, 2H), 2.19 – 2.16 (m, 2H), 1.67 – 1.64 (m, 2H), 1.50 – 1.46 (m, 2H), 1.37 – 1.28 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

173.6, 39.1, 37.0, 28.4, 26.8, 26.4, 26.3, 25.8, 25.4, 25.0, 24.7, 24.0.

N-(4-hydroxyphenyl)benzamide and 4-hydroxy-N-phenylbenzamide (3v and 3w).[47,48] Prepared from the oxime **2v** (213.2 mg, 1 mmol) following the general procedure. Reaction time: 15 min. Purification by flash column chromatography (PE/EA = 10/1 – 2/1) furnished a 1.5:1 isomeric mixture of **3v** and **3w** (194.0 mg, 91% overall yield) as a yellow solid. R_f = 0.41 (hexane/EtOAc, 1/1); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.11 (brs, 1H), 10.03 (s, 1H), 9.99 (s, 1H), 9.27 (brs, 1H), 7.92 (d, *J* = 7.2 Hz, 2H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 7.6 Hz, 2H), 7.56 – 7.49 (m, 5H), 7.32 (t, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.2, 165.0, 160.6, 153.8, 139.5, 135.2, 131.3, 130.8, 129.8, 128.6, 128.4, 127.6, 125.5, 123.3, 122.4, 120.3, 115.04, 114.97; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{11}NO_2Na$ 236.0682; Found 236.0682.

*3*β*-acetoxy-5-androstene-17*β*-acetamide (3x)*.[28,49] Prepared from the oxime **2x** (373.5 mg, 1 mmol) following the general procedure. Reaction time: 1 h. Purification by flash column chromatography (PE/EA = 4/1 – 3/2) furnished **3x** (336.2 mg, 90% yield) as a colorless solid. R_f = 0.38 (hexane/EtOAc, 1/3); mp 188.6−191.5 °C; $[\alpha]_D^{20}$ = −116 (*c* 1.0, C_2H_5OH); IR (KBr) ν_{max} 2937, 2902, 1733, 1652, 1370, 1254, 1038 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (m, 1H), 5.30 (d, *J* = 9.2 Hz, 1H), 4.62 – 4.55 (m, 1H), 3.88 (q, *J* = 9.2 Hz, 1H), 2.36 – 2.32 (m, 2H), 2.15 – 2.08 (m, 1H), 2.02 (s, 3H), 1.98 (s, 3H), 1.85 (d, *J* = 10.0 Hz, 2H), 1.72 – 1.10 (m, 13H), 1.01 (s, 3H), 0.99 – 0.95 (m, 1H), 0.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 170.0, 139.8, 122.4, 74.0, 58.9, 52.8, 50.1, 42.8, 38.2, 37.0, 36.8, 36.7, 32.1, 31.6, 28.7, 27.8, 23.74, 23.68, 21.5, 20.6, 19.4, 12.0; HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{35}NO_3Na$ 396.2509; Found 396.2507.

ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for all synthesized compounds and details of mechanistic study. The Supporting Information is available free of charge on the ACS Publications website at DOI:

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Notes

The authors declare no competing finacial interest.

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