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Oxidative N-heterocyclic carbene (NHC) catalysis for the rapid access to functionalized pyrrolo-oxazinones

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ABSTRACT

The N-heterocyclic carbene (NHC)-catalyzed intramolecular cyclization of *N*-substituted pyrrole 2-carboxaldehydes under oxidative conditions allowing the facile synthesis of pyrrolo-oxazinone derivatives is reported. The keys to the success of this strategy are the generation of acylazoliums using NHC and the base-mediated formation of the enolate. Subsequent intramolecular acylation of the enolate with the acylazoliums afforded the desired product. Mild reaction conditions, good functional group compatibility and high yields of products are the advantages of the present annulation.

1. Introduction

Functionalized pyrroles are endowed with remarkable biological properties as this heterocyclic scaffold is frequently found in a variety of natural products and drugs [1]. Among the various pyrrole natural products, pyrrolo-oxazinones are important as this core is found in marine natural products including Lukianol A and B having cytotoxic and antitumor activity (Fig. 1) [2]. Moreover, peramine is a naturally occurring pyrrolo-pyrazine alkaloid found application as insect feeding deterrent [3]. The intramolecular cyclization of the *N*-alkyne-functionalized pyrrole derivative has been a convenient method for the direct access to pyrrolo-oxazinones [4]. Herein, we demonstrate the potential of N-heterocyclic carbene (NHC) organocatalysis for the one-step synthesis of pyrrolo-oxazinones from *N*-substituted pyrrole 2-carboxaldehydes under oxidative conditions [5].

In the last three decades, NHC catalysis has been widely applied for the synthesis of various heterocycles [6]. In addition to the traditional reactivity of polarity reversal using NHCs, these catalytically active species are also useful for the non-umpolung transformations [7]. The generation of acylazolium intermediates is one of the important modes in this domain and this intermediate can be generated by the stoichiometric oxidation of the initially formed Breslow intermediate [8]. In 2010, Studer and co-workers reported an elegant NHC-catalyzed chemoselective acylation of alcohols leading to the formation of esters using the bisquinone oxidant (Scheme 1, eq 1) [9,10]. Since then, this oxidative strategy has been conveniently employed for the generation of activated carboxylates from aldehydes [11,12]. Recently, Lang and Wang utilized the oxidative NHC catalysis for the efficient synthesis of benzoxazinones from *N*-(2-formylphenyl)benzamide derivatives (eq 2) [13]. The reaction proceeded via a tandem isomerization-cyclization strategy. Inspired by this work, and given the significance of pyrrolo-oxazinones [2,3], we envisioned the NHC-catalyzed intramolecular cyclization of *N*-substituted pyrrole 2-carboxaldehydes leading to the synthesis of pyrrolo-oxazinones, where the reaction proceeds via the acylazolium intermediate (eq 3).

2. Results and discussion

The present study was initiated by the treatment of pyrrole-2-carbaldehyde **1a** with the carbene engendered from the *N*-mesityl triazolium salt **A** using Cs_2CO_3, and oxidative conditions using the bisquinone **3** in THF. Interestingly, under these conditions, the desired pyrrolo-oxazinone derivative **2a** was formed in 67% yield (based on ^{1}H NMR yield, Table 1, entry 1). Screening various NHC pre-catalysts revealed that the carbene generated from the

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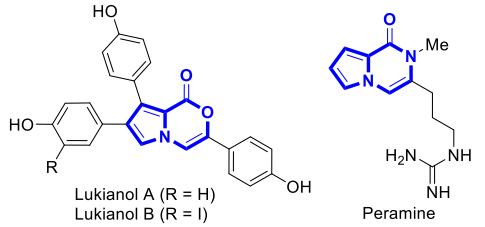
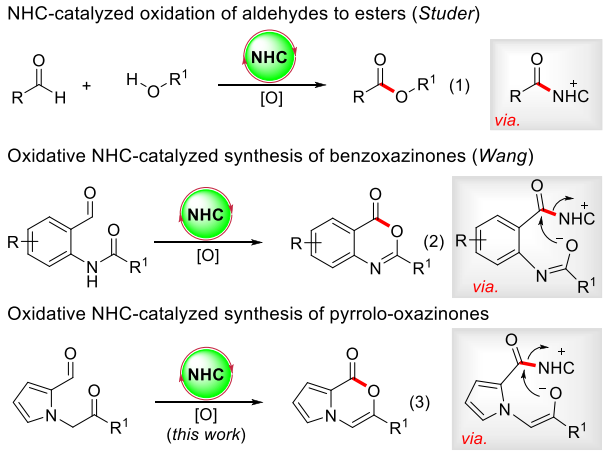
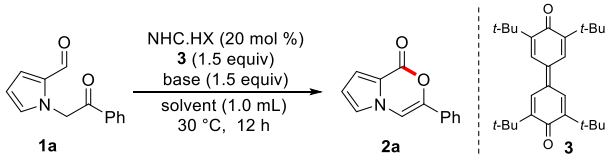


Fig. 1. Naturally occurring pyrrolo-oxazinones and an analogue.

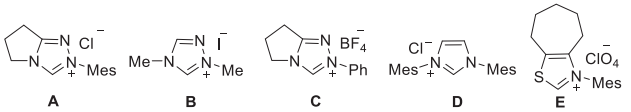


Scheme 1. NHC catalysis under oxidative conditions.

Table 1
Optimization studies[a].



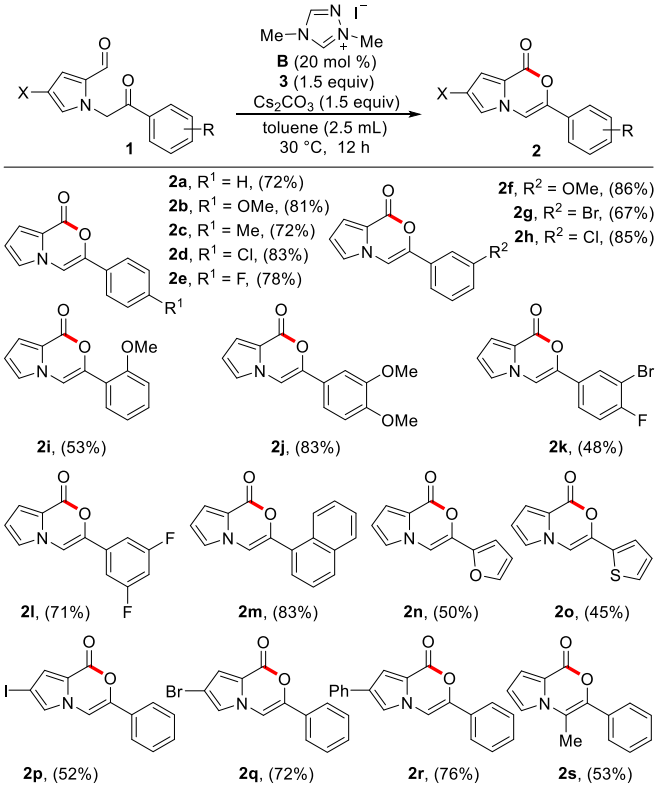
entry[a]	NHC.HX	base	solvent	yield of **2a** (%)[b]
1	**A**	Cs_2CO_3	THF	67
2	**B**	Cs_2CO_3	THF	70
3	**C**	Cs_2CO_3	THF	13
4	**D**	Cs_2CO_3	THF	32
5	**E**	Cs_2CO_3	THF	<5
6	**B**	Cs_2CO_3	$CHCl_3$	69
7	**B**	Cs_2CO_3	CH_3CN	39
8	***B***	*Cs_2CO_3*	*toluene*	*73 (72)*
9	**B**	Cs_2CO_3	DME	59
10	**B**	DBU	toluene	34
11	**B**	K_2CO_3	toluene	11
12	**B**	Na_2CO_3	toluene	<5
13[c]	**B**	Cs_2CO_3	toluene	57
14	-	Cs_2CO_3	toluene	<5



[a] Standard conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), **3** (0.15 mmol) base (0.15 mmol), NHC.HX (20 mol %), solvent (1.0 mL), 30 °C, 12 h.
[b] The yields were determined by ^{1}H NMR analysis of crude product using CH_2Br_2 as the internal standard. Isolated yield is provided in parenthesis.
[c] Reaction carried out using 10 mol % of **B**.

triazolium salt **B** afforded **2a** in an enhanced yield of 70% (entry 2) whereas other NHC pre-catalysts provided reduced yield of **2a** (entries 3–5). Further experiments were performed using NHC derived from **B**. The reactions performed in various solvents indicated that toluene is the so far best solvent furnishing **2a** in 72% yield, and the reactions performed in other solvents such as $CHCl_3$, DME and CH_3CN returned moderate yield of **2a** (entries 6–9). Cs_2CO_3 was found to be the optimal base for this reaction, and the other bases such as DBU, Na_2CO_3 and K_2CO_3 are less effective (entries 10–12). Notably, reducing the catalyst loading of **B** to 10 mol % reduced the formation of **2a** to 57% (entry 13). Control experiments indicated that there is no product formation in the absence of the NHC pre-catalyst **B** (entry 14). So far the best condition for this transformation is use of NHC pre-catalyst **B** (20 mol %) in the presence of Cs_2CO_3 (1.5 equiv), and bisquinone **3** (1.5 equiv) in toluene (1.0 mL) at 30 °C for 12 h (entry 8).

Having established the adequate reaction conditions, the scope and limitations of this intramolecular cyclization has been evaluated (see Scheme 2). The unsubstituted benzoyl methyl substituted pyrrole substrate worked well and various electronically dissimilar substituents at the 4-position of the benzoyl ring worked well and the corresponding substituted pyrrolo-oxazinones were formed in good yields (**2a-2e**). Moreover, substitution at the 3-position as well as 2-position of the arene did not affect the outcome of the reaction and the desired annulated products are formed in moderate to good yields (**2f-2i**). In addition, versatile pyrrolo-oxazinones bearing the disubstituted aryl moiety at the 3-position was smoothly synthesized starting from the corresponding pyrrole aldehydes (**2j-2m**). Interestingly, 3-heteroaryl pyrrolo-



[a] General conditions: **1** (0.25 mmol), **B** (20 mol %), **3** (1.5 equiv), Cs_2CO_3 (1.5 equiv), toluene (2.5 mL), 30 °C and 12 h. Yields of the chromatographically purified products are provided.

Scheme 2. Substrate Scope of the Reaction[a].

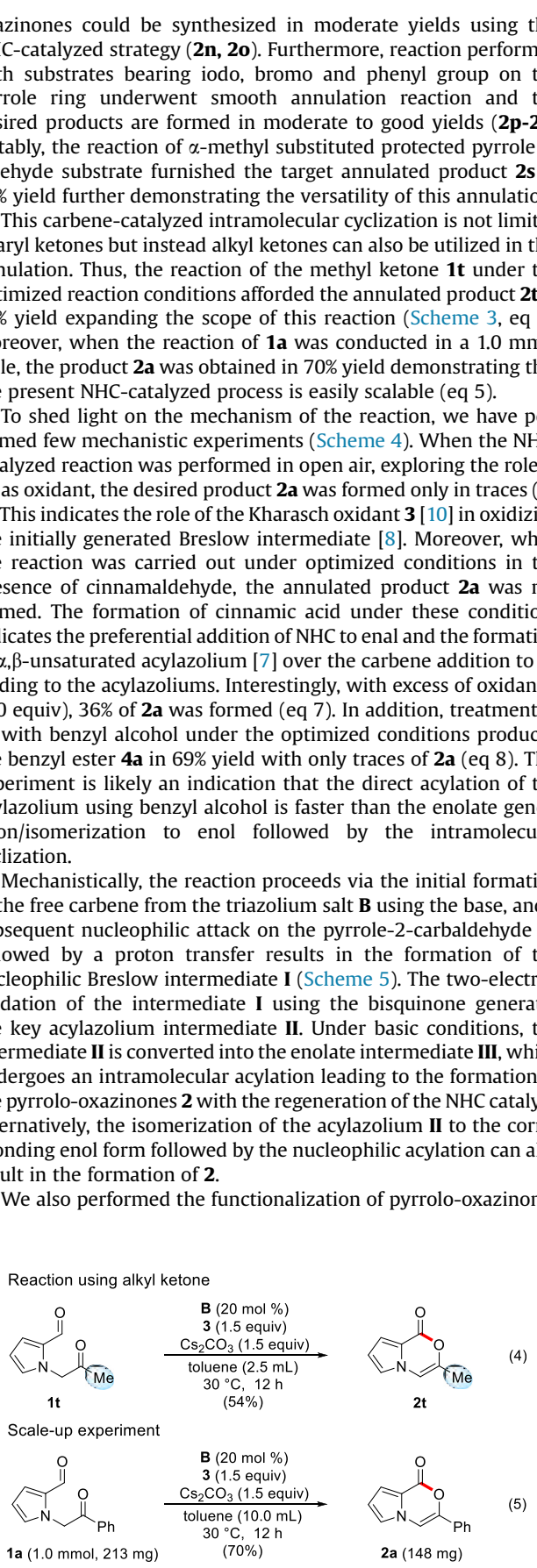
oxazinones could be synthesized in moderate yields using this NHC-catalyzed strategy (**2n, 2o**). Furthermore, reaction performed with substrates bearing iodo, bromo and phenyl group on the pyrrole ring underwent smooth annulation reaction and the desired products are formed in moderate to good yields (**2p-2r**). Notably, the reaction of α-methyl substituted protected pyrrole 2-aldehyde substrate furnished the target annulated product **2s** in 53% yield further demonstrating the versatility of this annulation.

This carbene-catalyzed intramolecular cyclization is not limited to aryl ketones but instead alkyl ketones can also be utilized in this annulation. Thus, the reaction of the methyl ketone **1t** under the optimized reaction conditions afforded the annulated product **2t** in 54% yield expanding the scope of this reaction (Scheme 3, eq 4). Moreover, when the reaction of **1a** was conducted in a 1.0 mmol scale, the product **2a** was obtained in 70% yield demonstrating that the present NHC-catalyzed process is easily scalable (eq 5).

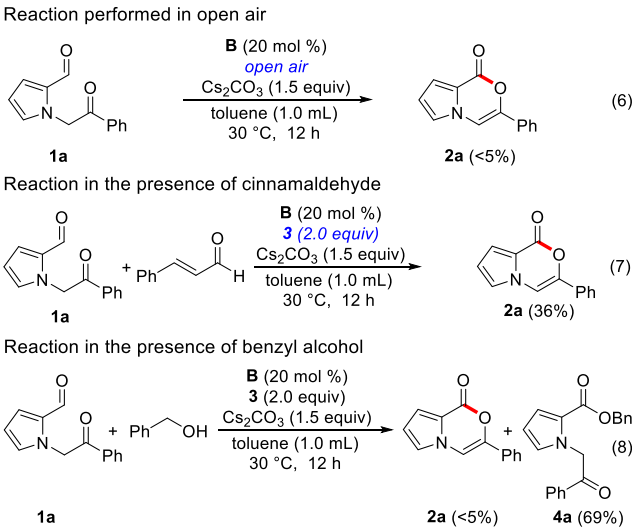
To shed light on the mechanism of the reaction, we have performed few mechanistic experiments (Scheme 4). When the NHC-catalyzed reaction was performed in open air, exploring the role of air as oxidant, the desired product **2a** was formed only in traces (eq 6). This indicates the role of the Kharasch oxidant **3** [10] in oxidizing the initially generated Breslow intermediate [8]. Moreover, when the reaction was carried out under optimized conditions in the presence of cinnamaldehyde, the annulated product **2a** was not formed. The formation of cinnamic acid under these conditions indicates the preferential addition of NHC to enal and the formation of α,β-unsaturated acylazolium [7] over the carbene addition to **1a** leading to the acylazoliums. Interestingly, with excess of oxidant **3** (2.0 equiv), 36% of **2a** was formed (eq 7). In addition, treatment of **1a** with benzyl alcohol under the optimized conditions produced the benzyl ester **4a** in 69% yield with only traces of **2a** (eq 8). This experiment is likely an indication that the direct acylation of the acylazolium using benzyl alcohol is faster than the enolate generation/isomerization to enol followed by the intramolecular cyclization.

Mechanistically, the reaction proceeds via the initial formation of the free carbene from the triazolium salt **B** using the base, and a subsequent nucleophilic attack on the pyrrole-2-carbaldehyde **1a** followed by a proton transfer results in the formation of the nucleophilic Breslow intermediate **I** (Scheme 5). The two-electron oxidation of the intermediate **I** using the bisquinone generates the key acylazolium intermediate **II**. Under basic conditions, the intermediate **II** is converted into the enolate intermediate **III**, which undergoes an intramolecular acylation leading to the formation of the pyrrolo-oxazinones **2** with the regeneration of the NHC catalyst. Alternatively, the isomerization of the acylazolium **II** to the corresponding enol form followed by the nucleophilic acylation can also result in the formation of **2**.

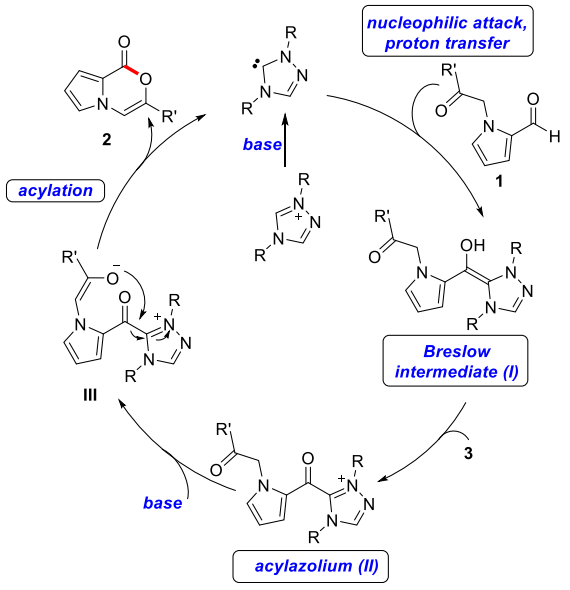
We also performed the functionalization of pyrrolo-oxazinones



Scheme 3. Synthetic Utility of the Reaction.

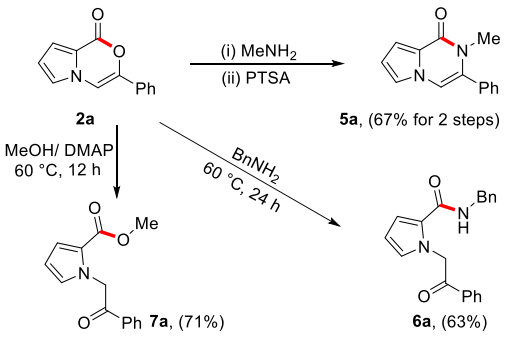


Scheme 4. Mechanistic Experiments.



Scheme 5. Proposed Mechanism of the Reaction.

(Scheme 6). Treatment of **2a** with 40% aqueous methyl amine solution resulted in the formation of the aminal, which was subsequently dehydrated using catalytic amount of PTSA resulting in the



Scheme 6. Functionalization of Pyrrolo-oxazinones.

formation of the pyrrolo-pyrazine derivative **5a** in 67% yield (for two steps). Moreover, ring-opening of **2a** using benzyl amine afforded the amide derivative **6a** in 63% yield. In addition, ring-opening using methanol furnished the methyl ester **7a** in 71% yield. The conversion to **6a** and **7a** can be considered as the two-step transformation of the aldehyde **1a** to the amide and ester respectively via the NHC-catalyzed annulation/ring-opening strategy.

3. Conclusion

In summary, we have developed a mild, scalable and one-pot strategy for the synthesis of pyrrolo-oxazinone derivatives. The NHC-catalyzed intramolecular cyclization of *N*-substituted pyrrole 2-carboxaldehydes under oxidative conditions afforded the products in moderate to good yields with good functional group tolerance. The key step in this annulation reaction is the generation of acylazolium intermediates under oxidative conditions. The application of the present strategy to the synthesis of marine natural products Lukianol A and B starting from the phenol derivatives appears interesting.

4. Experimental section

4.1. General information

Unless otherwise specified, all reactions were performed under argon atmosphere using oven-dried reaction vessels with Teflon screw caps. 30 °C corresponds to the room temperature (rt) of the lab when the experiments were carried out. Dry toluene was purchased from commercial sources and stored under argon over sodium wire. The pyrrole-2-carboxaldehyde was purchased from commercial sources. All the 1-(2-oxo-2-phenylethyl)-1*H*-pyrrole-2-carbaldehyde derivatives were prepared following the literature procedure [14]. The triazolium salt **B** was synthesized following the literature procedure [15]. Cs_2CO_3 was purchased from commercial sources and was used without further purification. Analytical thin layer chromatography was performed on TLC Silica gel 60 F254. Visualization was accomplished with short wave UV light or $KMnO_4$ staining solutions followed by heating. Flash chromatography was performed on silica gel (230–400 mesh) by standard techniques eluting with Pet. Ether-EtOAc solvent system. All compounds were fully characterized. ^1H and ^{13}C NMR spectra were recorded on Bruker AV 400 or Bruker Ultra shield spectrometer in solvents as indicated. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: $\delta_H = 7.26$ ppm, $\delta_C = 77.16$ ppm). Infrared (FT-IR) spectra were recorded on a Bruker Alfa FT-IR, ν-max in cm^{-1}. HRMS (ESI) data were recorded on a Waters Xevo G2-XS Q-TOF instrument.

4.2. General procedure for the synthesis of pyrrolo-oxazinones

To an oven-dried Schlenk reaction vessel equipped with a magnetic stir bar was taken the 1-(2-oxo-2-phenylethyl)-1*H*-pyrrole-2-carbaldehydes **1** (0.25 mmol, 1.0 equiv), triazolium salt **B** (11.3 mg, 0.05 mmol), oxidant **3** (153.2 mg, 0.375 mmol). The mixture was kept under argon atmosphere. To this mixture was added toluene (2.5 mL), followed by Cs_2CO_3 (122.2 mg, 0.375 mmol) under a positive pressure of argon and the reaction mixture was stirred at 30 °C for 12 h. Then, the solvent was evaporated and the crude mixture was purified using silica gel flash column chromatography (eluent: Pet. ether/EtOAc) to afford the pyrrolo-oxazinone derivatives **2**.

4.2.1. 3-Phenyl-1H-pyrrolo[2,1-c][1,4]oxazin-1-one (**2a**) [4a]

White solid (39 mg on 0.25 mmol scale, 72% yield). R_f (Pet. ether/EtOAc = 85/15): 0.52; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71–7.69 (m, 2H), 7.46–7.36 (m, 4H), 7.27–7.26 (m, 1H), 7.19–7.18 (m, 1H), 6.58–6.57 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 142.3, 130.6, 129.52, 129.0, 124.5, 121.6, 116.9, 115.8, 113.7, 104.5. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{13}H_{10}NO_2$ 212.0706; found 212.0711. FTIR (cm^{-1}) 3122, 2923, 1714, 1535, 1477, 1360, 1255, 1191, 1054, 913.

3-(4-Methoxyphenyl)-1H-pyrrolo[2,1-c][1,4]oxazin-1-one (**2b**) [4a]: White solid (49 mg, on 0.25 mmol scale, 81% yield). R_f (Pet. ether/EtOAc = 80/20): 0.55; ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, $J = 8.7$ Hz, 2H), 7.33 (s, 1H), 7.23 (d, $J = 3.4$ Hz, 1H), 7.15 (m, 1H), 6.92 (d, $J = 8.7$ Hz, 2H), 6.56–6.54 (m, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 154.4, 141.6, 125.2, 122.3, 120.8, 116.0, 114.8, 113.7, 112.8, 102.5, 54.8. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{12}NO_3$ 242.0812; found 242.0816. FTIR (cm^{-1}) 3123, 2921, 1710, 1536, 1469, 1365, 1254, 1194, 1054, 905.

3-(p-Tolyl)-1*H*-pyrrolo[2,1-*c*][1,4]oxazin-1-one (**2c**): White solid (41 mg, on 0.25 mmol scale, 72% yield). R_f (Pet. ether/EtOAc = 85/15): 0.53; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, $J = 8.2$ Hz, 2H), 7.40 (s, 1H), 7.24–7.16 (m, 4H), 6.56–6.55 (m, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 142.3, 139.6, 129.6, 127.7, 124.3, 121.6, 116.8, 115.6, 113.6, 103.9, 21.4. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{12}NO_2$ 226.0863; found 226.0869. FTIR (cm^{-1}) 3121, 2923, 1714, 1539, 1470, 1358, 1255, 1192, 1058, 905.

3-(4-Chlorophenyl)-1*H*-pyrrolo[2,1-*c*][1,4]oxazin-1-one (**2d**): White solid (51 mg, on 0.25 mmol scale, 83% yield). R_f (Pet. ether/EtOAc = 90/10): 0.46; ^1H NMR (400 MHz, $CDCl_3$) δ 7.65–7.62 (m, 2H), 7.46 (s, 1H), 7.41–7.39 (m, 2H), 7.28–7.27 (m, 1H), 7.20–7.19 (m, 1H), 6.61–6.59 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6, 141.3, 135.4, 129.3, 129.1, 125.7, 121.8, 116.8, 116.15, 113.9, 104.7. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{13}H_9ClNO_2$ 246.0322; found 246.0320. FTIR (cm^{-1}) 3123, 2918, 1722, 1710, 1476, 1469, 1393, 1362, 1187.

3-(4-Fluorophenyl)-1*H*-pyrrolo[2,1-*c*][1,4]oxazin-1-one (**2e**): White solid (45 mg, on 0.25 mmol scale, 78% yield). R_f (Pet. ether/EtOAc = 85/15): 0.51; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71–7.68 (m, 2H), 7.43 (s, 1H), 7.28 (s, 1H), 7.21 (s, 1H), 7.15–7.12 (m, 2H), 6.60 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4 (d, $J = 250$ Hz), 154.7, 141.5, 126.8 (d, $J = 3.4$ Hz), 126.5 (d, $J = 8.7$ Hz), 121.7, 116.2 (d, $J = 20$ Hz), 116.1, 115.9, 113.8, 104.3. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{13}H_9FNO_2$ 230.0612; found 230.0615. FTIR (cm^{-1}) 3111, 2966, 2923, 2841, 1721, 1607, 1473, 1358, 1254, 1187, 1037, 951.

3-(3-Methoxyphenyl)-1*H*-pyrrolo[2,1-*c*][1,4]oxazin-1-one (**2f**): White solid (52 mg, on 0.25 mmol scale, 86% yield). R_f (Pet. ether/EtOAc = 90/10): 0.34; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.33–7.19 (m, 5H), 6.91 (d, $J = 8.2$, 1H), 6.58 (s, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 154.8, 141.9, 131.9, 129.9, 121.7, 116.9, 116.6, 115.8, 115.3, 113.7, 109.8, 104.7, 55.5. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{14}H_{12}NO_3$ 242.0812; found 242.0817. FTIR (cm^{-1}) 3100, 2965, 2921, 2840, 1730, 1604, 1477, 1363, 1256, 1180, 1037, 951.

3-(3-Bromophenyl)-1*H*-pyrrolo[2,1-*c*][1,4]oxazin-1-one (**2g**): White solid (49 mg, on 0.25 mmol scale, 67% yield). R_f (Pet. ether/EtOAc = 90/10): 0.47; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (m, 1H), 7.66 (d, $J = 7.8$ Hz, 1H), 7.54–7.50 (m, 2H), 7.35–7.29 (m, 2H), 7.23 (m, 1H), 6.64–6.63 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 140.8, 132.7, 132.4, 130.5, 127.4, 123.3, 122.9, 121.9, 116.9, 116.3, 114.1, 105.2. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{13}H_9BrNO_2$ 289.9817; found 289.9819. FTIR (cm^{-1}) 2926, 1771, 1740, 1646, 1515, 1454, 1365, 1287.

3-(3-Chlorophenyl)-1*H*-pyrrolo[2,1-*c*][1,4]oxazin-1-one (**2h**): White solid (52.2 mg, on 0.25 mmol scale, 85% yield). R_f (Pet. ether/EtOAc = 90/10): 0.38; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.59–7.57 (m, 1H), 7.48 (s, 1H), 7.38–7.35 (m, 2H), 7.29–7.26 (m, 1H), 7.20 (bs, 1H), 6.61–6.60 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 140.9, 135.2, 132.4, 130.3, 129.5, 124.5, 122.4, 121.9, 116.9, 116.3, 114.1, 105.2. HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $C_{13}H_9ClNO_2$

246.0316; found 246.0322. FTIR (cm^{-1}) 3110, 2966, 2923, 2841, 1731, 1607, 1475, 1361, 1254, 1183, 1037, 949.

3-(2-Methoxyphenyl)-1*H*-pyrrolo[2,1-*c*][1,4]oxazin-1-one (**2i**): White solid (32 mg, on 0.25 mmol scale, 53% yield). R_f (Pet. ether/EtOAc = 90/10): 0.35; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.94 (d, J = 7.6 Hz, 1H), 7.33 (t, J = 7.7 Hz, 1H), 7.26 (d, J = 3.7 Hz, 1H), 7.18 (s, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 6.57 (m, 1H), 3.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 155.2, 138.4, 130.0, 127.8, 121.8, 121.1, 119.0, 117.1, 115.4, 113.6, 111.2, 109.2, 55.7. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{12}NO_3$ 242.0812; found 242.0816. FTIR (cm^{-1}) 3145, 2961, 2922, 2850, 1734, 1598, 1452, 1388, 1349, 1252, 1183, 1052.

3-(3,4-Dimethoxyphenyl)-1*H*-pyrrolo[2,1-*c*][1,4]oxazin-1-one (**2j**): White solid (56.3 mg, on 0.25 mmol scale, 83% yield). R_f (Pet. ether/EtOAc = 90/10): 0.35; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 1H), 7.25–7.22 (m, 2H), 7.19–7.17 (m, 2H), 6.88 (d, J = 8.3, 1H), 6.57–6.55 (m, 1H), 3.93–3.90 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 150.1, 149.2, 142.1, 123.3, 121.5, 117.2, 116.6, 115.5, 113.5, 111.2, 107.5, 103.5, 56.1, 55.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{14}NO_4$ 272.0917; found 272.0923. FTIR (cm^{-1}) 3011, 2965, 2935, 2837, 1731, 1591, 1416, 1331, 1258, 1188, 1021, 952.

3-(3-Bromo-4-fluorophenyl)-1*H*-pyrrolo[2,1-*c*][1,4]oxazin-1-one (**2k**): White solid (37 mg, on 0.25 mmol scale, 48% yield). R_f (Pet. ether/EtOAc = 85/15): 0.51; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (m, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.54–7.50 (m, 2H), 7.35–7.29 (m, 2H), 7.23 (m, 1H), 6.64–6.63 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7 (d, J = 253 Hz), 154.4, 140.2, 129.8, 128.3 (d, J = 4.2 Hz), 125.1 (d, J = 7.5 Hz), 121.9, 117.2 (d, J = 23.6 Hz), 116.8, 116.4, 114.1, 110.1 (d, J = 23.6 Hz), 104.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_8FBrNO_2$ 307.9722; found 307.9720. FTIR (cm^{-1}) 2920, 1725, 1646, 1513, 1478, 1395, 1362, 1045.

3-(3,5-Difluorophenyl)-1*H*-pyrrolo[2,1-*c*][1,4]oxazin-1-one (**2l**): White solid (44.0 mg, on 0.25 mmol scale, 71% yield). R_f (Pet. ether/EtOAc = 90/10): 0.17; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.31 (d, J = 3.7 Hz, 1H), 7.26–7.21 (m, 3H), 6.86–6.81 (m, 1H), 6.64–6.62 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5 (dd, J_1 = 249.5 Hz, J_2 = 13.5 Hz), 154.1, 140.0, 131.9, 122.0, 116.9, 116.7, 114.3, 107.4 (dd, J_1 = 19.6 Hz, J_2 = 8.1 Hz), 105.1, 104.8 (t, J = 25.4 Hz). HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_8F_2NO_2$ 248.0518; found 248.0526. FTIR (cm^{-1}) 2956, 2917, 2869, 2842, 1725, 1706, 1590, 1448, 1361, 1118, 99, 860, 732.

3-(Naphthalen-1-yl)-1*H*-pyrrolo[2,1-*c*][1,4]oxazin-1-one (**2m**): White solid (54.1 mg, on 0.25 mmol scale, 83% yield). R_f (Pet. ether/EtOAc = 90/10): 0.40; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18–8.16 (m, 1H), 7.94–7.88 (m, 2H), 7.62 (d, J = 7.0 Hz, 1H), 7.56–7.46 (m, 3H), 7.32 (d, J = 3.7 Hz, 1H), 7.26 (s, 1H), 7.20 (s, 1H), 6.63–6.61 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 142.6, 133.8, 131.2, 130.7, 128.7, 128.5, 127.8, 127.2, 126.5, 125.1, 121.6, 116.9, 115.8, 113.6, 108.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{12}NO_2$ 262.0863; found 262.0865. FTIR (cm^{-1}) 3050, 2953, 2920, 2851, 1730, 1601, 1430, 1390, 1280, 1207, 1180, 952.

3-(Furan-2-yl)-1*H*-pyrrolo[2,1-*c*][1,4]oxazin-1-one (**2n**) [4a]: White solid (25.2 mg, on 0.25 mmol scale, 50% yield). R_f (Pet. ether/EtOAc = 90/10): 0.53; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 2H), 7.28 (d, J = 3.9 Hz, 1H), 7.17 (s, 1H), 6.80 (d, J = 3.3 Hz, 1H), 6.58 (t, J = 3.2 Hz, 1H), 6.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 145.4, 143.2, 135.6, 121.9, 116.8, 116.5, 113.8, 112.1, 109.1, 103.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_8NO_3$ 202.0499; found 202.0504. FTIR (cm^{-1}) 3610, 3104, 2957, 2921, 2365, 1727, 1571, 1495, 1348, 1194, 1107, 873.

3-(Thiophen-2-yl)-1*H*-pyrrolo[2,1-*c*][1,4]oxazin-1-one (**2o**): White solid (24.6 mg, on 0.25 mmol scale, 45% yield). R_f (Pet. ether/EtOAc = 90/10): 0.40; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 3.5 Hz, 1H), 7.36 (s, 1H), 7.33 (d, J = 5.0 Hz, 1H), 7.28 (d, J = 3.8 Hz, 1H), 7.16 (s, 1H), 7.09–7.07 (m, 1H), 6.59–6.57 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 138.5, 133.5, 128.1, 126.2, 125.3, 121.7, 116.8, 116.3, 113.8, 103.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{11}H_8NO_2S$ 218.0270; found 218.0274. FTIR (cm^{-1}) 3610, 2958, 2923, 2849, 2364, 1731, 1529, 1517, 1465, 1238, 1080, 852.

7-Iodo-3-phenyl-1*H*-pyrrolo[2,1-*c*][1,4]oxazin-1-one (**2p**): White solid (44.2 mg, on 0.25 mmol scale, 52% yield). R_f (Pet. ether/EtOAc = 90/10): 0.48; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 6.9 Hz, 2H), 7.45–7.38 (m, 4H), 7.34 (s, 1H), 7.23 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 142.8, 130.1, 129.9, 129.1, 125.7, 124.6, 122.3, 118.8, 103.5, 66.15. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_9INO_2$ 337.9672; found 337.9674. FTIR (cm^{-1}) 3125, 2956, 2918, 2844, 1711, 1448, 1379, 1341, 1222, 1051, 1024.

7-Bromo-3-phenyl-1*H*-pyrrolo[2,1-*c*][1,4]oxazin-1-one (**2q**): White solid (52.1 mg, on 0.25 mmol scale, 72% yield). R_f (Pet. ether/EtOAc = 90/10): 0.47; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 6.1 Hz, 2H), 7.44–7.39 (m, 4H), 7.26–7.25 (m, 1H), 7.18 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 143.0, 130.1, 129.9, 129.1, 124.6, 121.1, 117.5, 117.2, 103.7, 101.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_9BrNO_2$ 289.9811; found 289.9818. FTIR (cm^{-1}) 3127, 2957, 2918, 2845, 1710, 1447, 1387, 1256, 1221, 1166, 1049.

3,7-Diphenyl-1*H*-pyrrolo[2,1-*c*][1,4]oxazin-1-one (**2r**): White solid (55 mg, on 0.25 mmol scale, 76% yield). R_f (Pet. ether/EtOAc = 90/10): 0.47; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.2 Hz, 2H), 7.58–7.54 (m, 3H), 7.47–7.40 (m, 7H), 7.30 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 142.6, 133.2, 130.5, 129.8, 129.6, 129.2, 129.1, 127.5, 125.9, 124.5, 117.9, 117.7, 112.9, 104.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{14}NO_2$ 288.1019; found 288.1021. FTIR (cm^{-1}) 3108, 2959, 2924, 2851, 1709, 1406, 1222, 1028, 994.

4-Methyl-3-phenyl-1*H*-pyrrolo[2,1-*c*][1,4]oxazin-1-one (**2s**): White solid (30.0 mg, on 0.25 mmol scale, 53% yield). ***Rf*** (Pet. ether/EtOAc = 90/10): 0.37; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.53 (m, 2H), 7.48–7.42 (m, 3H), 7.33–7.32 (m, 1H), 7.23–7.22 (m, 1H), 6.64 (dd, J_1 = 3.9 Hz, J_2 = 2.6 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 139.2, 131.8, 129.4, 128.5, 119.4, 117.7, 115.9, 113.6, 113.3, 13.6. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{12}NO_2$ 226.0863; found 226.0871. FTIR (cm^{-1}) 3133, 2959, 2922, 2850, 1721, 1469, 1352, 1304, 1195, 1130, 1038, 739.

3-Methyl-1*H*-pyrrolo[2,1-*c*][1,4]oxazin-1-one **(2t):** White solid (20 mg, on 0.25 mmol scale, 54% yield). R_f (Pet. ether/EtOAc = 90/10): 0.42; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 4.0 Hz, 1H), 7.03–7.02 (m, 1H), 6.79 (s, 1H), 6.51–6.49 (m, 1H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 141.2, 120.8, 116.6, 115.3, 112.9, 105.0, 16.9. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_8H_8NO_2$ 150.0555; found 150.0558. FTIR (cm^{-1}) 2958, 1726, 1687, 1533, 1481, 1353, 1219.

2-Methyl-3-phenylpyrrolo[1,2-*a*]pyrazin-1(2*H*)-one (**5a**) [16]: To a dry Schlenk tube containing compound **2a** (26.4 mg, 0.125 mmol) 40% aqueous $MeNH_2$ (55 μL, 0.5 mmol) was added. The resulting mixture was allowed to stir overnight at 30 °C. Then the solution was concentrated under reduced pressure and the residue was purified by flash column chromatography using silica gel and petroleum ether/EtOAc (70:30) as eluent. The aminal thus formed was treated with catalytic PTSA (1.0 mg) in benzene (1.0 mL) and the mixture was heated under reflux for 1 h. The reaction mixture was cooled, and the solvent was evaporated and the residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (80:20) to afford the 2-methyl-3-phenylpyrrolo[1,2-*a*]pyrazin-1(2*H*)-one **5a** as a white solid (19 mg, 67% yield). R_f (Pet. ether/EtOAc = 70/30): 0.48; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.43 (m, 3H), 7.39–7.36 (m, 2H), 7.11–7.10 (m, 1H), 7.07–7.06 (m, 1H), 6.89 (m, 1H), 6.57–6.55 (m, 1H), 3.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 133.2, 130.4, 129.5, 129.2, 128.8, 123.5, 118.1, 112.7, 109.9, 107.9, 32.1. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{13}N_2O_4$ 225.1028; found 225.1026. FTIR (cm^{-1}) 2920, 2367, 1668, 1627, 1473, 1424, 1366, 1292.

N-Benzyl-1-(2-oxo-2-phenylethyl)-1*H*-pyrrole-2-carboxamide

(6a): To a dry Schlenk tube containing compound **2a** (26.4 mg, 0.125 mmol) was added $BnNH_2$ (68.3 mg, 0.625 mmol). The resulting mixture was allowed to stir for 24 h at 60 °C. Then the residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (75:25) to afford the *N*-benzyl-1-(2-oxo-2-phenylethyl)-1*H*-pyrrole-2-carboxamide **6a** as a white solid (25 mg, 63% yield). R_f (Pet. ether/EtOAc = 70/30): 0.41; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 7.5 Hz, 2H), 7.64–7.60 (m, 1H), 7.53–7.49 (m, 2H), 7.37–7. 26 (m, 5H), 6.80 (m, 1H), 6.68–6.66 (m, 1H), 6.29–6.23 (m, 2H), 5.90 (s, 2H), 4.49 (d, J = 5.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 161.8, 138.5, 135.1, 133.8, 128.9, 128.8, 128.7, 128.4, 128.2, 127.8, 127.5, 126.7, 125.4, 112.2, 108.2, 55.3, 43.3. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{19}N_2O_2$ 319.1447; found 319.1443. FTIR (cm^{-1}) 2923, 2370, 1696, 1644, 1628, 1545, 1513, 1461, 1225, 1115.

Methyl 1-(2-oxo-2-phenylethyl)-1*H*-pyrrole-2-carboxylate **(7a)** [17] To a dry Schlenk tube containing compound **2a** (26.4 mg, 0.125 mmol), MeOH (3.0 mL) and DMAP (15.3 mg, 0.125 mmol) were added. The resulting mixture was allowed to stir overnight at 60 °C. Then the solution was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel using petroleum ether/EtOAc (90:10) to afford the methyl 1-(2-oxo-2-phenylethyl)-1*H*-pyrrole-2-carboxylate **7a** as a white solid (21.6 mg, 71% yield). R_f (Pet. ether/EtOAc = 80/20): 0.48; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.5 Hz, 2H), 7.64–7.60 (m, 1H), 7.53–7.49 (m, 2H), 7.06–7.05 (m, 1H), 6.85–6.84 (m, 1H), 6.27–6.25 (m, 1H), 5.76 (s, 2H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 161.9, 134.9, 133.8, 129.9, 128.9, 128.1, 122.3, 118.4, 108.8, 55.2, 51.2. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{14}H_{13}NO_3Na$ 266.0793; found 266.0790. FTIR (cm^{-1}) 2921, 2346, 1701, 1574, 1532, 1438, 1406, 1330, 1224.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.132330.

References

[1] For selected reviews, see: (a) J.M. Wood, D.P. Furkert, M.A. Brimble, Nat. Prod. Rep. 36 (2019) 289;
(b) S. Ahmad, O. Alam, M.J. Naim, M. Shaquiquzzaman, M.M. Alam, M. Iqbal, Eur. J. Med. Chem. 157 (2018) 527;
(c) V. Bhardwaj, D. Gumber, V. Abbot, S. Dhimana, P. Sharma, RSC Adv. 5 (2015) 15233;
(d) A. Domagala, T. Jarosz, M. Lapkowski, Eur. J. Med. Chem. 100 (2015) 176;
(e) H. Fan, J. Peng, M.T. Hamann, J.-F. Hu, Chem. Rev. 108 (2008) 264.
[2] (a) D. Morikawa, K. Morii, Y. Yasuda, A. Mori, K. Okano, J. Org. Chem. 85 (2020) 8603;
(b) I. Satyanarayana, D.-Y. Yang, T. Liou, J. *RSC Adv.* 10 (2020) 43168;
(c) K. Takamura, H. Matsuo, A. Tanaka, J. Tanaka, T. Fukuda, F. Ishibashi, M. Iwao, Tetrahedron 69 (2013) 2782;
(d) Y. Lu, B.A. Arndtsen, Org. Lett. 11 (2009) 1369;
(e) S. Kim, S. Son, H. Kang, Bull. Kor. Chem. Soc. 22 (2001) 1403;
(f) W.Y. Yoshida, K.K. Lee, A.R. Carrol, P. Scheuer, J. *Helv. Chim. Acta* 75 (1992) 1721.
[3] (a) B.J. Reinus, S.M. Kerwin, Synthesis 49 (2017) 2544;
(b) D. Dumas, J. Org. Chem. 53 (1988) 4650.
[4] (a) L. Habert, R. Sallio, M. Durandetti, C. Gosmini, I. Gillaizeau, Eur. J. Org Chem. (2019) 5175;
(b) I. Yenice, S. Basceken, M. Balci, Beilstein J. Org. Chem. 13 (2017) 825;
(c) S. Taskaya, N. Menges, M. Balci, Beilstein J. Org. Chem. 11 (2015) 897.
[5] For reviews on NHC organocatalysis, see: (a) X. Chen, H. Wang, Z. Jin, Y.R. Chi, Chin. J. Chem. 38 (2020) 1167;
(b) X.-Y. Chen, Z.-H. Gao, S. Ye, Acc. Chem. Res. 53 (2020) 690;
(c) S. Barik, A.T. Biju, Chem. Commun. 56 (2020) 15484;
(d) H. Ohmiya, ACS Catal. 10 (2020) 6862;
(e) T. Ishii, K. Nagao, H. Ohmiya, Chem. Sci. 11 (2020) 5630;
(f) T.K. Das, A.T. Biju, Chem. Commun. 56 (2020) 8537;
(g) K.J.R. Murauski, A.A. Jaworski, K.A. Scheidt, Chem. Soc. Rev. 47 (2018) 1773;
(h) X.-Y. Chen, Q. Liu, P. Chauhan, D. Enders, Angew. Chem. Int. Ed. 57 (2018) 3862;
(i) S. Mukherjee, A.T. Biju, Chem. Asian J. 13 (2018) 2333;
(j) M.H. Wang, K.A. Scheidt, Angew. Chem. Int. Ed. 55 (2016) 14912;
(k) R.S. Menon, A.T. Biju, V. Nair, Beilstein J. Org. Chem. 12 (2016) 444;
(l) D.M. Flanigan, F. Romanov-Michailidis, N.A. White, T. Rovis, Chem. Rev. 115 (2015) 9307;
(m) Menon, R. S.; Biju, A. T.; Nair, V. Chem. Soc. Rev. 2015, 44, 5040. (n) S.R. Yetra, A. Patra, A.T. Biju, Synthesis 47 (2015) 1357;
(o) M.N. Hopkinson, C. Richter, M. Schedler, F. Glorius, Nature 510 (2014) 485;
(p) J. Mahatthananchai, J.W. Bode, Acc. Chem. Res. 47 (2014) 696;
(q) M. Fevre, J. Pinaud, Y. Gnanou, J. Vignolle, D. Taton, Chem. Soc. Rev. 42 (2013) 2142;
(r) H.U. Vora, P. Wheeler, T. Rovis, Adv. Synth. Catal. 354 (2012) 1617;
(s) D.T. Cohen, K.A. Scheidt, Chem. Sci. 3 (2012) 53;
(t) X. Bugaut, F. Glorius, Chem. Soc. Rev. 41 (2012) 3511;
(u) J. Izquierdo, G.E. Hutson, D.T. Cohen, K.A. Scheidt, Angew. Chem. Int. Ed. 51 (2012) 11686;
(v) A.T. Biju, N. Kuhl, F. Glorius, Acc. Chem. Res. 44 (2011) 1182;
(w) V. Nair, R.S. Menon, A.T. Biju, C.R. Sinu, R.R. Paul, A. Jose, V. Sreekumar, Chem. Soc. Rev. 40 (2011) 5336;
(x) D. Enders, O. Niemeier, A. Henseler, Chem. Rev. 107 (2007) 5606.
[6] A.T. Biju, N-heterocyclic Carbenes in Organocatalysis, vol. 12, Wiley-VCH Verlag GmbH & Co. KGa A, Boschstr., Weinheim, Germany, 2019, p. 69469.
[7] For reviews on NHC-catalyzed non-umpolung chemistry, see:. (a) A. Ghosh, A.T. Biju, Angew. Chem. Int. Ed. 60 (2021) 13712;
(b) S. Mondal, S.R. Yetra, S. Mukherjee, A.T. Biju, Acc. Chem. Res. 52 (2019) 425;
(c) C. Zhang, J.F. Hooper, D.W. Lupton, ACS Catal. 7 (2017) 2583;
(d) S. De Sarkar, A. Biswas, R.C. Samanta, A. Studer, Chem. Eur J. 19 (2013) 4664;
(e) S.J. Ryan, L. Candish, D.W. Lupton, Chem. Soc. Rev. 42 (2013) 4906.
[8] R. Breslow, J. Am. Chem. Soc. 80 (1958) 3719.
[9] S. De Sarkar, S. Grimme, A. Studer, J. Am. Chem. Soc. 132 (2010) 1190.
[10] M.S. Kharasch, B.S. Joshi, J. Org. Chem. 22 (1957) 1439.
[11] For selected recent reports, see: (a) X.-Y. Duan, Z. Tian, B. Liu, T. He, L.-L. Zhao, M. Dong, P. Zhang, J. Qi, Org. Lett. 23 (2021) 3777;
(b) C.-L. Zhang, Y.-Y. Gao, H.-Y. Wang, B.-A. Zhou, S. Ye, Angew. Chem., Int. Ed. 60 (2021) 13918;
(c) J. Jin, X. Huang, J. Xu, T. Li, X. Peng, X. Zhu, J. Zhang, Z. Jin, Y.R. Chi, Org. Lett. 23 (2021) 3991;
(d) Z. Chen, X. Kong, S. Niu, S. Yang, J. Liu, B. Chen, B. Luo, C. Zhou, C. Ding, X. Fang, Org. Lett. 23 (2021) 3403;
(e) T. Li, C. Mou, P. Qi, X. Peng, S. Jiang, G. Hao, W. Xue, S. Yang, L. Hao, Y.R. Chi, Z. Jin, Angew. Chem. Int. Ed. 60 (2021) 9362;
(f) G. Wang, Q. Zhang, C. Wei, Y. Zhang, L. Zhang, J. Huang, D. Wei, Z. Fu, W. Huang, Angew. Chem. Int. Ed. 60 (2021) 7913;
(g) Y.-F. Han, Z.-H. Gao, C.-L. Zhang, S. Ye, Org. Lett. 22 (2020) 8396;
(h) Z.-Y. Wang, T. Yang, K.-K. Wang, R. Chen, M. Liu, H. Liu, Org. Chem. Front. 7 (2020) 1011.
[12] For selected reports from our group, see:. (a) K. Balanna, K. Madica, S. Mukherjee, A. Ghosh, T. Poisson, T. Besset, G. Jindal, A.T. Biju, Chem. Eur J. 26 (2020) 818;
(b) S. Mukherjee, S. Shee, T. Poisson, T. Besset, A.T. Biju, Org. Lett. 20 (2018) 6998;
(c) S. Mukherjee, A. Ghosh, U.K. Marelli, A.T. Biju, Org. Lett. 20 (2018) 2952;
(d) S. Mukherjee, S. Joseph, A. Bhunia, R.G. Gonnade, S.R. Yetra, A.T. Biju, Org. Biomol. Chem. 15 (2017) 2013;

(e) S. Premaletha, A. Ghosh, S. Joseph, S.R. Yetra, A.T. Biju, Chem. Commun. 53 (2017) 1478;
(f) S.R. Yetra, S. Mondal, S. Mukherjee, R.G. Gonnade, A.T. Biju, Angew. Chem. Int. Ed. 55 (2016) 268;
(g) S.R. Yetra, S. Mondal, E. Suresh, A.T. Biju, Org. Lett. 17 (2015) 1417. For a related cascade reaction using similar pyrrole derivative bearing a -COCF3 group, see: Ghosh, A.; Shee, S.; Barik, S.; Gonnade, R. G.; Biju, A. T. Org. Lett. 2021, 23, 5223.

[13] M. Lang, J. Wang, Org. Chem. Front. 6 (2019) 1367.
[14] J.H. Lee, I. Kim, J. Org. Chem. 78 (2013) 1283.
[15] J.L. Belletire, R.A. Bills, S.A. Shackelford, Synth. Commun. 38 (2008) 738.
[16] M. Ying, Z. Hongwei, L. Zehua, Z. Shanchao, Z. Hongwei, S. Chiyu, Z. Lijuan, Z. Mingming, W. Guan, J. Mengying, S. Wei, S. Hongrui, Chem. Res. Chin. Univ. 30 (2014) 624.
[17] F. Wang, J. Wang, S. Zhang, Molecules 9 (2004) 574.