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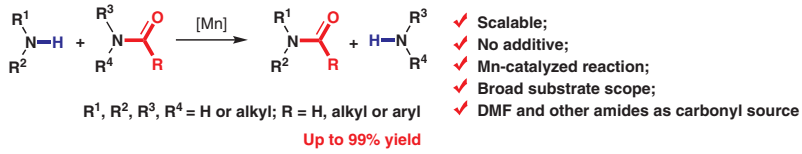
Mn(II)-Catalyzed *N*-Acylation of Amines

Juan Ma
Jingyu Zhang
Hang Gong*

The Key Laboratory for Green Organic Synthesis and Application of Hunan Province; The Key Laboratory of Environmentally Friendly Chemistry and Application of the Ministry of Education College of Chemistry, Xiangtan University, Xiangtan 411105, P. R of China
hgong@xtu.edu.cn



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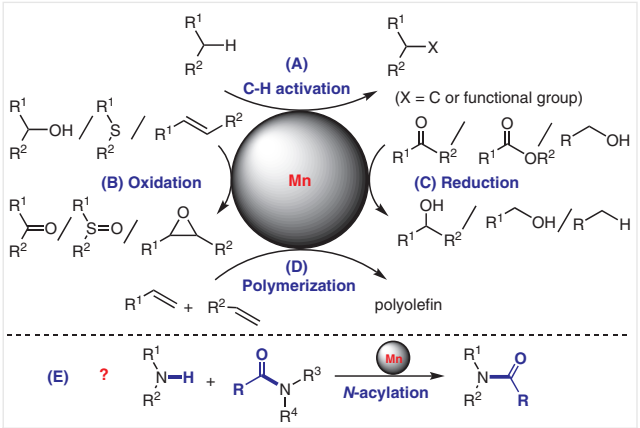
Abstract A practical protocol has been developed here for the Mn(II)-catalyzed *N*-acylation of amines with high yields using *N*,*N*-dimethylformamide and other amides as the carbonyl source. The protocol is simple, does not require any acid, base, ligand, or other additives, and encompasses a broad substrate scope for primary, secondary, and heterocyclic amines.

Key words synthetic methodology, *N*-acylation, manganese, amide, catalytic reaction

Metal-catalyzed reactions have recently been well developed, with reliance on the noble metals for major advances.[1] There is great interest in using earth-abundant, inexpensive, and non-toxic metals to replace the noble metals in catalytic reactions due to their sustainable development and economic considerations. However, it is a considerable challenge to use non-toxic metals because of their relatively lower catalytic activity. In this respect, manganese, which is known as the twelfth most abundant element in the Earth's crust and the third most abundant transition metal, has exhibited low toxicity[2] and low cost,[3] and is strongly competitive with traditional noble metal catalysts.[4]

Recently, many Mn-catalyzed organic reactions have been developed, resulting in an upsurge in Mn-catalyzed chemistry. Among them, the Mn-catalyzed C–H activation reactions are some of the most widely investigated (Scheme 1, A).[4a,5] Other Mn-catalyzed reactions, such as oxidation (Scheme 1, B),[6] reduction (Scheme 1, C),[7] polymerization (Scheme 1, D),[8] and other types of reactions[9] have also been reported. Despite the considerable development of Mn-catalyzed chemistry, the *N*-acylation of amines has not yet been reported (Scheme 1, E).



Scheme 1 Mn-catalyzed reactions

N-Acylation of amines is a very important organic reaction.[10] Moreover, the amide building block is widely present in pharmaceuticals, such as formoterol,[11a] lacosamide,[11b] tetrahydrolipstatin,[11c] leucovorin,[11d] natural products,[11e] and functional materials[11f] (Figure 1). Several carbonyl sources, such as *N*,*N*-dimethylformamide (DMF)/*N*,*N*-dimethylacetamide (DMA),[12] formic acid/formate,[13] methanol,[14] esters,[15] and others[16] have been applied to the *N*-acylation of amines. DMF is widely used as an inexpensive and readily available solvent in the organic synthesis industry and laboratory research. As a compound that contains an aldehyde and an amino group, DMF has been widely applied as a versatile precursor in forms such as -NMe_2, -CHO, -CO, -$CONMe_2$, and -Me.[17] *N*-Acylation of amines has been reported using DMF as a carbonyl source in the presence of various catalysts, such as Pd,[18] Ni,[12a] Ce,[12b] Fe,[12c,d] Cu,[12e] L-proline,[12f] boronic acid[12g] and its derivatives,[12h,i] imidazole[12j] and its derivatives,[12k] and hydroxylamine hydrochloride.[12l] However, these reactions frequently suffer from

drawbacks: the use of complex and costly catalysts or stoichiometric catalysts, requirement of additives, limited substrate scope, difficulty in isolation and purification, or lengthy preparation. Thus, a more optimal reaction consists of using the earth-abundant metal manganese to catalyze the *N*-acylation of amines.

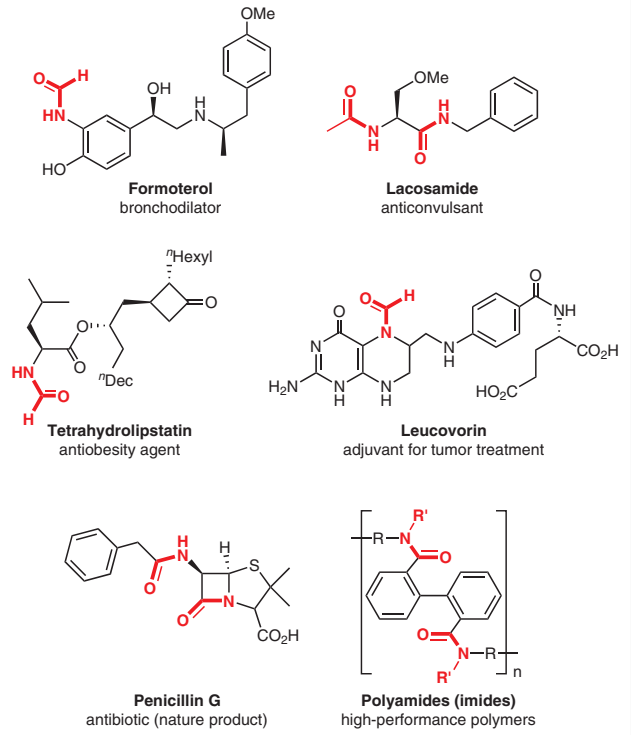
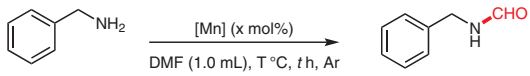


Figure 1 Amide-containing biologically active molecules and polymers

Herein, a highly efficient $MnCl_2·4H_2O$-catalyzed strategy for the *N*-acylation of amines using DMF and other amides as a carbonyl sources is reported (Scheme 1, E). This strategy is simple and cost-effective because the reagents and catalyst are inexpensive and do not require any acid, base, ligand, or other additives. A broad substrate scope is given, and primary, secondary, and heterocyclic amines with various functional groups can be converted into the desired *N*-acylation product with moderate to excellent yields. Furthermore, other amides such as formamide, *N*-methylformamide, *N*-ethylformamide, and acetamide can also serve as carbonyl sources to achieve the *N*-amidation reaction with excellent yields.

Initially, the reaction of benzylamine with DMF in the presence of $MnCl_2·4H_2O$ was selected as the model reaction (Table 1). Various reaction conditions were confirmed, including the type and the amount of Mn catalyst, reaction temperature, reaction time, and the reaction atmosphere. The results indicated that the conversion rate is very poor in the absence of Mn catalyst (entry 1). An excellent yield of 91% was achieved when using $MnCl_2·4H_2O$ (15 mol%) as the catalyst (entry 4). Other metal salts, such as $CoCl_2$, $CuCl_2·2H_2O$, $FeCl_3$, $PdCl_2$, and $NiCl_2·6H_2O$ were also investigated as catalysts, and only moderate yields were achieved (entries 7–11). Decreasing the reaction temperature (entry 12) or reducing the reaction time (entry 13) proved to be unfavorable to this transformation. Additionally, the presence of air is harmful to this reaction (entry 14).

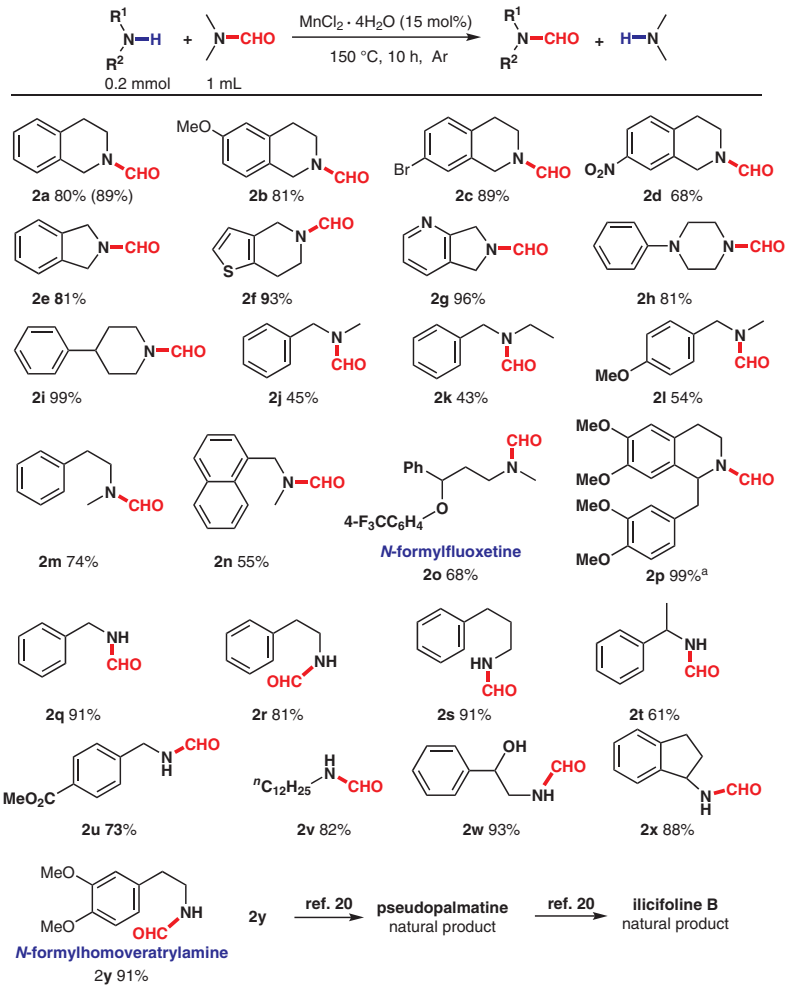
Table 1 Selected Optimization Results[a]



Entry	[Mn] (mol%)	Temp (°C)	Time (h)	Yield (%)
1	–	150	10	23
2	$MnCl_2·4H_2O$ (5)	150	10	66
3	$MnCl_2·4H_2O$ (10)	150	10	73
4	$MnCl_2·4H_2O$ (15)	150	10	91
5	$Mn(OAc)_3·2H_2O$ (15)	150	10	73
6	$Mn(OAc)_2·4H_2O$ (15)	150	10	76
7	$CoCl_2$ (15)	150	10	41
8	$CuCl_2·2H_2O$ (15)	150	10	48
9	$FeCl_3$ (15)	150	10	55
10	$PdCl_2$ (15)	150	10	43
11	$NiCl_2·6H_2O$ (15)	150	10	57
12	$MnCl_2·4H_2O$ (15)	130	10	58
13	$MnCl_2·4H_2O$ (15)	150	6	60
14[b]	$MnCl_2·4H_2O$ (15)	150	10	62

[a] Reaction conditions: benzylamine (0.2 mmol), catalyst (x mol%), DMF (1.0 mL), under argon unless otherwise indicated. Yields were determined by ^1H NMR spectroscopy using nitroethane as an internal standard.
[b] Under an atmosphere of air.

After optimization, *N*-formylation of various amines, such as primary, secondary, and heterocyclic amines, using DMF as the reagent was conducted (Scheme 2). The reaction proceeded well when using tetrahydroisoquinoline or its analogues as secondary amine substrates giving **2a–g** in good to excellent yields. Different functional groups on the benzene ring such as methoxy, bromide, and nitro were compatible with this reaction. However, the nitro group, which is known as an electron-withdrawing group, has a negative influence on this transformation, i.e. the reaction of 7-nitro-1,2,3,4-tetrahydroisoquinoline with DMF gave **2d** in only 68% yield. When using heterocyclic amines as substrates, excellent yields were also achieved, i.e. the formation of **2f,g**. Other secondary amines, including circular and linear amines, smoothly underwent the transformation to give products **2h–p** in moderate to excellent yields in most cases. In particular, *N*-formylfluoxetine (**2o**), which has been applied as a marker for fluoxetine,[19] was obtained in a good 68% yield. However, the alkyl substitution on nitrogen resulted in obvious steric hindrance and subsequent lower 45–74% yields in the formation of **2j–o**.



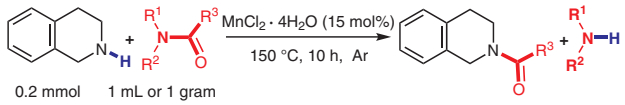
Scheme 2 Substrate scope of amines. *Reagents and conditions*: amine (0.2 mmol), $MnCl_2{\cdot}4H_2O$ (15 mol%), DMF (1.0 mL), sealed tube, argon atmosphere, 150 °C, 10 h. Isolated yields are given (NMR yield is given in brackets, nitroethane as internal standard). [a] H_2NCHO as carbonyl source.

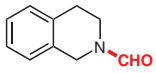
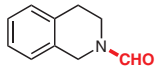
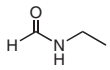
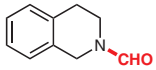
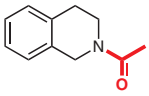
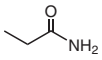
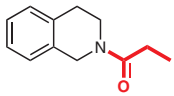
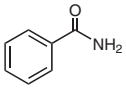
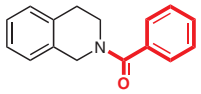
This successful protocol for the *N*-formylation of secondary amines was expanded to primary amines, and an efficiency greater than that for secondary amines was obtained i.e. for **2q–y**. This efficiency was likely the result of the less alkyl substituent on nitrogen, and subsequently, a smaller steric hindrance, which resulted in an increased yield. However, the methyl substituent at the α-position of nitrogen also results in obvious steric hindrance, e.g. in the formation of **2t**. Remarkably, a substrate with an acid/base sensitive ester group also proceeded well to give **2u**.

Additionally, a hydroxy group in the substrate had no adverse effect on this reaction, e.g. the formation of **2w**. The *N*-formylation of primary amines is a valuable organic reaction. For instance, the natural molecule homoveratrylamine (3,4-dimethoxyphenethylamine) was converted to *N*-formylation product **2y**, which can then be applied as a precursor for preparing the natural products pseudopalmatine, 8-oxopseudopalmatine, and ilicifoline B.[20] Phenylglycine methyl ester also was examined as substrate, however, only decarboxylation product **2q** was isolated in 59% yield.

To validate the practicability of the strategy, further extrapolation for the *N*-acylation of tetrahydroisoquinoline using various carbonyl sources was conducted (Table 2). The results indicated that formamide, *N*-methylformamide, and *N*-ethylformamide can also serve as carbonyl sources to achieve the *N*-acylation reaction in excellent yields (entries 1–3). Moreover, when acetamide and propanamide were used, the *N*-acetylation and *N*-propanoylation products were obtained in excellent 86% and 87% yields, respectively (entries 4 and 5). Benzamide was also tested as the carbonyl source, but the product **2zb** was obtained in only 25% yield, which may be due to the steric hindrance of the carbonyl source.

Table 2 Substrate Scope of Amides[a]



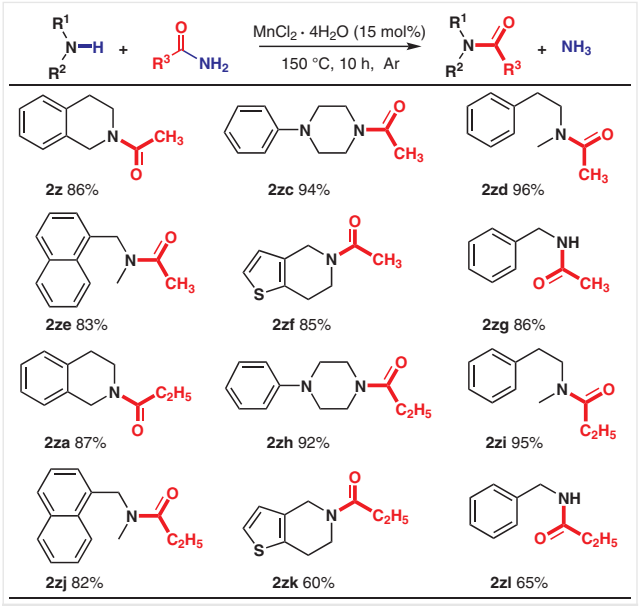
Entry	Amide	Product	Yield (%)
1		**2a** 	91
2		**2a** 	93 (98)[b]
3		**2a** 	89 (93)[b]
4		**2z** 	86
5		**2za** 	87
6		**2zb** 	25

[a] Reaction conditions: amine (0.2 mmol), $MnCl_2{\cdot}4H_2O$ (15 mol%), amide (1.0 mL; entries 4–6, 1 g), sealed tube, argon atmosphere, 150 °C, 10 h. Isolated yields are given.
[b] NMR yield with nitroethane as an internal standard.

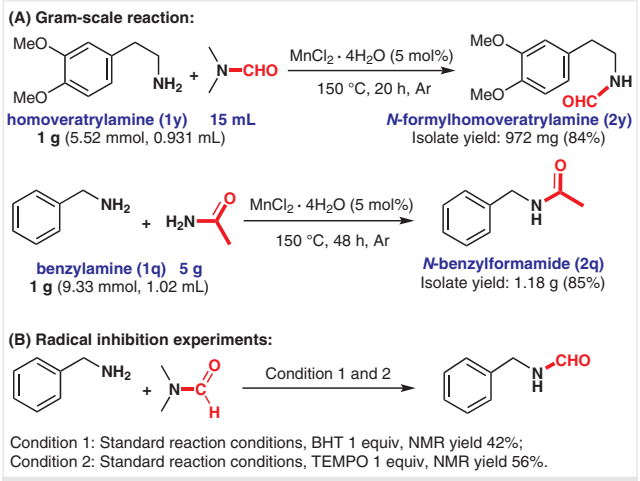
Based on the good results of *N*-acetylation and *N*-propanoylation of **1a**, the *N*-acylation and *N*-propanoylation were extrapolated to several amines (Scheme 3). As expected, both the primary and secondary amine are converted into the desired products **2z**,**za**,**zc**–**zl** in good to excellent yields.

Importantly, the gram-scale reaction of natural compound **1y** using only 5 mol% $MnCl_2{\cdot}4H_2O$ as catalyst was conducted (Scheme 4), and an excellent yield of 84% was achieved with a slightly extended reaction time (20 h). The gram-scale *N*-acetylation reaction of benzylamine (**1q**) also achieved with an excellent yield of 85%. To examine the reaction mechanism, radical inhibition experiments were conducted using benzylamine/DMF/$MnCl_2{\cdot}4H_2O$ together with 1 equiv butylated hydroxytoluene (BHT) or 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as blocker, resulting in the desired product **2q** in 42% and 56% yield (NMR yield), respectively. In our opinion, this reaction is not a radical process, but instead, is a nucleophilic process.

Based on the radical inhibition experiments and the reported metal-catalyzed *N*-formylation reactions,[12a] a reasonable mechanism is proposed (Scheme 5). First, the carbonyl group of DMF is activated by $MnCl_2$ via coordination. Subsequently, the activated DMF undergoes nucleophilic attack by the amine, which results in the formation of a tetrahedral intermediate **I**. Afterward, with a proton transfer, the sterically congested intermediate **I** eliminates dimethylamine to give intermediate **II**. Finally, the target molecule **T.M.** in intermediate **II** is replaced by DMF to finish the catalytic cycle.

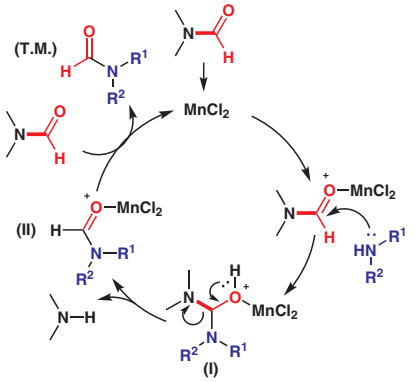


Scheme 3 Substrate scope of acetylation and propanoylation of amine. *Reagents and conditions*: amine (0.2 mmol), $MnCl_2{\cdot}4H_2O$ (15 mol%), amide (1 g), sealed tube, argon atmosphere, 150 °C, 10 h. Isolated yields are given.



Scheme 4 Gram-scale reactions and radical inhibition experiments

In summary, an efficient manganese-catalyzed *N*-acylation of amines using DMF and other amides as carbonyl sources was developed. The advantages of this strategy are the use of a metal as the catalyst that is richly abundant and inexpensive, the unencumbered availability of various in-



Scheme 5 Proposed mechanism for *N*-formylation using $MnCl_2·4H_2O$ as catalyst

expensive amides as the carbonyl source, the lack of requirement for any acid, base, ligand, or other additives, broad substrate scopes, and high yields.

Preparative TLC was performed for product purification using Sorbent Silica Gel 60 F254 TLC plates and visualized with UV light. IR spectra were recorded on a new FT infrared spectrometer. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on 400, 100, and 377 MHz NMR spectrometers using $CDCl_3$ as solvent unless otherwise stated. HRMS were made by means of ESI. Melting points were measured on micromelting point apparatus and uncorrected. Unless otherwise noted, all reagents were weighed and handled in air, and all reactions were carried out in a sealed tube under an atmosphere of argon. Unless otherwise noted, all reagents were purchased from reagent company, and used without further purifications.

In NMR spectra ** indicates the major rotamer and * indicates the minor rotamer.

N-Substituted Formamides 2; General Procedure

A solution of amine (0.2 mmol) and $MnCl_2·4H_2O$ (5.9 mg, 15 mol%) in DMF (1.0 mL) was stirred in a sealed microwave reaction tube under an atmosphere of argon at 150 °C for 10 h. The mixture was cooled to r.t., and water (10 mL) was added; the mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were dried (anhyd Na_2SO_4), the solvent was evaporated under vacuum, and the crude product was purified by preparative TLC (silica gel, petroleum ether/EtOAc) to obtain the pure product.

N-(3,4-Dimethoxyphenethyl)formamide (2y); Gram-Scale Synthesis

A solution of homoveratrylamine (**1y**; 1 g, 5.52 mmol) and $MnCl_2·4H_2O$ (54.3 mg, 5 mol%) in DMF (15 mL) was stirred in a sealed microwave reaction tube (120 mL) under an atmosphere of argon at 150 °C for 20 h. The mixture was cooled to r.t., and water (50 mL) was added; the mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were dried (anhyd Na_2SO_4), the solvent was evaporated under vacuum, and the crude product was purified column chromatography (silica gel, petroleum ether/EtOAc 2:1 with 1% Me_3N) to obtain the pure product; yield: 972 mg (84%).

N-Benzylformamide (2q); Gram-Scale Synthesis

A solution of benzylamine (**1q**; 1 g, 9.33 mmol), $MnCl_2·4H_2O$ (92.4 mg, 5 mol%) in acetamide (5 g) was stirred in a sealed microwave reaction tube (120 mL) under an atmosphere of argon at 150 °C for 48 h. The mixture was cooled to r.t., and water (30 mL) was added; the mixture was extracted with CH_2Cl_2 (4 × 20 mL). The combined organic layers were dried (anhyd Na_2SO_4), the solution was evaporated under vacuum, and the residue was purified by column chromatography (silica gel, petroleum ether/EtOAc 3:1 with 1% Me_3N) to obtain the pure product; yield: 1180 mg (85%).

1,2,3,4-Tetrahydroisoquinoline-2-carbaldehyde (2a)[21]

Purified by TLC; yellow oil; isolated yield: 25.8 mg (80%); ^1H NMR yield: 89%.

IR (neat): 3151, 1672, 1584, 1498, 1282, 1164, 1049, 930, 882, 751 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.25 (s, 0.38 H)*, 8.19 (s, 0.62 H)**, 7.22–7.08 (m, 4 H), 4.68 (1.24 H)**, 4.54 (0.75 H)*, 3.78 (t, *J* = 6.2 Hz, 0.74 H)*, 3.64 (t, *J* = 5.8 Hz, 1.27 H)**, 2.92–2.85 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6**, 161.1*, 134.3*, 133.4**, 132.1*, 131.6**, 129.1*, 128.8**, 127.0, 126.6–126.4 (m), 125.8, 47.2*, 43.1**, 42.2**, 37.9*, 29.6**, 27.8*.

HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{10}H_{11}NNaO$: 184.0733; found: 184.0733.

6-Methoxy-1,2,3,4-tetrahydroisoquinoline-2-carbaldehyde (2b)[22]

Purified by TLC; yellow solid; yield: 30.9 mg (81%); mp 63–64 °C.

IR (neat): 3140, 1672, 1612, 1508, 1402, 1312, 1277, 1241, 1119 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.22 (s, 0.40 H)*, 8.17 (s, 0.60 H)**, 7.04–6.99 (m, 1 H), 6.78–6.74 (m, 1 H), 6.65 (d, *J* = 10.0 Hz, 1 H), 4.60 (s, 1.24 H)**, 4.47 (s, 0.77 H)*, 3.77–3.73 (m, 3.76 H), 3.61 (t, *J* = 5.8 Hz, 1.24 H)**, 2.87–2.81 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5**, 161.1*, 158.4*, 158.1**, 135.6*, 134.7**, 127.5**, 126.8*, 124.3*, 123.7**, 113.6*, 113.4**, 112.9**, 112.7*, 55.2 (s), 46.7*, 43.1**, 41.7**, 37.8*, 29.9**, 28.1*.

HRMS (ESI): *m*/*z* $[M + HCO_2H - H]^-$ calcd for $C_{12}H_{14}NO_4$: 236.0917; found: 236.0921.

7-Bromo-1,2,3,4-tetrahydroisoquinoline-2-carbaldehyde (2c)

Purified by TLC; yellow solid; yield: 42.5 mg (89%); mp 58–60 °C.

IR (neat): 3140, 1672, 1402, 1191, 1157, 1116, 1075, 932, 829 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.24 (s, 0.37 H)*, 8.19 (s, 0.63 H)**, 7.34–7.26 (m, 2 H), 7.02 (t, *J* = 8.8 Hz, 1 H), 4.66 (s, 1.31 H)**, 4.52 (s, 0.72 H)*, 3.78 (t, *J* = 6.2 Hz, 0.72 H)*, 3.65 (t, *J* = 5.8 Hz, 1.32 H)**, 2.86 (t, *J* = 5.8 Hz, 1.28 H)**, 2.82 (t, *J* = 6.0 Hz, 0.80 H)*.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6**, 161.0*, 134.2*, 133.8**, 133.3*, 132.4**, 130.8*, 130.5**, 130.1*, 129.7**, 129.3**, 128.7*, 120.2**, 119.9*, 46.8*, 42.9**, 41.7**, 37.6*, 29.2**, 27.4*.

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{10}H_{14}BrN_2O$: 257.0284; found: 257.0275.

7-Nitro-1,2,3,4-tetrahydroisoquinoline-2-carbaldehyde (2d)

Purified by TLC; brown oil; yield: 28.0 mg (68%).

IR (neat): 3129, 1672, 1525, 1402, 1347, 1088, 855, 744, 531 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (s, 0.37 H)* 8.24 (s, 0.63 H)**, 8.08–8.04 (m, 2 H), 7.33 (t, *J* = 9.0 Hz, 1 H), 4.79 (s, 1.25 H)**, 4.66 (s, 0.74 H)*, 3.85 (t, *J* = 6.0 Hz, 0.72 H)*, 3.72 (t, *J* = 6.0 Hz, 1.27 H)**, 3.03 (t, *J* = 6.0 Hz, 1.23 H)**, 2.99 (t, *J* = 6.0 Hz, 0.76 H)*.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5**, 161.0*, 146.7**, 146.5*, 142.1*, 141.1**, 133.7*, 133.4**, 130.3*, 130.0**, 122.1*, 121.9**, 121.6**, 121.2*, 47.0*, 42.4**, 42.0**, 37.2*, 29.9**, 28.1*.

HRMS (ESI): *m*/*z* [M + CH_3CO_2H – H]$^-$ calcd for $C_{12}H_{13}N_2O_5$: 265.0819; found: 265.0824.

1,3-Dihydro-2*H*-isoindole-2-carbaldehyde (2e)[23]

Purified by TLC; black oil; yield: 23.8 mg (81%).

IR (neat): 3140, 1668, 1465, 1402, 1159, 1092, 747 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (s, 1 H), 7.31–7.27 (m, 4 H), 4.89 (s, 2 H), 4.76 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5, 135.9, 135.2, 128.0, 127.6, 123.2, 122.8, 51.4, 49.8.

HRMS (ESI): *m*/*z* [M + Cl]$^-$ calcd for C_9H_9ClNO: 182.0367; found: 182.0368.

4,5,6,7-Tetrahydrothieno[3,2-*c*]pyridine-5-carbaldehyde (2f)[12a]

Purified by TLC; yellow oil; yield: 31.1 mg (93%).

IR (neat): 3129, 1705, 1670, 1433, 1402, 1314, 1176, 1043, 1018 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (s, 0.38 H)*, 8.20 (s, 0.62 H)**, 7.17–7.15 (m, 1 H), 6.80 (t, *J* = 4.4 Hz, 1 H), 4.60 (s, 1.28 H)**, 4.47 (s, 0.74 H)*, 3.86 (t, *J* = 5.8 Hz, 0.74 H)*, 3.69 (t, *J* = 5.8 Hz, 1.28 H)**, 2.93 (t, *J* = 5.8 Hz, 1.26 H)**, 2.88 (t, *J* = 5.8 Hz, 0.75 H)*.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7**, 161.4*, 133.8*, 132.1**, 130.8**, 130.7*, 125.0**, 124.3*, 123.8 (s), 45.7*, 43.7**, 40.6**, 37.9*, 25.8**, 24.4*.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_8H_{13}N_2SO$: 185.0743; found: 185.0735.

5,7-Dihydro-6*H*-pyrrolo[3,4-*b*]pyridine-6-carbaldehyde (2g)

Purified by TLC; black oil; yield: 28.4 mg (96%).

IR (neat): 3140, 1668, 1584, 1469, 1387, 1262, 1159, 1110 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55–8.52 (m, 1 H), 8.48 (s, 0.60 H)**, 8.44 (s, 0.40 H)*, 7.67–7.62 (m, 1 H), 7.29–7.23 (m, 1 H), 4.95 (s, 0.79 H)*, 4.93 (s, 1.22 H)**, 4.81 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 157.1*, 156.5**, 149.7*, 149.4**, 131.4**, 130.9*, 129.7**, 129.0*, 122.8**, 122.4*, 51.8**, 50.4*, 49.9*, 48.5**.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_8H_9N_2O$: 149.0709; found: 149.0710.

4-Phenylpiperazine-1-carbaldehyde (2h)[24]

Purified by TLC; yellow solid; yield: 30.8 mg (81%); mp 86–87 °C.

IR (neat): 3131, 1664, 1402, 1152, 1115, 529 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08 (s, 1 H), 7.30–7.27 (m, 2 H), 6.94–6.90 (m, 3 H), 3.69 (t, *J* = 5.2 Hz, 2 H), 3.51 (t, *J* = 5.0 Hz, 2 H), 3.15 (dt, *J* = 15.2, 5.2 Hz, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.6, 150.8, 129.1, 120.7, 116.9, 50.3, 49.2, 45.4, 39.8.

HRMS (ESI): *m*/*z* [M + K]$^+$ calcd for $C_{11}H_{14}N_2KO$: 229.0738; found: 229.0742.

4-Phenylpiperidine-1-carbaldehyde (2i)[25]

Purified by TLC; yellow solid; yield: 37.4 mg (99%); mp 98–99 °C.

IR (neat): 3140, 1675, 1653, 1402, 1170, 1064, 759, 699, 529 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (s, 1 H), 7.31 (t, *J* = 7.4 Hz, 2 H), 7.24–7.18 (m, 3 H), 4.56 (d, *J* = 13.6 Hz, 1 H), 3.73 (d, *J* = 13.2 Hz, 1 H), 3.19 (td, *J* = 12.9, 2.6 Hz, 1 H), 2.81–2.67 (m, 2 H), 1.92 (t, *J* = 15.8 Hz, 2 H), 1.67–1.54 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.8, 144.8, 128.5, 126.6, 126.5, 46.4, 42.8, 40.1, 33.8, 32.3.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{15}NNaO$: 212.1046; found: 212.1048.

***N*-Benzyl-*N*-methylformamide (2j)**[26]

Purified by TLC; yellow oil; yield: 13.4 mg (45%).

IR (neat): 3122, 1664, 1402, 1379, 1140, 1066, 1081, 705, 529 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.29 (s, 0.57 H)**, 8.17 (s, 0.43 H)*, 7.40–7.20 (m, 5 H), 4.53 (s, 0.84 H)*, 4.40 (s, 1.16 H)**, 2.85 (s, 1.30 H)*, 2.79 (s, 1.75 H)**.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.8**, 162.6*, 135.9*, 135.6**, 128.9**, 128.7*, 128.2**, 128.1*, 127.6*, 127.4**, 53.5**, 47.7*, 34.0*, 29.4**.

HRMS (ESI): *m*/*z* [M + CH_3CO_2H – H]$^-$ calcd for $C_{11}H_{14}NO_3$: 208.0968; found: 208.0971.

***N*-Benzyl-*N*-ethylformamide (2k)**[27]

Purified by TLC; yellow oil; yield: 14.0 mg (43%).

IR (neat): 3140, 1672, 1497, 1402, 1109, 1079, 740, 703, 528 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (s, 0.50 H)*, 8.23 (s, 0.50 H)**, 7.39–7.21 (m, 5 H), 4.56 (s, 1.05 H)**, 4.40 (s, 1.00 H)*, 3.29 (q, *J* = 7.2 Hz, 0.99 H)*, 3.21 (q, *J* = 7.2 Hz, 1.08 H)**, 1.15 (t, *J* = 7.2 Hz, 1.54 H)**, 1.07 (t, *J* = 7.2 Hz, 1.49 H)*.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6, 136.4**, 136.1*, 128.8*, 128.6**, 128.1**, 128.00*, 127.5*, 127.4**, 50.8*, 44.7**, 41.4**, 36.7*, 14.3**, 12.1*.

HRMS (ESI): *m*/*z* [M + CH_3CO_2H – H]$^-$ calcd for $C_{12}H_{16}NO_3$: 222.1125; found: 222.1119.

***N*-(4-Methoxybenzyl)-*N*-methylformamide (2l)**

Purified by TLC; yellow oil; yield: 19.3 mg (54%).

IR (neat): 3140, 1671, 1612, 1515, 1402, 1303, 1176, 1079, 1032 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (s, 0.58 H)**, 8.08 (s, 0.42 H)*, 7.14 (d, *J* = 8.4 Hz, 0.86 H)*, 7.08 (d, *J* = 8.4 Hz, 1.15 H)**, 6.86–6.81 (m, 2 H), 4.41 (s, 0.86 H)*, 4.28 (s, 1.20 H)**, 3.76 (s, 1.78 H)**, 3.75 (s, 1.23 H)*, 2.78 (s, 1.30 H)*, 2.71 (s, 1.75 H)**.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.5**, 162.4*, 159.3**, 159.0*, 130.3, 129.5*, 128.7**, 128.0*, 127.5**, 114.1**, 113.9*, 113.5, 55.2 (d, *J* = 4.4 Hz)**, 52.8*, 47.0**, 44.7*, 33.8*, 29.1**.

HRMS (ESI): *m*/*z* [M + NH_4]$^+$ calcd for $C_{10}H_{17}N_2O_2$: 197.1285; found: 197.1304.

***N*-Methyl-*N*-phenethylformamide (2m)**[28]

Purified by TLC; yellow oil; yield: 24.1 mg (74%).

IR (neat): 3140, 1666, 1402, 1152, 1529 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (s, 0.37 H)*, 7.80 (s, 0.63 H)**, 7.33–7.22 (m, 4 H), 7.14 (d, *J* = 7.2 Hz, 1 H), 3.56 (t, *J* = 7.6 Hz, 0.79 H)*, 3.47 (t, *J* = 7.0 Hz, 1.25 H),** 2.90–2.82 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.6**, 162.4*, 138.5*, 137.6**, 128.7**, 128.7*, 128.6**, 128.5*, 126.7**, 126.4*, 51.2**, 45.9*, 35.0*, 34.7**, 33.1*, 29.7*.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{13}NO$: 164.1070; found: 164.1071.

N-Methyl-*N*-(naphthalen-1-ylmethyl)formamide (2n)

Purified by TLC; yellow oil; yield: 21.9 mg (55%).

IR (neat): 3140, 1672, 1510, 1402, 1258, 1161, 1081, 803, 779, 529 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.39 (s, 0.40 H)*, 8.17 (s, 0.60 H)**, 8.11 (d, *J* = 8.0 Hz, 0.64 H), 7.91–7.82 (m, 2.46 H), 7.55–7.30 (m, 4 H), 4.98 (s, 1.22 H)**, 4.88 (s, 0.78 H)*, 2.86 (s, 1.23 H)*, 2.75 (s, 1.78 H)**.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.2*, 162.2**, 133.7, 131.4, 131.2**, 131.1*, 131.0*, 130.9**, 129.0*, 128.8**, 128.7*, 128.6**, 127.6*, 126.6*, 126.0**, 125.4*, 125.3*, 125.0**, 123.7*, 122.20, 50.9*, 45.8**, 33.9**, 29.9*.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{14}NO$: 200.1070; found: 200.1069.

N-Formylfluoxetine (2o)

Purified by TLC; yellow oil; yield: 45.8 mg (68%).

IR (neat): 3140, 1675, 1616, 1519, 1329, 1251, 1161, 1113, 1068 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (s, 0.41 H)*, 7.99 (s, 0.59 H)**, 7.43 (d, *J* = 8.8 Hz, 2 H), 7.37–7.27 (m, 5 H), 6.90–6.86 (m, 2 H), 5.20 (dd, *J* = 8.8, 4.4 Hz, 0.42 H)*, 5.14 (dd, *J* = 8.8, 4.0 Hz, 0.61 H)**, 3.59–3.52 (m, 1.42 H)**, 3.42–3.35 (m, 0.62 H)*, 2.94 (s, 1.21 H)*, 2.90 (s, 1.84 H)**, 2.27–2.17 (m, 1.06 H), 2.15–2.04 (m, 1.15 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.7**, 162.6*, 160.1*, 159.8**, 140.3*, 139.8**, 129.0**, 128.8*, 128.2**, 128.0*, 126.9–126.7 (m), 125.6*, 125.5**, 123.3–122.7 (m), 115.7*, 115.6**, 78.1*, 76.8**, 45.9**, 41.5*, 36.9**, 35.8*, 34.8*, 29.5**.

^{19}F NMR (377 MHz, $CDCl_3$): δ = –61.52 (s)*, –61.59 (s)**.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{18}F_3NNaO_2$: 360.1182; found: 360.1178.

1-(3,4-Dimethoxybenzyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline-2-carbaldehyde (2p)[29]

Purified by TLC; white solid; yield: 73.5 mg (99%); mp 147–148 °C.

IR (neat): 3138, 1664, 1517, 1402, 1260, 1236, 1113, 1027 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (s, 0.39 H)*, 7.69 (s, 0.61 H)**, 6.83–6.56 (m, 4.76 H), 6.33 (s, 0.37 H), 5.52 (t, *J* = 6.2 Hz, 0.39 H), 4.60–4.56 (m, 0.61 H), 4.49–4.45 (m, 0.62 H), 3.87–3.84 (m, 9.71 H), 3.76 (s, 1.23 H), 3.69 (s, 1.28 H), 3.58–3.54 (m, 0.41 H), 3.31–3.24 (m, 0.40 H), 3.17–2.77 (m, 3.76 H), 2.73–2.59 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.4**, 161.3*, 149.1**, 148.7*, 148.3, 148.1, 147.9, 147.8, 147.6**, 147.3*, 130.0*, 129.7**, 127.4**, 127.1*, 126.2**, 125.4*, 122.0*, 121.8**, 112.8, 112.5, 111.6, 111.4, 111.3, 110.9, 110.4, 109.9, 59.0, 56.1, 56.0, 55.9, 55.9, 55.8, 55.8, 52.1, 43.1, 41.5, 40.9, 34.2, 29.1, 27.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{26}NO_5$: 372.1806; found: 372.1812.

N-Benzylformamide (2q)[14c]

Purified by TLC; yellow solid; yield: 24.6 mg (91%); mp 54–58 °C.

IR (neat): 3140, 1666, 1402, 699, 526 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25 (s, 0.87 H)**, 8.16 (d, *J* = 12 Hz, 0.13 H)*, 7.35–7.27 (m, 5 H), 6.08 (br s, 1 H), 4.48 (d, *J* = 6.0 Hz, 1.73 H)**, 4.41 (d, *J* = 6.4 Hz, 0.34 H)*.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.7*, 161.0**, 137.5**, 137.4*, 128.9*, 128.7**, 127.9*, 127.7**, 127.6**, 126.9*, 45.6*, 42.1**.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_8H_{10}NO$: 136.0757; found: 136.0747.

N-Phenethylformamide (2r)[21]

Purified by TLC; yellow oil; yield: 24.1 mg (81%).

IR (neat): 3140, 1670, 1402, 1154, 689, 527 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (s, 0.84 H)**, 7.89 (d, *J* = 12 Hz, 0.16 H)*, 7.32–7.20 (m, 5 H), 5.83 (br s, 1 H), 3.59–3.46 (m, 2 H), 2.86–2.82 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5*, 161.2**, 138.4**, 137.5*, 128.8–128.6 (m), 126.8*, 126.6**, 43.1*, 39.1**, 37.6*, 35.4**.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_9H_{11}NNaO$: 172.0733; found: 172.0741.

N-(3-Phenylpropyl)formamide (2s)[14b]

Purified by TLC; yellow oil; yield: 29.7 mg (91%).

IR (neat): 3122, 1666, 1402, 1154, 1113, 749, 701, 529 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (s, 0.82 H)**, 7.99 (d, *J* = 12 Hz, 0.18 H)*, 7.32–7.17 (m, 5 H), 6.04 (br s, 1 H), 3.31 (q, *J* = 6.8 Hz, 1.64 H)**, 3.20 (q, *J* = 6.8 Hz, 0.36 H)*, 2.68–2.64 (m, 2 H), 1.89–1.82 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8*, 161.3**, 141.1**, 140.5*, 128.5*, 128.4**, 128.3**, 126.2*, 126.0**, 41.0*, 37.7**, 33.0**, 32.4*, 32.4*, 31.0**.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_{13}NNaO$: 186.0889; found: 186.0897.

N-(1-Phenylethyl)formamide (2t)[30]

Purified by TLC; yellow oil; yield: 18.2 mg (61%).

IR (neat): 3100, 1662, 1534, 1497, 1402, 1238, 1118 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (s, 1 H), 7.38–7.25 (m, 5 H), 6.33 (br s, 1 H), 5.22–5.15 (m, 0.82 H)**, 4.71–4.64 (m, 0.19 H)*, 1.55 (d, *J* = 6.8 Hz, 0.53 H)*, 1.50 (d, *J* = 6.8 Hz, 2.47 H)**.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.3, 142.5, 128.8*, 128.6**, 127.7*, 127.4**, 126.0**, 125.7*, 51.6*, 47.5**, 23.5*, 21.7**.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_9H_{12}NO$: 150.0913; found: 150.0912.

Methyl 4-(Formamidomethyl)benzoate (2u)

Purified by TLC; white solid; yield: 28.2 mg (73%); mp 119–120 °C.

IR (neat): 3153, 1731, 1655, 1400, 1280, 1101, 1019, 766, 705 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (s, 0.87 H)**, 8.19 (d, *J* = 12 Hz, 0.13 H)*, 8.04–7.98 (m, 2 H), 7.36–7.32 (m, 2 H), 6.21 (br s, 1 H), 4.53 (d, *J* = 6.0 Hz, 1.79 H)**, 4.48 (d, *J* = 6.4 Hz, 0.27 H)*, 3.92 (s, 0.40 H)*, 3.91 (s, 2.68 H)**.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.8**, 164.7*, 161.2, 142.8**, 142.6*, 130.2*, 130.0**, 129.9*, 129.5**, 127.5**, 126.8*, 52.2*, 52.2**, 45.3*, 41.8**.

HRMS (ESI): *m*/*z* [M + Li]$^+$ calcd for $C_{10}H_{11}NLiO_3$: 200.0894; found: 200.0892.

***N*-Dodecylformamide (2v)**[26]

Purified by TLC; gray solid; yield: 34.9 mg (82%); mp 33–34 °C.

IR (neat): 3122, 1670, 1401, 1150, 1113, 529 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (s, 0.82 H)**, 8.03 (d, *J* = 12 Hz, 0.18 H)*, 5.63 (br s, 1 H), 3.28 (q, *J* = 6.8 Hz, 1.66 H)**, 3.20 (q, *J* = 6.8 Hz, 0.44 H)*, 1.53–1.48 (m, 2 H), 1.29–1.24 (m, 18 H), 0.87 (t, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.7*, 161.0**, 41.8*, 38.2**, 31.9**, 31.2*, 29.6–29.1 (m), 26.8**, 26.3*, 22.6, 14.1.

HRMS (ESI): *m*/*z* [M + K]$^+$ calcd for $C_{13}H_{27}NKO$: 252.1724; found: 252.1724.

***N*-(2-Hydroxy-2-phenylethyl)formamide (2w)**[31]

Purified by TLC; yellow oil; yield: 30.7 mg (93%).

IR (neat): 3140, 1670, 1523, 1495, 1402, 1239, 1198, 1096, 915 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (s, 0.83 H)**, 7.86 (d, *J* = 12 Hz, 0.17 H)*, 7.34–7.27 (m, 5 H), 6.35 (br s, 1 H), 4.80 (dd, *J* = 8.6, 3.4 Hz, 0.84 H)**, 4.70 (dd, *J* = 7.4, 3.8 Hz, 0.18 H)*, 3.73–3.67 (m, 1.80 H)**, 3.45–3.37 (m, 0.19 H)*, 3.33–3.27 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4*, 162.2**, 141.4**, 140.8*, 128.7*, 128.5**, 128.2*, 128.0**, 125.8*, 125.8**, 73.3*, 72.9**, 49.2*, 45.7**.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_9H_{12}NO_2$: 166.0863; found: 166.0860.

***N*-Indan-1-ylformamide (2x)**[32]

Purified by TLC; yellow solid; yield: 28.3 mg (88%); mp 109–110 °C.

IR (neat): 3118, 1640, 1547, 1402, 1154, 1115, 751, 529 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (s, 0.89 H)**, 8.21 (s, 0.11 H)*, 7.30–7.19 (m, 4 H), 6.00 (br s, 1 H), 5.55 (q, *J* = 8.0 Hz, 0.80 H)**, 4.99 (q, *J* = 8.0 Hz, 0.19 H)*, 3.03–2.96 (m, 1 H), 2.92–2.84 (m, 1 H), 2.64–2.55 (m, 1 H), 1.92–1.79 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.8*, 160.9**, 143.3**, 142.5*, 128.4*, 128.1**, 127.0*, 126.8**, 125.0*, 124.8**, 123.9**, 123.7*, 57.4*, 53.2**, 35.1*, 33.9**, 30.2**, 29.8*.

HRMS (ESI): *m*/z [M + CH_3CO_2H – H]$^-$ calcd for $C_{12}H_{14}NO_3$: 220.0968; found: 220.0971.

***N*-(3,4-Dimethoxyphenethyl)formamide (2y)**[33]

Purified by TLC; yellow oil; yield: 38.0 mg (91%).

IR (neat): 3140, 3006, 2941, 1668, 1593, 1467, 1400, 1265, 1029 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (s, 0.85 H)**, 7.87 (d, *J* = 12 Hz, 0.15 H)*, 6.79–6.65 (m, 3 H), 5.93 (br s, 1 H), 3.83 (s, 3.73 H)**, 3.82 (s, 2.25 H)*, 3.51 (q, *J* = 6.4 Hz, 1.64 H)**, 3.41 (q, *J* = 6.4 Hz, 0.36 H)*, 2.77–2.71 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.5*, 161.2**, 148.9*, 148.8**, 147.7*, 147.5**, 130.8**, 128.0*, 120.8*, 120.5**, 111.8*, 111.6**, 111.3*, 111.1**, 55.8**, 55.7*, 43.2*, 39.2**, 37.2*, 34.9**.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{16}NO_3$: 210.1125; found: 210.1122.

***N*-Acetyl-1,2,3,4-tetrahydroisoquinoline (2z)**[34]

Purified by TLC; yellow oil; yield: 30.1 mg (86%).

IR (neat): 3159, 3029, 2933, 1661, 1634, 1456, 1403, 1299, 1034 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.09 (m, 4 H), 4.72 (s, 1.13 H)**, 4.61 (0.87 H)*, 3.81 (t, *J* = 5.8 Hz, 0.85 H)*, 3.67 (t, *J* = 5.8 Hz, 1.15 H)**, 2.90 (t, *J* = 5.8 Hz, 1.22 H)**, 2.84 (t, *J* = 5.8 Hz, 0.89 H)*, 2.18 (s, 1.26 H)*, 2.17 (s, 1.67 H)**.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.5**, 169.5*, 135.0*, 133.9**, 133.4**, 132.4*, 128.9*, 128.2**, 126.9*, 126.6**, 126.5**, 126.5*, 126.3**, 126.0*, 48.0*, 44.0**, 43.9**, 39.4*, 29.4**, 28.434*, 21.9*, 21.6**.

HRMS (ESI): *m*/*z* [M + HCO_2H – H]$^-$ calcd for $C_{12}H_{14}NO$: 220.0968; found: 220.0981.

***N*-Propanoyl-1,2,3,4-tetrahydroisoquinoline (2za)**[35]

Purified by TLC; yellow oil; yield: 32.9 mg (87%).

IR (neat): 3120, 2983, 1694, 1646, 1454, 1401, 1310, 1053 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.08 (m, 4 H), 4.73 (s, 1.16 H)**, 4.61 (s, 0.94 H)*, 3.83 (t, *J* = 6.0 Hz, 0.96 H)*, 3.67 (t, *J* = 5.8 Hz, 1.12 H)**, 2.89 (t, *J* = 6.0 Hz, 1.30 H)**, 2.84 (t, *J* = 5.8 Hz, 0.88 H)*, 2.47–2.40 (m, 2 H), 1.21–1.16 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.8**, 172.8*, 135.2*, 134.1**, 133.7**, 132.7*, 128.9*, 128.2**, 126.9, 126.7, 126.5, 126.5, 126.3, 126.0, 47.2*, 44.2**, 43.1**, 39.7*, 29.5**, 28.5*, 27.0*, 26.8**, 9.4**, 9.3*.

HRMS (ESI): *m*/*z* [M + HCO_2H – H]$^-$ calcd for $C_{13}H_{16}NO_3$: 234.1125; found: 234.1125.

***N*-Benzoyl-1,2,3,4-tetrahydroisoquinoline (2zb)**[36]

Purified by TLC; yellow oil; yield: 11.9 mg (25%).

IR (neat): 3153, 2363, 2345, 1633, 1402, 1299, 1258, 1107, 934 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44 (m, 5 H), 7.22–7.17 (m, 4 H), 4.90 (s, 1.13 H)**, 4.59 (s, 0.87 H)*, 4.00 (s, 0.83 H)*, 3.65 (s, 1.20 H)**, 2.98–2.88 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.0, 136.1, 132.9, 129.8, 128.5, 127.1–126.6 (m), 49.8, 45.3, 44.9, 40.5, 29.6, 28.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{16}NO$: 238.1226; found: 238.1222.

***N*-(4-Phenylpiperazin-1-yl)acetamide (2zc)**[37]

Purified by TLC; white solid; yield: 38.4 mg (94%); mp 80–82 °C.

IR (neat): 3138, 2822, 1655, 1500, 1402, 1232, 1158, 999, 760, 695 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.27 (m, 2 H), 6.94–6.89 (m, 3 H), 3.77 (t, *J* = 5.2 Hz, 2 H), 3.62 (t, *J* = 5.2 Hz, 2 H), 3.19–3.13 (m, 4 H), 2.14 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.1, 151.0, 129.3, 120.6, 116.7, 49.8, 49.4, 46.3, 41.4, 21.4.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{16}N_2NaO$: 227.1155; found: 227.1157.

***N*-Methyl-*N*-phenethylacetamide (2zd)**

Purified by TLC; pale yellow oil; yield: 34.1 mg (96%).

IR (neat): 3029, 2935, 1651, 1402, 1202, 1129, 1079, 1033, 1005 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.15 (m, 5 H), 3.58 (t, *J* = 7.6 Hz, 0.98 H), 3.51 (t, *J* = 7.2 Hz, 1.02 H), 2.95 (s, 1.50 H), 2.88 (s, 1.50 H), 2.84 (t, *J* = 7.4 Hz, 2 H), 2.07 (s, 1.45 H), 1.85 (s, 1.48 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.5, 170.4, 139.1*, 138.1**, 128.7, 128.7, 128.6, 128.4, 126.7, 126.2, 52.5**, 49.6*, 36.8*, 34.6**, 33.6**, 33.3*, 21.8*, 20.8**.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{11}H_{15}NNaO$: 200.1046; found: 200.1039.

N-Methyl-*N*-(naphthalen-1-ylmethyl)acetamide (2ze)[38]

Purified by TLC; yellow oil; yield: 35.4 mg (83%).

IR (neat): 3140, 1655, 1402, 1262, 1163, 792 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 8.0 Hz, 0.66 H), 7.86–7.79 (m, 2.39 H), 7.58–7.21 (m, 4.17 H), 5.06 (s, 1.28 H)**, 4.98 (s, 0.72 H)*, 3.05 (s, 1.12 H)*, 2.83 (s, 1.89 H)**, 2.17 (s, 1.99 H)**, 2.12 (s, 1.23 H)*.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.6*, 170.4**, 133.8**, 133.7*, 132.6, 131.6, 131.3, 130.6, 129.0, 128.5, 128.4, 128.0, 126.9, 126.5, 126.4, 126.0, 125.9, 125.5, 125.1, 123.8, 122.3*, 121.9**, 52.0*, 48.3**, 34.8**, 34.3*, 22.0**, 21.2*.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{15}NNaO$: 236.1046; found: 236.1041.

5-Acetyl-4,5,6,7-tetrahydrothieno[3,2-*c*]pyridine (2zf)[39]

Purified by TLC; pale yellow oil; yield: 30.8 mg (85%).

IR (neat): 3111, 3014, 2928, 2850, 1634, 1403, 1241, 1217, 1010 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16–7.13 (m, 1 H), 6.81–6.78 (m, 1 H), 4.67 (s, 1.05 H)**, 4.55 (s, 0.95 H)*, 3.91 (t, *J* = 5.6 Hz, 0.95 H)*, 3.74 (t, *J* = 5.6 Hz, 1.07 H)**, 2.92 (t, *J* = 5.6 Hz, 1.08 H)**, 2.86 (t, *J* = 5.6 Hz, 0.93 H)*, 2.19 (s, 1.59 H)**, 2.17 (s, 1.38 H)*.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.6*, 169.4**, 134.3*, 132.3**, 132.0*, 131.0**, 125.1**, 124.3*, 123.5*, 123.3**, 46.3*, 44.1**, 42.3**, 39.4*, 25.5**, 24.6*, 21.9*, 21.5**.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_9H_{11}NSNaO$: 204.0454; found: 204.0452.

N-Benzylacetamide (2zg)[40]

Purified by TLC; colorless solid; yield: 25.6 mg (86%); mp 62–63 °C.

IR (neat): 3282, 1651, 1556, 1402, 1290, 1079, 1031 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.25 (m, 5 H), 6.13 (br s, 1 H), 4.39 (d, *J* = 6.0 Hz, 2 H), 1.99 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.0, 138.2, 128.6, 127.8, 127.4, 43.6, 23.2.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_9H_{11}NNaO$: 172.0733; found: 172.0728.

1-(4-Phenylpiperazin-1-yl)propan-1-one (2zh)

Purified by TLC; yellow oil; yield: 40.2 mg (92%).

IR (neat): 3137, 1653, 1601, 1498, 1402, 1230, 1157, 1029 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.27 (m, 2 H), 6.94–6.89 (m, 3 H), 3.78 (t, *J* = 4.8 Hz, 2 H), 3.62 (t, *J* = 4.6 Hz, 2 H), 3.18–3.14 (m, 4 H), 2.39 (q, *J* = 7.6 Hz, 2 H), 1.18 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.2, 150.9, 129.1, 120.4, 116.5, 49.6, 49.3, 45.2, 41.3, 26.4, 9.4.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{18}N_2NaO$: 241.1311; found: 241.1305.

N-Methyl-*N*-phenethylpropanamide (2zi)

Purified by TLC; yellow oil; yield: 36.3 mg (95%).

IR (neat): 3152, 1649, 1402, 1152, 531 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.15 (m, 5 H), 3.58 (t, *J* = 7.6 Hz, 1.08 H)**, 3.50 (t, *J* = 7.4 Hz, 0.92 H)*, 2.96 (s, 1.39 H)*, 2.87 (s, 1.58 H)**, 2.84 (t, *J* = 7.4 Hz, 2 H), 2.30 (q, *J* = 7.2 Hz, 1.06 H)**, 2.12 (q, *J* = 7.6 Hz, 0.91 H)*, 1.14 (t, *J* = 7.4 Hz, 1.61 H)**, 1.03 (t, *J* = 7.4 Hz, 1.38 H)*.

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.7*, 173.5**, 139.3**, 138.2*, 128.8*, 128.7**, 128.4, 126.7*, 126.2**, 51.5*, 50.0**, 35.9*, 34.9**, 33.8**, 33.5*, 26.8**, 25.9*, 9.5*, 9.2**.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{18}NO$: 192.1383; found: 192.1379.

N-Methyl-*N*-(naphthalen-1-ylmethyl)propanamide (2zj)

Purified by TLC; yellow oil; yield: 37.3 mg (82%).

IR (neat): 3144, 1651, 1510, 1403, 1256, 1120, 1066, 794 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 8.0 Hz, 0.64 H), 7.92–7.78 (m, 2.39 H), 7.58–7.50 (m, 3.11 H), 7.32 (d, *J* = 7.2 Hz, 0.64 H), 7.20 (d, *J* = 7.2 Hz, 0.37 H), 5.07 (s, 1.27 H)**, 4.99 (s, 0.73 H)*, 3.07 (s, 1.06 H)*, 2.82 (s, 1.89 H)**, 2.44–2.32 (m, 2 H), 1.22 (t, *J* = 7.4 Hz, 1.90 H), 1.14 (t, *J* = 7.6 Hz, 1.19 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.7*, 173.6**, 133.8**, 133.7*, 132.9**, 131.7**, 131.6*, 130.6*, 129.0*, 128.5**, 128.3**, 127.9*, 127.0*, 126.4**, 126.0*, 125.9**, 125.6*, 125.1**, 123.9, 122.3*, 121.9**, 51.0*, 48.5**, 34.5*, 34.0**, 26.9**, 26.1*, 9.5*, 9.4**.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{17}NNaO$: 250.1202; found: 250.1196.

1-(4,5,6,7-Tetrahydrothieno[3,2-*c*]pyridin-5-yl)propan-1-one (2zk)

Purified by TLC; pale yellow oil; yield: 23.4 mg (60%).

IR (neat): 3122, 1648, 1429, 1402, 1264, 1224, 1046, 889, 706 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16–7.13 (m, 1 H), 6.82–6.78 (m, 1 H), 4.68 (s, 1.06 H)**, 4.55 (s, 0.94 H)*, 3.93 (t, *J* = 5.6 Hz, 0.96 H)*, 3.75 (t, *J* = 5.8 Hz, 1.05 H)**, 2.91 (t, *J* = 5.6 Hz, 1.11 H)**, 2.86 (t, *J* = 5.6 Hz, 0.95 H)*, 2.48–2.39 (m, 2 H), 1.22–1.16 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9, 172.7, 134.5, 132.6, 132.1, 131.2, 125.2, 124.4, 123.5, 123.3, 45.4*, 43.3**, 42.6**, 39.7*, 27.0*, 26.8**, 25.7**, 24.7*, 9.5**, 9.3*.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_{13}NSNaO$: 218.0610; found: 218.0603.

N-Benzylpropanamide (2zl)[41]

Purified by TLC; yellow oil; yield: 21.2 mg (65%).

IR (neat): 3289, 1651, 1554, 1402, 1236, 1105, 1031, 732, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.27 (m, 5 H), 5.93 (br s, 1 H), 4.42 (d, *J* = 5.6 Hz, 2 H), 2.24 (q, *J* = 7.6 Hz, 2 H), 1.17 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.6, 138.3, 128.6, 127.7, 127.4, 43.5, 29.6, 9.8.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_{13}NNaO$: 186.0889; found: 186.0890.

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Supporting Information

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