Accepted Manuscript

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PII: S0040-4020(17)30330-7

DOI: 10.1016/j.tet.2017.03.073

Reference: TET 28579

To appear in: *Tetrahedron*

Received Date: 31 January 2017

Revised Date: 24 March 2017

Accepted Date: 26 March 2017

Please cite this article as: Yuan C, Du B, Xun M-M, Liu B, Oxidative cleavage of hydroxamic acid promoted by sodium periodate, *Tetrahedron* (2017), doi: 10.1016/j.tet.2017.03.073.

Graphical Abstract

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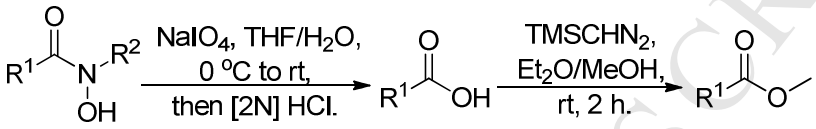

Tetrahedron
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Oxidative Cleavage of Hydroxamic Acid Promoted by Sodium Periodate

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

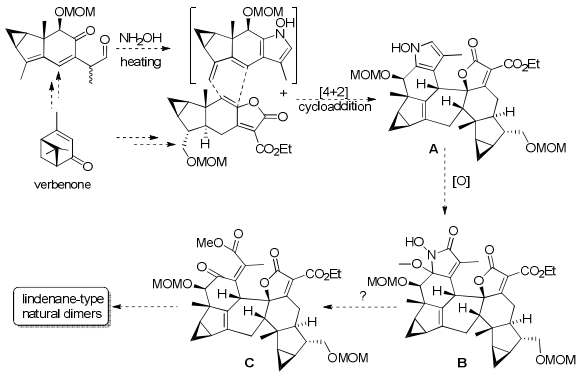
Keywords:
hydroxamic acid
ester
carboxylic acid
oxidative cleavage

ABSTRACT

A series of hydroxamic acids, involving aliphatic, aromatic and cyclic substrates, were transformed to the corresponding carboxylic acids through $NaIO_4$-mediated oxidative cleavage in mild conditions. Esterification of these acids with $TMSCHN_2$ could result in formation of the corresponding methyl ester. This methodology makes good compensation for the existing methods transforming amides to esters. Our results also pave the way to harness hydroxamic acids as useful synthetic building blocks.

1. Introduction

Hydroxamic acids are widely found in natural products with various biological activities,[1] synthetic intermediates,[2] and chiral ligands.[3] Accordingly, numerous synthetic approaches to hydroxamic acids have been developed, involving acylation of hydroxylamines,[2g,4] oxidation of arylacyl amides,[5] reaction of aromatic nitroso compounds with oxoacids,[6] coupling of carboxylic acids or their derivatives (acyl halides, anhydrides, and esters) with hydroxylamine or protected hydroxylamines,[7] and NHC-catalyzed coupling of aldehydes with *N*-arylnitroso compounds.[8] However, on the other hand, conversion of hydroxamic acids into other carboxylic acid derivatives through C-N oxidative cleavage has not been systematically studied, although scattered examples were reported though utilizing such oxidants as $NaIO_4$,[9] NaClO[10] and $K_3Fe(CN)_6$.[11] In other words, the potential of hydroxamic acids serving as synthetic building blocks toward carboxylic acid derivatives in organic synthesis need to be well exploited, which arouse our interest during our efforts on total synthesis of lindenane-type sesquiterpnoid dimers.[12] We actually conceived different strategies to realize the final transformation toward tetrasubstituted alkenes in the target molecules, one of which are depicted in scheme 1. Synthetically, a [4+2] cycloadduct **A** might be accessed from a diene fragment and a dienophile fragment, both achievable from verbenone. After oxidative elaboration of pyrrole in the intermediate **A**, a lactam could be generated to afford **B**. Oxidative cleavage of cyclic hydroxamic acid and esterification would produce the intermediate **C**, which would be transformed to different ~~lindenane~~-type natural dimers.



Scheme 1 A plausible application of oxidative cleavage of hydroxamic acid.

Structurally, hydroxamic acids can be regarded as special amides with one of the amide N-H bond replaced by a N-OH bond. Because of the electon-donating effect of nitrogen to carbonyl, amides are well-known as poor electrophiles.[13] So transformation of amides to other more labile carboxylic acid derivatives is really challenging. To solve this problem, synthetically useful methods for conversion of amides into esters and carboxylic acids were developed,[13,14] involving applicatiion of a trialkyloxonium tetrafluoroborate salt,[15] electrophilic preactivation of amides with trifluoromethanesulfonic anhydride (Tf_2O) and base,[16] copper-mediated methanolysis of bispicolylamine-substituted amides at room teperature,[17] nickel-catalyzed methanolysis of amides,[14,18] and so on.[19] In addition,

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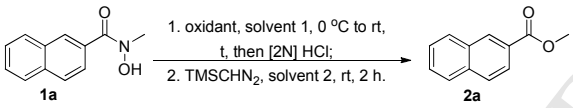
N,*N*´-dialkylhydrazides, as analogs of hydroxamic acids, can be efficiently cleaved to generate the corresponding carboxylic acids upon treatment with PhI(OH)OTs.[20] Herein, we present a mild method for conversion of hydroxamic acids to methyl esters or carboxylic acids by treatment with $NaIO_4$ in mild reaction conditions, which may greatly extend their potential application in organic synthesis.[17,21]

2. Results and Discussion

Initial studies were focused on the cleavage of a model substrate, *N*-hydroxy-*N*-methyl-2-naphthamide (**1a**), with various oxidants (Table 1, entries 1-9). Lead (IV) acetate was employed to promote the reaction in benzene, whereas formation of 2-naphthoic acid was not observed even though full conversion of **1a** (Table 1, entry 1). So was the case in which $NaClO_2$ was attempted in mixed THF/H_2O as solvents (Table 1, entry 2). Interestingly, treating **1a** with $NaClO_2$ in aqueous methanol afforded 2-naphthoic acid smoothly,[10] which was subsequently transformed to **2a** in 66% yield over two steps through esterification with $TMSCHN_2$ (Table 1, entry 3). As for $K_3Fe(CN)_6$, methyl 2-naphthoate was generated in 57% yield, and the presence of NaOH is crucial; otherwise, there is no reaction at all (Table 1, entry 4).[11] When we utilized Dess-Martin periodinane as the oxidant, an inferior yield was obtained (Table 1, entry 5). Other oxidants involving IBX, $PhI(OCOCF_3)_2$ and $PhI(OAc)_2$ were effective as well and delivered the desired products in moderate yields (Table 1, entries 6-8). To our delight, utilization of $NaIO_4$ provided **2a** in the highest yield (94%; Table 1, entry 9). Accordingly, $NaIO_4$ was selected as the optimal oxidant for this reaction.

Table 1. Optimization of the Reaction Conditions[a]

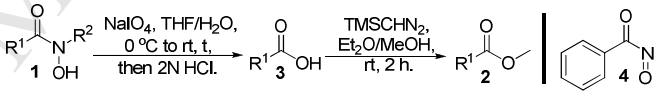


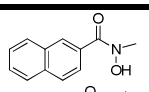
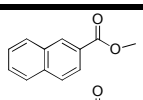
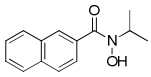
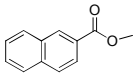
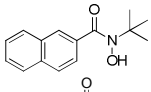
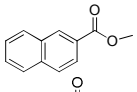
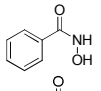
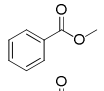
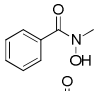
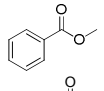
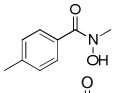
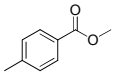
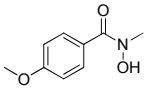
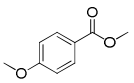
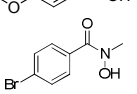
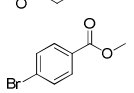
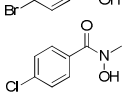
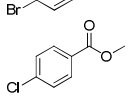
entry	oxidant	solvent 1	t (h)	solvent 2	yield[b] (%)
1[c]	$Pb(OAc)_4$	bezene	0.5	--	--
2[c]	$NaClO_2$	THF/H_2O	0.5	--	--
3[d]	$NaClO_2$	MeOH/H_2O	15	THF/MeOH	66
4[e]	$K_3Fe(CN)_6$	THF/H_2O	4	THF/MeOH	57
5	DMP	THF/H_2O	0.5	THF/MeOH	38[f]
6	IBX	THF/H_2O	0.5	THF/MeOH	65
7	$PhI(OCOCF_3)_2$	THF/H_2O	0.5	THF/MeOH	61
8	$PhI(OAc)_2$	THF/H_2O	0.5	THF/MeOH	72
9	$NaIO_4$	THF/H_2O	0.5	THF/MeOH	94
10	$NaIO_4$	acetone/H_2O	0.5	THF/MeOH	94
11	$NaIO_4$	MeOH/H_2O	0.5	THF/MeOH	90
12	$NaIO_4$	MeCN/H_2O	0.5	THF/MeOH	80
13	$NaIO_4$	THF/H_2O	0.5	Et_2O/MeOH	98
14[g]	$NaIO_4$	THF/H_2O	0.5	DCM/MeOH	98
15[h]	$NaIO_4$	THF/H_2O	0.5	MeOH	98

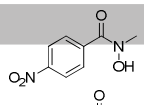
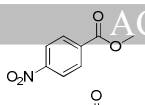
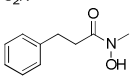
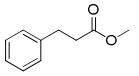
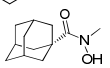
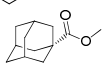
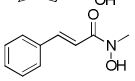
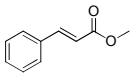
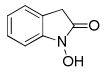
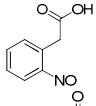
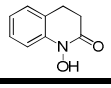
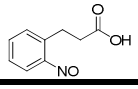
[a] Unless otherwise specified, the reaction was carried out with **1a** (1.0 mmol) and the oxidant (2.0 mmol) in solvent 1 (10 mL, v/v = 4/1) and was monitored by TLC. After complete conversion, 0.5 mL of 2N HCl solution was added to quench the reaction. After workup and concentration, esterification of the resultant acid with $TMSCHN_2$ (2.0 mmol) in solvent 2 (9 ml, v/v = 2/1) afforded methyl 2-naphthoate (**2a**). [b] Isolated yield. [c] 2-Naphthoic acid could not be obtained in this entry. [d] This reaction was performed with $NaClO_2$ (3.0 mmol) in MeOH (7.5 mL) and H_2O (2.5 ml). [e] $K_3Fe(CN)_6$ (4.0 mmol) and NaOH (4.0 mmol) was added. [f] The yield was determined by ^1H NMR with 4-bromoacetophenone as internal standard. [g] $TMSCHN_2$ (3.5 mmol) was added to ensure complete esterification. [h] $TMSCHN_2$ (7.0 mmol) was added to ensure complete esterification.

Subsequently, various solvent system were investigated for conversion of **1a** to 2-naphthoic acid. We noticed that the mixed THF/H_2O system behaved as well as the mixed acetone/H_2O system to afford **2a** in the same yields (Table 1, entries 9 and 10). Lower yields were obtained in the MeOH/H_2O system and the MeCN/H_2O system (Table 1, entries 11-12). Then the solvent effect in esterification of 2-naphthoic acid with $TMSCHN_2$ was investigated. Among mixed solvent systems, including THF/MeOH, Et_2O/MeOH and DCM/MeOH, and absolute methanol, the Et_2O/MeOH solvent system was determined to be the best (Table 1, entry 13), considering more $TMSCHN_2$ required to ensure complete transformation of 2-naphthoic acid in mixed DCM/MeOH and absolute methanol (Table 1, entries 14-15). Thus, the optimal reaction conditions for transformation from **1a** to **2a** were established: 1.0 mmol of hydroxamic acid was reacted with 2.0 mmol of $NaIO_4$ in a mixture of THF and H_2O (8 mL/2 mL) at 0 °C to rt until complete conversion; then the reaction was acidized with 0.5 mL of 2N HCl solution; after workup and concentration, esterification of the resultant acid with $TMSCHN_2$ (2.0 mmol) in mixed Et_2O and MeOH (6 mL/3 mL).

Table 2. Scope of the reaction of **1** to generate **2** or **3**[a]

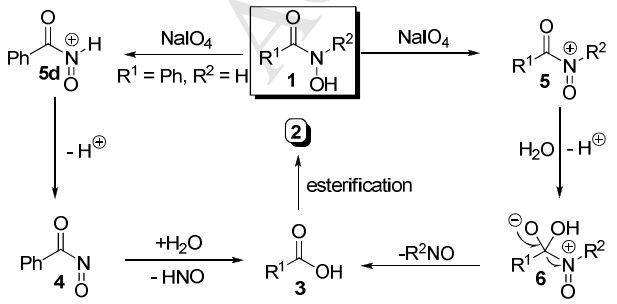


entry	substrate (**1**)		t (h)	Product (**2**/**3**)		yield[b] (%)
1		**1a**	0.5		**2a**	98
2		**1b**	6.5		**2a**	95
3		**1c**	12.0		**2a**	91
4[c]		**1d**	12.5		**2d**	83
5		**1e**	0.5		**2d**	89
6		**1f**	0.5		**2f**	92
7		**1g**	0.5		**2h**	96
8		**1h**	0.5		**2h**	95
9		**1i**	0.5		**2i**	92

10		**1j**	0.5	 **2j**	98
11		**1k**	0.5	 **2k**	96
12		**1l**	1.0	 **2l**	92
13		**1m**	0.5	 **2m**	96
14		**1n**	0.5	 **3n**	81[d]
15		**1o**	0.5	 **3o**	84[d]

[a] Unless otherwise specified, the reaction was carried out with **1** (1.0 mmol) and $NaIO_4$ (2.0 mmol) in THF (8 mL) and H_2O (2 mL) and was monitored by TLC to ensure complete conversion. After quenching the reaction with 0.5 mL of 2N HCl solution and routine workup, esterification of the resultant acid with $TMSCHN_2$ (2.0 mmol) in Et_2O (6 ml) and MeOH (3 mL) afforded **2**. [b] Isolated yield. [c] This reaction was carried out with **1d** (1.0 mmol) and $NaIO_4$ (2.0 mmol) in THF (8 mL) and H_2O (2 mL) and stirred for 30 min. After THF was removed, the residue was diluted in MeOH (8 mL) and HCl solution (2.0 M, 1.0 mL) and the solution was stirred at rt for 12 h; then esterification with $TMSCHN_2$ afforded **2d**. [d] Isolated yield of **3**; esterification was not conducted.

With the optimized reaction conditions in hand, we set out to investigate oxidative cleavage of versatile hydroxamic acids. As shown in Table 2, both the aromatic and the aliphatic hydroxamic acids were testified to be applicable into this methodology. Replacing methyl group in **1a** by more bulky aliphatic group such as isopropyl and *tert*-butyl resulted in slower reaction albeit in similar yields (Table 2, entries 1-3). Interestingly, when benzohydroxamic acid **1d** was treated with $NaIO_4$, an acyl nitroso **4** was firstly generated as known chemistry.[22] Compound **4** could be then slowly converted into benzoic acid in MeOH/H_2O at acidic condition at room temperature, and subsequent esterificatioin produced **2d** (Table 2, entry 4). Subsequently, different substituted aromatic hydroxamic acids **1e**-**1j**, with both electron-donating and electron-withdrawing groups at the para positions, produced the corresponding methyl esters without significant difference (Table 2, entries 5-10), indicating that electronic factor is not pivotal for this reaction. An aliphatic hydroxamic acid **1k** provided **2k** similarly in 96% yield, while compound **1l** with bulky admantyl group provided **2l** in excellent yield as well albeit after a little bit longer time (Table 2, entries 11-12). Similarly, α,β-unsaturated hydroxamic acid **1m** provided the desired products **2m** in satisfying yield (Table 2, entry 13). However, when cyclic substrates **1n** and **1o** was attempted, only the corresponding carboxylic acids **3n** and **3o** could be achieved respectively (Table 2, entries 14 and 15). Esterification failed to give methyl esters, probably due to lability of nitroso groups in **3n** and **3o**.



Scheme 2 Proposed reaction mechanism

Based on the above examples and previous research by other groups,[11,22] a plausible mechanisn for this reaction is shown in scheme 2. Periodate oxidation of hydroxamic acid **1** in THF/H_2O might yield the oxoammonium **5,** which could be nucleophilicly attacked by water to generate the intermediate **6**. After removal of one molecule of nitroso compound, the corresponding carboxylic acid **3** could be produced. Esterification of the resultant acid with $TMSCHN_2$ accomplishes methyl ester **2**. This mechanism was supported by formation of the stable acyl nitroso species **4** through oxidation of benzohydroxamic acid.[22] Compound **4** with less electrophilic character than **5** can be attacked by water in acidic condition to generate HNO after longer time, as illustrated in entry 4, table 2. Isolation of compound **3n** and **3o** supports this mechanism as well.

3. Conclusion

In conclusion, we have demonstrated a mild conversion of hydroxamic acids to methyl esters or carboxylic acids through $NaIO_4$-mediated oxidative cleavage of amide C-N bonds. This methodology is potentially applicable in organic synthesis as an surrogate to the existing synthetic methods transforming amides to esters or acids.

4. Experimental Section

4.1. General information

All non-aqueous reactions were carried out using flame-dried round-bottomed flasks under an inert atmosphere of argon with dry solvents. Dichloromethane (DCM) and triethylamine (TEA) were distilled from calcium hydride under argon; Tetrahydrofuran (THF) and ethyl ether were distilled from Na/benzophenone under argon; Methanol (MeOH) was distilled from dry magnesium turnings and iodine under argon. All the other chemicals were purchased commercially and used without further purification, unless otherwise stated. Flash chromatography was performed using silica gel (200-300 mesh). Reactions were monitored by thin layer chromatography (TLC). Visualization was achieved under a UV lamp (254 nm and 365 nm), I_2 and by developing the plates with *p*-anisaldehyde or phosphomolybdic acid. ^1H and ^{13}C NMR were recorded on Bruker DRX-400 MHz NMR spectrometer with TMS as the internal standard and were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: ^1H NMR = 7.26, ^{13}C NMR = 77.16; $(CD_3)_2SO$: ^1H NMR = 2.50 and 3.30, ^{13}C NMR = 39.52). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Coupling constants (*J*) are reported in Hertz (Hz). High resolution mass spectra (HRMS) were recorded by using FTMS-7 spectrometers. Infrared (IR) spectra were recorded on a NEXUS 670 FT-IR Fourier transform infrared spectrophotometer and are reported in wavenumbers (cm^{-1}).

4.2. General procedure for the preparation of compounds 1a, 1e, 1g, 1h and 1j

To a solution of MeNHOH•HCl (1.62 g, 19.4 mmol, 1.5 equiv) and DMAP (158 mg, 1.29 mmol, 0.1 equiv) in DCM (100 mL) was added Et_3N (3.92 g, 5.38 mL, 38.7 mmol, 3.0 equiv) at room temperature. Then the mixture was cooled to 0 °C and a solution of the corresponding acyl chloride (12.9 mmol, 1.0 equiv) in DCM (30 mL) was added dropwise. After stirring for 4.5 h at rt, the resulting mixture was quenched with H_2O (150 mL) at 0 °C. The layers were separated and the aqueous layer was extracted with DCM (3 × 100 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column

chromatography on silica gel to furnish the corresponding product (**1a, 1e, 1g, 1h** or **1j)**.

4.2.1. *N-hydroxy-N-methyl-2-naphthamide* (**1a**)

DCM-MeOH (v/v = 40:1), white solid, 2.29 g, 88% yield; IR (thin film): 3165, 2923, 1607, 1496, 1430, 1388, 1273, 1250, 1196, 1170, 1125, 1067, 963, 906, 865, 822, 756, 577, 477 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.87 (br s, 1H), 8.04 (s, 1H), 7.90 - 7.87 (m, 3H), 7.61 - 7.53 (m, 3H), 3.46 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 168.8, 133.5, 132.3, 132.0, 128.6, 128.3, 127.6, 127.3, 127.1, 126.6, 125.6, 37.4; HRMS (ESI): m/z calcd for $C_{12}H_{11}NO_2Na$ $[M+Na]^+$ 224.0682 found 224.0678.

4.2.2. *N-hydroxy-N-methylbenzamide* (**1e**)

Petroleum ether-EtOAc (v/v = 1:1), orange oil, 1.30 g, 67% yield; IR (thin film): 3438, 2925, 1607, 1570, 1430, 1388, 1218, 1182, 1071, 935, 909, 786, 708, 646, 556 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.54 - 7.41 (m, 5H), 3.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 132.8, 130.7, 128.3, 127.9, 38.4; HRMS (ESI): m/z calcd for $C_8H_9NO_2Na$ $[M+Na]^+$ 174.0525 found 174.0523.

4.2.3. *N-hydroxy-4-methoxy-N-methylbenzamide* (**1g**)

DCM-MeOH (v/v = 40:1), white solid, 2.06 g, 88% yield; IR (thin film): 3155, 2928, 2845, 1605, 1568, 1464, 1433, 1384, 1304, 1254, 1221, 1178, 1117, 1027, 842, 757, 596 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.49 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 3.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 161.7, 130.1, 124.5, 113.8, 55.5, 38.8; HRMS (ESI): m/z calcd for $C_9H_{10}NO_3$ $[M]^-$ 180.0666 found 180.0666.

4.2.4. *4-bromo-N-hydroxy-N-methylbenzamide* (**1h**)

DCM-MeOH (v/v = 40:1), white solid, 2.10 g, 71% yield; IR (thin film): 3165, 2923, 1597, 1560, 1473, 1431, 1391, 1264, 1218, 1181, 1074, 1012, 933, 836, 744, 553 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 3.38 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 167.7, 134.0, 130.8, 130.5, 123.6, 37.2; HRMS (ESI): m/z calcd for $C_8H_7BrNO_2$ $[M]^-$ 227.9666 found 227.9667.

4.2.5. *N-hydroxy-N-methyl-4-nitrobenzamide* (**1j**)

DCM-MeOH (v/v = 40:1), brown solid, 2.14 g, 84% yield; IR (thin film): 3738, 3437, 3109, 2875, 1630, 1591, 1512, 1468, 1389, 1219, 1182, 1107, 1069, 860, 720, 677, 559 cm^{-1}; ^1H NMR (400 MHz, $(CD_3)_2SO$) δ 10.27 (s, 1H), 8.27 - 8.25 (m, 2H), 7.82 (d, *J* = 8.8 Hz, 2H), 3.28 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 167.0, 148.0, 141.2, 129.5, 123.1, 36.8; HRMS (ESI): m/z calcd for $C_8H_7N_2O_4$ $[M]^-$ 195.0411 found 195.0409.

4.3. General procedure for preparation of compounds 1b, 1c, 1f, 1i, 1k, 1l and 1m[7c]

To a solution of MeNHOH•HCl (459.0 mg, 5.50 mmol, 1.1 equiv; for **1f, 1i**, **1k**, **1l** and **1m**) or ^{i}PrNHOH•HCl (614 mg, 5.50 mmol, 1.1 equiv; for **1b**) or ^{t}BuNHOH•HCl (691 mg, 5.5 mmol, 1.1 equiv; for **1c**) in DCM (70 mL) was added $NaHCO_3$ (1.05 g, 12.5 mmol, 2.5 equiv) at room temperature. Then the mixture was cooled to 0 °C and a solution of the corresponding acyl chloride (5.00 mmol, 1.0 equiv) in DCM (30 mL) was added. After stirring overnight at rt, the insoluble precipitate was filtered off and the solvent was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to provide the corresponding hydroxamic acid (**1b**, **1c**, **1f**, **1i**, **1k**, **1l** or **1m**).

4.3.1. *N-hydroxy-N-isopropyl-2-naphthamide* (**1b**)

DCM-MeOH (v/v = 70:1), brown solid, 676 mg, 59% yield; IR (thin film): 2986, 2776, 1585, 1562, 1477, 1362, 1331, 1192, 1129, 1057, 903, 865, 820, 784, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.92 - 7.87 (m, 3H), 7.60 - 7.54 (m, 3H), 4.29 (dt, *J* = 12.8, 6.4 Hz, 1H), 1.34 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 134.4, 132.7, 130.1, 128.8, 128.7, 128.0, 127.8, 127.1, 124.3, 52.8, 19.9; HRMS (ESI): m/z calcd for $C_{14}H_{15}NO_2Na$ $[M+Na]^+$ 252.0995 found 252.0996.

4.3.2. *O-(2-naphthoyl)-N-(tert-butyl)hydroxylamine* (**1c'**) and *N-(tert-butyl)-N-hydroxy-2-naphthamide* (**1c**)

1c': petroleum ether-EtOAc (v/v = 20:1), colourless oil, 916 mg, 75% yield; IR (thin film): 3223, 3061, 2974, 1716, 1630, 1599, 1508, 1471, 1431, 1389, 1365, 1282, 1222, 1194, 1130, 1083, 989, 955, 914, 865, 765, 593, 474 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.91 - 7.88 (m, 2H), 7.69 (br s, 1H), 7.63 - 7.54 (m, 2H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 135.7, 132.6, 131.0, 129.5, 128.6, 128.5, 127.9, 127.0, 125.8, 124.8, 56.3, 26.8; HRMS (ESI): m/z calcd for $C_{15}H_{17}NO_2Na$ $[M+Na]^+$ 266.1151 found 266.1153.

1c: petroleum ether-EtOAc (v/v = 2:1), white solid, 174 mg, 14% yield; IR (thin film): 3126, 2967, 2847, 1715, 1587, 1470, 1418, 1361, 1275, 1205, 1151, 1122, 1089, 1029, 953, 905, 863, 820, 755, 476 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.92 (s, 1H), 7.86 - 7.83 (m, 3H), 7.57 - 7.49 (m, 3H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 134.0, 133.7, 132.5, 128.6, 128.1, 128.0, 127.6, 127.4, 126.9, 124.7, 62.1, 29.0; HRMS (ESI): m/z calcd for $C_{15}H_{17}NO_2Na$ $[M+Na]^+$ 266.1151 found 266.1150.

4.3.3. *N-hydroxy-N,4-dimethylbenzamide* (**1f**)

Petroleum ether-EtOAc (v/v = 1:1), white solid, 761 mg, 92% yield; IR (thin film): 3099, 2876, 1598, 1560, 1495, 1464, 1433, 1390, 1219, 1180, 1119, 1073, 836, 785, 744, 684 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 3.39 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 141.3, 129.5, 129.1, 128.1, 38.6, 21.5; HRMS (ESI): m/z calcd for $C_9H_{11}NO_2Na$ $[M+Na]^+$ 188.0682 found 188.0680.

4.3.4. *4-chloro-N-hydroxy-N-methylbenzamide* (**1i**)

Petroleum ether-EtOAc (v/v = 1:1), white solid, 862 mg, 93% yield; IR (thin film): 3150, 2925, 1600, 1562, 1514, 1475, 1431, 1390, 1309, 1262, 1218, 1179, 1092, 1016, 841, 797, 749, 684, 553, 507, 469 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.66 (br s, 1H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 3.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 137.2, 130.8, 129.6, 128.9, 38.5; HRMS (ESI): m/z calcd for $C_8H_8ClNO_2Na$ $[M+Na]^+$ 208.0136 found 208.0134.

4.3.5. *N-hydroxy-N-methyl-3-phenylpropanamide* (**1k**)

Petroleum ether-EtOAc (v/v = 1:1), brown gum, 672 mg, 75% yield; IR (thin film): 3173, 2928, 1615, 1496, 1449, 1391, 1199, 1112, 1075, 1030, 964, 750, 700, 558, 486 cm^{-1}; ^1H NMR (400 MHz, $(CD_3)_2SO$) δ 9.84 (s, 1H), 7.28 - 7.15 (m, 5H), 3.09 (s, 3H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.64 (t, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 172.1, 141.6, 128.3, 125.8, 35.8, 33.4, 30.1; HRMS (ESI): m/z calcd for $C_{10}H_{14}NO_2$ $[M+H]^+$ 180.1019 found 180.1027.

4.3.6. *(3r,5r,7r)-N-hydroxy-N-methyladamantane-1-carboxamide* (**1l**)

Petroleum ether-EtOAc (v/v = 4:1), white solid, 805 mg, 77% yield; IR (thin film): 3179, 2906, 2853, 1590, 1451, 1414, 1383,

1315, 1264, 1205, 1104, 1062, 979, 922, 811 733 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.62 (br s, 1H), 3.42 - 3.38 (m, 3H), 2.02 - 2.00 (m, 9H), 1.74 - 1.67 (m, 6H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 175.7, 40.7, 37.9, 37.6, 36.4, 27.8; HRMS (ESI): m/z calcd for $C_{12}H_{20}NO_2$ $[M+H]^+$ 210.1489 found 210.1496.

4.3.7. *N-hydroxy-N-methylcinnamamide* (**1m**)

Petroleum ether-EtOAc (v/v = 1:1), white solid, 744 mg, 84% yield; IR (thin film): 3734, 3131, 2924, 2854, 2784, 1731, 1635, 1575, 1534, 1451, 1388, 1187, 1107, 988, 799, 763, 700, 677, 574, 484, 451 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.73 (br s, 1H), 7.72 (d, *J* = 15.6 Hz, 1H), 7.52 (s, 2H), 7.37 (s, 3H), 6.68 (br s, 1H), 3.50 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 165.6, 140.9, 135.0, 129.7, 129.0, 128.8, 127.9, 117.3, 36.1; HRMS (ESI): m/z calcd for $C_{10}H_{11}NO_2Na$ $[M+Na]^+$ 200.0682 found 200.0686.

4.4. General procedure for the preparation of compounds 1n and 1o

Compounds **1n** and **1o** can be prepared according to known procedure.[2b]

4.4.1. *1-hydroxyindolin-2-one* (**1n**)

^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.2 Hz, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 3.52 (s, 2H); ^1H NMR (400 MHz, $(CD_3)_2SO$) δ 10.66 (s, 1H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.00 (t, *J* = 7.3 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 3.55 (s, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 169.4, 143.7, 127.7, 124.4, 122.0, 121.2, 106.8, 33.4.

4.4.2. *1-hydroxy-3,4-dihydroquinolin-2(1H)-one* (**1o**)

^1H NMR (400 MHz, $CDCl_3$) δ 9.63 (br s, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.04 (td, *J* = 7.6, 0.8 Hz, 1H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.77 - 2.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 137.5, 127.8, 127.4, 123.9, 123.7, 113.3, 30.2, 24.6.

4.5. General procedure for conversion of hydroxamic acids (1a-c and 1e-m) to methyl esters

To a solution of hydroxamic acids (1.0 mmol, 1.0 equiv) in THF (8.0 mL) and H_2O (2.0 mL) was added $NaIO_4$ (428 mg, 2.00 mmol, 2.0 equiv) at 0 °C. Then the reaction was warmed to rt with stirring and was monitored by TLC to ensure complete conversion. The solution was concentrated under reduced pressure to remove THF, and the residue mixture was diluted with H_2O (15 mL), acidized with aqueous HCl solution (2.0 M, 0.5 mL). The aqueous layer was extracted with EtOAc (4 × 50 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure to provide the crude carboxylic acid, which was directly used for next step.

To a solution of the above crude carboxylic acid in Et_2O (6.0 mL) and MeOH (3.0 mL) was added $TMSCHN_2$ (2.0 M in hexane, 1.0 mL, 2.0 equiv) at rt. After stirring for 2 h at rt, the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to provide the corresponding methyl ester (**2**).

4.5.1. *methyl 2-naphthoate* (**2a**)

Petroleum ether-EtOAc (v/v = 50:1), white solid, for **1a**: t = 0.5 h, 182 mg, 98% yield; for **1b**: t = 6.5 h, 177 mg, 95% yield; for **1c**: t = 12.0 h, 170 mg, 91% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.07 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.61 - 7.52 (m, 2H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 135.6, 132.6, 131.2, 129.5, 128.3, 128.3, 127.9, 127.5, 126.8, 125.3, 52.4.

4.5.2. *methyl benzoate* (**2d**)

^{n}Pentane/Et_2O (v/v = 40:1), pale yellow oil, for **1f**: t = 0.5 h, 120 mg, 89% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 - 8.03 (m, 2H), 7.57 - 7.53 (m, 1H), 7.46 - 7.42 (m, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 133.0, 130.3, 129.7, 128.5, 52.2.

4.5.3. *methyl 4-methylbenzoate* (**2f**)

^{n}Pentane/Et_2O (v/v = 30:1), white solid, t = 0.5 h, 138 mg, 92% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 143.7, 129.7, 129.2, 127.5, 52.1, 21.8.

4.5.4. *methyl 4-methoxybenzoate* (**2g**)

Petroleum ether-EtOAc (v/v = 30:1), white solid, t = 0.5 h, 160 mg, 96% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 - 7.97 (m, 2H), 6.93 - 6.89 (m, 2H), 3.88 (s, 3H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 163.4, 131.6, 122.60, 113.6, 55.4, 51.9.

4.5.5. *methyl 4-bromobenzoate* (**2h**)

Petroleum ether-EtOAc (v/v = 50:1), white solid, t = 0.5 h, 204 mg, 95% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 - 7.88 (m, 2H), 7.58 - 7.56 (m, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 131.9, 131.3, 129.2, 128.2, 52.4.

4.5.6. *methyl 4-chlorobenzoate* (**2i**)

Petroleum ether-EtOAc (v/v = 30:1), white solid, t = 0.5 h, 157 mg, 92% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 139.5, 131.1, 128.9, 128.7, 52.4.

4.5.7. *methyl 4-nitrobenzoate* (**2j**)

Petroleum ether-EtOAc (v/v = 30:1), white solid, t = 0.5 h, 178 mg, 98% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.8 Hz, 2H), 8.20 (d, *J* = 8.4 Hz, 2H), 3.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 150.6, 135.6, 130.8, 123.7, 53.0.

4.5.8. *methyl 3-phenylpropanoate* (**2k**)

^{n}Pentane/Et_2O (v/v = 30:1), pale yellow oil, t = 0.5 h, 157 mg, 96% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 - 7.28 (m, 2H), 7.23 - 7.20 (m, 3H), 3.68 (s, 3H), 2.96 (t, *J* = 8.0 Hz, 2H), 2.66 - 2.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 140.6, 128.6, 128.4, 126.4, 51.8, 35.8, 31.1.

4.5.9. *(3r,5r,7r)-methyl adamantane-1-carboxylate* (**2l**)

^{n}Pentane/Et_2O (v/v = 60:1), white solid, t = 1.0 h, 179 mg, 92% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 3.63 (s, 3H), 1.99 (s, 3H), 1.87 (d, *J* = 2.8 Hz, 6H), 1.74 - 1.65 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.3, 51.6, 40.8, 39.0, 36.6, 28.0.

4.5.10. *methyl 3-phenylpropanoate* (**2m**)

^{n}Pentane/Et_2O (v/v = 40:1), pale yellow solid, t = 0.5 h, 156 mg, 96% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.55 - 7.50 (m, 2H), 7.39 - 7.37 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 145.0, 134.5, 130.4, 129.0, 128.2, 117.9, 51.8.

4.6. Procedure for conversion of benzohydroxamic acid (1d) to methyl benzoate (2d)

To a solution of benzohydroxamic acid (137 mg, 1.00 mmol, 1.0 equiv) in THF (8.0 mL) and H_2O (2.0 mL) was added $NaIO_4$ (428 mg, 2.00 mmol, 2.0 equiv) at 0 °C. After being stirred for 30 min at rt, the mixture was concentrated under reduced pressure to remove THF, diluted with H_2O (15 mL) and acidized with HCl

(2.0 M in H_2O, 1.0 mL). Then MeOH (8.0 mL) was added to the mixture. After stirring for 12 h at rt, the resulting mixture was concentrated under reduced pressure to remove MeOH and extracted with EtOAc (4 × 50 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure to provide crude benzoic acid, which was directly used for next step.

To a solution of the above crude benzoic acid in Et_2O (6.0 mL) and MeOH (3.0 mL) was added $TMSCHN_2$ (2.0 M in hexane, 1.0 mL, 2.0 equiv) at rt. After stirring for 2 h at rt, the mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (^{n}pentane/Et_2O v/v = 40:1) to obtain methyl benzoate (**2d**, 113 mg, 83%) as a pale yellow oil.

4.7. General procedure for conversion of cyclic hydroxamic acids (1n and 1o) to carboxylic acids (3n and 3o)

To a solution of cyclic benzohydroxamic acid (**1n** or **1o**, 1.00 mmol, 1.0 equiv) in THF (8.0 mL) and H_2O (2.0 mL) was added $NaIO_4$ (428 mg, 2.00 mmol, 2.0 equiv) at 0 °C. After being stirred for 30 min at rt, the mixture was concentrated under reduced pressure to remove THF, diluted with H_2O (15 mL), acidized with HCl (2.0 M in H_2O, 0.5 mL) and extracted with EtOAc (4 × 50 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to furnish the corresponding products (**3n** or **3o)**.

4.7.1. *2-(2-nitrosophenyl)acetic acid* (**3n**)

Petroleum ether-EtOAc (v/v = 1:1) to EA, yellow solid, 134 mg, 81% yield; IR (thin film): 3154, 2930, 1945, 1712, 1621, 1555, 1453, 1408, 1252, 1170, 814, 752, 618 cm^{-1}; ^1H NMR (400 MHz, $(CD_3)_2SO$) δ 12.60 (br s, 1H), 7.82 (td, *J* = 7.6, 1.2 Hz, 1H), 7.75 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.41 - 7.37 (m, 1H), 6.38 (dd, *J* = 8.0, 0.8 Hz, 1H), 4.73 (s, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 172.6, 164.1, 138.9, 137.2, 133.4, 127.5, 107.4, 36.8; HRMS (ESI): m/z calcd for $C_8H_8NO_3$ $[M+H]^+$ 166.0499 found 166.0498.

4.7.2. *3-(2-nitrosophenyl)propanoic acid* (**3o**)

Petroleum ether-EtOAc (v/v = 1:1), yellow solid, 151 mg, 84% yield; IR (thin film): 3066, 2924, 2844, 1711, 1524, 1486, 1448, 1348, 1280, 1207, 1164, 1071, 1020, 989, 757 cm^{-1}; ^1H NMR (400 MHz, $(CD_3)_2SO$) δ 12.27 (br s, 1H), 7.83 - 7.76 (m, 2H), 7.32 - 7.28 (m, 1H), 6.18 (d, *J* = 8.0 Hz, 1H), 4.04 (t, *J* = 8.0 Hz, 2H), 2.83 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 173.5, 164.4, 145.3, 137.5, 132.3, 126.6, 105.8, 36.2, 25.7; HRMS (ESI): m/z calcd for $C_9H_9NO_3Na$ $[M+Na]^+$ 202.0475 found 202.0472.

Acknowledgments

We acknowledge financial support from the NSFC (21672153 and 21290180). Financial support from the Open Fund of State Key Laboratory of Natural Medicines in China Pharmaceutical University is acknowledged (SKLNMKF201601).

Supplementary Material

The supplementary data associated with this article can be found in the online version.

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