Tetrahedron Letters 53 (2012) 1413–1416

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

An efficient copper (II)-catalyzed direct access to primary amides from aldehydes under neat conditions

Nemai C. Ganguly *, Sushmita Roy, Pallab Mondal

Department of Chemistry, University of Kalyani, Kalyani 741235, WB, India

ARTICLE INFO

Article history:
Received 11 November 2011
Revised 6 January 2012
Accepted 8 January 2012
Available online 13 January 2012

Keywords:
Aldehydes
Primary amides
Copper sulfate pentahydrate
Sodium acetate
Hydroxylamine hydrochloride

ABSTRACT

A simple expeditious one-pot conversion of a wide assortment of aldehydes to corresponding primary amides in good to excellent yields has been accomplished employing hydroxylamine hydrochloride (1 mol equiv), sodium acetate (1.1 mol equiv), and copper sulfate pentahydrate (5 mol %) under neat conditions at 110 °C. The protocol based upon ligand-free copper (II)-catalysis avoids the use of relatively expensive late transition metal-based catalysts, and is performed under operationally simple conditions without any demanding procedure of isolation and purification of products.

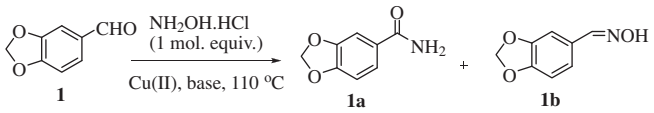
Amide functionality is widely prevalent in pharmaceuticals and drug candidates as well as various industrial materials including detergents and lubricants.[1] Amides are commonly prepared by the reaction of activated carboxylic acid derivatives such as acid chlorides, acid anhydrides, or esters with amines or direct coupling of acids with amines assisted by carbodiimides/*N*,*N*′-dicarbonyldiimidazole.[2] These methods are low in atom efficiency, often involve potentially explosive molecules as catalysts and generate substantial waste[3] making their environmental profile unfavorable. This is the compelling reason for identifying atom-economical, safe, and efficient amide bond formation as a key thrust area of green chemistry research.[4] Mild, highly selective enzymatic methods of hydrolysis of nitriles by nitrile hydrolases and lipase-catalyzed amidation of acids and esters with ammonia represent greener approaches but prohibitive isolation costs and applicability to a limited range of substrates constitute serious drawbacks.[5] The Beckmann rearrangement of ketoximes to secondary amides under electrophilic catalysis of Lewis and Bronsted acids provides efficient atom-economic access to secondary amides.[6] Similar isomerization of aldoximes to primary amides is ordinarily precluded due to poor migratory aptitude of hydrogen. To circumvent this difficulty expensive late transition metal-based catalysts such as those of Rh,[7] Ru,[8] Ir,[9] Au–Ag,[10] and Pd[11] have been employed which usually involve sequential dehydration of aldoximes to nitriles and their controlled hydration to primary amides. Very recently, utilization of indium and zinc salts[12] for this purpose has been also reported. We became interested in step-economic direct conversion of aldehydes to primary amides avoiding isolation of aldoximes. Available literature reports on Cu^{II}-catalyzed synthesis of nitriles from aldoximes[13,14] motivated us to explore one-pot Cu^{II}-catalyzed conversion of aldehydes to primary amides. The success of this endeavor primarily hinges upon identifying an appropriate Cu(II) salt as Lewis acid activator and finding out right conditions that would favor dehydration of oxime to nitrile and its facile concomitant hydration to amide rather than its cleavage to parent aldehyde. To this end, copper sulfate pentahydrate was considered an attractive candidate in view of its attenuated Lewis acidity, ability to coordinate with oximic hydroxy group and excellent performance as an alcohol dehydration catalyst.[15] Herein, we reveal a simple direct method of copper sulfate pentahydrate-catalyzed conversion of aromatic aldehydes into primary amides via aldoximes under neat conditions.

Exploratory experiments were carried out with piperonal (3,4-methylenedioxybenzaldehyde) **1**, a DOPA precursor, as a representative aromatic aldehyde. We chose piperonal as its oxime is hydrolytically labile under Lewis acid-catalyzed conditions[16] and, therefore, expected to provide a good feel of mildness and selectivity of amide formation against competing deprotection process. We screened a number of Cu(II)-salt catalysts such as $CuSO_4{\cdot}5H_2O$, $Cu(OTf)_2$, $Cu(NO_3)_2$, $Cu(OAc)_2{\cdot}H_2O$, the results of which are exhibited in Table 1. Initially, an equimolar mixture of piperonal (**1**), hydroxylamine hydrochloride and fused sodium acetate together with a catalytic amount of $CuSO_4{\cdot}5H_2O$ (10 mol %) was submitted to reaction in refluxing toluene for 3 h to yield 3,4-methylenedi-

* Corresponding author. Fax: +91 33 25828282.
E-mail address: nemai_g@yahoo.co.in (N.C. Ganguly).

0040-4039/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2012.01.029

Table 1
Optimization experiments of Cu(II)-catalyzed conversion of aldehyde **1** to amide **1a**.



Entry	Cu(II) salt (mol %)	Base (mol equiv)	Solvent	Reaction[a] time (h)	% Yield[b] of	
					1a	**1b**
1	$CuSO_4{\cdot}5H_2O$ (10)	NaOAc (1)	Toluene	3	70	15
2	$Cu(OTf)_2$ (10)	NaOAc (1)	Toluene	3	62	20
3	CuSO4.5H2O (10)	NaOH (1)	Toluene	3	65	25
4	$CuSO_4{\cdot}5H_2O$ (10)	Et_3N (1)	Toluene	3	10	75
5	$CuSO_4{\cdot}5H_2O$ (10)	Na_2CO_3 (1)	Toluene	3	68	23
6	$CuSO_4{\cdot}5H_2O$ (10)	K_2CO_3 (1)	Toluene	3	64	22
7	$CuSO_4{\cdot}5H_2O$ (10)	NaOAc (1.1)	—	2	96	—
8	$CuSO_4{\cdot}5H_2O$ (5)	NaOAc (1.1)	—	2	98	—
9	$CuSO_4{\cdot}5H_2O$ (5)	NaOAc (2)	—	2	95	—
10	$CuSO_4$ (5)	NaOAc (1.1)	—	2	96	—
11	$CuSO_4{\cdot}5H_2O$ (5), MS 4 Å	NaOAc (1.1)	—	2	94	—
12	$CuSO_4{\cdot}5H_2O$ (5)	K_2CO_3 (1.1)	—	2	90	—
13	$CuSO_4{\cdot}5H_2O$ (5)	Na_2CO_3 (1.1)	—	2	88	—
14	$Cu(OTf)_2$ (5)	NaOAc (1.1)	—	2	80	5
15	$Cu(NO_3)_2$ (5)	NaOAc (1.1)	—	2	90	—
16	$Cu(OAc)_2.H_2O$ (5)	NaOAc (1.1)	—	2	89	—

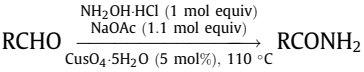
[a] Reactions were performed on 1 mmolar scale.
[b] Isolated yields after column chromatoghaphy.

oxybenzamide **1a** as the major product (70%) accompanied with a considerable amount of piperonal oxime **1b** (entry 1). There was further erosion in the selectivity of amide formation when copper triflate replaced copper sulfate pentahydrate (entry 2). Sodium hydroxide, triethylamine, anhydrous sodium carbonate, and potassium carbonate were tried as bases to demask hydroxylamine from its hydrochloride but only to deliver poorer results under identical reaction conditions in terms of selectivity and yield of amide (entries 3–6). The failure of triethylamine is presumably linked with its ability to deactivate Cu(II)-catalyst by offering nucleophilic nitrogen as an alternative coordination site. A serious synthetic constraint of all these liquid phase experiments (entries 1–6) was the persistent contamination of the desired amide with the oxime **1b**.

To circumvent this difficulty, we decided to explore solvent-free variation of the reaction. To protect against the cleavage of oximes triggered by protons released by hydrolysis of copper salts,[15,17] it was envisaged that mild basic conditions might be conducive and this was bolstered by previous reports of base-assisted conversions of aldoximes to nitriles.[18] Gratifyingly, treatment of an equimolar mixture of **1**, $NH_2OH.HCl$ together with a slight excess of fused NaOAc (1.1 mol equiv) and 10 mol % of $CuSO_4{\cdot}5H_2O$ at 110 °C under neat conditions vastly biased the reaction in favor of amide formation providing **1a** exclusively in a 96% yield within 2 h (entry 7). Optimization of catalyst loading further revealed that an impressive yield of 98% could be attained even with a lower catalyst loading of 5 mol % (entry 8). Interestingly, anhydrous copper sulfate, prepared by heating the pentahydrate at 200–300 °C under reduced pressure, delivered similar excellent yield of amide. The presence of dessicant, 4 Å molecular sieves did not alter the outcome of the reaction significantly. The results clearly suggest that 'external' water released from the hydrated copper salt has no important role in the reaction sequence. A few Cu(II)-salts such as $Cu(OTf)_2$, $Cu(NO_3)_2$, $Cu(OAc)_2{\cdot}H_2O$ were tested for their efficacy under identical solvent-free conditions (entry 14–16) but copper sulfate pentahydrate showed best catalytic performance among copper salts.

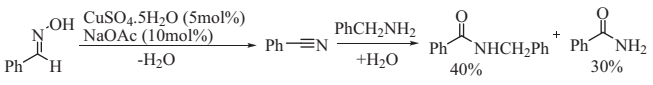
To assay the scope and generality of the protocol, a wide range of aldehydes, mainly aromatic and heteroaromatic ones, were subjected to optimized reaction conditions and the results are summarized in Table 2.

Table 2
Cu(II)-catalyzed conversion of aldehydes to primary amides under neat conditions



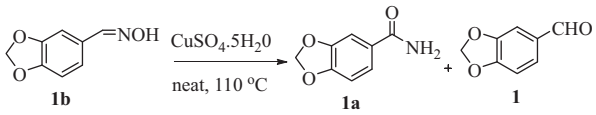
Entry	R	Time[a]/h	% Yield of amide[b]
1	3,4-(-OCH_2O-)C_6H_3	2	98
2	C_6H_5	2	95
3	2-Cl C_6H_4	6	45
4	4-Cl C_6H_4	3	90
5	2-NO_2 C_6H_4	6	40
6	4-NO_2 C_6H_4	4	86
7	4-Me C_6H_4	2	98
8	4-OH C_6H_4	6	78[c]
9	4-OMe C_6H_4	2	97
10	4-Allyloxy C_6H_4	3	95
11	4-Propargyloxy C_6H_4	3	98
12	4-Allyloxy,3-OMe C_6H_3	4	96
13	3-(2-Methylallyloxy) C_6H_4	4	98
14	4-OH,3-OMe C_6H_3	6	70[c]
15	9-Anthracyl	7	50
16	2-Thiophenyl	5	90
17	2-Furyl	5	92
18	2-Styryl	5	90
19	$C_6H_5CH_2$	5	95
20	$(CH_3)_2CH$	5	66

[a] Reaction conditions: aldehyde (1 mmol), $NH_2OH.HCl$ (1 mmol), NaOAc (1.1 mmol), $CuSO_4.5H_2O$ (5 mol %), 110 °C, under air.
[b] Isolated yield upon column chromatography over silica gel; the products were characterized by spectral data (FTIR, ^1H and ^{13}C NMR and MS).
[c] Varying amounts (10–20%) of unreacted aldehydes were isolated.



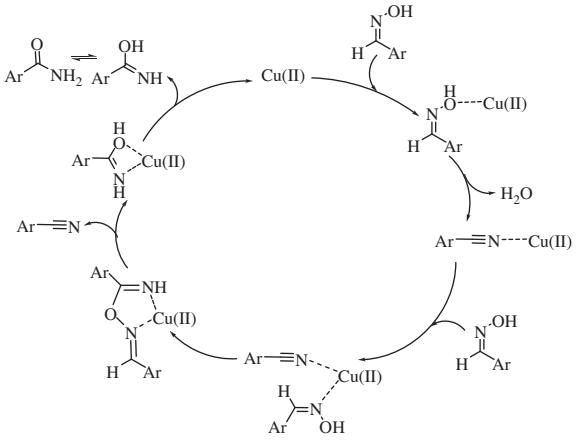
Scheme 1. Synthesis of *N*-benzylbenzamide by traping benzonitrile with benzylamine.

Table 3
Control experiments to assess the role of Cu(II)-catalysis in amide formation



Entry	Cu(II) salt (mol %)	Additive (mol %)	Reaction[a] time (h)	% Yield[b] of	
				1a	1
1	—	NaOAc (10)	2	—	—
2	$CuSO_4{\cdot}5H_2O$ (5)	NaOAc (10)	2	97	—
3	$CuSO_4{\cdot}5H_2O$ (5)	—	2	36	40
4	$CuSO_4{\cdot}5H_2O$ (5)	K^+Na^+ Tartrate(10)	2	—	—

[a] Reactions were performed on 1 mmolar scale.
[b] Isolated yields after column chromatoghaphy.



Scheme 2. Tentative catalytic cycle for the synthesis of primary amide using Cu(II)-catalyst.

Different aromatic moieties bearing deactivating *para*-nitro, electron-releasing methoxy, allyloxy, propargyloxy, or electroneutral methyl group could be accommodated to afford amides in excellent yields (86–98%) (entries 6, 7, 9–13). The presence of substituents *ortho* to the aldehyde group consistently lowered yield and required extended reaction time (entries 3, 5). Steric impediment to initial Cu (II) complex formation might be responsible for this and it is further supported by sluggish and incomplete conversion of sterically encumbered anthracene-9-carbaldehyde to the corresponding amide (50%, 7 h) (entry 15). The protocol has been successfully extended to heteroaromatic, aliphatic, and aromatic aldehydes with extended conjugation (entries 16–20). The stereochemical identity of the aldoxime (*E*/*Z*) did not affect the outcome of the reaction. Interconversion of the diastereoisomers under the conditions of the reaction is a distinct possibility.

Remarkably, the present methodology did not work for ketoximes as well as oxime methyl ether thereby implying juxtaposition of aldehydic hydrogen and oximic hydroxy group is essential for its success. We separately prepared 4-chlorobenzonitrile following literature procedure[19] and subjected it to optimized reaction conditions to afford the corresponding amide (94%) in 2 h. This observation is compatible with intermediacy of nitrile, although attempt to isolate it in case of 4-chlorobenzaldoxime as substrate by stopping the reaction short of completion after 1 h failed. However, we could successfully intercept the putative benzonitrile intermediate by reacting benzaldoxime with a primary amine, benzylamine having fairly high boiling point (bp 182–185 °C) under copper sulfate pentahydrate (5 mol %) catalyzed reaction condition to yield *N*-benzylbenzamide (40%) along with benzamide (Scheme 1).

To ascertain the role of Cu(II), piperonal oxime was treated with NaOAc (10 mol %), with and without $CuSO_4{\cdot}5H_2O$, in two separate control experiments (entries 1, 2, Table 3). Non-formation of amide without copper sulfate and its excellent yield (97%) in its presence strongly suggest implication of Cu(II)-catalyst in the formation of amide. When piperonal oxime was exposed to 5 mol % of $CuSO_4{\cdot}5H_2O$ without NaOAc, substantial deoximation occurred leading to concomitant formation of piperonal and the amide in ca. 10:9 ratio (entry 3, Table 3). Literature precedents are available on $CuSO_4$-promoted deoximation for example acetophenone oxime is cleaved to the ketone with 10 mol % $CuSO_4$ in toluene under reflux after 24 h.[20] Removal of Cu^{II} by complexation with sodium potassium tartrate, resulted in the recovery of unreacted oxime in almost quantitative yield further attesting to the essentiality of Cu(II) catalyst (entry 4, Table 3).

The strong propensity of oxime to bind with Cu(II) presumably activates it toward dehydration to nitrile. Analogous mechanistic scenario has been suggested for $NiCl_2{\cdot}6H_2O$-catalyzed acylation of amines with aldoximes.[21] Aromatic nitriles have stronger propensity to hydration than their aliphatic counterparts.[22] Therefore, water released by the way of dehydration of oximes might possibly hydrate nitriles strongly bound and activated to azaphilic Cu(II). Another equally plausible mechanistic hypothesis is the involvement of a second molecule of oxime as a surrogate of water for delivery onto nitrile carbon in a Cu(II) complex that binds together nitrile as well as oxime, as suggested in Rh-catalyzed 'anhydrous hydration' of nitriles.[23] A tentative catalytic cycle for the entire reaction sequence is depicted below (Scheme 2).

In conclusion, the current ligand-free Cu(II)-catalyzed method with low catalyst loading avoids use of strong bases under harsh conditions; it has been carried out under air in solvent-free conditions; it is operationally simple and uses organic solvent only in the post-reaction stage for the isolation of product.[24] No demanding or solvent-intensive isolation and purification of product are involved due to almost exclusive amide formation in most cases. The key greener features combined with generality, cost effectiveness, high selectivity, and efficiency make the present protocol synthetically appealing.

Acknowledgements

The authors (SR and PM) are thankful to UGC, New Delhi, India and CSIR, New Delhi, India for financial assistance by way of research fellowships. We are grateful to DST-FIST and UGC-SAP programmes for providing infrastructural facilities to the Department of Chemistry, University of Kalyani.

References and notes

1. Loudon, M. G. *Organic Chemistry*; Oxford University Press: New York, NY, 2002. pp. 982–983.
2. For reviews of amide formation, see: (a) Valeur, E.; Bradley, M. *Chem. Soc. Rev.* **2009**, *38*, 606; (b) Montalbetti, C.; Falque, V. *Tetrahedron* **2005**, *61*, 10827.
3. Sheldon, R. A. *Chemtech* **1994**, 38.
4. Constable, D. J. C.; Dunn, P. J.; Hayler, J. D.; Humphrey, G. R.; Leazer, J. L., Jr.; Linderman, R. J.; Lorenz, K.; Manley, J.; Pearlman, B. A.; Wells, A.; Zaks, A.; Zhang, T. Y. *Green Chem.* **2007**, *9*, 411.
5. (a) Wang, M.-X. *Top. Catal.* **2005**, *35*, 117; (b) Kumar, D.; Bhalla, T. C. *Appl. Microbial. Biotechnol.* **2005**, *68*, 726.
6. (a) Ganguly, N. C.; Mondal, P. *Synthesis* **2010**, 3705; (b) Gawley, R. E. *Org. React.* **1988**, *35*, 1; (c) Maruoka, K.; Yamamoto, H. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; pp 763–765. Vol. 6.
7. (a) Fujiwara, H.; Ogasawara, Y.; Yamaguchi, K.; Mizuno, N. *Angew. Chem., Int. Ed.* **2007**, *46*, 5202; (b) Kim, M.; Lee, J.; Lee, H.-Y.; Chang, S. *Adv. Synth. Catal.* **2009**, *351*, 1807.
8. Owston, N. A.; Parker, A. J.; Williams, J. M. *Org. Lett.* **2007**, *9*, 3599.
9. Owston, N. A.; Parker, A. J.; Williams, J. M. *Org. Lett.* **2007**, *9*, 73.
10. Ramon, R. S.; Bosson, J.; Diez-Gonzalez, S.; Marion, N.; Nolan, S. P. *J. Org. Chem.* **2010**, *75*, 1197.
11. Ali, M. A.; Punniyamurthy, T. *Adv. Synth. Catal.* **2010**, *352*, 288.
12. Kim, E. S.; Lee, H. S.; Kim, S. H.; Kim, J. N. *Tetrahedron Lett.* **2010**, *51*, 1589.
13. Jiang, N.; Ragauskas, A. J. *Tetrahedron Lett.* **2010**, *51*, 4479.
14. Attanasi, O.; Palna, P.; Serra-Zanetti, F. *Synthesis* **1983**, 741.
15. Hofmann, R. V.; Bishop, R. D.; Fitch, P. N.; Hardeustein, R. *J. Org. Chem.* **1980**, *45*, 917.
16. (a) Hirano, M.; Ukawa, K.; Yakabe, S.; Clark, J. H.; Morimoto, T. *Synthesis* **1997**, 858; (b) Ganguly, N. C.; Nayek, S.; Barik, S. K. *Synth. Commun.* **2009**, *39*, 4053.
17. Wabnitz, T. C.; Yu, J. Q.; Spencer, J. B. *Chem. Eur. J.* **2004**, *10*, 848.
18. (a) Saednya, A. *Synthesis* **1983**, 748; (b) Saednya, A. *Synthesis* **1982**, 190.
19. Chill, S. T.; Mebane, R. C. *Synth. Commun.* **2009**, *39*, 3601.
20. De, P.; Nonappa; Pandurangan, K.; Maitra, U.; Wailes, S. *Org. Lett.* **2007**, *9*, 2767.
21. Allen, C. L.; Davulcu, S.; Williams, J. M. J. *Org. Lett.* **2010**, *12*, 5096.
22. Kim, M.; Lee, J.; Lee, H.-Y.; Chang, S. *Adv. Synth. Catal.* **2009**, *351*, 1807.
23. Lee, J.; Kim, M.; Chang, S.; Lee, H.-Y. *Org. Lett.* **2009**, *11*, 5598.
24. *Typical procedure for synthesis of primary amide **1a** from aldehyde **1***: To an intimate mixture of neat piperonal **1** (150 mg, 1 mmol), $NH_2OH.HCl$ (69 mg, 1 mmol) and NaOAc (90 mg, 1.1 mmol) taken in a dried round bottomed flask was added $CuSO_4.5H_2O$ (13 mg, 5 mol %) and the mixture was heated at 110 °C on an oil bath with thorough stirring for 2 h (TLC monitoring). After cooling the reaction mixture, water (2 mL) was added to it to quench the reaction followed by extraction with EtOAc (3 × 6 mL). The combined extract was washed with brine (2 × 3 mL), dried (Na_2SO_4) and concentrated under reduced pressure. The crude product so obtained was filtered through a short pad of silica gel (60–120 mesh, Spectrochem, India) using EtOAc–*n*-hexane (1:1) as eluent to afford 3,4-methylenedioxybenzamide **1a** as a white crystalline solid (161 mg, 98%), mp 166–168 °C (lit 169 °C).[10]
Spectral data for selected products:
4-Allyloxybenzamide (entry 10): White solid; mp: 144–146 °C; IR (KBr): 3371, 3170, 1655, 1621, 1574, 1420, 1397, 1246, 1148, 1012, 939, 842 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.79 (dd, J = 8, 1.6 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2 H), 6.10–6.02 (m, 1H), 6 (br s, 2H), 5.43 (dd, J = 17.2, 1.2 Hz, 1H), 5.32 (dd, J = 10.4, 1.2 Hz, 1H), 4.59 (dd, J = 2.4,1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9, 161.6, 132.6, 129.3, 125.7, 118.2, 114.5, 68.9; LC–MS: m/z = 178 [M+1].
4-(Prop-2-ynyloxy)benzamide (entry 11): White solid; Mp: 120–122 °C; IR (KBr): 3442, 3279, 3145, 1673, 1652, 1608, 1567, 1424, 1396, 1246, 1189, 1016, 855 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 7.81 (d, J = 8.7 Hz, 2H), 7.74 (br s, 1H), 7.19 (br s, 1H), 6.97 (d, J = 8.7 Hz, 2H), 4.81 (d, J = 2.1 Hz, 2H), 3.57 (d, J = 2.1 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 167.4, 159.5, 129.3, 127.3, 114.3, 78.9, 78.5, 55.6; LC–MS: m/z = 176 [M+1].
4-Allyloxy-3-methoxybenzamide (entry 12): White solid; Mp: 178–180 °C; IR (KBr): 3367, 3169, 1646, 1619, 1578, 1426, 1381, 1278, 1260, 1151, 1124, 1010, 994, 874 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 7.81 (br s, 1 H), 7.42 (d, J = 6.6 Hz, 2H), 7.15 (br s, 1H), 6.95 (d, J = 8.7 Hz, 1H), 6.06–5.93 (m, 1H), 5.35 (dd, J = 17.1, 1.8 Hz, 1H), 5.22 (d, J = 10.5 Hz, 1H), 4.56 (dd, J = 5.4, 1.2 Hz, 2H), 3.75 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 167.5, 150.2, 148.5, 133.6, 126.9, 120.7, 117.9, 112.4, 111.3, 68.9, 55.7; LC–MS: m/z = 208 [M+1].
3-(2-Methylallyloxy)benzamide (entry 13): White solid; Mp: 108–110 °C; IR (KBr): 3364, 3192, 3077, 1658, 1620, 1601, 1582, 1390, 1249, 1017, 895 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 7.9 (br s, 1H), 7.41 (d, J = 6.9 Hz, 2H), 7.3 (br s, 1H), 7.29 (t, J = 7.8 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 5.02 (s, 1H), 4.92 (s, 1H), 4.47 (s, 2H), 1.74 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 167.6, 158.2, 140.8, 135.8, 129.3, 119.9, 117.7, 113.7, 112.3, 71.0, 19.2; LC–MS: m/z = 192 [M+1].
Anthracene-9-carboxamide (entry 15): Brown solid; Mp: 206–208 °C; IR (KBr): 3426, 3168, 1668, 1650, 1605, 1426, 1387, 1314, 1275, 888 cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 8.6 (br s, 1H), 8.24 (br s, 1H), 8.09–8.02 (m, 5H), 7.99 (br s, 1H), 7.57–7.48 (m, 4H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 170.4, 133.8, 130.8, 128.4, 126.9, 126.4, 125.6, 125.5, 117.8; LC–MS: m/z = 222 [M+1].