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An easy access to unsymmetrical ureas: a photocatalytic approach to the Lossen rearrangement†

Arvind K. Yadav, Vishnu P. Srivastava and Lal Dhar S. Yadav*

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An efficient and operationally simple method for the synthesis of unsymmetrical ureas from various hydroxamic acids and amines has been developed. Plausibly, the protocol involves visible-light-initiated *in situ* formation of Vilsmeier–Haack reagent and $COBr_2$ with CBr_4 and a catalytic amount of DMF in the presence of $Ru(bpy)_3Cl_2$ as a photocatalyst to bring about the Lossen rearrangement at room temperature.

Introduction

The Curtius, Hofmann, and Lossen rearrangements are inter related and well known textbook rearrangements that bring about the transformation of carboxylic acid derivatives (azides, amides and hydroxamic acids, respectively) into the corresponding isocyanates. Of these, the Lossen rearrangement has received comparatively less attention.[1] The literature reports several methods for activation of hydroxamic acids to execute the Lossen rearrangement,[2] but there are one or more serious problems associated with them such as competitive dimerisation, complexity of procedures and the formation of stoichiometric amounts of by-products that limit the application of the Lossen rearrangement on a large scale. The isocyanates formed as intermediates in the Lossen rearrangement undergo degradation to primary amines in the presence of water, whereas carbamates and urea derivatives are obtained under non-aqueous conditions.[1–3]

The synthesis of urea derivatives traditionally requires reagents based on either phosgene, phosgene surrogates,[2a,b] $R_3N{\cdot}SO_3$ (ref. 2c) and BDMS (bromodimethylsulfonium bromide)[4] or starting directly from isocyanates prepared in various ways.[5] However, these are noxious, unstable and require special care for handling as well as are ecologically and environmentally non-benign. Lessard and Spino[6] have reported photochemical Lossen rearrangement of cyclic hydroxamic acids and their esters to afford *N*-heterocycles, but they have used deleterious UV irradiation at −78 °C. Unsymmetrical ureas have attracted significant interest due to their extensive pharmaceutical (A and B), agricultural (C), and biological (D) applications (Fig. 1).[1–7] Urea derivatives are also important in organic synthesis as intermediates and bifunctional organocatalysts.[8] Thus, a convenient, catalytic and environmentally benign procedure for the synthesis of unsymmetrical ureas is highly demanded.

Recently, Stephenson *et al.* have reported visible-light-initiated *in situ* formation of Vilsmeier–Haack reagent.[9] Inspired by this work, we have very recently executed visible-light-driven Beckmann rearrangement and nitrile synthesis.[10] In view of the above points and our investigations on rearrangement reactions involving electron deficient nitrogen terminus,[4,10b,11] the Lossen rearrangement was chosen for the present study. Visible-light-photoredox catalysis has emerged as a new technique for the synthesis of fine chemicals under mild reaction conditions. The pioneering work in this area by MacMillan[12a] and Yoon[12b] groups using photocatalysts such as $Ru(bpy)_3Cl_2$ (bpy = 2,2′-bipyridine) and $Ir(dtbbpy)_3Cl_2$ (dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) are capable to initiate powerful transformations in organic synthesis, both for the target oriented and method driven.[13] Very recently, Tan *et al.* reported the aerobic oxidation of hydroxamic acids to give acylnitroso ene reaction *via* photoredox catalysis.[14] Visible-light-initiated *in situ* formation Vilsmeier–Haack reagent and $COBr_2$ might be an efficient electrophilic species for the activation of hydroxamic acids to form isocyanates, which are further trapped by amines to afford unsymmetrical ureas (Scheme 1).

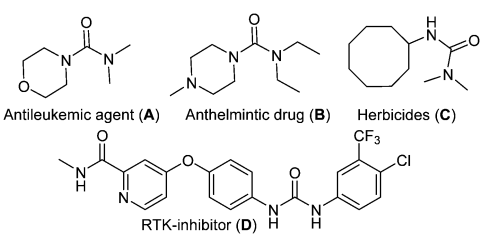
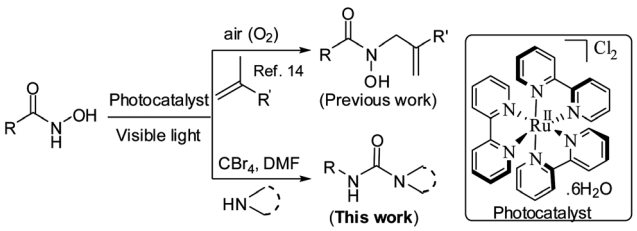


Fig. 1 Examples of bioactive unsymmetrical ureas.

Green Synthesis Lab, Department of Chemistry, University of Allahabad, Allahabad 211002, India. E-mail: ldsyadav@hotmail.com; Fax: +91 5322460533; Tel: +91 5322500652

† Electronic supplementary information (ESI) available: Copies of ^1H and ^{13}C NMR spectra of all the products. See DOI: 10.1039/c4ra03805c



Scheme 1 Visible-light-triggered activation of hydroxamic acids.

Results and discussion

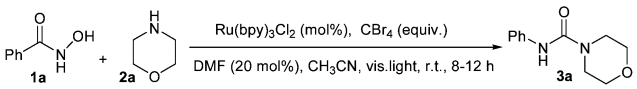
We started our work with a model reaction of hydroxamic acid **1a** (1.0 mmol), morpholine **2a** (1.0 mmol) and CBr_4 (2.0 mmol) in DMF (2 mL) under irradiation with blue LEDs in the presence of $Ru(bpy)_3Cl_2$ (1 mol%) as a photoredox catalyst. The reaction delivered 94% yield of the desired unsymmetrical urea **3a** (Table 1, entry 1). This encouraging result and the reported mechanism of hydroxyl group activation by using the Vilsmeier–Haack reagent,[9,10] led us to hypothesis that the reaction could be rendered catalytic with respect to DMF.

Accordingly, the above reaction was conducted using a catalytic amount (20 mol%) of DMF. To our delight, it was successful and produced the target urea **3a** without affecting the yield (94%) and required the same reaction time (8 h) (Table 1, entry 2). The control experiments were performed to see the role of different catalytic and reagent components in the present reaction, which indicated that in the absence of any one of the reagents/reaction parameters, there was a trace or no product formation (Table 1, entries 7–10). The use of compact fluorescent light (CFL) was not so effective in comparison to blue LEDs (Table 1, entry 2 *versus* 5) probably because the former has far less intensity of the blue light ($\lambda = 447.5$ nm) required to bring about the reaction. These results conclude that the photocatalyst in the presence of blue LEDs is essential for the reaction and support the photocatalytic model for the reaction.

Next, we optimized reaction conditions with respect to base and catalyst loading. It was noted that the reaction was sensitive to reaction media because in all the tested solvents, *viz.* MeCN, DCE, THF and CH_3NO_2 the yield was >56% (Table 2). The highest yield (94%) was in the case of MeCN and it was used as solvent throughout the present study. The optimum catalyst loading of $Ru(bpy)_3Cl_2$ was found to be 1 mol% (Table 1, entry 2). On lowering the catalyst loading from 1 mol% to 0.5 mol% there was a significant decrease in the yield (Table 1, entry 6). Moreover, an increase in the catalyst loading from 1 mol% to 1.5 mol% did not improve the yield (Table 1, entry 11). The effective catalytic amount of DMF to deliver the desired urea without affecting time and high yield was 20 mol% (Table 2, entry 1 *versus* 2 and 3), while CBr_4 (oxidative quencher and source of Vilsmeier–Haack reagent) requires 2.0 equiv. because the yield was considerably reduced with 1.0 equiv. and unaffected with 3.0 equiv. (Table 1, entry 2 *versus* 3, 4). Under the established conditions in hand, variation in hydroxamic acids **1** and amines **2** affords the corresponding ureas in good to excellent yields (Table 3).

As expected, hydroxamic acids and amines with an electron-withdrawing group afforded slightly lower yield in longer time in comparison to those with an electron-donating group. Moreover, it was found that aliphatic amines were marginally more effective in comparison to aromatic (Table 3). It is obvious from the results that the reaction is very mild, efficient and

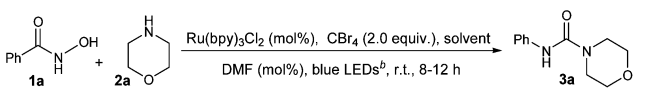
Table 1 Screening and control experiments[a]



Entry	Visible light	Ru(II) (mol%)	CBr_4 (equiv.)	Time (h)	Yield[b] (%)
1	Blue LEDs[c]	1	2	8	94[d]
2	Blue LEDs	1	2	8	94
3	Blue LEDs	1	1	8	52[e]
4	Blue LEDs	1	3	8	94
5	CFL (18 W)[f]	1	2	12	36
6	Blue LEDs	0.5	2	8	58
7	Blue LEDs	0	2	12	n.d.
8	Blue LEDs	1	0	12	n.d.
9	In the dark	1	2	12	n.d.
10	Blue LEDs	1	2	8	n.d.[g]
11	Blue LEDs	1.5	2	8	94

[a] The reaction was conducted with **1a** (1.0 mmol), **2a** (1.0 mmol), $Ru(bpy)_3Cl_2$ (mol%), DMF (20 mol%) in MeCN (3 mL) under a nitrogen atmosphere for each entry. [b] Isolated yield of **3a** after aqueous work up followed by column chromatography; n.d. = not detected. [c] Blue LEDs 4.45 W, $\lambda = 447.5$ nm (for details, see Experimental section) were used for irradiation at 2 cm distance from the flask bottom side at r.t. [d] The reaction was performed in DMF (2 mL). [e] 46% of **1a** was recovered. [f] 18 W CFL (compact fluorescent lamp, Philips, 6500 K, 1010 lm, 85 mA) was used for irradiation. [g] The reaction was performed without using DMF.

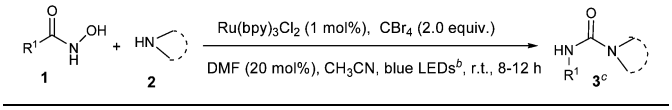
Table 2 Optimization of reaction condition[a]

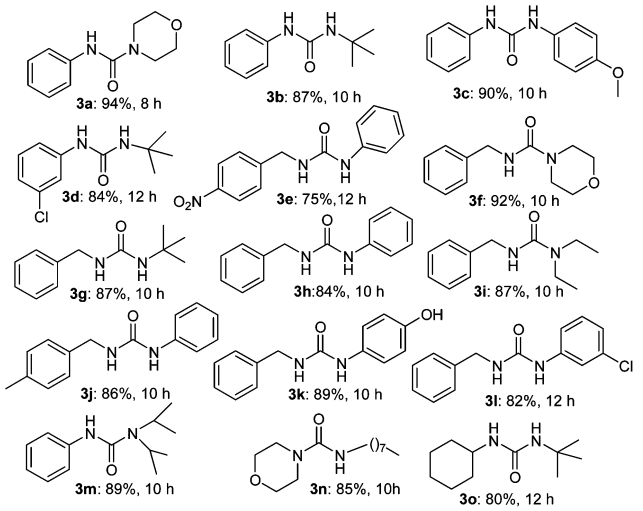


Entry	DMF (mol%)	Solvent	Time (h)	Yield[c] (%)
1	20	MeCN	8	94
2	15	MeCN	8	63
3	30	MeCN	8	94
4	15	MeCN	12	69
5	20	DCE	12	68
6	20	THF	12	57
7	20	$MeNO_2$	12	75

[a] The reaction was carried out with **1a** (1.0 mmol), **2a** (1.0 mmol), DMF (mol%), $Ru(bpy)_3Cl_2$ (1 mol%) and CBr_4 (2.0 equiv.) in solvent (3 mL) under a nitrogen atmosphere for each entry. [b] Blue LEDs 4.45 W, $\lambda = 447.5$ nm (for details, see Experimental section) were used for irradiation at 2 cm distance from the from the flask bottom side at r.t. [c] Isolated yield of **3a** after aqueous work up followed by column chromatography.

Table 3 Synthesis and scope of unsymmetrical ureas[a]



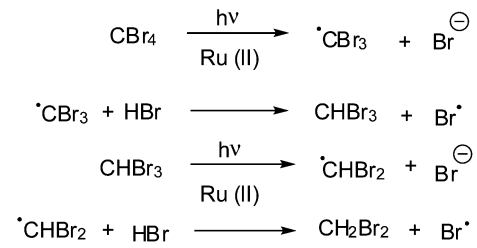


[a] The reaction was carried out with **1** (1.0 mmol), **2** (1.0 mmol), DMF (20 mol%), $Ru(bpy)_3Cl_2$(1 mol%) and CBr_4(2.0 equiv.) in CH_3CN (3 mL) under a nitrogen atmosphere. [b] Blue LEDs 4.45 W (for details, see Experimental section) were used for irradiation at 2 cm distance from the from the flask bottom side at r.t. [c] Isolated yield of 3 after aqueous work up followed by column chromatography.

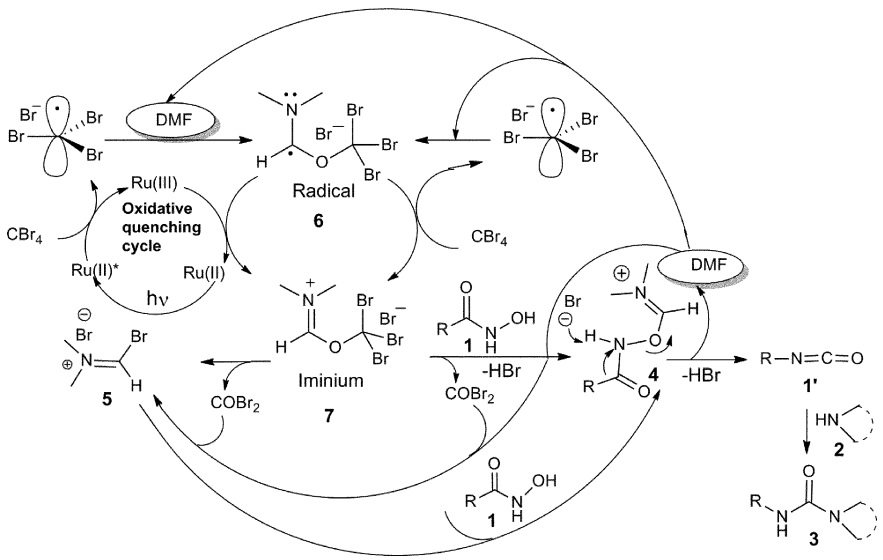
tolerates many functionalities like MeO, OH, *tert*-butyl, Cl and NO_2 (Table 3).

On the basis of our observations and the literature reports,[3,4,9,10] a plausible mechanism for the formation of unsymmetrical ureas **3** *via* the Lossen rearrangement is depicted in Scheme 2. The photoredox catalyst Ru(II) is excited on absorption of visible light and undergoes single electron transfer (SET) to CBr_4 to form $^{\bullet}CBr_3$, which reacts with DMF to generate radical **6** and Ru(III). Again, SET from the radical **6** reduces to Ru(III) to Ru(II) and iminium **7** to complete the redox cycle. Possibly, the iminium ion **7** reacts with hydoxamic acid to form **4** or it is converted into Vilsmeier–Haack reagent **5** and $COBr_2$, which react with the hydroxyl group of hydroxamic acids to form an intermediate **4**. In analogy with the traditional use of phosgene, the rearrangement might be driven by the reaction of hydroxamic acid with $COBr_2$. However, none of these possibilities could be ruled out. The intermediate **4** undergoes rearrangement to form reactive isocyanate **1′**, which is trapped by appropriate amines to give the desired products **3**. Furthermore, $COBr_2$ formed as a by-product pathway reacts with DMF to generate **5** as reported earlier.[15]

The mechanistic pathway shows that two molecules of HBr are formed during the conversion of each molecule of hydroxamic acid into isocyanate, even then no additional base is required for scavenging the HBr formed. This is understandable because two equivalents of CBr_4 have been used in the reaction, which generate $^{\bullet}CBr_3$ and subsequently $CHBr_2$ radicals.[16] The amounts of these radicals would be enough to bring about the rearrangement as well as to completely scavenge the HBr formed (Scheme 3).



Scheme 3 Scavenging of HBr formed.



Scheme 2 Plausible mechanistic pathway for photocatalytic Lossen rearrangement.

Conclusions

In conclusion, we have developed an efficient and operationally simple photocatalytic synthesis of unsymmetrical ureas using visible-light and CBr_4 as reagent, $Ru(bpy)_3Cl_2$ and DMF as catalyst at r.t. The protocol brings about the Lossen rearrangement under non-basic reaction condition to afford the unsymmetrical ureas in high yields. The present work opens up a new aspect of the synthetic utility of visible-light-mediated *in situ* formation of hydroxyl group activating reagents.

Experimental

General

General information. All commercially available reagents were obtained from commercial suppliers (DMF purchased from Merck, CBr_4 from Sigma Aldrich and amines from Loba) and used without further purification. Solvents were purified by the usual methods and stored over molecular sieves. All reactions were performed using oven-dried glassware under a nitrogen atmosphere. Organic solutions were concentrated using a Buchi rotatory evaporator. Column chromatography was carried out over silica gel (Merck 100–200 mesh) and TLC was performed using silica gel GF254 (Merck) plates. Melting points were determined by open glass capillary method and are uncorrected. IR spectra in KBr/neat were recorded on a Perkin-Elmer 993 IR spectrophotometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AVII spectrometer in $CDCl_3$ or DMSO-d_6 using TMS as internal reference with chemical shift value being reported in ppm. All coupling constants (*J*) are reported in Hertz (Hz). MS (EI) spectra were recorded on double focusing mass spectrometer. Blue LEDs (447.5 nm, 4.45 W) Rebel LED, mounted on a 25 mm Cool Base 161 lm@ 700 mA was purchased from Commercial Supplier Luxeon Star LEDs Quadica Developments Inc. 47 6th Concession Rd. Brantford, Ontario N 32 5L7, Canada.

Photocatalytic synthesis of unsymmetrical ureas 3 from hydroxamic acids

A round bottom flask was charged with hydroxamic acid **1** (1 mmol), amine **2** (1 mmol), $Ru(bpy)_3Cl_2$ (1 mol%), DMF (20 mol%), CBr_4 (2.0 equiv.) and CH_3CN (3 mL), and the contents were irradiated with the blue LEDs from bottom side of the flask for 8–12 h while stirring at r.t. under a nitrogen atmosphere. After completion of the reaction as indicated by TLC, the reaction mixture was quenched with saturated aqueous sodium hydrogen carbonate (10 mL) and extracted with ethyl acetate (3 × 10 mL). The organic phase was dried over anhydrous magnesium sulfate and concentrated *in vacuo* to yield the crude product, which was purified by silica gel column chromatography (EtOAc–hexane) to give the corresponding urea **3** in high yield.

The characterization data of the synthesised compounds **3** are summarized below with relevant ref. 17.

Compound 3a (ref. 17a). Brown solid; Mp 154–155 °C (Lit. 154–156 °C). IR (KBr): 3265, 3126, 3056, 2950, 2858, 1632, 1538, 1441, 1416, 1302, 1244, 1113, 992, 873, 859, 746 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42–7.02 (m, 5H), 6.59 (s, 1H), 3.46 (t, *J* = 4.8, 4H), 3.20 (t, *J* = 4.8, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 155.3, 138.6, 129.1, 123.4, 120.0, 66.6, 43.4. HRMS calcd for $C_{11}H_{14}N_2O_2$ = 206.1055; found 206.1057.

Compound 3b (ref. 17a). White solid; Mp 171–173 °C (Lit. 172–174 °C). IR (KBr): 3357, 2965, 2838, 1639, 1535, 1272, 1109, 1020, 839, 569 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.39–7.16 (m, 5H), 6.68 (br s, 1H), 5.93 (br s, 1H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 156.0, 140.7, 128.7, 121.1, 117.8, 49.4, 29.0. HRMS calcd for $C_{11}H_{16}N_2O$ = 192.1263; found 192.1260.

Compound 3c (ref. 17b). Brown solid; Mp 194–196 °C (Lit. 195–196 °C). IR (KBr): 3413, 2853, 1646, 1508, 1249, 1146, 1023, 752 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$); δ = 8.32 (br s, 1H), 8.22 (br s, 1H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 9.1 Hz, 2H), 7.26 (t, *J* = 7.9 Hz, 2H), 6.94 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 9.1 Hz, 2H), 3.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 133.4, 133.1, 126.2, 121.1, 120.0, 119.7, 117.1, 109.2, 29.7. HRMS calcd for $C_{14}H_{14}N_2O_2$ 242.1055, found 242.1051.

Compound 3d (ref. 17a). White solid; Mp 175–176 °C (Lit. 175–177 °C). IR (KBr): 3462, 2971, 1662, 1528, 1248, 1149, 1041, 789, 751, 682 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.70 (d, *J* = 8.1 Hz, 1H), 7.20–6.90 (m, 3H), 6.16 (br s, 1H), 5.43 (br s, 1H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 158.1, 137.7, 132.8, 128.1, 127.1, 123.5, 120.6, 42.0, 30.3. HRMS calcd for $C_{11}H_{15}ClN_2O$ = 226.0873; found 226.0869.

Compound 3e (ref. 17a). Yellow solid; Mp. 195–198 (Lit. 196–198 °C). IR (KBr): 3421, 3097, 2853, 1657, 1508, 1238, 1145, 1000, 799, 736 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.05 (s, 1H), 7.84–7.80 (m, 2H), 7.42–7.18 (m, 6H), 6.89–6.80 (m, 1H), 5.80 (s, 1H), 4.08 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 158.2, 142.6, 140.3, 138.0, 130.9, 128.2, 121.8, 119.0, 116.8, 50.1. HRMS calcd for $C_{14}H_{13}N_3O_3$ = 271.0957; found 271.0960.

Compound 3f (ref. 17a). White solid; Mp 140–142 °C (Lit. 139–141 °C). IR (KBr): 3335, 2921, 2855, 1626, 1539, 1267, 1114, 1067, 1017, 957, 851, 730 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.32–7.16 (m, 5H), 6.44 (br s, 1H), 4.65 (s, 2H), 4.24–4.21 (m, 4H), 3.24 (s, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 156.5, 139.8, 127.7, 127.0, 126.9, 65.6, 45.4, 43.5. HRMS calcd for $C_{12}H_{16}N_2O_2$ = 220.1212; found 220.1210.

Compound 3g (ref. 17a). White solid; Mp 112–114 °C (Lit. 111–114 °C). IR (KBr): 3363, 2962, 2850, 1638, 1506, 1334, 1248, 1116, 1026, 751 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.32–7.21 (m, 5H), 6.06 (t, *J* = 6.0 Hz, 1H), 5.73 (br s, 1H), 4.16 (d, *J* = 5.9 Hz, 2H), 1.25 (s, 9H); ^{13}C NMR (100 MHz DMSO-d_6) δ = 157.5, 141.0, 128.3, 127.0, 126.6, 49.3, 42.6, 29.4. HRMS calcd for $C_{12}H_{18}N_2O$ = 206.1419; found 206.1423.

Compound 3h (ref. 17a). White solid; Mp 186–188 °C (Lit. 186–188 °C). IR (KBr): 3343, 2951, 2840, 1641, 1508, 1218, 1117, 1010, 756 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.50 (s, 1H), 7.39–6.84 (m, 10H), 6.26 (t, *J* = 6.0 Hz, 1H), 4.17 (d, *J* = 5.9 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 156.1, 140.5, 128.5, 121.2, 117.7, 44.2. HRMS calcd for $C_{14}H_{14}N_2O$ = 226.1106; found 226.1108.

Compound 3i (ref. 17a). White solid; Mp 90–92 °C (Lit. 89–93 °C). IR (KBr): 3307, 2972, 1629, 1532, 1408, 1302, 1242, 1248,

1116, 1000, 975, 694 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ = 7.34–7.21 (m, 5H), 6.40 (t, J = 4.4 Hz, 1H), 4.20 (s, 2H), 3.31 (q, J = 4.8 Hz, 4H), 2.50 (t, J = 4.8 Hz, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 158.0, 141.0, 128.1, 126.9, 126.5, 44.2, 42.9, 13.3. HRMS calcd for $C_{12}H_{18}N_2O$ = 206.1419; found 206.1416.

Compound 3j (ref. 17a). White solid; Mp 176–177 °C (Lit. 176–178 °C). IR (KBr): 3358, 2914, 2863, 1651, 1508, 1248, 1116, 1000, 751 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ = 7.71 (s, 1H), 7.39–7.16 (m, 8H), 6.92–6.86 (m, 1H), 6.25 (s, 1H), 4.19 (s, 2H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 156.7, 140.9, 132.5, 128.7, 126.8, 121.0, 118.3, 49.0, 26.2. HRMS calcd for $C_{15}H_{16}N_2O$ = 240.1263; found 240.1265.

Compound 3k (ref. 17a). White solid; Mp 196–198 °C (Lit. 197–198 °C). IR (KBr): 3409, 2927, 2854, 1645, 1508, 1248, 1116, 1018, 816 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ = 9.16 (br s, 1H), 7.91 (br s, 1H), 7.34–7.20 (m, 9H), 6.40 (t, J = 4.8 Hz, 1H), 4.23 (d, J = 4.8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 155.6, 142.5, 139.8, 136.3, 132.5, 129.0, 127.3, 122.5, 121.1, 121.0, 43.5. HRMS calcd for $C_{12}H_{14}N_2O_2$ = 242.1055, found 242.1051.

Compound 3l (ref. 17a). White solid; Mp 174–176 °C (Lit. 175–176 °C). IR (KBr): 3373, 2953, 1636, 1508, 1248, 1116, 1000, 752, 659 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.11–8.03 (m, 1H), 7.38–6.90 (m, 8H), 6.36 (s, 1H), 5.54 (br s, 1H), 4.26 (d, J = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 155.4, 139.8, 136.3, 132.5, 129.1, 127.3, 122.5, 121.2, 121.0, 43.5. HRMS calcd for $C_{14}H_{13}ClN_2O$ = 260.0716, found 260.0718.

Compound 3m (ref. 17c). Brown solid; Mp 113–115 °C (Lit. 112–115 °C). IR (KBr): 3381, 2969, 2928, 1626, 1588, 1447, 1336, 1230. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.35 (d, J = 7.6 Hz, 2H), 7.25–7.19 (m, 2H), 7.10–7.06 (m, 1H), 6.24 (s, 1H), 3.99 (septet, J = 6.8 Hz, 2H), 1.34 (d, J = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.0, 139.5, 122.7, 121.3, 119.9, 45.6, 21.6. HRMS calcd for $C_{13}H_{20}N_2O$ 220.1576, found 220.1572.

Compound 3n (ref. 17d). Yellowish oil; IR (neat): 3337, 2921, 2863, 1624, 1518, 1248, 1116, 1000, 811, 687 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.25 (s, 1H), 3.72 (t, J = 6 Hz, 4H), 3.35 (t, J = 6.0 Hz, 4H), 3.25 (t, J = 6.0 Hz, 2H), 1.52 (m, 2H), 1.35–1.17 (br s, 10H), 0.89 (t, J = 6 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.0, 66.8, 44.3, 41.1, 32.3, 30.5, 29.5, 27.2, 22.8, 21.3, 14.4. HRMS calcd for $C_{13}H_{26}N_2O_2$ = 242.1994, found: 242.1995.

Compound 3o (ref. 17a). White solid; Mp 223–226 °C (Lit. 224–226 °C). IR (KBr): 3313, 2927, 2851, 1622, 1538, 1278, 1106, 1026, 633 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ = 5.81 (br s, 1H), 5.32 (br s, 1H), 3.29–3.27 (m, 1H), 1.74–1.59 (m, 4H), 1.02–1.24 (m, 6H), 0.95 (s, 9H); ^{13}C NMR (100 MHz, DMSO-d_6) δ = 158.1, 47.7, 33.0, 30.0, 25.4, 24.5, 22.0. HRMS calcd for $C_{11}H_{22}N_2O$ = 198.1732; found 198.1729.

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