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Visible-light-mediated eosin Y catalyzed aerobic desulfurization of thioamides into amides

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

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A novel method for the metal-free efficient synthesis of amides from thioamides using visible light and in an air atmosphere in the presence of eosin Y as an organophotoredox catalyst is reported. The protocol involves aerobic desulfurization–oxygenation of thioamides into amides in good to excellent yields at r.t. in a one-pot operation under mild conditions with the formation of nontoxic elemental sulfur as the only by-product. On the basis of several relevant experiments performed, it has been shown that the present photooxidation does not involve a singlet oxygen and accordingly a plausible organocatalytic photoredox mechanism is proposed.

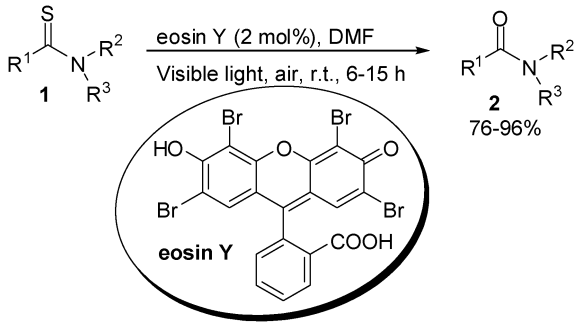
Introduction

The development of numerous available visible light photoredox systems is the outcome of efforts to mimic nature's ability to utilize solar energy in photosynthesis. Visible light photoredox catalysis has emerged as a powerful technique for organic synthesis owing to sustainability, ready availability, non-toxicity, ease of handling and potential applications of visible light.[1] Photosensitizers or photocatalysts are generally required to induce visible-light-driven reactions because most organic compounds do not absorb light in the visible region (400–800 nm).[2] In most studies ruthenium and iridium complexes have been used as visible light photoredox catalysts.[1] In their pioneering work in this area, MacMillan *et al.*,[3] Yoon *et al.*[4] and Stephenson *et al.*[1b,j] have used $Ru(bpy)_3^{2+}$ (where bpy = 2,2′-bipyridine) as the photoredox catalyst, which has inspired the development of several powerful methods for various chemical transformations useful in organic synthesis.[1]

However, these metal based methods suffer from disadvantages such as potential toxicity, high cost and low sustainability of the ruthenium and iridium complexes. As a superior alternative to transition metal photoredox catalysts, especially metal-free organic dyes have been recently utilized, which are easy to handle, eco-friendly and have great potential for applications in visible-light-mediated organic synthesis.[5] The amide functionality is among the most vital structural motifs in life and material sciences, and has fascinated chemists in both academia and industry.[6] The conversion of thiocarbonyl compounds into their oxygen analogues represents significant functional group manipulation in organic chemistry. The literature records a variety of methods and reagents to accomplish the transformation of thioamides into amides, for example, dimethylselenoxide,[7] diaryltelluroxide,[8] dimethylsulphoxide-acids,[9] sulphoxide-iodine,[10] sodium peroxide,[11] mercuric acetate,[12] trifluoroacetic anhydride,[13] and Caro's acid supported on a silica gel,[14] $H_2O_2/ZrCl_4$ (ref. 15) and bismuth(III) nitrate.[16]

Surprisingly, none of the above methods utilize molecular oxygen (air) for the oxidation of thioamides into amides although it is the best oxidant in terms of green chemistry theme and ready availability. However, there are only a few methods described in the literature to convert thiocarbonyl compounds into the corresponding carbonyl compounds using molecular oxygen as an oxidant.[17] Of these, the photooxidation reactions reported by Crank *et al.*[17a] and Ameta *et al.*[17b] most probably involve a singlet oxygen because they take place in visible light in the presence of Rose Bengal, a well known singlet oxygen sensitizer. Ameta *et al.*[17b] have also compared eosin Y with Rose Bengal and found that the yield was 10% and 15%, respectively. However, these reactions suffer from disadvantages such as longer time, bubbling of oxygen gas, poor yields and limited substrate scope. The other methods require transition-metal catalysis, O_2 (balloon) and heating at 80 °C.[17c] The removal of transition metals from products is often problematic, especially in the case of drugs and drug intermediates, where their presence even in traces is undesirable. In continuation of our recent work on transition-metal-free reactions enabling the amide–thioamide linkage[18] and stimulated by the fact that organosulfur compounds are widely involved in radical reactions because they form radicals very readily, we hypothesized the present visible-light-mediated eosin Y catalyzed aerobic desulfurization of thioamides **1** into **2** as depicted in Scheme 1.

Green Synthesis Lab, Department of Chemistry, University of Allahabad, Allahabad 211 002, India. E-mail: ldsyadav@hotmail.com; Fax: +91 532-246-0533; Tel: +91 532-250-0652

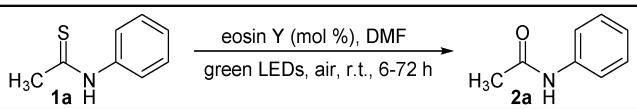


Scheme 1 Aerobic desulfurization of thioamides into amides.

Results and discussion

In order to verify the practicability of the envisaged protocol, a model reaction was carried out with thioamide (**1a**), thus its solution in DMF containing 2 mol% of eosin Y was exposed to an air atmosphere (but with no air bubbling) and irradiated with visible light (green light-emitting diodes (LEDs), λ_{max} = 535 nm) at r.t. It was highly satisfying that the reaction delivered the desired amide (**2a**) in 93% isolated yield after 6 h (Table 1, entry 1). Following this experiment a series of control experiments were performed, which demonstrated that either there was no product formation or it was formed in traces in the absence (−) of any one of the reagents/catalyst (Table 1, entries 2–5, 8 and 12). The reaction did not proceed satisfactorily when daylight or a household 18 W fluorescent lamp was used instead of green LEDs (Table 1, entries 6 and 7). The same result was obtained in the case of air or O_2 (balloon) (Table 1, entry 1 *versus* 9). These results establish that visible light, the photocatalyst and air all are essential (+) for the reaction and support the photocatalytic model of the reaction.

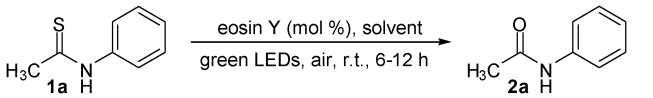
Table 1 Screening and control experiments[a]



Entry	Visible light	Eosin Y	Air	Time (h)	Yield[b] (%)
1	+	+	+	6	93
2	—	+	+	12	n.r.[c]
3	+	—	+	12	n.r.
4	+	+	—	12	n.r.
5	+	+	N_2	18	Trace
6	+	+	+	18	15[d]
7	+	+	+	12	49[e]
8	+	+	N_2	18	Trace
9	+	+	O_2	6	94
10	+	+	+	6	89[f]
11	+	+	+	72	27[g]
12	+	+	+	72	Trace[h]

[a] Reaction conditions: **1a** (1.0 mmol), eosin Y (2 mol%), DMF (3 mL), green LEDs (2.6 W, 161 lm) irradiation under an air atmosphere at r.t. [b] Isolated yield of the product **2a**, n.r. = no reaction. [c] The reaction was carried out in the dark. [d] The reaction was carried out in daylight. [e] The reaction was carried out using 18 W CFL (compact fluorescent lamp). [f] The reaction did not quench either in the presence of 2,3-dimethyl-2-butene (2.0 mol%) or DABCO (2.0 mol%). [g] TPP (tetraphenylporphyrin) (0.1 mol%) was used instead of eosin Y. [h] TDCPP (5,10,15,20-tetrakis-(2,6-dichlorophenyl)-21,23*H*-porphyrin) (2 mol%) was used instead of eosin Y.

Table 2 Optimization of reaction conditions[a]



Entry	Eosin Y (mol%)	Solvent	Time (h)	Yield[b] (%)
1	2	DMF	6	93
2	2	Dioxane	12	51
3	2	THF	12	46
4	2	DMSO	8	76
5	2	MeCN	12	65
6	2	MeOH	12	55
7	2	EtOH	12	58
8	3	DMF	12	93
9	1	DMF	12	67
10	2	$MeNO_2$	12	78

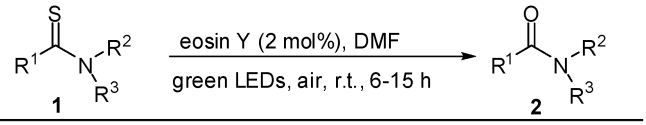
[a] Reaction conditions: **1a** (1.0 mmol), eosin Y (1–3 mol%), solvent (3 mL), green LEDs (2.6 W, 161 lm) irradiation under an air atmosphere at r.t. [b] Isolated yield of the product **2a**.

Then, reaction conditions were optimized with respect to solvents and the catalyst loading. In all the tested solvents (DMF, dioxane, THF, DMSO, MeCN, MeOH, EtOH and $MeNO_2$) the yield of amide **2a** was >45% (Table 2), which indicates that the reaction is not very sensitive to reaction media. DMF was the best solvent in terms of the reaction time and yield (Table 2, entry 1), hence it was used throughout the present work. When the amount of the catalyst was decreased from 2 mol% to 1 mol%, the yield of the amide **2a** considerably reduced (Table 2, entry 9), but the use of 3 mol% of the catalyst did not affect the yield (Table 2, entry 8).

Under the established reaction conditions, we surveyed the generality and scope of the present photocatalytic protocol across a range of substrates **1** incorporating aryl, alkyl and heterocyclic moieties as well as functional groups such as MeO, NO_2, and Br (Table 3). In all cases the yield was >75%, which clearly shows that the reaction is very mild and tolerates considerable structural and functional group variations in the substrate **1**. Regardless of differences in the electronic and steric properties of substrates **1**, they afford the desired product **2** in good to excellent yields (76–96%). However, thioamides with an electron-donating group on the aromatic ring appear to react faster and afford marginally higher yields in comparison to those bearing an electron-withdrawing group (Table 3, entries 2, 3, 7 *versus* entries 4, 5, 8; and 13–15 *versus* 16). Whilst the reaction works very well for secondary and tertiary thioamides, it is not applicable to primary thioamides because they dimerise to afford 1,2,4-thiadiazoles under the present reaction conditions.[19]

To investigate the possibility of involvement of singlet oxygen in the reaction, we performed several known experiments[20] such as: (i) the use of O_2 (balloon) instead of open air did not have a significant effect on the yield[20a] (Table 1, entry 9); (ii) the reaction was not quenched either in the presence of 2,3-dimethyl-2-butene[20b] or DABCO,[20c] a specific singlet oxygen quencher (Table 1, entry 10); (iii) the use of TPP and TDCPP

Table 3 Substrate scope for the desulfurization of thioamides into amides[a]



1 2

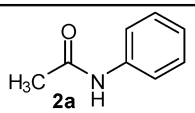
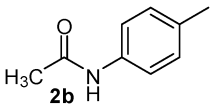
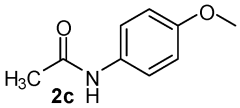
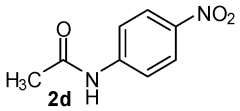
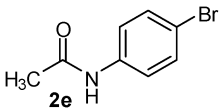
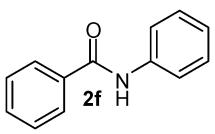
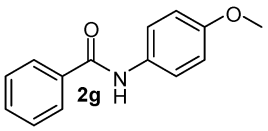
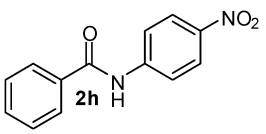
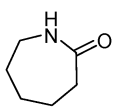
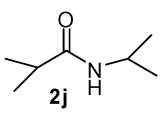
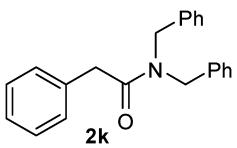
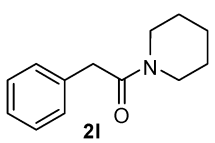
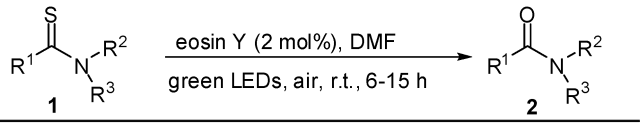
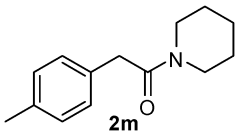
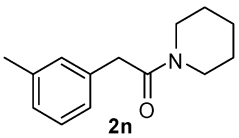
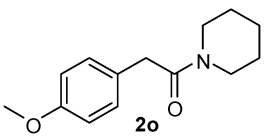
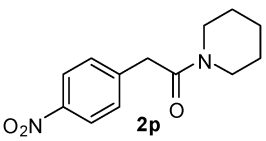
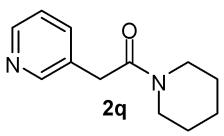
Entry	Product 2	Time (h)	Yield[b] (%)
1		6	93
2		6	95
3		6	96
4		10	79
5		10	81
6		8	85
7		6	92
8		10	76
9		10	87
10		10	84
11		10	81
12		10	86

Table 3 (*continued*)



1 2

Entry	Product 2	Time (h)	Yield[b] (%)
13		10	88
14		10	85
15		10	90
16		15	78
17		12	79

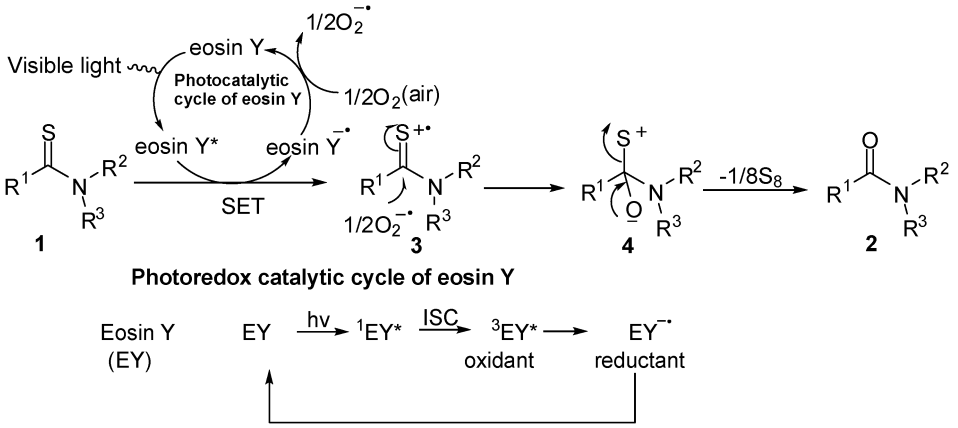
[a] See the Experimental section for general procedure. [b] Isolated yield of the products **2**.

gives very poor yield even after 72 h (Table 1, entries 11 and 12);[20a] (iv) the formation of a superoxide radical anion during the reaction was confirmed by the detection of the resulting H_2O_2 using a KI/starch indicator.[20d]

All these experiments suggested that singlet oxygen is not involved in the reaction. On the basis of these observations and the literature precedents,[21–23] a plausible mechanism involving photoredox catalysis for the desulfurization of thioamides **1** into the amides **2** is depicted in Scheme 2. On absorption of visible light, the organophotoredox catalyst eosin Y (EY) is excited to its singlet state ^{1}EY*, which through intersystem crossing (ISC) comes to its more stable triplet state ^{3}EY* and undergoes a single electron transfer (SET).[22] ^{3}EY* may undergo both reductive and oxidative quenching.[21] A SET from the C=S of **1** to ^{3}EY* generates radical cation **3**, which is attacked by $1/2O_2^{-\bullet}$ to form even electron cation **4** and product **2**, successively, along with detection of elemental sulfur as the only by-product of the reaction.

Conclusions

In conclusion, we have developed a novel metal-free method for visible-light-mediated oxidation of thioamides into amides using molecular oxygen (air) as an oxidant and inexpensive



Scheme 2 Photoredox catalytic cycle of eosin Y for the aerobic desulfurization of thioamides into amides.

eosin Y as a powerful organophotoredox catalyst. The reaction utilizes thioamides as substrates, and visible light and oxygen as reagents, hence it does not require any sacrificial electron donor or acceptor. This protocol is a superior alternative to the existing desulfurization of thioamides for syntheses of amides with several advantages in terms of green chemistry parameters such as sustainability, eco-friendly reagents, high efficiency, one-pot simple operation under mild conditions and formation of nontoxic elemental sulfur as the only by-product. This methodology widens the scope of substrates for visible light photoredox reactions.

Experimental section

General

Reagents were obtained from a commercial supplier 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 an aerobic atmosphere. Organic solutions were concentrated using a Buchi rotary evaporator. Column chromatography was carried out over a silica gel (Merck 100–200 mesh) and TLC was performed using silica gel GF254 (Merck) plates. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker AVII (400 MHz) spectrometer in $CDCl_3$–DMSO-d_6 using TMS as internal reference with the chemical shift value being reported in ppm. All coupling constants (J) are reported in Hertz (Hz). MS (EI) spectra were recorded on a double focusing mass spectrometer. Green LEDs (535 nm), Rebel LEDs, mounted on a 25 mm Cool Base 161 lm@ 700 mA were purchased from Commercial Supplier Luxeon Star LEDs Quadica Developments Inc. 47 6th Concession Rd. Brantford, Ontario N 32 5L7 Canada.

General procedure for the aerobic oxidation of thioamides 1 into amides 2 (Table 3). To a solution of thioamide **1** (1.0 mmol) in DMF (3 mL) eosin Y (2.0 mol%) was added and the mixture was irradiated with green LEDs (2.6 W, 161 lm) with stirring under an air atmosphere at r.t. for 6–15 h. After completion of the reaction (monitored by TLC), water (5 mL) was added and the mixture was extracted with EtOAc (3 × 5 mL). The combined organic phase was dried over $MgSO_4$, filtered and evaporated under reduced pressure. The resulting product was purified by silica gel column chromatography using a gradient mixture of hexane–ethyl acetate as an eluent to afford an analytically pure sample of **2**. All the products are known compounds and were characterized by comparison of their spectral data with those reported in the literature.[15,18a,24]

Compound 2a (ref. 24*a*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (br, 1H), 7.53 (d, J = 7.7 Hz, 2H), 7.25 (t, J = 7.6 Hz, 2H), 7.06 (t, J = 7.4 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.91 138.2, 129.1, 124.4, 120.2, 24.5; HRMS (EI): calcd for C_8H_9NO 135.0684, found 135.0682.

Compound 2b (ref. 24*a*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (br, 1H), 7.35 (d, J = 8.2 Hz, 2H), 7.08 (d, J = 8.2 Hz, 2H), 2.33 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 168.4, 135.4, 133.9, 129.4, 120.1, 24.5, 20.8; HRMS (EI): calcd for $C_9H_{11}NO$ 149.0841, found 149.0838.

Compound 2c (ref. 24*b*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (d, J = 9.0 Hz, 2H), 7.08 (br, 1H), 6.82 (d, J = 9.0 Hz, 2H), 3.82 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 156.5, 130.9, 121.9, 114.1, 55.5, 24.4; HRMS (EI): calcd for $C_9H_{11}NO_2$ 165.0790, found 165.0792.

Compound 2d (ref. 24*c*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.07 (br, 1H), 8.32 (d, J = 9.0 Hz, 2H), 8.20 (d, J = 9.0 Hz, 2H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 140.8, 138.4, 128.8, 124.0, 24.9; HRMS (EI): calcd for $C_8H_8N_2O_3$ 180.0535, found 180.0532.

Compound 2e (ref. 24*b*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (d, J = 8.5 Hz, 1H), 7.66 (br s, 1H), 7.55 (dd, J = 8.0 Hz; 1.5 Hz, 1H), 7.30 (dt, J = 1.3 Hz; 8.0 Hz, 1H), 6.95 (t, J = 7.3 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 139.6, 138.1, 132.4, 128.4, 122.1, 121.7, 24.8; HRMS (EI): calcd for C_8H_8BrNO 112.9789, found 112.9788.

Compound 2f (ref. 24*a*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, J = 8.1 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.0 Hz, 2H), 7.38–7.35 (m, 2H), 7.31 (t, J = 7.0 Hz, 2H), 7.14 (t, J = 7.3 Hz, 1H), 7.10–7.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9, 138.1, 132.0, 129.3, 128.9, 128.3, 127.2, 124.7, 120.4; HRMS (EI): calcd for $C_{13}H_{11}NO$ 197.0841, found 197.0840.

Compound 2g (ref. 18*a*). ^{1}H NMR (400 MHz; DMSO-d_6); δ = 10.11 (br, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.55–7.51 (m, 3H), 7.05

(d, J = 9.0 Hz, 2H), 6.95 (d, J = 9.0 Hz, 2H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 134.4, 132.3, 129.2, 128.4, 127.9, 126.8, 114.7, 56.4, 56.1; HRMS (EI): calcd for $C_{14}H_{13}NO_2$ 227.0946, found 227.0943.

Compound 2h (ref. 15). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.89 (br, 1H), 8.36 (d, J = 9.0 Hz, 2H), 7.86–7.15 (m, 5H), 8.23 (d, J = 9.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 149.6, 141.1, 139.0, 128.6, 127.2, 124.2, 123.5, 120.2; HRMS (EI): calcd for $C_{13}H_{10}N_2O_3$ 242.0691, found 242.0693.

Compound 2i (ref. 24*a*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.48 (br s, 1H), 3.18–3.23 (m, 2H), 2.44–2.47 (m, 2H), 1.60–1.76 (m, 6H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.3, 43.0, 36.9, 30.7, 29.9, 23.3; HRMS (EI): calcd for $C_6H_{11}NO$ 113.0841, found 113.0840.

Compound 2j (ref. 18*a*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.29 (br, 1H), 4.00–4.14 (m, 1H), 2.30 (septet, J = 6.9 Hz, 1H), 1.18 (d, J = 6.9 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.6, 41.6, 36.1, 23.5, 19.8; HRMS (EI): calcd for $C_7H_{15}NO$ 129.1154, found 129.1152.

Compound 2k (ref. 24*d*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (br t, J = 7.4 Hz, 2H), 7.34–7.21 (m, 9H), 7.21 (d, J = 7.2 Hz, 2H), 7.09 (d, J = 7.4 Hz, 2H), 4.60 (s, 2H), 4.45 (s, 2H), 3.77 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 137.3, 136.3, 135.1, 128.9, 128.7, 128.5, 128.3, 128.0, 127.8, 127.4, 126.9, 126.6, 50.3, 48.2, 41.1; HRMS (EI): calcd for $C_{22}H_{21}NO$ 315.1623, found 315.1620.

Compound 2l (ref. 24*c*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (t, J = 7.7 Hz, 2H), 7.30–7.19 (m, 3H), 3.73 (s, 2H), 3.60 (br t, J = 5.3 Hz, 2H), 3.38 (br t, J = 5.4 Hz, 2H), 1.59–1.53 (m, 2H), 1.50–1.48 (m, 2H), 1.35–1.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$); δ 169.5, 135.4, 128.7, 128.4, 126.7, 47.3, 43.0, 41.1, 26.3, 25.4, 24.5; HRMS (EI): calcd for $C_{13}H_{17}NO$ 203.1310, found 203.1312.

Compound 2m (ref. 24*d*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16–7.08 (m, 4H), 3.70 (s, 2H), 3.54 (br t, J = 5.2 Hz, 2H), 3.33 (br t, J = 5.4 Hz, 2H), 2.32 (s, 3H), 1.59–1.54 (m, 2H), 1.51–1.48 (m, 2H), 1.39–1.33 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 136.1, 132.4, 129.3, 128.6, 47.3, 43.0, 40.8, 26.3, 25.6, 24.4, 21.1; HRMS (EI): calcd for $C_{14}H_{19}NO$ 217.1467, found 217.1465.

Compound 2n (ref. 24*d*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 (br t, J = 7.6 Hz, 1H), 7.10 (s, 1H), 7.03 (br d, J = 7.4 Hz, 2H), 3.71 (s, 2H), 3.55 (br t, J = 5.5 Hz, 2H), 3.35 (br t, J = 5.5 Hz, 2H), 2.33 (s, 3H), 1.62–1.56 (m, 2H), 1.54–1.48 (m, 2H), 1.40–1.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 138.4, 135.5, 129.3, 128.4, 127.4, 125.5, 47.4, 42.8, 41.1, 26.3, 25.6, 24.5, 21.3; HRMS (EI): calcd for $C_{14}H_{19}NO$ 217.1467, found 217.1469.

Compound 2o (ref. 24*d*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 3.81 (s, 3H), 3.66 (s, 2H), 3.54 (br t, J = 5.3 Hz, 2H), 3.40 (br t, J = 5.5 Hz, 2H), 1.63–1.55 (m, 2H), 1.53–1.47 (m, 2H), 1.40–1.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 158.2, 129.6, 127.6, 114.2, 55.3, 47.1, 43.0, 40.3, 26.2, 25.6, 24.5; HRMS (EI): calcd for $C_{14}H_{19}NO_2$ 233.1416, found 233.1415.

Compound 2p (ref. 24*d*). ^{1}H NMR (400 MHz, $CDCl_3$,): δ = 8.20 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 3.60 (s, 2H), 3.60 (t, J = 5.5 Hz, 2H), 3.40 (t, J = 5.5 Hz, 2H), 1.65–1.60 (m, 2H), 1.58–1.50 (m, 2H), 1.46–1.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 147.0, 143.1, 130.0, 123.9, 47.3, 43.1, 40.6, 26.3, 25.5, 24.3; HRMS (EI): calcd for $C_{13}H_{16}N_2O_3$ 248.1161, found 248.1158.

Compound 2q (ref. 24*d*). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (br t, J = 5.1 Hz, 2H), 7.66 (d, J = 7.8 Hz, 1H), 7.30–7.23 (m, 1H), 3.72 (s, 2H), 3.55 (br t, J = 5.5 Hz, 2H), 3.45 (br t, J = 5.5 Hz, 2H), 1.66–1.60 (m, 2H), 1.57–1.50 (m, 2H), 1.47–1.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 149.9, 148.3, 136.5, 130.6, 122.8, 25.3, 26.4, 37.9, 43.1, 47.1, 24.5; HRMS (EI): calcd for $C_{12}H_{16}N_2O$ 204.1263, found 204.1265.

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