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Copper catalyzed oxidative deamination of Betti bases: an efficient approach for benzoylation/formylation of naphthols and phenols

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An efficient route for benzoylation or formylation of naphthols/phenols is developed *via* oxidative deamination of Betti bases. A copper salt catalyst with TBHP as an oxidant is used. Water is used as a reagent as well as solvent. The reaction proceeds through a regioselective radical pathway. Most importantly, the position of acylation is unambiguous. The method is also applicable to non-hydroxy substrates.

Betti bases,[1] *o*-(α-aminoalkyl)-naphthols or phenols have many applications such as, they are very good precursors for the synthesis of several nitrogen containing bio-active compounds and key intermediates for many multistep organic syntheses.[2] A small number of Betti base derivatives are reported to have biological activity.[3] From the last two decades, Betti bases were widely used as ligands in organometallic and asymmetric catalysis.[4] Despite these progresses, exploration in search of more applications of Betti bases are still highly enviable. The tertiary amine moiety of Betti bases is highly useful to incorporate nucleophile/functional groups into the α-CH of nitrogen through C–H activation.[1b,e]

C–H functionalization has attracted great attention in the past decades since it offers maximum step and atom economy for the formation of carbon–carbon or carbon–hetero bond compared to the routine cross coupling based methods where extra steps are required for the pre-functionalization of substrates.[5] The functionalization of sp^3 C–H bonds adjacent to a nitrogen atom has usually been realized utilizing transition metal salt catalysts with co-oxidants, such as *tert*-butyl hydroperoxide (TBHP), di-*tert*-butyl peroxide (DTBP), H_2O_2, molecular oxygen, to generate iminium ion intermediate, which can react with different nucleophiles.[6] Metals like Pd,[7] Ru,[8] Fe,[9] Rh,[10] V,[11] are often used for this purpose. However, there are many advantages of using copper salts, such as low cost, little toxicity, ready availability, high-efficiency and, therefore, have established to be the most efficient catalysts for the α-functionalization of tertiary amines.[12] However, C–H functionalization *via* oxidative deamination catalyzed by metal or non-metal is less explored.[13]

Our target was to synthesize hydroxyaryl ketones and aldehydes as they are highly useful intermediates in the synthesis of many pharmaceuticals,[14] natural products,[15] and some cosmetic products.[16] Therefore, the development of simple and efficient synthetic methods of this structural moiety is in demand. A few bio-active derivatives of hydroxyaryl ketones are shown (Fig. 1), where **A** is potent against HIV-1 reverse transcriptase,[17] **B** is cancer chemo-preventive[15d] and **C** is cGMP-dependent protein kinase.[15a] By tradition, Friedel–Crafts type acylation reactions have been used to obtain acylated phenol or naphthol compounds,[18] but these methods have been found to be difficult in controlling product regioselectivity.[18b,c] Moreover, Friedel–Crafts reaction of naphthols and phenols give low yield,[18d,e] and in some cases reaction has to be performed at higher temperature.[18f] Another common route to hydroxyaryl ketones is from the corresponding naphthyl/phenyl esters *via* Fries-rearrangement in the presence of Lewis acid catalyst.[19] Although, the yields are good in some cases, but require prolonged heating using stoichiometric amount of Lewis acid.[19a,b] Some reactions are reported with expensive triflate catalysts like $Hf(OTf)_4$ and $Sc(OTf)_3$.[19c,d] Moreover, Fries-rearrangement gives mixture of *o*/*p*-acylated product,[19e,f] and deacylated product.[19g] Recently, transition-metal catalyzed C–H functionalization technique has been used to form aryl ketones.[20] In addition,

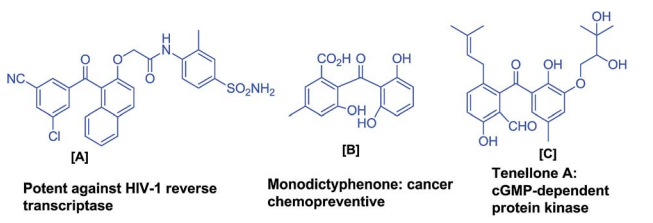

Fig. 1 Few bioactive derivatives of hydroxyaryl ketones.

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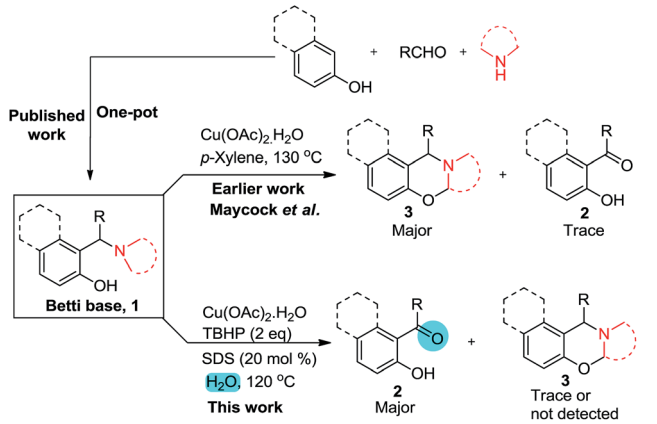
other methods for their synthesis have also been developed. For instance, transformation from *ortho*-functionalized diaryl ketones[21] or chromones,[22] acylation of benzoquinone,[23] or related arenes,[24] coupling reactions of nitriles with boronic acids,[25] and addition of lithium or magnesium reagents to carboxylic derivatives.[26] Though these methods are effective for the acylation, few of the reactions experience harsh reaction conditions,[26] inconvenient operation[24a,26] and handling hazardous substances.[24a]

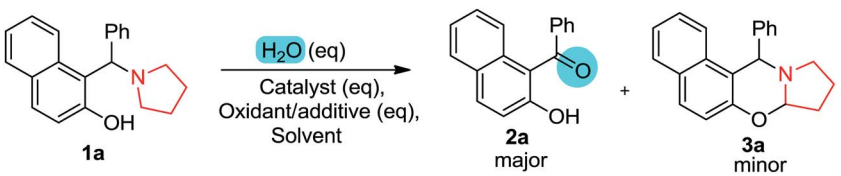


Scheme 1 Synthesis of hydroxyaryl ketones.

Encouraged by the results of Maycock *et al.*, where they obtained dihydro-1,3-oxazines along with traces of ketones from Betti bases (Scheme 1)[1b] and in continuation of our work[27] on the application of Betti bases in organic synthesis, herein we report an efficient method for benzoylation/formylation of naphthols and phenols from Betti bases *via* oxidative deamination under $Cu(OAc)_2 \cdot H_2O$/TBHP catalytic system using water as reagent and solvent (Scheme 1). We used sodium dodecyl sulphate (SDS) in the reaction to solubilize organic materials into water *via* micelle formation.[28] To the best of our knowledge there is no such report of transformation of Betti bases to hydroxyaryl ketones in the literature. Betti bases were efficiently prepared by the 3-component Mannich reaction of naphthol/phenol, aldehydes, and amines and obtained solely *ortho*-substituted naphthol/phenol product (**1**, Scheme 1).[1]

To test our hypothesis, we initiated a model study by considering the transformation of **1a** to **2a** as a representative example. Diverse solvents, metal catalysts and oxidants were screened (Table 1). We found that most of the organic solvents were inefficient for the successful reaction. When we performed the reaction in water as solvent, no product was indeed formed which might be due to insolubility of organic substrates in water. We obtained the best result while performing the reaction in presence of $Cu(OAc)_2 \cdot H_2O$ (0.1 eq.), TBHP (2 eq.) and SDS (0.2 eq.) in water at 120 °C (entry 6, Table 1). Among the two types of sp^3 C–H bonds adjacent to the nitrogen atom, α-

Table 1 Optimization of the reaction conditions[a]



Entry	Catalyst (eq.)	Oxidant/additive (eq.)	H_2O (eq.)	Solvent[b]	Temp. °C	Time (h)	Yield,[c] **2a** (**3a**)%
1	$Cu(OAc)_2 \cdot H_2O$ (0.1)	—	5	*p*-Xylene	130	2	5 (85)
2	$Cu(OAc)_2 \cdot H_2O$ (0.1)	—	10	*p*-Xylene	130	2	5 (85)
3	$Cu(OAc)_2 \cdot H_2O$ (0.1)	TBHP (2)	10	*p*-Xylene	130	2	15 (70)
4	$Cu(OAc)_2 \cdot H_2O$ (0.1)	TBHP (2)	—	H_2O	120	3	NR
5	$Cu(OAc)_2 \cdot H_2O$ (0.08)	TBHP (2), SDS (0.2)	—	H_2O	120	3	70 (trace)
6	**$Cu(OAc)_2 \cdot H_2O$ (0.1)**	**TBHP (2), SDS (0.2)**	**—**	**H_2O**	**120**	**3**	**90 (5)**
7	$Cu(OAc)_2 \cdot H_2O$ (1.0)	SDS (0.2)	—	H_2O	120	3	15 (ND)
8	—	TBHP (2), SDS (0.2)	—	H_2O	120	3	NR
9	$Cu(OAc)_2 \cdot H_2O$ (0.1)	TBHP (2), SDS (0.2)	—	H_2O	100	3	40 (trace)
10	$Cu(OAc)_2 \cdot H_2O$ (0.1)	TBHP (1), SDS (0.2)	—	H_2O	120	3	60 (5)
11	$Cu(OAc)_2 \cdot H_2O$ (0.1)	TBHP (3), SDS (0.2)	—	H_2O	120	3	90 (5)
12	$Cu(OAc)_2 \cdot H_2O$ (0.1)	H_2O_2 (2), SDS (0.2)	—	H_2O	120	3	20 (5)
13	$CuSO_4 \cdot 5H_2O$ (0.1)	TBHP (2), SDS (0.2)	—	H_2O	120	3	50 (trace)
14	CuBr (0.1)	TBHP (2), SDS (0.2)	—	H_2O	120	3	55 (ND)
15	$FeCl_3 \cdot 6H_2O$ (0.1)	TBHP (2), SDS (0.2)	—	H_2O	120	3	40 (5)
16	$Cu(OAc)_2 \cdot H_2O$ (0.1)	TBHP (2), SDS (0.2)	10	DMF	120	3	10 (ND)
17	$Cu(OAc)_2 \cdot H_2O$ (0.1)	TBHP (2), SDS (0.2)	10	DMSO	120	3	10 (ND)
18	$Cu(OAc)_2 \cdot H_2O$ (0.1)	TBHP (2), SDS (0.2)	10	Toluene	120	3	15 (60)

[a] Unless otherwise mentioned, all the reactions were performed by using **1a** (1 mmol, 303 mg). [b] 3 ml of solvent was used in each case. [c] Products were purified by column chromatography using silica gel (100–200 mesh) and yields are of isolated products. NR = No Reaction. ND = Not Detected.

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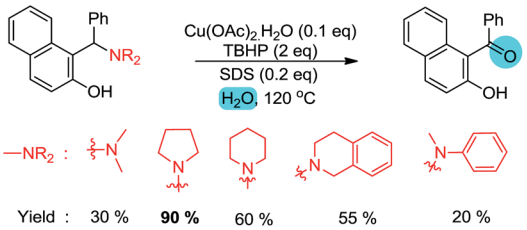
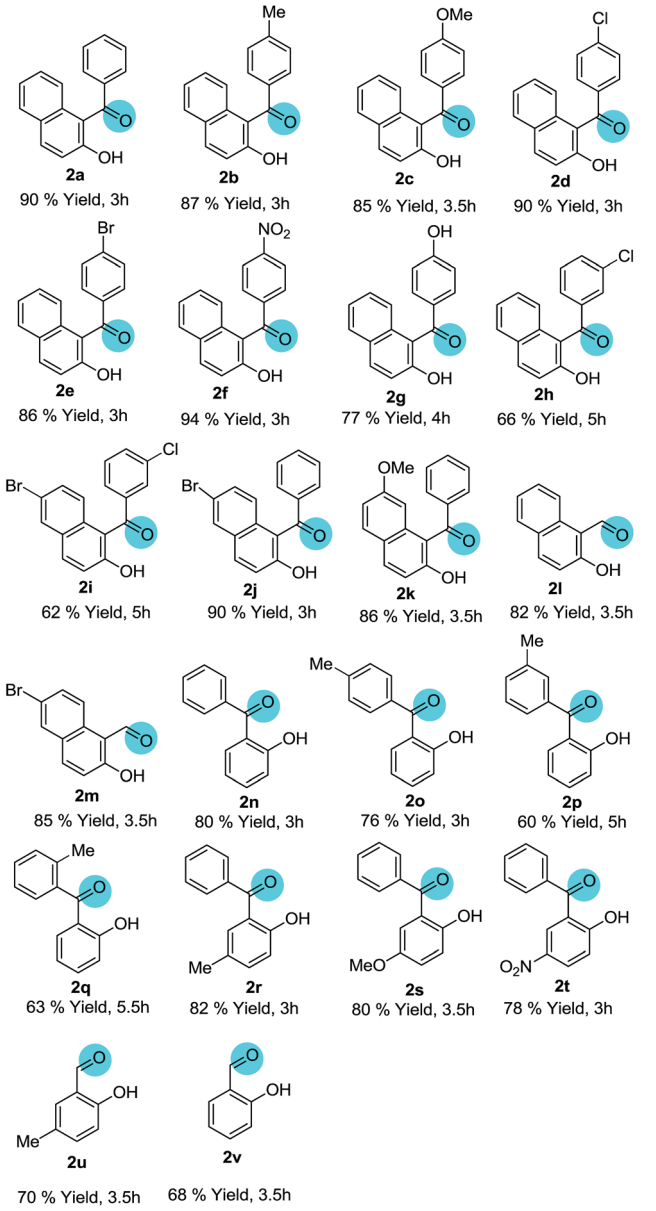


Scheme 2 Screening of *tert*-amine groups of Betti base.

functionalization occurred regioselectively at the benzylic carbon. A trace amount of dihydro-1,3-oxazine (**3a**) was also obtained as side product through the intramolecular α-functionalization of non-benzylic carbon. We next examined the effect of catalyst/oxidant loading on the reaction. Decrease in the loading of TBHP from two to one equivalent reduces the product yield whereas, increasing the amount from two to three equivalents could not further improve the yield (entry 10 & 11, Table 1). Also 0.1 equivalent of $Cu(OAc)_2 \cdot H_2O$ was established to be the lowest level of catalyst loading to offer good yield (Table 1). A series of *tert*-amine moieties of the Betti bases were screened to obtain the best possible yield of the product. We used various aliphatic cyclic, acyclic, aromatic amines, and found that Betti bases prepared from pyrrolidine furnished highest yield (Scheme 2), which was also observed in our previous report.[27]

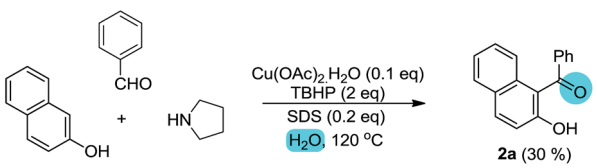
With the optimized conditions in hand, we next investigated the substrate scope of the reaction (Scheme 3). We used a variety of Betti base derivatives of naphthol and phenol. The resultant acylated products which contain a broad range of substituents could be obtained in moderate to excellent yield. *o*/*m*-Substituted aryl ring of Betti base (R in **1**, Scheme 1) offered relatively lower yield of product with longer time (**2h–i** and **2p–q**, Scheme 3). Electron withdrawing group on the R of Betti base increases the product yield, whereas electron releasing group decreases the yield (Scheme 3). We did not observe significant reactivity difference between the substrates containing electron donating and withdrawing groups on the aromatic ring bearing the –OH group. We then attempted our model reaction under 3-component one pot protocol using β-naphthol, benzaldehyde and pyrrolidine in water using the optimized conditions. Unfortunately, we obtained only 30% of yield of **2a** (Scheme 4).

There are two possible mechanisms for the reaction: either a radical mechanism or an ionic mechanism.[29] To establish the reaction mechanism, we performed our model reaction under the optimized conditions in presence of couple of radical scavengers such as, 2,6-di-*tert*-butyl-4-methyl phenol (BHT, 2 eq.) and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, 2 eq.). When we used BHT, there was no formation of product at all and we completely recovered the unreacted Betti base, while a significant drop in the product yield was noticed using TEMPO and only a trace of product **2a** was isolated, which suggest that the reaction follows a radical pathway. We also looked for the feasibility of the reaction without using TBHP or copper catalyst (entry 1, 2 and 8, Table 1). Without TBHP, the reaction gave dihydro-1,3-oxazine with trace of ketone whereas,



Scheme 3 Substrate scope for the synthesis of hydroxyaryl ketones. Reaction conditions: **1** (1 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.1 eq.), TBHP (2 eq., 70% in H_2O), SDS (0.2 eq.) and H_2O (3 ml) at 120 °C. Products were purified by column chromatography and yields are of isolated products.

without copper catalyst no reaction was indeed observed. A tentative mechanism for the reaction was proposed on the basis of these experiments and some relevant reports on α-C–H functionalization of *tert*-amine (Scheme 5).[1b,5f] The benzylic



Scheme 4 Three-component route to hydroxyaryl ketone.

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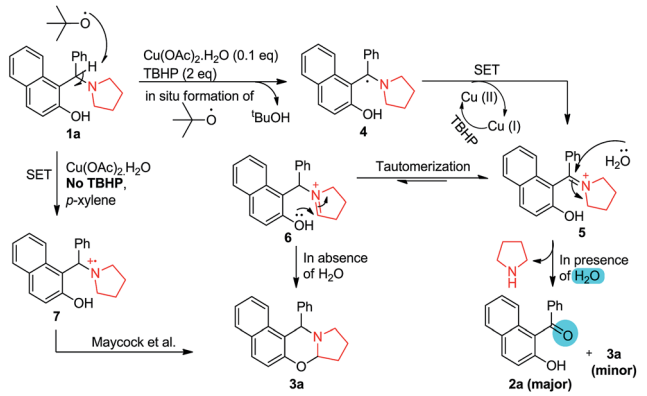
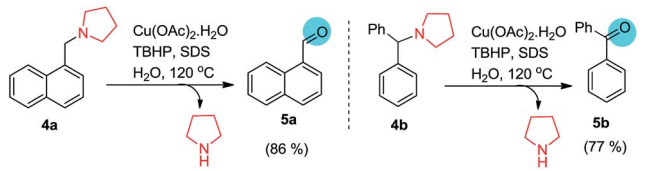


Scheme 5 A tentative mechanism for the reaction.



Scheme 6 Reaction without *ortho*-hydroxyl group.

radical **4** could be formed through H-abstraction by *tert*-butoxy radical (formed by copper catalyzed decomposition of TBHP),[5f] which followed by a single-electron transfer (SET) from **4** to generate the benzylic iminium carbocation **5**. Subsequently, the intermediate **5** was attacked by a molecule of water giving ketone **2**. On the other hand, the intermediate **5** can undergo tautomerization to the less stable non-benzylic iminium carbocation **6**. In absence of water or if water is present in less amount (entries 1–3, Table 1), the intermediate **6** can intramolecularly cyclise to the dihydro-1,3-oxazine **3**. According to Maycock *et al.*, copper catalyst alone provides dihydro-1,3-oxazines through the formation of intermediate ammoniumyl radical cation **7**.[1b]

From the proposed mechanism it is obvious that *ortho*-hydroxyl group does not play any role in obtaining the product. To justify this, we performed two experiments where the substrates do not contain *ortho*-hydroxyl group (Scheme 6). In both the cases we obtained good yield of oxidative deaminated product, indicating that the method is equally applicable to non-*ortho*-hydroxyl substrates as well. **4a** and **4b** were prepared according to the reported procedure.[30a,b]

Conclusion

In conclusion we have developed a simple and efficient method for the benzoylation/formylation of naphthols and phenols. The reaction neither uses any hazardous metal, Lewis acid catalyst nor the corrosive and irritant acyl halide reagent is required. Moreover, water is used as solvent. The method gives sole acylated product and most importantly the position of acylation is unambiguous. A most plausible mechanism is proposed based on some control experiments. We anticipate that this method would offer an efficient procedure to obtain this important class of compounds.

Experimental

General method

All the commercially available reagents were used as received. NMR spectra were recorded on a Bruker Avance DPX-400 NMR spectrometer with TMS as the internal standard at room temperature. Chemical shifts (δ) are quoted in ppm and coupling constants (J) are measured in Hertz (Hz). Mass spectra were recorded in Bruker Daltonics ESQUIRE 3000 LC ESI ion trap mass spectrometer. All the experiments were monitored by thin layer chromatography (TLC) on pre-coated silica gel plates (Merck) and visualized under UV lamp at 254 nm for UV active materials. Further visualization was achieved by staining $KMnO_4$ warming in a hot air oven or by iodine vapour. Column chromatography was performed on silica gel (100–200 mesh), using ethyl acetate : hexane as eluent.

General procedure for the synthesis of 1a–m[1]

To a solution of naphthol (2.0 mmol) in 5 ml ethanol, aldehyde (2.5 mmol) and amine (2.5 mmol) were added. The reaction mixture was stirred at room temperature for 12–15 h (**1a–k**) and 2 h (**1l–m**). The precipitate was filtered and washed with 20% ethanol in hexane to isolate the pure compound.

General procedure for the synthesis of 1n–v[1]

A mixture of phenol (2.0 mmol), aldehyde (2.5 mmol) and amine (2.5 mmol) was stirred at 80 °C for 4–5 h (**1n–t**) and 60 °C for 2 h (**1u–v**). The reaction mixture was brought to room temperature and purified by column chromatography using silica gel (100–200 mesh), and ethyl acetate–hexane as eluent.

The representative example of the synthesis of 2a

To a mixture of **1a** (1.0 mmol, 303 mg), $Cu(OAc)_2 \cdot H_2O$ (0.1 mmol, 20 mg), TBHP (2.0 mmol, 70% in H_2O, 257 mg) and SDS (0.2 mmol, 58 mg) added 3 ml water. The reaction mixture was then refluxed at 120 °C. After 3 h, the reaction was completed (monitored by TLC). Then the reaction mixture was brought to room temperature and extracted with ethyl acetate (2 × 50 ml). Dried the organic fraction with anhydrous sodium sulphate and concentrated in rotavapor under vacuum. Purified the product by column chromatography using silica gel (100–200 mesh), and ethyl acetate–hexane as eluent.

2a[1b]

White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.22 (s, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.64–7.62 (m, 2H), 7.58–7.55 (m, 1H), 7.43–7.39 (m, 2H), 7.32–7.24 (m, 3H), 7.18–7.14 (m, 1H); MS: m/z = 249.1 $[M + H]^+$.

2b[30c]

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.02 (s, 1H), 7.91 (d, J = 8.8 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 2H),

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7.36 (d, J = 8.8 Hz, 1H), 7.29–7.15 (m, 5H), 2.41 (s, 3H); MS: m/z = 263.1 $[M + H]^+$.

2c[30c]

Brownish solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.58 (s, 1H), 7.91 (d, J = 9.2 Hz, 1H), 7.75 (d, J = 9.2 Hz, 1H), 7.68–7.65 (m, 2H), 7.43–7.42 (d, J = 8.8 Hz, 1H), 7.29–7.17 (m, 3H), 6.89–6.86 (m, 2H), 3.86 (s, 3H). MS: m/z = 279.1 $[M + H]^+$.

2d[30c]

White powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.08 (s, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.76–7.73 (m, 1H), 7.57–7.54 (m, 2H), 7.38–7.36 (m, 2H), 7.30–7.18 (m, 4H); MS: m/z = 283.0 $[M + H]^+$.

2e[30d]

Brownish powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.07 (s, 1H), 7.93 (d, J = 8.8 Hz, 1H), 7.75–7.73 (m, 1H), 7.53–7.46 (m, 4H), 7.29–7.26 (m, 2H), 7.23–7.16 (m, 2H); MS: m/z = 327.0 $[M + H]^+$ (100%), 329.0 $[M + H]^+$ (100%).

2f[30e]

Brownish solid; mp = 186–188 °C; ^{1}H NMR (400 MHz $CDCl_3$) δ 11.25 (s, 1H), 8.32–8.29 (m, 2H), 8.06–8.04 (m, 2H), 7.98 (d, J = 8.8 Hz, 1H), 7.79–7.75 (m, 1H), 7.46–7.24 (m, 4H); MS: m/z = 316.0 $[M + Na]^+$.

2g[30c,f]

Off white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.65 (s, 1H), 7.90 (d, J = 9.2 Hz, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.63–7.58 (m, 2H), 7.43–7.41 (m, 1H), 7.31–7.19 (m, 3H), 6.84–6.81 (m, 2H); MS: m/z = 265.1 $[M + H]^+$.

2h[30g]

White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.18 (s, 1H), 7.98 (d, J = 7.5 Hz, 1H), 7.82–7.78 (m, 1H), 7.56–7.52 (m, 2H), 7.42–7.38 (m, 2H), 7.31–7.20 (m, 4H); MS: m/z = 283.0 $[M + H]^+$.

2i[30g]

White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.21 (s, 1H), 7.99–7.86 (m, 2H), 7.71 (s, 1H), 7.62–7.51 (m, 2H), 7.50–7.42 (m, 2H), 7.32–7.24 (m, 2H); MS: m/z = 362.8 $[M + H]^+$.

2j[30c]

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.13 (s, 1H), 7.86 (s, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.62–7.55 (m, 3H), 7.42–7.39 (m, 2H), 7.26–7.12 (m, 3H); MS: m/z = 327.0 $[M + H]^+$ (100%), 329.0 $[M + H]^+$ (100%).

2k[30c]

Reddish brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.62 (s, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.63–7.61 (m, 3H), 7.58–7.54 (m, 1H), 7.45–7.42 (m, 2H), 7.09 (d, J = 8.8 Hz, 1H), 6.89 (d, J = 8.8 Hz, 1H), 6.58 (s, 1H), 3.28 (s, 3H). MS: m/z = 279.1 $[M + H]^+$.

2l[30h]

Light brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.12 (s, 1H), 10.80 (s, 1H), 8.35 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 8.5 Hz, 1H), 7.61–7.58 (m, 1H), 7.46–7.44 (m, 1H), 7.12 (d, J = 8.9 Hz, 1H); MS: m/z = 172.0 $[M + H]^+$.

2m[30i]

White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.11 (s, 1H), 10.79 (s, 1H), 8.22 (d, J = 8.8 Hz, 1H), 7.98 (d, J = 2.4 Hz, 1H), 7.91 (d, J = 9.2 Hz, 1H), 7.71–7.69 (m, 1H), 7.21 (d, J = 9.2 Hz, 1H); MS: m/z = 251.0 $[M + H]^+$ (100%), 253.0 $[M + H]^+$ (100%).

2n[30j]

Low melting solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.01 (s, 1H), 7.69–7.67 (m, 2H), 7.61–7.58 (m, 2H), 7.53–7.50 (m, 3H), 7.10–7.07 (m, 1H), 6.89–6.85 (m, 1H); MS: m/z = 197.0 $[M - H]^+$.

2o[30d]

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.04 (s, 1H), 7.61–7.56 (m, 3H), 7.51–7.48 (m, 1H), 7.33 (d, J = 7.8 Hz, 2H), 7.08–7.05 (m, 1H), 6.91–6.85 (m, 1H), 2.44 (s, 3H); MS: m/z = 213.1 $[M + H]^+$.

2p[30k]

Low melting solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.82 (s, 1H), 7.70 (d, J = 7.2 Hz, 2H), 7.65–7.61 (m, 1H), 7.54 (t, J = 8.8 Hz, 2H), 7.38–7.34 (m, 2H), 7.0 (d, J = 8.4 Hz, 1H), 2.28 (s, 3H); MS: m/z = 213.1 $[M + H]^+$.

2q[30k]

Brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 12.27 (s, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.45–7.41 (m, 1H), 7.33–7.28 (m, 4H), 7.07 (d, J = 8.6 Hz, 1H), 6.84 (t, J = 7.8 Hz, 1H), 2.32 (s, 3H); MS: m/z = 213.0 $[M + H]^+$.

2r[30l]

Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.88 (s, 1H), 7.71–7.32 (m, 7H), 7.02 (d, J = 8.6 Hz, 1H), 2.22 (s, 3H); MS: m/z = 213.1 $[M + H]^+$.

2s[30j]

Light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.61 (s, 1H), 7.71–7.68 (m, 2H), 7.62–7.58 (m, 1H), 7.53–7.50 (m, 2H), 7.16–7.13 (m, 1H), 7.07–7.01 (m, 2H), 3.71 (s, 3H); MS: m/z = 229.1 $[M + H]^+$.

2t[30j]

Brown solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.98 (s, 1H), 8.49 (d, J = 2.8 Hz, 1H), 8.44–8.42 (m, 1H), 7.85–7.83 (m, 2H), 7.76–7.72 (m, 1H), 7.65–7.62 (m, 2H), 7.26 (d, J = 8.8 Hz, 1H); MS: m/z = 244.1 $[M + H]^+$.

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2u[30m]

Gummy; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.82 (s, 1H), 9.83 (s, 1H), 7.33–7.30 (m, 2H), 6.91 (d, J = 9.2 Hz, 1H), 2.26 (s, 3H), MS: m/z = 137.1 $[M + H]^+$.

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