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A general and practical oxidation of alcohols to primary amides under metal-free conditions†‡

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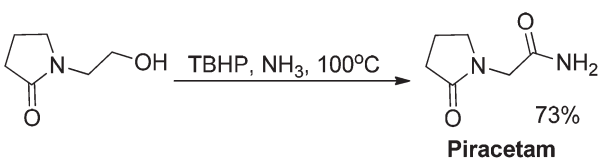
A general procedure for oxidation of both benzyl alcohols and alkyl alcohols to primary amides under catalyst free conditions has been developed. 34 examples of primary amides were produced from their corresponding alcohols in moderate to excellent yields. This is a practical procedure for primary amides synthesis; water and *tert*-butanol are the only by-products. A commercial drug, Piracetam, was prepared in one step with 73% yield as well.

Primary amides are an important class of compounds that are used as starting materials for engineering plastics, detergents, and lubricants.[1] In organic synthesis, primary amides are potent substrates for primary amines, nitriles, amino acid derivates, and heterocycles preparation.[2] Biologically, primary amides are present in numerous biologically active molecules.[3] Based on their importance, several methodologies have been developed for their synthesis,[4–8] such as the hydration of the corresponding nitriles[4] and the reaction of benzoic acids or acid chlorides with ammonia.[5] Other synthetic strategies involve the rearrangement of benzaldoximes,[6] and palladium-catalyzed carbonylation of organo halides with ammonia.[7] The direct oxidation of benzyl amines to the corresponding benzamides was also developed.[8] From the synthetic point of view, the oxidation of alcohols with ammonia to primary amides is more interesting in view of the availability and price of starting materials.[9] The reported methodologies for this transformation either needed a heterogeneous catalyst [OMS-2/O_2(3 bar), 130 °C] or the combination of I_2/H_2O_2, I_2/TEMPO/$FeCl_3/K_2CO_3$, and $PhI(OAc)_2/NaN_3$.

Sustainable development has been accepted as a common knowledge by our society. From the aspect of organic synthesis, the development of green reactions, with high atom efficiency, high selectivity, free from hazard reagents and using green solvent as the medium are the main targets.[10]

From the aspect of oxidation reaction, the development of selective and convenient processes is still challenging.[11] Based on our recent study on oxidation reactions,[12] we wish to report our new discovery for the oxidation of alcohols to primary amides under metal-free conditions in aqueous solution. This is a general procedure that can oxidize both benzyl alcohols and alkyl alcohols under catalyst free conditions. 34 examples of primary amides were produced from their corresponding alcohols in moderate to excellent yields. This is a practical procedure for primary amides synthesis; water and *tert*-butanol are the only by-products. Notably, a commercial drug, Piracetam, was prepared in one step with 73% yield (Scheme 1).

As shown in Table 1, various aromatic amides were produced in good yields. Electron donating groups at *para*-, *meta*-, and *ortho*-positions are all tolerable and gave the corresponding amides in 80–96% yields (Table 1, entries 1–6). 4-(Methylthio)benzamide was produced in 83% yield from the corresponding 4-methylthiobenzyl alcohol without the oxidation of sulfur (Table 1, entry 7). Naphthyl can be tolerated as well and the desired amides were isolated in 64–70% yields (Table 1, entries 8 and 9). The numbers of electron withdrawing groups at different positions were tested as well; the benzyl alcohols were oxidized into primary amides in good yields without further optimization (Table 1, entries 10–19).



Scheme 1 Synthesis of Piracetam.

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†Dedicated to Professor Irina Beletskaya.

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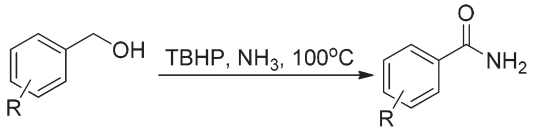
Table 1 Aromatic primary amides synthesis[a]



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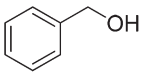
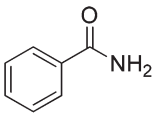
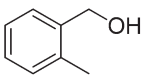
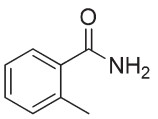
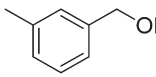
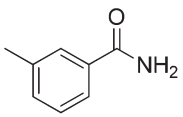
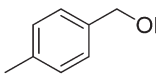
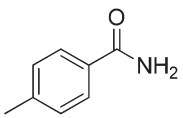
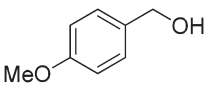
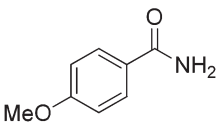
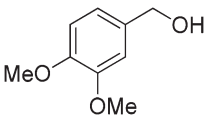
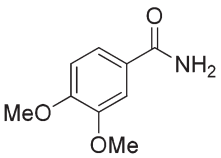
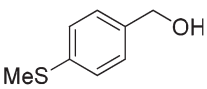
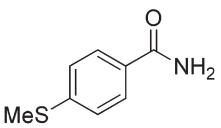
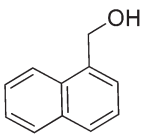
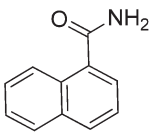
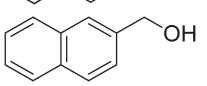
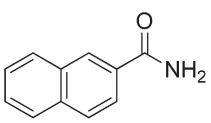
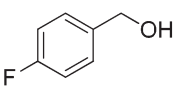
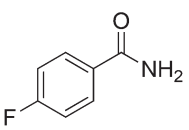
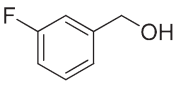
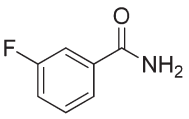
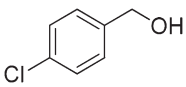
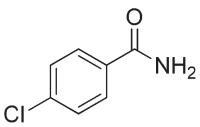
1			80
2			87
3			96
4			89
5			96
6			80
7			83
8			64
9			70
10			72
11			68
12			91

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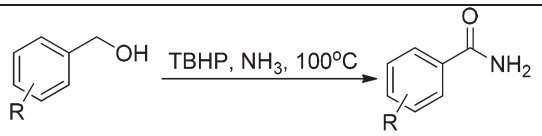
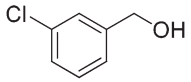
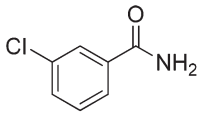
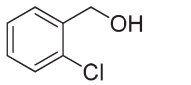
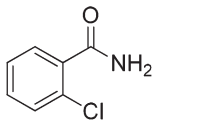
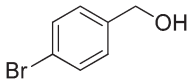
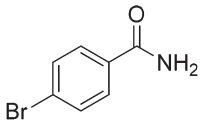
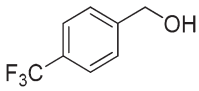
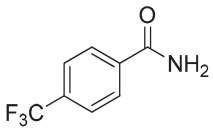
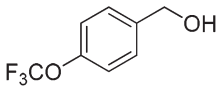
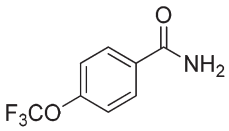
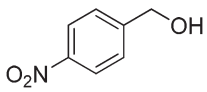
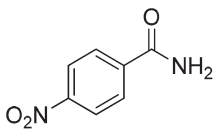
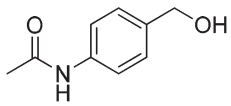
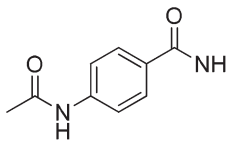


Entry	Benzyl alcohol	Product	Yield[b][%]
13			89
14			95
15			58
16			85
17			89
18			90
19			67

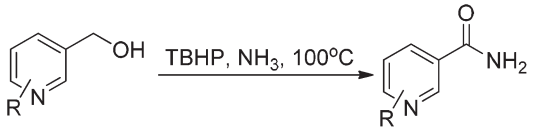
[a] Benzyl alcohols (1 mmol), NH_3 (25 wt% in H_2O; 1 mL), TBHP (70% in H_2O; 8 mmol), 100 °C, 16 h (reaction time was not optimized). [b] Isolated yields.

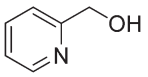
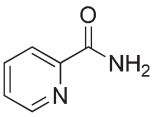
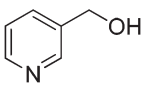
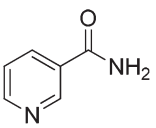
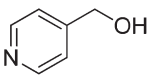
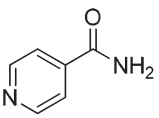
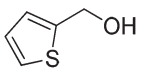
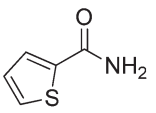
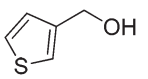
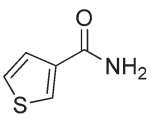
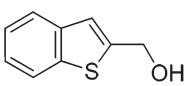
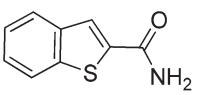
Additionally, 6 examples of heterocyclic amides were produced to prove the generality of this methodology (Table 2). Not only pyridines and thiophenes, but also benzothiophene can be tolerated. The solubility of the amide in water is responsible for the decreased yield in some cases.

Remarkably, various aliphatic primary amides were produced in a one step manner as well (Table 3). Even cinnamamide and 3-phenylpropiolamide can be produced from the corresponding alcohols in 41–65% yields (Table 3, entries 7 and 8).

Moreover, Piracetam, a nootropic drug, with trade names such as Breinox, Dinagen, Lucetam, Nootropil, Nootropyl, Oikamid and many others, with the ability to increase the performance in a variety of cognitive tasks among dyslexic

Table 2 Heteroaromatic primary amides synthesis[a]



Entry	Benzyl alcohol	Product	Yield[b][%]
1			70
2			82
3			95
4			61
5			71
6			60

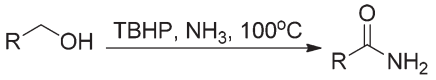
[a] Alcohols (1 mmol), NH_3 (25 wt% in H_2O; 1 mL), TBHP (70% in H_2O; 8 mmol), 100 °C, 16 h (reaction time was not optimized). [b] Isolated yields.

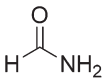
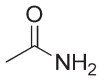
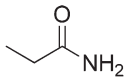
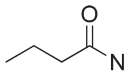
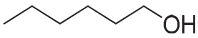
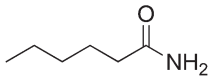
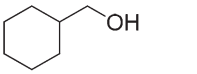
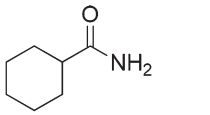
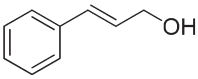
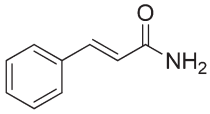
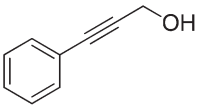
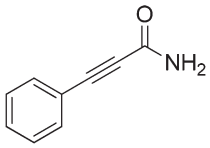
children and also inhibit brain damage caused by a variety of factors including hypoxia and excessive alcohol consumption, was prepared in a one-step manner in 73% yield.[13]

As to the reaction mechanism, it is not clear yet. However, some control experiments were also carried out. If ammonia was replaced with *N*-butylamine, amide was not formed under the same conditions. Several zinc salts [$ZnCl_2$, $ZnBr_2$, $Zn(OAc)_2$ and $Zn(OTf)_2$] were tested as an additional catalyst for the oxidative amidation of benzyl alcohol, but the yield of benzamide was decreased. A possible reaction mechanism has been proposed (Scheme 2). More detailed mechanistic studies are ongoing in our group.

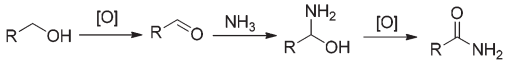
In conclusion, a general and practical methodology for the oxidation of alcohols to primary amides in aqueous solution under metal free conditions has been developed. 34 different kinds of primary amides were produced in good yields. A commercial drug, Piracetam, was prepared in one step with 73% yield as well. The mechanism of this transformation is under investigation in our group based on DFT calculation, *in situ* IR and related tools.

Table 3 Aliphatic primary amides synthesis[a]



Entry	Benzyl alcohol	Product	Yield[b][%]
1			76
2			85
3			86
4			69
5			80
6			79
7			65
8			41

[a] Alcohols (1 mmol), NH_3 (25 wt% in H_2O; 1 mL), TBHP (70% in H_2O; 8 mmol), 100 °C, 16 h (reaction time was not optimized). [b] Isolated yields.



Scheme 2 Proposed reaction mechanism.

Experimental section

Typical reaction procedure for the oxidation of benzyl alcohol to benzamide

In a 25 mL pressure tube equipped with a stirring bar, benzyl alcohol (1 mmol), an aqueous ammonia solution (25 wt% in H_2O; 1 mL) and *tert*-butyl peroxide (70% in H_2O; 8 mmol) were injected by a syringe. Then the tube was closed and heated up to 100 °C for 16 hours. When the reaction was completed, the reaction mixture was cooled to room temperature. The pure product was isolated after a simple filtration. When necessary, the crude product was purified by chromatography using ethyl acetate and hexane as the eluent.

Benzamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 7.40 (s, 1H), 7.47–7.59 (m, 3H), 7.92–7.95 (m, 2H), 8.10 (s, 1H); **^{13}C NMR** (DMSO-d_6): δ = 127.9 ($2CH_2$), 128.6 ($2CH_2$), 131.7 (CH), 134.7 (C), 168.4 (CO).

2-Methylbenzamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 2.67 (s, 3H), 7.32–7.52 (m, 2H), 7.64–7.65 (m, 2H), 8.32–8.44 (m, 2H); **^{13}C NMR** (DMSO-d_6): δ = 22.2 (CH_3), 126.6, 131.5, 131.7, 132.2 (CH), 133.6, 135.8 (C), 169.6 (CO).

3-Methylbenzamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 2.37 (s, 3H), 7.32–7.39 (m, 2H), 7.67–7.73 (m, 2H), 7.95 (s, 1H), 8.00–8.05 (m, 1H); **^{13}C NMR** (DMSO-d_6): δ = 22.2 (CH_3), 126.6, 131.5, 131.7, 132.2 (CH), 133.6, 135.8 (C), 169.6 (CO).

4-Methylbenzamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 2.36 (s, 3H), 7.27 (d, J = 8.23 Hz, 2H), 7.34 (s, 1H, NH_2), 7.83 (d, J = 8.23 Hz, 2H), 7.96 (s, 1H); **^{13}C NMR** (DMSO-d_6): δ = 21.9 (CH_3), 128.5 (2CH), 129.7 (2CH), 132.2 (C), 142.0 (C), 168.9 (CO).

4-Methoybenzamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 3.38 (s, 1H), 3.87 (s, 3H), 7.04 (d, J = 9.18 Hz, 2H), 7.92 (d, J = 9.18 Hz, 2H), 12.6 (s, 1H); **^{13}C NMR** (DMSO-d_6): δ = 56.3 (OCH_3), 114.6 (2CH), 123.8 (C), 132.2 (2CH), 163.7 (C), 167.8 (CO).

3,4-Dimethoybenzamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 3.82 (s, 3H), 3.84 (s, 3H), 6.99–7.05 (m, 2H), 7.23 (s, 1H), 7.47–7.56 (m, 2H), 7.90 (s, 1H); **^{13}C NMR** (DMSO-d_6): δ = 56.4, 56.5 ($2OCH_3$), 111.6, 121.6, 127.5 (CH), 149.1, 152.2 (C), 168.4 (CO).

Picolinamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 7.58–7.62 (m, 1H), 7.71 (s, 1H, NH_2), 7.98–8.03 (m, 1H), 8.07 (s, 1H, NH_2), 8.07–8.09 (m, 1H), 8.17 (s, 1H, NH_2), 8.64–8.66 (m, 1H); **^{13}C NMR** (DMSO-d_6): δ = 122.7 (CH), 127.3 (CH), 138.5 (CH), 149.3 (CH), 151.1 (C), 166.9 (CO).

Nicotinamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 7.48–7.53 (m, 1H), 7.69 (s, 1H, NH_2), 8.24–8.30 (m, 2H), 8.71–8.76 (m, 2H); **^{13}C NMR** (DMSO-d_6): δ = 124.4, 130.6, 136.2, 149.7 (CH), 152.9 (C), 167.6 (CO).

Isonicotinamide. **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 7.79–7.84 (m, 3H), 8.72–8.75 (s, 3H); **^{13}C NMR** (DMSO-d_6): δ = 122.5 (2CH), 123.9 (C), 142.3 (C), 151.2 (2CH), 167.5 (CO).

3-Fluorobenzamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 7.38–7.42 (m, 1H), 7.51–7.57 (m, 2H), 7.67–7.71 (m, 1H), 7.74–7.77 (m, 1H), 8.09 (s, 1H, NH_2); **^{13}C NMR** (DMSO-d_6): δ = 114.0 (d, J_{3CF} = 24.4 Hz, CH), 118.1 (d, J_{3CF} = 22.2 Hz, CH), 123.6 (d, J_{4CF} = 3.01 Hz, CH), 130.3 (d, J_{3CF} = 8.15 Hz, CH), 136.7 (d, J_{3CF} = 6.91 Hz, C), 161.9 (d, J_{CF} = 244.1 Hz, CF), 166.4 (CO).

4-Fluorobenzamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 7.29–7.35 (m, 2H), 7.43 (s, 1H), 7.96–8.00 (m, 2H), 8.03 (s, 1H, NH_2); **^{13}C NMR** (DMSO-d_6): δ = 115.8 (d, J = 23.8 Hz, 2CH), 130.9 (d, J = 9.40 Hz, 2H), 131.6 (C), 164.7 (d, J = 248.8 Hz, CF), 167.6 (CO).

2-Chlorobenzamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 6.83–8.13 (m, 6H); **^{13}C NMR** (DMSO-d_6): δ = 127.9 (d, J = 13.5 Hz), 129.7, 130.6, 130.9 (CH), 138.0 (C), 169.3 (CO).

3-Chlorobenzamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 7.50–7.55 (m, 1H), 7.57 (s, 1H, NH_2), 7.60–7.64 (m, 1H), 7.85–7.89 (m, 1H), 7.94–7.96 (m, 1H), 8.12 (s, 1H, NH_2); **^{13}C NMR** (DMSO-d_6): δ = 127.0 (CH), 128.1 (CH), 131.1 (CH), 131.9 (CH), 134.0 (C), 137.1 (C), 167.3 (CO).

4-Chlorobenzamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 7.49 (s, 1H, NH_2), 7.54–7.58 (m, 2H), 7.91–7.95 (m, 2H), 8.08 (s, 1H, NH_2); **^{13}C NMR** (DMSO-d_6): δ = 129.2 (2CH), 130.3 (2CH), 133.9 (C), 137.0 (C), 167.7 (CO).

4-Bromobenzamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 7.53 (s, 1H, NH_2), 7.66–7.71 (m, 2H), 7.83–7.89 (m, 2H), 8.10 (s, 1H, NH_2); **^{13}C NMR** (DMSO-d_6): δ = 126.0 (C), 130.5 (2CH), 132.2 (2CH), 134.3 (C), 167.9 (CO).

4-(Trifluoromethyl)benzamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 7.69 (s, 1H, NH_2), 7.85–7.89 (m, 2H), 8.10–8.13 (m, 2H), 8.26 (s, 1H, NH_2); **^{13}C NMR** (DMSO-d_6): δ = 124.7 (d, J_{CF3} = 273.1 Hz, CF_3), 126.2 (2CH), 129.3 (2CH), 132.1 (d, J = 31.5 Hz, C), 139.1 (C), 167.7 (CO).

4-(Trifluoromethoxy)benzamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 7.43–7.49 (m, 2H), 7.58 (s, 1H), 8.03–8.08 (m, 2H), 8.16 (s, 1H); **^{13}C NMR** (DMSO-d_6): δ = 121.1 (d, J_{CF3} = 253.9 Hz, OCF_3), 121.3 (2CH), 130.6 (2CH), 132.4, 134.2, 151.2 (C), 167.5 (CO).

4-(Thiomethyl)benzamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 3.31 (s, 3H), 7.70 (s, 1H), 8.01–8.09 (m, 2H), 8.10–8.16 (m, 2H), 8.25 (s, 1H); **^{13}C NMR** (DMSO-d_6): δ = 44.2 (CH_3), 127.9 (2CH), 129.3 (2CH), 139.7, 143.8 (C), 167.5 (CO).

4-Acetamidobenzamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 2.11 (s, 3H), 7.26 (s, 1H), 7.65–7.68 (m, 2H), 7.83–7.89 (m, 3H), 10.2 (s, 1H); **^{13}C NMR** (DMSO-d_6): δ = 124.2 (2CH), 129.6 (2CH), 140.7, 149.8 (C), 166.9 (CO).

Thiophene-2-carboxamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 7.15–7.17 (m, 3H), 7.40 (s, 1H), 7.76–7.79 (m, 2H), 7.99 (s, 1H); **^{13}C NMR** (DMSO-d_6): δ = 128.8, 129.6, 131.9 (CH), 141.3 (C), 163.8 (CO).

Thiophene-3-carboxamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 7.27 (s, 1H), 7.51–7.53 (m, 1H), 7.58–7.59 (m, 1H), 7.82 (s, 1H), 8.18–8.17 (m, 1H); **^{13}C NMR** (DMSO-d_6): δ = 127.4, 128.0, 129.9 (CH), 138.9 (C), 164.6 (CO).

Benzo[*b*]thiophene-2-carboxamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 7.43–7.54 (m, 2H), 7.67 (s, 1H), 7.93–7.98 (m, 1H), 8.02–8.07 (m, 1H), 8.09–8.12 (m, 1H), 8.28 (m, 1H); **^{13}C NMR** (DMSO-d_6): δ = 123.7, 125.7, 125.9, 126.1, 127.0 (CH), 140.1, 141.2, 141.3 (C), 164.2 (CO).

1-Naphthamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 7.54–7.70 (m, 5H), 7.98–8.07 (m, 3H), 8.33–8.38 (m, 1H); **^{13}C NMR** (DMSO-d_6): δ = 125.7, 125.9, 126.4, 126.9, 127.3, 128.9, 130.4 (CH), 130.5, 133.7, 133.9, 135.4 (C), 171.2 (CO).

2-Naphthamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 7.60–7.77 (m, 3H), 7.79–8.04 (m, 4H), 8.13–8.17 (m, 1H), 8.64 (s, 1H); **^{13}C NMR** (DMSO-d_6): δ = 126.2,

127.8, 128.7, 129.1, 129.3, 129.4, 130.5 (CH), 131.4, 133.2, 135.9 (C), 168.6 (CO).

Formamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 5.52 (s, 2H), 7.37 (m, 1H); **^{13}C NMR** (DMSO-d_6): δ = 160.6 (CO).

Acetamide. Ethyl acetate–hexane (2 : 1); **^{1}H NMR** (300 MHz, DMSO-d_6): δ = 1.79 (s, 3H), 6.71 (s, 1H), 7.31 (s, 1H); **^{13}C NMR** (DMSO-d_6): δ = 23.4 (CH_3), 160.6 (CO).

Notes and references

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