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Piper-Betle-Shaped Nano-S-Catalyzed Synthesis of 1-Amidoalkyl-2-naphthols under Solvent-Free Reaction Condition: A Greener "Nanoparticle-Catalyzed Organic Synthesis Enhancement" Approach

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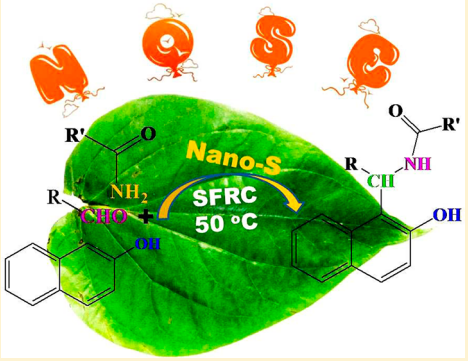
Supporting Information

ABSTRACT: Nano-S prepared by an annealing process showed excellent catalytic activity for the synthesis of 1-amidoalkyl-2-naphthols under solvent-free reaction condition at 50 °C. The catalyst could be reused up to the fifth cycle without loss in its action. The green-ness of the present protocol was also measured using green metrics drawing its superiority.



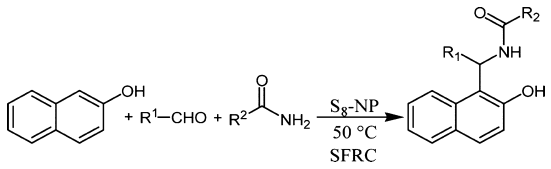
Recently, nanotechnology is mastering intricacies for the synthesis and application of interesting nanomaterials.[1] Nanoparticles have evoked tremendous awareness as nanocatalysts,[2] bridging the homogeneous and heterogeneous catalysis.[3] Hence, nanocatalysis should proffer the prospects for the synthesis of challenging compounds.[4]

The synthesis of sulfur in bulk or micro- or nanoform has been pursued significantly due to its remarkable applications[5] in sulfur nanocomposites,[6] modified carbon nanostructures,[7] and sulfur nanowires,[8] etc. There are some reports for the preparation and properties of sulfur nanoparticles.[9]

The multicomponent reactions[10] (MCRs) are promising constructive sources for devising large molecules with economic viability.[11] In the premise of green chemistry,[12] MCR under solvent-free reaction condition (SFRC)[13a,b] are fascinating since it involves the best reaction medium with "no medium".[13c] The synthesis of amidoalkyl naphthols[14] is important as the 1,3-amino-oxygenated moiety is ubiquitous to a variety of biologically significant compounds.[15]

There are numerous approaches described in the literature for the synthesis of 1-amidoalkyl-2-naphthols. These protocols[16] suffer from shortcomings such as large waste production, higher reaction temperature, prolonged reaction time, low yields, harsh conditions, undesirable byproducts, toxicity, low recovery, and reusability of the catalyst. Therefore, to overcome those drawbacks and in our continual interest in the growth of "NOSE" (nanoparticle-catalyzed organic synthesis enhancement) chemistry,[17] we herein report a convenient protocol for novel sulfur nanoparticle-catalyzed synthesis of 1-amidoalkyl-2-naphthols under SFRC at 50 °C (Scheme 1). To the best of our knowledge, nano-S-catalyzed synthesis of 1-amidoalkyl-2-naphthols is not yet reported.

Scheme 1. Synthesis of 1-Amidoalkyl-2-naphthols



The preparation of nano-S was accomplished by annealing elemental sulfur, which in turn was achieved by catalytic conversion of H_2S.[18] To characterize the sulfur nanoparticles synthesized at 120 and 180 °C, the EDX analysis was performed to find the elemental composition. EDX confirmed the presence of sulfur element only (Figure 1a). Both atomic and weight percent for pure nano-S was found to be 100%. SEM image (Figure 1b) of pure nano-S explored its sheet-like structure that might be due to the stronger intermolecular forces of attraction among the sulfur molecules.

The TGA curve (Figure 1c) indicated the thermal stability having a two-step pattern of weight loss within 180−290 °C. The first weight loss (<180 °C) is attributed to the evaporation of physically absorbed water, and the second weight loss at 290 °C is accompanied by the active liberation of H_2S (Figure 1c).

The X-ray diffraction patterns (Figure 2) for (a) bulk-S, (b) nano-S_8 synthesized at 120 °C and (c) at 180 °C revealed that the samples (a), (b), and (c) showed peaks corresponding to (222), (026), (117), (313), (044), (062), (066), (357), and (551) planes, indicating the presence of cubic orthorhombic

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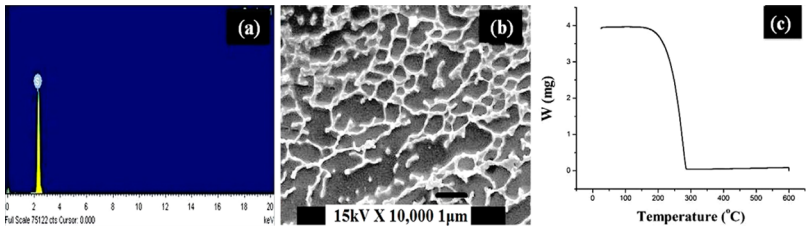


Figure 1. (a) EDX analysis, (b) SEM image, and (c) TGA curve of pure nano-S.

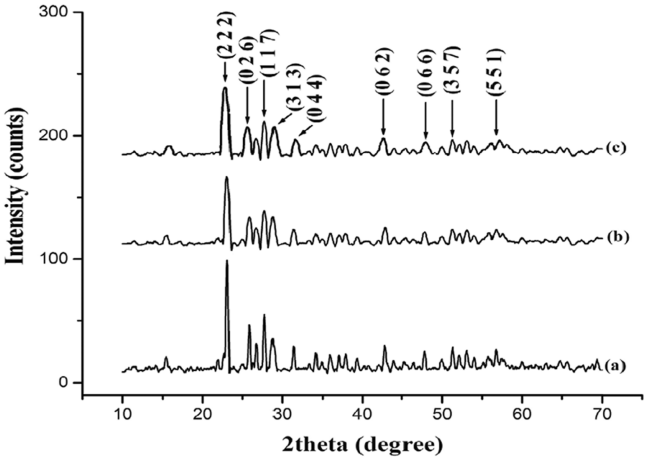


Figure 2. XRD pattern of (a) pure bulk sulfur, (b) nano-sulfur annealed at 120 °C and (c) nano-sulfur annealed at 180 °C.

face-centered S_8 (i.e., α-form) with face-centered lattice sites (JCPDS PDF #78-1889). The sharp XRD peaks of bulk sulfur (Figure 2a) were broadened on annealing to 120 and 180 °C (Figure 2b,c), which confirmed the transformation into the nanoform.

The crystallite sizes were found to lie between 13.8 and 25.6 nm in (b) and 7.3−5.4 nm in (c) calculated from the X-ray line broadening by applying the full width at half-maximum (fwhm) of characteristic peaks (222) and (117) to the Scherrer equation. These sizes are consistent with those measured from the TEM images, indicating the single crystal structure of nanoparticles.

High-resolution TEM (Figure 3) showed that the majority of isolated particles had piper betle shape and a very few were of

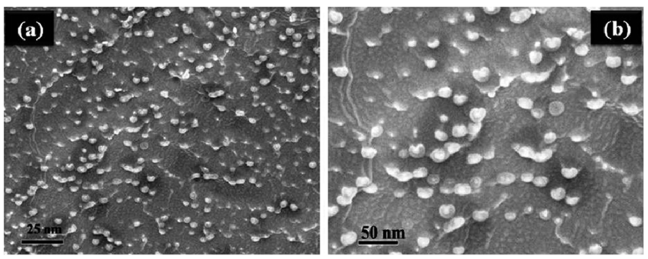


Figure 3. TEM micrographs of nano-S at (a) 25 nm and (b) 50 nm scale.

spherical structure with an average diameter of 5.2 nm (Figure 3a) and 18.3 nm (Figure 3b).

With the idea of developing a green procedure with almost no waste produced for the synthesis of amidoalkyl naphthol derivatives, the optimization of the reaction condition (Table 1) was performed by considering the model reaction (Scheme 2) among 2-naphthol **1**, urea **2**, and benzaldehyde **3** at room temperature under neat condition by grinding with mortar and pestle, but the reaction did not proceed (entry 1). Stirring the reaction mixture at 50 °C/70 °C/120 °C aerobically (16 h) also could not form any product (entries 2−4). These negative results indicated the necessity of a catalyst. Next, we investigated the reaction by using nanocatalysts (3.5 mol %) under SFRC at 50 °C (entries 5−9). To our surprise, the mentioned nanocatalysts furnished the products in trace to poor yields, but nano-sized S_8 showed outstanding activity in the formation of desired product **4** (entry 8) in excellent yields within much shorter time. The reaction was very clean with no side product formation.

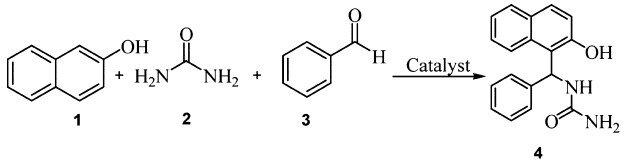
In order to check the effect of solvents (if any) in the reaction, several solvents were screened. The reactions were sluggish and gave poor yield with longer reaction time and

Table 1. Optimization of Reaction Condition[a]

entry	catalyst	solvent	T (°C)	t (h)	yield (%)[b]
1	none	SFRC	rt[h]	3	NR[c]
2	none	SFRC	50	16	NR[c]
3	none	SFRC	70	16	NR[c]
4	none	SFRC	120	16	NR[c]
5	nano-MgO[d]	SFRC	50	5	32
6	nano-Al_2O_3[e]	SFRC	50	5	25
7	nano-TiO_2[f]	SFRC	50	6	*j*
8	nano-S_8[g]	SFRC	50	30[k]	98
9	nano-S_8[g]	SFRC	60[i]	30[k]	52
10	nano-S_8[g]	EtOAc	50	6	48
11	nano-S_8[g]	MeOH	50	7	24
12	nano-S_8[g]	EtOH	50	7	26
13	nano-S_8[g]	THF	50	9	44
14	nano-S_8[g]	toluene	50	5	*j*
15	nano-S_8[g]	H_2O	50	12	12
16	pyridine	SFRC	50	8	17
17	imidazole	SFRC	50	8	17
18	Et_3N	SFRC	50	8	15
19	PPh_3	SFRC	50	8	17

[a]Reaction condition: benzaldehyde (0.3 mL, 3 mmol), urea (0.180 g, 3 mmol), naphthol (0.432 g, 3 mmol), SFRC, or solvent (5 mL). [b]Isolated yields. [c]No reaction was observed, 3.5 mol % of catalyst was used. Particle sizes. [d]17.4−16.4 nm. [e]37.4−39.7 nm. [f]<80 nm. [g]5.2−18.3 nm. [h]Grinded. [i]Ultrasound. [j]Trace. [k]Minute.

Scheme 2. Model Reaction



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tiresome catalyst isolation in the presence of solvents (entries 10−15). This may be attributed to the aggregation of sulfur nanoparticles which might reduce its surface area and block the active sites. Notably, the bulk basic catalysts were not effective in the reaction (entries 16−19).

We also examined the influence of catalyst loading in the model reaction (Scheme 2). The results are summarized in Table S1 and graphically in Figure S1 (Supporting Information), which indicated that the catalytic efficiency of nano-S_8 increased from 1 to 3 mol % and showed the maximum efficiency at 3.5 mol % loading. Increasing catalyst loading, keeping the reaction time constant (30 min), did not improve the yield (entries 8−12).

To generalize the reaction, various benzaldehyde derivatives were tested with naphthol and urea/acetamide under the standardized condition, and the outcomes are summarized in Table 2. Vaghei et al. reported the synthesis of (4-hydroxyphenyl)-(2-hydroxynaphthalen-1-yl)methyl using a catalytic amount of TBBDA.[17] Since then and before there was no report involving 4-hydroxybenzaldehyde as a starting material, but using nano-S, it reacted efficiently with urea/acetamide/benzamide and naphthol, furnishing the desired product in excellent yields (entries 5, 15, and 20). No byproducts were formed. Overall, the aldehydes in the liquid state favored the product formation efficiently due to the best possible mixing, although the reactions were conducted under SFRC.

Table 2. Nano-S-Catalyzed Synthesis of Amidoalkyl Naphthols

entry	R^1	R^2	time (min)	yield (%)[a,b]
1	C_6H_5	NH_2	30	98
2	4-ClC_6H_4	NH_2	15	94
3	3-$NO_2C_6H_4$	NH_2	15	94
4	4-$OCH_3C_6H_4$	NH_2	35	92
5	4-OHC_6H_4	NH_2	45	92
6	*trans*-C_6H_4CHCH	NH_2	30	92
7	2-furyl	NH_2	30	94
8	2-thienyl	NH_2	30	95
9	2-$CH_3C_6H_4$	CH_3	30	91
10	CH_3CH_2	CH_3	60	84
11	$CH_3CH_2CH_2$	CH_3	60	85
12	3-$NO_2C_6H_4$	CH_3	10	90
13	2-ClC_6H_4	CH_3	25	91
14	C_6H_5	CH_3	30	95
15	4-OHC_6H_4	CH_3	25	90
16	*trans*-C_6H_4CHCH	CH_3	45	90
17	C_6H_5	C_6H_5	30	95
18	4-$CH_3C_6H_4$	C_6H_5	30	95
19	4-ClC_6H_4	C_6H_5	30	95
20	4-OHC_6H_4	C_6H_5	25	95
21	$CH_3CH_2CH_2$	C_6H_5	40	90

[a]Yields refer to the isolated pure products. [b]Products were characterized by IR and NMR (^1H and ^{13}C spectroscopy, MS, and also by comparing their melting points with the authentic ones.

A plausible mechanism explaining the sequence of the events is tailored in Figure S2 (Supporting Information). We presumed that the reaction proceeded via *ortho*-quinone methides (*o*-QMs)[19] (I) formed by the nucleophilic addition of 2-naphthol to an aldehyde which was activated by nano-S. Finally, (I) reacted with amides/urea via Michael addition to produce amidoalkyl naphthols. The activation of the aldehydes akin to it has been previously reported with the sulfur-containing catalysts.[16d,23]

The data assembled from the catalyst recyclability test (Supporting Information, Table S2) delineated that the nano-S was equally active in the synthesis of **4** (Scheme 2) from fresh up to the fifth cycle, and after that, its yield slightly decreased with a bit longer reaction time. The TONs (turnover numbers) were also maintained from fresh up to the fifth cycle and then dropped off to some extent.

The XRD patterns of the reused nano-S after the third and fifth run were compared with the fresh one (Supporting Information, Figure S3a). The reused nano-S after the third run demonstrated unchanged morphology, but after the fifth run, it showed a slight diminution in the intensity of the highest peak (222) and an increase in the intensity of the (551) peak. It might be due to the dislocation in the crystal planes[17] during the consecutive cycles.

The TEM micrograph (Supporting Information, Figure S3b) after the fifth run portrayed the aggregation of the particles that might have reduced the activity of nano-S, affording poorer yield.

The recycled catalyst could not be used directly because some organic matter may get adsorbed on its surface. Therefore, the regeneration of the activity of nano-S after the fifth run was accomplished. To verify the decomposition of catalyst after the fifth run (if any), EDX analysis was performed. Interestingly, nano-S after the fifth run confirmed the existence of sulfur only (Figure S4a, Supporting Information). With this pleasing observation, the recycled catalyst was first washed with hot deionized water to remove most organic adsorbates and impurities. Calcination was then performed at 60 °C under sonication (45 min) by putting in distilled THF to reactivate the catalyst by collapsing the agglomeration.

The XRD pattern (Figure S4b, Supporting Information) of reactivated nano-S after calcination under sonication revealed the enhancement in the intensity and broadening of the peaks (026), (117), (313), (044), (062), (066), and (357) and a slight decrease in the intensity of (222) and (551) planes.

The TEM image (Figure S5, Supporting Information) of reactivated nano-S explored the spherical particles with an average diameter of 37 nm. The reusability test of reactivated nano-S was performed from the model reaction (Scheme 2), and the consequences are shown in Table S3 (Supporting Information). Our data showed that the reactivated nano-S could be reused up to the third consecutive run without significant loss in its activity, and after that, its action slowed down.

The "green-ness" of the present methodology was evaluated by different parameters of green chemistry (Supporting Information, Table S4) by considering Scheme 2 that established the supremacy of nano-S over other catalysts. The waste produced during the course of the reaction is the least in our protocol compared to the other methodologies. Moreover, the issues like solvent reusability and catalyst recyclability are omitted by *E*-factor which absolutely raises the accuracy.

In conclusion, we have introduced a potent, benign, highly active, and reusable nano-S for the one-pot synthesis of 1-amidoalkyl naphthols under SFRC using our NOSE approach. The method for the synthesis of nano-S is cheaper, and its utilization in industry will leave almost zero waste production along with easy isolation and regeneration of its activity. The chemistry of nano-S as a catalyst is not explored yet in organic

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synthesis; therefore, we believe that this protocol is going to be a breakthrough for its catalytic application.

EXPERIMENTAL SECTION

Typical Procedure for the Synthesis of Nano-S. Elemental sulfur (1 g) was taken in a silica crucible and heated in an oven preset at 120 °C for 25 min. The melted substance was brought down to room temperature and then placed over an ice bath. Finally, it was grinded with mortar and pestle. This process was repeated thrice. After that, it was washed with double distilled water (3 × 15 mL) and dried in oven at 100 °C. The synthesis of nano-S at 180 °C was accomplished akin to the above.

Representative Procedure for Synthesis of Amidoalkyl Naphthols (Table 2, entry 1). A 1:1:1 mixture of 2-naphthol (0.144 g, 1 mmol), benzaldehyde (0.102 mL, 1 mmol), urea (0.060 g, 1 mmol), and nano-S (S_8-NP) (0.00896 g, 3.5 mol %) was taken in a mortar and grinded with a pestle. The grinded mixture was transferred in a round-bottom flask (50 mL) and placed in a preheated oil bath at 50 °C under SFRC by stirring under aerobic condition for the required time. The progress of the reaction was monitored by TLC. After completion (confirmed by TLC), the reaction mixture was brought down to room temperature and ethyl acetate (5 mL) was added to it. It was then ultracentrifuged (3500 rpm) to pellet out the nano-S. The separated catalyst was washed with hot ethanol (3 × 10 mL), decanted, and finally dried in an oven at 100 °C. The reaction mixture containing the desired product was purified either by column chromatography or TLC preparative or in few cases by recrystallization from hot ethanol. The analytical data of this product (0.28616 g, 98% yield) are in good accord with the reported data.[19a] This procedure was followed for all of the products listed in Table 2.

Analytical Data for All Products. *[(2-Hydroxynaphthalen-1-yl)phenylmethyl]urea[14a] (Table 2, entry 1):* White solid (286.16 mg, 98%); mp 171.2−173.5 °C, R_f = 0.37 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 9.99 (br, s, 1H, OH), 7.75−7.70 (m, Ar−H), 7.35 (br, s, 1H, NH), 7.17−7.13 (m, Ar−H), 6.90 (s, 1H, CH), 5.79 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6, TMS) δ 159.1, 153.3, 144.7, 132.5, 131.1, 129.5, 129.1, 128.3, 126.4, 126.2, 122.9, 121.2,119.7, 48.6; IR (KBr pellets) ν_{max} (cm^{-1}) 3453 (N−H), 3382 (O−H), 3231 (NH_2), 2956 (C−H), 1661 (C═O); m/z (GC-MS) 292.12 [M$^+$]. Anal. Calcd (%) for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52; N, 9.58. Found: C, 74.04; H, 5.22; N, 9.64.

[(4-Chlorophenyl)-(2-hydroxynaphthalen-1-yl)methyl]urea[21] (Table 2, entry 2): White solid (306.44 mg, 94%); mp 210.6−212.7 °C, R_f = 0.35 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 9.96 (br, s, 1H, OH), 7.79−7.71 (m, Ar−H, 6H), 7.36 (br, s, 1H, NH), 7.24−7.10 (m, Ar−H, 4H), 6.86 (s, 1H, CH), 5.80 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6, TMS) δ 159.0, 153.4, 144.0, 132.5, 130.8, 129.7, 129.1, 128.3, 128.1, 127.1, 123.0, 118.9, 49.9; IR (KBr pellets) ν_{max} (cm^{-1}) 3485 (N−H), 3390 (O−H), 3192 (NH_2), 2955 (C−H), 1650 (C═O); m/z (GC-MS) 326.08 [M$^+$]. Anal. Calcd (%) for $C_{18}H_{15}ClN_2O_2$: C, 66.16; H, 4.63; N, 8.57. Found: C, 66.08; H, 4.43; N, 8.67.

[(2-Hydroxynaphthalen-1-yl)-(3-nitrophenyl)methyl]urea[21] (Table 2, entry 3): Light yellow powder (316.78 mg, 94%); mp 186.6−188.1 °C, R_f = 0.31 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 9.91 (br, s, 1H, OH), 8.11−8.07 (m, 6H, Ar−H), 7.91−7.85 (m, 4H, Ar−H), 7.34 (br, s, 1H, NH), 6.84 (s, 1H, CH), 5.82 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6, TMS) δ 161.7, 153.4, 147.3, 145.0, 133.4, 132.1, 130.2, 129.2, 128.9, 128.6, 128.1, 127.3, 123.3, 119.1, 49.4; IR (KBr pellets) ν_{max} (cm^{-1}) 3484 (N−H), 3374 (O−H), 3260 (NH_2), 2971 (C−H), 1632 (C═O); m/z (GC-MS) 337.11 [M$^+$]. Anal. Calcd for $C_{18}H_{15}N_3O_4$: C, 64.09; H, 4.48; N, 12.46. Found: C, 64.14; H, 4.49; N, 12.66.

[(2-Hydroxynaphthalen-1-yl)-(4-methoxyphenyl)methyl]urea[10a] (Table 2, entry 4): White solid (296.24 mg, 92%); mp 182.3−184.7 °C, R_f = 0.38 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 10.03 (br, s, 1H, OH), 7.95−7.89 (m, 6H, Ar−H), 7.44 (br, s, 1H, NH), 7.28−7.23 (m, 4H, Ar−H), 6.88 (s, 1H, CH), 5.79 (s, 2H, NH_2), 3.57 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.2, 153.4, 142.5, 135.5, 133.6, 129.5, 128.9, 128.2, 126.1, 123.5, 122.1, 118.6, 56.1, 50.1; IR (KBr pellets) ν_{max} (cm^{-1}) 3481 (N−H), 3370 (O−H), 3265 (NH_2), 2977 (C−H), 1637 (C═O); m/z (GC-MS) 322.13 [M$^+$]. Anal. Calcd for $C_{19}H_{18}N_2O_3$: C, 70.79; H, 5.63; N, 8.69. Found: C, 70.73; H, 5.33; N, 8.61.

[(2-Hydroxynaphthalen-1-yl)-(4-hydroxyphenyl)methyl]urea[16e] (Table 2, entry 5): White solid (283.36 mg, 92%); mp 146.7−148.6 °C, R_f = 0.31 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 10.51 (br, s, 1H, OH), 8.13−7.95 (m, 6H, Ar−H), 7.57 (br, s, 1H, NH), 7.20−6.98 (m, 4H, Ar−H), 6.69 (s, 1H, CH), 5.79 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.7, 150.5, 143.5, 132.5, 129.0, 129.6, 128.1, 127.8, 127.3, 125.6, 124.8, 122.6, 122.1, 119.8, 47.5; IR (KBr pellets) ν_{max} (cm^{-1}) 3458 (N−H), 3340 (O−H), 3287 (NH_2), 2965 (C−H), 1656 (C═O); m/z (GC-MS) 308.12 [M$^+$]. Anal. Calcd for $C_{18}H_{16}N_2O_3$: C, 70.12; H, 5.23; N, 9.09. Found: C, 70.19; H, 4.93; N, 9.03.

[1-(2-Hydroxynaphthalen-1-yl)-3-phenylallyl]urea (This Work) (Table 2, entry 6): Pale yellow solid (292.56 mg, 92%); mp 169.7−173.2 °C, R_f = 0.25 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 10.54 (br, s, 1H, OH), 8.11 (d, J = 7.5 Hz, 1H), 8.35 (d, J = 7.5 Hz, 1H), 7.75−7.71 (m, 6H, Ar−H), 7.55 (br, s, 1H, NH), 6.91 (s, 1H, CH), 5.82 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.6, 153.3, 150.6, 144.8, 136.3, 132.3, 129.3, 128.6, 128.0, 127.5, 127.1, 126.6, 126.1, 123.5, 122.1, 118.9, 118.1, 49.8; IR (KBr pellets) ν_{max} (cm^{-1}) 3418 (N−H), 3353 (O−H), 3278 (NH_2), 2970 (C−H), 1653 (C═O); m/z (GC-MS) 318.14 [M$^+$]. Anal. Calcd for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.30; H, 5.96; N, 8.89.

[Furan-2-yl-(2-hydroxynaphthalen-1-yl)methyl]urea[20] (Table 2, entry 7): Off white solid (265.08 mg, 94%); mp 162.3−163.7 °C, R_f = 0.35 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 9.97 (s, 1H, OH), 7.75−7.69 (m, 6H, Ar−H), 7.39 (s, 1H, NH), 6.86−6.88 (m, 3H, Ar−H), 6.02 (s, 1H, CH), 5.76 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6, TMS) δ 159.6, 156.8, 153.7, 141.8, 132.8, 129.7, 129.0, 128.7, 126.9, 122.9, 119.0, 118.2, 110.8, 105.6, 50.2; IR (KBr pellets) ν_{max} (cm^{-1}) 3471 (N−H), 3392 (O−H), 3254 (NH_2), 2987 (C−H), 1669 (C═O); m/z (GC-MS) 282.10 [M$^+$]. Anal. Calcd (%) for $C_{16}H_{14}N_2O_3$: C, 68.07; H, 5.00; N, 9.92. Found: C, 68.45; H, 4.93; N, 10.12.

[(2-Hydroxynaphthalen-1-yl)-thiophen-2-yl-methyl]urea[16b] (Table 2, entry 8): Light yellow solid (283.10 mg, 95%); mp 159.2−161.7 °C, R_f = 0.36 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 9.95 (s, 1H, OH), 7.77−7.71 (m, 6H, Ar−H), 7.33 (s, 1H, NH), 6.83−6.88 (m, 3H, Ar−H), 6.22 (s, 1H, CH), 5.80 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6, TMS) δ 160.1, 157.3, 154.4, 141.9, 133.4, 129.8, 129.2, 128.8, 126.2, 122.7, 119.2, 118.5, 110.3, 105.9, 49.8; IR (KBr pellets) ν_{max} (cm^{-1}) 3474 (N−H), 3398 (O−H), 3258 (NH_2), 2982 (C−H), 1672 (C═O); m/z (GC-MS) 298.08 [M$^+$]. Anal. Calcd (%) for $C_{16}H_{14}N_2O_2S$: C, 64.41; H, 4.73; N, 9.39. Found: C, 64.58; H, 4.99; N, 9.43.

N-[(2-Hydroxynaphthalen-1-yl)-o-tolylmethyl]acetamide[22] (Table 2, entry 9): Off white solid (277.55 mg, 91%); mp 200.3−202.7 °C, R_f = 0.38 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 9.98 (br, s, 1H, OH), 8.04−7.89 (m, 6H, Ar−H), 7.30−7.21 (m, 4H, Ar−H), 6.65 (br, s, 1H, NH), 5.77 (s, 1H, CH), 2.27 (s, 3H, CH_3), 1.89 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.5, 152.7, 143.5, 139.5, 134.3, 132.4, 129.2, 128.6, 128.1, 126.3, 125.4, 123.4, 122.0, 118.3, 50.1, 22.7, 19.4; IR (KBr pellets) ν_{max} (cm^{-1}) 3422 (N−H), 3322 (O−H), 2993 (C−H), 1625 (C═O); m/z (GC-MS) 305.14 [M$^+$]. Anal. Calcd (%) for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.60; H, 6.57; N, 4.64.

N-[1-(2-Hydroxynaphthalen-1-yl)-propyl]-acetamide[23] (Table 2, entry 10): White solid (204.12 mg, 84%); mp 172.9−174.4 °C, R_f = 0.42 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 10.05 (br, s, 1H, OH), 8.64 (br, s, 1H, NH), 7.82−7.75 (m, 6H, Ar−H), 6.24 (t, 1H, J = 7.3 Hz, CH), 2.17 (s, 3H, CH_3), 1.91−1.97 (m, 1H, CH_2), 0.93 (t, 3H, J = 7.3 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.4, 152.3, 134.6, 132.0, 131.3, 128.6, 128.1, 127.7, 127.2, 126.8, 126.1, 122.6, 119.4, 118.0, 48.6, 36.2, 19.8, 13.7; IR (KBr pellets) ν_{max} (cm^{-1}) 3418 (N−H), 3228 (O−H), 3004 (C−H), 1636 (C═O); m/z (GC-MS) 243.13 [M$^+$]. Anal. Calcd (%) for

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$C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 74.12; H, 7.37; N, 5.56.

N-[1-(2-Hydroxynaphthalen-1-yl)butyl]acetamide[23] *(Table 2, entry 11):* White solid (218.45 mg, 85%); mp 221.3−223.8 °C, R_f = 0.40 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 10.15 (br, s, 1H, OH), 8.60 (br, s, 1H, NH), 7.80−7.73 (m, 6H, Ar−H), 6.04 (t, 1H, J = 7.7 Hz, CH), 2.12 (s, 3H, CH_3), 1.81−1.73 (m, 1H, CH_2), 1.36−1.29 (m, 1H, CH_2), 0.96 (t, 3H, J = 7.7 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.4, 152.1, 134.6, 132.4, 131.3, 129.1, 128.7, 128.2, 127.3, 126.7, 126.1, 122.0, 119.1, 118.3, 47.9, 36.6, 19.8, 13.7; IR (KBr pellets) ν_{max} (cm^{-1}) 3451 (N−H), 3234 (O−H), 3041 (C−H), 1636 (C═O); m/z (GC-MS) 257.14 [M^+]. Anal. Calcd (%) for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 74.93; H, 7.62; N, 5.74.

N-[(2-Hydroxynaphthalen-1-yl)-(3-nitrophenyl)methyl]-acetamide[14b] *(Table 2, entry 12):* Pale yellow solid (302.40 mg, 90%); mp 240.2−241.6 °C, R_f = 0.36 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 10.03 (br, s, 1H, OH), 8.03−7.73 (m, 6H, Ar−H), 7.51 (br, s, 1H, NH), 7.11−7.02 (m, 4H, Ar−H), 6.10 (s, 1H, CH), 1.95 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 162.3, 154.2, 132.5, 130.1, 129.4, 128.8, 128.1, 127.3, 126.4, 123.3, 122.9, 122.1, 118.3, 117.0, 115.3, 114.1, 43.9, 22.3; IR (KBr pellets) ν_{max} (cm^{-1}) 3436 (N−H), 3258 (O−H), 2997 (C−H), 1644 (C═O); m/z (GC-MS) 336.11 [M^+]. Anal. Calcd (%) for $C_{19}H_{16}N_2O_4$: C, 67.85; H, 4.79; N, 8.33. Found: C, 67.49; H, 4.86; N, 8.40.

N-[(2-Chlorophenyl)-(2-hydroxynaphthalen-1-yl)methyl]-acetamide[24] *(Table 2, entry 13):* Off white solid (295.75 mg, 91%); mp 212.8−214.5 °C, R_f = 0.38 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 9.98 (br, s, 1H, OH), 7.94−7.88 (m, 6H, Ar−H), 7.47 (br, s, 1H, NH), 7.29−7.36 (m, 4H, Ar−H), 6.03 (s, 1H, CH), 1.91 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, TMS) δ 165.6, 154.1, 140.4, 133.5, 133.4, 132.8, 132.1, 130.3, 129.8, 129.1, 128.7, 127.6, 127.0, 123.1, 123.6, 119.2, 117.4, 48.6, 23.5; IR (KBr pellets) ν_{max} (cm^{-1}) 3440 (N−H), 3251 (O−H), 2990 (C−H), 1645 (C═O); m/z (GC-MS) 325.09 [M^+]. Anal. Calcd (%) for $C_{19}H_{16}ClNO_2$: C, 70.05; H, 4.95; N, 4.30. Found: C, 69.96; H, 4.55; N, 4.45.

N-[(2-Hydroxynaphthalen-1-yl)-phenylmethyl]acetamide[14a] *(Table 2, entry 14):* White solid (276.45 mg, 95%); mp 228.3−229.5 °C, R_f = 0.46 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 9.70 (br, s, 1H, OH), 7.94−7.88 (m, 6H, Ar−H), 7.53 (br, s, 1H, CH), 7.21−7.07 (m, 5H, Ar−H), 2.01 (s, 3H, CH_3); ^{13}C (100 MHz, DMSO-d_6, TMS) δ 167.6, 152.7, 144.7, 134.6, 128.9, 128.7, 128.1, 127.8, 127.1, 125.5, 124.7, 123.6, 122.3, 122.1, 118.2, 43.6, 21.7; IR (KBr pellets) ν_{max} (cm^{-1}) 3459 (N−H), 3388 (O−H), 3007 (C−H), 1660 (C═O); m/z (GC-MS) 291.13 [M^+]. Anal. Calcd (%) for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.70; H, 5.93; N, 4.91.

N-[(2-Hydroxynaphthalen-1-yl)-(4-hydroxyphenyl)methyl]-acetamide (This Work) (Table 2, entry 15): Light crimson solid (276.30 mg, 90%); mp 185.8−189.6 °C, R_f = 0.29 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 10.07 (br, s, 1H, OH), 7.71−7.68 (m, 6H, Ar−H), 7.44 (br, s, 1H, NH), 7.22−7.17 (m, 4H,, Ar−H), 6.41 (s, 1H, CH), 1.97 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6, TMS) δ 167.2, 148.1, 140.3, 130.4, 129.7, 129.1, 128.4, 127.7, 127.2, 125.6, 124.1, 122.7, 122.1, 120.5, 119.0, 49.3 22.1; IR (KBr pellets) ν_{max} (cm^{-1}) 3480 (N−H), 3365 (O−H), 2992 (C−H), 1675 (C═O); m/z (GC-MS) 307.12 [M^+]. Anal. Calcd (%) for $C_{19}H_{17}NO_3$: C, 74.25; H, 5.58; N, 4.56. Found: C, 74.33; H, 5.52; N, 4.26.

N-[1-(2-Hydroxynaphthalen-1-yl)-3-phenylallyl]acetamide[16c] *(Table 2, entry 16):* Off white solid (285.30 mg, 90%); mp 174.5−176.0 °C, R_f = 0.28 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 11.03 (br, s, 1H, OH), 8.29 (d, J = 6.9 Hz, 1H), 8.17 (d, J = 6.9 Hz, 1H), 7.80−7.74 (m, 6H, Ar−H), 7.51 (br, s, 1H, NH), 6.23 (s, 1H, CH), 2.05 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.1, 155.2, 151.4, 145.2, 134.4, 133.0, 130.2, 129.1, 128.7, 128.0, 127.5, 126.7, 126.2, 123.4, 122.3, 118.7, 118.2, 48.7, 21.3; IR (KBr pellets) ν_{max} (cm^{-1}) 3411 (N−H), 3350 (O−H), 2989 (C−H), 1659 (C═O); m/z (GC-MS) 317.14 [M^+]. Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.51; H, 6.09; N, 4.77.

N-[(2-Hydroxynaphthalen-1-yl)-phenylmethyl]benzamide[14a] *(Table 2, entry 17):* White solid (335.35 mg, 95%); mp 235.1−237.5 °C, R_f = 0.25 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 10.34 (br, s, 1H, OH), 8.17−8.11 (m, 6H, Ar−H), 7.92−7.87 (m, 5H, Ar−H), 7.40 (br, s, 1H, NH), 7.20−7.14 (m, 5H, Ar−H), 6.07 (s, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.5, 153.4, 148.2, 145.2, 134.8, 133.4, 132.8, 132.2, 130.8, 130.3, 129.7, 128.4, 128.1, 127.7, 127.1, 123.8, 122.6, 122.6, 121.0, 119.3, 118.1, 49.7; IR (KBr pellets) ν_{max} (cm^{-1}) 3475 (N−H), 3361 (O−H), 2984 (C−H), 1656 (C═O); m/z (GC-MS) 353.14 [M^+]. Anal. Calcd for $C_{24}H_{19}NO_2$: C, 81.56; H, 5.42; N, 3.96. Found: C, 81.73; H, 5.51; N, 3.90.

N-[(2-Hydroxynaphthalen-1-yl)-p-tolylmethyl]benzamide[14b] *(Table 2, entry 18):* Light yellow solid (348.65 mg, 95%); mp 207.5−209.8 °C, R_f = 0.27 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 9.91 (br, s, 1H, OH), 8.04−7.98 (m, 6H, Ar−H), 7.63 (br, s, 1H, NH), 7.23−7.14 (m, 9H, Ar−H), 6.07 (s, 1H, CH), 1.91 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.8, 153.1, 143.3, 139.5, 134.7, 132.9, 129.1, 128.8, 128.2, 126.3, 125.5, 123.4, 122.6, 119.4, 118.1, 48.7, 20.3; IR (KBr pellets) ν_{max} (cm^{-1}) 3419 (N−H), 3317 (O−H), 3071 (C−H), 1623 (C═O); m/z (GC-MS) 367.16 [M^+]. Anal. Calcd for $C_{25}H_{21}NO_2$: C, 81.72; H, 5.76; N, 3.81. Found: C, 81.53; H, 6.11; N, 3.87.

N-[(4-Chlorophenyl)-(2-hydroxynaphthalen-1-yl)methyl]-benzamide[23] *(Table 2, entry 19):* Off white solid (367.65 mg, 95%); mp 179.0−181.6 °C, R_f = 0.24 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 10.06 (br, s, 1H, OH), 8.06−7.97 (m, 6H, Ar−H), 7.43 (br, s, 1H, NH), 7.28−7.23 (m, 4H, Ar−H), 7.07−7.01 (m, 5H, Ar−H), 6.12 (s, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.0, 153.3, 138.7, 134.1, 132.5, 132.1, 131.2, 130.6, 129.7, 128.4, 128.2, 128.0, 127.8, 127.3, 126.7, 126.2, 122.9, 122.4, 118.7, 116.6, 48.9; IR (KBr pellets) ν_{max} (cm^{-1}) 3440 (N−H), 3325 (O−H), 3070 (C−H), 1644 (C═O); m/z (GC-MS) 387.10 [M^+]. Anal. Calcd for $C_{24}H_{18}ClNO_2$: C, 74.32; H, 4.68; N, 3.61. Found: C, 74.26; H, 4.60; N, 3.86.

N-[(2-Hydroxynaphthalen-1-yl)-(4-hydroxyphenyl)methyl]-benzamide (This Work) (Table 2, entry 20): Light brown solid (350.55 mg, 95%); mp 191.3−193.3 °C, R_f = 0.21 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 11.24 (br, s, 1H, OH), 8.94 (br, s, 1H, NH), 8.11−8.05 (m, 6H, Ar−H), 7.81−7.76 (m, 4H, Ar−H), 7.21−7.15 (m, 5H, Ar−H), 6.79 (s, 1H, CH); ^{13}C NMR (100 MHz, DMSO-d_6, TMS) δ 169.6, 156.4, 152.4, 149.2, 144.7, 139.2, 134.5, 132.5, 132.1, 130.0, 129.6, 129.2, 128.8, 128.1, 127.9, 127.1, 125.2, 124.4, 122.9, 122.2, 120.8, 119.3, 50.3 ; IR (KBr pellets) ν_{max} (cm^{-1}) 3488 (N−H), 3366 (O−H), 2955 (C−H), 1655 (C═O); m/z (GC-MS) 369.14 [M^+]. Anal. Calcd for $C_{24}H_{19}NO_3$: C, 78.03; H, 5.18; N, 3.79. Found: C, 77.67; H, 5.22; N, 4.08.

N-[1-(2-Hydroxynaphthalen-1-yl)butyl]benzamide[23] *(Table 2, entry 21):* White solid (287.10 mg, 90%); mp 240.1−242.7 °C, R_f = 0.33 (50% AcOEt/hexane); ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ 10.08 (br, s, 1H, OH), 8.11−8.05 (m, 6H, Ar−H), 7.83−7.79 (m, 5H, Ar−H), 7.31 (br, s, 1H, NH), 6.34 (t, 1H, J = 6.5 Hz, CH), 2.15 (s, 3H, CH_3), 1.84−1.78 (m, 1H, CH_2), 1.39−1.33 (m, 1H, CH_2), 0.97 (t, 3H, J = 6.5 Hz, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.7, 155.3, 148.1, 144.6, 139.7, 139.2, 135.1, 133.7, 132.4, 129.3, 128.8, 128.3, 127.7, 126.2, 125.3, 122.8, 119.6, 118.4, 48.7, 36.3, 19.4, 13.3; IR (KBr pellets) ν_{max} (cm^{-1}) 3469 (N−H), 3239 (O−H), 3010 (C−H), 1659 (C═O); m/z (GC-MS) 319.16 [M^+]. Anal. Calcd (%) for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.39. Found: C, 79.11; H, 6.92; N, 4.45.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Recycling potential of nano-S, turnover number (TON) for nano-S, green metrics, Tables S1, S2, S3, and S4, list of figures, and ^{1}H and ^{13}C NMR spectra of new compounds. This

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Notes

The authors declare no competing financial interest.

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