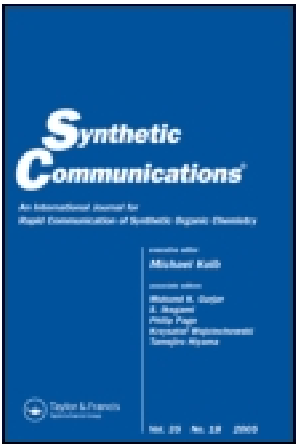

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Glycerol as an Alternative Green Reaction Medium for Multicomponent Reactions Using PS-PEG-OSO_3H as Catalyst

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GLYCEROL AS AN ALTERNATIVE GREEN REACTION MEDIUM FOR MULTICOMPONENT REACTIONS USING PS-PEG-OSO$_3$H AS CATALYST

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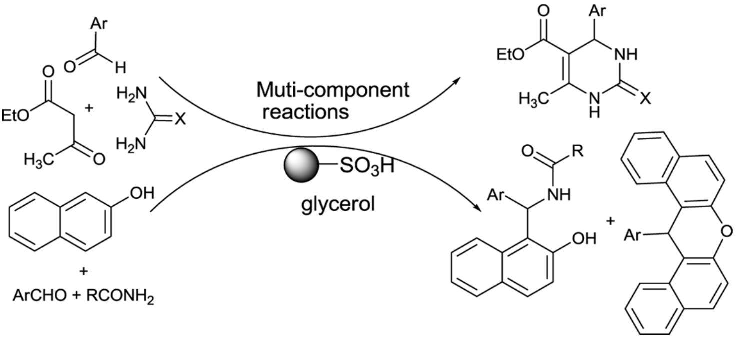
GRAPHICAL ABSTRACT



Abstract *Development of green solvents from renewable resources has gained much attention recently, because of the extensive uses of solvents in almost all of the chemical industry and the predicted disappearance of fossil oil. Here we show that glycerol and PS-PEGOSO$_3$H as a green and recyclable catalyst system were used in the multicomponent reactions for the synthesis of 3,4-dihydropyrimidinones, amidoalkyl naphthols, and dibenzoxanthenes, respectively. Excellent products yields and good recyclability of catalyst and glycerol were achieved. It demonstrates that glycerol is a renewable and recyclable green solvent that is nontoxic, biodegradable, and able to dissolve organic substrates. It was easy to isolate the reaction products by simple extraction.*

Keywords 3,4-Dihydropyrimidinones; glycerol; green chemistry; polymer-supported acid catalyst

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INTRODUCTION

The use of large volumes of volatile hazardous organic solvents in industrial processes poses a serious threat to the environment. Thus, procedures involving alternative benign solvents in reaction, isolation, and purification are of high priority in industry and academic research. Solvent-free processes have been developed,[1] which to some extent have succeeded in some organic reactions. However, in performing the majority of organic transformations, solvents play a critical role in mixing the ingredients to be more efficient. The solvent can also deliver the thermal energy needed for the reaction. In addition, the choice of solvent may affect the reaction activity and selectivity. Meanwhile, using water as a green solvent has also been well documented,[2,3] but the practical utilization is limited because of the hydrophobic nature of organic compounds and the sensitivity of catalysts to moisture. Ionic liquid has also been used as reaction media instead of water and organic solvents. However, ionic liquids, especially imidazolium-based systems containing PF_6 and BF_4 anions, are toxic in nature as they liberate hazardous HF, and their high cost and disposability make their utility limited.[4–6]

Glycerol as a green solvent, previously uncharted, has become an emerging field recently.[7] Wolfson's group[8–10] and Jérôme's group[11–12] have documented that glycerol could be used as a green solvent for some catalytic and noncatalytic organic transformations. As a solvent, glycerol has also promising physical and chemical properties, which allows its use as an alternative environmentally friendly solvent. It has a very high boiling point and negligible vapor pressure; it is stable up to its boiling temperature, is compatible with most organic and inorganic compounds, and does not requiring special handling or storage. In addition, like water, glycerol is natural, highly hydrophilic, nontoxic, abundant, biodegradable, and very cheap. Different hydrophobic solvents such as ethers and hydrocarbons, which are immiscible in glycerol, allow removal of the products by simple extraction. Distillation of products is also feasible because of the high boiling point of glycerol.

Multicomponent reactions (MCRs) have emerged as an important tool for building diverse and complex organic molecules through carbon–carbon and carbon–hetero atom bond formations taking place in a tandem manner.[13,14] Therefore, the design of novel MCRs has attracted great attention from research groups working in medicinal chemistry, drug discovery, and materials science. Among many kinds of multi-component condensations, the Biginelli reaction is the most widely exploited examples of MCRs.[15–17] We previously reported the synthesis of Polyethylene Glycol (PEG)-bound sulfonic acid[18] and polystyrene-poly(ethylene glycol) (PS-PEG) resin-supported sulfonic acid[19] and their utilization in the Biginelli reaction.

The purpose of this study is to explore the scope and limitation of glycerol as an alternative green solvent using PS-PEG-supported sulfonic acid as a catalyst in three typical MCRs. These included the Biginelli reaction to synthesize 3,4-dihydropyrimidones; reaction of amide, 2-naphthol, and aldehydes to produce amidoalkyl naphthols; and the condensation of two molecules of 2-naphthol with one molecular of aldehyde to produce dibenzoxanthenes.

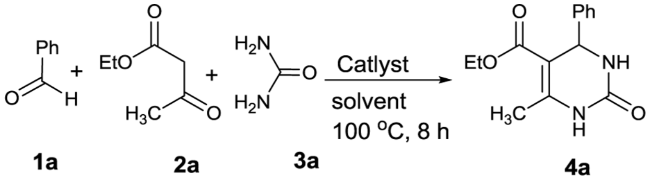
RESULTS AND DISCUSSION

PS-PEG-OSO$_3$H was prepared according to our previous work.[19] Elemental analysis found C 52.78%, H 6.41%, and S 11.64%, which indicated that the SO$_3$H group capacity of PS-PEG-OSO$_3$H was 3.6 mmol/g. The SO$_3$H group capacity of PS-PEG-SO$_3$H was found to be 3.3 mmol/g by titration using 20% NaOH aqueous as standard solution.

First, we started the investigation of the acid-catalyzed Biginelli reaction of acetoacetate **1a**, benzaldehyde **2a**, and urea **3a** in glycerol. When this reaction was performed at 100 °C using acid catalysts, such as *p*-toluene sulfonic acid (*p*-TSA), poly(ethylene glycol)-supported sulfonic acid (PEGOSO$_3$H), PS-PEGOSO$_3$H, and acetic acid, the desired product **4a** was obtained with 73–88% yields after 8 h (Table 1, entries 1–4). All acids used in this reaction could effectively catalyze this three-component reaction. When the reaction was performed without any catalyst, the product **4a** was obtained with 20% yield (entry 5). The combination solvent system of equal amounts of glycerol with H$_2$O and pure water were also tested as the reaction solvents (entries 6 and 7). Because of the good recyclability, we selected PS-PEG-OSO$_3$H as the catalyst to perform the synthesis of compounds **4a–k** (Table 2). From Table 2, it is evident that our methodology is reasonably general and can be applied to the synthesis of 3,4-dihydropyrimidinone derivatives.

The recyclability of the glycerol and PS-PEGOSO$_3$H was also investigated. At the end of the reaction, because glycerol and PS-PEGOSO$_3$H are not soluble in the organic phase, the product can be easily extracted with ethyl acetate. After simple filtration and washing with ethyl acetate and ether, the recycled PS-PEGOSO$_3$H was used directly in the next run. The solutions were combined and washed with

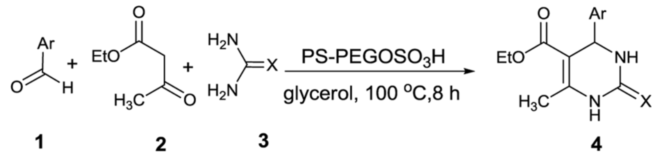
Table 1. Biginelli reaction in glycerol in the presence of acid catalysts[a]



Entry	Catalyst	Solvent	Yield (%)[b]
1	*p*-TSA	Glycerol	84
2	PEGOSO$_3$H	Glycerol	87
3	PS-PEGOSO$_3$H	Glycerol	88
4	Acetic acid	Glycerol	73
5	No catalyst	Glycerol	20
6	PS-PEGOSO$_3$H	Glycerol/water	48[c]
7	PS-PEGOSO$_3$H	Water	44

[a] **1a**: 1 mmol, **2a**: 1 mmol, **3a**: 1.2 mmol, solvent: 2.0 g, catalyst: 30% mmol.
[b] Isolated yield.
[c] At 120 °C for 12 h.

Table 2. Biginelli reaction in glycerol using PS-PEGOSO$_3$H as catalyst[a]



Entry	**1**/Ar	**3**/X	Product	Yield (%)[b]
1	C_6H_5	O	**4a**	88
2	4-MeOC_6H_4	O	**4b**	82
3	4-$NO_2C_6H_4$	O	**4c**	76
4	2-ClC_6H_4	O	**4d**	85
5	4-ClC_6H_4	O	**4e**	89
6	C_6H_5	S	**4f**	84
7	4-MeOC_6H_4	S	**4g**	85
8	3-$NO_2C_6H_4$	S	**4h**	81
9	4-$NO_2C_6H_4$	S	**4i**	75
10	4-ClC_6H_4	S	**4j**	88
11	4-MeC_6H_3	S	**4k**	93

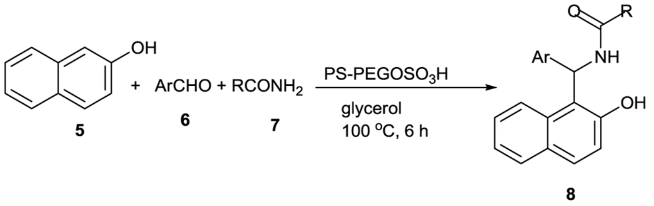
[a] Isolated yield.

[b] Reaction conditions: **1**: 1 mmol, **2**: 1 mmol, **3**: 1.2 mmol, glycerol: 2.0 g, PS-PEGOSO$_3$H: 0.2 g, at 100 °C for 8 h.

ethyl acetate and ether. It was then dried with anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to give glycerol. The recycled glycerol was used directly in the next run. The yields obtained after five cycles were comparable to those of fresh glycerol and PS-PEGOSO$_3$H. After the first run of the preparation of **4a**, the recovered glycerol and PS-PEGOSO$_3$H were subjected to the second use without an additional charge of glycerol or PS-PEGOSO$_3$H to give **4a** in 74% yield. The yields of **4a** observed in the third to fifth reuses were 68%, 62%, and 60%, respectively, demonstrating high recyclability of the PS-PEG resin-supported sulfonic acid.

Second, the coupling reaction of amides, 2-naphthol, and aldehydes to produce the amidoalkyl naphthols using glycerol and PS-PEGOSO$_3$H as reaction system was investigated. The reaction conditions were investigated in glycerol at 100 °C in the presence of various acid catalysts using the reaction of **5**, **6a**, and **7a** as a model. When *para*-toluenesulfonic acid (*p*-TSA) was used as catalyst in glycerol, amidoalkyl naphthol **8a** was obtained in poor yield; however, a good yield of dibenzoxanthene **9a** was obtained (84%). Interestingly, we found that PEGOSO$_3$H, and PS-PEGOSO$_3$H can effectively drive the condensation of amides, 2-naphthol, and aldehydes to give amidoalkyl naphthols in good yields (86% and 80%). Only a trace of amount of desired product **8a** was detected using acetic acid as catalyst (5%). PEG-400, water, and 1,2-dichloroethane were also studied as solvents. This reaction could also be carried out in PEG-400 and 1,2-dichloroethane to give the products in good yields (81% and 83%). Compared to the reaction in 1,2-dichloroethane, the reaction in glycerol has the advantages of easy isolation of products, good recyclability, and environmental friendliness. Other aromatic aldehydes as substrates were also

Table 3. Reactions of amides, 2-naphthol, and aldehydes for amidoalkylnaphthols in glycerol[a]



Entry	**6**/Ar	**7**/R	Product	Yield (%)[b]
1	C_6H_5	CH_3	**8a**	80
2	4-MeOC_6H_4	CH_3	**8b**	85
3	4-MeC_6H_4	CH_3	**8c**	81
4	4-ClC_6H_4	CH_3	**8d**	85
5	4-$NO_2C_6H_4$	CH_3	**8e**	89
6	3-$NO_2C_6H_5$	C_6H_5	**8f**	82
7	4-MeC_6H_3	C_6H_5	**8g**	86

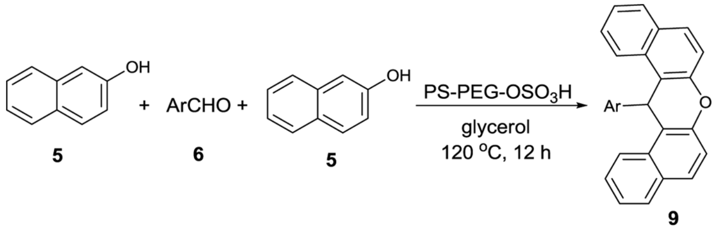
[a] **5**: 1 mmol, **6**: 1 mmol, **7**: 1.2 mmol, glycerol: 2.0 g, and PS-PEGOSO$_3$H: 0.15 g.

[b] Isolated yield.

successfully used in this condensation, giving amidoalkyl naphthols in the presence of PS-PEGOSO$_3$H in glycerol (Table 3).

We then moved on to the three-component reaction of two of molecules of 2-naphthol and one molecular of aldehyde to investigate the versatility of glycerol

Table 4. Reaction of 2-naphthol and aldehydes for synthesis of dibenzoxanthene[a]



Entry	**6**/Ar	Product	Yield (%)[b]
1	C_6H_5	**9a**	81
2	4-MeOC_6H_4	**9b**	77
3	4-MeC_6H_4	**9c**	90
4	2-ClC_6H_4	**9d**	86
5	4-ClC_6H_4	**9e**	88
6	3-$NO_2C_6H_4$	**9f**	78
7	4-$NO_2C_6H_4$	**9g**	76

[a] **5**: 2 mmol, **6**: 1 mmol, glycerol: 2.0 g, PS-PEGOSO$_3$H: 0.15 g.

[b] Isolated yield.

in the synthesis of dibenzoxanthene. Dibenzoxanthenes (**9a–g)** were synthesized in glycerol catalyzed by PS-PEGOSO$_3$H with good yields (Table 4). In this reaction, *p*-TSA, PEGOSO$_3$H, and PS-PEGOSO$_3$H all were shown to be greatly effective, resulting dibenzoxanthene in good yield. Though this reaction can also be performed in 1,2-dichloroethane or under solvent-free conditions, the product separation and the catalyst recycling is difficult. Furthermore, the organic solvent is not environmentally friendly.

CONCLUSIONS

In conclusion, we have investigated that the combination of glycerol and PS-PEGOSO$_3$H could be an environmentally friendly system for conducting MCRs such as Biginelli condensation; the three-component reactions of 2-naphthol, amides, and aldehydes; and the condensation of 2-naphthol with aldehydes (molar ratio of β-naphthol to aryl aldehyde is 2:1). To the best of our knowledge, the utilization of glycerol and PS-PEGOSO$_3$H as reaction system in these three-component reactions virtually has not been reported in the open literature. Glycerol is a safe and very cheap green solvent. We believe that the use of glycerol as a solvent will provide improved results compared with those observed in water, and further investigations are currently under way in our group on this topic.

EXPERIMENTAL

Typical Procedure for Compounds 4a–k

A mixture of aldehyde **1** (1 mmol), ethyl acetoacetate **2** (1 mmol), urea or thiourea **3** (1.2 mmol), and PS-PEG-SO$_3$H (0.2 g) in glycerol (2.0 g) under air was heated at 100 °C for 8 h. After the reaction, the products were extracted with ethyl acetate (6 mL × 3). After concentration of the organic phase, the crude products were recrystallized from EtOH to give pure compounds **4a–k**.

Selected Data

Compound 4a. Mp: 206–207 °C (lit.[20] 202–204 °C). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.14 (t, $J = 7.2$ Hz, 3H), 2.34 (s, 3H), 4.06 (q, $J = 7.2$ Hz, 2H), 5.37 (s, 1H,), 7.24–7.31 (m, 5H), 7.16 (brs, 1H), 7.76 (brs, 1H) ppm; IR (KBr) v: 3320, 3160, 3100, 2980, 1725, 1701, 1645, 1570, 1460, 1365, 1320, 1280 cm^{-1}.

Compound 4b. Mp: 199–201 °C (lit.[20] 202–204 °C); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.10 (t, $J = 7.0$ Hz, 3H), 2.24 (s, 3H), 3.71 (s, 3H), 3.98 (q, $J = 7.0$ Hz, 2H), 5.09 (s, 1H), 6.88 (d, $J = 8.5$ Hz, 2H), 7.15 (d, $J = 8.6$ Hz, 2H), 7.66 (brs, 1H), 9.14 (brs, 1H) ppm; IR (KBr) v: 3313, 3172, 1700, 1667, 1575, 1508, 1460 cm^{-1}.

Compound 4c. Mp: 207–209 °C (lit.[20] 207–209 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.10 (t, $J = 7.2$ Hz, 3H), 2.28 (s, 3H), 3.99 (q, $J = 7.2$ Hz, 2H), 5.29 (s, 1H), 7.53 (d, $J = 8.6$ Hz, 2H), 7.91 (brs, 1H), 8.23 (d, $J = 8.6$ Hz, 2H), 9.37 (brs, 1H) ppm; IR (KBr) v: 3238, 3172, 3119, 2976, 1728, 1699, 1645, 1595, 1520, 1513 cm^{-1}.

Compound 4d. Mp: 221–223 °C (lit.[20] 222–224 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.02 (t, $J = 7.2$ Hz, 3H), 2.28 (s, 3H), 3.89 (q, $J = 7.2$ Hz, 2H), 5.61 (s, 1H), 7.29–7.38 (m, 4H), 7.71 (brs, 1H), 9.21 (brs, 1H) ppm; IR (KBr) v: 3430, 3331, 3112, 2979, 1723, 1688, 1524 cm^{-1}.

Compound 4e. Mp: 212–214 °C (Lit.[20] 212–214 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.17 (t, $J = 7.2$ Hz, 3H), 2.33 (s, 3H), 4.08 (q, $J = 7.2$ Hz, 2H), 5.36 (s, 1H), 7.23–7.29 (m, 4H), 6.08 (brs, 1H), 8.39 (brs, 1H) ppm; IR (KBr) v: 3242, 3175, 3116, 2982, 1703, 1688, 1648, 1525 cm^{-1}.

Compound 4f. Mp: 207–209 °C (lit.[20] 208–210 °C). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.18 (t, $J = 6.4$ Hz, 3H), 2.31 (s, 3H), 4.10 (t, $J = 6.4$ Hz, 2H), 5.40 (s, 1H), 7.50–754 (m, 5H), 9.07 (brs, 1H), 9.41 (brs, 1H) ppm; IR (KBr) v: 3326, 3173, 3103, 1670, 1573, 1464, 1284, 1192 cm^{-1}.

Compound 4g. Mp: 153–154 °C (lit.[20] 150–152 °C). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.17 (t, $J = 7.2$ Hz, 3H), 2.42 (s, 3H), 3.77 (s, 3H), 4.09 (q, $J = 7.2$ Hz, 2H), 5.35 (s, 1H), 6.89 (d, $J = 8.6$ Hz, 2H), 7.26 (d, $J = 8.6$ Hz, 2H), 7.96 (brs, 1H), 8.18 (brs, 1H) ppm; IR (KBr) v: 3323, 3171, 3102, 2985, 1678, 1575, 1521, 1467, 1200 cm^{-1}.

Compound 4h. Mp: 208–209 °C (lit.[20] 208–209 °C). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.09 (t, $J = 7.2$ Hz, 3H), 2.35 (s, 3H), 4.01 (q, $J = 7.2$ Hz, 2H), 5.32 (s, 1H), 7.64–7.68 (m, 2H), 8.05–8.15 (m, 2H), 7.21 (brs, 1H), 8.23 (brs, 1H) ppm; IR (KBr) v: 3324, 3177, 3102, 2988, 1660, 1594, 1531, 1475, 1189 cm^{-1}.

Compound 4i. Mp: 212–214 °C (lit.[20] 210–213 °C). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.09 (t, $J = 7.2$ Hz, 3H), 2.31 (s, 3H), 4.02 (q, $J = 7.2$ Hz, 2H), 5.30 (s, 1H), 7.48 (d, $J = 8.6$ Hz, 2H), 8.24 (d, $J = 8.6$ Hz, 2H), 7.20 (brs, 1H), 8.45 (brs, 1H) ppm; IR (KBr) v: 3323, 3170, 3102, 2985, 1678, 1606, 1521, 1467, 1374, 1320, 1284, 1268, 1202 cm^{-1}.

Compound 4j. Mp: 190–192 °C (lit.[20] 192–194 °C). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.10 (t, $J = 7.2$ Hz, 3H), 2.30 (s, 3H), 4.02 (q, $J = 7.2$ Hz, 2H), 5.20 (s, 1H), 7.23 (d, $J = 8.6$ Hz, 2H), 7.43 (d, $J = 8.6$ Hz, 2H), 7.28 (brs, 1H), 7.80 (brs, 1H) ppm; IR (KBr) v: 3327, 3176, 2982, 1673, 1614, 1573, 1464, 1370, 1322, 1280, 1268, 1209 cm^{-1}.

Compound 4k. Mp: 190–192 °C (lit.[20] 192–194 °C). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 1.17 (t, $J = 7.2$ Hz, 3H), 2.22 (s, 3H), 2.43 (s, 3H), 4.09 (q, $J = 7.2$ Hz, 2H), 5.25 (s, 1H), 7.00 (d, $J = 8.6$ Hz, 2H), 7.20 (d, $J = 8.6$ Hz, 2H), 7.91 (brs, 1H), 8.45 (brs, 1H) ppm; IR (KBr) v: 3324, 3169, 3108, 3068, 1669, 1606, 1526, 1492, 1464, 1374, 1320, 1284, 1268, 1241 cm^{-1}.

Typical Procedure for Compounds 8a–g

A mixture of 2-naphthol **5** (2 mmol), aldehydes **6** (2 mmol), urea or acetamide **7** (2.5 mmol), and PS-PEGOSO$_3$H (0.15 g) in glycerol (2.0 g) was heated at 100 °C for 6 h. After the reaction, the products were extracted with ethyl acetate (6 mL × 3).

After removal of the solvent, the residual solid was purified by flash chromatography over silica to give pure amidoalkyl naphthols.

Selected Data

Compound 8a. Mp: 238–240 °C (lit.[21] 245–246 °C); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.03 (s, 3H), 7.11–7.23 (m, 8H), 7.32 (t, $J = 7.6$ Hz, 1H), 7.74 (d, $J = 7.8$ Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.85 (s, 1H), 8.46 (d, $J = 8.0$ Hz, 1H), 10.05 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ: 23.2, 40.3, 118.8, 119.6, 122.8, 123.6, 126.2, 126.8, 127.4, 128.5, 128.9, 129.2, 129.6, 132.8, 143.2, 153.8, 168.8 ppm; IR (KBr) ν: 3449, 3230–2229, 1642, 1602, 1579, 1503, 1433, 1370, 1232, 832 cm^{-1}.

Compound 8b. Mp: 185–187 °C (lit.[21] 182–183.5 °C); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.01 (s, 3H), 3.66 (s, 3H), 6.88–7.39 (m, 8H), 7.74–7.79 (m, 2H), 7.85 (d, $J = 8.0$ Hz, 1H), 8.45 (d, $J = 8.0$ Hz, 1H), 10.05 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 22.7, 47.5, 55.1, 113.4, 118.5, 119.0, 122.3, 123.2, 126.2, 127.2, 128.5, 129.0, 132.3, 134.4, 143.5, 153.0, 157.7, 169.0; IR (KBr) ν: 3426, 3055, 1625, 1582, 1513, 1436, 1250, 1042, 810 cm^{-1}.

Compound 8c. Mp: 220–222 °C (lit.[21] 222–223 °C); ^{1}H NMR ^{1}H NMR (400 MHz, DMSO-d_6) δ: 1.98 (s, 3H), 2.21 (s, 3H), 6.87–7.34 (m, 8H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.80 (d, $J = 8.0$ Hz, 1H), 7.83 (br, 1H), 8.37 (d, $J = 8.0$ Hz, 1H), 9.98 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): 21.3, 23.6, 48.2, 117.1, 118.8, 122.4, 123.6, 125.9, 126.7, 128.6, 128.8, 129.4, 129.8, 133.5, 134.9, 138.5, 153.2, 168.1 ppm; IR (KBr, cm^{-1}): 3433, 3055, 1628, 1578, 1515, 1437, 1276, 1181, 813 cm^{-1}.

Compound 8d. Mp: 226–228 °C (lit.[21] 223–225 °C); ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 2.03 (s, 3H), 7.06 (d, $J = 8.6$ Hz, 1H), 7.12 (d, $J = 8.6$ Hz, 1H), 7.16–8.48 (m, 10H), 10.01 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d$_6$): 22.7, 48.3, 118.3, 119.5, 123.6, 127.1, 128.3, 128.9, 129.3, 129.5, 129.8, 130.1, 131.3, 132.9, 143.4, 153.3, 168.9 ppm; IR (KBr) ν: 3392, 2962, 1638, 1577, 1493, 1436, 1278, 1245, 1172, 820 cm^{-1}.

Compound 8e. Mp: 247–249 °C (lit.[21] 248–250 °C); ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 2.03 (s, 3H), 7.20 (d, $J = 8\ .0$ Hz, 1H), 7.24 (d, $J = 8.0$ Hz, 1H), 7.26 (t, $J = 7.5$ Hz, 1H), 7.40 (t, $J = 7.5$ Hz, 1H), 7.54–7.53 (m, 2H), 7.75–8.63 (m, 6H), 10.11 (s, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d$_6$) δ: 22.9, 47.7, 116.9, 118.6, 120.2, 120.9, 123.3, 126.7, 128.6, 129.2, 129.8, 132.1, 133.4, 145.6, 148.1, 153.7, 169.8 ppm; IR (KBr) ν: 3396, 3267, 1648, 1603, 1522, 1438, 1063, 825 cm^{-1}.

Compound 8f. Mp: 218–220 °C (lit.[22] 216–217 °C); ^{1}H NMR (400 MHz, DMSO-d$_6$) δ: 6.15 (brs, 1H), 6.55 (brs, 1H), 7.65–6.95 (m, 11H), 8.10–7.85 (m, 4H), 10.30 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d$_6$) δ: 48.7, 115.4, 118.6, 118.9, 122.5, 123.2, 123.5, 124.6, 126.3, 127.5, 128.3, 128.8, 128.9, 130.2, 132.2, 133.5, 134.2, 134.4, 143.7, 148.9, 153.5, 167.9. IR (KBr) ν: 3372, 3229, 3092, 1645, 1576, 1520, 1435, 1346, 1299, 1062, 858 cm^{-1}.

Compound 8g. Mp: 188–190 °C (lit.[22] 192–193 °C); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 2.24 (s, 3H), 6.98–7.02 (m, 2H), 7.46–7.20 (m, 11H), 7.90–7.68 (m, 2H), 8.14 (d, 1H, $J = 8.0$ Hz), 8.86 (d, 1H, $J = 8.0$ Hz), 9.88 (brs, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 21.3, 49.1, 99.7, 114.9, 118.8, 122.4, 123.8, 126.5, 127.2, 127.8, 128.5, 128.6, 128.7, 129.4, 130.6, 132.3, 134.0, 135.2, 138.5, 153.2, 166.6; IR (KBr) ν: 3396, 1638, 1601, 1523, 1436, 1351,1258, 1054, 826 cm^{-1}.

Typical Procedure for Compounds 9a–g

2-Naphthol (2 mmol), benzaldehydes (1 mmol), and PS-PEGOSO$_3$H (0.15 g) were mixed with glycerol (2.0 g). The mixture was stirred for 12 h at 120 °C. After the reaction, the products were extracted with ethyl acetate (6 mL × 3). The organic phase was concentrated, and the crude products were recrystallized from EtOH to give pure product **9**.

Selected Data

Compound 9a. Mp: 181–183 °C (lit.[23] 185 °C); ^{1}H NMR (CDCl$_3$, 400 MHz): 6.49 (s, 1H), 6.99 (t, 1H, $J = 7.6$ Hz), 7.15 (t, 2H, $J = 7.6$ Hz), 7.41 (t, 2H, $J = 7.6$ Hz), 7.48–7.60 (m, 6H), 7.78–7.84 (m, 4H), 8.41 (2H, d, $J = 8.5$ Hz) ppm; IR (KBr) ν: 3073, 1612, 1593, 1460, 1255, 1081, 968 cm^{-1}.

Compound 9b. Mp: 202–203 °C (lit.[23] 204 °C); ^{1}H NMR (CDCl$_3$, 400 MHz): 3.67 (s, 3H), 6.56 (s, 1H), 7.72 (d, 2H, $J = 9.4$ Hz), 7.39–7.96 (m, 12H), 8.43 (d, 2H, $J = 9.4$ Hz) ppm; IR (KBr) ν: 3043, 1616, 1582, 1397, 1246, 1160, 960 cm^{-1}.

Compound 9c. Mp: 225–227 °C (lit.[23] 229 °C); ^{1}H NMR (CDCl$_3$): 2.15 (s, 3H), 6.50 (s, 1H), 7.00–7.60 (m, 10H), 7.75–8.45 (m, 6H) ppm; IR (KBr) ν: 3077, 2918, 1594, 1506, 1459, 1239, 964 cm^{-1}.

Compound 9d. Mp: 215–217 °C (lit.[23] 215 °C); ^{1}H NMR (CDCl$_3$): 6.47 (s, 1H), 7.11–8.24 (m, 16H); IR (KBr) ν: 3041, 2920, 1628, 1595, 1513, 1456, 1250, 964 cm^{-1}.

Compound 9e. Mp: 283–285 °C (lit.[23] 289 °C); ^{1}H NMR (CDCl$_3$): 6.43 (s, 1H), 6.90–7.12 (m, 2H), 7.28–7.61 (m, 8H), 7.73–7.86 (m, 4H), 8.28 (d, $J = 8.59$ Hz, 2H) ppm; IR (KBr) ν: 3066, 2925, 1623, 1590, 1514, 1456, 1245, 959, 812 cm^{-1}.

Compound 9f. Mp: 213–215 °C (lit.[23] 211 °C); ^{1}H NMR (CDCl$_3$, 400 MHz): 6.66 (s, 1H), 7.08–8.67 (m, 16H); IR (KBr) ν: 3033, 2938, 1628, 1585, 1450, 1246, 812 cm^{-1}.

Compound 9g. Mp > 300 °C (lit.[23] mp > 310 °C); ^{1}H NMR (CDCl$_3$, 400 MHz): 6.63 (s, 1H), 7.46 (t, $J = 8.0$ Hz, 2H),7.50 (d, $J = 8.8$ Hz, 2H), 7.62 (t, $J = 8.0$ Hz, 2H), 7.65 (d, $J = 8.8$ Hz, 2H), 7.82 (d, $J = 5.6$ Hz, 2H), 7.86 (d, $J = 5.6$ Hz, 2H), 8.00 (d, $J = 8.6$ Hz, 2H), 8.30 (d, $J = 8.6$ Hz, 2H) ppm; IR (KBr) ν: 3062, 2930, 1627, 1591, 1457, 1202, 1145, 964 cm^{-1}.

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