Tetrahedron Letters 50 (2009) 7024–7027

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

# An efficient organocatalyzed multicomponent synthesis of diarylmethanes via Mannich type Friedel–Crafts reaction

Atul Kumar *, Mukesh Kumar, Maneesh Kumar Gupta

*Medicinal and Process Chemistry Division, Central Drug Research Institute, Council of Scientific & Industrial Research, Lucknow 226001, India*

ARTICLE INFO

*Article history:*
Received 21 July 2009
Revised 25 September 2009
Accepted 28 September 2009
Available online 1 October 2009

*Keywords:*
Organocatalyst
Friedel–Crafts reaction
Diarylmethane derivatives
Multicomponent reaction

ABSTRACT

We have developed an efficient organocatalyzed, multicomponent synthesis of diarylmethane derivatives from tertiary aromatic amines, formaldehyde and 2-naphthols via Mannich type Friedel–Crafts reaction. Several organocatalysts such as (−)-chinchonidine, L-proline, L-thiaproline, and L-pipecolonic acid have been screened for the reaction but the best results were obtained with L-proline. In this Mannich type Friedel–Crafts alkylation, tertiary aromatic amines react with formaldehyde–proline adduct to generate 1-(4-(dimethylamino)benzyl)pyrrolidinium-2-carboxylate intermediate, which undergoes nucleophilic addition to give substituted diarylmethanes in excellent yields.



Multicomponent reactions (MCRs) are involved in some of the most interesting and challenging transformation in organic synthesis. MCRs have been receiving much attention[1] because of their efficiency and diversity of products, which is now considered as important tools in the modern drug discovery process.[2] Besides, these MCRs have been effectively used in the total synthesis of complex natural products.[3] Many studies for the improvement and application of already known classical MCRs, such as the Mannich reaction,[4]Ugi reaction,[5] and Biginelli reaction[6] have been reported. However, the development of new MCRs is still an important issue in the field of medicinal and organic chemistry.

Organocatalysts have exhibited immense promise in the synthesis of multicomponent reactions.[7] The catalytic property of small organic molecules like cinchona alkaloids and amino acids are well known.[8] However much attention has been focused on L-proline, an inexpensive, and efficient catalyst. L-Proline has been found to be very effective in enamine-based direct catalytic asymmetric aldol,[9] Mannich,[10] Diels–Alder,[11] and Knoevenagel type of reactions.[12]

Friedel–Crafts alkylation is one of the most powerful C–C bond forming reaction in organic synthesis.[13] Friedel–Crafts reactions are especially given by electron-rich arenes. Naphthols have been shown to be good donors in Friedel–Crafts alkylation and the nucleus has interesting biological activity as well as catalytic properties.[14,15] Micheal-type Friedel–Crafts reaction of 2-naphthols with activated species such as iminium ions,[16] α,β-unsaturated olefins,[15a] and aza-dicarboxylate[14b] are well known. In continuation of our efforts toward the development of organocatalyzed multicomponent reactions,[17] we wish to report here a new organocatalyzed Mannich type three-component Friedel–Crafts reaction of tertiary aromatic amine, formaldehyde, and 2-naphthol. In this Mannich type Friedel–Crafts alkylation, tertiary aromatic amines react with formaldehyde–proline adduct to generate 1-(4-(dimethylamino)benzyl)pyrrolidinium-2-carboxylate intermediate, which undergoes nucleophilic addition reaction with 2-naphthol to afford substituted diaryl methane derivatives **4a** in high yields (Scheme 1).

Diaryl and triaryl methane derivatives are important constituents of dyes and have shown a wide range of biological activities.[18]

Katritzky et al. reported the synthesis of diaryl methane derivatives from benzotrizole analogues of *N*,*N*-dialkylanilines and naphthol in moderate yields. The procedure involves multi-step synthesis and drastic conditions such as the use of hydrochloric acid.[19] Recently, Rong et al. reported a homocoupling of *p*-xylene to afford biarylmethane as major product using $Pd(OAc)_2/CF_3COOH$ (TFA)/$K_2S_2O_8$ catalytic system along with biaryls as minor product.[20]

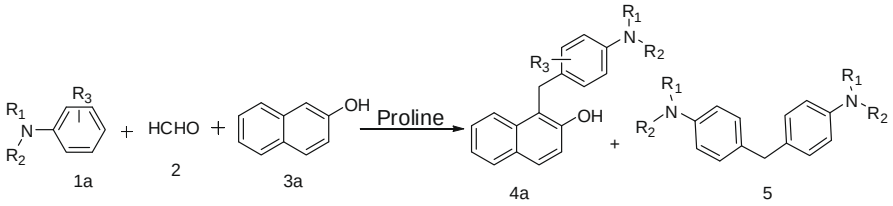
We have developed an organocatalyzed three-component synthesis of diarylmethane derivatives from tertiary aromatic amines, formaldehyde, and 2-naphthols in high yields.

Initial efforts were focused on the search of an efficient catalyst for the three-component coupling of 2-naphthol, formaldehyde, and *N*,*N*-dimethylaniline. It was observed that when the acid catalysts such as acetic acid, *p*-toluene sulfonic acid (PTSA), or boric acid were used, it led to the formation of **5** as major products and **4a** (diarylmethane derivatives) as a minor product in a low yield (Table 1).

We then screened a number of organocatalysts such as (−)-chinchonidine, L-proline, L-thiaproline, and L-pipecolonic acid for

* Corresponding author. Tel.: +91 522 2612411; fax: +91 522 26233405.
*E-mail address:* dratulsax@gmail.com (A. Kumar).

0040-4039/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2009.09.155




**Scheme 1.** Synthesis of diarylmethane derivatives via Mannich type Friedel–Crafts reaction.

**Table 1**
Screening of catalysts for coupling of 2-naphthol, formaldehyde, and *N*,*N*-dimethylaniline[a]

| Entry | Catalyst | Catalyst (mol %) | Yields **4a**[b] (%) | Yields **5**[b] (%) |
|---|---|---|---|---|
| 1 | Acetic acid | 20 | Trace | 90 |
| 2 | PTSA | 20 | Trace | 88 |
| 3 | Boric acid | 20 | Trace | 85 |
| 4 | (−)-Chinchonidine | 20 | 40 | 25 |
| 5 | L-Pipecolonic acid | 20 | 65 | 10 |
| 6 | L-Thiaproline | 20 | 65 | 15 |
| 7 | L-Proline | 20 | 85 | Trace |
| 8 | L-Proline | 10 | 55 | <5 |
| 9 | L-proline | 30 | 85 | Trace |

[a] Reaction conditions: *N*,*N*-dimethylaniline (1.0 mmol), formaldehyde (1.0 mmol), 2-naphthol (1.0 mmol), EtOH, rt, 12 h stirr.
[b] Isolated yield.

the efficient synthesis of **4a**. All these organocatalysts showed better selectivity for **4a** in comparison to **5**. L-Proline was found to be the best catalyst for the synthesis of diarylmethane derivatives (**4a**). In the presence of acid catalysts bis compound **5** was obtained as a major product, which probably formed by the reaction of aza quinone methide intermediate with *N*,*N*-dimethylaniline and 2-naphthol was unable to compete with dialkylaniline. Whereas in the case of organocatalyst (proline) reacts with formaldehyde to form an adduct, which reacts with dialkylaniline to generate an intermediate 1-(4-(dimethylamino)benzyl) pyrrolidinium-2-carboxylate, which on reaction with 2-naphthol gives diarylmethanes **4a** as a major product and small amounts of **5** (Fig. 1).

Decreasing the amount of L-proline (10 mol %) resulted in a decrease in the yield of **4a,** and **5** were formed in reasonable amounts. Increasing the amount of L-proline (30 mol %), no significant increase in the yield of **4a** was observed.

Thus, 20 mol % of L-proline was found to be the optimum for efficient synthesis of **4a**. The optimization data is summarized in Table 1.

We further studied the effect of solvent on L-proline-catalyzed coupling reaction of 2-naphthol, formaldehyde, and *N*,*N*-dimethylaniline (Table 2). In aprotic solvents such as dichloromethane and

**Table 2**
Solvent effect on L-proline catalyzed the three-component reaction of *N*,*N*-dimethylaniline, formaldehyde, and 2-naphthol[a]

| Entry | Solvents | Time (h) | Yield of **4a**[b] (%) |
|---|---|---|---|
| 1 | Dichloromethane | 12 | 35 |
| 2 | Tetrahydrofuran | 12 | 28 |
| 3 | Acetonitrile | 12 | 72 |
| 4 | Methanol | 12 | 84 |
| 5 | Ethanol | 12 | 85 |
| 6[c] | Ethanol | 5 | 45 |

[a] Reaction conditions: *N*,*N*-dimethylaniline (1 mmol), formaldehyde (1 mmol), 2-naphthol (1 mmol), L-proline (20 mol %), rt, stirr.
[b] Isolated yield.
[c] Reflex.

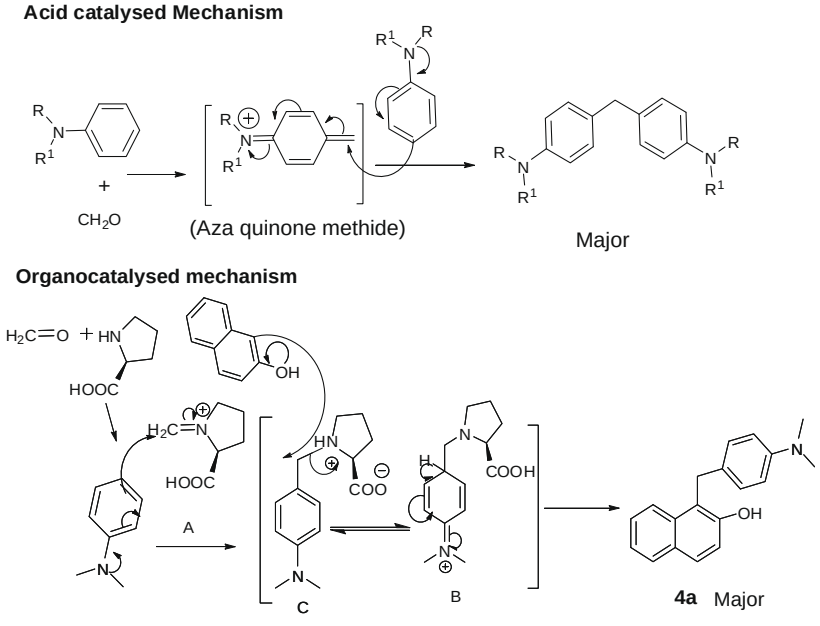
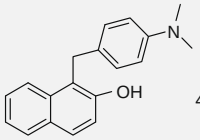
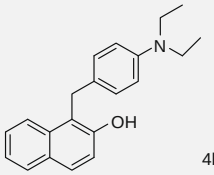
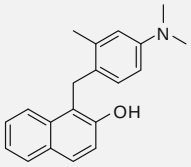
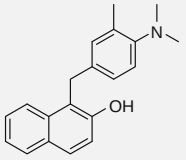
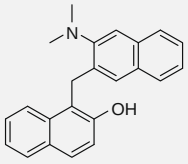
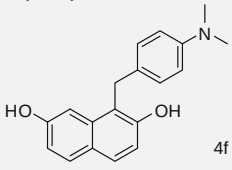
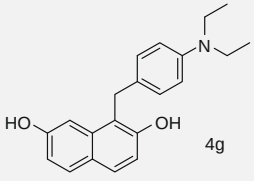
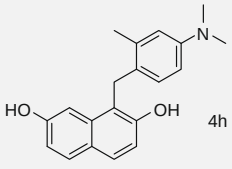
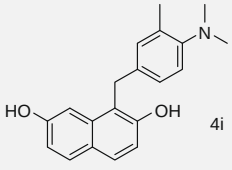
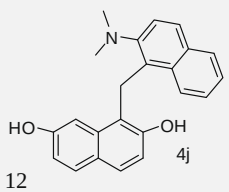


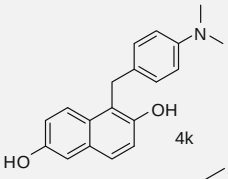
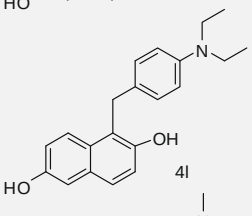
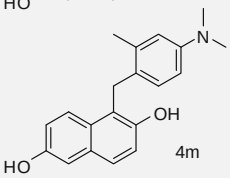
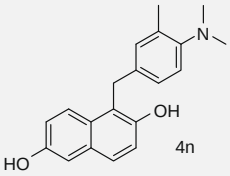

**Figure 1.** Possible mechanism of reaction.

**Table 3**
Proline catalyzed three-component Mannich type Friedel–Crafts coupling of tertiary aromatic amines, formaldehyde, and 2-naphthol[a]

| S.No. | $R_1/R_2$ | $R_3$ | Product | Yield[b] (%) |
|---|---|---|---|---|
| 1 | $CH_3$ | H |  4a | 80 |
| 2 | $C_2H_5$ | H |  4b | 78 |
| 3 | $CH_3$ | *m*-$CH_3$ |  4c | 81 |
| 4 | $CH_3$ | *o*-$CH_3$ |  4d | 80 |
| 5 | $CH_3$ | H |  4e | 76 |
| 6 | $CH_3$ | H |  4f | 80 |
| 7 | $C_2H_5$ | H |  4g | 80 |
| 8 | $CH_3$ | *m*-$CH_3$ |  4h | 82 |
| 9 | $CH_3$ | *o*-$CH_3$ |  4i | 80 |
| 10 | $CH_3$ | H |  4j | 74 |

12

**Table 3** (*continued*)

| S.No. | $R_1/R_2$ | $R_3$ | Product | Yield[b] (%) |
|---|---|---|---|---|
| 11 | $CH_3$ | H |  4k | 80 |
| 12 | $C_2H_5$ | H |  4l | 80 |
| 13 | $CH_3$ | *m*-$CH_3$ |  4m | 82 |
| 14 | $CH_3$ | *o*-$CH_3$ |  4n | 81 |

[a] Reaction conditions: *N*,*N*-dialkylaniline (1.0 mmol), formaldehyde (1.0 mmol), 2-naphthol (1.0 mmol), EtOH, rt, 12 h stirr.
[b] Isolated yields.

tetrahydrofuran, poor yield of **4a** was obtained with significant formation of **5**. However, acetonitrile gave moderate yield of **4a**. Whereas in protic solvents such as methanol and ethanol, **4a** was obtained in higher yields. Stirring the reaction mixture in ethanol for 12 h was found to be the optimal condition. Upon heating, the reaction mixture gave a complex mixture and **4a** was obtained in 45% yield.

In order to generalize the reaction we carried out the organocatalyzed three-component reaction of substituted tertiary aromatic amines, 2-naphthols, and formaldehyde[21] (Table 3).

In conclusion, we have developed an efficient organocatalyzed multicomponent Mannich type Friedel–Crafts reaction of tertiary aromatic amines, formaldehyde, and 2-naphthol for the synthesis of diarylmethane derivatives. Further development of this Mannich type Friedel–Crafts reaction and its application to the synthesis of bioactive compounds are in progress.

## Acknowledgments

Mukesh Kumar and Maneesh Kumar Gupta are thankful to CSIR–UGC, New Delhi, for the award of SRF.

## References and notes

1. For recent reviews, see: (a) Domling, A. *Chem. Rev.* **2006**, *106*, 17–89; (b) Banfi, L.; Riva, R. *Org. React.* **2005**, *65*, 1–140; (c) Ramón, D. J.; Yus, M. *Angew. Chem.* **2005**, *117*, 1628–1661. *Angew. Chem., Int. Ed.* **2005**, *44*, 1602–1634; (d) Zhu, J. *Eur. J. Org. Chem.* **2003**, 1133–1144.
2. (a) Armstrong, R. W.; Combs, A. P.; Tempest, P. A.; Brown, S. D.; Keating, T. A. *Acc. Chem. Res.* **1996**, *29*, 123–131; (b) Schreiber, S. L. *Science* **2000**, *287*, 1964–1969; (c) Werner, S.; Turner, D. M.; Lyon, M. A.; Huryn, D. M.; Wipf, P. *Synlett* **2006**, 2334–2338. and references cited therein.
3. (a) Inanaga, K.; Takasu, K.; Ihara, M. *J. Am. Chem. Soc.* **2004**, *126*, 1352–1353; (b) Powell, D. A.; Batey, R. A. *Org. Lett.* **2002**, *4*, 2913–2916.

4. For reviews, see: (a) Marques, M. M. B. *Angew. Chem.* **2006**, *118*, 356–360. *Angew. Chem., Int. Ed.* **2006**, *45*, 348–352; (b) Córdova, A. *Acc. Chem. Res.* **2004**, *37*, 102–112.
5. For reviews, see: (a) Domling, A.; Ugi, I. *Angew. Chem.* **2000**, *112*, 3300–3344. *Angew. Chem., Int. Ed.* **2000**, *39*, 168–3210; For recent studies, see: (b) Giovenzana, G. B.; Tron, G. C.; Paola, S. Di; Menegotto, I. G.; Pirali, T. *Angew. Chem.* **2006**, *118*, 1117–1120. *Angew. Chem., Int. Ed.* **2006**, *45*, 1099–1102; (c) Kaim, L. El.; Grimaud, L.; Oble, J. *Angew. Chem.* **2005**, *117*, 8175–8178. *Angew. Chem., Int. Ed.* **2005**, *44*, 7961–7964; (d) Bonnaterre, F.; Bois-Choussy, M.; Zhu, J. *Org. Lett.* **2006**, *8*, 4351–4354.
6. Movassaghi, M.; Jacobsen, E. N. *Science* **2002**, *298*, 1904–1905; Hongming, Li.; Wang, B.; Deng, Li. *J. Am. Chem. Soc.* **2006**, *128*, 732–733.
7. For reviews, see: (a) Kappe, C. O. *Acc. Chem. Res.* **2000**, *33*, 879–888; (b) Kappe, C. O. *QSAR Comb. Sci.* **2003**, *22*, 630–645; For recent research, see: (c) Nilsson, B. L.; Overman, L. E. *J. Org. Chem.* **2006**, *71*, 7706–7714; (d) Cohen, F.; Overman, L. E. *J. Am. Chem. Soc.* **2006**, *128*, 2604–2608; (e) Suzuki, I.; Suzumura, Y.; Takeda, K. *Tetrahedron Lett.* **2006**, *47*, 7861–7864; (f) Debache, A.; Boumoud, B.; Amimour, M.; Belfaitah, A.; Rhouati, S.; Carboni, B. *Tetrahedron Lett.* **2006**, *47*, 5697–5699; (g) Huang, Y.; Yang, F.; Zhu, C. *J. Am. Chem. Soc.* **2005**, *127*, 16386–16387.
8. Kumar, A.; Maurya, R. A. *Tetrahedron* **2007**, *63*, 1946–1952.
9. (a) Bogevig, A.; Kumaragurubaran, N.; Juhl, K.; Zhuang, W.; Jorgensen, K. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1790–1793; (b) Janey, J. M.; Hsiano, Y.; Armstrong, J. D., III *J. Org. Chem.* **2006**, *71*, 390–392.
10. (a) Kumaragurubaran, N.; Juhl, K.; Zhuang, W.; Bogevig, A.; Jorgensen, K. A. *J. Am. Chem. Soc.* **2002**, *124*, 827–833; (b) Kotrusz, P.; Toma, S. Molecules **2006**, *11*, 197–205. For recent reviews, see: (a) Domling, A. *Chem. Rev.* **2006**, *106*, 17–89. (b) Banfi, L.; Riva, R. *Org. React.* **2005**, *65*, 1–140. (c) Ramón, D. J.; Yus, M. *Angew. Chem.* **2005**, *117*, 1628–1661; *Angew. Chem., Int. Ed.* **2005**, *44*, 1602–1634. (d) Zhu, J. *Eur. J. Org. Chem.* **2003**, 1133–1144.
11. Armstrong, R. W.; Combs, A. P.; Tempest, P. A.; Brown, S. D.; Keating, T. A. *Acc. Chem. Res.* **1996**, *29*, 123–131.
12. Endo, A.; Yanagisawa, A.; Abe, M.; Tohma, S.; Kan, T.; Fukuyama, T. *J. Am. Chem. Soc.* **2002**, *124*, 6552–6554.
13. (a) Olah, G. A. In *Friedel–Crafts and Related Reaction*; Wiley: New York, 1963; (b) Olah, G. A. In *Friedel–Crafts Chemistry*; Wiley: New York, 1973.
14. For limited examples of naphthols in asymmetric Friedel–Craft reaction, see: (a) Erker, G.; van der Zeijden, A. A. H. *Angew. Chem., Int. Ed.* **1990**, *29*, 512; (b) Brandes, S.; Bella, M.; Kjaersgaard, A.; Jorgensen, K. A. *Angew. Chem., Int. Ed.* **2006**, *45*, 1147.
15. For limited examples of naphthols in Michael-type Friedel–Crafts reaction in a racemic form, see: (a) Kidwai, M.; Saxena, S.; Khan, M. K. R.; Thukral, S. S. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 4295; (b) Aoki, S.; Amamoto, C.; Oyamada, J.; Kitamura, T. *Tetrahedron* **2005**, *61*, 9291; (c) Nakazawa, T.; Furukawa, H.; Torii, K.; Itabashi, K. *Nippon Kagaku Kaishi* **1989**, 244.
16. Saidi, M. R.; Azizi, N. *Tetrahedron: Asymmetry* **2003**, *14*, 189.
17. (a) Kumar, A.; Maurya, R. A. *Tetrahedron Lett.* **2008**, *49*, 5471–5474; (b) Kumar, A.; Maurya, R. A. *Tetrahedron* **2008**, *64*, 3471–3482; (c) Kumar, A.; Maurya, R. A. *Tetrahedron Lett.* **2007**, *48*, 3887–3890.
18. Washburn, W. N. *J. Med. Chem.* **2009**, *52*, 1785–1794.
19. Katritzky, A. R.; Lan, X.; Lam, J. N. *J. Org. Chem.* **1991**, *56*, 4397–4403.
20. Rong, Y.; Ruoshi, Li.; Wenjun, Lu. *Organometallics* **2007**, *26*, 4376–4378.
21. *General procedure for the synthesis of compound* **4**: In a round-bottom flask equipped with a magnetic stirrer, β-naphthol (1 mmol), *N*,*N*-dimethylaniline (1 mmol), formaldehyde (1 mmol), L-proline (20 mol %), and 5 ml ethanol were taken. The reaction mixture was then stirred at room temperature for an appropriate time and the progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed and the residue was extracted with ethyl acetate. Evaporation of the solvent gave a crude product which was purified by column chromatography (silica gel, ethylacetate:hexane). Analytical data for few representative compounds. *1-(4-(Dimethylamino)-2-methylbenzyl)naphthalen-2-ol* (**4c**) brown solid; mp = 138–140 °C, $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 2.46 (s, 3H, $CH_3$), 2.88 (s, 6H, $N(CH_3)_2$), 4.27 (s, 2H, $CH_2$), 5.17 (s, 1H, OH), 6.36 (d, 1H, ArH, $J$ = 2.6 Hz), 6.56 (d, 1H, ArH, $J$ = 8.4 Hz), 6.67 (d, 1H, ArH, $J$ = 2.5 Hz), 7.11 (d, 1H, ArH, $J$ = 8.8 Hz), 7.30–7.47 (m, 2H, ArH), 7.75 (d, 1H, ArH, $J$ = 8.8 Hz), 7.80 (d, 2H, ArH $J$ = 8.1 Hz) ppm; $^{13}$C NMR (200 MHz, $CDCl_3$): $\delta$ 20.83, 28.16, 41.25, 111.31, 115.58, 117.98, 118.60, 123.55, 123.75, 125.52, 126.96, 128.63, 128.76, 128.92, 129.85, 134.24, 137.59, 149.91, 152.24. IR (KBr): $\gamma_{max}$ 3779, 2921, 2364, 1611, 1439, 1271, 804, 747, 687 cm$^{-1}$. ESIMS: $m/z$ 292 (M+H), Anal. Calcd for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.18. Found: C, 82.36; H, 7.16; N, 4.12. *1-(4-(Dimethylamino)-2-methylbenzyl)naphthalene-2,7-diol* (**4h**) brown solid, mp = 157–160 °C $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 2.47 (s, 3H, $CH_3$), 3.21 (s, 6H, $N(CH_3)_2$), 4.09 (s, 2H, $CH_2$), 6.27 (d, 2H, ArH, $J$ = 2.5 Hz), 6.34–6.59 (m, 1H, ArH), 6.79–7.02 (m, 3H, ArH), 7.47–7.69 (m, 2H, ArH), 8.89 (s, 1H, OH), 9.06 (s, 1H, OH) ppm; $^{13}$C NMR (300 MHz, $CDCl_3$ + DMSO-$d_6$): $\delta$ 25.23, 31.74, 43.97, 110.24, 115.32, 119.54, 119.70, 119.89, 120.71, 128.11, 132.07, 132.23, 132.68, 134.61, 140.59, 141.17, 153.61, 158.25, 160.55. IR (KBr): $\gamma_{max}$ 3778, 3325, 2957, 2364, 1626, 1504, 1319, 819, 773, 688 cm$^{-1}$ ESIMS: $m/z$ 308 (M+H). Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.10; H, 6.81; N, 4.46. *1-((2-(Dimethylamino)naphthalen-1yl)methyl)naphthalen-2-ol* (**4e**) solid, mp = 196–198 °C $^1$H NMR (200 MHz, $CDCl_3$ + DMSO-$d_6$): $\delta$ 2.79 (s, 6H, $N(CH_3)_2$), 4.80 (s, 2H, $CH_2$), 6.58 (d, 1H, ArH, $J$ = 7.7 Hz), 6.75 (d, 1H, ArH, $J$ = 7.7 Hz), 7.24–7.32 (m, 3H, ArH), 7.51–7.80 (m, 6H, ArH), 8.29–8.41 (m, 2H, ArH), 8.51 (s, 1H, OH) ppm; $^{13}$C NMR (300 MHZ, $CDCl_3$ + DMSO-$d_6$): $\delta$ 27.09, 45.41, 114.20, 116.99, 118.64, 122.72, 123.56, 124.48, 124.67, 124.79, 125.34, 126.32, 126.63, 128.41, 128.76, 128.88, 131.07, 133.37, 134.35, 149.20, 153.60. IR (KBr): $\gamma_{max}$ 3774, 2955, 2367, 1587, 1438, 1275, 1149, 809, 755, 682 cm$^{-1}$. ESIMS: $m/z$ 328 (M+H). Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28. Found: C, 84.317; H, 6.38; N, 4.22. *1-(4-(Dimethylamino)benzyl)naphthalen-2-ol* (**4a**) brown solid, mp = 127–130 °C $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (s, 6H, $(NCH_3)_2$), 4.37 (s, 2H, $CH_2$), 5.82 (s, 1H, OH), 6.65 (d, 2H, ArH, $J$ = 8.5 Hz), 7.09–7.18 (m, 3H, ArH), 7.29–7.46 (m, 2H, ArH), 7.67 (d, 1H, ArH, $J$ = 8.7 Hz), 7.77 (d, 1H, ArH, $J$ = 8.0 Hz), 7.95 (d, $J$ = 8.5 Hz, 1H, ArH) ppm; $^{13}$C NMR (200 MHz, $CDCl_3$): $\delta$ 30.17, 41.29, 113.83, 118.49, 123.52, 123.76, 126.97, 128.70, 128.91, 129.25, 130.61, 134.11, 142.24, 151.81. IR (KBr): $\gamma_{max}$ 3772, 2920, 2366, 1619, 1440, 1265, 806, 745, 684 cm$^{-1}$. ESIMS: $m/z$ 278 (M+H). Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.22; H, 6.82; N, 4.97. *1-(4-(Diethylamino)benzyl)naphthalene-2,7-diol* (**4g**) brown solid, mp = 130–134 °C $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 0.95 (t, 6H, $CH_2CH_3$, $J$ = 6.9 Hz), 3.12 (q, 4H, $NCH_2$, $J$ = 6.9 Hz), 4.13 (s, 2H, $CH_2$), 6.44 (d, 2H, ArH, $J$ = 5.4 Hz), 6.76 (d, 1H, ArH, $J$ = 1.8 Hz), 6.79 (d, 1H, ArH, $J$ = 1.9 Hz), 6.88–7.12 (m, 3H, ArH), 7.36 (d, 1H, ArH, $J$ = 8.7 Hz), 7.44 (d, 1H, ArH, $J$ = 8.7 Hz), 8.15 (s, 1H, OH), 8.61 (s, 1H, OH) ppm; $^{13}$C NMR (300 MHz, $CDCl_3$): $\delta$ 12.44, 29.57, 44.66, 105.82, 112.70, 114.93, 115.25, 117.34, 123.84, 127.42, 129.16, 129.81, 135.48, 140.54, 141.19, 152.65, 155.37. IR (KBr): $\gamma_{max}$ 3780, 2950, 2356, 1625, 1430, 1260, 805, 744, 687 cm$^{-1}$. ESIMS: $m/z$ 322 (M+H). Anal. Calcd for $C_{21}H_{23}NO_2$: C, 78.47; H, 7.21; N, 4.36. Found: C, 78.22; H, 7.12; N, 3.89.