Tetrahedron Letters 52 (2011) 5157–5160

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

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

New three-component condensation reaction: synthesis of 1-[(alkylthio)(phenyl)methyl]-naphthalene-2-ol catalyzed by bromodimethylsulfonium bromide (BDMS)

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ARTICLE INFO

Article history:
Received 8 May 2011
Revised 24 July 2011
Accepted 26 July 2011
Available online 31 July 2011

Keywords:
Bromodimethylsulfonium bromide (BDMS)
2-Naphthol
Thiols
Aromatic aldehyde
o-Quinone methides (*o*-QMs)
Thia-Michael reaction

ABSTRACT

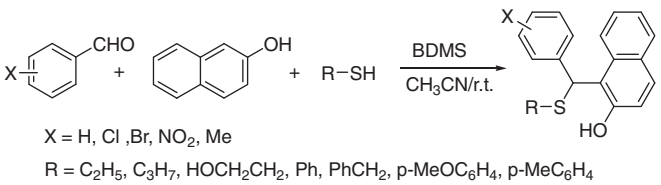
Bromodimethylsulfonium bromide acts as an efficient catalyst for one pot three component condensation reactions of aldehydes, 2-naphthol, and thiols in acetonitrile at room temperature. Various aliphatic and aromatic thiols undergo conjugate addition with in situ generated enone in acetonitrile and provide good yields. The main features of this procedure are mild reaction conditions, good yields, and operational simplicity.

Carbon–sulfur bond formation has versatile application in organic synthesis[1] in view of many recent sulfur-containing natural and pharmaceutical products, which have potent antibiotic, antimicrobial, analgesic, anti-inflammatory, antipsychotic, anti-HIV, and anti-tumor activities.[2] 1,4 Conjugate addition of a thiol nucleophile to an acceptor (alkene or alkyne) activated by an electron-withdrawing group namely the thia-Michael addition constitutes an important C–S bond forming strategy in organic synthesis.[3] The reported methods for thia-Michael addition are mainly focused on the use of acidic and basic catalysts for the direct addition of thiols to Michael acceptors in organic solvents.

Both from an atom-economic point of view as well as simplicity of the procedure, the thia-Michael addition is the preferred method for the preparation of organosulfur compounds. An acid or a base can be used as a promoter for this transformation. Over the years, numerous methods have been reported using a variety of catalysts, such as Cinchona alkaloid-squareamide,[4a] [**L**$Ni_2(CH_3CN)(THF)](ClO_4)_3$,[4b] $InCl_3$,[4c] silica nanoparticles,[4d] (IMesPr)AuCl,[4e] [Ru(acetone)(R,R-BIPHOP-F)Cp][SbF_6],[4f] cinchona alkaloid-derived urea,[4g] NEt_3,[4h] SDS/$NaHCO_3$,[4i] Co/SBA-15,[4j] $VO(OTf)_2$,[4k] silica–alumina supported NEt_3.[4l] It is highly desirable to develop a convenient, environment friendly method for the thia-Michael addition reaction. In this paper, we report the use of BDMS as a highly useful catalyst for the addition of thiols to the in situ generated enones from the reaction of aromatic aldehydes and 2-naphthol. To the best of our knowledge, these compounds are not reported till now.

Bromodimethylsulfonium bromide (BDMS) is a readily available, cheap, and highly efficient reagent[5] as well as a catalyst for various organic transformations.[5] In continuation of the present work on the development of new synthetic method, it has been observed that bromodimethylsulfonium bromide efficiently catalyzes the conjugate addition of various thiols to the in situ generated enones at room temperature (as shown in Scheme 1).

In the beginning of our study, benzaldehyde, 2-naphthol, and ethanethiol were chosen as model substrates. The reaction conditions were optimized for the synthesis of the 1-[(ethylthio)(phenyl)methyl]naphthalene-2-ol in terms of the yield and reaction time. Several reactions were scrutinized using different catalysts and various solvents, such as CH_3CN, DCM, and EtOH. The optimal amount of the reactants, such as benzaldehyde, 2-naphthol, thiol, and BDMS was found to be 1.0, 1.0, 1.1, and 0.1 equiv, respectively (Table 1, entry 3). We have noted that no



X = H, Cl ,Br, NO_2, Me

R = C_2H_5, C_3H_7, $HOCH_2CH_2$, Ph, $PhCH_2$, p-$MeOC_6H_4$, p-MeC_6H_4

Scheme 1. Synthesis of 1-[(alkylthio)(phenyl)methyl]naphthalene-2-ol.

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0040-4039/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2011.07.113

Table 1
Optimization for reaction conditions[a]

Entry	Catalyst	Solvent	Amount of catalyst (mol %)	Reaction Time (h)	Yield[b] (%)
1	No catalyst	Acetonitrile	0	6.0	0
2	BDMS	Acetonitrile	5	6.0	35
3	BDMS	Acetonitrile	10	6.0	74
4	BDMS	Acetonitrile	15	6.0	75
5	$Fe_2(SO_4)_3H_2O$	Acetonitrile	10	12.0	0
6	CH_3COOH	Acetonitrile	10	12.0	0
7	SiO_2–$HClO_4$	Acetonitrile	10	6.0	60
8	HBr–CH_3COOH	Acetonitrile	10	6.0	64
9	BDMS	DCM	10	6.0	71
10	BDMS	Ethanol	10	6.0	20

[a] All the reactions were carried out with 1 mmol scale.
[b] Isolated yield.

Table 2
Synthesis of 1-[(alkylthio)(phenyl)methyl]naphthalene-2-ol[7]

Entry	Aldehydes	Thiols	Time (h)	Yield[a] (%)
1	Bezaldehyde	Ethanethiol	6	74
2	Benzaldehyde	*n*-Propanethiol	6	73
3	Benzaldehyde	Thiophenol	8	21
4	*p*-Nitrobenzaldehyde	Ethanethiol	5	77
5	*p*-Nitrobenzaldehyde	*n*-Propanethiol	5	78
6	*p*-Nitrobenzaldehyde	Thiophenol	7	62
7	*p*-Chlorobenzaldehyde	*n*-Propanethiol	6	81
8	*p*-Chlorobenzaldehyde	Benzylthiol	6	71
9	*p*-Chlorobenzaldehyde	Thiophenol	8	30
10	*p*-Bromobenzaldehyde	*n*-Propanethiol	6	80
11	*p*-Bromobenzaldehyde	*p*-Methoxythiophenol	5	72
12	*p*-Methylbenzaldehyde	Ethanethiol	6	59
13	*m*-Nitrobenzaldehyde	Ethanethiol	5	77
14	*m*-Nitrobenzaldehyde	Mercaptoethanol	5	65
15	*m*-Bromobenzaldehyde	*p*-Thiocresol	5	70
16	*o*-Nitrobenzaldehyde	Ethanethiol	6	20
17	2-Naphthaldehyde	*p*-Thiocresol	6	73
18	*o*-Chlorobenzaldehyde	Ethanethiol	7	—

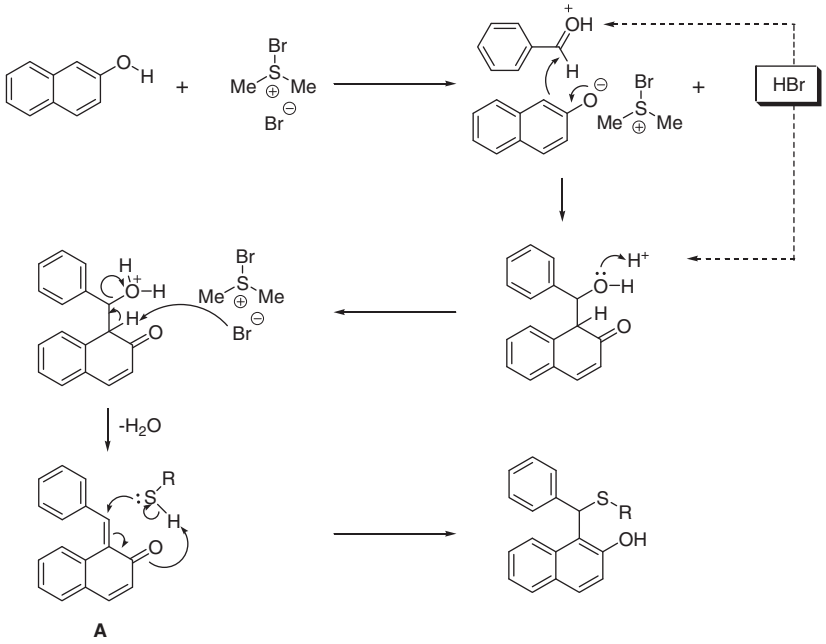
[a] Isolated yield.

product is formed in the absence of the catalyst. From this observation, it is obvious that BDMS plays an important role in the formation of the product.

The reaction was studied with other catalysts namely acetic acid, ferric sulfate, silica supported perchloric acid, and HBr–CH_3COOH. The best-suited catalyst for the reaction is BDMS. When 10 mol % of BDMS was used, the reaction proceeded smoothly and the yield was 74% (Table 1, entry 3). Moreover, the yield was found to be affected by the amount of BDMS added. When 0.0, 5, and 15 mol % of BDMS were used, the yield was 0.0%, 35%, and 75%, respectively (Table 1, entries 1, 2, and 4). It was noted that 10 mol % of BDMS was sufficient enough to carry out the reaction. Similarly, the role of solvent in this reaction was studied. Accordingly, the reaction was carried out in various solvents, such as acetonitrile, dichloromethane, and ethanol. It was found that acetonitrile is the most suitable solvent for this reaction.

Having established the optimized reaction condition, it was decided to explore the scope of this domino thia-Michael condensation reaction. Thus, several thiols were treated with a variety of aromatic aldehydes bearing different substituents NO_2, Br, Cl, Me at different positions and 2-naphthol in the presence of BDMS at room temperature in acetonitrile and the results were summarized in Table 2. Almost all reactions worked well with a variety of aromatic aldehydes including those bearing electron-withdrawing and electron-donating groups, such as NO_2, Br, Cl, and Me with ethanethiol, *n*-propanethiol, 2-mercaptoethanol, *p*-thiocresol, *p*-methoxythiophenol, benzylthiol, and thiophenol. The desired compounds were obtained in good to high yields within short reaction time (Table 2, entries 1, 2, 4–8, 10–15, and 17). It was shown that the aromatic aldehydes with electron withdrawing groups reacted faster than the aromatic aldehydes bearing electron donating groups as would be expected. With thiophenol, *p*-chlorobenzaldehyde gives a low yield of 30% (Table 2, entry 9) due to low electrophilicity of C-atom of the aldehyde group in comparison to arylaldehyde bearing nitro group at *para* position (62% yield, Table 2, entry 6). Similarly, the reaction of thiophenol, benzaldehyde, and 2-naphthol provides only 21% yield due to less nucleophilicity of the thiophenol. From these observations, it is quite clear that both electrophilicity of the aldehydic carbon and nucleophilicity of thiols play a crucial role for the formation of product. Furthermore, when *o*-nitrobenzaldehyde along with ethanethiol was taken, then the desired product was obtained in low yield (20%) due to steric hindrance of nitro group at *ortho*-position (Table 2, entry 16). In addition, when o-chlorobenzaldehyde along with ethanethiol was used, then no desired product was obtained (Table 2, entry 18). All these products were characterized by recording melting point, IR, ^1H NMR, ^{13}C NMR spectra, and elemental analysis.[7]

The formation of the 1-[(alkylthio)(phenyl)methyl]naphthalene-2-ol products can be explained as follows: It has been anticipated that bromodimethylsulfonium bromide may react with 2-naphthol to generate dry HBr in the reaction medium. The in situ generated dry HBr catalyzes Knoevenagel condensation between aromatic aldehydes and 2-naphthol to generate intermediate *ortho*-quinone methides (*o*-QMs, **A**)[6] as shown in Scheme 2. Then the intermediate A reacts with thiol to give the desired thia-Michael product.



Scheme 2. Proposed mechanism for the formation of product.

In summary, a simple and efficient method for the one pot multicomponent reaction for the synthesis of 1-[(alkylthio) (phenyl) methyl] naphthalene-2-ol using aromatic aldehydes, 2-naphthol, and thiols catalyzed by bromodimethylsulfonium bromide (BDMS) has been devised. The catalyst used is inexpensive and efficient.

Acknowledgments

S.A., A.A.D, and M.L. are thankful to UGC (New Delhi), IIT Guwahati and CSIR (New Delhi) for their research fellowships, respectively. The authors are also grateful to the Director, IIT Guwahati for providing the general research facility to carry out this work. We are thankful to the referees for their valuable comments and suggestions.

Reference and notes

1. (a) Kondo, T.; Mitsudo, T.-A. *Chem. Rev.* **2000**, *100*, 3205; (b) Gilchrist, T. L. *Heterocyclic Chemistry*, 3rd ed.; Addison Wesley Longman: Essex, 1997; (c) Okazaki, R. In *Organosulfur Chemistry*; Academic: London, 1995; Vol. 1, p 225.
2. (a) Czarnik, A. W. *Acc. Chem. Res.* **1996**, *29*, 112; (b) Nguyen-Ba, N.; Brown, W. L.; Chan, L.; Lee, N.; Brasili, L.; Lafleur, D.; Zacharie, B. *Chem. Commun.* **1999**, 1245; (c) Ashizawa, T.; Kawashima, K.; Kanda, Y.; Gomi, K.; Okabe, M.; Ueda, K.; Tamaoki, T. *Anticancer Drugs* **1999**, *10*, 829; (d) Dewick, P. M. *Medicinal Natural Products*, 2nd ed.; John Wiley & Sons: West Sussex, England, 2002; (e) Vardanyan, R. S.; Hruby, V. J. *Synthesis of Essential Drugs*; Elsevier: Amsterdam, 2006.
3. Perlmutter, P. *Conjugate Addition Reactions in Organic Synthesis*; Pergamon: Oxford, 1992.
4. (a) Dai, L.; Wang, S.-X.; Chen, F.-E. *Adv. Synth. Catal.* **2010**, *352*, 2137; (b) Lee, W.-Z.; Tseng, H.-S.; Wang, T.-L.; Tsai, H.-L.; Kuo, T.-S. *Organometallics* **2010**, *29*, 2874; (c) Dia, R.-M.; Belaqziz, R.; Romane, A.; Antoniotti, S.; Dunach, E. *Tetrahedron Lett.* **2010**, *51*, 2164; (d) Banerjee, S.; Das, J.; Alvarez, R. P.; Santra, S. *New J. Chem.* **2010**, *34*, 302; (e) Corma, A.; Gonzalez-Arellano, C.; Iglesias, M.; Sanchez, F. *App. Catal. A General* **2010**, *375*, 49; (f) Badoiu, A.; Bernardinelli, G.; Besnard, C.; Kundig, E. P. *Org. Biomol. Chem.* **2010**, *8*, 193; (g) Rana, N. K.; Selvakumar, S.; Singh, V. K. *J. Org. Chem.* **2010**, *75*, 2089; (h) O'Byrne, A.; Murray, C.; Keegan, D.; Palacio, C.; Evans, P.; Morgan, B. S. *Org. Biomol. Chem.* **2010**, *8*, 539; (i) Firouzabadi, H.; Iranpoor, N.; Abbasi, M. *Adv. Synth. Catal.* **2009**, *351*, 755; (j) Rajabi, F.; Razavi, S.; Luque, R. *Green Chem.* **2010**, *12*, 786; (k) Chen, C.-T.; Lin, Y.-D.; Liu, C.-Y. *Tetrahedron* **2009**, *65*, 10470; (l) Motokura, K.; Tanaka, S.; Tada, M.; Iwasawa, Y. *Chem. Eur. J.* **2009**, *15*, 10871. and references cited therein.
5. Choudhury, L. H.; Parvin, T.; Khan, A. T. *Tetrahedron* **2009**, *65*, 9513. and references cited therein.
6. (a) Singh, R.; Panda, G. *Org. Biomol. Chem.* **2010**, *8*, 1097; (b) Snyder, S. A.; Breazzano, S. P.; Ross, A. G.; Lin, Y.; Zografos, A. L. *J. Am. Chem. Soc.* **2009**, *131*, 1753; (c) Van De Water, R. W.; Pettus, T. T. R. *Tetrahedron* **2002**, *58*, 5367.
7. *General procedure*: To a mixture of aldehyde (1 mmol) and 2-naphthol (1 mmol) in 3 mL of acetonitrile was added BDMS (0.1 mmol) and kept for stirring at room temperature. Then the corresponding thiol (1.1 mmol) was added into it. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. After completion of the reaction, ethyl acetate (25 mL) was added into it and the organic layer was washed with 10 mL of water. The water layer was further extracted using ethyl acetate (2 × 25 mL). The combined organic layer dried over anhydrous sodium sulfate and it was concentrated under rotary evaporator. The crude mixture was purified through silica gel column chromatography and the desired product was obtained by eluting with ethyl acetate and hexane (1:99) mixture.
Spectral data:
1-((Ethylthio)(phenyl)methyl)naphthalen-2-ol (Table 2, entry 1): pale yellow semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (t, J = 7.6 Hz, 3H), 2.45–2.59 (m, 2H), 6.33 (s, 1H), 7.22 (d, J = 9.2 Hz, 2H), 7.27 (t, J = 8.0 Hz, 2H), 7.32 (d, J = 7.6 Hz, 1H), 7.38–7.44 (m, 3H), 7.78 (d, J = 7.6 Hz, 2H), 7.86 (d, J = 7.2 Hz, 1H), 9.08 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 26.8, 46.3, 113.5, 120.3, 121.8, 123.3, 127.2, 127.8, 128.4 (2C), 129.0 (2C), 129.2, 129.5, 130.5, 133.4, 138.6, 155.4; IR (KBr, cm^{-1}): 3429 (OH); Anal. Calcd $C_{19}H_{18}OS$ (294.41): requires C, 77.51; H, 6.16. Found C, 77.41; H, 6.22.
1-(Phenyl(propylthio)methyl)naphthalen-2-ol (Table 2, entry 2): pale yellow semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, J = 8.0 Hz, 3H), 1.55–1.64 (m, 2H), 2.39–2.46 (m, 1H), 2.52–2.58 (m, 1H), 6.28 (s, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.26–7.33 (m, 3H), 7.39–7.43 (m, 3H), 7.79 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.4 Hz, 1H), 9.14 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5, 22.4, 34.6, 46.7, 113.6, 120.3, 121.8, 123.3, 127.2, 127.8, 128.3 (2C), 128.9 (2C), 129.2, 129.5, 130.4, 133.4, 138.8, 155.3; IR (KBr, cm^{-1}): 3439 (OH); Anal. Calcd $C_{20}H_{20}OS$ (308.44): requires C, 77.88; H, 6.54. Found C, 77.78; H, 6.49.
1-(Phenyl(phenylthio)methyl)naphthalen-2-ol (Table 2, entry 3): pale yellow semisolid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.62 (s, 1H), 7.10–7.16 (m, 4H), 7.23–7.36 (m, 7H), 7.51 (dd, J_1 = 1.2 Hz, J_2 = 6.4 Hz, 2H), 7.69–7.73 (m, 2H), 7.80 (d, J = 8.8 Hz, 1H), 8.25 (s, 1H, OH) ppm; ^{13}C NMR (100 Hz, $CDCl_3$): δ 50.6, 115.4, 119.8, 122.3, 123.3, 127.0, 127.7, 127.9, 128.5 (2C), 129.0 (3C), 129.1 (2C), 129.5, 130.4, 131.0 (2C), 132.9, 134.1, 138.5, 154.1 ppm; IR (KBr, cm^{-1}: 3445 (–OH); Anal. Calcd $C_{23}H_{18}OS$ (342.45): requires C, 80.67; H, 5.30. Found C, 80.49; H, 5.21.
1-((Ethylthio)(4-nitrophenyl)methyl)naphthalen-2-ol (Table 2, entry 4): pale yellow solid, mp 127–129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (t, J = 7.6 Hz, 3H), 2.49–2.65 (m, 2H), 6.36 (s, 1H), 7.22 (d, J = 8.8 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.77–7.83 (m, 3H), 8.11 (d, J = 8.8 Hz, 2H), 8.61 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 27.1, 45.4, 113.2, 120.1, 121.7, 123.7, 124.0 (2C), 127.5, 129.4 (3C), 129.6, 131.0, 133.0, 146.6, 147.3, 154.9; IR (KBr, cm^{-1}: 3432 (OH), 1514 (NO_2), 1346 (NO_2); Anal. Calcd $C_{19}H_{17}NO_3S$ (339.41): requires C, 67.24; H, 5.05; N, 4.13. Found C, 67.12; H, 4.97; N, 4.05.
1-((4-Nitrophenyl)(propylthio)methyl)naphthalen-2-ol (Table 2, entry 5): pale yellow semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (t, J = 7.6 Hz, 3H), 1.58–1.65 (m, 2H), 2.44–2.51 (m, 1H), 2.57–2.63 (m, 1H), 6.32 (s, 1H), 7.23

(d, J = 8.4 Hz, 1H), 7.35 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 9.2 Hz, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 9.2 Hz, 1H), 8.13 (d, J = 8.8 Hz, 2H), 8.71 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 22.5, 35.0, 45.9, 113.4, 120.2, 121.7, 123.8, 124.1 (2C), 127.6, 129.5 (3C), 129.7, 131.1, 133.1, 146.8, 147.4, 155.1; IR (KBr, cm^{-1}: 3437 (OH), 1518 (NO_2), 1346 (NO_2); Anal. Calcd $C_{20}H_{19}NO_3S$ (353.43): requires C, 67.97; H, 5.42; N, 3.96. Found C, 67.84; H, 5.31; N, 3.87.

1-((4-Nitrophenyl)(phenylthio)methyl)naphthalen-2-ol (Table 2, entry 6): pale yellow semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.68 (s, 1H), 7.05 (t, J = 7.2 Hz, 1H), 7.10–7.18 (m, 5H), 7.29 (d, J = 7.6 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.60–7.64 (m, 3H), 7.95 (d, J = 8.8 Hz, 2H), 9.52 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 49.0, 116.8, 118.6, 123.1, 123.5, 123.6 (2C), 126.9, 127.5, 129.0 (2C), 129.1 (3C), 129.6, 130.5, 130.7 (2C), 132.2, 134.7, 146.6, 147.8, 152.3; IR (KBr, cm^{-1}: 3437 (OH), 1515 (NO_2), 1345 (NO_2); Anal. Calcd $C_{23}H_{17}NO_3S$ (387.45): requires C, 71.30; H,4.42; N, 3.62. Found C, 71.19; H, 4.33; N, 3.51.

1-((4-Chlorophenyl)(propylthio)methyl)naphthalen-2-ol (Table 2, entry 7): Pale yellow solid, mp 88–91 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (t, J = 7.2 Hz, 3H), 1.46–1.56 (m, 2H), 2.31–2.38 (m, 1H), 2.43–2.50 (m, 1H), 6.15 (s, 1H), 7.15 (t, J = 8.4 Hz, 3H), 7.23–7.27 (m, 3H), 7.35 (t, J = 7.6 Hz, 1H), 7.68–7.73 (m, 3H), 8.94 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5, 22.4, 34.7, 45.9, 113.3, 120.3, 121.6, 123.5, 127.3, 129.1 (2C), 129.3, 129.5, 129.8 (2C), 130.7, 133.2, 133.6, 137.3, 155.3; IR (KBr, cm^{-1}: 3436 (OH); Anal. Calcd $C_{20}H_{19}ClOS$ (342.88): requires C, 70.06; H, 5.59. Found C, 69.93; H, 5.49.

1-((Benzylthio)(4-chlorophenyl)methyl)naphthalen-2-ol (Table 2, entry 8): pale yellow semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.51 (d, J = 13.2 Hz, 1H), 3.61 (d, J = 13.6 Hz, 1H), 5.85 (s, 1H), 6.90 (d, J = 6.8 Hz, 2H), 7.07–7.23 (m, 9H), 7.37 (d, J = 8.4 Hz, 2H), 7.71 (t, J = 8.8 Hz, 2H), 8.81 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.0, 45.2, 112.8, 120.2, 121.9, 123.5, 127.1, 127.6, 128.8 (2C), 129.0 (2C), 129.1, 129.2 (2C), 129.5, 129.9 (2C), 130.8, 133.1, 133.6, 136.5, 136.8, 155.3; IR (KBr, cm^{-1}: 3430 (OH); Anal. Calcd $C_{24}H_{19}ClOS$ (390.93): requires C, 73.74; H, 4.90. Found C, 73.61; H, 4.99.

1-((4-Chlorophenyl)(phenylthio)methyl)naphthalen-2-ol (Table 2, entry 9): pale yellow semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.56 (s, 1H), 7.12–7.15 (m, 3H), 7.24–7.29 (m, 3H), 7.32–7.38 (m, 4H), 7.42 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 8.04 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 50.0, 115.2, 119.9, 122.2, 123.5, 127.2, 128.0, 129.2 (3C), 129.3 (2C), 129.6, 129.9 (3C), 130.6, 131.2 (2C), 132.8, 133.7, 137.2, 154.0; IR (KBr, cm^{-1}: 3450 (OH); Anal. Calcd $C_{23}H_{17}ClOS$ (376.90): requires C, 73.29; H, 4.55. Found C, 73.09; H, 4.46.

1-((4-Bromophenyl)(propylthio)methyl)naphthalen-2-ol (Table 2, entry 10): pale yellow solid, mp 96–99 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.93 (t, J = 7.2 Hz, 3H), 1.54–1.64 (m, 2H), 2.39–2.45 (m, 1H), 2.51–2.58 (m, 1H), 6.21 (s, 1H), 7.21 (d, J = 8.8 Hz, 1H), 7.27 (d, J = 9.2 Hz, 2H), 7.33 (t, J = 7.6 Hz, 1H), 7.39 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 6.8 Hz, 1H), 7.80 (d, J = 8.8 Hz, 3H), 9.01 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 22.4, 34.8, 46.0, 113.2, 120.4, 121.6, 121.8, 123.5, 127.3, 129.3, 129.5, 130.1 (2C), 130.7, 132.1 (2C), 133.3, 137.9, 155.3; IR (KBr, cm^{-1}: 3423 (OH); Anal. Calcd $C_{20}H_{19}BrOS$ (387.33): requires C, 62.02; H, 4.94. Found C, 61.93; H, 4.99.

1-((4-Bromophenyl)((4-methoxyphenyl)thio)methyl)naphthalen-2-ol (Table 2, entry 11): pale yellow semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.61 (s, 3H), 6.39 (s, 1H), 6.62 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 8.8 Hz, 1H), 7.23 (t, J = 8.0 Hz, 1H), 7.29–7.35 (m, 5H), 7.37–7.40 (m, 2H), 7.66–7.71 (m, 3H), 8.38 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 51.8, 55.3, 114.8 (2C), 115.0, 119.8, 121.7, 122.1, 123.36, 123.45, 127.0, 129.0, 129.5, 130.2 (2C), 130.5, 132.0 (2C), 132.9, 134.7 (2C), 137.7, 154.0, 160.0; IR (KBr, cm^{-1}: 3437 (OH); Anal. Calcd $C_{24}H_{19}BrO_2S$ (451.38): requires C, 63.86; H, 4.24. Found C, 63.93; H, 4.30.

1-((Ethylthio)(p-tolyl)methyl)naphthalen-2-ol (Table 2, entry 12): pale yellow semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (t, J = 7.6 Hz, 3H), 2.24 (s, 3H), 2.40–2.55 (m, 2H), 6.28 (s, 1H), 7.05 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.8 Hz, 1H), 7.27 (t, J = 8.8 Hz, 1H), 7.28 (d, J = 7.6 Hz, 2H), 7.38 (t, J = 8.4 Hz, 1H), 7.75 (d, J = 8.8 Hz, 2H), 7.84 (d, J = 8.8 Hz, 1H), 9.09 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.3, 21.2, 26.7, 46.0, 113.7, 120.2, 121.8, 123.2, 127.1, 128.2 (2C), 129.1, 129.4, 129.6 (2C), 130.3, 133.3, 135.6, 137.5, 155.3; IR (KBr, cm^{-1}: 3417 (OH); Anal. Calcd $C_{20}H_{20}OS$ (308.44): requires C, 77.88; H, 6.54. Found C, 77.79; H, 6.46.

1-((Ethylthio)(3-nitrophenyl)methyl)naphthalen-2-ol (Table 2, entry 13): pale yellow semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (t, J = 7.2 Hz, 3H), 2.50–2.65 (m, 2H), 6.37 (s, 1H), 7.24 (d, J = 8.8 Hz, 1H), 7.35 (d, J = 7.2 Hz, 1H), 7.40–7.47 (m, 2H), 7.67 (d, J = 8.0 Hz, 1H), 7.78–7.84 (m, 3H), 8.09 (d, J = 8.4 Hz, 1H), 8.35 (s, 1H), 9.30 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.4, 27.1, 45.3, 115.0, 120.3, 121.5, 122.8, 123.6, 123.7, 127.5, 129.4, 129.7, 129.9, 130.1, 133.0, 134.5, 141.2, 148.7, 155.2; IR (KBr, cm^{-1}: 3445 (OH), 1527 (NO_2), 1349 (NO_2); Anal. Calcd $C_{19}H_{17}NO_3S$ (339.41): requires C, 67.24; H, 5.05, N, 4.13. Found C, 67.12; H, 5.14, N, 4.21.

1-(((2-Hydroxyethyl)thio)(3-nitrophenyl)methyl)naphthalen-2-ol (Table 2, entry 14): pale yellow solid, mp 142–145 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.31 (brs, 1H), 2.75 (q, J = 5.6 Hz, 2H), 3.81 (s, 2H), 6.50 (s, 1H), 7.20 (d, J = 8.8 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.39 (t, J = 9.2 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.4 Hz, 2H), 8.08 (d, J = 8.0 Hz, 1H), 8.39 (s, 1H), 9.80 (s, 1H, OH); ^{13}C NMR (100 MHz, CD_3OD): δ 36.3, 45.0, 62.4, 118.6, 119.3, 122.3, 123.7, 123.8, 125.8, 126.8, 129.9, 130.2, 131.0, 133.1, 135.3, 145.6, 149.4, 154.1; IR (KBr, cm^{-1}: 3531 (OH), 1531 (NO_2), 1351 (NO_2); Anal. Calcd $C_{19}H_{17}NO_4S$ (355.41): requires C, 64.21; H, 4.82, N, 3.94. Found C, 64.12; H, 4.71, N, 3.81.

1-((3-Bromophenyl)(*p*-tolylthio)methyl)naphthalen-2-ol (Table 2, entry 15): pale yellow semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.20 (s, 3H), 6.57 (s, 1H), 6.97 (d, J = 8.0 Hz, 2H), 7.16 (t, J = 8.0 Hz, 1H), 7.21 (d, J = 8.8 Hz, 1H), 7.31 (t, J = 7.2 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.38–7.43 (m, 2H), 7.46 (d, J = 7.6 Hz, 1H), 7.73–7.77 (m, 3H), 7.80 (d, J = 8.8 Hz, 1H), 8.32 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 50.7, 115.0, 119.7, 122.2, 122.9, 123.4, 127.1 (2C), 129.0, 129.5, 130.0 (2C), 130.4, 130.5, 130.9, 131.5 (2C), 131.8 (2C), 132.8, 138.3, 141.2, 153.9; IR (KBr, cm^{-1}: 3436 (OH); Anal. Calcd $C_{24}H_{19}BrOS$ (435.38): requires C, 66.21; H, 4.40. Found C, 66.12; H, 4.34.

1-((Ethylthio)(2-nitrophenyl)methyl)naphthalen-2-ol (Table 2, entry 16): pale yellow semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.25 (s, J = 7.6 Hz, 3H), 2.56–2.64 (m, 2H), 7.23 (s, 1H), 7.25 (d, J = 9.2 Hz, 1H), 7.28 (dd, J_1 = 3.6 Hz, J_2 = 5.6 Hz, 1H), 7.34 (t, J = 6.8 Hz, 1H), 7.38 (dd, J_1 = 3.6 Hz, J_2 = 6.4 Hz, 2H), 7.46 (t, J = 7.6 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 9.2 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.95 (dd, J_1 = 3.6 Hz, J_2 = 5.6 Hz, 1H), 9.55 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 27.7, 41.4, 111.4, 120.5, 121.9, 123.7, 125.7, 127.8, 129.0, 129.2, 129.6, 130.6, 131.2, 133.0, 133.5, 133.6, 149.1, 156.5; IR (KBr, cm^{-1}: 3433 (OH), 1528 (NO_2), 1353 (NO_2); Anal. Calcd $C_{19}H_{17}NO_3S$ (339.41): requires C, 67.24; H, 5.05, N, 4.13. Found C, 67.12; H, 5.14, N, 4.19.

1-(Naphthalen-2-yl(p-tolylthio)methyl)naphthalen-2-ol (Table 2, entry 17): White solid, mp 117–120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.20 (s, 3H), 6.68 (s, 1H), 6.95 (d, J = 7.6 Hz, 2H), 7.21 (d, J = 9.2 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 7.33 (t, J = 7.6 Hz, 1H), 7.41–7.46 (m, 2H), 7.67 (dd, J_1 = 2.0 Hz, J_2 = 8.8 Hz, 1H), 7.72–7.76 (m, 3H), 7.77–7.82 (m, 3H), 7.87 (s, 1H), 8.51 (s, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 51.9, 115.0, 120.2, 122.2, 123.3, 126.4 (2C), 126.7, 127.1, 127.4, 127.7, 128.3, 128.9, 129.0, 129.5, 130.0 (2C), 130.5, 131.7 (3C), 133.0, 133.1, 133.6, 135.9, 138.2, 154.6; IR (KBr, cm^{-1}: 3434 (OH); Anal. Calcd $C_{28}H_{22}OS$ (406.54): requires C, 82.72; H, 5.45. Found C, 82.82; H, 5.54.