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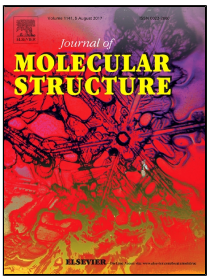

Sulfonated polynaphthalene as an effective and reusable catalyst for the one-pot preparation of amidoalkyl naphthols: DFT and spectroscopic studies

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Highlights

- The application of Sulfonated polynaphthalene (S-PNP) on the synthesis of amidoalkyl naphthols was investigated.
- The thermochemical parameters of reactions were investigated.
- Optimized structure, molecular orbitals, electrostatic potential (ESP) map of three amidoalkyl naphthol derivatives was studied.
- FT-IR spectra and ^{1}H nuclear magnetic resonance (NMR) spectra of selected amidoalkyl naphthols were recorded and compared with the theoretical results.

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Abstract

Sulfonated polynaphthalene (S-PNP) as a carbon-based solid acid efficiently catalyzed the one-pot three-component synthesis of amidoalkyl naphthols. The three-component process of substituted aryl aldehydes, 2-naphthol, and amide (benzamide and acetamide) or urea in the presence of S-PNP under thermal solvent-free conditions is described. Short reaction times, high yields and easy work-up are the advantages of this protocol. Furthermore, the catalyst can be readily recycled and reused without obvious significant loss of activity. Also, density functional theory (DFT) with the aid of M06-2X and B3LYP methods was used for studying of the optimized structure, molecular orbitals, electrostatic potential (ESP) map and spectroscopic analysis of some selected amidoalkyl naphthols. The thermochemical parameters of reactions including enthalpy, internal energy, entropy and Gibbs free energy were also investigated. The theoretically calculated infrared (IR) and ^{1}H nuclear magnetic resonance (NMR) spectra of title compounds were compared to the experimental data. Based on the results, the synthesis of amidoalkyl naphthols is exothermic. A good consistency between the calculated and observed spectral data was found.

Keywords: Amidoalkyl naphthols, Multicomponent reaction, Sulfonated polynaphthalene, DFT, Thermochemistry.

Introduction

Since the first multicomponent process (MCP) was described by Strecker in 1850,[1] multicomponent processes (MCPs) have been demonstrated to be a highly valuable tool for the expedient creation of the numerous chemical compounds.[2-7] Carrying out MCPs will be one of the most suitable methods, which will be a significant component of green chemistry.[8-12] The Betti 3-component reaction (Betti-3CR) is one pot three-components reaction (3CR) in the organic synthetic that generates 1-amido-2-naphthols via an MCR. Betti-3CR, a very well-known process was introduced by Italian chemist Mario Betti in 1900.[13] The Betti-3CR

represents an efficient protocol to produce amidoalkyl naphthols, which are also named the Betti base analogous (Fig. 1). Betti bases and the related molecules have attracted a lot of attention due to applications in asymmetric synthesis.[14] Computational studies on this field were also reported in recent years.[15]

[**Fig. 1.**]

A variety of natural products containing 1,3-amino-oxygenated functional groups acts as potential drugs, as antibiotic,[16] antitumors,[17] antimalarial,[18] antianginal,[19] antihypertensive,[20] antirheumatic,[21] and HIV protease inhibitors. The bradycardia effects of these motifs have also been reported.[22,23] Owing to the biological importance of 1-amidoalkyl-2-naphthol derivatives, efforts have been made by various researchers in developing MCRs for the synthesis of 1-amidoalkyl-2-naphthols from aldehydes, beta-naphthol, and amides or urea under thermal or sonication conditions using various catalysts such as cellulose-SO_3H,[24] silica sulfuric acids,[25] *p*-TSA,[26] $HClO_4$-SiO_2,[27] $Fe(HSO_4)_3$,[28] sulfamic acid,[29] heteropolyanion-based SO_3H,[30] saccarin sulfonic acid,[31] pyridinium-based ionic liquid,[32] N-(4-sulfonic acid) butyl triethylammonium hydrogen sulfate ([TEBSA][HSO_4]),[33] 2-methylpyridinium trifluoromethanesulfonate ([2-MPyH]OTf),[34] 2,4,6-trichloro-1,3,5-triazine (TCT),[35] 1,3-dibromo-5,5-dimethylhydantoin (DBH),[36] N-bromophthalimide (NBPI),[37] 2-Hydroxy-5-sulfobenzoic acid (2-HSBA).[38] Although some of these methods have convenient protocol with good to high yield, the majority suffer from at least one of the following disadvantages: unsatisfactory yeilds, the use of toxic halogenated solvents or catalysts and long reaction times. Despite these procedures, newer methodologies for the synthesis of amidoalkyl naphthol derivatives are still in demand.

The development of heterogeneous catalyst in chemical synthesis have become a major area of research. These catalyst have the potential to make the cleaner, safer, higher-yielding and relatively inexpensive processes.[39-42] In order to overcome to the problem associat of toxicity and volatile nature of many organic solvents, the design of solvent-free reactions has received significant attention in the area of green synthesis. The toxicity and volatile nature of many organic solvents have posed a serious threat to the environment. Thus, design of solvent free conditions and catalytic reaction has received tremendous attention in recent times in the area of green synthesis. In addition, reactions performed in the absence of a solvent typically require shorter reaction time and simpler work-up procedures.[43,44]

During the course of our recent studies directed towards the development of practical and environmentally procedures for the synthesis of organic compounds using reusable catalysts,[45,46] we investigated the application of a carbon-based solid acid (S-PNP) in the preparation of amidoalkyl naphthols. According to reported method,[47-50] this solid acid is easily prepared by polymerization of naphthalene in the presence of $FeCl_3$ and subsequent sulfonation by chlorosulfonic acid and represents a potential catalyst for the synthesis of amidoalkyl naphthols (Scheme 1).

[**Scheme 1**]

Experimental

General

The mid-IR spectrum was obtained using KBr pellets on a Perkin-Elmer RXI Fourier Transform spectrophotometer. The ultraviolet absorption spectra were examined in the range 200–600 nm using Perkin-Elmer lambda 25 recording spectrophotometer equipped with a 10 mm quartz cell. The NMR Spectra were acquired at the ambient temperatures on a Brucker AVANCE DRX 400. The development of reactions was monitored by thin layer chromatography (TLC) on Merck pre-coated silica gel 60 F_{254} aluminum sheets, visualized by UV light.

Preparation of PNP

To a solution of naphthalene (10.2 g, 80 mmol) in nitrobenzene (137 ml) was added $FeCl_3$ (28.6 g, 176 mmol) with vigorous stirring at room temperature under nitrogen. The solution was stirred at 90 °C for 1h and then at 150 °C for 24 h. The mixture was poured into methanol (686 ml) containing a small amount of concentrate HCl (3 ml). The precipitate was filtered and washed with methanol. It was dispersed in chloroform (200 ml). The precipitate was filtered, washed with chloroform, and dried at 120 °C for 3 h under reduced pressure. PNP (8.3 g, 83%) was obtained as the black powder (Scheme 2).

[**Scheme 2**]

Preparation of S-PNP by chlorosulfonic acid

A solution of chlorosulfonic acid (3.9 ml, 60 mmol) in dichloromethane (24 ml) was slowly added to the mixture of the PNP (2.5 g, 15 mmol) in dichloromethane (60 ml) with stirring under nitrogen. The mixture was stirred at 25 °C for 24 h. The precipitate was collected by filtration and washed with dichloromethane. The precipitate was dispersed in 0.5 *M* NaOH solution (200 ml) and stirred at 80 °C for 4 h. The mixture was filtered and the

precipitate was washed with distilled water. The precipitate was dispersed in 2*M* sulfuric acid solution (200 ml) and stirred at room temperature for 1 h. The mixture was filtered and the precipitate was washed with distilled water until the wash water reached a PH of 7. The precipitate was dried at 150 °C for 3h under reduced pressure to give the sulfonated polymer as the hygroscopic black powder. [50]

General procedure for the synthesis of amidoalkyl naphthols

A mixture of 2-naphthol (1 mmol), an aromatic aldehyde (1 mmol), acetamide or benzamide or urea (1 mmol), and S-PNP (0.05 g) was heated in oil bath at 80 °C for 10-70 min while monitoring the reaction process by TLC. Upon completion of the transformation, next, hot ethyl acetate (15 ml) was added to the resulting mixture, the solid residue was dissolved in EtOAc and the mixture filtered off. Then solvent was evaporated, the remained solid product was recrystallized in EtOH (15 ml).

Spectral data:

N-[(2-Hydroxynaphthalen-1-yl) (phenyl) methyl] acetamide (4a): ^{1}H NMR (500MHz, DMSO-d_6): δ 1.95 (s, 3H), 7.05-7.25 (m, 8H), 7.32 (t, 1H, *J*= 7.2 Hz), 7.73 (d, 1H, *J*= 8.8 Hz), 7.77 (d,1H, *J*=7.9 Hz), 7.81 (br, 1H), 8.40 (d, 1H, *J*= 8.3Hz), 9.95 (s, 1H).

N-[(4-chlorophenyl) (2-hydroxynaphthalen-1-yl) methyl] acetamide (4b): ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.99 (s, 3H), 7.10 (d, 1H, *J*=8.2 Hz), 7.16 (d, 2H, *J*= 8.3 Hz), 7.22 (d, 1H, *J*= 8.8 Hz), 7.25-7.35 (m, 3H), 7.38 (t, 1H, *J*=7.3 Hz), 7.78 (d, 1H, *J*= 8.8 Hz), 7.81 (a doublet overlapped with a broad signal, 2H, *J*= 7.5 Hz), 8.46 (d, 1H, *J*= 8.2 Hz), 10.03 (s, 1H).

N-[(2-Hydroxynaphthalen-1-yl) (4-nitrophenyl) methyl] acetamide (4f): ^{1}H NMR (500 MHz, DMSO-d_6): δ 1.98 (s, 3H), 7.14 (d, 1H, *J*= 7.9 Hz), 7.19 (d, 1H, *J*=8.8 Hz), 7.25 (t, 1H, *J*=7.5 Hz), 7.33-4.40 (m, 3H), 7.74-7.82 (m, 3H), 8.10 (d, 2H, *J*=8.8 Hz), 8.53 (d, 1H, *J*=7.9 Hz), 10.07(s, 1H).

N-[(2-Hydroxynaphthalen-1-yl) (phenyl) methyl] benzamide (4o): ^{1}H NMR (500MHz, DMSO-d_6): δ 7.24-7.88 (m, 13H), 7.82 (m, 3H), 8.08 (d, 1H, *J*= 8.0 Hz), 9.03 (d, 1H, *J*= 8.0 Hz), 10.38 (s,1H).

N-[(2-Hydroxynaphthalen-1-yl) (phenyl) methyl] urea (4w): ^{1}H NMR (500MHz, DMSO-d_6): δ 5.86 (s,2H, NH_2), 6.94 (s, 1H), 7.12-7.41 (m, 7H, Ar-H), 7.82 (d, 1H, NH), 7.75-7.83 (m, 3H, Ar-H), 9.97 (s, 1H, OH).

Computational details

Since the reactivity of the various derivatives of amidoalkyl naphthols are all quite similar, it was only necessary to study some of them as representatives of these derivatives. Three derivatives of amidoalkyl naphthols (compounds 1-3) (Scheme 4) were optimized through recently developed M06-2X meta hybrid density functional and 6-311G (d, p) polarized basis function. The vibrational frequencies were calculated to check the nature of the minima, prediction of IR spectrum and calculation of thermochemical data for multicomponent reactions of Scheme 3.

[**Scheme 4**]

M06-2X is one of the recommended density functional methods for the applications involving main-group thermochemistry[51] which was used in this article. The difference of the sum of electronic energy and thermal enthalpy for the reactants and the products was used for calculation of standard enthalpy of reactions (Δ_rH°). The difference of the sum of electronic energy and thermal energy for reactants and the products was used for the calculation of internal energy of reactions (Δ_rU°). The entropy of reactions (Δ_rS°) was evaluated on the basis of the thermodynamic functions obtained by vibrational analysis results and the statistical thermodynamic method. The Gibbs free energy of reactions (Δ_rG°) was calculated via equation (1). These thermochemical data were calculated at ambient and reaction temperatures (T = 298.15 and 353.15 K).

$$\Delta_rG^\circ = \Delta_rH^\circ - T\Delta_rS^\circ \quad (1)$$

^{1}H NMR chemical shifts (δ, ppm) versus TMS were calculated by gauge-independent atomic orbitals (GIAO) method, [52, 53] using more convenient B3LYP/6-311+G (2d, p) density functional. All calculations were performed using Gaussian 09 program package.[54]

Results and discussion

Preparation and characterization of S-PNP catalyst:

According to Tanemura method,[50] S-PNP was prepared by oxidative coupling polymerization of naphthalene in nitrobenzene by $FeCl_3$ under heating conditions and then sulfonation by chlorosulfonic acid in dichloromethane as solvent (Scheme 2).

The XRD pattern of catalyst exhibits a broad and a weak diffraction peaks (2θ = 15-35°) attributable to amorphous carbon (Fig. 2).

[**Fig. 2**]

Synthesis of amidoalkyl naphthols using S-PNP catalyst

After characterization of the sulfonated CBSA we decided to examine the catalyst efficacy in the preparation of amidoalkyl naphthols. Initially to find the best reaction conditions, three-component condensation of 2-naphthol, benzaldehyde and acetamide was employed as the template reaction. At first, screening trials were performed to optimize various reaction parameters, including temperature, catalyst amount, solvent and molar ratio, with the results summarized in Table 1.

[**Table 1**]

Among them, to check the effect of solvent on the yield of the product, the template reaction was carried out in various solvents (Table 1). Markedly low yields were observed when EtOH, CH_3CN, $CHCl_3$, THF, n-hexane were utilized as the reaction media (entries 12-16), the reaction proceeded most readily to give the highest yield of the product under solvent-free conditions. The best result was obtained when the reaction was conducted at 80 °C in the presence of 0.05 g of the catalyst under solvent-free conditions (Table1, entry 2). A further increase in temperature and catalyst amount did not improve the product yield.

Encouraged by the remarkable results obtained with above reaction conditions, and to show the generality and scope of this new protocol, a range of amidoalkyl naphthols were prepared in the presence of S-PNP under optimized conditions, with the results shown in Table 2.

[**Table 2**]

With the optimized reaction conditions in hand, the expediency of this method was well evaluated using a variety of aryl aldehydes and amides, a series of compounds were synthesized with this simple approach. Most of the reactions proceeded very efficiently and no side-products were observed. As can be seen from Table 2, the nature and position of functional groups on phenyl ring were not affected yields of products and reaction times, aromatic aldehydes bearing either electron-donating groups such as $–OCH_3$, $-CH_3$, -OH or

electron-withdrawing groups such as $–NO_2$, -F, -Cl reacted successfully with 2-naphthol and amide or urea to give the corresponding amidoalkyl naphthol products in high yields over short reaction time. The results also show that the amides with electron-withdrawing substituent react slowly and produce lower yields compared to amides without electron-with drawing groups.

To further evaluate the overall utility of the current methodology, we compared our results with those obtained using other techniques previously reported for the synthesis of amidoalkyl naphthols. As show in Table 3, it is clear that our method both reduces the required temperature and the reaction time and generates higher yields of the products.

[**Table 3**]

Also, in exploration to reusability of the catalyst after completion of the reaction, upon completion of the transformation, next, hot ethyl acetate (15 ml) was added to the resulting mixture, the solid residue was dissolved in EtOAc and the mixture filtered and the recovery solid catalyst was applied as such for the consecutive runs in four series of the same model reaction under the optimized conditions for up to four runs (1^{th} use: 90%, isolated yield, 2^{th} use: 87% isolated yield, 3^{th} use: 79% isolated yield, 4^{th} use: 73% isolated yield) (Fig. 3). Decreasing the yield is probably related to slight reduction in the catalytic activity of the catalyst or decreasing the amount of catalyst recovery which is attributed to the handling.

[**Fig. 3**]

Structural, electronic, thermochemical and spectroscopic properties of amidoalkyl naphthols

As shown in Scheme 3, a chiral center is generated during the reaction of β-naphthol, benzaldehyde, and amides (acetamide or benzamide) or urea. Therefore, it is possible to have two stereoisomers for these compounds with enantiomeric relationship. The product of reactions is racemic mixture and optically inactive. The optimized structure and structural parameters for selected amidoalkyl naphthols 1-3 (Scheme 4) calculated at M06-2X/6-311G(d,p) level of theory are shown in Fig. 4. In all structures, the amidic -NH (acetamide, benzamide or urea fragments) orients to the side of -OH group of β-naphthol to make favored intramolecular hydrogen bond. The NH…O distances for compounds 1-3 are Å, 2.312, 2.261 and 2.252, respectively (Fig and Table. 4).

[**Fig. 4**]

[**Table 4**]

Figure 5 displays the highest and the lowest molecular orbitals (HOMO and LUMO) and the calculated HOMO-LUMO energy separation for amidoalkyl naphthols 1-3. As shown that the HOMO and LUMO are localized on the naphthol part of molecules. The theoretically estimated energy gap for these molecules is around 6.6 eV.

[**Fig. 5**]

The calculated electrostatic potential (ESP) map for amidoalkyl naphthols 1-3 are shown in Fig. 6. The red and blue signs in the ESP maps indicate the most negative (the amidic oxygen atoms) and the most positive (hydrogen bonded hydrogen atoms) electrostatic potentials, respectively (unit for the legend is in Ha).

[**Fig. 6**]

Table 5 lists the calculated thermochemical data for the synthesis of amidoalkyl naphthols 1-3 through multi-component reaction of β-naphthol, benzaldehyde, and amides (acetamide or benzamide) or urea (Scheme 4). The gas phase enthalpy (Δ_rH°), internal energy (Δ_rU°), Gibbs free energy (Δ_rG°) and entropy (Δ_rS°) of reactions are calculated for 298.15 and 353.15 K via M06-2X/6-311G(d,p) level of theory. It is found that the enthalpy and internal energy of reactions are negative (exothermic), i.e. -13 to -14 kcal/mol. The entropy of reactions is also negative, i.e. -0.05 kcal/mol K. The decrease in entropy of reactions is due to the number of product molecules is less than the number of molecules of starting material in the same phase. Except for compound 3 at 298.15 K, the calculated Gibbs free energies of reactions are positive, which indicate that the mentioned reactions cannot be occurred spontaneously. The values of Δ_rG° rise as temperature increases (Table 5).

[**Table. 5**]

The calculated and recorded IR spectrum for amidoalkyl naphthols 1-3 are shown in Fig. 7. More important vibrational modes compared to experimental data are listed in Table 6. Due to the harmonic approximation, most of theoretical methods overestimate the vibrational frequencies; therefore the scaling factors of 0.89 and 0.93 are used to improve the calculated vibrational frequencies via M06-2X/6-311G(d,p) method for the modes above and below 2500 cm^{-1}, respectively. The O-H stretching vibration of compounds 1-3 occurs at 3400, 3419 and 3446 cm-1, respectively. The N-H stretching modes of these compounds appear at 3249, 3021 and 3246 cm^{-1}, respectively. Other peaks are assigned in Table 6.

[**Table 6**]

Table 7 lists the ^{1}H NMR chemical shifts (δ, ppm) for amidoalkyl naphthols 1-3 calculated via B3LYP/6-311G(d,p) level of theory in the gas phase and in DMSO as solvent (versus TMS). The observed spectra recorded in DMSO are shown in Fig. 8.

Conclusion

In conclusion, the synthesis of amidoalkyl naphthol derivatives is reported, *via* a one-pot three-component condensation of β-naphthol, aryl aldehydes, and amides (acetamid or benzamid) or urea in the presence of S-PNP as the catalyst under solvent-free conditions has been developed. The reaction exhibited merits such as mild conditions, easy wok-up, completion reaction in shorter reaction times, reuse of catalyst, safe, and no organic solvent is from the ecologically point of view. The structural and spectroscopic properties of various number of amidoalkyl naphthols with different substituents were investigated by calculation of optimized geometry, frontier molecular orbitals, electrostatic potential map, IR vibrational modes and H NMR chemical shifts. In all structures, the -NH group (acetamide, benzamide or urea fragments) orients to the side of -OH group of β-naphthol to make favored intramolecular hydrogen bond. The MO and ESP calculations show that the electronic and surface properties of these compounds (with 6.6 eV energy gap) are quite similar. Based on the thermochemical calculations, the formation of amidoalkyl naphthols is an exothermic process with decrease in entropy. The changes of Gibbs free energy during the reactions show that the formation of compound 3 with urea fragment is thermodynamically more favored than compounds 1 and 2 with amidic fragments. Comparison between the calculated ΔrG° values at different temperatures predicts that the reactions are less favorable with the increasing temperature. The theoretically calculated infrared (IR) and 1H nuclear magnetic resonance (NMR) spectra of title compounds confirm the experimental data about the formation of amidoalkyl naphthols.

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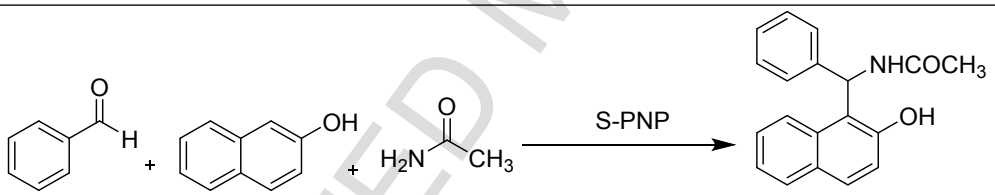
Table 1. Synthesis of N-((2-hydroxynaphthalen-1-yl) (phenyl)methyl) acetamide as a template under various conditions.



Entry	Catalyst Amount (g)	Solvent	T (^{o}C)	Time [a](min)	Yield [b]%
1	0.025	-	80	50	60
2[c]	**0.05**	**-**	**80**	**25**	**80**
3	0.075	-	80	20	80
4	0.1	-	80	13	80
5	-	-	80	180	40
6	0.05	-	25	180	-
7	0.05	-	50	180	47
9	0.05	-	100	25	87
12	0.05	CH_3CN	Reflux	120	40

13	0.05	$CHCl_3$	Reflux	60	20
14	0.05	THF	Reflux	75	30
15	0.05	EtOH	Reflux	60	20
16	0.05	n-hexane	Reflux	90	40

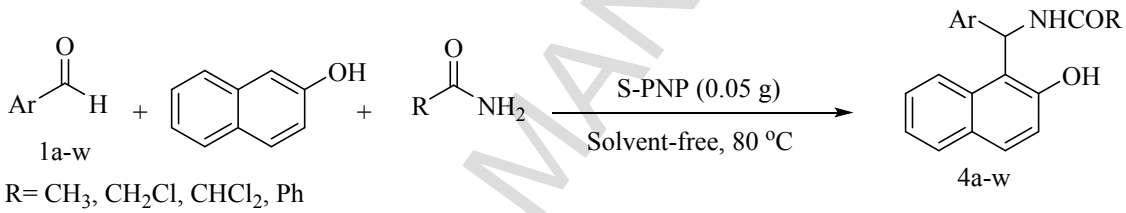
Reaction conditions: a well-ground mixture of 1-naphthol (1mmol), benzaldehyde (1mmol), acetamide (1mmol), and the catalyst (S-PNP) under different conditions.

[a] Progress of the reaction monitored with TLC analysis.

[b] Isolated yields.

[c] Optimized conditions shown in bold.

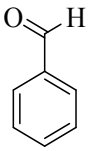
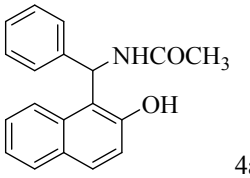
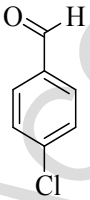
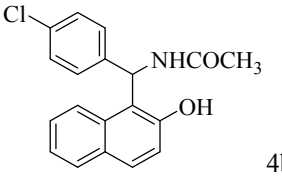
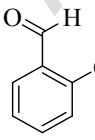
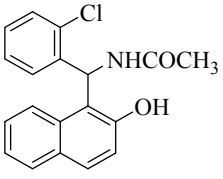
Table 2. The solvent-free synthesis of 1-amidoalkyl-2-naphthols from β-naphthol, aromatic aldehydes and amides derivatives using sulfonated polynaphthalene.

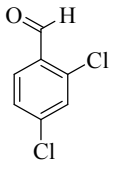
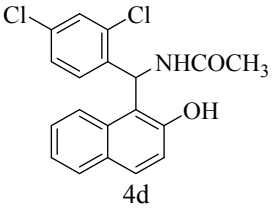
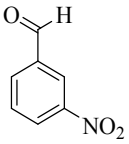
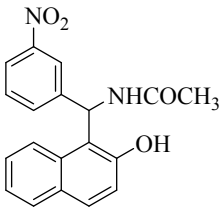
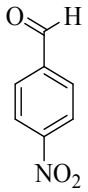
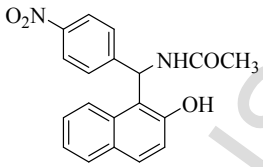
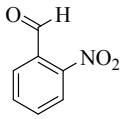
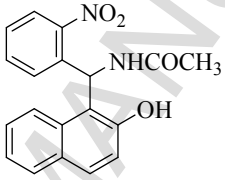
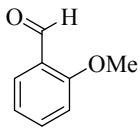
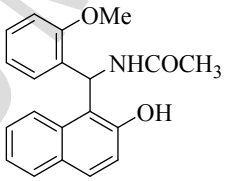
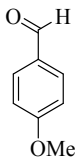
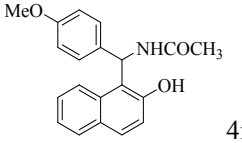
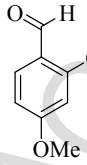
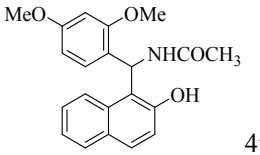
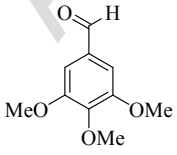
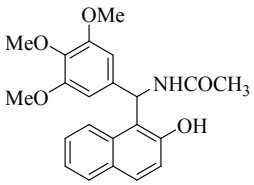


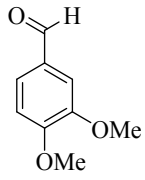
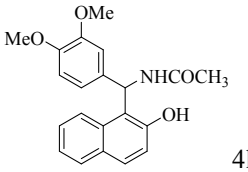
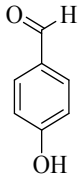
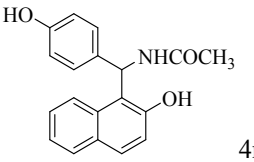
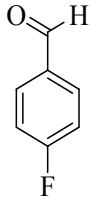
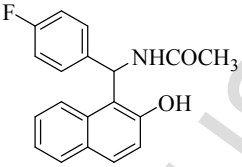
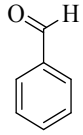
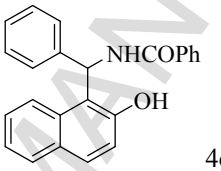
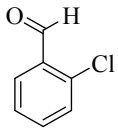
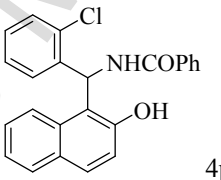
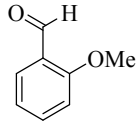
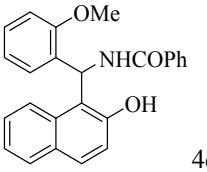
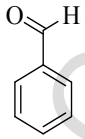
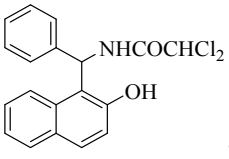
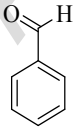
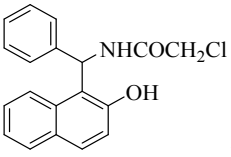
1a-w

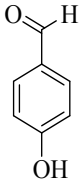
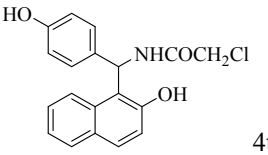
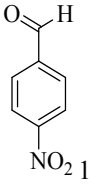
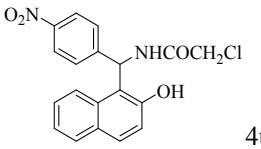
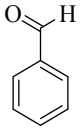
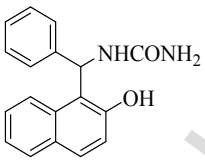
R= CH_3, CH_2Cl, $CHCl_2$, Ph

4a-w

Entry	Aldehyde	Amide	Product	Time (min)	Yield (%)	mp. °C (Ref.)
1	 1a	CH_3CONH_2	 4a	25	90	232-233 (238-240)[55a]
2	 1b	CH_3CONH_2	 4b	30	90	235-236 (237-238)[55b]
3	 1c	CH_3CONH_2	 4c	35	96	194-196 (197-199)[55a]

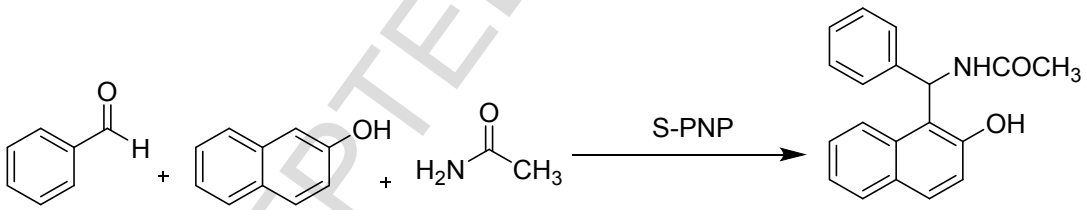
4	 1d	CH_3CONH_2	 4d	35	87	227-229 (228-230)[55c]
5	 1e	CH_3CONH_2	 4e	30	94	240-242 (238-240)[55a]
6	 1f	CH_3CONH_2	 4f	40	97	240-242 (237-238)[55b]
7	 1g	CH_3CONH_2	 4g	40	86	208-210 (218-219)[55b]
8	 1h	CH_3CONH_2	 4h	30	78	240-241 (241-242)[55b]
9	 1i	CH_3CONH_2	 4i	35	96	180-181 (183-185)[55d]
10	 1j	CH_3CONH_2	 4j	40	81	189-191 (190-192)[55c]
11	 1k	CH_3CONH_2	 4k	70	94	198-200 (192-194)[55c]

12	 1l	CH_3CONH_2	 4l	50	82	233-234 (235-237)[55d]
13	 1m	CH_3CONH_2	 4m	36	81	199-200 (205-207)[55e]
14	 1n	CH_3CONH_2	 4n	18	89	225-227 (230-232)[55d]
15	 1o	$PhCONH_2$	 4o	11	88	234-236 (238-240)[55b]
16	 1p	$PhCONH_2$	 4p	15	90	224-226 (284-285)[55b]
17	 1q	$PhCONH_2$	 4q	20	80	265-267 (266-267)[55b]
18	 1r	$NH_2COCHCl_2$	 4r	45	75	227-229
19	 1s	NH_2COCH_2Cl	 4s	25	76	198-200(206-207)[55b]

20	 1t	NH_2COCH_2Cl	 4t	43	77	213-215
21	 1u	NH_2COCH_2Cl	 4u	40	84	219-221 (217-218)[55b]
22	 1w	NH_2CONH_2	 4w	60	80	175-177 (172-176) [55a]

Reaction condition: Aldehyde (1 mmol), beta-naphthol (1 mmol), amide-benzamide-2-chloroacetamide-2,2-dichloroacetamide or urea (1 mmol) under thermal solvent-free condition, oil bath 80 °C.

Table 3. Comparison results of S-PNP with recently reported catalyst in the synthesis of amidoalkyl naphthols.



Entry	Catalyst	Conditions	Time	Yield[a] %
1	P_2O_5/SiO_2 [52]	Solvent-free 100 °C	5 min	94
2	[2-MPyH]OTf [42]	Solvent-free 125 °C	45 min	91
3	Succinic acid [53]	Solvent-free 120 °C	38 min	92
4	Montmorillonite K10 clay [54]	Solvent-free 125 °C	1.5 h	89
5	H-BEA [55]	Solvent-free 120 °C	5-7 min	85
6	2-HSBA [38]	Solvent-free 100 °C	5 min	95

7	$Fe(HSO_4)_3$ [28]	Solvent-free 85 °C	65 min	83
8	$Fe(HSO_4)_3$ [28]	Microwave oven at 450W	7 min	90
9	S-PNP	Solvent-free 80°C	25 min	90

Reaction conditions: a well-ground mixture of 1-naphthol (1 mmol), benzaldehyde (1 mmol), acetamide (1 mmol), and the catalyst (S-PNP) under different conditions

[a] Isolated yields

Table 4. The calculated bond lengths for amidoalkyl naphthols 1-3 at M06-2X/6-311G(d,p) level of theory.

Compound 1

Bond length	(Å)	Bond length	(Å)	Bond length	(Å)
C1-C2	1.416	C18-C20	1.484	C30-C36	1.516
C1-C6	1.368	C20-C21	1.395	C30-O35	1.209
C2-C3	1.368	C20-C29	1.392	C30-N15	1.367
C3-C4	1.421	C21-C23	1.386	N15-H16	1.007
C4-C5	1.422	C23-C25	1.394		
C4-C12	1.414	C25-C27	1.391		
C5-C6	1.418	C27-C29	1.390		
C5-C7	1.417				
C7-C9	1.368				
C9-C11	1.417				
C11-C12	1.371				
C11-O13	1.361				
O13-H14	0.960				

Compound 2

Bond length	(Å)	Bond length	(Å)	Bond length	(Å)
C1-C2	1.416	C18-C20	1.484	C30-N15	1.370
C1-C6	1.368	C20-C21	1.395	C30-O35	1.210

C2-C3	1.368	C20-C29	1.392	C30-C36	1.503
C3-C4	1.421	C21-C23	1.386	C36-C37	1.394
C4-C5	1.422	C23-C25	1.394	C36-C38	1.393
C4-C12	1.414	C25-C27	1.391	C37-C39	1.390
C5-C6	1.418	C27-C29	1.390	C38-C41	1.388
C5-C7	1.417			C39-C43	1.390
C7-C9	1.368			C41-C43	1.392
C9-C11	1.417			N15-H16	1.008
C11-C12	1.371				
C11-O13	1.361				
O13-H14	0.960				

Compound 3

Bond length	(Å)	Bond length	(Å)	Bond length	(Å)
C1-C2	1.416	C18-C20	1.484	C30-N15	1.385
C1-C6	1.368	C20-C21	1.395	C30-N36	1.385
C2-C3	1.368	C20-C29	1.392	C30-O35	1.207
C3-C4	1.421	C21-C23	1.386	N36-H37	1.008
C4-C5	1.422	C23-C25	1.394	N36-H38	1.008
C4-C12	1.414	C25-C27	1.391	N15-H16	1.008
C5-C6	1.418	C27-C29	1.390		
C5-C7	1.417				
C7-C9	1.368				
C9-C11	1.417				
C11-C12	1.371				
C11-O13	1.361				
O13-H14	0.960				

Table 5. Thermochemical properties for multi-component reactions for synthesis of amidoalkyl naphthols 1-3 (Scheme 1), calculated at M06-2X/6-311G(d,p) level of theory.

Property	Compound 1	Compound 2	Compound 3

	298.15 K	353.15 K	298.15 K	353.15 K	298.15 K	353.15 K
Δ_rH° (kcal/mol)	-14.05	-13.83	-13.94	-14.00	-14.10	-13.85
Δ_rU° (kcal/mol)	-13.46	-13.13	-13.35	-13.30	-13.51	-13.14
Δ_rS° (kcal/mol K)	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05
Δ_rG° (kcal/mol)	1.30	4.11	0.14	2.61	-0.03	2.54

Table 6. Calculated and scaled vibrational frequencies for amidoalkyl naphthols 1-3 at M06-2X/6-311G(d,p) level of theory in comparison to experimental data.

Compound 1				Compound 2				Compound 3			
Exp.	Calc.	Scal.	Assignment	Exp.	Calc.	Scal.	Assignment	Exp.	Calc.	Scal.	Assignment
3400	3917	3486	OH(Str)	3419	3640	3240	OH(Str)	3446	3911	3481	OH(Str)
3249	3644	3243	NH(Str)	3021	3639	3239	NH(Str)	3246	3609	3212	NH(Str)
1640	1806	1680	C=O(Str)	1622	1788	1663	C=O(Str)	3405	3615	3217	NH_2(Str)
1582	1541	1433	C=C(Str)	1532	1531	1424	C=C(Str)	3206	3730	3320	NH_2(Str)
1436	1401	1303	CH_3(bend)	822	838	779	Ring[1] (OOP)	1640	1827	1699	C=O(Str)
807	755	702	Ring[1] (OOP)	751	759	706	Ring[2] (OOP)	1522	1538	1430	C=C(Str)
742	755	702	Ring[2] (OOP)	696	684	636	Ring[2] (OOP)	814	822	764	Ring[1] (OOP)
696	664	618	Ring[2] (OOP)					746	758	705	Ring[2] (OOP)
								698	680	632	Ring[2] (OOP)

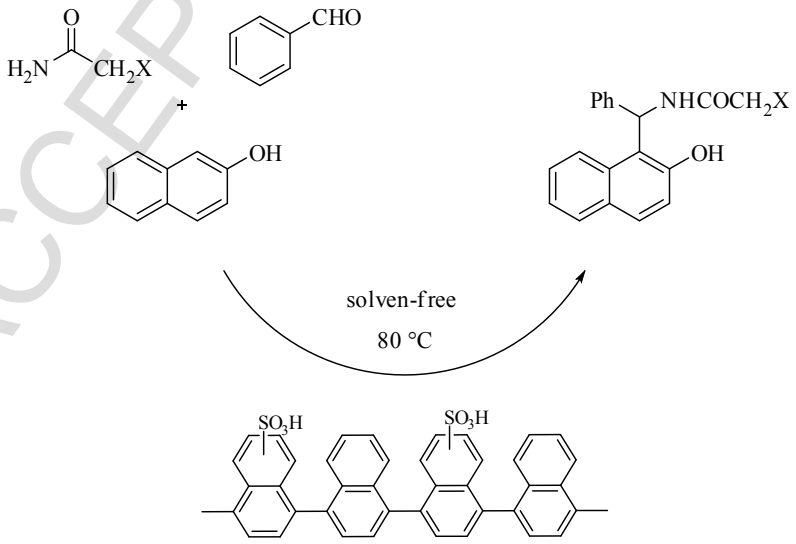
[1] Phenyl Ring
[2] 2-naphthole ring

Table 7. Calculated ^{1}H NMR chemical shifts (δ, ppm) for compounds 1-3 at the B3LYP/6-311 + G(2d,p) level of theory, as well as the corresponding experimental data for these compounds

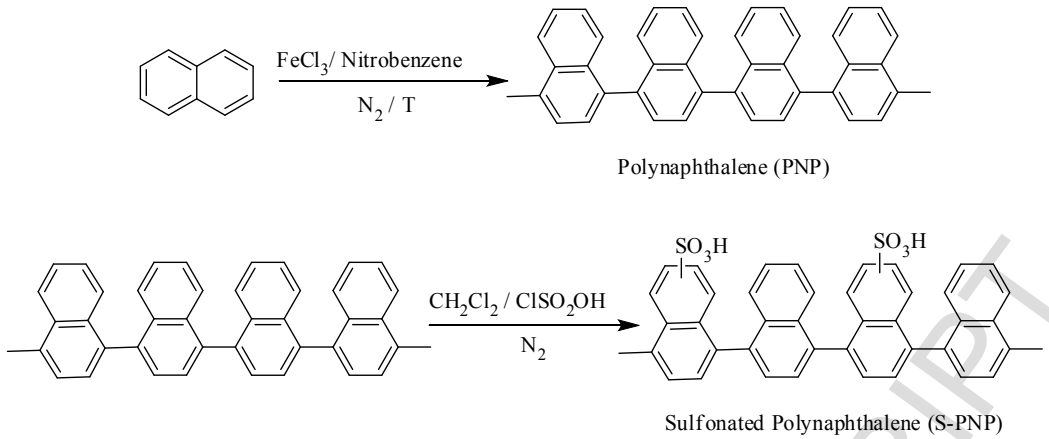
Compound 1				Compound 2				Compound 3			
Atom number	Exp.	Calc.[1]	Calc.[2]	Atom number	Exp.	Calc.[1]	Calc.[2]	Atom number	Exp.	Calc.[1]	Calc.[2]
OH	9.95	9.25	8.93	OH	10.38	9.33	9.10	OH	9.97	9.26	9.05
NH	8.40	8.14	8.11	NH	9.03	8.46	8.32	NH	7.82	8.07	8.16
H_a	7.81	7.58	7.64	H_a	8.08	7.97	8.07	H_a	6.94	7.58	7.64
2-naphthole ring (H_b,H_c,H_d)	7.05-7.27	7.29-7.50	7.24-7.62	2-naphthole ring(H_b,H_c,H_d)	7.24-7.88	7.64-8	7.76-8.13	2-naphthole ring(H_b,H_c,H_d)	7.75-7.83	7.29-8.01	7.22-8.10
Phenyl ring(H_e)	7.11-7.16	6.79-7.17	6.76-7.19	Phenyl ring (H_e,H_f)	7.12-7.40	7.20-7.60	7.29-7.70	Phenyl ring (H_e)	7.12-7.41	6.86-7.13	7.06-706-7.18
								NH_2	5.86	6.51	6.62
Me	1.95	1.80	1.82								

[1] Gas phase

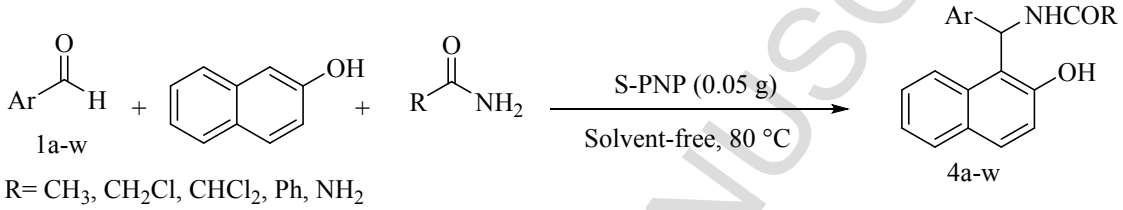
[2] In DMSO



Scheme 1. One-pot 3C synthesis of 1-amidoalkyl-2-naphthols catalysis by S-PNP.

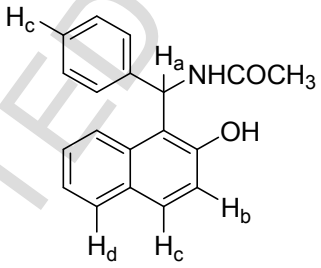


Scheme 2. Preparation of PNP (top) and S-PNP (bottom).

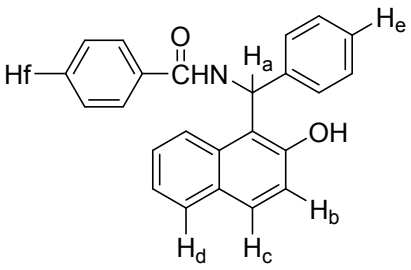


Scheme 3. Synthesis of 1-amidoalkyl-2-naphthols catalysis by S-PNP.

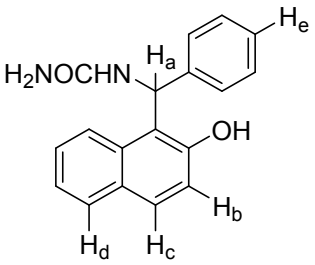
N-[(2-Hydroxynaphthalen-1-yl) (phenyl)methyl] acetamide (Compound 1)



N-[(2-Hydroxynaphthalen-1-yl) (phenyl)methyl] benzamide (Compound 2)



N-[(2-Hydroxynaphthalen-1-yl) (phenyl)methyl] urea (Compound 3)



Scheme 4. Three derivatives of amidoalkyl naphthols (compounds 1-3) (Scheme 4). were optimized.

Figure captions:

Figure 1. General structure of Betti bases (A) and amidoalkylNaphthols (B).

Figure 2. The XRD pattern of S-PNP catalyst.

Figure 3. Reusability of S-PNP in the synthesis of amidoalkyl naphthol 1a

Figure 4. The optimized structure for amidoalkyl naphthols 1-3 at M06-2X/6-311G(d,p) level of theory.

Figure 5. The calculated frontier molecular orbitals shape and energy for compounds 1-3 (from left to right, respectively).

Figure 6. The calculated ESP map for compounds 1-3 (from left to right, respectively).

Figure 7. Experimental (solid line) and calculated (dotted line) IR spectra for compounds 1-3.

Figure 8. Experimental ^{1}H NMR spectra for compounds 1-3.

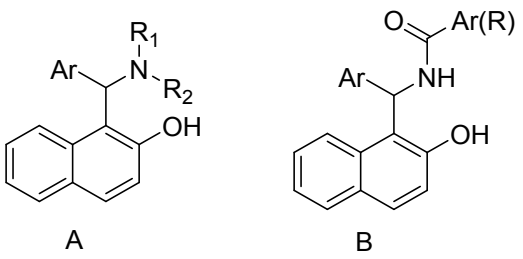


Figure 1.

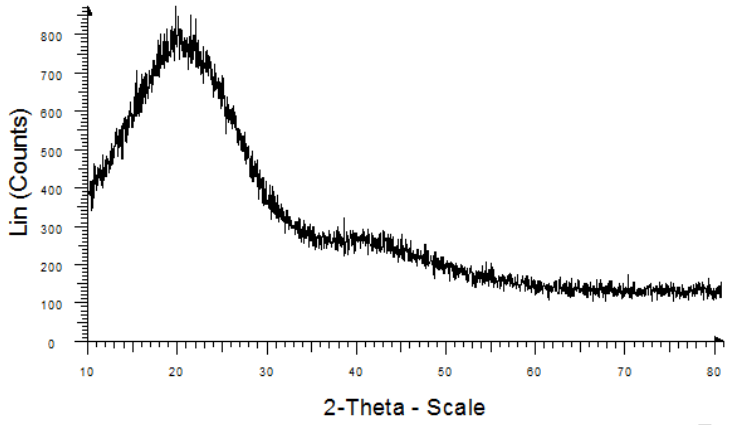


Figure 2.

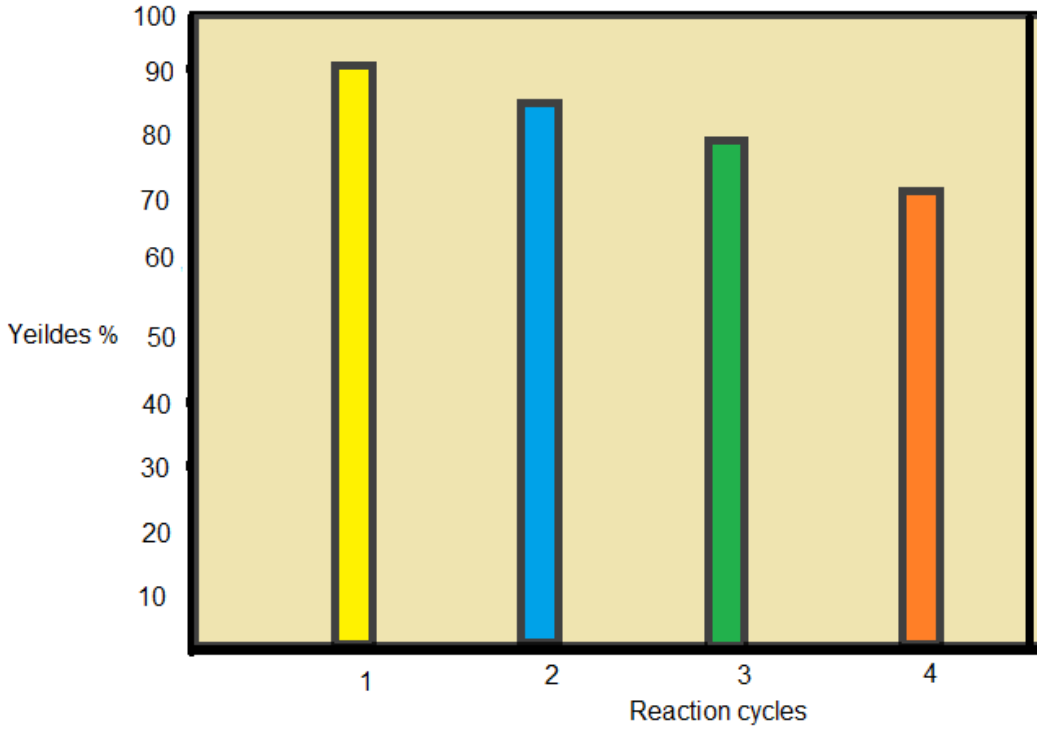
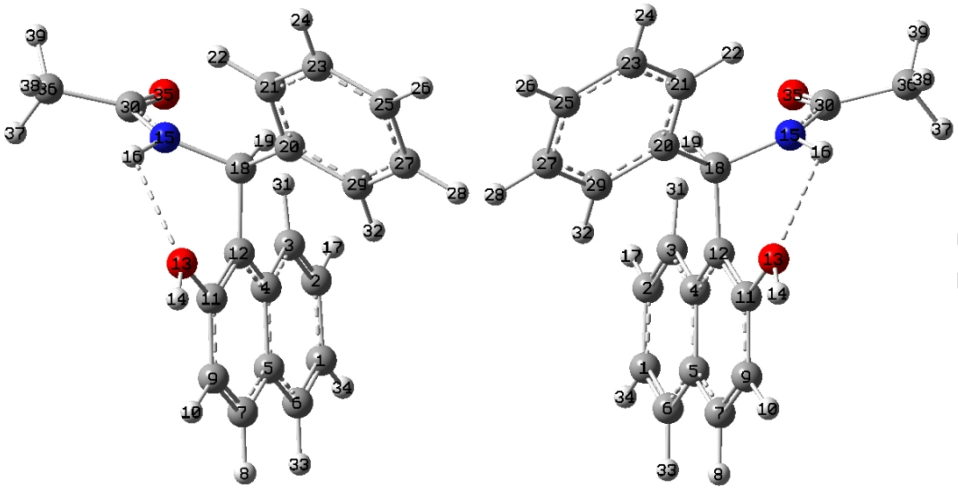
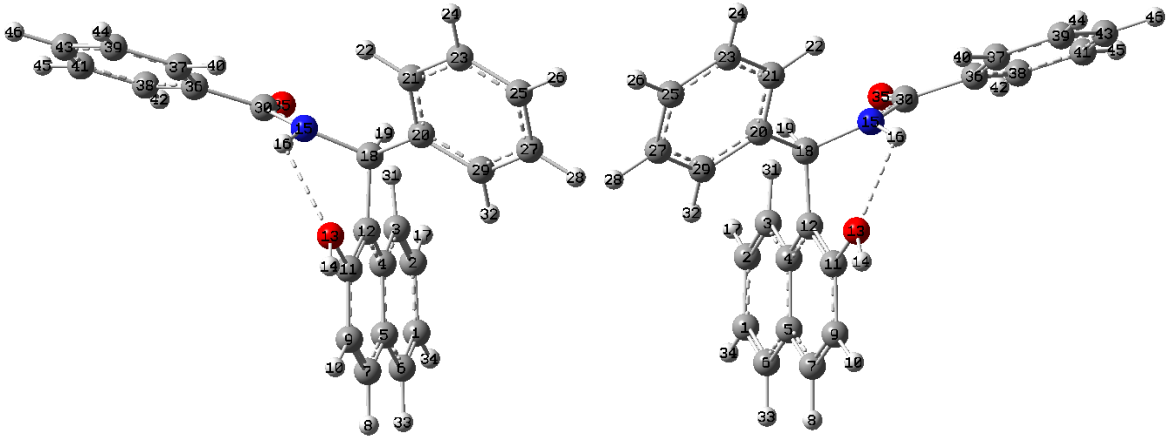


Figure 3.

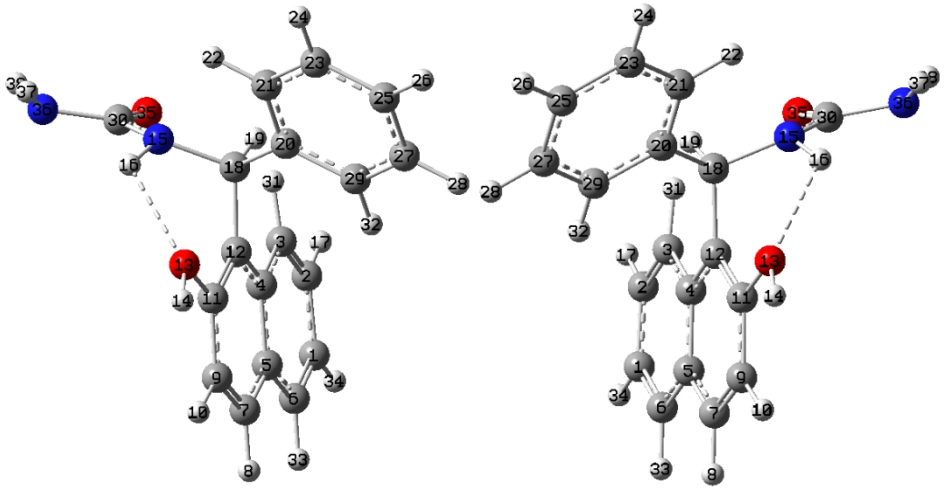


Compound 1



Compound 2

Fig. 4. Continued



Compound 3

Figure 4.

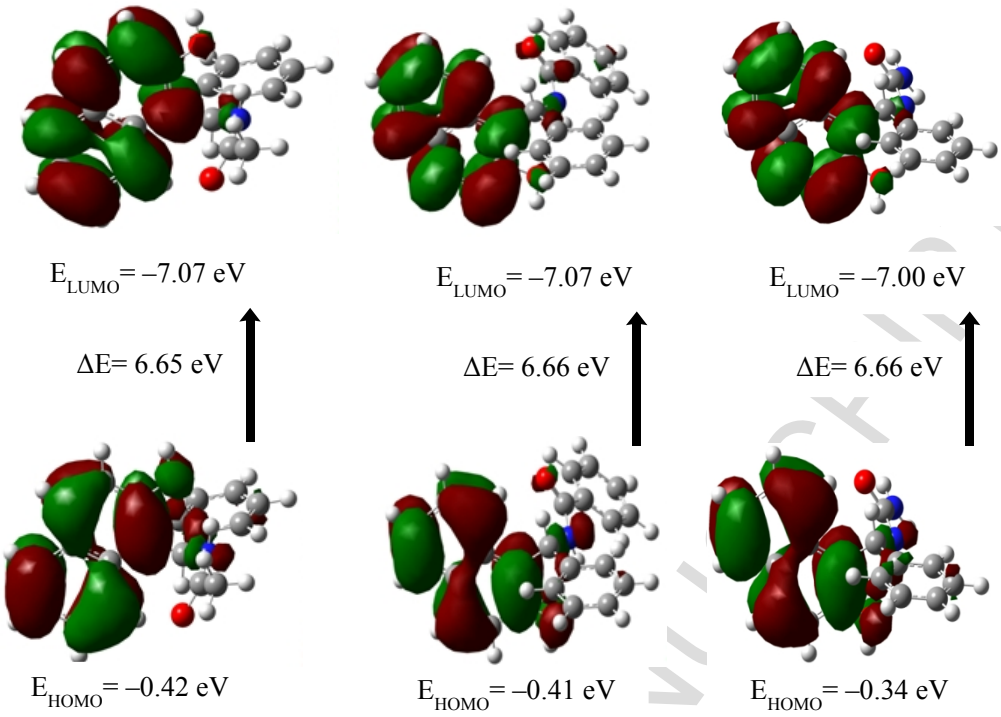


Figure 5.

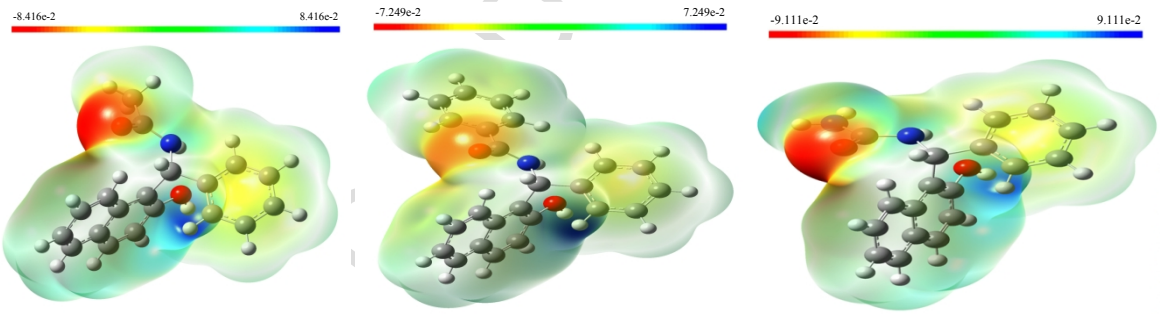


Figure 6.

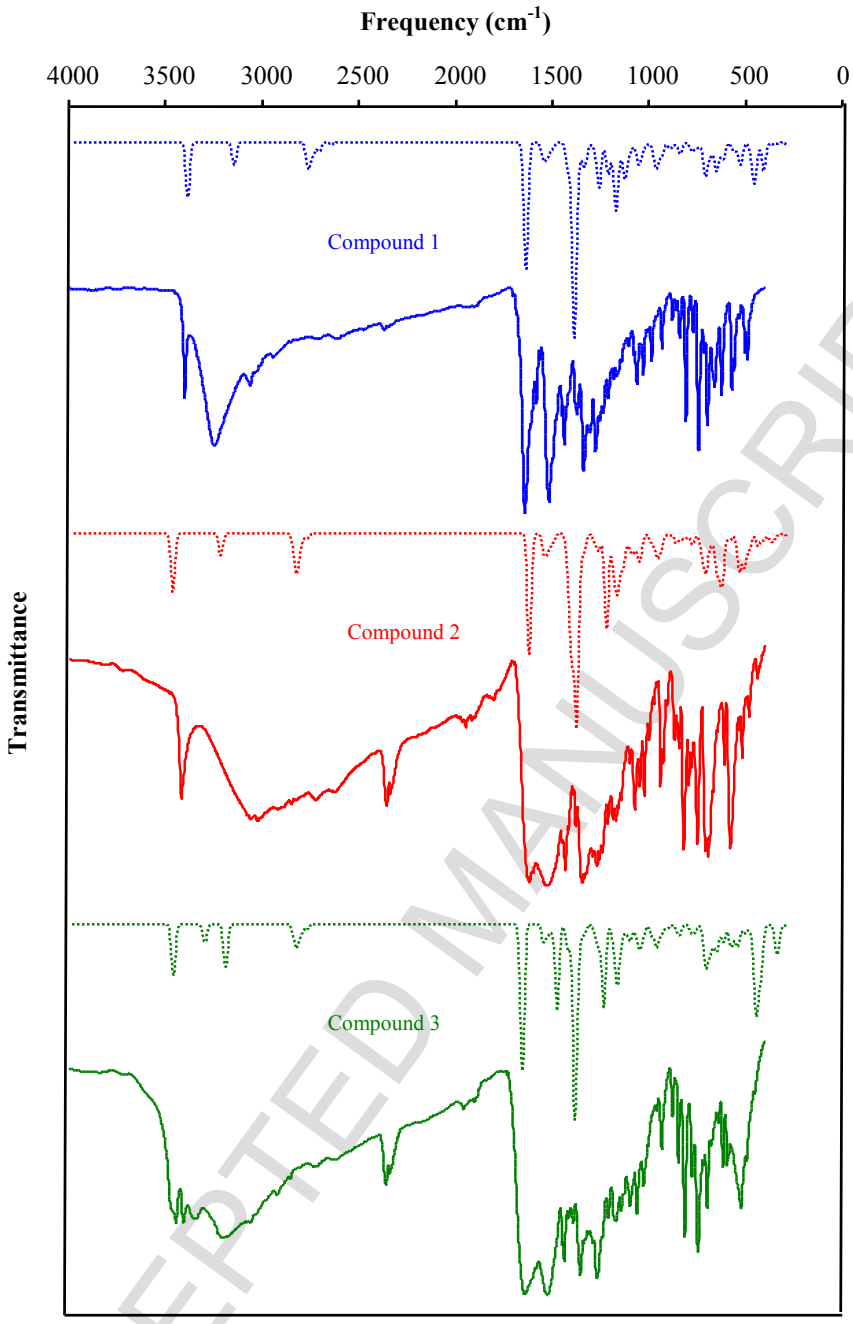
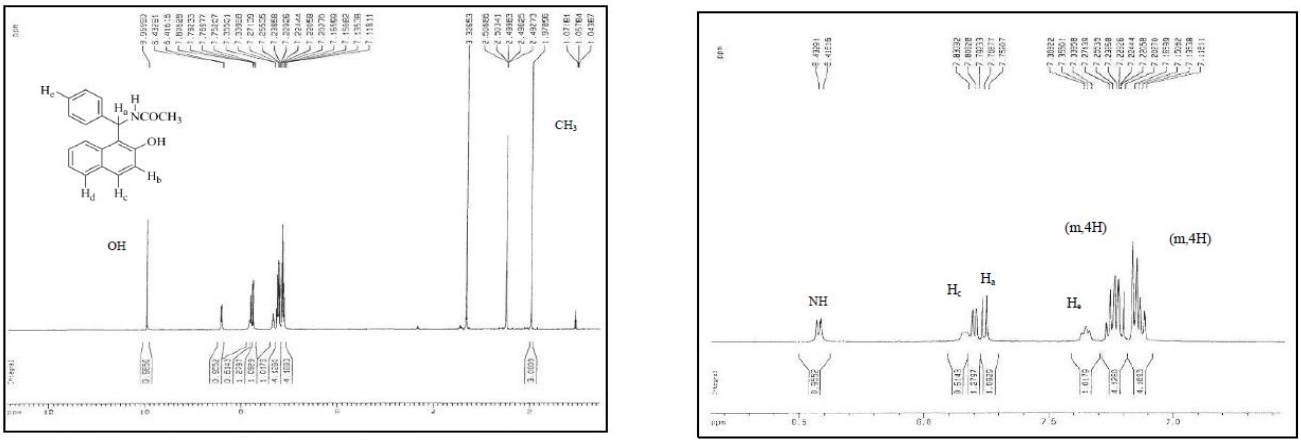
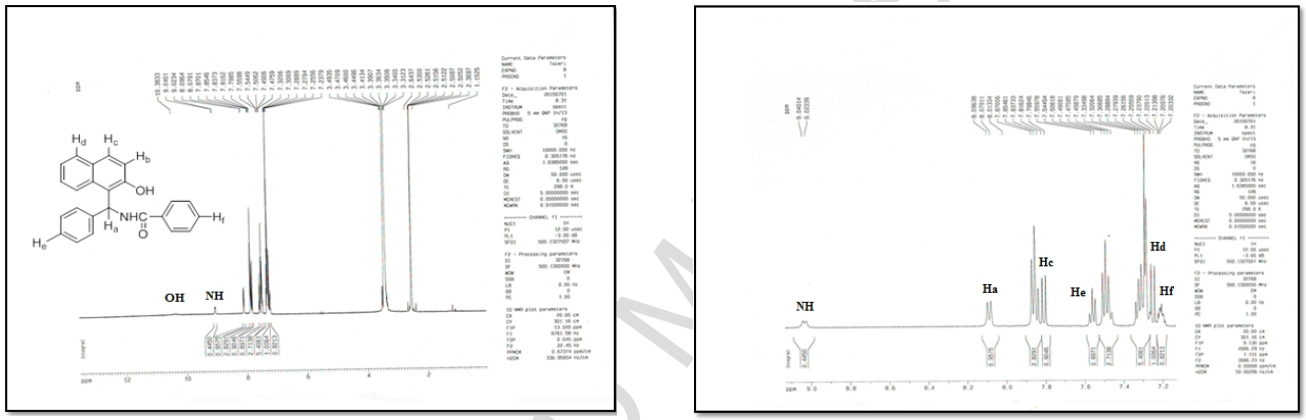


Figure 7.

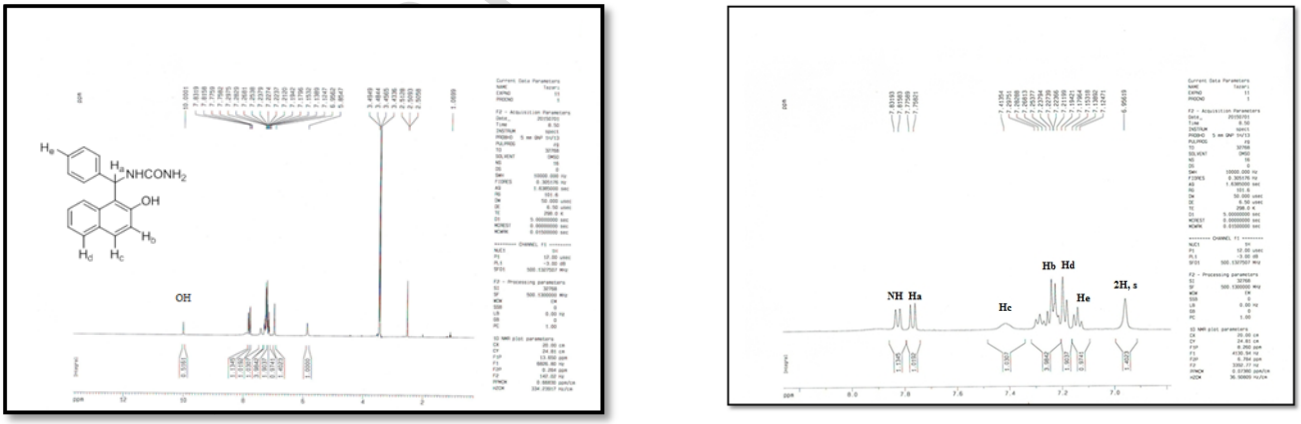
[2] In DMSO



(Compound 1)



(Compound 2)



(Compound 3)

Figure. 8.