Supplementry Information for

Role of basicity, catalytic activity and recyclability of heterogeneous catalyst for efficient synthesis of 1-[(2-benzothiazolylamino)arylmethyl]-2-naphthalenols

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Experimental section

General

The ^{1}H NMR spectra were measured by BRUKER AVANCE II 400 NMR spectrometer with tretramethylsilane as an internal standard at 20-25 ^{o}C; data for ^{1}H NMR are reported as follow: chemical shift (ppm), integration, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and br, broad), coupling constant (Hz). IR spectra were recorded by SHIMADZU, IR spectrometer of sample dispersed in KBr pellet and are reported in terms of frequency of absorption (cm^{-1}). E-Merck pre-coated TLC plates and RANKEM silica gel G were used for preparative thin-layer chromatography. Melting points were determined on electrical melting point apparatus in open capillary and were uncorrected. 2-Amino benzothiazole was purchased from Sigma Aldrich and other chemicals were purchased from Himedia, Mumbai India and used without any purifications.

KOH-loaded catalyst preparation

The catalyst was prepared by magnesia with an aqueous solution of KOH. The catalysts were dried at 393 K for 16 h and calcined at 773 K for 5 h. X-ray powder diffraction patterns were obtained from calcined catalyst samples with a PC X-ray diffractometer using Cu Kα radiation at 40 kV and 40 mA and a scan speed of 2 °C/min. The surface morphology of the prepared catalysts was investigated by a scanning electron microscope.

Preparation of hydrotalcite

The catalyst hydrotalcite was synthesized using literature procedure.[16]

Typical procedure. One-pot hydrothermal reactions at higher temperature and autogenous pressure in aqueous media were carried out to obtain small and high surface area particles. In a typical reaction Mg^{2+} and Al^{3+} hydroxide (metallic ratio of 3:1) were taken and corresponding

ratio of sodium bicarbonate was added to maintaining the *p*H 8.5. After aging the slurry, the precipitate was filtered, washed, and dried.

One-pot three component reaction

Typical procedure with KOH-loaded MgO. A mixture of aldehydes (2 mmol), 2-naphthol (2 mmol) and 2-amino benzothiazole (2 mmol) were heated at 70 ^{o}C under solvent free conditions using KOH-loaded MgO as a catalyst. The time taken by different aldehydes in reaction has mentioned in table 2. After completion of the reaction (TLC analysis), the reaction mixture was cooled to room temperature and filtered. Solid cake was washed with ethyl acetate. Filtrate having product was washed with water and extracted with ethanol and concentrated the ethanol to crystallize the product. Recycled KOH/MgO catalyst was washed with ethyl acetate to remove organic impurity.

Typical procedure using Hydrotalcite.

A mixture of aldehydes (2 mmol), 2-naphthol (2 mmol) and 2-amino benzothiazole (2 mmol) were heated at 70 ^{o}C under solvent free conditions using hydrotalcite (Mg-Al-CO_3, 80 mg) as a catalyst. The time taken by different aldehydes in reaction has mentioned in table 2. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and poured in cold water. The solid mass was filtered and dissolved in ethanol then filtered again so that product was dissolved in ethanol and hydrotalcite has been separated. Concentrate the ethanol to crystallize the product. Recycled hydrotalcite was washed with ethanol to remove organic impurity.

Characterization data

*1-[(2-Benzothiazolylamino)phenylmethyl]-2-naphthalenol (**1a**)*

White powder, mp 203-204°C; IR (KBr) (υ_{max}, cm^{-1}): 3381 (OH_{str}), 1599 ($C{=}C_{str}$), 1542 ($N\text{-}H_{ben}$), 1515 ($C\text{-}H_{ben}$), 1449 ($C\text{-}H_{ben}$); ^{1}H NMR (400 MHz, DMSO): δ_H 6.69-7.93 (16H, m, 15H-arom and 1H-CH), 8.67 (1H, s, NH), 10.11 (1H, s, OH); ^{13}C NMR (100 MHz, DMSO): 53.36, 118.02, 118.57, 118.81, 120.49, 120.84, 122.27, 123.58, 125.23, 126.04, 127.83, 128.34, 128.56, 129.28, 130.59, 132.12, 142.25, 151.96, 153.19, 166.33; ESI-MS: m/z Calculated for $C_{24}H_{18}N_2OS$ 382; Found $[M+H]^+$ 283.3.

*1-[(2-Benzothiazolylamino)(4-nitrophenyl)methyl]-2-naphthalenol (**1d**)*

White powder, mp 120-122°C; IR (KBr) (υ_{max}, cm^{-1}): 3348 (OH_{str}), 2933 ($C\text{-}H_{str}$), 1625 ($C{=}C_{str}$), 1510 ($N\text{-}H_{ben}$), 1267($C\text{-}N_{str}$), 962-812 ($C\text{-}H_{def}$); ^{1}H NMR (400 MHz, DMSO): δ_H 6.88-7.75 (15H, m, 14H-arom and -CH), 8.65 (1H, s, NH), 10.00 (1H, s, OH); ^{13}C NMR (100 MHz, DMSO): 53.43, 117.81, 118.31, 118.58, 119.59, 120.41, 121.46, 122.54, 122.91, 123.24, 122.98, 125.20, 125.33, 126.65, 127.32, 128.57, 128.98 129.89, 145.99, 150.68, 153.38, 166.69; ESI-MS: m/z Calculated for $C_{24}H_{17}N_3O_3S$ 427.2 Found $[M+H]^+$ 428.1.

*1-[(2-Benzothiazolylamino)(2-hydroxyphenyl)methyl]-2-naphthalenol (**1e**)*

Off white powder, mp 162-163°C; IR (KBr) (υ_{max}, cm^{-1}): 3504 (OH_{str}), 2941 ($C\text{-}H_{str}$), 1627 ($C{=}C_{str}$), 1508 ($N\text{-}H_{ben}$), 1280 ($C\text{-}N_{str}$), 962-813 ($C\text{-}H_{def}$); ^{1}H NMR (400 MHz, DMSO): δ_H 6.68-7.49 (15H, m, 14H-arom and -CH), 8.68 (1H, s, NH), 10.04 (1H, s, OH), 10.34 (1H, s, OH); ^{13}C NMR (100 MHz, DMSO): 51.82, 116.74, 116.95, 117.76, 118.84, 119.40, 120.60, 121.11, 121.24, 125.54, 122.52, 126.31, 128.20, 128.98, 129.80, 131.73, 132.12, 136.31, 150.86, 152.65, 154.47, 160.83, 166.54; ESI-MS: m/z Calculated for $C_{24}H_{18}N_2O_2S$ 398.2 Found $[M+H]^+$ 399.1.

*1-[(2-Benzothiazolylamino)(4-methoxyphenyl)methyl]-2-naphthalenol (**1f**)*

Off white powder, mp 172-173°C; IR (KBr) (υ_{max}, cm^{-1}): 3510 (OH_{str}), 3012 ($C\text{-}H_{str}$), 2922 ($C\text{-}H_{str}$), 1625 ($C{=}C_{str}$), 1500 ($N\text{-}H_{ben}$), 1278 ($C\text{-}N_{str}$); ^{1}H NMR (400 MHz, DMSO): δ_H 3.69 (3H, s, OCH_3), 6.69-7.87 (15H, m, 14H-arom and -CH), 8.51 (1H, s, NH), 10.53 (1H, s, OH); ^{13}C NMR (100 MHz, DMSO): 54.81, 59.12, 113.33, 118.11, 119.03, 119.12, 120.58, 122.53, 125.52, 126.22, 127.42, 128.47, 128.79, 129.38, 130.22, 132.16, 133.56, 151.69, 153.35, 158.00, 166.84; ESI-MS: m/z Calculated for $C_{25}H_{20}N_2O_2S$ 412.2 Found $[M+H]^+$ 413.1.

*1-[(2-Benzothiazolylamino)(4-methylphenyl)methyl]-2-naphthalenol (**1g**)*

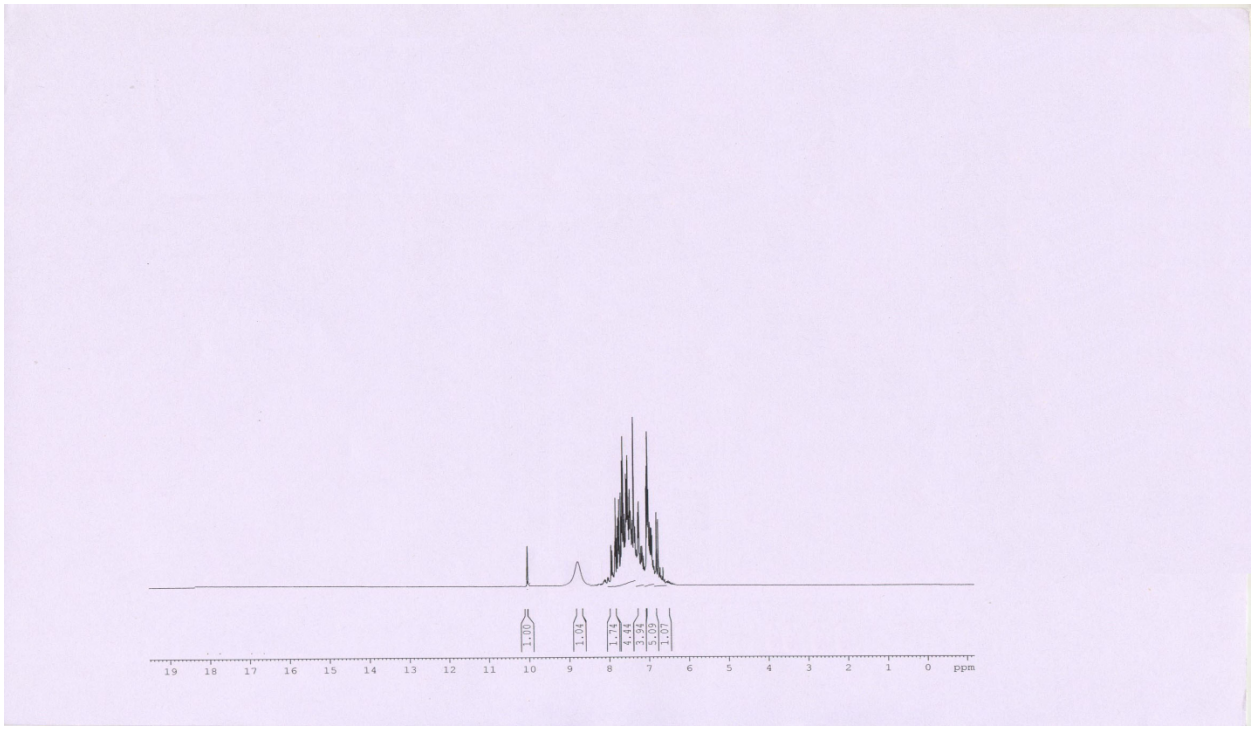
White powder, mp 180-181°C; IR (KBr) (υ_{max}, cm^{-1}): 3007 ($C\text{-}H_{str}$), 2922 ($C\text{-}H_{str}$), 1625 ($C{=}C_{str}$), 1510 ($N\text{-}H_{ben}$), 1267 ($C\text{-}N_{str}$); ^{1}H NMR (400 MHz, DMSO): δ_H 2.23 (3H, s, CH_3), 6.75-7.80 (15H, m, 14H-arom and -CH), 8.66 (1H, s, NH), 10.14 (1H, s, OH); ^{13}C NMR (100 MHz, DMSO): 20.60, 53.33, 118.00, 118.66, 118.92, 120.51, 120.85, 122.27, 125.26, 126.03, 128.34, 128.50, 128.60, 129.22, 130.55, 132.13, 135.17, 139.13, 151.97, 153.20, 166.39; ESI-MS: m/z Calculated for $C_{25}H_{20}N_2OS$ 396.2 Found $[M]^+$ 396.1.

*1-[(2-Benzothiazolylamino)(4-chlorophenyl)methyl]-2-naphthalenol (**1h**)*

White powder, mp 208-209 °C; IR (KBr) (υ_{max}, cm^{-1}): 3504 (OH_{str}), 1627 ($C{=}C_{str}$), 1267 ($C\text{-}N_{str}$), 1122 ($C\text{-}H_{ben}$); ^{1}H NMR (400 MHz, DMSO): δ_H 6.97-7.98 (15H, m, 14H-arom and -CH), 8.57 (1H, s, NH); ^{13}C NMR (100 MHz, DMSO): 53.48, 117.71, 118.13, 118.44, 118.96, 120.95, 121.12, 122.43, 122.47, 125.81, 126.82, 127.30, 127.78, 128.22, 129.54, 130.32, 131.39, 134.52, 138.16, 151.61, 153.28, 155.11, 166.89; ESI-MS: m/z Calculated for $C_{24}H_{17}N_2OClS$ 416.4 Found $[M+H]^+$ 417.2.

^{1}H NMR Spectra

*1-[(2-benzothiazolylamino)phenylmethyl]-2-naphthalenol (**1a**)*



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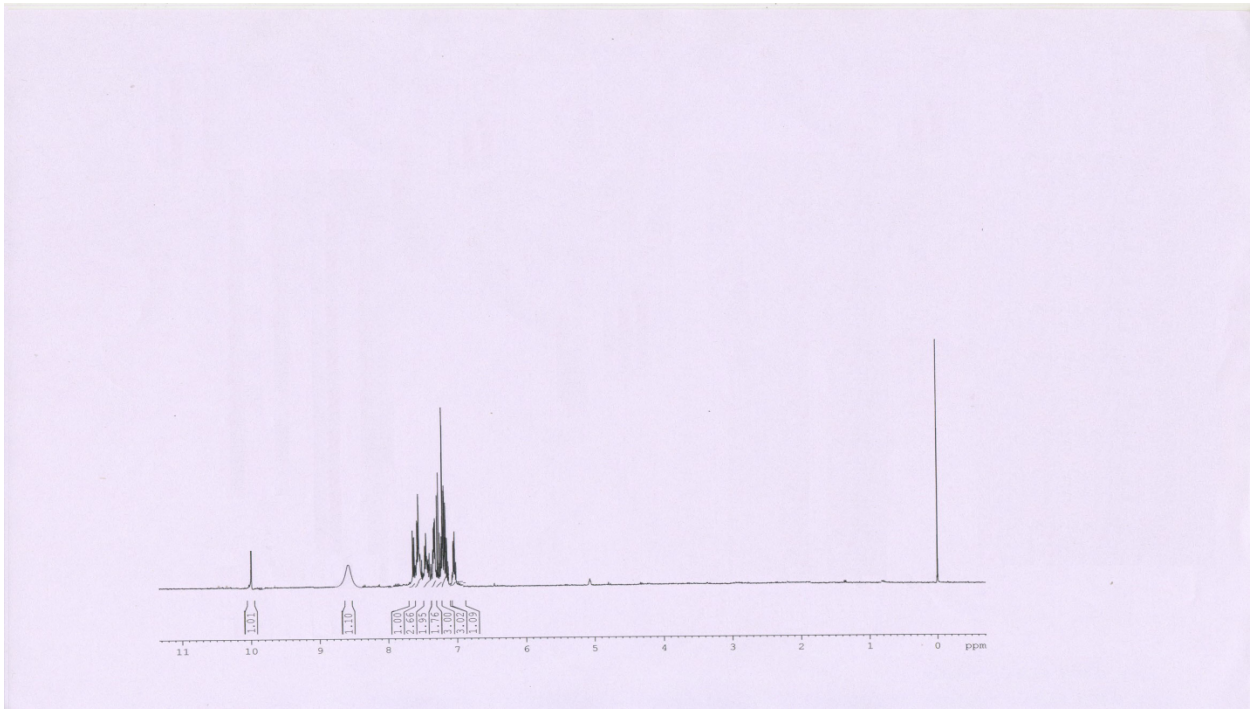

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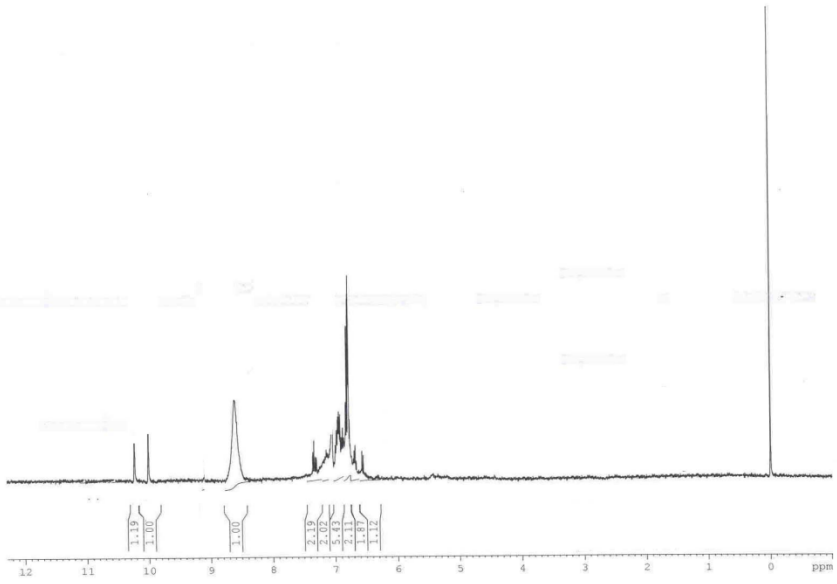

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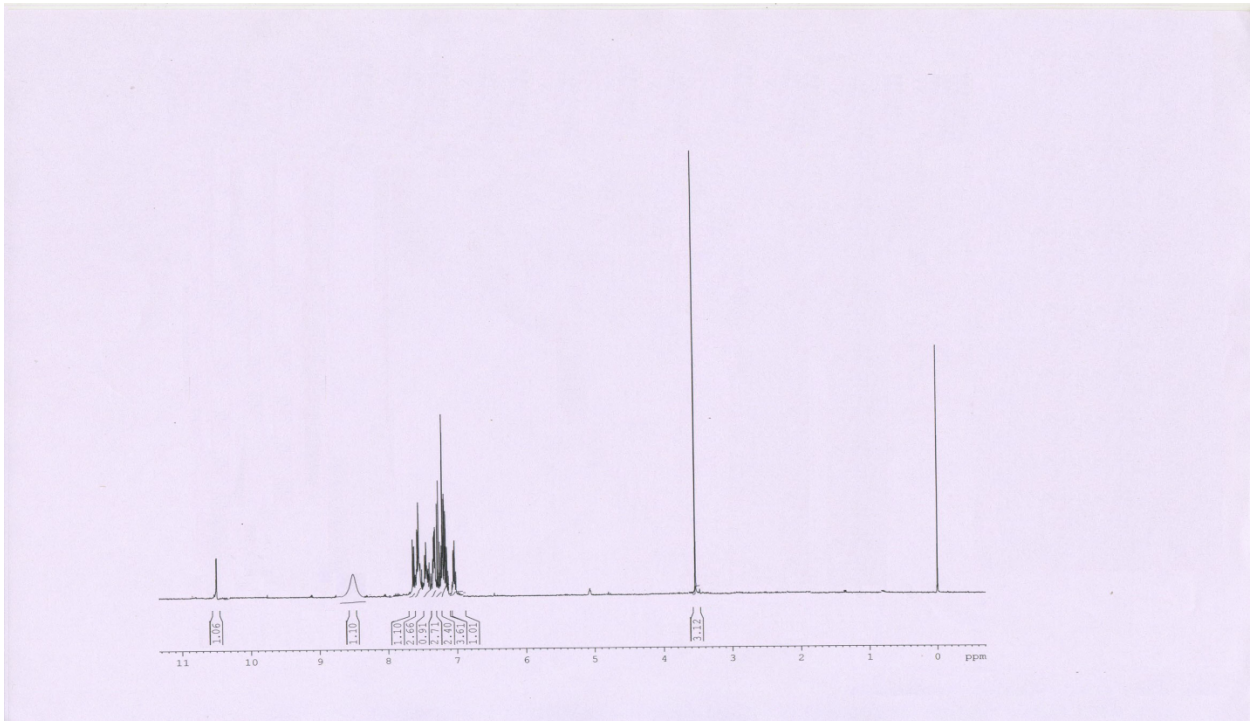
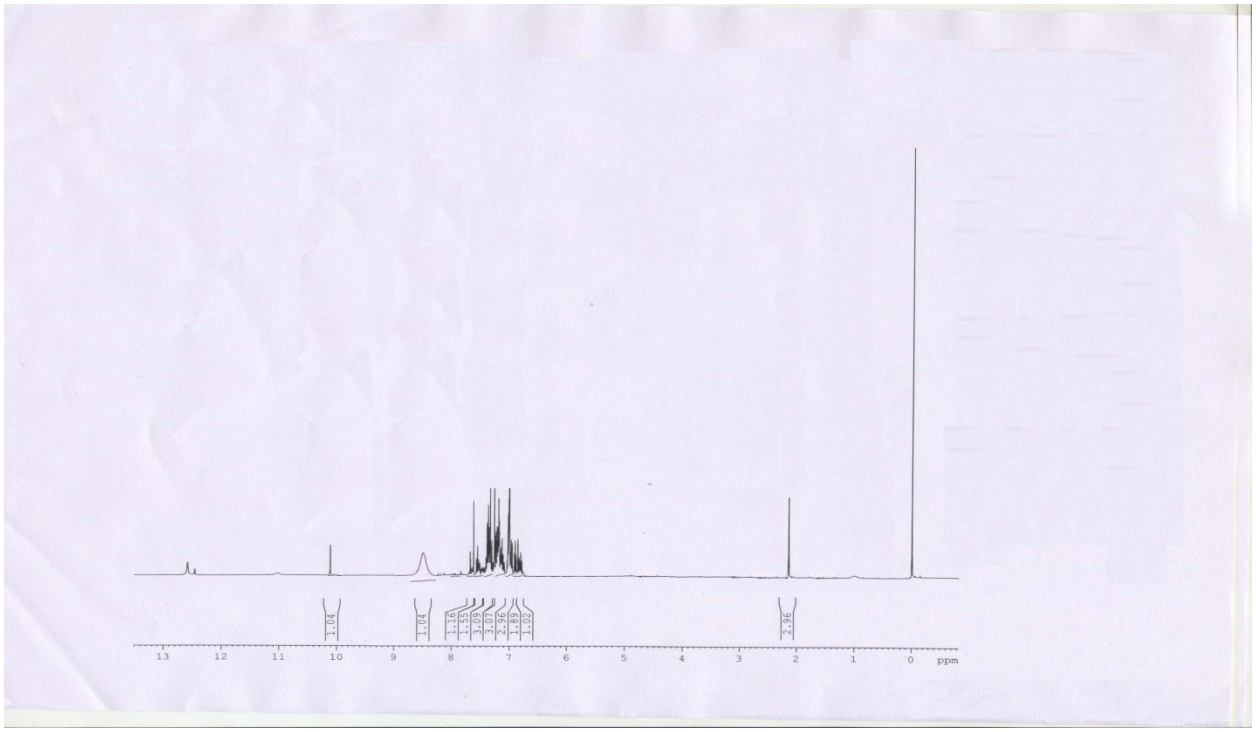


*1-[(2-benzothiazolylamino)(4-methylphenyl)methyl]-2-naphthalenol (**1g**)*



*1-[(2-benzothiazolylamino)(4-chlorophenyl)methyl]-2-naphthalenol (**1h**)*