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Acid catalyzed and thermal rearrangements of 1-(α-branched alkoxy) naphthalenes

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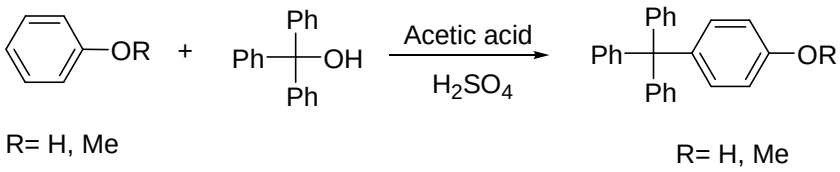
ABSTRACT

Acid catalyzed and thermal rearrangements of 1-(α-branched alkoxy) naphthalenes are studied. The intermediate carbonium ion is established by crossover experiments under acidic rearrangement conditions. The disubstituted product of the acidic rearrangement is corroborated by single crystal structure analysis. Thermal rearrangements are studied in detail.

Key words: Ethers; Acidic rearrangements; Thermal rearrangements; Crossover experiment; Trityl ether; t-Butyl ether.

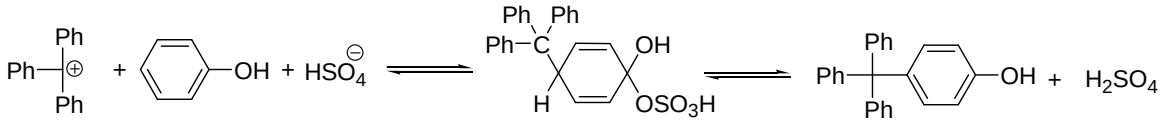
INTRODUCTION

The development of synthetic organic chemistry mostly depends on new C-C bond forming reactions and rearrangements. Early 1900, Baeyers [1] et al. observed that phenol and anisole in presence of acetic and sulphuric acids condense with triphenyl carbinol at room temperature to give 4-hydroxy and 4-methoxy tetra phenyl methane respectively as shown in scheme 1.



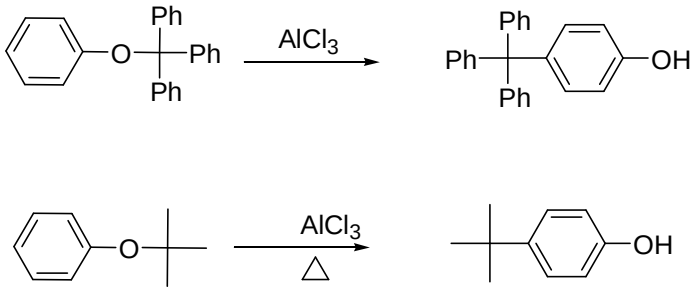
Scheme 1: Preparation of Tetraphenylmethane derivatives

Later these results were confirmed by Boyd [2] et al. They proposed the stable trityl cation formation and the reaction with phenol or anisole at para position as shown in scheme 2.



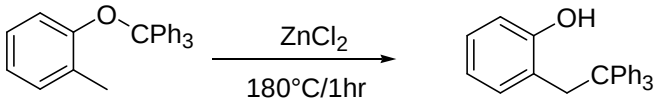
Scheme 2: Proposed mechanism for the tritylation of phenols

During 1930's Parsons [3a] et al. and Smith [3b] et al. reported the acid catalyzed rearrangement of triphenyl methyl ethers and t-butyl ethers as shown in Scheme 3.



Scheme 3: Rearrangement of tert-alkyl phenyl ethers under acidic and thermal conditions

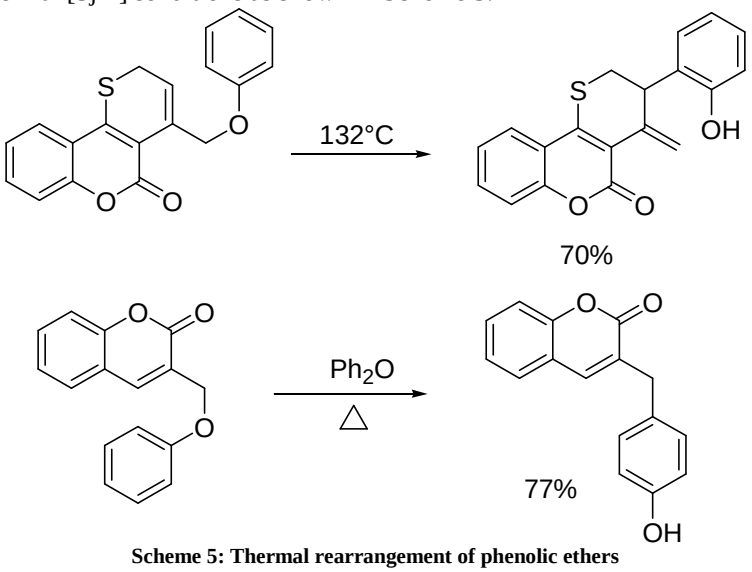
In the same paper Parsons [3a] et al. described the thermal rearrangement of O-tolyl triphenyl methyl ether was reported to give 1-(2-hydroxyphenyl)-2, 2, 2-triphenylethane as shown in Scheme 4.



Scheme 4: Rearrangement of tert-aryl phenyl ether under thermal conditions

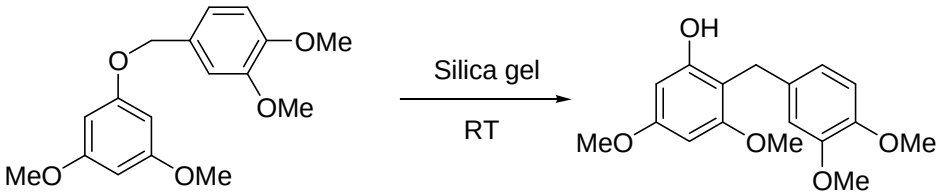
During 1940's Iddles [4a,b] and coworkers studied the rearrangement of both triphenylmethyl and diphenylmethyl ethers and concluded that under acidic conditions migration of diary methyl or triaryl methyl carbonium ion takes place to either the ortho or para position or both in some cases. The rearranged products are also confirmed by independent synthesis.

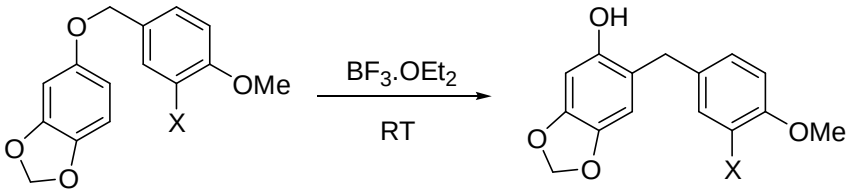
Lately Majumdar [5a-i] et al. studied the sigmatropic rearrangement of ethers. They studied phenolic ethers rearrangement under thermal [5j-k] conditions as shown in Scheme 5.



Scheme 5: Thermal rearrangement of phenolic ethers

Krans and Chaudhary [6a], Luzzio and Chen [6b] reported silica and acid catalysed rearrangement of benzyl ethers as shown in Scheme 6.





Scheme 6: Rearrangement of benzyl ethers on silica and under acidic conditions

MATERIALS AND METHODS

General: Most of the reagents used in this work were obtained from commercial suppliers and were of LR/AR grade. Solvents were purified before use by standard procedures. Melting points were determined using open capillary tubes on POLMON melting points apparatus (Model-96) and are uncorrected. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded by using a Bruker 400 Spectrometer with TMS as internal standard. IR spectra were recorded on a Perkin-Elmer Spectrum 100 FTIR Spectrophotometer as KBr pellets or with the neat products. Mass spectra were recorded on an API 2000 LCMS/MS Applied BioSystems MDS Sciex spectrometer. Analytical TLC was conducted on E-Merck 60F254 aluminum-packed plates of silica gel (0.2 mm). Developed plates were visualized by using UV light or in an iodine chamber. HPLC was performed by using a Shimadzu 2010 instrument.

General procedure:

Thermal reaction: The 1-(1-phenyl-ethoxy)-naphthalene **1** (5.0g, 0.02 moles) was heated (neat) to 170-175°C in test-tube and maintained for 10 hours. (Reaction was monitored by TLC). After completion of the reaction, the reaction mass was cooled to room temperature and the compound was purified by column chromatography over silica gel (50 g, hexane/EtOAc, 8:2 and Rf value of each compound 0.81, 0.56 and 0.48 respectively) to give pure 2-(1-phenyl-ethyl)-naphthalen-1-ol **2** (1.15g, 23.54 %), 4-(1-phenyl-ethyl)-naphthalen-1-ol **3** (1.5g, 30.13 %), 1-naphthol 5 (0.9g, 18.80 %) and a new product 2,4-bis-(1-phenyl-ethyl)-naphthalen-1-ol **4** (1.2g, 24.14%).

Acid reaction: The ether (1.0 mole) was dissolved in ethyl acetate (10 Vol). The acid (2.0 moles) ($HClO_4$, BF_3: OEt_2, HCl) was slowly added using an addition funnel while the mixture was stirred for 2-3 hr at RT (20-25°C). After the TLC confirmed the absence of starting material water (20 Vol) was added and stirred at RT for 30 minutes. The layers were separated and the aqueous layer was extracted with ethyl acetate (5 Vol). The organic layers were combined, dried and concentrated under vacuum to give crude compound. The crude compound was purified on silica gel column chromatography to get pure ortho **2**, para **3** and disubstituted product **4**.

General procedure for the synthesis of 5-7: The hydroxyl compound **(2- 4)** (1.0 mole) was dissolved in DCM (10 Vol). 4-nitro benzene sulfonyl chloride (1.1 moles) was slowly added using a solid dropping funnel while the mixture was stirred in an ice bath (0-5°C). TEA (0.5 moles) was added and the mixture was continuously stirred at 0-5°C for 1h. After the TLC confirmed the absence of starting material. Water (20 Vol) was added and stirred at RT for 30 minutes. The layers were separated and the aqueous layer was extracted using DCM (10 Vol). The organic layers were combined, dried and concentrated under vacuum to give pure products (**5-7**). The structure of the product was confirmed by its analytical data.

2-(1-(3,4-dimethoxyphenyl)ethyl)naphthalen-1-ol (2j):

White solid; Mp. 129.5-132.6°C; IR (KBr): 3455, 2964, 1513, 1254, 1230, 1141, 1028, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.71-1.73 (d, 3H, *J* = 7.20 Hz), 3.78 (s, 3H), 3.86 (s, 3H), 4.36-4.42 (q, 1H, *J* = 14 Hz), 5.24 (s, 1H), 6.77-6.78 (d, 1H, *J* = 1.6 Hz), 6.82-6.84 (d, 1H, *J* = 8.20 Hz), 6.893-6.896 (d, 1H, *J* = 1.24 Hz), 7.40-7.48 (m, 4H), 7.78-7.80 (m, 1H), 8.08-8.09 (m, 1H); ^{13}C NMR (100 MHz, DMSO): δ 21.01, 39.08, 55.75, 55.81, 110.92, 111.34, 119.02, 120.31, 121.37, 125.03, 125.21, 125.22, 125.70, 125.85, 127.45, 133.40, 137.19, 147.91, 148.56, 149.37.

4-(1-(4-methoxyphenyl) ethyl) naphthalen-1-ol (3g):

White solid; Mp. 144.8-147.1°C; IR (KBr): 3316, 2982, 1586, 1509, 1236, 1024, 830, 766 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.70-1.72 (d, 3H, *J* = 7.05 Hz), 3.76 (s, 3H), 4.76-4.81 (q, 1H, *J* = 14 Hz), 5.21 (s, 1H), 6.79-6.81 (d, 3H, *J* = 8.62 Hz), 7.13-7.15 (d, 2H, *J* = 8.52 Hz), 7.22-7.24 (d, 1H, *J* = 7.81 Hz), 7.43-7.46 (m, 2H), 7.98-8.00 (m, 1H), 8.20-8.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.70, 39.26, 55.15, 107.87, 113.70, 122.12, 123.94, 124.64, 124.74, 126.28, 128.40, 132.62, 134.28, 139.17, 150.04, 157.53.

4-(1-(3,4-dimethoxyphenyl)ethyl)naphthalen-1-ol (3j):
White solid; Mp. 213.9-218.5°C; IR (KBr): 3420, 3000, 2964, 1592, 1515, 1268, 1138, 1026, 768 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.70-1.72 (d, 3H, *J* = 7.16 Hz), 3.77 (s, 3H), 3.84 (s, 3H), 4.75-4.78 (q, 1H, *J* = 14 Hz), 5.26 (s, 1H), 6.73-6.80 (m, 4H), 7.19-7.21 (d, 1H, *J* = 7.80 Hz), 7.44-7.46 (m, 2H), 7.99-8.01 (m, 1H), 8.21-8.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.44, 44.42, 60.39, 60.44, 112.28, 115.82, 123.99, 127.51, 128.31, 128.63, 128.65, 128.99, 130.08, 130.56, 136.84, 137.27, 144.70, 151.61, 153.33, 156.58.

2,4-bis(1-(2-chlorophenyl)ethyl)naphthalen-1-ol (4i):
Colourless oil; IR(Neat): 3431, 2989, 1516, 1252, 1235, 1139, 1028, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.67-1.69 (d, 3H, *J* = 6.96 Hz), 1.71-1.73 (d, 3H, *J* = 7.04 Hz), 4.86-4.89 (q, 1H, *J* = 14 Hz), 5.18-5.23 (q, 1H, *J* = 14.4 Hz), 6.87-6.88 (d, 1H, *J* = 7.32 Hz), 7.03-7.08 (m, 2H), 7.18-7.24 (m, 2H), 7.25-7.26 (m, 1H), 7.34 (s, 1H), 7.37-7.40 (m, 4H), 7.78-7.80 (m, 1H), 8.12 (m, 1H); ^{13}C NMR (100 MHz, DMSO): δ 20.04, 20.55, 35.59, 36.87, 121.84, 123.39, 123.64, 124.96, 125.24, 125.99, 126.89, 127.12, 127.30, 127.88, 128.23, 128.28, 129.39, 129.71, 131.33, 132.64, 133.13, 142.26, 144.39, 147.13.

2-(1-phenylethyl)naphthalen-1-yl 4-nitrobenzenesulfonate (5a):
Offwhite solid; Mp. 166.5-168.0°C; IR(KBr): 3121, 3068, 2979, 1527, 1365, 1345, 1191, 1031, 771 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.66-1.68 (d, 3H, *J* = 6.10 Hz), 4.68-4.73 (q, 1H, *J* = 14 Hz), 7.21-7.23 (m, 3H), 7.27-7.30 (m, 3H), 7.33-7.35 (d, 1H, *J* = 8.59 Hz), 7.49 (m, 1H), 7.73-7.78 (t, 2H, *J* = 9.66 Hz), 7.83-7.85 (d, 1H, *J* = 8.12 Hz), 8.21-8.23 (d, 2H, *J* = 8.76 Hz), 8.39-8.41 (d, 2H, *J* = 8.74 Hz); ^{13}C NMR ($CDCl_3$) : δ 20.75, 37.83, 122.19, 124.49, 126.00, 126.45, 127.01, 127.61, 127.85, 128.06, 128.44, 129.60, 133.50, 136.80, 142.39, 142.58, 144.26, 150.95.

2-(1-(3-methoxyphenyl)ethyl)naphthalen-1-yl 4-nitrobenzenesulfonate (5b):
White solid; Mp. 139.3-141.0°C; IR (KBr): 2973, 1597, 1531, 1373, 1190, 1036, 884, 782 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.61-1.63 (d, 3H, *J* = 7.08 Hz), 3.74 (s, 3H), 4.59-4.65 (q, 1H, *J* = 14 Hz), 6.70-6.77 (m, 3H), 7.17 (m, 1H), 7.30-7.32 (d, 1H, *J* = 8.61 Hz), 7.39-7.41 (t, 1H, *J* = 7.77 Hz), 7.44-7.46 (t, 1H, *J* = 7.70 Hz), 7.72-7.74 (d, 2H, *J* = 8.48 Hz), 7.79-7.81 (d, 1H, *J* = 8.04 Hz), 8.15-8.18 (d, 2H, *J* = 8.65 Hz), 8.34-8.37 (d, 2H, *J* = 8.63 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.69, 37.66, 55.01, 110.90, 113.97, 119.83, 122.09, 124.31, 125.81, 126.30, 126.84, 127.49, 127.69, 127.90, 129.20, 129.43, 133.40, 136.39, 142.25, 142.46, 145.78, 150.78, 159.47.

2-(1-(2-methoxyphenyl)ethyl)naphthalen-1-yl 4-nitrobenzenesulfonate (5c):
Offwhite solid; Mp. 139.9-141.6°C; IR (KBr): 3102, 2979, 1594, 1529, 1379, 1349, 1187, 1037, 799, 782 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.62-1.64 (d, 3H, *J* = 6.79 Hz), 3.74 (s, 3H), 4.61-4.66 (q, 1H, *J* = 13.8 Hz), 6.71-6.73 (d, 1H, *J* = 7.68 Hz), 6.76-6.78 (d, 1H, *J* = 7.44 Hz), 7.15-7.17 (t, 1H, *J* = 7.59 Hz), 7.31-7.33 (d, 1H, *J* = 8.54 Hz), 7.39-7.41 (t, 1H, *J* = 7.73 Hz), 7.44-7.46 (t, 2H, *J* = 7.56 Hz), 7.73-7.75 (d, 2H, *J* = 7.68 Hz), 7.79-7.81 (d, 1H, *J* = 7.88 Hz), 8.15-8.17 (d, 2H, *J* = 8.36 Hz), 8.33-8.35 (d, 2H, *J* = 8.38 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.70, 37.67, 45.68, 55.02, 110.90, 113.98, 119.83, 122.10, 124.32, 125.82, 126.31, 126.86, 127.50, 127.90, 127.91, 129.22, 129.43, 133.40, 136.40, 142.22, 142.46, 145.79, 150.78, 159.48.

2-(1-p-tolylethyl)naphthalen-1-yl 4-nitrobenzenesulfonate (5d):
White solid; Mp. 146.3-148.2°C; IR (KBr): 3112, 2965, 1526, 1373, 1190, 1037, 780 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.60-1.61 (d, 3H, *J* = 6.01 Hz), 2.30 (s, 3H), 4.57-4.63 (q, 1H, *J* = 14 Hz), 7.04-7.07 (m, 4H), 7.29-7.31 (d, 1H, *J* = 8.63 Hz), 7.37-7.41 (t, 1H, *J* = 7.62 Hz), 7.44-7.47 (t, 1H, *J* = 7.32 Hz), 7.72-7.74 (d, 2H, *J* = 8.49 Hz), 7.79-7.81 (d, 1H, *J* = 8.04 Hz), 8.16-8.18 (d, 2H, *J* = 8.72 Hz), 8.34-8.36 (d, 2H, *J* = 8.72 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.73, 20.83, 37.26, 122.07, 124.29, 125.86, 126.24, 126.81, 127.30, 127.51, 127.67, 127.88, 128.94, 129.46, 133.34, 135.87, 136.76, 141.09, 142.28, 142.41, 150.80.

2-(1-(4-bromophenyl)ethyl)naphthalen-1-yl 4-nitrobenzenesulfonate (5e):
Light yellow solid; Mp. 158.2-160.0°C; IR (KBr): 3107, 2979, 2940, 1528, 1366, 1191, 1030, 784, 776 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.64-1.65 (d, 3H, *J* = 7.10 Hz), 4.68-4.73 (q, 1H, *J* = 14 Hz), 7.09-7.11 (d, 2H, *J* = 8.32 Hz), 7.24 (s, 1H), 7.32-7.39 (m, 3H), 7.43-7.45 (t, 1H, *J* = 7.57 Hz), 7.58-7.60 (d, 1H, *J* = 8.46 Hz), 7.73-7.75 (d, 1H, *J* = 8.60 Hz), 7.79-7.81 (d, 1H, *J* = 8.14 Hz), 8.18-8.20 (d, 2H, *J* = 8.71 Hz), 8.38-8.40 (d, 2H, *J* = 8.72 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.45, 37.33, 120.21, 121.87, 124.40, 125.55, 126.41, 126.90, 127.31, 127.76, 128.06, 129.28, 129.52, 131.34, 133.43, 136.30, 142.21, 142.38, 143.20, 150.91.

2-(1-(4-fluorophenyl)ethyl)naphthalen-1-yl 4-nitrobenzenesulfonate (5f):
White solid; Mp. 154.4-156.2°C; IR (KBr): 3111, 2968, 1529, 1373, 1190, 1035, 780 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.64-1.66 (d, 3H, *J* = 7.04 Hz), 4.71-4.76 (q, 1H, *J* = 14 Hz), 6.93-6.97 (t, 2H, *J* = 8.44 Hz), 7.18-7.21 (m, 2H), 7.25-7.27 (d, 1H, *J* = 8.47 Hz), 7.35 (m, 1H), 7.44 (m, 1H), 7.60 (m, 1H), 7.72-7.74 (d, 1H, *J* = 8.60 Hz), 7.78-7.80 (d, 1H, *J* = 8.06 Hz), 8.18-8.20 (d, 2H, *J* = 8.52 Hz), 8.38-8.40 (d, 2H, *J* = 8.46 Hz); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 20.67, 37.09, 114.94, 115.15, 121.89, 124.40, 125.62, 126.38, 126.87, 127.22, 127.32, 127.74, 128.02, 128.92, 133.38, 136.75, 139.82, 142.30, 150.90, 160.10.

2-(1-(4-methoxyphenyl)ethyl)naphthalen-1-yl 4-nitrobenzenesulfonate (5g):
White solid; Mp. 117.3-119.3°C; IR (KBr): 3070, 2972, 2931, 1536, 1380, 1189, 1039, 1028, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.52 (s, 3H), 3.66 (s, 3H), 4.42 (s, 1H), 6.77-6.79 (m, 2H), 7.05-7.06 (m, 2H), 7.42-7.44 (m, 3H), 7.67 (m, 1H), 7.88-7.92 (m, 2H), 8.35-8.36 (d, 2H, *J* = 4.39 Hz), 8.48-8.49 (d, 2H, *J* = 4.45 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.78, 36.87, 55.12, 133.60, 122.00, 124.31, 125.83, 126.23, 126.81, 127.44, 127.69, 127.88, 128.41, 129.45, 133.80, 136.20, 137.01, 142.28, 157.96.

2-(1 - (2 – methoxy - 4 - methyl phenyl) ethyl) naphthalen - 1 - yl 4 - nitrobenzenesulfonate (5h):
White solid; Mp. 160.2-162.5°C; IR (KBr): 3115, 2967, 2932, 1528, 1373, 1187, 1031, 782 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.51-1.52 (d, 3H, *J* = 7.16 Hz), 2.30 (s, 3H), 3.61 (s, 3H), 4.60-4.65 (s, 1H), 6.53 (s, 1H), 6.68-6.70 (d, 1H, *J* = 7.72 Hz), 7.01-7.03 (d, 1H, *J* = 7.64 Hz), 7.33-7.35 (d, 1H, *J* = 8.64 Hz), 7.45-7.48 (m, 2H), 7.71-7.73 (d, 1H, *J* = 8.60 Hz), 7.79-7.81 (m, 1H), 7.95 (m, 1H), 8.18-8.20 (d, 2H, *J* = 8.76 Hz), 8.32-8.34 (d, 2H, *J* = 8.76 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.98, 21.23, 32.18, 54.95, 111.40, 120.73, 122.36, 124.03, 126.02, 126.06, 126.74, 126.88, 127.36, 127.53, 127.84, 129.28, 129.60, 133.26, 135.83, 137.52, 142. 55. 142.64. 150.58. 156.70.

2-(1-(2-chlorophenyl)ethyl)naphthalen-1-yl 4-nitrobenzenesulfonate (5i):
Light yellow solid; Mp. 187.0-190.0°C; IR (KBr): 3106, 2982, 2940, 1528, 1367, 1191, 1031, 777 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.66-1.68 (d, 3H, *J* = 7.12 Hz), 4.82-4.87 (q, 1H, *J* = 108 Hz), 7.14-7.35 (m, 5H), 7.46-7.49 (pen, 2H), 7.75-7.77 (d, 1H, *J* = 8.57 Hz), 7.80-7.82 (d, 1H, *J* = 7.92 Hz), 7.89 (s, 1H), 8.23-8.25 (d, 2H, *J* = 8.60 Hz), 8.39-8.41 (d, 2H, *J* = 8.46 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.50, 35.48, 122.23, 125.54, 126.16, 127.07, 127.43, 127.77, 128.15, 128.27, 128.65, 128.83, 129.79, 129.96, 133.41, 133.42, 134.59, 141.19, 141.63, 142.21, 151.47.

2-(1-(4-chlorophenyl)ethyl)naphthalen-1-yl 4-nitrobenzenesulfonate (5k):
White solid; Mp. 159.5-160.6°C; IR (KBr): 3109, 2979, 1530,1 191, 1367, 1031, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.64-1.66(d, 3H, *J* = 7.12 Hz), 4.70-4.75 (q, 1H, *J* = 14 Hz), 7.14-7.17 (d, 2H, *J* = 8.30 Hz), 7.22-7.24 (d, 3H, *J* = 8.15 Hz), 7.34-7.36 (t, 1H, *J* = 7.68 Hz), 7.43-7.45 (t, 1H, *J* = 7.57 Hz), 7.58-7.60 (d, 1H, *J* = 8.45 Hz), 7.73-7.75 (d, 1H, *J* = 8.59 Hz), 7.79-7.81 (d, 1H, *J* = 8.12 Hz), 8.18-8.20 (d, 2H, *J* = 8.68 Hz), 8.38-8.41 (d, 2H, *J* = 8.68 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.50, 37.27, 121.88, 124.39, 125.57, 126.40, 126.90, 127.32, 127.75, 128.05, 128.39, 128.88, 129.52, 132.12, 133.42, 136.41, 142.22, 142.38, 142.67, 150.92.

2-(1-(thiophen-2-yl) ethyl)naphthalen-1-yl 4-nitrobenzenesulfonate (5l):
White solid; Mp. 168.4-170.0°C; IR (KBr): 3123, 2976, 1526, 1362, 1192, 1032, 774 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.69-1.71 (d, 3H, *J* = 6.91 Hz), 4.75-4.80 (q, 1H, *J* = 13.4 Hz), 6.75 (s, 1H), 6.89-6.92 (m, 1H), 7.16-7.17 (d, 1H, *J* = 4.82 Hz), 7.39-7.49 (m, 3H), 7.76-7.78 (d, 2H, *J* = 8.47 Hz), 7.80-7.82 (d, 1H, *J* = 8.00 Hz), 8.16-8.18 (d, 2H, *J* = 8.67 Hz), 8.34-8.36 (d, 2H, *J* = 8.60 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.49, 34.17, 122.18, 123.98, 124.31, 124.47, 125.52, 126.49, 126.94, 127.43, 127.73, 128.04, 129.48, 133.58, 135.85, 141.96, 142.00, 148.63, 150.85.

2-(1-(furan-2-yl)ethyl)naphthalen-1-yl 4-nitrobenzenesulfonate (5m):
White solid; Mp. 138-142°C; IR (KBr): 3117, 2981, 1533, 1373, 1190, 1040, 786 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.53-1.56 (m, 3H), 4.47 (m, 1H), 6.04 (s, 1H), 6.28 (s, 1H), 7.23-7.47 (m, 4H), 7.74-7.80 (m, 3H), 8.16-8.16 (m, 2H), 8.36-8.37 (d, 2H, *J* = 4.68 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.64, 32.89, 105.87, 110.02, 122.17, 124.28, 125.38, 126.45, 126.90, 127.54, 127.68, 127.94, 129.54, 133.60, 133.90, 141.50, 141.95, 142.34, 150.82, 157.14.

1-(1-phenylethyl)naphthalen-4-yl 4-nitrobenzenesulfonate (6a):
White solid; Mp. 134.2-138.5°C; IR(KBr): 3107, 2971, 2876, 1532, 1379, 1353, 1189, 1024, 825, 742 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.77-1.78 (d, 3H, *J* = 7.13 Hz), 4.87-4.92 (q, 1H, *J* = 14 Hz), 7.20-7.23 (m, 3H), 7.28-7.30 (m, 2H), 7.37-7.39 (d, 1H, *J* = 8.02 Hz), 7.42-7.45 (m, 3H), 7.85 (m, 1H), 8.04-8.07 (d, 1H, *J* = 8.30 Hz), 8.14-8.16 (d, 2H, *J* = 8.70 Hz), 8.35-8.37 (d, 2H, *J* = 8.71 Hz); ^{13}C NMR ($CDCl_3$): δ 22.55, 40.56, 117.76, 121.78, 123.65, 124.34, 126.34, 126.53, 127.03, 127.08, 127.54, 128.62, 129.89, 132.94, 141.51, 141.78, 144.22, 145.85.

1-(1-(3-methoxyphenyl) ethyl)naphthalen-4-yl 4-nitrobenzenesulfonate (6b):
Offwhite solid; Mp. 135.8-140.0°C; IR (KBr): 3078, 2970, 1599, 1529, 1381, 1187, 784 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.72-1.73 (d, 3H, *J* = 5.8 Hz), 3.74 (s, 3H), 4.81-4.83 (q, 1H, *J* = 14 Hz), 6.68-6.79 (m, 3H), 7.17-7.42 (m, 5H), 7.81-7.83 (d, 1H, *J* = 6.93 Hz), 8.00-8.02 (d, 1H, *J* = 7.24 Hz), 8.08-8.10 (d, 2H, *J* = 7.55 Hz), 8.29-8.31 (d,

2H, *J* = 7.46 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.33, 40.41, 55.01, 110.65, 113.91, 117.63, 119.92, 121.61, 123.47, 124.19, 126.39, 129.45, 129.76, 129.91, 132.81, 141.28, 141.43, 144.11, 147.49, 150.81, 159.63.

1-(1-(2-methoxyphenyl) ethyl)naphthalen-4-yl 4-nitrobenzenesulfonate (6c):
White solid; Mp. 135.7-138.1°C; IR (KBr): 3105, 2970, 1599, 1528, 1380, 1351, 1187, 1040, 814 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.72-1.74 (d, 3H, *J* = 7.00 Hz), 3.74 (s, 3H), 4.80-4.85 (q, 1H, *J* = 14 Hz), 6.68-6.72 (m, 2H), 6.78-6.80 (d, 1H, *J* = 7.48 Hz), 7.19-7.26 (m, 2H), 7.35-7.42 (m, 3H), 7.81-7.83 (d, 1H, *J* = 8.00 Hz), 8.00-8.02 (d, 1H,. *J* = 8.23 Hz), 8.08-8.10 (d, 2H, *J* = 8.55 Hz), 8.29-8.32 (d, 2H, *J* = 8.55 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.33, 40.42, 55.02, 110.66, 113.92, 117.63, 119.93, 121.62, 123.47, 124.19, 126.39, 126.91, 129.45, 129.76, 132.82, 141.28, 141.43, 144.11, 147.50, 150.82, 159.63.

1-(1-p-tolylethyl)naphthalen-4-yl 4-nitrobenzenesulfonate (6d):
White solid; Mp. 150.3-156.3°C; IR (KBr): 3080, 2975, 1528, 1375, 1189, 1025, 863 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.71-1.73 (d, 3H, *J* = 7.08 Hz), 2.29 (s, 3H), 4.80-4.85 (q, 1H, *J* = 14 Hz), 7.07 (s, 4H), 7.22-7.26 (t, 1H, *J* = 8.05 Hz), 7.33-7.43 (m, 3H), 7.81-7.83 (d, 1H, *J* = 8.07 Hz), 8.02-8.04 (d, 1H, *J* = 8.38 Hz), 8.09-8.11 (d, 2H, *J* = 8.76 Hz), 8.31-8.33 (d, 2H, *J* = 8.75 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.85, 22.47, 40.00, 117.62, 121.61, 123.41, 124.19, 124.22, 126.35, 126.85, 126.91, 127.26, 129.16, 129.75, 132.80, 135.72, 141.39, 141.89, 142.71, 144.02.

1-(1-(4-bromophenyl)ethyl)naphthalen-4-yl 4-nitrobenzenesulfonate (6e):
Light yellow solid; Mp. 138.5-140.0°C; IR (KBr): 3108, 2974, 1529, 1375, 1189 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.71-1.72 (d, 3H, *J* = 7.16 Hz), 4.78-4.84 (q, 1H, *J* = 14.2 Hz), 7.04-7.06 (d, 2H, *J* = 8.24 Hz), 7.23-7.26 (m, 1H), 7.31-7.33 (d, 1H, *J* = 8.04 Hz), 7.37-7.42 (m, 4H), 7.8 (m, 1H), 7.94-7.96 (d, 1H, *J* = 8.12 Hz), 8.11-8.13 (d, 2H, *J* = 8.76 Hz), 8.33-8.35 (d, 2H, *J* = 8.76 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.27, 39.96, 117.61, 119.98, 121.79, 123.54, 124.02, 124.26, 126.53, 127.02, 127.05, 129.15, 129.73, 131.58, 132.66, 140.91, 141.39, 144.25, 144.78, 150.86.

1-(1-(4-fluorophenyl)ethyl)naphthalen-4-yl 4-nitrobenzenesulfonate (6f):
White solid; Mp. 118.6-120.0°C; IR (KBr): 3110, 2969, 2873, 1603, 1525, 1509, 1382, 1187, 817 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.71-1.73 (d, 3H, *J* = 7.08 Hz), 4.82-4.87 (q, 1H, *J* = 14 Hz), 6.92-6.97 (t, 2H, *J* = 8.49 Hz), 7.11-7.15 (t, 2H, *J* = 6.78 Hz), 7.22-7.24 (d, 1H, *J* = 7.98 Hz), 7.31-7.33 (d, 1H, *J* = 8.00 Hz), 7.40-7.42 (p, 2H), 7.83-7.87 (m, 1H), 7.97-7.99 (d, 1H, *J* = 8.15 Hz), 8.10-8.13 (d, 2H, *J* = 8.57 Hz), 8.32-8.34 (d, 2H, *J* = 8.62 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.52, 39.73, 115.17, 115.38, 117.62, 121.76, 123.47, 124.08, 124.25, 126.49, 126.98, 128.76, 129.74, 132.69, 141.38, 141.41, 144.18, 150.85, 159.99, 162.42.

1 - (1 - (2 - methoxy - 4 - methyl phenyl) ethyl) naphthalen- 4 - yl 4 - nitrobenzenesulfonate (6h):
White solid; Mp. 170.5-179.0°C; IR (KBr): 3067, 2964, 2932, 1532, 1377, 1191, 1039, 1026, 820 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.61-1.63 (d, 3H, *J* = 7.04 Hz), 2.30 (s, 3H), 3.84 (s, 3H), 5.18-5.23 (q, 1H, *J* = 14 Hz), 6.59-6.61 (d, 1H, *J* = 7.68 Hz), 6.71-6.75 (t, 2H, *J* = 7.90 Hz), 7.24-7.26 (m, 1H), 7.33-7.40 (m, 3H), 7.77-7.79 (d, 1H, *J* = 8.24 Hz), 7.99-8.01 (d, 1H, *J* = 8.28 Hz), 8.08-8.10 (d, 2H, *J* = 8.72 Hz), 8.29-8.31 (d, 2H, *J* = 8.72 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.93, 21.31, 32.59, 55.34, 111.38, 117.51, 121.11, 121.38, 122.20, 124.12, 124.36, 126.24, 126.71, 126.79, 127.29, 129.76, 131.36, 132.95, 137.12, 141.41, 142.51, 143.88, 155.84.

1-(1-(2-chlorophenyl)ethyl)naphthalen-4-yl 4-nitrobenzenesulfonate (6i):
Offwhite solid; Mp. 142.1-146.8°C; IR (KBr): 3071, 2971, 1533, 1385, 1190, 765, 744 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.68-1.70 (d, 3H, *J* = 7.04 Hz), 5.22-5.27 (q, 1H, *J* = 14 Hz), 6.95-7.11 (m, 3H), 7.26-7.28 (d, 1H, *J* = 8.36 Hz), 7.33-7.44 (m, 4H), 7.80-7.84 (d, 1H, *J* = 8.21 Hz), 7.88-7.90 (d, 1H, *J* = 8.48 Hz), 8.08-8.10 (d, 2H, *J* = 8.72 Hz), 8.30-8.32 (d, 2H, *J* = 8.72 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.61, 37.10, 117.53, 121.60, 123.29, 124.04, 124.18, 126.51, 126.91, 127.04, 127.17, 127.59, 128.20, 129.62, 129.75, 132.79, 133.17, 140.81, 141.28, 143.24, 144.27, 150.82.

1-(1-(4-chlorophenyl)ethyl)naphthalen-4-yl 4-nitrobenzenesulfonate (6k):
White solid; Mp. 127.1-130.0°C; IR (KBr): 3106, 2966, 1536, 1380, 1189, 846 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.71-1.73 (d, 3H, *J* = 7.10 Hz), 4.80-4.86 (q, 1H, *J* = 14 Hz), 7.09-7.11 (d, 2H, *J* = 8.25 Hz), 7.22-7.25 (m, 3H), 7.31-7.33 (d, 1H, *J* = 8.02 Hz), 7.40-7.44 (m, 2H), 7.83-7.85 (d, 1H, *J* = 7.96 Hz), 7.94-7.96 (d, 1H, *J* = 8.22 Hz), 8.11-8.13 (d, 2H, *J* = 8.69 Hz), 8.33-8.35 (d, 2H, *J* = 8.70 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.33, 39.89, 117.61, 121.77, 123.52, 124.03, 124.25, 126.52, 127.01, 128.63, 128.75, 129.74, 131.92, 132.67, 141.00, 141.39, 144.24.

1-(1-(thiophen-2-yl)ethyl)naphthalen-4-yl 4-nitrobenzenesulfonate (6l):
White solid; Mp. 113.5-115.6°C; IR (KBr): 3076, 2976, 1529, 1376, 1188, 1021, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.82-1.83 (d, 3H, *J* = 7.01 Hz), 5.09-5.14 (q, 1H, *J* = 14 Hz), 6.793-6.798 (d, 1H, *J* = 2.0 Hz), 6.91-6.93 (t, 1H, *J* = 3.80 Hz), 7.15-7.16 (d, 1H, *J* = 4.95 Hz), 7.21-7.23 (d, 1H, *J* = 7.97 Hz), 7.32-7.34 (d, 1H, *J* = 8.00 Hz), 7.43-7.45 (t, 1H, *J* = 7.80 Hz), 7.48-7.50 (t, 1H, *J* = 8.00 Hz), 7.85-7.87 (d, 1H, *J* = 8.34 Hz), 8.09-8.11 (d, 3H, *J* = 8.30 Hz), 8.30-8.32 (d, 2H, *J* = 8.26 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.14, 35.87, 117.80, 121.79, 123.40, 123.65, 123.68, 124.14, 124.21, 126.54, 126.56, 126.93, 127.06, 129.77, 132.37, 141.29, 141.72, 144.21, 149.50.

1-(1-(furan-2-yl)ethyl)naphthalen-4-yl 4-nitrobenzenesulfonate (6m):
White solid; Mp. 116-118°C; IR (KBr): 3066, 2979, 1525, 1371, 1180, 746 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.70-1.71 (d, 3H, *J* = 7.08 Hz), 4.87-4.93 (q, 1H, *J* = 14 Hz), 6.09-6.10 (d, 1H, *J* = 2.92 Hz), 6.32-6.33 (t, 1H, *J* = 2.32 Hz), 7.12-7.17 (q, 2H), 7.33 (s, 1H), 7.42-7.46 (t, 1H, *J* = 7.48 Hz), 7.51-7.53 (d, 1H, *J* = 7.56 Hz), 7.85-7.87 (d, 1H, *J* = 8.28 Hz), 8.09-8.11 (d, 3H, *J* = 8.68 Hz), 8.32-8.34 (d, 2H, *J* = 8.68 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.95, 34.57, 105.87, 110.03, 117.80, 121.81, 123.43, 123.46, 124.20, 125.02, 126.92, 126.97, 129.73, 132.40, 140.12, 141.39, 141.41, 144.16, 150.86, 157.78.

1,3-bis(1-phenylethyl)naphthalen-4-yl 4-nitrobenzenesulfonate (7a):
White solid; Mp. 177.5-180.3°C; IR(KBr): 3105, 3064, 2972, 2933, 1601, 1531, 1377, 1347, 1313, 1186, 1042, 837, 741 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.60-1.63 (m, 6H), 4.63-4.68 (q, 1H, *J* = 14.2 Hz), 4.75-4.81 (q, 1H, *J* = 14.2 Hz), 7.14-7.23 (m, 7H), 7.24-7.27 (m, 2H), 7.28-7.31 (m, 4H), 7.71-7.73 (d, 1H, *J* = 8.0 Hz), 7.93-7.96 (d, 1H, *J* = 8.4 Hz), 8.14-8.16 (d, 2H, *J* = 8.74 Hz), 8.32-8.34 (d, 2H, *J* = 8.72Hz); ^{13}C NMR ($CDCl_3$) : δ 21.05, 22.61, 38.02, 40.83, 122.83, 124.27, 124.44, 124.52, 126.31, 126.39, 126.45, 127.51, 127.60, 128.02, 128.39, 128.44, 128.64, 129.59, 131.77, 135.65, 141.48, 141.62, 142.41, 144.34, 145.99, 150.91.

2-benzhydrylnaphthalen-1-ol (9):
White solid; Mp. 85.5-87.7°C; IR (KBr): 3555, 3055, 3021, 1597, 1572, 1492, 1394, 1381, 1173, 1077, 805, 748, 699 cm^{-1}; ^1H NMR (400 MHz, DMSO): δ 6.22 (s, 1H), 6.99-7.01 (d, 1H, *J* = 7.20 Hz), 7.10-7.12 (d, 4H, *J* = 7.42 Hz), 7.17-7.20 (t, 2H, *J* = 7.20 Hz), 7.26-7.30 (t, 4H, *J* = 7.44 Hz), 7.33-7.35 (d, 1H, *J* = 8.55 Hz), 7.42-7.44 (t, 2H, *J* = 3.75 Hz), 7.76-7.78 (q, 1H), 8.21-8.23 (q, 1H), 9.39 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 49.15, 119.46, 122.48, 125.27, 125.29, 125.67, 125.98, 126.39, 127.87, 128.02, 128.57, 129.48, 133.34, 144.23, 149.66.

4-benzhydrylnaphthalen-1-ol (10):
White solid; Mp. 166.3-169.0°C; IR (KBr): 3505, 3024, 2864, 1601, 1589, 1376, 1256, 1234, 1207, 1138, 1049, 758, 704 cm^{-1}; ^1H NMR (400 MHz, DMSO): δ 6.21 (s, 1H), 6.64-6.66 (d, 1H, *J* = 7.88 Hz), 6.74-6.76 (d, 1H, *J* = 7.84 Hz), 7.07-7.09 (d, 4H, *J* = 7.44 Hz), 7.17-7.20 (t, 2H, *J* = 7.20 Hz), 7.26-7.29 (t, 4H, *J* = 7.42 Hz), 7.37-7.39 (q, 2H), 7.900-7.908 (q, 1H), 8.13-8.15 (q, 1H), 10.05(s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 51.95, 107.39, 122.87, 124.38, 124.53, 125.43, 126.48, 126.53, 127.68, 128.63, 129.58, 130.31, 132.66, 144.38, 152.45.

2,4-dibenzhydrylnaphthalen-1-ol (11):
White solid; Mp. 149.8-150.9°C; IR (KBr): 3562, 3080, 3058, 3024, 1599, 1492, 1449, 1387, 1249, 1076, 746, 699 cm^{-1}; ^1H NMR (400 MHz, DMSO): δ 6.12 (s, 1H), 6.16 (s, 1H), 6.57 (s, 1H), 6.89-6.95 (m, 8H), 7.10-7.19 (m, 12H), 7.35-7.42 (m, 2H), 7.90-7.92 (d, 1H, *J* = 8.23 Hz), 8.22-8.24 (d, 1H, *J* = 8.14 Hz), 9.32 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 48.95, 51.91, 123.13, 123.99, 124.38, 124.88, 126.08, 126.23, 126.27, 126.37, 128.39, 128.48, 129.17, 129.29, 130.23, 130.99, 131.29, 144.06, 148.44.

2-benzhydryl-1,3,5-trimethoxybenzene (12):
The (naphthalen-1-yloxy) diphenylmethane (1.0 mole) and 1, 3, 5 trimethoxy benzene (TMB) (1.0 mole) was dissolved in ethyl acetate (10 Vol) and $BF_3 \cdot OEt_2$ (2.0 mole) was slowly added using an addition funnel while the mixture was stirred for 2-3 hr at RT (20-25°C). After the TLC confirmed the absence of starting material water (20 Vol) was added and stirred at RT for 30 minutes. The layers were separated and the aqueous layer was extracted with ethyl acetate (5 Vol). The organic layers were combined, dried and concentrated under vacuum to give crude compound. The crude compound was purified on silica gel column chromatography to get pure ortho, Para, disubstituted and 2-benzhydryl-1, 3, 5-trimethoxybenzene **12** products.

White solid; Mp. 106.4-112.1°C; IR (KBr): 3081, 2958, 2837, 1602, 1593, 1492, 1452, 1437, 1226, 1147, 1113, 953, 696 cm^{-1}; ^1H NMR (400 MHz, DMSO): δ 3.54 (s, 6H), 3.75 (s, 3H), 5.89 (s, 1H), 6.23 (s, 2H), 7.04-7.06 (d, 4H, *J* = 7.48 Hz), 7.10-7.13 (t, 2H, *J* = 7.20 Hz), 7.18-7.22 (t, 4H, *J* = 7.44 Hz); ^{13}C NMR (100 MHz, CDCl3): δ 45.03, 55.15, 55.59, 91.54, 113.51, 125.21, 126.95, 127.44, 128.71, 128.74, 128.97, 129.01, 129.29, 144.01, 159.01, 159.90.

4-tritylphenol (14):
White solid; Mp. 283-286°C; IR (KBr): 3550, 3082, 3052, 3029, 1610, 1591, 1507, 1488, 1440, 1262, 1176, 1160, 826, 750, 701 cm^{-1}; ^1H NMR (400 MHz, DMSO): δ 6.50-6.52 (d, 1H, *J* = 8.68 Hz), 6.63-6.65 (d, 1H, *J* = 8.68 Hz), 6.91-6.92 (d, 3H, *J* = 7.56 Hz), 7.15-7.17 (m, 2H), 7.21-7.31 (m, 10H), 7.36-7.38 (d, 3H, *J* = 7.60 Hz); ^{13}C NMR (100 MHz, DMSO): δ 64.07, 114.71, 126.14, 127.89, 130.80, 131.91, 136.92, 147.18, 155.60.

2-tert-butylphenol (19):
Yellow oil; IR(Neat): 3531, 2958, 2912, 2871, 1605, 1583, 1443, 1364, 1249, 1085, 853, 809, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.38 (s, 9H), 4.80 (s, 1S), 6.66-6.68 (d, 1H, *J* = 7.91 Hz), 6.86-6.90 (t, 1H, *J* = 7.30 Hz), 6.99-7.06 (m, 1H), 7.08-7.10 (t, 1H, *J* = 3.85 Hz).

4-tert-butylphenol (20):
White solid; Mp. 88.3-90.5°C; IR (KBr): 3245, 2961, 1599, 1514, 1450, 1361, 1242, 1183, 1111, 827, 545 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.32 (s, 9H), 2.0-2.5 (s, br, 1H), 6.76-6.78 (d, 2H, *J* = 8.56 Hz), 7.25-7.27 (d, 2H, *J* = 8.42 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.45, 33.99, 114.72, 126.38, 143.49, 152.93.

RESULTS AND DISCUSSION

During our studies on ether rearrangements [7a-d] under acidic conditions we observed similar type of rearrangement and the studies were extended towards the synthesis of Tolterodine [7b], and Mimosifoliol [7c] (Fig 1). In this paper we would like to report our systematic studies of both acidic and thermal rearrangement of various ethers.

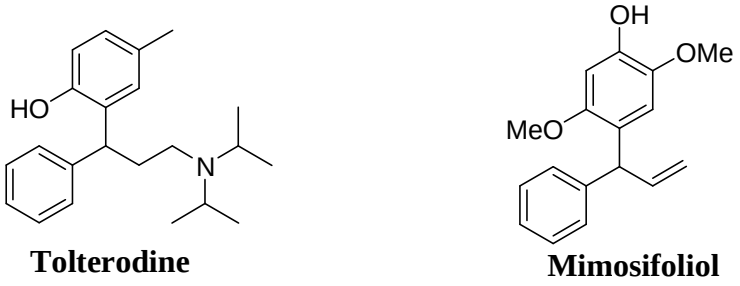
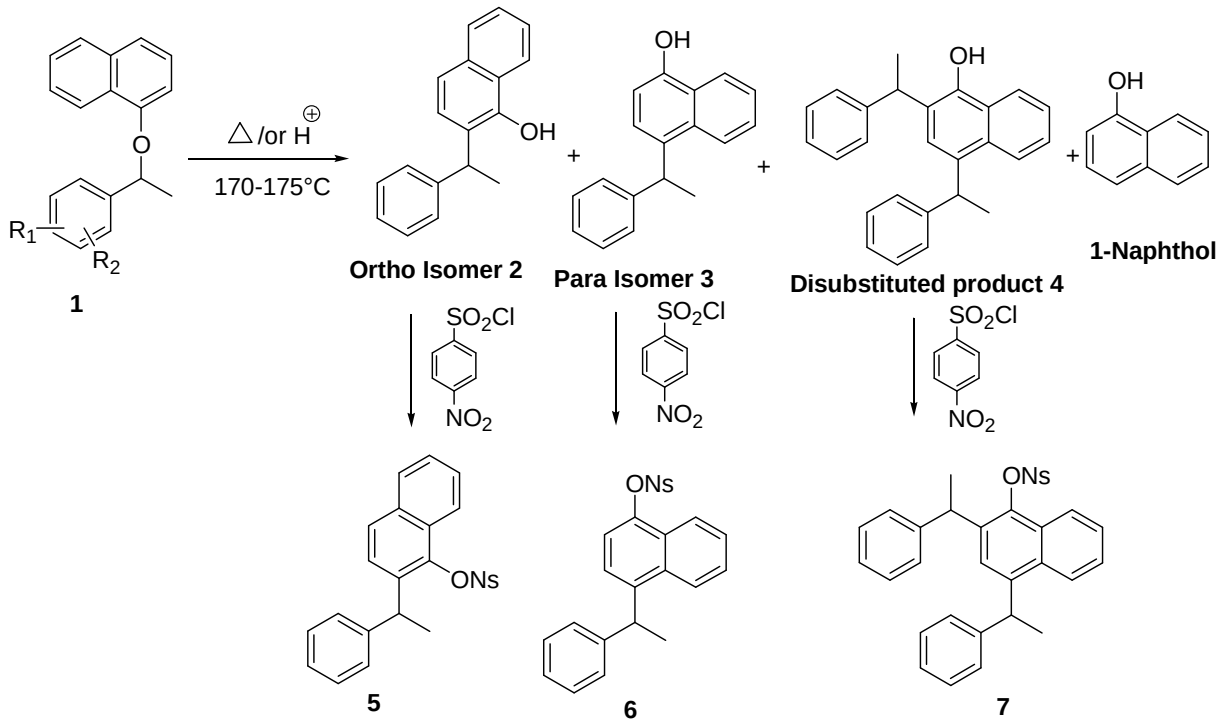


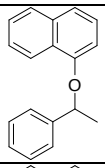
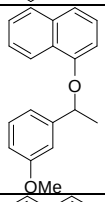
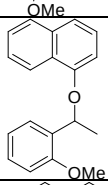
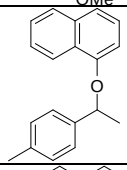
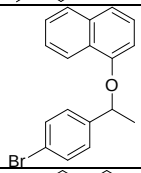
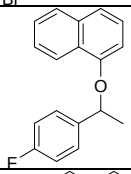
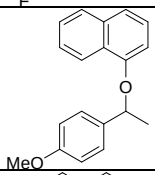
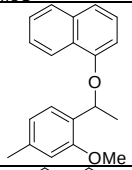
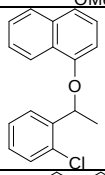
Figure 1. Structures of Tolterodine and Mimosifoliol

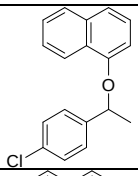
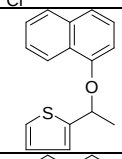
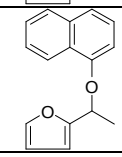


Scheme 7: Rearrangement of 1-(1-phenylethoxy) naphthalene's under acidic and thermal conditions

In the case of (1-phenylethyl)-1-naphthyl ether **1** both thermal and acidic condition gave four products, which are characterized as ortho isomer **2,** para isomer **3,** 1-naphthol and a disubstituted product **4** as shown in Scheme 7. Only (2-chlorophenyl) ethyl 1-naphthyl ether (**1i**) did not undergo thermal rearrangement (decomposition of the ether is observed). In majority of the thermal rearrangement cases ortho isomer is observed as a major product where as para isomer is major under acidic conditions. Ortho isomer, para isomer and disubstituted products are characterized as p-nitro benzene sulfonates. All the isolated products are confirmed by spectral analysis.

Table 1: Rearrangement of 1-(1-phenylethoxy) naphthalene's under acidic and thermal conditions

Entry	Compounds	Reaction, Time	Ortho Isomer[a] **2** %	Para Isomer[a] **3** %	Disubstituted product[a] **4** %	α-Naphthol[a]%
1a		H^+	17	30	25	15
		Δ, 10 hr	24	30	24	19
1b		H^+	23	24	23	13
		Δ, 21 hr	40	12	16	25
1c		H^+	20	25	23	7
		Δ, 22 hr	46	16	21	16
1d		H^+	21	30	26	13
		Δ, 5hr	41	14	19	16
1e		H^+	32	19	14	17
		Δ, 21 hr	39	9	11	5
1f		H^+	32	20	15	14
		Δ, 50 hr	36	16	10	14
1g		H^+	17	36	13	20
		Δ, 15 hr	39	12	11	20
1h		H^+	30	21	-	16
		Δ, 5 hr	33	18	-	11
1i		H^+	18	51	11	19
		Δ, 5 hr	-	-	-	-
1j		H^+	21	23	15	19

		Δ, 18 hr	17	23	16	22
1k		H^+	26.	15	15	11
		Δ, 32 hr	35	5	18	12
1l		H^+	23	27	13	20
		Δ, 5 hr	30	34	13	16
1m		H^+	23	18	-	12
		Δ, 5 hr	38	16	-	9

[a]*Yields determined by HPLC[8] analysis of the crude reaction mixture.*

The structure of the ortho isomer **5a** and the disubstituted product **7a** were confirmed by single crystal X-ray [9] structure analyses as shown in fig 2.

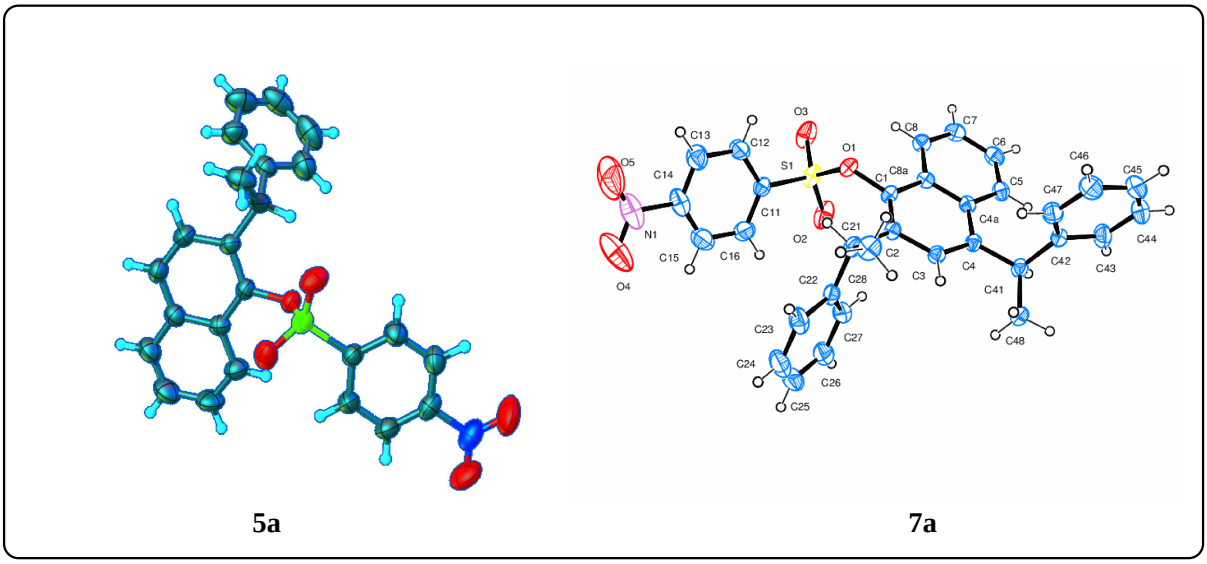
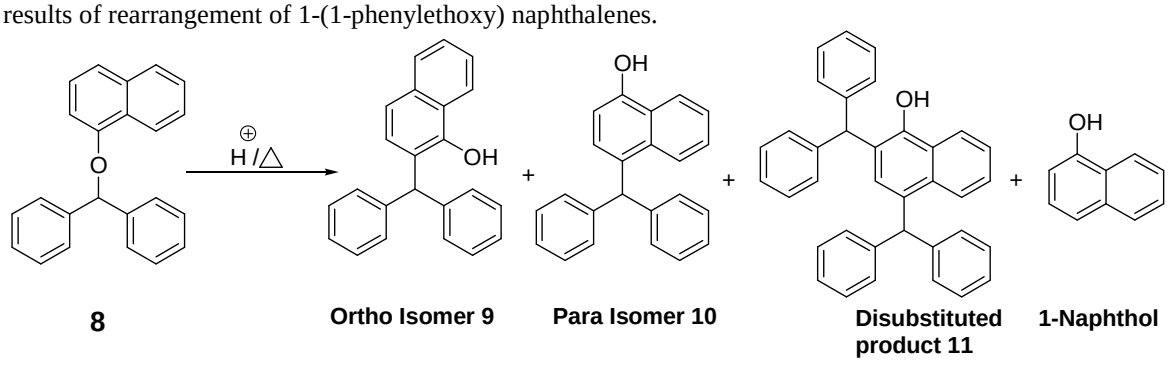


Figure 2: The ORTEP Diagrams of 5a and 7a

The results of the rearrangement of benzyl naphthyl ether **8** under both acidic and thermal conditions are similar to the results of rearrangement of 1-(1-phenylethoxy) naphthalenes.



Scheme 8: Rearrangement of benzhydryl 1-naphthyl ether under acidic and thermal conditions

The benzhydryl 1-naphthyl ether rearrangement is studied under different acidic conditions. Under all acidic conditions the para isomer is the major product, which may be due to steric encumbrance of the ortho position, whereas the ortho isomer is the major one in thermal rearrangements.

Table 2: Benzhydryl 1-naphthyl ether rearrangement studies

SNo	Reagent	Time	Ortho[a] **9,** %	Para[a] **10,** %	Disubstituted product[a] **11,** %	1-Naphthol[a] , %
01	$AlCl_3$	30 min	11	40	30	17
02	$HClO_4$	30 min	13	38	30	18
03	$BF_3 \cdot OEt_2$	3 h	38	32	19	10
04	Δ, 160°C	10 h	32	11	25	8

[a]*Yields determined by HPLC analysis of the crude reaction mixture.*

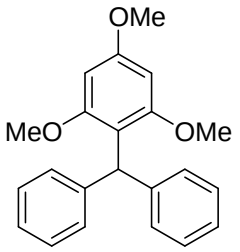
It is expected that the formation of **11** is concentration dependent. To study the effect of dilution the reaction is studied under different dilutions with ethyl acetate and as expected it is found that the formation of the disubstituted product **11** has decreased from 22% to 8 % at 1-100 ml of dilution. The HPLC results are given in Table 3.

Table 3: Rearrangement of benzhydryl 1-naphthyl ether under different dilutions

Entry	Ethyl acetate ml	Reagent	Time	Ortho[a] **9** %	Para[a] **10** %	**Di substituted product[a] 11 %**	1-Naphthol[a] %
01	1 ml	$BF_3 \cdot OEt_2$	10 min	22	43	**22**	12
02	10 ml	$BF_3 \cdot OEt_2$	3 h	38	32	**19**	11
03	50 ml	$BF_3 \cdot OEt_2$	6 h	54	28	**11**	6
04	100 ml	$BF_3 \cdot OEt_2$	8 h	43	20	**8**	4

[a]*Yields determined by HPLC analysis of the crude reaction mixture.*

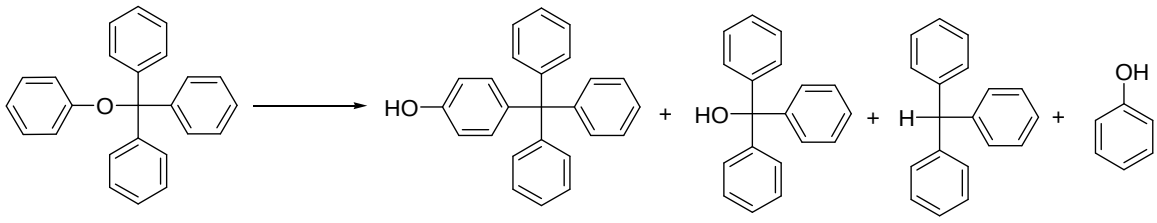
To confirm the mechanism of carbonium ion formation during acidic rearrangements, the reaction is performed in the presence of 1, 3, 5-trimethoxy benzene (TMB). Compound **12** is formed in ~15% along with other products. The structure of **12** is confirmed by its spectral data.



12

This crossover experiment is performed in various concentrations of 1,3,5-trimethoxy benzene (TMB) but it was found that the latter had little effect on the formation of **12,** instead, the formation of the disubstituted product increased from 0.05% to 6.83%.

Phenyl trityl ether behaved differently to what was reported by Parsons[3a] and Smith[3b]. These authors reported only the formation of the 4-substituted phenol **14,** while we isolated trityl alcohol and triphenylmethane under acidic conditions. We were unable to explain the formation of triphenylmethane **16,** under these conditions.



13 **14** **15** **16** **17**

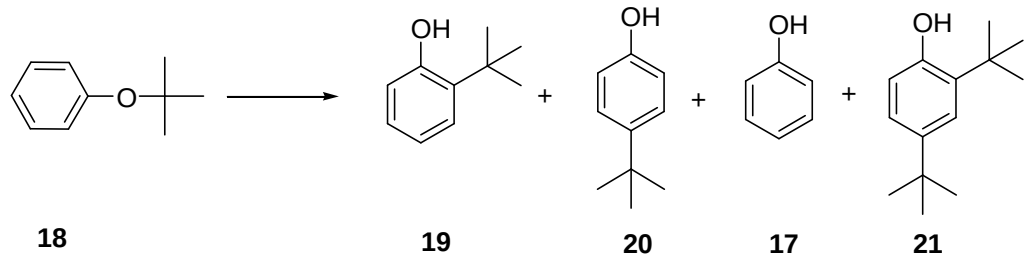
Scheme 9: Rearrangement of l phenyl trity ether

Table 5: Trityl phenyl ether rearrangement studies

Entry	Reagent	Temp	Time	**14**[a] %	**15**[a] %	**16**[a] %	**17**[a] %
01	BF_3· OEt_2	room temp	3 h	22.5	30.10	28.6	9.5
02	$HClO_4$	room temp	3 h	5.13	61.70	-	0.64
03	Silica gel	room temp	24 h	18.0	61.12	-	17.31
04	Δ, 185°C	180-185°C	8 h	12.6	50.63	18.3	13.6

[a]*Yields determined by HPLC analysis of the crude reaction mixture.*

The t-butyl ether of phenol behaved differently under thermal and certain acidic conditions (HCl and BF_3· OEt_2). Rearrangement with BF_3· OEt_2 depended on solvent also.



18 **19** **20** **17** **21**

Scheme 10: Rearrangement of phenyl-t-butyl ether

Table 6: Phenyl t-butyl ether rearrangement studies

Entry	Reagent	Solvent	Temp	Time	**19**[a] %	**20**[a] %	**17**[a] %	**21**[a]%
01	$HClO_4$	Neat	room temp	5 h	2	85	1	9
02	$AlCl_3$	Neat	room temp	3 h	0.5	83	8	1
03	HCl	Ethyl acetate	room temp	1 h	-	-	99	-
04	BF_3· OEt_2	Ethyl acetate	room temp	1 h	-	-	98	-
05	BF_3· OEt_2	DCM	RT	1 h	9	10	62	5
06	Δ, 190°C	Neat	180-185°C	8h	b	b	b	b

[a]*Yields determined by HPLC analysis of the crude reaction mixture.*
[b] *No reaction*

CONCLUSION

During our systemic study of the rearrangement of ethers under acidic and thermal conditions, we confirmed that the rearrangements are taking place via carbonium ion formation in acidic conditions.

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A. Veera Reddy; M. Sashibhushan; T. Sreenivasula Reddy. *Synth. Comm*. **2012**, *42*, 3545-3552. d). A. Veera Reddy; B. Sreenivasula Reddy; M. Sashibhushan; G. Narayanaswamy; T. Sreenivasula Reddy. *Der Pharma Chemica*, **2011**, *3*, 464-485.
[8] HPLC instrumentation and conditions:Waters Alliance 2695 separation module (Waters Corporation, Milford, USA) equipped with 2996 PDA detector (for specificity and forced degradation studies) and 2487 UV/visible detector with Empower software was used for the analysis. YMC Pack C18 column (250 X 4.6 mm, 5µm, YMC Corporation, Japan) and a gradient mixture of solvent A and B were used as stationary and mobile phases, respectively. 0.1 % TFA in 1000mL of water. Buffer was used as solvent A. Acetonitrile was used as solvent B. The gradient program (T/%B) was set as 0/30, 5/30, 15/70, 25/70, 25.1/90, 40/90, 40.1/30 and 40.0/30. 1.0ml/min flow rate and 20.0µl injection volume were maintained. The eluted compounds were monitored at 210 nm. The column oven temperature was maintained at 25°C.
[9] 5a: CCDC-972918, 7a: CCDC-970590.