# CHAPTER III

## Graphene oxide (GO)-mediated one-pot sequential dehydration-hydrothiolation of *sec*. aryl alcohols

## III.A. Introduction

Exploration of the applicability of GO as the carbocatalyst for various synthetic reactions is one of the recent cherished goals.[1] GO possesses rich chemical functionality and is slightly acidic (pH 4.5 at 0.1 $mgmL^{-1}$),[2] and has long been recognized as having strong oxidizing properties.[1c,3]

As discussed previously, Bielawski and subsequently some other groups have revealed an intriguing new direction for metal-free catalytic use of GO in organic reactions.[4] Bielawski and co-workers reported GO-facilitated oxidation of benzylic alcohols to the corresponding aldehyde or ketone in varying yields.[4a] The oxidation was carried out using 200 w% GO and heating at 100 $^oC$ for 24h. One consideration from their observations is that diphenylmethanol afforded >98% conversion to the corresponding ketone, while 1-phenylethanol gave rise to only 26% acetophenone. They also observed minimal oxidation of benzyl alcohol to benzaldehyde with low catalyst loading or reaction temperature. Interestingly, oxidation reactions of alcohols did not proceed under a $N_2$-blanketed atmosphere. GO as oxidation catalyst has also been demonstrated for conversion of amine to imine.[4f] Use of GO as metal-free catalyst is a growing area of interest. Here we represent a unique example of diverse reactivity of the material to afford complex products.

## III.B. Background and objectives

Thioethers are very useful building blocks in the synthesis of organosulfur compounds.[5a-b] They also play very important role in biological and chemical processes.[5c] Hence a convenient synthetic process for thioethers is highly wanted. Basically reaction between thiols and alkenes can produce thioethers either via electrophilic pathway leading to Markovnikov adduct or free radical pathway to anti-Markovnikov adduct. (Figure III.B.2).

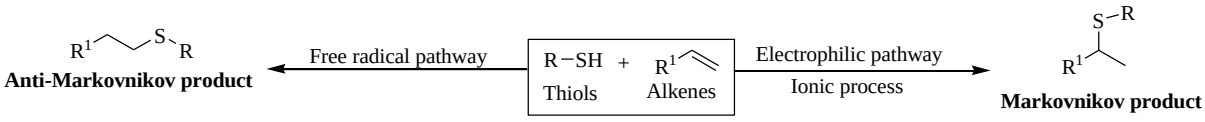
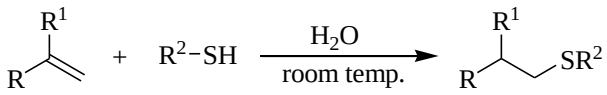


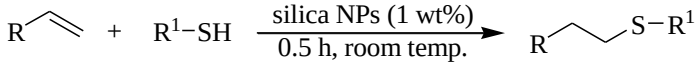

**Figure III.B.1.** Different way of addition reaction

Ranu & Mandal developed a simple and green procedure for anti-Markovnikov addition of thiols to unactivated alkenes on water at room temperature without the use of any additive.[6a]



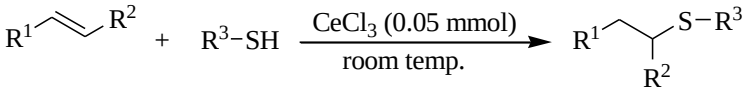

**Scheme III.B.1.** On-water anti-Markovnikov addition of thiols to unactivated alkenes

Silica nanoparticles can effectively catalyze anti-Markovnikov addition of thiols to alkenes leading to linear thioethers.[6b-c] Banerjee et al. utilised these nanoparticles to catalyze a straightforward route towards thioethers from thiols and alkenes under neutral conditions.[6d]



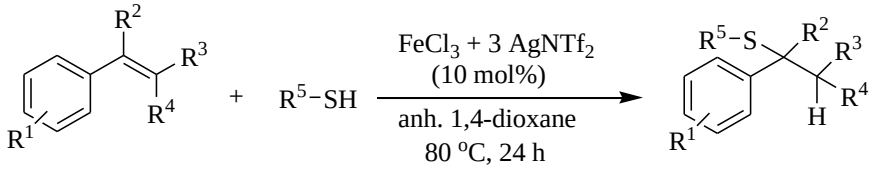

**Scheme III.B.2.** Silica nanoparticles-catalyzed addition of thiols to alkenes

Another anti-Markovnikov addition of thiols to alkenes was introduced by Silveira et al.,[6e] The products were obtained in good to excellent yields under solvent-free condition at room temperature using anhydrous cerium(III)chloride as catalyst.




**Scheme III.B.3.** Anhydrous cerium(III)chloride-promoted anti-Markovnikov addition

A sustainable and economic synthetic route has been developed by Perez and Corma et al. where bis(triflimide)iron(III) salt-catalyzed selective hydrothiolation of styrenes following Markovnikov addition.[6f] Iron(III) salt played a unique role in terms of regioselectivity.

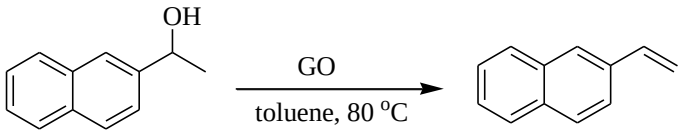



**Scheme III.B.4.** Bis(triflimide)iron(III) salt-catalyzed selective hydrothiolation of styrenes

Thus mostly the anti-Markovnikov additions of thiols to alkenes have been explored to synthesize thioethers except the last scheme where Markovnikov addition took place using bis(triflimide)iron which played the key role. Hence we aimed to choose easily available or easy to prepare and relatively low cost green catalyst for this synthesis. Graphene oxide (GO) here emerged as the promising one with lots of potentiality. Recent works on the utilization of this green carbocatalyst in oxidation-hydration reactions,[4a] Friedel-Crafts addition of indoles to *α,β*-unsaturated ketones,[4e] C-H oxidation,[4d] aerobic oxidative coupling of amines to imines,[4f] have accounted for its versatile behaviour. It can be used as highly efficient and selective oxidant of thiols and sulphides.[4b] Exploration of catalytic activities of GO is still under progress. In this context we have developed an efficient and mild one-pot graphene oxide (GO) catalyzed sequential dehydration-hydrothiolation from a mixture of *sec*. aryl alcohols and thiols resulting unsymmetrical thioethers under metal-free conditions. It may be mentioned here that the reaction followed entirely selective Markovnikov addition.

## III.C. Results and discussion

Usually GO has been utilised as oxidation catalyst such as in the oxidation of thiols and *sec*. aryl alcohols to the corresponding disulfides and aryl aldehydes respectively.[5a] Now *sec*. aryl alcohols when treated with mineral acids are prone towards dehydration. Preliminary studies with 1-(2-naphthyl)ethanol revealed that the dehydration is indeed possible by heating its solution of toluene ($N_2$- bubbled) at 80-100 $^oC$ in the presence of GO (5-20 w%), but not to the extent that is well acceptable (Scheme III.C.5). The dehydration was accompanied by the recovery of the starting alcohol and some unidentified product. Another experiment was conducted taking a mixture of styrene and GO in toluene which showed partial decomposition after stirring for 12 h. All reactions were performed in screw-capped vials flushed with $N_2$.




**Yield - 40%**

**Scheme III.C.5.** GO-promoted dehydration of 1-(2-naphthyl)ethanol

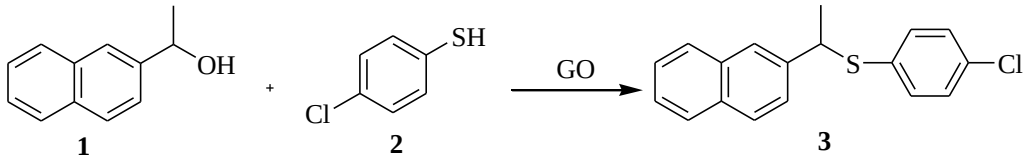
Hence we envisaged that the course of the reaction might be altered and driven towards dehydration depending upon some variations, such as lower loading of GO (w%), carrying out the reaction under milder conditions and $N_2$-atmosphere as well as one-pot further reaction of the generated olefin.

We reasoned that the dehydration may perhaps be driven, if the resulting alkene is reacted immediately with some other reactant. While a combination of alkene and thiol represents an atom-economic 'click' reaction,[7] Bielawski and coworkers,[4b,g] reported GO-catalyzed thiol oxidation to disulfide and also polymerization of styrene under solvent-free condition. Based on this background, we designed experiments starting from a mixture of *sec*. aryl alcohol and thiol. Graphene oxide (GO) was synthesized by some variation of the Hummers method,[8a-b] and compared with reported FT-IR spectrum.[8c]

As summarized in Table III.C.1, gentle magnetic stirring of an equimolar mixture of 1-(2-naphthyl)ethanol and 4-chlorobenzenethiol in toluene at different temperatures in the presence of varying amounts of GO furnished diverse results. Initial stirring up to 50 $^oC$ yielded no desired product except certain amount of disulfide, formed by oxidative dimerization of thiol (entries 1-2). Increasing reaction temperature and quantity of thiol however gave our expected thiol-addition product (67-79%), characterized as [(4-

chlorophenyl)(1-phenylethyl)sulfane], occurring through sequential dehydration-hydrothiolation in entirely Markovnikov fashion (entries 3-4), with minimal amounts of

**Table III.C.1. Optimization of sequential dehydration-hydrothiolation reaction conditions[a]**



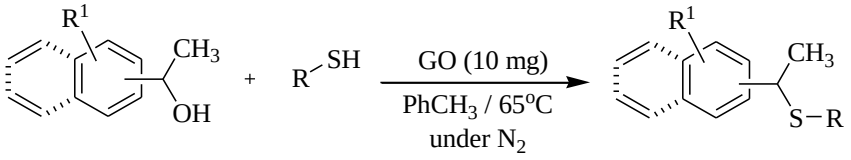

**1** **2** **3**

| entry | GO (mg / w%) | solvent | temp (oC) | time (h) | product yield (%)b | | |
|---|---|---|---|---|---|---|---|
| | | | | | **3** | disulfide | 2-vinylnaphthalene |
| 1 | 10 / 6 | toluene | rt | 24 | nil | 14 | nil |
| 2 | 10 / 6 | toluene | 50 | 24 | nil | 22 | nil |
| 3 | 10 / 6 | toluene | 65 | 2 | 67 | 8 | 12 |
| **4** | **10 / 6** | **toluene** | **65** | **2** | **79** | **8** | **nil** |
| 5 | 10 / 6 | toluene | 80 | 1.5 | 65 | 16 | nil |
| 6 | 20 / 12 | toluene | 65 | 1.5 | 47 | 23 | nil |
| 7 | 5 / 3 | toluene | 65 | 6 | 49 | 17 | nil |
| 8 | 10 / 6 | 1,4-dioxane | 65 | 3.5 | 51 | 20 | nil |
| 9 | 10 / 6 | THF | 65 | 3 | 48 | 22 | nil |
| 10 | 10 / 6 | MeCN | 65 | 2 | 58 | 15 | nil |
| 11 | 10 / 6 | DMF | 65 | 24 | nil | 31 | nil |
| 12 | nil | toluene | 65 | 24 | nil | 10 | nil |

[a] Reactions were performed in 1 (1 mmol), 2 (1 mmol) for entries 1-3 and 1 (1 mmol), 2 (1.2 mmol) for entries 4-11 in solvents (2 mL). [b] Isolated yield.

diphenyldisulfide (8%). Further heating (80 $^{o}$C) did not show significant improvement except slightly more disulfide formation (entry 5). Increase/decrease of GO (wt%) or changing the solvents were not effective either (entry 6-10). Reactions carried out in DMF or without GO did not produce traces of the desired thioether (entries 11-12). Since the findings are new and thioethers are important building blocks for the synthesis of biologically active compounds,[9] we became interested to extend the reaction protocol, as in entry 4, with varieties of *sec*. aryl alcohols and thiols to finally constitute a general and practical method for preparing

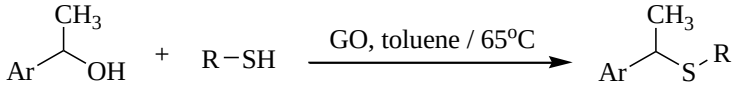
unsymmetrical thioethers via one-pot GO-facilitated metal-free sequential dehydration-hydrothiolation reactions (Scheme III.C.6). Preparation of thioethers from *sec*. aryl alcohols has been reported via Pd-catalyzed $S_N1$ reactions.[10]



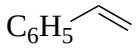
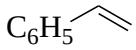
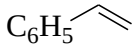

**Scheme III.C.6.** Graphene oxide (GO) catalyzed one-pot sequential dehydration-hydrothiolation reaction

First few examples in Table III.C.2 illustrate the reaction of a mixture of 1-(2-naphthyl)ethanol and different aromatic thiols bearing –Cl, –Me, –F and $–NH_2$ groups (Table III.C.2, entries 1-5). The reaction protocol was found to be successful, except in entry 5 with $–NH_2$ group, yielding corresponding thioethers in 67-79% yields along with 8-10% of diaryldisulfides. However, the separation was easy by column chromatography over silica gel. Similar reaction sequence was also observed with 1-(1-naphthyl)ethanol and different arylthiols (entries 6-7). In the series of 1-phenylethanol, variation of functional groups in either aryl moiety was also successful and corresponding unsymmetrical thioethers were realized in good yields (entries 8-10 and 12). However, reaction with aryl alcohol bearing $NO_2$ group was unsuccessful, even after continuing the reaction for 24 h (entry 11). The disulfide was isolated along with the starting alcohol 1-(3-nitrophenyl)ethanol. To broaden the scope of the reaction, we attempted similar reaction sequence with aliphatic thiols. Both long chain and alicyclic thiols worked without any difficulty. Entries 13-17 displayed that the reactions did occur quite well furnishing desired unsymmetrical thioethers in fairly good yields (68-81%), along with minimal formation of the thiol-corresponding disulfides. It was observed that presence of electron-donating groups in the aryl ring of the alcohol worked better towards dehydration-hydrothiolation sequence.

**Table III.C.2. Graphene oxide (GO)-catalyzed reaction of *sec*. aryl alcohols with different thiols[a]**




**1** **2** **3**

| entry | Ar | R | time (h) | yield (%) **3**[b] |
|---|---|---|---|---|
| 1 | 2-$C_{10}H_7$ | 4-$ClC_6H_4$ | 2 | **3a**: 79 |
| 2 | 2-$C_{10}H_7$ | 4-$CH_3C_6H_4$ | 1.5 | **3b**: 67 |
| 3 | 2-$C_{10}H_7$ | 2,5-$(CH_3)_2C_6H_3$ | 2 | **3c**: 70 |
| 4 | 2-$C_{10}H_7$ | 4-$FC_6H_4$ | 2 | **3d**: 77 |
| 5 | 2-$C_{10}H_7$ | 4-$NH_2C_6H_4$ | 3 | nil |
| 6 | 1-$C_{10}H_7$ | 4-$ClC_6H_4$ | 2.5 | **3e**: 72 |
| 7 | 1-$C_{10}H_7$ | 4-$FC_6H_4$ | 2.5 | **3f**: 74 |
| 8 | $C_6H_5$ | 4-$CH_3C_6H_4$ | 1.5 | **3g**: 69 |
| 9 | $C_6H_5$ | $C_6H_5$ | 1.5 | **3h**: 73 |
| 10 | 3,4-$(OCH_3)_2C_6H_3$ | $C_6H_5$ | 2 | **3i**: 78 |
| 11 | 3-$NO_2C_6H_4$ | 4-$FC_6H_4$ | 24 | nil |
| 12 | 3,4-$(OCH_3)_2C_6H_3$ | 4-$ClC_6H_4$ | 2 | **3j**: 78 |
| 13 | 2-$C_{10}H_7$ | $CH_3(CH_2)_4$ | 2.5 | **3k**: 68 |
| 14 | 2-$C_{10}H_7$ | Cy | 1 | **3l**: 71 |
| 15 | 1-$C_{10}H_7$ | $CH_3(CH_2)_6$ | 2 | **3m**: 81 |
| 16 | 4-$CH_3C_6H_4$ | $CH_3(CH_2)_4$ | 3 | **3n**: 69 |
| 17 | 3,4-$(OCH_3)_2C_6H_3$ | $CH_3(CH_2)_4$ | 3 | **3o**: 80 |
| 18[c] | $C_6H_5$  | 4-$CH_3C_6H_4$ | 2 | **3p**: 82 |
| 19[d] | $C_6H_5$  | 4-$CH_3C_6H_4$ | 4 | **3p**: 74 |
| 20[e] | $C_6H_5$  | 4-$CH_3C_6H_4$ | 4 | **3p**: 74 |

[a] Reaction conditions: 1 (1 mmol), 2 (1.2 mmol), GO (10 mg) in toluene (2 mL), gentle magnetic stirring in a screw-capped vial under $N_2$. [b] Isolated yield. [c] In the absence of GO. [d] In the presence of GO. [e] In the presence of graphite.

In order to suggest a plausible mechanism and to test whether GO also catalyzes the hydrothiolation providing entirely Markovnikov addition product, we performed experiments taking solution of styrene and 4-tolylthiol in toluene under similar reaction conditions, both in the absence and presence of GO. It is interesting to observe that the resulting thioether **3p** is now obtained completely through anti-Markovnikov fashion (Table III.C.2, entries 18 and 19). Further reaction using graphite also gave **3p** by anti-Markovnikov addition (entry 20). We initially observed partial conversion of aryl alcohol to styrene, when stirred with GO in the absence of any thiol and stirring the mixture of styrene and GO in toluene showed partial

decomposition even after 12h. Carrying out the experiments under a blanket of $N_2$ might suppress the possibility of polymerization,[4g] as well as further oxidation of disulfide to thione. Since we obtained reverse addition products in other cases (i.e. Markovnikov addition product), we presume that the GO participates in the overall process, i.e. one-pot dehydration-hydrothiolation reactions, via acid-catalyzed Markovnikov addition.[9e]

The reusability of the GO as heterogeneous carbocatalyst was also checked with the same combination of reactants used for the optimization of reaction conditions. The recovered GO from the first batch of reaction was washed with diethyl ether, dried and reused for subsequent four batches with appreciable conversions and without any loss of catalytic activity. In each run, minimal formation of disulfide (8-10%) was noticed (Table III.C.3). The FT-IR spectrum of the recovered GO (after the first run) was checked, which displayed essentially similar absorptions, signifying apparently no changes of its functional groups.

**Table III.C.3. Recyclability test of GO in carbocatalysis of one-pot sequential dehydration-hydrothiolation of 1(2- naphthyl)ethnol and 4- chlorobenzenethiol[a]**

| Entry | Yield (%)[b] | Yield (%)[c] |
|---|---|---|
| 1st run | 79 | 8 |
| 2nd run | 79 | 8 |
| 3rd run | 78 | 10 |
| 4th run | 76 | 8 |
| 5th run | 76 | 10 |

[a]Reaction conditions: alcohol (1 mmol) and thiol (1.2 mmol) in toluene (2 mL) at 65 oC. [b]Isolated yield of thioether (3a). [c]Isolated yield of disulfide.

## III.D. Conclusions

Thus we have successfully developed graphene oxide catalysed dehydration-hydrothiolation of a mixture of sec. aryl alcohol and thiols to prepare unsymmetrical thioethers. Here benzyl alcohols undergo oxidation and thiols are reported to produce disulfides under GO-catalyzed conditions. It is a new, straight-forward and mild reaction procedure where dehydration and subsequent regioselective hydrothiolation occur on the resulting alkene in one-pot catalyzed by GO.

## III.E. Experimental section:

### III.E.1. General information

General informations of experimental section are given in Chapter II under II.E.1. general information (Page–47).

### III.E.2. Preparation of graphene oxide (GO)

GO was prepared according to the modified Hummer's method.[8a-b] To an ice-cold concentrated sulfuric acid (46 mL) was slowly added sodium nitrate (0.1 g) and then graphite powder (2 g) with vigorous magnetic stirring. After the complete addition of graphite powder, potassium permanganate (6 g) was added to the reaction mixure very slowly, keeping the temperature within 0–5 $^{o}$C to avoid any possible explosion. The mixture was allowed to stir at room temperature for 6 h forming a thick paste. It was diluted with double distilled water (92 mL) under stirred condition. The temperature of the solution was raised to about 90 $^{o}$C and the mixture was allowed to stir for 30 min. Finally, 280 mL water was added followed by slow addition of 3 mL $H_2O_2$ (30%). The colour of the solution changes from dark brown to yellow and the product was filtered off, washed repeatedly with water to makes it free from acid. Finally, the brown mass was collected and dried at 60 $^{o}$C under vacuum to obtain grapheme oxide. Prepared GO was characterized by IR spectroscopy in KBr, which was comparable with literature data.[8c] IR (in KBr): 3359, 1719, 1618, 1411, 1218, 1052 $cm^{-1}$.

### III.E.3. General procedure for one-pot sequential dehydration-hydrothiolation

To a solution of alcohol (**1**) (1 mmol) and thiol (**2**) (1.2 mmol) in toluene (2 mL) was added graphene oxide (10 mg), and the mixture was bubbled with $N_2$ gas for 2-3 min and immediately screw-capped to ensure the reaction mixture under nitrogen atmosphere. The sealed tube was stirred with a magnetic spin bar at 65 $^{o}$C for hours as mentioned in Table 2. After the reaction, the catalyst was filtered off, washed with diethyl ether (3 x 5 mL) and the combined filtrate was concentrated to afford a mixture of thioether and disulfide. The crude mixture was separated by column chromatography over silica gel and elution with pet ether afforded the desired thioether in pure form.

### III.E.4. Characterization of GO

Prepared G.O was characterized by IR spectroscopy in KBr, which was comparable with literature data.

| Sl. No. | Functional group | Wave number ($cm^{-1}$) | |
|---|---|---|---|
| | | Observe | Literature |
| 1 | –OH | 3359 | 3368 |
| 2 | –COOH | 1719 | 1718 |
| 3 | –C=C | 1618 | 1620 |
| 4 | –C-OH | 1411 | 1413 |
| 5 | –C-O-C | 1218 | 1227 |
| 6 | –C-O-C | 1052 | 1060 |

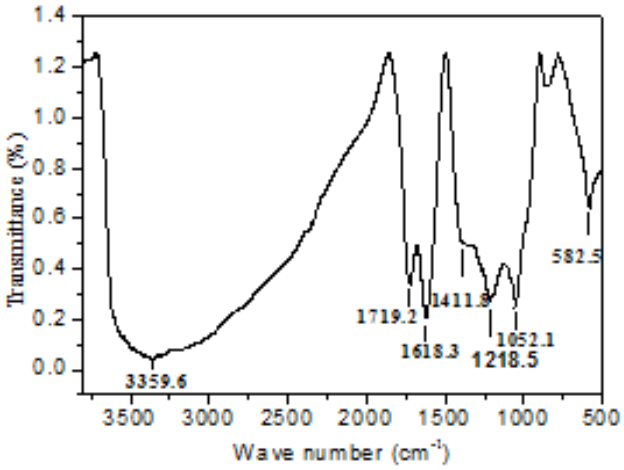
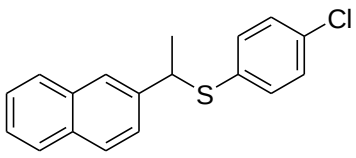


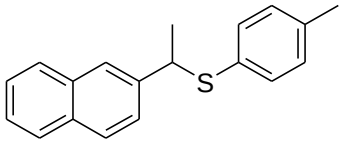

**Figure III.E.4.2. The FT-IR Spectra of GO**

### III.E.5. Spectral data



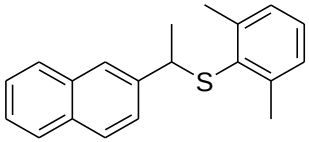

**3a**

**(4-Chlorophenyl)(1-(naphthalene-6-yl)ethyl)Sulfane (3a):** white crystalline solid, mp 72-74 $^{o}$C. $^{1}$H NMR (300 MHz, $CDCl_3$): δ 1.69 (d, *J* = 7.2 Hz, 3H, $CH_3$), 4.43 (q, *J* = 6.9 Hz, 1H, CH), 7.10-7.19 ( m, 4H ArH), 7.40-7.51 (m, 3H ArH), 7.58 (s, 1H ArH), 7.71-7.79 (m, 3H ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 22.1, 48.4, 125.4, 125.7, 125.8, 126.1, 127.6, 127.7, 128.3, 128.8, 132.6, 133.1, 133.3, 133.9, 140.2.



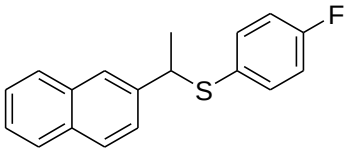

**3b**

**(1-(Naphtyalen-6-yl)ethyl)(*p*-tolyl)sulfane (3b):** white solid, mp 69-71 $^{o}$C. $^{1}$H NMR ($CDCl_3$, 300 MHz): δ 1.69 (d, *J* = 6.9 Hz, 3H, $CH_3$), 2.27 (s, 3H, $ArCH_3$), 4.42 (q, *J* = 6.9 Hz, 1H, CH), 6.99 (d, *J* = 8.1 Hz, 2H, ArH), 7.16-7.21 (m, 2H, ArH), 7.40-7.46 (m, 2H, ArH), 7.52 (dd, *J* = 8.4 and 1.8 Hz, 1H, ArH), 7.59 (s, 1H, ArH), 7.71-7.81 (m, 3H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 21.1, 22.2, 48.6, 125.6, 125.69, 125.7, 126.0, 127.6, 127.8, 128.1, 129.4, 131.1, 132.6, 133.2, 137.4, 140.7.



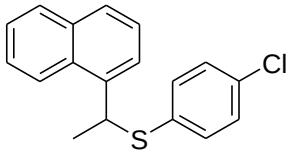

**3c**

**2,5-Dimethylphenyl)(1-(naphthalene-6-yl)sulfane (3c): pale yellow liquid.** $^{1}$H NMR ($CDCl_3$, 300 MHz): δ 1.69 (d, *J* = 7.2 Hz, 3H, $CH_3$), 2.14 (s, 3H, $ArCH_3$), 2.27 (s, 3H, $ArCH_3$), 4.41 (q, *J* = 6.9 Hz, 1H, CH), 6.86 (dd, *J* = 7.5 and 1.2 Hz, 1H, ArH), 6.98 (d, *J* = 7.8 Hz, 1H, ArH), 7.09 (s, 1H, ArH), 7.37-7.42 (m, 2H, ArH), 7.48-7.51 (dd, *J* = 8.4 and 1.8 Hz, 1H, ArH), 7.58 (s, 1H, ArH), 7.67- 7.76 (m, 3H, ArH) $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 20.2, 20.7, 22.1, 47.6, 125.5, 125.61, 125.64, 125.9, 127.5, 127.7, 128.0, 128.1, 129.9, 132.6, 133.2, 133.6, 133.9, 135.6, 136.9, 140.6.



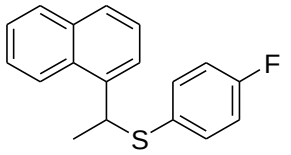

**3d**

**(4-Fluorophenyl)(1-(naphthalene-6-yl)ethyl)sulfane (3d):** white solid, mp 73-75 $^{o}$C. $^{1}$H NMR ($CDCl_3$, 300 MHz): δ 1.69 (d, *J* = 6.9 Hz, 3H, $CH_3$), 4.38 (q, *J* = 6.9 Hz, 1H, CH), 6.82-6.90 (m, 2H, ArH), 7.19-7.25 (m, 2H, ArH), 7.39-7.47 (m, 3H, ArH), 7.50-7.51 (m, 1H, ArH), 7.69-7.74 (m, 1H, ArH), 7.77-7.81 (m, 2H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 21.9, 49.1, 115.6, 115.8, 125.5, 125.8, 126.1, 127.6, 127.7, 128.2, 132.6, 133.1, 135.6, 135.8, 140.3, 160.9, 164.2.



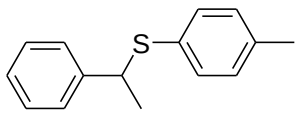

**3e**

**(4-Chlorophenyl)(1-(naphthalene-8-yl)ethyl)sulfane (3e):**[11] white crystalline solid, mp 96-98 $^{o}$C. $^{1}$H NMR ($CDCl_3$, 300 MHz): δ 1.73 (d, *J* = 6.9 Hz, 3H, $CH_3$), 5.10 (q, *J* = 6.9 Hz, 1H, CH), 7.10-7.18 (m, 4H, ArH), 7.36 (t, *J* = 7.5 Hz 1H, ArH), 7.44-7.55 (m, 3H, ArH), 7.72 (d, *J* = 8.1 Hz, 1H, ArH), 7.82-7.85 (m, 1H, ArH), 8.16 (d, *J* = 8.4 Hz, 1H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 21.9, 43.0, 122.9, 124.2, 125.3, 125.6, 126.1, 128.0, 128.8, 129.0, 130.7, 133.2, 133.4, 133.6, 133.9, 137.7.



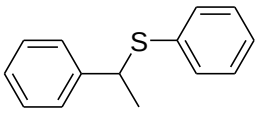

**3f**

**(4-Fluorophenyl)(1-(naphthalene-8-yl)ethyl)sulfane (3f):** white solid. mp 83-85 $^{o}$C. $^{1}$H NMR ($CDCl_3$, 300 MHz): δ 1.70 (d, *J* = 6.9 Hz, 3H, $CH_3$), 5.02 (q, *J* = 6.9 Hz, 1H, CH), 6.80-6.86 (m, 2H, ArH), 7.15-7.21 (m, 2H, ArH), 7.31-7.52 (m, 4H, ArH), 7.69 (d, *J* = 8.1 Hz, 1H, ArH), 7.79-7.82 (m, 1H, ArH), 8.16 (d, *J* = 8.4 Hz, 1H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 21.7, 43.4, 115.5, 115.8, 123.0, 124.2, 125.2, 125.5, 126.0, 127.8, 128.9, 129.49, 129.5, 130.7, 133.8, 135.5, 135.6, 137.9, 160.8, 164.1.



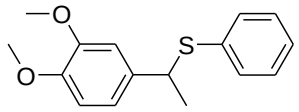

**3g**

**(1-Phenylethyl)(*p*-tolyl)sulfane (3g):**[11] colourless liquid. $^{1}$H NMR ($CDCl_3$, 300 MHz) δ 1.60 (d, *J* = 7.2 Hz, 3H, $CH_3$), 2.29 (s, 3H, $ArCH_3$), 4.26 (q, *J* = 6.9 Hz, 1H, CH), 7.02 (d, *J* = 8.1 Hz 2H, ArH), 7.17-7.27 (m, 7H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 21.1, 22.1, 48.3, 127.0, 127.3, 128.3, 129.4, 131.2, 133.2, 137.3, 143.3.



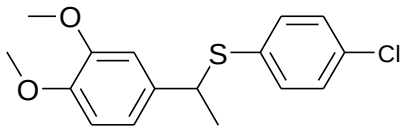

**3h**

**Phenyl(1-phenylethyl)sulfane (3h):**[11] Pale yellow liquid. $^{1}$H NMR ($CDCl_3$, 300 MHz): δ 1.63 (d, *J* = 6.9 Hz, 3H, $CH_3$), 4.34 (q, *J* = 6.9 Hz, 1H, CH), 7.19-7.31 (m, 10H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 22.3, 48.0, 127.1, 127.2, 128.4, 128.6, 132.5, 135.1, 143.2.



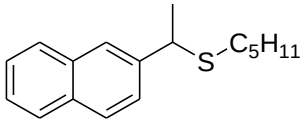

**3i**

**(1-(3,4-Dimethoxyphenyl)ethyl)(phenyl)sulfane (3i):** pale yellow solid, mp 53-55 $^{o}$C. $^{1}$H NMR ($CDCl_3$, 300 MHz): δ 1.61 (d, *J* = 6.9 Hz, 3H, $CH_3$), 3.81 (s, 3H, $OCH_3$), 3.83 (s, 3H, $OCH_3$), 4.30 (q, *J* = 6.9 Hz, 1H, CH), 6.72-6.75 (m, 1H, ArH), 6.79-6.82 (m, 2H, ArH), 7.17-7.31 (m, 5H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 22.2, 47.7, 55.6, 55.7, 110.3, 110.7, 119.1, 127.0, 128.5, 132.5, 135.0, 135.6, 147.9, 148.6.



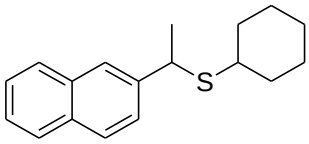

**3j**

**(4-Chloro phenyl)(1-(3,4-dimethoxyphenyl)ethyl)sulfane (3j):** Colourless liquid. $^{1}$H NMR ($CDCl_3$, 300 MHz): δ 1.60 (d, *J* = 6.9 Hz, 3H, $CH_3$), 3.84 (s, 3H, $OCH_3$), 3.85 (s, 3H, $OCH_3$), 4.26 (q, *J* = 6.9 Hz, 1H, CH), 6.73-6.80 (m, 3H, ArH), 7.18 (s, 4H, ArH); $^{13}$C NMR ($CDCl_3$, 75Mz): 22.2, 48.1, 55.7, 55.8, 110.3, 110.7, 119.3, 128.7, 133.3, 133.5, 134.0, 135.3, 148.1, 148.7.



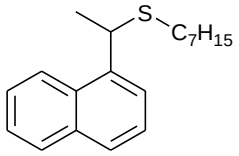

**3k**

**(1-(Naphthalen-6-yl)ethyl)(pentyl)sulfane (3k):** Colourless liquid. $^{1}$H NMR ($CDCl_3$, 300 MHz): δ 0.82 (t, *J* = 6.9 Hz, 3H, $CH_3$), 1.19-1.28 (m, 4H, -$CH_2$-$CH_2$-), 1.45-1.52 (m, 2H, $CH_2$), 1.64 (d, *J* = 7.2 Hz, 3H, $CH_3$), 2.23-2.33 (m, 2H, S-$CH_2$), 4.11 (q, *J* = 6.9 Hz, 1H, S-CH-Ar), 7.42-7.49 (m, 2H, ArH), 7.53-7.57 (dd, *J* = 8.4 and 1.8 Hz, 1H, ArH), 7.68 (s, 1H, ArH), 7.78-7.83 (m, 3H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 13.9, 22.2, 22.5, 29.0, 31.1, 31.2, 44.3, 125.4, 125.6, 125.7, 126.1, 127.6, 127.7, 128.4, 132.6, 133.2, 141.5.



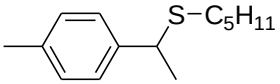
**3l**

**Cyclohexyl(1-(naphthalene-6-yl)ethyl)sulfane (3l):** Colourless liquid. $^{1}$H NMR ($CDCl_3$, 300 MHz): δ 1.43-1.73 (m, 9H, Cy-H ), 1.61 (d, *J* = 6.9 Hz, 3H, $CH_3$), 1.99 (m, 1H, CyH), 2.35-2.39 (m, 1H, S-CyH), 4.21 (q, *J* = 7.2 Hz, 1H, S-CH-Ar), 7.42-7.49 (m, 2H, ArH), 7.56 (dd, *J* = 8.7 and 1.8 Hz ,1H, ArH), 7.70 (s, 1H, ArH), 7.79-7.83 (m, 3H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 23.1, 25.7, 25.8, 25.9, 33.3, 33.9, 42.7, 42.75, 125.4, 125.6, 126.0, 127.6, 127.7, 128.3, 132.6, 133.3, 142.1.



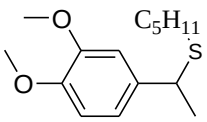
**3m**

**Heptyl(1-(naphthalene-5-yl)ethyl)sulfane (3m):** Colourless liquid. $^{1}$H NMR ($CDCl_3$, 300 MHz): δ 0.84 (t, *J* = 6.6 Hz, 3H, $CH_3$), 1.17-1.27 (m, 8H, $C_4H_8$), 1.43-1.52 (m, 2H, $CH_2$), 1.72 (d, *J* = 7.2 Hz, 3H, $CH_3$), 2.35-2.41 (m, 2H, S-$CH_2$), 4.80 (q, *J* = 6.9 Hz, 1H, S-CH-Ar), 7.41-7.53 (m, 3H, ArH), 7.67-7.73 (m, 2H, ArH), 7.81-7.85 (m, 1H, ArH), 8.19 (d, *J* = 8.4 Hz, 1H, ArH); 13C NMR (CDCl3), 75 MHz): δ 14.0, 22.5, 28.76, 28.8, 29.4, 31.3, 31.6, 39.4, 123.0, 124.3, 125.4, 125.8, 127.4, 128.9, 131.0, 133.9, 139.3.



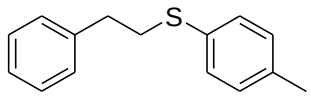
**3n**

**Pentyl(1-*p*-tolyiethyl)sulfane (3n):** Colourless liquid $^{1}$H NMR ($CDCl_3$, 300 MHz): δ 0.85 (t, *J* = 6.9 Hz, 3H, $CH_3$), 1.21-1.29 (m, 4H, $CH_2$-$CH_2$), 1.45-150 (m, 2H, $CH_2$), 1.54 (d, *J* = 6.9 Hz, 3H, CH-C$\underline{H}_3$), 2.24-2.34 (m, 5H, $CH_2$ & $ArCH_3$), 3.91 (q, *J* = 7.2 Hz, 1H, CH), 7.11 (d, *J* = 7.8 Hz, 2H, ArH), 7.21-7.24 (m, 2H, ArH); $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 13.9, 21.0, 22.2, 22.6, 29.0, 31.1, 31.2, 43.7, 127.1, 129.0, 136.5, 141.1.



**3o**

**(1-(3,4-dimethoxyphenyl)ethyl)(pentyl)sulfane (3o):** Colourless liquid. $^{1}$H NMR ($CDCl_3$, 300 MHz): δ 0.83-0.88 (m, 3H, $CH_3$), 1.25-1.30 (m, 4H, $CH_2$-$CH_2$), 1.47-1.52 (m, 2H, $CH_2$), 1.54 (d, *J* = 7.2 Hz, 3H, $CH_3$), 2.26-2.34 (m, 2H, S-$CH_2$), 3.86 (s, 3H, $OCH_3$), 3.89 (s, 3H, $OCH_3$), 3.92 (q, *J* = 7.2 Hz, 1H, C<u>H</u>-$CH_3$), 6.77-6.92 (m, 2H, ArH), 6.93 (d, *J* = 1.8 Hz, 1H, ArH); $^{13}$C NMR (CDCl3, 75 MHz): δ 13.8, 22.1, 22.7, 28.9, 31.0, 31.1, 43.8, 55.69, 55.7, 110.0, 110.6, 119.2, 136.6, 147.8, 148.9.




**3p**

**Phenethyl(*p*-toyl)sulfane (3p):** Colourless liquid. $^{1}$H NMR ($CDCl_3$, 300 MHz): δ 2.31 (s, 3H, $CH_3$), 2.88 (t, *J* = 7.2 Hz, 2H, $CH_2$-Ar), 3.08-3.13 (m, 2H, S-$CH_2$), 7.08-7.28 (m, 9H, ArH), $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 20.9, 35.67, 35.7, 126.3, 128.4, 128.44, 129.6, 130.0, 132.4, 136.1, 140.2.

## III.F. References

References for chapter III are given in Bibliography section (page 139–140).