SUPPORTING INFORMATION FOR

Bimetallic BaMoO$_4$ Nanoparticle for C-S Cross-Coupling of Thiols with Haloarene

Subhalaxmi Panda, Santosh Kumar Sahu, Pradyota K. Behera, Reba Panigrahi, Bamaknta Garnaik, and Prof. Laxmidhar Rout

[a] Dept. of Chemistry, Berhampur University, Odisha-760007, India.

Corresponding Author: ldr.chem@buodisha.edu.in, routlaxmi@gmail.com
# Table of Contents

<table>
<thead>
<tr>
<th>Sl No</th>
<th>Content</th>
<th>Page No</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Table of Contents</td>
<td>S2</td>
</tr>
<tr>
<td>2</td>
<td>General Information</td>
<td>S3</td>
</tr>
<tr>
<td>3</td>
<td>The Synthesis of Bimetallic BaMoO₄ Nano Catalyst</td>
<td>S4-S5</td>
</tr>
<tr>
<td>4</td>
<td>Catalyst Characterisation, SEM, EDX, XPS, IR</td>
<td>S6-S12</td>
</tr>
<tr>
<td>5</td>
<td>General experimental set up and procedure</td>
<td>S13</td>
</tr>
<tr>
<td>6</td>
<td>Optimization and Control Experiments</td>
<td>S14</td>
</tr>
<tr>
<td>7</td>
<td>Recyclability test</td>
<td>S15-S18</td>
</tr>
<tr>
<td>8</td>
<td>Proposed Mechanism</td>
<td>S19</td>
</tr>
<tr>
<td>9</td>
<td>Multi-Gram scale reaction and General Procedure</td>
<td>S20</td>
</tr>
<tr>
<td>10</td>
<td>Characterizations of products</td>
<td>S21-S32</td>
</tr>
<tr>
<td>11</td>
<td>'H NMR and '¹³C NMR Spectra of New Compounds</td>
<td>S33-S76</td>
</tr>
</tbody>
</table>
GENERAL INFORMATION

DMSO (99.9%), Toluene (99.8%), DMF (99.8%), t-BuOH (99.5%), 1,4-Dioxane (99.8%), Acetonitrile (99.8%) and Deuteriated NMR solvents CDCl₃ (99.8%) and CD₃CN (99.8%) is purchased from Sigma-Aldrich. All other solvents is purchased from Merck of high purity grade. Acetonitrile (99.8%) was sparged with nitrogen (N₂) for 10 min at room temperature and stored under nitrogen atmosphere. 4-Bromoacetophenone (99%), 4-Chloroacetophenone (99%), 4-nitroiodobenzene (98%), Iodobenzene (98%), 4-Methoxyiodobenzene (98%), 4-Methyliodobenzene (99%), Bromobenzene (98%), Chlorobenzene (99.8%). All thiols such as Thiophenol(98%), Cyclohexane thiol(97%), Cyclopentane thiol(97%), 2-bromobenzene thiol(97%), 4-bromobenzenethiol(95%), 2-chlorobenzene thiol(97%), 4-methoxybenzene thiol(97%), 4-methylbenzenethiol(98%), Barium Nitrate Ba(NO₃)₂ (99.99%), (NH₄)₆Mo₇O₂₄.4H₂O (99.98%), and Cs₂CO₃ (ReagentPlus®, 99%) and KOH (99%), K₂CO₃ (99%), KO⁻Bu(99%) was purchased from Sigma-Aldrich.

Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. The ¹H and ¹³C NMR spectra were recorded at 300 MHz, 400 MHz or 500 MHz for ¹H or at 75 MHz, 100 MHz or 125 MHz for ¹³C NMR, respectively. Deuterated solvents were purchased from Sigma-aldrich and used as received. All ¹H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvents. Data for ¹H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets…etc, br = broad), coupling constant (Hz) and integration. All ¹³C NMR spectra are reported in ppm relative to CDCl₃ (77.0 ppm). 1,4-diiodobenzene was used as an internal standard for NMR yields from proton analysis for the C-S bond formation reaction. Elemental analysis is performed in 2400 Series II CHNS/O analyser in CHNS mode.

Flash column chromatography was performed by using a 100-150 times weight excess of flash silica gel 40-63 μm from Aldrich. Fractions were analyzed by TLC using TLC silica gel F254 250 μm precoated-plates from Merck and permanganate stain was used for UV-inactive compounds. ESI mass spectrometry analysis was performed at the University of Hyderabad and IIT Guwahati, mass spectrometry facility with multi-mode (combined ESI and APCI). Melting point is determined in Digital melting point apparatus, Electronics India (EI)-2935 model; Visualised through LCD Screen and is uncorrected by ±5 °C. Sample purity was determined using 2,4,6-trimethoxybenzene, Internal Standard. Sample purity was determined using 2,4,6-trimethoxybenzene, Internal Standard. XPS is with Al-Kα line at IIT Roorke. HRMS is done at University of Hyderabad in ESI mode.
The Synthesis of Bimetallic BaMoO₄ Nano Catalyst

1gm of \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}.4\text{H}_2\text{O}\) (Purchased from Sigma-aldrich, 99.98%) dissolved in 150 ml distilled water and (1.19 gm) of \(\text{Ba(NO}_3)_2\) (Purchased from Sigma-aldrich 99.99%) dissolved in 150 ml distilled water, respectively. Then \(\text{Ba(NO}_3)_2\) solution was heated at 50 °C for 10 min and finally the ammonium molybdate solution was added drop wise to this solution. After adding two-third portion a white precipitate was obtained and added completely. The solution was heated at 50 °C and finally treated with ultrasonic irradiation with power 100W. The white product was filtered with whatman filterpaper 42, washed with distilled water and ethanol several times. The final product obtained was dried at 100°C for 60 min. The product was characterized in TEM and IR.

**Figure-1:** Clear aqueous solution of both before mixing them
Figure 2: Formation of BaMoO$_4$ nanoparticle after Mixing

Figure 3: BaMoO$_4$ nanoparticles after Sonication and drying
Catalyst Characterization

The catalyst obtained was dried at 100°C for 60 minutes. The catalyst has been characterized by SEM, EDX, XPS and IR spectroscopy. The SEM reveals that the nanocatalyst has rectangular rod shaped structure with particle size 6-15 nm in width and 15-30 nm in length (Figure 4-7). The XPS and IR study reveals presence of species Mo(VI) along with Mo-O-Ba bond. The strong, broad intensive band peak observed at 796 cm⁻¹ was due to symmetric or antisymmetric stretching vibrations of the molybdate ion (MoO₄²⁻) (Busy and Keller 1964). The very weak line observed at 1650 cm⁻¹ was the first overtone of the line at 796 cm⁻¹. The strong line at 370 cm⁻¹ was the antisymmetric bending vibration and the lines at 325 and 290 cm⁻¹ were due to the symmetric bending vibration of the molybdate ion (Clark and Doyle 1966). The band at 1330 cm⁻¹ was indicative of the vibration of oxygen ion for pure molybdenum and barium. The peaks at 516 cm⁻¹ and 478 cm⁻¹ were related to the Mo-O-Mo bands which agreed with Tsutomu et al (1980) and Nakamoto (1978). The peaks at 796, 370 cm⁻¹ were assigned to the characteristic absorption bands relating to (MoO₄)⁴⁻; Mo=O bond 1022, 912 cm⁻¹; Ba-O-Mo (796, 396, 1695 cm⁻¹) Ba-O (636.5, 584.4, 504.3 cm⁻¹).

2. A. Phuruangrat, B. Kuntalue, T. Thongtem, S. Thongtem, Materials Science-poland, 2015, 33, 537
Figure 4: Morphology of BaMoO$_4$ Nanoparticles showing average particle size 6-30nm in SEM
**Figure 5: EDXRF of BaMoO₄ nanocatalyst**

<table>
<thead>
<tr>
<th>Element</th>
<th>App Conc.</th>
<th>Intensity</th>
<th>Weight%</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>25.01</td>
<td>0.8143</td>
<td>35.03</td>
<td>0.78</td>
<td>78.49</td>
</tr>
<tr>
<td>Mo L</td>
<td>29.81</td>
<td>0.8408</td>
<td>40.44</td>
<td>0.79</td>
<td>15.11</td>
</tr>
<tr>
<td>Ba L</td>
<td>17.89</td>
<td>0.8320</td>
<td>24.52</td>
<td>0.68</td>
<td>6.40</td>
</tr>
<tr>
<td>Totals</td>
<td></td>
<td></td>
<td>100.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
X-RAY PHOTOELECTRON Spectra of BaMoO4 catalyst

Al mono 24.6 W 100.0 _ 45.0_ 55.00 eV

Figure: 6a XPS Spectra of Ba$^{2+}$ of Catalyst
Figure: 6b XPS Spectra of Mo$^{4+}$ and Mo$^{6+}$ of Catalyst
Figure 7: IR spectra of Original Catalyst;
Figure 7a: IR spectra of Original Catalyst; (Expanded Version)
General experimental set up and procedure

An oven dried 25 mL of 3-necked round bottom flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with KOH (78 mg, 1.4 eq.), 4-nitriiodobenzene (248.93 mg, 1 mmol), Thiophenol (110.02 mg, 1 mmol), BaMoO$_4$ 3 mol% (9 mg) and 1 mL CH$_3$CN. The reaction mixture was evacuated and purged with inert gas (N$_2$) three times. The reaction mixture was then placed into an oil bath with stirring maintained at 75°C. The three necked flask is equipped with condenser in one neck, N$_2$ ballon in second neck and third neck was stopped with Teflon cork as showed in Figure 6. The reaction is monitored after every 2 hr up to 24hr with the help of TLC and KMnO$_4$ Stain.

![General Reaction set up at Dept. Of Chemistry, Berhampur University, Odisha, India on 22/06/2018](image)

After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. Then 5 ml of CH$_2$Cl$_2$ is added and catalyst was filtered with whatmann filter paper-40. The filtrate was washed with water, concentrated in rotor and subjected for flash column chromatography using with 230-400 Silica Gel using ethylacetate and hexane as eluent to afford corresponding product. All yields are reported after column chromatography.
**Optimization and Control Experiments**

**Table 1.** Standardisation table for reaction of Benzene thiol with iodobenzene

<table>
<thead>
<tr>
<th>SI No</th>
<th>Solvent</th>
<th>Base</th>
<th>Temp.(°C)</th>
<th>Yield%[^a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Toluene</td>
<td>KOH</td>
<td>80</td>
<td>15</td>
</tr>
<tr>
<td>2</td>
<td>1,4-dioxane</td>
<td>KOH</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>t-BuOH</td>
<td>KOH</td>
<td>80</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>CH₃CN</td>
<td>KOH</td>
<td>80</td>
<td>92</td>
</tr>
<tr>
<td>5</td>
<td>DMF</td>
<td>KOH</td>
<td>80</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>CH₃CN</td>
<td>KOH</td>
<td>75</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>CH₃CN</td>
<td>Pyridine</td>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>CH₃CN</td>
<td>NE₅</td>
<td>80</td>
<td>5</td>
</tr>
<tr>
<td>9</td>
<td>CH₃CN</td>
<td>Cs₂CO₃</td>
<td>80</td>
<td>35</td>
</tr>
<tr>
<td>10</td>
<td>CH₃CN</td>
<td>K₂CO₃</td>
<td>80</td>
<td>25</td>
</tr>
<tr>
<td>11</td>
<td>CH₃CN</td>
<td>t-BuOK</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>12</td>
<td>CH₃CN</td>
<td>KOH</td>
<td>80</td>
<td>0[^i]</td>
</tr>
<tr>
<td>13</td>
<td>CH₃CN</td>
<td>KOH</td>
<td>80</td>
<td>0[^i]</td>
</tr>
<tr>
<td>14</td>
<td>CH₃CN</td>
<td>K₃PO₄</td>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>CH₃CN</td>
<td>KOH</td>
<td>80</td>
<td>0[^i]</td>
</tr>
<tr>
<td>16</td>
<td>CH₃CN</td>
<td>KOH</td>
<td>80</td>
<td>0[^i]</td>
</tr>
</tbody>
</table>

[^a]: Catalyst 3 mol% (3 mg), Thiophenol(0.3 mmol), iodobenzene(0.33 mmol), Base 1.4 equiv. is stirred under N₂ atmosphere for 12h. [^b]: isolated yield. [^c]: No catalyst. [^d]: No base. [^e]: Ba(NO₃)₂ as catalyst. [^f]: (NH₄)MoO₄ as catalyst. All are isolated yields.
RECYCLABILITY TEST:

After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. Then 5 ml of CH$_2$Cl$_2$ is added and catalyst was filtered with whatmann filter paper-40. The filtrate was washed with water, concentrated in rotor and subjected for column chromatography using with 230-400 Silica Gel using ethylacetate and hexane as eluent to afford corresponding product. All yields are reported after column chromatography.

The Catalyst in the Whatmann filter paper-40 was washed with 5 ml of dichloromethane and 5 ml of water. The catalyst in filter paper was dried with suction pump followed by 100 °C in Oven for 2h. IR spectra of catalyst reveals the same peak after the catalyst is recovered (See Spectra, Fig.-8-9). The catalyst is subjected to further reaction of fresh batch of thiols and haloarene in presence of base KOH. The reaction proceeded with >80% of yield under similar condition. The catalyst has been tested for another two cycles for catalyzing the reaction.

\[
\begin{align*}
\text{Catalyst} & \quad \text{Thiol} \quad \text{Iodobenzene} \quad \text{Base} & \quad \text{Product} \\
& \quad \quad \text{9 mg} \quad \text{1 mmol} \quad \text{1.1 mmol} & \quad \text{CH$_3$CN} \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Sl No</th>
<th>Runs</th>
<th>Catalyst</th>
<th>Recovered Catalyst</th>
<th>Yield%$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>First Run</td>
<td>9 mg</td>
<td>8.7 mg</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>Second Run</td>
<td>8.7 mg</td>
<td>8.5 mg</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>Third Run</td>
<td>8.5 mg</td>
<td>8.3 mg</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td>Forth Run</td>
<td>8.3 g</td>
<td>8.1 mg</td>
<td>91</td>
</tr>
<tr>
<td>5</td>
<td>Fifth Run</td>
<td>8.1 mg</td>
<td>8 mg</td>
<td>91</td>
</tr>
</tbody>
</table>

$^a$Catalyst 3 mol% (9 mg), Thiol(1 mmol), iodobenzene(1.1 mmol), Base 1.4 equiv. $^b$Isolated yield.
Figure 9: IR of recovered catalyst after reaction
X-RAY PHOTOELECTRON Spectra of Recycled BaMoO4 catalyst

Al mono 24.6 W 100.0 _ 45.0_ 55.00 eV

Figure: 10 XPS Spectra of Ba^{+2} after recycle of Catalyst
Mo in +6 oxidation state

Figure: 11 XPS Spectra of Mo$^{6+}$ after recycle of Catalyst

Mechanism Study
From the result obtained in the manuscript, it is clear that, the reaction has a characteristic of Oxidative addition followed by reductive elimination. With substituted iodobenzene, we did not found any regioselective product or benzyne products.

We have attempted to figure out a possible mechanism for the above reaction (Figure 12). The result of scheme 1-4 reveals that, the reaction has a characteristic of oxidative addition followed by reductive elimination. The XPS and IR study reveals presence of species Mo(VI) along with Mo-O-Ba bond. In BaMoO$_4$ nanocluster, Mo(VI) has high reduction potential than barium(II). We anticipate that molybdenum might be completing the cycle through possible intermediates a-e. The nanocluster is stabilised well by acetonitrile solvent. It is anticipated that, the above intermediates were stabilised by the nanocluster electrons in acetonitrile solvent.

**Figure 12.** Proposed Mechanism for BaMoO$_4$ catalysed C-S cross-coupling reaction
GRAM SCALE REACTION:

An oven dried 100 mL of 3-necked round bottom flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with KOH (784 mg, 1.4 eq., 14 mmol), iodobenzene (2.24 g, 11 mmol), Thiophenol (1.1 g, 10 mmol), BaMoO$_4$ 1 mol% (29 mg) and 5 mL CH$_3$CN. The reaction mixture was evacuated and purged with inert gas (N$_2$) three times. The reaction mixture was then placed into an oil bath maintained at 80°C. The three necked flask is equipped with condenser in One neck, N$_2$ ballon in second neck and third neck was stopped with Teflon cork as showed in Figure. After the reaction is over. The solution is cooled and subjected to rotor. It was worked up with 25 ml of ethyl acetate and 20 ml of water. The layers are separated. Organic layer is collected and concentrated. The Cross-coupled C-S product was isolated by flash chromatography (1:40 EtOAc:hexanes) as pale yellow solid (1.56 g, 84%). Physical State: Colorless liquid. ; Mp: 53 °C

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.28-7.25(m, 4H), 7.24-7.20 (m, 4H,) 7.18-7.14 (m, 2H),

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 135.3, 131.0, 129.2, 127.0.

General Procedure C-S Cross Couplings:

A oven dried 25 mL of 3-necked round bottom flask was charged with a stir bar, flame dried under vacuum and back filled with nitrogen three times. The flask was then charged with KOH (23.5 mg, 1.4 eq.), Haloarenes (0.33 mmol), Aryl/alkyl thiols (0.3 mmol), 3 mol% BaMoO$_4$ (3 mg) and 1 mL CH$_3$CN. The reaction mixture was evacuated and purged with inert gas (N$_2$) three times. The reaction mixture was then placed into an oil bath maintained at 75-80°C as reported in the scheme. The three necked flask is equipped with condenser in One neck, N$_2$ ballon in second neck and third neck was stopped with Teflon cork as showed in Figure 6. The reaction is monitored after every 2 hr up to 24hr with the help of TLC and KMnO$_4$ Stain. After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. Then 5 ml of CH$_2$Cl$_2$ is added and catalyst was filtered with whatmann filter paper-40. The filtrate was washed with water, concentrated in rotor and subjected for flash column chromatography using with 230-400 Silica Gel using ethylacetate and hexane as eluent to afford corresponding product. All yields are reported after column chromatography. The products were identified and cited with reorted literature
CHARACTERIZATIONS OF PRODUCTS

RECATIVITY OF THIOLS WITH HALOARENES

(Phenyl)(phenylsulfane (3a)

The flask was charged with Thiophenol (33 mg, 0.3 mmol), KOH (23 mg, 1.4 eq.), Iodobenzene (67 mg, 0.33 mmol), 3 mol% BaMoO$_4$ (3 mg) and 1 mL CH$_3$CN. After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as colorless oil (51 mg, 92%).

Physical State: Liquid

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.28-7.25 (m, 4H), 7.24-7.20 (m, 4H), 7.18-7.14 (m, 1H), 7.07 (d, $J = 8.0$ Hz, 2H), 7.19-7.17 (m, 4H), 7.13-7.10 (m, 1H), 7.07 (d, $J = 8.0$ Hz, 2H), 2.27 (S, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 135.3, 131.0, 129.2, 127.0.

Phenyl(p-tolyl)sulfane (3b)

The flask was charged with 4-methyl thiophenol (37 mg, 0.3 mmol), KOH (23 mg, 1.4 eq.), Iodobenzene (67 mg, 0.33 mmol), 3 mol% BaMoO$_4$ (3 mg) and 1 mL CH$_3$CN. After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as colorless oil (54 mg, 90%).

Physical State: Liquid

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.24 (d, $J = 8.0$, Hz, 2H), 7.19-7.17 (m, 4H), 7.13-7.10 (m, 1H), 7.07 (d, $J = 8.0$, Hz, 2H), 2.27 (S, 3H).

$^{13}$H NMR (400 MHz, CDCl$_3$) $\delta$ 137.6, 137.1, 132.3, 130.1, 129.7, 129.1, 126.4, 21.2.
(4-methoxyphenyl)(phenyl)sulfane (3c)\(^1\)

The flask was charged with 4-methoxy thiophenol (42 mg, 0.3 mmol), KOH (23 mg, 1.4 eq.), iodobenzene (67 mg, 0.33 mmol), 3 mol\% BaMoO\(_4\) (3 mg) and 1 mL CH\(_3\)CN. After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as colorless oil (54 mg, 84%).

Physical State: Liquid

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.52 – 7.49 \text{ (m, 2H)}, 7.31 – 7.25 \text{ (m, 5H)}, 6.97 \text{ (d, } J = 8 \text{ Hz, 2H)}, 3.87 \text{ (s, 3H)}\)

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 159.7, 138.5, 135.3, 128.8, 128.1, 125.6, 124.2, 114.9, 55.2\)

(Phenyl)(4-bromo phenyl)sulfane (3d)\(^1\)

The flask was charged with 4-bromothiophenol (56 mg, 0.3 mmol), KOH (23 mg, 1.4 eq.), iodobenzene (67 mg, 0.33 mmol), 3 mol\% BaMoO\(_4\) (3 mg) and 1 mL CH\(_3\)CN. After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as colorless oil (65 mg, 82%).

Physical State: Liquid

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.34 \text{ (d, } J = 8.0 \text{ Hz, 2H)}, 7.27 \text{ (t, } J = 8.0 \text{ Hz, 2H)}, 7.25-7.18 \text{ (m, 5H)}\).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta 137.4, 135.7, 132.2, 132.0, 131.5, 130.2, 129.3, 127.5, 127.4, 121.5\).
The flask was charged with 2-chlorothiophenol (43 mg, 0.3 mmol), KOH (23 mg, 1.4 eq.), iodobenzene (67 mg, 0.33 mmol), 3 mol% BaMoO$_4$ (3 mg) and 1 mL CH$_3$CN. After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as pale yellow oil (53 mg, 81%).

Physical State: Liquid

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.46-7.43 (m, 2H), 7.41-7.36 (m, 4H), 7.13-7.10 (m, 2H), 6.98-6.96 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 135.2, 133.6, 132.0, 131.3, 129.3, 129.3, 128.3, 127.4.

The flask was charged with 2-bromothiophenol (56 mg, 0.3 mmol), KOH (23 mg, 1.4 eq.), iodobenzene (67 mg, 0.33 mmol), 3 mol% BaMoO$_4$ (3 mg) and 1 mL CH$_3$CN. After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as pale yellow oil (63 mg, 80%).

Physical State: Liquid; CAS: 15861-48-0

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.45 (d, $J = 8.0$ Hz, 1H), 7.36-7.33 (m, 2H), 7.28-7.24 (m, 3H), 7.02 (t, $J = 8.0$ Hz, 1H), 6.92 (t, $J = 8.0$ Hz, 1H), 6.382 (d, $J = 8.0$ Hz, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 138.3, 133.4, 132.9, 132.7, 129.6, 129.6, 128.4, 127.7, 127.2, 122.9.
The flask was charged with cyclopentane thiol (31 mg, 0.3 mmol), KOH (23 mg, 1.4 eq.), iodobenzene (67 mg, 0.33 mmol), 3 mol% BaMoO$_4$ (3 mg) and 1 mL CH$_3$CN. After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as color less (47 mg, 89%).

Physical State: Liquid; CAS No. 19744-72-0

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.29-7.26 (m, 2H), 7.19 (t, $J = 8.0$ Hz, 2H), 7.09 (t, $J = 8.0$ Hz, 1H), 3.55-3.48 (m, 1H), 2.0-1.94 (m, 2H), 1.71-1.66 (m, 2H), 1.58-1.50 (m, 4H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 137.2, 129.8, 128.7, 125.8, 45.8, 33.5, 33.07, 24.7.

(Phenyl)(cyclohexyl)sulfane (3h)$^3$

The flask was charged with cyclohexane thiol (35 mg, 0.3 mmol), KOH (23 mg, 1.4 eq.), iodobenzene (67 mg, 0.33 mmol), 3 mol% BaMoO$_4$ (3 mg) and 1 mL CH$_3$CN. After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as colorless oil (49 mg, 85%).

Physical State: Liquid

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 (d, $J = 8.0$ Hz, 2H), 7.19 (t, $J = 8.0$ Hz, 2H), 7.12 (t, $J = 8.0$ Hz, 1H), 3.06-3.03 (m, 1H), 1.91-1.89 (m, 2H), 1.70-1.68 (m, 2H), 1.54-1.52 (m, 1H), 1.30-1.19 (m, 5H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 137.4, 135.1, 131.8, 128.7, 126.5, 46.5, 33.3, 26.0, 25.7.

3-(phenylthio)pyridine (3h1)

The flask was charged with 3-mercaptopyridine (111 mg, 1 mmol), Cs$_2$CO$_3$ (389 mg, 1.2 eq.), iodobenzene (223 mg, 1.1 mmol), 2.6 mol% CuMoO$_4$ (6 mg) and 1 mL DMSO. After the time specified in the reaction schemes, the reaction mixture
was cooled and worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as colorless oil (153 mg, 82%).

Physical State: Yellow Liquid

\[ ^1H\text{ NMR (400 MHz, CDCl}_3] \delta 8.58-8.47 (m, 2H), 7.57 (d, J = 8z, 1H), 7.38 – 7.28 (m, 5H), 7.20 (t, J = 8z, 1H), \]

\[ ^{13}C\text{ NMR (100 MHz, CDCl}_3] \delta 150.8, 147.6, 144.0, 137.6, 133.7, 131.6, 129.0, 128.9, 127.7, 127.4, 127.0. \]

\[
\begin{array}{c}
\text{N} \\
\text{S} \\
\text{H} \\
\end{array}
\]

3-(p-tolylthio)pyridine (3h2)

The flask was charged with 3-mercaptopyridine (111 mg, 1 mmol), Cs\textsubscript{2}CO\textsubscript{3} (389 mg, 1.2 eq.), 4-methyl iodobenzene (238 mg, 1.1 mmol), 2.6 mol\% CuMoO\textsubscript{4} (6 mg) and 1 mL DMSO. After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as colorless oil (160 mg, 80%).

Physical State: Yellow Liquid

\[ ^1H\text{ NMR (400 MHz, CDCl}_3] \delta 8.55-8.44 (m, 2H); 7.97 (d, J = 8 Hz, 1H), 7.30-7.26 (m, 2H), 7.15 –7.13 (m, 3H); 2.33 (s, 1H). \]

\[ ^{13}C\text{ NMR (100 MHz, CDCl}_3] \delta 149.8, 146.7, 144.1, 138.3, 136.6, 132.7, 130.2, 129.7, 129.4, 128.4. 20.89. \]

3-(Phenylthio)-1H-1,2,4-triazole

The flask was charged with 1H-1,2,4-triazole-5-thiol (101 mg, 1 mmol), Cs₂CO₃ (389 mg, 1.2 eq.), iodobenzene (223 mg, 1.1 mmol), 2.6 mol% CuMoO₄ (6 mg) and 1 mL DMSO. After the time specified in the reaction schemes, the reaction mixture was cooled and worked up with ethylacetate and water (20 x 5) ml. The organic layer was separated and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as colorless oil (143 mg, 81%).

Physical State: Yellow Oil

¹H NMR (400 MHz, less Soluble in CDCl₃) δ 8.34 (s, 1H), 8.14 (d, J=8.0 Hz, 2H), 7.53 (d, J=8.0 Hz, 2H),

REACTIVITY OF THIOLS WITH 4-ACETYLHALOARENES

![Chemical Reaction Diagram]

1-(4-(Phenylthio)phenyl)ethan-1-one (3i)

The flask was charged with thiophenol (33 mg, 0.3 mmol), KOH (23 mg, 1.4 eq.), 4-acetyl bromobenzene (65 mg, 0.33 mmol), 3 mol% BaMoO₄ (3 mg) and 1 mL CH₃CN. After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as white solid (64 mg, 95%).
**Physical State:** white solid; Mp: 64°C

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 (d, $J=8.0$ Hz, 2H), 7.51-7.49 (m, 2H), 7.41-7.39 (m, 3H), 7.22 (d, $J=8.0$ Hz, 2H), 2.55 (s, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.1, 144.9, 134.4, 133.9, 132.9, 129.7, 128.9, 128.8, 127.5, 26.5.

![Chemical structure](image)

1-(4-(p-Tolylthio)phenyl)ethan-1-one (3j)$^{11}$

The flask was charged with 4-methyl thiophenol (37 mg, 0.3 mmol), KOH (23 mg, 1.4 eq.), 4-acetyl bromobenzene (65 mg, 0.33 mmol), 3 mol% BaMoO$_4$ (3 mg) and 1 mL CH$_3$CN. After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as white solid (63 mg, 88%).

**Physical State:** white solid; Mp: 97°C

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J=8.0$ Hz, 2H), 7.42 (d, $J=8.0$ Hz, 2H), 7.24 (d, $J=8.0$ Hz, 2H), 7.16 (d, $J=8.0$ Hz, 2H), 2.54 (s, 3H), 2.40 (s, 3H)

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 197.1, 145.9, 140.4, 134.8, 134.5,130.5, 128.8, 127.2, 126.6, 26.5, 21.3.

![Chemical structure](image)

1-(4-((4-bromophenyl)thio)phenyl)ethanone (3k)$^{11}$

The flask was charged with 4-bromo thiophenol (56 mg, 0.3 mmol), KOH (23 mg, 1.4 eq.), 4-acetyl bromobenzene (65 mg, 0.33 mmol), 3 mol% BaMoO$_4$ (3 mg) and 1 mL CH$_3$CN. After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as white solid (81 mg, 88%).

**Physical State:** white solid; MP: 181 °C

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87 (d, $J=8.0$ Hz, 2H), 7.52 (d, $J=8.0$ Hz, 2H), 7.34 (d, $J=8.0$ Hz, 2H), 7.23 (d, $J=8.0$ Hz, 2H), 2.55 (s, 3H)
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 197.1, 143.8, 134.9, 132.9, 132.1, 131.9, 129.9, 128.9, 127.9, 126.5, 26.4.

1-(4-(benzylthio)phenyl)ethanone (3l)$^{12}$
The flask was charged with Benzyl mercaptan (37 mg, 0.3 mmol), KOH (23 mg, 1.4 eq.), 4-acetyl bromobenzene (65 mg, 0.33 mmol), 3 mol% BaMoO$_4$ (3 mg) and 1 mL CH$_3$CN. After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor.
The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as pale white needles (63 mg, 87%).
Physical State: white needles; MP: 112 °C
$Rf$ = 0.5 (silica gel, 1:4 EtOAc:hexanes)
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.82 (d, $J$=8.0 Hz, 2H), 7.36-7.30 (m, 7H), 4.22 (s, 2H), 2.56 (s, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 197.2, 144.2, 136.3, 134.2, 128.7, 128.7, 127.5, 126.9, 37.2, 24.4.

1-(4-(cyclohexylthio)phenyl)ethanone (3m)$^{13}$
The flask was charged with cyclohexane thiol (35 mg, 0.3 mmol), KOH (23 mg, 1.4 eq.), 4-acetyl bromobenzene (65 mg, 0.33 mmol), 3 mol% BaMoO$_4$ (3 mg) and 1 mL CH$_3$CN. After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as White Solid (59 mg, 85%).
Physical State: White Solid; Mp: 67 °C
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 (d, $J$=8.0 Hz, 2H), 7.38 (d, $J$=8.0 Hz, 2H), 3.36-3.32 (m, 1H), 2.59 (s, 3H), 2.07-2.06 (m, 2H), 1.84-1.81 (m, 2H), 1.64-1.47 (m, 2H), 1.44-1.35 (m, 4H).
$^{13}$C NMR (100 MHz, CDCl$_3$) δ 197.4, 143.6, 134.3, 128.7, 128.3, 44.9, 33.1, 29.7, 26.4, 25.9, 25.6.
1-(4-((4-Hydroxyphenyl)thio)phenyl)ethan-1-one (3n)\textsuperscript{11}

The flask was charged with 4-hydroxy thiophenol (38 mg, 0.3 mmol), KOH (23 mg, 1.4 eq.), 4-acetyl bromobenzene (65 mg, 0.33 mmol), 3 mol\% BaMoO\textsubscript{4} (3 mg) and 1 mL CH\textsubscript{3}CN. After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as white solid (63 mg, 86%).

**Physical State:** white solid; Mp: 190 °C

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.80 (d, \(J = 8.0\) Hz, 2H), 7.44 (d, \(J = 8.0\), Hz, 2H), 7.11 (d, \(J = 8.0\), Hz, 2H), 6.91 (d, \(J = 8.0\) Hz, 2H), 5.18 (s, 1H), 2.50 (s, 3H).

\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 197.5, 159.4, 146.7, 137.1, 128.8, 125.9, 116.9, 26.4.

1-(4-((4-Aminophenyl)thio)phenyl)ethan-1-one (3o)\textsuperscript{11}

The flask was charged with 4-amino thiophenol (37 mg, 0.3 mmol), KOH (23 mg, 1.4 eq.), 4-acetyl bromobenzene (65 mg, 0.33 mmol), 3 mol\% BaMoO\textsubscript{4} (3 mg) and 1 mL CH\textsubscript{3}CN. After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as white solid (61 mg, 84%).

**Physical State:** White solid; Mp: 145 °C

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.78 (dt, \(J = 8.0\) Hz, 2H), 7.35 (d, \(J = 8.0\), Hz, 2H), 7.09 (d, \(J = 8.0\) Hz, 2H), 6.73 (d, \(J = 8.0\) Hz, 2H), 3.91 (s, 2H), 2.53 (s, 3H).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 197.2, 147.8, 137.1, 133.6, 128.7, 125.3, 117.8, 116.1, 26.4.

**REACTIVITY OF THIOLS WITH 4-NITROHALOARENES**
The flask was charged with Thiophenol (33 mg, 0.3 mmol), KOH (23 mg, 1.4 eq.), 4-nitroiodobenzene (82 mg, 0.33 mmol), 3 mol% BaMoO₄ (3 mg) and 1 mL CH₃CN. After the time specified in the reaction scheme, the reaction mixture was cooled and concentrated in rotor.

**Physical State:** Yellow Solid; **Mp:** 53 °C

**1H NMR (400 MHz, CDCl₃)** δ 8.08 (d, J = 8.0, Hz, 2H), 7.56 (dd, J = 8.0, Hz, 2H), 7.47 – 7.45 (m, 3H), 7.19 (d, J = 8.0, Hz, 2H).

**13C NMR (100 MHz, CDCl₃)** δ 149.3, 145.3, 134.8, 130.4, 129.7, 126.7, 124.0.

---

**(4-nitrophenyl)(phenyl)sulfane (3p)**

The flask was charged with 4-methyl-thiophenol (37 mg, 0.3 mmol), KOH (23 mg, 1.4 eq.), 4-nitroiodobenzene (82 mg, 0.33 mmol), 3 mol% BaMoO₄ (3 mg) and 1 mL CH₃CN. After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as pale yellow solid (64 mg, 95%).

**Physical State:** White Solid; **Mp:** 86 °C

**1H NMR (400 MHz, CDCl₃)** δ 7.98 (d, J = 8.0, Hz, 2H), 7.37 (d, J = 8.0, Hz, 2H), 7.21 (8, J = 8.0, Hz, 2H), 7.05 (d, J = 8.0, Hz, 2H), 2.34(S, 3H).

**13C NMR (100 MHz, CDCl₃)** δ 149.3, 145.1, 140.2, 135.1, 130.8, 126.5, 126.1, 123.9, 21.3
The flask was charged with 4-methoxy-thiophenol (42 mg, 0.3 mmol), KOH (23 mg, 1.4 eq.), 4-nitroiodobenzene (82 mg, 0.33 mmol), 3 mol% BaMoO$_4$ (3 mg) and 1 mL CH$_3$CN. After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as pale yellow oil (66 mg, 85%).

Physical State: Liquid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.05 (d, $J = 8.0$, Hz, 2H), 7.5 (d, $J = 8.0$, Hz, 2H), 7.1 (d, $J = 8.0$, Hz, 2H), 7.0 (d, $J = 8.0$, Hz, 2H), 3.87 (S, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 161.1, 150.1, 144.9, 137.1, 132.0, 125.5, 123.9, 120.1, 115.6, 55.4.

The flask was charged with Cyclohexane thiol (35 mg, 0.3 mmol), KOH (23 mg, 1.4 eq.), 4-nitroiodobenzene (82 mg, 0.33 mmol), 3 mol% BaMoO$_4$ (3 mg) and 1 mL CH$_3$CN. After the time specified in the reaction schemes, the reaction mixture was cooled and concentrated in rotor. The product was isolated by flash chromatography (1:40 EtOAc:hexanes) as pale yellow solid (66 mg, 93%).

Physical State: Yellow Solid; Mp: 53 °C

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.12 (d, $J = 8.0$, Hz, 2H), 7.37 (d, $J = 8.0$, Hz, 2H), 3.38-3.32 (m, 1H), 2.07-2.04 (m, 2H), 1.84-1.80 (m, 2H), 1.69-1.66 (m, 1H), 1.48-1.30 (m, 5H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.9, 145.2, 127.7, 123.9, 44.9, 32.9, 29.7, 25.8, 25.6
<table>
<thead>
<tr>
<th>Compound Characterization</th>
<th>Reference</th>
</tr>
</thead>
</table>
| (Phenyl)(phenylsulfane (3a)

| 1 | (Phenyl)(2-chloro phenyl)sulfane (3e)

| 8 |
| Phenyl(p-tolyl)sulfane (b)

| 1 | (Phenyl)(2-bromo phenyl)sulfane (3f)

| 9 |
| (4-methoxyphenyl)(phenyl)sulfane (3c)

| 1 | (Phenyl)(cyclopentyl)sulfane (3g)

| 10 |
| (Phenyl)(4-bromo phenyl)sulfane (3d)

| 1 | (Phenyl)(cyclohexyl)sulfane (3h)

| 3 |
| 1-(4-(Phenylthio)phenyl)ethan-1-one (3i)

| 11 | 1-(4-(cyclohexylthio)phenyl)ethanone (3m)

| 13 |
| (4-nitrophenyl)(phenyl)sulfane (3p)

| 1 | (4-nitrophenyl)(4-methoxyphenyl)sulfane (3r)

| 3 |
| (4-nitrophenyl)(4-methyl phenyl)sulfane (3q)

| 2 | (4-nitrophenyl)(cyclohexyl)sulfane (3s)

| 7 |

$^{1}\text{H}$ and $^{13}\text{C}$ NMR Spectra of Products
6.10.2018_CS Carbon L3C of HKS-CS-3
$\text{ST}_\text{01-4-nitrobenzenes dodecane methods}$

$\text{ST}_\text{01} 12062019$

$3s$

![Chemical Structure](attachment:image.png)

$\frac{\text{f1 (ppm)}}{9.5 \ 9.0 \ 8.5 \ 8.0 \ 7.5 \ 7.0 \ 6.5 \ 6.0 \ 5.5 \ 5.0 \ 4.5 \ 4.0 \ 3.5 \ 3.0 \ 2.5 \ 2.0 \ 1.5 \ 1.0 \ 0.5 \ 0.0 \ -0.5}$