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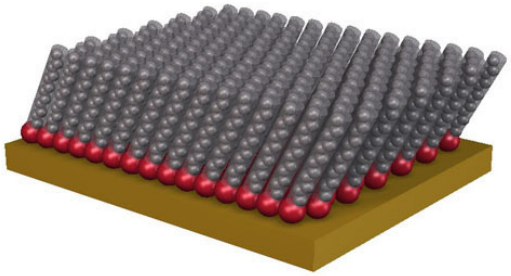
Product Information

Technical Bulletin AL-267

Thioacetate Deprotection Procedure

Product Description
The reactivity of the free thiols is a growing concern when synthesizing increasingly complex compounds for self-assembled monolayers (SAMs, Figure 1).

Figure 1.
Schematic showing an ordered self-assembled monolayer of densely packed alkane thiols.



One way to address this problem is to protect the free thiol groups. Several methods have been reported to accomplish this, such as using thioether, thioester, and disulfide functionalities.[1] More recently, the direct use of a thioacetate group for the preparation of SAMs on the gold surface was demonstrated.[2] However, SAMs produced using thioacetates are not as densely packed or as well ordered as SAMs produced by the free thiol analogs.[2] Thioacetates also take longer to absorb on the gold surface than the free thiols.[2]

This problem can be addressed by deprotecting a free thiol from its protected derivative just prior to use. One method to obtain inherently unstable free thiols quickly and easily is from the hydrolysis of thioacetate using hydrolyzing agents[1] such as:

Sodium hydroxide (Catalog Number 221465)
Potassium hydroxide (Catalog Number 221473)
Potassium carbonate (Catalog Number 209619)
Sodium methoxide (Catalog Number 164992)

The resulting free thiol can be used immediately or stored for hours to days at room temperature, depending on the stability of the free thiol. The deprotection of S-(10-undecenyl) thioacetate (1) to generate 11-mercapto-1-undecene (2) is described in this bulletin. This compound is a good candidate for this technique, as it is difficult to store for an extended period of time due to the reactivity of thiol group with the alkenyl functionality.

Precautions and Disclaimer
Please consult the Material Safety Data Sheet for information regarding hazards and safe handling practices.

Procedure
Deprotection of S-(10-Undecenyl) thioacetate (Figure 2)

1. Dissolve S-(10-Undecenyl) thioacetate (1) (2.0 g, 8.76 mmol) in 10 ml of ethanol (Catalog Number 459844) using a 250 mL, three neck, round bottom flask (Catalog Number Z418668) under inert atmosphere.

2. Add NaOH solution (700 mg, 18 mmol in 2.5 ml of H_2O) in a drop-wise fashion.

3. Reflux reaction mixture for 2 hours before cooling to room temperature.

4. Neutralize mixture with 6 mL of degassed 2 M HCl solution (Catalog Number 653799) and transfer it to a separatory funnel under inert atmosphere.

5. Add 20 mL of degassed diethyl ether (Catalog Number 346136) and 10 mL of degassed water to the separatory funnel before separating the organic layer.

6. Wash organic layer with 10 mL of degassed water and dry over Na_2SO_4 (Catalog Number 238597).

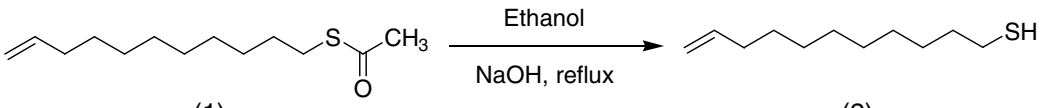
7. Remove the solvent at 40 °C using a rotary evaporator.

Results

This procedure resulted in 1.3 g of 11-mercapto-1-undecene[3] with 95% purity, which can be stabilized by adding small amount of 4-*tert*-butylcatechol (Catalog Number 124249).

Figures 3 and 4 show the H^1-NMR of the thioacetate (1) and the resulting free thiol (2) respectively. This free thiol can be directly used to create self-assembled monolayers.

Figure 2.
Deprotection of S-(10-Undecenyl) thioacetate



(1) (2)

Figure 3.
H^1-NMR of S-(10-Undecenyl) thioacetate (1) prior to following deprotection protocol.

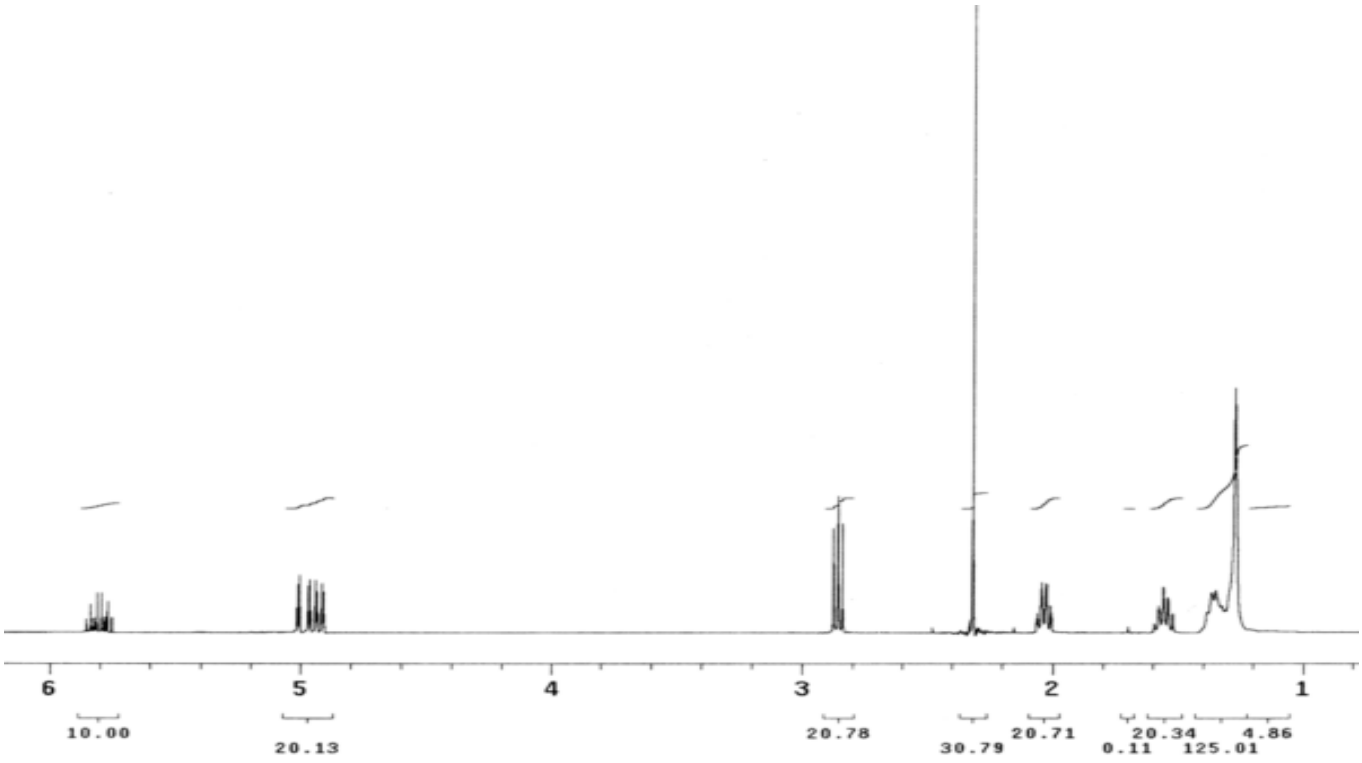
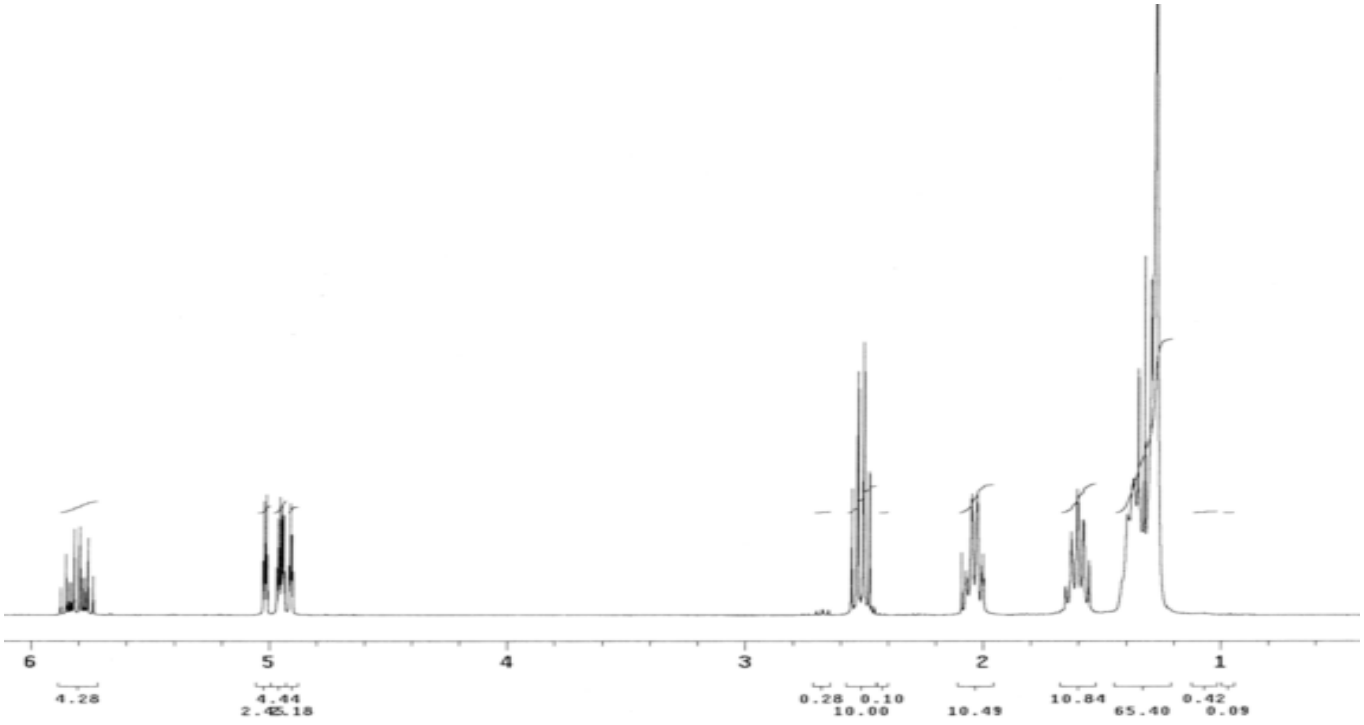


Figure 4.
H^1-NMR of 11-mercapto-1-undecene (2) after following deprotection protocol.



References

1. Witt D. et al., *Current Organic Chemistry*, **8**, 1 (2004).
2. Bethencourt M.I., et al., *Langmuir*, **25**, 1265 (2009).
3. McGovern, M.E., and Thompson, M., *Can. J. Chem.*, **77**, 1678 (1999).

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