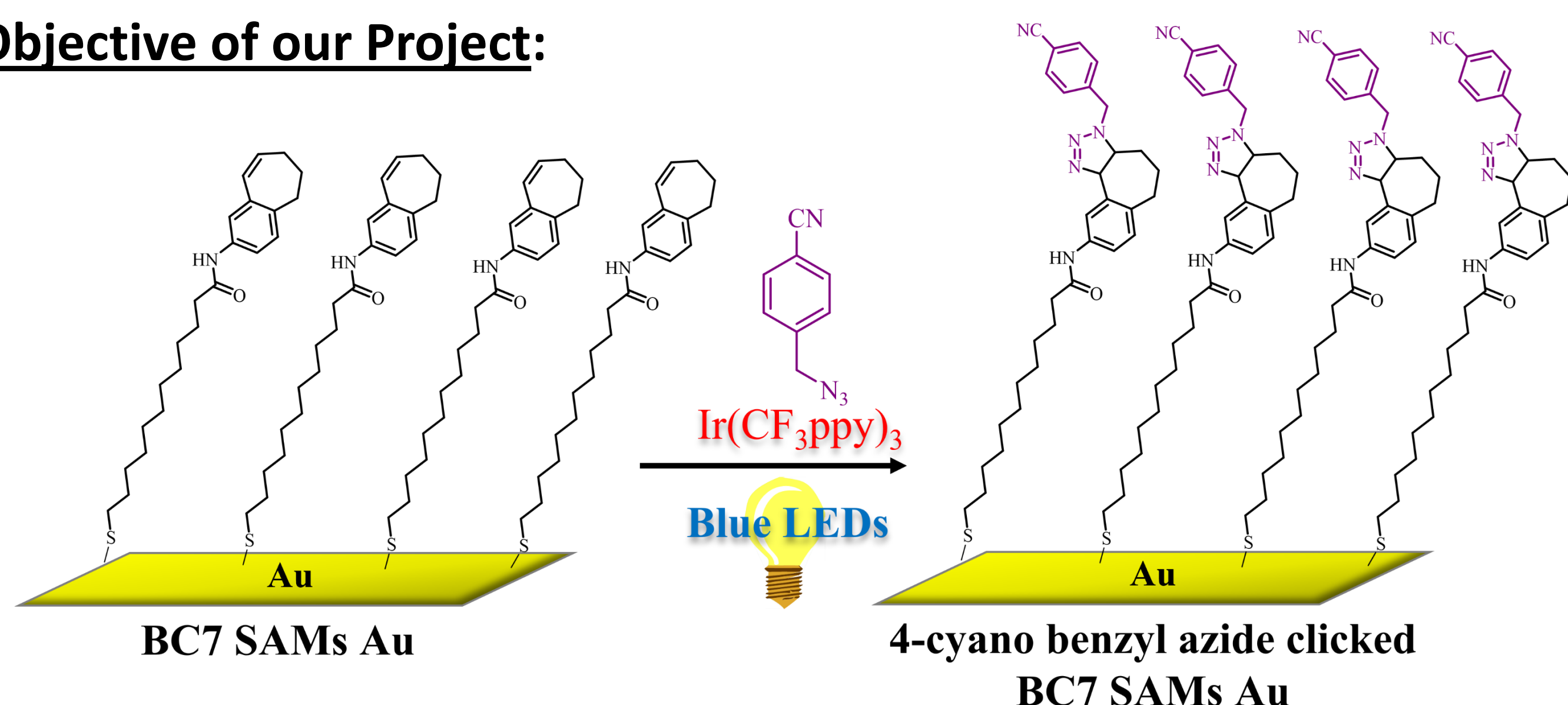


Abstract:

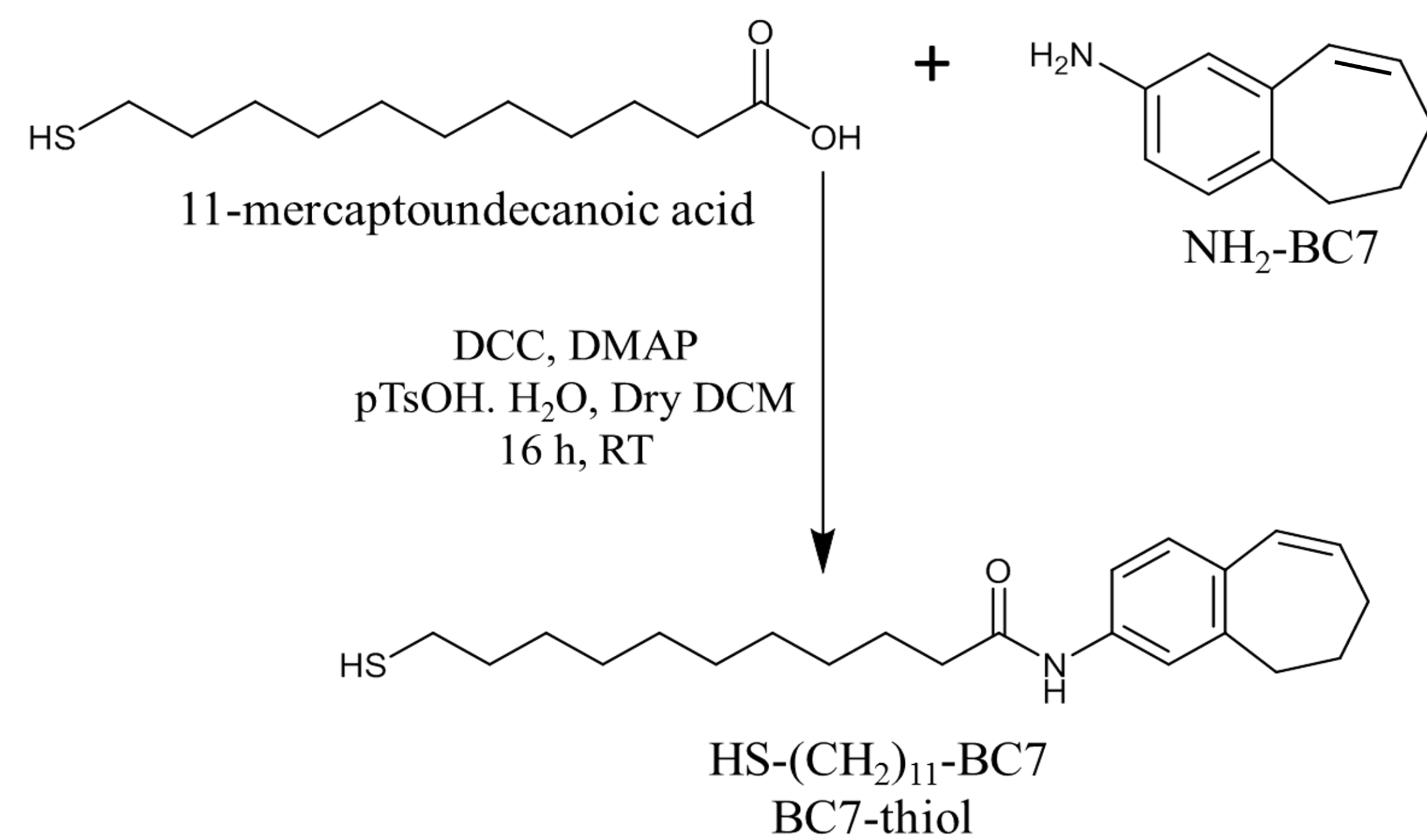
In this work, a visible light-mediated [3+2] cycloaddition reaction between azide molecule and benzocycloheptene (BC7) terminated gold (Au) surface will be investigated. Exposure of the BC7 to photocatalyst and visible light facilitated the double bond isomerization of benzofused-cycloheptene, Z-BC7 to a strained and kinetically unstable alkene, E-BC7 to undergo cycloaddition with azide molecule to form triazoline ring structure. Control reaction with BC7 thioacetate was investigated and the reaction progress was monitored via attenuated total reflectance-Fourier transform infrared (ATR-FTIR). The strategy reported here offers spatial and temporal control of functionalization along with catch and release mechanisms due to the cleavable nature of the linker.

Objective of our Project:



Scheme 1: Preparation of BC7 SAMs on gold surface and click reaction.

Synthesis and Characterization of BC7-thiol:



Scheme 2: Synthesis strategy for BC7-thiol.

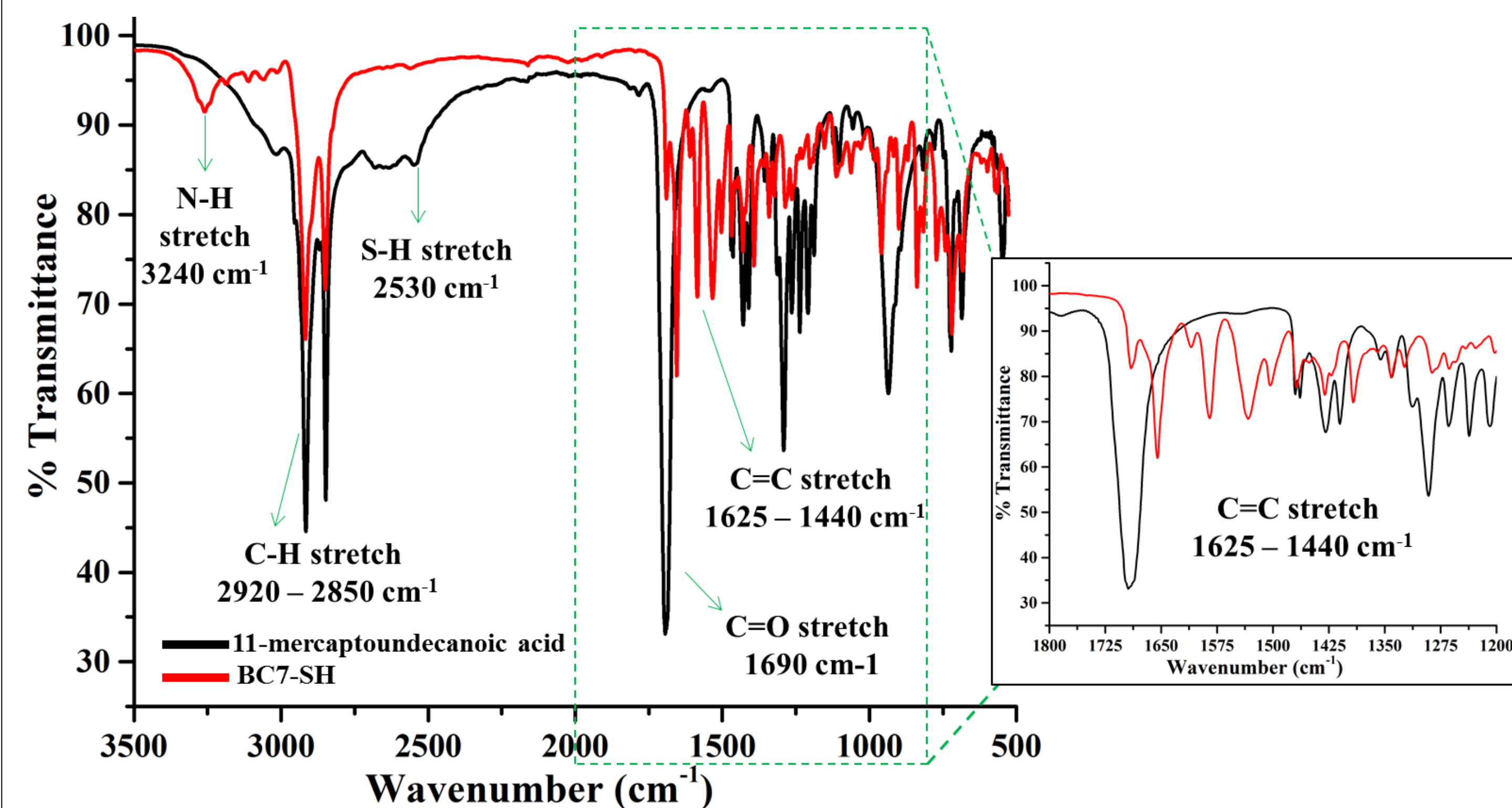
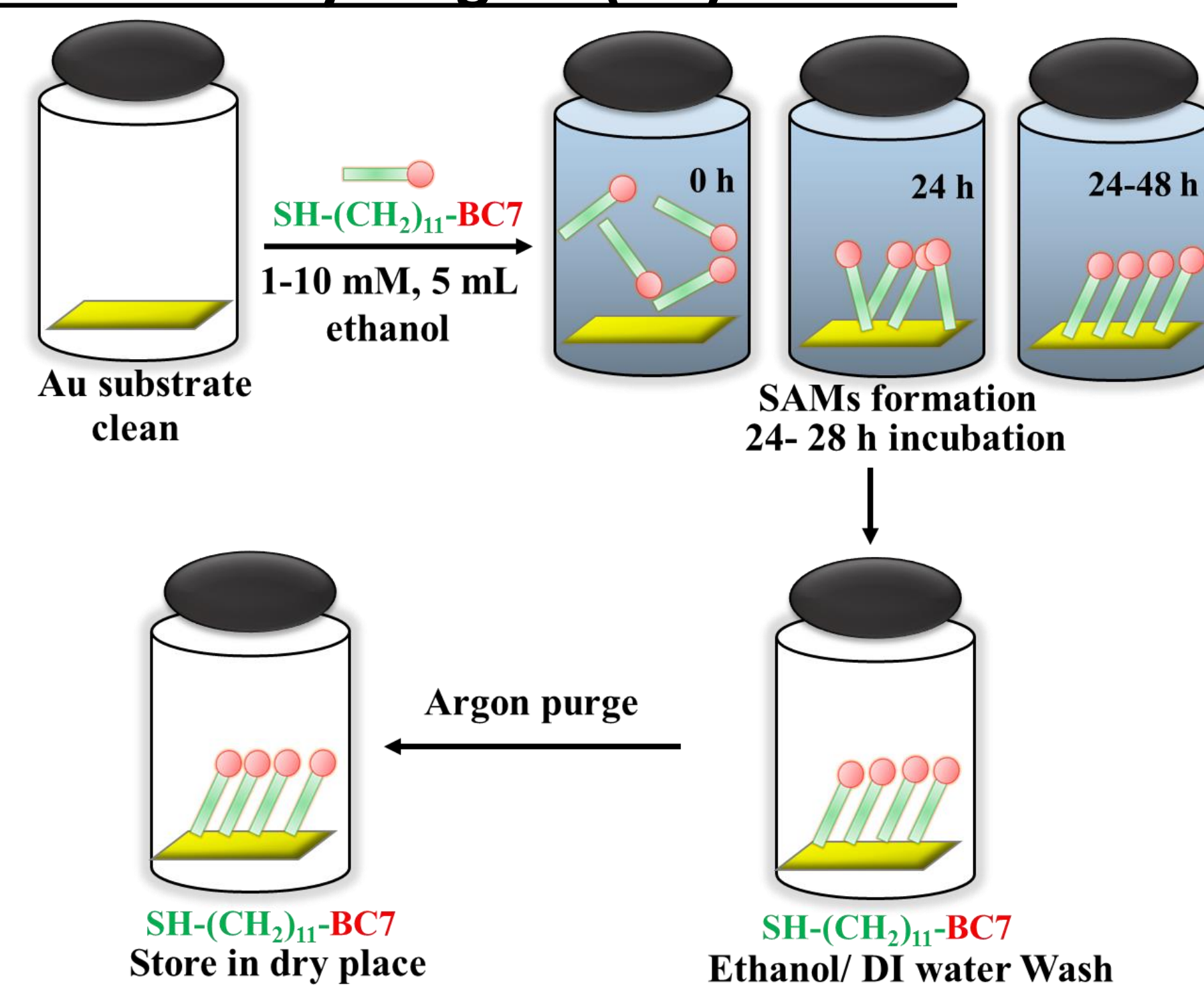


Figure 1: ATR-FTIR spectra of 11-mercaptoundecanoic acid (black) and BC7-SH (red).

BC7-thiol Self Assembly on gold (Au) surface:



Scheme 3: Schematic representation of BC7-thiol SAMs formation on the gold surface.

Characterization of BC7 SAMs on gold Surface:

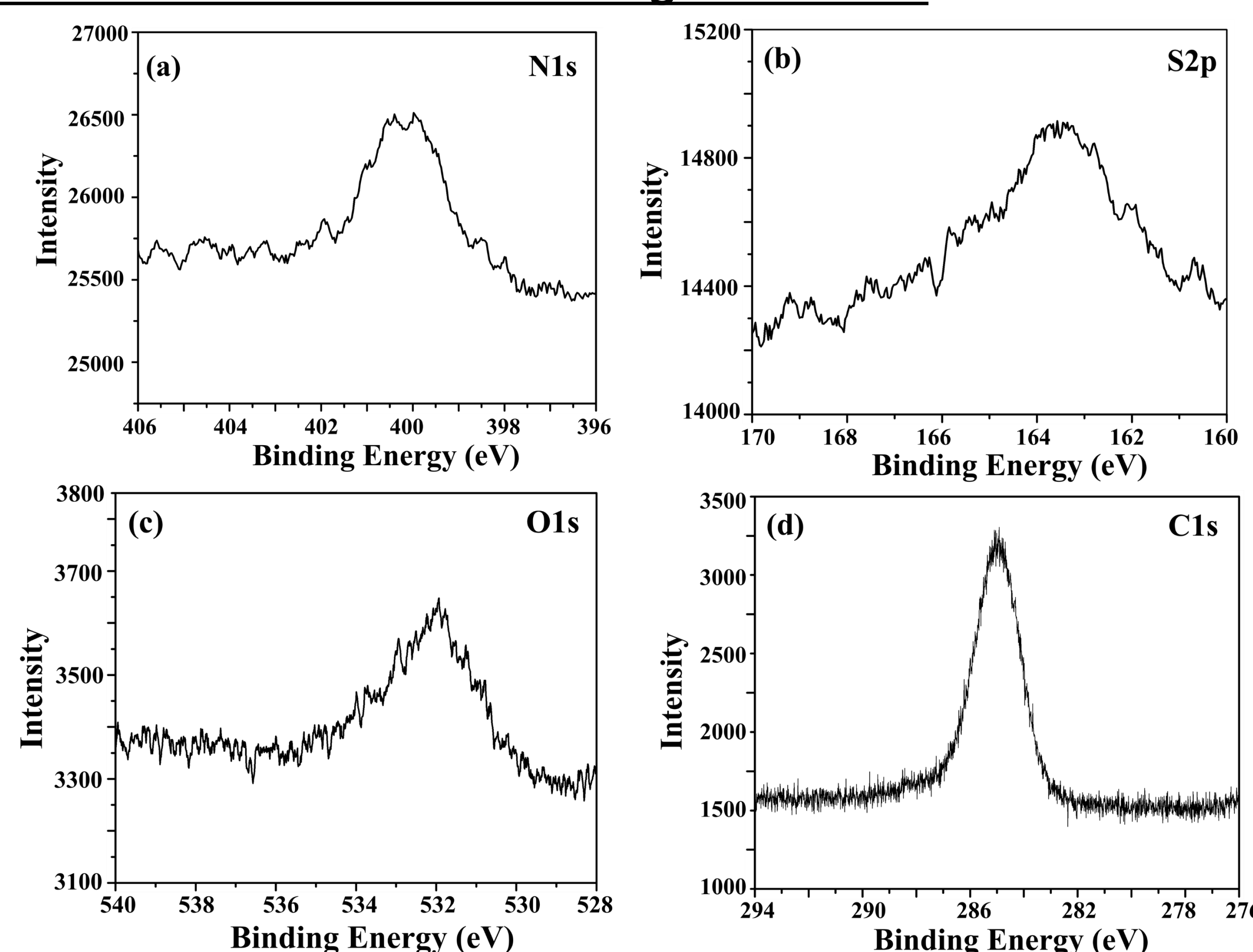
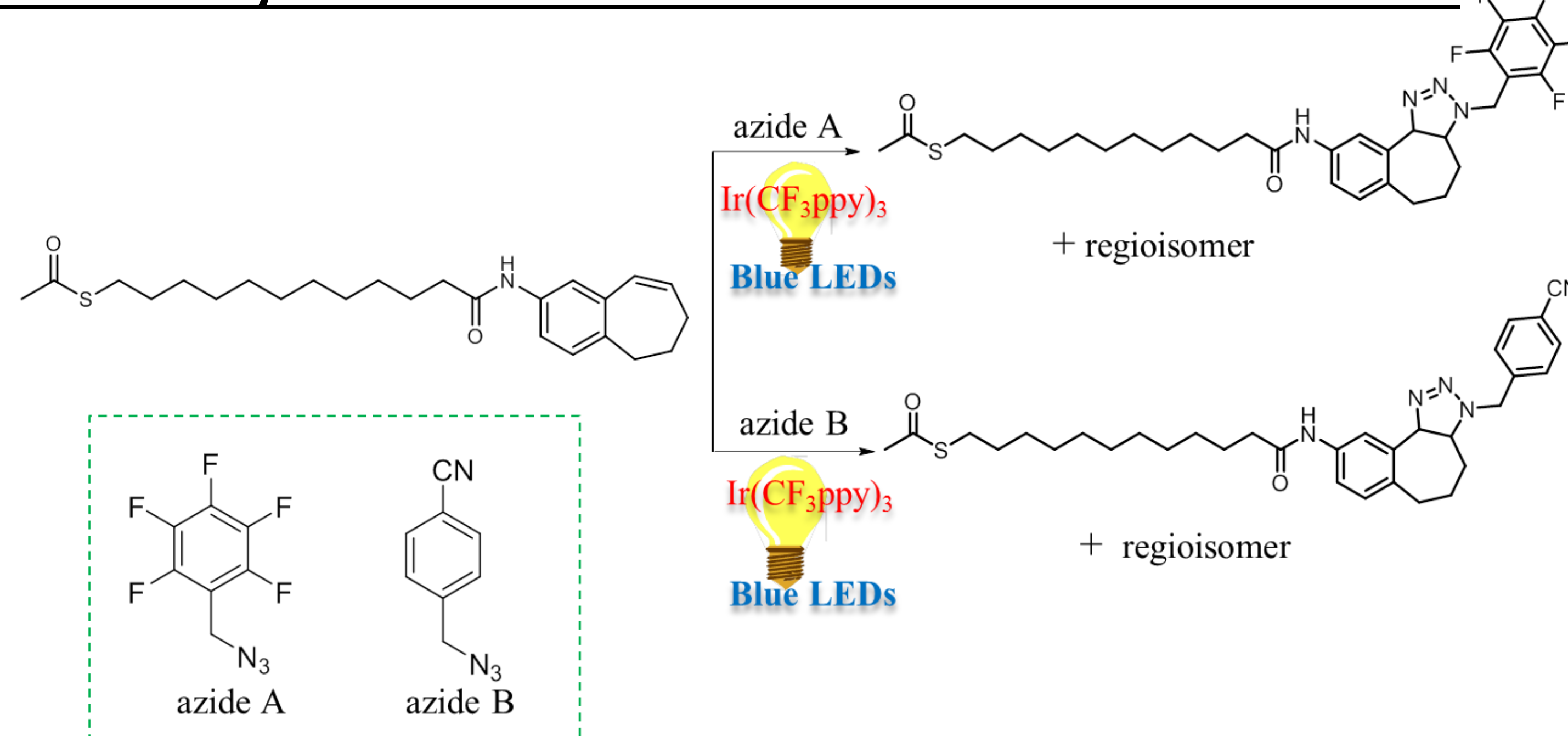


Figure 2: High-resolution XPS spectra of BC7 thiol SAMs on gold surface; (a) N1s region, (b) S2p, (c) C1s, and (d) O1s.

Photocatalytic Click Reaction on BC7-thioacetate with Azides:



Scheme 4: Overall click reaction strategy on BC7 thioacetate.

Characterization of Click Reaction on BC7-thioacetate:

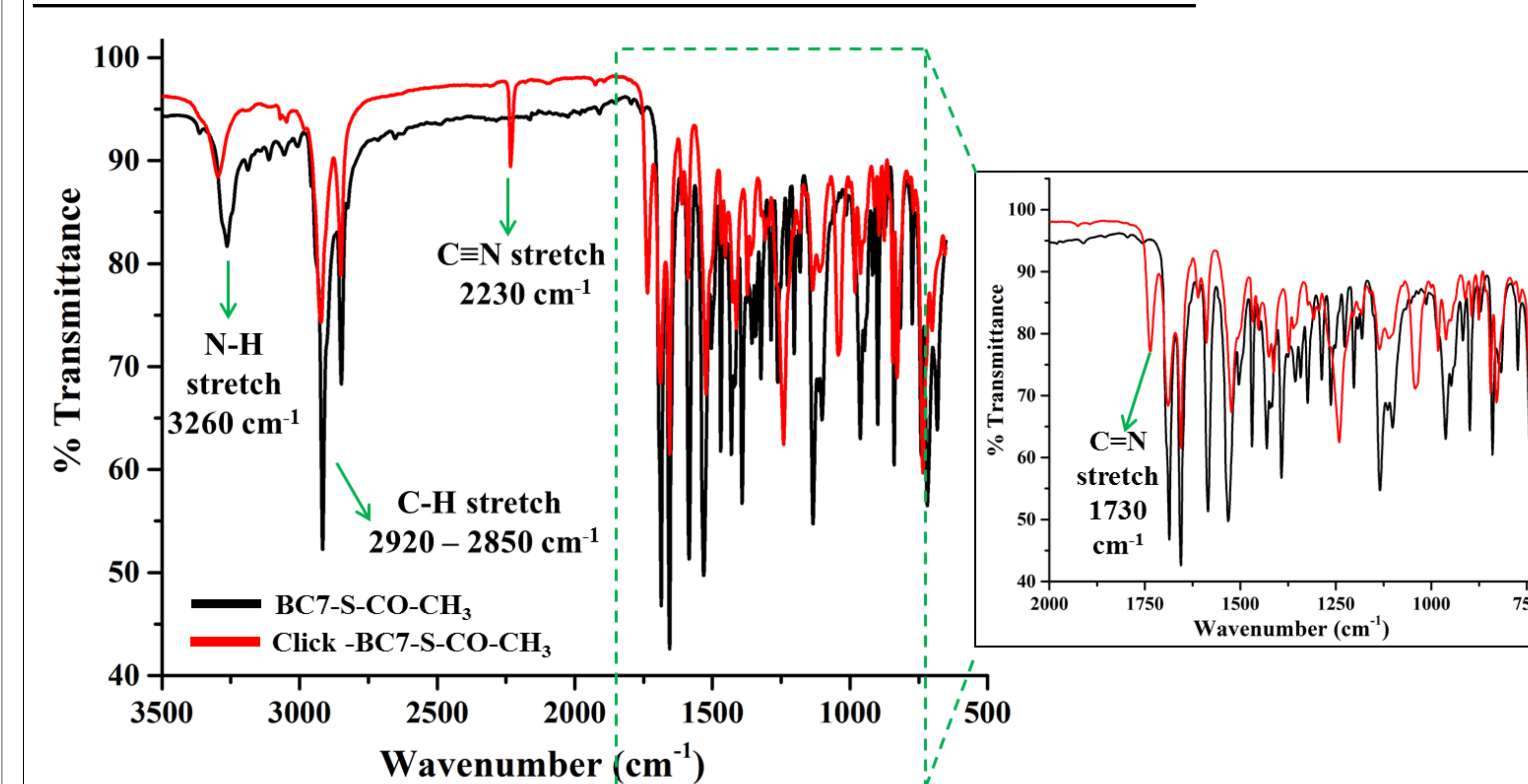


Figure 3: ATR-FTIR spectra of BC7-thioacetate (black) and BC7-thioacetate and 4-cyano benzyl azide click product (red).

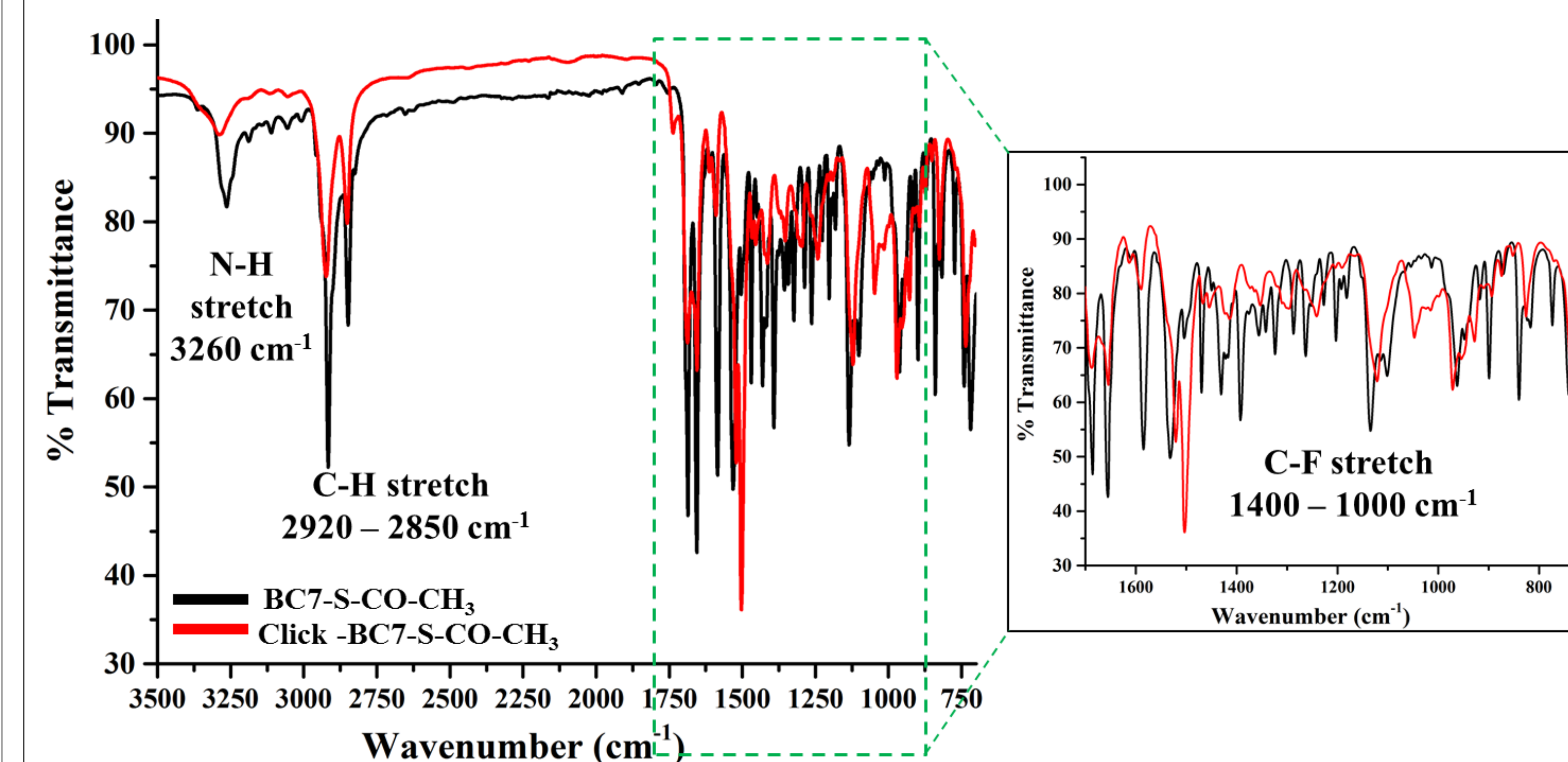


Figure 4: ATR-FTIR spectra of BC7-thioacetate (black) and BC7-thioacetate and 2,3,4,5,6-pentafluorobenzyl azide click product (red).

Conclusion and Future Directions:

BC7 SAMs were immobilized on the Au surface. The presence of BC7 on Au was characterized by XPS spectroscopy. To investigate BC7 SAMs Au click reaction efficiency, control experiments were first carried out using BC7-thioacetate with 4-cyanobenzyl azide and 2,3,4,5,6-pentafluorobenzyl azide. Reaction progress was successfully monitored by ATR-FTIR. Our future experiments will be focused on photocatalytic click reaction of BC7 SAMs on Au with 4-cyanobenzyl azide and 2,3,4,5,6-pentafluorobenzyl azide.

References:

- Brennan, J. L.; Hatzakis, N. S.; Tshikhudo, T. R.; Dirvianskyte, N.; Razumas, V.; Patkar, S.; Vind, J.; Svendsen, A.; Nolte, R. J. M.; Rowan, A. E.; Brust, M. *Bioconjugate Chem.* **2006**, *17*, 1373–1375
- X. Wang, P. Gobbo, M. Suchy, M. S. Workentin and R. H. E. Hudson, *RSC Adv.*, **2014**, *4*, 43087–43091.

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