

Supplementary Information

Using Silyl Protecting Group to Enable Post-deposition C-C Coupling Reactions of Alkyne-functionalized N-Heterocyclic Carbene Monolayers on Au surfaces

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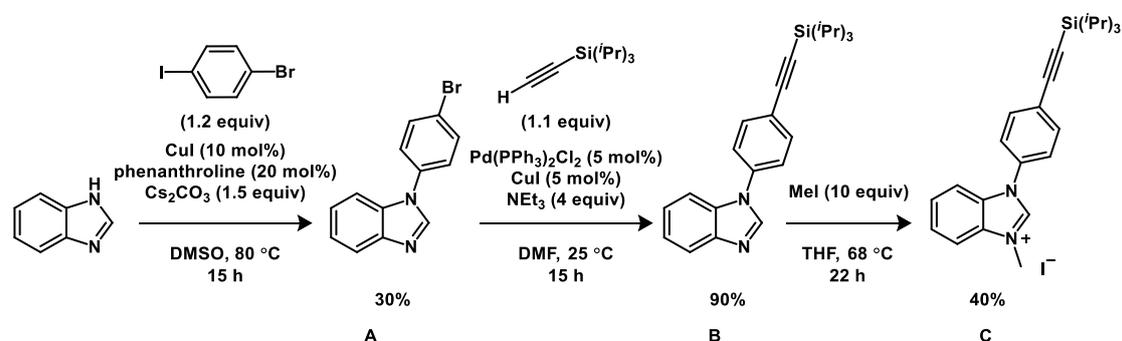
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Supplementary experimental

Potassium tert-butoxide (99.99%), tetrabutylammonium fluoride (TBAF) (1.0 M solution in THF), 4-nitrophenyltrifluoromethylsulfonate (99%), 4-fluoroiodobenzene (99%), 1-bromo-4-iodobenzene (98%), triethylamine (99.5%), CuI (98%), and PdPPh₃Cl₂ (98%), Cs₂CO₃ (99%), phenanthroline (99%), trimethylsilylacetylene (98%), triethylamine (99%), and iodomethane (99%) were purchased from Sigma-Aldrich and were used without further purification. Au films were prepared by evaporation of 10 nm Cr film on piranha-cleaned Si (110) wafer, followed by evaporation of 100 nm Au.

The TIPS-protected NHC salt, 3-methyl-1-(4-((triisopropylsilyl)ethynyl)phenyl)-1H-benzo[d]imidazol-3-ium iodide, was synthesized in three steps according to Scheme S1.

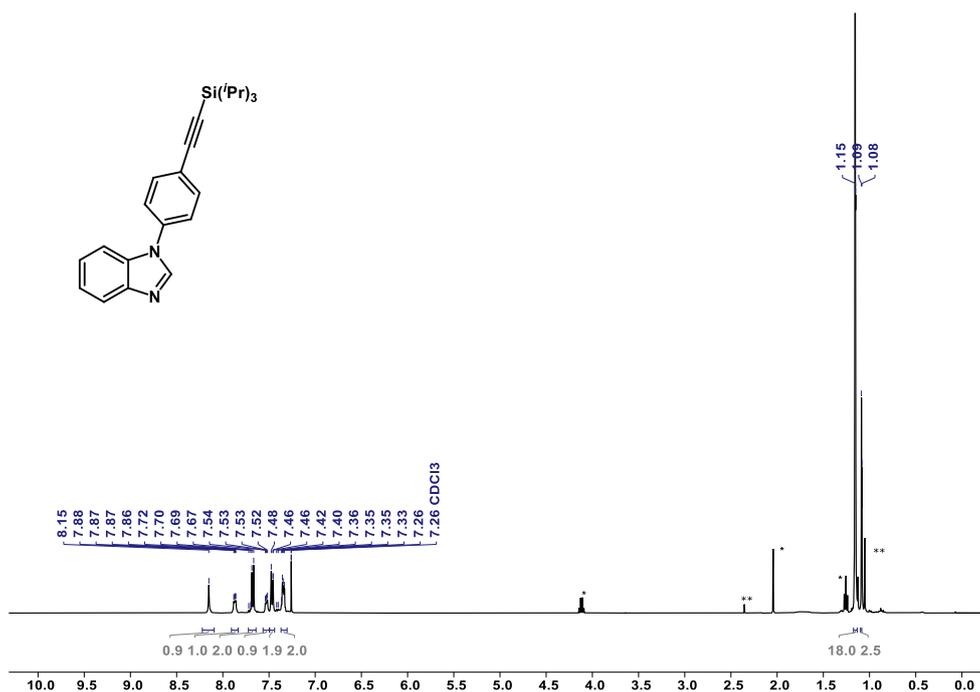


Scheme S1: Synthesis of TIPS protected alkyne-NHCs

1-(4-bromophenyl)-1H-benzo[d]imidazole (A) was prepared using modified procedure reported by Buchwald et. al.¹ Benzimidazole (709 mg, 6 mmol), 1-bromo-4-iodobenzene (1.75g, 6.2 mmol), Cs₂CO₃ (3.91 g, 12 mmol), CuI (114 mg, 0.6 mmol), and phenanthroline (216 mg, 1.2 mmol) were added to an oven dried 100 mL round bottom flask equipped with a stir bar. The flask was fitted with a rubber septum, then evacuated and backfilled with nitrogen three times. After the third cycle, 50 mL DMSO was added and the reaction was placed in an oil bath pre-heated to 80 °C and stirred for 15h. After 15h, the reaction was cooled to room temperature, diluted with dichloromethane, and filtered through a plug of celite, eluting with additional dichloromethane. The filtrate was concentrated by rotary evaporation, and the resulting residue was purified by recrystallization in hexane and ethyl acetate to provide **A** as a white solid (492 mg, 30% yield). ¹H NMR analysis of **A** in CDCl₃ was consistent with reported literature.²

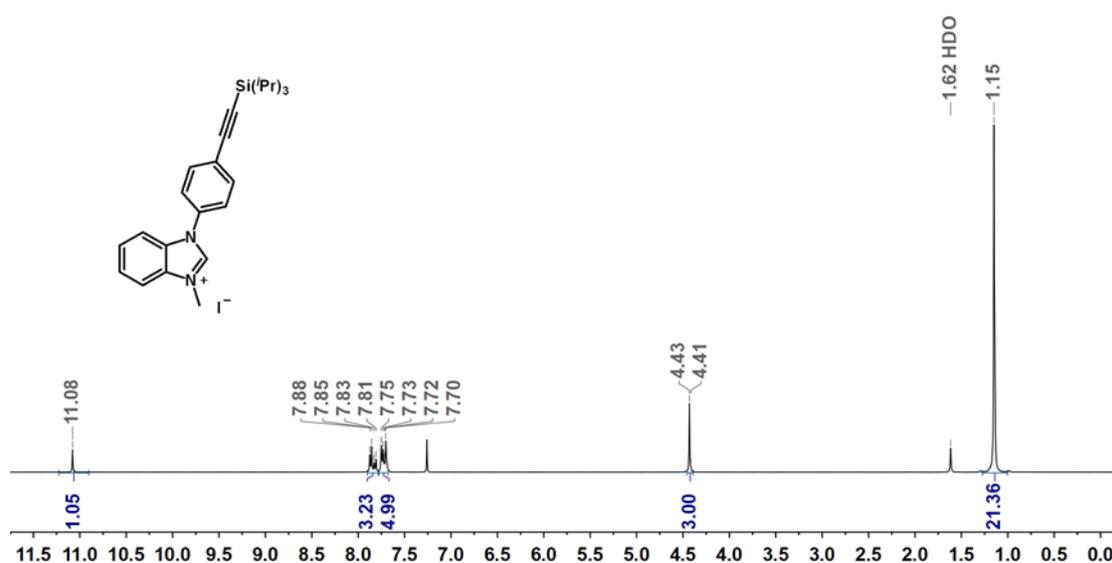
1-(4-((triisopropylsilyl)ethynyl)phenyl)-1H-benzo[d]imidazole (B) Bromo-functionalized aryl benzimidazole **A** (471 mg, 1.73 mmol), trimethylsilylacetylene (427 uL, 1.90 mmol), triethylamine (1.0 mL, 7.18 mmol), and DMF (50 mL) were combined in an oven dried 100 mL Schlenk flask equipped with a stir bar. The mixture was sparged with N₂ for approximately

15 minutes, then Pd(PPh₃)₂Cl₂ (60.7 mg, 0.087 mmol) and CuI (16.5 mg, 0.087 mmol) were added and the mixture was sparged for an additional 5 minutes. During this time a color change was from yellow to deep red was observed. The mixture was stirred at room temperature under an N₂ atmosphere and reaction progress was monitored by thin layer chromatography using an eluent mixture (1:1) of hexane and ethyl acetate. After 15h the mixture was filtered through celite and eluted further with ethyl acetate. The filtrate was then washed with water (3 x 75 mL), and the organic fraction was collected and dried over MgSO₄. Volatile organics were removed by rotary evaporation to provide an orange oil. The product was purified by column chromatography (silica gel stationary phase, hexane/ethyl acetate (1:1) as eluent. Collection of product fractions and removal of volatiles by rotary evaporation yielded an orange oil, which solidified upon standing overnight (584 mg, 90% yield). The ¹H NMR spectrum was consistent with product **B**. Minor impurities were observed and identified as ethyl acetate (*) and remaining trimethylsilylacetylene (**). The product was used in the subsequent step without further purification. ¹H NMR (400 MHz, Chloroform-d) δ 8.15 (s, 1H), 7.87 (dd, J = 5.8, 3.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.53 (dd, J = 5.6, 3.4 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.35 (q, J = 4.9, 4.4 Hz, 2H), 1.15 (d, J = 1.8 Hz, 19H), 1.09 (d, J = 2.1 Hz, 3H).



3-methyl-1-(4-((triisopropylsilyl)ethynyl)phenyl)-1H-benzo[d]imidazol-3-ium (C). TIPS-protected benzimidazole **B** (432 mg, 1.15 mmol) was added to an oven dried 100 mL Schlenk flask equipped with stir bar. The flask was fitted with a rubber septum, then evacuated and backfilled with nitrogen three times. After the third cycle, anhydrous THF (20 mL) and methyl iodide (1.02 mL, 16.3 mmol) were added and the reaction was stirred in an oil bath pre-heated

to 70 °C. After approximately 2h, a white precipitate was observed. The reaction was continued for an additional 2h. After cooling to room temperature, the mixture was filtered to collect the solid and washed with small portions of THF, followed by diethyl ether. The solid was dried under vacuum overnight to provide 227 mg of the desired TIPS-protected NHC (230 mg, 40 % yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 11.08 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.78 – 7.64 (m, 5H), 4.43 (s, 3H), 1.15 (s, 21H).



Alkyne-functionalized imidazolium salt was dissolved in THF (30 mM) in a glove box and mixed with a THF solution of potassium tert-butoxide (60 mM) for 2 hours for deprotonation and formation of 3-methyl-1-(4-((triisopropylsilyl)ethynyl)phenyl)-1H-benzo[d]imidazol-2-ylidene. The freshly prepared solution with the TIPS-alkyne-NHC was transferred to a vial in which the metal-coated Si wafers were deposited. After 18 hours, the wafers were removed from the glove box and rinsed three times with tetrahydrofuran, three times with distilled water and two times with ethanol. The samples were then flushed with N₂ for 5 minutes.

Removal of TIPS protecting group was conducted by immersing the TIPS-NHC covered surfaces in 0.01 M TBAF solution in THF. After 24 hours, the solution was removed, and the surfaces were rinsed with THF, TDW (Triple Distilled Water) and ethanol and dried with N₂ for 5 minutes.

Sonogashira coupling reactions were conducted by immersing Au films that were coated with alkyne-NHC in 10 ml THF solution containing 40 mg CuI (0.2 mmol), 10 mg Pd(PPh₃)₂Cl₂ (0.01 mmol), and 60 mg 4-nitrophenyltrifluoromethylsulfonate or 100 μl 4-fluoriodobenzene (0.8 mmol). The solutions were bubbled with N₂ for 20 min, followed by addition of 2 ml

triethylamine. The samples were put in a shaker at 120 rpm. After 24 hours, the solution was removed, and the surfaces were rinsed thoroughly with THF and ethanol and then dried with N₂ for 5 minutes.

X-ray photoelectron spectroscopy (XPS) measurements were performed using Kratos AXIS Supra spectrometer (Kratos Analytical) with Al K α monochromatic X-ray source (1486.6 eV). The XPS spectra were acquired with a takeoff angle of 90° (normal to analyzer); vacuum condition in the chamber was 2·10⁻⁹ Torr. High-resolution XPS spectra were acquired with a pass energy of 20 eV and step size of 0.1 eV. The binding energies were calibrated according to the Au4f_{7/2} XPS peak position (B.E. = 84.0 eV). Data were collected and analyzed by using ESCApe processing program (Kratos Analytical Ltd.) and Casa XPS (Casa Software Ltd.).

Polarization-modulation infrared reflection absorption spectroscopy (PM-IRRAS) measurements were performed at room temperature under positive nitrogen pressure in a reflection-absorption cell (Harrick, Inc.) with a PM-FTIR spectrometer (PMA-50 coupled to Vertex 70, Bruker). 2048 scans were performed with a resolution of 4 cm⁻¹ while using a mercury-cadmium-telluride (MCT) detector.

Tapping-mode AFM measurements were performed using a nanoIR3 system (Bruker).

UV-Vis measurements were performed using Cary Series UV-Vis-NIR spectrometer (Agilent Technologies) with data interval of 1 nm and scan rate of 600 nm/min. Samples for UV-Vis measurements were prepared by evaporating 1 nm Cr (as an adhesion layer) and 10 nm Au on a quartz slide, followed by deposition of TIPS-alkyne NHCs according to the previously described procedure.

Raman measurements were conducted using InVia Confocal Raman Microscope (Renishaw) equipped with a 785 nm laser (300 mW). The samples were exposed to 0.1% laser intensity for 30 sec. The measurements were conducted on Au SERS substrates (purchased from Silmeco) coated with TIPS-alkyne, or immersed in a potassium tert-butoxide (60 mM) THF solution for 18 hours as a control experiment.

Cyclic and linear voltammetry experiments were carried out using a BioLogic SP-150 potentiostat connected to a three-electrode setup. The working electrode was a typical Au surface coated with TIPS-alkyne molecules following removal of the protecting group, and the counter electrode was a Pt wire. The potential was measured against Ag quasi-reference electrode prepared by immersing an Ag wire in an aqueous solution containing 0.2M HCl and 0.25M FeCl₃. The measurements were performed in 0.1 M NaClO₄ in acetonitrile and a scan rate of 0.05 V/sec. Cyclic and linear voltammetry experiments for quantification of the NO₂ groups after Sonogashira coupling reactions were performed in 0.1 M HCl aqueous solutions and a scan rate of 0.05 V/sec.

Quantitative analysis of NHCs density based on LSV measurements:

Peak area = $6.4\text{E-}8 \text{ [A}\cdot\text{V]} / 0.05 \text{ [V}\cdot\text{sec}^{-1}] = 1.28\text{E-}6 \text{ [C]}$ (total charge)

$1.28\text{E-}6 \text{ [C]} / 1 \text{ electron} = 1.28\text{E-}6 \text{ [C]}$ (total charge normalized to # of molecules)

$1.28\text{E-}6 \text{ [C]} / 96485 \text{ [C}\cdot\text{mol}^{-1}] = 1.326\text{E-}11 \text{ [mol]}$

$1.326\text{E-}11 \text{ [mol]} / 1 \text{ [cm}^2] = 1.3 \pm 0.4\text{E-}11 \text{ [mol/cm}^2]$ (Surface coverage)

Quantitative analysis of NO₂ groups density based on LSV measurements:

Area = $1.75\text{E-}7 \text{ [A}\cdot\text{V]} / 0.05 \text{ [V}\cdot\text{sec}^{-1}] = 3.5\text{E-}6 \text{ [C]}$ (total charge)

$3.5\text{E-}6 \text{ [C]} / 6 \text{ electrons} = 5.83\text{E-}7 \text{ [C]}$ (total charge normalized to # of molecules)

$5.83\text{E-}7 \text{ [C]} / 96485 \text{ [C}\cdot\text{mol}^{-1}] = 6.05\text{E-}12 \text{ [mol]}$

$6.05\text{E-}12 \text{ [mol]} / 0.5 \text{ [cm}^2] = 1.2 \pm 0.5\text{E-}11 \text{ [mol/cm}^2]$ (Surface density)

Supplementary references

1. Altman, R. A., Koval, E. D. & Buchwald, S. L. Copper-catalyzed N-arylation of imidazoles and benzimidazoles. *J. Org. Chem.* **72**, 6190–6199 (2007).
2. Janíková, K., Jedinák, L., Volná, T. & Cankař, P. Chan-Lam cross-coupling reaction based on the Cu₂S/TMEDA system. *Tetrahedron* **74**, 606–617 (2018).

Table S1: Contact angle of Au film with and without alkyne-functionalized NHCs

Surface	Water contact angle
Clean Au	117°
TIPS-alkyne, as deposited	116°
TIPS-alkyne, following TIPS removal	95°
TIPS-alkyne, following Sonogashira reaction	86°

Supplementary figures

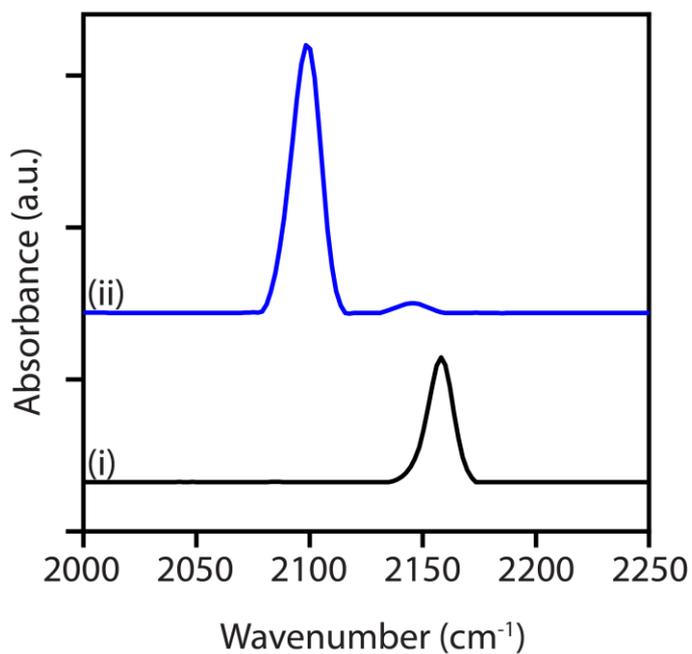


Figure S1: (i) PM-IRRAS spectrum of TIPS protected alkyne-functionalized benzimidazolium that was deprotonated and drop-casted on Si wafer; (ii) PM-IRRAS spectrum of drop-casted alkyne-functionalized benzimidazolium on Si wafer following deprotonation and TIPS removal.

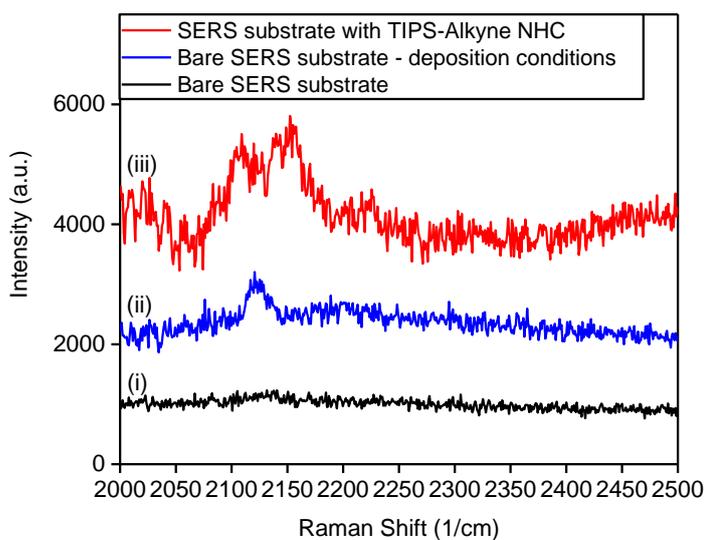


Figure S2: Raman scattering spectra of the bare Au SERS substrate (i), following exposure to deposition conditions (KO^tBu in THF) without TIPS-protected imidazolium precursor (ii); and following exposure to deposition conditions with the TIPS-protected imidazolium precursor (iii). Raman signal was detected at 2153 cm⁻¹ following surface anchoring of TIPS-protected NHC and this signal was correlated to the alkyne-phenyl group.

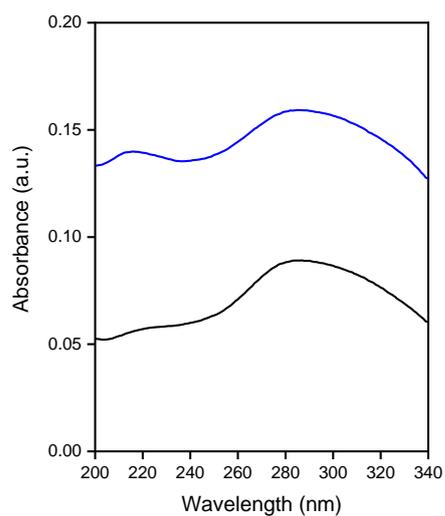


Figure S3: UV-Vis absorption measurements of Au film that was evaporated on quartz slide. Measurements were conducted before and after surface anchoring of TIPS-protected NHC (black and blue colored spectra, respectively). The additional peak that was detected at 220 nm following surface anchoring of TIPS-protected NHC indicates the presence of NHCs on the Au surface.

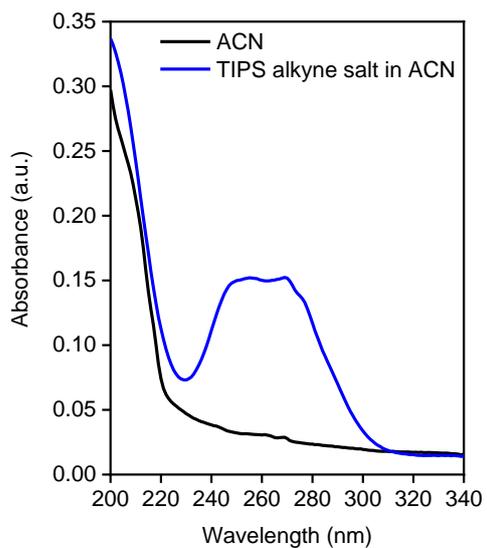


Figure S4: UV-Vis absorption measurements of acetonitrile and TIPS-protected imidazolium salt in acetonitrile (black and blue colored spectra, respectively).

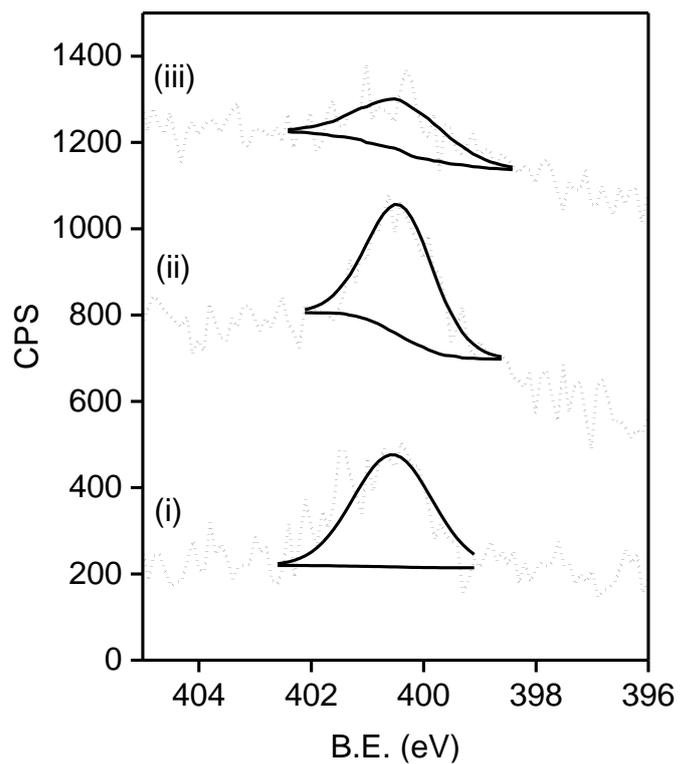


Figure S5: N1s XPS spectra of TIPS-protected NHCs that were anchored on Au film before (i) and after annealing to 100 (ii) and 200 °C (iii) for 2 h under N₂ environment. TIPS-protected NHCs showed high stability following annealing to 100 °C with no indication for NHCs desorption or deformation. Exposure of the sample to 200 °C led to partial desorption of NHCs.

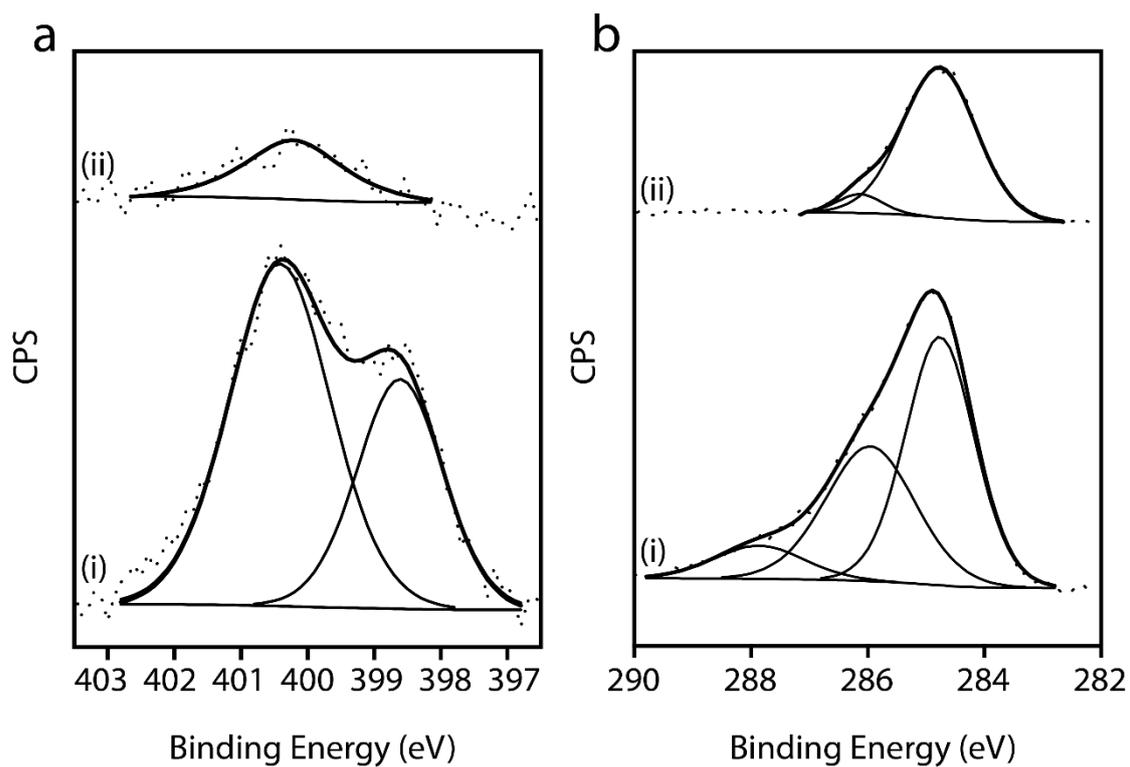


Figure S6: N1s (a) and C1s (b) XPS spectra of alkyne-NHCs that were deposited on Au film without (i) and with (ii) TIPS protection of the alkyne group.

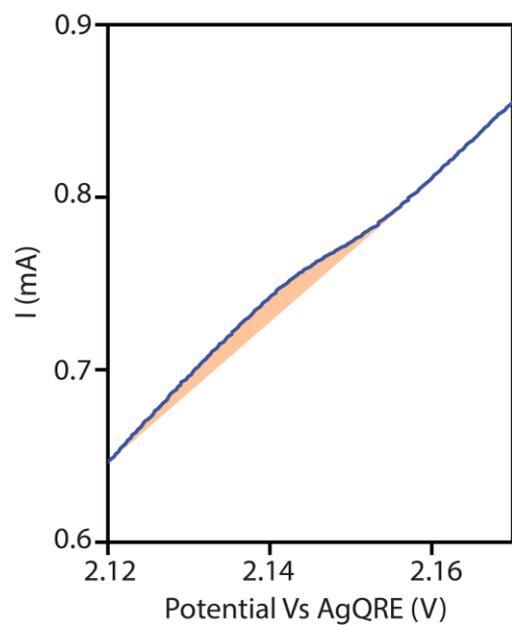


Figure S7: Linear sweep voltammogram of alkyne-NHCs SAM on Au film. LSV conditions: 0.1M NaClO₄ and scan rate of 0.05 V/sec.

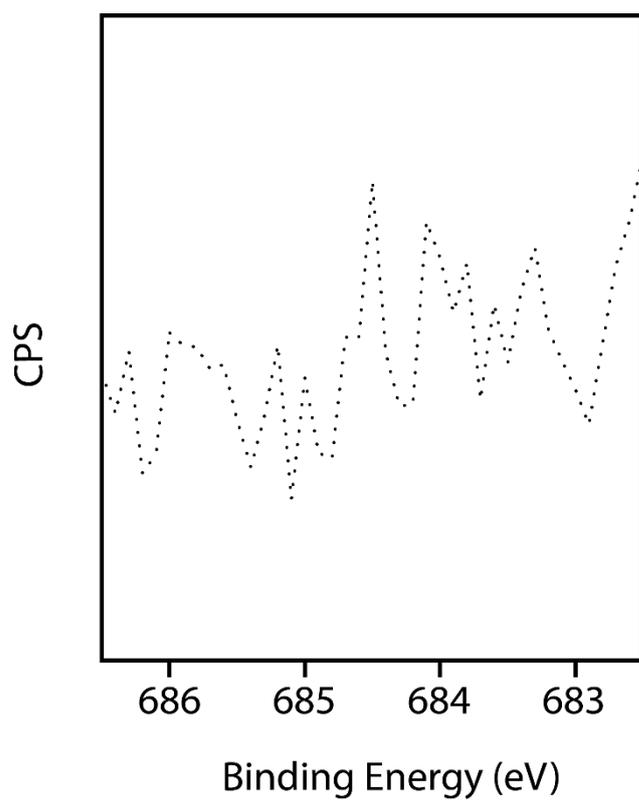


Figure S8: F1s XPS signal following exposure to Sonogashira-like reaction with 4-fluoriodobenzene without the presence of surface-anchored alkyne-NHCs on the Au film.

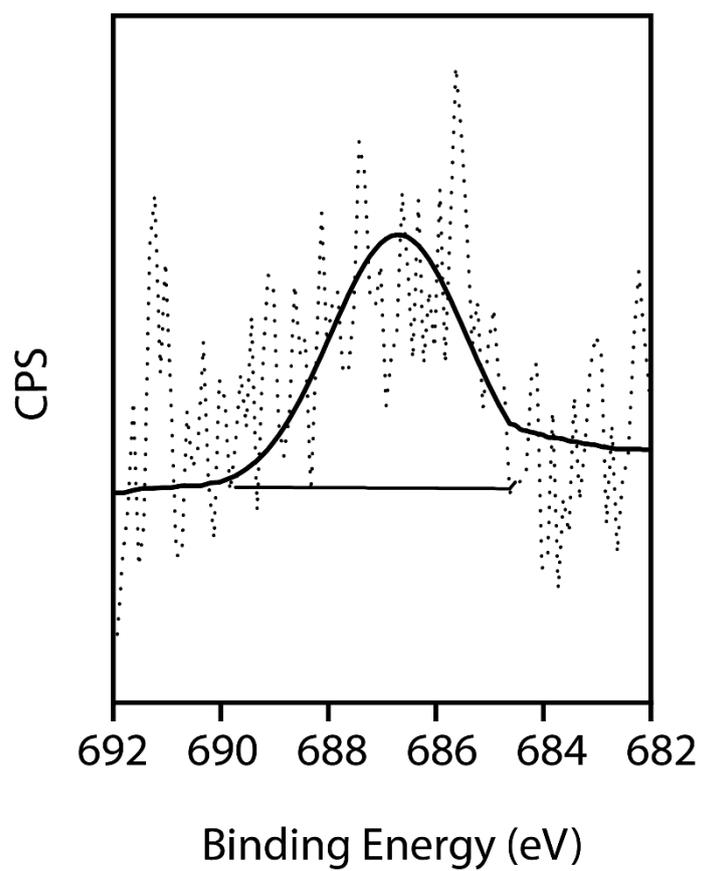


Figure S9: F1s XPS signal of 4-fluoriodobenzene drop-casted on a silicon wafer.

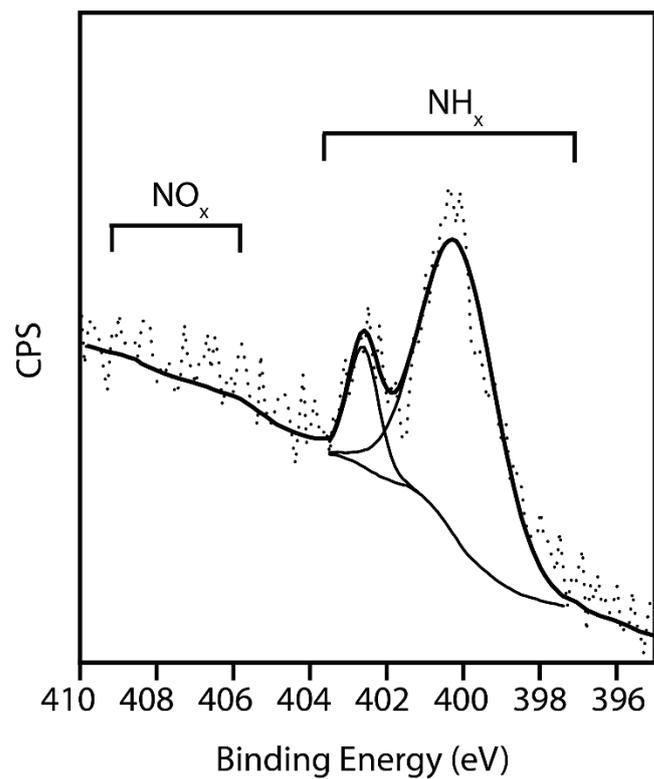


Figure S10: N1s XPS signal of Sonogashira-like coupling reaction with 4-nitrophenyltrifluoromethylsulfonate without surface-anchored alkyne-NHCs on the Au film.

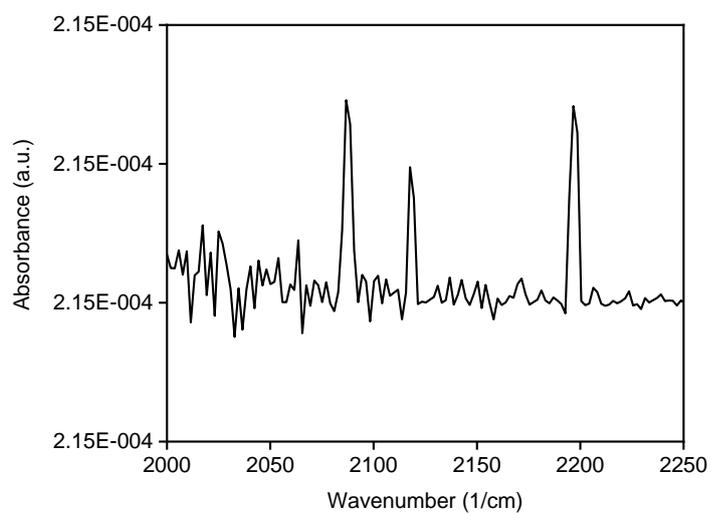


Figure S11: PM-IRRAS signal of alkyne-NHCs following the Sonogashira coupling reaction with 4-nitrophenyltriflate.

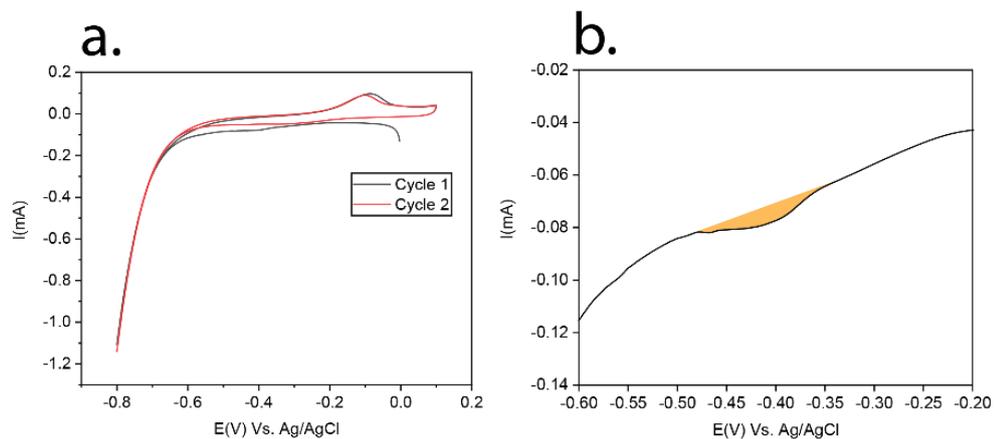


Figure S12: (a) Cyclic voltammogram of alkyne-NHCs SAM on Au film following Sonogashira coupling with 4-nitrophenyltriflate. (b) Linear sweep voltammogram used for quantitative analysis of nitro reduction. CV and LSV conditions: 0.1 M HCl and scan rate of 0.05 V/sec.

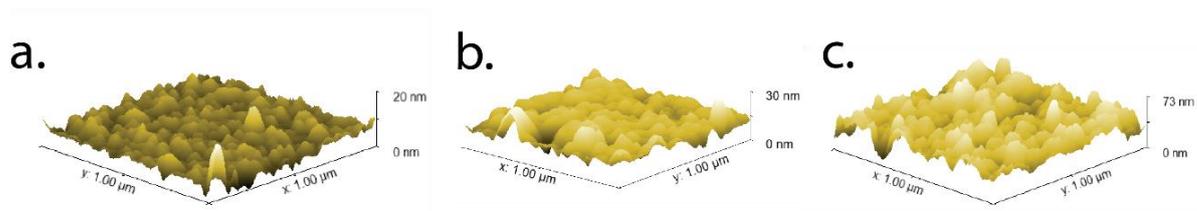


Figure S13: AFM topography maps of (a) TIPS-protected NHCs on Au film; (b) alkyne-functionalized NHCs on Au film, following TIPS removal; (c) Sonogashira coupling reaction of alkyne-functionalized NHC with 4-nitrophenyltriflate.