Supporting Information for

Support Curvature and Conformational Freedom Control Chemical Reactivity of Immobilized Species

Tino Zdobinsky, Pradipta Sankar Maiti and Rafal Klajn*

Department of Organic Chemistry
Weizmann Institute of Science
Rehovot 76100, Israel

Experimental Section

General Information
All chemical reagents were purchased from commercial suppliers and used without purification. Dichloromethane (DCM), 1,2-dichloroethane, N,N-dimethylformamide (DMF), dioxane, N,N-diisopropylethylamine (DIPEA) and triethylamine (TEA) were heated at reflux for 1 h over calcium hydride and distilled. Preparative low pressure chromatography was performed by using silica gel 60 µm (230-400 mesh, Merck). TLC analysis was performed on silica gel 60 F254 (Merck) and detection was conducted under UV light (254 nm) and staining with potassium permanganate. NMR spectra were recorded on an AVIII 300 MHz NMR (Bruker) spectrometer. Transmission electron microscopy was done on a CM120 Super Twin TEM (Philips) operating at 120 kV. High-resolution FD-mass spectra were measured on a Waters Micromass GCT_Premier Mass spectrometer. High resolution ESI-mass spectra were measured on a SYNAPT High Definition, Q-TOF Mass Spectrometer. UV-Vis spectra were recorded on a UV-3600 UV-VIS-NIR spectrophotometer (Shimadzu). As UV light source for the irradiation experiments was used a 4 W hand-held UV lamp (UVP, LLC; Upland, CA; model number UVGL-25). The abbreviations used for the proton spectra multiplicities: s, singlet; br, broad; d, doublet; dd, double doublet; t, triplet; q, quartet; m, multiplet; ψ, pseudo. Further abbreviations used: ethyl acetate, EA; hexane, Hex; ethanol, EtOH; methanol, MeOH; tetrahydrofuran, THF; acetyl, Ac; N,N'-dimethylthlylenediamine, DMED; dodecylamine, DDA; didodecyldiammonium bromide, DDAB; N,N-dimethylacetamide, DMAc; HV, high vacuum; Mesyl, Ms; tetrabutylammonium borohydride, TBAB; minutes, min.
Synthetic Procedures

Reagents and conditions: (a) 1.) Zn, Me₂Cl₂Si, DMAc, 1,2-dichloroethane, reflux, 2 h, 2.) AcCl, 50°C, 15 min, 64%; (b) 4-pentyn-1-ol, Pd(PPh₃)₂Cl₂, Cul, piperidine, toluene, 30°C, 16 h, 93%; (c) H₂, EtOH, 18 h, 96%; (n=1) NaI, Cul, DMED, n-BuOH, reflux, 18 h, 77%; (e) n=1) Ms-Cl, DIPEA, DCM, -20°C-rt, 17 h, 91%; n=4) Ms-Cl, DIPEA, DCM, -20°C-rt, 16 h, 88%; (f) AcSH, Cs₂CO₃, DMF, 15 h, rt, 95% (n=1), 91% (n=4).

S-(4-iodophenyl) ethanethioate (5)
To a stirred suspension of zinc (powder; 197 mg, 3.01 mmol) and dichlorodimethylsilane (280 µL, 2.31 mmol) in 1,2-dichloroethane (5 mL) was added a solution of 4-iodobenzene-sulfonyl chloride (4) (222 mg, 0.73 mmol) and DMAc (200 µL, 2.16 mmol) in 1,2-dichloroethane (5 mL). The mixture was stirred at 80°C for 80 minutes and additional dichlorodimethylsilane (200 µL, 1.65 mmol) was added. After further 40 minutes the reaction mixture was cooled to 50°C, and acetyl chloride (200 µL, 2.81 mmol) was added. After further 15 min the reaction mixture was poured into water. The aqueous layer was extracted with DCM, and the combined organic layers were dried (MgSO₄), filtered and evaporated to dryness. After column chromatography the thioacetate 5 (131.1 mg, 0.47 mmol, 64%) was obtained as colorless solid.

H NMR (CDCl₃): δ = 2.42 (s, 3H), 7.12 (d, J = 8.39 Hz, 2H), 7.73 (d, J = 8.35 Hz, 2H).

C NMR (CDCl₃): δ = 30.28, 95.99, 127.73, 135.98, 138.37, 193.27. Rf: 0.39 (Hex:DCM, 1:1).

5-(4-Bromophenyl)pent-4-yn-1-ol (7)
To 1-bromo-4-iodobenzene (6) (5.01 g, 17.72 mmol) and 4-pentyn-1-ol (1.70 mL, 18.37 mmol) in toluene (25 mL) was added piperidine (3.45 mL, 34.9 mmol) and the mixture was degassed with argon for 10 minutes. PdCl₂(PPh₃)₂ (200 mg, 0.28 mmol) and Cul (135 mg, 0.71 mmol) were added and the mixture was stirred at 30°C overnight. Afterwards the volatiles were evaporated and the residue was purified by column chromatography (Hex:EA, 3:1). The alcohol 7 (3.96 g, 16.56 mmol, 93%) was obtained as orange/brown solid.
$^1$H NMR (CDCl$_3$): $\delta = 1.82$ (q, $J = 6.6$ Hz, 2H), 2.10 (s, br., 1H), 2.49 (t, $J = 7.0$ Hz, 2H), 3.77 (t, $J = 6.2$ Hz, 2H), 7.22 (d, $J = 8.5$ Hz, 2H), 7.38 (d, $J = 8.5$ Hz, 2H). $^{13}$C NMR (CDCl$_3$): $\delta = 15.98$, 31.26, 61.59, 80.10, 90.69, 121.78, 122.70, 131.45, 133.02. $R_f$: 0.13 (Hex:EA, 3:1).

5-(4-Bromophenyl)pentan-1-ol (8a)

To the alkyne 7 (3.43 g, 14.4 mmol) in EtOH (150 mL) was added Pd/C 10% (226.1 mg) and the mixture was degassed by applying vacuum and refilling with hydrogen several times. Afterwards the reaction mixture was stirred under hydrogen (1 bar) for 40 h. Further Pd/C was added, the degassing procedure repeated and the reaction was stirred for another 64 hours under hydrogen. The crude mixture was filtrated over Celite and purified by column chromatography (Hex:EA, 3:1). The saturated alcohol 8a (2.12 g, 8.71 mmol, 60%) was obtained as colorless liquid.

$^1$H NMR (CDCl$_3$): $\delta = 1.37$ (m, 2H), 1.52-1.65 (m, 4H), 2.55 (t, $J = 7.6$ Hz, 2H), 3.61 (t, $J = 6.5$ Hz, 2H), 7.02 (d, $J = 8.1$ Hz, 2H), 7.37 (d, $J = 8.2$ Hz, 2H). $^{13}$C NMR (CDCl$_3$): $\delta = 25.32$, 31.09, 32.52, 35.28, 62.72, 119.35, 130.18, 131.30, 141.49. $R_f$: 0.13 (Hex:EA, 3:1).

2-(4-Iodophenyl)ethanol (9b)

To a mixture of 2-(4-bromophenyl)ethanol (8b) (2.20 g, 10.93 mmol) in dioxane (10 mL) were added CuI (208 mg, 1.09 mmol), sodium iodide (3.16 g, 21.1 mmol) and DMED (216 µL). The reaction mixture was refluxed for 18 h. Aqueous ammonia solution (5%, 30 mL) was added and the mixture was extracted two times with EA (30 mL). The combined organic extracts were washed with aqueous ammonia solution and water. The unified organic phases were dried over MgSO$_4$ and concentrated to dryness. The aryl iodide 9b (2.60 g, 10.49 mmol, 96%) as slightly brown solid.

$^1$H NMR (CDCl$_3$): $\delta = 2.37$ (s, br., 1H), 2.75 (t, $J = 6.55$ Hz, 2H), 3.75 (t, $J = 6.61$ Hz, 2H), 6.94 (d, $J = 8.01$ Hz, 2H), 7.60 (d, $J = 8.26$ Hz, 2H). $^{13}$C NMR (CDCl$_3$): $\delta = 38.62$, 63.20, 91.68, 131.15, 137.54, 138.38. $R_f$: 0.32 (DCM).

5-(4-Iodophenyl)pentan-1-ol (9a)

To a mixture of the aryl bromide 8a (1.92 g, 7.89 mmol) in n-butanol (15 mL) were added CuI (150 mg, 0.79 mmol), sodium iodide (2.365 g, 15.78 mmol) and DMED (170 µL, 1.58 mmol). The reaction mixture was refluxed for 18 h. Aqueous ammonia solution (5%, 30 mL) was added and the mixture was extracted two times with EA (30 mL). The combined organic extracts were washed with aqueous ammonia solution and water. The organic phases were dried over MgSO$_4$ and concentrated to dryness. The crude product was purified by column chromatography (DCM) to obtain the aryl iodide 9a (1.76 g, 6.07 mmol, 77%) as slightly brown solid.

$^1$H NMR (CDCl$_3$): $\delta = 1.37$ (m, 2H), 1.52-1.65 (m, 4H), 2.55 (t, $J = 7.7$ Hz, 2H), 3.61 (t, $J = 6.5$ Hz, 2H), 6.91 (d, $J = 8.2$ Hz, 2H), 7.57 (d, $J = 8.26$ Hz, 2H). $^{13}$C NMR (CDCl$_3$): $\delta = 25.32$, 31.06, 32.55, 35.58, 62.82, 90.66, 130.56, 137.29, 142.16. $R_f$: 0.13 (Hex:EA, 3:1).
4-Iodophenethyl methanesulfonate (10b)
To a solution of the aryl iodide 9b (2.60 g, 10.5 mmol) in DCM (100 mL) was added DIPEA (2.50 mL, 15.1 mmol) at room temperature and the mixture was stirred for 30 min. The solution was cooled to −20°C and stirred at the same temperature for 1 h after Ms-Cl (1.10 mL, 13.9 mmol) was added dropwise. The mixture was allowed to warm up to room temperature and stirred for further 16 h at this temperature. Afterwards water (100 mL) was added and the phases were separated. The water layer was extracted with DCM (2x 50 mL), the combined organic phases were dried over MgSO4 and concentrated to dryness. Column chromatography (Hex:EA, 3:1) affords the mesylate 10b (3.109 g, 9.53 mmol, 91%) as a white solid.

1H NMR (CDCl3): δ = 2.86 (s, 3H), 2.97 (t, J = 6.87 Hz, 2H), 4.36 (t, J = 6.83 Hz, 2H), 6.97 (d, J = 8.30 Hz, 2H), 7.62 (d, J = 8.37 Hz, 2H). 13C NMR (CDCl3): δ = 35.12, 37.40, 69.75, 92.46, 131.06, 136.10, 137.77. Rf: 0.56 (DCM).

5-(4-Iodophenyl)pentyl methanesulfonate (10a)
To a solution of the alcohol 9a (1.55 g, 5.35 mmol) in DCM (5 mL) was added TEA (0.96 mL, 6.96 mmol) at room temperature and the mixture was stirred for 30 min. The solution was cooled to −20°C and stirred at the same temperature for 1 h after Ms-Cl (550 µL, 6.96 mmol) was added dropwise. The mixture was allowed to warm up to room temperature and stirred for further 16 h at this temperature. Afterwards water (100 mL) was added and the phases were separated. The water layer was extracted with DCM (2x 50 mL), the combined organic phases were dried over MgSO4 and concentrated to dryness. Column chromatography (DCM:Hex, 3:1) affords the mesylate 10a (1.729 g, 4.69 mmol, 87.8%) as a slightly brown solid.

1H NMR (CDCl3): δ = 1.40 (m, 2H), 1.61 (m, 2H), 1.74 (m, 2H), 2.54 (t, J = 7.7 Hz, 2H), 2.96 (s, 3H), 4.18 (t, J = 6.5 Hz, 2H), 6.90 (d, J = 8.1 Hz, 2H), 7.56 (d, J = 8.2 Hz, 2H). 13C NMR (CDCl3): δ = 24.96, 28.97, 30.61, 35.15, 37.33, 70.00, 90.82, 130.20, 137.35, 141.79. HR-FD-MS: calculated: 367.9943; found: 367.9952. Rf: 0.35 (DCM).

S-[2-(4-Iodophenyl)ethyl]thioacetate (11b)
To a solution of the mesylate 10b (3.04 g, 9.32 mmol) in DMF (100 mL) was added Cs2CO3 (9.77 g, 30.0 mmol) and the suspension was stirred for 30 minutes. Thioacetic acid (2.14 mL, 30 mmol) was then added and the mixture was stirred at room temperature overnight. The mixture was poured into water and extracted with diethyl ether (3x 100 mL). The combined organic phases were dried over MgSO4 and concentrated to dryness. Column chromatography (Hex:EA, 20:1) affords the thioacetate 11b (2.71 g, 4.69 mmol, 87.8%) as a slightly brown solid.

1H NMR (CDCl3): δ = 2.31 (s, 3H), 2.79 (t, J = 7.58 Hz, 2H), 3.06 (t, J = 7.63 Hz, 2H), 6.95 (d, J = 8.32 Hz, 2H), 7.60 (d, J = 8.34 Hz, 2H). 13C NMR (CDCl3): δ = 30.20, 30.74, 35.33, 91.88, 130.69, 137.55, 139.54, 195.43. HR-ESI-MS: calculated: 306.9654; found: 306.9640. Rf: 0.27 (Hex:EA, 20:1).
**S-(5-(4-iodophenyl)pentyl) ethanethioate (11a)**

To a solution of the mesylate 10a (1.68 g, 4.56 mmol) in DMF (50 mL) Cs₂CO₃ (4.47 g, 13.68 mmol) was added and the suspension was stirred for 30 minutes. Thioacetic acid (978 µL, 13.68 mmol) was then added and the mixture was stirred at room temperature overnight. The mixture was poured into water and extracted with diethyl ether (3x 100 mL). The combined organic phases were dried over MgSO₄ and concentrated to dryness. Column chromatography (Hex:DCM, 1:1) affords the thioacetate 11a (1.46 g, 4.20 mmol, 92%) as pale brown solid.

**¹H NMR (CDCl₃):** δ = 1.37 (m, 2H), 1.58 (m, 4H), 2.31 (s, 3H), 2.53 (t, J = 7.7 Hz, 2H), 2.84 (t, J = 7.4 Hz, 2H), 6.90 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.2 Hz, 2H).

**¹³C NMR (CDCl₃):** δ = 28.27, 28.98, 29.37, 30.69, 30.71, 35.22, 90.74, 130.56, 137.30, 142.03, 195.90.

**HR-FD-MS:** calculated: 348.0045; found: 348.0056.

**Rf:** 0.45 (Hex:DCM, 1:1).

**Reagents and conditions:** (a) trimethylsilylacetylene, Pd(PPh₃)₂Cl₂, CuI, piperidine, TEA, 110°C, 17 h, 94%; (b) K₂CO₃, THF, MeOH, rt, 6 h, 100%; (c) R-Ar-I (5, 11a, 11b), Pd(PPh₃)₂Cl₂, Cu, PPh₃, TEA, 50°C, 14 h, (15a 75%; 15b 70%; 15c 74%).

**Trimethyl anthracenylethylnilsilane (13)**

9-Bromoanthracene (12) (402 mg, 1.56 mmol), Pd(PPh₃)₂Cl₂ (105 mg, 0.15 mmol) and Cul (33.6 mg, 0.176 mmol) were dried under HV in a two-neck flask. Piperidine (1.2 mL), TEA (12 mL) and TMS-acetylene (600 µL) were added slowly, and the mixture was debubbled with argon for 10 minutes. Afterwards the reaction mixture was stirred and heated at 110°C overnight (17 h). Saturated NH₄Cl solution (10 mL) was added and the resulting mixture was extracted with Hex (3x 15 mL). The organic phase was dried over MgSO₄ and the solvent was evaporated. The residue was subjected to column chromatography on silica gel (Hex + 0.5% toluene) to obtain the silane 13 as a yellow solid (402 mg, 1.47 mmol, 94%).

**¹H NMR (CDCl₃):** δ = 0.44 (s, 9H), 7.50 (ddd, J = 1.27 Hz, J = 6.67 Hz, J = 8.01 Hz, 2H), 7.60 (ddd, J = 1.36 Hz, J = 6.63 Hz, J = 8.68 Hz, 8.00 (m, 2H), 8.42 (s, 1H), 8.57 (m, 2H).

**¹³C NMR (CDCl₃):** δ = 0.43, 101.68, 106.33, 117.24, 125.78, 126.83, 126.91, 128.03, 131.19, 133.03. Rf: 0.21 (Hex + 0.5% toluene).

**9-Ethynylanthracene (14)**

The silane 13 (413 mg, 1.50 mmol) and potassium carbonate (1.43 g, 7.78 mmol) were combined in THF:MeOH (1:1, 30 mL). The mixture was stirred for 16 h and poured into a mixture of ether and water (1:1, 30 mL). The phases were separated and the organic phase was dried over MgSO₄.
and concentrated. The crude solid was passed through a silica gel plug (Hex) to yield 9-ethynylanthracene (14) (299 mg, 1.48 mmol, 99%) as yellow solid. Due to the instability of this compound over prolonged storage it is used directly for the following reaction.

\(^1\)H NMR (CDCl\(_3\)): δ = 4.06 (s, 1H), 7.53 (Pt, J = 7.45 Hz, 2H), 7.65 (dd, J = 7.47 Hz, J = 8.67 Hz, 2H), 7.99 (d, J = 8.33 Hz, 2H), 8.39 (s, 1H), 8.68 (d, J = 8.69 Hz, 2H). \(^1^3\)C NMR (CDCl\(_3\)): δ = 80.58, 88.42, 116.11, 125.74, 126.65, 126.94, 128.38, 128.80, 131.09, 133.27. R\(_f\) 0.21 (Hex + 0.5% toluene).

S-(4-(anthracen-9-ylethynyl)phenyl) ethanethioate (15a)

To the acetylene 14 (294 mg, 1.46 mmol) dissolved in TEA (15 mL), was added the iodide 5 (308 mg, 2.18 mmol), PdCl\(_2\)(PPh\(_3\))\(_2\) (28.4 mg, 40.0 µmol), CuI (21.8 mg, 0.12 mmol) and PPh\(_3\) (33.9 mg, 0.13 mmol). The mixture was degassed with argon for 10 min and afterwards heated to 50°C for 14 h. After cooling down to room temperature the reaction mixture was filtered over Celite and the solvent was evaporated. Column chromatography (Hex:DCM, 1:1) afforded compound 15a (388 mg, 1.10 mmol, 75%) as yellow solid.

\(^1\)H-NMR (CDCl\(_3\)): 2.47 (s, 3H), 7.47-7.54 (m, 4H), 7.58-7.64 (m, 2H), 7.80 (d, J = 8.2 Hz, 2H), 8.00 (d, J = 8.4 Hz, 2H), 8.42 (s, 1H), 8.62 (d, J=8.7 Hz, 2H). \(^1^3\)C-NMR (CDCl\(_3\)): δ = 30.36, 88.12, 99.94, 116.80, 124.88, 125.76, 126.65, 128.17, 128.80, 131.09, 132.21, 132.70, 134.44, 193.55. HR-FD-MS: calculated: 352.0922; found: 352.0933. R\(_f\) 0.40 (Hex).

S-4-(anthracen-9-ylethynyl)phenethyl ethanethioate (15b)

To the acetylene 14 (328 mg, 1.62 mmol) dissolved in TEA (20 mL), was added the iodide 11b (717 mg, 2.34 mmol), PdCl\(_2\)(PPh\(_3\))\(_2\) (31.1 mg, 44.3 µmol), CuI (38.9 mg, 0.204 mmol) and PPh\(_3\) (37.5 mg, 0.14 mmol). The mixture was degassed with argon for 10 min and afterwards heated to 50°C for 15 h. After cooling down to room temperature the solvent was evaporated. Column chromatography (Hex:DCM, 1:1) afforded compound 15b (433 mg, 1.14 mmol, 70%) as yellow solid.

\(^1\)H NMR (CDCl\(_3\)): δ = 2.36 (s, 3H), 2.93 (t, J = 7.66 Hz, 2H), 3.17 (t, J = 7.49 Hz, 2H), 2.30 (d, J = 8.15 Hz, 2H), 7.51 (ddd, J = 7.43 Hz, J = 6.58 Hz, J = 0.98 Hz, 2H), 7.61 (ddd, J = 7.57 Hz, J = 6.64 Hz, J = 1.28 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H), 8.00 (d, J = 8.42 Hz, 2H), 8.41 (s, 1H), 8.67 (d, J = 8.68 Hz, 2H). \(^1^3\)C NMR (CDCl\(_3\)): δ = 30.30, 30.74, 35.79, 86.26, 100.76, 117.38, 121.86, 125.71, 126.62, 126.81, 127.68, 128.74, 128.86, 131.23, 131.82, 132.61, 140.55, 195.63. HR-FD-MS: calculated: 380.1235; found: 380.1247. R\(_f\) 0.90 (DCM), 0.24 (Hex:DCM, 1:1), 0.15 (Hex:DCM, 2:1).

S-(5-(4-(anthracen-9-ylethynyl)phenyl)pentyl) ethanethioate (15c)

The acetylene 14 (311 mg, 1.53 mmol) and the iodine 11a (595 mg, 1.71 mmol) were dissolved in dry TEA (20 mL) and the solution was degassed with argon for 10 minutes. Afterwards PdCl\(_2\)(PPh\(_3\))\(_2\) (50.8 mg, 72.4 µmol), CuI (29.0 mg, 152 µmol) and PPh\(_3\) (57.2 mg, 218 µmol) were added and the solution degassed for further 5 minutes. The mixture was heated for 14 h to 50°C and afterwards filtrated over Celite. The solvent was evaporated and the crude product purified by
column chromatography (Hex: DCM, 3:2) to obtain compound 15c (478 mg, 1.13 mmol, 74%) as yellow oil.

$^1$H NMR (CDCl$_3$): $\delta = 1.41$ (m, 2H), 1.57-1.70 (m, 4H), 2.36 (s, 3H), 2.64 (t, $J = 7.6$ Hz, 2H), 2.89 (t, $J = 7.3$ Hz, 2H), 7.24 (d, $J = 7.9$ Hz, 2H), 7.52 (Ψt, $J = 7.5$ Hz, 2H), 7.63 (Ψt, $J = 7.6$ Hz, 2H), 7.73 (d, $J = 7.8$ Hz, 2H), 8.00 (d, $J = 8.3$ Hz, 2H), 8.38 (s, 1H), 8.72 (d, $J = 8.6$ Hz, 2H).

$^{13}$C NMR (CDCl$_3$): $\delta = 28.44, 29.10, 29.47, 30.74, 30.76, 35.78, 85.94, 101.16, 117.59, 120.98, 125.73, 126.62, 126.89, 127.62, 128.79, 131.17, 132.61, 143.27, 196.00.

HR-FD-MS: calculated: 422.1704; found: 422.1713.

$R_f$: 0.57 (Hex:EA, 1:1).

Reagents and conditions: $h\nu$ (365 nm), toluene, 21 h, 79% (16a), 83% (16b), 82% (16c).

S-((9s,10s)-11-((4-(acetylthio)phenyl)-12-(anthracen-9-yl)-9,10-dihydro-9,10-ethenoanthracen-9-yl)ethyl)phenethyl ethanethioate (16a)

20.0 mg of the acetylene 15a (56.0 µmol) were dissolved in toluene (1.5 mL) and irradiated for 21 h with long-wave UV light (365 nm). The crude mixture was transferred to a silica-gel column and purified using toluene:dichloromethane (1:1). The photocycloadduct 16a (15.9 mg, 23 µmol, 79%) were obtained as slightly yellow solid.

$^1$H NMR (CDCl$_3$): $\delta = 2.26$ (s, 3H), 2.27 (s, 3H), 5.74 (s, 1H), 6.47 (d, $J = 8.4$ Hz, 2H), 6.93 (d, $J = 8.7$ Hz, 2H), 7.00-7.11 (m, 8H), 7.14-7.25 (m, 6H), 7.32 (d, $J = 1.4$ Hz, $J = 6.3$ Hz, $J = 7.8$ Hz, 2H), 7.59 (dd, $J = 1.2$ Hz, $J = 6.8$ Hz, 2H), 7.69 (dd, $J = 1.5$ Hz, $J = 6.9$ Hz, 2H), 7.92 (d, $J = 8.5$ Hz, 2H), 8.35 (s, 1H).

$^{13}$C NMR (CDCl$_3$): $\delta = 30.09, 30.22, 56.08, 58.47, 86.42, 90.45, 122.77, 123.09, 123.75, 125.10, 125.29, 125.53, 125.73, 126.41, 126.51, 126.75, 127.04, 127.51, 128.39, 130.43, 131.29, 131.94, 132.34, 133.76, 133.83, 139.04, 144.42, 144.94, 145.63, 148.04, 193.65, 194.12. $R_f$: 0.41 (Tol:DCM, 2:1), 0.51 (Hex:DCM, 2:1).

S-((9s,10s)-11-((4-(2-(acetylthio)ethyl)phenyl)-12-(anthracen-9-yl)-9,10-dihydro-9,10-ethenoanthracen-9-yl)ethyl)phenethyl ethanethioate (16b)

The acetylene 15b (55.6 mg, 145 µmol) was dissolved in toluene (4 mL) and irradiated for 21 h with long-wave UV light (365 nm). The crude mixture was transferred to a silica-gel column and purified using toluene:dichloromethane (1:1). The photocycloadduct 16b (45.7 mg, 60 µmol, 83%) was obtained as slightly yellow solid.

$^1$H NMR (CDCl$_3$): $\delta = 2.21$ (s, 3H), 2.31 (s, 3H), 2.56 (t, $J = 7.45$ Hz, 2H), 2.72 (t, $J = 7.62$ Hz, 2H), 2.87 (t, $J = 7.70$ Hz, 2H), 2.99 (t, $J = 7.63$ Hz, 2H), 5.72 (s, 1H), 6.39 (d, $J = 8.23$ Hz, 2H), 6.74 (d, $J = 8.41$ Hz, 2H), 6.91 (m, 4H), 7.06 (Ψd, $J = 3.78$ Hz, 4H), 7.17 (m, 4H), 7.31 (m, 2H), 7.34 (t, $J = 7.62$ Hz, 2H), 7.59 (d, $J = 8.53$ Hz, 2H), 7.69 (d, $J = 8.54$ Hz, 2H), 7.94 (d, $J = 8.6$ Hz, 2H), 8.35 (s, 1H).
7.58 (d, J = 6.95 Hz, 2H), 7.70 (d, J = 7.25 Hz, 2H), 7.92 (d, J = 8.34 Hz, 2H), 8.35 (s, 1H).

$^{13}$C NMR (CDCl$_3$): $\delta$ = 30.14, 30.28, 30.70, 30.81, 35.38, 35.69, 56.42, 58.47, 84.60, 91.03, 120.90, 122.87, 123.06, 125.09, 125.24, 125.34, 125.62, 126.51, 126.95, 128.15, 128.25, 128.41, 130.68, 131.46, 131.55, 132.13, 133.20, 136.25, 138.74, 139.83, 144.18, 144.79, 145.47, 148.53, 195.71, 195.81. $R_f$: 0.48 (Hex:DCM, 2:1).

S-(5-(4-((9s,10s)-11-((9s,10s)-11-(4-(acetylthio)pentyl)phenyl)-12-(anthracen-9-yl)-9,10-dihydro-9,10-ethenoanthracen-9-yl)ethynyl)phenyl)pentyl) ethanethioate (16c)

48.1 mg of 15c (113 µmol) were dissolved in toluene (4 mL) and irradiated for 21 h with long-wave UV light (365 nm, ~0.7 mW/cm$^2$). The crude mixture was transferred to a silica-gel column and purified using toluene/dichloromethane (1:1). The photocycloadduct 16c (39.2 mg, 46 µmol, 82%) was obtained as slightly yellow solid.

$^1$H NMR (CDCl$_3$): $\delta$ = 1.16-1.69 (m, 12H), 2.28 (s, 3H), 2.32 (s, 3H), 2.32 (t, $J$ = 7.3 Hz, 3H), 2.46 (t, $J$ = 7.6 Hz, 2H), 2.75 (t, $J$ = 7.4 Hz, 2H), 2.83 (t, $J$ = 7.3 Hz, 2H), 5.74 (s, 1H), 6.39 (d, $J$ = 8.3 Hz, 2H), 6.69 (d, $J$ = 8.2 Hz, 2H), 6.84 (d, $J$ = 8.1 Hz, 2H), 6.91 (d, $J$ = 8.2 Hz, 2H), 7.06 – 7.10 (m, 4H), 7.13-7.23 (m, 4H), 7.29-7.36 (m, 2H), 7.59 (dd, $J$ = 1.5 Hz, $J$ = 6.6 Hz, 2H), 7.72 (dd, $J$ = 1.5 Hz, $J$ = 6.8 Hz, 2H), 7.93 (d, $J$ = 8.5 Hz, 2H), 8.35 (s, 1H). $^{13}$C NMR (CDCl$_3$): $\delta$ = 28.35, 28.37, 29.05, 29.08, 29.34, 29.43, 29.83, 30.52, 30.74, 30.78, 35.28, 35.82, 56.44, 58.45, 84.15, 91.22, 120.03, 122.86, 123.03, 125.04, 125.18, 125.24, 125.54, 126.33, 126.43, 127.05, 127.96, 128.03, 128.35, 130.70, 131.36, 131.47, 133.41, 135.43, 141.27, 142.43, 143.76, 144.87, 145.60, 148.65, 196.15, 196.18. $R_f$: 0.51 (Hex:DCM, 2:1).

Preparation of 2.45 (± 0.28) nm Au NPs

DDAB stock solution was first prepared by dissolving DDAB (833 mg, 1.80 mmol) in toluene (18 mL) (with sonication). HAuCl$_4$·3H$_2$O (50 mg, 125 µmol) and DDA (450 mg, 2.43 mmol) were added to 12.5 mL of the stock solution and sonicated until completely dissolved. Gold (III) was then reduced by fast addition of TBAB (125 mg, 486 µmol) in DDAB stock solution under vigorous stirring. The NPs were functionalized 1 h after the synthesis.

Preparation of 5.52 (± 0.54) nm Au NPs

DDAB stock solution was first prepared by dissolving 925 mg DDAB in 20 mL toluene. 50 mg of HAuCl$_4$·3H$_2$O and 450 mg DDA were added to 12.5 mL of the stock solution and sonicated until dissolved. Gold (III) was then reduced by rapid injection of 125 mg of TBAB in 5 mL of the DDAB stock solution under vigorous stirring. Thus prepared solution of ~2.5 nm NPs (“seeds”) was aged for 24 hours. Growth solution was prepared by adding to 50 mL of pure toluene the following reagents, in the following order: 1) 1.00 g DDAB, 2) 1.85 g DDA, 3) 200 mg of HAuCl$_4$·3H$_2$O, 4) 7 mL of the aged seed solution. Finally, 131 µL of hydrazine dissolved in 20 mL of the DDAB stock solution was added dropwise (~1 drop / sec) to the growth solution under vigorous stirring.
**Preparation of 7.46 (± 0.84) nm Au NPs**
DDAB stock solution was first prepared by dissolving 925 mg DDAB in 20 mL toluene. Erlenmeyer flask was charged with 20 mL of toluene and the following reagents were added, in the following order: 1) 400 mg DDAB (dissolves with sonication), 2) 740 mg DDA, 3) 80 mg HAuCl\(_4\)·3H\(_2\)O (dissolves with sonication), 4) 10.4 mL of as-prepared 5.5 nm Au NPs. Finally, a reducing solution was prepared by injecting N\(_2\)H\(_4\)·H\(_2\)O (52.4 µL) to 8 mL of the DDAB stock solution, and the resulting solution was added dropwise (~1 drop / sec) to the growth solution under vigorous stirring. Reaction mixture was stirred overnight in the dark.

**Preparation of 2.59 (± 0.33) nm Pd NPs**
DDAB stock solution was first prepared by dissolving DDAB (370 mg, 800 µmol) in toluene (8 mL). Pd(acac)\(_2\) (12 mg, 39.4 µmol) and DDA (180 mg, 971 µmol) were added to 5 mL of the stock solution and sonicated until completely dissolved. Pd was reduced by fast addition of TBAB (50 mg, 194 µmol) dissolved in the DDAB stock solution (2 mL) under vigorous stirring. The NPs were surface-modified 1 h after the synthesis.

**Surface modification of Au and Pd NPs**
The 2.5 nm Au and Pd NPs were used directly for surface modification without prior purification. For 5.5 nm and 7.5 nm NPs, as-prepared NPs were first quenched with one volume of MeOH and the mixture was left undisturbed (with occasional stirring) for two hours. The resulting black precipitate was collected by decantation (do not centrifuge) and redissolved in the initial amount of toluene. A 4-fold excess of ligand was used for surface modification. The number of binding sites on the surface of NPs was calculated assuming that a single thiolate ligand occupies a surface area of 0.214 nm\(^2\). Due the low stability of 1, we generated this and other thiols in situ during the surface modification procedure as follows: an 8-fold excess of DDAB (with respect to the number of thiol molecules) was dissolved in toluene with sonication. Afterwards, an 8-fold excess of TBAB (with respect to the number of thiol molecules) was added and the solution was sonicated. This mixture was added to the acetylated ligand (15a, 15b or 15c) and the resulting solution was added to the NP solution and left for 24 h. Due to the low solubility of the 5.5 nm and 8.5 nm NPs after workup, these NPs were used for irradiation without any purification. For Pd NPs and 2.5 nm Au NPs, one volume of MeOH was added and the mixture was centrifuged. The supernatants were discarded and the remaining solids were washed several times with pure MeOH, dried and redissolved in pure toluene. We verified that the functionalization procedure does not affect the size of the NPs, and that the number of ligands on NPs does not increase further for incubation times longer than 24 hr (i.e., saturation is reached within 24 hr).

**Etching of Au NPs**
Toluene solution of NPs was placed in a 20 mL vial and the volume was reduced to 1 mL by in vacuo. Water (0.5 mL) and MeCN (3 mL) were added. KCN (10 mg) was added and the mixture was vigorous stirred. After 1 h, brine (3 mL) and toluene (3 mL) were added and the mixture was stirred for an additional 30 min. The phases were separated and the organic phase was evaporated to dryness. The residue was dissolved in toluene (3 mL) and brine (3 mL) was added. After phase separation the organic phase was evaporated and dried under HV for several minutes. The residue was dissolved in EtOH and analyzed by UV-Vis spectroscopy.
Calculation of the surface coverage of Pd NPs
To calculate the number of ligands per single Pd NP, the spectrum of dodecanethiol-functionalized Pd NPs was subtracted from the spectra of the ligand-functionalized NPs after purification. Using the resulting absorbance at 400.5 nm and the regression line of the calibration of the acetylated ligands, the actual concentration of ligands in the UV-Vis sample was calculated. The entire amount of ligand in solution was determined using known dilution from UV-VIS analysis. After calculating the number of NPs using the known size and the amount of Pd used for synthesis the overall number of ligands can be correlated to the number of NPs.

Fig. S1. UV-Vis spectra of 15a (18 µg/mL, blue), 15b (14 µg/mL, red) and 15c (15 µg/mL, green) in toluene.

Fig. S2. UV-Vis spectra of 16a (27 µg/mL, blue), 16b (41 µg/mL, red) and 16c (37 µg/mL, green) in toluene.
**Fig. S3.** Evolution of the UV-Vis spectrum of 15b in toluene exposed to UV light ($\lambda \sim 365$ nm; $I \sim 0.7$ mW/cm$^2$). The spectra were recorded after the following times of irradiation (from top to bottom): 30 min, 90 min, 180 min, 300 min, 390 min, 480 min, 570 min, 660 min, 1260 min.

**Fig. S4.** Plot of 1/absorbance at 422 nm against the reaction time.

\[ y = 0.0063x + 0.2933 \]
Fig. S5. UV-Vis spectra of 15a at 0.36 µg/mL (red), 1.8 µg/mL (green), 5.4. µg/mL (blue), 9.0 µg/mL (violet), 18 µg/mL (cyan).

Fig. S6. Plot of absorbance of 15a at 400.5 nm against the concentration.
**Fig. S7.** UV-Vis spectra of **15b** at 0.56 μg/mL (blue), 2.8 μg/mL (red), 8.4. μg/mL (green), 14 μg/mL (violet), 28 μg/mL (cyan).

**Fig. S8.** Plot of the absorbance of **15b** at 400.5 nm against the concentration.

\[ y = 34.983x - 0.0107 \]
**Fig. S9.** UV-Vis spectra of 15c at 0.6 µg/mL (blue), 3.0 µg/mL (red), 9.0. µg/mL (green), 15 µg/mL (violet), 30 µg/mL (cyan).

**Fig. S10.** Plot of the absorbance of 15c at 400.5 nm against the concentration.

\[
y = 36.082x - 0.0097
\]
NMR spectra

Fig. S11. $^1$H NMR spectrum of 5.

Fig. S12. $^{13}$C NMR spectrum of 5.
Fig. S13. $^1$H NMR spectrum of 7.

Fig. S14. $^{13}$C NMR spectrum of 7.
Fig. S15. $^1$H NMR spectrum of 8a.

Fig. S16. $^{13}$C NMR spectrum of 8a.
Fig. S17. $^1$H NMR spectrum of 9b.

Fig. S18. $^{13}$C NMR spectrum of 9b.
Fig. S19. $^1$H NMR spectrum of 9a.

Fig. S20. $^{13}$C NMR spectrum of 9a.
Fig. S21. $^1$H NMR spectrum of 10b.

Fig. S22. $^{13}$C NMR spectrum of 10b.
Fig. S23. $^1$H NMR spectrum of 10a.

Fig. S24. $^{13}$C NMR spectrum of 10a.
Fig. S25. $^1$H NMR spectrum of 11b.

Fig. S26. $^{13}$C NMR spectrum of 11b.
Fig. S27. $^1$H NMR spectrum of 11a.

Fig. S28. $^{13}$C NMR spectrum of 11a.
Fig. S29. $^1$H NMR spectrum of 13.

Fig. S30. $^{13}$C NMR spectrum of 13.
Fig. S31. $^1$H NMR spectrum of 14.

Fig. S32. $^{13}$C NMR spectrum of 14.
Fig. S33. $^1$H NMR spectrum of 15a.

Fig. S34. $^{13}$C NMR spectrum of 15a.
Fig. S35. $^1$H NMR spectrum of 15b.

Fig. S36. $^{13}$C NMR spectrum of 15b.
Fig. S37. $^1$H NMR spectrum of 15c.

Fig. S38. $^{13}$C NMR spectrum of 15c.
Fig. S39. $^1$H NMR spectrum of 16a.

Fig. S40. $^{13}$C NMR spectrum of 16a.
Fig. S41. $^1$H NMR spectrum of 16b.

Fig. S42. $^{13}$C NMR spectrum of 16b.
Fig. S43. $^1$H NMR spectrum of 16c.

Fig. S44. $^{13}$C NMR spectrum of 16c.
Fig. S45. COSY spectrum of 16c.

Fig. S46. NOESY spectrum of 16c in the aromatic region, the significant NOE is indicated with pink arrows.